Oxidative Transformations of Allenes (Part I)
and
Enyne Ring-Closing Metathesis (Part II)

BY

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THESIS

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This thesis is dedicated to my beloved family

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TABLE OF CONTENTS

CHAPTER PAGE

PART I

OXIDATIVE TRANSFORMATIONS OF ALLENES

1. Nitration of Silylallenes to Form Functionalized Nitroalkenes 1
1.1. Introduction and Background Information 2
1.2. Synthesis of Nitro Compounds 2
1.2.1. Nitration of Aromatic Compounds 2
1.2.2. Nitration of Alkanes 4
1.2.3. Nitration of Alkyl Halides 4
1.2.4. Nitration of Alkenes 5
1.2.5. Nitration of Alkynes 9
1.2.6. Nitration of Allenes 10
1.3. Reactions of Nitro Compounds 11
1.3.1. Henry Reaction 12
1.3.2. Michael Reactions 13
1.3.2.1. Conjugate addition to Nitroalkenes 13
1.3.2.2. Addition of Nitroalkanes to α,β-Unsaturated Enones 15
1.3.3. Nef Reaction 15
1.4. Nitration of Silylallenes 16
1.5. Summary 24
1.6. Experimental Details 24
1.6.1. General Information 24
1.6.2. General Procedure for Silylallene Synthesis 25
1.6.3. General Procedures for Nitration of Silylallenes with $NaNO_2$/AcOH 25
1.6.4. General Procedure for Nitration of Silylallenes with $Fe(NO_3)_3 \cdot 9H_2O/FeCl_3$ 25
1.6.5. General Procedure for the Conversion of Silyloximes to Isooxazolidinones 26
1.6.6. Selected Characterization Data 26
1.7. References 32

2. Oxidative Dimerization of Silylallenes via Activation of the Allenic C(sp^2)–H Bond Catalyzed by Copper(I) Chloride and *N*-Hydroxyphthalimide 37
2.1. Introduction 38
2.2. Phthalimide *N*-Oxyl Radical Reactions 40
2.2.1. Phthalimide *N*-Oxyl Radical-Catalyzed Reactions 40
2.2.2. Stoichiometric Reactions of Phthalimide *N*-Oxyl Radical 43
2.2.2.1. Cu-Catalyzed Allylic and Benzylic C–H Bond Activation Reactions 43
2.2.2.2. Cu-Catalyzed Phthalimide *N*-Oxyl Radical Addition to Alkenes 45
2.3. Results and Discussion 47
2.4. Summary 54
2.5. Experimental Details 54
2.5.1. General Information 54
2.5.2. General Procedure for Dimerization of Silylallenes 54
2.5.3. Selected Characterization Data 55
2.6. References 59

TABLE OF CONTENTS (continued)

CHAPTER PAGE

3. Facile Alder Ene Reactions of Silylallenes Involving an Allenic C(sp^2)–H Bond 63
3.1. Introduction 64
3.2. Types of Ene Reactions 64
3.2.1. Ene Reaction with Azodicarboxylates 65
3.2.2. Carbonyl Ene Reaction 67
3.2.3. Nitroso Ene Reaction 71
3.2.4. Imino Ene Reaction 72
3.2.5. Aryne Ene Reaction 74
3.2.6. Singlet Oxygen Ene Reaction 75
3.3. Ene Reaction of Silylallenes with Triplet Molecular Oxygen 77
3.4. Results and Discussion 79
3.5. Summary 88
3.6. Experimental Details 88
3.6.1. General Information 88
3.6.2. General Procedure for Ene Reaction of Silylallenes 88
3.6.3. Selected Characterization Data 89
3.7. References 96

4. Iron-Catalyzed Complementary Oxidative Transformations of Allenes with Different Oxidants 101
4.1. Introduction 102
4.2. Iron-Catalyzed Oxidative Transformations Using DDQ 103
4.3. Iron-Catalyzed Oxidative Transformations Using *t*-BuOOH 107
4.4. Allenes to Indenes via an Allylic Cation 111
4.5. Results and Discussion 114
4.6. Summary 126
4.7. Experimental Details 126
4.7.1. General Information 126
4.7.2. Representative Procedure for Alkyl and Silylallenes Preparation 127
4.7.3. General Procedure of Aryl-Substituted Allenes with DDQ 127
4.7.4. General Procedure of Aryl-Substituted Allenes with *t*-BuOOH 128
4.7.5. General Procedure of Silyl-Substituted Allenes with DDQ 128
4.7.6. General Procedure of Silyl-Substituted Allenes with *t*-BuOOH 128
4.7.7. Selected Characterization Data 129
4.8. References 139

PART II

RING-CLOSING ENYNE METATHESIS

5. Structure and Reactivity of Sulfonamide- and Acetate-Chelated Ruthenium Alkylidene Complexes 145
5.1. Introduction 146
5.1.1. Brief Historical Background 146
5.1.2. Metathesis Reaction Types and Catalysts 146
5.1.2.1. Classification of Metathesis Reactions 146
5.1.2.2. Grubbs-Type Ruthenium Alkylidene Complexes 148

TABLE OF CONTENTS (continued)

CHAPTER PAGE

5.1.2.3. Schrock-Type Molybdenum and Tungsten Complexes 150
5.1.2.4. Diyne Metathesis Complexes 152
5.2. Enyne Metathesis 153
5.3. Metallotropic [1,3]-Shift in Enyne Metathesis 157
5.4. Results and Discussion 160
5.5. Summary 171
5.6. Experimental Details 171
5.6.1. General Information 171
5.6.2. General Procedure for Starting Material Preparation 172
5.6.3. General Procedure for Metal Complex Formation 172
5.6.4. Selected Characterization Data 173
5.7. References 179

6. Structure and Reactivity of Hydroxy- and Ether-Chelated Ruthenium Alkylidene Complexes 187
6.1. Introduction 188
6.2. Results and Discussion 191
6.3. Summary 199
6.4. Experimental Details 199
6.4.1. General Information 199
6.4.2. General Procedure for Preparation of Starting Materials 199
6.4.3. General Procedure for Metal Complex Formation 200
6.4.4. Selected Characterization Data 200
6.5. References 205

7. Structure and Reactivity of Alkene-Chelated Ruthenium Alkylidene Complexes 209
7.1. Introduction 210
7.2. Alkene-Chelated Ruthenium Alkylidenes 211
7.3. Results and Discussion 213
7.3.1. Ring-Closing Metathesis (RCM) of 1,7-Diynes 215
7.3.2. RCM of 1,n-Diynes to Form *trans*-1,5-Chelates 217
7.3.3. Enyne RCM-Induced Formation of *trans*-1,5-Chelates 220
7.3.4. New Reactivity of Enediynes to Form *trans*-1,5-Chelates 220
7.3.5. Enyne RCM of 1,n-Enynes to Form η^3-Complexes 223
7.3.6. Metathesis Activity of Alkene-Chelated Ruthenium Alkylidenes 225
7.4. Summary 228
7.5. Experimental Details 228
7.5.1. General Information 228
7.5.2. General Procedure for Metal Complex Formation 228
7.5.3. Selected Characterization Data 229
7.6. References 241

8. Thermal Bicyclization of Ynamide-Tethered 1,3,8-Triynes 243
8.1. Introduction 244
8.2. Intramolecular [4+2] Cycloaddition Reactions of Ynamide Derivatives 244
8.2.1. Cycloaddition of Ynamide-Tethered 1,3-Enynes 245
8.2.2. Cycloaddition of Ynamide-Tethered Triynes and Tetraynes 247

TABLE OF CONTENTS (continued)

CHAPTER PAGE

8.3. Intramolecular [2+2+2] Cycloaddition Reactions Ynamide-Tethered Triynes 250
8.4. Gold-Catalyzed Cyclization of Ynamide Tethered Alkynes 251
8.5. Results and Discussion 252
8.6. Summary 261
8.7. Experimental Details 262
8.7.1. General Procedure for Substrate Preparation 262
8.7.2. General Procedure for Thermal Bicyclization 263
8.7.3. Selected Characterization Data 263
8.8. References 274

APPENDICES 279
Appendix I Selected NMR Spectra for Chapter 1 279
Appendix II Selected NMR Spectra for Chapter 2 313
Appendix III Selected NMR Spectra for Chapter 3 331
Appendix IV Selected NMR Spectra for Chapter 4 383
Appendix V Selected NMR Spectra for Chapter 5 443
Appendix VI Selected NMR Spectra for Chapter 6 467
Appendix VII Selected NMR Spectra for Chapter 7 477
Appendix VIII Selected NMR Spectra for Chapter 8 525
Appendix IX Copyright Permissions 571

VITA 585

LIST OF SCHEME

SCHEME PAGE

1.1. Aromatic Nitration of Toluene 3

1.2. Nitration of Adamantane 4

1.3. Nitration in Greenery Solvent PEG-400 5

1.4. Nitration of Alkyl Halides in Ionic Liquids 5

1.5. Nitration with Amberlite Resin 5

1.6. Nitration of Alkene Using Nitric Acid 6

1.7. Nitration of Methyl Acrylate 6

1.8. Nitration of Styrene Derivatives 6

1.9. Nitration of Alkene with CAN 7

1.10. Proposed Nitration Mechanism with CAN 7

1.11. Iron-Mediated Nitro-Cyclization of 1,6-Dienes 8

1.12. Iron-Mediated Halo-Nitration of Alkenes 8

1.13. Nitration of Olefins with $AgNO_2$ and TEMPO 9

1.14. Nitration of Alkynes to Nitroalkynes 10

1.15. Nitration of Terminal Alkynes to Nitroalkenes 10

1.16. Nitration of Enynes 10

1.17. Nitration of Di-*tert*-butylallenes 11

1.18. Nitration of Monosubstituted Allenes 11

1.19. Reactions of Nitroalkenes 11

1.20. Henry Reaction with Common Bases 12

1.21. Transformations of Nitro-Aldol Product 13

1.22. Conjugate Addition to Nitroalkenes 14

LIST OF SCHEME (continued)

SCHEME PAGE

1.23. Transformations of Michael Adducts Derived from Nitroalkenes 14

1.24. Addition of Nitroalkanes to α,β-Unsaturated Enones 15

1.25. Nef Reaction in Presence of Acid 15

1.26. Nef Reaction with Oxidation Method 16

1.27. Nitroalkenes to Ketones 16

1.28. Nitration of Simple Alkene versus Silylallene 17

1.29. One-Step Synthesis of Silylallenes 17

1.30. Plausible Mechanism for the Formation of α-Nitro α,β-Unsaturated Silyl Oximes 24

2.1. Total Synthesis of (–)-Histrionictoxin 39

2.2. Nitration of Silylallenes 40

2.3. First *N*-hydroxyphthalimide Catalyzed Reactions 40

2.4. Oxidation of Cyclohexane to Adipic Acid 41

2.5. Oxidation of Arylic C(sp^3)–H Bonds 41

2.6. Oxidation of Alcohols to Ketones 42

2.7. Allylic and Propargylic Oxidation of Alcohols 42

2.8. Aerobic Oxidation of Indane 43

2.9. Proposed Mechanism for Oxygenation with Stoichiometric NHPI 45

2.10. Cu(II)-Catalyzed Dioxygenation of Alkenes Using NHPI 45

2.11. Proposed Mechanism of Cu-Catalyzed Dioxygenation of Alkenes 46

2.12. Cu(I)-Catalyzed Dioxygenation of Alkenes Using NHPI 46

2.13. Catalyst-Control Dioxygenation of Alkenes 47

2.14. Initial Observation of Silylallene Dimerization 48

LIST OF SCHEME (continued)

SCHEME PAGE

2.15. A Proposed Reaction Mechanism 53

3.1. Ene Reaction 64

3.2. Aza-Ene Reaction of Allenes 67

3.3. Carbonyl Ene Reaction 67

3.4. Titanium-BINOL Catalyzed Intermolecular Carbonyl Ene Reaction 68

3.5. Menthol Synthesis Using Type-I Intramolecular Ene Reaction 69

3.6. Type II Ene Reaction for Carbocyles Synthesis 70

3.7. Type III Carbonyl Ene Cyclization in Total Synthesis of (–)-Laurenyne 70

3.8. Intramolecular Imino Ene Reaction 72

3.9. Intamolecular Imino Ene Reaction in Total Synthesis of Papuamine 73

3.10. Intramolecular Alkene Imino Ene Reaction 73

3.11. Intramolecular Direct Imino Ene Reaction 73

3.12. Intermolecular Enantioselective Imino Ene Reaction 74

3.13. Intramolecular Aryne Ene Reaction 74

3.14. Applications of Allylic Hydroperoxides 76

3.15. Autooxidation of Disubstituted Silylallenes 77

3.16. Alder-Ene Reactions of Alkyl-Substituted Allenes with Azodicarboxylate 81

3.17. Application to a Chiral Pyrazoline Containing an Amino-Tertiary Centre 86

3.18. Ene Reactions of Silylallenes with Ethyl Glyoxylate and Benzyne 87

4.1. Polar Reaction vs. Radical Mediated Processes of Allenes 102

4.2. $FeCl_2$-Catalyzed Benzylic Alkylation and Proposed Mechanism 104

4.3. Proposed Mechanism Iron-Catalyzed Oxidative Arylation of a Benzylic C–H Bond 105

LIST OF SCHEME (continued)

SCHEME PAGE

4.4. Iron-Catalyzed Dehydrogenative Coupling of Indoles and Benzylic C–H Bonds 106

4.5. Iron-Catalyzed C–O Bond Forming Reaction and Plausible Mechanism 106

4.6. Iron-Catalyzed Benzylic Oxidation 107

4.7. Iron-Catalyzed Oxidative C–H Amination 109

4.8. Iron-Catalyzed Oxidative Coupling Reactions of 1,3-Dicarbonyl Compounds 109

4.9. Plausible Mechanism of Iron-Catalyzed Carbonylation–Peroxidation of Alkenes 110

4.10. Arylvinylidenecyclopropanes with Acetals 112

4.11. Electrophilic Addition of Carbocations to Allenes 113

4.12. Imino-Nazarov Cyclization of Allenamides 114

4.13. Summary of Initial Proof of Complementary Reactivity of non-Silylated and Silylated Allenes with DDQ and TBHP 117

4.14. Abnormal Reactivity of Silyl-Substituted Allenes with DDQ with $FeCl_2$ 122

4.15. Mechanisms for the Transformations of Alkyl- and Silylsubstituted Allenes with DDQ Relative Free Energies (in $kcalmol^{-1}$) were Calculated at the M06-2X/6-31+G* Level of Theory 124

4.16. Mechanism of Iron-Catalyzed Reaction of Silylallenes with TBHP 125

5.1. Tungsten-Catalyzed RCM for Synthesis of Nakadomarin A and Epothilone C 151

5.2. Example of First Enyne Metathesis 153

5.3. Pd-Catalyzed Enyne Metathesis 154

5.4. Pt-Catalyzed Ring-Closing Enyne Metathesis 154

5.5. First Catalytic Ruthenium Carbene-Based Enyne RCM 154

5.6. Tandem Ring-Closing Metathesis of Dienynes 155

5.7. Possible Mechanism for Enyne RCM 156

LIST OF SCHEME (continued)

SCHEME PAGE

5.8. Mode Selectivity in Enyne RCM 157

5.9. Metallotropic [1,3]-Shift Induced by Enyne RCM 158

5.10. Reactivity of Alkynyl Ruthenium Alkylidenes 158

5.11. Formation of Oligoenynes via Metallotropic [1,3]-Shift 159

5.12. Enyne RCM and Metallotropic [1,3]-Shift for Natural Product Synthesis 159

5.13. RCM Strategy for the Formation of Chelated Ruthenium Alkylidene 162

5.14. Designing New Structural Motifs of Sulfonamide-Chelates 163

5.15. Designing New Structural Motifs of Acetate-Chelates 163

5.16. Unexpected Formation of Carbon Monoxide Complex 165

5.17. Formation of Octahedral Complex with trans NHC–Carbene Geometry Induced by CO Coordination 165

5.18. Metathesis Activity of CO-Bound Octahedral Complex and Sulfonamide-Chelates 166

5.19. RCM of Sulfonamide-Tethered 1,6-Enynes 167

5.20. Metathesis Activity of Acetate-Chelate 170

5.21. CO-Binding to a 6-Membered Acetate-Chelate Promote Acetate Migration with Concurrent Ru=C Cleavage 170

6.1. Chelation Effect in Enyne Cross Metathesis 188

6.2. Intramolecular Chelation with Hydroxy-Alkyl Functionalities 190

6.3. Enyne Cross Metathesis to Form Ether- and Hydroxy-Chelated Ruthenium Alkylidenes 190

6.4. Designing of Enyne RCM Substrates 191

6.5. Initial Attempts for Hydroxy-Chelated Ruthenium Alkylidene 192

6.6. Effect of *gem*-Dialkyl Substituent in Alkyne-Chelated Ruthenium Alkylidenes 193

LIST OF SCHEME (continued)

SCHEME PAGE

6.7. Strategy for the Hydroxy-Chelated Ruthenium Alkylidenes 193

6.8. Unexpected Behaviors of Related Enynes 198

6.9. Competing Chelation between Hydroxyl and Sulfonamide or Acetate Moieties 198

7.1. Initial Steps in G-I and G-II Catalyzed Olefin Metathesis 210

7.2. G-I Derived First Alkene-Chelated Ruthenium Alkylidene 211

7.3. η^3-Vinylcarbene Complexes Derived from Ruthenium-Based Olefin Metathesis 212

7.4. Alkene-Chelated Ruthenium *N*-Heterocyclic Alkylidene 212

7.5. Alkene-Chelated Ruthenium Alkylidene Derived from 7-8 with Acenaphthylene 213

7.6. Alkyne-Chelated Ruthenium Alkylidene 213

7.7. RCM of 1,n-Diynes for the Formation Various Alkene Chelated Ruthenium Alkylidenes 214

7.8. RCM of 1,7-Diynes Without *gem*-Dimethyl Group 215

7.9. RCM of *gem*-Dimethyl Group Containing 1,7-Diynes with G-I, G-II and HG-II 216

7.10. RCM of 1,7-Diynes in Presence of an External Alkenes 216

7.11. Possible Mechanism for the Formation of **7-25c** 225

7.12. Metathesis Activity of *trans*-1,5-Chelates Derived from 1,n-Diynes 225

7.13. Metathesis Activity of *trans*-1,5-Chelates Derived from Dienynes 226

7.14. Metathesis Activity of Alkene Chelated η^3-Complex **7-24b** 227

7.15. Metathesis Activity of Sulfonamide Chelate **7-26d** 227

8.1. Intramolecular [4+2] Cycloaddition of Ynamide-Tethered 1,3-Dienes 245

8.2. Thermal [4+2] Cycloaddition of 1,3-Eneynamide Tethered Alkynes 246

8.3. [4+2] Cycloaddition of Aryl Substituted 1,3-Eneynamide Tethered Alkynes 246

8.4. [4+2] Cycloaddition of Ynamide Tethered 1,3-Enynes for 247

LIST OF SCHEME (continued)

SCHEME PAGE

8.5. HDDA Reaction of Triynes 247

8.6. Alkane C−H Activation by Aryne Intermediates Catalyzed by Silver 248

8.7. Hydrogenation of Arynes with Silyl C_β–H Bonds 248

8.8. Hydroarylation of Arynes Catalyzed by a Silver Ion 249

8.9. Aryne Ene Reaction with Ynamide having Tetraynes 249

8.10. Regioselectivity in the Nucleophile Trapping of Arynes 250

8.11. [2+2+2] Cycloaddition Reactions Ynamide-Tethered Triynes 250

8.12. [2+2+2] Cycloaddition Reaction for the Synthesis of Antiostatin A_1 251

8.13. [2+2+2] Cycloaddition Reaction for Synthesis of (−)-Herbindole 251

8.14. Possible Cyclization Pathways of 1,5-Diynes 252

8.15. Possible Cyclization Pathways of Ynamide-Tethered Alkynes 252

8.16. RCM Strategy for Synthesis of Herbindole Core 253

8.17. Model Substrate for RCM 254

8.18. Unexpected Bicyclization During Ynamide Synthesis 254

8.19. Modified Synthetic Sequence for Ene-ynamide-Tethered Diyne **8-47a** 255

8.20. Unexpected Cyclization of Ynamide-Tethered Triyne Functionality 255

8.21. Plausible Mechanism for Cyclization of a Ynamide-Tethered Triyne 256

8.22. Ene-Reaction Followed Diels-Alder Cyclization of Ynamide 259

8.23. Different Cyclization Behaviors 259

8.24. Deuterium Labelling Experiments 260

8.25. Possibility of Intramolecular Cation Trapping 261

8.26. Probes for a Radical Intermediate 261

LIST OF TABLE

TABLE		PAGE
1.1.	Optimization of Reaction Conditions	19
1.2.	Scope of the Reaction with $NaNO_2$/AcOH with and without CAN	20
1.3.	Nitration Reaction with Iron(III) Nitrate	22
1.4.	Conversion of α-Nitro α,β-Unsaturated Silyl Oximes to Isooxazolidinones	23
2.1.	Cu-Catalyzed Oxygenation with Stoichiometric NHPI	44
2.2.	Optimization of Reaction Condition for Dimerization of Silylallenes	48
2.3.	Dimerization of Silylallenes Derived from Cyclic Ketones	51
2.4.	Dimerization/Oxidation of Silylallenes Derived from Acyclic Ketones	52
3.1.	First Lewis Acid Promoted Aza-Ene Reaction	65
3.2.	First Metal-Catalyzed Aza-Ene Reaction	66
3.3.	First Catalytic Asymmetric Carbonyl Ene Reaction	68
3.4.	Cu-Catalyzed Asymmetric Carbonyl Ene Reaction	69
3.5.	Intramolecular Nitroso Ene Reaction	71
3.6.	Intermolecular Nitroso Ene Reaction	72
3.7.	Aryne Ene Reaction of Tetraynes	75
3.8.	Regioselectivity in Schenck Ene Reaction	77
3.9.	Autooxidation of Trisubstituted Silylallenes	78
3.10.	Alder-Ene Reaction of Silylallenes with Azodicarboxylate	80
3.11.	Ene Reaction Selectivity of Cycloalkyl-Based Silylallenes	85
3.12.	Computational Results for Selected Allenes (in kcal/mol)	86
4.1.	Iron-Catalyzed Oxidative Arylation of the Benzylic C–H Bond	105
4.2.	Synthesis of *tert*-Butyl Peroxyacetals via Iron-Catalysis	108

LIST OF TABLE (continued)

TABLE		PAGE
4.3.	Iron-Catalyzed Carbonylation–Peroxidation of Alkenes	110
4.4.	Rearrangement of Arylvinylidenecyclopropanes	111
4.5.	Lewis Acid Promoted Reaction of Allenes to Indenes	112
4.6.	$FeCl_3$-Catalyzed Allenes to Indenes	113
4.7.	Optimization of Reaction Conditions with DDQ for non-Silylated Allene	114
4.8.	Optimization of Reaction Conditions with TBHP for non-Silylated Allene	115
4.9.	Optimization of Reaction Conditions with DDQ for Silylallene	115
4.10.	Optimization of Reaction Conditions with TBHP for Silylallene	116
4.11.	Iron-Catalyzed Reaction of Alkyl, Aryl-Substituted Allenes with DDQ	118
4.12.	Iron-Catalyzed Reaction of Alkyl, Aryl-Substituted Allenes with TBHP	119
4.13.	Iron-Catalyzed Oxidative Transformation of Silylallenes with DDQ	121
4.14.	Iron-Catalyzed Oxidative Transformation of Silylallenes and TBHP	123
5.1.	Formation of Various Sulfonamide-Chelates	164
5.2.	Acetate-Chelated Ruthenium Alkylidene Complexes	169
6.1.	Formation of Hydroxy- and Ether-Chelated Ruthenium Alkylidenes by Relying on Exo-Thorp-Ingold-Effect	195
6.2.	Formation of Hydroxy- and Ether-Chelated Ruthenium Alkylidenes	197
7.1.	RCM of 1,n-Diynes to Form *trans*-1,5-Chelates	218
7.2.	Enyne RCM-Induced Formation of *trans*-1,5-Chelates	219
7.3.	New Reactivity of Enediynes to Form *trans*-1,5-Chelates	221
7.4.	Enyne RCM of 1,n-Enynes to Form η^3- Vinylcarbene Complexes	224

LIST OF TABLE (continued)

TABLE PAGE

8.1. First Thermal [4+2] Cycloaddition of Ynamide Tethered Triynes 245

8.2. Cyclization Reaction of Ynamide Tethered Triyne 258

LIST OF FIGURES

FIGURE PAGE

1.1. Most Common Transformations of Nitro Group into Other Functional Groups 2

1.2. Selected for Synthesis of Nitro Compounds 2

2.1. Homopropargylic Alcohols from Allenyl Reagents 38

3.1. Intramolecular Ene Reaction Classification 64

3.2. Calculated Energies and Geometries for the Ene Reaction of *t*-Bu- and Me_3Si-Substituted Allenes with Azodicarboxylate 83

5.1. Classifications of Metathesis Reactions 147

5.2. Elementary Steps in Diene, Enyne and Diyne Metathesis 148

5.3. Grubbs-Type Ruthenium Alkylidene Complexes 149

5.4. Schrock-Type Molybdenum and Tungsten Complexes 150

5.5. Diyne Metathesis Complexes 152

5.6. Possibility of Metallotropic [1,3]-Shift in Enyne RCM 157

5.7. Chelated Ruthenium Alkylidene Complexes 161

6.1. Hoveyda-Grubbs 1st and 2nd Generation Catalysts 189

6.2. X-ray Structures of **6-14d** and **6-14e** 196

7.1. X-Ray Structures 222

8.1. Structure of Herbindole A, B and C 253

LIST OF ABBREVIATIONS

Ac	Acetyl (CH3C=O)
BINOL	1,1'-Bi-2-naphthol
Boc	*t*-Butyloxycarbonyl [$COC(CH_3)_3$]
Bn	Benzyl
Bu	Butyl
BTCEAD	bis(2,2,2- trichloroethyl)azodicarboxylate
CAN	Ceric ammonium nitrate
Cat.	Catalyst
DBU	1,8-Diazabicyclo[5.4.0]undec-7-ene
DCE	1,2-Dichloroethane
DCM	Dichloromethane
DDQ	2,3-Dichloro-5,6-dicyano-1,4-benzoquinone
de	Diastereomeric excess
DEAD	Diethyl azodicarboxylate
DIAD	Diisopropyl azodicarboxylate
DIBAL	Diisobutylaluminum Hydride
DMAP	4-Dimethylaminopyridine (base catalyst)
DMF	Dimethylformamide (solvent)
DMSO	Dimethyl sulfoxide (solvent)
DTBP	Di-*tert*-butylperoxide
ee	Enantiomeric Excess
LA	Lewis acid
LAH	Lithium aluminum hydride ($LiAlH_4$)
LDA	Lithium diisopropylamide

LIST OF ABBREVIATIONS (continued)

LHMDS	Lithium hexamethyldisilazide ($LiN(SiMe_3)_2$)
MCPBA	*meta*-Chloroperoxybenzoic acid
Ms	Methanesulfonyl (Mesyl, CH_3SO_2)
NBS	*N*-Bromosuccinimide
NHPI	*N*-Hydroxyphthalimide
NMO	*N*-Methylmorpholine *N*-oxide
PCC	Pyridiniumchlorochromate
PDC	Pyridinium dichromate
PEG	Polyethylene glycol
PINO	Pthalimide *N*-oxyl radical
PMB	*p*-Methoxybenzyl
PPTS	pyridinium *p*-toluenesulfonate
Pyr	pyridine; solvent, base, catalyst
RCM	Ring-closing metathesis
RT	Room temperature
SET	Single electron transfer
TASF	Tris(dimethylamino)sulfoniumdifluorotrimethylsilicate
TBAF	Tetra-*n*-butylammonium fluoride
TBDMS	*t*-Butyldimethylsilyl
TBDPS	*t* -Butyldiphenylsilyl
TBHP	*t*-Butylhydroperoxide
TBS	*t*-Butyldimethylsilyl (also TBDMS)
TEA	Triethylamine
TEMPO	2,2,6,6-Tetramethyl-1-piperidinyloxy

LIST OF ABBREVIATIONS (continued)

TES	Triethylsilyl
Tf	Trifluoromethanesulfonyl
TFA	Trifluoroacetic acid
THF	Tetrahydrofuran
THP	Tetrahydropyran
TIPS	Triisopropylsilyl
TMEDA	*N*,*N*,*N*',*N*'-Tetramethylethylenediamine
TMG	1,1,3,3-Tetramethylguanidine
TMP	2,2,6,6-Tetramethylpiperidide
TMS	Trimethylsilyl
TPAP	Tetrapropylammonium perruthenate
Tol	*p*-Tolyl
Troc	2,2,2-Trichloroethoxycarbonyl
Ts	*p*-Toluenesulfonyl

SUMMARY

This thesis has two main parts. Part I is composed of four chapters describing new oxidative transformations of silylallenes comparing with alkyl allenes. Part II consists of four chapters describing the enyne ring-closing metathesis derived sulfonamide, acetate, hydoxy, ether and alkene chelated Grubbs type ruthenium alkylidenes and their reactivity. Part II also consists the unexpected thermal bicyclization of metathesis substrates ynamide tethered diynes.

More specifically, in Chapter 1; nitration of silylallenes with nitrogen dioxide radical, generated from $NaNO_2$ and AcOH, to form α-nitro-α,β-unsaturated silyl oximes and also using $Fe(NO_3)_3 \cdot 9H_2O$ and $FeCl_3 \cdot 6H_2O$, to form regioisomeric chloride-trapped products depending on the steric bulk of the silyl group. Another novel class of compound isooxazolidinones were obtained upon treating the initially formed α-nitro-α,β-unsaturated silyl oximes with TBAF. In Chapter 2; silylallenes with a catalytic system of copper(I) chloride and *N*-hydroxyphthalamide (*N*-Hpth) along with a stoichiometric amount of a terminal oxidant diacetoxyiodobenzene were favored mainly for the formation of dimer products with or without 1,3-enynes, and *N*-Hpth adducts.

In Chapter 3, activation of allenic C(sp^2)–H bond over an allylic C(sp^3)–H bond was described. In this ene reaction linear silylallenes preferentially engage an allenic C(sp^2)–H bond with high selectivity but cycloalkyl-substituted silylallenes showed low or reversed selectivity. On the other hand, non-silylated allenes engage allylic C(sp^3)–H bonds favorably regardless of their structural feature. DFT calculations were provided for further insight into the selectivity trend. In Chapter 4, substituent and oxidant-dependent transformations of allenes are described using alkyl- and silyl-substituted allenes with DDQ (2,3-dichloro-5,6-dicyano-p-benzoquinone) and TBHP (*tert*-butyl hydroperoxide). The reactions of non-silylated allenes involve allylic cation intermediate via forming C–O bond at the *sp*-hybridized C2 carbon and the reactions of silylated allenes favor the formation of propargylic cation intermediates via transferring the allenic hydride to the oxidant, generating 1,3-enynes or propargylic TBHP ethers.

In Chapter 5, sulfonamide-, and acetate-chelated ruthenium alkylidenes were prepared via enyne ring-closing metathesis. All 5-membered sulfonamide chelates and 6-membered acetate chelates have the chelated oxygen and the NHC ligand in cis relationship. Upon exposure to carbon monoxide, the sulfonamide chelates formed unprecedented CO-bound octahedral ruthenium alkylidene complex and the corresponding acetate chelate decomposed to generate vinyl acetates as pure organic product concurrently with dimeric ruthenium CO-complex. In Chapter 6, structure and reactivity of 5-membered hydroxy- and ether-chelated ruthenium alkylidenes were described. The chelated oxygen bound to the metal center in cis to the NHC ligand. In Chapter 7, alkene-chelated ruthenium alkylidene complexes are prepared via enyne ring-closing metathesis (RCM), and their structures and reactivity are explored. The RCM of diynes, enediynes and ynamide tethered alkynes using stoichiometric amount of Grubbs 2nd-generation complex led the formation of alkene-chelated ruthenium alkylidenes, where the chelated alkene is trans to the NHC. This chelation behavior is somewhat different from that observed by Grubbs. On the other hand, the reaction with ene-ynamides generate η^3-vinylcarbene complexes. These complexes show very good metathesis activity contrary to a related η^3-vinylcarbene complex generated from diphenyl acetylene by Grubbs, which was metathesis-inactive.

Finally, in Chapter 8, the unexpected thermal bicyclization of metathesis substrates ynamide tethered triynes to generate novel class of tetrahydropyranopyridines were explored. Where the ynamide tethered triynes smoothly underwent 6-*exo*-mode ring-closure reaction by heating at 85 ^{o}C. The reaction has been explored by varying anion- and cation-stabilizing groups, including the ether side chain, and the alkyne substituent to provide broad range of tetrahydropyranopyridine derivatives.

PART I

OXIDATIVE TRANSFORMATIONS OF ALLENES

CHAPTER 1

NITRATION OF SILYLALLENES TO FORM FUNCTIONALIZED NITROALKENES

1.1. Introduction and Background Information*

Nitro group is one of the most extensively studied among the functional groups. Its strong electron-withdrawing nature and its facile conversion to other functional groups makes nitro compounds versatile building blocks in chemical synthesis (**Figure 1.1**).[1] Nitro compounds are avoided for long time to be used in medicine due to potential toxicity issues; however, later many nitro group-containing drugs are successfully used in medicine for the treatment of several diseases.[2] Nitro compounds are also widely used as fuel, solvents and raw material in chemical industry.[3]

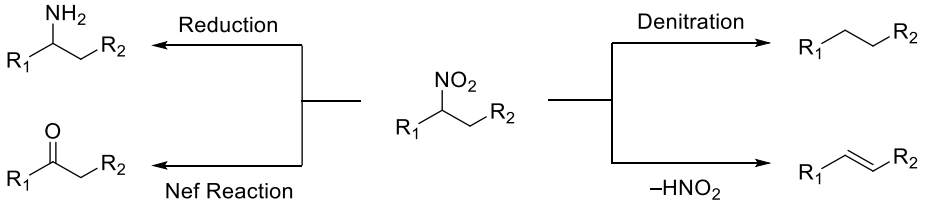


Figure 1.1 Most Common Transformations of Nitro Group into Other Functional Groups

1.2. Synthesis of Nitro Compounds

The nitro group can be easily introduced to organic molecules (**Figure 1.2**) and easily exploited in the complex molecule synthesis. The most common method to introduce nitro group into organic compounds is the nitration of alkanes, alkenes, and aromatic compounds. Also, nucleophilic substitution of alkyl halides with metal nitrites is widely utilized. Other functional groups such as amines, oximes, azides, as well as carbonyl compounds were also converted to nitro compounds.[1]

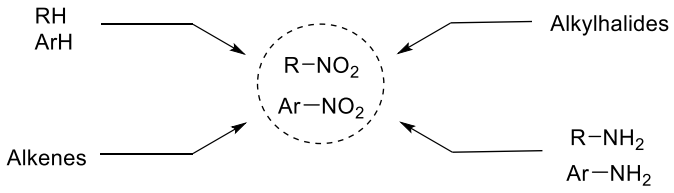


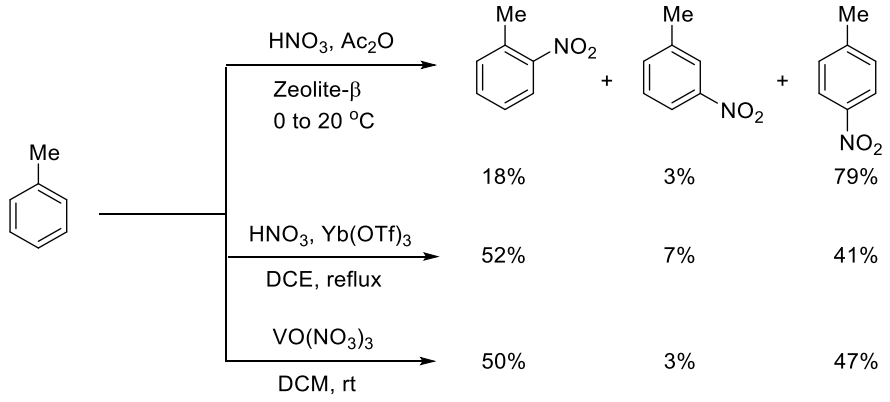
Figure 1.2 Selected for Synthesis of Nitro Compounds

1.2.1. Nitration of Aromatic Compounds

Aromatic nitration is one of the most widely studied reactions, which was extensively used in the

* Reproduced in part with permission from Sabbasani, V. R.; Lee, D. "Nitration of Silylallenes to Form Functionalized Nitroalkenes" *Org. Lett.* **2013**, *15*, 3954–3957.

synthesis of useful materials in industrial processes such as plastics, perfumes, pharmaceuticals and dyes as well as explosives. The most classical method of aromatic nitration is the use of an excess nitric acid in the presence of concentrated sulfuric acid. This classical method, however, generates large amounts of highly polluted nitrogen oxide fumes and waste acids. Later several methods of acid catalyzed nitration reactions were developed using strong acids or Lewis acid and nitric acid, alkyl nitrate, nitryl chloride and dinitrogen tetra-/pent-oxides are the source of nitrating agent. Also, other methods using a nitronium ion source such as nitronium tetrafluoroborate, nitronium hexafluorophosphate, and *N*-nitropyridinium salts were studied to minimize the byproducts in classical nitration reactions. To minimize acid waste, several recoverable and easily removable environmentally friendly solid acid catalysts were developed. Solid acid resins such as Nafion-H and other polysulfonic acid catalysts reduces the harshness of the reaction. However, these reactions suffer from low regioselectivity by forming mixtures of ortho- and para-nitration products. The other type of solid acid catalysts with high surface area are Nafion resin within porous silica, copper nitrate on montmorillonite K-10, zeolite ZSM-5 and iron nitrate clay, have improved the regioselectivity and reduced the amount of acid wastes.[4]



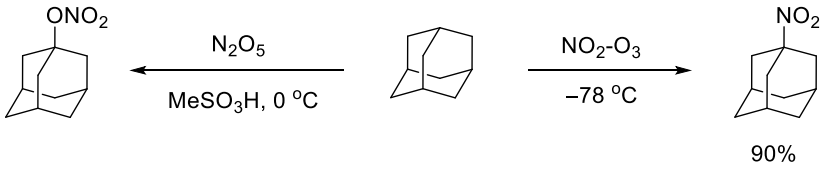
Scheme 1.1 Aromatic Nitration of Toluene

Aromatic nitration using stoichiometric amount of nitric acid in the presence of recoverable zeolite-β catalyst and acetic anhydride provided *para*-nitration product as a major product in 79% yield by forming acetic acid the only byproduct in the reaction (**Scheme 1.1**).[5] The catalytic reaction with recoverable lanthanide triflate ($Yb(OTf)_3$) also reduced the acid waste in the reaction, but did not improve the

regioselectivity.[6] The nitration reaction with 2 to 3 equivalents of vanadium(V) oxytrinitrate as the direct source of nitrating agent, devoid of acids in the reaction provided ortho-, meta- and para-nitration products in 99% yield with low regioselectivity (**Scheme 1.1**).[7]

1.2.2. Nitration of Alkanes

Nitration of saturated aliphatic hydrocarbons requires forced reaction conditions due to the low reactivity of the substrate towards the conventional nitrating reagents. Although the gas phase nitration in the synthesis of nitro alkanes (eg; nitromethane, nitroethane, 1-nitropropane etc.) was used in the industry,[4] the same reaction in typical laboratory operations is often challenging because of the difficulty in selective C(sp^3)─H functionalization under the conditions. There are several attempts reported for the nitration of adamantane to form 1-nitroadamantane,[8] and the best results were observed using nitrogen dioxide in the presence of ozone at low temperature, providing 1-nitroadamantane in 90% yield (**Scheme 1.2**).[9] On the other hand, the nitration with dinitrogen pentoxide in the presence of methane sulfonic acid gave a mixture of several compounds.[10]

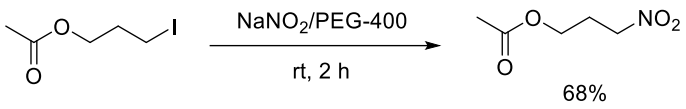


Scheme 1.2 Nitration of Adamantane

1.2.3. Nitration of Alkyl Halides

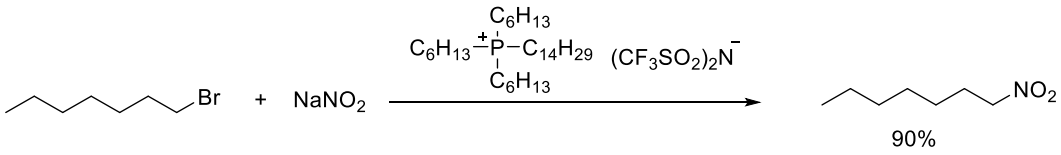
Nucleophilic substitution of alkyl halides with metal nitrites is widely utilized for the synthesis of primary and secondary nitro alkanes. The most common metal nitrites used in the substitution reaction are silver nitrite ($AgNO_2$), sodium nitrite ($NaNO_2$), and potassium nitrite (KNO_2). The reaction with primary and secondary alkyl halides (bromides and iodides) with $NaNO_2$ in DMF or DMSO provided nitration products in good to moderate yields (50─70%). On the other hand, the reaction with $AgNO_2$ with primary alkyl halides provided nitro alkanes in higher yields (75─80%), whereas the reaction with secondary alkyl halides delivered only about 15% yield.[11]

To avoid using traditional volatile organic solvents, nitration of alkyl halides with $NaNO_2$ in the presence of greenery solvent PEG-400 was developed. The reaction of 3-iodopropyl acetate using $NaNO_2$ in PEG-400 provided 3-nitro propyl acetate in good yield (**Scheme 1.3**).[12]



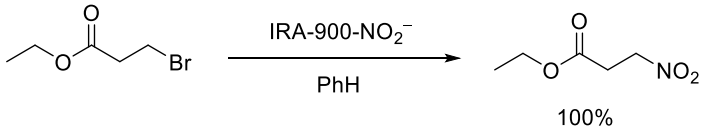
Scheme 1.3 Nitration in Greenery Solvent PEG-400

Nitration of primary alkyl halides using phosphonium bistriflimide ionic liquids were also demonstrated, where the reaction of alkyl halide with $NaNO_2$ in the presence of ionic liquids provided nitration products in 80─90% yields (**Scheme 1.4**).[13]



Scheme 1.4 Nitration of Alkyl Halides in Ionic Liquids

In the synthesis of primary and secondary nitro alkanes using strong nucleophiles ($NaNO_2$ and/or $AgNO_2$) in polar aprotic solvents (DMF or DMSO), the initially formed primary and secondary nitro alkanes were further oxidized to the corresponding aldehydes and ketones (Nef reaction). To avoid such side reactions and tedious work-up procedures, several nitrite ion-bounded macroporous quaternary ammonium amberlite resin were developed, and the amberlite IRA-900-NO_2^- showed a good nitrite transforming profile. The reaction of ethyl-3-bromo propionate with amberlite resin delivered ethyl-3- nitro propionate in 100% yield by avoiding other side reactions (**Scheme 1.5**).[14]

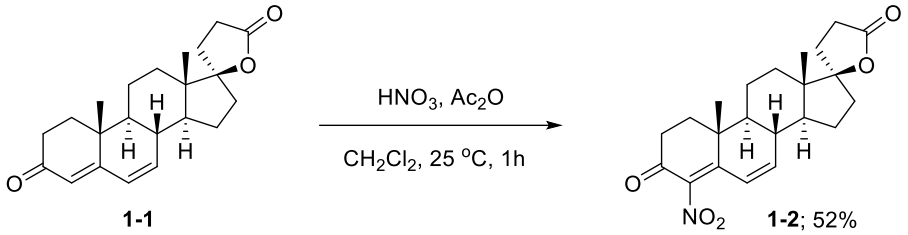


Scheme 1.5 Nitration with Amberlite Resin

1.2.4. Nitration of Alkenes

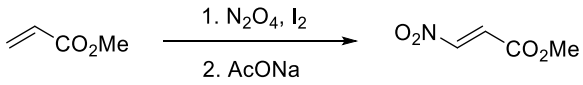
Nitration of alkenes to form conjugated nitroalkenes, is a very useful synthetic method to form versatile

intermediates in organic synthesis. The most common methods to synthesize nitroalkene are the nitration of alkenes or the dehydration of 2-nitro alcohols. In early days, nitration of alkenes employed nitric acid but, the use of corrosive nitric acid often led to the decomposition of alkene and/or the lack of selectivity with low yields. The first example of unusual nitration using nitric acid was demonstrated with steroid **1-1** in the presence of acetic anhydride, which provided nitration product **1-2** in 52% yield (**Scheme 1.6**).[15]



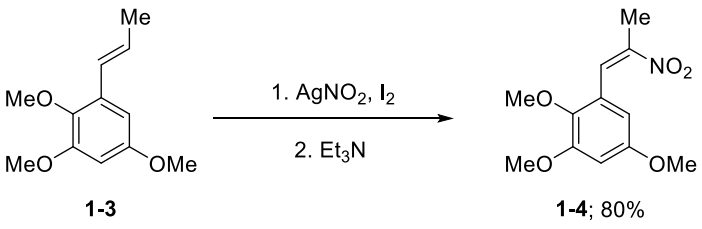
Scheme 1.6 Nitration of Alkene Using Nitric Acid

There are several methods reported for synthesis of nitroalkenes using various nitrating agents.[16] The most important breakthrough came from the nitration of methyl acrylate using two step protocol of dinitrogen tetraoxide (N_2O_4) and iodine addition followed by treatment of the reaction mixture with sodium acetate, which provided methyl-3-nitroacrylate (**Scheme 1.7**).[17] However, the disadvantage of this reaction is to use gaseous N_2O_4.



Scheme 1.7 Nitration of Methyl Acrylate

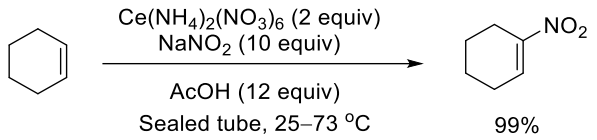
Later, the reaction conditions were further simplified by using in situ generated nitryl iodide from $AgNO_2$ and iodine. The nitration of trimethoxy styrene **1-3** using $AgNO_2$ and iodine followed by triethyl amine treatment provided potent serotonine agonists **1-4** in very good yield as a single stereoisomer



Scheme 1.8 Nitration of Styrene Derivatives

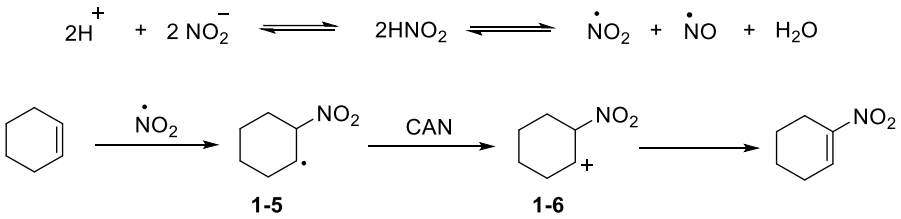
(**Scheme 1.8**).[18] An alternative protocol was developed by replacing $AgNO_2/I_2/Et_3N$ with KNO_2/I_2/pyridine in 18-crown-6 to generate conjugate nitroalkenes in 49─89% yields.[19]

In 1996, Hwu and coworkers developed one of the most efficient nitration methods by employing a new ultra-sonication method, where cerium ammonium nitrate (CAN), $NaNO_2$ and acetic acid (AcOH) were irradiated in a sealed tube at 600 W and 22─55 °C. The nitration of cyclohexene in the presence of CAN, excess of $NaNO_2$ and AcOH provided nitrocyclohexene in excellent yield (99%) (**Scheme 1.9**).[20]



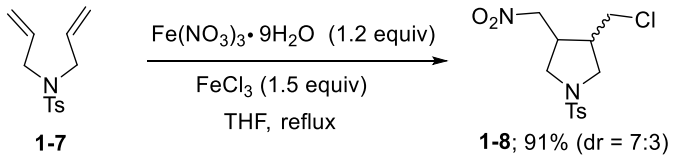
Scheme 1.9 Nitration of Alkene with CAN

The proposed mechanism of nitration with CAN, acetic acid and sodium nitrite involves the formation of nitrogen dioxyl, which then reacts with alkene to form a carbon centered radical intermediate **1-5**. Subsequently, radical intermediate **1-5** is oxidized to carbocation **1-6** by transforming the single electron to CAN. Carbocation **1-6** then undergoes elimination to provide the observed conjugated nitro alkene (**Scheme 1.10**). When the reaction is performed in acetonitrile, carbocation **1-6** trapped with acetonitrile to form *N*-(2-nitrocyclohexyl)acetamide in 58% yield.[21]



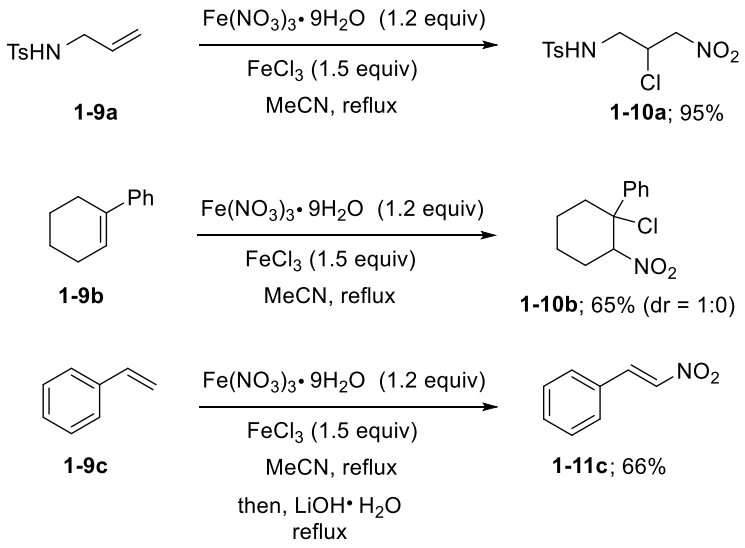
Scheme 1.10 Proposed Nitration Mechanism with CAN

In 2010, Taniguchi and Ishibashi developed iron-mediated radical nitro-cyclization of 1,6-dienes. The reactions of 1,6-dine **1-7** in the presence of $Fe(NO_3)_3 \cdot 9H_2O$ and $FeCl_3$ provided **1-8** in 91% yield (**Scheme 1.11**). The proposed mechanism of the reaction involves thermal decomposition of $Fe(NO_3)_3 \cdot 9H_2O$ to nitrogen dioxyl, which then reacts with alkene moiety followed by radical cyclization to form a new propagating radical, which then trapped with chloride salt to afford the five-membered-cyclized products.[22]



Scheme 1.11 Iron-Mediated Nitro-Cyclization of 1,6-Dienes

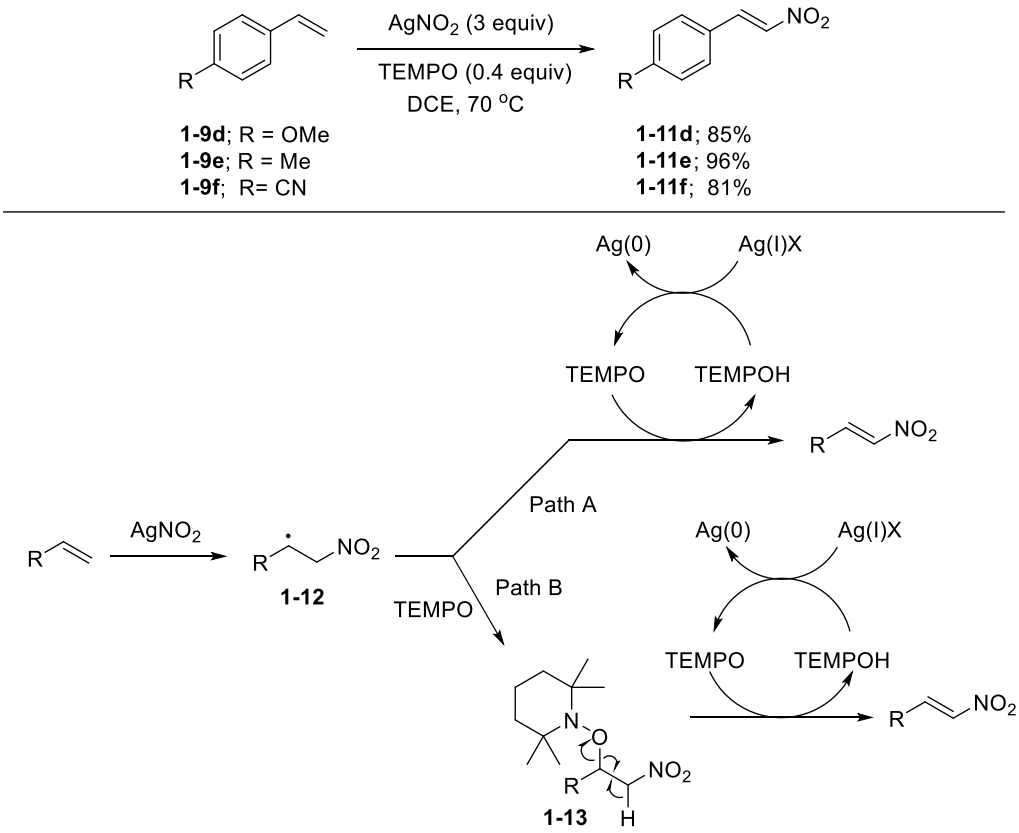
The authors extended the iron-mediated radical nitration to simple alkenes; alkenes **1-9a** and **1-9b** under the optimized conditions by replacing THF with acetonitrile provided **1-10a** and **1-10b** in good yields (**Scheme 1.12**). On the other hand, by treating the initially formed halo-nitration product derived from **1-9c** with lithium hydroxide, conjugated nitro alkene **1-11c** was obtained.[23]



Scheme 1.12 Iron-Mediated Halo-Nitration of Alkenes

Most recently Maiti and coworkers reported highly efficient regio- and stereoselective nitration of mono- and disubstituted olefins using the $AgNO_2$ and TEMPO. The Alkenes **1-9d–f** in the presence of excess $AgNO_2$ and 40 mol % TEMPO in DCE at 70 ^oC delivered nitration products **1-11d–f** in excellent yields and stereoselectivity (**Scheme 1.13**). The proposed mechanism of the reaction, involves the formation of nitro radical from $AgNO_2$, which then reacts with mono- or disubstituted alkene to generate carbon centered radical intermediate **1-12**. From **1-12**, nitroalkene can be formed via Path A or B. TEMPOH is generated upon abstraction of hydrogen atom either directly from **1-12** (Path A) or from **1-13** (Path B). Most likely, TEMPOH oxidize back to TEMPO by reacting with an excess $AgNO_2$.[24] The authors also

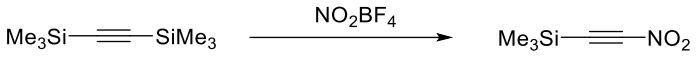
reported the facile nitration of alkenes with ferric nitrate and catalytic TEMPO in the presence of air, which provides conjugated nitroalkenes in good to excellent yields (56─90%).[25] Similar concept extended to the metal free nitration of alkenes using *t*BuONO and TEMPO to provide nitroolefins stereoselectively in 46─89% yields.[26]



Scheme 1.13 Nitration of Olefins with $AgNO_2$ and TEMPO

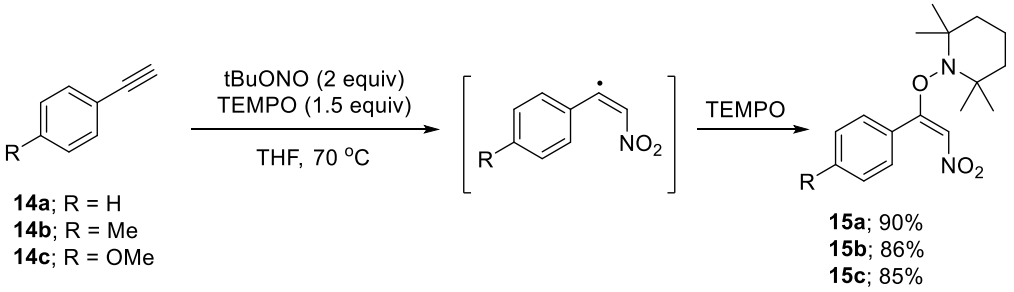
1.2.5. Nitration of Alkynes

Alkynes can undergo two types of nitration reaction; 1) the direct functionalization of terminal alkynes to form nitroalkynes, and 2) the direct addition of nitro group to provide nitroalkenes. Nitroalkynes are very useful substrates in organic synthesis, but these compounds are very unstable under thermal reaction conditions.[27] In 1986, Bedford and coworkers reported mild reaction condition for the synthesis of nitroalkynes. Relaying on this method l-nitro-2-(trimethylsilyl)acetylene was synthesized from bis(trimethylsily1)acetylene and nitronium tetrafluoroboroate (**Scheme 1.14**).[28]



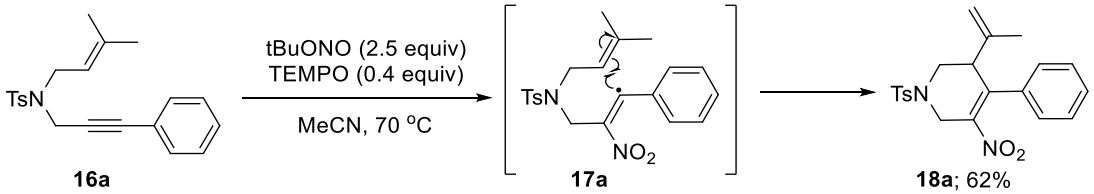
Scheme 1.14 Nitration of Alkynes to Nitroalkynes

Maiti et al. reported metal free nitration of terminal alkynes to form nitroalkenes by using the *t*BuNO and TEMPO. Aryl substituted alkynes **14a-c** under the optimized conditions provided nitroalkenes **15a-c** in excellent yields. However, the reaction of alkylated terminal alkynes delivered the nitration product in low yield from (23─35%). Mechanistically, *t*BuONO is proposed to decompose to NO radical and subsequent oxidation to NO_2 radical, which then reacts with alkyne **14** to generate a carbon centered vinyl radical followed by trapping with TEMPO to provide nitro-oxoamination product **15**.[29]



Scheme 1.15 Nitration of Terminal Alkynes to Nitroalkenes

Most recently the similar reaction condition (*t*BuONO/TEMPO) was used for the nitration of 1,6-enynes. Enyne **16a** under the optimized reaction conditions provided carbocyclic product **18a** in good yield (**Scheme 1.16**). Mechanistically, the generated nitro radical reacts with an internal alkyne to generate carbon centered aryl vinyl radical **17a**, which then undergoes carbocyclization followed by β─H elimination to deliver the carbocylic nitration product.[30]

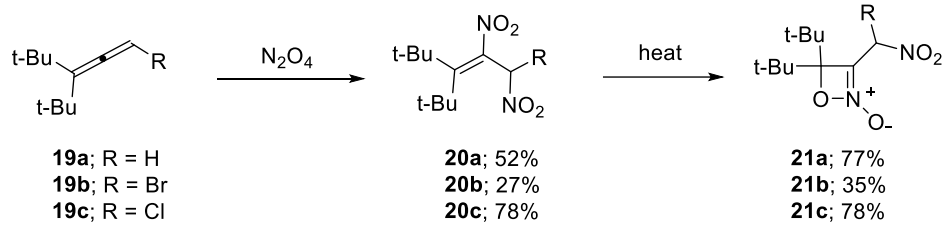


Scheme 1.16 Nitration of Enynes

1.2.6. Nitration of Allenes

In 1975, Berndt and Wieser were reorted the first nitration reaction of allenes. In this study the nitration

of di-*tert*-butylallene **19** was treated with dinitrogen tetraoxide. After careful work-up at 0 °C dinitration product **20** was observed. Upon heating, nitroalkene **20** smoothly underwent first order cyclization to provide oxazete *N*-oxides **21** in good yields (**Scheme 1.17**).[31]



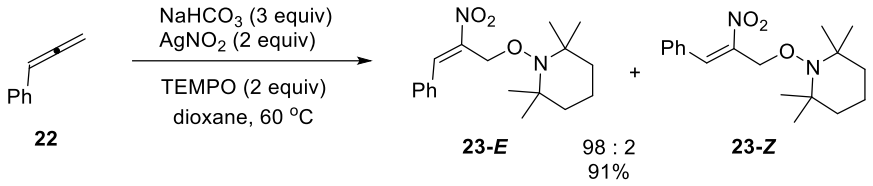
19a; R = H
19b; R = Br
19c; R = Cl

20a; 52%
20b; 27%
20c; 78%

21a; 77%
21b; 35%
21c; 78%

Scheme 1.17 Nitration of Di-*tert*-butylallenes

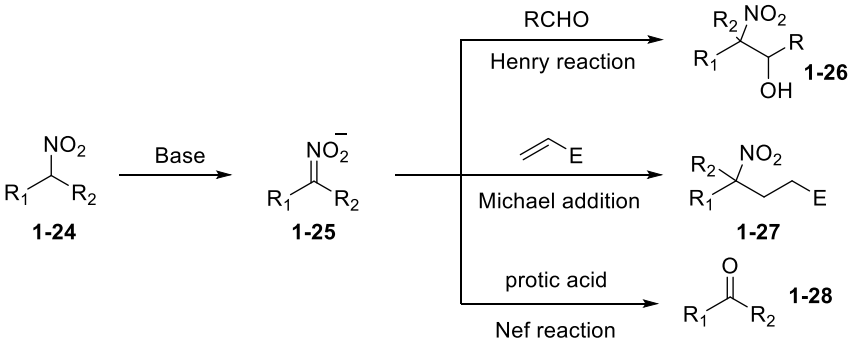
Most recently, Ma and coworkers reported the nitro-oxoamination of monosubstituted allenes by optimizing known olefin nitration conditions. Allene **22** upon treatment of $NaHCO_3$, $AgNO_2$ and TEMPO, provided nitro-oxoamination product **23** in 91% with high regio- and stereoselectivity (**Scheme 1.18**).[32]



Scheme 1.18 Nitration of Monosubstituted Allenes

1.3. Reactions of Nitro Compounds

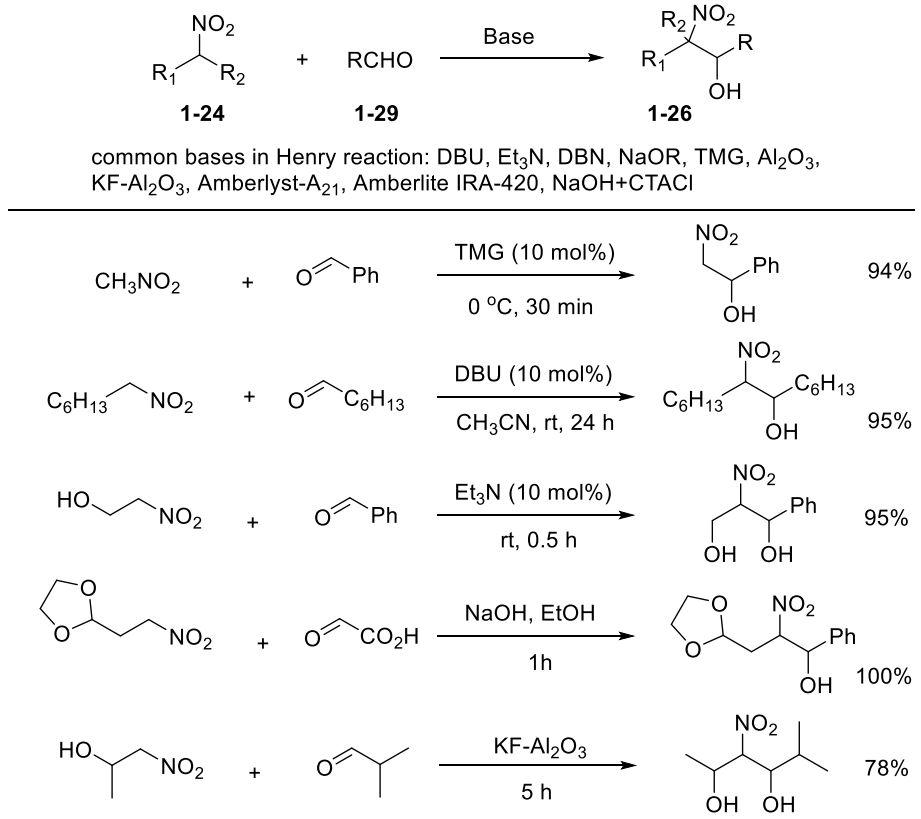
Nitro compounds constitute a powerful source of stabilized carbanion because of the strong electron withdrawing nature of a nitro group. Nitroalkane **1-24** in the presence of base is converted to nitronate anion **1-25** (**Scheme 1.19**).[1,2] This anion can be used for various reactions employing a broad range of



Scheme 1.19 Reactions of Nitroalkenes

electrophiles. The reaction of nitronate anion with an aldehyde to produce nitro aldol product **1-26**, which is called Henry reaction. The reaction with electron deficient alkenes provides **1-27** via a Michel reaction. Quenching nitronate anion **1-25** with protic acid delivers the corresponding carbonyl compound **1-28**, which is known as Nef reaction. While other electrophiles can be used to trap the nitronate anion **1-25**, nitro alkenes themselves are also used as Michael acceptors.

1.3.1. Henry Reaction



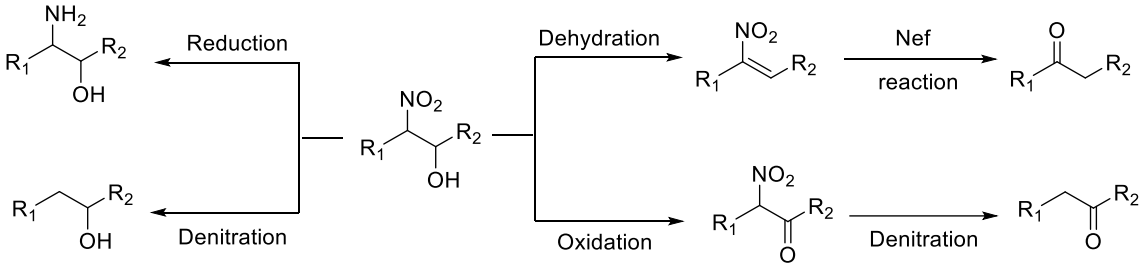
Scheme 1.20 Henry Reaction with Common Bases

In 1985, Henry discovered nitro-aldol reaction between nitroalkanes and carbonyl compounds to produce β-nitro alcohols.[33] Since then, the nitro-aldol reaction was studied extensively and used in many synthetic transformations. In general, the Henry reaction provides a mixture of diastereomers. The lack of stereoselectivity is due to the reversible nature of the reaction as well as easy epimerization at the nitro carbon center.

General reaction conditions for the Henry reaction involves a catalytic amount of base to generate a

nitronate anion. The most common bases for the classical nitro-aldol reactions are hydroxides, alkoxides, carbonates, and bicarbonates in common solvents such as water or ethanol.[1] Nitro-aldol reaction between nitroalkanes **1-24** and aldehydes **1-29** with some common bases are briefly summarized in **Scheme 1.20**.[34]

The general transformations of nitro-aldol products to other functional groups are shown in **Scheme 1.21**. The nitro-aldol product can be reduced to form an amino alcohol or denitrated to form alcohols also oxidation followed by radical denitration provides corresponding ketones. The most well studied reaction of these compounds is the direct formation of nitro alkenes by dehydration during the nitro-aldol reaction, which after careful acidic work-up, ultimately provides corresponding ketone.[1]



Scheme 1.21 Transformations of Nitro-Aldol Product

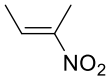
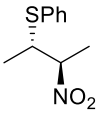
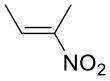
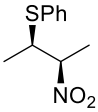
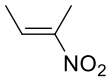
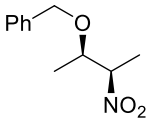
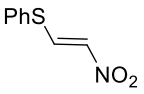
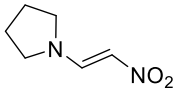
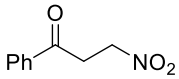
1.3.2. Michael Reaction

Michael addition is the one of most important tools in organic synthesis for the creation of carbon-carbon bond and carbon-hetereoatom bond. Nitro compounds were used as Michael acceptors as well as Michael donors. Nitroalkenes are good Michael acceptors because of the strong electron withdrawing nature of the nitro group. On the other hand, nitroalkanes are good Michael donors for 1,4-addition to electron deficient conjugated alkenes, under basic reaction conditions.[1]

1.3.2.1. Conjugate addition to Nitroalkenes

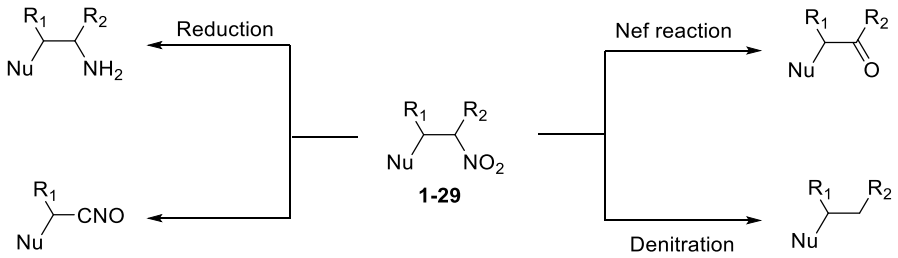
Michael addition of nitroalkenes using some selected nucleophiles were showed in **Scheme 1.22**. Nitroalkene **1-27a**, with in situ generated sulfur, selenium, and oxygen centered nucleophiles from the corresponding alcohols, smoothly formed Michael adducts **1-29a**, **1-29b** and **1-29c** in good yields.[35] The reaction of nitroalkenes **1-27b** and **1-27c** with amines and carbon-centered nucleophiles were provided Michael adducts **1-29d** and **1-29e** in good yields.[36]

1-27 **1-28** **1-29**

nitroalkene	HNu/MNu		product	yield (%)
 **1-27a**	+ LiSPh **1-28a**	–78 °C, AcOH	 **1-29a**; dr = 91:9	71
 **1-27a**	+ NaSePh **1-28b**	–78 °C, AcOH	 **1-29b**; dr = 91:9	68
 **1-27a**	+ $NaOCH_2Ph$ **1-28c**	–78 °C, AcOH	 **1-29c**; dr = 91:9	73
 **1-27b**	+ **1-28d**	THF, rt	 **1-29d**	85
1-27c	+ **1-28e**	LDA	 **1-29e**	81

Scheme 1.22 Conjugate Addition to Nitroalkenes

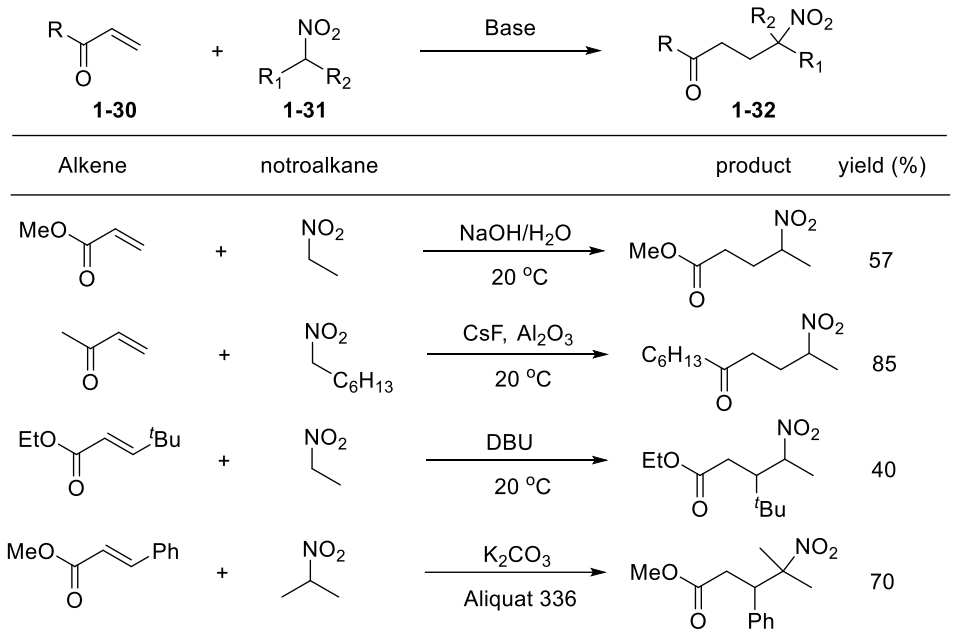
The newly formed carbon-carbon and/or carbon-heteroatom bonded Michael adducts were used for various oxidative and reductive transformations. The most classical transformation of Michael adducts derived from conjugate addition of nucleophiles to nitroalkenes are shown in **Scheme 1.23**. These adducts can be oxidized to ketones, can be reduced to amines, denitrated to alkanes/functionalized hydrocarbons, and nitrile oxides.[1]



Scheme 1.23 Transformations of Michael Adducts Derived from Nitroalkenes

1.3.2.2. Addition of Nitroalkanes to α,β-Unsaturated Enones

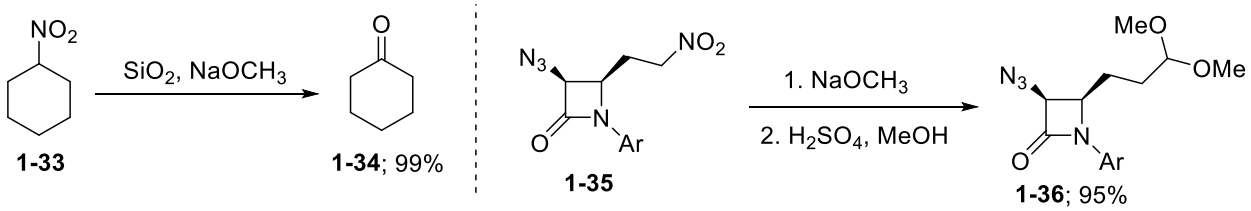
Nitroalkanes were widely used as Michael donors under basic conditions. Bases are used to generate nitronate anions are same as the Henry reaction. The selected examples of Michael reaction of nitroalkanes under basic reaction conditions are briefly summarized in **Scheme 1.24**.[37]



Scheme 1.24 Addition of Nitroalkanes to α,β-Unsaturated Enones

1.3.3. Nef Reaction

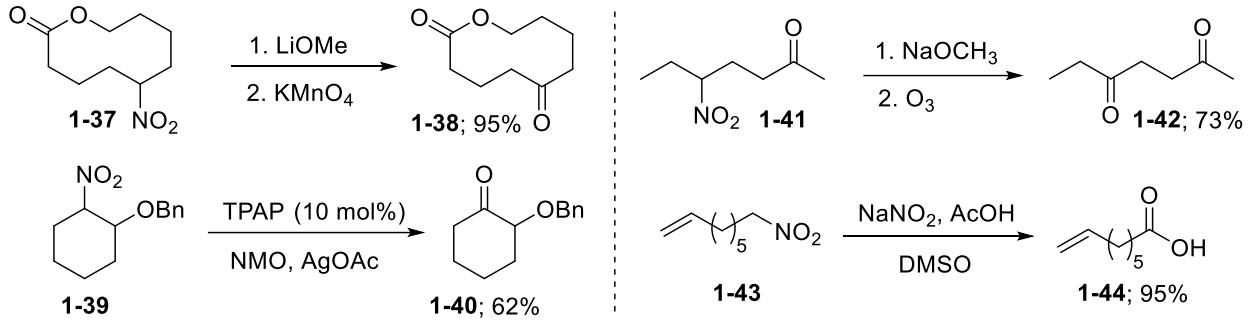
Nef reaction is one of the most useful transformations of nitro compounds, where the conversion of primary/secondary nitroalkanes and nitroalkens to the corresponding aldehydes, ketones and/or carboxylic acids. The most classical method for these transformations is the treatment of nitronate with acid. The other possible methods are oxidation of nitronates and the reduction of nitroalkenes.[1,38] The general example for classical method of Nef reaction is shown in **Scheme 1.25**, where nitroalkanes **1-33** and **1-35** are converted



Scheme 1.25 Nef Reaction in Presence of Acid

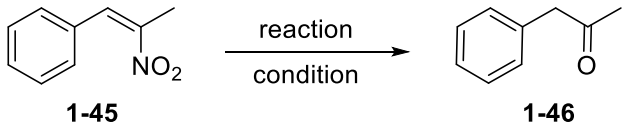
to the corresponding ketone **1-34** and acetal **1-36** using silica gel and sulfuric acid.[39]

Selected examples of nitronate oxidation using different oxidants are shown in **Scheme 1.26**. The nitronate derived from nitroalkanes **1-37**, **1-39**, **1-41** and **1-43** in the presence of $KMnO_4$, TPAP, O_3, and $NaNO_2$/AcOH, were converted to ketones **1-38**, **1-40**, **1-42** and **1-44** in good yields.[40]



Scheme 1.26 Nef Reaction with Oxidation Method

Nitroalkenes are directly converted to corresponding ketones using various reaction conditions such as Raney Ni, $CrCl_2$, $CdCl_2$, and electrochemical-Pb to provide ketone **1-46** in good yield as shown in **Scheme 1.27**.[41]



reaction condition	yield (%)
Raney Ni/NaH_2PO_2	88
$CrCl_2$	80
$LiBHR_3$, HCl	80
$CdCl_2$-Mg-H_2O	80
Pb	80

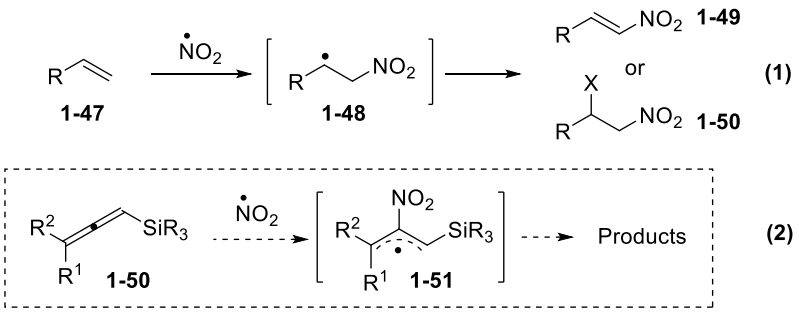
Scheme 1.27 Nitroalkenes to Ketones

1.4. Nitration of Silylallenes[†]

The most representative nitration method is based on the addition of nitrogen dioxide with an alkene starting material (**Scheme 1.28**, eq 1).[1] Alkene **1-47** reacts with nitrogen dioxyl radical to form carbon centered radical **1-48**, which can deliver the addition or the elimination product **1-49** or **1-59**. To generate structurally more elaborate nitro compounds, we envisioned the corresponding nitration of silylallenes **1-**

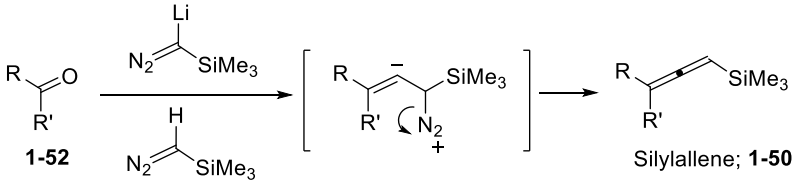
[†] Reproduced with permission from Sabbasani, V. R.; Lee, D. "Nitration of Silylallenes to Form Functionalized Nitroalkenes" *Org. Lett.* **2013**, *15*, 3954–3957.

50, which so far has not been reported in the literature (eq 2).[31] Compared to the addition of a nitrogen dioxyl with alkene, we expected that the addition of a radical species with silylallenes **1-50** should be more favorable due to the formation of a relatively more stable allylic radical intermediate **1-51**. The resulting radical intermediate will be directly captured by another radical species or be oxidized to the corresponding allylic cation, which then reacts with a nucleophile. Herein we studied the result of our investigation for the nitration of silylallenes under two different conditions, and facile 5-*endo-dig* cyclization of the products of nitroso-nitration of silylallenes, α-nitro- α,β-unsaturated silyl oximes, upon treatment with TBAF to form isooxazolidinone derivatives.



Scheme 1.28 Nitration of Simple Alkene versus Silylallene

While developing a method for the synthesis of differently substituted allenes and exploring their reactivities,[42] we prepared a series of trisubstituted silylallenes **1-50** via a three component coupling reaction involving ketone **1-52**, lithium trimethylsilyldiazomethane, and free trimethylsilyldiazomethane (**Scheme 1.29**).[42a] Occasionally in this study, we observed the instability of some of these silylallenes under air.[43] Unaware of any reported instability of the corresponding alkylsubstituted allenes, we inferred that the instability of silylallenes should be caused by the silyl substituent. This property, we envisioned, can be exploited in developing new chemical processes such as nitration, which were extensively studied with



Scheme 1.29 One-Step Synthesis of Silylallenes

alkenes under conditions that generate nitrogen dioxyl, and most representative conditions are: $NaNO_2$/AcOH/cerium ammonium nitrate (CAN),[21] $AgNO_2$/TEMPO,[24] $Fe(NO_3)_3 \cdot 9H_2O/FeCl_3$,[23] and tBuONO/TEMPO.[26]

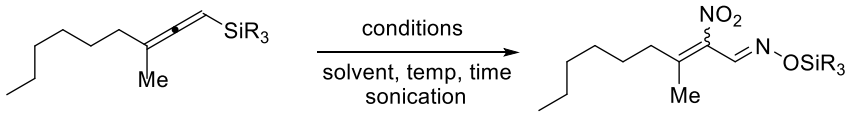
Not knowing which conditions are most suitable for silylallenes, we decided to screen these systems to find the optimal conditions (**Table 1.1**).When trimethylsilylallene **1-50a** was used as the substrate under sodium nitrite ($NaNO_2$)/acetic acid (AcOH)/cerium ammoniumnitrate (CAN) in chloroform ($CHCl_3$) or acetonitrile (CH_3CN), only decomposition of the substrate was observed (entry 1 and 2). Changing the conditions to silver nitrite/TEMPO in chloroform or 1,2-dichloroethane resulted in the same negative outcome (entry 3 and 4). Then, we changed the substrate from **1-50a** to **1-50b** where the trimethylsilyl group is replaced with a tertbutyldimethylsilyl group since we believed that substrate **1-50a** containing a trimethylsilyl group might not be compatible with the acidic conditions that cause protodesilylation.[44]

Gratifyingly, tert-butyldimethylsilyl allene **1-50b** smoothly participated in the addition reaction under $NaNO_2$/AcOH/CAN in $CHCl_3$ at room temperature to deliver the product α-nitro- α,β-unsaturated silyl oxime **1-53b** in 81% yield with a 1:1 ratio of E/Z isomers (entry 5). Running the reaction at higher temperature (50 ^oC) considerably shortened the reaction time and further improved the yield to 89% (entry 6). Reactions without AcOH or $NaNO_2$ did not proceed at all and returned the starting material intact (entry 7 and 8). On the other hand, the same reaction without CAN showed a similar reaction profile as that with CAN, providing product **1-53b** in 85% yield (entry 9). When another reagent combination of $AgNO_2$/TEMPO was tried, product **1-53b** was produced but only in 45% yield (entry 10). For the better solubility of $NaNO_2$ in AcOH, ultra-sonication method was used at 50 ^oC.

With the optimized reaction condition for nitration of silylallene in hand, we examined the substrate scope by using a variety of silylallenes (**Table 1.2**). Although CAN additive did not play any major role for the reaction of **1-50b**, we ran additional reactions with other substrates with and without CAN in parallel (entries 1, 2, 4, 5, and 8). From these data, we conclude that not only with **1-50b** but also with most of other silylallenes examined in general the CAN additive was unnecessary.

First, we probed the influence of the steric bulk of the silyl group by comparing the reactivity between

triethyl and triisopropylsilyl allenes **1-50c** and **1-50d**. Both substrates reacted smoothly to provide silyl oxime products **1-53c** and **1-53d** in 91 and 85% yield, respectively, both with 1:1 ratio of *E*/*Z* isomers (entries 1 and 2). The slightly inferior yield of the latter implies that the steric bulk of the silyl group plays a certain role but only to a minor extent. On the other hand, tert-butyl-substituted allene **1-50e** decomposed when treated under identical conditions (entry 3), which clearly indicates the important role of the silyl group to promote the current nitration reaction.



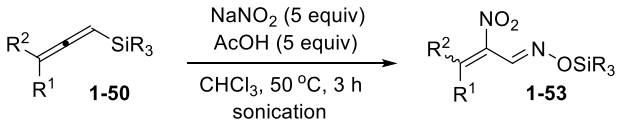
1-50a SiR_3= $SiMe_3$, **1-50b** SiR_3 = $SiMe_2{}^tBu$ **1-53a, 1-53b**

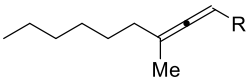
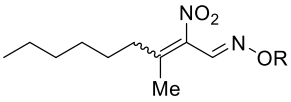
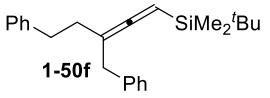
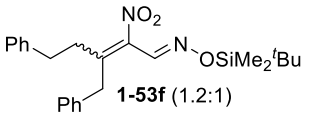
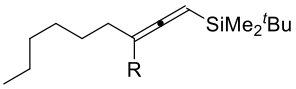
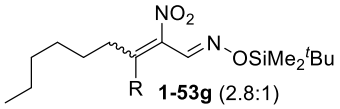
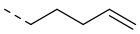
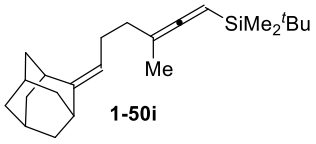
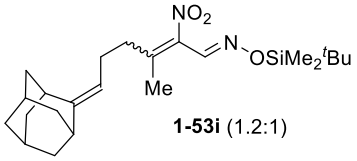
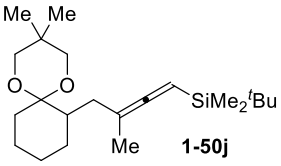
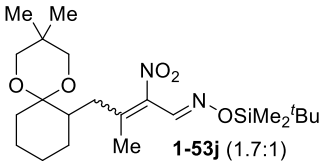
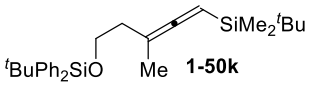
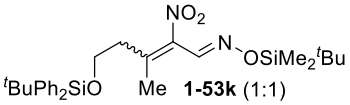
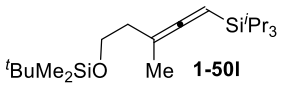
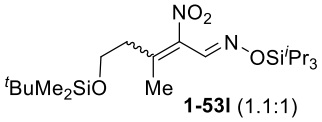
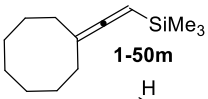
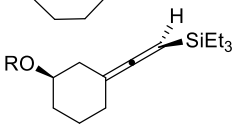
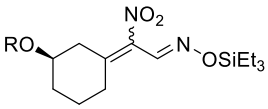
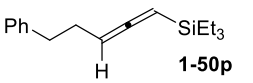
entry	allene	conditions	solvent	T (^oC)	time (h)	product	yield (%)[a]
1	**1-50a**	$NaNO_2$/AcOH/CAN	$CHCl_3$	25	2	decompose	-
2	**1-50a**	$NaNO_2$/AcOH/CAN	CH_3CN	25	2	decompose	-
3	**1-50a**	$AgNO_2$/ TEMPO	$ClCH_2CH_2Cl$	25	8	decompose	-
4	**1-50a**	$AgNO_2$/TEMPO	$CHCl_3$	25	8	decompose	-
5	**1-50b**	$NaNO_2$/AcOH/CAN	$CHCl_3$	25	24	**1-53b**	81 (1:1)[b]
6	**1-50b**	$NaNO_2$/AcOH/CAN	$CHCl_3$	50	3	**1-53b**	89 (1:1)[b]
7	**1-50b**	$NaNO_2$/CAN	$CHCl_3$	50	3	no reaction[c]	-
8	**1-50b**	AcOH/CAN	$CHCl_3$	50	3	no reaction[c]	-
9	**1-50b**	$NaNO_2$/AcOH	$CHCl_3$	50	3	**1-53b**	85 (1:1)[b]
10[d]	**1-50b**	$AgNO_2$/TEMPO	$ClCH_2CH_2Cl$	60	10	**1-53b**	45 (1:1)[b]

[a] Isolated yields after purification by flash chromatography. [b] *E*/*Z* ratio were determined by ^1H NMR. [c] Most starting material was recovered. [d] Similar yield in $CHCl_3$

Table 1.1 Optimization of Reaction Conditions

Next, we examined the effect of extra π-systems on the allene containing benzyl/phenethyl (**1-50f**), phenyl (**1-50g**), 4-pentenyl (**1-50h**), and 3-adamentylidene (**1-50i**) groups (entries 4─7). Other than a slight difference in yields, no byproducts involving these extra π-systems were observed. While benzyl-substituted substrate **1-50f** provided product **1-53f** in 83% yield (entry 4), phenyl and 4-pentenyl group-substituted substrate **1-50g** and **1-50h** afforded **1-53g** and **1-53h** in 88 and 86% yield, respectively (entry 5 and 6). The differences in *E*/*Z* ratio for the products should be the consequence of the steric bias of these



entry	allene	product (*E*/*Z*)[b]	yield (%)[a]
			
1	**1-50c** R = $SiEt_3$	**1-53c** (1:1)	91 (87)[c]
2	**1-50d** R = Si^iPr_3	**1-53d** (1:1)	85 (80)[c]
3	**1-50e** R = *t*-Bu	decomposed	—
4	 **1-50f**	 **1-53f** (1.2:1)	83 (86)[c]
5	 **1-50g** R = Ph	 **1-53g** (2.8:1)	88 (85)[c]
6	**1-50h** R = 	**1-53h** (1:1)	86
7	 **1-50i**	 **1-53i** (1.2:1)	67
8	 **1-50j**	 **1-53j** (1.7:1)	93
9	 **1-50k**	 **1-53k** (1:1)	96 (91)[c]
10	 **1-50l**	 **1-53l** (1.1:1)	83
11	 **1-50m**	decomposed	—
12	 R = $SiMe_2(t\text{Bu})$ **1-50n**	 **1-53n** (1.3:1)	88 (86)[c]
13	R = Ac **1-50o**	**1-53o** (1.1:1)	81
14	 **1-50p**	no reaction[d]	—

[a] Isolated yields. [b] *E*/*Z* ratios were determined by ^{1}H NMR. [c] The yields in the parentheses are for the reactions with CAN. [d] Starting material was recovered even after heating to 70 °C.

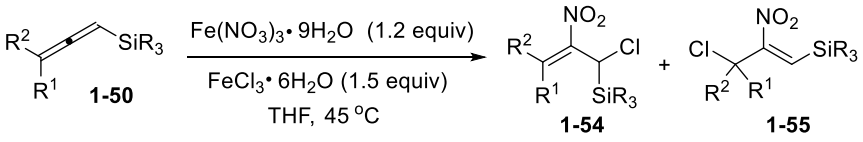
Table 1.2 Scope of the Reaction with $NaNO_2$/AcOH with and without CAN

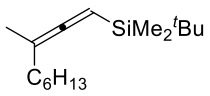
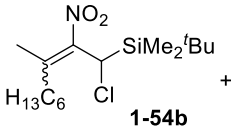
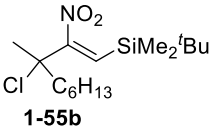
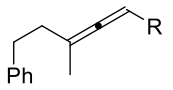
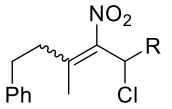
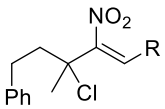
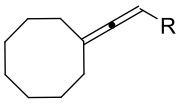
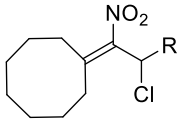
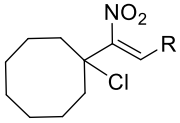
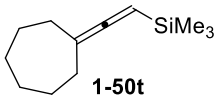
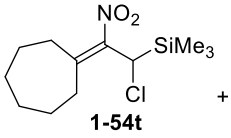
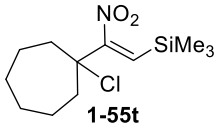
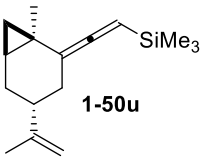
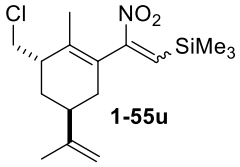
substituents. Allene **1-50i** containing a 3-adamantylidene moiety provided product **1-53i** in 67% yield without complication by the trisubstituted alkenyl functionality (entry 7). Based on these results, we concluded that the silyl allene moiety is much more reactive than simple alkene functionality toward nitrogen dioxyl. Other silyl allenes **1-50j, 1-50k** and **1-50l** containing oxygen-based functional groups such as ketal or silyl ether moieties were tested (entries 8─10). While, ketal functional group containing silylallene **1-50j** smoothly afforded nitration product **1-53j** in 93% yield with the E/Z ratio 1.7:1 (entry 8). Allenes **1-50k** and **1-50l** having the silyl ether functionality delivered the nitration products **1-53k** and **1-53l** in 96, and 83% yield with *E/Z* ratios are almost 1:1 (entries 9 and 10).

Even though cyclooctanylidene allene **1-50m** containing trimethylsilyl substituent decomposed (entry 11), cyclohexanylidene allene **1-50n** and **1-50o** substituted with triethysilyl group smoothly afforded nitration products **1-53n** and **1-53o** in 88% and 81% yield, respectively (entries 12 and 13). Unexpectedly, disubstituted silyl allene **1-50p** was recovered intact under identical reaction conditions (entry 14), which is probably due to the difficulty in forming a relatively unstable secondary carbon-centered radical intermediate form **1-50p** as opposed to the tertiary from trisubstituted silyl allenes.

Having silylallenes successfully engaged in nitration with metal nitrites, we next examined their nitration using $Fe(NO_3)_3 \cdot 9H_2O$ as the source of nitrite under oxidative conditions (**Table 1.3**). Even though silylallene **1-50b** decomposed when exposed to $Fe(NO_3)_3 \cdot 9H_2O$ alone, by adding an oxidant such $FeCl_3 \cdot 6H_2O$ to the reaction, chlorinated nitroalkenes **1-54b** and **1-55b** were obtained in 83% yield with a 1:1 ratio (entry 1). Gratifyingly, silylallene **1-50q** containing a sterically less encumbered trimethylsilyl group, not a viable substituent in the previous reaction, is not only compatible with the conditions but also controlled the regioselectivity, affording products **1-54q** and **1-55q** in 82% yield with a 10:1 ratio (entry 2). The reaction of tert-butyl allene **1-50r** afforded **1-54r** and **1-55r** in 70% combined yield without regioselectivity (entry 3). A related pair of cyclooctanylidene allenes **1-50m** and **1-50s** showed similar behaviors where both trimethylsilyl and tert-butyl groups efficiently controlled the regioselectivity, providing **1-54m**/**1-55m** and **1-54s**/**1-55s** in 78 and 80% yield with 25:1 and 20:1 ratio, respectively (entries 4 and 5). Cycloheptanylidene allene **1-50t** also afforded a mixture of **1-54t** and **1-55t** in 79% yield with

20:1 selectivity (entry 6). Carvone-derived cyclopropane-containing silylallene **1-50u** resulted in 64% yield of only the cyclopropane ring-opened product **1-55u** in a 2:1 ratio (entry 8).



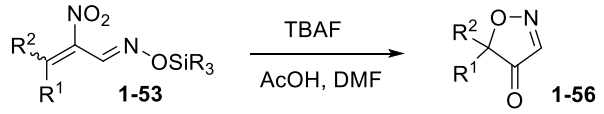
entry	silylallene	product	yield (%)[a]	**1-54**:**1-55**[b,c]
1	 **1-50b**	 **1-54b** +  **1-55b**	83	1:1
2	 **1-50q**, R = $SiMe_3$	 **1-54q** +  **1-55q**	82	10:1
3	**1-50r**, R = *t*-Bu	**1-54r** + **1-55r**	70	1:1
4	 **1-50m**, R = $SiMe_3$	 **1-54m** +  **1-55m**	78	25:1
5	**1-50s**, R = *t*-Bu	**1-54s** + **1-55s**	80	20:1
6	 **1-50t**	 **1-54t** +  **1-55t**	79	20:1
7	 **1-50u**	 **1-55u**	64	2:1

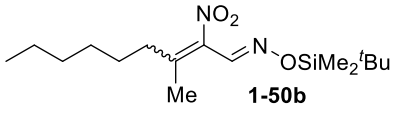
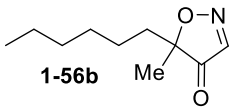
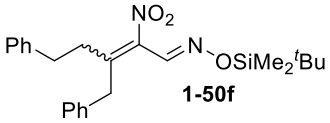
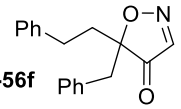
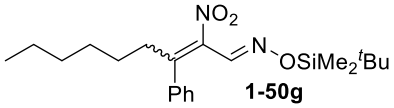
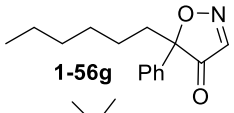
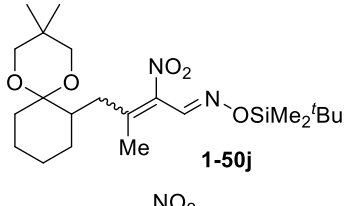
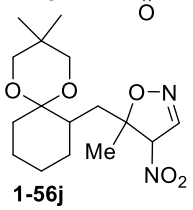
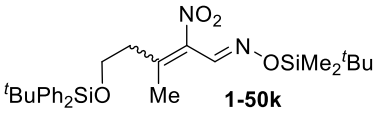
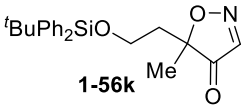
[a] Combined yields after purification. [b] The ratios of **1-54** and **1-55** were determined by ^{1}H NMR analysis. [c] The double-bond geometry of **1-55** was determined by NOE experiments

Table 1.3 Nitration Reaction with Iron(III) Nitrate

Next, we examined the behavior of functionalized nitroalkenes **1-53** by treating them with desilylating agent (**Table 1.4**). Upon treatment of **1-53** with TBAF, novel isooxazolidinone derivatives **1-56** were obtained in moderate yields, which is the consequence of a spontaneous Nef reaction initiated by 5-*endo-dig* Michael addition of the oxime oxygen onto the electron-deficient nitroalkene moiety. Nitroalkenes **1-50b**, **1-50f** and **1-50g** in presence of TBAF/AcOH provided isooxalidinones **1-56b**, **1-56f** and **1-56g** in

moderate yield 54, 58 and 35% respectively (entries 1─3). In the case of **1-50j** (dr = 1.7:1), the nitronate intermediate, however, was not hydrolyzed, preserving the nitro group delivered **1-56j** in 68% yield (entry 4). The desilylation of **1-50k** was chemoselective such that even a primary silyl ether moiety in **1-50k** was untouched while the silyl ether of oxime moiety was desilylated and participated in subsequent Michael reaction (entry 5) gave the cyclized product **1-56k** in 52% yield (entry 5).



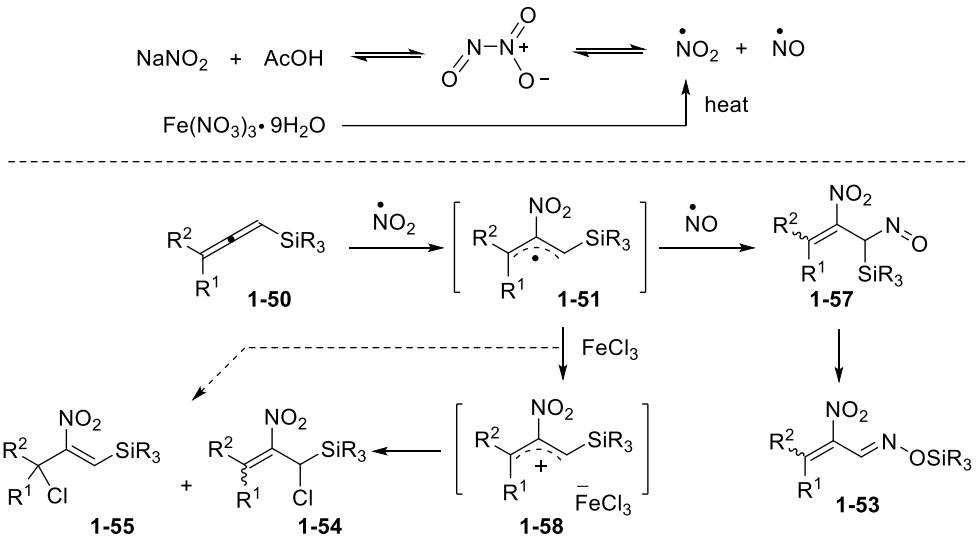
entry	substrate **1-53**	product	yield(%)[a]
1			54
2			58
3			35[b]
4			68
5			52

[a] Isolated yields. [b] A 1:1 mixture with 1-phenylheptan-1-one.

Table 1.4 Conversion of α-Nitro α,β-Unsaturated Silyl Oximes to Isooxazolidinones

A plausible reaction mechanism for the formation of **1-53** and **1-54**/**1-55** are depicted in **Scheme 1.30**. The given reagents combinations would generate nitrogen dioxyl, which then react with silylallene **1-50** to generate allylic radical **1-51**. In the case with $NaNO_2$/AcOH, **1-51** reacts with nitroxyl, resulting in the formation of **1-57**, which then undergoes tautomerization to provide observed product **1-53**. On the other hand, under the conditions with $Fe(NO_3)_3{\cdot}9H_2O/FeCl_3$, intermediate radical **1-51** would react with ferric

chloride either directly or indirectly via an electron-transfer process to form ion pair **1-58** followed by chloride transfer to give **1-54** or **1-55** depending on the substituents on **1-58**.



Scheme 1.30 Plausible Mechanism for the Formation of α-Nitro α,β-Unsaturated Silyl Oximes

1.5. Summary

In summary, an efficient method for the nitration of silylallenes with two different reaction conditions $NaNO_2$/AcOH and $Fe(NO_3)_3{\cdot}9H_2O/FeCl_3$ has been developed. The reaction with $NaNO_2$/AcOH provided a new class of nitroalkenes, α-nitro-α,β-unsaturated silyl oximes, and the reaction with $Fe(NO_3)_3{\cdot}9H_2O/FeCl_3$, allylic chloro substituted nitroalkenes were generated. Another novel class of compounds isooxazolidinones were obtained upon treating the initially formed α-nitro-α,β-unsaturated silyl oximes with TBAF in acetic acid.

1.6. Experimental Details

1.6.1. General Information

Reactions were carried out in oven or flame-dried glassware unless otherwise noted. Compounds were purchased from Aldrich or Acros or TCI America unless otherwise noted. Chloroform ($CHCl_3$) was purchased from Aldrich and used as received. Tetrahydrofuran (THF) was distilled over sodium and benzophenone under nitrogen atmosphere. Flash chromatography was performed using silica gel 60 Å (32−63 mesh) purchased from Silicycle Inc. Analytical thin layer chromatography (TLC) was performed

on 0.25 mm E. Merck pre-coated silica gel 60 (particle size 0.040−0.063 mm). Yields refer to chromatographically and spectroscopically pure compounds unless otherwise stated. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer and DPX-400 spectrometers. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), sext (sextet), m (multiplet), b (broad), and app (apparent). ^{1}H NMR signals that fall within a ca. 0.3 ppm range are generally reported as a multiplet, with a single chemical shift value corresponding to the center of the peak. Coupling constants, J, are reported in Hz (Hertz). Electrospray ionization (ESI) mass spectra were recorded on a Waters Micromass Q-Tof Ultima in the University of Illinois at Urbana-Champaign. Electron impact (EI) mass spectra and Chemical Ionization (CI) mass spectra were obtained using a Micromass 70-VSE in the University of Illinois at Urbana– Champaign.

1.6.2. Representative Procedure for Silylallene Synthesis

Silylallenes **1-50m**, **1-50q**, **1-50t** and **1-50u** were prepared by published three component coupling involving ketones, lithiated trimethylsilyl diazomethane and trimethylsilyl diazomethane as shown.[42a] Silylallenes **1-50a**–**l**, **1-50n** and **1-50o** were prepared by the reported procedure from the corresponding propargylic alcohols via the Brook rearrangement followed by mesylation and cuprated-based S_N2' substitution.[45]

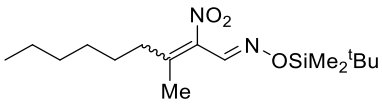
1.6.3. General Procedures for Nitration of Silylallenes with $NaNO_2$/AcOH: Silylallene **1-50b** (0.40 mmol, 1 equiv) in 10 mL chloroform ($CHCl_3$) was taken into a thick walled Schlenk tube, and then $NaNO_2$ (2 mmol, 5 equiv) and AcOH (2 mmol, 5 equiv) were added to the reaction tube. The reaction mixture was degassed under vacuum at -78 ^{o}C, and then sonicated for 3 hours at 50 ^{o}C. The tube was opened to air at room temperature and 10 mL water added to the reaction mixture, which than extracted with dichloromethane (CH_2Cl_2) and dried ($MgSO_4$). After removal of the solvent, the crude product was purified by column chromatography (EtOAc/hexanes, 1:9) to give α-nitro-α,β-unsaturated silyl oximes **1-53b** as yellow oil (89%).

1.6.4. General Procedures for Nitration of Silylallenes with $Fe(NO_3)_3{\cdot}9H_2O/FeCl_3$: Substrate silylallene **1-50b** (0.20 mmol, 1 equiv), $Fe(NO_3)_3{\cdot}9H_2O$ (0.24 mmol, 1.2 equiv) and $FeCl_3{\cdot}6H_2O$ (0.30 mmol, 1.5

equiv) were dissolved in THF in a thick-walled Schlenk tube equipped with a magnetic stir bar. The reaction mixture was degassed under vacuum at -78 °C, and then stirred at 45 °C for 8 hours. The tube was opened to air at room temperature and the solvent was removed under reduced pressure. The organic product was isolated by flash column chromatography on silica gel (EtOAc/hexanes, 1:9) to give nitro alkene **1-54b** and **1-55b** (83%).

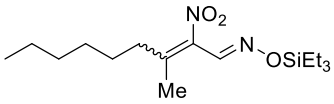
1.6.5. General Procedure for the Conversion of Silyloximes to Isooxazolidinones: α-Nitro-α,β-unsaturated silyl oximes **1-53b** (0.20 mmol, 1 equiv) and DMF (6 mL) were taken into a round bottom flask under nitrogen, and then AcOH (0.20 mmol, 1 equiv) and 1 M tetrabutyl ammonium fluoride (TBAF) in THF (0.20 mmol, 1 equiv) were added to the reaction mixture. The reaction mixture was then stirred for 5 hours at room temperature, which was quenched with saturated aqueous NH_4Cl solution, extract with ethyl acetate and dried ($MgSO_4$). After concentration, the crude product was purified by column chromatography (EtOAc/hexanes, 1:9) to give isooxazolidinones **1-56b** (54%).

1.6.6. Selected Characterization Data



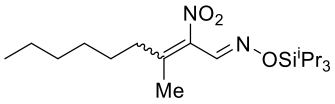
1-53b (*E/Z* = 1:1)

1-53b (1:1 mixture of *E/Z* isomers, 89% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 and 7.40 (2S, 1H), 2.27-2.25 (m, 1H), 2.19-2.17 (m, 1H), 1.99 and 1.90 (2S, 3H), 1.50 (m, 2H), 1.32-1.26 (m, 6H), 0.89-0.86 (m, 12H), 0.14 (S, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 146.4, 141.5, 141.4, 139.8, 139.2, 34.6, 34.4, 31.5, 31.4, 29.2, 28.8, 27.7, 27.3, 25.6, 22.4, 19.0, 18.9, 17.9, 13.9; HRMS (ESI**)** calcd for $C_{16}H_{22}N_2O_3Si$ $[M+H]^+$ 329.2260, found 329.2260.



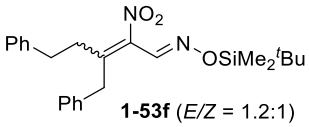
1-53c (*E/Z* = 1:1)

1-53c (1:1 mixture of *E/Z* isomers, 91% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42 and 7.40 (2S, 1H), 2.30-2.27 (m, 1H), 2.20-2.17 (m, 1H), 2.01 and 1.90 (2S, 3H), 1.53-1.48 (m, 2H), 1.28-1.24 (m, 6H), 0.98-0.86 (m, 12H), 0.70-0.65 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.9, 146.6, 141.6, 141.4, 139.7, 139.2, 34.8, 34.4, 31.5, 31.4, 29.7, 29.2, 28.9, 27.6, 27. 4, 22.5, 22.4, 19.1, 18.9, 13.9, 6.4, 6.3, 4.1; HRMS (ESI**)** calcd for $C_{16}H_{22}N_2O_3Si$ $[M+H]^+$ 329.2263, found 329.2261.



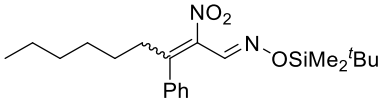
1-53d (*E/Z* = 1:1)

1-53d (1:1 mixture of *E/Z* isomers, 85% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 and 7.39 (2S, 1H), 2.31-2.27 (m, 1H), 2.21-2.18 (m, 1H), 2.01 and 1.91 (2S, 3H), 1.52-1.48 (m, 2H), 1.34-1.28 (m, 6H), 1.22-1.16 (m, 3H), 1.04-1.00 (m, 18H), 0.89-0.86 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.6, 146.3, 141.2, 141.0, 139.7, 139.1, 34.8, 34.4, 31.5, 31.4, 29.2, 28.9, 27.7, 27.5, 22.5, 22.4, 19.1, 19.0, 18.5, 18.4, 17.6, 14.0, 12.0, 11.8; HRMS (ESI**)** calcd for $C_{19}H_{39}N_2O_3Si$ $[M+H]^+$ 371.2730, found 371.2738.



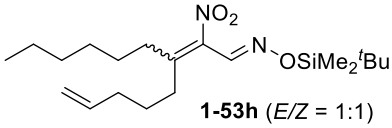
1-53f (*E/Z* = 1.2:1)

1-53f (1.2:1 mixture of *E/Z* isomers, 83% yield): **Major Isomer**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32-7.05 (m, 11H), 3.65 (s, 2H), 2.67 (t, *J* = 7.8 Hz, 2H), 2.39 (t, *J* = 7.8 Hz, 2H), 0.92 (s, 9H), 0.17 (s, 6H); **Minor Isomer**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.60 (s, 1H), 7.32-7.05 (m, 10H), 3.52 (s, 2H), 2.78-2.74 (m, 2H), 2.54-2.51 (m, 2H), 0.94 (s, 9H), 0.20 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.7, 145.6, 141.8, 141.2, 140.8, 140.7, 140.5, 139.7, 136.2, 135.7, 129.2, 129.0, 128.8, 128.7, 128.5, 128.3, 127.4, 127.1, 126.7, 126.4, 38.3, 37.7, 34.5, 34.3, 33.6, 25.6, 17.9, -5.4, -5.5.



1-53g (*E/Z* = 2.2:1)

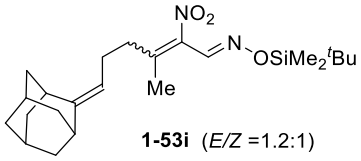
1-53g (2:1 mixture of *E/Z* isomers, 88% yield): **Major Isomer**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.42-7.22 (m, 5H), 6.86 (s, 1H), 2.53-2.49 (m, 2H), 1.41-1.18 (m, 8H), 0.93 (s, 9H), 0.84 (t, *J* = 7.0 Hz, 3H), 0.16 (s, 6H); **Minor Isomer**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.35-7.18 (m, 5H), 2.55-2.53 (m, 2H), 1.41-1.18 (m, 8H), 0.89 (s, 9H), 0.86-0.85 (m, 3H), 0.16 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7, 147.2, 142.2, 140.8, 140.6, 136.3, 135.6, 129.7, 129.0, 128.8, 128.6, 128.5, 126.6, 34.4, 34.2, 31.4, 31.3, 29.1, 28.9, 28.0, 27.1, 25.7, 25.6, 22.4, 17.9,14.0, -5.5; HRMS (ESI**)** calcd for $C_{21}H_{35}N_2O_3Si$ $[M+H]^+$ 391.2417, found 391.2416.



1-53h (*E/Z* = 1:1)

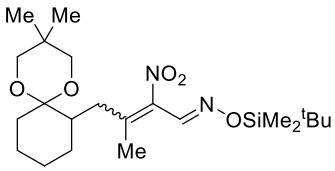
1-53h (1:1 mixture of *E/Z* isomers, 86% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 1H), 5.79-5.72 (m, 1H), 5.05-4.96 (m, 2H), 2.28-2.25 (m, 2H), 2.20-2.16 (m, 2H), 2.10-2.06 (m, 2H), 1.63-1.56 (m, 2H), 1.50-1.45 (m, 2H), 1.33-1.27 (m, 6H), 0.90-0.85 (s, 12H), 0.14 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.8, 149.7, 141.4, 139.7, 139.6, 137.5,

137.2, 115.8, 115.4, 33.7, 33.3, 32.3, 32.1, 31.6, 31.5, 31.4, 29.4, 29.1, 28.0, 27.2, 27.1, 22.4, 17.9, 14.0, -5.5.



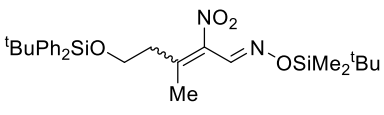
1-53i (*E/Z* =1.2:1)

1-53i (1.2:1 mixture of *E/Z* isomers, 67% yield): **Major Isomer**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (s, 1H), 5.00-4.98 (m, 1H), 2.72 (s, 1H), 2.25-2.21 (m, 6H), 1.92 (m, 6H), 1.88-1.65 (m, 8), 0.89 (s, 9H), 0.14 (s, 6H); **Minor Isomer**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 1H), 5.02-4.96 (m, 1H), 2.79 (s, 1H), 2.35-2.32 (m, 6H), 2.00 (s, 3H), 1.88-1.81 (m, 11H), 0.90 (s, 9H), 0.15 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 149.6, 146.3, 145.8, 141.6, 141.4, 140.2, 139.5, 113.9, 113.2, 40.6, 40.5, 39.0, 38.9, 37.2, 37.1, 35.3, 35.1, 32.2, 32.1, 28.6, 28.5, 26.3, 26.2, 25.7, 24.9, 24.6, 19.4, 19.1, 17.9, -5.5; HRMS (ESI**)** calcd for $C_{23}H_{39}N_2O_3Si$ $[M+H]^+$ 419.2742, found 419.2740.



1-53j (*E/Z* =1.7:1)

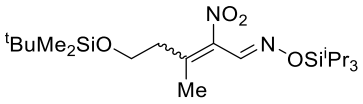
1-53j (1.7:1 mixture of *E/Z* isomers, 93% yield): ***E*-Isomer**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (s, 1H), 3.70 (d, *J* = 15 Hz, 1H), 3.50 (d, *J* = 10 Hz, 1H), 3.31-3.28 (m, 2H), 2.78 (dd, *J* = 13.2, 2.4 Hz, 1H), 2.68 (d, *J* = 13.2 Hz, 1H), 2.29 (dd, *J* = 13.0, 10.91 Hz, 1H), 1.96 (s, 3H), 1.70-1.49 (m, 4H), 1.30-1.10 (m, 7H), 0.87 (s, 9H), 0.72 (s, 3H), 0.12 (s, 3H), 0.12 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.3, 141.9, 140.9, 98.0, 69.7, 69.5, 44.9, 33.2, 29.9, 27.4, 27.3, 27.1, 26.3, 25.9, 25.8, 25.6, 25.2, 23.4, 22.5, 22.2, 19.2, -5.5; ***Z*-Isomer**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (s, 1H), 3.73 (d, *J* = 11.3 Hz, 1H), 3.56 (d, *J* = 11.3 Hz, 1H), 3.29 (d, *J* = 11.3 Hz, 2H), 2.74 (dd, *J* = 13.4, 3.0 Hz, 1H), 2.63 (dd, J = 13.4, 10.5 Hz, 2H), 1.89 (s, 3H), 1.74-1.69 (m, 1H), 1.62-1.1.46 (m, 3H), 1.36-1.20 (m, 2H), 1.19-0.99 (m, 5H), 0.88 (s, 9H), 0.71 (s, 3H), 0.13 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.2, 141.6, 140.5, 98.1, 69.8, 69.4, 44.4, 32.4, 29.8, 27.4, 27.1, 25.6, 25.2, 23.4, 22.3, 22.2, 19.0, -5.5; HRMS (ESI**)** calcd for $C_{22}H_{40}N_2O_5Si$ $[M+H]^+$ 441.2785, found 441.2775.



1-53k (*E/Z* =1:1)

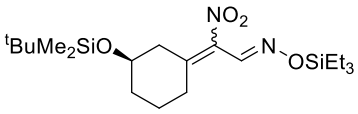
1-53k (1:1 mixture of *E/Z* isomers, 96% yield): **Isomer-1**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70-7.41 (m, 11H), 3.92 (t, *J* = 6.2 Hz, 2H), 2.64 (t, *J* = 6.2 Hz, 2H), 1.94 (s, 3H), 1.10 (s, 9H), 0.95 (s, 9H), 0.21 (s, 6H);

Isomer-2: 7.70-7.41 (m, 11H), 3.84 (t, *J* = 6.0 Hz, 2H), 2.49 (t, *J* = 6.0 Hz, 2H), 1.90 (s, 3H), 1.10 (s, 9H), 0.95 (s, 9H), 0.20 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 142.7, 141.6, 141.5, 141.4, 140.4, 135.8, 135.6, 133.3, 132.9, 130.0, 129.8, 127.9, 127.8, 62.0, 61.0, 37.2, 26.9, 25.7, 19.9, 19.2, 19.1, 18.8, 18.0, -5.4; HRMS (ESI**)** calcd for $C_{28}H_{43}N_2O_4Si_2$ $[M+H]^+$ 527.2761, found 527.2765.



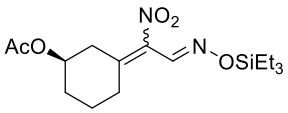
1-53l (*E/Z* =1.1:1)

1-53l (1:1 mixture of *E/Z* isomers, 83% yield): **Major isomer**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41 (s, 1H), 3.85 (t, *J* = 6.2 Hz, 2H), 2.56 (t, *J* = 6.2 Hz, 2H), 1.99 (s, 3H), 1.22-1.15 (m, 3H), 1.04 (m, 18H), 0.87 (s, 9H), 0.04 (s, 6H); **Minor Isomer**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (s, 1H), 3.78 (t, *J* = 6.0 Hz, 2H), 2.44 (t, *J* = 6.0 Hz, 2H), 2.01 (s, 3H), 1.22-1.15 (m, 3H), 1.03 (m, 18H), 0.07 (m, 9H), 0.03 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.5, 142.9, 141.3, 141.1, 140.0, 61.6, 60.6, 37.6, 37.5, 25.9, 25.8, 20.4, 19.2, 10.7, 17.6, 11.8, 11.5, -5.4, -5.5; HRMS (ESI**)** calcd for $C_{22}H_{45}N_2O_4Si_2$ $[M+H]^+$ 445.2918, found 445.2910.



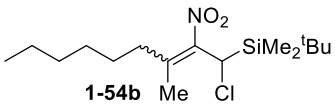
1-53n (*E/Z* =1.3:1)

1-53n (1.3:1 mixture of *E/Z* isomers, 88% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (s, 1H), 3.91-3.87 (m, 1H), 2.69 (dd, *J* = 13.4, 3.1 Hz, 1H), 2.33-2.27 (m, 2H), 2.18-2.16 (m, 2H), 1.96-1.95 (m, 1H), 1.86-1.83 (m, 1H), 1.58-1.48 (m, 1H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.86 (s, 9H), 0.69 (q, *J* = 7.9 Hz, 6H), 0.05 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 146.0, 141.0, 138.4, 70.1, 39.4, 34.5, 30.4, 25.7, 22.7, 18.0, 6.4, 4.1, -4.8, -4.9; HRMS (EI**)** calcd for $C_{20}H_{40}O_4N_2Si_2$ $[M]^+$ 428.2526, found 428.2531.



1-53o (*E/Z* =2.2:1)

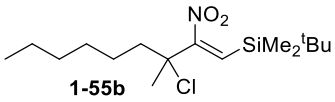
1-53o (1.3:1 mixture of *E/Z* isomers, 81% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (s, 1H), 5.05-5.03 (m, 1H), 2.70 (dd, *J* = 14.2, 6.6 Hz, 1H), 2.57 (dd, *J* = 14.2, 3.5 Hz, 1H), 2.36-2.23 (m, 2H), 2.03 (s, 3H), 1.91-1.70 (m, 4H), 0.94 (t, *J* = 7.9 Hz, 9H), 0.68 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.1, 144.0, 141.0, 136.3, 70.6, 34.6, 30.2, 30.0, 22.5, 21.1, 6.3, 4.1.



1-54b

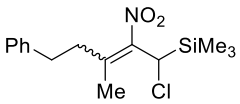
1-54b (1:1 mixture of *E/Z* isomers): ***E*-Isomer**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.47 (s, 1H), 2.20-2.16 (m, 2H), 1.90 (s, 3H), 1.34-1.25 (m, 8H), 0.97 (s, 9H), 0.93-0.89 (m, 3H), 0.28 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7, 138.5, 41.3, 35.2,

34.9, 31.6, 31.5, 29.3,27.7, 26.9, 26.4, 22.5, 19.8, 17.8, 14.0, 6.5; ***Z*-Isomer**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.42 (s, 1H), 2.15-2.12 (m, 2H), 1.87 (s, 3H), 1.34-1.25 (m, 8H), 0.97 (s, 9H), 0.91-0.86 (m, 3H), 0.28 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.3, 137.0, 41.5, 35.2, 31.6, 31.5, 29.3, 27.7, 27.6, 26.9, 22.6, 18.7, 14.1, 6.7; HRMS (EI**)** calcd for $C_{16}H_{32}O_2ClNSi$ $[M]^+$ 333.1890, found 333.1894.



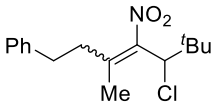
1-55b

1-55b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.03 (s, 1H), 2.05-2.01 (m, 2H), 1.79 (s, 3H), 1.45-1.25 (m, 8H), 0.91 (s, 9H), 0.89 (t, *J* = 6.8 Hz, 3H), 0.09 (s, 3H), 0.08 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.4, 123.9, 69.9, 43.3, 31.5, 29.9, 28.9, 26.3, 25.0, 22.5, 16.8, 14.0, -6.9; HRMS (EI**)** calcd for $C_{16}H_{32}O_2ClNSi$ $[M]^+$ 333.1890, found 333.1891.



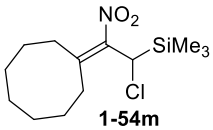
1-54q (*E/Z* = 1:1)

1-54q (1:1 mixture of *E/Z* isomers): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.17 (m, 5H), 4.22-isomer1, 4.17-isomer2 (s, 1H), 2.90-2.73 (m, 2H), 2.58-2.36 (m, 2H), 1.91-isomer1, 1.90-isomer2 (s, 3H), 0.19-isomer1, 0.17-isomer2 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.7, 148.3, 140.4, 140.0, 138.0, 136.4, 128.9, 128.8, 128.6, 128.5, 128.4, 128.3, 128.2, 126.7, 126.4, 126.2, 45.2, 44.7, 37.1, 36.5, 34.1, 34.0, 19.7, 18.7, -2.3, -2.4; HRMS (EI**)** calcd for $C_{15}H_{22}O_2ClNSi$ $[M]^+$ 311.1108, found 311.1113.



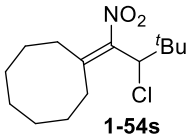
1-54r (*E/Z* = 1:1)

1-54r (1:1 mixture of *E/Z* isomers): I**somer-1**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.16 (m, 5H), 4.70 (s, 1H), 2.79 (t, *J* = 5 Hz, 2H), 2.53 (t, *J* = 5 Hz, 2H) 1.79 (s, 3H), 1.04 (s, 9H); I**somer-2**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35-7.16 (m, 5H), 4.70 (s, 1H), 2.90-2.83 (m, 2H), 2.35-2.27 (m, 2H), 1.91 (s, 3H), 1.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ147.6, 147.0, 140.2, 140.0, 137.6, 134.2, 128.8, 128.6, 128.5, 128.3, 128.2, 126.7, 126.4, 64.2, 63.9, 45.5, 37.6, 37.3, 37.1, 35.5, 34.1, 33.6, 31.5, 29.7, 29.0, 28.9, 26.8, 19.2, 18.2; HRMS (EI**)** calcd for $C_{16}H_{22}O_2ClN$ $[M]^+$ 295.1339, found 293.1341.



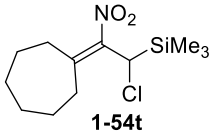
1-54m

1-54m (78% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.27 (s, 1H), 2.36 (t, *J* = 5 Hz, 2H), 2.25-2.22 (m, 2H), 1.77-1.44 (m, 10H), 0.21 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.1, 144.1, 45.3, 32.6, 30.5, 28.5, 27.6, 26.0, 25.4, 24.1, -2.0; HRMS (EI**)** calcd for $C_{13}H_{24}O_2ClNSi$ $[M]^+$ 289.1264, found 289.1260.



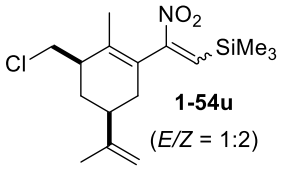
1-54s

1-54s (80% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.73 (s, 1H), 2.38-2.33 (m, 2H), 2.21-2.15 (m, 2H), 1.84-1.45 (m, 10H), 1.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.7, 143.5, 64.2, 37.2, 31.9, 29.6, 29.2, 27.2, 26.8, 25.8, 25.0, 23.8; HRMS (EI**)** calcd for $C_{14}H_{24}O_2ClN$ $[M]^+$ 273.1495, found 273.1490.



1-54t

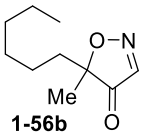
1-54t (80% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.26 (s, 1H), 2.41-2.34 (m, 2H), 2.31-2.25 (m, 2H), 1.81-1.79 (m, 1H), 1.71-1.67 (m, 2H), 1.62-1.52 (m, 4H), 1.47-1.41 (m, 1H), 0.20 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.8, 142.5, 44.6, 32.3, 31.7, 28.6, 28.1, 27.0, 26.7, -2.3; HRMS (EI**)** calcd for $C_{12}H_{22}O_2ClNSi$ $[M]^+$ 275.1108, found 275.1104.



1-54u

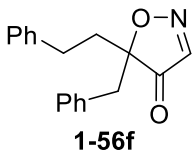
(*E/Z* = 1:2)

1-54u (2:1 mixture of *E/Z* isomers): ***Z*-isomer**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.97 (s, 1H), 4.78 (s, 1H), 4.77 (s, 1H), 3.72-3.70 (m, 1H), 3.50-3.46 (m, 1H), 2.52-1.97 (m, 6H), 1.76 (s, 3H), 1.70 (s, 3H), 0.21 (s, 9H); ***E*-isomer**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.18 (s, 1H), 4.73-4.70 (m, 2H), 3.74-3.70 (m, 1H), 3.41-3.36 (m, 1H), 2.52-1.97 (m, 6H), 1.76 (s, 3H), 1.66 (s, 3H), 0.16 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.0, 136.1, 134.4, 131.9, 130.0, 128.1, 109.6, 45.9, 45.6, 13.1, 36.0, 35.8, 35.7, 35.1, 29.7, 29.0, 28.8, 20.8, 19.4, 19.0, -1.0, -1.2.



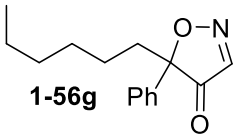
1-56b

1-56b (54% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (s, 1H), 1.78 (m, 2H), 1.35 (s, 3H), 1.33-1.07 (m, 8H), 0.86 (t, J = 6.91 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.1, 146.2, 85.5, 36.6, 31.3, 29.1, 22.8, 22.4, 20.8, 13.9; HRMS (ESI**)** calcd for $C_{22}H_{28}NO_3Si$ $[M+H]^+$ 184.1374, found 184.1371.



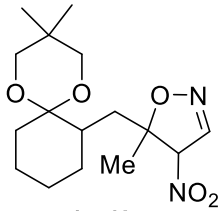
1-56f

1-56f (58% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (s, 1H), 7.28-7.10 (m, 10H), 3.12 (d, *J* = 15.0, 1H), 3.02 (d, *J* = 15.0, 1H), 2.61-2.58 (m, 1H), 2.41-2.35 (m, 1H), 2.19-2.13 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 205.6, 147.0, 140.2, 133.1, 130.2, 128.5, 128.3, 127.4, 126.3, 87.9, 42.0, 37.8, 29.1; HRMS (EI**)** calcd for $C_{18}H_{17}O_2N$ $[M]^+$ 279.1259, found 279.1254.



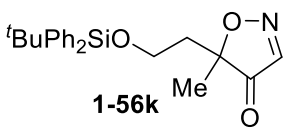
1-56g

1-56g (58% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (s, 1H), 7.49-7.44 (m, 2H), 7.38-7.30 (m, 3H), 2.17-2.01 (m, 2H), 1.37-1.21 (m, 8H), 0.84 (t, *J* = 5.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 203.1, 146.2, 135.3, 128.6, 128.1, 124.9, 87.7, 38.5, 31.4, 24.4, 23.4, 22.6, 22.5, 14.1; HRMS (EI**)** calcd for $C_{15}H_{19}O_2N$ $[M]^+$ 245.1415, found 245.1412.



1-56j

1-56j (68% yield): Major diastereomer: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (s, 1H), 6.32 (s, 1H), 3.75 (d, *J* = 11.4 Hz, 1H), 3.61 (d, *J* = 11.6 Hz, 1H), 3.34-3.31 (m, 2H), 2.71 (dd, *J* = 15.1, 2.3 Hz, 1H), 2.62 (d, *J* = 14.6 Hz, 1H), 1.78-1.74 (m, 1H), 1.61-1.53 (m, 4H), 1.37 (s, 3H), 1.45-1.14 (m, 4H), 1.22 (s, 3H), 0.74 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.4, 98.5, 95.3, 89.0, 69.6, 69.5, 41.7, 40.1, 31.8, 26.8, 25.3, 23.7, 22.4, 22.3, 22.1, 21.2; HRMS (ESI**)** calcd for $C_{16}H_{27}N_2O_5$ $[M+H]^+$ 327.1923, found 327.1920.



1-56k

1-56k (52% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (s, 1H), 7.60 (dd, *J* = 15.8, 6.7 Hz, 4H), 7.44-7.37 (m, 6H), 3.70-3.66 (m, 1H), 3.70-3.51 (m, 1H), 2.28-2.22 (m, 1H), 2.02-1.99 (m, 1H), 1.39 (s, 3H), 0.98 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 204.9, 146.8, 135.6, 135.5, 133.0, 132.8, 129.8, 129.7, 127.7, 82.6, 58.6, 40.4, 26.6, 22.2, 19.0; HRMS (ESI**)** calcd for $C_{22}H_{28}NO_3Si$ $[M+H]^+$ 382.1838, found 382.1845.

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CHAPTER 2

OXIDATIVE DIMERIZATION OF SILYLALLENES VIA ACTIVATION OF THE ALLENIC C(sp^2)–H BOND CATALYZED BY COPPER(I) CHLORIDE AND *N*-HYDROXYPHTHALIMIDE

2.1. Introduction*

Allenes play an important role for the development of new synthetic methods especially with transition metal catalysts.[1] The vast array of reactions involving allenes is the consequence of the two cumulated alkenes connected by an *sp*-hydridized central carbon, which ultimately provides the increased reactivity of their π-bonds in allenes. Especially, stannylallenes,[2] boronylallenes,[3] chromylallenes and silylallenes[4] are important class of building blocks in organic synthesis. These allenes have been extensively used for the synthesis of homopropargylic alcohols due to their versatile reactive nature of these allenes with the carbonyl compounds (**Figure 2.1**).[5,6,7,8] Allenyl metal species are known to undergo two types of reactions with aldehydes, where, allene **2-1** reacts with the aldehydes **2-2** in the presence of a Lewis acid to deliver the homopropargylic alcohols **2-3** (eq 1). On the other hand, silylallene **2-4** is also known to undergo ene type reaction with aldehydes to provide the homopropargyl alcohols **2-5** (eq 2). These homopropargylic alcohols are important synthetic intermediates in various settings because of their versatility for further elaboration in subsequent steps.[1,9]

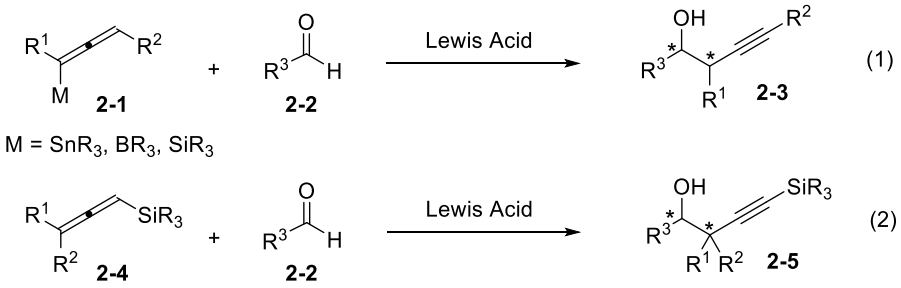
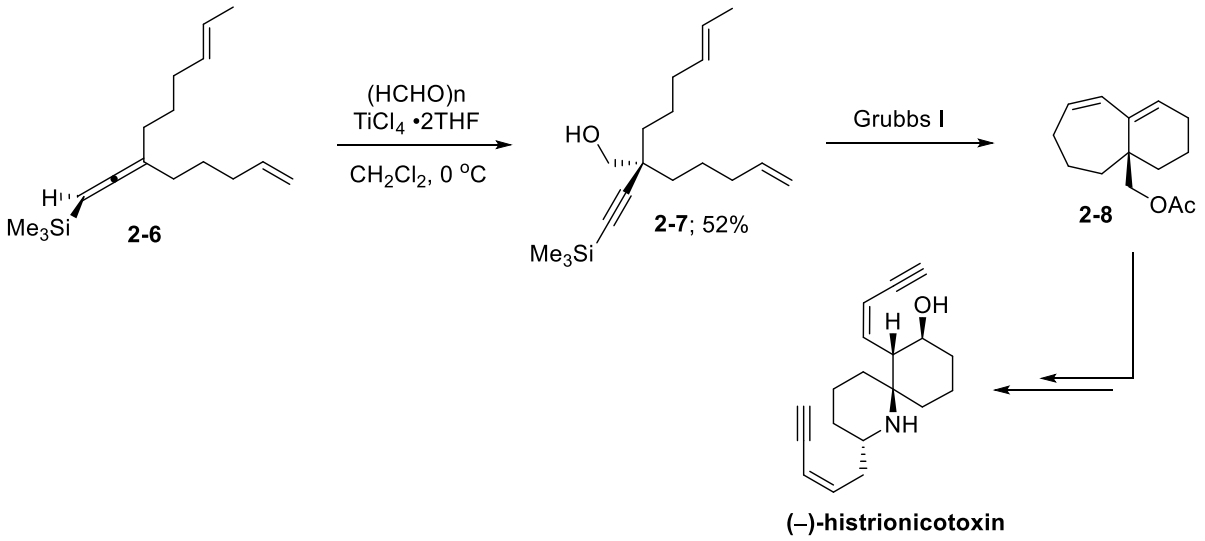


Figure 2.1 Homopropargylic Alcohols from Allenyl Reagents

The applications of these homopropargylic alcohols for the synthesis of natural products has been extensively studied.[1b] Most recently, Fukuyama and coworkers reported the total synthesis of (−)-histrionictoxin using silylallene **2-6** as a chirality transfer substrate (**Scheme 2.1**),[8g] **w**here the silylallene

* Reproduced in part with permission from Sabbasani, V. R.; Lee, D. "Oxidative Dimerization of Silylallenes via Activation of the Allenic C(sp^2)−H Bond Catalyzed by Copper(I) Chloride and *N*-Hydroxyphthalimide" *Org. Lett.* **2015**, *17*, 4878−4881.

was reacted with paraformaldehyde in the presence of titanium tetrachloride to provide homopropargylic alcohol **2-7**. Alcohol **2-7** was treated with Grubbs first-generation catalyst to form bicyclic ring-closing metathesis product **2-8**, which was further converted to a natural product (—)-histrionictoxin.



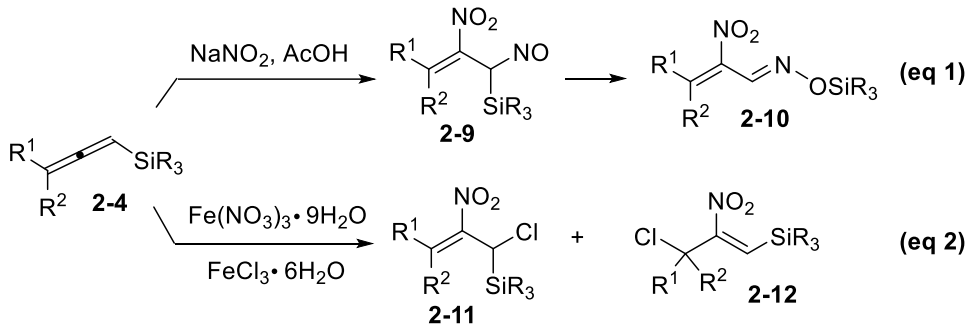
Scheme 2.1 Total Synthesis of (—)-Histrionictoxin

Recently, the Lee group reported a one-step protocol for the synthesis of trisubstituted silylallenes by treating with ketones with (trimethylsilyl)diazomethane (**Scheme 2.1**).[10] The easy access as well as the unknown reactions of these silylallenes prompts us to explore their unique reactivity. Although silylallenes have been employed in many synthetic transformations their utility has not been broadly defined especially for trisubstituted silylallenes.

The availability of these silylallenes allowed us to examine their reactivity, which resulted in novel nitration to form functionalized nitroalkenes (**Scheme 2.2**).[11] In this transformation, the initial addition of a nitrogendioxyl radical occurs on the *sp*-hybridized carbon to form an allylic radical intermediate which is then trapped by the nitroxyl radical or by the chloride nucleophile (Sn1 reaction) depending on the reaction conditions (Eqs 1 and 2).

Based on this facile addition of radical species with silylallenes, we envisioned that various other radical species might also react with these silylallenes under appropriate conditions to generate diversely

functionalized alkene products. We thus studied the behavior of silylallenes with the oxygen-centered radical reactions. For this new reactivity we have chosen a well-known oxygen-centered phthalimide *N*-oxyl radical that could be easily generated from the *N*-hydroxyphthalimide using environmental friendly Cu-catalyst.

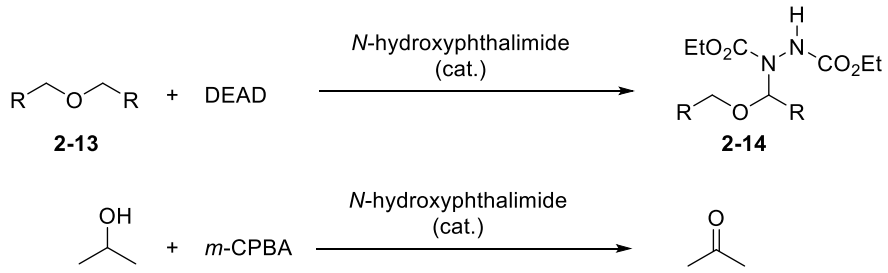


Scheme 2.2 Nitration of Silylallenes

2.2. Phthalimide *N*-Oxyl Radical Reactions

Phthalimide *N*-oxyl radical (PINO) is one of the most studied oxygen-centered radicals that can generate in situ from *N*-hydroxyphthalimide in the presence and/or absence of metal complexes. *N*-Hydroxyphthalimide (NHPI) is cheap and nontoxic material that can be easily synthesized from phthalic anhydride and hydroxylamine.[12] It has been extensively used for the radical functionalization of C─H bonds, which also, used for the direct addition to double bonds to produce the hydroxylamine derivatives.

2.2.1. Phthalimide *N*-Oxyl Radical-Catalyzed Reactions

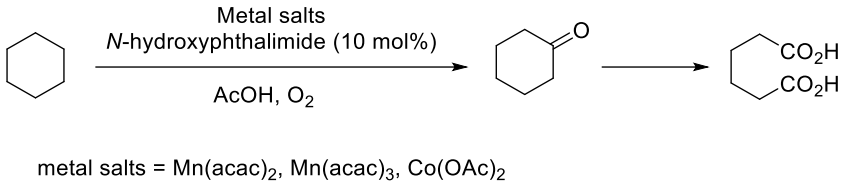


Scheme 2.3 First *N*-hydroxyphthalimide Catalyzed Reactions

PINO-catalyzed reactions were first reported by Grochowski and coworkers, where they used NHPI as

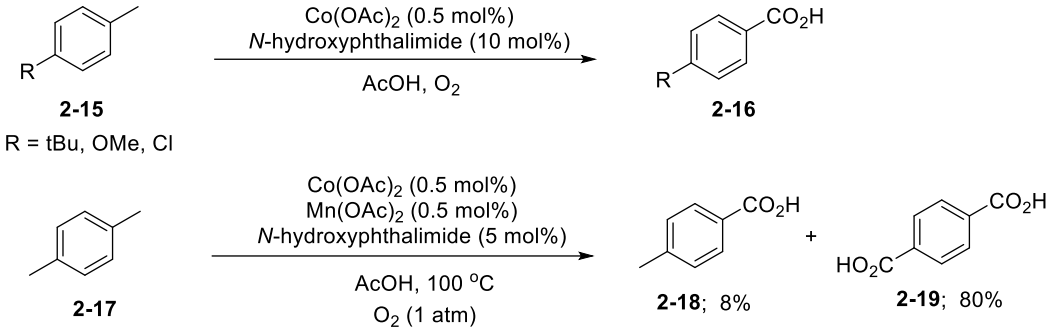
a catalyst for the transformations of C(sp^3)─H amination of ethers using ethyl diazodicarboxylate (DEAD), and for the oxidation of 2-propanol to acetone using *m*-chloroperbenzoic acid (*m*-CPBA) (**Scheme 2.3**).[13] Mechanistically, DEAD reacts with NHPI to generate PINO radical, which then abstract a hydrogen to generate an alkoxy alkyl carbon-centered radical, which added to DEAD.

Later, PINO radical-catalyzed reactions have been extensively used for the oxidation of allylic, benzylic and propagylic C(sp^3)─H bonds as well as the oxidation of alkanes, alcohols and also epoxidation of alkenes. Industrial two-step protocol for the oxidation of cyclohexane to adipic acid is based on the use of air followed by nitric acid. Because of the environmental issues, it requires to avoid the use of nitric acid.



Scheme 2.4 Oxidation of Cyclohexane to Adipic Acid

To solve this problem Ishi and coworkers developed a new method using NHPI and metal salts as a catalyst in acetic acid (**Scheme 2.4**). In this reaction, they used Mn(II), Mn(III) and Co(II) salts as catalysts and oxygen as an oxidant.[14] For commercial applications, this process has been further evaluated in pilot scale.[15] Thereafter, several studies has been made for the oxidation of alkanes using NHPI and related radicals.[16]

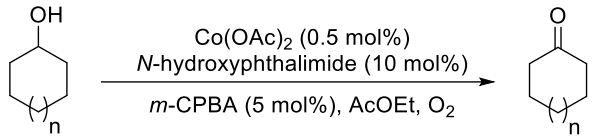


Scheme 2.5 Oxidation of Arylic C(sp^3)─H Bonds

The oxidation of benzylic C(sp^3)─H bonds was studied using various oxidants, and NHPI is one of the

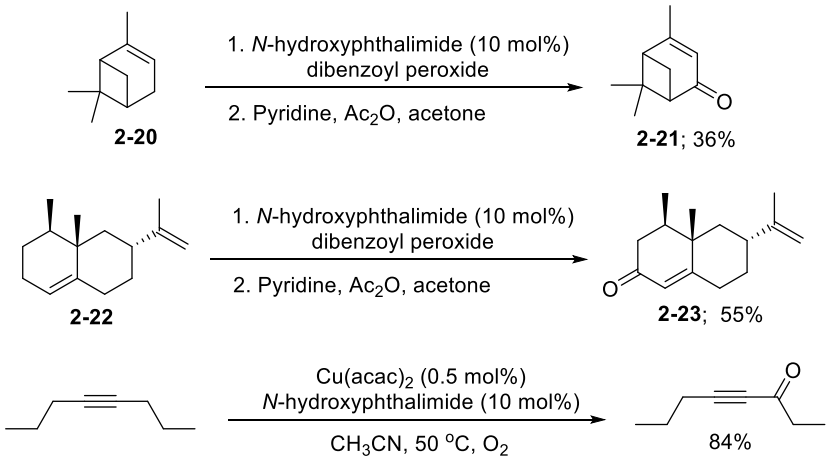
most studied catalysts together with many metal catalysts. The combination of $Co(OAc)_2$ and NHPI catalysts under aerobic oxidation has been utilized for oxidation of toluene derivatives **2-15** to benzoic acid derivatives **2-16** (**Scheme 2.5**).[17] Similar conditions, by adding $Mn(OAc)_2$ as an extra catalyst was converted the *p*-xylene **2-17** to terephthalic acid **2-19**, which is used in industries to produce tons of polyethylene terephthalate.[18]

The aerobic oxidation of alcohols to ketones was first reported in 1977 using PINO radical-catalyzed electrolytic method.[19] After that, non-electrolytic aerobic oxidation of alcohols to ketones using various metal complexes were reported.[20] The best conversions and yields were observed using catalytic combination of cobalt acetate, NHPI and *m*-CPBA (**Scheme 2.6**).[21]



Scheme 2.6 Oxidation of Alcohols to Ketones

The allylic oxidation of alkenes has been studied extensively, where alkenes **2-20** and **2-22** in the presence of NHPI catalyst and dibenzoyl peroxide provided the corresponding ketones **2-21** and **2-23** in low to moderate yields (**Scheme 2.7**).[18] The low yields of the reaction was due to low conversion, and the



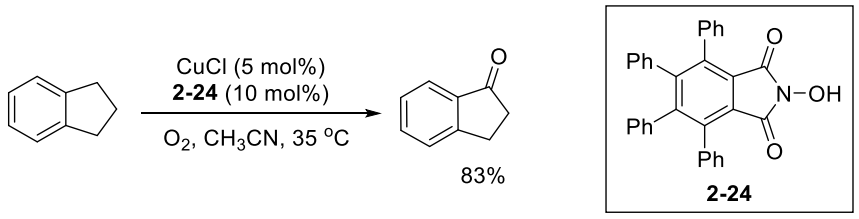
Scheme 2.7 Allylic and Propargylic Oxidation of Alcohols

side reactions induced by the generated peroxy radicals as well as PINO-radical.[22] PINO radical also oxidize propargylic position of alkynes, where the reaction with 4-octyne using catalytic amounts of Cu(II) and NHPI in the presence of oxygen provided 4-octyn-3-one with good conversion and yield.

NHPI was also widely used as catalyst for the epoxidation of alkenes as well as oxidation of silyl ethers, acetals, amines, amides, sulfides and silanes.[14]

2.2.2. Stoichiometric Reactions of Phthalimide *N*-Oxyl Radical

Aerobic oxidation of benzylic compounds using catalytic combination of CuCl and NHPI was first reported by Einhorn and coworkers. They have studied the oxidation of benzylic compounds by using various NHPI derivatives. They found that the NHPI is less efficient for the conversion Inadane to indanone in presence of oxygen. The best results was obtained with **2-24**, which provided indanone in very good yield (**Scheme 2.8**).[23]



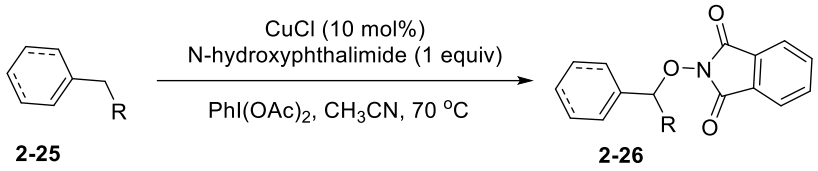
Scheme 2.8 Aerobic Oxidation of Indane

Thereafter, several groups published copper-catalyzed stoichiometric NHPI reactions for allylic and benzylic C(sp^3)─H oxidation to form an oxygenated products, along with addition reactions of in situ generated PINO radical to alkenes to form phthalimidoxy derivatives. In these transformations, various oxidants ranging from diacetoxy iodobenzene, dialkylpeoxides, hydroperoxides and oxygen have been used.

2.2.2.1. Cu-Catalyzed Allylic and Benzylic C–H Bond Activation Reactions

In 2008, Chang and coworkers reported a Cu-catalyzed new C─O bond forming method using NHPI and diacetoxy iodobenzene as an oxidant. In this study a broad range of substrates are selectively

oxygenated at allylic and benzylic positions using stoichiometric amounts of NHPI and diacetoxy iodobenzene in the presence of CuCl catalyst (**Table 2.1**).[24]



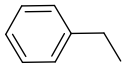
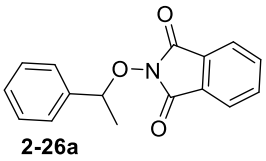
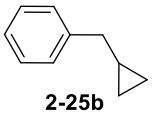
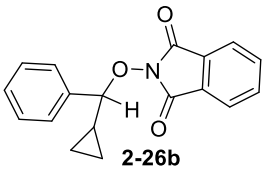
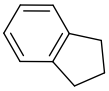
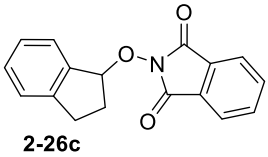
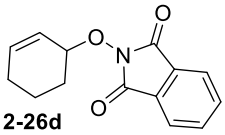
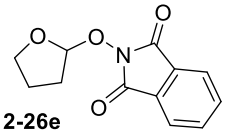
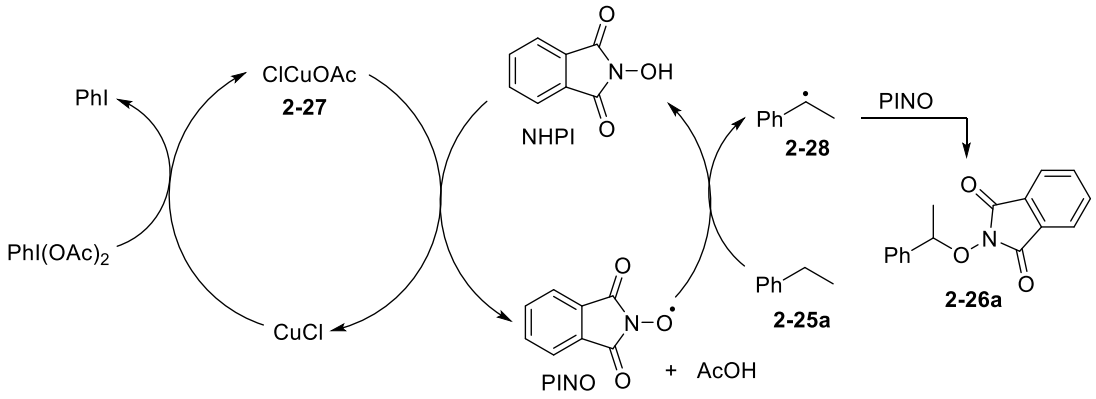
entry	substrate	product	yield (%)
1	 **2-25a**	 **2-26a**	78
2	 **2-25b**	 **2-26b**	82
3	 **2-25c**	 **2-26c**	75
4	**2-25d**	 **2-26d**	76
5	**2-25e**	 **2-26e**	70

Table 2.1 Cu-Catalyzed Oxygenation with Stoichiometric NHPI

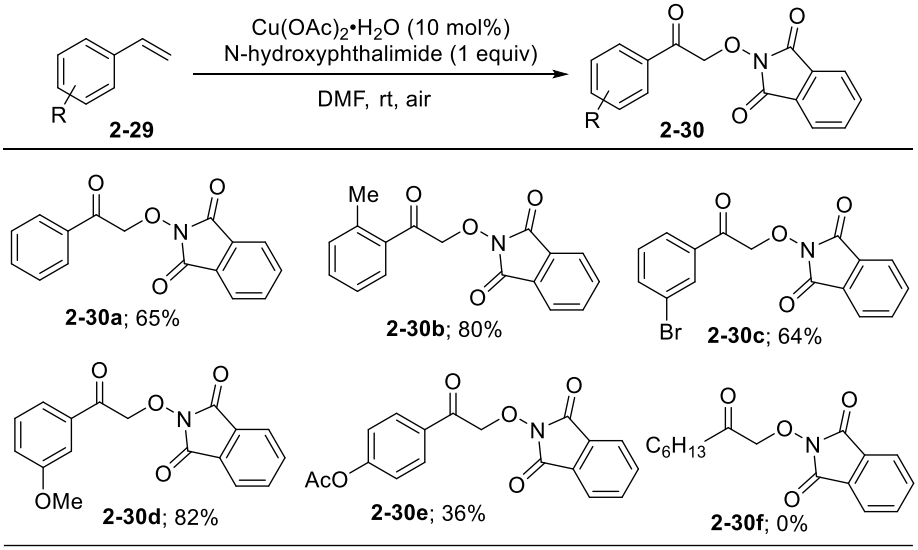
The proposed mechanism of the Cu-catalyzed oxygenation reaction commences with CuCl reacting with the diacetoxy iodobenzene to form acetoxychlorocopper **2-27**, which converts NHPI into PINO radical by regenerating CuCl catalyst. The resulting PINO radical abstracts an allylic/benzylic hydrogen to form allylic/benzylic carbon centered radical **2-28**. The carbon-centered radical combines with a nitroxyl radical to form oxygenated product **2-26** (**Scheme 2.9**).



Scheme 2.9 Proposed Mechanism for Oxygenation with Stoichiometric NHPI

2.2.2.2. Cu-Catalyzed Phthalimide *N*-Oxyl Radical Addition to Alkenes

Copper-catalyzed deoxygenation of styrene derivatives using stoichiometric NHPI in the presence of

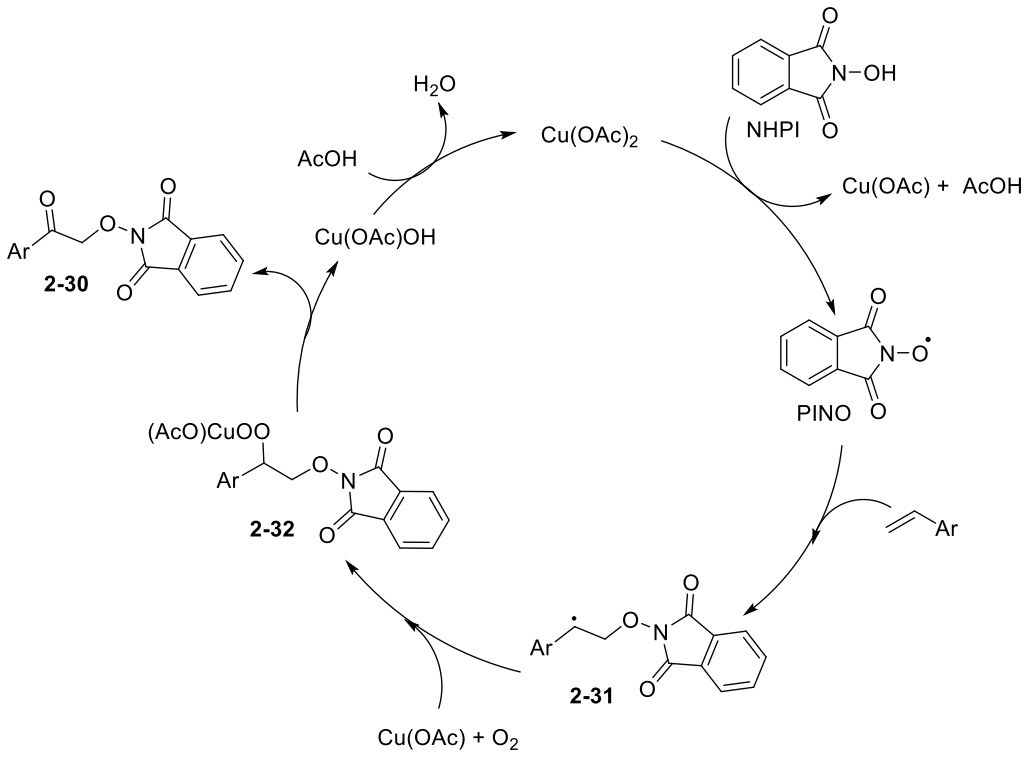


Scheme 2.10 Cu(II)-Catalyzed Dioxygenation of Alkenes Using NHPI

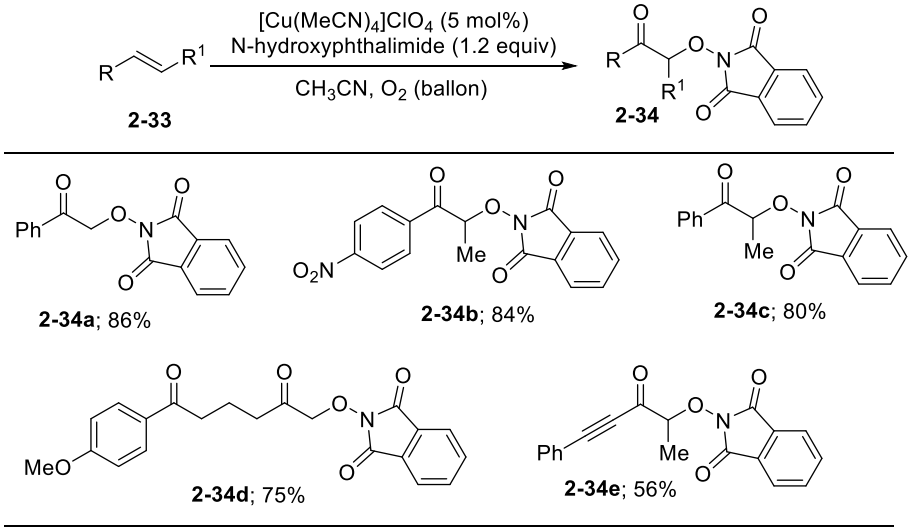
air to form *β*-keto-*N*-alkoxyphthalimides has been described by Punniyamurthy and coworkers. The described reaction is relatively mild and efficient with a broad range of aryl substituted alkene substrates (**Scheme 2.10**).[25] However, no reaction was observed with 1-octene to form alkoxyphthalimide **2-30f**.

The proposed mechanism of the reaction an initial reaction between $Cu(OAc)_2$ and NHPI to produce a PINO radical, CuOAc and AcOH. The resulting PINO radical then added to an alkene to form carbon-

centered radical **2-31**, which then reacts with oxygen in presence of CuOAc to generate intermediate **2-32**. Metal peroxy intermediate **2-32** decomposes to dioxygenated product **2-30** by releasing Cu(OAc)OH. The released Cu(OAc)OH further reacts with AcOH to regenerate $Cu(OAc)_2$ catalyst (**Scheme 2.11**).



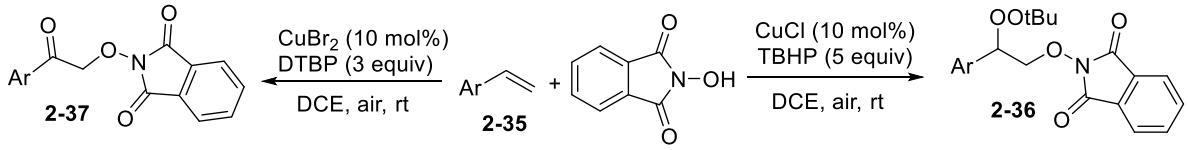
Scheme 2.11 Proposed Mechanism of Cu-Catalyzed Dioxygenation of Alkenes



Scheme 2.12 Cu(I)-Catalyzed Dioxygenation of Alkenes Using NHPI

Woerpel and coworkers also reported the similar oxidation protocol using different a copper-catalyst. In this dioxygenation reaction, 5 mol% of $[Cu(MeCN)_4]ClO_4$ catalyst and 1.2 equivalence of NHPI under oxygen balloon were used. Compared to this reaction, the previous reaction is less efficient when the alkenyl substituent is electron-withdrawing aryl group and/or inactive for the alkyl substituted alkenes. In Woerpel's method the electron withdrawing-group-containing styrene derivatives and terminal alkens are also reactive, and provided high yields of *β*-keto-*N*-alkoxyphthalimides (**Scheme 2.12**).[26]

Xia and coworker also reported catalyst control dioxygenation of olefins using stoichiometric NHPI (**Scheme 2.13**). The CuCl-catalyzed deoxygenation of alkenes using *tert*-butylhydroperoxide (TBHP) and NHPI provided dioxygenated dialkyl peroxide products in good to moderate yields. On the other hand, the reaction catalyzed by $CuBr_2$ using di-*tert*-butylperoxide (DTBP) provided *β*-keto-*N*-alkoxyphthalimides in moderate yields.[27]



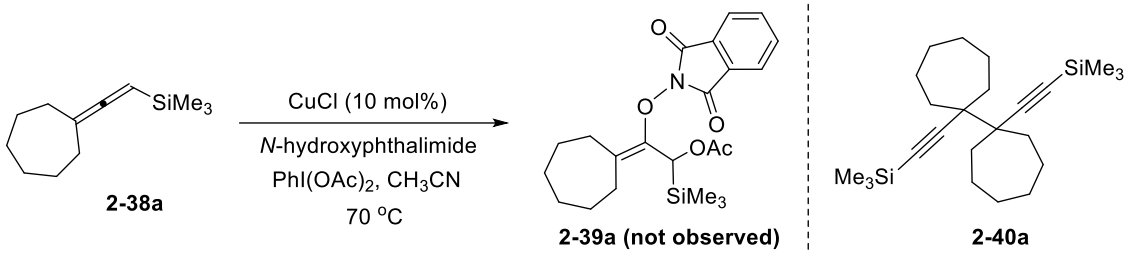
Scheme 2.13 Catalyst-Control Dioxygenation of Alkenes

2.3. Results and Discussion[†]

Based on the Cu-catalyzed dioxygenation of alkenes using NHPI and the behavior of silylallenes in nitration reaction (**Scheme 2.14**), we expected that silylallene **2-38** in the presence of CuCl and NHPI might behave similarly to form bis-oxygenated product **2-39**. Surprisingly, however, dimer **2-40** was isolated as a sole product (Scheme 2.3.1). Clearly, this dimerization event to form 1,5-enynes implies that the putative PINO radical derived from NHPI did not add to the central carbon of silylallene. Instead it abstracted the allenic C(sp^2)─H hydrogen[28] to generate a propargylic radical, which then dimerize[29] to form structurally

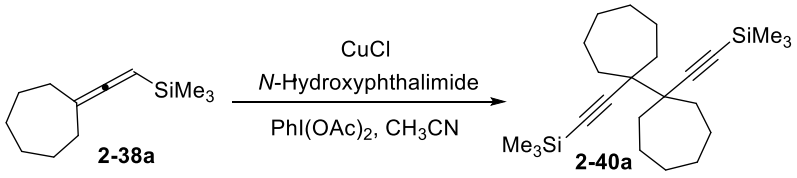
[†] Reproduced with permission from Sabbasani, V. R.; Lee, D. "Oxidative Dimerization of Silylallenes via Activation of the Allenic C(sp^2)−H Bond Catalyzed by Copper(I) Chloride and *N*-Hydroxyphthalimide" *Org. Lett.* **2015**, *17*, 4878−4881.

demanding 1,5-enynes having two quaternary carbons next to each other.



Scheme 2.14 Initial Observation of Silylallene Dimerization

On the basis of this initial observation of silylallene dimerization, we further investigated the dimerization behavior of silylallenes containing different structural features. We commenced our investigation with optimizing the reaction conditions in terms of the catalyst loading, stoichiometry of reagents and oxidant, reaction time, and temperature (**Table 2.2**). Using cycloheptanylidyl allene **2-38a** as a test substrate with catalytic amount of CuCl (10 mol %) and a stoichiometric amounts of N-hydroxyphthalimide (NHPI) and $PhI(OAc)_2$ in CH_3CN at 70 °C gave the dimer product of 1,5-diyne **2-40a** in 76% yield (entry 1). By lowering the reaction temperature from 70 °C to 36 °C, slightly increased the



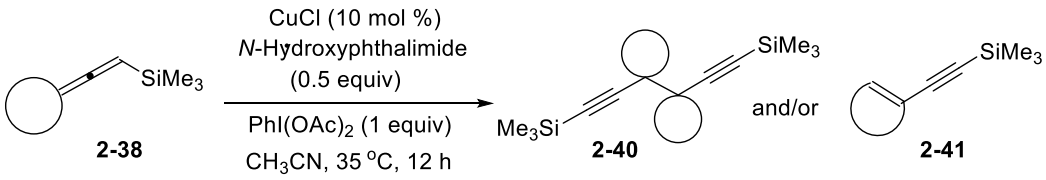
entry	catalyst (10 mol%)	*N*-Hpth (equiv)	$PhI(OAc)_2$ (equiv)	temp (° C)	time (h)	yield (%)[a]
1	CuCl	1	1	70	12	76
2	CuCl	1	1	36	14	78
3	CuCl	1	0	36	14	N/R
4	CuCl	0	1	36	14	N/R
5	**CuCl**	**0.5**	**1**	**36**	**14**	**78**
6	CuCl	0.3	1	36	14	40
7	CuOAc	0.5	1	36	12	unknown
8	$Cu(OAc)_2$	0.5	1	36	12	unknown

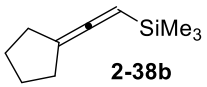
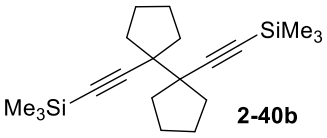
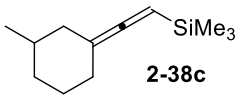
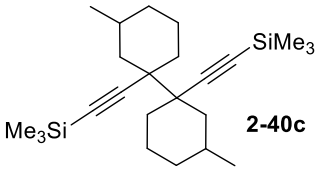
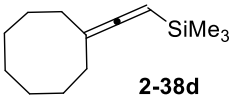
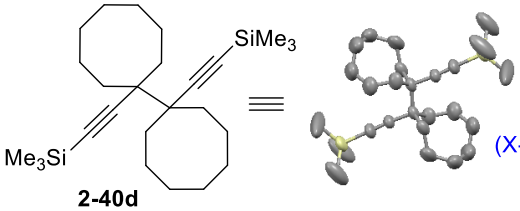
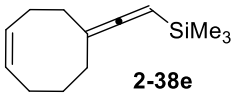
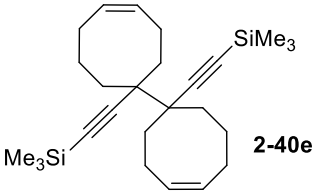
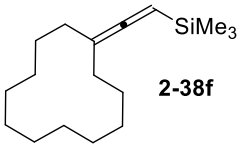
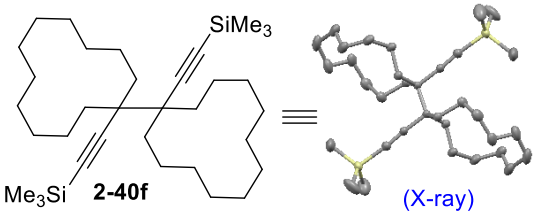
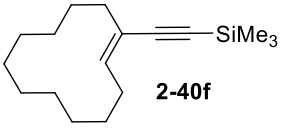
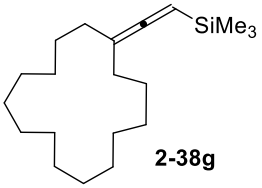
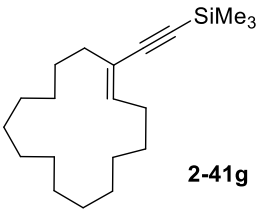
[a] Isolated yields

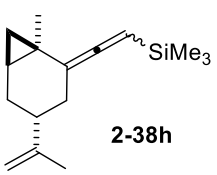
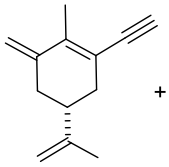
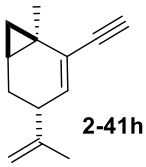
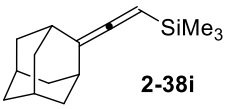
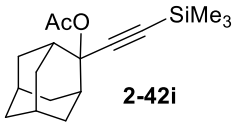
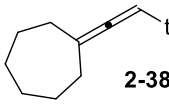
Table 2.2 Optimization of Reaction Condition for Dimerization of Silylallenes

yield of reaction up to 78% (entry 2). Next, we explored the effect of the amounts of NHPI and $PhI(OAc)_2$; without oxidant and/or NHPI, no reaction occurred (entries 3 and 4). Lowering the amount of NHPI down to 50 mol % did not affect the yield of the reaction (entry 5). However, further lowering NHPI to 30 mol % significantly lower the yield of **2-40a** (entry 6). Changing the catalyst from CuCl to CuOAc or $Cu(OAc)_2$ provided unknown mixture of products (entries 7 and 8).

With the optimized reaction condition for the dimerization of silylallenes in hand, we next examined the substrates differing in their ring sizes ranging from five to eight, twelve and fifteen as well as the substitution pattern around the allene skeleton (**Table 2.3**). A small ring-based allenes **2-38b** and **2-38c** having five and six membered rings derived from cyclopentanone and 3-methyl cyclohexanone afforded dimers **2-40b** and **2-40c** in 62 and 58% yield (entries 1 and 2), and cyclooctanone derived silylallene **2-38d** containing cyclooctylidene moiety provided dimeric product **2-40d** in 72% yield (entry 3). For the reaction of allene **2-38e** containing an extra double bond on the eight-membered ring also yielded only dimer **2-40e** in 68% yield, without any other side-product derived from the involvement of the double bond to form bis-oxygenated product and/or oxygenation of the allylic C(sp^3)–H bond cyclooctene moiety (entry 4). Unexpectedly, however, increasing the ring size beyond eight diverted the product distribution. The reaction of allenes **2-38f** with twelve-membered ring afforded 2:1 mixture of dimer **2-40f** and 1,3-enyne **2-41f** in 70% combined yield (entry 5), and that of **2-38g** containing 15-membered ring generated 1,3-enyne **2-41g** in 75% yield as a sole product (entry 6). Carvone-derived cyclopropane-containing silyallene **2-38h** resulted in 55% combined yield of cyclopropane-opened[30] conjugated dienyne **2-41h** and 1,3-enyne **2-41h'** in a 2:1 ratio (entry 7). On the other hand, adamantanone-derived silyallene **2-38h** generated an acetoxy group-trapped product **2-42i** in 45% yield (entry 8). The reaction of **2-38a-t-Bu** where trimethylsilyl of **2-38a** is replaced with a tert-butyl group led to only decomposition under identical conditions (entry 9). The stark difference in reactivity between silylallene **2-38a** and the corresponding tert-butylallene counterpart **2-38a-t-Bu** suggests that silyl group plays a crucial role in weakening the allenic C(sp^2)–H bond.



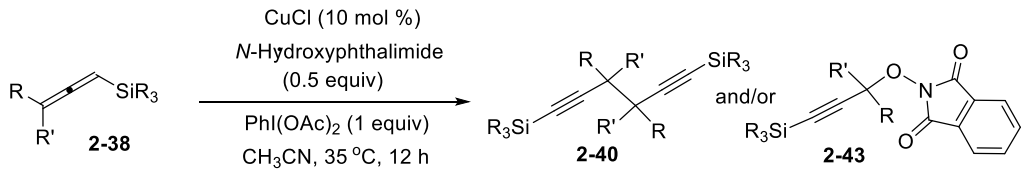
entry	silylallene	product	yield (%)[a]
1	 **2-38b**	 **2-40b**	62
2	 **2-38c**	 **2-40c**	58
3	 **2-38d**	 **2-40d**	72
4	 **2-38e**	 **2-40e**	68
5	 **2-38f**	 **2-40f** +  **2-40f** **2-40f:2-41f** = 2:1[b]	70
6	 **2-38g**	 **2-41g**	75

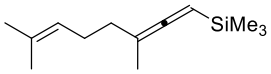
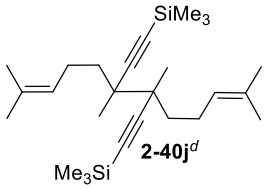
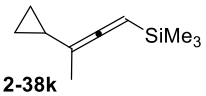
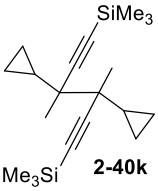
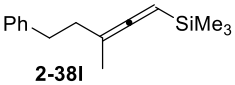
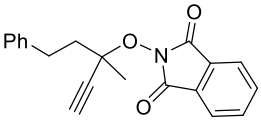
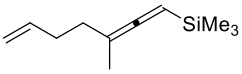
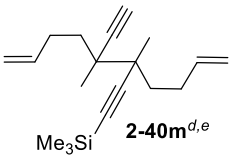
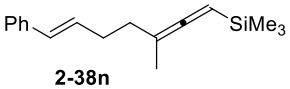
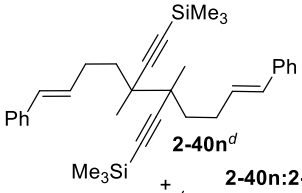
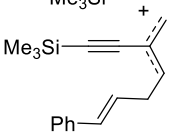
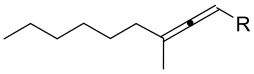
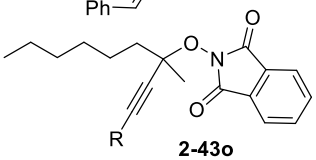
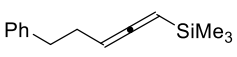
7	 **2-38h**	 **2-41h** +  **2-41'**	**2-41h:2-41'** = 1:2[c]	55
8	 **2-38i**	 **2-42i**		45
9	 **2-38a-t-Bu**	Decomposed		---

[a] Isolated yields. [b] The ratio was determined by 1H NMR. [c] Protodesilylation of $SiMe_3$ was observed.

Table 2.3 Dimerization of Silylallenes Derived from Cyclic Ketones

Having seen the general trend of reactivity of cycloalkane-based silylallenes in dimerization, we next examined the reactivity of acyclic alkane-based silylallenes toward dimerization (**Table 2.4**). Silylallene **2-38j** bearing a prenyl group afforded dimer **2-40j** as a single diastereomer in 72% yield (entry 1), yet a cyclopropyl group-containing silylallene **2-38k** derived from cyclopropyl methyl ketone resulted in severe decomposition with only a trace amount of dimer **2-40k** (entry 2). Surprisingly, silylallene **2-38l** did not generate an expected dimer product, instead pthalamide *N*-oxyl radical trapped product **2-43l** was generated in 34% yield. By employing a stoichiometric amount of NHPI, the yield of **2-43l** increased to 61% (entry 3). The results obtained from silylallenes **2-38j**, **2-38k** and **2-38l** imply that even a remote unsaturated functional groups such as a prenyl or a phenyl group may significantly affects the dimerization of these silylallenes. This notion is further strengthened by the reaction of silylallenes **2-38m**– **2-38p**. Although the reaction of silylallene **2-38m** containing a terminal double delivered only single diastereomer of dimer product **2-40m** in good yields (entry 4) the corresponding silylallene **2-38n** containing a styryl group afforded a mixture of dimer **2-40n** and 1,3-enyne **2-41n** in 69% combined yield (entry 5). Interestingly, silylallenes **2-38o** and **2-38p** containing different silyl groups such as $SiEt_3$ and $SiMe_2$t-Bu, respectively, delivered only the propargylic aminoxy ethers **2-43o** and **2-43p** in moderate yields (entries 6 and 7). On the

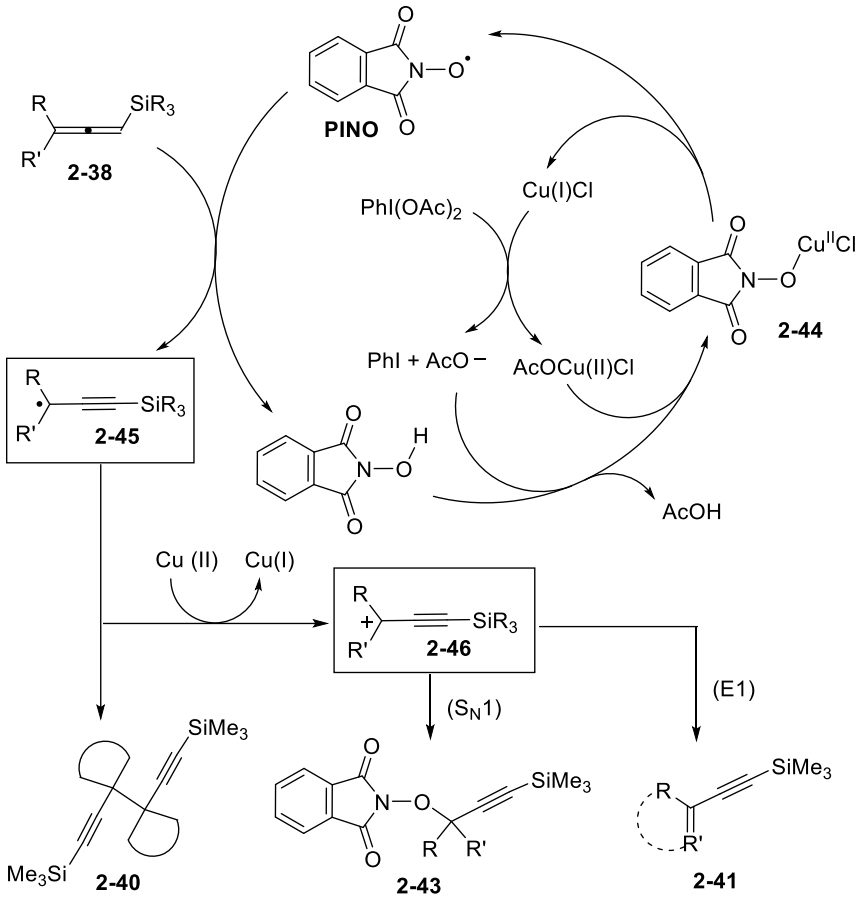


entry	Silylallene	Product	yield (%)[a]
1	 **2-38j**	 **2-40j**[d]	72
2	 **2-38k**	 **2-40k**	trace[b]
3	 **2-38l**	 **2-43l**[e]	34 (61)[c,d]
4	 **2-38m**	 **2-40m**[d,e]	66
5	 **2-38n**	 **2-40n**[d] **2-40n:2-41n** = 1.3:1  **2-41n**	69
6	 **2-38o**, R = $SiEt_3$	 **2-43o**	38 (67)[c]
7	**2-38p**, R = $SiMe_2{}^tBu$	**2-43p**	31 (58)[c]
8	 **2-38q**	Decmposed	---

[a] Isolated yields. [b] Trace amounts of dimeric product was observed by HRMS. [c] Yields in the parenthesis are from reactions with 1 equiv of *N*-hydroxypthalimide. [d] Single diastereomer was observed. [e] Protodesilylation was observed.

Table 2.4 Dimerization/Oxidation of Silylallenes Derived from Acyclic Ketones

other hand, disubstituted silylallene **2-38q** did not produce any identifiable product but decomposition under identical reaction conditions (entry 8).



Scheme 2.15 A Proposed Reaction Mechanism

On the basis of this general trend and selectivity we proposed a tentative mechanism for the dimerization (**Scheme 2.15**). As the first step in the catalytic cycle, Cu(I)Cl is oxidized to AcOCu(II)Cl by $PhI(OAc)_2$, which then reacts with *N*-hydroxyphthalimide to generate adduct **2-44**. Upon homolysis of **2-44**, phthalimide *N*-oxyl radical[31] PINO is generated together with Cu(I)Cl which is oxidized back to AcOCu(II)Cl to reenter the catalytic cycle. In the next step, PINO radical reacts with a substrate silylallene by abstracting the allenic C(sp^2)–H hydrogen to generate a propargylic carbon-centered radical **2-45** and *N*-hydroxyphthalimide, which complete the full catalytic cycle. The main downstream events of radical **2-5** are its dimerization to form product **2-40** or further oxidation to the corresponding carbocation **2-46**, which

then undergoes an elimination and/or substitution to generate products **2-41** and/or **2-43**, respectively.

2.4. Summary[‡]

In summary, a novel oxidative dimerization reaction of silylallenes using a catalytic system of copper(I) chloride and *N*-hydroxyphthalamide along with a stoichiometric amount of a terminal oxidant diacetoxyiodobenzene. Noticeable dependency on substrate structure for the formation of dimers, 1,3-enynes, and phathalamide *N*-oxyl adducts was recognized; silylallenes containing a small ring substructure afforded only head-to-head dimers whereas large ring-containing silylallenes provide 1,3-enynes as an accompanying minor or exclusive product depending on the size of the macrocycle. On the other hand, silylallenes containing an acyclic substituent generated dimers except in a few cases where phathalamide *N*-oxyl radical react at the propargylic center predominantly to form the corresponding aminoxy ethers. Inferred from these different products, we proposed a plausible mechanism for the reaction, which involved the abstraction of the allenic C(sp^2)–H hydrogen by phathalamide *N*-oxyl radical to generate a propargylic carbon-centered radical as the key intermediate.

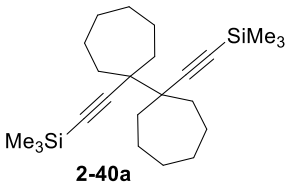
2.5. Experimental Details

2.5.1. General Information: See **chapter 1** section **1.6.1** for general information

2.5.2. General Procedure for Dimerization of Silylallenes: CuCl (2.5 mg, 0.0125 mmol, 0.1 equiv) and *N*-hydroxyphthalimide (20.5 mg, 0.125 mmol, 0.5 equiv) were dissolved in 2 mL CH_3CN in a thick-walled Schlenk tube under nitrogen followed by addition of silylallene **2-38a** (50 mg, 0.25 mmol, 1equiv) in 2 mL CH_3CN and iodobenzene diacetate (161 mg, 0.5 mmol, 1 equiv) at room temperature. The reaction mixture was degassed under vacuum at –78 °C and stirred at 35 °C for 14 h. The tube was opened to air at room temperature and the solvent was removed under reduced pressure. The residual crude oil was purified was purified by column chromatography (Hexanes) to give dimer **2-40a** as a white solid (37.5 mg, 78%).

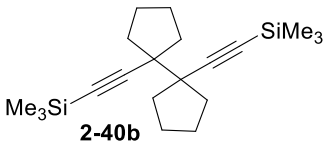
[‡] Reproduced with permission from Sabbasani, V. R.; Lee, D. "Oxidative Dimerization of Silylallenes via Activation of the Allenic C(sp^2)−H Bond Catalyzed by Copper(I) Chloride and *N*-Hydroxyphthalimide" *Org. Lett.* **2015**, *17*, 4878−4881.

2.5.3. Selected Characterization Data



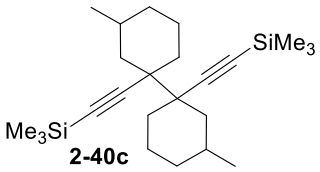
2-40a

2-40a (37.5 mg, white solid, 78%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.92–1.89 (m, 4H), 1.73–1.64 (m, 16H), 1.46 (m, 4H), 0.14 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 112.4, 87.5, 48.9, 35.3, 27.8, 24.3, 0.3; HRMS (EI) calcd for $C_{24}H_{42}Si_2$ $[M]^+$ 386.2825, found 386.2834.



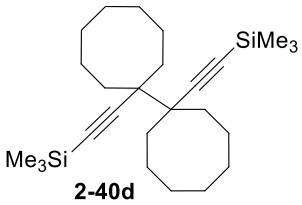
2-40b

2-40b (25.6 mg, white solid, 62%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.98–1.97 (m, 4H), 1.79–1.78 (m, 8H), 1.67–1.65 (m, 4H), 0.12 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ113.5, 85.4, 50.7, 37.7, 25.3, 0.3; HRMS (EI) calcd for $C_{20}H_{34}Si_2$ $[M]^+$ 330. 2199, found 330.2204.



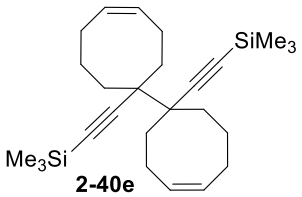
2-40c

2-40c (28 mg, white solid, 58%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.77–1.62 (m, 12H), 1.54–1.50 (m, 2H), 1.25–1.20 (m, 4H), 0.89–0.87 (m, 6H), 0.14 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 111.3, 88.8, 45.5, 40.5, 37.1, 34.9, 32.6, 31.7, 31.5, 29.2, 0.4; HRMS (EI) calcd for $C_{24}H_{42}Si_2$ $[M]^+$ 386.2825, found 386.2816.



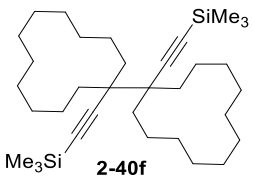
2-40d

2-40d (37.5 mg, white solid, 72%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.99–1.94 (m, 4H), 1.86–1.78 (m, 8H), 1.69–1.64 (m, 10H), 1.46–1.43 (m, 6H), 0.13 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 113.1, 87.1, 47.4, 32.5, 28.4, 24.8, 23.6, 0.2; HRMS (EI) calcd for $C_{26}H_{46}Si_2$ $[M]^+$ 414.3138, found 414.3130.



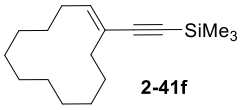
2-40e

2-40e (35 mg, white solid, 68%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.82–5.77 (m, 2H), 5.52–5.47 (m, 2H), 2.64–2.52 (m, 4H), 2.05–1.78 (m, 10H), 1.54–1.45 (m, 6H), 0.16 (s, 18H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.9, 129.2, 110.0, 89.8, 36.9, 29.7, 26.4, 24.3, 23.6, 0.3; HRMS (EI) calcd for $C_{26}H_{42}Si_2$ $[M]^+$ 410.2825, found 410.2822.



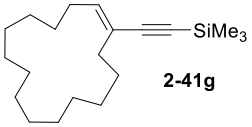
2-40f

2-40f (31 mg, white solid, 47%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.88–1.82 (m, 4H), 1.63–1.56 (m, 8H), 1.37–1.34 (m, 32H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 112.8, 87.9, 44.3, 32.2, 27.1, 26.2, 22.9, 22.4, 21.0, 0.1; HRMS (EI) calcd for $C_{34}H_{62}Si_2$ $[M]^+$ 526.4390, found 526.4397.



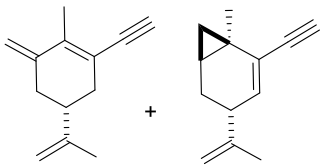
2-41f

2-41f (15 mg, color less liquid, 23% yield)**:**^{1}H NMR (500 MHz, $CDCl_3$) δ 5.81 (t, *J* = 7.7 Hz, 1H), 2.34–2.31 (m, 2H), 2.16–2.14 (m, 2H), 1.57 (m, 4H), 1.39–1.28 (m, 12H), 0.19 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 122.4, 104.5, 98.2, 36.1, 30.2, 26.9, 26.1, 25.8, 25.2, 24.8, 24.6, 24.4, 0.1; IR (neat): 2927, 2855, 1710, 1678, 1466, 1445, 1248 cm^{-1}.



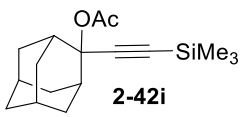
2-41g

2-41g (57 mg, colorless liquid, 75%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.66 (5.66 (t, *J* = 7.4 Hz, 1H), 2.35–2.32 (m, 2H), 2.15–2.13 (m, 2H), 1.56–1.53 (m, 2H), 1.48–1.46 (m, 2H), 1.36–1.26 (m, 18H), 0.20 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.0, 123.5, 104.4, 98.1, 36.0, 29.6, 28.5, 27.6, 27.3, 27.2, 27.1, 26.9, 26.8, 26.6, 25.7, 0.2; HRMS (EI) calcd for $C_{20}H_{36}Si$ $[M]^+$ 304.2586, found 304.2589.



2-41h 1:2 **2-41h'**

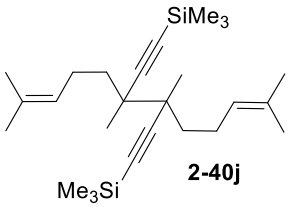
2-41h:2-41h' (12 mg, colorless liquid, 55%)**: 2-41h'** (major isomer)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.89 (d, *J* = 2.5 Hz, 1H), 4.76 (s, 1H), 4.73 (s, 1H), 2.95 (s, 1H), 1.71 (s, 3H), 2.56–2.52 (m, 1H), 1.31 (s, 3H), 1.27–1.24 (m, 1H), 1.15–1.11 (m, 1H), 0.88 (t, *J* = 7.0 Hz, 1H), 0.74 (t, *J* = 5.1 Hz, 1H), 0.61–0.59 (m, 1H); **2-41h** (minor isomer)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ5.05 (s, 1H), 4.91 (s, 1H), 4.77 (s, 1H), 4.74 (s, 1H), 3.30 (s, 1H), 2.31–2.23 (m, 2H), 2.08 (m, 3H), 2.01–1.99 (m, 1H), 1.75 (s, 3H), 1.63–1.57 (m, 2H); **2-41h** and **2-41h':** ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.2, 147.5, 144.0, 135.4, 126.3, 111.5, 110.9, 109.5, 83.6, 82.8, 76.9, 41.3, 39.9, 37.0, 36.2, 24.9, 22.9, 22.4, 21.1, 20.7, 20.6, 18.3, 16.9, 15.7, 14.1; HRMS (EI) calcd for $C_{13}H_{17}$ $[M+H]^+$ 173.1330, found 173.1332.



2-42i

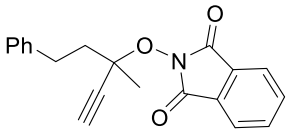
2-42i (32 mg, colorless liquid, 45%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.43 (s, 2H), 2.21–2.18 (m, 2H), 2.07 (s, 3H), 1.98–1.95 (m, 2H), 1.82–1.72 (m, 6H), 1.61–1.59

(m, 2H), 0.17 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.8, 105.7, 91.6, 80.2, 37.6, 36.0, 35.5, 34.9, 32.0, 26.9, 26.4, 21.9, 0.0; HRMS (ESI) calcd for $C_{17}H_{26}O_2SiNa$ $[M+Na]^+$ 313.1600, found 313.1608.



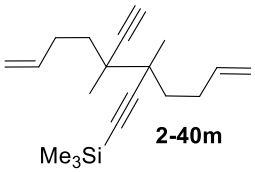
2-40j

2-40j (37 mg, white solid, 72%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.19–5.16 (m, 2H), 2.27–2.19 (m, 2H), 2.08–2.91 (m, 2H), 1.70 (s, 6H), 1.63 (s, 6H), 1.51–1.47 (m, 2H), 1.25 (s, 3H), 1.30–1.26 (m, 2H), 1.23 (s, 3H), 0.13 (s, 18); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.5, 124.8, 111.2, 87.0, 43.4, 36.6, 36.3, 25.7, 24.5, 24.4, 21.6, 21.3, 17.6, 0.3; HRMS (EI) calcd for $C_{26}H_{46}Si_2$ $[M]^+$ 414.3138, found 414.3153.



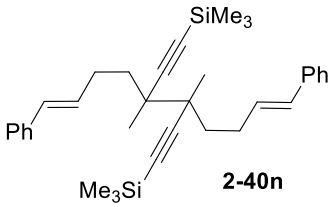
2-43l

2-43l (49 mg, colorless liquid, 61%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.88–7.86 (m, 2H), 7.78–7.76 (m, 2H), 7.32–7.27 (m, 4H), 7.22–7.19 (m, 1H), 3.11–3.05 (m, 1H), 3.02–2.96 (m,1H), 2.60 (s, 1H), 2.34–2.28 (m, 1H), 2.24–2.18 (m, 1H), 1.77 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.8, 141.5, 134.5, 129.2, 128.5, 128.5, 126.0, 123.6, 84.7, 82.6, 76.4, 42.5, 31.0, 26.9; HRMS (ESI) calcd for $C_{20}H_{18}NO_3$ $[M+H]^+$ 320.1287, found 320.1274.



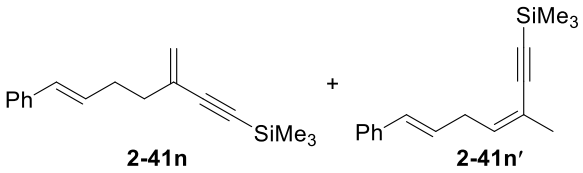
2-40m

2-40m (47 mg, colorless liquid, 74%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.90–5.85 (m, 2H), 5.07–5.04 (m, 2H), 4.97–4.95 (m, 2H), 2.32–2.29 (m, 2H), 2.20–2.17 (m, 2H), 2.15 (s, 1H), 1.80–1.75 (m, 2H), 1.62–1.56 (m, 2H), 1.29 (s, 3H), 0.13 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.3, 139.1, 114.3, 114.3, 110.4, 87.9, 87.8, 71.6, 43.3, 42.5, 35.8, 35.4, 30.2, 30.1, 21.8, 21.6, 0.2; HRMS (EI) calcd for $C_{19}H_{29}Si$ $[M–H]^+$ 285.2038, found 285.2043.

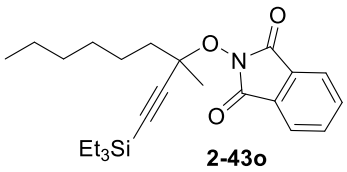


2-40n

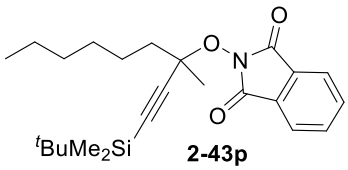
2-40n (24 mg, white solid, 37%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.7 Hz, 2H), 7.29 (t, *J* = 7.6 Hz, 2H), 7.20 (d, *J* = 7.1 Hz, 1H), 6.43 (d, *J* = 15.8 Hz, 1H), 6.32–6.27 (m, 1H), 2.51–2.48 (m, 1H), 2.37–2.31 (m, 1H), 1.88–1.82 (m, 1H), 1.70–1.84 (m, 1H), 1.30 (s, 9H), 0.15 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.9, 131.3, 129.7, 128.5, 126.8, 125.9, 110.7, 87.7, 43.4, 36.3, 29.5, 21.7, 0.3; HRMS (EI) calcd for $C_{34}H_{46}Si_2$ $[M]^+$ 510.3138, found 510.3129.



2-41n:2-41n' (2:1, 20 mg, colorless liquid, 32%)**:** **Major isomer 2-41n**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.4 Hz, 2H), 7.3 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.45–6.42 (m, 1H), 6.27–6.17 (m, 1H), 5.42 (d, *J* = 1.2 Hz, 1H) 5.30 (d, *J* = 1.2 Hz, 1H), 2.49–2.44 (m, 2H), 2.33 (t, *J* = 7.5 Hz, 1H), 0.22 (s, 9H); **Minor isomer 2-41n'**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.4 Hz, 2H), 7.3 (t, *J* = 7.6 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 6.45–6.42 (m, 1H), 6.27–6.17 (m, 1H), 5.79–5.76 (m, 1H), 3.18 (t, *J* = 7.0 Hz, 2H), 1.89 (s, 3H), 0.28 (s, 9H); **2-41n+2-41n'**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.7, 136.1, 131.0, 130.6, 130.5, 129.6, 128.5, 128.3, 127.9, 127.0, 127.0, 126.0, 122.5, 105.4, 104.4, 98.2, 94.4, 36.9, 34.4, 31.6, 22.9, 0.2, 0.1; HRMS (EI) calcd for $C_{17}H_{22}Si$ $[M]^+$ 254.1490, found 254.1487.



2-43o (colorless liquid, 67%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83–7.82 (m, 2H), 7.74–7.73 (m, 2H), 2.05–1.90 (m, 1H), 1.92–1.86 (m, 1H), 1.73–1.66 (m, 1H), 1.71 (s, 3H), 1.61–1.57 (s, 1H), 1.40–1.32 (m, 6H), 0.90 (t, *J* = 6.5 Hz, 3H), 0.83 (t, *J* = 7.9 Hz, 9H), 0.43 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.5, 134.2, 129.3, 123.3, 123.1, 105.1, 91.1, 86.7, 41.1, 31.7, 29.4, 27.3, 24.9, 22.6, 14.1, 7.3, 4.1; HRMS (ESI) calcd for $C_{24}H_{36}NO_3Si_2$ $[M+H]^+$ 414.2464, found 414.2463.



2-43p (60 mg, colorless liquid, 58%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.84–7.82 (m, 2H), 7.74–7.73 (m, 2H), 2.04–1.98 (m, 1H), 1.92–1.86 (m, 1H), 1.70 (s, 3H), 1.69–1.65 (m, 1H), 1.60–1.54 (m, 1H), 1,40–1.31 (m, 6H), 0.90 (t, *J* = 6.7 Hz, 3H), 1.70 (s, 9H), –0.06 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 164.4, 134.2, 129.2, 123.4, 104.6, 91.9, 86.6, 41.9, 31.7, 29.4, 27.2, 25.9, 24.9, 22.6, 14.1, -5.0; HRMS (ESI) calcd for $C_{24}H_{36}NO_3Si_2$ $[M+H]^+$ 414.2464, found 414.2472.

2.6. References

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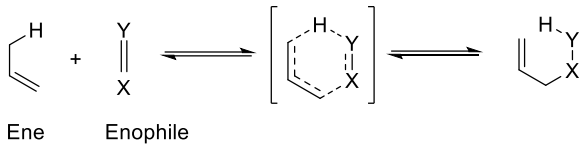
CHAPTER 3

FACILE ALDER-ENE REACTIONS OF SILYLALLENES INVOLVING AN ALLENIC C(sp^2)─H BOND

3.1. Introduction*

The ene reaction is a sigmatropic process by which an allylic H–C bond is activated by the π-bond of an enophile, replacing a H–C bond with a C–C or C–X (X = O, N) bond with a concomitant double bond transposition. This sigmatropic process was first made known by Alder in 1943 and documented in his Nobel Lecture in 1950.[1] Alkenes having allylic C–H bonds in a substrate with enophile (X=Y) undergoes 1,5-H shift[2] to form a new a C–C or C–X bond as shown in **Scheme 3.1**. The formal ene reaction proceeds through a concerted process via suprafacial interaction between HOMO of ene and the LUMO of enophile. On the other hand, it may proceeds through a stepwise radical process when the system is too strained to achieve a necessary geometry. In step wise mechanism, the observed side reaction is the cyclobutane formation.[3]



Scheme 3.1 Ene Reaction

3.2. Types of Ene Reactions

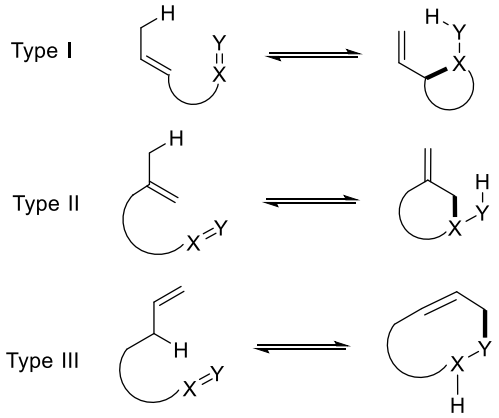


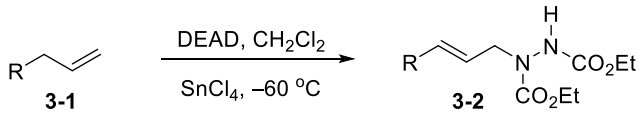
Figure 3.1 Intramolecular Ene Reaction Classification

* Reproduced in part with permission from Sabbasani, V. R.; Lee, D. "Facile Alder-Ene Reactions of Silylallenes Involving an Allenic C(sp^2)─H Bond" *Chem.−Eur. J.* **2015**, *21*, 17210–17214.

Both the inter- and intramolecular ene reactions are well developed by using various enophiles and they have been widely utilized in the organic synthesis.[4] The most common enophiles used in ene reactions are azo-compounds, carbonyls, nitroso compounds, imino compounds, arynes, and singlet oxygen. The mode of reactivity and connectivity of the ene donor and enophiles in intramolecular ene reaction is classified into three major types Type I, Type II and Type III (**Figure 3.1**).

3.2.1. Ene Reaction with Azodicarboxylates

Azodicarboxylates have been widely studied as enophiles in ene reactions with alkenes and allenes. The reaction of azo compounds with alkene provides useful allylic amination products by activating allylic C(sp^3)–H bond. The earlier developments of thermal ene reaction with azodicarboxylates were often required elevated temperature.[5] The most improved thermal azodicarboxylate-based ene reaction was developed by Leblanc and coworkers by employing more reactive bis(2,2,2-trichloroethyl) azodicarboxylate (BTCEAD) as an enophile.[6] Later in 1993, Heathcock and coworkers reported the first Lewis acid-promoted diazocarboxylate ene reaction with various alkenes (**Table 3.1**). The aza-ene reaction of alkenes **3-1** with diethylazodicarboxylate (DEAD) in the presence of stoichiometric amount of $SnCl_4$

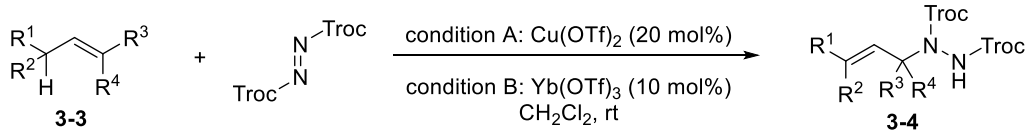


entry	alkene	ene adduct	yield (%)
1	**3-1a**	**3-2a** (*E*:*Z* = 11:1)	86
2	**3-1b**	**3-2b**	74
3	**3-1c**	**3-2c**	72

Table 3.1 First Lewis Acid Promoted Aza-Ene Reaction

provided allylic amination products **3-2** in good yield and excellent *E/Z* selectivity in case of **3-2a** (entries 1 to 3).[7] The other Lewis acids such as $BF_3{\cdot}OEt_2$, Et_2BBr, $ZnBr_2$ and $Ti(OiPr)_4$ were also tested, however they were ineffective, leading to no reaction or the decomposition of the azo-compounds.

Recently, Jørgensen and coworkers reported the first transition metal-catalyzed aza-ene reaction using BTCEAD (**Table 3.2**). This metal-catalazed aza-ene reaction was optimized by testing series of metal trifilates, and it was found that $Cu(OTf)_2$ and $Yb(OTf)_2$ were most effective in providing amination products **3-4** in good yields up to 99%.[8]



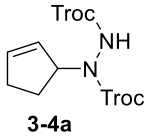
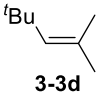
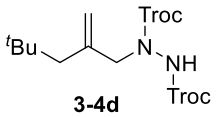
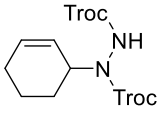
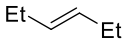
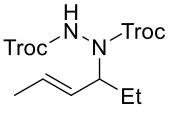
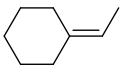
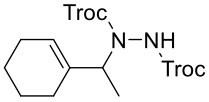
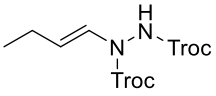
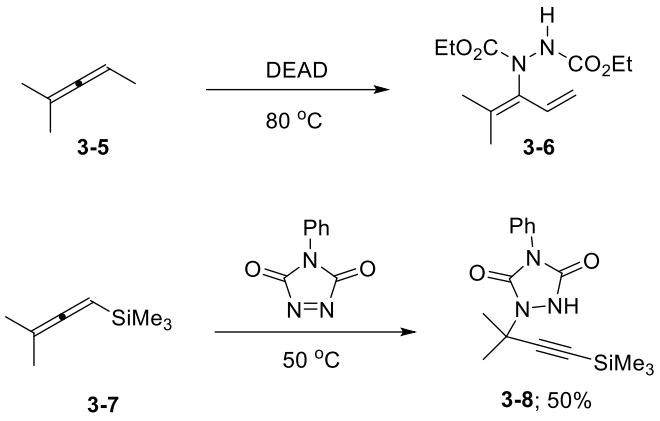
entry	alkene	product	condition	yield	entry	alkene	product	condition	yield
1	**3-3a**	 **3-4a**	A B	76% 95%	4	 **3-3d**	 **3-4d**	A	96%
2	**3-3b**	 **3-4b**	A B	44% 43%	5	 **3-3e**	 **3-4e**	A B	85% 92%
3	 **3-3c**	 **3-4c**	A B	98% 99%	6	**3-3f**	 **3-4f**	A B	98% 93%

Table 3.2 First Metal-Catalyzed Aza-Ene Reaction

Corey and coworkers developed the reverse aza-indolene reaction, where the ene reaction with indole derivative in the presence of 4-methyl-1,2,4-triazoline-3,5-dione in dichloromethane at 0 °C provided indole-ene product, the reverse reaction was performed at 150 °C to remove the enophile. This protection and deprotection strategy was utilized in the total synthesis of a natural product okaramine N.[9]

Aza-ene reactions of alkyl- and silylallenes were also briefly studied (**Scheme 3.2**). Thermal aza-ene reaction of alkylallene **3-5** in the presence of DEAD at 80 °C provided diene **3-6** by activating allylic C(sp^3)–

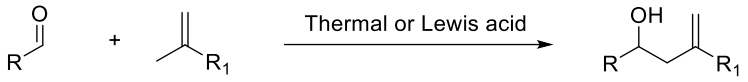
H bond.[10] On the other hand, thermal aza-ene reaction of silylallene **3-7** with 4-phenyl-1,2,4-triazoline-3,5-dione at 80 °C afforded only the propargyl amination product **3-8** via the activation of an allenic C(sp^2)–H bond.[11]



Scheme 3.2 Aza-Ene Reaction of Allenes

3.2.2. Carbonyl Ene Reaction

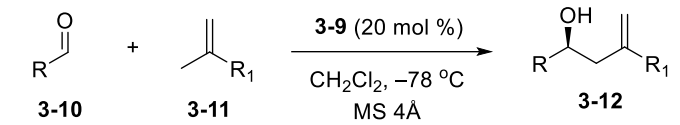
The carbonyl ene reaction is one of the most extensively investigated ene reactions, where the carbonyl containing enophiles and the all carbon ene-donor are widely used to generate synthetically valuable homoallylic alochols (**Scheme 3.3**). Thermal as well as Lewis and Brønsted acid-catalyzed carbonyl ene reactions were developed.



Scheme 3.3 Carbonyl Ene Reaction

In 1982, the first asymmetric intermolecular carbonyl ene reaction was developed by Whitesell and coworkers by using chiral glyoxylate as an enophile in the presence of stoichiometric amounts of Lewis acid, which provided diastereomeric excess up to 99%.[12] In 1988, the first catalytic asymmetric intermolecular carbonyl ene reaction was reported by Yamamoto and coworkers. In this transformations, they have used chiral binaphthol-derived aluminum complex **3-9**, and achieved enantioselectivity of the

reaction up to 88% with good to moderate yields of homoallylic alcohols (**Table 3.3**).[13]



entry	R	R_1	yield (%)	ee (%)
1	C_6F_5	Ph	35	78
2	Cl_3C	Ph	43	73
3	C_6F_5	SPh	88	88
4	Cl_3C	Me	79	78

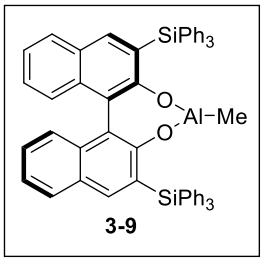
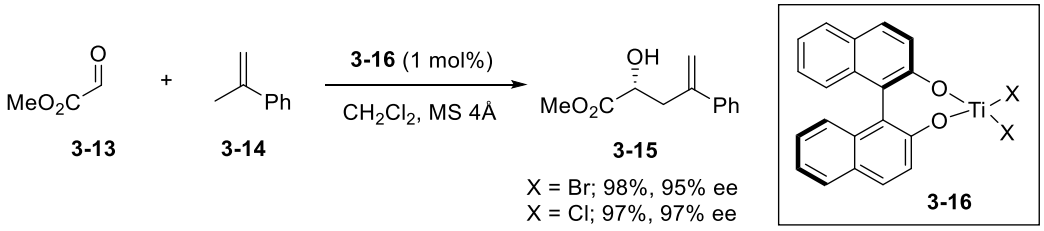


Table 3.3 First Catalytic Asymmetric Carbonyl Ene Reaction

Mikami and coworkers developed an asymmetric carbonyl ene reaction with an in situ generated chiral titanium-BINOL complex from diisopropoxytitanium dihalide and optically active binaphthol (BINOL).[14] The best results were obtained with (R)-BINOL and $TiCl_2(^iPrO)_2$ to form chiral homoallylic alcohol up to 86% ee with 82% yield. After this report, various asymmetric carbonyl ene reactions were developed extensively by using chiral titanium complexes. For example, the ene reaction between enophile **3-13** and alkene **3-14** using dihalo titanium-BINOL complex **3-16** provided an homoallylic alcohol in excellent yield and enatioselectivity (**Scheme 3.4**). Even the chiral complex derived from (R)-BINOL having 33% ee also provided ene product with 92% ee in 92% yield. It was believed that, the high enatioselectivity obtained from this titanium-BINOL complex is the result of isostructural dinuclear chelate complex. The dimerized

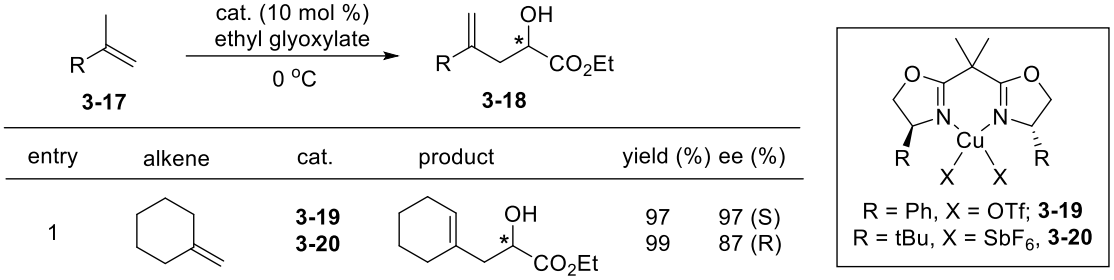


Scheme 3.4 Titanium-BINOL Catalyzed Intermolecular Carbonyl Ene Reaction

dinuclear complexes may exist as (*R*,*R*) or (*S*,*S*) and meso-forms, and the authors believed that the less reactive meso-compound may allowing excess (*R*)-BINOL to form preferentially (*R*,*R*)-dimer after

consumption of (S)-BINOL. The formed (R,R)-BINOL dimer complex resulting the high enantioselctivite homoallylic alcohol.[15,16]

A Cu-catalyzed asymmetric carbonyl ene reaction was developed by Evans and coworkers, where the carbonyl-ene reaction of alkene **3-17** with ethyl glyoxylate using Cu-Box catalyst **3-19** and/or **3-20** provided homoallylic alcohol **3-18** in excellent yields and enatioselectivity (**Table 3.4**).[17]



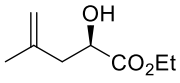
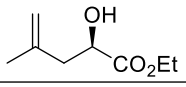
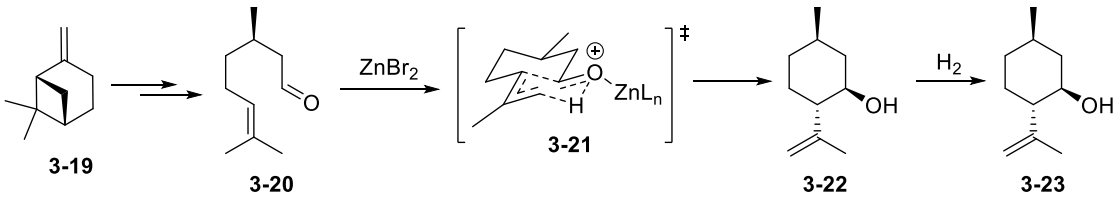
entry	alkene	cat.	product	yield (%)	ee (%)
1		**3-19** **3-20**		97 99	97 (S) 87 (R)
2		**3-19**		92	92
3		**3-19**		99	89

Table 3.4 Cu-Catalyzed Asymmetric Carbonyl Ene Reaction

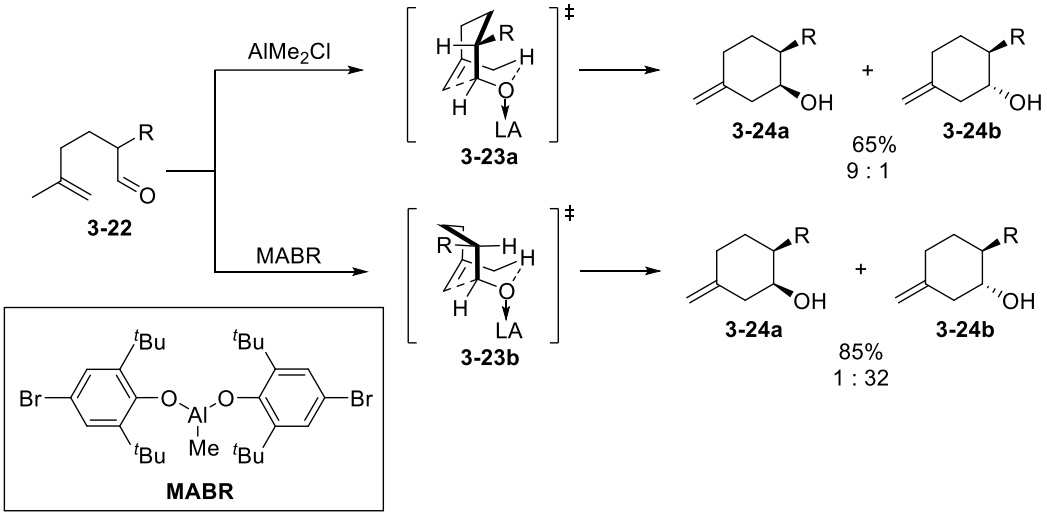
Intramolecular carbonyl ene reactions have been extensively utilized in the natural product synthesis. For example, in industrial process intramolecular carbonyl ene reaction for the facile and quicker production of menthol from β-pinene (**Scheme 3.5**). The established menthol synthesis starts from readily available



Scheme 3.5 Menthol Synthesis Using Type-I Intramolecular Ene Reaction

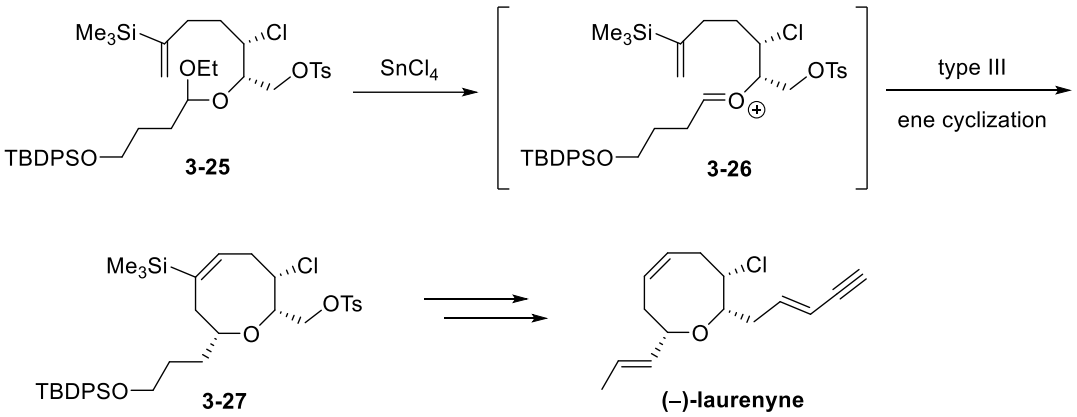
β-pinene **3-19** by converting it to (*R*)-citronellal **3-20**, which then was easily converted to L-isopulegol **3-22** via Type I carbonyl ene cyclization using Lewis acid $ZnBr_2$. The stereoselective formation of **3-22** can be explained by adopting chair like transition state **3-21**. L-Isopulegol **3-22** can be easily converted to

menthol **3-23** by hydrogenation.[18]



Scheme 3.6 Type II Ene Reaction for Carbocyles Synthesis

The Snider group and also the Yamamoto group reported the Lewis acid promoted carbonyl ene cyclization to form carbocyles in high selectivity (**Scheme 3.6**). In Snider's work, carbonyl-ene reaction of **3-22** in presence of dimethylaluminum chloride afforded *syn*- and *anti*-carbocyles **3-24a** and **3-24b** in 9:1 ratio.[19] On the other hand, in Yamamoto's work the same carbonyl-ene substrate **3-22** provided *anti*-carbocyle **3-24b** in high selectivity upon treating with MABR.[20] The reversal of selectivity of these



Scheme 3.7 Type III Carbonyl Ene Cyclization in Total Synthesis of (−)-Laurenyne

reactions can be explained by two different transition states, where substrate **3-22** with $AlMeCl_2$ proceed

via transition state **3-23a** whereas that with MABR proceeds preferentially via boat-like transition state **3-23b**.[21]

A type III carbonyl ene cyclization was successfully employed by Overman in the total synthesis of (−)-laurenyne (**Scheme 3.7**). Acetal **3-25** in the presence of $SnCl_4$ afforded carbocylization product **3-27** via oxocarbonium intermediate **3-26**. The type III carbonyl ene cyclization is an enabling tool for the effective construction of the required oxocene core of (−)-laurenyne.[22]

3.2.3. Nitroso Ene Reaction

The most common method for acylnitroso ene reaction was first developed by the Keck and Kirby groups. In their two-step protocol, the generated acylnitroso intermediate was reacted with alkene under thermal condition.[23] Most recently, Read de Alaniz and coworkers developed an efficient acylnitroso ene reaction from the corresponding oximes,[24] where *N*-hydroxycarbamate **3-28** was treated with CuCl in the

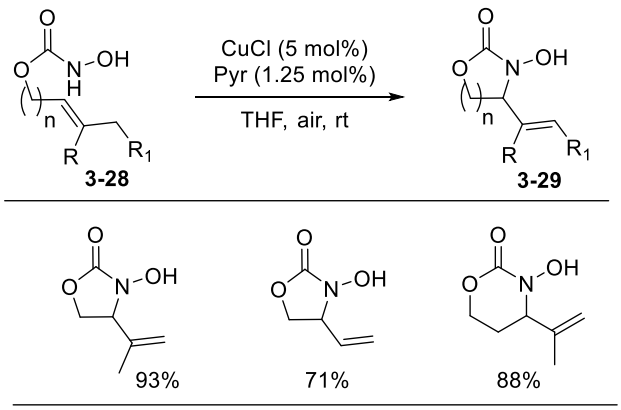


Table 3.5 Intramolecular Nitroso Ene Reaction

presence of base and air to provide intramolecular nitroso ene product **3-29** in excellent yield (**Table 3.5**). In this transformation, mild reaction conditions were employed for the formation of acylnitroso intermediate. Similarly, inter molecular nitrosoene reactions under optimized conditions, by using the excess alkene was achieved (**Table 3.6**). Srivastava and coworkers also developed an iron(II)-catalyzed intermolecular nitrso ene reaction for β-alkyl-*N*-aryl aza Baylis−Hillman adducts in good to moderate yields.[25]

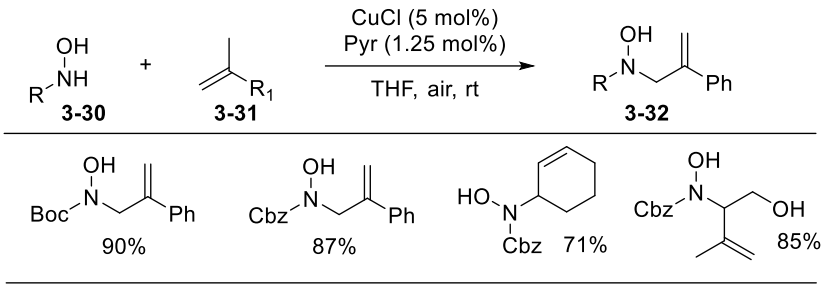
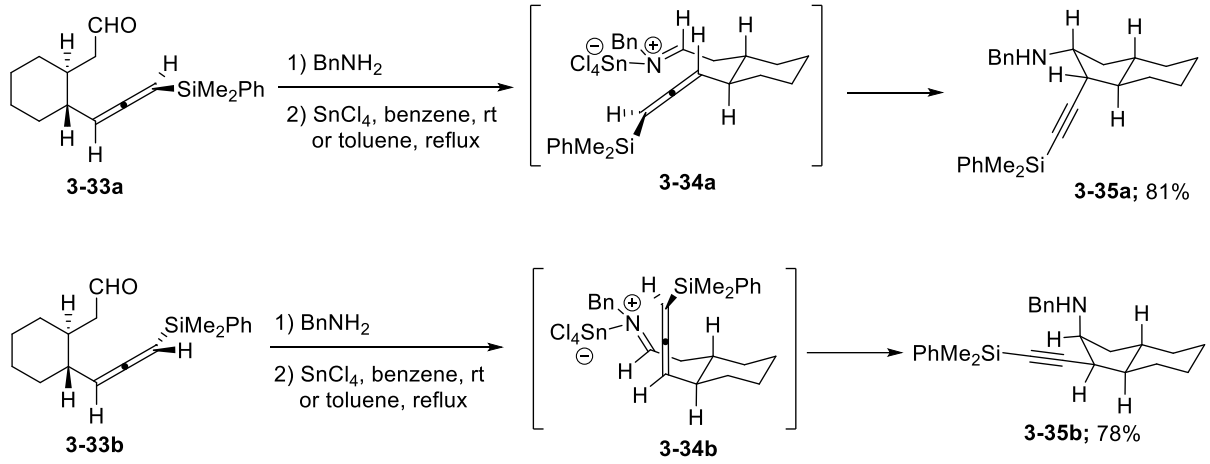


Table 3.6 Intermolecular Nitroso Ene Reaction

3.2.4. Imino Ene Reaction

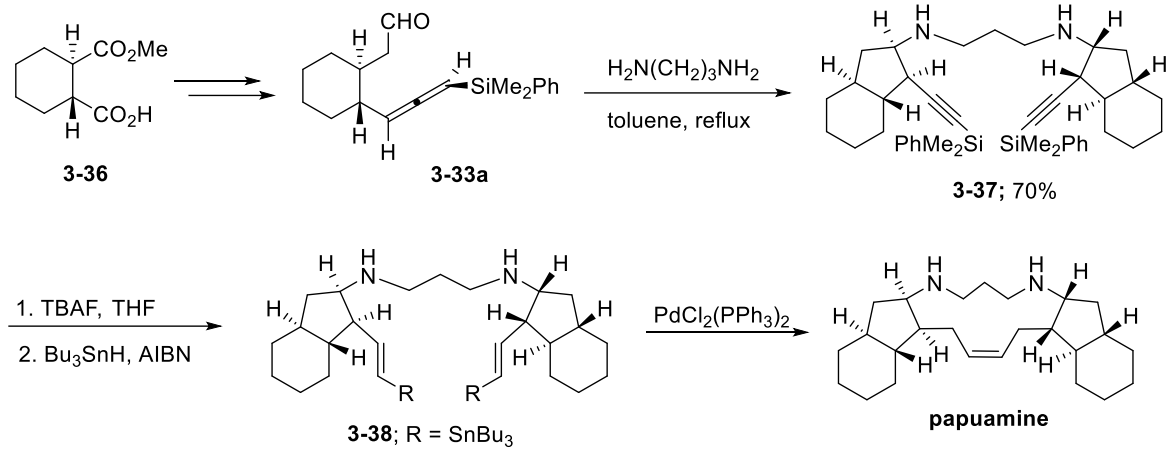
The imino ene reaction is a powerful synthetic method to generate homoallylic and homopropargylic amines, although the imino ene reaction was less developed compared to the carbonyl ene. First, the intramolecular imono ene cyclization of silylallenes were extensively studied by Weinreb. This cyclization



Scheme 3.8 Intramolecular Imino Ene Reaction

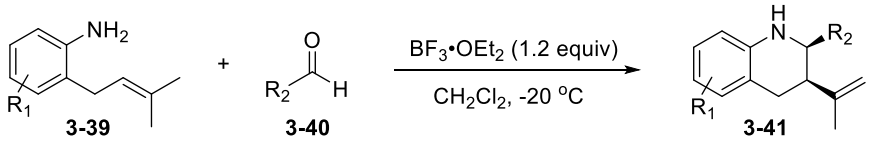
protocol cleverly utilized in the natural product synthesis (**Scheme 3.8**). The first report of intramolecular imino ene reaction employed two different diastereomers of silylallenes **3-33a** and **3-33b** having a tethered aldehyde. Treating these compounds with benzyl amine and Lewis acid under reflux afforded bicyclic homopropargyl amines **3-35a** and **3-35b** in good yield. The stereochemistry of the allene moiety was effectively transferred to the products via transition states **3-34a** and **3-34b** generate **3-35a** and **3-35b**, respectively. This intramolecular ene reaction was used in the total synthesis of papuamine, where

silylallene aldehyde **3-33a** was refluxed with propylenediamine to provide the tetracyclic bis-homopropargyl amine **3-37** stereoselectively in 70% yield. The resulting dimeric product **3-37** was further converted to a natural product in three steps.[26] The intramolecular ene reaction was also applied to the total synthesis of (−)-monanine, (−)-coccinine, (−)-pancracine, (−)-brunsvigine and (−)-manthine alkaloids.[27]

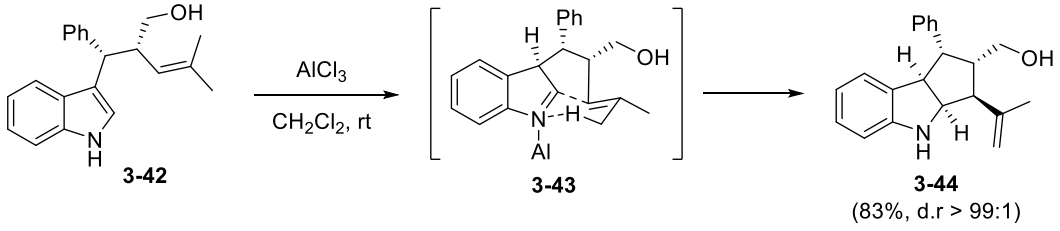


Scheme 3.9 Intamolecular Imino Ene Reaction in Total Synthesis of Papuamine

The intramolecular ene reaction of in situ generated iminium ion from alkenyl amines **3-39** with an aldehyde **3-40** in the presence of Lewis acid provided the cyclized product **3-41** in good to moderate yields (**Scheme 3.10**).[28]



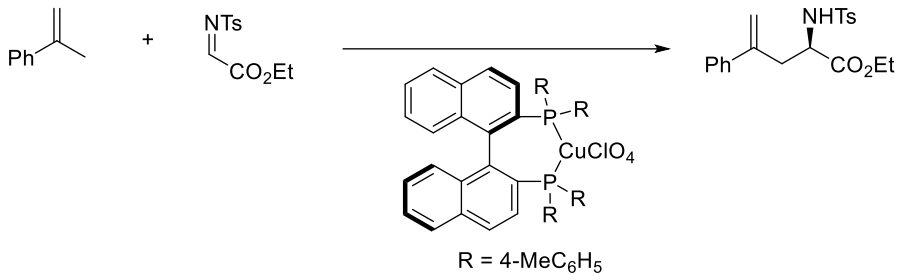
Scheme 3.10 Intramolecular Alkene Imino Ene Reaction



Scheme 3.11 Intramolecular Direct Imino Ene Reaction

Recently, Chen and coworkers reported a Lewis acid-catalyzed intramolecular imino ene reaction of indoles. In this study the authors described alkene tethered indole **3-42** upon treating with of $AlCl_3$ provided cyclic product **3-44** with complete diastereoselectivity via intermediate **3-43** (**Scheme 3.11**).[29]

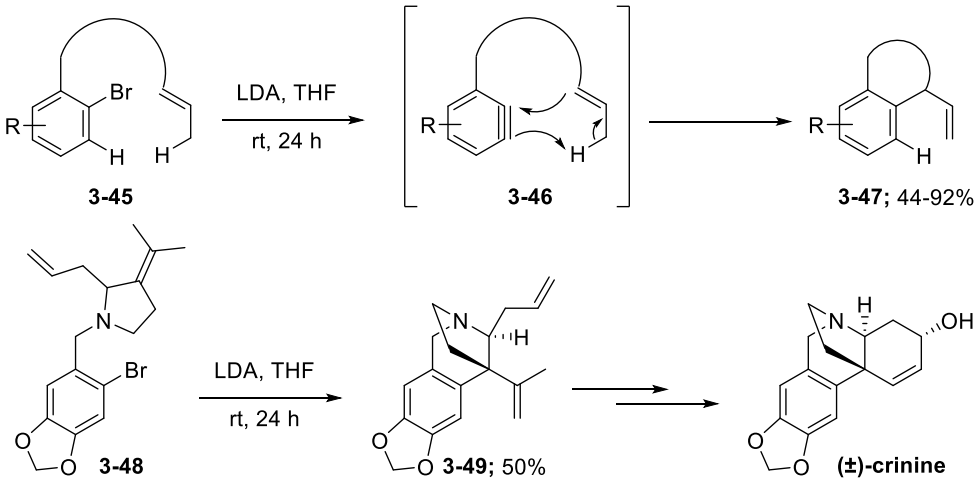
Intermolecular imino ene reaction with alkenes and imines have also been reported. The best enantioselective imino ene reactions to obtain α-imino esters was reported by Lectka and Jørgensen using a chiral Lewis acid copper-BINAP system (**Scheme 3.12**). In this reaction, high enantioselctivity was achieved up to 92% with good yields.[30]



Scheme 3.12 Intermolecular Enantioselective Imino Ene Reaction

3.2.5. Aryne Ene Reaction

The strong electrophilic nature of arynes invites investigations on their ene reaction behavior by several groups after the first report in 1969 by Oda. The application of this aryne ene reaction have also been used



Scheme 3.13 Intramolecular Aryne Ene Reaction

in natural product synthesis. Recently, Lautens and coworkers reported an intramolecular aryne ene reaction with alkene tethered with bromobenzenes and its application to total synthesis of (±)-crinine (**Scheme 3.13**). The internal alkene containing aryl bromide **3-45**, upon treatement with LDA, afforded aryne ene cyclization product **3-47** in good to moderate yields. For the synthesis of natural product, aryl bromide **3-48** was subjected to LDA to provide **3-49** in 50% yield.

Recently, The Lee and Hoye groups also reported the aryne ene reaction, the aryne has been generated from tetrayne and/or triyne via hexadehydro Diels-Alder (HDDA) reaction. In Lee's report, tetraynes **3-50** has been used to generate aryne **3-51** in refluxing toluene (**Table 3.7**), which underwent cyclization with a tethered alkene to form **3-52** in good to moderate yields depending on the ring size as well as the substituents in the ene tether.

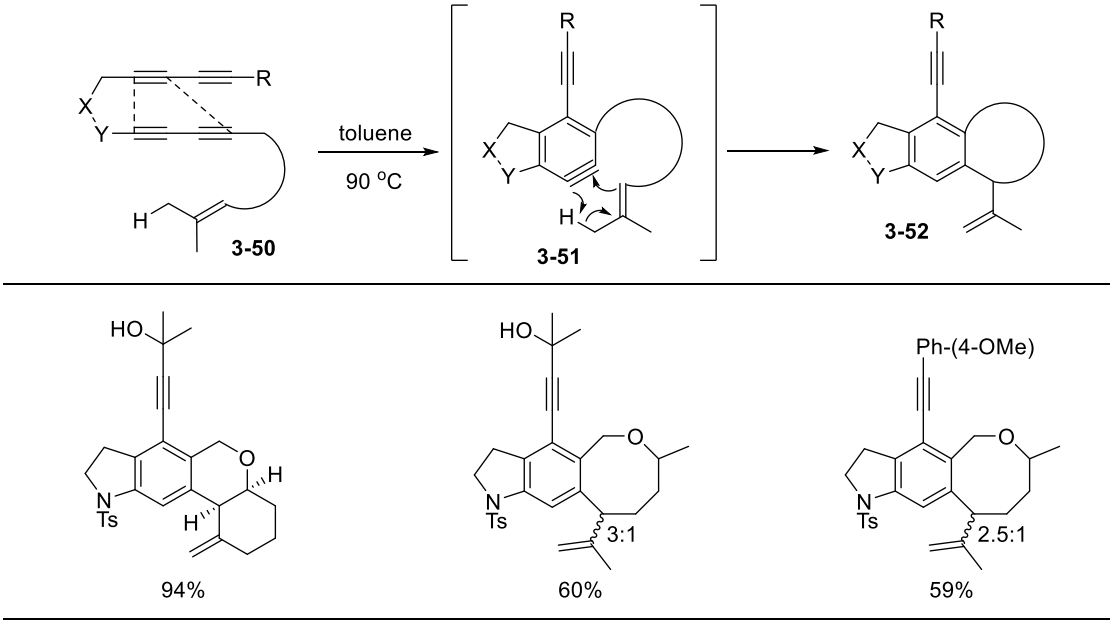
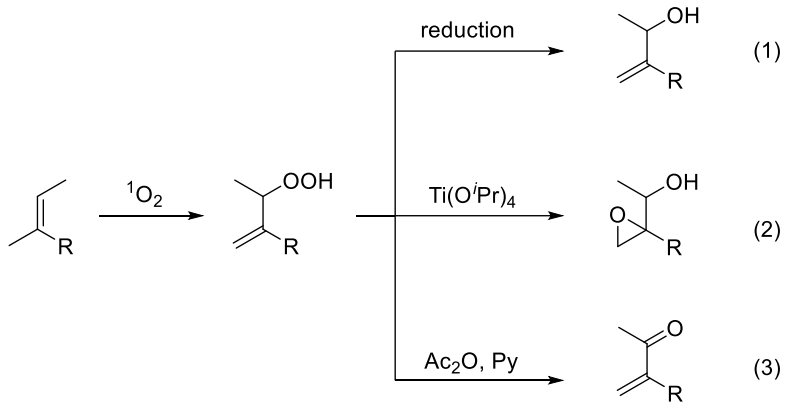


Table 3.7 Aryne Ene Reaction of Tetraynes

3.2.6. Singlet Oxygen Ene Reaction

Ene reactions with singlet oxygen were first discovered by Schenck. Due to the abundance of molecular oxygen, Schenck ene reaction has been studied extensively and also extensively used in organic synthesis. The products in Shenck ene reaction are allylic hydroperoxides, which are important synthetic intermediates

that can be used for various transformations. The most common transformations are reduction to allylic alochols (**Scheme 3.14**, eq 1), epoxidation with Ti(IV) (eq 2), and dehydration to form α,β-unsaturated carbonyl compounds (eq 3).



Scheme 3.14 Applications of Allylic Hydroperoxides

The regioselectivity in Schenck ene reaction can be controlled by using classical *cis*-effect, *gem*-directing and non-bonded interactions of large group as well as the silyl and stannyl substituent effects. Stephenson and Rautenstrauch demonstrated the *cis*-substituent effect (**Table 3.8**, eq 1) in the Schenck ene reaction, where they have observed high selectivity by abstracting the hydrogen at more-hindered side (**3-53a** to **3-53d**).[31] Based on the observed results, several models have been proposed. However, most of the models and the calculations data suggests the existence of interaction between the incoming singlet-oxygen and two allylic hydrogens that are on the same side highly preferred.[32]

On the other hand, several groups have studied the large group germinal substituent effect in oxygen ene reaction (**Table 3.8**, eq 2). It was observed that the allylic hydrogens next to a large alkyl substituent are more reactive than the allylic hydrogen next to small alkyl substituent in the ene reaction of non-symmetrical *cis*- and *trans*-alkylsubstituted alkenes (**3-54a** to **3-54c**). It was rationalized through a repulsive 1,3-nonbonded interactions of oxygen with small and large group in the transition state.[33]

The highly regioselective allylic hydrogen abstraction from the group that is *geminal* to larger substituent of the double bond occurred predominately in the reaction with singlet oxygen (**Table 3.8**, eq

3).[34] The allylic hydrogen abstraction can also be affected by silicon-substituent, which is similar to the *germinal* large group effect (**Table 3.8,** eq 4).[35]

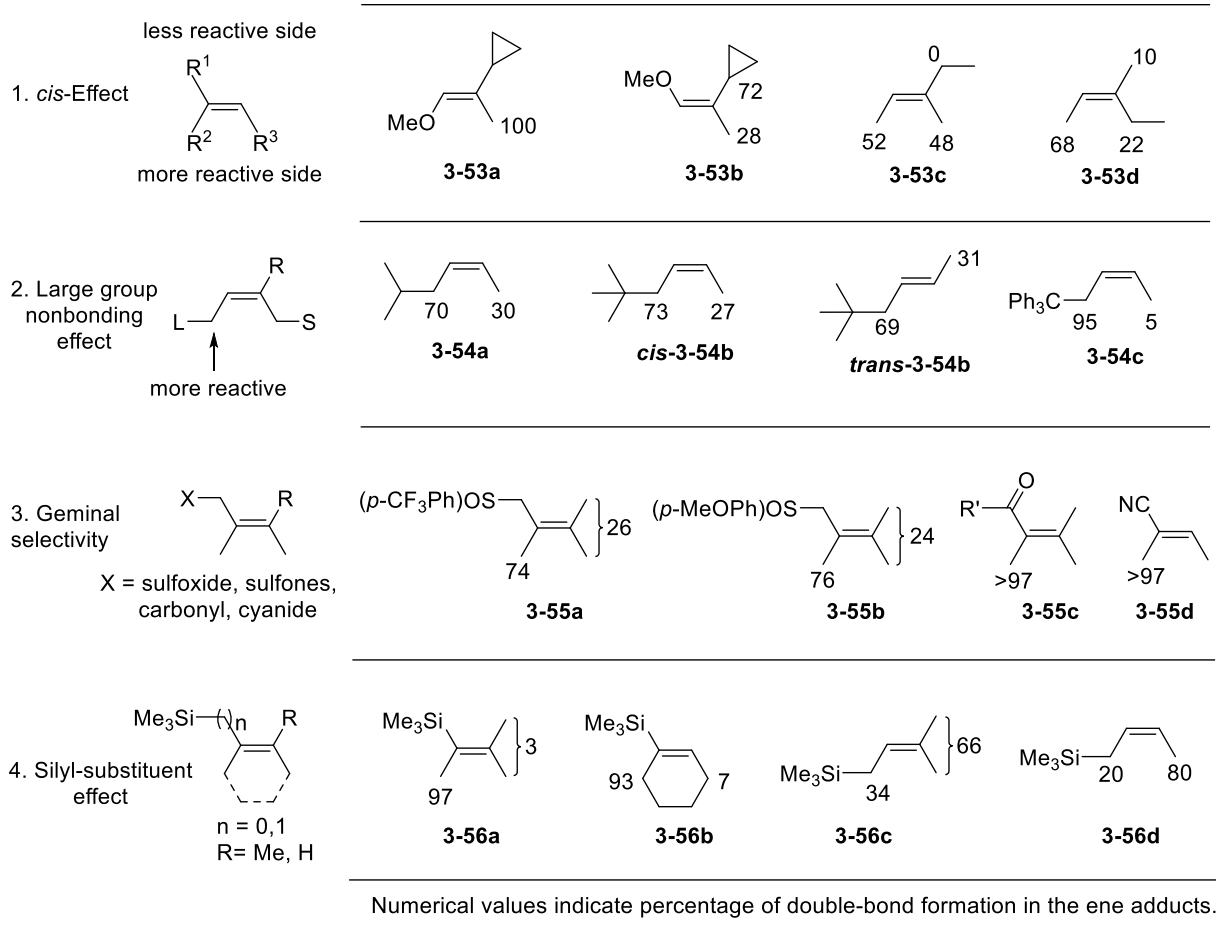
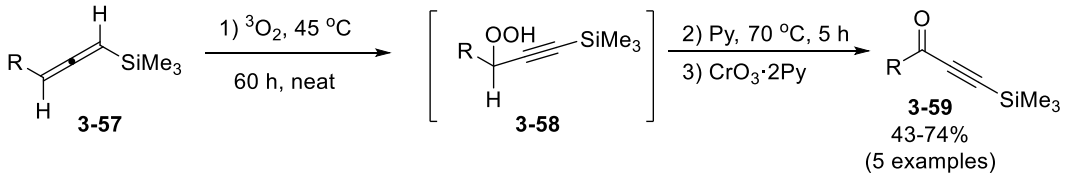


Table 3.8 Regioselectivity in Schenck Ene Reaction

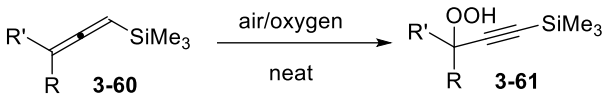
3.3. Ene Reaction of Silylallenes with Triplet Molecular Oxygen



Scheme 3.15 Autooxidation of Disubstituted Silylallenes

Suziki and coworkers briefly studied the oxidation of disubstituted silylallenes with triplet oxygen. In this transformation silylallene **3-57** in the presence of triplet oxygen at 45 °C afforded peroxide **3-58**, which

then was directly oxidized to ketone **3-59** in good to moderate yields (**Scheme 3.15**).[36]



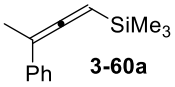
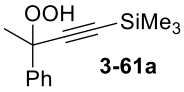
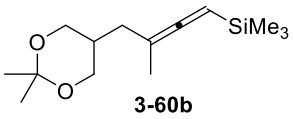
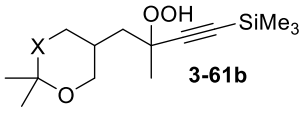
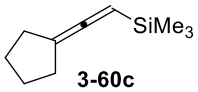
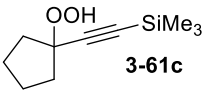
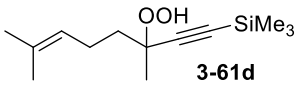
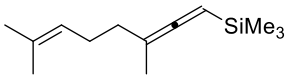
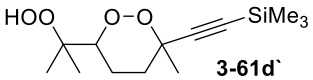
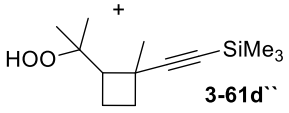
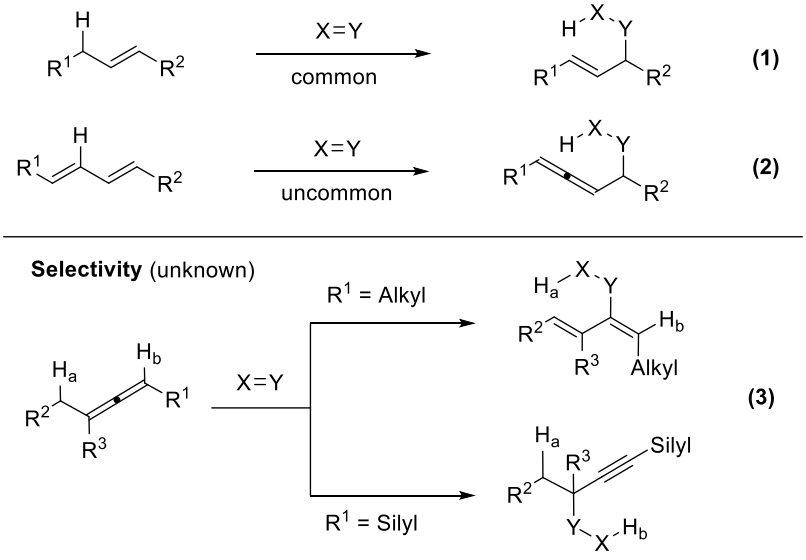
entry	allene	peroxide	yield (%)
1			86 (air, 16 h)
2			>95 (air, 24 h)
3			>95 (air, 48 h)
			9% (air, 48 h) 8% (O_2, 24 h)
4			50% (air, 48 h) 64% (O_2, 24 h)
		(2:1 mixture of diasteromers)	
			32% (air, 48 h) 17% (O_2, 24 h)

Table 3.9 Autooxidation of Trisubstituted Silylallenes

Our group has extensively studied the autooxidation of trisubstituted silylallenes to afford propargy hydroperoxides (**Table 3.9**). Acyclic as well as cyclic ketones-derived silylallenes provided the corresponding peroxides in excellent yields (entries 1−3). The reaction with prenyl tethered silylallene **3-60d** delivered a mixture of peroxide and the double bond involved endoperoxides in different ratio's depending on the reaction conditions (entry 4). The mechanism for the formation of propargyl hydroperoxides is proposed to involve ene-type reaction by abstracting hydrogen selectively from the allenic carbon.[37]

3.4. Results and Discussion[†]

In general, ene reactions involve electron-rich ene-donors containing allylic C–H bonds and enophiles of electron-withdrawing π-systems, and the orbital alignment of the allylic C(sp^3)–H bonds is an important factor (eq 1). Although less common, ene reactions involving the activation of C(sp^2)–H bond that generate allene or alkyne products are reported (eq 2), where the involvement of allylic C–H bonds is to be nullified. To the best of our knowledge, the favorable participation of an allenic C(sp^2)–H over an equally available allylic C(sp^3)–H bond in Alder ene reaction has not been reported (eq 3).

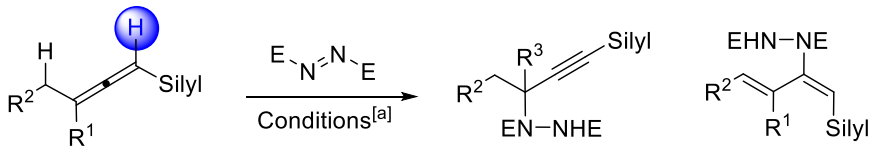


Based on the reactivity of silyl allenes sporadically reported in literature, we surmised that the reactivity and selectivity of silylallenes toward ene reaction would be strongly influenced by the silyl substituent on the allene moiety whereby the less common reaction involving allenic C(sp^2)–H under typical environment might become more favorable. To explore this possibility, we examined the azodicarboxylate-mediated ene reaction profiles of various silyallenes derived from acyclic and cyclic ketones, and herein we report the general trend of the ene reactions of silylallenes favorably engaging allenic C(sp^2)–H over C(sp^3)–H bonds.

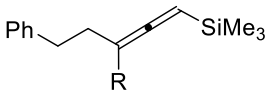
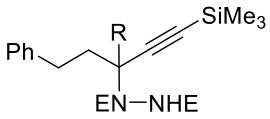
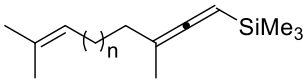
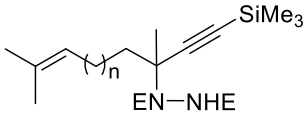
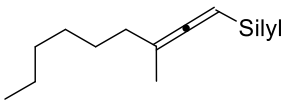
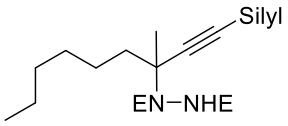
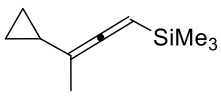
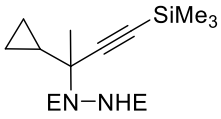
We commenced our investigation by examining the ene reaction of acyclic ketone-derived silyallenes

[†] Reproduced in part with permission from Sabbasani, V. R.; Lee, D. "Facile Alder-Ene Reactions of Silylallenes Involving an Allenic C(sp^2)─H Bond" *Chem.−Eur. J.* **2015**, *21*, 17210–17214.

3-62a–g with systematic variation in their structural characteristics (**Table 3.10**). Under typical reaction conditions (1.2 equiv diisopropyl-azodicarboxylate, CH_2Cl_2, 28 °C, 16–24 h), tri- and disubstituted silylallenes **3-62a** and **3-62b** provided tertiary and secondary propargylic hydrozodicarboxylate **3-63a** and **3-63b** in 76 and 63% yield, respectively, without forming **3-64a** and **3-64b** (entries 1 and 2). The ene reaction of silylallenes **3-62c** and **3-62d** with a prenyl group tethered with one or two methylene units provided products **3-63c** and **3-62d** in 68 and 55% yields (entries 3 and 4). Ene reaction product of the



3-62 **3-63** **3-64** (not formed)

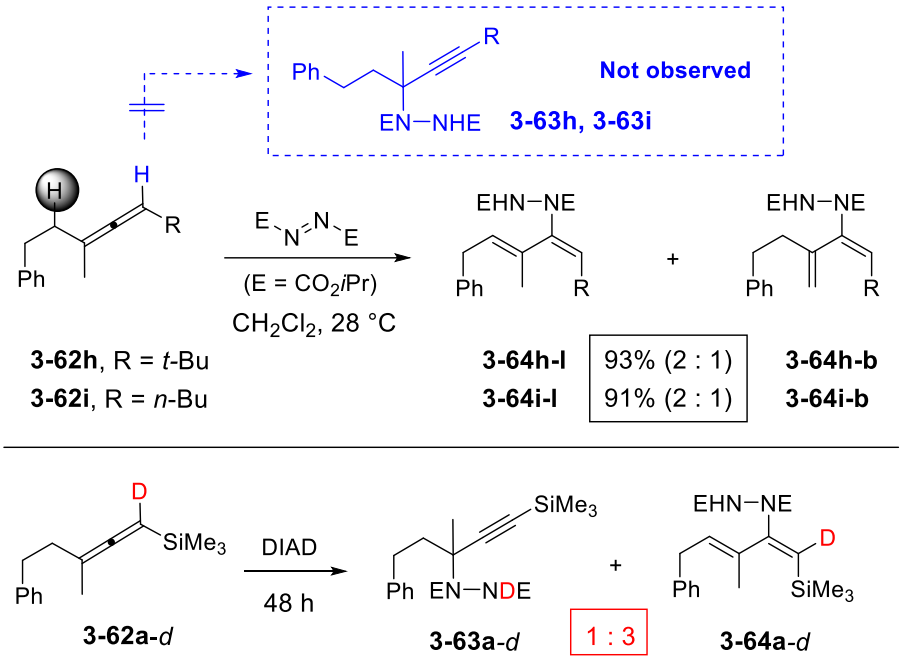
entry	Silylallene	Product	ratio (**2-63 : 2-64**)	yield (%)[b]
				
1	**3-62a** R = Me	**3-63a**	1 : 0	76
2	**3-62b** R = H	**3-63b**	1 : 0	63
				
3	**3-62c** n = 1	**3-63c**	1 : 0	68
4	**3-62d** n = 2	**3-63d**	1 : 0	55
				
5	**3-62e** Silyl = $SiEt_3$	**3-63e**	1 : 0	77
6	**3-62f** Silyl = $SiMe_2$t-Bu	**3-63f**	1 : 0	72
				
7	**3-62g**	**3-63g**	1 : 0	72

[a] Conditions: diisopropylazodicarboxylate (1.2 equiv), CH_2Cl_2 , 28 °C, 16–24 h.
[b] Isolated yields after purification.

Table 3.10 Alder-Ene Reaction of Silylallenes with Azodicarboxylate

tethered prenyl group was not observed in appreciable amounts. Different silyl groups other than trimethylsilyl ($SiMe_3$) in allene **3-62e** ($SiEt_3$) and **3-63f** ($SiMe_2$t-Bu) did not affect the reaction efficiency and thus products **3-63e** and **3-63f** were obtained in 77 and 72% yields, respectively (entries 5 and 6). Similarly, silylallene **3-62g** containing a cyclopropyl group afforded **3-63g** in 72% yield (entry 7).

The most salient features of these ene reactions in **Table 3.10** is the selective participation of the allenic C(sp^2)–H bond next to the silyl group without involvement of allylic C(sp^3)–H bonds. The contrasting reactivity of the corresponding alkyl group-substituted allenes clearly demonstrated with the ene reaction of **3-62h** and **3-62i** (**Scheme 3.16**). When subject to the identical conditions, *t*-butyl and *n*-butyl-substituted allenes **3-62h** and **3-62i** provided **3-64h-l** and **3-64h-b** (2:1) in 93% yield, and **3-64i-l** and **3-64i-b** (2:1) in 91% yield, respectively. The ene reaction products **3-63h** and **3-63i** involving allenic C(sp^2)–H bonds were not observed. This contrasting ene reaction preference of **3-62h** and **3-62i** compared to silylated allenes implies a strong activating role of the silyl substituent for the Alder ene reactions involving allenic C(sp^2)–H bonds.

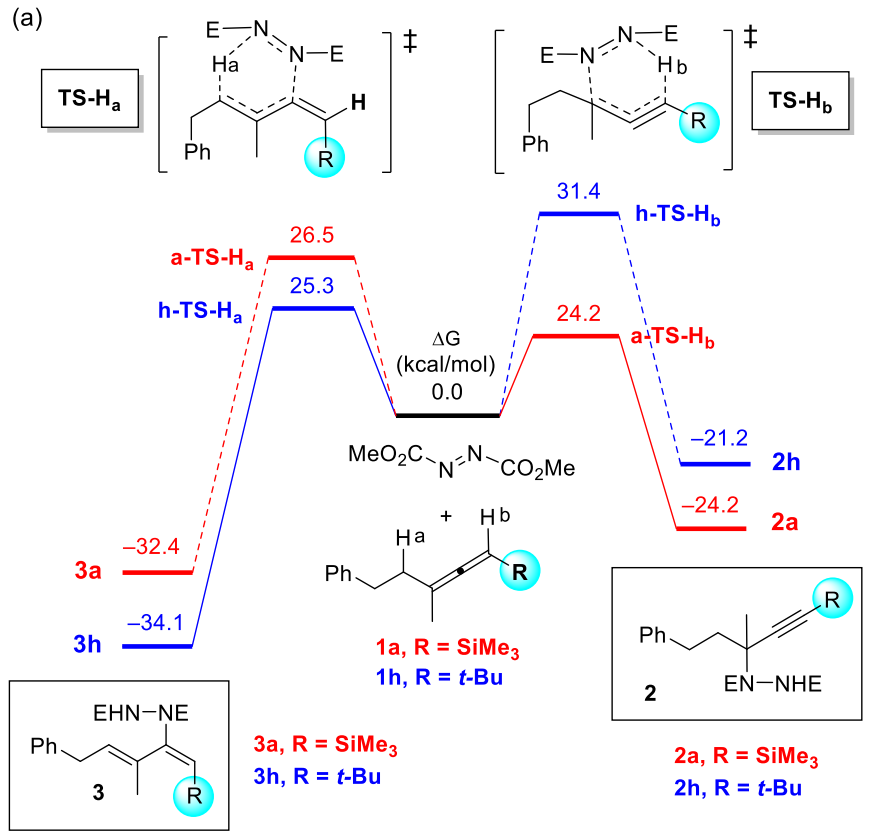


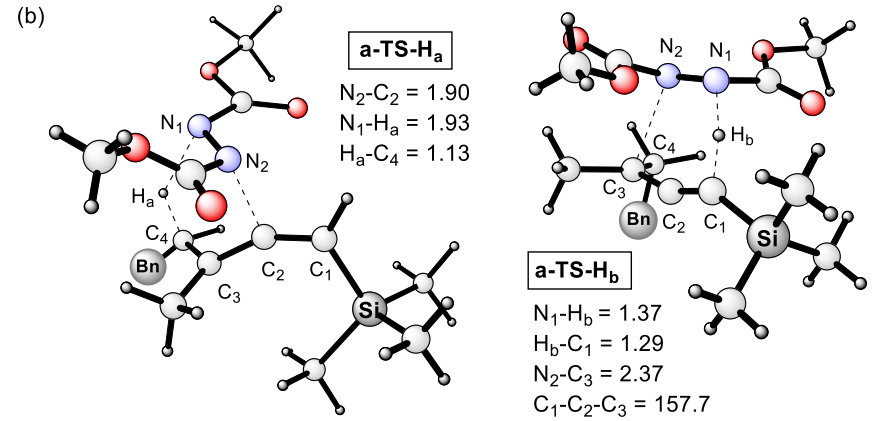
Scheme 3.16 Alder-Ene Reactions of Alkyl-Substituted Allenes with Azodicarboxylate

The delicate influence of the substituent on allenes for their reactivity was further illustrated by a deuterium-labeled allene **3-62a-*d***. Compared to **3-62a** that exclusively engaged allenic C(sp^2)–H for its ene reaction within 20 h, generating **3-63a**, the corresponding mono-deuterated substrate **3-62a-*d*** provided a mixture of **3-64a**-*d* and **3-64a**-*d* in a 1:3 ratio after 48 h. This stark contrast in reactivity between **1a** and **3-62a-*d*** clearly indicates that silylallene **3-62a-*d*** has significantly lower reactivity for the ene reaction involving allenic C(sp^2)–H bond (high deuterium kinetic isotope effect), such that the other mode of ene reaction involving allylic C–H bonds outcompete to afford **3-64a**-*d* predominantly.

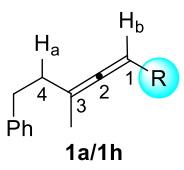
To understand the substituent-dependent ene reactivity and selectivity of allenic C(sp^2)–H and allylic C(sp^3)–H bonds, Density Functional Theory (DFT) calculations for the reactions of **3-62a** and **3-62h** were carried out with a slightly simplified azodicarboxylate (CO_2Me instead of CO_2i-Pr) (**Figure 3.2**). Optimization and frequency calculations were performed in CH_2Cl_2 at the (SMD)M06-2X/6-311++G(2d,p) level of theory.[38] The calculated free energy values (ΔG) are in good agreement with the experimental results where the silyl-substituted transition state **a-TS-H$_b$** is preferred to **a-TS-H$_a$** by 2.3 kcal/mol for **3-62a**, leading favorably to **3-63a** (**Figure 3.4.1a**). On the contrary, the reaction of *tert*-butyl-substituted allene **3-62h** proceeds via **h-TS-H$_a$**, which is 6.1 kcal/mol lower in energy than **h-TS-H$_b$**, thus only **3-64h** was obtained.

Based on these geometric structures, we surmised that the activation energy for the reaction with allylic C(sp^3)–H bond via **TS-H$_a$** should be determined predominately by the interaction between N_2 and C_2, and thus the electron-rich allene should be more reactive. This is further supported by the fact that the relative energy for **h-TS-H$_a$** is 1.2 kcal/mol lower than that for **a-TS-H$_a$**, as natural population analysis (NPA) showed the C_2 atom is less positively charged in **1h** than in **1a** (**Figure 3.2c**).[39] On the other hand, the energy required for allenic C(sp^2)–H activation should be more relevant to the strength of the C_1–H_b bond, which is substantially being broken in **TS-H$_b$**. Theoretical support for this supposition was obtained by the calculated bond dissociation energies in **Figure 3.2c**, where the D_0 (C_1–H_b) is quite close to the D_0 (C_4–H_a) for *t*-butyl-substituted allene **1h**, and only marginal variation in D_0 (C_4–H_a) is predicted upon changing





(c)



1a/1h

R	D_0 (C_4–H_a)[a]	D_0 (C_1–H_b)[a]	NPA (C_2)
$SiMe_3$ (**1a**)	87.5	82.2	0.084e
t-Bu (**1h**)	87.4	87.2	0.037e

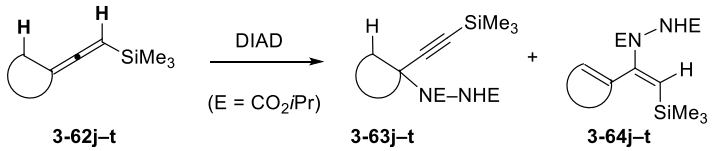
[a] In kcal/mol

Figure 3.2 Calculated Energies and Geometries for the Ene Reaction of *t*-Bu- and Me_3Si-Substituted Allenes with Azodicarboxylate

t-butyl to $SiMe_3$ for **1a**. On the other hand, lowering as much as 5 kcal/mol in D_0 (C_1–H_b) was calculated for **1a**, indicating dramatic activation of the α-C(sp^2)–H bond by the silyl group.[40]

The relatively low bond dissociation energy of the α-C(sp^2)–H bond in silylallenes is believed to be a major factor rendering different reactivity and selectivity for silylallenes in their Alder ene reaction, otherwise **TS-H_b** would be disfavored due to the higher energy required for distortion of the silylated allene moiety and its hybridization pattern change.

Next, we examined the reactivity of cyclic silylallenes **3-62j–t** derived from cyclic ketones (**Table 3.11**), and the results of typical substrates were subsequently validated by DFT calculations (**Table 3.12**). Under the typical conditions, 3-phenylcyclobutanone-derived allene **3-62j** generated two ene reaction products **3-63j** and **3-64j** with a 4.6:1 ratio in 76% yield (entry 1), but cyclopentanone derived allene **3-62k** provided only **3-64k** in 92% yield without forming **3-62k** (entry 2). The calculated energy difference between **TS-H_a** and **TS-H_b** for **3-62k** was found to be 1.6 kcal/mol, favoring **3-64k** over **3-63k**, which is in qualitative agreement with the observed ratio of these products. Cyclohexanone-derived allenes **3-62l** provided **3-63l** and **3-64l** in 90% combined yield with a 1.8:1 ratio (entry 3). The low selectivity in this reaction is consistent with the marginal energy difference between **l-TS-H_b** (28.5 kcal/mol) and **l-TS-H_a** (29.1 kcal/mol). The reaction of more substituted cyclohexanone derived silylallenes **3-62m** and **3-62n** showed much higher selectivity but in opposite preference, generating only **3-63m** and **3-64n** in good yields (entries 4 and 5). These contrasting behavior of **2-62m** and **2-62n** can be explained by the steric effect of their substituents in the vicinity of the allene moiety. Probably, the isopropyl group in **2-62m** significantly hinders the approach of the reacting azodicarboxylate to the allylic hydrogen prohibiting the formation of **3-64m**. On the other hand, the quaternary carbon on the bicyclo[4.1.0]heptane system in **2-62n** would hiders the formation of the incipient C–N bond at the vicinity, prohibiting the formation of **2-63m**. Cycloheptyl-containing silylallene **3-62o** afforded **3-63o** and **3-64o** in 75% combined yield with a 1:2 ratio (entry 6), yet the corresponding *t*-butyl and *n*-butyl substituted allenes **3-62p** and **3-62q** afforded **3-64p** and **3-64q** exclusively (entries 7 and 8). These examples further bolster the conclusion that the silyl group promotes



3-62j–t **3-63j–t** **3-64j–t**

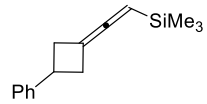
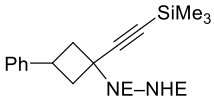
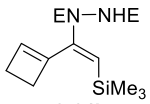
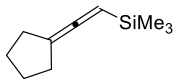
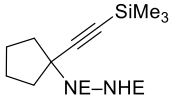
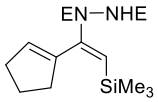
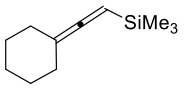
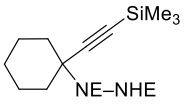
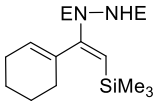
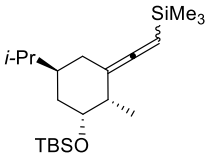
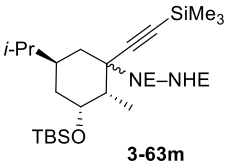
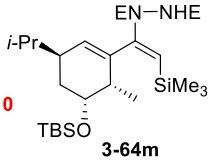
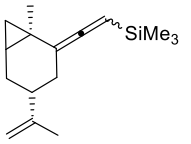
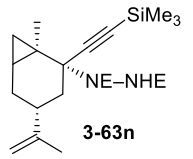
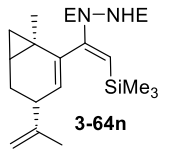
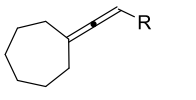
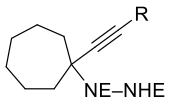
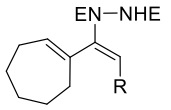
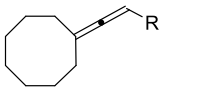
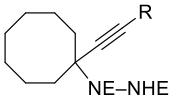
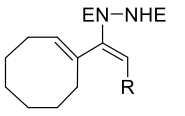
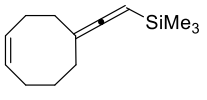
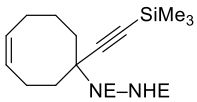
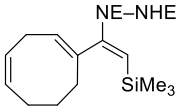
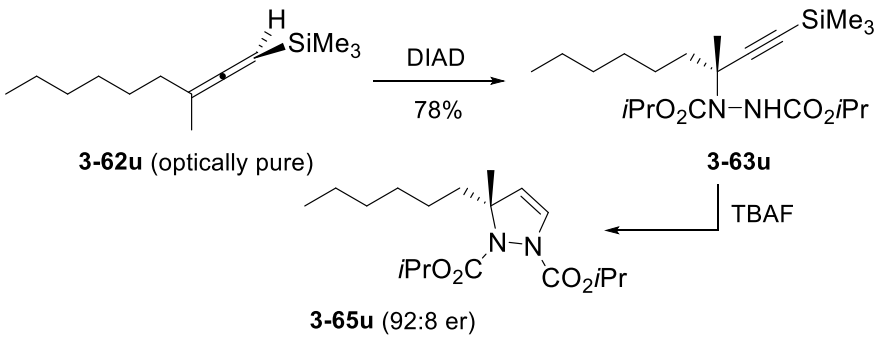
entry	Silylallene	Product Ratio (3-63 : 3-64)	Product	Yield (%)[a]
1	 **3-62j**	 **3-63j**	**4.6 : 1**	 **3-64j**	76
2	 **3-62k**	 **3-63k**	**0 : 1**	 **3-64k**	92
3	 **3-62l**	 **3-63l**	**1.8 : 1**	 **3-64l**	90
4	 **3-62m**	 **3-63m**	**1 : 0**	 **3-64m**	73
5	 **3-62n**	 **3-63n**	**0 : 1**	 **3-64n**	91
6	 **3-62o** R = $SiMe_3$	 **3-63o**	**1.5 : 1**	 **3-64o**	75
7	**3-62p** R = *t*-Bu	**3-63p**	**0 : 1**	**3-64p**	94
8	**3-62q** R = *n*-Bu	**3-63q**	**0 : 1**	**3-64q**	78
9	 **3-62r** R = $SiMe_3$	 **3-63r**	**1 : 0**	 **3-64r**	72
10	**3-62s** R = *t*-Bu	**3-63s**	**0 : 1**	**3-64s**	80
11	 **3-62t**	 **3-63t**	**1 : 0**	 **3-64t**	84

Table 3.11 Ene Reaction Selectivity of Cycloalkyl-Based Silylallenes

Allene	ΔG(TS-H_a)	ΔG(TS-H_b)	ΔΔG[a]	2 : 3
3-62k	25.2	26.8	-1.6	0 : 1
3-62l	29.1	28.5	0.6	1.8 : 1
3-62r	26.9	25.7	1.2	1 : 0
3-62s	26.0	31.9	-5.9	0 : 1

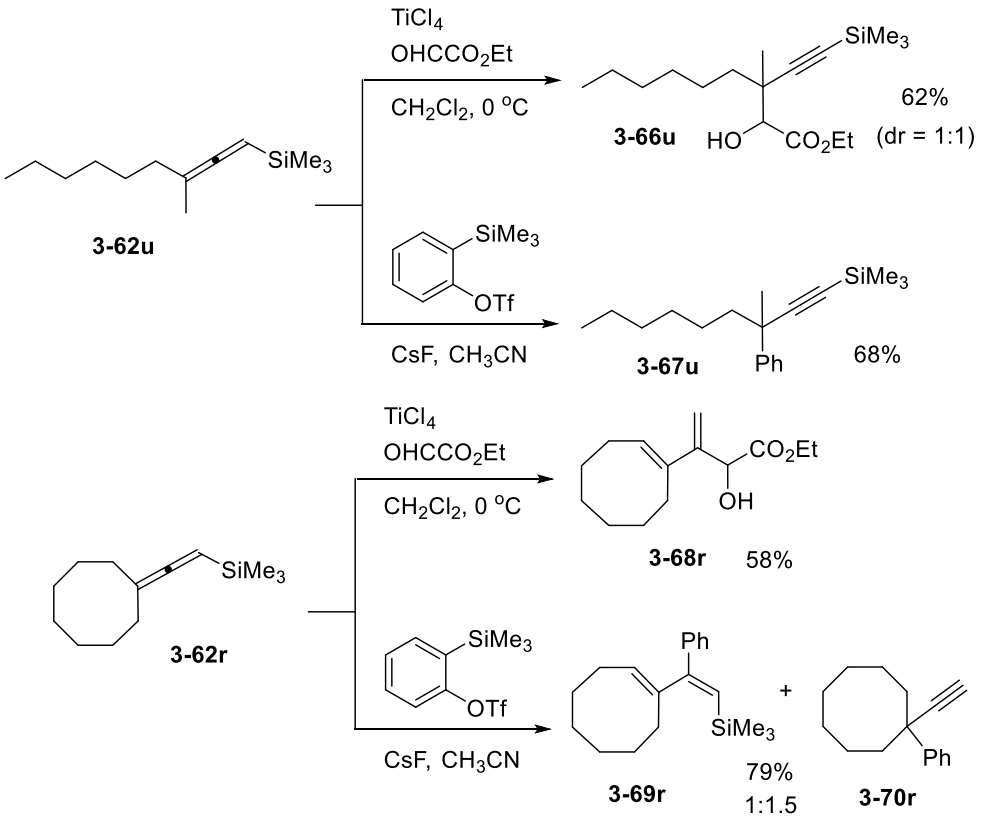
Table 3.12 Computational Results for Selected Allenes (in kcal/mol)

the ene reaction with the allenic C(sp^2)–H bond, which is further demonstrated by the contrasting reactivity between cyclooctane-based allenes **3-62r** and **3-62s** (entries 9 and 10). The reaction of silyl group-containing allene **3-62r** engaged an allenic C(sp^2)–H bond, affording product **3-63r** in 72% yield (entry 9), while that of *t*-butyl-containing allene **3-62s** afforded an alternative ene product **3-64s** (80% yield) involving an allylic C(sp^3)–H bond (entry 10). The contrasting behaviors of **3-62r** and **3-62s** were reproduced by computations, where the activation energy for the allenic C(sp^2)–H bond of **3-62r** is 1.2 kcal/mol lower than that with the allylic C(sp^3)–H bond. On the other hand, *t*-butyl-substituted allenes **3-62s** showed the opposite preference by 5.9 kcal/mol, which is consistent with the formation of **3-64s** as the sole product. Cyclooctadiene-derived silylallene **3-62t** containing an extra double bond provided **3-63t** in 84% yield without any other product involving the activation of its allylic C–H bonds (entry 11).



Scheme 3.17 Application to a Chiral Pyrazoline Containing an Amino-Tertiary Centre

The concerted nature of the Alder ene reaction of silylallenes with azodicarboxylate was illustrated by the reaction of chiral silylallene **3-62u** (optically pure) (**Scheme 3.17**). After the conversion of **3-63u** (the *e.e* was not determined at this stage) to pyrazoline **3-65u**, its enantiomeric ratio was determined to be 92:8, which suggests that the ene reaction proceeded mainly in a concerted manner.[41] The result not only validates the DFT predictions for the concerted mechanism but also bodes well for potential utility of the process to construct various chiral molecules containing an amino-tertiary center.[42]



Scheme 3.18 Ene Reactions of Silylallenes with Ethyl Glyoxylate and Benzyne

The general trend of the ene reaction of representative silylallenes **3-62u** and **3-62r** was further illustrated by other enophile such as ethyl glyoxylate and benzyne[43] (**Scheme 3.18**). For linear silylallene **3-62u**, ene reactions with both ethyl glyoxylate and benzyne enophiles preferred to generate allenic C(sp^2)–H ene product **3-66u** and **3-67u** in 62% and 68% yield. On other hand, from the corresponding cycloalkyl-substituted silylallene **3-62r**, C(sp^3)–H ene product **3-68r** with ethyl glyoxylate and **3-69r** with benzyne

became major products. On other hand, from the corresponding cycloalkyl-substituted silylallene **3-62r**, the reaction with ethyl glyoxylate provided only protodesilylated C(sp^3)─H ene product **3-68r**, whereas that with benzyne delivered protodesilylated C(sp^2)─H ene product **3-70r** as a major product.

3.5. Summary

In summary, we have observed an unexpected ene reaction selectivity of silylallenes with azodicarboxylates. In general, regardless of the substituent pattern, acyclic ketone-derived silylallenes promote ene reaction with an allenic C(sp^2)–H bond exclusively. On the other hand, the selectivity between allenic C(sp^2)–H vs allylic C(sp^3)–H bonds in cyclic ketone-derived silylallenes are significantly affected by the ring size and the substituent pattern in the vicinity of the allene moiety. Comparison of the reactivity of silylallenes with the corresponding alkyl-substituted allenes clearly indicates that silyl group has a critical role for the allenic C(sp^2)–H bond to participation in the ene reaction. DFT calculations provide further insight into these reactions that the distortion energies for both the reacting allene and azodicarboxylate moieties to reach the transition state is one of the major factors that dictate the selectivity between the two reaction pathways.

3.6. Experimental Details

3.6.1. General Information: See **chapter 1** section **1.6.1** for general information

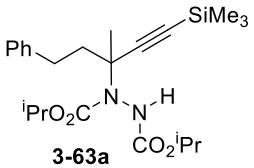
3.6.2. General Procedure for Ene Reaction of Silylallenes

Ene Reaction with Diisopropyl Azodicarboxylate: Silylallene **3-62a** (100 mg, 0.43 mmol) and diisopropyl azodicarboxylate (0.1 mL, 0.52 mmol) were dissolved in CH_2Cl_2 in a thick-walled Schlenk tube equipped with a magnetic stir bar. The reaction mixture was degassed briefly under vacuum at -78 ^oC, and stirred at 28 ^oC for 20 h. The tube was opened to air at room temperature and the solvent was removed under reduced pressure. Product **3-63a** (yield 76%) was isolated by flash column chromatography (EtOAc/hexanes, 1:4) on silica gel.

Ene Reaction with Ethyl Glyoxylate: Titanium tetrachloride (31 μL, 0.29 mmol) in CH_2Cl_2 (3 mL) was added to THF (3 mL) dropwise at 0 °C. The mixture was warmed to room temperature over 10 min, which than concentrated and the residue was redissolved in CH_2Cl_2 (5 mL). To this solution, were added ethyl glyoxylate (50% in toluene, 75 μL, 0.38 mmol) followed by silylallene **3-62u** (40 mg, 0.19mmol) at 0 °C. The mixture was stirred for 20 min at the same temperature, quenched with saturated aqueous sodium bicarbonate, extracted with dichloromethane (2x10 mL), and dried over magnesium sulfate. The filtrate was concentrated and purified by column chromatography (EtOAc/hexanes, 5:1) to give product **3-66u** in 62% yield.

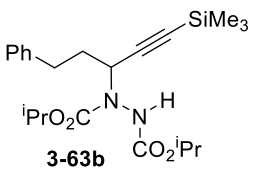
Ene Reaction with Ethyl Benzyne: A solution containing 2-(trimethylsilyl)phenyl trifluoromethanesulfonate (92 μL, 0.38 mmol), silylallene **3-62u** (40 mg, 0.19 mmol) and CsF (58 mg, 0.38 mmol) in CH_3CN (3 mL) was stirred at 0 ^oC for 5 h. The reaction mixture was concentrated and the residue was redissolved in EtOAc (15 mL), washed with water (8 mL) and dried over magnesium sulfate. The filtrate was concentrated and purified by column chromatography (EtOAc/hexanes, 20:1) to give product **3-66u** in 68% yield.

3.6.3. Selected Characterization Data



3-63a

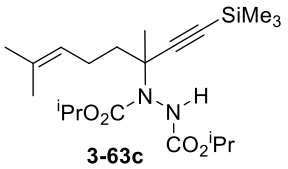
3-63a: (colorless oil, 76% yield): ^1H NMR (500 MHz, $CDCl_3$) δ 7.27-7.26 (bm, 2H), 7.21-7.18 (bm, 3H), 6.45-6.06 (bs, 1H), 4.96-4.91 (m, 2H), 2.86-2.63 (m, 2H), 2.49-2.04 (m, 2H), 1.76 (S, 3H), 1.27-1.24 (m, 12H), 0.18 (S, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.1, 142.2, 128.5, 128.3, 125.9, 106.8, 89.5, 70.2, 63.4, 42.4, 31.7, 26.8, 22.0, 0.04; HRMS (ESI) calcd for $C_{23}H_{37}N_2O_4Si$ $[M+1]^+$ 433.2523, found 433.2523.



3-63b

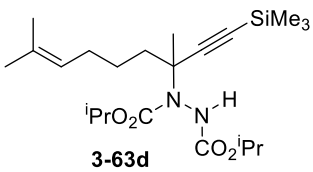
3-63b: (colorless oil, 3 days, 63% yield): ^1H NMR (500 MHz, $CDCl_3$) δ 7.27-7.22 (m, 5H), 6.35-6.19 (bs, 1H), 4.97-4.95 (m, 2H), 2.77 (m, 2H), 2.10-1.96 (bm, 2H), 1.28-1.24 (m, 12H), 0.17 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0, 141.3,

128.6, 128.3, 125.9, 102.5, 89.4, 70.1, 50.8, 35.1, 32.2, 22.0, 0.0; HRMS (ESI) calcd for $C_{22}H_{35}N_2O_4Si$ $[M+1]^+$ 419.2366, found 419.2359.



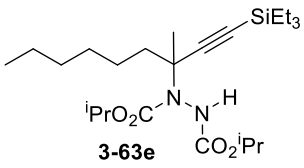
3-63c

3-63c: (colorless oil, 68% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.40-6.37 (bs, 1H), 5.12-5.11 (m, 1H), 4.94-4.88 (m, 2H), 2.37-2.29 (m, 2H), 2.01-2.00 (m, 2H) 1.72-1.71 (s, 6H), 1.67 (s, 3H), 1.61 (s, 1H), 0.14 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.7, 139.8, 126.7, 106.5, 89.4, 69.8, 69.3, 63.6, 39.8, 29.9, 25.6, 24.1, 24.0, 22.0, 17.5, 0.0; HRMS (ESI) calcd for $C_{21}H_{39}N_2O_4Si$ $[M+1]^+$ 411.2679, found 411.2679.



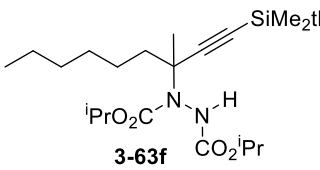
3-63d

3-63d: (colorless oil, 55% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.42-6.36 (bs, 1H), 5.11 (m, 1H), 4.94-4.90 (m, 2H), 2.25-1.82 (m, 6H), 1.69 (s, 6H), 1.58 (s, 3H), 1.26-1.22 (m, 12H), 0.13 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.9, 131.6, 124.4, 106.83, 88.7, 69.6, 63.2, 39.9, 28.0, 26.8, 25.7, 25.3, 22.0, 17.7, 0.0; HRMS (ESI) calcd for $C_{22}H_{41}N_2O_4Si$ $[M+1]^+$ 411.2836, found 425.2838.



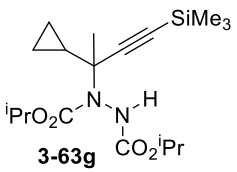
3-63e

3-63e: (colorless oil 77% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.44-6.16 (bs, 1H), 4.96-4.88 (m, 2H), 2.35-1.76 (m, 2H), 1.70 (s, 3H), 1.50-1.46 (m, 2H), 1.28-1.21 (m, 18H), 0.97 (t, J = 7.9 Hz, 9H), 0.87 (t, J = 6.1 Hz, 3H), 0.56 (q, J = 7.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.7, 154.4, 108.0, 86.1, 69.7, 63.7, 40.2, 31.7, 29.4, 29.1, 26.8, 25.0, 22.5, 22.0, 21.9, 14.0, 7.4, 4.4; HRMS (ESI) calcd for $C_{24}H_{47}N_2O_4Si$ $[M+1]^+$ 455.3305, found 455.3299.



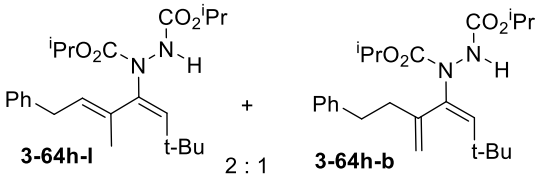
3-63f

3-63f: (colorless oil, 72% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.44-6.20 (bs, 1H), 4.91-4.86 (m, 2H), 2.27-1.75 (m, 2H), 1.67 (s, 3H), 1.56-1.44 (m, 2H), 1.25-1.19 (m, 18H), 0.99 (s, 9H), 0.85 (t, J = 6.1 Hz, 3H), 0.04 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.7, 107.3, 87.0, 69.7, 63.5, 40.1, 31.6, 29.3, 29.1, 26.7, 26.3, 26.0, 22.5, 22.0, 21.9, 16.5, 14.0, -4.6; HRMS (ESI) calcd for $C_{24}H_{47}N_2O_4Si$ $[M+1]^+$ 455.3305, found 455.3300.



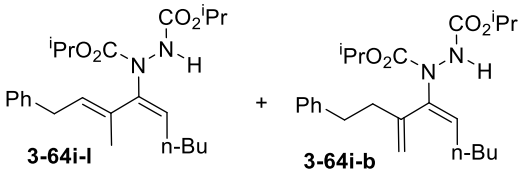
3-63g

3-63g: (colorless oil, 72% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.45-6.23 (bs, 1H), 4.95-4.94 (m, 2H), 1.82-1.74(bs, 3H), 1.35-1.23 (m, 13H), 0.87-0.44 (m, 4H), 0.12 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0, 103.4, 88.1, 69.4, 63.8, 29.7, 28.0, 27.8, 22.0, 18.5, -0.0; HRMS (ESI) calcd for $C_{18}H_{33}N_2O_4Si$ $[M+1]^+$ 369.2210, found 369.2215.



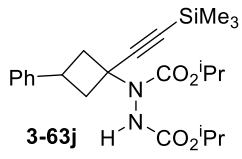
3-64h-l **3-64h-b**

3-64h-I & **3-64h-b**: (colorless oil, 25 h, 93% yield, 2:1); **3-64h-l**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.59 (m, 1H), 3.47-3.29 (m, 2H), 1.85-1.81 (bs, 3H), 1.10 (s, 9H). 2h-b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.55 (m, 1H), 5.23 (s, 1H), 5.05 (s, 1H), 2.81-2.78 (m, 2H), 2.45-2.41 (m, 2H), 1.04 (s, 9H); **3-64h-l & 3-64h-b**: ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.5, 141.9, 140.9, 140.7, 130.4, 130.3, 136.1, 132.6, 131.3, 128.4, 128.3, 125.9, 125.8, 118.8, 70.17, 69.4, 36.4, 36.3, 34.4, 34.0, 32.8, 32.6, 30.8, 30.6, 29.7, 22.0. **3-64h-I**; HRMS (ESI) calcd for $C_{24}H_{37}N_2O_4$ $[M+1]^+$ 417.2753, found 417.2747.



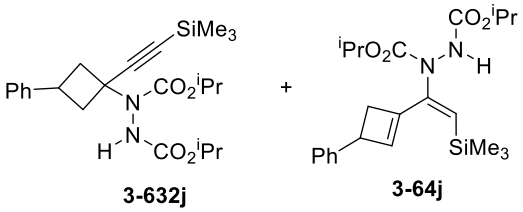
3-64i-l **3-64i-b**

3-64i-I & **3-64i-b**: (colorless oil, 25 h, 91% yield, 2:1); **3-64i-l**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.50-3.28 (m, 2H), 1.87 & 1.80 (s, 3H). **3-64i-b**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.82-2.73 (m, 2H), 2.54-2.39 (m, 2H), 2.16-2.01 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.7, 143.1, 141.9, 141.7, 140.9, 133.4, 131.0, 128.4, 128.3, 125.9, 125.8, 118.1, 113.5, 70.7, 70.6, 70.4, 70.2, 69.8, 69.6, 36.2, 35.6, 35.3, 35.2, 34.5, 34.4, 34.3, 31.9, 31.2, 13.9.

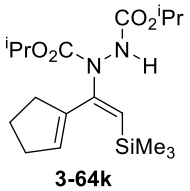


3-63j

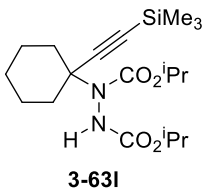
3-63j: (colorless oil, 62% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.31-7.20 (m, 5H), 6.36 (bs, 1H), 5.02-4.96 (m, 2H), 3.73 (bm, 1H), 3.49-3.46 (m, 1H), 2.94 (m, 1H), 2.62-2.47 (m, 2H), 1.29-1.27 (m, 12H), 0.18 & 0.12 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.6, 144.5, 128.4, 126.8, 126.3, 126.1, 107.1, 87.4, 70.8, 69.8, 55.7, 33.0, 32.7, 29.7, 22.0, 0.0; HRMS (ESI) calcd for $C_{23}H_{35}N_2O_4Si$ $[M+1]^+$ 431.2366, found 431.2368.



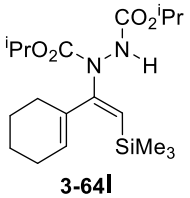
Mixture of isomers: **3-64J** (14% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.67 (bs, 1H), 6.33 (m, 1H), 5.75 (bs, 1H), 3.88 (d, *J* = 4.5 Hz, 1H), 3.17-3.13 (m, 1H), 2.56-2.55 (m, 2H); **3-63j** & **3-64j** ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.7, 144.3, 142.8, 136.4, 128.4, 128.3, 126.8, 126.3, 126.1, 110.0, 87.4, 70.8, 70.5, 69.8, 55.7, 43.4, 41.3, 33.0, 32.7, 21.9, 0.0.



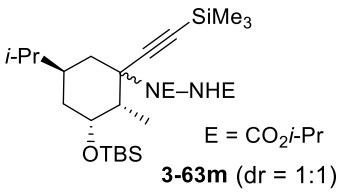
3-64k: (colorless oil, 92% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.53-6.36 (bs, 1H), 5.80 (m, 1H), 5.44 (bs, 1H), 4.99-4.90 (m, 2H), 2.40-2.37 (m, 4H), 1.94-1.89 (m, 2H), 1.31-1.22 (m, 12H), 0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.7, 148.6, 141.3, 132,7, 119.4, 70.3, 34.8, 32.7, 23.5, 22.0, 21.9, 0.3; HRMS (ESI) calcd for $C_{18}H_{33}N_2O_4Si$ $[M+1]^+$ 369.2210, found 369.2214.



3-63l: (colorless oil, 58% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.37-6.18 (bs, 1H), 4.94-4.90 (m, 2H), 2.40-1.58 (m, 8H), 1.36-1.12 (m, 14H), 0.13 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.5, 106.4, 89.7, 69.7, 62.16, 36.0, 25.1, 23.5, 23.3, 22.1, 0.0; HRMS (ESI) calcd for $C_{19}H_{35}N_2O_4Si$ $[M+1]^+$ 383.2366, found 383.2359.

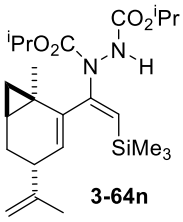


3-64l: (colorless oil, 32% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.49-6.34 (bs, 1H), 5.78 (m, 2H), 5.34 (bs, 1H), 4.98-4.89 (m, 2H), 2.08-2.02 (m, 4H), 1.63-1.58 (m, 4H), 1.31-1.22 (m, 12H), 0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.8, 136.0, 129.5, 118.6, 70.3, 27.1, 25.2, 22.4, 22.4, 22.0, 21.0, 0.4; HRMS (ESI) calcd for $C_{19}H_{35}N_2O_4Si$ $[M+1]^+$ 383.2366, found 383.2372.



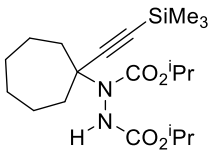
3-63m: (colorless oil, 73% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.43 and 6.11 (s, 1H), 4.91-4.86 (m, 2H), 3.92-3.91 (m, 1H), 2.84-2.73 (m, 1H), 2.43-2.34 (m, 1H), 2.15-1.94 (m, 2H), 1.72-1.45 (m, 2H), 1.29-1.14 (m, 13H), 0.90-0.97 (m, 3H), 0.9 (s, 9H), 0.86-0.84 (m, 6H), 0.13 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.4, 104.9, 93.6, 72.3, 70.2, 69.4, 39.4, 39.0, 38.9, 37.4, 36.9, 36.6, 35.2, 34.9, 31.9, 20.1,

22.1, 20.0, 19.3, 18.3, 14.2, 0.1, -4.6. HRMS (ESI) calcd for $C_{29}H_{57}N_2O_5Si_2$ $[M+1]^+$ 569.3806, found 569.3801.



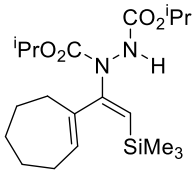
3-64n

3-64n: (colorless oil, 22h, 91% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.50 & 6.29 (bs, 1H), 5.60-5.54 (m, 2H), 4.96-4.92 (m, 2H), 4.74-4.72 (m, 2H), 2.47 (bm, 1H), 2.01-1.99 (bm, 1H), 1.70 (s, 3H), 1.66-1.64 (m, 1H), 1.23-1.22 (m, 12H), 1.14-1.13 (m, 1H), 1.08 (s, 3H), 0.82 (m, 1H), 0.56 (m, 1H), 0.07 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.0, 154.3, 147.4, 140.7, 129.6, 119.8, 119.7, 110.5, 70.3, 69.4, 39.4, 24.0, 22.6, 22.1, 22.0, 21.9, 21.2, 17.6, 15.4, 0.4; HRMS (ESI) calcd for $C_{24}H_{41}N_2O_4Si$ $[M+1]^+$ 449.2836, found 449.2845.



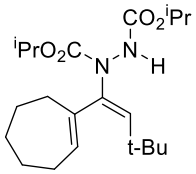
3-63o

3-63o: (colorless oil, 25% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.37 & 6.14 (s, 1H), 4.96-4.91 (m, 2H), 2.35-2.06 (m, 4H), 1.66-1.53 (m, 8H), 1.25-1.21 (m, 12H), 0.15 (s, 9H).



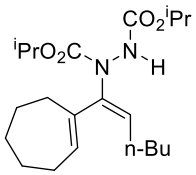
3-64o

3-64o: (colorless oil, 50% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.49 (bs, 1H), 5.32 (t, *J* = 5.3 Hz, 1H), 5.32 (bs, 1H), 4.97-4.89 (m, 2H), 2.16 (m, 4H), 1.71-1.70 (m, 2H), 1.55-1.54 (m, 4H), 1.23-1.22 (m, 12H), 0.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.7, 141.5, 134.5, 118.3, 117.4, 70.3, 69.6, 31.9, 31.0, 29.0, 26.4, 26.3, 22.1, 22.0, 0.7; HRMS (ESI) calcd for $C_{20}H_{37}N_2O_4Si$ $[M+1]^+$ 397.2523, found 397.2524.



3-64p

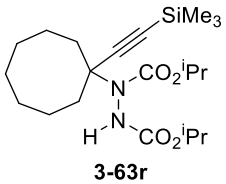
3-64p: (colorless oil, 25h, 94% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.33 (bs, 1H), 5.73 (t, *J* = 6.2 Hz, 1H), 5.48 (bs, 1H), 4.95-4.89 (m, 2H), 2.18-2.12 (m, 4H), 1.71-1.67 (m, 2H), 1.52 (m, 4H), 1.25-1.21 (m, 12H), 1.06 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.3, 138.8, 138.2, 137.9, 135.6, 69.9, 32.4, 32.0, 31.8, 30.9, 28.8, 26.8, 26.6, 22.0; HRMS (ESI) calcd for $C_{21}H_{37}N_2O_4$ $[M+1]^+$ 381.2753, found 381.2758.



3-64q

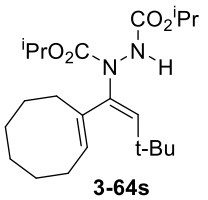
3-64q: (colorless oil, 28h, 78% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.46, 5.81 (t, *J* = 6.4 Hz, 1H), 5.51 (bs, 1H), 4.95-4.89 (m, 2H), 2.18-2.11 (m, 6H), 1.74-1.71 (m, 2H), 1.52-1.49 (m, 4H), 1.33-1.28 (m, 4H), 1.28-1.20 (m, 12H), 0.86 (t, *J* = 6.8 Hz, 3H); ^{13}C

NMR (125 MHz, $CDCl_3$) δ 155.6, 141.2, 138.2, 134.8, 127.2, 70.0, 69.5, 32.4, 31.8, 31.2, 28.7, 28.0, 26.9, 26.4, 22.1, 21.9, 21.7,13.9; HRMS (ESI) calcd for $C_{21}H_{37}N_2O_4$ $[M+1]^+$ 381.2753, found 381.2756.



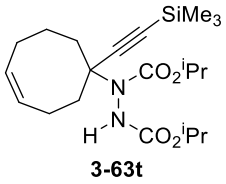
3-63r

3-63r: Colorless oil (72% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 6.36 & 6.14 (s, 1H), 4.94-4.89 (m, 2H), 2.53-2.26 (m, 2H), 2.03-1.99 (m, 2H), 1.70-1.47 (m, 10H), 1.31-1.21 (m, 12H), 0.13 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.1, 107.3, 88.4, 69.7, 65.9, 35.2, 33.8, 28.3, 27.5, 24.4, 22.0, 22.5, 22.1, 0.0; $C_{21}H_{39}N_2O_4Si$ $[M+1]^+$ 411.2679, found 411.2672.



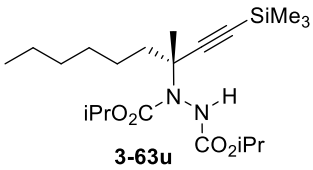
3-64s

3-64s: (colorless oil, 25h, 80% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 6.29 (bs, 1H), 5.64-5.62 (bs, 1H), 5.57 (t, *J* = 8.1 Hz, 1H), 4.94-4.86 (m, 2H), 2.22 (m, 2H), 2.13-2.09 (m, 2H), 1.51-1.44 (m, 8H), 1.22-1.16 (m, 12H), 1.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.1, 140.0, 138.5, 134.9, 134.0, 69.8, 69.4, 32.3, 30.8, 29.6, 29.5, 28.9, 26.5, 26.3, 21.9; HRMS (ESI) calcd for $C_{22}H_{39}N_2O_4$ $[M+1]^+$ 395.2910, found 395.2903.



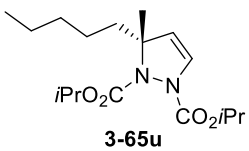
3-63t

3-63t: (colorless oil, 84% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 6.45-6.24 (bs, 1H), 5.77-5.76 (m, 1H), 5.53-5.47 (m, 1H), 4.94-4.88 (m, 2H), 2.50-2.31 (m, 3H), 2.12-1.76 (m, 6H), 1.52-1.47 (m, 1H), 1.25-1.20 (m, 12H), 0.16 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.0, 131.3, 128.8, 104.8, 93.0, 70.0, 69.5, 66.9, 37.9, 34.9, 34.4, 24.8, 24.0, 23.9, 23.4, 23.0, 22.1, 22.0, 0.0.



3-63u

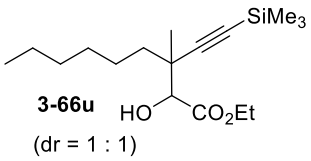
3-63u: (colorless oil, 78% yield); ^1H NMR (500 MHz, $CDCl_3$) δ 6.43, 6.37 and 6.18 (S, 1H), 4.94-4.89 (m, 2H), 2.26-1.77 (m, 2H), 1.66 (s, 3H), 1.45-1.43 (m, 2H), 1.26-1.20 (m, 18H), 0.87-0.84 (m, 3H), 0.12 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.8, 106.9, 88.6, 69.8, 63.2, 40.0, 31.6, 29.3, 26.7, 24.8, 22.5, 22.0, 14.0, 0.0; HRMS (ESI) calcd for $C_{21}H_{41}N_2O_4Si$ $[M+1]^+$ 413.2836, found 413.2836.



3-65u

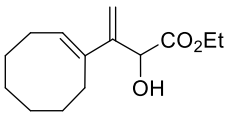
3-65u: (colorless oil, 55% yield, 92:8 er); ^1H NMR (500 MHz, $CDCl_3$) δ 6.58 (d, *J* = 4.4 Hz, 1H), 5.00-4.98 (m, 2H), 4.95 (d, *J* = 4.5 Hz, 1H), 1.51 (s, 3H), 1.29-1.23 (m, 22H), 0.86-0.84 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.0, 126.5, 115.5,

72.0, 70.6, 69.5, 31.7, 29.3, 24.2, 22.5, 22.1, 21.9, 14.0; HRMS (ESI) calcd for $C_{18}H_{33}N_2O_4$ $[M+1]^+$ 341.2440, found 341.2438.



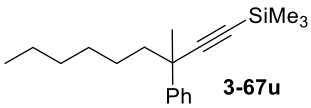
3-66u
(dr = 1 : 1)

3-66u: (colorless oil, 62% yield, dr = 1:1); ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.30-4.22 (m, 2H), 4.00-3.91 (m, 1H), 2.96-2.91 (m, 1H), 1.65-1.61 (m, 1H), 1.46-1.42 (m, 3H), 1.34-1.27 (m, 12H), 0.88 (m, 3H), 0.14 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 173.1, 109.0, 87.6, 76.1, 75.4, 73.0, 61.6, 38.1, 37.8, 31.7, 29.6, 24.5, 24.3, 22.9, 22.6, 22.3, 14.3, 14.1, 0.2; HRMS (EI) calcd for $C_{17}H_{32}O_3Si$ $[M]^+$ 312.2121, found 312.2126.



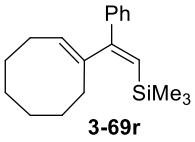
3-68r

3-68r: (colorless oil, 58% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.91 (t, *J* = 8.2 Hz, 1H), 5.26 (s, 1H), 5.15 (s, 1H), 4.86 (d, *J* = 5.3 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 3.11 (d, *J* = 5.3 Hz, 1H), 2.41-2.39 (m, 2H), 2.20-2.18 (m, 2H), 1.54-1.45 (m, 8H), 1.25 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 174.2, 145.8, 137.4, 129.3, 114.3, 72.9, 61.9, 30.1, 28.7, 27.4, 27.0, 26.4, 26.0, 14.1; HRMS (EI) calcd for $C_{14}H_{22}O_3$ $[M]^+$ 238.1563, found 238.1635.



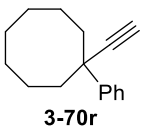
3-67u

3-67u: (colorless oil, 68% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55-7.54 (m, 2H), 7.36-7.31 (m, 3H), 1.79-1.74 (m, 2H), 1.56 (s, 3H), 1.23 (m, 8H), 0.86 (t, *J* = 10.0 Hz, 3H), 0.38 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.5, 128.1, 127.5, 126.4, 112.2, 87.4, 44.2, 36.3, 31.9, 30.3, 29.5, 25.4, 22.7, 14.1; HRMS (EI) calcd for $C_{19}H_{30}Si$ 286.2117, found 286.2122.



3-69r

3-69r: (colorless oil, 46% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39-7.37 (m, 2H), 7.30-7.24 (m, 3H), 5.73 (t, *J* = 8.1 Hz, 1H), 5.57 (s, 1H), 2.26-2.22 (m, 2H), 2.16-2.14 (m, 2H), 1.67-1.61 (m, 4H), 1.52-1.50 (m, 2H), 1.28-1.26 (m, 2H), 0.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 161.4, 143.6, 142.3, 129.6, 128.3, 127.7, 127.6, 127.3, 30.7, 29.4, 29.2, 26.5, 26.3, 26.2, 0.6; HRMS (EI) calcd for $C_{19}H_{28}Si$ $[M]^+$ 284.1960, found 284.1947.



3-70r

3-70r: (colorless oil, 33% yield); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.7 Hz, 2H), 7.22 (t, *J* = 7.3 Hz, 1H), 2.36 (s, 1H), 2.12-2.00 (m, 4H), 1.88-1.85

(m, 2H), 1.63-1.62 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 148.8, 128.2, 126.3, 90.5, 70.9, 44.1, 37.0, 28.3, 24.3, 23.2; HRMS (EI) calcd for $C_{16}H_{20}$ $[M]^+$ 212.1565, found 212.1566.

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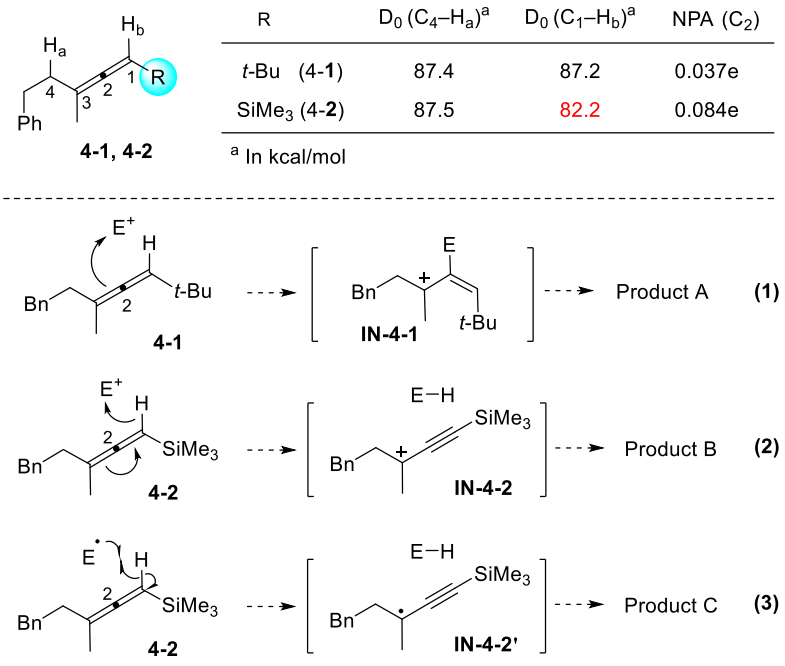
CHAPTER 4

IRON-CATALYZED COMPLEMENTARY OXIDATIVE TRANSFORMATIONS OF ALLENES WITH DIFFERENT OXIDANTS

4.1. Introduction*

Our investigations on new reactions of silylated allenes toward nitration chemistry,[1] oxidative dimerization reaction[2] and Alder ene reactions[3] using various reacting counterparts revealed that the silyl substituent has profound influence on their reaction course. For example, in Alder ene reaction, allenic C(sp^2)–H bond becomes more prone to participate in the reaction than allylic C(sp^3)–H bonds.[3] Density Functional Theory (DFT) calculations revealed that the main reason for this unexpected reactivity is the weakening of the allenic C(sp^2)–H bond (**Scheme 4.1**). Compared to non-silylated allene **4-1**, the corresponding silylated counterpart **4-2** has an unusually low bond strength of the allenic C(sp^2)–H bond (82.2 kcal/mol), which is even lower than that of a typical allylic C(sp^3)–H bond by 5 kcal/mol. In addition, the natural population analysis (NPA) indicates that the *sp*-hybridized C2 carbon in **4-2** imparts significantly less positively charged character relative to that of **4-1**.



Scheme 4.1 Polar Reaction vs. Radical-Mediated Processes of Allenes

* Reproduced in part with permission from Sabbasani, V. R.; Lee, H.; Xia, Y.; Lee, D. "Iron-Catalyzed Complementary Iron(II)-Catalyzed Oxidative Transformations of Allenes with Different Oxidants" *Angew. Chem., Int. Ed.* **2015**, *54*, DOI: 10.1002/anie.201510006.

Based on this strong electronic impact of a silyl substituent on allene moiety (**Scheme 4.1**, Eq 1 and 2), we expected that non-silylated and silylated allenes may show complementary reactivity toward other electrophiles or oxidants. We expect that typical tri-substituted alkyl allene **4-1** would prefer to interact with an electrophile at the more positively charged C2 carbon to generate an allylic cation **IN-4-1** (Eq 1), whereas the corresponding silylated counterpart **4-2** with less positive nature at the C2 may favor electron movements involving both the π-bond and C–H bond to generate propargyl cation **IN-4-2** (Eq 2). Therefore, depending on the choice of electrophiles or oxidants, the subtle difference in reactivity of structurally different allenes can be manifested to generate different final products. We have chosen the DDQ (2,3-dichloro-5,6-dicyano-*p*-benzophenone) and/or *t*-BuOOH (tert-butyl hydroperoxide) as oxidants and non-toxic, environmentally friendly iron-catalyst as an initiator.

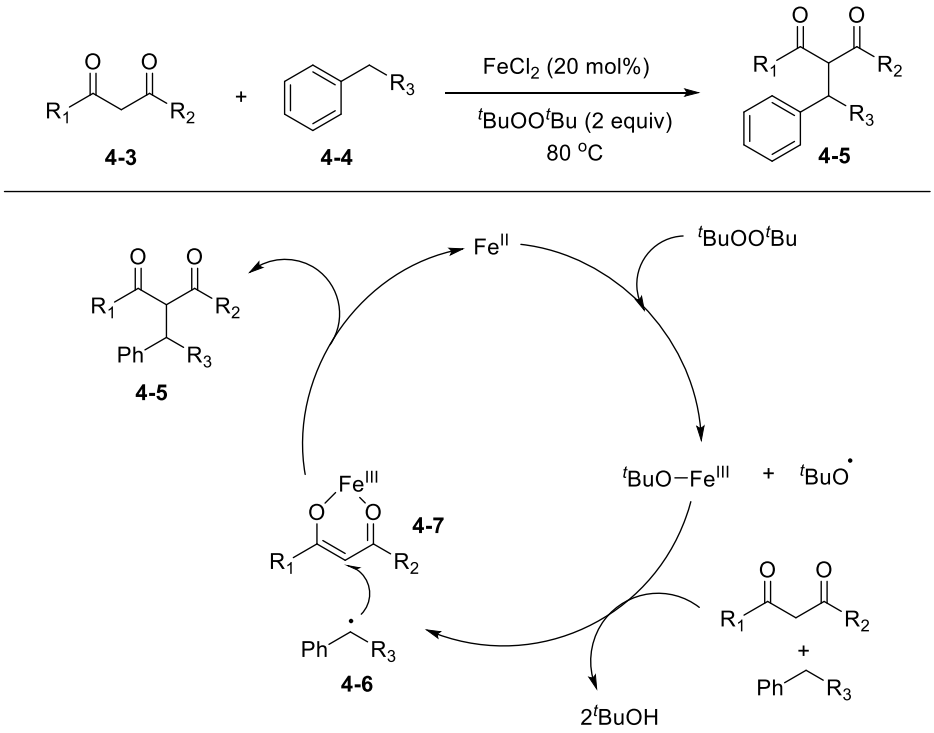
4.2. Iron-Catalyzed Oxidative Transformations Using DDQ

Among oxidizing agents available to chemists, 2,3-dichloro-5,6-dicyano-*p*-benzophenone (DDQ) has played an indispensable role in organic chemistry because of its high oxidizing power and readily soluble nature in typical organic solvent.[4] DDQ has been employed for the oxidation of ketones to the corresponding α,β-unsaturated ketones,[5] alcohols to the corresponding carbonyls,[6] for the formation of phenols,[7] and heterocycles,[8] and various allylic and benzylic C–H bonds to form C─heteroatom[9] and C─C bonds.[10,11]

The reaction of DDQ with cyclic silylenol ethers was first reported by Bhattacharya, which was recently further investigated by Mayr through kinetic studies with the employment of various other π-nucleophiles (electron-rich alkenes), such as cyclic and acyclic silyl enol ethers derived from aldehydes and ketones, silyl ketene acetals, enamino esters, and allylsilanes.[12]

In 2007, Li and coworkers reported the first example of Iron-catalyzed cross dehydroginative coupling between two C(sp^3)–H bonds for the construction of a C–C bond reaction (**Scheme 4.2**).[13] In this method, a cross dehydroginative coupling between 1,3-dicarbonyl compounds and benzylic C–H bond as a coupling partners using di-*tert*-butyl peroxide as an oxidant to provide α-branched alkyl-β-dicarbonyl compounds in

25–87% yield. The proposed mechanism of the reaction involves oxidative cleavage of di-*tert*-butyl by Fe(II) to generate radical intermediates Fe(III)O^{t}Bu and *tert*-butoxyl radical, which then abstracts a benzylic hydrogen to generate carbon centered benzyl radical **4-6**. On the other hand, Fe(III) compound reacts with dicarbonyl compound to form intermediate **4-7**. Combining both the generated radicals delivers the cross coupled product **4-5** and regenerate the Fe(II)-catalyst. Thereafter, several more Iron-catalyzed oxidative cross coupling reaction have been published.[14]



Scheme 4.2 $FeCl_2$-Catalyzed Benzylic Alkylation and Proposed Mechanism

Based on Li's Fe-catalyzed dehydrogenative coupling using ^{t}BuOO^{t}Bu, Shi reported the first iron-catalyzed cross dehydrogenative arylation of benzylic C─H bonds with arenes by using DDQ as an oxidant.[15] After screening several catalysts and oxidants, $FeCl_2$ and DDQ are the choice of a catalyst and an oxidant to generate coupling products in excellent yields (**Table 4.1**). They also conducted mechanistic studies and proposed a plausible mechanism. The reaction is initiated by single electron transfer from Fe(II) to DDQ followed by abstraction of a benzylic hydrogen to generate carbon centered benzyl radical **4-11**

and Fe(III) complex **4-12**. Single electron transfer from benzyl radical **4-11** to the Fe(III) complex to form benzyl cation **4-13** and then Friedel–Crafts-type alkylation with **4-8** followed by abstraction of proton to afford the product **4-10** and reduced DDQ with regenerated catalyst (**Scheme 4.3**).

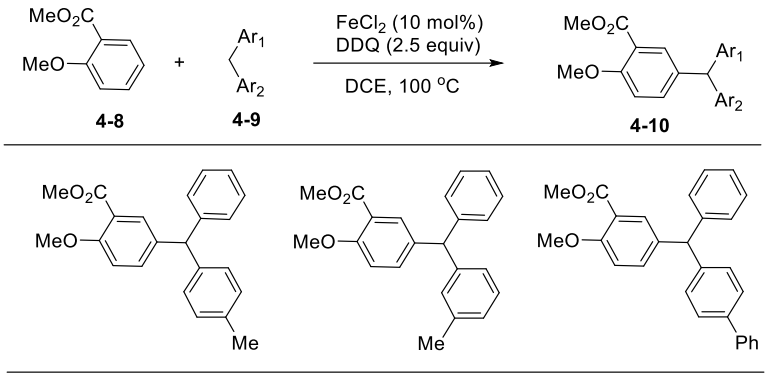
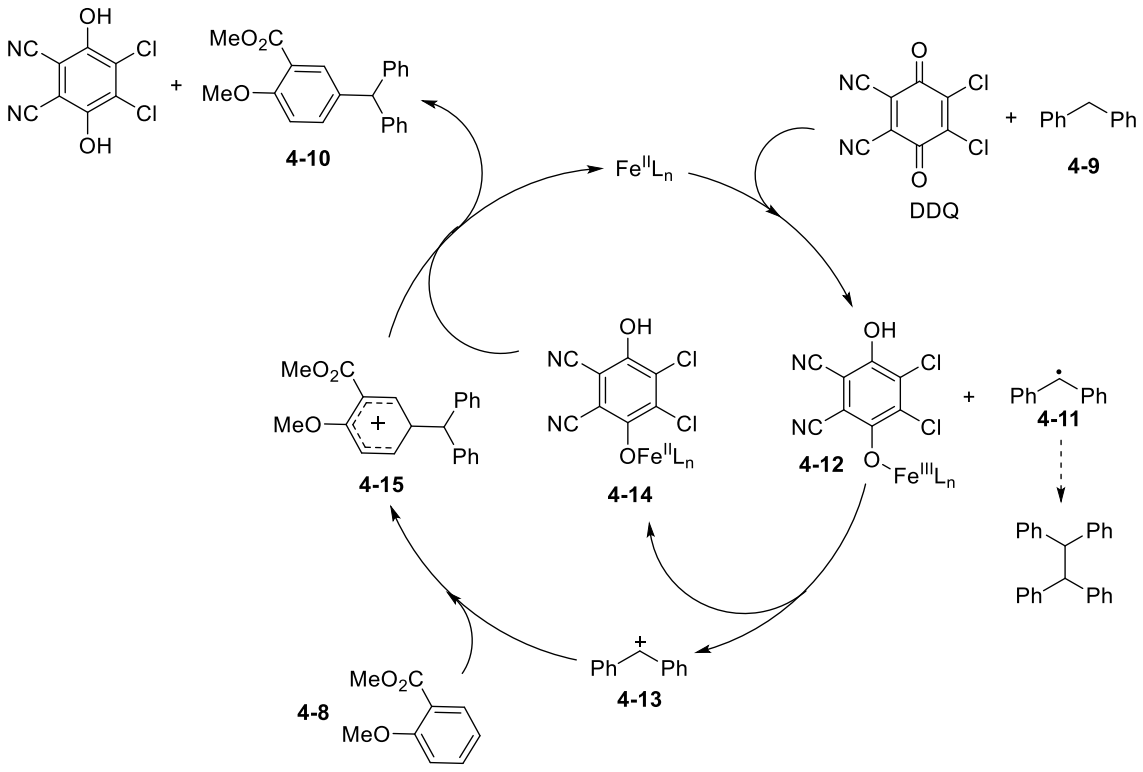


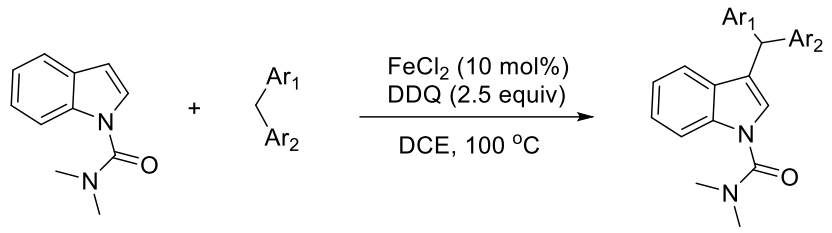
Table 4.1 Iron-Catalyzed Oxidative Arylation of the Benzylic C–H Bond



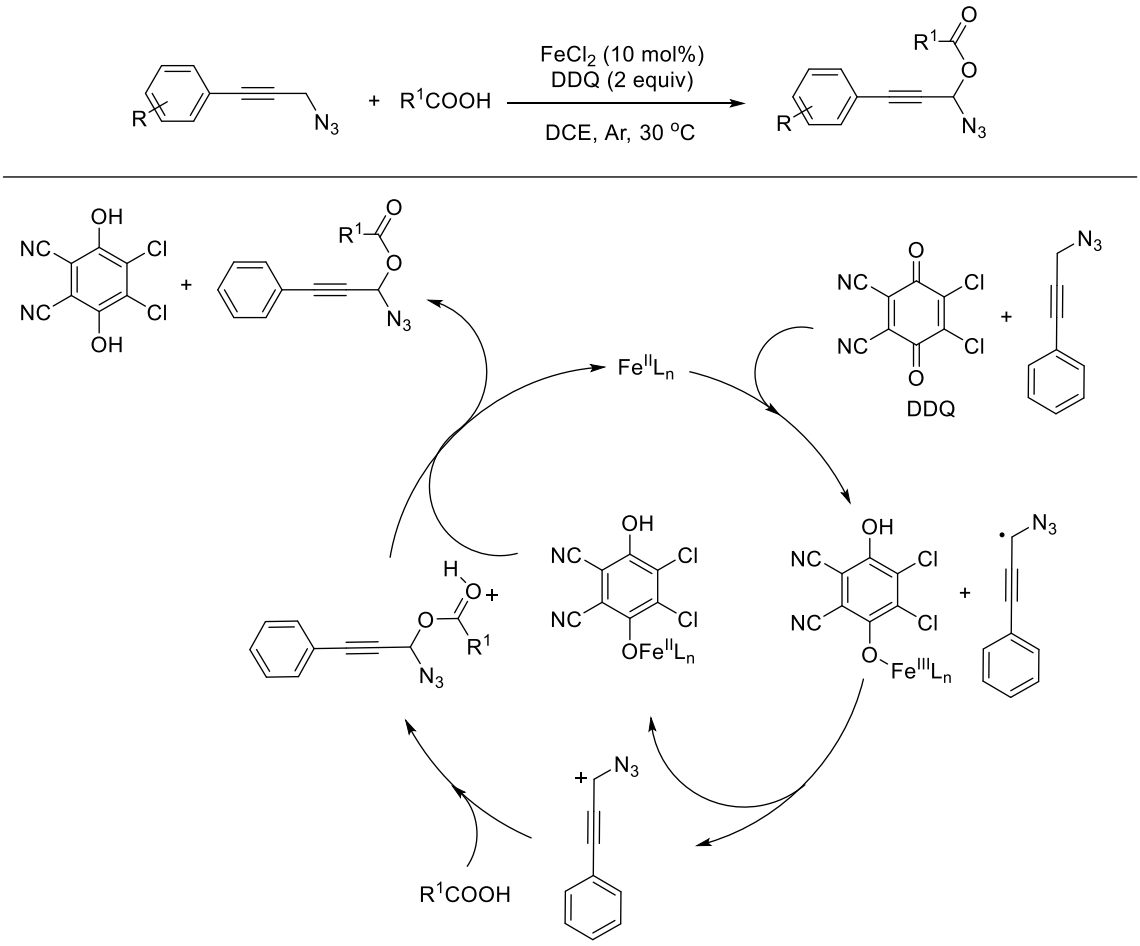
Scheme 4.3 Proposed Mechanism Iron-Catalyzed Oxidative Arylation of a Benzylic C–H Bond

Most recently, Chen and coworkers utilized the same method for the cross dehydrogenative coupling

of indoles and benzylic C─H bonds.[16] In this transformation, the oxidative cross-coupling reaction of indoles at the C-3 position with diarylmethane derivatives was achieved with good to moderate yields (**Scheme 4.4**). The proposed mechanism of the reaction is similar to that of Shi's mechanism.



Scheme 4.4 Iron-Catalyzed Dehydrogenative Coupling of Indoles and Benzylic C–H Bonds



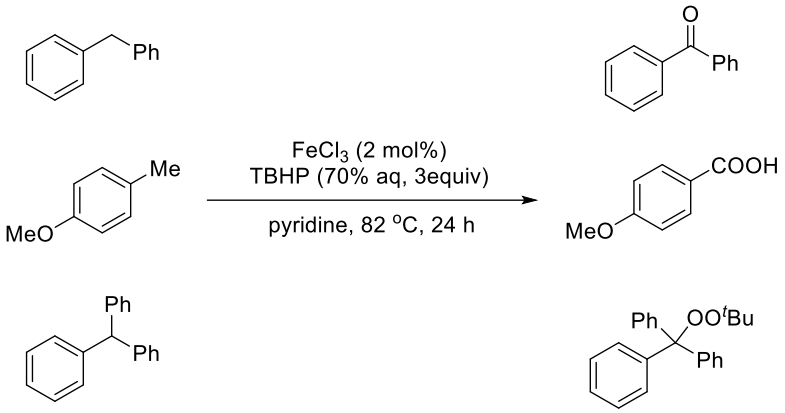
Scheme 4.5 Iron-Catalyzed C–O Bond Forming Reaction and Plausible Mechanism

In 2012, the Jiao group reported an iron-catalyzed oxidative dehydrogenative coupling for formation

C–O bond. The authours used arylpropargyl azides derivied from the corresponding propargyl halides followed by oxidative coupling with carboxylic acids (**Scheme 4.5**).[17] They have used $FeCl_2$ as a catalyst and DDQ as an oxidant were employed for smooth coupling to form a new C–O bond at the propargyl center. This reaction was also tested with other oxidants and solvents, which were were not successful. The proposed mechanism of the reaction is similar to that depicted in **Scheme 4.2**. The reaction proceeds through a propargyl radical, which is then oxidized to the corresponding propargyl cation and trapped with a carboxylic acid.

4.3. Iron-Catalyzed Oxidative Transformations Using *t*-BuOOH

After Li's first report on the oxidative transformation using $FeCl_2$ and $^tBuOO^tBu$ (**Scheme 4.6**), several methods have been developed using *tert*-butyl hydroperoxide (TBHP). In 2007, Bolm and coworkers reported the oxidation of benzylic C−H bonds to the corresponding carbonyl derivatives. In this new oxidation protocol, several benzylic compounds were oxidized to ketones in good to excellent yields (**Scheme 4.3.1**).[18] On the other hand, the reaction with *p*-methoxy toluene under the optimized condition directly generated *p*-methoxy benzoic acid, but the reaction with triphenyl methane delivered ^tBuOO radical/anion-trapped products.



Scheme 4.6 Iron-Catalyzed Benzylic Oxidation

In 2012, Urabe and coworkers further investigated the iron-catalyzed C–H bond oxygenation for the synthesis of *tert*-butyl peroxyacetals. Under the optimized conditions, a series of *tert*-butyl peroxyacetals

were synthesized in good yields (**Table 4.2**). The proposed mechanism of the reaction has two possible pathways to explain the formation of the observed products. The initiation step generating a *tert*-butyl peroxy radical may start efficiently in the presence of iron-catalyst. Then the peroxy radical abstracts a hydrogen atom on ether substrates to form a benzylic radical. This benzylic radical may directly combine with *tert*-butyl peroxy radical or its further oxidized to carbocation, which then captured with *tert*-butyl peroxy anion to provide peroxyacetal products.

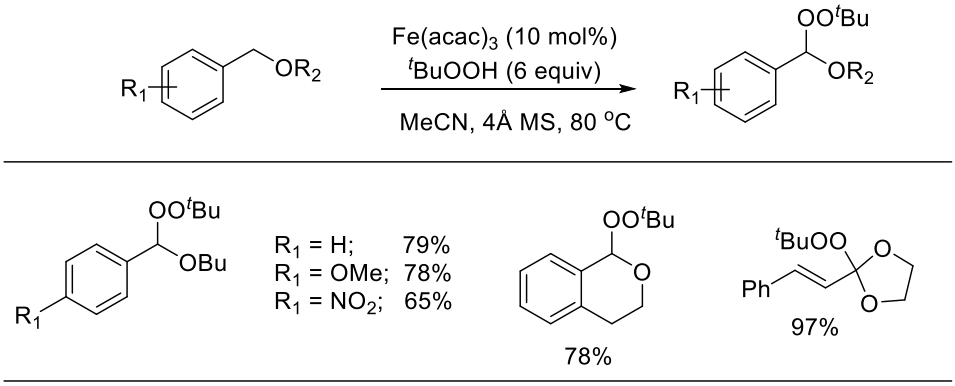
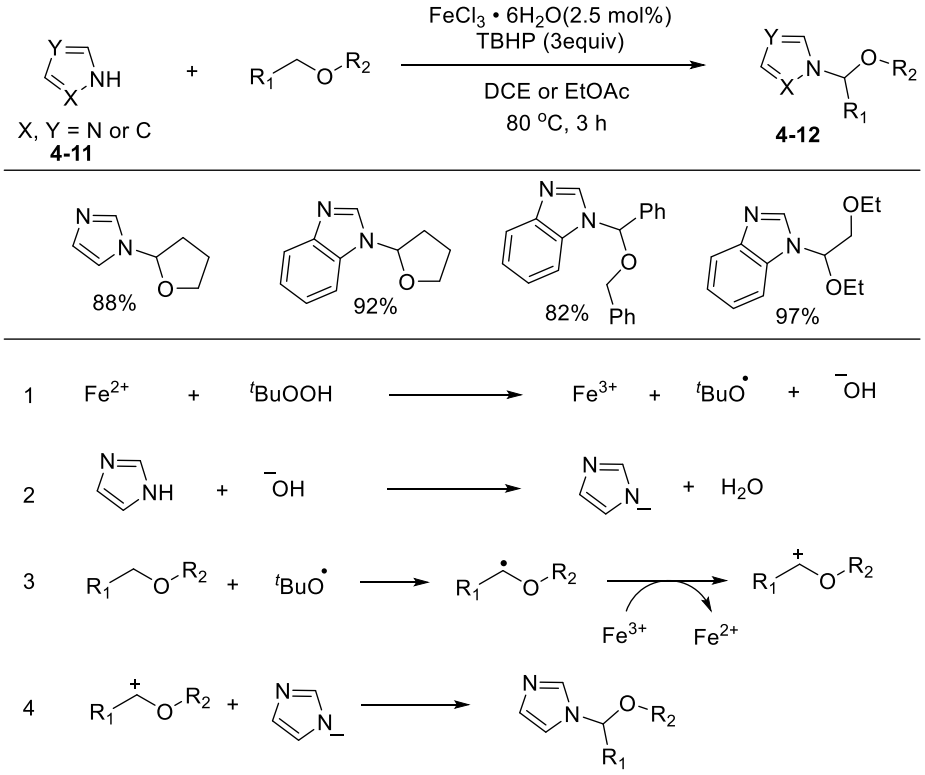


Table 4.2 Synthesis of *tert*-Butyl Peroxyacetals via Iron-Catalysis

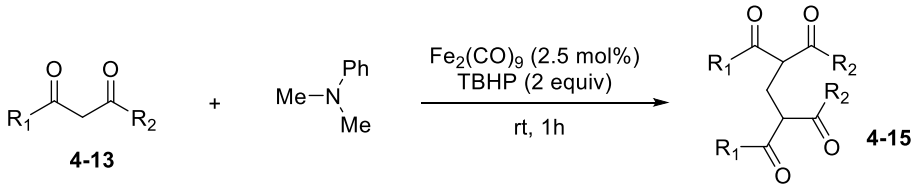
Hong and coworkers reported an iron-catalyzed oxidative cleavage of alkenes and alkynes by using TBHP. The reaction with styrene derivatives and/or aryl acetylenes provided aromatic carboxylic acids in good yields. However, the reaction with linear alkenes or alkynes provided the carboxylic acids in low yields.[19]

In 2010, Lee and coworkers reported an iron-catalyzed oxidative C─N bond formation using TBHP as an oxidant. In this method, authors used azoles and ethers for oxidative coupling to provide C─N bond forming products in good yields (**Scheme 4.7**).[20] The proposed mechanism of the reaction is initiated by iron-catalyzed oxidative cleavage of TBHP into a *tert*-butoxyl radical and hydroxide (step 1). The generated hydoxy anion deprotonates the azole to afford the corresponding anion (step 2). On the other hand, the *tert*-butoxyl radical abstracts hydrogen from the carbon adjacent to the oxygen atom to generate a carbon centered radical, which is oxidized to oxonium ion (step 3) and trapped with an azole anion (step 4).



Scheme 4.7 Iron-Catalyzed Oxidative C─H Amination

In 2009, Li and coworkers reported highly efficient synthesis of methylene-bridged bis-1,3-dicarbonyl compounds using an iron-catalyst and TBHP. In this transformation, 1,3-dicarbonyl compound and phenyl dimethyl amine can undergo oxidative coupling to generate γ-amino-1,3-dicarbony compounds, and which can undergo direct substitution with another 1,3-dicarbonyl compound to afford methylene-bridged bis-1,3-dicarbonyl compounds (**Scheme 4.8**).[21]



Scheme 4.8 Iron-Catalyzed Oxidative Coupling Reactions of 1,3-Dicarbonyl Compounds

In 2011, Li and coworkers reported a highly novel protocol of carbonylation-peroxidation of alkenes with an iron catalyst in excess of TBHP. In this protocol the authors synthesized a series of β-peoxy ketones

4-18 by three component coupling reaction of alkenes **4-16**, aldehydes **4-17** and TBHP (**Table 4.3**).[22]

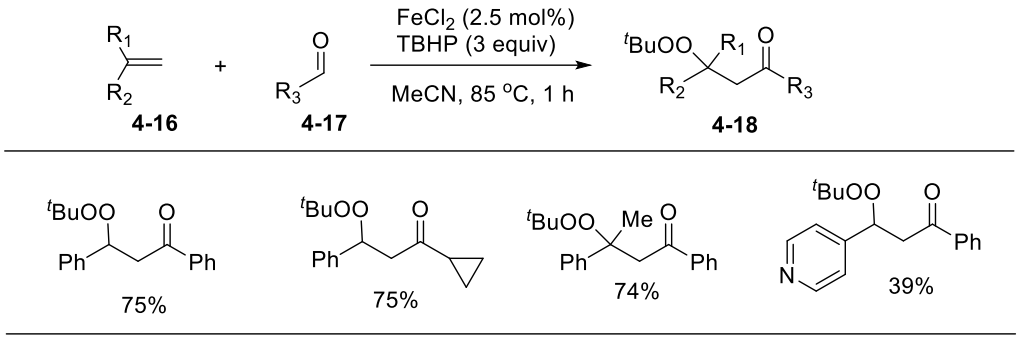
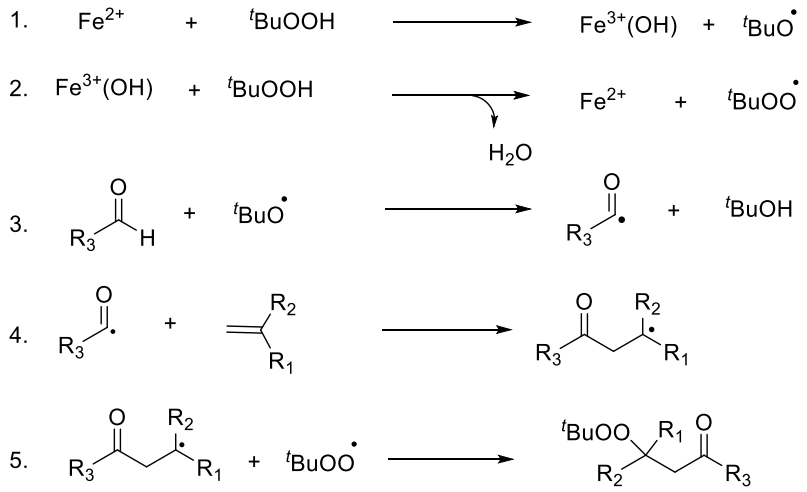


Table 4.3 Iron-Catalyzed Carbonylation–Peroxidation of Alkenes

Based on the observed results and the reaction in presence of TEMPO, they have proposed a plausible reaction mechanism (**Scheme 4.9**). The reaction of Fe(II) with TBHP generates *tert*-butyloxyl and *tert*-butylperoxyl radicals (step 1 and 2). Hydrogen abstraction by *tert*-butyloxyl radical from an aldehyde generates acyl radical intermediate (step 3), adds to alkene to provide carbon centered β-radical ketones (step 4). The generated β-ketone radical reacts with *tert*-butylperoxyl radical to produce β-peoxy ketones. The authors believe the oxidation of the β-ketone radical to the corresponding carbocation might be difficult under the reaction conditions.[23] The reaction in the presence of TEMPO provided only the acyl radical trapped TEMPO-adduct in quantitative yield.



Scheme 4.9 Plausible Mechanism of Iron-Catalyzed Carbonylation–Peroxidation of Alkenes

4.4. Allenes to Indenes via an Allylic Cation

Indenes are important class of compounds in organic chemistry mainly because of their novel core structure that can serve as building blocks for many pharmaceutical compounds[24] and bioactive materials.[25] Indenes have also been used in catalysis as ligands in metallocene-based olefin polymerization reactions.[26] The synthesis of a novel class of indenes have been widely studied[27] and one of the most common methods using the Lewis acid catalyzed Friedel−Crafts reactions of arynes.[28] Recently, the formation of indene derivatives from allenes by using Lewis acid and/or metal-complex has been reported.

Shi and coworkers developed an efficient Lewis acid-catalyzed rearrangement of arylvinylidenecyclopropanes **4-19** having different substituents on cyclopropane to generate a novel class of indene derivatives **4-20** via a double intramolecular Fridel-Crafts reaction under mild reaction conditions using $Sn(OTf)_2$ as a Lewis acid catalyst (**Table 4.4**).[29]

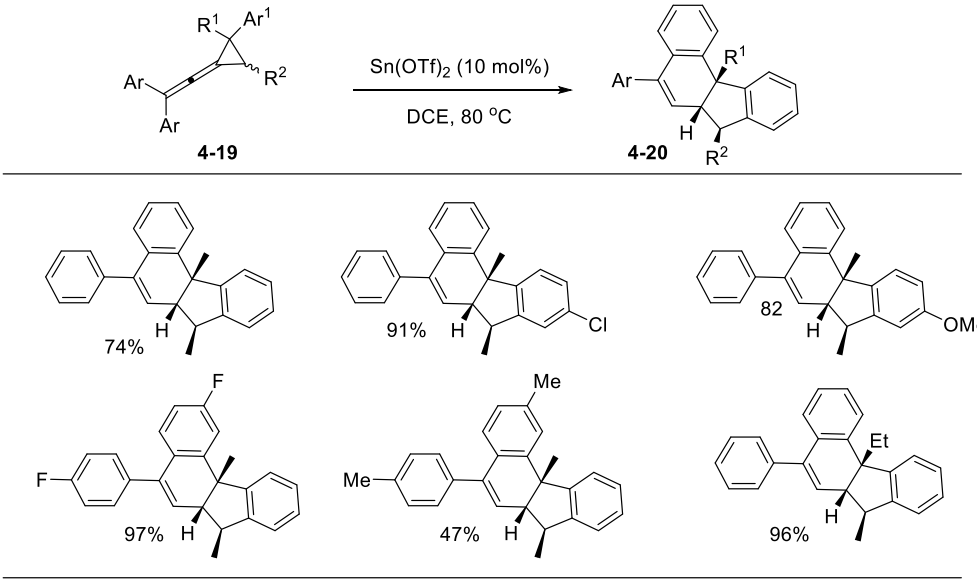
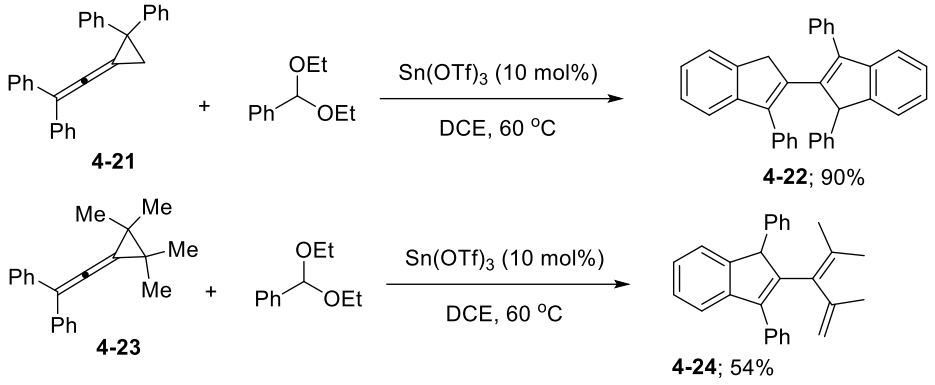


Table 4.4 Rearrangement of Arylvinylidenecyclopropanes

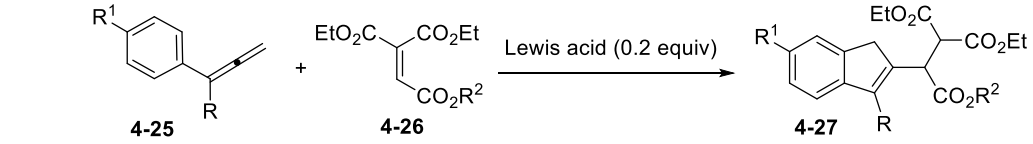
The same group also reported a facile synthetic protocol for preparation of different types of indene derivatives by using Lewis acid-catalyzed reaction of arylvinylidenecyclopropanes **4-21** and **4-22** with acetals (**Scheme 4.10**).[30] In this transformation best results were observed with $Sn(OTf)_3$, where the Lewis

acid first reacts with acetals to generate an oxonium ion, which then adds regioselectivity to the allene generates an allylic cation and further cyclization, providing the indene derivatives **4-22** and **4-24**.



Scheme 4.10 Arylvinylidenecyclopropanes with Acetals

In 2010, Yamazaki and coworkers reported the synthesis of indenes from the reaction between aryl-allene **4-25** and ethenetricarboxylates **4-26** in the presence of various Lewis acids (**Table 4.5**). The best results were observed with $SnCl_4$ as catalytic and/or stoichiometric amounts. The other Lewis acids $AlCl_3$ and ZnI_2 were also effective for the indene formation. Mechanistically, the ethenetricarboxylates **4-26** is activated by a Lewis acid and a Michael addition of central carbon of allene generates an allylic cation, which further cyclizes to generate indene product.[31]



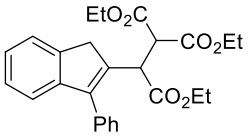
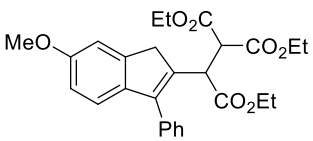
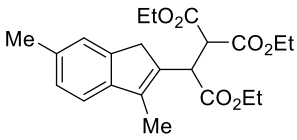
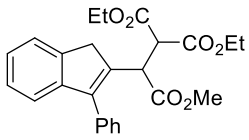
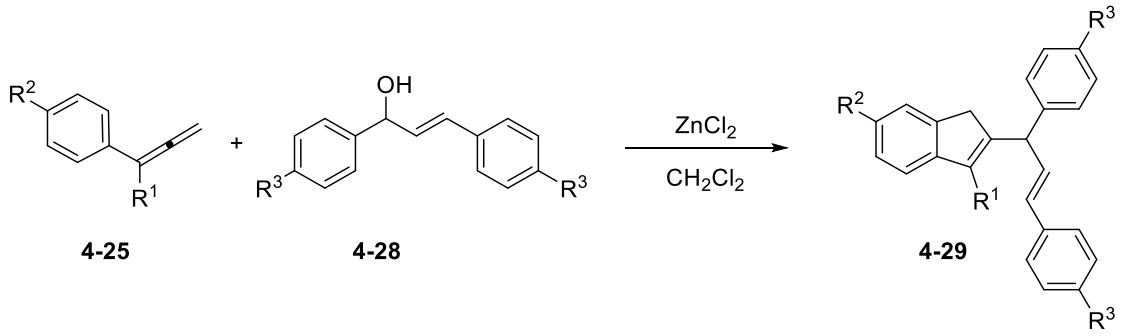
			
$SnCl_4$; 99% $AlCl_3$; 69% ZnI_2; 71%	$SnCl_4$; 0% $AlCl_3$; 44% ZnI_2; 30%	$SnCl_4$; 65%	$SnCl_4$; 81%

Table 4.5 Lewis Acid Promoted Reaction of Allenes to Indenes

Ma and Meng reported the electrophilic addition of a carbocation to allenes. The disubstituted aryl

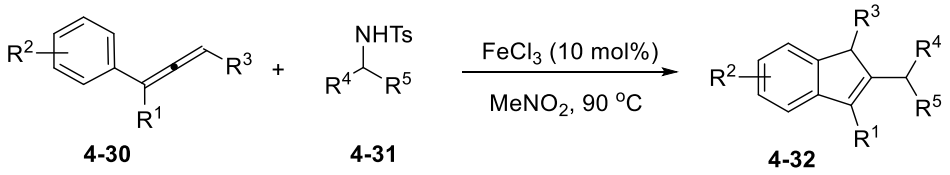
allene **4-25** reacts with an allylic carbocation generated from the corresponding allylic alcohol **4-28** upon treating with stoichiometric amount Lewis acid $ZnCl_2$. The generated carbocation regioselectively added to the central allenic carbon and followed by Friedel-Crafts cyclization provides indene derivative **4-29** in good yields (**Scheme 4.11**).[32]



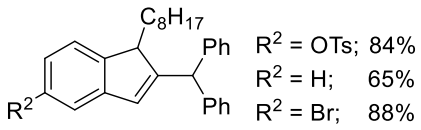
4-25 **4-28** **4-29**

Scheme 4.11 Electrophilic Addition of Carbocations to Allenes

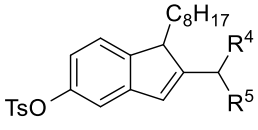
Tian and coworkers reported an approach similar to Ma's for the synthesis of indene derivatives by generating carbocation intermediates from *N*-benzylic/allylic sulfonamides with iron-catalyst (**Table 4.6**). In this reaction the di- and trisubstituted allenes **4-30** and sulfonamides **4-31** catalyzed by $FeCl_3$ provided alkylated indene derivatives **4-32** in good to moderate yields.[33]



4-30 **4-31** **4-32**



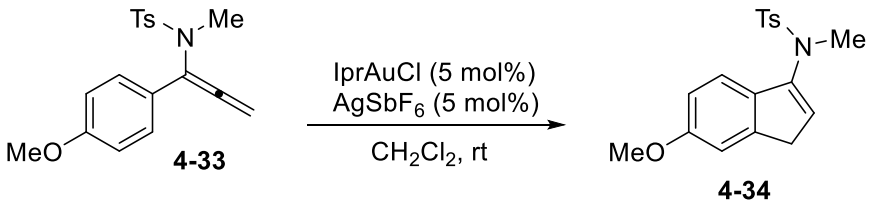
R^2 = OTs; 84%
R^2 = H; 65%
R^2 = Br; 88%



R^4 = Ph, R^5 = Me; 87%
R^4 = R^5 = 4-$MeOC_6H_4$; 71%
R^4 = (*E*)-PhCH=CH, R^5 = Ph; 66%
R^4 = (*E*)-PhCH=CH, R^5 = Me; 70%

Table 4.6 $FeCl_3$-Catalyzed Allenes to Indenes

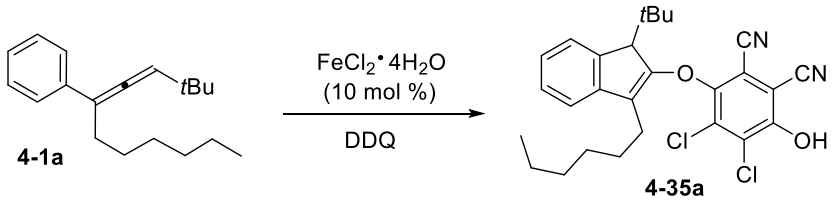
Hsung et al. reported a gold catalyzed imino-Nazarov cyclization of α-aryl-substituted allenamides (**Scheme 4.12**). In this transformation, allenamide **4-30** in the presence of gold catalyst produces an allylic cation type intermediate that further cyclized to form indene products **4-31** in excellent yields.[34]



Scheme 4.12 Imino-Nazarov Cyclization of Allenamides

4.5. Results and Discussion[†]

Described herein are clear demonstrations of novel complementary reactivity of allenes under different reaction conditions to generate structurally diverse oxidation products. In general, non-silylated allenes provided products via traditional reaction pathways involving cation intermediate **IN-1** (**Scheme 1.1**), whereas the corresponding silylated counterparts led to either E1 or S_N1 products via unprecedented oxidation pathways involving propargylic cation intermediate **IN-2**. The mechanistic aspects of these two different modes of reactions were further verified by DFT calculations.



entry	$FeCl_2 \cdot 4H_2O$ (mol %)	DDQ (equiv)	solvent	temp (^oC)	time (h)	yield (%)[a]
1	10	1.5	$ClCH_2CH_2Cl$	70	0.5	78
2	10	1.5	CH_3CN	70	0.5	86
3	10	1.0	CH_3CN	70	0.5	84
4	10	1.0	CH_3CN	25	2.0	91

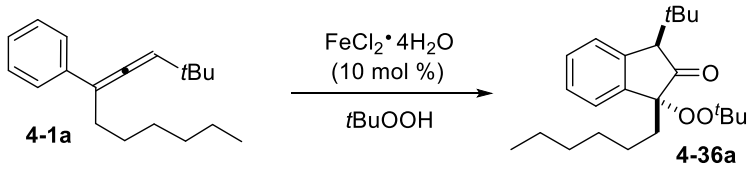
[a] Isolated yield after purification

Table 4.7 Optimization of Reaction Conditions with DDQ for non-Silylated Allene

The initial differentiation of the reactivity between allenes **4-1a** and **4-2a** was made with two different

[†] Reproduced in part with permission from Sabbasani, V. R.; Lee, H.; Xia, Y.; Lee, D. "Iron-Catalyzed Complementary Iron(II)-Catalyzed Oxidative Transformations of Allenes with Different Oxidants" *Angew. Chem., Int. Ed.* **2015**, *54*, DOI: 10.1002/anie.201510006.

oxidants, DDQ and TBHP under iron-catalyzed conditions. First, the reaction of phenyl substituted allene **4-1a** with DDQ was briefly optimized by changing the solvents, amount of DDQ and mainly the reaction temperature (**Table 4.7**). The reaction of **4-1a** with DDQ (1.5 equivalence) and 10 mol% $FeCl_2 \cdot 4H_2O$ in dichloroethane (DCE) at 70 °C provided the indene-DDQ adduct **4-35a** in 78% yield (entry 1). By changing the reaction solvent from DCE to acetonitrile (CH_3CN) the reaction yield was improved to 86% (entry 2). The reaction by using stoichiometric amount of DDQ did not change yield of the reaction (entry 3). However, the reaction at 25 °C afforded the indene derivative **4-35a** in 91% yield (entry 4).

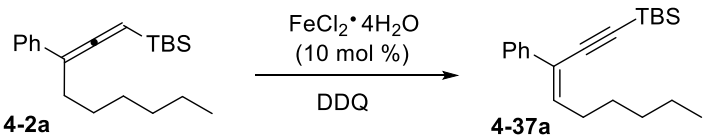


entry	$FeCl_2 \cdot 4H_2O$ (mol %)	*t*BuOOH (equiv)	solvent	temp (°C)	time (h)	yield (%)[a]
1	10	2.0	CH_3CN	25	32	36
2	10	2.0	CH_3CN	70	8	48
3	10	4.0	CH_3CN	70	4	90
4	10	4.0	CH_3CN	50	4	91

[a] Isolated yield after purification

Table 4.8 Optimization of Reaction Conditions with TBHP for non-Silylated Allene

After the optimization of **4-1a** with DDQ, we used same allene to optimize the reaction with TBHP (**Table 4.8**). The reaction of allene **4-1a** with two equivalence of TBHP at 25 °C and/or 70 °C provided only the indanone **4-36a** in very low yield (entries 1 and 2). However, the reaction with 4 equivalence of TBHP



entry	$FeCl_2 \cdot 4H_2O$ (mol %)	DDQ (equiv)	solvent	temp (°C)	time (h)	yield (%)[a]
1	10	1.0	CH_3CN	25	24	76
2	10	1.0	CH_3CN	80	8	98

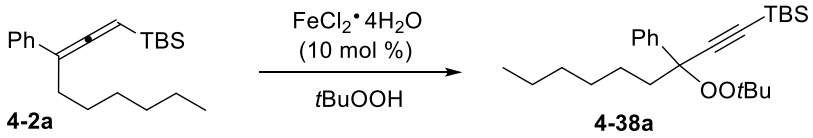
[a] Isolated yield after purification

Table 4.9 Optimization of Reaction Conditions with DDQ for Silylallene

at 70 °C afforded indanone **4-36a** in 90% yield (entry 3). Also, even the lowering of the reaction temperature to 50 °C, the yield was slightly increased to 91% (entry 4). In this transformation single diastereomerer of **4-36a** was obtained.

Optimization of non-silylallene **4-1a** with DDQ and TBHP, we next turned our attention to test the behavior of silylallene **4-2a** with DDQ and TBHP using $FeCl_2 \cdot 4H_2O$ catalyst. Initially, the reaction of silylallene **4-2a** with DDQ at room temperature afforded the 1,3-enyne **4-37a** as a single isomer in 76% yield (**Table 4.9**, entry 1). By increasing the reaction temperature to 80 °C not only shorten the reaction time from 24 h to 8 h, but also increased yield of the reaction to 98% (entry 2).

Similarly, the reaction of silylallene **4-2a** with TBHP also optimized and the best results were obtained by using 2.5 equivalence of TBHP and 10 mol % of $FeCl_2 \cdot 4H_2O$ at 70 °C afforded the propargyl peroxy ether 4-38a in excellent yield (**Table 4.10**, entry 2).

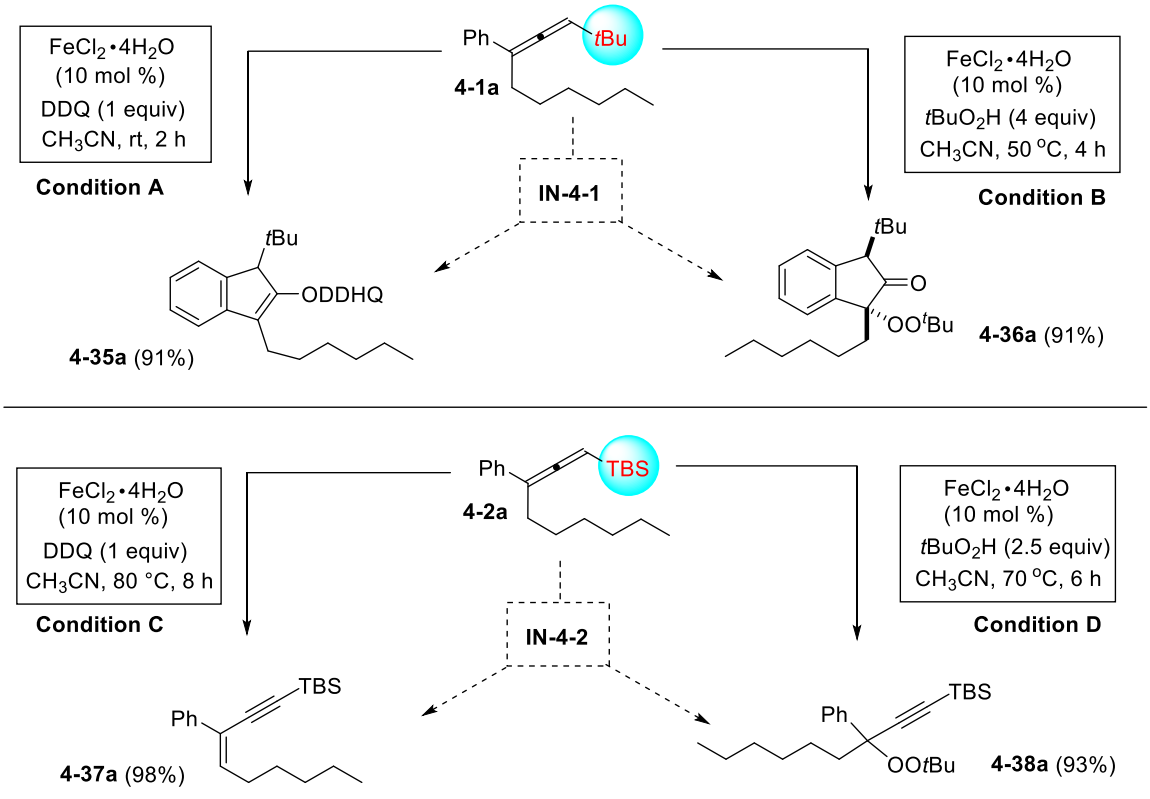


entry	$FeCl_2 \cdot 4H_2O$ (mol %)	*t*BuOOH (equiv)	solvent	temp (°C)	time (h)	conv (%)	yield (%)[a]
1	10	2.5	CH_3CN	25	32	~ 20	---
2	10	2.5	CH_3CN	70	6	100	93

[a] Isolated yield after purification

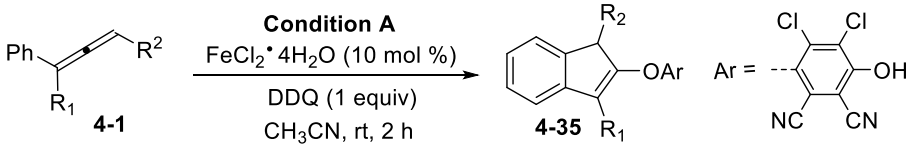
Table 4.10 Optimization of Reaction Conditions with TBHP for Silylallene

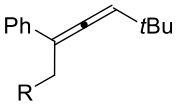
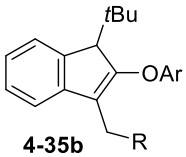
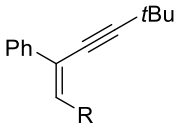
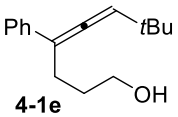
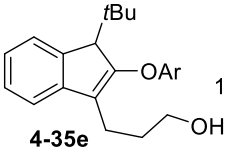
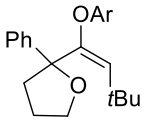
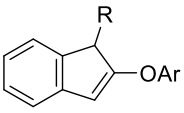
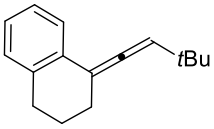
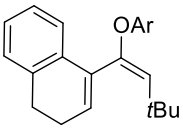
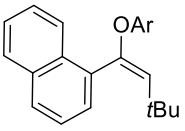
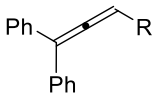
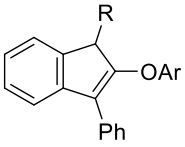
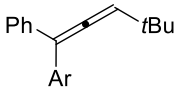
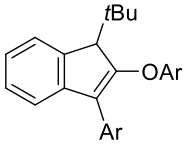
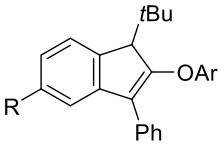
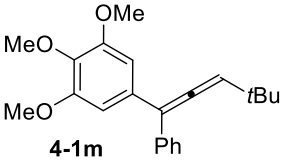
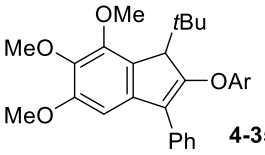
The optimized reaction conditions with allenes **4-1a** and **4-2a** with DDQ and TBHP in presence of $FeCl_2 \cdot 4H_2O$ catalyst were summarized in **Scheme 4.13**. Condition A and B are the non-silylated allene **4-1a** with DDQ and TBHP to provide the indene derivatives **4-35a** and **4-36a** via an intermediate **IN-4-1**. On the other hand, conditions C and D are the reaction of silyllated allene **4-2a** with DDQ and TBHP to provide corresponding substitution and elimination products **4-37a** and **4-38a** via an intermediate **IN-4-2**.



Scheme 4.13 Summary of Initial Proof of Complementary Reactivity of non-Silylated and Silylated Allenes with DDQ and TBHP

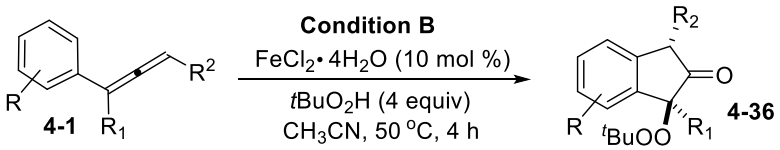
On the basis of these diverse reactivity of allenes observed, we further explore reactions of other allenes with the variation of steric and electronic factors. First, a series of phenyl group-containing trisubstituted allenes were examined under Condition A (**Table 4.11**). Both *gem*-phenyl, methyl- and *gem*-phenyl, benzyl-substituted allenes **4-1b** and **4-1c** provided 1,3-enynes **4-35b′** and **4-35c′** as a minor component together with major product **4-35b** and **4-35c** in 76% (**4-35b′**:**4-35b** = 1:18) and 88% (**4-35c′**:**4-35c** = 1:7.8) yields, respectively (entries 1 and 2), while trisubstituted allene **4-1d** containing γ-silyloxypropyl group provided **4-35d** exclusively in good yield (81%, entry 3). When a competing nucleophile such as a hydroxyl group exists on the allene **4-1e**, it participated preferentially over a phenyl group, generating a mixture of **4-35e** and **4-35e′** in 84% combined yield and 1:6.5 ratio (entry 4). Disubstituted allenes **4-1f** and **4-1g** with *tert*-butyl and phenyl groups did not afford products **4-35f** and **4-35g** instead the starting material was recovered (entry 5). Cycloalkyl-based allene **4-1h** afforded DDQ-incorporated 1,3-diene **4-35h** and

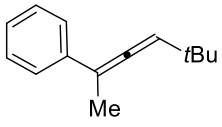
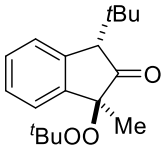
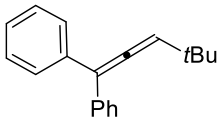
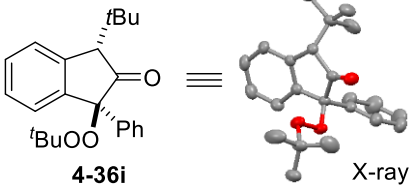
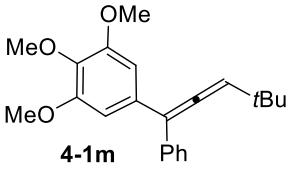
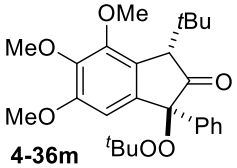
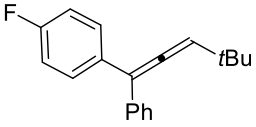
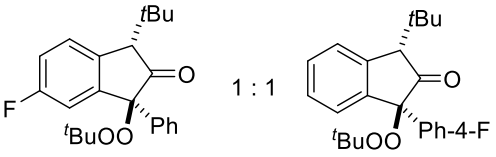
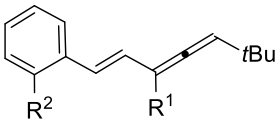
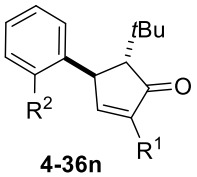


entry	allene	product			yield (%)[a]
1	 **4-1b**, R = H	 **4-35b**	18 : 1[b]	 **4-35b'**	76
2	**4-1c**, R = Ph	**4-35c**	7.8 : 1[b]	**4-35c'**	88
3	**4-1d**, R =CH_2CH_2OTBS	**4-35d**	1 : 0		81
4	 **4-1e**	 **4-35e**	1 : 6.5[b]	 **4-35e'**	84
5	**4-1f**, R = *t*Bu **4-1g**, R = Ph		**4-35f, 4-35g** (not observed)[c]		—
6	 **4-1h**	 **4-35h**		 **4-35h'**[d]	78
7	 **4-1i**, R = *t*Bu			**4-35i**	85
8	**4-1j**, R = Et			**4-35j**	93
9	 **4-1k**, Ar = 4-F-Ph	 **4-35k**	10 : 1[b]	 **4-35k'**	92
10	**4-1l**, R = 4-OMe-Ph	**4-35l**	1 : 3.5[b]	**4-35l'**	78
11	 **4-1m**	 **4-35m**			92

[a] Yield of isolated product. [b] The ratio was determined by ^{1}H NMR analysis. [c] Recovered starting material. [d] During purification 3h was oxidized to the corresponding naphthalene derivative 3h' (ca. 10%).

Table 4.11 Iron-Catalyzed Reaction of Alkyl, Aryl-Substituted Allenes with DDQ



entry	Allene	Products	yield (%)[a,b]
1	 **4-1b**	 **4-36b**	83
2	 **4-1i**	 **4-36i** X-ray	91
3	 **4-1m**	 **4-36m**	89
4	 **4-1k**	 **4-36k** 1 : 1 **4-36k'**	80
5	 **4-1n** R^1 = Me, R^2 = H	 **4-36n**	58
6	**4-1o** R^1 = H, R^2 = H	**4-36o**	52
7	**4-1p** R^1 = Me, R^2 = OMe	**4-36p**	56

[a] Isolated yields after purification.[b] Single diastereome.

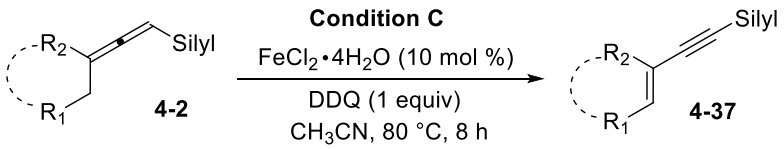
Table 4.12 Iron-Catalyzed Reaction of Alkyl, Aryl-Substituted Allenes with TBHP

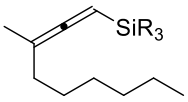
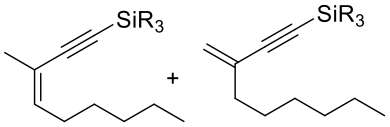
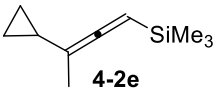
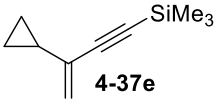
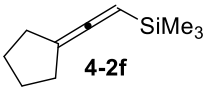
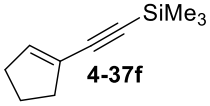
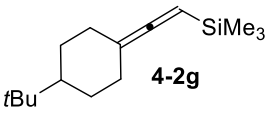
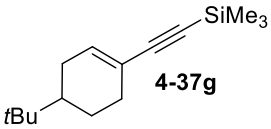
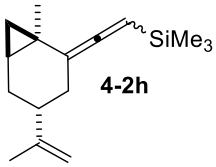
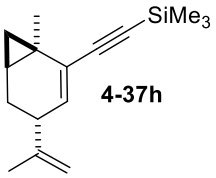
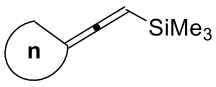
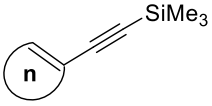
oxidized naphthalene derivative **4-35′** in 78% yield (entry 6). *gem*-Diphenyl-substituted allenes **1-4i** and **1-4j** bearing *tert*-butyl and ethyl groups behaved similarly, generating **4-35i** and **4-35j** in 85 and 93% yield, respectively (entries 7 and 8). Unsymmetrical *gem*-diphenyl-substituted allenes **4-1k** and **4-1l** carrying *p*-fluoro and *p*-methoxy substituent provided a mixture of **4-35k**/**4-35k′** (10:1) and **4-35l**/**4-35l′** (1:3.5),

showing the preferential participation of the more electron-rich aryl group (entries 9 and 10). This is further demonstrated by allene **4-1m** with phenyl and 3,4,5-trimethoxyphenyl groups, which exclusively afforded indene derivative **4-35m** in excellent yield (entry 11).

We further examined the reactivity of these phenyl-substituted allenes under Condition B (**Table 4.12**). *gem*-phenyl, methyl-substituted allene **4-1b** provided the indanone peroxy ether derivative **4-36b** as single diastereomer in 83% yield (entry 1). The reaction with *gem*-diphenyl-substituted allenes **4-1j** delivered the indanone derivative **4-36j** in excellent yield (91%, entry 2). The relative stereochemistry of indanone peroxy ethers **4-36** was further confirmed by single x-ray diffraction analysis of compound **4-36j**. Also, allene **4-1m** with phenyl and 3,4,5-trimethoxyphenyl groups generated indanone **4-36m** as a single regioisomer involving the electron rich trimethoxyphenyl in very good yield (89%, entry 3). On the other hand, allene **4-1k** containing phenyl and 4-fluorophenyl groups generated isomeric products **4-36k** and **4-36k′** in a 1:1 ratio (entry 4). Allenes **4-1n–4-1p** bearing a cinnamyl group were provided cyclopentenone derivatives **4-36n–4-36p** without incorporation of peroxy ether in marginal yields (entries 5–7). The relative stereochemistry of **4-36n–4-36p** was confirmed by nOe experiments.

Next, we investigated the reaction profiles of structurally diversified silylated allenes under condition C (**Table 4.13**). Unsymmetrically substituted silylallenes **4-2b**, **4-2c** and **4-2d** having different silyl groups TES, TBS and TIPS afforded regioisomeric 1,3-enynes **4-37b**, **4-37c** and **4-37d** in good to moderate yields, where different silyl substitution has little effect the 1,3-enyne yields (entries 1, 2 and 3). A cyclopropyl-substituted silylallene **4-2e** derivied from cyclopropyl methyl ketone afforded 1,3-enyne **5e** in low yield, which is mainly due to its volatility (entry 4). Cyclpentanone, 4-*tert*-butyl cyclohexanone and carvone derived silylallenes **4-2f**, **4-2g** and **4-2h** provided the 1,3-enynes **4-37f**, **4-37g** and **4-37h** in 64%, 67%, and 78% yields, respectively (entries 5, 6 and 7). The Symmetrical cyclic *gem*-dialkyl-substituted silylallenes **4-2i**–**4-2l** derived from cycloheptanone, cyclooctanone, cyclododecanone and cyclopentadecanone provided 1,3-enynes **4-37i**–**4-37l** as the only products in 73%, 81%, 75% and 74% yields, respectively (entries 8, 9, 10 and 11).



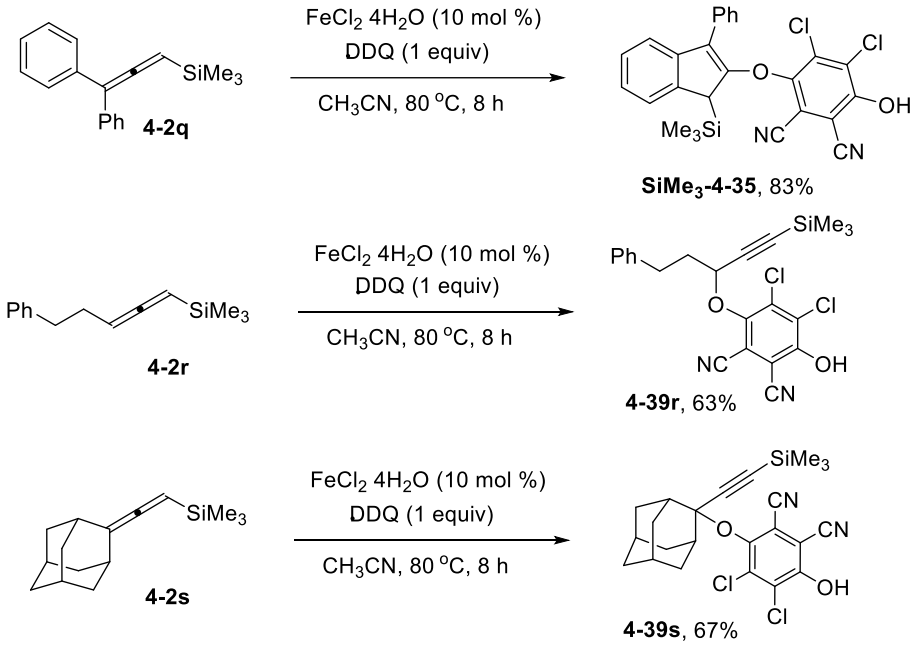
entry	silylallene	product	yield (%)[a]
			
1	**4-2b**, SiR_3 = $SiEt_3$	**4-37b** (1 : 1)[b]	62
2	**4-2c**, SiR_3 = $SiMe_2tBu$	**4-37c** (1.6 : 1)[b]	82
3	**4-2d**, SiR_3 = $Si\textit{i}Pr_3$	**4-37d** (1.6 : 1)[b]	75
4	 **4-2e**	 **4-37e**	36
5	 **4-2f**	 **4-37f**	64
6	 **4-2g**	 **4-37g**	67
7	 **4-2h**	 **4-37h**	78
			
8	**4-2i**, n = 7	**4-37i**	73
9	**4-2j**, n = 8	**4-37j**	81
10	**4-2k**, n = 12	**4-37k**	75
11	**4-2l**, n = 15	**4-37l**	74

[a] Isolated yields. [b] The ratio was determined by ^{1}H NMR

Table 4.13 Iron-Catalyzed Oxidative Transformation of Silylallenes with DDQ

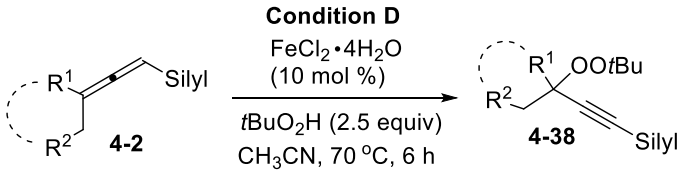
Products other than 1,3-enynes were also observed for certain silylallenes (**Scheme 4.14**). For example, the reaction of *gem*-diphenyl-substituted allene **4-2q** afforded DDQ-incorporated indene derivative **$SiMe_3$-4-35** similar to that of non-silylated allenes, which is the consequence of the lack of any protons to be eliminated from an intermediate involved. For disubstituted silyl allene **4-2r** and adamantane-derived

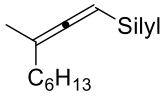
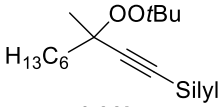
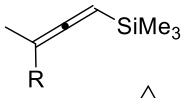
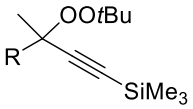
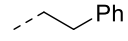
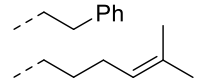
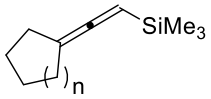
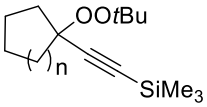
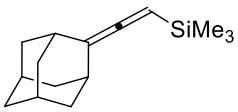
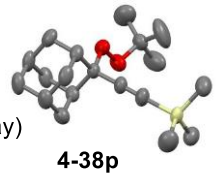
silylallene **4-2s** provided H_2-DDQ-added aryl propargylic ethers **4-39r** and **4-39s**. The formation of **4-39r** can be justified by a favorable nucleophilic substitution over elimination pathway at the sterically less hindered secondary carbon center, whereas **4-39s** is the consequence of a favorable substitution over the unlikely elimination of the bridgehead protons.



Scheme 4.14 Abnormal Reactivity of Silyl-Substituted Allenes with DDQ with $FeCl_2$

The reactivity of these silylated allenes were further explored under Condition D (**Table 4.14**). Different silyl groups having silylallenes **4-2b** ($SiEt_3$), **4-2c** ($SiMe_2tBu$) and **4-2d** ($SiiPr_3$) reacted smoothly to provide propargylic peroxides **4-38b**, **4-38c** and **4-38d** in good yields (entry 1, 2 and 3). While cyclopropyl methyl ketone derived silylallene **4-2e** delivered the *tert*-butyl propargylic peroxide **4-38e** in 70% yield (entry 4). On other hand, benzyl acetone derived silylallene **4-2m** obtained the propargylic peroxide **4-38m** in excellent yields (93%, entry 5). Silylallene **4-2n** with a prenyl group tether was interestingly formed only the corresponding propargylic peroxide product **4-38n** in very good yields, without affecting the double bond on the prenyl group (93%, entry 6). Cyclopentanone, cyclohexanone, cycloheptanone, cyclooctanone, cyclododecanone and cyclopentadecanone derived silylallenes **4-2f**, **4-2o**, **4-2i**, **4-2j**, **4-2k**, and **4-2l** were reacted smoothly to provide corresponding propargylic *tert*-butyl propargylic



entry	Silylallene	product	yield (%)[a]
			
1	**4-2b**, Silyl = $SiEt_3$	**4-38b**	73
2	**4-2c**, Silyl = $SiMe_2tBu$	**4-38c**	93
3	**4-2d**, Silyl = $Si*i*Pr_3$	**4-38d**	82
			
4	**4-2e**, R =	**4-38e**	70
5	**4-2m**, R = 	**4-38m**	93
6	**4-2n**, R = 	**4-38n**	93
			
7	**4-2f**, n = 1	**4-38f**	72
8	**4-2o**, n = 2	**4-38o**	88
9	**4-2i**, n = 3	**4-38i**	85
10	**4-2j**, n = 4	**4-38j**	82
11	**4-2k**, n = 7	**4-38k**	73
12	**4-2l**, n = 10	**4-38l**	89
13	 **4-2p**	(X-ray)  **4-38p**	56

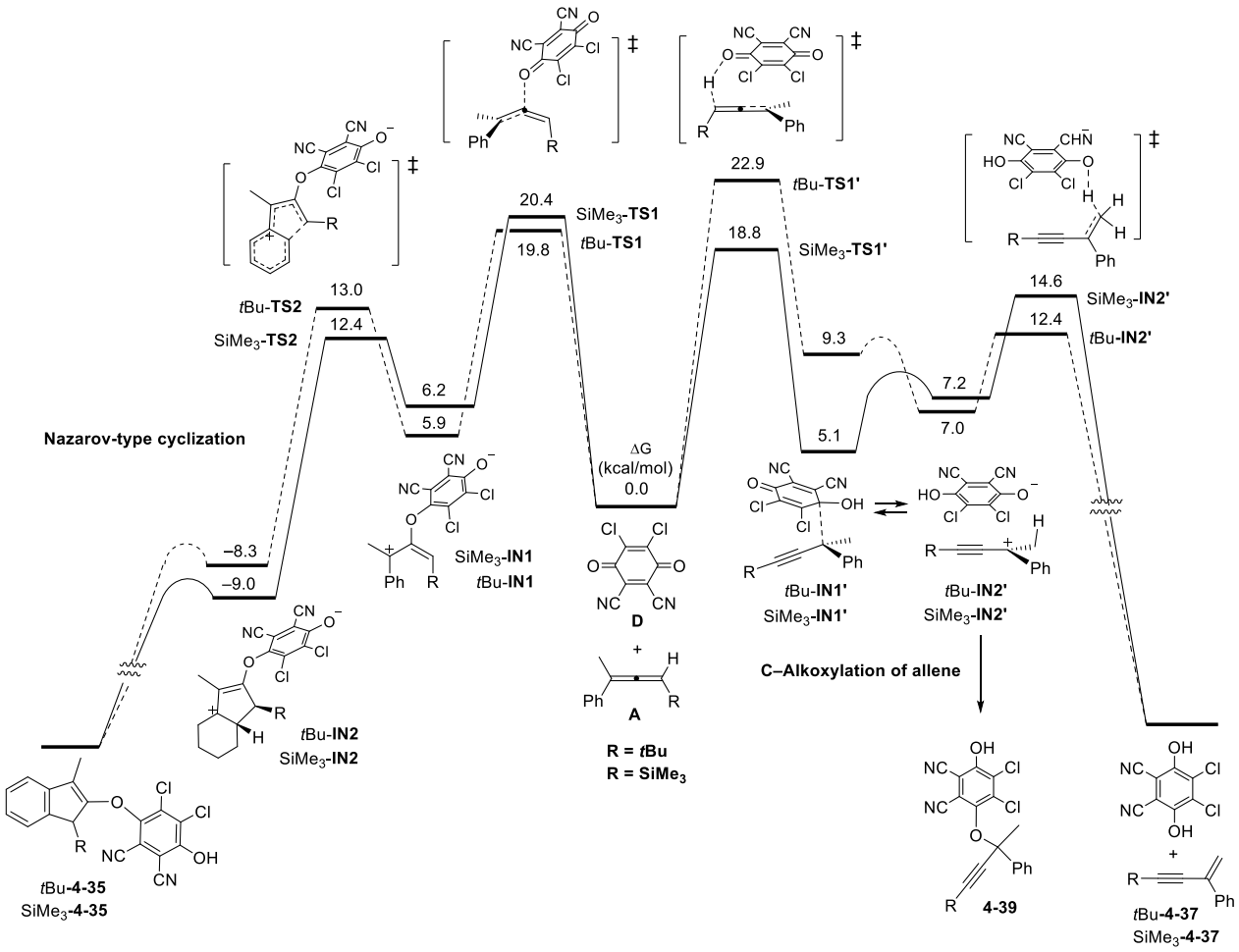
[a] Yield of isolated product

Table 4.14 Iron-Catalyzed Oxidative Transformation of Silylallenes and TBHP

peroxides **4-38i**, **4-38j**, **4-38k**, and **4-38l** in excellent yields (entries 7 to 12). Cycloadamantanone derived silylallene **4-2p** afforded the propargylic peroxide product **4-38p** in moderate yield (56%, entry 13).

To gain further insights into the reactivity and selectivity of these allene-based transformations, DFT calculations were carried out (**Scheme 4.15**). For non-silylated allene, clearly the *t*Bu-**TS1** (19.8 kcal/mol)

with DDQ interacting at the C2 carbon to generate *t*Bu-**IN1** (5.9 kcal/mol) is significantly more favorable than its reaction through *t*Bu-**TS1′** (22.9 kcal/mol) involving a hydride transfer to generate *t*-Bu-**IN1′** (5.1 kcal/mol). On the contrary, silylated allenes show the opposite preference; the reaction through transition state $SiMe_3$-**TS1′** (18.8 kcal/mol) involving a hydride transfer to generate $SiMe_3$-**IN1′** (5.1 kcal/mol) is



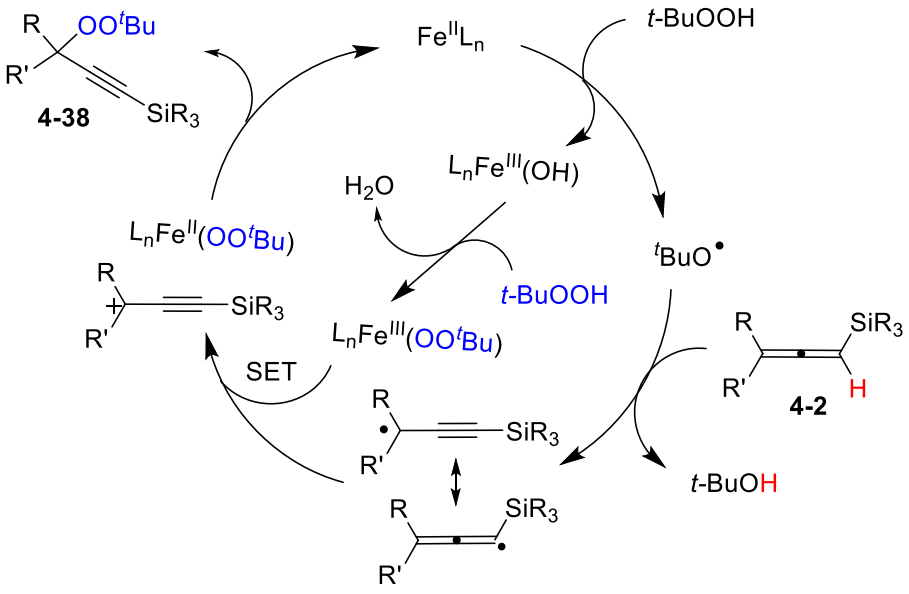
Scheme 4.15 Mechanisms for the Transformations of Alkyl- and Silylsubstituted Allenes with DDQ

Relative Free Energies (in kcalmol^{-1}) were Calculated at the M06-2X/6-31+G* Level of Theory

lower in energy by 1.6 kcal/mol than that of transition state $SiMe_3$-**TS1** (20.4 kcal/mol) where DDQ interacts at the C2 carbon to generate $SiMe_3$-**IN1** (6.2 kcal/mol). These calculated energy profiles of the initial bond-forming step leading to different products clearly support the observed mode-selective transformations of non-silylated and silylated allenes. The generated allylic cation further undergo Nazarov

cyclization to lead the DDQ incorporated products **4-35**. On the other hand, the generated propargylic cation can undergo deprotenation and/or substitution lead to the corresponding 1,3-enynes **4-37** and/or H_2-DDQ-added aryl propargylic ethers **4-39**.

A plausible mechanism for this iron-catalyzed propargylic peroxide formation is proposed in **Scheme 4.16**. In the initial Fe(II)-promoted homolytic cleavage of the weak O–O bond of *tert*-butyl hydroperoxide would generate a tert-butoxyl radical, which abstract the allenic C(sp^2)–H hydrogen from substrate silylallene **4-2** to generated a propargylic radical by forming *t*-BuOH as by product. The resulting carbon-centered propargylic radical then undergoes an electron transfer process with Fe(III)– OO*t*Bu to an ion-pair of propargylic cation and [Fe(II)–OOtBu], which then form the observed *tert*-butyl propargylic peroxide products **4-38** and regenerated Fe(II)-catalyst. However, formation of C–OO*t*Bu bond directly by the initially formed carbon-centered propargyl radical and a free or metal-bounded *tert*-butylperoxyl radical cannot be excluded.



Scheme 4.16 Mechanism of Iron-Catalyzed Reaction of Silylallenes with TBHP

4.6. Summary[‡]

In summary, we have discovered efficient and mode-specific reactions of non-silylated and silylated allenes with DDQ and/or tBuOOH in presence of iron catalyst. Trisubstituted allenes containing geminal aryl-aryl or aryl-alkyl substitution patterns provide oxidant-incorporated indene/indanone derivatives via the addition of oxidant to the central carbon of the allenes to generate an allylic cation followed by electrophilic aromatic substitution/Nazarov cyclization on one of the existing aryl/alkenyl groups on the allene moiety. On the other hand, silyl-substituted allenes regardless of the nature of the other substituents consistently generate a formal 1,4-dehydogenated 1,3-enynes as the major products with DDQ with few exceptions. For certain structural characteristics of silylallenes, however, disfavor the 1,4-dehydrogenation pathway, and thus selectively generate DDQ-incorporated propargylic ethers. However, silyl-substituted allenes with *t*-BuOOH consistently delivered the *tert*-butyl propargylic peroxides. The DFT-calculated energy profiles associated the initial bond-forming step in each reaction pathway with DDQ was nicely justify the experimental observations.

4.7. Experimental Details

4.7.1. General Information

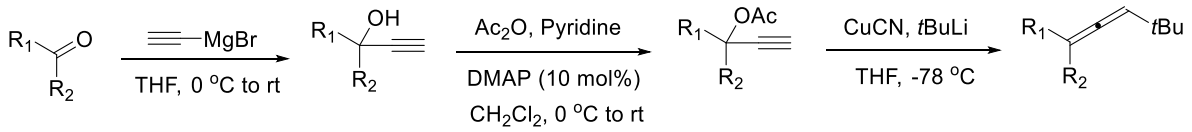
Reactions were carried out in oven or flame-dried glassware unless otherwise noted. Compounds were purchased from Aldrich or Acros or TCI America unless otherwise noted. Acetonitrile (CH_3CN) was distilled over calcium hydride under nitrogen atmosphere. Tetrahydrofuran (THF) was distilled over sodium and benzophenone under nitrogen. Flash chromatography was performed using silica gel 60 Å (32−63 mesh) purchased from Silicycle Inc. Analytical thin layer chromatography (TLC) was performed on 0.25 mm E. Merck pre-coated silica gel 60 (particle size 0.040–0.063 mm). Yields refer to chromatographically and

[‡] Reproduced in part with permission from Sabbasani, V. R.; Lee, H.; Xia, Y.; Lee, D. "Iron-Catalyzed Complementary Iron(II)-Catalyzed Oxidative Transformations of Allenes with Different Oxidants" *Angew. Chem., Int. Ed.* **2015**, *54*, DOI: 10.1002/anie.201510006.

spectroscopically pure compounds unless otherwise stated. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DR-500 spectrometer. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), sext (sextet), m (multiplet), b (broad), and app (apparent). ^{1}H NMR signals that fall within a ca. 0.3 ppm range are generally reported as a multiplet, with a single chemical shift value corresponding to the center of the peak. Coupling constants, *J*, are reported in Hz (Hertz). Electrospray ionization (ESI) mass spectra were recorded on a Waters Micromass Q-Tof Ultima in the University of Illinois at Urbana–Champaign. Electron impact (EI) mass spectra and Chemical Ionization (CI) mass spectra were obtained using a Micromass 70-VSE in the University of Illinois at Urbana-Champaign.

4.7.2. Representative Procedure for Alkyl and Silylallenes Preparation

Alkyl allenes **4-1** were prepared from the corresponding ketones via their conversion to propargylic alcohols followed by acetylation and cuprate-based S_N2' substitution.



Preparation of silylallenes see section **1.6.2.**

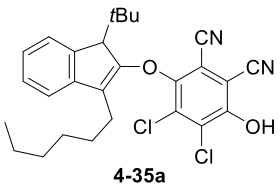
4.7.3. General Procedure of Aryl-Substituted Allenes with DDQ: Arylalkylallene **4-1a** (50 mg, 0.2 mmol) and $FeCl_2 \cdot 4H_2O$ (4 mg, 0.02 mmol) in 3 mL acetonitrile (CH_3CN) was taken into a thick walled Schlenk tube equipped with a magnetic stir bar, and then DDQ (50 mg, 0.22 mmol) was added to the reaction tube under nitrogen and stirred for 2 hours at room temperature. The tube was opened to air and the solvent was removed under reduced pressure. The organic product isolated by flash column chromatography on silica gel (EtOAc/hexanes, 20:1) to give indene product **4-35a** (88 mg, 91%).

4.7.4. General Procedure of Aryl-Substituted Allenes with *t*-BuOOH: Arylalkylallene **4-1a** (50 mg, 0.2 mmol) and $FeCl_2 \cdot 4H_2O$ (3 mg, 0.02 mmol) in 3 mL acetonitrile (CH_3CN) was taken into a round-bottom flask equipped with a magnetic stir bar, and then *tert*-BuOOH (5─6 M in decane, 0.16 mL, 0.8 mmol) was added to the flask under nitrogen and stirred for 4 hours at 50 ^oC. The reaction was opened to air and the solvent was removed under reduced pressure. The organic product isolated by flash column chromatography on silica gel (EtOAc/hexanes, 20:1) to give peroxyindanone product **4-36a** (65 mg, 91%).

4.7.5. General Procedure of Silyl-Substituted Allenes with DDQ: Silylallene **4-2a** (50 mg, 0.16 mmol) and $FeCl_2 \cdot 4H_2O$ (3.1 mg, 0.016 mmol) in 3 mL acetonitrile (CH_3CN) was taken into a thick walled Schlenk tube equipped with a magnetic stir bar under nitrogen, and then DDQ (38.6 mg, 0.17 mmol) was added to the reaction tube under nitrogen. The reaction mixture was degassed under vacuum at –78 ^oC, and then stirred at 80 ^oC for 8 hours. The tube was opened to air and the solvent was removed under reduced pressure. The organic product isolated by flash column chromatography on silica gel (EtOAc/hexanes, 1:50) to give 1,3-enyne product **4-37a** (49 mg, 98%).

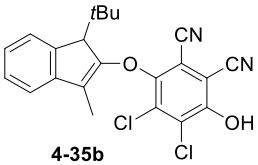
4.7.6. General Procedure of Silyl-Substituted Allenes with *t*-BuOOH: Silylallene **4-2a** (50 mg, 0.16 mmol) and $FeCl_2 \cdot 4H_2O$ (3 mg, 0.016 mmol) in 3 mL acetonitrile (CH_3CN) was taken into a thick walled Schlenk tube equipped with a magnetic stir bar under nitrogen, and then *tert*-BuOOH (5─6 M in decane, 80 mL, 0.4 mmol) was added to the reaction tube under nitrogen. The reaction mixture was degassed under vacuum at –78 ^oC, and then stirred at 70 ^oC for 6 hours. The tube was opened to air and the solvent was removed under reduced pressure. The organic product isolated by flash column chromatography on silica gel (EtOAc/hexanes, 1:50) to give 1,3-enyne product **4-38a** (60 mg, 93%).

4.7.7. Selected Characterization Data



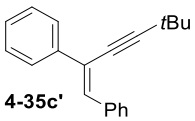
4-35a

4-35a (92% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.5 Hz, 1H), 7.27–7.25 (m, 1H), 7.21–7.19 (m, 1H), 7.15–7.12 (m, 1H), 6.41 (bs, 1H), 3.42 (s, 1H), 2.25–2.23 (bm, 1H), 2.09–2.01 (bm, 1H), 1.39–1.35 (m, 1H), 1.30–1.25 (m, 7H), 1.12 (s, 9H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.9, 151.8, 150.9, 142.5, 140.1, 131.7, 129.3, 129.3, 128.2, 128.5, 126.8, 126.6, 125.3, 124.5, 119.2, 112.0, 111.6, 101.7, 58.6, 34.8, 31.5, 30.3, 29.5, 28.6, 27.9, 23.8, 22.6, 14.1; IR (neat): 3182, 2955, 2929, 2859, 2244, 1736, 1634, 1410, 1251, 1202, 1163, 1148 cm^{-1}; HRMS (ESI**)** calcd for $C_{27}H_{29}N_2O_2Cl_2$ $[M+H]^+$ 483.1606, found 483.1601.



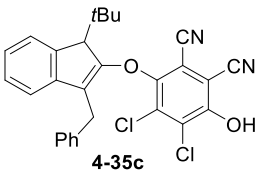
4-35b

4-35b (76% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.5 Hz, 1H), 7.26 (t, *J* = 7.5 Hz, 1H), 7.16–7.14 (m, 2H),6.60 (bs, 1H), 3.42 (s, 1H), 1.67 (s, 3H), 1.12 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.5, 151.4, 151.0, 143.2, 139.7, 132.0, 128.6, 127.9, 126.9, 126.7, 125.1, 124.6, 122.6, 121.1, 118.7, 111.6, 111.4, 101.6, 58.6, 34.8, 28.6, 8.6; IR (neat): 3167, 2957, 2248, 1644, 1412, 1395, 1364, 1345, 1198, 1163, 1148, 1105, 1081 cm^{-1}; HRMS (ESI**)** calcd for $C_{22}H_{19}N_2O_2Cl_2$ $[M+H]^+$ 413.0824, found 413.0829.



4-35c'

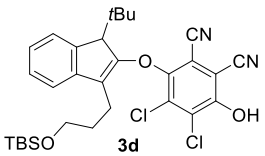
4-35c′ (10% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.01 (d, *J* = 7.7 Hz, 2H), 7.73 (d, *J* = 7.8 Hz, 2H), 7.39 (dt, *J* = 7.7, 2.9 Hz, 4H), 7.30 (dd, *J* = 14.2, 7.2 Hz, 2H), 7.11 (s, 1H), 1.40 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.2, 136.9, 133.2, 129.0, 128.4, 128.1, 128.0, 127.7, 126.4, 122.2, 106.7, 78.3, 32.1, 30.8; IR (neat): 2964, 2926, 2864, 2211, 1597, 1494, 1450, 1361, 1255, 1203, 1185 cm^{-1}; HRMS (EI**)** calcd for $C_{20}H_{20}$ $[M+H]^+$ 260.1565, found 260.1568.



4-35c

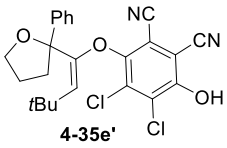
4-35c (78% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.4 Hz, 1H), 7.26 (t, *J* = 7.2 Hz, 1H), 7.19–7.14 (m, 5H), 6.86 (bm, 2H), 6.29 (bs, 1H), 3.74–3.72 (m, 1H), 3.59 (s, 1H), 3.47–3.46 (m, 1H), 1.18 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.9, 151.3, 150.7, 143.2, 139.5, 137.5, 132.0, 128.4, 127.3, 127.1, 126.7, 125.3, 124.7, 123.4, 119.1, 111.6, 111.3, 101.2, 59.2, 35.1, 29.3, 28.7; IR (neat): 3357, 2957, 2917, 2238, 1630, 1494, 1479, 1440,

1417, 1359, 1334, 1210, 1078, 1030 cm^{-1}; HRMS (ESI**)** calcd for $C_{28}H_{23}N_2O_2Cl_2$ $[M+H]^+$ 489.1137, found 489.1137.



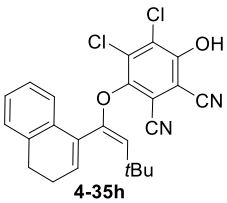
3d

4-35d (81% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.4 Hz, 1H), 7.34–7.24 (m, 2H), 7.16–7.13 (m, 1H), 6.29 (bs, 1H), 3.59 (t, *J* = 5.7 Hz, 2H), 3.41 (s, 1H), 2.35 (bm, 1H), 2.13–2.07 (bm, 1H), 1.75–1.74 (bm, 1H), 1.62–1.61 (bm, 1H), 1.10 (s, 9H), 0.88 (s, 9H), 0.03 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.8, 151.5, 150.9, 140.0, 131.5, 128.5, 128.2, 126.9, 126.4, 125.4, 124.6, 119.3, 111.8, 111.5, 101.8, 85.8, 62.9, 58.6, 34.8, 31.8, 28.5, 26.9, 20.3, 18.4, –5.3; IR (neat): 3300, 2954, 2928, 2857, 2231, 1643, 1417, 1360, 1253, 1214, 1162 cm^{-1}; HRMS (ESI**)** calcd for $C_{30}H_{37}N_2O_3Cl_2Si$ $[M+H]^+$ 571.1951, found 571.1956.



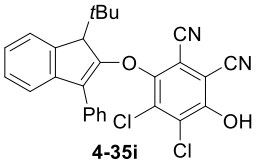
4-35e'

4-35e′ (84% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 7.3 Hz, 2H), 7.32 (t, *J* = 7.02 Hz, 2H), 7.25 (m, 1H), 4.14–4.11 (m, 1H), 4.14 (s, 1H), 4.05–4.04 (m, 1H), 2.89–2.83 (m, 1H), 2.51–2.49 (m, 1H), 2.08–2.06 (m, 1H), 1.88–1.83 (m, 1H), 1.08 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.8, 152.5, 147.0, 144.6, 135.1, 127.8, 127.1, 126.2, 116.4, 111.7, 111.6, 110.5, 101.6, 87.0, 68.4, 39.3, 32.8, 31.6, 24.8; IR (neat): 3236, 2951, 2256, 2235, 1738, 1644, 1480, 1439, 1418, 1268, 1242, 1190 cm^{-1}; HRMS (ESI**)** calcd for $C_{24}H_{23}N_2O_3Cl_2$ $[M+H]^+$ 457.1086, found 457.1079.



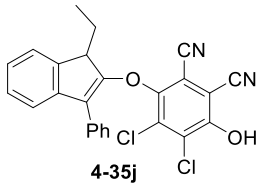
4-35h

4-35h (78% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.5 Hz, 1H), 7.25–7.23 (m, 1H), 7.18 (t, *J* = 7.3 Hz, 1H), 7.13 (d, *J* = 7.3 Hz, 1H), 6.38 (t, *J* = 4.5 Hz, 1H), 4.89 (s, 1H), 2.89 (bm, 2H), 2.42–2.38 (m, 2H), 1.03 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.0, 149.9, 147.9, 135.4, 135.2, 134.1, 132.7, 132.5, 127.7, 127.6, 127.2, 126.9, 126.8, 125.4, 121.7, 111.9, 111.6, 110.3, 101.5, 31.7, 30.9, 27.3, 23.2; IR (neat): 3239, 2959, 2233, 1679, 1557, 1475, 1434, 1416, 1361, 1344, 1262, 1200, 1131, 1091, 1043 cm^{-1}; HRMS (ESI**)** calcd for $C_{24}H_{21}N_2O_2Cl_2$ $[M+H]^+$ 439.0980, found 439.0977.



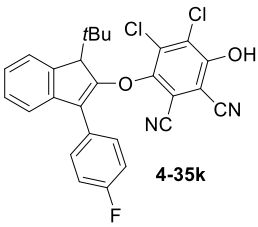
4-35i

4-35i (85% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.51 (d, *J* = 7.3 Hz, 1H), 7.24–7.10 (m, 8H), 6.22 (bs, 1H), 3.62 (s, 1H), 1.30 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.9, 151.8, 149.6, 144.3, 139.1, 132.9, 131.8, 128.8, 128.1, 127.8, 127.0, 125.1, 124.3, 122.4, 119.4, 112.0, 111.3, 58.7, 35.2, 28.7; IR (neat): cm^{-1}; IR (neat): 3271, 2958, 2239, 1632, 1596, 1479, 1458, 1442, 1366, 1343, 1276, 1210, 1099 cm^{-1}; HRMS (ESI**)** calcd for $C_{27}H_{21}N_2O_2Cl_2$ $[M+H]^+$ 475.0980, found 475.0981.



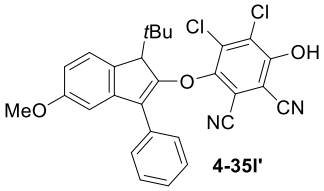
4-35j

4-35j (93% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.41–7.39 (m, 1H), 7.25–7.19 (m, 5H), 7.13–7.12 (m, 2H), 6.90–6.89 (m, 1H), 3.84 (t, *J* = 5.5 Hz, 1H), 2.25–2.19 (m, 1H), 2.15–2.09 (m, 1H), 1.05 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 157.8, 152.0, 148.9, 144.1, 139.9, 133.3, 131.7, 128.8, 128.1, 127.6, 127.1, 126.9, 124.8, 122.8, 120.3, 119.5, 111.4, 111.2, 109.1, 100.8, 49.1, 23.1, 9.8; IR (neat): 3305, 2960, 2927, 2873, 2231, 1633, 1595, 1491, 1416, 1344, 1312, 1299, 1274, 1201, 1162, 1093, 1073, 1028 cm^{-1}; HRMS (ESI**)** calcd for $C_{25}H_{17}N_2O_2Cl_2$ $[M+H]^+$ 447.0667, found 447.0663.



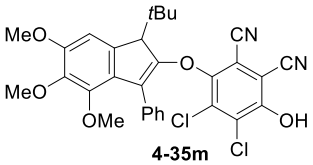
4-35k

4-35k (92% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 (d, *J* = 7.2 Hz, 1H), 7.21–7.10 (m, 4H), 6.93 (t, *J* = 8.4 Hz, 2H), 6.83 (bm, 1H), 6.62 (bs, 1H), 3.60 (s, 1H), 1.27 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 163.2, 161.2, 151.6, 139.1, 132.7, 130.6, 127.7, 127.1, 126.9, 125.2, 124.5, 124.3, 119.2, 115.3, 115.2, 111.1, 58.7, 35.2, 28.7; IR (neat): 3253, 2954, 2243, 1638, 1598, 1478, 1448, 1396, 1366, 1253, 1098, 1090 cm^{-1}; HRMS (ESI**)** calcd for $C_{27}H_{20}N_2O_2Cl_2F$ $[M+H]^+$ 493.0886, found 493.0888.



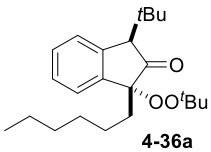
4-35l'

4-35l′ (78% yield): ^{1}H NMR (500 MHz, acetone–D_6) δ 7.26–7.20 (m, 3H), 7.14–7.09 (m, 3H), 6.78–6.76 (m, 2H), 6.71 (bs, 1H), 3.79 (s, 3H), 3.62 (s, 1H), 1.28 (s, 9H); ^{13}C NMR (125 MHz, acetone–D_6) δ 157.5, 140.8, 132.4, 132.1, 129.9, 128.6, 128.1, 127.7, 127.0, 124.9, 119.4, 113.6, 113.0, 111.9, 111.4, 50.4, 54.9, 28.1, 28.0; IR (neat): 3191, 2957, 2868, 2251, 1693, 1640, 1604, 1584, 1440, 1397, 1350, 1314 cm^{-1}; HRMS (ESI**)** calcd for $C_{28}H_{23}N_2O_3Cl_2$ $[M+H]^+$ 505.1086, found 505.1084.



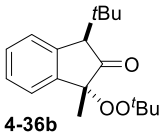
4-35m

4-35m (92% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.22–7.19 (m, 3H), 7.10 (bm, 2H), 6.93 (bs, 1H), 6.18 (s, 1H), 3.92 (s, 3H), 3.84 (s, 3H), 3.69 (s, 3H), 3.69 (s, 1H), 1.23 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 160.4, 153.1, 151.8, 150.5, 149.6, 141.7, 132.6, 131.6, 128.9, 128.2, 128.0, 127.0, 123.5, 111.8, 111.3, 100.8, 100.0, 61.1, 60.6, 57.7, 56.2, 36.7, 29.3; IR (neat): 3250, 2940, 2236, 1695, 1597, 1463, 1442, 1411, 1365, 1343 cm^{-1}; HRMS (ESI**)** calcd for $C_{30}H_{27}N_2O_5Cl_2$ $[M+H]^+$ 565.1297, found 565.1299.



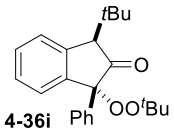
4-36a

4-36a (colorless oil, 91%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.47–7.42 (m, 2H), 7.34–7.30 (m, 2H), 3.23 (s, 1H), 1.89–1.81 (m, 2H), 1.22-1.28 (m, 6H) 1.11 (s, 9H), 0.99 (s, 9H) 0.89–0.84 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ ^{13}C NMR (126 MHz, $CDCl_3$) δ 215.93, 171.92, 142.47, 140.76, 128.14, 127.17, 126.44, 125.28, 87.37, 79.73, 60.53, 35.73, 35.01, 28.95, 26.33, 22.62, 14.07; IR (neat): 2957, 2930, 2872, 1759, 1464, 1363, 1272, 1243cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{36}O_3Na$ $[M+Na]^+$ 383.2562, found 383.2560.



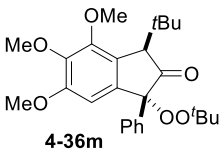
4-36b

4-36b (colorless oil, 83%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.44 (dd, *J*=5.5Hz, *J*=7.8Hz, 1H), 7.34 (dd, *J*=5.5Hz, *J*=9.1Hz, 1H), 3.26 (s, 1H), 1.46 (s, 3H), 1.08 (s, 9H), 0.98 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 216.4, 142.7, 140.6, 128.3, 127.4, 126.4, 124.6, 85.1, 79.5, 60.5, 35.6, 28.6, 26.3, 20.0; IR (neat): 2975, 2932, 2870, 1756, 1477, 1387, 1363, 1312 cm^{-1}; HRMS (ESI) calcd for $C_{18}H_{26}O_3Na$ $[M+Na]^+$ 313.1780, found 313.1783.



4-36i

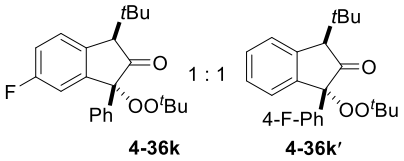
4-36i (colorless oil, 73%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57–7.54 (m, 4H), 7.47–7.45 (m, 2H), 7.33–7.30 (m, 4H), 3.32 (s, 1H), 1.09 (s, 9H), 0.87 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.2, 141.8, 140.4, 135.6, 128.8, 128.7, 128.4, 127.9, 127.5, 127.4, 126.6, 121.6, 80.1, 60.9, 35.4, 30.9, 28.6, 26.4; IR (neat): 2969, 1755, 1600, 1465, 1448, 1413, 1363, 1342 cm^{-1}; HRMS (EI) calcd for $C_{23}H_{28}O_3Na$ $[M+Na]^+$ 375.1936, found 375.1935.



4-36m

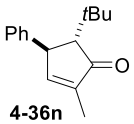
4-36m (yellow oil, 89%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65–7.60 (m, 2H), 7.35 (m, 3H), 6.84 (s, 1H), 3.90 (s, 3H), 3.81 (s, 3H) , 3.78 (s, 3H) , 3.30 (s, 1H) , 1.00 (s, 9H) , 0.70 (s, 9H) ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.3, 153.9, 150.5, 143.0, 135.7, 135.0,

129.1, 128.0, 105.7, 79.8, 61.0, 60.3, 59.6, 56.1, 36.3, 29.3, 26.3; IR (neat): 2973, 2934, 1755, 1587, 1504, 1463, 1432, 1363, 1334, 1235 cm^{-1}; HRMS (EI) calcd for $C_{22}H_{27}O_3$ $[M+H]^+$ 339.1960, found 339.1960.



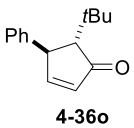
4-36k **4-36k′**

4-36k (colorless oil, 79%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.57–7.48 (m, 4H), 7.36–7.29 (m, 2H), 7.01 (t, *J* = 8.5 Hz, 1H), 3.30 (d, *J* = 9.3 Hz, 1H), 1.08 (dd, *J* = 8.3, 1.2 Hz, 9H), 0.87 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.03, 212.26, 163.99, 161.83, 143.97, 141.80, 140.13, 135.33, 131.43, 130.76, 129.14, 128.66, 128.02, 126.67, 114.98, 114.81, 113.34, 80.24, 61.03, 28.60, 26.36; IR (neat): 2968, 2926, 1725, 1600, 1505, 1448, 1362, 1266, 1226 cm^{-1}.



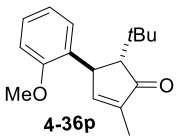
4-36n

4-36n (colorless oil, 58%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.30–7.22 (m, 5H), 7.13 (d, *J*=7.1Hz, 1H), 3.80 (t, *J*=2.2Hz, 1H), 2.18 (d, *J*=2.1Hz, 1H), 1.82 (s, 3H), 1.02 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.2, 158.9, 142.9, 141,4 128.8, 127.6, 126.8, 64.1, 48.6, 34.5, 27.8. 10.0; IR (neat): 2956, 1697, 1494, 1475, 1364, 1327, 1226 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{21}O$ $[M+H]^+$ 229.1592, found 229.1590.



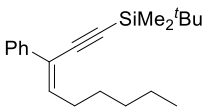
4-36o

4-36o (colorless oil, 52%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.52–7.48 (m, 1H), 7.33–7.31 (m, 2H), 7.25–7.23 (m, 1H), 7.16–7.14 (m, 2H), 6.22–6.20 (m, 1H), 3.94 (s, 1H), 2.15 (d,, *J*=2.4Hz, 1H), 1.04 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 211.6, 165.1, 134.0, 128.9, 127.6, 63.9, 51.1, 34.5, 27.8; IR (neat): 2955, 2868, 1729, 1594, 1494, 1464, 1453, 1396, 1367, 1334 cm^{-1}; HRMS (EI) calcd for $C_{15}H_{19}O$ $[M+H]^+$ 215.1436, found 215.1437.



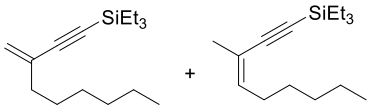
4-36p

4-36p (colorless oil, 50%): ^1H NMR (500 MHz, $CDCl_3$) δ 7.22–7.18 (m, 1H), 7.06 (d, *J*=1.2Hz, 1H), 7.01–6.99 (m, 1H), 6.89 (dd, *J*=7.9Hz, *J*=15.0Hz, 1H), 4.28 (d, *J*=2.2Hz, 1H), 3.83 (s, 1H), 2.27 (d, *J*=2.2Hz, 1H), 1.78 (s, 1H), 0.99 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) 211.7, 159.3, 140.6, 130.4, 128.4, 127.7, 120.8, 110.9, 63.0, 55.3, 41.6, 34.2, 27.6, 10.0; IR (neat): 2953, 1694, 1598, 1490, 1462, 1438, 1366, 1326, 1288, 1244 cm^{-1}; HRMS (EI) calcd for $C_{17}H_{23}O_2$ $[M+H]^+$ 259.1698, found 259.1705.



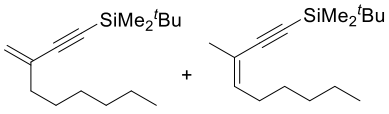
4-37a

4-37a (98% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (d, *J* = 7.8 Hz, 2H), 7.34 (t, *J* = 7.6 Hz, 2H), 7.28–7.25 (m, 1H), 6.48 (t, *J* = 7.6 Hz, 1H), 2.53 (q, *J* = 7.5 Hz, 2H), 1.55–1.52 (m, 2H), 1.39–1.37 (m, 4H), 1.03 (s, 9H), 0.93 (t, *J* = 7.0 Hz, 3H), 0.21 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.9, 138.0, 128.3, 127.3, 125.9, 123.7, 103.0, 98.5, 31.6, 31.3, 28.7, 26.2, 22.5, 16.7, 14.1, –4.4; IR (neat): 2954, 2928, 2857, 2172, 1729, 1647, 1494, 1449, 1410, 1250, 1036 cm^{-1}; HRMS (EI) calcd for $C_{21}H_{32}Si$ $[M]^+$ 312.2273, found 312.2276.



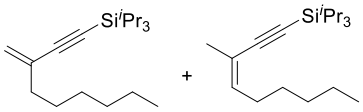
4-37b-1 4-37b 4-37b-2

4-37b–1: Characteristic signals: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.35 (s, 1H), 5.22 (s, 1H), 2.15 (t, *J* = 7.4 Hz, 2H); **4-37b–2: Characteristic signals:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.70 (t, *J* = 7.4 Hz, 1H), 2.25 (q, *J* = 7.3 Hz, 1H), 1.83 (s, 3H); **4-37b–1** and **4-37b–2:** ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.5, 132.1, 121.6, 118.0, 107.1, 106.1, 94.5, 91.2, 37.2, 31.7, 31.5, 30.7, 28.7, 28.5, 28.0, 23.0, 22.6, 22.5, 14.1, 7.5, 4.6; IR (neat): 2955, 2933, 2874, 2171, 1458, 1414, 1264 cm^{-1}.



4-37-1 4-37c 4-37-2

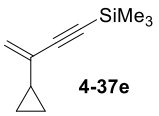
4-37c–1: Characteristic signals: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.35 (d, *J* = 1.9 Hz, 1H), 5.25 (s, 1H), 2.15 (t, *J* = 7.5 Hz, 2H); **4-37c–2: Characteristic signals:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.72–5.68 (m, 1H), 2.27–2.23 (m, 2H), 1.83 (d, *J* = 1.1 Hz, 3H); **4-37c–1** and **4-37c–2:** ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.6, 132.0, 121.6, 118.0, 106.4, 105.5, 95.4, 92.0, 37.1, 31.7, 31.5, 30.7, 28.8, 28.0, 26.1, 22.9, 22.6, 22.5, 16.7, 16.6, 14.1, –4.5, –4.6; IR (neat): 2954, 2927, 2856, 2142, 1462, 1389 cm^{-1}; HRMS (EI) calcd for $C_{16}H_{30}Si$ $[M]^+$ 250.2117, found 250.2126.



4-37-1 4-37d 4-37-2

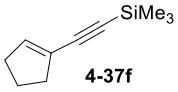
4-37d–1: Characteristic signals[9]**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.34 (d, *j* = 1.5 Hz, 1H), 5.22 (s, 1H), 2.16 (t, *J* = 7.45 Hz, 2H); **4-37d–2: Characteristic signals**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.70 (t, *J* = 7.4 Hz, 1H), 2.27 (q, *J* = 7.4 Hz, 2H), 1.84 (s, 3H); **4-37d–1** and **4-37d–2:** ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.1, 139.0, 132.3, 121.3, 118.3, 107.7, 106.7, 93.3, 90.8, 37.3, 31.7, 31.6, 30.8, 28.8, 28.5, 28.0, 23.0, 22.6, 22.5,

18.7, 14.1, 11.3; IR (neat): 2941, 2864, 2171, 1649, 1462, 1367, 1193 cm^{-1}; HRMS (EI) calcd for $C_{19}H_{36}Si$ $[M]^+$ 292.2586, found 292.2591.



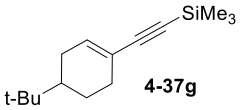
4-37e

4-37e: ^1H NMR (500 MHz, $CDCl_3$) δ 5.35 (d, *J* = 1.4 Hz, 1H), 5.32 (d, *J* = 1.7 Hz, 1H), 1.53 (s, 3H), 1.52–1.51 (m, 1H), 0.70–0.65 (m, 4H), 0.17 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 119.5, 16.0, 5.8, –0.06; HRMS (EI) calcd for $C_{10}H_{17}Si$ $[M+1]^+$ 165.1099, found 165.1096.



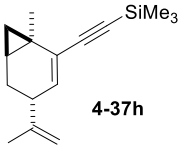
4-37f

4-37f (64% yield): ^1H NMR (500 MHz, $CDCl_3$) δ 6.12–6.11 (m, 1H), 2.48–2.39 (m, 4H), 1.92–1.86 (m, 2H), 0.10 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.4, 124.6, 102.6, 95.3, 36.4, 33.3, 23.4, 0.0; IR (neat): 2955, 2853, 2150, 1713, 1463, 1248 cm^{-1}.



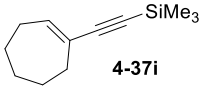
4-37g

4-37g (67% yield): ^1H NMR (500 MHz, $CDCl_3$) δ 6.18 (bm, 1H), 2.23–2.14 (m, 3H), 1.87–1.80 (m, 2H), 1.29–1.13 (m, 2H), 0.85 (s, 9H), 0.17 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.6, 120.5, 107.0, 91.1, 43.1, 32.1, 30.6, 27.4, 27.1, 23.7, 0.1.



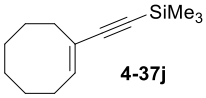
4-37h

4-37h (58% yield)**:** ^1H NMR (500 MHz, $CDCl_3$) δ 5.85 (d, *J* = 2.6 Hz, 1H), 4.75 (s, 1H), 4.72 (s, 1H), 2.54–2.50 (m, 1H), 2.02–1.97 (m, 1H), 1.70 (s, 3H), 1.59–1.53 (m, 1H), 1.28 (s, 3H), 1.14–1.10 (m, 1H), 0.75 (t, *J* = 5.2 Hz, 1H), 0.58 (dd, *J* = 8.3, 4.61 Hz, 1H), 0.20 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147.6, 134.7, 127.2, 110.7, 105.1, 93.8, 39.9, 24.7, 23.0, 21.1, 20.5, 18.0, 15.7, 0.0; HRMS (EI) calcd for $C_{16}H_{24}Si$ $[M+1]^+$ 245.1330, found 245.1324.



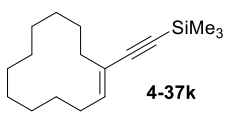
4-37i

4-37i (73% yield)**:** ^1H NMR (500 MHz, $CDCl_3$) δ 6.36 (t, *J* = 6.7 Hz, 1H), 2.33–2.31 (m, 2H), 2.19–2.17 (m, 2H), 1.72–1.71 (m, 2H), 1.57–1.55 (m, 2H), 1.51–1.49 (m, 2H), 0.17 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.3, 126.9, 108.9, 90.6, 34.0, 32.0, 29.2, 26.5, 26.4, 0.1; IR (neat): 2924, 2858, 2170, 1677, 1456, 1249 cm^{-1}; HRMS (EI) calcd for $C_{12}H_{20}Si$ $[M]^+$ 192.1334, found 192.1328.



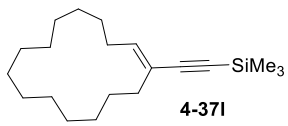
4-37j

4-37j (81% yield)**:** ^1H NMR (500 MHz, $CDCl_3$) δ 6.1 (t, *J* = 8.4 Hz, 1H), 2.30–2.27 (m, 2H), 2.17–2.13 (m, 2H), 1.60–1.48 (m, 8H), 0.17 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.8, 123.9, 108.0, 90.2, 29.9, 29.6, 28.4, 27.0, 26.3, 25.8, 0.2.



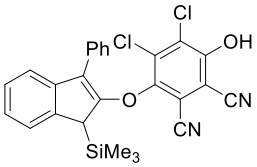
4-37k

4-37k (75% yield)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.81 (t, *J* = 7.7 Hz, 1H), 2.34–2.31 (m, 2H), 2.16–2.14 (m, 2H), 1.57 (m, 4H), 1.39–1.28 (m, 12H), 0.19 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.2, 122.4, 104.5, 98.2, 36.1, 30.2, 26.9, 26.1, 25.8, 25.2, 24.8, 24.6, 24.4, 0.1; IR (neat): 2927, 2855, 1710, 1678, 1466, 1445, 1248 cm^{-1}.



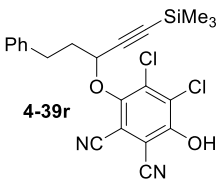
4-37l

4-37l (74% yield)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.66 (t, *J* = 7.4 Hz, 1H), 2.35–2.31 (m, 2H), 2.15–2.13 (m, 2H), 1.55–1.1.53 (m, 2H), 1.48–1.45 (m, 2H), 1.35–1.25 (m, 18H), 0.19 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.0, 123.4, 104.4, 98.1, 35.9, 29.5, 28.4, 27.5, 27.2, 27.1, 27.0, 26.9, 26.8, 26.5, 25.7, 0.1; IR (neat): 2924,2855, 1679, 1459, 1249 cm^{-1}; HRMS (EI) calcd for $C_{20}H_{36}Si$ $[M]^+$ 304.2586, found 304.2589.



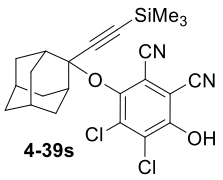
SiMe$_3$-4-35q

SiMe$_3$-4-35q (83% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.40–7.39 (m, 3H), 7.19–7.15 (m, 5H), 7.09–7.08 (m, 2H), 6.97 (bs, 1H), 3.81 (s, 1H), 0.23 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.8, 151.7, 149.3, 143.4, 137.9, 132.2, 129.1, 128.0, 127.5, 125.5, 123.8, 122.7, 119.5, 111.6, 111.3, 100.9, 44.3, –2.3; HRMS (ESI**)** calcd for $C_{26}H_{21}N_2O_2Cl_2Si$ $[M+H]^+$ 491.0749, found 491.0748.



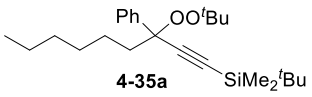
4-39r

4-39r (63% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32–7.22 (m, 5H), 5.10 (t, *J* = 6.2 Hz, 1H), 2.98 (t, *J* = 7.9 Hz, 2H), 2.42–2.32 (m, 2H), 0.12 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.4, 150.3, 140.6, 135.5, 128.5, 126.9, 126.2, 112.4, 111.7, 100.8, 100.2, 97.1, 74.9, 37.3, 31.1, –0.5; IR (neat): 3225, 2951, 2250, 1603, 1496, 1450, 1411, 1278, 1249, 1157, 1081 cm^{-1}; HRMS (ESI) calcd for $C_{22}H_{21}N_2O_2SiCl_2$ $[M+1]^+$ 443.0749, found 443.0753.



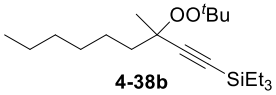
4-39s

4-39s (67% yield): ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.58 (bs, 2H), 2.51 (d, *J* = 12.4 Hz, 2H), 2.12–2.09 (m, 2H), 1.91–1.72 (m, 8H), 0.01 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.9, 151.5, 137.6, 126.2, 113.5, 112.4, 111.9, 103.0, 100.5, 98.9, 93.3, 39.3, 37.4, 36.5, 31.9, 26.5, 26.4, –0.5; IR (neat): 3211, 2902, 2857, 2257, 1704, 1556, 1438, 1417, 1249, 1210 cm^{-1}; HRMS (ESI) calcd for $C_{23}H_{25}N_2O_2SiCl_2$ $[M+1]^+$ 459.1062, found 459.1075.



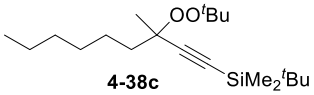
4-35a

4-38a (colorless liquid, 93%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ ^{1}H NMR 7.62 (d, *J* = 7.3 Hz, 2H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.28 (d, *J* = 7.3 Hz, 1H), 2.00–1.95 (m, 1H), 1.82–1.77 (m, 1H), 1.26 (m, 17H), 1.01 (s, 9H), 0.87 (t, *J* = 6.9 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.9, 127.8, 127.4, 126.5, 106.7, 89.5, 83.4, 79.9, 42.6, 31.6, 29.3, 26.8, 26.2, 24.6, 22.6, 16.7, 14.1, –4.6; HRMS (ESI) calcd for $C_{18}H_{34}O_2NaSi$ $[M+Na]^+$ 425.2852, found 425.2852.



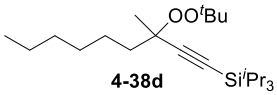
4-38b

4-38b (colorless liquid, 73%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.76–1.70 (m, 1H), 1.61–1.54 (m, 1H), 1.44 (s, 3H), 1.30–1.26 (m, 8H), 1.24 (s, 9H), 1.00–0.97 (m, 6H), 0.89–0.87 (m, 3H), 0.60–0.56 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 109.4, 85.2, 79.4, 78.2, 39.9, 31.7, 29.4, 26.7, 25.6, 24.4, 22.5, 14.0, 7.4, 4.4; HRMS (ESI) calcd for $C_{20}H_{40}O_2NaSi$ $[M+Na]^+$ 363.2695, found 363.2710.



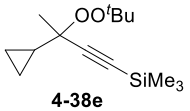
4-38c

4-38c (colorless liquid, 93%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.76–1.70 (m, 1H), 1.62–1.56 (m, 1H), 1.49–1.44 (m, 5H), 1.32–1.29 (m, 6H), 1.24 (s, 9H), 0.93 (s, 9H), 0.89–0.87 (m, 3H), 0.09 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 108.8, 86.2, 79.4, 78.1, 39.8, 31.7, 29.4, 26.7, 26.0, 25.5, 24.3, 22.5, 16.6, 14.0, –4.6; HRMS (ESI) calcd for $C_{20}H_{40}O_2NaSi$ $[M+Na]^+$ 363.2695, found 363.2702.



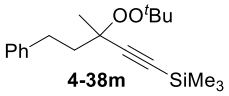
4-38d

4-38d (colorless liquid, 82%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.77–1.71 (m, 1H), 1.63–1.56 (m, 1H), 1.54–1.48 (m, 5H), 1.32–1.26 (m, 6H), 1.24 (s, 9H), 1.09–1.01 (m, 18H), 0.89–0.87 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 110.1, 84.0, 79.2, 78.2, 39.9, 31.7, 29.5, 26.7, 24.5, 22.5, 18.6, 14.0, 11.2; HRMS (ESI) calcd for $C_{23}H_{46}O_2NaSi$ $[M+Na]^+$ 405.3165, found 405.3165.



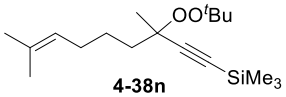
4-38e

4-38e (colorless liquid, 70%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.53 (s, 3H), 1.25 (s, 9H), 1.06–1.00 (m, 1H), 0.72–0.67 (m, 1H), 0.49–0.39 (m, 3H), 0.14 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 104.5, 88.9, 80.6, 79.6, 26.7, 26.2, 17.8, 2.8, 1.5, 0.0; HRMS (EI) calcd for $C_{14}H_{25}O_2Si$ $[M–H]^+$ 253.16239, found 253.16316.



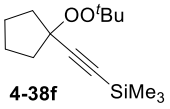
4-38m

4-38m (colorless liquid, 93%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.29–7.17 (m, 4H), 2.83–2.79 (m, 2H), 2.10–2.05 (m, 1H), 1.97–1.86 (m, 1H), 1.50 (s, 1H), 1.26 (s, 9H), 0.21 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.3, 128.4, 128.3, 125.7, 107.6, 88.6, 79.6, 77.7, 41.8, 30.9, 26.7, 25.4, 0.0; HRMS (ESI) calcd for $C_{19}H_{30}O_2NaSi$ $[M+Na]^+$ 341.1913, found 341.1913.



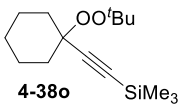
4-38n

4-38n (colorless liquid, 58%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.13–5.10 (m, 1H), 1.99–1.98 (m, 2H), 1.75–1.70 (m, 2H), 1.68 (s, 1H), 1.62–1.57 (m, 5H), 1.53–1.49 (m, 2H), 1.43 (s, 3H), 1.24 (s, 9H), 0.16 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 131.5, 124.5, 108.1, 87.9, 79.5, 78.0, 39.5, 28.1, 26.7, 25.7, 25.4, 24.6, 17.2, 0.0; HRMS (ESI) calcd for $C_{18}H_{34}O_2NaSi$ $[M+Na]^+$ 333.2226, found 333.2233.



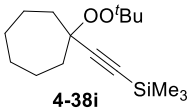
4-38f

4-38f (colorless liquid, 72%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.14–2.10 (m, 2H), 1.88–1.83 (m, 2H), 1.71–1.67 (m, 4H), 1.24 (s, 9H), 0.15 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 108.7, 87.1, 84.4, 79.3, 38.6, 26.5, 24.1, –0.1; HRMS (ESI) calcd for $C_{14}H_{26}O_2NaSi$ $[M+Na]^+$ 277.1600, found 277.1613.



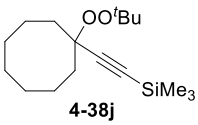
4-38o

4-38o (colorless liquid, 88%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.94–1.91 (2H, m), 1.67–1.64 (m, 2H), 1.58–1.50 (m, 6H), 1.25 (s, 9H), 0.16 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 108.0, 89.1, 79.3, 78.4, 35.6, 26.7, 25.5, 22.8, 0.0; HRMS (ESI) calcd for $C_{15}H_{28}O_2NaSi$ $[M+Na]^+$ 291.1756, found 291.1768.



4-38i

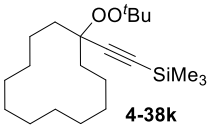
4-38i (colorless liquid, 85%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.02–1.97 (m, 2H), 1.85–1.80 (m, 2H), 1.64–1.52 (m, 8H), 1.24 (s, 9H), 0.15 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 109.2, 88.2, 81.8, 79.3, 38.0, 28.7, 26.7, 22.5, 0.0; HRMS (ESI) calcd for $C_{16}H_{30}O_2NaSi$ $[M+Na]^+$ 305.1913, found 305.1923.



4-38j

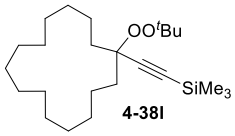
4-38j (colorless liquid, 82%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.99–1.95 (m, 2H), 1.90–1.85 (m, 2H), 1.61–1.44 (m, 10H), 1.25 (s, 9H), 0.15 (s, 9H); ^{13}C NMR (125 MHz,

$CDCl_3$) δ 108.7, 88.2, 81.5, 79.3, 33.4, 28.0, 26.8, 26.7, 24.9, 22.2, 0.0; HRMS (ESI) calcd for $C_{17}H_{32}O_2NaSi$ $[M+Na]^+$ 319.2069, found 319.2078.



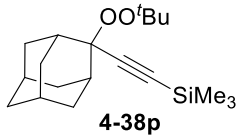
4-38k

4-38k (white solid, 73%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.84–1.79 (m, 2H), 1.67–1.61 (m, 2H), 1.50–1.28 (m, 18H), 1.24 (s, 9H), 0,19 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 108.7, 87.9, 80.7, 79.3, 31.6, 26.8, 26.1, 22.4, 22.1, 19.3, 0.0; HRMS (ESI) calcd for $C_{21}H_{40}O_2NaSi$ $[M+Na]^+$ 375.2695, found 375.2681.



4-38l

4-38l (white solid, 89%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.77–1.63 (m, 4H), 1.36–1.27 (m, 24H), 1.24 (s, 9H), 0.15 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 108.6, 88.1, 80.8, 79.3, 35.3, 27.5, 26.9, 26.8, 26.7, 26.4, 21.9, 0.0; HRMS (ESI) calcd for $C_{24}H_{46}O_2NaSi$ $[M+Na]^+$ 417.3165, found 417.3172.



4-38p

4-38p (colorless liquid, 56%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.15–2.12 (m, 6H), 1.73–1.68 (m, 4H), 1.50 (d, J = 11.74 Hz, 2H), 1.26 (s, 9H), 0.16 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 109.0, 88.9, 81.4, 78.9, 37.7, 35.1, 34.9, 31.7, 27.3, 26.7, 0.0; HRMS (ESI) calcd for $C_{19}H_{32}O_2NaSi$ $[M+Na]^+$ 343.2069, found 343.2079.

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PART II

ENYNE RING-CLOSING METATHESIS

CHAPTER 5

STRUCTURE AND REACTIVITY OF SULFONAMIDE- AND ACETATE-CHELATED RUTHENIUM ALKYLIDENE COMPLEXES

5.1. Introduction

5.1.1. Brief Historical Background

Metathesis has emerged as a powerful synthetic tool to create molecular complexity in modern organic synthesis.[1] First olefin metathesis reaction was known as double bond scrambling reaction, which was reported in mid-1950s.[2] Earlier, the mechanism of metathesis reaction was unclear, and it was first proposed by Chauvin in 1971 to use a propagating metal carbene species that reacts with an alkene via a [2+2]-cycloaddition to form metallocyclobutane intermediate.[3] Since Chauvin's proposed the metal alkylidene-bond mechanism of olefin metathesis, extensive investigations have been devoted to the developments of catalytically active metathesis catalysts, and the first major breakthroughs came in early 1990's from the Schrock and Grubbs groups. In 1990, Schrock reported highly metathesis active first well-defined molybdenum-based alkylidene complex.[4] However, the molybdenum-based alkylidenes are sensitive to air and moisture, and typical polar functional groups intolerant. In 1992, Grubbs reported the first air stable and efficient ruthenium-alkylidene metathesis catalyst.[5] After this, the development of more effective and user-friendly catalyst[6] systems as well as their application to a variety of metathesis reactions have been realized.

5.1.2. Metathesis Reaction Types and Catalysts

5.1.2.1. Classification of Metathesis Reactions

Depending on the type of unsaturated π–systems involved in the events of metathesis, it can be classified into three major types (a) diene, (b) enyne, and (c) diyne metathesis (**Figure 5.1**).[7] Based on the structural change involved in the metathesis, these metathesis events are further categorized into different classes and the most general three major class of these events are cross metathesis (CM), ring-closing metathesis (RCM), and ring-opening metathesis (ROM).

The most developed diene metathesis can be further categorized into four types: (1) an intermolecular metathesis reaction between two alkenes to form a new alkene product and ethylene as by-product is called

as diene cross metathesis,[8] (2) an intramolecular metathesis reaction between two alkenes

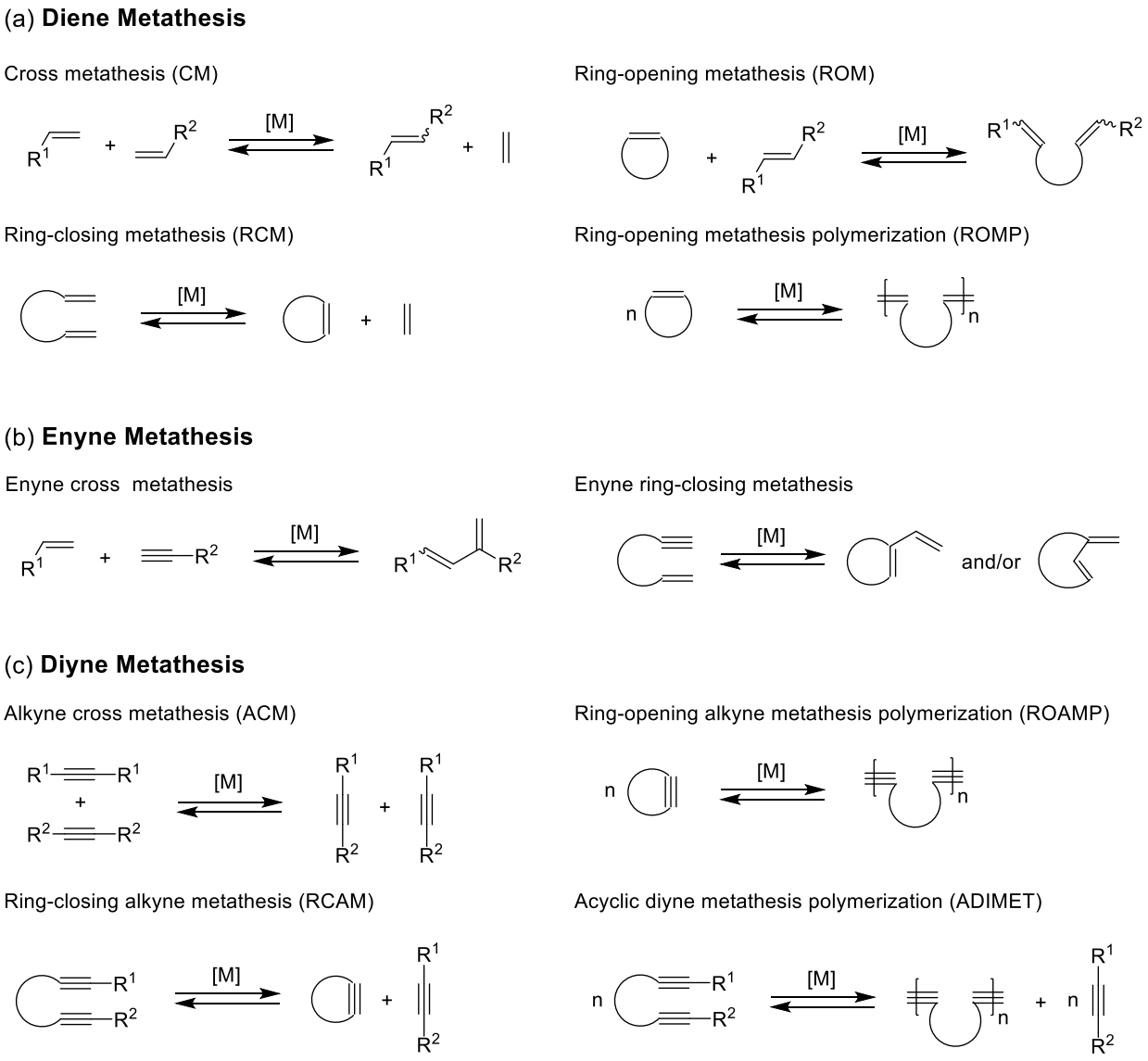


Figure 5.1 Classifications of Metathesis Reactions

to form a new cycloalkene product and ethylene side product is called diene ring-closing metathesis,[9] (3) an intermolecular metathesis reaction between a cyclic- and acyclic alkene to form an acyclic diene product is named as ring-opening metathesis, and (4) a self-metathesis process of strained cycloalkene to generate a polymeric acyclic alkene is called ring-opening metathesis polymerization.[10] The metathesis reaction between an alkene and alkyne to generate a conjugated 1,3-diene is known as enyne metathesis, which is

classified into two major categories; enyne cross metathesis and enyne ring-closing metathesis.[11] Similar to diene metathesis, diyne metathesis is also categorized into four types; cross metathesis, ring-closing metathesis, ring-opening metathesis polymerization and ring-opening metathesis.[12]

Although each of these three metathesis processes involves different combinations of unsaturated functionalities, all of them share two identical elementary steps. These are [2+2] cycloaddition between metal alkylidene or alkylidyne with appropriate π-systems to form metallacyclobutane (in diene metathesis), metallacyclobutene (in enyne metathesis), and metallacyclobutadiene (in diyne metathesis) intermediate, and their cycloreversion in subsequent step (**Figure 5.2**).

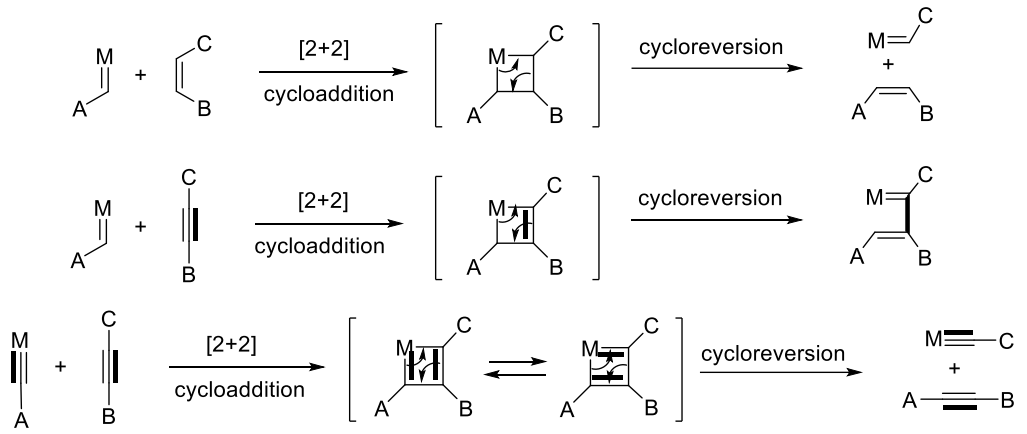


Figure 5.2 Elementary Steps in Diene, Enyne and Diyne Metathesis

5.1.2.2. Grubbs-Type Ruthenium Alkylidene Complexes

Based on the availability, functional group tolerance, and their relatively air-stable nature, Grubbs ruthenium-carbene complexes ranging from **Ru-1** to **Ru-10** are extensively used as common initiators in diene and enyne metathesis reaction (**Figure 5.3**). In 1992, Grubbs and coworkers first reported the well-defined ruthenium-based alkylidene complex **Ru-1a** of type $[RuCl_2(PPh_3)(=CH-CH=CPh_2)]$.[5] To improve the catalytic activity of this ruthenium alkylidene complex, triphenylphosphine (PPh_3) ligand of **Ru-1a** was replaced with tricyclohexylphosphine (PCy_3), which has shown much increased metathesis activity with a very good functional group tolerance.[13] After that, in 1995, a new ruthenium alkylidene complex **G-I** (**Ru-2**) having benzylidene carbene known as Grubbs first-generation catalyst (**G-I**) was reported by Grubbs.[14]

The **G-I** complex has been extensively used in diene and enyne metathesis of variety substrate classes. Thereafter, in 1999 Grubbs and coworkers further modified **G-I** complex by replacing the PCy_3 ligand with a *N*-heterocyclic carbene (NHC) ligand, which is known as the second-generation Grubbs catalyst (**G-II** or **Ru-3**).[15] The replacement of PCy_3 with a stronger σ-donor NHC ligand, thus facilitates the dissociation of PCy_3 to activate the catalyst as a 14-electron species, which is essential for the initiation of metathesis catalytic cycle. In 1999, Hoveyda and coworkers made an important discovery by replacing one of the L-type PCy_3 ligand of **G-I** with a *o*-isopropoxybenzylidene ligand which further improved the stability of the catalyst.[16] Shortly thereafter, variations of *o*-isopropoxybenzylidene **G-II** has been developed by both Hoveyda and Blechert groups (**Ru-5**).[17] The replacement of PCy_3 ligand with chelated *o*-isopropoxybenzylidene was found to impart exceptional stability especially with respect to air and moisture.

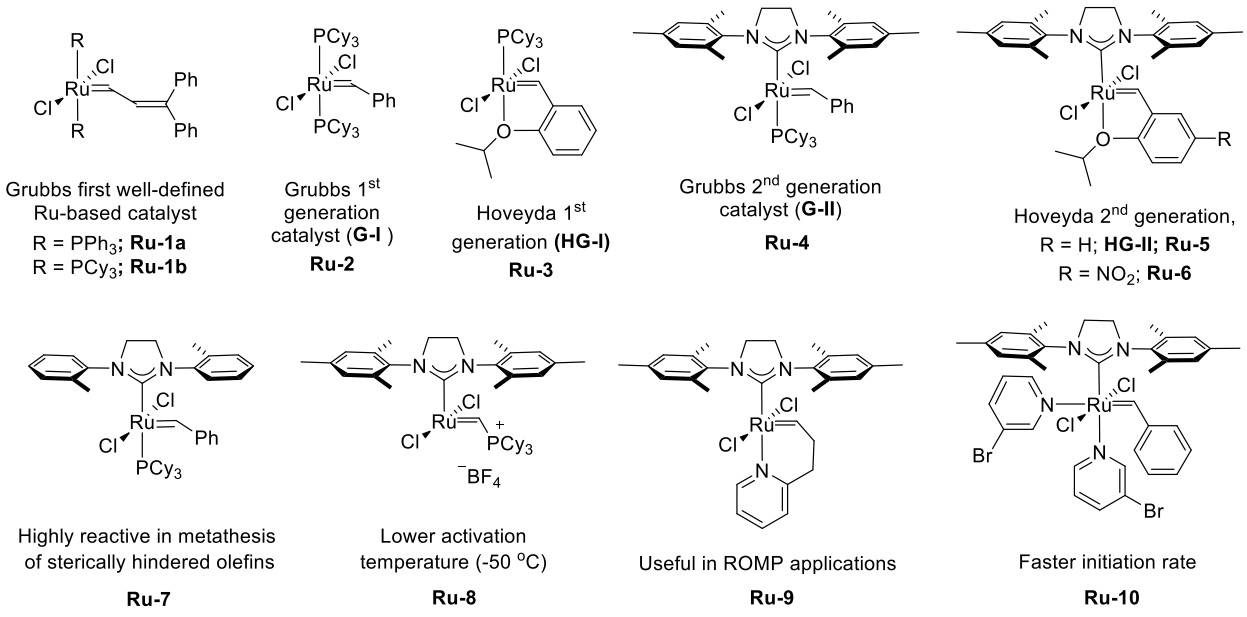


Figure 5.3 Grubbs-Type Ruthenium Alkylidene Complexes

Moreover, the use of phosphine-free complexes can prevent the phosphine-mediated catalyst decomposition pathways. The introduction of a nitro group to the *o*-isopropoxybenzylidene of **HG-II** further improves metathesis reactions (**Ru-6**).[18] Also, there are several other commercially available ruthenium alkalidene complexes **Ru-7** to **Ru-10** are known, which further improve the thermal stability of

the original catalyst. Complex **Ru-7** is known to be highly reactive even with sterically hindered alkenes, and **Ru-8** is known to catalyze reactions even at very low temperatures. Complex **Ru-9** is widely used for ring-opening polymerizations, and **Ru-10** is known to initiate metathesis reaction rapidly.[19]

5.1.2.3. Schrock-Type Molybdenum and Tungsten Complexes

Molybdenum- and tungsten-based catalysts have been widely used in metathesis reactions, and some of the most common complexes that are used extensively in the diene metathesis are summarized in **Figure 5.4**. Molybdenum- and tungsten-based alkylidene complexes **Mo-1**/**W-1** were first prepared by Schrock and coworkers. The general formula of these complexes is [M(=CHMe$_2$Ph)(=N-Ar)(OR$_2$)] where M is Mo or W.[4] These Schrock-type alkylidene complexes are the most reactive alkene metathesis catalysts. However, the high oxophilicity of the metal center makes these catalysts are extremely air and moisture

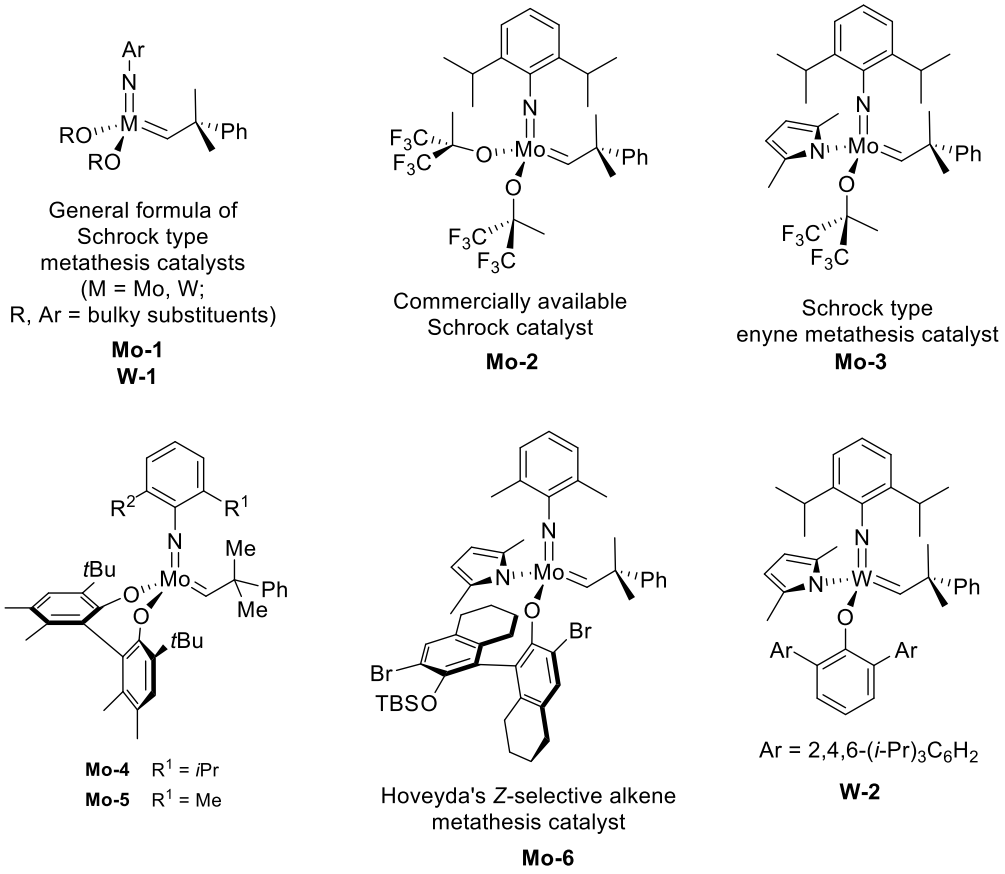
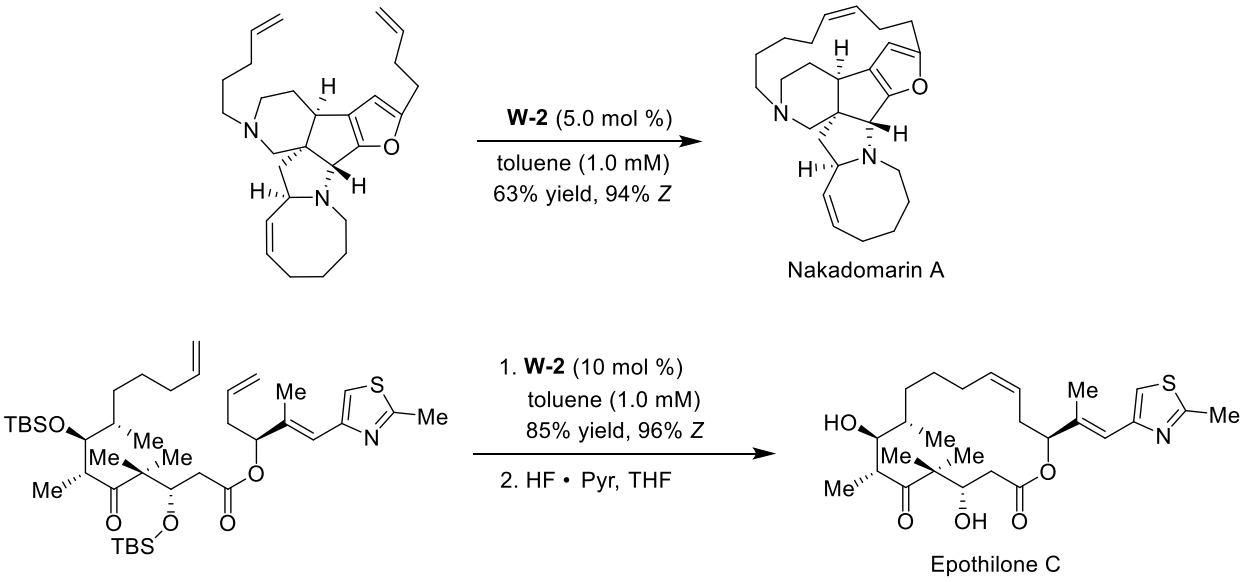


Figure 5.4 Schrock-Type Molybdenum and Tungsten Complexes

sensitive.[20] Although Schrock-type molybdenum-based alkylidene complex **Mo-2** is commercially available, it requires thoroughly purified reagents and solvents, and even under these reaction conditions, its use is limited only to a relatively narrow range.[21] Hoveyda and coworkers demonstrated Schrock-type **Mo-3** complex having stereogenicity Mo-center was tested for *endo*-selective enyne ring-closing metathesis. Similar molybdenum-based alkylidene complexes **Mo-4**, **Mo-5** and **Mo-6** were well developed for enantioselective diene ring-closing metathesis, and highly *Z*-selective diene ring-closing metathesis of dienes using bulky and freely rotating monodentate alkoxide ligand in **Mo-6**.[22] It was also demonstrated that **Mo-6** catalyst can overcome the inherent thermodynamic preference of the metathesis process in forming *E*-alkene products such that a non-reversible reaction regime operates to selectively generate *Z*-alkenes.[23]



Scheme 5.1 Tungsten-Catalyzed RCM for Synthesis of Nakadomarin A and Epothilone C

Hoveyda and coworkers also reported high *Z*-selective diene ring-closing metathesis using tungsten-based alkylidene complex **W-1**. This complex has been employed for the synthesis of natural products such as epothilone C and nakadomarin A. The *Z*-cycloalkenes in these macrocyclic natural products was obtained in high *Z*-selectivity in excellent yields (**Scheme 5.1**).[24]

5.1.2.4. Diyne Metathesis Complexes

The development of new catalysts with good functional group tolerance and high catalytic activity is required for their practical use. All alkyne metathesis catalysts known to date belong to either in situ generated systems (Mortreux's system) or well-defined single-component catalysts (Schrock-type complexes) (**Figure 5.5**).[25] All well-defined single-component catalysts are variants of Schrock-type alkylidyne complexes of high oxidation state molybdenum or tungsten complexes. Except the Mortreux's system, all classical Schrock-type alkylidyne complexes suffer from high sensitivity toward moisture, molecular oxygen, and even molecular nitrogen for catalyst **Mo-8**. The first well-defined, commercially available and widely used alkyne metathesis catalyst is Schrock complex **W-3**, which is benefited by having

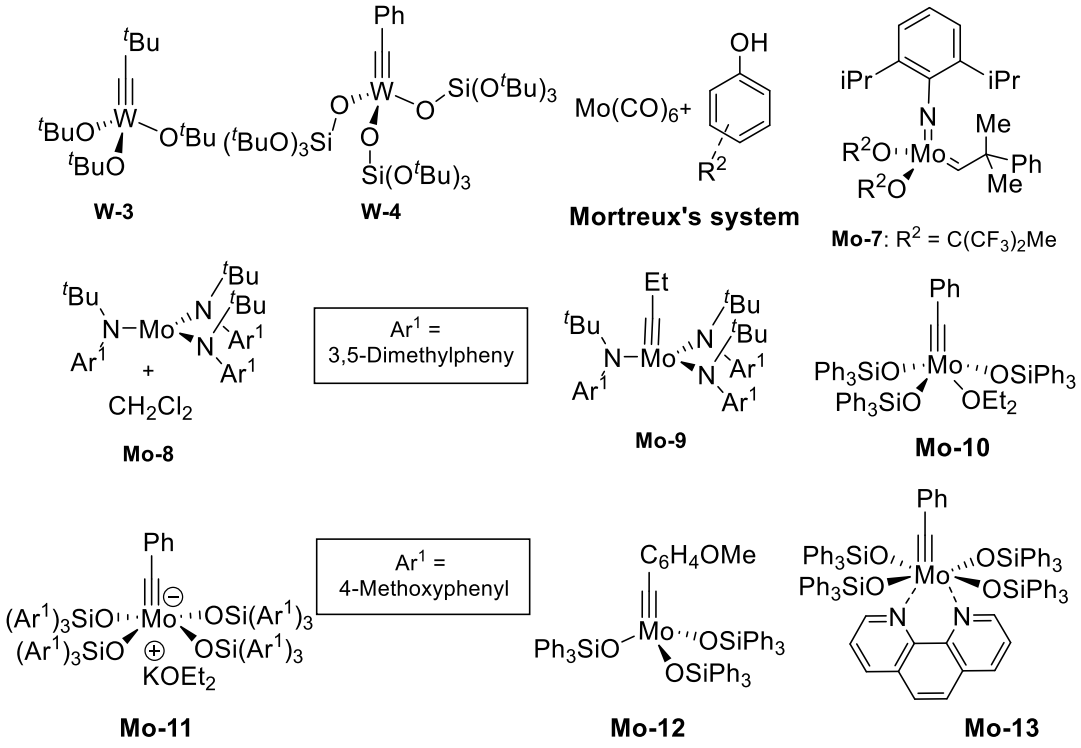


Figure 5.5 Diyne Metathesis Complexes

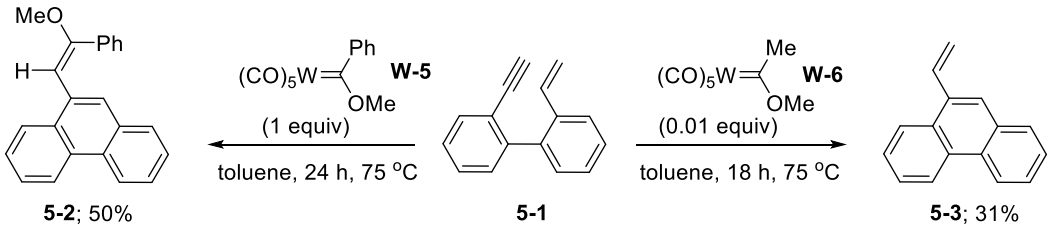
the bulky alkoxide ligands to prevent or slow down bimolecular decomposition of the alkylidyne intermediates in the catalytic cycle. Bulky ligands having thiolates, alkyl, and amides did not show much improvement for catalyst activity. Recently, significant improvements of the performance of Schrock-type

complexes have been realized mainly by the Fürstner group, and their broad range of applications in complex natural product synthesis have been demonstrated. Complex **Mo-13** is air stable for several weeks and also capable of performing large scale reactions.[26]

5.2. Enyne Metathesis

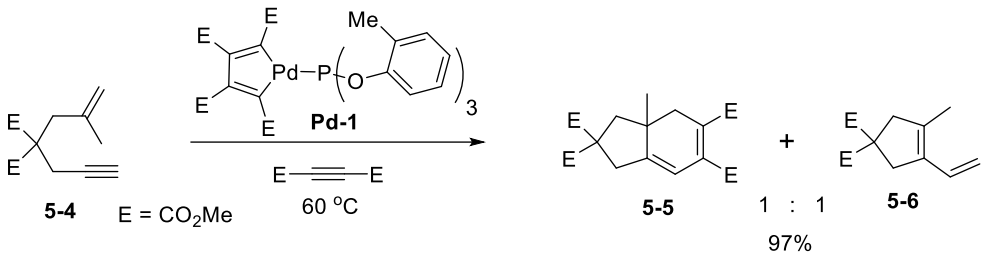
Among diene, enyne and diyne metathesis, enyne metathesis is the most atom economical process that can generate conjugated 1,3-diene via a formal addition reaction between an alkene and alkyne both in inter and intra manners. In enyne metathesis (cross metathesis and/or ring-closing metathesis), the generated propagating ruthenium alkylidene species can easily undergo tandem reaction sequences that would enable the formation of multiple bonds and rings in one step.

In 1985, Katz and coworkers reported the first example of enyne ring-closing metathesis using Fischer tungsten complexes **W-5** and **W-6** (**Scheme 5.2**). In this intramolecular enyne metathesis, enyne **5-1** in the presence of catalytic and/or stoichiometric amount of tungsten complexes provided the metathesis products **5-2** and **5-3**. The proposed mechanism involves metallocyclobutene formation and its cycloreversion to generate a vinyl carbene complex.[27] Thereafter, Hoye and Mori independently studied chromium Fischer carbene mediated enyne ring-closing metathesis. These reactions however suffers with high catalyst loading, low yields with undesired product formation and poor functional group tolerance.[28]



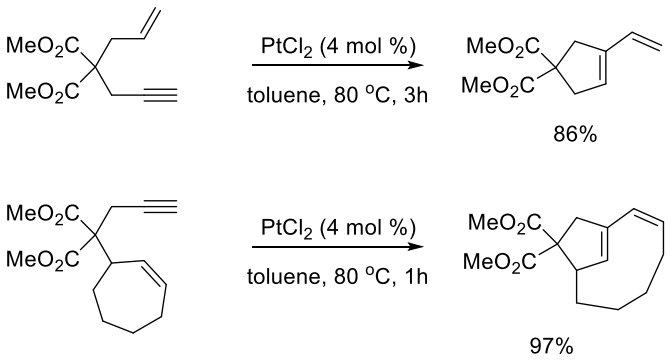
Scheme 5.2 Example of First Enyne Metathesis

Trost and coworkers disclosed the palladium-catalyzed enyne RCM reactions (**Scheme 5.3**).[29] In this metathesis transformation, low valent palladium complex **Pd-1** has been used, and two products **5-5** and **5-6** were obtained in a 1:1 ratio.



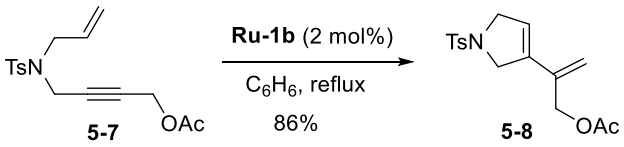
Scheme 5.3 Pd-Catalyzed Enyne Metathesis

Murai reported platinum-catalyzed enyne ring-closing metathesis. In this study, 1,6-enynes were treated with a catalytic amount of $PtCl_2$ to generate 1-vinylcycloalkene in high yields (**Scheme 5.4**).[30] The suggested mechanism for the formation of ring-closer products might involve non-classical carbocations.[31]



Scheme 5.4 Pt-Catalyzed Ring-Closing Enyne Metathesis

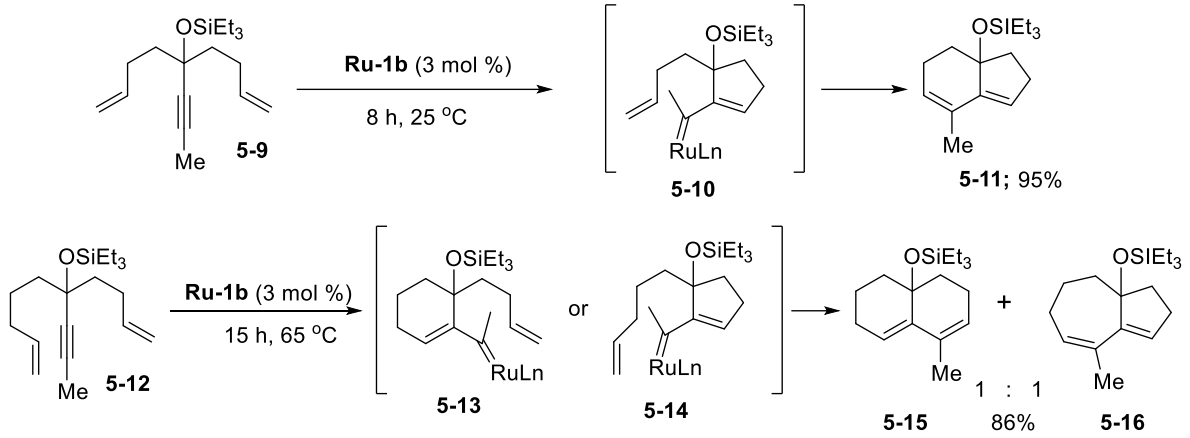
Ruthenium-catalyzed enyne metathesis was first reported by Mori and Kinoshita.[32] Enyne **5-7** upon treatment a catalytic amount of **Ru-1b** (2 mol%), efficiently provided diene **5-8** in 86% yield (**Scheme 5.5**).



Scheme 5.5 First Catalytic Ruthenium Carbene-Based Enyne RCM

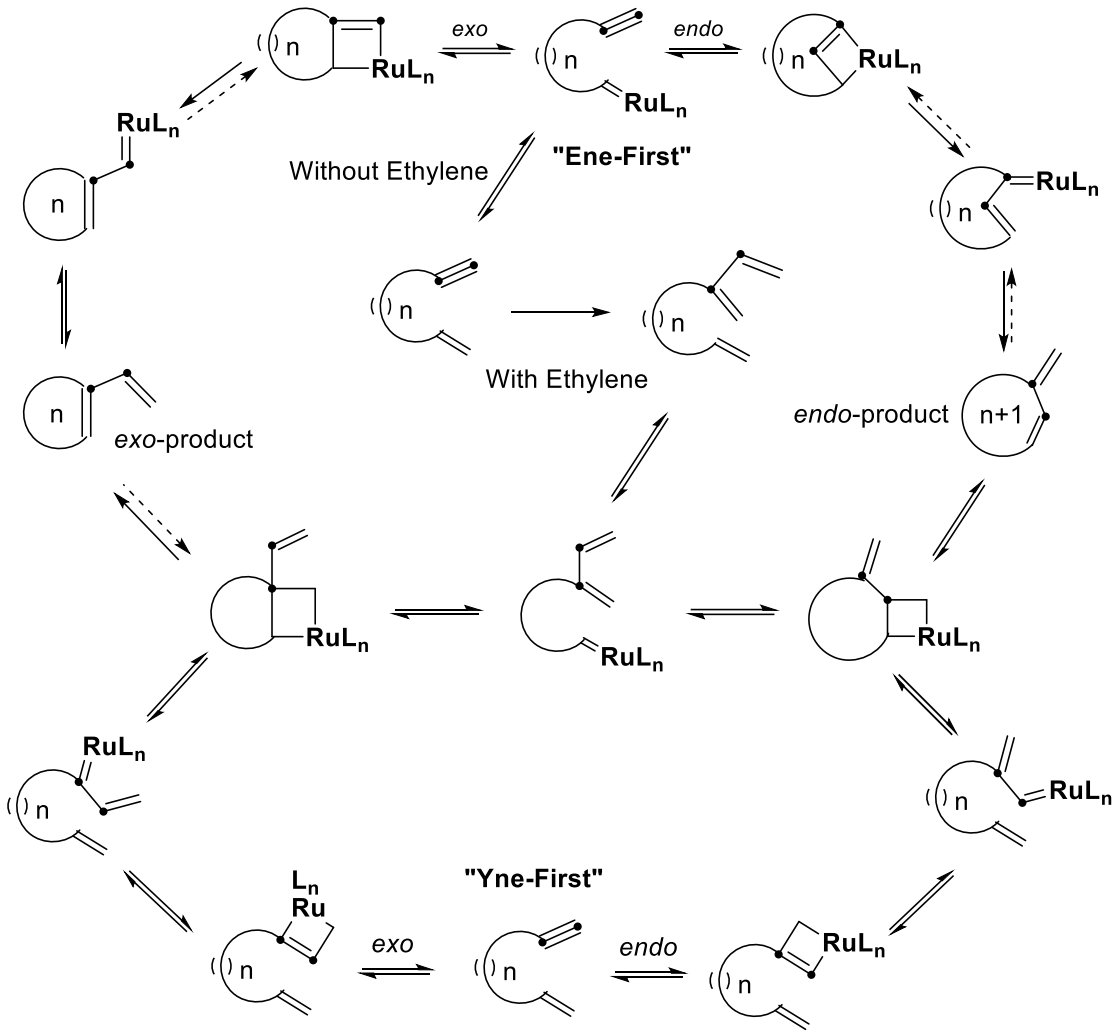
After the first report from Mori group, Grubbs and coworkers extended this RCM of enyne metathesis to dienynes using **Ru-1b** (**Scheme 5.6**).[33] Dienyne **5-9** having a symmetrical alkenyl tether provided bicyclic product **5-11** in excellent yield when treated with **Ru-1b**. However, the reaction with dienyne **5-**

12 having unsymmetrically tethered alkene afforded a mixture of bicyclic products in 1:1 ratio. Thereafter, numerous synthetic applications of enyne metathesis has been evolved by using various Grubbs-type ruthenium alkylidenes.[34,35]



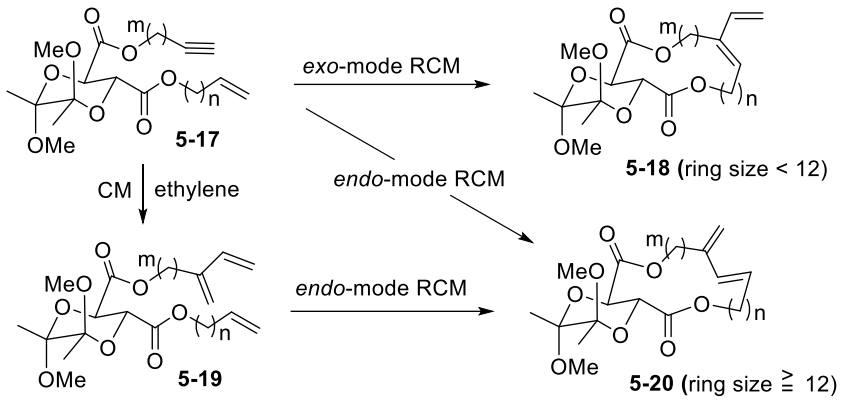
Scheme 5.6 Tandem Ring-Closing Metathesis of Dienynes

Comparing to the ring-closing metathesis of dienes and diynes, which ultimately generate only one product regardless of the initiation events, ring-closing metathesis of enynes has potentially three different initiation events, which lead to two different "Ene-First" pathways and two different "Yne-First" pathways. These pathways involve unique propagating alkylidene species, yet ignored only two distinct RCM products are observed (1,2-substituted or 1,3-substituted dienes) via isomeric vinyl ruthenium alkylidene intermediates (**Scheme 5.7**). Several groups have investigated the mechanism of enyne metathesis, however, there are still some uncertainties.[36] Mori and coworkers observed the formation of *endo*-RCM products when disubstituted alkenes are present in the substrate.[37] Hoveyda and coworkers also demonstrated the enyne metathesis catalyzed by group VI metals (W, Mo) which generally initiates at an alkyne counterpart. Computational studies did not show any preference for "Ene-First" and "Yne-First" mechanism, yet calculations showed the preferential formation either *endo*- or *exo*-product depending on the nature of substituents.



Scheme 5.7 Possible Mechanism for Enyne RCM

The *exo*/*endo*-selectivity in enyne RCM has been nicely demonstrated by Lee and Hansen by varying the ring sizes from small to medium and to macrocycles (**Scheme 5.8**). In their study, the small and medium ring forming substrates generally favor the formation of *exo*-mode ring-closer product **5-18**. On the other hand, the RCM to form macrocycles preferentially generates the *endo*-mode ring-closer products. The formation of *endo*-products rationalized by the "Ene-First" mechanism, where the initially formed ruthenium alkylidene favors to add to the tethered alkyne such a way to generate a more alkyl substituted alkylidene intermediate. However, the reactions under ethylene provides 1,3-diene **5-17**, which then underwent diene RCM to generate formal *endo*-mode products **5-20** exclusively.[38]



Scheme 5.8 Mode Selectivity in Enyne RCM

5.3. Metallotropic [1,3]-Shift in Enyne Metathesis

Alkynyl alkylidene complexes can undergo [1,3]-transposition known as metallotropic [1,3]-shift. It can be considered as a special case RCM of enynes, where metallotropic [1,3]-shift can be initiated by *exo*-mode ring closure by a propagating alkylidene species. The regioselective termination with an appropriate substituent on the alkyne moiety seems to be necessary (**Figure 5.6**).

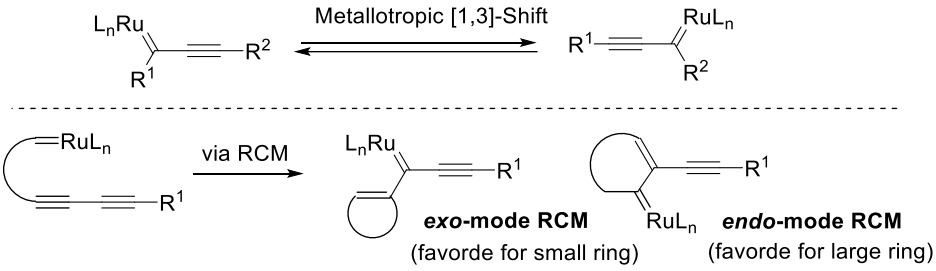
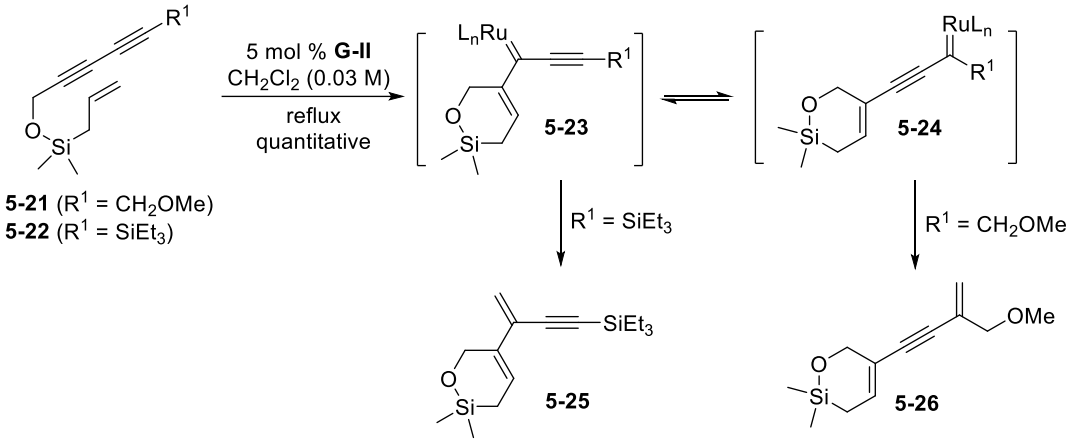


Figure 5.6 Possibility of Metallotropic [1,3]-Shift in Enyne RCM

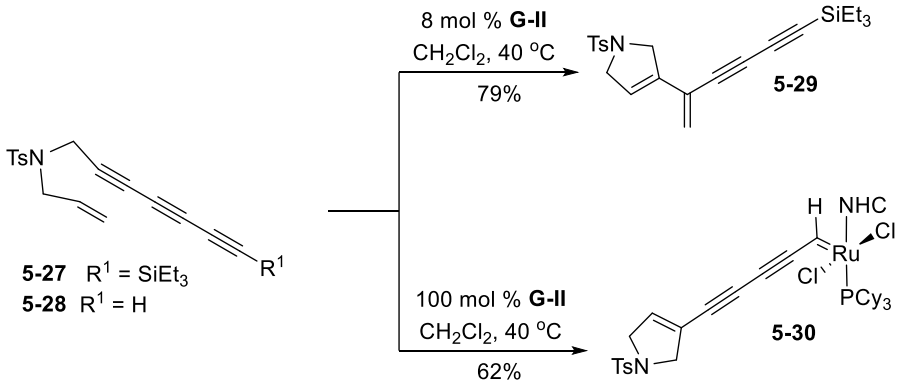
The regioselective RCM of ene-1,3-diynes followed by metallotropic [1,3]-shift was reported by Lee and coworkers (**Scheme 5.9**).[39] In their report, metallotropic [1,3]-shift of an initial generated alkynyl alkylidene was controlled by the R^1 substituent at the terminus of the 1,3-diyne moiety. In the reaction, if R^1 is hydrogen and/or unhindered alkyl group such as in **5-21**, the metallotropic shift occurs to generate 1,5-diene-3-yne **5-26** via initially formed **5-23** to **5-24**. However, if the R^1 is sterically hindered substituent such as a triethylsilyl group **5-25** was generated without metallotropic shift. It can be concluded that the

equilibrium between alkynyl alkylidenes **5-23** and **5-24** would mainly depend on the nature of the substituent on the diyne tethers.



Scheme 5.9 Metallotropic [1,3]-Shift Induced by Enyne RCM

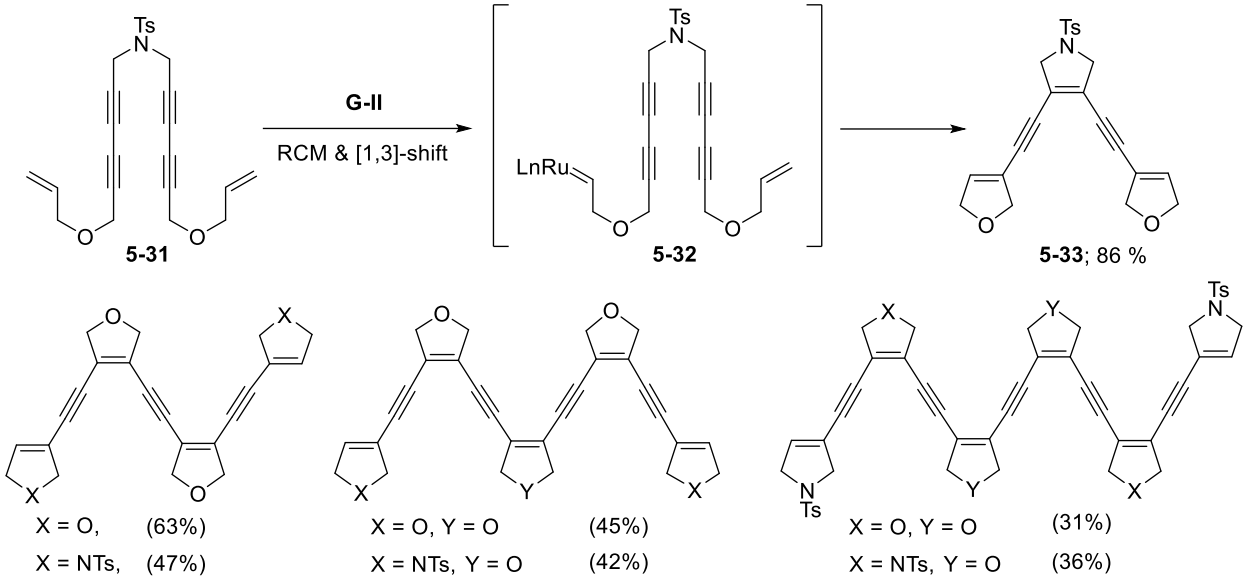
The substituent effect on metallotropic shift in RCM of enynes was further probed by Lee and coworkers (**Scheme 5.10**).[40] Ene-triyne **5-27** having triethyl silyl substituent upon treatment with a catalytic amount **G-II**, provided simple RCM product **5-29** as a sole product. However, the reaction of triyne **5-28** with stoichiometric amount of **G-II** afforded alkynyl alkylidene complex **5-30**.



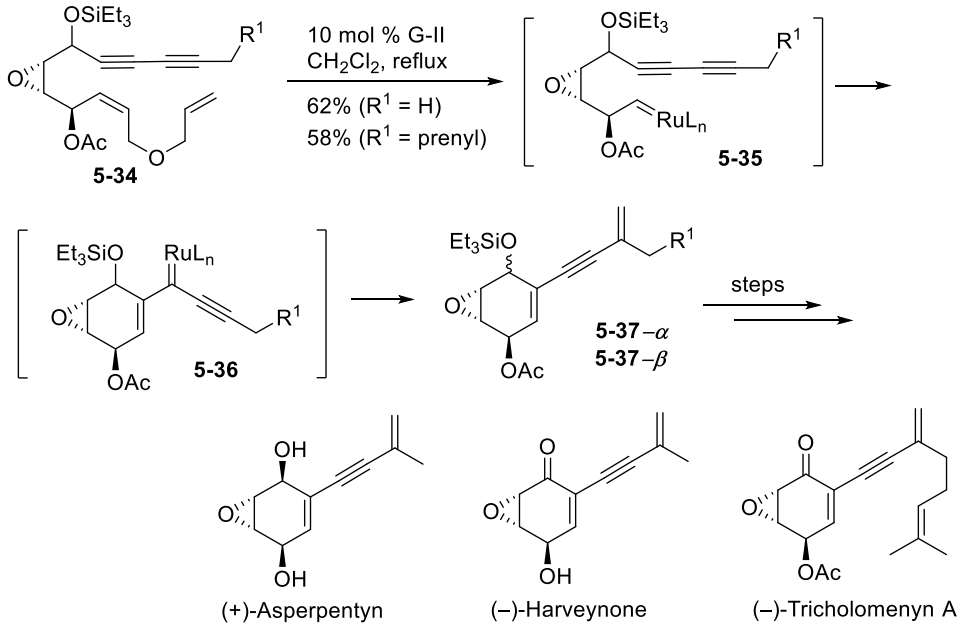
Scheme 5.10 Reactivity of Alkynyl Ruthenium Alkylidenes

Lee and coworkers nicely utilized this enyne RCM followed by metallotropic [1,3]-shift for the synthesis of oligoenynes (**Scheme 5.11**).[41] Diene tethered multiynes in the presence of catalytic amount of **G-II** catalyst underwent multiple enyne RCM with multiple metallotropic [1,3]-shift to afford oligoenynes

in good to moderate yields.



Scheme 5.11 Formation of Oligoenynes via Metallotropic [1,3]-Shift



Scheme 5.12 Enyne RCM and Metallotropic [1,3]-Shift for Natural Product Synthesis

This metallotropic shift process also successfully implemented in the total synthesis of natural products, such as (+)-asperpentyne, (−)-harveynone and (−)-tricholomenyn (**Scheme 5.12**).[42] The relay tethered ene-diynes in the presence of **G-II** complex, undergoes RCM to generate ruthenium alkylidene **5-35**. After

RCM with the tethered alkyne to produce alkynyl alkylidene **5-36**, a metallotropic shift process followed by termination affords 1,5-diene-3-yne **5-37**. Further functional group modifications of **5-37** led to the target natural products. A similar metalltropic shift process was also applied to the synthesis of (3*R*,9*R*,10*R*)-panaxytriol.[43]

5.4. Results and Discussion

The favorable coordination of alkene or alkyne to the coordinatively unsaturated ruthenium metal center along the catalytic cycle is necessary for productive alkene and enyne metathesis catalyzed by Grubbs-type ruthenium alkylidene complexes.[1] Occasionally, however, other polar functional groups containing lone pair electrons, alkenes, or alkynes near the metal center preferentially occupy the coordination site over the substrate such that the catalytic cycle is arrested at various resting stages either temporarily or permanently in alkene and enyne metathesis. To minimize these non-productive metathesis events involving the trapped propagating alkylidene species, it is crucial to understand what functionality and structural features and how they promote or discourage such events.

There are many known heteroatom-chelated ruthenium alkylidenes, and the earliest and most prominent complex of this type is **HG-I** (**Ru-3**),[16] an oxygen-chelate discovered by Hoveyda and coworkers, which is now developed as the Grubbs-Hoveyda complex **HG-II** (**Ru-5**)[17] and its variants.[18,44] The development of this phosphine-free complex gave an important breakthrough for metathesis because of its exceptionally stability to air and moisture. Thus, other phosphine-free heteroatom-chelated ruthenium alkylidenes complexes are emerged, and many research groups have continued to develop heteroatom-chelated ruthenium alkylidene complexes and studied their structure and reactivity.

Sulfur-chelated ruthenium alkylidene complexes **Ru-11** and **Ru-12** were reported by Lemkoff [45] and Grela,[46] respectively (**Figure 5.7**). Six-membered chelates with sulfonyl oxygen[47] (**Ru-13**, **Ru-14**) and imino-nitrogen[48] (**Ru-15**) were also reported. All these ruthenium alkylidenes have a chelated heteroatom and the *N*-heterocyclic carbene (NHC) ligands with a trans-relationship. In earlier study, Snapper reported alkene-chelated ruthenium complex **Ru-16**, where an alkene is chelated to the metal trans to the phosphine

ligand.[49] Vinyl alkylidene complex[50] **Ru-17** and styryl-chelated complex **Ru-18** were also reported by Grubbs,[51] which display a cis-relationship between the NHC ligand and the chelated alkene.

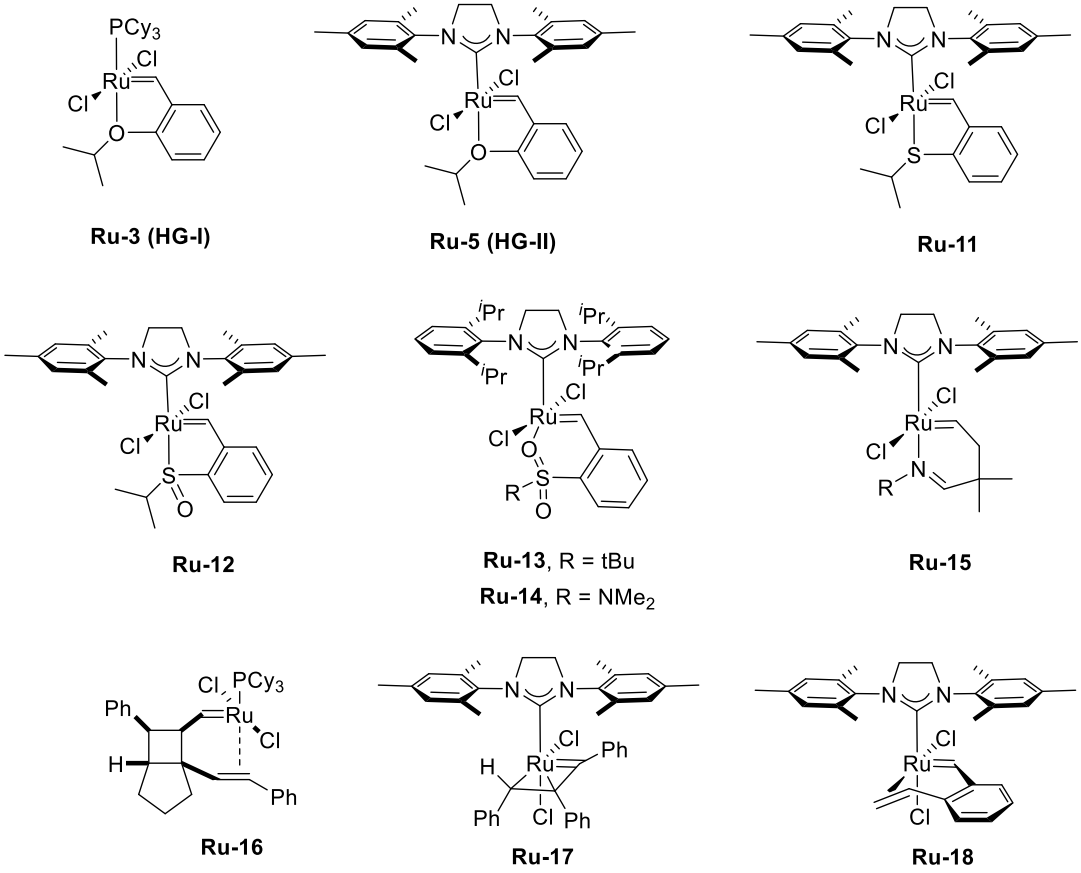
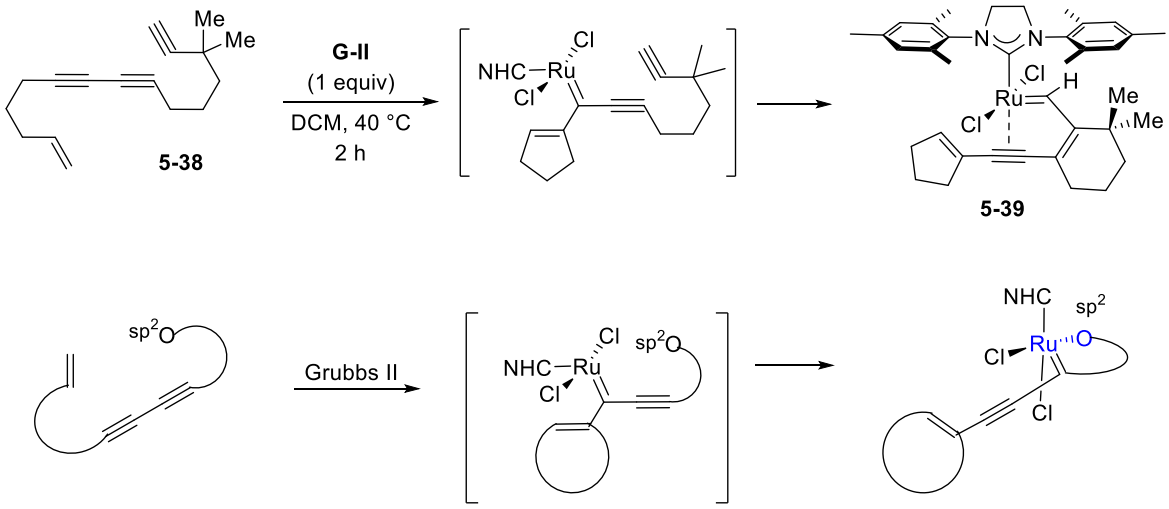


Figure 5.7 Chelated Ruthenium Alkylidene Complexes

Recently, our group also reported the first well-defined alkyne-chelated ruthenium alkylidene complex **5-39**, which was generated by employing a sequential process of tandem ring-closing enyne metathesis and metallotropic [1,3]-shift of enetriyne **5-38** (**Scheme 5.13**).[52] Interestingly complex **5-39** shows that the alkyne is coordinated to the metal center trans to the NHC ligand. On the basis of the reactivity of ruthenium based alkylidene complex in enyne metathesis and metallotropic [1,3]-shift, we envisioned that the RCM of enediynes would be one of most effective methods to deliver the ruthenium alkylidene moiety at an appropriate location such that the metal center and the installed chelating group would interact to form heteroatom chelates. For the RCM of enediynes, the metallotropic [1,3]-shift of the initially formed

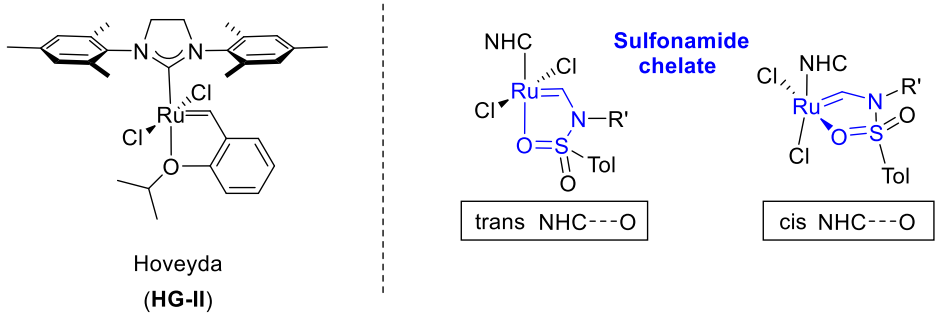
ruthenium alkylidene would be facilitated by a chelation event and vice versa and the thermodynamic advantage of metallotropic [1,3]-shift to generate a fully conjugated system would force the metal center to be positioned near the chelating group. Here in we studied the structure and reactivity of acetate- and sulfonamide-chelated ruthenium alkylidene complexes formed via a tandem reaction involving enyne ring-closing metathesis and metallotropic [1,3]-shift. Also, we tested the behavior of these acetate- and sulfonamide-chelates toward carbon monoxide.



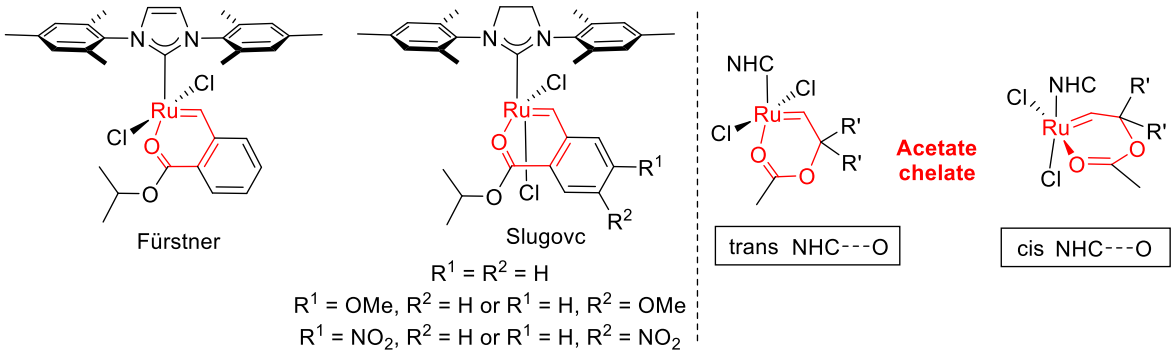
Scheme 5.13 RCM Strategy for the Formation of Chelated Ruthenium Alkylidene

To gain further insight into the chelation behavior of ruthenium alkylidenes, we investigated the factors that promote chelation by oxygen functionality (**Scheme 5.14** and **Scheme 5.15**). The design of 5-membered sulfonamide chelates is modeled by replacing the sp^2–sp^2 carbon moiety of the phenyl group in the Hoveyda complex with a N–S(O) moiety of sulfonamides (**Scheme 5.14**). We believe that the 1-ene-6,8-diyne having a sulfonamide attached to the diyne as an ynamide can undergo enyne RCM followed by metallotropic shift might generate a sulfonamide chelated ruthenium alkylidene more favorably. Similarly, for a less common 6-membered ester chelates, the sp^2–sp^2 carbon moiety of the phenyl group in the complexes reported by Fürstner[53] and Slugovc[54] are modeled by the $(R'_2)C$–O moiety of acetate chelates (**Scheme 5.15**). We expected that the formation of acetate-based chelates might be less favorable than that of Fürstner's ester chelate because of the more flexible nature of the C–O linker than the phenyl linker,

which will be partially compensated by the *gem*-dialkyl effect of the (R′$_2$)C–O linker.



Scheme 5.14 Designing New Structural Motifs of Sulfonamide-Chelates



Scheme 5.15 Designing New Structural Motifs of Acetate-Chelates

First, to prove the validity of the 5-membered sulfonamide chelates, terminal ynamide-containing enediynes **5-40** were tested with a stoichiometric amount of Grubbs second-generation catalyst (**G-II**) (**Table 5.1**). In the reaction of yanamide-containing enediyne **5-40a** with a stoichiometric amount of **G-II** complex in CH_2Cl_2 at 45 °C, spectroscopic characterization of the newly formed material (78%) clearly indicates the characteristics of structure **5-41a**, which was further confirmed by single crystal X-ray diffraction analysis. Unexpectedly, the complex shows a cis relationship between the NHC and the chelated oxygen of the sulfonyl group. The favorable formation of a cis sulfonamide-chelate can be explained by the steric repulsion, between alkyne substituent of ruthenium alkylidene and NHC ligand, in the trans chelated complex that might cause a ligand rearrangement to form a more stable cis complex. An enediyne substrate **5-40b** containing a hydroxyl group was subjected to a stoichiometric amount of **G-II**, which

generated the corresponding ruthenium sulfonamide-chelate **5-41b** in 62% yield with a 1:1 diastereomeric ratio. The chelation behavior and the cis relationship between NHC and the chelated oxygen of the sulfonyl group were further confirmed by X-ray structure of **5-41b**, which shows that the ligand disposition around the metal center in **5-41b** is virtually identical to that of **5-41a**. Enediyne **5-40c** was also tested with **G-II** to afford sulfonamide-chelate **5-41c** in 62% yield.

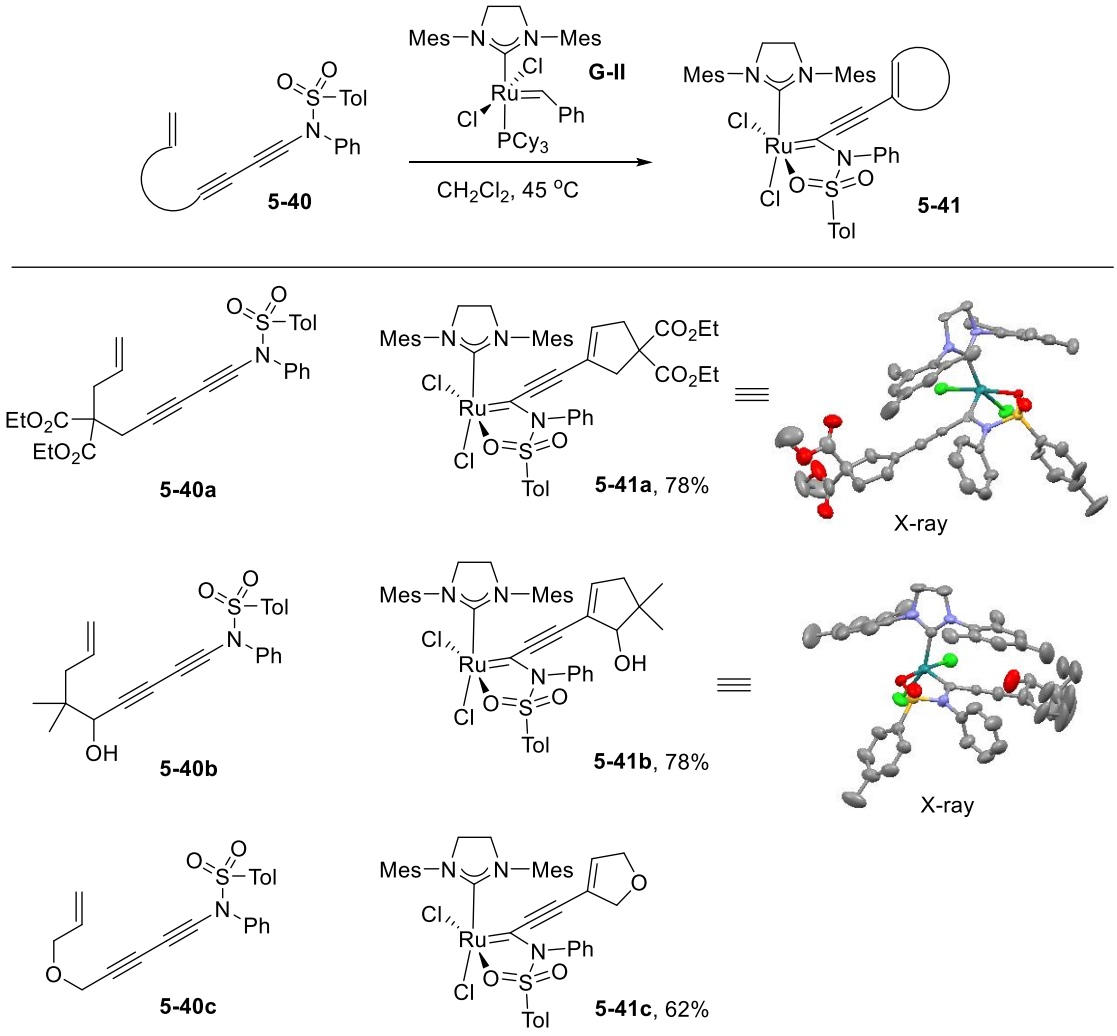
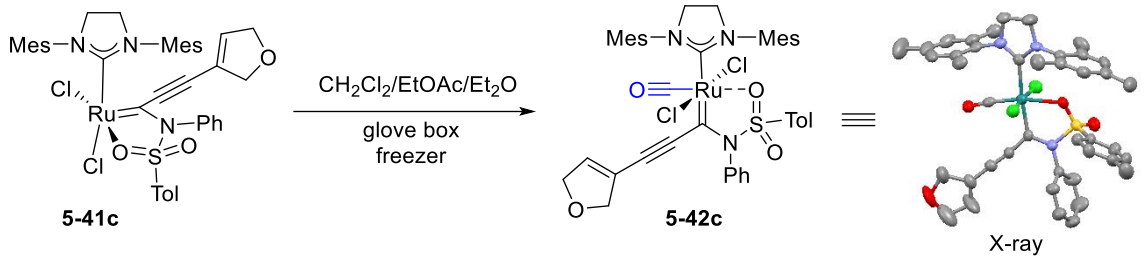


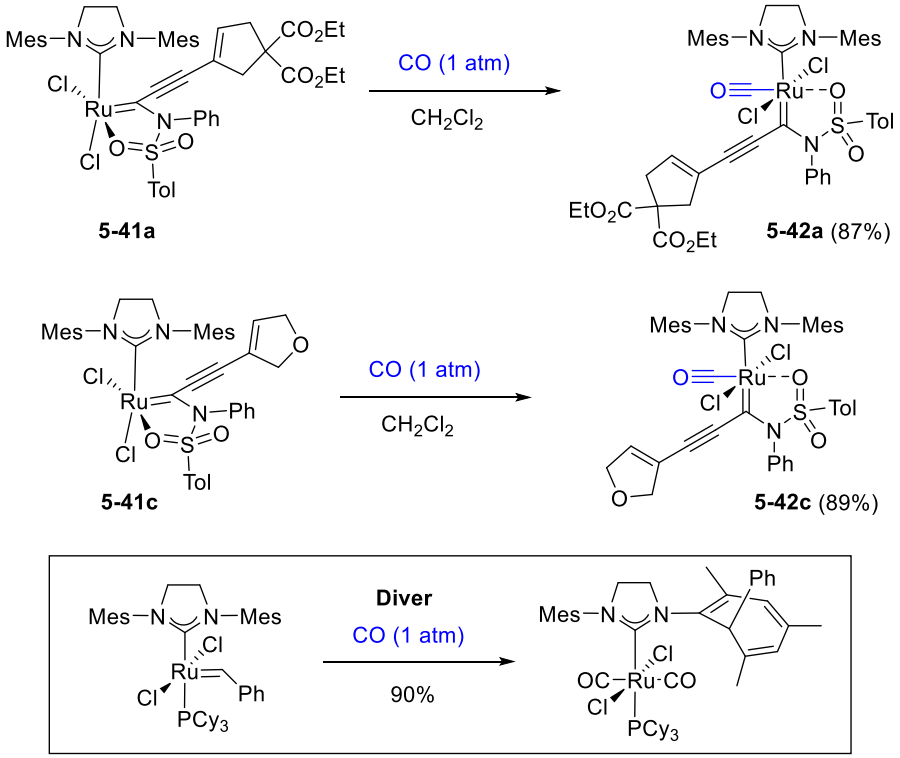
Table 5.1 Formation of Various Sulfonamide-Chelates

To our surprise, however, when **5-41c** was kept in a mixed solvent system of CH_2Cl_2/EtOAc/Et_2O over 10 days, high quality single crystals were obtained, X-ray diffraction analysis of showed that the obtained

material was not the expected sulfonamide-chelate **5-41c** but its carbon monoxide-coordinated form **5-42c** (**Scheme 5.16**).



Scheme 5.16 Unexpected Formation of Carbon Monoxide Complex

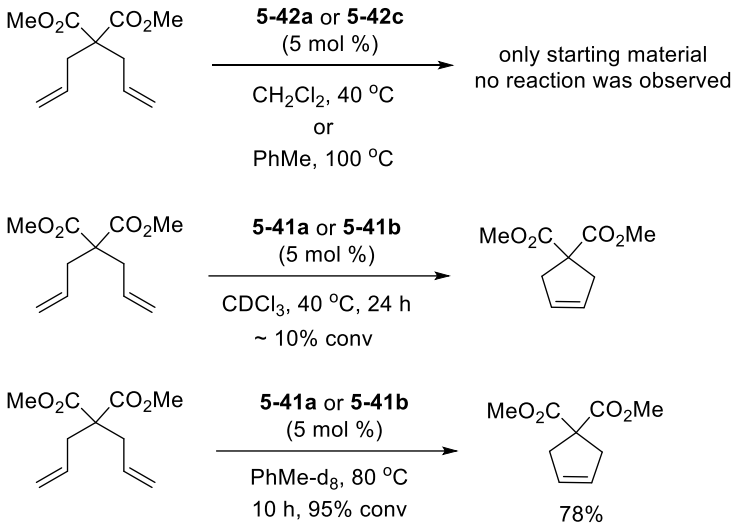


Scheme 5.17 Formation of Octahedral Complex with trans NHC–Carbene Geometry Induced by CO Coordination

To further confirm this CO coordination event, both **5-41a** and **5-41c** were treated with CO (balloon) in CH_2Cl_2, which provided the same type of complex **5-42a** and **5-42c** within 15 minutes in 87% and 89%

yield, respectively (**Scheme 5.17**). During this time a characteristic green color of **5-41a** and **5-41c** changed to pink. The formation of CO-coordinated complexes **5-42a** and **5-42c** is in stark contrast to Diver's observation where Buchner reaction products were formed upon treating Grubbs-II with carbon monoxide,[55] and Grubbs-Hoveyda chelate did not generate Buchner products.[56]

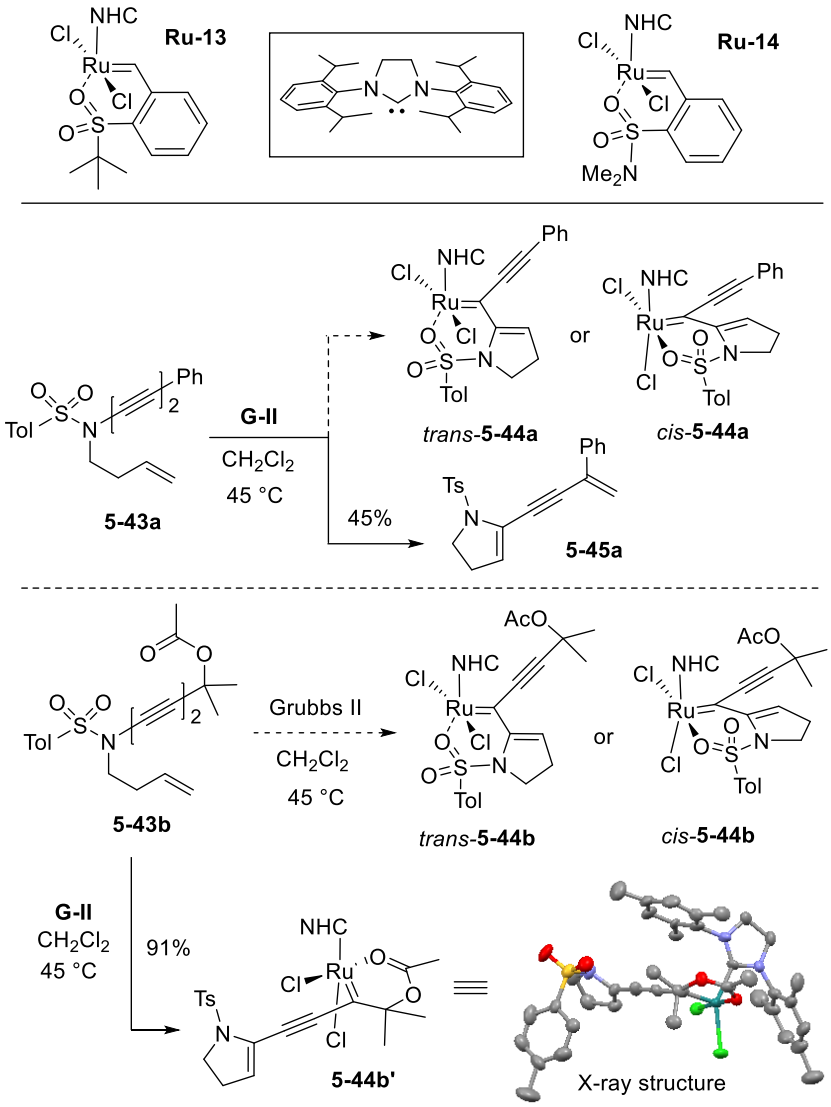
These CO-bound octahedral ruthenium alkylidene complexes chelated with a sulfonamide moiety display a trans relationship between NHC ligand and the carbenic carbon ligand. This is a rare example of Grubbs-type ruthenium alkylidenes to have this unique ligand geometry. This can be explained by the electronic effect of the initially coordinated CO ligand to the ruthenium center of the complex **5-41**, which might force the rearrangement of ligands through pseudorotation at the metal center.



Scheme 5.18 Metathesis Activity of CO-Bound Octahedral Complex and Sulfonamide-Chelates

Next, the metathesis activity of CO-bound octahedral complexes with dimethyl-2,2-diallylmalonate was tested at 40 °C in CH_2Cl_2 or 100 °C in toluene (**Scheme 5.18**). However, as expected, complexes **5-42a** and **5-42c** are devoid of metathesis activity because of their coordinatively saturated environment, which would not allow either associative nor dissociate ligand-substrate exchange with alkene substrates. On the other hand, sulfonamide-bound octahedral complex precursor **5-41a** is metathesis-active. Upon treating dimethyl-2,2-diallylmalonate with **5-41a** (5 mol %) in toluene-d_8 at 80 °C, the corresponding RCM product

was obtained in 78% yield (95% conversion) after 10 h, but at 45 °C in $CDCl_3$, only around 10 % conversion was observed after 24 h.

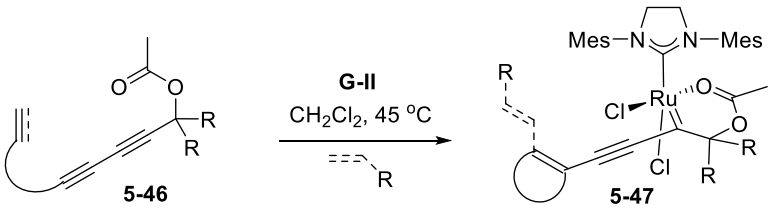


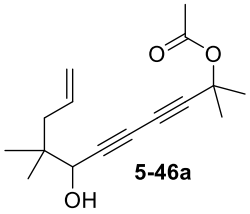
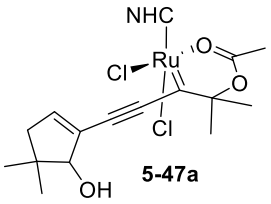
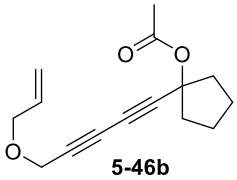
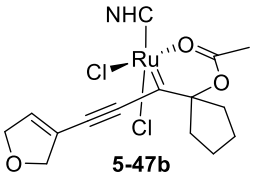
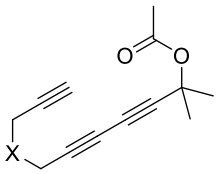
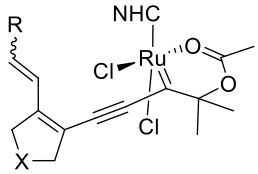
Scheme 5.19 RCM of Sulfonamide-Tethered 1,6-Enynes

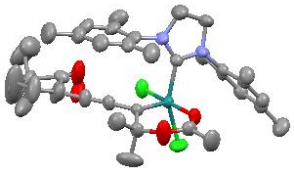
Next, we explore the formation of 6-membered sulfonamide chelates and their ligand disposition. Grela and coworkers have demonstrated that the chelated oxygen of the 6-membered sulfone and sulfonamide maintain a trans relationship to the NHC (**Scheme 5.19**).[47] Based on these examples, we expected that the RCM of ynamide-tethered 1,6-enyne **5-43a,b** would undergo ring-closure to form either *trans*-**5-44a,b** or *cis*-**5-44a,b**. Although C–C–N–S of **5-44a,b** connecting the metal center and a chelated oxygen is different

from C–C–C–S of **Ru-13** or **Ru-14**, the overall ligand disposition of these complexes are expected to be similar. To our surprise, however, ynamide **5-43a** upon treating with stoichiometric **G-II** provided only metathesis product **5-45a** instead of either sulfonamide chelate *trans*-**5-44a** or *cis*-**5-44a**. From the reaction of **5-43b**, under otherwise identical conditions, only acetate-chelated *cis*-complex **5-44b′** was obtained in 91% yield without forming the expected *trans*-**5-44b** or *cis*-**5-44b**. The result from the reaction of **5-43a** and **5-43b** suggest that, as opposed to the 5-membered sulfonamide chelates, the corresponding 6-membered chelates **5-44a** and **5-44b** should be relatively unfavorable, thus favorably generating **5-45a** and **5-44b′**, respectively. The ligand environment of the formed acetate-chelated complex **5-44b′** was further confirmed by single crystal X-ray diffraction analysis.

The formation of these 5- and 6-membered sulfonamide chelates of ruthenium alkylidenes prompted us to further explore carbonyl-based sp^2-oxygen chelates. To facilitate the delivery of the ruthenium alkylidene moiety near the chelating acetate functionality, we first employed a ring-closing metathesis strategy rather than cross metathesis with substrates 1,3-diynes **5-46a**–**5-46d** (**Table 5.2**). Upon treatment of 1,3-diynyl propargylic acetates **5-46a** a containing hydroxyl group with a stoichiometric amount of **G-II**, the corresponding acetate-chelated complex **5-47a** was formed in 86% yield (entry 1). The cis relationship between the NHC and the chelated oxygen of the acetate in complex **5-47a** is evident in its X-ray structure. Enediyne of cyclopentyl propargylic acetate **5-46b** with a stoichiometric amount of **G-II** complex generated acetate chelate **5-47b** only in 45% (entry). The low yield of **5-47b** is the consequence of its turn over to the final metathesis product (13%). Propargyl-sulfonamide tethered diyne propargyl acetate **5-46c** with **G-II** in the presence of 1-octene undergoes cross metathesis with propagyl sulfonamide followed by enyne RCM and metallotropic [1.3]-shift afforded acetate chelated complex **5-47c** in good yield (85%, entry 3). For triynyl propargylic acetate **5-46d**, its cross metathesis with styrene and 1-octene followed by metallotropic [1,3]-shift provided chelates **5-47d**, and **5-47d′** in 78% and 81% yield, respectively (entries 4 and 5).



entry	enediyne	acetate-chelates	yield (%)
1			86%
2			45%
			
3	**5-46c**, X = NTs	**5-47c**, R = C_6H_{13} (*E*/*Z* = 3.5 : 1)	85%
4	**5-46d**, X = $C(CO_2Me)_2$	**5-47d**, R = C_6H_{13} (*E*/*Z* = 4.1 : 1)	78%
5	**5-46d**, X = $C(CO_2Me)_2$	**5-47d'**, R = Ph (*E*/*Z* = 6.3 : 1)	81%

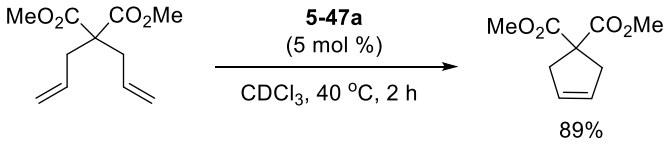


X-ray structure of **5-47a**

Table 5.2 Acetate-Chelated Ruthenium Alkylidene Complexes

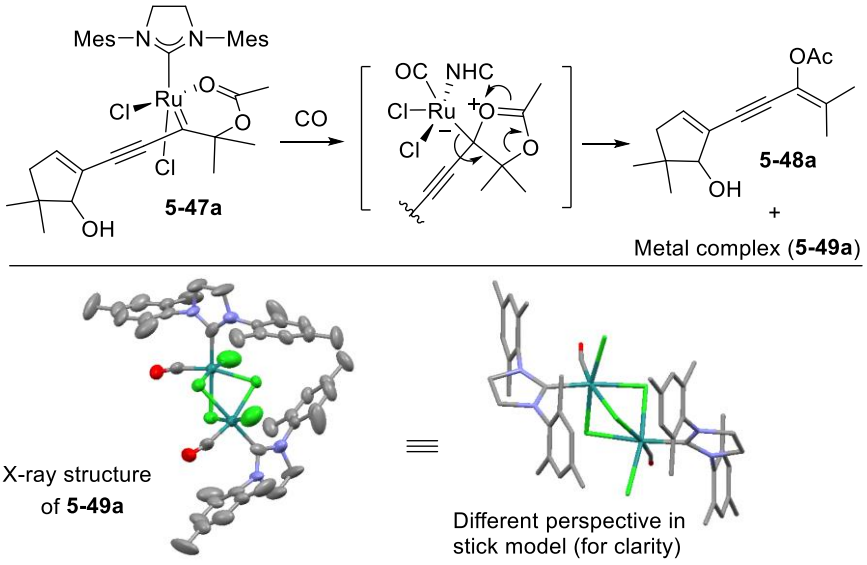
These results suggest that the subtle steric and electronic influence of the substituent on the carbenic carbon is critical for the formation of these chelates. The corresponding substrates devoid of a *gem*-dialkyl substituent at the propargylic carbon did not form chelates. Compared to Fürstner's and Slugovc's trans chelates containing either a vinyl group or a proton, the formation of 6-membered cis chelates is primarily due to the presence of an alkynyl group at the carbenic carbon. For **5-47a**–**5-67d** and **5-47d′** to form trans

chelates, 90° rotation of the Ru=C axis is required, which will bring the linear alkynly group to the same space where one of the mesityl groups. Metathesis activity of this acetate-chelate **5-47a** was tested with dimethyl-2,2-diallylmalonate; RCM of dimethyl-2,2-diallylmalonate catalyzed by **5-47a** (5 mol %) provided the corresponding ring-closed product in 89% within 2 h (**Scheme 5.20**).



Scheme 5.20 Metathesis Activity of Acetate-Chelate

The complexation behavior of these acetate-chelated ruthenium alkylidenes toward carbon monoxide was found to be different from that of sulfonamide chelates. Upon exposure of a green colored CH_2Cl_2 solution of **5-47a** to carbon monoxide, the solution became colorless as opposed to pink with sulfonamide chelates. Characterization of the newly formed material shows that CO-promoted decomplexation of **5-47a** to generate vinyl acetates **5-48a** and CO-bound C_2-symmetrical dimeric ruthenium complex[57] **5-49a** in quantitative yield (**Scheme 5.21**). The structure of **5-49a** was further confirmed by single X-ray



Scheme 5.21 CO-Binding to a 6-Membered Acetate-Chelate Promote Acetate Migration with Concurrent Ru=C Cleavage

crystallography. Regarding this transformation, we propose that the CO-coordination would decrease the electron density from the carbenic carbon because of the strong π-acceptor capacity of CO, which promotes the acetate to rearrange with concurrent cleavage of Ru=C bond.

5.5. Summary

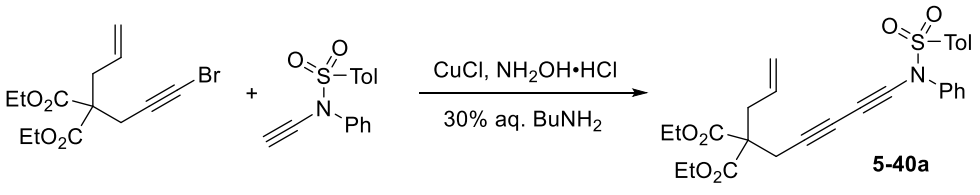
In summary, novel sulfonamide- and acetate-chelated ruthenium alkylidene complexes were synthesized from appropriately functionalized enediynes via ring-closing metathesis. In all 5-membered sulfonamide- and 6-membered acetate-chelated complexes prepared in this study, the sulfonamide and acetate moieties are disposed in a cis relationship relative to the NHC ligands. Upon exposure to carbon monoxide, the sulfonamide chelates generated a CO-bound octahedral ruthenium alkylidene complex where the alkylidene carbene moiety and the NHC ligand maintain a trans relationship. This is the first example of Grubbs-type ruthenium alkylidenes to have this unique trans geometry. On the other hand, under the same conditions, the corresponding acetate chelate decomposed to generate a vinyl acetate as pure organic product concurrently with a dimeric ruthenium CO-complex. The CO-bound octahedral ruthenium alkylidenes are metathesis inactive because the ligand environment of the ruthenium center is completely locked, which does not allow ligand-substrate exchange.

5.6. Experimental Details

5.6.1. General Information: Reactions were carried out in oven or flame-dried glassware unless otherwise noted. Compounds were purchased from Aldrich or Acros or TCI America or Oakwood or GFS or Strem chemicals unless otherwise noted. Dichloromethane (DCM) were distilled over calcium hydride (CaH_2) under nitrogen atmosphere. Flash chromatography was performed using silica gel 60 Å (32−63 mesh) purchased from Silicycle Inc. Analytical thin layer chromatography (TLC) was performed on 0.25 mm E. Merck precoated silica gel 60 (particle size 0.040−0.063 mm). Yields refer to chromatographically and spectroscopically pure compounds unless otherwise stated. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-500 spectrometer. Multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), qn (quintet), sext (sextet), m (multiplet), b (broad), and app (apparent). 1H NMR signals that fall

within a ca. 0.3 ppm range are generally reported as a multiplet, with a single chemical shift value corresponding to the center of the peak. Coupling constants, *J*, are reported in Hz (Hertz). Electrospray ionization (ESI) mass spectra were recorded on a Waters Micromass Q-Tof Ultima in the University of Illinois at Urbana-Champaign. Electron impact (EI) mass spectra and Chemical Ionization (CI) mass spectra were obtained using a Micromass 70-VSE in the University of Illinois at Urbana–Champaign. Single-crystal X-ray diffraction (XRD) studies were performed using a Bruker SMART X2S benchtop diffractometer fitted with a Oxford Cryostreams Desktop Cooler. Solution and refinement was accomplished with the SHELXTL suite of programs, using standard methods.

5.6.2. General Procedure for Starting Material Preparation: Cuprous chloride (7.3 mg, 0.074 mmol) was added to an aqueous solution of n-$BuNH_2$ (30%, 6 mL) at 0 ºC. A few crystals of hydroxylamine hydrochloride were added to discharge the blue color. A solution of *N*-phenyl *p*-toluensulfonylynamide (200 mg, 0.74 mmol) in CH_2Cl_2 (2 mL) was added to the solution, upon which the color of the solution became yellow. Bromoalky diethyl 2-allyl-2-(3-bromoprop-2-yn-1-yl)malonate (285 mg, 0.90 mmol) in CH_2Cl_2 (15 mL) was added dropwise to this solution for 15 min under nitrogen purging. During the addition, a small amount of hydroxylamine hydrochloride was added occasionally to keep the color of the reaction light yellow. After the addition of the bromoalkyne, the reaction was stirred while warming up to room temperature over 20 min and then quenched with water (10 mL). The organic layer was separated and the aqueous layer was further extracted with CH_2Cl_2 (10 mL x 3). The combined organic layers were dried over anhydrous Mg_2SO_4, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography (SiO_2, hexane: EtOAc = 3 : 2), affording enediyne **5-40a** (259 mg, 69 %).

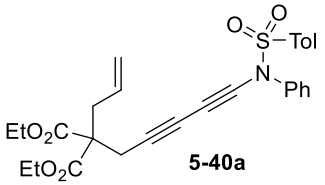


5.6.3. General Procedure for Metal Complex Formation: Compound **5-40a** (36 mg, 0.071 mmol) and Grubbs second generation complex (55 mg, 0.065 mmol) was dissolved in CH_2Cl_2 (6 mL) in an air-free

sealed tube and heated up to 45 °C over 3 h. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (SiO_2, hexane: EtOAc : CH_2Cl_2 = 1 : 2 : 1) to afford **5-41a** (49.3 mg, 78%) as a green solid.

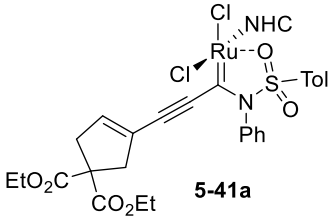
General Procedure for Carbon Monoxide Complexes: Compound **5-41a** (10 mg, 0.010 mmol) in CH_2Cl_2 (5 mL) was subjected to carbon monoxide ballon and stirred for 15 minutes at room temperature. The reaction mixture filtered through a short pad of silica using EtOAc/CH_2Cl_2 (1:1) and concentred to afford **5-42a** as a pink solid.

5.6.4. Selected Characterization Data



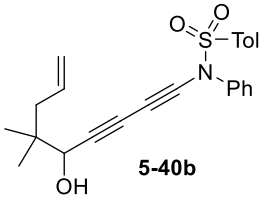
5-40a

Characterization data of 5-40a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (d, ^3J = 8.3Hz, 2H), 7.29−7.25 (m, 5H), 7.16−7.15 (m, 2H), 5.64−5.55 (m, 1H), 5.17−5.09 (m, 2H), 4.18 (q, J = 7.1 Hz, 4H), 2.91 (s, 2H), 2.76 (d, ^3J = 7.4 Hz, 2H), 2.41 (s, 3H), 1.22 (t, ^3J = 7.1 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.49 (CO_2Et), 145.41, 137.99, 132.91, 131.64, 129.74, 129.27, 128.72, 128.15, 126.37, 120.04, 78.59, 68.52, 67.26, 61.81, 57.82, 56.80, 36.69, 23.87, 21.74, 14.10; HRMS (ESI) calcd for $C_{28}H_{30}NO_6S$ $[M+H]^+$ 508.1794 found, 508.1793.



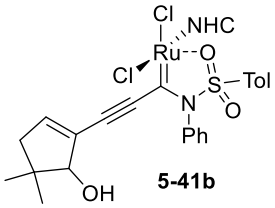
5-41a

Characterization data of 5-41a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, ^3J = 8.1 Hz, 2H), 7.25−7.23 (m, 2H), 7.12−7.08 (m, 5H), 7.01−7.00 (m, 2H), 6.22 (bs, 2H), 6.63 (s, 1H), 5.66 (s, 1H), 4.37−4.14 (m, 8H), 2.90−2.64 (m, 7H), 2.49 (s, 3H), 2.42 (s, 3H), 2.35 (s, 3H), 2.33 (s, 3H), 2.28 (s, 3H), 2.13 (s, 3H), 1.24−1.21 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 225.06 (Ru=CN), 214.29 (Ru=C(N)C), 171.37 (CCO_2Et), 171.31 (CCO_2Et), 146.11, 140.50, 140.06, 139.59, 138.37, 137.96, 137.21, 136.38, 136.19, 135.57, 130.69, 130.59, 130.18, 130.05, 129.93, 129.79, 129.69, 129.36, 129.16, 128.17, 124.14, 111.40, 96.86, 61.83, 58.71, 52.40, 51.11, 42.22, 42.03, 21.80, 21.46, 20.94, 20.14, 19.45, 18.89, 18.40, 14.07; HRMS (ESI) calcd for $C_{49}H_{50}Cl_2N_3O_7SRu$ [M+CO−3H]+ 996.1790 found, 996.2591.



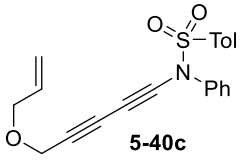
5-40b

Characterization data of 5-40b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.58 (d, ^{3}J = 8.2 Hz, 2H), 7.33−7.26 (m, 5H), 7.21−7.19 (m, 2H), 5.85−5.78 (m, 1H), 5.10−5.07 (m, 2H), 4.18 (d, ^{3}J = 5.5 Hz, 1H), 2.44 (s, 3H), 2.19−2.09 (m, 2H), 1.94 (d, ^{2}J = 5.7 Hz), 0.98 (s, 3H), 0.97 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.46, 137.94, 134.64, 132.98, 129.78, 129.33, 128.79, 128.20, 126.42, 118.04, 82.28, 71.22, 70.89, 70.33, 57.30, 42.78, 39.24, 22.77, 22.64, 21.77; HRMS (ESI) calcd for $C_{24}H_{26}NO_3S$ $[M+H]^+$ 408.1633 found, 408.1634.



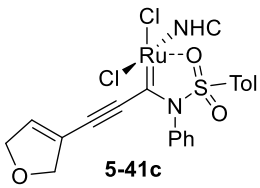
5-41b

Characterization data of 4-41b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.00−7.96 (m, 2H), 7.14−7.01 (m, 10H), 6.87−6.81 (m, 1H), 6.67− 6.61 (s, 1H), 5.75−5.66 (s, 1H), 4.38−4.11 (m, 5H), 3.09 (s, 1H), 2.69−2.14 (m, 23H), 1.08−0.92 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 225.86 (Ru=CN), 225.29 (Ru=CN), 214.11 (Ru=C(N)C), 213.95 (Ru=C(N)C), 146.15, 145.02, 140.59, 140.53, 140.26, 140.09, 139.55, 139.19, 138.32, 138.23, 138.05, 137.81, 137.44, 137.06, 136.39, 136.34, 136.26, 135.61, 135.55, 130.68, 130.60, 130.55, 130.10, 129.95, 129.89, 129.69, 129.46, 129.43, 129.23, 129.09, 128.34, 128.16, 116.10, 115.95, 97.55, 97.44, 83.64 (HC─OH), 52.35, 52.30, 51.19, 47.43, 47.34, 42.56, 27.74, 27.54, 26.42, 22.39, 22.16, 21.79, 21.45, 21.03, 20.98, 20.14, 19.47, 19.07, 18.93, 18.37; HRMS (ESI) calcd for $C_{44}H_{49}Cl_1N_3O_3SRu$ $[M-Cl]^+$ 836.2227 found, 836.2266.



5-40c

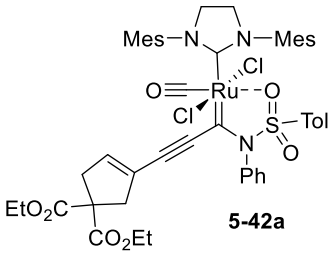
Characterization data of 5-40c: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.57 (d, ^{3}J = 8.3 Hz, 2H), 7.32−7.31 (m, 3H), 7.28 (d, ^{3}J =8.2 Hz, 2H), 7.20−7.18 (m, 2H), 5.92−5.84 (m, 1H), 5.30 (dd, ^{3}J = 1.5 Hz, ^{3}J = 17.2 Hz, 1H), 5.21 (dd, ^{3}J = 1.1 Hz, ^{3}J = 10.4 Hz, 1H), 4.25 (s, 2H), 4.05 (d, ^{3}J = 5.7 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.53, 137.92, 133.80, 132.94, 129.80, 129.34, 128.81, 128.17, 126.33, 118.10, 79.12, 71.19, 70.79, 70.58, 57.90, 57.48, 21.77; HRMS (ESI) calcd for $C_{21}H_{20}NO_3S$ $[M+H]^+$ 366.1164 found, 366.1155.



5-41c

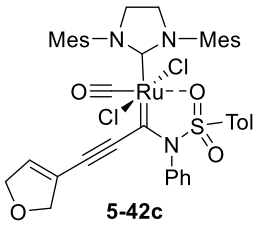
Characterization data of 5-41c: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, ^{3}J = 8.2 Hz, 2H), 7.27−7.24 (m, 1H), 7.12−7.09 (m, 5H), 7.04 (s, 1H), 7.00 (s, 1H), 6.79 (s, 1H), 6.78 (s, 1H), 6.63 (s, 1H), 6.07 (s, 1H), 4.36−4.16 (m, 8H), 2.64 (s, 3H),

2.49 (s, 3H), 2.42 (s, 3H), 2.35 (s, 3H), 2.33 (s, 3H), 2.29 (s, 3H), 2.17 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 224.49 (Ru=CN), 214.07 (Ru=C(N)C), 146.20, 140.57, 140.06, 139.48, 138.29, 137.92, 137.23, 136.42, 135.62, 133.83, 130.70, 130.61, 130.06, 129.95, 129.89, 129.71, 129.46, 129.24, 128.19, 123.30, 106.51, 98.74, 77.01, 75.39, 52.43, 51.14, 21.78, 21.44, 21.03, 20.13, 19.44, 18.86, 18.36; HRMS (ESI) calcd for $C_{42}H_{40}S_1Cl_2O_4N_3Ru$ $[M+CO-3H]^+$ 854.1155 found, 854.1961.



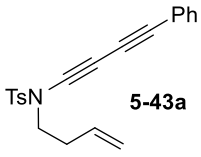
5-42a

Characterization data of 5-42a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, ^3J = 7.6 Hz, 2H), 7.32−6.91 (m, 11H), 5.85 (s, 1H), 4.13−4.05 (m, 8H), 2.89 (s, 2H), 2.76 (s, 2H), 2.55−2.24 (m, 21H), 1.19 (t, ^3J = 6.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 264.50 (Ru=CN), 213.12 (Ru=C(N)C), 198.86 (RuC≡O), 170.97 (CCO_2Et), 146.77, 143.21, 138.35, 137.68, 131.98, 131.08, 130.05, 129.63, 129.39, 122.52, 93.82, 61.89, 58.78, 51.89, 42.22, 41.91, 21.93, 19.03, 18.99, 13.98; HRMS (ESI) calcd for $C_{49}H_{50}Cl_2N_3O_7SRu$ $[M-3H]^+$ 996.1785 found, 996.2591.



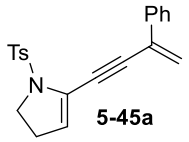
5-42c

Characterization data of 5-42c: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 (d, ^3J = 7.8 Hz, 2H), 7.33−6.86 (m, 11H), 6.12 (s, 1H), 4.52 (s, 2H), 4.19 (s, 2H), 4.06 (s, 3H), 3.84 (s, 1H), 2.56 (s, 6H), 2.52 (s, 6H), 2.44 (s, 3H), 2.31−2.25 (m, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 264.53 (Ru=CN), 212.73 (Ru=C(N)C), 198.83 (RuC≡O), 146.99, 139.50, 137.64, 131.11, 130.21, 129.83, 129.72, 129.27, 121.74, 121.59, 96.14, 76.80, 75.63, 51.94, 51.88, 21.98, 19.02, 18.89; HRMS (ESI) calcd for $C_{42}H_{40}S_1Cl_2O_4N_3Ru$ $[M-3H]^+$ 854.1155 found, 854.1961.



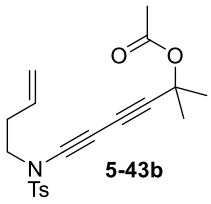
5-43a

Characterization data of 5-43a: ; ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, ^3J = 8.3 Hz, 2H), 7.75−7.73 (m, 2H), 7.40−7.28 (m, 5H), 6.05 (s, 1H), 5.82 (s, 1H), 5.62 (t, ^3J = 3.1 Hz, 1H), 3.81 (t, ^3J = 9.0 Hz, 2H), 2.47−2.42 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.81, 136.50, 133.92, 130.15, 129.60, 128.51, 128.14, 126.21, 125.42, 122.38, 122.07, 93.54, 81.42, 49.52, 29.74, 28.44, 21.60; HRMS (ESI) calcd for $C_{21}H_{20}NO_2S$ $[M+H]^+$ 350.1215 found, 350.1213.



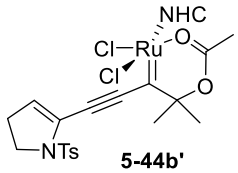
5-45a

Characterization data of 5-45a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, ^{3}J = 8.3 Hz, 2H), 7.75−7.73 (m, 2H), 7.40−7.28 (m, 5H), 6.05 (s, 1H), 5.82 (s, 1H), 5.62 (t, ^{3}J = 3.1 Hz, 1H), 3.81 (t, ^{3}J = 9.0 Hz, 2H), 2.47−2.42 (m, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.81, 136.50, 133.92, 130.15, 129.60, 128.51, 128.14, 126.21, 125.42, 122.38, 122.07, 93.54, 81.42, 49.52, 29.74, 28.44, 21.60; HRMS (ESI) calcd for $C_{21}H_{20}NO_2S$ $[M+H]^+$ 350.1215 found, 350.1213.



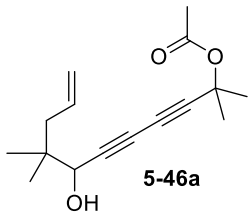
5-43b

Characterization data of 5-43b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, J = 8.3 Hz), 7.34 (d, J = 8.1 Hz, 2H), 5.67−5.60 (m, 1H), 5.06 (dd, J = 1.4 Hz, 17.1 Hz, 1H), 5.02 (d, J = 10.3 Hz, 1H), 3.35 (t, J = 7.4 Hz, 2H), 2.44 (s, 3H), 2.37−2.32 (m, 2H), 2.00 (s, 3H), 1.65 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.29 (O=C(Me)O), 145.10, 134.61, 133.17, 130.01, 127.58, 118.07, 82.68, 72.09, 71.62, 68.75, 58.10, 50.91, 32.19, 28.79, 21.84, 21.70; HRMS (ESI) calcd for $C_{20}H_{24}NO_4S$ $[M+H]^+$ 374.1426 found, 374.1420.



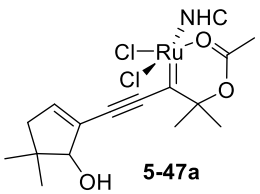
5-44b'

Characterization data of 5-44b′: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 (d, ^{3}J = 8.1 Hz, 2H), 7.27 (d, ^{3}J = 7.3 Hz, 2H), 7.12 (bs, 1H), 7.06 (bs, 1H), 6.89 (bs, 2H), 6.20 (t, ^{3}J = 3.1 Hz, 1H), 4.36 (bs, 1H), 4.12−4.10 (m, 2H), 3.98 (bs, 1H), 3.92−3.87 (m, 1H), 3.52−3.46 (m, 1H), 2.70 (s, 3H), 2.43 (s, 3H), 2.35 (s, 9H), 2.27 (s, 3H), 2.18 (s, 3H), 1.93 (s, 3H), 1.53 (s, 3H), 1.49 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 260.71 (Ru=CN), 214.74 (Ru=C(C)C), 179.81 (RuO=C(Me)O), 143.87, 132.90, 130.82, 129.90, 129.78, 129.38, 129.24, 127.93, 126.80, 114.99, 111.92, 98.96, 52.18, 51.27, 49.20, 30.45, 25.03, 24.91, 23.17, 21.56; HRMS (ESI) calcd for $C_{40}H_{47}Cl_1N_3O_4RuS$ $[M-Cl]^+$ 802.2026 found, 802.2016.



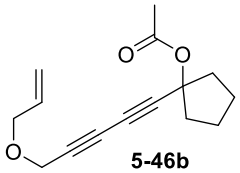
5-46a

Characterization data of 5-46a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.83−5.75 (m, 1H), 5.07−5.04 (m, 2H), 4.11 (s, 1H), 2.16 2.16−2.12 (m, 2H), 2.08−2.04 (m, 1H), 2.00 (s, 3H), 1.64 (s, 6H), 0.95 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.31 (O=C(Me)O), 134.57, 117.99, 80.01, 79.43, 71.79, 70.56, 70.14, 68.50, 42.67, 39.11, 28.69, 22.68, 22.53, 21.77; HRMS (ESI) calcd for $C_{16}H_{22}O_3Na$ $[M+Na]^+$ 285.1467 found, 285.1463.



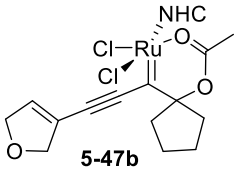
5-47a

Characterization data of 5-47a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (bs, 2H), 6.84−6.76 (m, 2H), 6.15 and 6.11 (s, 1H), 4.56 and 4.42 (s, 1H), 4.12−3.85 (m, 4H), 3.84 and 3.63 (s, 1H), 2.64−2.61 (m, 2H), 2.35−2.16 (m, 15H), 1.86−1.66 (m, 3H), 1.42−0.98 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 262.52 (Ru=CN), 261.93 (Ru=CN), 214.12 (Ru=C(C)C), 214.04 (Ru=C(C)C), 179.99 (RuO=C(Me)O), 140.63, 140.45, 139.54, 138.21, 138.04, 137.62, 135.47, 134.49, 133.31, 133.26, 133.12, 132.44, 130.69, 130.24, 129.33, 128.89, 123.11, 122.84, 110.24, 97.84, 97.60, 83.89, 83.67, 52.36, 51.34, 47.89, 47.83, 42.43, 27.96, 27.70, 27.03, 26.94, 26.41, 26.07, 25.36, 25.20, 25.02, 23.22, 22.63, 22.33, 21.31, 21.11, 20.50, 18.89, 17.49; HRMS (ESI) calcd for $C_{36}H_{46}ClN_2O_3Ru$ $[M-Cl]^+$ 691.2235 found, 691.2244.



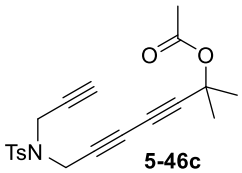
5-46b

Characterization data of 5-46b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.89−5.81 (m, 1H), 5.28 (dd, ^{3}J = 1.4 Hz, ^{3}J = 17.2 Hz, 1H), 5.19 (d, ^{3}J = 10.4 Hz, 1H), 4.19 (s, 2H), 4.03−4.02 (m, 2H), 2.15−2.14 (m, 4H), 2.00 (s, 3H), 1.73−1.71 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.41 (O=C(Me)O), 133.72, 118.06, 80.23, 78.98, 76.59, 70.69, 70.45, 68.90, 57.58, 40.35, 23.41, 21.55.



5-47b

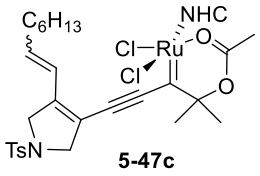
Characterization data of 5-47b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.97−6.88 (m, 4H), 6.42 (s, 1H), 4.77 (bs, 2H), 4.34 (bs, 2H), 4.12−4.08 (m, 4H), 2.30−2.27 (bm, 18H), 2.17 (s, 3H), 1.86−1.83 (m, 4H), 1.68−1.61 (m, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 260.59 (Ru=CN), 215.06 (Ru=C(C)C), 179.27 (RuO=C(Me)O), 135.18, 130.89, 129.73, 125.62, 114.76, 109.80, 108.60, 77.39, 75.68, 51.73, 38.77, 37.65, 29.69, 25.87, 24.03, 23.09, 21.08; HRMS (ESI) calcd for $C_{35}H_{42}Cl_1N_2O_3Ru$ $[M-Cl]^+$ 675.1934 found, 6751936.



5-46c

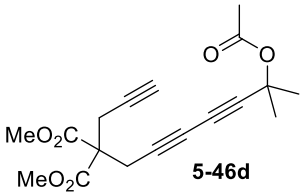
Characterization data of 5-46c: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, ^{3}J = 8.3 Hz, 2H), 7.29 (d, ^{3}J = 8.1 Hz), 4.20 (s, 2H), 4.08 (d, ^{3}J = 2.1 Hz, 2H), 2.40 (s, 3H), 2.16 (t, ^{3}J = 2.4 Hz, 1H), 1.99 (s, 3H), 1.60 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.07 (O=C(Me)O), 144.15, 134.82, 129.68, 127.88, 79.02, 76.04, 74.43, 72.87, 71.45, 69.84, 68.11,

36.93, 36.56, 28.64, 21.72, 21.57; HRMS (ESI) calcd for $C_{20}H_{21}NO_4NaS$ $[M+Na]^+$ 394.1089 found, 394.1085.



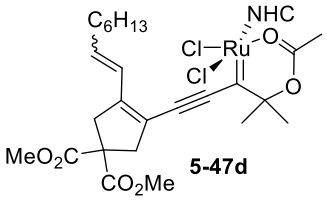
5-47c

Characterization data of 5-47c: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J = 8.1 Hz, 2H), 7.32 (d, ^3J = 8.1 Hz, 2H), 7.10−6.64 (m, 4H), 6.48−6.20 (m, 1H), 5.91−5.73 (m, 1H), 4.36−3.85 (m, 8H), 2.70 (bs, 2H), 2.40−2.01 (m, 21H),1.40−1.25 (m, 14H), 0.97−0.87 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 285.59 (Ru=CN), 214.29 (Ru=C(C)C), 179.68 (RuO=C(Me)O), 143.83, 138.97, 136.78, 133.59, 130.01, 127.56, 125.12, 118.45, 115.09, 114.43, 97.63, 57.09, 55.59, 55.43, 54.29, 52.32, 51.22, 33.69, 31.72, 28.96, 28.48, 25.51, 25.45, 23.15, 22.64, 21.59, 14.16.



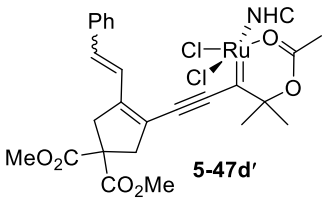
5-46d

Characterization data of 5-46d: ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.75 (s, 6H), 3.08 (s, 2H), 2.98 (d, ^3J = 2.6 Hz, 1H), 2.95 (d, ^3J = 2.5 Hz, 1H), 2.02 (s, 1H), 1.99 (s, 3H), 1.62 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.17 (O=C(Me)O), 168.77 (CCO_2Et), 78.14, 75.48, 72.03, 71.78, 71.73, 68.79, 67.63, 56.43, 53.28, 28.69, 23.60, 22.94, 22.68, 21.78; HRMS (ESI) calcd for $C_{18}H_{20}O_6K$ $[M+K]^+$ 371.0891 found, 371.0898.

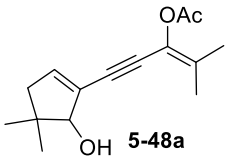


5-47d

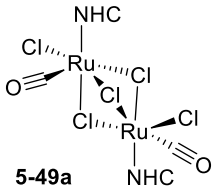
Characterization data of 5-47d: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.12 (s, 1H), 7.06 (s, 1H), 6.52 (s, 1H), 6.75 (s, 1H), 6.50 (d, ^3J = 15.8 Hz, 1H), 6.02─5.96 (m, 1H), 4.36─4.34 (m, 1H), 4.11─4.06 (m, 2H), 3.93─3.91 (m, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.54─3.43 (m, 2H), 2.78─2.73 (m, 5H), 2.41 (s, 3H), 2.35 (s, 3H), 2.25 (s, 3H), 2.22 (s, 3H), 2.18 (s, 6H), 2.04─2.01 (m, 2H), 1.89 (s, 3H), 1.48 (s, 3H), 1.45 (s, 3H), 1.31─1.27 (m, 8H), 0.91─0.88 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 259.82 (Ru=CN), 215.18 (Ru=C(C)C), 179.55 (RuO=C(Me)O), 172.21 (CCO_2Me), 172.11 (CCO_2Me), 142.57, 140.51, 139.77, 138.20, 137.53, 135.71, 135.57, 130.90, 130.54, 129.31, 128.83, 127.32, 121.02, 120.04, 114.38, 97.84, 57.65, 53.04, 52.33, 51.15, 43.00, 41.58, 33.74, 31.82, 29.08, 28.71, 25.81, 25.70, 23.18, 22.70, 21.37, 21.05, 20.57, 19.31, 18.80, 17.44, 14.21; HRMS (ESI) calcd for $C_{46}H_{60}Cl_1N_2O_6Ru$ $[M-Cl]^+$ 873.3193 found, 873.3195.



Characterization data of 5-47d′: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.74 (d, ^{3}J = 7.3 Hz, 2H), 7.59 (d, ^{3}J = 16.2 Hz, 1H), 7.32−7.25 (m, 2H), 7.09−6.86 (bm, 4H), 6.82 (d, ^{3}J = 16.2 Hz, 1H), 4.34−4.07 (m, 4H), 3.82 (s, 3H), 3.80 (s, 3H), 3.54−3.44 (m, 2H), 2.97−2.86 (m, 2H), 2.31 (bs, 18H), 2.19 (s, 3H), 1.51 (s, 3H), 1.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 259.19 (Ru=CN), 214.66 (Ru=C(C)C), 179.60 (RuO=C(Me)O), 172.13 (CCO_2Me), 171.86 (CCO_2Me), 144.63, 137.84, 132.20, 128.88, 128.73, 127.97, 127.73, 127.48, 126.41, 123.65, 118.89, 115.39, 97.89, 57.73, 53.15, 42.94, 41.37, 25.83, 25.66, 23.16, 27.17; HRMS (ESI) calcd for $C_{46}H_{52}Cl_1N_2O_6Ru$ $[M-Cl]^+$ 865.2567 found, 865.2551.



Characterization data of 5-48a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.14 (s, 1H), 4.19 (s, 1H), 2.17 (s, 3H), 1.94 (s, 3H), 1.83 (bm, 2H), 1.69 (s, 3H), 1.09 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 168.77, 137.57, 133.08, 126.77, 125.64, 88.82, 85.71, 84.98, 46.21, 42.37, 27.90, 22.24, 21.20, 20.78, 17.70; HRMS (ESI) calcd for $C_{15}H_{20}O_3Na$ $[M+Na]^+$ 271.1310 found, 271.1310.



Characterization data of 5-49a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.00 (s, 4H), 4.09 (s, 4H), 2.42 (s, 12 H), 2.33 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 206.64 (Ru=CN), 187.75 (RuC≡O), 184.14 (RuC≡O), 140.79, 139.44, 137.57, 51.42, 18.53; HRMS (ESI) calcd for $C_{44}H_{54}Cl_4N_4O_2Ru_2$ $[M-Cl+2H]^+$ 1014.1082 found, 1014.1406.

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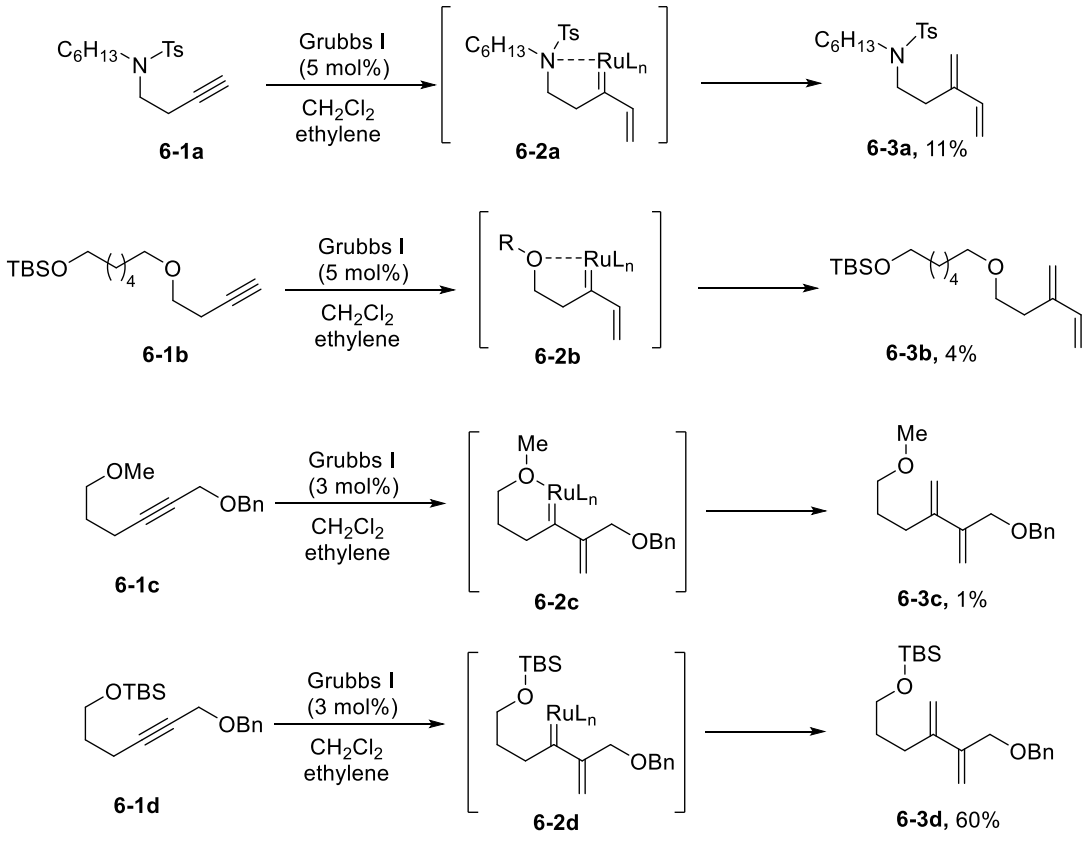
CHAPTER 6

STRUCTURE AND REACTIVITY OF HYDROXY- AND ETHER-CHELATED RUTHENIUM ALKYLIDENE COMPLEXES

6.1. Introduction

The coordination of an alkene or alkyne of a substrate to the unsaturated ruthenium metal center is required for the productive alkene and enyne metathesis catalyzed by Grubbs-type ruthenium alkylidene complexes. However, polar functional groups contains lone pair electrons near the reacting metal center occasionally occupy the coordination site more favorably over the substrate alkenes or alkynes such that the catalytic cycle is arrested at various resting states either temporarily or permanently. In the earlier developments of metathesis, it was found that, the involvement of lone pair to chelate with metal center was recognized as a potential problem.[1] In 1999, Mori and coworkers widely studied the cross metathesis of enynes, and they found that the alkynes having heteroatoms

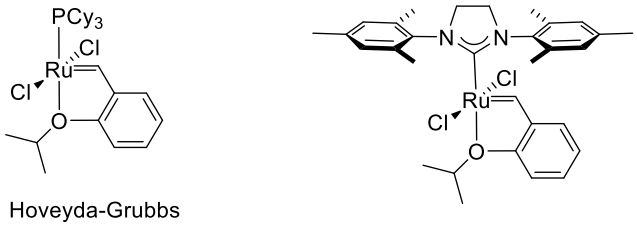


Scheme 6.1 Chelation Effect in Enyne Cross Metathesis

close to the reactive site was harmful and led to lower yields of expected products (**Scheme 6.1**).[2] For example, the reaction of homopropargyl sulfonamide **6-1a** with 5 mol% first-generation Grubbs catalyst

under ethylene provided cross metathesis product **6-3a** in 11% yield. Also, the homopropargyl ether tethered alkyne **6-1b** generated the cross metathesis product **6-3b** only in 4%. The low yields of these reactions can be rationalized by the involvement of the lone pairs on the substrates to chelate with the metal center to generate relatively stable **6-2a** and **6-2b**. Contrasting behavior of alkynes **6-1c** and **6-1d** having the methyl ether and silyl ether provided cross metathesis products **6-3c** were observed, which the former yielded, whereas the latter provided **6-3d** in 60% yield, respectively. This can be explained by strongest chelation of the methyl ether compared to that of silyl ether. However, there were only limited evidences for observed chelates of a heteroatom with a metal center. Therefore, it is important to understand the structure and dynamic properties of chelated ruthenium alkylidene complexes to design more effective catalysts and their substrates.

In this regard, known heteroatom-chelated ruthenium alkylidenes would provide important insight. The earliest and most important heteroatom-chelated ruthenium alkylidene is **HG-I**, discovered by Hoveyda and it involves oxygen-chelated alkylidene ligand with one phosphine (Figure 1).[3] Subsequently, a highly active and more stable oxygen-chelated *N*-heterocyclic ruthenium alkylidene **HG-II** was developed, which is commercially available as Hoveyda-Grubbs catalyst second-generation.[4] Thereafter, several heteroatom-chelated *N*-heterocyclic ruthenium alkylidenes were widely explored.[5]



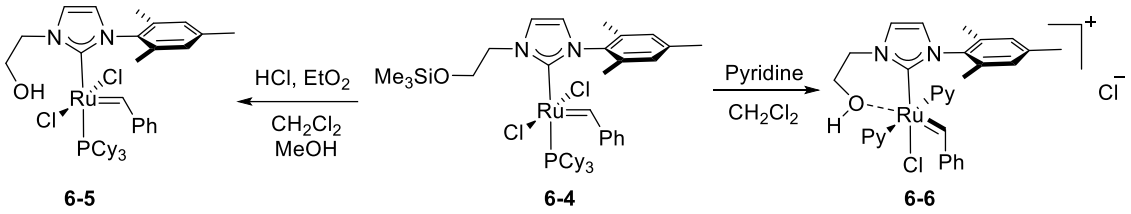
Hoveyda-Grubbs 1st generation **(HG-I)**

Hoveyda-Grubbs 2nd generation, **(HG-II)**

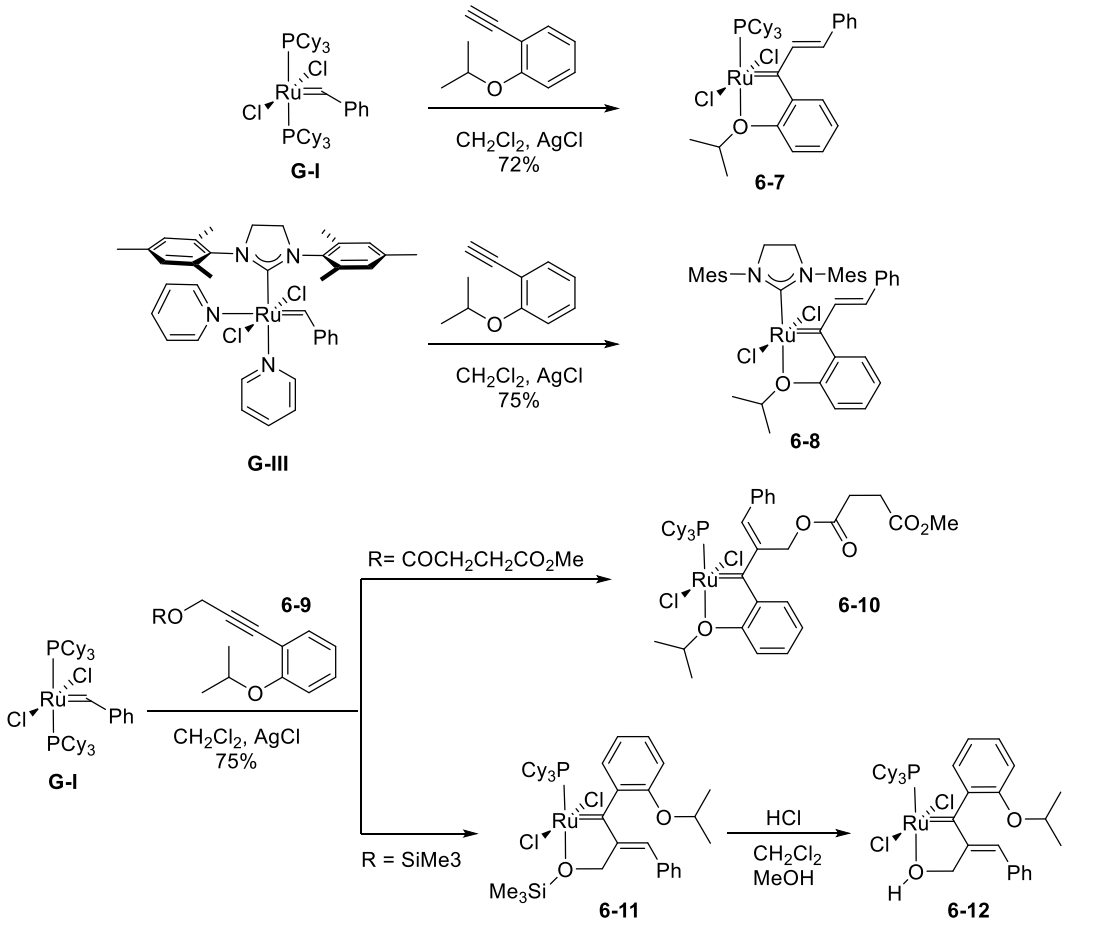
Figure 6.1 Hoveyda-Grubbs 1st and 2nd Generation Catalysts

Fürstner and coworkers first reported the hydroxy-chelated ruthenium alkylidine (**Scheme 6.2**).[6] Trimethylsilyl ether containing *N*-heterocyclic ruthenium alkylidene **6-4** was treated with ethereal solution

HCl to provide a free hydroxy ethyl-containing ruthenium alkylidene **6-5**. On the other hand, the same complex upon treating with pyridine generated a bench-stable hydroxy ethyl side chain chelated octahedral complex **6-6**. This is the first example of new type of Grubbs complex. However, this octahedral complex was found to be metathesis inactive due to the pyridine ligands that are tightly bound to the metal center, which is stable even upon adding *p*-TsOH.



Scheme 6.2 Intramolecular Chelation with Hydroxy-Alkyl Functionalities



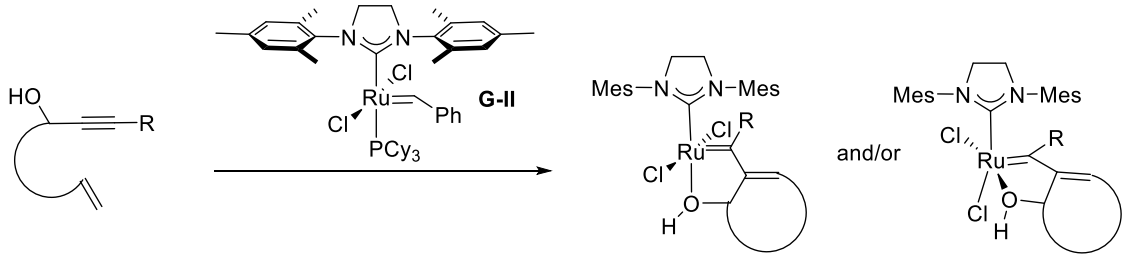
Scheme 6.3 Enyne Cross Metathesis to Form Ether- and Hydroxy-Chelated Ruthenium Alkylidenes

Based on this initial observation, they further studied the ether and hydroxy-chelation behaviors (**Scheme 6.3**).[7] They first tested the chelation behavior relying on enyne metathesis with the Grubbs first-generation and third-generation complexes (**G-I** and **G-III**). Cross metathesis of both complexes with 1-ethylene 2-*iso*-propoxybenzene afforded the Hoveyda type ether-chelated complexes **6-7** and **6-8**. Next, they examined the behavior of the internal alkyne **6-9** having a methyl succinate moiety and trimethlsilyl ether moiety with **G-I** complex. The reaction with methyl succinate derived propargyl ether favored the formation of complex **6-10**, whereas the latter delivered only silyl ether oxygen-chelated ruthenium alkylidene **6-11**. Deprotection of trimethyl silyl group from **6-11** with HCl provided hydroxy-chelated ruthenium alkylidene **6-12**. The metathesis activity of these complexes were tested and the best results were observed with the silyl ether oxygen-chelated complex **6-11**.

The hydroxy-chelated *N*-heterocyclic ruthenium alkylidene derivatives were synthesized by using second-generation Grubbs complexes except *N*-heterocyclic alkyl tethered hydroxy-chelated octahedral complex **6-6**. To generate other types of hydroxy-chelated ruthenium alkylidenes, which are structurally similar to the Hoveyda complexes, we plan on using enyne RCM of alkenyl tethered propargylic alcohols and Grubbs second-generation complex.

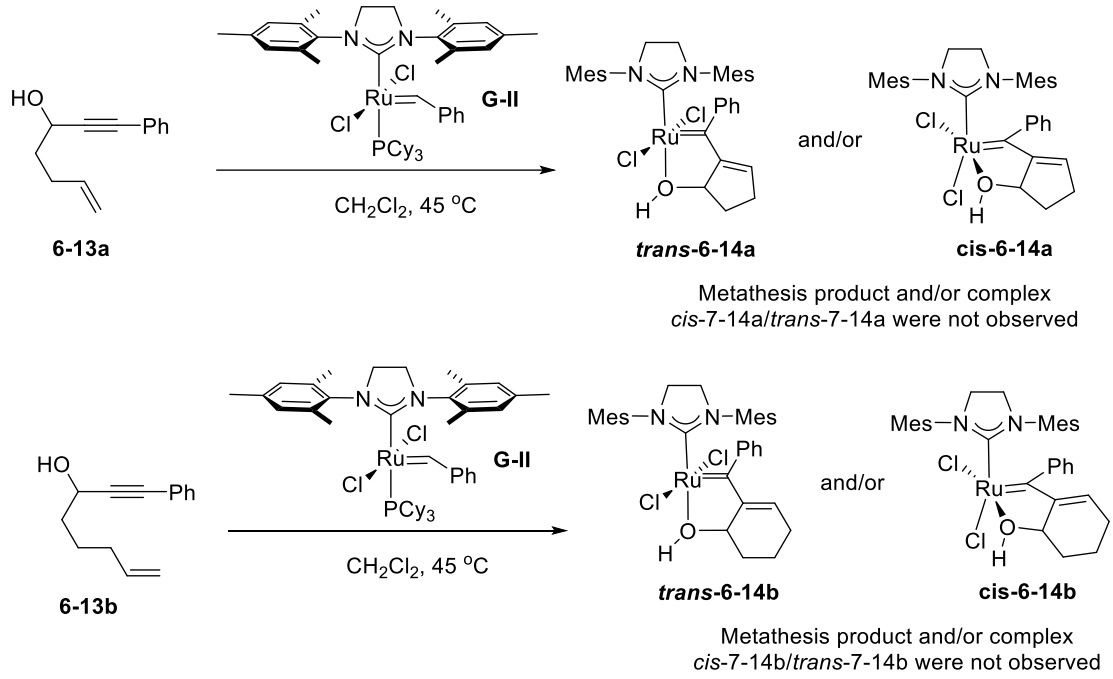
6.2. Results and Discussion

To gain further insight into the hydroxy- and ether-chelation behaviors of ruthenium alkylidenes, we plan to explore the factors that facilitate the chelate formation with the oxygen functionality in enyne ring-closing metathesis (**Scheme 6.4**). In this regard, we envisioned that the ring-closing metathesis (RCM) of



Scheme 6.4 Designing of Enyne RCM Substrates

enynes would be one of most effective method to allocate the ruthenium alkylidene moiety at an appropriate location such that the metal center and the installed chelating group would interact to form the expected oxygen-chelates. Toward this goal, we have designed several enynes such as **6-13a** and **6-13b** propagylic alcohol, and subjected to a typical enyne RCM conditions with a stoichiometric amount of **G-II** (**Scheme 6.5**).

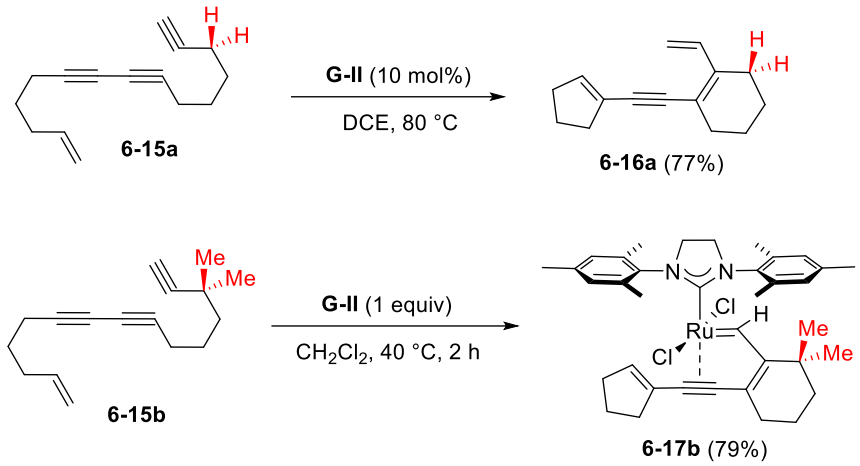


Scheme 6.5 Initial Attempts for Hydroxy-Chelated Ruthenium Alkylidene

First, 1,6-enyne **6-13a** was treated with a stoichiometric amount of **G-II** in CH_2Cl_2 at 45 °C, however, the expected chelate ***cis/trans*-6-14a**, nor the ring-closed product were not observed. We believe that the ring size of the chelates may play a crucial role for stability of the ruthenium alkylidene generated after the ring-closing metathesis of enyne. Thus, we have further tested 1,7-enyne **6-13b**, but neither trapped propagating alkylidene ***cis/trans*-6-14b** nor the ring-closed metathesis product was observed.

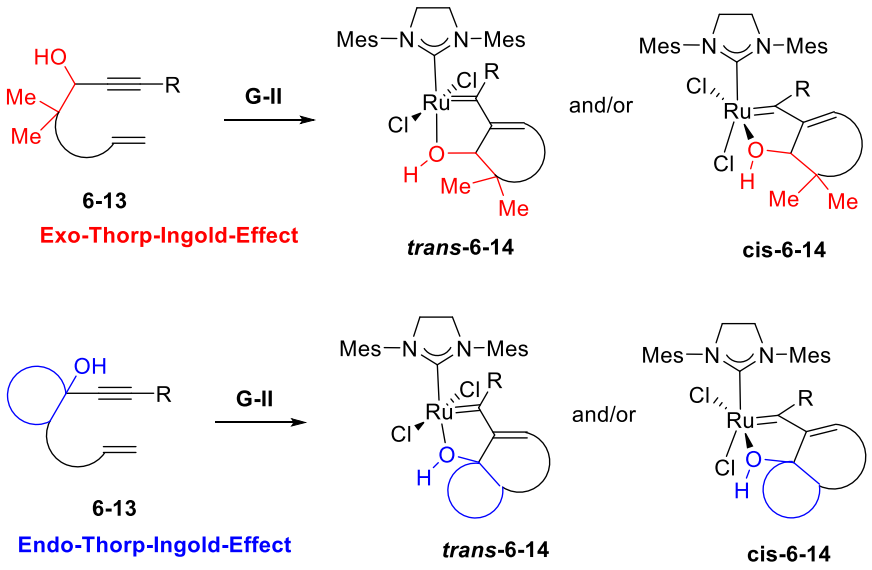
The negative results from 1,n-enynes **6-13a** and **6-13b** were assumed to be the consequence of lacking *gem*-dialkyl substituent, which is crucial for the formation of alkyne chelated ruthenium alkylidenes (**Scheme 6.6**). For example, the tandem enyne RCM of substrate **6-15a** having no *gem*-dialkyl substituent

provided only metathesis product 1,5,7-trienyne **6-16a** in 77% yield, whereas that of substrate **6-15b** having *gem*- dimethyl substituent delivered alkyne-chelated ruthenium alkylidene complex **6-17b** in 79% yield, without forming any metathesis product.[8]



Scheme 6.6 Effect of *gem*-Dialkyl Substituent in Alkyne-Chelated Ruthenium Alkylidenes

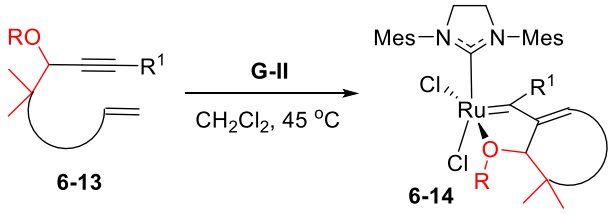
Based on the *gem*-dialkyl substituent effect in the formation of alkyne chelated ruthenium alkylidenes, we installed the *gem*-dialkyl substituents in alkenynol **6-13** (**Scheme 6.7**). due to presence of this gem-dialkyl substituent we expected that the Thorpe-Ingold effect-based control of not only the structural



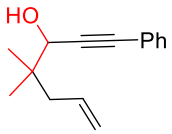
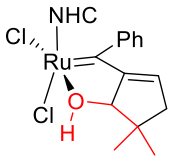
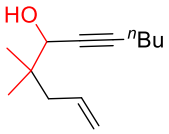
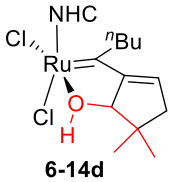
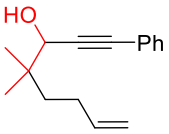
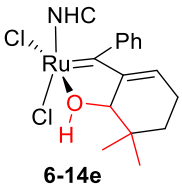
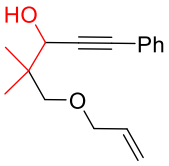
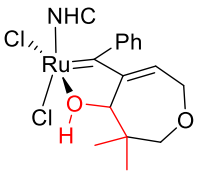
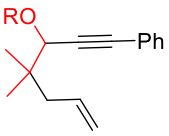
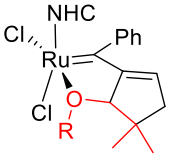
Scheme 6.7 Strategy for the Hydroxy-Chelated Ruthenium Alkylidenes

properties of trapped complexes stabilized by this structural elements. Compared to the traditional Thorp-Ingold effect of *gem*-dialkyl group for the RCM, the beneficial effect induced by this functionality can be defined as the exo-Thrope-Ingold effect because it exists outside of the ring system of the chelate.

In order to prove the validity of exo- and endo-Thorpe-Ingold effect to form oxygen-chelated ruthenium alkylidenes, 1,n-enynes containing propagylic alcohols and ethers **6-13c—6-13h** were treated with a stoichiometric amount of Grubbs second-generation complex (**G-II**) in CH_2Cl_2 at 45 °C (**Table 6.1**). Gratifyingly, 1,6-enyne **6-13c** reacted smoothly with **G-II** to afford hydroxy-chelated ruthenium alkalidene **6-14c** in 92% yield (entry 1). The spectroscopic characterization of the newly formed material clearly indicates the characteristics of structure **6-14c**. The cis relationship between the chelated oxygen and NHC was further confirmed by single X-ray diffraction analysis. The formation of complex **6-14c** further supports the importance of *gem*-dimethyl substituent effect because the corresponding structure **6-14a** could not be generated. The enyne **6-13d** containing a *n*-butyl substituent on the alkyne in **6-13c** instead of phenyl group, also reacted smoothly to generate 5-membered hydroxy-chelated complex **6-14d** in 84% yield (entry 2). 1,7-Enyne and 1,8-enyne **6-13d** and **6-13e**, also provided 5-membered hydroxy-chelated ruthenium alkylidenes **6-14d** and **6-14e** in 94% and 80% yield, respectively (entries 3 and 4). We further examined the behavior the 1,6-enynes **6-13f** and **6-13g** having methy propargyl ether and a trimethylsilyl propargyl ether, and both compounds smoothly underwent enyne ring-closing metathesis followed by chelate formation to provide 5-membered methyl ether and trimethyl silyl ether chelated ruthenium alkalidenes **6-14f** and **6-14g** in 86% and 92% yield, respectively (entries 5 and 6). These results are not only validate the exo-Thorp-Ingold effect in forming the oxygen-chelated ruthenium alkylidenes. Also, it is interesting note that all cis ruthenium alkalidene chelates obtained in the current study shows a cis relationship between the NHC ligand and the oxygen chelated moiety. The ligand disposition around the metal center of hydoxy-chelated ruthenium alkalidenes **6-14d** and **6-14e** were further confirmed by single crystal X-ray diffraction analysis (**Figure 6.2**).



6-13 **6-14**

entry	enyne	Product	yield (%)[a]
1	 **6-13c**	 **6-14c**	92
2	 **6-13d**	 **6-14d**	84
3	 **6-13e**	 **6-14e**	94
4	 **6-13f**	 **6-14f**	80
5	 **6-13g**; R = Me	 **6-14g**	86
6	**6-13h**; R = $SiMe_3$	**6-14h**	92

[a] Isolated yield after purification

Table 6.1 Formation of Hydroxy- and Ether-Chelated Ruthenium Alkylidenes by Relying on Exo-Thorp-Ingold-Effect

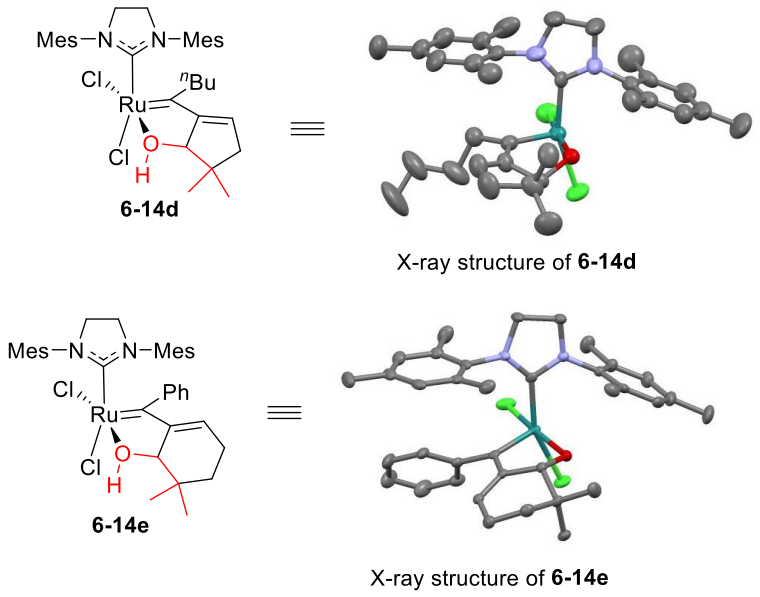
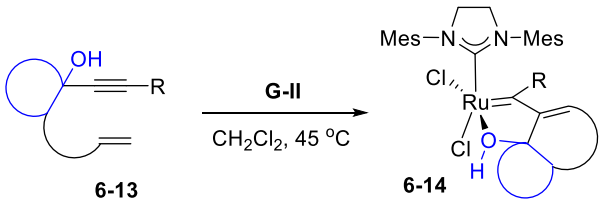
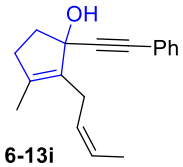
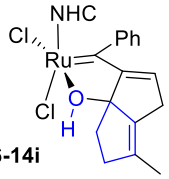
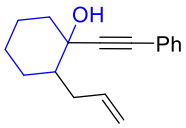
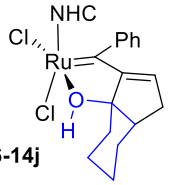
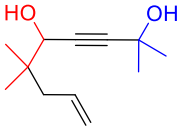
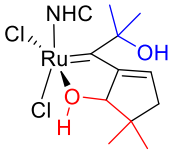


Figure 6.2 X-ray Structures of 6-14d and 6-14e

After successful formation of hydroxy- and ether-chelates putatively promoted by the exo-Thorp-Ingold effect, we next studied the endo-Thrope-Ingold effect with 1,6-enynes under the same reaction condition (**Table 6.2**). 1,6-Enynes **6-13i** and **6-13j** derived from jasmone and 2-allylcyclohexanone were subjected to a stoichiometric amount of **G-II**. Both enynes reacted smoothly to deliver 5-membered alcohol-chelated ruthenium alkylidenes **6-14i** and **6-14j** in 91% and 90% yield, respectively (entries 1 and 2). Based on these results, we conclude that the endo-*gem*-dialkyl substituent also plays an important role for chelation. 1,5-Enyne **6-13k** having two dimethyl substituents, underwent enyne RCM to generate 5-memmbered hydroxy-chelated ruthenium alkalidene **6-14k**, in 82% yield without forming a 4-membered hydroxy-chelated ruthenium alkalidene (entry 3).

After demonstrating that enynes **6-13c—6-13k** form oxygen-chelates successfully, we next examined the behavior of the enynes having two possible chelating elements to form 5-membered and/or 6-membered chelates (**Scheme 6.8**). Enyne **6-13l** having the possibility to form 5-membered exo-cyclic hydroxy-chelate **6-14l** and/or 6-membered endo-cyclic **6-14l′** was converted exclusively to enyne RCM product **6-18l** without forming any chelated ruthenium alkylidene. On the other hand, enyne **6-13m**, upon treating with



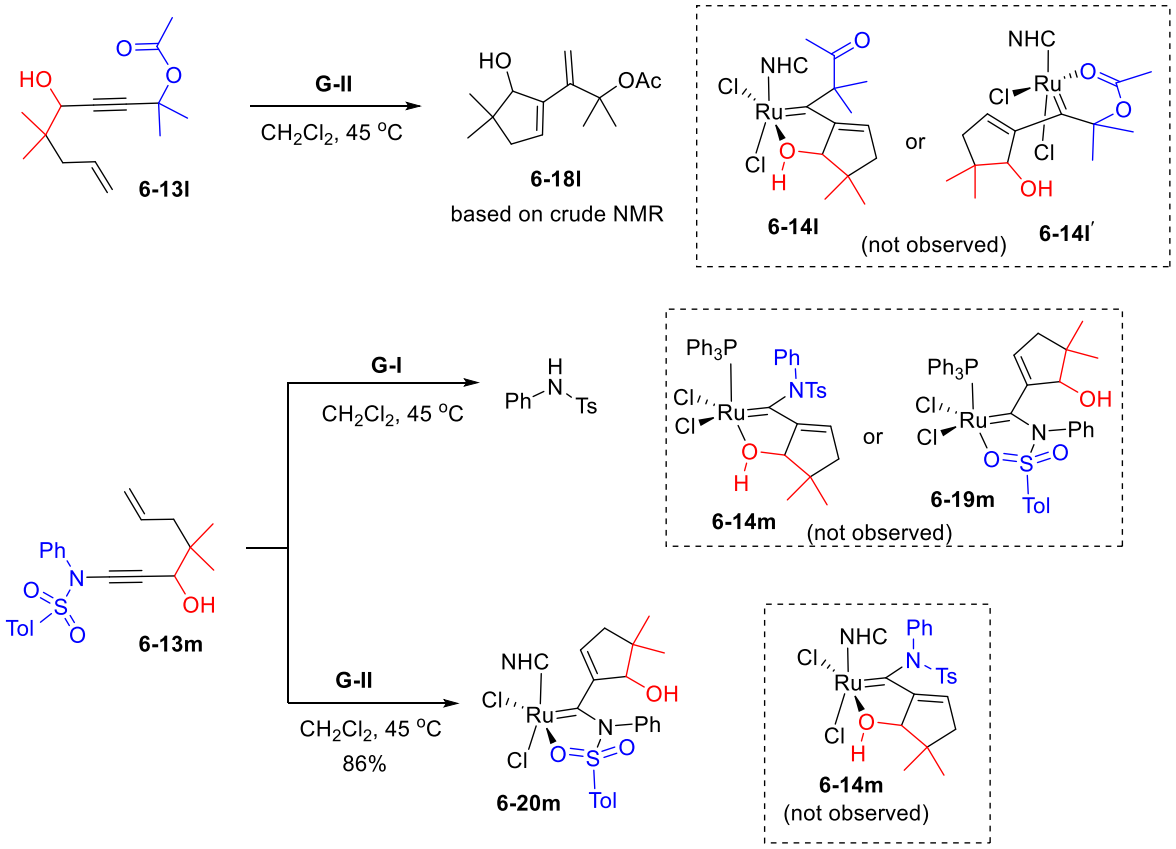
entry	enyne	Product	yield (%)[a]
1	 6-13i	 6-14i	91
2	 6-13j	 6-14j	90
3	 6-13k	 6-14k	82

[a] Isolated yield after purification

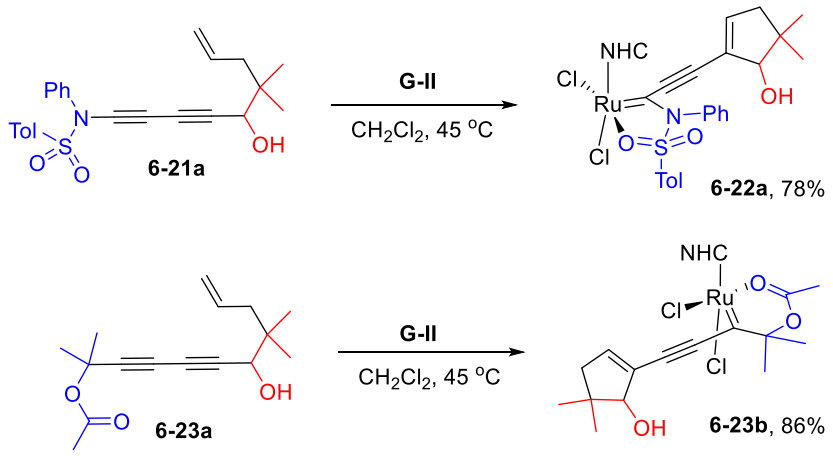
Table 6.2 Formation of Hydroxy- and Ether-Chelated Ruthenium Alkylidenes

Grubbs first-generation complex **G-I**, provided only the corresponding *N*-phenyl sulfonamide, derived from C−N bond cleavage. However, with Grubbs second-generation complex (**G-II**) smoothly converted to endo-cyclic 5-memered sulfonamide-chelate **6-20m**, without forming the exo-cyclic 5-membered hydroxy-chelate **6-14m**. The single X-ray diffraction analysis of **6-20m** shows a cis relationship between the NHC and the chelated sulfonyl oxygen. This clearly indicates the endo *gem*-dialkyl substituent of **6-13m** has more steric and electronic influence on the carbenic carbon to stabilize the generated ruthenium alkylidene to provide only **6-20m**.

To further probe the steric and electronic influence for chelate formation, we next examined the chelation behavior of the ruthenium alkylidenes derived from enediynes **6-21a** and **6-23a**. These enediynes



Scheme 6.8 Unexpected Behaviors of Related Enynes



Scheme 6.9 Competing Chelation between Hydroxyl and Sulfonamide or Acetate Moieties

can undergo metallotropic [1,3]-shift of the initially formed ruthenium alkylidene species, which would be even more facilitated by the chelation event and vice versa (**scheme 6.9**). The thermodynamic advantage

of the metallotropic [1,3]-shift to generate a fully conjugated system would force the metal center to be positioned near the strong chelating group. The reaction of enediyne **6-21a** with **G-II** provided only sulfonamide-chelated ruthenium alkylidene **6-22a** in 78% yield. Enediyne **6-23a** also prefer to form 6-membered acetate-chelated ruthenium alkylidene **6-24a** (86%). In both cases, the corresponding hydroxy-chelation was not observed, this might be the consequence of forming more conjugated 1,5-diene-3-yne rather than 1,3-dien-4-yne.

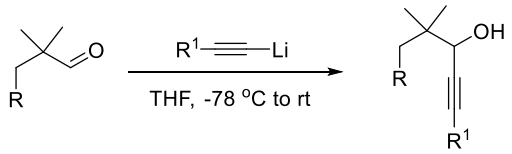
6.3. Summary

In summary, we have examined the chelation behavior of hydroxy and ether functional groups that can capture propagating ruthenium alkylidene intermediate to prevent the expected metathesis process. We trapped propagating ruthenium alkylidenes in enyne ring-closing metathesis by relying on the exo and endo *gem*-dialkyl substituent effect. The structural features of stable oxygen-chelates are explored by single crystal X-ray diffraction analysis. All chelates generated in this study have the disposition of the oxygen and NHC ligands in cis relationship. The competing chelation between hydroxyl vs a sulfonamide or an acetate-chelate was were also examined.

6.4. Experimental Details

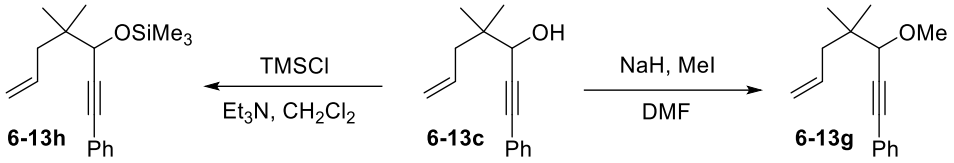
6.4.1. General Information: For general information see section 6.6.1.

6.4.2. General Procedure for Preparation of Starting Materials:



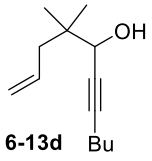
Enynes **6-13a─6-13f**, **6-13i** and **6-13j** were synthesized from the know aldehydes and/or ketones using the alkynyl lithium.[9]

Enynes **6-13g** and **6-13h** were prepared from **6-13c** by methylation and trimethylsilyl protection of an alcohol.

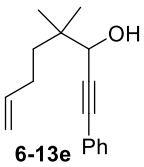


6.4.3. General Procedure for Metal Complex Formation: Compund **6-13c** (16 mg, 0.074 mmol) and Grubbs second generation complex (59 mg, 0.07 mmol) was dissolved in CH_2Cl_2 (4 mL) in an air-free sealed tube and heated up to 45 ^oC over 3 h. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (SiO_2, EtOAc : CH_2Cl_2 = 1 : 1) to afford **6-14c** (43.7 mg, 92%) as a green solid.

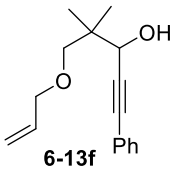
6.4.4. Selected Characterization Data



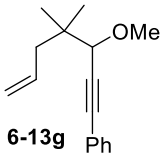
Characterization data of 6-13d: ^1H NMR (500 MHz, $CDCl_3$) δ 5.89-5.81 (m, 1H), 5.08-5.05 (m, 2H), 4.05 (s, 1H), 2.22 (dt, *J* = 2.0 Hz, 7.0 Hz, 2H), 2.18-2.07 (m, 2H), 1.69 (bs, 1H), 1.52-1.47 (m, 2H), 1.45-1.39 (s, 2H), 0.95 (s, 3H), 0.95 (s, 3H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.19, 117.49, 86.76, 79.50, 70.53, 42.83, 38.75, 30.82, 22.67, 22.55, 21.97, 18.41, 13.59; HRMS (ESI**)** calcd for $C_{13}H_{23}O$ $[M+H]^+$ 195.1749, found 195.1751.



Characterization data of 6-13e: ^1H NMR (500 MHz, $CDCl_3$) δ 7.44-7.42 (m, 2H), 7.32-7.31 (m, 3H), 5.89-5.81 (m, 1H), 5.06-5.03 (m, 1H), 4.96-4.94 (m, 1H), 4.32 (s, 1H), 2,12-2.07 (m, 2H), 1.83 (bs, 1H), 1.57-1.52 (m, 2H), 1.05 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.39, 131.70, 128.37, 128.32, 122.78, 114.18, 88.77, 86.08, 70.91, 38.63, 37.56, 28.43, 22.76, 22.54; HRMS (ESI**)** calcd for $C_{16}H_{21}O$ $[M+H]^+$ 229.1592, found 229.1592.

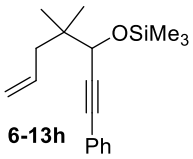


Characterization data of 6-13f: ^1H NMR (500 MHz, $CDCl_3$) δ 7.45-7.43 (m, 2H), 7.31-7.29 (m, 3H), 5.94-5.86 (m, 1H), 5.30-5.27 (m, 1H), 5.20-5.17 (m, 1H), 4.43 (s, 1H), 4.02-4.00 (m, 2H), 3.68 (d, *J* = 8.9 Hz, 1H), 3.62 (bs, 1H), 3.30 (d, *J* = 8.9 Hz, 1H), 1.15 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.41, 131.71, 128.27, 128.23, 123.05, 117.14, 88.90, 85.47, 78.11, 72.53, 70.99, 39.48, 22.25, 21.17; HRMS (ESI**)** calcd for $C_{16}H_{20}O_2$ $[M]^+$ 244.1463, found 244.1462.



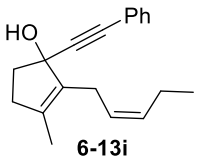
6-13g

Characterization data of 6-13g: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48-7.46 (m, 2H), 7.33-7.31 (m, 3H), 5.91-5.82 (m, 1H), 5.11-5.08 (m, 2H), 3.83 (s, 1H), 3.49 (s, 3H), 2.26-2.17 (m, 2H), 1.06 (s, 3H), 1.04 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.99, 131.75, 128.29, 128.21, 123.10, 117.55, 86.98, 86.94, 79.63, 57.45, 43.22, 38.67, 29.77, 23.33, 22.97; HRMS (ESI**)** calcd for $C_{16}H_{21}O$ $[M+H]^+$ 229.1592, found 229.1590.



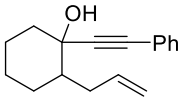
6-13h

Characterization data of 6-13h: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.44 (m, 2H), 7.33-7.31 (m, 3H), 5.91-5.84 (m, 1H), 5.11-5.08 (m, 2H), 4.27 (s, 1H), 2.20 (d, *J* = 7.3 Hz, 2H), 1.02 (s, 3H), 1.01 (s, 3H), 0.23 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 135.28, 131.52, 128.28, 128.07, 123.35, 117.30, 89.67, 85.53, 70.84, 42.78, 39.24, 22.80, 22.56, 0.25; HRMS (ESI**)** calcd for $C_{18}H_{27}OSi$ $[M+H]^+$ 287.1826, found 287.1823.



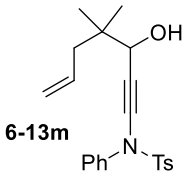
6-13i

Characterization data of 6-13i: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45-7.42 (m, 2H), 7.32-7.30 (m, 3H), 5.53-5.42 (m, 2H), 3.22 (dd, *J* = 7.1 Hz, 14.7 Hz, 1H), 3.10-3.04 (m, 1H), 2.63-2.57 (m, 1H), 2.47-2.40 (m, 1H), 2.24-2.21 (m, 2H), 2.07-1.97 (m, 2H), 1.38 (s, 3H), 0.99 (t, *J* = 7.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 152.87, 132.82, 131.70, 128.33, 128.17, 126.26, 94.48, 86.06, 84.40, 62.96, 43.34, 40.14, 32.82, 25.95, 25.02, 20.71, 14.20; HRMS (ESI**)** calcd for $C_{18}H_{21}O$ $[M+H]^+$ 253.1592, found 253.1589.



6-13j

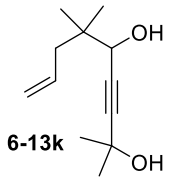
Characterization data of 6-13j: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46-7.44 (m, 2H), 7.32-7.31 (m, 3H), 5.95-5.87 (m, 1H), 5.15-5.04 (m, 1H), 2.74-2.68 (m, 1H), 2.63 (s, 1H), 2.14-2.01 (m, 2H), 1.80-1.50 (m, 5H), 1.32-1.22 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 138.31, 131.72, 128.31, 122.96, 116.27, 90.33, 86.59, 73.38, 47.92, 41.61, 41.12, 36.15, 29.64, 25.54, 24.18; HRMS (ESI**)** calcd for $C_{17}H_{20}O$ $[M]^+$ 240.1514, found 240.1518.



6-13m

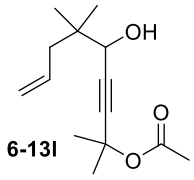
Characterization data of 6-13m: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.32-7.23 (m, 7H), 5.87-5.79 (m, 1H), 5.06-5.03 (m, 2H), 4.21 (s, 1H), 2.41 (s, 3H), 2.19-2.06 (m, 2H), 0.97 (s, 3H), 9,95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 138.8,

134.9, 133.0, 129.6, 129.1, 128.3, 128.2, 126.2, 117.7, 79.8, 70.4, 70.2, 42.9, 39.2, 22.9, 22.8, 21.7; HRMS (ESI**)** calcd for $C_{22}H_{26}NO_3S$ $[M+H]^+$ 384.1633, found 384.1626.



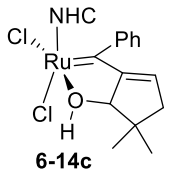
6-13k

Characterization data of 6-13k: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.87-5.78 (m, 1H), 5.07-5.04 (m, 2H), 4.07 (s, 1H), 2.62 (bs, 1H), 2.37 (bs, 1H), 2.17-2.06 (m, 2H), 1.51 (s, 6H), 0.95 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.92, 117.70, 90.91, 81.58, 69.96, 65.16, 42.82, 38.69, 31.47, 31.41, 22.73, 22.53; HRMS (ESI**)** calcd for $C_{12}H_{19}O$ $[M-H+H_2O]^+$ 179.1436, found 179.1433.



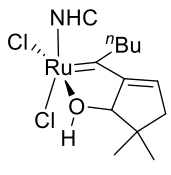
6-13l

Characterization data of 6-13l: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.86−5.77 (m, 1H), 5.08−5.02 (m, 2H), 4.06 (s, 1H), 2.33 (s, 1H), 2.16−2.05 (m, 2H), 1.99 (s, 3H), 1.63 (s, 6H), 0.94 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.34, 135.05, 117.55, 86.88, 83.84, 71.95, 69.87, 42.76, 38.82, 29.04, 28.97, 22.66, 22.54, 21.93; HRMS (ESI) calcd for $C_{14}H_{22}O_3Na$ $[M+Na]^+$ 261.1467 found, 261.1466.



6-14c

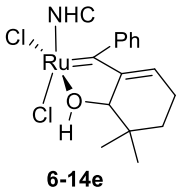
Characterization data 6-14c (43.7 mg, 92%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 (d, *J* = 7.2 Hz, 1H), 7.08-7.06 (m, 3H), 7.00-6.95 (m, 4H), 6.70 (s, 1H), 5.78 (s, 1H), 4.97 (d, *J* = 11.1 Hz, 1H), 4.28-4.23 (m, 2H), 4.12-4.08 (m, 1H), 3.92-3.90 (m, 1H), 2.51 (s, 3H), 2.44 (s, 3H), 2.36 (s, 9H), 2.20 (d, *J* = 11.2 Hz, 1H), 1.84 (m, 5H), 1.20 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 285.24, 216.84, 164.91, 155.07, 140.22, 140.07, 139.01, 138.09, 137.98, 135.65, 135.13, 131.26, 131.03, 130.58, 129.31, 128.49, 127.37, 126.11, 124.29, 112.16, 93.61, 53.10, 51.06, 42.78, 26.42, 21.60, 21.34, 21.08, 20.16, 19.01, 18.57, 18.28; HRMS (ESI**)** calcd for $C_{35}H_{40}Cl_1N_2ORu$ $[M-Cl-2H]^+$ 641.1879, found 641.1875.



6-14d

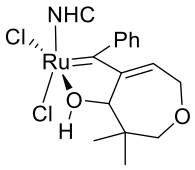
Characterization data 6-14d: (39 mg, 84%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.17 (s, 1H), 6.96 (s, 2H), 6.81 (s, 1H), 5.78 (s, 1H), 4.93 (s, 1H), 4.34-4.30 (m, 1H), 4.11-4.04 (s, 2H), 3.99-3.94 (m, 1H), 3.33-3.30 (m, 2H), 2.76 (s, 3H), 2.51 2.76 (s, 3H), 2.37 (s, 3H), 2.33 (s, 3H), 2.21 (s, 3H), 2.11-2.07 (m, 1H), 1.92 (s, 3H), 1.90-1.86 (m, 4H), 1.51-1.47 (m, 1H), 1.08 (s, 3H), 0.90 (s, 3H), 0.73 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 305.80, 218.08, 160.42,

140.33, 139.97, 138.69, 138.52, 137.81, 136.20, 135.97, 136.20, 135.97, 131.17, 130.02, 129.06, 128.51, 107.64, 106.11, 92.16, 52.68, 52.27, 52.17, 50.74, 41.39, 28.43, 26.76, 24.25, 22.73, 21.27, 21.04, 19.92, 19.31, 19.09, 18.46, 13.50; HRMS (ESI**)** calcd for $C_{33}H_{46}Cl_1N_2ORu$ $[M\text{-}Cl]^+$ 623.2348, found 623.2346.



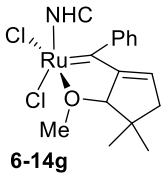
6-14e

Characterization data 6-14e (45.6 mg, 94%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.14 (m, 3H), 7.08-6.83 (m, 6H), 6.19 (s, 1H), 4.27-4.17 (m, 3H), 4.06-4.02 (m, 1H), 3.91-3.87 (m, 1H), 2.55 (s, 3H), 2.46 (d, *J* = 11.2 Hz, 1H), 2.43 (s, 3H), 2.39 (s, 3H), 2.36 (s, 3H), 2.29 (s, 3H), 1.96 (s, 3H), 1.49-1.44 (m, 2H), 1.26-1.20 (m, 2H), 1.10 (s, 3H), 0.64 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 294.66, 216.79, 156.52, 155.68, 140.22, 139.20, 138.17, 137.89, 135.90, 135.03, 131.21, 131.00, 129.21, 128.52, 126.58, 120.91, 84.21, 53.19, 50.94, 35.09, 34.22, 27.76, 24.38, 21.38, 21.14, 20.20, 19.13, 18.86, 18.17, 17.65; HRMS (ESI**)** calcd for $C_{36}H_{41}N_2ORu$ $[M{-}2Cl{-}3H]^+$ 619.2262, found 619.2269.



6-14f

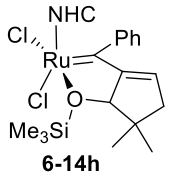
Characterization data 6-14f (39.7 mg, 80%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.11-7.08 (m, 2H), 7.01-6.96 (m, 4H), 6.84 (s, 1H), 6.41 (s, 1H), 6.39 (s, 1H), 5.99 (bs, 1H), 4.79 (d, *J* = 8.0 Hz, 1H), 4.34-4.28 (m, 1H), 4.18-3.97 (m, 3H), 3.65 (dd, *J* = 4.5 Hz, 17.5 Hz, 1H), 3.56 (d, *J* = 12.5 Hz), 3.43 (d, *J* = 12.4 Hz, 1H), 3.28 (d, *J* = 17.4 Hz, 1H), 2.76 (d, *J* = 8.7 Hz, 1H), 2.60 (s, 3H), 2.42 (s, 3H), 2.35 (s, 3H), 2.34 (s, 3H), 2.26 (s, 3H), 2.23 (s, 3H), 1.01 (s, 3H), 0.70 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 214.44, 160.57, 157.68, 140.26, 139.75, 139.03, 138.63, 137.42, 136.05, 135.88, 130.77, 130.49, 128.97, 128.33, 126.43, 126.30, 122.77, 114.04, 84.15, 80.58, 71.13, 52.74, 51.23, 40.71, 24.95, 21.36, 21.12, 19.95, 19.27, 19.15, 18.77, 18.12; HRMS (ESI**)** calcd for $C_{36}H_{42}Cl_1N_2O_2Ru$ $[M{-}Cl{-}2H]^+$ 671.1985, found 671.1985.



6-14g

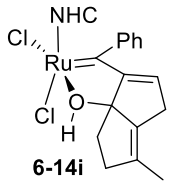
Characterization data 6-14g (42 mg, 86%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.24 (bs, 2H), 7.55 (t, *J* = 7.3 Hz, 1H), 7.18 (t, *J* = 7.5 Hz, 2H), 7.06 (s, 1H), 7.02 (s, 1H), 6.40 (s, 1H), 5.90 (s, 1H), 4.99 (d, *J* = 5.2 Hz), 4.34 (s, 1H), 4.24-4.18 (m, 2H), 3.88-3.86 (m, 1H), 3.70-3.68 (m, 1H), 2.81 (s, 3H), 2.79 (s, 3H), 2.57 (s, 3H), 2.30 (s, 3H), 2.19 (s, 3H), 1.98-1.94 (m, 1H), 1.86 (s, 3H), 1.85 (s, 3H), 1.68 (m, 1H), 1.18 (s, 3H), 1.05 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 281.29, 214.66, 141.92, 139.66, 139.41, 138.35, 137.51, 135.78, 134.31, 130.75, 130.37, 129.86, 129.46, 128.94, 128.05,

88.58, 86.65, 79.65, 60.73, 52.41, 52.25, 49.50, 46.10, 27.01, 26.38, 14.63, 23.38, 21.26, 20.84, 20.38, 18.96, 18.89, 17.91.



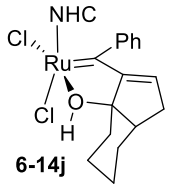
6-14h

Characterization data 6-14h (44 mg, 92%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.08 (bs, 1H), 7.54 (t, *J* = 7.0 Hz, 2H), 7.17 (bm, 2H), 7.06 (s, 1H), 7.17 (s, 1H), 6.37 (s, 1H), 5.91 (s, 1H), 4.96 (s, 1H), 4.86 (d, *J* = 3.5 Hz, 1H), 4.25-4.17 (m, 2H), 3.87-3.86 (m, 1H), 3.70-3.68 (m, 1H), 2.79 (s, 3H), 2.58 (s, 3H), 2.30 (s, 3H), 2.20 (s, 3H), 1.94 (dd, *J* = 5.4 Hz, 14.0Hz, 1H), 1.86 (s, 3H), 1.83 (s, 3H), 1.59 (d, *J* = 14.3 Hz, 1H), 1.16 (s, 3H), 0.96 (s, 3H), -0.43 (s, 9H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 281.44, 214.57, 142.63, 139.69, 139.45, 138.19, 137.43, 135.83, 134.74, 134.13, 133.04, 130.74, 129.87, 129.48, 128.83, 91.47, 79.23, 52.40, 52.34, 50.22, 45.21, 24.17, 22.78, 21.25, 20.87, 20.46, 18.97, 17.85, 0.15; HRMS (ESI**)** calcd for $C_{38}H_{51}Cl_2N_2ORuSi$ $[M+H]^+$ 751.2195, found 751.1168.



6-14i

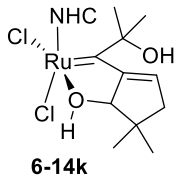
Characterization data 6-14i (45 mg, 91%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.61 (t, *J* = 7.3 Hz, 2H), 7.24 (m, 3H), 7.13 (s, 1H), 7.03 (s, 1H), 6.24 (s, 1H), 6.11 (s, 1H), 4.81 (d, *J* = 2.3 Hz, 1H), 4.33-4.25 (m, 2H), 3.96-3.90 (m, 1H), 3.84-3.80 (m, 1H), 2.94 (s, 3H), 2.71-2.66 (m, 1H), 2.60 (s, 3H), 2.49 (s, 1H), 2.34 (s, 3H), 2.32 (s, 3H), 2.15-2.00 (m, 3H), 1.79 (s, 3H), 1.72 (s, 3H), 1.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 213.41, 166.26, 143.12, 141.92, 140.07, 139.28, 137.63, 135.79, 134.91, 134.53, 132.88, 130.92, 130.80, 130.14, 129.49, 128.66, 87.97, 79.38, 74.37, 52.25, 52.09, 44.32, 35.13, 26.40, 26.15, 25.02, 21.28, 20.80, 20.45, 19.25, 19.01, 17.79; HRMS (ESI**)** calcd for $C_{37}H_{45}Cl_2N_2Ru$ $[M+4H-OH]^+$ 689.1998, found 689.1983.



6-14j

Characterization data 6-14j (44 mg, 90%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (bm, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.19 (t, *J* = 7.6 Hz, 2H), 7.10 (s, 1H), 7.05 (s, 1H), 6.27 (s, 1H), 6.03 (s, 1H), 4.34 (s, 1H), 4.30-4.14 (m, 2H), 3.87-3.69 (m, 2H), 2.83 (s, 3H), 2.64 (s, 3H), 2.41 (bs, 1H), 2.33 (s, 3H), 2.24 (s, 3H), 1.85 (s, 3H), 1.81-1.75 (m, 2H), 1.51-1.28 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 283.37, 212.49, 142.86, 139.66, 139.04, 138.28, 137.56, 135.46, 134.61, 134.17, 133.97, 130.95, 130.73, 130.00, 129.49, 128.73, 128.61, 96.43, 80.84, 73.82, 52.36, 41.03, 36.93, 33.09, 22.93,

21.24, 20.98, 20.84, 20.60, 20.48, 19.31, 19.17, 17.88; HRMS (ESI**)** calcd for $C_{37}H_{43}N_2ORu$ $[M-2Cl-H]^+$ 633.2413, found 633.2411.



6-14k

Characterization data 6-14k (38 mg, 82%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.06 (s, 1H), 6.92 (s, 1H), 6.84 (s, 1H), 6.80 (s, 1H), 5.16 (s, 1H), 4.91 (s, 1H), 4.34-4.37 (bs, 1H), 4.25-4.21 (m, 1H), 4.12-4.07 (m, 2H), 3.70 (s, 1H), 2.51 (s, 3H), 2.32 (s, 3H), 2.28 (s, 6H), 2.26 (s, 3H), 2.25 (s, 3H), 2.04-1.99 (m, 2H), 1.40 (s, 3H), 1.17 (s, 3H), 1.14 (s, 3H), 0.93 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 283.59, 216.98, 159.01, 140.76, 140.22, 138.78, 138.12, 137.65, 135.69, 135.48, 130.65, 130.48, 130.34, 129.99, 129.83, 128.81, 119.51, 116.16, 95.15, 84.13, 52.67, 51.03, 46.74, 41.99, 27.28, 27.05, 26.96, 26.43, 26.21, 25.06, 23.10, 21.60, 21.34, 20.98, 20.07, 18.90, 18.35.

6.5. References

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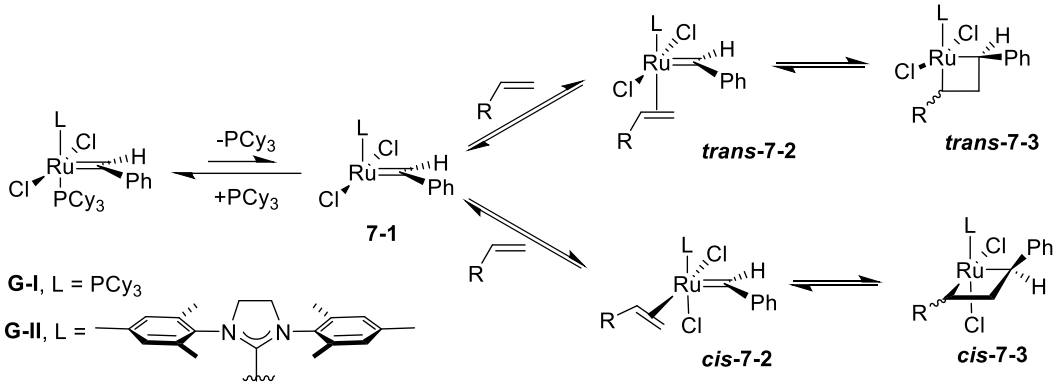
CHAPTER 7

STRUCTURE AND REACTIVITY OF ALKENE-CHELATED RUTHENIUM ALKYLIDENE COMPLEXES

7.1. Introduction

Olefin metathesis catalyzed by ruthenium alkylidenes developed by Grubbs and others is one of the most versatile synthetic tools for carbon-carbon double bond construction.[1] The catalysts **G-I**[2] and **G-II**[3] developed by Grubbs and coworkers, have received significant attention and widely used in the diverse areas of chemistry, because of their relatively high catalytic activity, functional group tolerance, and commercial availability.[4] The general steps in Chauvin's proposed mechanism of olefin metathesis catalyzed by metal alkylidenes involve olefin binding to the metal alkylidene to generate a metallocyclobutane followed by cycloreversion to produce another olefin chelated metal alkalidene species (**Scheme 7.1**).[5] Based on the Chauvin's proposed mechanism, Grubbs and coworker's initial mechanistic studies on **G-I**[6] and **G-II**[7] in olefin metathesis mainly focused on the catalyst initiation to generate coordinatively unsaturated species **7-1**. In their catalyst initiation studies, it was found that the loss of poshphine ligand is the rate-limiting step to generate catalytically active 14-electron intermediate **7-1**, particularly for the catalyst **G-II**.[8] The generated active species **7-1** interact with an alkene in two possible orientations relative to ligand L to produce alkylidene/olefin complex *trans*-**7-2** and *cis*-**7-2**. Cycloaddition of **7-2** to afford metallacyclobutane **7-3**, followed by cycloreversion and olefin dissociation regenerates



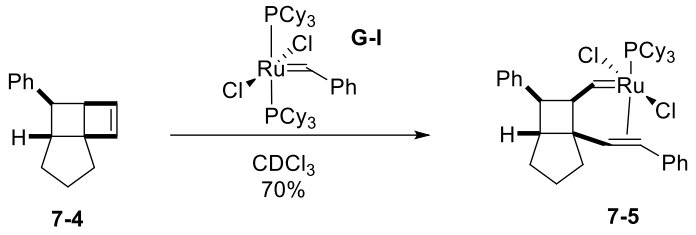
Scheme 7.1 Initial Steps in G-I and G-II Catalyzed Olefin Metathesis

active species **7-1**. It is important to understand the key intermediate's ligand disposition around the metal center to design more metathesis active, diastereoselective, and enantioselective as well as *Z*-selective olefin

metathesis catalysts.[9] Even though a lot of information provided by mechanistic studies, the ligand orientation of the alkene-chelated ruthenium alkyldene[10] **7-2** and metallacyclobutane[11] complexes **7-3** relative to ligand (L) remained unclear. In this chapter, the ligand orientation of the alkene-chelated ruthenium alkyldene **7-2** is mainly described.

7.2. Alkene-Chelated Ruthenium Alkylidenes

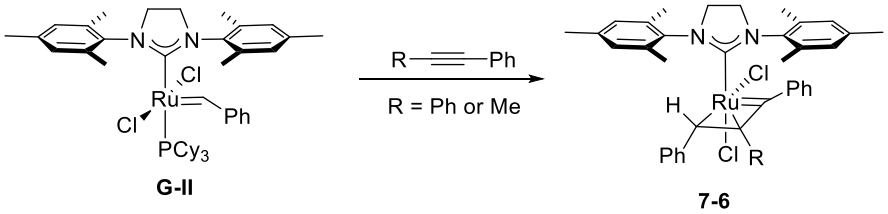
The first alkene-chelated ruthenium alkylidene was derived from the Grubbs first-generation complex **G-I** was reported by Snapper and coworkers.[12] The ring-opening metathesis of cyclobutene **7-4** with stoichiometric amount of **G-I** afforded alkene-chelated ruthenium alkylidene **7-5** in 70 % yield (**Scheme 7.2**). The crystal structure of **7-5** shows the alkene chelated to the metal center trans to the PCy_3 ligand, which is also called bottom bound alkene chelated ruthenium alkylidene. The newly generated bottom bound complex **7-5** showed good metathesis activity.



Scheme 7.2 G-I Derived First Alkene-Chelated Ruthenium Alkylidene

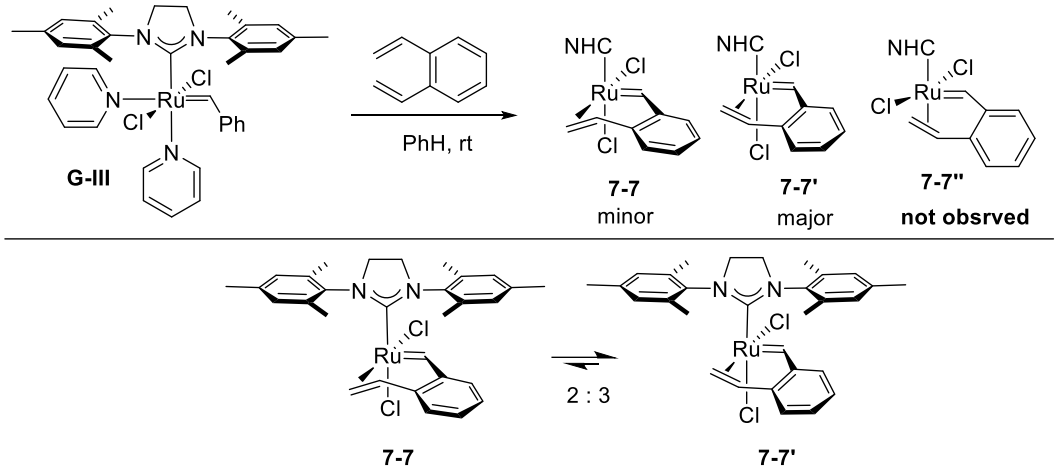
In 2001, Grubbs and coworkers reported **G-II**-derived η^3-vinylcarbene complexes (**Scheme 7.3**).[13] The Grubbs second-generation complex **G-II** reacted cleanly with an excess amount of diphenyl acetylene and/or 1-phenyl-1-propyne to afford phosphine free complex **7-6**. The crystal structure of **7-6** shows several interesting features where the alkene bound cis to the *N*-heterocyclic (NHC) ligand. The newly generated η^3-vinylcarbene complex **7-6** was found to be metathesis inactive.

In 2006, Grubbs and coworkers reported the *N*-heterocyclic ruthenium complex derived chelated with an alkene moiety (**Scheme 7.4**).[14] The reaction of Grubbs third-generation complex **G-III** with divinyl benzene afforded a mixture of two alkene-chelated ruthenium alkylidenes. The minor isomer was



Scheme 7.3 η^3-Vinylcarbene Complexes Derived from Ruthenium-Based Olefin Metathesis

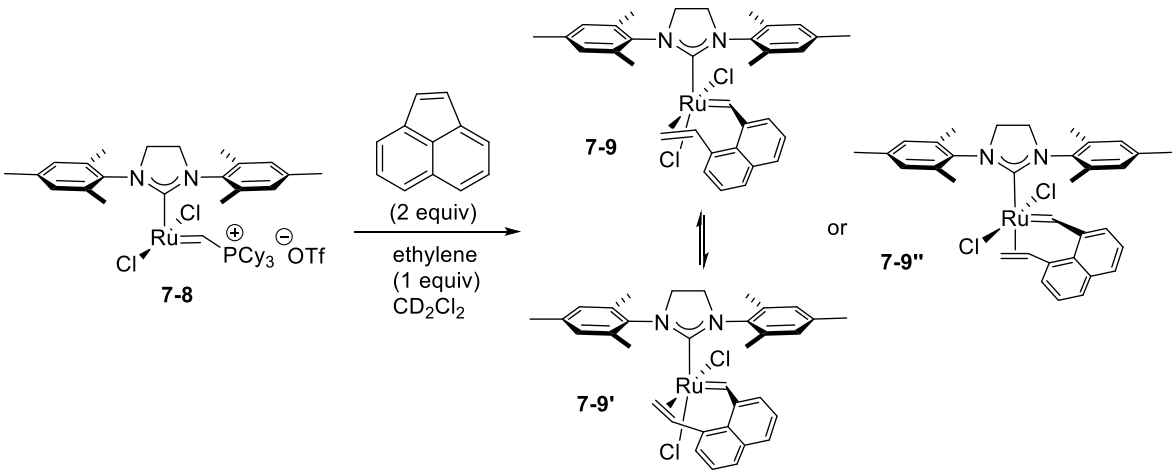
crystallized and its crystal structure shows the alkene-chelated to ruthenium center in cis to the NHC ligand (side bound). After the careful NMR analysis of the mixture under various temperature the major isomer was assigned as **7-7′**, which is also the side bound ruthenium alkylidene. The equilibrium ratio of these alkylidenes **7-7** and **7-7′** is 2:3. More interestingly, the authors did not observe the bottom bound complex **7-7′′**, which is similar to the Snapper alkene-chelated ruthenium alkylidene. Based on the observed cis alkene-chelated complex, further investigation was carried out with the variation of both NHC and a ligand precursor. All these studies preferentially favored the alkene-chelation cis to the NHC ligand.[15]



Scheme 7.4 Alkene-Chelated Ruthenium *N*-Heterocyclic Alkylidene

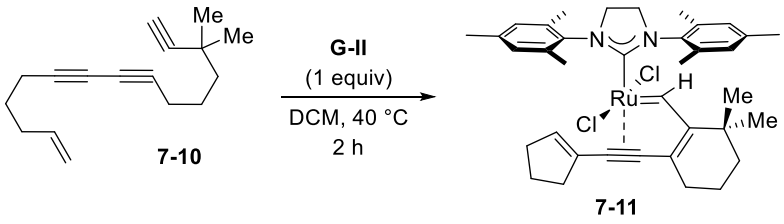
Similarly, alkene chelated complexes using ruthenium complex **7-8** and acenaphthylene was reported by Piers and coworkers.[16] Based on the NMR characterization data, they believed that alkene-chelation occurs trans to the NHC ligand (bottom bound complex **7-9′′**) rather than with a cis relationship (side bound complex). However, without having more definitive evidences, they are unable to assign geometry of the

observed complex. Based on the DFT calculations of **7-9**, **7-9′** and **7-9′′**, Goddard and coworkers predicted that more favorable complex is **7-9**.[17]



Scheme 7.5 Alkene-Chelated Ruthenium Alkylidene Derived from 7-8 with Acenaphthylene

Recently, the closely related alkyne-chelated complex have been reported by our group (**Scheme 7.6**). Well-defined alkyne-chelated ruthenium alkylidene complex **7-11** was generated by employing the tandem ring-closing enyne metathesis and metallotropic [1,3]-shift of enetriyne **7-10**.[18] Interestingly complex **7-11** shows that a chelated alkyne binds to the metal center trans to the NHC ligand. Interestingly, it was found that the alkyne chelated complex **7-11** was metathesis inactive.

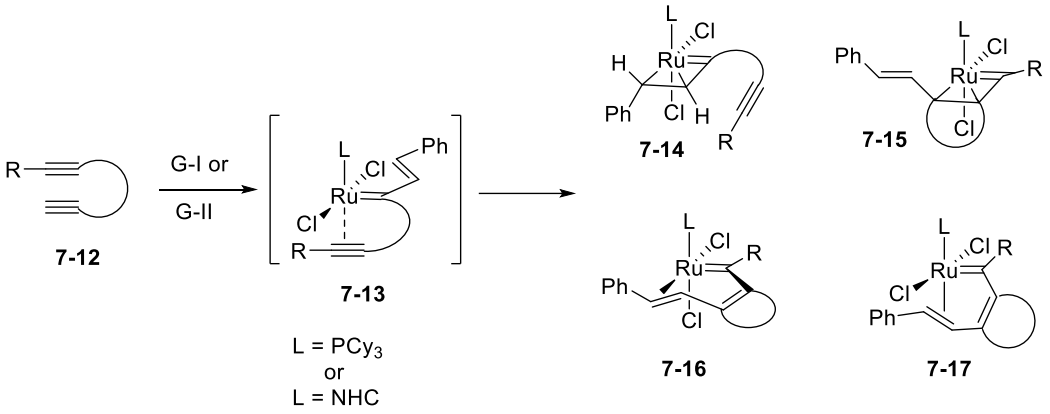


Scheme 7.6 Alkyne-Chelated Ruthenium Alkylidene

7.3. Results and Discussion

Because of only a small set of examples of π-system-bound complexes, observed by Snapper, Grubbs and Piers, it is premature to generalize or predict the preferred chelation mode of a tethered alkene or alkyne to the ruthenium center, which call for further investigations. We assume that the combined effect of the

ligand on the metal and the structure of the tether between the metal and the chelating alkene should play a crucial role to dictate the preference for different mode of alkene chelation. To examine the involvement of these parameters, we envisioned that the ring-closing metathesis (RCM) of 1,n- diyne **7-12** would provide an ideal platform for systematic exploration (**Scheme 7.7**).



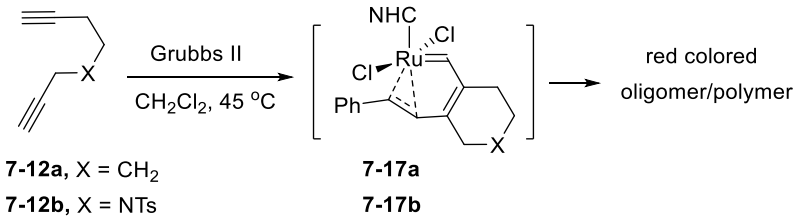
Scheme 7.7 RCM of 1,n-Diynes for the Formation Various Alkene Chelated Ruthenium Alkylidenes

It is expected that the cross metathesis (CM) between one of the terminal alkyne moieties in **7-12** and ruthenium alkylidene initiator **G-I** or **G-II** would generate the first propagating alkylidene species, where the generated ruthenium alkylidene complex has two possibilities to chelate with an alkyne or alkene. If the tethered alkyne is chelated with the metal center complex **7-13** would be formed, which might have a similar ligand orientation as reported complex **7-11**. On the other hand, if the metal center prefers to be chelated with an alkene, then η^3-vinylcarbene complex **7-14** will be formed. The ligand disposition of complex **7-14** would be is expected to have a similarity to Grubbs η^3-vinylcarbene complex **7-6**. If the RCM of **7-13** is kinetically viable, it would generate three possible alkene-chelated alkylidenes, one might be η^3-vinylcarbene complex **7-15**, and the other possible alkene-chelates are the side-bound and bottom bound complexes **7-16** and **7-17**. It will be interesting to note the possibility of competition between cis-1,3-chelate **7-14** and cis-1,5-chelate **7-16**, as well as cis-1,5-chelate **7-16** and *trans-1,5-chelate* **7-17**. The requirement for this reaction (with a stoichiometric amount of an initiator) to generate one of these alkene-chelates is a rapid initiation and strong chelation such that these complexes don't enter the next catalytic cycle that

ultimately leads to oligomerization/polymerization.

7.3.1. Ring-Closing Metathesis (RCM) of 1,7-Diynes

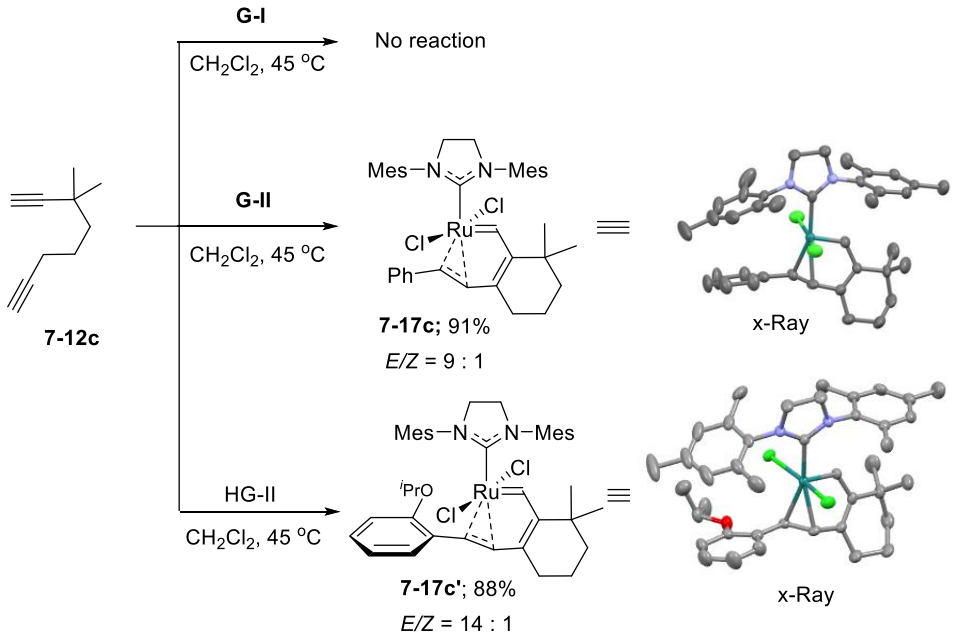
The alkene-chelation behavior to the ruthenium center was first examined with simplest 1,7-diyne **7-12a** (X = CH_2) and **7-12b** (X = NTs) and Grubbs second-generation catalyst **G-II** (**Scheme 7.8**); treating **7-12a** with a stoichiometric amount of **G-II** in CH_2Cl_2 at 45 °C led to a full conversion but the isolated red-colored material was identified as oligomers of **7-12a**. Similarly, **7-12b** was treated with a stoichiometric amount of **G-II**, but again led the same result as with **7-12a**. Presumably, the expected **7-17a** and **7-17b** were indeed generated, but due to their relatively weak chelation of the styryl moiety to the ruthenium center, they readily react with diyne **7-12a**,**b** to enter into next catalytic cycle, leading to oligomerization or polymerization.



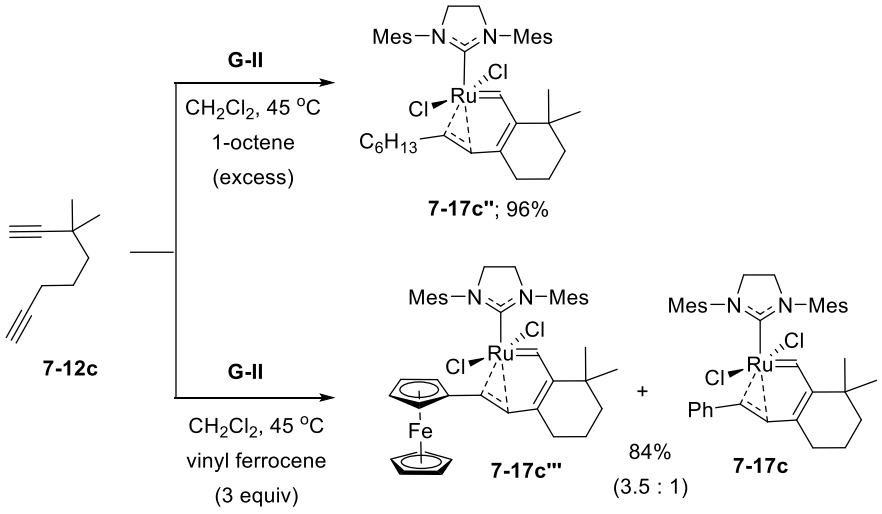
Scheme 7.8 RCM of 1,7-Diynes Without *gem*-Dimethyl Group

On the basis of our previous studies where the *gem*-dimethyl group at the β-position on the alkyne-chelated ruthenium alkylidene **7-11** is indispensable for it stability, we expected the same stabilizing effect by a *gem*-dimethyl group for structurally related alkene-chelates (**Scheme 7.9**). To our delight, treatment of 1,7-diyne **7-12c** containing a *gem*-dimethyl moiety with **G-II**, under otherwise identical conditions, provided a crystalline material in 91% yield (*E/Z* = 9 : 1). The spectroscopic characterization data ^{1}H- and ^{13}C-NMR signals of newly formed complex are consistent with trans chelated ruthenium alkylidene **7-17c**, which was further confirmed by single X-ray crystallography analyses. There was no evidence for the formation of the corresponding *cis*-complex in this reaction. We next tested the same diyne **7-12c** with stoichiometric **G-I**, but no reaction was observed. However, diyne **7-12c** with Hoveyda-Grubbs second-generation complex (**HG-II**) smoothly reacted to afford an alkene-bound ruthenium alkylidene **7-17c′** in

88% yield (*E/Z* = 14 : 1), the ligand disposition around the metal center was further confirmed by X-ray crystallography analyses.



Scheme 7.9 RCM of *gem*-Dimethyl Group Containing 1,7-Diynes with G-I, G-II and HG-II



Scheme 7.10 RCM of 1,7-Diynes in Presence of an External Alkenes

After the successful formation of alkene-chelated ruthenium alkylidenes from diyne **7-12c** with **G-II** and **HG-II**, we next tested the same diyne **7-12c** with **G-II** in the presence of an external alkenes (**Scheme**

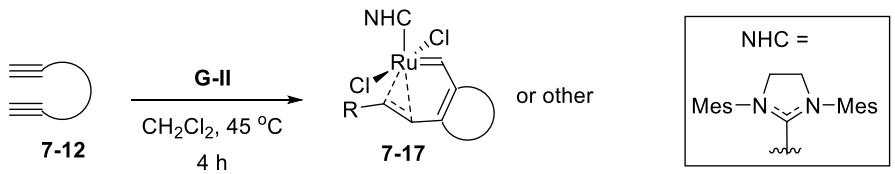
7.10). The reaction with excess 1-octene provided alkene chelated product **7-17c″** in 96% yield. On the other hand, the reaction with 3 equivalent of vinyl ferrocene afforded a mixture of vinyl ferrocene cross metathesis followed by ring-closed product **7-17c‴** and benzylidene cross metathesized product **7-17c** in a 3.5:1 ratio with 84% combined yield.

The selective formation of *trans*-1,5-chelates **7-17c**, **7-17c′**, **7-17c″**, and **7-17c‴** from 1,7-diyne **7-12c** contrasts to the preferred formation of cis-1,5-chelates **7-7** from *o*-vinylstyryl system of Grubbs and coworkers. These contrasting chelation behaviors imply that the seemingly minor differences in the structure of alkene ligand such as a substituent on the terminal position on the vinyl group and the *gem*-dimethyl group at the β-carbon from the carbene center may favor the formation of these trans chelates.

7.3.2. RCM of 1,n-Diynes to Form *trans*-1,5-Chelates

Encouraged by the results in **Scheme 7.9** and **Scheme 7.10**, an RCM approach for the formation 1,5-trans alkene chelates was further implemented for structurally diverse 1,n-diynes (**Table 7.1**). 1,6-Enyne **7-12d** derived from 1,1-dimethylpropargylamine was subjected to a stoichiometric amount of **G-II** in CH_2Cl_2 at 45 °C. Although a full conversion of enyne was observed the isolated red-colored material was identified as oligomers of **7-12d**, and *trans*-1,5-chelate **7-17d** in 5% yield (entry 1). On the other hand, 1,6-enyne **7-12e** derived from 1,1-dimethylpropargylalochol was completely converted to oligomers without forming any alkene-chelated complex (entry 2). The oligomerization of these enynes suggests that the 5-membered ring's bond angels are not suitable to form the expected chelates so that these complexes promote oligomerizations and polymerizations. By replacing the propargyl carbon of **7-12e** with diphenyl silyl group, gratifyingly, silyl ether tethered 1,6-enyne **7-2f** under otherwise identical conditions, provided *trans*-1,5-chelate **7-17f** in 82% yield without forming any oligomer or polymer (entry 3).

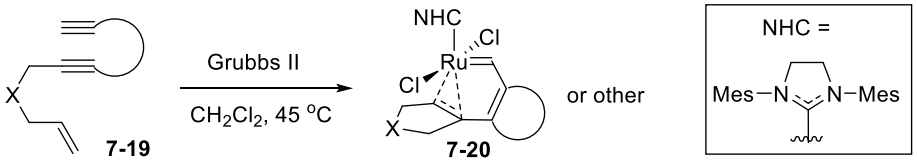
Having these results in hand, we next examined the behavior of 1,7-enynes having the propygl ether moiety. The 1,7-enyne **7-12g** containing a 1,3-dioxolane moiety was treated with **G-II** provide a 1:10 mixture of alkene- and ether-chelated products **7-17g** and **7-18g** in 78% combined yield. This indicates the generated ruthenium alkylidene favorably form a chelate with an oxygen functionalized to generate a



entry	1,n-diyne	product(s)	yield (%)
1	**7-12d**; X = NTs	**7-17d** and/or oligomers	5
2	**7-12e**; X = O	**7-17e**	0
3	**7-12f**	**7-17f**	82
4	**7-12g**	**7-17g** (*E*/*Z* = 4 :1) + **7-18g** (1:10)	78
5	**7-12h**	**7-17h**	93
6	**7-12i**	decomposed	
7	**7-12j**	**7-17j** (x-Ray)	92
8	**7-12k;** R = Et	**7-17k**	81
9	**7-12l;** R = *t*-Bu	**7-17l**	83

Table 7.1 RCM of 1,n-Diynes to Form *trans*-1,5-Chelates

Hoveyda type complex (entry 4). Enyne **7-12h** was treated with **G-II** in the presence of an excess 1-octene afforded *trans*-1,5-chelate **7-17h** in 93% yield (entry 5).



7-19 **7-20**

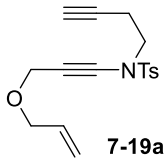
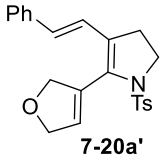
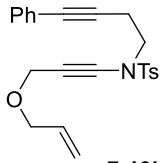
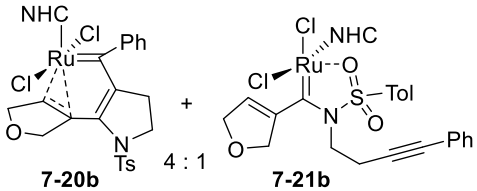
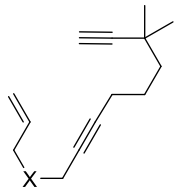
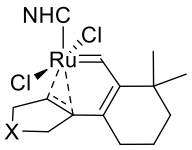
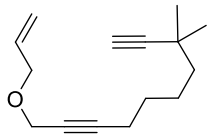
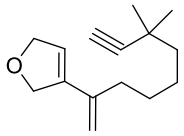
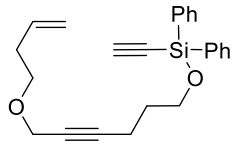
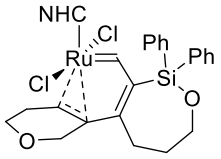
entry	enediyne	product(s)	yield (%)
1	 **7-19a**	 **7-20a'**	43
2	 **7-19b**	 **7-20b** + 4 : 1 **7-21b**	71
3	 **7-19c**; X = O	 **7-20c**	71
4	**7-19d**; X = NTs	**7-20d**	78
5	 **7-19e**	 **7-20e'**	42
6	 **7-19f**	 **7-20f**	84

Table 7.2 Enyne RCM-Induced Formation of trans-1,5-Chelates

Subsequently, formation of *trans*-1,5-chelates with 1,8-enynes (entries 6–9) were explored. 1,8-Enyne **7-12i** having a *gem*-dimethyl moiety was treated with **G-II** under otherwise identical conditions but only

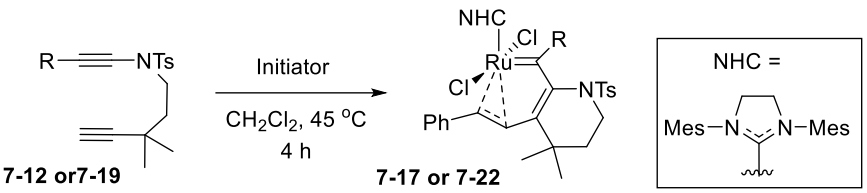
decomposition was observed (entry 6). By replacing the *gem*-dimethyl group of **7-12i** with a diphenyl silyl ether moiety (**7-12j**), smooth conversion was observed to generate *trans*-1,5-chelate **7-17j** in excellent yield (92%, entry 7). Also, 1,8-enynes **7-12k** and **7-12l** afforded only *trans*-1,5-chelates **7-17k** and **7-17l** in 81% and 83% yield, respectively (entries 8 and 9). Interestingly, ether-chelated Hoveyda-type ruthenium alkylidene complexes were not observed with both ethyl silyl ether **7-12k** and *tert*-butyl silyl ether **7-12l**.

7.3.3. Enyne RCM-Induced Formation of *trans*-1,5-Chelates

Next, we investigated the formation of *trans*-1,5-chelates using tandem enyne RCM of endiynes (**Table 7.2**). Enediyne **7-19a** derived from 3-butynamine upon treating with **G-II**, provided only metathesis product 1,3,6-triene **7-20a′** in 43% yield, by initiating the reaction at the terminal alkyne instead of the terminal alkene (entry 1). On the other hand, the reaction of endiyne **7-19b** containing an internal alkyne provided *trans*-1,5-chelate **7-20b** and sulfonamide-chelated ruthenium alkylidene **7-21b** in a 4:1 ratio (71%, entry 2). Tandem RCM of endiynes **7-19c** and **7-19d** smoothly afforded *trans*-1,5-chelates **7-20c** and **7-20d** in 71% and 78% yield, respectively (entries 3 and 4). Linear endiyne **7-19e** underwent enyne RCM catalyzed by **G-II** to generate ruthenium alkylidene, which did not further cyclize to form a seven-membered ring, instead underwent cross metathesis occurred to produce **7-20e′** in 42% yield (entry 5). On the other hand, endiyne **7-19f** containing a diphenyl silyl ether reacted smoothly with **G-II** to afford **7-20f** in 84% yield (entry 6).

7.3.4. New Reactivity of Enediynes to Form *trans*-1,5-Chelates

The successful use of 1,n-diynes and endiynes to form *trans*-1,5-chelates, we next examined ynamide containing endiynes (**Table 7.3**). It is interesting to note that the metathesis reaction of **7-19a** intiates at the alkyne moiety not the alkene to provide **7-20a′**. The chemoselectivity for the initiation at terminal alkyne instead of terminal alkene is somewhat unusual. To further probe this unusual initiation, we have synthesized endiyne **7-19g** having *gem*-dimethyl moiety at the propargylic carbon.



7-12 or7-19 → **7-17 or 7-22**

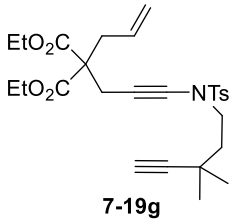
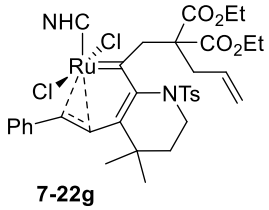
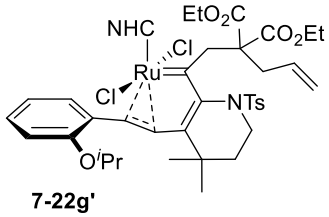
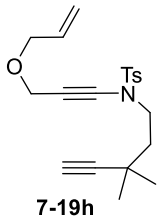
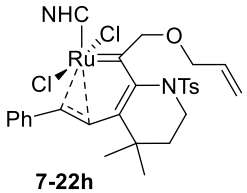
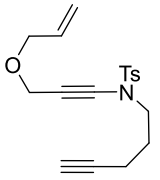
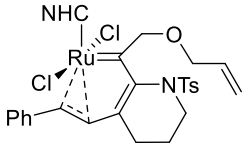
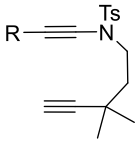
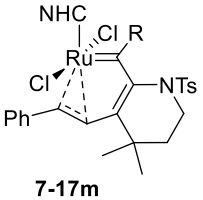
entry	1,n-diyne	initiator	product(s)	yield (%)
1	 **7-19g**	**G-II**	 **7-22g**	87
2	**7-19g**	**HG-II**	 **7-22g'**	91
3	**7-19g**	**G-I**	75% SM recovered	---
4	 **7-19h**	**G-II**	 **7-22h**	88
5	 **7-19i**	**G-II**	 **7-22i**	34
6	 **7-12m**, R = H	**G-II**	 **7-17m**	68
7	**7-12n**, R = Ph	**G-II**	decomposed	---

Table 7.3 New Reactivity of Enediynes to Form *trans*-1,5-Chelates

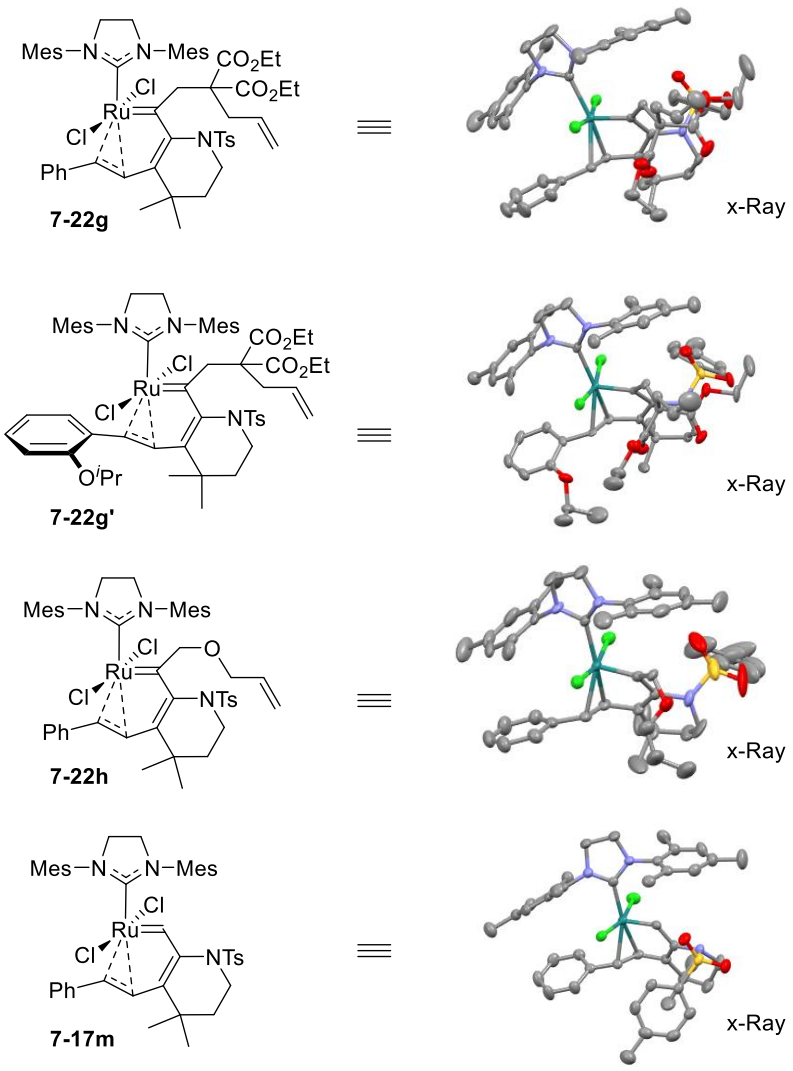


Figure 7.1 X-Ray Structures

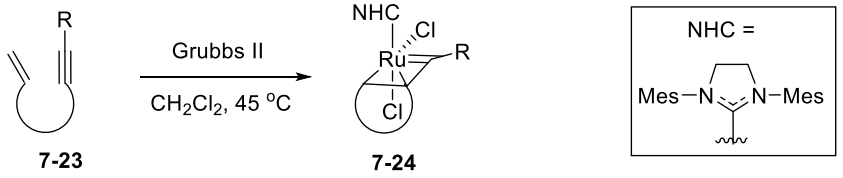
Endiyne **7-19g** reacted smoothly to provide *trans*-1,5-chelate **7-22g** via initiating the reaction at sterically hindered terminal alkyne (entry 1). Interestingly, the reaction not only generate an alkyne-initiated *trans*-1,5-chelate but also was prevented from further cyclization with the tethered alkene moiety. The same substrate **7-19g** was also tested with **HG-II** and **G-I** complexes. The reaction with **HG-II** led the alkene-chelated complex **7-22g′** (entry 2), whereas with **G-I** no reaction was observed (entry 3). The structures of *trans*-1,5-chelates **7-22g** and **7-22g′** were further confirmed by single crystal X-ray diffraction analysis (**Figure 7.1**). Less sterically hindered allyl ether-tethered endiyne **7-19h** reacted with **G-II** to afford *trans*-1,5-chelate **7-22h** in 88% yield. The structure of *trans*-1,5-chelate **7-22h** was further confirmed by X-ray

crystallography analysis (entry 4). On the other hand, substrate **7-19i** devoid of a *gem*-dimethyl group provided **7-22i** in 34% yield (entry 5). The formation *trans*-1,5-chelate can be explained by the increased flexibility of C−C bond rotation due to lack of *gem*-dimethyl group. The surprising new reactivity of these endiynes encouraged us to examine the reactivity of 1,7-diyne **7-12m**. Similar to the previous cases the reaction initiated at a more hindered alkyne near a *gem*-dimethyl substituent instead of an electron-rich terminal ynamide providing 1,5-chelate **7-17m** in 68% yield (entry 6). Unexpectedly, however, the reaction of diyne **7-12n** led only decompose product under the reaction conditions (entry 7). The new mode of enyne metathesis for ynamide-containing diynes and endiynes might be the consequence of the sulfonamide coordination with the reacting ruthenium complex such that initiation occurs selectively even at the alkyne near the *gem*-dimethyl substituent.

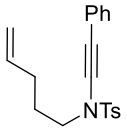
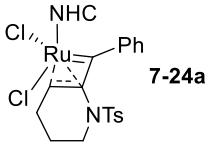
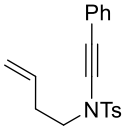
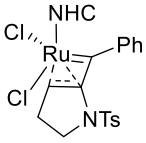
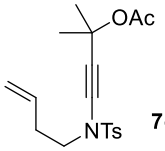
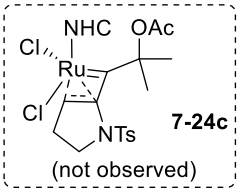
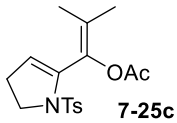
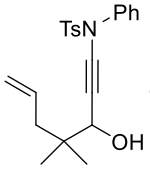
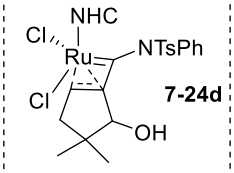
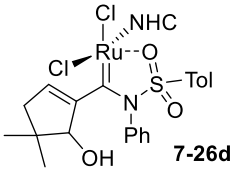
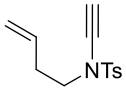
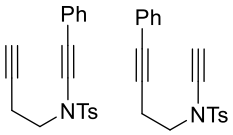
7.3.5. Enyne RCM of 1,n-Enynes to Form η^3-Complexes

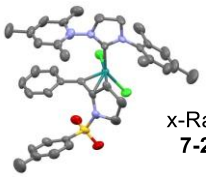
The failure of forming the expected chelate from diyne **7-12n** in **Table 7.3**, promoted us to introduce an alkene instead of the terminal alkyne. Surprisingly, treatment of enyne **7-23a** with **G-II** under otherwise identical conditions smoothly afforded a green solid in 94% yield (**Table 7.4**, entry 1). The spectroscopic data of this green complex agree with *cis*-dichloro complex chelated either with the sulfonyl oxygen or the alkene. The crystal structure of this green solid clearly identifies cis alkene-chelated η^3-complex **7-24a**. 1,5-Enyne **7-23b** also provided alkene-chelated η^3-complex **7-24b** in 92% yield (entry 2), and a propargyl acetate substituent 1,5-enyne of **7-23c** provided **7-25c** in 88% yield (entry 3). The formation of compound **7-25c** can be explained by the formation of ruthenium alkylidene **7-24c** followed by its rearrangement via an intermediate **7-27c** and **7-28c** (**Scheme 7.11**). The enynes were further modified by changing the sulfonamide position. Enyne **7-23d** with stoichiometric **G-II** smoothly generated a new crystalline red colored complex **7-26d** in 86% yield (entry 4). The X-ray crystallographic analysis of the red colored crystal clearly identified the sulfonamide-chelated ruthenium alkylidene rather than alkene-chelated ruthenium alkylidene **7-24d**. Interestingly, a terminal alkyne tethered enyne **7-23e** just decomposed under the same reaction condition (entry 5). The reaction of differently substituted 1,6-diynes **7-23f** and **7-23g** with **G-II**

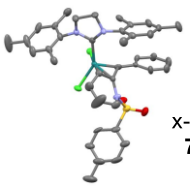
also led only decomposition (entry 6).



7-23 **7-24**

entry	1,n-diyne	product(s)	yield (%)
1	 **7-23a**	 **7-24a**	94
2	 **7-23b**	 **7-24b**	92
3	 **7-23c**	 **7-24c** (not observed)  **7-25c**	88
4	 **7-23d**	 **7-24d** (not observed)  **7-26d**	86
5	 **7-23e**	decomposed	--
6	 **7-23f** **7-23g**	decomposed	--


x-Ray of **7-24a**


x-Ray of **7-24b**

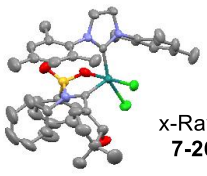
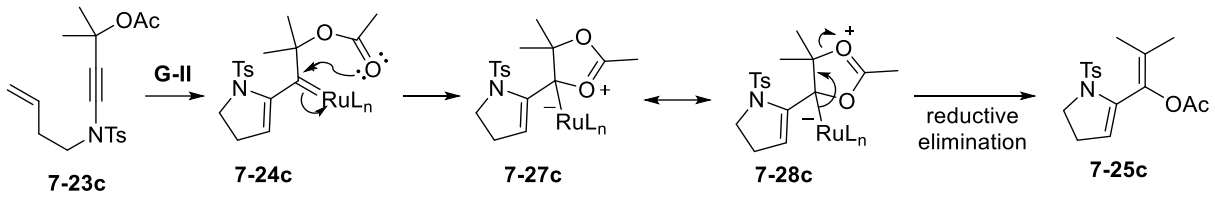

x-Ray of **7-26d**

Table 7.4 Enyne RCM of 1,n-Enynes to Form η^3- Vinylcarbene Complexes

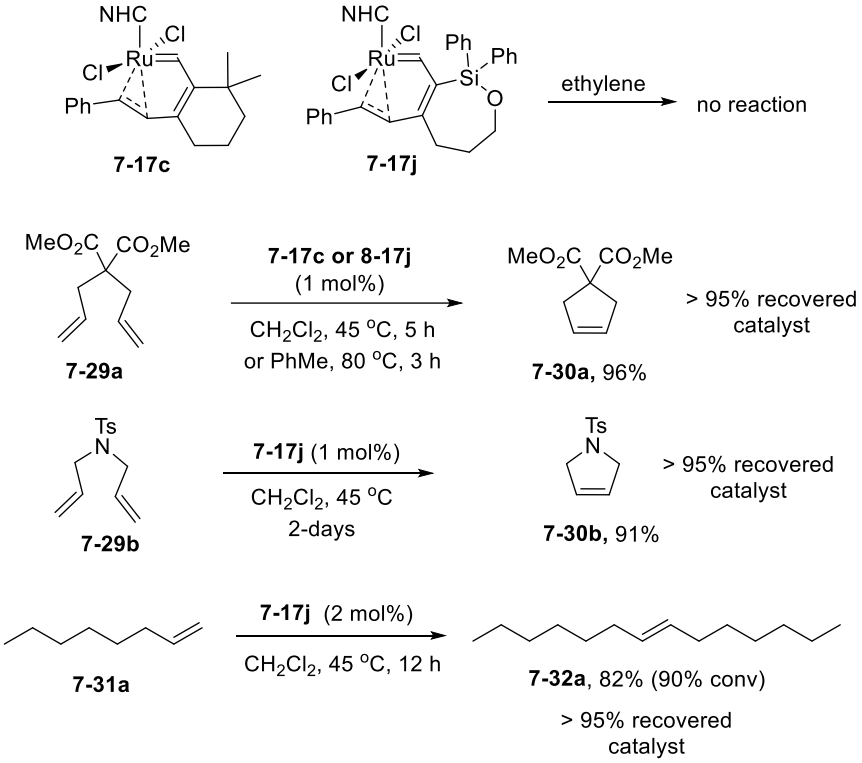


Scheme 7.11 Possible Mechanism for the Formation of 7-25c

The chelation behavior of 1,n-diynes, enynes, and enediynes suggest that the subtle steric and electronic influence of the substituent on the carbenic carbon is critical for the formation of these chelates. The corresponding diynes and endiynes devoid of the *gem*-dialkyl substituent at the propargylic carbon did not form *trans*-1,5-chelates rather provided the oligomerization/polymerization.

7.3.6. Metathesis Activity of Alkene-Chelated Ruthenium Alkylidenes

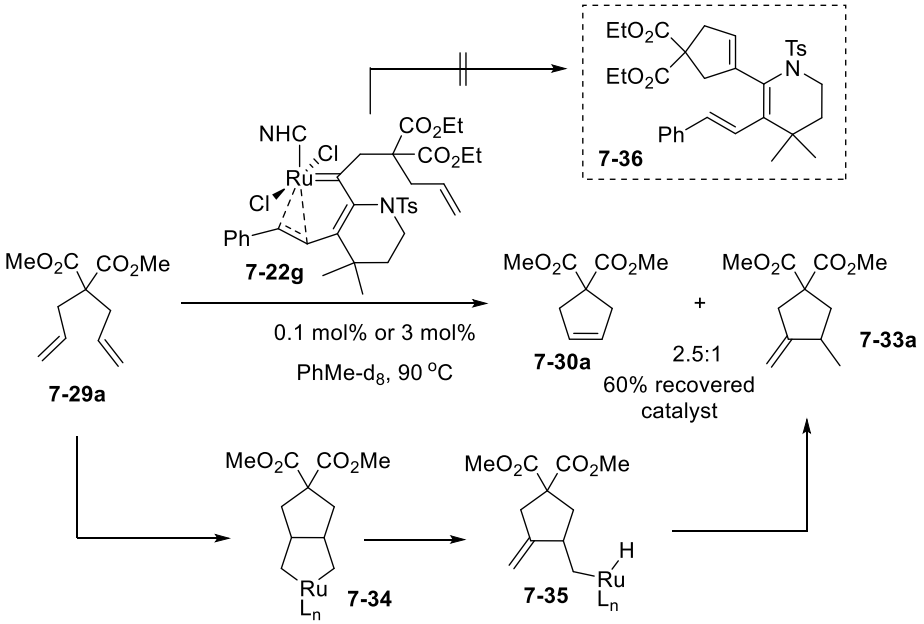
The metathesis activity of some of these new ruthenium chelates was examined (**Scheme 7.12**). Chelates **7-17c** and **7-17j**, when treated with ethylene were recovered unchanged. On the other hand, RCM



Scheme 7.12 Metathesis Activity of *trans*-1,5-Chelates Derived from 1,n-Diynes

of dienes **7-29a** and **7-29b** using 1−3 mol% of diyne-derived chelates in CH_2Cl_2 at 40 °C provided ring-closed products **7-30a** and **7-30b**. Cross metathesis with these chelates was also examined for 1-octene, the at 45 °C for 12 h, which provided cross metathesis product **7-32a** in 82% yield. Interestingly, in all cases >95% of catalyst was recovered.

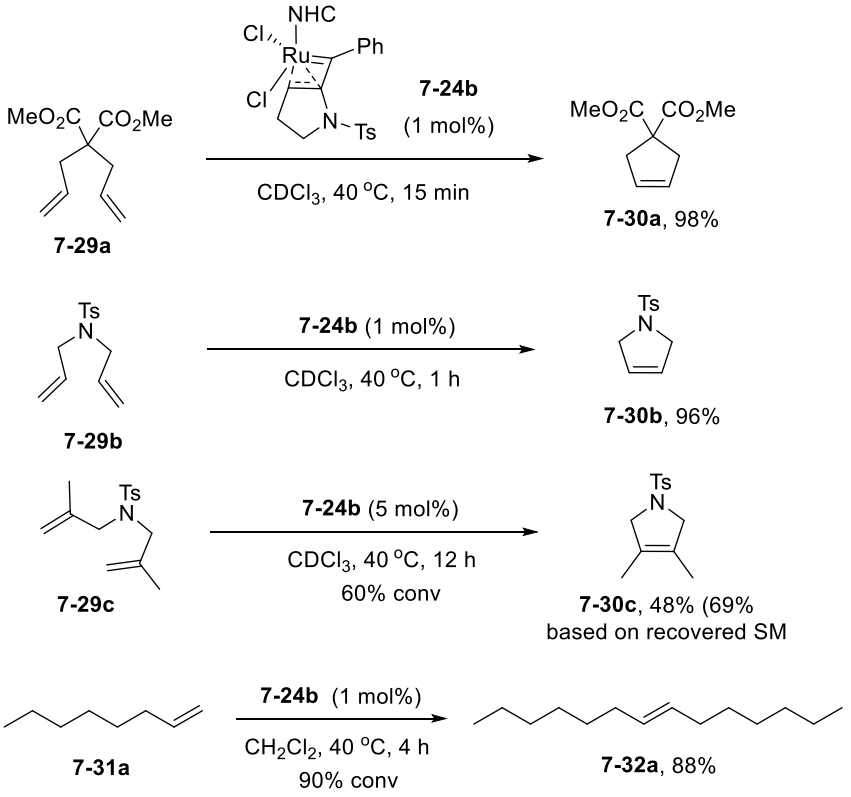
Next, metathesis activity of *trans*-1,5-chelate **7-22** derived from endiynes were tested (**Scheme 7.13**). The RCM of diene **7-29a** in the presence of a catalytic amount of **7-22g** for 12 h in toluene-d_8 at 90 °C provided a mixture of metathesis products **7-30a** and **7-33a** in a 2.5:1 ratio, whereas no reaction was observed in $CDCl_3$ at 45 °C. The formation of product **7-33a** can be explained by the ruthenium catalyzed cyclization of diene to generate **7-34** and which then undergo β–hydride elimination (**7-35**) followed by reductive elimination to provide product **7-33a**.



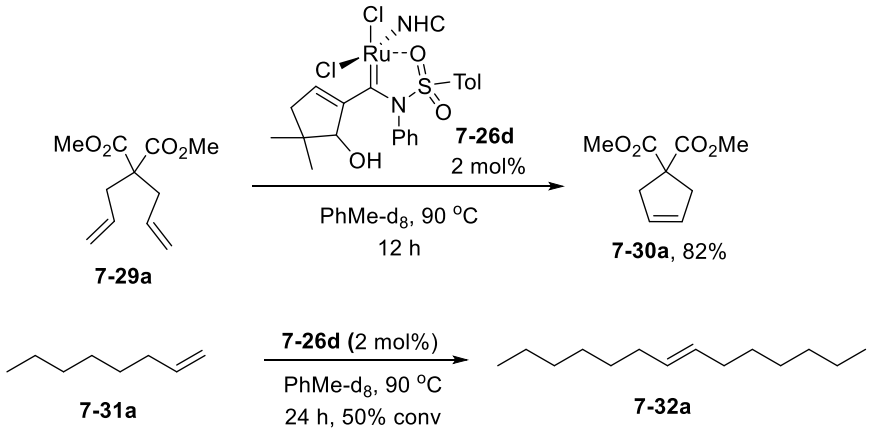
Scheme 7.13 Metathesis Activity of *trans*-1,5-Chelates Derived from Dienynes

Finally, η^3-vinylcarbene complex **7-24b** was tested in both RCM and CM reactions (**Scheme 7.14**). The RCM of dienes **7-29a** and **7-29b** with 1 mol% of **7-24b** in $CDCl_3$ at 40 °C smoothly converted ring-closed products **7-30a** and **7-30b** in 98% and 96% yield, respectively. After the purification, 90% of catalyst **7-24b** was recovered. The RCM of highly hindered diene **7-29c** was also tested with 5 mol% of **7-24b** under

the same reaction conditions to provide cyclized product **7-30c** in 69% yield with some recovered starting material. The cross metathesis of 1-octene with 1 mol% of **7-24b** afforded the cross metathesis product in 88% yield. (Note: η^3-vinylcarbene complexes **7-6** reported by Grubbs were found to be metathesis inactive.)



Scheme 7.14 Metathesis Activity of Alkene Chelated η^3-Complex 7-24b



Scheme 7.15 Metathesis Activity of Sulfonamide Chelate 7-26d

The metathesis activity of sulfonamide-chelate **7-26d** was also tested (**Scheme 7.15**). The RCM of diene **7-29a** with 2 mol % of **7-26d** in $CDCl_3$ at 40 ^oC, returned only starting materials, however, the same reaction in toluene-d_8 at 90 ^oC slowly promoted cyclization to provide **7-30b** in 82% yield. The cross metathesis of this catalyst was very slow, leading to 50% converstion after 24 h.

7.4. Summary

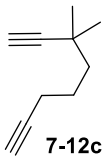
In summary, novel metathesis active *trans*-1,5-alkene-chelated ruthenium alkylidene complexes were prepared via enyne cross metathesis (CM) and ring-closing metathesis (RCM). The RCM of 1,n-diynes and ene-1,n-diynes using stoichiometric amount of Grubbs second-generation complex led to the formation of alkene-chelated ruthenium alkylidenes, where the chelated alkene is trans to the *N*-heterocyclic carbene. This chelation behavior is somewhat different from that observed by Grubbs where a 2:3 equilibrium ratio of cis chelates were observed upon treatment of 1,2-divinyl styrene with the Grubbs third-generation complex. The diyne derived *trans*-1,5-alkene-chelates showed metathesis activity with dienes and a recovered catalyst. On the other hand, under the same conditions ene-ynamides generate η^3-vinylcarbene complexes. These complexes show good metathesis activity contrary to a related η^3-vinylcarbene complexes generated from diphenyl acetylene/phenyl-1-propyne by Grubbs, which were metathesis-inactive.

7.5. Experimental Details

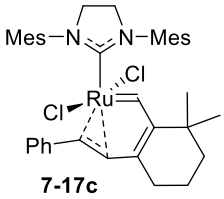
7.5.1. General Information: For general information see section 6.6.1.

7.5.2. General Procedure for Metal Complex Formation: Compund **7-12c** (9 mg, 0.066 mmol) and Grubbs II (51 mg, 0.06 mmol) was dissolved in CH_2Cl_2 (4 mL) in an air-free sealed tube and heated up to 45 ^oC over 4 h. The solvent was removed under reduced pressure and the crude product was purified by flash column chromatography (SiO2, Hexanes : EtOAc = 5 : 1) to afford **7-17c** (38 mg, 91%) as a red solid.

7.5.3. Selected Characterization Data

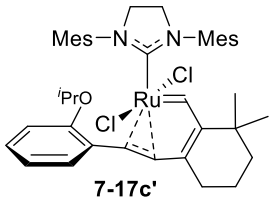

7-12c

7-12c: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.20 (dt, *J* = 7.1, 2.8 Hz, 2H), 2.06 (s, 1H), 1.94 (t, *J* = 2.6 Hz, 1H), 1.71─1.65 (m, 2H), 1.50─1.46 (m, 2H), 1.20 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 91.5, 84.3, 68.5, 68.0, 42.2, 30.8, 29.1, 24.4, 18.8; HRMS (ESI**)** calcd for $C_{10}H_{13}$ $[M─H]^+$ 133.1017, found 133.1018.


7-17c

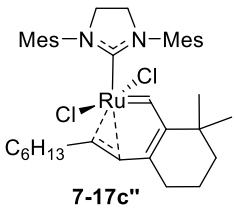
E/Z = 9 : 1

7-17c (38 mg, 91%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 16.56 (s, 1H), 7.20 (t, *J* = 7.0 Hz, 1H), 7.10─7.03 (m, 5H), 6.99 (bs, 1H), 6.54 (bs, 1H), 5.41 (d, *J* = 13.0 Hz, 1H), 4.48 (d, J = 13.0 Hz, 1H), 4.01─3.95 (m, 4H), 2.32─2.23 (m, 15H), 1.32 (m, 4H), 0.71 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 312.7, 207.1, 167.0, 160.4, 138.4, 137.7, 137.5, 137.1, 135.3, 134.1, 130.0, 129.5, 128.5, 126.6, 123.3, 107.6, 52.2, 51.7, 38.3, 34.5, 33.5, 28.6, 27.7, 26.6, 26.2, 21.1, 21.0, 19.7, 18.8, 18.6; HRMS (ESI**)** calcd for $C_{38}H_{46}N_2Cl_2Ru$ $[M]^+$ 702.2082 found, 702.2083.


7-17c'

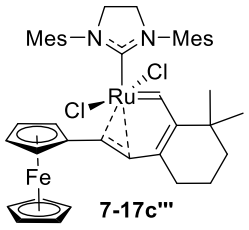
E/Z = 14 : 1

7-17c′ (40 mg, 88%)**:** ^{1}H NMR (500 MHz, $CDCl_3$) δ 16.65 (s, 1H), 7.15 (d, *J* = 7.1 Hz, 1H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.98 (s, 2H), 6.68 (d, *J* = 8.2 Hz, 1H), 6.62 (s, 2H), 6.54 (t, *J* = 7.4 Hz, 1H), 5.22─5.21 (m, 2H), 4.41─4.38 (m, 1H), 4.02─3.95 (m, 4H), 2.49 (s, 6H), 2.32 (s, 3H), 2.30 (s, 6H), 2.26 (s, 3H), 1.72─1.63 (m, 4H), 1.36─1.33 (m, 2H), 1.24 (s, 3H), 1.23 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 212.3, 207.5, 166.9, 160.6, 154.8, 138.3, 137.9, 137.5, 137.3, 134.6, 130.0, 129.7, 127.5, 126.7, 126.4, 125.1, 121.3, 113.5, 102.0, 70.2, 52.3, 51.9, 38.5, 34.7, 33.6, 28.7, 22.0, 21.2, 21.0, 19.9, 18.9, 18.7; HRMS (ESI**)** calcd for $C_{41}H_{52}Cl_2N_2ORu$ $[M]^+$ 760.2505, found 760.2486.


7-17c"

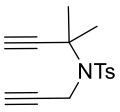
7-17c″ (41 mg, 96%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 16.52 (s, 1H), 6.96 (s, 2H), 6.91 (s, 2H), 4.78 (d, *J* = 12.9 Hz, 1H), 4.10 (m, 4H), 3.76─3.70 (m, 1H), 2.57 (s, 6H), 2.29 (s, 3H), 2.27 (s, 3H), 1.27─1.25 (m, 6H), 1.77─1.13 (m, 16H), 0.87 (t, *J* = 7.2 Hz, 6H), 0.64 (bs, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 311.1, 208.3, 167.2, 158.2, 139.2, 138.8, 138.5, 137.6, 136.9, 129.8, 129.3, 128.0, 113.1, 52.3, 51.2, 38.2, 34.0, 33.5, 31.7, 31.3, 31.2,

30.8, 30.7, 29.2, 27.8, 27.7, 26.6, 22.7, 21.1, 21.0, 20.6, 14.2; HRMS (ESI**)** calcd for $C_{38}H_{53}N_2Ru$ $[M-2Cl-H]^+$ 639.3252 found, 639.3285.



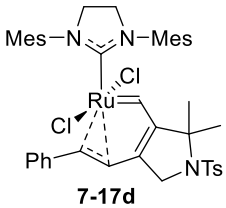
7-17c'''

7-17c'''(31.6 mg, 65%): ^{1}H NMR (500 MHz, $CDCl_3$) δ16.51 (s, 1H), 6.97 (bs, 2H), 6.65 (s, 2H), 5.01 (d, *J* = 13.0 Hz, 1H), 4.47 (d, *J* = 13.0 Hz, 1H), 4.09─3.97 (m, 13 H), 2.30 (s, 12 H), 2.23 (s, 6H), 1.65 (m, 2H), 1.54 (m, 2H), 1.34 (m, 2H), 0.70 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 312.2, 208.0, 167.0, 159.2, 138.4, 137.7, 137.6, 137.2, 134.3, 130.0, 129.9, 129.7, 129.5, 128.6, 126.6, 121.0, 108.4, 69.1, 52.2, 51.7, 38.4, 34.9, 21.2, 21.0, 20.0, 18.8, 18.7; HRMS (ESI**)** calcd for $C_{42}H_{50}N_2Cl_2FeRu$ $[M]^+$ 810.1744, found 810.1743.



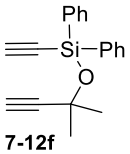
7-12d

7-12d: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 2H), 4.38 (d, *J* = 2.3 Hz, 2H), 2.41 (s, 3H), 2.39 (s, 1H), 2.31 (t, *J* = 2.3 Hz, 1H), 1.72 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.2, 139.6, 129.4, 127.3, 85.8, 81.2, 72.4, 72.3, 56.7, 36.9, 30.1.



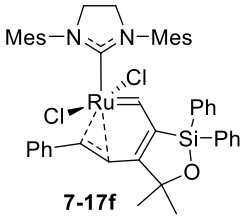
7-17d

7-17d (2.5 mg, 5%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 16.17 (s, 1H), 7.85─7.83 (m, 1H), 7.69 (d, *J* = 8.2 Hz, 2H), 7.48─7.47 (m, 1H), 7.36─7.32 (m, 2H), 7.26─7.25 (m, 2H), 6.96─6.94 (m, 1H), 6.57─6.52 (m, 1H), 5.35 (d, *J* = 14.0 Hz, 1H), 5.06 (d, *J* = 14.0 Hz, 1H), 3.98 (m, 2H), 3.13 (s, 2H), 2.40─2.27 (m, 18 H), 1.29 (s, 6H); HRMS (ESI**)** calcd for CHO $[M+H]^+$. HRMS (ESI**)** calcd for $C_{43}H_{48}N_3O_2SCl_2Ru$ $[M-H]^+$ 842.1888, found 842.1920.



7-12f

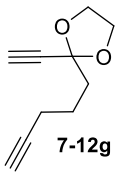
7-12f: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78─7.76 (m, 4H), 7.44─7.38 (m, 6H), 2.77 (s, 1H), 2.34 (s, 1H), 1.66 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.8, 134.7, 130.3, 127.8, 96.6, 87.7, 86.4, 72.0, 68.7, 32.4; HRMS (ESI**)** calcd for $C_{19}H_{19}OSi$ $[M+H]^+$ 291.1205, found 291.1204.



7-17f

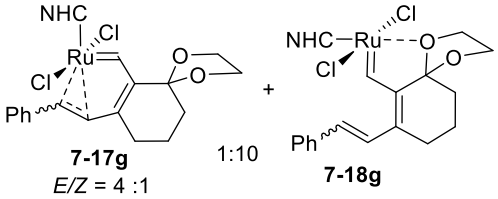
7-17f (42 mg, 82%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 16.02 (s, 1H), 7.51─7.49 (m, 2H), 7.42 (m, 8H), 7.23 (t, *J* = 7.0 Hz, 1H), 7.09─7.03 (m, 4H), 6.94 (s, 2H), 6.26 (bs, 2H), 5.77 (d, *J* = 13.5 Hz, 1H), 4.79 (d, *J* = 13.5 Hz, 1H), 4.02─3.99 (m, 4H), 2.32 (s, 9H), 2.21 (s, 6H), 2.01 (s, 3H), 1.53 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ

311.9, 204.9, 182.6, 159.8, 138.0, 137.9, 137.2, 137.0, 135.1, 134.3, 133.6, 130.6, 129.8, 129.4, 128.8, 128.0, 126.9, 126.3, 123.7, 107.8, 86.2, 51.8, 51.6, 28.2, 21.3, 21.1, 19.7, 18.8; HRMS (ESI**)** calcd for $C_{47}H_{49}N_2OSiRu$ $[M-2Cl-H]^+$ 787.2658, found 787.2637.

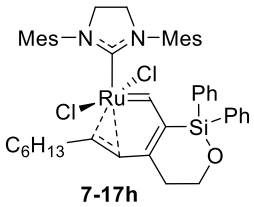


7-12g

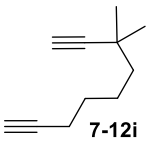
7-12g: ^{1}H NMR (500 MHz, $CDCl_3$) δ 4.08─4.05 (m, 2H), 3.97─3.95 (m, 2H), 2.49 (s, 1H), 2.24 (dt, *J* = 2.6 Hz, *J* = 7.1 Hz, 2H), 2.01─1.99 (m, 2H), 1.94 (t, *J* = 2.6 Hz, 1H), 1.79─1.74 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 102.6, 83.9, 81.4, 72.1, 68.7, 64.7, 37.9, 22.8, 18.2; HRMS (ESI**)** calcd for $C_{10}H_{11}O_2$ $[M-H]^+$ 163.0759, found 163.0766.



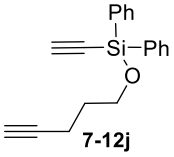
7-17g and **7-18g** (34 mg, 78%): ^{1}H NMR (500 MHz, $CDCl_3$) Characteristic signal of **7-18g** δ 18.04 (s, 1H); Characteristic signal of **7-17g** δ 16.43 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 285.2, 269.4, 218.1, 208.8, 160.0, 153.9, 138.6, 130.4, 230.3, 230.0, 129.9, 129.7, 129.6, 129.4, 129.3, 129.2, 129.9, 128.9, 128.9, 128.6, 128.2, 127.9, 127.1, 126.8, 126.7, 126.6, 124.4, 108.3, 107.4, 70.0, 67.8, 64.6, 64.4, 64.2, 52.8, 52.0, 51.7, 50.6, 35.7, 34.0, 29.7, 28.4, 27.0, 26.9, 26.8, 26.4, 26.2, 25.5, 21.4, 21.3, 21.2, 20.2, 19.3, 18.1; HRMS (ESI**)** calcd for C38 $H_{44}N_2O_2ClRu$ $[M-Cl]^+$ 697.2135, found 697.2134.



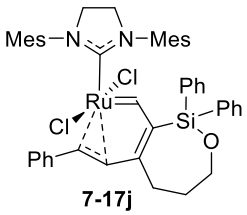
7-17h (47 mg, 93%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 16.43 (s, 1H), 7.47 (t, *J* = 7.4 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 4H), 7.31 (d, *J* = 7.1 Hz, 4H), 6.94 (s, 2H), 6.20 (s, 2 H), 5.07 (d, *J* = 13.0 Hz, 1H), 4.09─4.05 (m, 4H), 3.97─3.86 (m, 3H), 2.56 (s, 6H), 2.34 (s, 3H), 2.30 (s, 6H), 2.02 (t, *J* = 4.9 Hz, 2H), 1.73 (s, 3H), 1.60 (m, 2H), 1.28─1.12 (m, 8H), 0.88 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 312.2, 206.7, 171.7, 155.8, 139.3, 138.9, 138.1, 136.9, 136.4, 135.2, 133.7, 133.4, 131.7, 130.4, 130.0, 129.5, 129.4, 127.0, 112.7, 60.6, 52.3, 51.1, 37.9, 31.7, 30.8, 30.7, 29.1, 27.8, 26.3, 22.7, 20.9, 20.6, 18.8, 14.2; HRMS (ESI**)** calcd for $C_{46}H_{55}N_2OSiRu$ $[M-2Cl-H]^+$ 781.3127, found 781.3052.



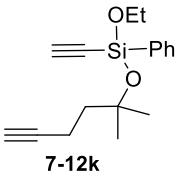
7-12i: ^{1}H NMR (500 MHz, $CDCl_3$) δ 2.21 (m, 2H), 2.07 (s, 1H), 1.94 (s, 1H), 1.55 (m, 4H), 1.42─1.40 (m, 2H), 1.21 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 91.8, 84.5, 68.2, 67.7, 42.6, 31.0, 29.1, 28.9, 24.5, 18.4; LRMS (EI**)** calcd for $C_{11}H_{15}$ $[M─H]^+$ 147.1, found 147.1.



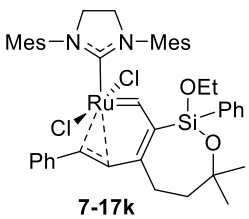
7-12j: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82─7.81 (m, 4H), 7.52─7.46 (m, 6H), 4.01 (t, *J* = 6.1 Hz, 2H), 2.78 (s, 1H), 2.41 (dt, *J* = 2.6 Hz, *J* = 7.1 Hz, 2H), 1.99 (t, *J* = 2.6 Hz, 1H), 1.94─1.91 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.7, 133.1, 130.7, 128.1, 96.8, 84.9, 84.1, 68.6, 62.8, 31.2, 15.1; HRMS (ESI**)** calcd for $C_{19}H_{19}OSi$ $[M+H]^+$ 291.1205, found 291.1201.



7-17j (47 mg, 92%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 16.38 (s, 1H), 7.50 (t, *J* = 7.2 Hz, 2H), 7.42 (t, *J* = 7.3 Hz, 4H), 7.35 (d, *J* = 7.0 Hz, 4H), 7.24─7.23 (m, 1H), 7.18 (d, *J* = 7.6 Hz, 2H), 7.09 (t, *J* = 7.53 Hz, 2H), 6.55 (bs, 2H), 6.05 (bs, 2H), 5.67 (d, *J* = 12.7 Hz, 1H), 4.91 (d, *J* = 12.7 Hz, 1H), 3.92 (bm, 6H), 2.29─2.24 (m, 18H), 1.46 (s, 4H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 315.1, 206.2, 181.2, 157.5, 137.8, 137.8, 136.3, 135.3, 135.1, 134.6, 133.9, 133.9, 130.2, 129.8, 129.5, 128.7, 128.3, 128.1, 128.0, 126.8, 126.6, 109.5, 65.3, 52.3, 51.7, 37.6, 28.9, 26.4, 26.2, 21.2, 20.5, 20.0, 19.9, 18.7, ; HRMS (ESI**)** calcd for $C_{44}H_{49}N_2O_2SiRu$ $[M─2Cl─H]^+$ 767.2618, found 767.2575.

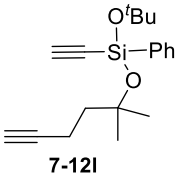


7-12k: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75─7.73 (m, 2H), 7.45─7.40 (m, 3H), 3.91 (q, *J* = 5.0 Hz, 2H), 2.55 (s, 1H), 2.39─2.35 (m, 2H), 1.94 (t, *J* = 2.6 Hz, 1H), 1.90─1.86 (m, 2H), 1.41 (s, 6H), 1.27 (t, *J* = 5.0 Hz, 3H), ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.1, 133.8, 130.5, 127.9, 93.8, 85.6, 85.1, 75.9, 67.9, 59.3, 43.2, 29.4, 29.3, 18.1, 13.7; HRMS (ESI**)** calcd for $C_{17}H_{22}O_2SiNa$ $[M+Na]^+$ 309.1287, found 309.1282.



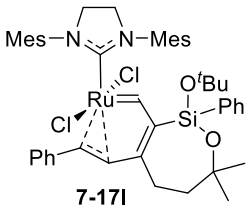
7-17k (41 mg, 81%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 16.17, 7.47─7.46 (m, 1H), 7.43─7.37 (m, 5H), 7.22─7.21 (m, 2H), 7.07─7.05 (m, 5H), 6.83 (bs, 1H), 6.44 (bs, 1H), 5.64 (d, *J* = 12.7 Hz, 1H), 4.64 (d, *J* = 12.3 Hz, 1H), 4.00─3.88 (m, 4H), 3.56─3.53 (m, 1H), 3.46─3.43 (m, 1H), 2.36─2.28 (m, 11H), 2.09─1.93 (m, 9H), 1.20─1.12 (m, 9H), 0.96 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 316.6, 206.2, 181.0, 156.3, 138.5, 137.7,

136.4, 136.2, 135.4, 134.7, 134.1, 130.0, 129.6, 129.5, 128.7, 127.6, 126.6, 126.4, 73.9, 58.9, 52.1, 51.8, 40.2, 35.6, 29.5, 21.2, 21.0, 20.0, 19.5, 19.1, 18.6, 18.2, ; HRMS (ESI**)** calcd for $C_{45}H_{54}N_2O_2ClRuSi$ $[M-Cl]^+$ 819.2687 found, 819.2675.



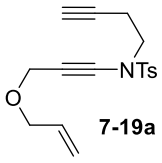
7-12l

7-12l: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80─7.78 (m, 2H), 7.44─7.40 (m, 3H), 2.57 (s, 1H), 2.40─2.36 (m, 2H), 1.95 (t, *J* = 2.6 Hz, 1H), 1.89─1.86 (m, 2H), 1.43─1.37 (m, 15H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.3, 134.0, 130.1, 127.7, 94.9, 93.3, 87.9, 85.2, 75.7, 67.9, 43.3, 31.8, 29.4, 13.7; HRMS (ESI**)** calcd for $C_{19}H_{26}O_2NaSi$ $[M+Na]^+$ 337.1600, found 337.1595.



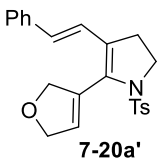
7-17l

7-17l (44 mg, 83%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 16.07 (s, 1H), 7.45─7.37 (m, 5H), 7.21─7.19 (m, 1H), 7.06─7.03 (m, 4H), 6.86 (s, 2H), 6.35 (s, 1H), 5.67 (d, *J* = 12.6 Hz, 1H), 5.22 (s, 1H), 4.45 (d, *J* = 12.6 Hz, 1H), 4.04─3.86 (m, 4H), 2.74 (s, 3H), 2.44 (s, 3H), 2.30 (s, 3H), 1.98 (s, 3H), 1.87 (s, 3H), 1.83 (s, 3H), 1.78 (m, 2H), 1.38 (m, 5H), 1.21 (s, 9H), 1.13 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 317.5, 206.4, 179.4, 158.4, 138.6, 138.3, 138.1, 137.6, 137.2, 136.0, 135.6, 134.6, 134.1, 130.2, 129.9, 129.7, 129.4, 129.1, 128.7, 127.4, 126.4, 126.2, 125.7, 104.9, 74.1, 73.5, 51.8, 40.2, 35.5, 31.8, 31.7, 31.5, 31.3, 31.2, 28.2, 27.7, 26.6, 21.2, 21.1, 20.1, 19.3, 19.2, 18.4; HRMS (ESI**)** calcd for $C_{47}H_{58}Cl_1N_2O_2RuSi$ $[M-Cl]^+$ 847.3009, found 847.2999.



7-19a

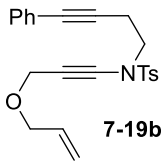
7-19a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.88─5.80 (m, 1H), 5.26─5.16 (m, 2H), 4.24 (s, 2H), 3.95 (d, *J* = 5.6 Hz, 2H), 3.48 (t, *J* = 7.6 Hz, 2H), 2.49 (dt, *J* = 2.4 Hz, 7.7 Hz, 2H), 2.41 (s, 3H), 1.96 (t, *J* = 2.4 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 134.5, 134.1, 129.9, 127.6, 117.7, 79.6, 79.0, 70.7, 70.1, 68.0, 57.5, 50.0, 18.4; HRMS (ESI**)** calcd for $C_{17}H_{20}O_3NS$ $[M+H]^+$ 318.1164, found 318.1160.



7-20a'

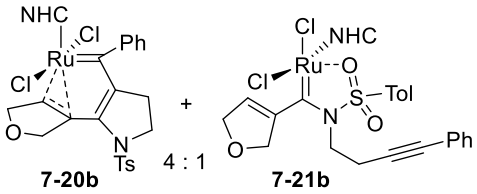
7-20a′ (11 mg, 43%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.34-7.22 (m, 7H), 6.96 (d, *J* = 16.0 Hz, 1H), 6.28 (d, *J* = 16.0 Hz, 1H), 6.08 (s, 1H), 4.97-4.91 (m, 4H), 3.86 (t, *J* = 8.4 Hz, 2H), 2.42 (s, 3H), 2.31-2.27 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$)

δ 144.1, 136.9, 133.1, 130.6, 129.7, 129.3, 128.8, 128.1, 127.9, 127.7, 126.4, 121.7, 76.0, 49.6, 29.2, 21.7; HRMS (ESI**)** calcd for $C_{23}H_{24}NO_3S$ $[M+H]^+$ 394.1477 found, 394.1472



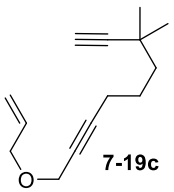
7-19b

7-19b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.36─7.26 (m, 7H), 5.89─5.84 (m, 1H), 5.30─5.19 (m, 2H), 4.28 (s, 2H), 3.98 (d, *J* = 5.7 Hz, 2H), 3.61 (t, *J* = 7.5 Hz, 2H), 2.76 (t, *J* = 7.5 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 134.7, 131.7, 129.9, 128.2, 128.0, 127.7, 123.2, 117.8, 85.2, 82.7, 79.2, 70.2, 68.0, 57.6, 50.2, 21.7, 19.5.



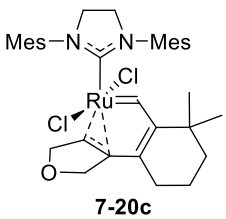
7-20b 4 : 1 **7-21b**

7-20b (36 mg, 71%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.31-6.86 (m, 8H), 6.46 (s, 1H), 6.29 (m, 2H), 4.92 (d, *J* = 12.1 Hz, 1H), 4.67 (s, 1H), 4.49 (d, *J* = 12.1 Hz, 1H), 4.22 (d, *J* = 18.4 Hz, 1H), 4.00-3.75 (m, 5H), 3.53-3.37 (m, 2H), 2.77 (s, 3H), 2.63 (s, 3H), 2.44 (m, 5H), 2.34 (s, 3H), 2.30 (s, 3H), 2.24 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 282.2, 203.9, 169.3, 145.0, 139.2, 129.1, 138.3, 137.4, 134.6, 131.0, 130.2, 130.0, 129.8, 129.4, 128.9, 128.2, 127.7, 125.6, 112.3, 96.1, 87.6, 69.8, 66.9, 53.1, 52.9, 52.0, 26.9, 26.4, 21.8, 21.2, 20.6, 19.3, 19.1, 18.8; HRMS (ESI**)** calcd for $C_{43}H_{46}N_3O_3SRu$ $[M-2Cl-H]^+$ 786.2303 found, 786.2277.



7-19c

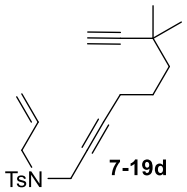
7-19c: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.93─5.85 (m, 1H), 5.28 (dd, *J* = 1.6 Hz, *J* = 17.2 Hz, 1H), 5.18 (dd, *J* = 1.5 Hz, *J* = 10.4 Hz, 1H), 4.12 (m, 2H), 4.04─4.02 (m, 2H), 2.25─2.22 (m, 2H), 2.06 (s, 1H), 1.69─1.65 (m, 2H), 1.49─1.46 (m, 2H), 1.19 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.2, 117.6, 91.5, 86.7, 76.1, 70.4, 68.0, 57.7, 42.4, 37.5, 29.1, 14.6, 19.2; HRMS (ESI**)** calcd for $C_{14}H_{21}O$ $[M+H]^+$ 205.1592, found 205.1588.



7-20c

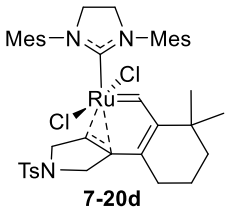
7-20c (36 mg, 71%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.31-6.86 (m, 8H), 6.46 (s, 1H), 6.29 (m, 2H), 4.92 (d, *J* = 12.1 Hz, 1H), 4.67 (s, 1H), 4.49 (d, *J* = 12.1 Hz, 1H), 4.22 (d, *J* = 18.4 Hz, 1H), 4.00-3.75 (m, 5H), 3.53-3.37 (m, 2H), 2.77 (s, 3H), 2.63 (s, 3H), 2.44 (m, 5H), 2.34 (s, 3H), 2.30 (s, 3H), 2.24 (s, 3H), 1.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 282.2, 203.9, 169.3, 145.0, 139.2, 129.1, 138.3, 137.4, 134.6, 131.0, 130.2, 130.0, 129.8, 129.4, 128.9, 128.2, 127.7, 125.6, 112.3, 96.1, 87.6, 69.8, 66.9, 53.1, 52.9, 52.0, 26.9,

26.4, 21.8, 21.2, 20.6, 19.3, 19.1, 18.8; HRMS (ESI**)** calcd for $C_{43}H_{46}N_3O_3SRu$ $[M-2Cl-H]^+$ 786.2303 found, 786.2277



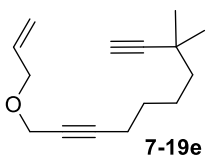
7-19d

7-19d: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 5.73─5.65 (m, 1H), 5.23 (d, *J* = 17.2 Hz, 1H), 5.16 (d, *J* = 10.1 Hz, 1H), 4.01 (s, 2H), 3.75 (d, *J* = 6.3 Hz, 2H), 2.37 (s, 3H), 2.03 (s, 1H), 1.88 (t, *J* = 6.9 Hz, 2H), 1.41─1.39 (m, 2H), 1.27─1.25 (m, 2H), 1.12 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.2, 136.2, 132.2, 129.3, 127.8, 119.5, 91.3, 85.9, 72.6, 68.1, 48.9, 42.3, 36.3, 30.7, 29.1, 24.3, 21.5, 18.8; HRMS (ESI**)** calcd for $C_{21}H_{28}NO_2S$ $[M+H]^+$ 358.1841, found 358.1837.



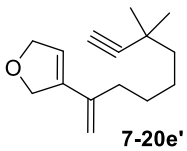
7-20d

7-20d (38 mg, 78%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 16.10 (s, 1H), 7.68 (d, *J* = 8.0 Hz, 2H), 7.32 (d, *J* = 7.9 Hz, 2H), 7.12─7.06 (m, 2H), 7.06 (s, 1H), 6.95 (s, 1H), 6.77 (s, 1H), 5.00 (d, *J* = 10.8 Hz, 1H), 4.19─4.01 (m, 4H), 3.82─3.80 (m, 1H), 3.50 (d, *J* = 5.2 Hz, 1H), 3.05 (d, *J* = 12.7 Hz, 1H), 2.94 (s, 3H), 2.63 (s, 3H), 2.58 (s, 3H), 2.42 (m, 5H), 2.32 (s, 3H), 2.25 (s, 3H), 2.18 (s, 3H), 1.93─1.83 (m, 2H), 1.46─1.44 (m, 2H), 0.78 (s, 3H), 0.34 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 313.7, 205.9, 167.3, 160.8, 143.4, 139.6, 137.5, 136.5, 132.9, 132.6, 130.5, 130.1, 129.6, 129.4, 128.9, 128.2, 127.4, 127.2, 125.7, 124.3, 101.4, 62.2, 53.6, 53.2, 52.1, 51.7, 51.3, 46.6, 46.4, 38.5, 38.1, 35.6, 35.1, 33.6, 33.0, 29.8, 27.8, 27.0, 26.9, 26.4, 26.2, 21.5, 20.9, 20.2, 19.3, 18.6, 18.1; HRMS (ESI**)** calcd for $C_{41}H_{52}N_3O_2SCl_2Ru$ $[M+H]^+$ 822.2201, found 822.2194.



7-19e

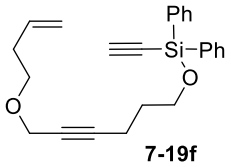
7-19e: ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.93─5.85 (m, 1H), 5.30─5.18 (m, 2H), 4.12 (t, *J* = 2.1 Hz, 2H), 4.03 (d, *J* = 5.7 Hz, 2H), 2.27─2.24 (m, 2H), 1.59─1.53 (m, 6H), 1.33 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.2, 125.1, 117.6, 86.2, 76.4, 70.5, 57.7, 40.6, 32.4, 28.5, 26.7, 24.5, 18.6.



7-20e'

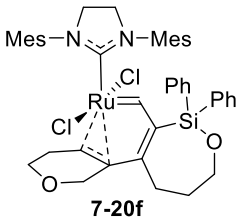
7-20e′ (16 mg, 84%, 10 mol% of Grubbs II used): ^{1}H NMR (500 MHz, $CDCl_3$) δ 5.84 (s, 1H), 5.00 (s, 1H), 4.76 (s, 4H), 2.30 (t, *J* = 7.0 Hz, 2 H), 2.08 (s, 1H), 1.52-1.41 (m, 6H), 1.21 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 140.7, 121.5, 118.6, 112.9, 92.0, 77.5, 76.6, 75.3, 67.7, 43.0, 34.1, 31.0, 29.7, 29.2, 28.9, 25.2; LRMS (ESI**)** calcd for $C_{15}H_{20}OLi$ $[M-2H+Li]^+$ 223.2,

found, 223.2.



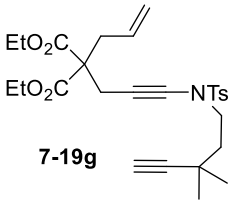
7-19f

7-19f: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73─7.72 (m, 4H), 7.43─7.39 (m, 6H), 5.85─5.80 (m, 1H), 5.13─5.09 (m, 1H), 5.08─5.04 (m, 1H), 4.10 (s, 2H), 3.92 (t, *J* = 5.9 Hz, 2H), 3.53 (t, *J* = 6.6 Hz, 2H), 2.75─2.72 (m, 4H), 2.37─2.33 (m, 3H), 1.86─1.83 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.6, 133.0, 130.6, 128.0, 96.6, 86.2, 84.8, 76.3, 69.1, 62.8, 58.6, 34.0, 31.2, 15.4. HRMS (ESI**)** calcd for $C_{24}H_{26}O_2SiNa$ $[M+Na]^+$ 397.1600, found 397.1596.



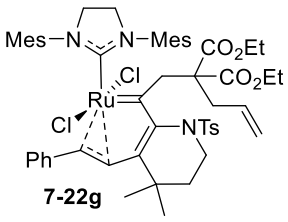
7-20f

7-20f: (42 mg, 84%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 16.51 (s, 1H), 7.50─7.44 (m, 2H), 7.41─7.34 (m, 5H), 7.31─7.30 (m, 2H), 6.97 (s, 1H), 6.87 (s, 1H), 6.30 (s, 1H), 5.89 (s, 1H), 5.45 (d, *J* = 14.4 Hz, 1H), 4.60 (d, *J* = 3.4 Hz, 1H), 4.52 (d, *J* = 14.4 Hz, 1H), 4.16─3.98 (m, 4H), 3.90─3.79 (m, 3H), 3.29 (td, *J* = 11.0, 5.4 Hz, 1H), 3.05─3.00 (m, 1H), 2.62 (s, 3H), 2.59 (s, 3H), 2.45 (s, 3H), 2.27 (s, 3H), 2.22 (s, 3H), 2.10─1.90 (m, 4H), 1.66─1.57 (m, 2H), 1.53 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 309.8, 205.0, 177.6, 155.6, 139.7, 139.2, 138.9, 137.7, 136.6, 136.2, 135.6, 135.2, 135.0, 134.5, 133.4, 132.7, 130.2, 130.1, 129.9, 129.1, 127.0, 102.7, 63.7, 62.8, 52.4, 51.0, 34.2, 27.9, 24.7, 21.0, 20.7, 20.6, 20.5, 18.9, 18.7; HRMS (ESI**)** calcd for $C_{44}H_{49}N_2O_2RuSi$ $[M-2Cl-H]^+$ 767.2618, found 767.2575.



7-19g

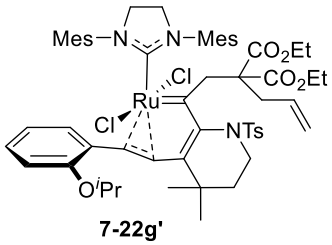
7-19g: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 5.03─5.55 (m, 1H), 5.14─5.03 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 4H), 3.45─3.41 (m, 2H), 2.83 (s, 3H), 2.71 (d, *J* = 7.4 Hz, 2H), 2.43 (s, 3H), 2.09 (s, 1H), 1.89─1.85 (m, 2H), 1.21 (t, *J* = 7.1 Hz, 6H), 1.18 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.8, 144.5, 134.8, 131.9, 129.8, 127.6, 119.7, 89.8, 75.9, 69.1, 65.0, 61.6, 57.0, 48.7, 40.2, 36.5, 29.5, 29.1, 22.8, 21.6, 14.1; HRMS (ESI**)** calcd for $C_{27}H_{36}NO_6S$ $[M+H]^+$ 502.2263, found 502.2259.



7-22g

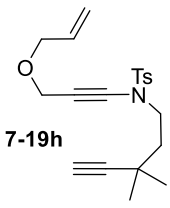
7-22g (56 mg, 87%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.92 (d, *J* = 7.1 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 7.04─7.00 (m, 4H), 6.92 (d, *J* = 7.7 Hz, 2H), 6.84 (s, 1H), 6.21 (2, 1H), 5.90─5.81 (m, 1H), 5.66 (d, *J* = 13.2 Hz, 1H), 5.04─4.97 (m, 2H), 4.42 (d, *J* = 15.9 Hz, 1H), 4.27─4.16 (m, 3H),

4.05─3.93 (m, 5H), 3.74─3.73 (m, 1H), 3.63 (d, *J* = 14.6 Hz, 1H), 3.25─3.18 (m, 1H), 2.66 (s, 3H), 2.69─2.67 (m, 1H), 2.46 (s, 3H), 2.40 (s, 3H), 2.38 (s, 3H), 2.30─2.27 (m, 4H), 2.20 (s, 3H), 2.10─2.07 (m, 1H), 1.98 (s, 3H), 1.31─1.24 (m, 6H), 0.91 (s, 3H), 0.83 (bm, 2H), 0.71 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 318.2, 205.0, 171.1, 169.4, 163.7, 155.9, 143.3, 138.6, 137.7, 137.6, 137.3, 137.0, 136.9, 136.2, 135.5, 133.9, 131.6, 130.7, 129.8, 129.4, 129.3, 128.5, 126.9, 126.6, 117.5, 104.0, 96.2, 61.7, 60.8, 60.7, 55.3, 53.0, 52.1, 45.1, 42.2, 37.2, 33.2, 30.4, 26.0, 21.5, 21.3, 20.5, 19.2, 18.8, 14.1, 13.9; HRMS (ESI**)** calcd for $C_{55}H_{67}N_3O_6SCl_2Ru$ $[M]^+$ 1069.3171 found, 1069.3180.



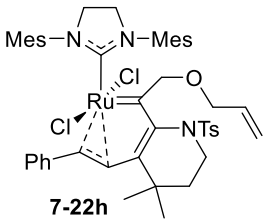
7-22g'

7-22g′ (61 mg, 91%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.2 Hz), 7.29 (d, *J* = 8.1 Hz, 2H), 7.04─7.00 (m, 1H), 6.96 (d, *J* = 2.8 Hz, 2H), 6.90 (s, 1H), 6.67 (d, *J* = 8.2 Hz, 1H), 6.54 (d, *J* = 7.5 Hz, 1H), 6.44 (s, 1H), 6.41 (t, *J* = 7.5 Hz, 1H), 5.87─5.80 (m, 1H), 5.75 (d, *J* = 13.1 Hz, 1H), 4.99 (d, *J* = 16.8 Hz, 1H), 4.92 (dd, *J* = 1.9 Hz, 10.1 Hz, 1H), 4.77─4.73 (m, 2H), 4.37─4.30 (m, 1H), 4.20─4.11 (m, 4H), 3.97 (m, 3H), 3.74─3.73 (m, 1H), 3.67─3.64 (m, 1H), 3.18─3.12 (m, 1H), 2.89 (s, 3H), 2.53 (s, 3H), 2.38 (s, 3H), 2.36 (s, 3H), 2.30 (s, 3H), 2.21 (m, 3H), 2.13 (s, 3H), 1.29 (t, *J* = 7.1Hz, 3H), 1.26─1.21 (m, 3H), 1.12 (d, *J* = 6.1 Hz, 3H), 0.91 (s, 3H), 0.68 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 318.0, 205.1, 171.0, 170.2, 163.2, 156.2, 155.7, 143.3, 138.6, 138.1, 137.6, 137.2, 136.9, 136.7, 135.7, 135.0, 131.5, 130.8, 129.9, 129.5, 129.4, 128.1, 126.3, 121.1, 117.4, 113.7, 107.4, 94.1, 70.6, 61.2, 60.5, 56.7, 53.0, 52.5, 45.3, 40.5, 36.9, 33.0, 30.4, 26.0, 22.5, 22.0, 21.5, 21.3, 20.5, 19.7, 19.5, 18.9, 14.2, 13.8; HRMS (ESI**)** calcd for $C_{58}H_{73}Cl_2N_3O_7RuS$ $[M─H]^+$ 1128.3608, found 1128.3564.



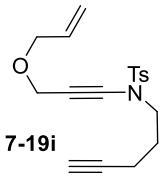
7-19h

7-19h: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 5.91─5.83 (m, 1H), 5.29─5.18 (m, 2H), 4.27 (s, 2H), 3.98 (d, *J* = 5.6 Hz, 2H), 3.53─3.50 (m, 2H), 2.43 (s, 3H), 2.11 (s, 1H), 1.75─1.71 (m, 2H), 1.20 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.7, 134.7, 134.1, 129.8, 127.6, 117.8, 89.8, 79.7, 70.1, 69.1, 67.4, 57.6, 48.8, 40.4, 29.6, 29.2, 21.2; HRMS (ESI**)** calcd for $C_{20}H_{26}NO_3S$ $[M+H]^+$ 360.1633, found 360.1628.



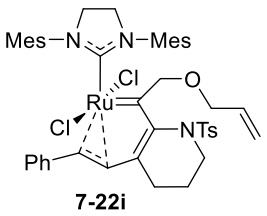
7-22h

7-22h (49 mg, 88%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.07 (t, *J* = 7.6 Hz, 2H), 7.00 (bs, 1H), 6.93 (m, 4H), 6.33 (s, 1H), 5.82 (m, 1H), 5.71 (d, *J* = 13.4 Hz, 1H), 5.21 (s, 1H), 5.18 (s, 1H), 5.08 (m, 1H), 4.10─3.71 (m, 8H), 2.97 (dd, *J* = 20.3, 7.9 Hz, 1H), 2.85 (s, 3H), 2.58 (d, *J* = 15.0 Hz, 1H), 2.46 (s, 3H), 2.39 (s, 3H), 2.32 (s, 6H), 2.11 (s, 3H), 1.83 (s, 3H), (d, *J* = 13.8 Hz, 1H), 0.85 (s, 6H), 0.81 (d, *J* = 3.7 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 318.5, 205.7, 162.6, 155.4, 143.3, 139.1, 138.0, 137.7, 137.2, 136.7, 136.1, 135.8, 133.9, 131.7, 131.0, 129.6, 129.4, 129.3, 128.8, 128.5, 127.1, 127.0, 115.2, 105.0, 98.7, 85.5, 72.2, 52.5, 52.3 44.5, 36.8, 34.1, 30.7, 26.4, 21.6, 21.2, 20.4, 19.1, 18.9, 18.8; HRMS (ESI**)** calcd for $C_{48}H_{57}N_3O_3SClRu$ $[M─Cl]^+$ 892.2853 found, 892.2845.



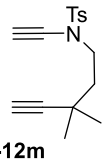
7-19i

7-19i: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.79 (d, *J* = 8.2 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 5.92─5.84 (m, 1H), 5.30─5.19 (m, 2H), 4.28 (s, 2H), 3.98 (d, *J* = 5.7 Hz, 2H), 3.44 (t, *J* = 7.0 Hz, 2H), 2.44 (s, 3H), 2.24 (dt, *J* = 2.5 Hz, 7.0 Hz, 2H), 1.97 (t, *J* = 2.5 Hz, 1H), 1.87 (p, *J* = 7.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8, 134.6, 134.1, 129.8, 127.7, 117.8, 82.7, 79.4, 70.2, 69.4, 67.6, 57.6, 50.3, 26.9, 21.7, 15.6; HRMS (ESI**)** calcd for $C_{18}H_{22}NO_3S$ $[M+H]^+$332.1320, found 332.1321.



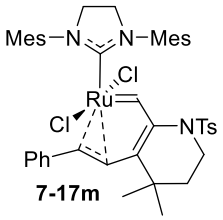
7-22i

7-22i (18 mg, 34%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.1 Hz, 2H), 7.21 (t, *J* = 7.3 Hz, 1H), 7.07 (t, *J* = 7.7 Hz, 2H), 7.00─6.88 (m, 4H), 6.33 (bs, 1H), 5.88─5.81 (m, 1H), 5.56 (d, *J* = 13.2 Hz, 1H), 5.23 (dd, *J* = 1.6 Hz, 17.3 Hz, 1H), 5.17─5.14 (m, 1H), 5.10 (dd, *J* = 1.3 Hz, 10.5 Hz, 1H), 4.17─4.10 (m, 2H), 4.06─3.90 (m, 7H), 2.84 (m, 2H), 2.47 (m, 2H), 2.43 (s, 3H), 2.33 (s, 3H), 2.31 (s, 3H), 2.11 (s, 3H), 1.82 (s, 3H), 1.57 (s, 3H), 1.26 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 316.3, 205.3, 157.9, 156.8, 143.3, 138.2, 137.9, 137.7, 136.0, 131.0, 129.7, 129.3, 128.5, 128.4, 127.1, 126.9, 115.4, 108.5, 97.6, 85.1, 72.2, 52.5, 52.2, 45.7, 30.1, 29.8, 21.6, 21.2, 21.2, 18.9, ; HRMS (ESI**)** calcd for $C_{46}H_{53}N_3O_3SClRu$ $[M─Cl]^+$ 864.2540, found 864.2545.



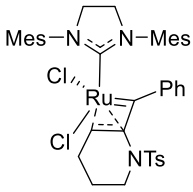
7-12m

7-12m: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.36 (d, *J* = 8.1 Hz, 2H), 3.54─3.50 (m, 2H), 2.74 (s, 1H), 2.46 (s, 3H), 2.12 (s, 1H), 1.77─1.74 (m, 2H), 1.22 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.8, 134.7, 129.9, 127.7, 89.7, 76.1, 69.1, 59.2, 48.6, 40.2, 29.6, 29.1, 21.7, 15.6; HRMS (ESI**)** calcd for $C_{16}H_{20}NO_2S$ $[M+H]^+$ 290.1215, found 290.1217.



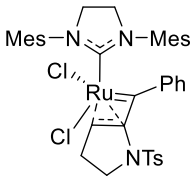
7-17m

7-17m (35 mg, 68%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 16.34 (s, 1H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.27─7.25 (m, 2H), 7.20─7.17 (m, 4H), 7.11 (t, *J* = 7.6Hz, 2H), 6.89 (s, 1H), 6.55 (s, 1H), 6.52 (s, 1H), 5.23 (d, *J* = 13.2 Hz, 1H), 4.72 (d, *J* = 13.2 Hz, 1H), 4.11─3.91 (m, 4H), 3.74 (td, *J* = 3.9 Hz, J = 14.4 Hz, 1H), 3.26─3.20 (m, 1H), 2.77 (s, 3H), 2.37 (s, 3H), 2.33 (s, 6H), 2.28 (s, 3H), 2.25 (s, 3H), 2.21 (s, 3H), 1.10 (s, 3H), 1.04─1.01 (m, 1H), 0.78─0.72 (m, 1H), 0.51 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 311.0, 205.6, 159.8, 152.2, 143.5, 138.7, 138.2, 137.7, 137.2, 137.1, 136.3, 136.1, 135.5, 134.7, 134.2, 131.0, 129.5, 129.4, 129.3, 128.6, 128.5, 127.3, 126.9, 115.2, 112.9, 52.4, 51.8, 44.1, 37.3, 33.8, 27.7, 27.2, 21.6, 21.2, 19.8, 19.8, 19.1, 18.7; HRMS (ESI**)** calcd for $C_{44}H_{51}N_3O_2SClRu$ $[M─Cl]^+$ 822.2434, found 822.2429.



7-24a

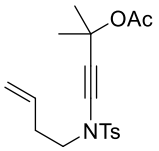
7-24a (45 mg, 94%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.13─7.12 (m, 2H), 7.05─6.96 (m, 7H), 6.11─6.08 (m, 1H), 4.38─4.27 (m, 1H), 4.24─4.12 (m, 2H), 4.09─4.07 (m, 1H), 3.99─3.92 (m, 1H), 3.82─3.78 (m, 1H), 3.49─3.31 (m, 1H), 2.98─2.92 (m, 1H), 2.57 (s, 3H), 2.47 (s, 3H), 2.41 (s, 3H), 2.35 (s, 3H), 2.32 (s, 3H), 2.30 (s, 3H), 1.98 (s, 3H), 1.28─1.26 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 280.8, 215.2, 160.4, 154.5, 145.1, 140.7, 140.2, 139.1, 138.4, 137.8, 136.8, 136.6, 133.8, 130.4, 130.4, 130.2, 130.1, 129.5, 128.9, 128.6, 128.4, 126.3, 125.6, 122.3, 52.1, 51.4, 45.8, 23.5, 21.7, 21.4, 21.2, 20.7, 19.4, 19.2, 18.8, 17.2; HRMS (ESI**)** calcd for $C_{40}H_{45}N_3O_2SClRu$ $[M─Cl]^+$ 768.1964, found 768.1977.



7-24b

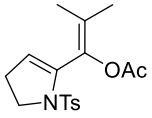
7-24b (43 mg, 92%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.53 (t, *J* = 7.4 Hz, 1H), 7.14─7.11 (m, 3H), 7.03─6.94 (m, 5H), 6.88─6.86 (m, 2H), 6.27 (s, 1H), 6.07 (s, 1H), 4.23─4.18 (m, 1H), 4.04─3.95 (m, 2H), 3.83─3.64 (m, 3H), 3.54 (d, *J* = 5.0 Hz, 1H), 2.62 (s, 3H), 2.61 (s, 3H), 2.36─2.35 (m, 2H), 2.29 (s, 6H), 2.19 (s, 3H), 1.94 (s, 3H), 1.69 (s, 3H);

^{13}C NMR (125 MHz, $CDCl_3$) δ 209.8, 144.3, 143.6, 140.5, 139.8, 138.4, 137.0, 135.6, 134.0, 133.8, 133.5, 131.6, 131.0, 130.1, 129.8, 129.4, 129.2, 129.0, 128.9, 128.6, 128.3, 127.9, 114.9, 104.9, 52.9, 52.2, 51.8, 51.6, 27.9, 27.0, 26.9, 26.3, 26.1, 21.6, 21.2, 20.9, 20.6, 19.0, 18.8, 17.7; HRMS (ESI**)** calcd for $C_{39}H_{42}N_3O_2RuS$ $[M-Cl_2-H]^+$ 718.2041, found 718.2075



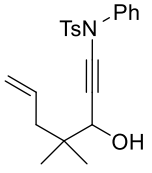
7-23c

7-23c: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.2 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.70─5.62 (m, 1H), 5.05─4.96 (m, 2H), 3.31 (t, *J* = 7.3 Hz, 2H), 2.40 (s, 3H), 2.33 (q, *J* = 7.1 Hz, 2H), 1.93 (s, 3H), 1.60 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.2, 144.5, 134.5, 133.8, 129.6, 127.8, 117.5, 72.8, 72.2, 50.6, 31.9, 29.0, 21.9, 21.6; HRMS (ESI**)** calcd for $C_{16}H_{22}NO_3S$ $[M+H-OCCH_3]^+$ 308.1315, found 308.1320.



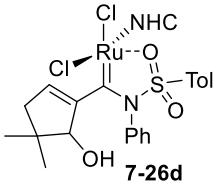
7-25c

7-25c (18 mg, 92%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 1H-NMR (501 MHz) ppm 7.71 (d, *J* = 8.2 Hz, 2H), 7.28 (d, *J* = 8.2 Hz, 2H), 5.43 (t, *J* = 2.8Hz, 1H), 3.84 (t, *J* = 8.4 Hz, 2H), 2.42 (s, 3H), 2.18 (s, 3H), 2.10 (dt, 1H, *J* = 2.8 Hz, 8.4 Hz, 2H), 1.82 (s, 3H), 1.72 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.4, 143.7, 137.1, 134.9, 129.4, 129.1, 128.0, 127.6, 126.4, 121.1, 50.4, 28.1, 21.6, 20.9, 20.1, 18.3



7-23d

7-23d: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.0 Hz, 2H), 7.32─7.23 (m, 7H), 5.87─5.79 (m, 1H), 5.06─5.03 (m, 2H), 4.21 (s, 1H), 2.41 (s, 3H), 2.19─2.06 (m, 2H), 0.97 (s, 3H), 9,95 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 138.8, 134.9, 133.0, 129.6, 129.1, 128.3, 128.2, 126.2, 117.7, 79.8, 70.4, 70.2, 42.9, 39.2, 22.9, 22.8, 21.7; HRMS (ESI**)** calcd for $C_{22}H_{26}NO_3S$ $[M+H]^+$ 384.1633, found 384.1626.



7-26d

7-26d (44 mg, 86%): ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 8.2 Hz, 2H), 7.22-7.14 (m, 3H), 7.10-7.02 (m, 4H), 6.86-6.82 (m, 2H), 6.86-6.57 (m, 2H), 5.53 (d, *J* = 2.0 Hz, 1H), 4.31-4.04 (m, 4H), 3.90 (s, 1H), 3.62 (d, *J* = 4.2 Hz, 1H), 2.59 (s, 3H), 2.56 (s, 3H), 2.42 (s, 3H), 2.36 (s, 3H), 2.34 (s, 3H), 2.29 (s, 3H), 2.24 (s, 3H), 1.79 (d, *J* = 16.6 Hz, 1H), 1.38 (d, *J* = 16.4 Hz, 1H), 0.96 (s, 3H), 0.46 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 262.6, 214.7, 153.9, 146.2, 140.5, 139.0, 138.4, 138.3, 137.2, 137.0, 136.3, 132.9, 130.6, 130.5, 130.0, 129.9, 129.7, 129.3,

129.1, 128.5, 127.8, 122.1, 88.1, 52.7, 51.1, 47.2, 41.7, 27.7, 23.5, 21.8, 21.4, 21.1, 20.5, 19.2, 19.0, 18.7; HRMS (ESI**)** calcd for $C_{43}H_{50}N_3O_4RuS$ $[M-2Cl+H+CO]^+$ 806.2560 found, 806.2483.

7.6. References

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CHAPTER 8

THERMAL BICYCLIZATION OF YNAMIDE-TETHERED 1,3,8-TRIYNES

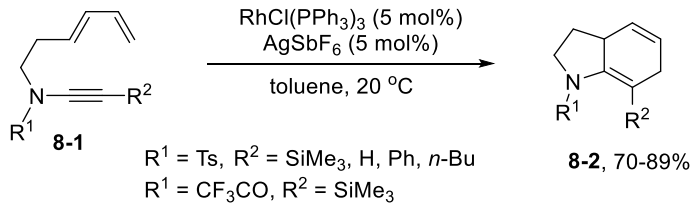
8.1. Introduction

Ynamines are a class of alkynes that have a nitrogen atom directly attached to a triple-bond.[1] Due to the strong electron donating nature of a nitrogen moiety, ynamines are highly reactive species compared to typical alkynes. In 1958, the formation of ynamines was observed by Zaugg and coworkers in the reaction of propargyl bromide with phenothiazine.[2] Thereafter, the synthesis and application of ynamines became popular,[3] yet the development of efficient and general synthetic methods was limited due to instability. To enhance their stability, an electron-withdrawing group was installed on the alkynyl nitrogen, which is now known as ynamides[4,5] The electron-withdrawing group not only stabilize the system but also it acts as an efficient directing group. In the last two decades, the chemistry of ynamides has been extensively developed. Ynamides can undergo various addition reactions, including hydroarylation, M−H/M−X additions, and radical addition reactions. Ynamides are also extensively employed in ring-forming reactions, which is not only due to the favorable reactivity of the electron-rich ynamide functionality, but also the usefulness of the resultant heterocyclic products.

8.2. Intramolecular [4+2] Cycloaddition Reactions of Ynamide Derivatives

Ynamides have been extensively studied in a variety of cycloaddition reactions, such as [2+1], [2+2], [3+2], [4+2], [2+2+1] and [2+2+2] cycloadditions. Among these, [4+2] cycloaddition reaction has been engaged most often for the synthesis of a novel class of indole derivatives.

In 2003, Witulski and coworkers reported the intramolecular [4+2] cycloaddition reaction of ynamide-tethered 1,3-dienes (**Scheme 8.1**).[6] In their study, the cycloaddition of diene-ynamides **8-1** provide a novel class of functionalized dihydroindolines **8-2**. For this transformation, an in situ generated cationic rhodium (I) catalyst form $RhCl(PPh_3)_3$ and $AgSbF_6$, was employed. The intermolecular version of this Diels-Alder reaction was further studied by Hsung and coworkers with chiral ynamides and symmetrical 1,3-dienes.[7]



Scheme 8.1 Intramolecular [4+2] Cycloaddition of Ynamide-Tethered 1,3-Dienes

8.2.1. Cycloaddition of Ynamide-Tethered 1,3-Enynes

Danheiser and coworkers reported an intramolecular Diels-Alder reaction of ynamide tethered 1,3-enynes to generate highly substituted indoline derivatives (**Table 8.1**).[8] Upon treating with a stoichiometric amount of BHT (butylated hydroxytoluene) under thermal reaction conditions, ynamide tethered 1,3-enynes **8-3** provided indoline derivatives **8-4** in good to moderate yields.

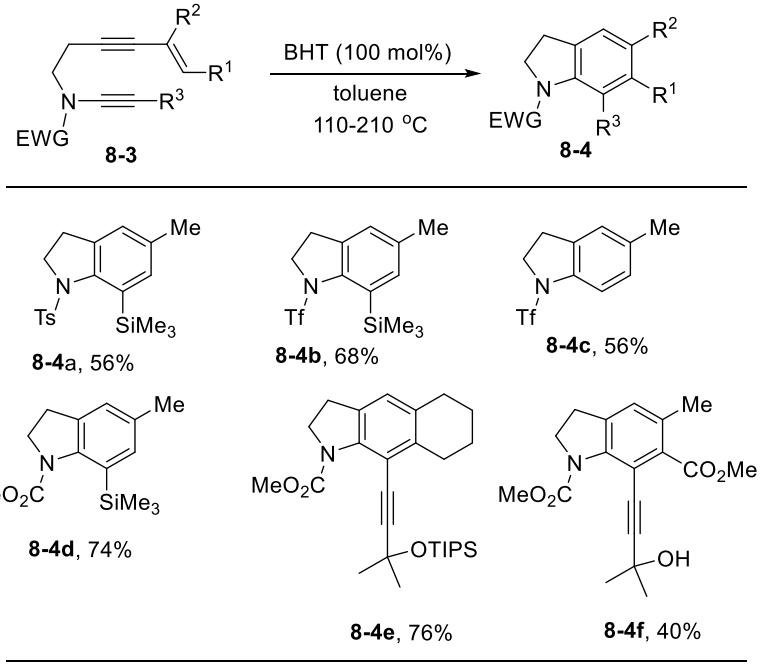
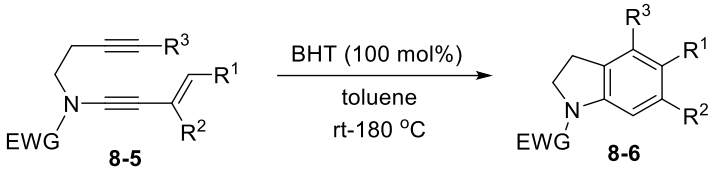


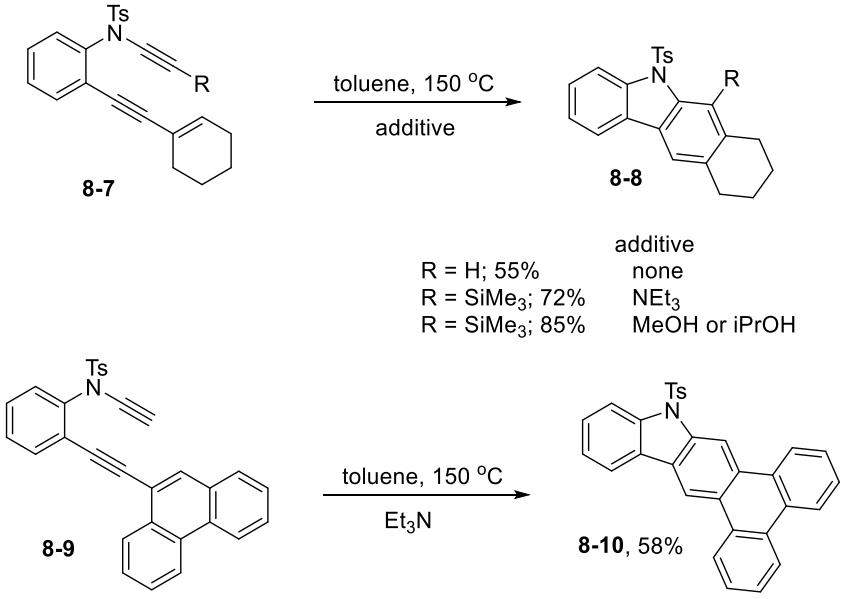
Table 8.1 Thermal [4+2] Cycloaddition of Ynamide Tethered 1,3-Enynes

This transformation was further extended to 1,3-enynamide tethered alkynes **8-5**, which generate differently substituted indoline derivatives **8-6** (**Scheme 8.2**).



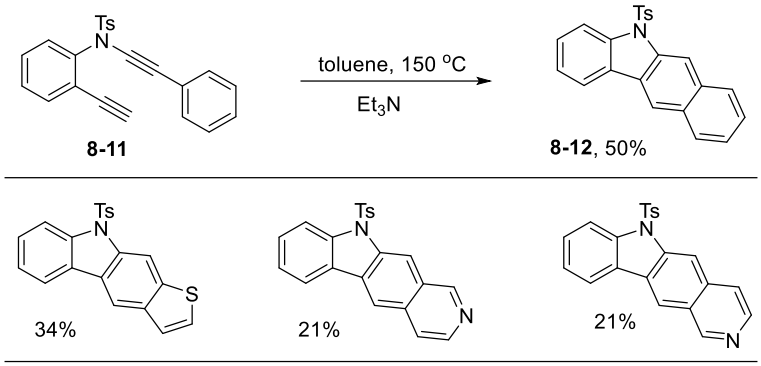
Scheme 8.2 Thermal [4+2] Cycloaddition of 1,3-Eneynamide-Tethered Alkynes

Saá and coworkers reported a similar Diels-Alder reaction for the synthesis of carbazole derivatives (**Scheme 8.3**).[9] Ynamide-tethered 1,3-enynes **8-7** having a different substituent on the ynamide moity provided cyclized products **8-8** in moderate yields in the presence of certain additives, such as Et_3N, MeOH, and i-PrOH. These additives were found to be crucial for optimum yields. Phenanthrene substituted diyne **8-9** was also engaged in the study, which generate carbocycle **8-10** in 58% yield.



Scheme 8.3 [4+2] Cycloaddition of Aryl-Substituted 1,3-Eneynamide-Tethered Alkynes

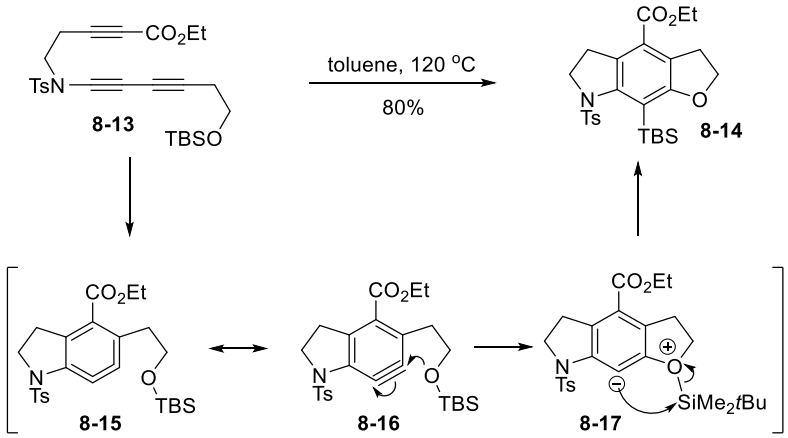
Saá and coworkers also studied dehydro Diels-Alder reaction of aryl-substituted *N*-terminal diynes (**Scheme 8.4**). [10] Aryl-substituted diynes **8-11**, in the presence of triethyl amine, provided the corresponding cyclized products **8-12** in low yield.



Scheme 8.4 [4+2] Cycloaddition of Ynamide-Tethered 1,3-Enynes

8.2.2. Cycloaddition of Ynamide-Tethered Triynes and Tetraynes

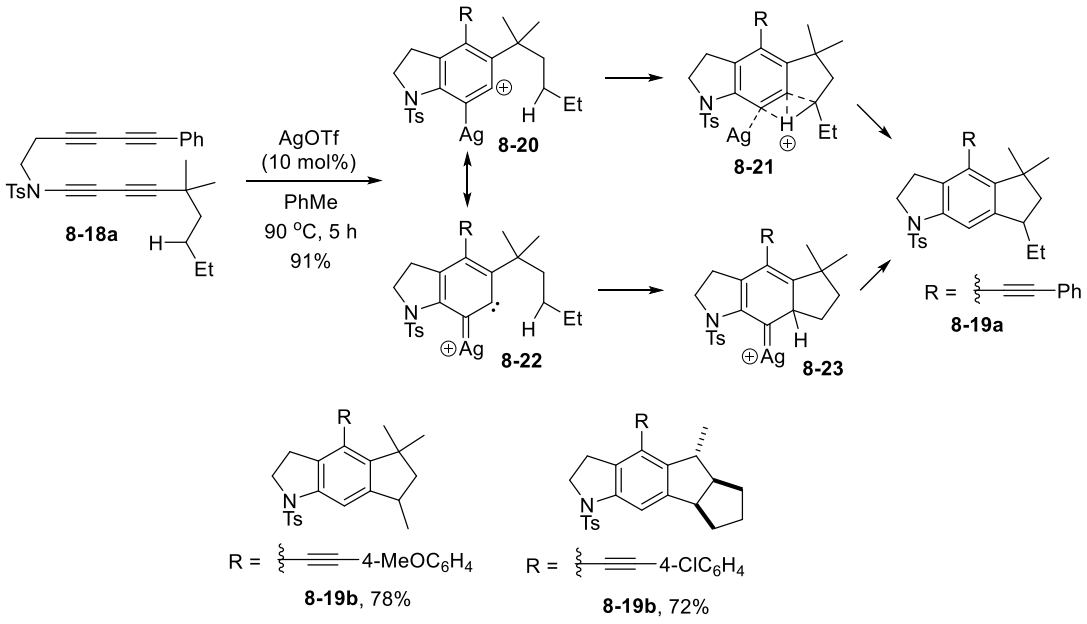
Hoye and coworkers reported the [4+2] cycloaddition of ynamide having triynes (**Scheme 8.5**).[11] Triyne **8-13** smoothly underwent hexadehydro Diels-Alder (HDDA) reaction to provide indoline **8-14** in 80% yield in toluene at 120 °C. The mechanism for the formation product **8-14** is rationalized by cycloaddition of **8-13** to generate aryne intermediate **8-16**, which then trapped with silyl ether.



Scheme 8.5 HDDA Reaction of Triynes

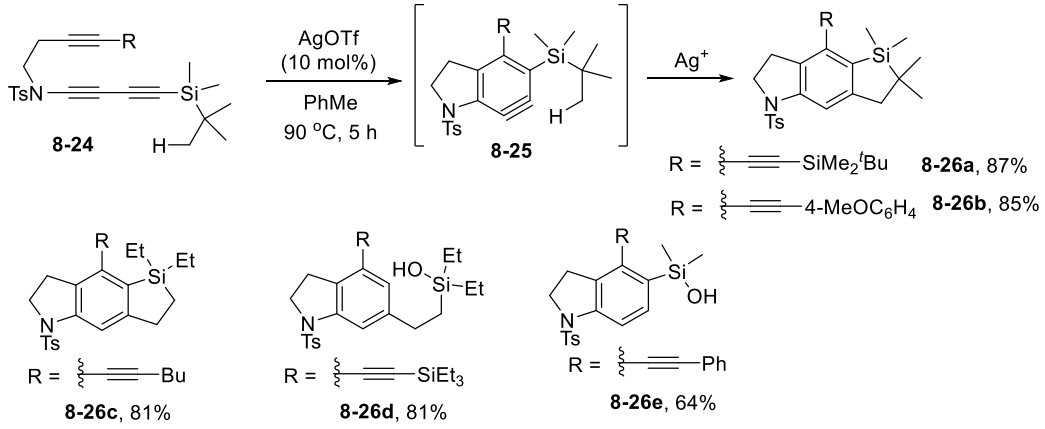
Lee and coworkers also reported HDDA reaction of tetraynes in the presence of a silver cation (**Scheme 8.6**).[12] Ynamide-containing tetraynes with catalytic amount of AgOTf in toluene at 90 °C provided indoline derivatives **8-19** in good yield. Mechanistically, the initially generated aryne intermediate is further activated by a silver ion to generate **8-20** or its alternative from **8-22**, which then

effectively reacts with primary, secondary, and tertiary alkane C−H bonds to afford carbocycles **8-19**.



Scheme 8.6 Alkane C−H Activation by Aryne Intermediates Catalyzed by a Silver Ion

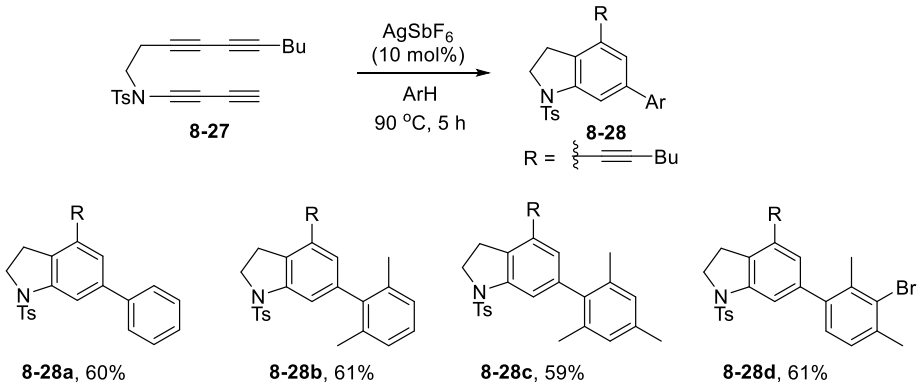
The C–H bond activation by arynes was further extended to the system containing a silyl substituent (**Scheme 8.7**).[13] A putative aryne generated from tetrayne **8-24** favors a direct C–H insertion if the reacting C–H bond is primary to generate **8-26a**–**8-26c**, whereas a hydride transfer process becomes more favorable if the reacting C–H is secondary or tertiary, affording **8-26d** and **8-26e**.



Scheme 8.7 Formal Hydrogenation of Arynes with Silyl C_β–H Bonds

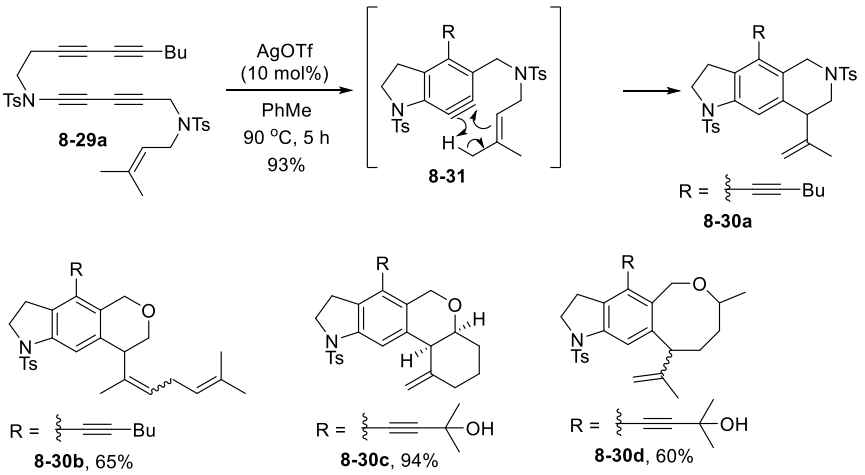
Lee and coworkers also reported a silver-catalyzed nucleophilic aromatic substitution reaction of

arynes (**Scheme 8.8**),[14] where yanamides **8-27** were effectively converted biaryl products **8-28** via an aryne intermediate followed by its trapping with variety of nucleophiles arenes. Complete regioselectivity was observed in these reactions involving yanamide-derived tetaraynes **8-27**.



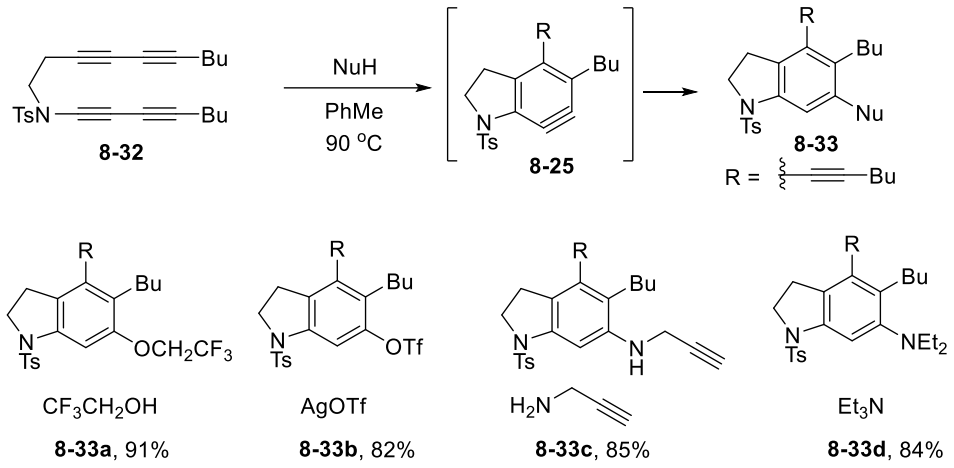
Scheme 8.8 Hydroarylation of Arynes Catalyzed by a Silver Ion

Silver-catalyzed ene reactions of arynes were also explored by Lee and coworkers (**Scheme 8.9**).[15] Ynamide **8-29** tethered with an alkenyl group, upon formation of aryne **8-31**, provide Alder-ene products **8-30** in good yields. This reaction showed identical reaction profiles and efficiency with and without the silver catalyst and it was concluded that the formation of the aryne intermediate and their ene reaction is not affected by the silver ion.



Scheme 8.9 Aryne Ene Reaction with Ynamide having Tetraynes

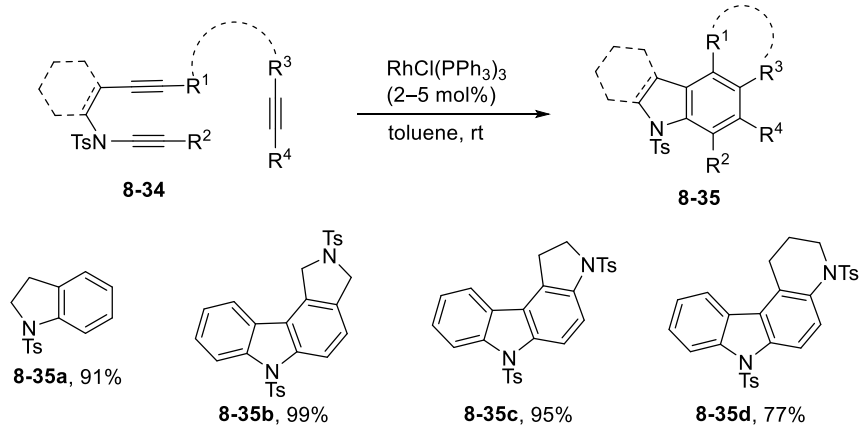
The highly regioselective nucleophile trapping of arynes generated from ynamides were widely exploited by Lee and coworkers (**Scheme 8.10**).[16] A variety of nucleophiles provided the corresponding adducts with high regioselectivity, and most cases single regioisomers were observed.



Scheme 8.10 Regioselectivity in the Nucleophile Trapping of Arynes

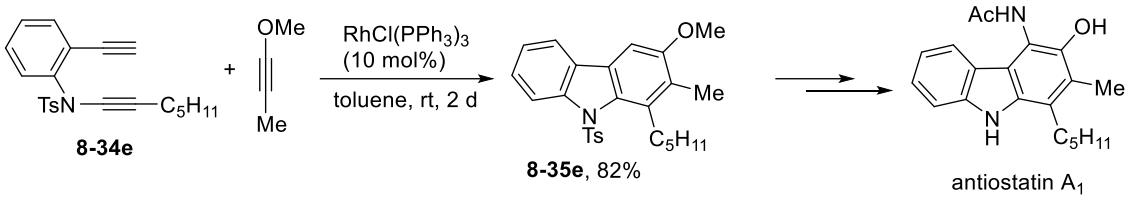
8.3. Intramolecular [2+2+2] Cycloaddition Reactions Ynamide-Tethered Triynes

Rhodium catalyzed [2+2+2] cycloaddition reactions of ynamide were first reported by Witulski and coworkers (**Scheme 8.11**).[17] In this transformation regioselective intermolecular cycloaddition of triyne was observed to generate indolines **8-35a**. This cycloaddition was then extended the intramolecular cycloaddition of ynamide **8-34** to generate polycyclic structures **8-35** in good yields.



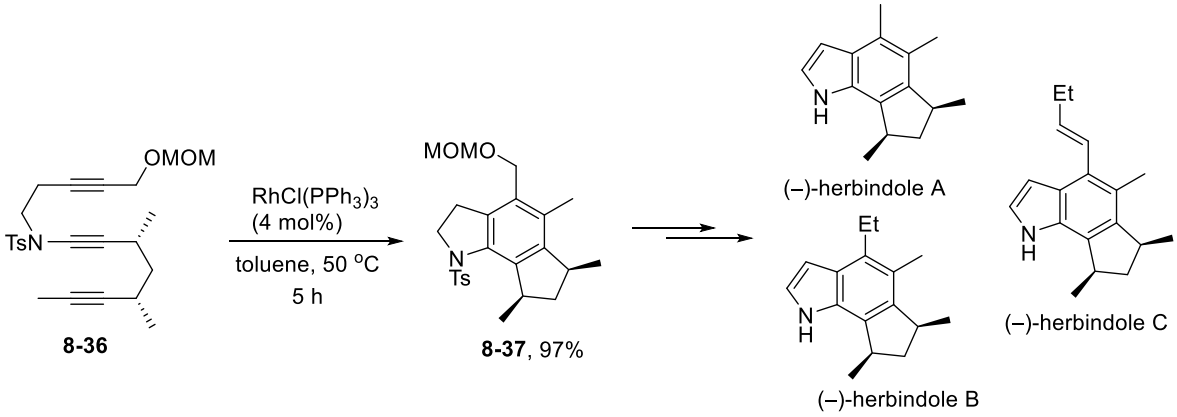
Scheme 8.11 [2+2+2] Cycloaddition Reactions Ynamide-Tethered Triynes

Witulski and coworkers applied this intermolecular [2+2+2] cycloaddition to the total synthesis of antiostatin A_1 (**Scheme 8.12**).[18] Intermolecular cycloaddition of diyne **8-34e** and 1-methoxy-1-propyne in the presence of Wilkinson's catalyst provided cycloaddition product **8-35e** in 82% yield, which was further converted to antiostatin A_1 and its derivatives.



Scheme 8.12 [2+2+2] Cycloaddition Reaction for the Synthesis of Antiostatin A_1

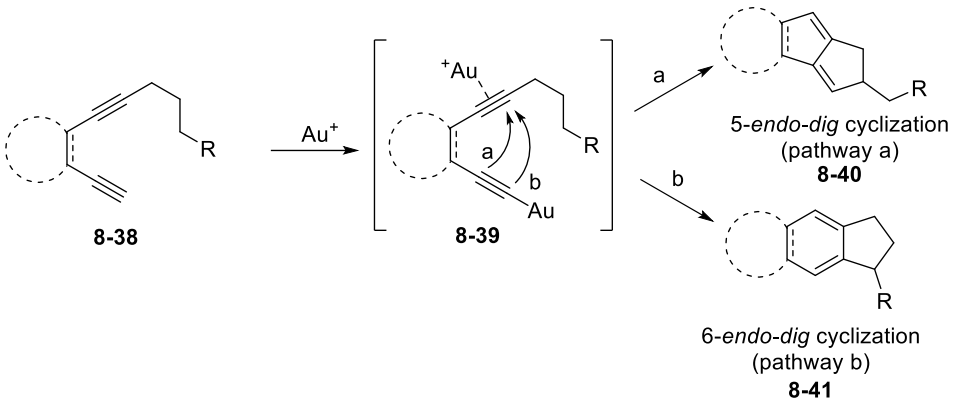
Sato and coworker cleverly employed an intramolecular [2+2+2] cycloaddition of triynes containing a ynamide tether for total synthesis of (−)-herbindole A, B and C (**Scheme 8.13**).[19] The cycloaddition of ynamide **8-36** in the presence of Wilkinson's catalyst afforded the core structure of natural products in 97% yield, which was converted to (−)-herbindole A, B and C.



Scheme 8.13 [2+2+2] Cycloaddition Reaction for Synthesis of (−)-Herbindole

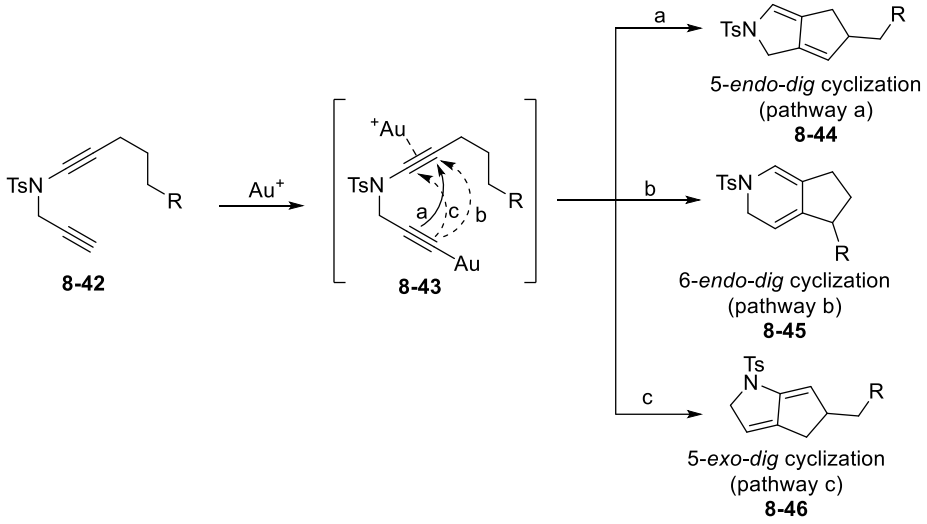
8.4. Gold-Catalyzed Cyclization of Ynamide-Tethered Alkynes

The metal-catalyzed cyclization reactions of 1,5-diynes were extensively studied (**Scheme 8.14**).[20] For example, diyne **8-38** in the presence of gold cation can undergo two types of *endo*-dig-cyclization to afford 5-*endo*-dig and 6-*endo*-dig cyclization products **8-40** and **8-41** (pathways a and b).



Scheme 8.14 Possible Cyclization Pathways of 1,5-Diynes

Similarly, *N*-propargyl ynamides would undergo three types of cyclizations leading to three different products **8-44**, **8-45**, and **8-46** (**Scheme 8.15**).[21] The pathway **a** and the pathway **b** are 5- and 6-*endo*-dig cyclization, and the third pathway **c** is 5-*exo*-dig cyclization (pathway c).[22,23]



Scheme 8.15 Possible Cyclization Pathways of Ynamide-Tethered Alkynes

8.5. Results and Discussion

After extensive study of structure and reactivity of ruthenium alkylidenes for enyne RCM, we became interest in utilizing RCM strategy in the total synthesis of (−)-herbindole A, B and C (**Figure 8.1**).[24,25] Herbindoles are polylalkylated cyclopent[g]indole alkaloids isolated from Western Australian sponge,

Axinella sp. These natural products show important biological activity such as cytotoxicity against KB cells and anti-feedant activity against fishes.[26]

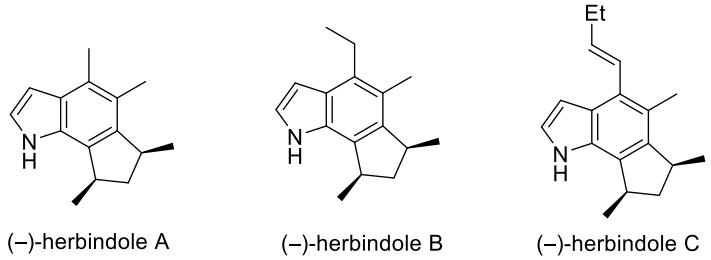
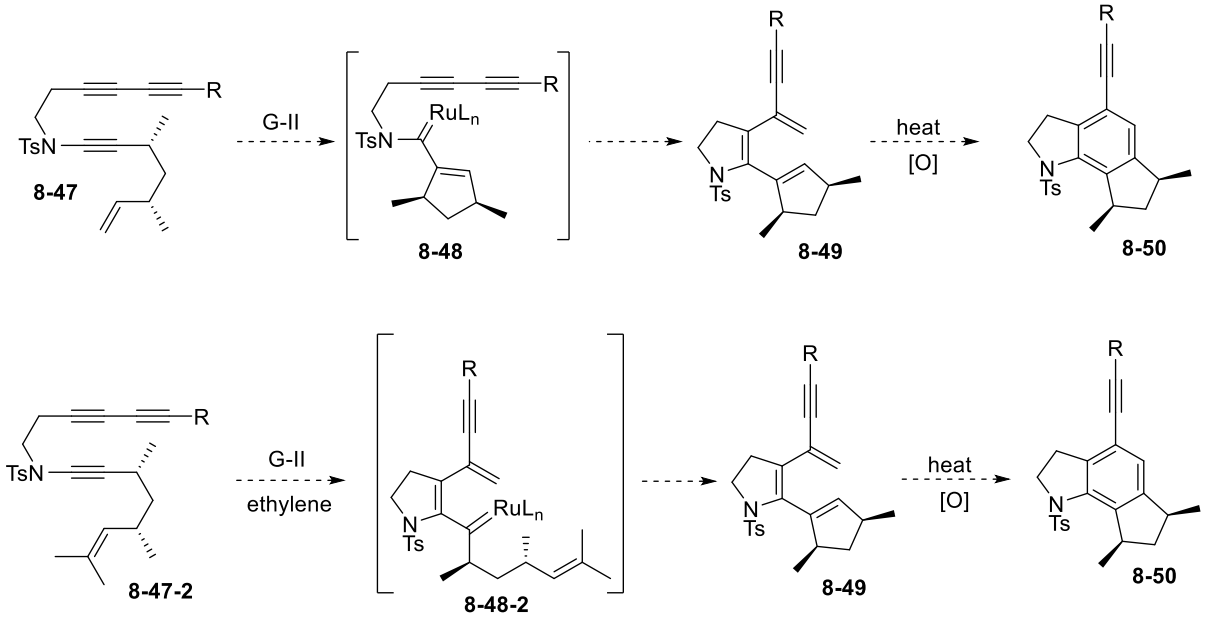


Figure 8.1 Structure of Herbindole A, B and C

To effect RCM strategy for the synthesis of herbindoles, we have designed enynamide-based substrate **8-47** (**Scheme 8.16**). It was expected that enyne-tethered diyne **8-47** should undergo tandem RCM to provide 1,3,5-triene **8-49** by initiating the metathesis reaction at terminal alkene. The resultant triene **8-49** would undergo electrocyclization under the reaction conditions to provide the core structure of natural product herbindole **8-50**.

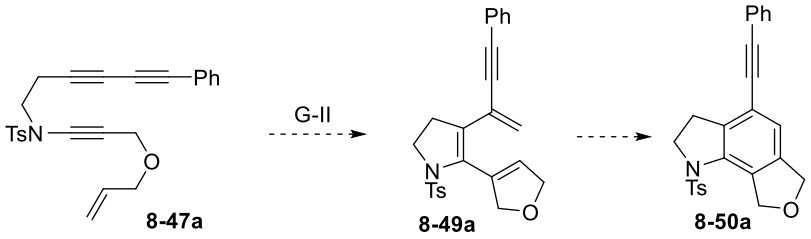


Scheme 8.16 RCM Strategy for Synthesis of Herbindole Core

The regioselective termination not involving metallotropic [1,3]-shift of ruthenium alkylidene

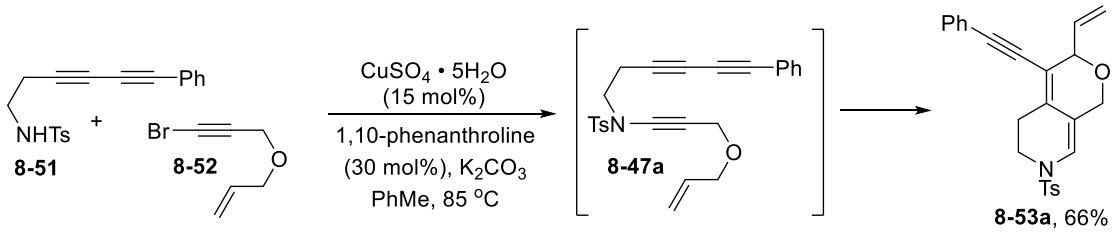
intermediate can be realized by installing a proper R group in **8-47**. On the other hand, in triyne **8-47-2**, the initiation of RCM is expected to occur at an internal alkyne of the diyne to generate same metathesis product **8-49** via intermediate **8-48-2**.

To test the feasibility of the proposed tandem enyne RCM strategy, we planned to use a simplified model substrate **8-47a** for initial study to examine whether indole core structure **8-49a** can be generated (**Scheme 8.17**).



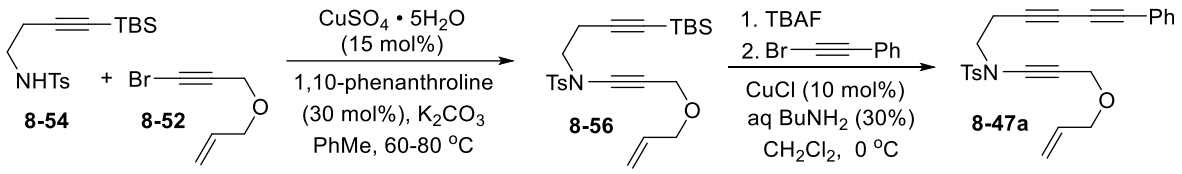
Scheme 8.17 Model Substrate for RCM

To prepare ene-ynamide tethered diyne **8-47a**, coupling of building blocks **8-51** and **8-52** were envisioned (**Scheme 8.18**). Upon subjecting diyne-tethered sulfonamide **8-51** and bromoalkyne **8-52** to typical coupling conditions involving copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$, 15 mol %), 1,10-phenanthroline (30 mol %) and excess of potassium carbonate (K_2CO_3) in toluene at 85 ^oC, a clean conversion occurred to provide a product in 66% yield.[5] The characteristic NMR signals of the isolated product did not corroborate the structure of the expected product **8-47a**. Extensive spectroscopic studies ultimately proved that the compound isolated from the reaction was bicyclic structure **8-53a**, which we believe, was derived from the initially formed coupling product **8-47a**.



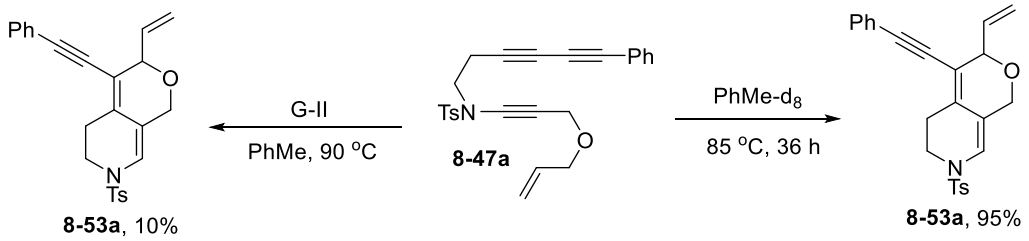
Scheme 8.18 Unexpected Bicyclization During Ynamide Synthesis

To get further confirmation for the initial formation of **8-47a** and its conversion to **8-53a**, we have modified the synthetic sequence such that the final step for the generation of **8-47a** is achieved at lower temperature (**Scheme 8.19**). In this modified synthesis, coupling between **8-54** and bromoalkyne **8-52** provided **8-56**, which then converted to ene-ynamide-tethered diyne **8-47a** via deprotecting the silyl group followed by coupling with phenylacetylene bromide at 0 °C catalyzed by CuCl in aqueous $BuNH_2$ and CH_2Cl_2.



Scheme 8.19 Modified Synthetic Sequence for Ene-ynamide-Tethered Diyne 8-47a

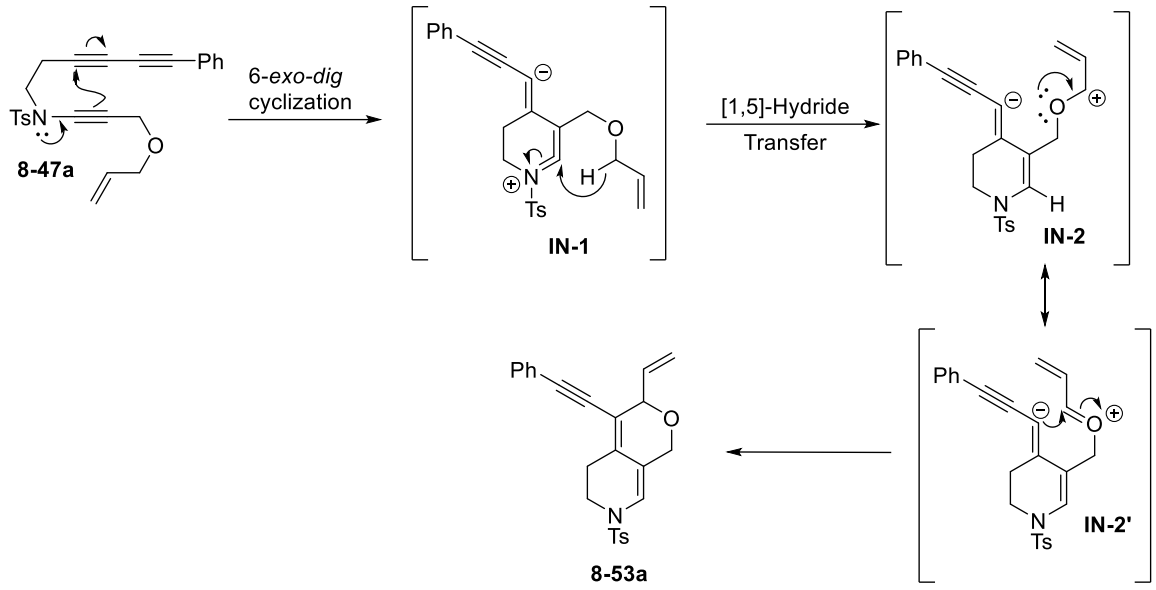
The freshly prepared compound **8-47a** was then heated in toluene-d_8 at 85 °C for 36 h, which provided 6-*exo*-*dig*-cyclized product **8-53a** in 95% yield (**Scheme 8.20**). This result not only confirms that **8-47a** is a direct precursor of **8-53a** but also the conversion of **8-47a** to **8-53a** is a purely thermal process not affected by the copper catalyst. Compound **8-47a** was tested for its RCM behavior with **G-II** catalyst in toluene at 90 °C to see whether it can generate ring-closed metathesis product **8-49a**. Under the conditions, no metathesis product was generated, and only a small amount (ca 10%) of **8-53a** together with other decomposed products were observed. On the basis of this initial discovery, we further explored the general scope of the unprecedented cyclization reaction of ynamide-tethered triyne functionality.



Scheme 8.20 Unexpected Cyclization of Ynamide-Tethered Triyne Functionality

Based on these results, we have formulated a plausible mechanism of the cyclization reaction

(**Scheme 8.21**). We believe that the most crucial aspect of the cyclization of **8-47a** to **8-53a** is the intramolecular interaction of the electron-donating ynamide functionality with the electron-withdrawing diyne moiety to provide 6-*exo*-*dig*-cyclized allenyliminium intermediate **IN-1**. The highly strained intermediate **IN-1** can abstract an hydride to induce [1,5]-hydride transfer to form a zewitterionic intermediate **IN-2**, which then undergo C−C bond formation to afford bicyclic product **8-53a**.



Scheme 8.21 Plausible Mechanism for Cyclization of a Ynamide-Tethered Triyne

With this proposed mechanism, we also hypothesized that the overall efficiency of the reaction would critically depend on the easiness of forming 6-*exo*-*dig*-cyclized intermediate **IN-1** and zewitterionic intermediate **IN-2**, which in turn should be dependent on the existence of the anion- and cation-stabilizing groups. To prove this hypothesis, we have prepared a range of substrates containing structural variations and tested their reaction profiles (**Table 8.2**).

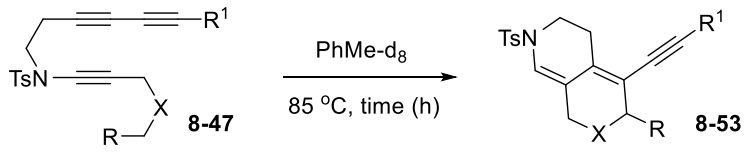
First, we compared the subtle electronic effect of the substituent on the diyne (entries 1−3). Ene-ynamide-tethered diynes **8-47b**, **8-47c**, and **8-47d** having a different substituent on the diyne, where **8-47b** and **8-47c** have an aryl group (phenyl and 4-chlorophenyl) and **8-47d** has a triethyl silyl group, upon heating in toluene-d_8 at 85 ºC, afforded cyclized products **8-53b 8-53c**, and **8-53d** in 81%, 88%, and 84%

yield, respectively (entries 1−3). The cyclization of **8-47b** and **8-47d** has significant reaction time difference; triethyl silyl substituent-containing triyne **8-47d** took 28 h for complete cycliation, whereas a phenyl substituted-triyne **8-47b** took 34 h.

Next, we explored the subtle electronic effect on the carbon involved in the [1,5]-hydride transfer (entries 4−10). Ynamide **8-47e** with benzylic C–Hs, ynamide **8-47f** with a 4-methoxy benzylic C–Hs, ynamide **8-47g** with a 4-nitro-benzylic C–Hs, and ynamide **8-47h** with 4-trifluromethyl benzylic C–Hs, afford cyclized products **8-53e**−**8-53h** in good yields (entries 4−7). Also, ynamide **8-47i** with a tertiary benzylic C–H bond cyclized smoothly to generate **8-53i** in 83% yield (entry 8). On the other hand, the reaction ynamide **8-47j** derived from cyclohexanemethanol took 48 h for complete conversion to provide product **8-53j** (76%, entry 9), and that of ynamide **8-47k** containing a myrtenol moity took 34 h to afford **8-53k** in 81% yield (entry 10). The reactivity difference in **8-47e**−**8-47k** clearly indicates the subtle electronic effect in [1,5]-hydride transfer step to form a zewitterionic intermediate **IN-2**. The hydride transfer from a benzylic carbon is much faster than that from an allylic carbon, which is still faster than that from a saturated alkyl group.

Subsequently, we compared examined the steric effect of the substituents at the propargyl ether carbon center (entries 11 and 12). While methyl-substituted propargyl ether **8-47l** took 48 h to provide cyclized product **8-53l** in 81% yield (entry 11), more sterically hindered *gem*-dimethyl substituted propargyl ether **8-47m** required high temperature (100 ºC) to provide cyclized product **8-53m** in 78% yield (entry 12). These results suggest that the increased steric effect induced by the substituents on the propargyl ether may increase the activation barrier to form intermediate **IN-1**.

We next studied the effect of ring size and requirement of propargyl oxygen (entries 13 and 14). As expected, homopropargyl-tethered substrate **8-47n** took 120 h to provide **8-53n** in 68% yield (entry 13). Interestingly, substrate ynamide **8-47o** derived from diethyl allylmalonate behaved differently to provide a mixture of 6-*exo*-*dig* cyclized product **8-53o** and **8-53o′** in 1.2:1 ratio with 78% combined yield (entry



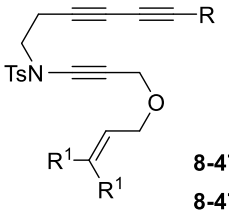
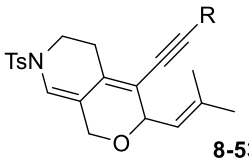
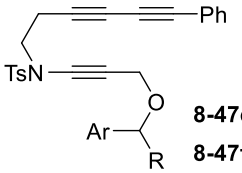
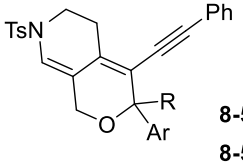
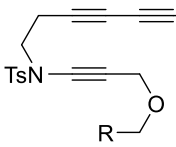
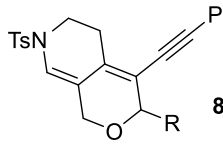
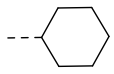
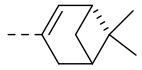
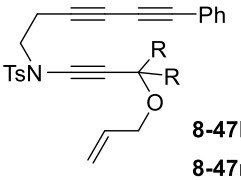
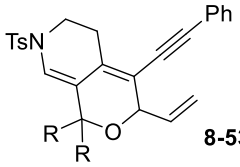
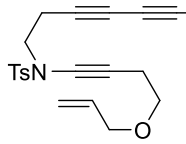
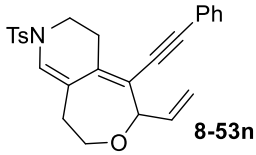
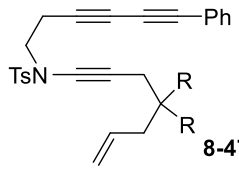
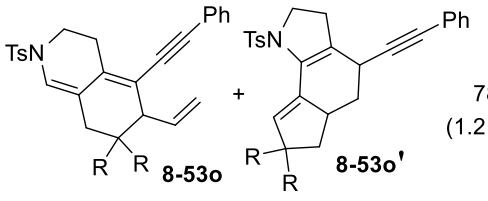
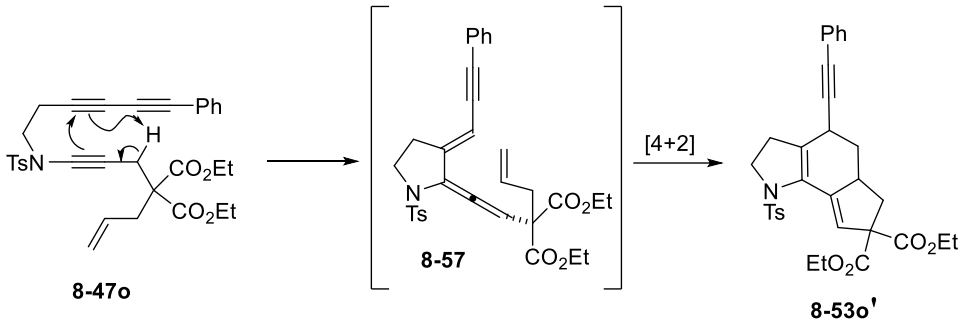
entry	substrate	time (h)	product	yield (%)
				
1	**8-47b**, R = Ph, R^1 = Me	34	**8-53b**	81
2	**8-47c**, R = 4-Cl-C_6H_4, R^1 = H	30	**8-53c**	89
3	**8-47d**, R = $SiEt_3$, R^1 = Me	28	**8-53d**	84
				
4	**8-47e**, Ar = Ph, R = H	24	**8-53e**	95
5	**8-47f**, Ar = 4-$MeOC_6H_4$, R = H	23	**8-53f**	83
6	**8-47g**, Ar = 4-$NO_2C_6H_4$, R = H	24	**8-53g**	88
7	**8-47h**, Ar = 4-$CF_3C_6H_4$, R = H	23	**8-53h**	89
8	**8-47i**, Ar = Ph, R = Me	28	**8-53i**	83
				
9	**8-47j**, R = 	48	**8-53j**	76
10	**8-47k**, R = 	34	**8-53k**	81
				
11	**8-47l**, R = H, Me	48	**8-53l**	81
12	**8-47m**, R = Me, Me	48	**8-53m**	78
				
13	**8-47n**	120	**8-53n**	68
				
14	**8-47o**, R = CO_2Et	72	**8-53o** + **8-53o'**	78 (1.2 : 1)

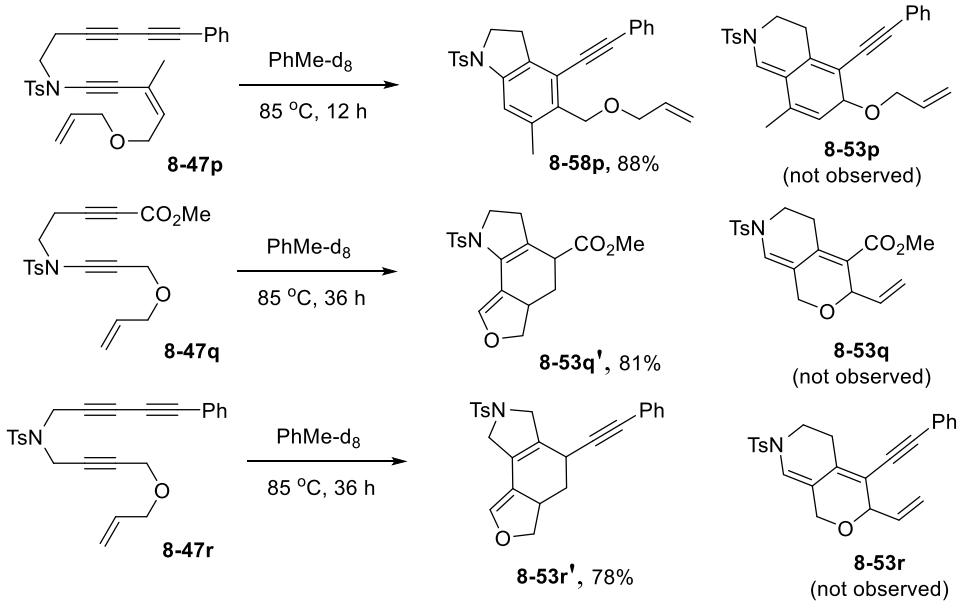
Table 8.2 Cyclization Reaction of Ynamide-Tethered Triynes

10). The formation of **8-53o′** is the consequence of an initial Alder-ene reaction followed by Diels-Alder reaction as shown in **Scheme 8.22**.



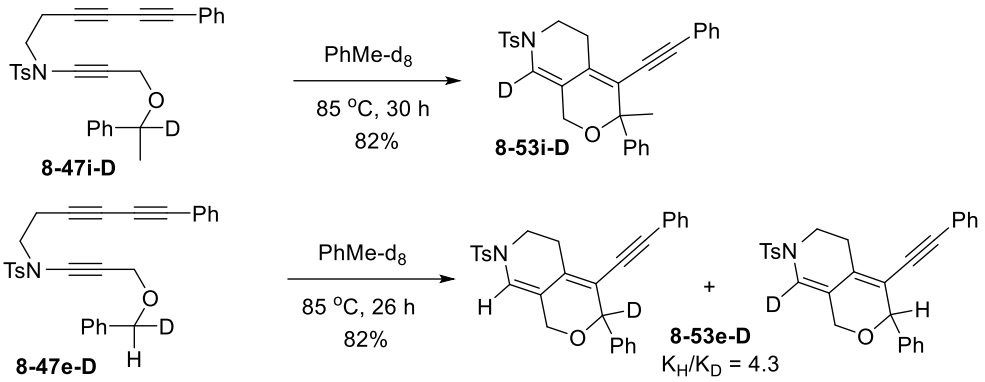
Scheme 8.22 Ene-Reaction Followed Diels-Alder Cyclization of Ynamide

We further examined the behavior of **8-47p** with 1,3-enyne tether, ynamide **8-47q** containing only two triple bonds, and **8-47r** containing a sulfonamide tether (**Scheme 8.23**). The reaction of **8-47p** provided only the [4+2] cycloaddition product[8,9,10] **8-58p** in 88% yield without forming the expected **8-53p**. The reaction of **8-47q** provided **8-53q′** in 81% yield via an initial ene-reaction followed by Diels-Alder reaction. Substrate **8-47r** having propagyl sulfonamide instead of ynamide also underwent only ene-reaction followed by Diels-Alder reaction to generate **8-53r′** in 78% yield.



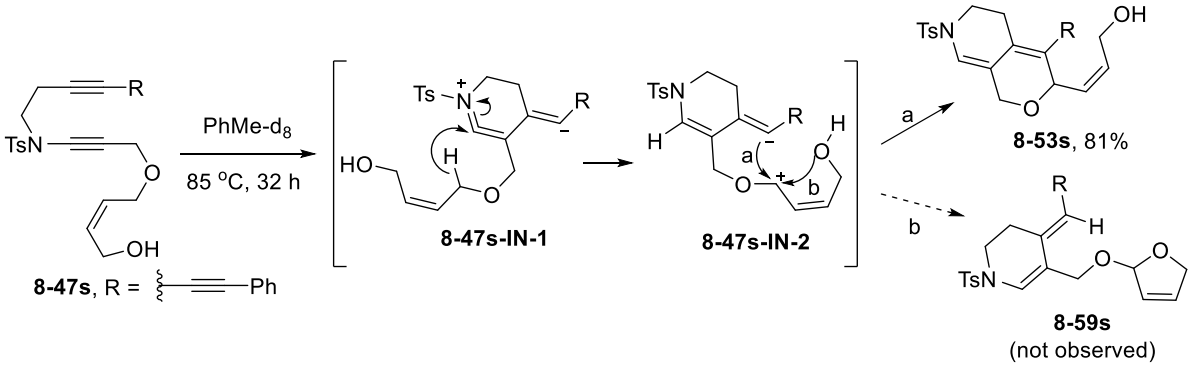
Scheme 8.23 Different Cyclization Behaviors

To gain further mechanistic insights into the cyclization, we deuterium labeling studies were carried out (**Scheme 8.24**). Upon thermal cyclization of 3° deuterated ynamide **8-47i-D**, complete deuterium incorporated on **8-53i-D** was observed with 82% isolated yield. On the other hand, 2° deuterated ynamide **8-47e-D** cyclized to provide **8-53e-D** in 82% yield with k_H/k_D = 4.3.



Scheme 8.24 Deuterium Labelling Experiments

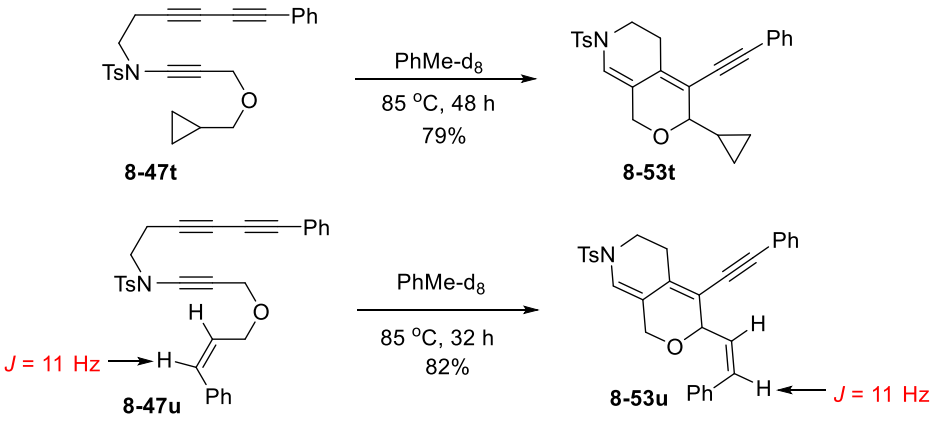
We next studied the possibility to trap the oxonium ion intermediate using an internal alcohol (**Scheme 8.25**). The ynamide **8-47s** having a free hydroxyl group may form oxonium ion intermediate **8-47s-IN-2** after hydride transfer from **8-47s-IN-1**. At this juncture, we expected that the generated oxonium ion should react with the tethered alcohol to provide **8-59s**, however, only **8-53s** was isolated in 81% yield.



Scheme 8.25 Possibility of Intramolecular Cation Trapping

The negative result of cation trapping with a tethered alcohol moiety, may suggest the possibility of

involving radical intermediates. To test this hypothesis, cyclopropyl-containing ynamide **8-47t** was synthesized and subjected to the typical reaction conditions, but product **8-53t** was obtained as only isolated product in 79% yield, where the cyclopropane ring was intact (**Scheme 8.26**). Additional probe ynamide **8-47u** for radical mechanism having a *cis*-alkene was examined, expecting that isomerization of the cis-alkene would happen to form a *trans*-alkene, if a radical intermediate is involved. Again the reaction of **8-47u** provided only the *cis*-alkenyl product **8-53u** in 82% yield. Even the reaction in presence of BHT or the radical trapping agents like TEMPO afforded **8-53u** with similar efficiency.



Scheme 8.26 Probes for a Radical Intermediate

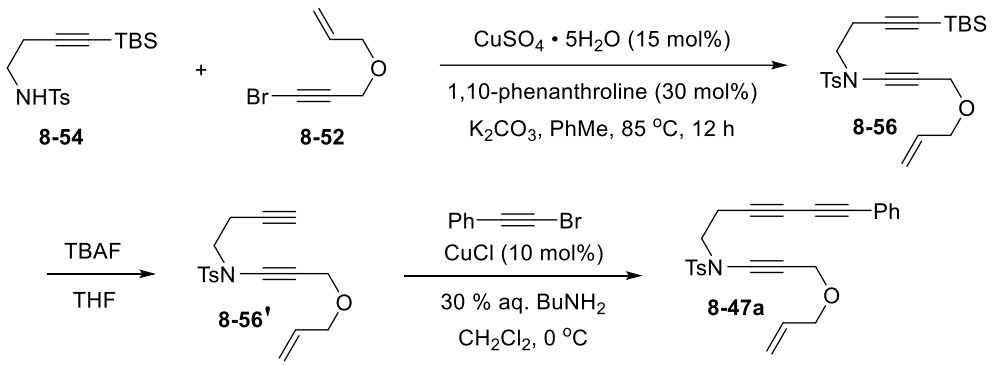
8.6. Summary

In summary, a novel and facile thermal 6-*exo*-*dig*-cyclization of ynamide-tethered triynes has been discovered. The overall reaction scope has been defined by examining substrates with variation of anion- and cation-stabilizing groups, the substituent on the diyne moiety, allyl propargylic-, benzyl propargylic-, alkyl propargylic-ethers and propargylic carbon substituents. Based on the observed reaction profiles, and preliminary mechanistic studies, the reaction is proposed to proceed through the interaction between an electron withdrawing 1,3-diyne moiety with an electron donating ynamide moiety to form a highly strained 6-*endo*-*dig*-cyclized zwitterionic intermediate with an allenyliminium ion followed by [1,5]-hydride shift, and final ring closure. Providing appropriate electronic activation by the substituents, this new cyclization reaction can be further developed to generate a broad range of novel bicyclic compounds

not readily accessible by other.

8.7. Experimental Details

8.7.1. General Procedure for Substrate Preparation:



Synthesis of 8-56 from 8-54: In a 100 mL flask **8-54** (600 mg, 1.8 mmol) was dissolved in 15 mL toluene under nitrogen. $CuSO_4$•$5H_2O$ (0.27 mmol), 1,10-phenanthroline (0.54 mmol), and K_2CO_3 (3.6 mmol) followed by **8-52** (2.7 mmol) was added to the reaction flask. The resulting mixture was heated in oil bath at 85 °C for 20 h. The flask cooled to room temperature and purified through column using hexane/EtOAc (7:3) as eluent to provid **8-56** (400 mg, 52%).

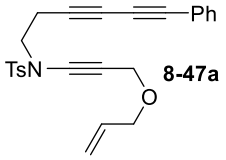
Synthesis of 8-56′ from 8-53: In a 250 mL flask **8-56** (400 mg, 0.9 mmol) was dissolved in 10 mL tetrahydrofuran and cooled to 0 °C. TBAF (1M in THF, 1.2 mL) was added drop wise. The reaction warmed to room temperature and stirred for 2 h. The reaction quenched with saturated aqueous NH_4Cl, extract with EtOAc, and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure and purified through column chromatography using hexane/EtOAc (7:3) an eluent to afford the **8-56′** (210 mg, 74%).

Synthesis of 8-47a from 8-56′: In a 100 mL round-bottom flask with septum-inlet **8-56′** (200 mg, 0.6 mmol) was dissolved in 10 mL CH_2Cl_2 and cooled to 0 °C. The flask was connected to continuous nitrogen purging adapter and added the 30% aq $BuNH_2$ (5 mL) and CuCl (0.06 mmol). The reaction turns into blue color which was discharged by adding few crystals of hydroxylamine hydrochloride.

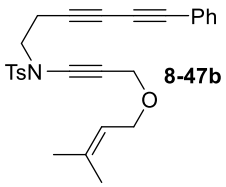
Phenylacetylene bromide (0.9 mmol) in 15 mL CH_2Cl_2 was added dropwise to the reaction mixture at 0 ^oC for 10 min. stirring was continued for 15 min, quenched with H_2O, extract with CH_2Cl_2, and dried over $MgSO_4$. The filtrate was concentrated under reduced pressure and purified through column using hexane/EtOAc (7:3) an eluent to afford the **8-47a** (210 mg, 74%).

8.7.2. General Procedure for Thermal Bicyclization: Ynamide tethered triyne **8-47a** (42 mg, 0.1 mmol) dissolved in 0.6 mL of toluene-d_8 in NMR tube was heated at 85 ^oC for 34 h (monitored by ^1H NMR). The reaction tube was cooled to room temperature and concentrated under reduced pressure. The crude residue was purified by silica gel column chromatography (hexane/EtOAc 7:3) to provide bicyclic product **8-53a** (38 mg, 95%).

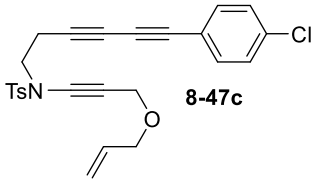
8.7.3. Selected Characterization Data



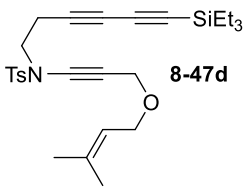
8-47a: ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 6.9 Hz, 2H), 7.35–7.31 (m, 5H), 5.88 (ddd, *J* = 5.7 Hz, *J* = 10.9 Hz, *J* = 16.2 Hz, 1H), 5.29 (dd, *J* = 1.4 Hz, *J* = 17.2 Hz, 1H), 5.20 (d, *J* = 10.4 Hz, 1H), 4.29 (s, 2H), 3.99 (d, *J* = 5.7 Hz, 2H), 3.56 (t, *J* = 7.4 Hz, 2H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145, 134.5, 134.1, 132.5, 129.9, 129.8, 129.1, 128.4, 127.6, 121.6, 117.7, 79.3, 78.8, 75.8, 73.9, 70.2, 68.3, 67.3, 57.5, 49.6, 26, 21.6, 19.6; HRMS (EI) calcd for $C_{25}H_{23}NO_3S$ $[M]^+$ 417.1399, found 417.1402.



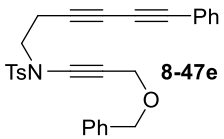
8-47b: ^1H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 6.9 Hz, 2H), 7.31 (td, *J* = 3.7 Hz, *J* = 15.9 Hz, 2H), 5.30 (ddd, *J* = 1.3 Hz, *J* = 4.3 Hz, *J* = 7.0 Hz, 1H), 4.25 (s, 2H), 3.97 (d, *J* = 7.0 Hz, 2H), 3.55 (t, *J* = 7.4 Hz, 2H), 2.70 (t, *J* = 7.4 Hz, 2H), 2.40 (s, 3H), 1.73 (s, 3H), 1.66 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 132.5, 129.9, 129.1, 128.4, 127.6, 121.6, 120.4, 79.4, 78.4, 75.8, 73.9, 68.6, 67.3, 65.6, 57.2, 49.6, 25.8, 21.6, 19.6, 18; HRMS (ESI) calcd for $C_{27}H_{28}NO_3S$ $[M+H]^+$ 446.1790, found 446.1787.



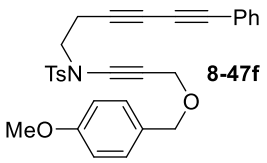
8-47c: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.37 (dd, *J*= 8.3 Hz, *J* = 19.6 Hz, 2H), 7.28 (m, 2H), 5.88 (ddd, *J* = 5.8 Hz, *J* = 11.1 Hz, *J* = 16.2 Hz, 2H), 5.29 (dd, *J* = 1.4 Hz, *J* = 17.2 Hz, 1H), 5.20 (d, *J* = 10.3 Hz, 1H), 4.29 (s, 2H), 3.99 (d, *J* = 5.7 Hz, 2H), 3.56 (t, *J* = 7.4 Hz, 2H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145, 135.3, 134.4, 134, 133.7, 129.9, 128.8, 127.6, 120.1, 117.8, 79.9, 78.8, 74.5, 70.2, 68.3, 67.1, 57.5, 49.5, 21.7, 19.6.



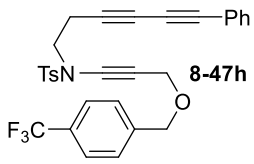
8-47d: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.1 Hz, 2H), 5.30–5.28 (m, 1H), 4.22 (s, 2H), 3.95 (d, *J* = 7.0 Hz, 2H), 3.49 (t, *J* = 7.6 Hz, 2H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.42 (s, 3H), 2.02 (s, 3H), 1.73 (s, 3H), 1.65 (s, 3H), 0.97 (t, *J* = 7.9 Hz, 9H), 0.60 (q, *J* = 7.9 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 138.1, 134.4, 129.9, 127.6, 120.3, 88.8, 82.5, 78.4, 73.9, 68.5, 67.7, 65.5, 57.2, 49.5, 25.7, 21.6, 19.2, 18.7,7.3, 4.2; HRMS (EI) calcd for $C_{25}H_{39}SiNO_3SNa$ $[M+Na]^+$ 484.2318, found 484.2323.



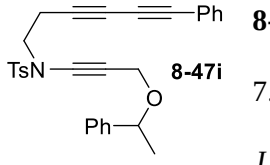
8-47e: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.85 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.35–7.32 (m, 10H), 4.56 (s, 2H), 4.35 (s, 2H), 3.60 (t, *J* = 7.3 Hz, 2H), 2.74 (t, *J* = 7.3 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 137.6, 134.4, 132.6, 130, 129.2, 128.5, 128.1, 127.8, 127.7 , 121.6, 79.5, 79.1, 77.5, 77.2, 77, 75.9, 74, 71.2, 68.4, 67.4, 57.6, 49.6, 21.7, 19.6; HRMS (ESI) calcd for $C_{29}H_{26}NO_3S$ $[M+H]^+$ 468.1633, found 468.1634.



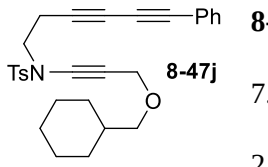
8-47f: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 7.0 Hz, 2H), 7.33–7.31 (m, 5H), 7.26 (d, *J* = 8.5 Hz, 4H), 6.87 (d, *J* = 8.5 Hz, 2H), 4.48 (s, 2H), 4.29 (s, 2H), 3.79 (s, 3H), 3.58 (t, *J* = 7.3 Hz, 2H), 2.73 (t, *J* = 7.3 Hz, 2H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.4, 145, 134.4, 132.5, 129.9, 129.8, 129.5, 129.2, 128.5, 128.4, 127.7, 127.1, 121.6, 113.8, 79.4, 78.9, 75.8, 73.9, 70.8, 68.4, 67.3, 57.1, 55.3, 49.6, 21.7, 19.6.



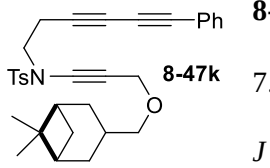
8-47h: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, *J* = 8.2 Hz, 2H), 7.58 (d, *J* = 8.1 Hz, 2H), 7.45 (m, 4H), 7.35–7.32 (m, 5H), 4.60 (s, 2H), 4.37 (s, 2H), 3.58 (t, *J* = 7.3 Hz, 2H), 2.72 (t, *J* = 7.3 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 141.8, 134.4, 132.5, 129.9, 129.7,129.2, 128.4, 127.9, 127.6, 125.3, 121.5, 79.5, 79.3, 75.9, 73.8, 70.2, 68, 67.4, 58, 49.5, 21.6, 19.7.



8-47i: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.47–7.45 (m, 2H), 7.35–7.32 (m, 10H) ppm 4.63 (q, *J* = 6.5 Hz, 1H), 4.24 (d, *J* = 16.3 Hz, 1H), 4.05 (d, *J* = 16.3 Hz, 1H), 3.55 (ddd, *J* =7.7 Hz, *J* = 13.9 Hz, *J* = 13.4Hz, 2H), 2.69 (t, *J* = 7.4 Hz, 2H), 2.43 (s, 3H), 1.46 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 142.6, 134.5, 132.5, 129.9, 129.1, 128.5, 128.4, 127.7, 127.7, 126.5, 121.6, 79.4, 78.4, 77.3, 77.1, 76.8, 76.1, 75.8, 73.9, 68.6, 67.3, 55.9, 49.5, 23.7, 21.7, 19.6; HRMS (ESI) calcd for $C_{30}H_{28}NO_3S$ $[M+H]^+$ 482.1790, found 482.1793.

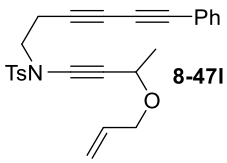


8-47j: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.46–7.44 (m, 2H), 7.33–7.29 (m, 5H), 4.24 (s, 2H), 3.56 (t, *J* = 7.4 Hz, 2H), 3.22 (d, *J* = 6.5 Hz, 2H), 2.70 (t, *J* = 7.4 Hz, 2H), 2.41 (s, 3H), 1.68 (m, 5H), 1.56–1.54 (m, 1H), 1.22–1.18 (m, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 134.5, 132.5, 129.9, 129.1, 128.4, 127.7, 121.6, 79.3, 78.3, 75.7, 75.5, 73.9, 68.7, 67.2, 58.5, 49.6, 37.9, 30.1, 26.6, 25.8, 21.6; HRMS (ESI) calcd for $C_{29}H_{32}NO_3S$ $[M+H]^+$ 474.2103, found 474.2098.



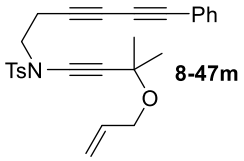
8-47k: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.46–7.44 (m, 2H), 7.33–7.29 (m, 5H), 5.52–5.50 (m, 1H) 4.24 (d, *J* = 2.3 Hz, 2H), 3.86 (dq, *J* = 1.3 Hz, *J* = 12.1 Hz, 2H), 3.56 (t, *J* = 7.4 Hz, 2H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.42 (s, 3H), 2.40 (dd, *J* = 3.0 Hz, *J* = 5.6 Hz, 1H), 2.28 (q, *J* = 17.9 Hz, 2H), 2.15 (dt, *J* = 1.1 Hz, *J* = 5.7 Hz, 2H), 2.12–2.10 (m, 1H), 1.29 (s, 3H), 1.17 (t, *J* = 8.5 Hz, 1H), 0.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ

144.9, 144.6, 134.5, 132.5, 129.9, 129.1, 128.4, 127.6, 121.6, 120.9, 79.3,78.5, 77.3, 77.1,76.8, 75.8, 73.9, 72.1, 68.5, 67.3; HRMS (ESI) calcd for $C_{32}H_{34}NO_3S$ $[M+H]^+$ 512.2259, found 512.2258.



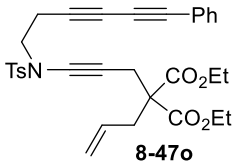
8-47l

8-47l: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.47–7.45 (m, 2H), 7.35–7.32 (m, 2H), 7.30 (dd, *J* = 4.5 Hz, *J* = 11.5 Hz, 3H), 5.89 (ddd, *J* = 5.7 Hz, *J* = 10.9 Hz, *J* = 22.3 Hz, 1H), 5.28 (dd, *J* = 1.5 Hz, *J* =17.2 Hz, 1H), 5.18 (d, *J* = 10.4 Hz,1H,), 4.34 (q, *J* = 6.6 Hz, 1H), 4.13 (dd, *J* = 5.2 Hz, *J* = 12.5 Hz, 1H,), 3.90 (dd, *J* = 6.2 Hz, *J* = 12.5 Hz, 1H), 3.57–3.55 (m, 2H), 2.70 (t, *J* = 7.4 Hz, 2H), 2.42 (s, 3H), 1.45 (d, *J* = 6.6 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 134.4, 132.5, 129.8, 129.1, 128.4, 127.7, 121.6, 117.3, 79.3, 77.6, 77.3, 77.1, 76.8, 75.8, 73.9, 71.5, 69.4, 67.3, 64.8, 49.6, 22.1, 21.6, 19.7.



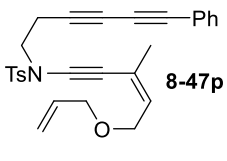
8-47m

8-47m: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 6.9 Hz, 2H), 7.35–7.32 (m, 5H), 5.89 (ddd, *J* = 5.5 Hz, *J* = 10.7 Hz, *J* = 22.6 Hz, 1H), 5.24 (dd, *J* = 1.6 Hz, *J* = 17.2 Hz, 1H), 5.12 (d, *J* = 10.4 Hz, 1H,), 3.99 (d, *J* = 5.5 Hz, 2H), 3.56 (t, *J* = 7.3 Hz, 2H), 2.69 (t, *J* = 7.3 Hz, 2H), 2.42 (s, 3H), 1.48 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 135.5, 132.5, 129.8, 129.1, 128.4, 127.7, 121.6, 116.2, 79.4, 77.1, 75.8, 73.5, 67.3, 65.4, 49.5, 28.9, 21.6, 19.7.



8-47o

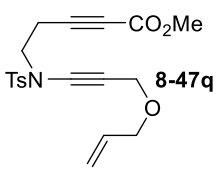
8-47o: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 5.56 (qd, *J* = 7.5 Hz, *J* = 9.9 Hz, 1H), 5.08–5.06 (m, 2H), 4.13 (q, *J* = 7.1 Hz, 4H), 3.37 (t, *J* = 7.6 Hz, 2H), 2.83 (s, 2H), 2.67 (d, *J* = 7.4 Hz, 2H), 2.42–2.40 (m, 4H), 1.92 (t, *J* = 2.5 Hz, 1H), 1.18 (t, *J* = 7.1 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ169.7, 144.6, 134.6, 131.8, 129.8, 127.5, 119.6, 79.6, 75.2, 70.5, 65.6, 61.5, 56.9, 49.9, 36.5, 22.7, 21.5, 18.1, 14.0.



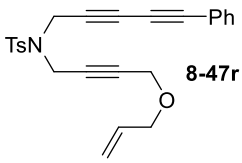
8-47p

8-47p: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.36–7.34 (m, 2H),7.31 (t, *J* = 7.2 Hz 3H), 5.92 (ddd, *J* = 5.7 Hz, *J* = 10.9 Hz, *J* = 22.6 Hz, 1H), 5.73 (t, *J* =6.7 Hz, 1H), 5.27 (d, *J* = 17.2 Hz, 1H), 5.17 (d, *J* = 10.4 Hz, 1H), 4.12 (d, *J* = 6.8 Hz, 2H), 3.97 (d, *J* = 5.6 Hz, 2H), 3.60 (t, *J* = 7.4 Hz, 2H), 2.71 (t, *J* = 7.4

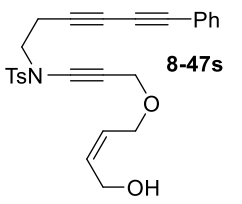
Hz, 2H), 2.43 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.0, 134.8, 134.4, 132.5, 131.3,129.9, 129.1, 128.4, 127.7, 121.6, 121.0, 117.0, 86.3, 79.2, 75.8, 73.8, 71.2, 70.5, 68.5, 67.4, 49.7, 23.1, 21.7, 19.7; HRMS (ESI) calcd for $C_{28}H_{28}NO_3S$ $[M+H]^+$ 458.1790, found 458.1776.



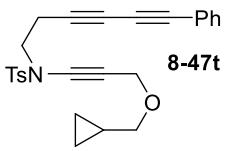
8-47q: ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (dd, *J* = 1.6 Hz, *J* = 8.2 Hz, 1H), 7.33 (d, *J* = 8.1 Hz, 1H), 5.84 (ddd, *J* = 5.5 Hz, *J* = 10.8 Hz, *J* = 22.7 Hz, 1H), 5.28 (dd, *J* = 1.5 Hz, *J* = 17.2 Hz, 1H), 5.15 (dd, *J* = 1.2 Hz, *J* = 10.4 Hz, 1H), 4.21 (p, *J* = 7.1 Hz, 1H), 3.88 (dd, *J* = 1.1 Hz, *J* = 5.4 Hz, 1H), 3.74 (d, *J* = 3.5 Hz, 1H), 3.55 (dt, *J* = 3.7 Hz, *J* = 7.1 Hz, 1H), 2.68 (t, *J* = 7.1 Hz, 1H), 2.44 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.6, 145.1, 134.3, 134, 130.1, 129.9, 127.6, 117.7, 84.2, 78.6, 77.3, 74.5, 70.2, 68.3, 57.4, 52.7, 48.9, 21.6, 18.7; HRMS (ESI) calcd for $C_{19}H_{21}NO_5S$ $[M+H]^+$ 376.1219, found 376.1208.



8-47r: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 5.83 (ddd, *J* = 5.7 Hz, *J* = 10.9 Hz, *J* = 16.2 Hz, 1H), 5.25 (dd, *J* = 1.4 Hz, *J* = 17.2 Hz, 1H), 5.18 (d, *J* = 10.4 Hz, 1H), 4.21 (s, 2H), 4.14 (s, 2H), 3.99 (s, 2H), 3.91 (d, *J* = 5.7 Hz, 2H), 2.39 (s, 3H), 0.91 (s, 9H), 0.10 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144, 134.9, 133.8, 129.6, 127.9, 117.8, 87.6, 85.4, 82.2, 78.5, 70.8, 70.5, 70, 57.1, 37.1, 37, 25.9, 21.5, –4.8; HRMS (ESI) calcd for $C_{23}H_{34}SiNO_3S$ $[M+H]^+$ 456.2029, found 456.2022.

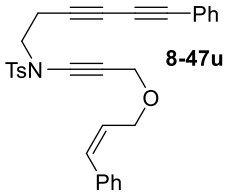


8-47s: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 7.1 Hz, 2H), 7.34–7.30 (m, 1H), 5.84–5.82 (m, 1H), 5.65–5.63 (m, 1H), 4.30 (s, 2H), 4.22 (d, *J* = 6.5 Hz, 2H), 4.11 (d, *J* = 6.6 Hz, 2H), 3.56 (t, *J* = 7.3 Hz, 2H), 2.71 (t, *J* = 7.3 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145.1, 134.4, 133.2, 132.5, 130, 129.2, 128.4, 127.6, 127.4, 121.6, 79.3, 79, 75.8, 68.1, 67.3, 64.5, 58.6, 57.5, 49.5, 21.7, 19.6; HRMS (ESI) calcd for $C_{26}H_{26}NO_4S$ $[M+H]^+$ 448.1583, found 448.1580.



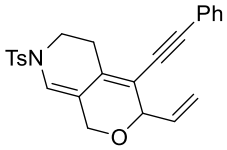
8-47t: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.46 (d, *J* = 7.0 Hz, 2H), 7.35–7.31 (m, 5H), 4.30 (s, 2H), 3.56 (t, *J* = 7.4 Hz, 2H), 3.28 (d, *J* = 7.0 Hz,

2H), 2.70 (t, *J* = 7.4 Hz, 2H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 134.5, 132.5, 129.9, 129.1, 128.4, 127.6, 121.6, 79.3, 78.5, 75.8, 68.5, 67.3, 57.8, 49.5, 26, 21.6, 19.6; HRMS (ESI) calcd for $C_{26}H_{26}NO_3S$ $[M+H]^+$ 432.1633, found 432.1636.



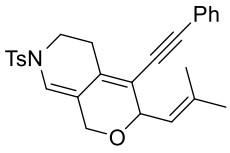
8-47u

8-47u: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.80 (d, *J* = 8.2 Hz, 2H), 7.48–7.44 (m, 2H), 7.35–7.30 (m, 10H), 7.22 (d, *J* = 7.5 Hz, 1H), 6.62 (d, *J* = 11.8 Hz, 1H), 5.83–5.81 (m, 1H), 4.33 (s, 2H), 4.29 (d, *J* = 6.4 Hz, 2H), 3.51 (t, *J* = 7.5 Hz, 2H), 2.64 (t, *J* = 7.5 Hz, 2H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 136.5, 134.4, 132.5, 132.2, 129.9, 129.1, 128.8, 128.6, 128.4, 128.3, 128.1, 127.8, 127.6, 127.6, 127.3, 126.5, 121.6, 79.3, 78.9, 75.8, 73.9, 69.8, 68.2, 67.3, 66.1, 57.9, 49.5, 21.6, 19.6; HRMS (ESI) calcd for $C_{31}H_{28}NO_3S$ $[M+H]^+$ 494.1790, found 494.1791.



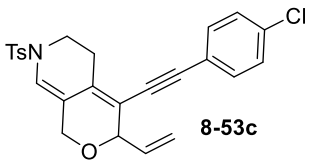
8-53a

8-53a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.37 (dd, *J* = 2.9 Hz, *J* = 6.5 Hz, 2H), 7.32–7.29 (m, 5H), 6.62 (s, 1H), 5.99–5.97 (m, 1H), 5.36 (dd, *J* = 13.8 Hz, *J* = 35.5 Hz, 1H), 4.75 (d, J = 5.6 Hz, 1H), 4.38 (d, *J* = 13.1 Hz, 1H), 4.20 (d, *J* = 13.1 Hz, 1H), 3.56 (ddd, *J* = 5.2 Hz, *J* = 7.0 Hz, *J* = 12.0 Hz, 1H), 3.45 (qd, *J* = 4.6 Hz, *J* = 8.4 Hz, 1H), 2.72–2.70 (m, 2H), 2.43 (s, 3H) ; ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 135.3, 132.2, 131.2, 130, 128.3, 127, 123, 120.4, 118.2, 114.5, 113.7, 98.6, 85.3, 63.4, 43.4, 26.1, 21.6; HRMS (EI) calcd for $C_{25}H_{23}NO_3S$ $[M]^+$ 417.1399, found 417.1402.



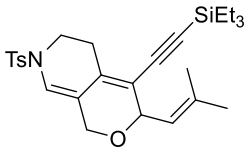
8-53b

8-53b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.32–7.28 (m, 7H), 6.60 (s, 1H), 5.31 (d, *J* = 8.8 Hz, 1H), 4.97 (d, *J* = 8.8 Hz, 1H), 4.36 (d, *J* = 13.1 Hz, 1H), 4.24–4.22 (m, 1H), 3.58 (m, 1H), 3.38 (ddd, *J* = 4.3 Hz, *J* = 8.7 Hz, *J* = 15.9 Hz, 1H), 2.69–2.67 (m, 2H), 2.43 (s, 3H), 1.80 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 139, 138.3, 137.5, 137, 135.5, 131.2, 130, 128.3, 128.2, 127, 122.6, 120.1, 117.4, 114, 86.1, 73.5, 64.4, 43.5, 26.1, 25.9, 21.6, 18.7; HRMS (ESI) calcd for $C_{27}H_{28}NO_3S$ $[M+H]^+$ 446.1790, found 446.1780.



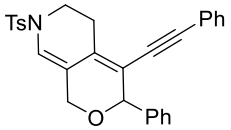
8-53c

8-53c: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.29 (t, *J* = 5.7 Hz, 3H), 6.63 (s, 1H), 5.97 (ddd, J = 5.9 Hz, J = 10.4 Hz, J = 16.7 Hz, 1H), 5.36 (dd, *J* = 13.8 Hz, *J* = 28.8 Hz, 2H), 4.73 (d, *J* = 5.3 Hz, 1H), 4.37 (d, *J* = 13.1 Hz, 1H), 4.20 (d, *J* = 13.2 Hz, 1H), 3.55–3.53 (m, 1H), 3.45–3.43 (m, 1H), 2.70–2.68 (m, 1H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 135.2, 134.5, 133, 132.4, 130, 128.7, 127.3, 127, 120.7, 118.4, 113.4, 97.7, 88.1, 63.4, 43.4, 26.1, 21.6.



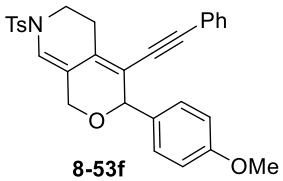
8-53d

8-53d: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.32 (dd, *J* = 8.3 Hz, *J* = 13.3 Hz, 2H), 6.57 (s, 1H), 5.23 (d, *J* = 8.9 Hz, 1H), 4.88 (d, *J* = 8.9 Hz, 1H), 4.31 (d, *J* = 13.1 Hz, 1H), 4.19 (d, *J* = 13.1 Hz, 1H), 3.91 (dd, *J* = 4.6 Hz, *J* = 10.5 Hz, 1H), 3.57–3.55 (m, 1H), 3.33 (ddd, *J* = 4.5 Hz, *J* = 9.3 Hz, *J* = 11.9 Hz, 1H), 2.63–2.61 (m, 2H), 2.43 (s, 3H), 1.73 (s, 6H), 0.95 (t, *J* = 7.9 Hz, 9H), 0.59 (qd, *J* = 7.9 Hz, *J* = 23.7 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 138.1, 132.7, 129.9, 127.5, 127, 122.7, 120.1, 116.4, 113.8, 102.4, 73.5, 65.1, 64.5, 43.4, 26.2, 21.6, 31.6, 31.3, 31.2, 31.1, 26.2, 26.1, 21.7, 21.1, 21, 19.6, 19.5.



8-53e

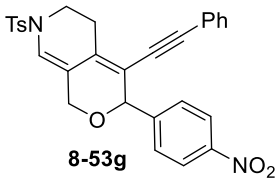
8-53e: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.37–7.33 (m, 7H), 7.22 (dd, *J* = 2.4 Hz, *J* =8.3 Hz, 3H), 7.14 (dd, *J* = 1.9 Hz, *J* = 7.4 Hz, 2H), 6.65 (s, 1H), 5.30 (s, 1H), 4.28–4.26 (m, 1H), 3.61 (ddt, *J* = 4.1 Hz, *J* = 7.2 Hz, *J* = 10.8 Hz, 1H), 3.48–3.46 (m, 1H), 2.85–2.83 (m, 1H), 2.74 (ddd, *J* = 5.2 Hz, *J* = 10.1 Hz, *J* = 20.6 Hz, 1H), 2.45 (s, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.3, 139.3, 134.7, 132.7, 132.5, 131.1, 130, 128.5, 128.2, 127.1, 123, 120.5, 115.2,113.9, 99.3, 86.2, 79, 63.7, 43.6, 26.2, 21.6; HRMS (EI) calcd for $C_{29}H_{25}NO_3S$ $[M]^+$ 467.1555, found 467.1565.



8-53f

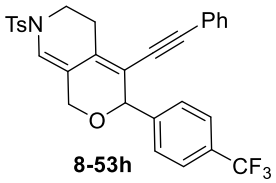
8-53f: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.3 Hz, 2H), 7.34 (d, *J* = 8.1 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 3H), 7.23–7.21 (m, 2H), 7.19–7.17 (m, 2H), 6.88 (d, *J* = 8.7 Hz, 1H), 6.64 (s, 1H), 5.27 (s, 1H), 4.23 (dd, *J* = 13.4 Hz, *J* = 30.6 Hz, 2H), 3.80 (s, 3H), 3.62 (ddd, *J* = 4.7 Hz, *J* = 7.1 Hz, *J* = 11.8 Hz, 1H), 3.48 (dq, *J* = 4.5 Hz, *J* = 9.0

Hz, 1H), 2.85–2.83 (m, 1H), 2.74–2.72 (m, 1H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 159.5, 144.2, 134.7, 132.6, 131.4, 131.2, 130, 129.8, 128.2, 127.1, 122.3, 120.4, 115.3, 114, 113.6, 99.1, 86.3, 78.4, 63.2, 55.3, 43.6, 26.2, 21.6, 31.6, 31.3, 31, 31.2, 31.1, 26.2, 26.1, 21.7, 21.1, 21, 19.6, 19.5.



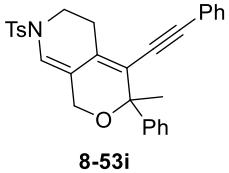
8-53g

8-53g: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.23–8.21 (m, 3H), 7.70 (d, *J* = 8.2 Hz, 2H),7.60 (d, *J* = 8.6 Hz, 2H), 7.52 (d, *J* = 8.5 Hz, 1H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.26–7.24 (m, 4H), 7.13 (d, *J* = 6.3 Hz, 2H), 6.70 (s, 1H), 5.37 (s, 1H), 4.70 (s, 1H), 4.34 (s, 2H), 4.31 (s, 3H), 3.66–3.64 (m, 1H), 3.45–3.43 (m, 1H), 2.83 (ddd, *J* = 3.4 Hz, *J* = 9.0 Hz, *J* = 14.9 Hz, 1H), 2.74–2.72 (m, 1H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 147, 144.4, 134.8, 132.9, 131, 130.1, 129.2, 128.6, 128.4, 128, 127.1, 123.7, 123.3, 121.2, 113.7, 113, 99.3, 85.6, 70.6, 64.4, 58.4, 43.4, 26.2, 21.6.



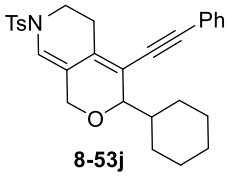
8-53h

8-53h: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.2 Hz, 2H), 7.62 (d, *J* = 8.1 Hz, 2H), 7.54 (d, *J* = 8.1 Hz, 2H), 7.35 (d, *J* = 8.1 Hz, 2H), 7.24–7.22 (m, 3H), 7.12 (dd, *J* = 1.5 Hz, *J* = 7.7 Hz, 2H), 6.68 (s, 1H), 5.34 (s, 1H), 4.28 (s, 2H), 3.64 (ddd, *J* = 4.8 Hz, *J* = 6.8 Hz, *J* = 11.7 Hz, 1H), 3.47–3.45 (m, 1H), 2.85–2.83 (m, 1H), 2.75–2.73 (m, 1H), 2.45 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.3, 143.4, 134.6, 133.1, 131.1, 130, 128.8, 128.4, 128.3, 127.1, 125.1, 121, 114.3, 113.4, 99.7, 85.8, 78.4, 64, 43.5, 26.2, 21.6.



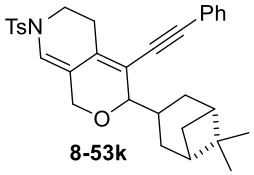
8-53i

8-53i: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.3 Hz, 2H), 7.54 (d, *J* = 7.3 Hz, 2H), 7.34–7.30 (m, 10H), 6.56 (s, 1H), 4.09 (d, *J* = 13.6 Hz, 1H), 3.98 (dd, *J* = 1.2 Hz, *J* = 13.5 Hz, 1H), 3.52 (t, *J* = 6.3 Hz, 2H), 2.84 (tq, *J* = 6.3 Hz, *J* = 16.3 Hz, 2H), 2.43 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 134.7, 132.6, 131.1, 130, 128.3, 128.3, 128.2, 127.5, 127, 120.4, 114, 99.6, 98.8, 87.4, 78.9, 61.4, 43.6, 29.4, 26.7, 21.6; HRMS (ESI) calcd for $C_{30}H_{28}NO_3S$ $[M+H]^+$ 482.1790, found 482.1780.



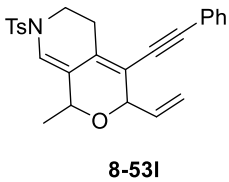
8-53j

8-53j: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.38 (dd, *J* = 3.0 Hz, *J* = 6.7 Hz, 2H), 7.32–7.29 (m, 5H), 7.26 (s, 1H), 6.56 (s, 1H), 4.32 (d, *J* = 13.1 Hz, 1H), 4.18 (d, *J* = 13.1 Hz, 1H), 4.09 (s, 1H), 3.63 (td, *J* = 5.6 Hz, *J* = 11.4 Hz, 1H), 3.34 (ddd, *J* = 4.2 Hz, *J* = 9.9 Hz, *J* = 11.8 Hz, 1H), 2.76–2.74 (m, 1H), 2.62–2.60 (m, 1H), 2.43 (s, 3H), 1.99 (ddd, *J* = 2.6 Hz, *J* = 8.5 Hz, *J* = 11.3 Hz, 1H), 1.79 (d, *J* = 12.6 Hz, 3H), 1.65 (s, 1H), 1.56 (s, 1H), 1.46 (ddd, *J* = 3.4 Hz, *J* = 12.7 Hz, *J* = 25.3 Hz, 1H),1.29–1.27 (m, 1H), 1.15 (ddd, *J* = 7.8 Hz, *J* = 13.0 Hz, *J* = 15.0 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 133.2, 131.2, 129.9, 128.4, 128.2, 127, 119.6, 116.4, 114.6, 86.1, 80.6, 65.4, 43.5, 41.4, 31.6, 31.3, 31.1, 26.2 , 21.7, 21.1, 19.5; HRMS (ESI) calcd for $C_{29}H_{32}NO_3S$ $[M+H]^+$ 474.2103, found 474.2103.



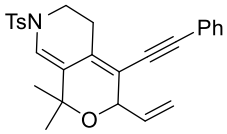
8-53k

8-53k: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.46–7.44 (m, 2H), 7.32–7.28 (m, 5H), 5.51 (m, 1H), 4.24 (d, *J* = 2.3 Hz, 2H), 3.86 (dq, *J* = 1.3 Hz, *J* = 12.1 Hz, 2H), 3.56 (t, *J* = 7.4 Hz, 2H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.42 (s, 3H), 2.31 (dd, *J* = 21.4 Hz, *J* = 39.3 Hz, 2H), 2.15 (dt, *J* = 1.1 Hz, *J* = 5.7 Hz, 1H), 2.10 (d, *J* = 1.0 Hz, 1H), 1.29 (s, 3H), 1.16 (d, *J* = 8.6 Hz, 1H), 0.83 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.9, 144.6, 134.5, 132.5, 129.9, 129.1, 128.4, 127.6, 121.6, 120.9, 79.3, 78.5, 75.8, 73.9, 72.1, 68.5, 67.3, 57.1, 49.6, 43.5, 40.9, 40.8, 38, 31.6, 31.3, 31.3, 31.2, 31.1, 26.2, 26.1, 21.7, 21, 19.6, 19.5; HRMS (ESI) calcd for $C_{32}H_{34}NO_3S$ $[M+H]^+$ 512.2259, found 512.2256.



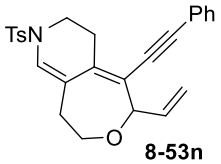
8-53l

8-53l: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.81 (d, *J* = 8.1 Hz, 2H), 7.47 (d, *J* = 7.2 Hz, 2H), 7.36 (d, *J* = 7.9 Hz, 2H), 7.31 (d, *J* = 7.3 Hz, 3H), 5.92 (ddt, *J* = 1.2 Hz, *J* = 3.8 Hz, *J* = 6.1 Hz, 1H), 5.73 (t, *J* = 6.7 Hz, 1H), 5.26 (t, *J* = 16.6 Hz, 1H), 5.17 (d, *J* = 10.4 Hz, 1H), 4.12 (d, *J* = 6.8 Hz, 2H), 3.97 (d, *J* = 5.6 Hz, 2H), 3.60 (t, *J* = 7.4 Hz, 2H), 2.71 (t, *J* = 7.4 Hz, 2H), 2.43 (s, 3H), 1.89 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 145, 134.8, 134.4, 132.5, 131.3, 129.9, 129.1, 128.4, 127.7, 121.6, 121, 117, 86.3, 79.2, 75.8, 73.8, 71.2, 70.5, 68.5, 67.4, 49.7, 23.1, 21.7, 19.7, 21.7, 19.6.



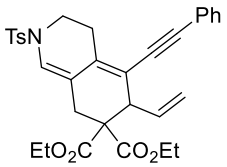
8-53m

8-53m: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (d, *J* = 8.2 Hz, 2H), 7.37–7.35 (m, 2H), 7.32–7.28 (m, 5H), 6.70 (s, 1H), 5.98 (ddd, *J* = 6.8 Hz, *J* = 10.2 Hz, *J* = 17.1 Hz, 1H), 5.44 (d, *J* = 17.1 Hz, 1H), 5.29 (d, *J* = 10.3 Hz, 1H), 4.70 (d, *J* = 6.4 Hz, 1H), 3.78–3.76 (m, 1H), 3.13 (dt, *J* = 3.8 Hz, *J* = 11.6 Hz, 1H), 2.83 (td, *J* = 4.0 Hz, *J* = 15.6 Hz, 1H), 2.43 (s, 3H), 1.46 (s, 3H), 1.35 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 136.6, 134.4, 131.2, 129.9, 128.3, 128.3, 127, 121.9, 119.9, 117.7, 114.1, 99.2, 85.9, 72.7, 43.1, 27.2, 26.3, 26.2, 21.0.



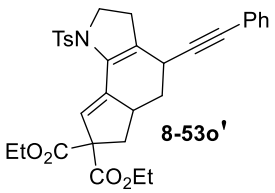
8-53n

8-53n: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.67 (d, *J* = 8.2 Hz, 2H), 7.33–7.28 (m, 10H), 6.65 (s, 1H), 6.17–6.15 (m, 1H), 5.32–5.30 (m, 2H), 4.93 (d, *J* = 5.8 Hz, 1H), 3.91 (dd, *J* = 3.7 Hz, *J* = 9.3 Hz, 2H), 3.60 (ddd, *J* = 4.3 Hz, *J* = 6.9 Hz, *J* = 11.5 Hz, 1H), 3.38 (ddd, *J* = 5.0 Hz, *J* = 11.2 Hz, *J* = 13.5 Hz, 1H), 2.84–2.82 (m, 2H), 2.71–2.69 (m, 2H), 2.43 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 139, 136.7, 132.5, 131, 129.9, 129.7, 129.1, 129, 128.3, 128.1, 127.7, 127.6, 127, 124.2, 117.3, 98.4, 88.5, 68.1, 43, 34.3, 28, 26, 21.5; HRMS (ESI) calcd for $C_{26}H_{26}NO_3S$ $[M+H]^+$ 432.1633, found 432.1622.



8-53o

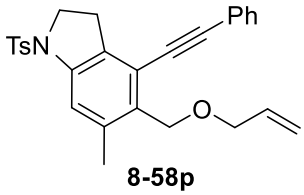
8-530: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.37 (dd, *J* = 3.0 Hz, *J* = 6.5 Hz, 2H), 7.30–7.26 (m, 5H), 6.63 (s, 1H), 5.59 (td, *J* = 9.4 Hz, *J* = 17.0 Hz, 1H), 5.20–5.18 (m, 2H), 4.18–4.14 (m, 7H), 4.05 (dddd, *J* = 3.7 Hz, *J* = 7.1 Hz, *J* = 10.7 Hz, *J* = 17.9 Hz, 2H), 3.77 (d, *J* = 8.8 Hz, 1H), 3.52–3.50 (m, 1H), 3.32–3.30 (m, 1H), 2.79–2.77 (m, 1H), 2.42 (s, 3H), 1.25–1.22 (m, 4H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 169.2, 144.1, 134, 132.5, 131.4, 129.9, 128.2, 128.1, 127, 123.5, 119.5, 114.8, 113.2, 96.5, 88.4, 61.6, 61.5, 57, 48.2, 43.7, 28.7, 26.7, 21.6; HRMS (ESI) calcd for $C_{32}H_{34}NO_6S$ $[M+H]^+$ 560.2107, found 560.2099.



8-53o'

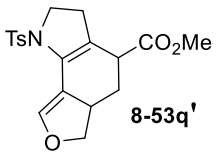
8-53o′: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.31–7.29 (m, 2H), 7.28–7.26 (m, 4H), 7.11 (d, *J* = 8.0 Hz, 2H), 6.40 (s, 1H), 4.24–2.22 (m, 4H), 4.09–2.07 (m, 1H), 3.82–3.84 (m, 1H), 3.39 (s, 1H), 3.31 (d, *J* = 8.6 Hz, 1H), 2.93 (dd, *J* = 7.2 Hz, *J* =13.1 Hz, 1H), 2.41–2.39 (m, 1H), 2.19–2.17 (m, 2H), 2.04 (s, 3H), 1.93

(ddd, *J* = 5.7 Hz, *J* = 11.2 Hz, *J* = 18.0 Hz, 2H), 1.55 (dt, *J* = 5.7 Hz, *J* = 12.8 Hz, 1H), 1.28 (dt, *J* = 4.7 Hz, *J* = 7.1 Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 171.2, 170.5, 143.6, 137.2, 134, 133.9, 133.3, 131.5, 129.5, 128.4, 128.2, 128, 127.6, 125, 123.1, 87.9, 81.8, 66.5, 61.7, 61.5, 51.2, 40.7, 38.2, 35.5, 31, 29.2, 21.1; HRMS (ESI) calcd for $C_{32}H_{34}NO_6S$ $[M+H]^+$ 560.2107, found 560.2095.



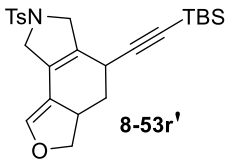
8-58p

8-58p: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.47–7.45 (m, 2H), 7.35–7.33 (m, 2H), 7.26–7.24 (m, 3H), 5.96 (ddd, *J* = 10.9 Hz, *J* = 16.1 Hz, *J* = 5.7 Hz, 1H), 5.31–5.29 (m, 1H), 5.17 (d, *J* = 10.4 Hz, 1H), 4.71 (s, 2H), 4.07–4.05 (m, 2H), 3.93 (t, *J* = 8.5 Hz, 2H), 3.02 (t, *J* = 8.4 Hz, 2H), 2.45 (s, 3H), 2.38 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 141.6, 141.4, 139.4, 138.8, 135, 132.3, 131.4, 129.7, 128.5, 128.4, 127.2, 122.6, 121.1, 117.1, 116.6, 96.5, 85.4, 71.4, 67.6, 49.9, 27.9, 21.5, 19.9.



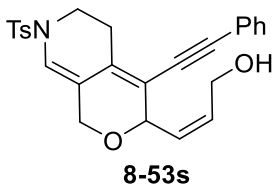
8-53q′

8-53q′: ^{1}H NMR (500 MHz, PhMe-d_8) δ 7.56 (d, *J* = 8.1 Hz, 2H), 7.36 (s, 1H), 6.75 (d, *J* = 8.1 Hz, 2H), 4.34–4.32 (m, 2H), 4.07 (s, 1H), 3.86–3.84 (m, 2H), 3.54–3.52 (m, 2H), 3.28 (d, *J* = 2.7 Hz, 2H), 3.10 (s, 3H), 1.93 (s, 3H).



8-53r′

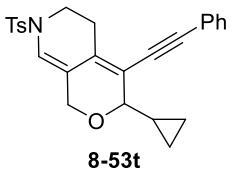
8-53r′: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.73 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 6.24 (s, 1H), 4.63 (t, *J* = 9.1 Hz, 1H), 4.23–4.21 (m, 2H), 4.08 (td, *J* = 11.6 Hz, *J* = 14.7 Hz, 2H), 3.73 (dd, *J* = 8.9 Hz, *J* = 12.5 Hz, 2H), 3.36 (dq, *J* = 3.3 Hz, *J* = 11.1 Hz, 2H), 3.21 (d, *J* = 4.8 Hz, 1H), 2.42 (s, 3H), 2.13 (dd, *J* = 3.6 Hz, *J* = 12.1 Hz, 1H), 1.54 (dt, *J* = 5.7 Hz, *J* = 12.4 Hz, 1H), 0.85 (s, 9H), 0.03 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.4, 139.2, 134.1, 129.9, 129.9, 129.8, 128.4, 127.4, 124.5, 111.3, 105.6, 84.6, 75.5, 55.6, 53.5, 37.8, 33.3, 27.1, 26, 21.5, 16.4, -4.5; HRMS (ESI) calcd for $C_{25}H_{34}SiNO_3S$ $[M+H]^+$ 456.2029, found 456.2015.



8-53s

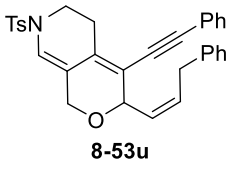
8-53s: 2s: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 2H), 7.35–7.31 (m, 7H), 6.63 (s, 1H), 5.95–5.93 (m, 1H), 5.70–5.68 (m, 1H), 5.09 (d, *J* = 8.0 Hz, 1H), 4.33–4.30 (m, 4H),

3.60–3.58 (m, 1H), 3.41–3.39 (m, 1H), 2.70–2.68 (m, 2H), 2.43 (s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.3, 134.6, 133.3, 132.6, 131.2, 130, 129.5, 128.5, 128.4, 127, 122.8, 120.7, 114.6, 113.3, 98.7, 85.7, 72.7, 64.3, 59.2, 43.4, 26.1, 21.6; HRMS (ESI) calcd for $C_{26}H_{26}NO_4S$ $[M+H]^+$ 448.1583, found 448.1587.



8-53t

8-53t: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.2 Hz, 2H), 7.39 (dd, *J* = 3.0 Hz, *J* = 6.5 Hz, 2H), 7.33–7.31 (m, 5H), 6.60 (s, 1H), 4.40 (d, *J* = 13.2 Hz, 1H), 4.18 (d, *J* = 13.2 Hz, 1H), 3.59 (ddd, *J* = 5.1 Hz, *J* = 6.9 Hz, *J* = 12.1 Hz, 1H), 3.50 (d, *J* = 8.9 Hz, 1H), 3.41–3.39 (m, 1H), 2.72–2.68 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.2, 134.7, 132, 131.1, 130, 128.4, 128.2, 127, 123.4, 120.1, 116.5, 114.1, 98.6, 86.2, 81, 64.7, 43.5, 26, 21.6, 15.1, 4.3, 2.4; HRMS (ESI) calcd for $C_{26}H_{26}NO_3S$ $[M+H]^+$ 432.1633, found 432.1627.



8-53u

8-53u: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.3 Hz, 2H), 7.47 (d, *J* = 7.4 Hz, 2H), 7.34 (t, *J* = 8.3 Hz, 10H), 6.82 (d, *J* = 11.6 Hz, 1H), 6.63 (s, 1H), 5.78 (dd, *J* = 9.6 Hz, *J* = 11.5 Hz, 1H), 5.15 (dd, *J* = 10.6 Hz, *J* = 19.7 Hz, 1H), 4.39 (d, *J* = 13.2 Hz, 1H),4.25 (d, *J* = 13.1 Hz, 1H), 3.60–3.58 (m, 1H), 3.46–3.44 (m, 1H), 2.73–2.71 (m, 1H), 2.44 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 144.1, 136.8, 134, 131.2, 130, 129.3, 129, 128.3, 128.3, 128.2, 127.4, 127, 120.4, 115.4, 113.1, 99.2, 87, 72.6, 64.8, 43.5, 26.2, 21.6; HRMS (ESI) calcd for $C_{31}H_{28}NO_3S$ $[M+H]^+$ 494.1790, found 494.1776.

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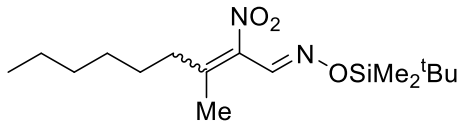
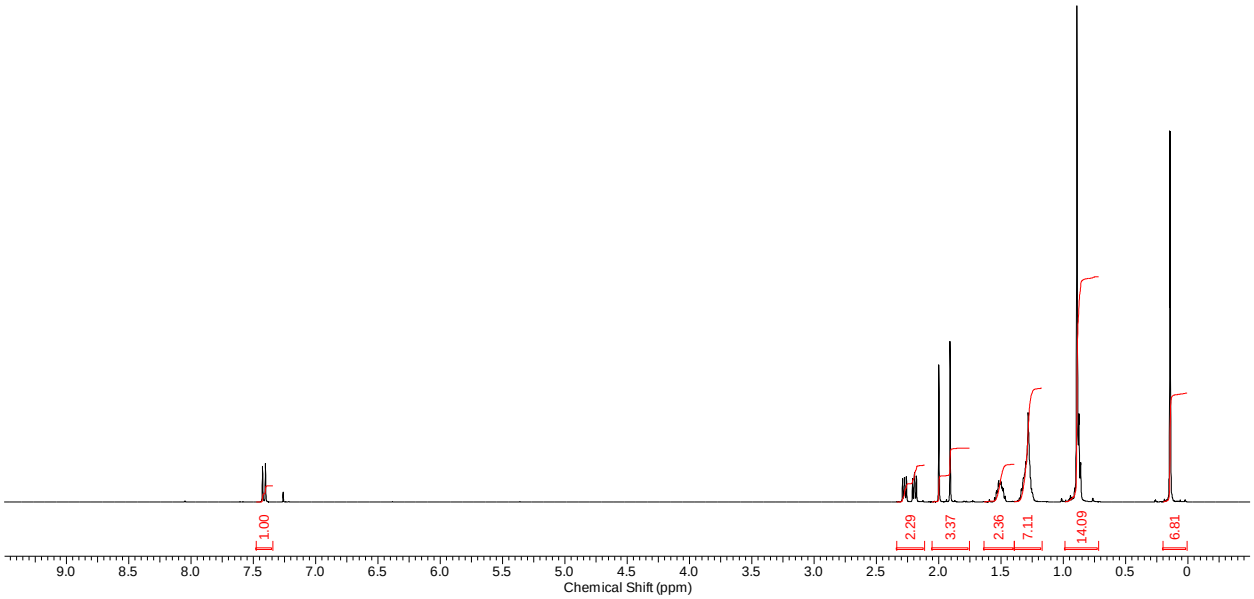
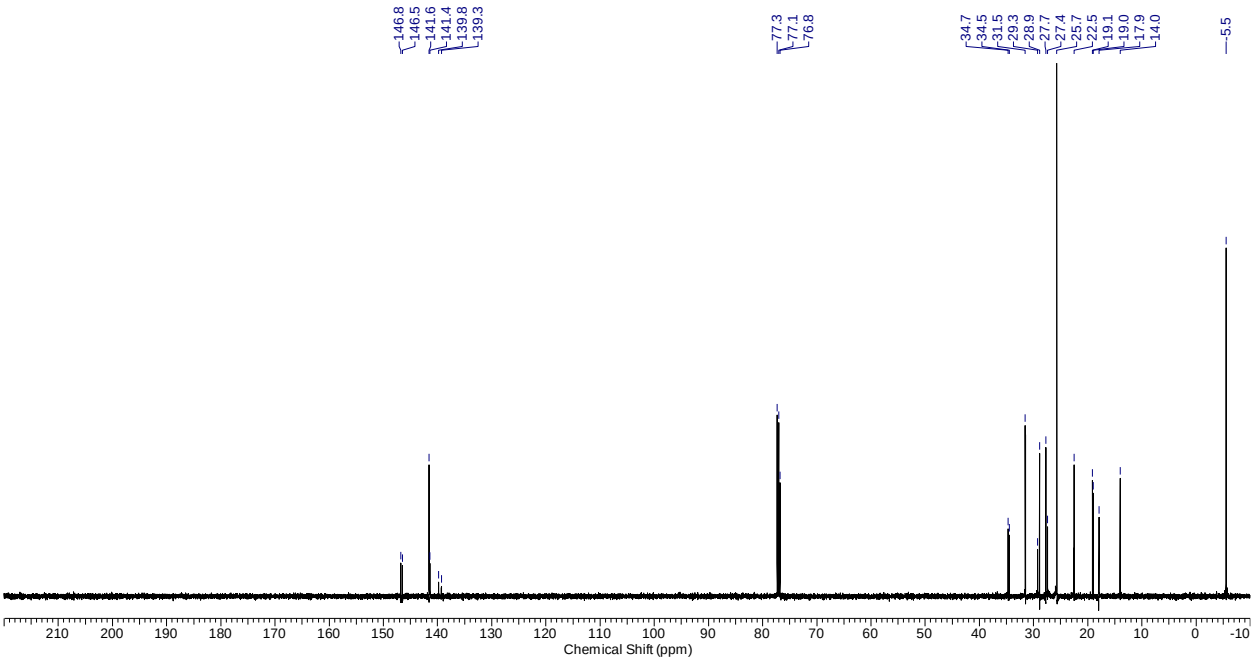
Appendix I

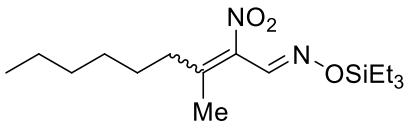
Selected NMR Spectra for Chapter 1


NO2
N
OSiMe2tBu
Me

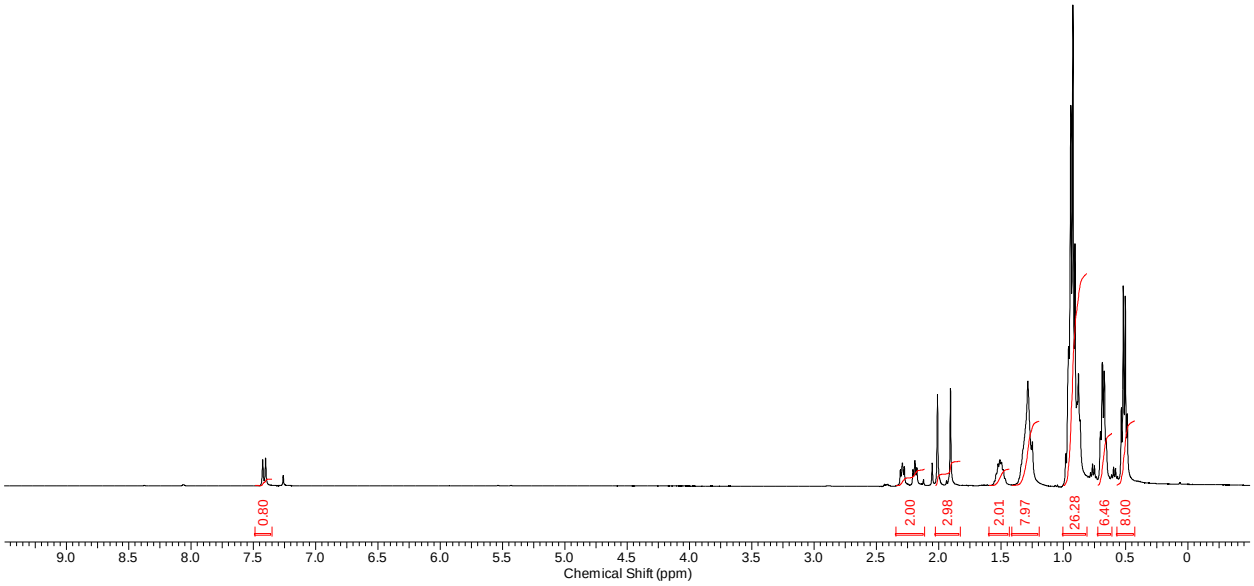
1-53b (*E*/*Z* = 1:1)

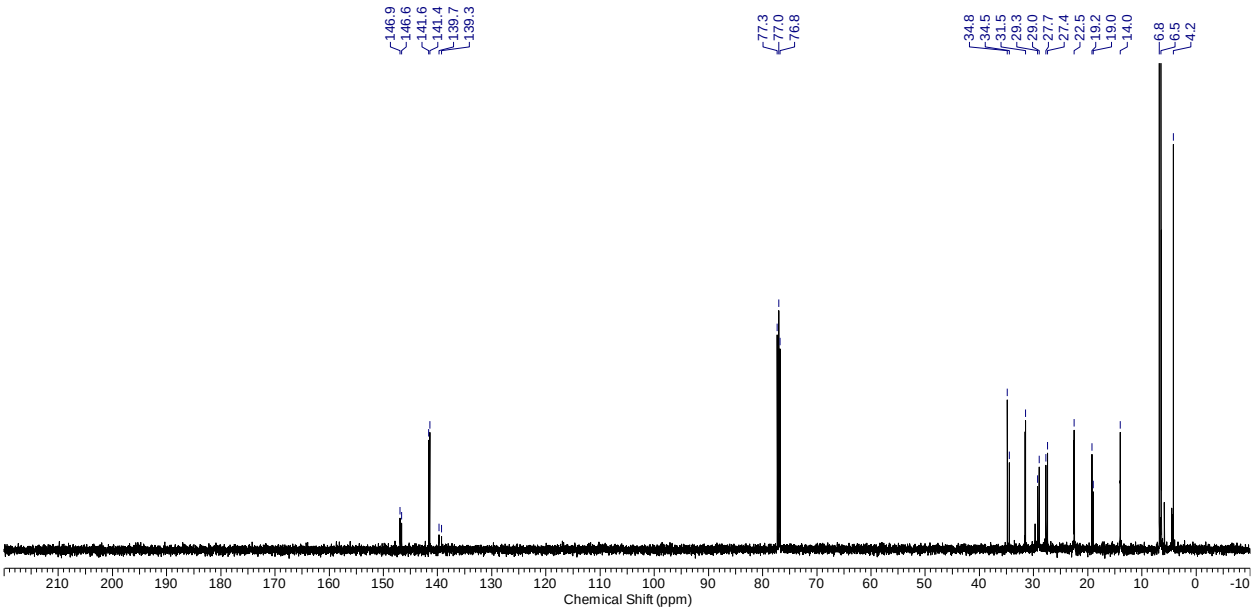

1.00
2.29
3.37
2.36
7.11
14.09
6.81
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

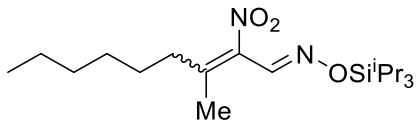

146.8
146.5
141.6
141.4
139.8
139.3
77.3
77.1
76.8
34.7
34.5
31.5
29.3
28.9
27.7
27.4
25.7
22.5
19.1
19.0
17.9
14.0
-5.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)


NO2
N
OSiEt3
Me

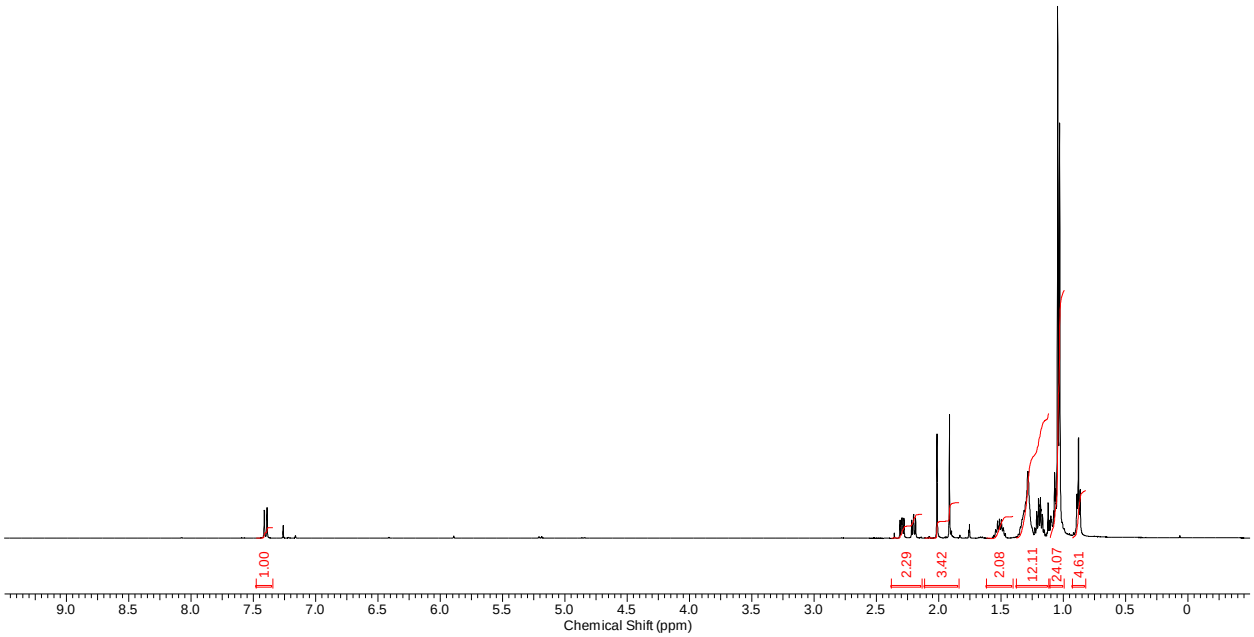
1-53c (*E*/*Z* = 1:1)

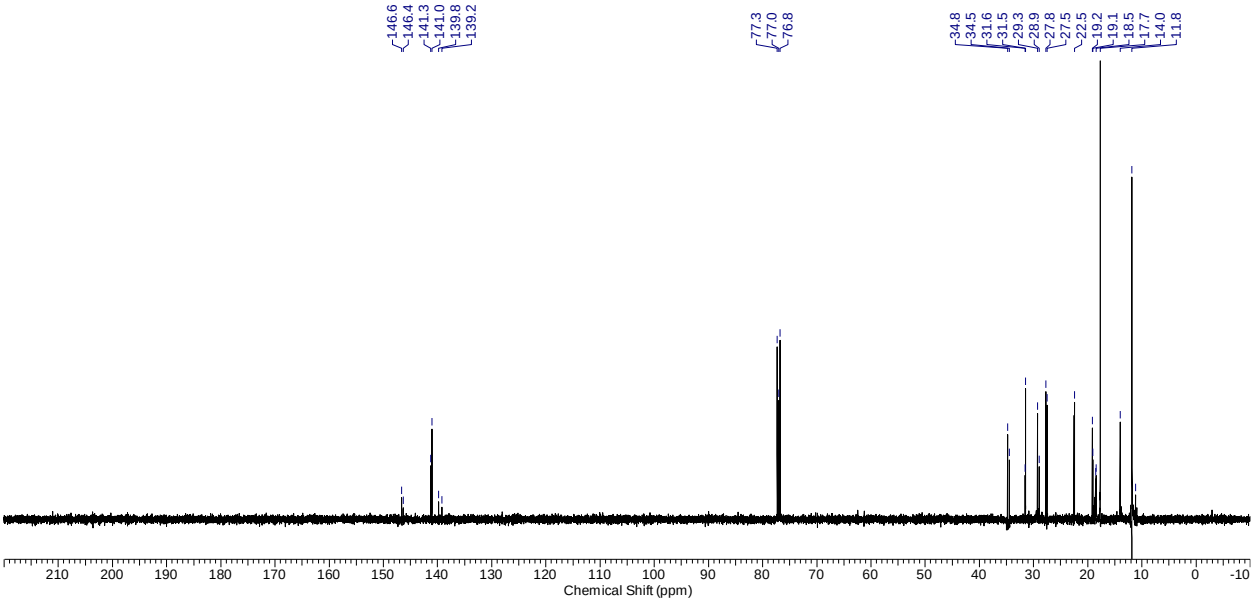

0.80
2.00
2.98
2.01
7.97
26.28
6.46
8.00
Chemical Shift (ppm)

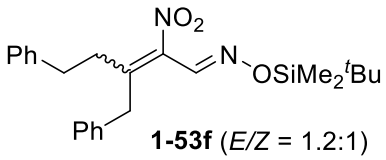

146.9
146.6
141.6
141.4
139.7
139.3
77.3
77.0
76.8
34.8
34.5
31.5
29.3
29.0
27.7
27.4
22.5
19.2
19.0
14.0
6.8
6.5
4.2
Chemical Shift (ppm)


NO2
N
OSiiPr3
Me

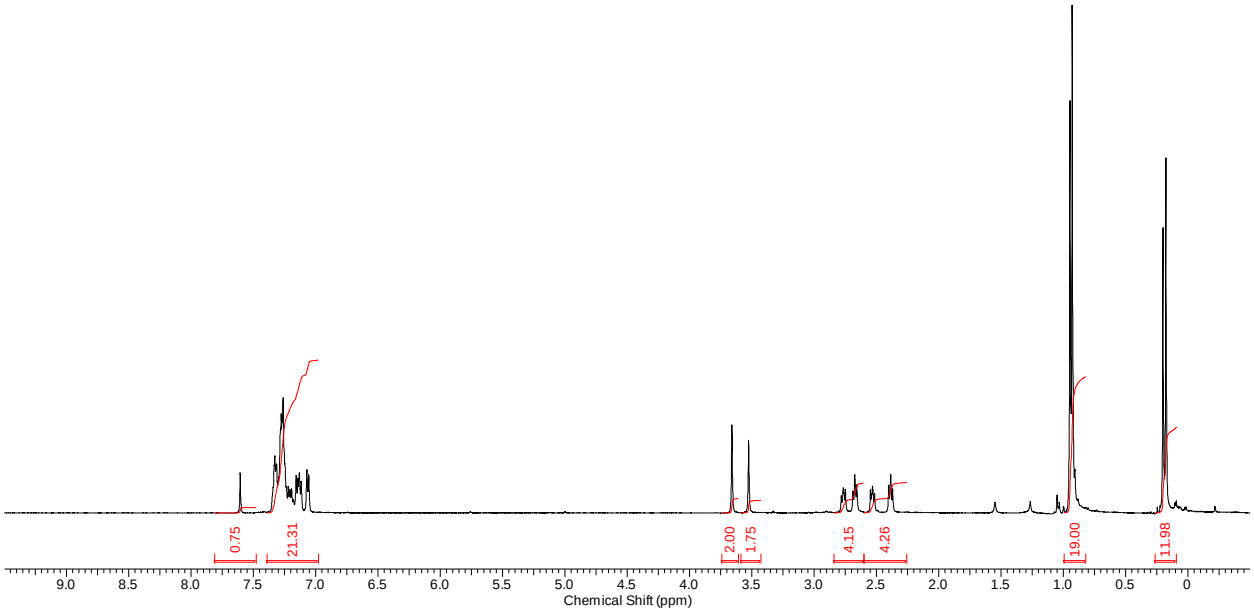
1-53d (*E*/*Z* = 1:1)

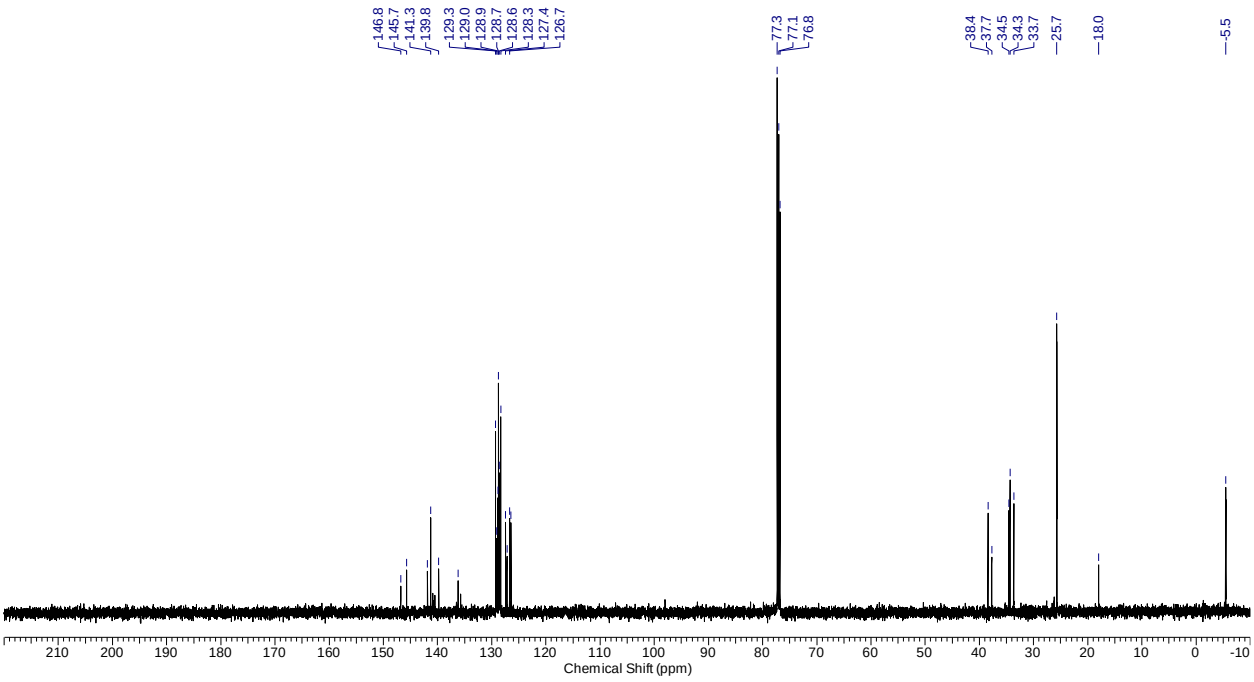

1.00
2.29
3.42
2.08
12.11
24.07
4.61
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

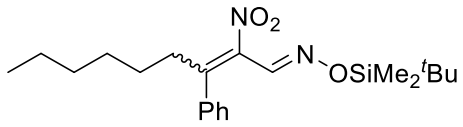

146.6
146.4
141.3
141.0
139.8
139.2
77.3
77.0
76.8
34.8
34.5
31.6
31.5
29.3
28.9
27.8
27.5
22.5
19.2
19.1
18.5
17.7
14.0
11.8
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Chemical Shift (ppm)


NO2
Ph
N
OSiMe2tBu
Ph

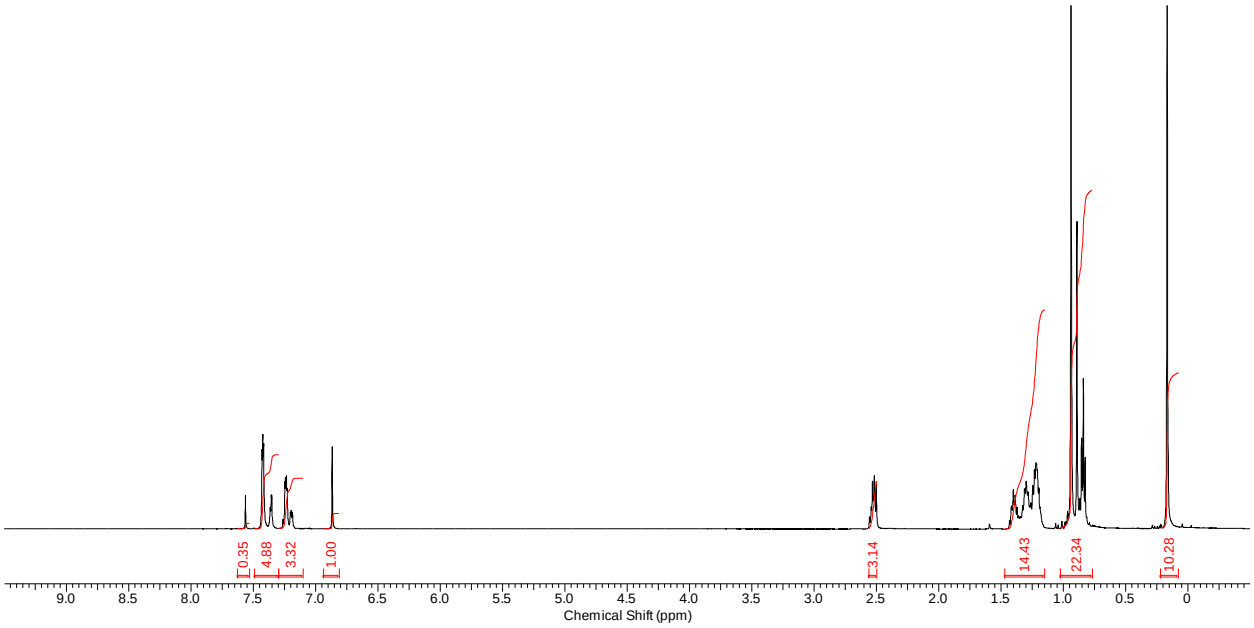
1-53f (*E*/*Z* = 1.2:1)

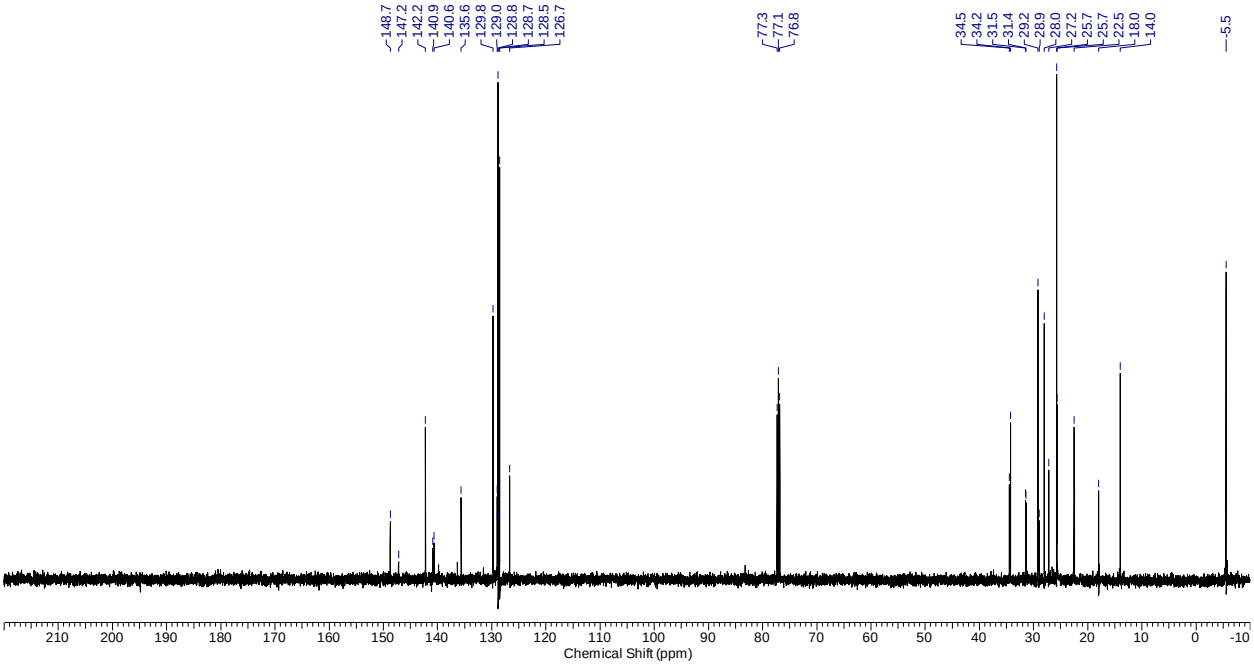

0.75
21.31
2.00
1.75
4.15
4.26
19.00
11.98
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

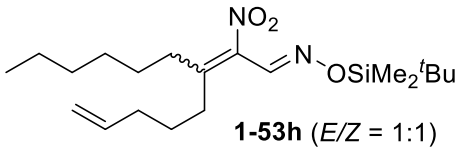

146.8
145.7
141.3
139.8
129.3
129.0
128.9
128.7
128.6
128.3
127.4
126.7
77.3
77.1
76.8
38.4
37.7
34.5
34.3
33.7
25.7
18.0
5.5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)


NO2
N
OSiMe2tBu
Ph

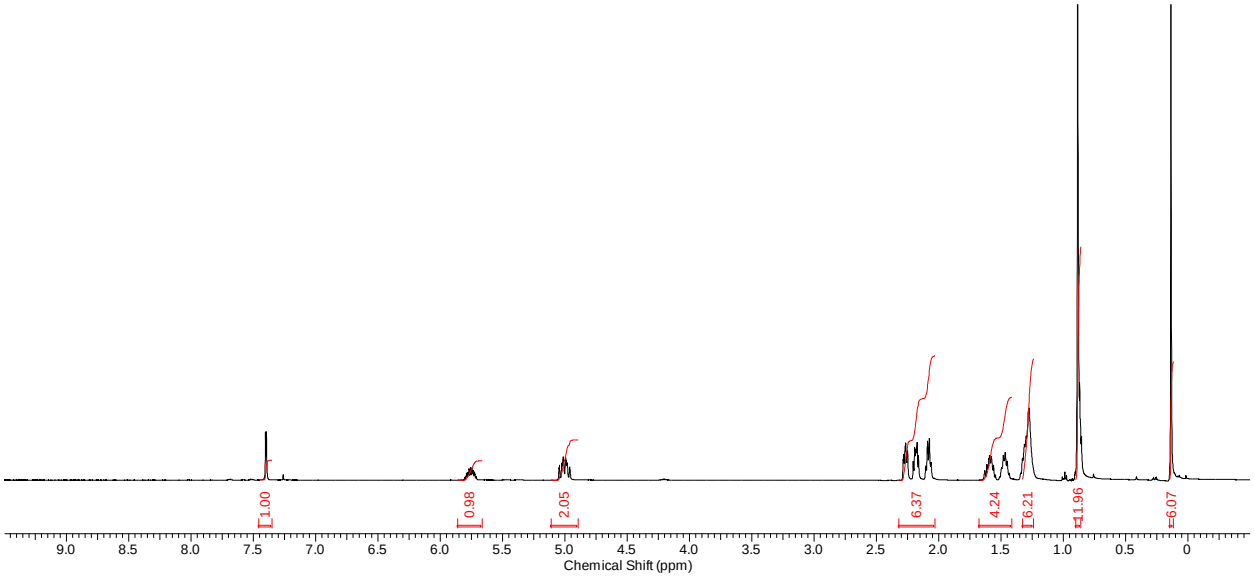
1-53g (*E*/*Z* = 2.2:1)


0.35
4.88
3.32
1.00
3.14
14.43
22.34
10.28
Chemical Shift (ppm)


148.7
147.2
142.2
140.9
140.6
135.6
129.8
129.0
128.8
128.7
128.5
126.7
77.3
77.1
76.8
34.5
34.2
31.5
31.4
29.2
28.9
28.0
27.2
25.7
25.7
22.5
18.0
14.0
-5.5
Chemical Shift (ppm)


NO2
N
OSiMe2tBu

1-53h (*E*/*Z* = 1:1)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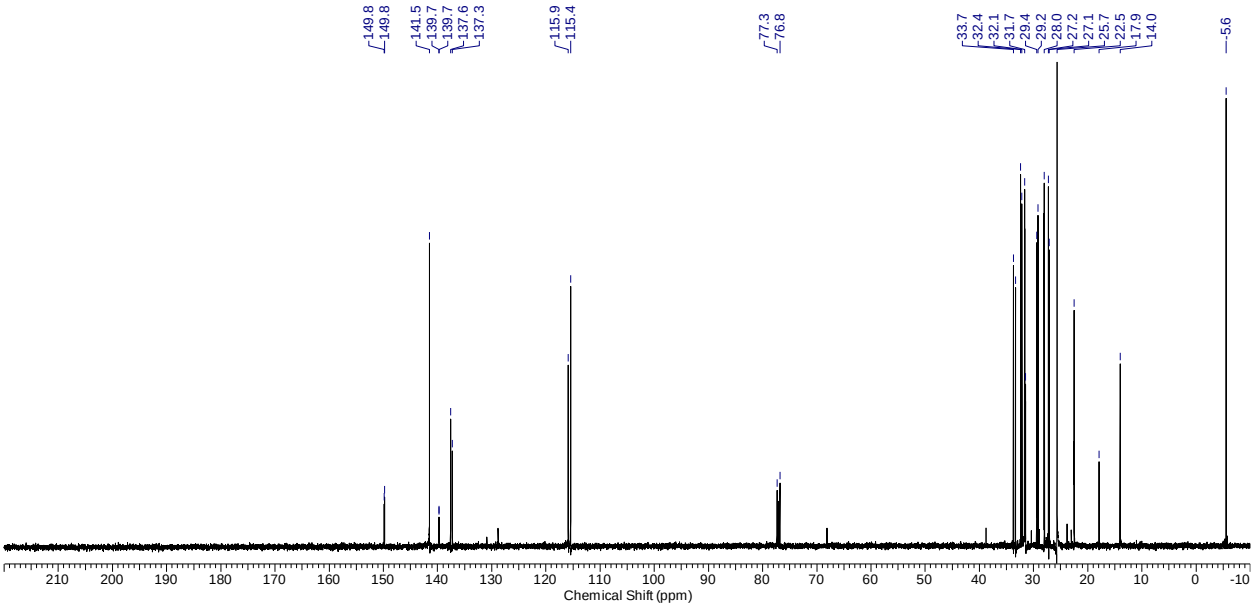
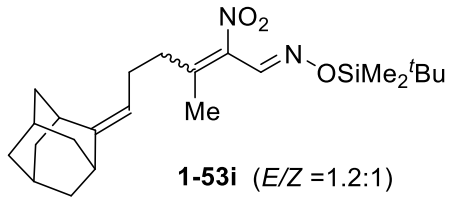
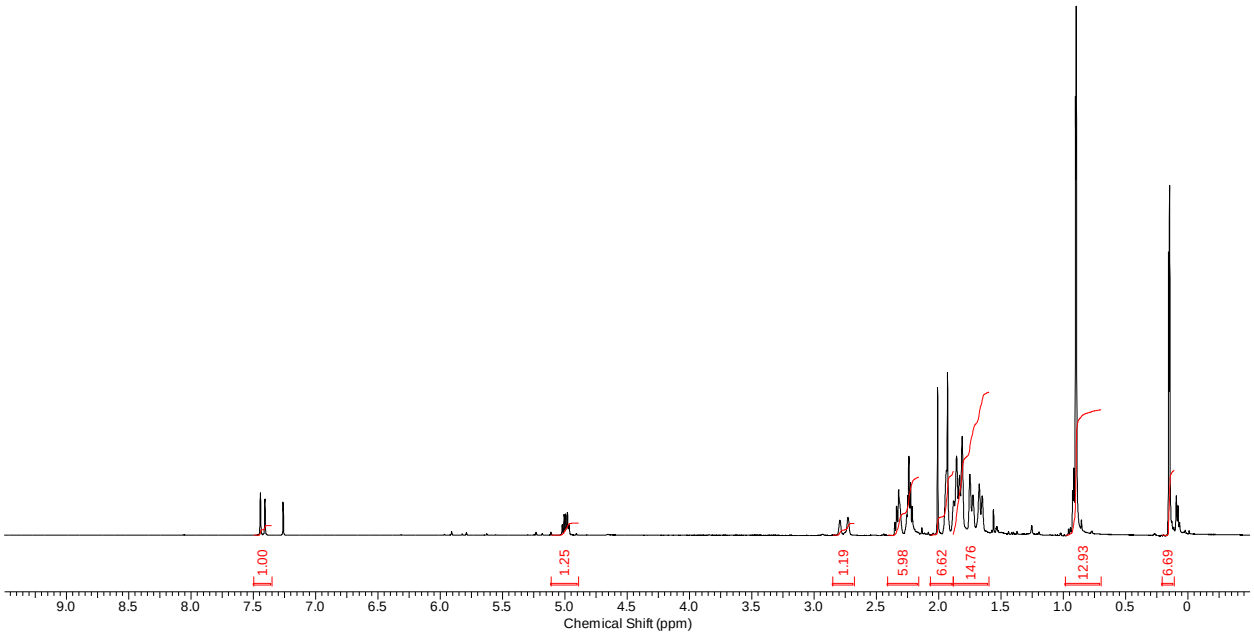
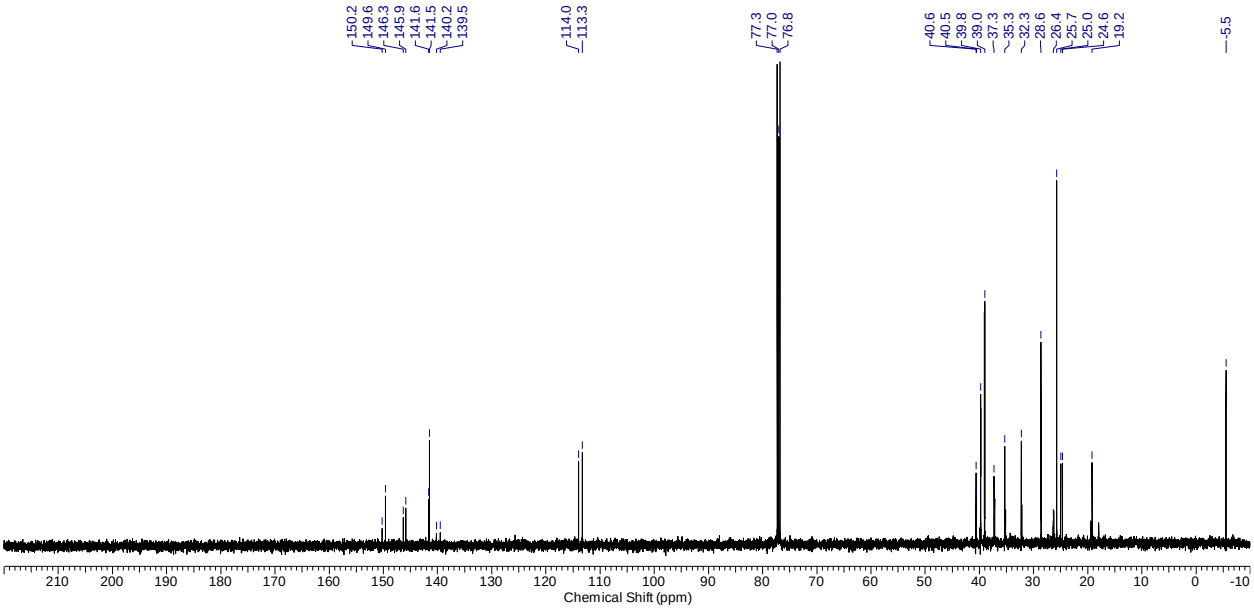
0.98
2.05
6.37
4.24
6.21
11.96
6.07
Chemical Shift (ppm)

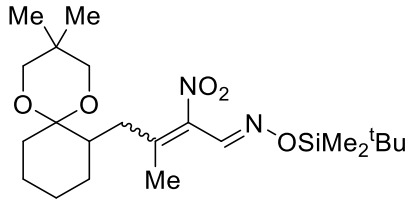

149.8
149.8
141.5
139.7
139.7
137.6
137.3
115.9
115.4
77.3
76.8
33.7
32.4
32.1
31.7
29.4
29.2
28.0
27.2
27.1
25.7
22.5
17.9
14.0
-5.6
Chemical Shift (ppm)


NO2
N
OSiMe2tBu
Me

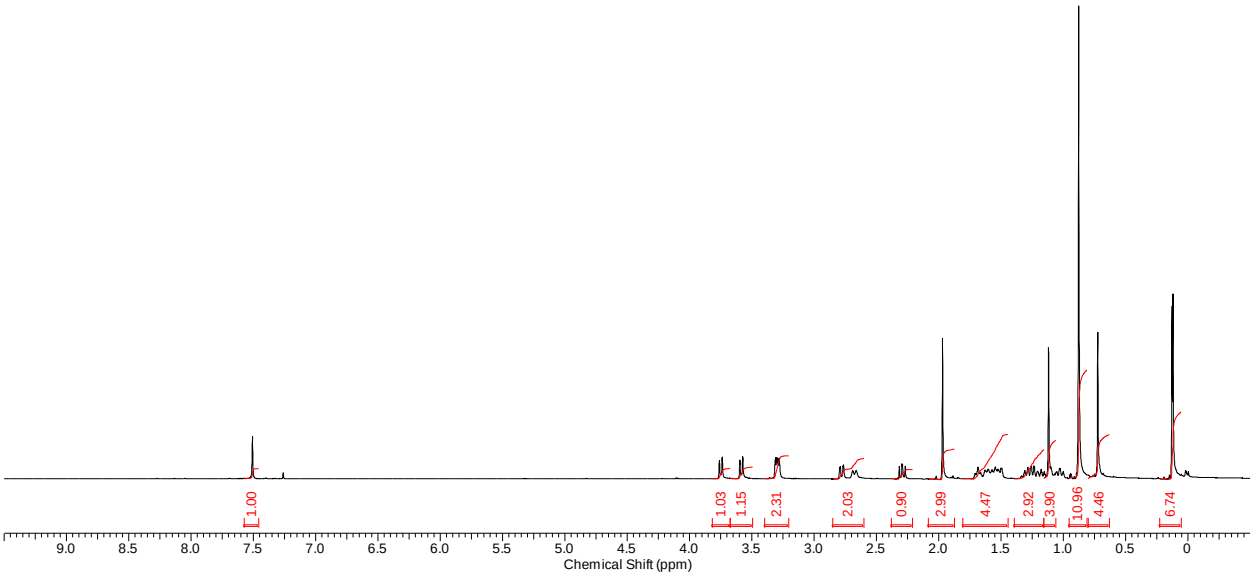
1-53i (*E*/*Z* =1.2:1)

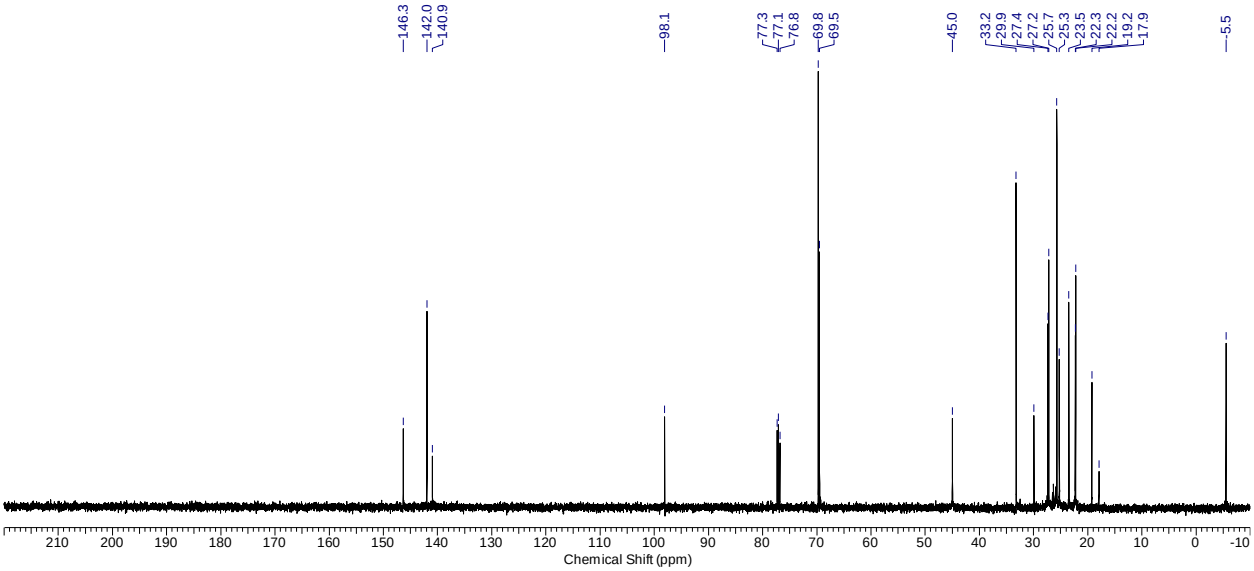

1.00
1.25
1.19
5.98
6.62
14.76
12.93
6.69
Chemical Shift (ppm)

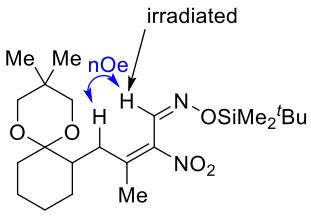

150.2
149.6
146.3
145.9
141.6
141.5
140.2
139.5
114.0
113.3
77.3
77.0
76.8
40.6
40.5
39.8
39.0
37.3
35.3
32.3
28.6
26.4
25.7
25.0
24.6
19.2
-5.5
Chemical Shift (ppm)


Me
Me
O
O
NO2
N
OSiMe2tBu
Me

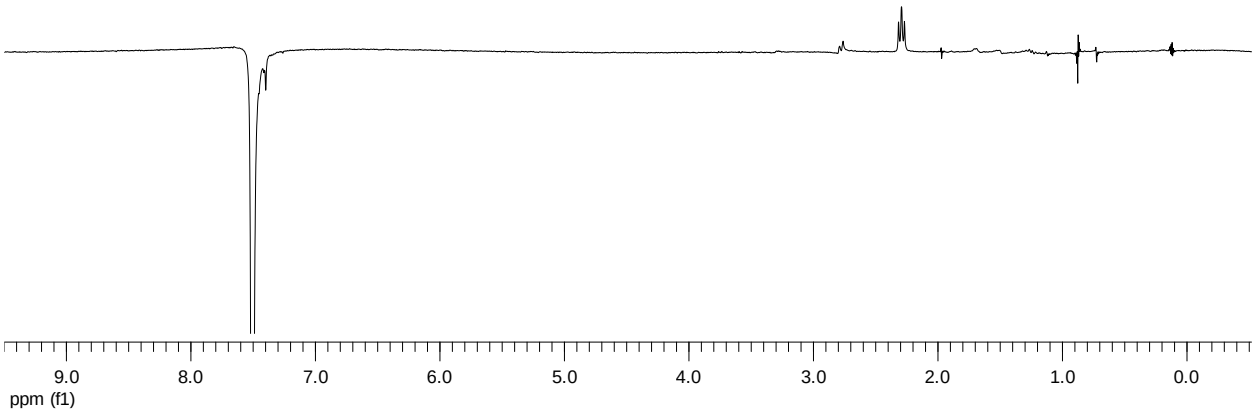
1-53j (*E/Z* =1.7:1)

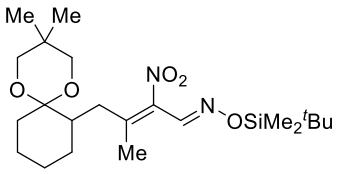

1.00
1.03
1.15
2.31
2.03
0.90
2.99
4.47
2.92
3.90
10.96
4.46
6.74
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)


146.3
142.0
140.9
98.1
77.3
77.1
76.8
69.8
69.5
45.0
33.2
29.9
27.4
27.2
25.7
25.3
23.5
22.3
22.2
19.2
17.9
5.5
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Chemical Shift (ppm)

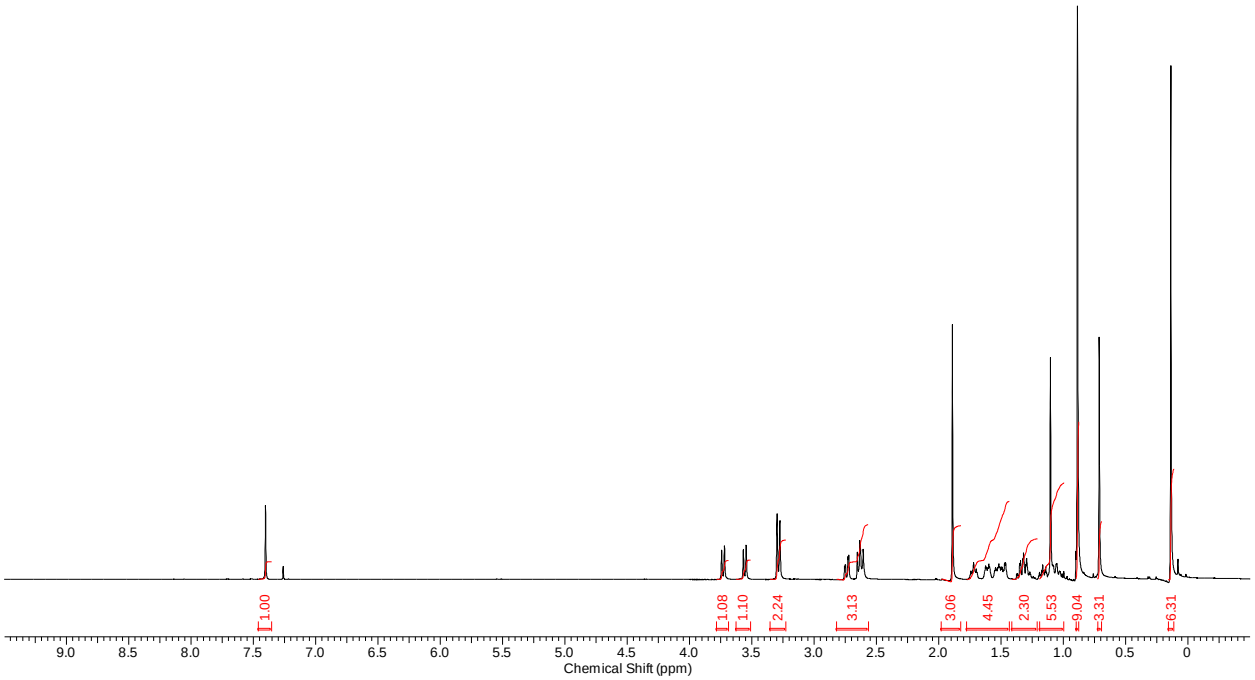


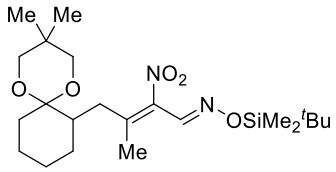
1-53j (*E*-isomer)



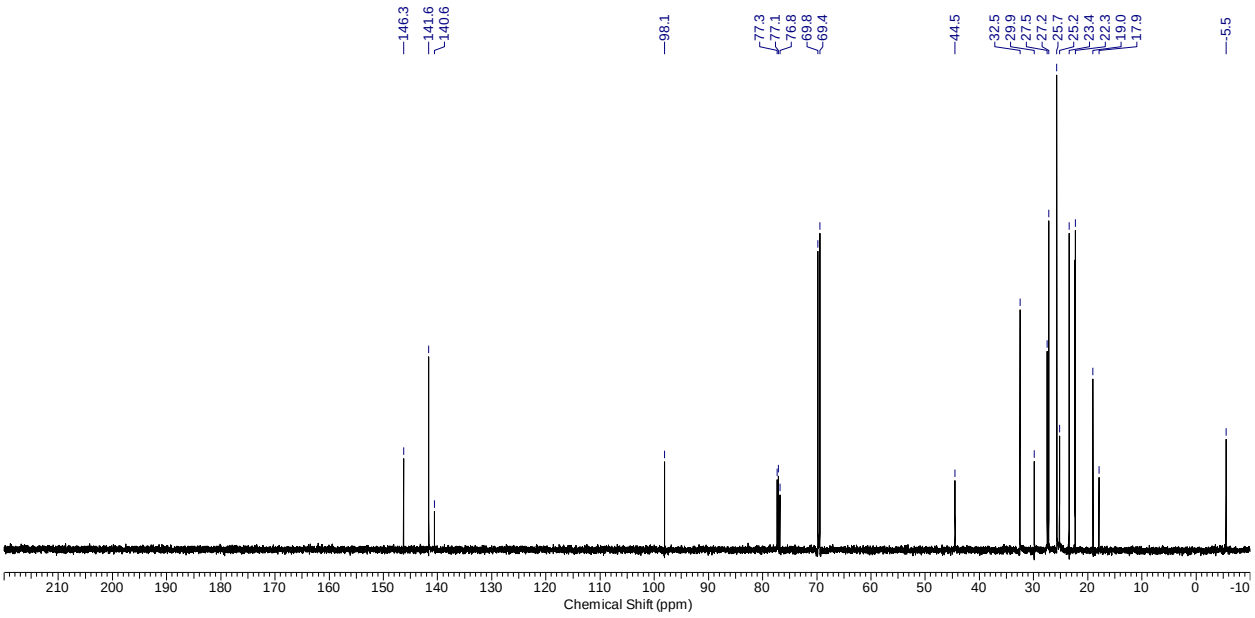


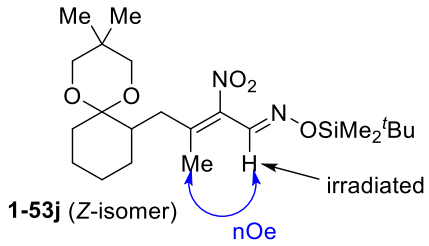
1-53j (*Z*-isomer)



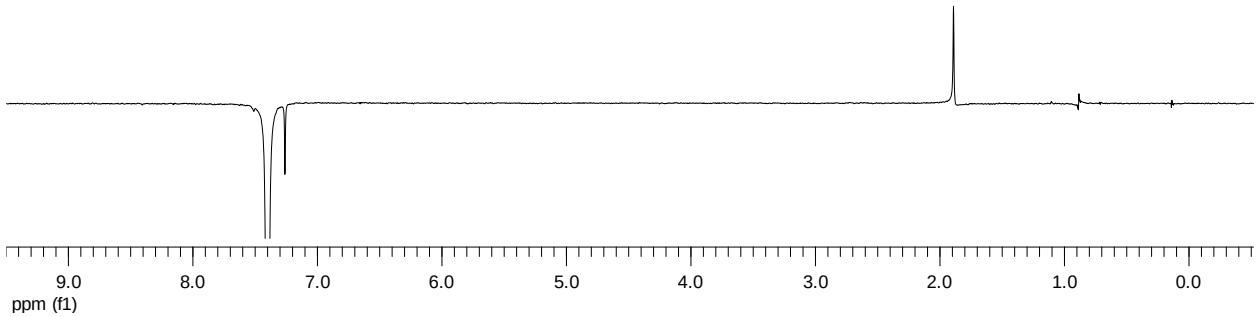


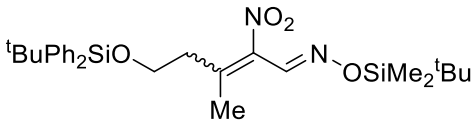
1-53j (*Z*-isomer)



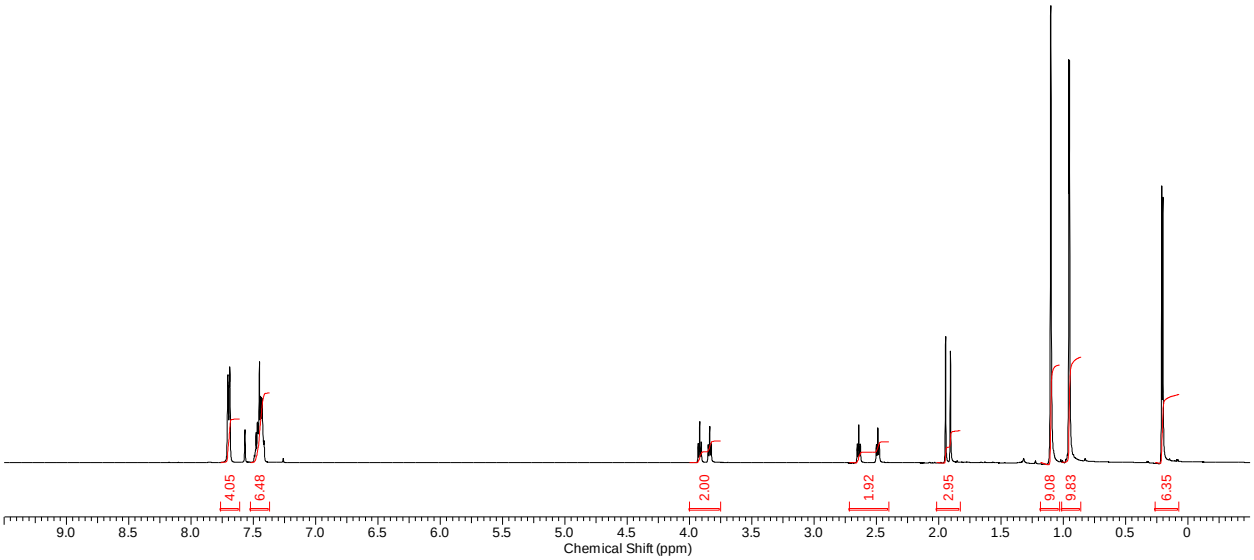


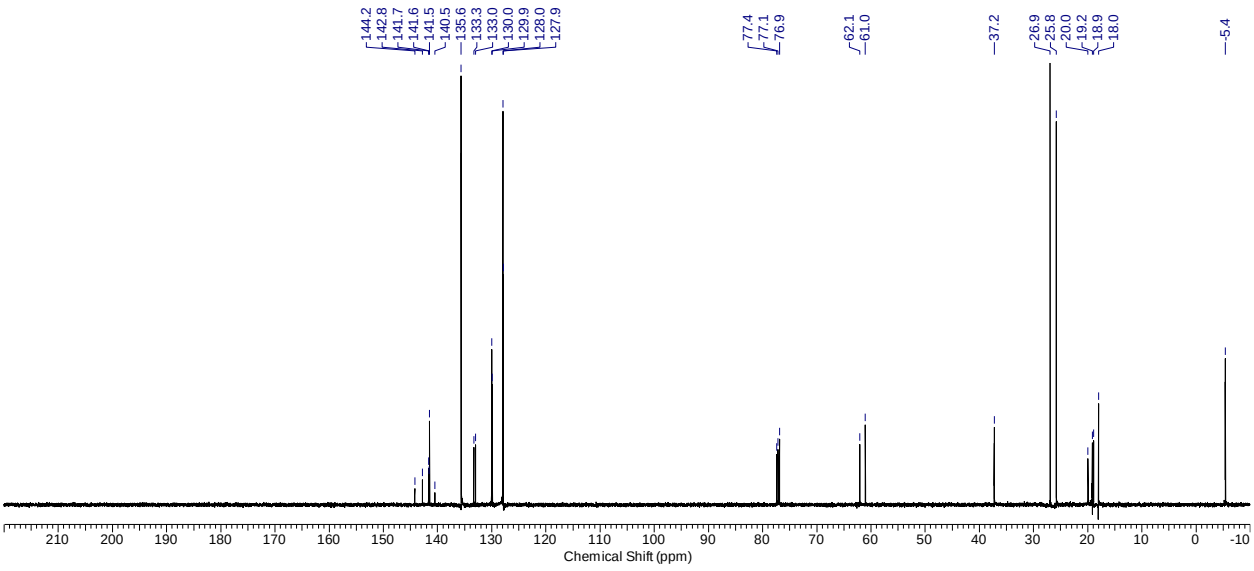
1-53j (*Z*-isomer)

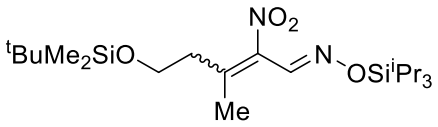



NO2
tBuPh2SiO
N
OSiMe2tBu
Me

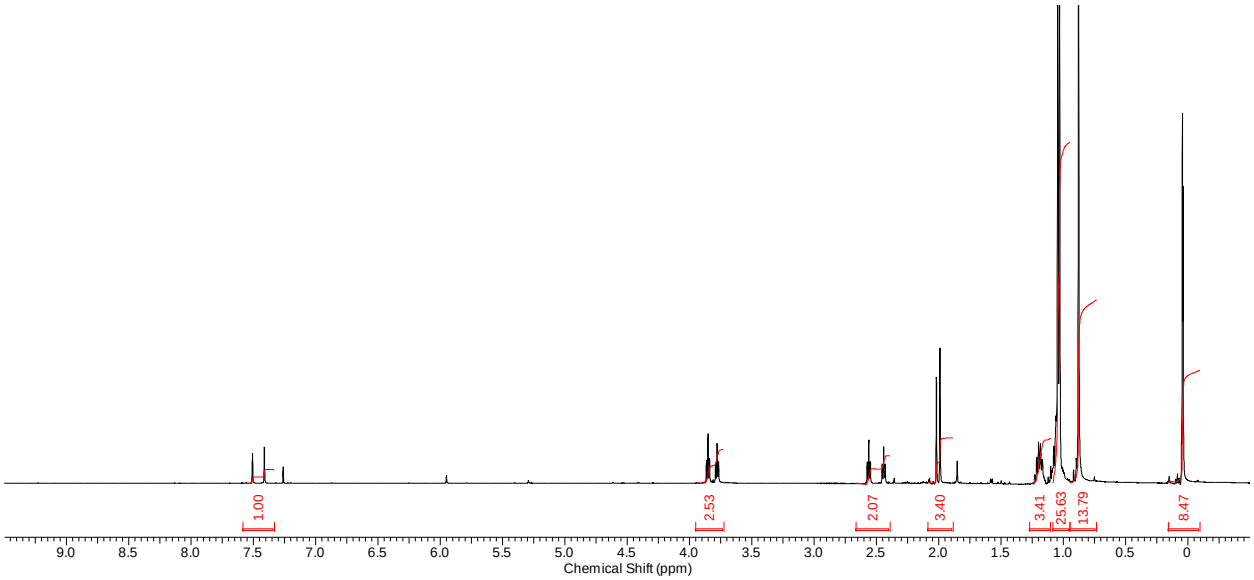
1-53k (*E/Z* =1:1)

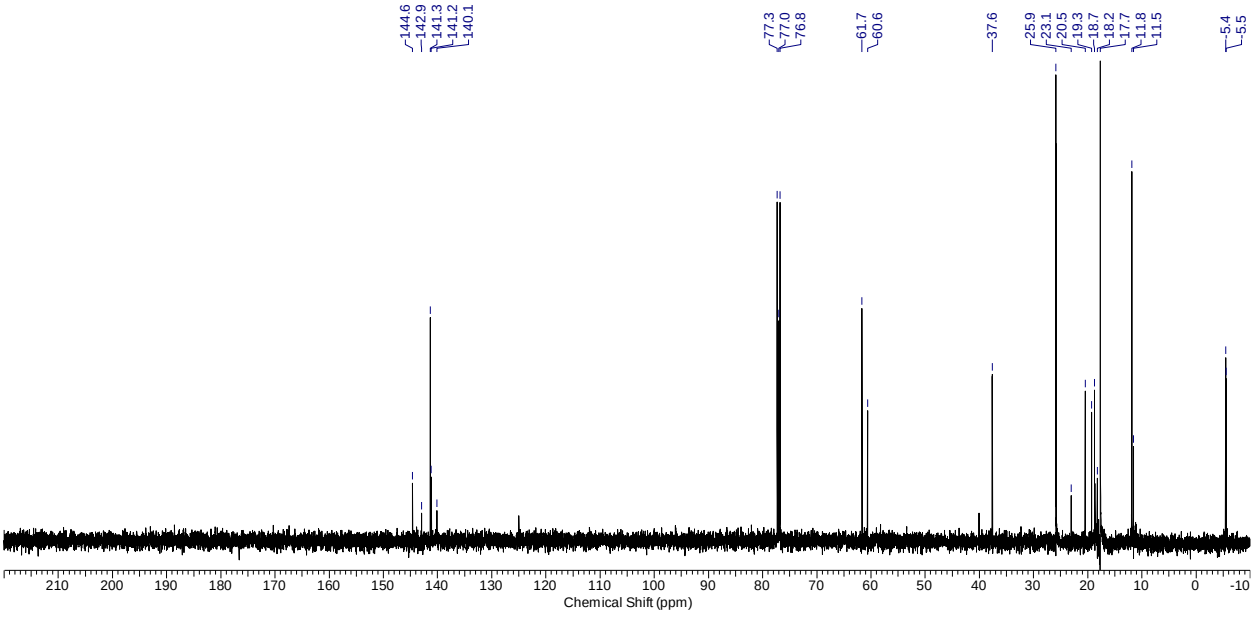

4.05
6.48
2.00
1.92
2.95
9.08
9.83
6.35
Chemical Shift (ppm)

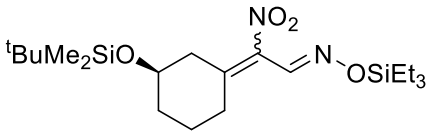

144.2
142.8
141.7
141.6
141.5
140.5
135.6
133.3
133.0
130.0
129.9
128.0
127.9
77.4
77.1
76.9
62.1
61.0
37.2
26.9
25.8
20.0
19.2
18.9
18.0
-5.4
Chemical Shift (ppm)


NO2
tBuMe2SiO
N
OSiiPr3
Me

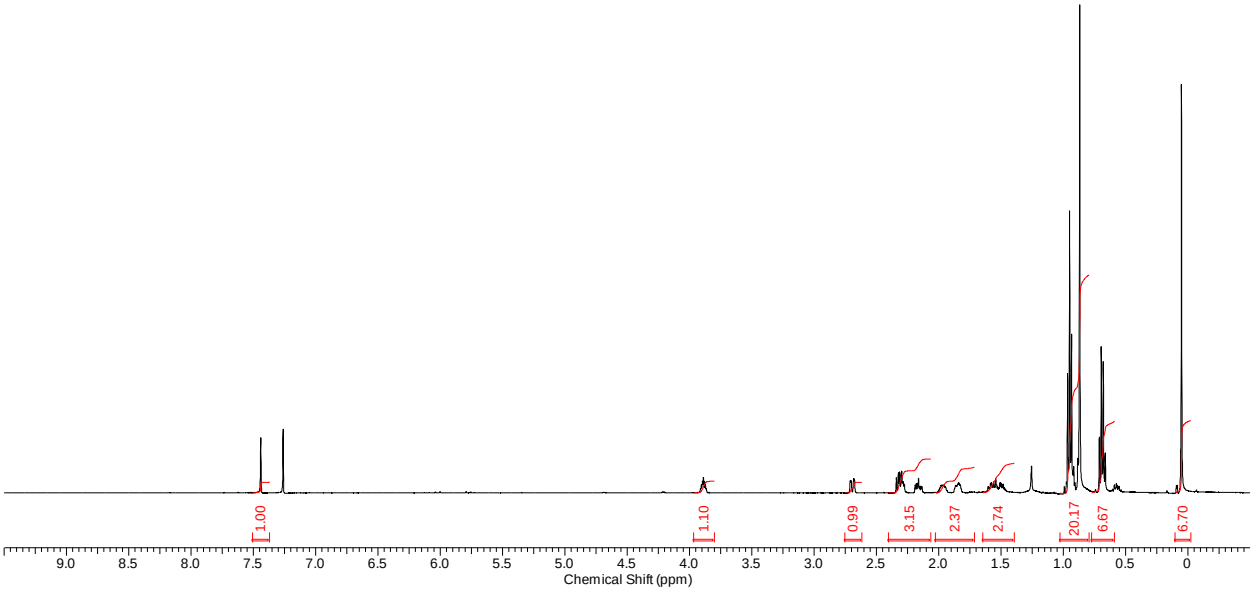
1-53l (*E*/*Z* =1.1:1)

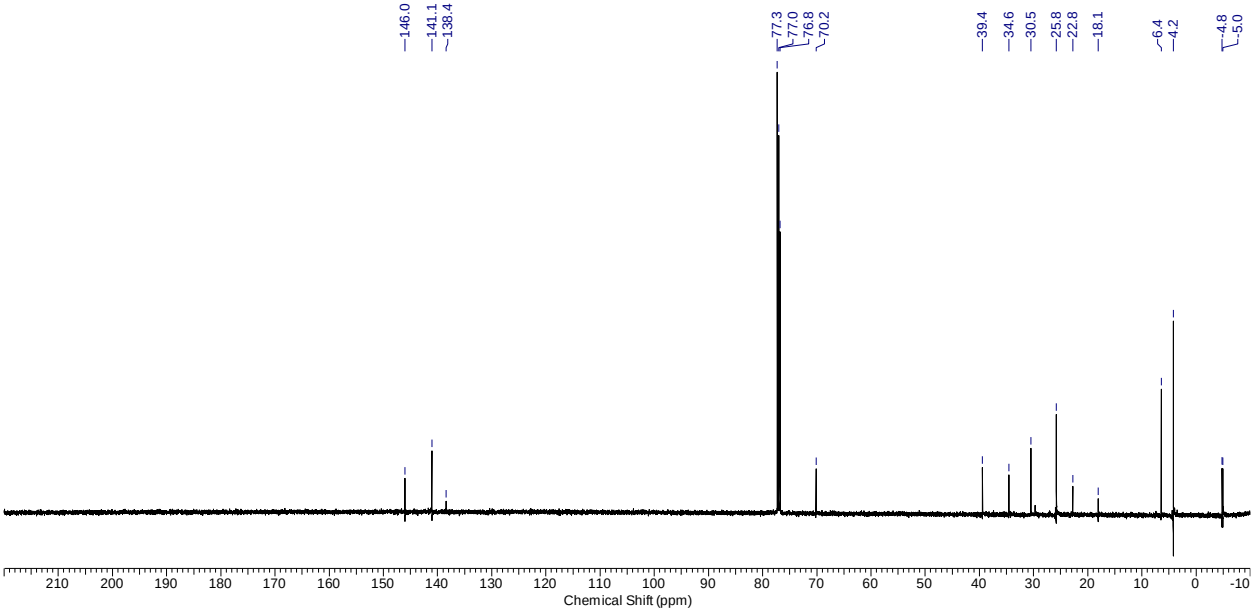

1.00
2.53
2.07
3.40
3.41
25.63
13.79
8.47
Chemical Shift (ppm)

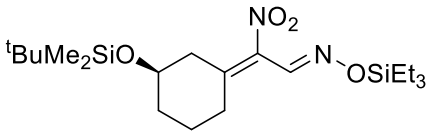

144.6
142.9
141.3
141.2
140.1
77.3
77.0
76.8
61.7
60.6
37.6
25.9
23.1
20.5
19.3
18.7
18.2
17.7
11.8
11.5
5.4
5.5
Chemical Shift (ppm)


NO2
tBuMe2SiO
N
OSiEt3

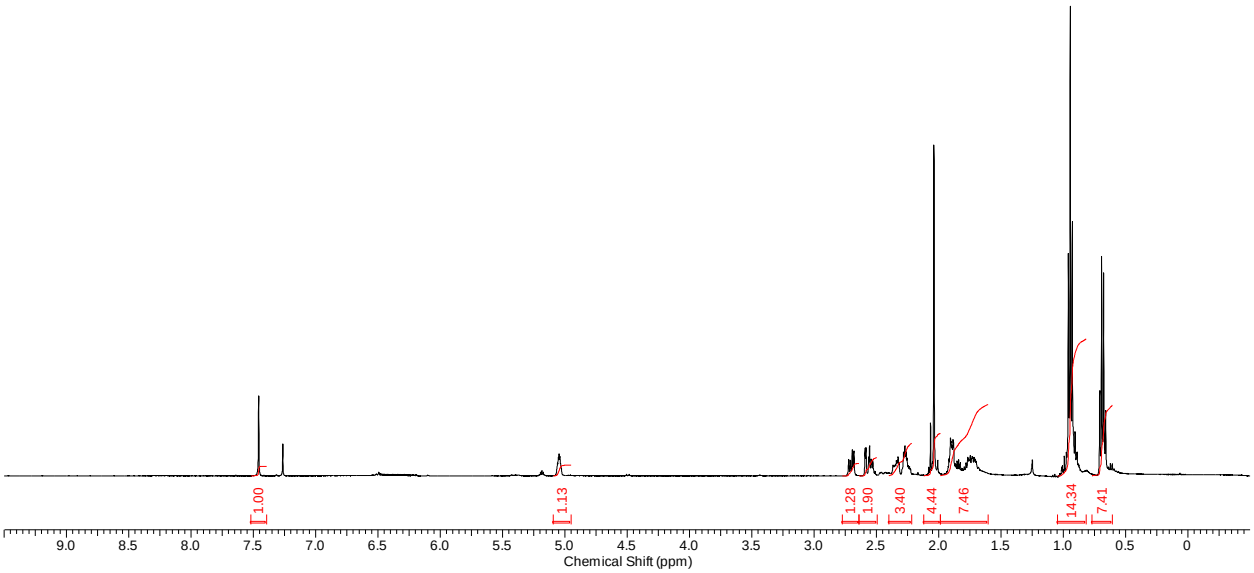
1-53n (*E/Z* =1.3:1)

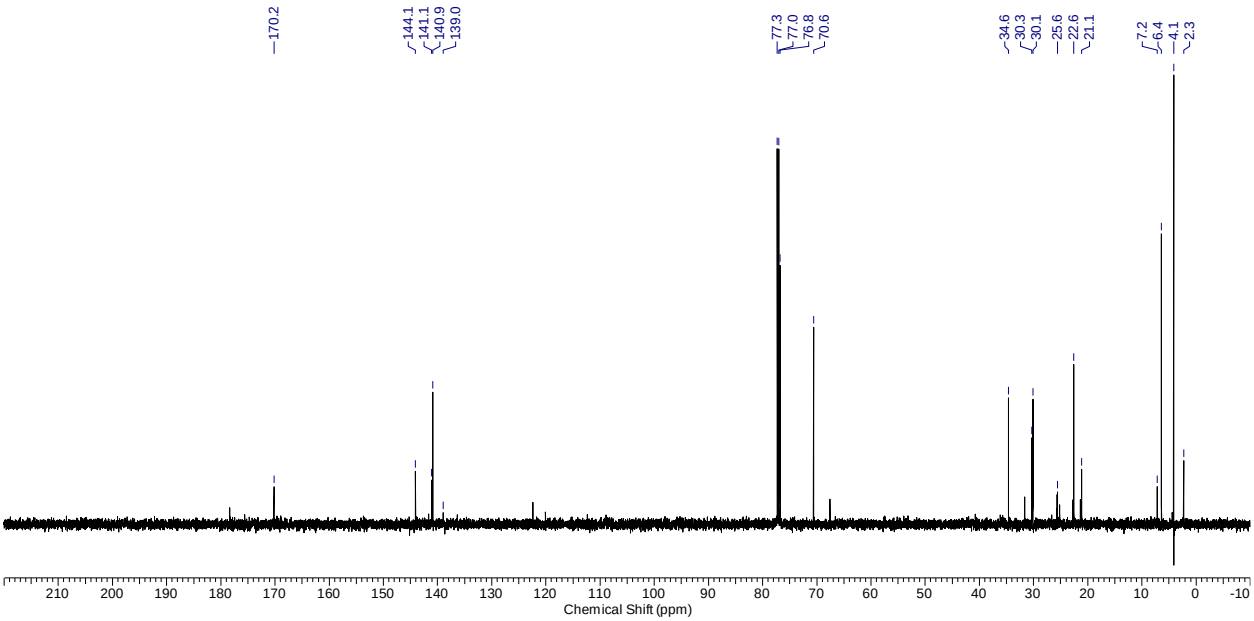

1.00
1.10
0.99
3.15
2.37
2.74
20.17
6.67
6.70
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

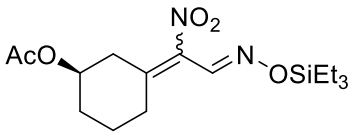

146.0
141.1
138.4
77.3
77.0
76.8
70.2
39.4
34.6
30.5
25.8
22.8
18.1
6.4
4.2
-4.8
-5.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)


NO2
tBuMe2SiO
N
OSiEt3

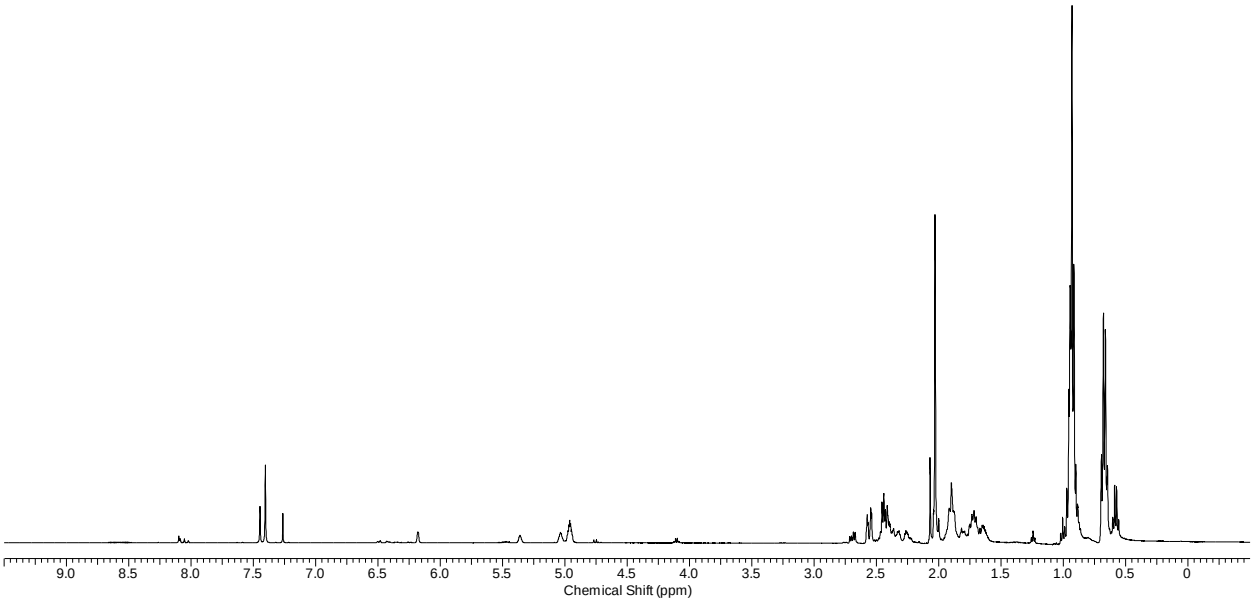
1-53n (*E/Z* =1.3:1)

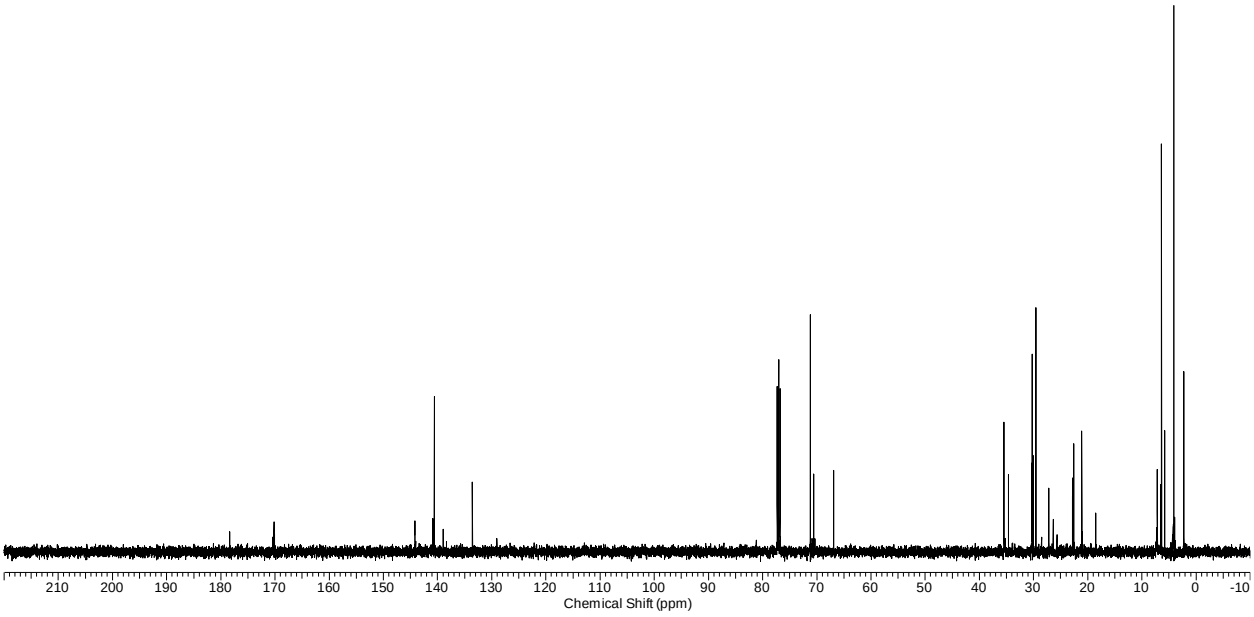

1.00
1.13
1.28
1.90
3.40
4.44
7.46
14.34
7.41
Chemical Shift (ppm)

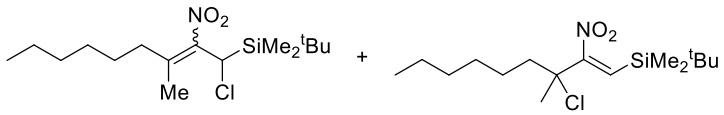

170.2
144.1
141.1
140.9
139.0
77.3
77.0
76.8
70.6
34.6
30.3
30.1
25.6
22.6
21.1
7.2
6.4
4.1
2.3
Chemical Shift (ppm)


NO2
AcO
N
OSiEt3

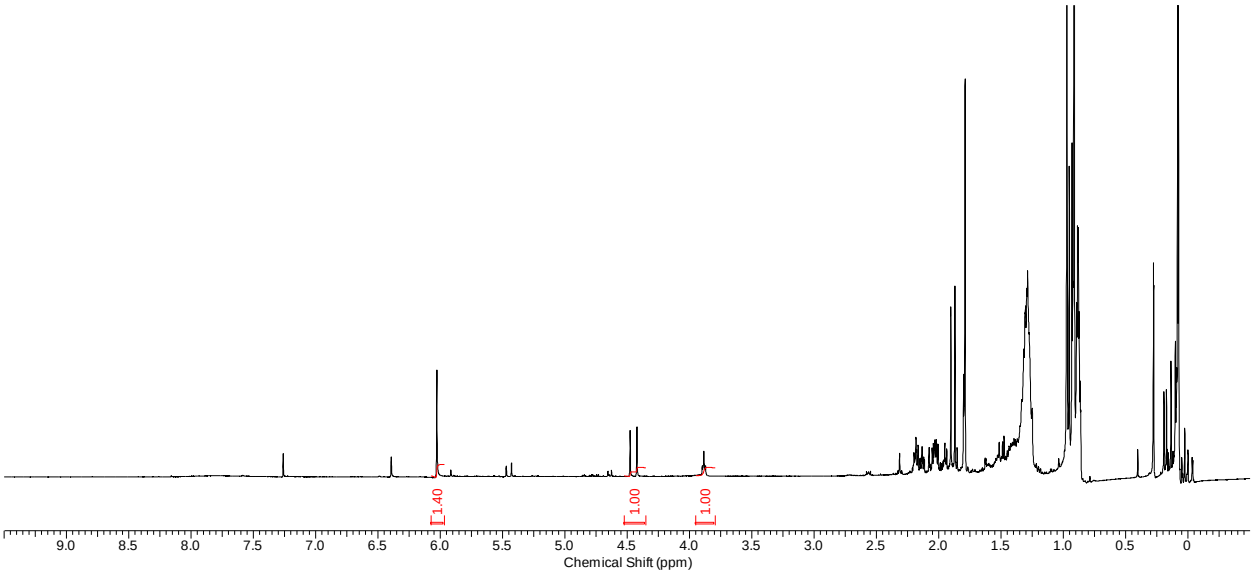
1-53o (*E/Z* =2.2:1)

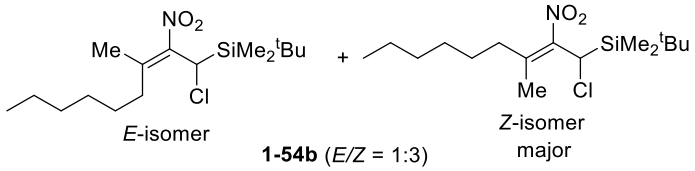

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)



1-54b crude NMR 1:1 **1-54b**

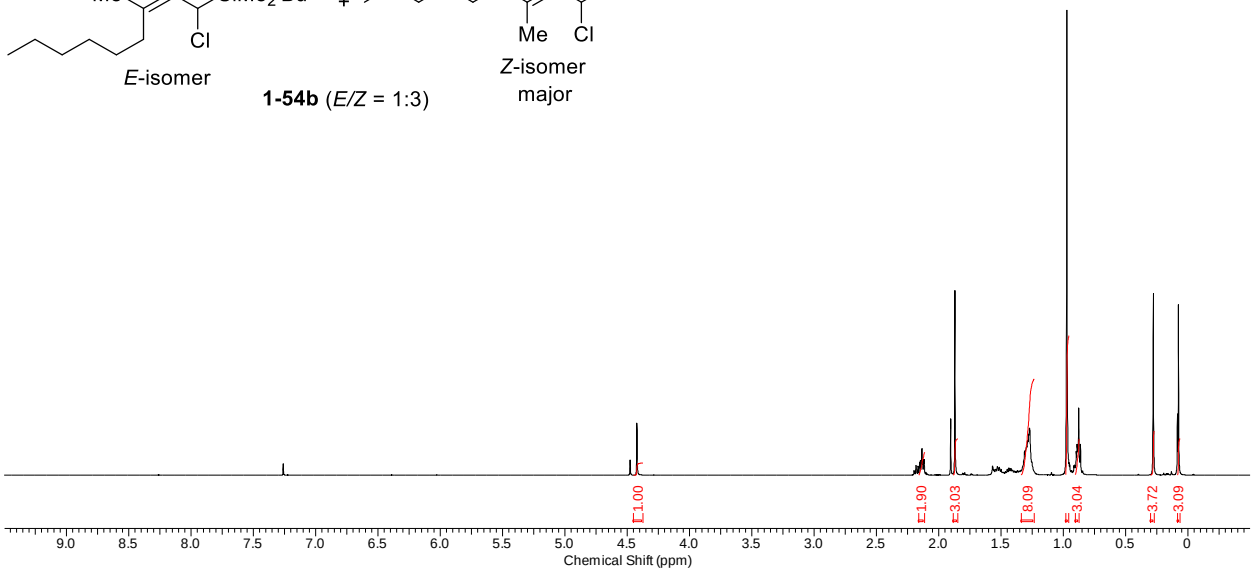


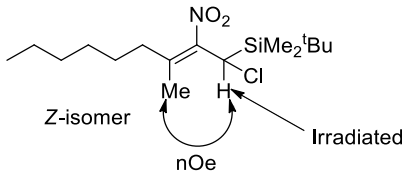


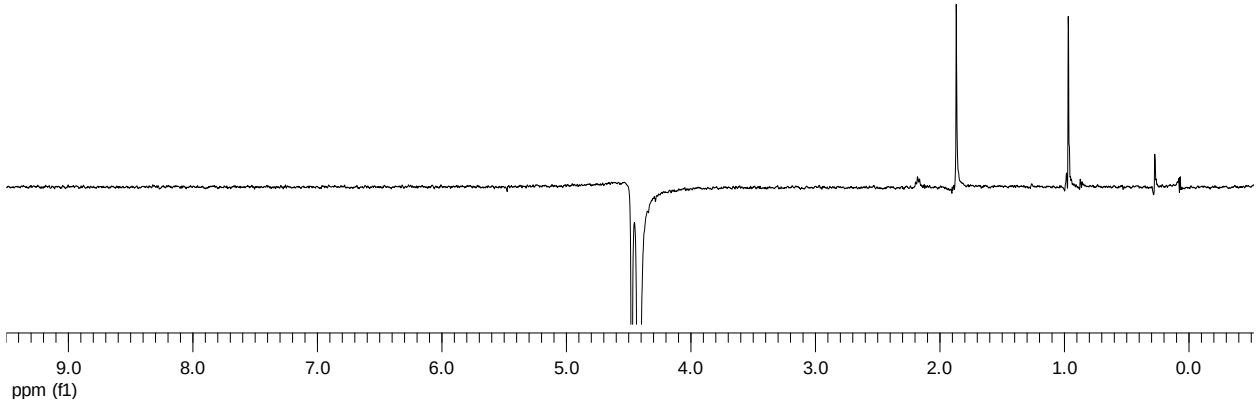
E-isomer

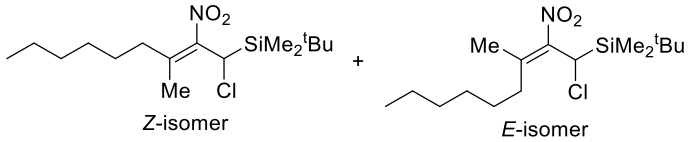
1-54b (*E*/*Z* = 1:3)

Z-isomer major

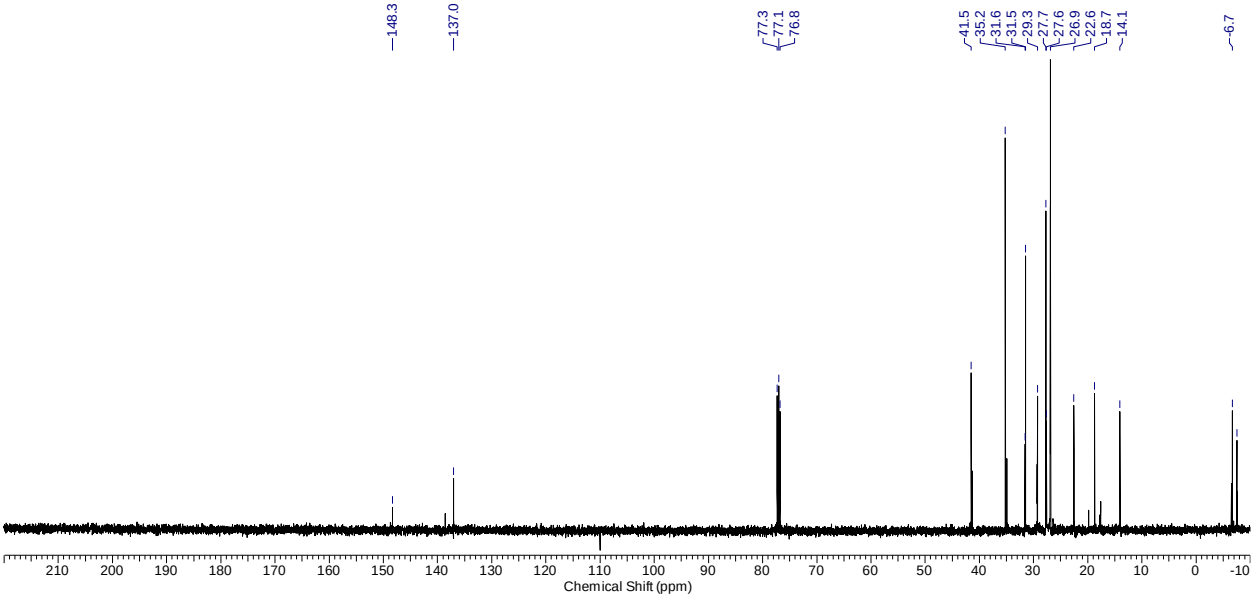


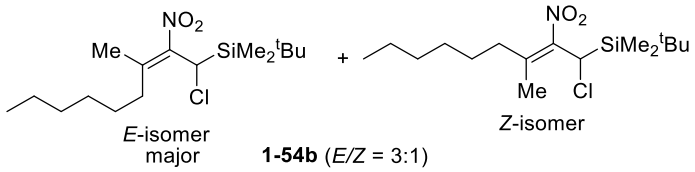

NO2
SiMe2tBu
Cl
Me
H
Z-isomer
Irradiated
nOe


9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

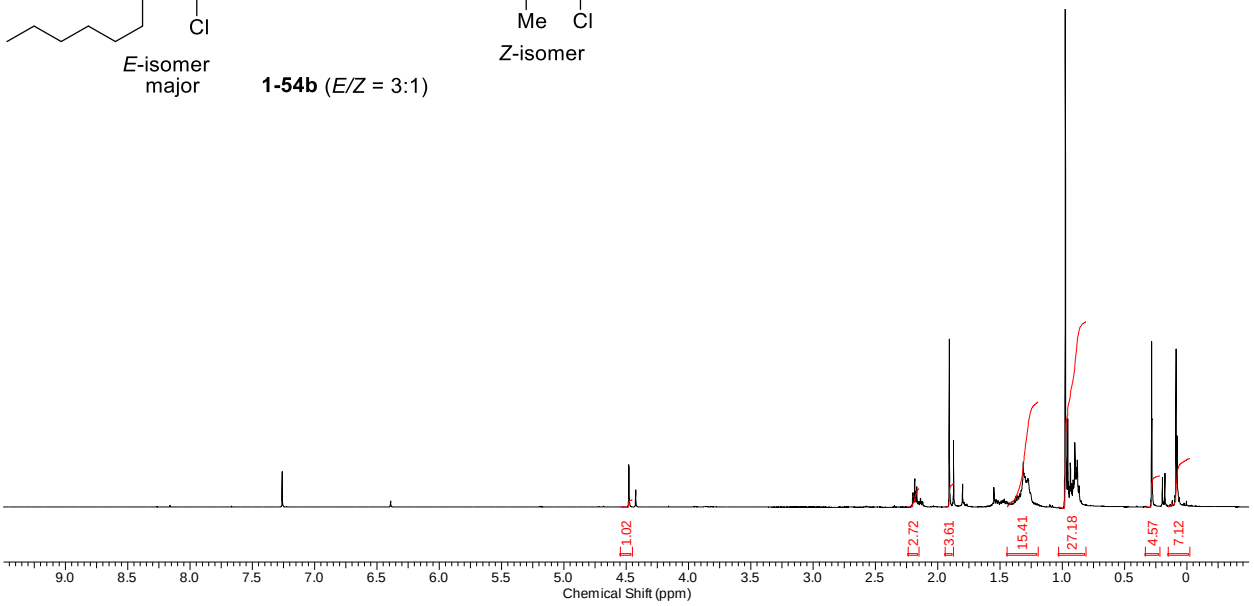

NO2
SiMe2tBu
Me
Cl
Z-isomer
+
NO2
Me
SiMe2tBu
Cl
E-isomer

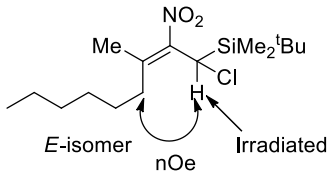
1-54b (*E*/*Z* = 1:3)

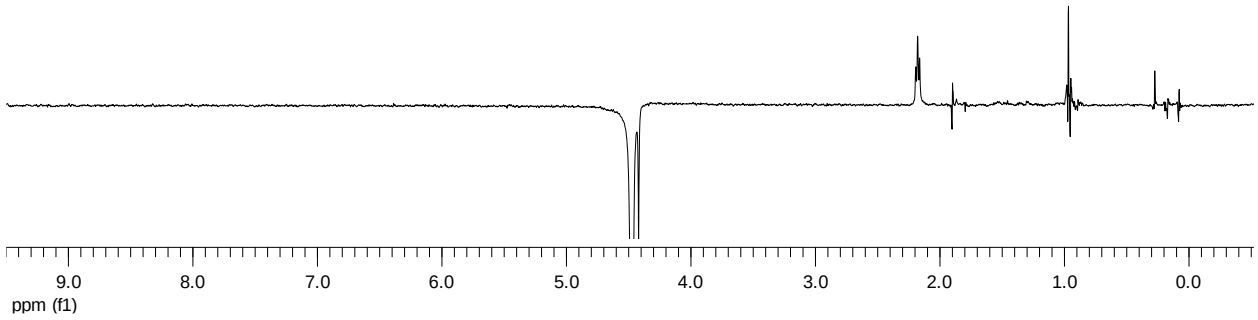

148.3
137.0
77.3
77.1
76.8
41.5
35.2
31.6
31.5
29.3
27.7
27.6
26.9
22.6
18.7
14.1
-6.7
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
Chemical Shift (ppm)

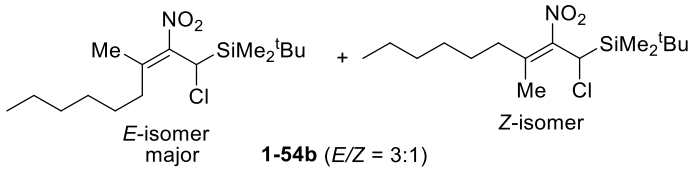

NO2
Me
SiMe2tBu
Cl
E-isomer
major
+
NO2
SiMe2tBu
Me
Cl
Z-isomer

1-54b (*E*/*Z* = 3:1)

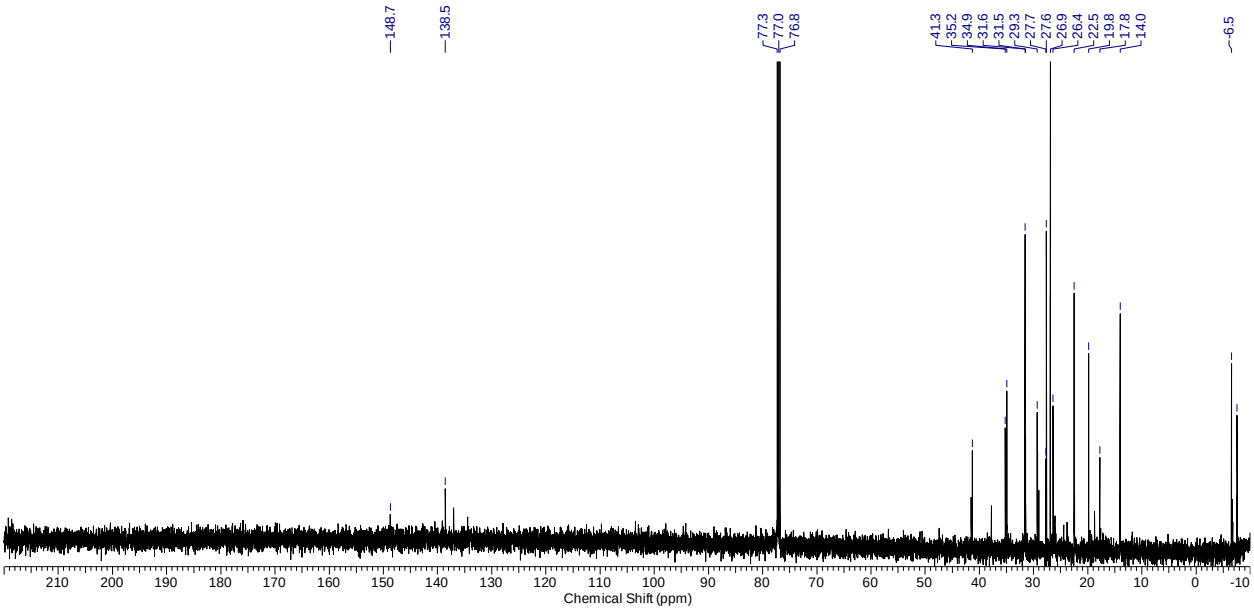

1.02
2.72
3.61
15.41
27.18
4.57
7.12
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
Chemical Shift (ppm)

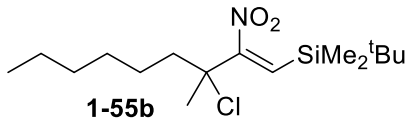

NO2
Me
SiMe2tBu
Cl
H
E-isomer
nOe
Irradiated


9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0.0
ppm (f1)

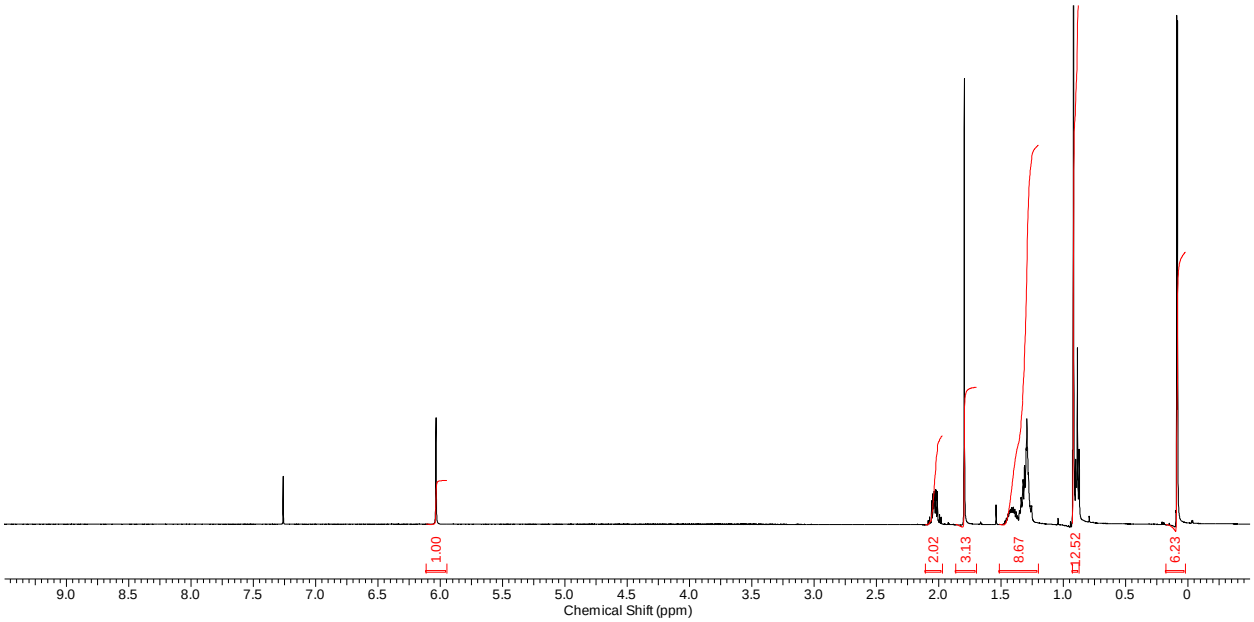


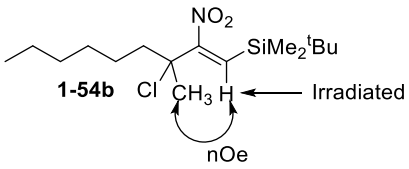
1-54b (*E*/*Z* = 3:1)

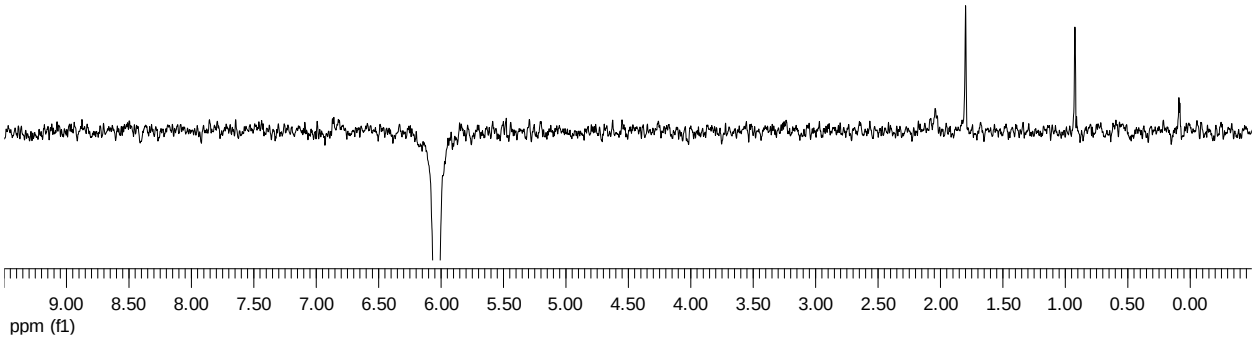


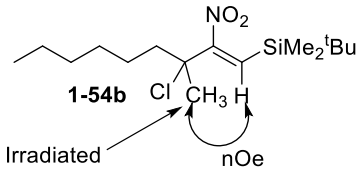


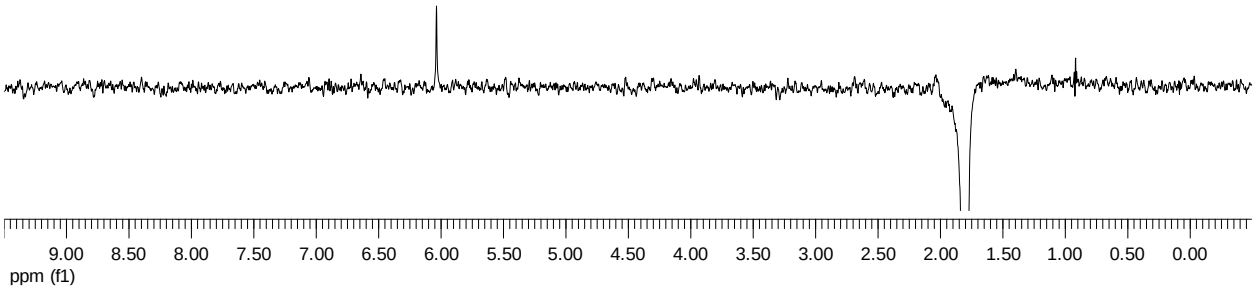
1-55b

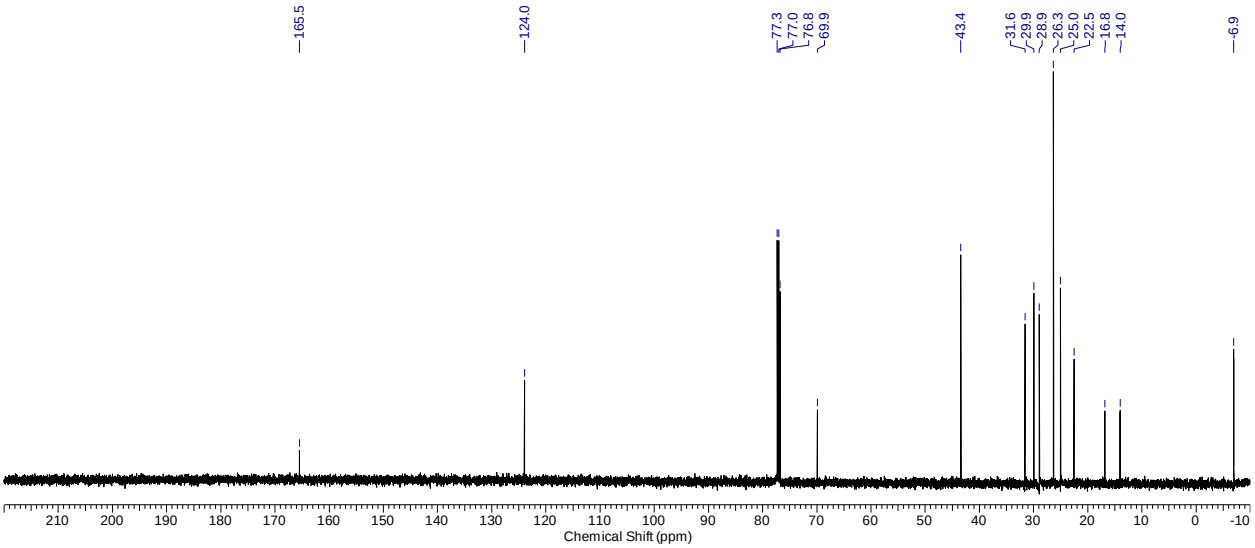


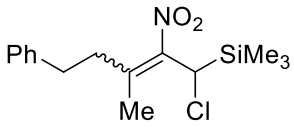

NO2
SiMe2tBu
1-54b
Cl
CH3
H
Irradiated
nOe


9.00 8.50 8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50 0.00
ppm (f1)

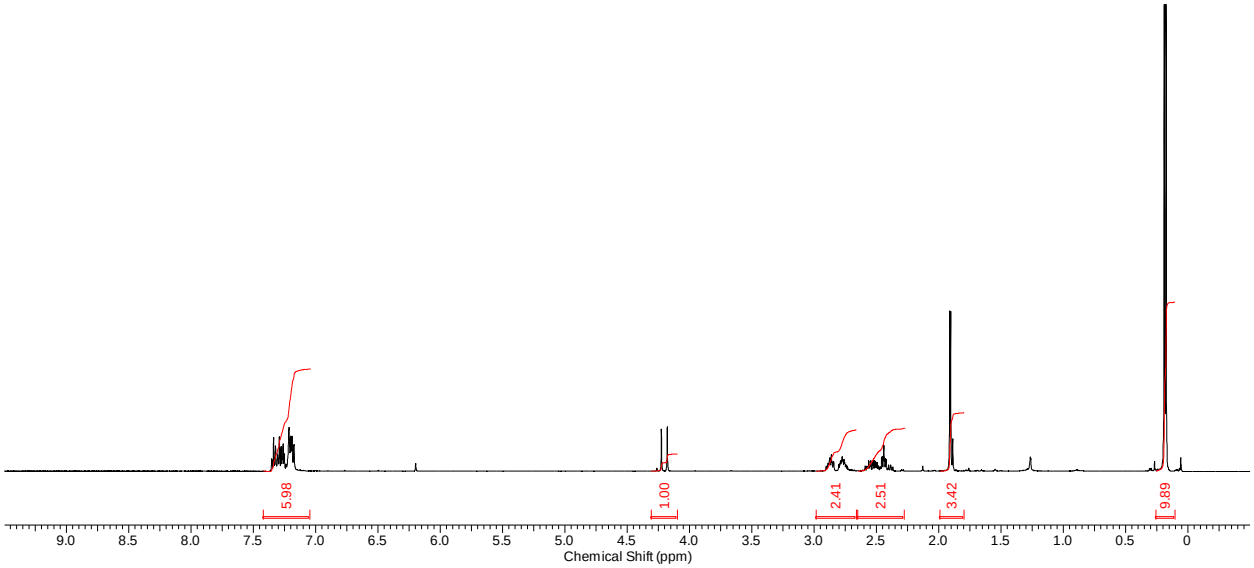

NO2
SiMe2tBu
1-54b
Cl
CH3
H
Irradiated
nOe

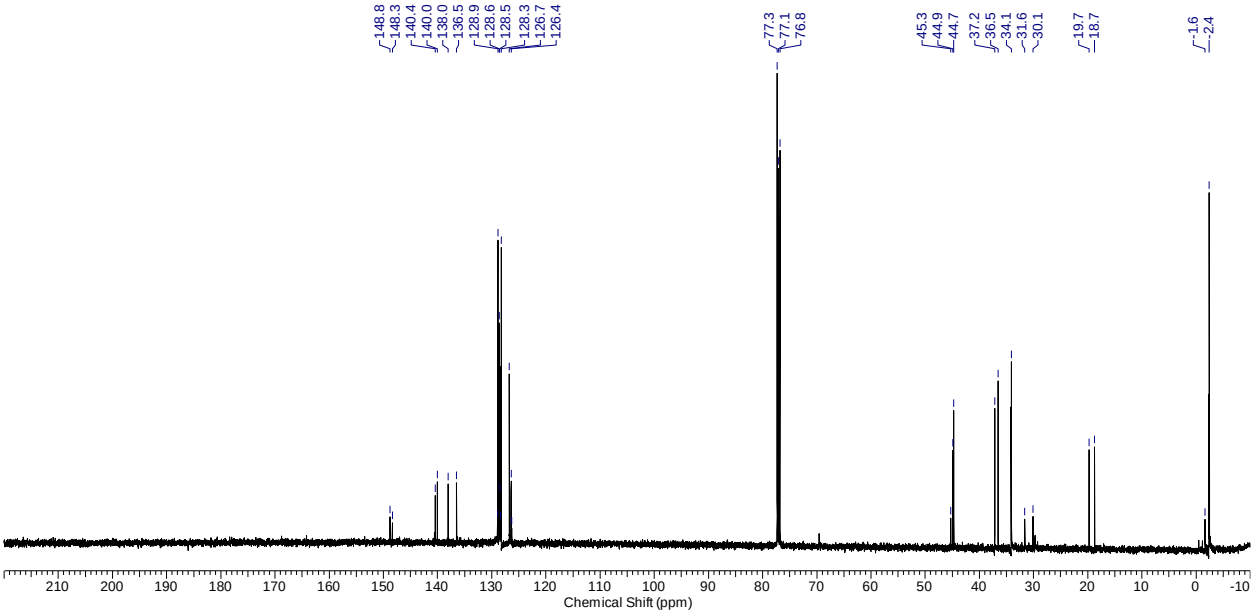

9.00 8.50 8.00 7.50 7.00 6.50 6.00 5.50 5.00 4.50 4.00 3.50 3.00 2.50 2.00 1.50 1.00 0.50 0.00
ppm (f1)

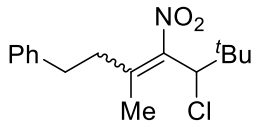

165.5
124.0
77.3
77.0
76.8
69.9
43.4
31.6
29.9
28.9
26.3
25.0
22.5
16.8
14.0
6.9
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)


NO2
Ph
SiMe3
Me
Cl

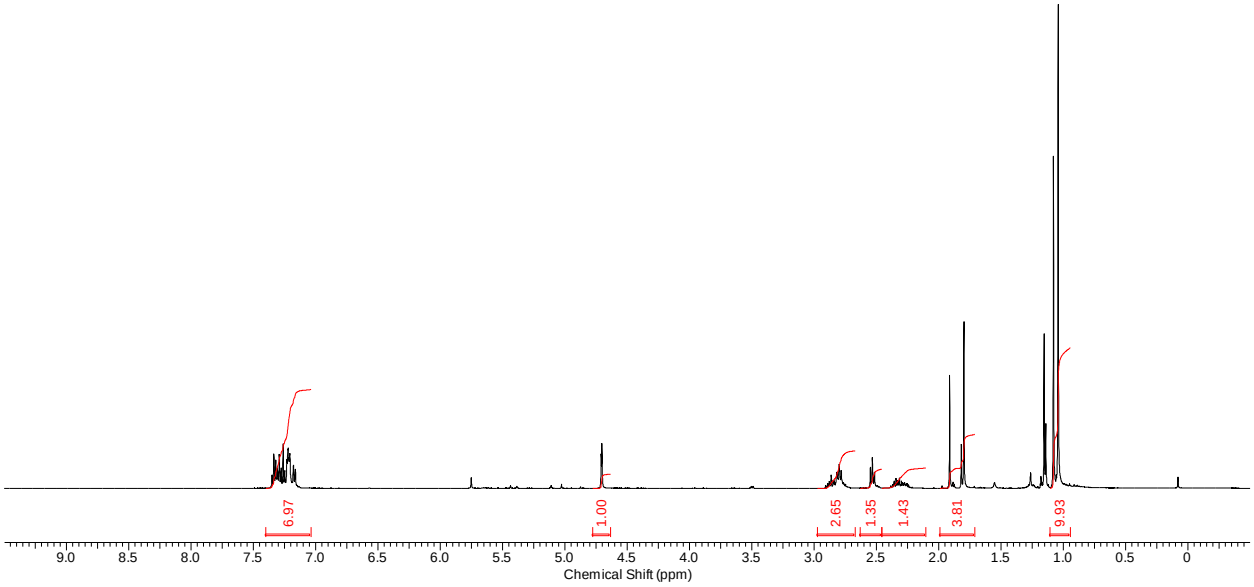
1-54q (*E*/*Z* = 1:1)

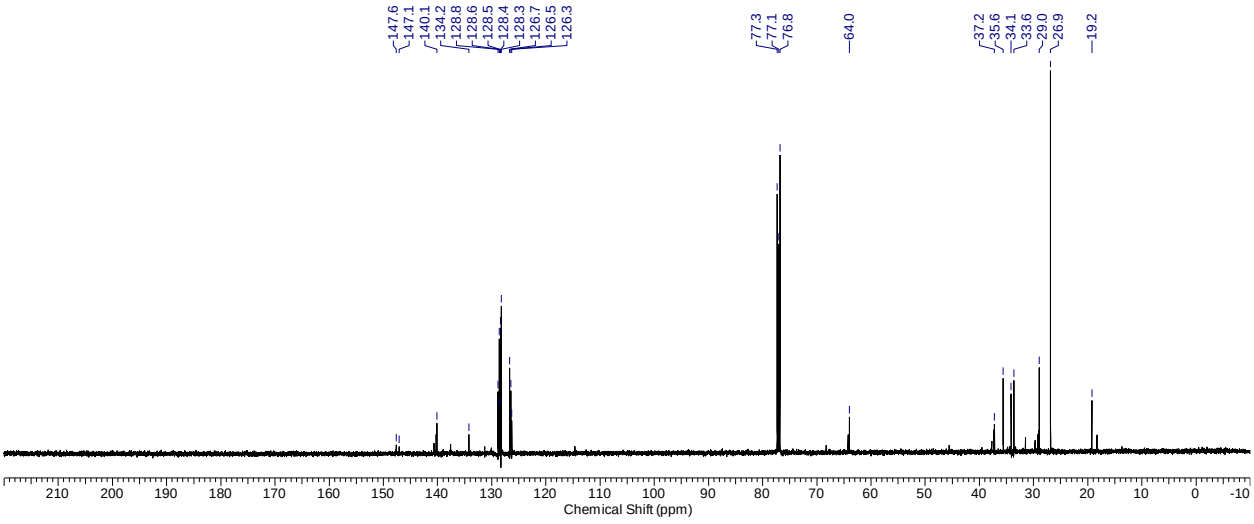

5.98
1.00
2.41
2.51
3.42
9.89
Chemical Shift (ppm)

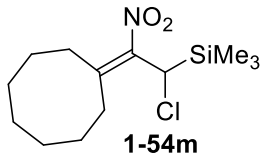

148.8
148.3
140.4
140.0
138.0
136.5
128.9
128.6
128.5
128.3
126.7
126.4
77.3
77.1
76.8
45.3
44.9
44.7
37.2
36.5
34.1
31.6
30.1
19.7
18.7
1.6
-2.4
Chemical Shift (ppm)


NO2
Ph
tBu
Me
Cl

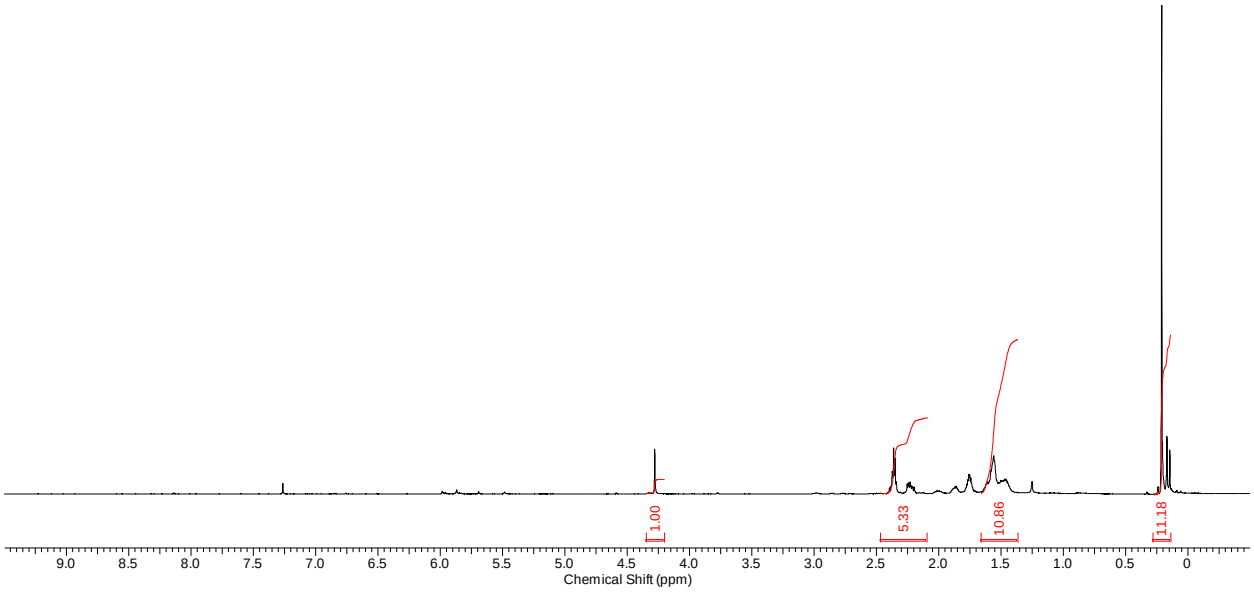
1-54r (*E*/*Z* = 1:1)

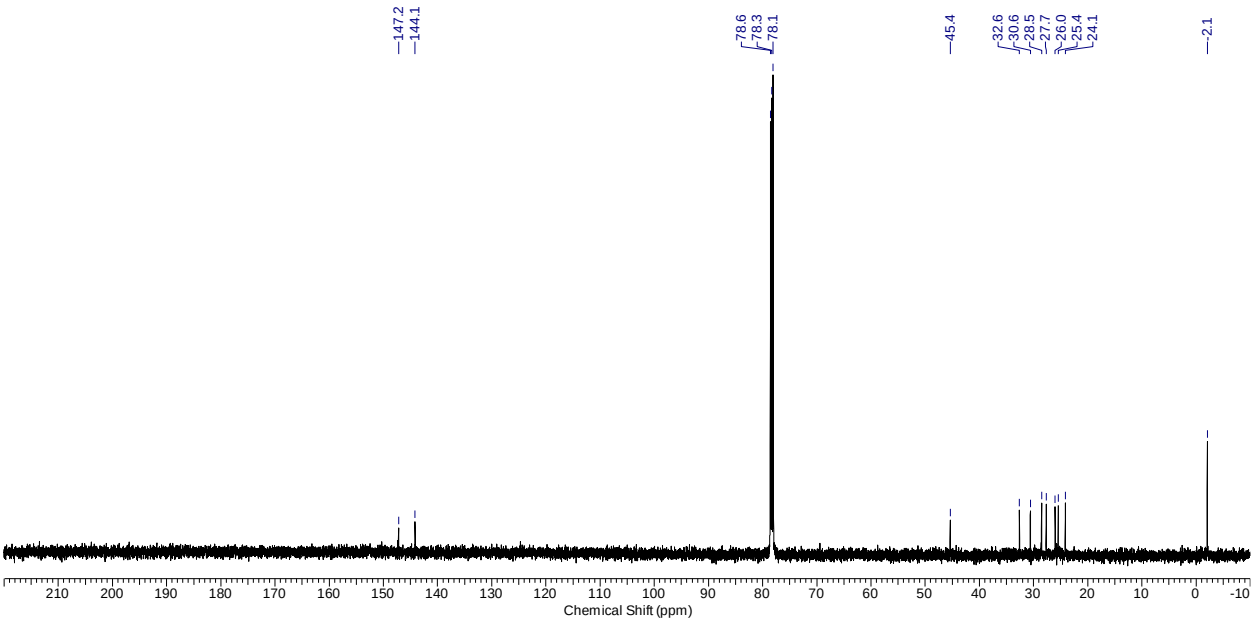

6.97
1.00
2.65
1.35
1.43
3.81
9.93
Chemical Shift (ppm)

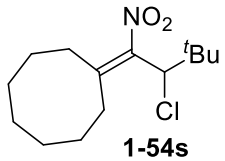

147.6
147.1
140.1
134.2
128.8
128.6
128.5
128.4
128.3
126.7
126.5
126.3
77.3
77.1
76.8
64.0
37.2
35.6
34.1
33.6
29.0
26.9
19.2
Chemical Shift (ppm)


NO2
SiMe3
Cl

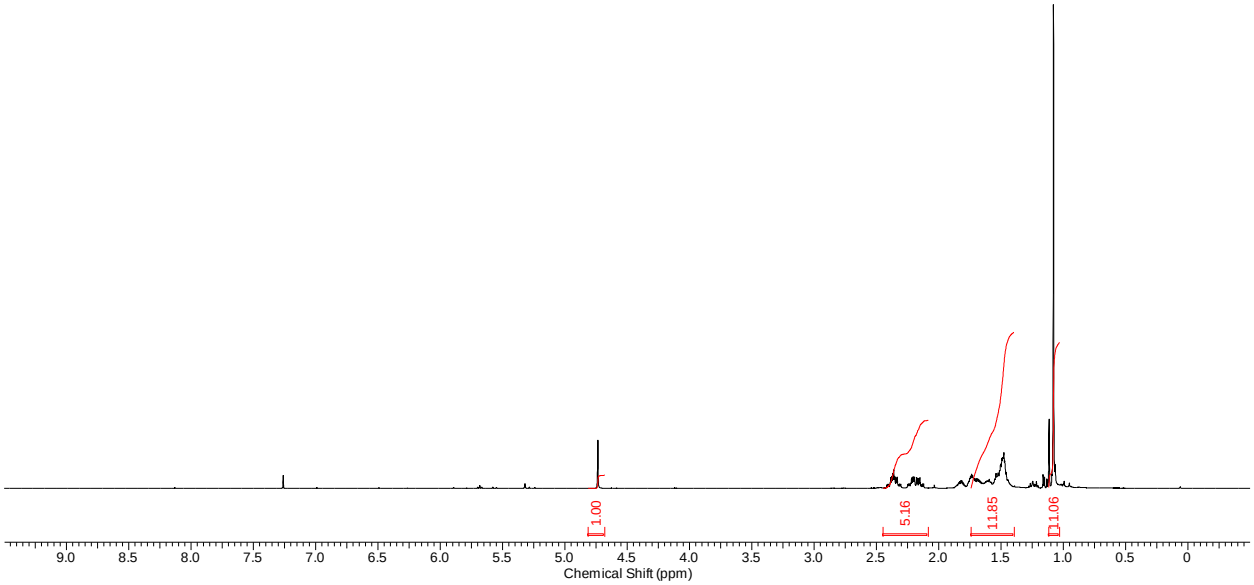
1-54m

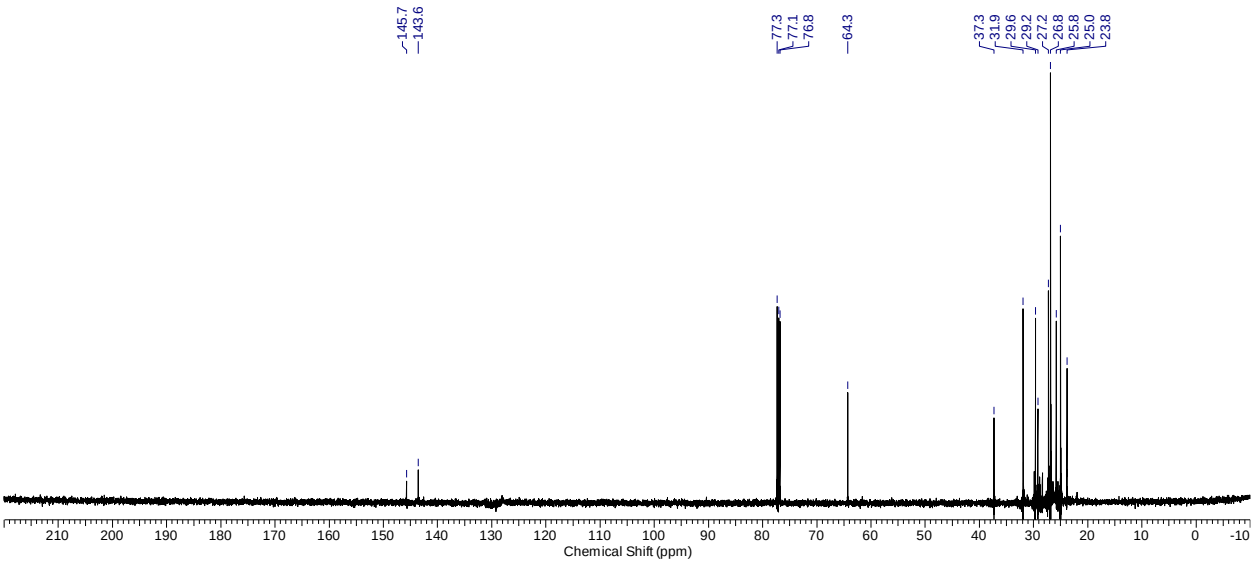

1.00
5.33
10.86
11.18
Chemical Shift (ppm)

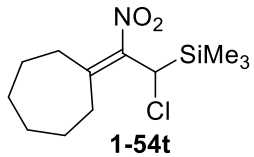

147.2
144.1
78.6
78.3
78.1
45.4
32.6
30.6
28.5
27.7
26.0
25.4
24.1
2.1
Chemical Shift (ppm)


NO2
tBu
Cl

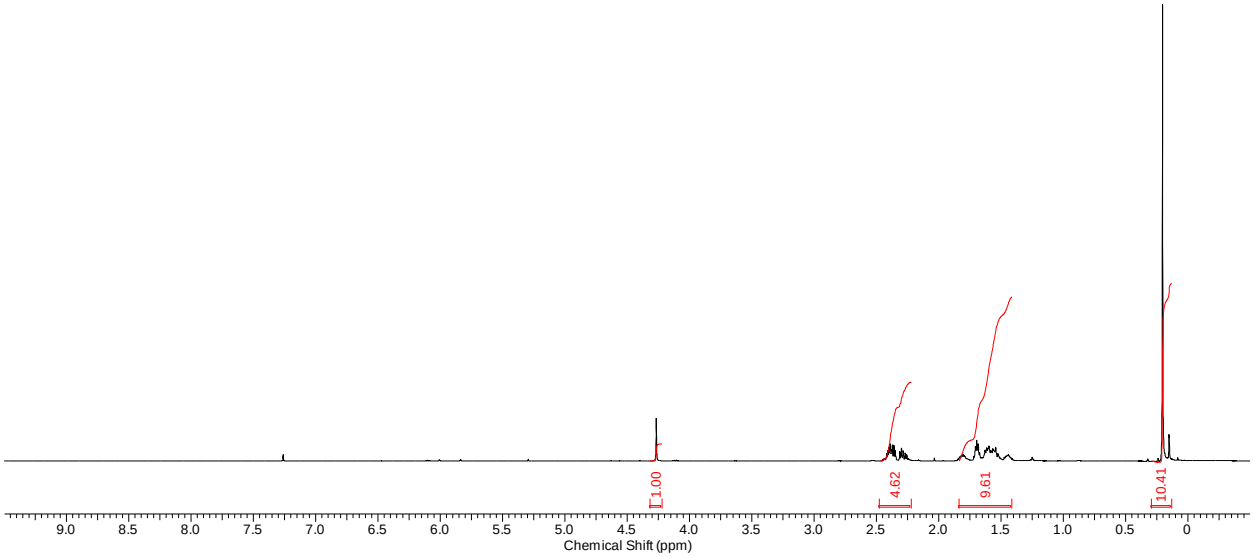
1-54s

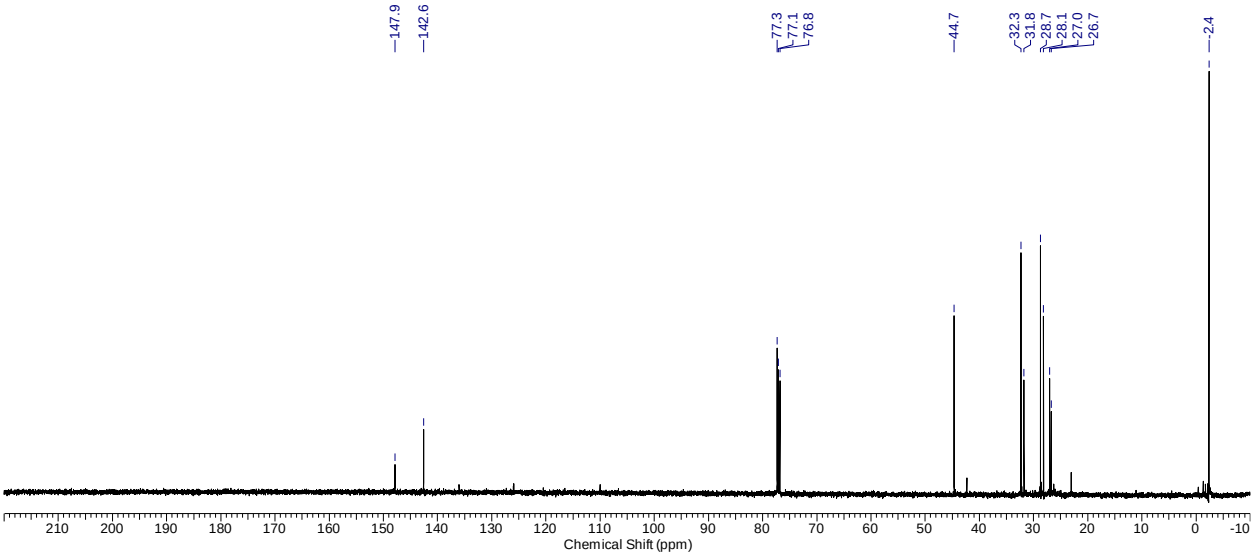

1.00
5.16
11.85
11.06
Chemical Shift (ppm)

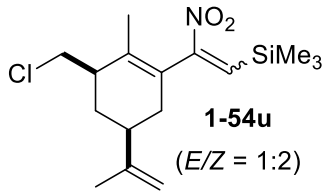

145.7
143.6
77.3
77.1
76.8
64.3
37.3
31.9
29.6
29.2
27.2
26.8
25.8
25.0
23.8
Chemical Shift (ppm)


NO2
SiMe3
Cl

1-54t

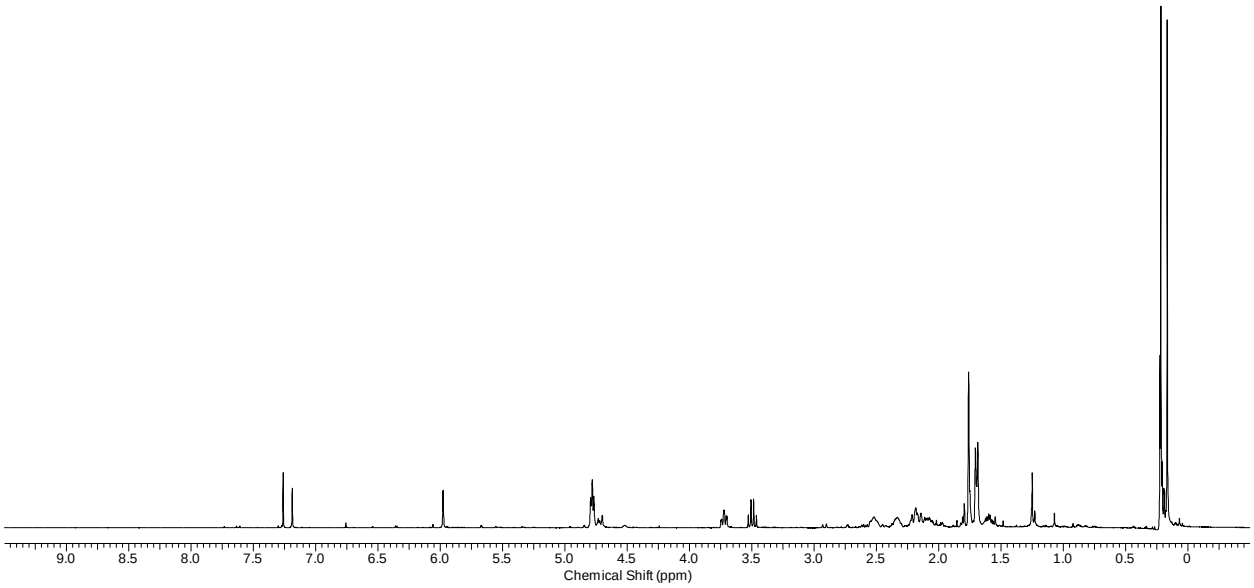

1.00
4.62
9.61
10.41
Chemical Shift (ppm)

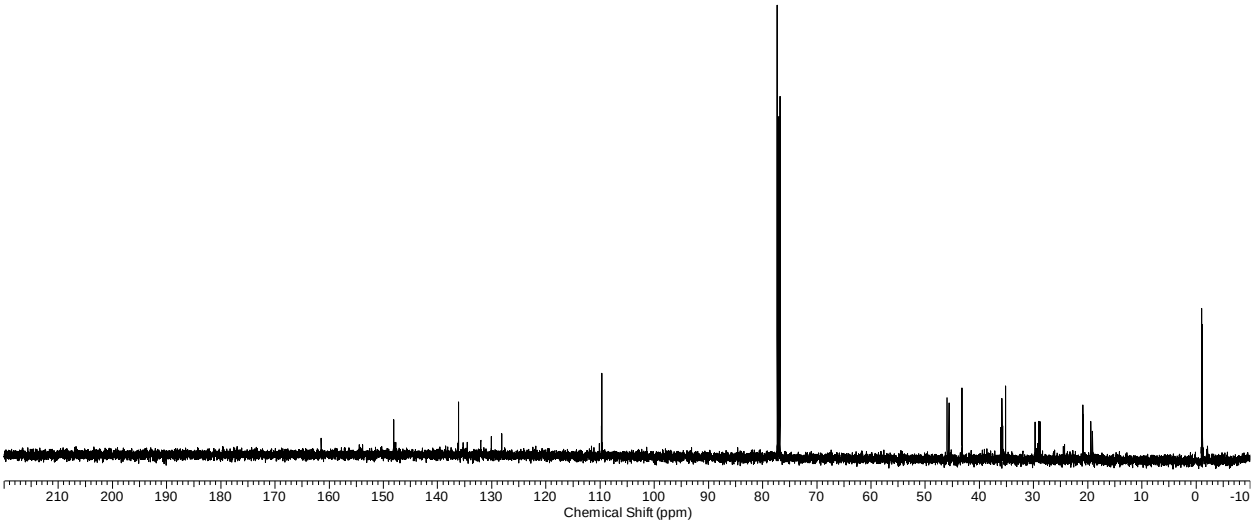

147.9
142.6
77.3
77.1
76.8
44.7
32.3
31.8
28.7
28.1
27.0
26.7
2.4
Chemical Shift (ppm)

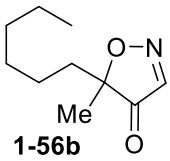

NO2
SiMe3
Cl

1-54u

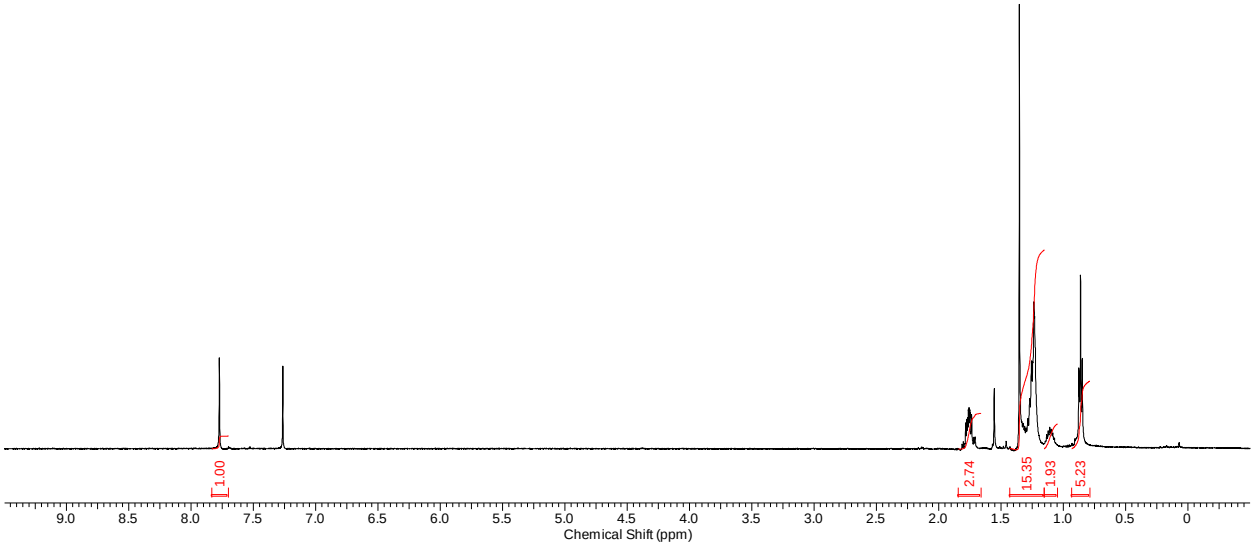
(*E*/*Z* = 1:2)

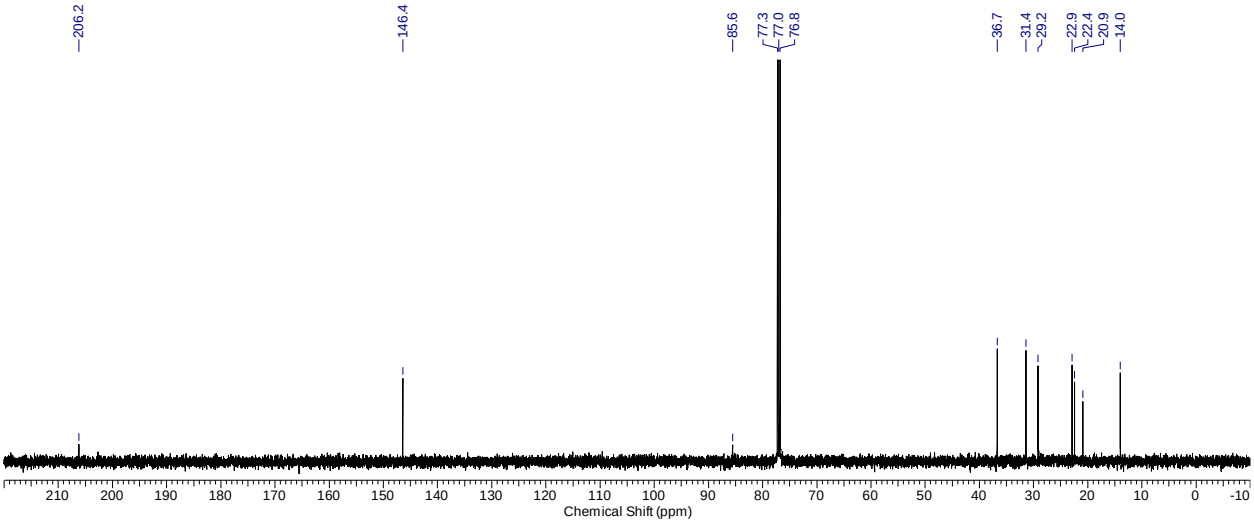

9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

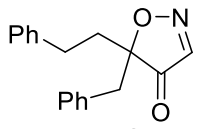

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)


O−N
Me
O

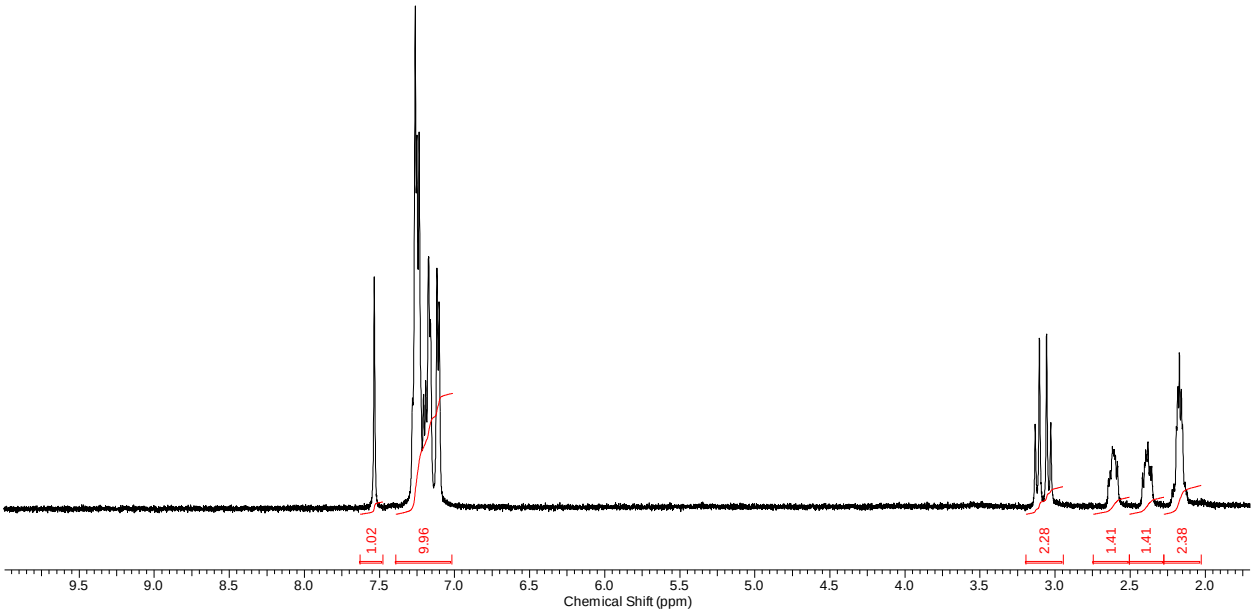
1-56b

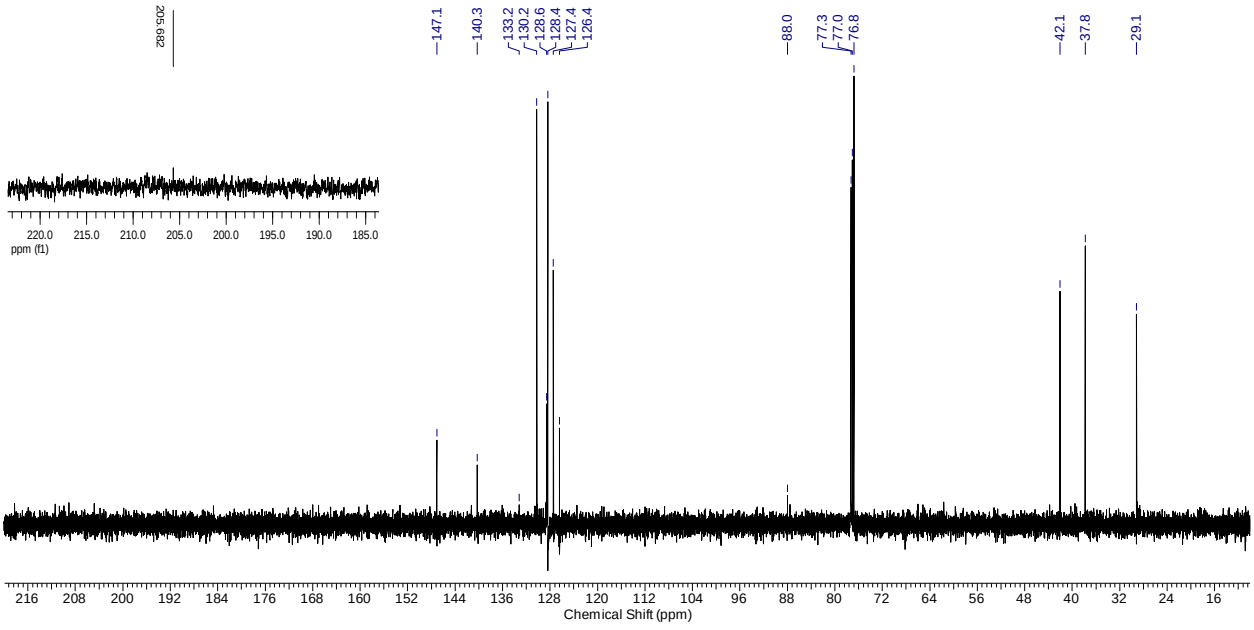

1.00
2.74
15.35
1.93
5.23
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

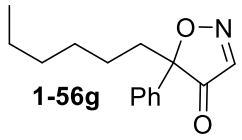

206.2
146.4
85.6
77.3
77.0
76.8
36.7
31.4
29.2
22.9
22.4
20.9
14.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

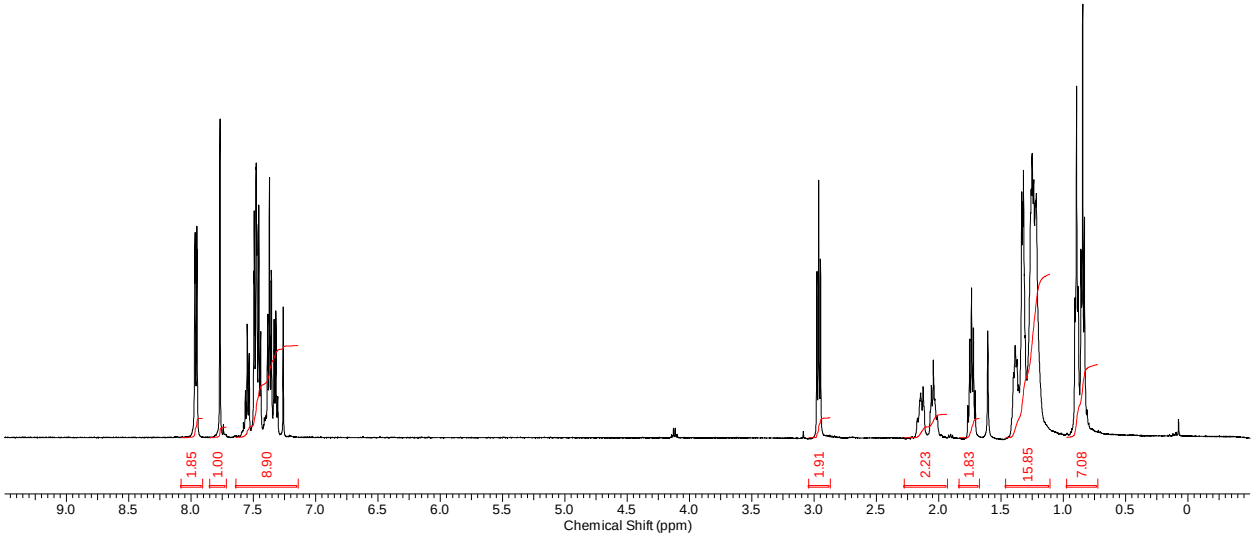

Ph
O
N
Ph
O

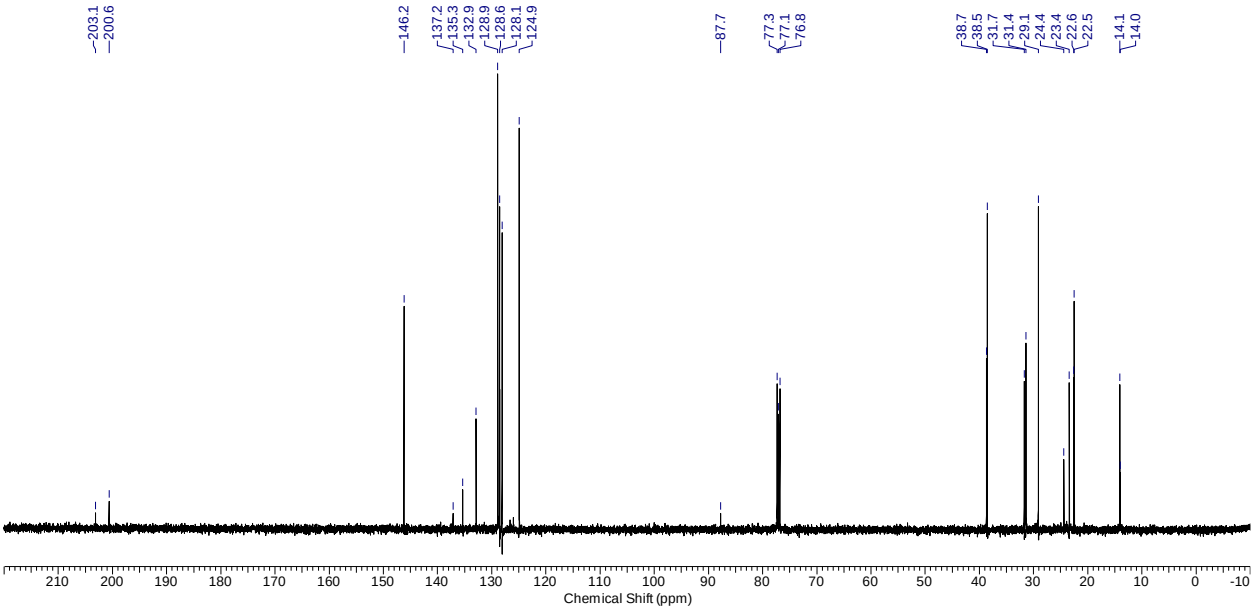
1-56f

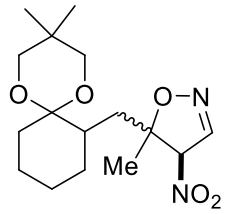

1.02
9.96
2.28
1.41
1.41
2.38
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
Chemical Shift (ppm)


205.682
147.1
140.3
133.2
130.2
128.6
128.4
127.4
126.4
88.0
77.3
77.0
76.8
42.1
37.8
29.1
220.0
215.0
210.0
205.0
200.0
195.0
190.0
185.0
ppm (f1)
216
208
200
192
184
176
168
160
152
144
136
128
120
112
104
96
88
80
72
64
56
48
40
32
24
16
Chemical Shift (ppm)

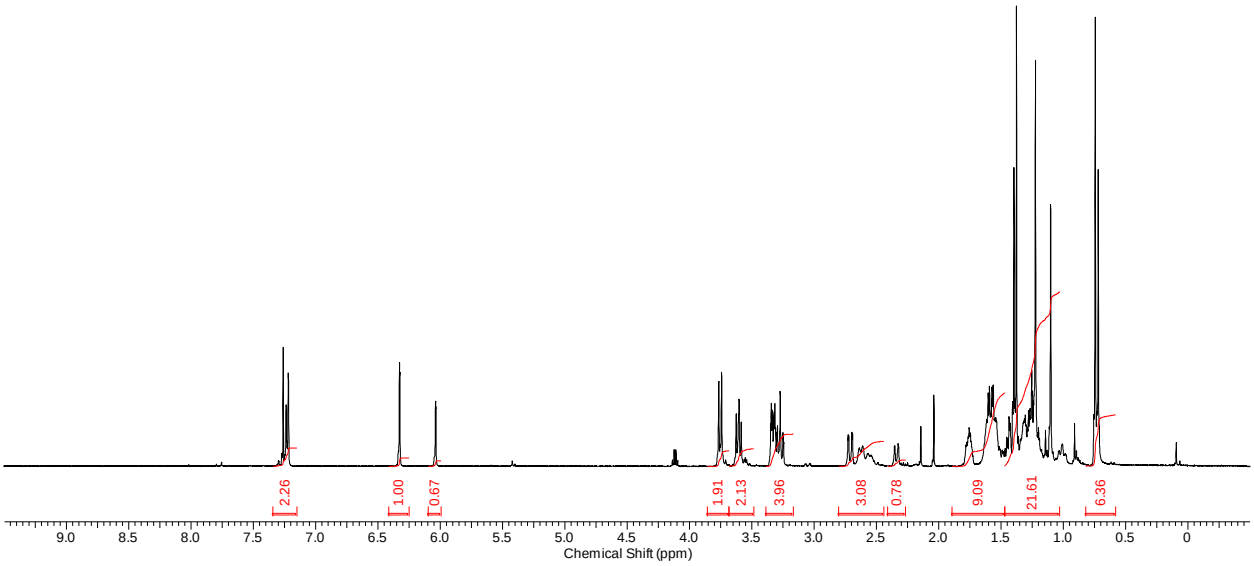

O–N
1-56g
Ph
O

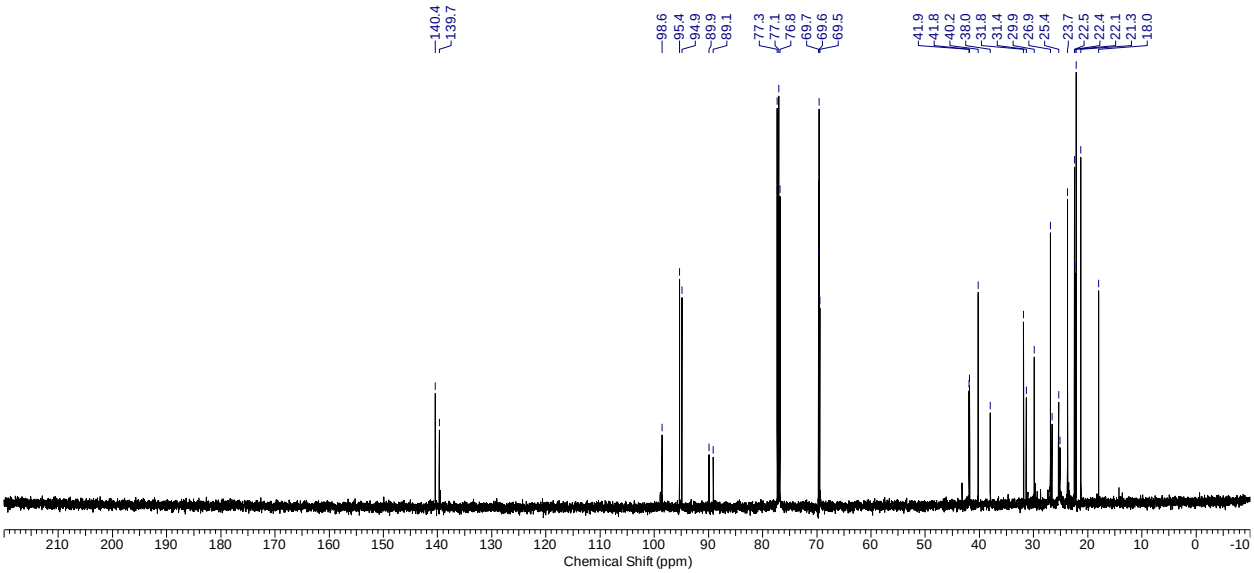

1.85
1.00
8.90
1.91
2.23
1.83
15.85
7.08
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

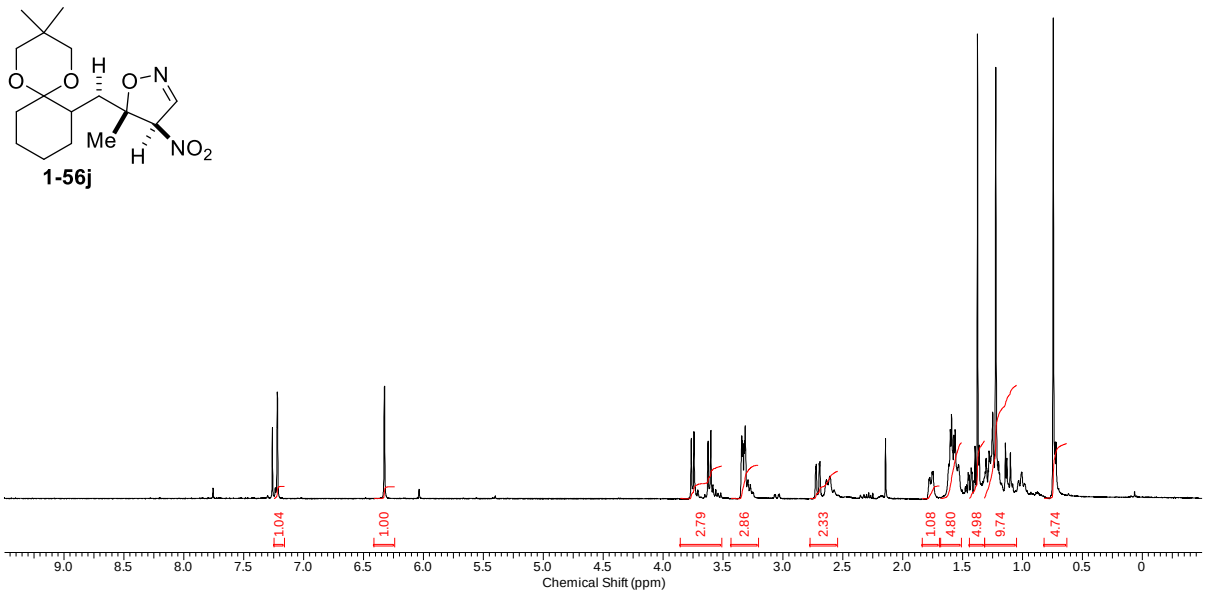

203.1
200.6
146.2
137.2
135.3
132.9
128.9
128.6
128.1
124.9
87.7
77.3
77.1
76.8
38.7
38.5
31.7
31.4
29.1
24.4
23.4
22.6
22.5
14.1
14.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

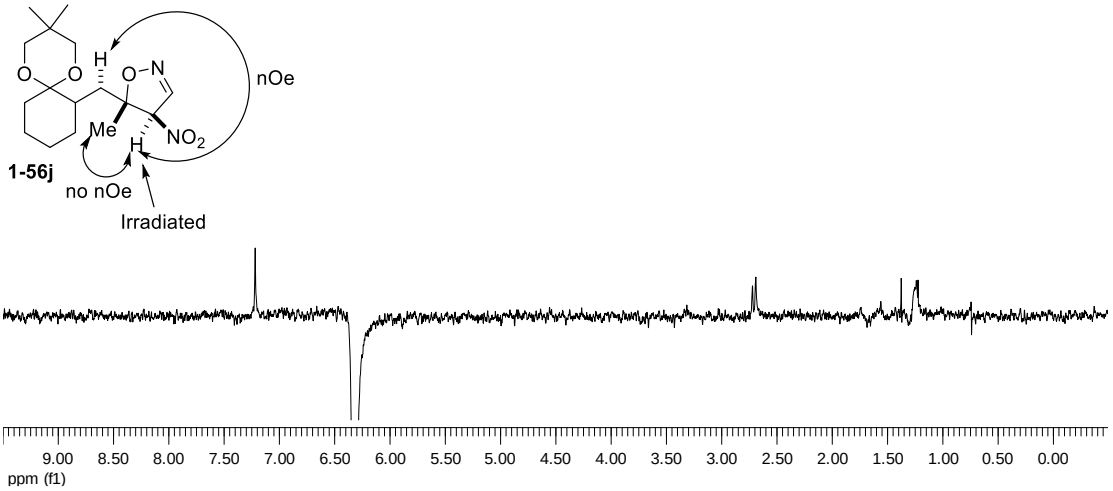

O
O
O–N
Me
NO2

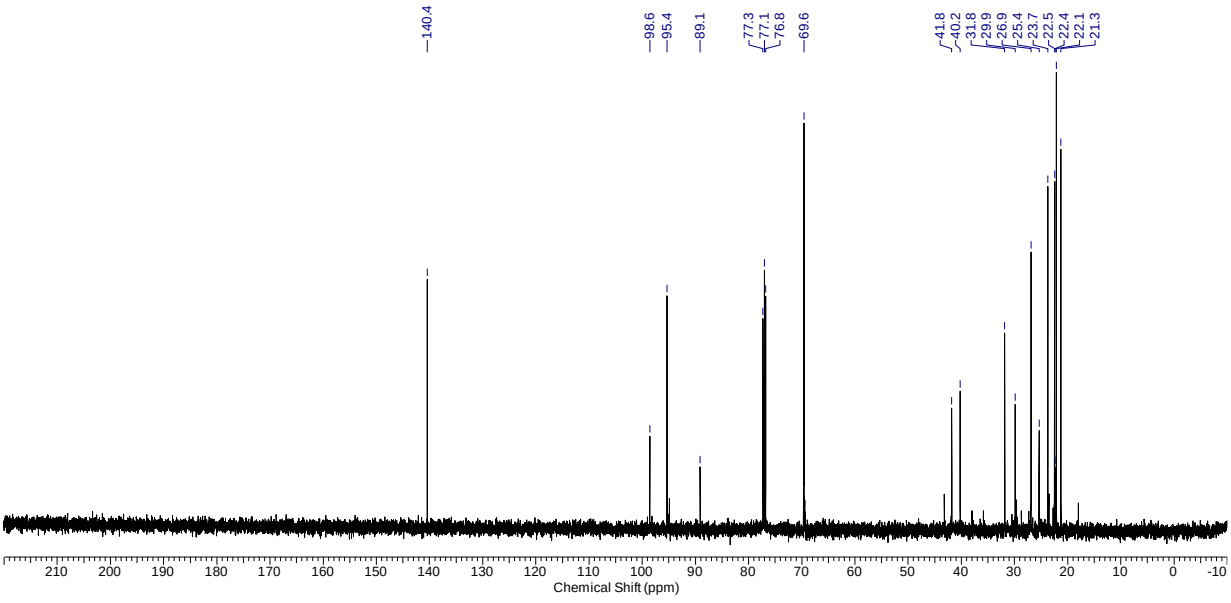
1-56j (1.7:1)

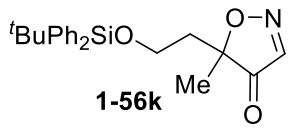

2.26
1.00
0.67
1.91
2.13
3.96
3.08
0.78
9.09
21.61
6.36
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)


140.4
139.7
98.6
95.4
94.9
89.9
89.1
77.3
77.1
76.8
69.7
69.6
69.5
41.9
41.8
40.2
38.0
31.8
31.4
29.9
26.9
25.4
23.7
22.5
22.4
22.1
21.3
18.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

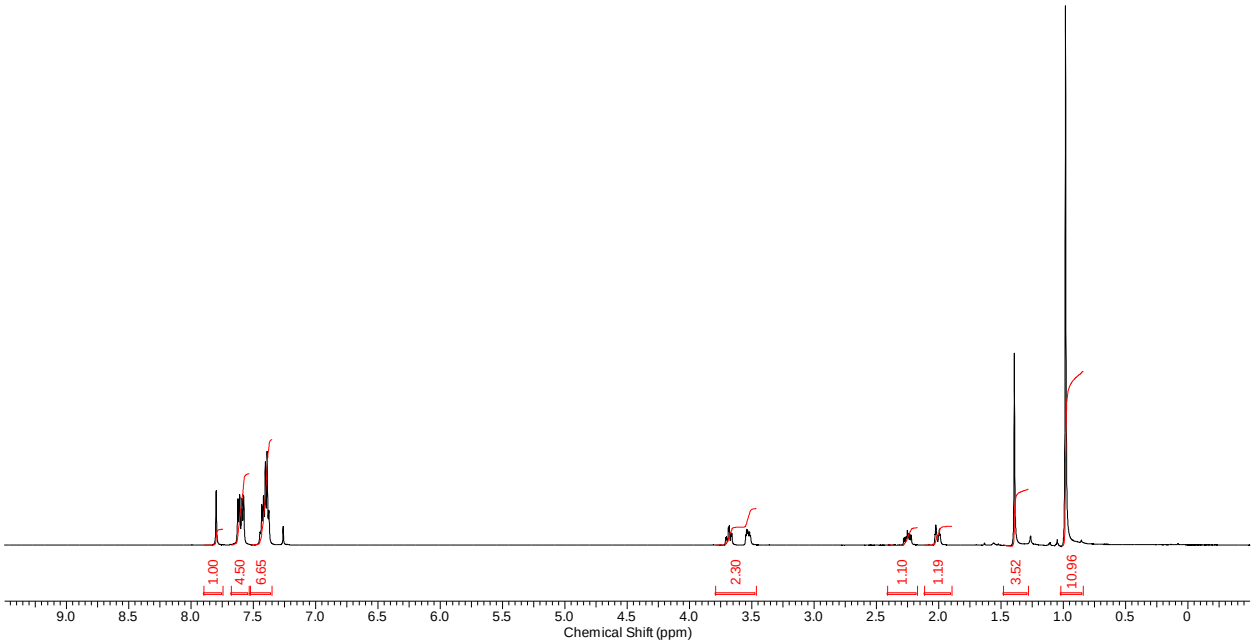

1-56j
1.04
1.00
2.79
2.86
2.33
1.08
4.80
4.98
9.74
4.74
Chemical Shift (ppm)

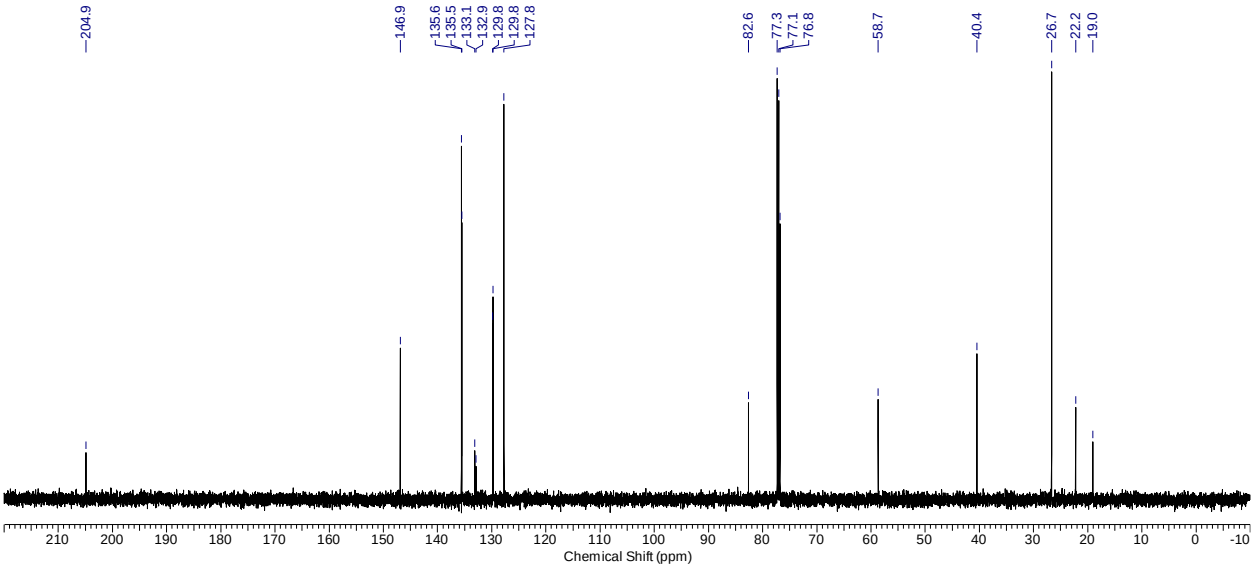

nOe
1-56j
no nOe
Irradiated
ppm (f1)


140.4
98.6
95.4
89.1
77.3
77.1
76.8
69.6
41.8
40.2
31.8
29.9
26.9
25.4
23.7
22.5
22.4
22.1
21.3
Chemical Shift (ppm)


tBuPh2SiO
O–N
Me
O

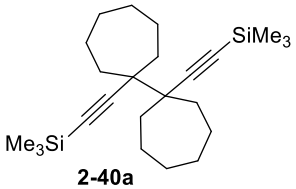
1-56k


1.00
4.50
6.65
2.30
1.10
1.19
3.52
10.96
Chemical Shift (ppm)

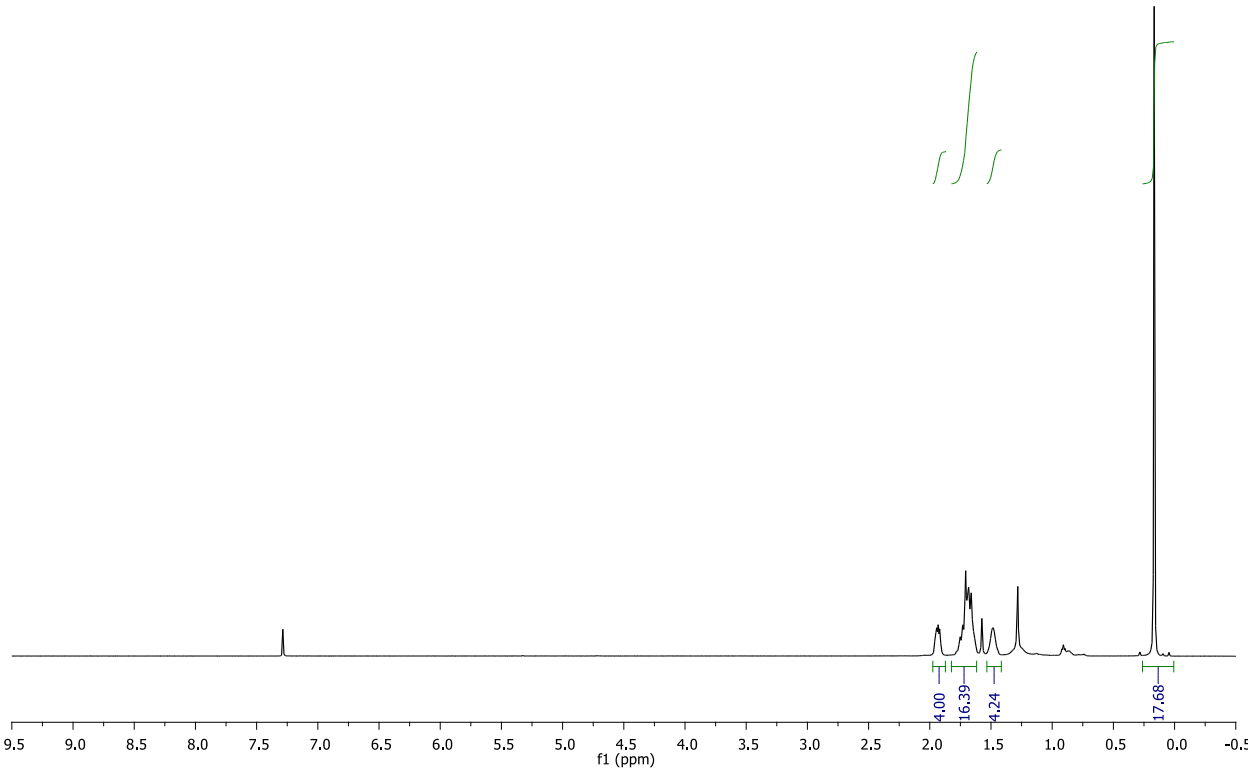

204.9
146.9
135.6
135.5
133.1
132.9
129.8
129.8
127.8
82.6
77.3
77.1
76.8
58.7
40.4
26.7
22.2
19.0
Chemical Shift (ppm)

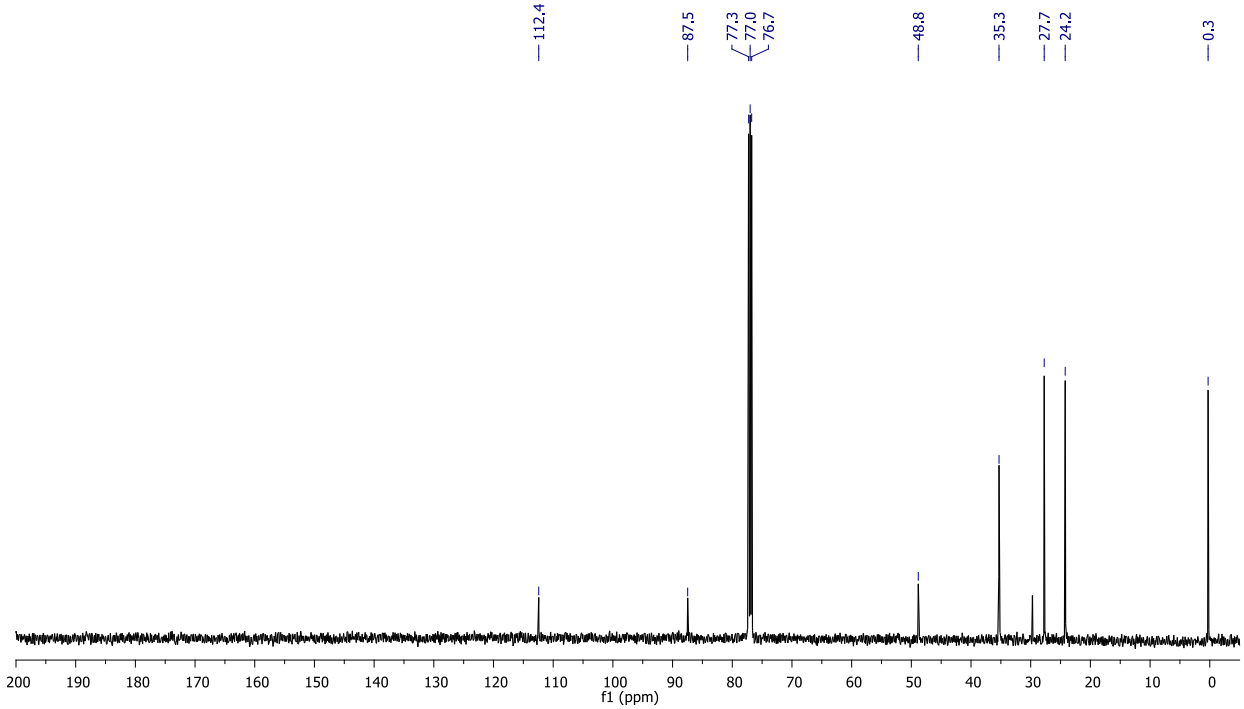
Appendix II

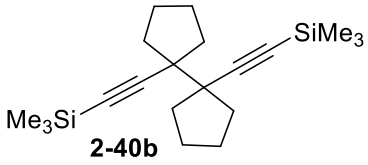
Selected NMR Spectra for Chapter 2


SiMe3
Me3Si

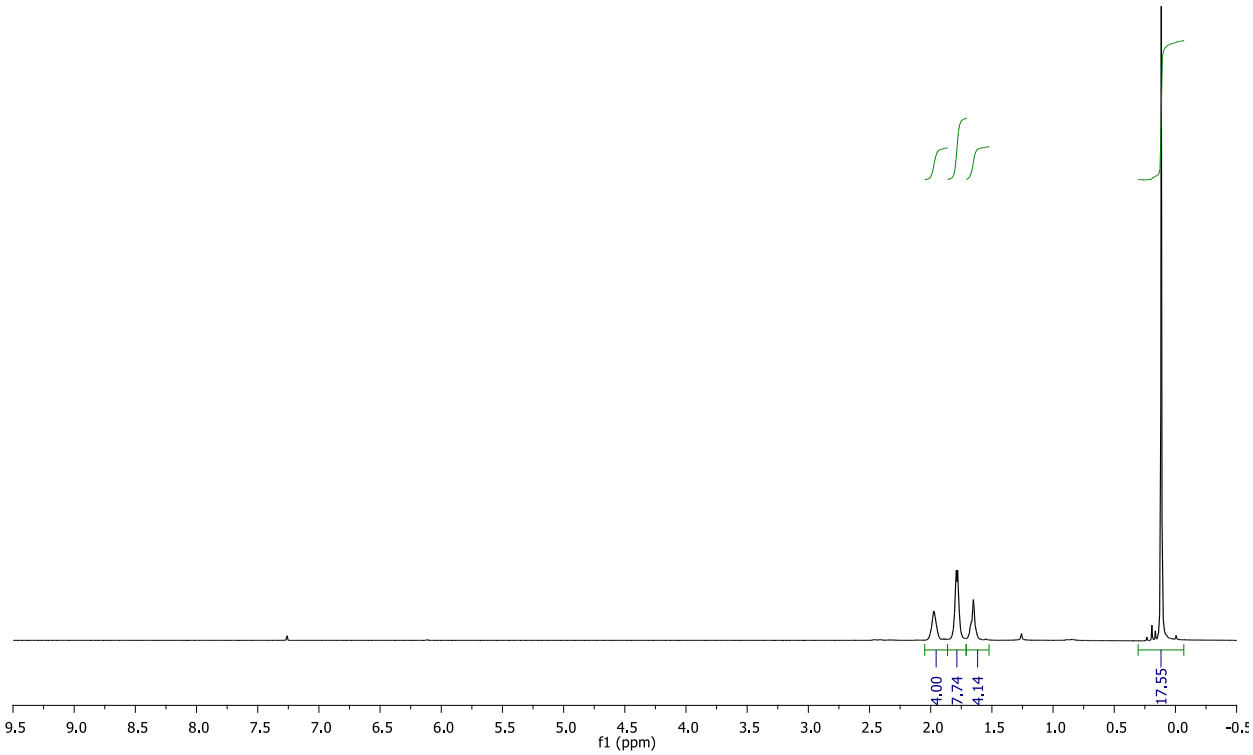
2-40a

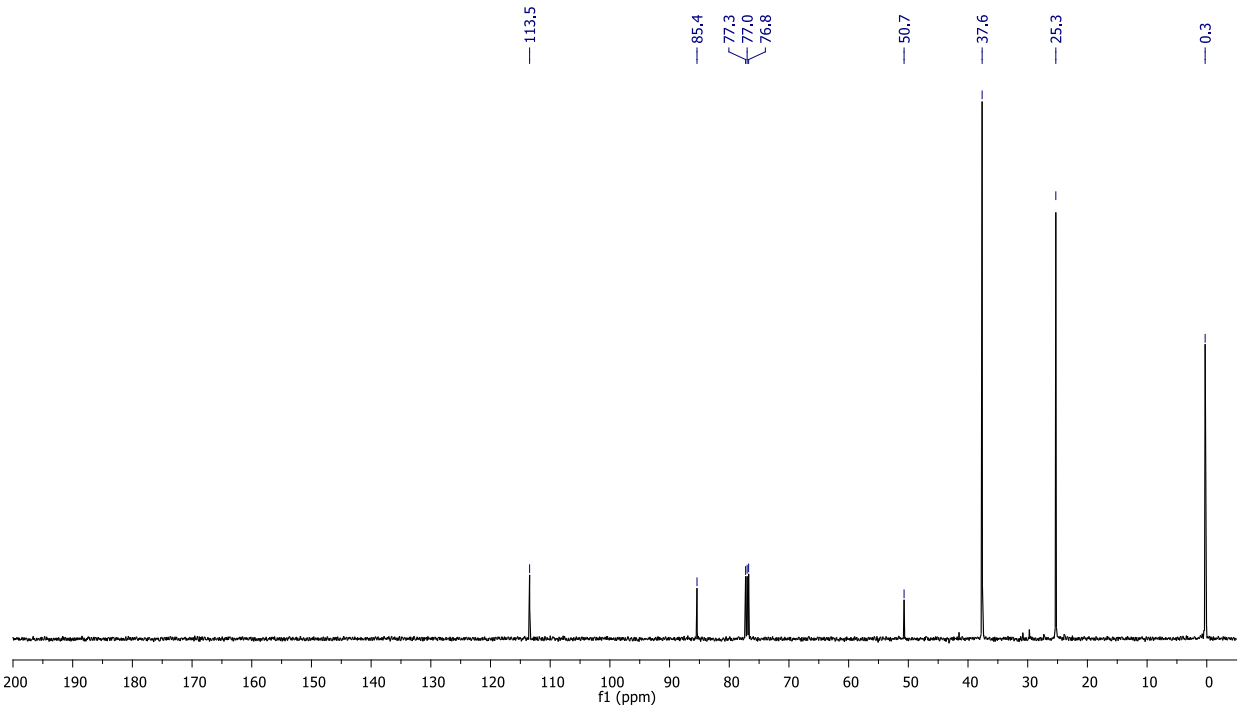

4.00
16.39
4.24
17.68
f1 (ppm)

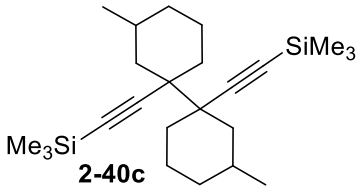

112.4
87.5
77.3
77.0
76.7
48.8
35.3
27.7
24.2
0.3
f1 (ppm)


SiMe3
Me3Si

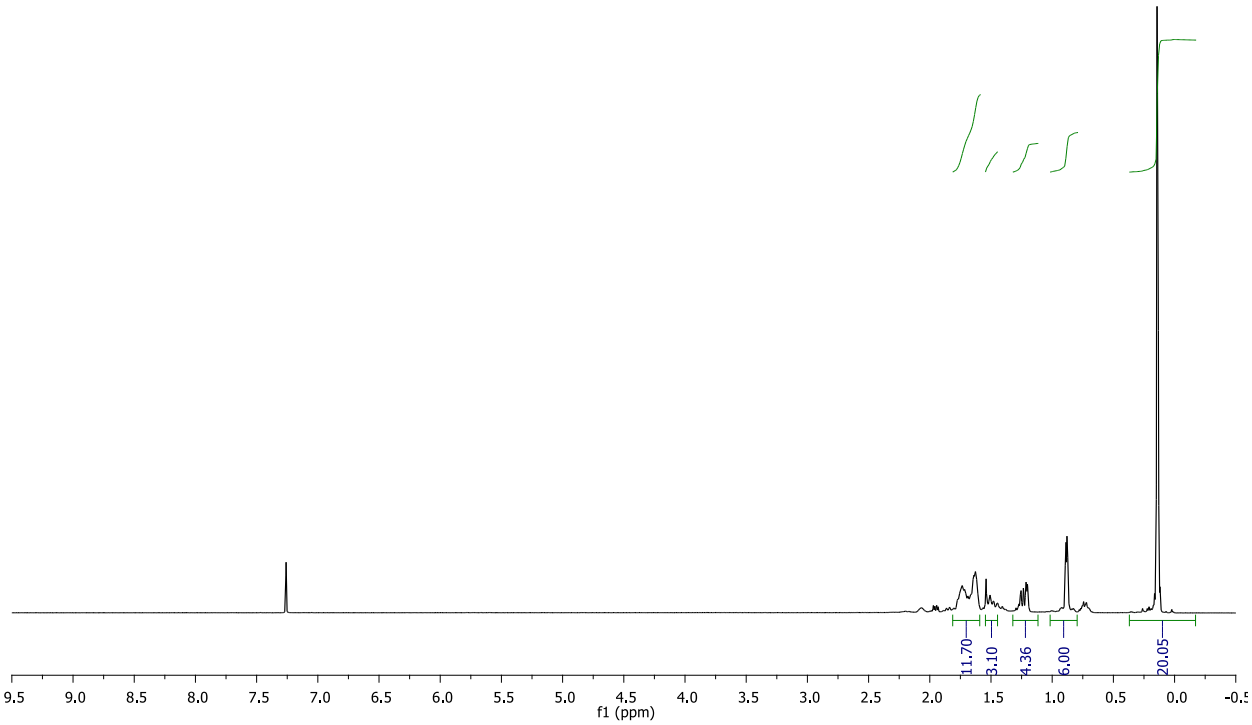
2-40b

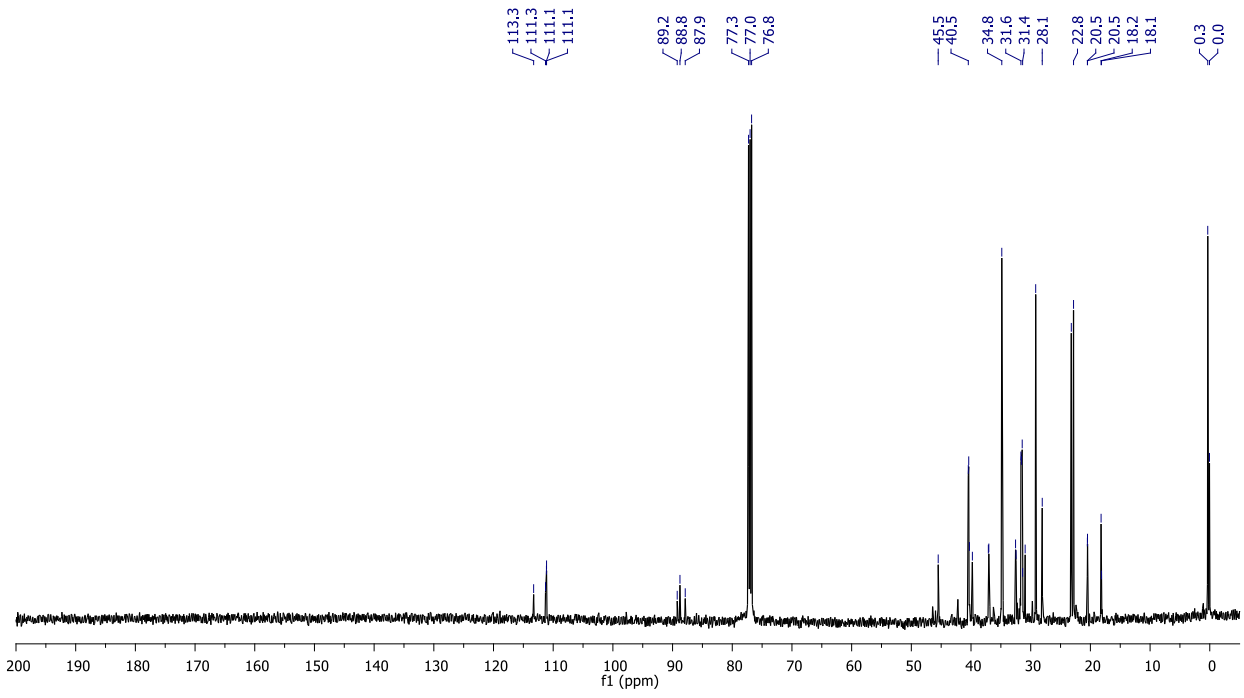

4.00
7.74
4.14
17.55
f1 (ppm)

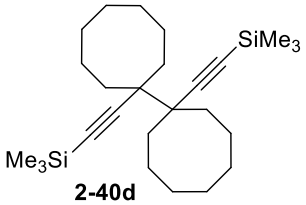

113.5
85.4
77.3
77.0
76.8
50.7
37.6
25.3
0.3
f1 (ppm)


SiMe3
Me3Si

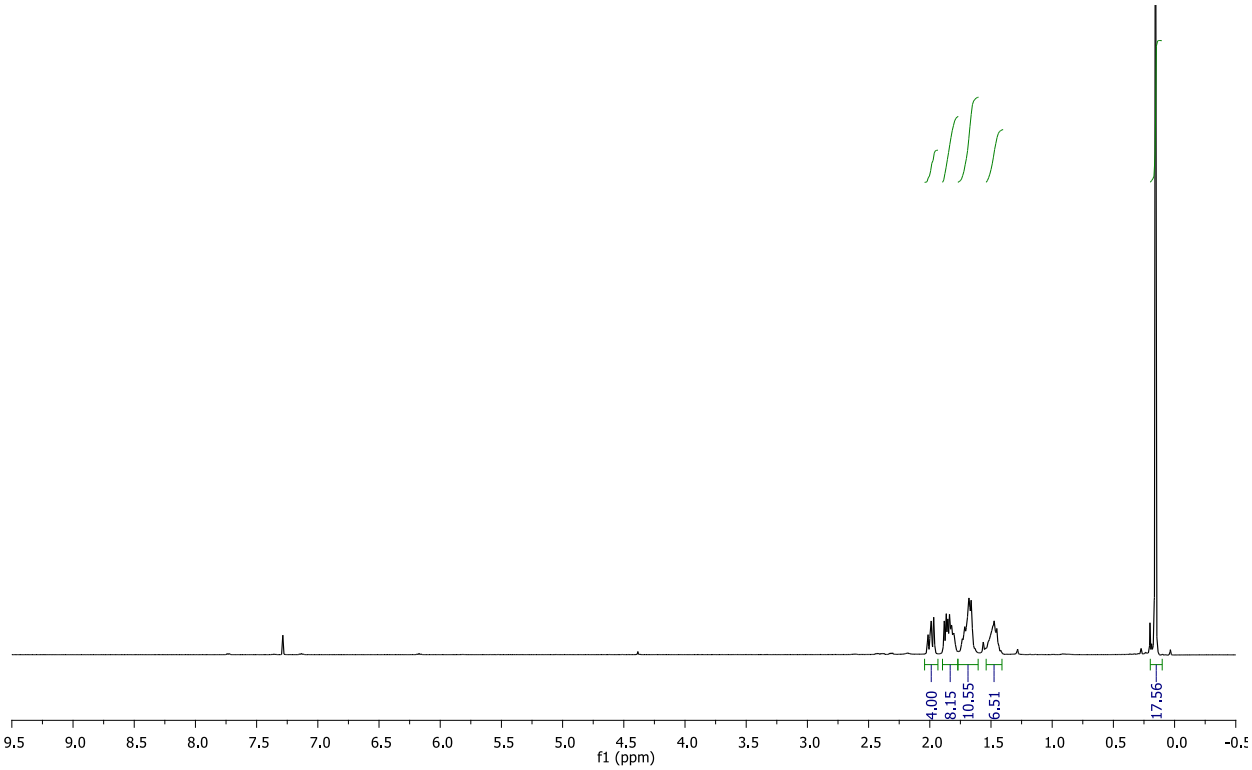
2-40c

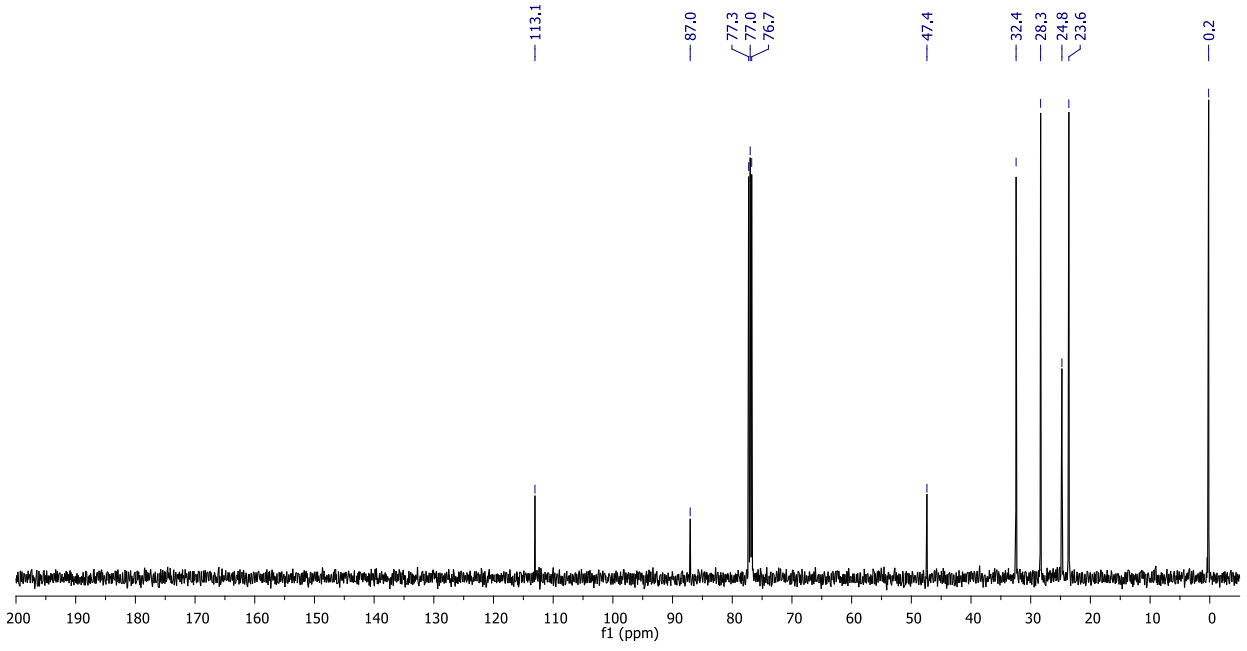

11.70
3.10
4.36
6.00
20.05
f1 (ppm)

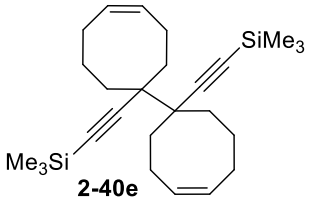

113.3
111.3
111.1
111.1
89.2
88.8
87.9
77.3
77.0
76.8
45.5
40.5
34.8
31.6
31.4
28.1
22.8
20.5
20.5
18.2
18.1
0.3
0.0
f1 (ppm)


SiMe3
Me3Si

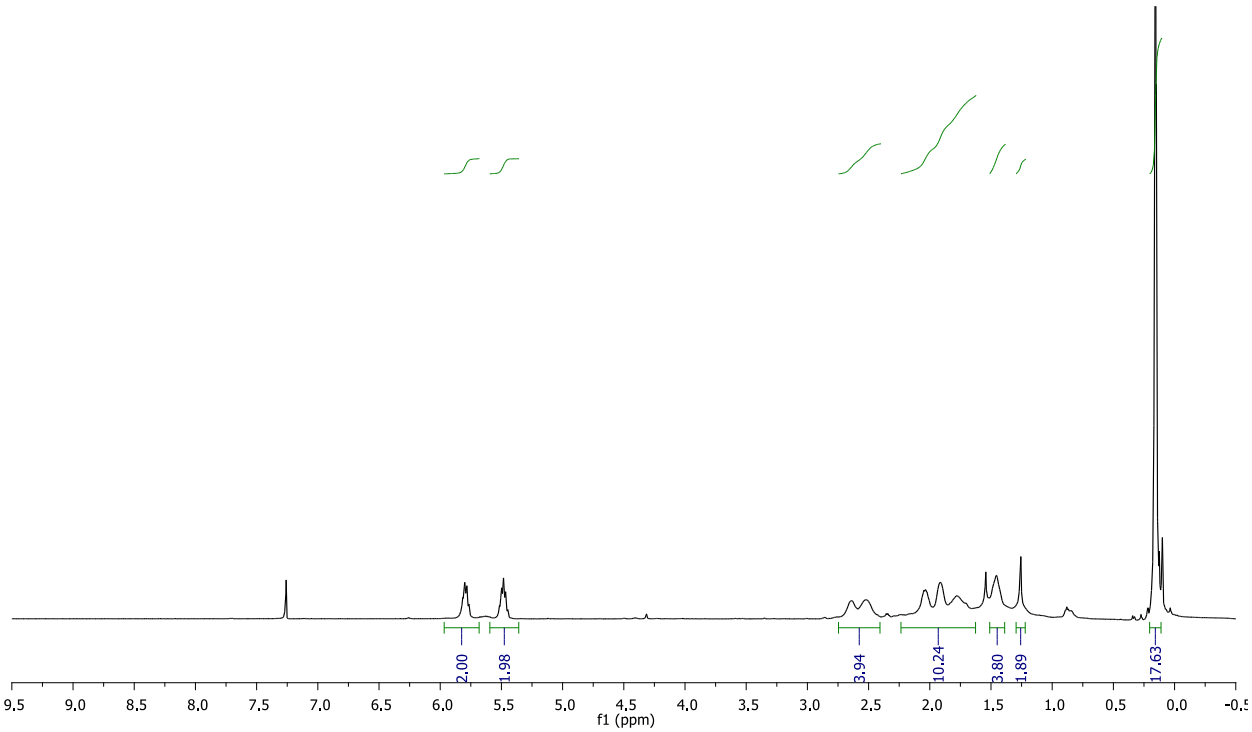
2-40d

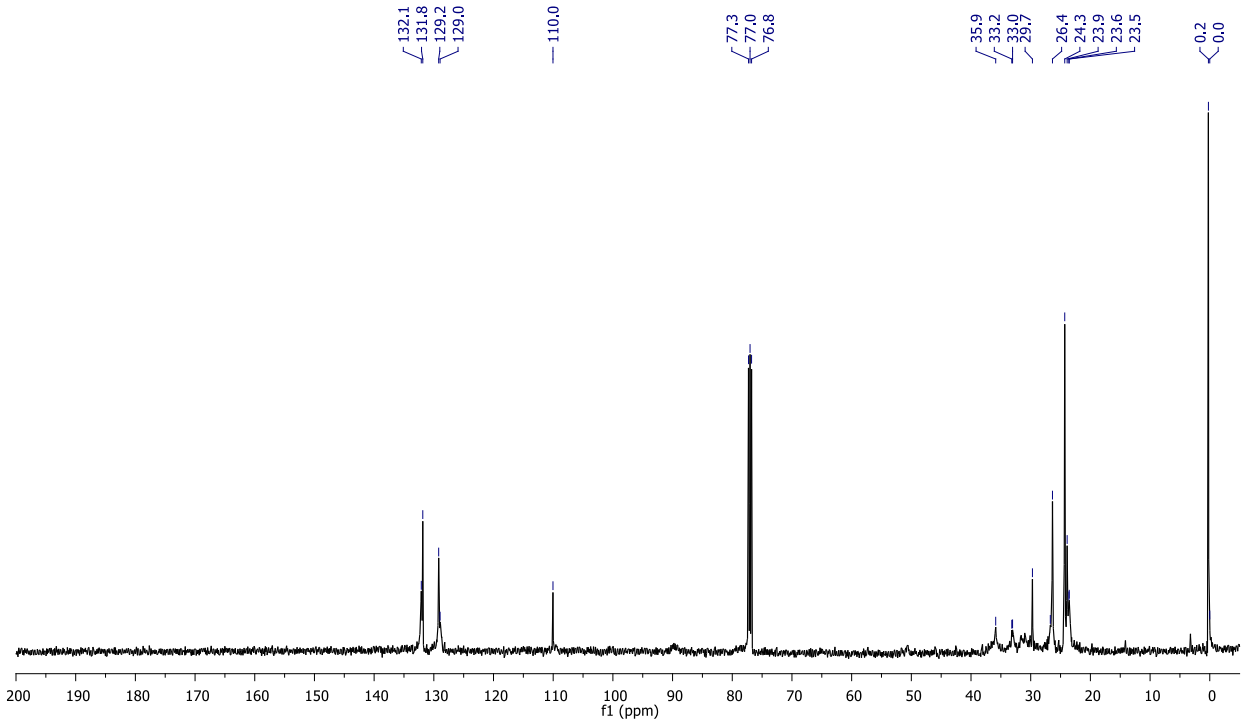

4.00
8.15
10.55
6.51
17.56
f1 (ppm)

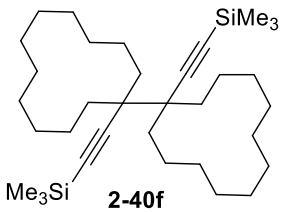

113.1
87.0
77.3
77.0
76.7
47.4
32.4
28.3
24.8
23.6
0.2
f1 (ppm)


SiMe3
Me3Si

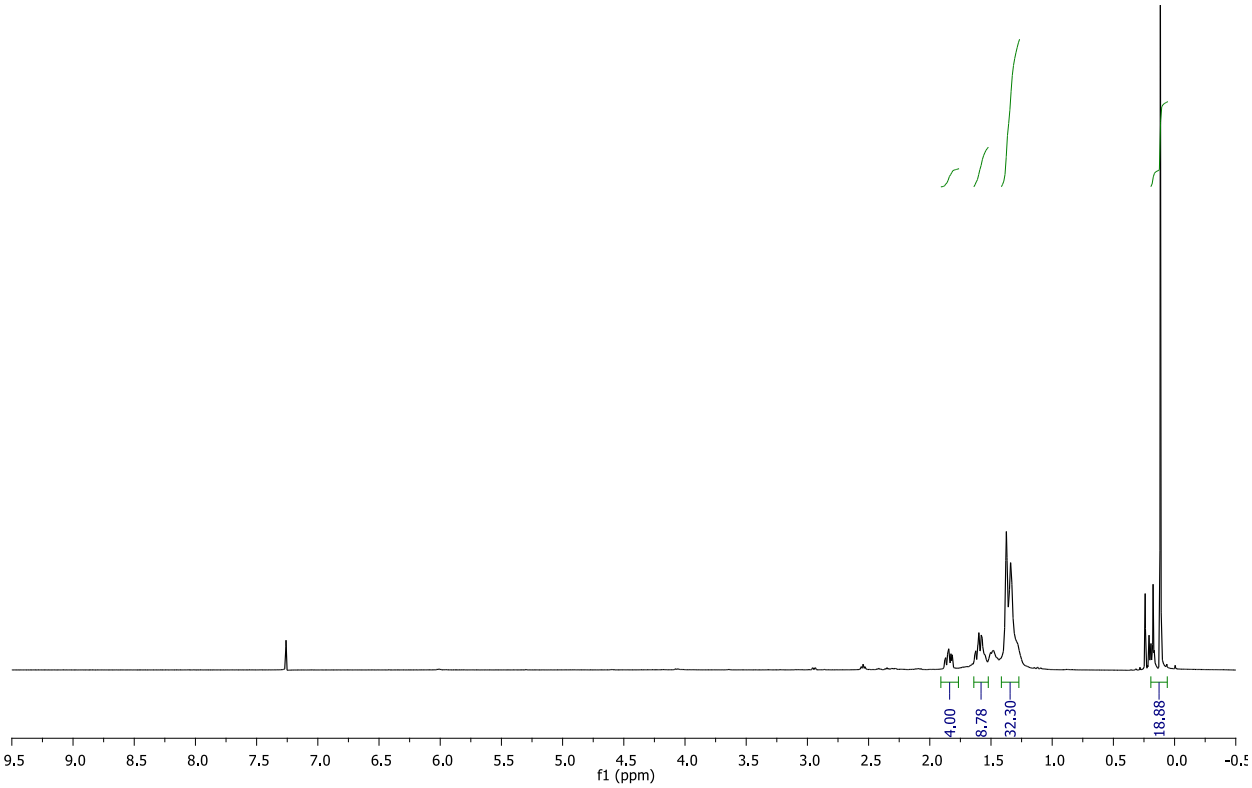
2-40e

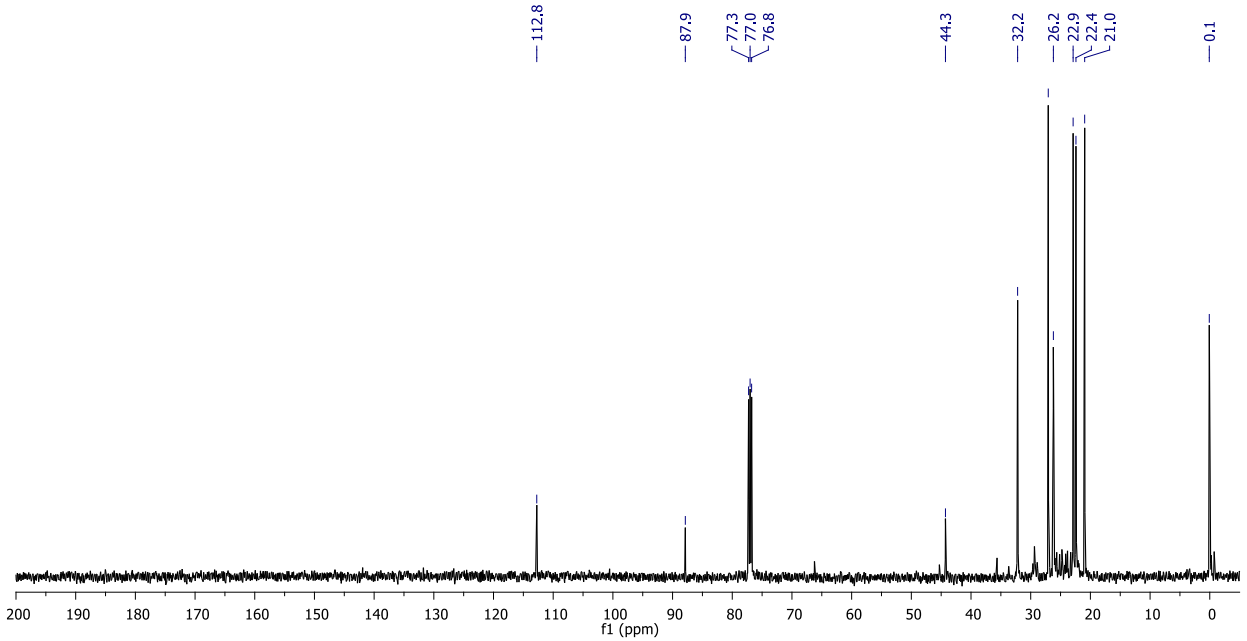

2.00
1.98
3.94
10.24
3.80
1.89
17.63
f1 (ppm)

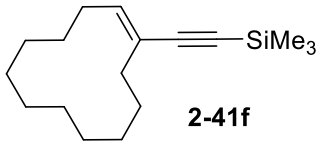

132.1
131.8
129.2
129.0
110.0
77.3
77.0
76.8
35.9
33.2
33.0
29.7
26.4
24.3
23.9
23.6
23.5
0.2
0.0
f1 (ppm)


SiMe3
Me3Si

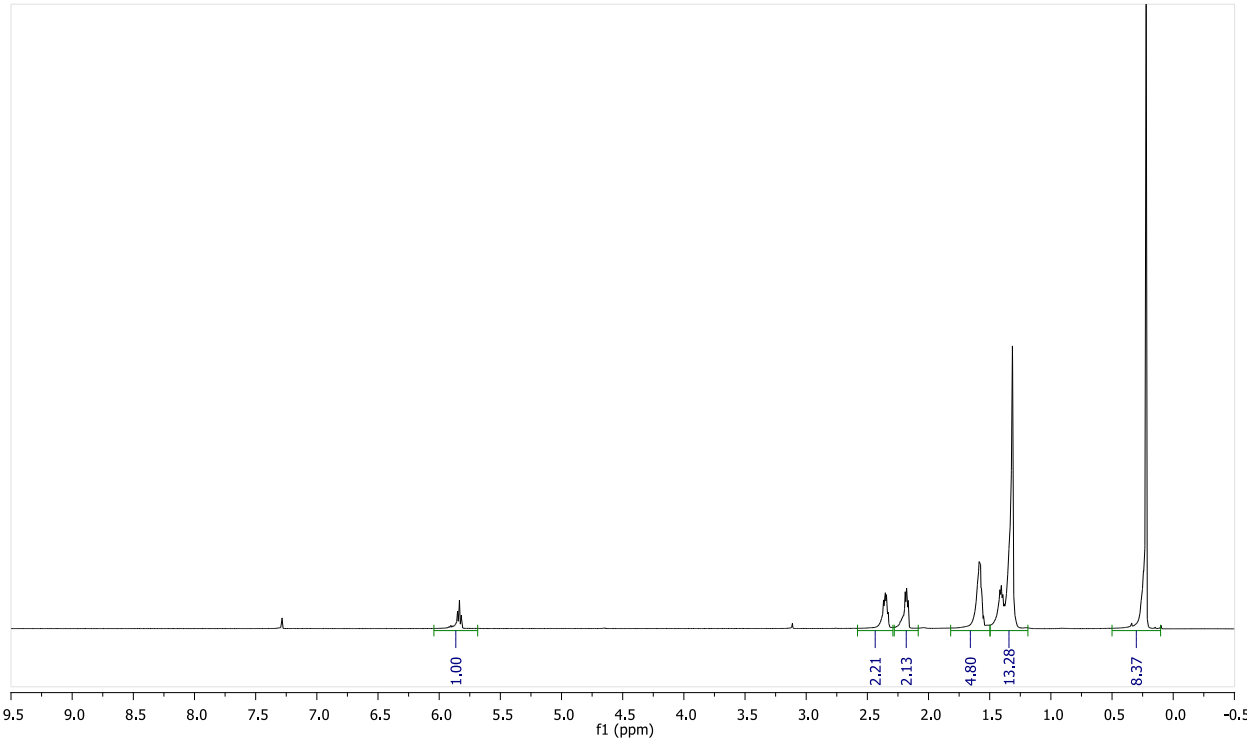
2-40f

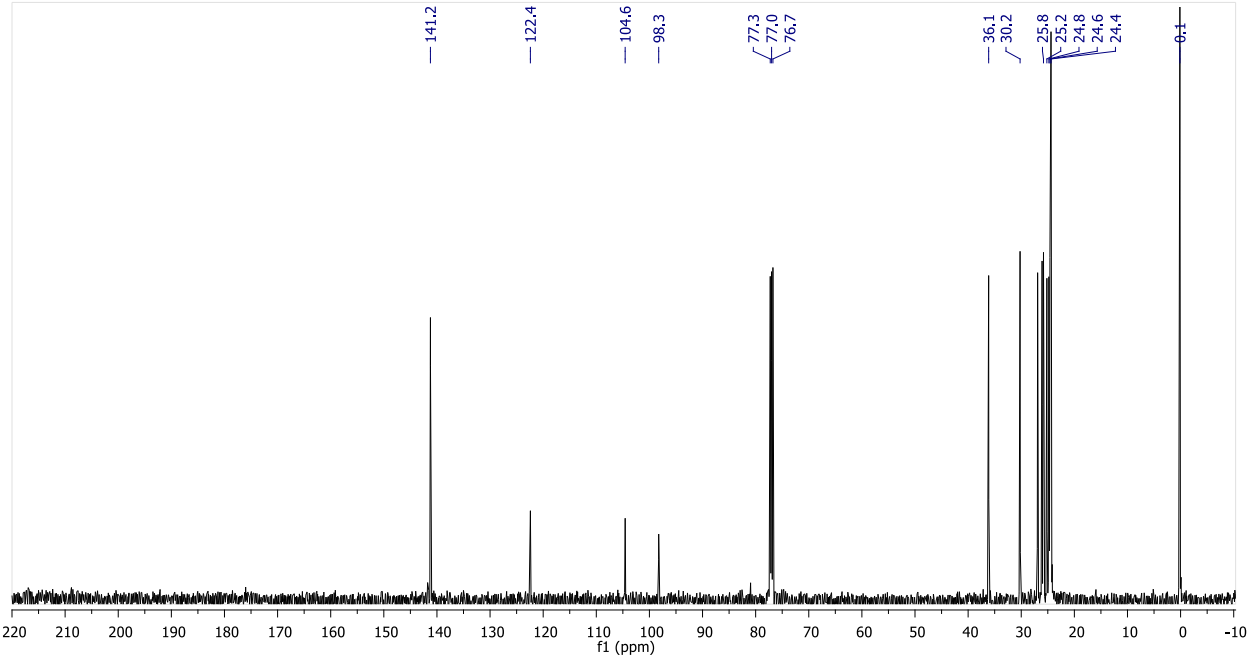

4.00
8.78
32.30
18.88
f1 (ppm)

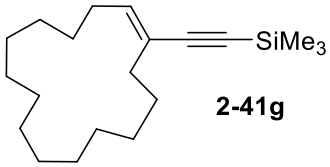

112.8
87.9
77.3
77.0
76.8
44.3
32.2
26.2
22.9
22.4
21.0
0.1
f1 (ppm)


SiMe3

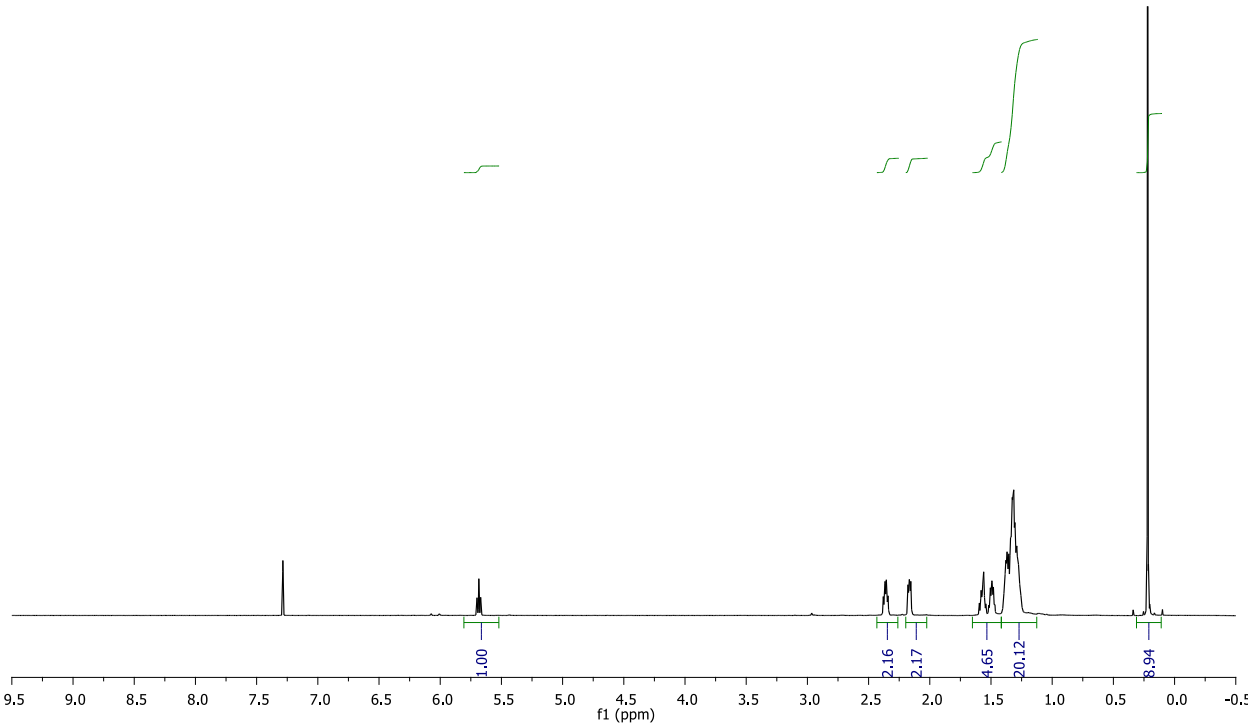
2-41f

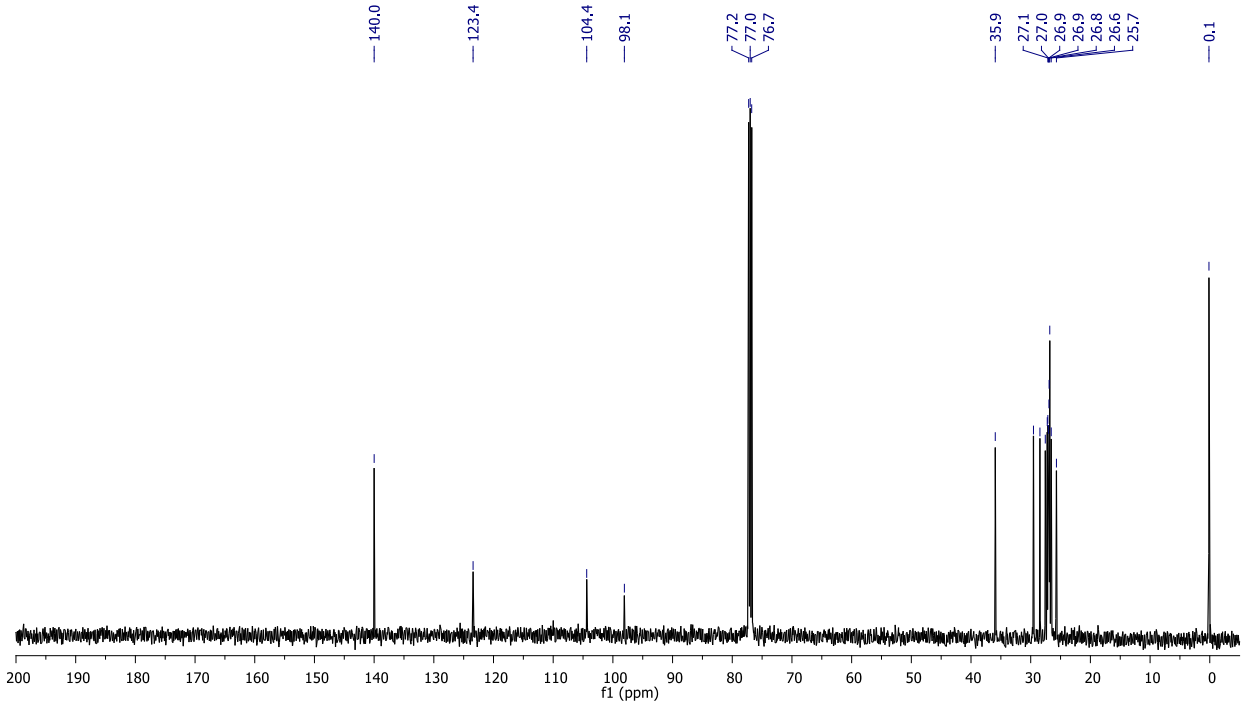

1.00
2.21
2.13
4.80
13.28
8.37
f1 (ppm)

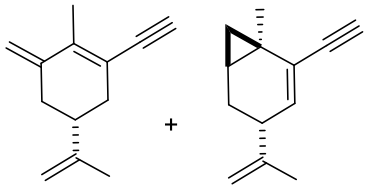

141.2
122.4
104.6
98.3
77.3
77.0
76.7
36.1
30.2
25.8
25.2
24.8
24.6
24.4
0.1
f1 (ppm)


SiMe3

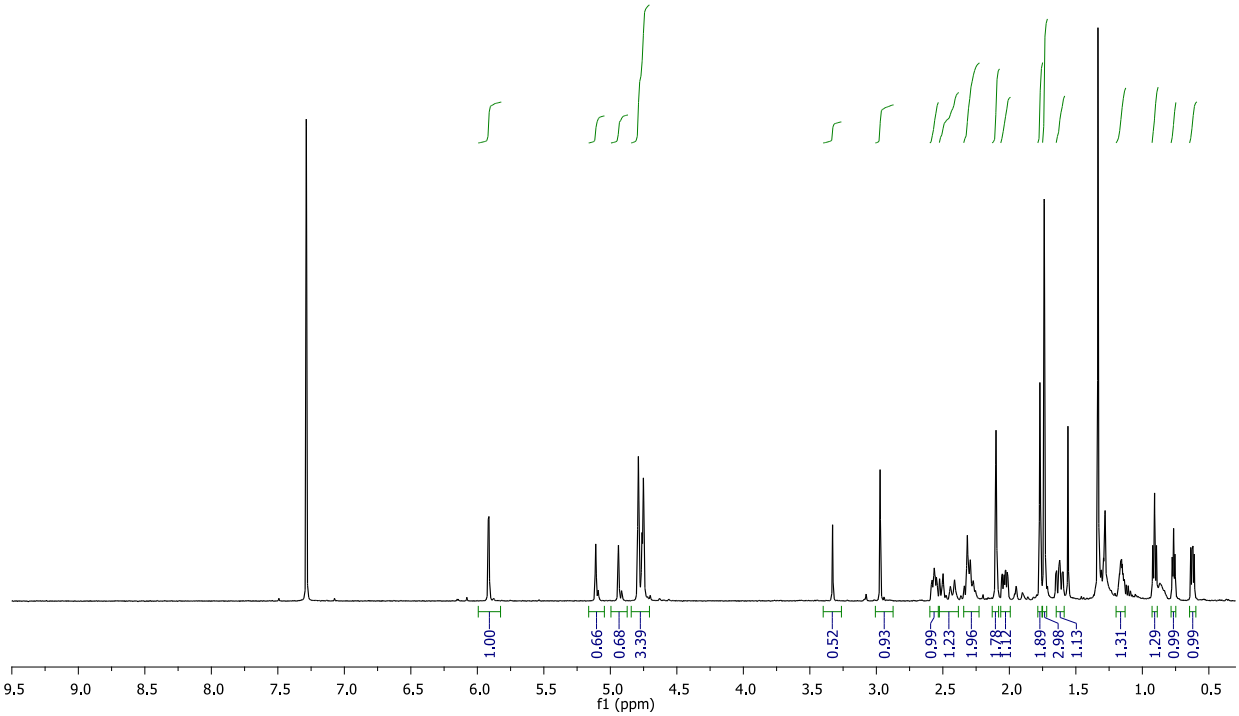
2-41g

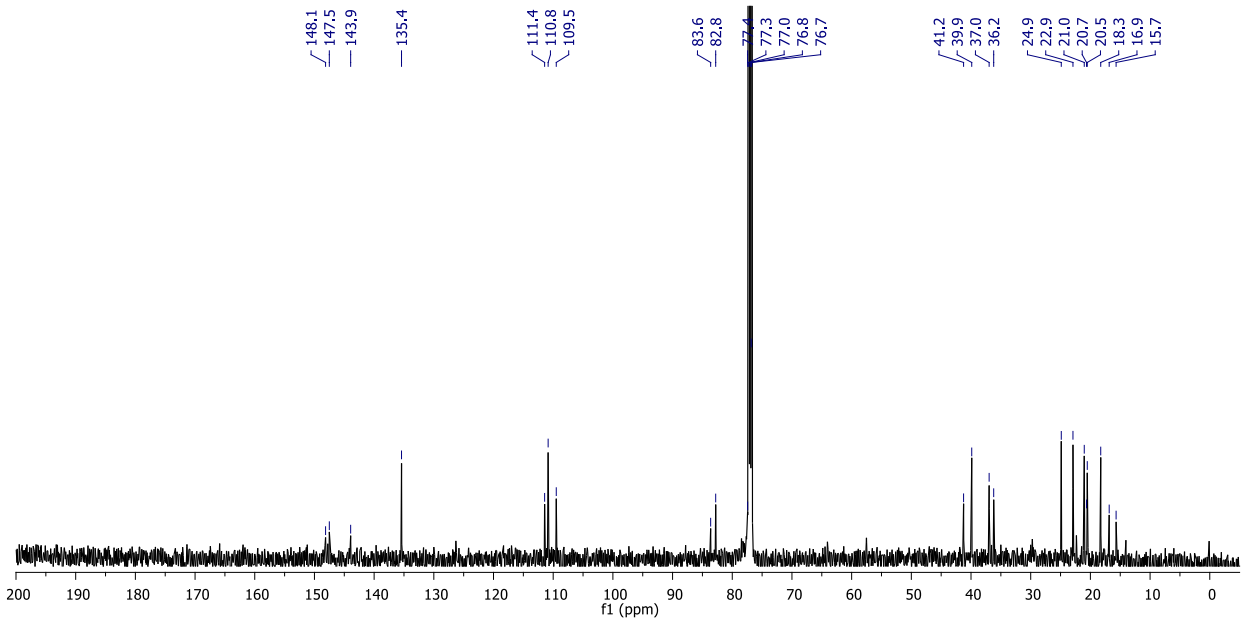

1.00
2.16
2.17
4.65
20.12
8.94
f1 (ppm)

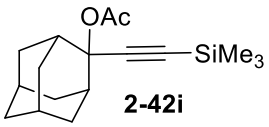

140.0
123.4
104.4
98.1
77.2
77.0
76.7
35.9
27.1
27.0
26.9
26.9
26.8
26.6
25.7
0.1
f1 (ppm)



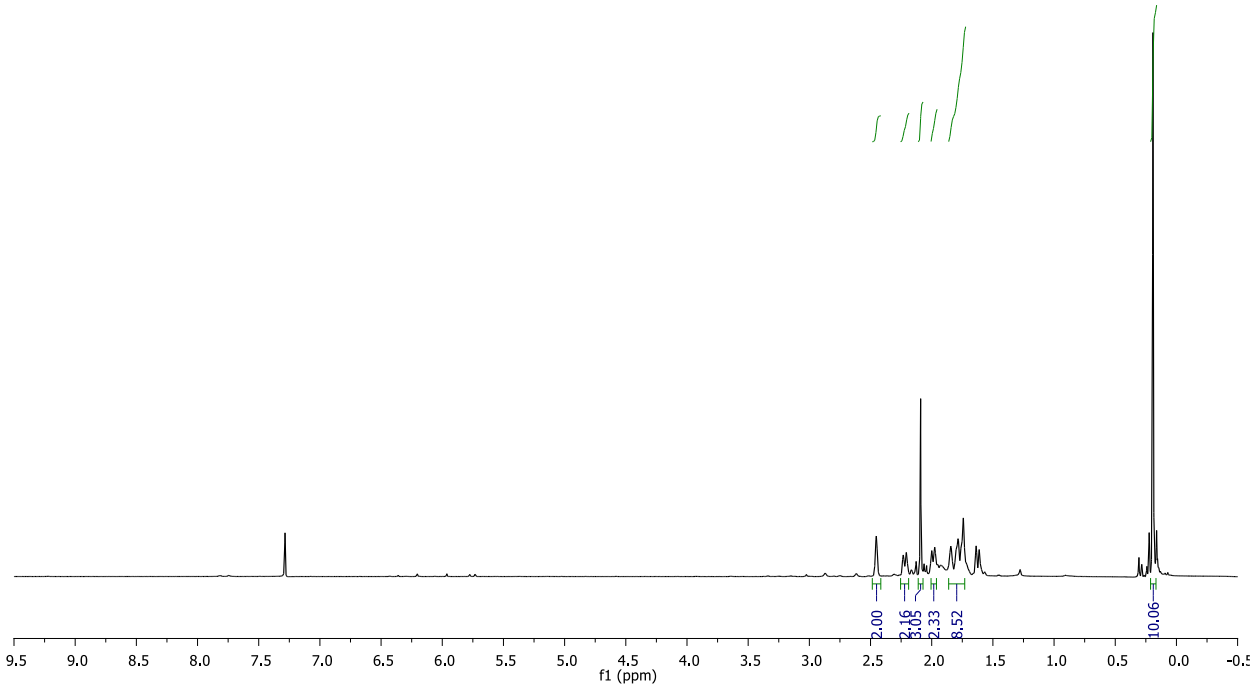
2-41h 1:2 **2-41h'**

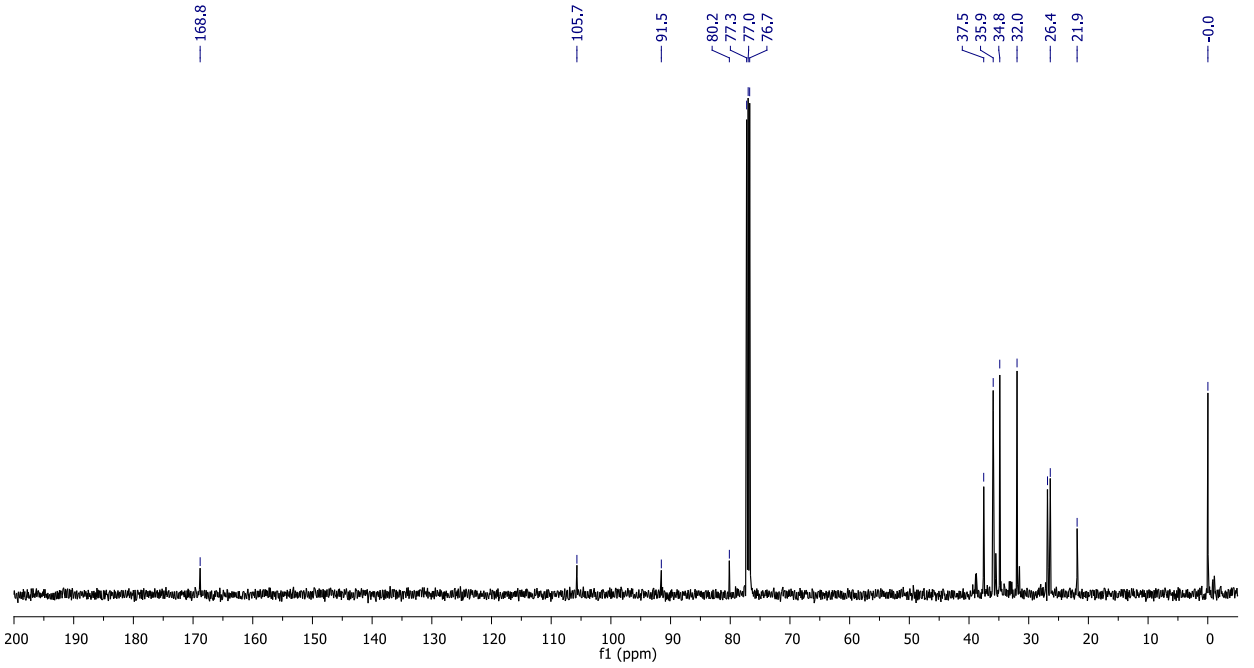

1.00
0.66
0.68
3.39
0.52
0.93
0.99
1.23
1.96
1.78
1.12
1.89
2.98
1.13
1.31
1.29
0.99
0.99
f1 (ppm)

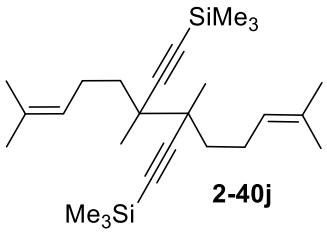

148.1
147.5
143.9
135.4
111.4
110.8
109.5
83.6
82.8
77.4
77.3
77.0
76.8
76.7
41.2
39.9
37.0
36.2
24.9
22.9
21.0
20.7
20.5
18.3
16.9
15.7
f1 (ppm)


OAc
SiMe3

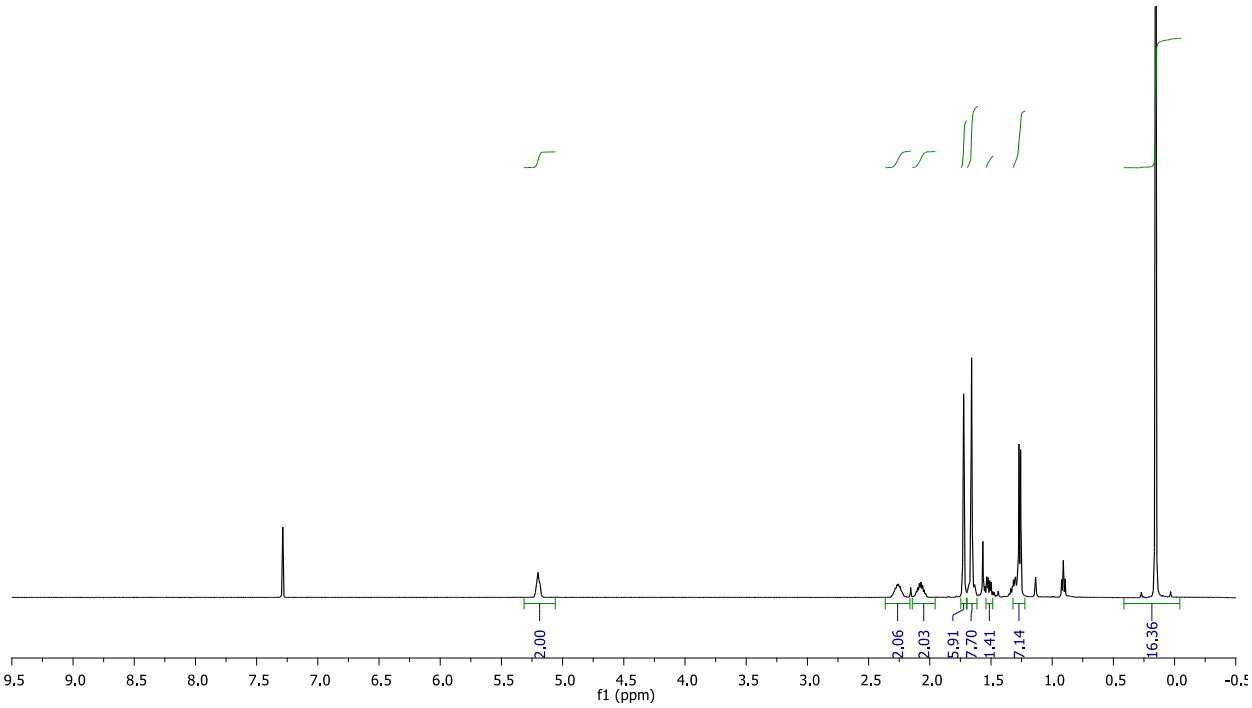
2-42i

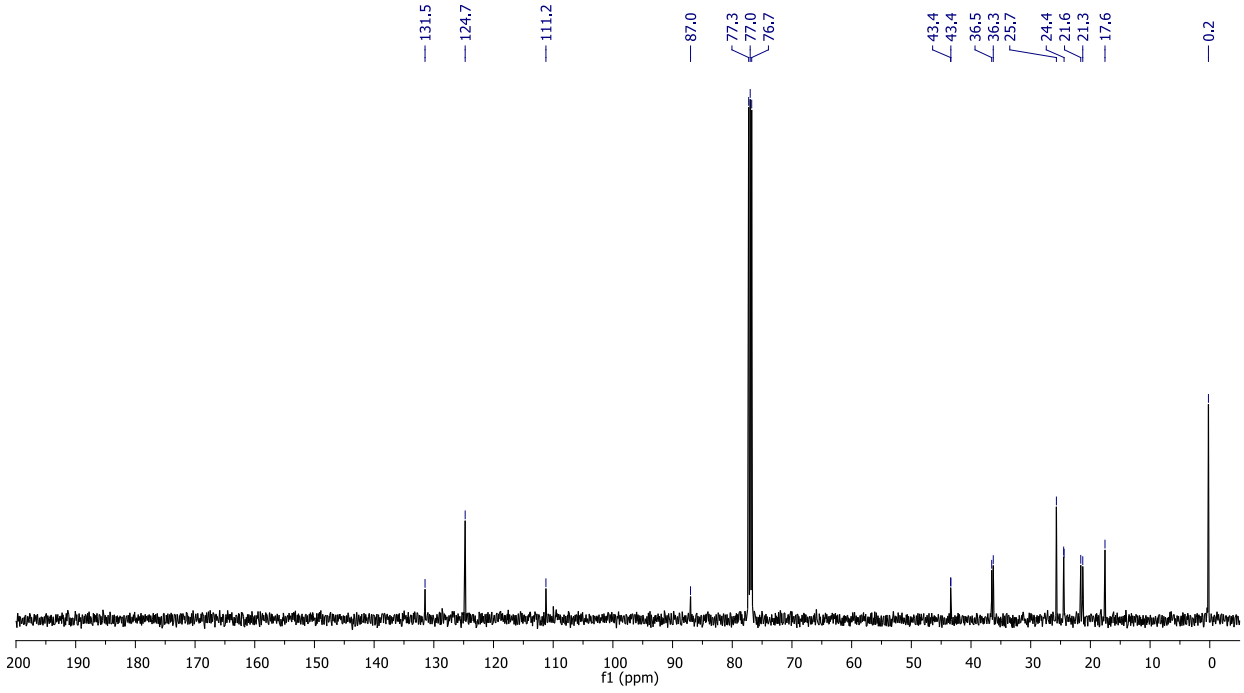

2.00
2.16
3.05
2.33
8.52
10.06
f1 (ppm)

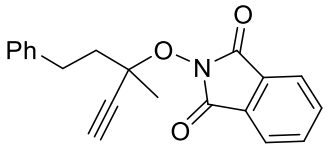

168.8
105.7
91.5
80.2
77.3
77.0
76.7
37.5
35.9
34.8
32.0
26.4
21.9
-0.0
f1 (ppm)


SiMe3
Me3Si

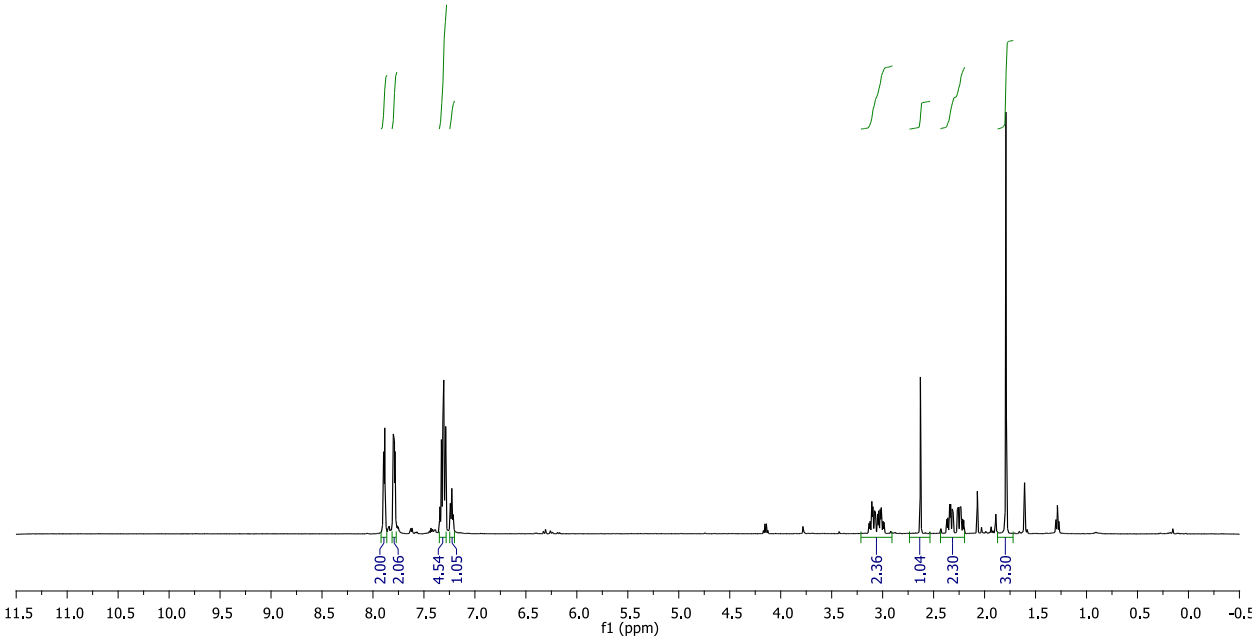
2-40j

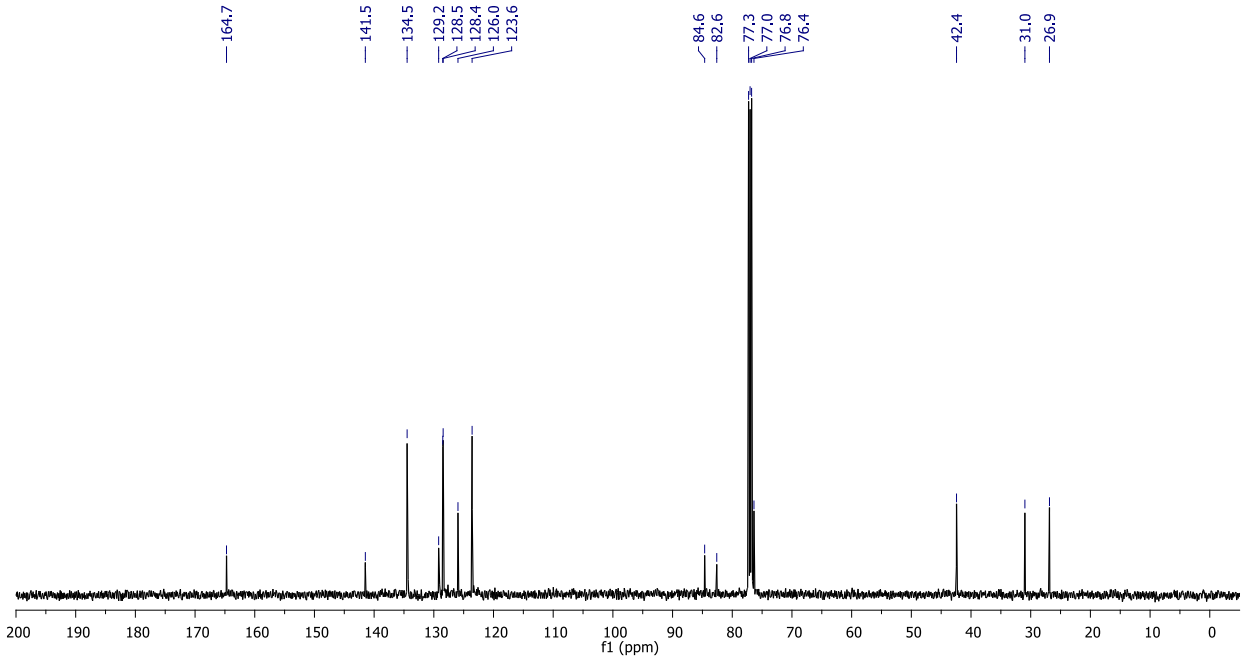

2.00
2.06
2.03
5.91
7.70
1.41
7.14
16.36
f1 (ppm)

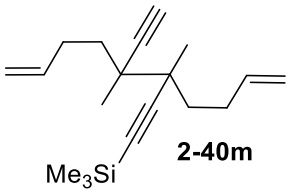

131.5
124.7
111.2
87.0
77.3
77.0
76.7
43.4
43.4
36.5
36.3
25.7
24.4
21.6
21.3
17.6
0.2
f1 (ppm)


Ph
O
N
O
O

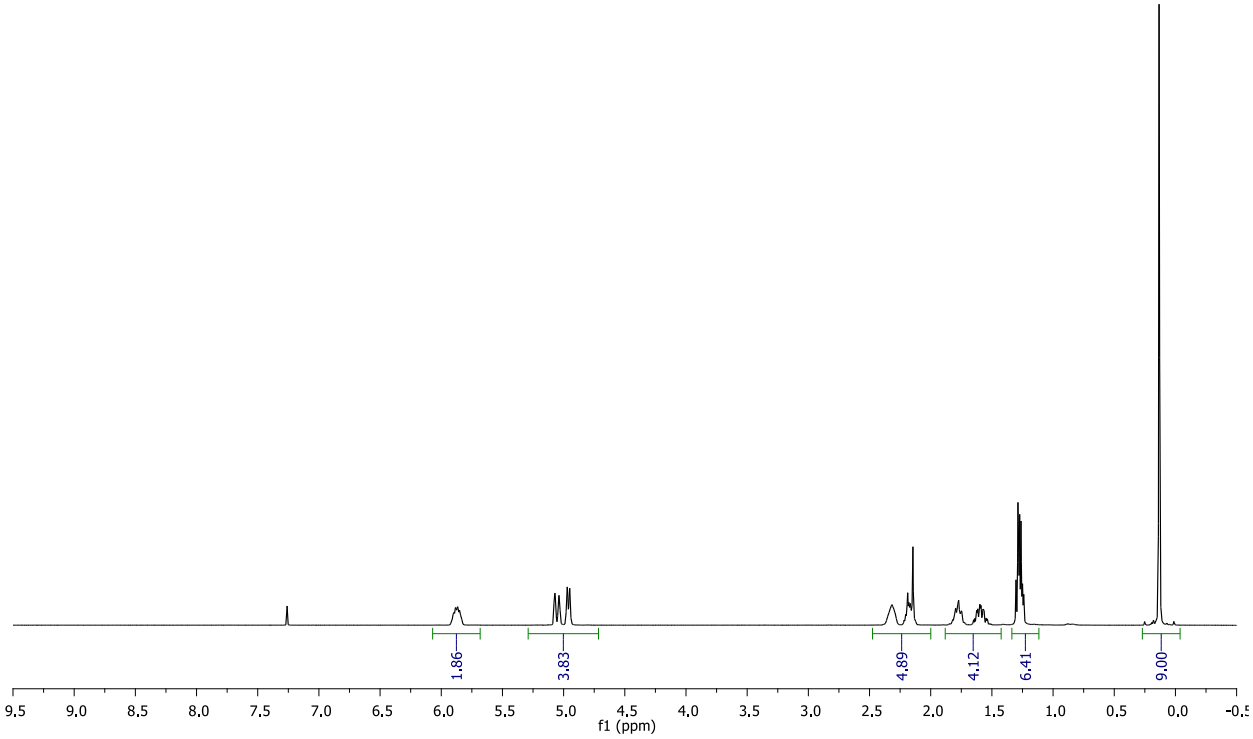
2-43l

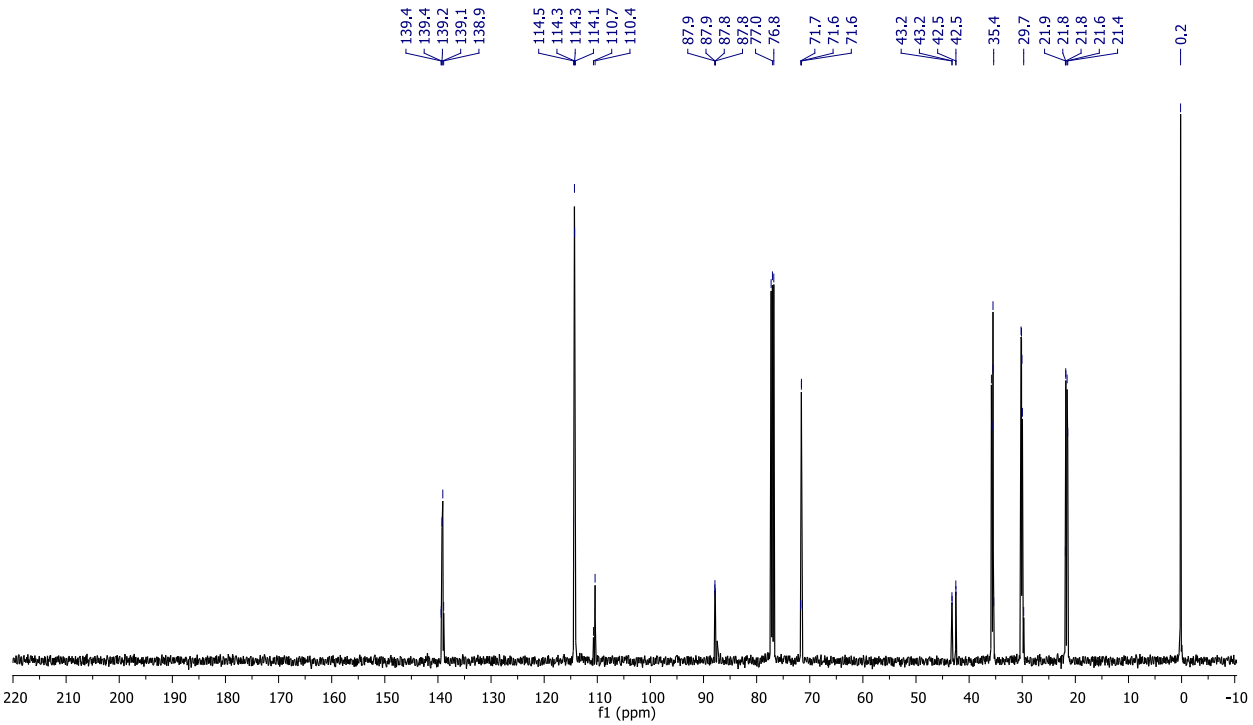

2.00
2.06
4.54
1.05
2.36
1.04
2.30
3.30
f1 (ppm)

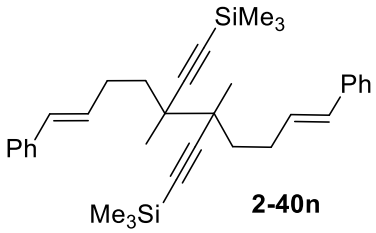

164.7
141.5
134.5
129.2
128.5
128.4
126.0
123.6
84.6
82.6
77.3
77.0
76.8
76.4
42.4
31.0
26.9
f1 (ppm)


Me3Si

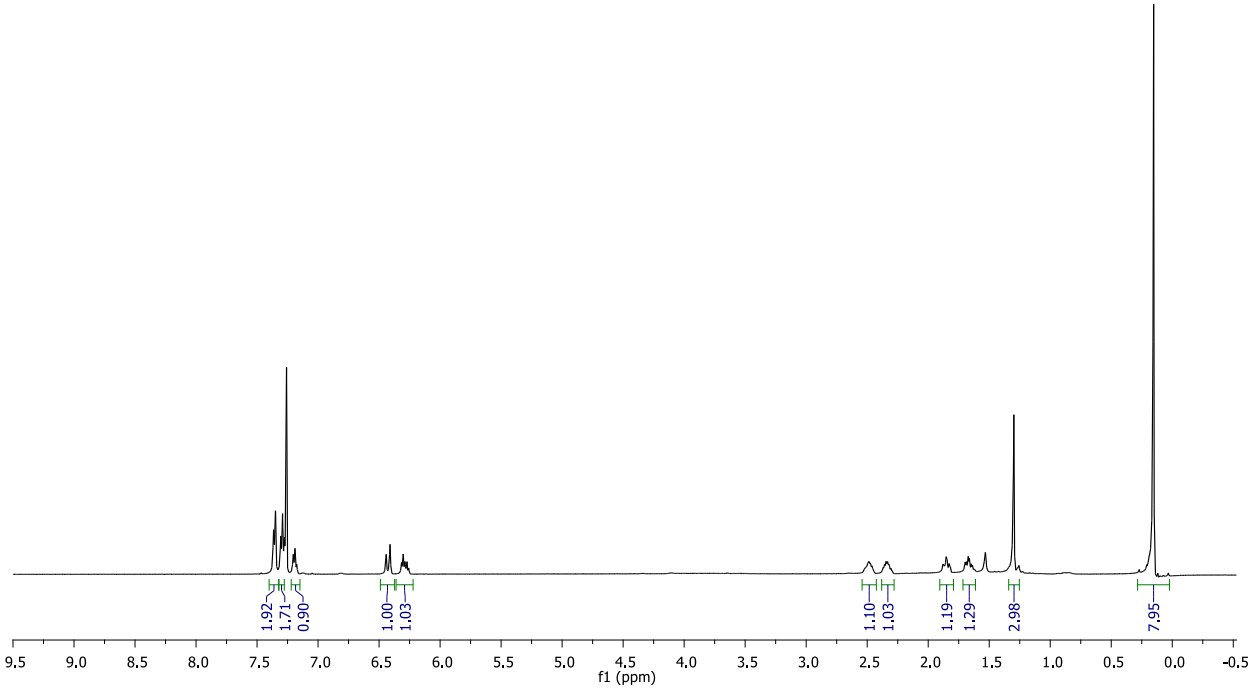
2-40m

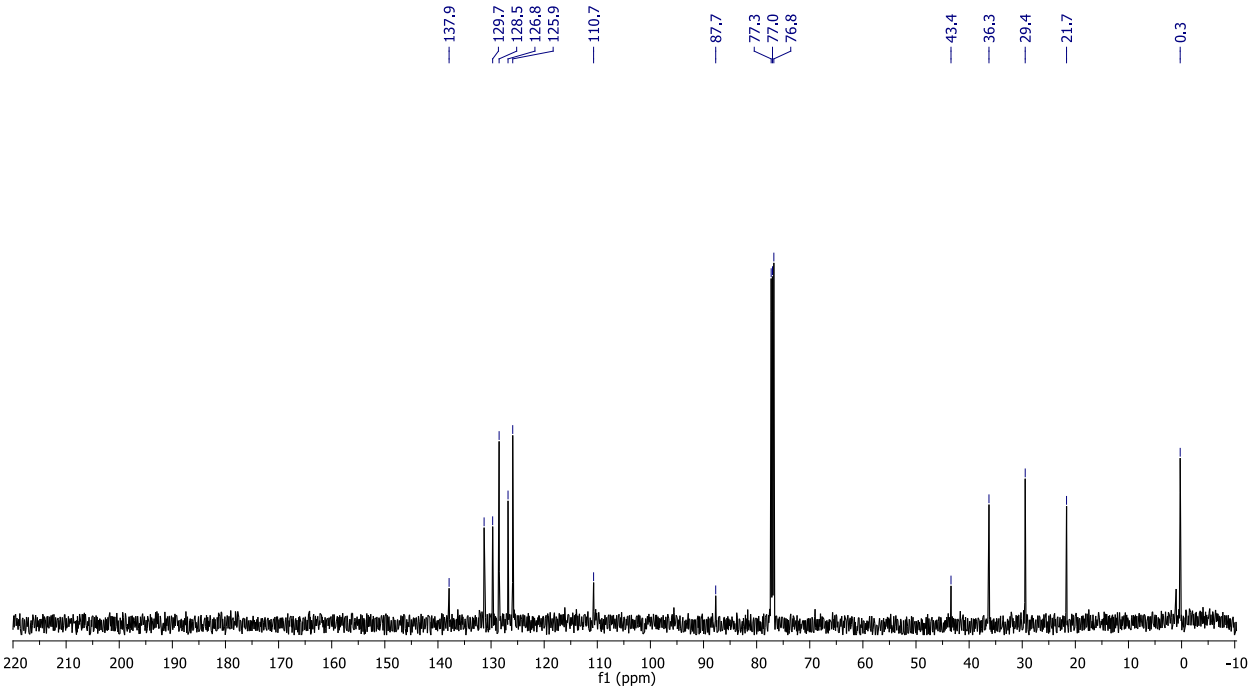

1.86
3.83
4.89
4.12
6.41
9.00
f1 (ppm)

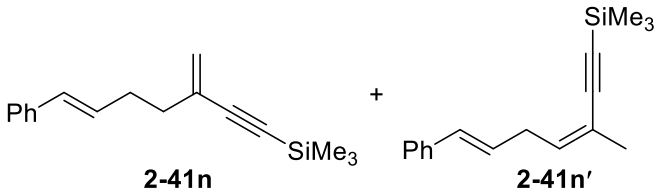

139.4
139.4
139.2
139.1
138.9
114.5
114.3
114.3
114.1
110.7
110.4
87.9
87.9
87.8
87.8
77.0
76.8
71.7
71.6
71.6
43.2
43.2
42.5
42.5
35.4
29.7
21.9
21.8
21.8
21.6
21.4
0.2
f1 (ppm)


SiMe3
Ph
Ph
Me3Si

2-40n

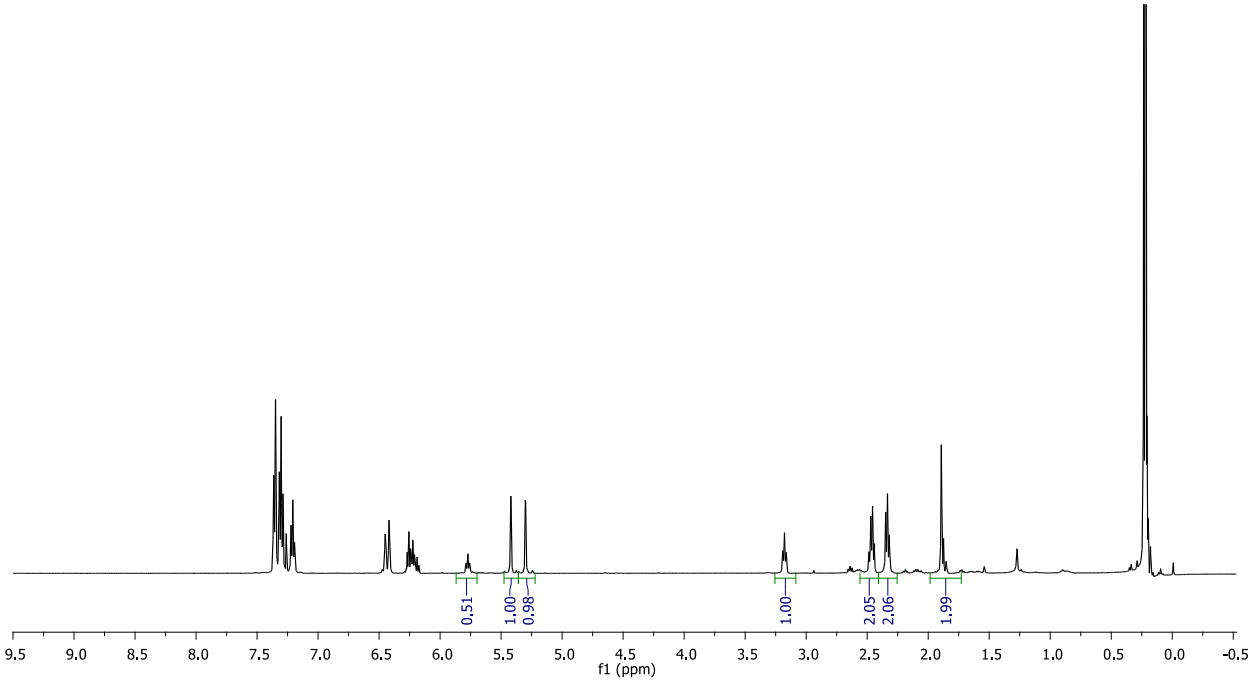

1.92
1.71
0.90
1.00
1.03
1.10
1.03
1.19
1.29
2.98
7.95
f1 (ppm)

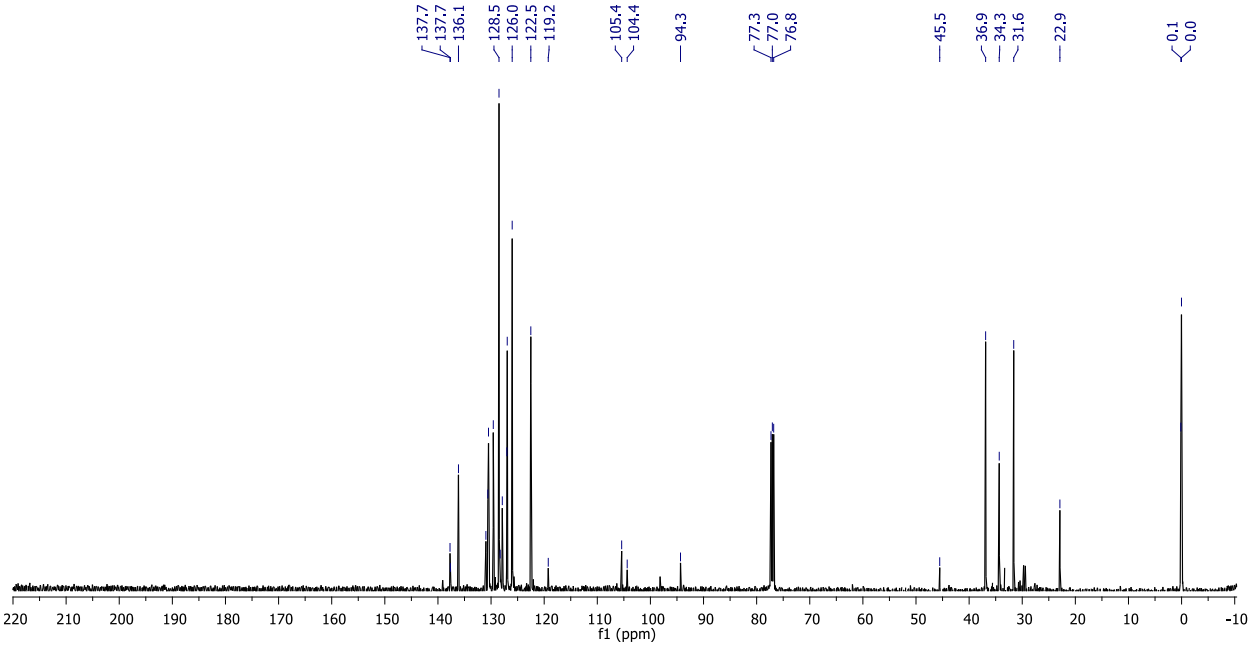

137.9
129.7
128.5
126.8
125.9
110.7
87.7
77.3
77.0
76.8
43.4
36.3
29.4
21.7
0.3
f1 (ppm)

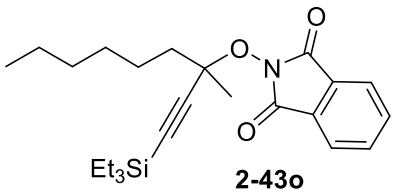

Ph
SiMe3
+
SiMe3
Ph

2-41n + **2-41n′**

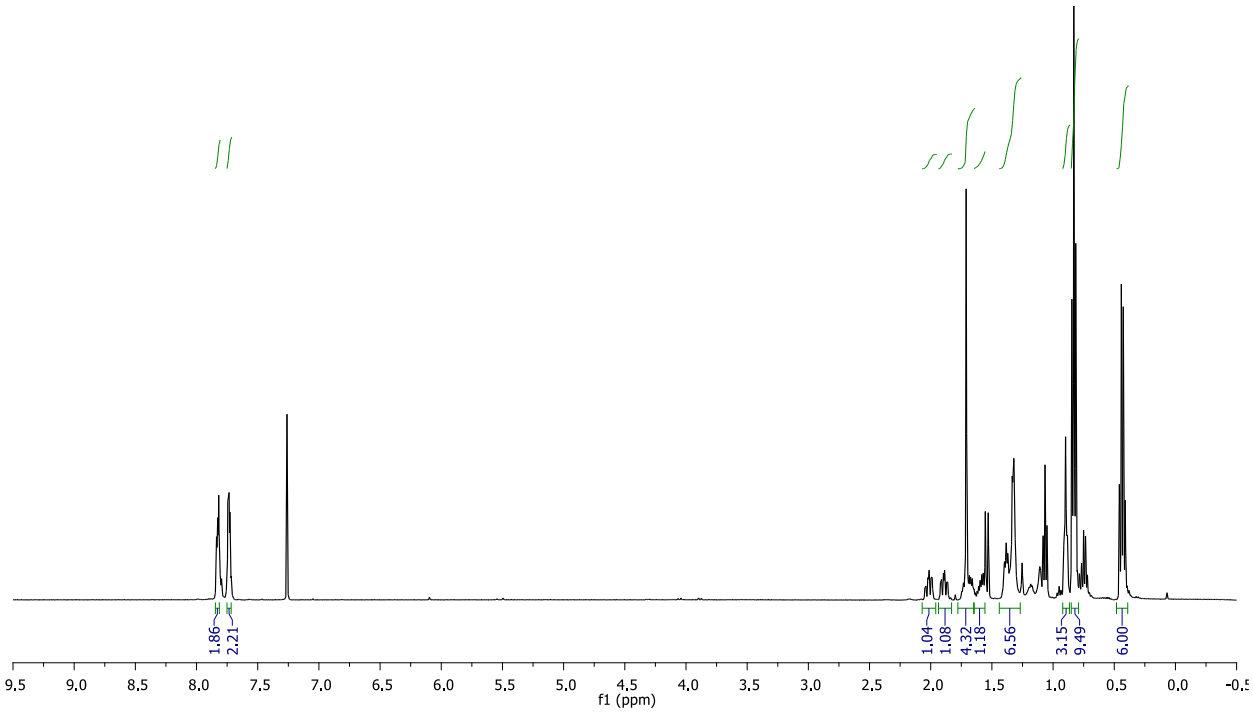
2 : 1

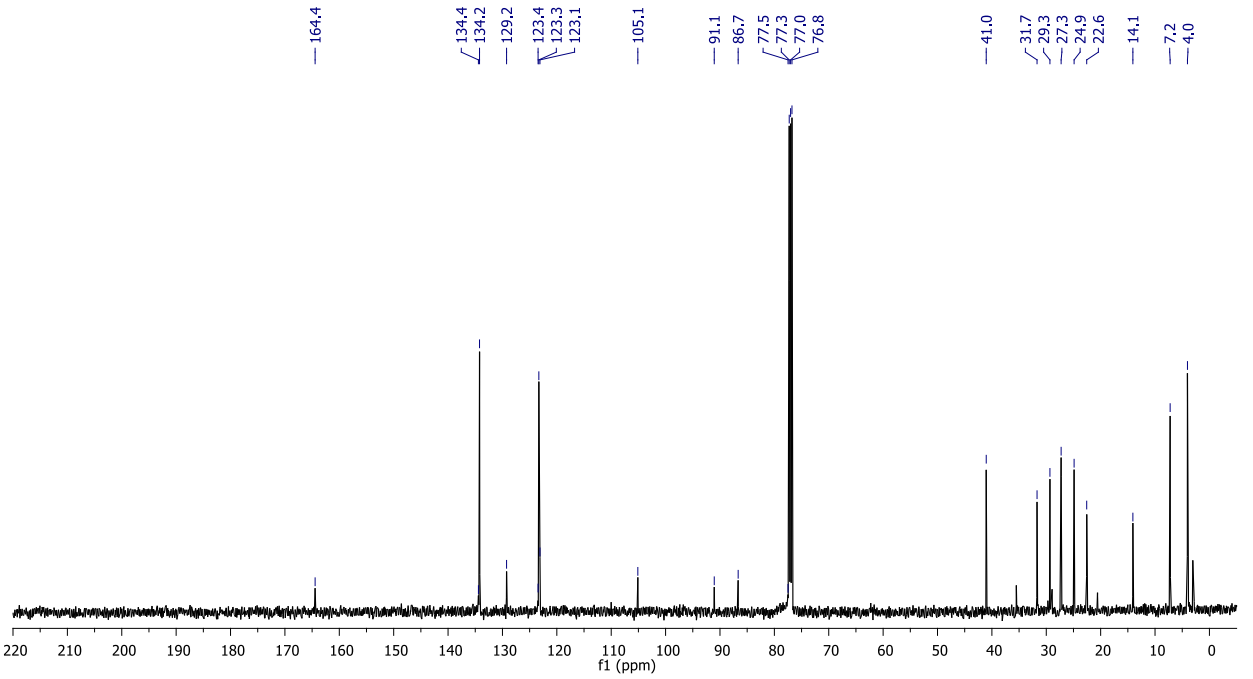

0.51
1.00
0.98
1.00
2.05
2.06
1.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

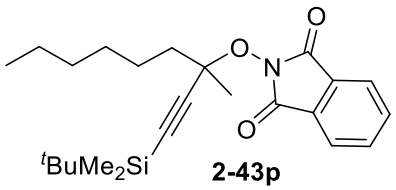

137.7
137.7
136.1
128.5
126.0
122.5
119.2
105.4
104.4
94.3
77.3
77.0
76.8
45.5
36.9
34.3
31.6
22.9
0.1
0.0
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O
O
N
O
O
Et3Si

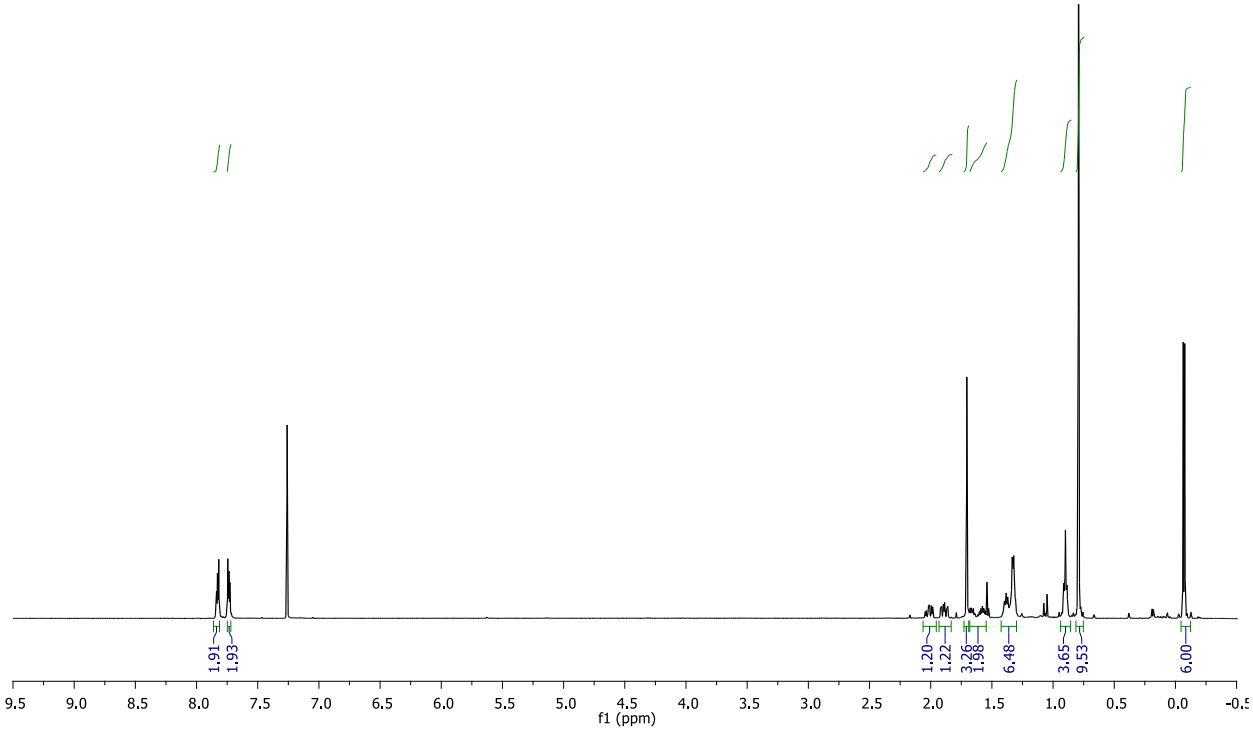
2-43o

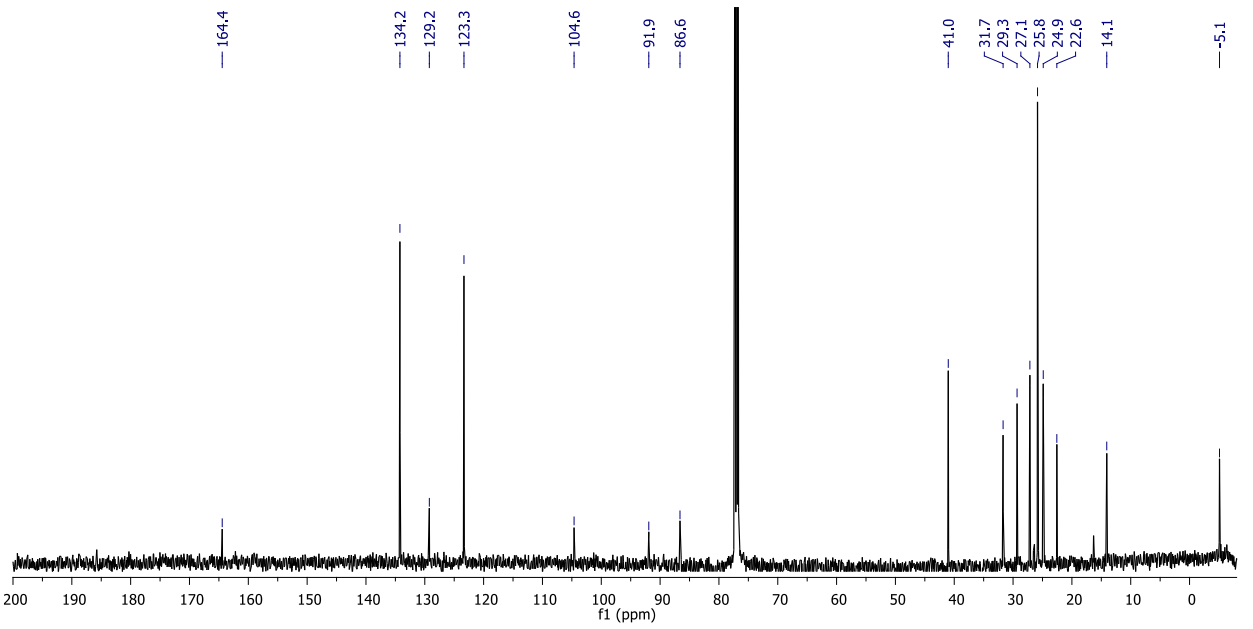

1.86
2.21
1.04
1.08
4.32
1.18
6.56
3.15
9.49
6.00
f1 (ppm)


164.4
134.4
134.2
129.2
123.4
123.3
123.1
105.1
91.1
86.7
77.5
77.3
77.0
76.8
41.0
31.7
29.3
27.3
24.9
22.6
14.1
7.2
4.0
f1 (ppm)


O
O
N
O
^{t}BuMe$_2$Si

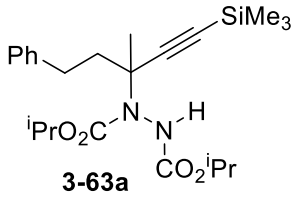
2-43p


1.91
1.93
1.20
1.22
3.26
1.98
6.48
3.65
9.53
6.00
f1 (ppm)

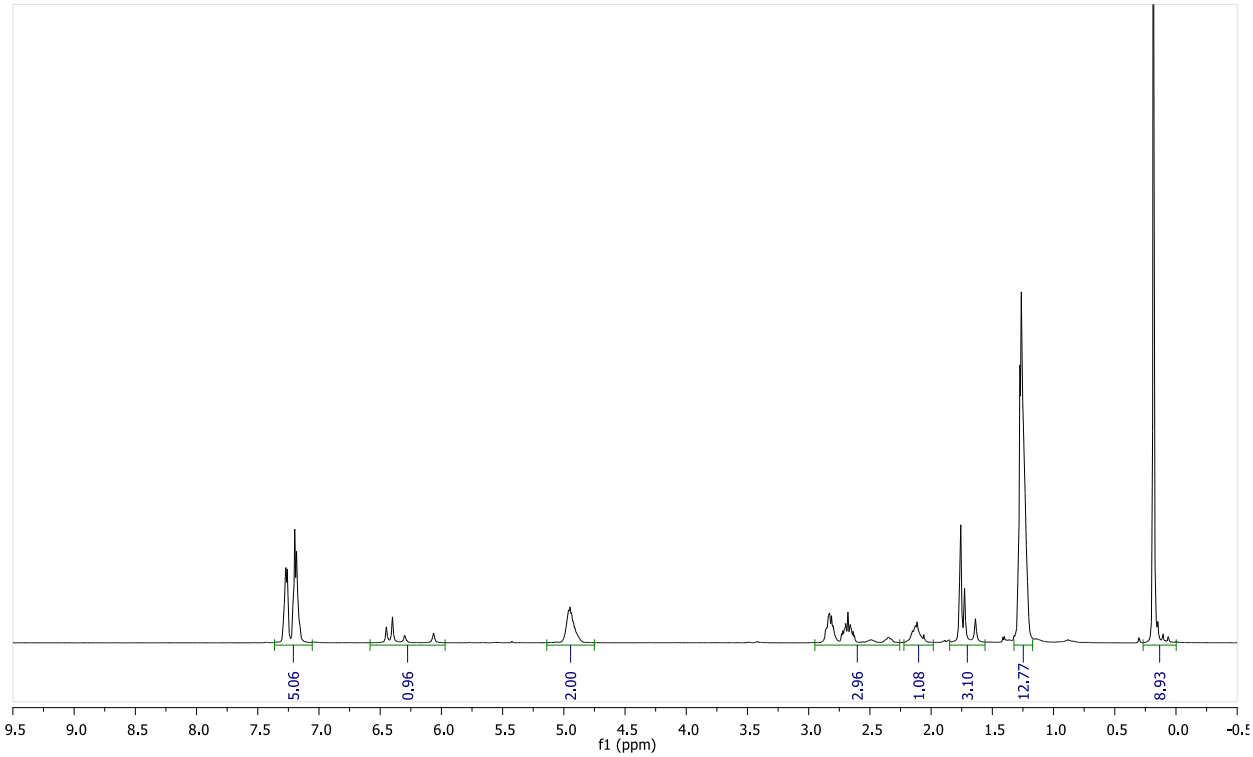

164.4
134.2
129.2
123.3
104.6
91.9
86.6
41.0
31.7
29.3
27.1
25.8
24.9
22.6
14.1
-5.1
f1 (ppm)

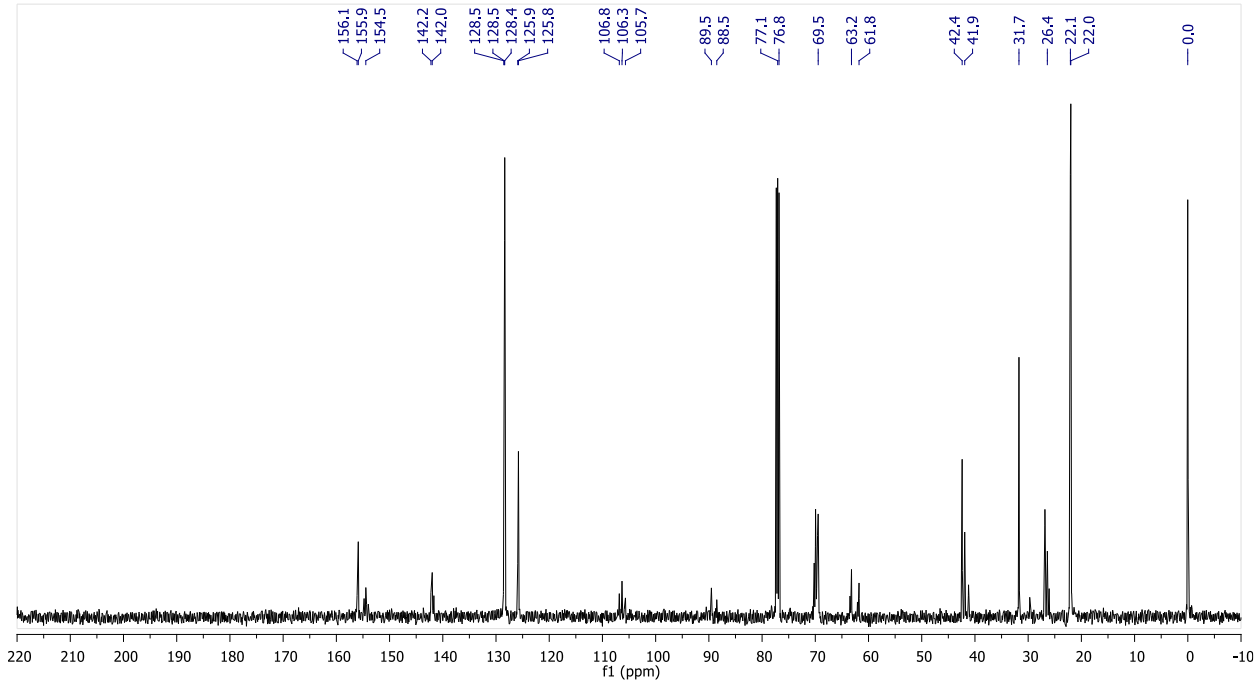
Appendix III

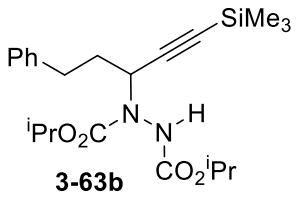
Selected NMR Spectra for Chapter 3


SiMe3
Ph
N
N
H
iPrO2C
CO2iPr

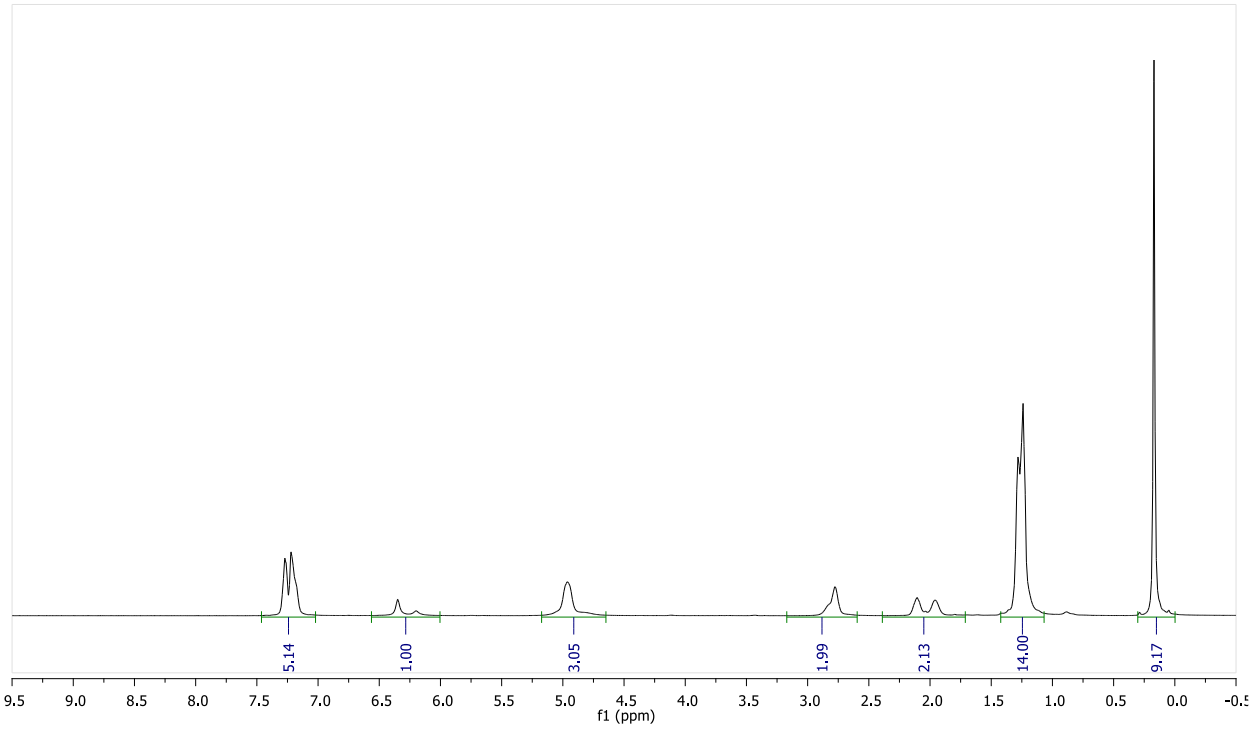
3-63a

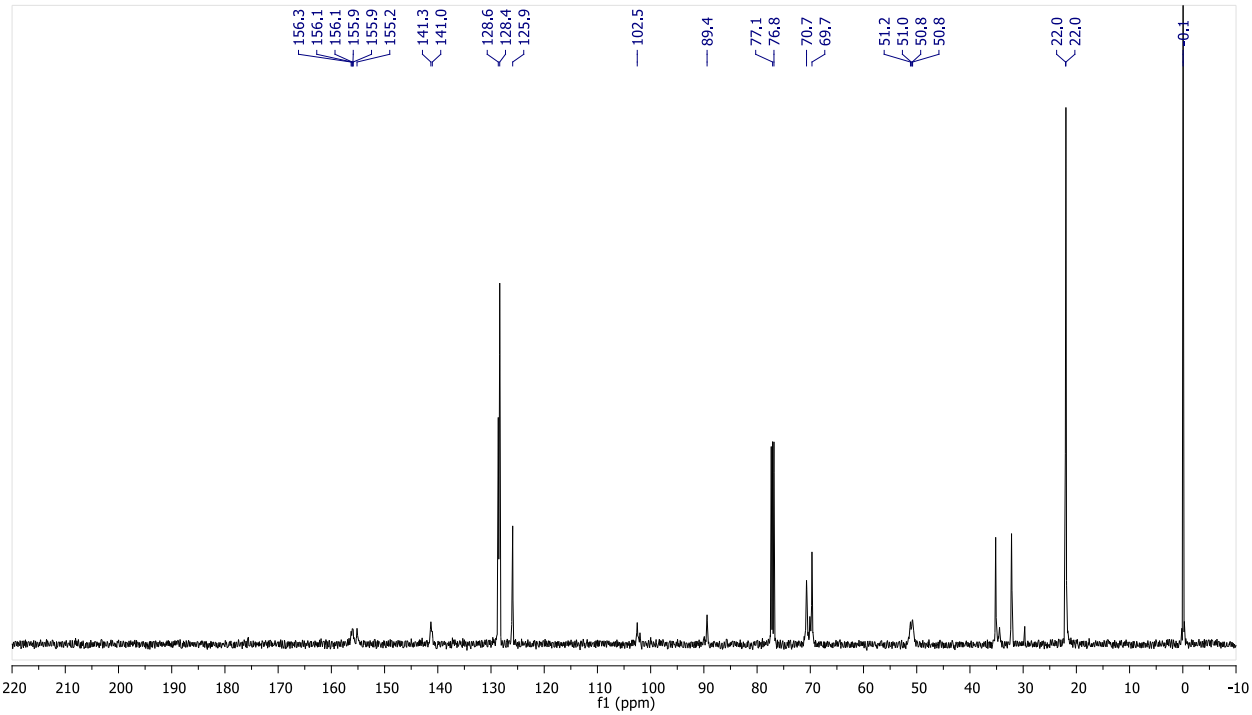

5.06
0.96
2.00
2.96
1.08
3.10
12.77
8.93
f1 (ppm)

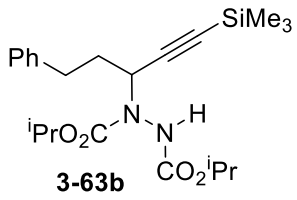

156.1
155.9
154.5
142.2
142.0
128.5
128.5
128.4
125.9
125.8
106.8
106.3
105.7
89.5
88.5
77.1
76.8
69.5
63.2
61.8
42.4
41.9
31.7
26.4
22.1
22.0
0.0
f1 (ppm)


SiMe3
Ph
iPrO2C
N
N
H
CO2iPr

3-63b

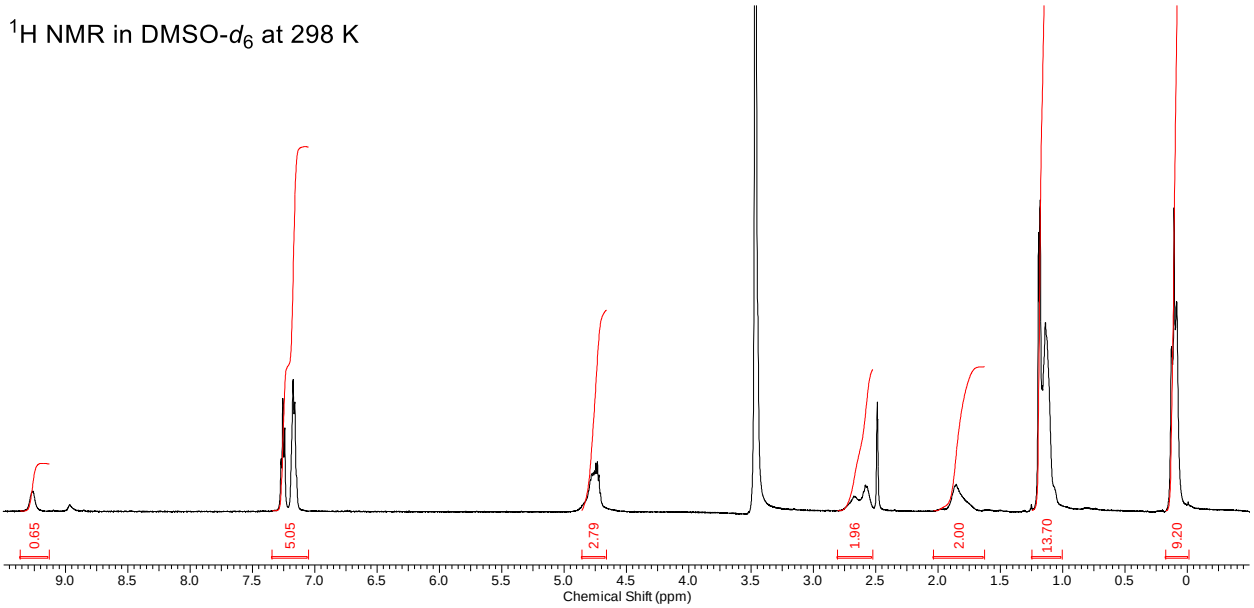

5.14
1.00
3.05
1.99
2.13
14.00
9.17
f1 (ppm)


156.3
156.1
156.1
155.9
155.9
155.2
141.3
141.0
128.6
128.4
125.9
102.5
89.4
77.1
76.8
70.7
69.7
51.2
51.0
50.8
50.8
22.0
22.0
0.1
f1 (ppm)

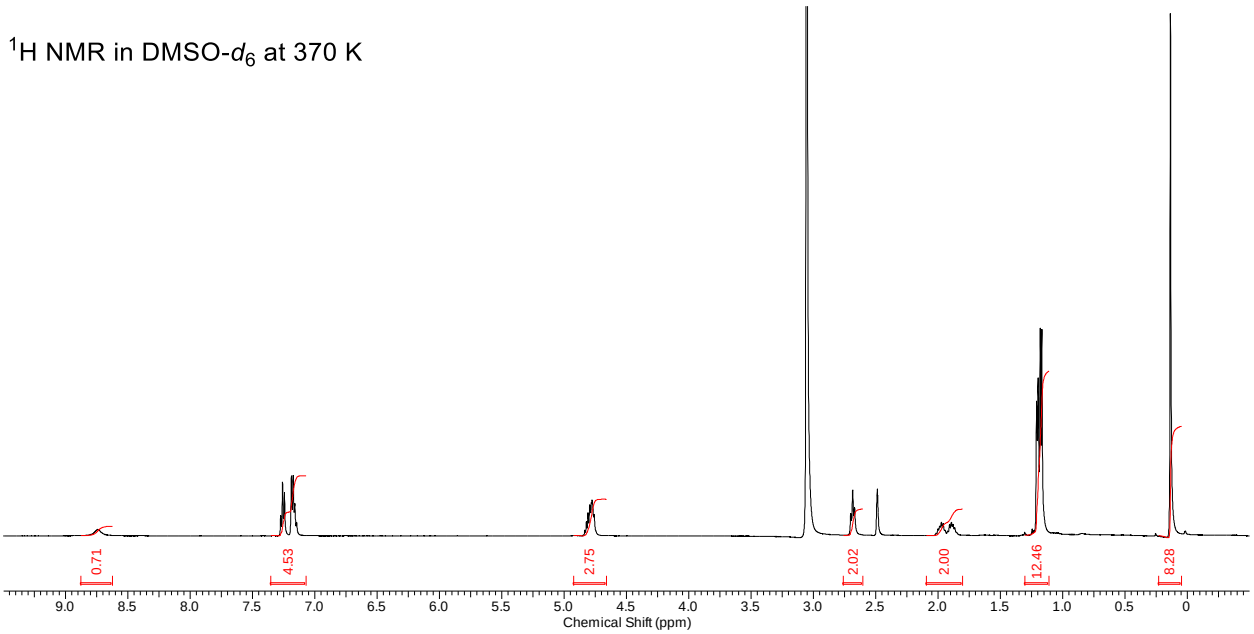


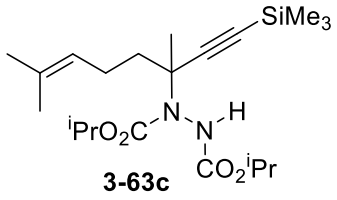
3-63b

^{1}H NMR in DMSO-d_6 at 298 K

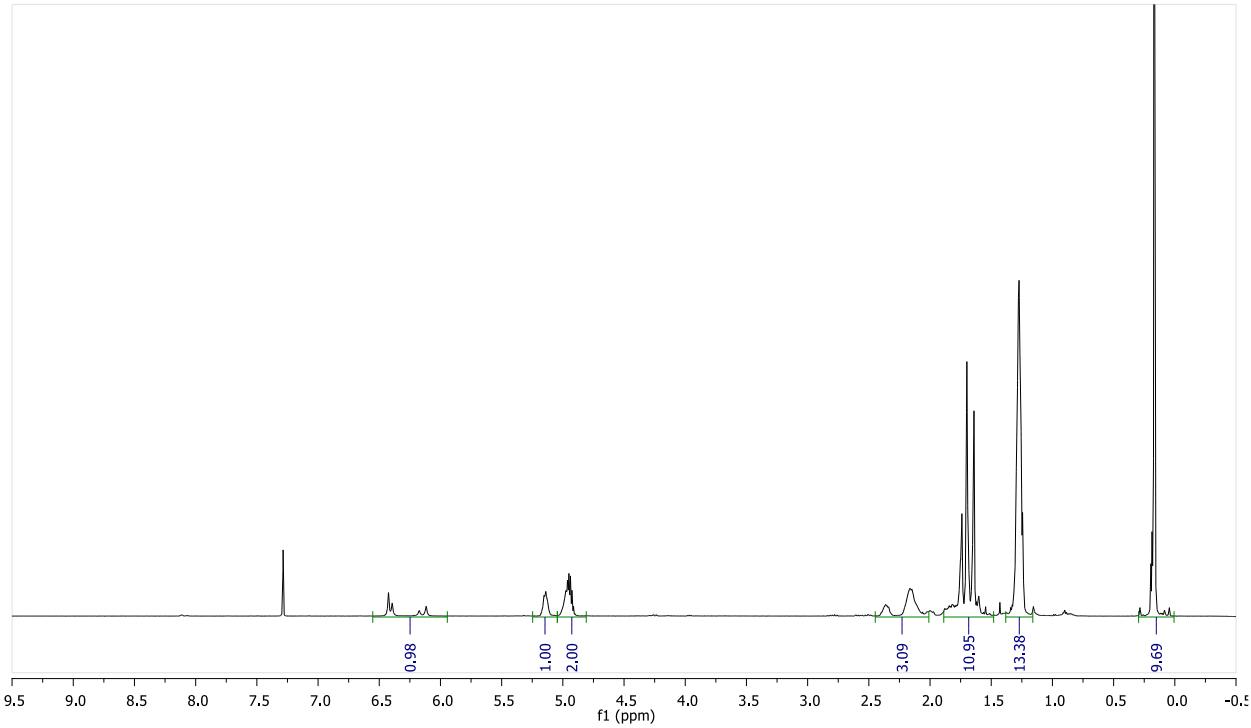


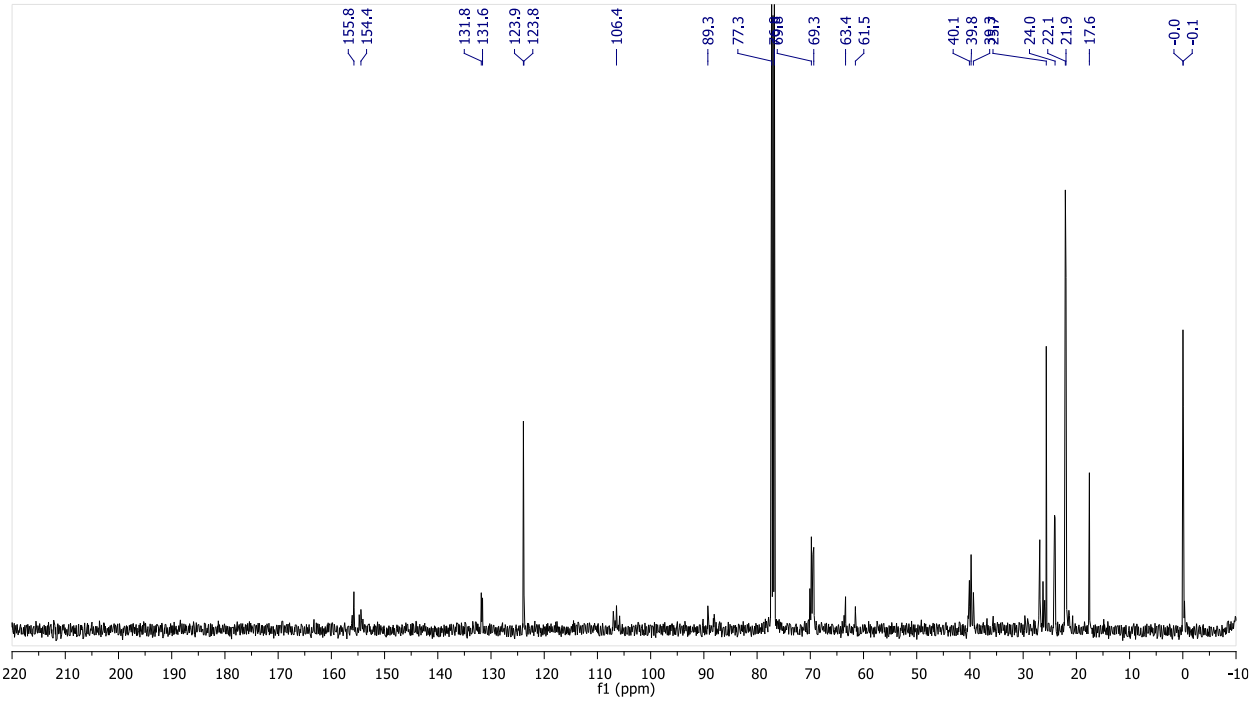
^{1}H NMR in DMSO-d_6 at 370 K

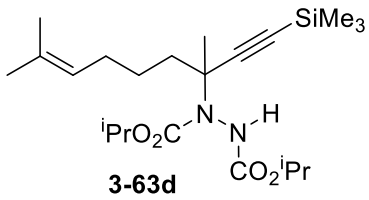



SiMe3
iPrO2C
N
N
H
CO2iPr

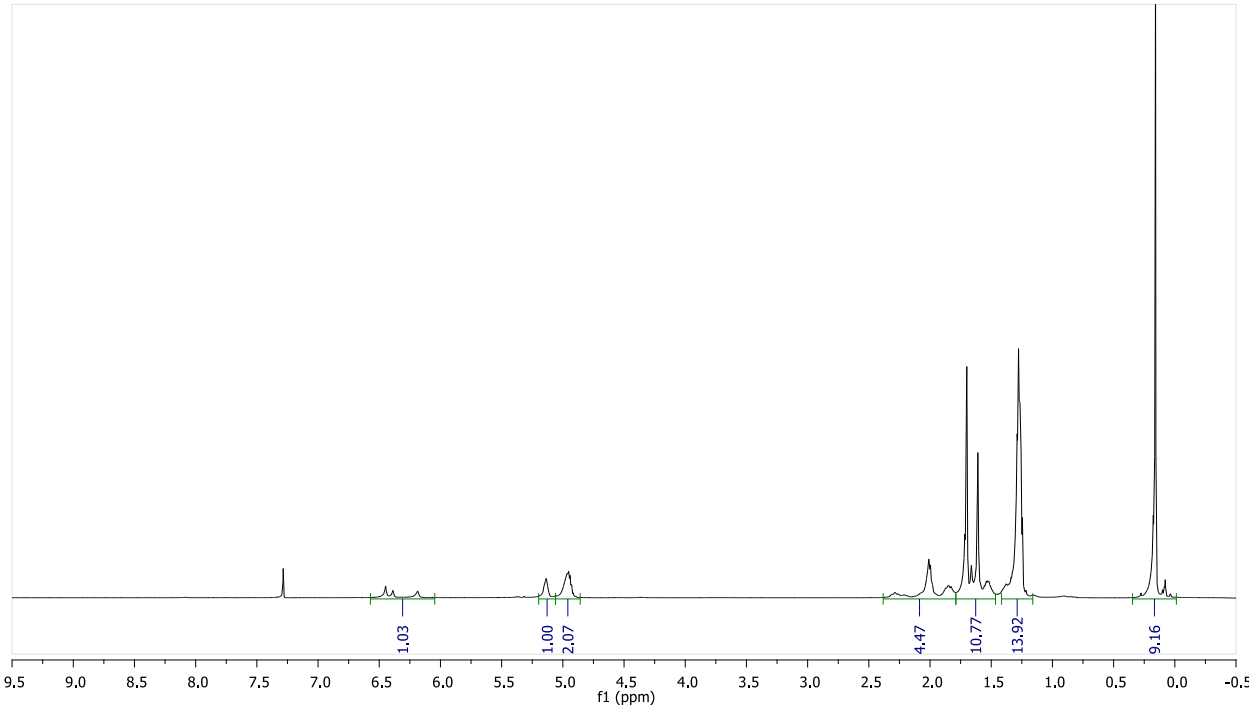
3-63c

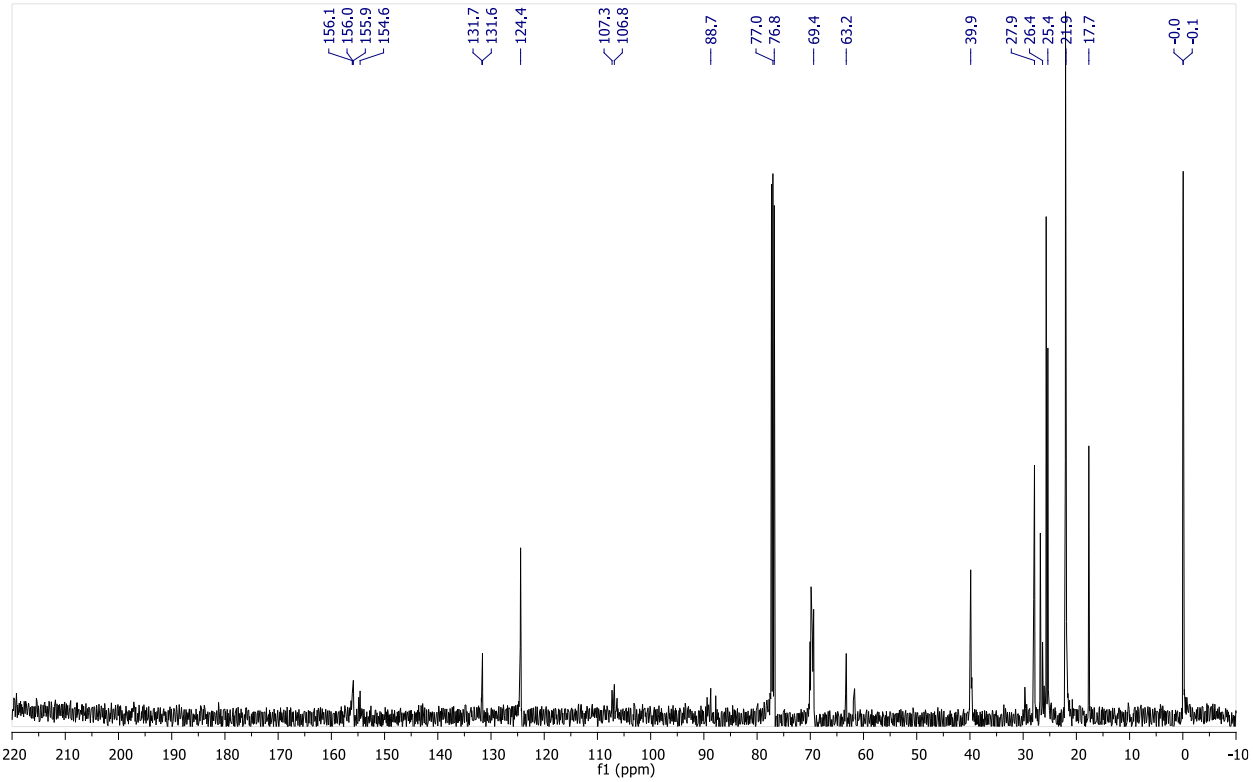

0.98
1.00
2.00
3.09
10.95
13.38
9.69
f1 (ppm)

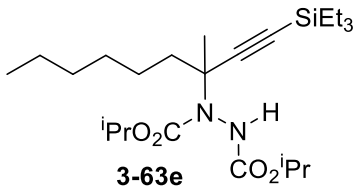

155.8
154.4
131.8
131.6
123.9
123.8
106.4
89.3
77.3
69.3
63.4
61.5
40.1
39.8
24.0
22.1
21.9
17.6
-0.0
-0.1
f1 (ppm)


SiMe3
iPrO2C
N
N
H
CO2iPr

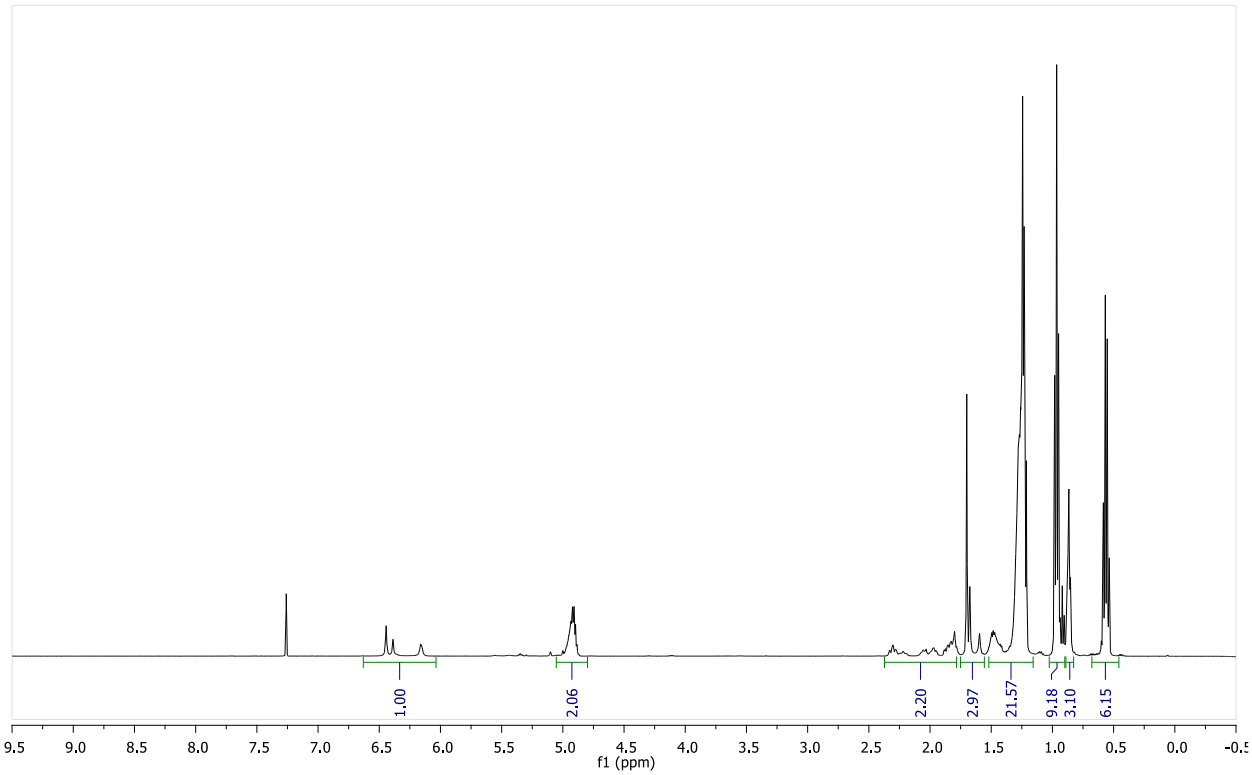
3-63d

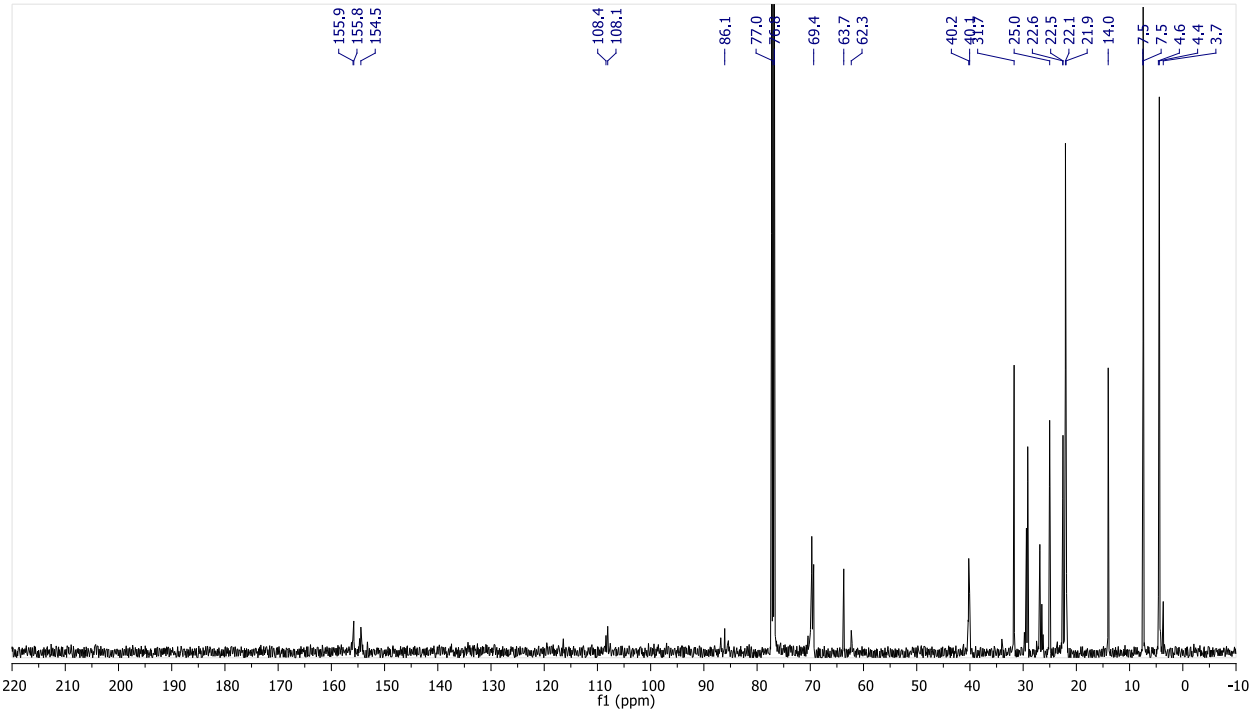

1.03
1.00
2.07
4.47
10.77
13.92
9.16
f1 (ppm)

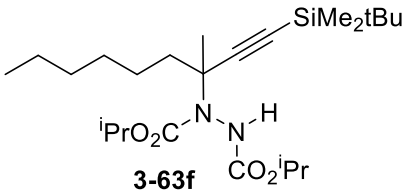

156.1
156.0
155.9
154.6
131.7
131.6
124.4
107.3
106.8
88.7
77.0
76.8
69.4
63.2
39.9
27.9
26.4
25.4
21.9
17.7
-0.0
-0.1
f1 (ppm)


SiEt3
iPrO2C
N
N
H
CO2iPr

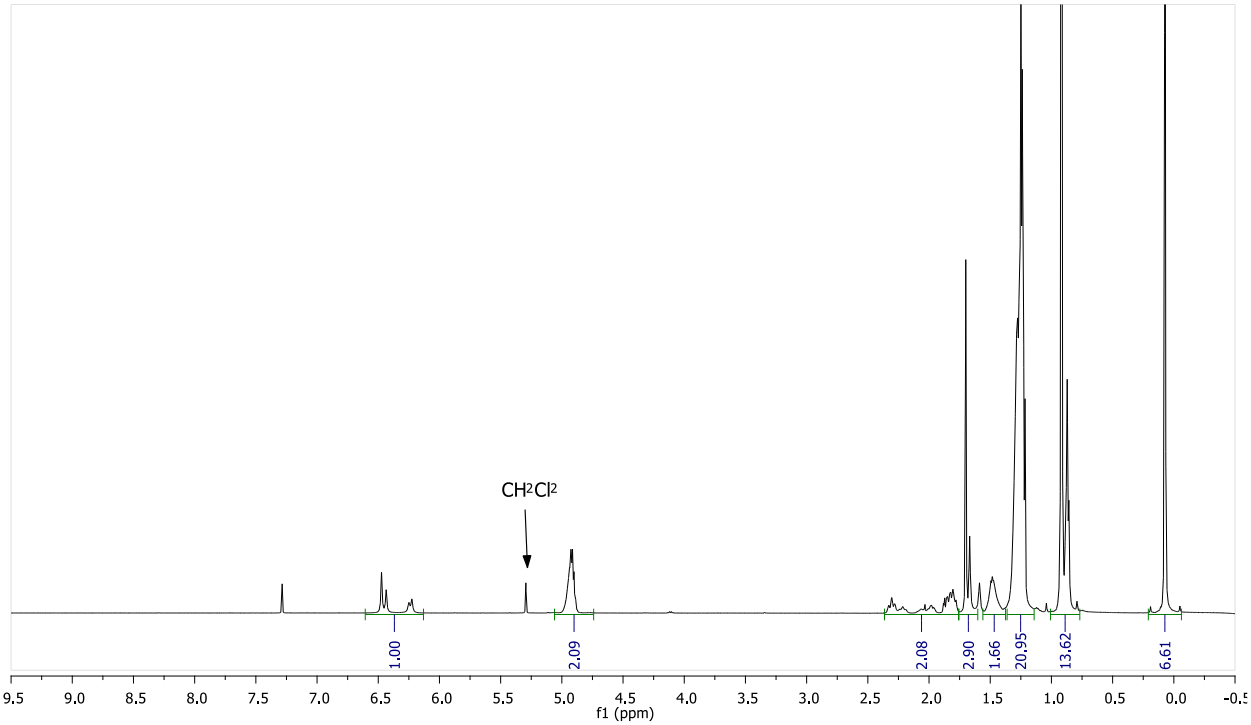
3-63e

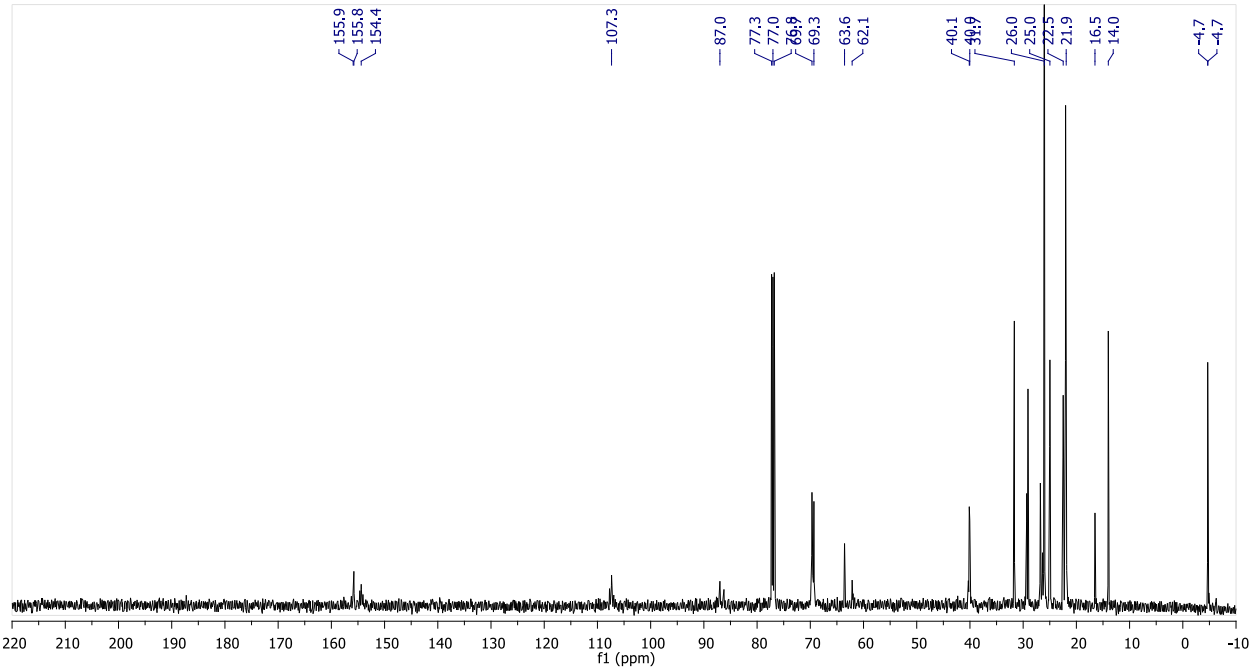

1.00
2.06
2.20
2.97
21.57
9.18
3.10
6.15
f1 (ppm)

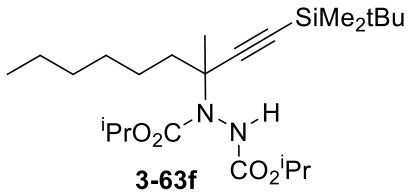

155.9
155.8
154.5
108.4
108.1
86.1
77.0
69.4
63.7
62.3
40.2
40.1
31.7
25.0
22.6
22.5
22.1
21.9
14.0
7.5
7.5
4.6
4.4
3.7
f1 (ppm)


SiMe2tBu
iPrO2C
N
N
H
CO2iPr

3-63f

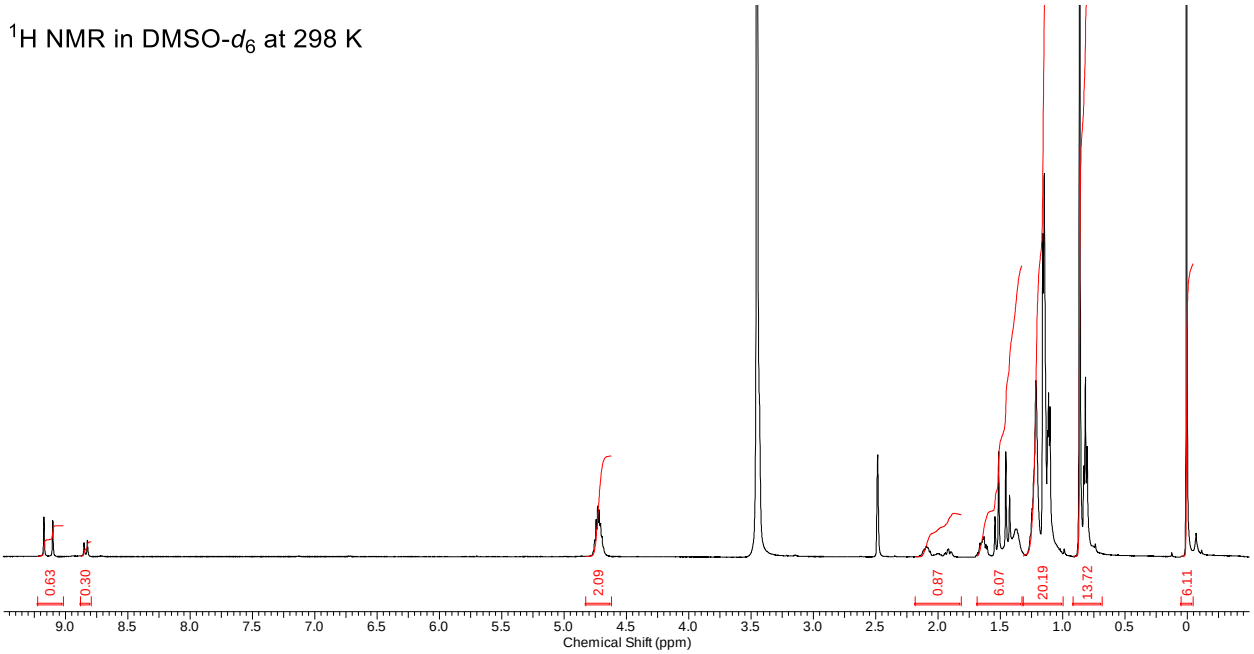

CH2Cl2
1.00
2.09
2.08
2.90
1.66
20.95
13.62
6.61
f1 (ppm)


155.9
155.8
154.4
107.3
87.0
77.3
77.0
69.3
63.6
62.1
40.1
26.0
25.0
22.5
21.9
16.5
14.0
-4.7
-4.7
f1 (ppm)

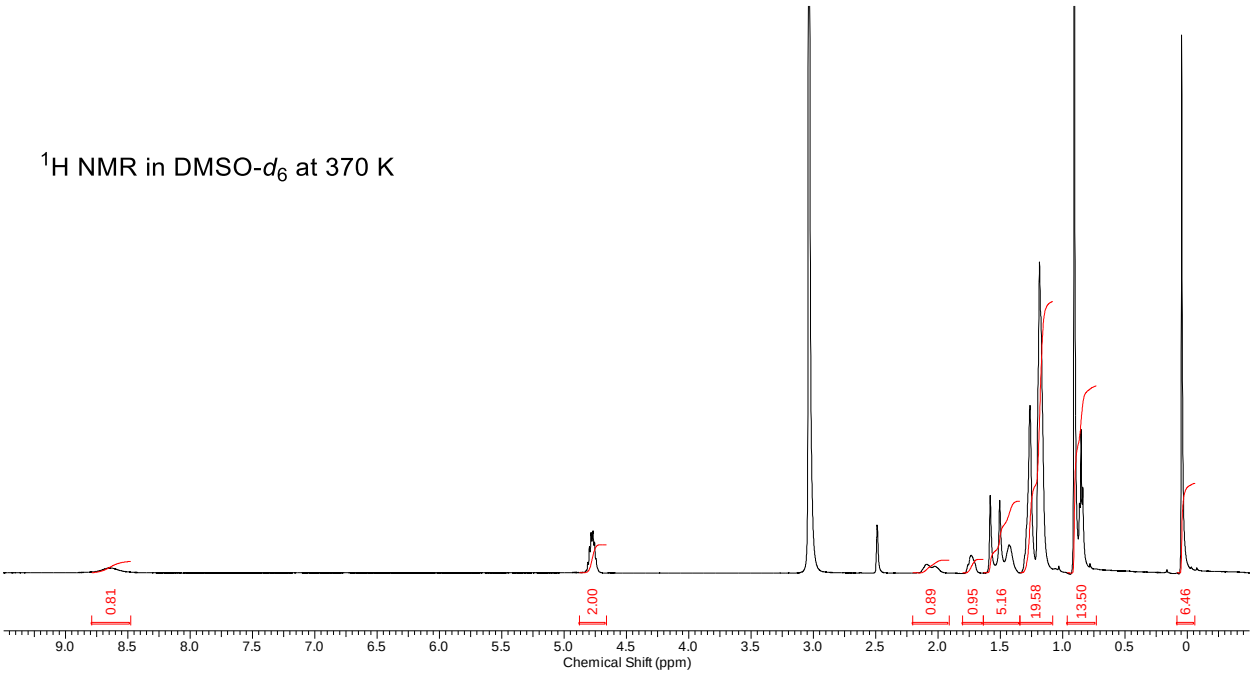


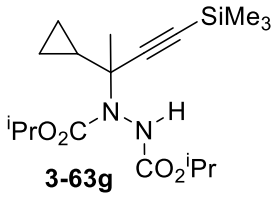
3-63f

^{1}H NMR in DMSO-d_6 at 298 K

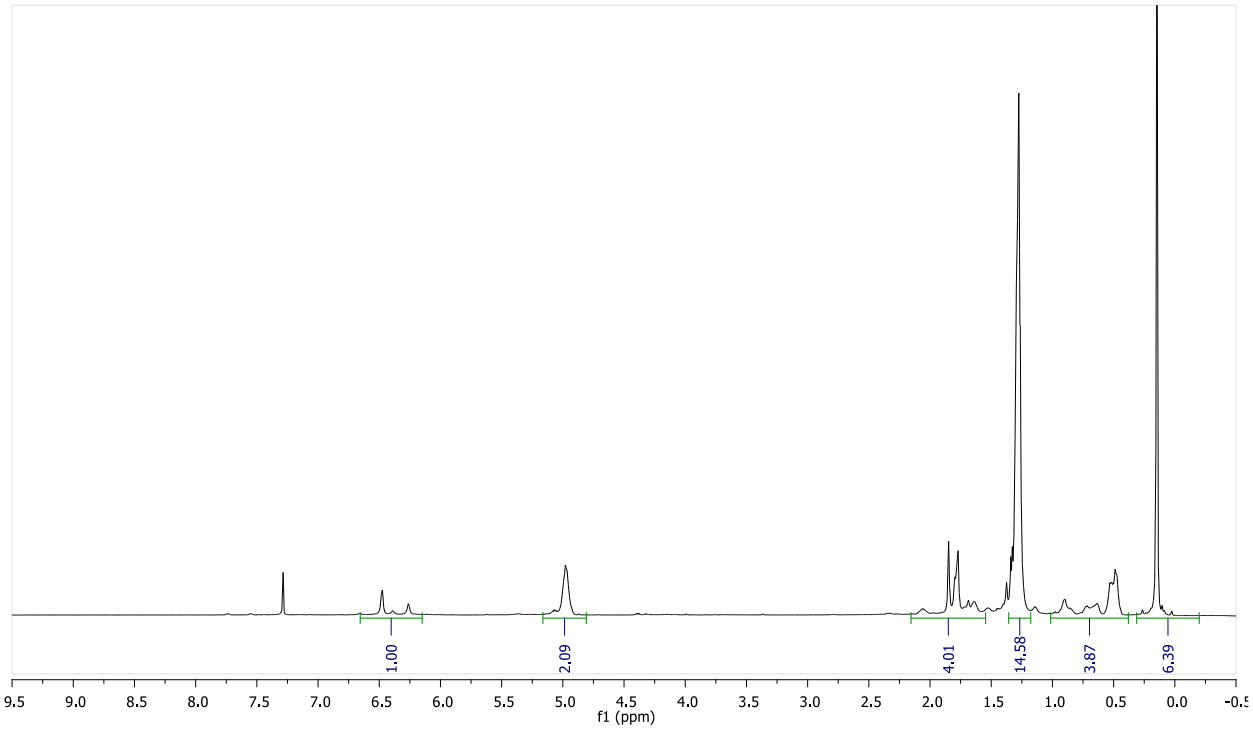


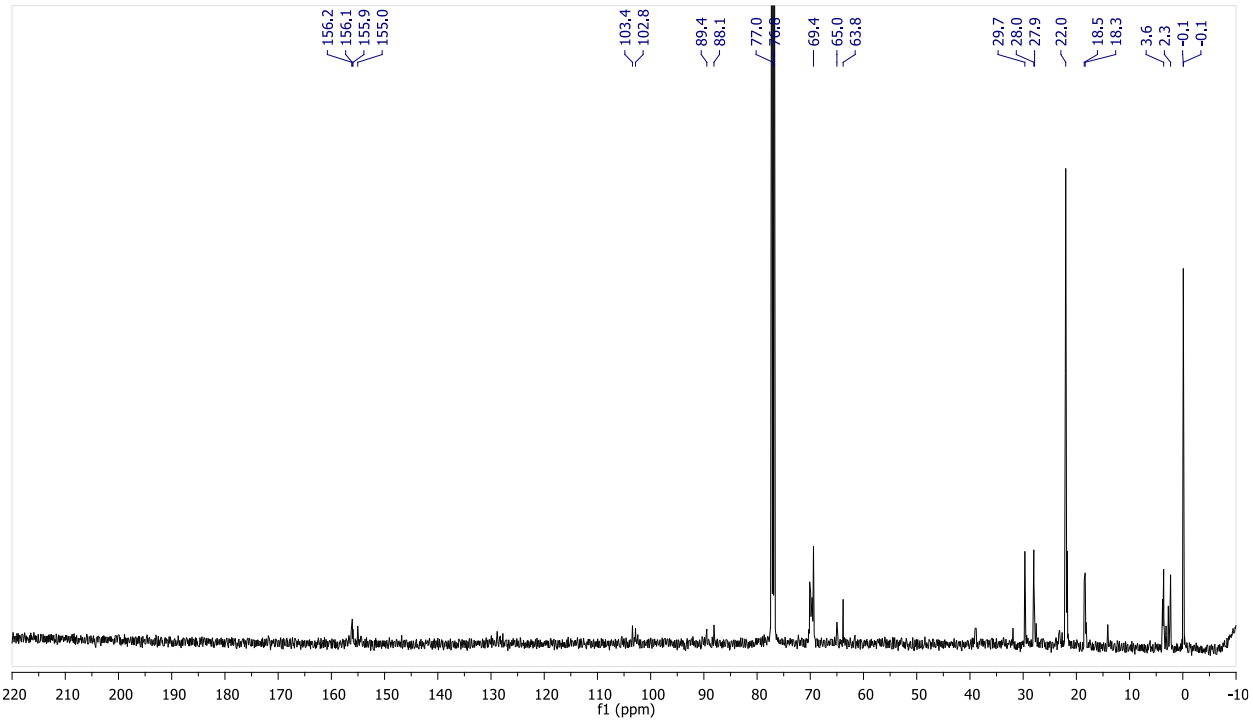
^{1}H NMR in DMSO-d_6 at 370 K

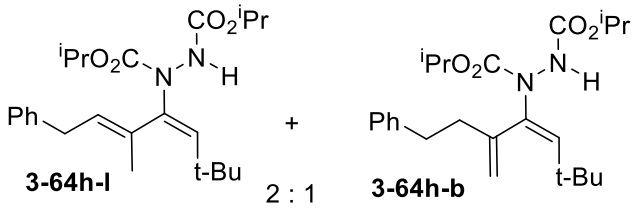


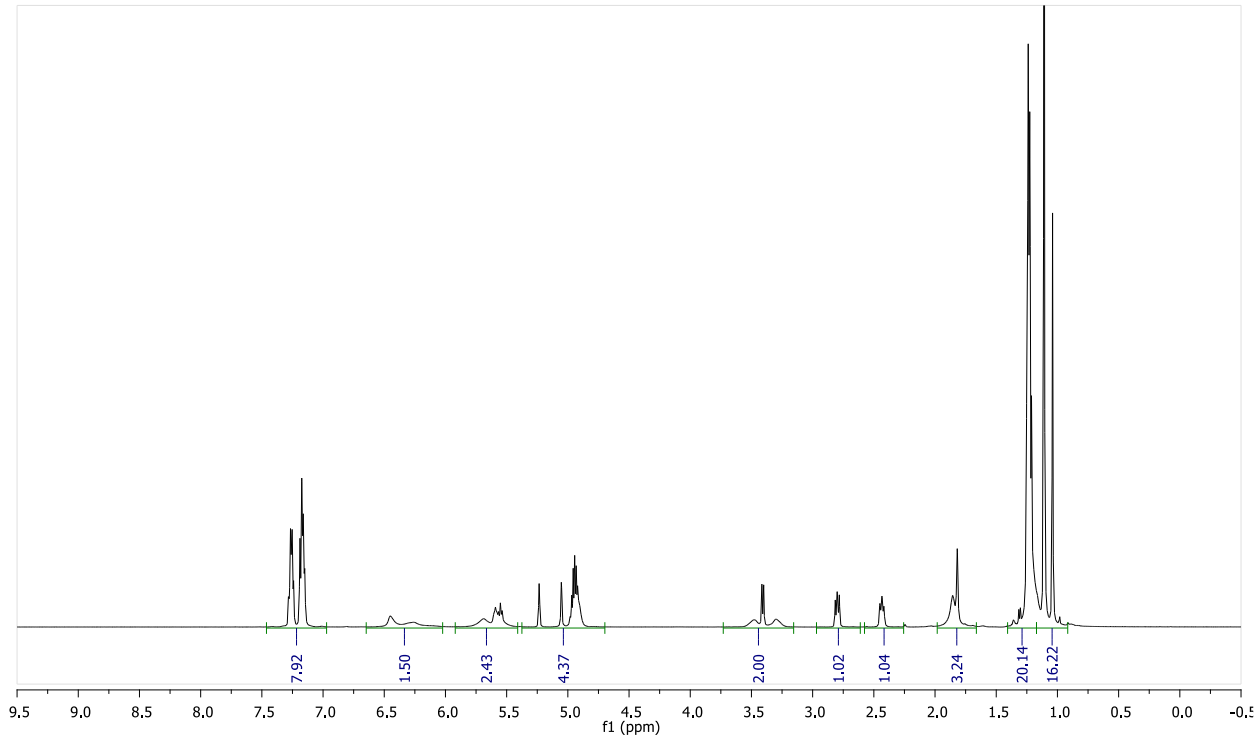

SiMe3
iPrO2C
N
N
H
CO2iPr

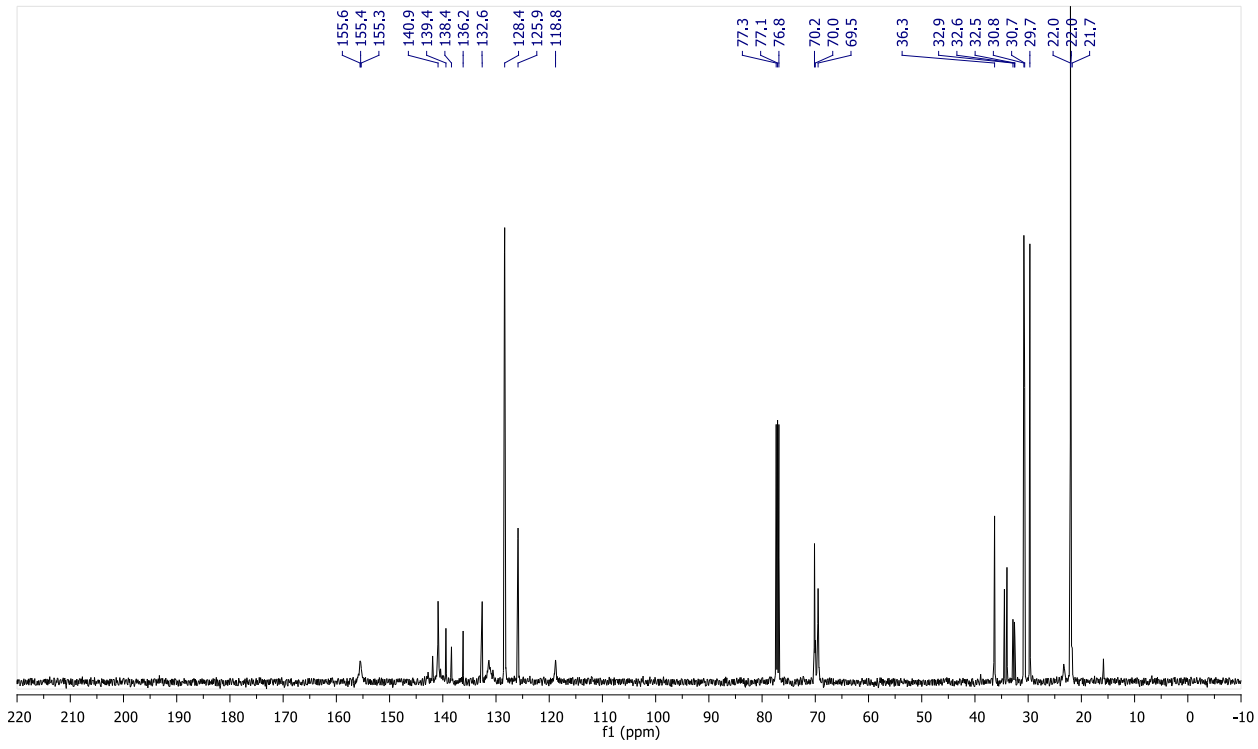
3-63g

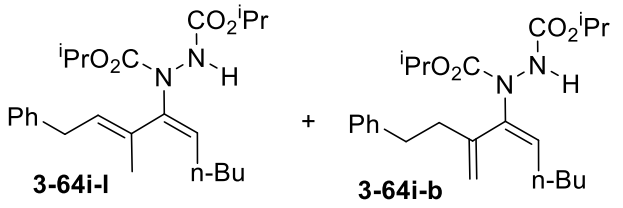

1.00
2.09
4.01
14.58
3.87
6.39
f1 (ppm)

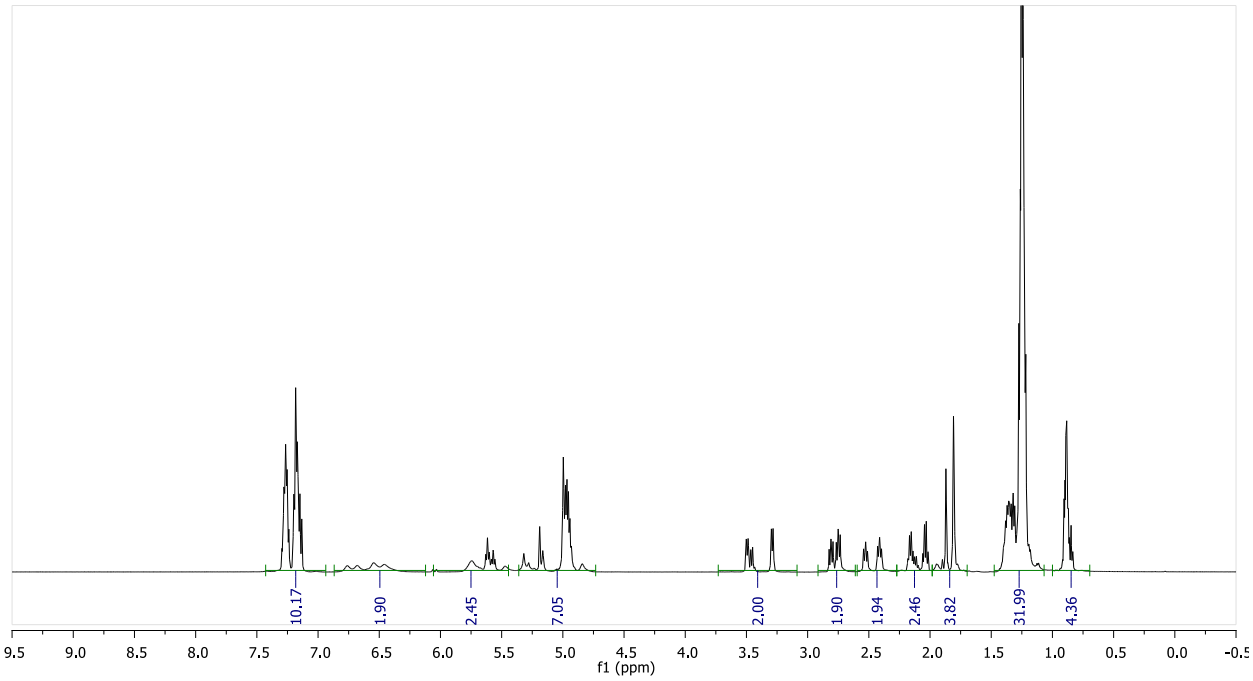

156.2
156.1
155.9
155.0
103.4
102.8
89.4
88.1
77.0
69.4
65.0
63.8
29.7
28.0
27.9
22.0
18.5
18.3
3.6
2.3
-0.1
-0.1
f1 (ppm)

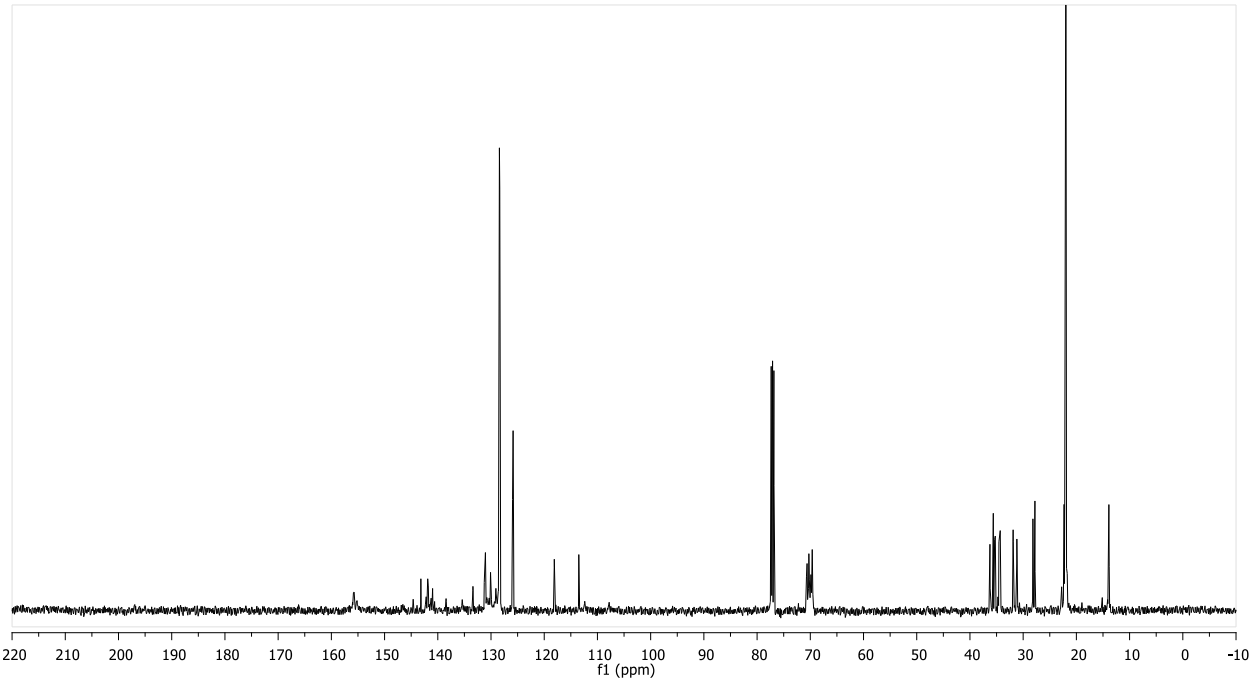

CO2iPr
iPrO2C
N
N
H
Ph
t-Bu
3-64h-l
+
2 : 1
3-64h-b

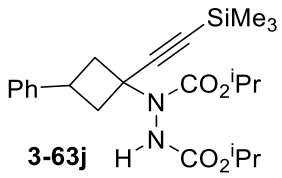

7.92
1.50
2.43
4.37
2.00
1.02
1.04
3.24
20.14
16.22
f1 (ppm)


155.6
155.4
155.3
140.9
139.4
138.4
136.2
132.6
128.4
125.9
118.8
77.3
77.1
76.8
70.2
70.0
69.5
36.3
32.9
32.6
32.5
30.8
30.7
29.7
22.0
22.0
21.7
f1 (ppm)

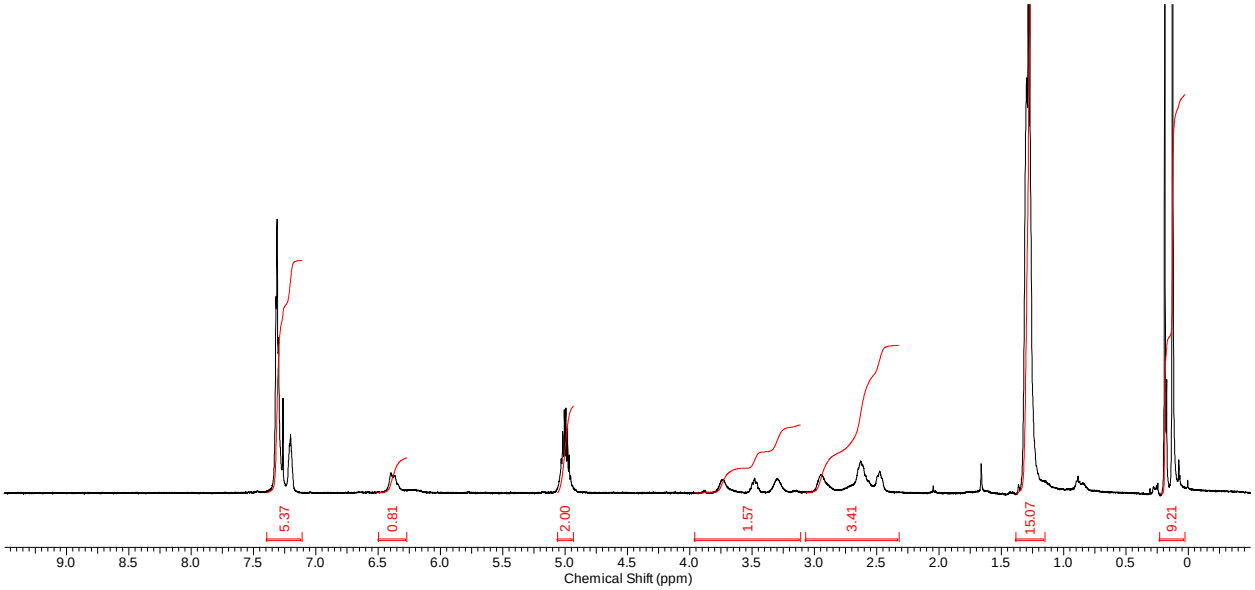

CO2iPr
iPrO2C
N
N
H
Ph
n-Bu
3-64i-l
+
CO2iPr
iPrO2C
N
N
H
Ph
n-Bu
3-64i-b

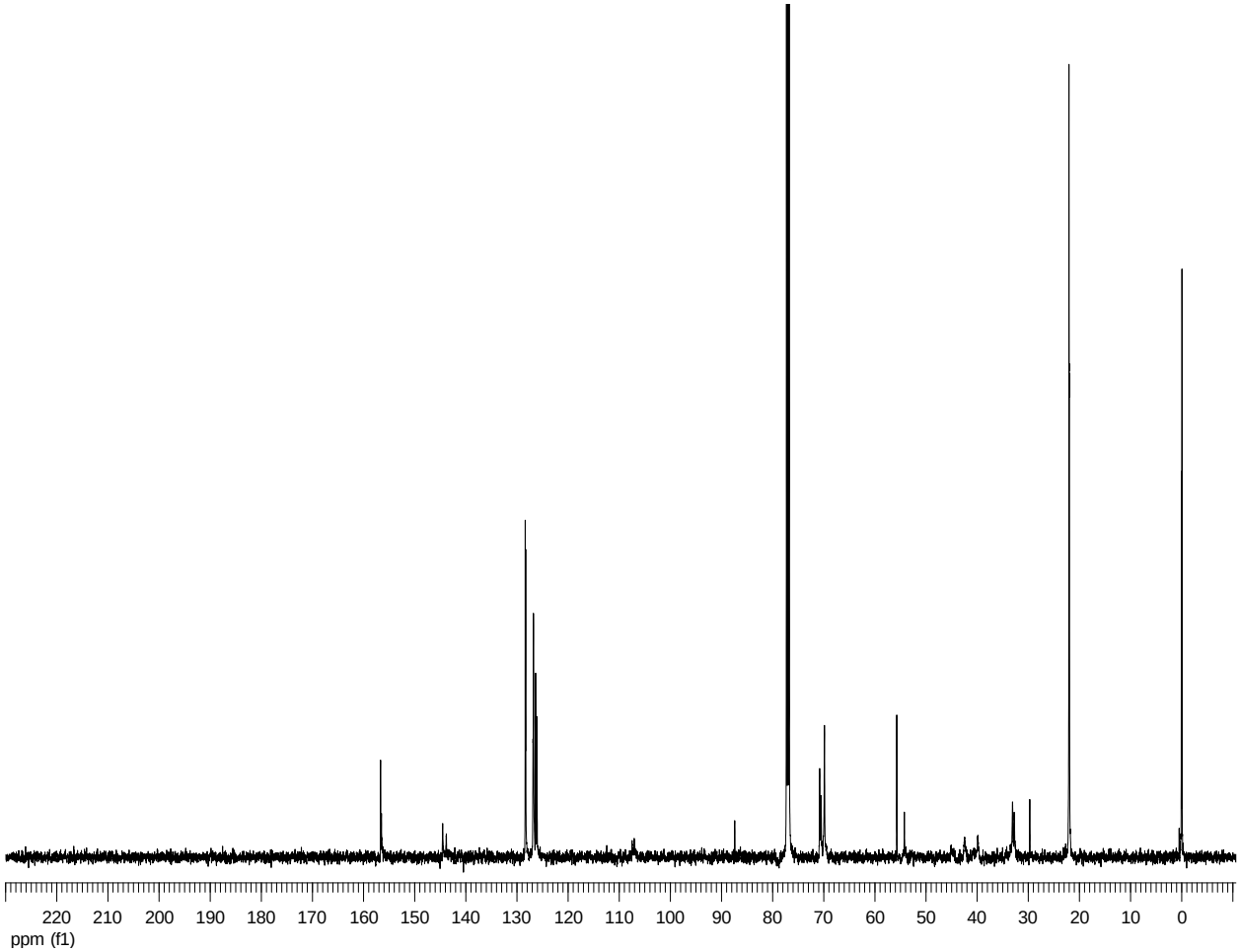

10.17
1.90
2.45
7.05
2.00
1.90
1.94
2.46
3.82
31.99
4.36
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

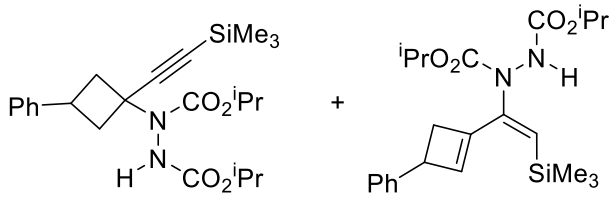

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


SiMe3
Ph
CO2iPr
N
N
H
CO2iPr

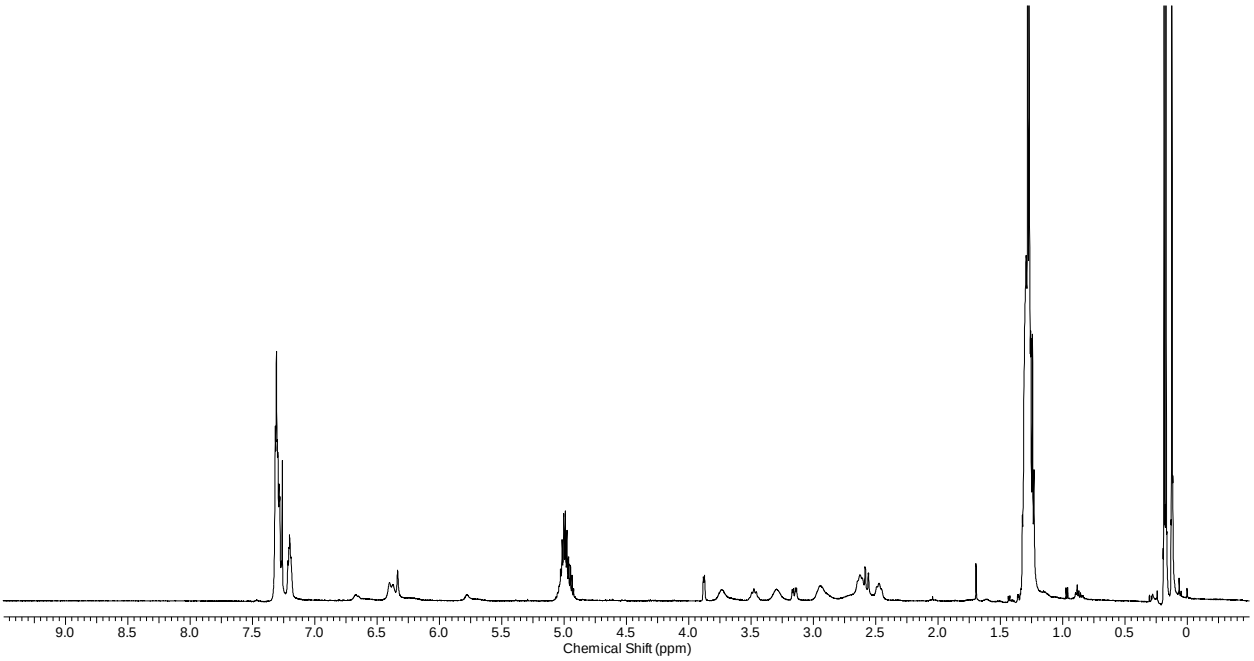
3-63j

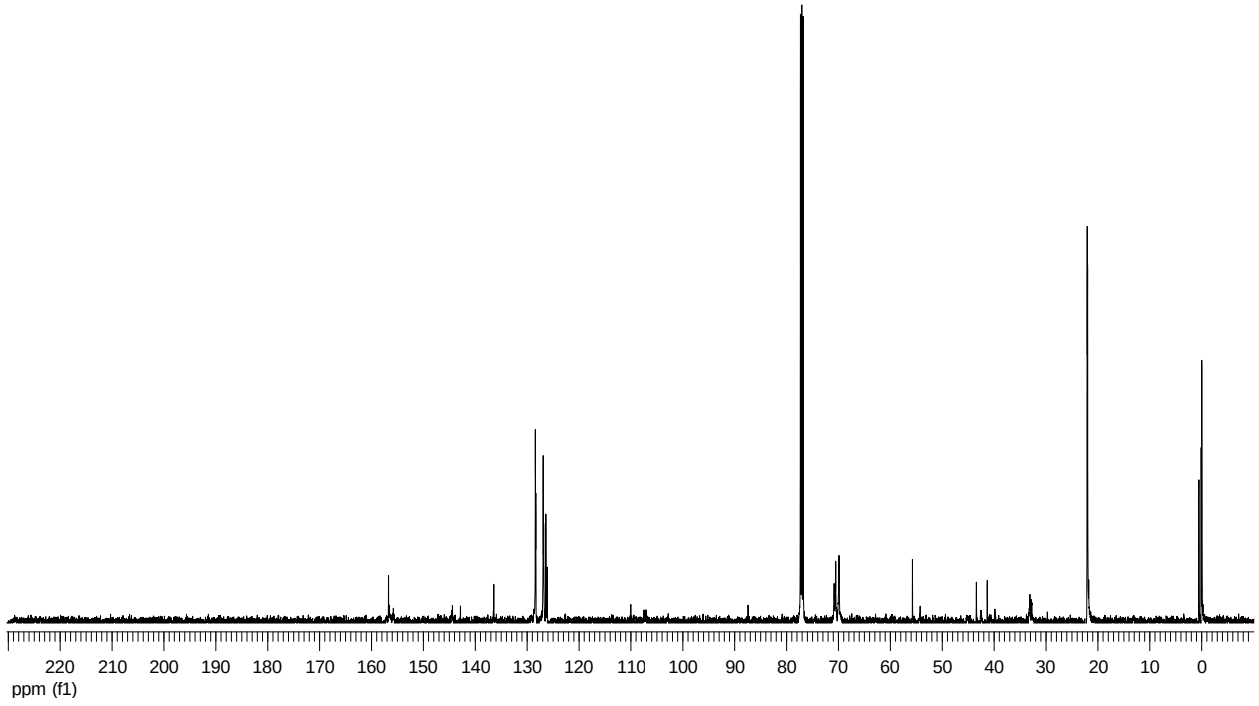

5.37
0.81
2.00
1.57
3.41
15.07
9.21
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

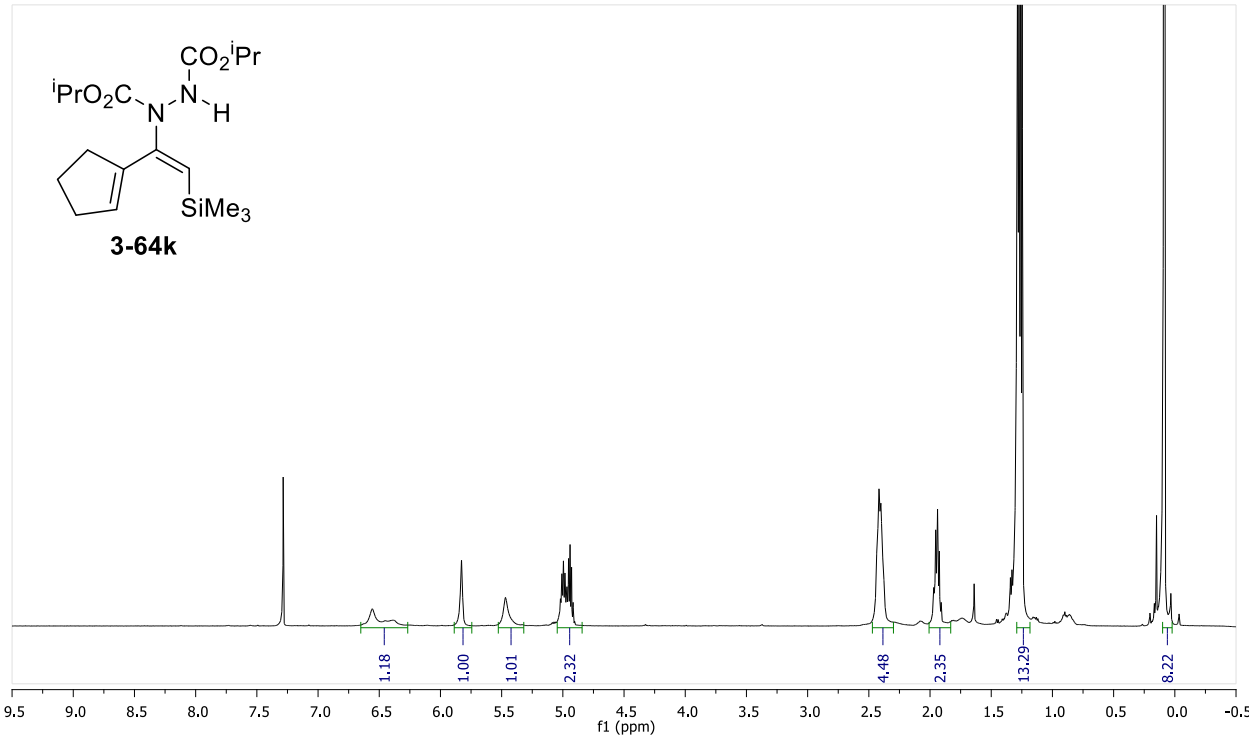

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (f1)

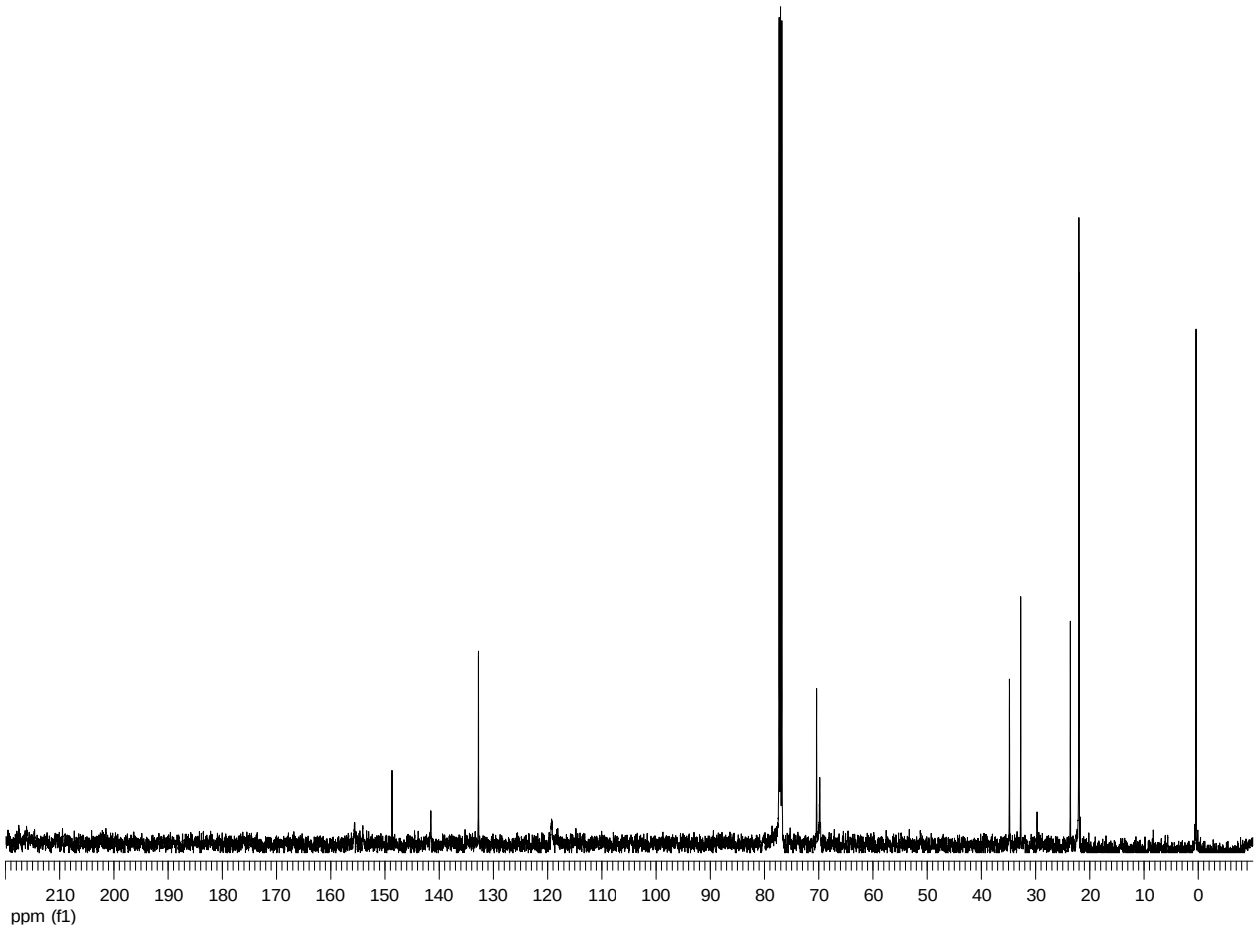

SiMe3
Ph
CO2iPr
N
N
H
CO2iPr
+
CO2iPr
iPrO2C
N
N
H
Ph
SiMe3

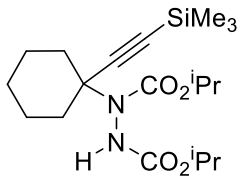
3-632j **3-64j**


9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

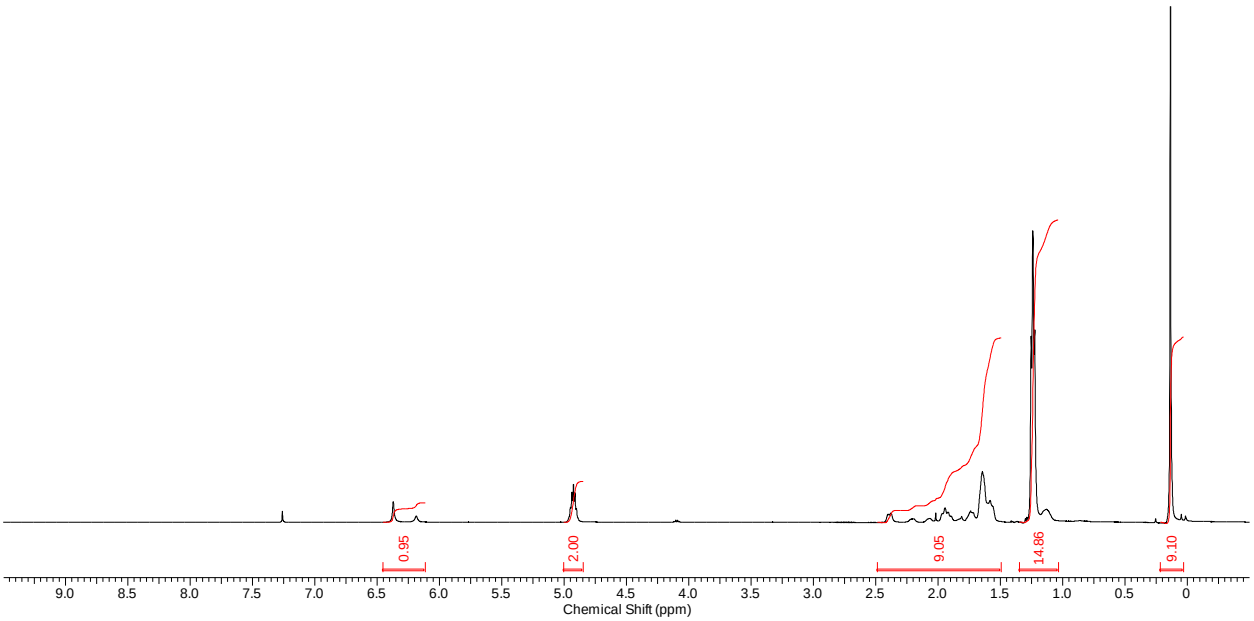

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (f1)

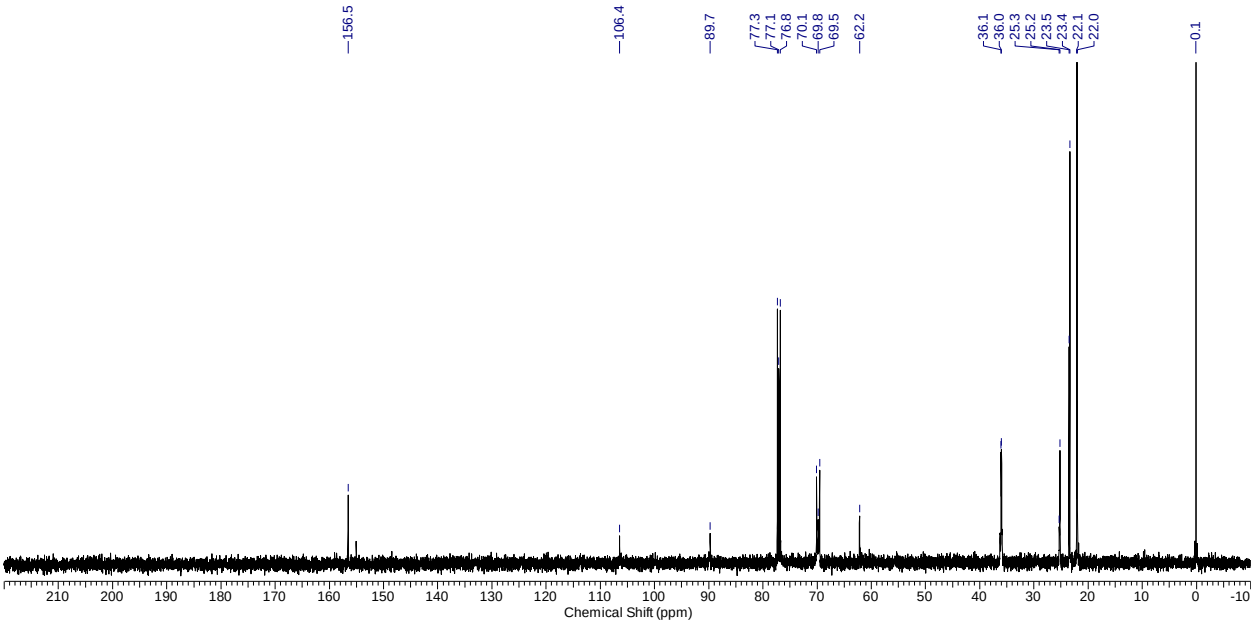

CO2iPr
iPrO2C
N
N
H
SiMe3
3-64k
1.18
1.00
1.01
2.32
4.48
2.35
13.29
8.22
f1 (ppm)

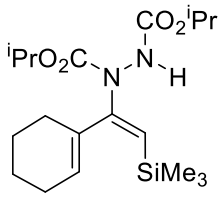

ppm (f1)


SiMe3
CO2iPr
N
N
H
CO2iPr

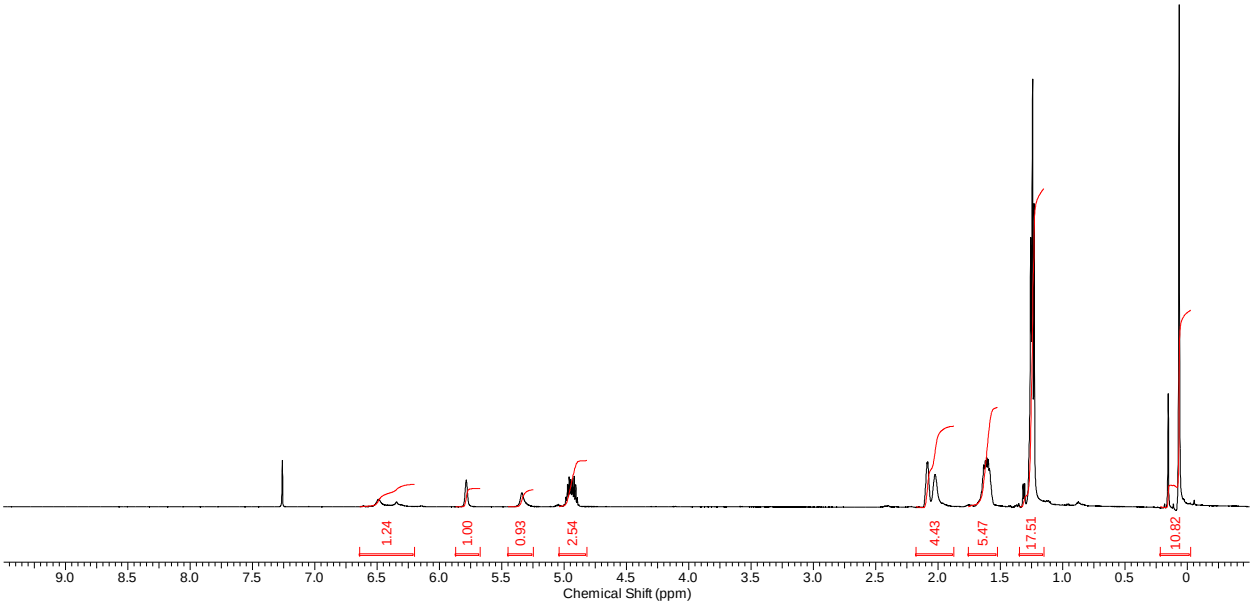
3-63l

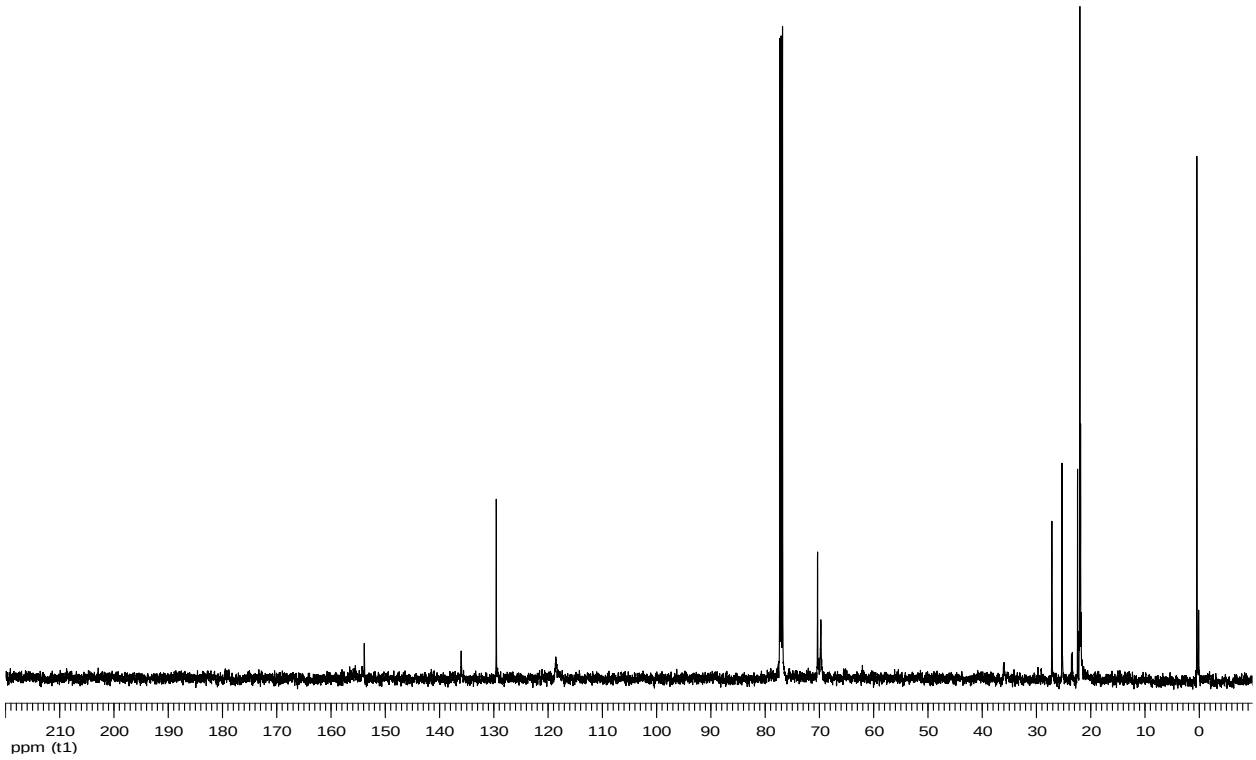

0.95
2.00
9.05
14.86
9.10
Chemical Shift (ppm)

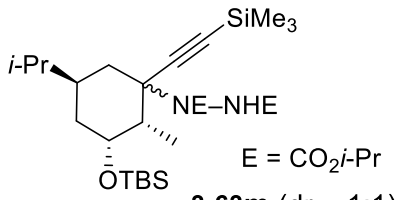

156.5
106.4
89.7
77.3
77.1
76.8
70.1
69.8
69.5
62.2
36.1
36.0
25.3
25.2
23.5
23.4
22.1
22.0
0.1
Chemical Shift (ppm)


CO2iPr
iPrO2C
N
N
H
SiMe3

3-64l

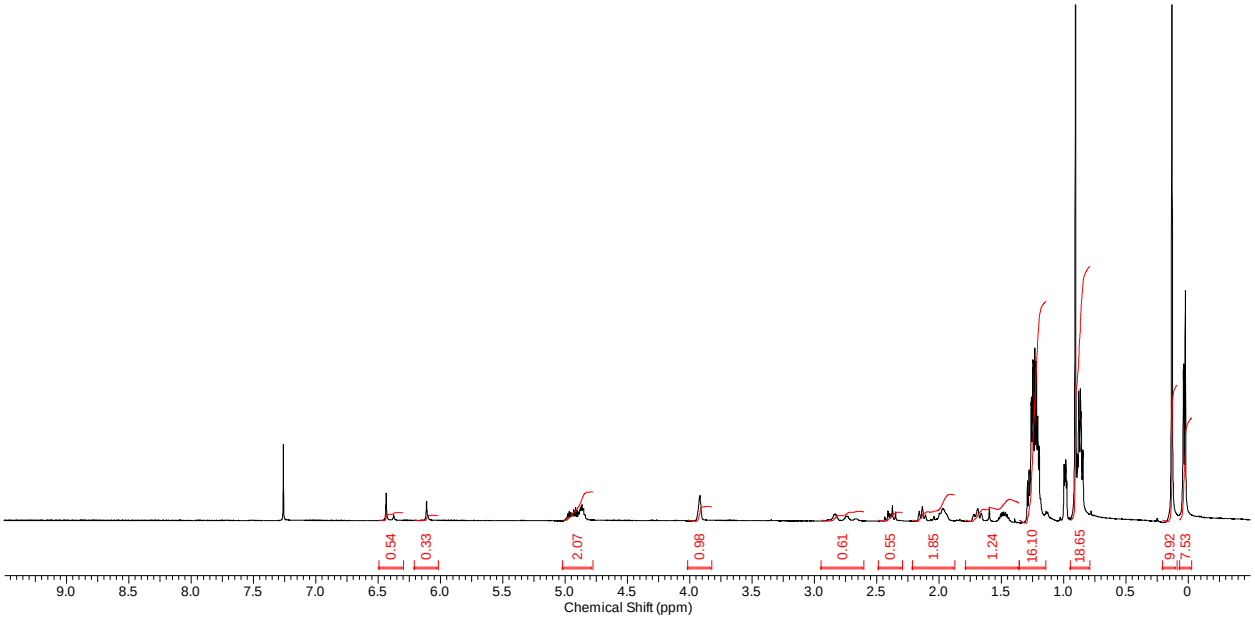

1.24
1.00
0.93
2.54
4.43
5.47
17.51
10.82
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

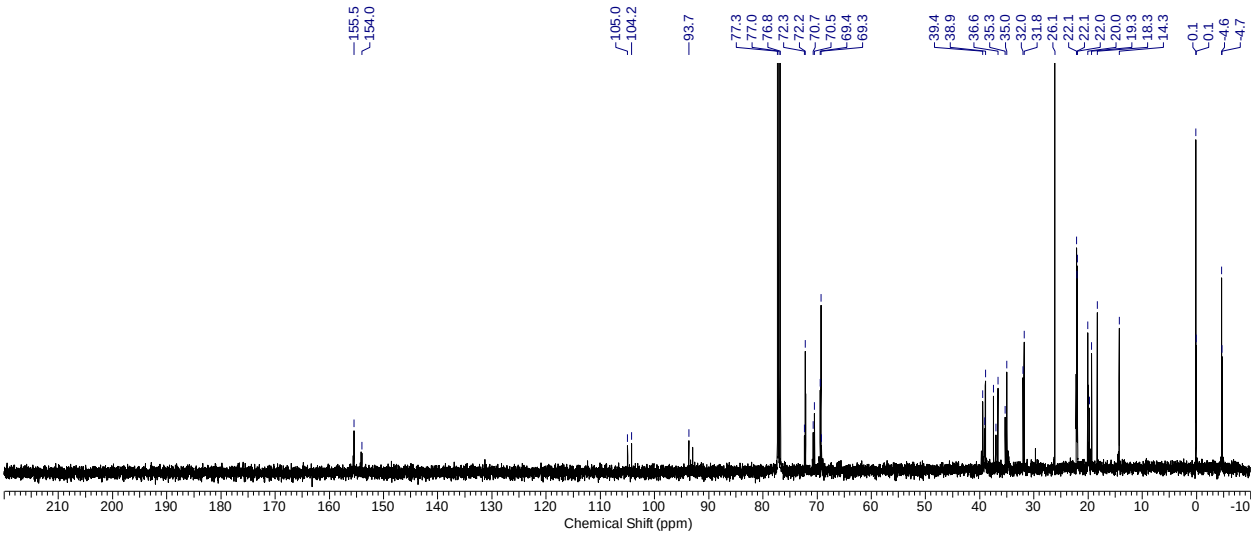

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (t1)

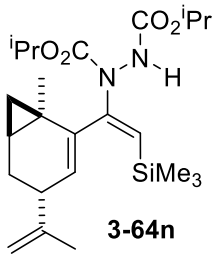


E = CO_2*i*-Pr

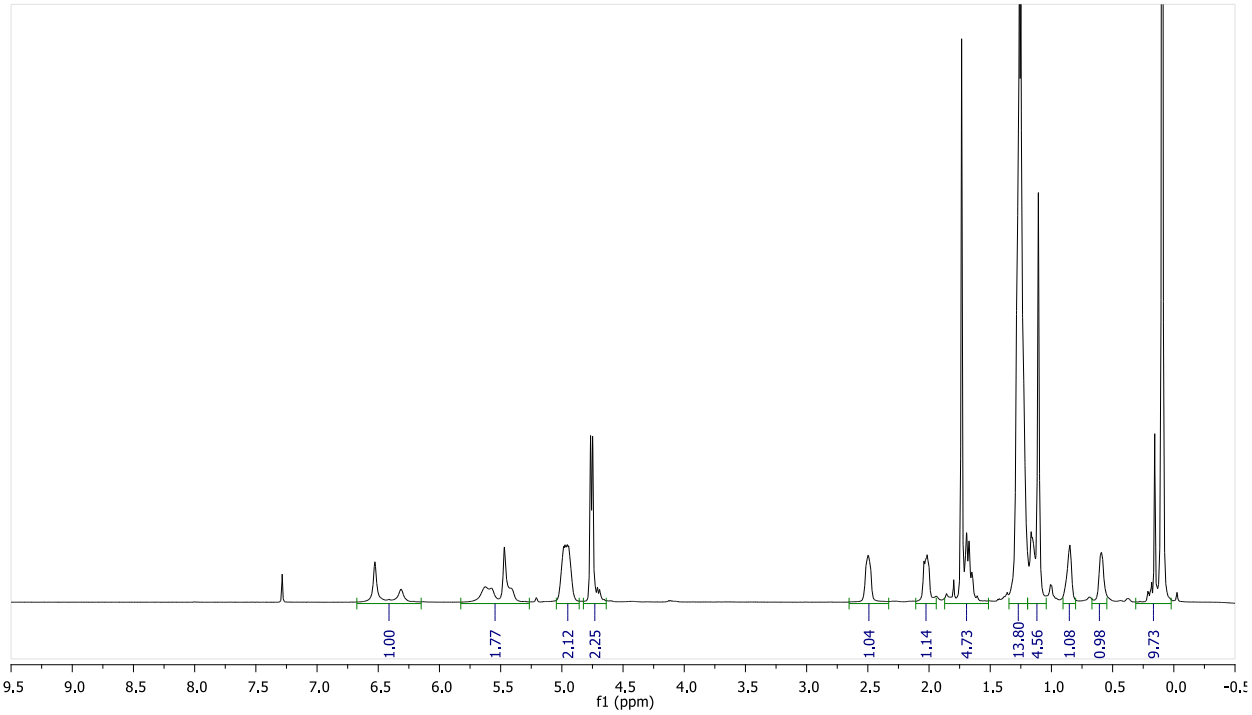
3-63m (dr = 1:1)

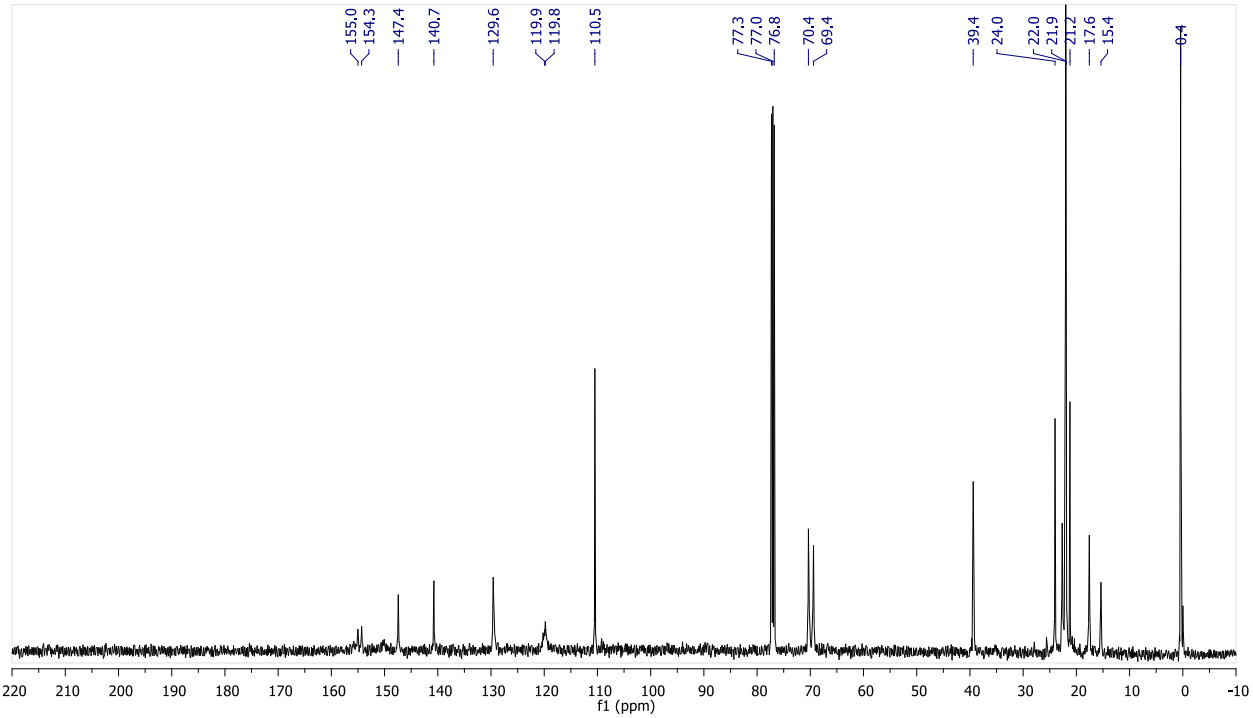


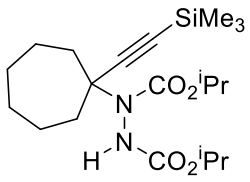



CO2iPr
iPrO2C
N
N
H
SiMe3

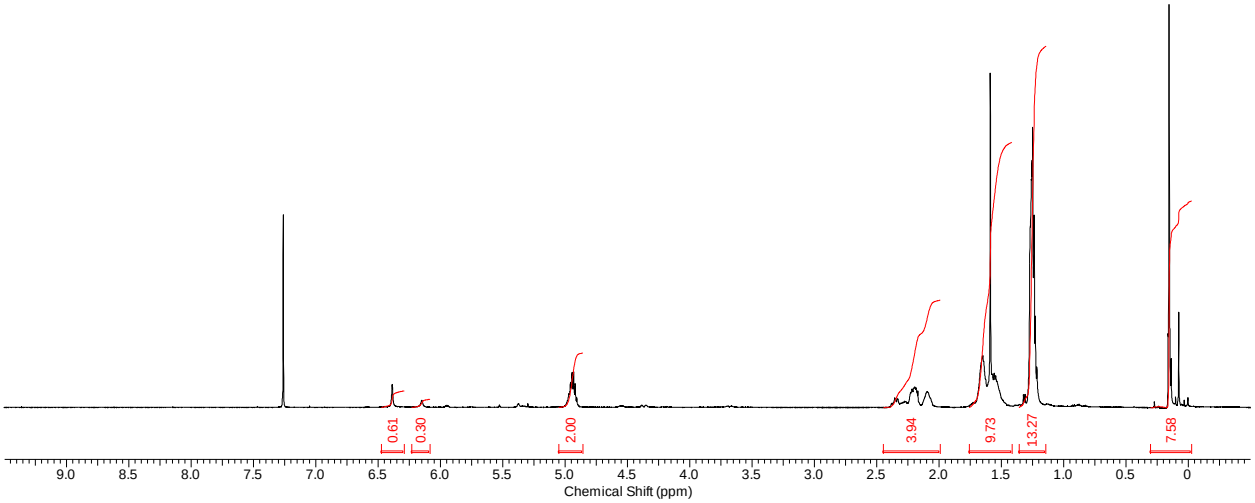
3-64n

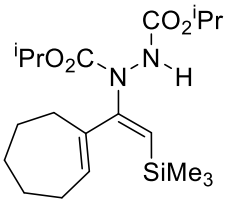

1.00
1.77
2.12
2.25
1.04
1.14
4.73
13.80
4.56
1.08
0.98
9.73
f1 (ppm)


155.0
154.3
147.4
140.7
129.6
119.9
119.8
110.5
77.3
77.0
76.8
70.4
69.4
39.4
24.0
22.0
21.9
21.2
17.6
15.4
0.4
f1 (ppm)

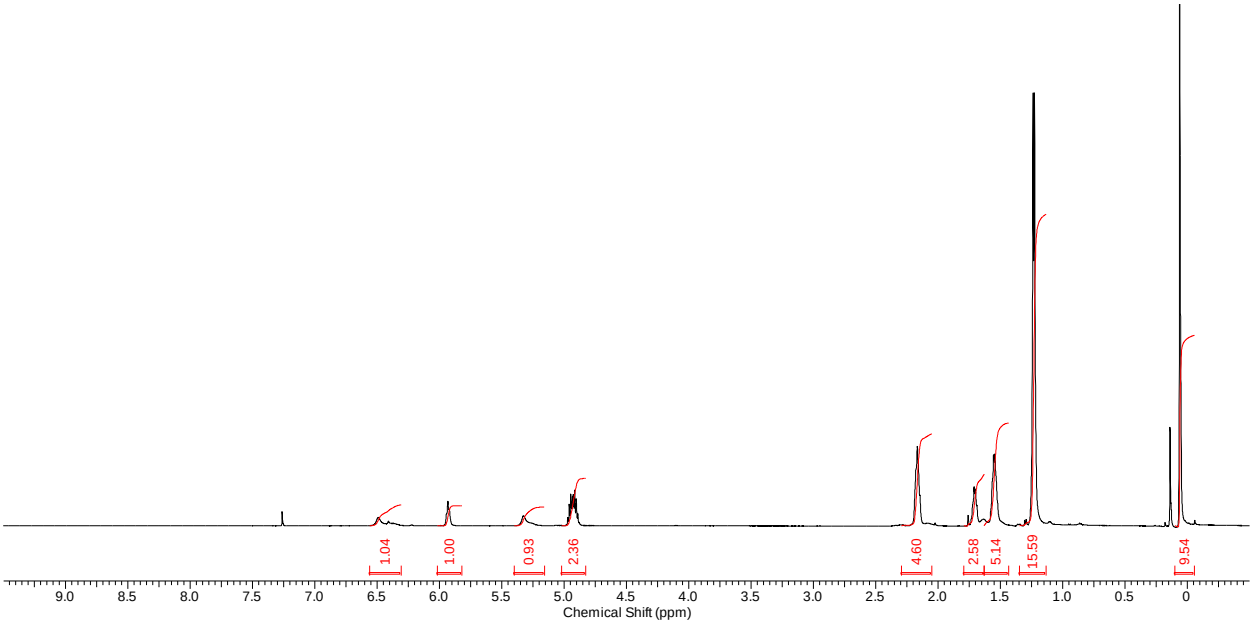

SiMe3
CO2iPr
N
N
H
CO2iPr

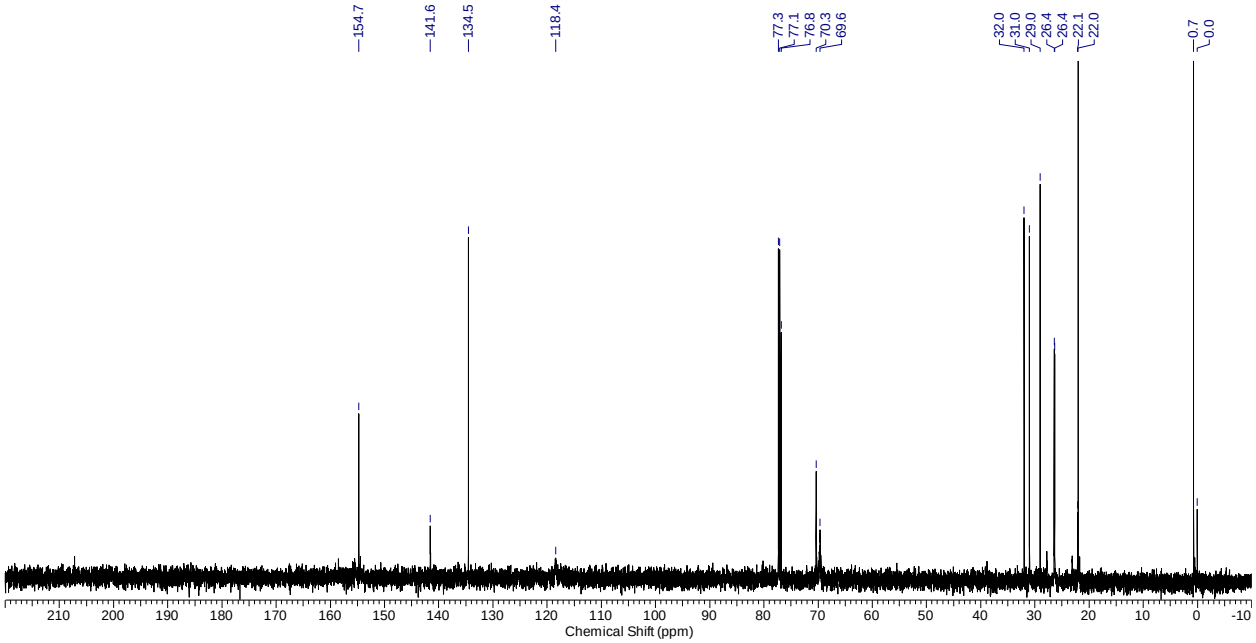
3-63o

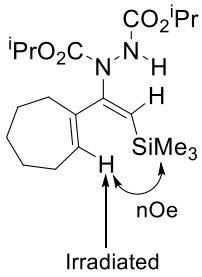

0.61
0.30
2.00
3.94
9.73
13.27
7.58
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

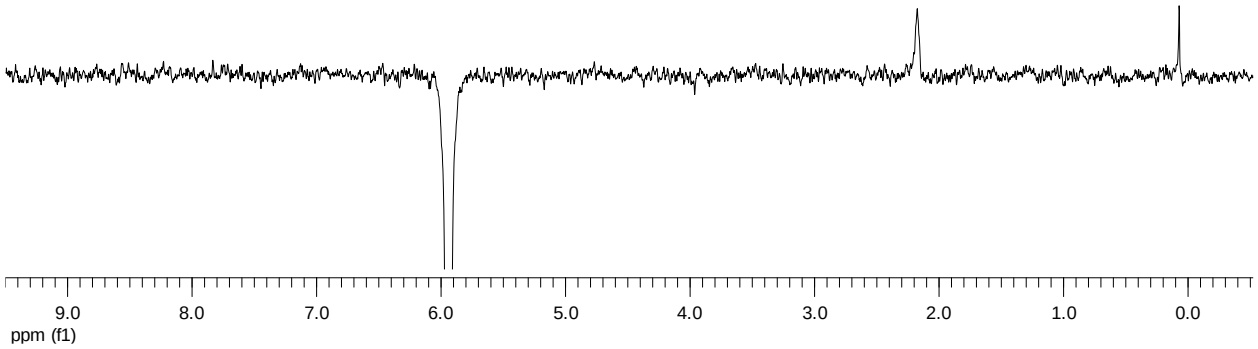

CO2iPr
iPrO2C
N
N
H
SiMe3

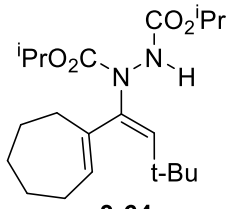
3-64o


1.04
1.00
0.93
2.36
4.60
2.58
5.14
15.59
9.54
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

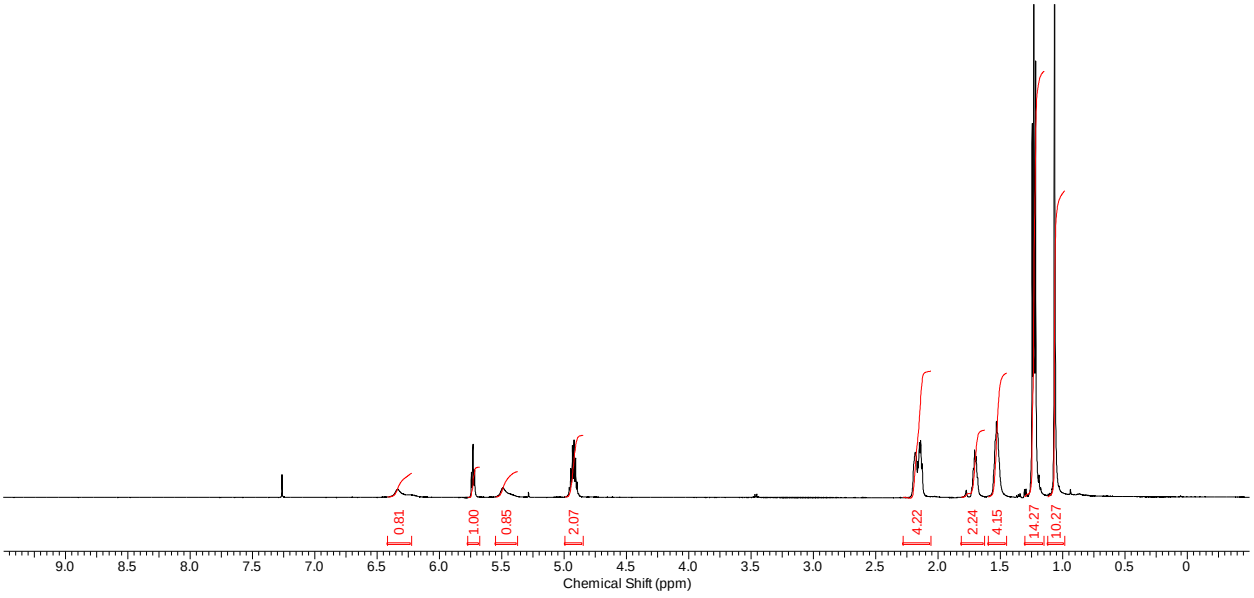

154.7
141.6
134.5
118.4
77.3
77.1
76.8
70.3
69.6
32.0
31.0
29.0
26.4
26.4
22.1
22.0
0.7
0.0
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
Chemical Shift (ppm)

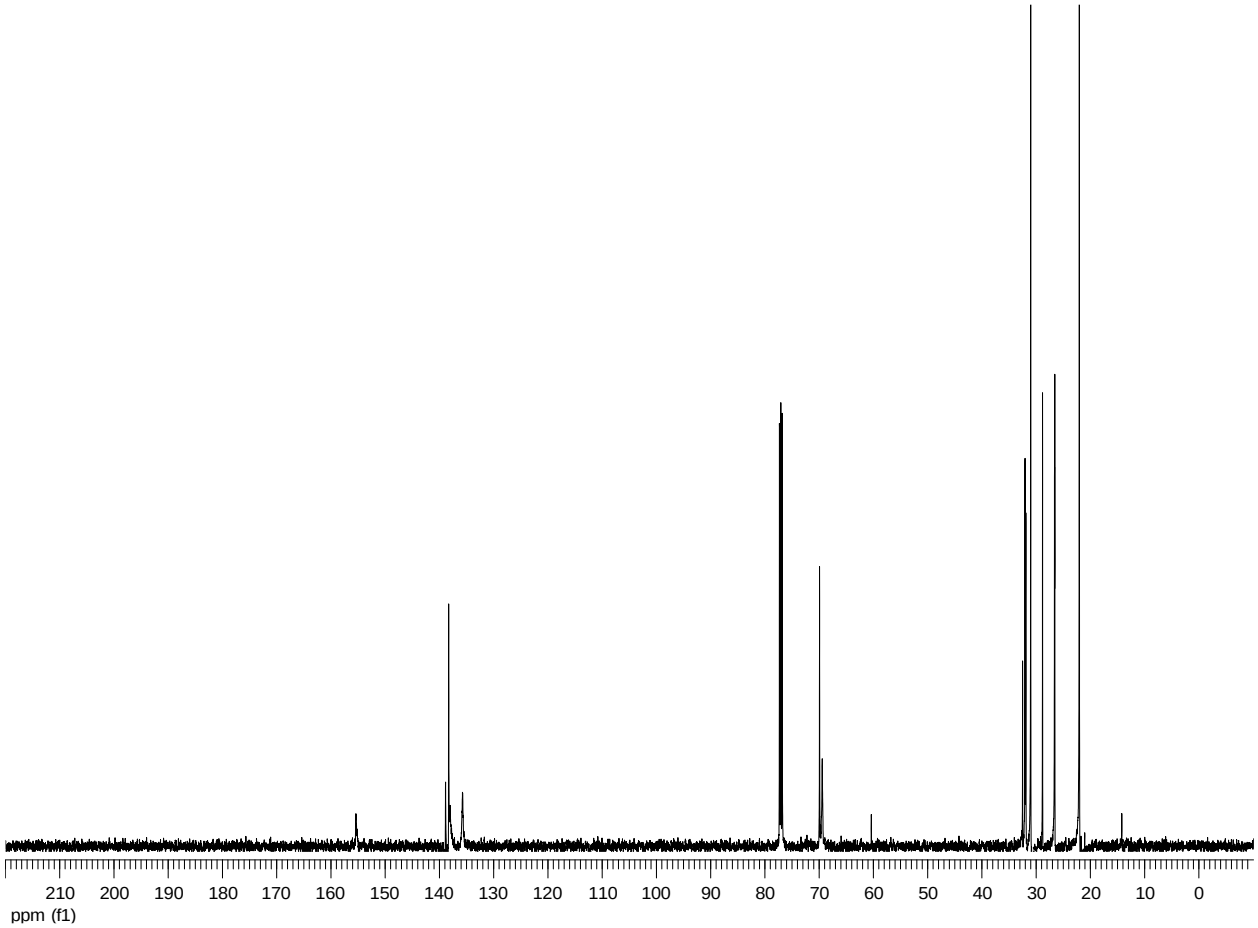

CO2iPr
iPrO2C
N
N
H
H
SiMe3
H
nOe
Irradiated

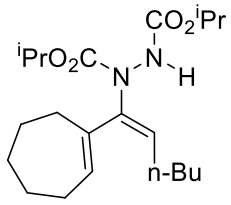

9.0 8.0 7.0 6.0 5.0 4.0 3.0 2.0 1.0 0.0
ppm (f1)


CO2iPr
iPrO2C
N
N
H
t-Bu

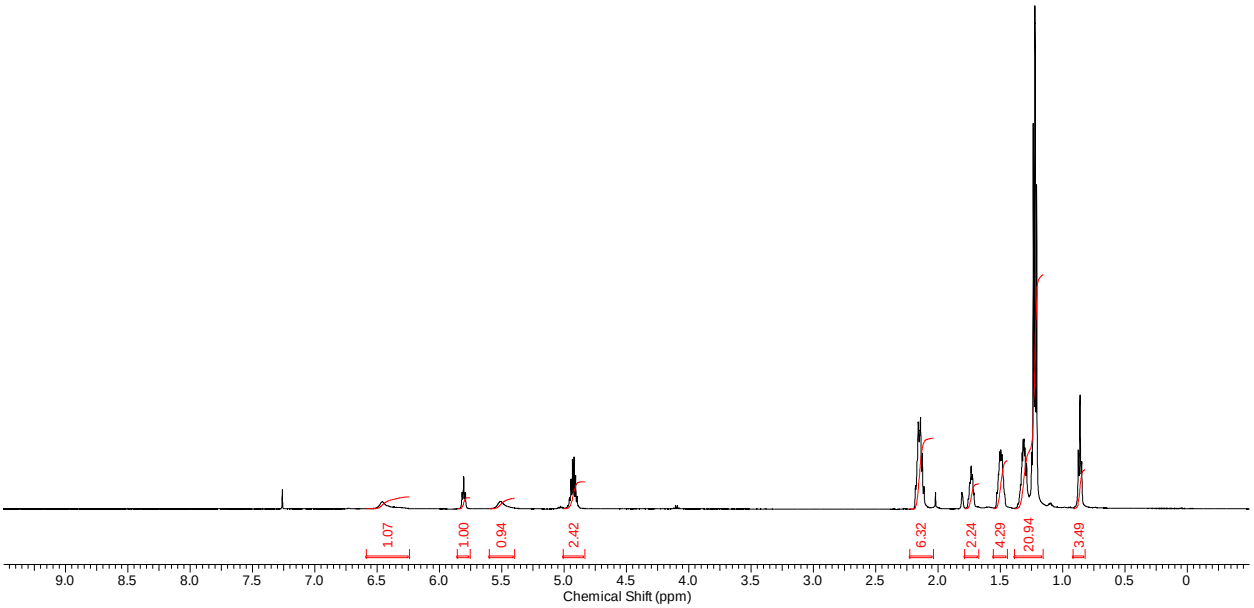
3-64p

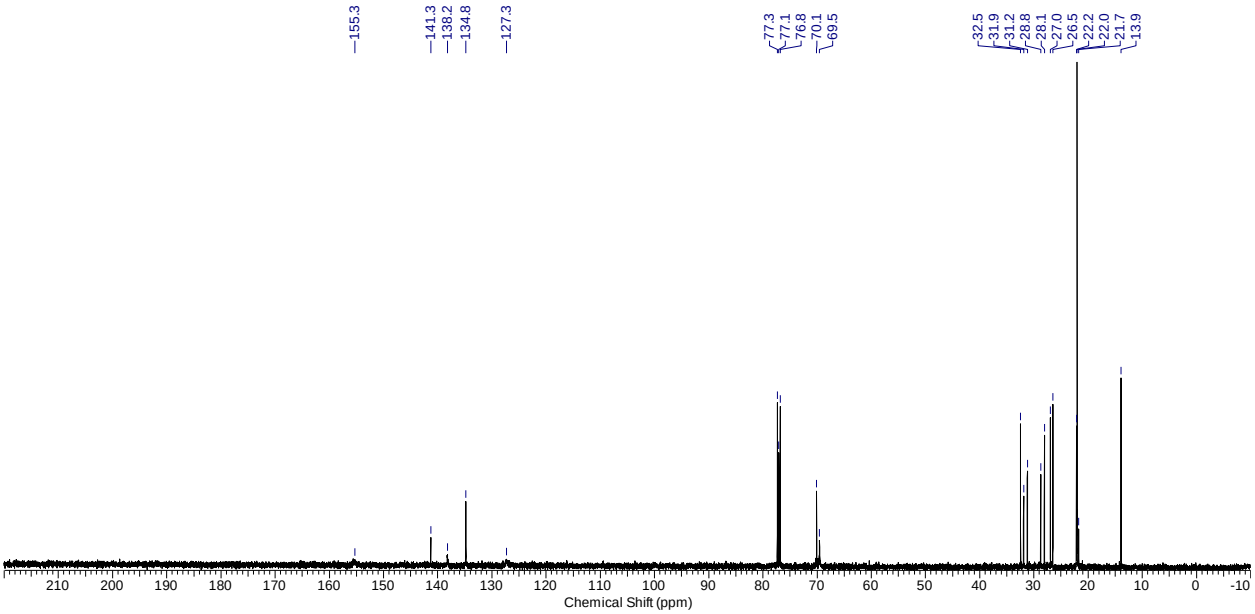

0.81
1.00
0.85
2.07
4.22
2.24
4.15
14.27
10.27
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
Chemical Shift (ppm)

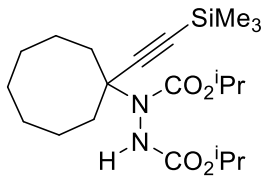

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
ppm (f1)


CO2iPr
iPrO2C
N
N
H
n-Bu

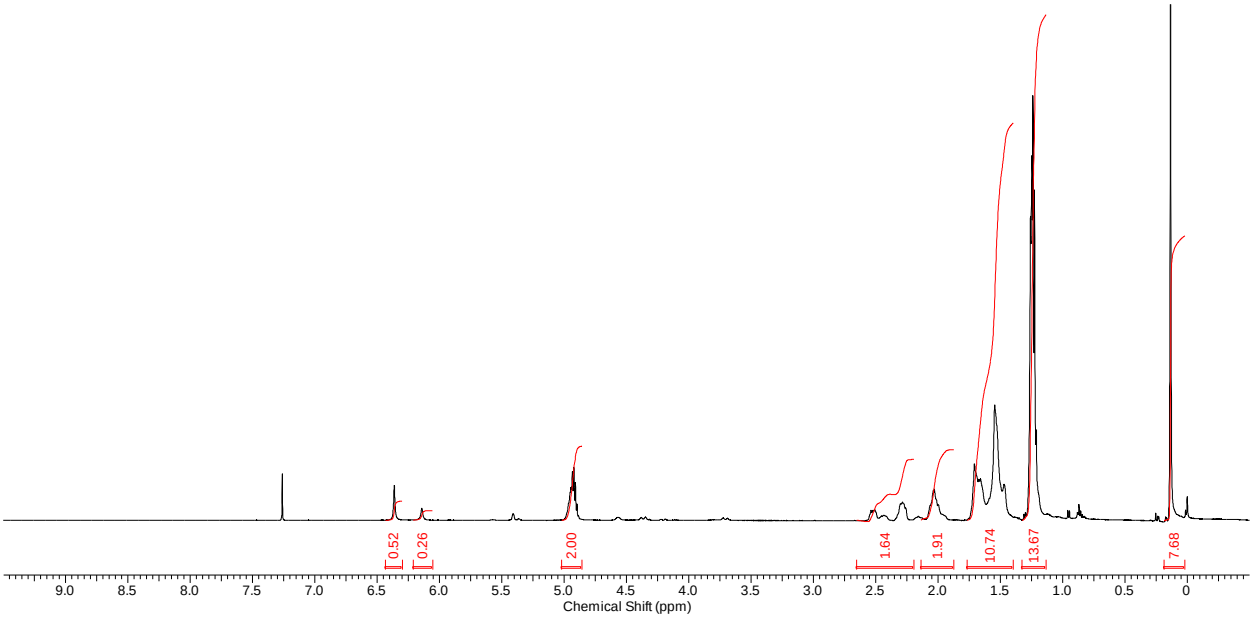
3-64q

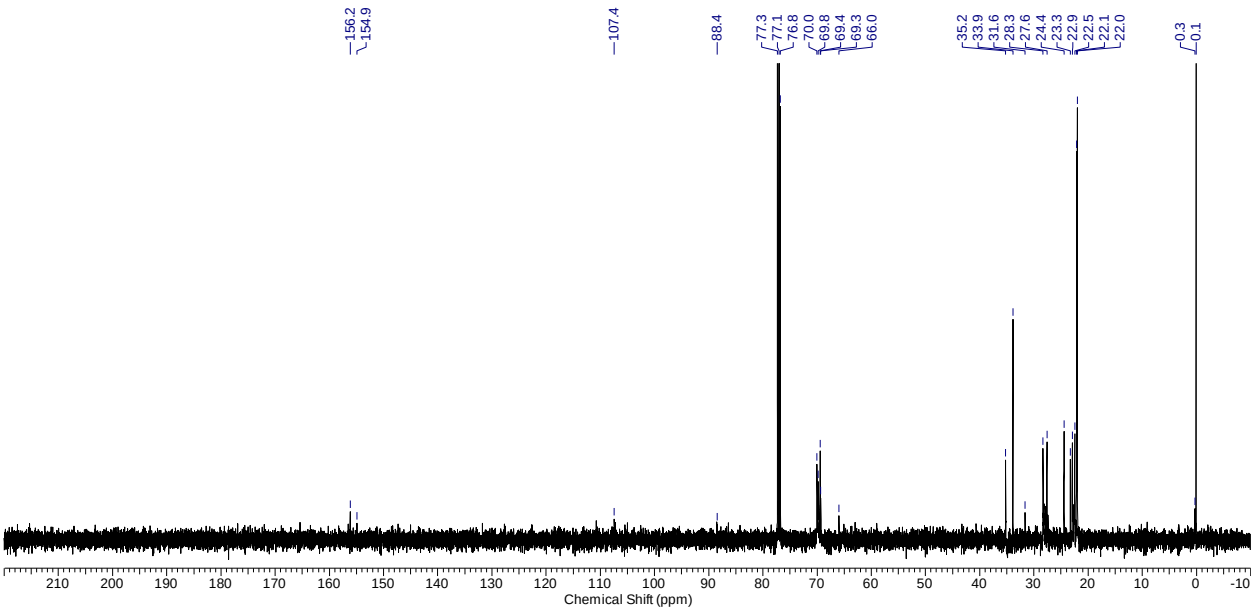

1.07
1.00
0.94
2.42
6.32
2.24
4.29
20.94
3.49
Chemical Shift (ppm)

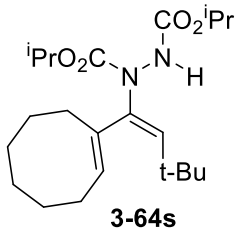

155.3
141.3
138.2
134.8
127.3
77.3
77.1
76.8
70.1
69.5
32.5
31.9
31.2
28.8
28.1
27.0
26.5
22.2
22.0
21.7
13.9
Chemical Shift (ppm)


SiMe3
CO2iPr
N
N
H
CO2iPr

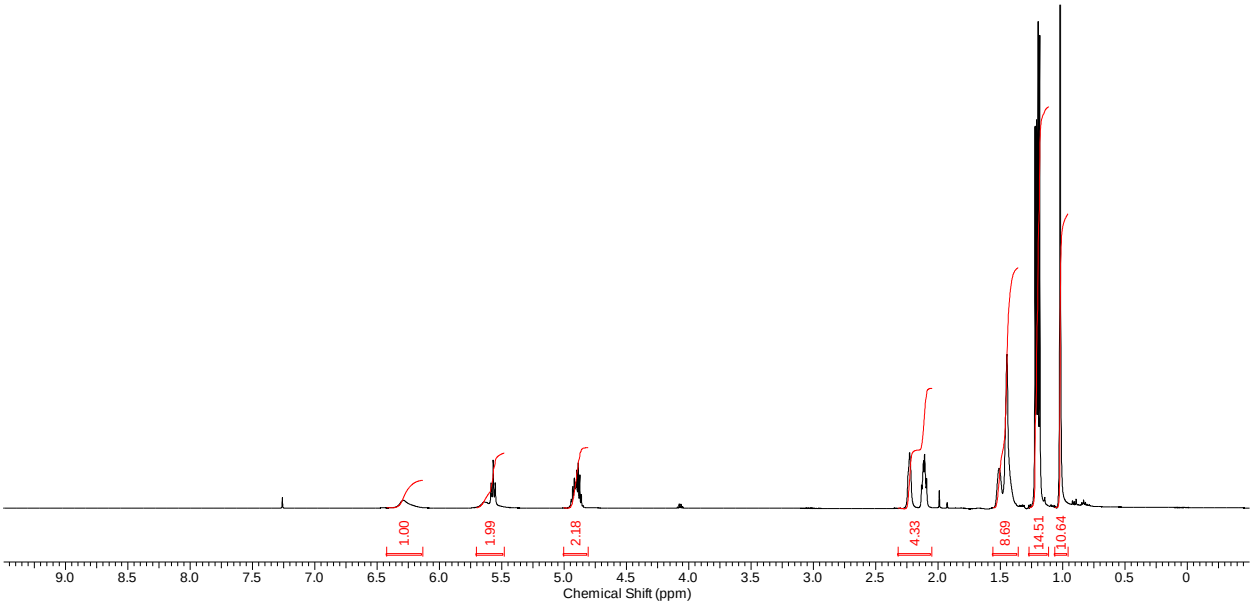
3-63r

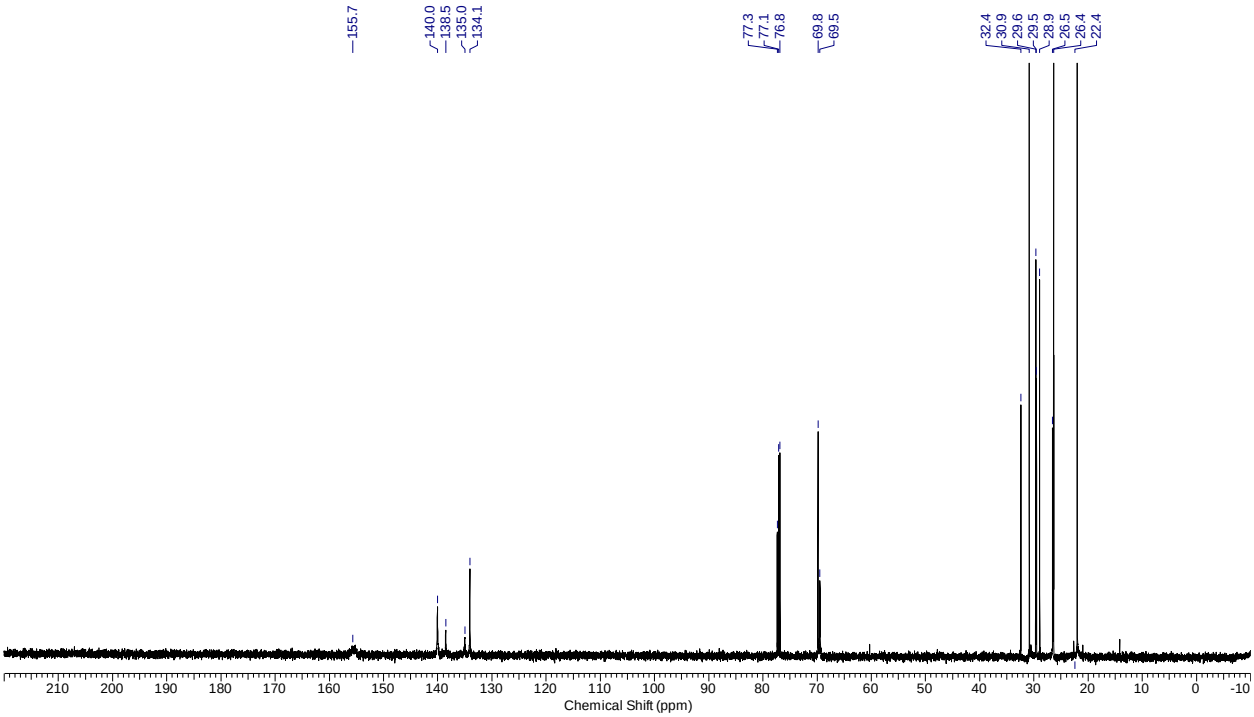

0.52
0.26
2.00
1.64
1.91
10.74
13.67
7.68
Chemical Shift (ppm)

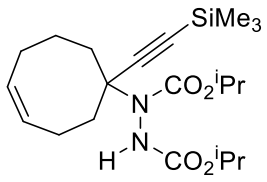

156.2
154.9
107.4
88.4
77.3
77.1
76.8
70.0
69.8
69.4
69.3
66.0
35.2
33.9
31.6
28.3
27.6
24.4
23.3
22.9
22.5
22.1
22.0
0.3
0.1
Chemical Shift (ppm)


CO2iPr
iPrO2C
N
N
H
t-Bu

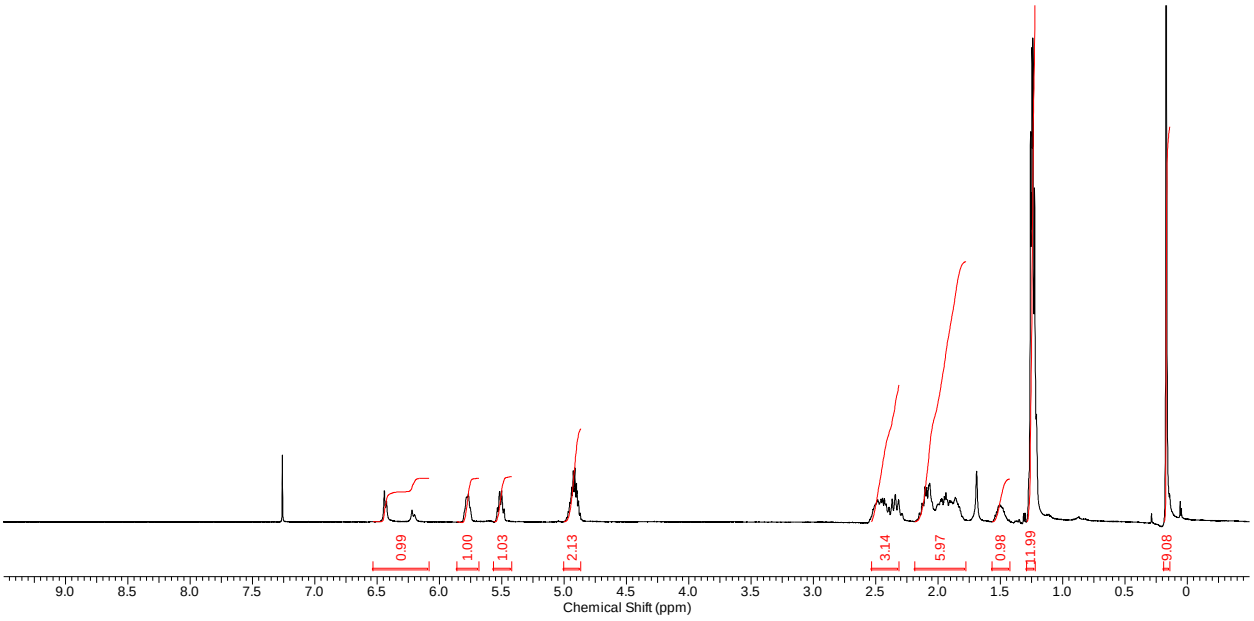
3-64s

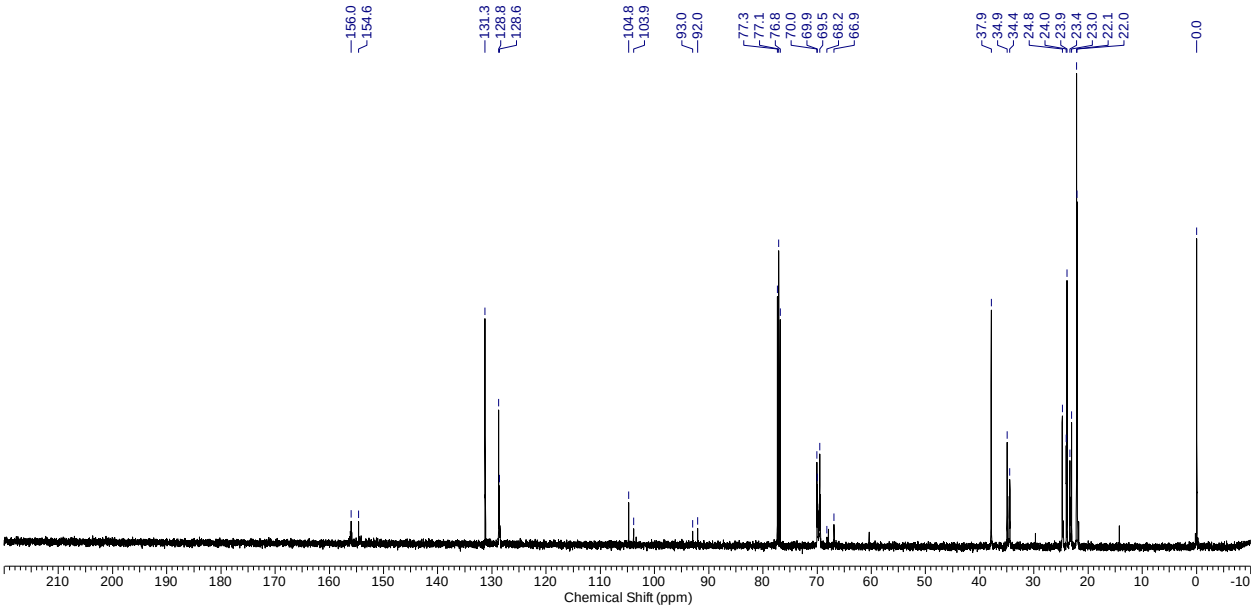

1.00
1.99
2.18
4.33
8.69
14.51
10.64
Chemical Shift (ppm)

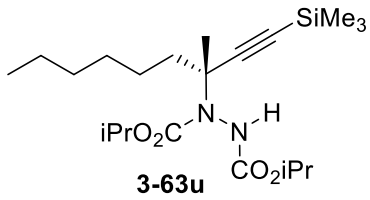

155.7
140.0
138.5
135.0
134.1
77.3
77.1
76.8
69.8
69.5
32.4
30.9
29.6
29.5
28.9
26.5
26.4
22.4
Chemical Shift (ppm)


SiMe3
CO2iPr
N
N
H
CO2iPr

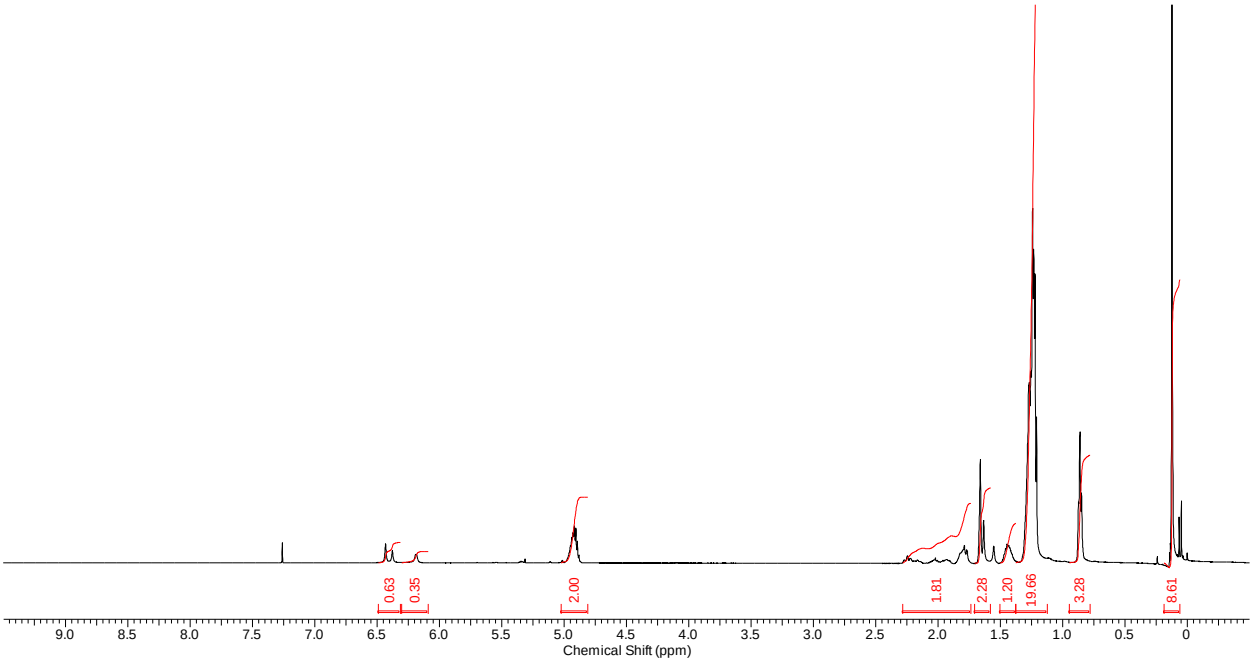
3-63t

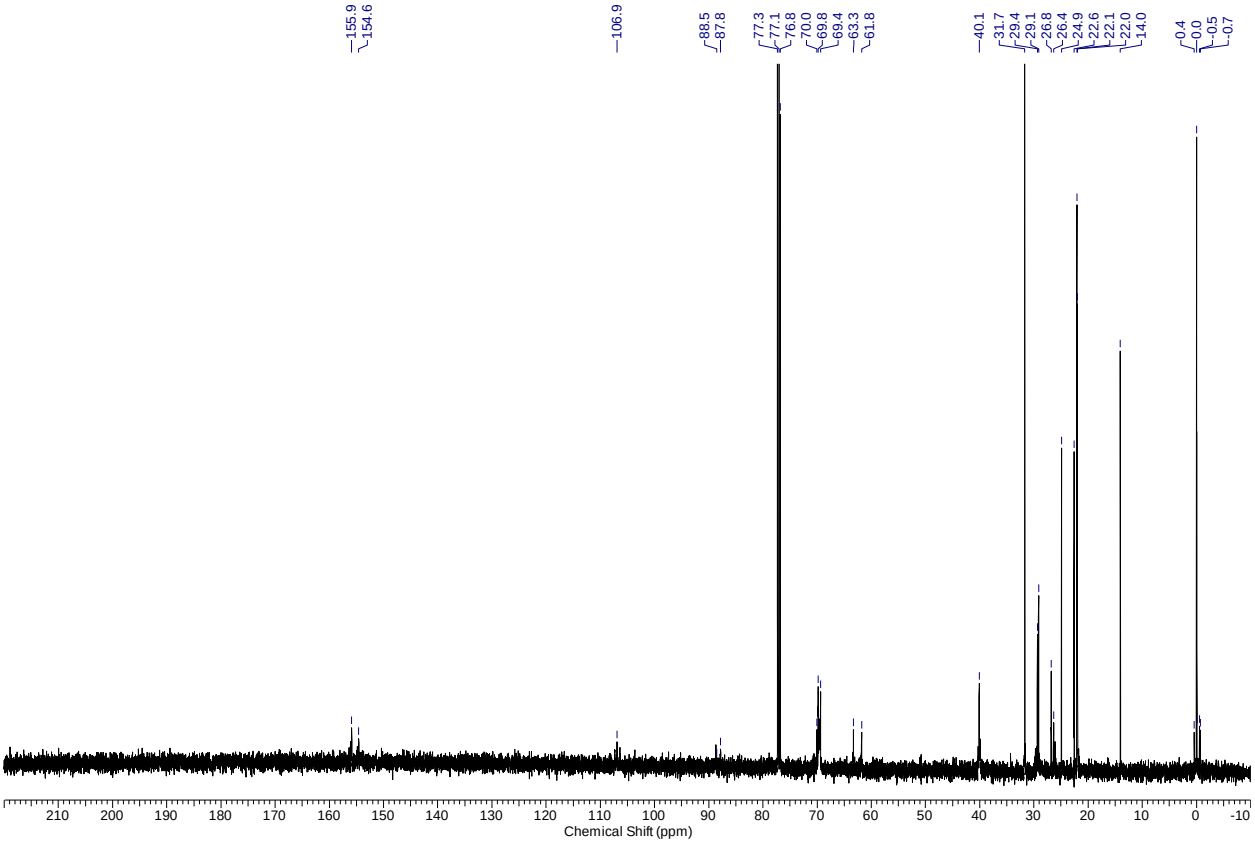

0.99
1.00
1.03
2.13
3.14
5.97
0.98
11.99
9.08
Chemical Shift (ppm)

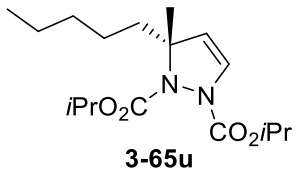

156.0
154.6
131.3
128.8
128.6
104.8
103.9
93.0
92.0
77.3
77.1
76.8
70.0
69.9
69.5
68.2
66.9
37.9
34.9
34.4
24.8
24.0
23.9
23.4
23.0
22.1
22.0
0.0
Chemical Shift (ppm)


SiMe3
iPrO2C
N
N
H
CO2iPr

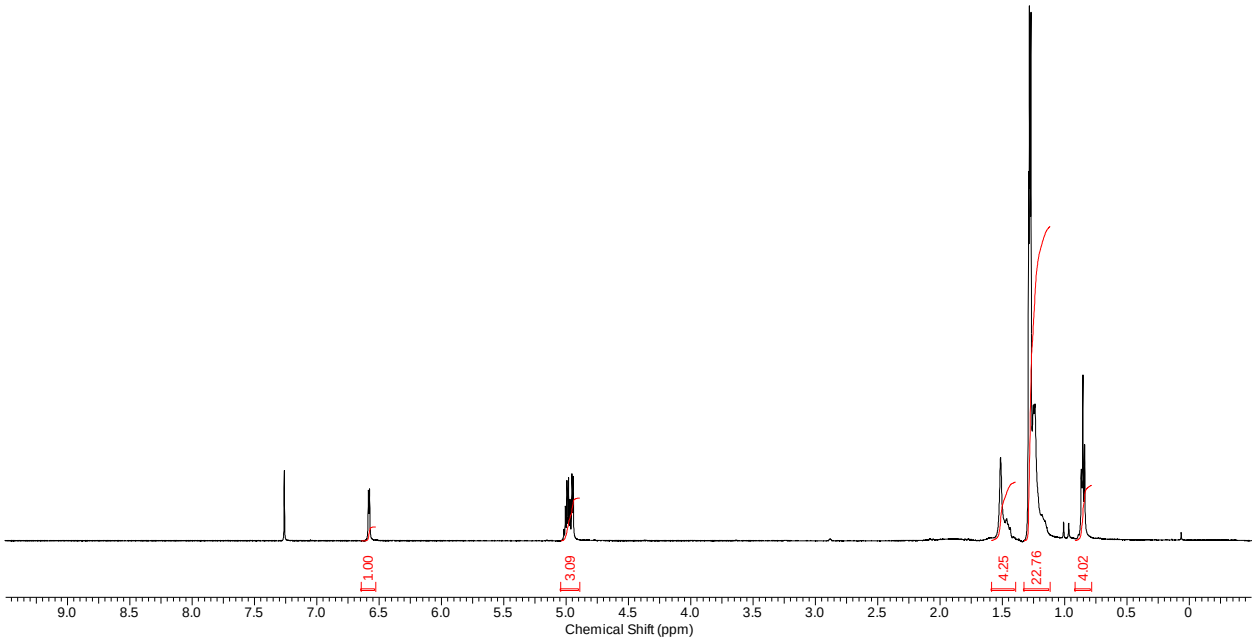
3-63u

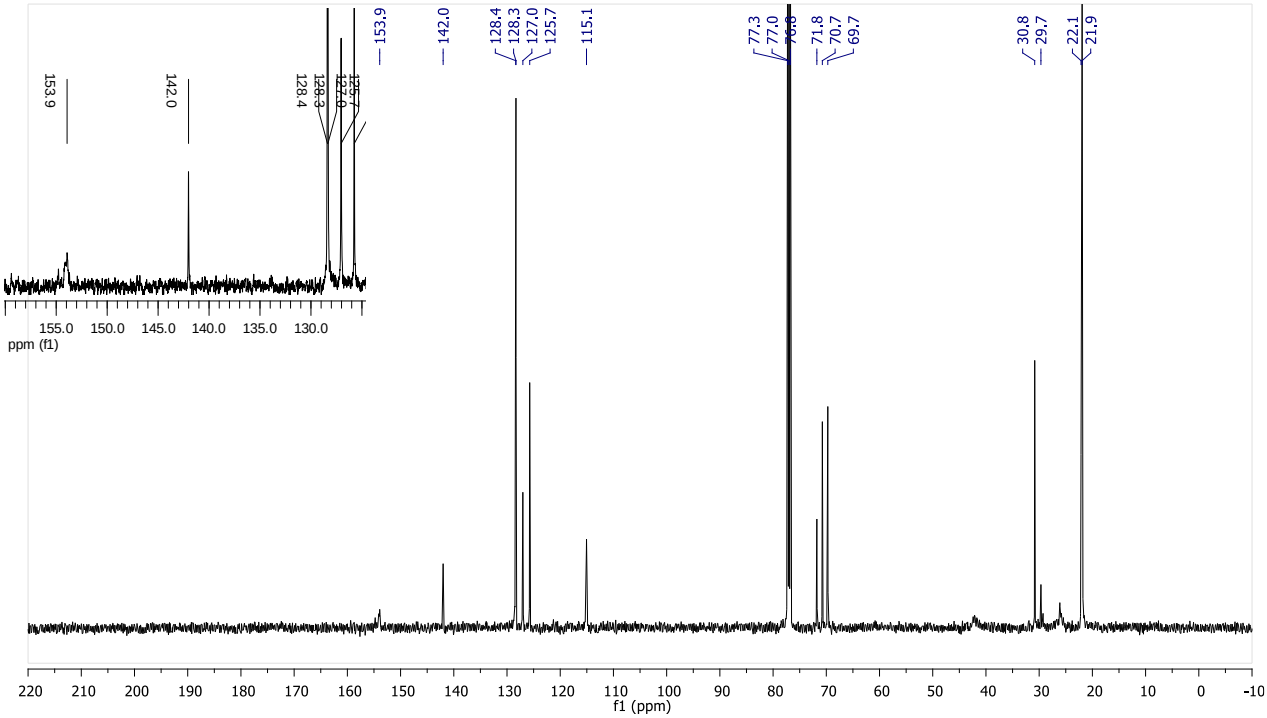

0.63
0.35
2.00
1.81
2.28
1.20
19.66
3.28
8.61
Chemical Shift (ppm)

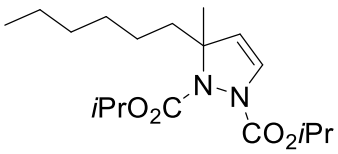

155.9
154.6
106.9
88.5
87.8
77.3
77.1
76.8
70.0
69.8
69.4
63.3
61.8
40.1
31.7
29.4
29.1
26.8
26.4
24.9
22.6
22.1
22.0
14.0
0.4
0.0
-0.5
-0.7
Chemical Shift (ppm)


iPrO2C
N
N
CO2iPr

3-65u

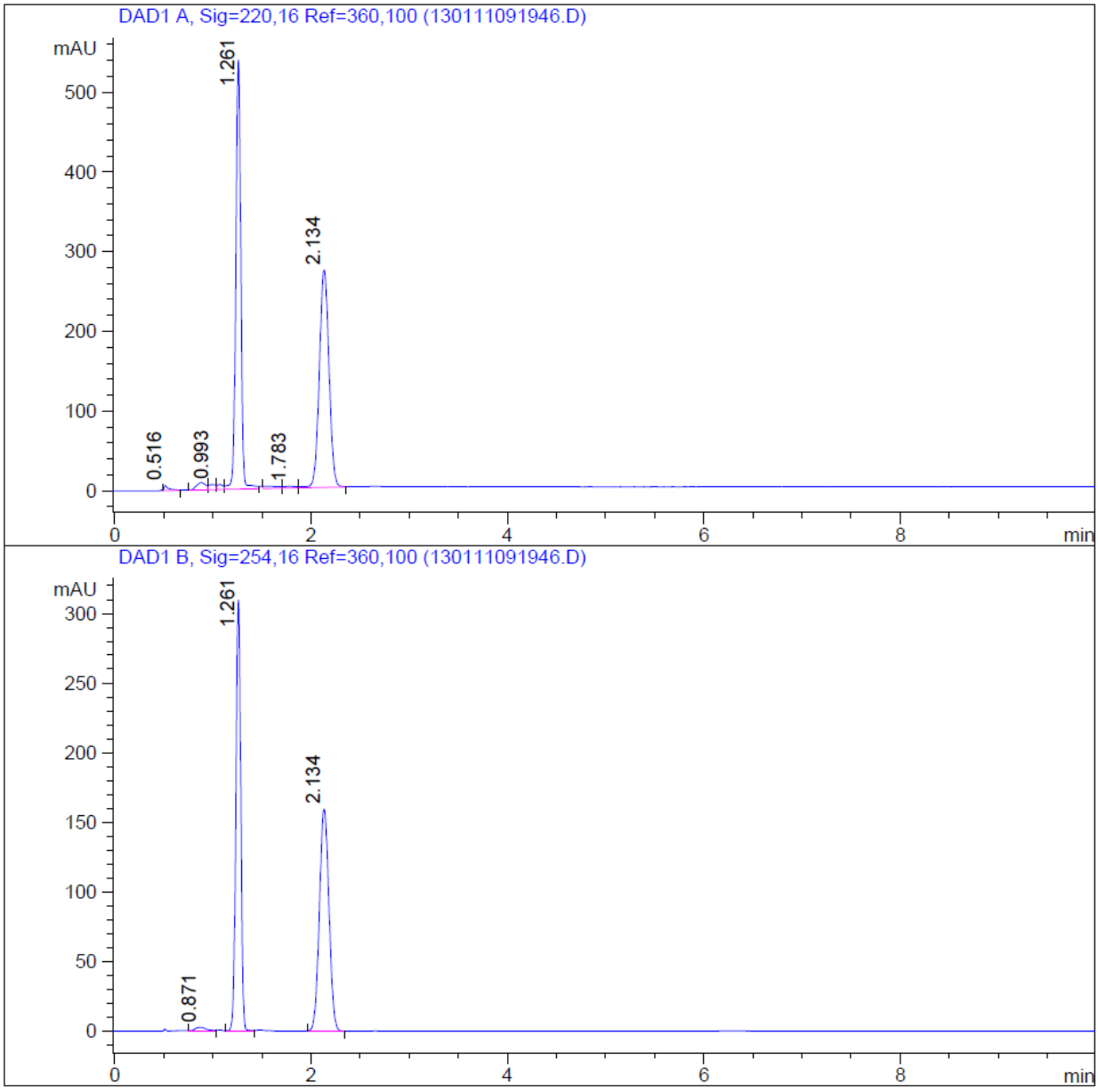

1.00
3.09
4.25
22.76
4.02
Chemical Shift (ppm)


153.9
142.0
128.4
128.3
127.0
125.7
115.1
77.3
77.0
76.6
71.8
70.7
69.7
30.8
29.7
22.1
21.9
ppm (f1)
f1 (ppm)



3-65u (racemic)

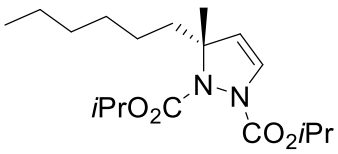
```
Acq. Method :  C:\CHEM32\1\METHODS\2_iso_MEOH_3ML_10MIN_150BAR.M
               isocratic 2% MeOH:CO2  10min @ 3ml/min  150bar
Column Position 6: ChiralPak IC
```



Signal Description : DAD1 A, Sig=220,16 Ref=360,100

#	RT [min]	Width	Height	Area	Area %
1	0.516	0.045	6.404	20.776	0.526
2	0.879	0.092	9.456	59.468	1.504
3	0.993	0.073	6.290	32.033	0.810
4	1.074	0.057	6.401	25.960	0.657
5	1.261	0.054	539.071	1.909e3	48.279
6	1.584	0.134	2.771	28.674	0.725
7	1.783	0.122	2.122	19.659	0.497
8	2.134	0.107	272.506	1.858e3	47.002

#	RT [min]	Width	Height	Area	Area %
1	0.871	0.122	2.726	23.694	1.089
2	1.261	0.054	310.066	1.072e3	49.288
3	2.134	0.106	159.510	1.079e3	49.622



3-65u (chiral)

```
Acq. Method :  C:\CHEM32\1\METHODS\2_iso_MEOH_3ML_10MIN_150BAR.M
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Column Position 6: ChiralPak IC
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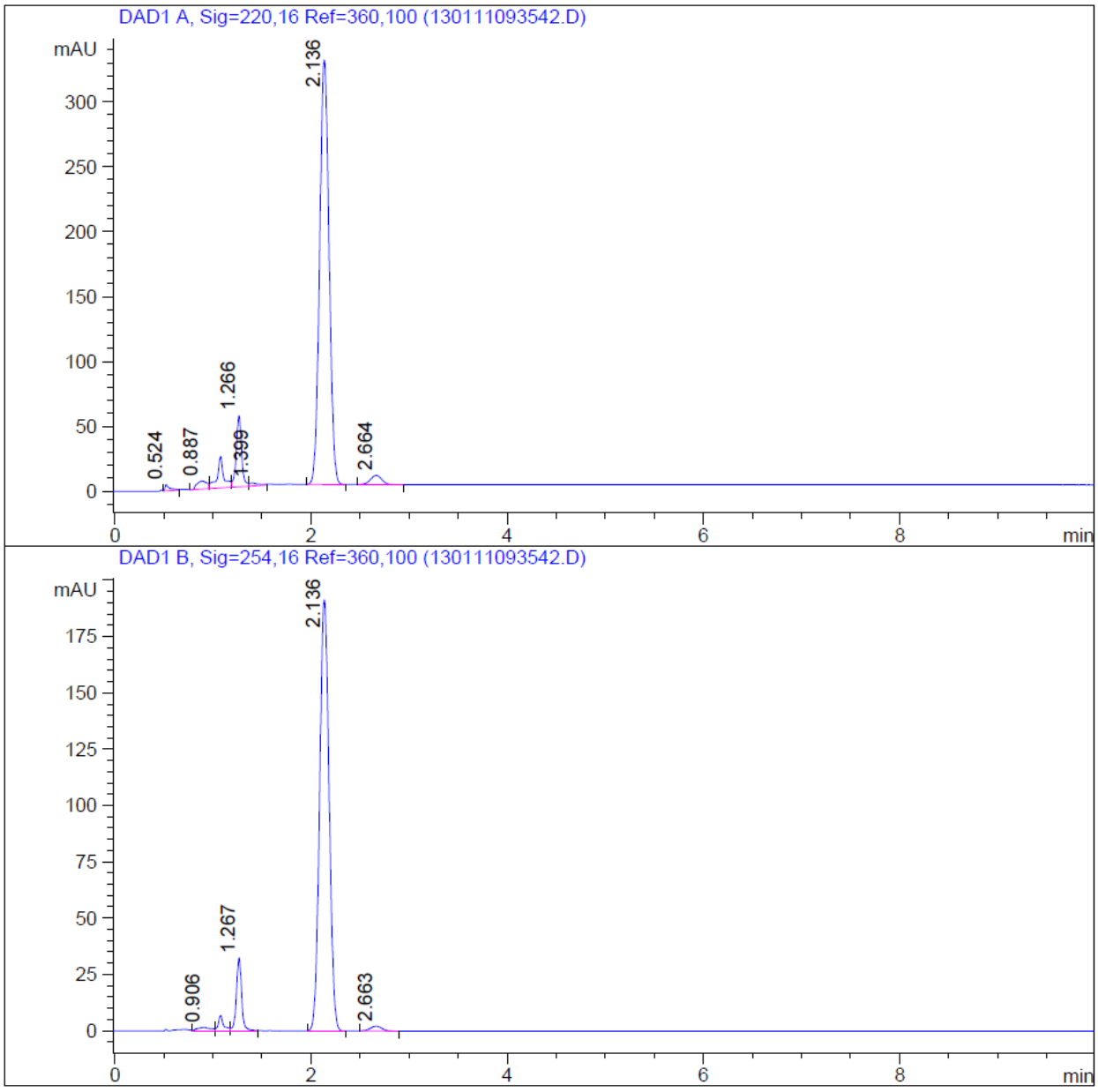
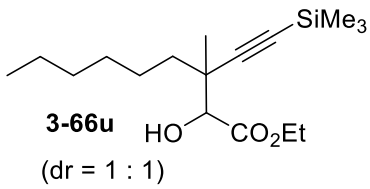


Signal Description : DAD1 A, Sig=220,16 Ref=360,100

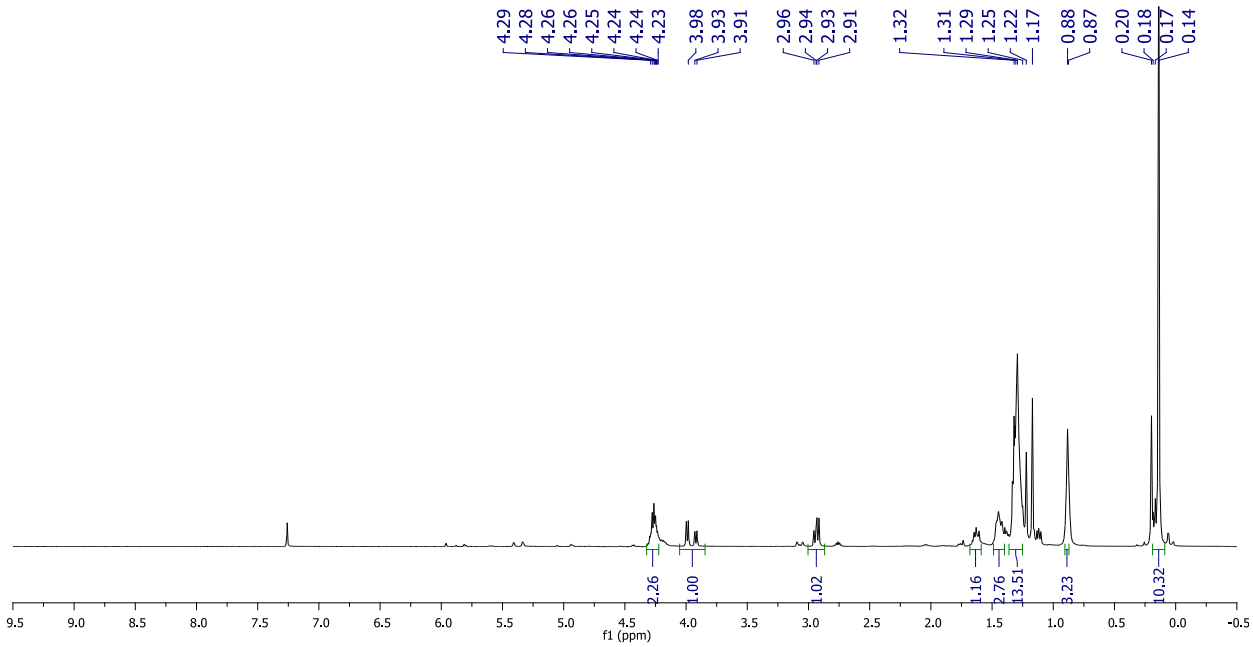
#	RT [min]	Width	Height	Area	Area %
1	0.524	0.048	4.677	16.640	0.633
2	0.887	0.100	6.159	42.211	1.606
3	1.079	0.065	24.045	114.140	4.342
4	1.266	0.059	54.713	208.777	7.943
5	1.399	0.090	2.222	14.408	0.548
6	2.136	0.104	326.995	2.174e3	82.703
7	2.664	0.129	7.195	58.486	2.225

#	RT [min]	Width	Height	Area	Area %
1	0.906	0.123	1.553	14.646	1.006
2	1.079	0.055	6.758	26.109	1.793
3	1.267	0.056	32.292	119.321	8.195
4	2.136	0.104	191.291	1.278e3	87.773
5	2.663	0.130	2.192	17.946	1.233


SiMe3
HO
CO2Et

3-66u

(dr = 1 : 1)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4.28
4.26
4.26
4.25
4.24
4.24
4.23
3.98
3.93
3.91
2.96
2.94
2.93
2.91
1.32
1.31
1.29
1.25
1.22
1.17
0.88
0.87
0.20
0.18
0.17
0.14
2.26
1.00
1.02
1.16
2.76
13.51
3.23
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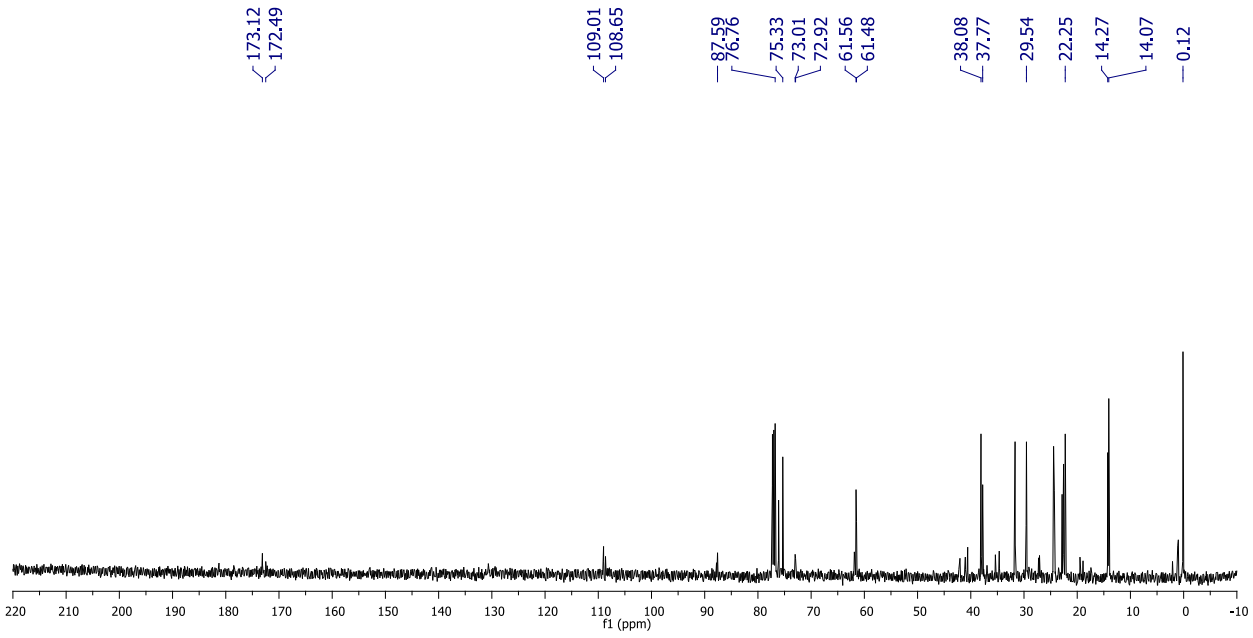
f1 (ppm)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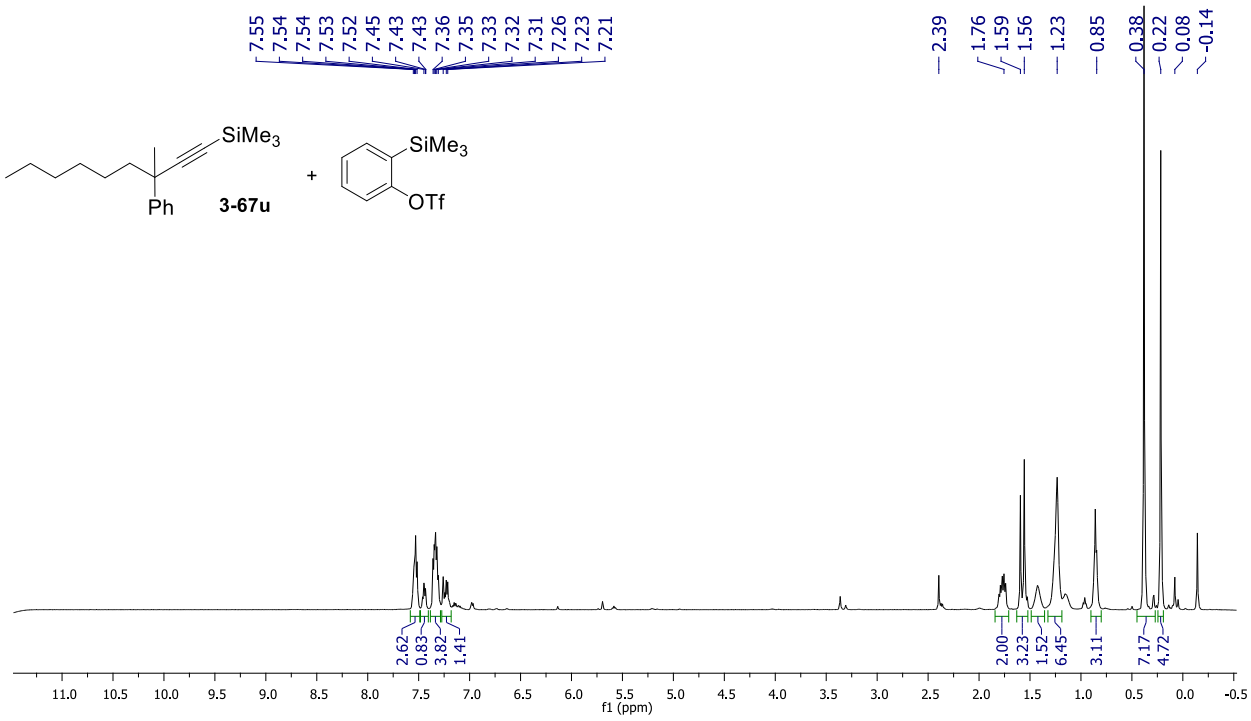
172.49
109.01
108.65
87.59
76.76
75.33
73.01
72.92
61.56
61.48
38.08
37.77
29.54
22.25
14.27
14.07
0.12
f1 (ppm)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7.54
7.54
7.53
7.52
7.45
7.43
7.43
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7.35
7.33
7.32
7.31
7.26
7.23
7.21
2.39
1.76
1.59
1.56
1.23
0.85
0.38
0.22
0.08
-0.14
SiMe3
Ph
3-67u
+
SiMe3
OTf
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0.83
3.82
1.41
2.00
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1.52
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3.11
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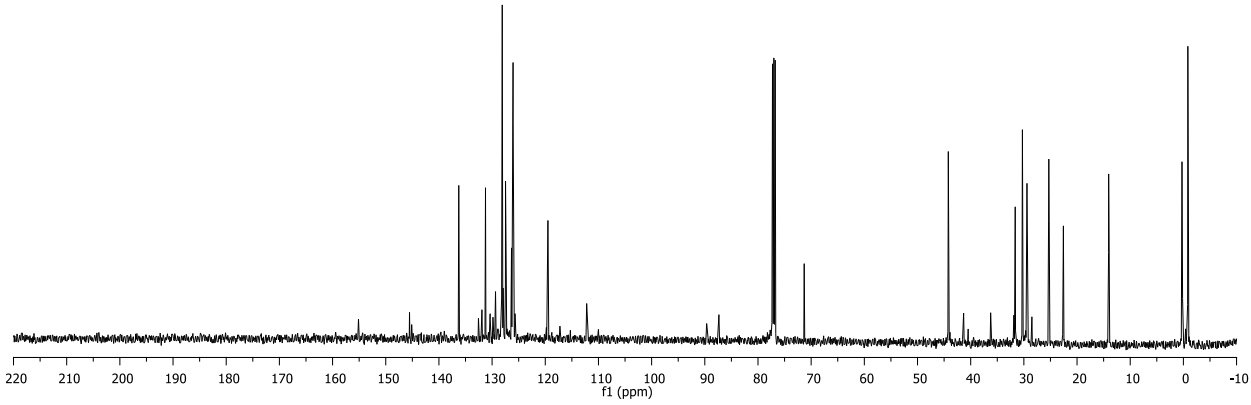
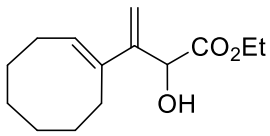
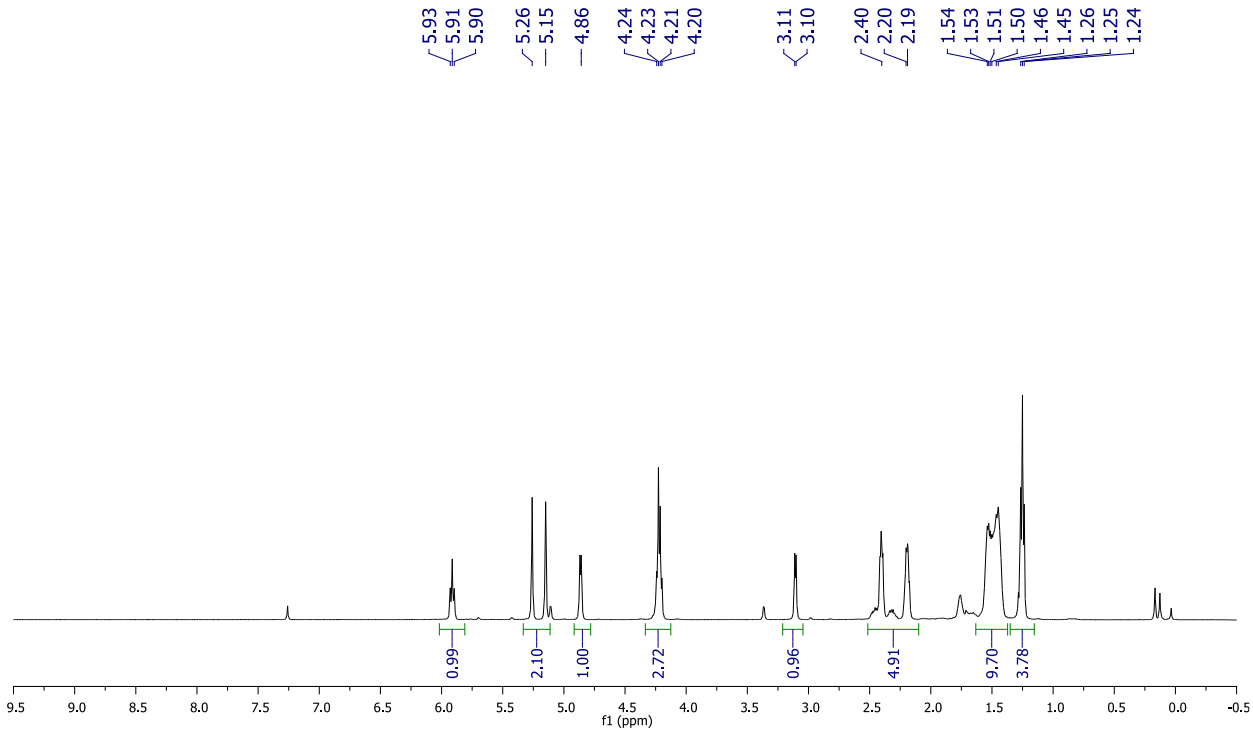
4.72
f1 (ppm)


f1 (ppm)


CO2Et
OH

3-68r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4.24
4.23
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4.20
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3.10
2.40
2.20
2.19
1.54
1.53
1.51
1.50
1.46
1.45
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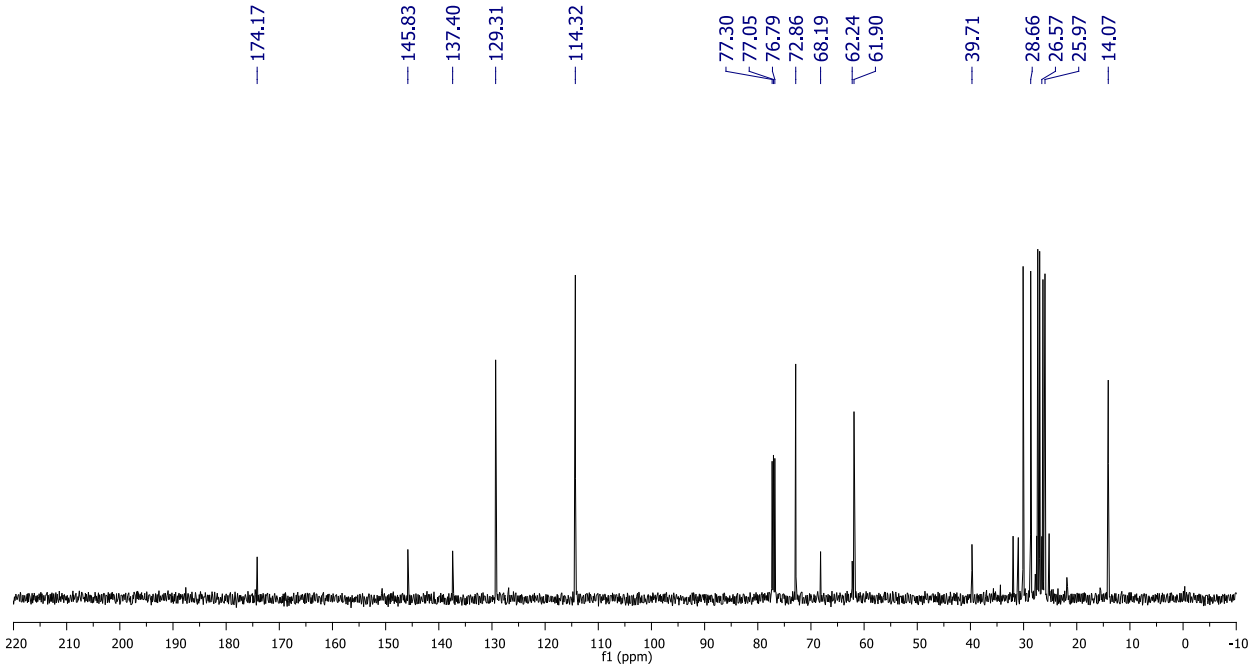
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68.19
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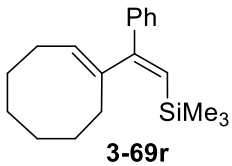
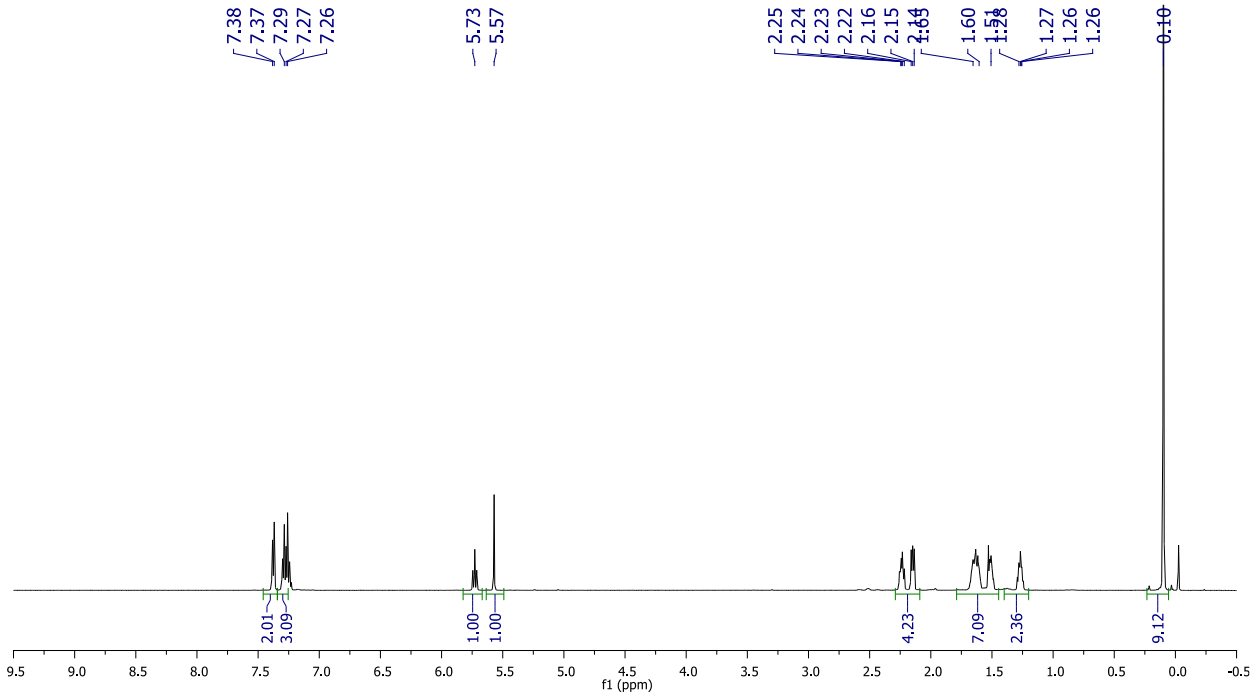
f1 (ppm)


Ph
SiMe3

3-69r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5.73
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2.25
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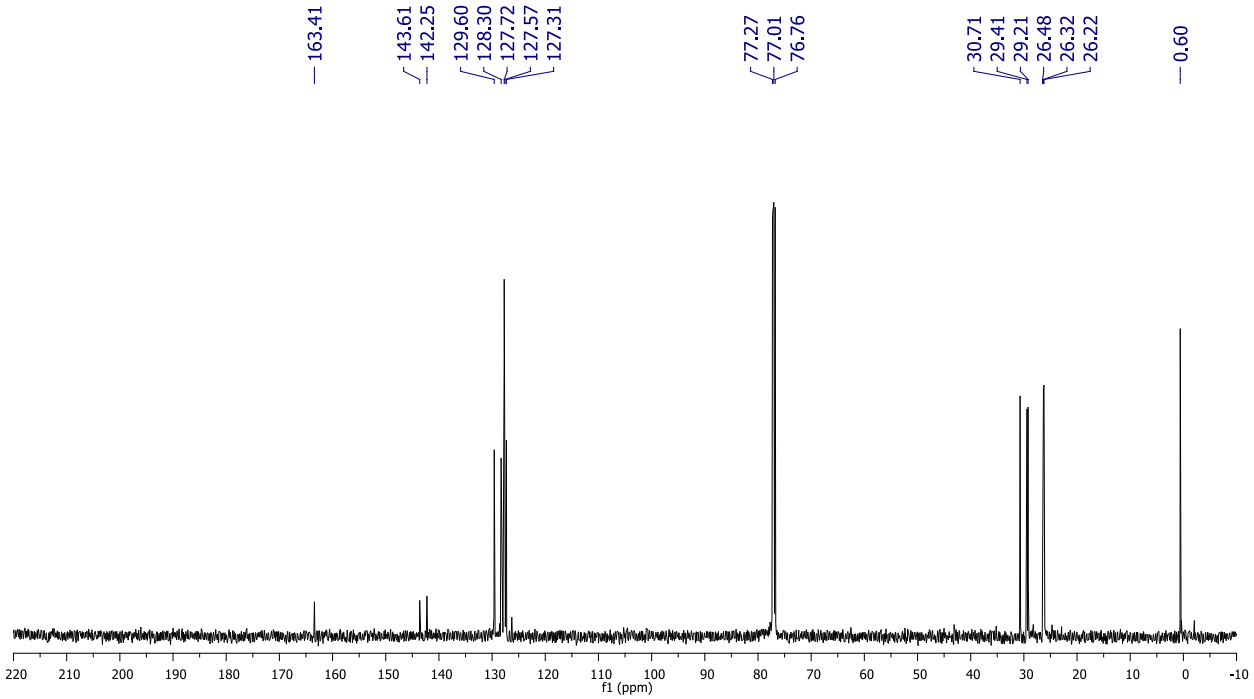
2.23
2.22
2.16
2.15
1.60
1.27
1.26
1.26
0.10
2.01
3.09
1.00
1.00
4.23
7.09
2.36
9.12
f1 (ppm)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127.57
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29.21
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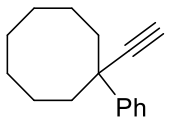
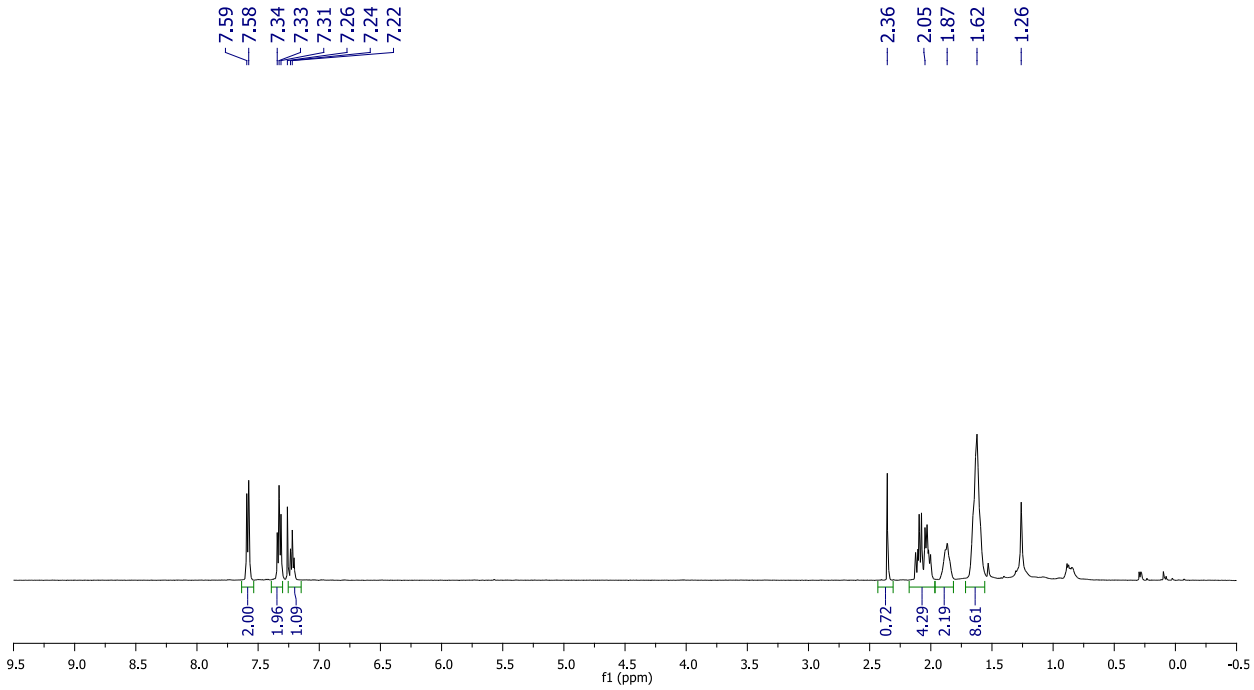
f1 (ppm)


Ph

3-70r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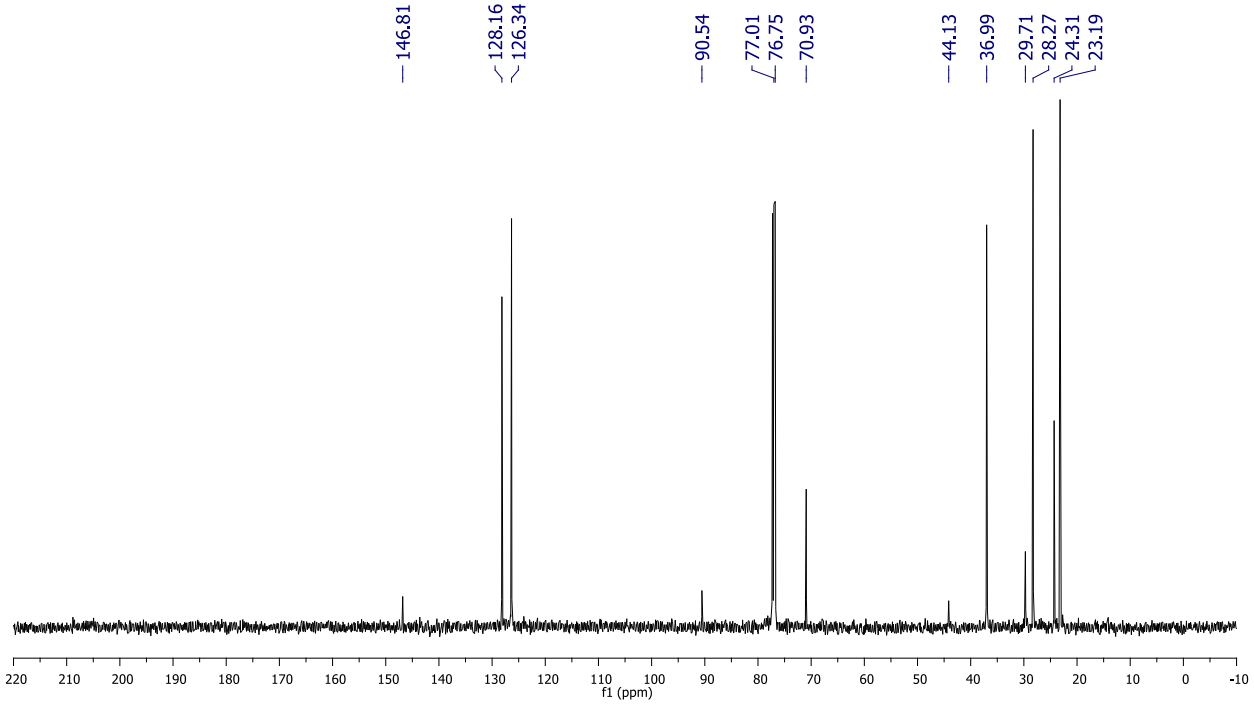
7.58
7.34
7.33
7.31
7.26
7.24
7.22
2.36
2.05
1.87
1.62
1.26
2.00
1.96
1.09
0.72
4.29
2.19
8.61
f1 (ppm)


146.81
128.16
126.34
90.54
77.01
76.75
70.93
44.13
36.99
29.71
28.27
24.31
23.19
f1 (ppm)

Computational Details

All DFT calculations were carried out with the Gaussian 09 suite of computational programs.[1] The geometries of all stationary points were optimized using the M06-2X hybrid functional[2] at the basis set level of 6-311++G(2d,p). Frequencies were analytically computed at the same level of theory to obtain the free energies and to confirm whether the structures are minima (no imaginary frequency) or transition states (only one imaginary frequency). The solvent effect (dichloromethane, ε =8.93) was included in all optimization and frequency calculations by using the SMD polarizable continuum model.[3] All transition state structures were confirmed to connect the proposed reactants and products by intrinsic reaction coordinate (IRC)[4] calculations.

The bond dissociation energy is the standard enthalpy change for the hemolytic cleavage of the bond at 0 K and was calculated with the above method. Calculations with other methods resulted in similar results (Table S1). The distortion energies in Table S2 are the energies required for the distortion of two reacting moieties to reach the geometries in the TS, which show that the allene is much more distorted in case of **TS-H$_b$** than in **TS-H$_a$**.

[1] Gaussian 09, Revision A.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö.Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian, Inc., Wallingford CT, **2009**.

[2] Y. Zhao, D. G. Truhlar, *Theor.Chem. Acc*. **2008**, *120*, 215.

[3] A. V. Marenich, C. J. Cramer, D. G. Truhlar, *J. Phys. Chem. B***2009**, *113*, 6378.

[4] a) C. Gonzalez, H. B. Schlegel, *J. Chem. Phys*. **1989**, *90*, 2154; b) C. Gonzalez, H. B. Schlegel, *J. Phys. Chem.* **1990**, *94*, 5523.

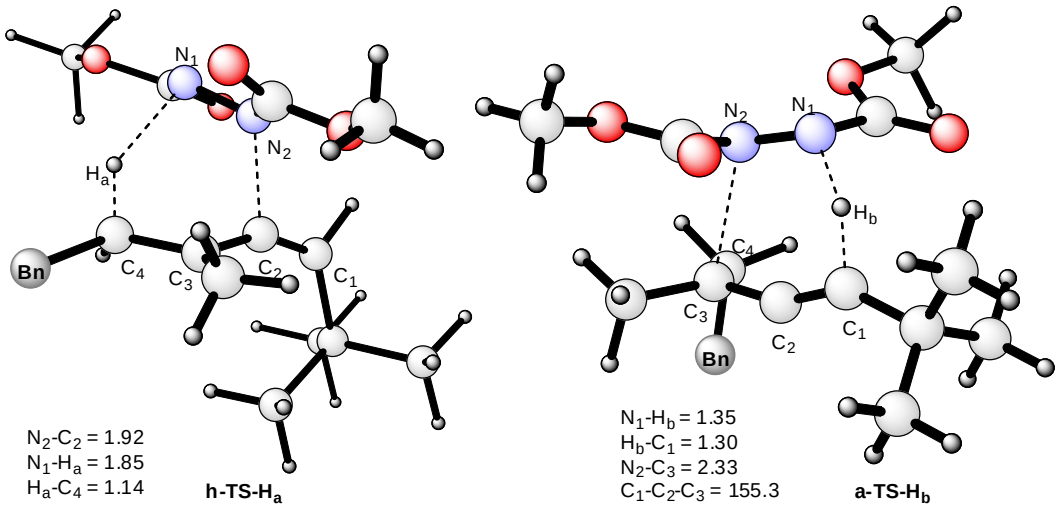
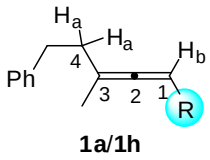


Figure SI. Geometric Structures for **h-TS-H$_a$** and **h-TS-H$_b$**, distances and angle are in Angstrom and degree, respectively.

Table S1. Bond Dissociation Energies Calculated with Other Methods



1a/1h

R	$D_0(C_4\text{-}H_a)^{a,b}$	$D_0(C_1\text{-}H_b)^{a,b}$
$SiMe_3$ (**1a**)	88.1 (84.0)	82.4 (77.9)
*t*Bu (**1h**)	88.2 (84.0)	87.6 (83.6)

[a] in kcal/mol
[b] values calculated at the M06-2X/6-31+G(d) and B3LYP/6-311++G(2d,p) (in parenthesis) levels, respectively.

Table S2. Distortion Energies for Key TS (in kcal/mol)

Allene	TS	ΔE_{dist}(EN=NE)[a]	ΔE_{dist} (Allene)[b]	ΔE_{dist}(Total)[c]
1a (R = $SiMe_3$)	**a-TS-H$_a$**	8.3	12.3	20.6
	a-TS-H$_b$	7.0	25.5	32.5
1h (R = *t*Bu)	**h-TS-H$_a$**	6.9	12.9	19.8
	h-TS-H$_b$	7.8	29.3	37.1

[a] Energy required for distortion of the azadicarboxylate to reach the geometry in the TS
[b] Energy required for distortion of the allene to reach the geometry in the TS
[c] ΔE_{dist}(Total) = ΔE_{dist}(EN=NE) + ΔE_{dist} (Allene)

The computational results in Figure S2 are in good agreement with the experimental observations in reaction of **1h**. The energy for **h-TS-Ha-I**, which will lead to product **3h-b'**, is about 0.3 kcal/mol higher than **h-TS-Ha**. This is consistent with the experimental ratio between **3h-l** and **3h-b** (2:1).

In experiments both **3h-l** and **3h-b** were obtained as *E*-isomers, calculation results showed that much higher energies are required for TS (**h-TS-Ha-II** and **h-TS-Ha-III**) leading to other isomers.

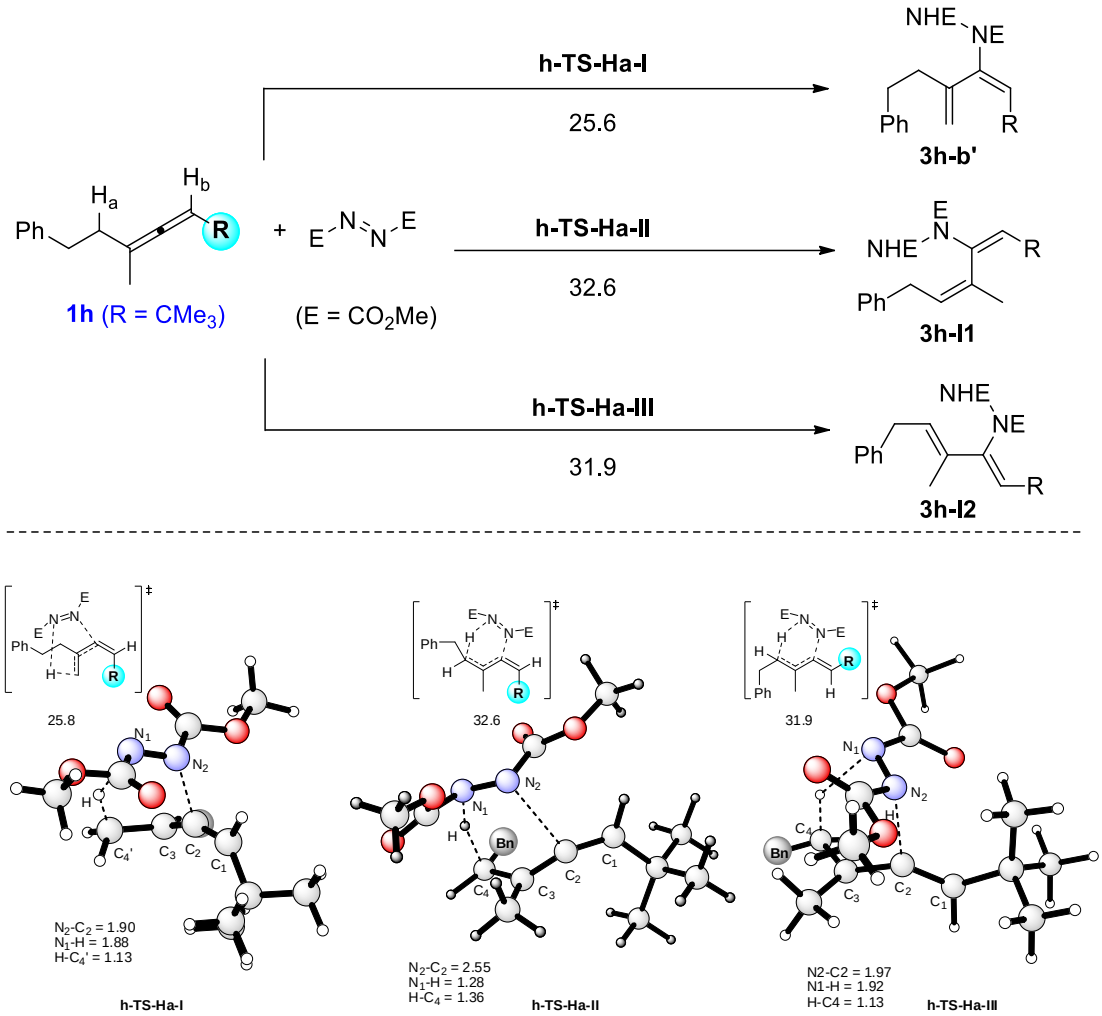


Figure S2. Computational Results Accounting for the Observed Regio- and Stereoselectivities in the Reactions Allene **1h** (distances are in Angstrom; energies are in kcal/mol).

Table S3. Calculated energies (in Hartree)

Species	E_0[a]	H_{298}[b]	G_{298}[c]
EN=NE	-566.238564	-566.226927	-566.276811
1a	-873.911437	-873.891038	-873.960318
1h	-622.481755	-622.463535	-622.52772
1k	-681.059524	-681.04405	-681.10135
1l	-720.344056	-720.327622	-720.387253
1r	-798.882994	-798.864326	-798.927732
1s	-547.454026	-547.437594	-547.495998
a-TS-Ha	-1440.133146	-1440.10233	-1440.194862
a-TS-Hb	-1440.131803	-1440.099998	-1440.198552
h-TS-Ha	-1188.703889	-1188.67516	-1188.764204
h-TS-Hb	-1188.693721	-1188.664654	-1188.754518
k-TS-Ha	-1247.283624	-1247.257863	-1247.337956
k-TS-Hb	-1247.279784	-1247.253437	-1247.335457
l-TS-Ha	-1286.561444	-1286.534355	-1286.617687
l-TS-Hb	-1286.560531	-1286.532945	-1286.618586
r-TS-Ha	-1365.103452	-1365.074293	-1365.161686
r-TS-Hb	-1365.104048	-1365.074388	-1365.163657
s-TS-Ha	-1113.674877	-1113.647733	-1113.731333
s-TS-Hb	-1113.665272	-1113.637875	-1113.721981
2a	-1440.228605	-1440.198098	-1440.288838
3a	-1440.212365	-1440.181189	-1440.275738
3h	-1188.797878	-1188.768939	-1188.858854
3h	-1188.777	-1188.747902	-1188.838262

[a] Sum of electronic and zero-point energies

[b] Sum of electronic and thermal enthalpies

[c] Sum of electronic and thermal free energies

Cartesian Coordinates

EN=NE

N	-3.22086000	2.23374500	0.93310400
N	-2.34864100	2.03796900	1.77173700
C	-1.08295700	2.63276200	1.38860200
O	-0.25302300	2.00495900	0.80383000
O	-1.01030500	3.85901300	1.84286200
C	0.24493000	4.53015800	1.60215900
H	0.42202100	4.60420900	0.53090100
H	0.13263200	5.51583300	2.04238200
H	1.05169700	3.98163900	2.08487400
C	-4.46213300	1.56282800	1.26891400
O	-4.78022400	0.55056500	0.72194400
O	-5.13555900	2.26082900	2.14881100
C	-6.43346700	1.72867200	2.48892400
H	-6.85296600	2.42922800	3.20396600
H	-7.05157900	1.67194800	1.59467300
H	-6.31868300	0.74312300	2.93600300

1a

C	-1.58691700	-0.37452500	1.00729900
C	-2.66136000	-0.99565800	0.60216100
H	-3.38783600	-0.44290900	0.00472400
Si	-2.96554100	-2.80602100	0.99904700
C	-4.46731500	-2.95367300	2.10837900
H	-4.68628100	-4.00355200	2.32277300
H	-4.30474900	-2.44055100	3.05944200
H	-5.35062500	-2.51677200	1.63547000
C	-1.45650900	-3.49732800	1.85817600
H	-0.55865900	-3.37758900	1.24640600
H	-1.28282900	-3.00354600	2.81729600
H	-1.59229800	-4.56497300	2.05220100
C	-3.28885800	-3.71817700	-0.60447500
H	-3.50974900	-4.77122800	-0.40939200
H	-4.14482200	-3.28780700	-1.13133200
H	-2.42373200	-3.67103900	-1.27029500
C	-0.48981100	0.19269600	1.43589200
C	0.78163500	0.16343400	0.62208900
H	1.16041800	1.17898000	0.47469500
H	1.56092600	-0.40246500	1.13915300
H	0.62069400	-0.29350000	-0.35375900
C	-0.44673700	0.90847900	2.76886500
H	-1.45558300	1.00645600	3.17440900
H	-0.05867300	1.92127200	2.61099200
C	0.44328200	0.19946500	3.80467700
H	0.04366200	-0.80134700	3.98771600
H	1.45276800	0.08415400	3.40433100
C	0.50007000	0.97420700	5.09557000
C	-0.46862800	0.78925300	6.08208600
C	1.49161300	1.93162100	5.30808900
C	-0.44704600	1.53926200	7.25187500
H	-1.24520400	0.04593700	5.93168100
C	1.51730700	2.68460400	6.47609800
H	2.25303800	2.08465800	4.54988100
C	0.54664800	2.49098900	7.45217700
H	-1.20565400	1.37990100	8.00923900
H	2.29700800	3.42241500	6.62490600
H	0.56569000	3.07540700	8.36412400

1h

C	-1.66610800	-0.23563600	0.94761500
C	-2.78641200	-0.75731900	0.52733800
H	-3.45643800	-0.14402400	-0.07604400
C	-4.60370600	-2.09435900	1.54495100
H	-5.01103500	-3.09664300	1.70299800
H	-4.47561500	-1.61766500	2.51992200
H	-5.33724900	-1.51636700	0.97685000
C	-2.25882900	-2.96260400	1.62452400
H	-1.29607500	-3.03138700	1.11194200
H	-2.09368400	-2.49241500	2.59702000
H	-2.62796500	-3.97701900	1.79488500
C	-3.48575400	-2.86752500	-0.55401700
H	-3.88968200	-3.87255300	-0.40543300
H	-4.19150900	-2.30622400	-1.17188700
H	-2.54519300	-2.95310300	-1.10359100
C	-0.54381400	0.28738700	1.36721200
C	0.72699200	0.19391400	0.55858200
H	1.16332900	1.18847600	0.42731000
H	1.47003800	-0.42200300	1.07136500
H	0.54358100	-0.24070300	-0.42330100
C	-0.46497200	1.01640100	2.69121900
H	-1.46508100	1.12814900	3.11443300
H	-0.06862300	2.02311800	2.51561100
C	0.43854700	0.30841600	3.71562600
H	0.04611500	-0.69527800	3.90016200
H	1.44477500	0.19922400	3.30568300
C	0.50407700	1.08047200	5.00775200
C	-0.45709300	0.89118800	6.00074900
C	1.49525100	2.03931300	5.21531900
C	-0.42849200	1.63813200	7.17222600
H	-1.23325600	0.14674200	5.85380600
C	1.52776700	2.78949900	6.38504200
H	2.25086700	2.19590000	4.45203100
C	0.56468900	2.59148100	7.36764700
H	-1.18128300	1.47528200	7.93462200
H	2.30684300	3.52876000	6.52993900
H	0.58909400	3.17368700	8.28087200
C	-3.26796800	-2.17353500	0.79623400

1k

C	-1.51557900	-0.13054500	-1.04651300
C	-0.79037900	-1.04951700	-1.62695000
Si	0.90085800	-1.53822000	-0.97294600
C	0.84126600	-3.31881100	-0.39348700
H	1.82350500	-3.64486900	-0.04028100
H	0.12834700	-3.44233700	0.42530700
H	0.53996200	-3.98444600	-1.20654500
C	1.34361600	-0.40469300	0.44617000
H	1.35865900	0.64080400	0.12782500

H	0.62477600	-0.50124700	1.26389400
H	2.33392500	-0.65461000	0.83644400
C	2.14507600	-1.38064400	-2.36435500
H	3.13772100	-1.69915900	-2.03461500
H	1.85972400	-2.00317800	-3.21647700
H	2.21780700	-0.34726400	-2.71216500
C	-2.18969800	0.79063200	-0.41798700
C	-3.16613500	0.54138900	0.72818200
C	-2.12919300	2.28783900	-0.70549200
C	-3.89891100	1.88162200	0.87246200
H	-2.60673000	0.32241700	1.64295900
H	-3.83065600	-0.30050100	0.53507000
C	-2.82749400	2.91273200	0.51030600
H	-2.69471100	2.51172900	-1.61486600
H	-1.10867500	2.64191400	-0.85291200
H	-4.71679400	1.93615500	0.14835100
H	-4.31880000	2.02595800	1.86834400
H	-3.23467500	3.90177700	0.29866300
H	-2.11673700	3.00770400	1.33614700
H	-1.18620000	-1.53917700	-2.51836900

1l

C	-1.09619500	0.01446600	-0.49272700
C	-0.64744100	-0.88378600	-1.32869500
Si	1.00425400	-1.73580000	-1.06327900
C	0.70422200	-3.58140400	-0.94658000
H	1.64694200	-4.12050000	-0.81952800
H	0.05726700	-3.82335100	-0.09978800
H	0.22407900	-3.95419500	-1.85528300
C	1.76321400	-1.08716900	0.51729700
H	1.91702600	-0.00616200	0.46843000
H	1.12520900	-1.30021300	1.37896300
H	2.73505000	-1.55709300	0.69222100
C	2.12807200	-1.38621100	-2.51961000
H	3.08705700	-1.89768400	-2.39806800
H	1.67932800	-1.73288300	-3.45421400
H	2.32527100	-0.31577900	-2.61655400
H	-1.26860000	-1.15919700	-2.18238700
C	-1.47937200	0.89222000	0.39490800
C	-2.26883400	0.50299400	1.62630600
C	-1.21520300	2.37538600	0.25096500
C	-3.56822500	1.31127800	1.71149900
H	-1.65756700	0.72775000	2.50947400
H	-2.47175000	-0.56852100	1.62847100
C	-2.52766200	3.16313000	0.34712600
H	-0.55663400	2.68980000	1.07018500
H	-0.69970600	2.58390400	-0.68731700
C	-3.29033800	2.81152900	1.62374500
H	-4.08855500	1.07459100	2.64284600
H	-4.22676600	1.01572900	0.88786000
H	-2.31582200	4.23455500	0.31337800
H	-3.14856800	2.92677500	-0.52357100
H	-4.22831800	3.37048300	1.66662400
H	-2.69537300	3.11734100	2.49224000

1r

C	-0.02988100	-0.03506200	1.38215900
C	0.09711900	-1.19993100	0.80423200
Si	-0.98090000	-1.70479600	-0.65126100
C	-1.03571000	-3.57416100	-0.71830300
H	-1.62970600	-3.91402600	-1.57090600
H	-0.03022300	-3.99042600	-0.82318700
H	-1.47946200	-3.98896600	0.19016500
C	-0.22441500	-1.02777800	-2.22682600
H	-0.17574000	0.06408700	-2.18691200
H	0.79091800	-1.40582300	-2.37104500
H	-0.81885700	-1.30949700	-3.10057900
C	-2.69944300	-0.99906400	-0.42829400
H	-3.33436000	-1.27095100	-1.27641800
H	-3.16736900	-1.38049500	0.48257900
H	-2.67136500	0.09219300	-0.36853800
C	-0.18749700	1.14969400	1.91340700
C	0.59845900	2.33073700	1.37707400
C	-1.15059600	1.35210200	3.06970700
C	-0.27863700	3.54793500	1.05589600
H	1.13548600	2.01589500	0.47902800
H	1.35203700	2.61884200	2.11859900
H	-0.78274500	2.16967700	3.69930700
H	-1.13118400	0.44949800	3.68343400
C	-2.62393800	1.62787900	2.69684400
C	-1.51614400	3.18716800	0.21548800
H	-0.58442400	4.02071300	1.99197800
H	0.34021300	4.28381600	0.53841000
C	-2.99305100	3.07872500	2.35762000
H	-2.92009200	0.95811800	1.88267500
H	-3.21832300	1.33397600	3.56593000
C	-2.85275000	3.50786300	0.89291500
H	-1.48561100	3.70379100	-0.74684100
H	-1.48765600	2.11843400	-0.01770800
H	-2.41217100	3.74400500	3.00358500
H	-4.03785300	3.24159900	2.63675100
H	-3.03111500	4.58717500	0.84382900
H	-3.65362500	3.03897100	0.31166200
H	0.87850700	-1.87392800	1.15838600

1s

C	-0.61679400	-0.15451700	1.41523800
C	0.15983700	-1.19005000	1.24229300
H	0.74121200	-1.55803500	2.08860000
C	1.83589300	-2.04982800	-0.36215200
H	2.00444500	-2.63391700	-1.27085200
H	2.26033400	-1.05388100	-0.51083600
H	2.37638900	-2.53206600	0.45655300
C	-0.38985400	-1.29336000	-1.21295500
H	-1.46097100	-1.20727100	-1.01356300
H	0.00456300	-0.28934600	-1.38910200
H	-0.25819600	-1.87715700	-2.12750500
C	-0.21234900	-3.38402500	0.15356400
H	-0.04081400	-3.99000600	-0.74035900
H	0.28021200	-3.87602500	0.99634600
H	-1.28635600	-3.35949700	0.35328800
C	-1.39434600	0.88223200	1.58834400
C	-0.86952700	2.28976700	1.38102900
C	-2.84388600	0.68770400	2.00061100

C	-1.78666900	3.14356300	0.49717800
H	0.12760000	2.23102200	0.93845600
H	-3.16273500	1.54793500	2.59915000
H	-2.88475800	-0.18462300	2.65538900
C	-3.86442500	0.45855400	0.86128100
C	-2.18219500	2.43211700	-0.80864100
H	-2.68198100	3.40255700	1.06679600
H	-1.28074600	4.08833500	0.28835500
C	-4.45895600	1.70830500	0.19597200
H	-3.41912200	-0.20121100	0.10855900
H	-4.69298900	-0.09993400	1.30430200
C	-3.69283600	2.28333800	-1.00264900
H	-1.76736000	2.95843700	-1.67157600
H	-1.73281900	1.43487200	-0.82145700
H	-4.59441500	2.47709000	0.96265800
H	-5.46668800	1.46574000	-0.15253700
H	-4.12848200	3.25777700	-1.24778300
H	-3.86656500	1.64134700	-1.87232500
C	0.33663400	-1.96699100	-0.05262400
H	-0.76190800	2.77259000	2.35870300

a-TS-H$_a$

C	-0.53477600	-0.26389600	1.98774100
C	0.17054700	-1.31531200	1.67268600
H	0.86157400	-1.71197700	2.41244100
C	1.66443400	-1.66781500	-0.93497800
H	1.65917500	-2.06699800	-1.95276500
H	1.82618600	-0.58810800	-0.99298000
H	2.51116100	-2.10774300	-0.40214000
C	-1.37785800	-1.24311000	-0.96818200
H	-2.33198900	-1.45272700	-0.47745400
H	-1.25286000	-0.15832900	-1.03068500
H	-1.43432800	-1.63145400	-1.98940300
C	-0.19947900	-3.88917400	0.08390000
H	-0.26390100	-4.34680500	-0.90700700
H	0.63052900	-4.35848400	0.61812600
H	-1.12200200	-4.11950000	0.62228800
C	-1.46710500	0.68578300	1.65152400
C	-0.94797500	2.01768800	1.31128800
H	0.00663200	1.92784500	0.78434000
H	-0.64445800	2.45014300	2.31473300
N	0.36858100	1.65084500	3.73646500
N	-0.12883400	0.45888400	3.67858000
C	-1.36129100	0.37159200	4.43128300
O	-1.86781000	1.26694500	5.04459100
O	-1.79428700	-0.88023600	4.40101200
C	-3.00640700	-1.12105900	5.12835100
H	-3.80190000	-0.47071400	4.76635300
H	-3.25329600	-2.16321700	4.94634500
H	-2.84317200	-0.94827200	6.19139200
C	1.67140800	1.67967200	3.20745500
O	2.33000100	0.74517800	2.82012900
O	2.09254100	2.94749500	3.19081200
C	3.41517000	3.13880800	2.68447300
H	3.59723600	4.20929900	2.72842000
H	4.13977500	2.60671000	3.30062600
H	3.48327600	2.78637900	1.65529600
Si	0.05168200	-2.04228600	-0.06334600
C	-1.88459500	2.97087600	0.56253900
H	-1.44025000	3.96809000	0.59203300
H	-2.85145600	3.03455800	1.06444800
C	-2.07135100	2.54009000	-0.87446800
C	-3.30195600	2.08952300	-1.34665200
C	-0.98317600	2.53867200	-1.75009300
C	-3.43890200	1.62142800	-2.65017000
H	-4.16392800	2.10218300	-0.68826500
C	-1.11581800	2.07772100	-3.05233800
H	-0.01935000	2.89825000	-1.40397900
C	-2.34494400	1.60717600	-3.50472900
H	-4.40305700	1.26761100	-2.99602100
H	-0.25878600	2.08247800	-3.71552600
H	-2.44856300	1.23929900	-4.51835300
C	-2.93172800	0.43405700	1.82634300
H	-3.37394300	1.15728100	2.52147700
H	-3.43783500	0.56688300	0.86585000
H	-3.12286600	-0.57719700	2.18039100

a-TS-H$_b$

C	-2.17362300	-1.17610300	-0.01350100
C	-2.89675300	-2.17450200	-0.27032400
H	-2.22772400	-3.11318400	0.31582500
Si	-4.38676300	-2.81128500	-1.21672700
C	-3.91201300	-2.92195100	-3.01695600
H	-4.75704300	-3.27576800	-3.61398600
H	-3.60843900	-1.94529600	-3.40158800
H	-3.08105300	-3.61811500	-3.14712700
C	-5.77687700	-1.59142800	-0.95536100
H	-6.03607500	-1.51815000	0.10328000
H	-5.49327900	-0.59696800	-1.30782900
H	-6.66854700	-1.90631200	-1.50439500
C	-4.80270500	-4.48568900	-0.51586900
H	-5.67364700	-4.91108900	-1.02104700
H	-3.96273900	-5.17186800	-0.64640500
H	-5.02785300	-4.41919000	0.55145800
C	-1.08778300	-0.48059200	0.38105300
C	-1.14711900	0.43836600	1.56941100
H	-0.16117800	0.53884100	2.02516900
H	-1.46319100	1.43260800	1.23987000
H	-1.86687000	0.09240900	2.31269000
C	0.04312200	-0.28600400	-0.59990200
H	0.06938900	-1.12734000	-1.29607600
H	0.98338400	-0.28697200	-0.04133100
C	-0.07991000	1.02906400	-1.39067400
H	-1.03791100	1.03570400	-1.91737300
H	-0.07403700	1.87499300	-0.69996200
C	1.04695600	1.17298400	-2.38032000
C	0.98210600	0.53593300	-3.61961400
C	2.19166900	1.90235900	-2.06429700
C	2.03340400	0.62796700	-4.52261900
H	0.09515600	-0.03406800	-3.87819900
C	3.24635200	1.99791900	-2.96527200
H	2.25462000	2.40403600	-1.10414000
C	3.17034500	1.36036400	-4.19752900
H	1.96412500	0.13121600	-5.48328500

H	4.12683600	2.57364700	-2.70509000
H	3.98924900	1.43628400	-4.90264700
N	-0.99401300	-3.57796300	0.65061300
N	-0.29395800	-2.62426400	1.16383400
C	-0.73222200	-2.37292400	2.49966100
O	-1.78286300	-2.70543100	2.98011600
O	0.21947300	-1.69777600	3.13050100
C	-0.09249100	-1.32255500	4.47721100
H	-0.25798700	-2.21098100	5.08580800
H	0.77223000	-0.77193400	4.83684000
H	-0.98177200	-0.69291600	4.49849200
C	-0.50954400	-4.05171300	-0.61039400
O	-1.24899900	-4.57870800	-1.39986600
O	0.79746700	-3.92626800	-0.74950100
C	1.33069600	-4.45844900	-1.97120700
H	2.39929400	-4.26866600	-1.92901500
H	1.13407200	-5.52800200	-2.03145100
H	0.88682500	-3.94952000	-2.82608300

h-TS-H_a

C	-0.45499300	-0.34697200	1.76471700
C	0.30006100	-1.39442700	1.55913700
H	0.91834200	-1.75154400	2.37814600
C	1.88165900	-2.14363600	-0.17306700
H	2.01092400	-2.72543400	-1.08943000
H	2.23015400	-1.12479300	-0.35896200
H	2.51272300	-2.58278100	0.60358200
C	-0.44564800	-1.52420400	-0.85220900
H	-1.50694000	-1.53372000	-0.59006100
H	-0.15148000	-0.48894500	-1.04362400
H	-0.32175100	-2.08897600	-1.77941000
C	-0.04684500	-3.59219800	0.49860100
H	0.07025000	-4.18257100	-0.41388800
H	0.54658200	-4.06074000	1.28756700
H	-1.09759700	-3.62225700	0.79676800
C	-1.38360100	0.57890800	1.38164600
C	-0.89471000	1.93529600	1.09986400
H	0.01958600	1.89809600	0.50093100
H	-0.50676100	2.28848900	2.11078400
N	0.37451500	1.55602000	3.56394600
N	-0.11711800	0.36811800	3.51885900
C	-1.42141600	0.32968400	4.15585500
O	-1.99078300	1.26648500	4.63756700
O	-1.84358500	-0.92405500	4.18165200
C	-3.12321400	-1.12282600	4.79728900
H	-3.88565100	-0.53807900	4.28389500
H	-3.33073800	-2.18492600	4.70230700
H	-3.08211800	-0.83599800	5.84734500
C	1.72082400	1.56354700	3.13093000
O	2.41461700	0.61103700	2.87935700
O	2.12495100	2.83111100	3.04380500
C	3.48477200	3.00687100	2.63746600
H	3.64988200	4.08057500	2.61442200
H	4.15854300	2.53666100	3.35326200
H	3.64398000	2.57798900	1.64833200
C	-1.89336700	2.95525100	0.55654500
H	-1.41752600	3.93863600	0.59972000
H	-2.76811400	3.00516200	1.20758400
C	-2.33810900	2.68721200	-0.86408000
C	-3.69181000	2.64190800	-1.19192600
C	-1.40230800	2.50333600	-1.88341200
C	-4.10405000	2.41825000	-2.50131400
H	-4.43195800	2.78227200	-0.41075600
C	-1.80891100	2.27811300	-3.19199000
H	-0.34267400	2.54222300	-1.65416900
C	-3.16302700	2.23415200	-3.50628700
H	-5.16196900	2.38665300	-2.73437800
H	-1.06649000	2.13995800	-3.96932100
H	-3.48078000	2.05845000	-4.52697300
C	-2.84988500	0.27968800	1.46980700
H	-3.34424500	0.94058700	2.19150100
H	-3.31769700	0.46914300	0.49882600
H	-3.02775600	-0.75751500	1.74823000
C	0.40693600	-2.14825500	0.24921000

h-TS-H_b

C	-2.26445200	-1.21110500	-0.11066700
C	-2.96340700	-2.21850700	-0.39438900
H	-2.24853900	-3.15267900	0.16413500
C	-3.87725000	-2.87089700	-2.59591500
H	-4.77304800	-3.20885600	-3.12360700
H	-3.55066700	-1.92640600	-3.03711000
H	-3.08946400	-3.61231200	-2.73543500
C	-5.29536300	-1.63322600	-0.93445700
H	-5.52902700	-1.48227900	0.12123000
H	-4.98112200	-0.67745200	-1.35915700
H	-6.20290300	-1.96042100	-1.44815100
C	-4.65784700	-4.02367000	-0.51001400
H	-5.56210600	-4.36409000	-1.01932900
H	-3.88457500	-4.78591800	-0.62928400
H	-4.87819700	-3.91972900	0.55492500
C	-1.15411700	-0.56632100	0.31761200
C	-1.20194600	0.33755700	1.51886900
H	-0.21487700	0.42849000	1.97296300
H	-1.51387700	1.33558800	1.19742800
H	-1.92322000	-0.00897500	2.26055400
C	-0.02360700	-0.35254300	-0.66059100
H	0.00923400	-1.18776700	-1.36395200
H	0.91708700	-0.34763800	-0.10337800
C	-0.16134900	0.96536200	-1.44386500
H	-1.12092300	0.96569100	-1.96792500
H	-0.16123400	1.80770200	-0.74877200
C	0.96080500	1.12520000	-2.43647600
C	0.89510200	0.49836700	-3.68090500
C	2.10185500	1.85962700	-2.11884000
C	1.94164100	0.60586700	-4.58775400
H	0.01081000	-0.07524100	-3.94062700
C	3.15177300	1.97060200	-3.02361800
H	2.16562900	2.35324600	-1.15455900
C	3.07481200	1.34340800	-4.26114600
H	1.87142100	0.11721000	-5.55249600
H	4.02941800	2.55010900	-2.76219700
H	3.88982300	1.43158700	-4.96931800
N	-1.03370900	-3.60223700	0.55170900

N	-0.39396300	-2.62693800	1.10913000
C	-0.88497800	-2.44253900	2.44032900
O	-1.94752300	-2.81015600	2.86433300
O	0.03459900	-1.79069300	3.13775400
C	-0.33249300	-1.48130700	4.48740300
H	-0.50087500	-2.39897200	5.04999000
H	0.50738700	-0.93144900	4.90264600
H	-1.23439000	-0.86976500	4.50362900
C	-0.46077400	-4.05696700	-0.67686400
O	-1.12839400	-4.61609800	-1.50641500
O	0.84747600	-3.88345000	-0.73706700
C	1.47162400	-4.39043400	-1.92537300
H	2.53093400	-4.18038200	-1.80934900
H	1.30165700	-5.46279000	-2.01139500
H	1.07593700	-3.87958700	-2.80265700
C	-4.19901700	-2.69106600	-1.10671600

k-TS-H_a

C	-0.37710200	-0.22978300	1.86733700
C	0.36318900	-1.29125000	1.69511700
H	0.98977100	-1.60934300	2.52524900
C	2.13488700	-1.98323800	-0.66113400
H	2.23690400	-2.52922200	-1.60302900
H	2.34384200	-0.92808900	-0.85383700
H	2.89344200	-2.35731800	0.03113800
C	-0.87337900	-1.48921500	-1.09587900
H	-1.87983400	-1.62779700	-0.69397800
H	-0.71152200	-0.42163900	-1.26655400
H	-0.82715300	-1.99375200	-2.06519800
C	0.08417600	-4.01565700	0.37661700
H	0.14866300	-4.59019100	-0.55139900
H	0.81265300	-4.42805600	1.07933800
H	-0.91330800	-4.16191500	0.79817300
C	-1.30141500	0.68530500	1.45243000
C	-0.94157600	2.06430400	1.10089200
C	-2.80088600	0.52924000	1.48406400
C	-2.26017200	2.74852500	0.71934300
H	-0.12425600	2.14804300	0.38146500
H	-0.51132200	2.49118500	2.06161900
H	-3.15289600	-0.11649100	2.28921600
H	-3.10154600	0.05972600	0.53811600
C	-3.30352400	1.97925400	1.53751700
H	-2.25377000	3.81695100	0.93089700
H	-2.44722000	2.61336300	-0.34937800
H	-4.31615900	2.08521700	1.14994300
H	-3.29075200	2.33121400	2.57206700
N	0.45328800	1.80977500	3.51595400
N	-0.03613300	0.61723800	3.54240900
C	-1.29706000	0.58427800	4.25096900
O	-1.81841700	1.51875300	4.78933200
O	-1.73447200	-0.66636400	4.29038800
C	-2.95404400	-0.85847600	5.02060200
H	-3.74149600	-0.21880200	4.62296800
H	-3.21060200	-1.90587600	4.88961500
H	-2.79423400	-0.63412100	6.07462500
C	1.78191900	1.79957700	3.04343800
O	2.46360700	0.83758300	2.78844700
O	2.19361900	3.06318000	2.92026200
C	3.54564000	3.22098100	2.48421100
H	3.71862700	4.29293800	2.44067100
H	4.23054000	2.75765600	3.19407000
H	3.68352500	2.77585100	1.49902100
Si	0.41869300	-2.20477100	0.05007500

k-TS-H_b

C	-1.44848500	-0.08366500	-0.59369200
C	-0.77078600	-1.06613900	-0.99448300
H	-1.68818100	-1.74308000	-1.64942300
Si	0.89745700	-1.92479300	-1.00755000
C	0.57071800	-3.71850100	-1.39181000
H	1.50040400	-4.29307900	-1.37643400
H	-0.11195700	-4.15446500	-0.65813000
H	0.11852100	-3.82500500	-2.38090900
C	1.64038200	-1.70581300	0.69179300
H	1.80058800	-0.64773800	0.91185100
H	0.98347100	-2.12057100	1.45965200
H	2.60487700	-2.21726300	0.75491700
C	1.97161900	-1.13048800	-2.31034300
H	2.94808600	-1.62233500	-2.33910900
H	1.52175300	-1.21597800	-3.30146000
H	2.13144300	-0.07152800	-2.09502600
N	-3.62767100	-0.85935500	-1.89261500
N	-2.77088200	-1.67627800	-2.41268700
C	-2.24055800	-1.18005500	-3.65139000
O	-2.70159900	-0.29577600	-4.31415100
O	-1.19004700	-1.92241900	-3.98084300
C	-0.58469700	-1.59111100	-5.23730500
H	-0.23537800	-0.55929600	-5.22699900
H	0.24971800	-2.27724600	-5.35257900
H	-1.30224600	-1.73038000	-6.04506300
C	-4.28046000	-1.49240600	-0.79847900
O	-3.88885600	-2.45074700	-0.18499300
O	-5.40728800	-0.83677000	-0.54575800
C	-6.18055100	-1.34167200	0.54811400
H	-7.02265900	-0.66283800	0.65135900
H	-6.53054900	-2.34922500	0.32482600
H	-5.59034300	-1.35543000	1.46420900
C	-2.46835400	0.77926600	-0.44922300
C	-3.29195300	0.92724000	0.81566000
C	-2.66305700	2.01708200	-1.31045000
C	-4.28441800	2.04283600	0.47680700
H	-2.61415400	1.26765800	1.60616700
H	-3.73420400	-0.00687800	1.16239700
C	-3.45791500	2.97769600	-0.41254300
H	-3.25219000	1.73086300	-2.18446800
H	-1.71454800	2.42167600	-1.66404400
H	-5.12183100	1.63359800	-0.09194900
H	-4.67706000	2.53368500	1.36719100
H	-4.06975400	3.66957400	-0.99075900
H	-2.77319800	3.56382900	0.20590000

l-TS-H_a

C	-1.63008400	-1.03282600	1.16395900
C	-0.85465900	-2.07670200	1.05251300

H	-1.18559500	-2.88643300	0.40657100
Si	0.75943800	-2.21121200	2.01187700
C	0.54164900	-3.50944200	3.34147800
H	1.47842400	-3.67091200	3.88172000
H	-0.22022500	-3.20288200	4.06260200
H	0.23116600	-4.46338600	2.90786200
C	1.15764500	-0.54559400	2.75925600
H	1.29510000	0.20724600	1.97876400
H	0.36379000	-0.20725200	3.43058500
H	2.08485900	-0.60256100	3.33643300
C	2.09367900	-2.73668200	0.81117900
H	3.05014400	-2.85871900	1.32659700
H	1.84085100	-3.69101700	0.34224000
H	2.22760500	-1.99586700	0.01915600
C	-1.93143500	0.21155500	1.64724700
C	-2.93155600	0.34056300	2.71326700
C	-1.43335700	1.47853200	1.01671500
C	-3.11116300	1.77963100	3.18417000
H	-3.88577900	-0.08123100	2.26206600
H	-2.71814300	-0.34670800	3.53886100
C	-0.93201400	2.47817400	2.08904000
H	-2.27817400	1.94521100	0.49102500
H	-0.66139700	1.27132900	0.27611800
C	-1.73324600	2.40787900	3.40238700
H	-3.69825500	1.79607300	4.10280300
H	-3.66700200	2.35202600	2.43572500
H	-1.00181800	3.47903400	1.65943400
H	0.12319900	2.28804400	2.28884200
H	-1.82874700	3.40497000	3.83474700
H	-1.19476200	1.79558500	4.13224900
N	-4.35654800	-1.32425400	0.96938600
N	-3.29037400	-1.27825100	0.24422900
C	-3.34982900	-0.18765700	-0.70230000
O	-4.27178700	0.56411300	-0.84484700
O	-2.25029900	-0.20140000	-1.44178800
C	-2.18365100	0.81180800	-2.45329200
H	-2.28879500	1.80065600	-2.00886700
H	-1.20458600	0.70271100	-2.91157000
H	-2.96806200	0.65368300	-3.19270800
C	-4.40751100	-2.51676700	1.72005900
O	-3.65432700	-3.45694500	1.66206200
O	-5.46286800	-2.45285200	2.53509400
C	-5.67642900	-3.61198000	3.34332300
H	-6.54555300	-3.38807800	3.95615400
H	-5.87141000	-4.48136500	2.71547900
H	-4.80829700	-3.80288200	3.97369000

l-TS-H_b

C	-0.35344800	0.66379700	0.18867500
C	-0.08283100	-0.49373300	-0.22823400
H	0.76190100	-0.89448100	0.66660100
C	0.81622200	-3.13827600	-1.32887400
H	0.62665200	-3.96287800	-2.02062900
H	1.79653400	-2.71517700	-1.56223600
H	0.85173900	-3.54266600	-0.31459000
C	-0.54883400	-1.06404000	-3.15721100
H	-1.28871100	-0.26155500	-3.20394100
H	0.42617600	-0.64514200	-3.41603800
H	-0.80959700	-1.81169200	-3.91147300
C	-2.18799900	-2.52488300	-0.99957900
H	-2.47467800	-3.32778300	-1.68428800
H	-2.16988500	-2.92731200	0.01541000
H	-2.95289100	-1.74598000	-1.04815500
N	1.13934400	-0.83727100	1.96283500
N	1.17489700	0.39084200	2.35534100
C	2.29909800	1.03455300	1.75103200
O	2.89337500	0.65778700	0.77597500
O	2.58868700	2.12646100	2.44404700
C	3.65680600	2.92109200	1.91636100
H	3.41952200	3.24827100	0.90404500
H	3.74582100	3.77541900	2.58185700
H	4.58380700	2.34894400	1.90980100
C	0.16647400	-1.64712700	2.62447200
O	-0.34306600	-2.58700700	2.07262600
O	-0.01418100	-1.30878000	3.88869500
C	-0.92014800	-2.15120900	4.61637400
H	-0.91987800	-1.76900100	5.63298100
H	-1.91840400	-2.08525700	4.18508800
H	-0.57267600	-3.18297300	4.59571300
C	-0.49115400	1.70290200	1.03399300
C	0.09800200	3.06320400	0.72935300
C	-1.64199500	1.63986500	2.01831500
C	0.13624400	4.02126000	1.92456600
H	-0.55104800	3.50335300	-0.03863800
H	1.08265600	2.95307500	0.26669900
C	-1.46113800	2.58620500	3.20185900
H	-2.55062400	1.93191700	1.47585700
H	-1.78247400	0.60641200	2.34250800
C	-1.16948000	4.00206200	2.71381800
H	0.34942100	5.02652800	1.55381300
H	0.94779400	3.74323800	2.59671100
H	-2.36476600	2.56429200	3.81474100
H	-0.63164300	2.23716800	3.82475600
H	-1.10041800	4.69007700	3.55923000
H	-1.99625700	4.34731300	2.08204300
Si	-0.51404300	-1.84060200	-1.45953200

r-TS-H_a

C	-0.47141300	-0.26166500	1.62483700
C	0.26693000	-1.30709800	1.36747300
H	0.99120000	-1.60366800	2.12277000
Si	0.20473100	-2.22472100	-0.27486900
C	1.74323200	-1.75010100	-1.22957900
H	1.79885600	-2.29476000	-2.17605200
H	1.74703300	-0.67934800	-1.44929200
H	2.64334700	-1.97913900	-0.65343500
C	-1.33705800	-1.73636900	-1.20895400
H	-2.23504700	-2.01714400	-0.65309300
H	-1.36671800	-0.66008700	-1.39787200
H	-1.36733400	-2.24919300	-2.17449600
C	0.20636400	-4.06043900	0.08153100
H	0.22190600	-4.63190200	-0.85043500
H	1.08629200	-4.34428500	0.66451800
H	-0.68287600	-4.35445500	0.64439200

C	-1.44128700	0.66115400	1.30088800
C	-0.94778600	1.97146400	0.89743000
C	-2.88183900	0.38621300	1.66967100
C	-1.94334800	3.01163900	0.41503000
H	-0.09167200	1.87844000	0.22025700
H	-0.43247700	2.33527200	1.87371100
H	-3.20315000	1.13044800	2.41052000
H	-2.90558000	-0.58616500	2.16194400
C	-3.93061300	0.36314900	0.52392100
C	-2.57263400	2.62571000	-0.93853400
H	-2.71748700	3.14997600	1.17303600
H	-1.42361000	3.96742400	0.33545600
C	-4.66222100	1.68493600	0.24027700
H	-3.48126000	-0.02976700	-0.39073000
H	-4.67592200	-0.37226200	0.83325400
C	-4.09755100	2.52894700	-0.90929500
H	-2.27793000	3.34144500	-1.70919900
H	-2.16656900	1.66091300	-1.25740700
H	-4.69271500	2.27450400	1.16077000
H	-5.70516000	1.46075400	0.00258500
H	-4.52985300	3.53252400	-0.84652500
H	-4.43256400	2.10732900	-1.86197900
N	0.52374500	1.77030800	3.17945100
N	0.07560200	0.56048300	3.27460300
C	-1.09196900	0.50988000	4.12002800
O	-1.60548100	1.44413100	4.66783800
O	-1.46752500	-0.75455700	4.25175100
C	-2.62547600	-0.96220200	5.06968700
H	-3.47024700	-0.39102900	4.68586200
H	-2.83243200	-2.02753900	5.01867900
H	-2.41546800	-0.66637800	6.09700300
C	1.80337200	1.78908600	2.57768400
O	2.48904100	0.84239300	2.28492900
O	2.15678700	3.06051000	2.38506000
C	3.45411000	3.24989000	1.81414800
H	3.57702800	4.32452500	1.70957200
H	4.22035800	2.84544700	2.47534600
H	3.51691200	2.76483100	0.84042700

r-TS-H_b

C	-0.54205800	0.19114600	1.06164000
C	-0.44738400	-0.91596900	0.47251900
H	0.53710500	-1.47012400	1.16721200
Si	-1.10048700	-1.99047900	-0.91908100
C	-0.58594800	-3.74401200	-0.55961700
H	-0.98672400	-4.42566700	-1.31443700
H	0.50232600	-3.83644900	-0.55646700
H	-0.95689800	-4.06546100	0.41676800
C	-0.37592800	-1.37063500	-2.52338900
H	-0.68265600	-0.33904300	-2.71234800
H	0.71537400	-1.40384000	-2.50522900
H	-0.72114900	-1.98642500	-3.35856700
C	-2.95826400	-1.80514000	-0.91230400
H	-3.40622100	-2.41582300	-1.70107300
H	-3.37675900	-2.12365600	0.04515700
H	-3.24479600	-0.76444000	-1.08293700
C	-0.30194000	1.22482300	1.89433300
C	0.60021000	2.35551200	1.46216900
C	-1.21969200	1.39987400	3.08178800
C	-0.13360100	3.69157200	1.27054300
H	1.10624400	2.06432500	0.53953500
H	1.36900400	2.47355500	2.23042900
H	-0.75849600	2.08251300	3.80063800
H	-1.32934300	0.42642400	3.56627000
C	-2.65442800	1.88408500	2.74894400
C	-1.42111400	3.57500400	0.43679200
H	-0.35927800	4.11514600	2.25162100
H	0.56946200	4.38364800	0.80334800
C	-2.85459400	3.39732300	2.59975600
H	-3.01634200	1.35478000	1.86140100
H	-3.27712900	1.54821500	3.58113800
C	-2.68892000	3.98422500	1.19331500
H	-1.34668900	4.18640900	-0.46519200
H	-1.53573400	2.54520900	0.08547300
H	-2.18955500	3.90572200	3.30380400
H	-3.86804000	3.64124200	2.92953100
H	-2.71788200	5.07525700	1.28151900
H	-3.55670800	3.70199500	0.58883500
N	1.68502000	-1.26842500	1.77761300
N	1.60082300	-0.24347200	2.56288200
C	0.92406800	-0.59932500	3.75820200
O	0.27530300	-1.59522500	3.95205500
O	1.11795500	0.36574100	4.65215600
C	0.47865700	0.16376800	5.91662300
H	0.86282100	-0.73787700	6.39289200
H	0.72204900	1.03918000	6.51254300
H	-0.60059400	0.07881900	5.79084900
C	2.58633600	-1.03536400	0.68720300
O	3.43755700	-0.19402200	0.64618200
O	2.37942600	-1.96642300	-0.23795800
C	3.27027200	-1.91772700	-1.35948900
H	2.96484600	-2.72982500	-2.01373100
H	3.18386800	-0.95921500	-1.86982100
H	4.29695700	-2.06796700	-1.02734100

s-TS-H_a

C	-0.44320900	-0.23794200	1.73347300
C	0.29079500	-1.28820000	1.46824400
H	0.96466500	-1.64427600	2.24252800
C	1.71200400	-1.84886300	-0.46356600
H	1.79582700	-2.42845600	-1.38687700
H	1.89227800	-0.79673600	-0.69700800
H	2.49383400	-2.18370900	0.22261300
C	-0.75174900	-1.55658800	-0.81689500
H	-1.75032500	-1.69698800	-0.39585200
H	-0.62537900	-0.49709400	-1.05429100
H	-0.69272000	-2.12277700	-1.74970300
C	0.10408600	-3.52863600	0.45950200
H	0.17001000	-4.11351600	-0.46148400
H	0.86152900	-3.89974400	1.15423900
H	-0.87970100	-3.69717200	0.90438000
C	-1.36569200	0.72620700	1.41956100
C	-0.82178100	2.05864900	1.15053500
C	-2.83563700	0.46886200	1.65175000

C	-1.76253500	3.12801800	0.61953500
H	0.08730200	1.98940400	0.54345000
H	-0.40355900	2.36032600	2.17783600
H	-3.21680000	1.20643500	2.36918700
H	-2.92079800	-0.51162900	2.12067600
C	-3.76313500	0.48278400	0.40348900
C	-2.24914800	2.79808900	-0.80583800
H	-2.60891800	3.24262700	1.30021700
H	-1.23401400	4.08227800	0.63216700
C	-4.45868000	1.81792900	0.09345200
H	-3.22013700	0.12045400	-0.47341000
H	-4.53680100	-0.26000600	0.60659000
C	-3.76804400	2.70965100	-0.94608700
H	-1.87167200	3.53881800	-1.51438700
H	-1.81341500	1.84276300	-1.11405000
H	-4.59417300	2.36665800	1.02954700
H	-5.46737300	1.60825100	-0.27150500
H	-4.20347400	3.71199600	-0.88570000
H	-3.99602400	2.33342100	-1.94809500
N	0.51693800	1.62119300	3.51854700
N	0.03945000	0.42511900	3.47726200
C	-1.19465100	0.34545000	4.23351200
O	-1.73605200	1.25894700	4.78774600
O	-1.58702400	-0.91841000	4.27404100
C	-2.79693900	-1.15467100	5.00629200
H	-3.61109600	-0.55794300	4.59599700
H	-3.00594900	-2.21447100	4.89069300
H	-2.65042900	-0.90819300	6.05729500
C	1.82701600	1.66116200	2.98505300
O	2.51280000	0.72589700	2.65916400
O	2.20631000	2.93664700	2.90292600
C	3.52939000	3.14547800	2.40227900
H	3.67341300	4.22238300	2.38807000
H	4.26168400	2.67603800	3.05883700
H	3.62502900	2.73755100	1.39626800
C	0.32045600	-2.04129900	0.15414000

s-TS-H_b

C	-0.55408600	0.49882700	0.40991500
C	-0.31510200	-0.61966800	-0.10914100
H	0.62283700	-1.05478400	0.73310800
C	0.52415600	-2.48503000	-1.51466000
H	0.27693200	-3.15247100	-2.34316100
H	1.41279600	-1.91084400	-1.78645400
H	0.76162700	-3.09220900	-0.63846300
C	-0.98187500	-0.72150600	-2.47436200
H	-1.82664300	-0.05590100	-2.28398300
H	-0.12238700	-0.11674900	-2.76999400
H	-1.24178400	-1.38485700	-3.30322700
C	-1.88843400	-2.38460900	-0.83164000
H	-2.14524900	-3.06945000	-1.64382700
H	-1.68935600	-2.97259600	0.06553900
H	-2.74591000	-1.73593400	-0.63998600
C	-0.53903700	1.48009400	1.34163000
C	0.15375300	2.78721500	1.05550400
C	-1.58493300	1.42225600	2.43286500
C	-0.83020400	3.92881100	0.72047100
H	0.85500600	2.64583200	0.22943000
H	0.72142100	3.08517300	1.93937800
H	-1.35104400	2.17627600	3.19009800
H	-1.49293500	0.44548000	2.90988200
C	-3.04971800	1.58837200	1.96838900
C	-1.95624500	3.54229100	-0.25165200
H	-1.25768200	4.30200400	1.65294900
H	-0.23531800	4.74938100	0.31559300
C	-3.54731000	3.02352900	1.75447800
H	-3.21551800	0.98595400	1.06834400
H	-3.66362300	1.13902500	2.75262600
C	-3.36087700	3.63112100	0.35827400
H	-1.92850700	4.18409200	-1.13479900
H	-1.79145300	2.52711700	-0.62137100
H	-3.08717900	3.66578500	2.51131400
H	-4.61957300	3.04699300	1.96741100
H	-3.65742900	4.68380400	0.41562500
H	-4.06459000	3.15303700	-0.33049700
N	1.12395100	-1.07387300	1.94363200
N	1.14924200	0.13416100	2.41372000
C	2.24953900	0.83135900	1.83343900
O	2.80801400	0.55467300	0.80452600
O	2.56939100	1.85090400	2.62196000
C	3.61792700	2.69236700	2.12729200
H	3.34103500	3.10960700	1.15908600
H	3.73361700	3.48345800	2.86284300
H	4.54313400	2.12527000	2.03212200
C	0.23630100	-1.92824500	2.67538200
O	-0.20609300	-1.71827300	3.76899700
O	0.05761900	-3.04061800	1.97385500
C	-0.79276200	-4.01900200	2.58519600
H	-0.84664800	-4.84332900	1.87956800
H	-0.36208700	-4.35482700	3.52758500
H	-1.78339600	-3.59964500	2.75906300
C	-0.65972400	-1.55747000	-1.22980900

2a

C	-0.79579900	0.24192800	2.15066800
C	-0.36149100	-0.90093800	1.61665000
H	0.26649900	-1.51814800	2.25718700
C	0.05095600	-1.05679500	-1.49868100
H	-0.17296500	-1.68885400	-2.36369800
H	-0.20279700	-0.02805800	-1.75933800
H	1.12829000	-1.10693600	-1.31737700
C	-2.74844000	-1.46912200	-0.25711200
H	-3.29301200	-1.97788400	0.54352000
H	-3.05369600	-0.42161400	-0.26482300
H	-3.05209400	-1.91767000	-1.20800800
C	-0.53250200	-3.50717500	0.18816400
H	-0.85172800	-4.06661900	-0.69534700
H	0.53859200	-3.67980500	0.32446400
H	-1.05263000	-3.92207900	1.05584100
C	-1.60270200	1.26127900	1.43047700
C	-1.09550300	1.80547200	0.32305300
H	-0.09025100	1.50526300	0.03536000
H	-0.68550400	2.42422000	4.36892200
N	-0.09433400	1.86642400	3.76285600

N	-0.54367500	0.58472200	3.52050900
C	-0.59697500	-0.24621700	4.62332600
O	-0.23985600	0.10761200	5.72294600
O	-1.12647500	-1.43419300	4.34625500
C	-1.23497200	-2.32025200	5.46738700
H	-1.91671200	-1.90950400	6.21099400
H	-1.63150000	-3.24819700	5.06430000
H	-0.25635300	-2.48846400	5.91403800
C	1.26822600	2.02329000	3.92835700
O	2.09735100	1.21623000	3.59642000
O	1.51965800	3.22182600	4.45593500
C	2.90916300	3.53327200	4.61992000
H	2.93736000	4.54704600	5.00927100
H	3.36688000	2.84320200	5.32756000
H	3.42452700	3.47983300	3.66214800
Si	-0.90102100	-1.67805600	-0.01012400
C	-1.74956400	2.78741300	-0.61189200
H	-1.24680000	3.75555800	-0.52524200
H	-2.80006300	2.93622900	-0.36376200
C	-1.61728500	2.28204000	-2.03114500
C	-2.57705600	1.42707700	-2.57008100
C	-0.48109500	2.57353700	-2.78318000
C	-2.39793200	0.86116100	-3.82675000
H	-3.46692700	1.19424000	-1.99479900
C	-0.29855200	2.01107600	-4.04122600
H	0.27251900	3.23805300	-2.37300300
C	-1.25424500	1.14745400	-4.56375100
H	-3.15007300	0.19280100	-4.22955600
H	0.59243900	2.24488100	-4.61212200
H	-1.11123200	0.70296000	-5.54148800
C	-2.93679400	1.58165400	2.04536700
H	-2.80441200	2.07457300	3.01348000
H	-3.53776600	2.23699400	1.41791000
H	-3.49999900	0.66229300	2.22941900

3a

C	-2.40910400	-1.53232100	-0.17338500
C	-3.39483800	-1.78965200	-0.82074800
H	-1.74696200	-4.09682900	1.16056700
Si	-4.87400600	-2.21444400	-1.85335400
C	-4.52839900	-1.61900600	-3.58763000
H	-5.37375100	-1.84622100	-4.24298600
H	-4.36520000	-0.53886600	-3.60520400
H	-3.63997300	-2.10505600	-3.99733300
C	-6.36009800	-1.34920400	-1.12924600
H	-6.53843700	-1.67322700	-0.10132400
H	-6.22099100	-0.26577000	-1.12681900
H	-7.25350800	-1.57629100	-1.71738500
C	-5.08391700	-4.06811500	-1.80311500
H	-5.94370400	-4.37076100	-2.40697000
H	-4.19731700	-4.57164900	-2.19535300
H	-5.24858000	-4.41658100	-0.78088200
C	-1.20637300	-1.12637300	0.57917900
C	-1.62639900	0.03675100	1.49508100
H	-0.76510100	0.59269300	1.85451400
H	-2.26578300	0.71097600	0.92661600
H	-2.19487300	-0.34192600	2.34527100
C	-0.09621800	-0.71382000	-0.40789200
H	0.10228600	-1.55858700	-1.07153200
H	0.81116900	-0.53169600	0.17496700
C	-0.43303600	0.52521900	-1.24311500
H	-1.39995200	0.38179900	-1.73311500
H	-0.51650000	1.39958900	-0.59404300
C	0.62876200	0.77036400	-2.28470900
C	0.54470800	0.16473700	-3.53810100
C	1.73967100	1.56292000	-2.00029100
C	1.54420200	0.34773900	-4.48594400
H	-0.31659800	-0.45314600	-3.77256800
C	2.74280400	1.74815000	-2.94494000
H	1.81727600	2.04194100	-1.02951100
C	2.64833600	1.13981500	-4.19103100
H	1.45962000	-0.12647100	-5.45673300
H	3.59850200	2.36928600	-2.70732500
H	3.42740600	1.28480600	-4.92971400
N	-0.98127200	-3.55726600	0.77553900
N	-0.76608200	-2.32514000	1.35790700
C	0.09524400	-2.33847900	2.43546500
O	0.41898000	-3.35134100	3.01065900
O	0.52623600	-1.12183700	2.76145000
C	1.36105500	-1.06706300	3.92558000
H	2.28444200	-1.61784500	3.75329600
H	1.57245500	-0.01252400	4.08114700
H	0.83833900	-1.47954600	4.78721800
C	0.06022300	-4.32477200	0.30627000
O	-0.06331900	-5.50348700	0.07103800
O	1.16580800	-3.61423600	0.10393100
C	2.27539300	-4.35650500	-0.41579300
H	3.07986500	-3.63511600	-0.52949800
H	2.56381300	-5.14072400	0.28287900
H	2.01948600	-4.79314100	-1.38011200

2h

C	-0.61719200	0.28968300	1.88534200
C	-0.07081300	-0.80971500	1.36933100
H	0.61419800	-1.33168600	2.03583100
C	1.03936300	-1.47827500	-0.72898200
H	0.95197700	-2.06398900	-1.64820500
H	1.28053800	-0.44770700	-1.00099600
H	1.86982300	-1.88154500	-0.14396400
C	-1.41925300	-1.03026300	-0.81814000
H	-2.34704600	-0.91996100	-0.25087400
H	-1.18803100	-0.07326800	-1.28270500
H	-1.59634600	-1.75518800	-1.61731200
C	-0.56424100	-3.00339900	0.43314700
H	-0.64519300	-3.61034700	-0.47198500
H	0.23491200	-3.41744000	1.05263700
H	-1.50317200	-3.08658600	0.98710500
C	-1.51902400	1.28764000	1.25353300
C	-1.05405700	2.04273700	0.25818500
H	-0.03025500	1.86892500	-0.06623800
H	-0.15362900	2.47209300	4.02698000
N	0.36147400	1.75771000	3.52464000
N	-0.32407100	0.59129500	3.26619600
C	-0.66825900	-0.16760500	4.35867700

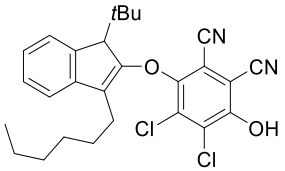
O	-0.36967200	0.13076000	5.49337100
O	-1.38730700	-1.23893200	4.02192900
C	-1.79456300	-2.05780600	5.12403900
H	-2.44371700	-1.49663600	5.79519500
H	-2.33681300	-2.88927300	4.68171800
H	-0.92492500	-2.42165700	5.66943300
C	1.70037400	1.63905700	3.83218700
O	2.37438100	0.66426000	3.61842700
O	2.14203900	2.78610800	4.35216100
C	3.54422700	2.82173800	4.64369400
H	3.72711300	3.80168500	5.07597100
H	3.80270000	2.03959500	5.35594400
H	4.12187300	2.69744000	3.72857200
C	-1.82127600	3.05354800	-0.55316400
H	-1.18468100	3.91977700	-0.74727400
H	-2.70612700	3.40080000	-0.02073500
C	-2.22922500	2.42220800	-1.86683100
C	-3.44127300	1.74167000	-1.97242900
C	-1.36333600	2.42288400	-2.95816600
C	-3.77863800	1.07028800	-3.14087800
H	-4.12038600	1.72962000	-1.12578000
C	-1.69565500	1.74922100	-4.12828000
H	-0.41705600	2.94944300	-2.88698400
C	-2.90385300	1.06859900	-4.22194400
H	-4.72471000	0.54587600	-3.20767200
H	-1.01025400	1.75600700	-4.96762200
H	-3.16341200	0.54134900	-5.13193900
C	-2.89961000	1.36386600	1.84718300
H	-2.84485600	1.40068200	2.93884600
H	-3.45964800	2.23320800	1.50730900
H	-3.46801000	0.46463600	1.58934000
C	-0.27572600	-1.53810100	0.06137600

3h

C	-2.49517500	-1.54133500	-0.24875100
C	-3.47489800	-1.75807400	-0.90859500
H	-1.89210000	-4.18517200	0.95161400
C	-4.42433500	-1.49516300	-3.15053800
H	-5.30375900	-1.69225500	-3.76834000
H	-4.24223100	-0.41867200	-3.13908700
H	-3.56370700	-1.98792300	-3.60709200
C	-5.88324700	-1.31913900	-1.11355500
H	-6.06861300	-1.67958200	-0.09990400
H	-5.72759100	-0.23926900	-1.07460900
H	-6.76980600	-1.52025100	-1.71981700
C	-4.91238600	-3.53953100	-1.77758600
H	-5.79428500	-3.75064400	-2.38724300
H	-4.05646700	-4.05645500	-2.21592000
H	-5.08084400	-3.93886600	-0.77546300
C	-1.28695200	-1.19971000	0.52744200
C	-1.68237700	-0.08576400	1.51271700
H	-0.81148000	0.42453900	1.91455000
H	-2.30015400	0.63943900	0.98466300
H	-2.26807900	-0.50269500	2.33307300
C	-0.16267800	-0.75442900	-0.42795400
H	0.01764600	-1.56262000	-1.14050000
H	0.74783600	-0.62732900	0.16468600
C	-0.46746600	0.53742800	-1.19272900
H	-1.43908300	0.44518500	-1.68580600
H	-0.52630400	1.37797200	-0.49814000
C	0.59692900	0.80873200	-2.22516700
C	0.51407800	0.23130400	-3.49225100
C	1.70832100	1.59338200	-1.92190800
C	1.51485700	0.43326000	-4.43433000
H	-0.34758800	-0.38077000	-3.74053300
C	2.71315700	1.79777600	-2.86117800
H	1.78584800	2.05011100	-0.94049000
C	2.61992300	1.21722500	-4.12033500
H	1.43121300	-0.01973500	-5.41528600
H	3.56962600	2.41204400	-2.60885400
H	3.40068500	1.37650900	-4.85424800
N	-1.11217000	-3.64575300	0.59653300
N	-0.86804400	-2.45035300	1.23995000
C	-0.00831800	-2.54131600	2.31395500
O	0.29325300	-3.59040700	2.83456300
O	0.45060700	-1.35404600	2.70523000
C	1.28926400	-1.38191400	3.86731400
H	2.19618700	-1.94924000	3.66400100
H	1.53059900	-0.34302100	4.07588400
H	0.75744900	-1.82313300	4.70895400
C	-0.09157600	-4.41134300	0.08336000
O	-0.24428800	-5.57215400	-0.21693300
O	1.03210800	-3.71918600	-0.08068900
C	2.12337800	-4.45894200	-0.64052300
H	2.94384000	-3.75095400	-0.71945400
H	2.39550700	-5.28420900	0.01614800
H	1.85622200	-4.83987600	-1.62511900
C	-4.66873700	-2.02492600	-1.73084400

Appendix IV

Selected NMR Spectra for Chapter 4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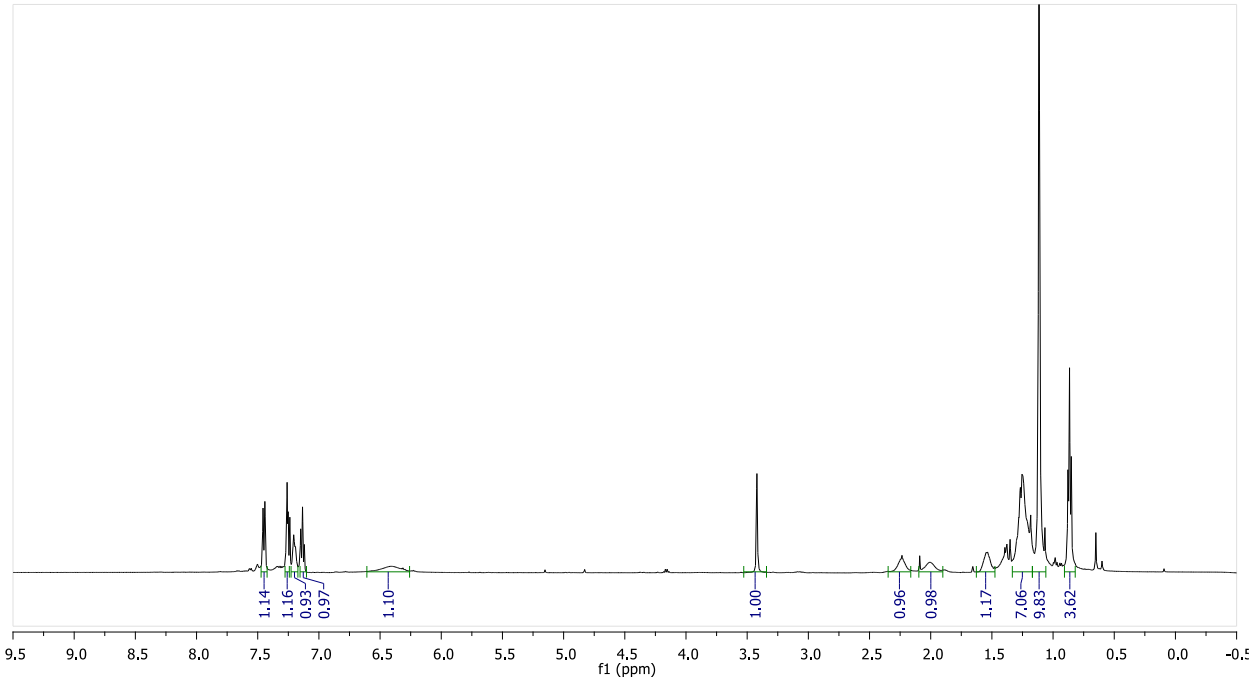
OH
Cl

4-35a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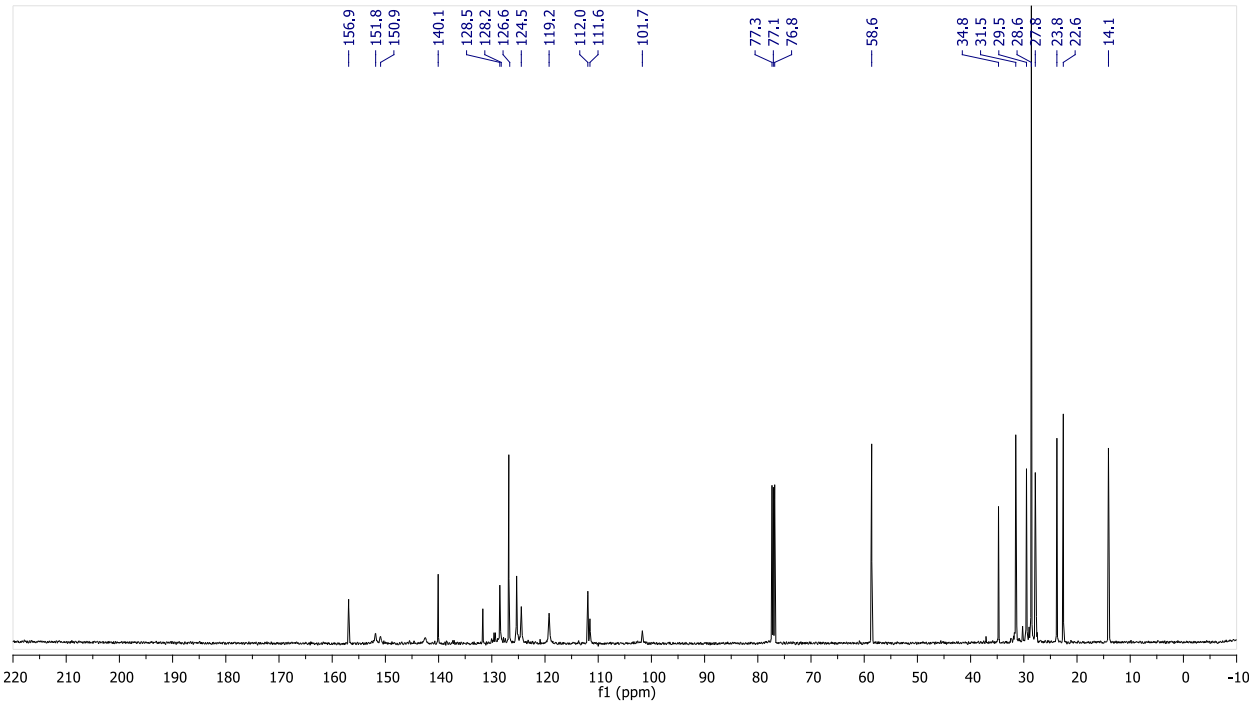
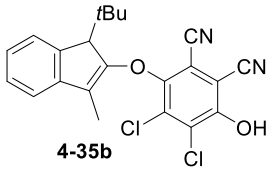
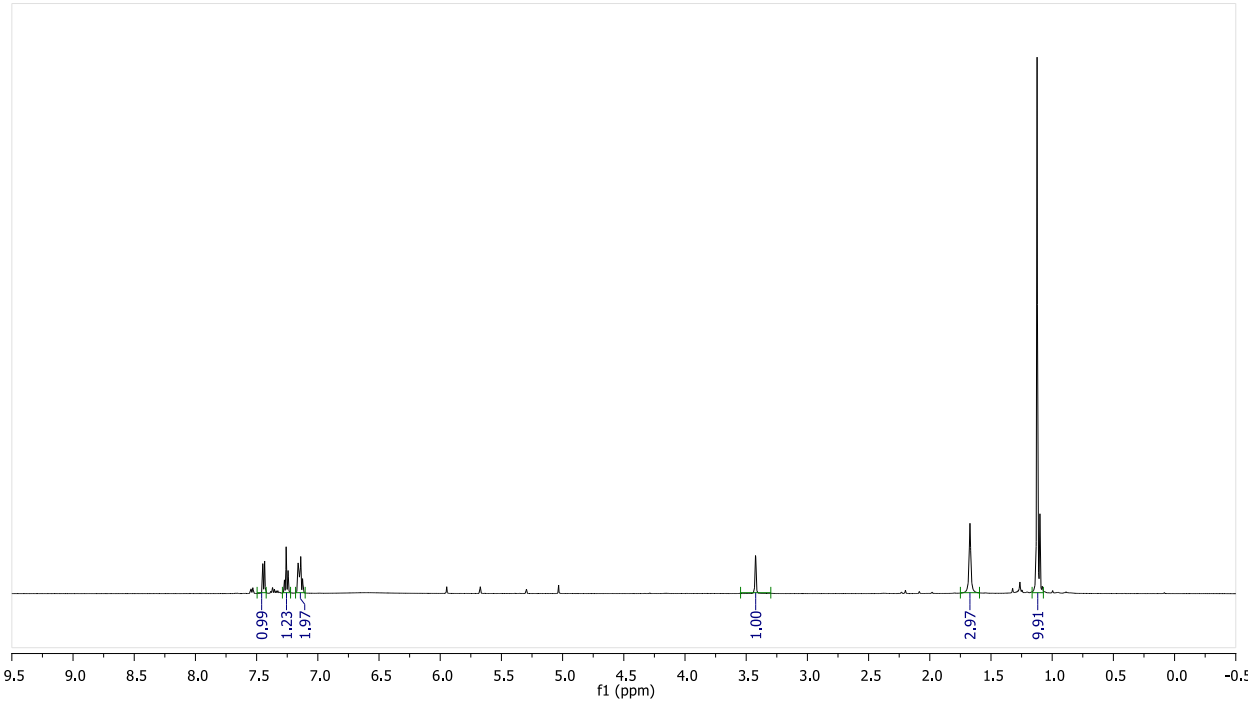
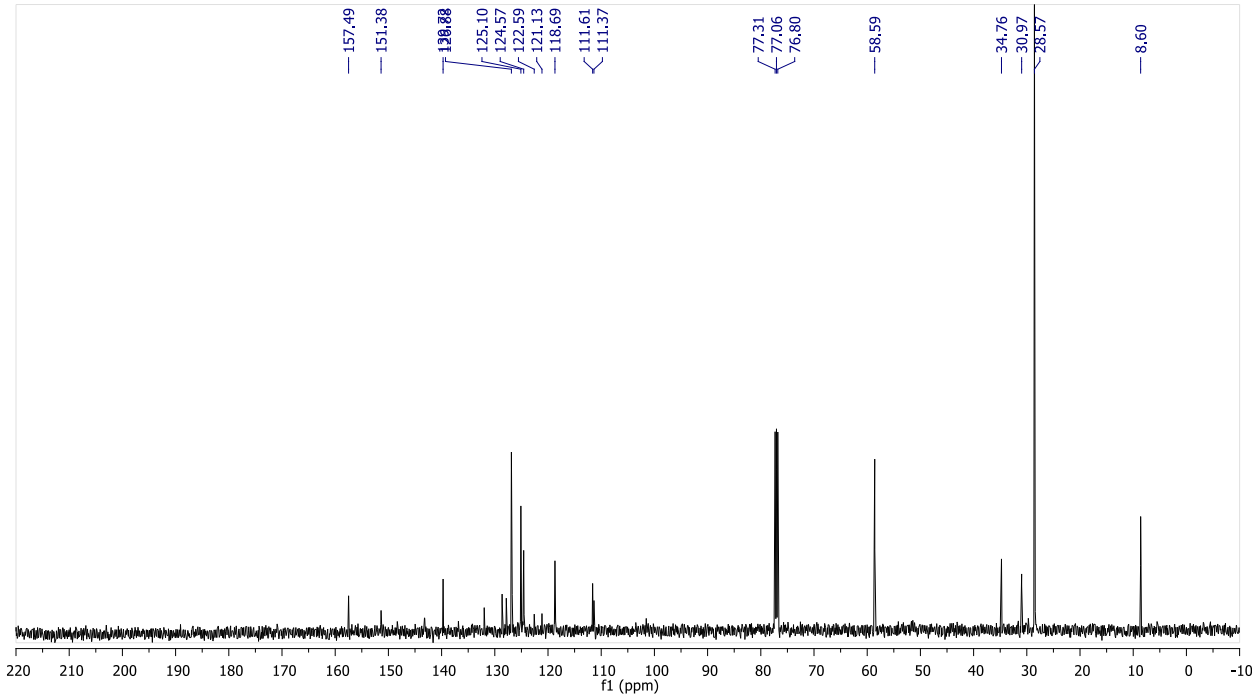
1.00
0.96
0.98
1.17
7.06
9.83
3.62
f1 (ppm)

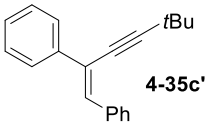

156.9
151.8
150.9
140.1
128.5
128.2
126.6
124.5
119.2
112.0
111.6
101.7
77.3
77.1
76.8
58.6
34.8
31.5
29.5
28.6
27.8
23.8
22.6
14.1
f1 (ppm)


tBu
CN
CN
O
Cl
OH
Cl

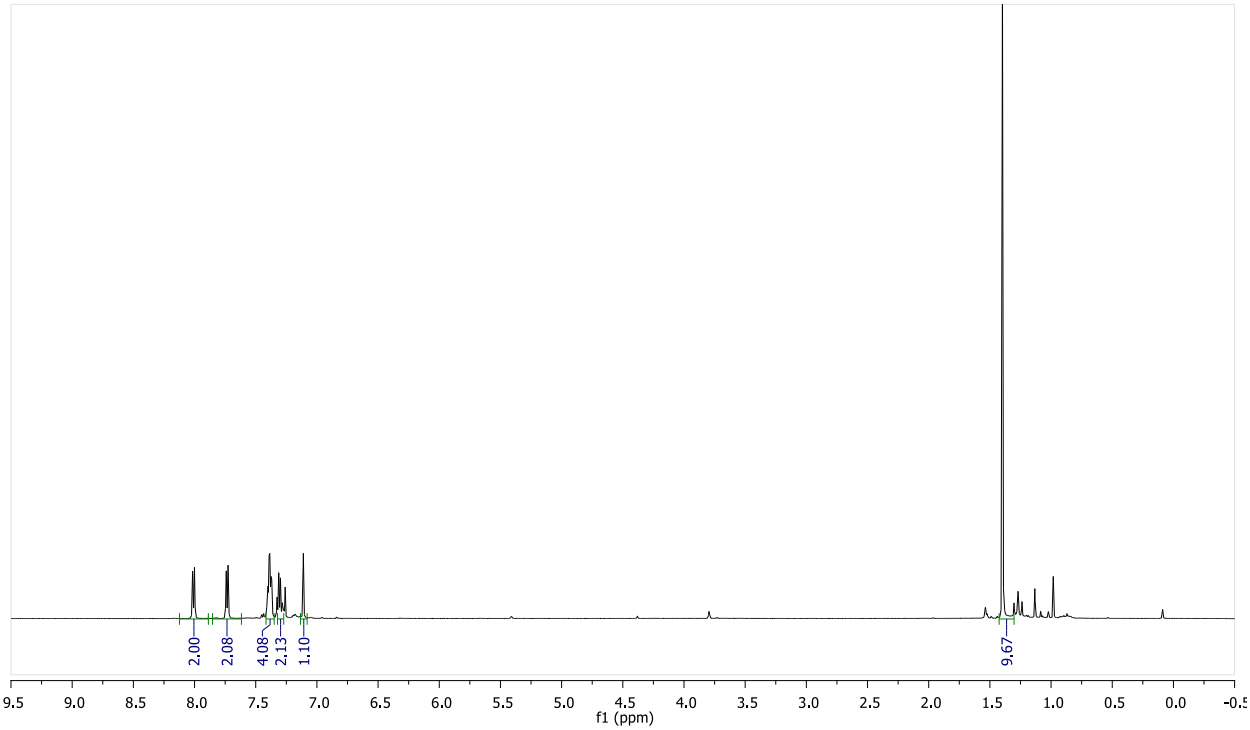
4-35b

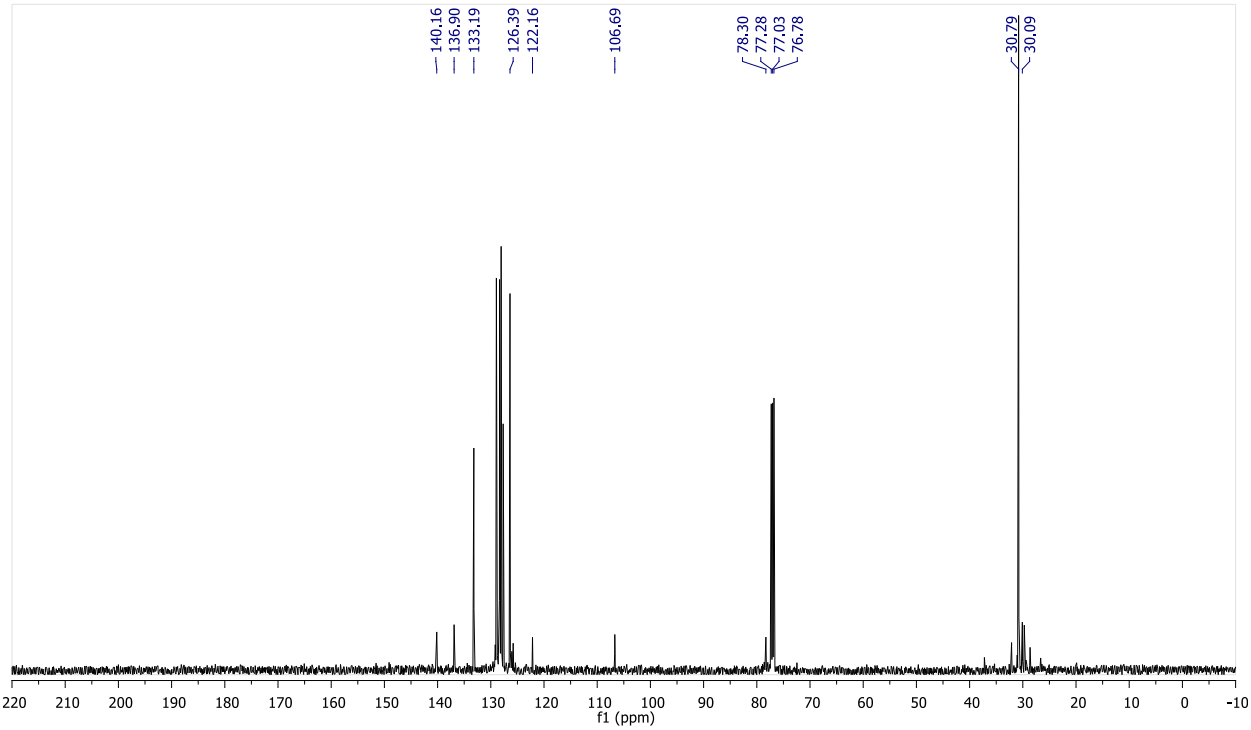

0.99
1.23
1.97
1.00
2.97
9.91
f1 (ppm)

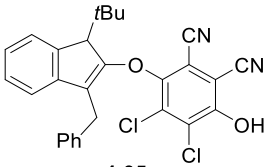

157.49
151.38
125.10
124.57
122.59
121.13
118.69
111.61
111.37
77.31
77.06
76.80
58.59
34.76
30.97
28.57
8.60
f1 (ppm)


tBu
Ph

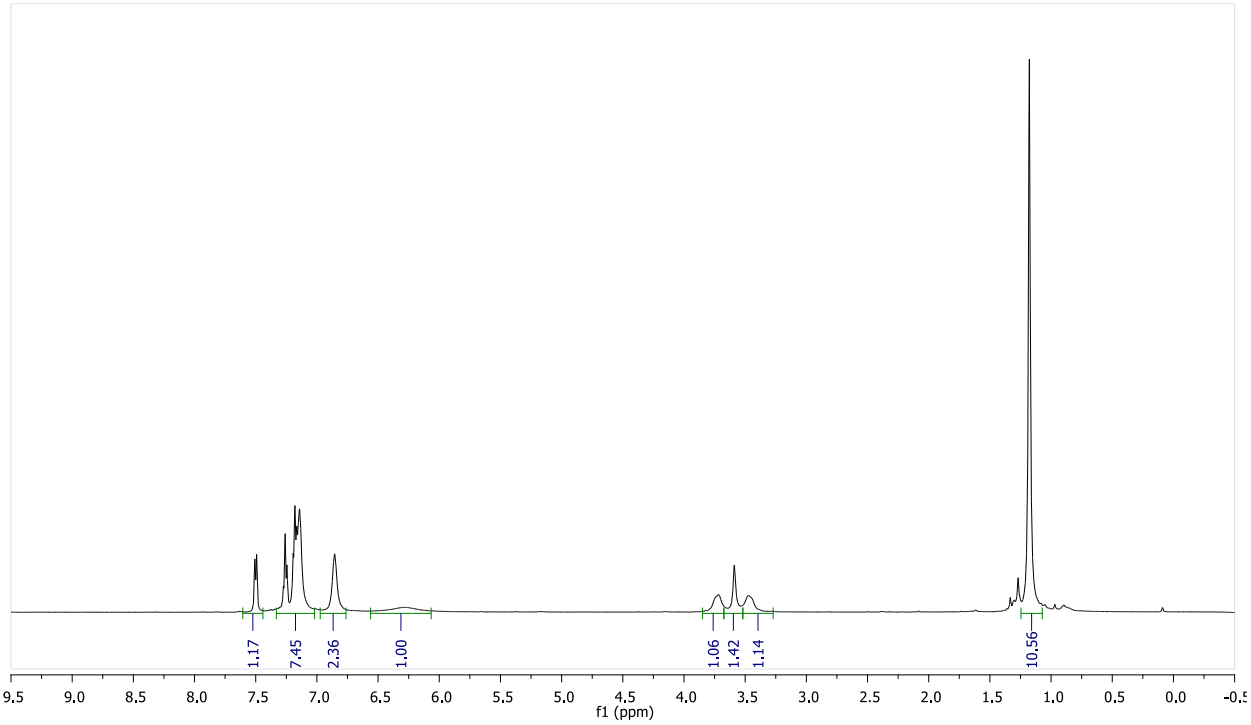
4-35c'

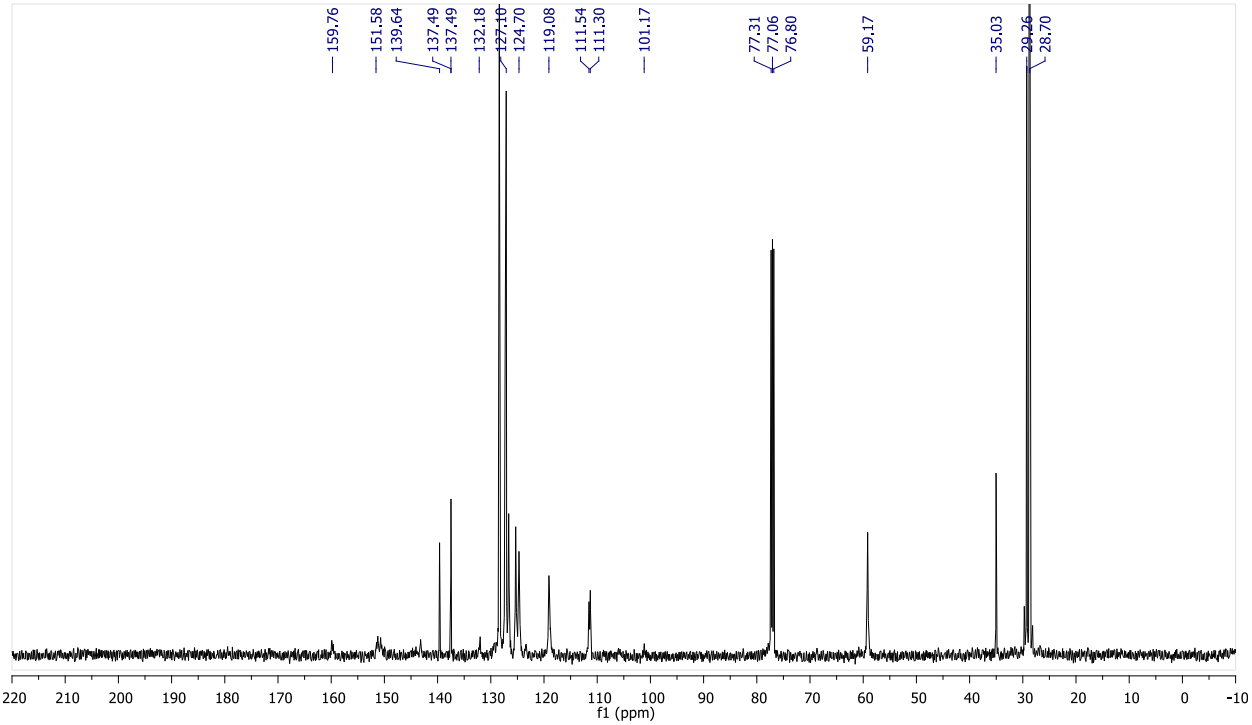

2.00
2.08
4.08
2.13
1.10
9.67
f1 (ppm)

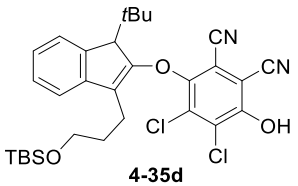

140.16
136.90
133.19
126.39
122.16
106.69
78.30
77.28
77.03
76.78
30.79
30.09
f1 (ppm)


tBu
CN
CN
O
Cl
OH
Cl
Ph

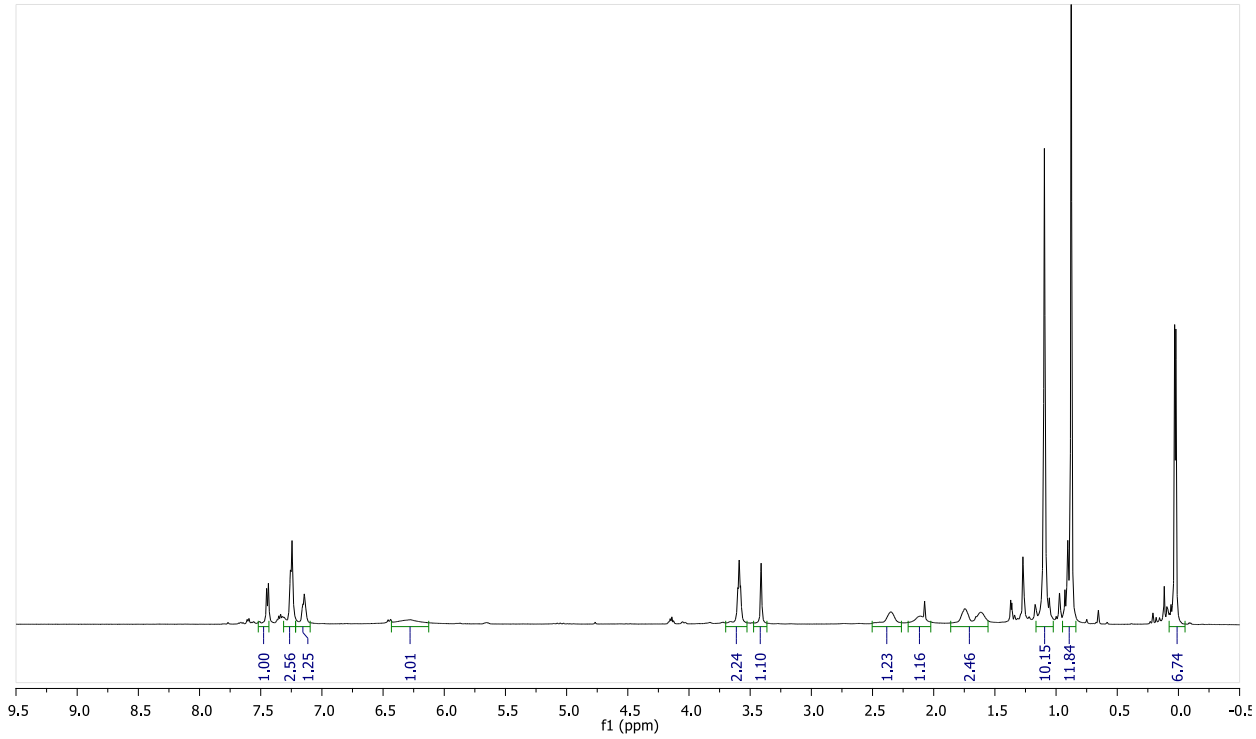
4-35c

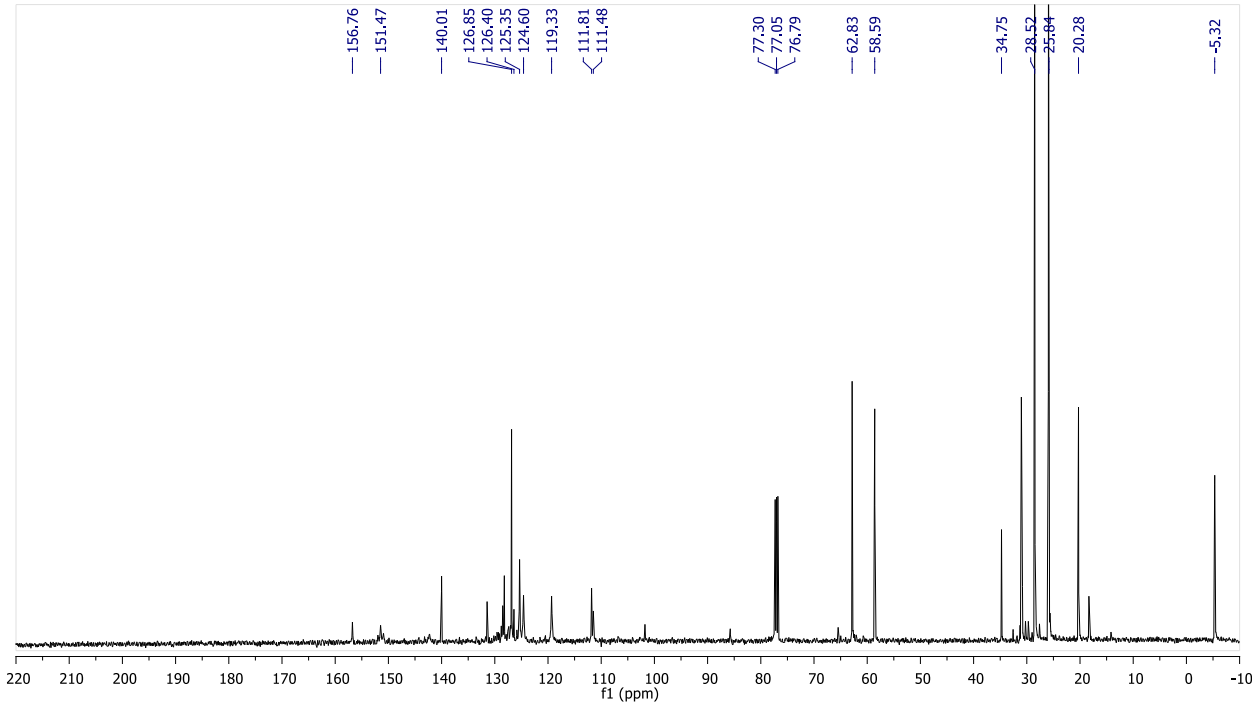

1.17
7.45
2.36
1.00
1.06
1.42
1.14
10.56
f1 (ppm)

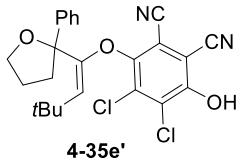

159.76
151.58
139.64
137.49
137.49
132.18
127.10
124.70
119.08
111.54
111.30
101.17
77.31
77.06
76.80
59.17
35.03
29.26
28.70
f1 (ppm)


tBu
CN
O
CN
Cl
OH
Cl
TBSO

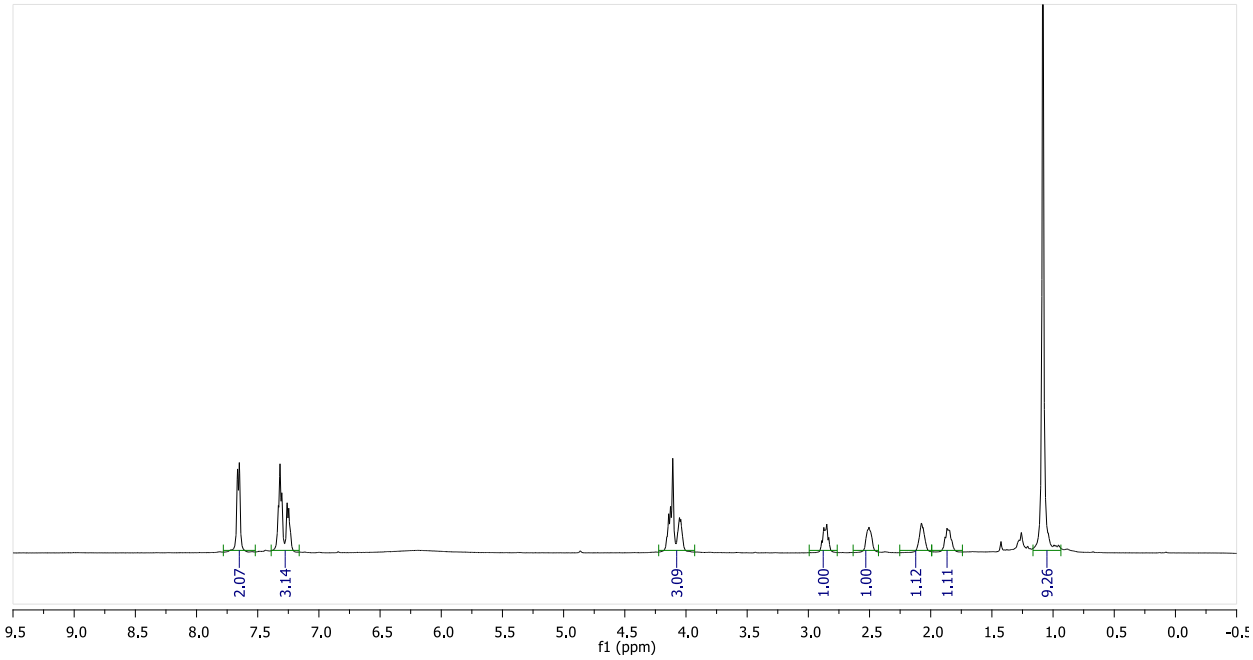
4-35d

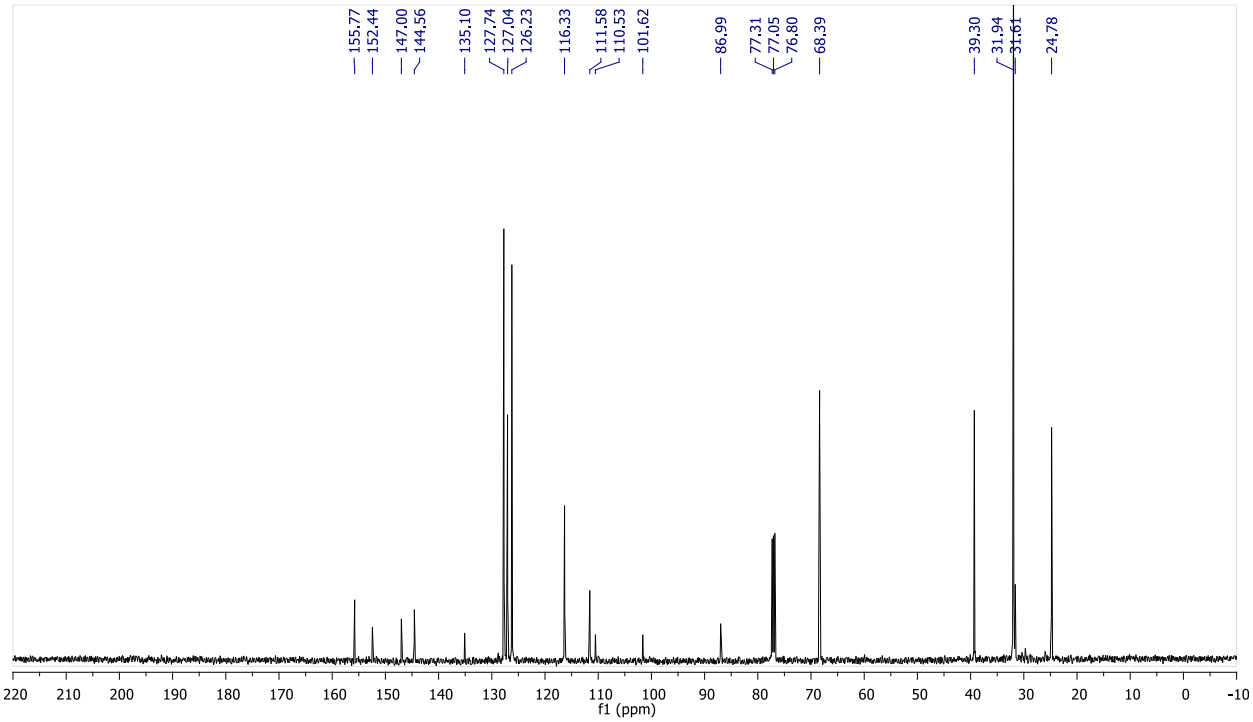

1.00
2.56
1.25
1.01
2.24
1.10
1.23
1.16
2.46
10.15
11.84
6.74
f1 (ppm)


156.76
151.47
140.01
126.85
126.40
125.35
124.60
119.33
111.81
111.48
77.30
77.05
76.79
62.83
58.59
34.75
28.52
25.84
20.28
-5.32
f1 (ppm)


Ph
O
O
NC
CN
tBu
Cl
OH
Cl

4-35e'


2.07
3.14
3.09
1.00
1.00
1.12
1.11
9.26
f1 (ppm)


155.77
152.44
147.00
144.56
135.10
127.74
127.04
126.23
116.33
111.58
110.53
101.62
86.99
77.31
77.05
76.80
68.39
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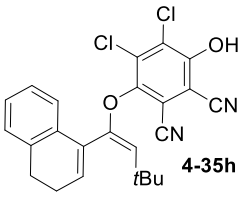
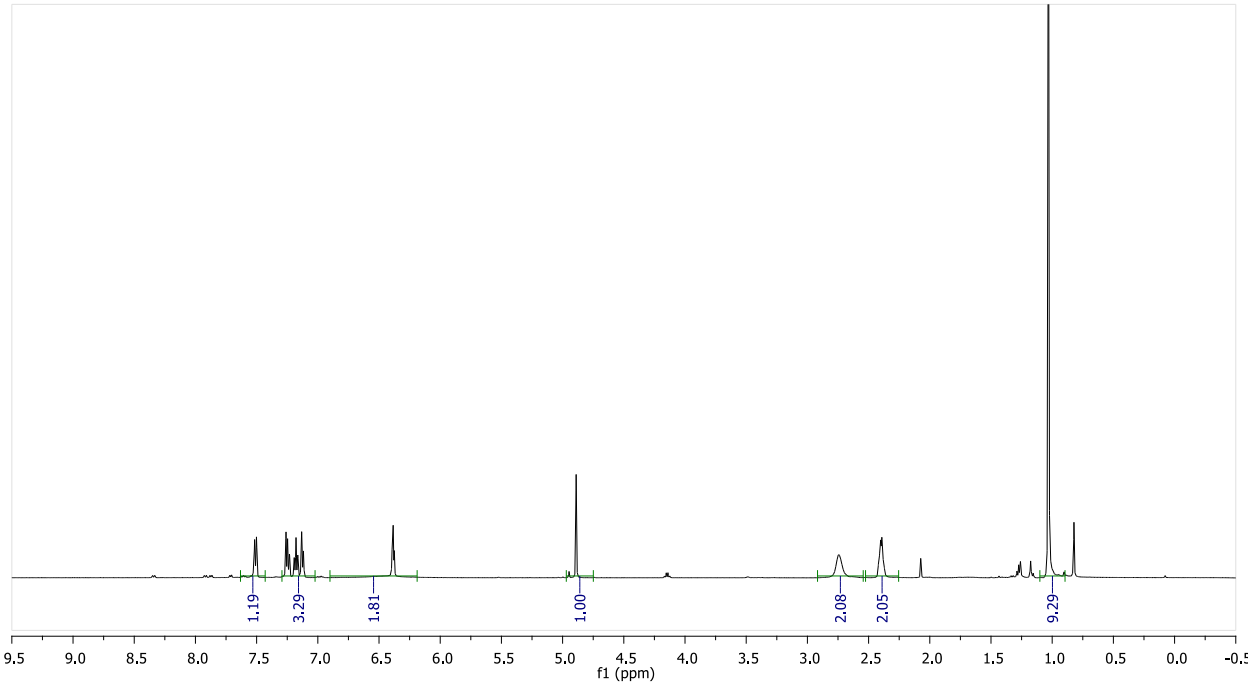
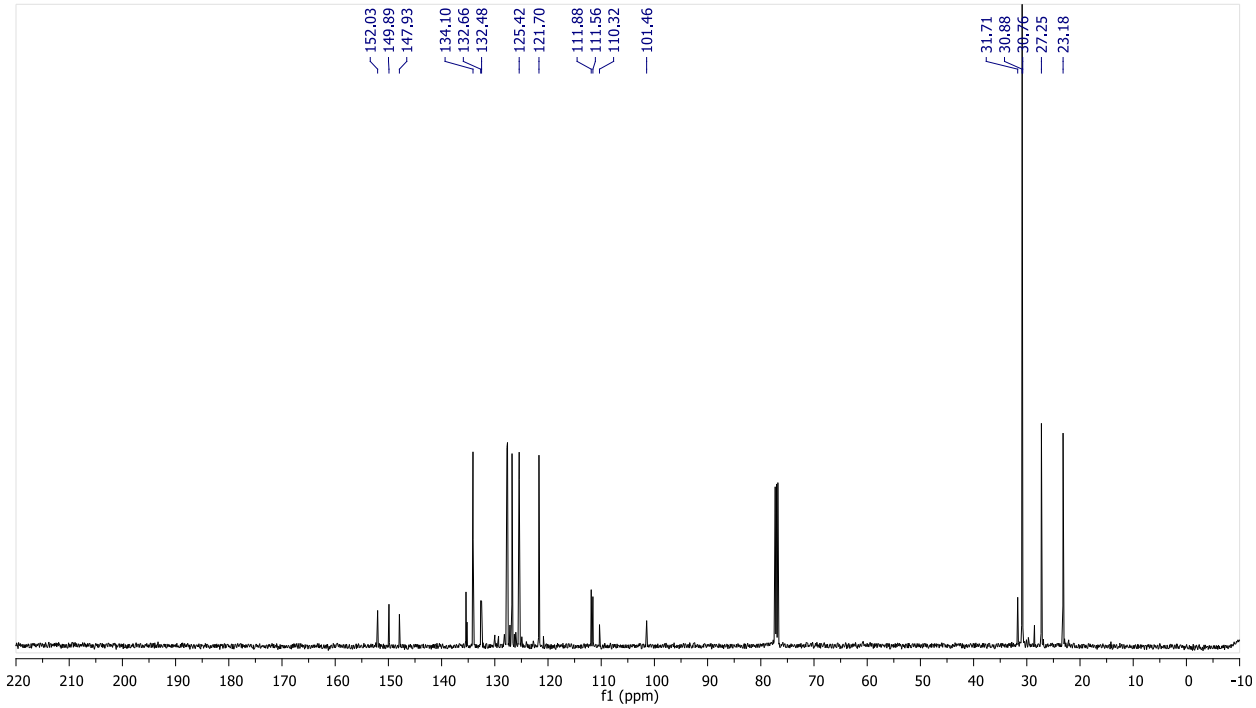
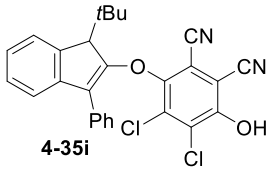
31.94
31.61
24.78
f1 (ppm)


Cl
Cl
OH
O
CN
CN
tBu

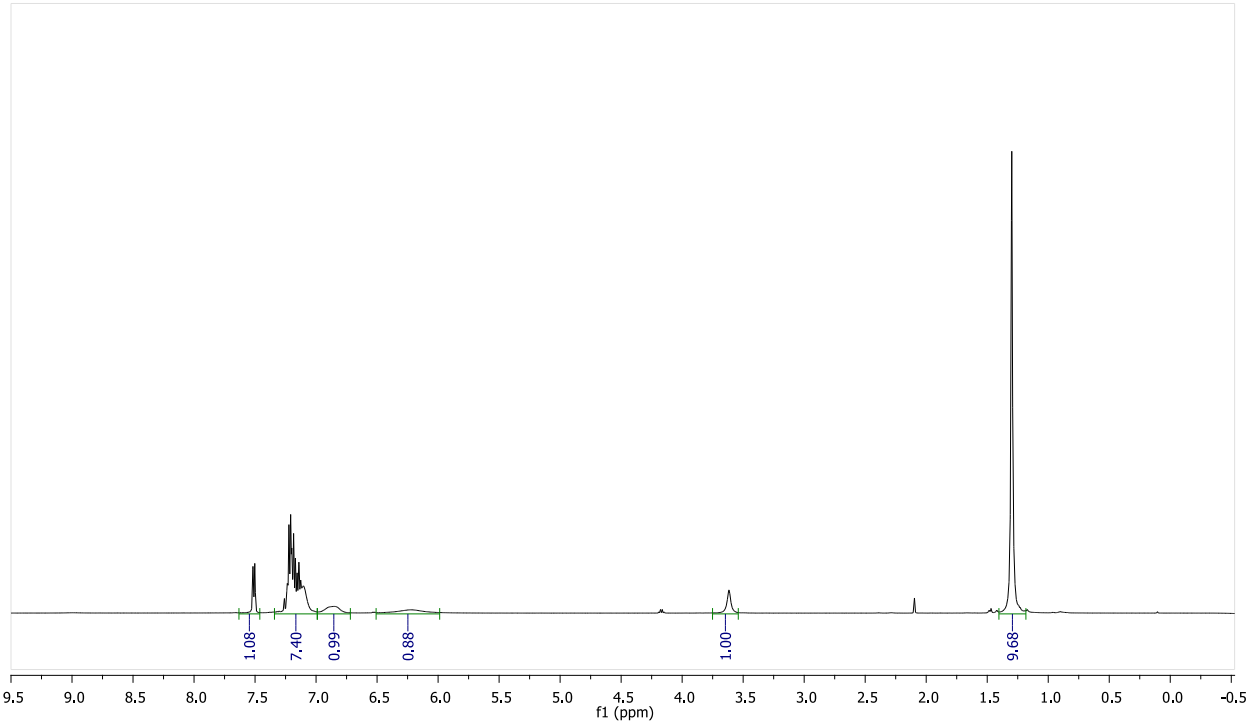
4-35h

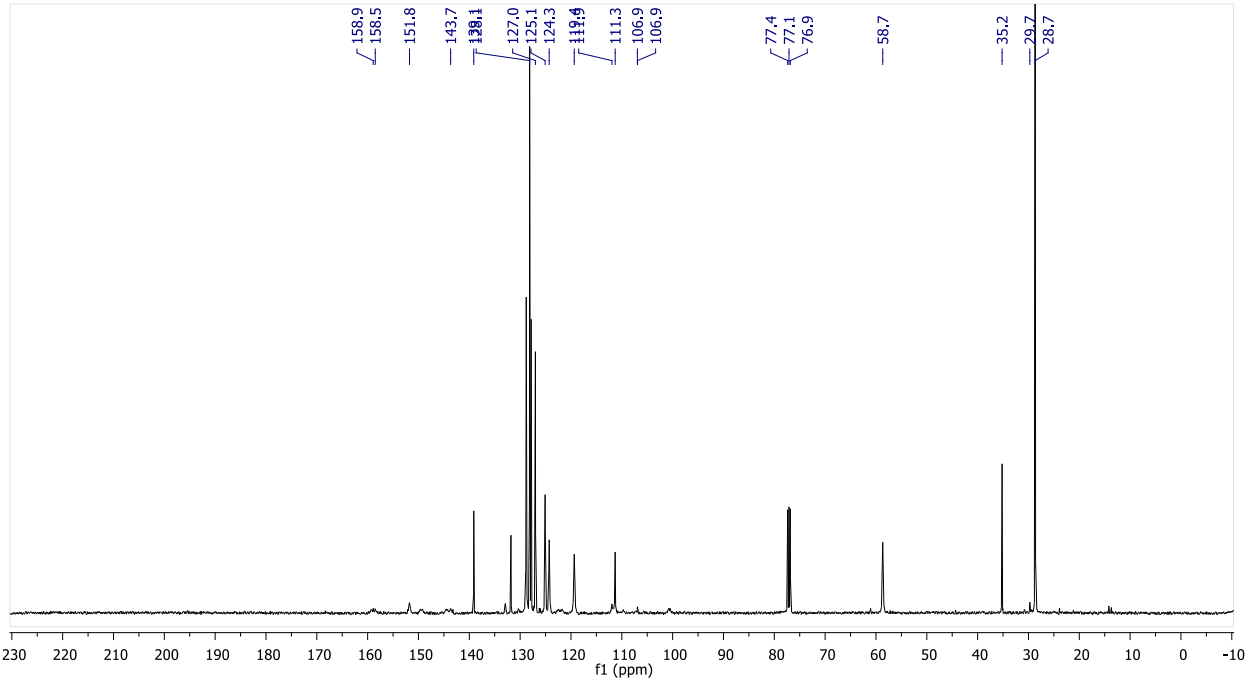

1.19
3.29
1.81
1.00
2.08
2.05
9.29
f1 (ppm)

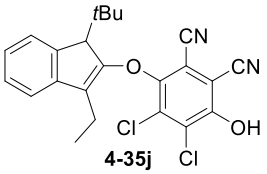

152.03
149.89
147.93
134.10
132.66
132.48
125.42
121.70
111.88
111.56
110.32
101.46
31.71
30.88
30.76
27.25
23.18
f1 (ppm)


tBu
CN
O
CN
Ph
Cl
OH
Cl

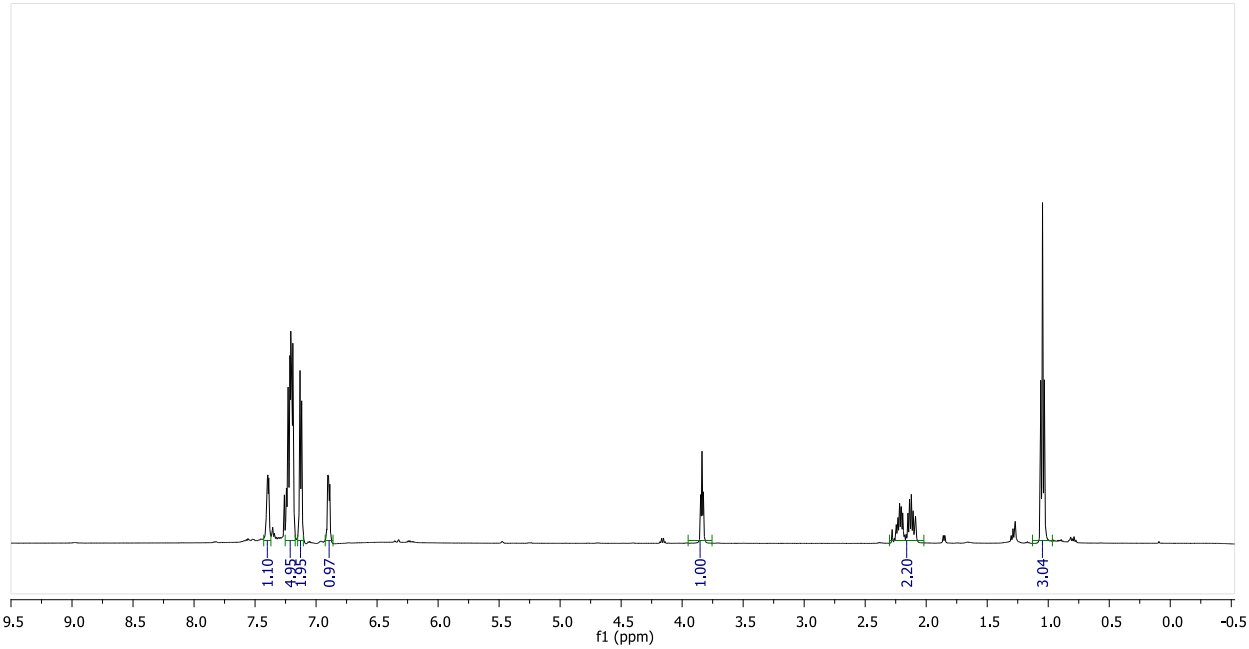
4-35i

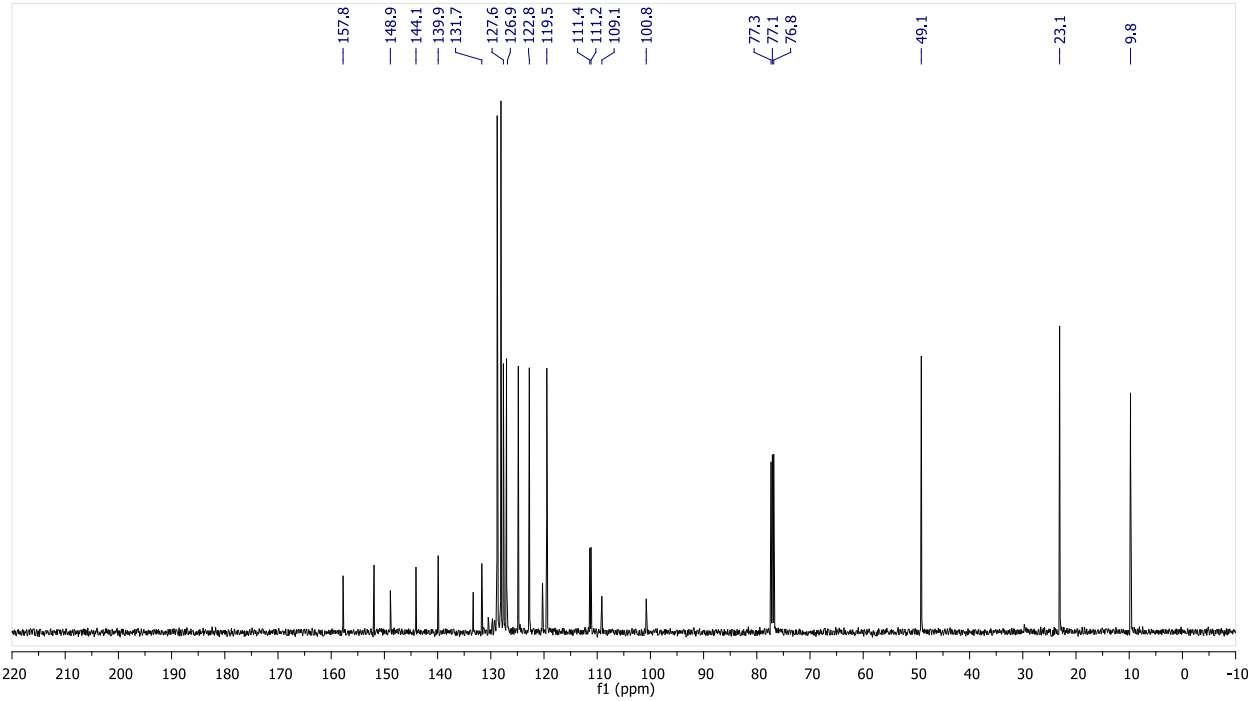

1.08
7.40
0.99
0.88
1.00
9.68
f1 (ppm)

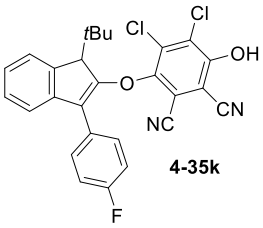

158.9
158.5
151.8
143.7
127.0
125.1
124.3
111.3
106.9
106.9
77.4
77.1
76.9
58.7
35.2
29.7
28.7
f1 (ppm)


tBu
CN
O
CN
Cl
OH
Cl

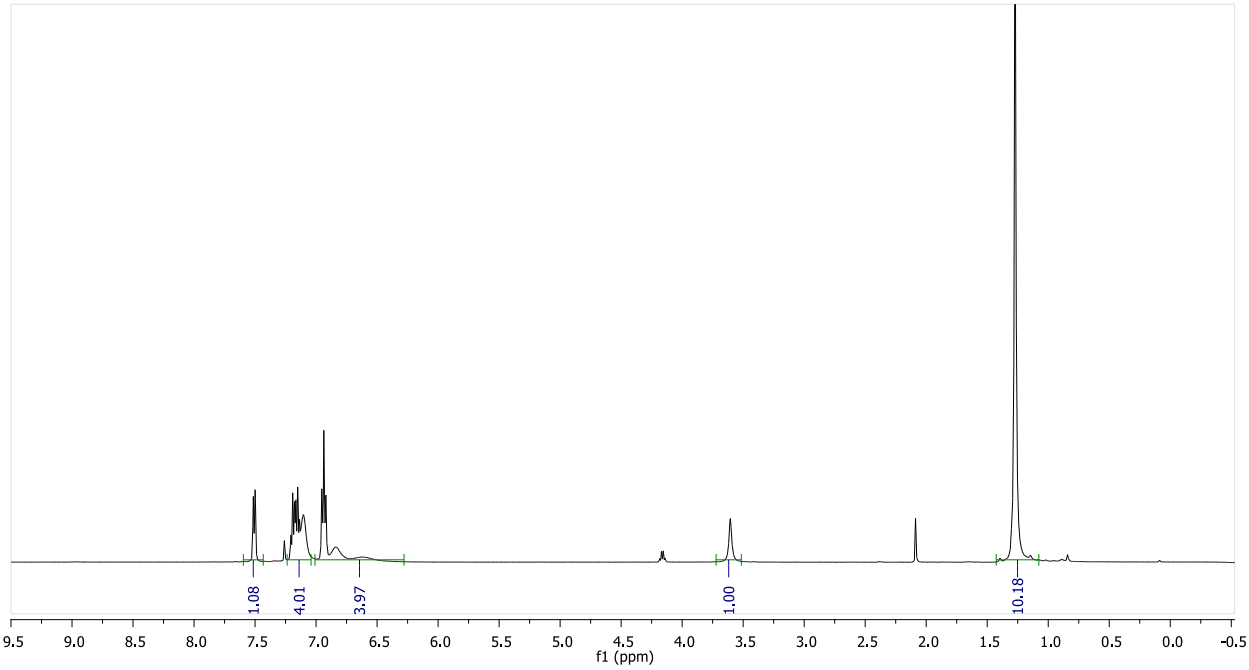
4-35j

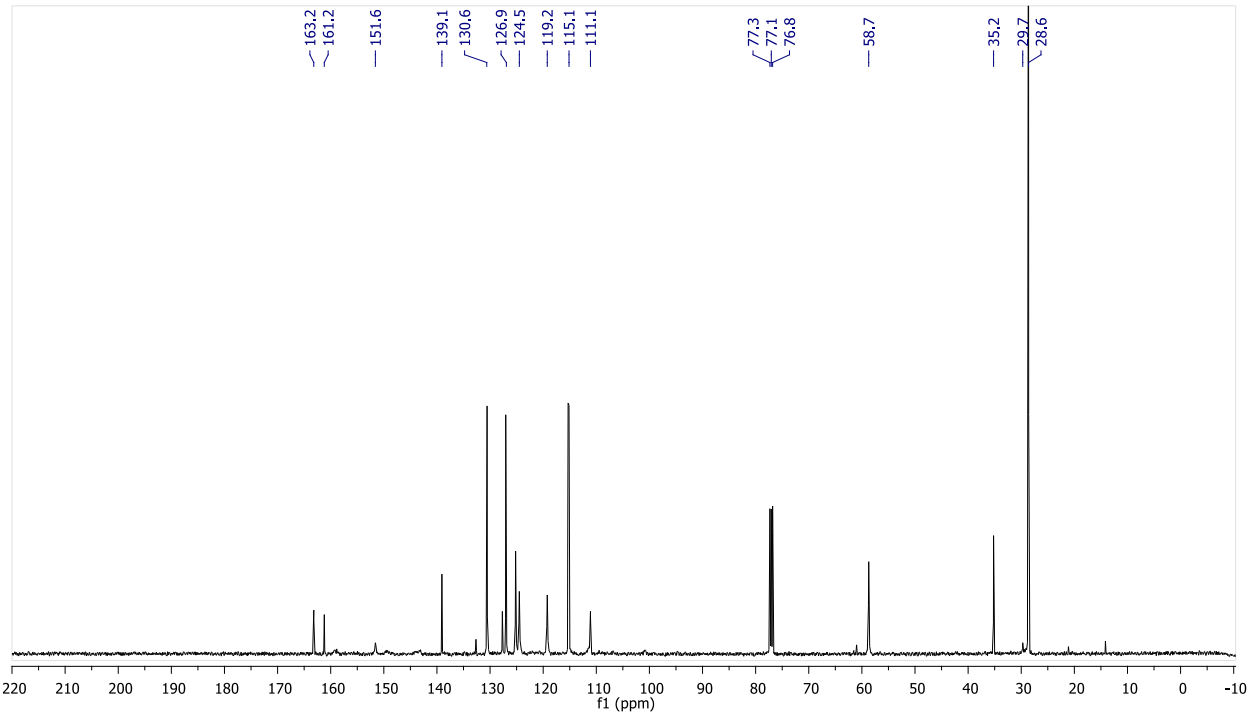

1.10
4.95
1.95
0.97
1.00
2.20
3.04
f1 (ppm)

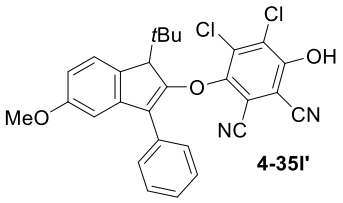

157.8
148.9
144.1
139.9
131.7
127.6
126.9
122.8
119.5
111.4
111.2
109.1
100.8
77.3
77.1
76.8
49.1
23.1
9.8
f1 (ppm)


tBu
Cl
Cl
OH
O
CN
NC
F

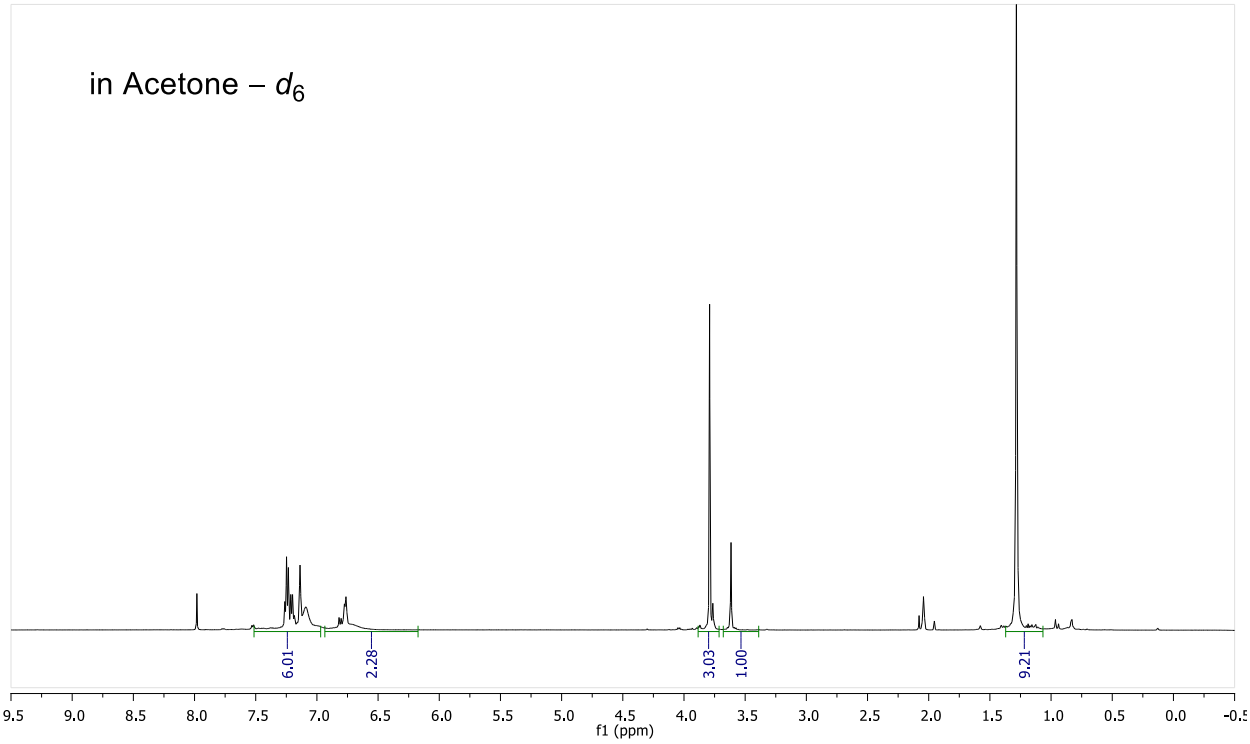
4-35k

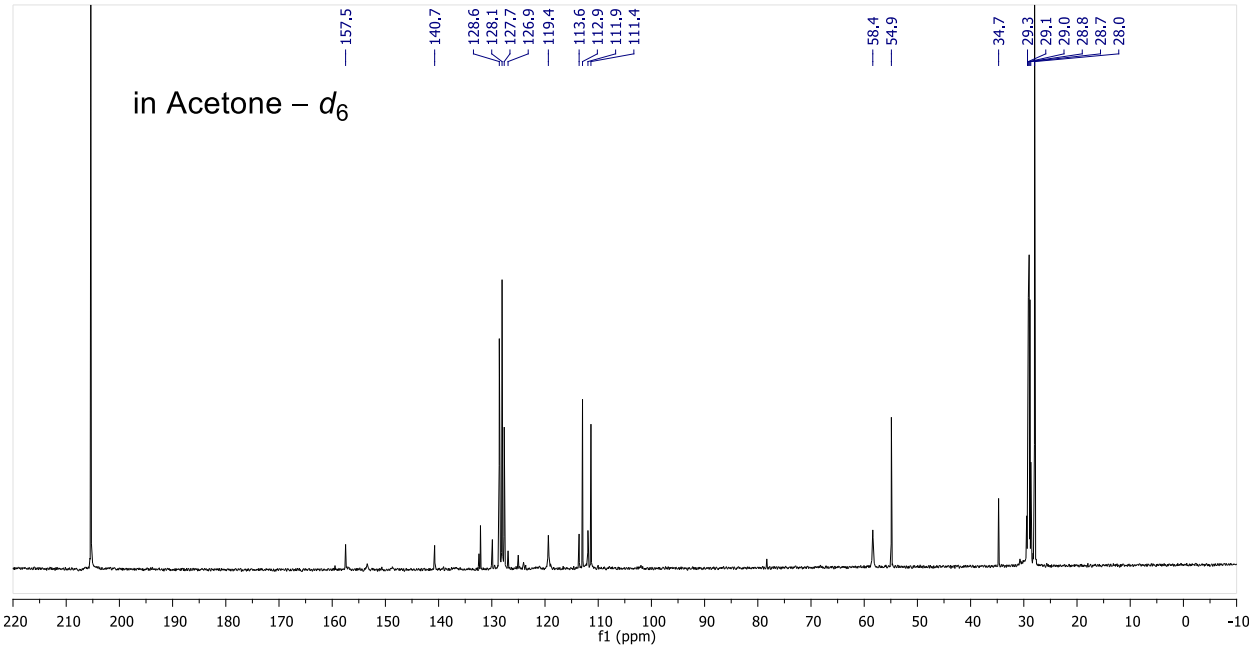

1.08
4.01
3.97
1.00
10.18
f1 (ppm)

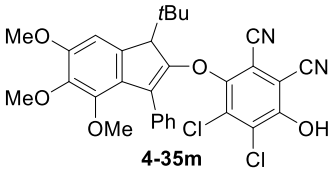

163.2
161.2
151.6
139.1
130.6
126.9
124.5
119.2
115.1
111.1
77.3
77.1
76.8
58.7
35.2
29.7
28.6
f1 (ppm)


tBu
Cl
Cl
OH
O
MeO
NC
CN

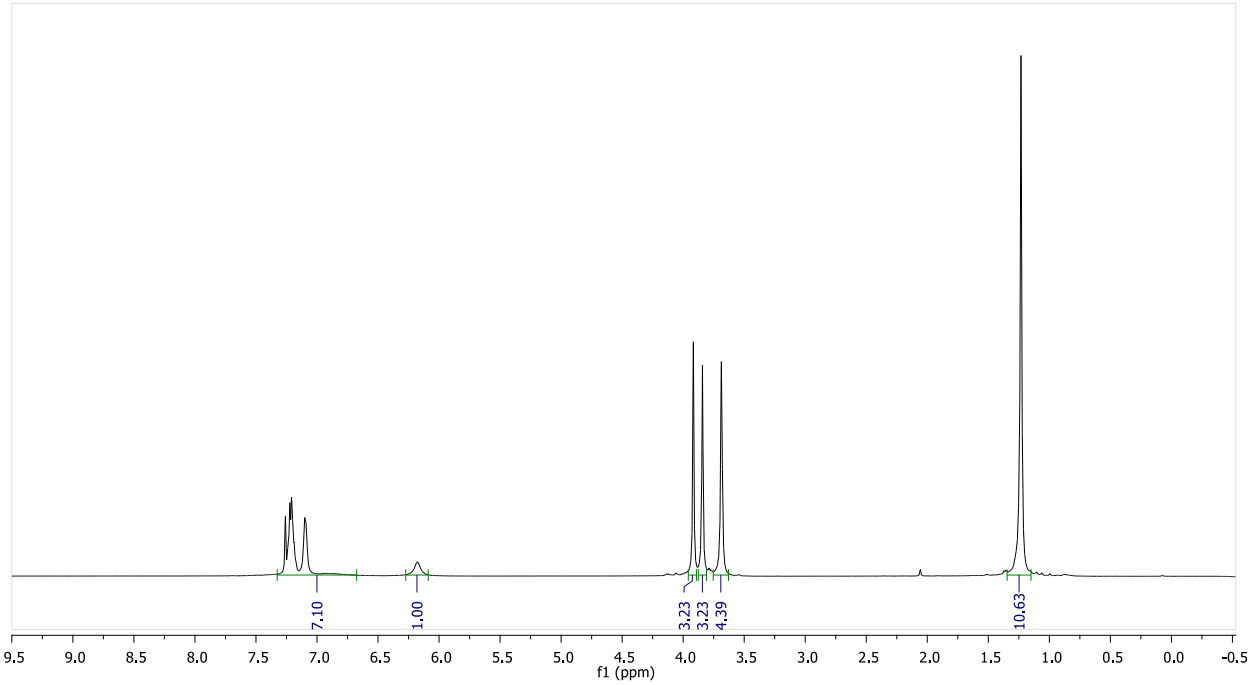
4-35l'

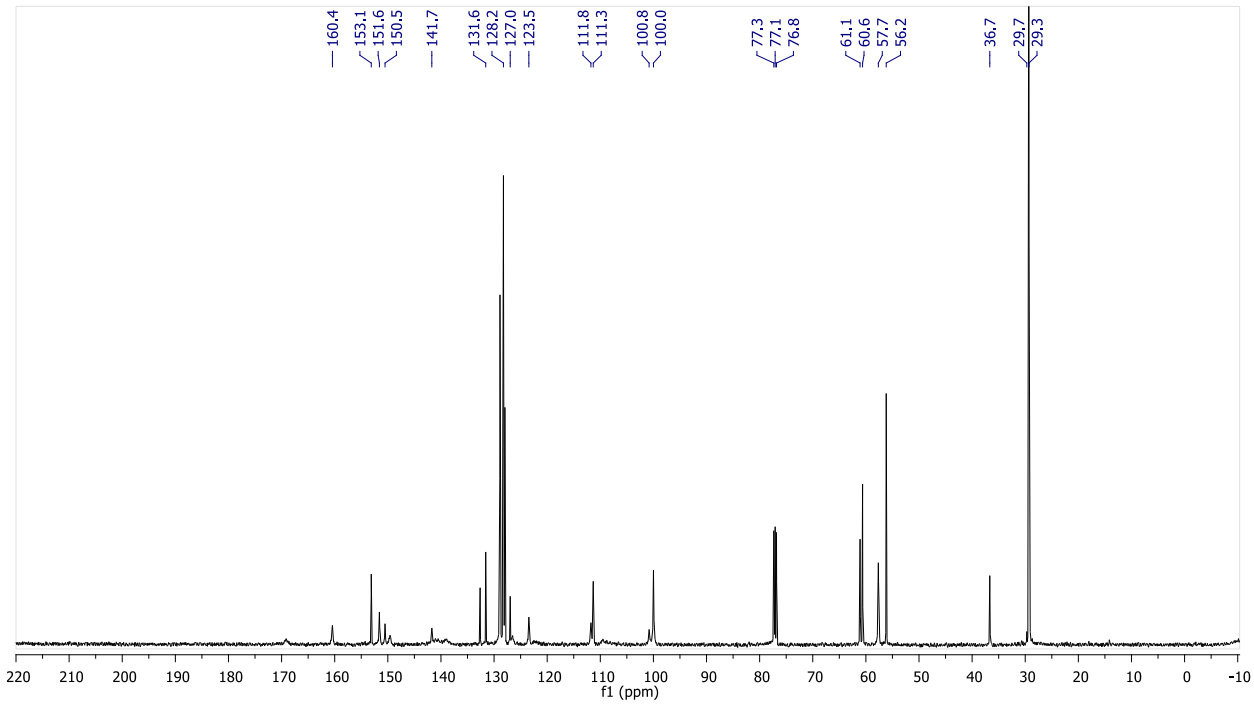

in Acetone – d_6
6.01
2.28
3.03
1.00
9.21
f1 (ppm)

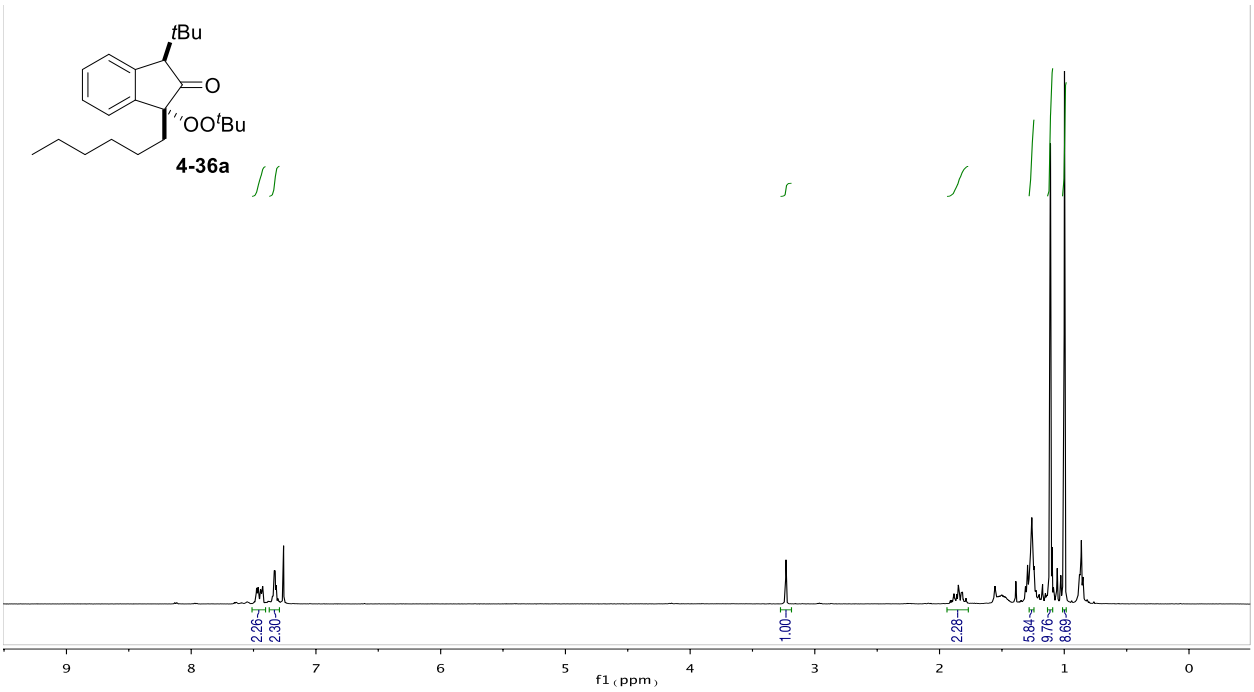

157.5
140.7
128.6
128.1
127.7
126.9
119.4
113.6
112.9
111.9
111.4
58.4
54.9
34.7
29.3
29.1
29.0
28.8
28.7
28.0
in Acetone – d_6
f1 (ppm)

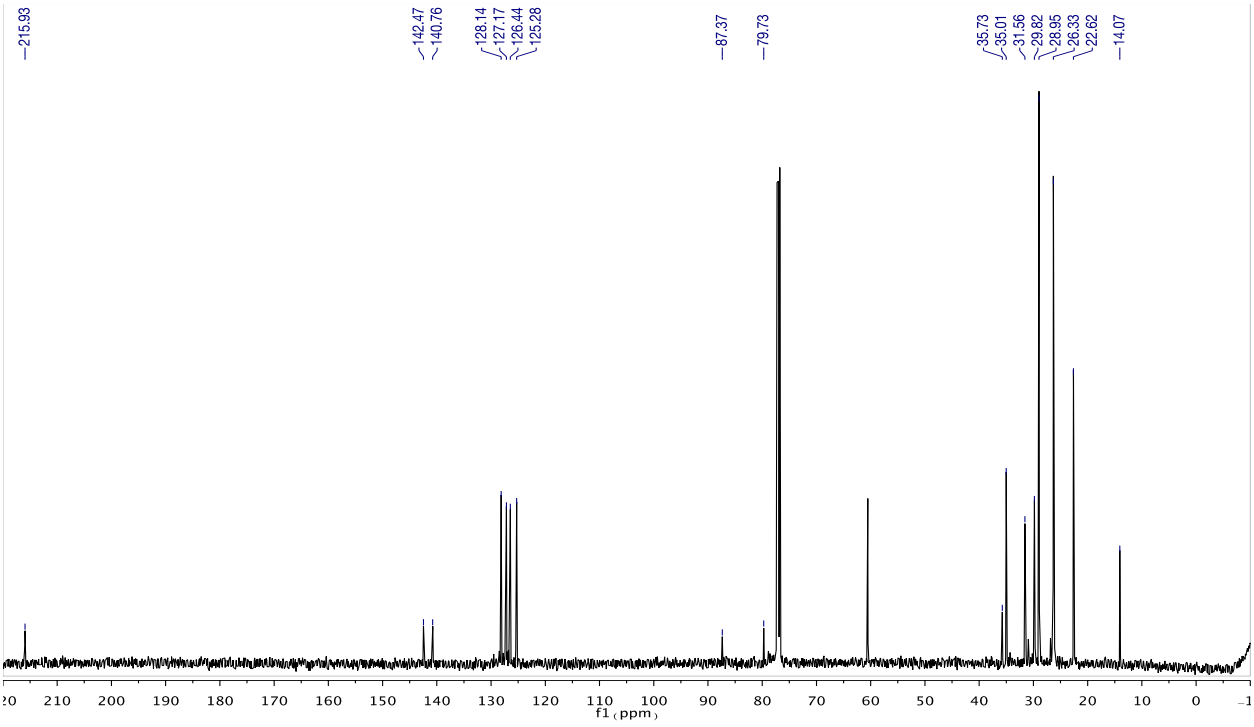

tBu
MeO
CN
CN
O
MeO
OMe
Ph
Cl
OH
Cl

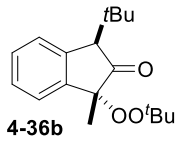
4-35m


7.10
1.00
3.23
3.23
4.39
10.63
f1 (ppm)

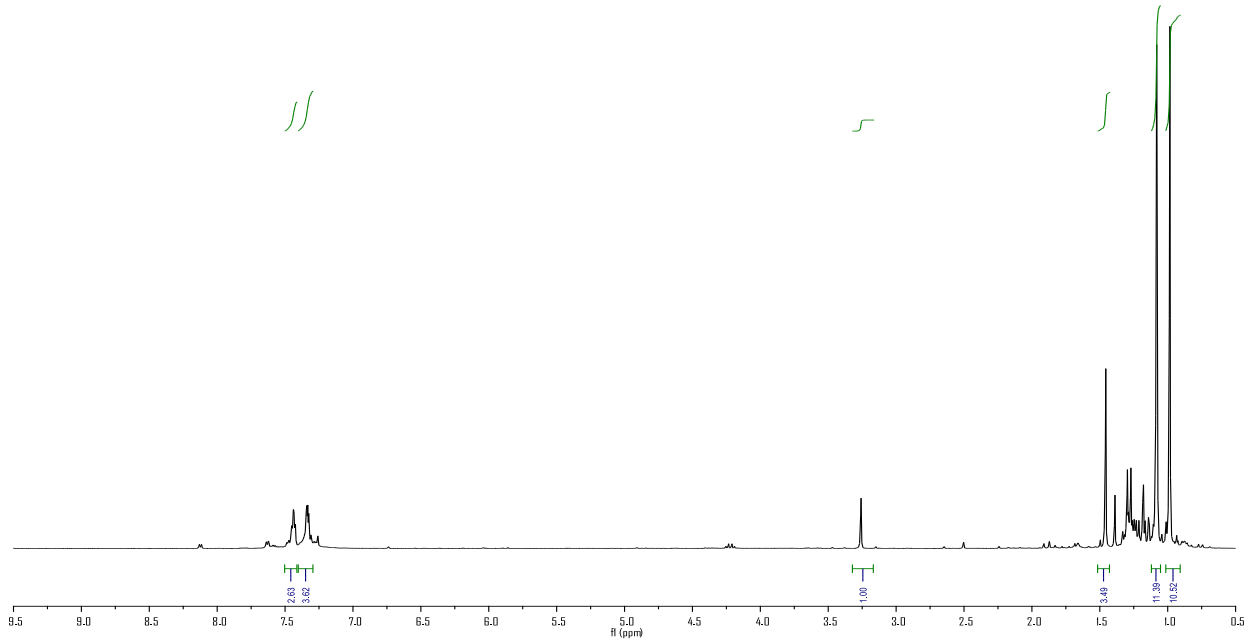

160.4
153.1
151.6
150.5
141.7
131.6
128.2
127.0
123.5
111.8
111.3
100.8
100.0
77.3
77.1
76.8
61.1
60.6
57.7
56.2
36.7
29.7
29.3
f1 (ppm)

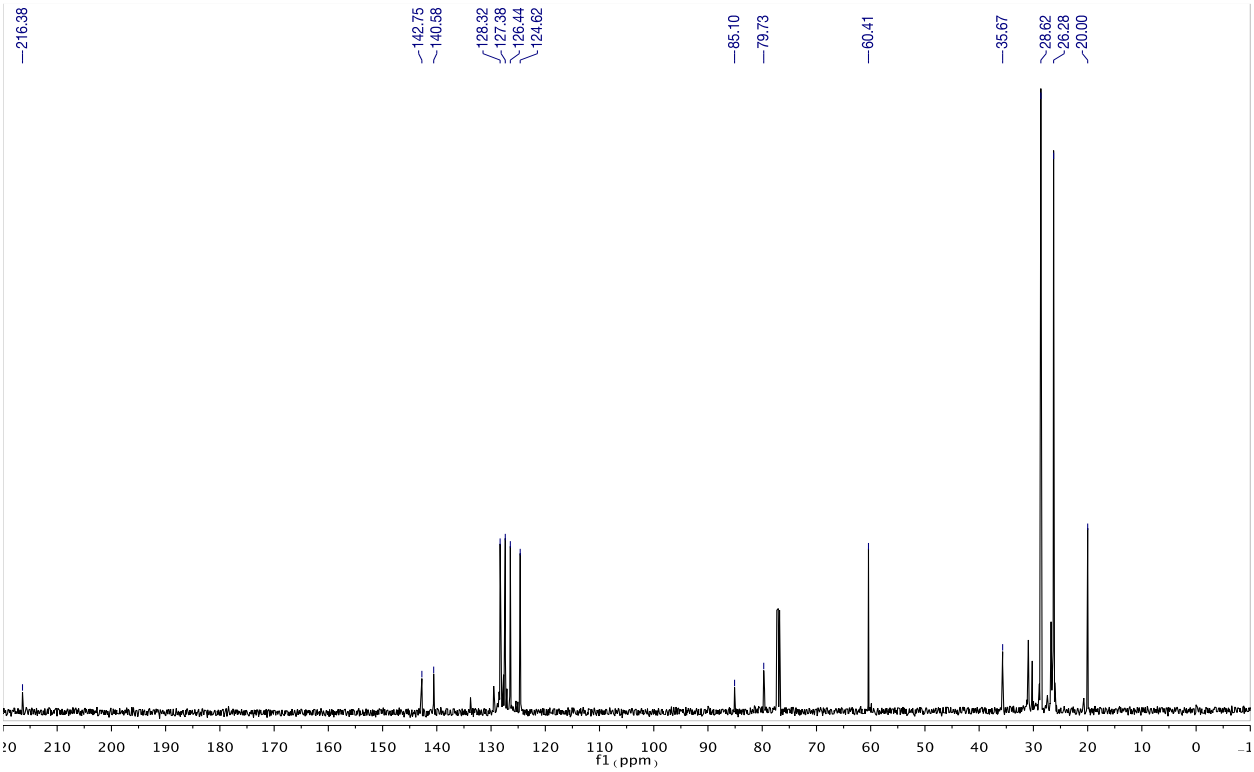

tBu
O
OOtBu
4-36a
2.26
2.30
1.00
2.28
5.84
9.76
8.69
f1 (ppm)

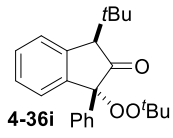

215.93
142.47
140.76
128.14
127.17
126.44
125.28
87.37
79.73
35.73
35.01
31.56
29.82
28.95
26.33
22.62
14.07
f1 (ppm)


tBu
O
OO'Bu

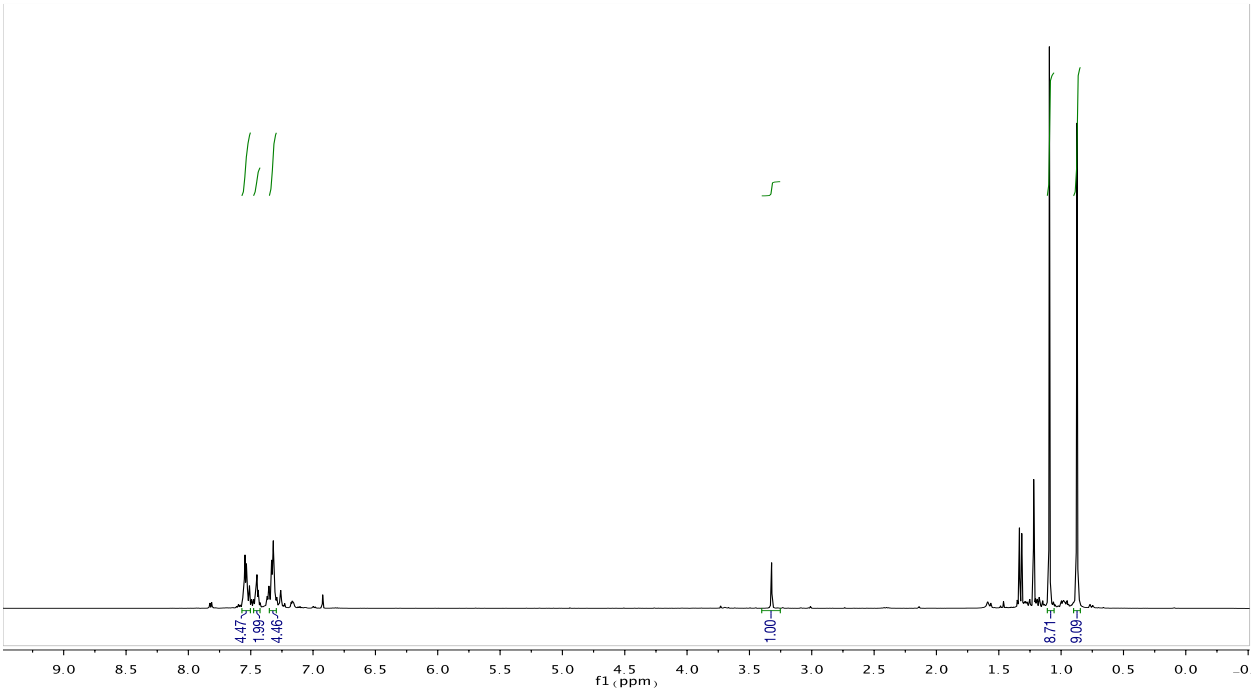
4-36b

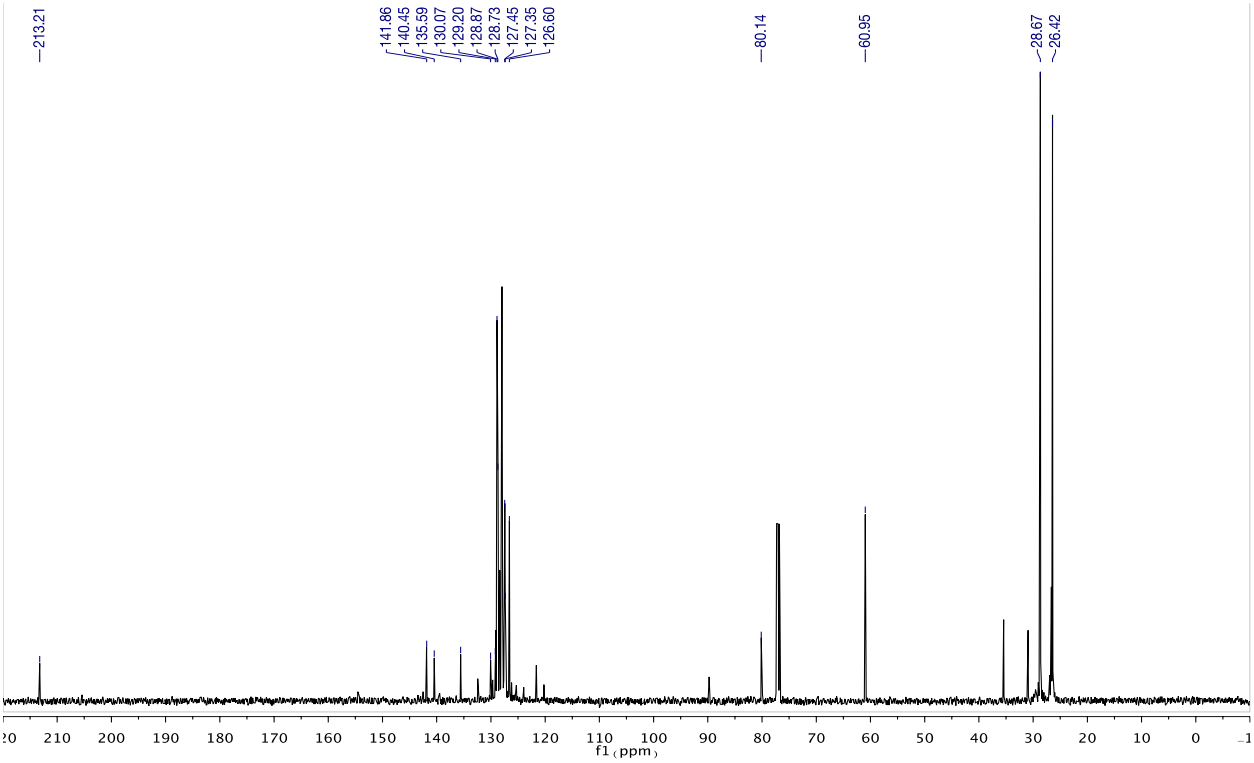

2.63
3.62
1.00
3.49
11.39
10.52
f1 (ppm)

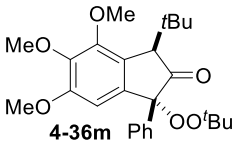

216.38
142.75
140.58
128.32
127.38
126.44
124.62
85.10
79.73
60.41
35.67
28.62
26.28
20.00
f1 (ppm)


tBu
O
Ph
OOtBu

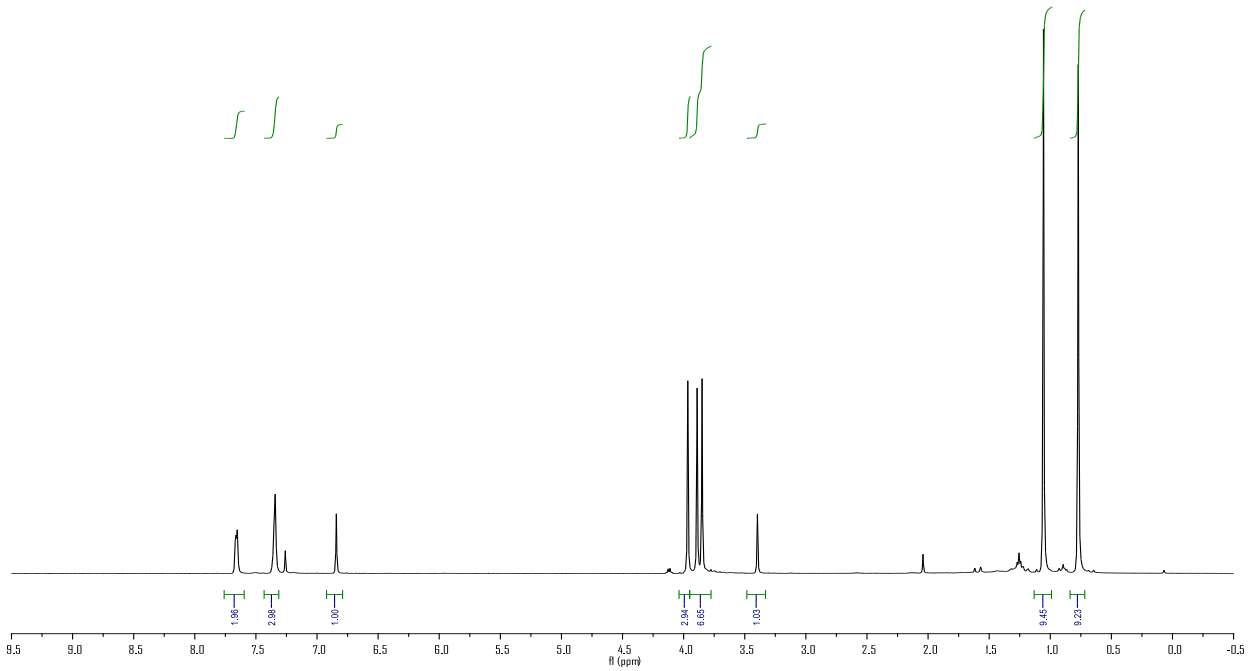
4-36i

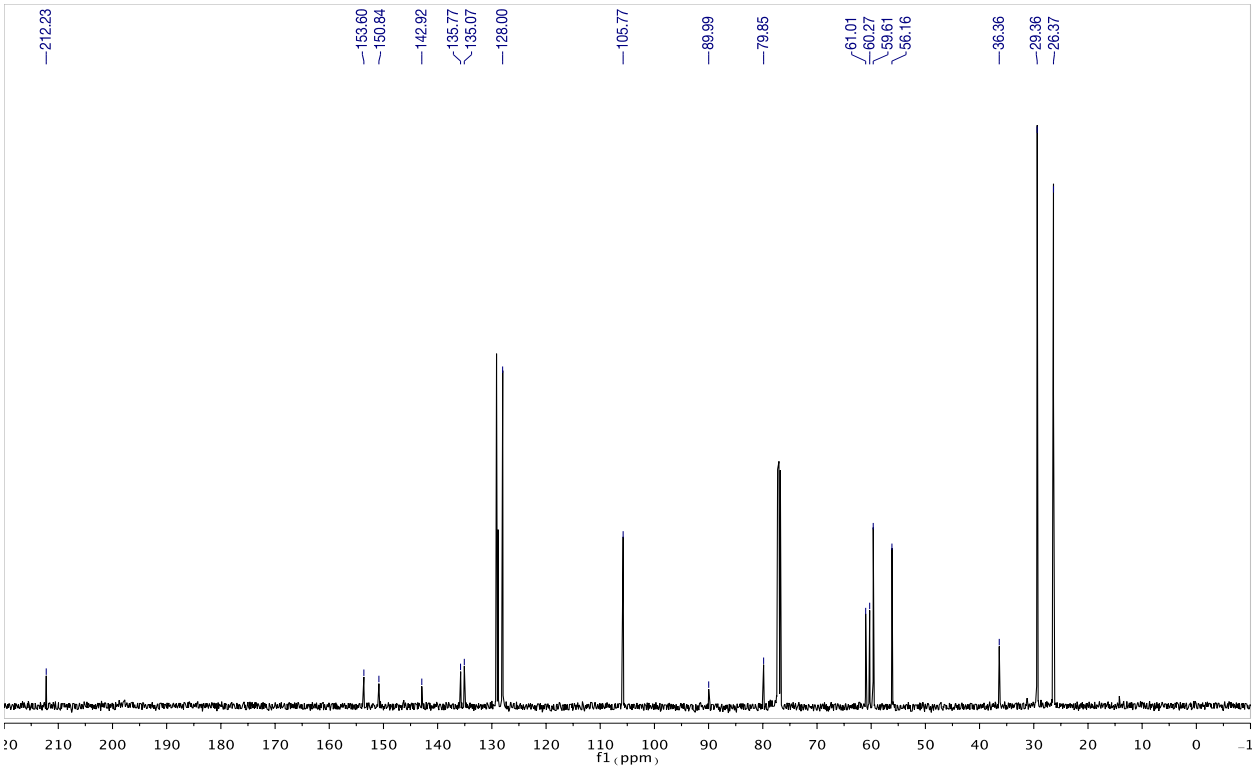

4.47
1.99
4.46
1.00
8.71
9.09
f1 (ppm)

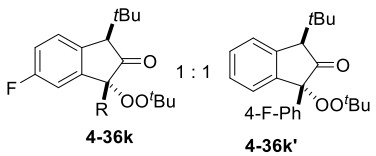

213.21
141.86
140.45
135.59
130.07
129.20
128.87
128.73
127.45
127.35
126.60
80.14
60.95
28.67
26.42
f1 (ppm)


OMe
tBu
MeO
O
MeO
OOtBu
Ph

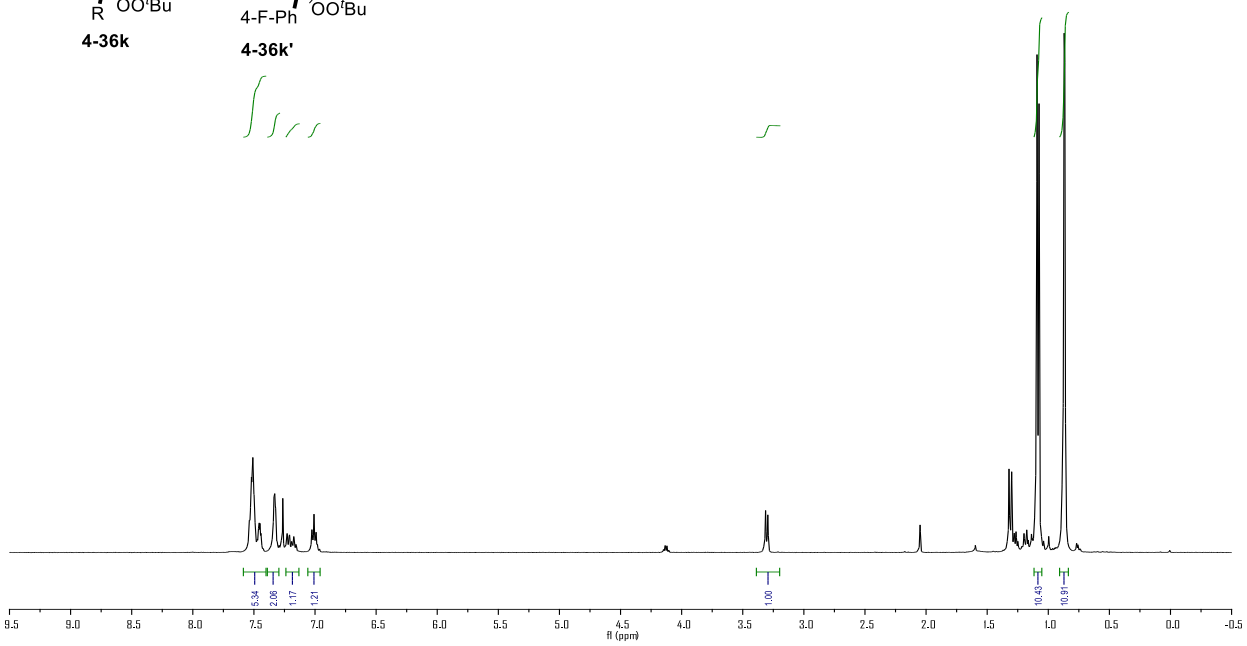
4-36m

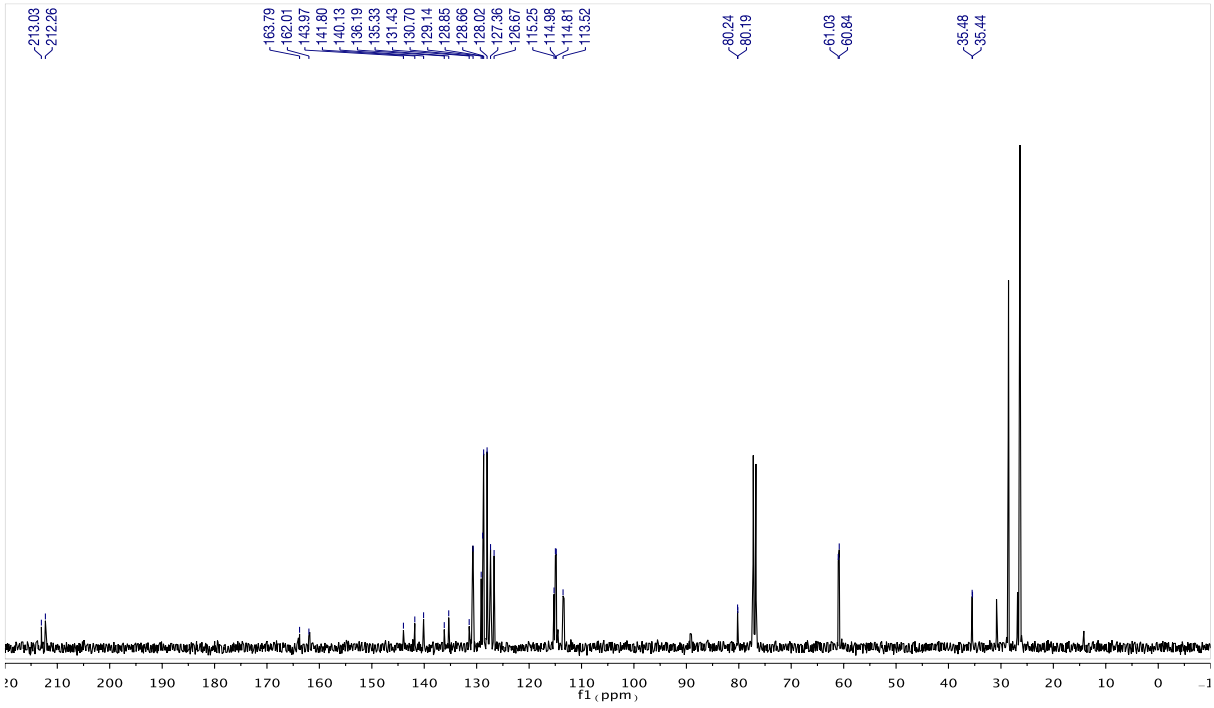

1.96
2.98
1.00
2.94
6.65
1.03
9.45
9.23
f1 (ppm)

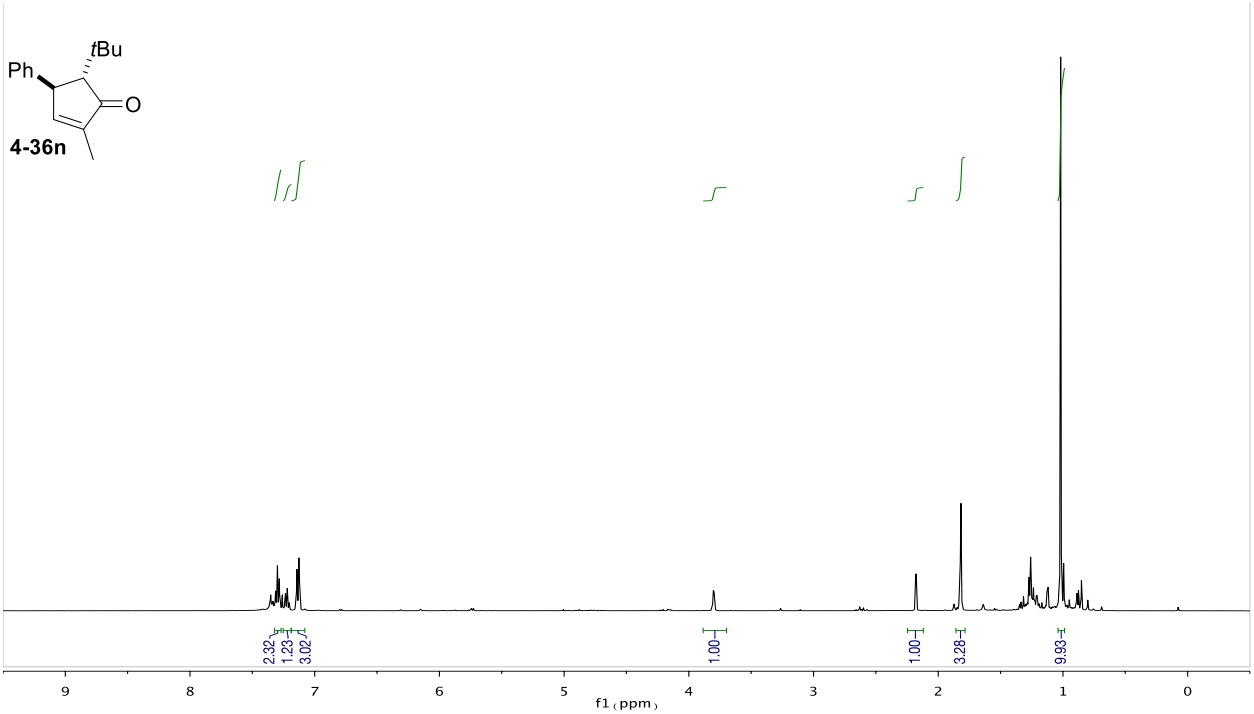

212.23
153.60
150.84
142.92
135.77
135.07
128.00
105.77
89.99
79.85
61.01
60.27
59.61
56.16
36.36
29.36
26.37
f1 (ppm)

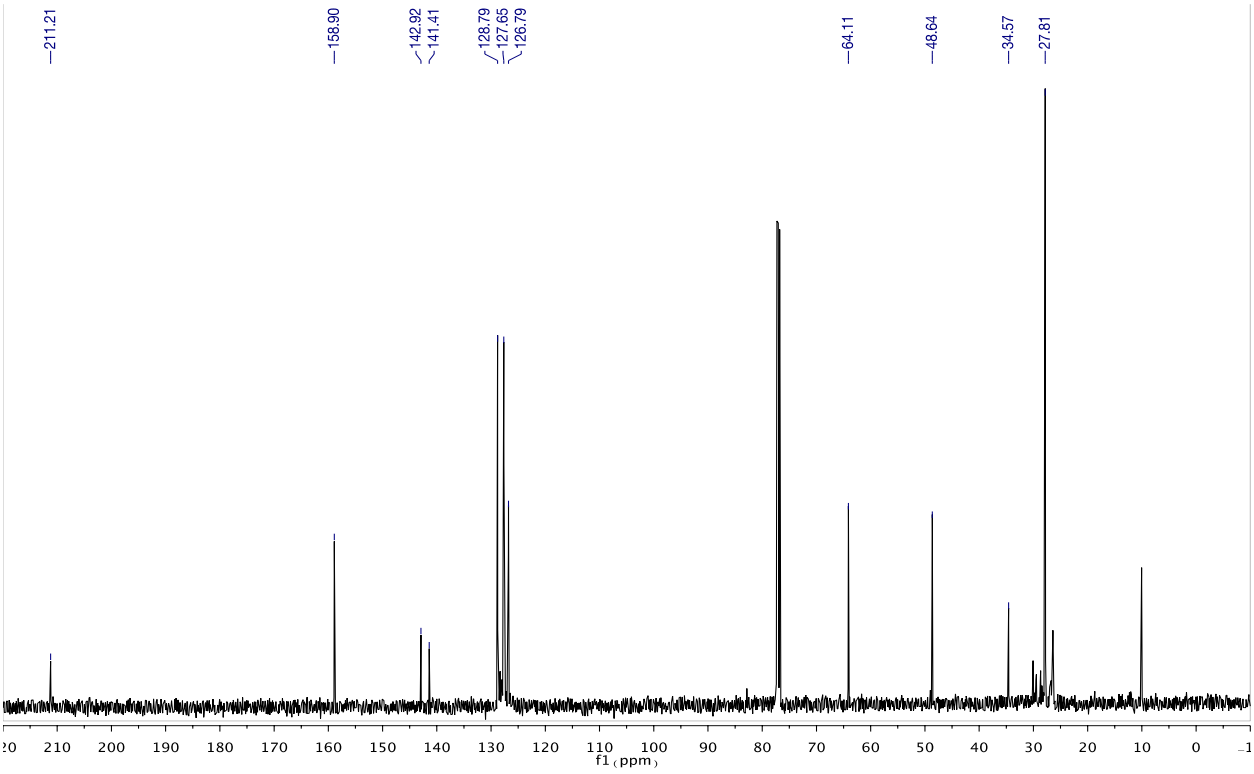

tBu
O
F
R
OOtBu
1 : 1
tBu
O
4-F-Ph
OOtBu

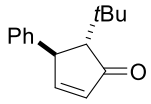
4-36k **4-36k'**


5.34
2.06
1.17
1.21
1.00
10.43
10.91
f1 (ppm)

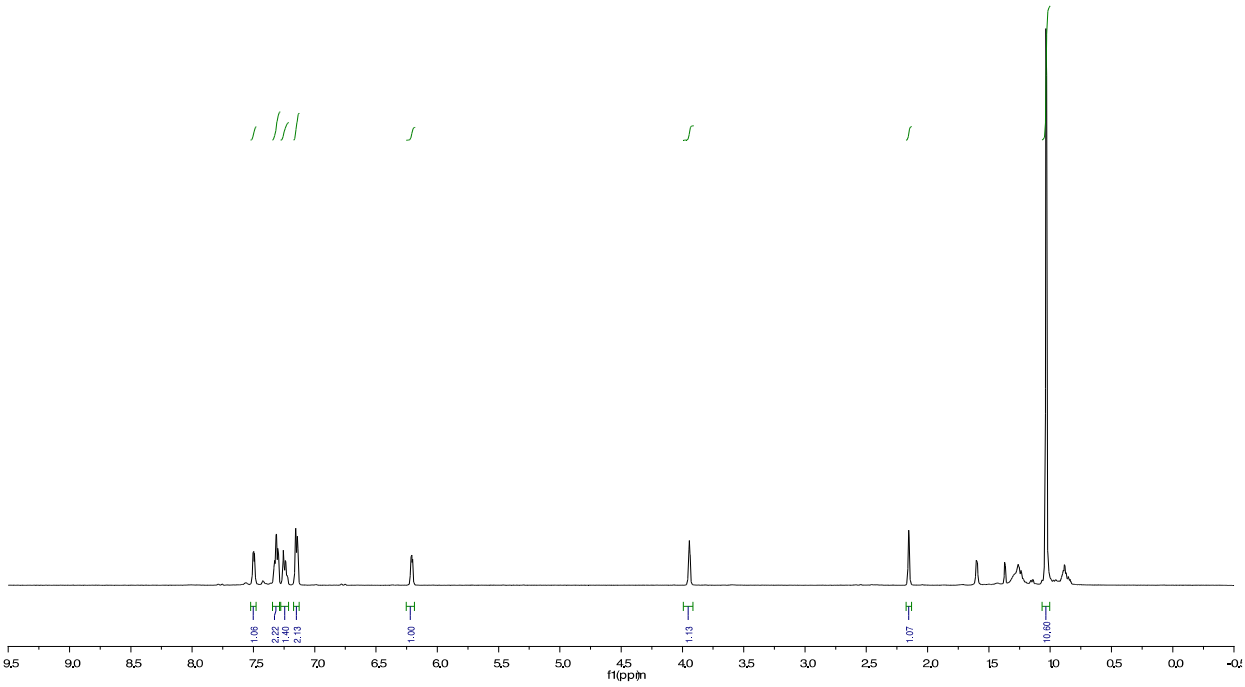

213.03
212.26
163.79
162.01
143.97
141.80
140.13
136.19
135.33
131.43
130.70
129.14
128.85
128.66
128.02
127.36
126.67
115.25
114.98
114.81
113.52
80.24
80.19
61.03
60.84
35.48
35.44
f1 (ppm)

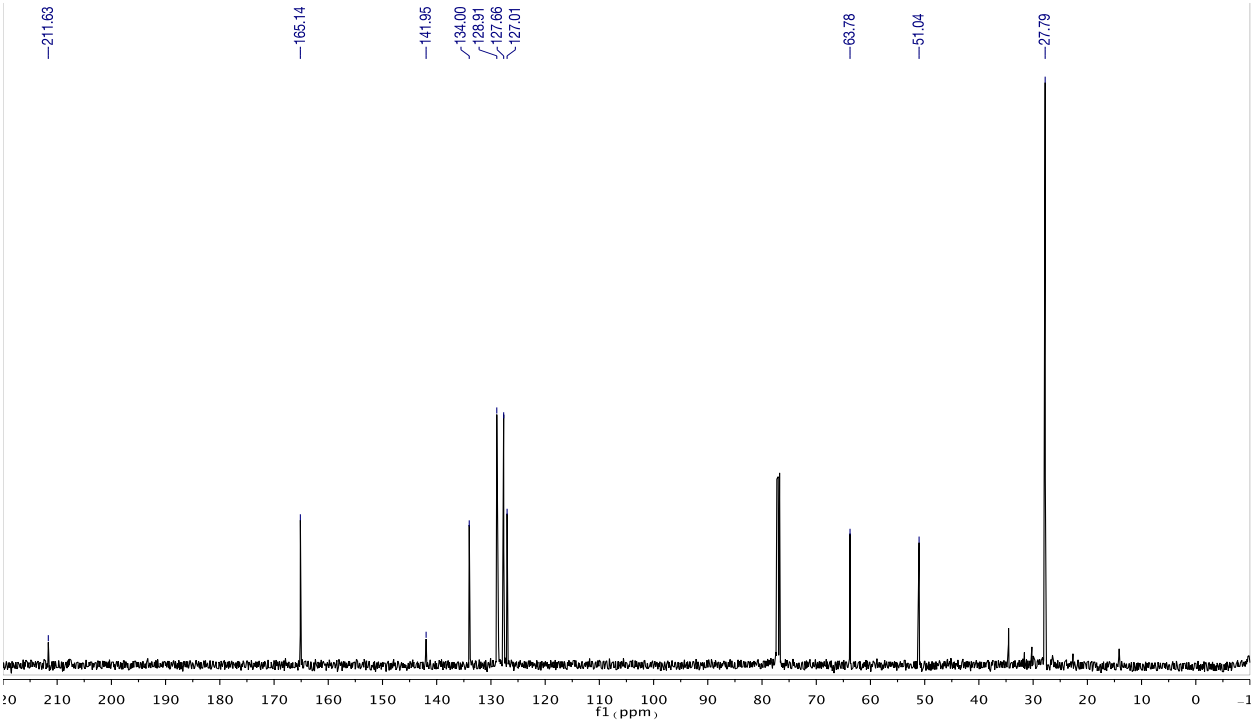

tBu
Ph
O
4-36n
2.32
1.23
3.02
1.00
1.00
3.28
9.33
f1 (ppm)

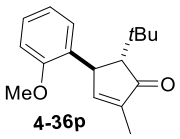

211.21
158.90
142.92
141.41
128.79
127.65
126.79
64.11
48.64
34.57
27.81
f1 (ppm)


tBu
Ph
O

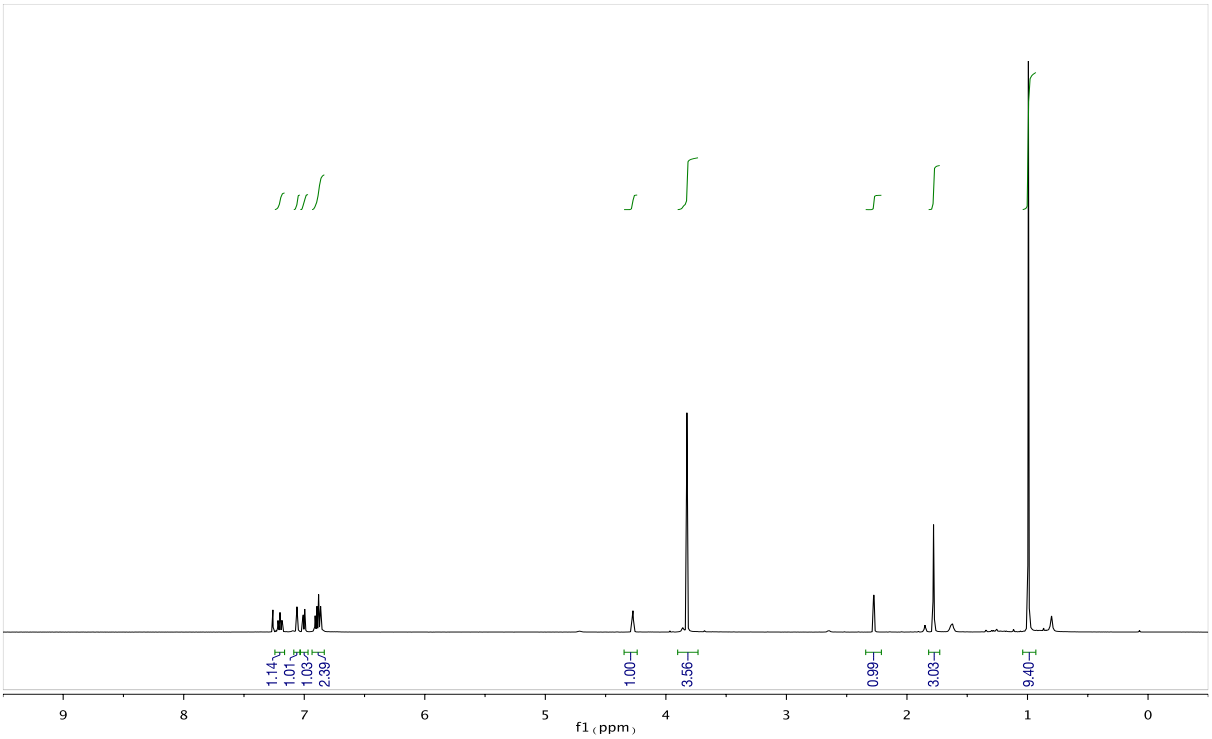
4-36o

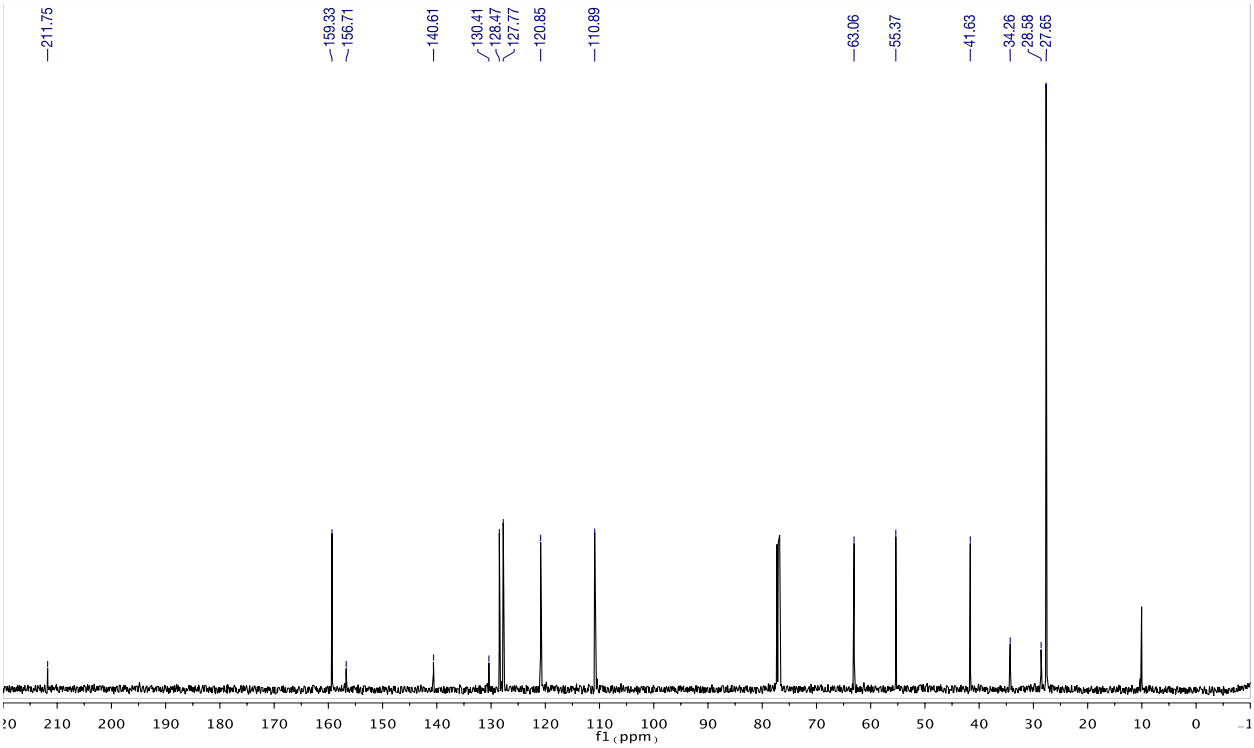

1.06
2.22
1.40
2.13
1.00
1.13
1.07
10.60
f1(ppm)

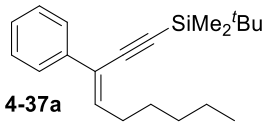

211.63
165.14
141.95
134.00
128.91
127.66
127.01
63.78
51.04
27.79
f1 (ppm)


tBu
MeO
O

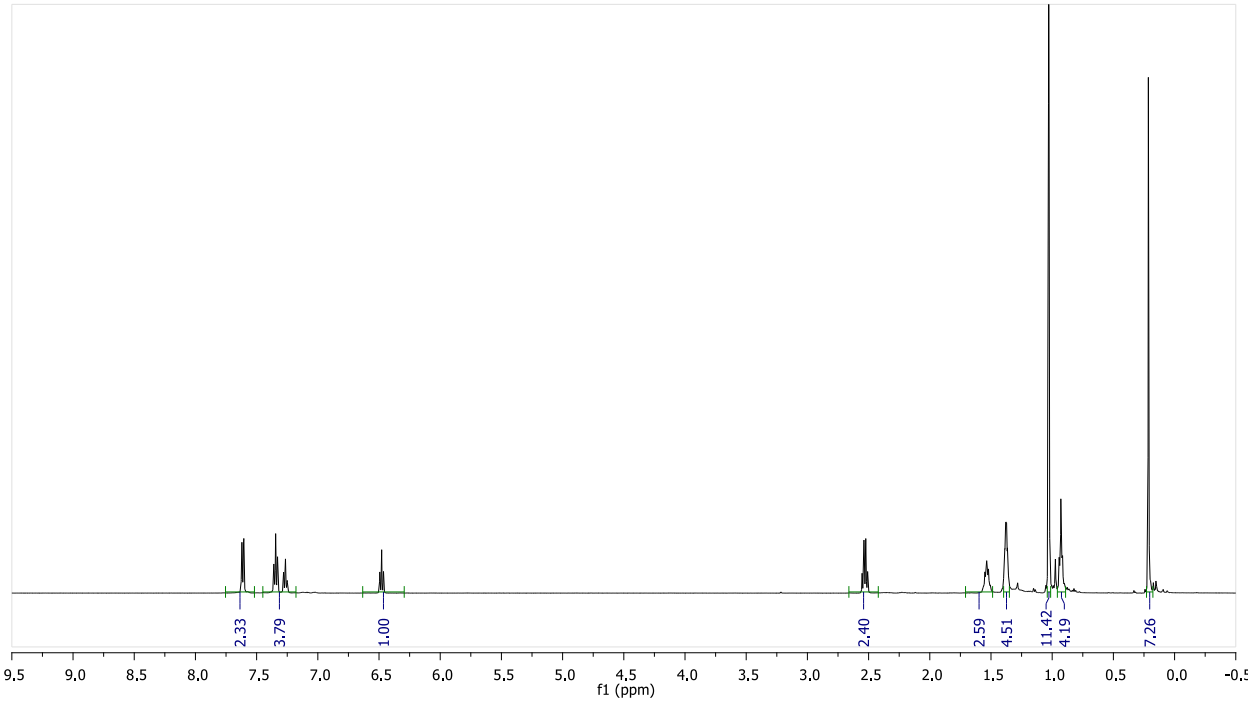
4-36p

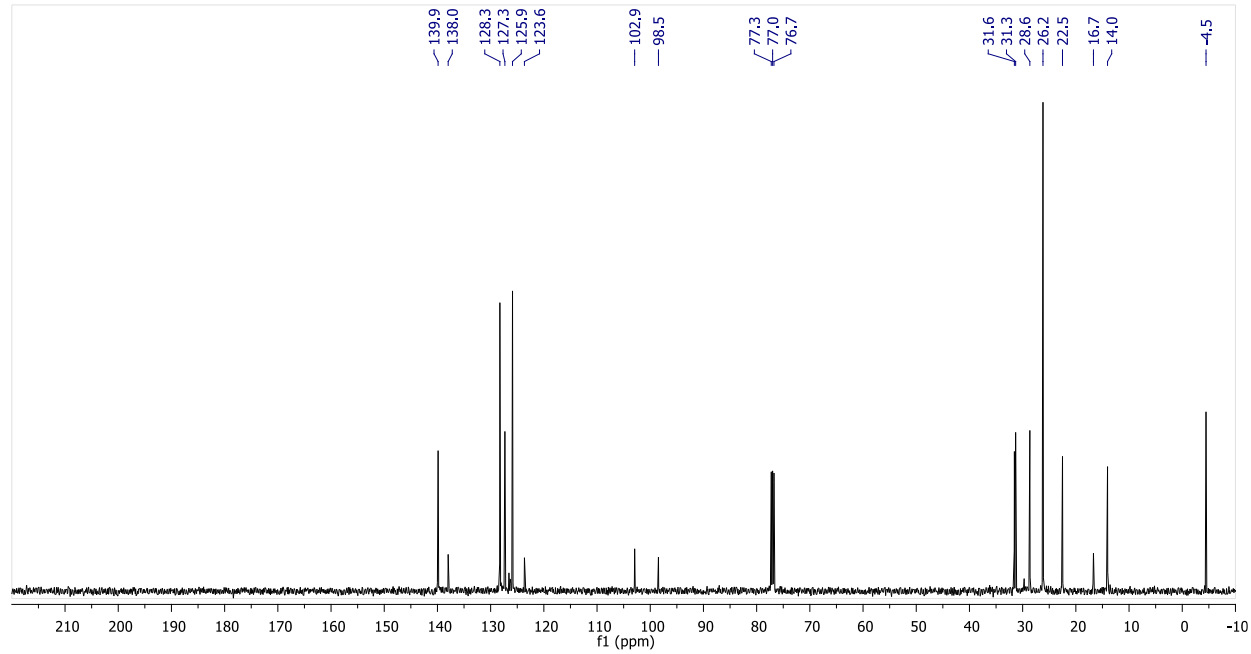

1.14
1.01
1.03
2.39
1.00
3.56
0.99
3.03
9.40
f1 (ppm)

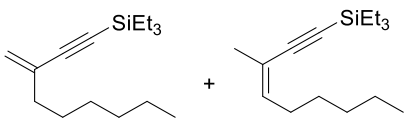

211.75
159.33
156.71
140.61
130.41
128.47
127.77
120.85
110.89
63.06
55.37
41.63
34.26
28.58
27.65
f1 (ppm)


SiMe2tBu

4-37a

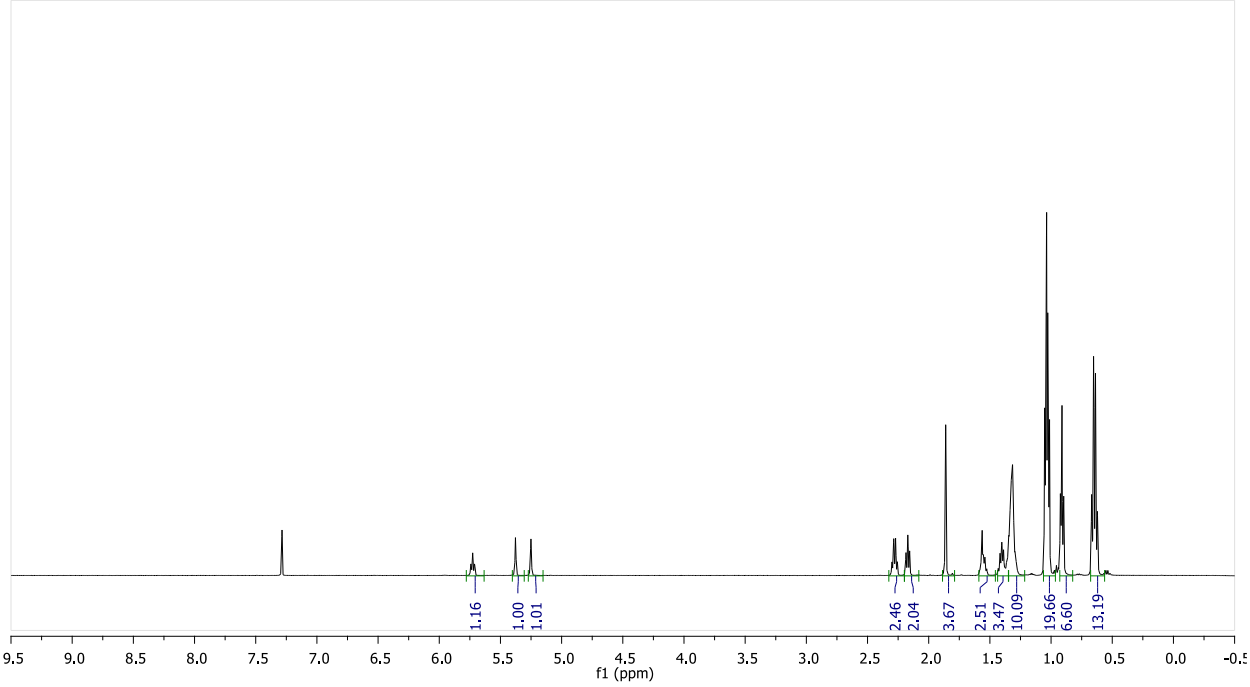

2.33
3.79
1.00
2.40
2.59
4.51
11.42
4.19
7.26
f1 (ppm)

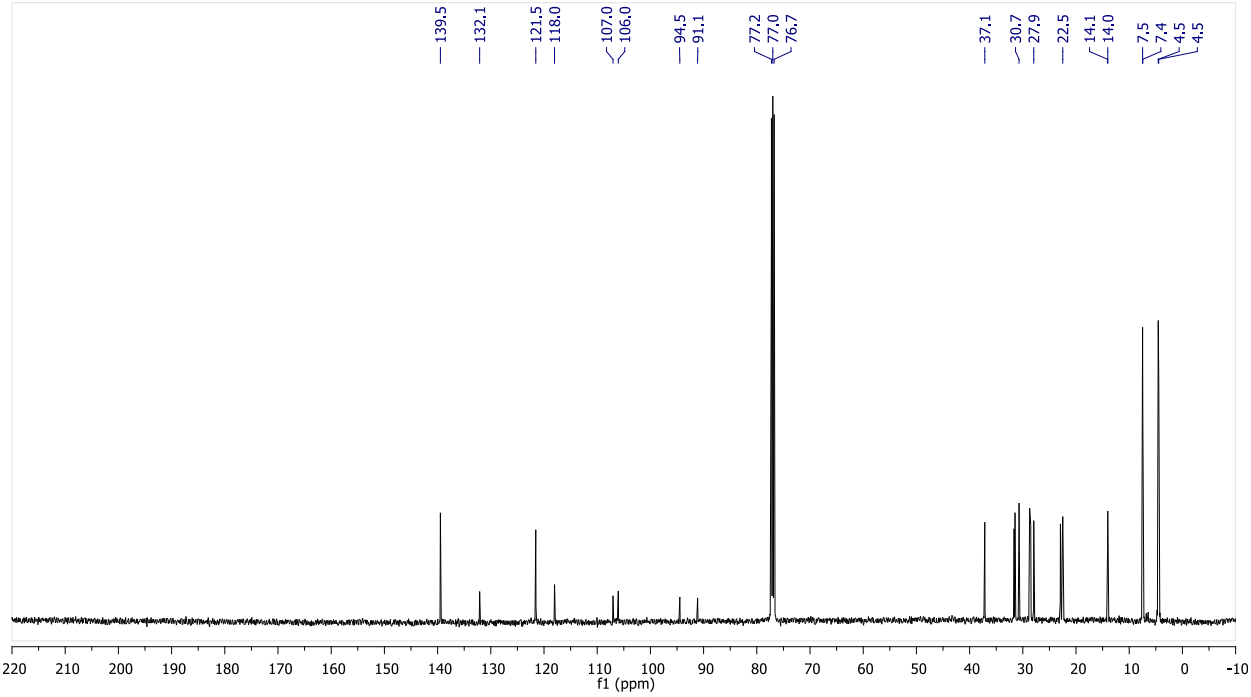

139.9
138.0
128.3
127.3
125.9
123.6
102.9
98.5
77.3
77.0
76.7
31.6
31.3
28.6
26.2
22.5
16.7
14.0
-4.5
f1 (ppm)

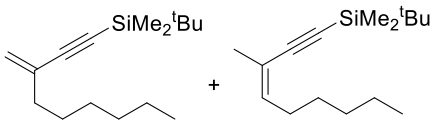


4-37b-1 **4-37b-2**

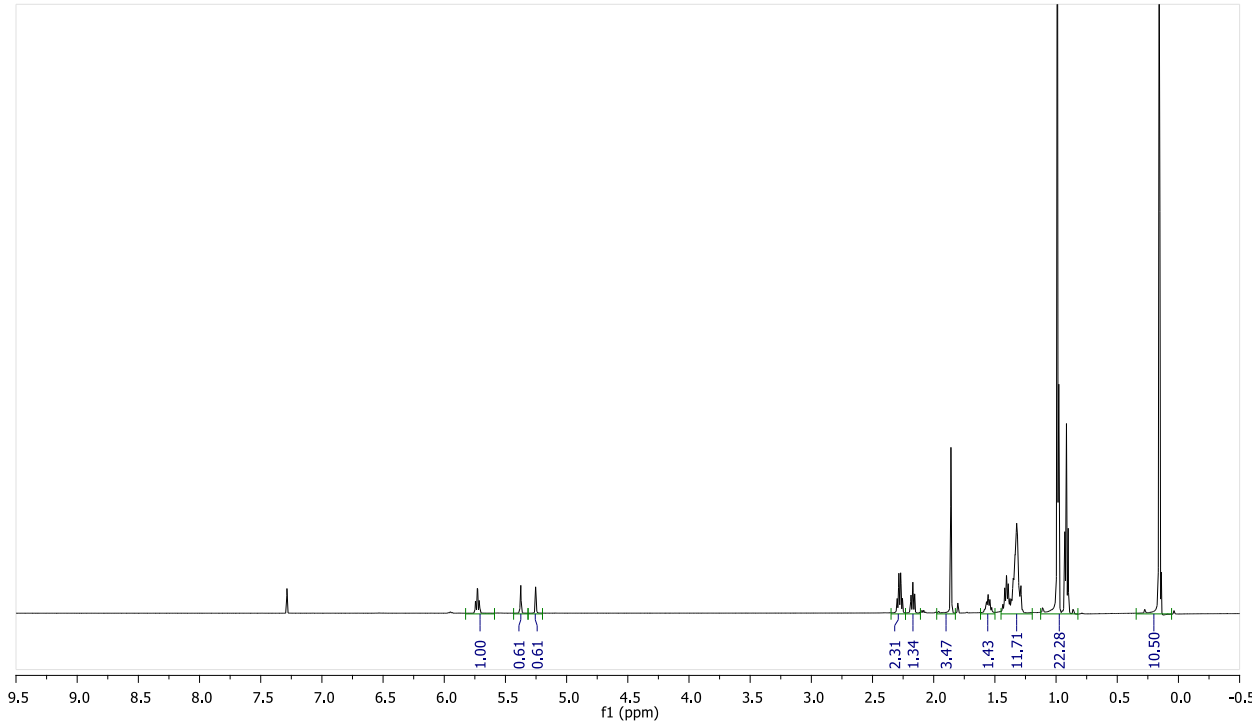
4-37b (1:1)

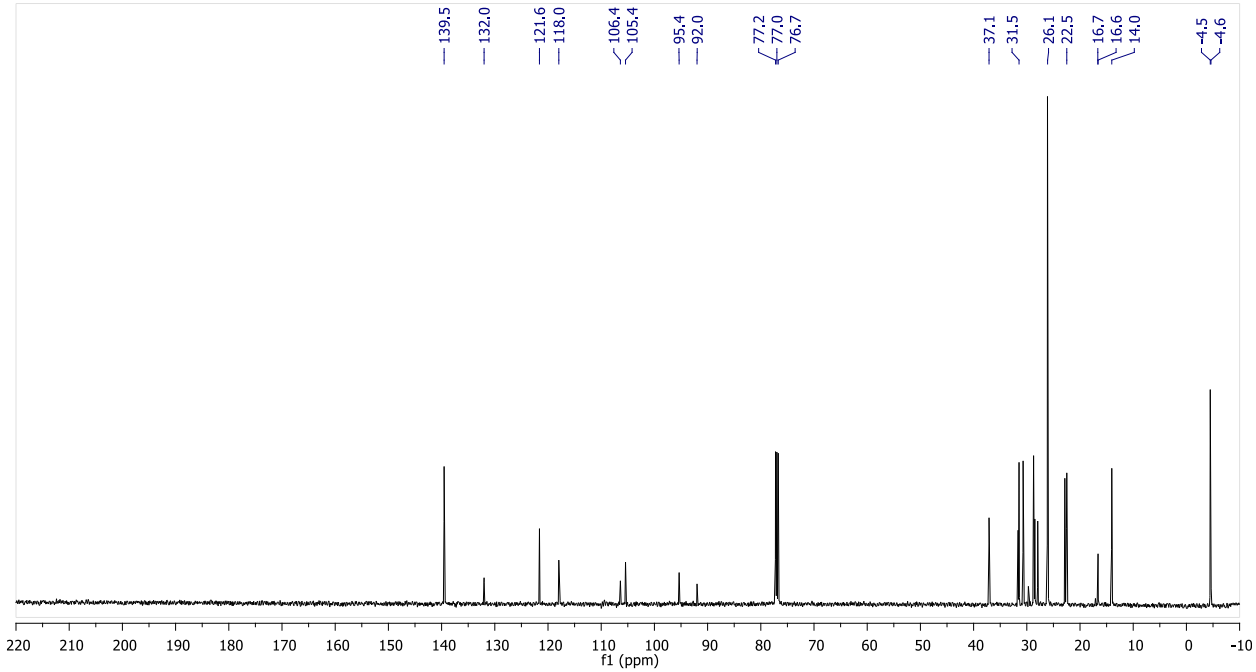


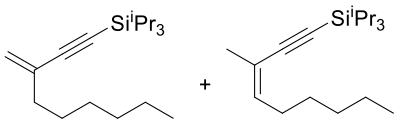



SiMe2tBu
+
SiMe2tBu

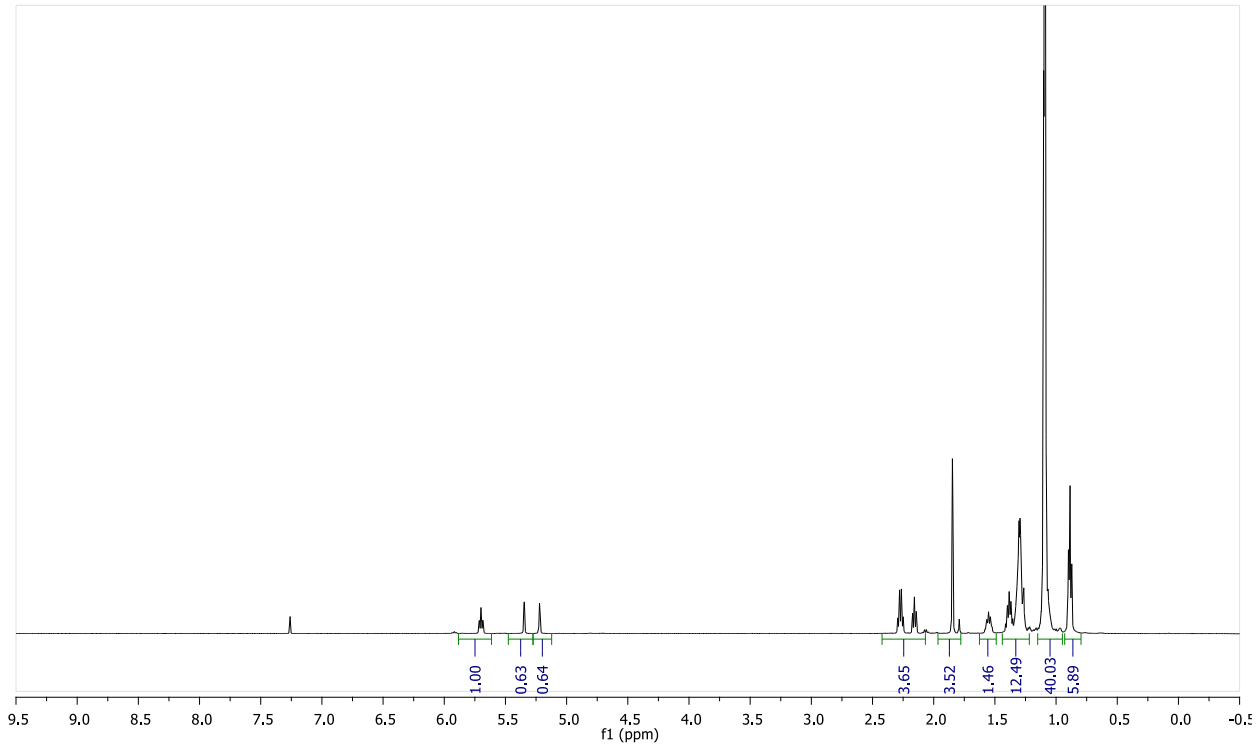
4-37c (1:1.5)

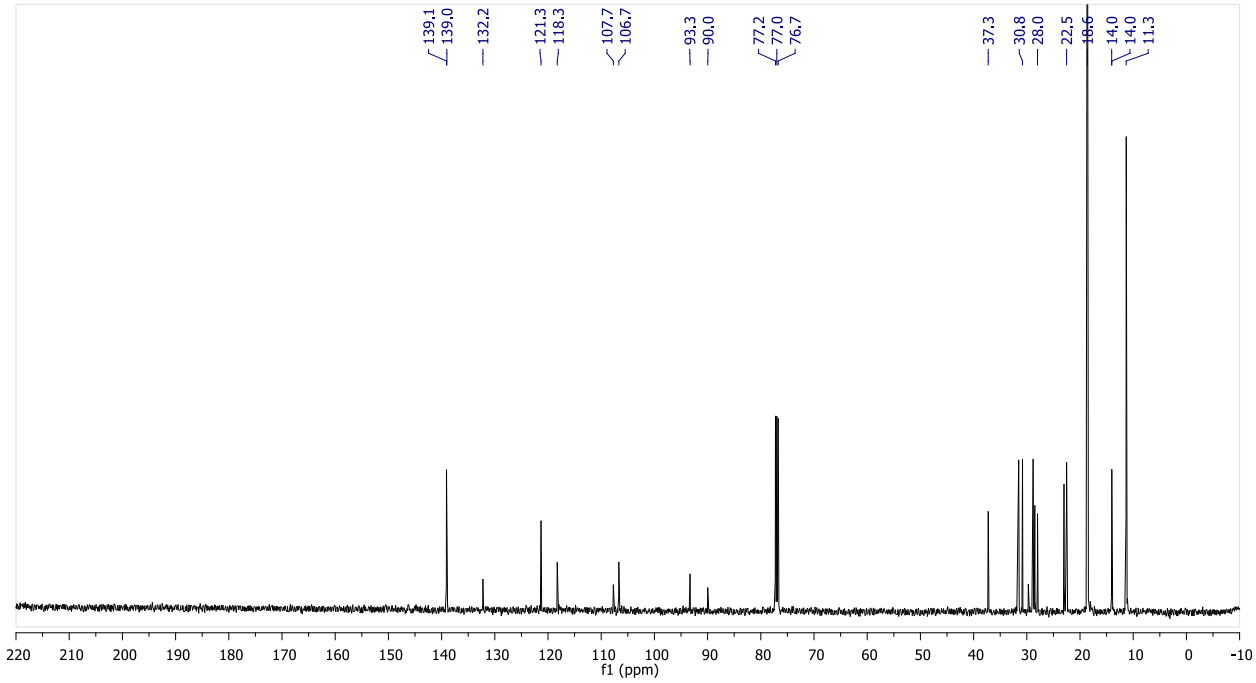

1.00
0.61
0.61
2.31
1.34
3.47
1.43
11.71
22.28
10.50
f1 (ppm)

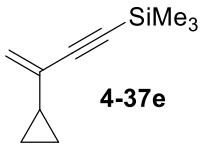

139.5
132.0
121.6
118.0
106.4
105.4
95.4
92.0
77.2
77.0
76.7
37.1
31.5
26.1
22.5
16.7
16.6
14.0
-4.5
-4.6
f1 (ppm)


Si^{i}Pr$_3$
+
Si^{i}Pr$_3$

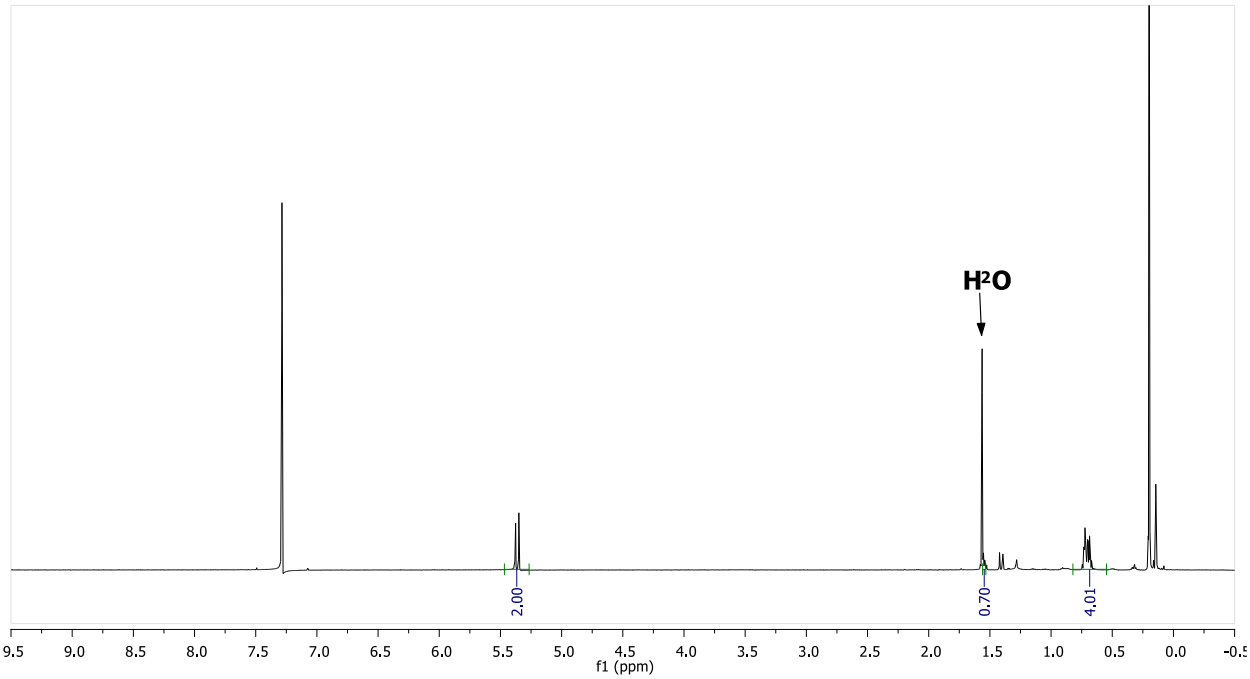
4-37d (1:1.5)

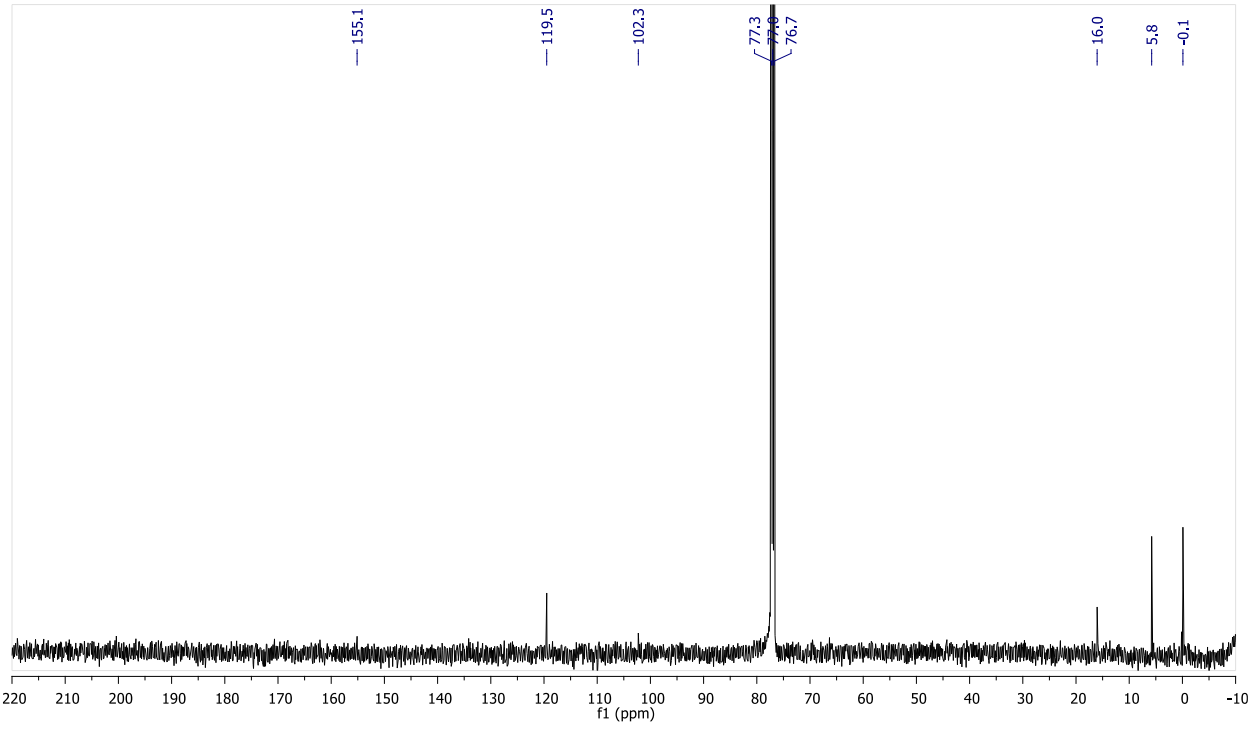

1.00
0.63
0.64
3.65
3.52
1.46
12.49
40.03
5.89
f1 (ppm)

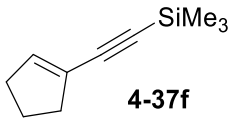

139.1
139.0
132.2
121.3
118.3
107.7
106.7
93.3
90.0
77.2
77.0
76.7
37.3
30.8
28.0
22.5
18.6
14.0
14.0
11.3
f1 (ppm)


SiMe3

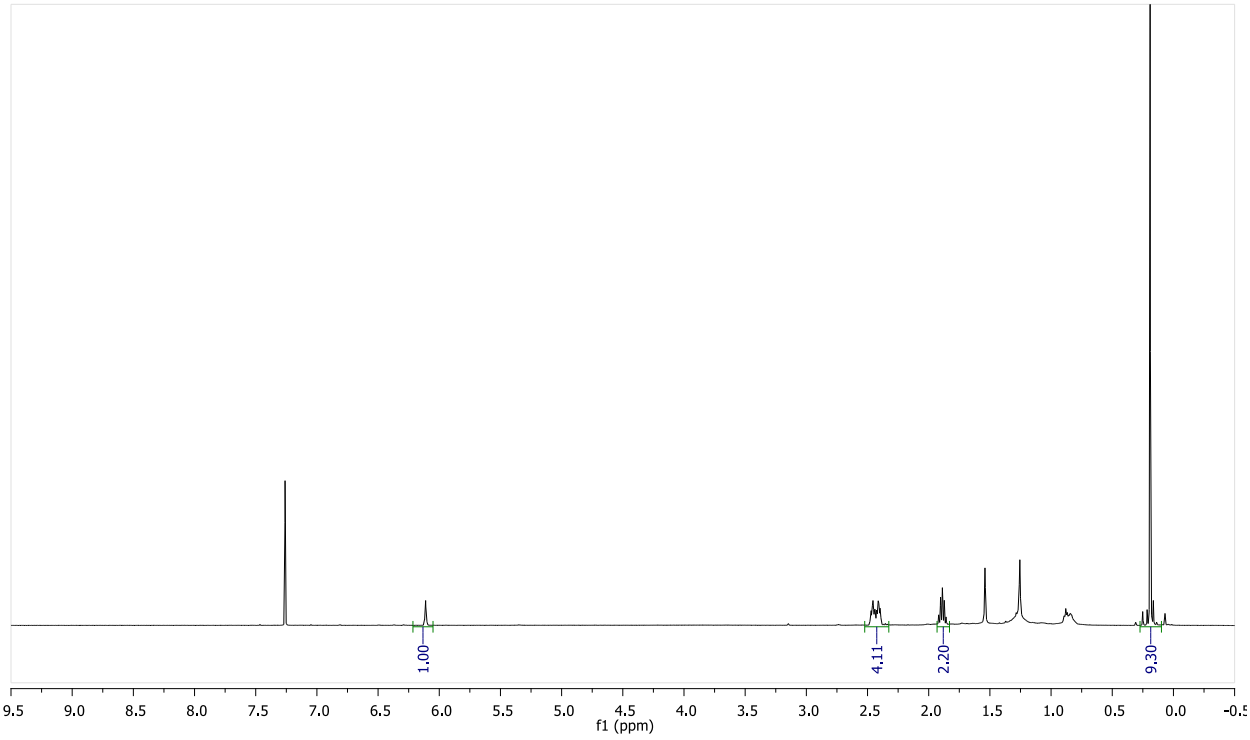
4-37e

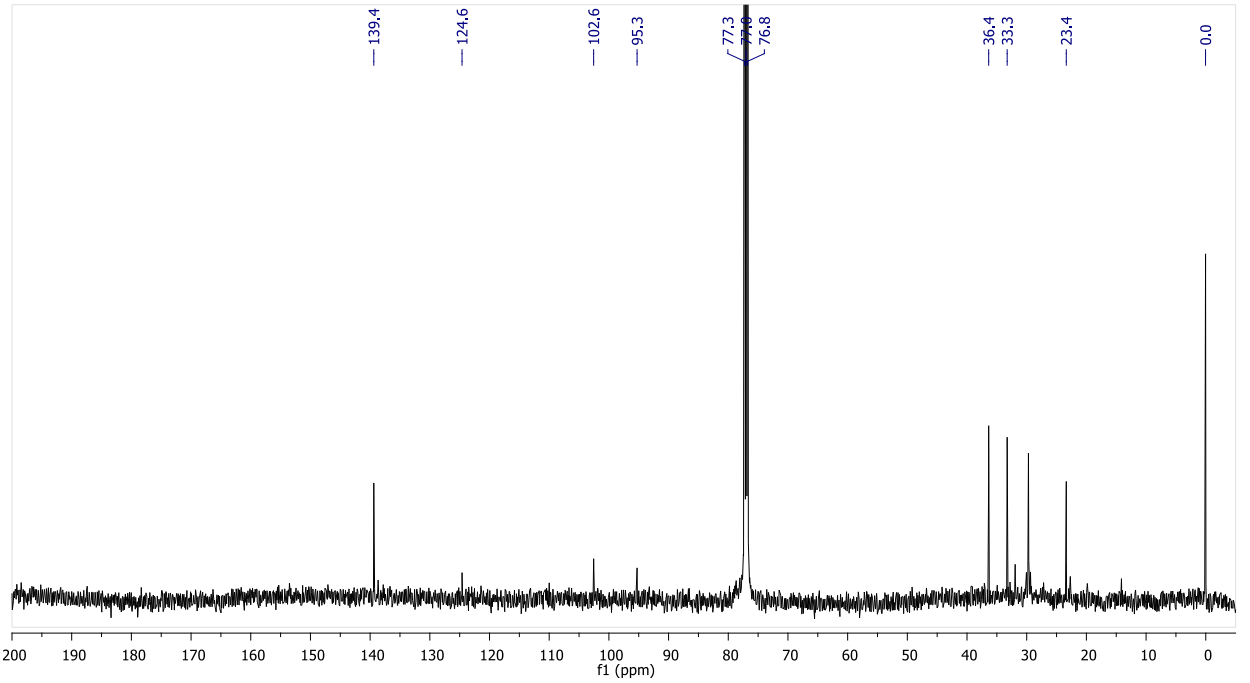

H2O
2.00
0.70
4.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

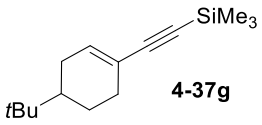

155.1
119.5
102.3
77.3
76.7
16.0
5.8
-0.1
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


SiMe3

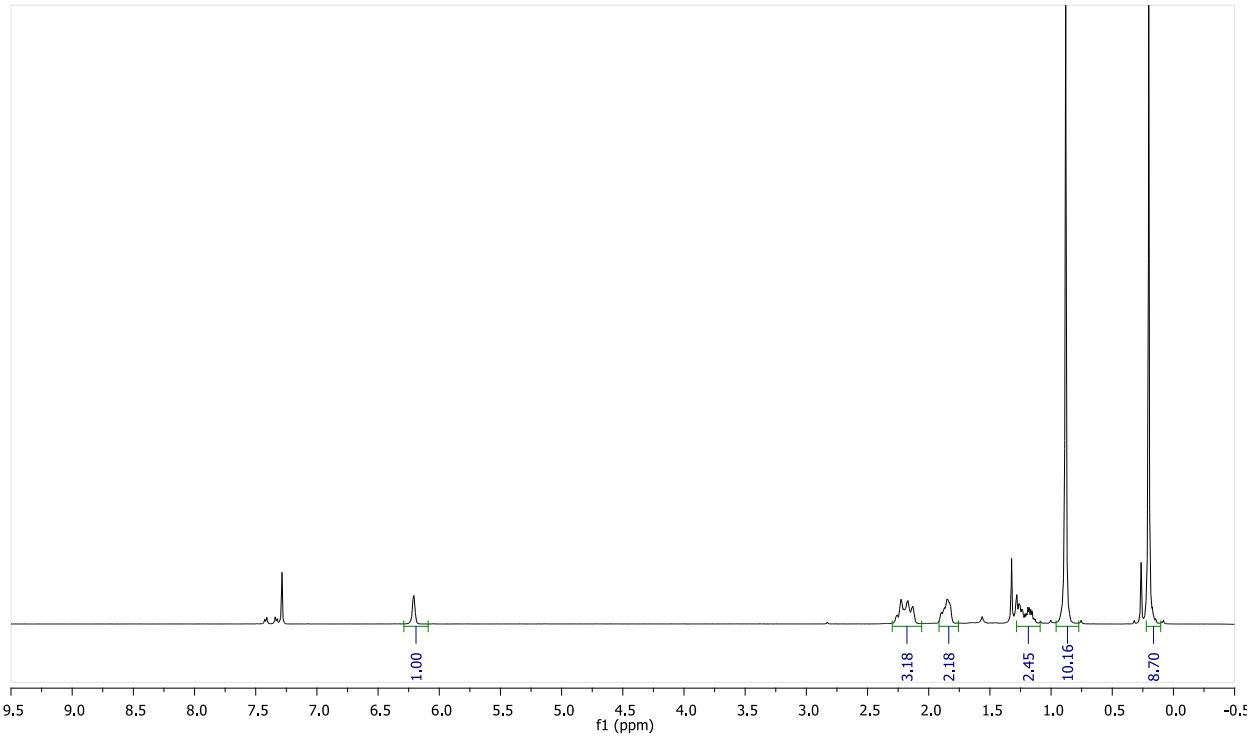
4-37f

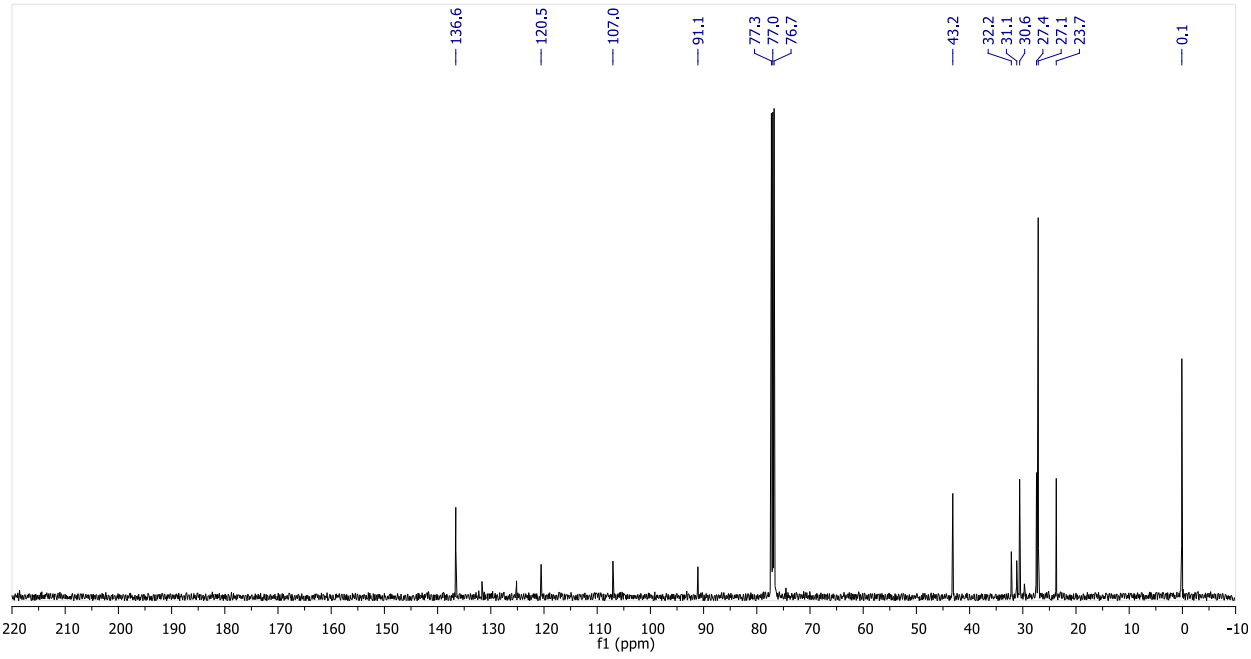

1.00
4.11
2.20
9.30
f1 (ppm)

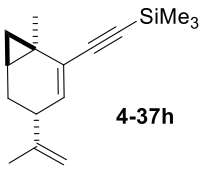

139.4
124.6
102.6
95.3
77.3
76.8
36.4
33.3
23.4
0.0
f1 (ppm)


SiMe3
tBu

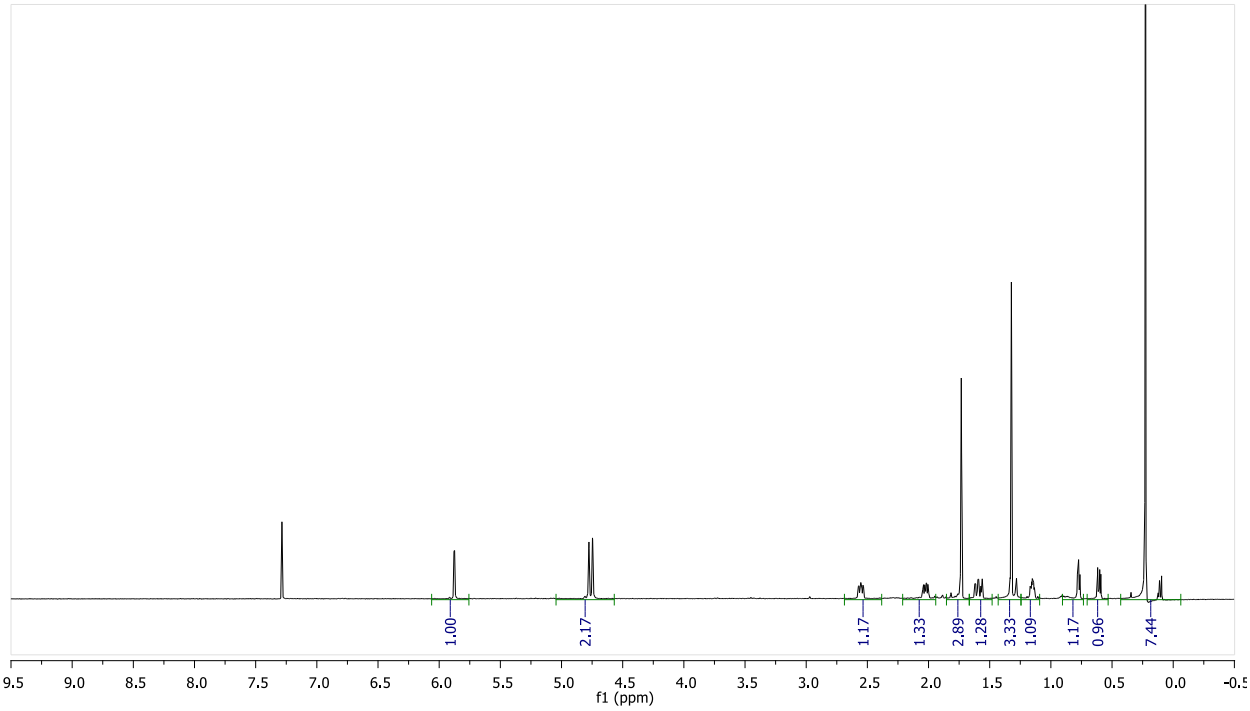
4-37g

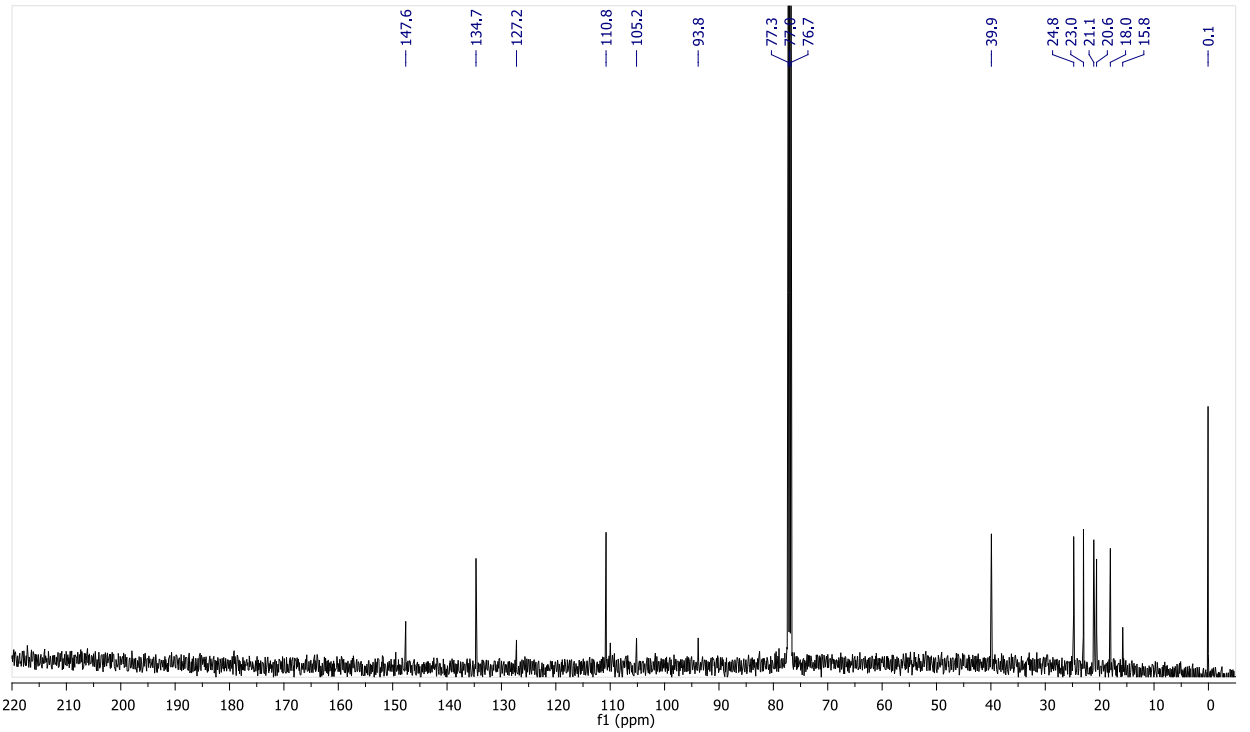

1.00
3.18
2.18
2.45
10.16
8.70
f1 (ppm)

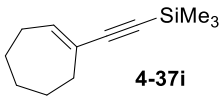

136.6
120.5
107.0
91.1
77.3
77.0
76.7
43.2
32.2
31.1
30.6
27.4
27.1
23.7
0.1
f1 (ppm)


SiMe3

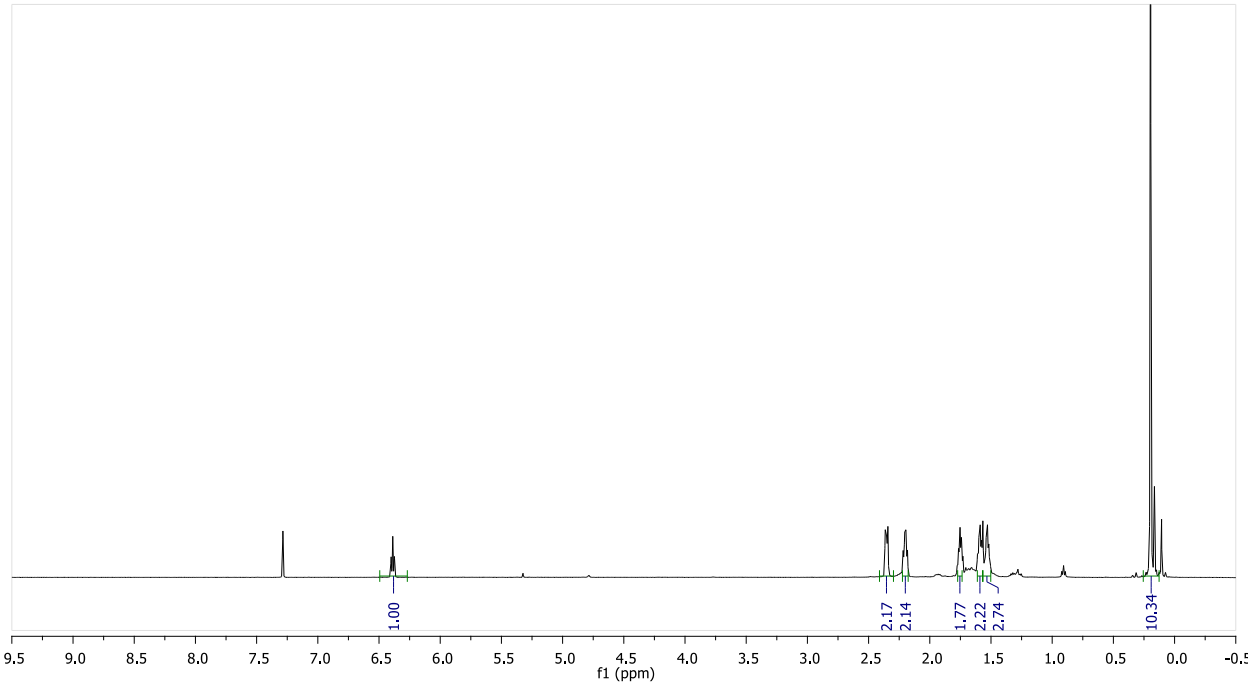
4-37h

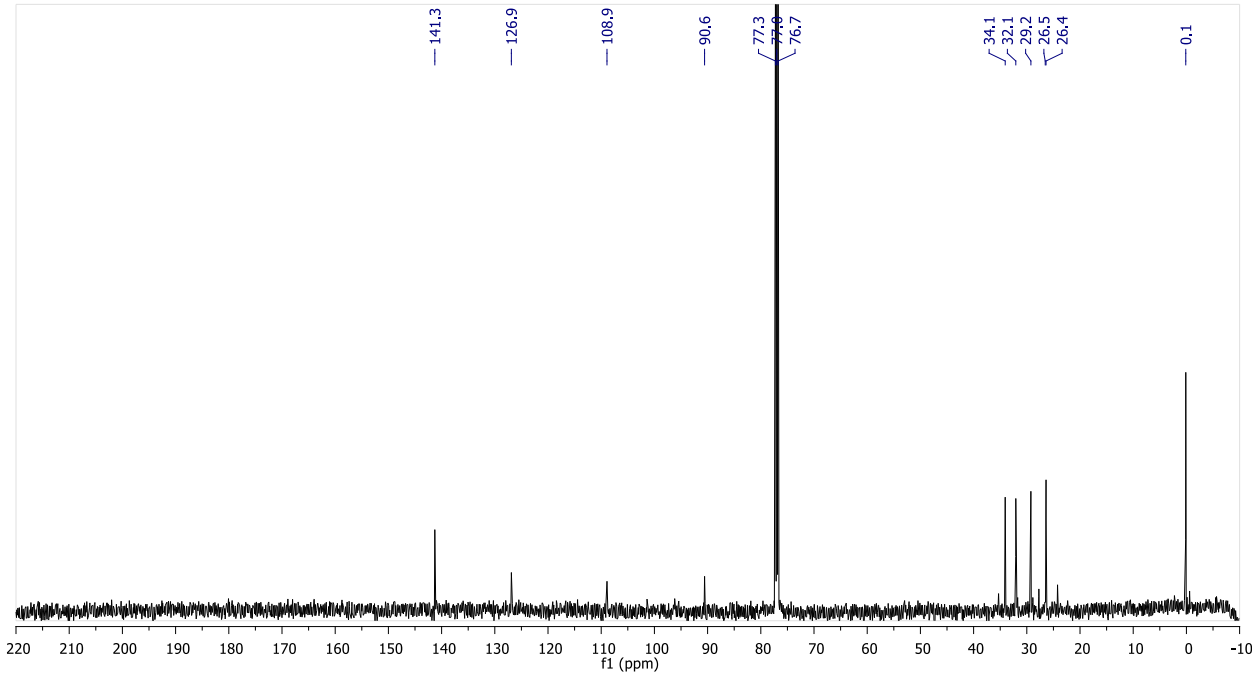

1.00
2.17
1.17
1.33
2.89
1.28
3.33
1.09
1.17
0.96
7.44
f1 (ppm)

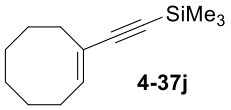

147.6
134.7
127.2
110.8
105.2
93.8
77.3
77.0
76.7
39.9
24.8
23.0
21.1
20.6
18.0
15.8
0.1
f1 (ppm)


SiMe3

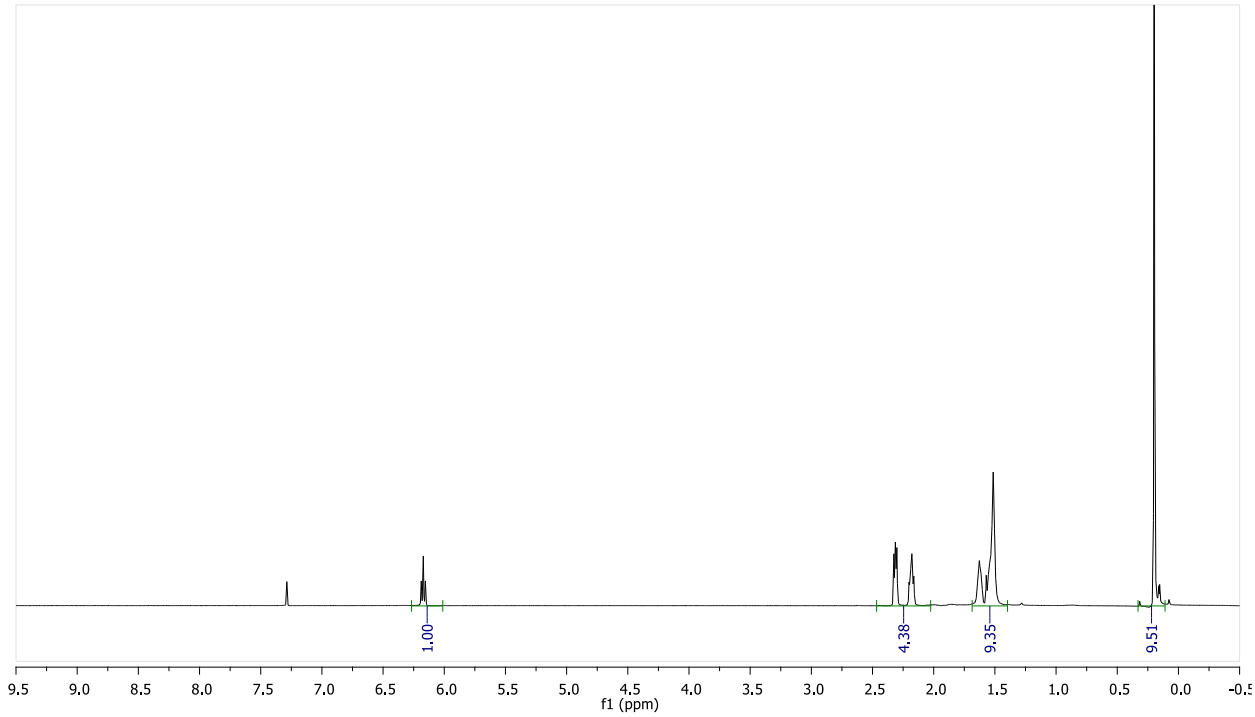
4-37i

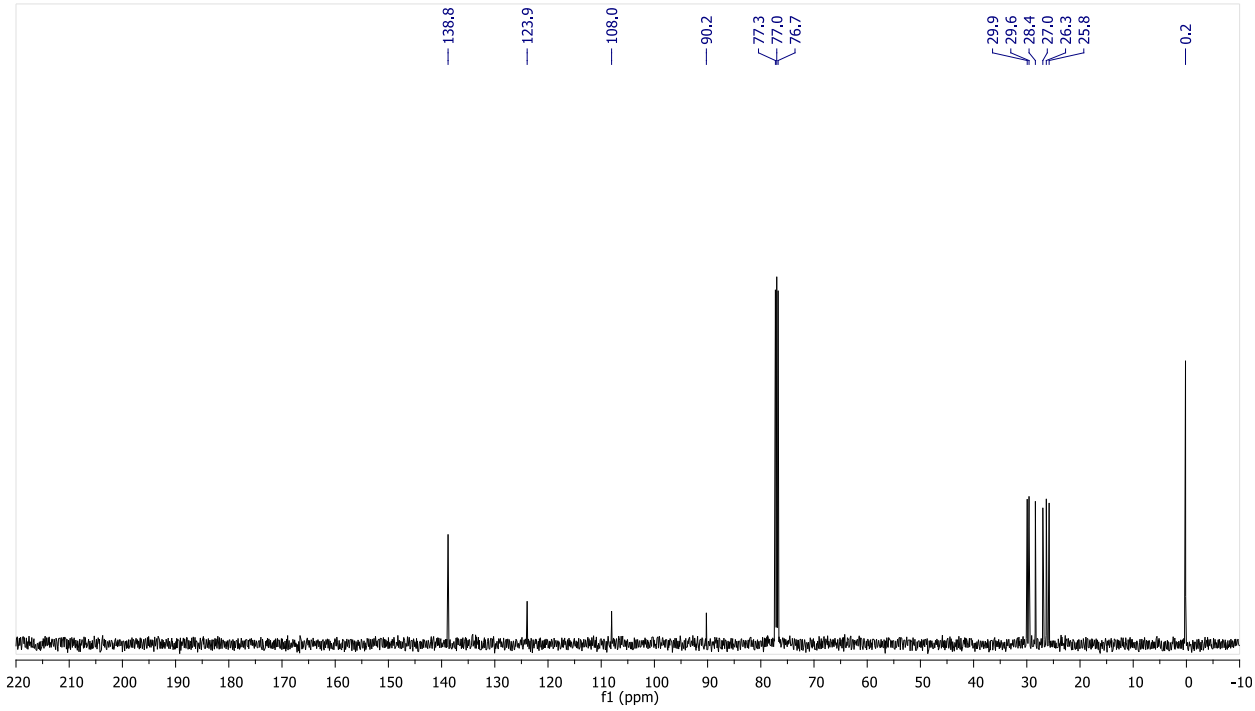

1.00
2.17
2.14
1.77
2.22
2.74
10.34
f1 (ppm)

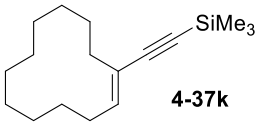

141.3
126.9
108.9
90.6
77.3
76.7
34.1
32.1
29.2
26.5
26.4
0.1
f1 (ppm)


SiMe3

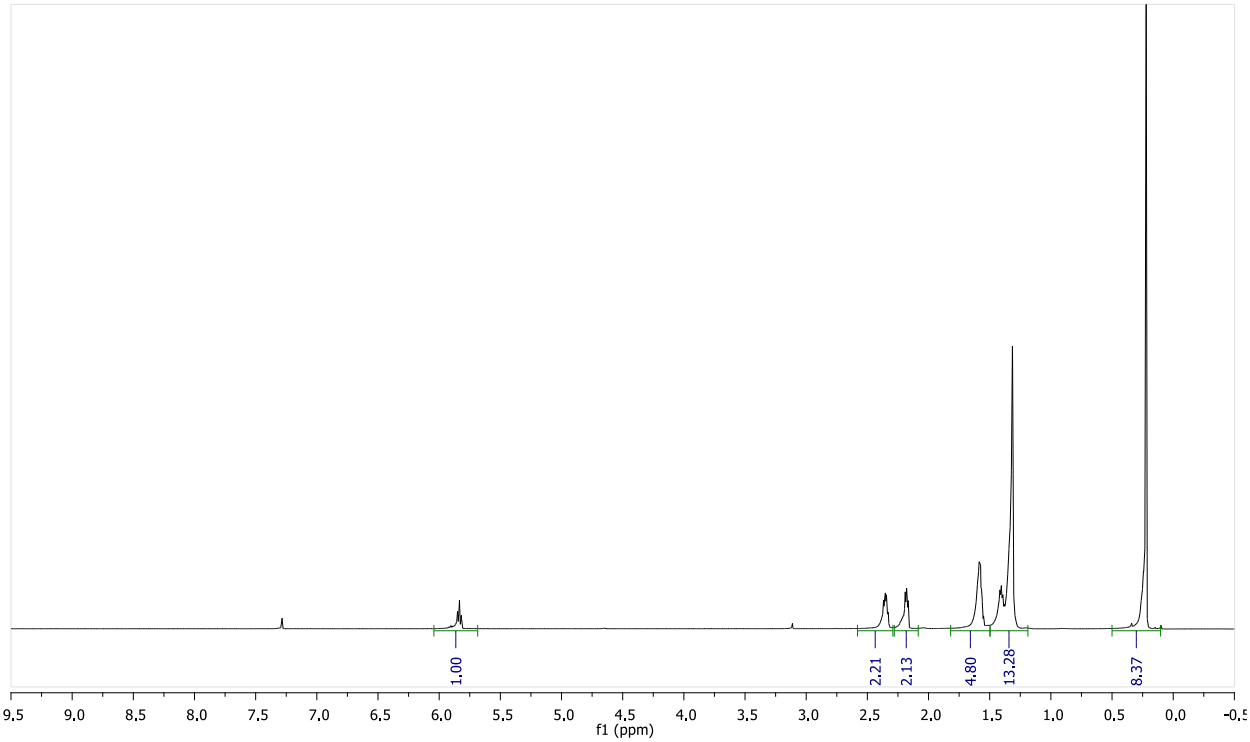
4-37j

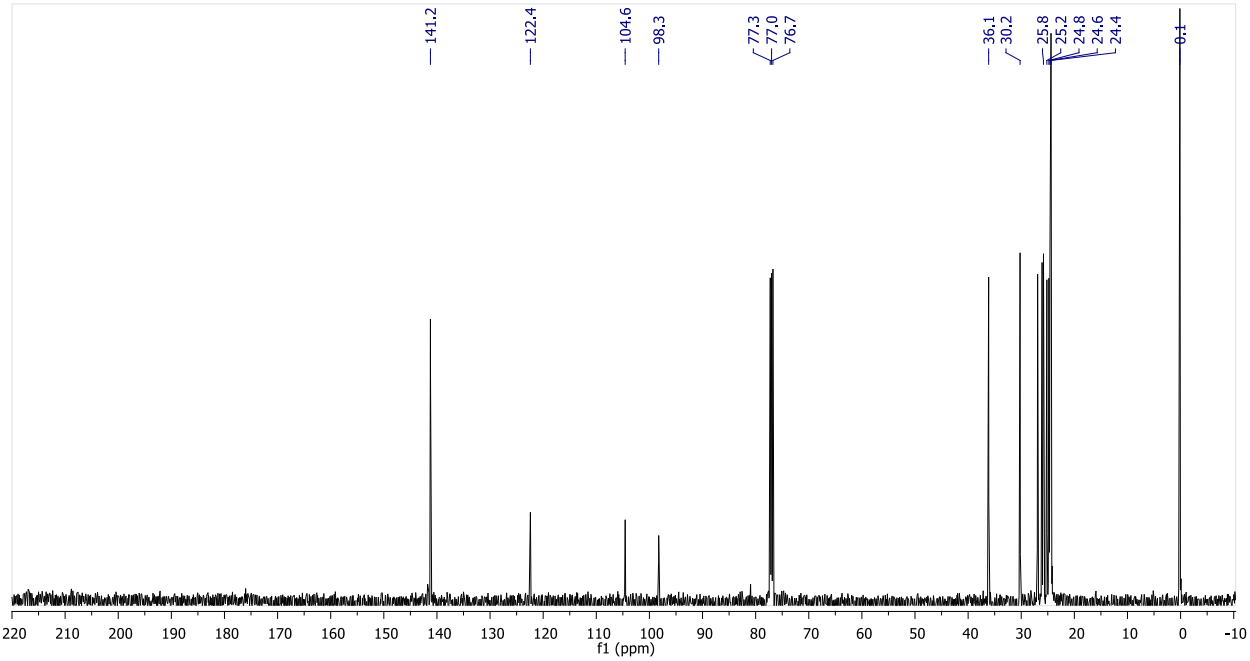

1.00
4.38
9.35
9.51
f1 (ppm)

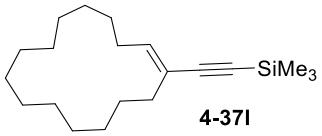

138.8
123.9
108.0
90.2
77.3
77.0
76.7
29.9
29.6
28.4
27.0
26.3
25.8
0.2
f1 (ppm)


SiMe3

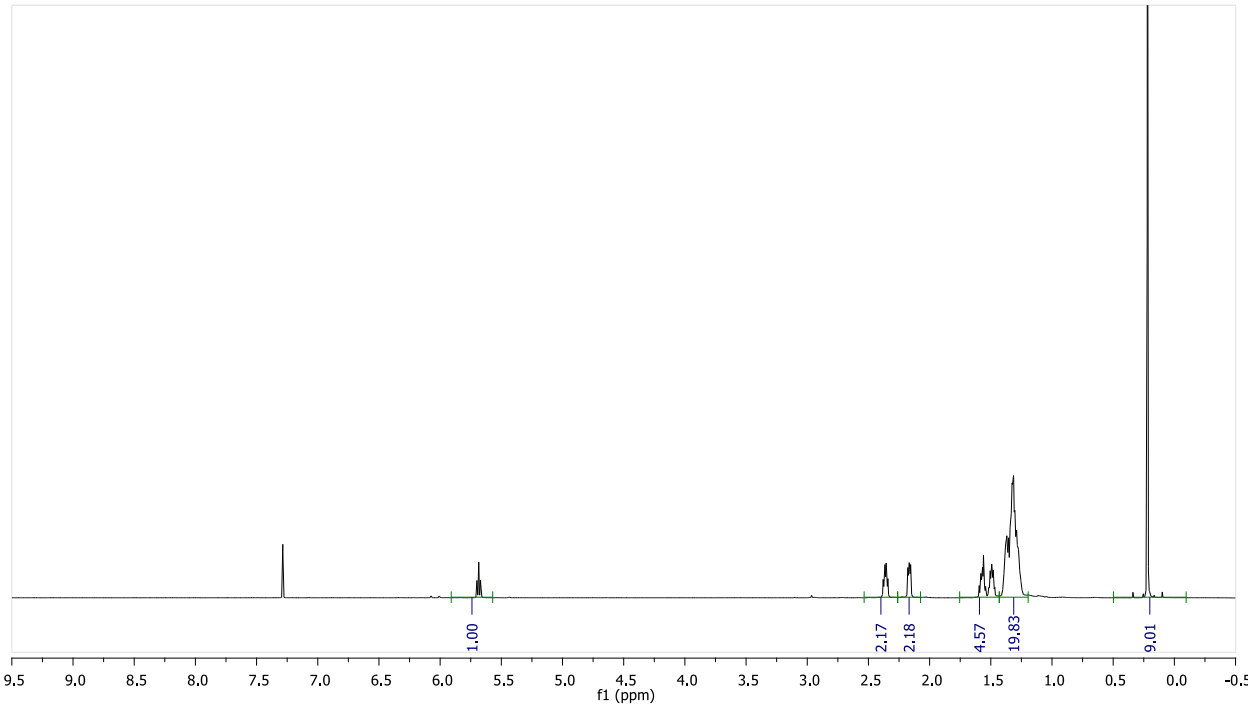
4-37k

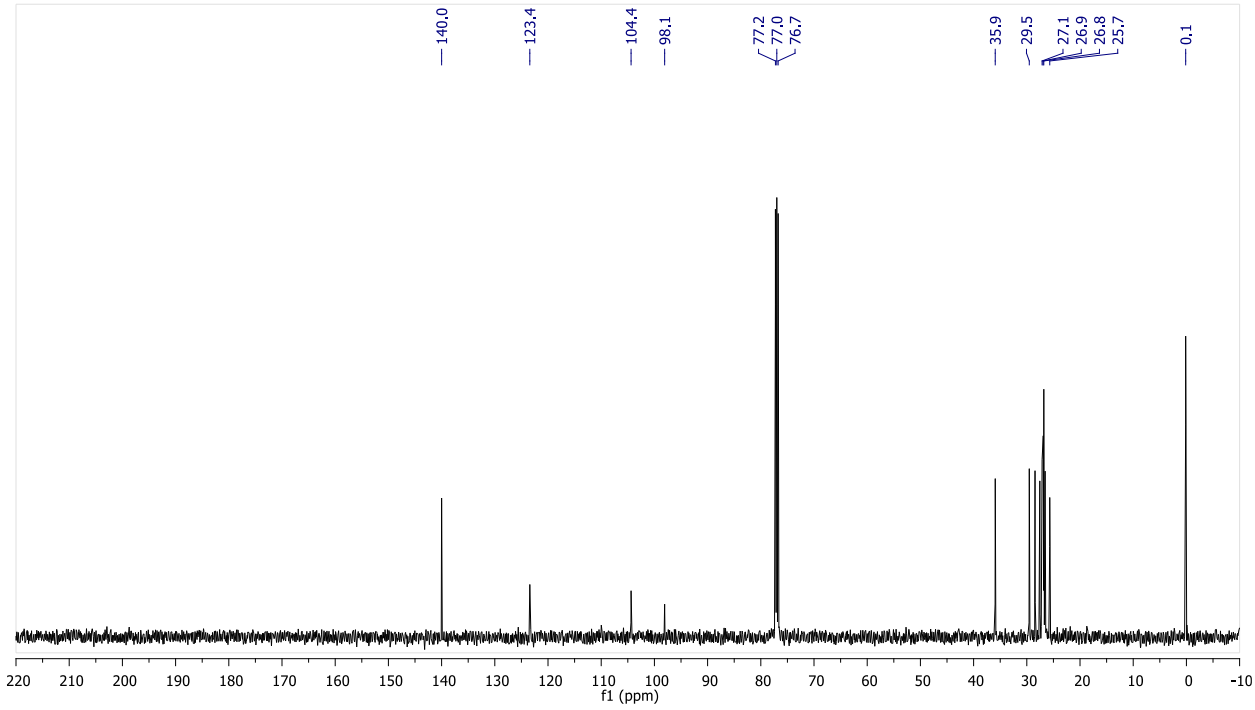

1.00
2.21
2.13
4.80
13.28
8.37
f1 (ppm)

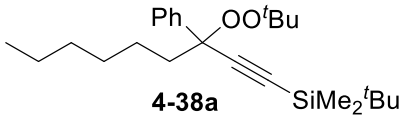

141.2
122.4
104.6
98.3
77.3
77.0
76.7
36.1
30.2
25.8
25.2
24.8
24.6
24.4
0.1
f1 (ppm)


SiMe3

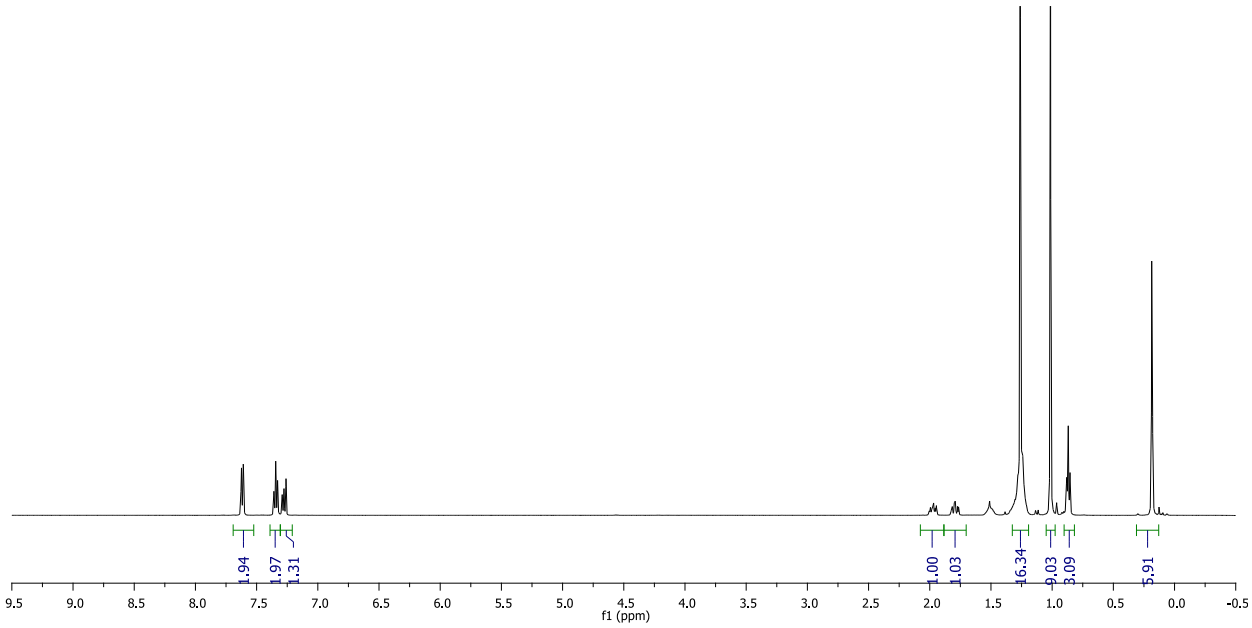
4-37l

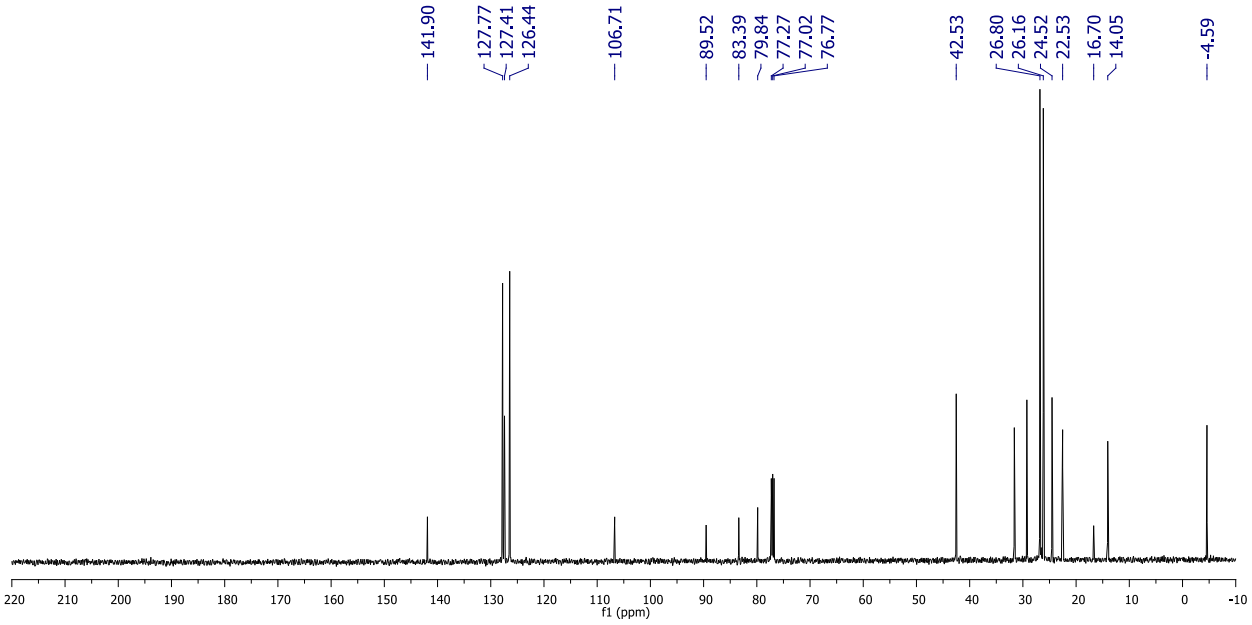

1.00
2.17
2.18
4.57
19.83
9.01
f1 (ppm)

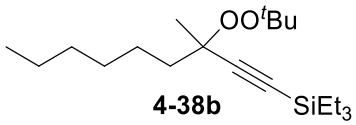

140.0
123.4
104.4
98.1
77.2
77.0
76.7
35.9
29.5
27.1
26.9
26.8
25.7
0.1
f1 (ppm)


Ph
OO^{t}Bu
SiMe$_2$^{t}Bu

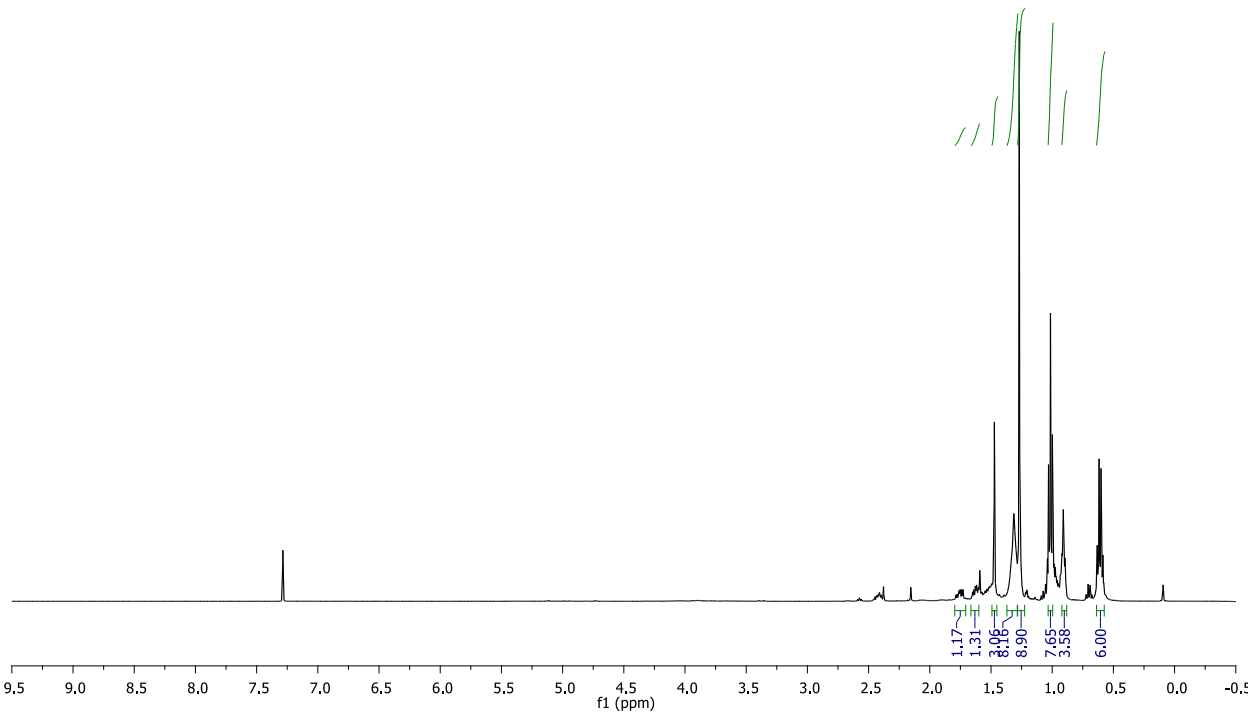
4-38a

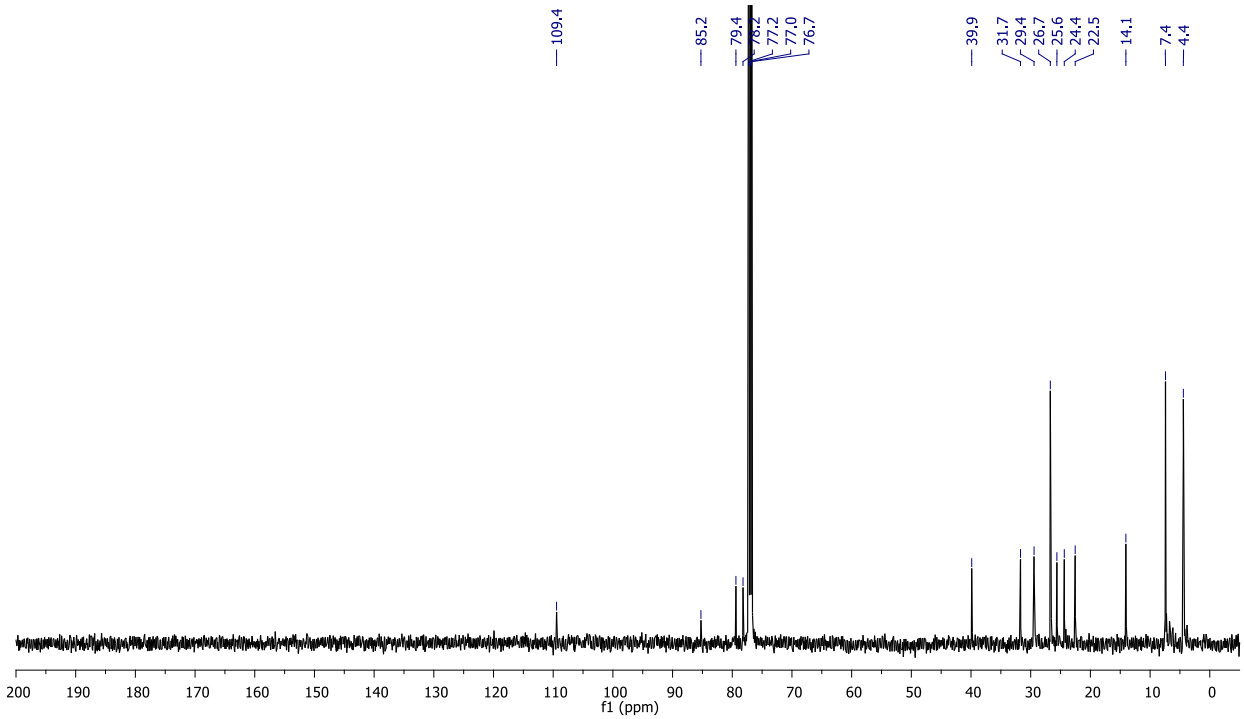

1.94
1.97
1.31
1.00
1.03
16.34
9.03
3.09
5.91
f1 (ppm)

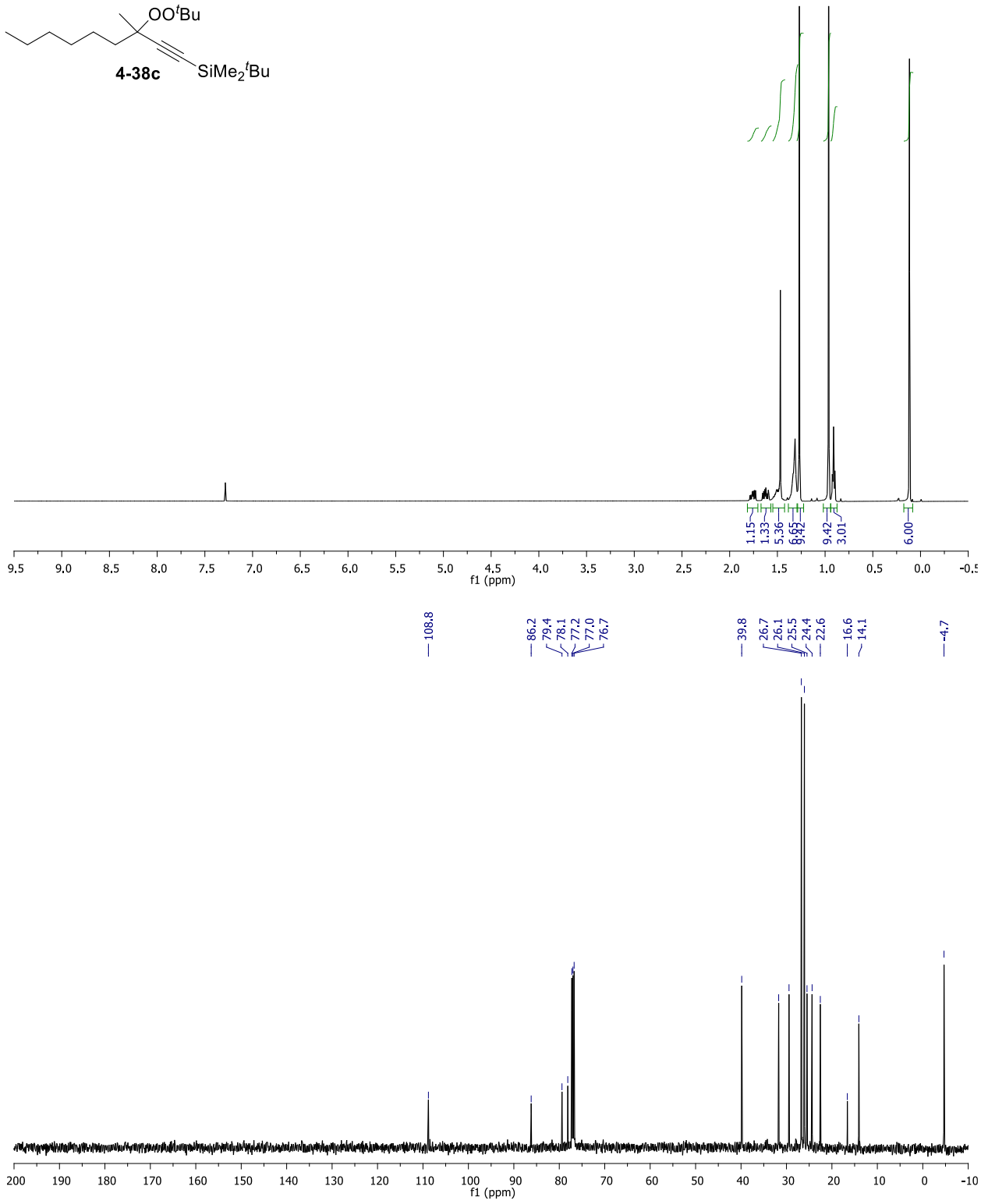

141.90
127.77
127.41
126.44
106.71
89.52
83.39
79.84
77.27
77.02
76.77
42.53
26.80
26.16
24.52
22.53
16.70
14.05
-4.59
f1 (ppm)

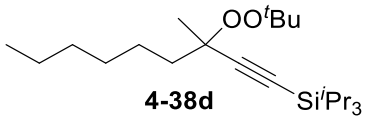

OO^{t}Bu
SiEt$_3$

4-38b

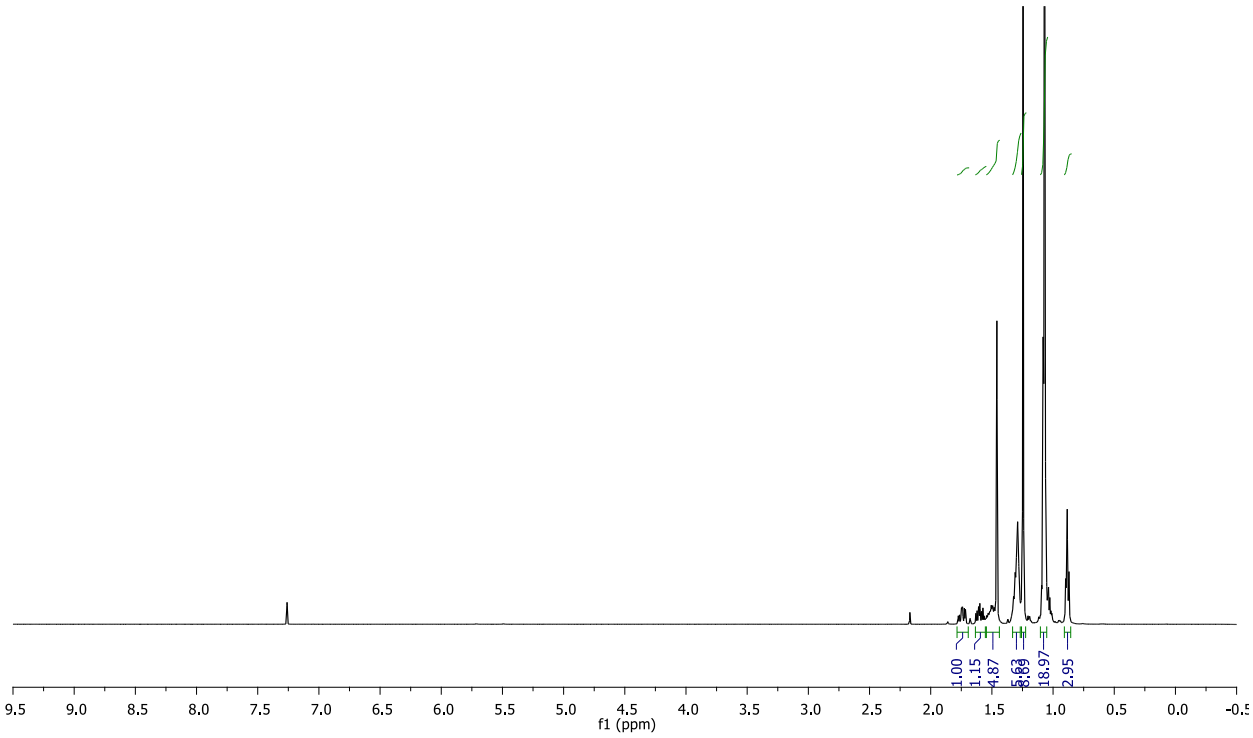

1.17
1.31
3.06
8.16
8.90
7.65
3.58
6.00
f1 (ppm)

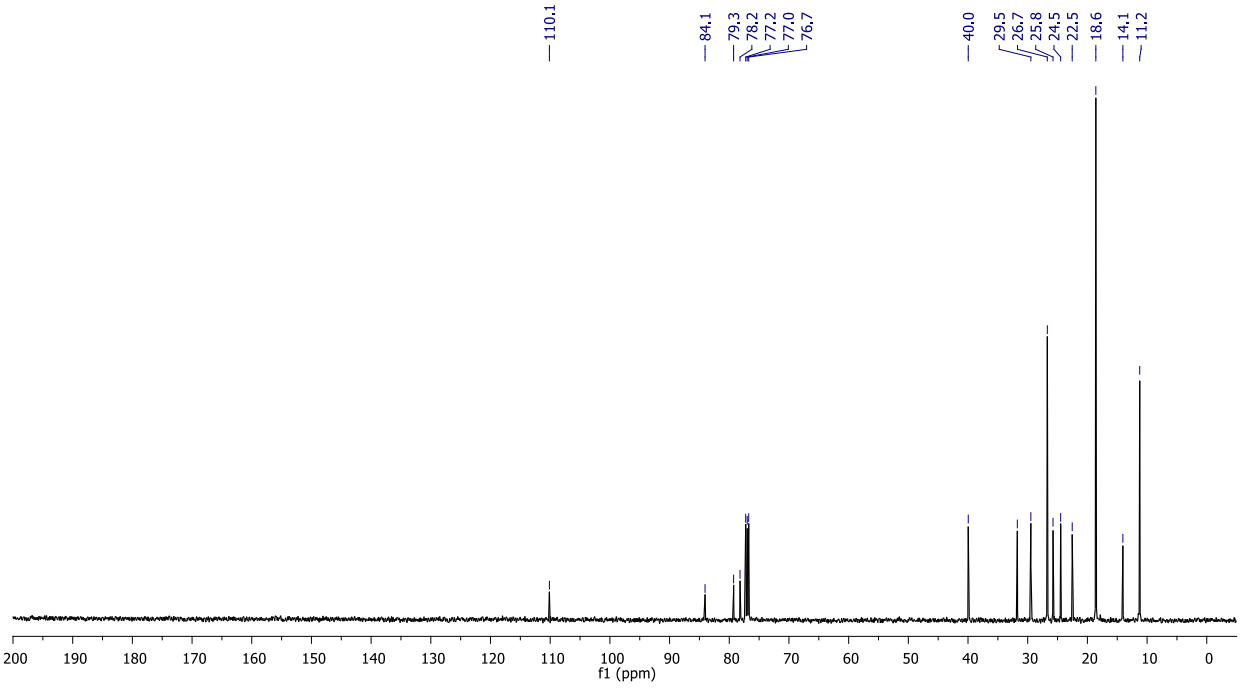

109.4
85.2
79.4
78.2
77.2
77.0
76.7
39.9
31.7
29.4
26.7
25.6
24.4
22.5
14.1
7.4
4.4
f1 (ppm)

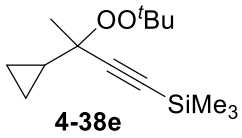

OO^{t}Bu
SiMe$_2$^{t}Bu
4-38c
1.15
1.33
5.36
6.55
9.42
3.01
6.00
f1 (ppm)
108.8
86.2
79.4
78.1
77.2
77.0
76.7
39.8
26.7
26.1
25.5
24.4
22.6
16.6
14.1
-4.7
f1 (ppm)


OO^{t}Bu
Si^{i}Pr$_3$

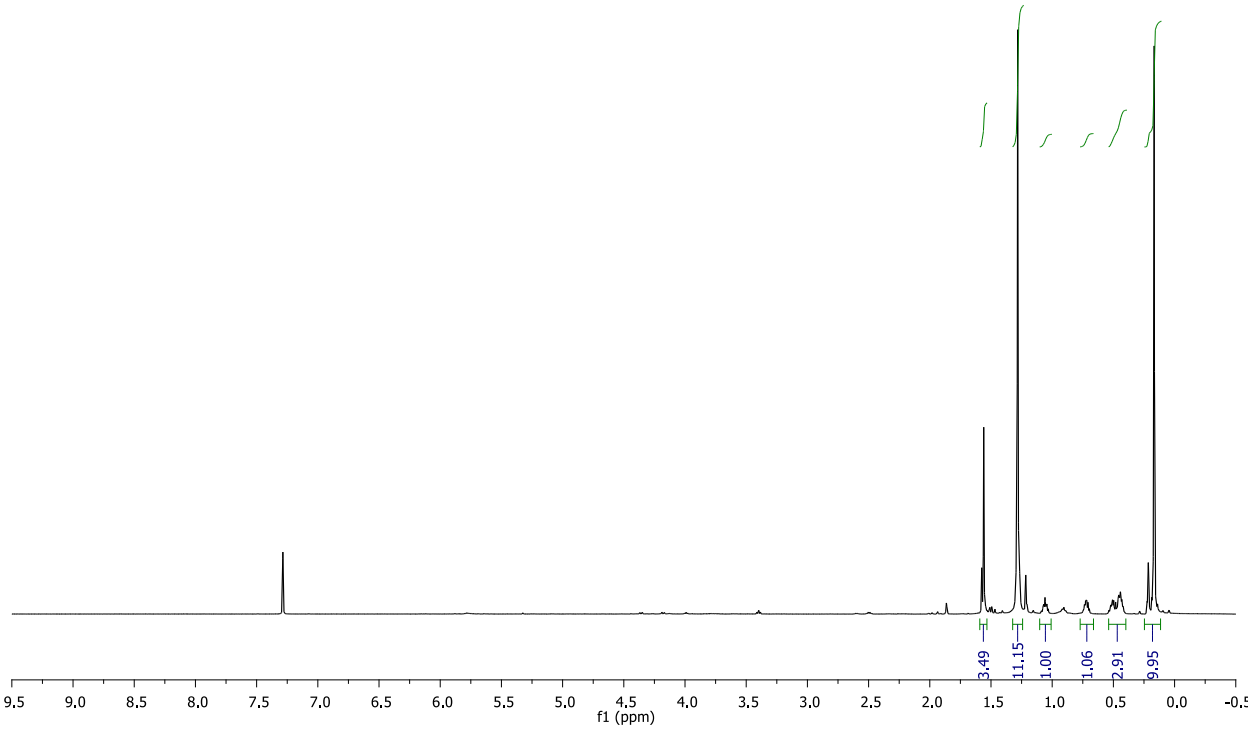
4-38d

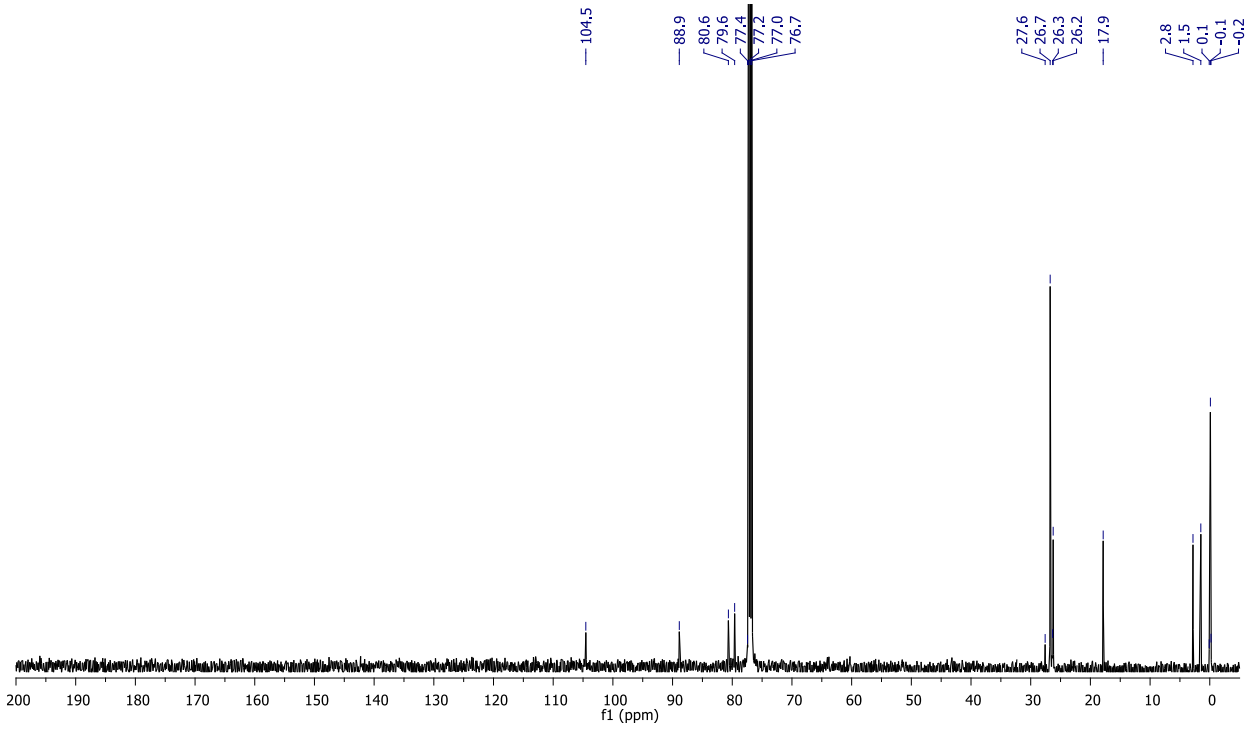

1.00
1.15
4.87
5.63
5.89
18.97
2.95
f1 (ppm)

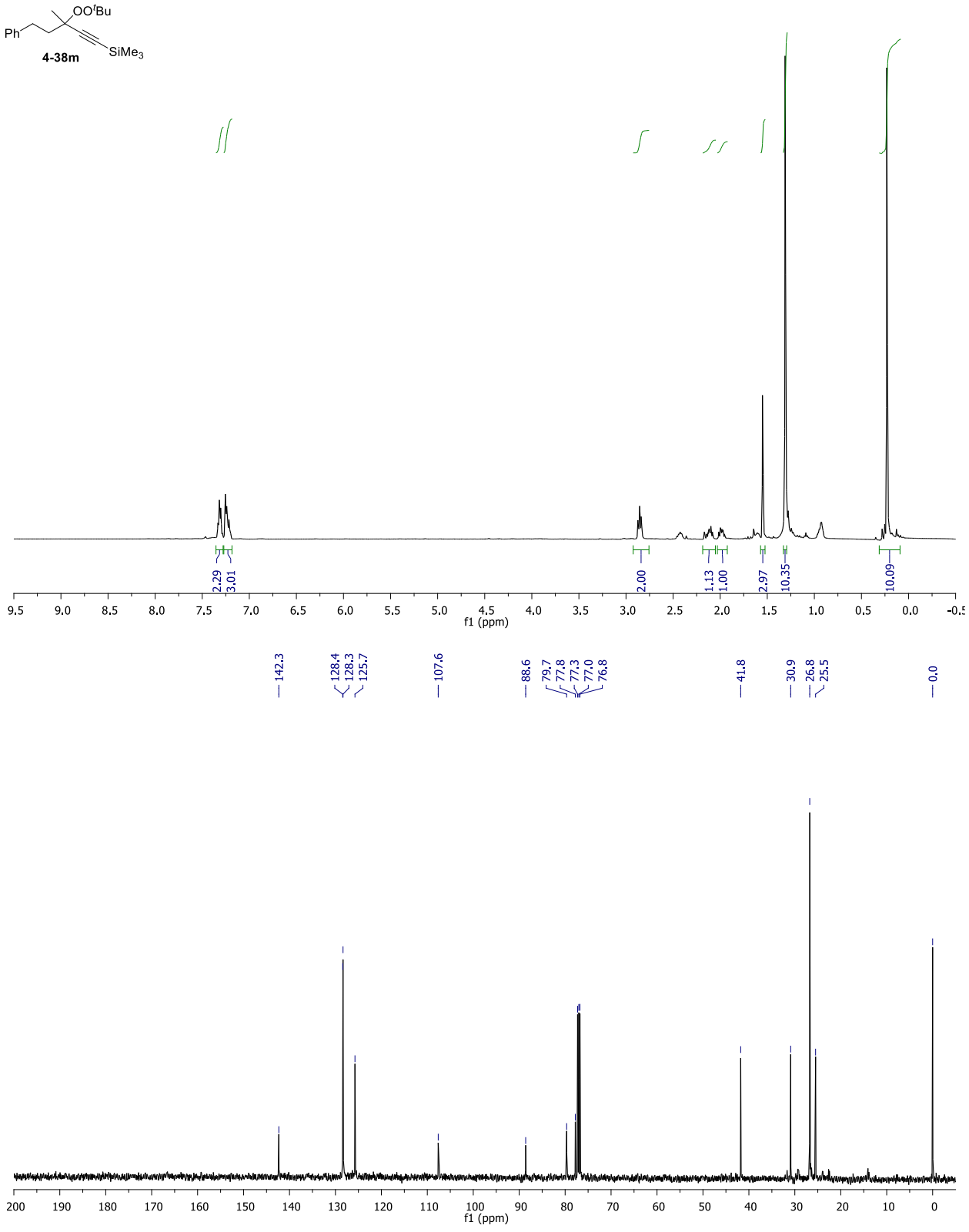

110.1
84.1
79.3
78.2
77.2
77.0
76.7
40.0
29.5
26.7
25.8
24.5
22.5
18.6
14.1
11.2
f1 (ppm)

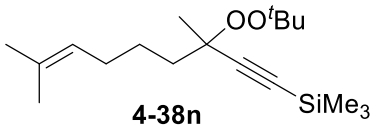

OO^{t}Bu
SiMe$_3$

4-38e

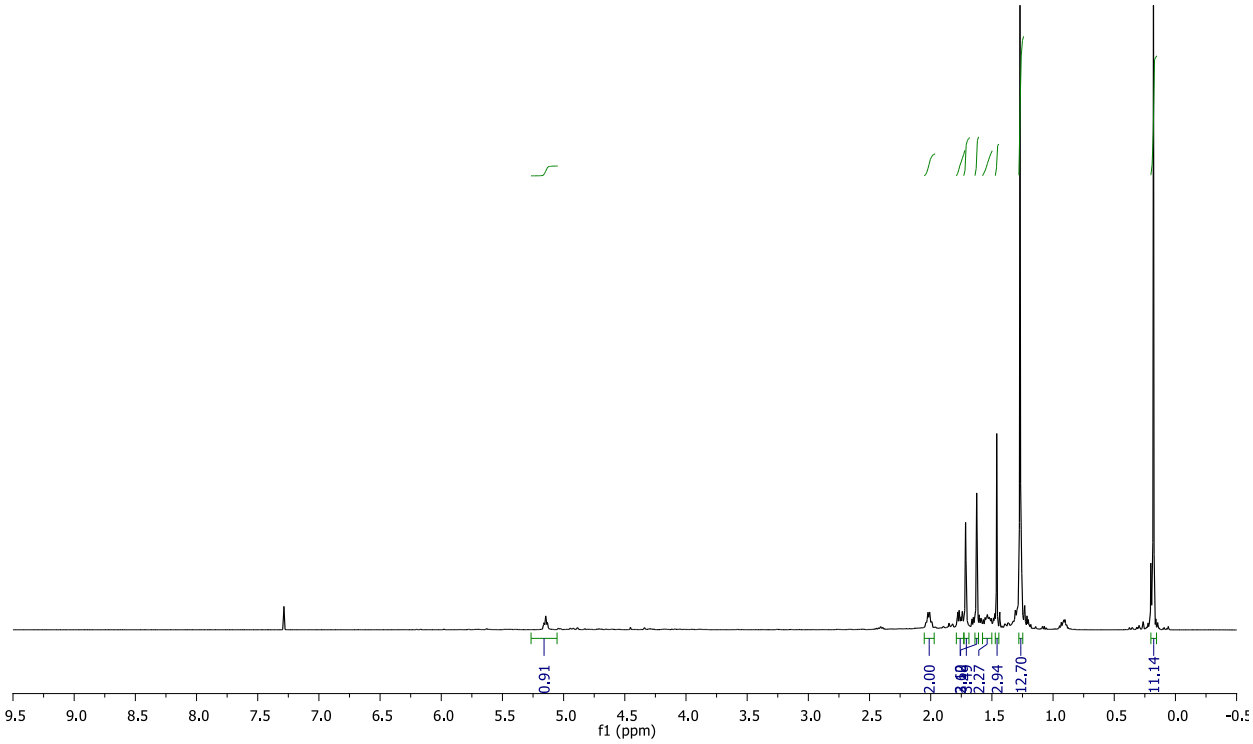

3.49
11.15
1.00
1.06
2.91
9.95
f1 (ppm)

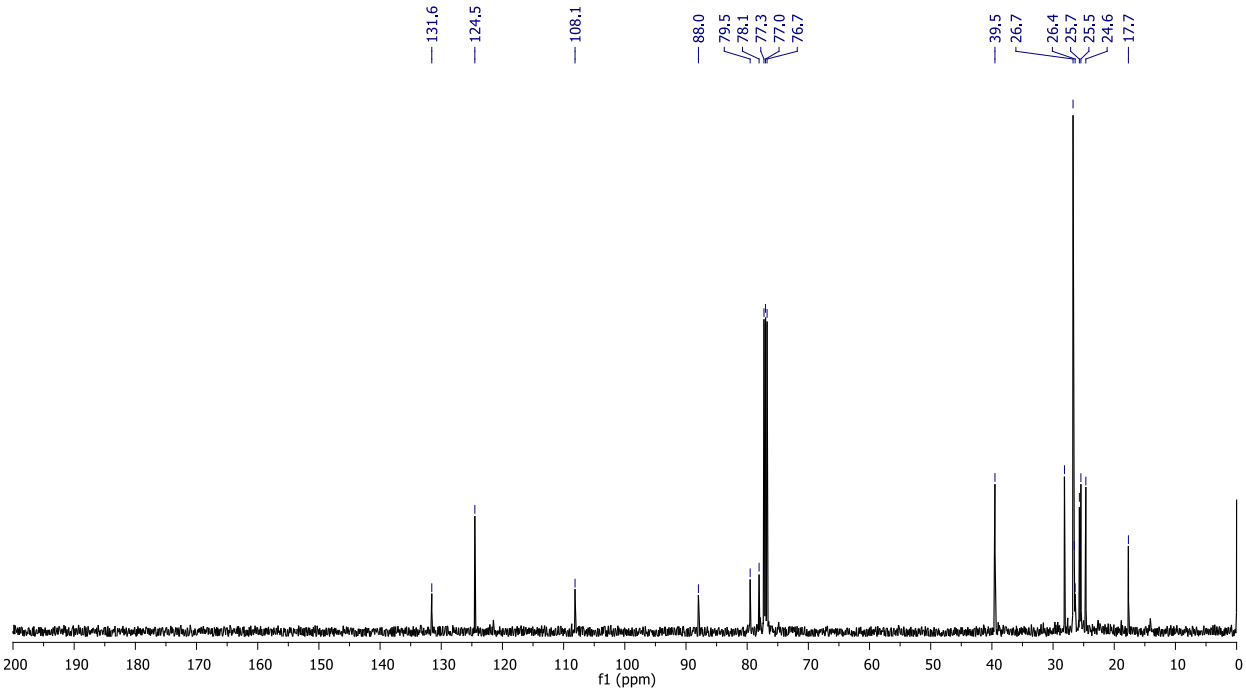

104.5
88.9
80.6
79.6
77.4
77.2
77.0
76.7
27.6
26.7
26.3
26.2
17.9
2.8
1.5
0.1
-0.1
-0.2
f1 (ppm)

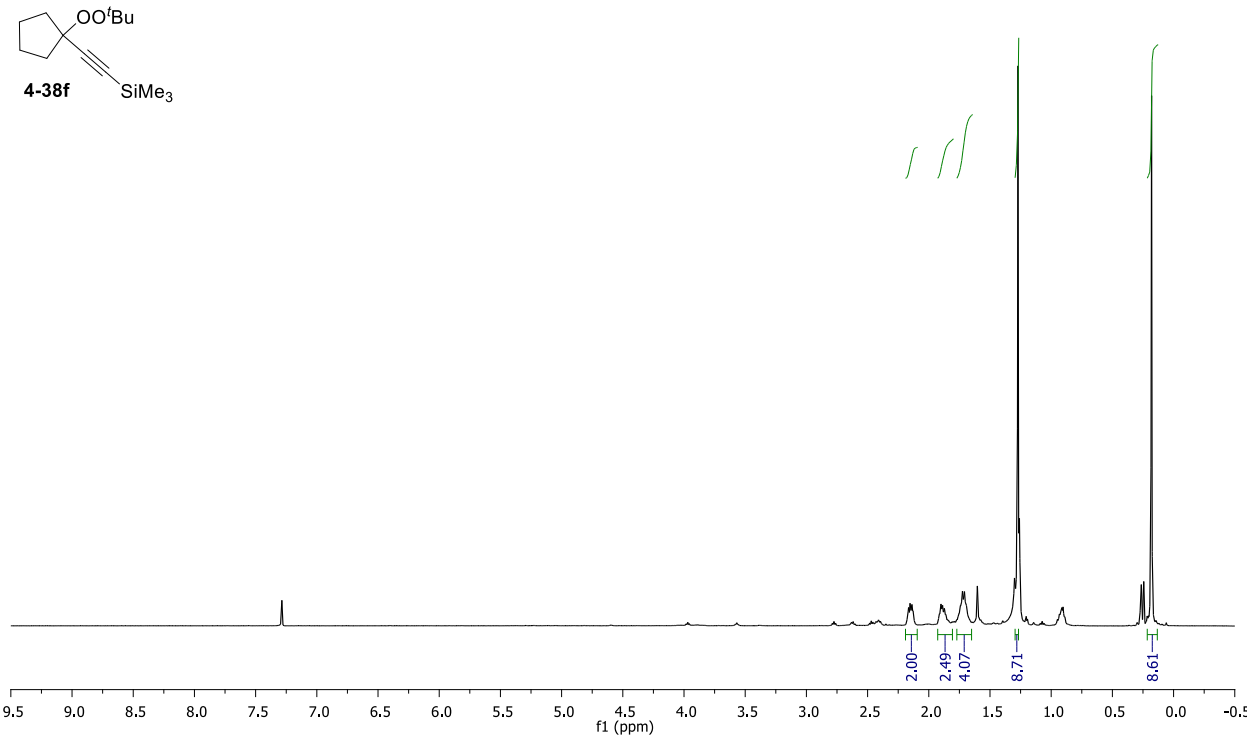

OO^{t}Bu
Ph
SiMe$_3$
4-38m
2.29
3.01
2.00
1.13
1.00
2.97
10.35
10.09
f1 (ppm)
142.3
128.4
128.3
125.7
107.6
88.6
79.7
77.8
77.3
77.0
76.8
41.8
30.9
26.8
25.5
0.0
f1 (ppm)

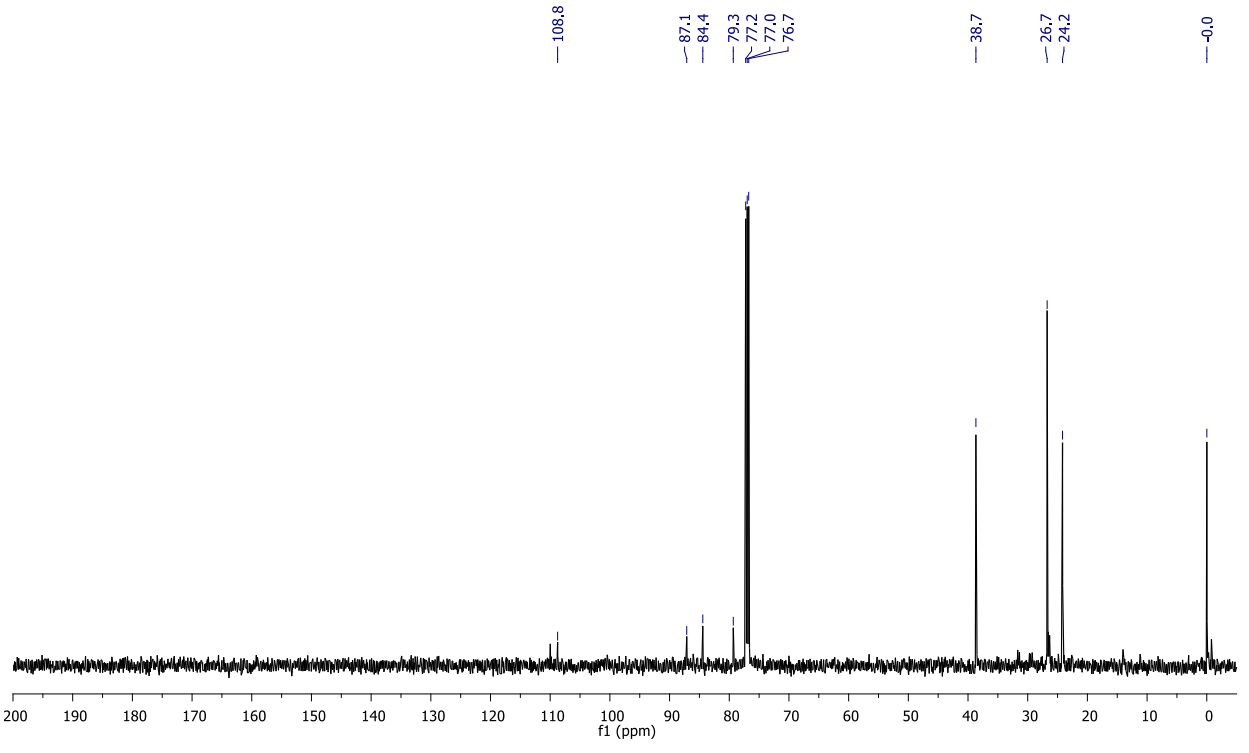

OO^{t}Bu
SiMe$_3$

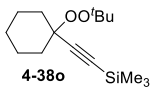
4-38n


0.91
2.00
2.27
2.94
12.70
11.14
f1 (ppm)

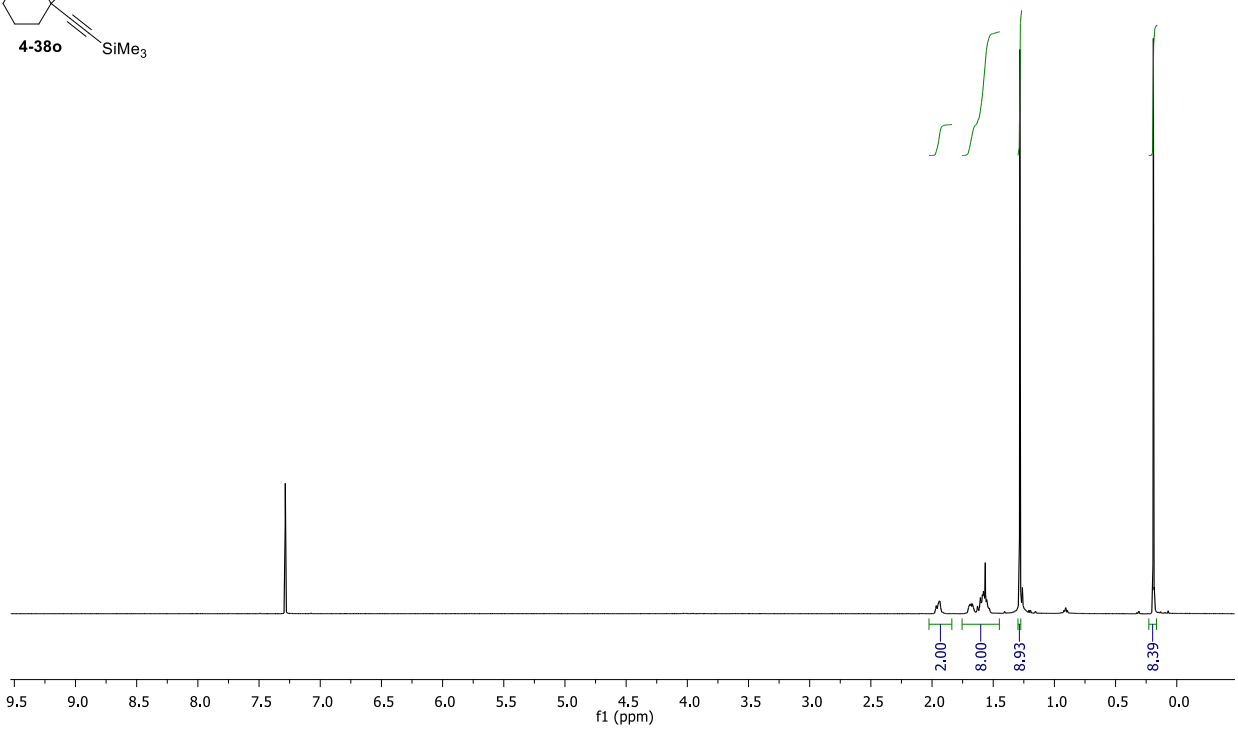

131.6
124.5
108.1
88.0
79.5
78.1
77.3
77.0
76.7
39.5
26.7
26.4
25.7
25.5
24.6
17.7
f1 (ppm)

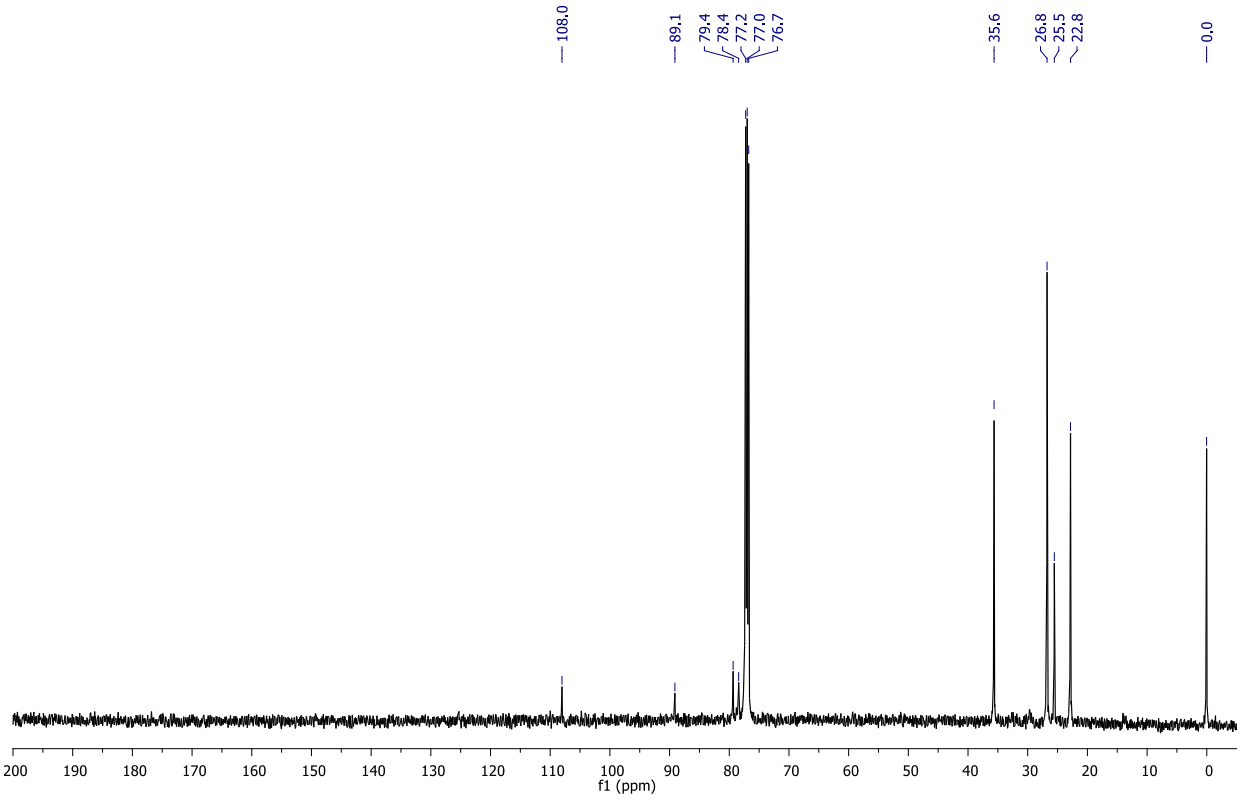

OO^{t}Bu
SiMe$_3$
4-38f
2.00
2.49
4.07
8.71
8.61
f1 (ppm)

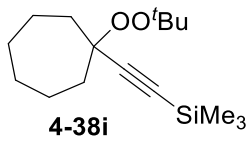

108.8
87.1
84.4
79.3
77.2
77.0
76.7
38.7
26.7
24.2
-0.0
f1 (ppm)


OO^{t}Bu
SiMe$_3$

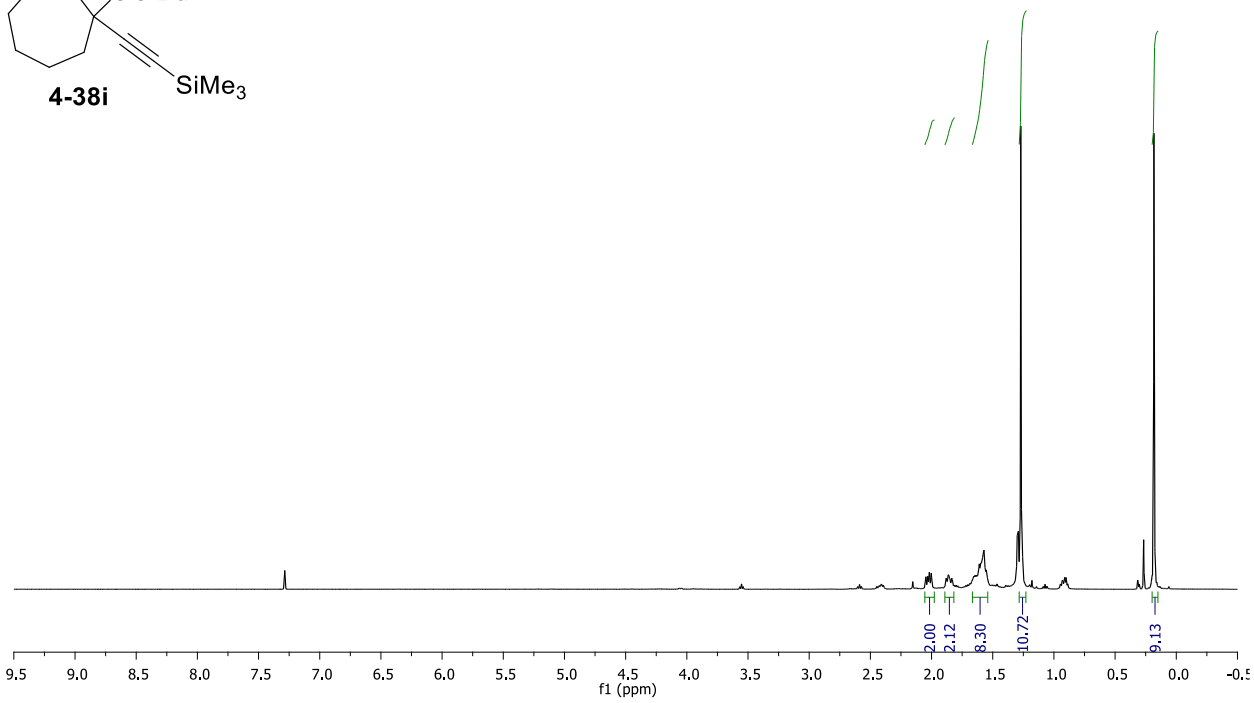
4-38o

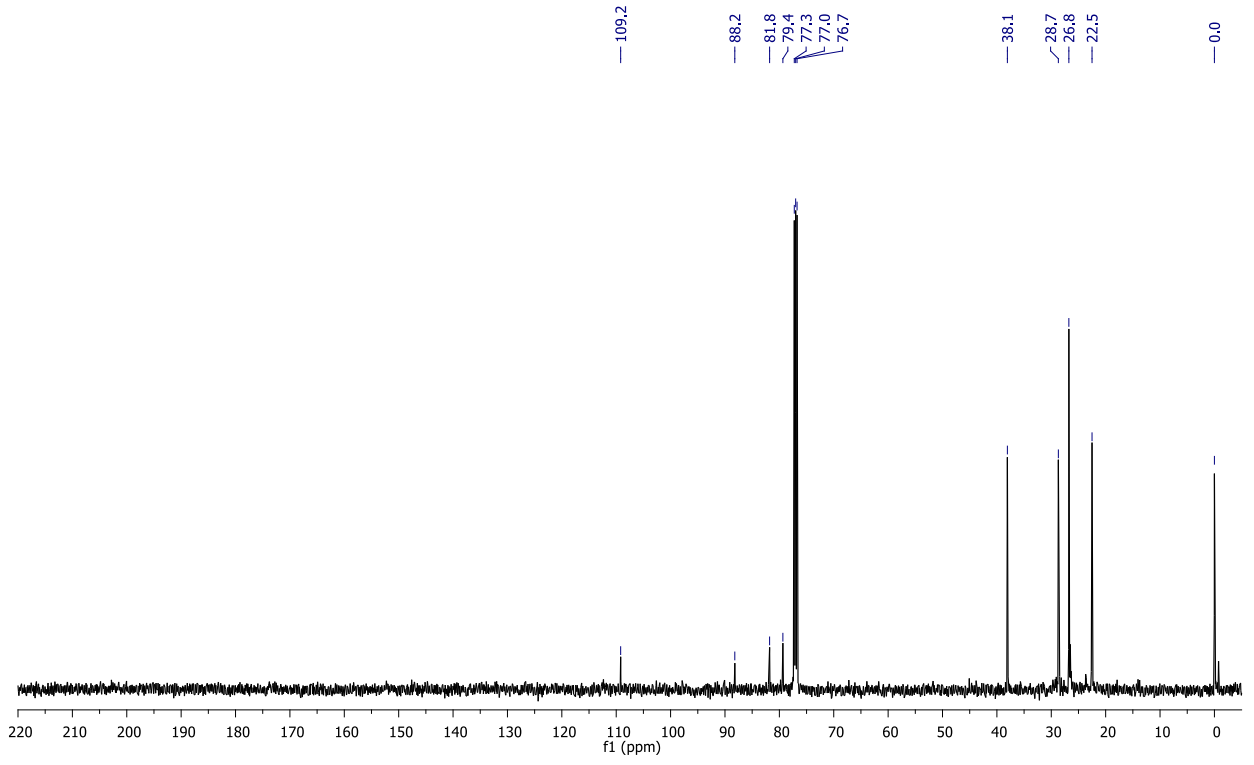

2.00
8.00
8.93
8.39
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

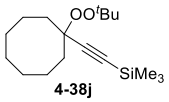

108.0
89.1
79.4
78.4
77.2
77.0
76.7
35.6
26.8
25.5
22.8
0.0
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


OO^{t}Bu
SiMe$_3$

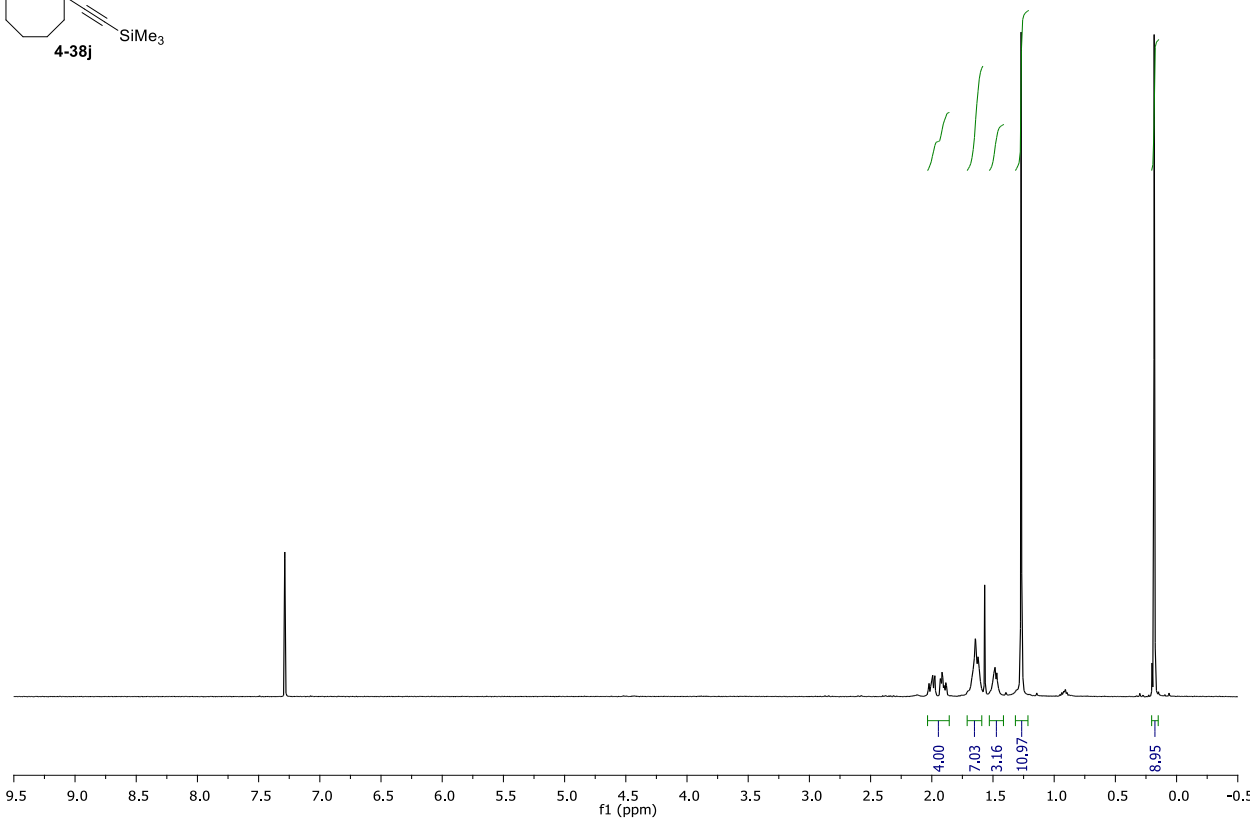
4-38i

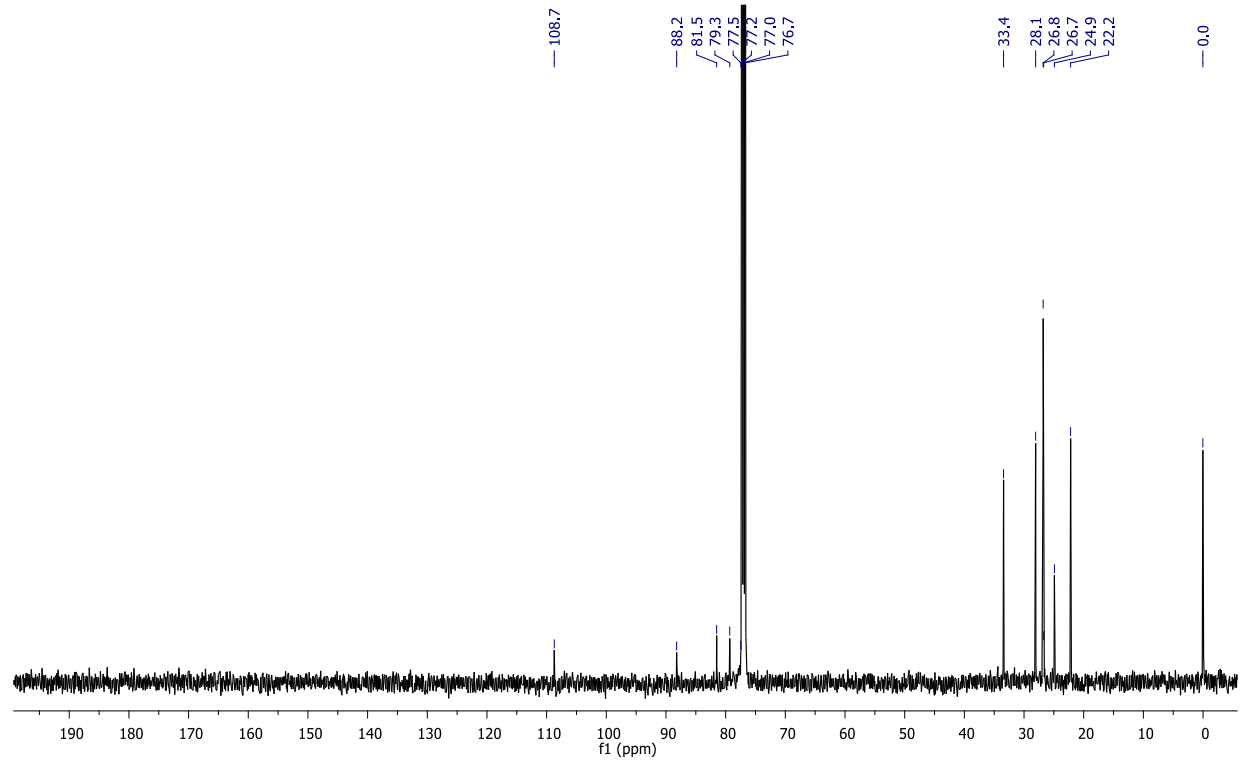

2.00
2.12
8.30
10.72
9.13
f1 (ppm)

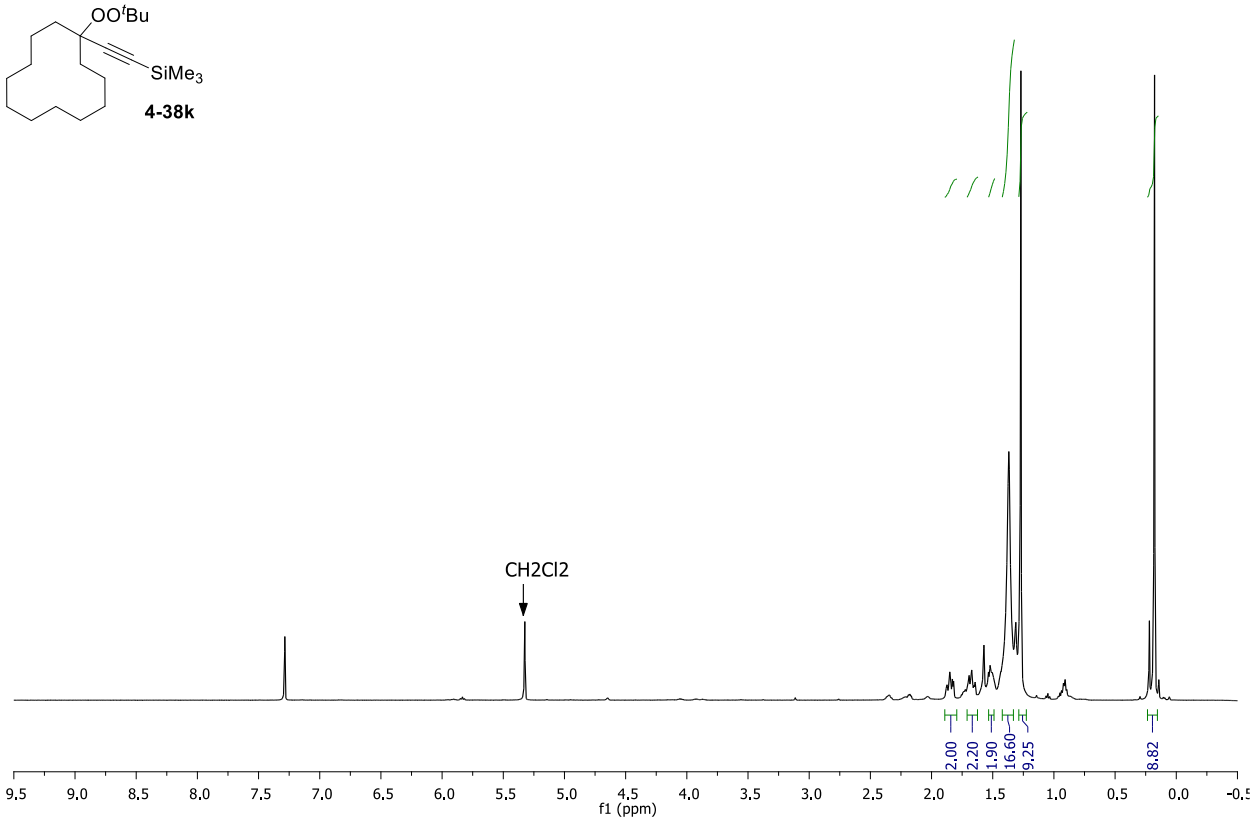

109.2
88.2
81.8
79.4
77.3
77.0
76.7
38.1
28.7
26.8
22.5
0.0
f1 (ppm)

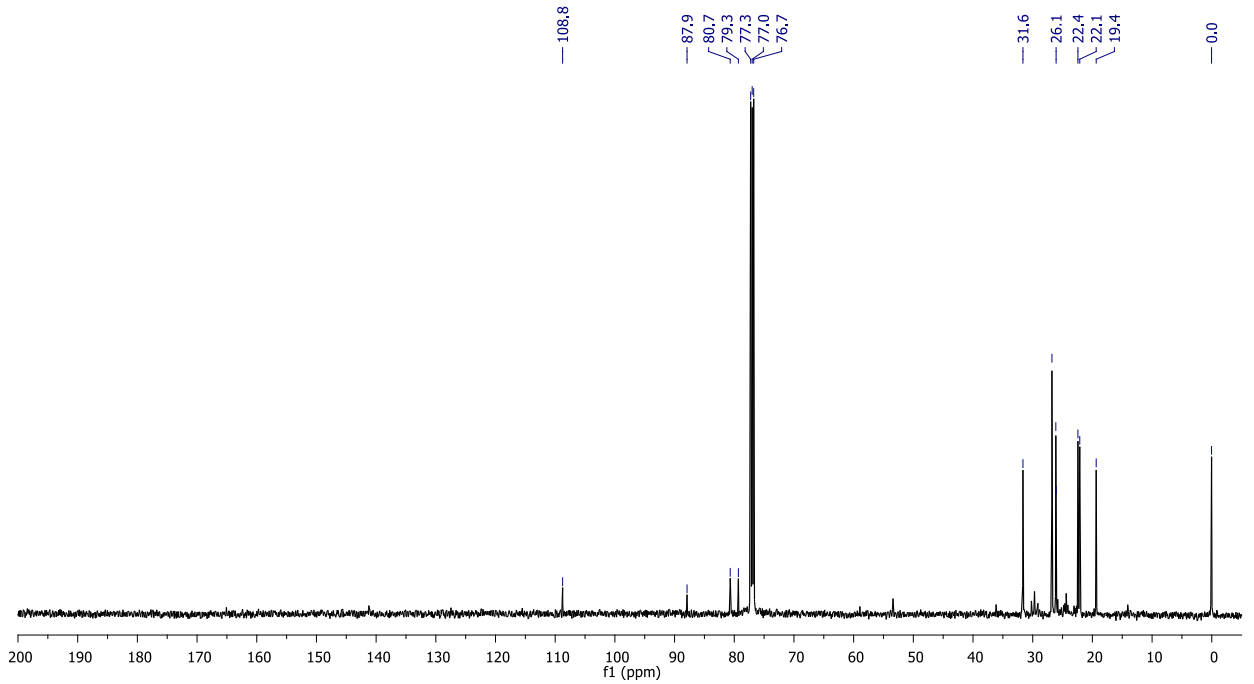

OO^{t}Bu
SiMe$_3$

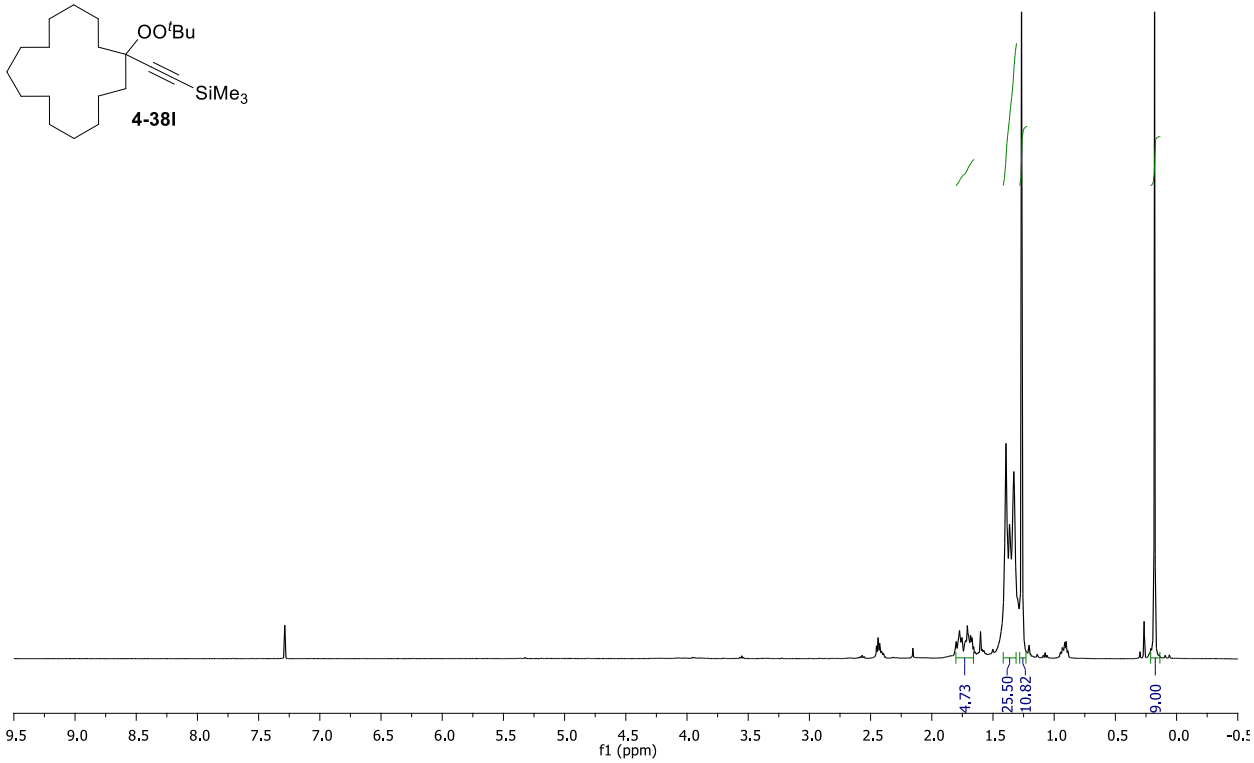
4-38j

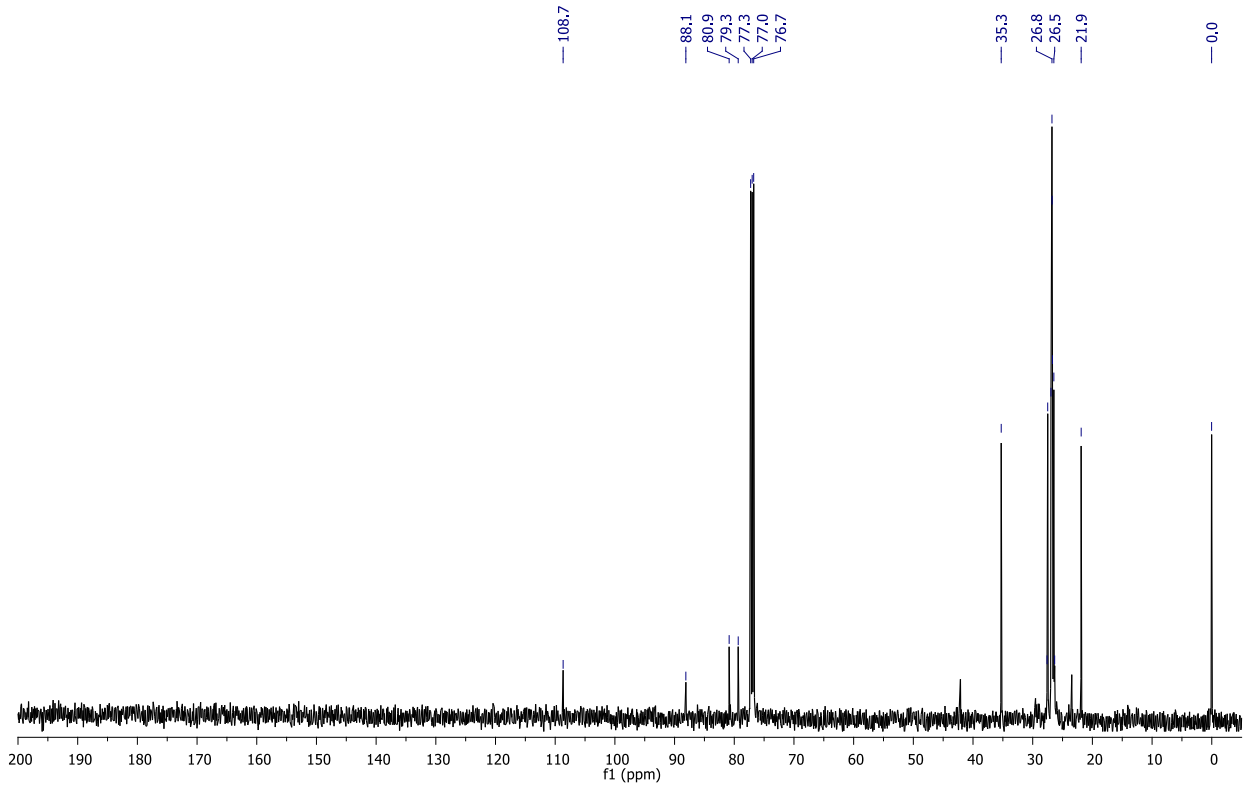

4.00
7.03
3.16
10.97
8.95
f1 (ppm)

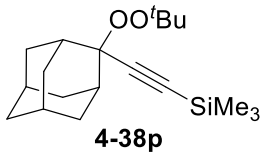

108.7
88.2
81.5
79.3
77.5
77.2
77.0
76.7
33.4
28.1
26.8
26.7
24.9
22.2
0.0
f1 (ppm)


OO^{t}Bu
SiMe$_3$
4-38k
CH2Cl2
2.00
2.20
1.90
16.60
9.25
8.82
f1 (ppm)

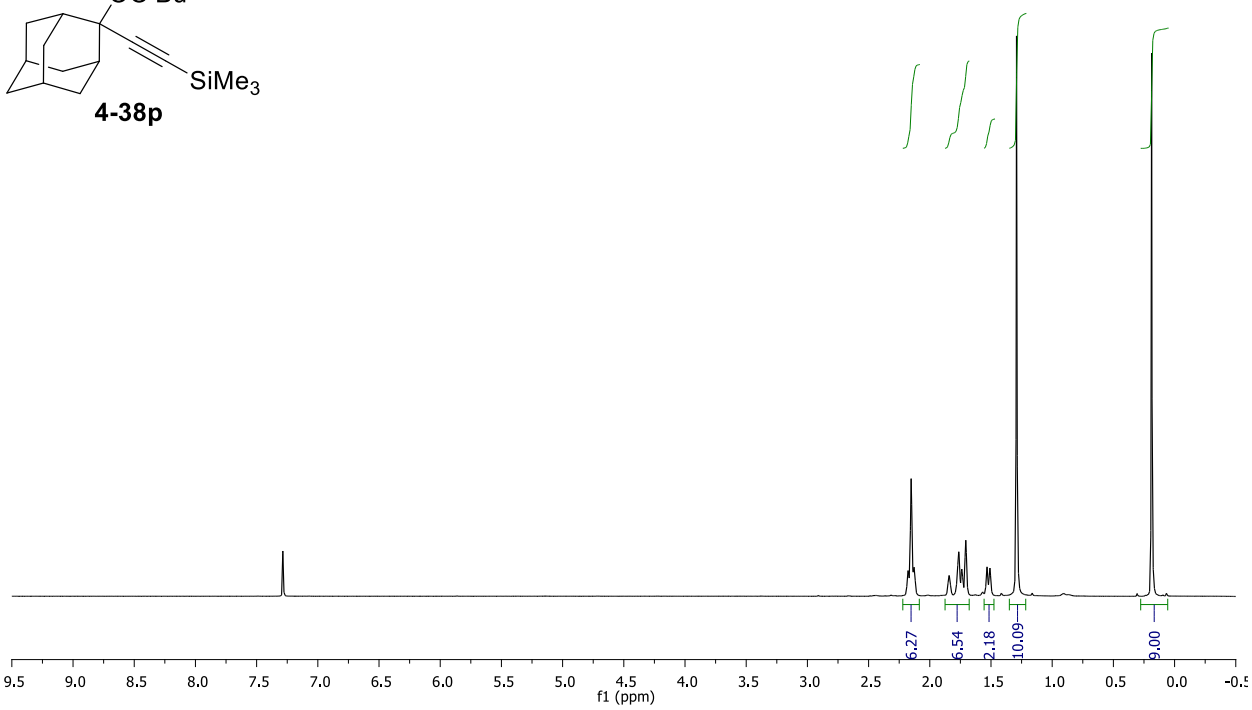

108.8
87.9
80.7
79.3
77.3
77.0
76.7
31.6
26.1
22.4
22.1
19.4
0.0
f1 (ppm)

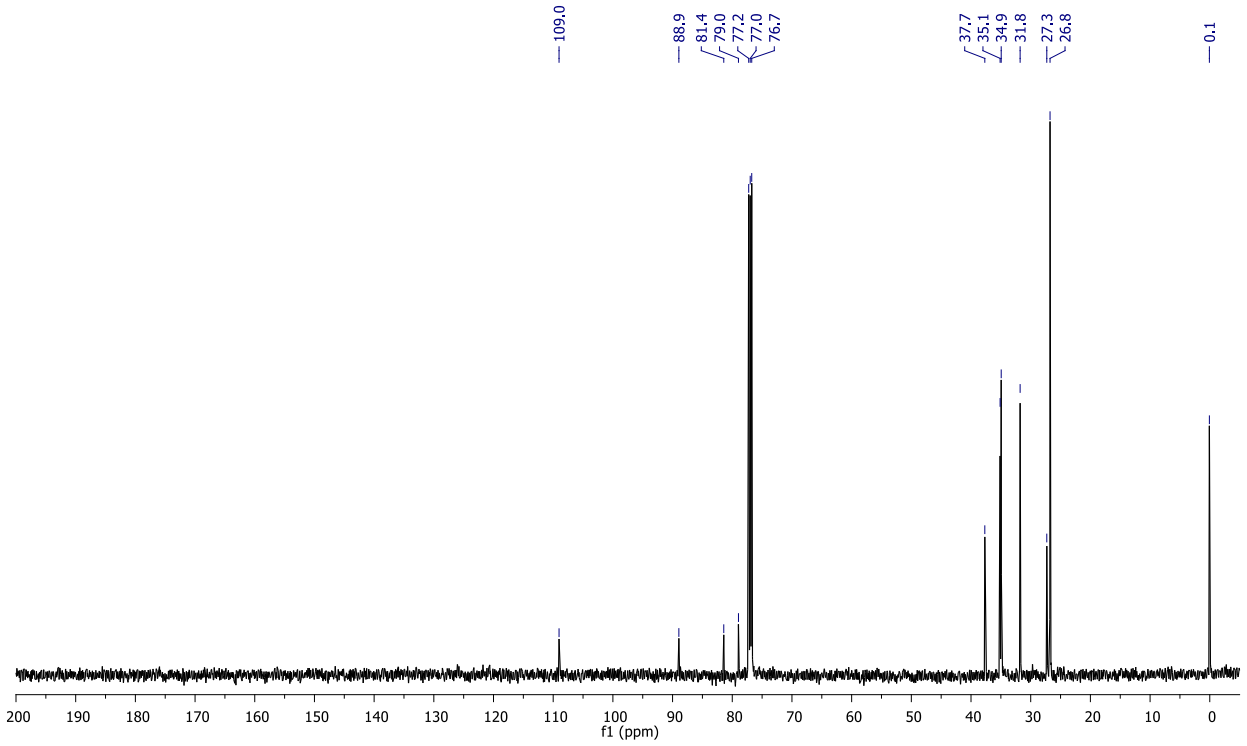

OO^{t}Bu
SiMe$_3$
4-38l
4.73
25.50
10.82
9.00
f1 (ppm)

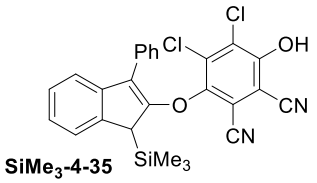

108.7
88.1
80.9
79.3
77.3
77.0
76.7
35.3
26.8
26.5
21.9
0.0
f1 (ppm)


OO^{t}Bu
SiMe$_3$

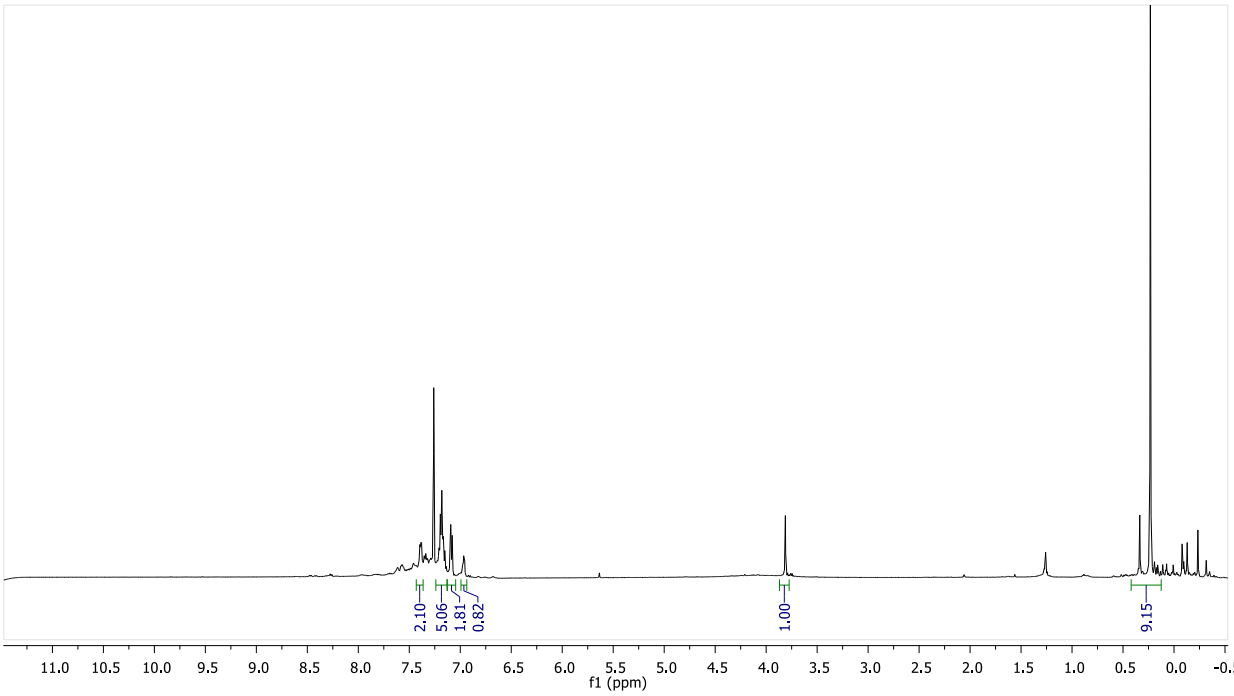
4-38p


6.27
6.54
2.18
10.09
9.00
f1 (ppm)


109.0
88.9
81.4
79.0
77.2
77.0
76.7
37.7
35.1
34.9
31.8
27.3
26.8
0.1
f1 (ppm)


Cl
Ph
Cl
OH
O
CN
CN
SiMe3

$SiMe_3$-4-35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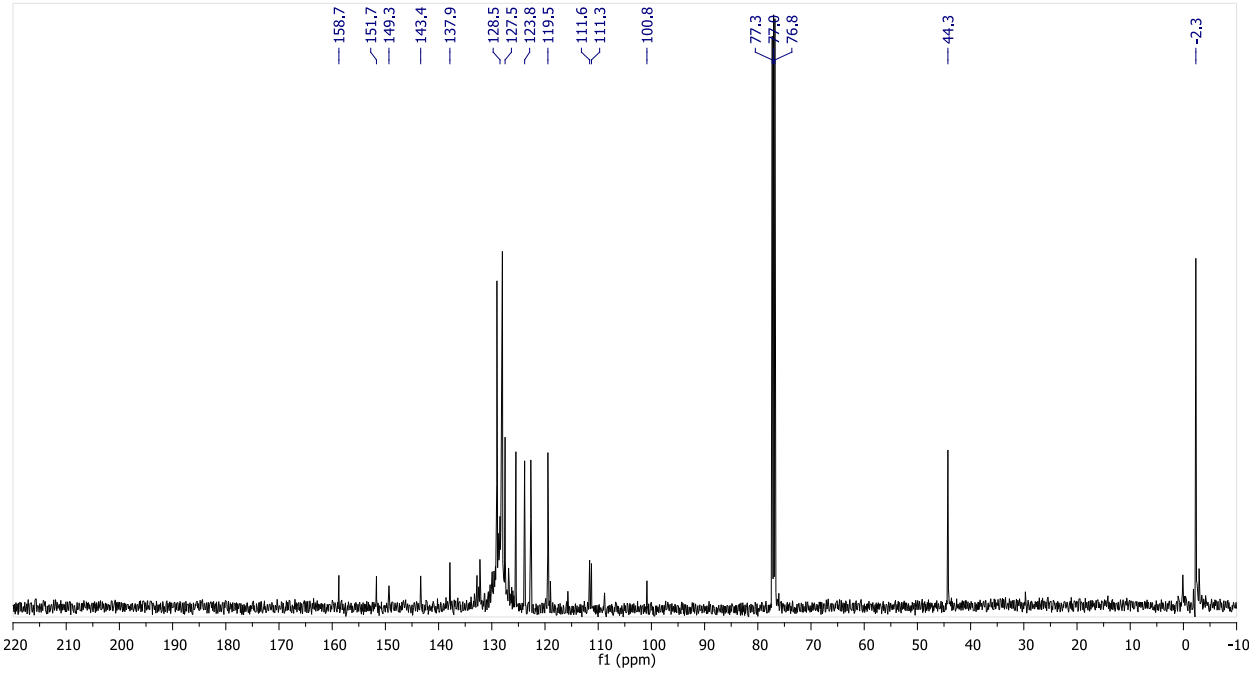
0.82
1.00
9.15
f1 (ppm)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151.7
149.3
143.4
137.9
128.5
127.5
123.8
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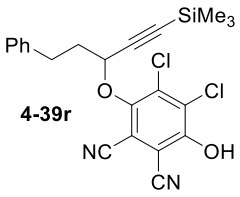
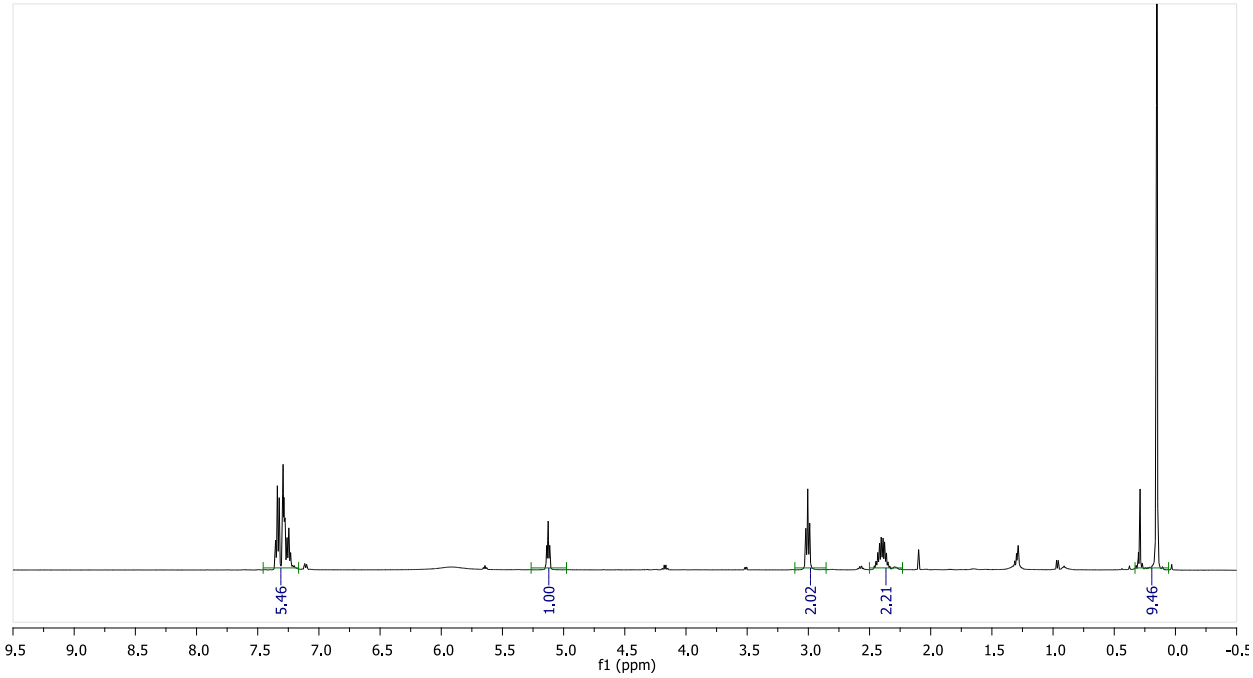
111.6
111.3
100.8
77.3
77.0
76.8
44.3
-2.3
f1 (ppm)


SiMe3
Ph
Cl
O
Cl
NC
OH
CN

4-39r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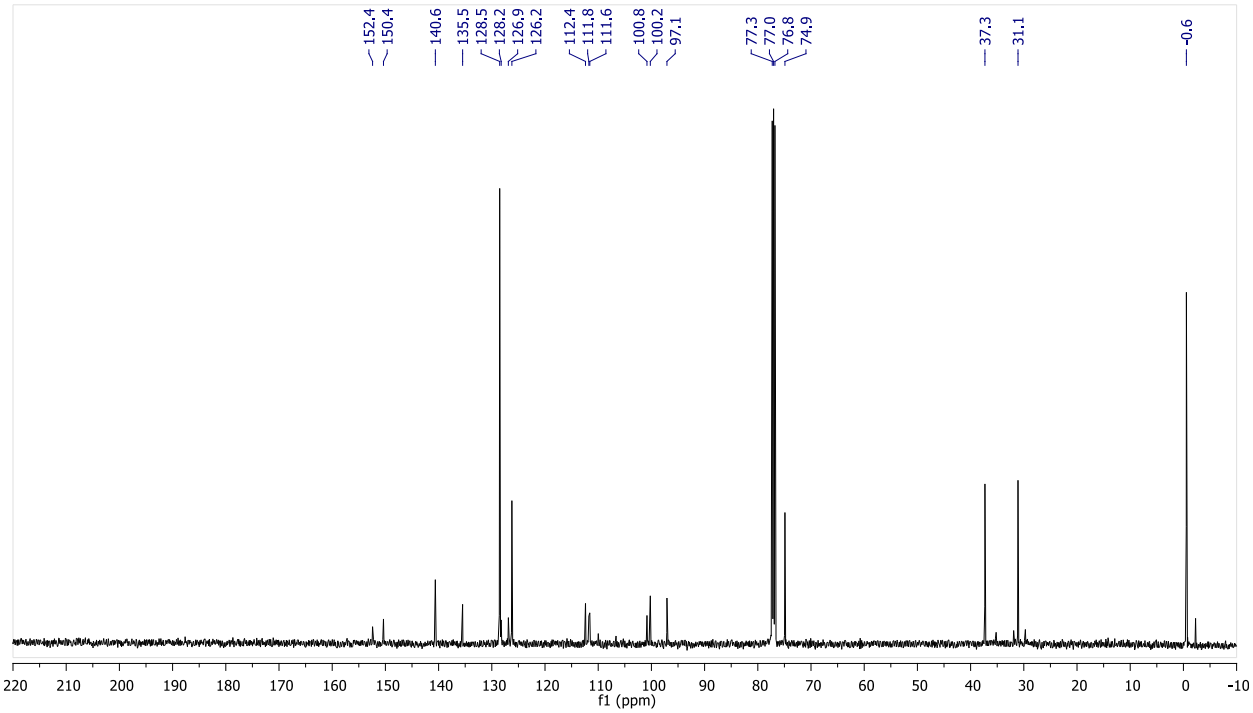
2.02
2.21
9.46
f1 (ppm)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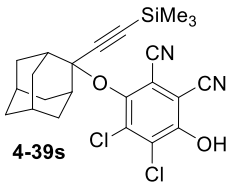
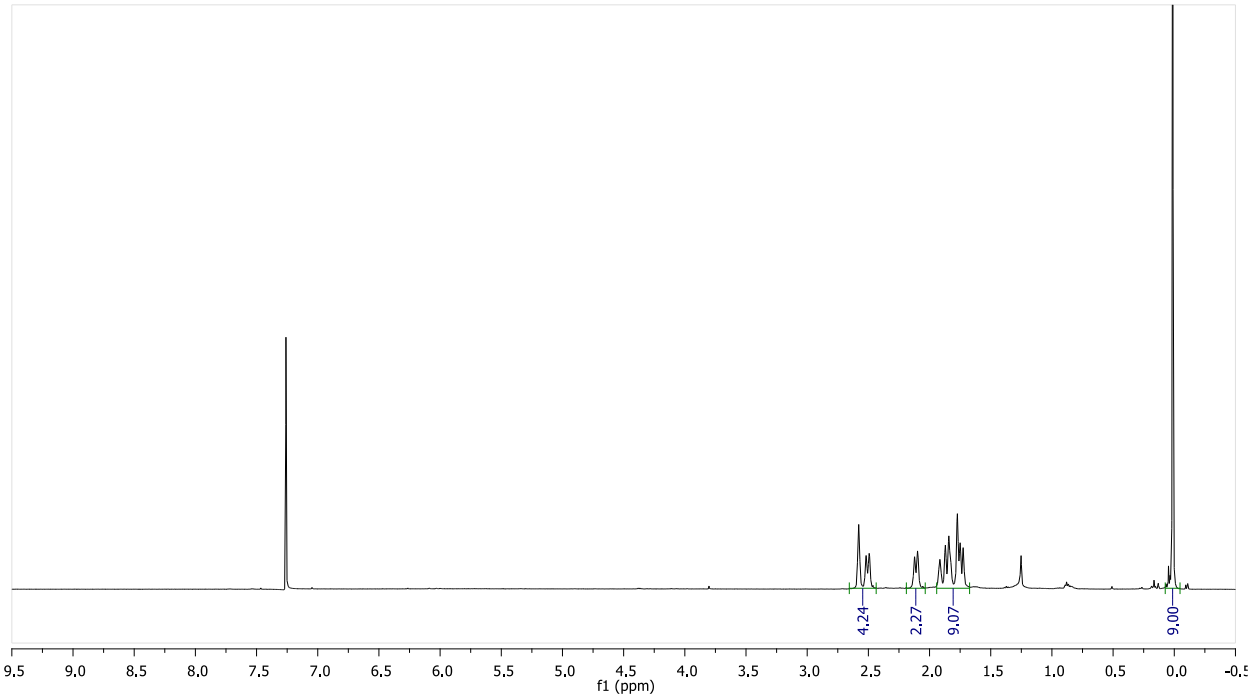
150.4
140.6
135.5
128.5
128.2
126.9
126.2
112.4
111.8
111.6
100.8
100.2
97.1
77.3
77.0
76.8
74.9
37.3
31.1
-0.6
f1 (ppm)


SiMe3
CN
O
CN
Cl
OH
Cl

4-39s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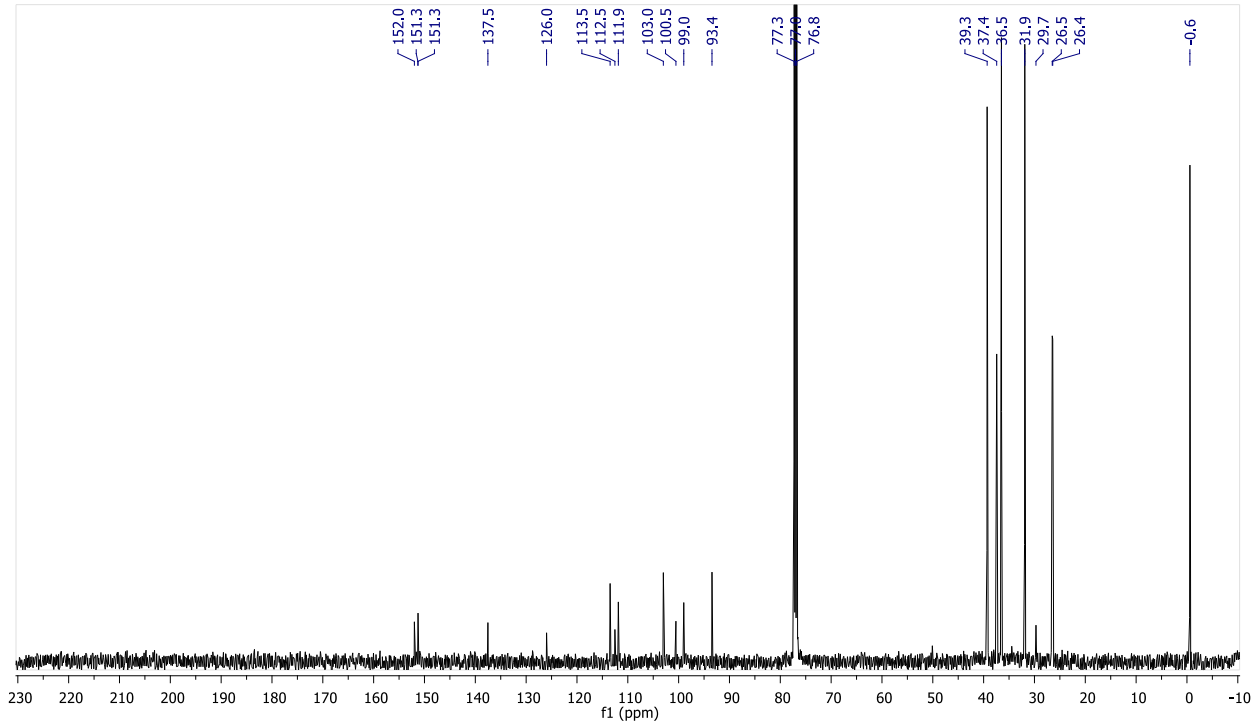
2.27
9.07
9.00
f1 (ppm)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151.3
151.3
137.5
126.0
113.5
112.5
111.9
103.0
100.5
99.0
93.4
77.3
77.0
76.8
39.3
37.4
36.5
31.9
29.7
26.5
26.4
-0.6
f1 (ppm)

Computational Details

All calculations were carried out with the Gaussian 09 suite of computational programs.[1] The geometry optimizations and frequency calculations were done at the M06/6-31+G(d) level of theory.[2] The effect of CH_3CN solvent was evaluated by single point calculations using the SMD model with the default UFF atomic radii. Unless stated otherwise, all the energy values discussed in the main text are relative free energies (ΔG_{sol}, kcal/mol). Only the intermediate or transition state that has the lowest energy value among all possible conformers is used for discussion.

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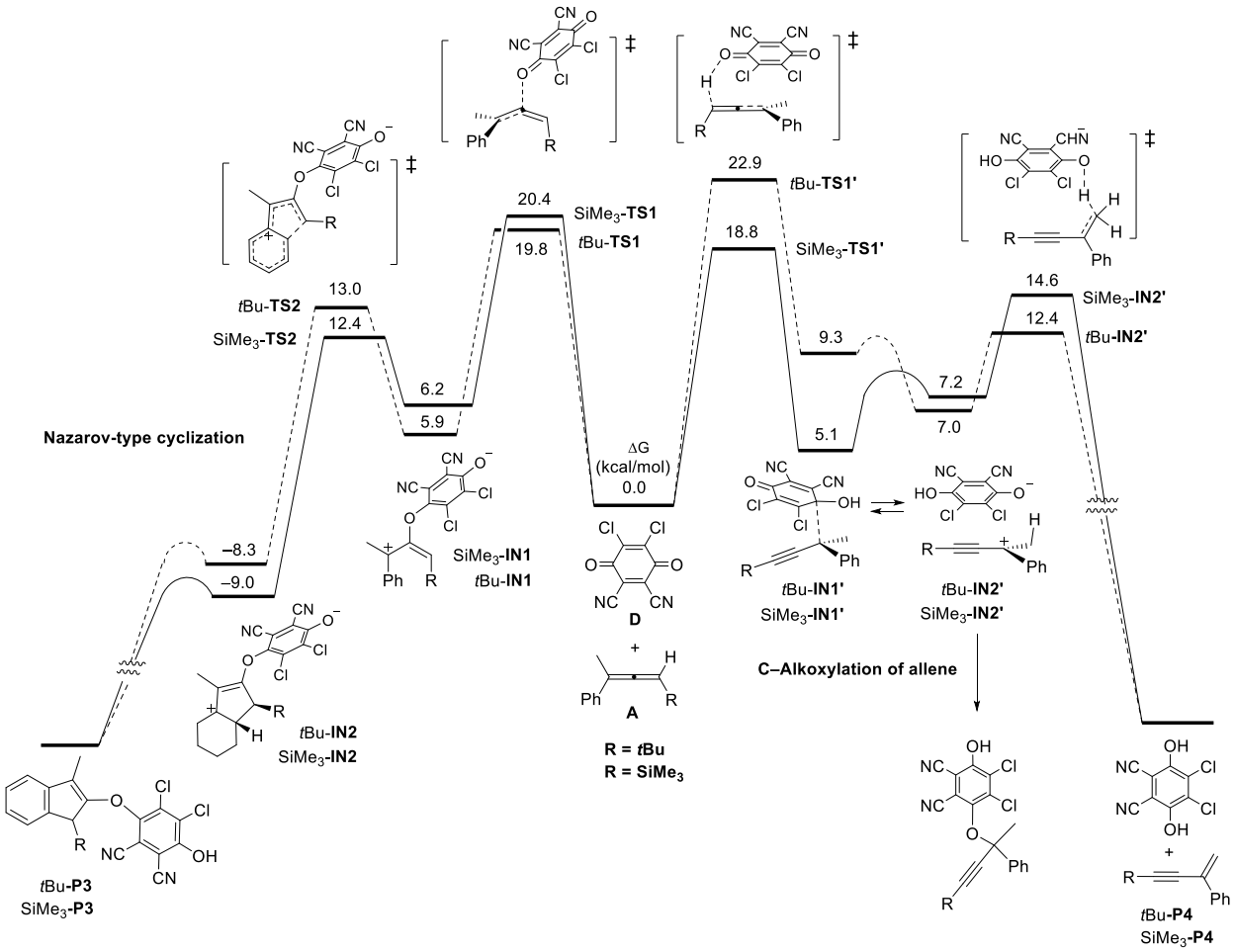
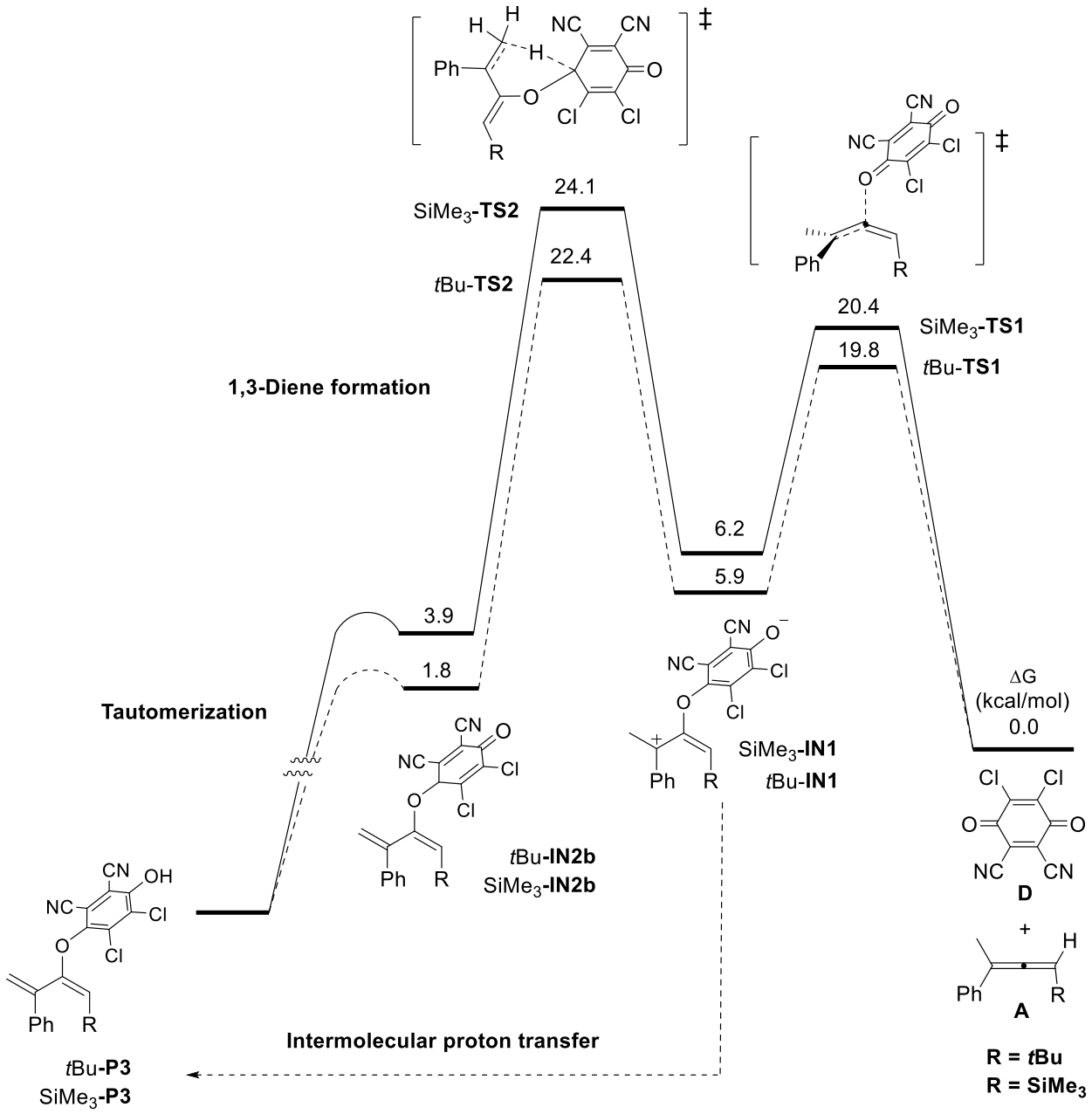
[1] Gaussian 09, Revision **D.01**, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Jr. Montgomery, J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, *Gaussian, Inc*., Wallingford CT, **2009**.

[2] a) Y. Zhao, D. G. Truhlar, *Theor. Chem. Acc.* **2008**, *120*, 215; b) Y. Zhao, D. G. Truhlar, *Acc. Chem. Res.* **2008**, *41*, 157.

1) Mechanisms for the transformations of alkyl- and silyl-substituted allenes with DDQ (relative free emergies (in kcal/mol) were calculated at the M06-2X/6-31+G* level)



2) Mechanisms for the possible pathway for the formation of 1,3-dienes



3) Mechanisms for the possible C-alkylation and C-alkoxylation of allenes

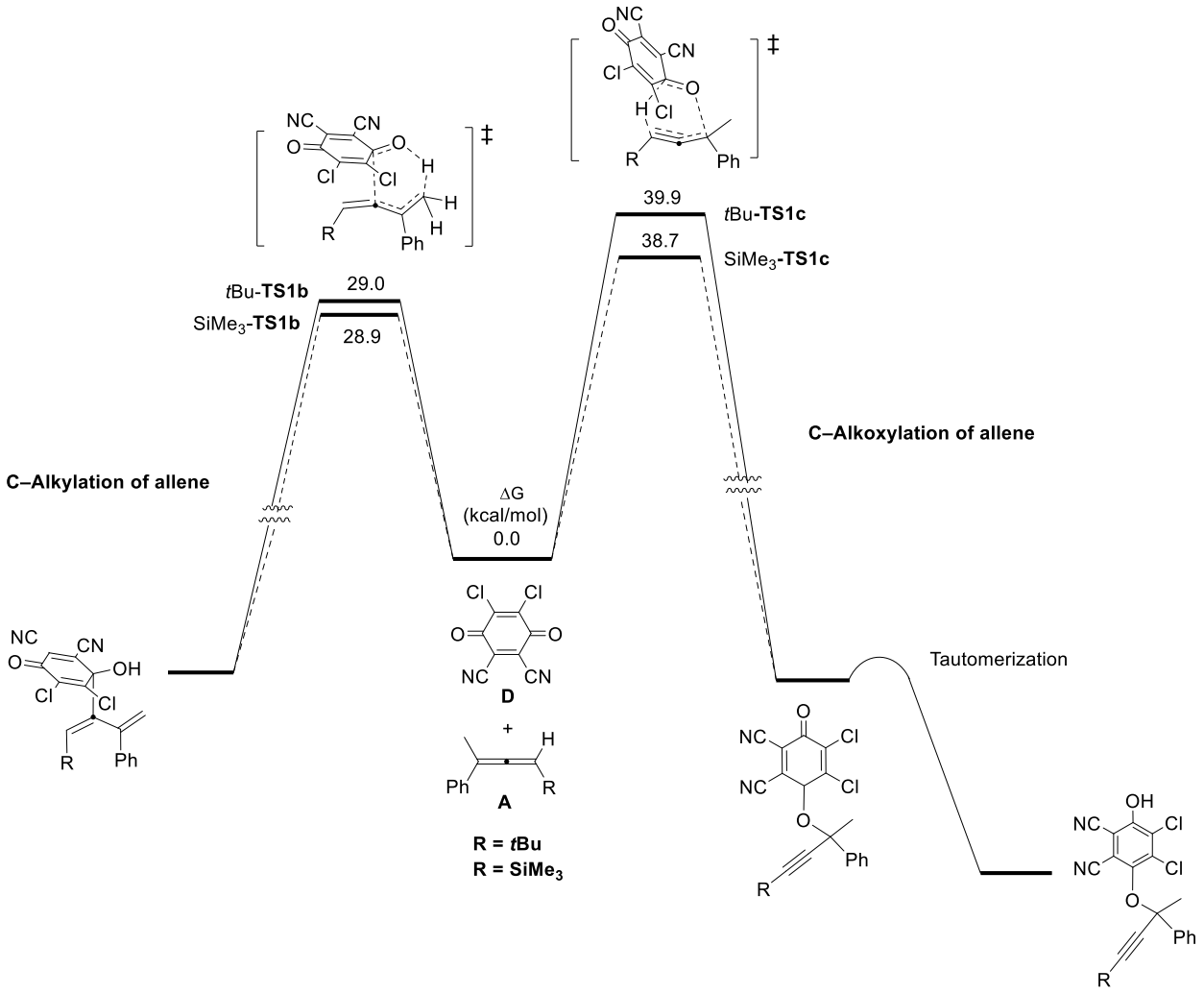


Table of Energy Values (in a.u.)

Species	Free energy	Electronic energy	Single point energy in solution
DDQ	-1484.822101	-1484.845405	-1484.865823
t-Bu-Allene	-543.805622	-544.045846	-544.0605809
t-Bu-TS1	-2028.598753	-2028.889793	-2028.922368
t-Bu-IN1	-2028.596258	-2028.887347	-2028.944577
t-Bu-TS2	-2028.583742	-2028.875021	-2028.933509
t-Bu-TS1'	-2028.595268	-2028.878745	-2028.909822
t-Bu-IN1'	-2028.620637	-2028.913265	-2028.940658
t-Bu-IN2'-Cation	-542.942028	-543.1693679	-543.2501869
t-Bu-IN2'-Anion	-1485.556704	-1485.591941	-1485.664039
$SiMe_3$-Allene	-795.21969	-795.4424618	-795.4553859
$SiMe_3$-TS1	-2280.01107	-2280.285738	-2280.317362
$SiMe_3$-IN1	-2280.004503	-2280.280946	-2280.341644
$SiMe_3$-TS2	-2279.997443	-2280.273837	-2280.331753
$SiMe_3$-TS1'	-2280.016505	-2280.284756	-2280.313484
$SiMe_3$-IN1'	-2280.04261	-2280.317708	-2280.342025
$SiMe_3$-IN2'-Cation	-794.357527	-794.5694272	-794.646712

Cartesian Coordinates

DDQ

C	-3.49778000	0.55625700	0.00026600
C	-1.99463700	0.58995200	0.00073300
C	-1.32044300	1.75742700	0.00023900
C	-2.04205900	3.07612600	-0.00093900
C	-3.53896400	3.03914100	-0.00157500
C	-4.21316800	1.87192300	-0.00086400
Cl	-4.30833800	4.56042100	-0.00334000
Cl	-5.91550400	1.77990600	-0.00139300
C	0.11126000	1.81822200	0.00078500
C	-1.33071000	-0.67986800	0.00179600
N	1.26650400	1.86493900	0.00126800
N	-0.79031100	-1.70200500	0.00267800
O	-1.42316400	4.10914800	-0.00132800
O	-4.08424100	-0.49584100	0.00074200

t-Bu-Allene

C	-1.66013000	-0.16443200	0.79746000
C	-2.75018600	-0.75351900	0.37965200
H	-2.90171700	-1.81143200	0.61184300
C	-4.00895500	-0.85328500	-1.75085100
H	-4.82689600	-0.42924600	-2.34547100
H	-3.08886200	-0.79749600	-2.34303300
H	-4.23409900	-1.91089200	-1.57041000
C	-3.52459700	1.37708100	-0.71235900
H	-3.40741500	1.94155000	0.21948500
H	-2.59068600	1.46818300	-1.27860200
H	-4.32863800	1.83930200	-1.29620900
C	-5.16335900	-0.18292600	0.37061000
H	-5.99339900	0.24852700	-0.20161300
H	-5.41334900	-1.22628000	0.59596300
H	-5.08008400	0.35902100	1.31892500
C	-0.56812800	0.45238400	1.19946900
C	-0.53861200	1.13148300	2.55133200
H	0.22228800	0.68296300	3.20051200
H	-0.30334500	2.19700500	2.44695000
H	-1.50794300	1.03710000	3.04442300
C	-3.85539900	-0.08830100	-0.42820100
C	0.64760900	0.50166600	0.34059300
C	1.83208600	1.08495400	0.80616700
C	0.63714800	-0.02845200	-0.95896700
C	2.97128200	1.13245700	0.00139100
H	1.87766500	1.50655500	1.80554000
C	1.77037300	0.01904900	-1.76040600
H	-0.27566600	-0.48213400	-1.33701200
C	2.94733600	0.60062200	-1.28362400
H	3.87952100	1.58749900	0.38662500
H	1.73641000	-0.39784300	-2.76314600
H	3.83388300	0.63716100	-1.90980400

t-Bu-TS1

C	-1.62888800	-0.46274200	1.28346600
C	-2.75304000	-0.85543400	0.71999900
H	-3.13698300	-1.83531500	1.00354000
C	-3.56773900	-0.99507700	-1.59360400
H	-4.17533800	-0.52389200	-2.37473700
H	-2.55739800	-1.14844800	-1.98885900
H	-3.99970300	-1.97787200	-1.37319800
C	-2.92232300	1.25006800	-0.68623500
H	-2.90587900	1.91919600	0.18116100
H	-1.89612800	1.14368900	-1.05575900
H	-3.51527300	1.73321200	-1.47042300
C	-4.96770700	0.08868000	0.18710700
H	-5.58472500	0.57619100	-0.57617500
H	-5.43248900	-0.87185500	0.43596200
H	-4.97438400	0.71393100	1.08635800
C	-0.72760500	0.56847700	1.52744800
C	-1.11817500	1.67879300	2.46698100
H	-0.72546400	1.49428100	3.47529400
H	-0.72242200	2.63816300	2.11710700
H	-2.20508600	1.75018100	2.54029500
C	-3.53674600	-0.10667200	-0.33852600
C	0.62222400	0.37424500	1.10656700
C	1.70563300	1.02812000	1.76124400
C	0.92807000	-0.60727300	0.12959500
C	3.00435100	0.63477600	1.52340100
H	1.49982700	1.77890200	2.51823700
C	2.24346100	-0.96370600	-0.14059300
H	0.11366200	-1.06407500	-0.42885000
C	3.27703000	-0.38846400	0.59340100
H	3.81929600	1.08391800	2.08260100
H	2.45817900	-1.72677700	-0.88396100
H	4.30162600	-0.71612700	0.43869700
C	2.68514800	-3.57110900	1.74689900
C	2.43804600	-2.52951900	2.76914800
C	1.19310000	-1.98084000	2.94668900
C	0.07366300	-2.34374600	2.11533700
C	0.28693900	-3.38767400	1.12268800
C	1.49648100	-3.98624100	0.96359700
Cl	-1.07146900	-3.81320000	0.15327500
Cl	1.77067500	-5.21383200	-0.20213700
C	0.95153300	-0.99978200	3.97133400
C	3.55490100	-2.11079000	3.56033500
N	0.75086300	-0.20616400	4.78881100
N	4.45508400	-1.74065000	4.18759100
O	-1.07202600	-1.80296300	2.31192600
O	3.79009000	-4.05089500	1.56651500

t-Bu-IN1

C	-1.32636000	-0.74332900	0.88189100
C	-2.28018600	0.05373500	0.30621500
H	-3.27092400	-0.40320600	0.33668300
C	0.03448800	-0.47984800	1.15730800
C	0.95296000	-1.64064800	1.27139500
H	0.79341300	-2.37925800	0.48273500
H	1.99876200	-1.33932600	1.33209700
H	0.69053300	-2.13244900	2.22373500
C	0.48046800	0.84744600	1.50386300
C	1.77248200	1.29223500	1.15277400
C	-0.36155600	1.70144300	2.24821000
C	2.17837300	2.57718300	1.47517500
H	2.42706500	0.64880900	0.57240400
C	0.06835700	2.97350500	2.60089400
C	1.32894200	3.41820700	2.20244600
H	3.15824600	2.92804300	1.16758100
H	-0.57271900	3.61241000	3.20011800
H	1.66075800	4.41609000	2.47331900
C	-5.40156800	-2.56638000	3.24794700
C	-4.18985600	-2.08263000	3.90360900
C	-2.99375000	-1.92565300	3.20466400
C	-2.89949400	-2.21013000	1.83790800
C	-4.04187900	-2.67678500	1.15041200
C	-5.23543300	-2.85583300	1.81042100
Cl	-3.87252200	-2.98650900	-0.55041200
Cl	-6.63632200	-3.41786000	0.99090700
C	-1.79159500	-1.43683100	3.82172100
C	-4.25607300	-1.75411100	5.29088500
N	-0.77705100	-1.02912900	4.20569600
N	-4.27362700	-1.46699400	6.41393700
O	-1.69500700	-2.06686400	1.19641600
O	-6.47270800	-2.71315600	3.83028600
C	-2.28806100	1.28132200	-0.56634500
C	-0.94319700	1.86930700	-0.99946800
H	-0.25147900	1.08994200	-1.33942900
H	-1.11993500	2.54622000	-1.84163500
H	-0.45897500	2.44941800	-0.21247800
C	-3.03044000	0.80377600	-1.84432300
H	-2.46713300	0.01773900	-2.35811300
H	-4.02622100	0.41401300	-1.61075200
H	-3.14427700	1.65132500	-2.52787200
C	-3.15324600	2.36095700	0.11483600
H	-2.65391500	2.76484800	1.00068600
H	-3.31941400	3.18164500	-0.59108300
H	-4.12967300	1.96594100	0.41423100
H	-1.31820200	1.32893600	2.60064800

t-Bu-TS2

C	-1.21346500	-0.67093500	1.49091000
C	-2.14919900	0.39897800	1.24064200
H	-2.90608700	0.52147500	2.01713200
C	0.12577600	-0.52571400	1.17946500
C	1.08000000	-1.67177600	1.24892400
H	0.63355400	-2.57438400	0.82436000
H	2.01876200	-1.44296000	0.73954500

H	1.31394300	-1.88687000	2.29928500
C	0.48100800	0.84385400	0.97367700
C	1.52388500	1.27428400	0.11644700
C	-0.33306400	1.81875400	1.62722400
C	1.65775300	2.61293700	-0.17359700
H	2.16424000	0.53971900	-0.36241400
C	-0.19558600	3.18401200	1.28593700
C	0.78049200	3.56974800	0.39257400
H	2.43165200	2.94227600	-0.86035300
H	-0.80658700	3.92637800	1.79052400
H	0.91566500	4.62089900	0.15625400
C	-5.70410700	-2.89581100	2.26354100
C	-5.11959400	-1.96965000	3.22498200
C	-3.76486600	-1.61705000	3.18347100
C	-2.92449400	-2.11416900	2.19295900
C	-3.42024000	-3.03374300	1.25117000
C	-4.74481400	-3.40608000	1.26685600
Cl	-2.31043400	-3.61954100	0.04601300
Cl	-5.38224200	-4.49537600	0.09996100
C	-3.18877700	-0.65862900	4.08831300
C	-5.97119300	-1.40200700	4.21975800
N	-2.64580100	0.16437000	4.69708900
N	-6.63713800	-0.91249400	5.03295200
O	-1.57228600	-1.76671800	2.18191800
O	-6.89034000	-3.21919000	2.26355300
H	-0.79355200	1.58225400	2.58489200
C	-2.64061700	0.92108600	-0.08423100
C	-1.63263300	0.95720200	-1.22718300
H	-0.89438700	1.75213200	-1.08587200
H	-1.10850900	0.00210000	-1.34032300
H	-2.16694200	1.15951800	-2.16075500
C	-3.32171500	2.28263300	0.09663200
H	-3.83657200	2.55693200	-0.82903100
H	-4.06591300	2.25435400	0.90002700
H	-2.59254000	3.06591600	0.32105000
C	-3.74918700	-0.12591000	-0.43261500
H	-3.31201300	-1.09801900	-0.67526500
H	-4.47698100	-0.25806100	0.37520200
H	-4.28137800	0.24801400	-1.31397000

t-Bu-TS1'

C	-1.92851700	0.20711400	0.72115600
C	-2.99615200	-0.22045900	0.22539500
H	-2.89629400	-1.53145300	0.72824700
C	-4.18562800	-1.04079400	-1.76812500
H	-5.08277200	-0.92188300	-2.38546500
H	-3.30510300	-0.86461200	-2.39508500
H	-4.14835100	-2.07381100	-1.40675000
C	-4.27218000	1.39514100	-1.12435400
H	-4.29309800	2.11175900	-0.29750300
H	-3.39797300	1.60850100	-1.74777200
H	-5.17401200	1.53736300	-1.73069700
C	-5.45631300	-0.32849000	0.28486400
H	-6.36933900	-0.21141000	-0.30912100
H	-5.43144700	-1.34922700	0.68041300
H	-5.49987700	0.36592300	1.12960900
C	-0.77544600	0.40817300	1.43695100
C	-0.88816200	0.98929600	2.82393700
H	-0.34072200	0.39173200	3.56257800
H	-0.44997400	1.99470900	2.83771600
H	-1.92959600	1.04897100	3.14128500
C	-4.23047100	-0.04728200	-0.59763100
C	0.52808100	0.20925500	0.83529900
C	1.68974600	0.22260600	1.63258700
C	0.66435800	-0.04609300	-0.54972600
C	2.94092400	-0.02211200	1.06905900
H	1.62236400	0.42004400	2.69816700
C	1.90969500	-0.26539200	-1.10622800
H	-0.22505900	-0.06026300	-1.17498400
C	3.05471200	-0.26362100	-0.29540800
H	3.82042300	-0.03949800	1.70425600
H	1.99888700	-0.45944000	-2.17090400
H	4.02904400	-0.45821100	-0.73354600
C	1.47387400	-2.82925000	2.14361100
C	0.47068500	-2.36198200	3.12269500
C	-0.85837700	-2.25916700	2.79001100
C	-1.33503200	-2.56191000	1.46496500
C	-0.36601200	-2.95138900	0.46574200
C	0.95302900	-3.08984000	0.77232000
Cl	-0.97188000	-3.20672200	-1.12490300
Cl	2.11203400	-3.61410000	-0.36723500
C	-1.84714200	-1.85020600	3.74973400
C	0.94479300	-2.02092600	4.42847700
N	-2.64172800	-1.49442000	4.51137800
N	1.32846500	-1.70452900	5.47442500
O	-2.59609600	-2.55840500	1.20317100
O	2.64361600	-2.99423800	2.43345000

t-Bu-IN1'

C	-2.02137600	-0.37881600	0.71646000
C	-2.96148300	-0.17141300	-0.01857500
H	-2.88769900	-2.18688400	1.86451900
C	-4.43023000	-1.12022200	-1.75597100
H	-5.24551500	-0.87833800	-2.44709500
H	-3.57488800	-1.47918000	-2.33570100
H	-4.75722500	-1.93516500	-1.10333000
C	-3.60254700	1.25132000	-1.89801500
H	-3.33504500	2.15492500	-1.34164800
H	-2.73190800	0.93200300	-2.47933800
H	-4.41241600	1.49667400	-2.59398300
C	-5.28584500	0.60992500	-0.14010900
H	-6.10503000	0.85453400	-0.82530200
H	-5.63226000	-0.17169300	0.54356800
H	-5.04496500	1.50209700	0.44627600
C	-0.93616800	-0.60116000	1.68820400
C	-1.31771600	0.17934300	2.96317700
H	-0.56033700	0.10221900	3.74316300
H	-1.43606500	1.23229700	2.69521000
H	-2.26135900	-0.19271000	3.36765700
C	-4.06692500	0.13452400	-0.94724100
C	0.41675400	-0.16570300	1.12373400
C	1.47145700	0.20220900	1.96903500
C	0.65334300	-0.18903800	-0.25712200
C	2.72714600	0.51348100	1.45219200
H	1.33470000	0.22966700	3.04556600
C	1.90799700	0.11768500	-0.77588100
H	-0.15409000	-0.46160700	-0.93300200
C	2.95260400	0.46382300	0.07914100
H	3.53280900	0.77853200	2.13006300
H	2.06974000	0.07395800	-1.84867900
H	3.93614600	0.68811100	-0.32218900
C	1.79885200	-2.90804200	1.39764300
C	0.70228700	-3.20021100	0.41697400
C	-0.58053100	-2.95390100	0.73864100
C	-0.95555200	-2.20807500	2.01262200
C	0.05337500	-2.51429200	3.10246900
C	1.34604400	-2.73717000	2.80905800
Cl	-0.50041300	-2.44249100	4.72503900
Cl	2.58010300	-2.86211100	3.99358700
C	-1.64530700	-3.31662600	-0.15020400
C	1.09481300	-3.73955500	-0.85230400
N	-2.51326600	-3.65130000	-0.83896400
N	1.40954900	-4.15817200	-1.88353400
O	-2.22239800	-2.58801400	2.45427600
O	2.95830100	-2.90368500	1.06408300

tBu-IN2'-Cation

C	-2.25602700	0.06854700	0.83607300
C	-3.17073800	0.16987300	0.02935700
C	-1.26783200	-0.06891800	1.80410500
C	-1.71146300	-0.48199800	3.17389400
H	-1.21602300	-1.41642800	3.46211100
H	-1.42286700	0.28185200	3.90564900
H	-2.79017200	-0.62341300	3.21269600
C	0.10353200	0.17510700	1.49370600
C	1.10537300	0.02191700	2.48694100
C	0.48132600	0.57328600	0.18495600
C	2.43112800	0.25754400	2.17723200
H	0.83774400	-0.28092100	3.49391200
C	1.80936100	0.80806700	-0.11556500
H	-0.28327300	0.69283100	-0.57676300
C	2.78224300	0.65029400	0.87902800
H	3.19733800	0.13910900	2.93569300
H	2.09800300	1.11277500	-1.11571300
H	3.82577600	0.83584100	0.64121500
C	-3.71804800	0.79054500	-2.28279400
H	-2.97815200	0.09804100	-2.69489900
H	-4.54700300	0.86769100	-2.99286300
H	-3.26180900	1.77958500	-2.18060900
C	-5.30320700	1.27250000	-0.36396800

H	-5.70333600	0.91929600	0.59012200
H	-4.87392100	2.26842000	-0.22444000
H	-6.12723700	1.34928900	-1.08015700
C	-4.89523200	-1.11417200	-1.09596900
H	-4.17285000	-1.83621100	-1.48623400
H	-5.29207800	-1.48291800	-0.14650500
H	-5.72044100	-1.03113000	-1.81004700
C	-4.26004700	0.28645500	-0.93490800

IN2'-Anion

H	-2.70512900	-2.94220800	0.91096100
C	2.00412900	-2.78371300	0.62032700
C	0.94679600	-2.62700800	-0.34641100
C	-0.42172400	-2.72454700	0.00877500
C	-0.83078600	-2.97614900	1.31124400
C	0.16673600	-3.13828600	2.29610400
C	1.50538200	-3.04812000	1.97631300
Cl	-0.36612800	-3.45357000	3.92203200
Cl	2.71819100	-3.24760300	3.19041600
C	-1.47033100	-2.56958700	-0.95624300
C	1.30491000	-2.36460600	-1.70022400
N	-2.40295600	-2.46594100	-1.63956200
N	1.56753600	-2.14777300	-2.81087900
O	-2.14084500	-3.07503800	1.68966300
O	3.21568000	-2.70766000	0.35850200

SiMe$_3$-Allene

C	-1.47971500	-0.43151200	1.05407900
C	-2.56393400	-1.03905300	0.64852700
H	-2.70730800	-2.09417300	0.89613000
Si	-3.83098100	-0.10429100	-0.39186300
C	-3.96938400	-0.94913700	-2.06992600
H	-4.71633000	-0.45073500	-2.69865000
H	-3.01169200	-0.92559700	-2.60161000
H	-4.26867400	-1.99777500	-1.96355500
C	-3.21927200	1.66033800	-0.58821300
H	-3.13418000	2.15743000	0.38467600
H	-2.22847200	1.68120400	-1.05657400
H	-3.90316500	2.24737300	-1.21126700
C	-5.50219700	-0.14778900	0.47413100
H	-6.26190000	0.37986600	-0.11395600
H	-5.84768000	-1.17778800	0.61746800
H	-5.44704600	0.32735800	1.45937400
C	-0.41102300	0.25587400	1.40552700
C	-0.38990500	0.99095700	2.72776100
H	0.40377900	0.60811700	3.37983800
H	-0.21038100	2.06160000	2.57465800
H	-1.34375900	0.87138700	3.24539200
C	0.77595400	0.32662600	0.51245700
C	1.93680800	0.99795700	0.91590900
C	0.76297300	-0.26439100	-0.76129200
C	3.04848900	1.07446300	0.07595900
H	1.98376400	1.46771400	1.89357200
C	1.86954800	-0.18836300	-1.59685100
H	-0.12888300	-0.79108100	-1.09232300
C	3.02218200	0.48301200	-1.18268900
H	3.93738400	1.60083200	0.41263400
H	1.83357900	-0.65439400	-2.57772500
H	3.88760100	0.54198700	-1.83607000

SiMe$_3$-TS1

C	-1.61257600	-0.64266800	1.41460600
C	-2.74043700	-1.03664600	0.86728100
H	-3.10004300	-2.03052400	1.13708900
C	-3.69060100	-1.04892400	-2.00191800
H	-4.23088000	-0.53250900	-2.80327400
H	-2.67484300	-1.25444400	-2.35758400
H	-4.18588500	-2.01082900	-1.82953400
C	-2.73461100	1.59973600	-0.72622500
H	-2.72286400	2.23311300	0.16757000
H	-1.69618000	1.42158800	-1.02813700
H	-3.22262900	2.16654700	-1.52758100
C	-5.39893500	0.30890400	0.19029200
H	-5.98099100	0.86203500	-0.55548700
H	-5.92543400	-0.62923800	0.39627300
H	-5.38793900	0.89772700	1.11374100
C	-0.73862200	0.42642200	1.63570400
C	-1.15707400	1.50894400	2.59442900
H	-0.78563500	1.30160600	3.60673300
H	-0.76159000	2.47947500	2.27781300
H	-2.24663300	1.57058000	2.64371900
C	0.59938200	0.29250900	1.17293900
C	1.67566300	0.99089100	1.79527100
C	0.91516900	-0.67703200	0.18551100
C	2.98034900	0.64955600	1.51816900
H	1.46257400	1.73116600	2.56056400
C	2.23514800	-0.97761100	-0.12680200
H	0.10365400	-1.16619100	-0.34930400
C	3.26571900	-0.36219800	0.57813200
H	3.79331000	1.12903400	2.05438100
H	2.45860700	-1.73081300	-0.87761600
H	4.29765600	-0.64798200	0.39240900
C	2.83978700	-3.56785200	1.72156700
C	2.59012800	-2.54077800	2.75663800
C	1.33134100	-2.04023100	2.98259700
C	0.20031500	-2.43503900	2.18523100
C	0.41580800	-3.46712700	1.18248200
C	1.64009900	-4.02202000	0.97898400
Cl	-0.95937500	-3.93840700	0.25835800
Cl	1.91532100	-5.23591000	-0.20097200
C	1.08945500	-1.07214700	4.01938800
C	3.71709300	-2.08152200	3.50987900
N	0.88565900	-0.28750600	4.84478500
N	4.62268400	-1.67483800	4.10616000
O	-0.95944400	-1.93488300	2.42506900
O	3.95490700	-4.00618400	1.49942300
Si	-3.65597200	-0.01137000	-0.43373700

SiMe$_3$-IN1

C	-1.12127300	-0.65272000	2.02865100
C	-2.28200300	0.05337000	1.77294000
H	-3.07842800	-0.18435200	2.48500000
C	0.15391400	-0.39964000	1.46583600
C	1.21065600	-1.42923400	1.65301900
H	0.82416600	-2.42466500	1.40956400
H	2.11784600	-1.20319500	1.09351300
H	1.47003900	-1.46441300	2.72132700
C	0.44891200	0.86831500	0.84381200
C	1.34227600	0.93377400	-0.25109100
C	-0.11037600	2.06960800	1.33664200
C	1.60689600	2.14296600	-0.86902500
H	1.77309600	0.01999600	-0.64902200
C	0.18036900	3.28365700	0.72268000
C	1.02654500	3.32172300	-0.38290100
H	2.26420800	2.17623400	-1.73196900
H	-0.23499500	4.20291100	1.12410300
H	1.25396800	4.27121800	-0.85838600
C	-4.91336200	-3.76852700	3.01378200
C	-4.42485700	-2.91186900	4.09065300
C	-3.19159200	-2.25690400	4.01580200
C	-2.37308600	-2.39370800	2.89725400
C	-2.78517800	-3.21939500	1.82921600
C	-3.99851600	-3.86555600	1.86419300
Cl	-1.72869400	-3.35075700	0.44989700
Cl	-4.53984100	-4.82898000	0.54654000
C	-2.74855600	-1.34438400	5.03612800
C	-5.26471500	-2.73014600	5.23019600
N	-2.36295600	-0.56046700	5.79572100
N	-5.93245800	-2.55995200	6.16239200
O	-1.14699700	-1.73673800	2.85787200
O	-5.99752000	-4.34641300	3.04688300
Si	-3.04382900	0.85610900	0.22023300
C	-4.46648700	-0.35127600	-0.02539000
H	-4.09827500	-1.36236200	-0.23703300
H	-5.11663100	-0.41056700	0.85432000
H	-5.08087500	-0.03515100	-0.87676500
C	-1.94384600	0.84126100	-1.29713800
H	-1.21961900	1.66066700	-1.32190300
H	-1.40568200	-0.10917500	-1.38844900
H	-2.58689400	0.93583000	-2.18055900
C	-3.66230200	2.57104800	0.65919800
H	-2.83886300	3.27717200	0.80672300
H	-4.29207100	2.95544100	-0.15098800
H	-4.26843900	2.55379100	1.57092600
H	-0.70365700	2.04978700	2.24502600

SiMe$_3$-TS2

C	-0.99616900	-0.65913500	1.87046100
C	-2.03722300	0.28699000	1.70436100
H	-2.74109900	0.30615100	2.54432800

C	0.27779700	-0.44325000	1.33217000
C	1.29451200	-1.53333300	1.30718100
H	0.86836800	-2.44935900	0.88753200
H	2.19047000	-1.24378200	0.75575500
H	1.59186600	-1.76763200	2.33745000
C	0.49736100	0.90694700	0.94885700
C	1.38684800	1.28909900	-0.09203200
C	-0.28717700	1.91392600	1.59348500
C	1.38564400	2.58400600	-0.55083700
H	2.00479300	0.53652800	-0.57222700
C	-0.29542500	3.22916100	1.08145300
C	0.52464900	3.55335700	0.02217400
H	2.03299500	2.86726500	-1.37496900
H	-0.88599000	3.99315700	1.57730300
H	0.55307900	4.57393500	-0.34805600
C	-5.16556100	-3.22755000	3.02495700
C	-4.54270400	-2.34200900	4.00268800
C	-3.23466000	-1.87072500	3.84753600
C	-2.47920400	-2.21400600	2.73057700
C	-3.02050200	-3.06888700	1.75256900
C	-4.30470800	-3.54657500	1.87248200
Cl	-2.02901800	-3.42492000	0.36621500
Cl	-5.01381500	-4.52524900	0.64886900
C	-2.63861400	-0.93263800	4.76096500
C	-5.31715300	-1.93887800	5.13210000
N	-2.10937200	-0.11783800	5.39163500
N	-5.92575900	-1.58843200	6.05449400
O	-1.15981300	-1.76820000	2.61047900
O	-6.31361300	-3.65462500	3.12912900
Si	-2.91715600	0.85526300	0.09715100
C	-4.30183200	-0.41021000	-0.00384800
H	-3.93552700	-1.38671900	-0.33712900
H	-4.81417900	-0.55410600	0.95486100
H	-5.04807300	-0.06445000	-0.72992700
C	-1.79519200	0.75945200	-1.39671000
H	-1.08286400	1.58854000	-1.44235100
H	-1.23947300	-0.18497000	-1.42031500
H	-2.41243500	0.79794600	-2.30193900
C	-3.63331300	2.56770300	0.36930800
H	-2.88807600	3.35912300	0.25154800
H	-4.42495500	2.74486200	-0.36752200
H	-4.08682600	2.66071400	1.36226200
H	-0.61647400	1.76316900	2.61862300

SiMe$_3$-TS1'

C	-2.00084300	0.12861500	0.80365800
C	-3.02705500	-0.27810800	0.20499100
H	-2.98126500	-1.62178700	0.57391500
C	-0.94937200	0.37973000	1.65043900
C	-1.29453100	0.79418400	3.06189200
H	-0.80781400	0.14645300	3.80011000
H	-0.95152500	1.81913300	3.24709100
H	-2.37050500	0.74146900	3.23045600
C	0.42690400	0.33035500	1.22879300
C	1.46446600	0.45488300	2.18391200
C	0.78648000	0.11740400	-0.12454200
C	2.79336700	0.35500400	1.80617200
H	1.22595800	0.61406300	3.23017100
C	2.11852600	0.05388000	-0.50016000
H	0.00132300	0.01976800	-0.87201500
C	3.12569500	0.14322200	0.46615100
H	3.57235800	0.41172000	2.55959700
H	2.37692500	-0.10690200	-1.54204300
H	4.16656500	0.04470700	0.17419300
C	1.52536100	-2.69224300	1.37956800
C	0.64143700	-2.52360100	2.54628100
C	-0.72876500	-2.52448100	2.41165000
C	-1.36314200	-2.68560200	1.12826700
C	-0.52051800	-2.88603400	-0.02801600
C	0.83593900	-2.91379000	0.08074200
Cl	-1.31850200	-3.04578300	-1.54481100
Cl	1.85653900	-3.21822400	-1.25599600
C	-1.59616500	-2.37061300	3.54628300
C	1.26778700	-2.33836400	3.81973800
N	-2.28910500	-2.22288700	4.46090200
N	1.76687200	-2.16131700	4.84970800
O	-2.64130400	-2.67990900	1.01008200
O	2.74217400	-2.65194400	1.45773400
Si	-4.52890300	0.04992400	-0.87538600
C	-4.40035600	1.80992600	-1.51465100
H	-3.49296800	1.94602100	-2.11214800
H	-5.26203600	2.05229200	-2.14708100
H	-4.37454800	2.52710000	-0.68784400
C	-6.03069400	-0.19252900	0.21832100
H	-6.05722400	-1.20764400	0.62875700
H	-6.02694600	0.51038300	1.05765700
H	-6.95329400	-0.03521400	-0.35168200
C	-4.48793600	-1.20152500	-2.26846100
H	-3.58627000	-1.08267000	-2.87876600
H	-4.49697900	-2.22428100	-1.87588300
H	-5.35925900	-1.08103800	-2.92207000

SiMe$_3$-IN1'

C	-2.11508900	-0.44079100	0.95485000
C	-3.05837300	-0.14929000	0.24342300
H	-2.78276100	-2.63442500	1.22672800
C	-1.01748200	-0.90978900	1.81352200
C	-1.49117800	-0.77175500	3.27442900
H	-0.73213400	-1.08644500	3.99039100
H	-1.72889300	0.27914800	3.45811100
H	-2.38774900	-1.37226000	3.44309100
C	0.27683100	-0.14579400	1.53906800
C	1.28863600	-0.06447100	2.50466200
C	0.51186000	0.43090200	0.28376100
C	2.50407600	0.55159400	2.21574300
H	1.15144000	-0.50221600	3.48876900
C	1.72707600	1.04393700	-0.00830400
H	-0.26362300	0.39047100	-0.47814500
C	2.73158100	1.09929300	0.95575300
H	3.27869000	0.58726300	2.97585200
H	1.88931100	1.46827700	-0.99447400
H	3.68572100	1.56352400	0.72623200
C	1.94780900	-2.60265500	0.67675500
C	0.87626600	-2.56005900	-0.37187900
C	-0.42190900	-2.60321400	-0.02100300
C	-0.85950300	-2.50279500	1.43539100
C	0.18947500	-3.12939000	2.33232300
C	1.49484900	-3.08132100	2.01538700
Cl	-0.35009200	-3.78928200	3.82165600
Cl	2.74792200	-3.56719800	3.08025000
C	-1.44977600	-2.66520800	-1.02024000
C	1.30736000	-2.47706600	-1.73695300
N	-2.28411700	-2.75308400	-1.81773100
N	1.64910900	-2.39412000	-2.83876900
O	-2.07096000	-3.16219300	1.63499400
O	3.09778700	-2.34979800	0.41411100
Si	-4.38684700	0.26187700	-0.99576100
C	-3.51868700	0.64046300	-2.61358600
H	-2.95896000	-0.23326200	-2.96324900
H	-4.24598500	0.90989400	-3.38798500
H	-2.81979700	1.47619300	-2.50125000
C	-5.33058800	1.75220700	-0.35514800
H	-5.80258900	1.53831500	0.60936100
H	-4.66821600	2.61420400	-0.22454300
H	-6.11915000	2.03613700	-1.06131300
C	-5.50020200	-1.23937100	-1.14438500
H	-4.92944800	-2.11187800	-1.47896200
H	-5.97623800	-1.47905700	-0.18747100
H	-6.29392600	-1.05456400	-1.87718200

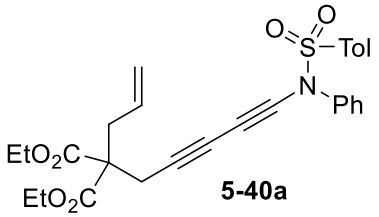
SiMe$_3$-IN2'-Cation

C	-2.10786800	0.04137700	0.94733000
C	-3.03122700	0.14178000	0.14303400
C	-1.11162600	-0.09571500	1.91168800
C	-1.54947900	-0.52545900	3.27795700
H	-1.04379800	-1.45711900	3.55726100
H	-1.26840900	0.23541300	4.01581200
H	-2.62663300	-0.67833800	3.31601700
C	0.25353100	0.16439100	1.59715900
C	1.26215800	0.01524700	2.58537900
C	0.62036000	0.57508800	0.28822500
C	2.58313700	0.26714500	2.27086000
H	1.00187100	-0.29682900	3.59151100
C	1.94433500	0.82565500	-0.01667800
H	-0.14970800	0.69082400	-0.46853600
C	2.92318000	0.67191500	0.97280400
H	3.35464500	0.15237700	3.02450200
H	2.22551300	1.13946300	-1.01612200
H	3.96357800	0.87009700	0.73130100
Si	-4.47275600	0.29415000	-1.08445900

C	-3.73467700	0.86800400	-2.70189800
H	-3.00328800	0.15158000	-3.08886400
H	-4.52472100	0.97307300	-3.45384500
H	-3.24614200	1.84205200	-2.59802200
C	-5.62538500	1.54893800	-0.31348900
H	-5.99852300	1.20928300	0.65730100
H	-5.14001300	2.52021500	-0.17896000
H	-6.48939400	1.69704300	-0.97145000
C	-5.20457800	-1.42447800	-1.17583900
H	-4.48236400	-2.15364800	-1.55520400
H	-5.56133700	-1.76435700	-0.19900100
H	-6.06031800	-1.41641200	-1.86051700

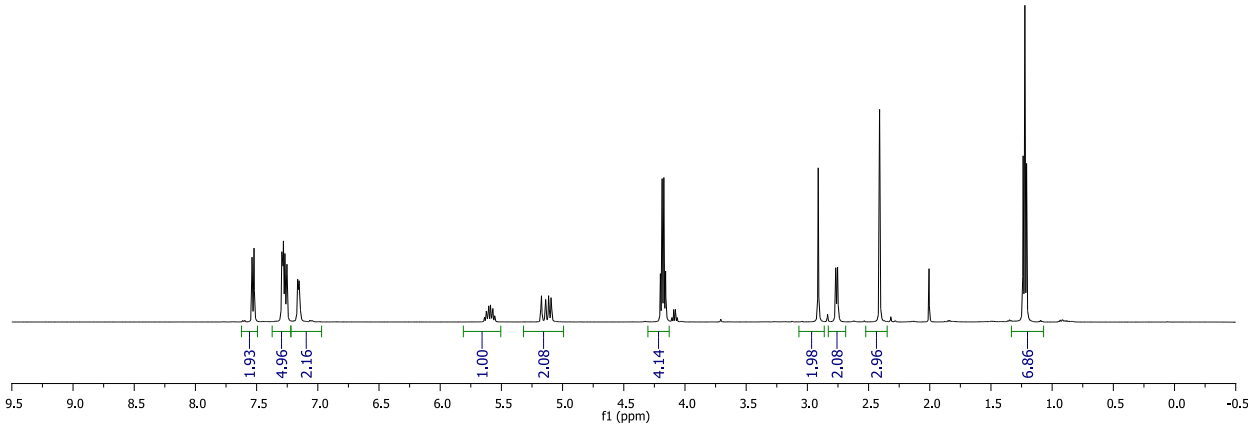
Appendix V

Selected NMR Spectra for Chapter 5

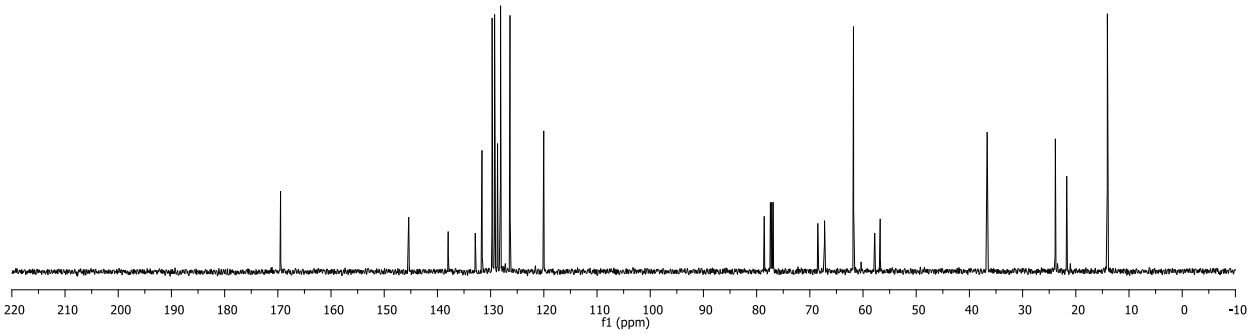

O
O
S
Tol
N
Ph
EtO2C
EtO2C

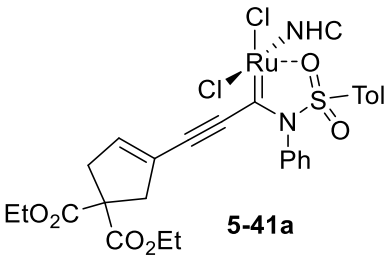
5-40a

7.54
7.53
7.28
7.16
7.16
7.16
7.15
7.15
5.60
5.59
5.58
5.57
5.57
5.17
5.14
5.11
5.09
4.19
4.17
2.91
2.77
2.75
2.41
1.24
1.22
1.21

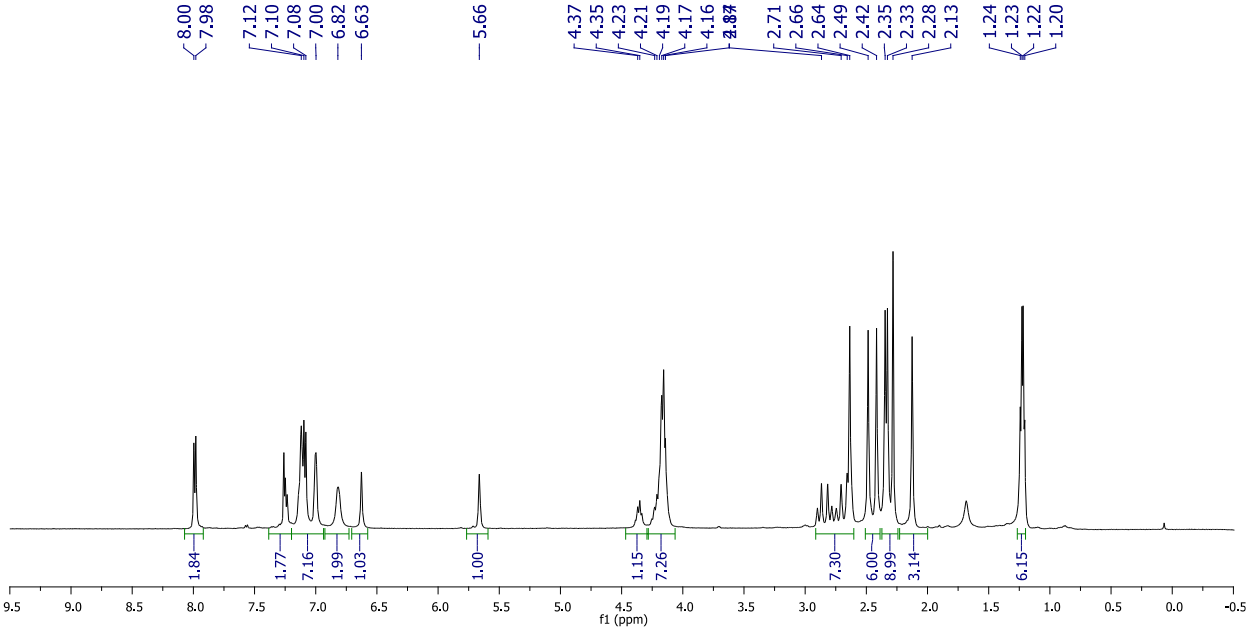

1.93
4.96
2.16
1.00
2.08
4.14
1.98
2.08
2.96
6.86
f1 (ppm)

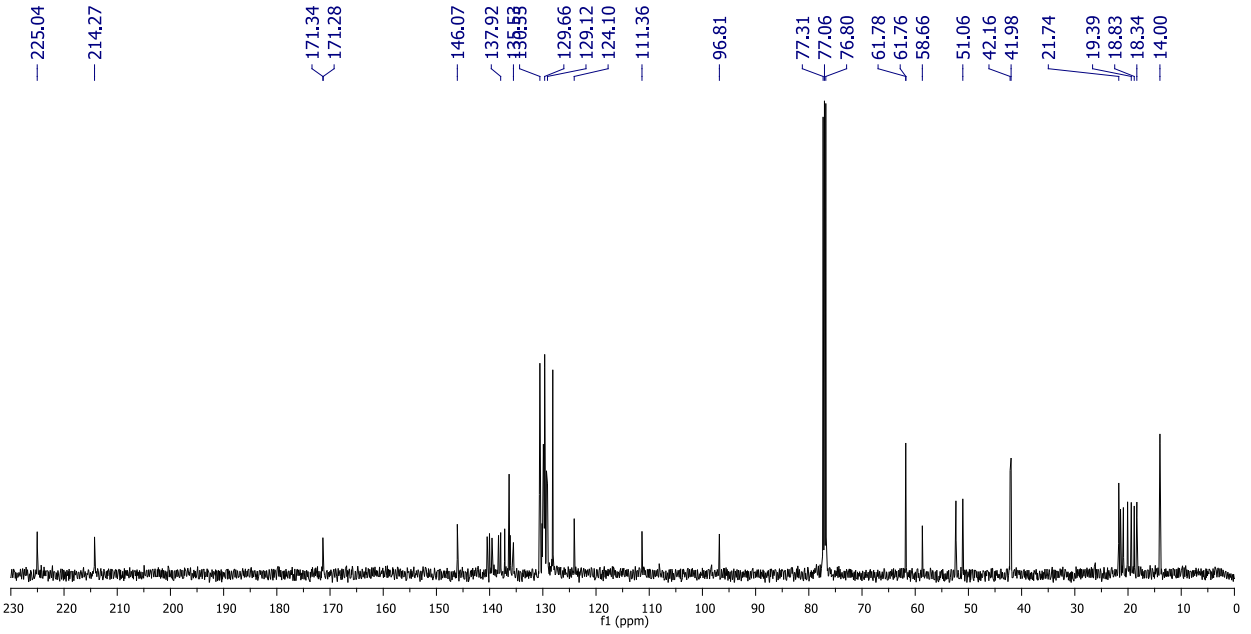
169.49
145.40
137.98
129.26
126.36
120.02
78.57
77.41
77.15
76.90
68.50
67.23
61.79
57.80
56.77
36.67
23.84
21.71
14.07

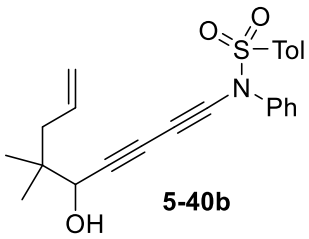

f1 (ppm)


Cl
NHC
Ru
O
Cl
S
Tol
O
N
Ph
EtO2C
CO2Et

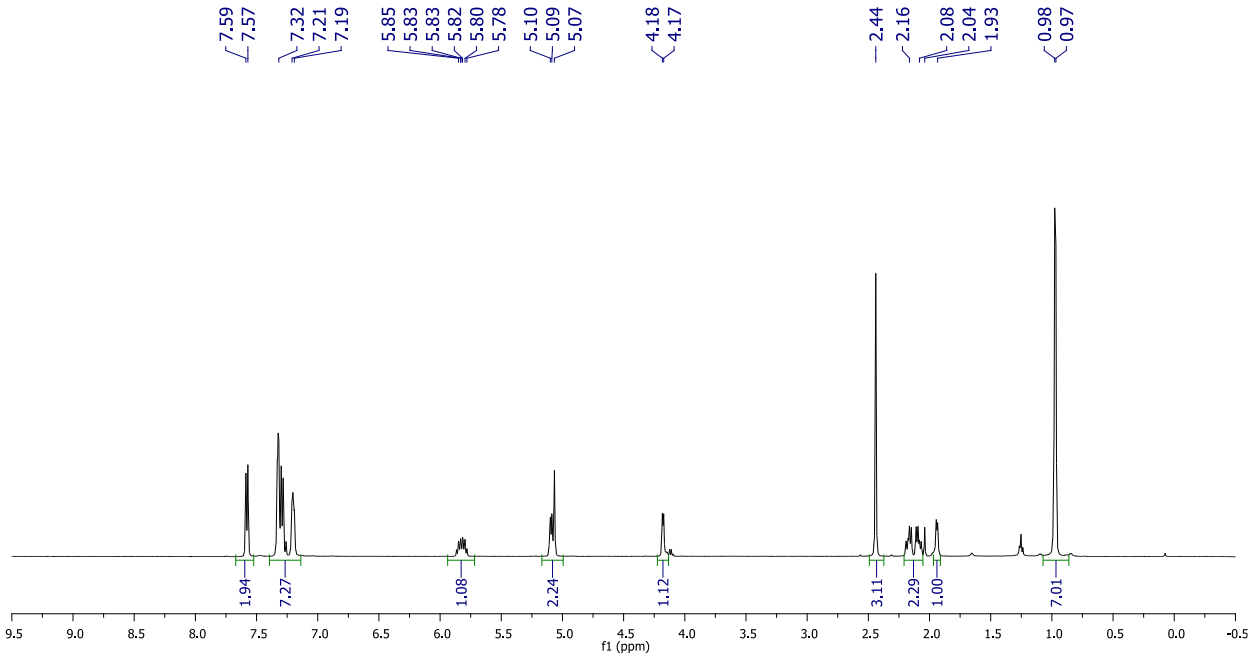
5-41a

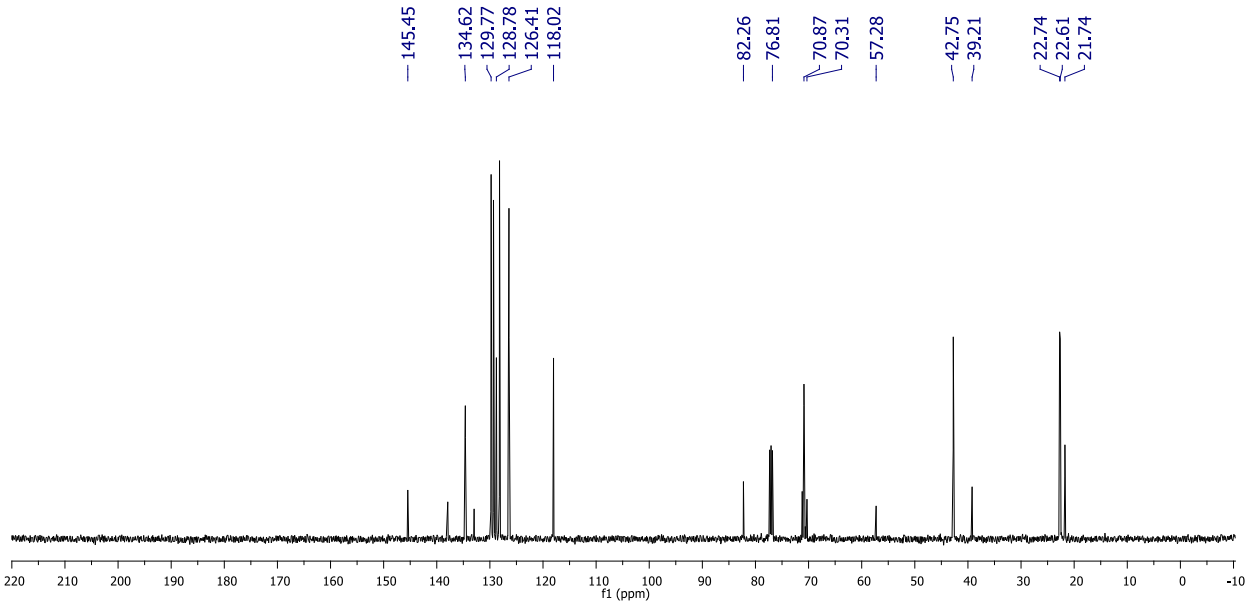

8.00
7.98
7.12
7.10
7.08
7.00
6.82
6.63
5.66
4.37
4.35
4.23
4.21
4.19
4.17
4.16
2.71
2.66
2.64
2.49
2.42
2.35
2.33
2.28
2.13
1.24
1.23
1.22
1.20
1.84
1.77
7.16
1.99
1.03
1.00
1.15
7.26
7.30
6.00
8.99
3.14
6.15
f1 (ppm)

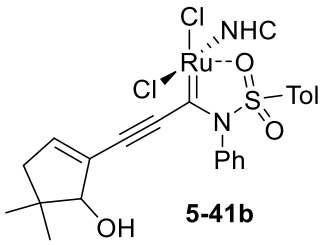

225.04
214.27
171.34
171.28
146.07
137.92
129.66
129.12
124.10
111.36
96.81
77.31
77.06
76.80
61.78
61.76
58.66
51.06
42.16
41.98
21.74
19.39
18.83
18.34
14.00
f1 (ppm)


O
O
S
Tol
N
Ph
OH

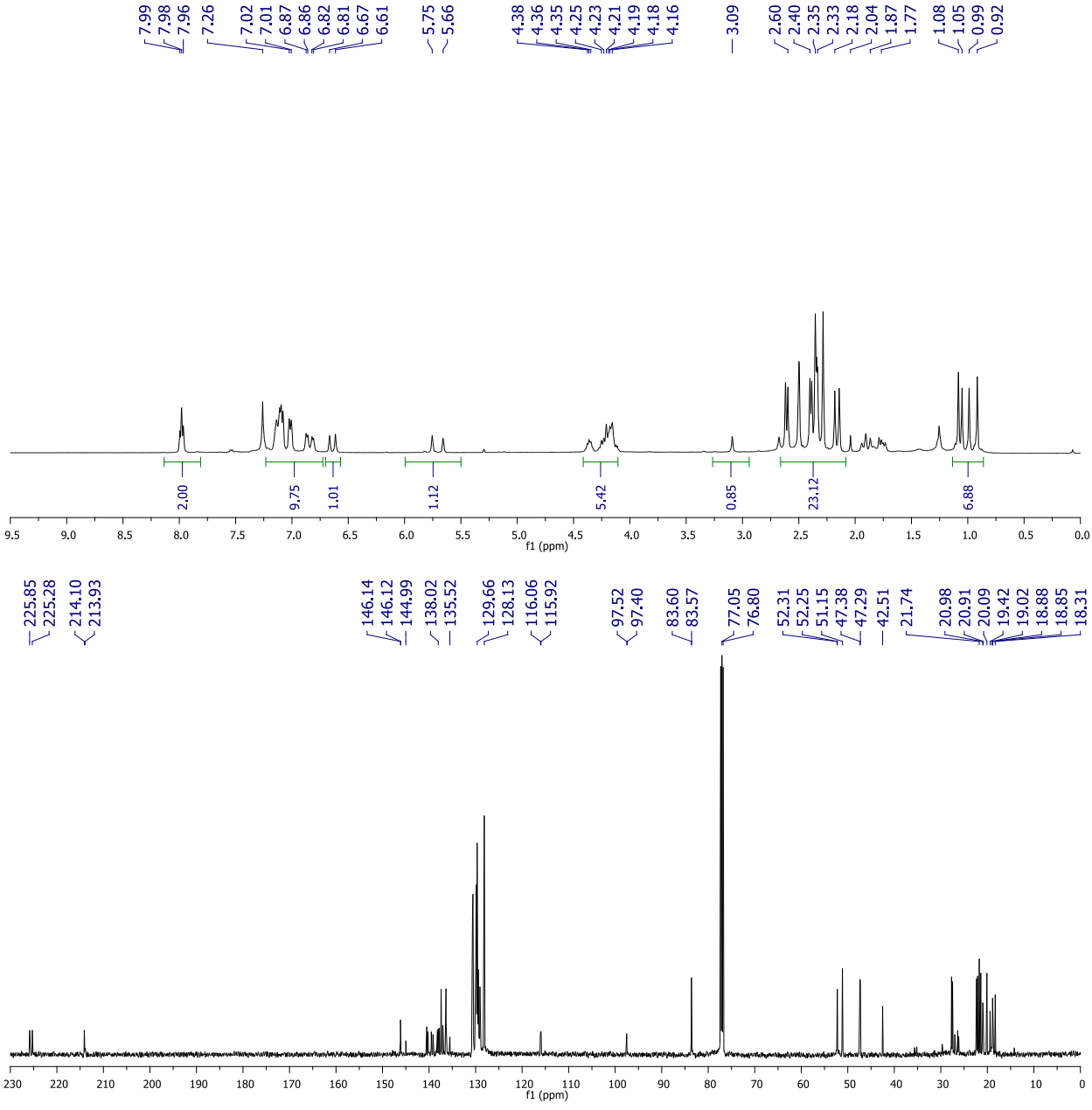
5-40b

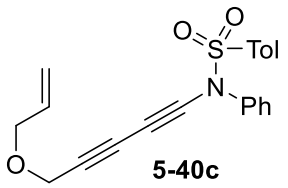

7.59
7.57
7.32
7.21
7.19
5.85
5.83
5.83
5.82
5.80
5.78
5.10
5.09
5.07
4.18
4.17
2.44
2.16
2.08
2.04
1.93
0.98
0.97
1.94
7.27
1.08
2.24
1.12
3.11
2.29
1.00
7.01
f1 (ppm)


145.45
134.62
129.77
128.78
126.41
118.02
82.26
76.81
70.87
70.31
57.28
42.75
39.21
22.74
22.61
21.74
f1 (ppm)

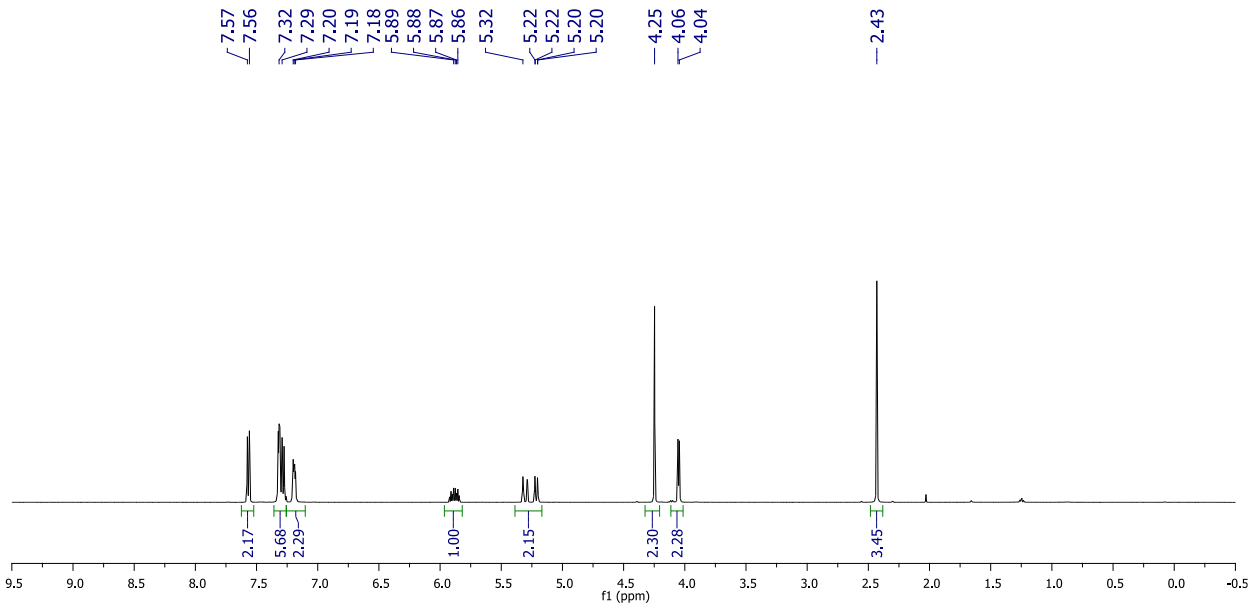

Cl
NHC
Ru
O
Cl
S
Tol
N
O
Ph
OH

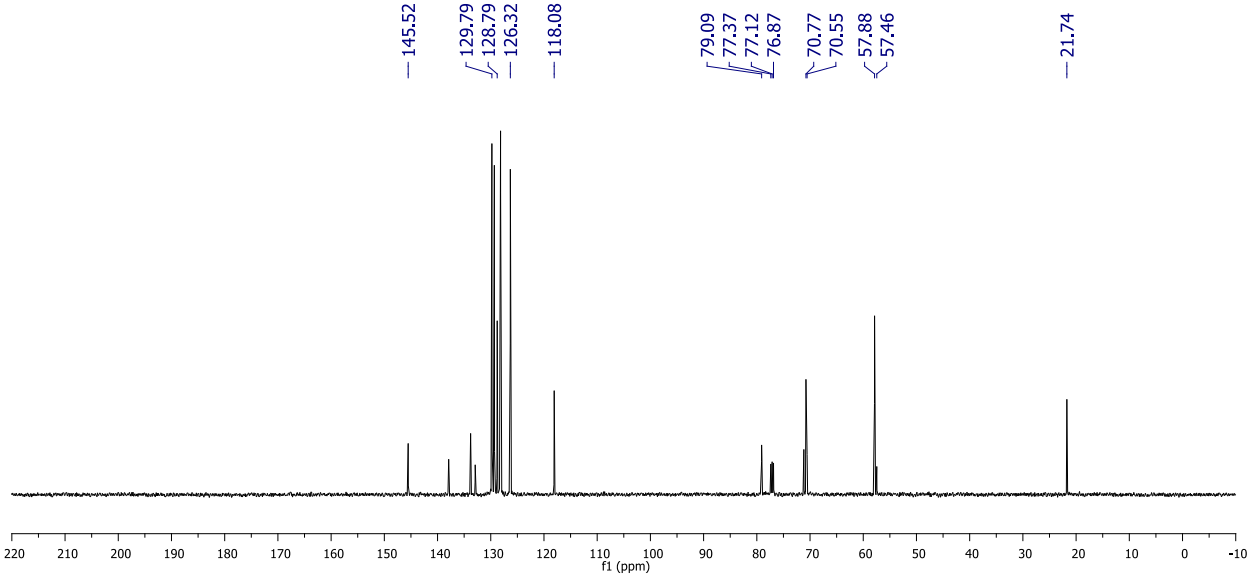
5-41b

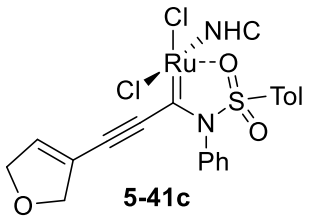

7.99
7.98
7.96
7.26
7.02
7.01
6.87
6.86
6.82
6.81
6.67
6.61
5.75
5.66
4.38
4.36
4.35
4.25
4.23
4.21
4.19
4.18
4.16
3.09
2.60
2.40
2.35
2.33
2.18
2.04
1.87
1.77
1.08
1.05
0.99
0.92
2.00
9.75
1.01
1.12
5.42
0.85
23.12
6.88
f1 (ppm)
225.85
225.28
214.10
213.93
146.14
146.12
144.99
138.02
135.52
129.66
128.13
116.06
115.92
97.52
97.40
83.60
83.57
77.05
76.80
52.31
52.25
51.15
47.38
47.29
42.51
21.74
20.98
20.91
20.09
19.42
19.02
18.88
18.85
18.31
f1 (ppm)


O
O
S
Tol
N
Ph
O

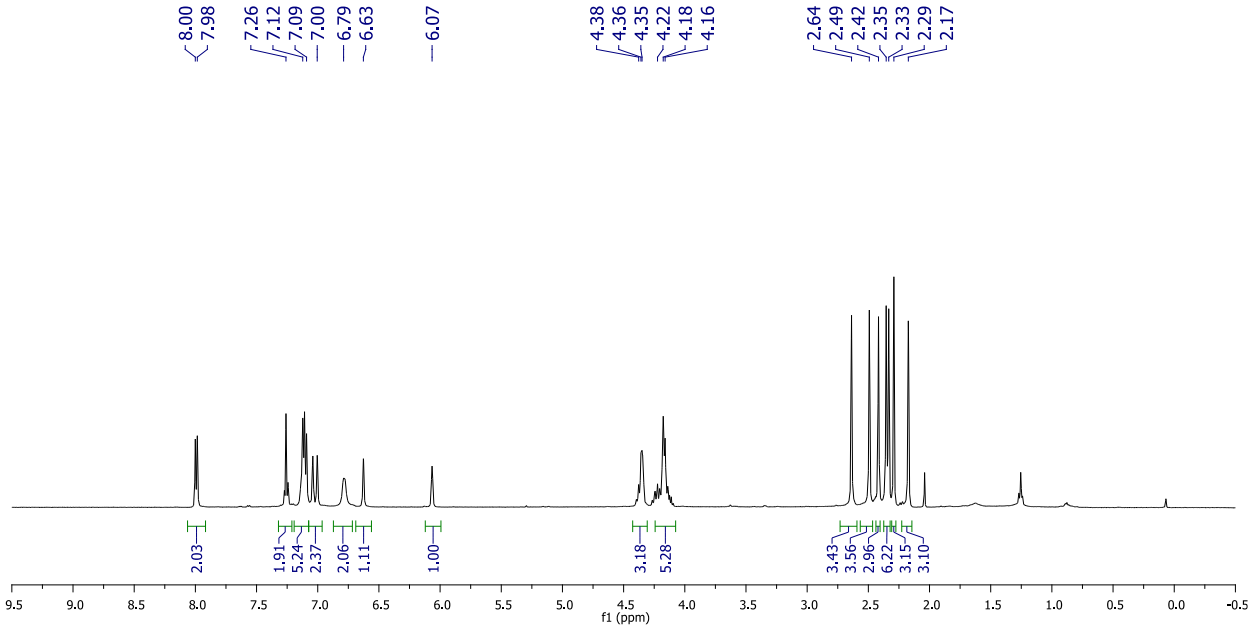
5-40c

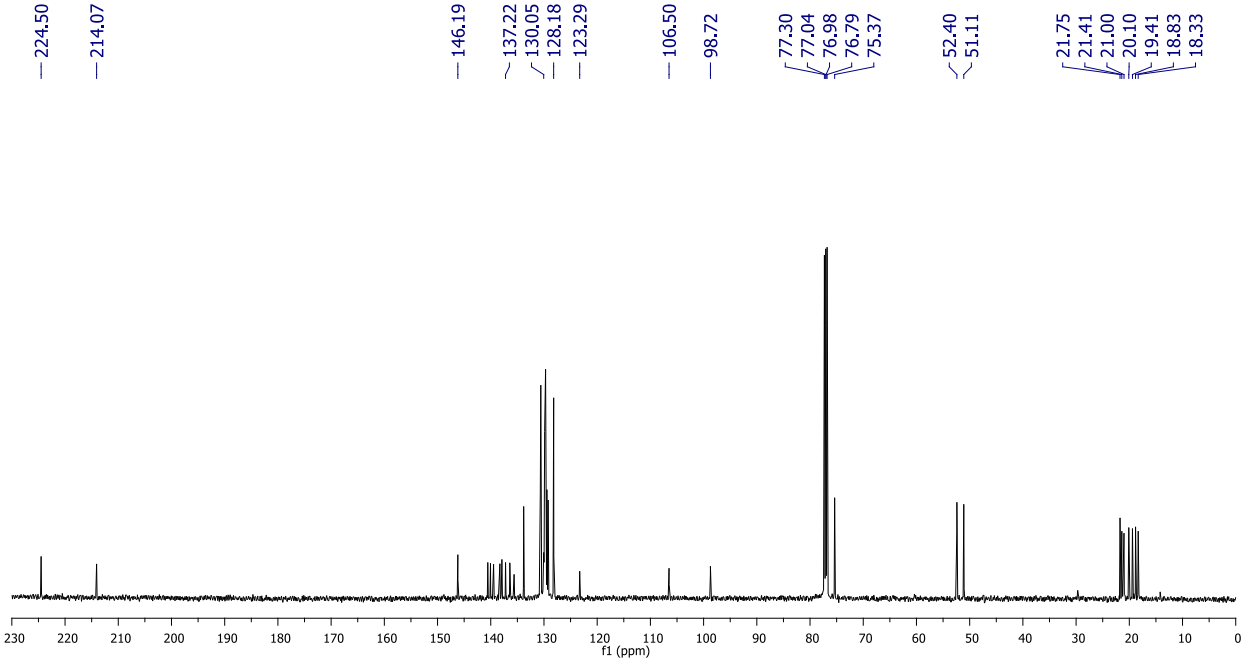

7.57
7.56
7.32
7.29
7.20
7.19
7.18
5.89
5.88
5.87
5.86
5.32
5.22
5.22
5.20
5.20
4.25
4.06
4.04
2.43
2.17
5.68
2.29
1.00
2.15
2.30
2.28
3.45
f1 (ppm)

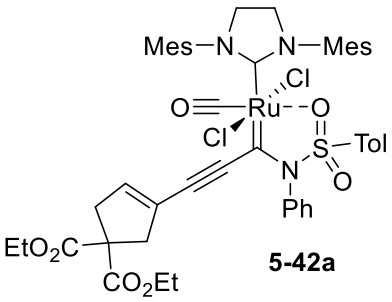

145.52
129.79
128.79
126.32
118.08
79.09
77.37
77.12
76.87
70.77
70.55
57.88
57.46
21.74
f1 (ppm)


Cl
NHC
Ru
O
Cl
S
Tol
O
N
Ph
O

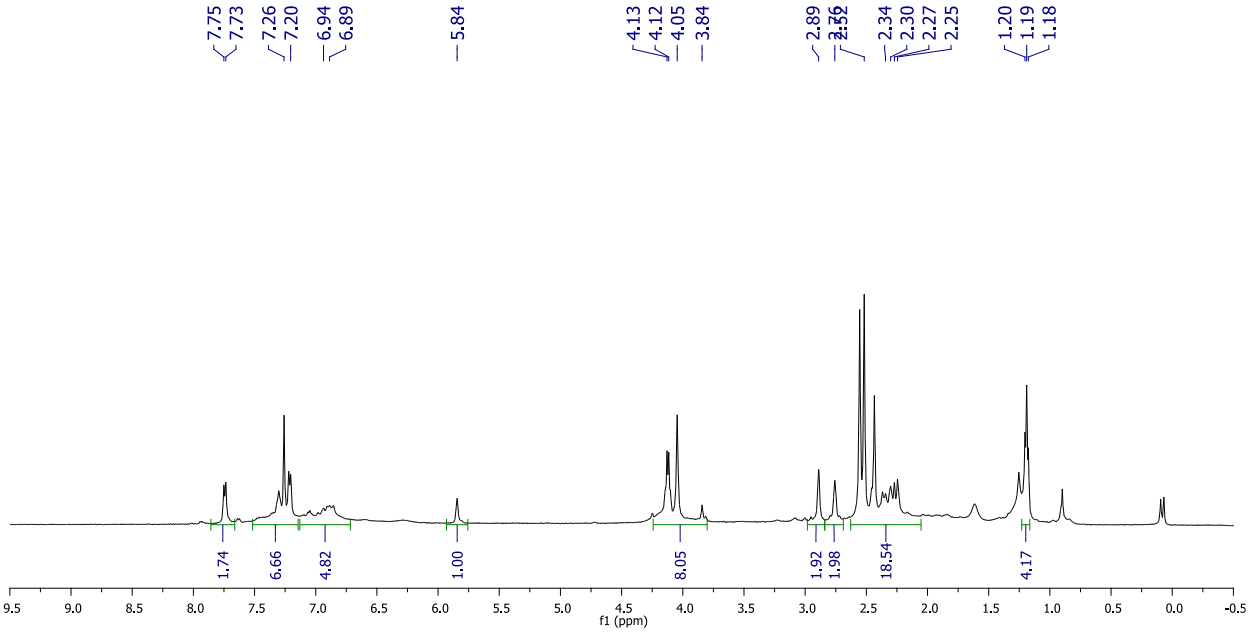
5-41c

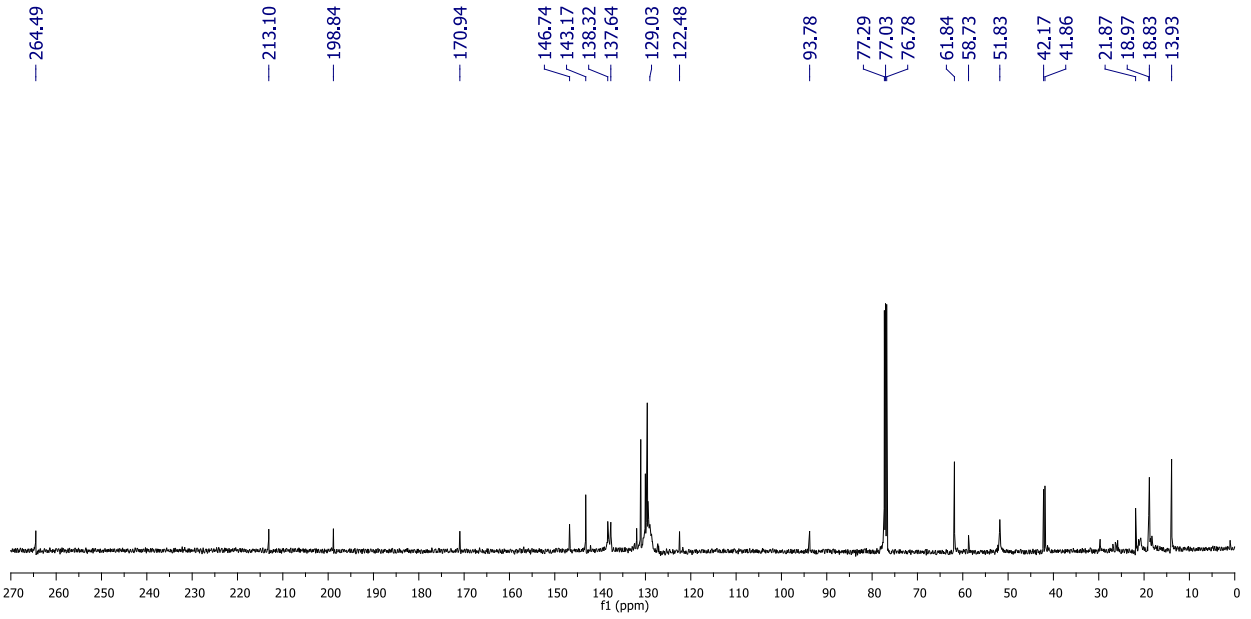

8.00
7.98
7.26
7.12
7.09
7.00
6.79
6.63
6.07
4.38
4.36
4.35
4.22
4.18
4.16
2.64
2.49
2.42
2.35
2.33
2.29
2.17
2.03
1.91
5.24
2.37
2.06
1.11
1.00
3.18
5.28
3.43
3.56
2.96
6.22
3.15
3.10
f1 (ppm)

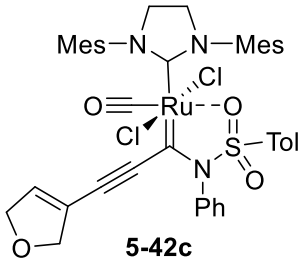

224.50
214.07
146.19
137.22
130.05
128.18
123.29
106.50
98.72
77.30
77.04
76.98
76.79
75.37
52.40
51.11
21.75
21.41
21.00
20.10
19.41
18.83
18.33
f1 (ppm)


Mes
N
N
Mes
Cl
O
Ru
O
Cl
S
Tol
N
O
Ph
EtO2C
CO2Et

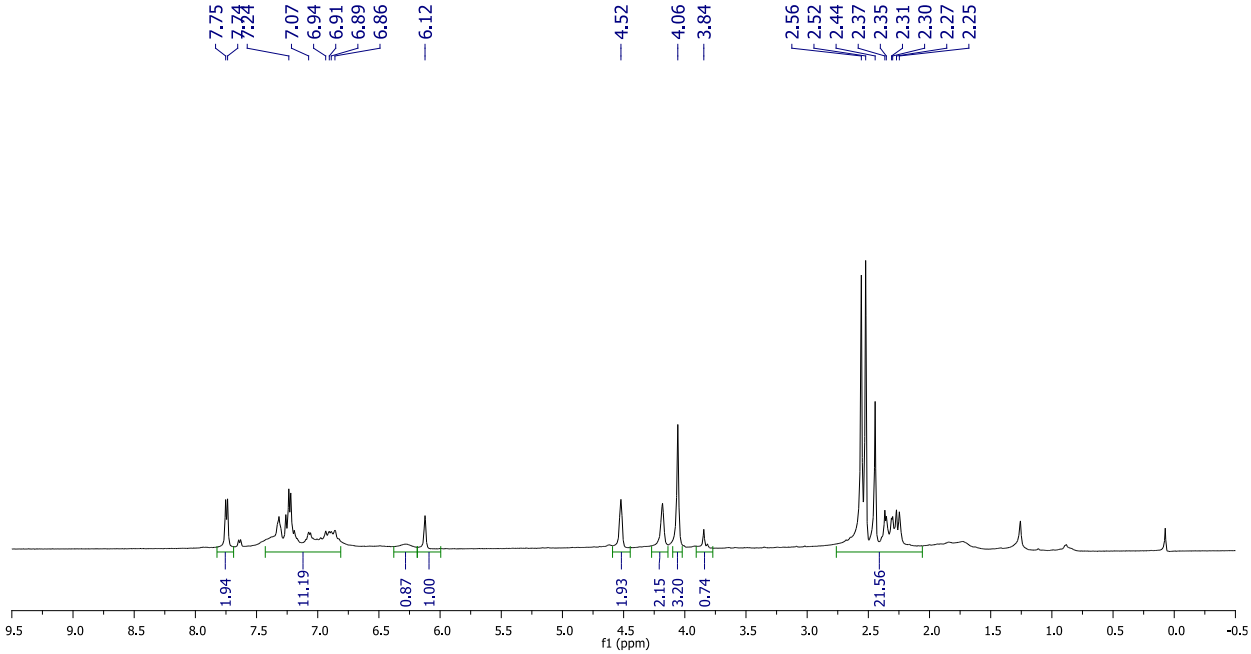
5-42a

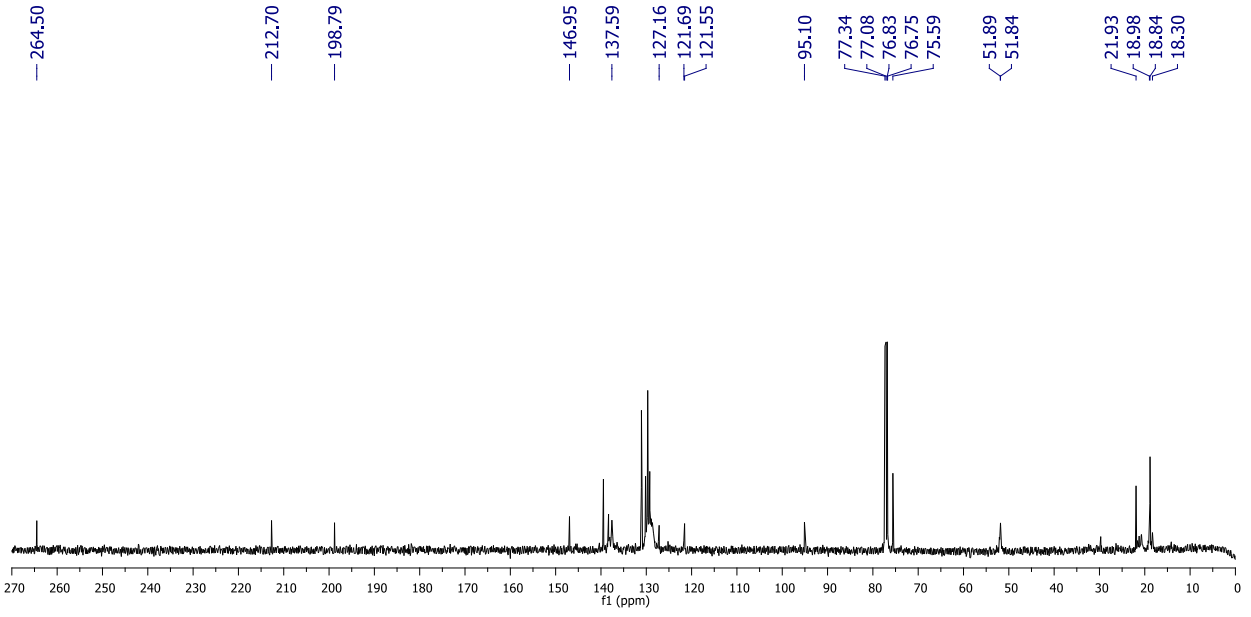

7.75
7.73
7.26
7.20
6.94
6.89
5.84
4.13
4.12
4.05
3.84
2.89
2.34
2.30
2.27
2.25
1.20
1.19
1.18
1.74
6.66
4.82
1.00
8.05
1.92
1.98
18.54
4.17
f1 (ppm)


264.49
213.10
198.84
170.94
146.74
143.17
138.32
137.64
129.03
122.48
93.78
77.29
77.03
76.78
61.84
58.73
51.83
42.17
41.86
21.87
18.97
18.83
13.93
f1 (ppm)


Mes
N
N
Mes
Cl
O
Ru
O
Cl
S
Tol
N
O
Ph
O

5-42c


7.75
7.74
7.24
7.07
6.94
6.91
6.89
6.86
6.12
4.52
4.06
3.84
2.56
2.52
2.44
2.37
2.35
2.31
2.30
2.27
2.25
1.94
11.19
0.87
1.00
1.93
2.15
3.20
0.74
21.56
f1 (ppm)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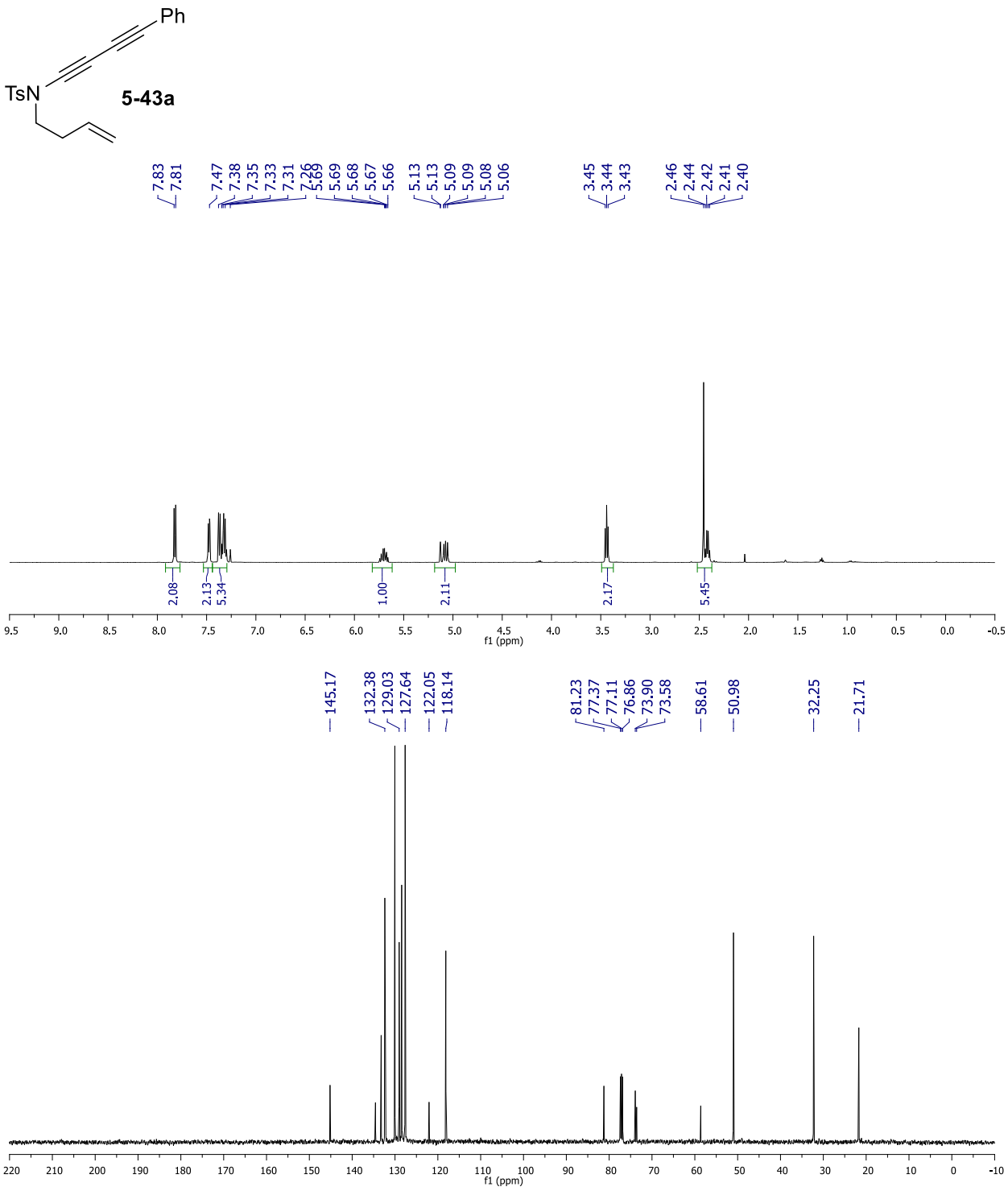
212.70
198.79
146.95
137.59
127.16
121.69
121.55
95.10
77.34
77.08
76.83
76.75
75.59
51.89
51.84
21.93
18.98
18.84
18.30
f1 (ppm)


Ph
TsN
5-43a
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7.81
7.47
7.38
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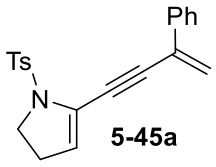
7.33
7.31
7.26
5.69
5.69
5.68
5.67
5.66
5.13
5.13
5.09
5.09
5.08
5.06
3.45
3.44
3.43
2.46
2.44
2.42
2.41
2.40
2.08
2.13
5.34
1.00
2.11
2.17
5.45
f1 (ppm)
145.17
132.38
129.03
127.64
122.05
118.14
81.23
77.37
77.11
76.86
73.90
73.58
58.61
50.98
32.25
21.71
f1 (ppm)


Ph
Ts
N

5-45a

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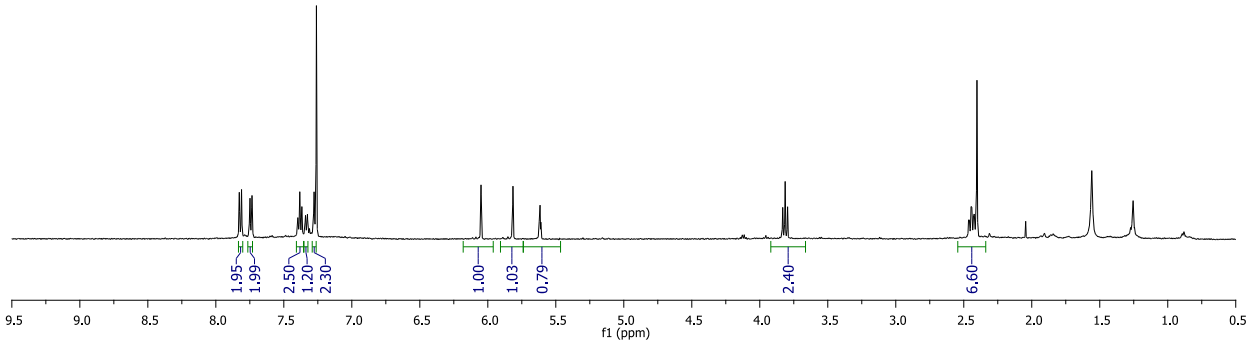
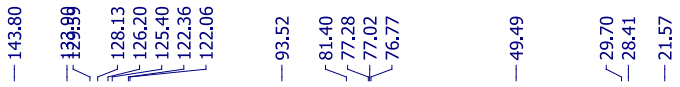
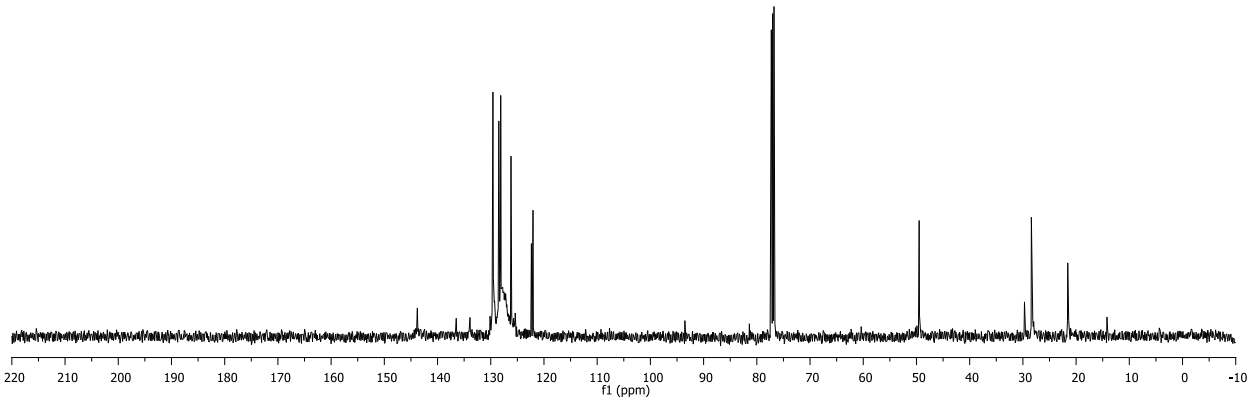
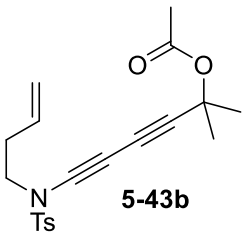
7.81
7.75
7.75
7.38
7.37
7.34
7.33
7.28
7.26
6.05
5.81
5.62
5.62
5.61
3.83
3.81
3.80
2.46
2.46
2.45
2.44
2.43
2.42
2.40

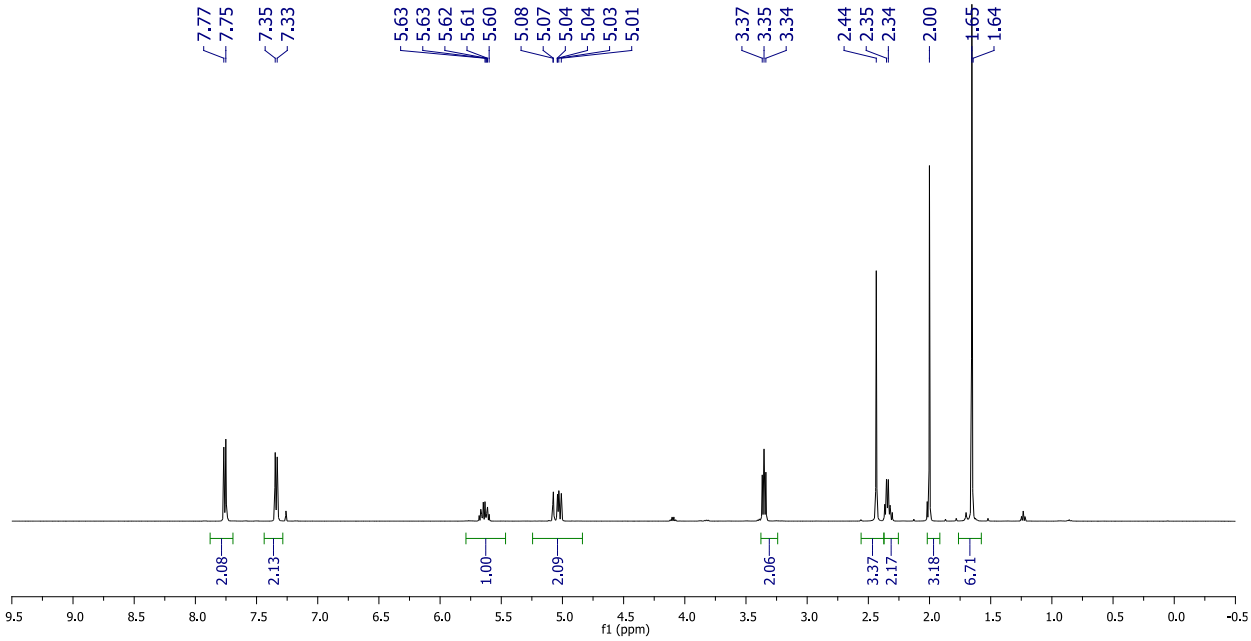

1.95
1.99
2.50
1.20
2.30
1.00
1.03
0.79
2.40
6.60
f1 (ppm)

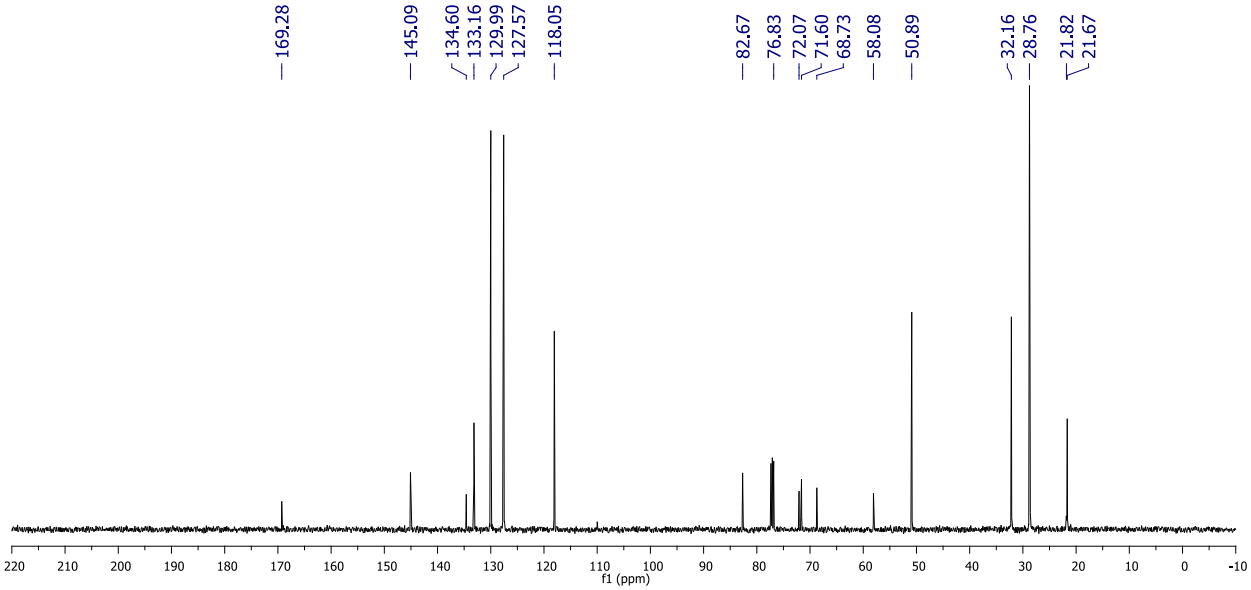

143.80
128.13
126.20
125.40
122.36
122.06
93.52
81.40
77.28
77.02
76.77
49.49
29.70
28.41
21.57

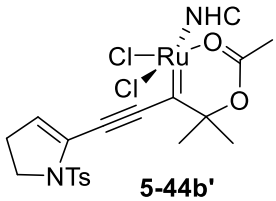

f1 (ppm)


O
O
N
Ts

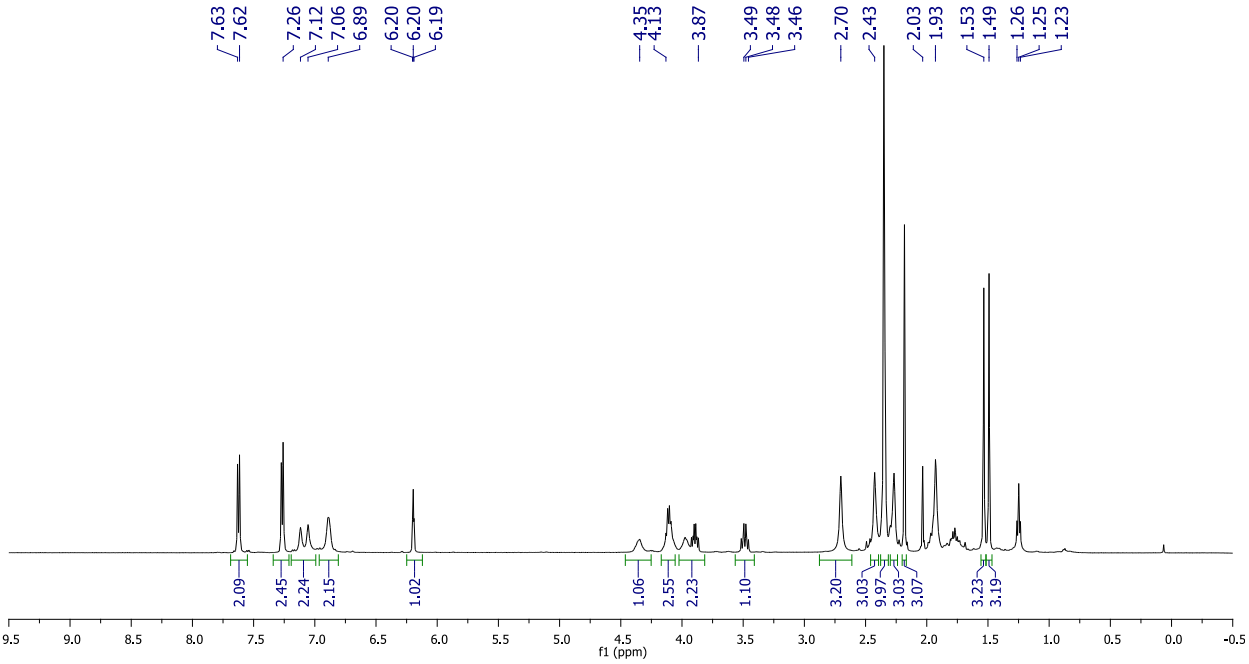
5-43b

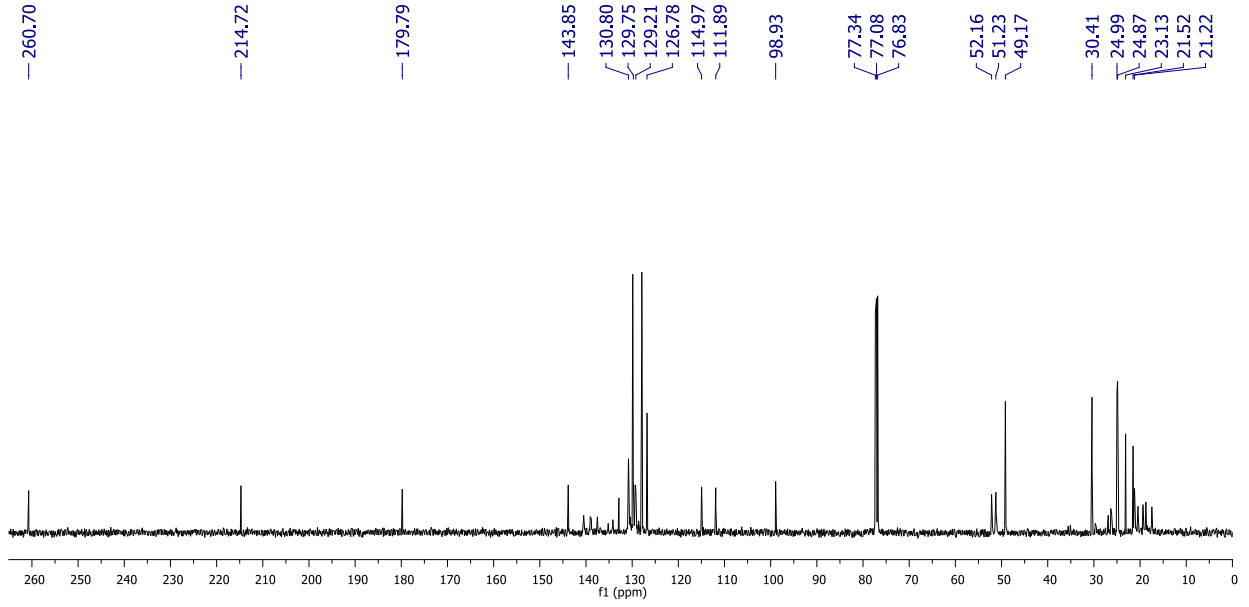

7.77
7.75
7.35
7.33
5.63
5.63
5.62
5.61
5.60
5.08
5.07
5.04
5.04
5.03
5.01
3.37
3.35
3.34
2.44
2.35
2.34
2.00
1.65
1.64
2.08
2.13
1.00
2.09
2.06
3.37
2.17
3.18
6.71
f1 (ppm)

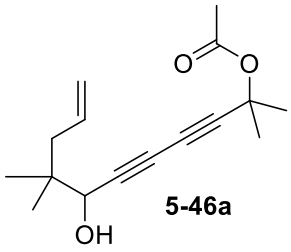

169.28
145.09
134.60
133.16
129.99
127.57
118.05
82.67
76.83
72.07
71.60
68.73
58.08
50.89
32.16
28.76
21.82
21.67
f1 (ppm)


NHC
Cl
Ru
O
Cl
O
NTs

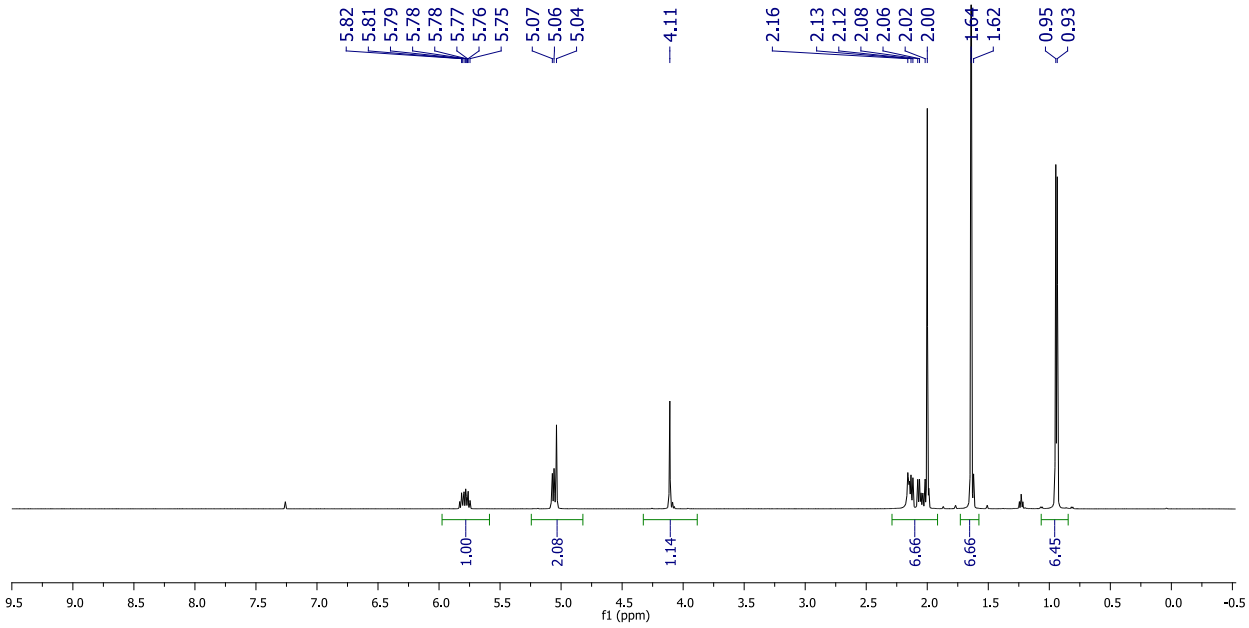
5-44b'

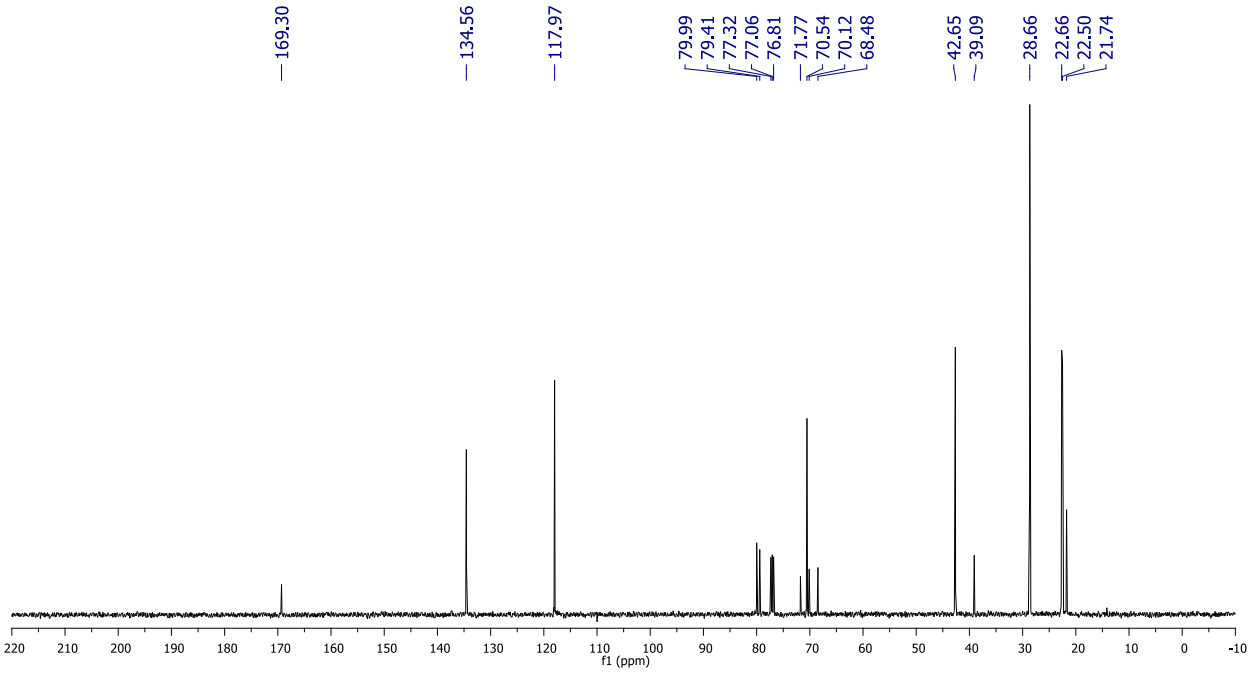

7.63
7.62
7.26
7.12
7.06
6.89
6.20
6.20
6.19
4.35
4.13
3.87
3.49
3.48
3.46
2.70
2.43
2.03
1.93
1.53
1.49
1.26
1.25
1.23
2.09
2.45
2.24
2.15
1.02
1.06
2.55
2.23
1.10
3.20
3.03
9.97
3.03
3.07
3.23
3.19
f1 (ppm)

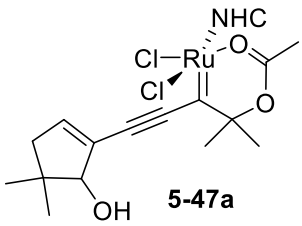

260.70
214.72
179.79
143.85
130.80
129.75
129.21
126.78
114.97
111.89
98.93
77.34
77.08
76.83
52.16
51.23
49.17
30.41
24.99
24.87
23.13
21.52
21.22
f1 (ppm)


O
O
OH

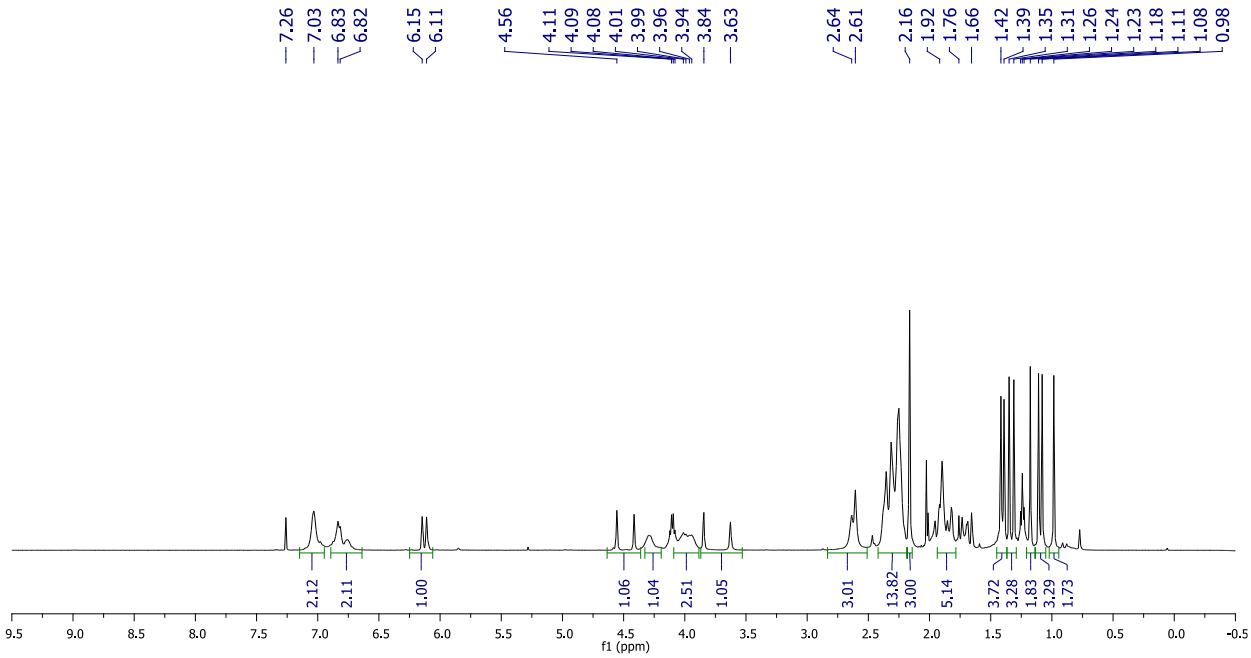
5-46a

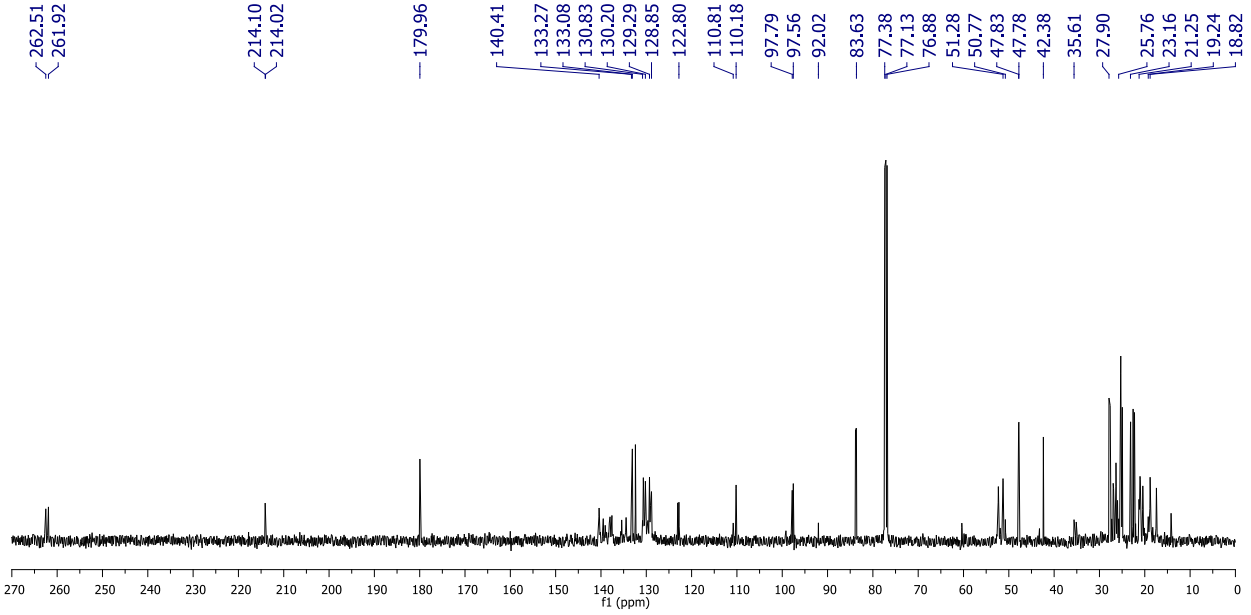

5.82
5.81
5.79
5.78
5.78
5.77
5.76
5.75
5.07
5.06
5.04
4.11
2.16
2.13
2.12
2.08
2.06
2.02
2.00
1.64
1.62
0.95
0.93
1.00
2.08
1.14
6.66
6.66
6.45
f1 (ppm)

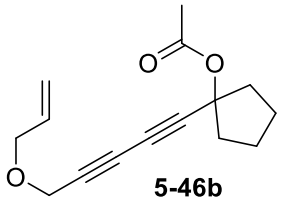

169.30
134.56
117.97
79.99
79.41
77.32
77.06
76.81
71.77
70.54
70.12
68.48
42.65
39.09
28.66
22.66
22.50
21.74
f1 (ppm)


NHC
Cl
Ru
O
Cl
O
OH

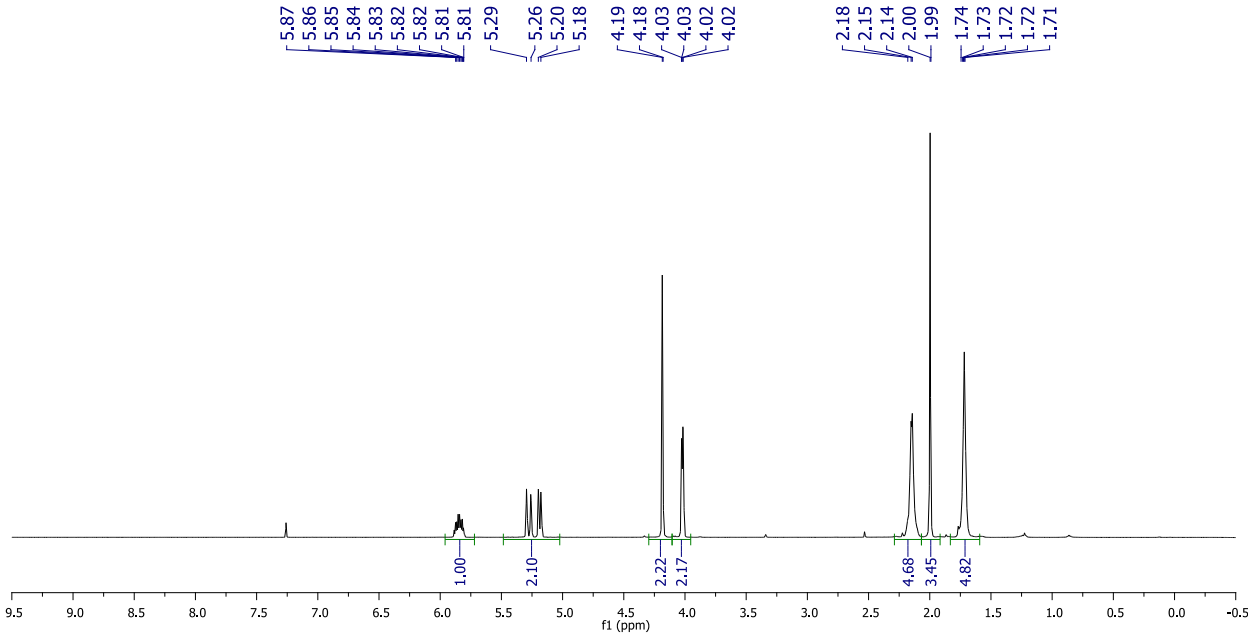
5-47a

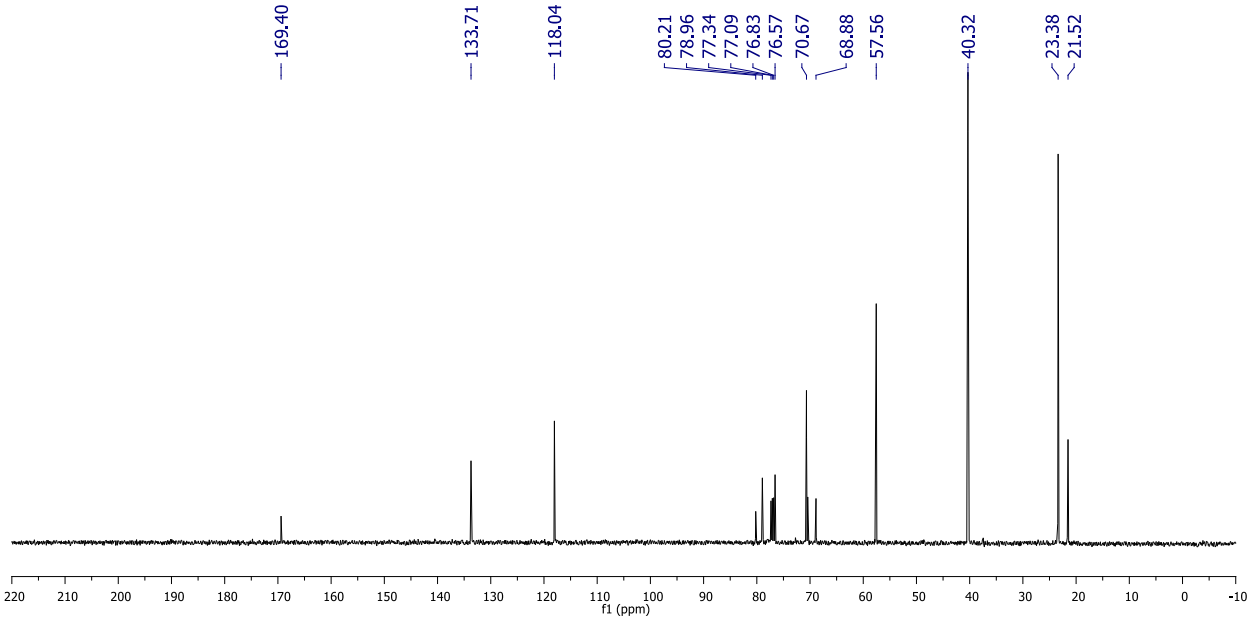

7.26
7.03
6.83
6.82
6.15
6.11
4.56
4.11
4.09
4.08
4.01
3.99
3.96
3.94
3.84
3.63
2.64
2.61
2.16
1.92
1.76
1.66
1.42
1.39
1.35
1.31
1.26
1.24
1.23
1.18
1.11
1.08
0.98
2.12
2.11
1.00
1.06
1.04
2.51
1.05
3.01
13.82
3.00
5.14
3.72
3.28
1.83
3.29
1.73
f1 (ppm)

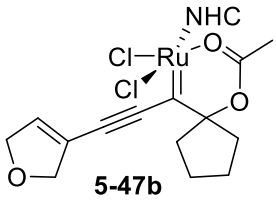

262.51
261.92
214.10
214.02
179.96
140.41
133.27
133.08
130.83
130.20
129.29
128.85
122.80
110.81
110.18
97.79
97.56
92.02
83.63
77.38
77.13
76.88
51.28
50.77
47.83
47.78
42.38
35.61
27.90
25.76
23.16
21.25
19.24
18.82
f1 (ppm)



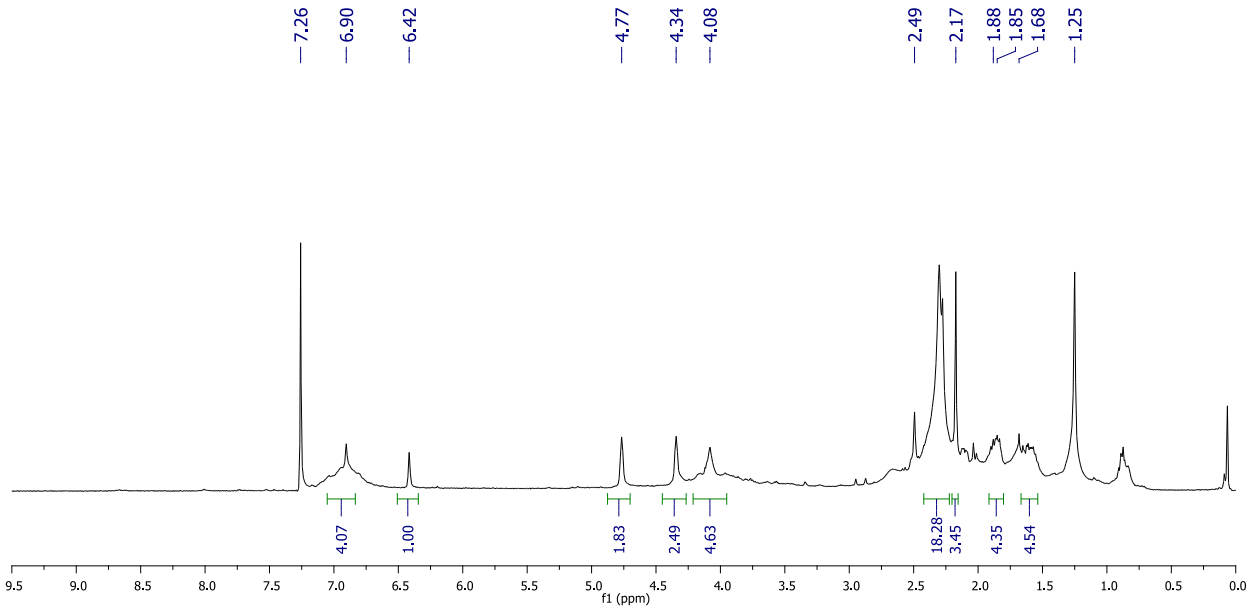
5-46b

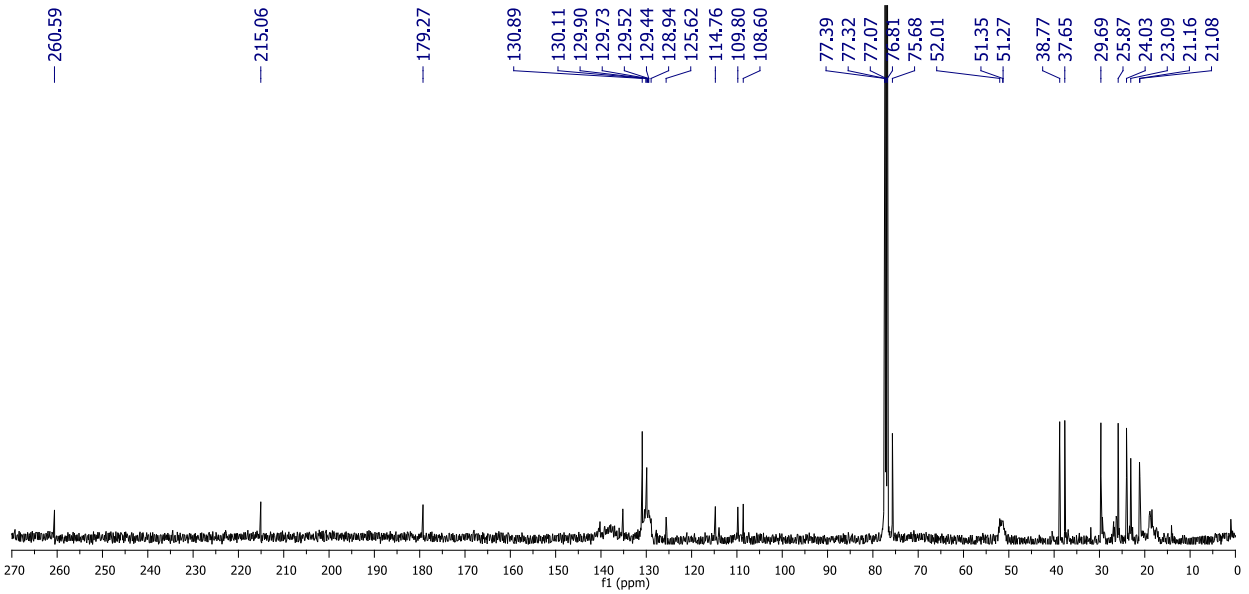

5.87
5.86
5.85
5.84
5.83
5.82
5.82
5.81
5.81
5.29
5.26
5.20
5.18
4.19
4.18
4.03
4.03
4.02
4.02
2.18
2.15
2.14
2.00
1.99
1.74
1.73
1.72
1.72
1.71
1.00
2.10
2.22
2.17
4.68
3.45
4.82
f1 (ppm)

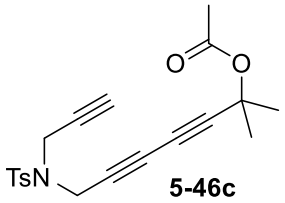

169.40
133.71
118.04
80.21
78.96
77.34
77.09
76.83
76.57
70.67
68.88
57.56
40.32
23.38
21.52
f1 (ppm)


NHC
Cl
Ru
O
Cl
O
O

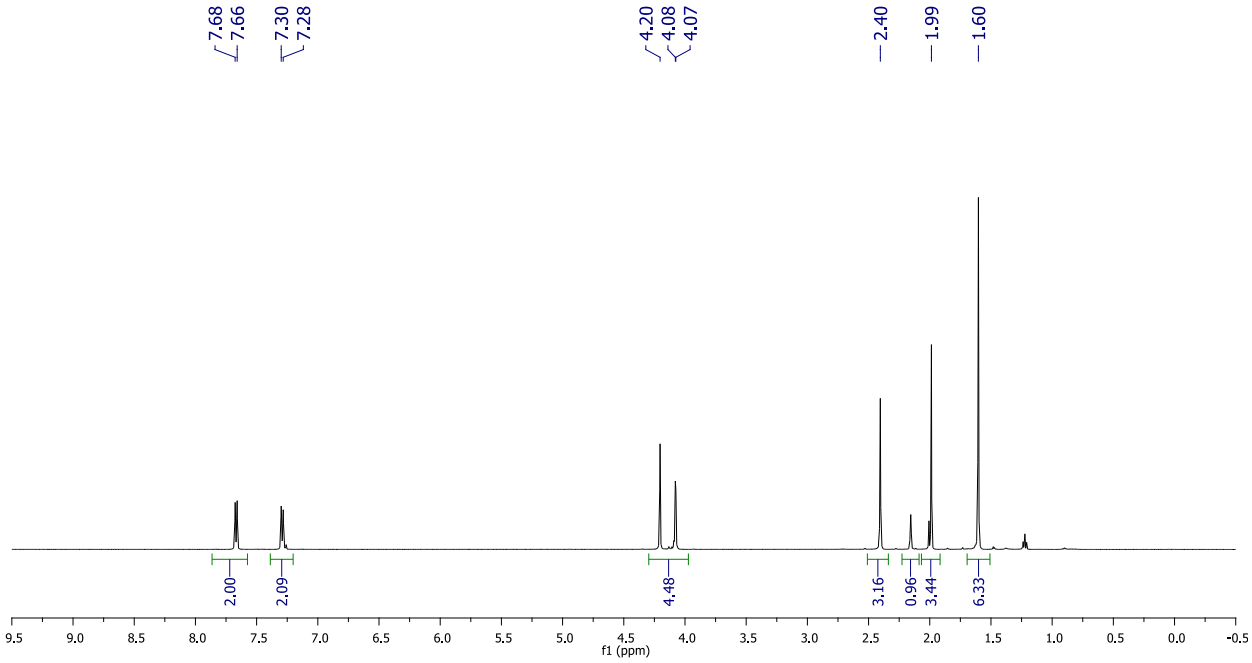
5-47b

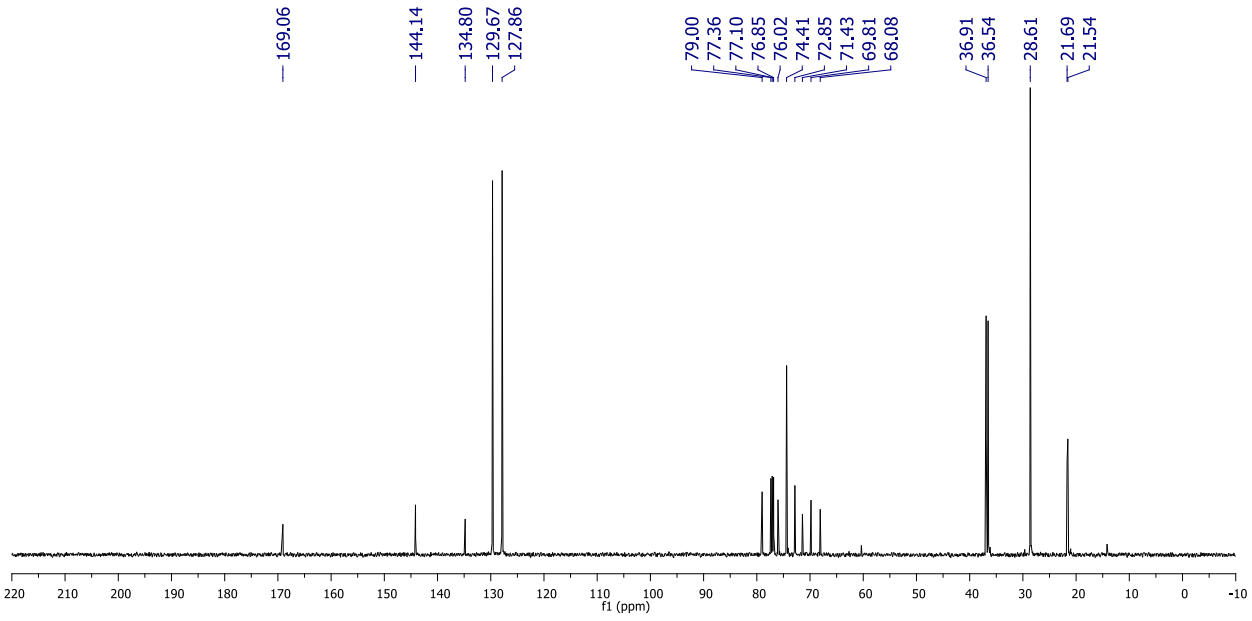

7.26
6.90
6.42
4.77
4.34
4.08
2.49
2.17
1.88
1.85
1.68
1.25
4.07
1.00
1.83
2.49
4.63
18.28
3.45
4.35
4.54
f1 (ppm)

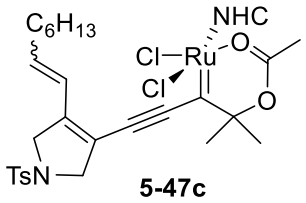

260.59
215.06
179.27
130.89
130.11
129.90
129.73
129.52
129.44
128.94
125.62
114.76
109.80
108.60
77.39
77.32
77.07
76.81
75.68
52.01
51.35
51.27
38.77
37.65
29.69
25.87
24.03
23.09
21.16
21.08
f1 (ppm)


O
O
TsN

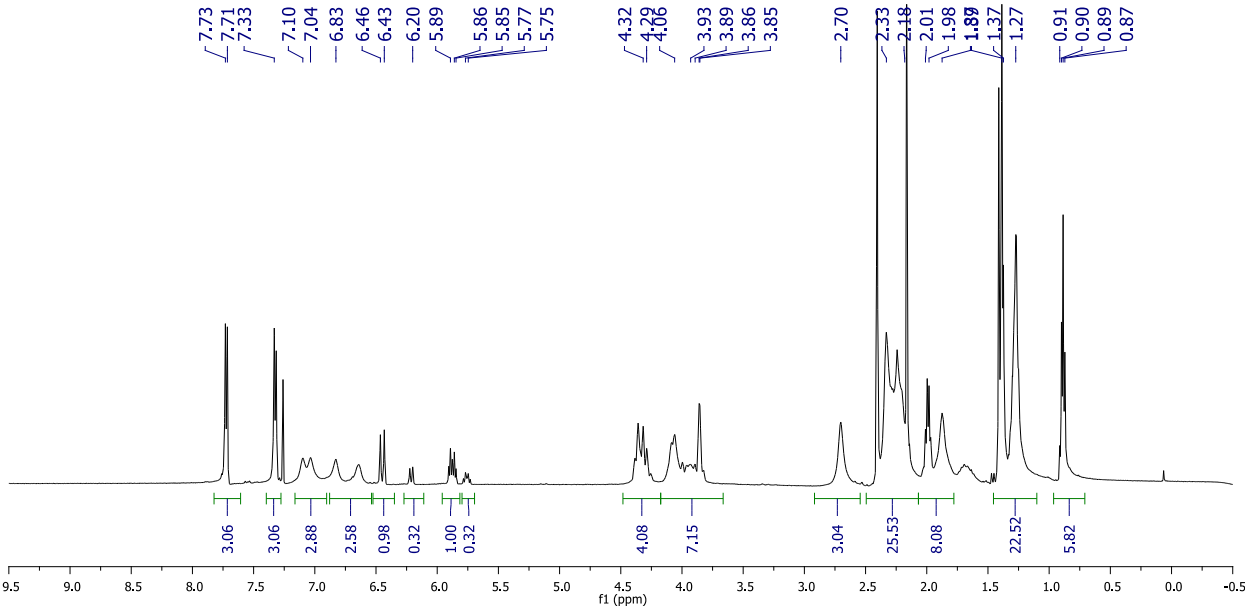
5-46c

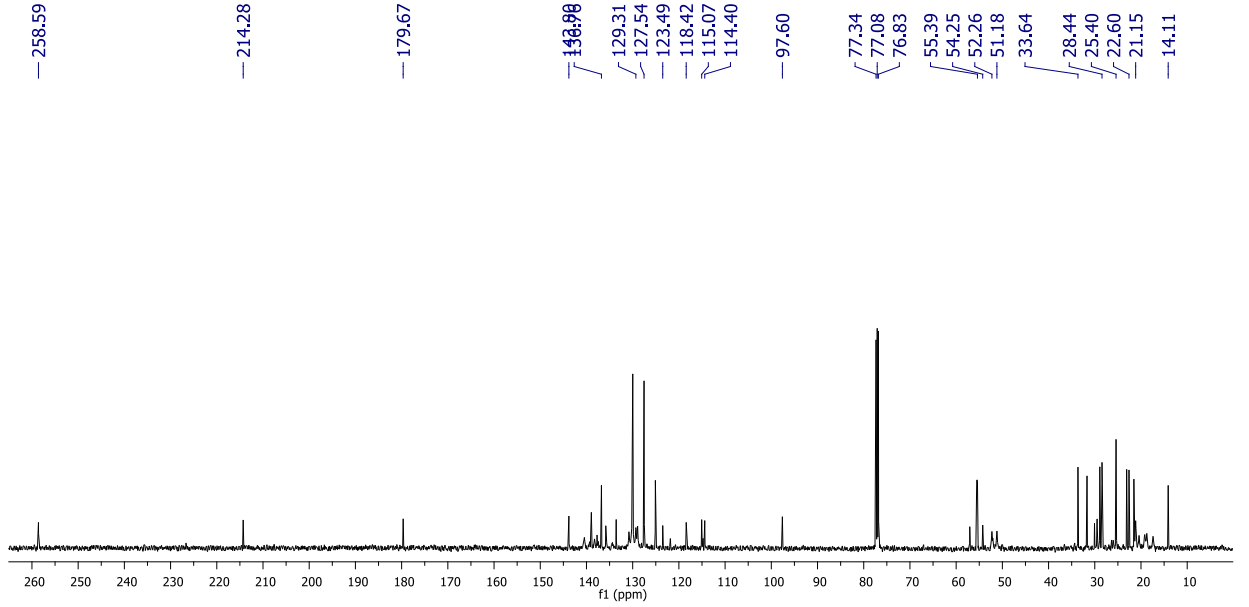

7.68
7.66
7.30
7.28
4.20
4.08
4.07
2.40
1.99
1.60
2.00
2.09
4.48
3.16
0.96
3.44
6.33
f1 (ppm)

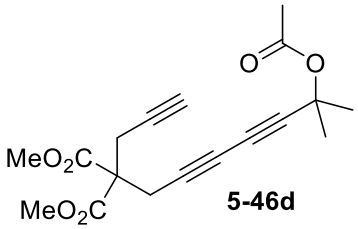

169.06
144.14
134.80
129.67
127.86
79.00
77.36
77.10
76.85
76.02
74.41
72.85
71.43
69.81
68.08
36.91
36.54
28.61
21.69
21.54
f1 (ppm)


C6H13
NHC
Cl—Ru
O
Cl
O
TsN

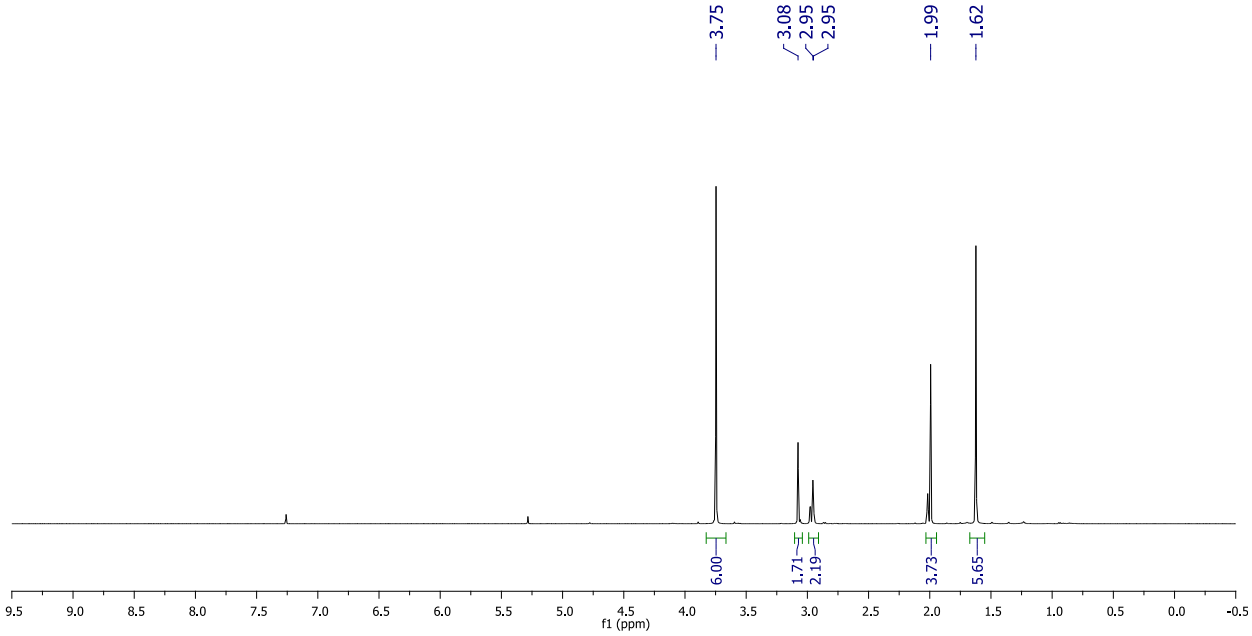
5-47c

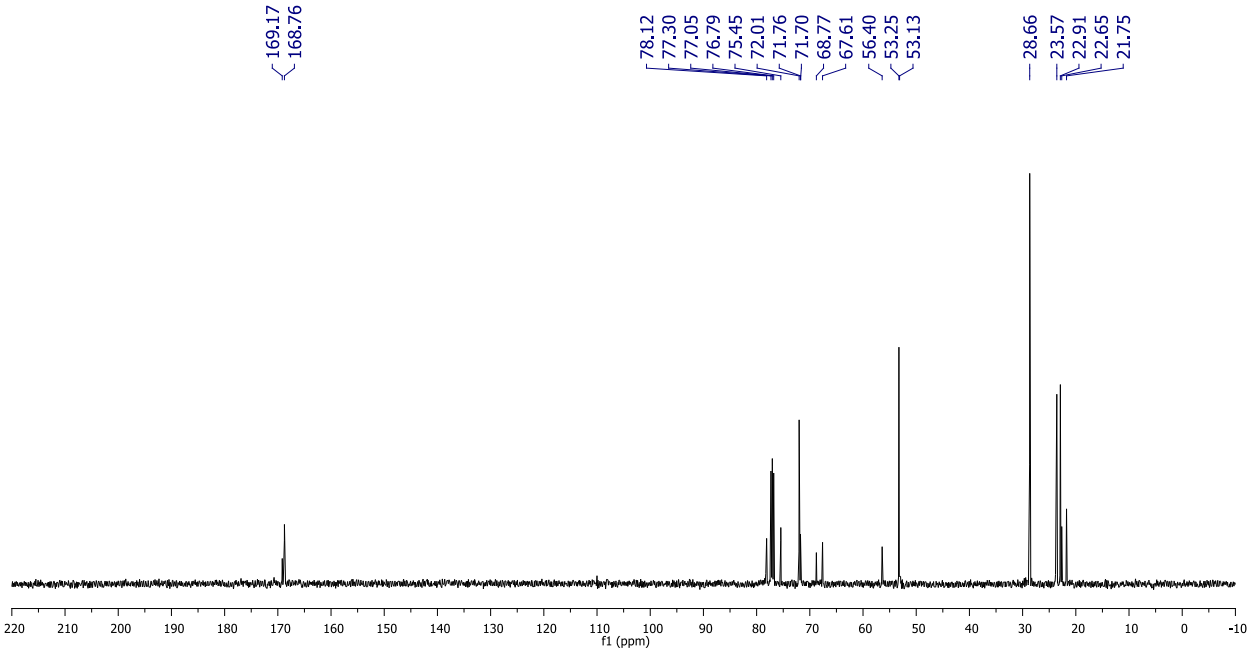

7.73
7.71
7.33
7.10
7.04
6.83
6.46
6.43
6.20
5.89
5.86
5.85
5.77
5.75
4.32
4.29
4.06
3.93
3.89
3.86
3.85
2.70
2.33
2.18
2.01
1.98
1.37
1.27
0.91
0.90
0.89
0.87
3.06
3.06
2.88
2.58
0.98
0.32
1.00
0.32
4.08
7.15
3.04
25.53
8.08
22.52
5.82
f1 (ppm)

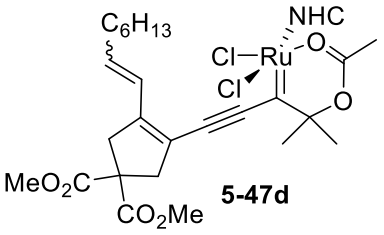

258.59
214.28
179.67
129.31
127.54
123.49
118.42
115.07
114.40
97.60
77.34
77.08
76.83
55.39
54.25
52.26
51.18
33.64
28.44
25.40
22.60
21.15
14.11
f1 (ppm)


O
O
MeO2C
MeO2C

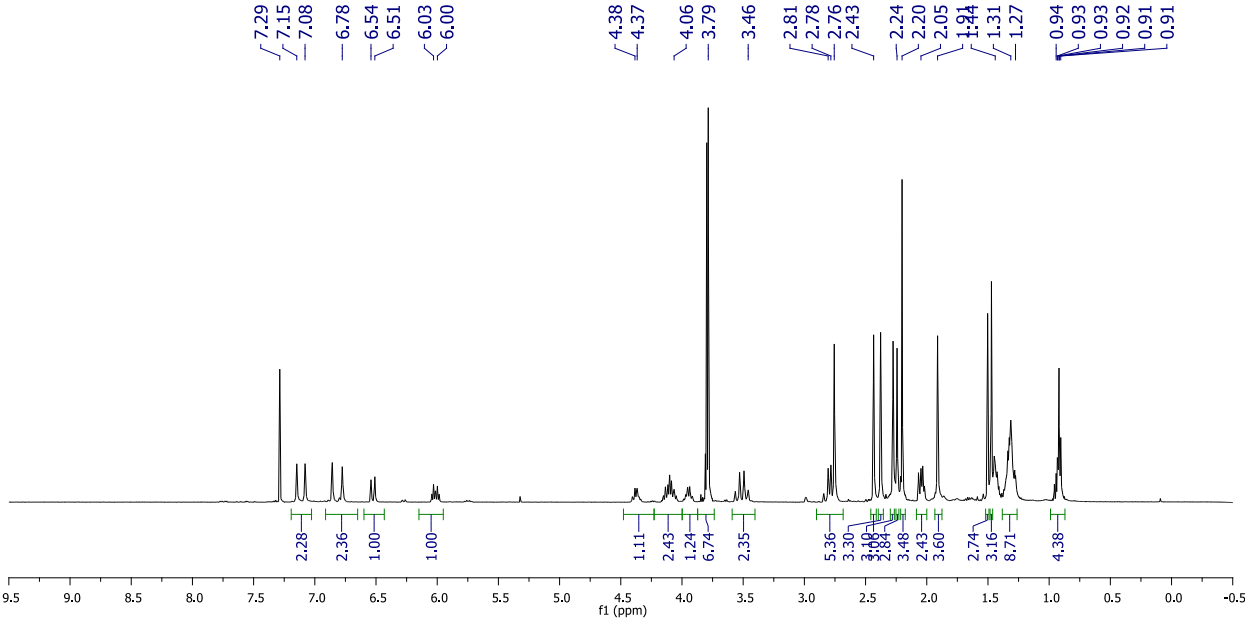
5-46d

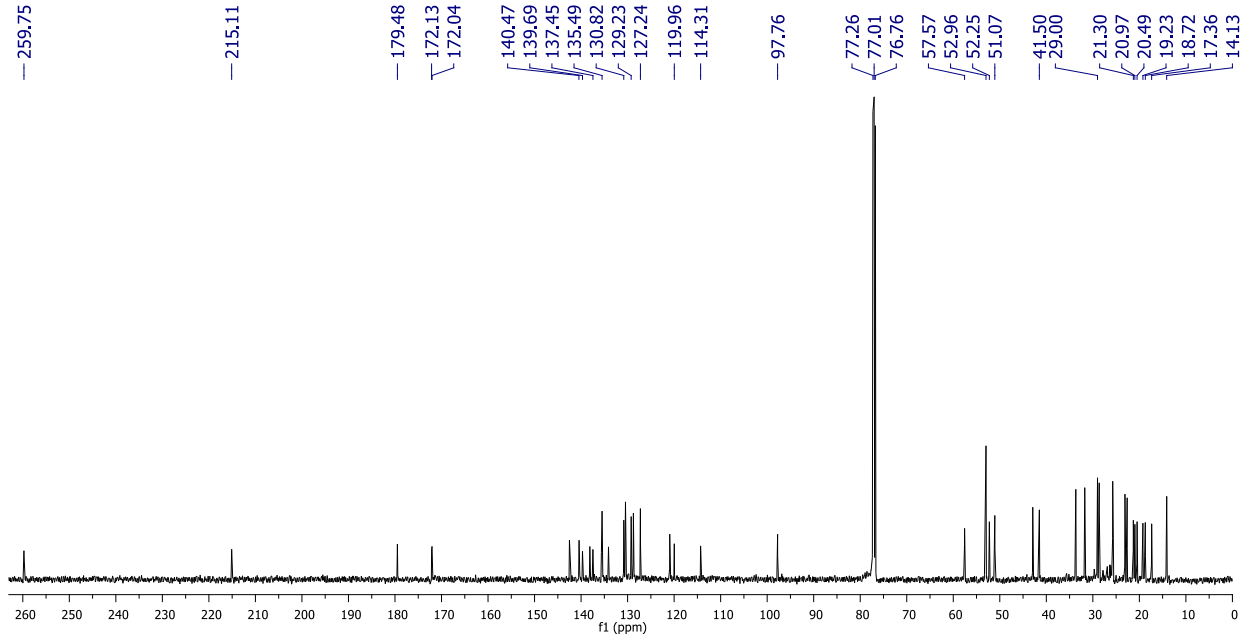

3.75
3.08
2.95
2.95
1.99
1.62
6.00
1.71
2.19
3.73
5.65
f1 (ppm)

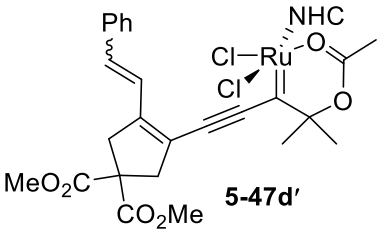

169.17
168.76
78.12
77.30
77.05
76.79
75.45
72.01
71.76
71.70
68.77
67.61
56.40
53.25
53.13
28.66
23.57
22.91
22.65
21.75
f1 (ppm)


C6H13
NHC
Cl—Ru
O
Cl
O
MeO2C
CO2Me

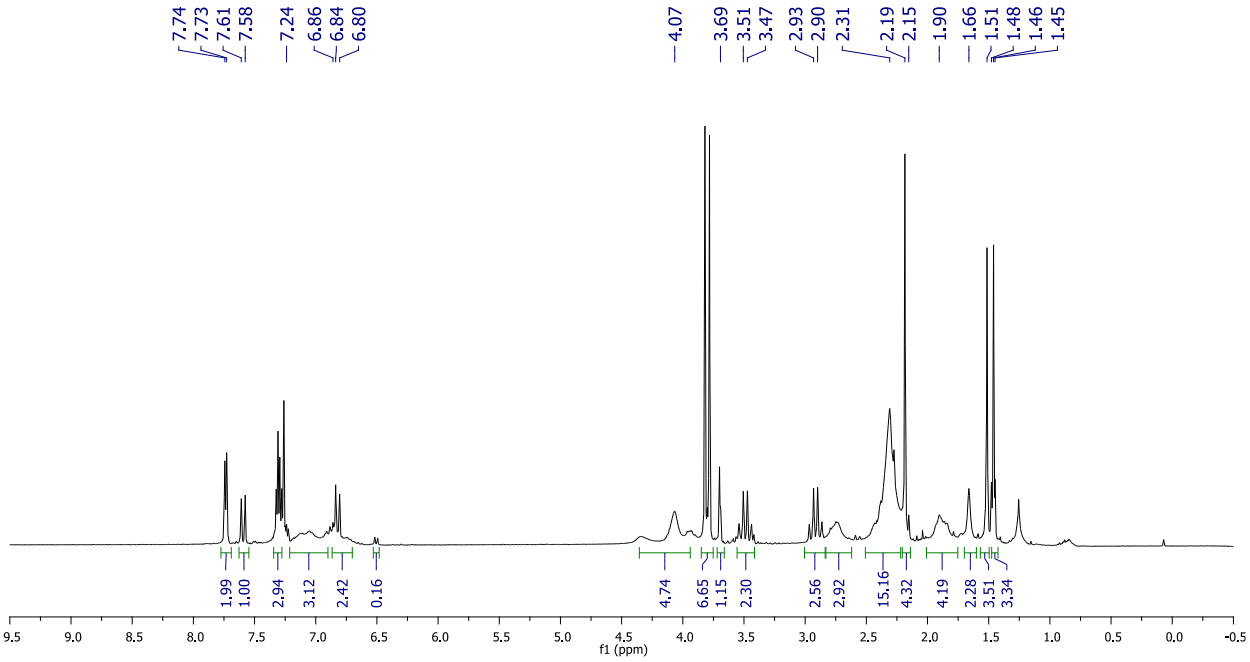
5-47d

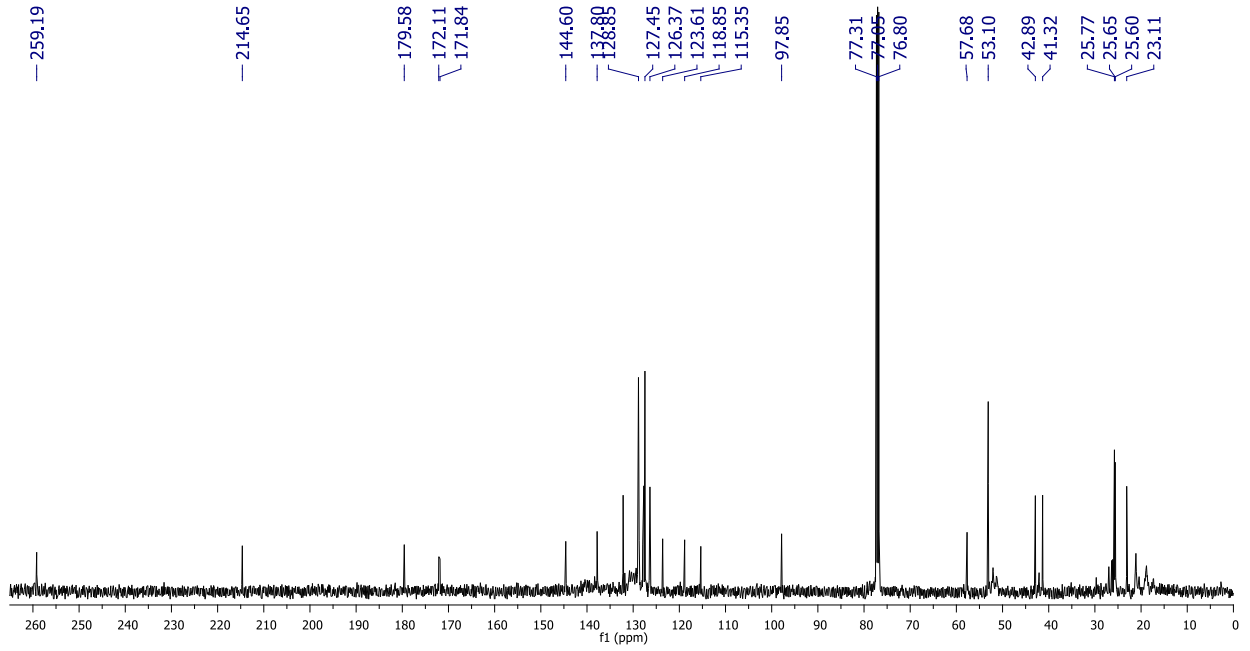

7.29
7.15
7.08
6.78
6.54
6.51
6.03
6.00
4.38
4.37
4.06
3.79
3.46
2.81
2.78
2.76
2.43
2.24
2.20
2.05
1.91
1.44
1.31
1.27
0.94
0.93
0.93
0.92
0.91
0.91
2.28
2.36
1.00
1.00
1.11
2.43
1.24
6.74
2.35
5.36
3.30
2.84
3.48
2.43
3.60
2.74
3.16
8.71
4.38
f1 (ppm)

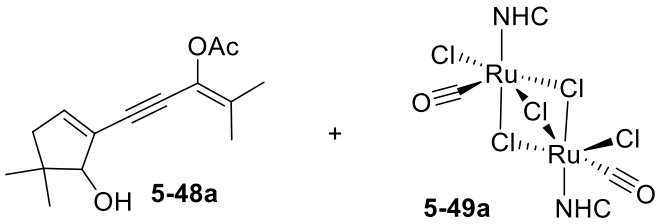

259.75
215.11
179.48
172.13
172.04
140.47
139.69
137.45
135.49
130.82
129.23
127.24
119.96
114.31
97.76
77.26
77.01
76.76
57.57
52.96
52.25
51.07
41.50
29.00
21.30
20.97
20.49
19.23
18.72
17.36
14.13
f1 (ppm)

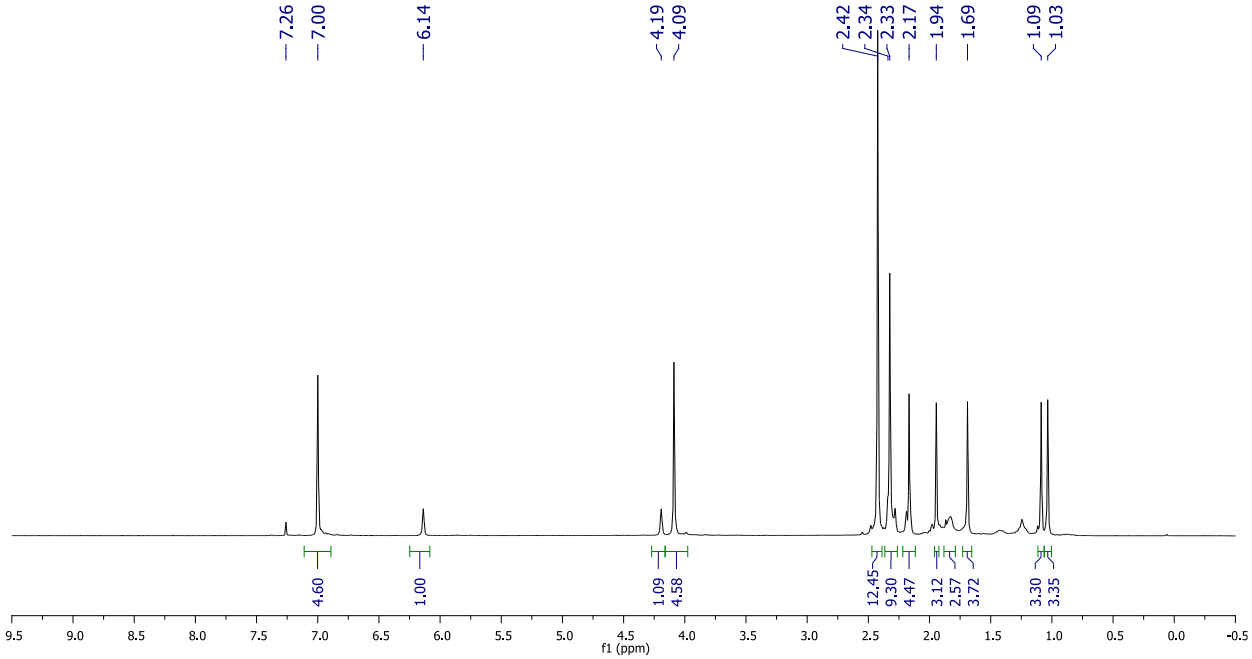

Ph
NHC
Cl—Ru
O
Cl
O
MeO2C
CO2Me

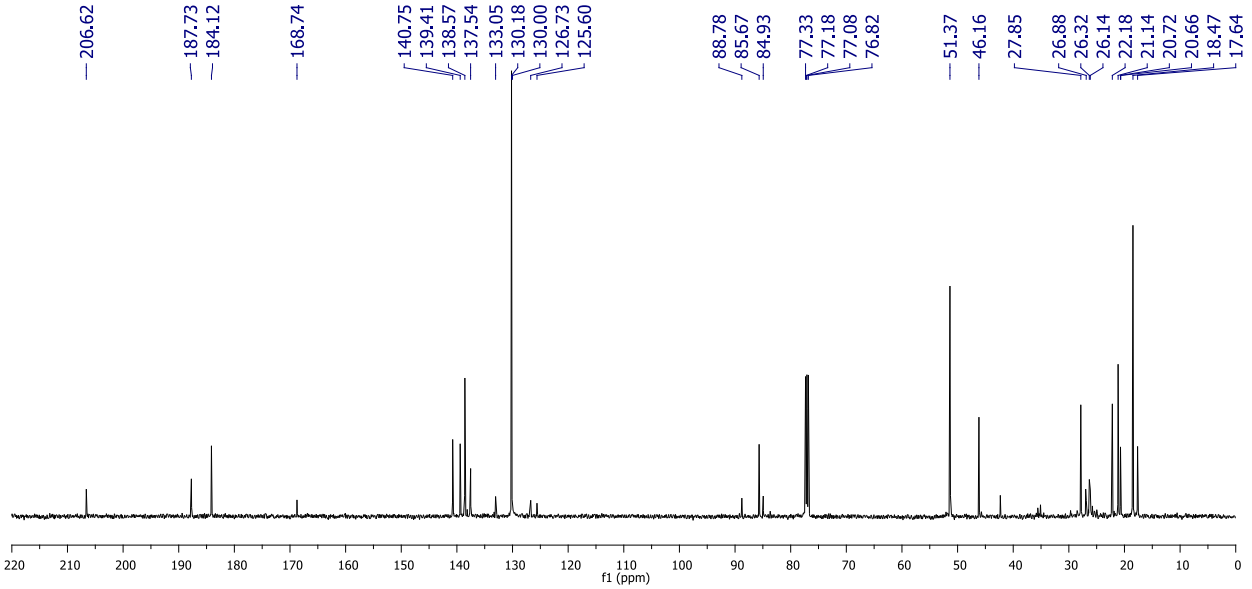
5-47d′


7.74
7.73
7.61
7.58
7.24
6.86
6.84
6.80
4.07
3.69
3.51
3.47
2.93
2.90
2.31
2.19
2.15
1.90
1.66
1.51
1.48
1.46
1.45
1.99
1.00
2.94
3.12
2.42
0.16
4.74
6.65
1.15
2.30
2.56
2.92
15.16
4.32
4.19
2.28
3.51
3.34
f1 (ppm)


259.19
214.65
179.58
172.11
171.84
144.60
137.80
128.85
127.45
126.37
123.61
118.85
115.35
97.85
77.31
77.05
76.80
57.68
53.10
42.89
41.32
25.77
25.65
25.60
23.11
f1 (ppm)

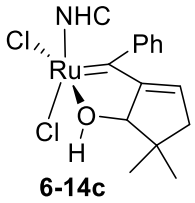

OAc
OH
5-48a
+
NHC
Cl
Ru
Cl
O
Cl
Cl
Ru
Cl
O
NHC
5-49a


7.26
7.00
6.14
4.19
4.09
2.42
2.34
2.33
2.17
1.94
1.69
1.09
1.03
4.60
1.00
1.09
4.58
12.45
9.30
4.47
3.12
2.57
3.72
3.30
3.35
f1 (ppm)

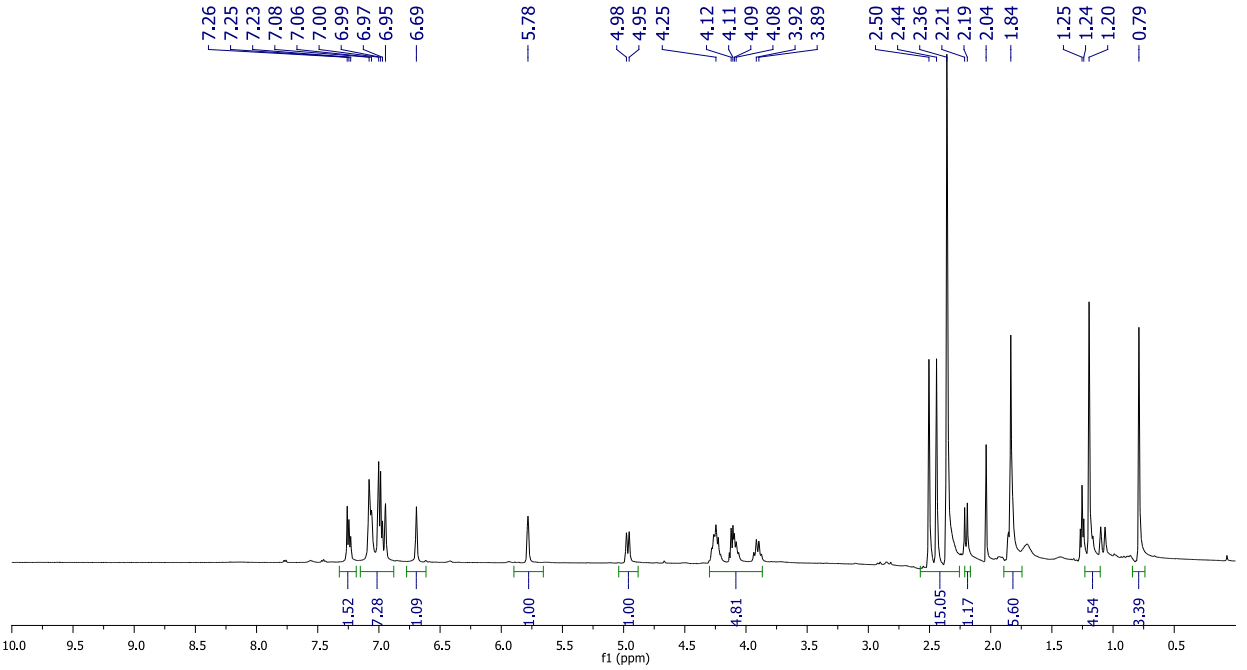

206.62
187.73
184.12
168.74
140.75
139.41
138.57
137.54
133.05
130.18
130.00
126.73
125.60
88.78
85.67
84.93
77.33
77.18
77.08
76.82
51.37
46.16
27.85
26.88
26.32
26.14
22.18
21.14
20.72
20.66
18.47
17.64
f1 (ppm)

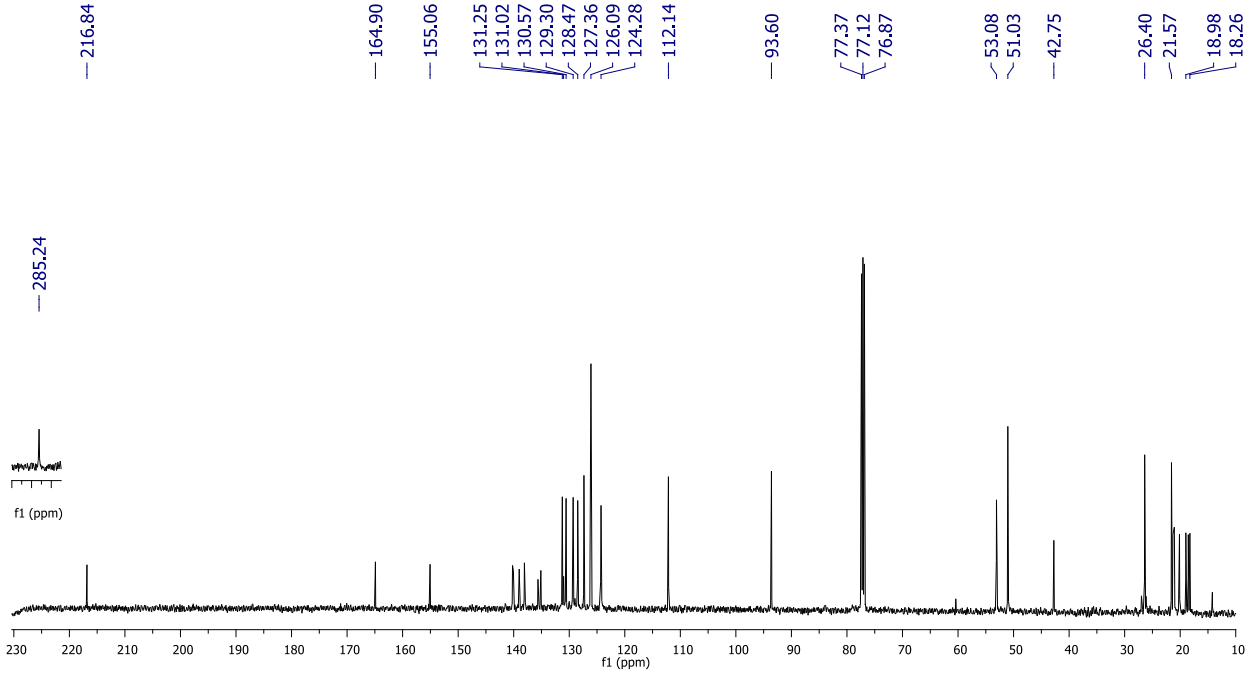
Appendix VI

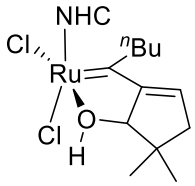
Selected NMR Spectra for Chapter 6


NHC
Cl
Ph
Ru
Cl
O
H

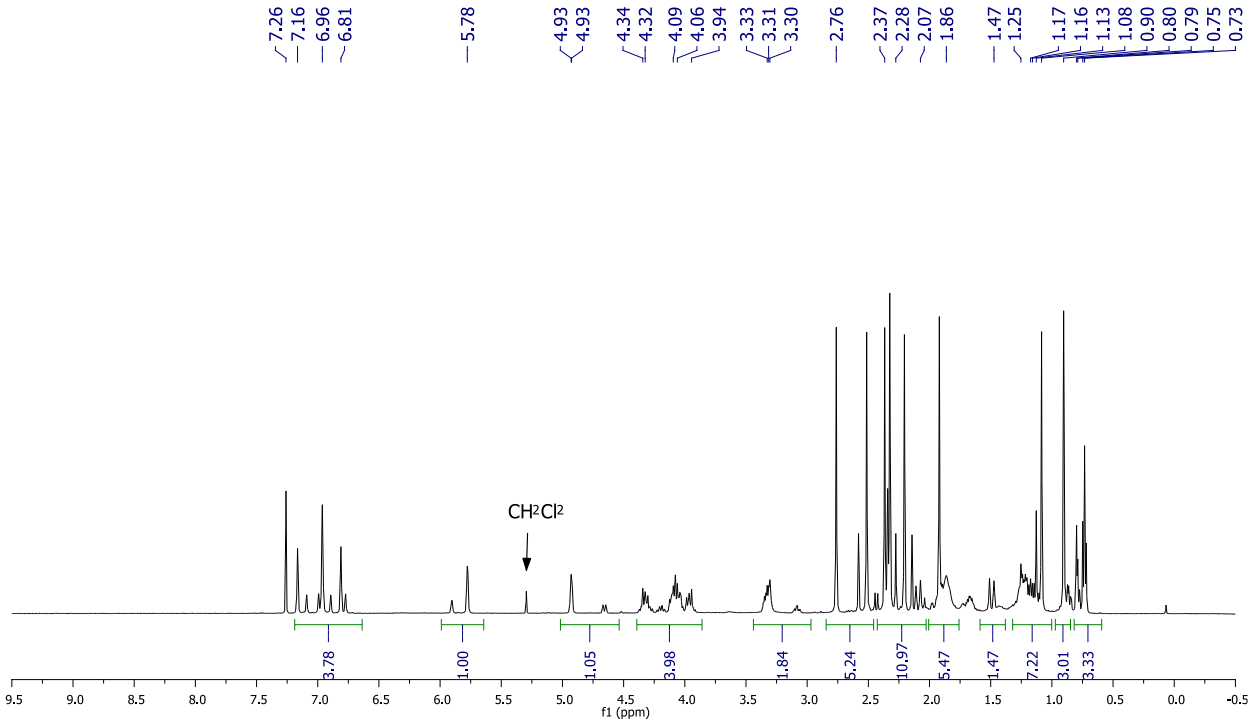
6-14c

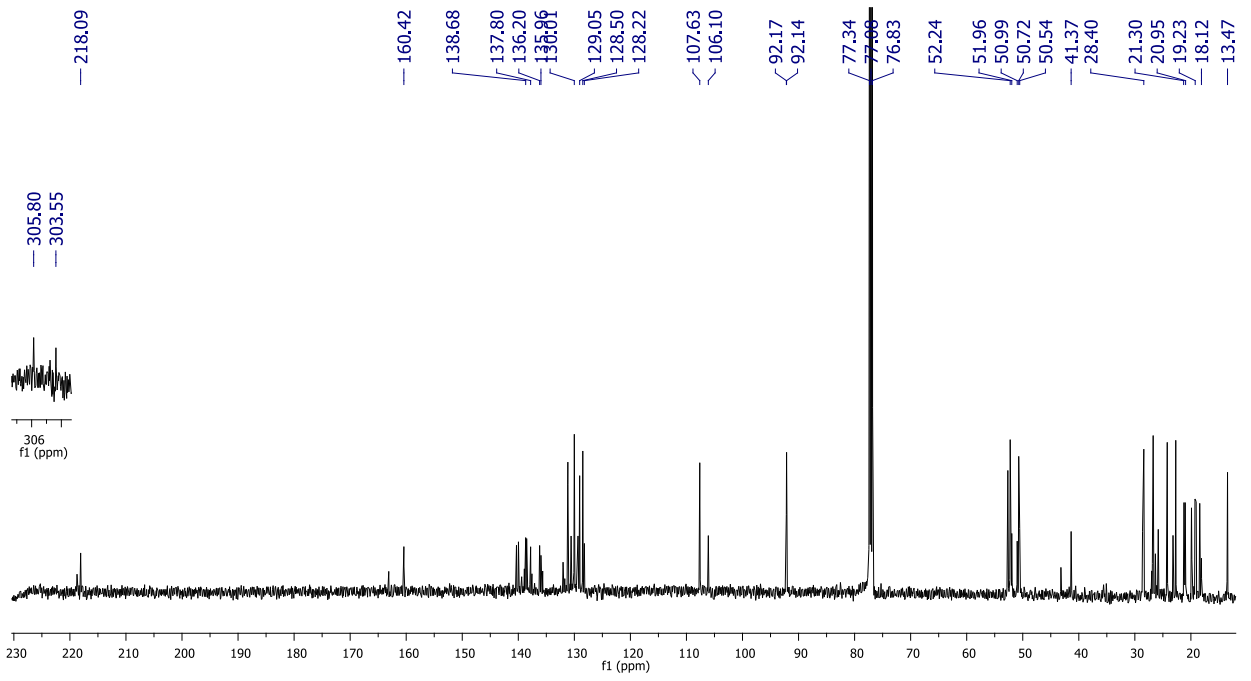

7.26
7.25
7.23
7.08
7.06
7.00
6.99
6.97
6.95
6.69
5.78
4.98
4.95
4.25
4.12
4.11
4.09
4.08
3.92
3.89
2.50
2.44
2.36
2.21
2.19
2.04
1.84
1.25
1.24
1.20
0.79
1.52
7.28
1.09
1.00
1.00
4.81
15.05
1.17
5.60
4.54
3.39
f1 (ppm)

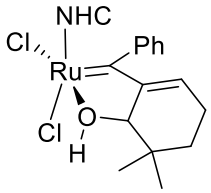

216.84
164.90
155.06
131.25
131.02
130.57
129.30
128.47
127.36
126.09
124.28
112.14
93.60
77.37
77.12
76.87
53.08
51.03
42.75
26.40
21.57
18.98
18.26
285.24
f1 (ppm)
f1 (ppm)


NHC
Cl
nBu
Ru
Cl
O
H

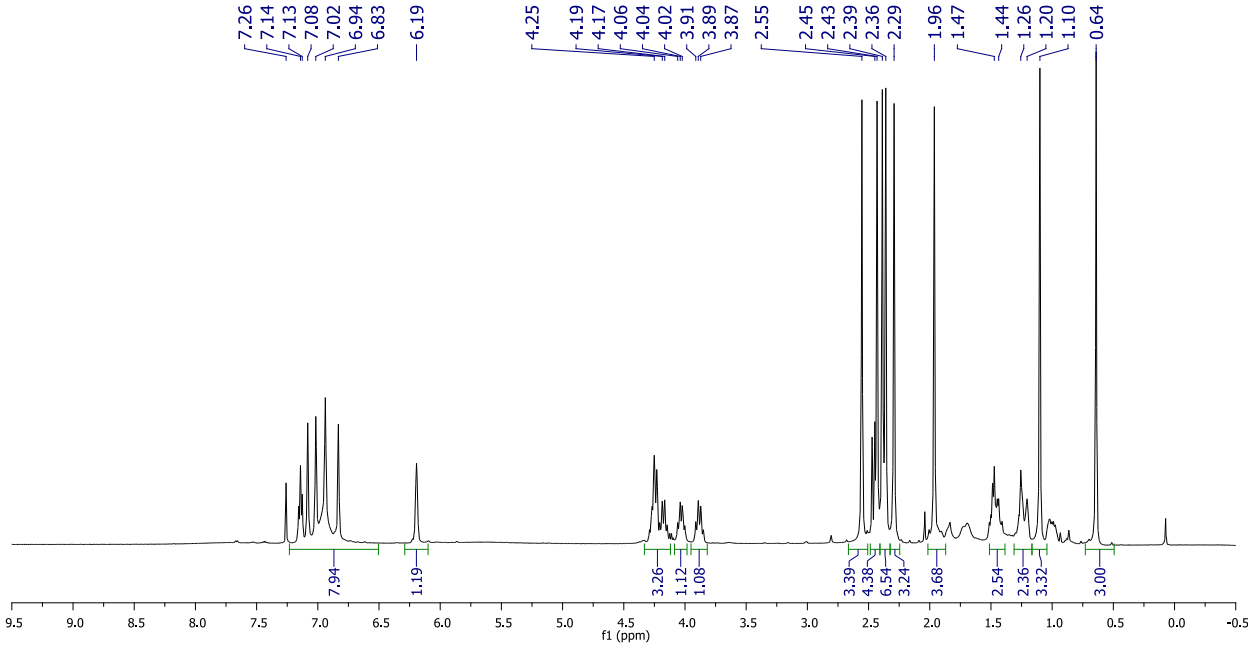
6-14d

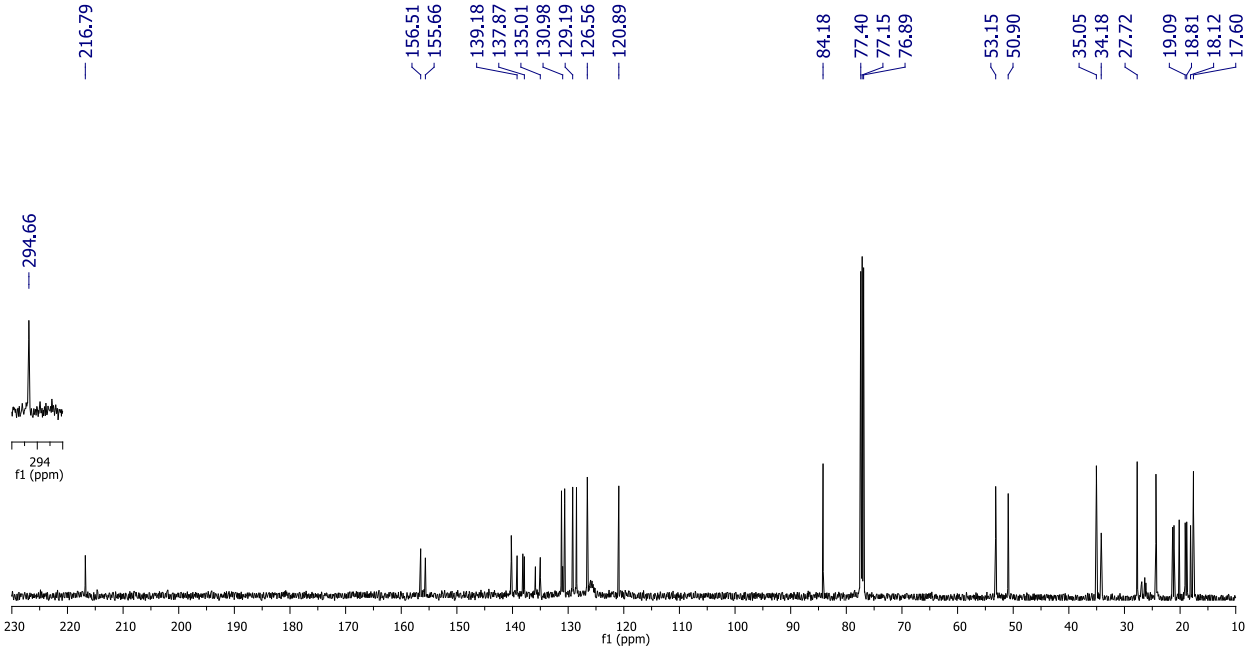

7.26
7.16
6.96
6.81
5.78
4.93
4.93
4.34
4.32
4.09
4.06
3.94
3.33
3.31
3.30
2.76
2.37
2.28
2.07
1.86
1.47
1.25
1.17
1.16
1.13
1.08
0.90
0.80
0.79
0.75
0.73
CH2Cl2
3.78
1.00
1.05
3.98
1.84
5.24
10.97
5.47
1.47
7.22
3.01
3.33
f1 (ppm)

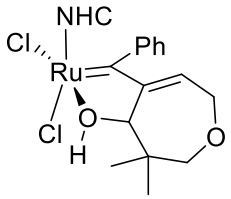

218.09
160.42
138.68
137.80
136.20
130.01
129.05
128.50
128.22
107.63
106.10
92.17
92.14
77.34
77.00
76.83
52.24
51.96
50.99
50.72
50.54
41.37
28.40
21.30
20.95
19.23
18.12
13.47
305.80
303.55
306
f1 (ppm)
f1 (ppm)


NHC
Cl
Ph
Ru
Cl
O
H

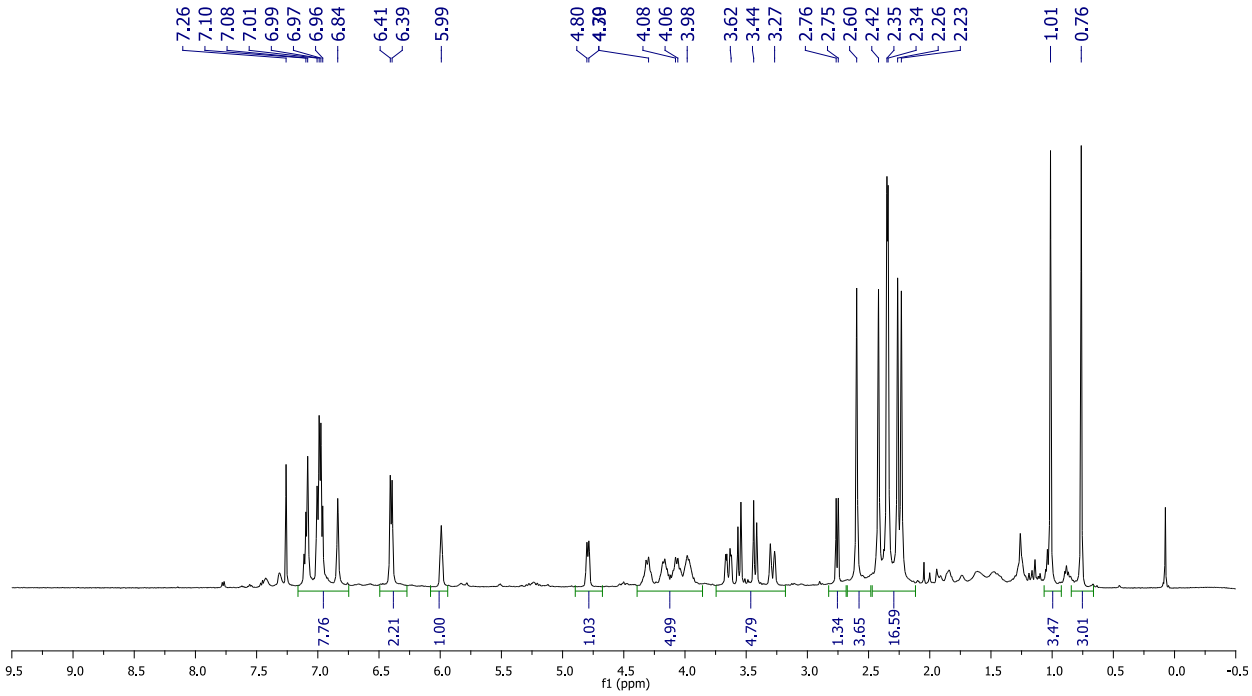
6-14e

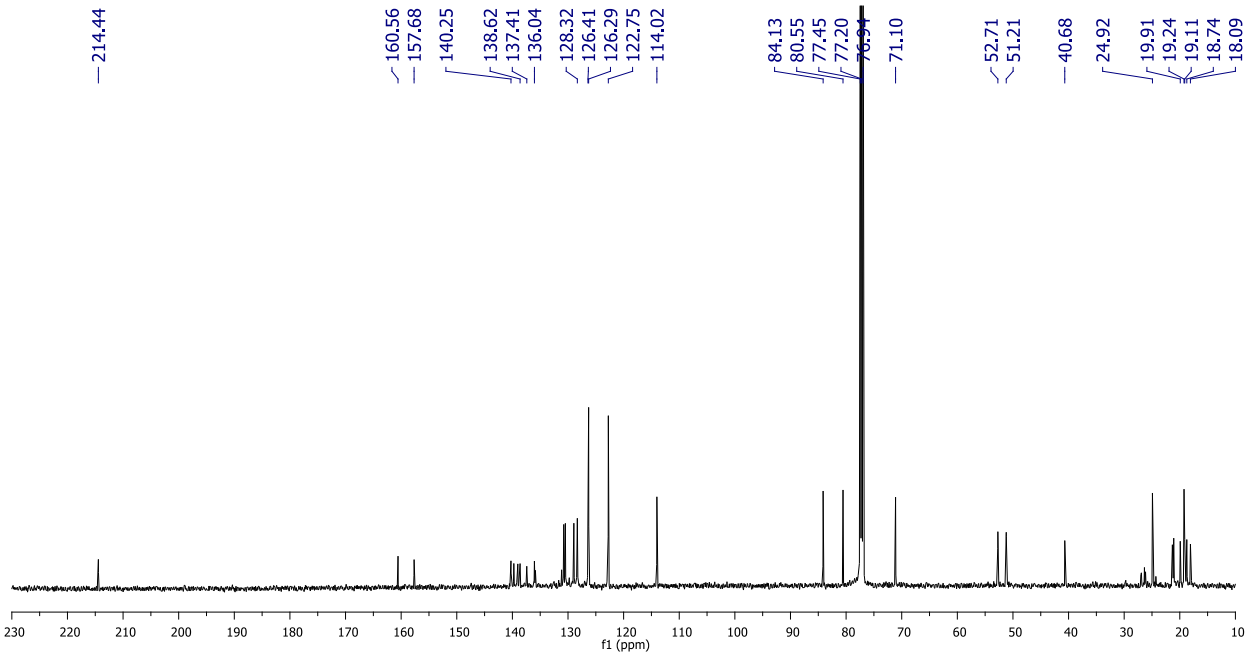

7.26
7.14
7.13
7.08
7.02
6.94
6.83
6.19
4.25
4.19
4.17
4.06
4.04
4.02
3.91
3.89
3.87
2.55
2.45
2.43
2.39
2.36
2.29
1.96
1.47
1.44
1.26
1.20
1.10
0.64
7.94
1.19
3.26
1.12
1.08
3.39
4.38
6.54
3.24
3.68
2.54
2.36
3.32
3.00
f1 (ppm)

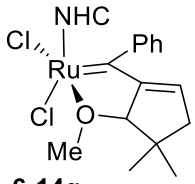

216.79
156.51
155.66
139.18
137.87
135.01
130.98
129.19
126.56
120.89
84.18
77.40
77.15
76.89
53.15
50.90
35.05
34.18
27.72
19.09
18.81
18.12
17.60
294.66
294
f1 (ppm)
f1 (ppm)


NHC
Cl
Ph
Ru
Cl
O
H
O

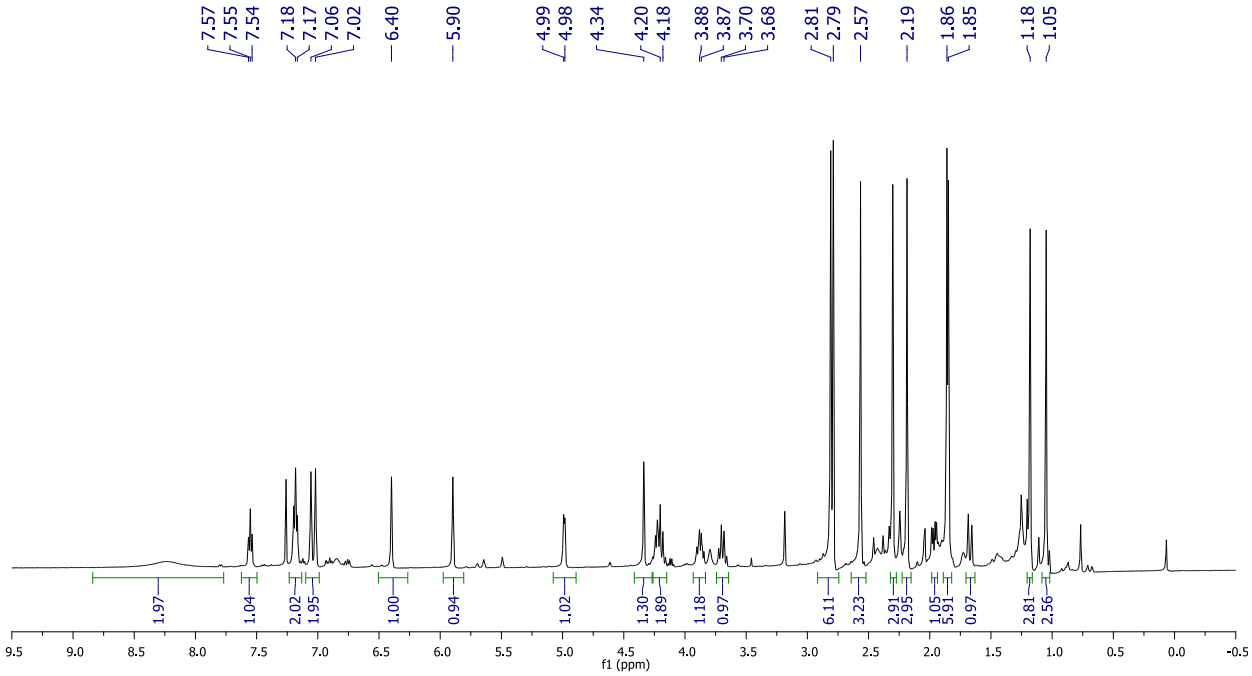
6-14f

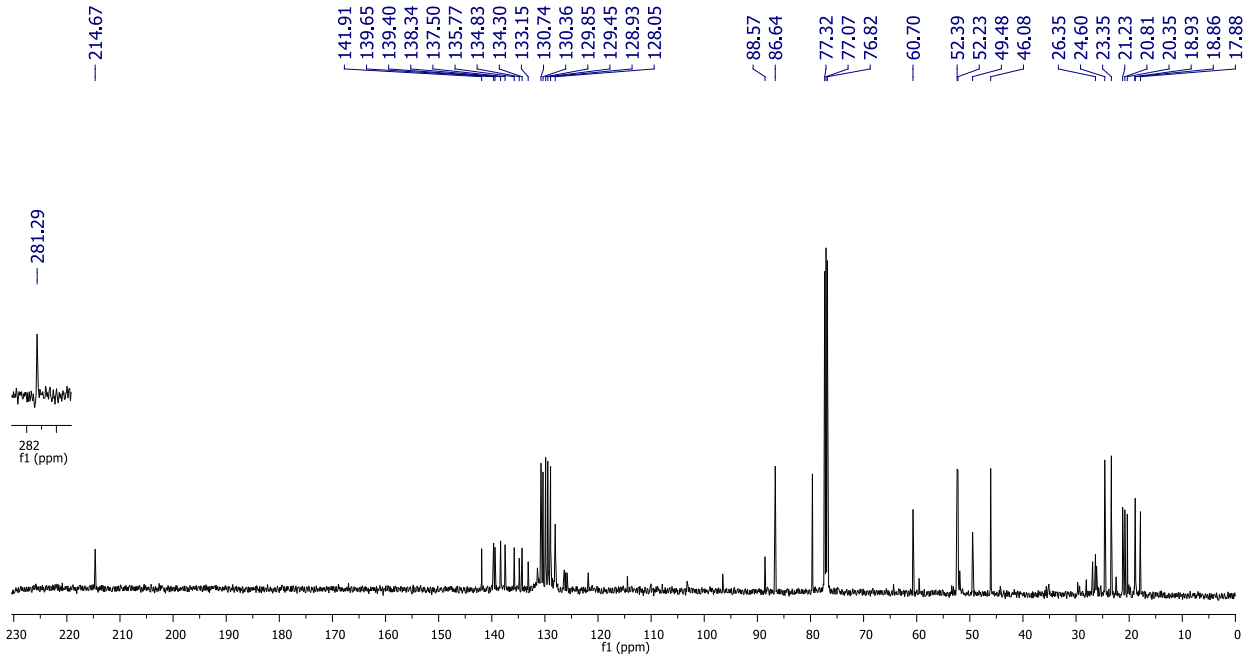

7.26
7.10
7.08
7.01
6.99
6.97
6.96
6.84
6.41
6.39
5.99
4.80
4.08
4.06
3.98
3.62
3.44
3.27
2.76
2.75
2.60
2.42
2.35
2.34
2.26
2.23
1.01
0.76
7.76
2.21
1.00
1.03
4.99
4.79
1.34
3.65
16.59
3.47
3.01
f1 (ppm)


214.44
160.56
157.68
140.25
138.62
137.41
136.04
128.32
126.41
126.29
122.75
114.02
84.13
80.55
77.45
77.20
76.94
71.10
52.71
51.21
40.68
24.92
19.91
19.24
19.11
18.74
18.09
f1 (ppm)


NHC
Cl
Ph
Ru
Cl
O
Me

6-14g


7.57
7.55
7.54
7.18
7.17
7.06
7.02
6.40
5.90
4.99
4.98
4.34
4.20
4.18
3.88
3.87
3.70
3.68
2.81
2.79
2.57
2.19
1.86
1.85
1.18
1.05
1.97
1.04
2.02
1.95
1.00
0.94
1.02
1.30
1.89
1.18
0.97
6.11
3.23
2.91
2.95
1.05
5.91
0.97
2.81
2.56
f1 (ppm)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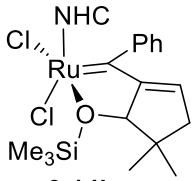
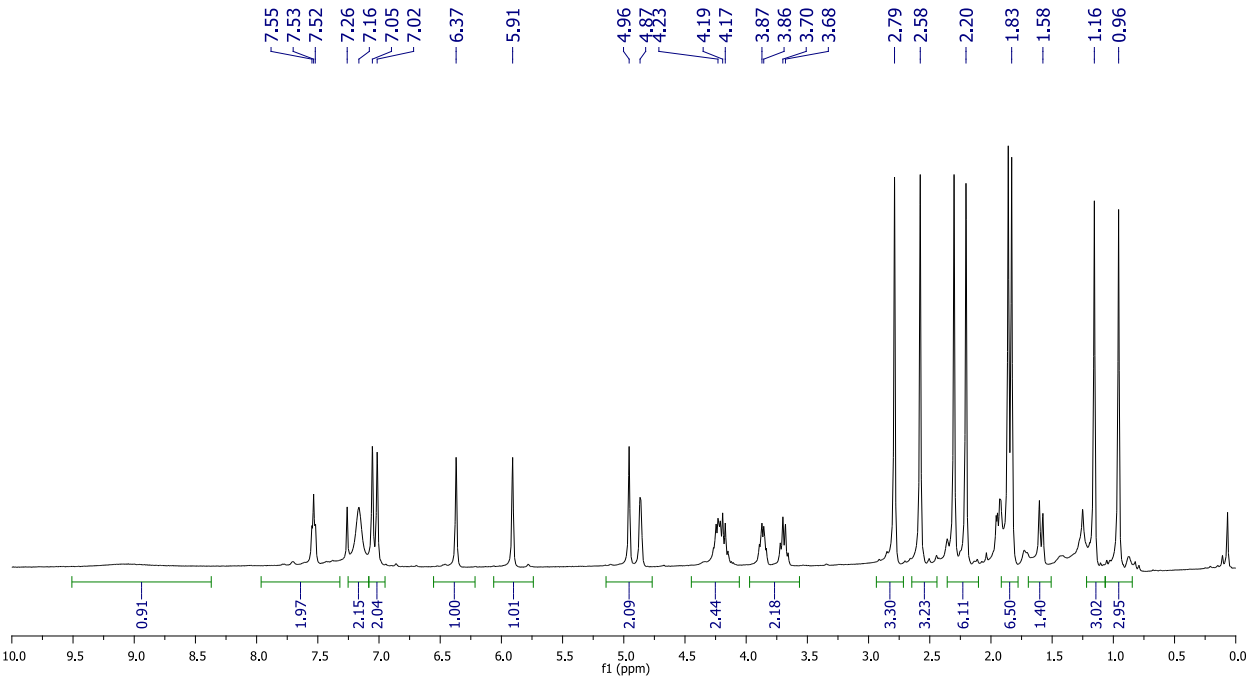
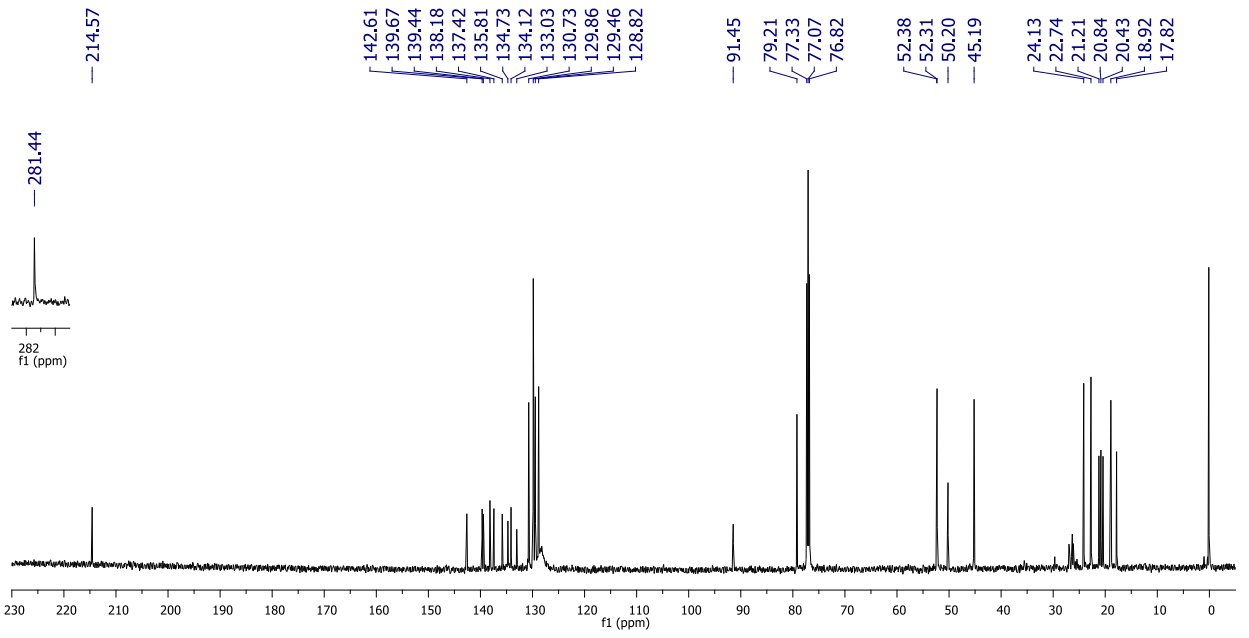
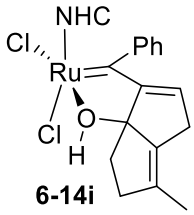
141.91
139.65
139.40
138.34
137.50
135.77
134.83
134.30
133.15
130.74
130.36
129.85
129.45
128.93
128.05
88.57
86.64
77.32
77.07
76.82
60.70
52.39
52.23
49.48
46.08
26.35
24.60
23.35
21.23
20.81
20.35
18.93
18.86
17.88
281.29
282
f1 (ppm)
f1 (ppm)


NHC
Cl
Ph
Ru
Cl
O
Me3Si

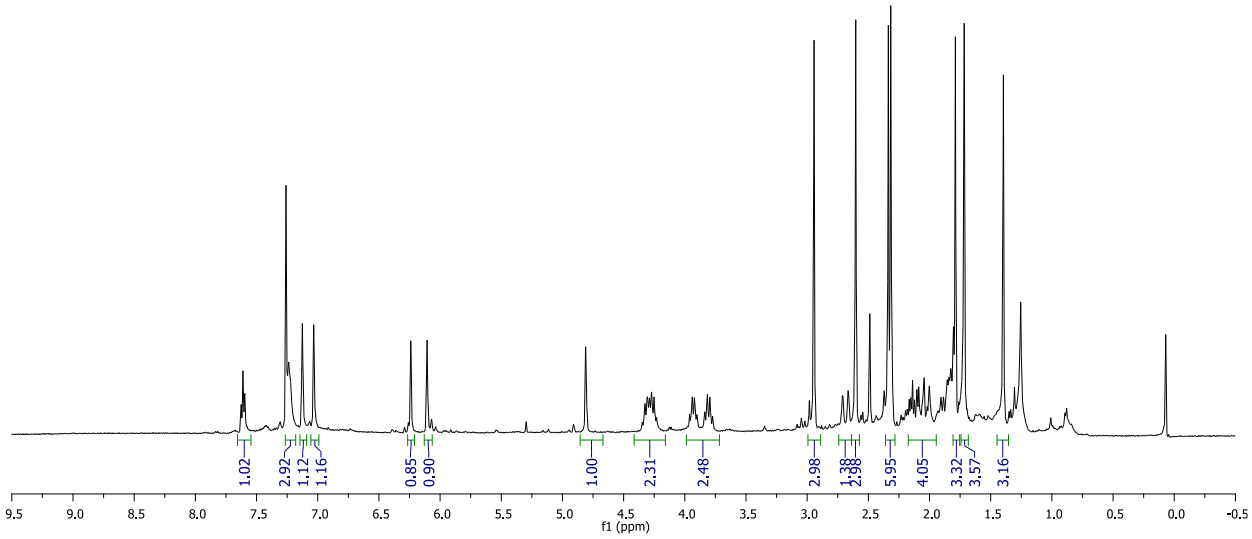
6-14h

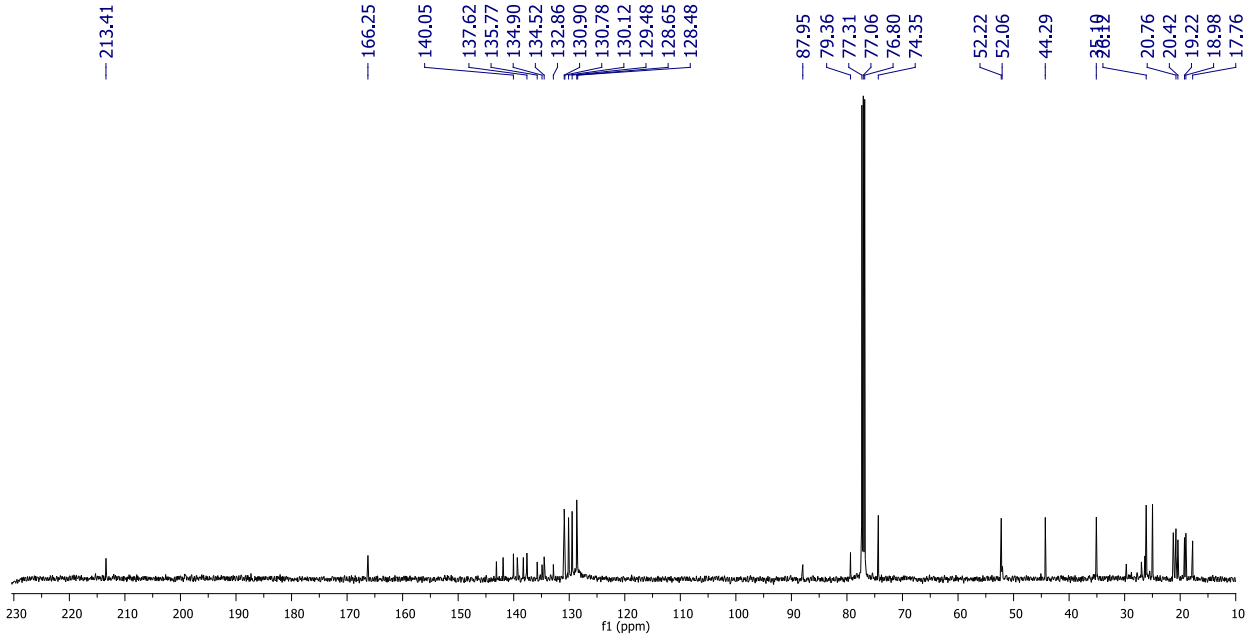

7.55
7.53
7.52
7.26
7.16
7.05
7.02
6.37
5.91
4.96
4.87
4.23
4.19
4.17
3.87
3.86
3.70
3.68
2.79
2.58
2.20
1.83
1.58
1.16
0.96
0.91
1.97
2.15
2.04
1.00
1.01
2.09
2.44
2.18
3.30
3.23
6.11
6.50
1.40
3.02
2.95
f1 (ppm)

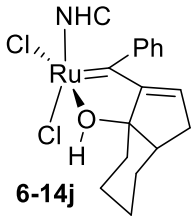

214.57
142.61
139.67
139.44
138.18
137.42
135.81
134.73
134.12
133.03
130.73
129.86
129.46
128.82
91.45
79.21
77.33
77.07
76.82
52.38
52.31
50.20
45.19
24.13
22.74
21.21
20.84
20.43
18.92
17.82
281.44
282
f1 (ppm)
f1 (ppm)


NHC
Cl
Ph
Ru
Cl
O
H

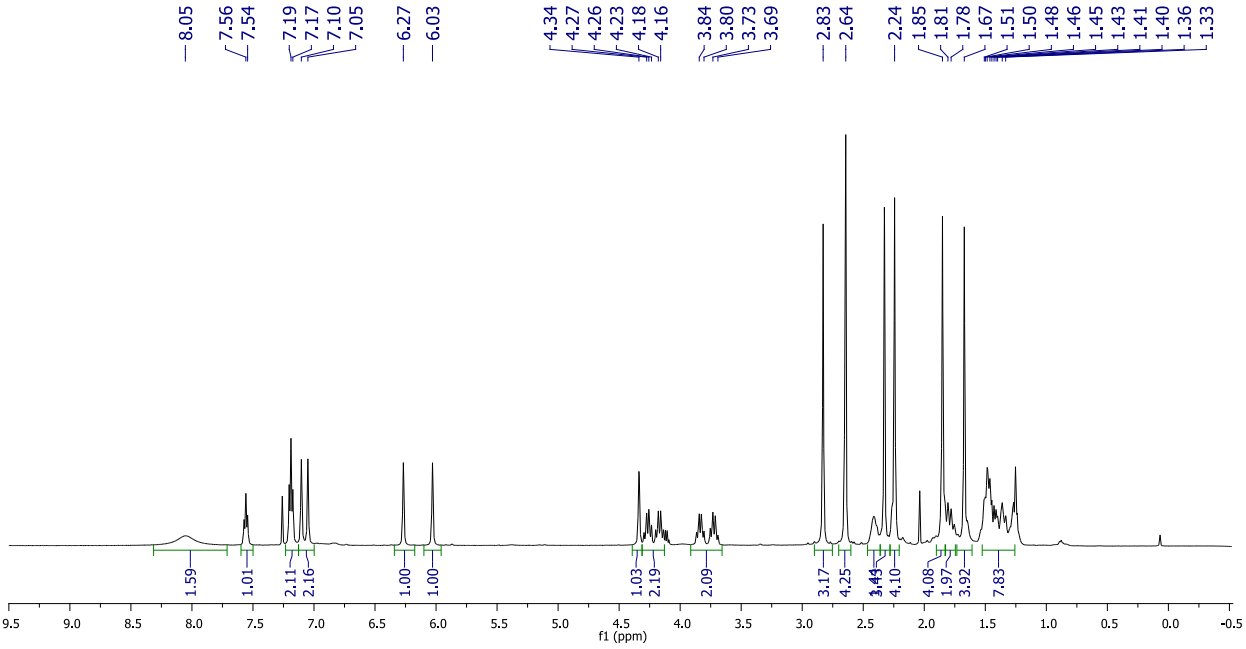
6-14i

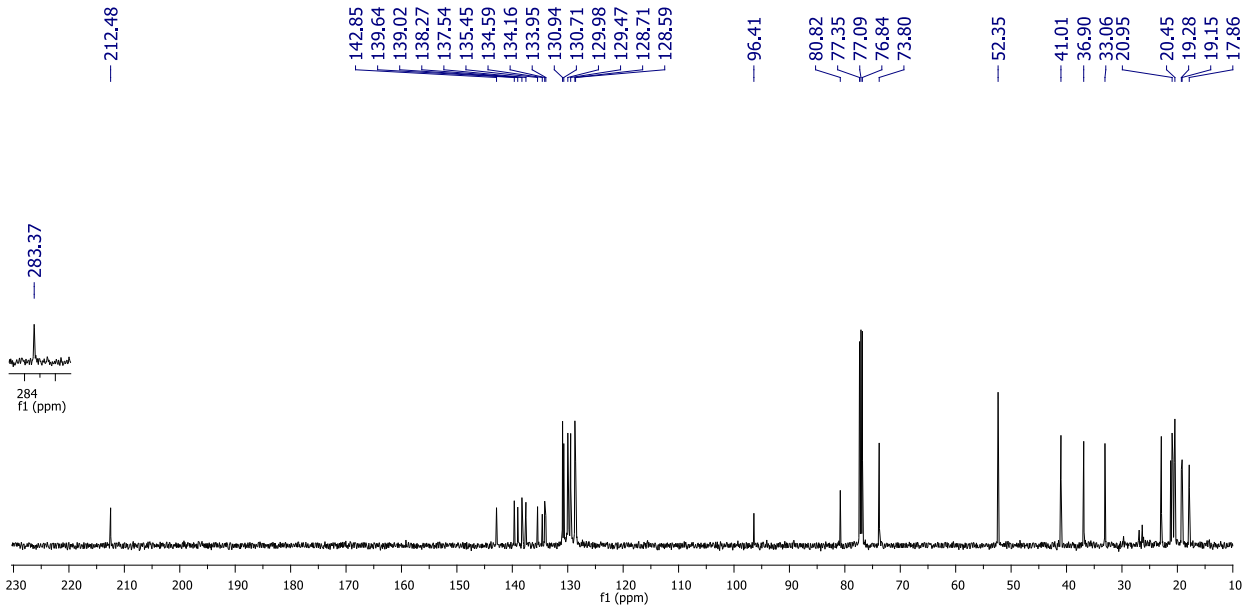

1.02
2.92
1.12
1.16
0.85
0.90
1.00
2.31
2.48
2.98
1.38
1.98
5.95
4.05
3.32
3.57
3.16
f1 (ppm)

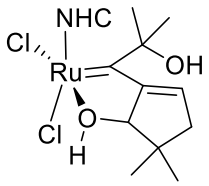

213.41
166.25
140.05
137.62
135.77
134.90
134.52
132.86
130.90
130.78
130.12
129.48
128.65
128.48
87.95
79.36
77.31
77.06
76.80
74.35
52.22
52.06
44.29
20.76
20.42
19.22
18.98
17.76
f1 (ppm)


NHC
Cl
Ph
Ru
Cl
O
H

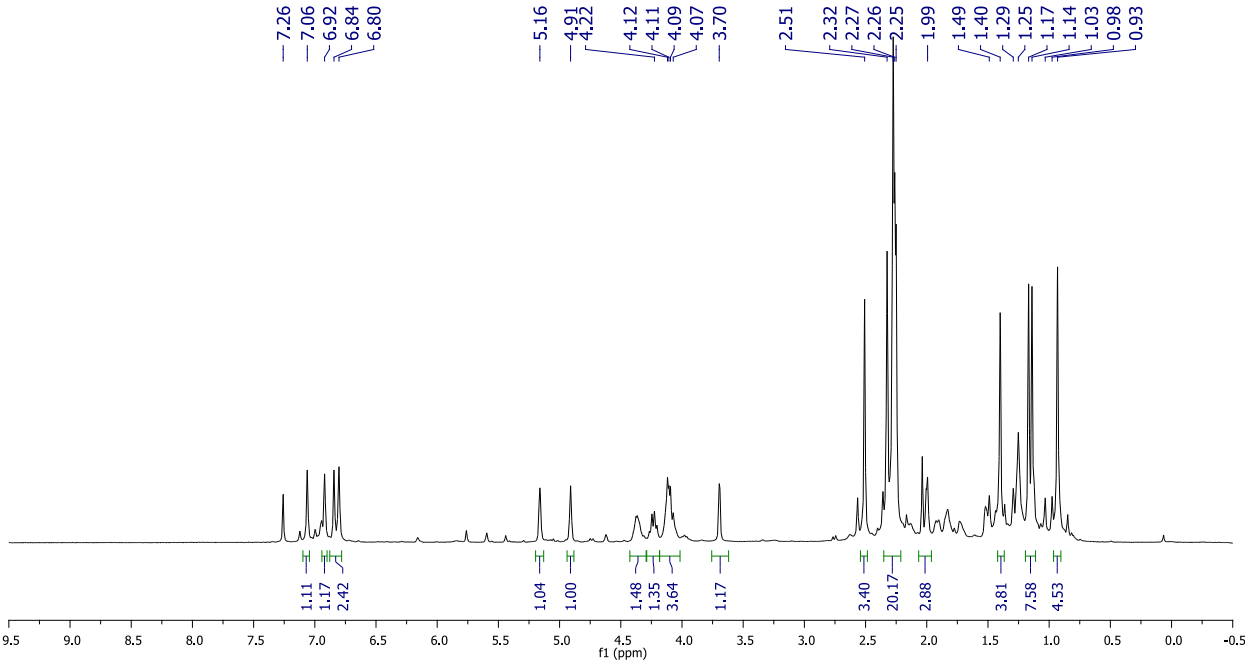
6-14j

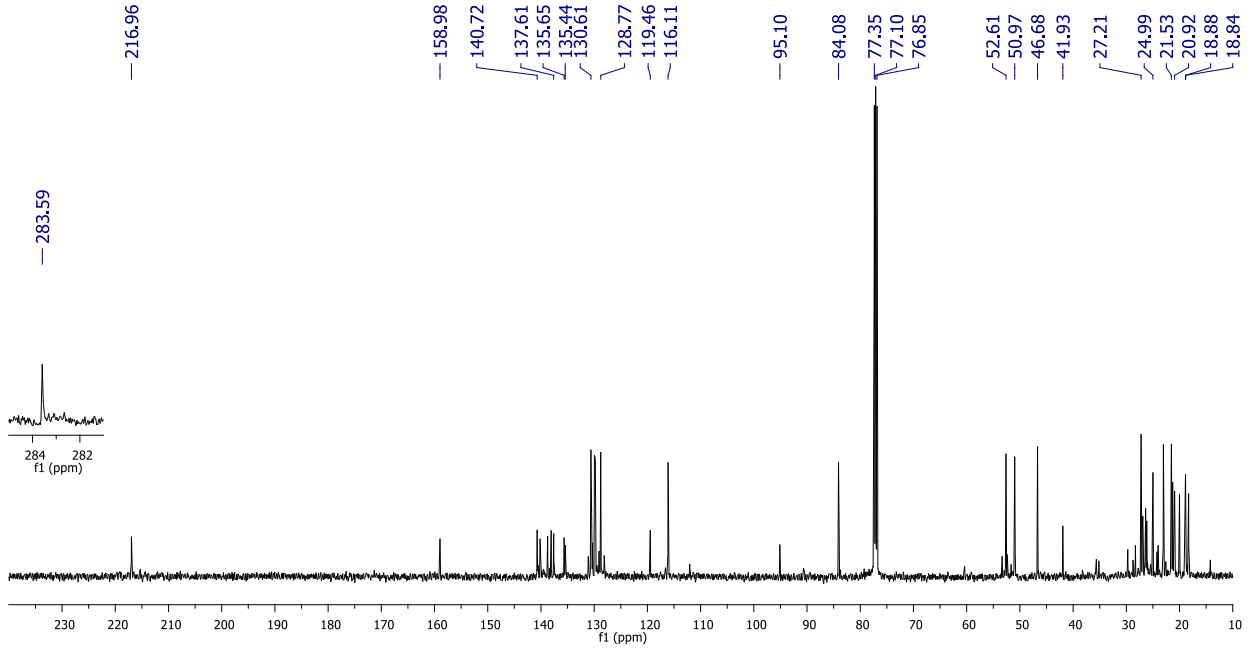

8.05
7.56
7.54
7.19
7.17
7.10
7.05
6.27
6.03
4.34
4.27
4.26
4.23
4.18
4.16
3.84
3.80
3.73
3.69
2.83
2.64
2.24
1.85
1.81
1.78
1.67
1.51
1.50
1.48
1.46
1.45
1.43
1.41
1.40
1.36
1.33
1.59
1.01
2.11
2.16
1.00
1.00
1.03
2.19
2.09
3.17
4.25
4.10
4.08
1.97
3.92
7.83
f1 (ppm)


212.48
142.85
139.64
139.02
138.27
137.54
135.45
134.59
134.16
133.95
130.94
130.71
129.98
129.47
128.71
128.59
96.41
80.82
77.35
77.09
76.84
73.80
52.35
41.01
36.90
33.06
20.95
20.45
19.28
19.15
17.86
283.37
284
f1 (ppm)
f1 (ppm)


NHC
Cl
Ru
OH
Cl
O
H

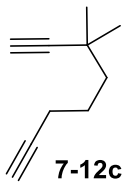
6-14k


7.26
7.06
6.92
6.84
6.80
5.16
4.91
4.22
4.12
4.11
4.09
4.07
3.70
2.51
2.32
2.27
2.26
2.25
1.99
1.49
1.40
1.29
1.25
1.17
1.14
1.03
0.98
0.93
1.11
1.17
2.42
1.04
1.00
1.48
1.35
3.64
1.17
3.40
20.17
2.88
3.81
7.58
4.53
f1 (ppm)

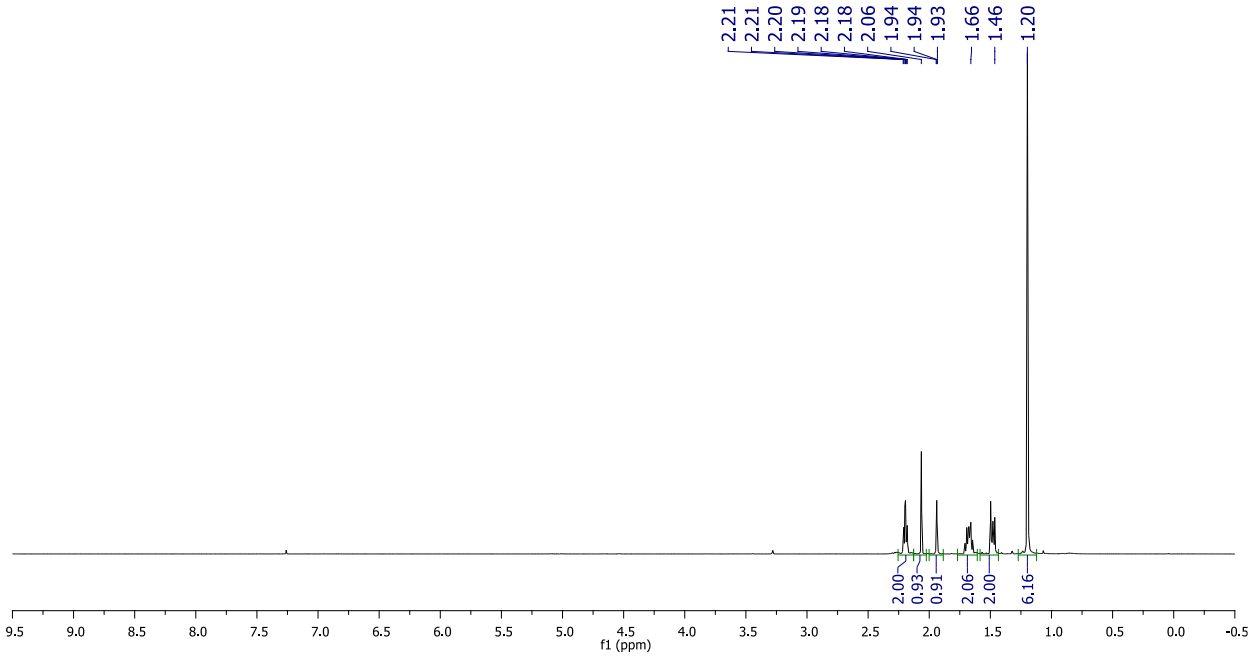

216.96
158.98
140.72
137.61
135.65
135.44
130.61
128.77
119.46
116.11
95.10
84.08
77.35
77.10
76.85
52.61
50.97
46.68
41.93
27.21
24.99
21.53
20.92
18.88
18.84
283.59
284
282
f1 (ppm)
f1 (ppm)

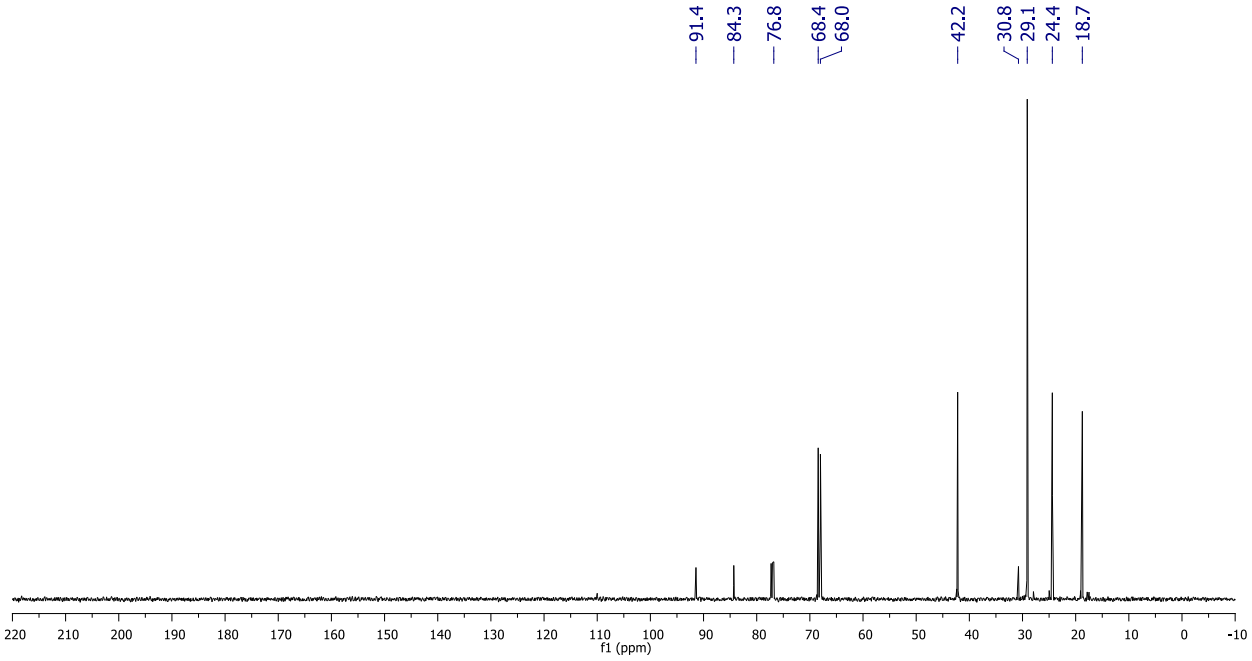
Appendix VII

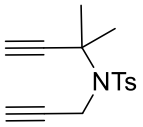
Selected NMR Spectra for Chapter 7



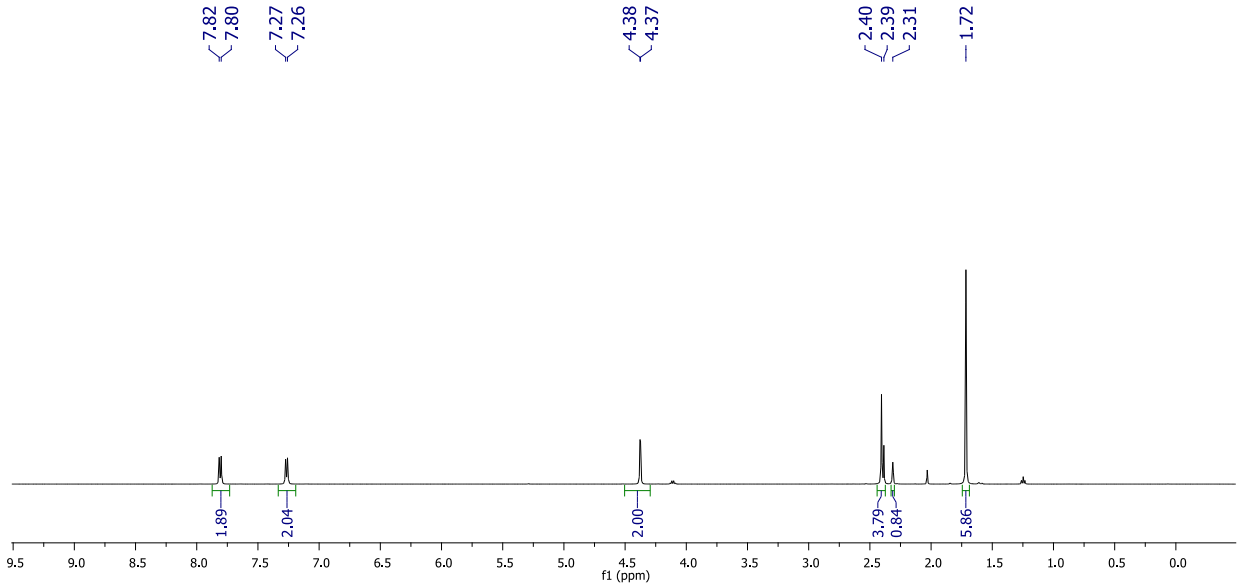
7-12c

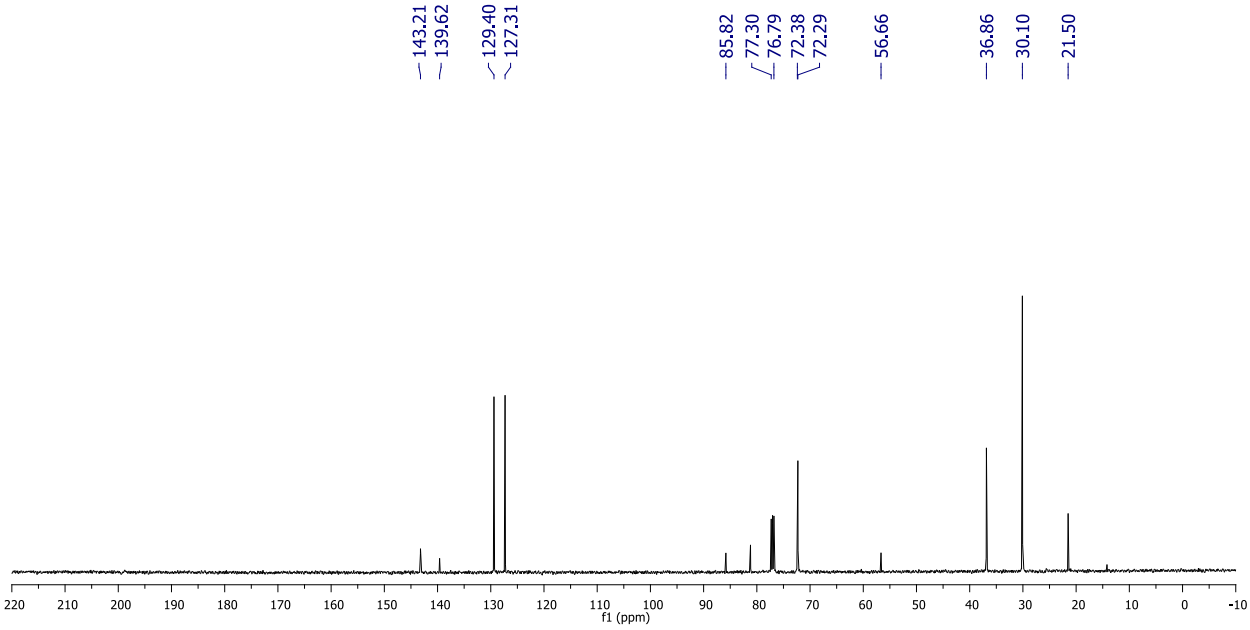

2.21
2.21
2.20
2.19
2.18
2.18
2.06
1.94
1.94
1.93
1.66
1.46
1.20
2.00
0.93
0.91
2.06
2.00
6.16
f1 (ppm)

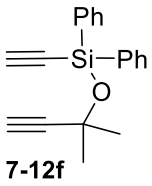

91.4
84.3
76.8
68.4
68.0
42.2
30.8
29.1
24.4
18.7
f1 (ppm)


NTs

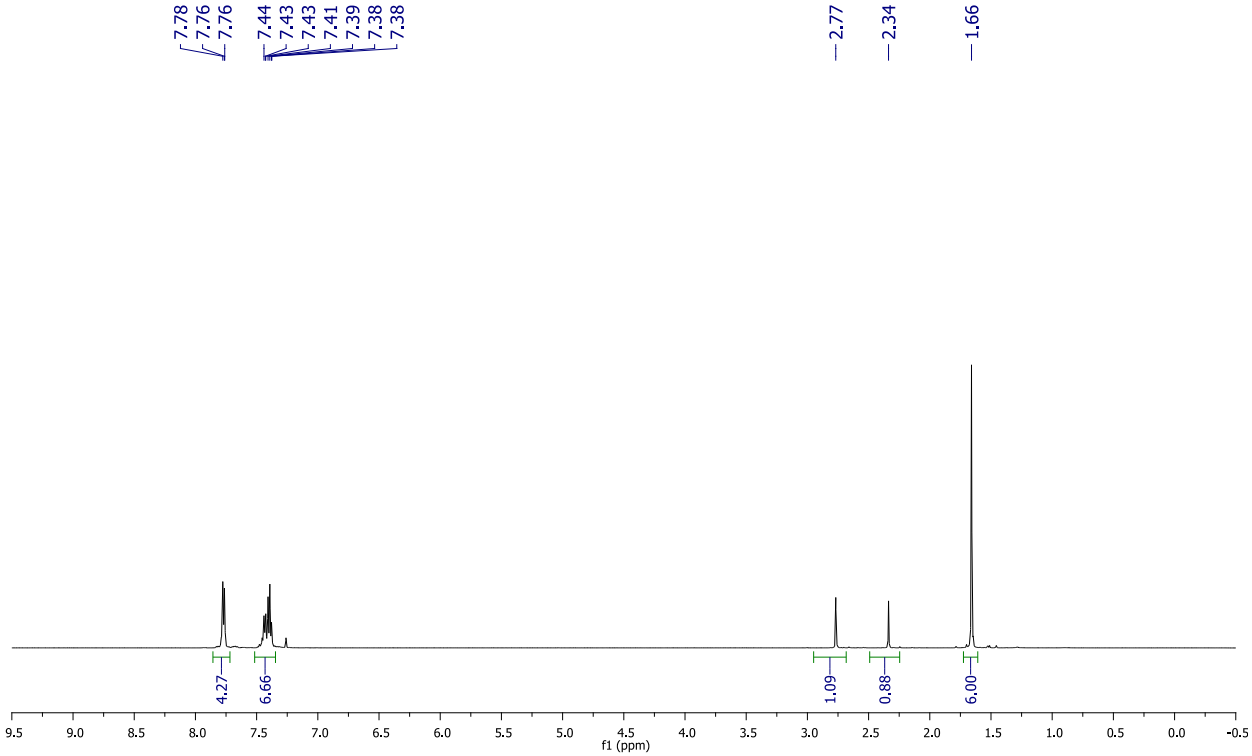
7-12d

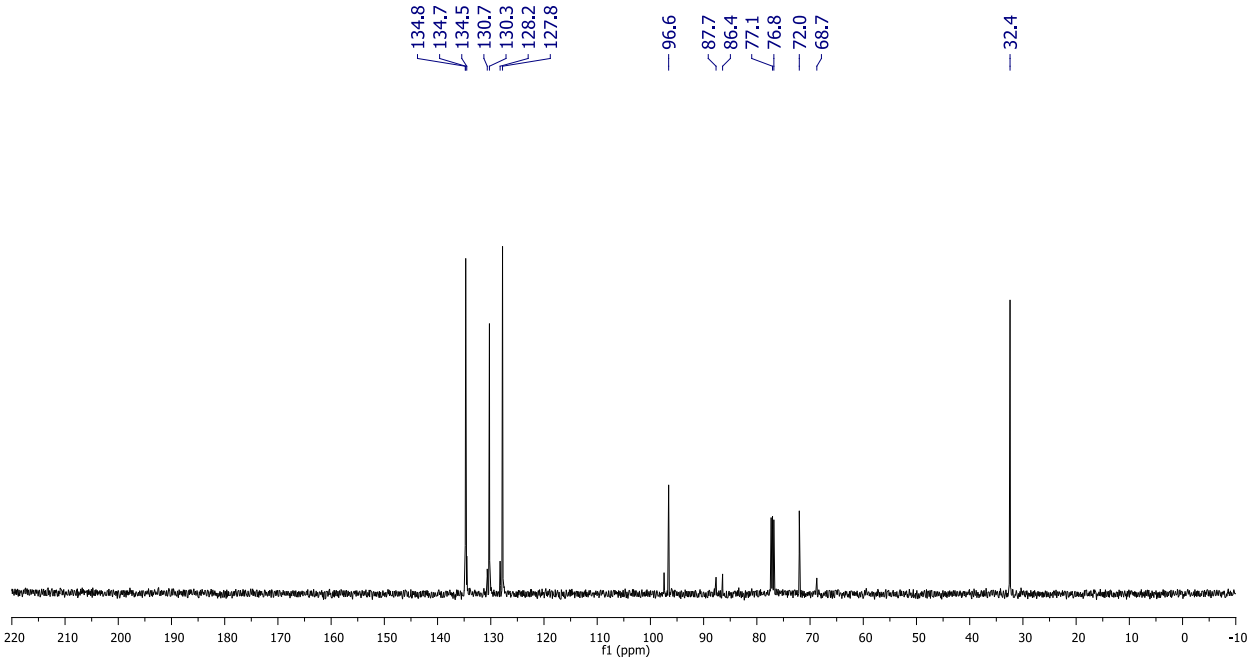

7.82
7.80
7.27
7.26
4.38
4.37
2.40
2.39
2.31
1.72
1.89
2.04
2.00
3.79
0.84
5.86
f1 (ppm)

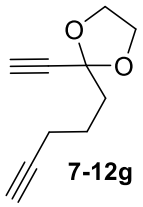

143.21
139.62
129.40
127.31
85.82
77.30
76.79
72.38
72.29
56.66
36.86
30.10
21.50
f1 (ppm)


Ph
Si
Ph
O

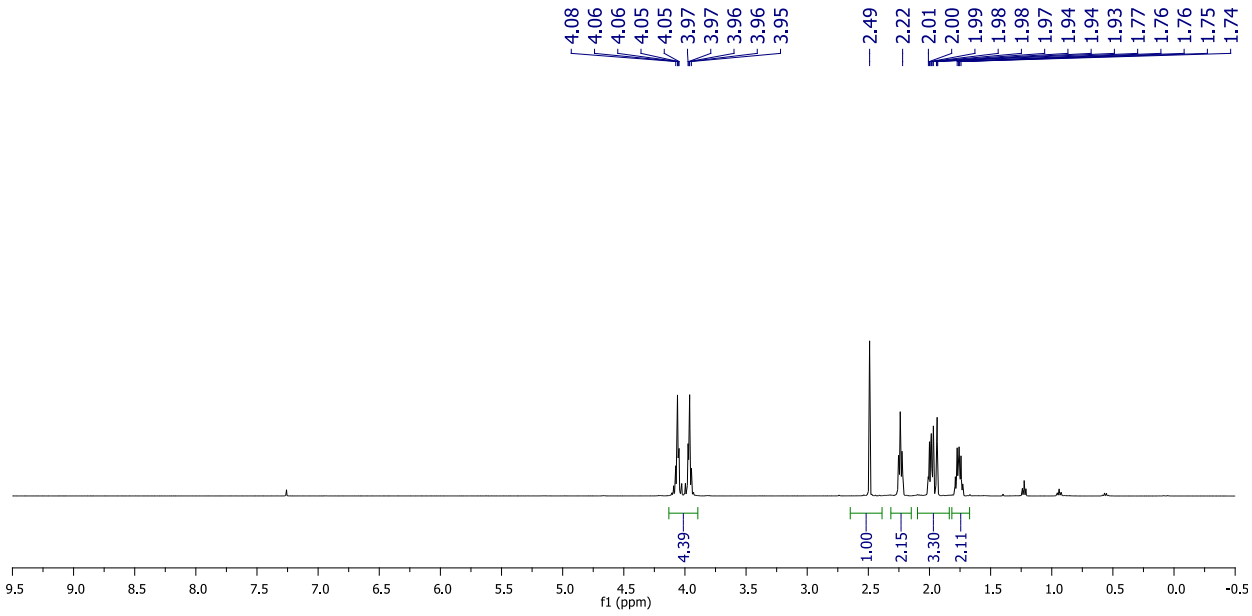
7-12f

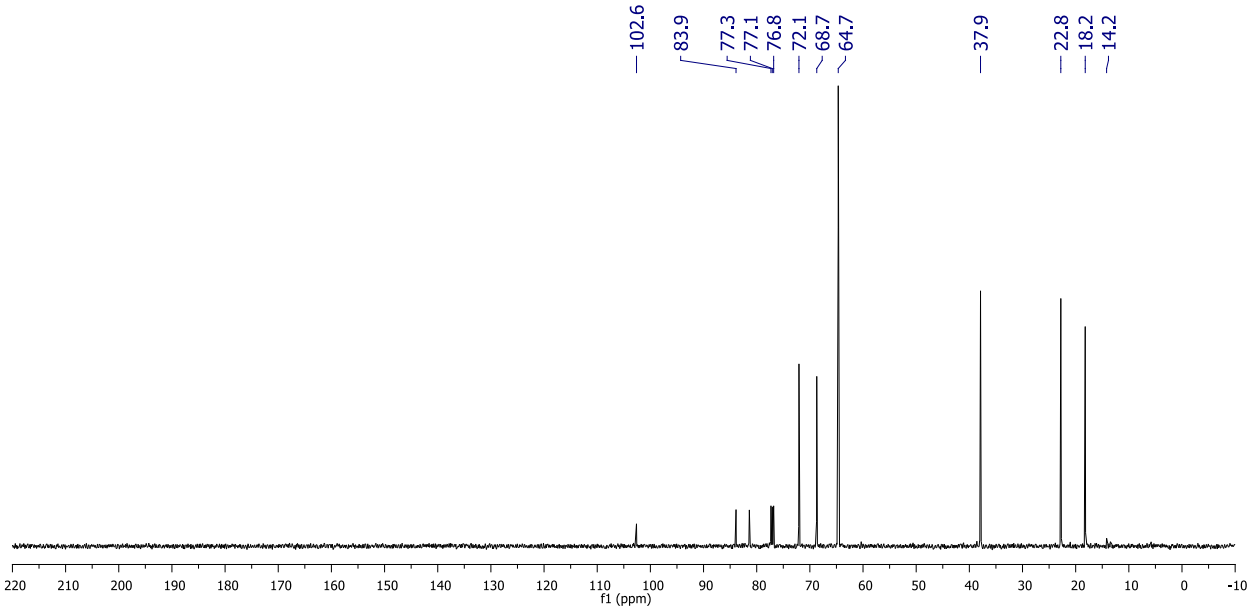

7.78
7.76
7.76
7.44
7.43
7.43
7.41
7.39
7.38
7.38
2.77
2.34
1.66
4.27
6.66
1.09
0.88
6.00
f1 (ppm)

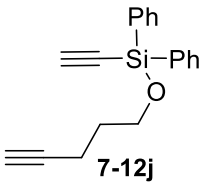

134.8
134.7
134.5
130.7
130.3
128.2
127.8
96.6
87.7
86.4
77.1
76.8
72.0
68.7
32.4
f1 (ppm)


O
O

7-12g

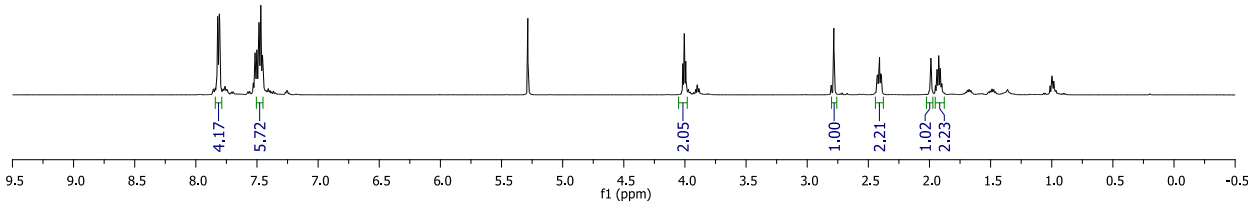

4.08
4.06
4.06
4.05
4.05
3.97
3.97
3.96
3.96
3.95
2.49
2.22
2.01
2.00
1.99
1.98
1.98
1.97
1.94
1.94
1.93
1.77
1.76
1.76
1.75
1.74
4.39
1.00
2.15
3.30
2.11
f1 (ppm)


102.6
83.9
77.3
77.1
76.8
72.1
68.7
64.7
37.9
22.8
18.2
14.2
f1 (ppm)

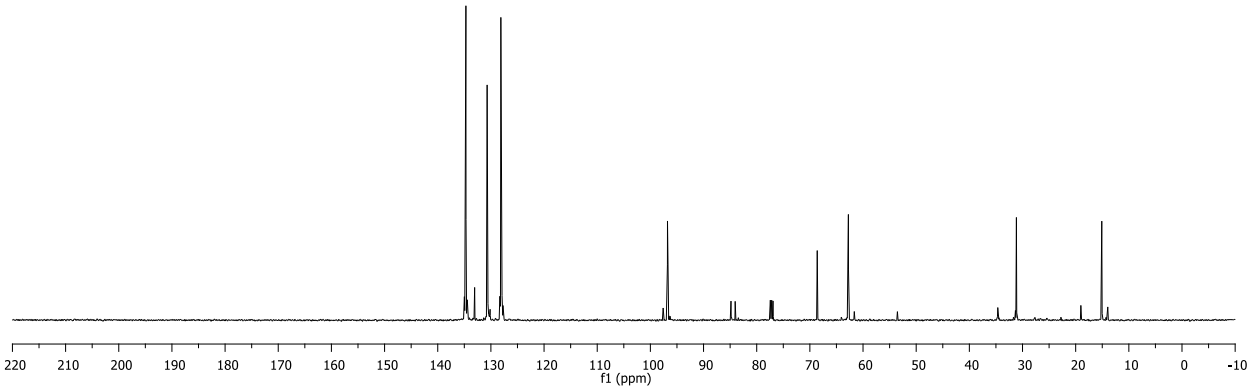

Ph
Si
Ph
O

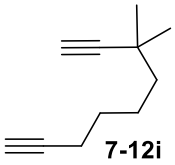
7-12j

7.82
7.82
7.81
7.81
7.52
7.50
7.50
7.48
7.47
7.46
7.45
5.29
4.02
4.01
3.99
2.78
2.39
1.99
1.99
1.98
1.94
1.92
1.91

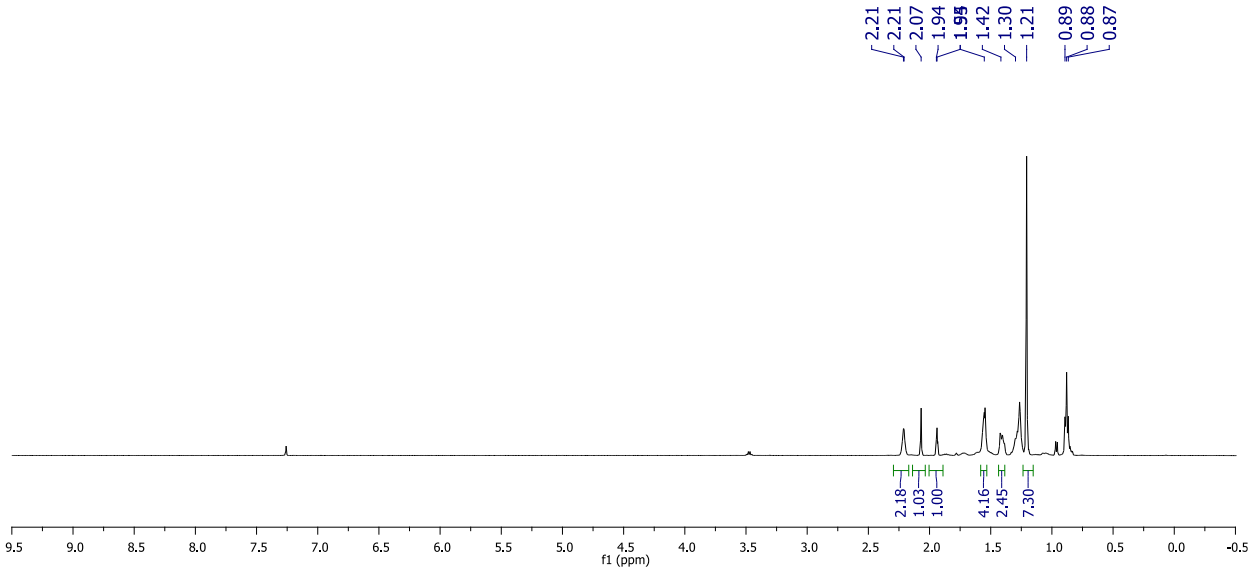

4.17
5.72
2.05
1.00
2.21
1.02
2.23
f1 (ppm)

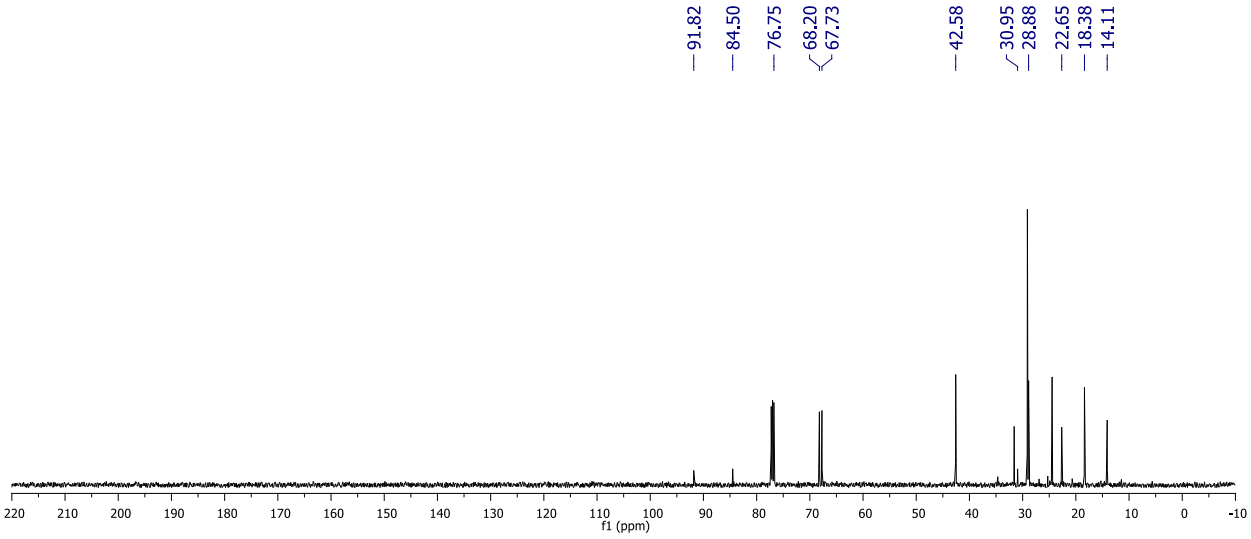
134.7
133.1
130.7
128.1
96.8
84.8
84.0
76.9
68.6
62.8
31.1
15.1

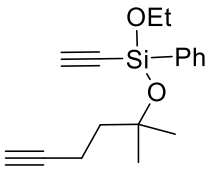

f1 (ppm)



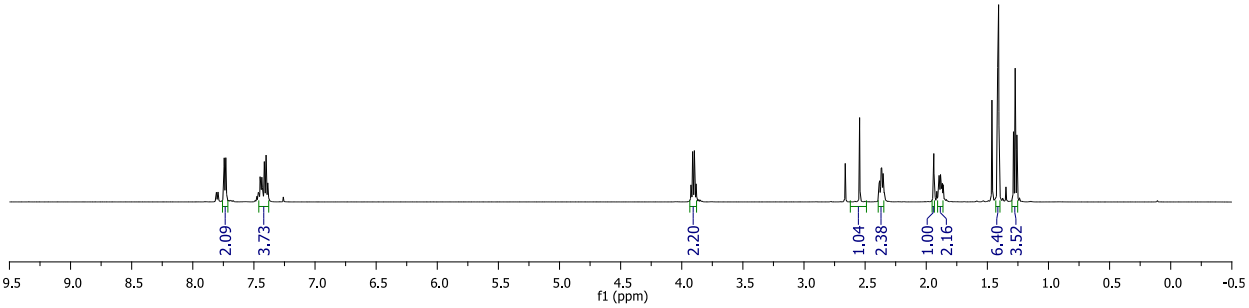
7-12i

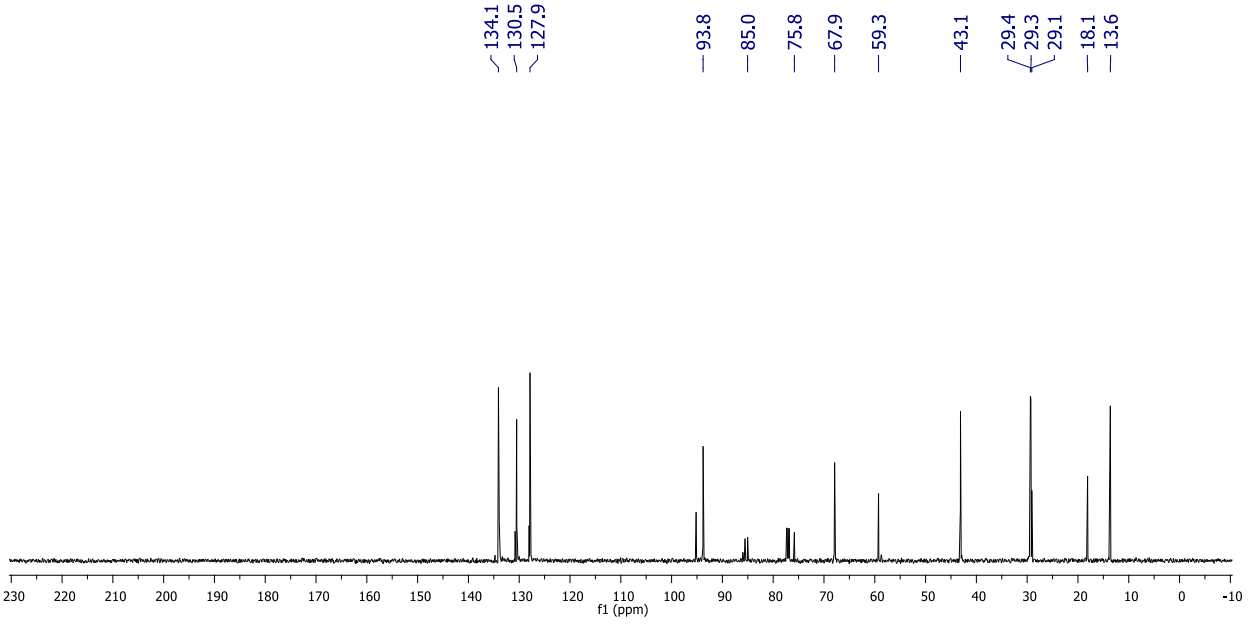

2.21
2.21
2.07
1.94
1.42
1.30
1.21
0.89
0.88
0.87
2.18
1.03
1.00
4.16
2.45
7.30
f1 (ppm)

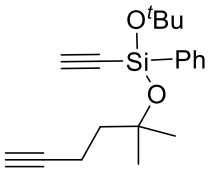

91.82
84.50
76.75
68.20
67.73
42.58
30.95
28.88
22.65
18.38
14.11
f1 (ppm)


OEt
Si
Ph
O

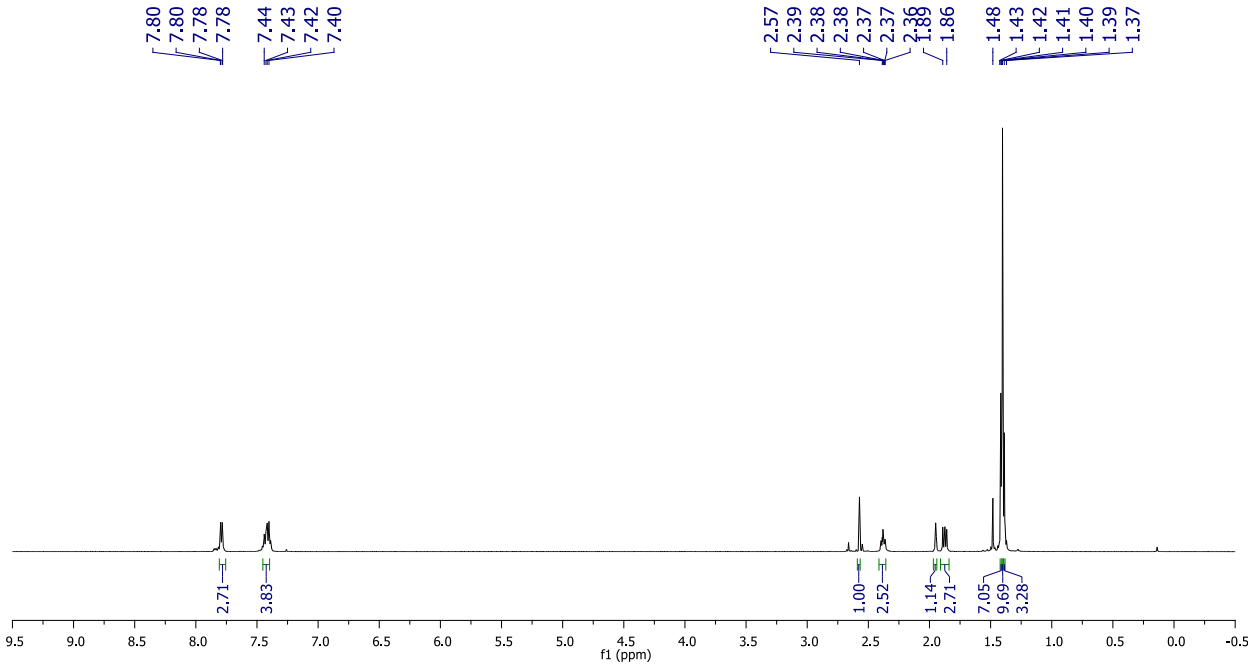
7-12k

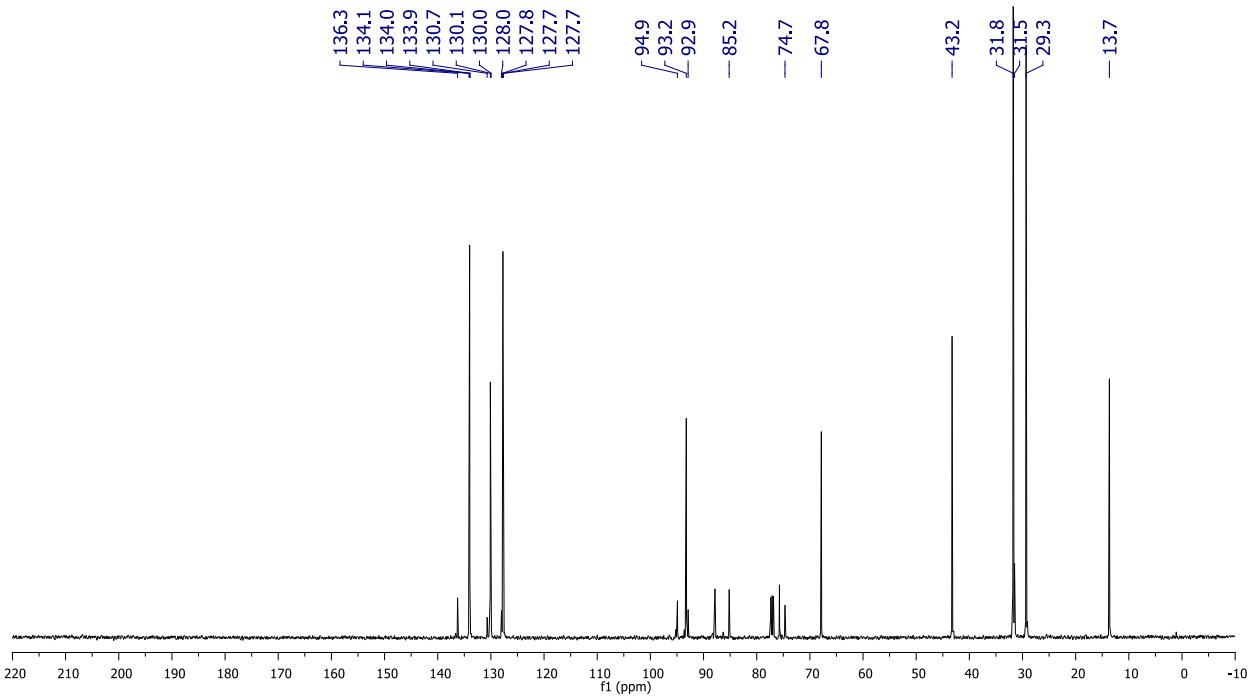

2.09
3.73
2.20
1.04
2.38
1.00
2.16
6.40
3.52
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

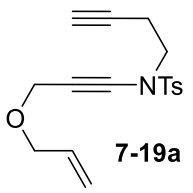

134.1
130.5
127.9
93.8
85.0
75.8
67.9
59.3
43.1
29.4
29.3
29.1
18.1
13.6
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


O^{t}Bu
Si
Ph
O

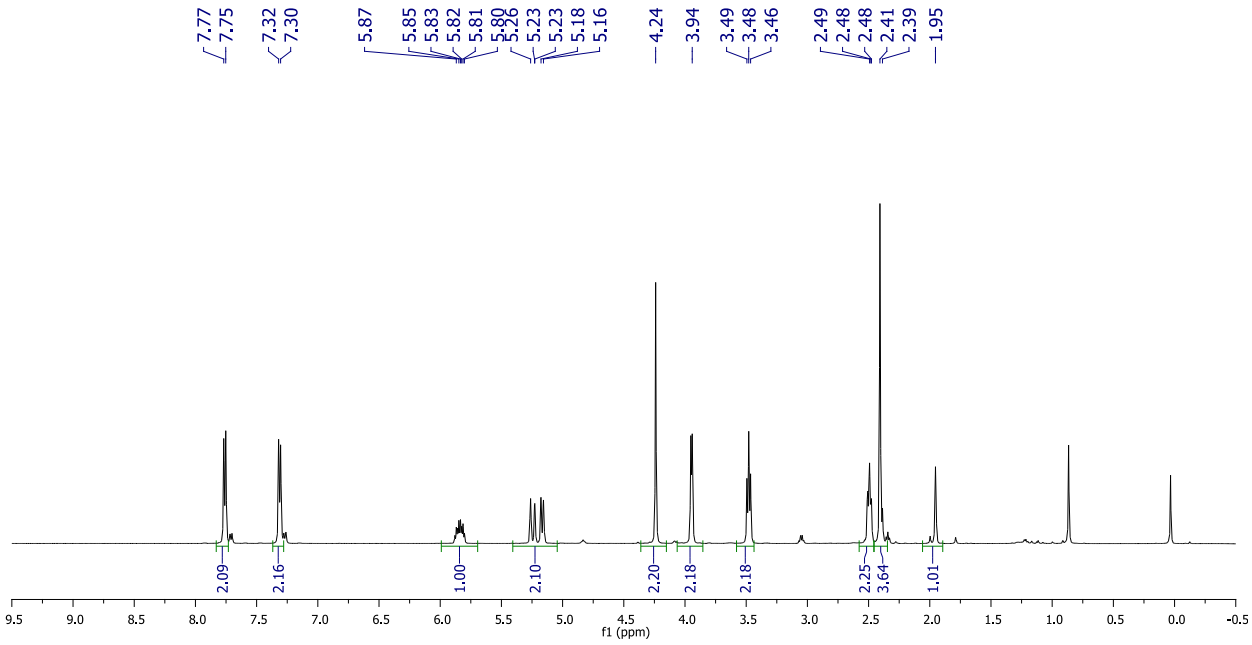
7-12l

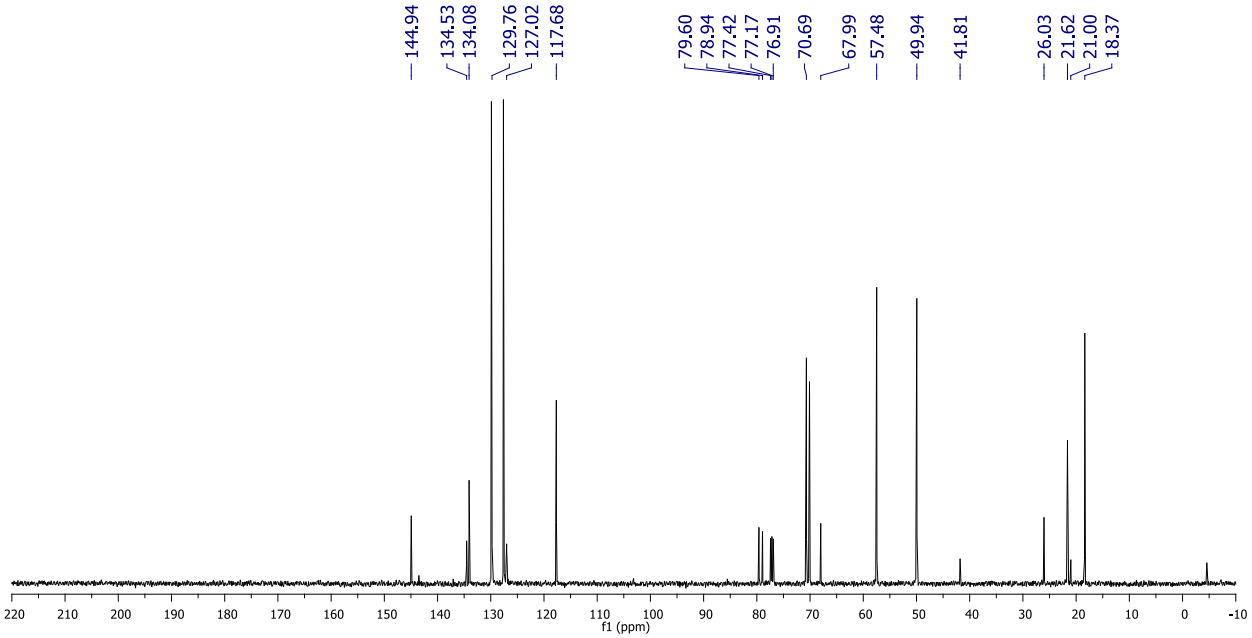

7.80
7.80
7.78
7.78
7.44
7.43
7.42
7.40
2.57
2.39
2.38
2.38
2.37
2.37
2.36
1.89
1.86
1.48
1.43
1.42
1.41
1.40
1.39
1.37
2.71
3.83
1.00
2.52
1.14
2.71
7.05
9.69
3.28
f1 (ppm)

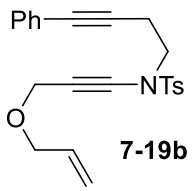

136.3
134.1
134.0
133.9
130.7
130.1
130.0
128.0
127.8
127.7
127.7
94.9
93.2
92.9
85.2
74.7
67.8
43.2
31.8
31.5
29.3
13.7
f1 (ppm)


NTs
O

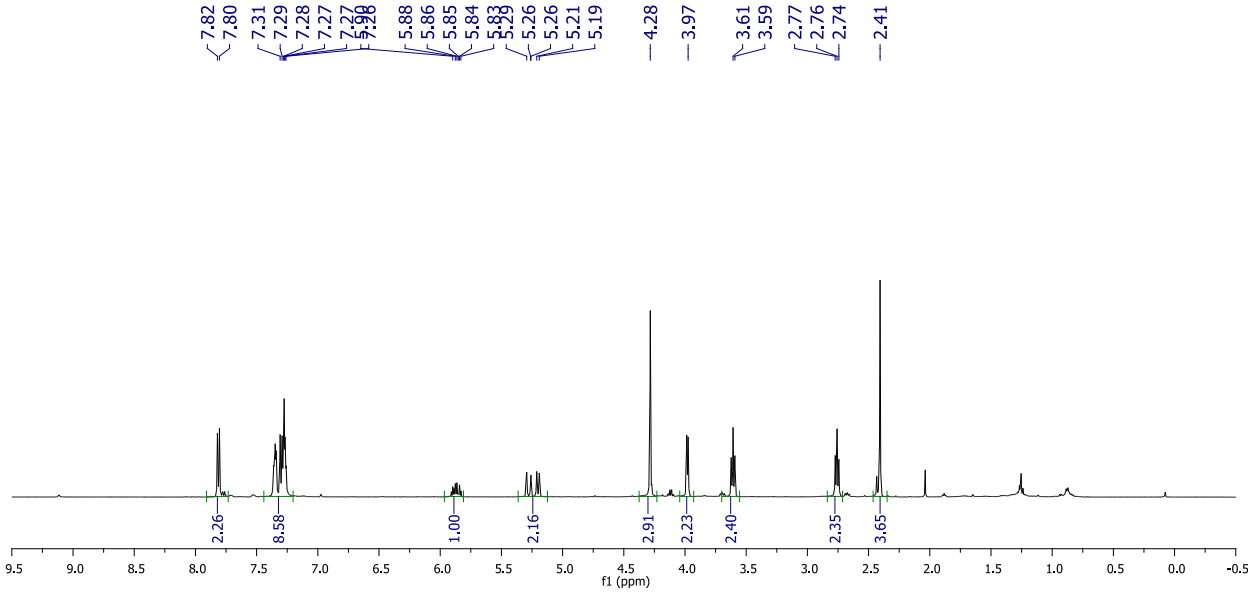
7-19a

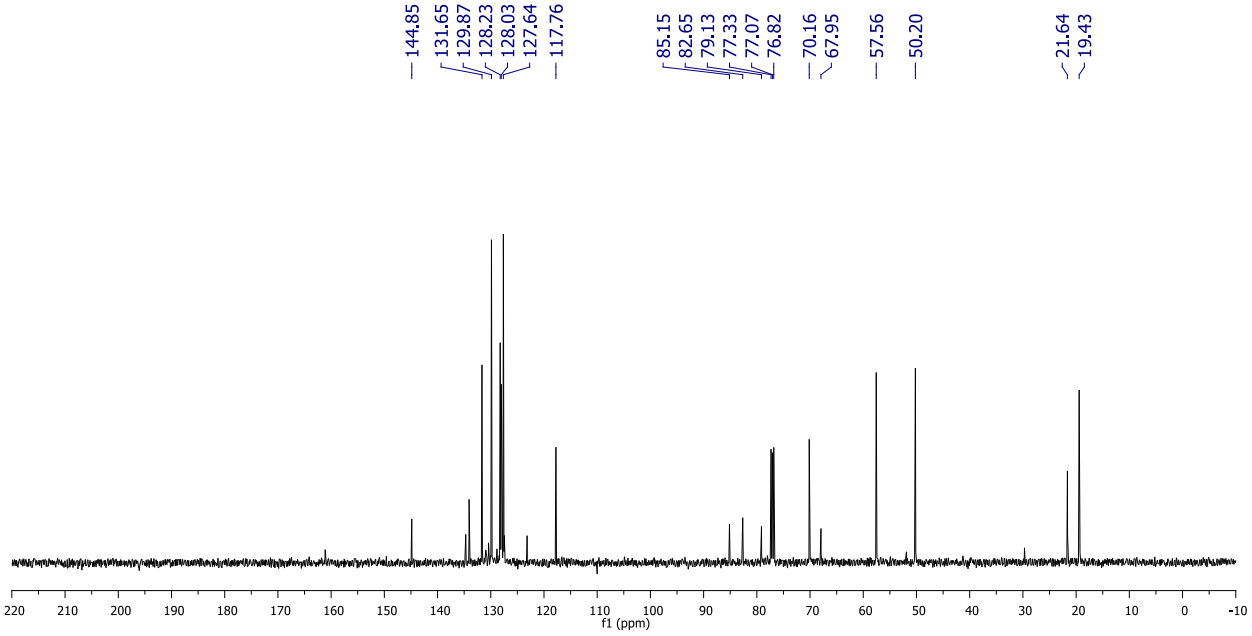

7.77
7.75
7.32
7.30
5.87
5.85
5.83
5.82
5.81
5.80
5.26
5.23
5.23
5.18
5.16
4.24
3.94
3.49
3.48
3.46
2.49
2.48
2.48
2.41
2.39
1.95
2.09
2.16
1.00
2.10
2.20
2.18
2.18
2.25
3.64
1.01
f1 (ppm)

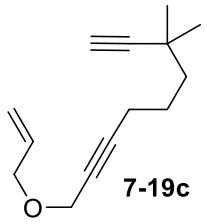

144.94
134.53
134.08
129.76
127.02
117.68
79.60
78.94
77.42
77.17
76.91
70.69
67.99
57.48
49.94
41.81
26.03
21.62
21.00
18.37
f1 (ppm)


Ph
NTs
O

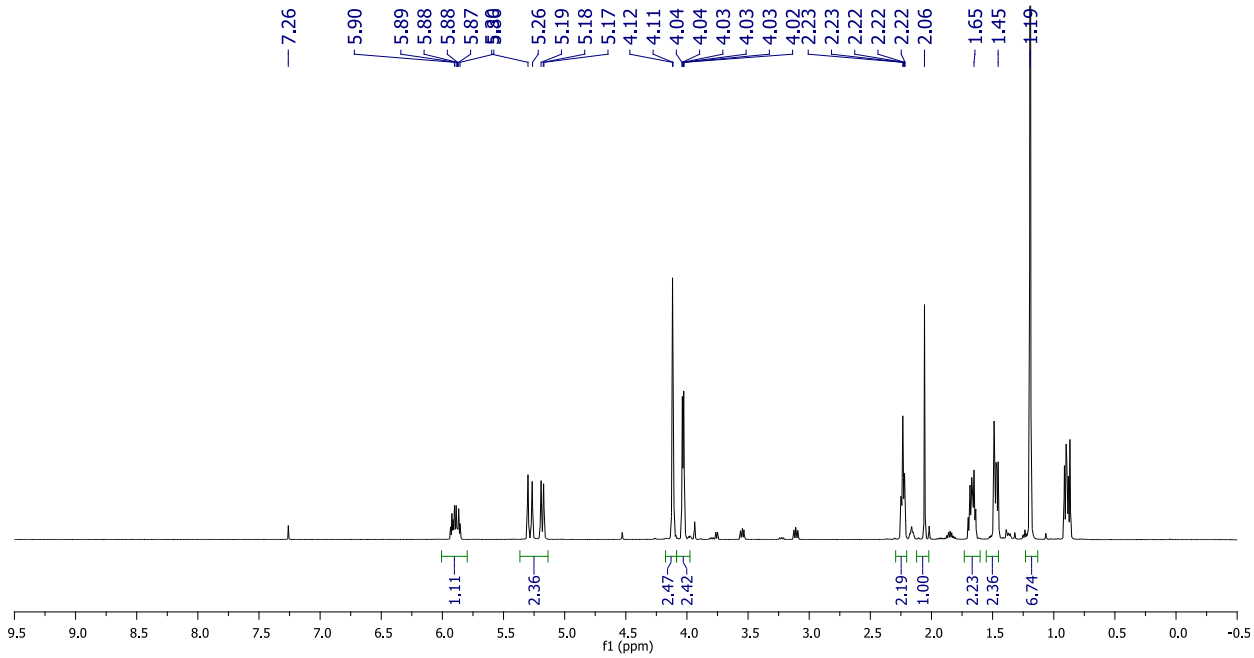
7-19b

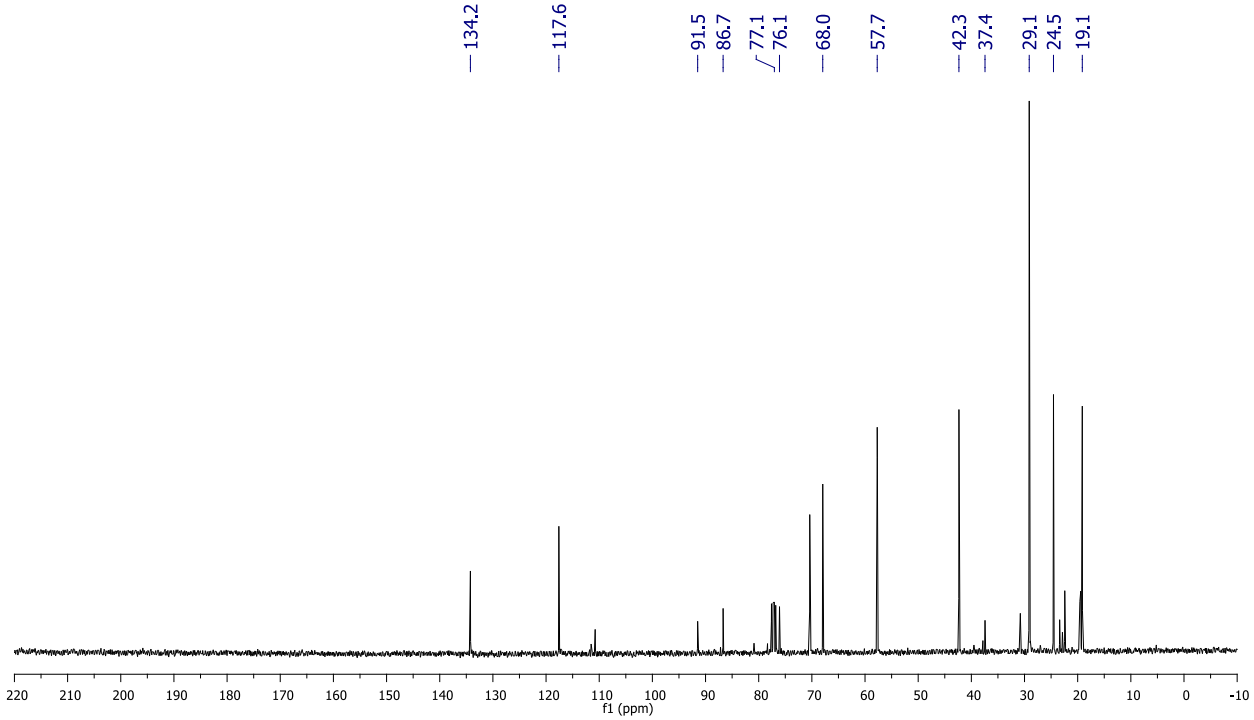

7.82
7.80
7.31
7.29
7.28
7.27
5.88
5.86
5.85
5.84
5.26
5.26
5.21
5.19
4.28
3.97
3.61
3.59
2.77
2.76
2.74
2.41
2.26
8.58
1.00
2.16
2.91
2.23
2.40
2.35
3.65
f1 (ppm)

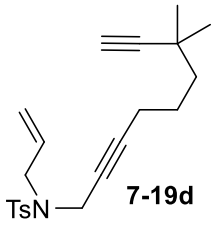

144.85
131.65
129.87
128.23
128.03
127.64
117.76
85.15
82.65
79.13
77.33
77.07
76.82
70.16
67.95
57.56
50.20
21.64
19.43
f1 (ppm)


O

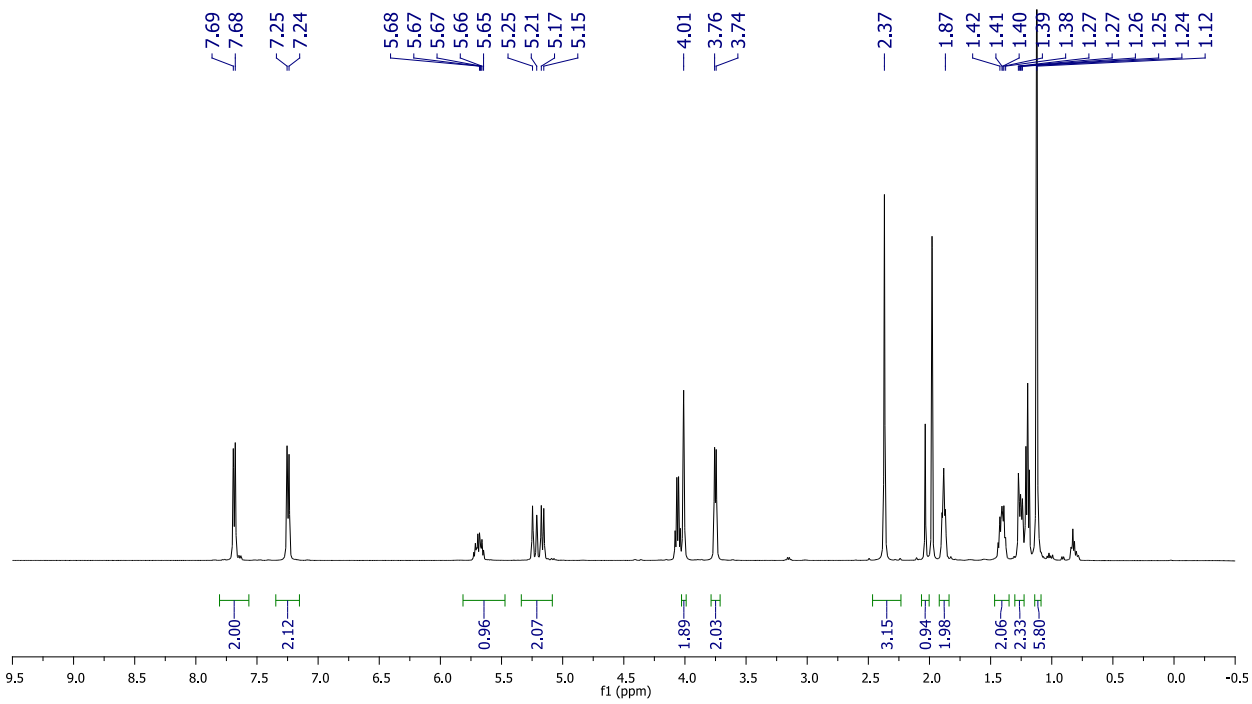
7-19c

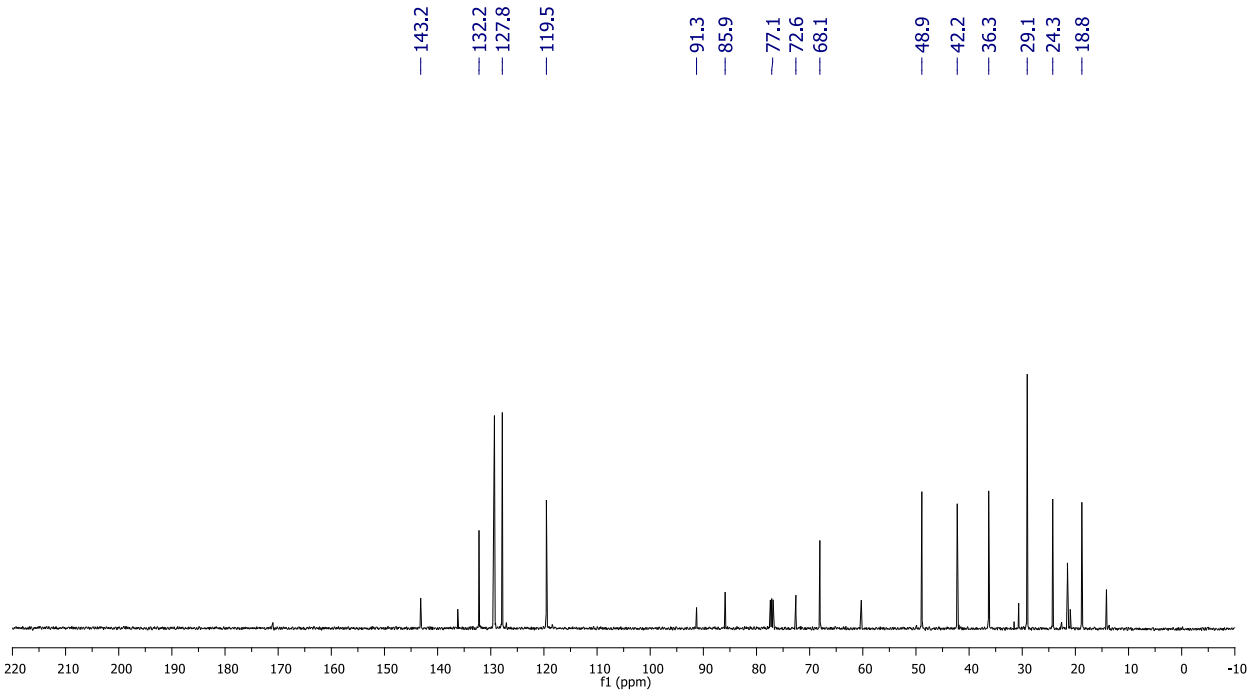

7.26
5.90
5.89
5.88
5.88
5.87
5.26
5.19
5.18
5.17
4.12
4.11
4.04
4.04
4.03
4.03
4.03
4.02
2.23
2.23
2.22
2.22
2.22
2.06
1.65
1.45
1.19
1.11
2.36
2.47
2.42
2.19
1.00
2.23
2.36
6.74
f1 (ppm)

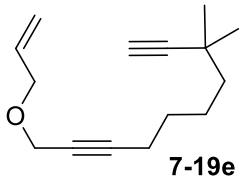

134.2
117.6
91.5
86.7
77.1
76.1
68.0
57.7
42.3
37.4
29.1
24.5
19.1
f1 (ppm)


TsN

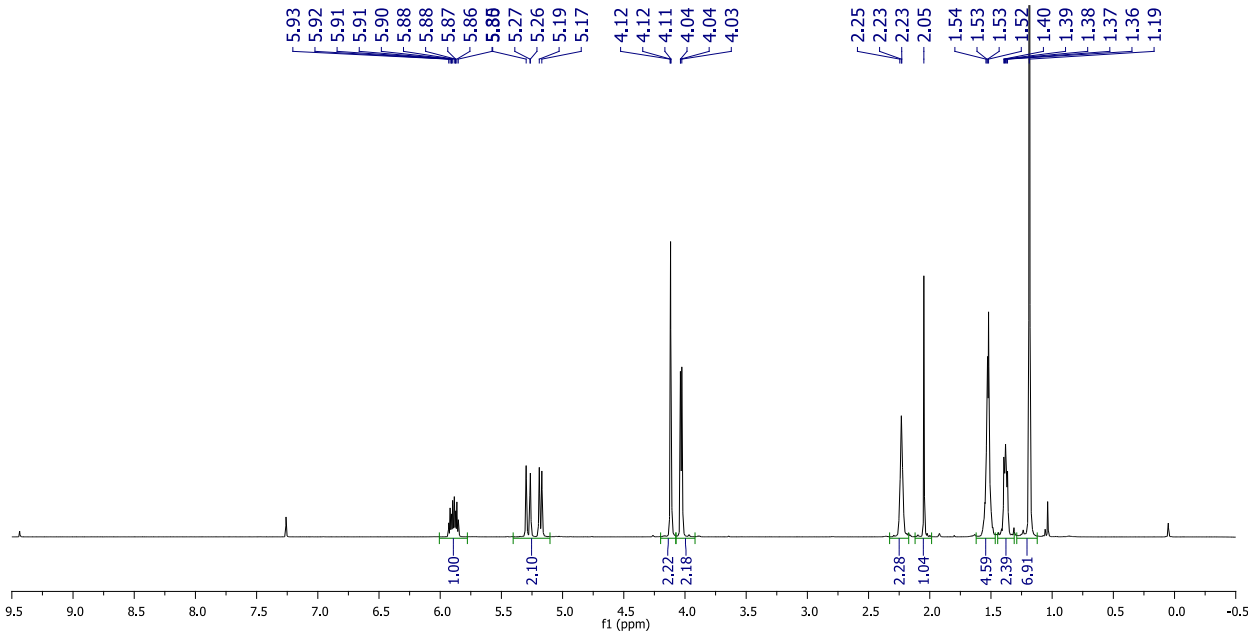
7-19d

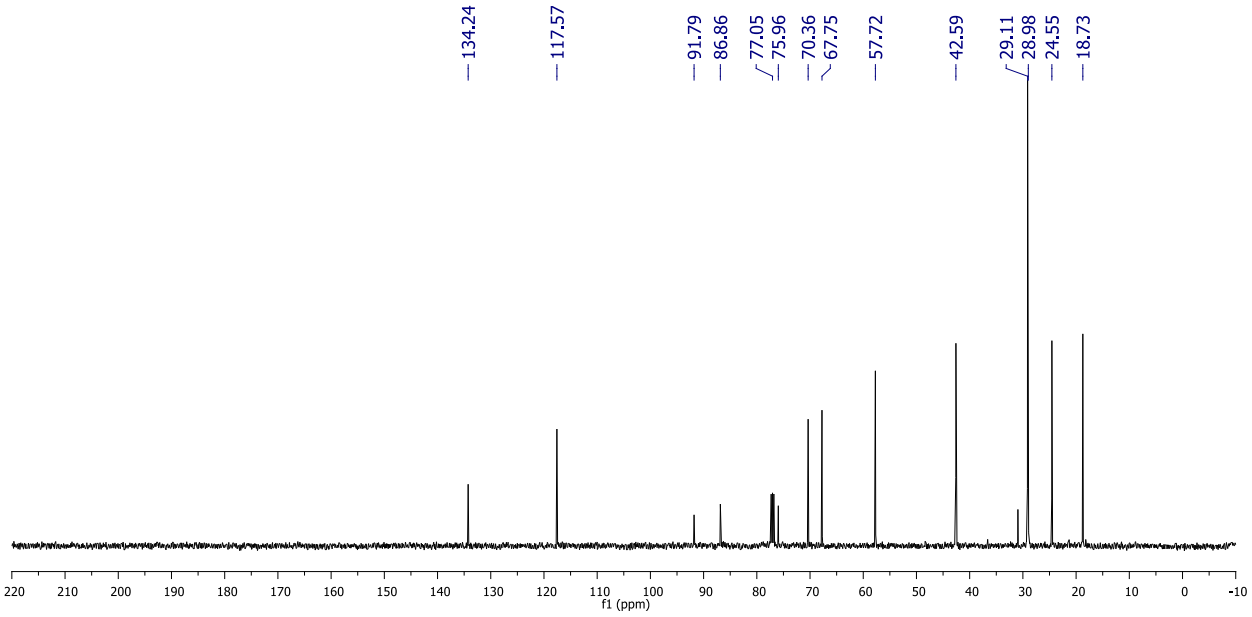

7.69
7.68
7.25
7.24
5.68
5.67
5.67
5.66
5.65
5.25
5.21
5.17
5.15
4.01
3.76
3.74
2.37
1.87
1.42
1.41
1.40
1.39
1.38
1.27
1.27
1.26
1.25
1.24
1.12
2.00
2.12
0.96
2.07
1.89
2.03
3.15
0.94
1.98
2.06
2.33
5.80
f1 (ppm)

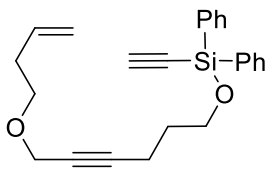

143.2
132.2
127.8
119.5
91.3
85.9
77.1
72.6
68.1
48.9
42.2
36.3
29.1
24.3
18.8
f1 (ppm)



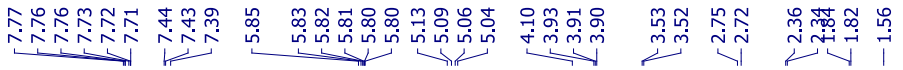
7-19e

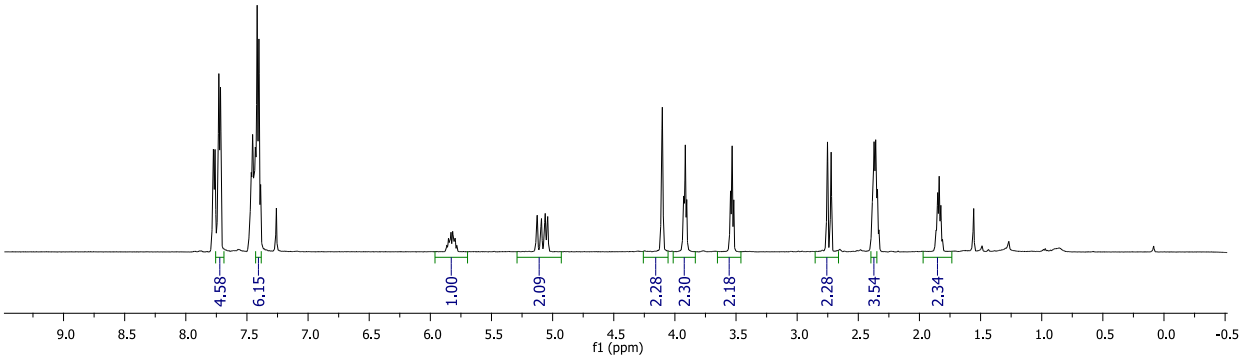

5.93
5.92
5.91
5.91
5.90
5.88
5.88
5.87
5.86
5.85
5.27
5.26
5.19
5.17
4.12
4.12
4.11
4.04
4.04
4.03
2.25
2.23
2.23
2.05
1.54
1.53
1.53
1.52
1.40
1.39
1.38
1.37
1.36
1.19
1.00
2.10
2.22
2.18
2.28
1.04
4.59
2.39
6.91
f1 (ppm)


134.24
117.57
91.79
86.86
77.05
75.96
70.36
67.75
57.72
42.59
29.11
28.98
24.55
18.73
f1 (ppm)

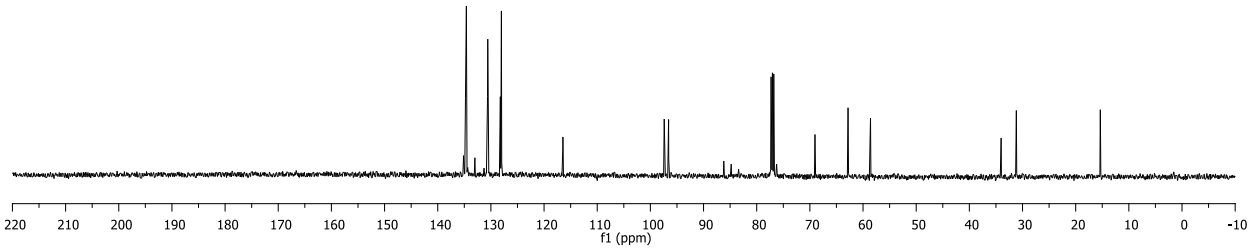

Ph
Si
Ph
O
O

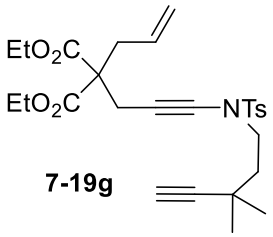
7-19f


7.77
7.76
7.76
7.73
7.72
7.71
7.44
7.43
7.39
5.85
5.83
5.82
5.81
5.80
5.80
5.13
5.09
5.06
5.04
4.10
3.93
3.91
3.90
3.53
3.52
2.75
2.72
2.36
2.34
1.84
1.82
1.56

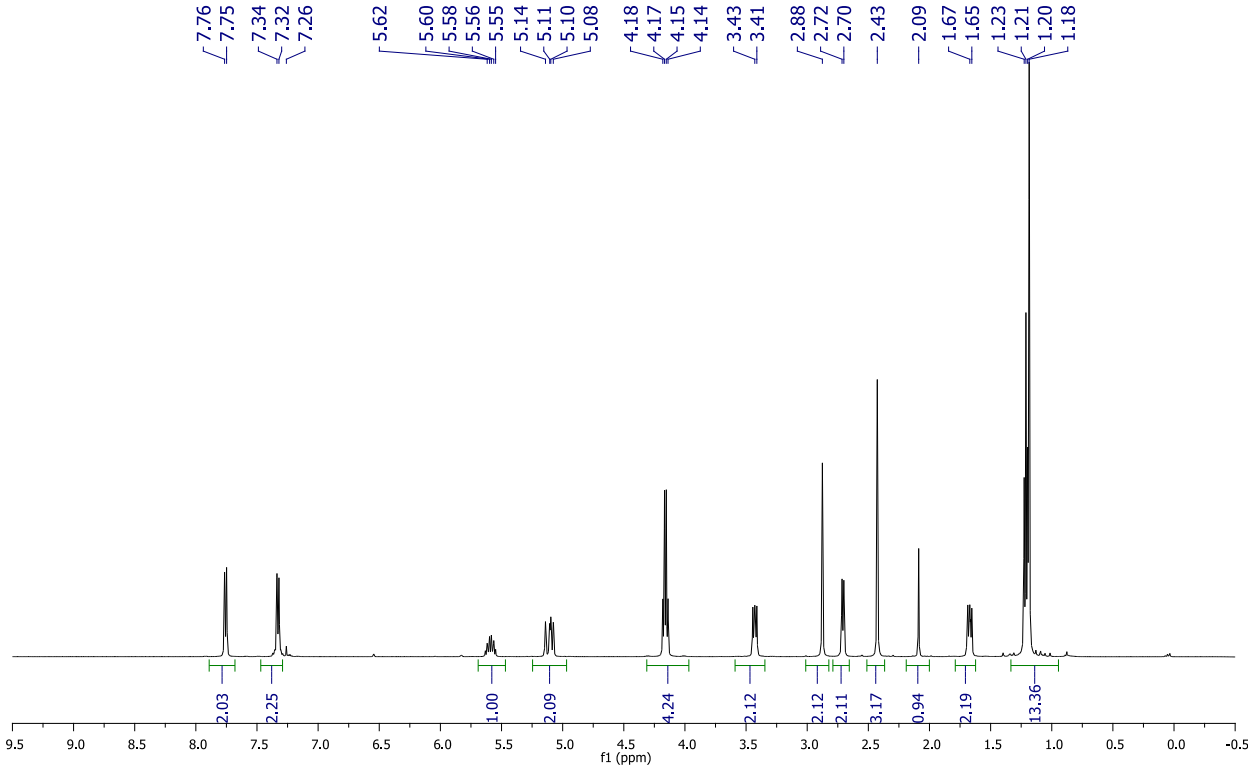

4.58
6.15
1.00
2.09
2.28
2.30
2.18
2.28
3.54
2.34
f1 (ppm)

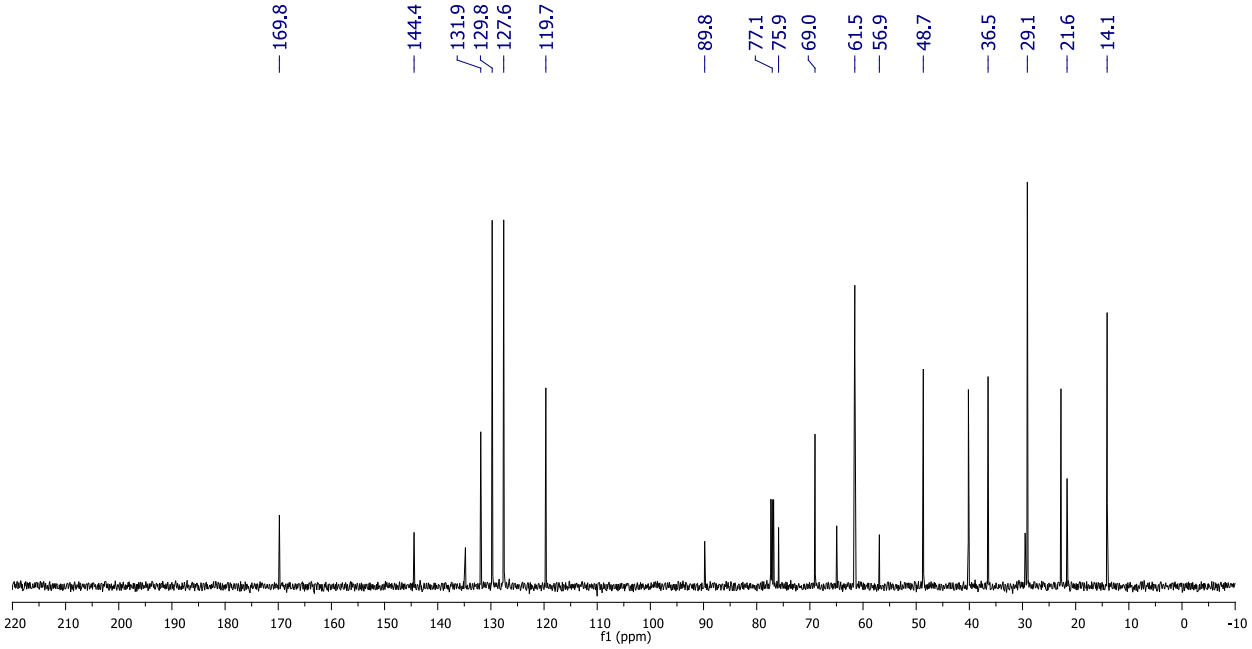
134.6
133.0
130.6
128.0
97.4
96.6
86.2
84.8
76.3
69.0
62.8
58.6
34.0
31.2
15.4

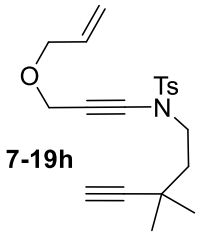

f1 (ppm)


EtO2C
EtO2C
NTs

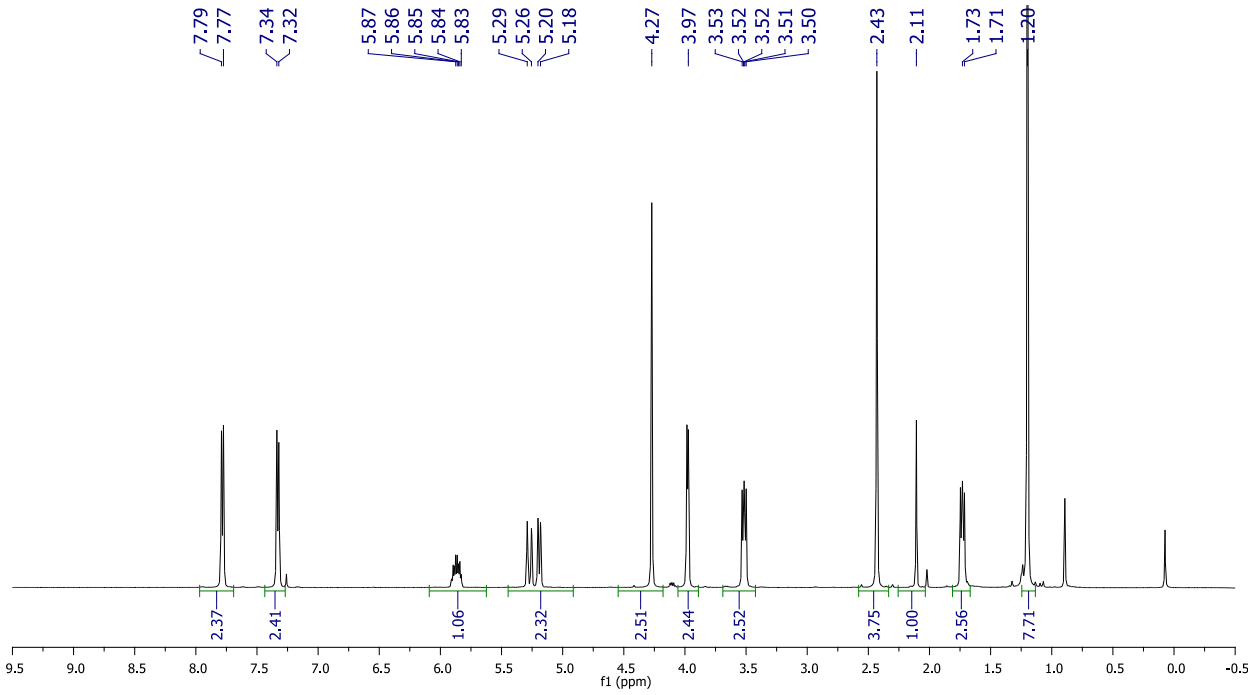
7-19g

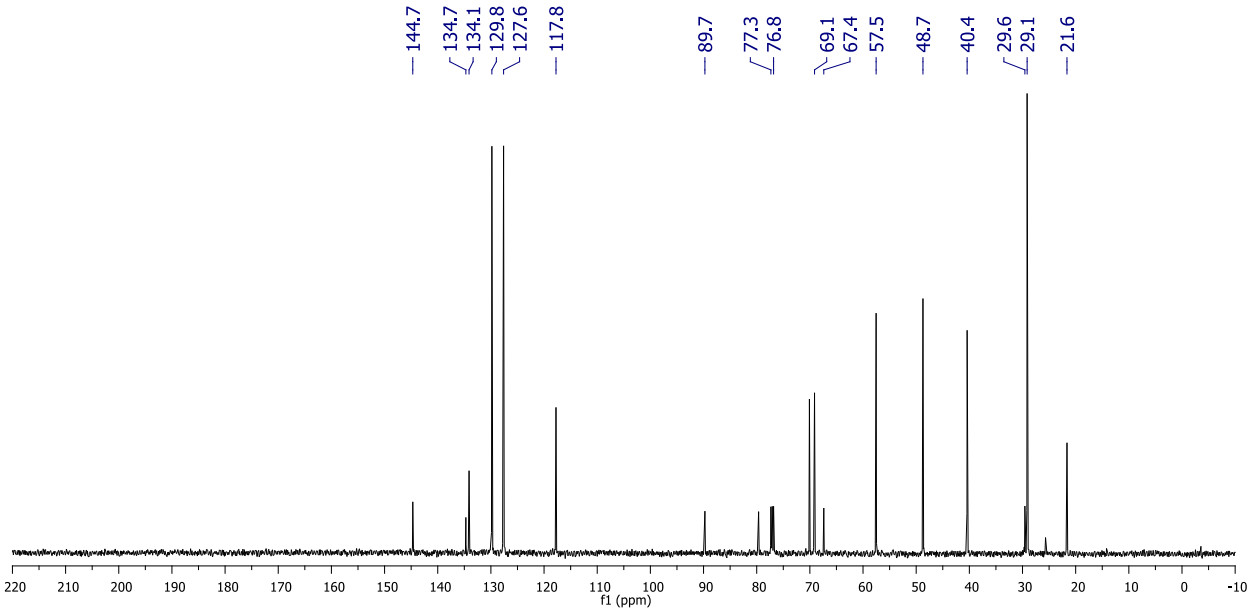

7.76
7.75
7.34
7.32
7.26
5.62
5.60
5.58
5.56
5.55
5.14
5.11
5.10
5.08
4.18
4.17
4.15
4.14
3.43
3.41
2.88
2.72
2.70
2.43
2.09
1.67
1.65
1.23
1.21
1.20
1.18
2.03
2.25
1.00
2.09
4.24
2.12
2.12
2.11
3.17
0.94
2.19
13.36
f1 (ppm)

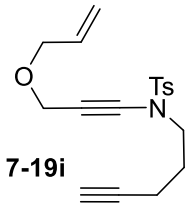

169.8
144.4
131.9
129.8
127.6
119.7
89.8
77.1
75.9
69.0
61.5
56.9
48.7
36.5
29.1
21.6
14.1
f1 (ppm)


O
Ts
N

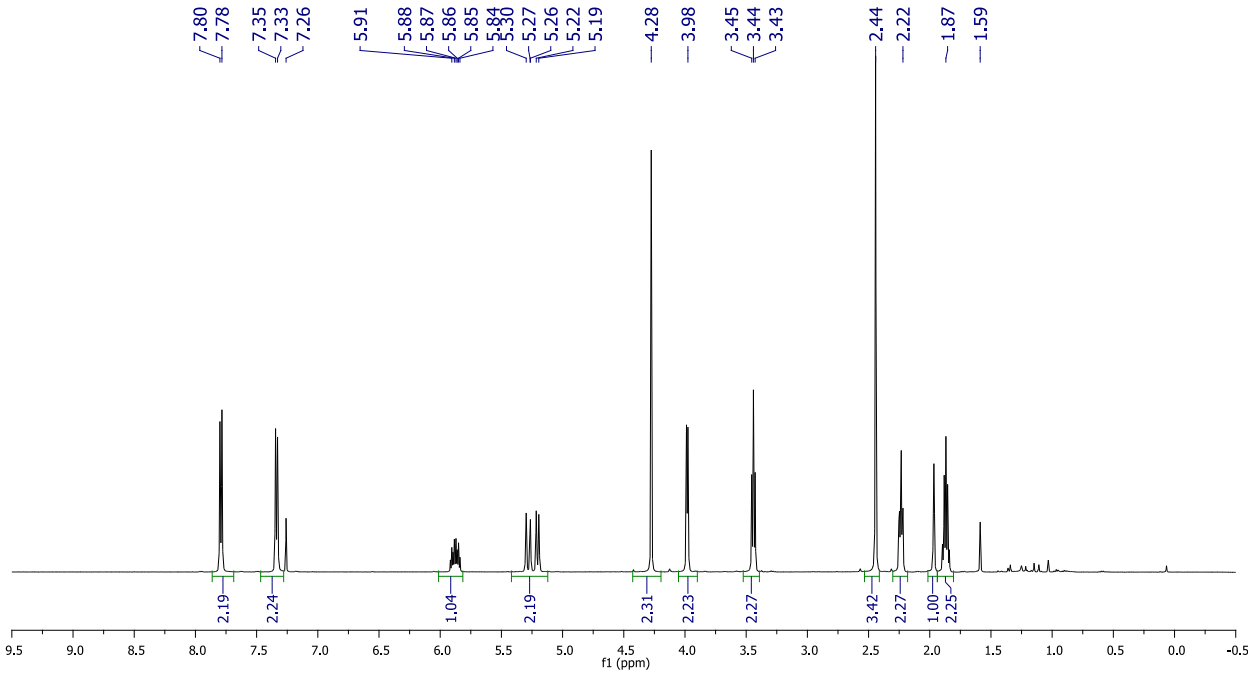
7-19h

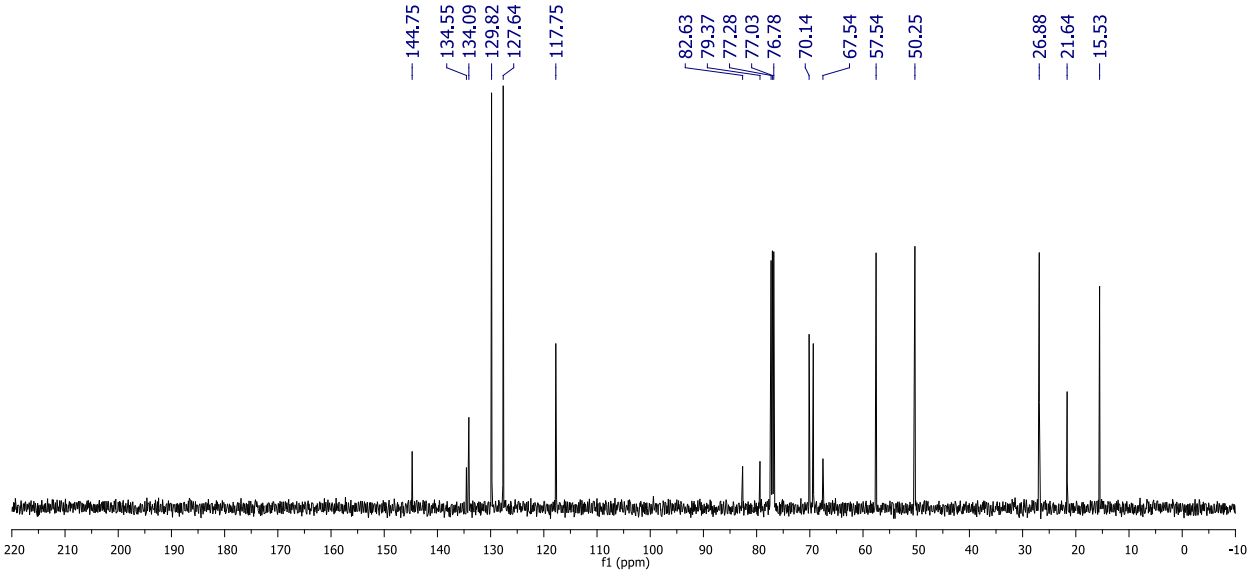

7.79
7.77
7.34
7.32
5.87
5.86
5.85
5.84
5.83
5.29
5.26
5.20
5.18
4.27
3.97
3.53
3.52
3.52
3.51
3.50
2.43
2.11
1.73
1.71
1.20
2.37
2.41
1.06
2.32
2.51
2.44
2.52
3.75
1.00
2.56
7.71
f1 (ppm)

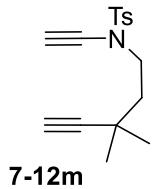

144.7
134.7
134.1
129.8
127.6
117.8
89.7
77.3
76.8
69.1
67.4
57.5
48.7
40.4
29.6
29.1
21.6
f1 (ppm)


O
Ts
N

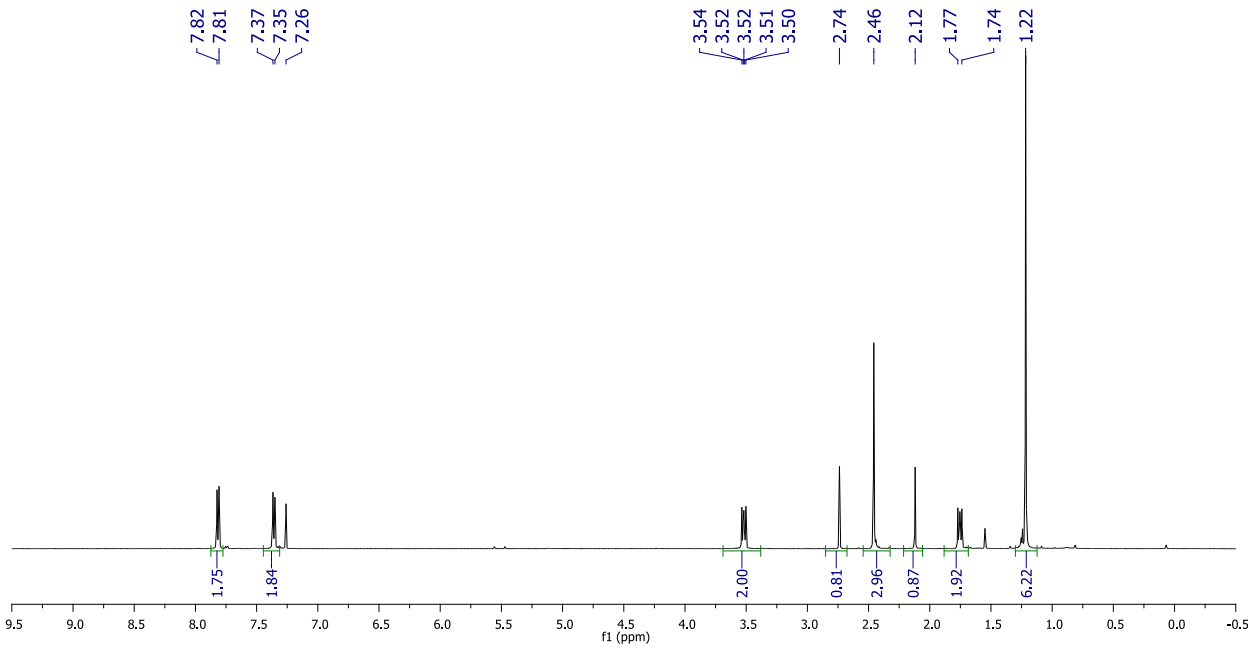
7-19i

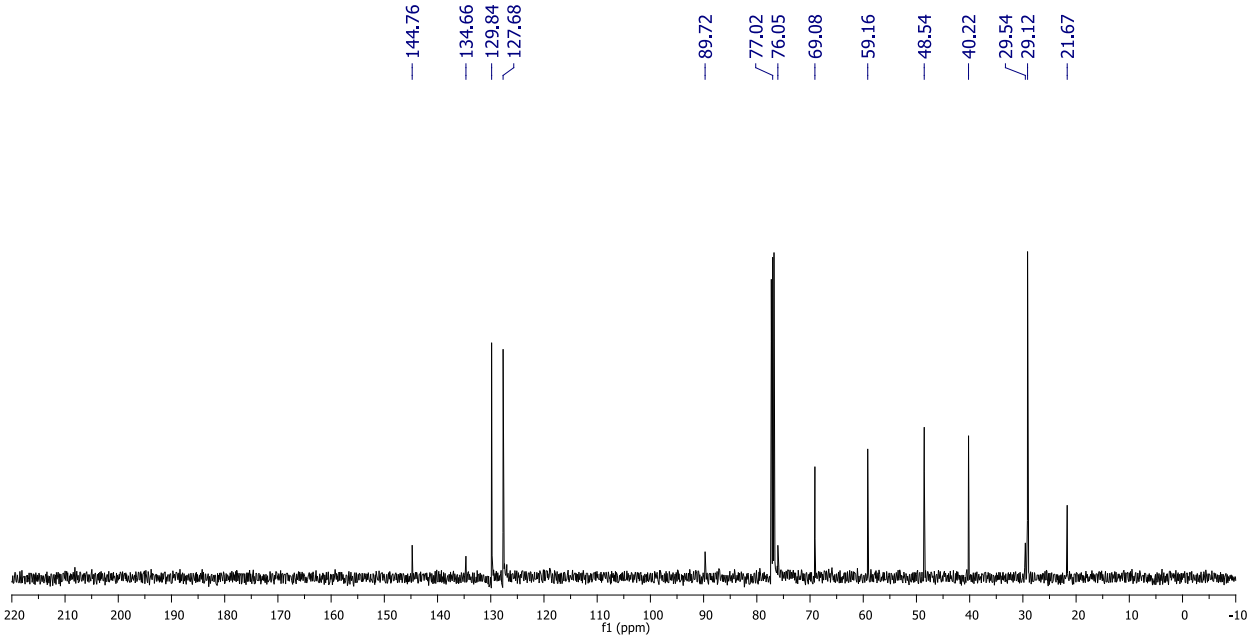

7.80
7.78
7.35
7.33
7.26
5.91
5.88
5.87
5.86
5.85
5.84
5.30
5.27
5.26
5.22
5.19
4.28
3.98
3.45
3.44
3.43
2.44
2.22
1.87
1.59
2.19
2.24
1.04
2.19
2.31
2.23
2.27
3.42
2.27
1.00
2.25
f1 (ppm)

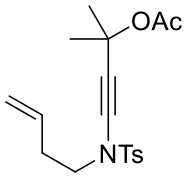

144.75
134.55
134.09
129.82
127.64
117.75
82.63
79.37
77.28
77.03
76.78
70.14
67.54
57.54
50.25
26.88
21.64
15.53
f1 (ppm)


Ts
N

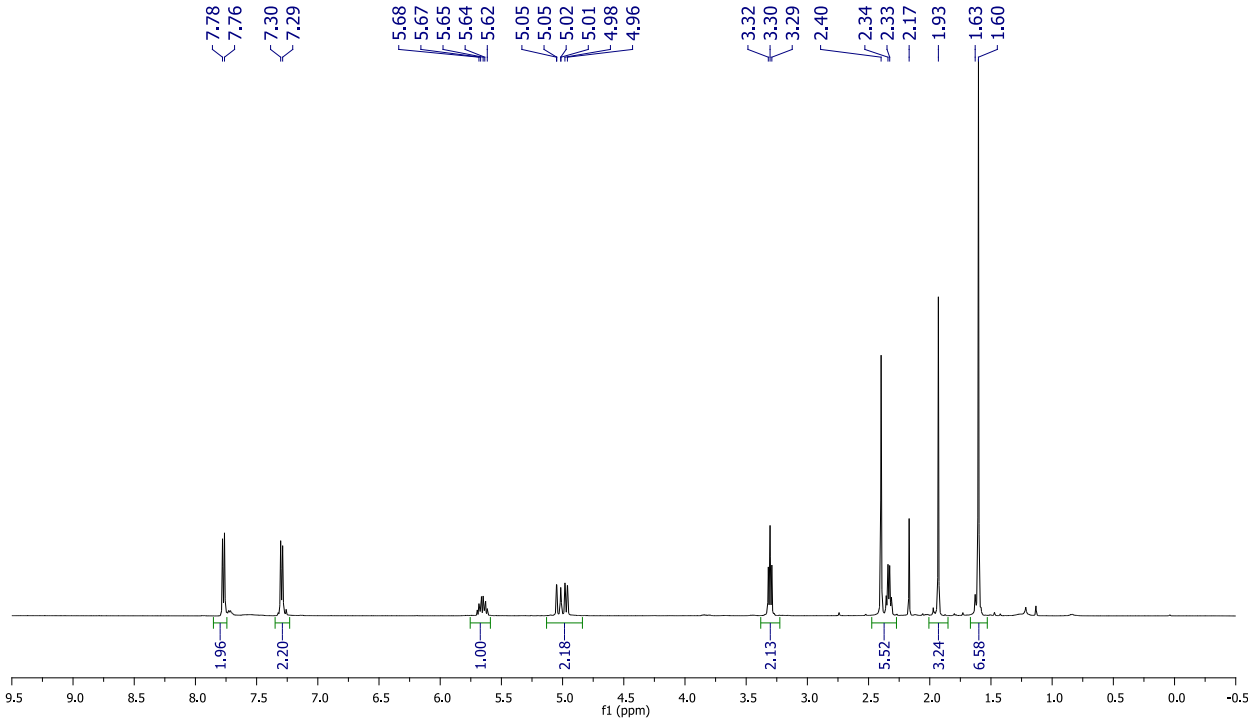
7-12m

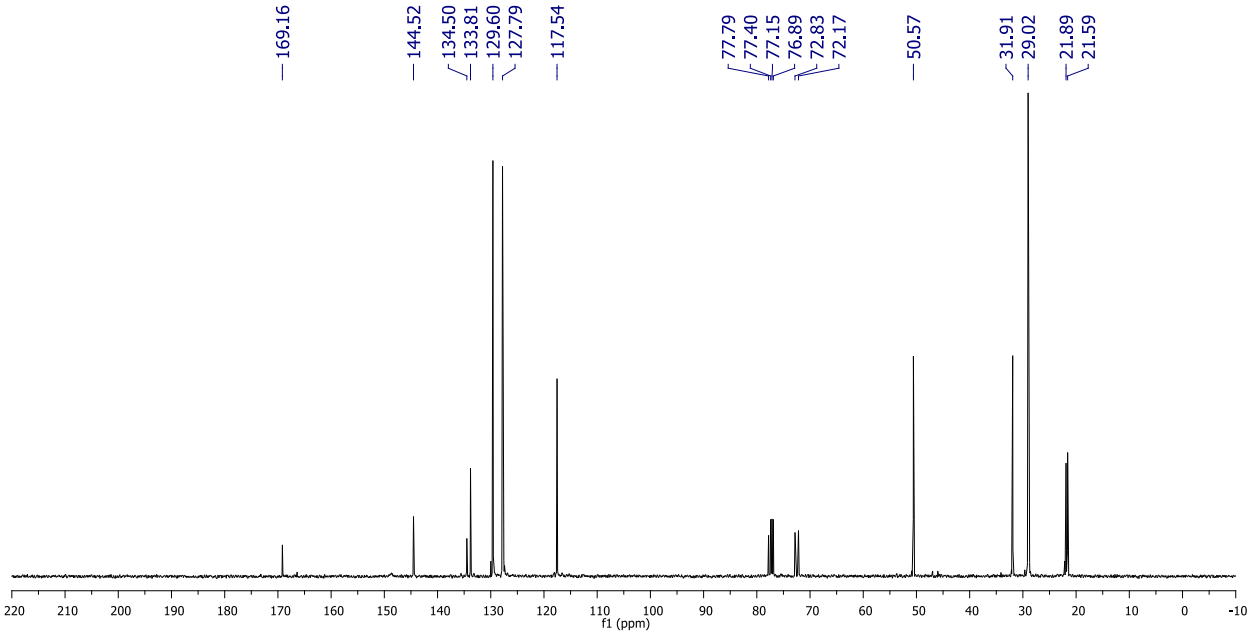

7.82
7.81
7.37
7.35
7.26
3.54
3.52
3.52
3.51
3.50
2.74
2.46
2.12
1.77
1.74
1.22
1.75
1.84
2.00
0.81
2.96
0.87
1.92
6.22
f1 (ppm)

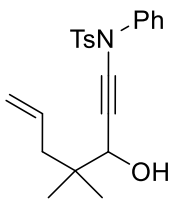

144.76
134.66
129.84
127.68
89.72
77.02
76.05
69.08
59.16
48.54
40.22
29.54
29.12
21.67
f1 (ppm)


OAc
NTs

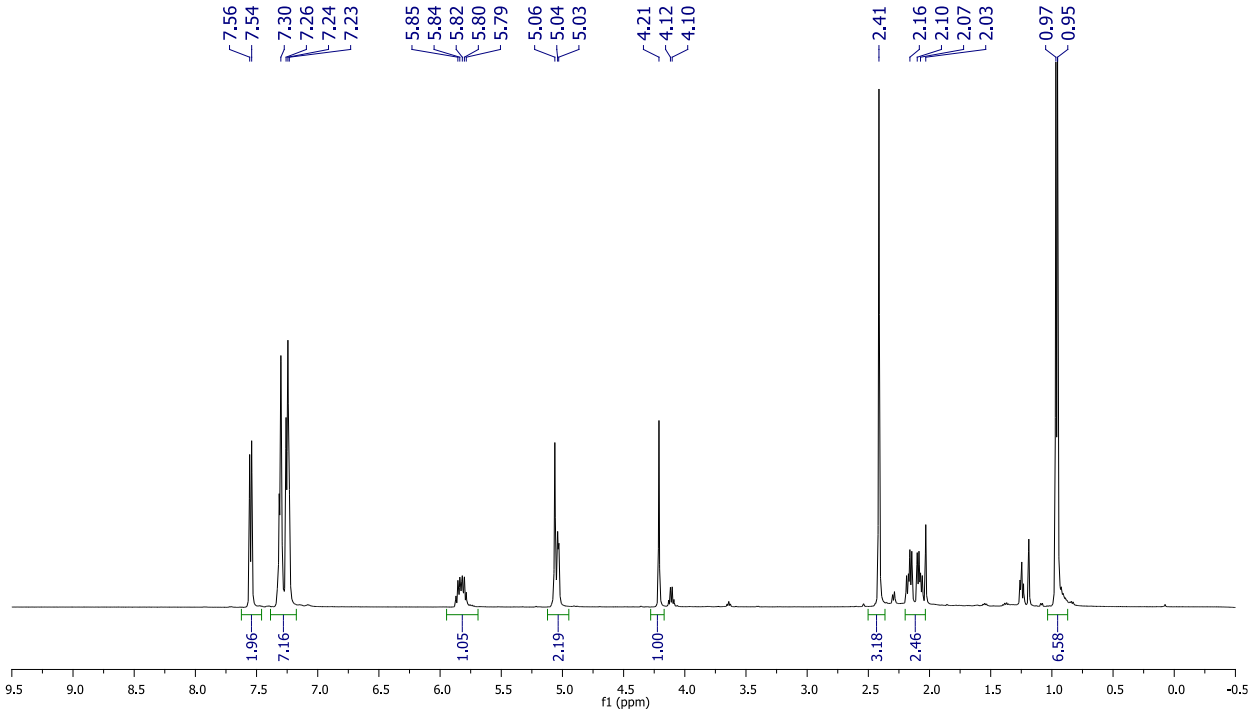
7-23c

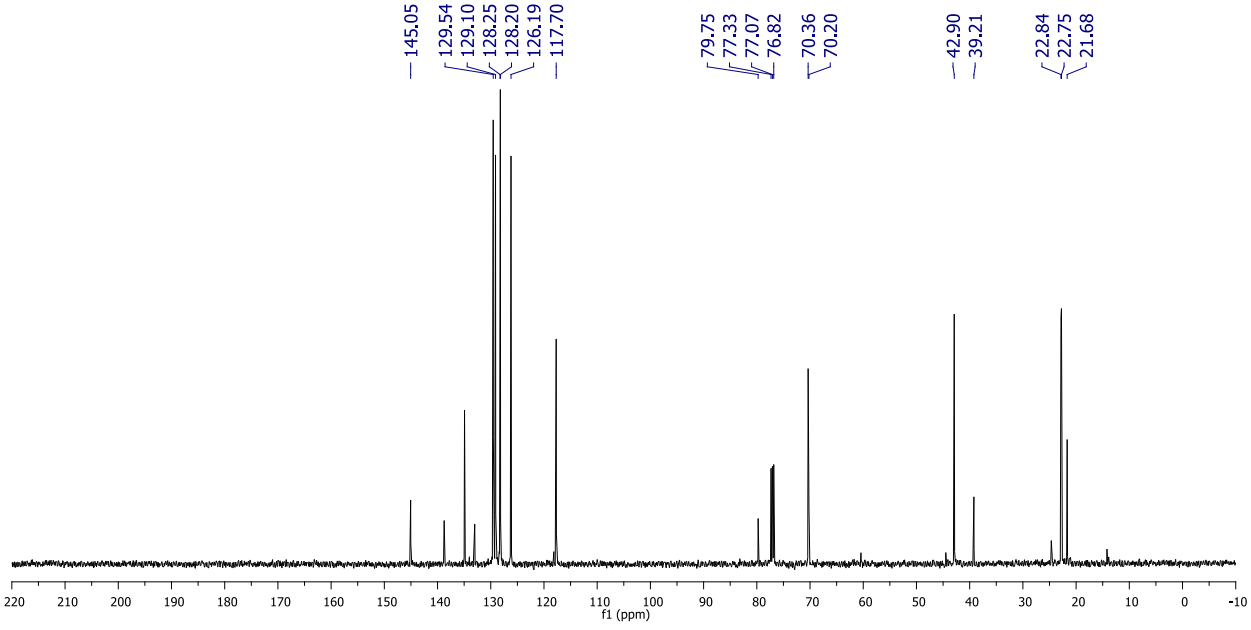

7.78
7.76
7.30
7.29
5.68
5.67
5.65
5.64
5.62
5.05
5.05
5.02
5.01
4.98
4.96
3.32
3.30
3.29
2.40
2.34
2.33
2.17
1.93
1.63
1.60
1.96
2.20
1.00
2.18
2.13
5.52
3.24
6.58
f1 (ppm)

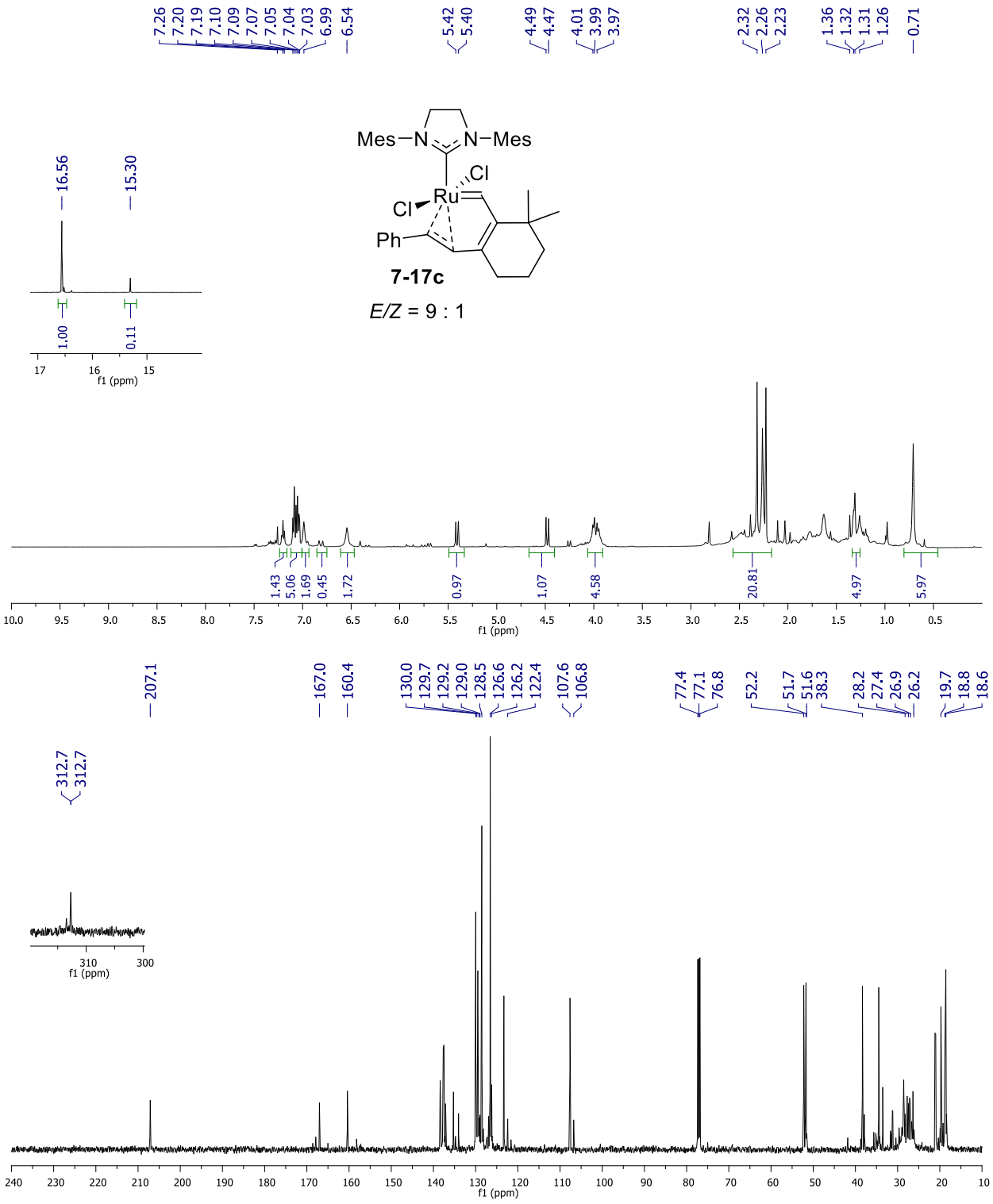

169.16
144.52
134.50
133.81
129.60
127.79
117.54
77.79
77.40
77.15
76.89
72.83
72.17
50.57
31.91
29.02
21.89
21.59
f1 (ppm)

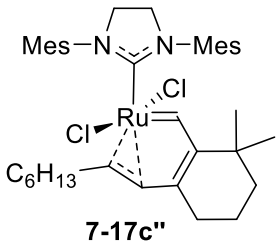

TsN
Ph
OH

7-23d

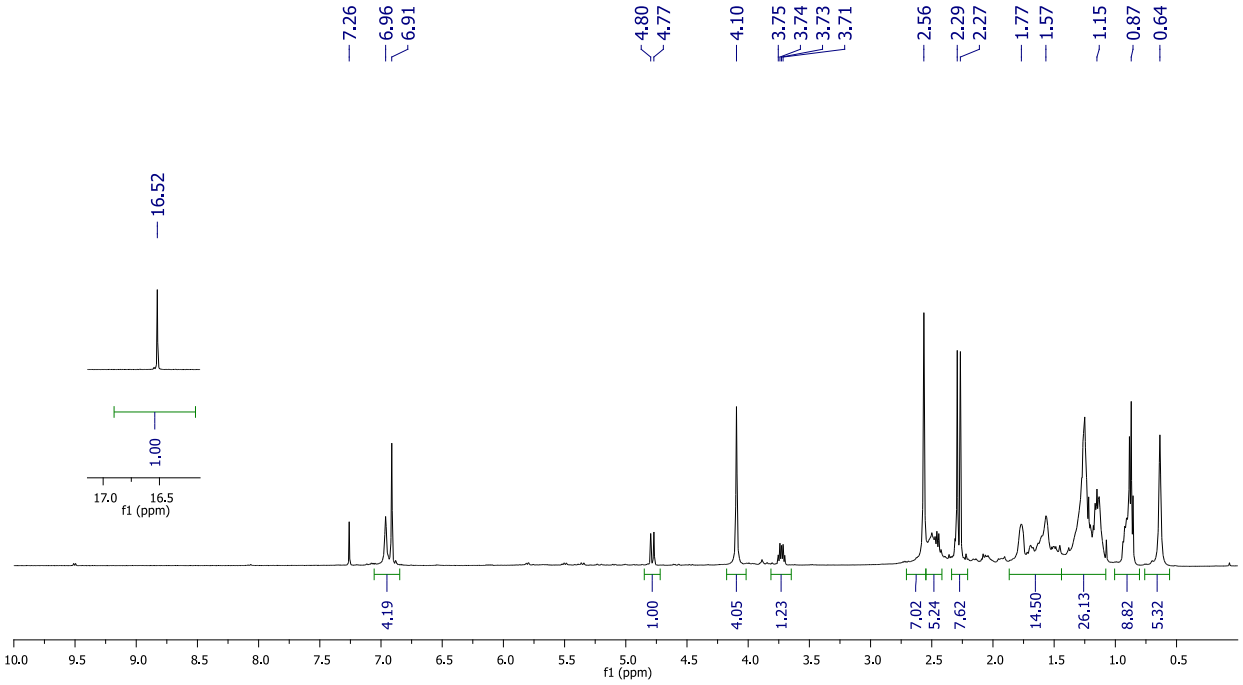

7.56
7.54
7.30
7.26
7.24
7.23
5.85
5.84
5.82
5.80
5.79
5.06
5.04
5.03
4.21
4.12
4.10
2.41
2.16
2.10
2.07
2.03
0.97
0.95
1.96
7.16
1.05
2.19
1.00
3.18
2.46
6.58
f1 (ppm)

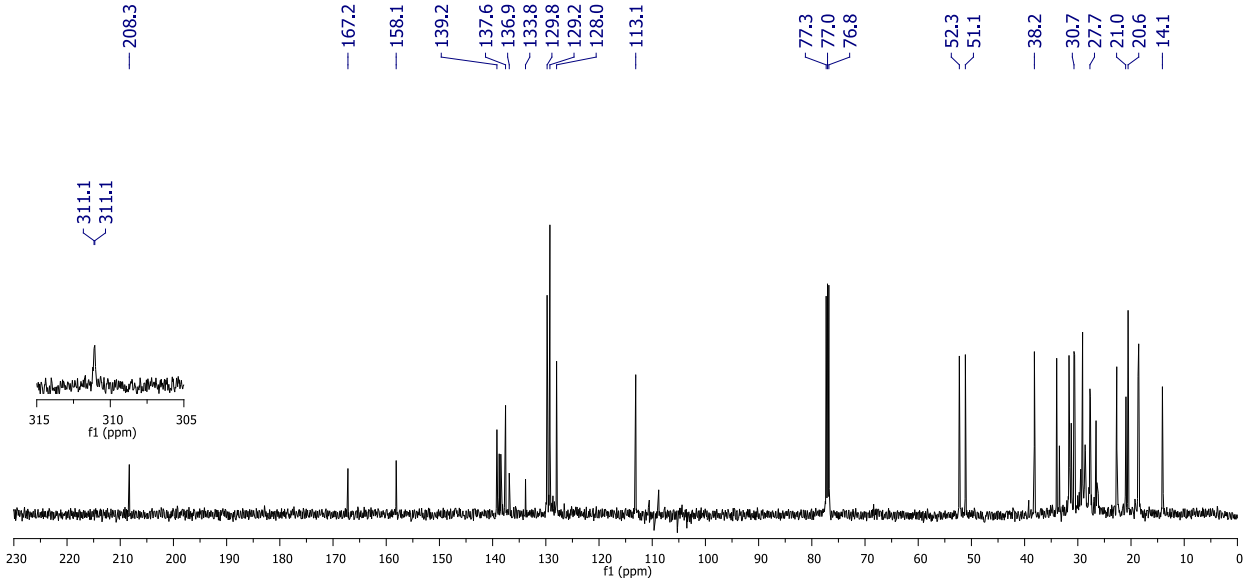

145.05
129.54
129.10
128.25
128.20
126.19
117.70
79.75
77.33
77.07
76.82
70.36
70.20
42.90
39.21
22.84
22.75
21.68
f1 (ppm)

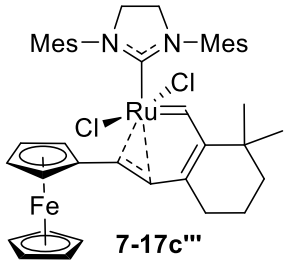

7.26
7.20
7.19
7.10
7.09
7.07
7.05
7.04
7.03
6.99
6.54
5.42
5.40
4.49
4.47
4.01
3.99
3.97
2.32
2.26
2.23
1.36
1.32
1.31
1.26
0.71
Mes−N
N−Mes
Cl
Ru
Cl
Ph
7-17c
E/Z = 9 : 1
16.56
15.30
1.00
0.11
f1 (ppm)
1.43
5.06
1.69
0.45
1.72
0.97
1.07
4.58
20.81
4.97
5.97
f1 (ppm)
207.1
167.0
160.4
130.0
129.7
129.2
129.0
128.5
126.6
126.2
122.4
107.6
106.8
77.4
77.1
76.8
52.2
51.7
51.6
38.3
28.2
27.4
26.9
26.2
19.7
18.8
18.6
312.7
312.7
f1 (ppm)
f1 (ppm)


Mes–N
N–Mes
Cl
Ru
Cl
C_6H_{13}

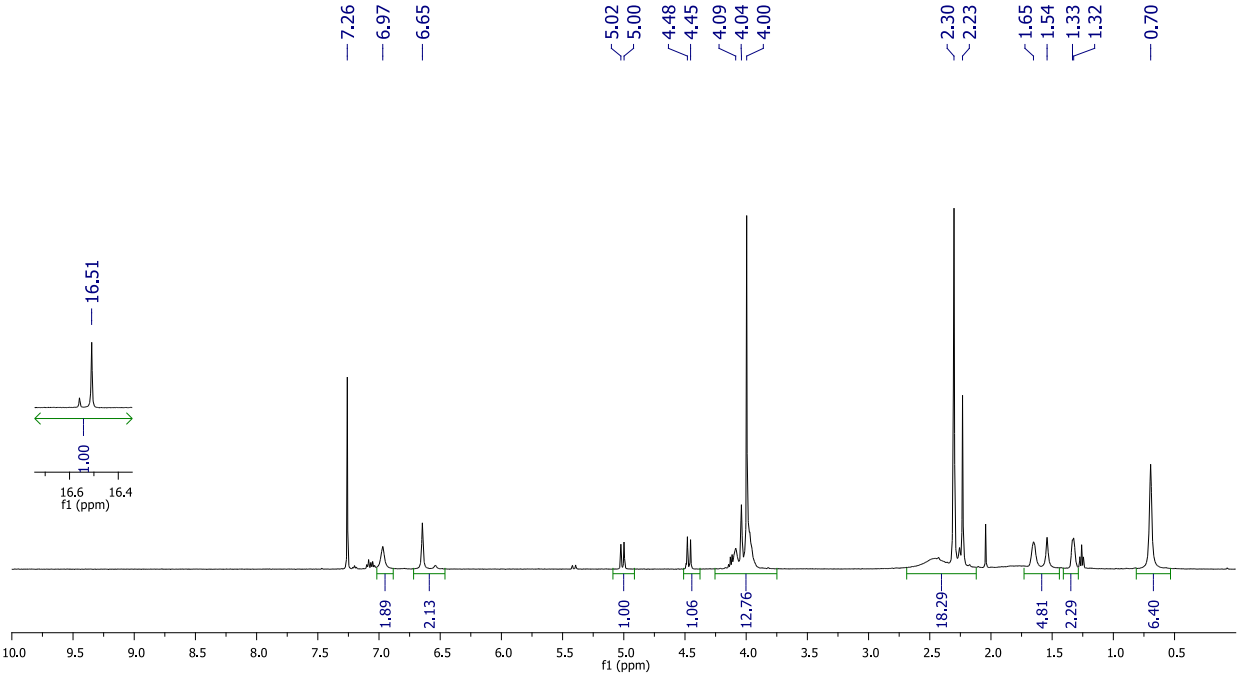
7-17c"

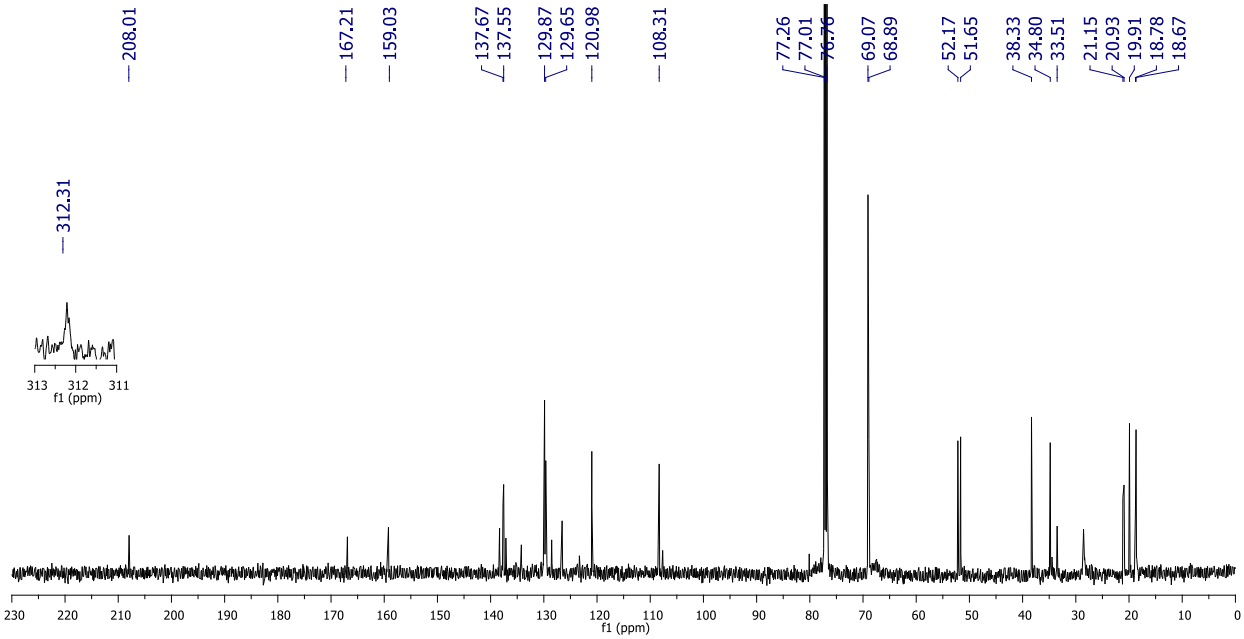

7.26
6.96
6.91
4.80
4.77
4.10
3.75
3.74
3.73
3.71
2.56
2.29
2.27
1.77
1.57
1.15
0.87
0.64
16.52
1.00
17.0
16.5
f1 (ppm)
4.19
1.00
4.05
1.23
7.02
5.24
7.62
14.50
26.13
8.82
5.32
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

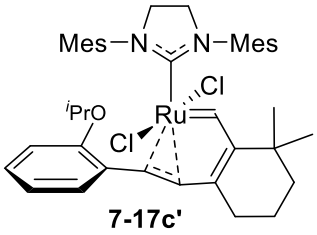

208.3
167.2
158.1
139.2
137.6
136.9
133.8
129.8
129.2
128.0
113.1
77.3
77.0
76.8
52.3
51.1
38.2
30.7
27.7
21.0
20.6
14.1
311.1
311.1
315
310
305
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Mes
N
N
Mes
Cl
Ru
Cl
Fe

7-17c'''

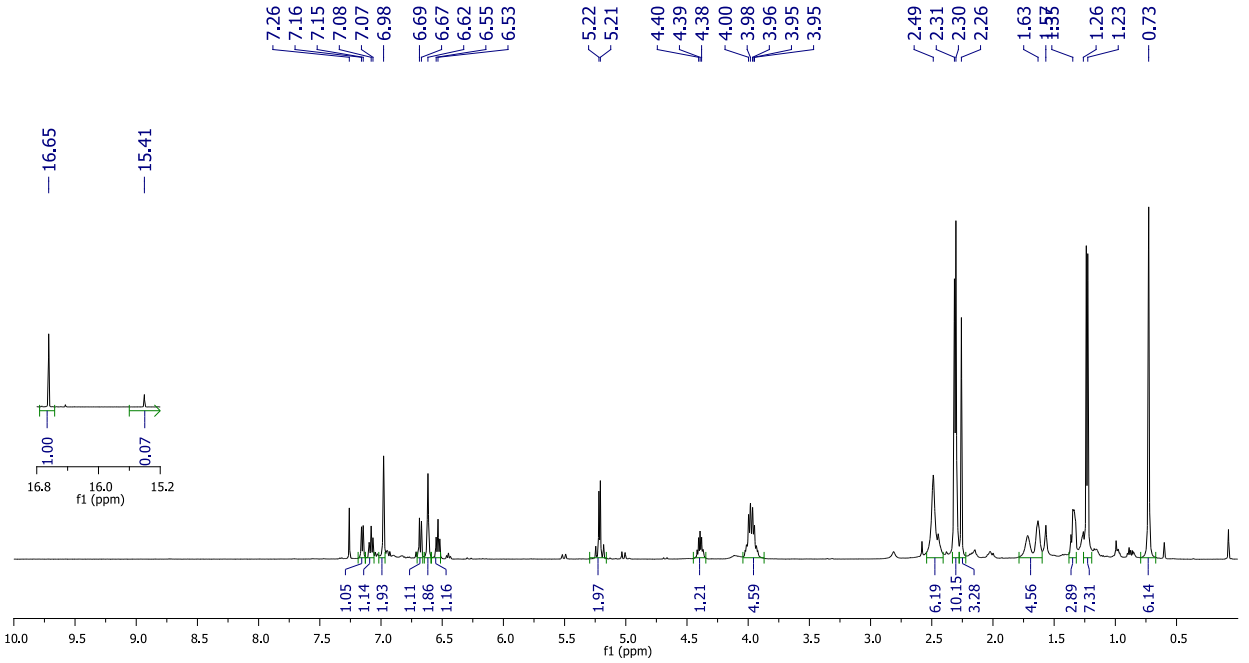

7.26
6.97
6.65
5.02
5.00
4.48
4.45
4.09
4.04
4.00
2.30
2.23
1.65
1.54
1.33
1.32
0.70
16.51
1.00
16.6
16.4
f1 (ppm)
1.89
2.13
1.00
1.06
12.76
18.29
4.81
2.29
6.40
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

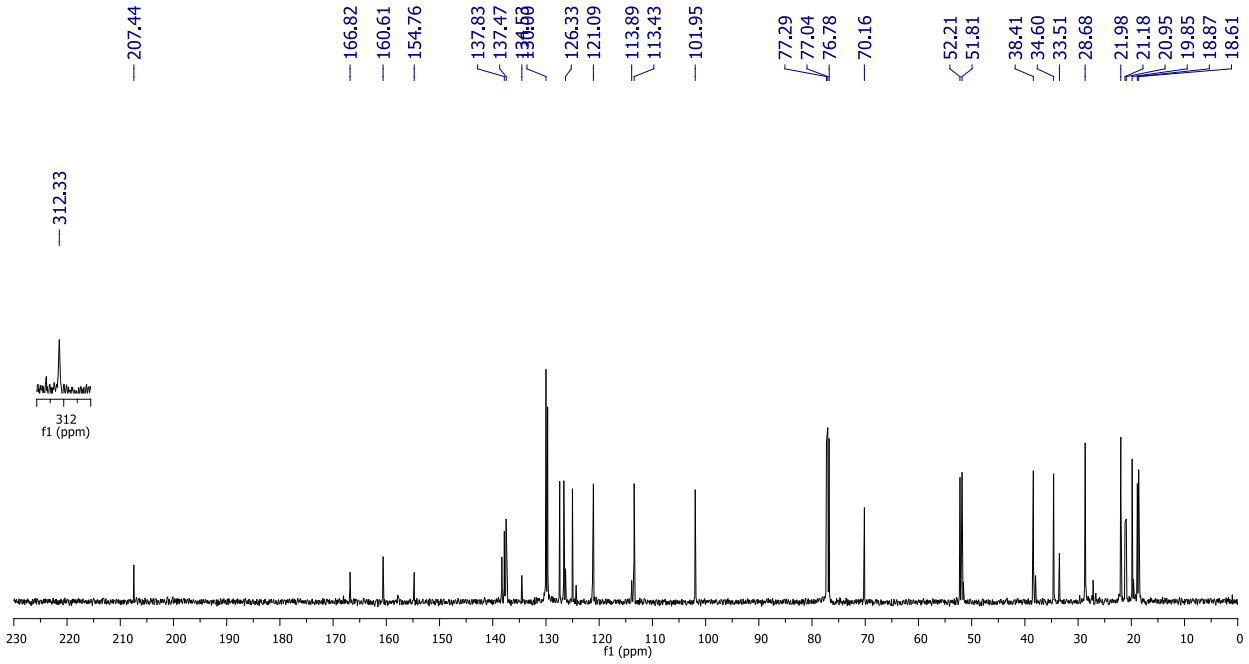

208.01
167.21
159.03
137.67
137.55
129.87
129.65
120.98
108.31
77.26
77.01
76.76
69.07
68.89
52.17
51.65
38.33
34.80
33.51
21.15
20.93
19.91
18.78
18.67
312.31
313
312
311
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

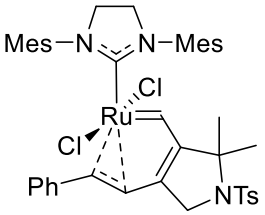

Mes−N
N−Mes
Cl
iPrO
Ru
Cl

7-17c'

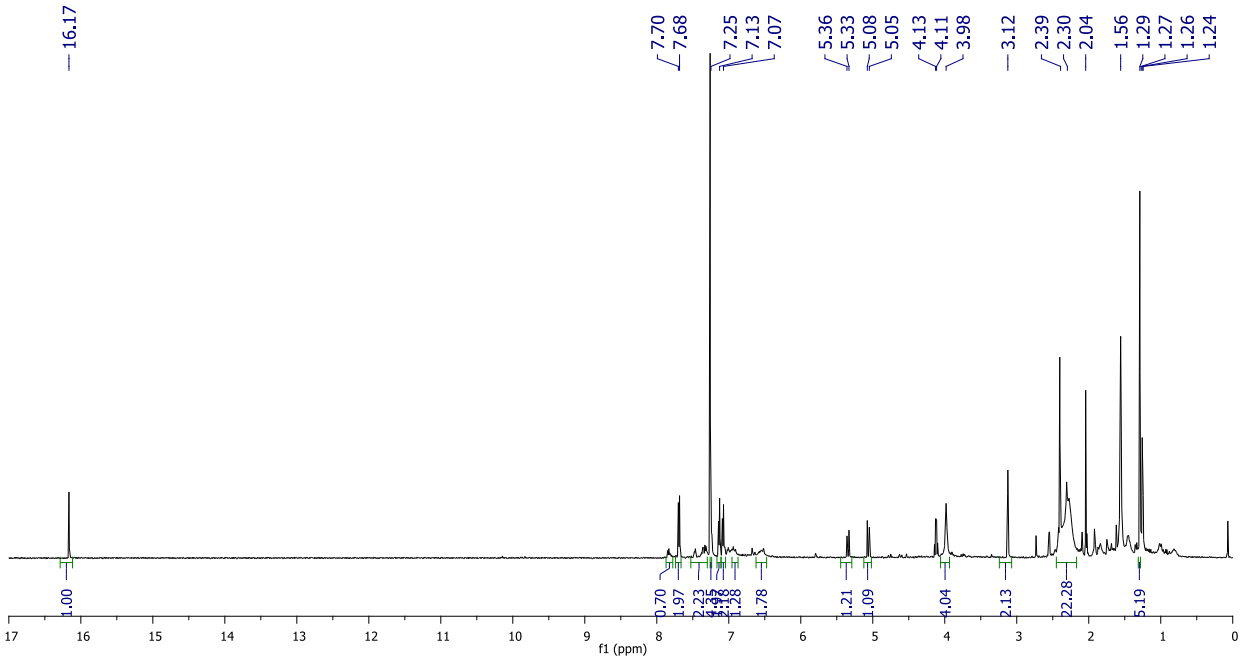
E/*Z* = 14 : 1

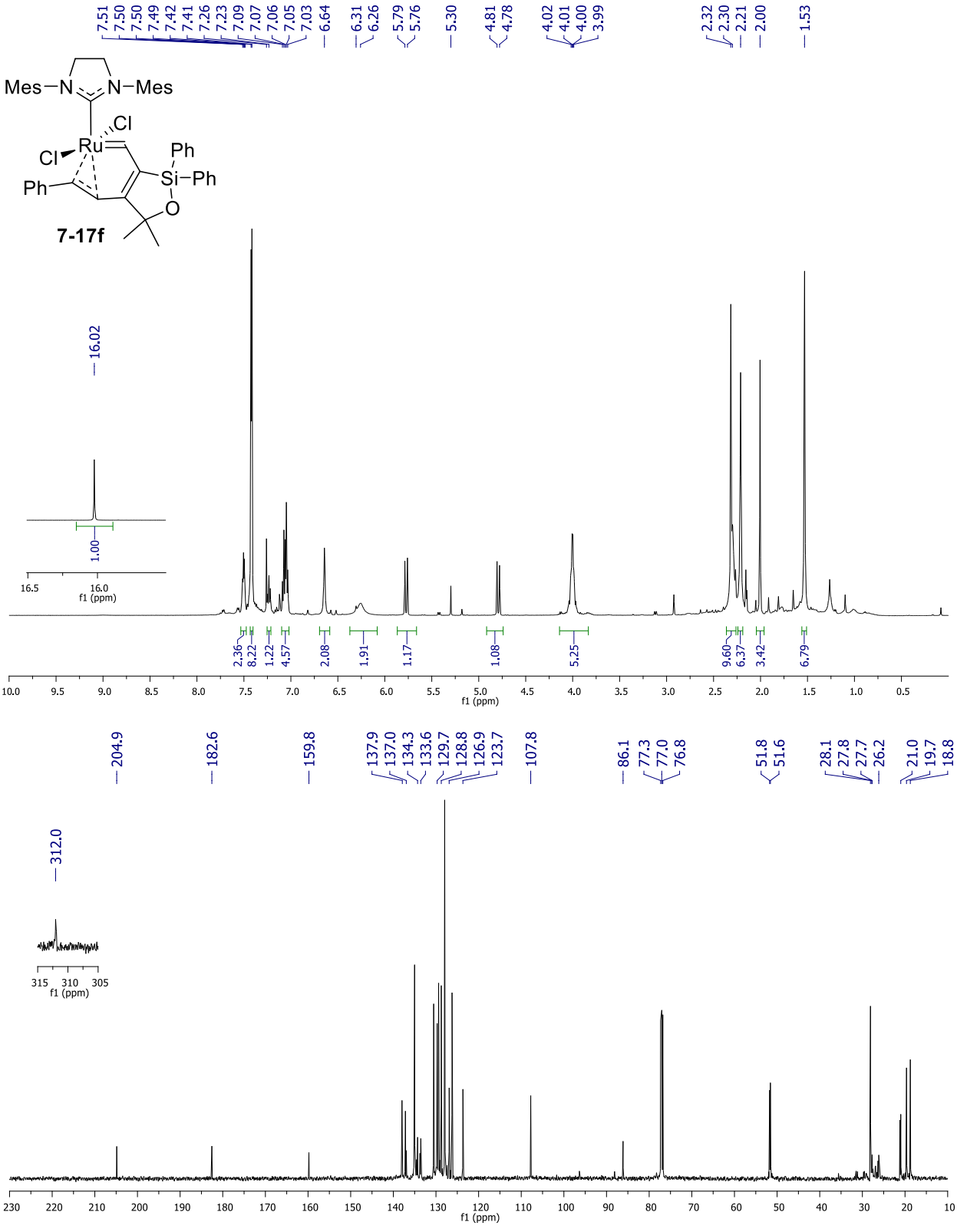

7.26
7.16
7.15
7.08
7.07
6.98
6.69
6.67
6.62
6.55
6.53
5.22
5.21
4.40
4.39
4.38
4.00
3.98
3.96
3.95
3.95
2.49
2.31
2.30
2.26
1.63
1.26
1.23
0.73
16.65
15.41
1.00
0.07
16.8
16.0
15.2
f1 (ppm)
1.05
1.14
1.93
1.11
1.86
1.16
1.97
1.21
4.59
6.19
10.15
3.28
4.56
2.89
7.31
6.14
f1 (ppm)

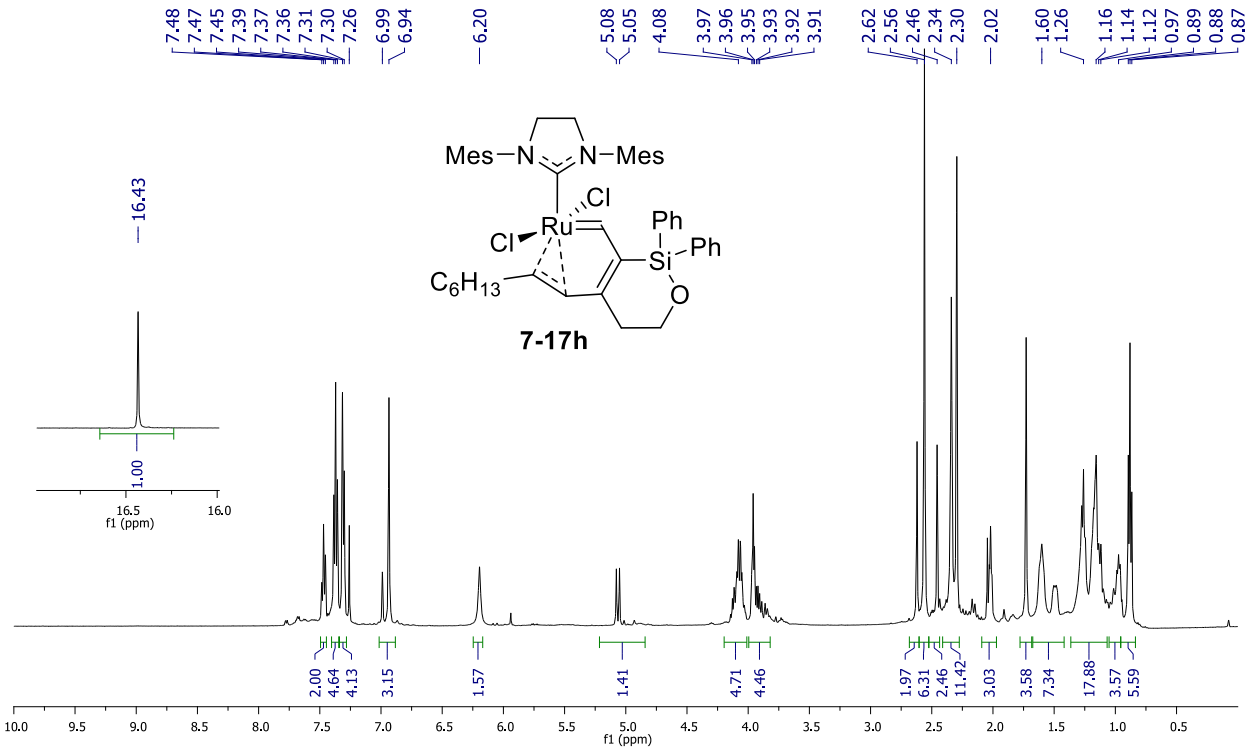

207.44
166.82
160.61
154.76
137.83
137.47
126.33
121.09
113.89
113.43
101.95
77.29
77.04
76.78
70.16
52.21
51.81
38.41
34.60
33.51
28.68
21.98
21.18
20.95
19.85
18.87
18.61
312.33
312
f1 (ppm)
f1 (ppm)

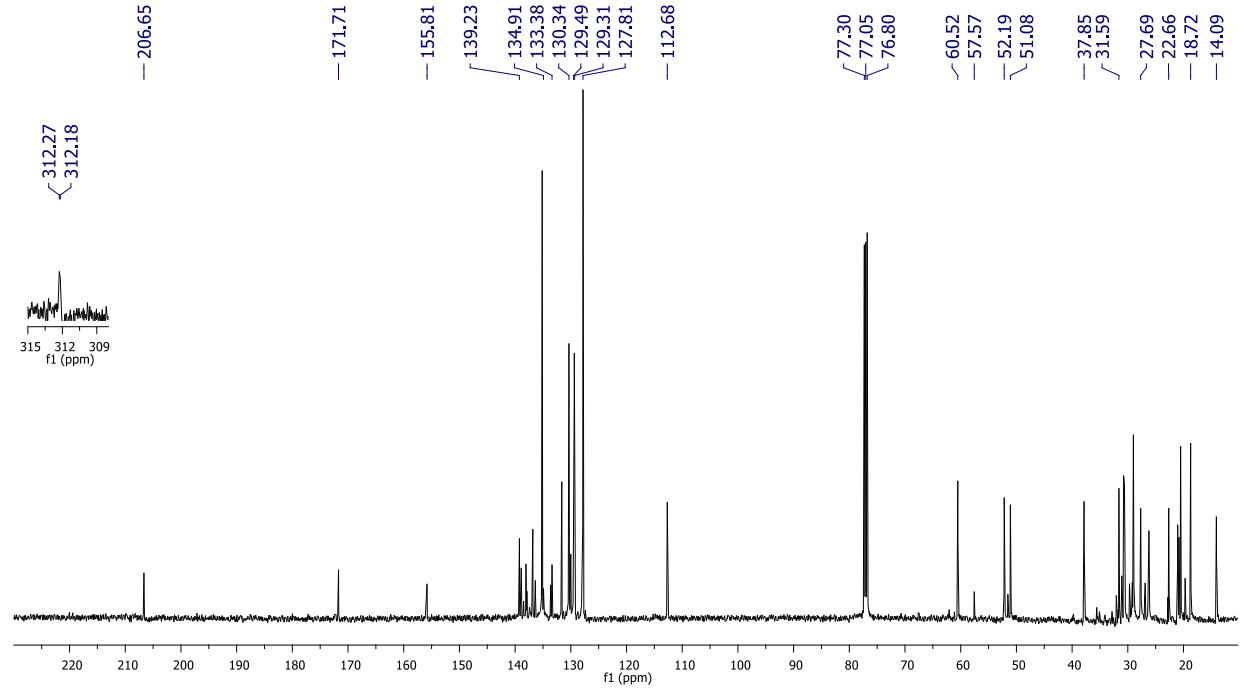

Mes
N
N
Mes
Cl
Ru
Cl
Ph
NTs

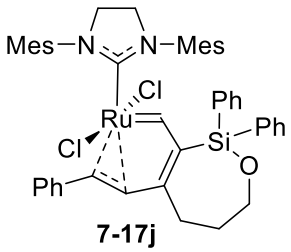
7-17d


16.17
7.70
7.68
7.25
7.13
7.07
5.36
5.33
5.08
5.05
4.13
4.11
3.98
3.12
2.39
2.30
2.04
1.56
1.29
1.27
1.26
1.24
1.00
0.70
1.97
2.23
1.28
1.78
1.21
1.09
4.04
2.13
22.28
5.19
f1 (ppm)

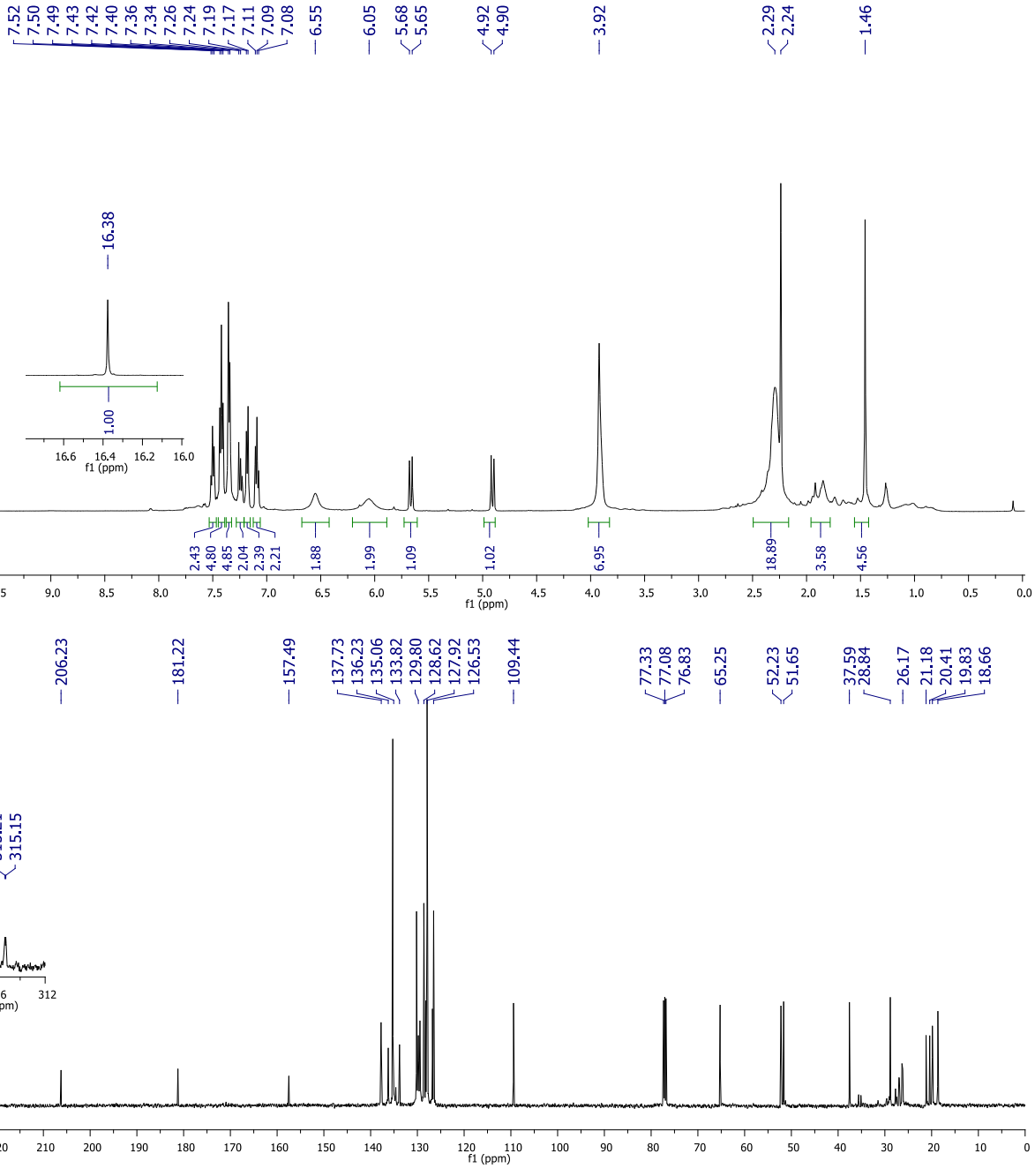

7.51
7.50
7.50
7.49
7.42
7.41
7.26
7.23
7.09
7.07
7.06
7.05
7.03
6.64
6.31
6.26
5.79
5.76
5.30
4.81
4.78
4.02
4.01
4.00
3.99
2.32
2.30
2.21
2.00
1.53
Mes−N
N−Mes
Cl
Ru
Cl
Ph
Ph
Si−Ph
O
7-17f
16.02
1.00
16.5
16.0
f1 (ppm)
2.36
8.22
1.22
4.57
2.08
1.91
1.17
1.08
5.25
9.60
6.37
3.42
6.79
f1 (ppm)
204.9
182.6
159.8
137.9
137.0
134.3
133.6
129.7
128.8
126.9
123.7
107.8
86.1
77.3
77.0
76.8
51.8
51.6
28.1
27.8
27.7
26.2
21.0
19.7
18.8
312.0
315
310
305
f1 (ppm)
f1 (ppm)

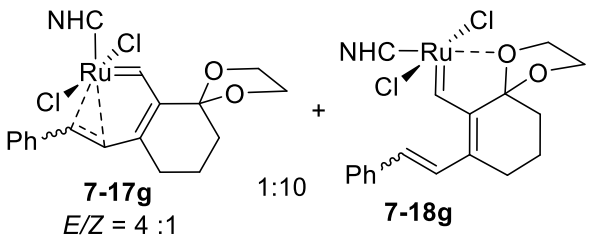

7.48
7.47
7.45
7.39
7.37
7.36
7.31
7.30
7.26
6.99
6.94
6.20
5.08
5.05
4.08
3.97
3.96
3.95
3.93
3.92
3.91
2.62
2.56
2.46
2.34
2.30
2.02
1.60
1.26
1.16
1.14
1.12
0.97
0.89
0.88
0.87
Mes−N
N−Mes
Cl
Ru
Cl
Ph
Si
Ph
O
C6H13
7-17h
16.43
1.00
16.5
16.0
f1 (ppm)
2.00
4.64
4.13
3.15
1.57
1.41
4.71
4.46
1.97
6.31
2.46
11.42
3.03
3.58
7.34
17.88
3.57
5.59
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


206.65
171.71
155.81
139.23
134.91
133.38
130.34
129.49
129.31
127.81
112.68
77.30
77.05
76.80
60.52
57.57
52.19
51.08
37.85
31.59
27.69
22.66
18.72
14.09
312.27
312.18
315
312
309
f1 (ppm)
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
f1 (ppm)


Mes
N
N
Mes
Cl
Ru
Cl
Ph
Si
Ph
Ph
O

7-17j


7.52
7.50
7.49
7.43
7.42
7.40
7.36
7.34
7.26
7.24
7.19
7.17
7.11
7.09
7.08
6.55
6.05
5.68
5.65
4.92
4.90
3.92
2.29
2.24
1.46
16.38
1.00
16.6
16.4
16.2
16.0
f1 (ppm)
2.43
4.80
4.85
2.04
2.39
2.21
1.88
1.99
1.09
1.02
6.95
18.89
3.58
4.56
f1 (ppm)
206.23
181.22
157.49
137.73
136.23
135.06
133.82
129.80
128.62
127.92
126.53
109.44
77.33
77.08
76.83
65.25
52.23
51.65
37.59
28.84
26.17
21.18
20.41
19.83
18.66
315.21
315.15
320
316
312
f1 (ppm)
f1 (ppm)

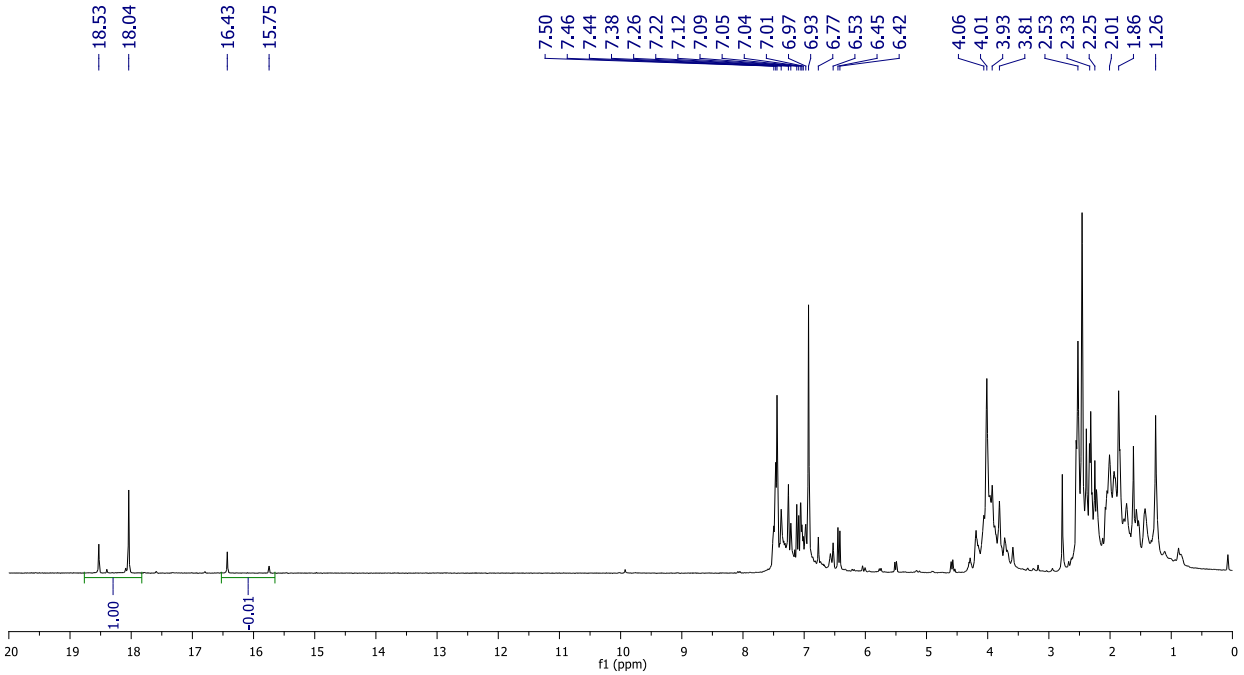


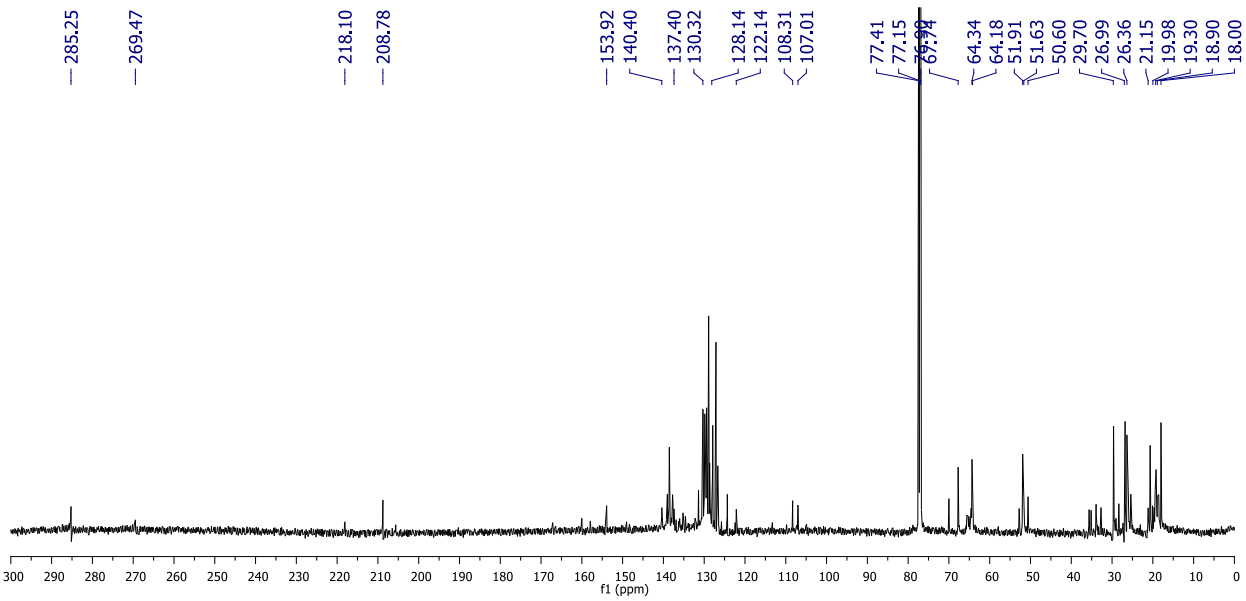
7-17g

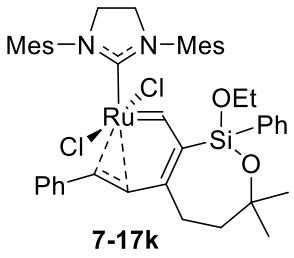
E/Z = 4 :1

1:10

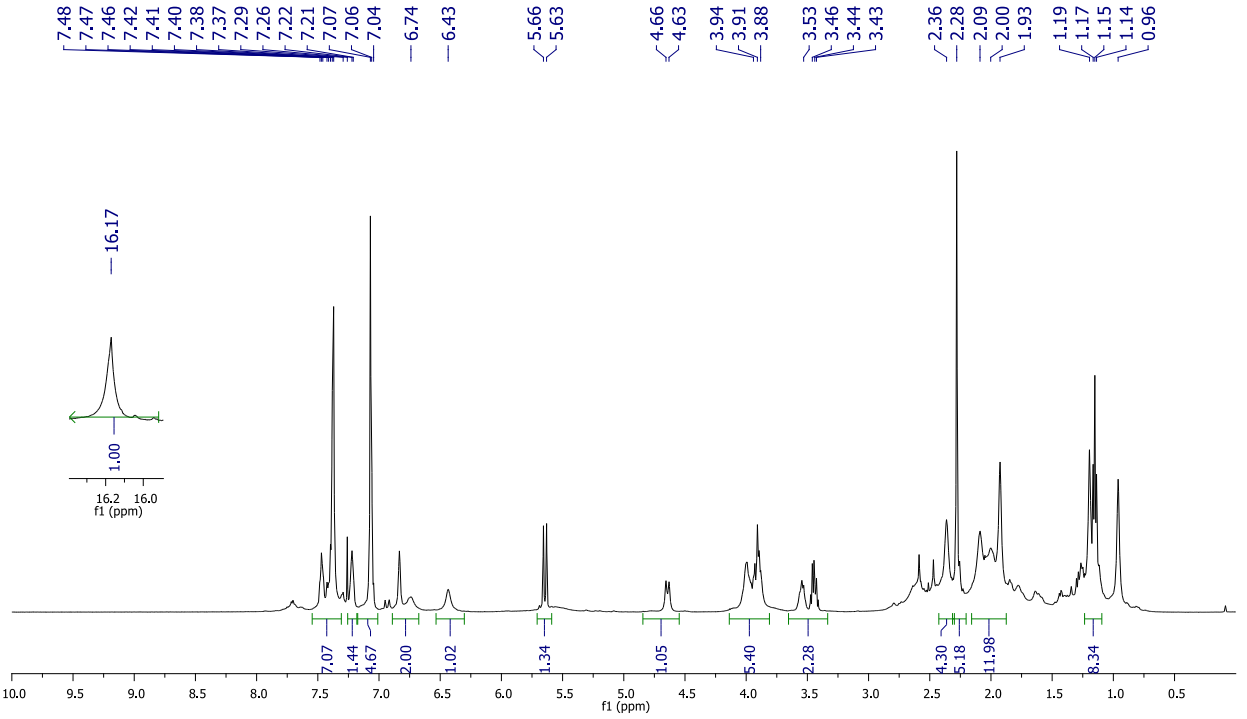
7-18g

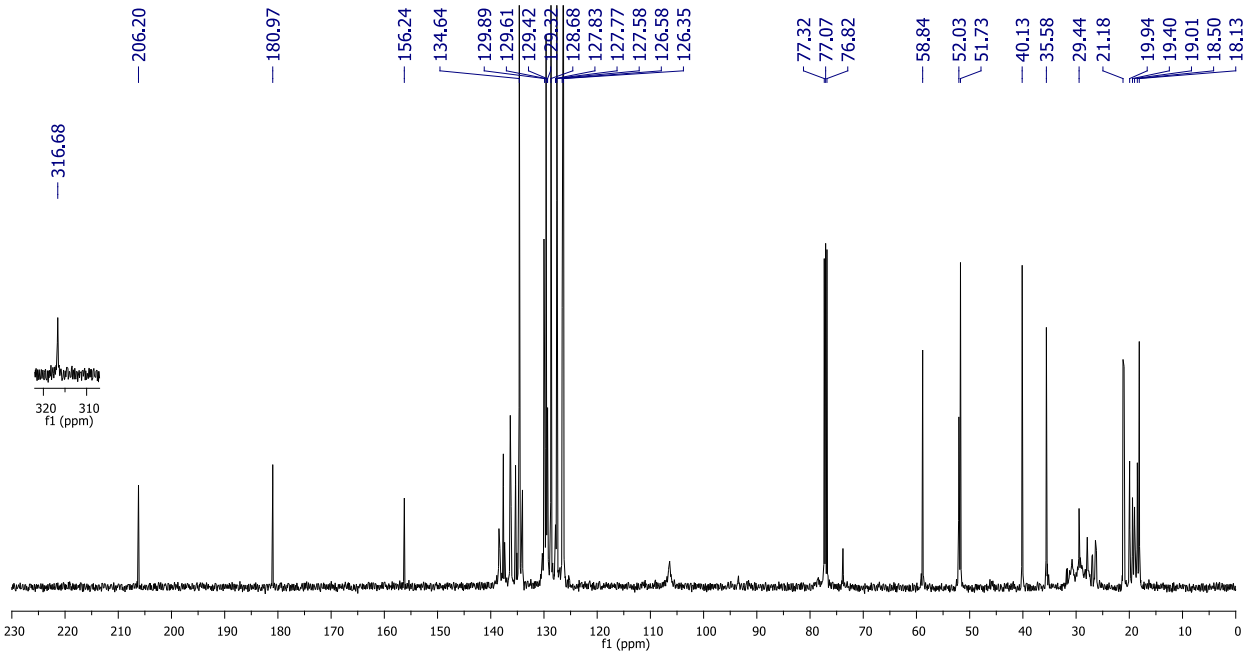


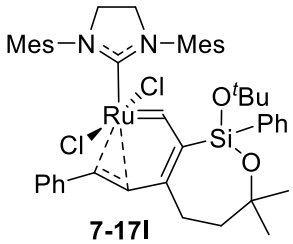



Mes
N
N
Mes
Cl
Ru
Cl
OEt
Si
Ph
O
Ph

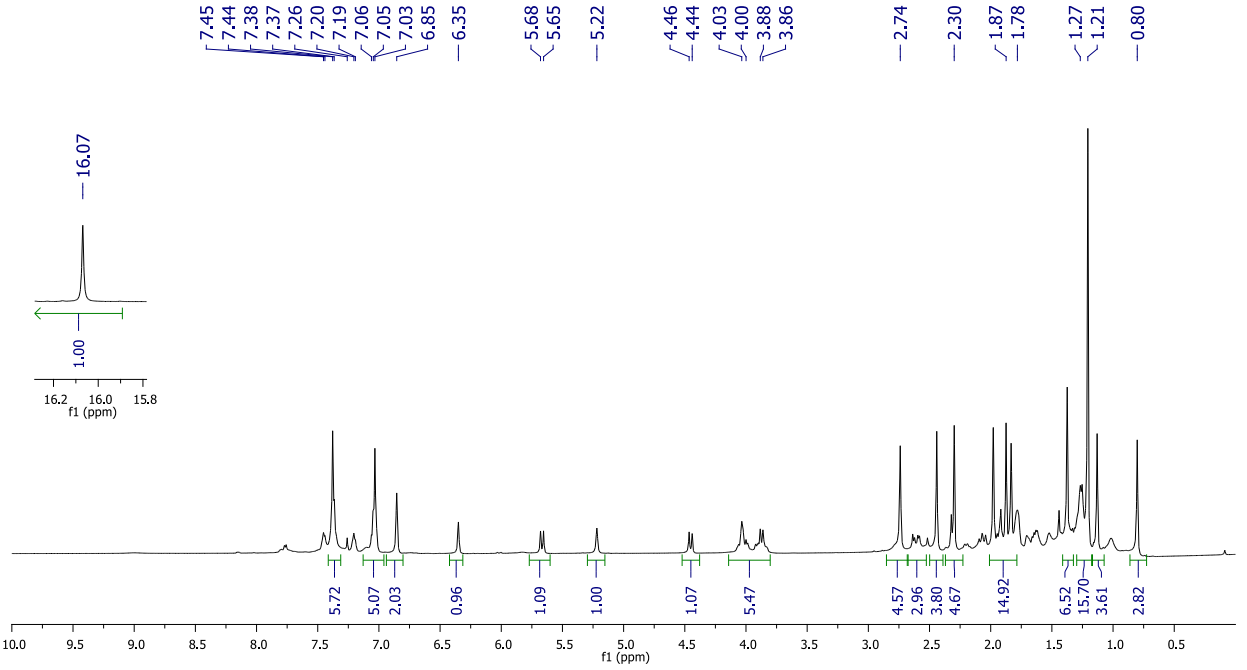
7-17k

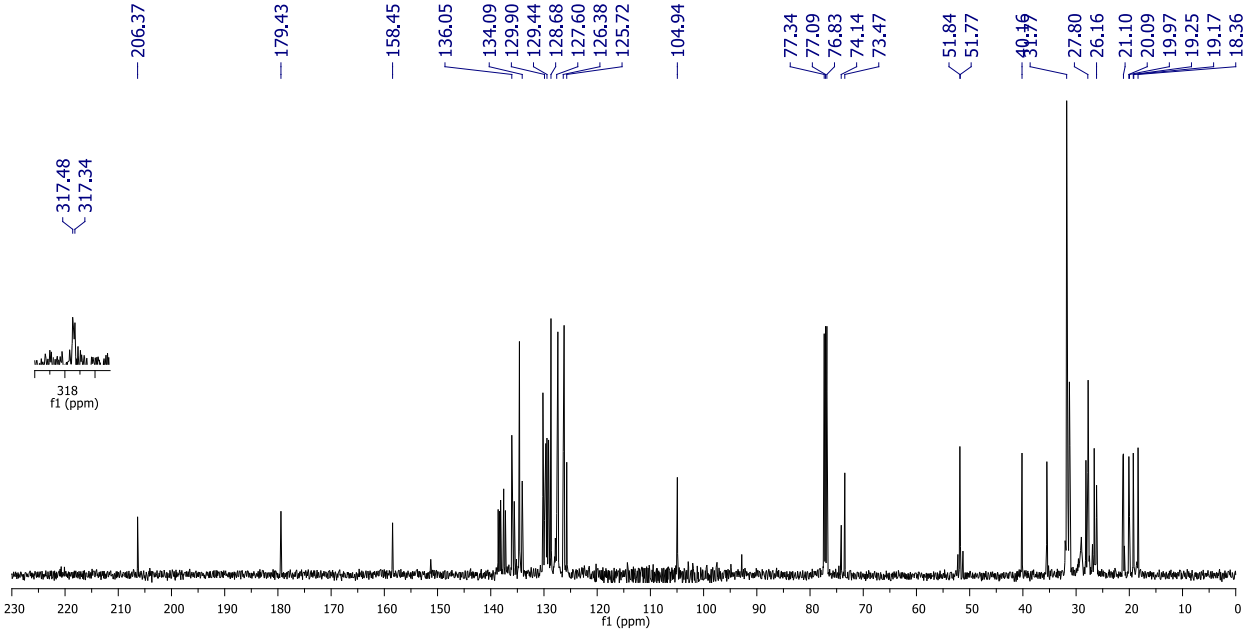

7.48 7.47 7.46 7.42 7.41 7.40 7.38 7.37 7.29 7.26 7.22 7.21 7.07 7.06 7.04 6.74 6.43 5.66 5.63 4.66 4.63 3.94 3.91 3.88 3.53 3.46 3.44 3.43 2.36 2.28 2.09 2.00 1.93 1.19 1.17 1.15 1.14 0.96
16.17
1.00
16.2 16.0
f1 (ppm)
7.07 1.44 4.67 2.00 1.02 1.34 1.05 5.40 2.28 4.30 5.18 11.98 8.34
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

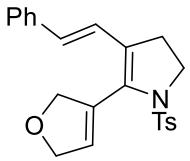

206.20 180.97 156.24 134.64 129.89 129.61 129.42 129.32 128.68 127.83 127.77 127.58 126.58 126.35 77.32 77.07 76.82 58.84 52.03 51.73 40.13 35.58 29.44 21.18 19.94 19.40 19.01 18.50 18.13
316.68
320 310
f1 (ppm)
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


Mes
N
N
Mes
Cl
Ru
Cl
O^{t}Bu
Si
Ph
Ph
O

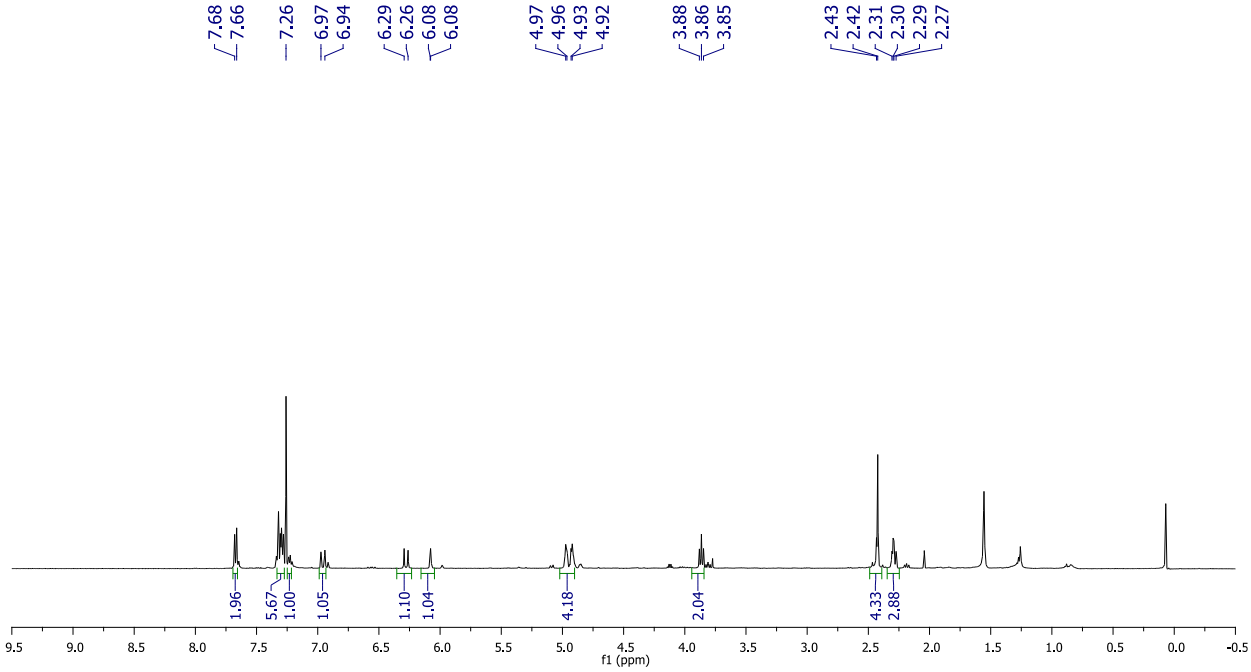
7-17l

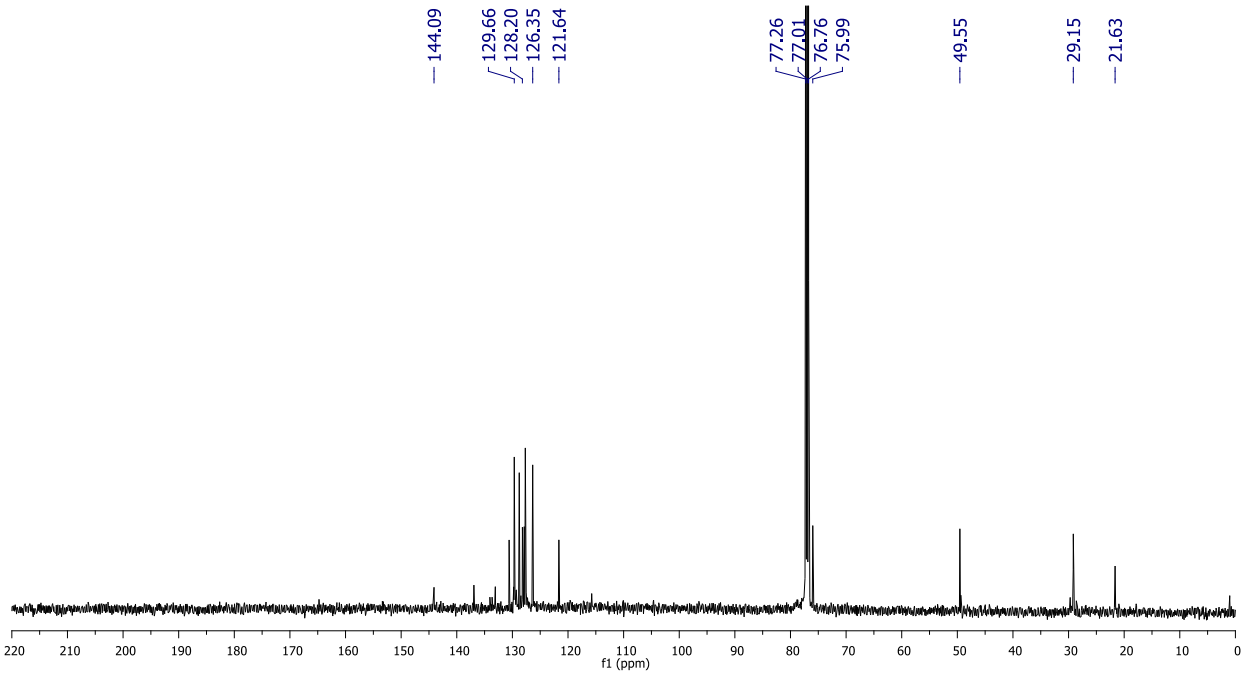

7.45
7.44
7.38
7.37
7.26
7.20
7.19
7.06
7.05
7.03
6.85
6.35
5.68
5.65
5.22
4.46
4.44
4.03
4.00
3.88
3.86
2.74
2.30
1.87
1.78
1.27
1.21
0.80
16.07
1.00
16.2
16.0
15.8
f1 (ppm)
5.72
5.07
2.03
0.96
1.09
1.00
1.07
5.47
4.57
2.96
3.80
4.67
14.92
6.52
15.70
3.61
2.82
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

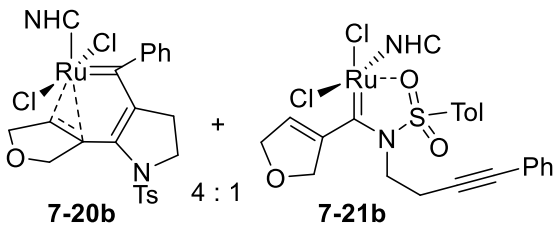

206.37
179.43
158.45
136.05
134.09
129.90
129.44
128.68
127.60
126.38
125.72
104.94
77.34
77.09
76.83
74.14
73.47
51.84
51.77
40.16
31.79
27.80
26.16
21.10
20.09
19.97
19.25
19.17
18.36
317.48
317.34
318
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


Ph
N
Ts
O

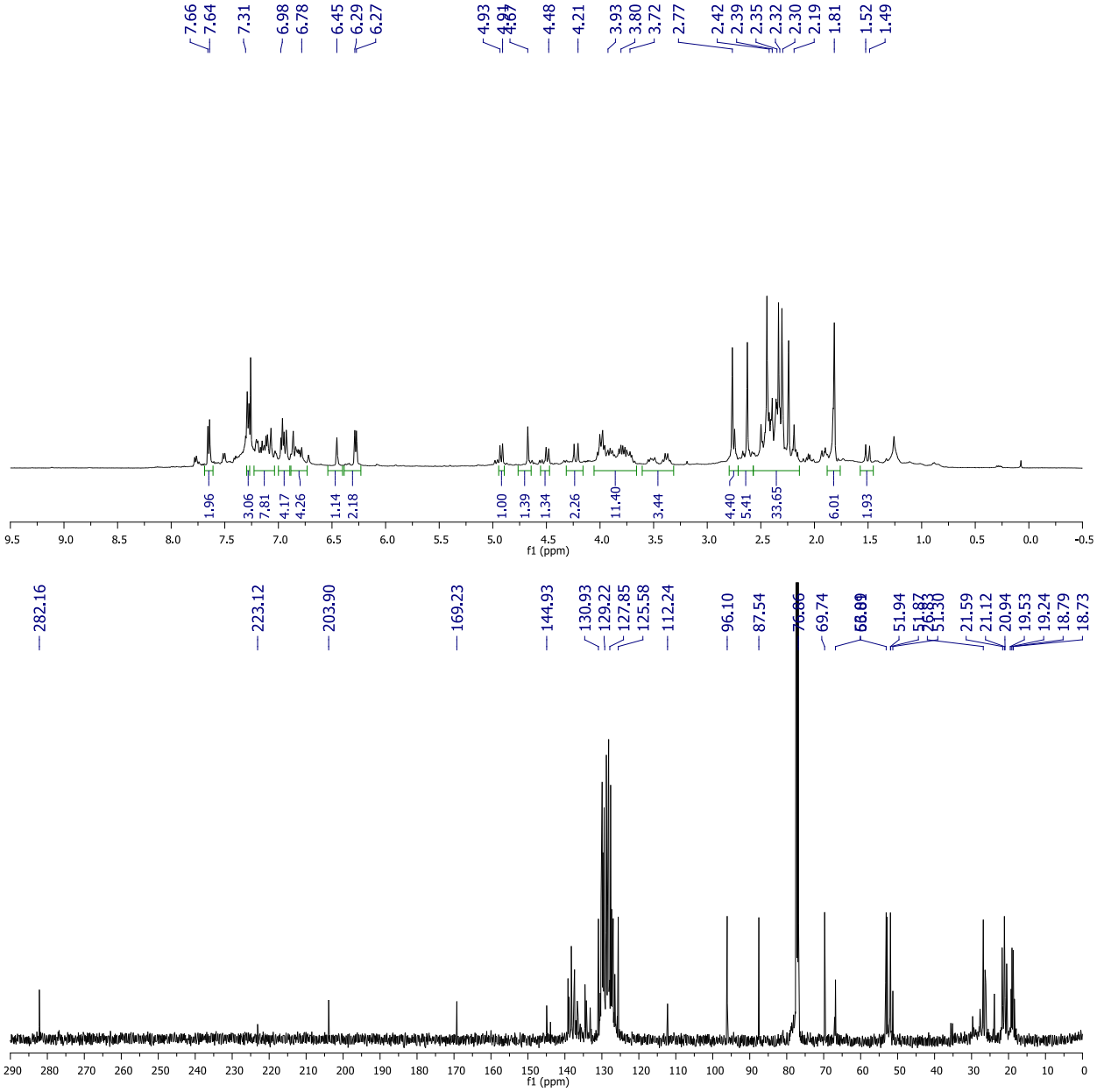
7-20a'

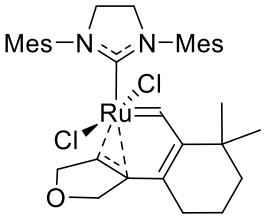

7.68
7.66
7.26
6.97
6.94
6.29
6.26
6.08
6.08
4.97
4.96
4.93
4.92
3.88
3.86
3.85
2.43
2.42
2.31
2.30
2.29
2.27
1.96
5.67
1.00
1.05
1.10
1.04
4.18
2.04
4.33
2.88
f1 (ppm)


144.09
129.66
128.20
126.35
121.64
77.26
77.01
76.76
75.99
49.55
29.15
21.63
f1 (ppm)

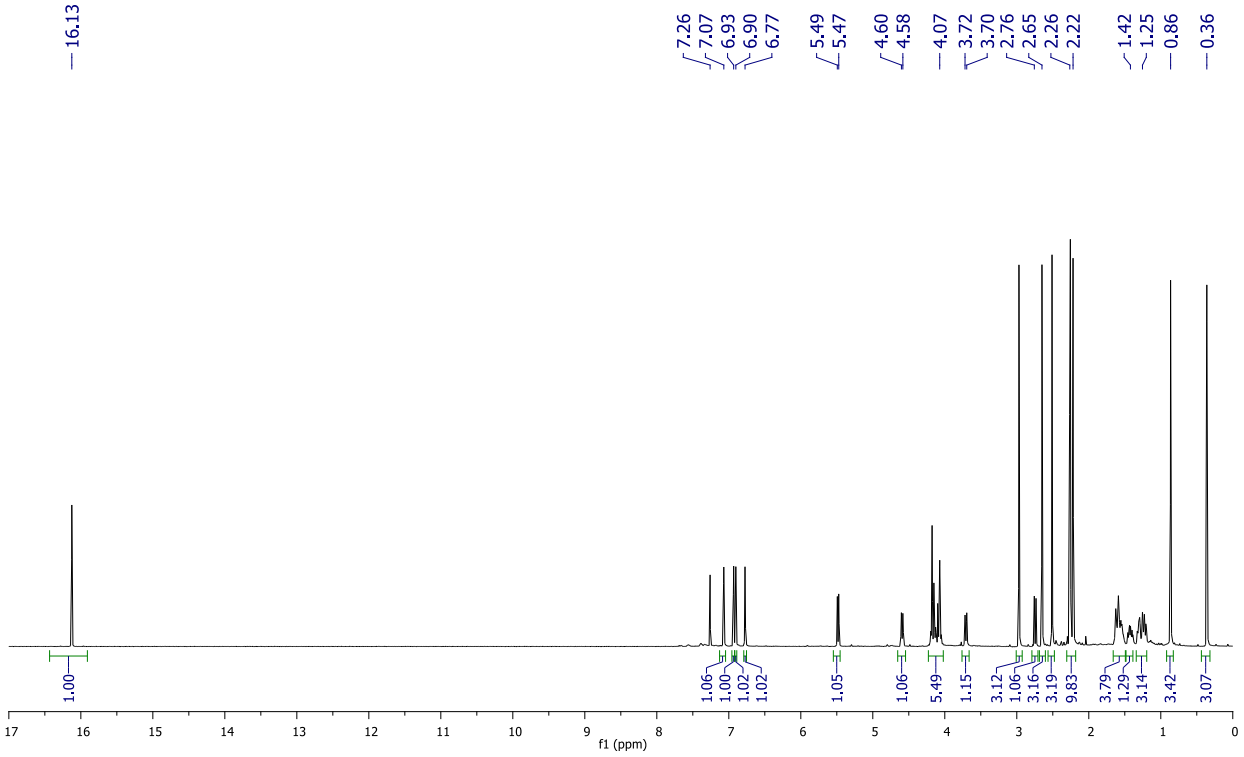

NHC
Cl
Ph
Ru
Cl
O
N
Ts
+
4 : 1
Cl
NHC
Ru
O
Cl
S
Tol
N
O
O
Ph

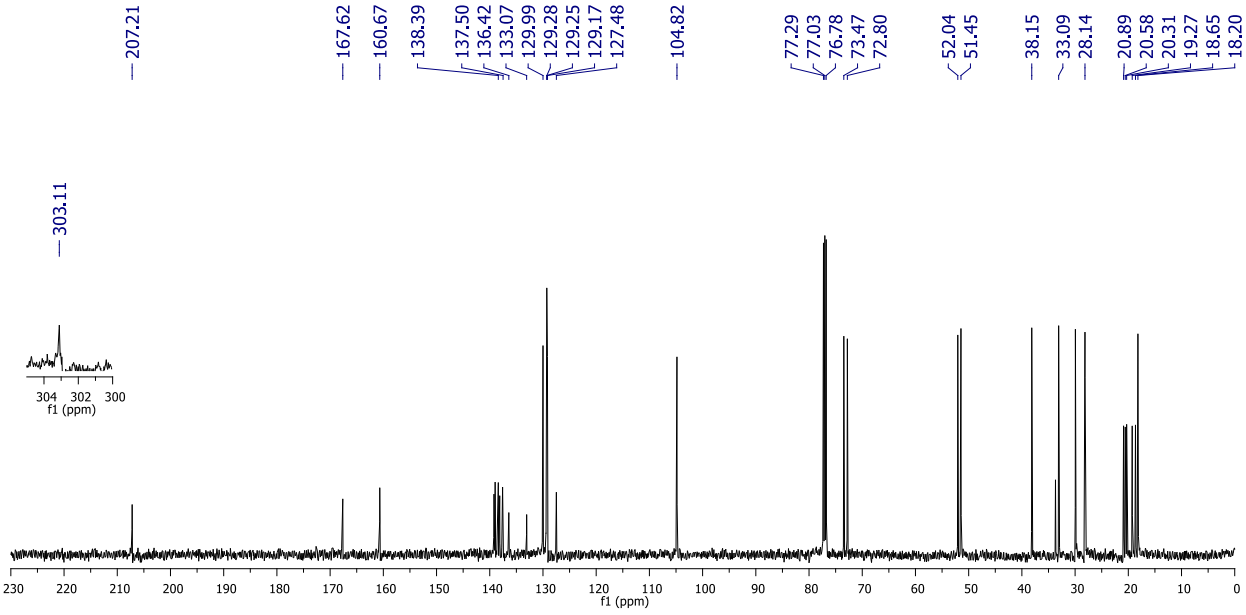
7-20b **7-21b**

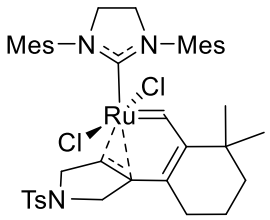

7.66
7.64
7.31
6.98
6.78
6.45
6.29
6.27
4.93
4.91
4.87
4.48
4.21
3.93
3.80
3.72
2.77
2.42
2.39
2.35
2.32
2.30
2.19
1.81
1.52
1.49
1.96
3.06
7.81
4.17
4.26
1.14
2.18
1.00
1.39
1.34
2.26
11.40
3.44
4.40
5.41
33.65
6.01
1.93
f1 (ppm)
282.16
223.12
203.90
169.23
144.93
130.93
129.22
127.85
125.58
112.24
96.10
87.54
76.86
69.74
58.89
51.94
51.87
51.83
51.30
21.59
21.12
20.94
19.53
19.24
18.79
18.73
f1 (ppm)


Mes−N
N−Mes
Cl
Ru
Cl
O

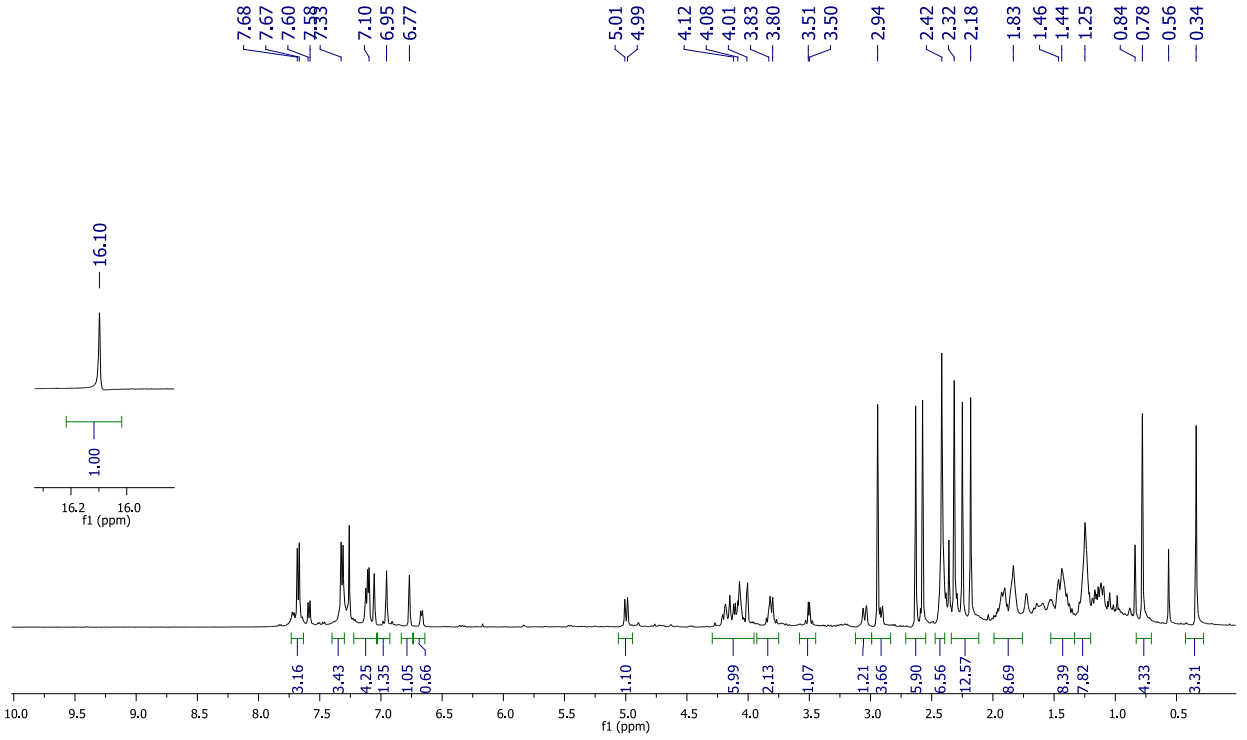
7-20c

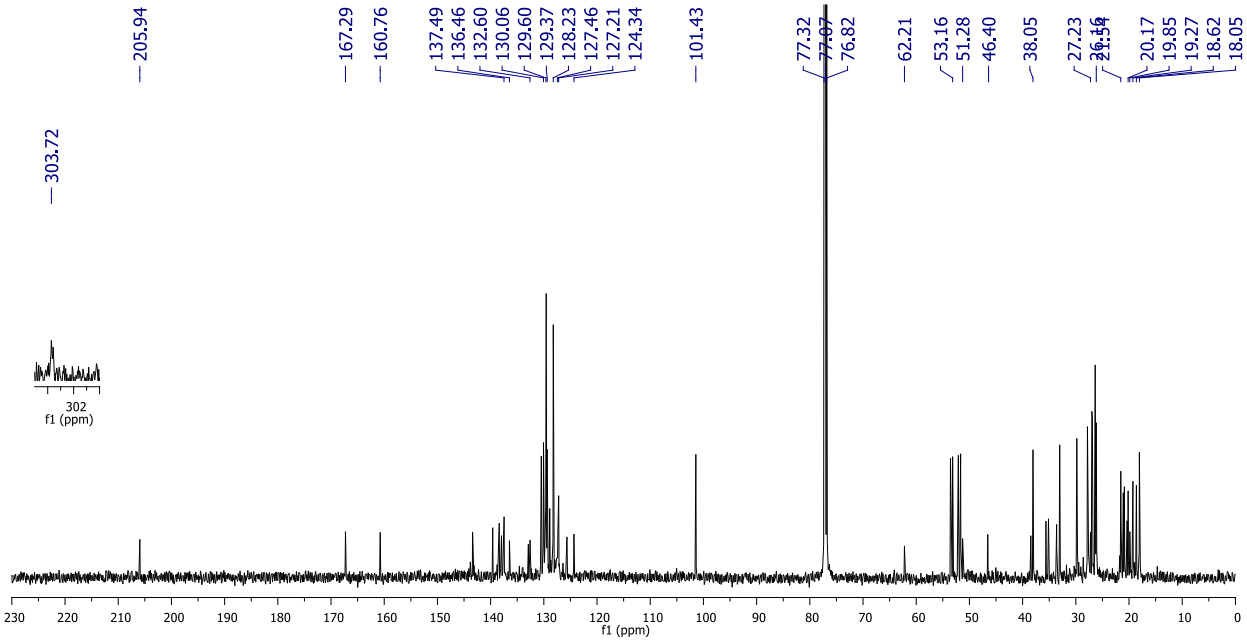

16.13
7.26
7.07
6.93
6.90
6.77
5.49
5.47
4.60
4.58
4.07
3.72
3.70
2.76
2.65
2.26
2.22
1.42
1.25
0.86
0.36
1.00
1.06
1.00
1.02
1.02
1.05
1.06
5.49
1.15
3.12
1.06
3.16
3.19
9.83
3.79
1.29
3.14
3.42
3.07
f1 (ppm)

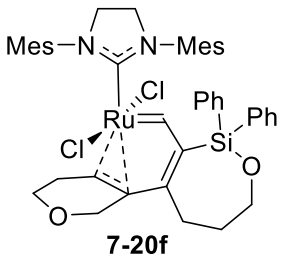

207.21
167.62
160.67
138.39
137.50
136.42
133.07
129.99
129.28
129.25
129.17
127.48
104.82
77.29
77.03
76.78
73.47
72.80
52.04
51.45
38.15
33.09
28.14
20.89
20.58
20.31
19.27
18.65
18.20
303.11
304
302
300
f1 (ppm)
f1 (ppm)


Mes–N
N–Mes
Cl
Ru
Cl
TsN

7-20d

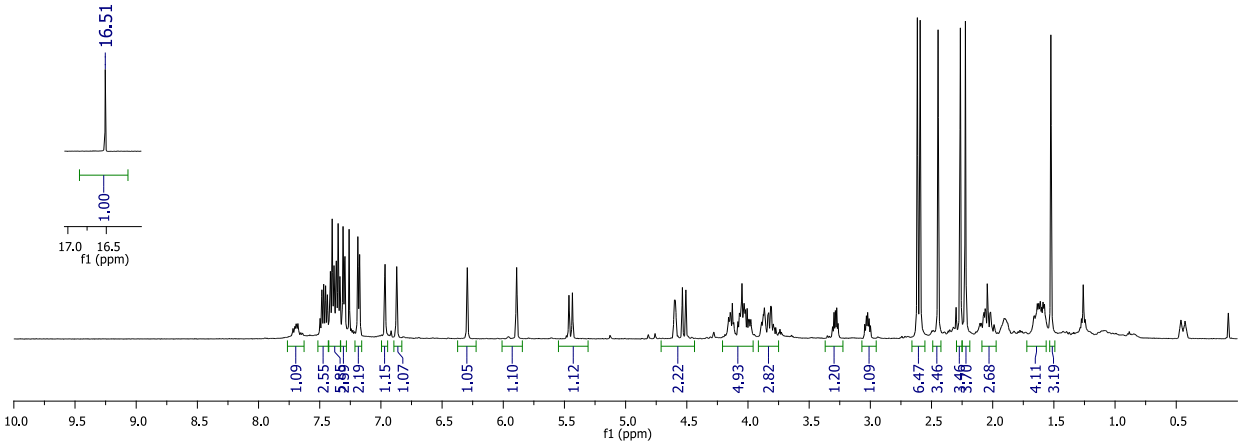

7.68
7.67
7.60
7.58
7.33
7.10
6.95
6.77
5.01
4.99
4.12
4.08
4.01
3.83
3.80
3.51
3.50
2.94
2.42
2.32
2.18
1.83
1.46
1.44
1.25
0.84
0.78
0.56
0.34
16.10
1.00
16.2
16.0
f1 (ppm)
3.16
3.43
4.25
1.35
1.05
0.66
1.10
5.99
2.13
1.07
1.21
3.66
5.90
6.56
12.57
8.69
8.39
7.82
4.33
3.31
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

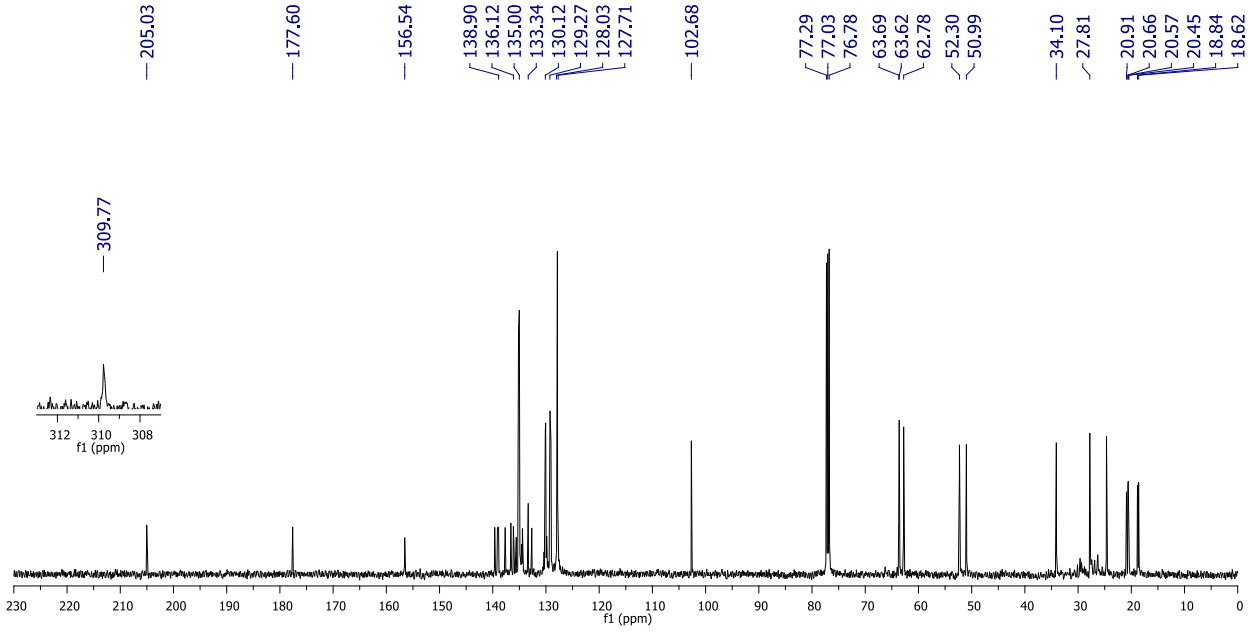

205.94
167.29
160.76
137.49
136.46
132.60
130.06
129.60
129.37
128.23
127.46
127.21
124.34
101.43
77.32
77.07
76.82
62.21
53.16
51.28
46.40
38.05
27.23
26.16
21.54
20.17
19.85
19.27
18.62
18.05
303.72
302
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

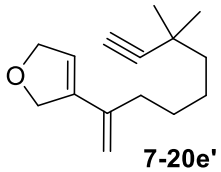

Mes–N
N–Mes
Cl
Ru
Ph
Ph
Si
Cl
O
O

7-20f

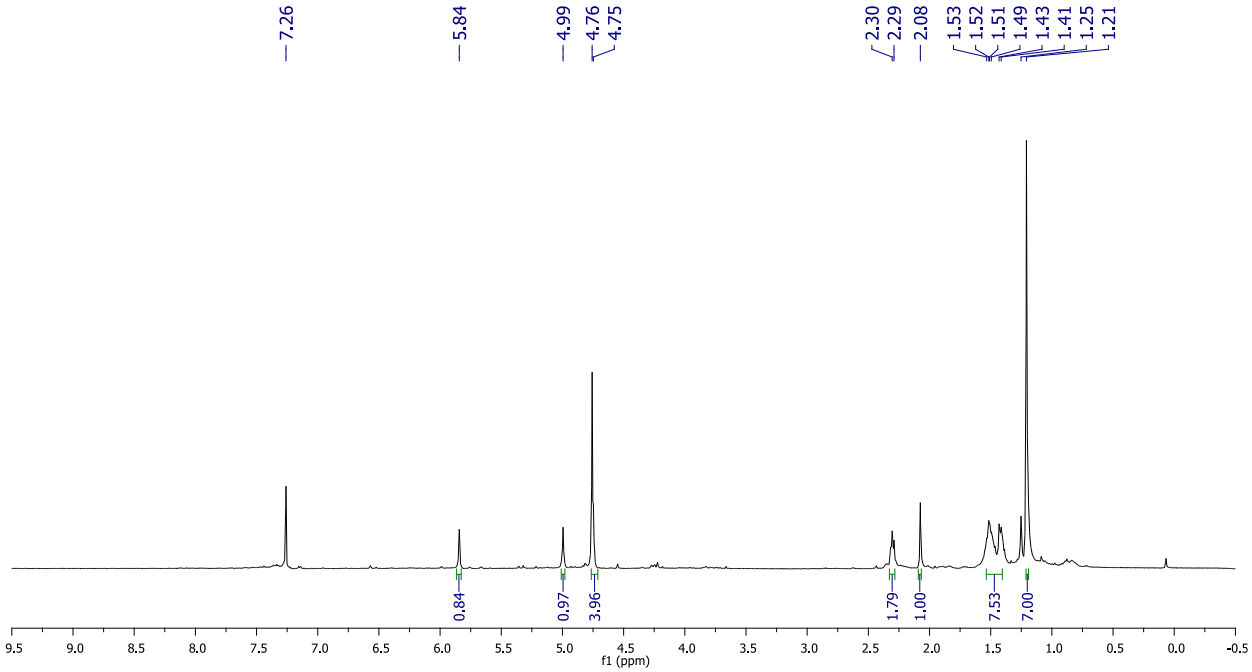
7.48
7.47
7.45
7.44
7.41
7.40
7.38
7.36
7.35
7.33
7.31
7.29
7.26
7.19
7.17
6.97
6.87
6.29
5.89
5.46
5.43
4.60
4.54
4.51
4.06
4.01
3.87
3.81
3.29
3.27
3.01
2.62
2.59
2.45
2.26
2.22
2.04
1.52
1.26

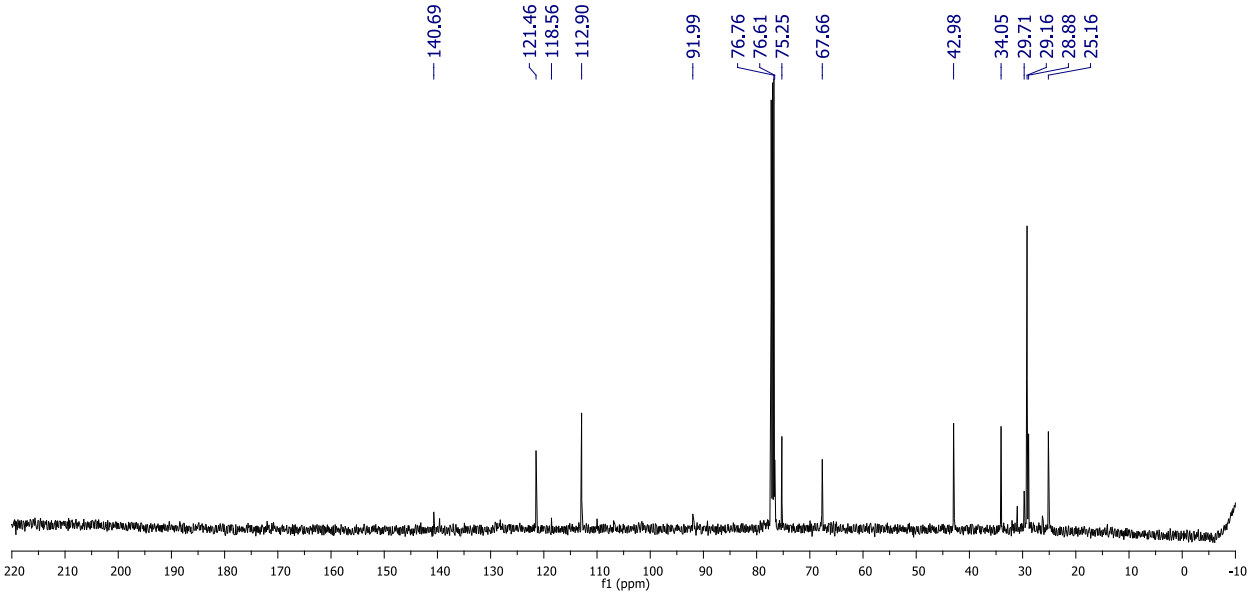

16.51
1.00
17.0
16.5
f1 (ppm)
1.09
2.55
5.85
2.19
1.15
1.07
1.05
1.10
1.12
2.22
4.93
2.82
1.20
1.09
6.47
3.46
2.68
4.11
3.19
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

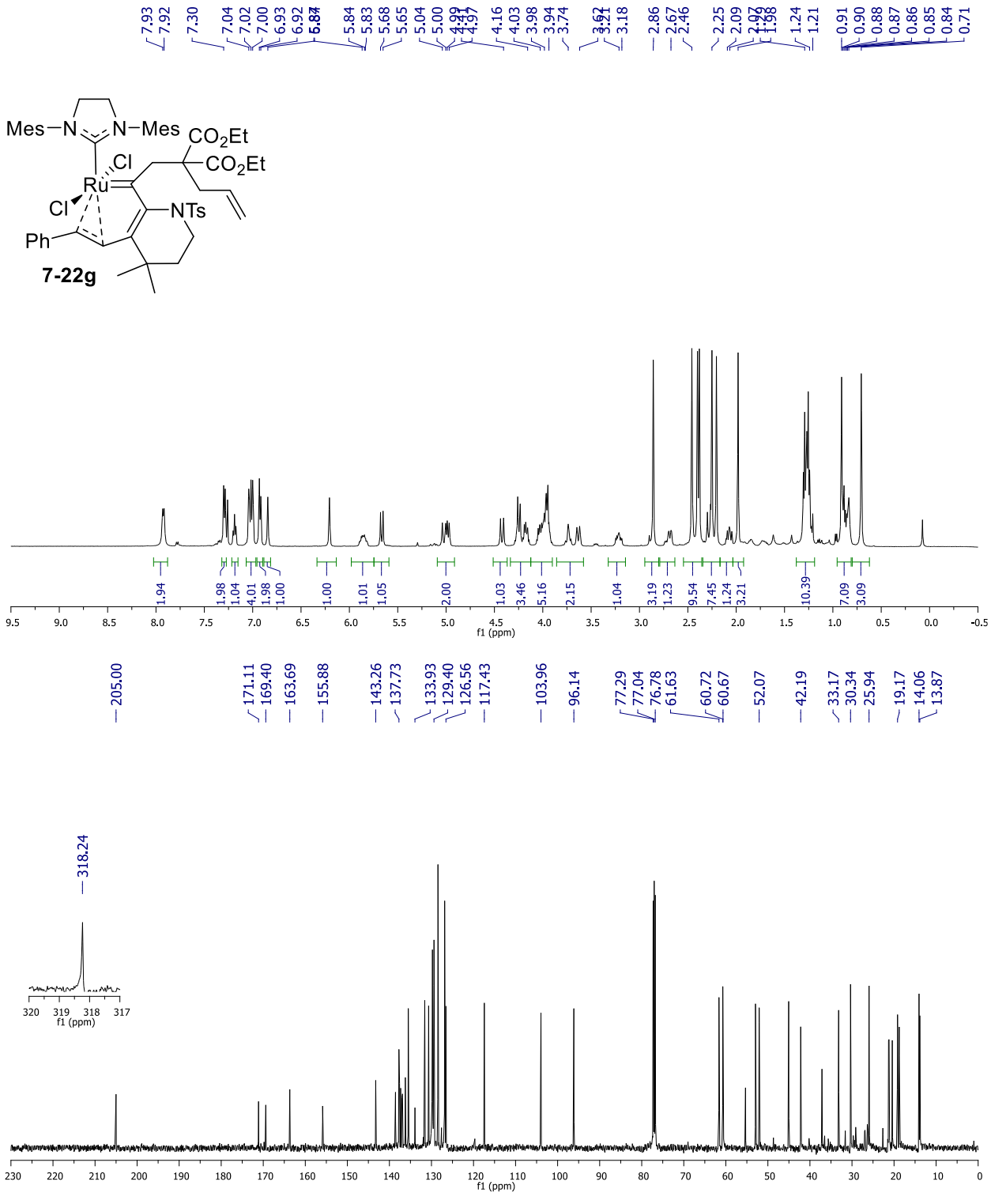

205.03
177.60
156.54
138.90
136.12
135.00
133.34
130.12
129.27
128.03
127.71
102.68
77.29
77.03
76.78
63.69
63.62
62.78
52.30
50.99
34.10
27.81
20.91
20.66
20.57
20.45
18.84
18.62
309.77
312
310
308
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

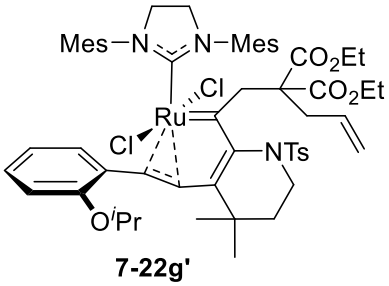


7-20e'

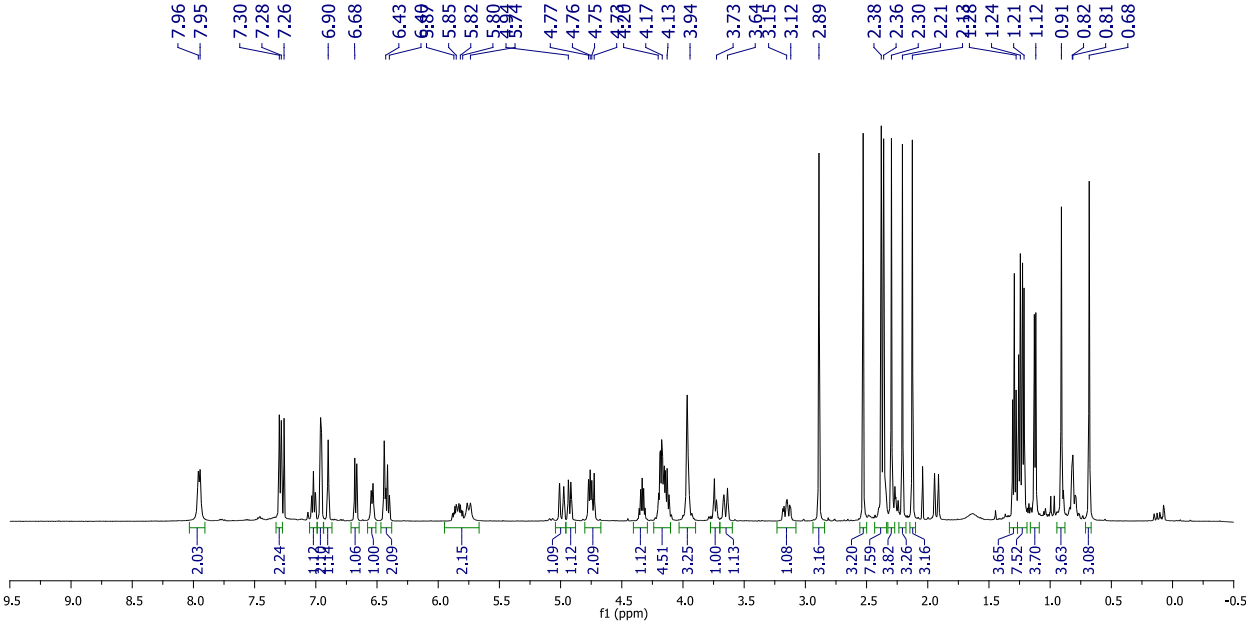

7.26
5.84
4.99
4.76
4.75
2.30
2.29
2.08
1.53
1.52
1.51
1.49
1.43
1.41
1.25
1.21
0.84
0.97
3.96
1.79
1.00
7.53
7.00
f1 (ppm)

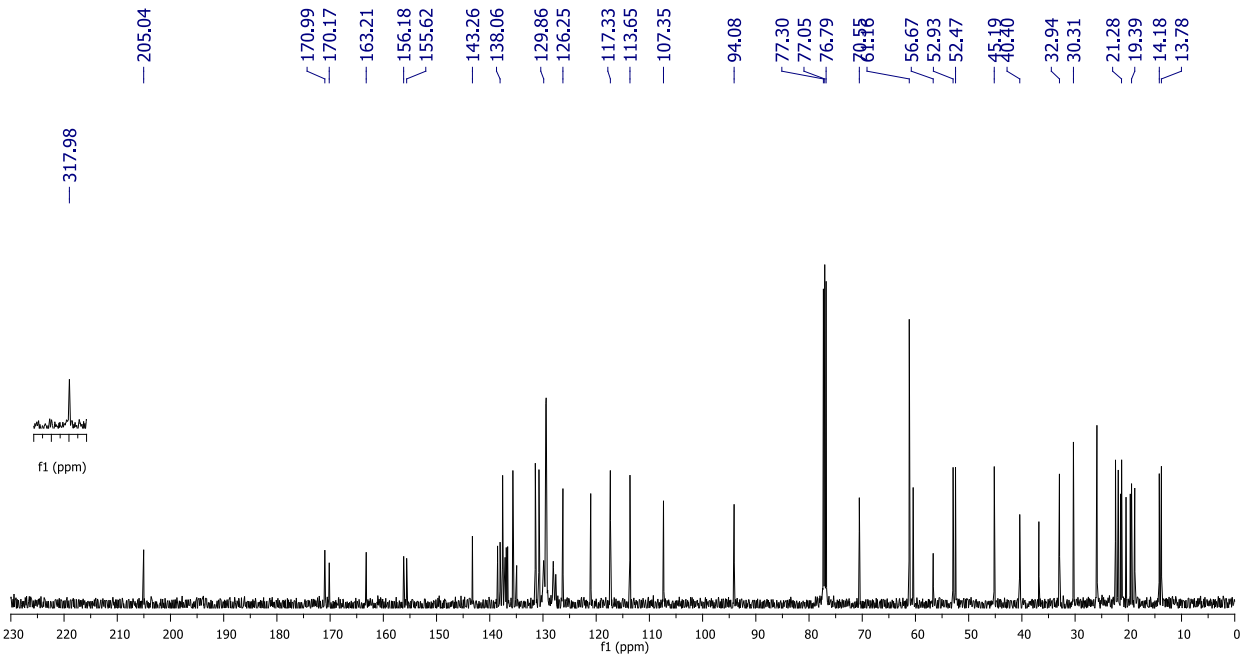

140.69
121.46
118.56
112.90
91.99
76.76
76.61
75.25
67.66
42.98
34.05
29.71
29.16
28.88
25.16
f1 (ppm)

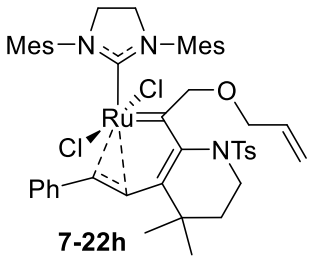

7.93
7.92
7.30
7.04
7.02
7.00
6.93
6.92
5.84
5.83
5.68
5.65
5.04
5.00
4.16
4.03
3.98
3.94
3.74
3.18
2.86
2.67
2.46
2.25
2.09
1.24
1.21
0.91
0.90
0.88
0.87
0.86
0.85
0.84
0.71
Mes
N
Mes
CO2Et
CO2Et
Cl
Ru
Cl
NTs
Ph
7-22g
1.94
1.98
1.04
4.01
1.98
1.00
1.00
1.01
1.05
2.00
1.03
3.46
5.16
2.15
1.04
3.19
1.23
9.54
7.45
1.24
3.21
10.39
7.09
3.09
f1 (ppm)
205.00
171.11
169.40
163.69
155.88
143.26
137.73
133.93
129.40
126.56
117.43
103.96
96.14
77.29
77.04
76.78
61.63
60.72
60.67
52.07
42.19
33.17
30.34
25.94
19.17
14.06
13.87
318.24
f1 (ppm)
f1 (ppm)


Mes–N
N–Mes
CO2Et
CO2Et
Cl
Ru
Cl
NTs
O'Pr

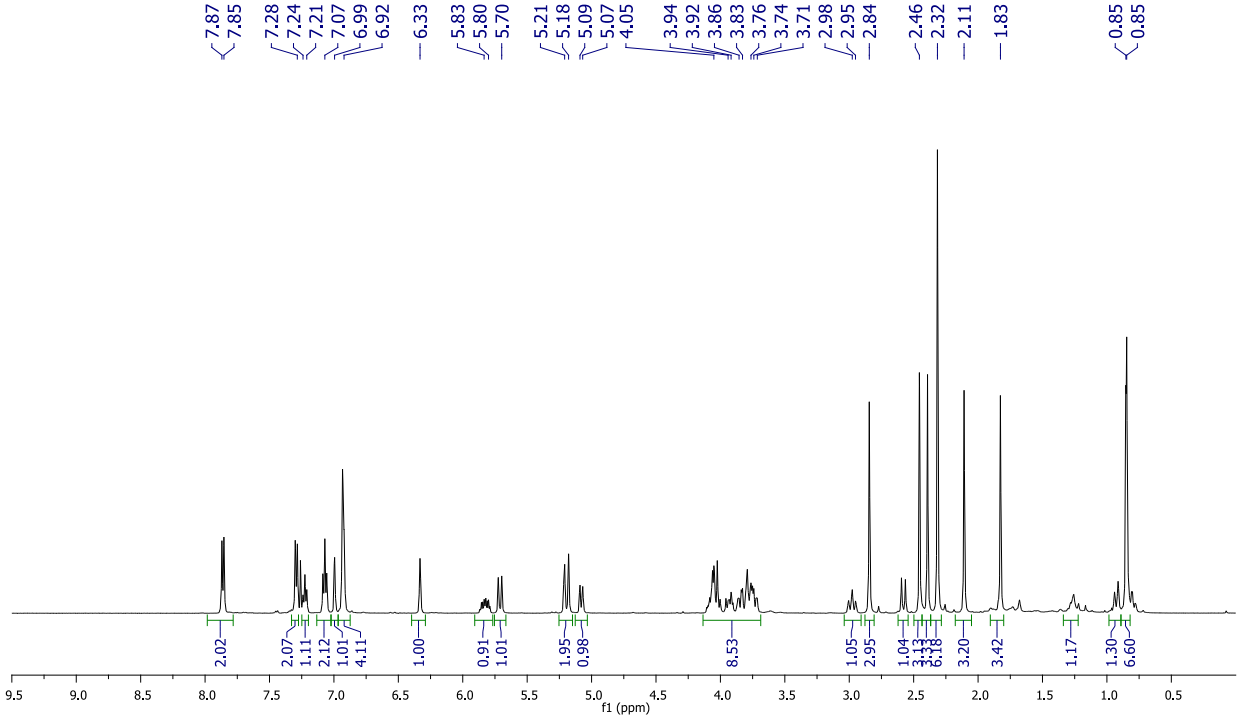
7-22g'

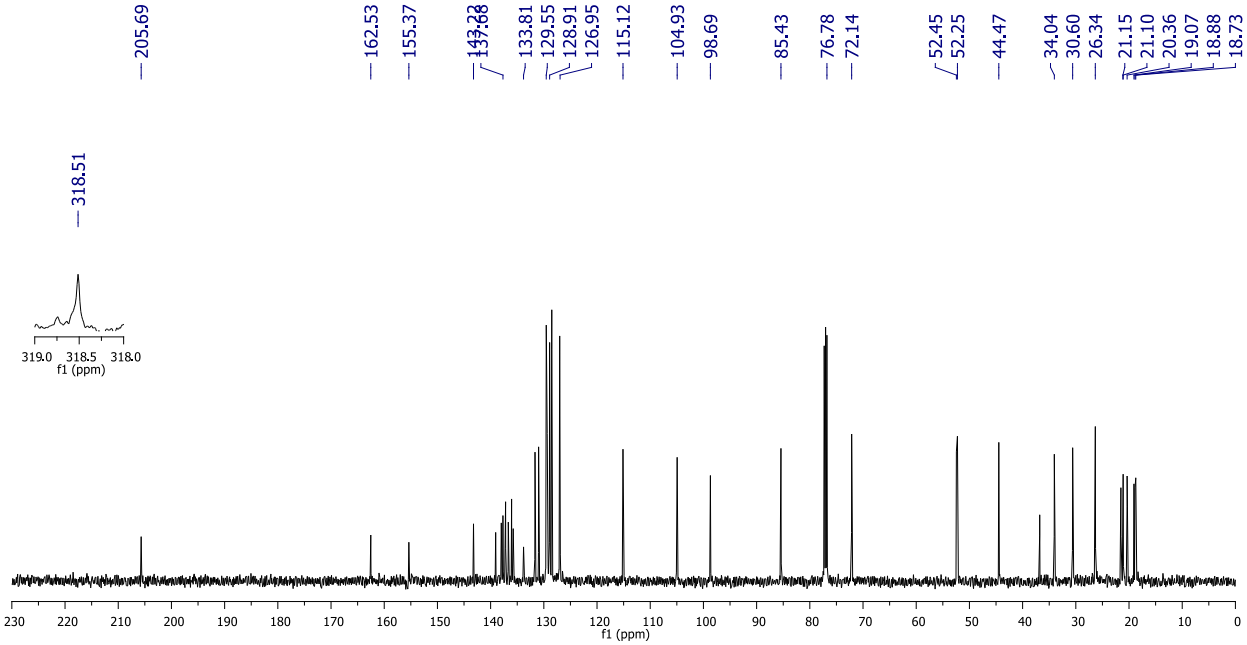

7.96
7.95
7.30
7.28
7.26
6.90
6.68
6.43
5.85
5.82
4.77
4.76
4.75
4.17
4.13
3.94
3.73
3.64
3.15
3.12
2.89
2.38
2.36
2.30
2.21
1.24
1.21
1.12
0.91
0.82
0.81
0.68
2.03
2.24
1.06
1.00
2.09
2.15
1.09
1.12
2.09
1.12
4.51
3.25
1.00
1.13
1.08
3.16
3.20
7.59
3.82
3.26
3.16
3.65
7.52
3.70
3.63
3.08
f1 (ppm)

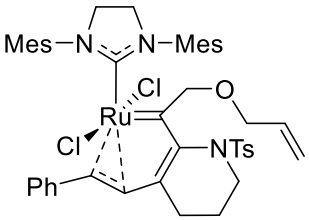

205.04
170.99
170.17
163.21
156.18
155.62
143.26
138.06
129.86
126.25
117.33
113.65
107.35
94.08
77.30
77.05
76.79
70.55
61.78
56.67
52.93
52.47
45.19
40.40
32.94
30.31
21.28
19.39
14.18
13.78
317.98
f1 (ppm)
f1 (ppm)


Mes
N
N
Mes
Cl
O
Ru
Cl
NTs
Ph

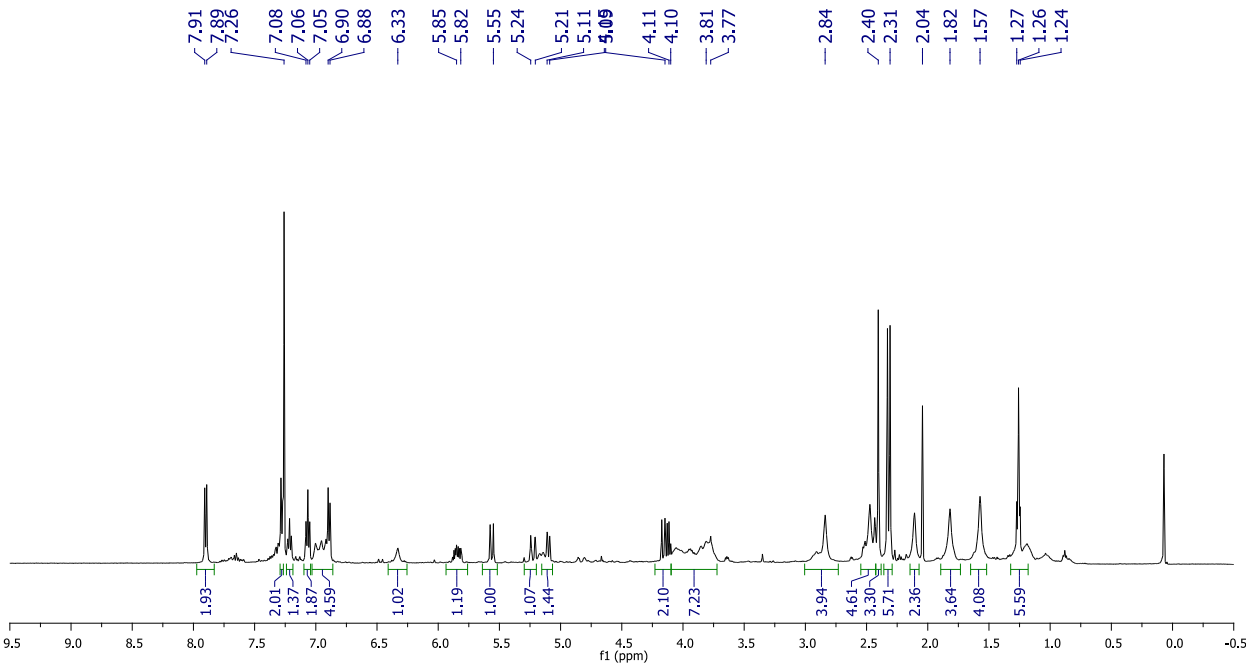
7-22h

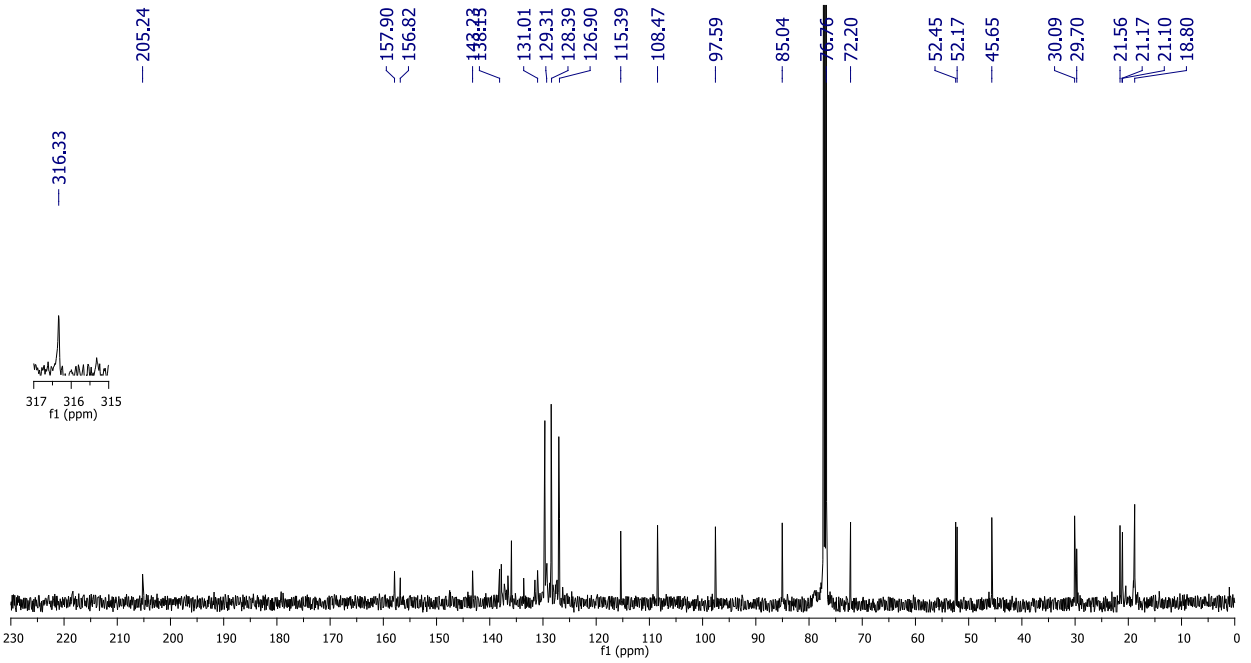

7.87
7.85
7.28
7.24
7.21
7.07
6.99
6.92
6.33
5.83
5.80
5.70
5.21
5.18
5.09
5.07
4.05
3.94
3.92
3.86
3.83
3.76
3.74
3.71
2.98
2.95
2.84
2.46
2.32
2.11
1.83
0.85
0.85
2.02
2.07
1.11
2.12
1.01
4.11
1.00
0.91
1.01
1.95
0.98
8.53
1.05
2.95
1.04
3.13
6.18
3.20
3.42
1.17
1.30
6.60
f1 (ppm)

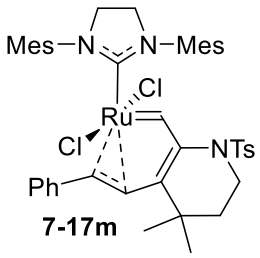

205.69
162.53
155.37
137.88
133.81
129.55
128.91
126.95
115.12
104.93
98.69
85.43
76.78
72.14
52.45
52.25
44.47
34.04
30.60
26.34
21.15
21.10
20.36
19.07
18.88
18.73
318.51
319.0
318.5
318.0
f1 (ppm)
f1 (ppm)


Mes
N
N
Mes
Cl
Ru
O
Cl
NTs
Ph

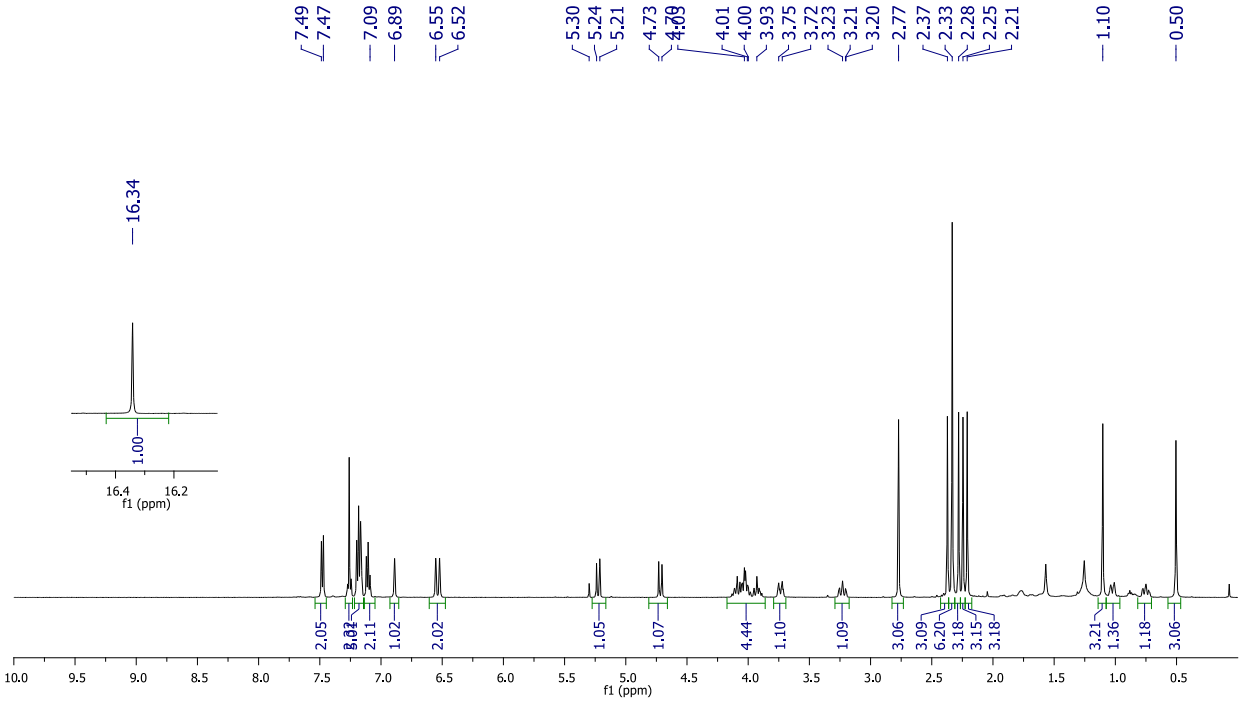
7-22i

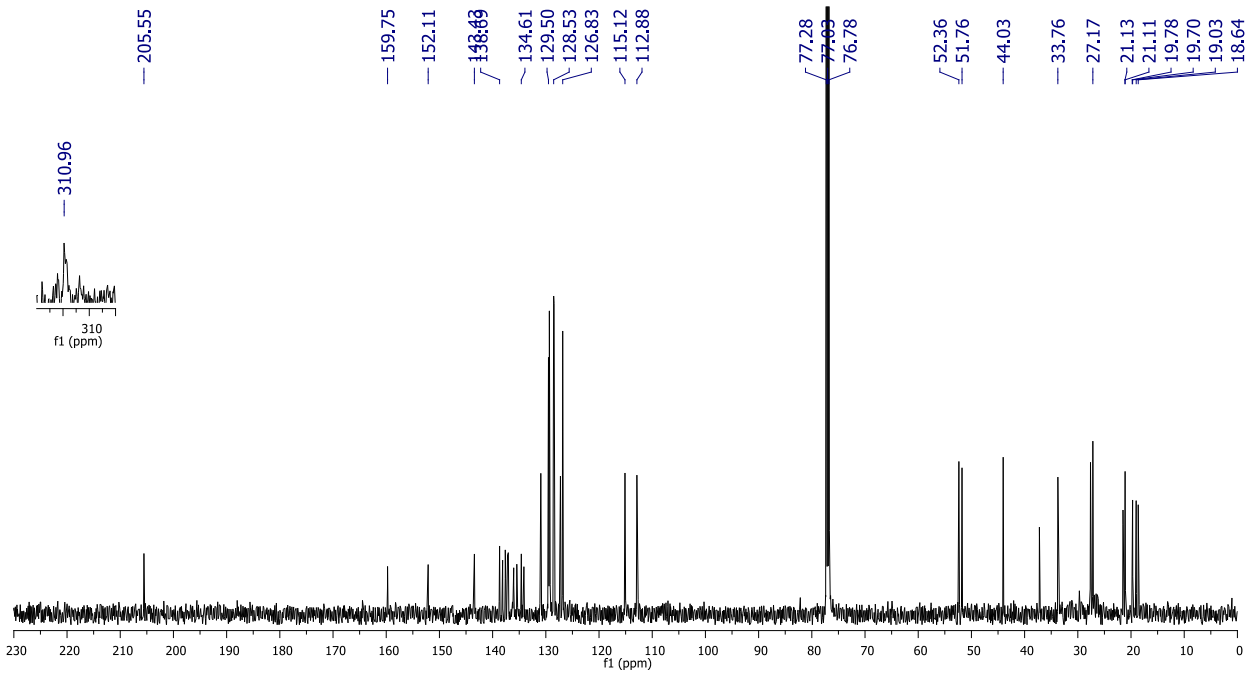

7.91
7.89
7.26
7.08
7.06
7.05
6.90
6.88
6.33
5.85
5.82
5.55
5.24
5.21
5.11
4.11
4.10
3.81
3.77
2.84
2.40
2.31
2.04
1.82
1.57
1.27
1.26
1.24
1.93
2.01
1.37
1.87
4.59
1.02
1.19
1.00
1.07
1.44
2.10
7.23
3.94
4.61
3.30
5.71
2.36
3.64
4.08
5.59
f1 (ppm)

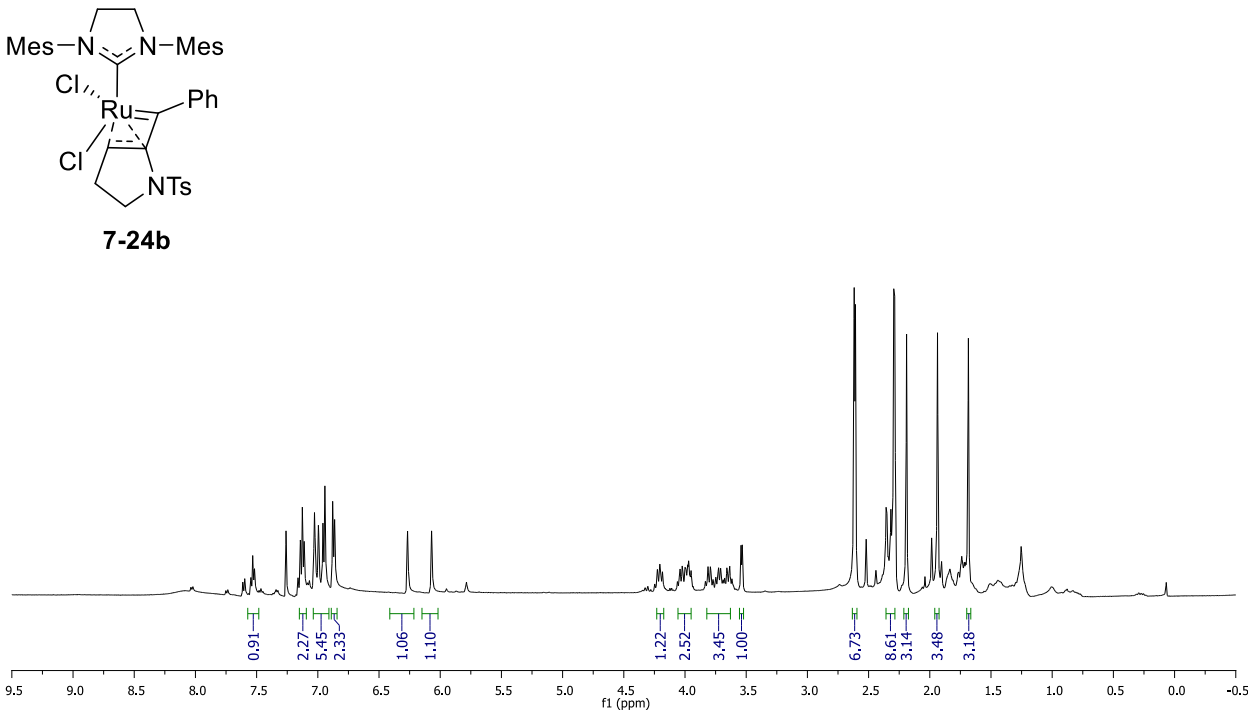

205.24
157.90
156.82
131.01
129.31
128.39
126.90
115.39
108.47
97.59
85.04
72.20
52.45
52.17
45.65
30.09
29.70
21.56
21.17
21.10
18.80
316.33
317
316
315
f1 (ppm)
f1 (ppm)


Mes
N
N
Mes
Cl
Ru
Cl
NTs
Ph

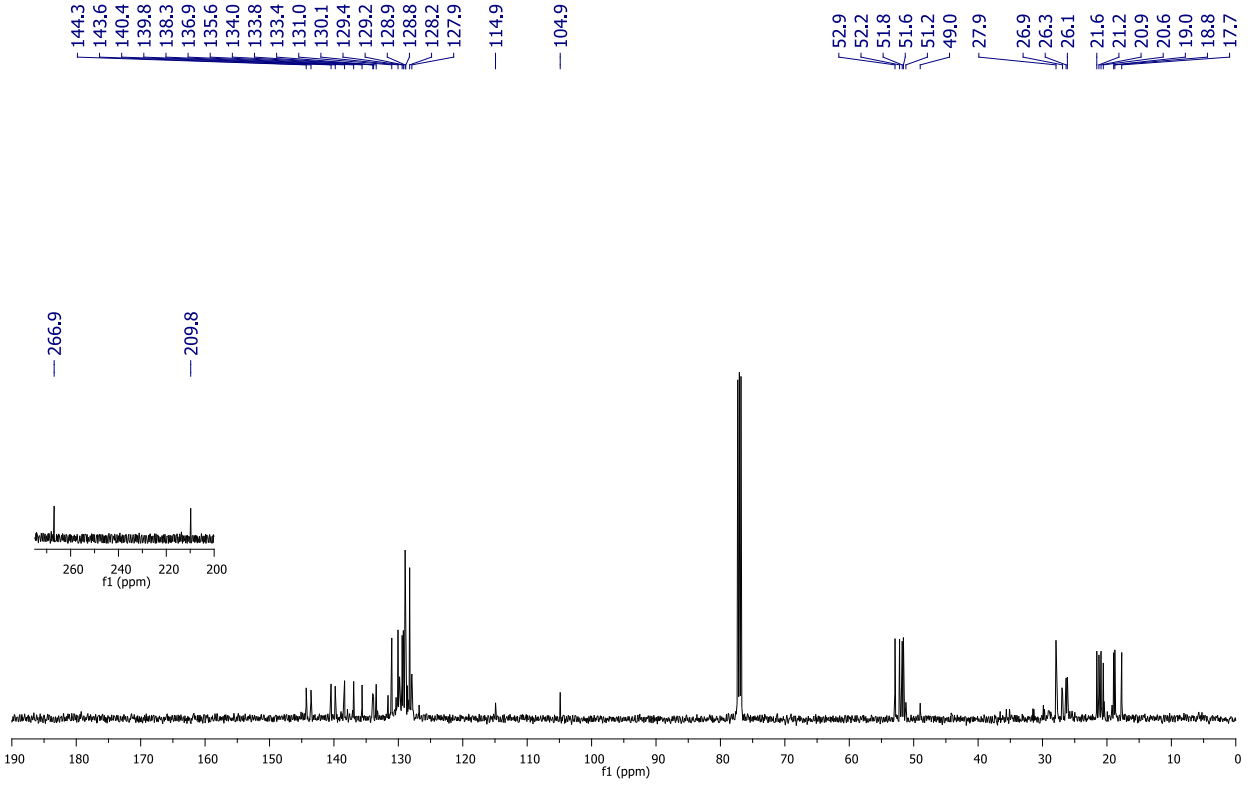
7-17m

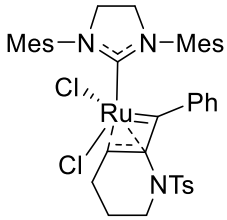

7.49
7.47
7.09
6.89
6.55
6.52
5.30
5.24
5.21
4.73
4.01
4.00
3.93
3.75
3.72
3.23
3.21
3.20
2.77
2.37
2.33
2.28
2.25
2.21
1.10
0.50
16.34
1.00
16.4
16.2
f1 (ppm)
2.05
2.11
1.02
2.02
1.05
1.07
4.44
1.10
1.09
3.06
3.09
6.20
3.18
3.15
3.18
3.21
1.36
1.18
3.06
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


205.55
159.75
152.11
134.61
129.50
128.53
126.83
115.12
112.88
77.28
77.03
76.78
52.36
51.76
44.03
33.76
27.17
21.13
21.11
19.78
19.70
19.03
18.64
310.96
310
f1 (ppm)
230
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

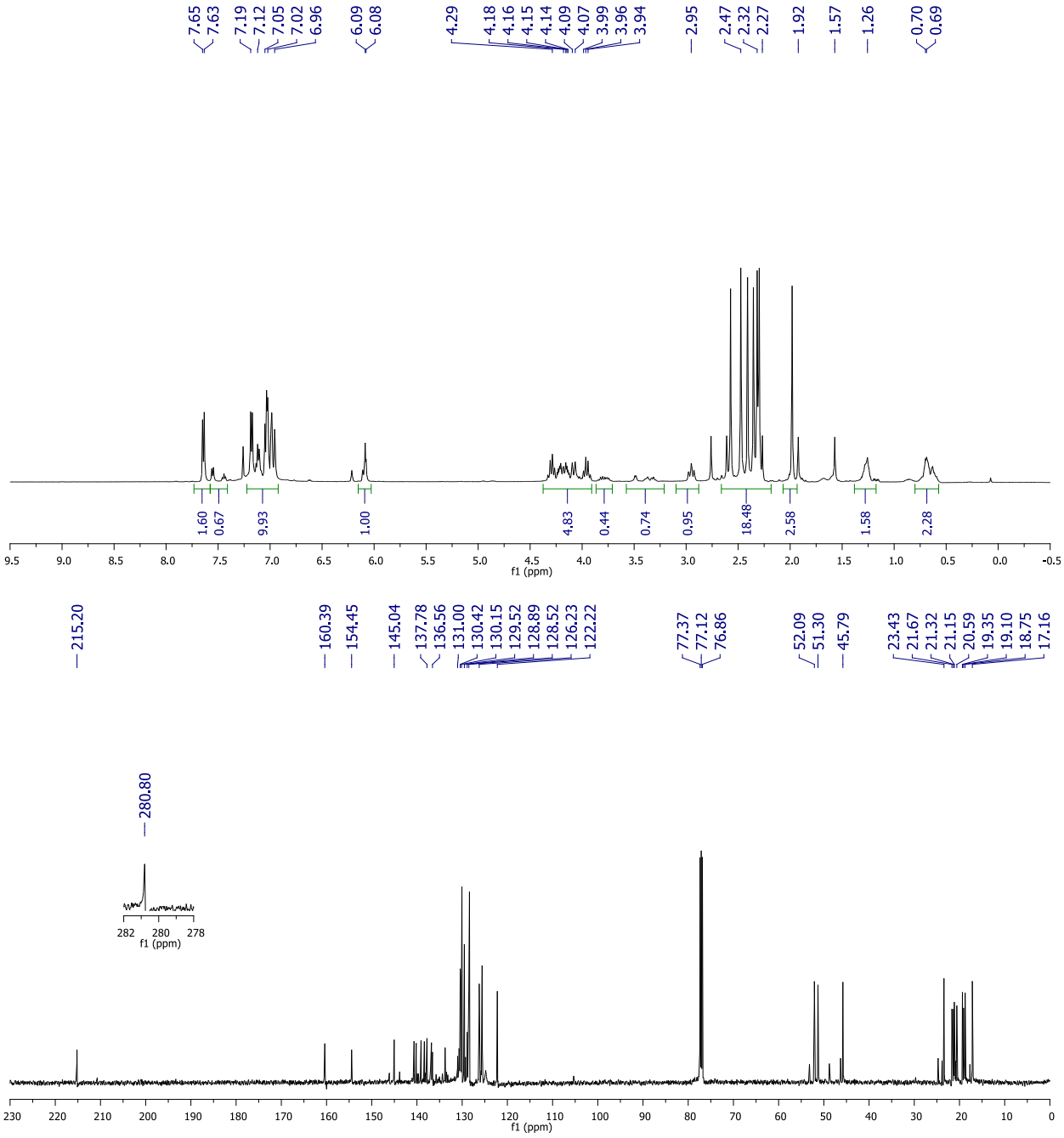

7.53
7.52
7.26
7.00
6.94
6.86
6.27
6.07
4.21
4.00
3.98
3.96
3.81
3.77
3.73
3.69
3.66
3.62
3.53
2.62
2.61
2.29
1.94
1.68
Mes
N
N
Mes
Cl
Ru
Ph
Cl
NTs
0.91
2.27
5.45
2.33
1.06
1.10
1.22
2.52
3.45
1.00
6.73
8.61
3.14
3.48
3.18
f1 (ppm)

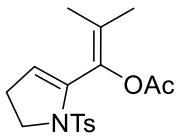
7-24b


144.3
143.6
140.4
139.8
138.3
136.9
135.6
134.0
133.8
133.4
131.0
130.1
129.4
129.2
128.9
128.8
128.2
127.9
114.9
104.9
52.9
52.2
51.8
51.6
51.2
49.0
27.9
26.9
26.3
26.1
21.6
21.2
20.9
20.6
19.0
18.8
17.7
266.9
209.8
f1 (ppm)

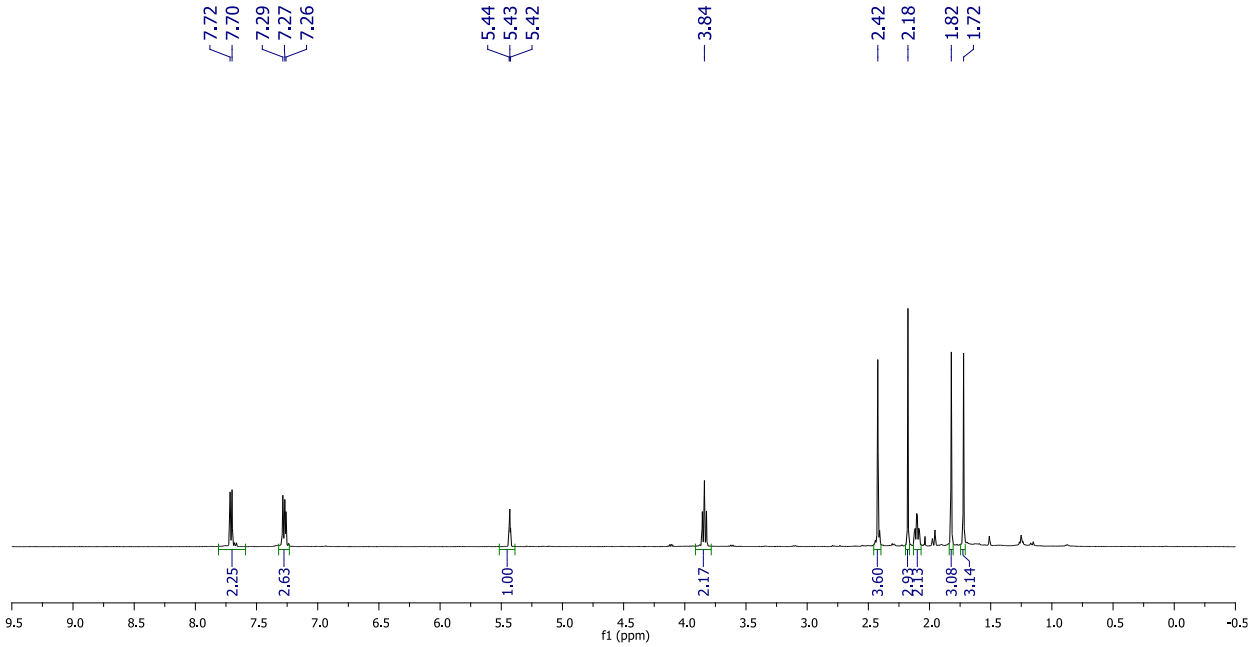

Mes
N
N
Mes
Cl
Ru
Ph
Cl
NTs

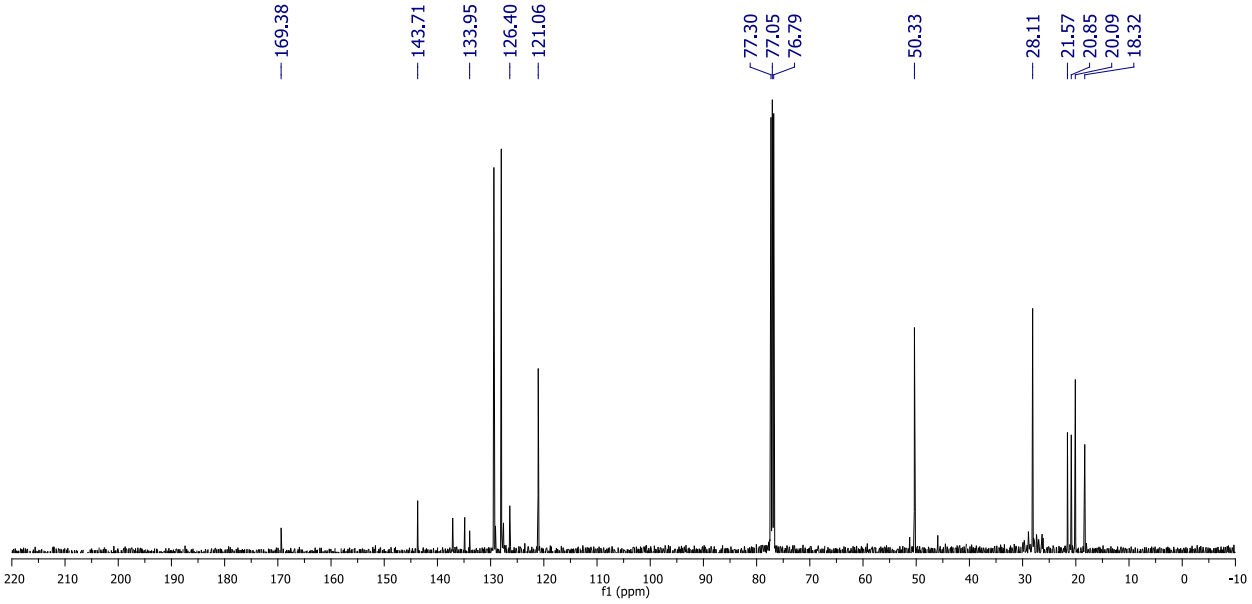
7-24a

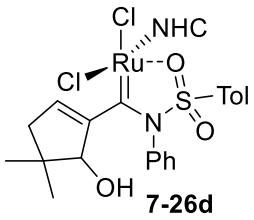

7.65
7.63
7.19
7.12
7.05
7.02
6.96
6.09
6.08
4.29
4.18
4.16
4.15
4.14
4.09
4.07
3.99
3.96
3.94
2.95
2.47
2.32
2.27
1.92
1.57
1.26
0.70
0.69
1.60
0.67
9.93
1.00
4.83
0.44
0.74
0.95
18.48
2.58
1.58
2.28
f1 (ppm)
215.20
160.39
154.45
145.04
137.78
136.56
131.00
130.42
130.15
129.52
128.89
128.52
126.23
122.22
77.37
77.12
76.86
52.09
51.30
45.79
23.43
21.67
21.32
21.15
20.59
19.35
19.10
18.75
17.16
280.80
f1 (ppm)


OAc
NTs

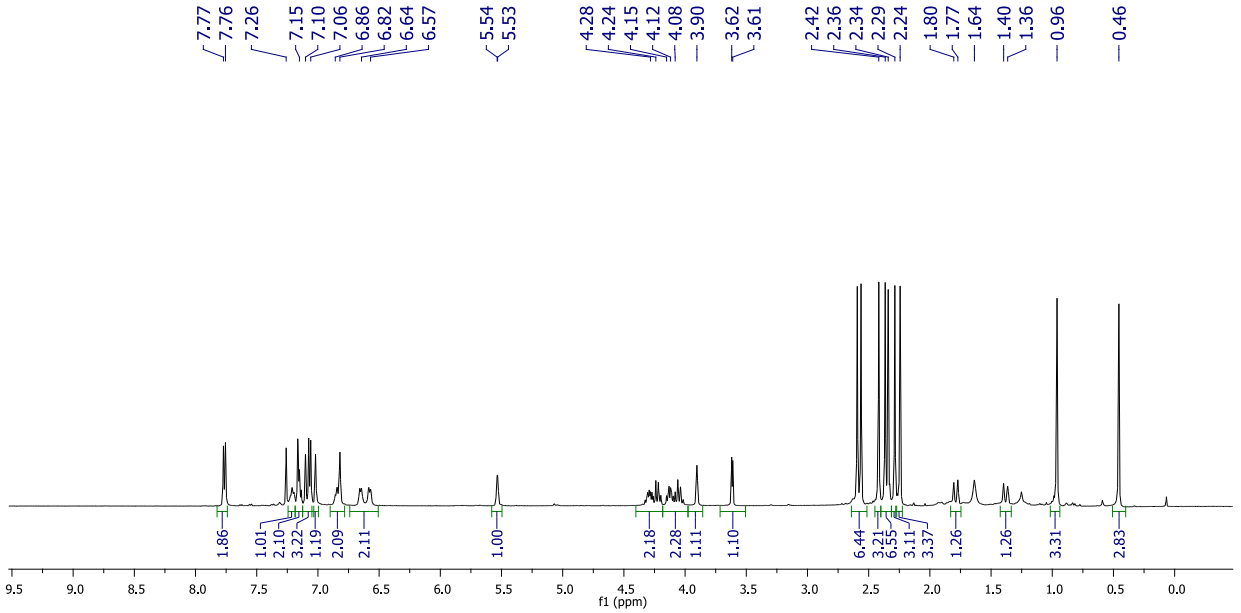
7-25c


7.72
7.70
7.29
7.27
7.26
5.44
5.43
5.42
3.84
2.42
2.18
1.82
1.72
2.25
2.63
1.00
2.17
3.60
2.93
2.13
3.08
3.14
f1 (ppm)


169.38
143.71
133.95
126.40
121.06
77.30
77.05
76.79
50.33
28.11
21.57
20.85
20.09
18.32
f1 (ppm)


Cl
NHC
Ru
O
Cl
S
Tol
N
O
Ph
OH

7-26d


7.77
7.76
7.26
7.15
7.10
7.06
6.86
6.82
6.64
6.57
5.54
5.53
4.28
4.24
4.15
4.12
4.08
3.90
3.62
3.61
2.42
2.36
2.34
2.29
2.24
1.80
1.77
1.64
1.40
1.36
0.96
0.46
1.86
1.01
2.10
3.22
1.19
2.09
2.11
1.00
2.18
2.28
1.11
1.10
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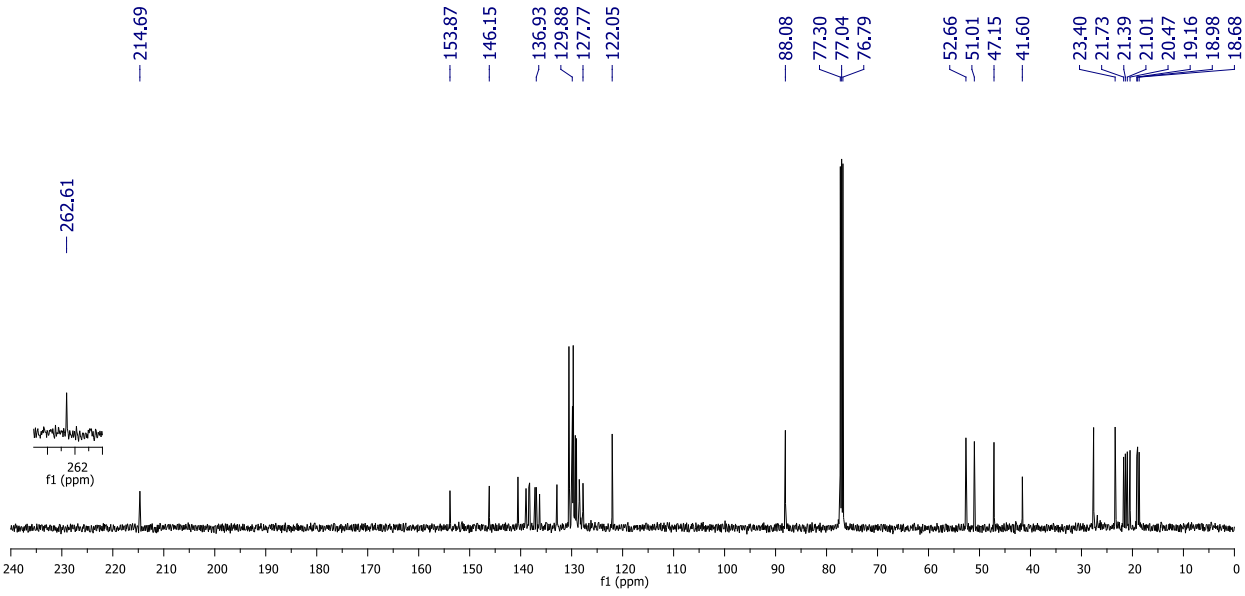
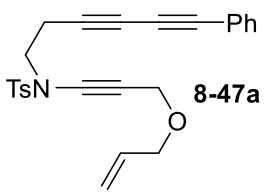
3.21
6.55
3.11
3.37
1.26
1.26
3.31
2.83
f1 (ppm)

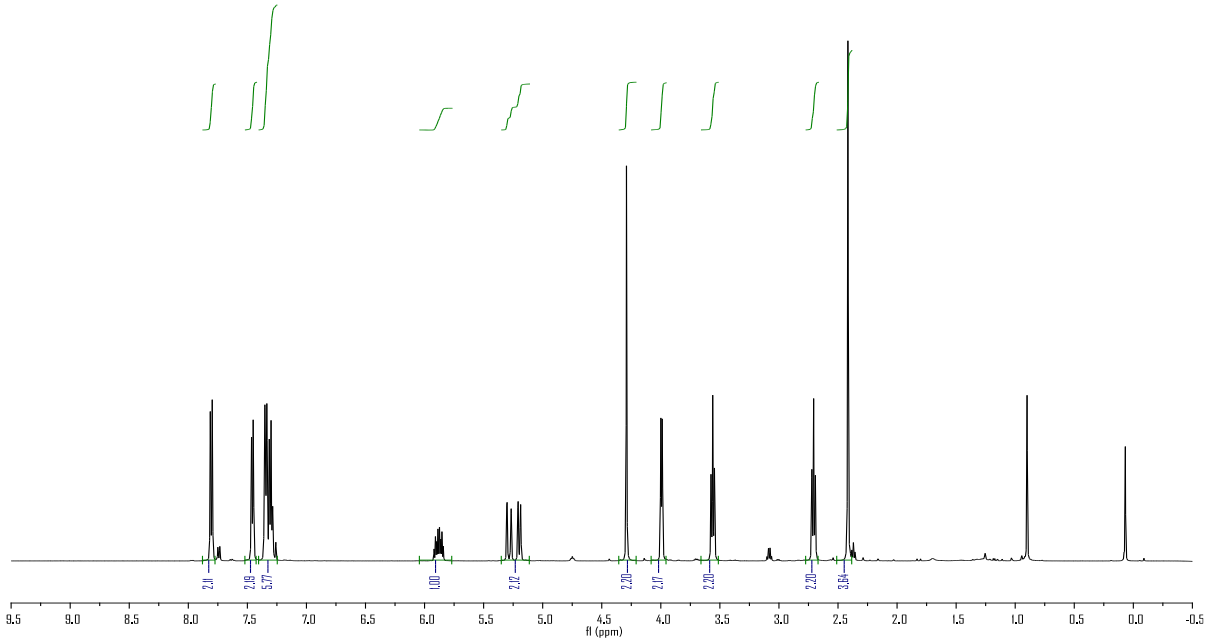

214.69
153.87
146.15
136.93
129.88
127.77
122.05
88.08
77.30
77.04
76.79
52.66
51.01
47.15
41.60
23.40
21.73
21.39
21.01
20.47
19.16
18.98
18.68
262.61
262
f1 (ppm)
f1 (ppm)

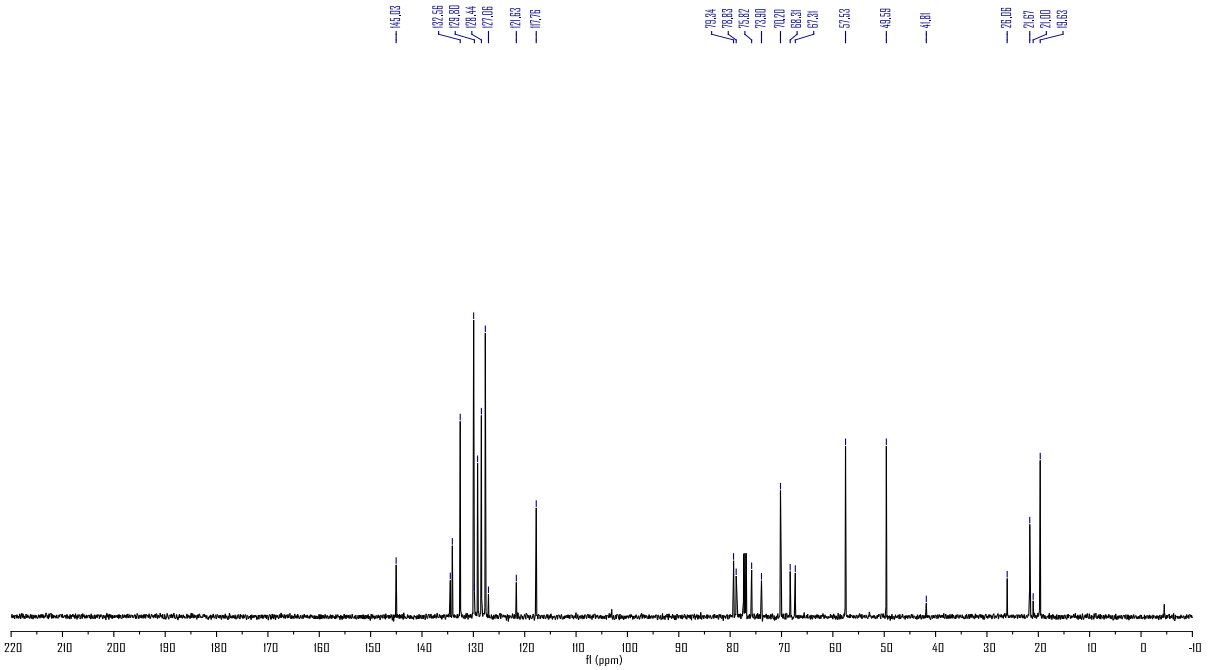
Appendix VIII

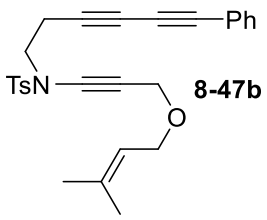
Selected NMR Spectra for Chapter 8


Ph
TsN
O

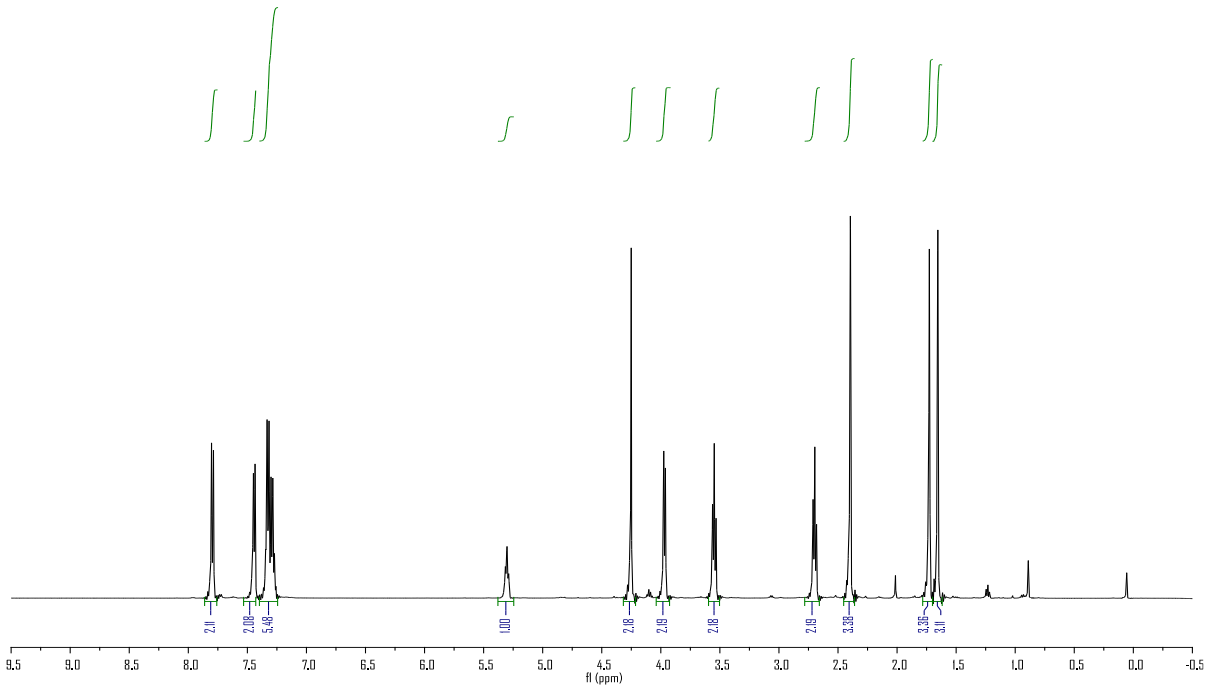
8-47a

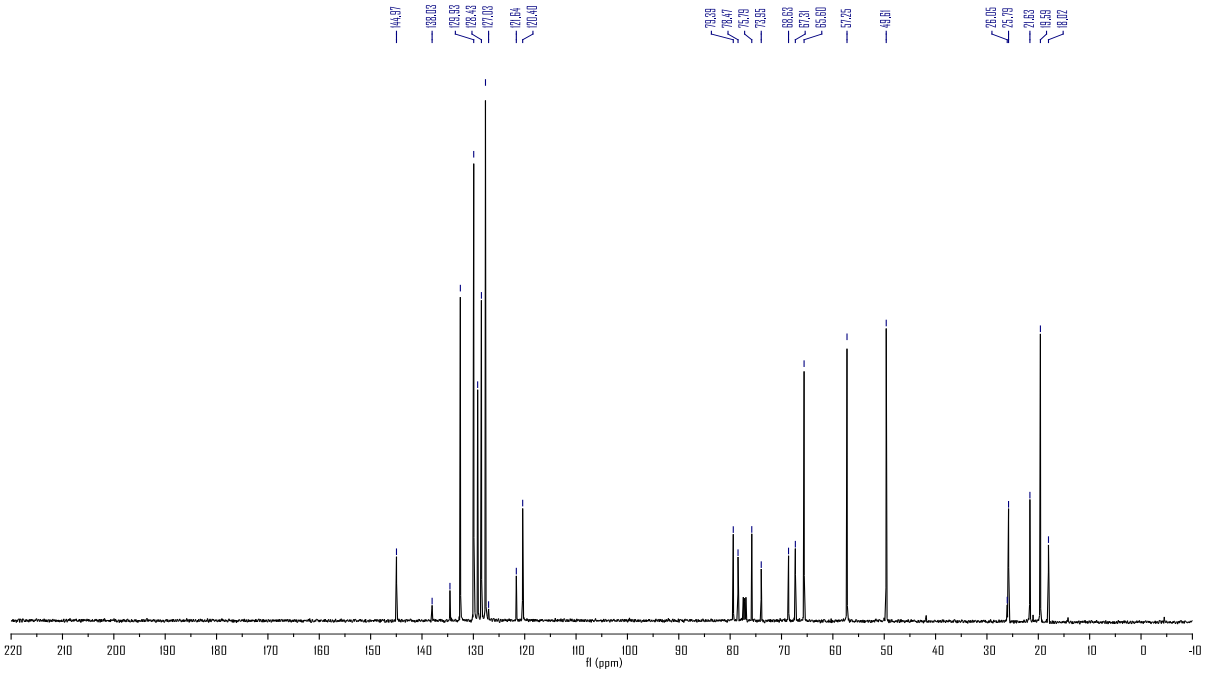

2.11
2.93
5.77
1.00
2.12
2.20
2.17
2.20
2.20
3.64
f1 (ppm)

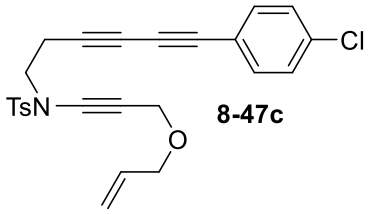

145.03
132.56
129.80
128.44
127.06
121.63
117.76
79.24
78.83
75.82
73.91
70.27
68.39
67.31
57.53
49.56
41.81
20.06
21.67
21.00
19.63
f1 (ppm)


Ph
TsN
O

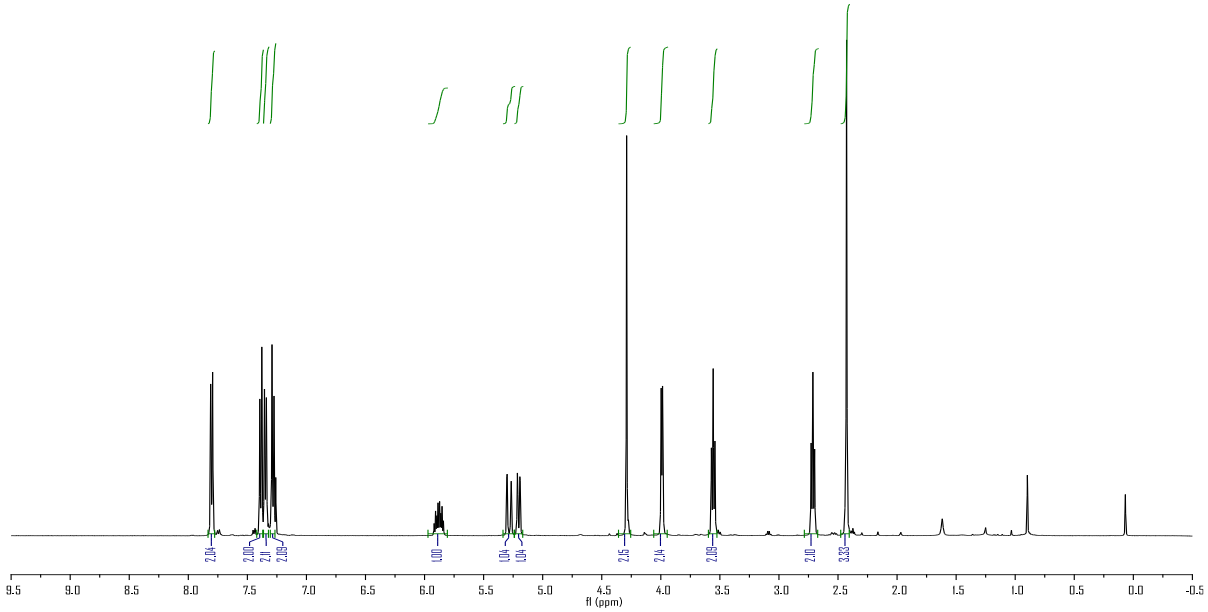
8-47b

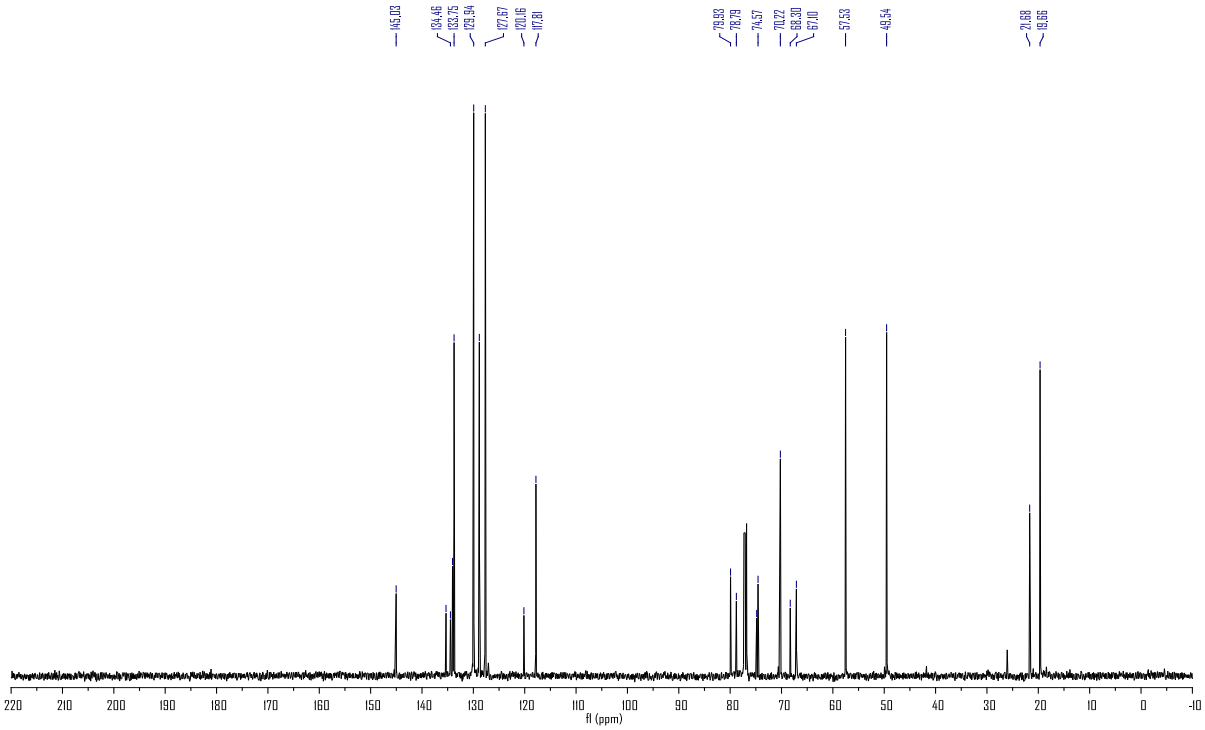

2.11
2.08
5.48
1.00
2.18
2.19
2.18
2.19
3.38
3.36
3.11
f1 (ppm)

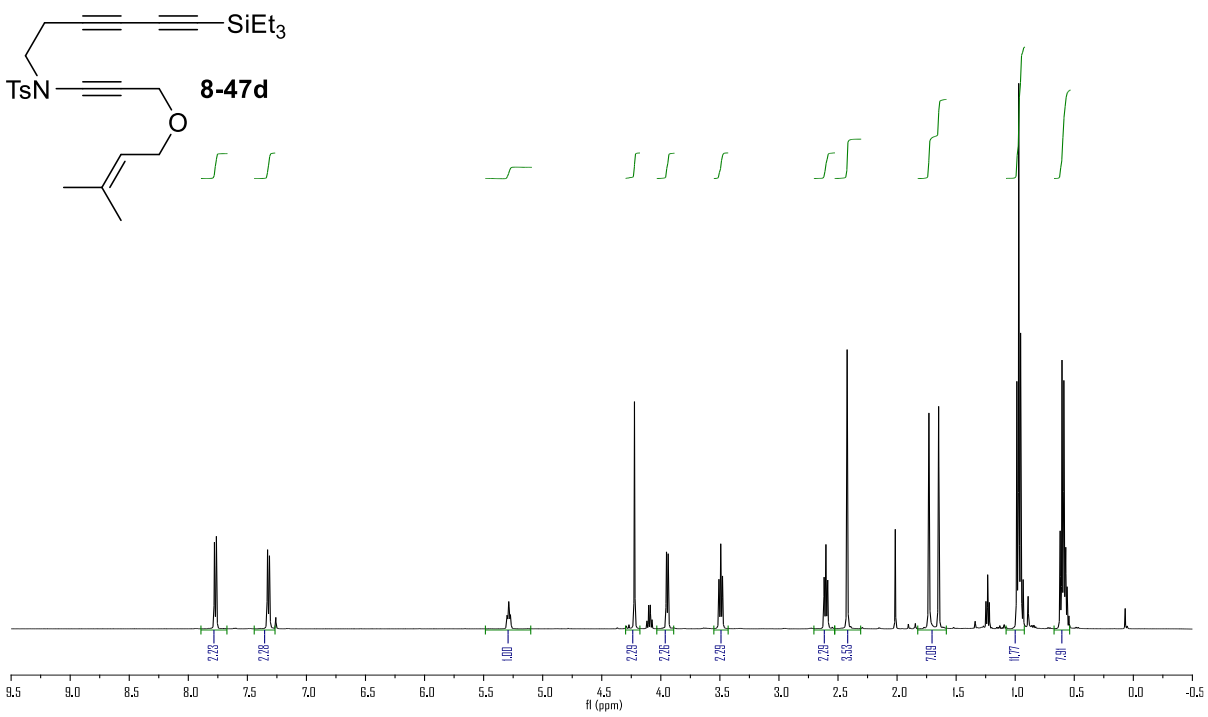

144.97
138.03
129.93
128.43
127.03
121.64
120.48
79.08
78.47
75.79
73.55
68.63
57.31
55.60
57.25
49.61
26.05
25.79
21.83
19.59
18.02
f1 (ppm)

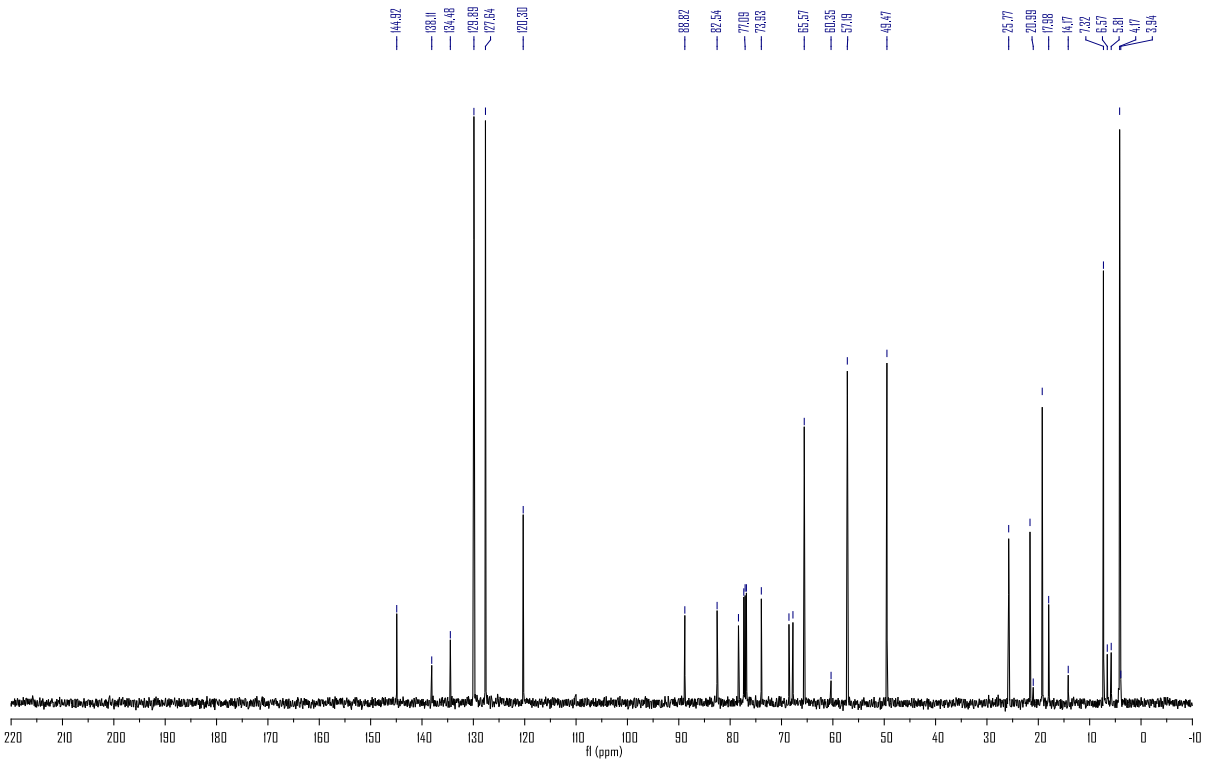

Cl
TsN
O

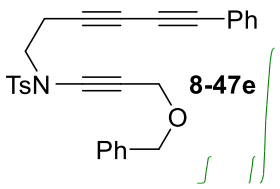
8-47c

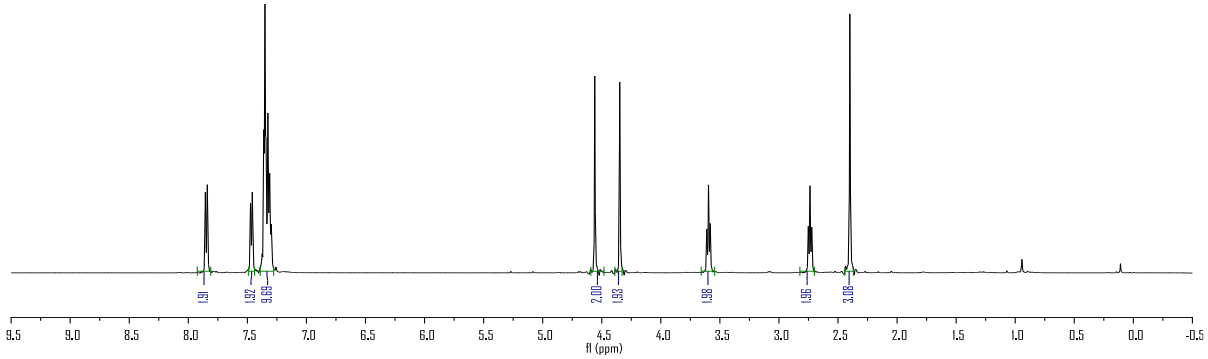

2.04
2.00
2.11
2.05
1.00
1.04
1.04
2.15
2.14
2.09
2.00
3.33
f1 (ppm)

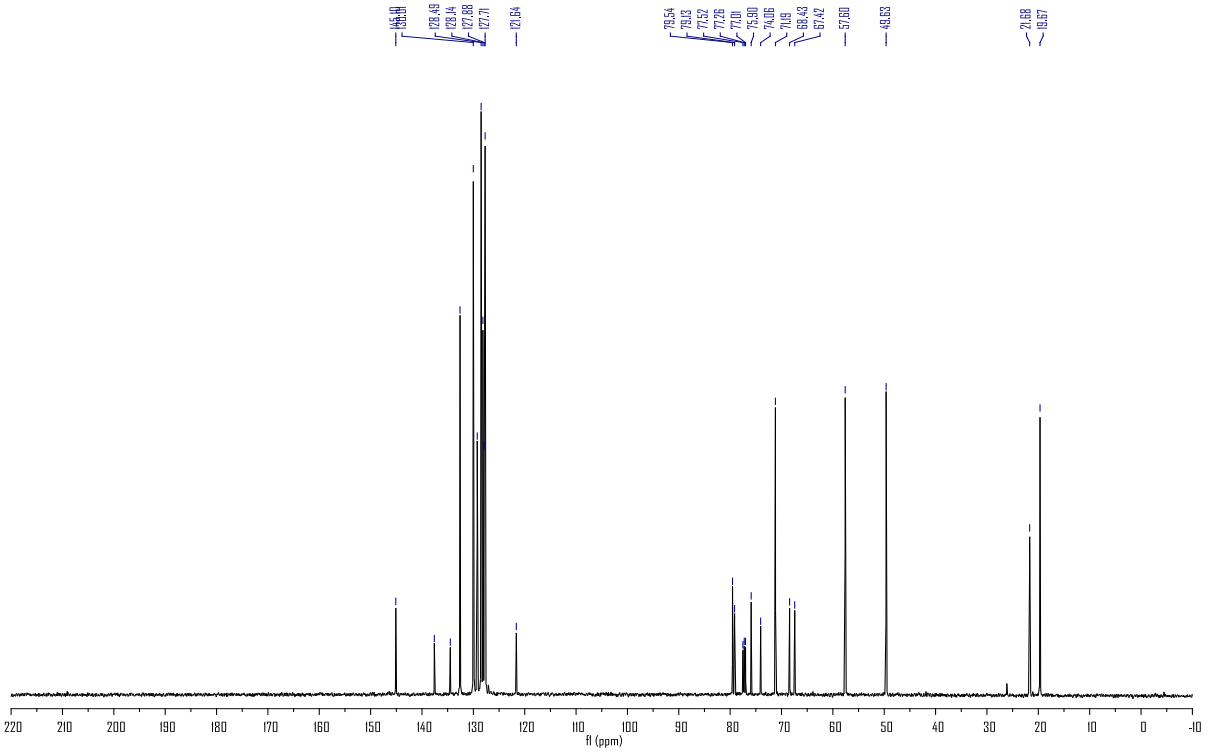

145.03
134.48
133.75
129.394
122.67
120.16
117.81
79.93
78.79
74.57
70.22
68.30
67.10
57.53
49.54
21.68
19.66
f1 (ppm)

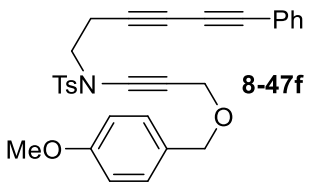

SiEt3
TsN
O
8-47d
2.23
2.28
1.00
2.29
2.26
2.29
2.29
3.53
7.09
11.77
7.91
f1 (ppm)


144.92
138.11
134.48
129.89
127.84
120.30
88.82
82.54
77.09
73.93
65.57
60.35
57.19
49.47
25.77
20.99
17.98
14.77
7.32
6.57
5.81
4.17
3.94
f1 (ppm)

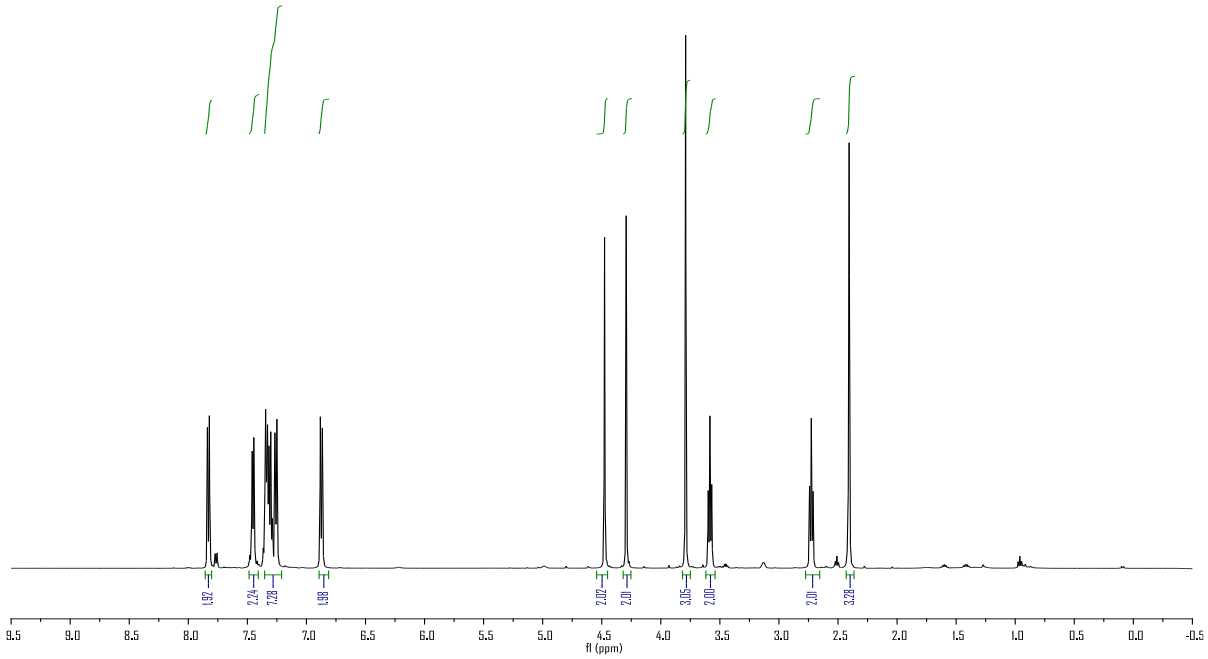

Ph
TsN
8-47e
O
Ph

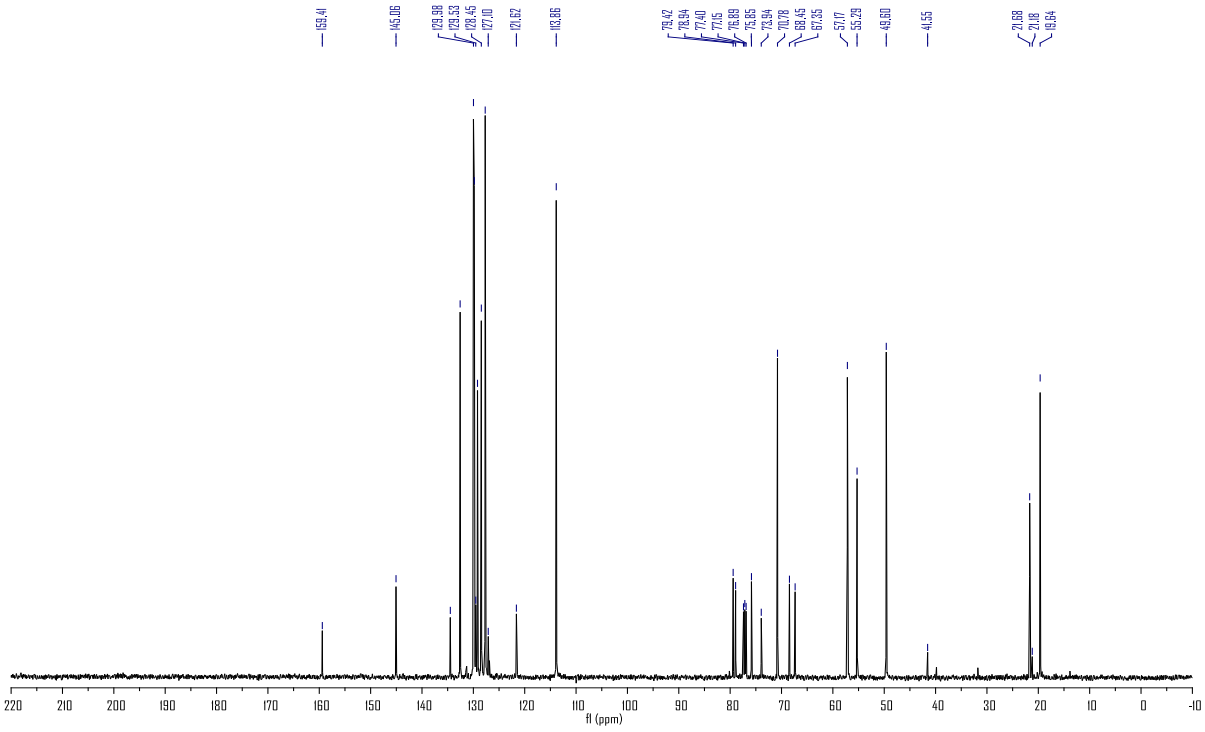

1.91
1.82
9.69
2.00
1.93
1.98
1.96
3.08
f1 (ppm)

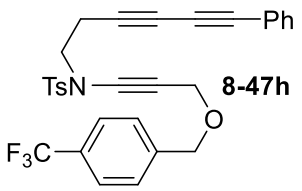

146.00
136.98
128.49
128.14
127.88
127.71
121.64
79.54
79.13
77.52
77.25
77.00
75.90
74.06
71.19
68.43
67.42
57.88
49.63
21.68
19.67
f1 (ppm)


Ph
TsN
O
MeO

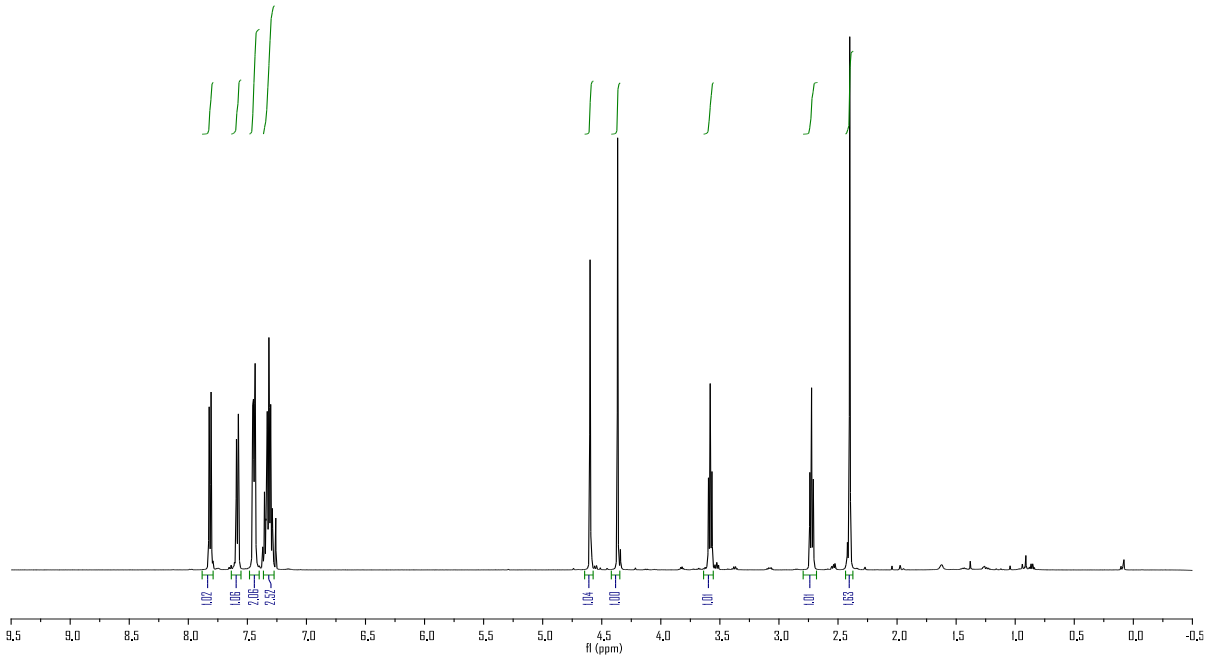
8-47f

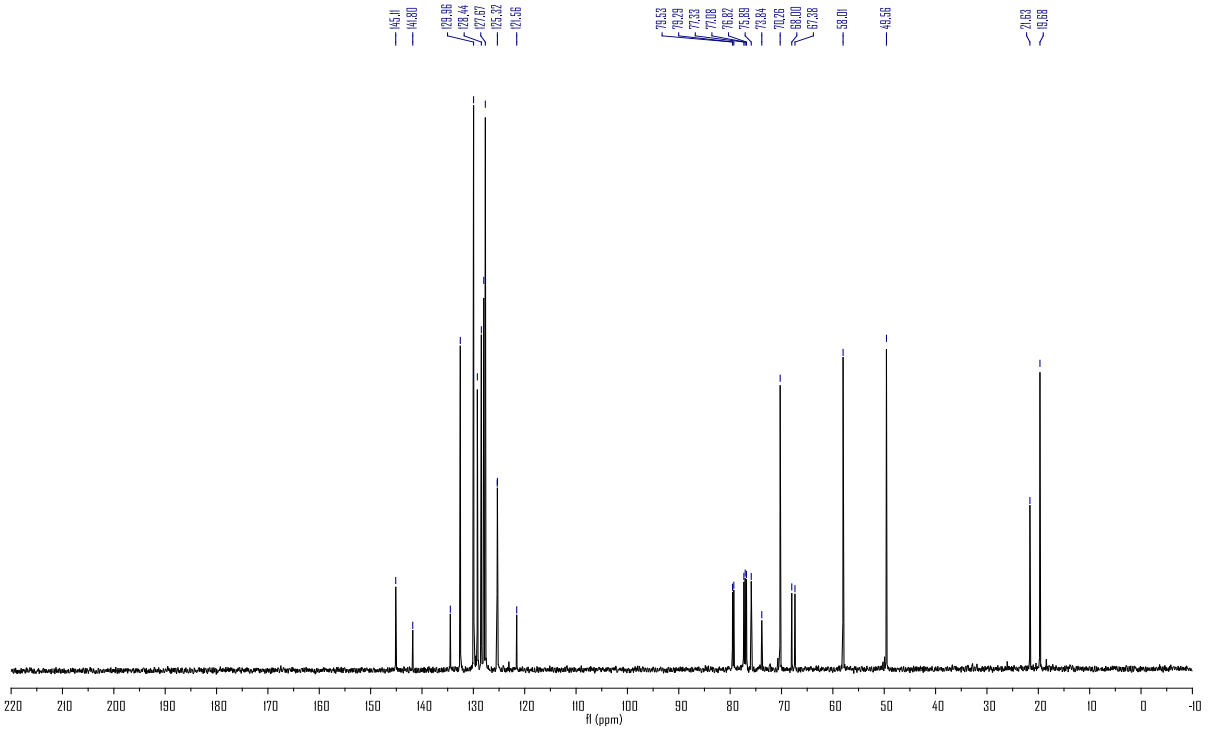

1.92
2.24
7.28
1.98
2.02
2.01
3.05
2.00
2.01
3.28
f1 (ppm)

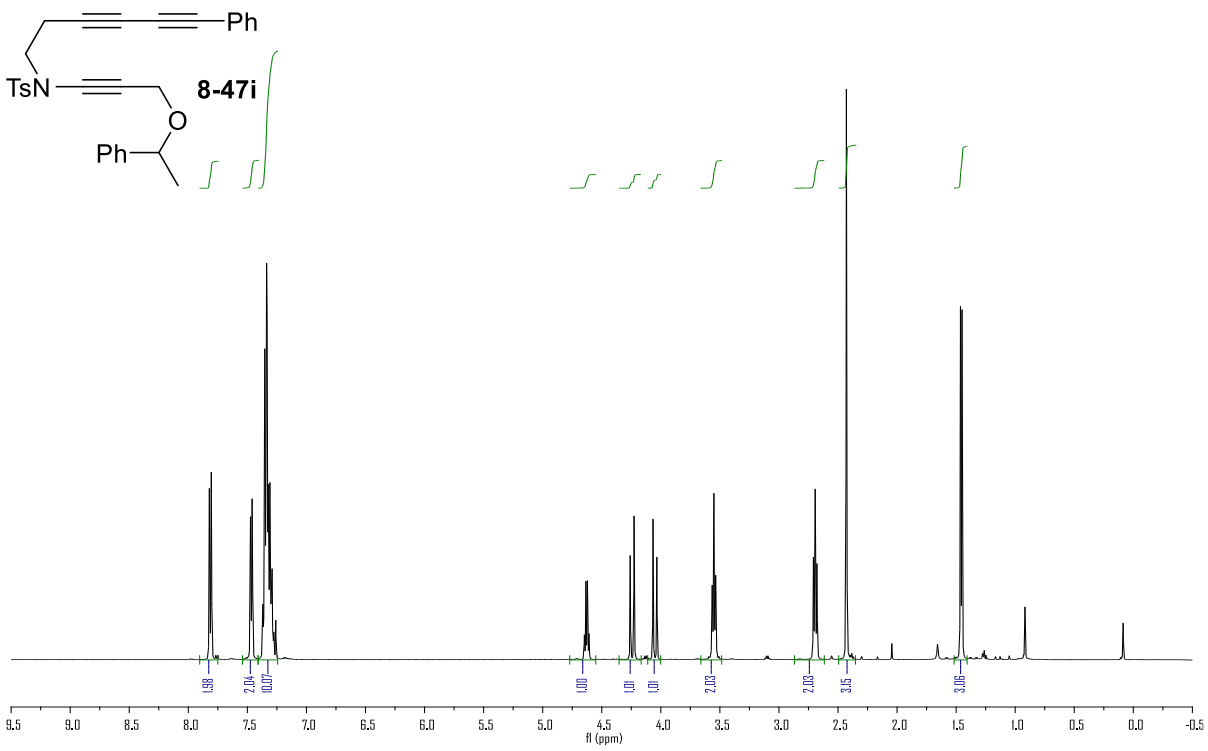

159.41
145.06
139.38
129.53
128.45
127.10
121.62
102.86
79.42
78.94
77.40
77.15
76.89
76.65
73.94
70.78
68.45
67.35
57.17
55.29
49.80
41.55
21.68
21.08
18.64
f1 (ppm)

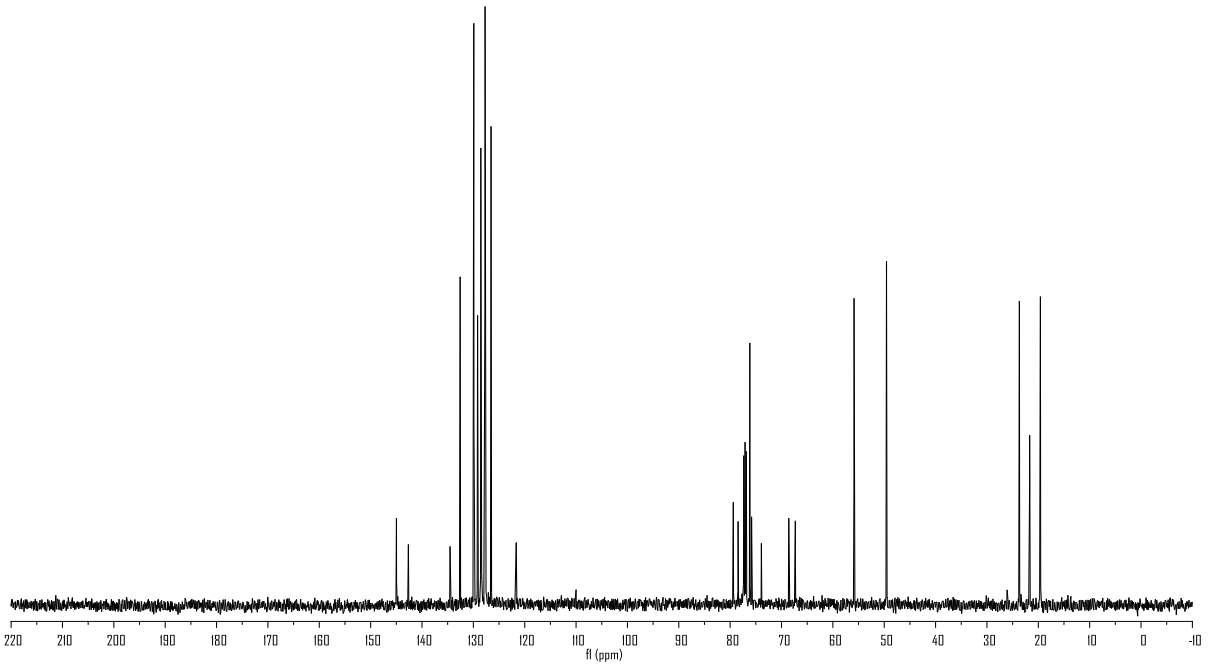

Ph
TsN
O
F3C

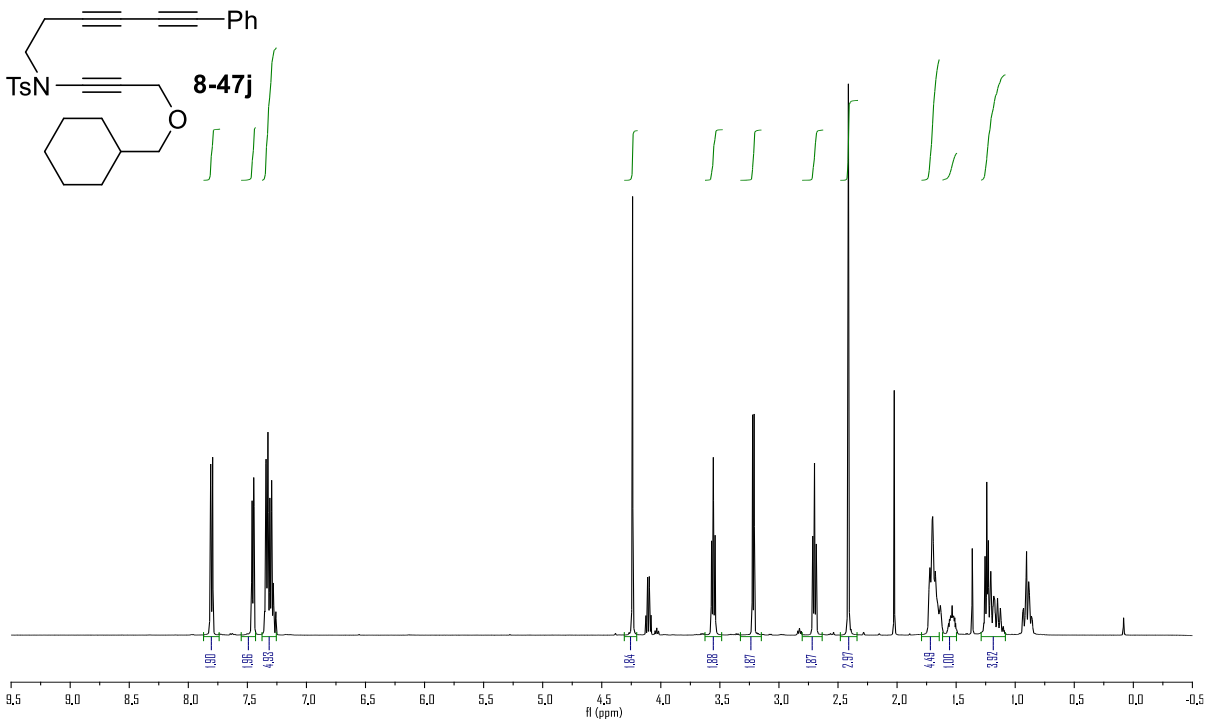
8-47h

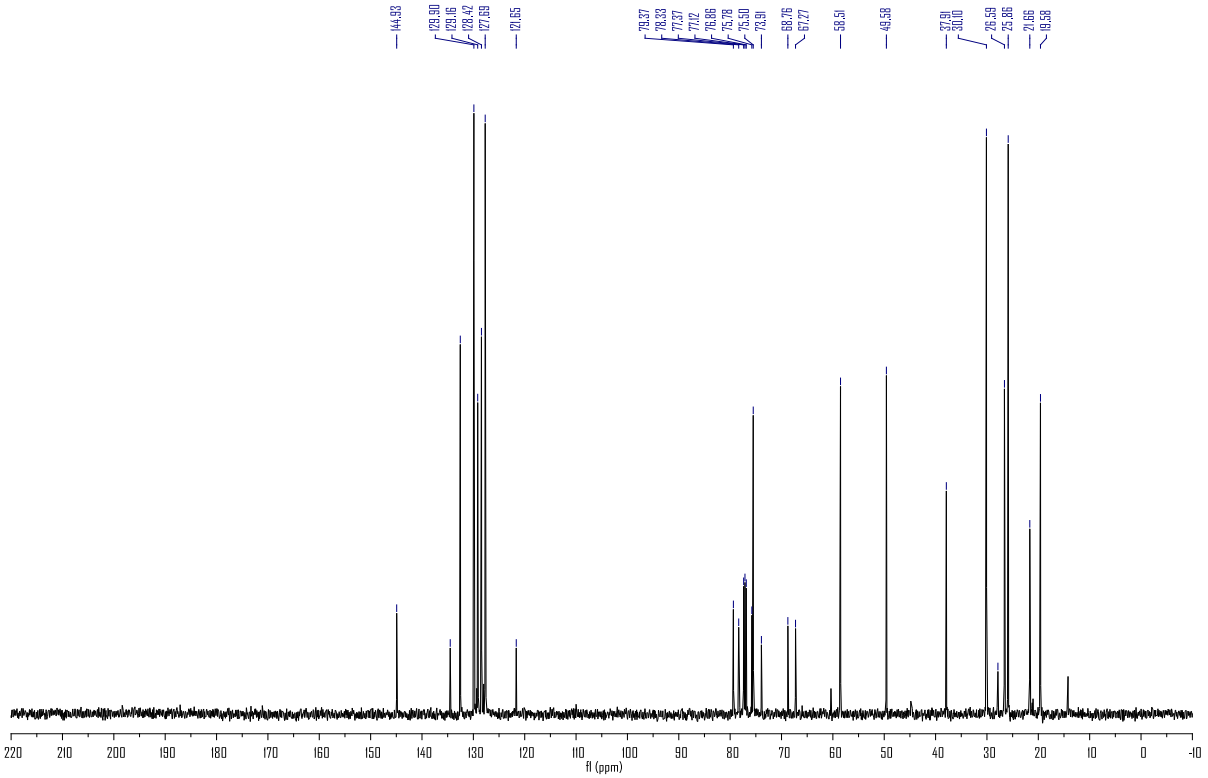

1.02
1.05
2.05
2.52
1.04
1.00
1.01
1.01
1.63
f1 (ppm)

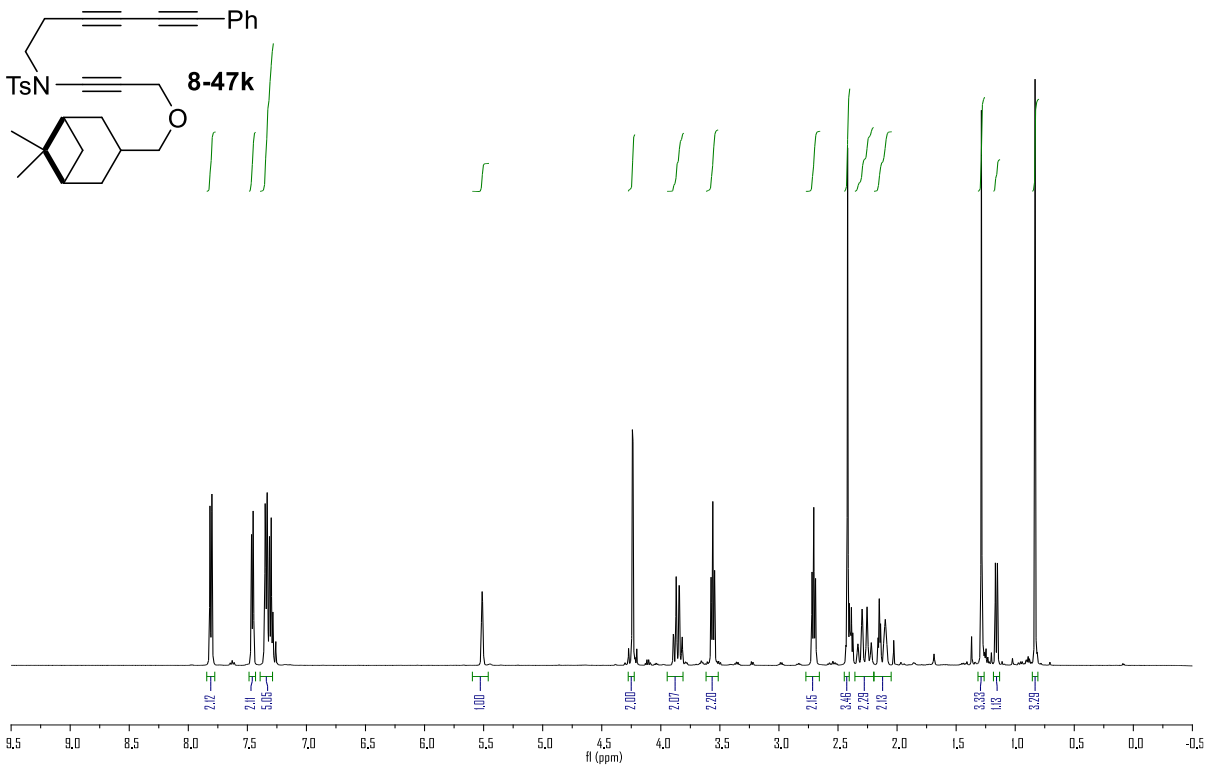

145.11
140.80
129.96
129.44
127.67
125.32
121.56
79.53
79.29
77.33
77.08
76.82
75.88
73.84
70.26
68.00
67.38
58.01
49.56
21.63
19.68
f1 (ppm)

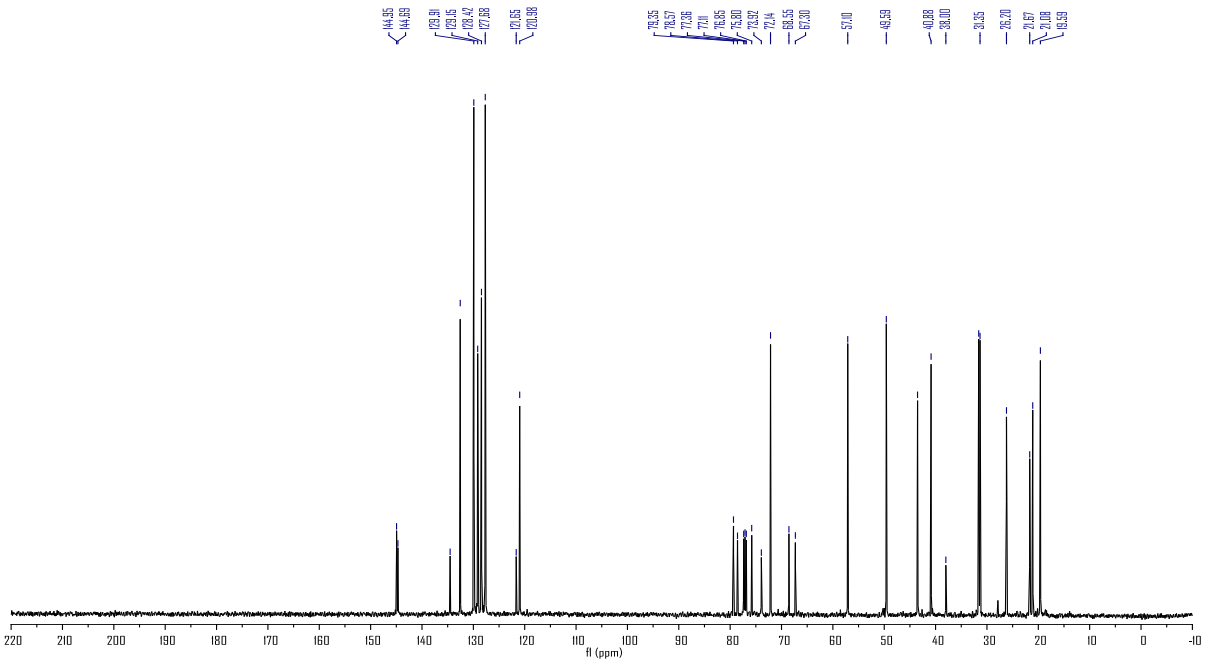

Ph
TsN
8-47i
O
Ph
1.98
2.04
10.07
1.00
1.01
1.01
2.03
2.03
3.15
9.06
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

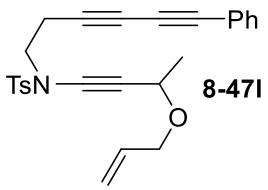

220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Ph
TsN
O
8-47j
1.90
1.86
4.93
1.84
1.88
1.87
1.87
2.97
4.48
1.00
3.92
f1 (ppm)

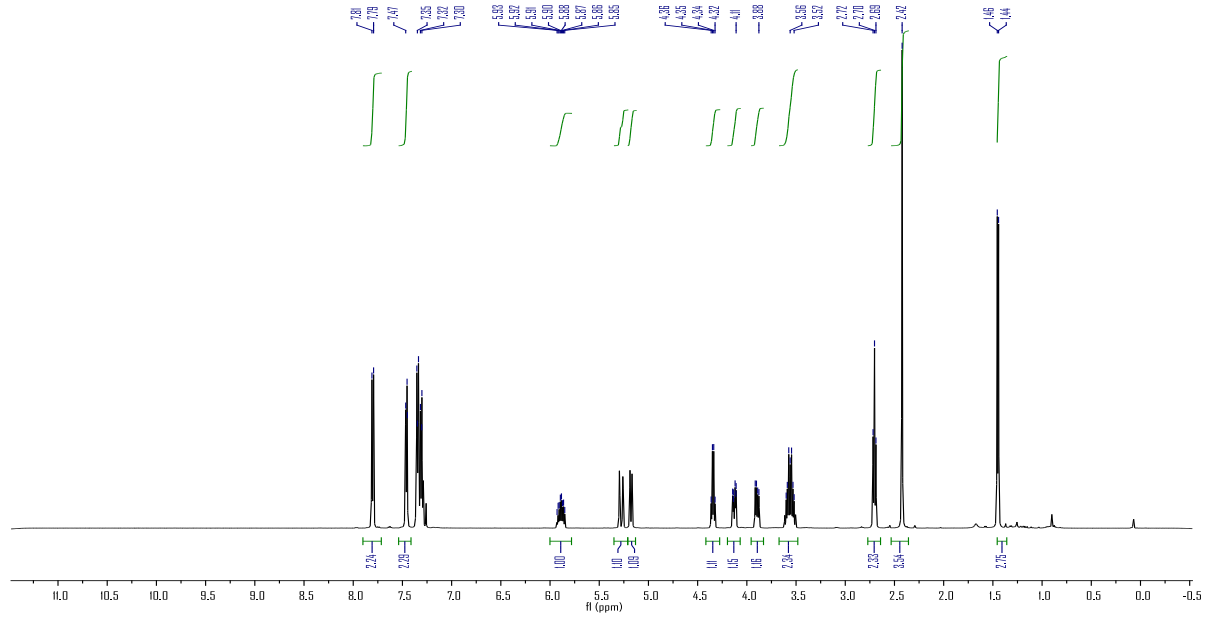

144.83
129.90
129.16
128.42
127.69
121.65
78.37
78.33
77.37
77.12
76.88
75.78
75.50
73.91
68.76
67.27
58.51
49.58
37.91
30.10
26.59
25.88
21.65
19.58
f1 (ppm)

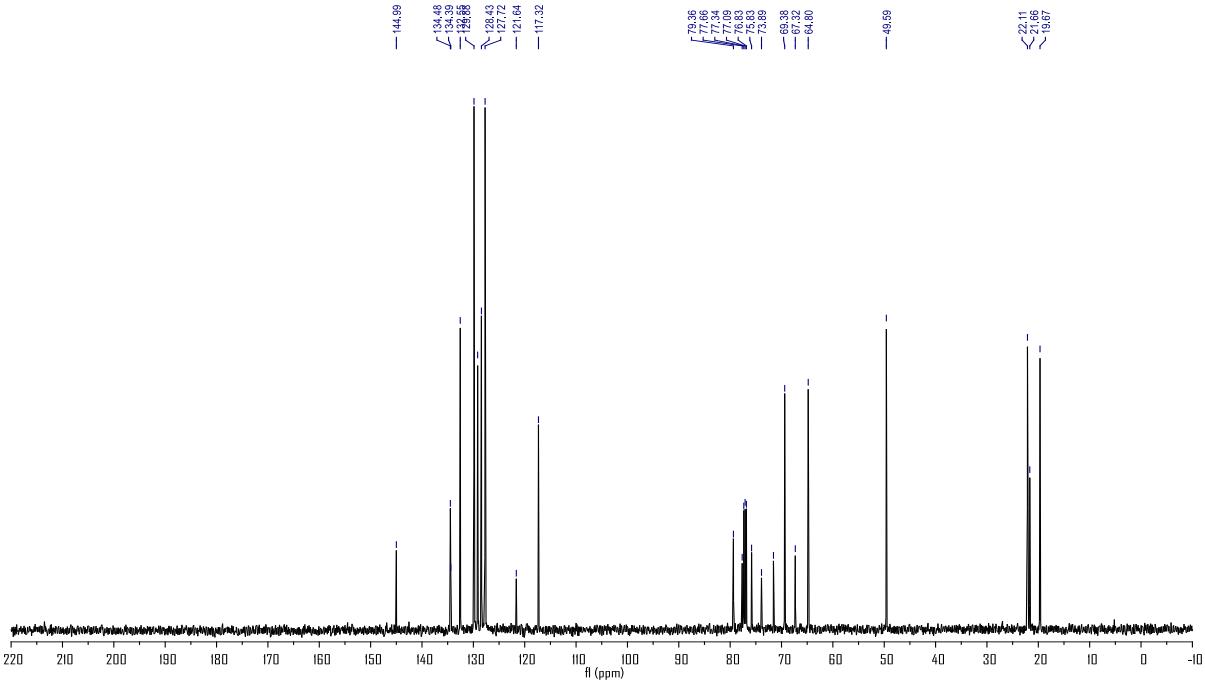

Ph
TsN
O
8-47k
2.12
2.11
5.05
1.00
2.00
2.07
2.20
2.15
3.46
2.29
2.13
3.33
1.13
3.29
f1 (ppm)

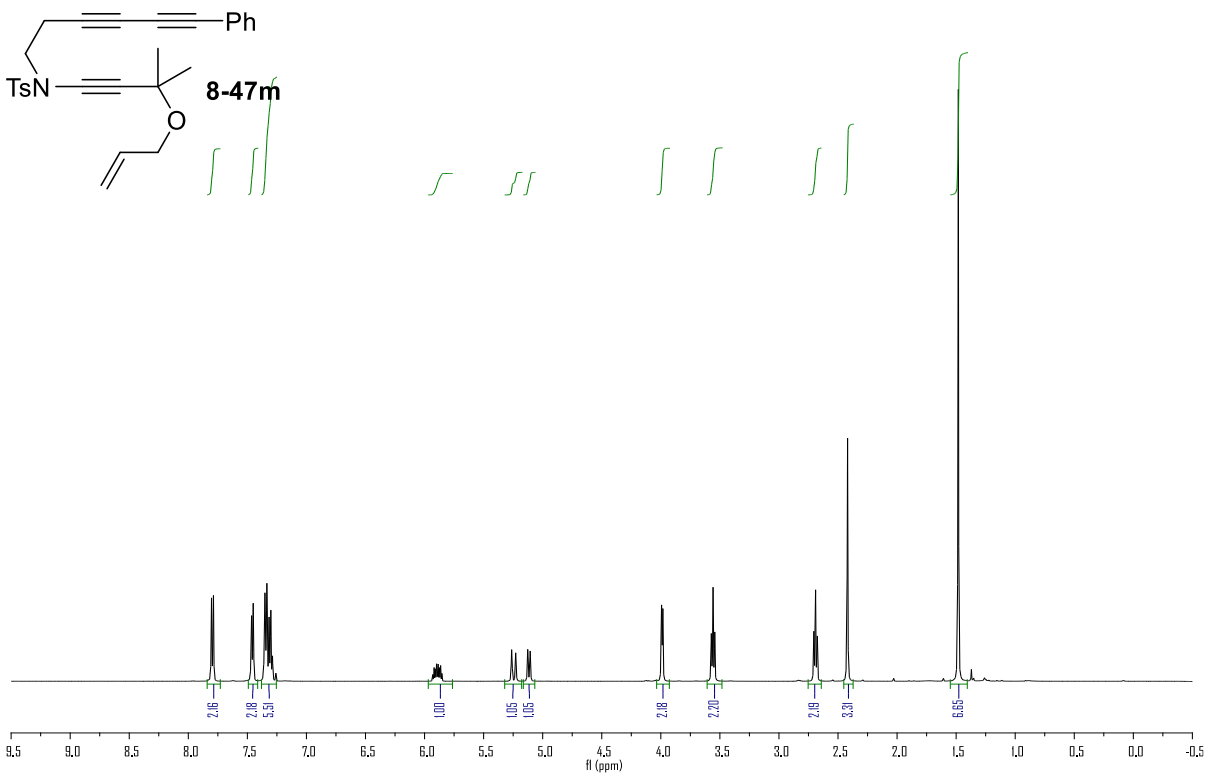

144.55
144.69
139.91
139.45
128.42
127.88
120.65
120.98
78.35
78.57
77.36
77.11
76.85
75.80
73.92
72.14
68.55
67.30
57.10
49.59
40.88
38.00
31.55
26.20
21.67
21.08
19.59
f1 (ppm)

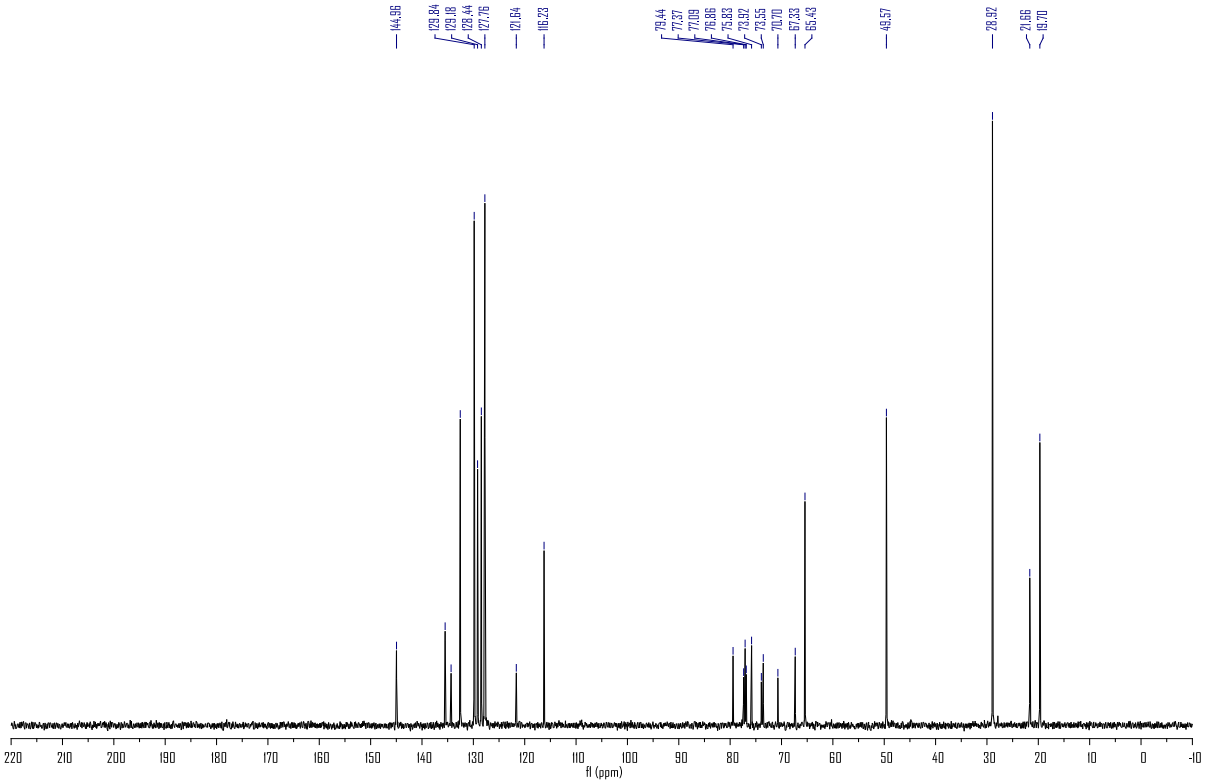

Ph
TsN
O

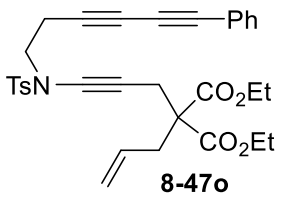
8-47l


7.80
7.79
7.47
7.35
7.32
7.30
5.93
5.92
5.91
5.90
5.88
5.87
5.86
5.85
4.36
4.35
4.34
4.32
4.11
3.88
3.56
3.52
2.72
2.70
2.69
2.42
1.45
1.44
2.24
2.09
4.00
1.01
1.09
1.11
1.15
1.16
2.34
2.33
3.54
2.75
f1 (ppm)

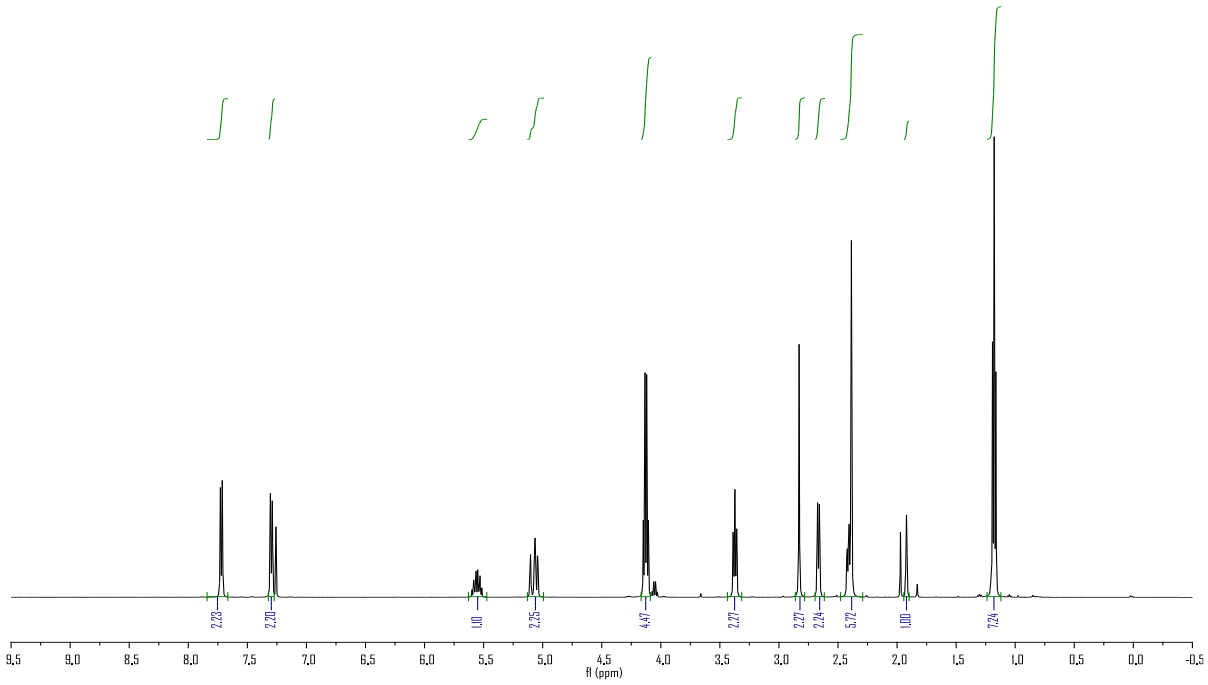

144.99
134.48
134.39
129.66
129.58
128.43
127.72
121.64
117.32
79.36
77.66
77.34
77.09
76.83
75.83
73.89
69.38
67.32
64.80
49.59
22.11
21.66
19.67
f1 (ppm)

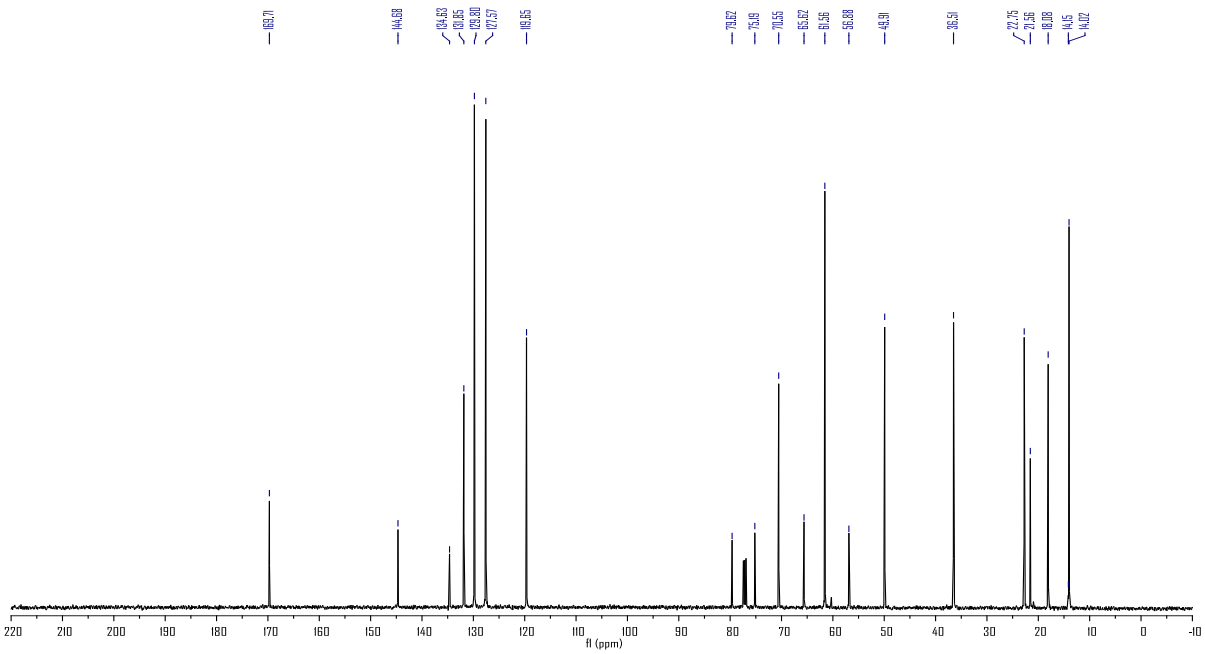

Ph
TsN
O
8-47m
2.16
2.18
5.51
1.00
1.05
1.05
2.18
2.20
2.19
3.31
6.65
f1 (ppm)

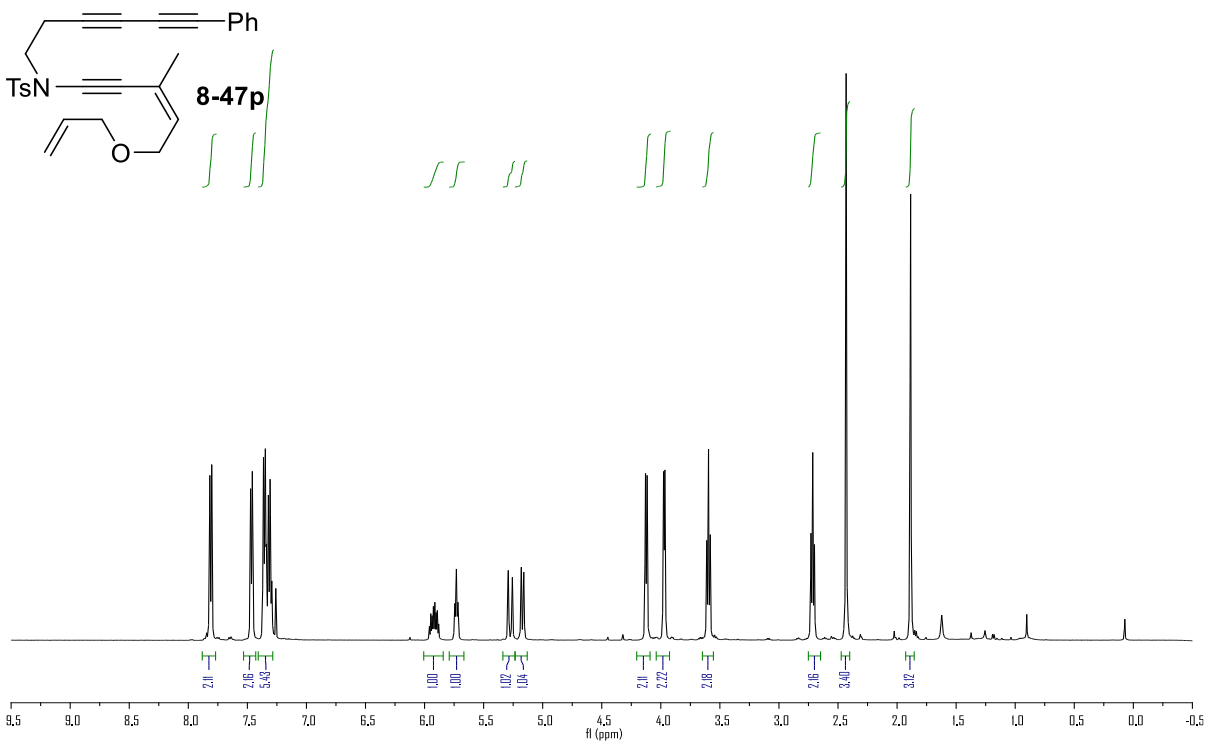

144.96
129.84
129.18
128.44
127.76
121.64
116.23
79.44
77.37
77.09
76.86
75.83
73.92
73.55
70.70
67.33
65.43
49.57
28.92
21.66
19.70
f1 (ppm)

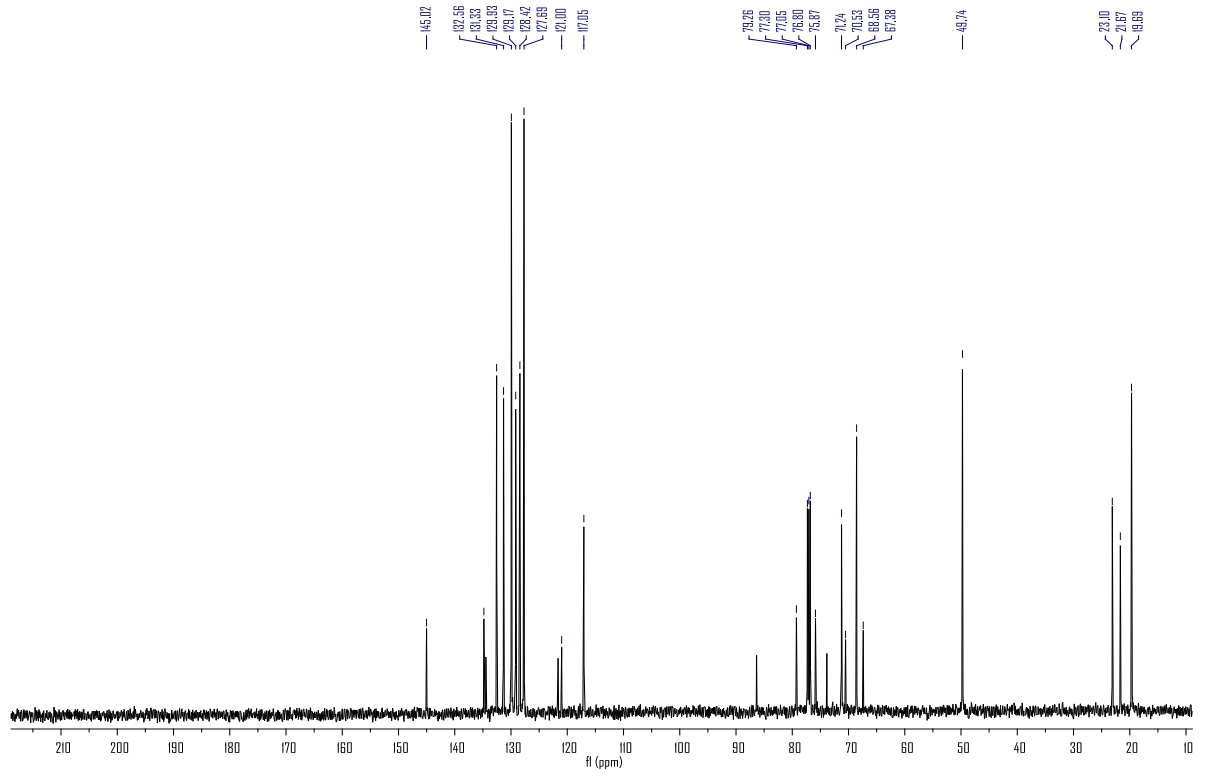

Ph
TsN
CO2Et
CO2Et

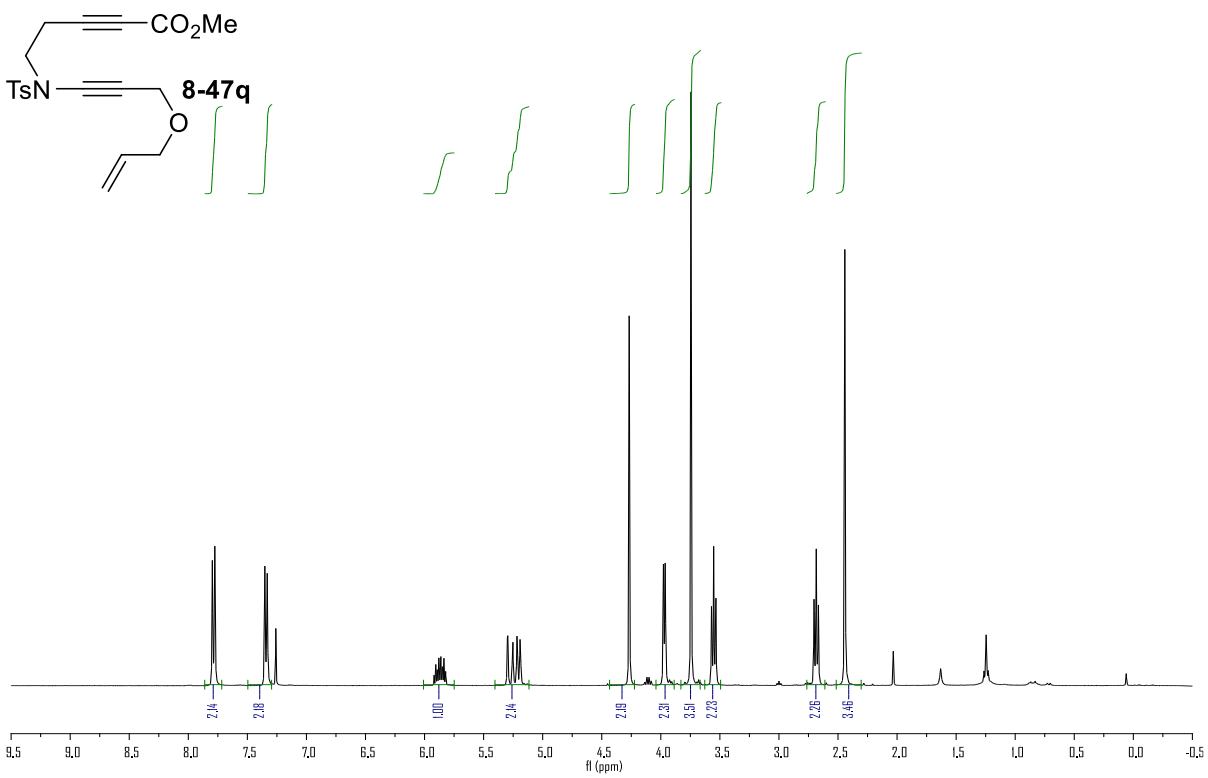
8-47o

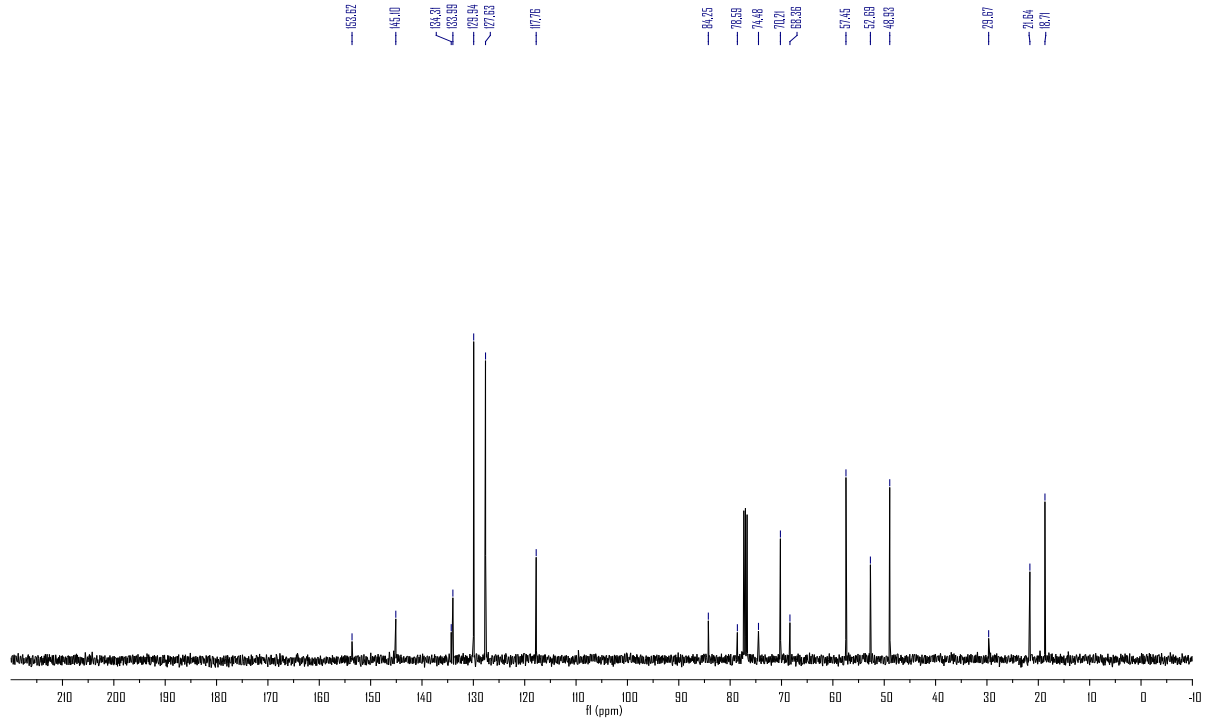

2.23
2.20
1.01
2.25
4.47
2.27
2.27
2.24
5.72
1.00
7.24
f1 (ppm)

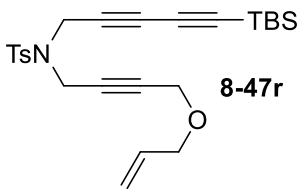

169.71
144.68
134.63
130.85
128.80
127.57
116.85
79.62
75.18
70.55
65.52
61.46
56.88
49.91
36.54
27.75
21.56
18.08
14.15
14.02
f1 (ppm)


Ph
TsN
O
8-47p
2.11
2.16
5.43
1.00
1.00
1.02
1.04
2.11
2.22
2.18
2.16
3.40
3.12
f1 (ppm)

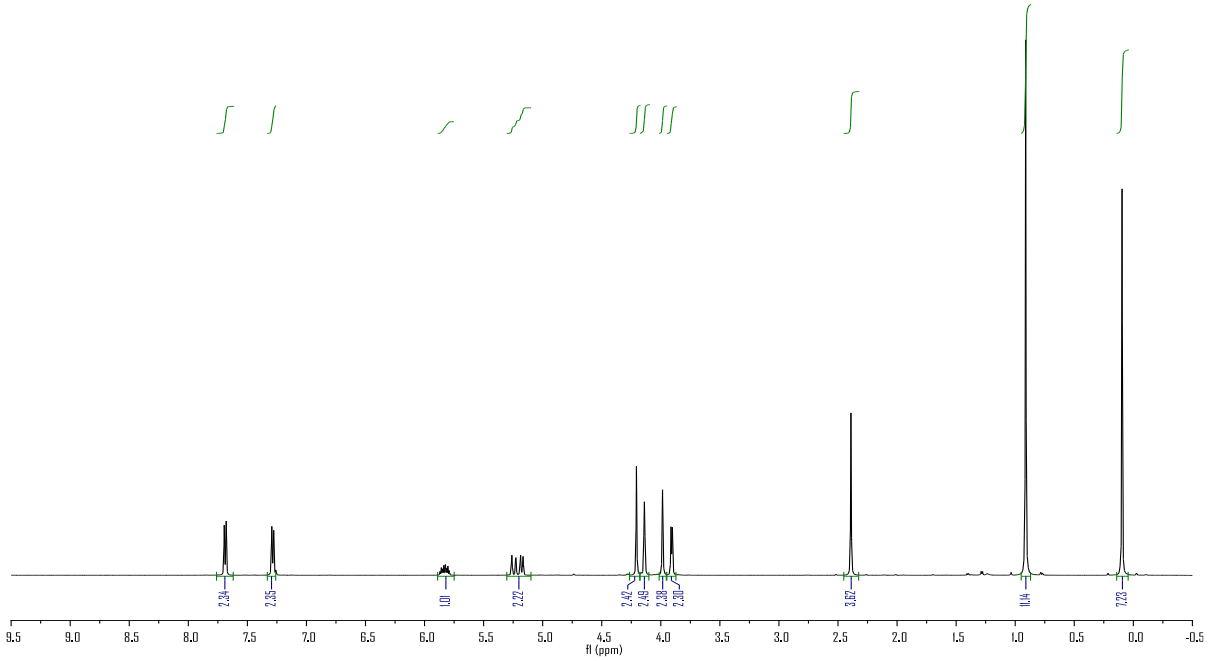

145.02
132.56
131.33
129.83
128.77
128.42
127.69
121.00
117.05
79.26
77.30
77.05
76.80
75.87
71.24
70.53
68.56
67.38
49.74
23.10
21.67
19.89
f1 (ppm)

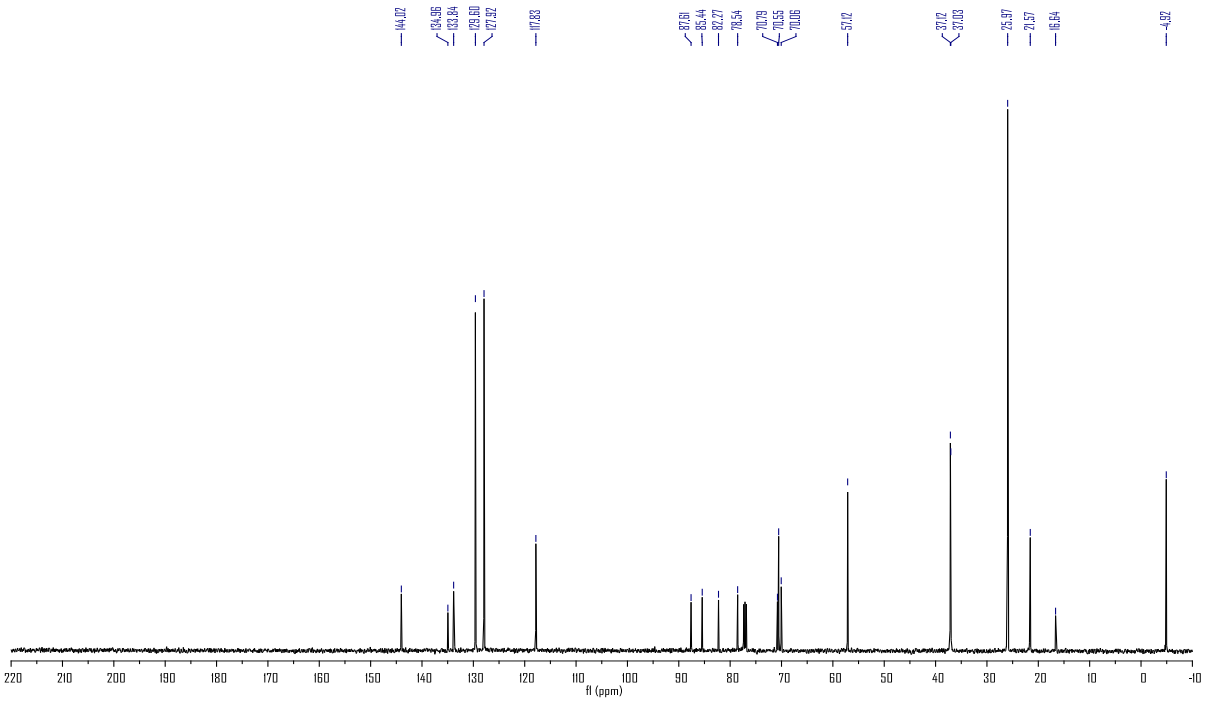

CO2Me
TsN
8-47q
O
2.14
2.18
1.00
2.14
2.19
2.31
3.51
2.23
2.26
3.46
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

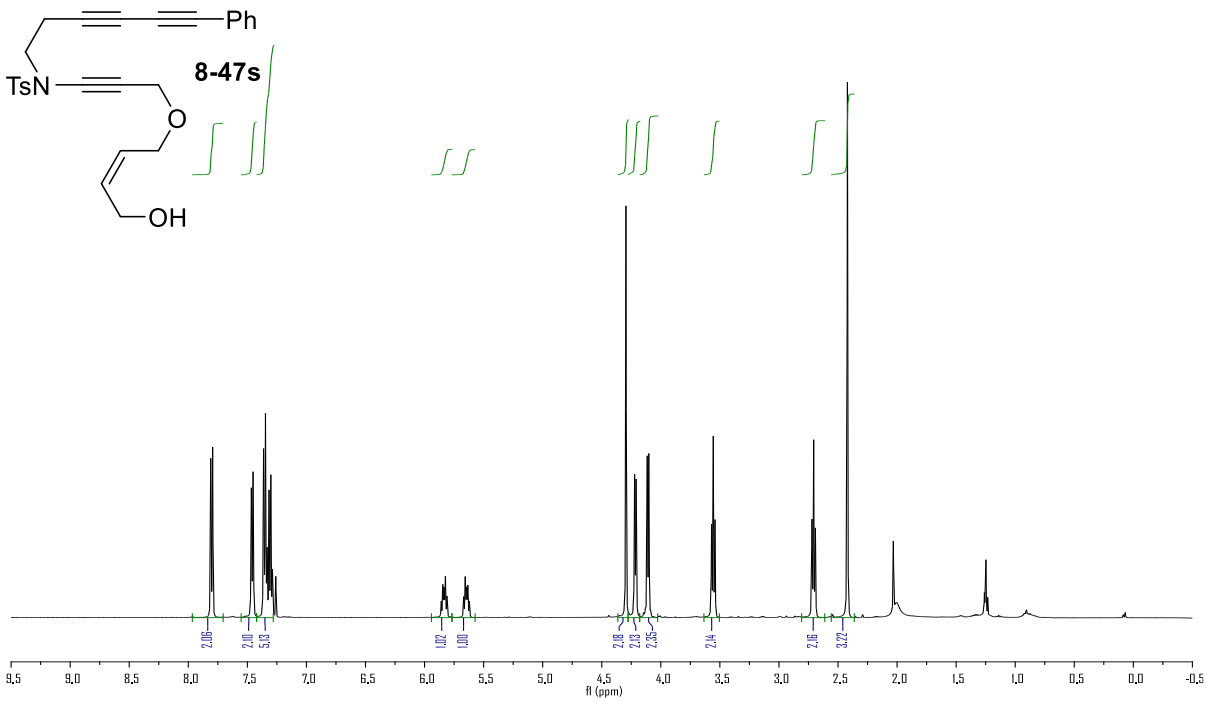

153.62
145.10
134.31
133.99
129.94
127.63
117.76
84.75
78.59
74.48
70.21
68.38
57.45
52.69
48.93
29.67
21.64
18.71
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

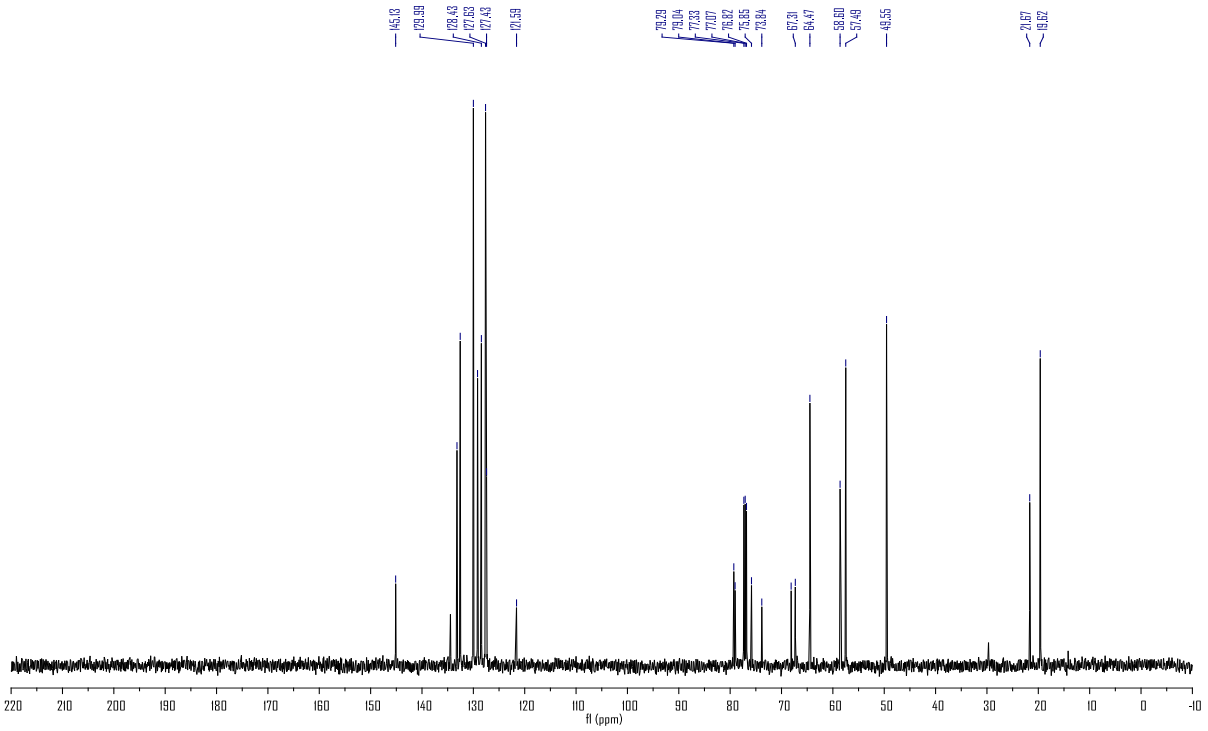

TBS
TsN
O

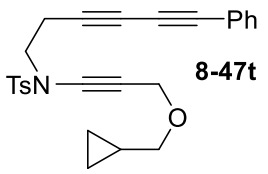
8-47r


2.34
2.35
1.01
2.22
2.42
2.49
2.38
2.30
3.82
11.14
2.23
f1 (ppm)

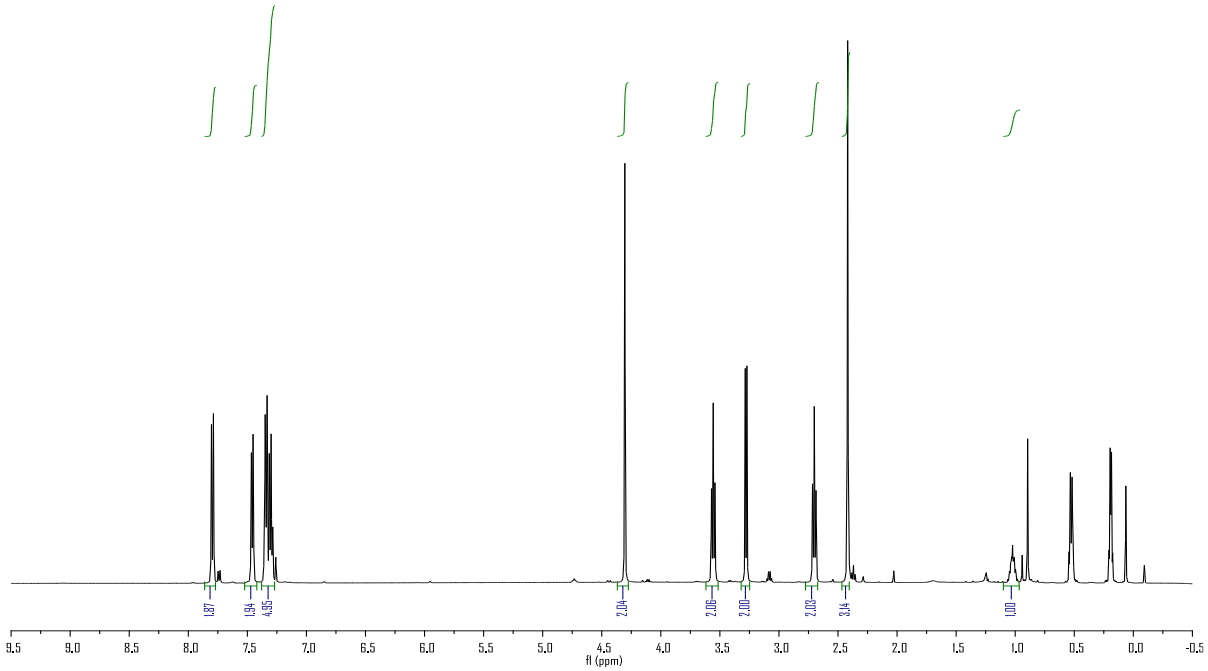

144.02
134.95
133.84
129.60
127.92
117.83
87.81
85.44
82.27
78.34
70.79
70.55
70.06
57.12
27.12
27.03
25.37
21.57
16.84
-4.92
f1 (ppm)

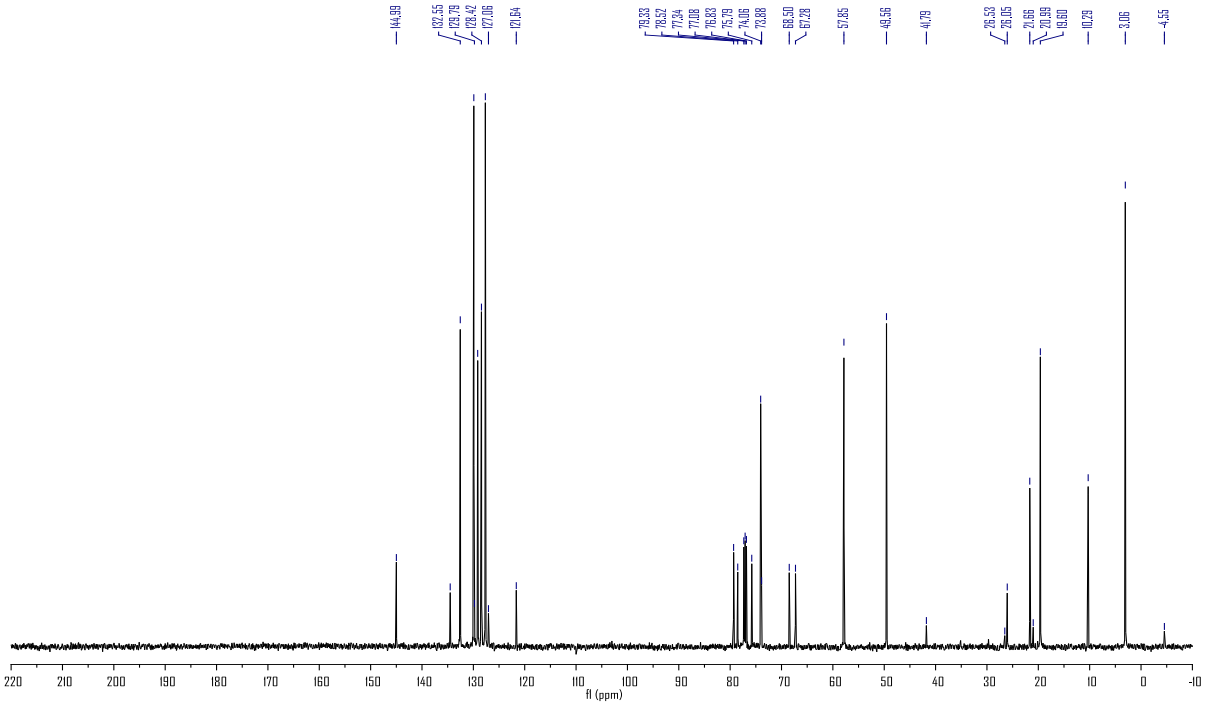

Ph
TsN
O
OH
8-47s
2.05
2.10
5.53
1.02
1.00
2.18
2.13
2.35
2.14
2.16
3.22
f1 (ppm)


145.13
129.99
128.43
127.63
127.43
121.59
79.29
83.04
77.33
77.07
76.82
75.85
73.84
67.31
64.47
58.80
57.49
49.55
21.67
19.62
f1 (ppm)


Ph
TsN
O

8-47t


1.87
1.94
4.95
2.04
2.06
2.00
2.03
3.14
1.00
f1 (ppm)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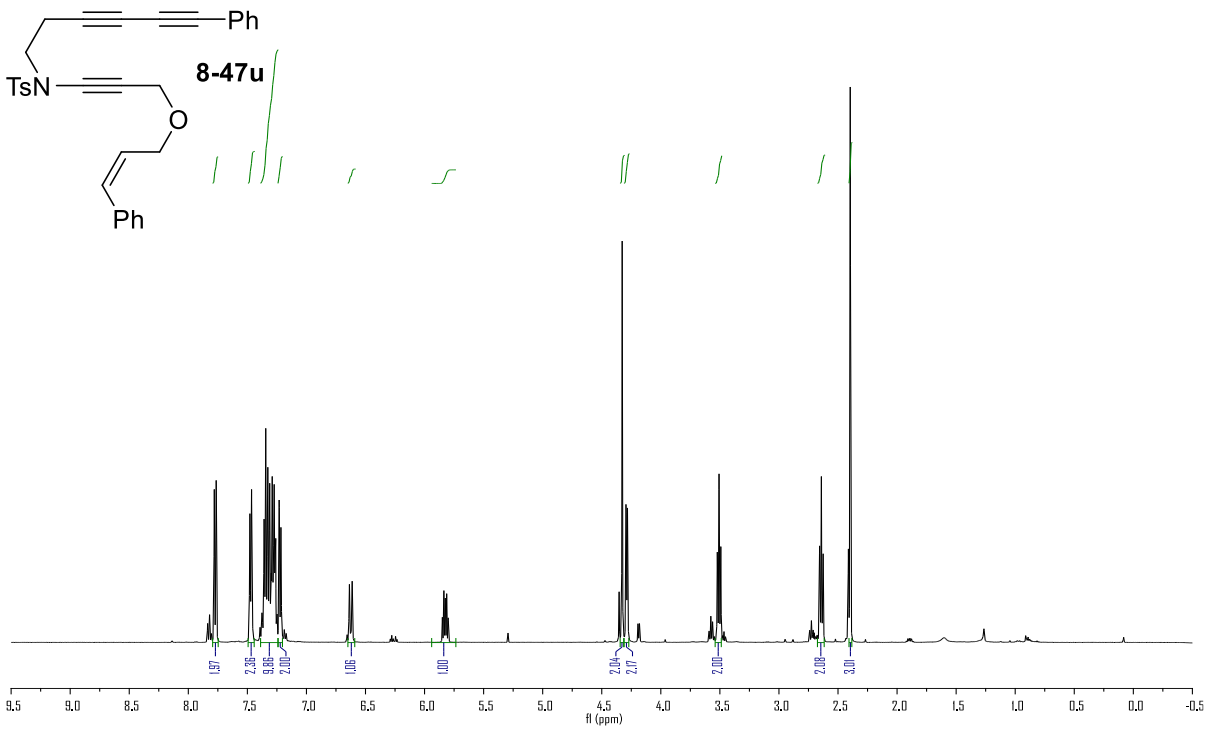
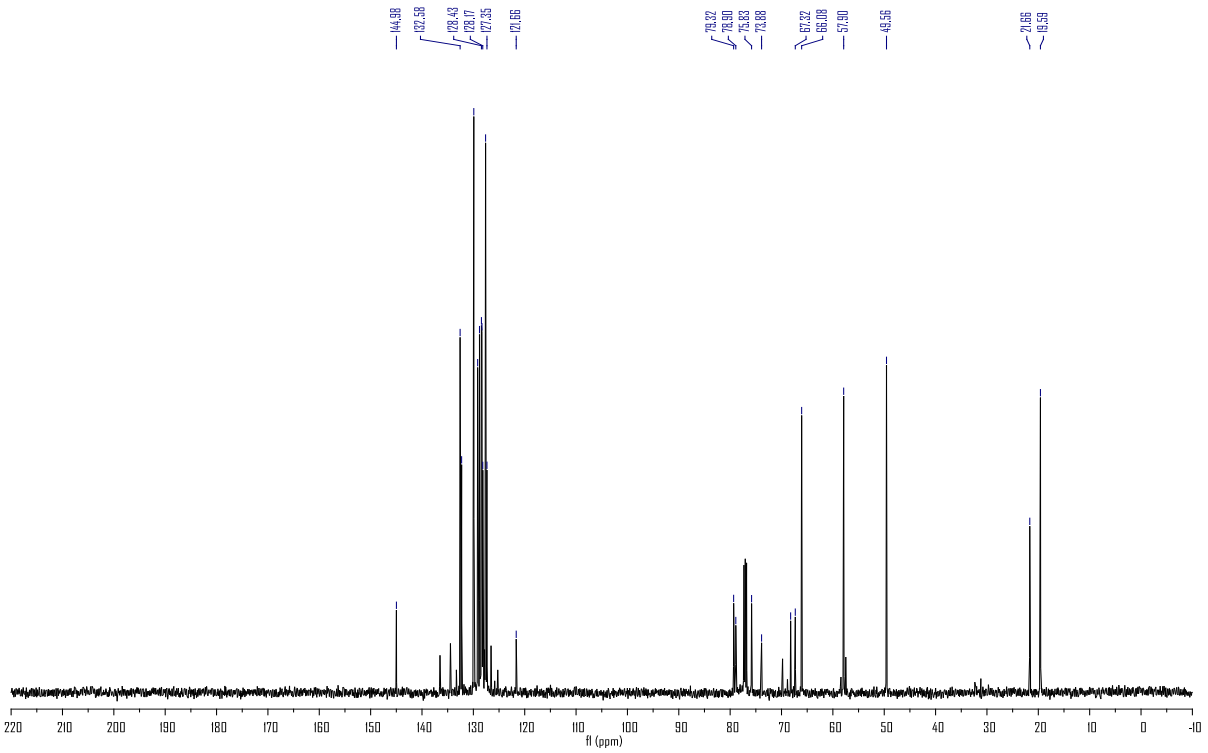
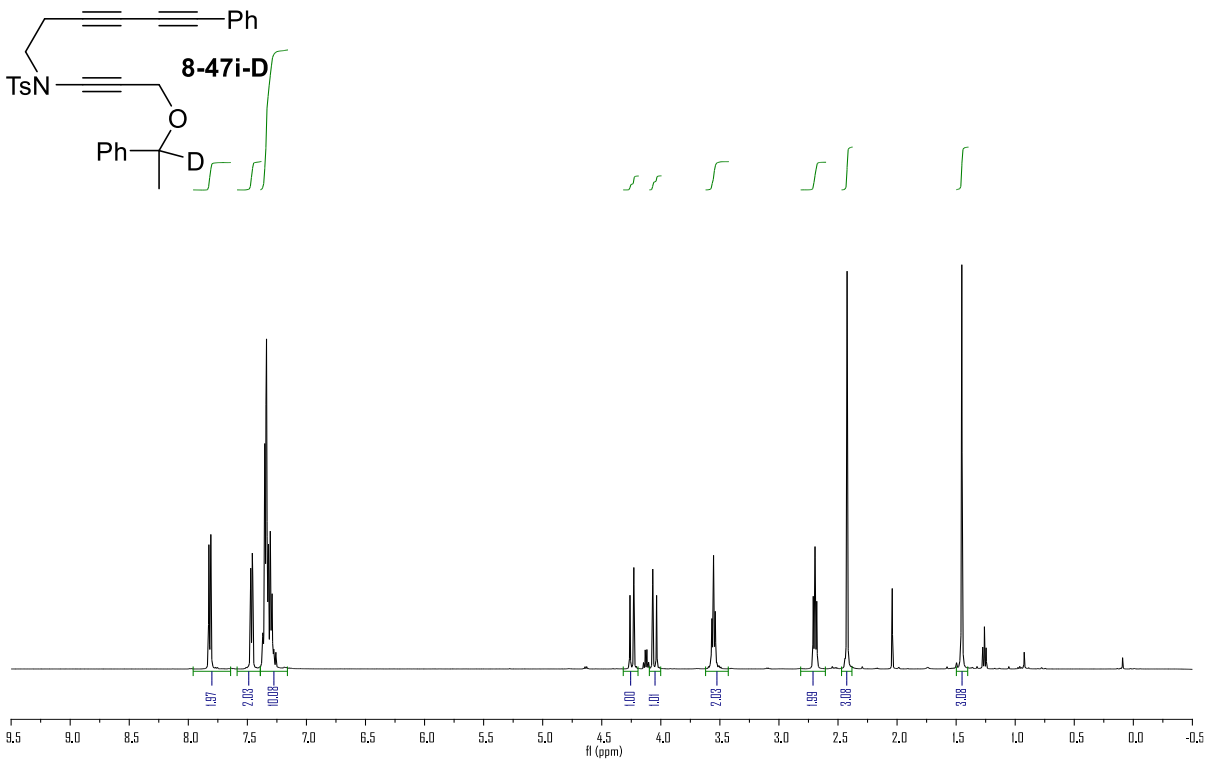
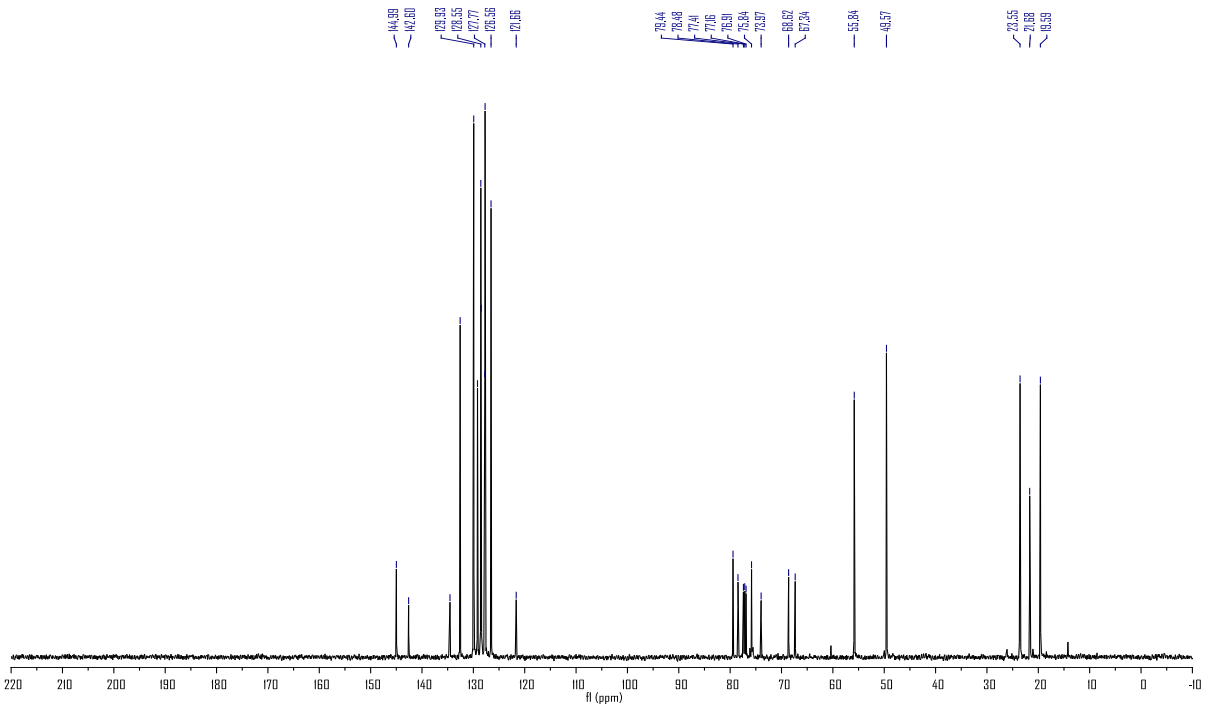
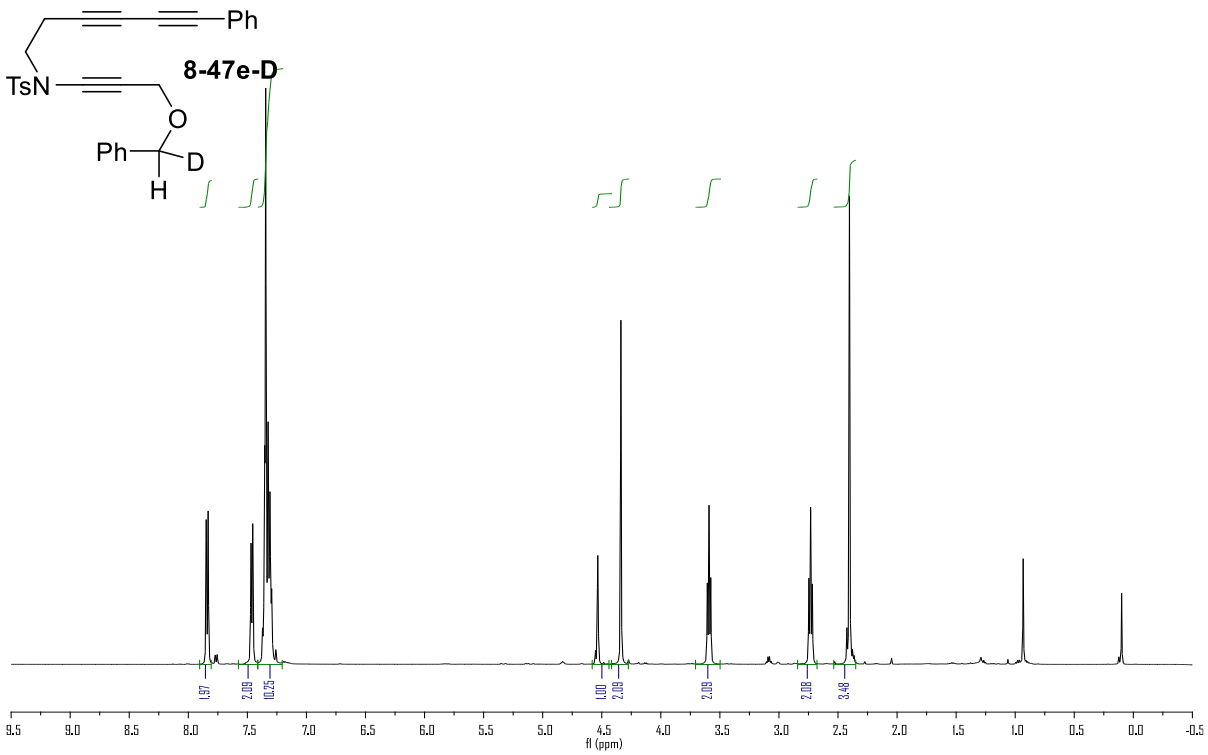
132.255
129.719
128.412
127.086
121.641
79.333
78.512
77.214
77.088
76.833
75.719
74.085
72.888
68.450
67.278
57.865
49.556
44.719
26.533
26.055
21.666
20.959
13.601
10.279
3.016
-4.555
f1 (ppm)

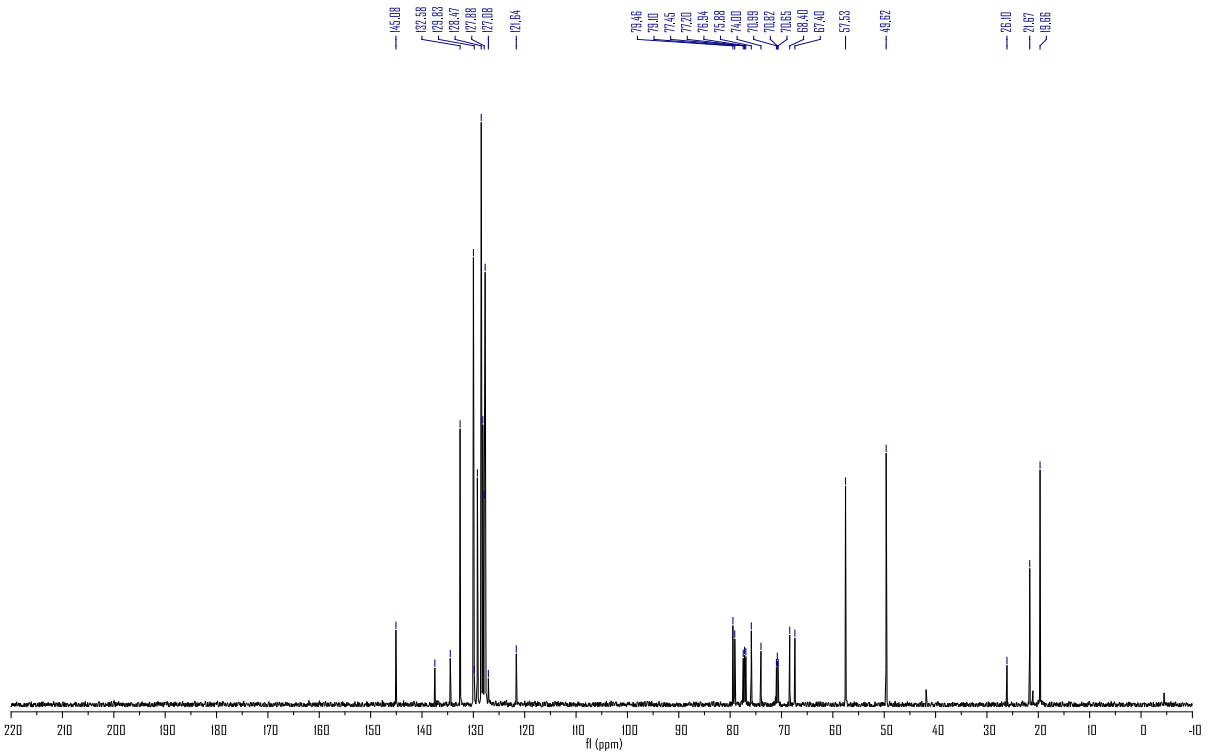

Ph
TsN
O
Ph
8-47u
1.97
2.38
9.86
2.00
1.06
1.00
2.04
2.17
2.00
2.08
3.01
f1 (ppm)

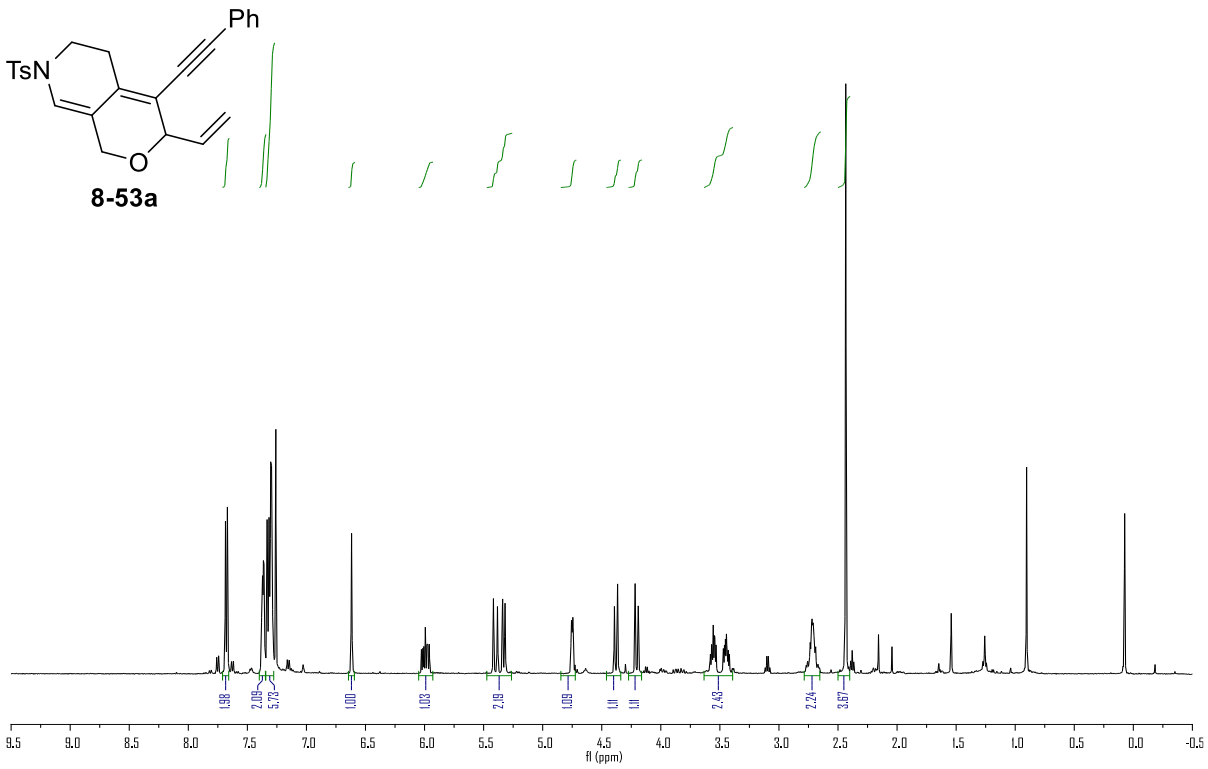

144.98
132.58
128.43
128.17
127.35
121.66
79.32
78.90
75.83
73.88
67.32
66.08
57.90
49.56
21.66
19.59
f1 (ppm)

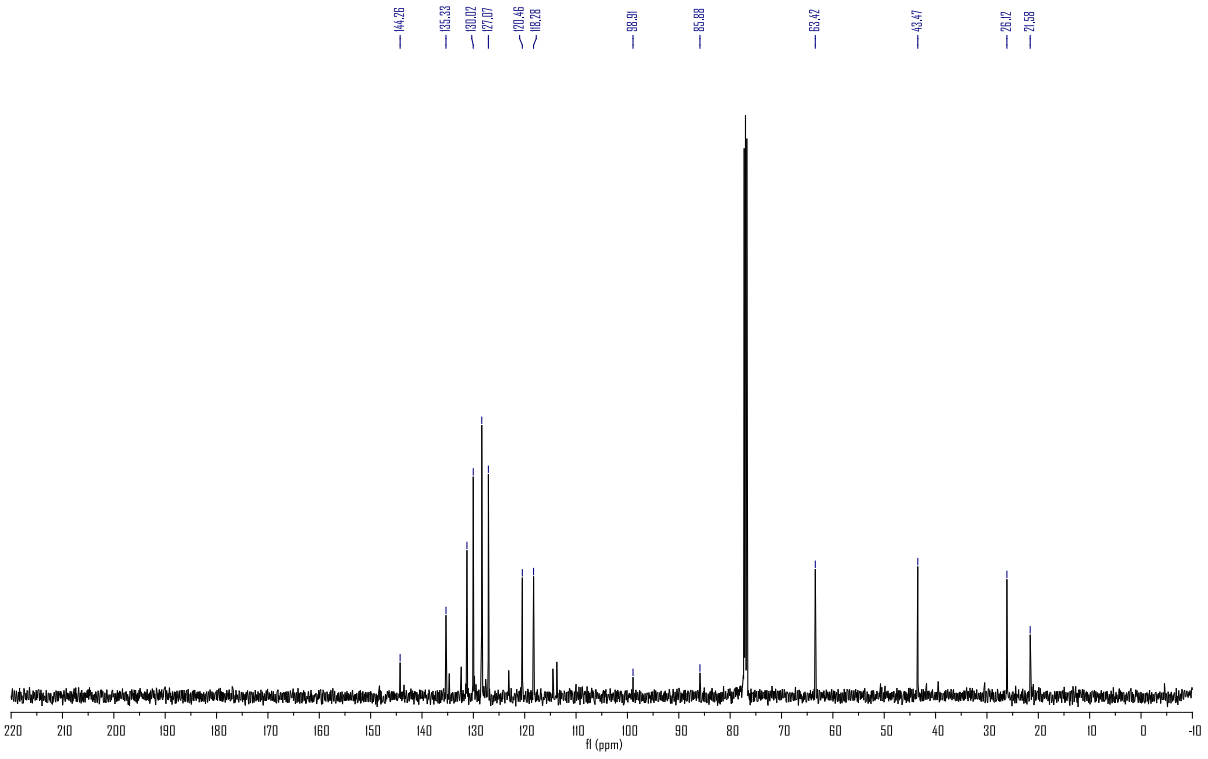

Ph
8-47i-D
TsN
O
Ph
D
1.97
2.03
10.08
1.00
1.01
2.03
1.99
3.08
3.08
f1 (ppm)

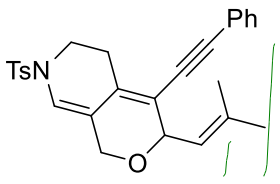

144.99
142.80
129.93
128.35
127.77
125.56
121.66
79.44
78.48
77.41
77.16
76.91
75.84
73.37
68.62
67.34
55.84
49.57
29.55
21.68
18.59
f1 (ppm)


Ph
TsN
O
Ph
D
H
8-47e-D
1.97
2.09
10.25
1.00
2.09
2.09
2.08
3.48
f1 (ppm)

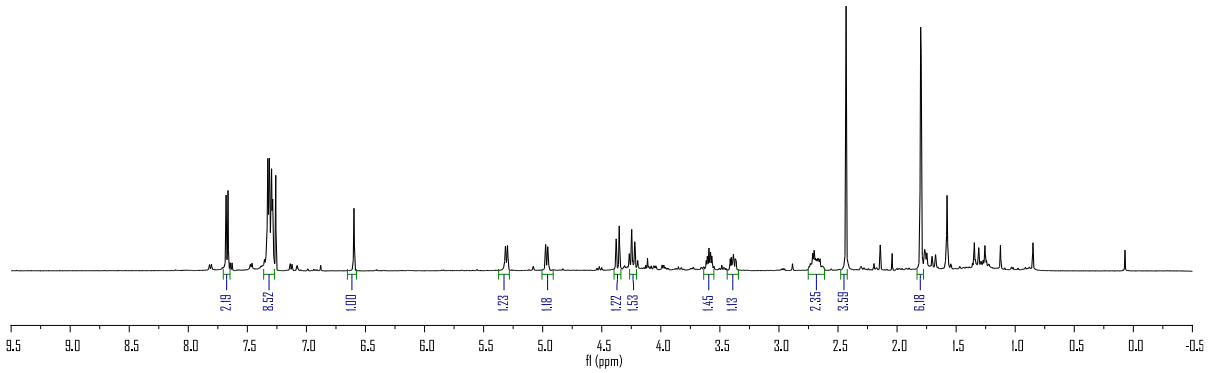

145.08
132.58
129.83
128.47
127.88
127.08
121.64
79.46
79.10
77.45
77.20
76.94
75.88
74.00
70.39
70.82
70.65
68.40
67.40
57.53
49.62
26.10
21.67
19.66
f1 (ppm)


Ph
TsN
O
8-53a
1.98
2.05
5.73
1.00
1.03
2.19
1.09
1.11
1.11
2.49
2.24
3.67
f1 (ppm)

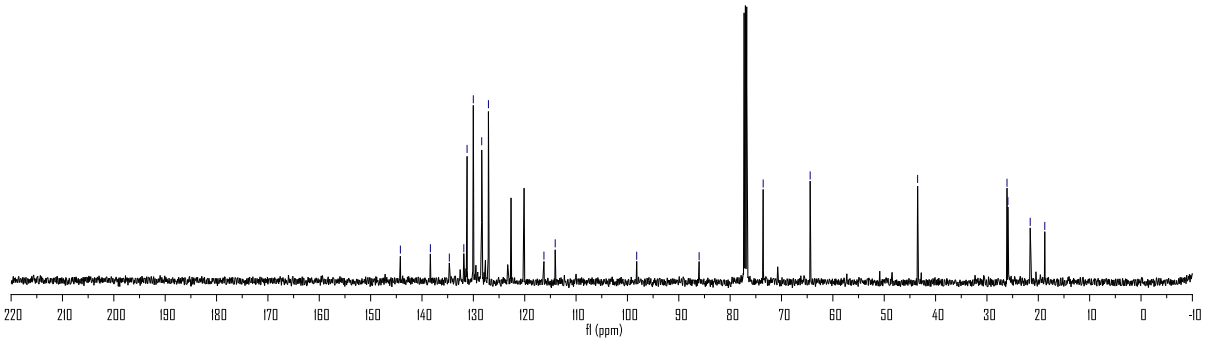

144.26
135.33
130.02
127.07
120.46
118.28
98.91
85.88
63.42
43.47
26.12
21.58
f1 (ppm)

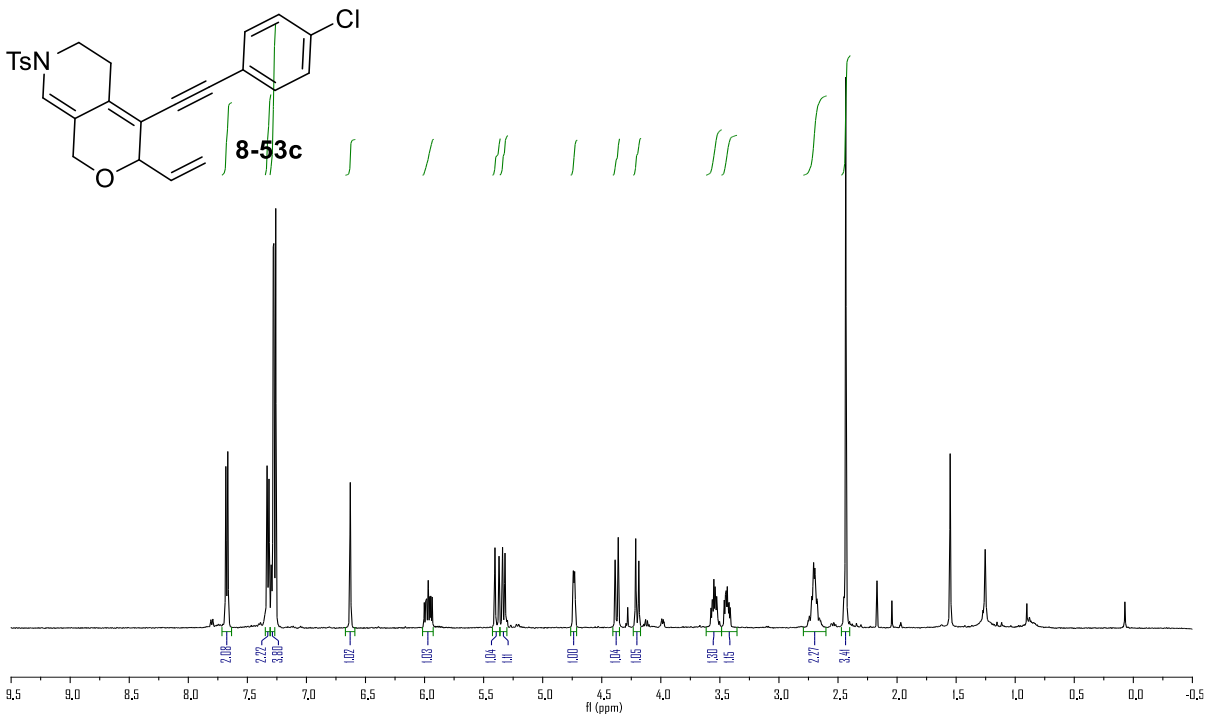

Ph
TsN
O

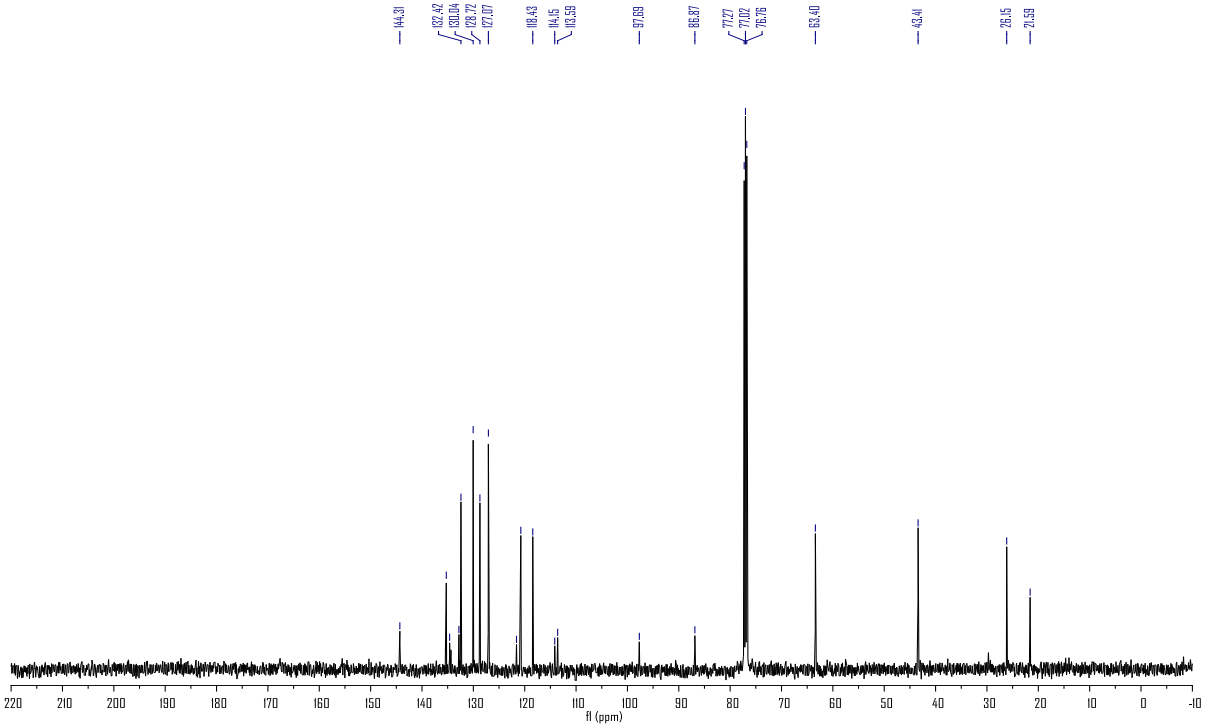
8-53b

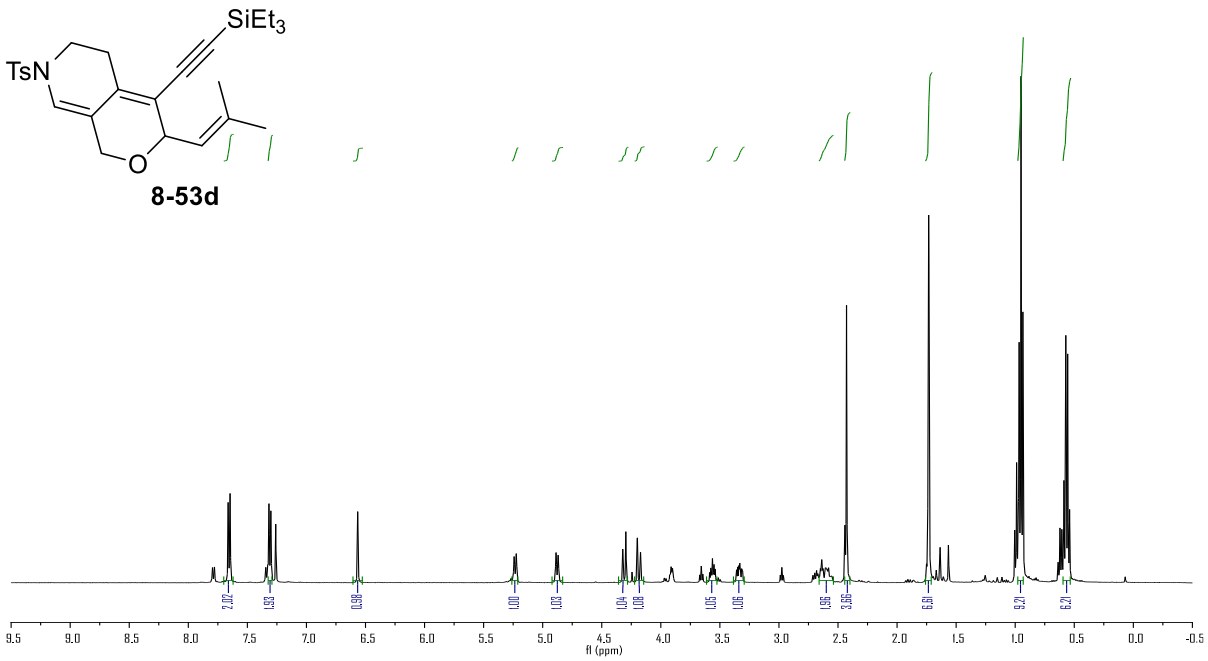

2.19
8.57
1.00
1.23
1.18
1.27
1.53
1.45
1.13
2.35
3.59
6.18
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

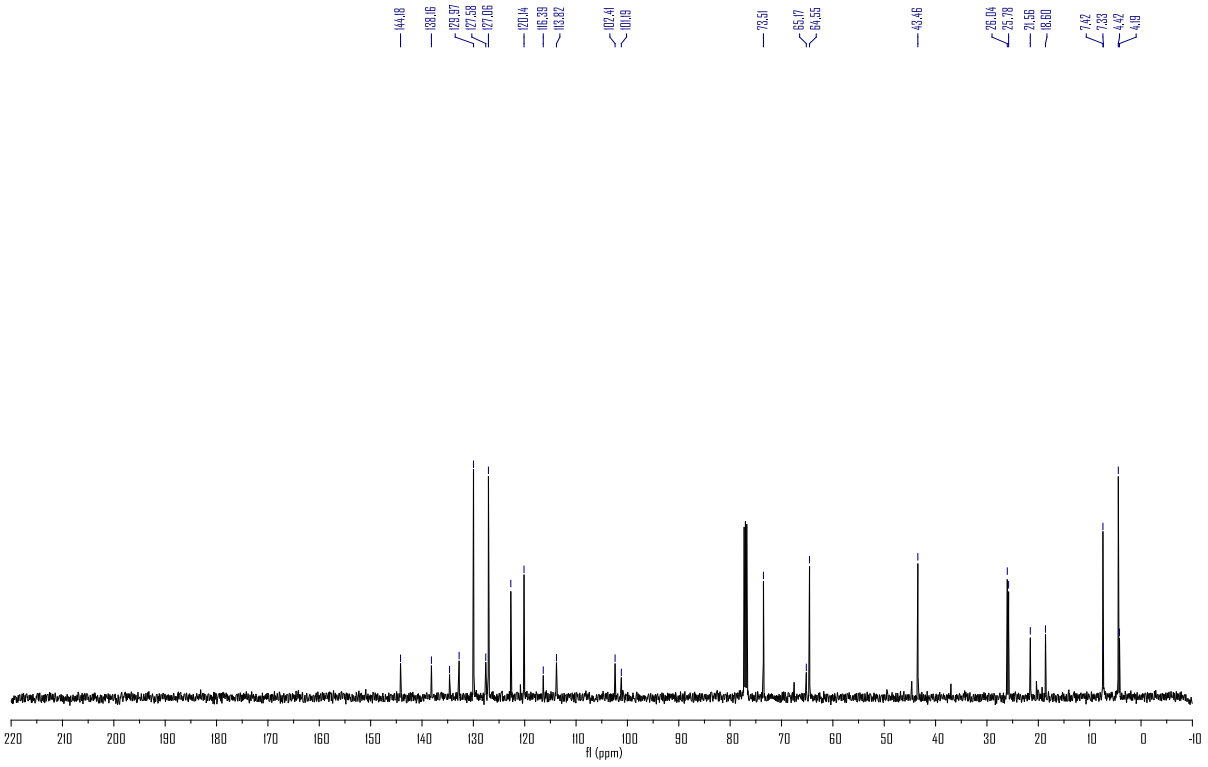
144.21
138.37
131.22
130.01
128.37
127.06
116.26
114.06
98.20
86.04
73.57
64.42
43.50
28.09
25.92
21.58
18.74


220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


TsN
Cl
O
8-53c
2.08
2.22
3.80
1.02
1.03
1.04
1.11
1.00
1.04
1.05
1.30
1.15
2.27
3.41
f1 (ppm)

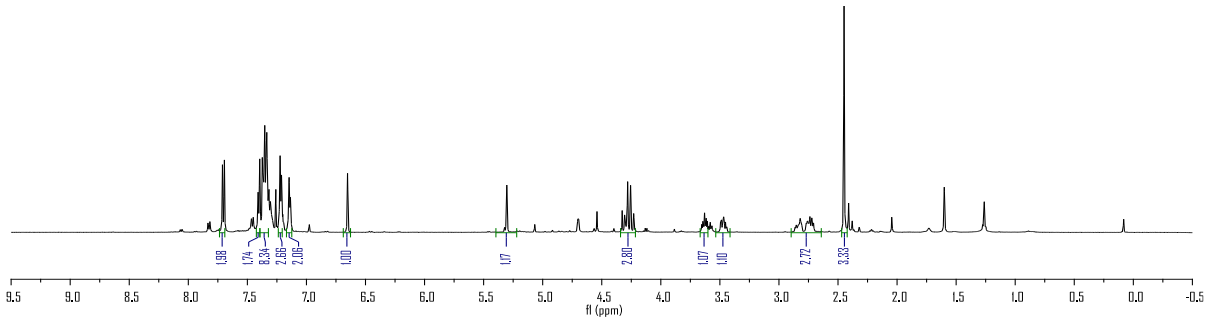

144.31
132.42
130.04
128.72
127.07
118.43
114.15
113.59
97.69
86.87
77.27
77.02
76.76
63.40
43.41
26.15
21.59
f1 (ppm)

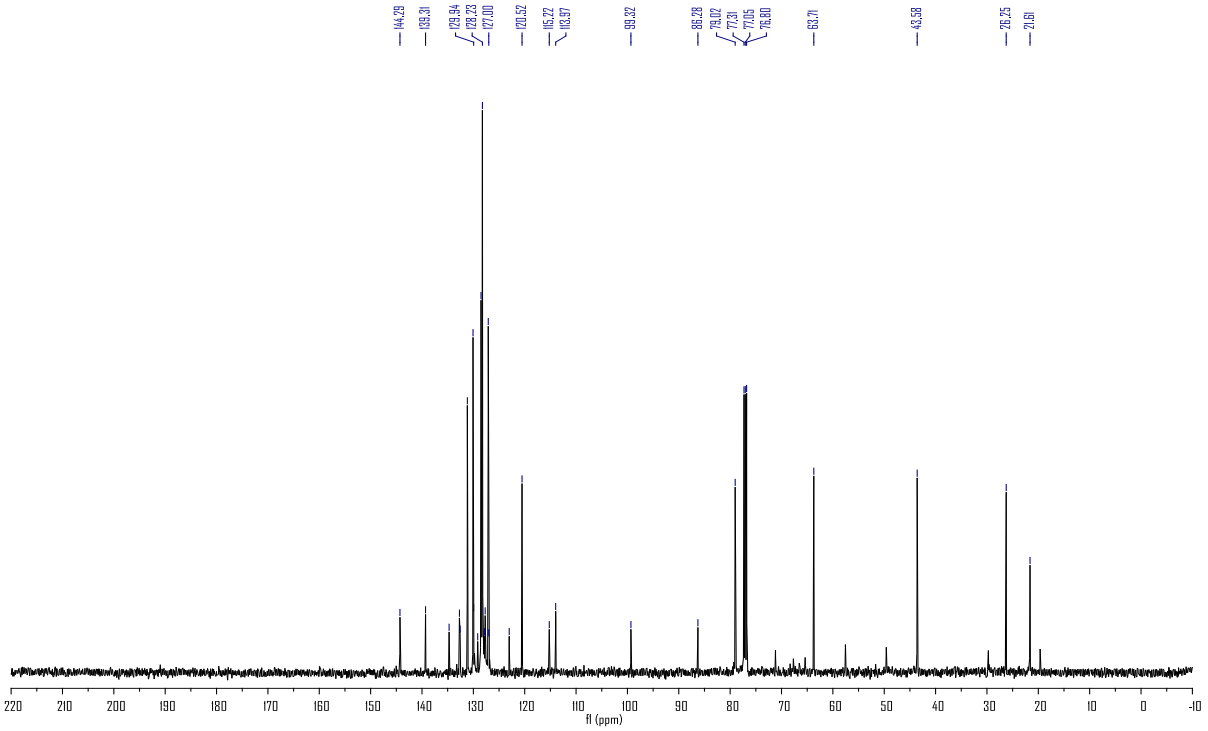

SiEt3
TsN
O
8-53d
2.02
1.93
0.98
1.00
1.03
1.04
1.08
1.05
1.06
1.96
3.86
6.81
9.21
6.21
f1 (ppm)

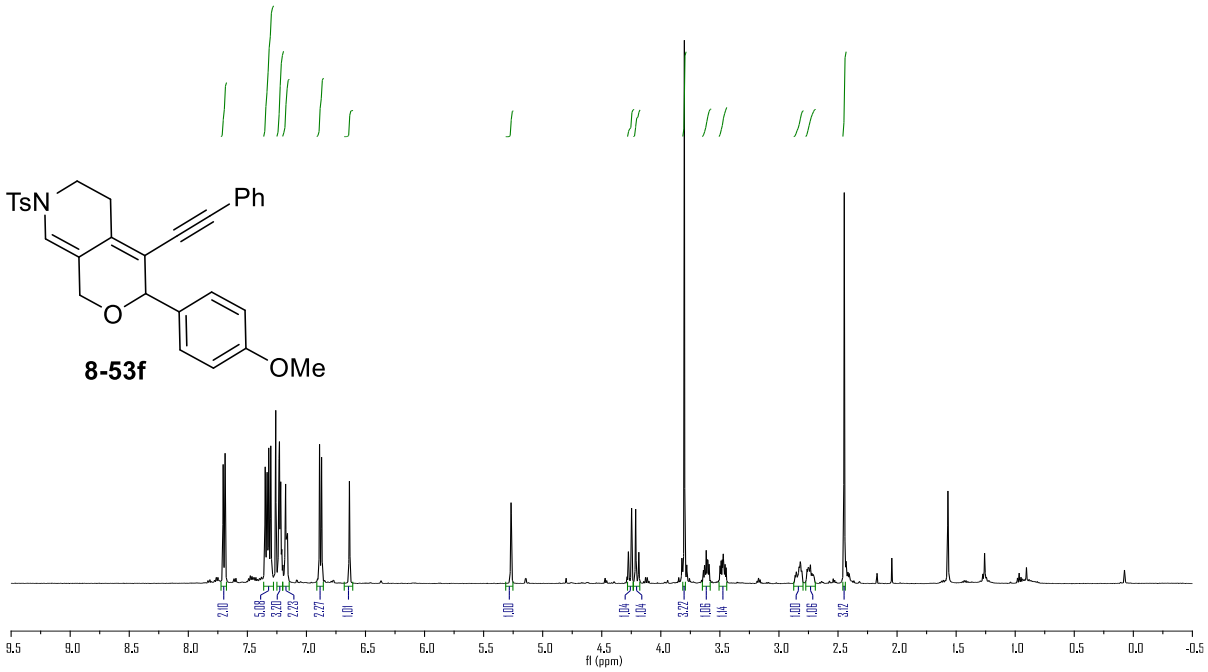

144.18
138.16
129.97
127.58
127.06
120.44
116.39
113.82
102.41
101.19
73.51
65.17
64.55
43.46
26.04
25.78
21.56
18.60
7.42
7.33
4.42
4.19
f1 (ppm)

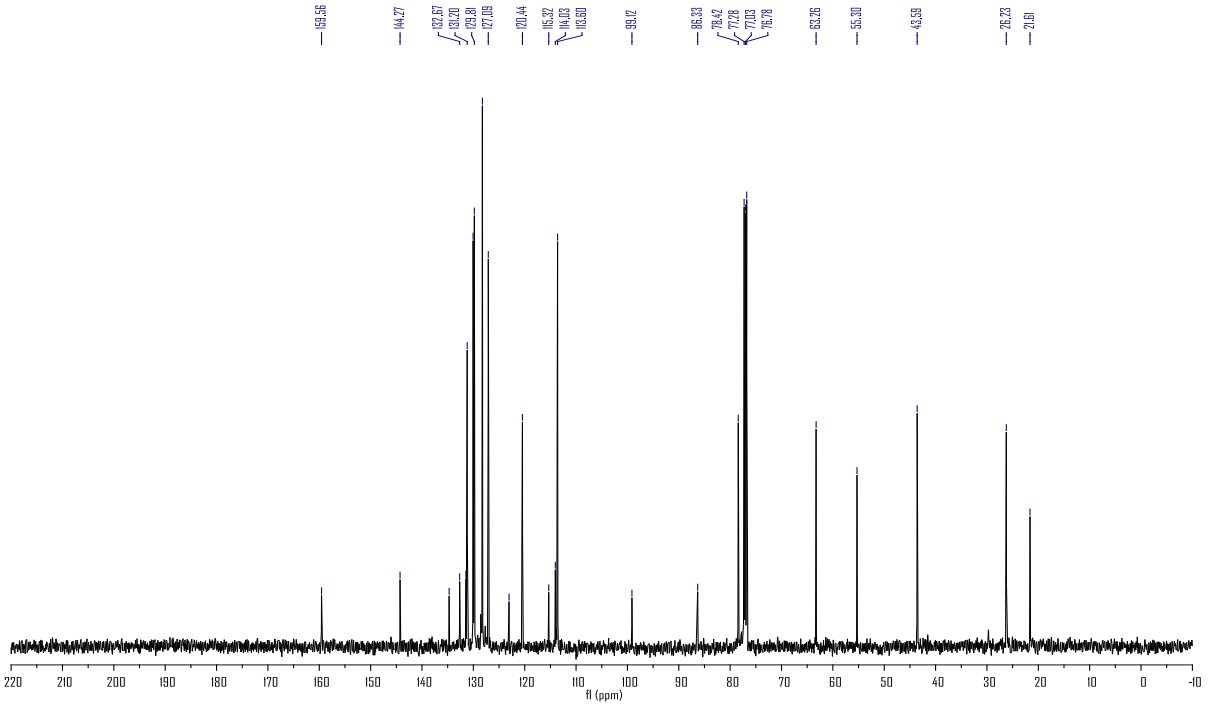
TsN
Ph
O
Ph

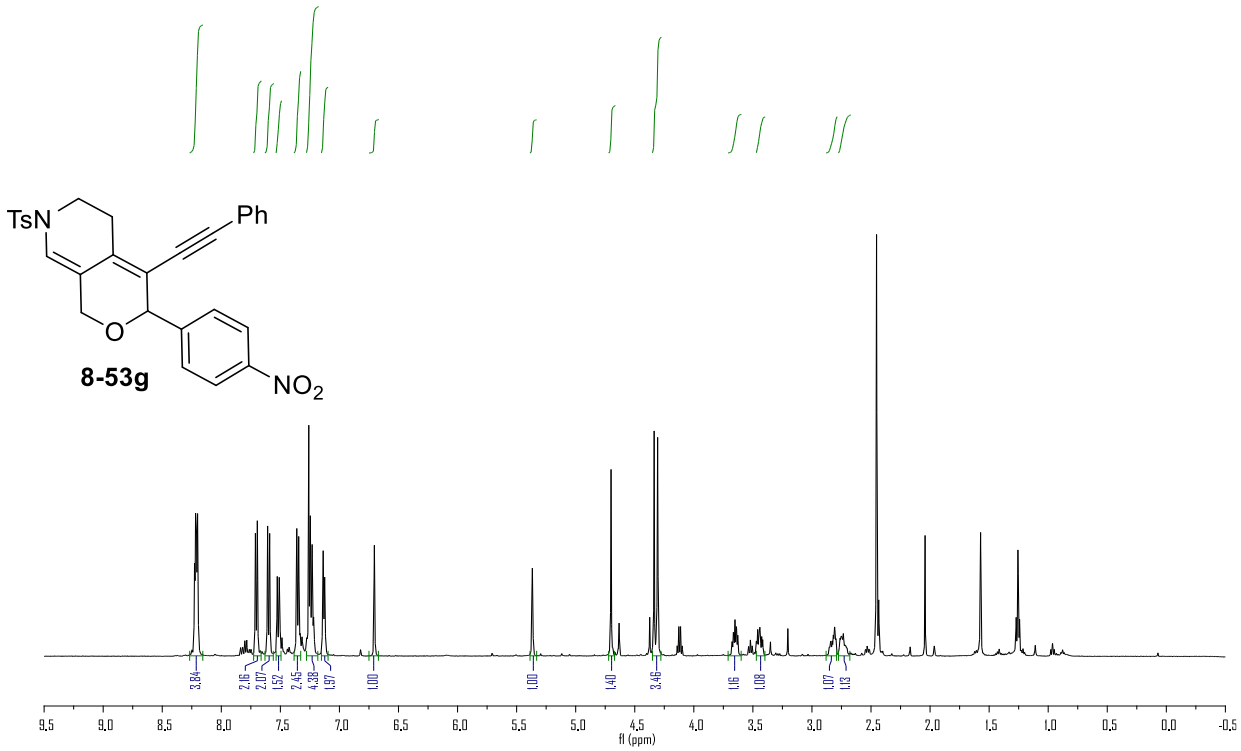
8-53e

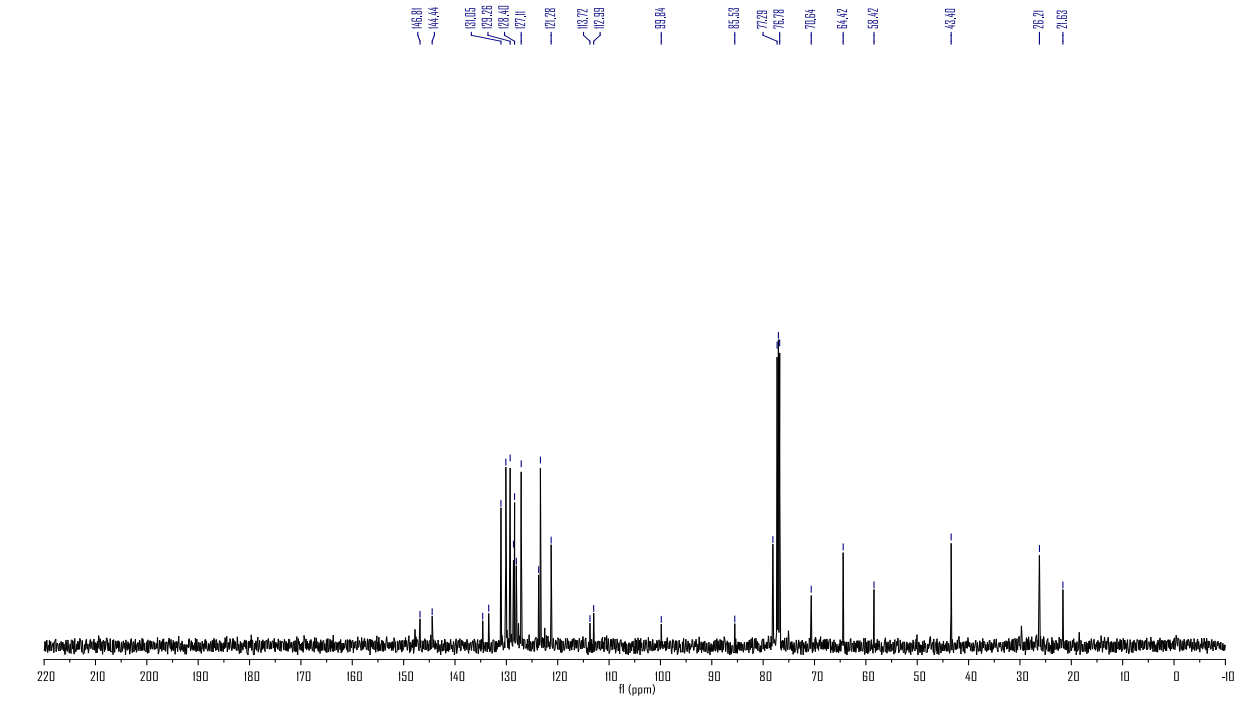

0.93
1.74
8.34
2.65
2.06
1.00
1.17
2.80
1.07
1.10
2.72
3.33
f1 (ppm)

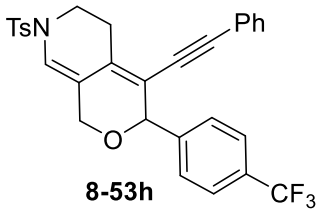

144.29
138.31
129.94
128.23
127.00
120.52
115.22
113.97
89.32
86.28
79.02
77.31
77.05
76.80
63.71
43.58
26.25
21.61
f1 (ppm)


TsN
Ph
O
OMe
8-53f
2.10
5.08
3.20
2.23
2.27
1.01
1.00
1.04
1.04
3.22
1.06
1.14
1.00
1.06
3.12
f1 (ppm)

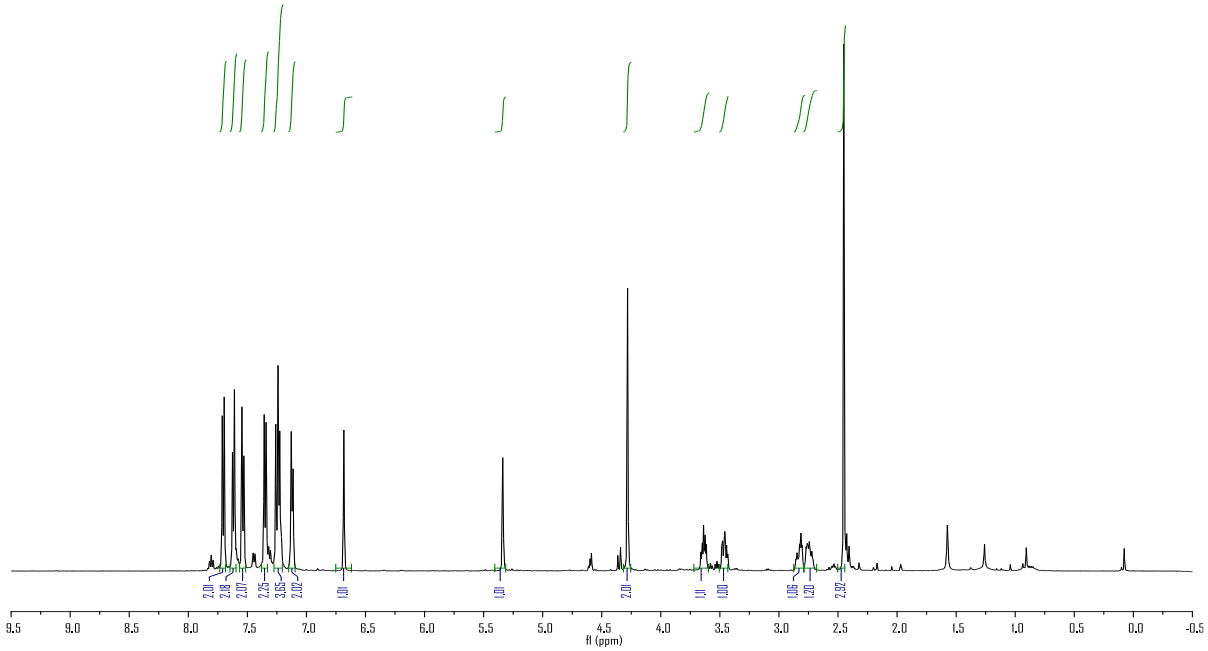

159.56
144.27
132.67
130.20
129.31
127.09
120.44
115.32
114.03
113.60
99.12
86.33
78.42
77.28
77.03
76.78
63.26
55.30
43.59
26.23
21.61
f1 (ppm)

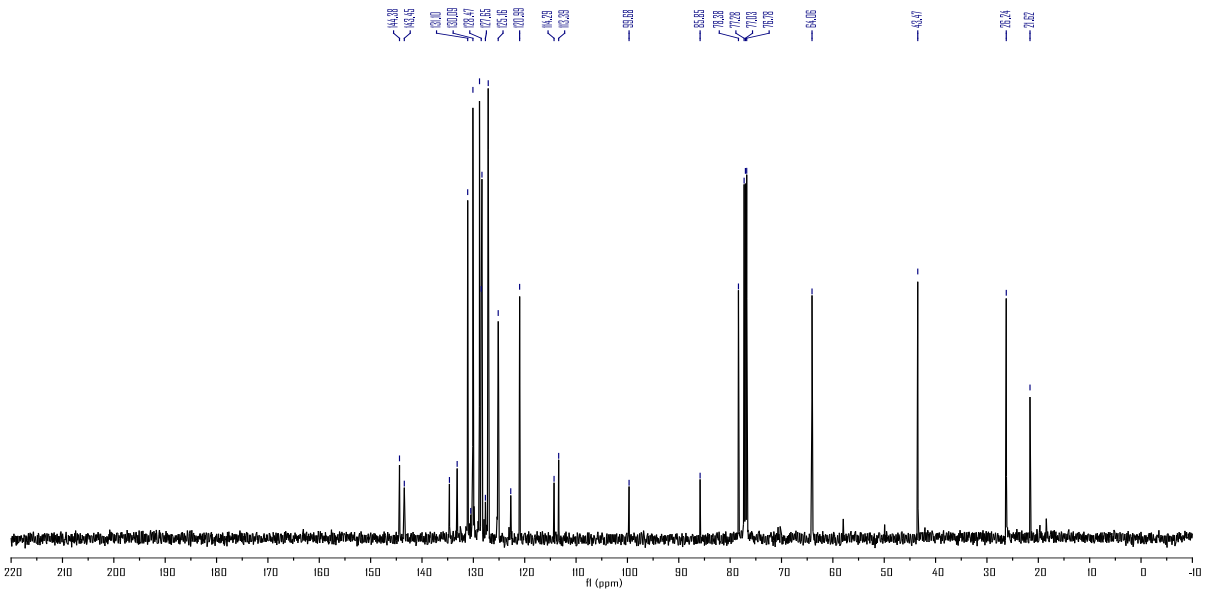

TsN
Ph
O
NO2
8-53g
3.84
2.16
2.07
1.52
2.45
4.38
1.97
1.00
1.00
1.40
8.46
1.16
1.08
1.07
1.13
f1 (ppm)

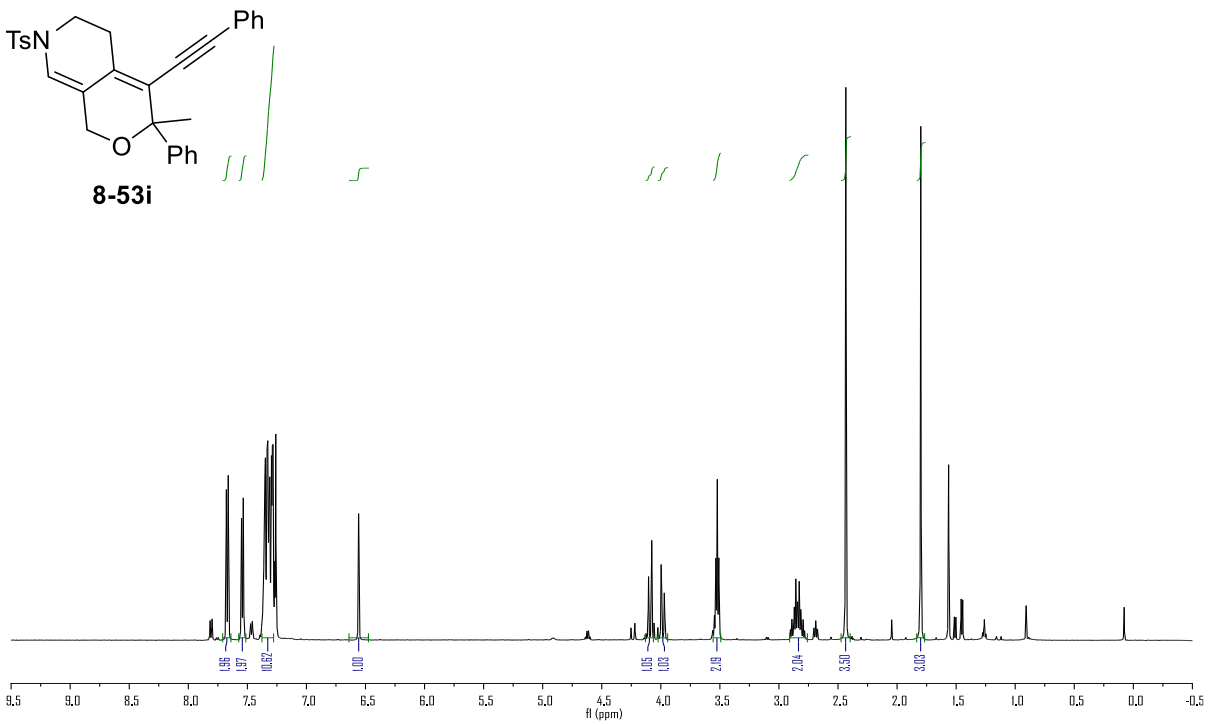

146.81
144.44
131.05
129.26
129.40
127.11
121.28
113.72
112.59
99.84
85.53
77.28
76.78
70.64
64.42
58.42
43.40
26.21
21.63
f1 (ppm)

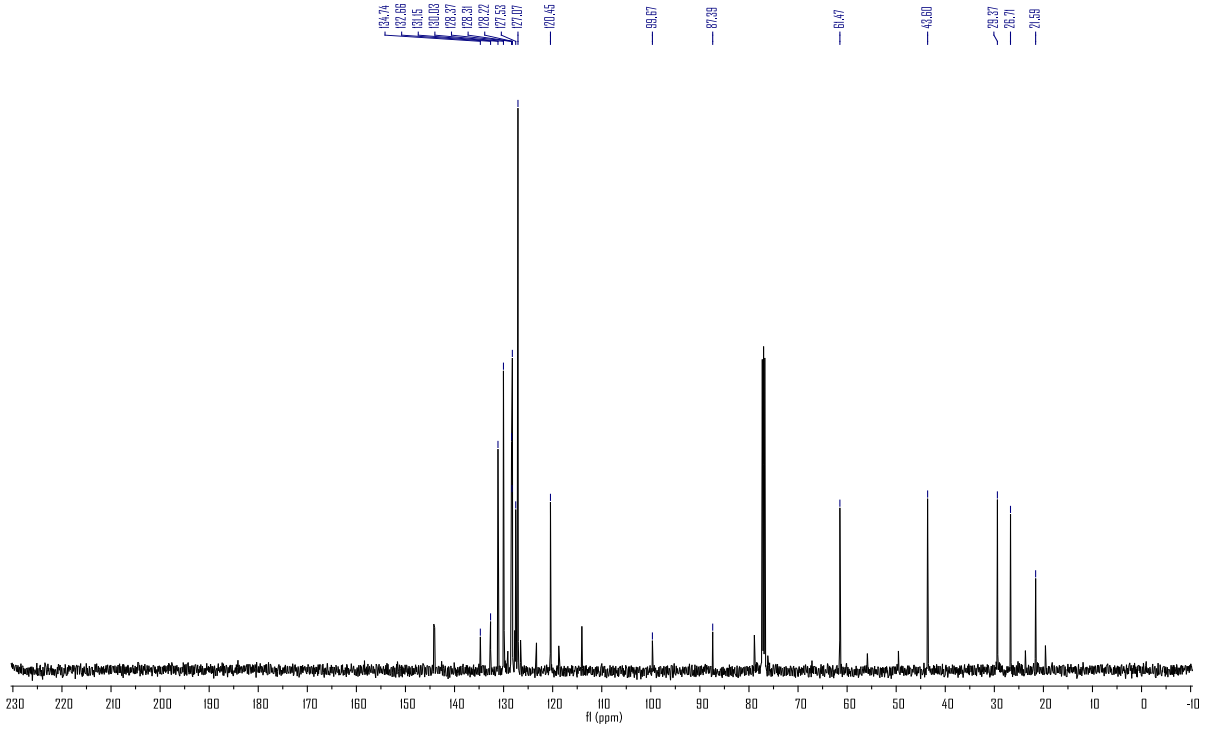

TsN
Ph
O
CF3

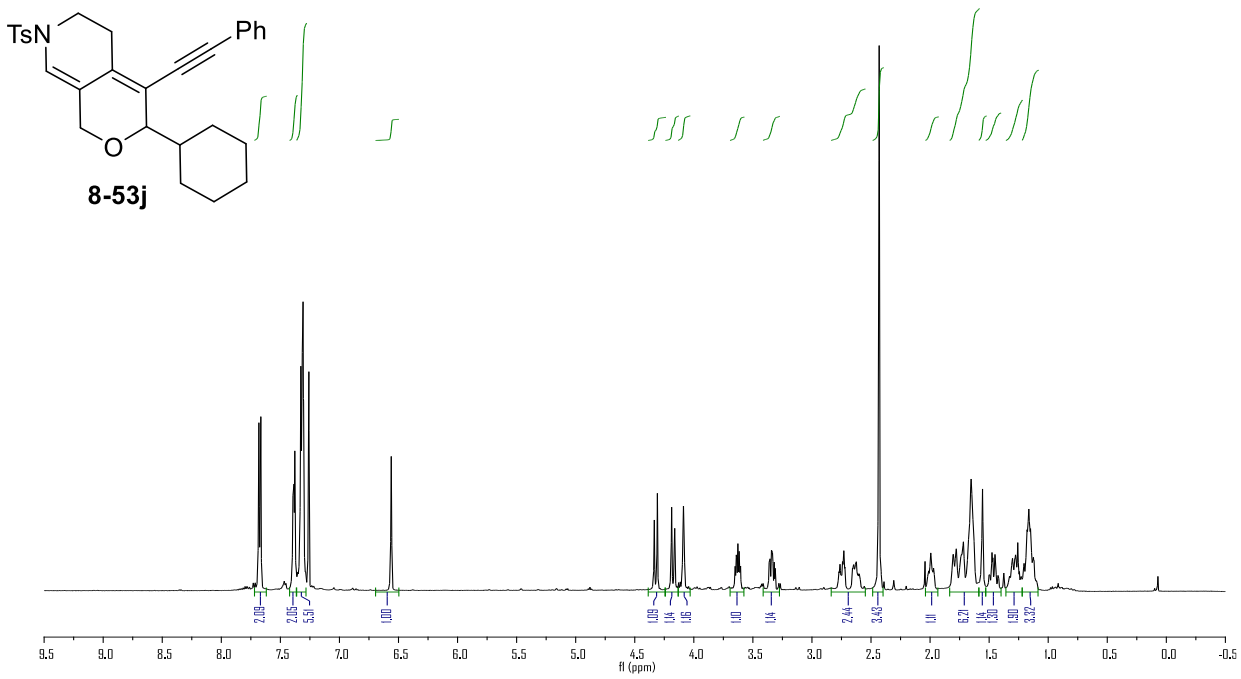
8-53h

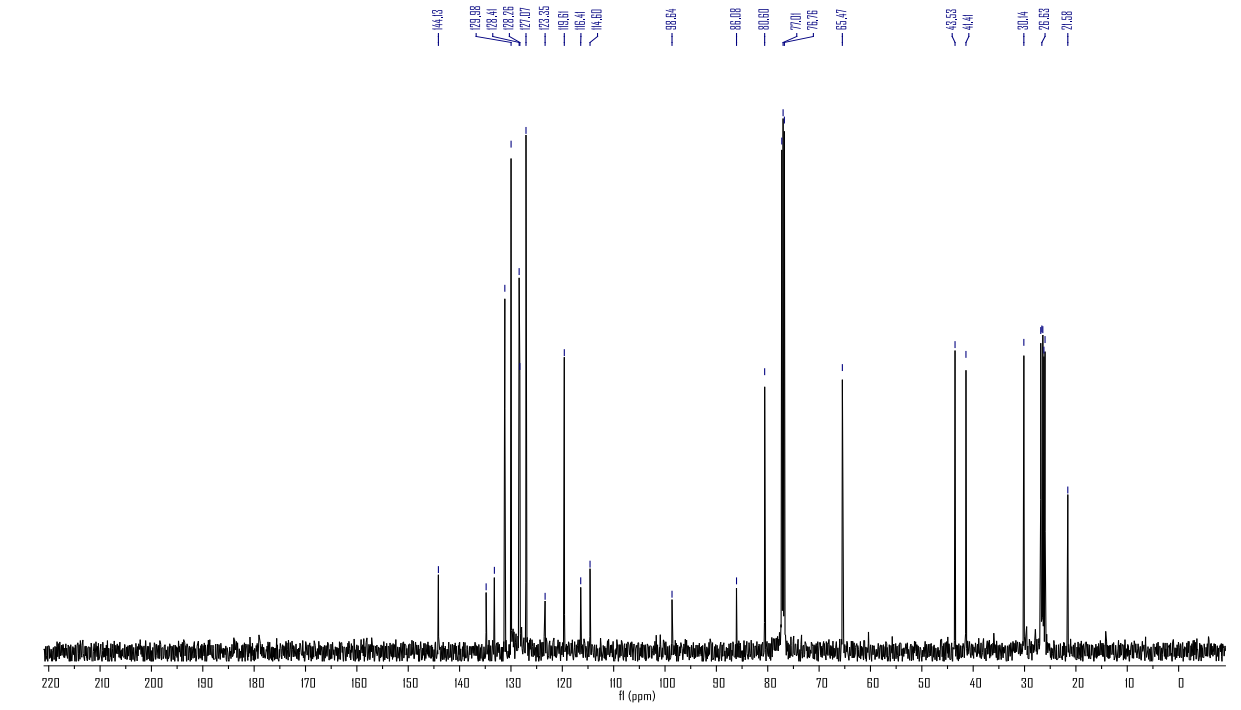

2.01
2.18
2.07
2.25
3.65
2.02
1.00
1.00
2.01
1.11
1.00
1.06
1.20
2.92
f1 (ppm)

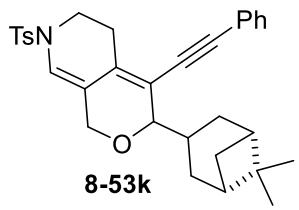

144.38
142.45
130.10
130.09
128.47
127.55
125.48
120.98
114.29
107.30
88.68
85.85
78.38
77.28
77.03
76.78
64.06
43.47
28.74
21.62
f1 (ppm)


TsN
Ph
O
Ph
8-53i
1.95
1.97
10.62
1.00
1.05
1.03
2.19
2.04
3.50
3.03
f1 (ppm)

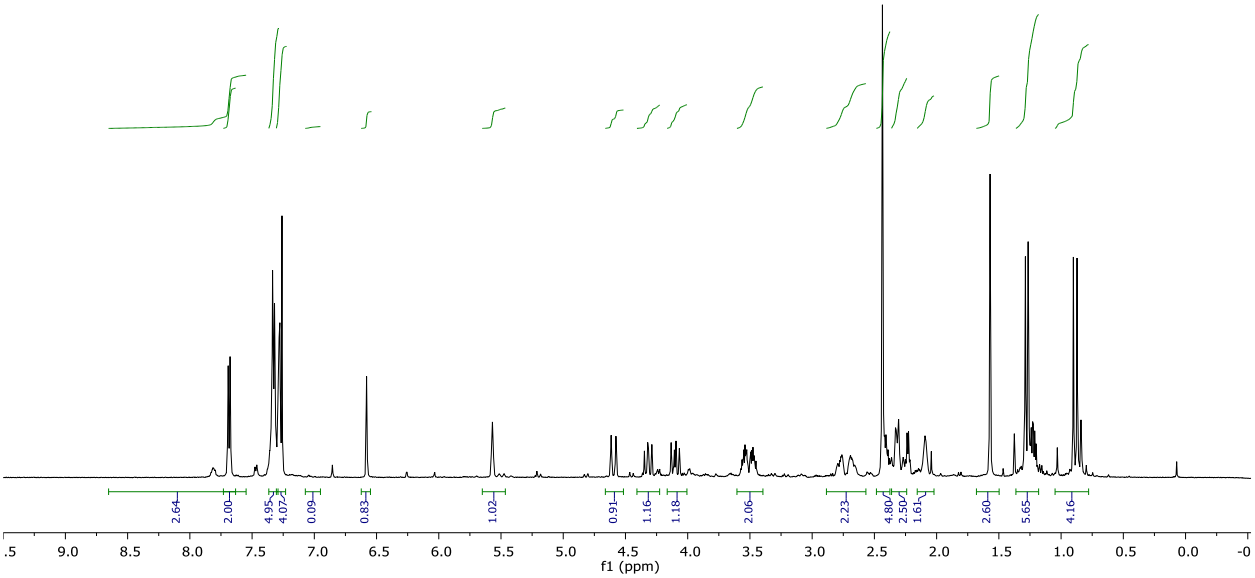

134.74
132.66
131.15
130.03
128.37
128.31
128.22
127.53
127.07
120.45
99.67
87.39
51.47
43.60
29.37
26.71
21.59
f1 (ppm)

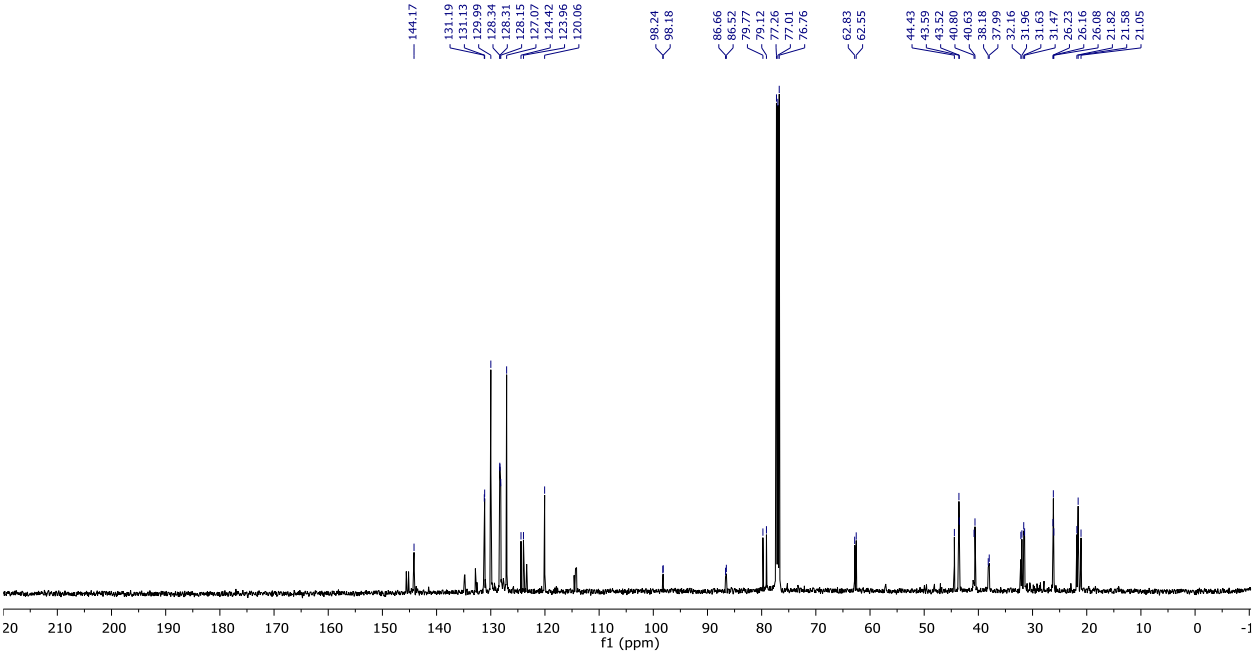

TsN
Ph
O
8-53j
2.09
2.05
5.51
1.00
1.09
1.04
1.16
1.10
1.04
2.44
3.43
1.11
6.21
1.04
1.30
1.90
3.32
f1 (ppm)

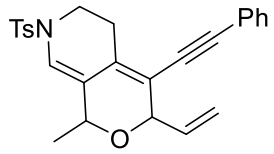

144.13
129.38
128.41
128.26
127.07
123.35
119.61
116.41
114.80
88.64
86.08
80.80
77.01
76.76
55.47
45.53
41.41
30.14
26.83
21.58
f1 (ppm)


TsN
Ph
O

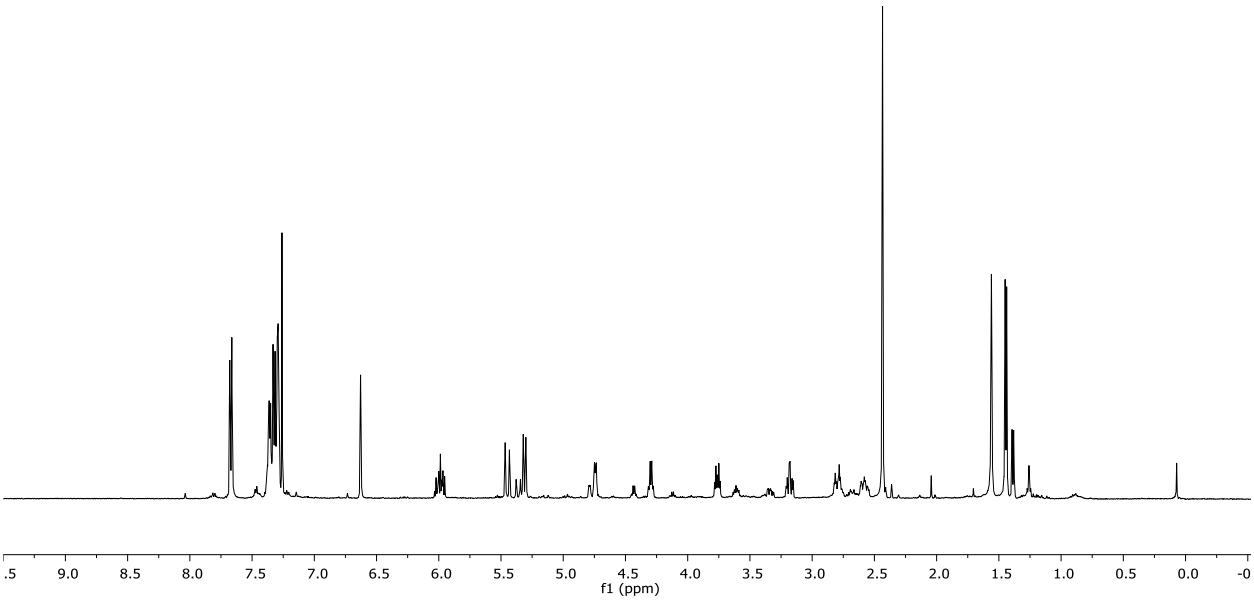
8-53k

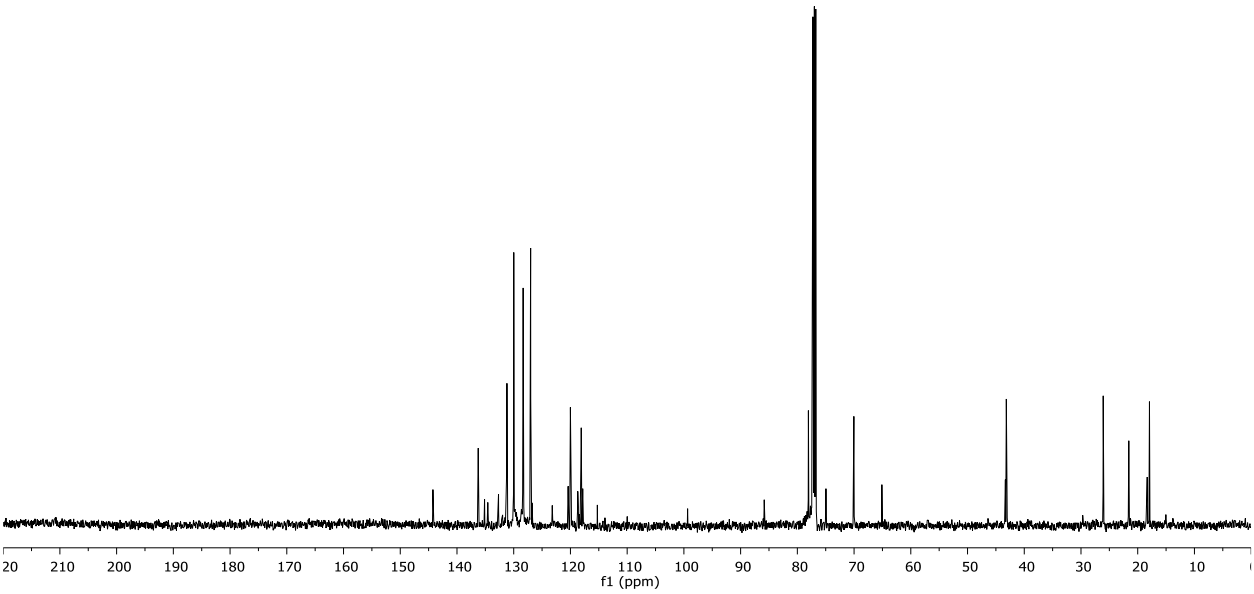

2.64
2.00
4.95
4.07
0.09
0.83
1.02
0.91
1.16
1.18
2.06
2.23
4.80
2.50
1.61
2.60
5.65
4.16
f1 (ppm)

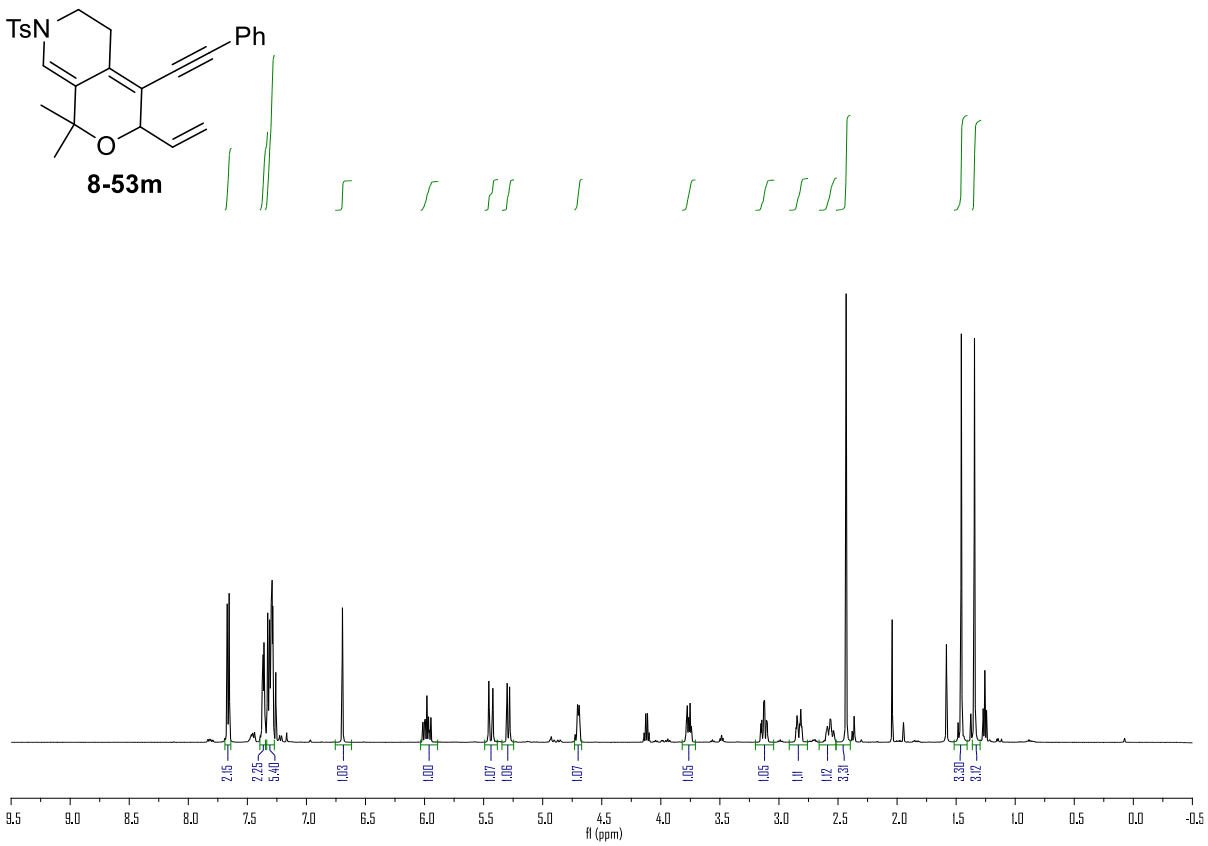

144.17
131.19
131.13
129.99
128.34
128.31
128.15
127.07
124.42
123.96
120.06
98.24
98.18
86.66
86.52
79.77
79.12
77.26
77.01
76.76
62.83
62.55
44.43
43.59
43.52
40.80
40.63
38.18
37.99
32.16
31.96
31.63
31.47
26.23
26.16
26.08
21.82
21.58
21.05
f1 (ppm)

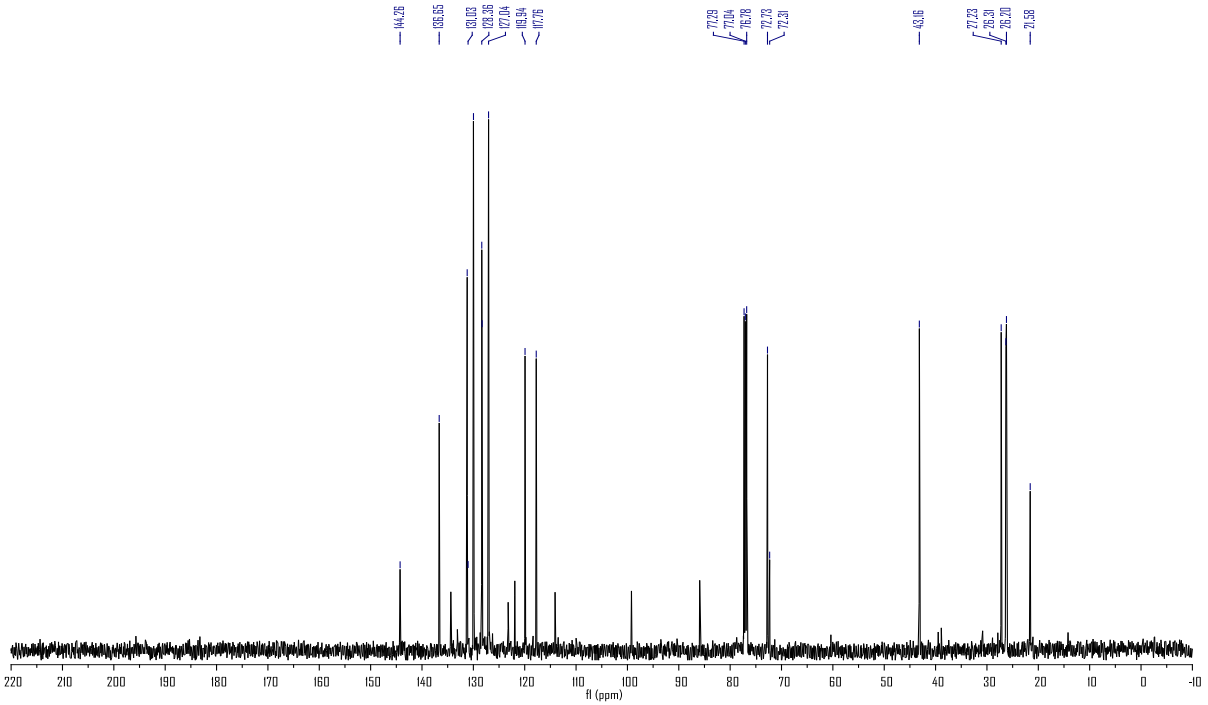

TsN
Ph
O

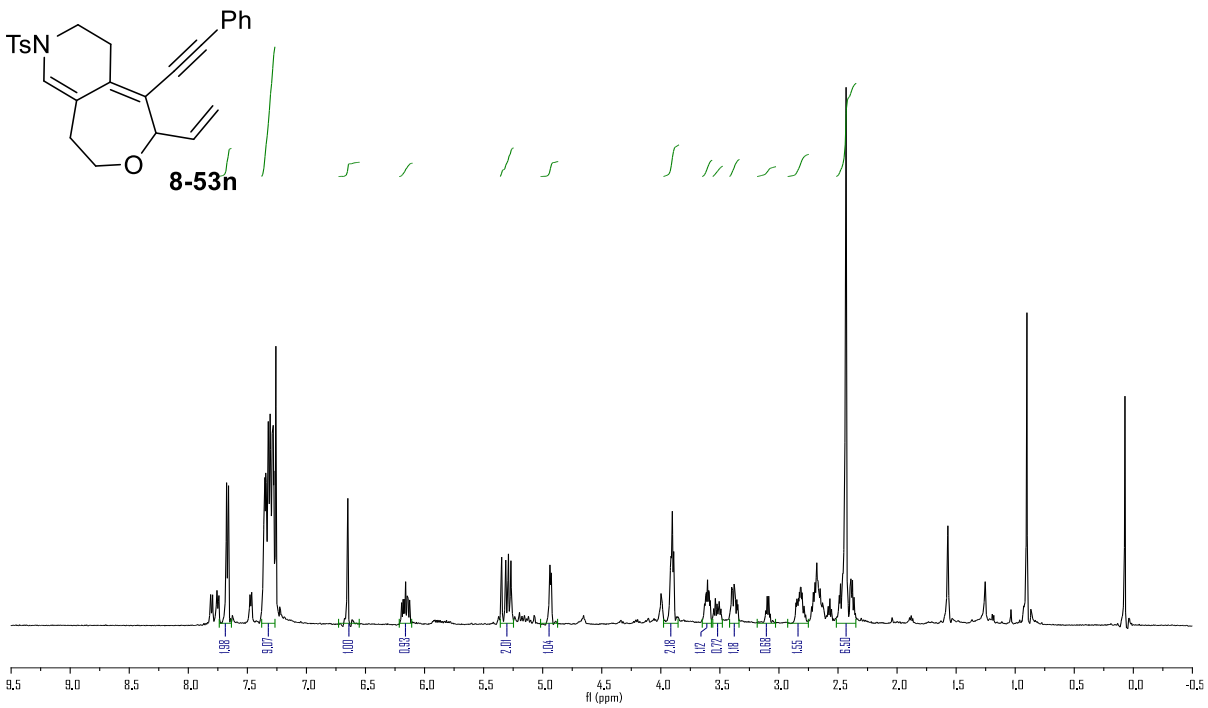
8-53l

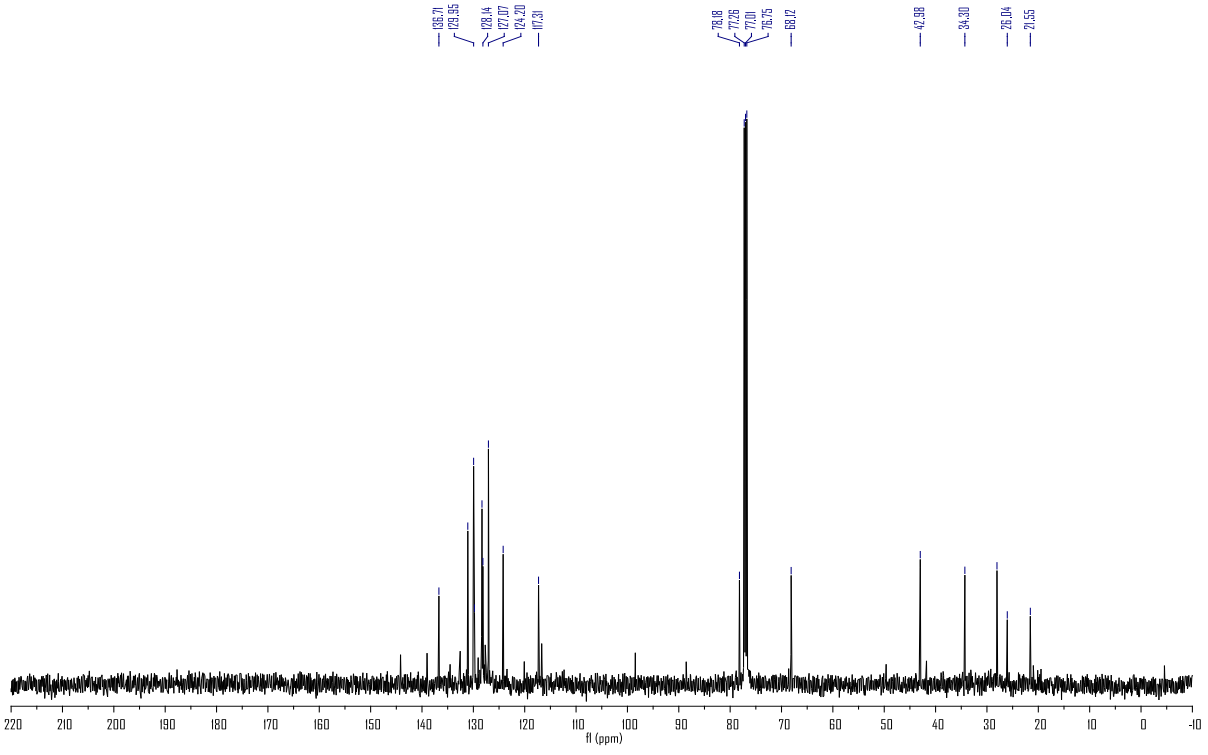

.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0
f1 (ppm)

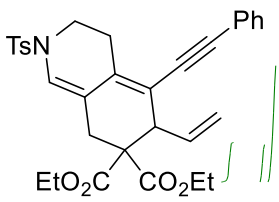

20 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


TsN
Ph
O
8-53m
2.15
2.25
5.40
1.03
1.00
1.07
1.06
1.07
1.05
1.05
1.11
1.12
3.31
3.30
3.12
f1 (ppm)

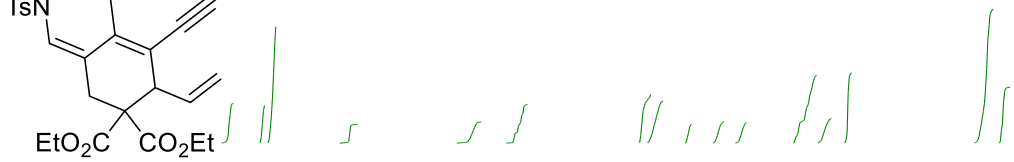

144.26
136.65
131.03
128.36
127.04
92.94
77.76
77.29
77.04
76.78
72.73
72.31
43.16
27.23
26.31
21.58
f1 (ppm)

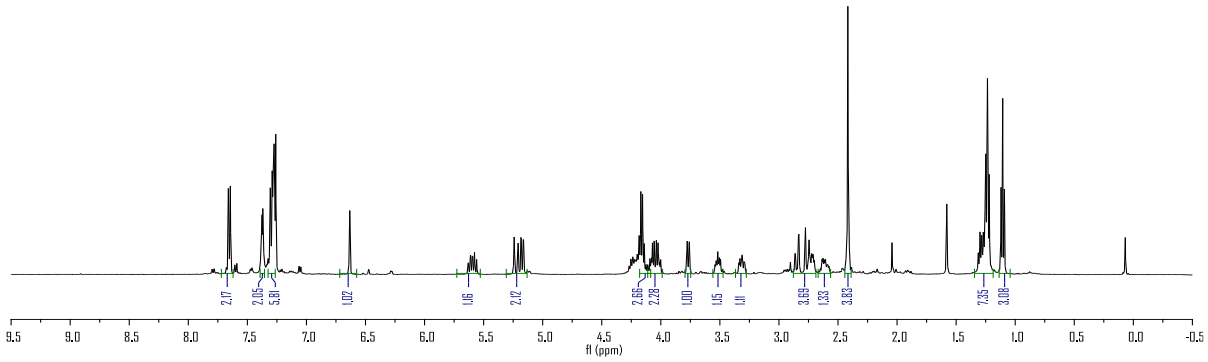

TsN
Ph
O
8-53n
1.98
9.07
1.00
0.93
2.01
1.04
2.08
1.12
0.72
1.01
0.98
1.55
6.36
f1 (ppm)

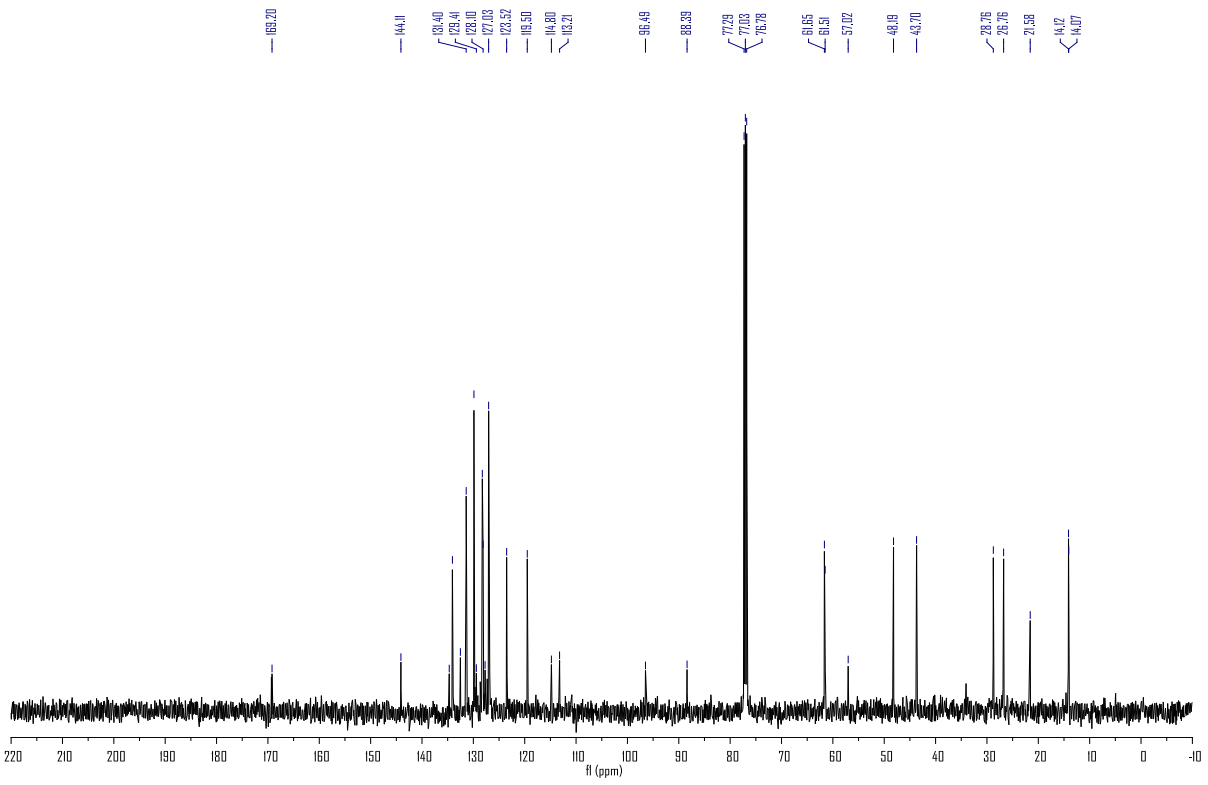

136.71
129.55
128.44
127.07
124.20
117.31
78.18
77.26
77.01
76.75
68.12
42.98
34.30
26.04
21.55
f1 (ppm)

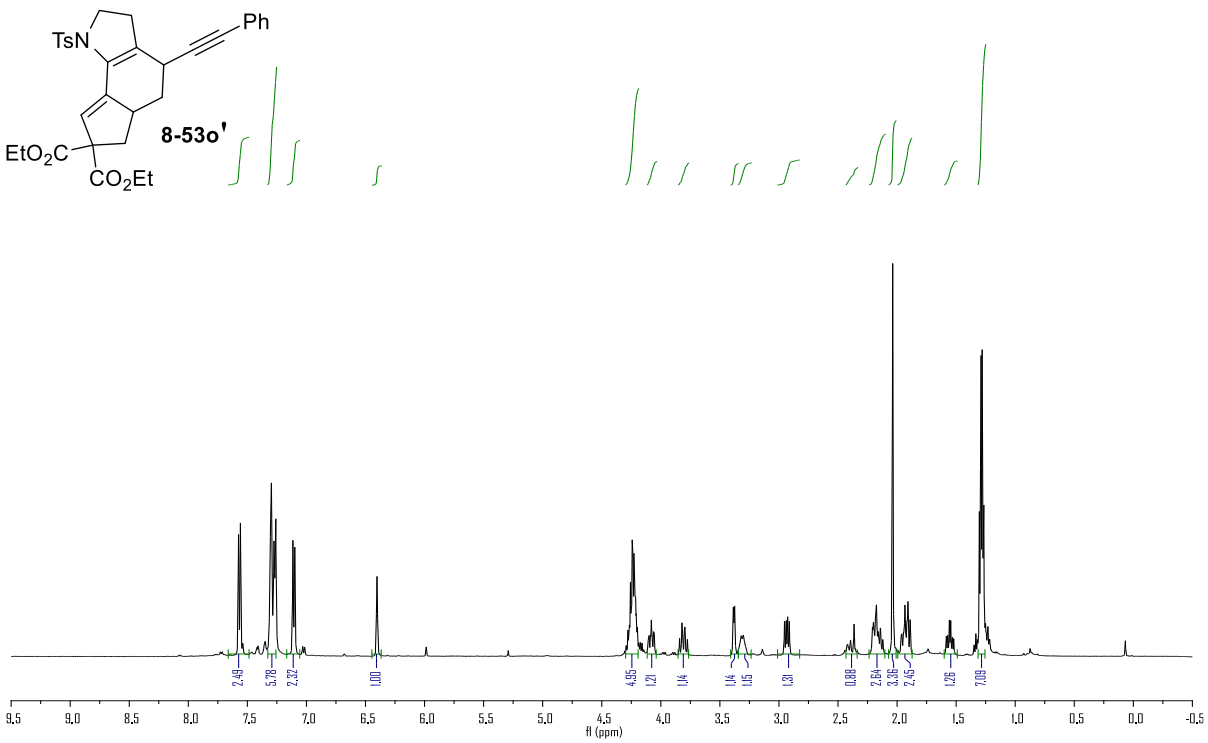

TsN
Ph
EtO2C
CO2Et

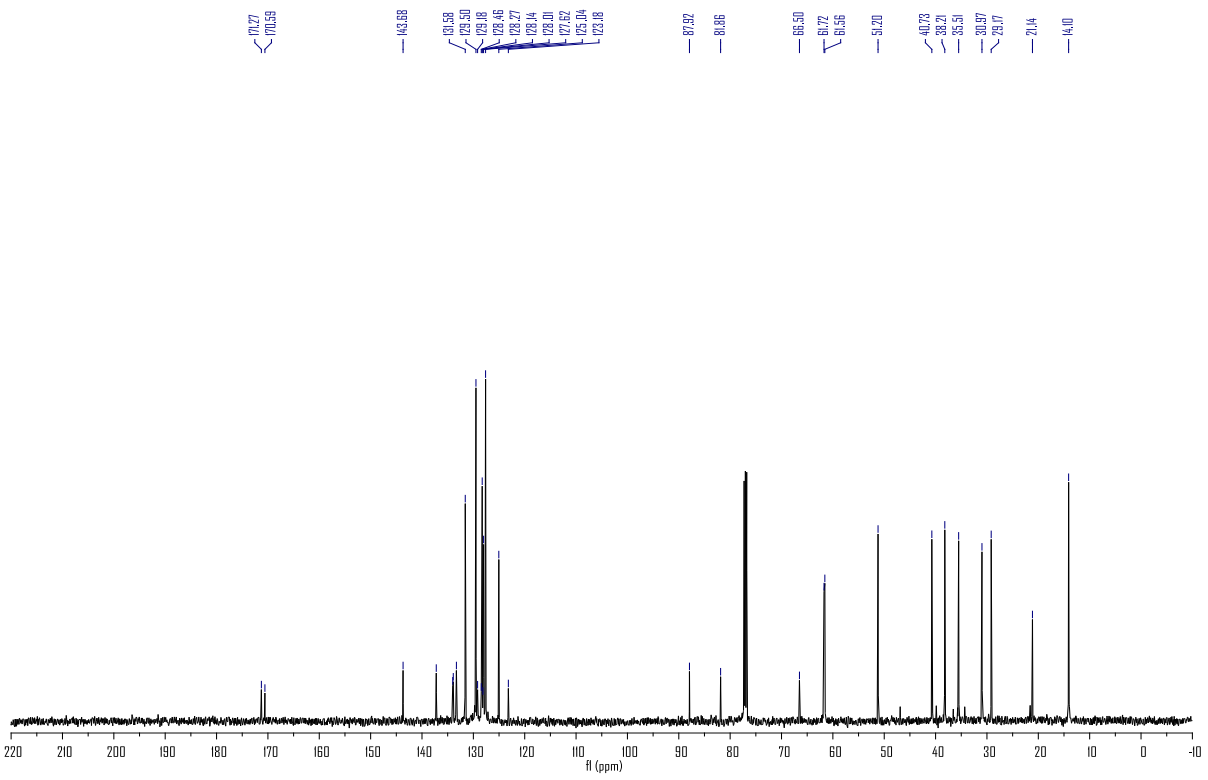
8-53o

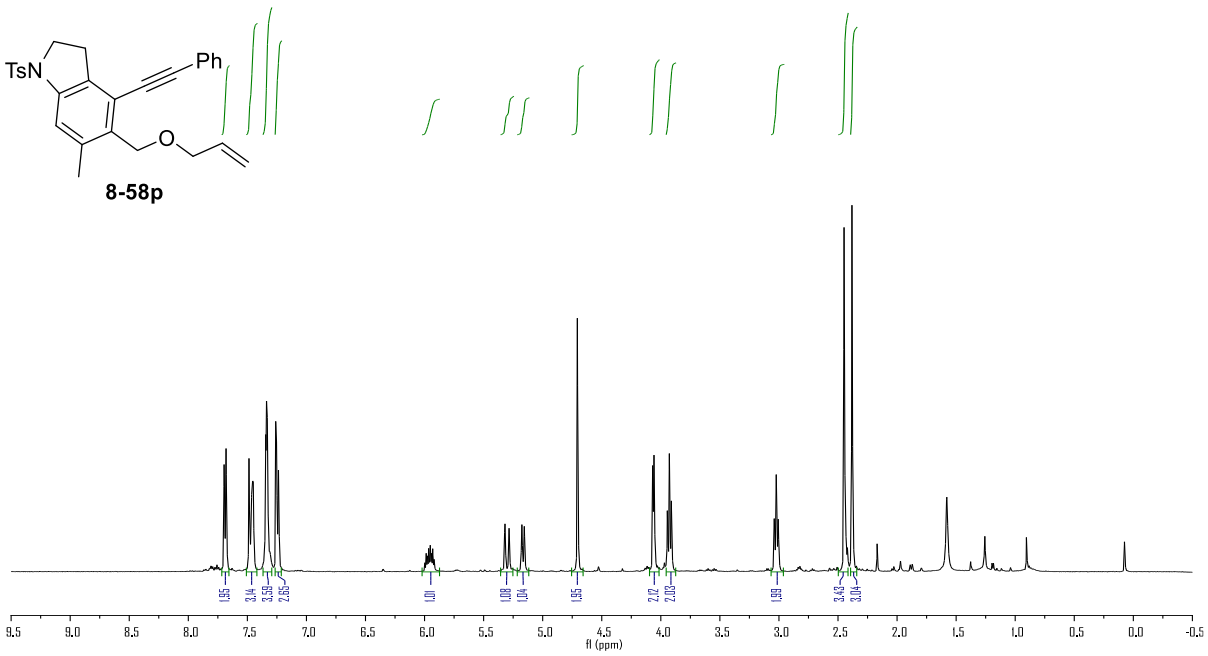


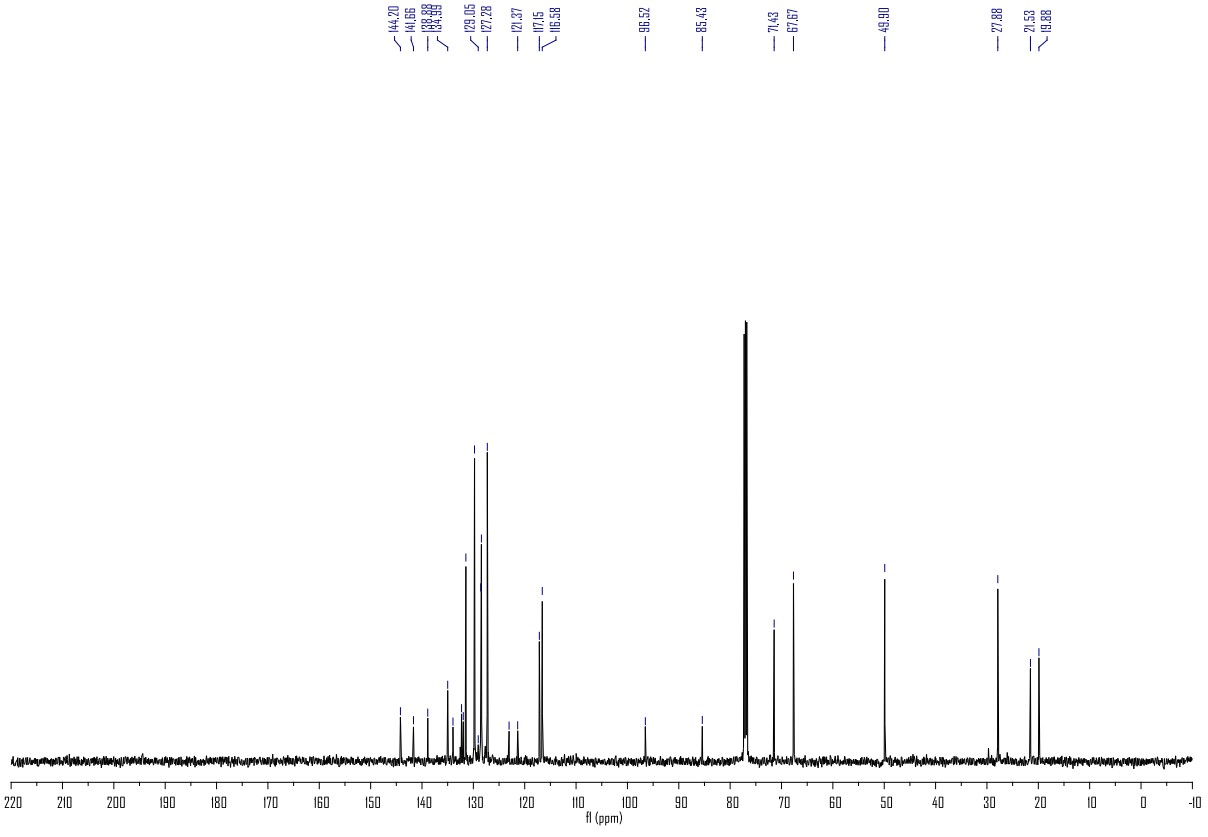

2.17
2.05
5.81
1.02
1.16
2.12
2.66
2.28
1.00
1.15
1.11
3.69
1.33
3.83
7.35
3.08
f1 (ppm)

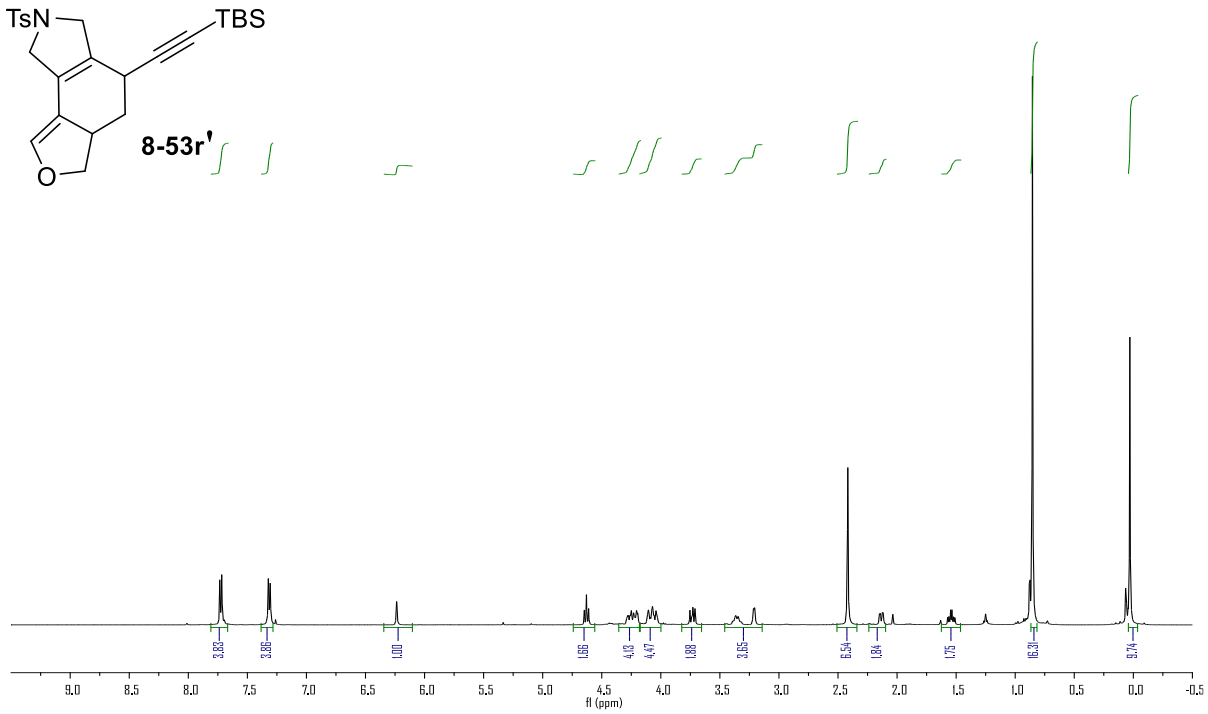

163.20
144.11
131.40
129.44
128.10
127.03
122.52
119.50
114.80
113.21
96.49
88.39
77.29
77.03
76.78
61.65
61.54
57.02
48.18
43.70
28.76
28.76
21.58
14.12
14.07
f1 (ppm)

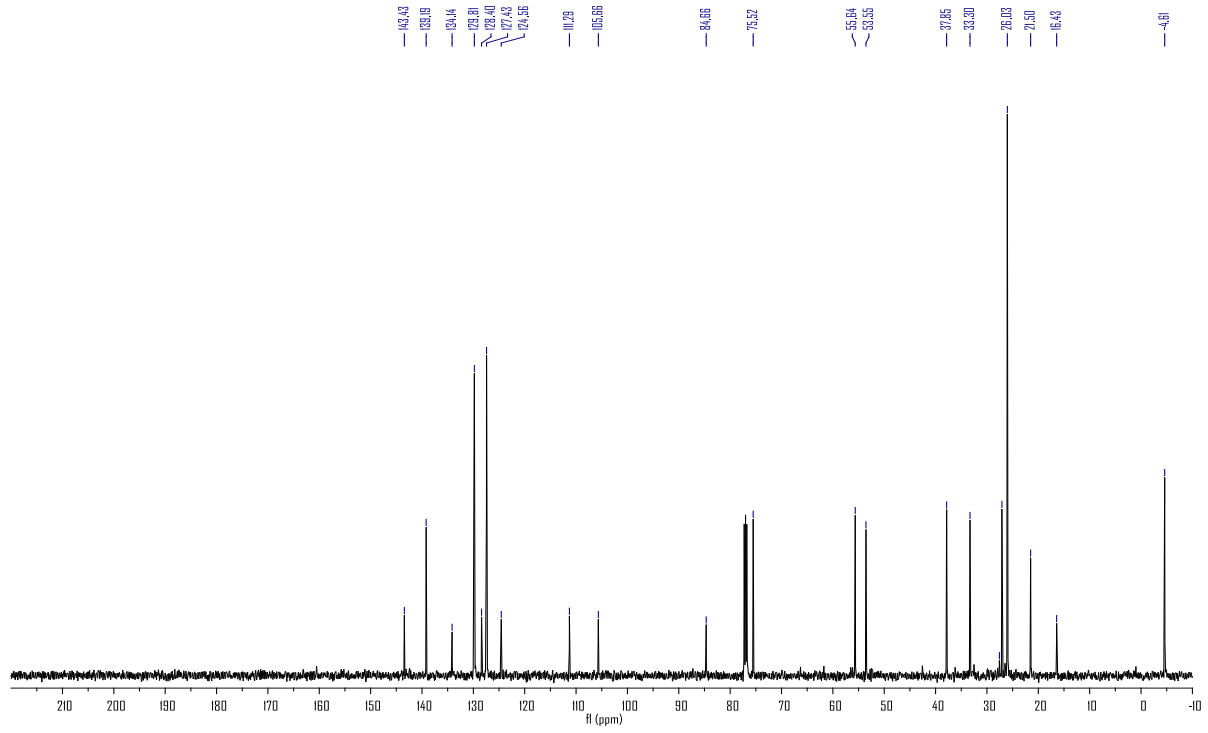

TsN
Ph
8-53o'
EtO2C
CO2Et
2.49
5.78
2.32
1.00
4.95
1.21
1.14
1.14
1.15
1.31
0.88
2.64
3.38
2.45
1.26
7.09
f1 (ppm)

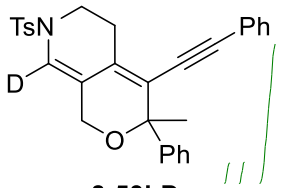

171.27
170.59
143.68
131.58
129.50
129.18
128.46
128.27
128.14
128.01
127.62
125.04
123.18
87.92
81.86
65.50
61.72
61.56
51.20
40.73
39.21
35.51
30.97
29.77
21.44
14.10
f1 (ppm)


TsN
Ph
O
8-58p
1.95
3.44
3.59
2.65
1.01
1.08
1.04
1.95
2.72
2.03
1.93
3.43
3.04
f1 (ppm)

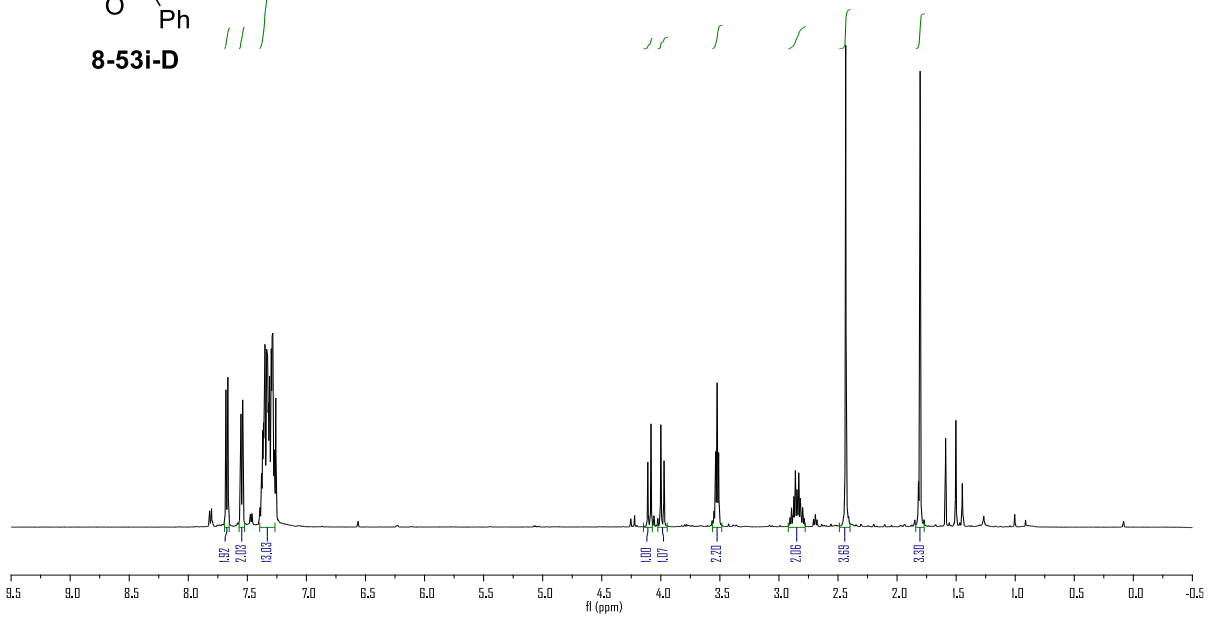

144.20
141.66
133.88
133.39
129.05
127.29
121.37
117.15
116.58
96.52
85.43
71.43
67.67
49.90
27.88
21.53
19.88
f1 (ppm)

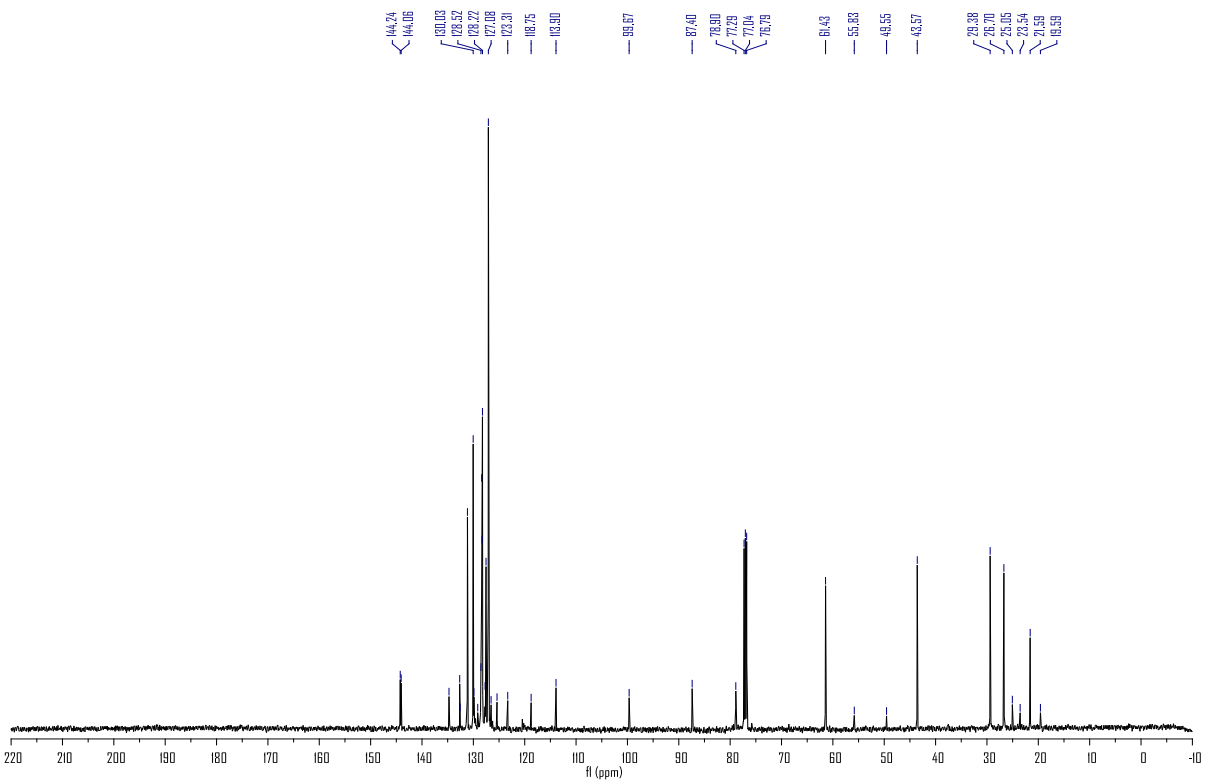

TsN
TBS
O
8-53r'
3.83
3.85
1.00
1.66
4.18
4.47
1.88
3.85
6.54
1.84
1.75
16.31
5.74
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)

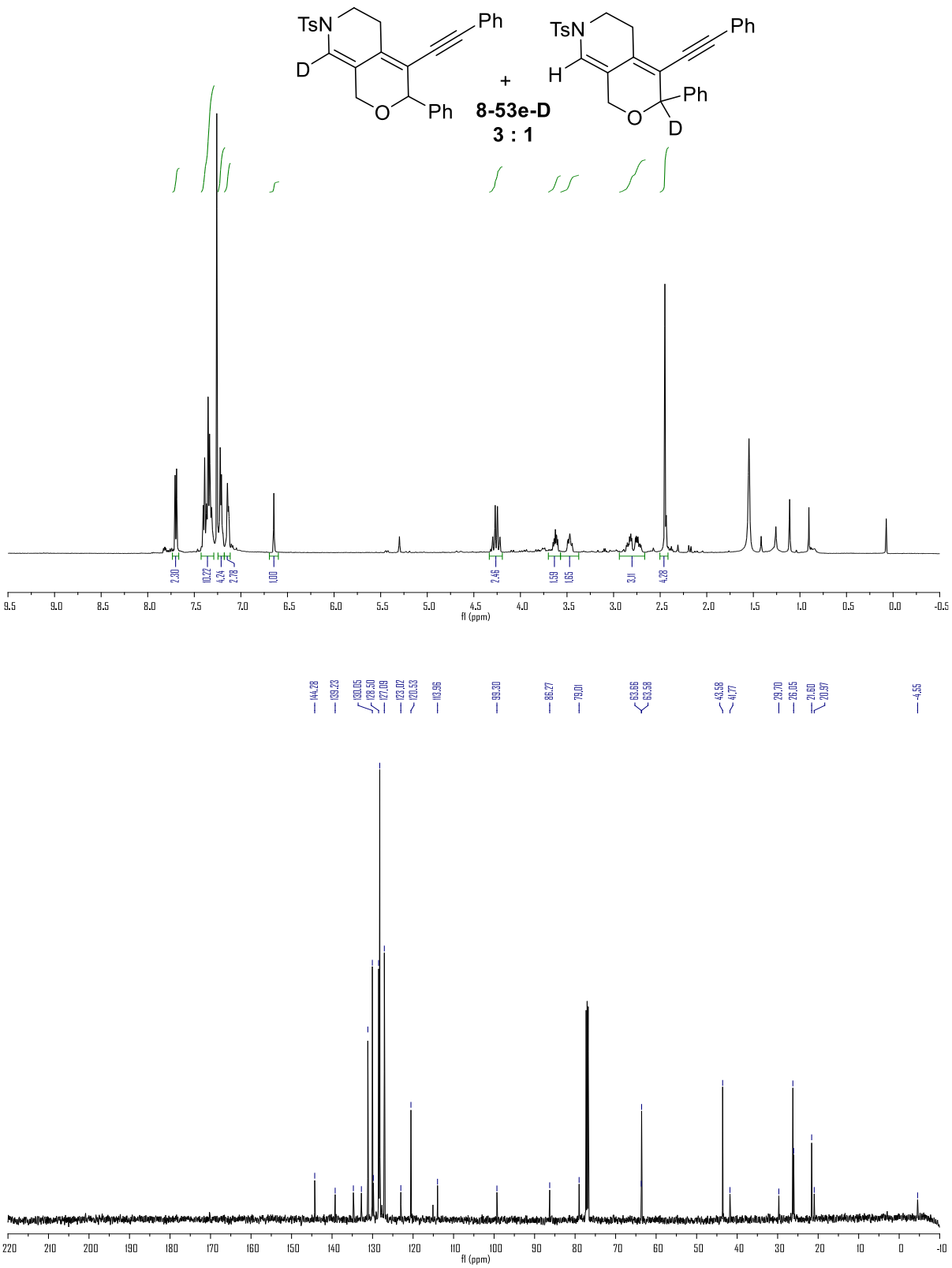

143.43
139.19
134.44
129.81
128.40
127.43
126.56
111.29
105.66
84.86
75.52
55.84
53.55
37.85
33.30
26.03
21.50
16.48
-4.61
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

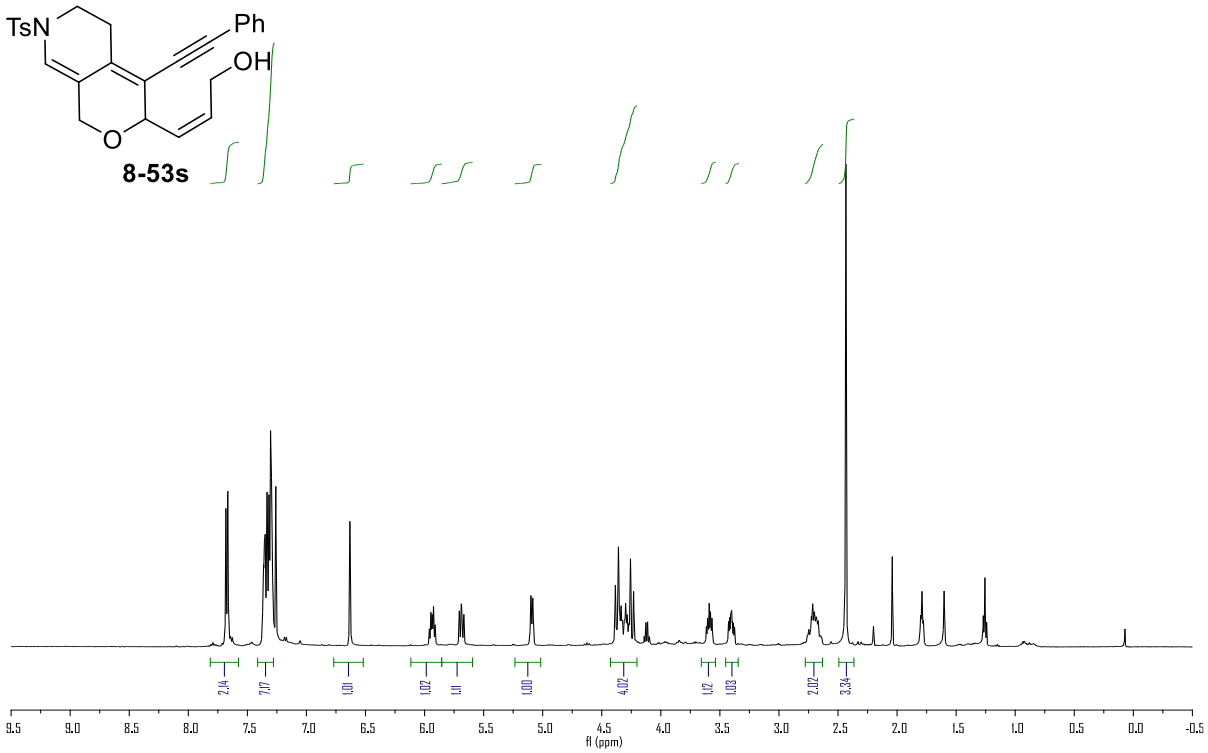

TsN
Ph
D
O
Ph

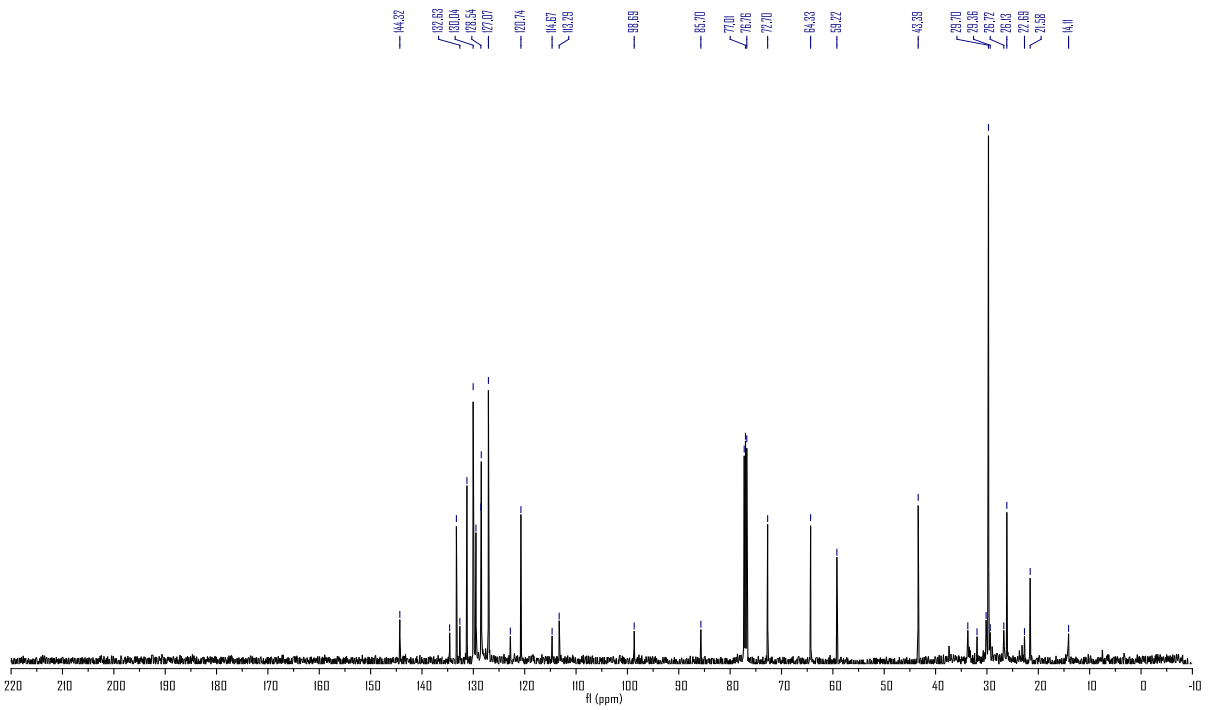
8-53i-D


1.92
2.03
13.03
1.00
1.07
2.20
2.06
3.69
3.30
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


144.24
144.06
130.03
128.52
128.22
127.08
123.31
118.75
113.90
89.67
87.40
78.90
77.29
77.04
76.79
61.43
55.83
49.55
43.57
29.38
26.70
25.05
23.54
21.58
15.39
220
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)


TsN
D
Ph
O
Ph
+
8-53e-D
3 : 1
TsN
H
Ph
Ph
O
D
2.301
10.272
4.74
2.78
1.000
2.461
1.589
1.165
3.111
4.278
f1 (ppm)
144.278
139.233
130.055
128.501
127.618
123.072
120.533
110.916
89.300
86.277
79.011
63.866
63.538
43.581
41.777
29.710
26.055
21.610
20.917
4.555
f1 (ppm)


TsN
Ph
OH
O
8-53s
2.14
7.17
1.01
1.02
1.11
1.00
4.02
1.12
1.03
2.02
3.34
f1 (ppm)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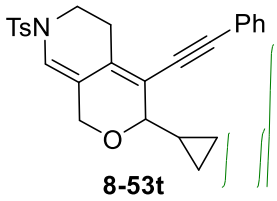
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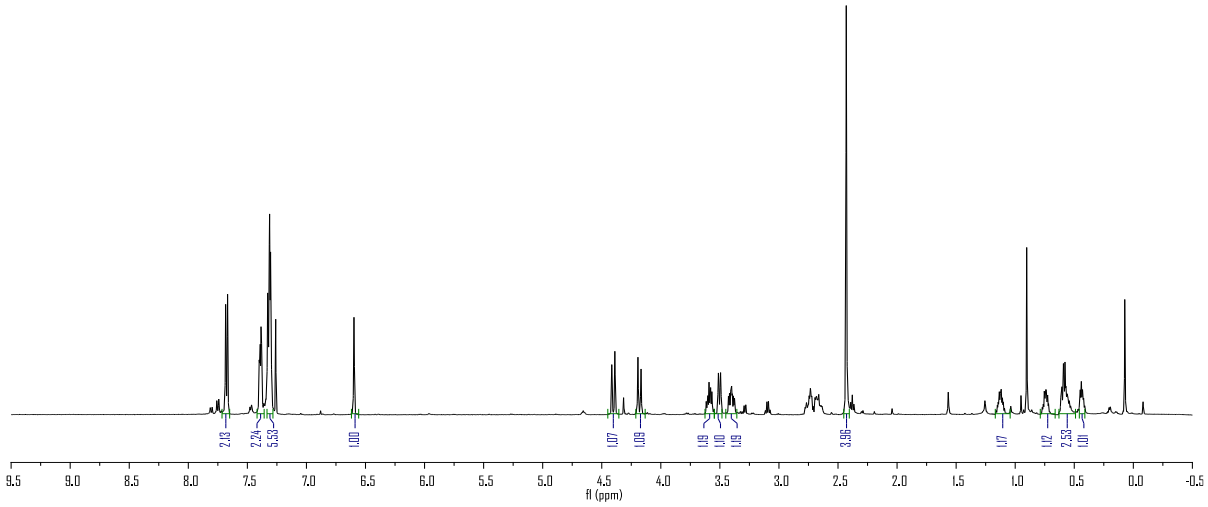
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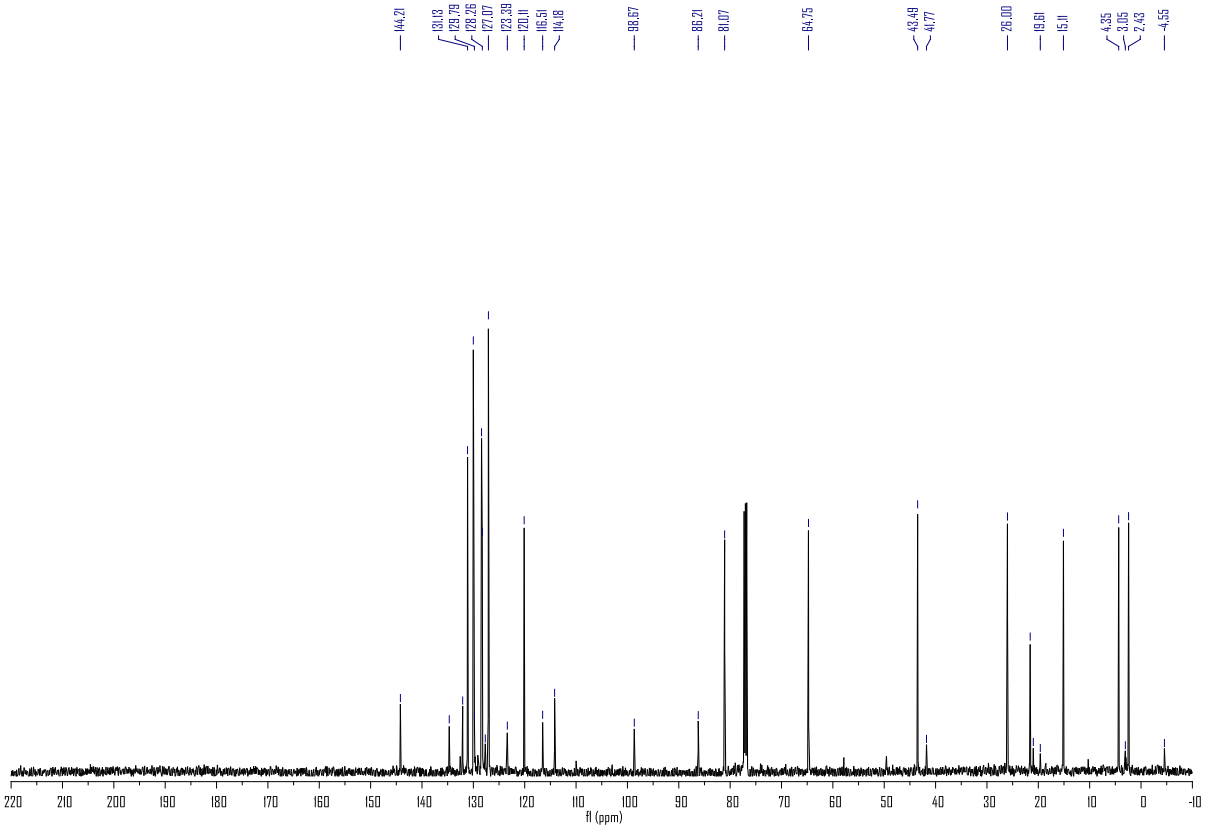
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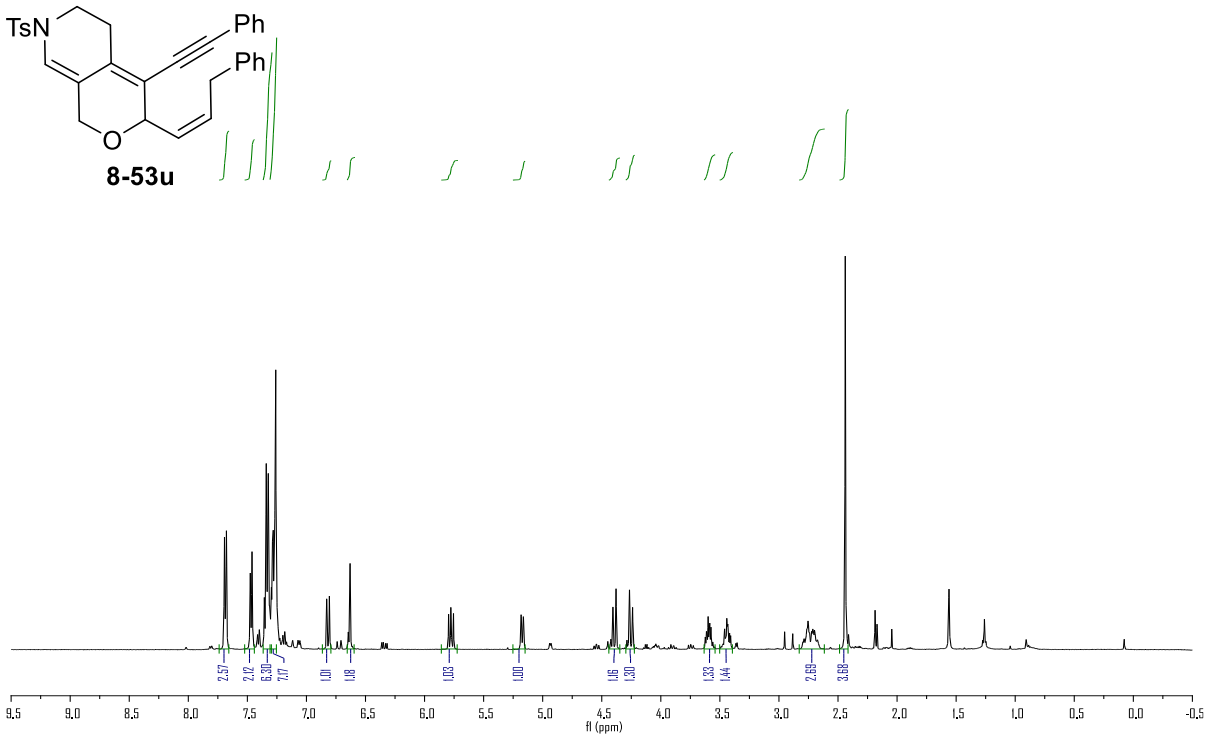
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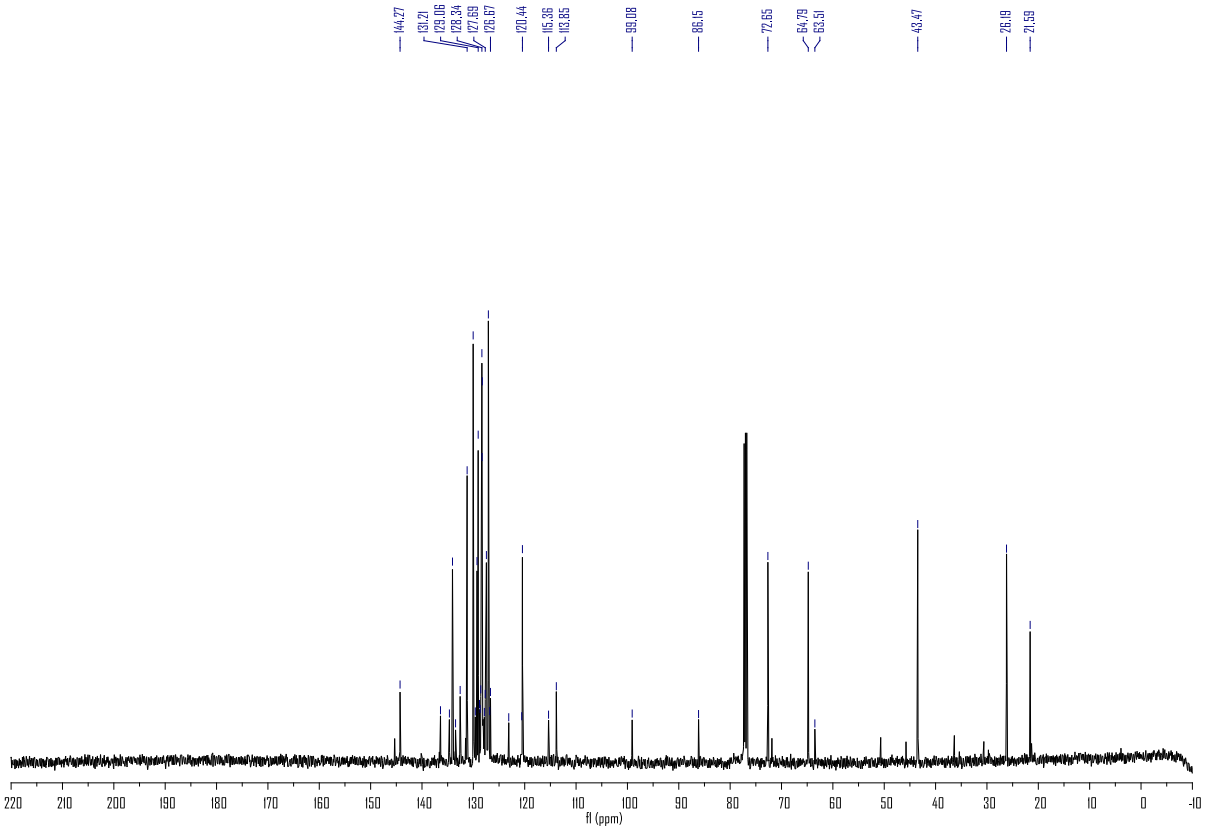
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Publication: Organic Letters

Publisher: American Chemical Society

Date: Aug 1, 2013

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Author: Venkata R. Sabbasani, Daesung Lee

Publication: Organic Letters

Publisher: American Chemical Society

Date: Oct 1, 2015

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