

STRATEGIES FOR ACHIEVING SELECTIVITY IN HOMOGENEOUS CATALYSIS

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ABSTRACT

Christina A. Roselli: Strategies for Achieving Selectivity in Homogeneous Catalysis
(Under the direction of Michel R. Gagné)

A hallmark of gold(I)-catalyzed enyne cycloisomerization reactions is their unique ability to generate complex scaffolds from simple unsaturated starting materials. Initial work focused on the development of a gold-catalyzed cascading cycloisomerization of alkylidene cyclopropane bearing 1,5-enynes that terminated in a cyclo-addition of aldehydes. In one pot, we transformed a simple enyne starting material into a complex terpene-like polycyclic scaffold. This diastereoselective reaction provides convergent access to novel molecular scaffolds and tolerates a diverse scope of aldehydes. Mechanistic studies revealed the catalyst rests as an off-cycle digold vinyl intermediate. Further investigations focused on expanding the scope and diversity of the products. We found that an enantioselective variant was not feasible and that electrophilic halogenation could not outcompete protodemettallation. Through the development of an alternate reactivity pathway, we incorporated ketone and nitrile nucleophiles into our scaffold to develop more diverse heterocycles.

A second area of research focused on a computational study on the transfer of silylum from triphenylphosphine to other heteroatom containing Lewis bases. In various examples of tris(pentafluorophenyl)borane (BCF) catalyzed hydrosilylative reductions, phosphine additives attenuate the reactivity of the system, acting as silylum ion carriers. With these studies in mind, we computed the relative “silaphilicity” of various Lewis bases to understand how Lewis base

preferences might correlate with the observed chemoselectivity in complex molecules. The relative free energies of various Lewis base relevant to catalysis were compared to develop a thermodynamic scale of stabilities. As expected from experimental studies, both the choice of phosphine and silane impact the thermodynamics of this transfer.

The final chapter focuses on the development of a living, chain-growth polymerization of a donor-acceptor (D-A)monomer. While donor-acceptor conjugated polymers have many applications in organic electric materials, they are typically synthesized through step-growth methods, leading to little control over polymer composition and molecular weight. We described the synthesis of a novel monomer and explored a variety of metal complexes for the living polymerization. While catalyst loading studies and chain extension experiments are not fully consistent with a living chain-growth mechanism, we identified a new D-A polymer and worked towards expanding the current methodologies to develop alternating D-A polymers.

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TABLE OF CONTENTS

LIST OF FIGURES	xii
LIST OF TABLES.....	xvii
LIST OF SCHEMES.....	xix
LIST OF EQUATIONS	xxii
LIST OF SYMBOLS AND ABBREVIATIONS	xxii
Chapter 1: Gold(I)-Catalyzed Addition of Aldehydes to Cyclopropylidene Bearing 6-Aryl-1,5-Enynes.....	1
1.1 Introduction	1
1.1.1 Transition metal catalyzed enyne cycloisomerizations.....	1
1.1.2 Alkylidene cyclopropane incorporation into substrates	1
1.1.3 Au-catalyzed couplings of enynes with carbonyl compounds.....	5
1.2 Initial reactivity of enyne with aldehydes	7
1.3 Substrate scope	10
1.4 Stereochemical analysis	14
1.5 Mechanistic studies	15
1.6 Conclusions	19
1.7 Acknowledgements	20
1.8 Experimental section	20
1.8.1 General methods	20

1.8.2 Preparation of starting materials	21
1.8.3 Synthesis of enyne 1.1c.....	25
1.8.4 Gold-catalyzed addition of aldehydes to 1,5-enynes	26
1.8.5 Isolation of di-gold vinyl 1.7.....	40
1.8.6 Isolation of cycloisomer 1.5.....	42
1.8.7 Experimental procedure for acid/base experiments	42
1.8.8 Experimental procedure for competition experiments.....	43
1.8.9 NMR spectra of new compounds.....	44
1.8.10 Gradient 1D NOESY stereochemical assignment	71
1.8.11 Single Crystal X-ray diffraction analysis.....	73
REFERENCES	75
Chapter 2: Expanding the Scope of the Intermolecular Addition of Aldehydes to Enynes.....	79
2.1 Introduction: addition of aldehydes to cyclopropylidene-bearing 1,5-enynes.....	79
2.2 Enantioselective catalysis.....	80
2.2.1 Background	80
2.2.2 Results and discussion	82
2.3 Intercepting protodemettalation with halonium sources	85
2.3.1 Background	85
2.3.2 Results and discussion	87

2.4	Moving beyond aldehydes: trapping with other unsaturated nucleophiles.....	91
	2.4.1 Introduction	91
	2.4.2 Gold-catalyzed addition of unsaturated nucleophiles to 1,5-enynes	92
	2.4.3 In-situ generation of tertiary carbocation for nucleophile incorporation	93
2.5	Conclusion.....	99
2.6	Experimental section	99
	2.6.1 General Methods	99
	2.6.2 Preparation of starting materials and products	100
	2.6.3 NMR spectra of new compounds	106
	REFERENCES	114
Chapter 3:	Computed thermodynamic stabilities of silylum Lewis base adducts	117
3.1	Introduction	117
	3.1.1 Silylum ions in catalysis	117
	3.1.2 Combination of BCF and silane for chemoselective reductions	119
	3.1.3 Research objective	120
3.2	Results and discussion.....	120
	3.2.1 Variation of silane	120
	3.2.2 Variation of phosphine.....	122
	3.2.3 Variation of heteroatom Lewis base silylum acceptors	124
	3.2.4 Rationalization of reactivity in complex natural products	130

3.3	Conclusions	132
3.4	Acknowledgements	133
3.5	Experimental Section	133
	3.5.1 Computational Methods.....	133
	3.5.2 Basis set comparison	134
	3.5.3 Table of summarized energies	135
3.6	Associated content.....	143
	REFERENCES	144
Chapter 4:	Towards a controlled Kumada catalyst-transfer polycondensation of a fluorine-incorporated donor-acceptor conjugated monomer	147
4.1	Introduction	147
	4.1.1 π -Conjugated polymers	147
	4.1.2 Catalyst transfer polycondensation	150
	4.1.3 Donor-acceptor conjugated polymers	152
4.2	Results and discussion.....	156
	4.2.1 Monomer synthesis and Grignard metathesis	156
	4.2.2 Initial reactivity	158
	4.2.3 Ligand screen	162
	4.2.4 The switch to palladium	163
4.3	Catalyst loading study and block co-polymer synthesis	166
4.4	Summary	169
4.5	Acknowledgements	169

4.6	Experimental Section	170
4.6.1	General methods	170
4.6.2	Preparation of starting materials	171
4.6.3	Polymerization reactions.....	175
4.6.4	NMR spectra of new compounds.....	177
4.6.5	Representative GPC traces.....	184
	REFERENCES	186
	APPENDIX A. OPTIMIZED COORDINATES AND GIBBS FREE ENERGIES.....	188

LIST OF FIGURES

Figure 1.1. Resonance forms of auro-allyl cation A	4
Figure 1.2. Diversity-oriented synthesis.	7
Figure 1.3. Mayr's π -nucleophilicity parameters.....	14
Figure 1.4. ORTEP representation of the solid state molecular structure of 1.4k ; ellipsoids drawn at 50% probability, only one enantiomer of the asymmetric unit, and majority of the hydrogen atoms omitted for clarity.	14
Figure 1.5. 1-D NOE spectra of 1.4j	15
Figure 1.6. Selected examples of di-gold intermediates.....	18
Figure 1.7. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of S1.2 in CDCl_3 at 25 °C.	44
Figure 1.8. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of S1.3 in CDCl_3 at 25 °C.	45
Figure 1.9. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of S1.4 in CDCl_3 at 25 °C.	46
Figure 1.10. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 1.1b in CDCl_3 at 25 °C.	47
Figure 1.11. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of S1.7 in CDCl_3 at 25 °C.	48
Figure 1.12. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 1.1c in CDCl_3 at 25 °C.....	49
Figure 1.13. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 1.4a in CDCl_3 at 25 °C.	50
Figure 1.14. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 1.4b in CDCl_3 at 25 °C.....	51
Figure 1.15. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 1.4c in CDCl_3 at 25 °C.....	52

Figure 1.16. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 1.4d in CDCl_3 at 25 °C.....	53
Figure 1.17. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 1.4e in CDCl_3 at 25 °C.....	54
Figure 1.18. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 1.4f in CDCl_3 at 25 °C.....	55
Figure 1.19. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 1.4g in CDCl_3 at 25 °C.....	56
Figure 1.20. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 1.4h in CDCl_3 at 25 °C.....	57
Figure 1.21. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 1.4i in CDCl_3 at 25 °C.....	58
Figure 1.22. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR of 1.4j in CDCl_3 at 25 °C.....	60
Figure 1.23. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 1.4k in CDCl_3 at 25 °C.....	61
Figure 1.24. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 1.4l in CDCl_3 at 25 °C.....	62
Figure 1.25. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 1.4m in CDCl_3 at 25 °C.....	63
Figure 1.26. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR of 1.4n in CDCl_3 at 25 °C.....	64
Figure 1.27. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 1.4o in CDCl_3 at 25 °C.....	65
Figure 1.28. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 1.4p in CDCl_3 at 25 °C.....	66
Figure 1.29. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 1.6a in CDCl_3 at 25 °C.....	67
Figure 1.30. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 1.6b in CDCl_3 at 25 °C.....	68
Figure 1.31. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR of 1.7 in CDCl_3 at 25 °C	70
Figure 1.32. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 1.5 in CDCl_3 at 25 °C	71

Figure 2.1. Linear coordination mode of gold(I).	80
Figure 2.2. Gold activation of alkynes.....	85
Figure 2.3. Common electrophilic halogen sources.....	86
Figure 2.4. The proposed use of other nucleophiles as cation traps.	92
Figure 2.5. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 2.11 in CDCl_3 at 25 °C.....	106
Figure 2.6. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 2.12 in CDCl_3 at 25 °C.	107
Figure 2.7. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 2.13b in CDCl_3 at 25 °C.	108
Figure 2.8. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of the major diastereomer of 2.13c in CDCl_3 at 25 °C.	109
Figure 2.9 Crude ^1H of 2.13c in CDCl_3 at 25 °C.	110
Figure 2.10. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 2.13d in CDCl_3 at 25 °C.	111
Figure 2.11 ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 2.13e in CDCl_3 at 25 °C.....	112
Figure 2.12. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 2.13f in CDCl_3 at 25 °C.	113
Figure 3.1. Isolated silylum ions.....	118
Figure 3.2. Phosphine-modified catalytic cycle for the BCF-catalyzed reduction of ethers.....	118
Figure 3.3. Thermodynamic Lewis base stabilities of various substrates. The numbers in bold indicate the Gibbs free energy (kcal/mol) for the transfer of Me_3Si^+ from $\text{Me}_3\text{Si}-\text{PPh}_3^+$ to the Lewis base. The	

heterolysis of $\text{Me}_3\text{Si}-\text{PPh}_3^+$ to PPh_3 and Lewis base free Me_3Si^+ is endergonic by 24.0 kcal/mol.....	127
Figure 3.4. Silylum Lewis base adducts of bio-mass derived sugar substrates.....	129
Figure 3.5. Free energy diagram for the demethylation of α - and β -OMe-glucose. Each horizontal line represents the energy of the most stable energy minimized conformer.....	130
Figure 3.6. Reactivity hierarchy observed experimentally with natamycin (using $\text{B}(3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3)_3$ and Me_2EtSiH).	131
Figure 4.1. Comparison of band gap in conjugated systems.....	148
Figure 4.2. Common structural features of conjugated polymers.....	149
Figure 4.3. Step-growth vs. chain-growth and living chain-growth polymerization.....	150
Figure 4.4. Proposed mechanism for Kumada CTP.....	152
Figure 4.5. Frontier molecular orbital interactions of D-A units.....	153
Figure 4.6. Our D-A conjugated monomer precursor.....	156
Figure 4.7. Synthesis of monomer precursor 3	157
Figure 4.8. Ni(diimine) complexes.....	159
Figure 4.9. Polymerization of 3 with (NHC) Ni complexes.....	163
Figure 4.10. Room temperature GPC trace.....	166
Figure 4.11. High temperature GPC trace.....	166

Figure 4.12. Catalyst loading screen.....	167
Figure 4.13. GPC trace of block copolymer	168
Figure 4.14. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR of 4 in CDCl_3	178
Figure 4.15. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR of 5 in CDCl_3	179
Figure 4.16. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR of 7 in CDCl_3	181
Figure 4.17. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR of 3 in CDCl_3	182
Figure 4.18. ^1H and $^{19}\text{F}\{^1\text{H}\}$ NMR of PTFTAZ in CDCl_3	183

LIST OF TABLES

Table 1.1. Gold(I)-catalyzed cyclo-coupling of 1.1b and aliphatic aldehydes. ^{a,b}	11
Table 1.2. Substrate scope with aromatic aldehydes. ^{a,b}	12
Table 1.3. Reaction optimization to favor the aldehyde trapped product 1.4	17
Table 1.4. Single crystal X-ray diffraction analysis of 1.4k	73
Table 2.1. Chiral gold complex screen. ^a	83
Table 2.2. Silver screen.	85
Table 2.3. Stoichiometric reactivity with halogen sources.	89
Table 2.4. Lewis acid screen with 2.11	96
Table 2.5. Reactivity of 2.12 with ketones and nitriles.	98
Table 3.1. Effect of substituents on free energy of transfer to 2-Me-THF.	122
Table 3.2. Steric and electrons perturbations of phosphine Lewis base acceptor.	123
Table 3.3. Effect of substitution on methyl ether silylum acceptors.....	125
Table 3.4. Calculations for the splitting of trimethylsilane with BCF and PPh ₃ . ^a	134
Table 3.5. Relevant energies of all optimized coordinates.	135
Table 4.1. Catalyst loading screen of 3-MgCl with (N-Mes-diimine)NiBr ₂	161

Table 4.2. Solvent screen for the polymerization of **3-MgCl** with
(N-Mes-diimine)NiBr₂.^a 162

Table 4.3. Concentration screen for the polymerization of **3** with
PEPPSI-IPr-PdCl₂. 164

LIST OF SCHEMES

Scheme 1.1. Recent gold-catalyzed transformations in the Gagné group.....	2
Scheme 1.2. Proposed mechanism for the formation of 1.2	3
Scheme 1.3. Methanol trapping experiment.....	4
Scheme 1.4. Proposed reactivity with aldehydes.	5
Scheme 1.5. Reactivity of 1,5- and 1,6-enynes with aldehydes.	6
Scheme 1.6. Initial aldehyde trapping experiments.....	8
Scheme 1.7. Reaction pathway for cycloisomerization vs. aldehyde addition.	8
Scheme 1.8. Gold-catalyzed intramolecular hydroarylation of allenes.....	9
Scheme 1.9. Synthetic route to 1.1b	9
Scheme 1.10. Reactivity of auro-allyl cation with aldehydes.	10
Scheme 1.11. Cyclo-coupling with enynes 1.1c and 1.1d	13
Scheme 1.12. Acid/base dependent competition from intermediate B	17
Scheme 1.13. Synthesis of di-gold vinyl 1.7	18
Scheme 1.14. Proposed catalytic cycle. $[Au]^+ = Ph_3PAu^+$; counterion [NTf ₂ ⁻] omitted for clarity.	19
Scheme 2.1. Intermolecular addition of aldehydes to 1,5-enynes.....	79

Scheme 2.2. Common approaches to enantioselective gold catalysis.....	81
Scheme 2.3. Enantioselective cycloisomerization of 1,5-enynes.....	82
Scheme 2.4. Synthesis and activation of chiral gold complexes.....	82
Scheme 2.5. Gold-mediated halogenation of pyranones.....	86
Scheme 2.6. Gold-catalyzed halocyclization.....	87
Scheme 2.7. Proposed reactivity pathway.....	88
Scheme 2.8. Synthesis of model gold vinyl compound 2.6	89
Scheme 2.9. Catalytic reactivity with enyne 2.3	90
Scheme 2.10. Addition of nitriles and imines to gold intermediates.....	92
Scheme 2.11. Reactivity of 2.1 with nucleophiles	93
Scheme 2.12. Proposed reactivity of key carbocation B	94
Scheme 2.13. Ritter reaction.	94
Scheme 2.14. Synthesis of water-trapped product.	95
Scheme 2.15. Nitrile trapping with 2.12	97
Scheme 3.1. BCF catalyzed reductions	119
Scheme 3.2. Chemoselective reduction of natamycin.....	120
Scheme 3.3. Silane-dependent reduction of isosorbide.....	121

Scheme 3.4. Potential reactivity pathway for N-methylacetamide.	126
Scheme 3.5. Bond lengths for the cis and trans 2,5-Me ₂ -THF silylum ions.	128
Scheme 3.6. Potential reactivity pathway for isobutyric acid.	128
Scheme 4.1. Discovery of living chain-growth mechanism for synthesis of P3HT.	151
Scheme 4.2. D-A conjugated polymers.	154
Scheme 4.3. Selective Grignard formation.	158
Scheme 4.4. Polymerization of 3	160
Scheme 4.5. Living chain growth polymerization using NHC-Pd pre-catalysts.	164
Scheme 4.6. Reversed order of block copolymerization.	169

LIST OF EQUATIONS

Equation 2.1. Proposed hydrolysis of Bi(OTf)₃. 97

LIST OF SYMBOLS AND ABBREVIATIONS

ACP	alkylidene cyclopropane
Å	angstrom
Ac	acetyl
aq	aqueous
Ar	aryl
ArF	fluoro-aryl
α	alpha (opposite side of pyranose ring)
β	beta (same side of pyranose ring)
B	base
BCF	tris(pentafluorophenyl)borane
calcd	calculated
CTP	catalyst transfer polycondensation
D-A	donor-acceptor
DABCO	1,4-diazabicyclo[2.2.2]octane
dba	dibenzylideneacetone
DCC	N,N'-dicyclohexylcarbodiimide
DCM	dichloromethane
1D	1-dimensional
°C	degrees Celcius
DFT	density functional theory
DIAD	diisopropyl azodicarboxylate
DIPA	diisopropylamine

DMAP	4-(dimethylamino)pyridine
DMS	dimethylsulfide
DOS	diversity-oriented synthesis
dppp	1,3-bis(diphenylphosphino)propane
dppe	1,2-bis(diphenylphosphino)ethane
DTBP	2,6-ditertbutylpyridine
Đ	Dispersity
δ	delta– chemical shift (NMR)
EDG	electron donating group
E _g	band gap
equiv.	equivalents
ESI	electrospray ionization
ΔG	free energy
g	gram
GC-MS	gas chromatography – mass spectrometry
GPC	gel permeation chromatography
h	hour
HOMO	highest occupied molecular orbital
HRMS	high resolution mass spectrometry
Hz	hertz (NMR coupling constant)
<i>i</i> -Pr	iso-propyl
K	Kelvin
kcal	kilocalorie

L	liter
LB	Lewis base
LC-TOF	liquid chromatography time-of-flight
LDA	lithium diisopropylamide
LTQ-FT	linear ion-trap quadrupole Fourier transform
LUMO	lowest unoccupied molecular orbital
<i>m</i> -	meta
M	molar
Me	methyl
mg	milligram
MHz	megahertz
min	minute
mL	milliliter
mmol	millimol
M _n	number average molecular weight
mol	mole
mol%	mole percent (catalyst loading)
MTBE	methyl tertbutyl ether
NaHMDS	sodium bis(trimethylsilyl)amide
NHC	N-heterocyclic carbene
NIS	N-iodosuccinimide
NMR	nuclear magnetic resonance
NOE	nuclear Overhauser effect

NR	no reaction
NTf ₂	bis(trifluoromethylsulfonyl)imide
Nu	nucleophile
<i>o</i> -	ortho
OTf	trifluoromethylsulfonyl
<i>p</i> -	para
P3HT	poly-3-hexylthiophene
PEPSSI	pyridine-enhanced precatalyst preparation stabilization and initiation
Ph	phenyl
ppm	parts per million
PTFTAZ	poly-thiophene-fluorobenzotriazole
π	pi – electrons involved in multiple bonds
π^*	anti-bonding π orbital
R	any unspecified carbon-containing group
RI	refractive index
RT	room temperature
σ	sigma – electrons involved in sigma bonds
σ_p	Hammet sigma constant (para)
SM	starting material
<i>t</i> -Bu	tert-butyl
TEA	triethylamine
THF	tetrahydrofuran
THP	tetrahydropyran

TLC thin layer chromatography

μm micrometer

UV ultraviolet

X halogen

xs excess

Chapter 1: Gold(I)-Catalyzed Addition of Aldehydes to Cyclopropylidene Bearing 6-Aryl-1,5-Enynes

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1.1 Introduction

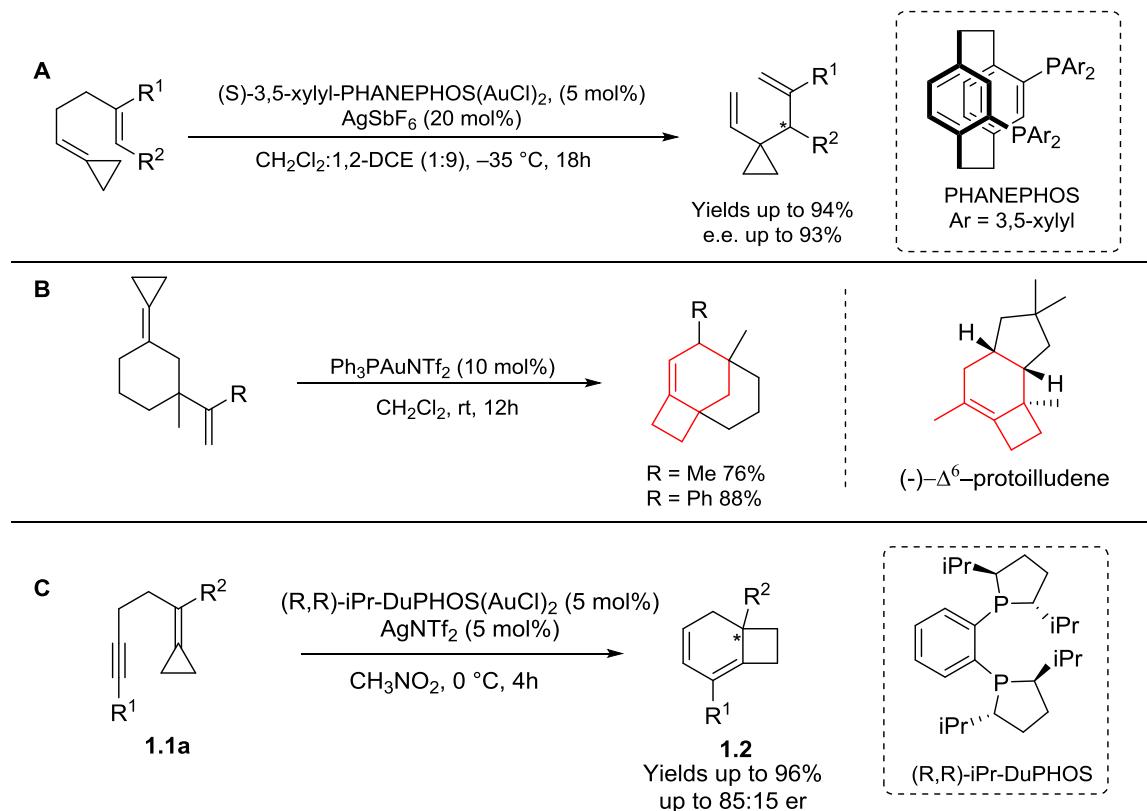
1.1.1 Transition metal catalyzed enyne cycloisomerizations

Transition metal catalyzed enyne cycloisomerizations proceeding via novel reaction pathways have enabled the construction of complex molecular scaffolds to be realized.^{2–8} The effectiveness of electrophilic gold(I) complexes for activating unsaturated carbon-carbon bonds⁹ is key to initiating and guiding the reactivity of these fragments. Coupling enyne cycloisomerization processes to the addition of heteronucleophiles, including alcohols^{10–12} and aldehydes,^{13–17} in enyne cycloisomerization reactions has created new transformations that multiply the molecular complexity of the products.

1.1.2 Alkylidene cyclopropane incorporation into substrates

Alkylidene cyclopropanes (ACPs) are versatile and reactive building blocks in organic synthesis, and several groups have been instrumental in developing their unique reactivity profiles.^{18–23} A key property is the inherent ring strain in the ACP moiety (ca. 40 kcal/mol),²² relief of which can provide a thermodynamic driving force for otherwise unfavorable reactions. Recent work in the Gagné group has explicitly sought ring strain release protocols through the strategic incorporation of ACPs into substrates.^{24–26} Our first use of this strategy was in the development of the first enantioselective Cope rearrangement of achiral 1,5-dienes (Scheme 1.1A).²⁴ Traditionally, the thermodynamic driving force for the Cope rearrangement is the

formation of the more substituted olefins in the products, limiting the synthesis of certain diene motifs through this reaction.²⁷ The reversibility of the rearrangement also presents a challenge in the development of enantioselective processes.²⁸ Our group overcame both of these challenges by installing a terminal ACP in the diene in combination with the use of a chiral bis-gold catalyst. Under these conditions, the diene products could be obtained in high yields with high enantioselectivities. Density functional theory (DFT) calculations suggest that the reaction is thermodynamically driven by the release of ring strain from the ACP and that the gold catalyst is significant in lowering the kinetic barrier of the transformation by roughly 20 kcal/mol.

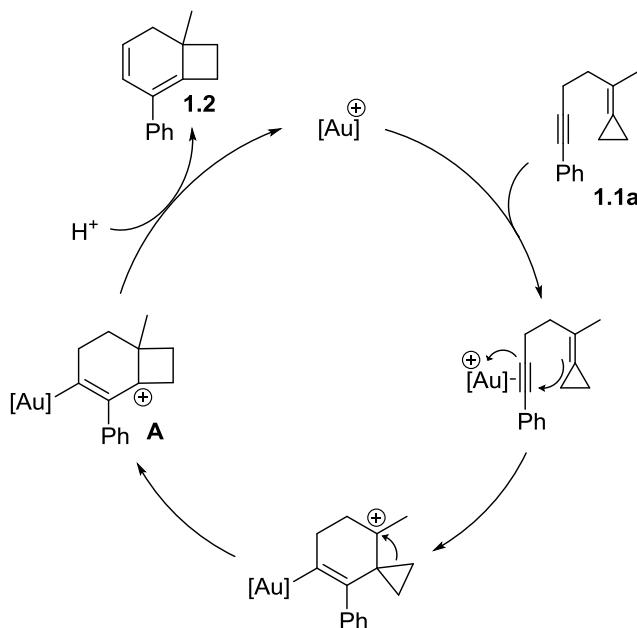


Scheme 1.1. Recent gold-catalyzed transformations in the Gagné group.

The group next looked to expand this Cope rearrangement to cyclic dienes that contained ACPs with the goal of developing a cyclooctene ring (Scheme 1.1B).²⁵ Surprisingly, upon treating these cyclic dienes with a gold catalyst, the expected Cope product was not formed—

instead, a fused tricyclic product was obtained. While the substrate scope was very limited, the reaction provided products that contained a bicyclo[4.2.0]oct-1-ene core, a structural motif common in a number of natural products.^{29,30}

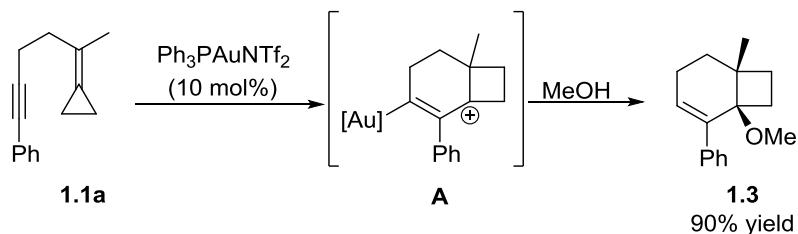
Next, the group looked to expand upon the synthesis of compounds that contained this [4.2.0]-skeleton by designing a 1,5-enyne that contained an ACP (Scheme 1.1C).³¹ When enyne **1.1a** was treated with the Gagosz catalyst ($\text{Ph}_3\text{PAuNTf}_2$),³² it underwent cycloisomerization to form the expected bicyclo[4.2.0]octadiene product **1.2**. The reaction was very versatile, tolerating a variety of different substituents on both the alkyne and the alkylidene cyclopropane. Expanding upon the method, the use of a chiral bis-gold catalyst enabled the development of an asymmetric reaction with chiral products obtained with good to moderate enantioselectivities.



Scheme 1.2. Proposed mechanism for the formation of **1.2**.

The proposed mechanism for this transformation is shown in Scheme 1.2. Gold coordination to the alkyne triggers a 6-*endo-dig* cyclization to afford a transient cyclopropyl methyl carbenium ion.^{33–35} This intermediate then ring expands to form the more stable auro-

allyl cation. The reaction turns over with a net 1,2-hydrogen shift to generate the bicyclic product **1.2** and regenerate the gold catalyst. To probe this mechanism, methanol was added to the catalytic reaction as an external nucleophile as a means to trap the auro-allyl cation. Consistent with this proposal, the [4.2.0] bicyclo methoxy compound **1.3** was obtained as a single diastereomer (Scheme 1.3). A control experiment was run in which **1.2** was treated with methanol and gold catalyst. Compound **1.3** was not obtained, suggesting the feasibility of the generation and subsequent trapping of auro-allyl cation **A**.



Scheme 1.3. Methanol trapping experiment.

This cycloisomerization project was the main inspiration for the development of our gold-catalyzed addition of aldehydes to 1,5-enyne **1.1a**. The key auro-allyl carbocation **A**, shown in Figure 1.1, can also be described as a cationic vinyl carbene, which rationalizes the electrophilic centers in the structure.

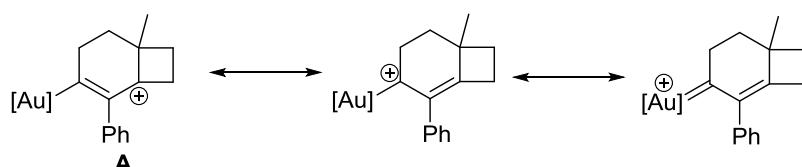
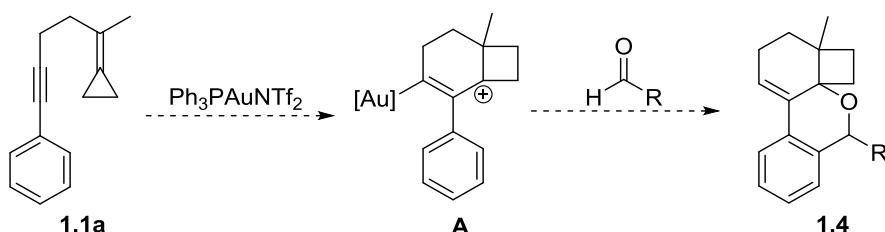


Figure 1.1. Resonance forms of auro-allyl cation **A**.

We hypothesized that the auro-allyl cation **A** might be sufficiently electrophilic to also be trapped by an aldehyde to generate an oxocarbenium ion poised to annulate a THP ring (Scheme 1.4). These results coupled with the precedent established by Helmchen (*vide infra*), suggested

that **A** might also be trapped by aldehydes, to yield oxo-carbenium ions that are poised to annulate to novel terpene-like ring structures.



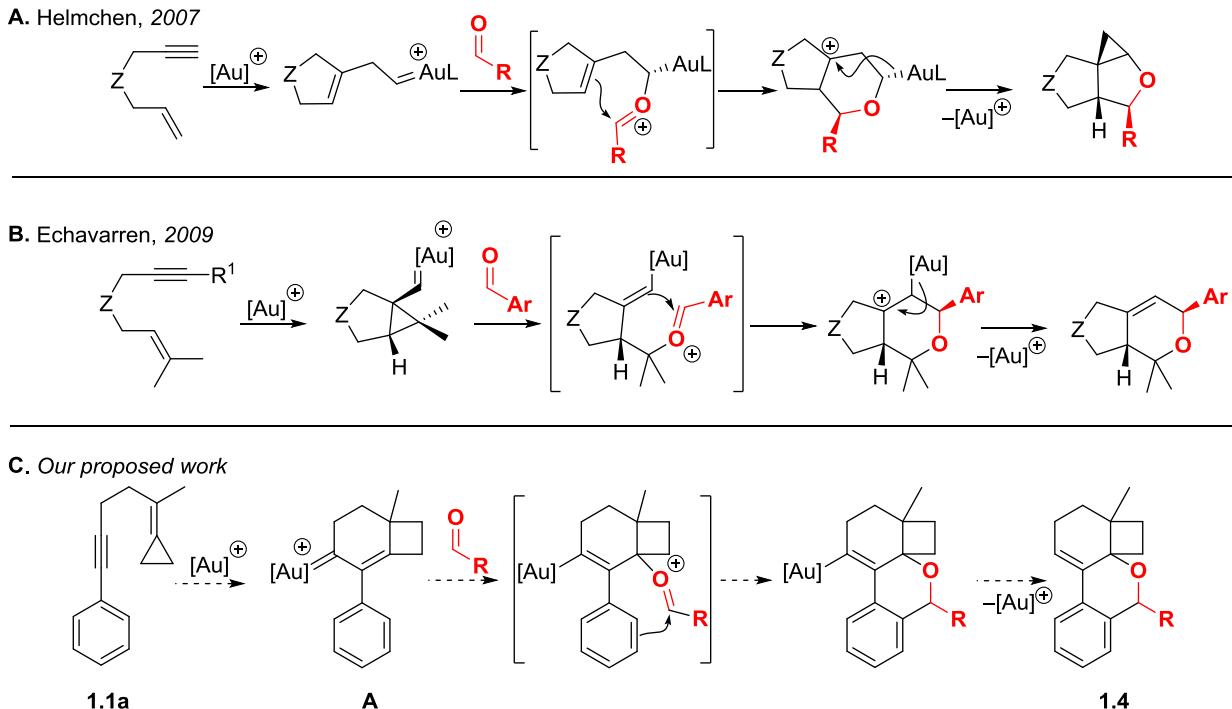
Scheme 1.4. Proposed reactivity with aldehydes.

1.1.3 Au-catalyzed couplings of enynes with carbonyl compounds

The most typical coupling reactivity of $1,n$ -enyne ($n = 6,7$) with carbonyl compounds are formal $[2 + 2 + 2]$ cycloadditions to yield O-heterocycles.^{15,16} Helmchen^{13,14} and later Echavarren¹⁵ in particular have studied the gold(I) catalyzed reaction of aldehydes with 1,6-enynes (Scheme 1.5). The reaction pathway is governed by the substituents on the olefin and the alkyne, as well as the identity of the nucleophile.¹⁷ In the system developed by Helmchen, 1,6-enynes with monosubstituted olefins first undergo a rearrangement to form a cationic gold carbene, which is then intercepted by an aldehyde (or ketone) to form the oxocarbenium intermediate (Scheme 1.5, A).¹³ This is followed by a Prins cyclization and demetallation to yield the novel tricyclic products. Helmchen later carried out an extensive mechanistic DFT study on this system, which supported the proposed addition of aldehydes to an electrophilic carbene intermediate.¹⁴

Echavarren looked at a closely related system in which the enyne was substituted at both the alkyne and the olefin (Scheme 1.5, B).¹⁵ Enynes of this type undergo a formal $[2 + 2 + 2]$ cycloaddition with aldehydes to give bicyclic products. The enyne first undergoes a gold catalyzed rearrangement to form the cyclopropyl gold carbene intermediate, which is then

attacked by the aldehyde to form the oxocarbenium. This then undergoes a Prins-type cyclization, followed by demetallation to yield the bicyclic product.



Scheme 1.5. Reactivity of 1,5- and 1,6-enynes with aldehydes.

In Scheme 1.5C, we propose a similar reactivity pathway for our 1,5-enyne. The reaction begins as previously described³¹ with a gold catalyzed 6-*endo-dig* cyclization followed by rearrangement to yield the cationic gold carbene intermediate **A**. This intermediate would then be intercepted by the aldehyde to form an oxocarbenium intermediate, which would then undergo a Friedel-Crafts annulation to form a new THP ring. Rearomatization would afford the gold vinyl, followed by protodemettalation to yield the novel polycyclic product. The convergence of these approaches, coupled with their rigid features and parallels to terpenoids, suggests a role in diversity-oriented synthesis.^{36,37}

Diversity-oriented synthesis (DOS) targets the development of novel molecular scaffolds in an effort to identify new drug candidates.³⁶ The goal is to expand the chemical space through the synthesis of a diverse range of structures, rather than to target or modify a known scaffold or natural product. DOS pathways typically transform a common intermediate into a diverse library of structures. Our reaction features a sequential cycloisomerization-cycloaddition to generate a complex, fused molecular scaffold in one step (Figure 1.2). Starting from a common linear enyne we generate a novel, rigid skeleton which can be easily diversified through variation of the unsaturated trapping nucleophile. Additionally, these products can be further manipulated at the olefin or through cross-coupling reactions on the arene to build chemical compound collections.

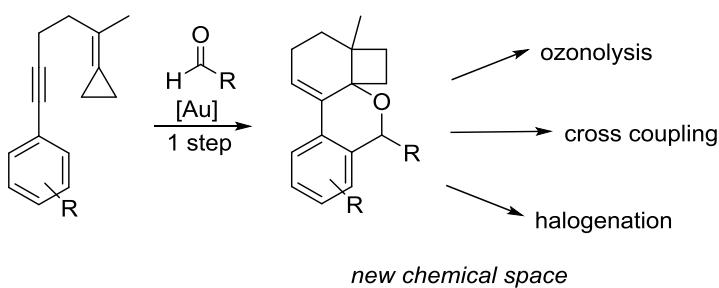
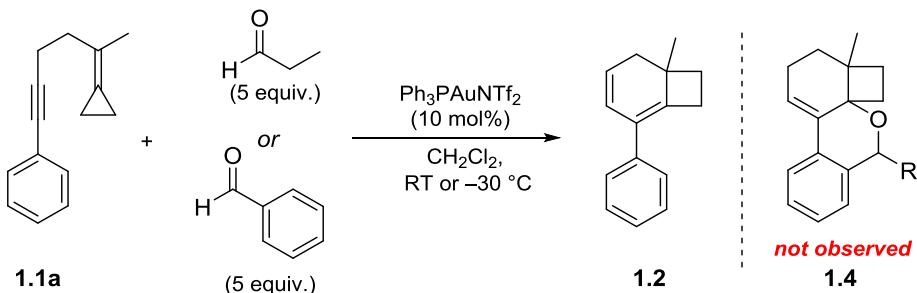


Figure 1.2. Diversity-oriented synthesis.

1.2 Initial reactivity of enyne with aldehydes

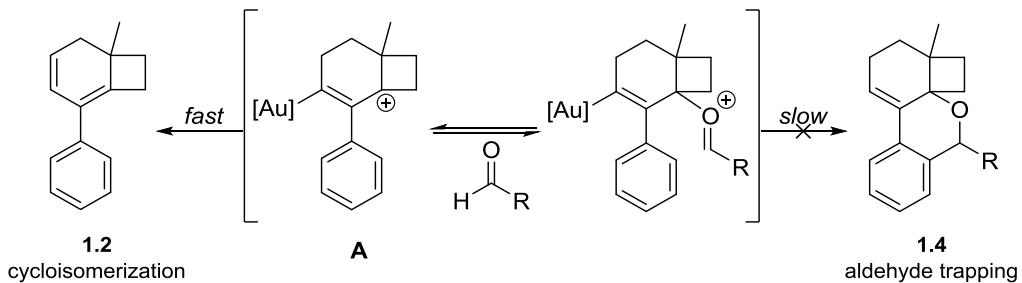
To test our hypothesis, we began looking at the reactivity of the phenyl-substituted enyne **1.1.a** that was previously developed in the group. Our initial hypothesis suggested an electron-rich aldehyde would best facilitate the trapping, as extra electron density would render the oxygen of the carbonyl more nucleophilic. We began using $\text{Ph}_3\text{PAuNTf}_2$ as a catalyst due to its success in the cycloisomerization chemistry and because it does not require pre-activation with silver salts. Preliminary studies focused on the use of p-anisaldehyde (5 equiv.) as the nucleophile. At room temperature, only the cycloisomerized product was observed (Scheme 1.6). Lowering the temperature of the reaction to -30°C did not result in conversion to the desired

trapped product. Propionaldehyde was also screened under these conditions and similarly only returned **1.2**.



Scheme 1.6. Initial aldehyde trapping experiments.

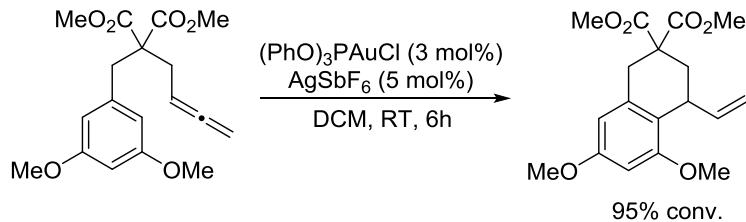
The rapid cycloisomerization at both ambient and reduced temperatures led us to propose that the phenyl ring of the enyne was insufficiently electron-rich to nucleophilically add to the oxocarbenium intermediate (Scheme 1.7). We proposed that the oxocarbenium could be forming, however the subsequent Friedel-Crafts annulation is unable to outcompete with the 1,2-hydrogen shift and protodemettalation.



Scheme 1.7. Reaction pathway for cycloisomerization vs. aldehyde addition.

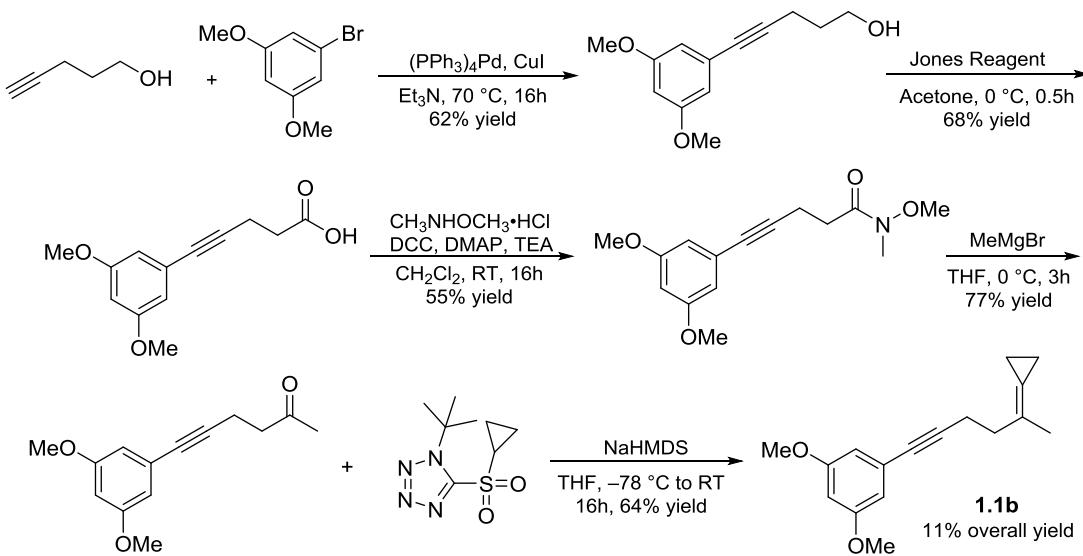
To overcome the limitations of our substrate, we designed the analogous 1,5-ene with dimethoxy substituents on the arene (compound **1.1b**). We proposed that incorporating electron-donating groups both ortho- and para- to the site of addition would be key in facilitating the Friedel-Crafts reaction. Previous studies in the lab on the gold-catalyzed intramolecular hydroarylation of allenes revealed that activated arenes were required to facilitate the

intramolecular Fridel-Crafts reaction (Scheme 1.8).³⁸ In this study, viable arenes for the Friedel-Crafts reaction included naphthalene, ethers and a pyrrole, but were limited when it came to those with electron-deficient groups and even a *t*-butyl group.



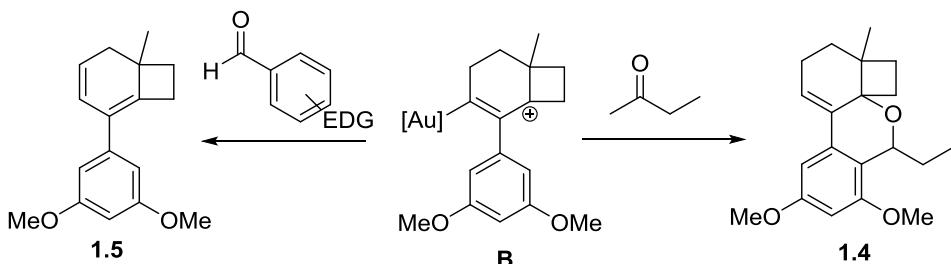
Scheme 1.8. Gold-catalyzed intramolecular hydroarylation of allenes.

Following this strategy, activated enyne **1.1b** was synthesized following a modified literature procedure (Scheme 1.9).³¹ The synthesis begins with a Sonogashira cross-coupling to afford the substituted alkyne in 62% yield. The corresponding alcohol was oxidized to the carboxylic acid with Jones reagent. Formation of the Weinreb amide, followed by methyl Grignard addition yielded the ketone. The final step in the synthesis was the modified Julia-Kocienski olefination to afford **1.1b** in an 11% overall yield.



Scheme 1.9. Synthetic route to **1.1b**.

We began screening **1.1b** with electron-rich aromatic aldehydes. With p-anisaldehyde at room temperature, only the cycloisomer **1.5** was obtained (Scheme 1.10). Lowering the temperature to 0 °C or –30 °C did not change the outcome of the reaction. Switching to more electron-rich aldehydes such as p-(dimethylamino)benzaldehyde or 3,4,5-trimethoxybenzaldehyde still only returned the cycloisomerized product. Acetonitrile and nitromethane were screened as alternative solvents, however this did not change the reaction outcome.



Scheme 1.10. Reactivity of auro-allyl cation with aldehydes.

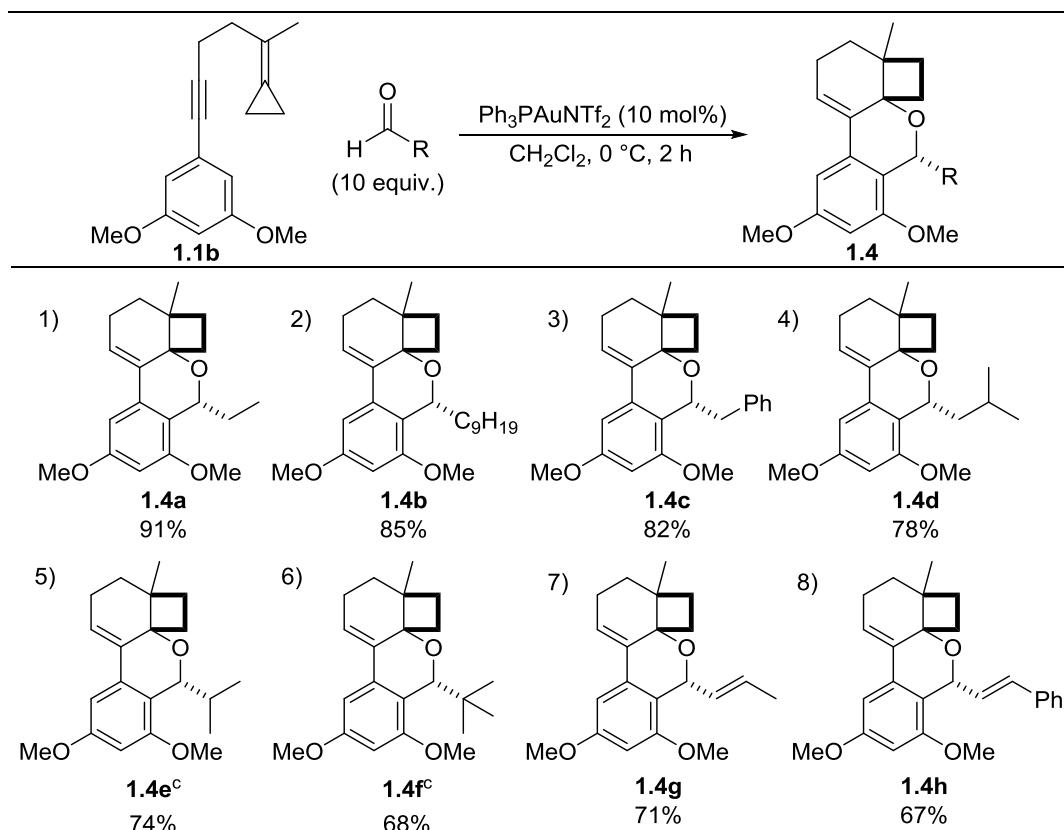
To our delight, upon switching to propionaldehyde (5 equiv, RT), we obtained a single diastereomer of **1.4** as the major product, along with a lesser quantity of **1.5** (3:1 ratio). We initially began screening protic additives to increase selectivity for **1.4** (see section 1.5). Ultimately, we found that by increasing the equivalents of aldehyde to 10 and lowering the temperature to 0 °C, we were able to obtain complete selectivity (>99%) to our desired product **1.4**.

1.3 Substrate scope

These latter optimized conditions were used to evaluate the scope with respect to the aldehyde partner. As shown in Table 1.1, a variety of aliphatic aldehydes were successfully incorporated, including aldehydes with linear and branched chains, as well as unsaturated moieties. With bulkier aldehydes, including pivaldehyde and isobutyraldehyde,

cycloisomerization became increasingly competitive as the resulting oxocarbenium intermediate is more sterically hindered at carbon, thus slowing down the subsequent Friedel-Crafts annulation. Lowering the temperature to $-35\text{ }^{\circ}\text{C}$ returned our desired selectivity for aldehyde trapping. In each case the products were isolated by column chromatography in good to excellent yields and as a single diastereomer. NMR analysis along with an X-ray structure of an aromatic aldehyde derivative (*vide infra*) led to our proposal of the indicated diastereomer.

Table 1.1. Gold(I)-catalyzed cyclo-coupling of **1.1b** and aliphatic aldehydes.^{a,b}

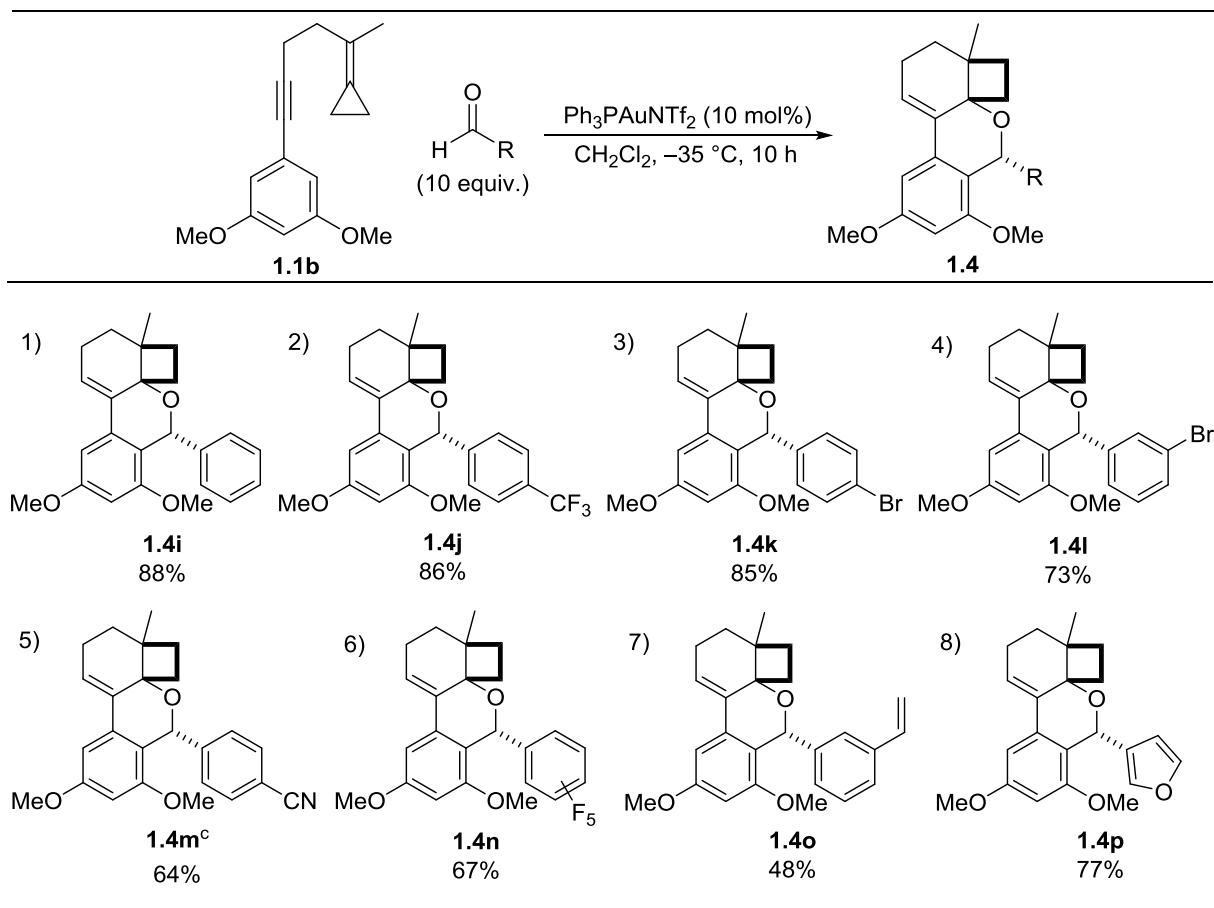


^aSee the experimental section for typical reaction procedure. ^bYields of chromatographically purified. ^cTemperature lowered to $-35\text{ }^{\circ}\text{C}$.

In contrast, aromatic aldehydes were found to not add to **B** as efficiently (1:1 mixture of **1.4 : 1.5**) under the conditions in Table 1.1, though cooling to $-35\text{ }^{\circ}\text{C}$ returned high chemo- and diastereoselectivities. In each case selectivities for the trapped product were very high (Table

1.2). Meta and para substituted arenes bearing electron-withdrawing groups showed excellent reactivity, as did vinyl arenes and furaldehyde. However, as demonstrated in our earlier optimization reactions, electron rich aldehydes, including p-anisaldehyde, 3,4,5-trimethoxybenzaldehyde, and p-(dimethylamino)benzaldehyde, only returned cycloisomerized product.

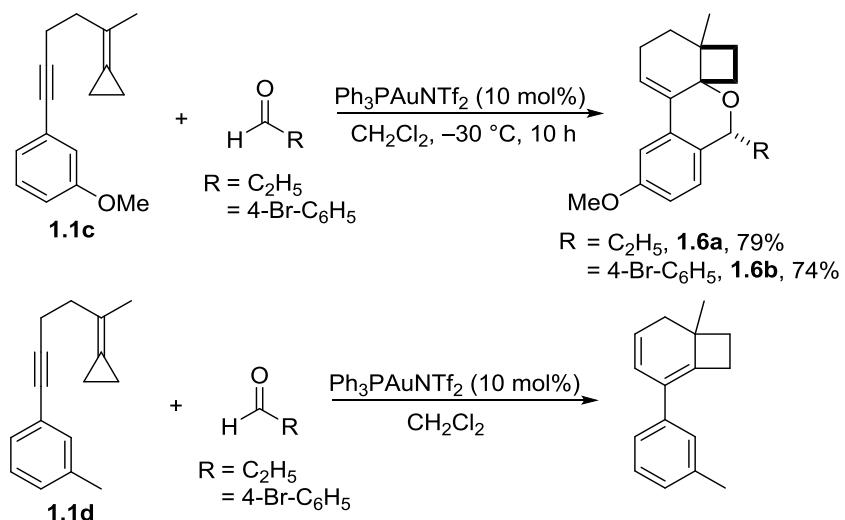
Table 1.2. Substrate scope with aromatic aldehydes.^{a,b}



^aSee the experimental section for typical reaction procedure. ^bYields of chromatographically purified. ^cReaction time extended to 20 h.

The meta-methoxy enyne **1.1c** was also tested, and under the optimized conditions for each class of aldehydes a single regio- and diastereomer of the polycycle was formed, in which the methoxy group of the arene was positioned para to the site of addition (**1.6a** and **1.6b**, Scheme 1.11). A similar reaction with a m-tolyl group (enye **1.1d**) did not successfully trap

aldehydes, providing only the cycloisomerized product. The requirement of at least a single activating group on the nucleophilic arene suggests that this Friedel-Crafts addition may be product determining (c.f. **1.1a**). This reactivity can be rationalized looking at both the Hammett parameters and nucleophilicity of the arene. Enyne substrates with electron donating groups such as p-OMe have a σ_p value of -0.27, which is significantly lower than that of p-Me ($\sigma_p = -0.17$) and benzene ($\sigma_p = 0$).³⁹ Alternatively, Mayr's nucleophilicity reactivity scales can be used to rationalize this reactivity. These scales measure the relative nucleophilicity of a variety of π -nucleophiles with a common electrophile. The nucleophilicity parameters for dimethoxybenzene and methoxybenzene, 2.48 and -1.18, respectively, are both higher than those of toluene (-4.36) and benzene (-6.3), confirming these arenes are more nucleophilic (Figure 1.3).⁴⁰



Scheme 1.11. Cyclo-coupling with enynes **1.1c** and **1.1d**.

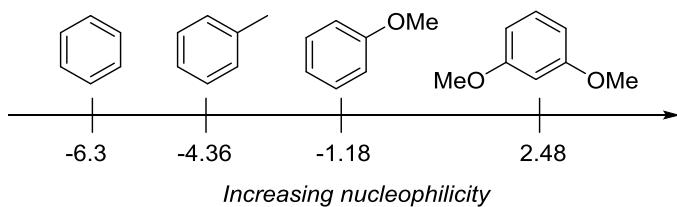


Figure 1.3. Mayr's π -nucleophilicity parameters.

1.4 Stereochemical analysis

To confirm the relative stereochemistry of the products an X-ray structure of crystalline **1.4k** was obtained. This product was chosen for the X-ray analysis as the incorporation of the bromoarene allowed for a crystalline product. Most of the products that incorporated aliphatic aldehydes resulted in oils rather than solid material. As shown in Figure 1.2, the proton from the aldehyde is cis to the cyclobutane ring. This relative stereochemistry suggested the indicated orientation of the oxocarbenium ion on attacking the arene (**C**, Figure 1.4).

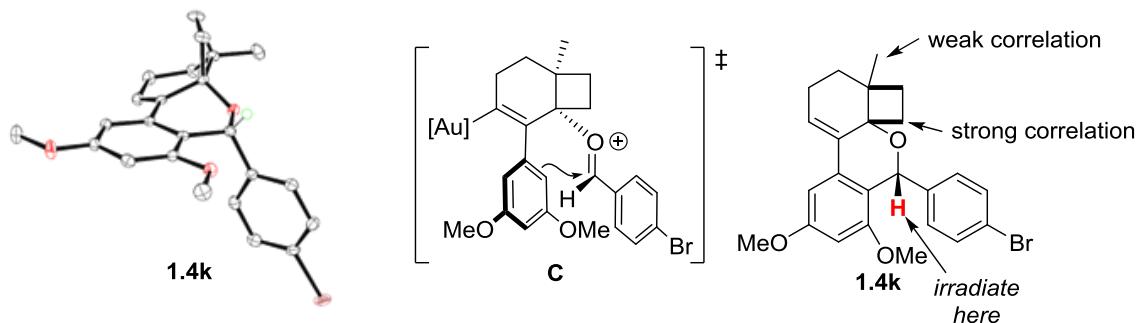


Figure 1.4. ORTEP representation of the solid state molecular structure of **1.4k**; ellipsoids drawn at 50% probability, only one enantiomer of the asymmetric unit, and majority of the hydrogen atoms omitted for clarity.

The single isomer of product obtained from the remaining aldehydes were assigned by analogy to **1.4k** and in the cases of **1.4a** and **1.4j**, were confirmed by comparative 1D-NOESY

experiments. For this analysis, we first looked at the 1D-NOE of compound **1.4k** as a starting point. In the NMR experiment, the α -ether proton was irradiated and correlations through space to the various nearby protons were measured (Figure 1.4). A relatively strong correlation to the cyclobutane protons was observed, with only a small correlation to the methyl protons. The analogous NMR experiment with **1.4a** was conducted to confirm the stereochemistry of an aliphatic aldehyde trapped product. This was also repeated with **1.4j** to confirm that other aromatic aldehydes provided the same relative stereochemistry (Figure 1.5). In all cases, stronger correlations to the cyclobutane protons than to the methyl group was observed. Had the other diastereomer been formed in which this α -ether proton was trans to the cyclobutene ring, we would not expect to observe such a strong NOE correlation (if any) to the cyclobutane protons.

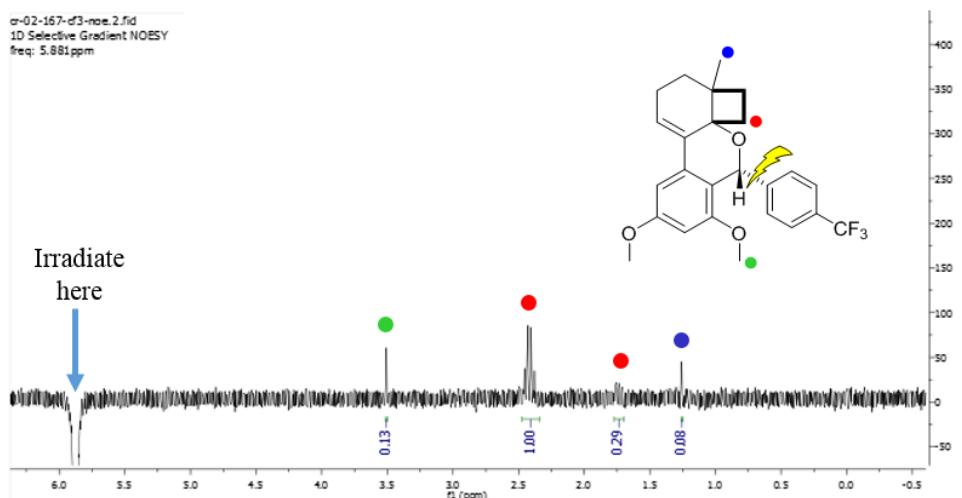


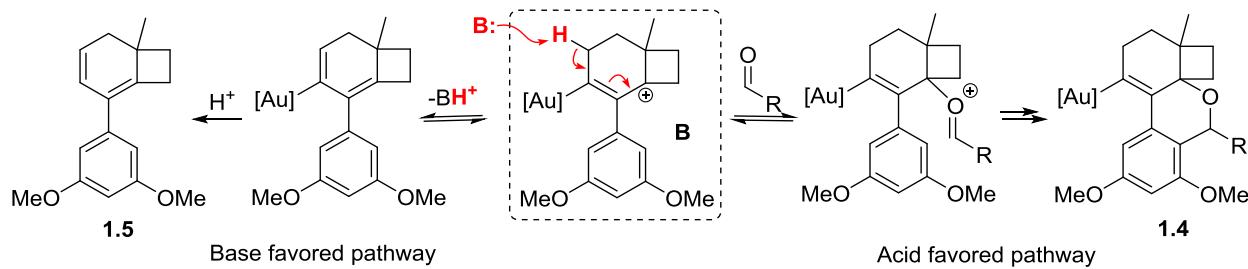
Figure 1.5. 1-D NOE spectra of **1.4j**.

1.5 Mechanistic studies

Our methodological studies sparked a number of mechanistic questions about additions to the putative auro-allyl cation, **B**. A competition experiment between benzaldehyde and p-CF₃-benzaldehyde (5 equiv. each) with enyne **1.1b** and Ph₃PAuNTf₂ (10 mol%) revealed that the more electron rich aldehyde was slightly favored (2:1 **1.4i** : **1.4j**). Competing p-anisaldehyde

(which is not viable in Table 1.2) and p-CF₃-benzaldehyde, however only provides the p-CF₃-benzaldehyde trapped product **1.4j**. These data, combined with the need for an electron-rich arene on the enyne, show that electron rich aldehydes can better trap the auro-allyl cation but the resulting oxo-carbenium ion is proportionately less electrophilic. This renders very electron rich aromatic aldehydes (p-OMe, p-NMe₂, etc), effectively incapable of competing with the 1,2-shift. If the addition of aldehyde to **B** is reversible, then the product determining step is the Friedel-Crafts annulation.

An analysis of the competing manifolds for the formation of **1.4** versus **1.5** in Scheme 1.12 suggested that the partitioning of **B** might be sensitive to protic additives. We reasoned that the net 1,2-H shift might be the result of an allylic proton loss followed by protodemettallation. To test this notion, the relatively strong acid [Ph₂NH₂][BF₄] ($pK_{aH2O} \sim 1$)⁴¹ was added to gauge its influence on selectivity. As shown in entries 2 and 3 of Table 1.3, increasing equivalents of acid enhanced the trapping efficiency (up to 10:1). With a build-up of acid in the system, proton loss via a 1,2-hydrogen shift is inhibited, building up more of the key intermediate **B** that allows for aldehyde incorporation. On the other hand, with N-methyldiphenylamine as base (entries 4 and 5) the selectivity was shifted towards cycloisomerization with increasing equivalents of base. Because the addition of base facilitates the formation of the cycloisomerized product **1.5**, this suggests that the competing 1,2-hydrogen shift does indeed initiate with a proton loss.



Scheme 1.12. Acid/base dependent competition from intermediate **B**.

Table 1.3. Reaction optimization to favor the aldehyde trapped product **1.4**.

Entry	Additive + Equiv.	Pdt ratio (1.4 : 1.5)	
1	None	3:1	
2	[Ph ₂ NH ₂][BF ₄], 1 equiv.	4:1	
3	[Ph ₂ NH ₂][BF ₄], 5 equiv.	10:1	
4	Ph ₂ NMe, 1 equiv.	1:2	
5	Ph ₂ NMe, 5 equiv.	1:10	

Information on the catalyst's resting state was obtained by *in situ* monitoring using ³¹P NMR spectroscopy ($-35\text{ }^{\circ}\text{C}$). These spectra revealed the presence of a single catalyst species, with two distinct singlets in a 1:1 ratio (33 and 38 ppm). Initially this species was proposed as a geminally diaurated vinyl intermediate, which our group and others have previously shown to be prevalent in gold-vinyl⁴²⁻⁴⁹ and aryl⁵⁰⁻⁵² reactivity (Figure 1.6). These aurophilic interactions

have been reported in both catalytic and stoichiometric reactions and are ubiquitous in gold catalysis.⁴²

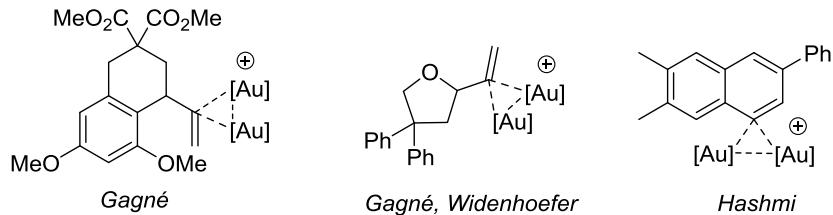
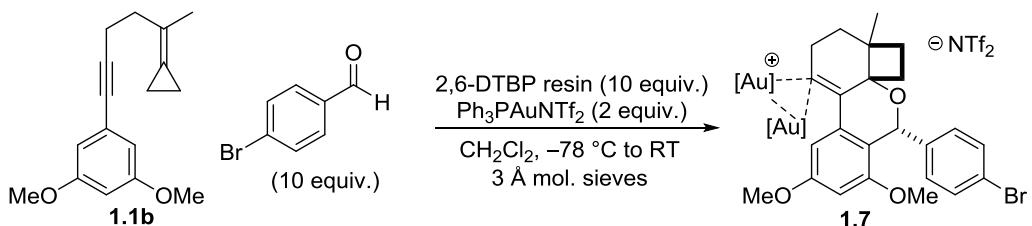


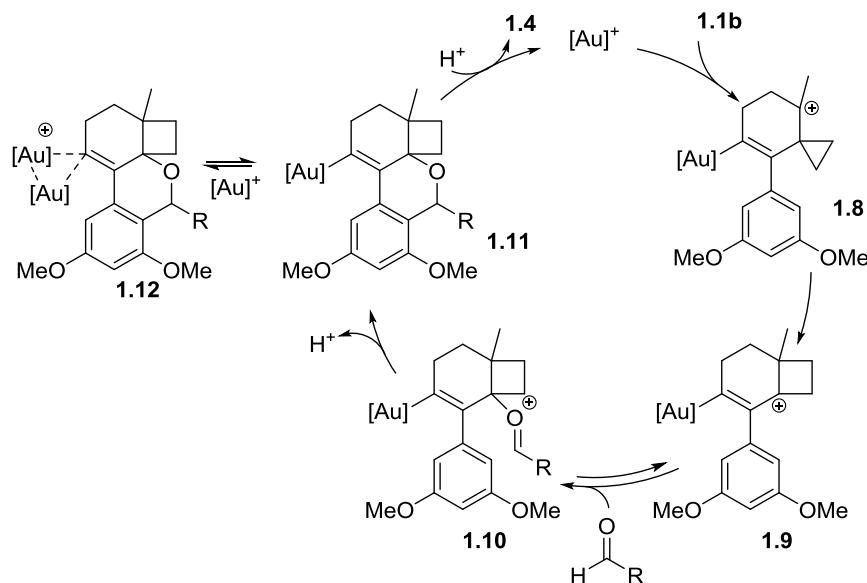
Figure 1.6. Selected examples of di-gold intermediates.

Evidence supporting the assignment of this species to a geminally diaurated vinyl intermediate⁴⁵ was obtained from stoichiometric reactions of **1.1b** with Ph₃PAuNTf₂ (2 equiv), 4-Br-benzaldehyde (10 equiv.), and a polymer-bound 2,6-di-*tert*-butylpyridine, which yielded a product with the same two distinct peaks as observed in the *in situ* ³¹P NMR experiments (Scheme 1.13). A combination of HRMS and NMR spectroscopy suggested di-gold vinyl complex **1.7**. Isolated **1.7** was always contaminated by traces of protodemetallated product **1.4k** and (Ph₃P)₂Au⁺, a common decomposition product in gold catalysis.⁵³ Several gold complexes and bases (to arrest protodemetallation) were screened, however the purity of the isolated **1.7** could not be improved above ~90% due to the sensitivity of the product in the removal of the excess aldehyde.



Scheme 1.13. Synthesis of di-gold vinyl **1.7**.

The proposed mechanism for this transformation is shown in Scheme 1.14. Au activation of alkyne **1.1b** triggers a 6-*endo-dig* cyclization to **1.8**, which ring expands to form the more stable auro-allyl cation **1.9** (equivalent to **B**). Distal attack of the aldehyde generates oxocarbenium intermediate **1.10**, which cyclizes, facilitated by the electron-rich methoxy groups. Re-aromatization affords gold-vinyl intermediate **1.11**, which may be directly protodemetallated to form **1.4** or trapped by $[\text{Au}]^+$ to yield the digold resting state **1.12**. Previous investigations of our group in collaboration with the Widenhoefer group⁴⁶ have shown that digold intermediates are usually off-cycle and that trapping of monogold vinyls by $[\text{Au}]^+$ is fast and can be competitive with protodemetallation.⁴⁹



Scheme 1.14. Proposed catalytic cycle. $[\text{Au}]^+ = \text{Ph}_3\text{PAu}^+$; counterion $[\text{NTf}_2^-]$ omitted for clarity.

1.6 Conclusions

In summary, we have developed a regio- and diastereoselective gold(I)-catalyzed addition of aldehydes to 1,5-enynes that sequences a series of C–C and C–O bond forming reactions to convergently create novel terpene-like polycyclic scaffolds. The scope with respect

to aldehydes is significant, and once again digold structures dominate the speciation of reactions generating a vinyl gold intermediate.

1.7 Acknowledgements

The National Institutes of Health (GM-60578) is gratefully acknowledged. We thank Drs. Peter White and Philippa Payne for assistance acquiring and analyzing crystallographic data. Dr. Mee-Kyung Chung and the UNC Dept. of Chemistry Mass Spec Core Laboratory are thanked for HRMS analyses.

1.8 Experimental section

1.8.1 General methods

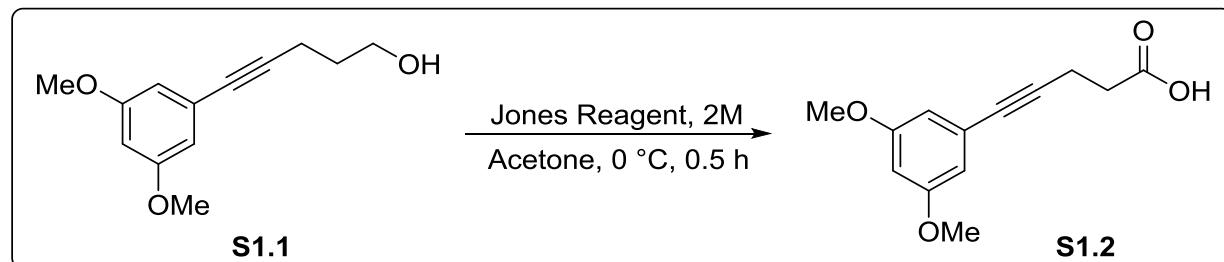
Unless otherwise stated, all commercially available reagents were used as received. Anhydrous tetrahydrofuran (THF, Stabilized, 99.9%, Acros Organics, purchased from Fisher Scientific) and anhydrous 1,4-dioxane (99.8%, purchased from Sigma Aldrich) were used as received. Anhydrous dichloromethane and diethyl ether were passed through a column of alumina.⁵⁴ The polymer-bound 2,6-di-tert-butylpyridine (200-400 mesh, ~1.8 mmol/g loading, 1 % cross-linked with divinylbenzene) was purchased from Sigma Aldrich. Column chromatography was performed using SilaFlash P60 40-63 µm (230-400 mesh). Thin layer chromatography (TLC) was performed on SiliCycle Silica Gel 60 F254 plates and was visualized with UV light and either KMnO₄ stain or 2,4-dinitrophenylhydrazine stain. NMR spectra were recorded on a Bruker Avance 400, 500 or 600 MHz spectrometer. All deuterated solvents were used as received from Cambridge Isotope Laboratories, Inc. The residual solvent protons (¹H) or the solvent carbons (¹³C) were used as internal standards. ¹H NMR data are presented as follows: chemical shift in ppm (δ) downfield from tetramethylsilane (multiplicity, coupling constant, integration). The following abbreviations are used in reporting NMR data: s, singlet; d, doublet;

t, triplet; q, quartet; dd, doublet of doublets; dt, doublet of triplets; ddd, doublet of doublet of doublets; m, multiplet. High resolution mass spectra for organic compounds were obtained on an Agilent Accurate LC-TOF Mass Spectrometer (Agilent Series 6220) operating in positive ion mode with an electrospray ionization source (fragmentor = 175 V) by Dr. Mee-Kyung Chung. The data were analyzed using an Agilent MassHunter Workstation Software, Qualitative Analysis (V.B.02.00). High resolution mass spectra for Au-containing intermediates were obtained with a hybrid LTQ FT (ICR 7T) (ThermoFisher, Bremen, Germany) mass spectrometer where samples were introduced via a micro-electrospray source and analyzed using Xcalibur (ThermoFisher, Breman, Germany) by the UNC Chapel Hill Chemistry Department Mass Spec Facility.

1.8.2 Preparation of starting materials

Synthesis of enyne **1.1b**.

Preparation of 5-(3,5-dimethoxyphenyl)pent-4-ynoic acid, **S1.2**

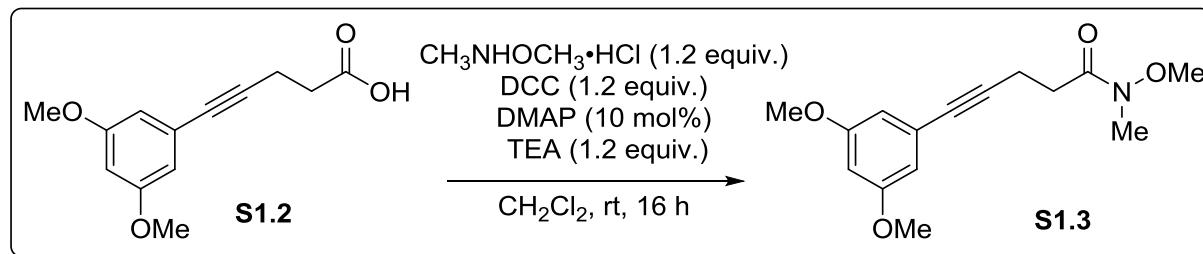


The alcohol **S1.1** was synthesized following a literature procedure.⁵⁵

To a solution of alcohol **S1.1** (2.33 g, 10.58 mmol) in acetone (107 mL) at 0 °C was added Jones Reagent (2M, 17 mL) dropwise. The resulting solution was stirred for 30 minutes at 0 °C. Isopropanol (~10 mL) was added to quench the reaction, and the reaction mixture was extracted with H₂O/Et₂O. The organic layer was concentrated and extracted between Et₂O and 1

M NaOH. The aqueous layer was washed with Et₂O and acidified by adding conc. HCl until reaching pH ~1. This was then extracted with Et₂O. The organic layer was washed with brine, dried over MgSO₄, filtered and concentrated to afford **S1.2** as a rusty orange solid, which was used without further purification (1.788 g, 72%). **¹H NMR** (600 MHz, CDCl₃) δ 6.55 (d, *J* = 2.3 Hz, 2H), 6.41 (t, *J* = 2.3 Hz, 1H), 3.77 (s, 6H), 2.75 – 2.68 (m, 4H). **¹³C NMR** (151 MHz, CDCl₃) δ = 176.6, 160.4, 124.7, 109.4, 101.4, 87.2, 81.3, 55.4, 33.1, 15.1. **HRMS** (ESI): calcd for C₁₃H₁₅O₄ [M+H]⁺ 235.0965, found 235.0971.

Preparation of 5-(3,5-dimethoxyphenyl)-N-methoxy-N-methylpent-4-ynamide, **S1.3**

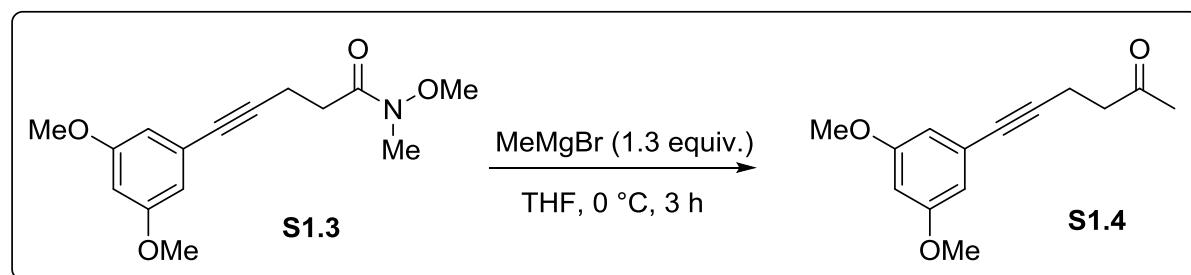


The following procedure was adapted from a literature procedure.³¹

To a solution of acid **S1.2** (0.871 g, 3.72 mmol) in CH_2Cl_2 (60 mL) at room temperature was added *N,O*-dimethylhydroxylamine hydrochloride (0.435 g, 4.46 mmol), *N,N'*-dicyclohexylcarbodiimide (0.920 g, 4.46 mmol), 4-(dimethylamino)pyridine (0.045 g, 0.372 mmol), and triethylamine (0.62 mL, 4.46 mmol). The reaction mixture was stirred at room temperature for 16 hours. H_2O (25 mL) was added to quench the reaction. The reaction mixture was extracted with CH_2Cl_2 , and the organics were washed with brine, dried over MgSO₄, filtered and concentrated under reduced pressure. The product was purified by silica gel column chromatography (Hexanes/EtOAc = 3:1) to afford the Weinreb amide as a viscous yellow oil (0.571 g, 55% yield). **¹H NMR** (600 MHz, CDCl₃): δ = 6.56 (d, *J* = 2.3 Hz, 2H), 6.40 (t, *J* = 2.3

Hz, 1H), 3.77 (s, 6H), 3.72 (s, 3H), 3.21 (s, 3H), 2.77 – 2.72 (m, 4H). **¹³C NMR** (151 MHz, CDCl₃) δ = 172.6, 160.4, 125.0, 109.4, 101.2, 88.7, 80.9, 61.4, 55.4, 32.2, 31.3, 14.9. **HRMS** (ESI): calcd for C₁₅H₂₀NO₄ [M+H]⁺ 278.1387, found 278.1397

Preparation of 6-(3,5-dimethoxyphenyl)hex-5-yn-2-one, S1.4

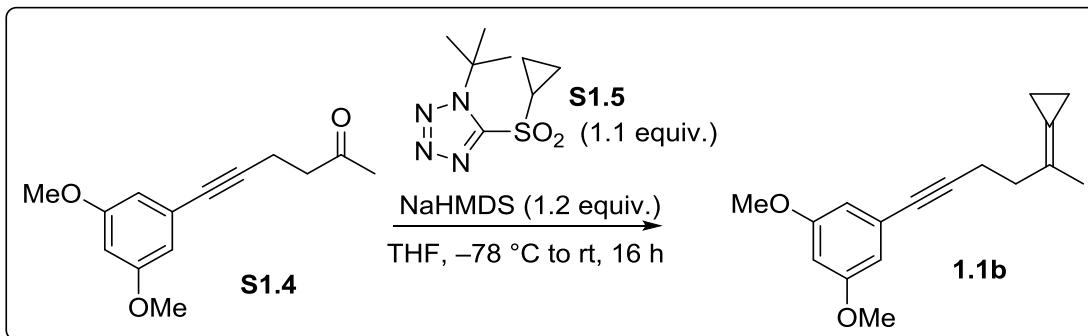


The following procedure was adapted from a literature procedure.³¹

To a solution of Weinreb amide **S1.3** (0.498 g, 1.80 mmol) in anhydrous THF (20 mL) at 0°C was slowly added a solution of MeMgBr (3 M in Et₂O, 0.78 mL, 2.34 mmol). The reaction mixture was stirred for 3 hours at 0°C. A saturated solution of NH₄Cl (25 mL) was added to quench the reaction, and the mixture was extracted with EtOAc. The organics were washed with brine, dried over MgSO₄, filtered and concentrated to afford the ketone as a pale yellow waxy solid (0.387 g, 92% yield). The product was taken to the next step without further purification.

¹H NMR (400 MHz, CDCl₃) δ = 6.53 (d, *J* = 2.2, 2H), 6.40 (t, *J* = 2.2, 1H), 3.76 (s, 6H), 2.77 (t, *J* = 7.1, 2H), 2.65 (t, *J* = 7.1, 2H), 2.20 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ = 206.7, 160.6, 125.0, 109.5, 101.4, 88.3, 81.1, 55.5, 42.6, 30.1, 14.1. **HRMS** (ESI): calcd for C₁₄H₁₇O₃ [M+H]⁺ 233.1172, found 233.1175.

Preparation of 1-(5-cyclopropylidenehex-1-yn-1-yl)-3,5-dimethoxybenzene, **1.1b**

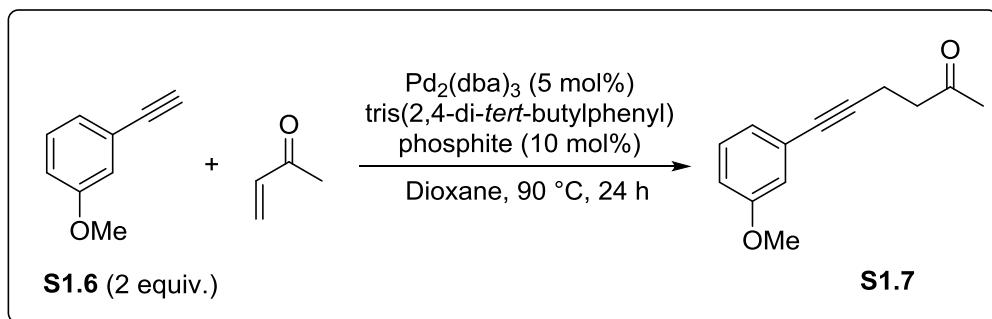


The Julia-Kocienski **S1.5** reagent was synthesized following a literature procedure.⁵⁶ The following procedure was adapted from a literature procedure.³¹

The ketone **S1.3** (0.387 g, 1.67 mmol) and Julia-Kocienski reagent **S1.5** (0.399 g, 1.73 mmol) were dissolved in anhydrous THF (20 mL) and cooled to -78 °C. Sodium bis(trimethylsilyl)amide (1 M in THF, 2 mL, 2 mmol) was added, and the reaction was allowed to warm to room temperature and stirred overnight. A saturated aqueous solution of NH₄Cl (10 mL) was added to quench, and the reaction mixture was extracted with Et₂O. The organics were washed with brine, dried over MgSO₄ and concentrated to afford a yellow oil. The crude product was purified by silica gel column chromatography (Hexanes:EtOAc 10:1) to give the title compound **1.1b** as a pale yellow oil (0.333 g, 78% yield). ¹H NMR (600 MHz, CDCl₃) δ 6.53 (d, *J* = 2.1 Hz, 2H), 6.39 (t, *J* = 2.0 Hz, 1H), 3.77 (s, 6H), 2.60 (t, *J* = 7.6 Hz, 2H), 2.47 (t, *J* = 7.4 Hz, 2H), 1.86 (s, 3H), 1.11 (t, *J* = 5.9 Hz, 2H), 0.98 (t, *J* = 6.2 Hz, 2H). ¹³C NMR (151 MHz, CDCl₃) δ = 160.6, 125.5, 122.9, 116.7, 109.4, 101.1, 90.4, 80.6, 55.5, 36.0, 20.8, 18.2, 3.2, 1.6. HRMS (ESI): calcd for C₁₇H₂₁O₂ [M+H]⁺ 257.1536, found 257.1535.

1.8.3 Synthesis of enyne **S1.6**

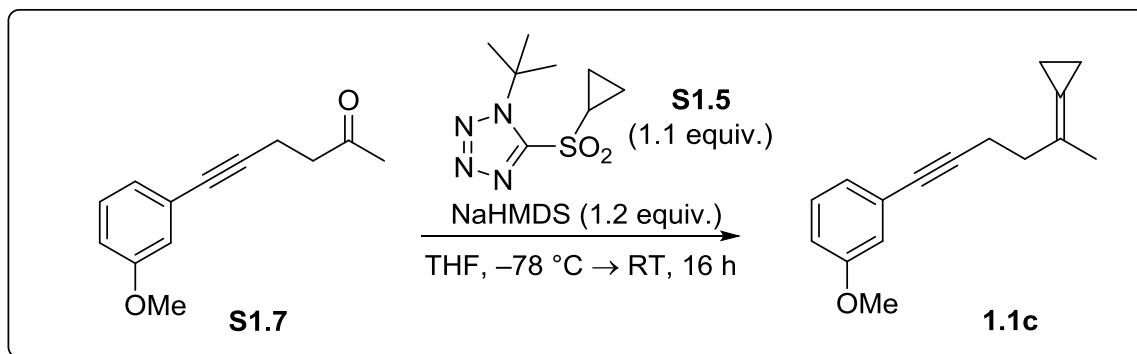
Preparation of 6-(3-methoxyphenyl)hex-5-yn-2-one, **S1.7**



The alkyne **S1.6** was synthesized following a literature procedure.⁵⁷ The following procedure was adapted from a literature procedure.⁵⁸

$\text{Pd}_2(\text{dba})_3$ (0.250 g, 0.242 mmol) and tris(2,4-di-*tert*-butylphenyl) phosphite (0.313 g, 0.483 mmol) were added to a flame-dried Schlenk flask under N_2 . Anhydrous dioxane (40 mL) was added and the resulting solution was sparged for 30 minutes. Methyl vinyl ketone (0.39 mL, 4.83 mmol) was added, and the reaction mixture was heated at 90 °C in a flask equipped with a reflux condenser under N_2 . A solution of alkyne **S1.6** (1.278 g, 9.66 mmol) in dioxane (10 mL) was added dropwise to the reaction mixture over the course of 10 h, then continued to reflux for 14 h. The reaction was allowed to cool to room temperature, diluted with Et_2O , and filtered through a plug of Florisil®, eluting with Et_2O . The filtrate was concentrated and purified via silica gel column chromatography (Hexanes:EtOAc 30:1/ 20:1/ 10:1) to afford the title compound **S1.7** as a dark yellow oil (0.228 g, 23% yield). **1H NMR** (600 MHz, CDCl_3): δ = 7.18 (t, J = 7.9 Hz, 1H), 6.97 (dt, J = 7.6, 1.2 Hz, 1H), 6.91 (dd, J = 2.7, 1.4 Hz, 1H), 6.83 (ddd, J = 8.2, 2.7, 0.9 Hz, 1H). 3.79 (s, 3H), 2.77 (t, J = 7.3 Hz, 2H), 2.66 (t, J = 7.3 Hz, 2H), 2.21 (s, 3H). **13C NMR** (151 MHz, CDCl_3) δ = 206.7, 159.2, 129.3, 124.5, 124.1, 116.4, 114.4, 88.4, 80.9, 55.3, 42.5, 30.0, 14.0. **HRMS** (ESI): calcd for $\text{C}_{13}\text{H}_{15}\text{O}_2$ [M+H]⁺ 203.1067, found 203.1067.

Preparation of 1-(5-cyclopropylidenehex-1-yn-1-yl)-3-methoxybenzene, **1.1c**



The ketone **S1.7** (0.228 g, 1.13 mmol) and Julia-Kocienski reagent **S1.5** (0.286 g, 1.24 mmol) were dissolved in anhydrous THF (15 mL) and cooled to -78 °C. Sodium bis(trimethylsilyl)amide (1 M in THF, 1.4 mL, 1.4 mmol) was added, and the reaction was allowed to warm to room temperature and stirred overnight. A saturated aqueous solution of NH₄Cl (~10 mL) was added to quench, and the reaction mixture was extracted with Et₂O. The organics were washed with brine, dried over MgSO₄ and concentrated to afford the product as a pale yellow oil. The crude product was purified by silica gel column chromatography (Hexanes:EtOAc 30:1) to give the title compound **1.1c** as a pale yellow oil (0.091 g, 37% yield).

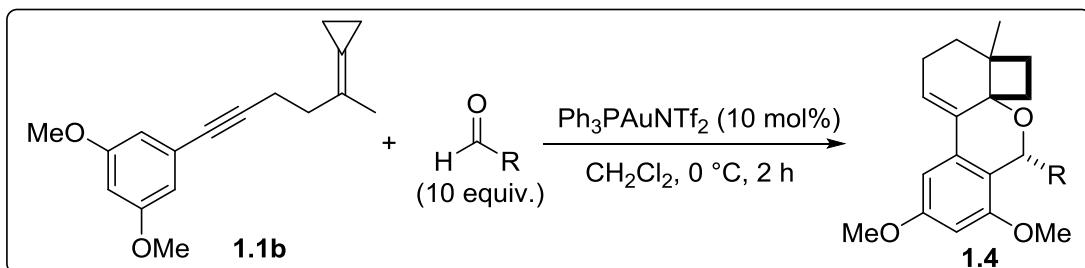
¹H NMR (600 MHz, CDCl₃): δ = 7.18 (t, *J* = 7.9 Hz, 1H), 6.96 (dt, *J* = 7.6, 1.2 Hz, 1H), 6.90 (dd, *J* = 2.6, 1.4 Hz, 1H), 6.82 (ddd, *J* = 8.4, 2.7, 0.9 Hz, 1H), 3.79 (s, 3H), 2.61 (t, *J* = 7.6 Hz, 2H), 2.47 (t, *J* = 7.5 Hz, 2H), 1.86 (s, 3H), 1.12 – 1.09 (t, *J* = 7.5 Hz, 2H), 0.99 – 0.97 (t, *J* = 7.4 Hz, 2H). **¹³C NMR** (151 MHz, CDCl₃) δ = 159.2, 129.2, 125.1, 124.0, 122.7, 116.5, 116.3, 114.1, 90.4, 80.4, 55.2, 35.9, 20.7, 18.1, 3.1, 1.4. **HRMS** (ESI): calcd for C₁₆H₁₉O [M+H]⁺ 227.1430, found 227.1432.

1.8.4 Gold-catalyzed addition of aldehydes to 1,5-enynes

Ph₃PAuNTf₂ was synthesized following a literature procedure.³²

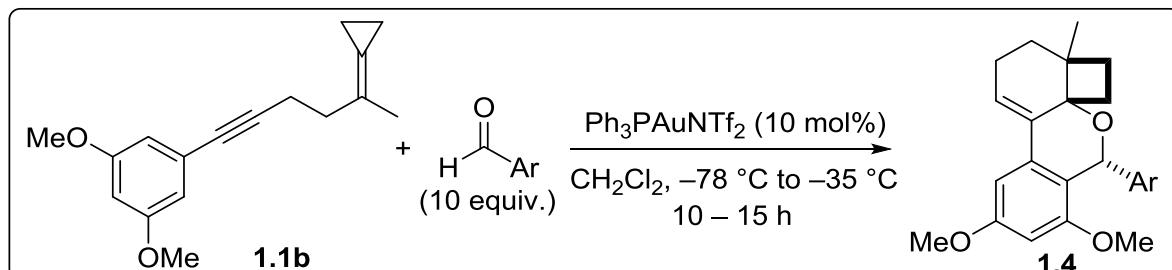
General procedure for Au-catalyzed addition of aldehydes to 1,5-enynes

Method A, procedure for aliphatic aldehydes, reaction run at 0 °C



The 1,5-enyne **1.1b** (0.1 mmol) was dissolved in anhydrous CH_2Cl_2 (1 mL) in an oven-dried 1 dram vial. The aldehyde (1.0 mmol, 10 equiv.) was added to the vial, and the contents were stirred and cooled to 0°C in an ice bath. $\text{Ph}_3\text{PAuNTf}_2$ (0.01 mmol, 0.1 equiv.) was added to the vial, and the reaction mixture was stirred for 2 hours. Upon evaporation of the solvent under reduced pressure, the residue was purified by silica gel column chromatography to afford the polycyclic product in pure form.

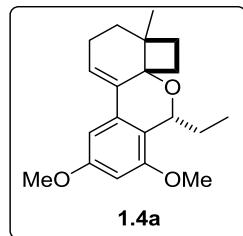
Method B, procedure for aromatic aldehydes, reaction run at –35 °C



The 1,5-enyne **1.1b** (0.1 mmol) was dissolved in anhydrous CH_2Cl_2 (1 mL) in an oven-dried 1 dram vial. The aldehyde (1.0 mmol, 10 equiv.) was added to the vial, and the contents were stirred and cooled to -78°C in a dry ice/acetone bath. $\text{Ph}_3\text{PAuNTf}_2$ (0.01 mmol, 0.1 equiv.) was added to the vial, and the reaction mixture was transferred to a cryobath at -35°C . The reaction was stirred for the appropriate reaction time (ca. 10-15 h), then warmed to room

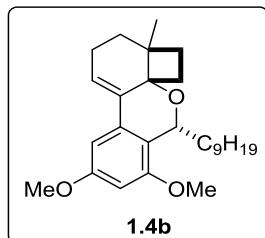
temperature. Upon evaporation of the solvent under reduced pressure, the residue was purified by silica gel column chromatography to afford the polycyclic product in pure form.

Synthesis of 7-ethyl-8,10-dimethoxy-3a-methyl-2,3,3a,4,5,7-hexahydrobenzo[c]cyclobuta[i]chromene, 1.4a



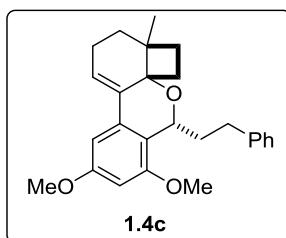
Propionaldehyde was distilled prior to use. The product **1.4a** was prepared following Method A and purified using hexanes: ethyl acetate (10:1), (pale yellow oil, 91% yield). **¹H NMR** (600 MHz, CDCl₃): δ = 6.58 (d, *J* = 2.3 Hz, 1H), 6.33 (d, *J* = 2.3 Hz, 1H), 6.25 (dd, *J* = 5.0, 3.5 Hz, 1H), 4.82 (dd, *J* = 7.4, 3.3 Hz, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 2.31 – 2.24 (m, 2H), 2.24 – 2.19 (m, 1H), 2.00 – 1.91 (m, 1H), 1.68 – 1.55 (m, 3H), 1.49 – 1.44 (m, 1H), 1.43 – 1.37 (m, 1H), 1.34 – 1.30 (m, 1H), 1.29 (s, 3H), 0.83 (t, *J* = 7.4 Hz, 3H). **¹³C NMR** (150 MHz, CDCl₃): δ = 159.0, 156.6, 135.6, 135.2, 120.1, 119.3, 99.8, 97.5, 71.7, 70.5, 55.3, 55.2, 42.3, 31.5, 29.2, 28.4, 22.6, 22.6, 22.0, 9.6. **HRMS** (ESI): calcd for C₂₀H₂₇O₃ [M+H]⁺ 315.1955, found 315.1959.

Synthesis of 8,10-dimethoxy-3a-methyl-7-nonyl-2,3,3a,4,5,7-hexahydrobenzo[c]cyclobuta[i]chromene, 1.4b



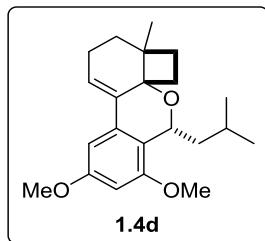
The product **1.4b** was prepared following Method A and purified using hexanes: ethyl acetate (10:1), (pale yellow oil, 85% yield). **¹H NMR** (600 MHz, CDCl₃): δ = 6.57 (d, *J* = 2.3 Hz, 1H), 6.33 (d, *J* = 2.3 Hz, 1H), 6.24 (dd, *J* = 5.3, 3.2 Hz, 1H), 4.85 (dd, *J* = 8.0, 3.1 Hz, 1H), 3.82 (s, 3H), 3.76 (s, 3H), 2.30 – 2.25 (m, 2H), 2.24 – 2.19 (m, 1H), 1.96 – 1.89 (m, 1H), 1.62 – 1.55 (m, 3H), 1.48 – 1.43 (m, 1H), 1.43 – 1.38 (m, 1H), 1.31 – 1.28 (m, 1H), 1.28 (s, 3H), 1.27 – 1.21 (m, 14H), 0.87 (t, *J* = 7.0 Hz, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ = 159.0, 156.5, 135.6, 135.0, 120.1, 119.8, 99.8, 97.5, 71.7, 69.5, 55.3, 55.2, 42.4, 35.4, 32.0, 31.5, 29.7, 29.6, 29.5, 29.4, 29.2, 25.3, 22.7, 22.6, 21.9, 14.2. **HRMS** (ESI): calcd for C₂₇H₄₁O₃ [M+H]⁺ 413.3050, found 413.3049.

Synthesis of 7-benzyl-8,10-dimethoxy-3a-methyl-2,3,3a,4,5,7-hexahydrobenzo[c]cyclobuta[i]chromene, 1.4c



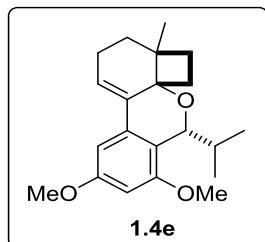
The product **1.4c** was synthesized following Method A and purified using hexanes: ethyl acetate (10:1), (yellow oil, 82% yield). **¹H NMR** (600 MHz, CDCl₃): δ = δ 7.27 (d, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 7.5 Hz, 2H), 7.17 (t, *J* = 7.1 Hz, 1H), 6.62 (d, *J* = 2.3 Hz, 1H), 6.34 (d, *J* = 2.3 Hz, 1H), 6.33 – 6.29 (m, 1H), 4.89 (d, *J* = 7.7 Hz, 1H), 3.85 (s, 1H), 3.76 (s, 1H), 2.71 (t, *J* = 8.0 Hz, 2H), 2.40 – 2.22 (m, 4H), 1.99 – 1.91 (m, 1H), 1.65 – 1.57 (m, 2H), 1.54 – 1.44 (m, 2H), 1.39 – 1.34 (m, 4H). **¹³C NMR** (151 MHz, CDCl₃) δ = 159.1, 156.6, 143.2, 135.4, 135.0, 128.6, 128.1, 125.3, 120.1, 119.0, 105.4, 99.8, 97.5, 71.8, 68.8, 55.3, 55.1, 42.2, 36.7, 31.5, 31.1, 29.2, 22.7, 22.6, 22.0. **HRMS** (ESI): calcd for C₂₅H₂₈NaO₃ [M+Na]⁺ 399.1931, found 399.1918.

Synthesis of 7-isobutyl-8,10-dimethoxy-3a-methyl-2,3,3a,4,5,7-hexahydrobenzo[c]-cyclobuta[i] chromene, **1.4d**



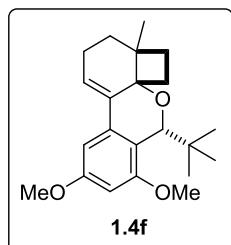
The product **1.4d** was synthesized following Method A and purified using hexanes: ethyl acetate (10:1), (pale yellow oil, 78% yield). **¹H NMR** (600 MHz, CDCl₃): δ = 6.59 (d, *J* = 2.3 Hz, 1H), 6.33 (d, *J* = 2.3 Hz, 1H), 6.26 (dd, *J* = 5.3, 3.2 Hz, 2H), 4.91 (dd, *J* = 9.2, 2.7 Hz, 1H), 3.82 (s, 3H), 3.77 (s, 3H), 2.31 – 2.19 (m, 3H), 1.94 – 1.87 (m, 1H), 1.80 (ddd, *J* = 13.5, 9.4, 2.8 Hz, 1H), 1.62 – 1.52 (m, 2H), 1.49 – 1.36 (m, 3H), 1.28 (s, 3H), 0.96 (d, *J* = 6.5 Hz, 3H), 0.88 (d, *J* = 6.7 Hz, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ = 159.0, 156.5, 135.5, 134.8, 120.2, 120.0, 99.9, 97.6, 71.7, 68.0, 55.3, 55.1, 44.5, 42.3, 31.2, 29.1, 24.7, 23.9, 22.7, 22.6, 21.9, 21.7. **HRMS** (ESI): calcd for C₂₂H₃₁O₃ [M+H]⁺ 343.2268, found 343.2271.

Synthesis of 7-isopropyl-8,10-dimethoxy-3a-methyl-2,3,3a,4,5,7-hexahydrobenzo[c]-cyclobuta[i] chromene, 1.4e



The product **1.4e** was synthesized following Method B and purified using hexanes: ethyl acetate (10:1), (waxy yellow solid, 74% yield). **¹H NMR** (600 MHz, CDCl₃): δ = 6.55 (d, *J* = 2.3 Hz, 1H), 6.33 (d, *J* = 2.2 Hz, 1H), 6.20 (t, *J* = 4.3 Hz, 1H), 4.75 (d, *J* = 3.7 Hz, 1H), 3.82 (s, 3H), 3.76 (s, 3H), 2.27 (m, 3H), 2.23 – 2.15 (m, 1H), 1.69 – 1.54 (m, 2H), 1.46 (dt, *J* = 13.6, 4.7 Hz, 1H), 1.41 – 1.36 (m, 1H), 1.32 – 1.29 (m, 1H), 1.29 (s, 3H), 0.96 (d, *J* = 6.9 Hz, 3H), 0.59 (d, *J* = 6.7 Hz, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ = 159.0, 156.6, 135.9, 135.8, 120.1, 119.0, 99.9, 97.4, 73.4, 71.5, 55.3, 55.2, 42.7, 32.4, 32.2, 29.4, 22.7, 22.6, 22.1, 19.7, 16.0. **HRMS** (ESI): calcd for C₂₁H₂₉O₃ [M+H]⁺ 329.2111, found 329.2114.

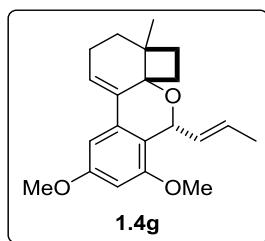
Synthesis of 7-(tert-butyl)-8,10-dimethoxy-3a-methyl-2,3,3a,4,5,7-hexahydrobenzo[c]-cyclobuta[i] chromene, 1.4f



The product **1.4f** was synthesized following Method B and purified using hexanes: ethyl acetate (10:1), (pale yellow oil, 68% yield). **¹H NMR** (600 MHz, CDCl₃): δ = 6.49 (d, *J* = 2.3

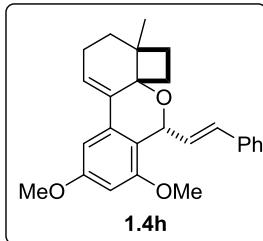
Hz, 1H), 6.34 (d, J = 2.3 Hz, 1H), 6.14 (t, J = 4.2 Hz, 1H), 4.87 (s, 1H), 3.84 (s, 3H), 3.72 (s, 3H), 2.31 – 2.25 (m, 2H), 2.13 – 2.06 (m, 1H), 1.53 – 1.46 (m, 2H), 1.46 – 1.40 (m, 2H), 1.34 (s, 3H), 1.28 – 1.19 (m, 1H), 0.77 (s, 9H). **^{13}C NMR** (151 MHz, CDCl_3) δ = 159.2, 157.4, 137.7, 137.4, 120.5, 116.9, 100.8, 97.0, 75.9, 72.1, 55.3, 54.8, 43.9, 39.7, 36.1, 29.1, 26.5, 23.1, 22.8, 21.8. **HRMS** (ESI): calcd for $\text{C}_{22}\text{H}_{31}\text{O}_3$ [M+H]⁺ 343.2268, found 343.2269.

Synthesis of (E)-8,10-dimethoxy-3a-methyl-7-(prop-1-en-1-yl)-2,3,3a,4,5,7-hexahydrobenzo[c]cyclobuta[i]chromene, 1.4g



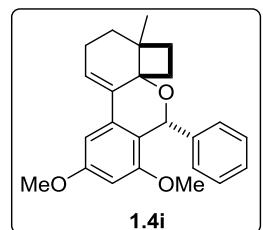
Crotonaldehyde (99% trans) was distilled prior to use. The product **1.4g** was synthesized following Method A and purified using hexanes: ethyl acetate (10:1), (white solid, 71% yield). **^1H NMR** (600 MHz, CDCl_3): δ = 6.58 (d, J = 2.4 Hz, 1H), 6.34 (d, J = 2.0 Hz, 1H), 6.26 (dd, J = 5.4, 3.2 Hz, 1H), 5.76 – 5.67 (m, 1H), 5.59 (ddd, J = 15.1, 6.1, 1.7 Hz, 1H), 5.29 (d, J = 6.1 Hz, 1H), 3.75 (s, 3H), 2.32 – 2.24 (m, 3H), 1.65 (d, J = 6.3 Hz, 3H), 1.64 – 1.55 (m, 3H), 1.47 – 1.40 (m, 2H), 1.31 (s, 3H). **^{13}C NMR** (151 MHz, CDCl_3) δ = 159.3, 156.6, 135.2, 134.6, 131.7, 126.0, 120.8, 118.5, 100.0, 97.8, 72.3, 70.1, 55.3, 53.4, 42.5, 31.8, 29.1, 22.9, 22.6, 22.0, 17.9. **HRMS** (ESI): calcd for $\text{C}_{21}\text{H}_{27}\text{O}_3$ [M+H]⁺ 327.1955, found 327.1960.

Synthesis of (E)-8,10-dimethoxy-3a-methyl-7-styryl-2,3,3a,4,5,7-hexahydrobenzo[c]-cyclobuta[i] chromene, 1.4h



The product **1.4h** was synthesized following Method A and purified using hexanes: ethyl acetate (10:1), (waxy yellow solid, 67% yield). **¹H NMR** (600 MHz, CDCl₃): δ = 7.34 (d, *J* = 6.8 Hz, 2H), 7.26 (t, *J* = 7.7 Hz, 2H), 7.17 (t, *J* = 7.3 Hz, 1H), 6.65 – 6.59 (m, 2H), 6.35 (d, *J* = 2.3 Hz, 1H), 6.36 – 6.30 (m, 1H), 6.30 (dd, *J* = 5.5, 3.0 Hz, 1H), 5.51 (d, *J* = 6.2 Hz, 2H), 3.83 (s, 3H), 3.76 (s, 3H), 2.37 – 2.27 (m, 3H), 1.69 (ddd, *J* = 11.0, 8.7, 2.6 Hz, 1H), 1.64 – 1.59 (m, 1H), 1.52 – 1.43 (m, 2H), 1.36 – 1.32 (m, 4H). **¹³C NMR** (151 MHz, CDCl₃) δ = 159.6, 156.7, 137.7, 135.1, 134.8, 130.6, 129.9, 128.3, 127.0, 126.5, 121.2, 117.8, 100.2, 97.8, 72.4, 70.2, 55.4, 55.3, 42.6, 32.0, 29.2, 22.9, 22.7, 22.0. **HRMS** (ESI): calcd for C₂₆H₂₉O₃ [M+H]⁺ 389.2111, found 389.2120.

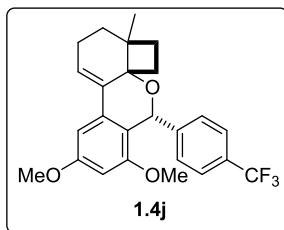
Preparation of 8,10-dimethoxy-3a-methyl-7-phenyl-2,3,3a,4,5,7-hexahydrobenzo[c]-cyclobuta[i] chromene, **1.4i**



The product **1.4i** was synthesized following Method B and purified using dichloromethane: petroleum ether (1:1), (white solid, 88% yield). **¹H NMR** (600 MHz, CDCl₃): δ = 7.24 – 7.19 (m, 4H), 7.20 – 7.15 (m, 1H), 6.65 (d, *J* = 2.3 Hz, 1H), 6.34 (dd, *J* = 5.1, 3.5 Hz, 1H), 6.26 (d, *J* = 2.2 Hz, 1H), 5.82 (s, 1H), 3.83 (s, 3H), 3.46 (s, 3H), 2.39 (q, *J* = 10.1 Hz, 1H),

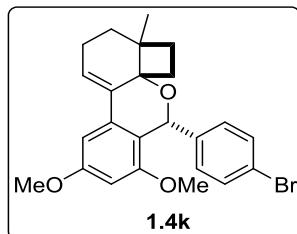
2.32 – 2.26 (m, 2H), 1.71 (ddd, J = 11.0, 8.7, 2.5 Hz, 1H), 1.61 (q, J = 9.8 Hz, 1H), 1.42 (ddd, J = 13.6, 5.3, 3.4 Hz, 1H), 1.37 – 1.30 (m, 2H), 1.23 (s, 3H). **^{13}C NMR** (151 MHz, CDCl_3): δ = 159.6, 156.8, 144.0, 135.1, 135.0, 128.1, 127.5, 126.8, 120.6, 118.7, 99.8, 98.0, 72.7, 72.7, 55.3, 55.1, 42.3, 31.3, 29.0, 22.8, 22.7, 21.9. **HRMS** (ESI): calcd for $\text{C}_{24}\text{H}_{27}\text{O}_3$ [M+H]⁺ 363.1955, found 363.1973.

Preparation of 8,10-dimethoxy-3a-methyl-7-(4-(trifluoromethyl)phenyl)-2,3,3a,4,5,7-hexa-hydro-benzo[c]cyclobuta[i]chromene, 1.4j



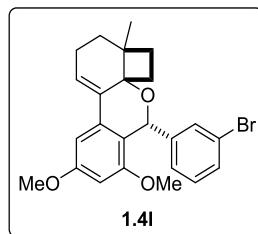
The product **1.4j** was synthesized following Method B and purified using dichloromethane: petroleum ether (1:1), (pale yellow crystalline solid, 86% yield). **^1H NMR** (600 MHz, CDCl_3): δ = 7.47 (d, J = 8.2 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 6.67 (d, J = 2.3 Hz, 1H), 6.38 (dd, J = 5.4, 3.2 Hz, 1H), 6.27 (d, J = 2.3 Hz, 1H), 5.86 (s, 1H), 3.83 (s, 3H), 3.48 (s, 3H), 2.40 (q, J = 10.1 Hz, 1H), 2.32 – 2.28 (m, 2H), 1.71 (ddd, J = 11.0, 8.7, 2.5 Hz, 1H), 1.63 (q, J = 9.5 Hz, 1H), 1.46 (ddd, J = 13.6, 5.2, 2.9 Hz, 1H), 1.39 – 1.33 (m, 2H), 1.23 (s, 3H). **^{13}C NMR** (150 MHz, CDCl_3): δ = 159.9, 156.6, 148.1, 135.0, 134.7, 128.9 (q, $^2J_{\text{CF}} = 32$ Hz), 128.4, 124.5 (q, $^3J_{\text{CF}} = 3.8$ Hz), 124.4 (q, $^1J_{\text{CF}} = 271.9$ Hz), 121.1, 117.6, 99.9, 97.9, 72.8, 72.3, 55.3, 55.0, 42.2, 31.2, 29.0, 22.7, 22.6, 22.0. **^{19}F NMR** (376.3 MHz, CDCl_3): δ = -62.25. **HRMS** (ESI): calcd for $\text{C}_{25}\text{H}_{26}\text{F}_3\text{O}_3$ [M+H]⁺ 431.1829, found 431.1833.

Preparation of 7-(4-bromophenyl)-8,10-dimethoxy-3a-methyl-2,3,3a,4,5,7-hexahydro-benzo[c] cyclobuta[i]chromene, 1.4k



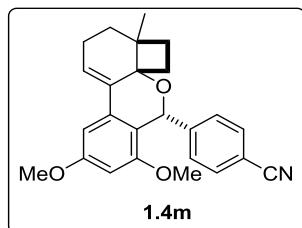
The product **1.4k** was synthesized following Method B and purified using dichloromethane: petroleum ether (1:1), (colorless crystalline solid, 85% yield). **¹H NMR** (600 MHz, CDCl₃) δ = 7.33 (d, *J* = 8.4 Hz, 1H), 7.09 (d, *J* = 8.4 Hz, 1H), 6.65 (d, *J* = 2.3 Hz, 1H), 6.35 (dd, *J* = 5.0, 3.5 Hz, 1H), 6.26 (d, *J* = 2.3 Hz, 1H), 5.77 (s, 1H), 3.83 (s, 3H), 3.49 (s, 3H), 2.37 (q, *J* = 9.9 Hz, 1H), 2.31 – 2.27 (m, 2H), 1.70 (ddd, *J* = 10.9, 8.7, 2.5 Hz, 1H), 1.61 (q, *J* = 9.5 Hz, 1H), 1.44 (ddd, *J* = 13.6, 5.4, 3.1 Hz, 1H), 1.37 – 1.32 (m, 2H), 1.22 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ = 159.9, 156.8, 143.3, 135.1, 135.0, 130.8, 130.1, 121.0, 120.7, 118.1, 100.0, 98.0, 72.9, 72.3, 55.4, 55.2, 42.3, 31.3, 29.2, 22.8, 22.8, 22.1. **HRMS** (ESI): calcd for C₂₄H₂₇BrO₃ [M+H]⁺ 441.1060, found 441.1044.

Preparation of 7-(3-bromophenyl)-8,10-dimethoxy-3a-methyl-2,3,3a,4,5,7-hexahydro-benzo[c] cyclobuta[i]chromene, 1.4l



The product **1.4l** was synthesized following Method B and purified using dichloromethane: petroleum ether (1:1), (pale yellow crystalline solid, 73% yield). **¹H NMR** (600 MHz, CDCl₃): δ = 7.36 (t, *J* = 1.8 Hz, 1H), 7.30 (ddd, *J* = 7.8, 2.1, 1.2 Hz, 1H), 7.14 (dt, *J* = 7.7, 1.4 Hz, 1H), 7.08 (t, *J* = 7.8 Hz, 1H), 6.65 (d, *J* = 2.3 Hz, 1H), 6.35 (dd, *J* = 5.4, 3.1 Hz, 1H), 6.27 (d, *J* = 2.2 Hz, 1H), 5.76 (s, 1H), 3.83 (s, 3H), 3.50 (s, 3H), 2.37 (q, *J* = 10.0 Hz, 1H), 2.31 – 2.27 (m, 2H), 1.69 (ddd, *J* = 11.0, 8.7, 2.5 Hz, 1H), 1.61 (q, *J* = 9.5 Hz, 1H), 1.44 (ddd, *J* = 13.6, 5.7, 2.8 Hz, 1H), 1.39 – 1.32 (m, 2H), 1.23 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ = 159.8, 156.7, 146.4, 135.0, 134.7, 131.2, 129.8, 129.2, 126.8, 121.5, 121.0, 117.8, 99.9, 98.0, 72.8, 72.2, 55.3, 55.1, 42.3, 31.2, 29.0, 22.7, 22.6, 22.0. **HRMS** (ESI): calcd for C₂₄H₂₅BrNaO₃ [M+Na]⁺ 463.0879, found 463.0871.

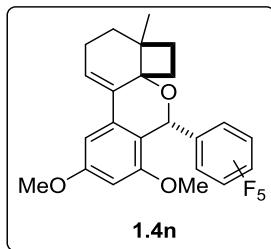
Preparation of 4-(8,10-dimethoxy-3a-methyl-2,3,3a,4,5,7-hexahydrobenzo[c]cyclobutyl[1]chromen-7-yl)benzonitrile, 1.4m



The product **1.4m** was synthesized following Method B and purified using dichloromethane: petroleum ether (1:1), (white crystalline solid, 64% yield). **¹H NMR** (600 MHz, CDCl₃): δ = 7.51 (d, *J* = 8.3 Hz, 2H), 7.32 (d, *J* = 8.3 Hz, 2H), 6.65 (d, *J* = 2.3 Hz, 1H), 6.38 (dd, *J* = 5.5, 3.1 Hz, 1H), 6.25 (d, *J* = 2.3 Hz, 1H), 5.82 (s, 1H), 3.83 (s, 3H), 3.48 (s, 3H), 2.37 (q, *J* = 10.0 Hz, 1H), 2.33 – 2.28 (m, 2H), 1.70 (ddd, *J* = 10.9, 8.7, 2.5 Hz, 1H), 1.61 (d, *J* = 9.8 Hz, 1H), 1.46 (ddd, *J* = 13.6, 5.7, 2.9 Hz, 1H), 1.38 – 1.32 (m, 2H), 1.22 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ = 160.0, 156.5, 149.5, 134.9, 134.4, 131.6, 128.9, 121.3, 119.3, 117.0,

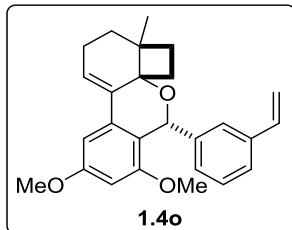
110.4, 99.9, 97.8, 72.9, 72.3, 55.3, 55.0, 42.2, 31.1, 29.0, 22.6, 22.6, 21.9. **HRMS** (ESI): calcd for C₂₅H₂₆NO₃ [M+H]⁺ 388.1907, found 388.1910.

Preparation of 8,10-dimethoxy-3a-methyl-7-(perfluorophenyl)-2,3,3a,4,5,7-hexahydro-benzo[c] cyclobuta[i]chromene, 1.4n



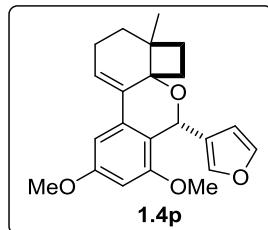
The product **1.4n** was synthesized following Method B and purified using dichloromethane: petroleum ether (1:1), (tan solid, 67% yield). **¹H NMR** (600 MHz, CDCl₃): δ = 6.66 (d, *J* = 2.3 Hz, 1H), 6.43 (dd, *J* = 5.9, 2.7 Hz, 1H), 6.25 (d, *J* = 2.3 Hz, 1H), 6.14 (s, 1H), 3.83 (s, 3H), 3.56 (s, 3H), 2.39 (q, *J* = 9.7, 8.7 Hz, 1H), 2.36 – 2.25 (m, 2H), 1.72 – 1.61 (m, 2H), 1.49 – 1.44 (m, 1H), 1.43 – 1.35 (m, 2H), 1.21 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ = 159.8, 156.1, 145.40 (d, *J*_{C-F} = 254.8 Hz), 140.21 (d, *J*_{C-F} = 251.8 Hz), 137.08 (d, *J*_{C-F} = 248.8 Hz), 136.3, 134.9, 133.5, 121.1, 117.3, 114.6, 99.6, 97.5, 73.0, 63.4, 55.3, 55.2, 41.8, 30.0, 29.0, 22.6, 22.5, 22.0. **¹⁹F NMR** (376 MHz, CDCl₃) δ = -143.20 (d, *J* = 16.3), -157.33 (t, *J* = 20.9), -164.19 (td, *J* = 21.3, 7.1). **HRMS** (ESI): calcd for C₂₄H₂₂F₅O₃ [M+H]⁺ 453.1484, found .453.1493.

Preparation of 8,10-dimethoxy-3a-methyl-7-(3-vinylphenyl)-2,3,3a,4,5,7-hexahydrobenzo[c]cyclobuta[i]chromene, 1.4o



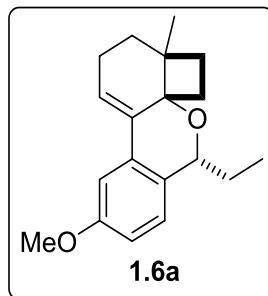
The product **1.4o** was synthesized following Method B and purified using dichloromethane: petroleum ether (1:1), (white solid, 48% yield). **¹H NMR** (600 MHz, CDCl₃): δ = 7.28 (s, 1H), 7.24 (d, J = 7.8 Hz, 1H), 7.17 (t, J = 7.6 Hz, 1H), 7.08 (d, J = 7.5 Hz, 1H), 6.67 (dd, J = 17.6, 10.9 Hz, 1H), 6.65 (d, J = 2.3 Hz, 1H), 6.34 (t, J = 4.3 Hz, 1H), 6.27 (d, J = 2.2 Hz, 1H), 5.82 (s, 1H), 5.68 (d, J = 17.6 Hz, 1H), 5.17 (d, J = 10.9 Hz, 1H), 3.83 (s, 3H), 3.47 (s, 3H), 2.39 (q, J = 10.1 Hz, 1H), 2.32 – 2.26 (m, 2H), 1.71 (ddd, J = 11.0, 8.6, 2.5 Hz, 1H), 1.61 (q, J = 9.7 Hz, 1H), 1.44 – 1.40 (m, 1H), 1.36 – 1.31 (m, 2H), 1.23 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ = 159.6, 156.8, 144.3, 137.3, 136.7, 135.1, 135.1, 127.7, 127.7, 126.4, 124.6, 120.7, 118.6, 113.1, 99.9, 98.0, 72.8, 72.6, 55.3, 55.2, 42.3, 31.4, 29.0, 22.8, 22.7, 21.9. **HRMS** (ESI): calcd for C₂₆H₂₉O₃ [M+H]⁺ 389.2111, found 389.2116.

Preparation of 7-(furan-3-yl)-8,10-dimethoxy-3a-methyl-2,3,3a,4,5,7-hexahydrobenzo-[c]cyclobuta [i]chromene, 1.4p



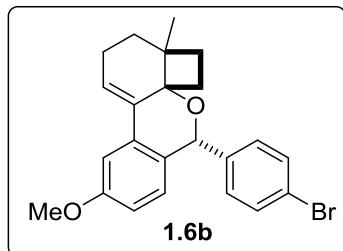
The product **1.4p** was synthesized following Method B and purified using dichloromethane: petroleum ether (1:1), (yellow solid, 77% yield). **¹H NMR** (600 MHz, CDCl₃): δ = 7.23 (t, *J* = 1.7 Hz, 1H), 7.19 – 7.17 (m, 1H), 6.60 (d, *J* = 2.3 Hz, 1H), 6.33 (d, *J* = 2.3 Hz, 1H), 6.26 – 6.24 (m, 2H), 5.91 (s, 1H), 3.83 (s, 3H), 3.67 (s, 3H), 2.32 (q, *J* = 10.0 Hz, 1H), 2.28 – 2.24 (m, 2H), 1.69 (ddd, *J* = 11.1, 8.7, 2.6 Hz, 1H), 1.59 (q, *J* = 9.5 Hz, 1H), 1.45 – 1.40 (m, 1H), 1.34 – 1.28 (m, 2H), 1.27 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ = 159.7, 156.5, 141.9, 140.2, 135.3, 135.2, 128.2, 121.3, 118.3, 110.2, 100.2, 97.7, 72.7, 64.6, 55.3, 55.2, 42.8, 32.5, 29.0, 22.9, 22.7, 21.8. **HRMS** (ESI): calcd for C₂₂H₂₅O₄ [M+H]⁺ 353.1747, found 353.1749.

Preparation of 7-ethyl-10-methoxy-3a-methyl-2,3,3a,4,5,7-hexahydrobenzo[c]cyclobuta[i]chromene, 1.6a



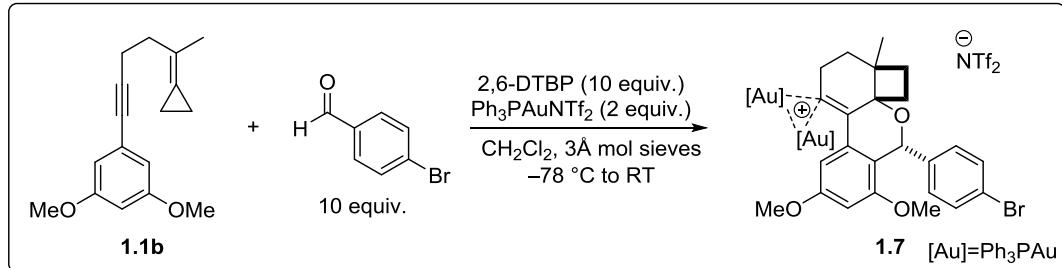
Propionaldehyde was distilled prior to use. The product **1.6a** was synthesized following Method A and purified using hexanes: ethyl acetate (9:1), (yellow oil, 79% yield). **¹H NMR** (600 MHz, CDCl₃): δ = 7.06 (d, *J* = 2.6 Hz, 1H), 6.99 (dd, *J* = 8.6, 0.9 Hz, 1H), 6.76 (dd, *J* = 8.5, 2.6 Hz, 1H), 6.36 – 6.31 (m, 1H), 4.67 (dd, *J* = 8.7, 3.2 Hz, 1H), 3.81 (s, 3H), 2.36 – 2.26 (m, 3H), 2.06 – 1.99 (m, 1H), 1.72 – 1.63 (m, 3H), 1.48 – 1.41 (m, 2H), 1.35 (td, *J* = 10.8, 10.1, 2.1 Hz, 1H), 1.30 (s, 3H), 0.98 (t, *J* = 7.3 Hz, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ = 158.1, 134.7, 133.6, 130.0, 125.3, 119.9, 113.4, 108.1, 72.5, 71.7, 55.2, 41.9, 29.8, 29.3, 28.8, 22.6, 22.5, 21.6, 9.7. **HRMS** (ESI): calcd for C₁₉H₂₅O₂ [M+H]⁺ 286.1883, found 286.1886.

Preparation of 7-(4-bromophenyl)-10-methoxy-3a-methyl-2,3,3a,4,5,7-hexahydrobenzo[c]cyclobuta[i]chromene, 1.6b



The product **1.6b** was synthesized following Method B and purified using dichloromethane: petroleum ether (1:1), (pale yellow crystalline solid, 74% yield). **1H NMR** (600 MHz, CDCl₃): δ = 7.45 (d, *J* = 8.4 Hz, 2H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.08 (d, *J* = 2.6 Hz, 1H), 6.64 (dd, *J* = 8.6, 2.6 Hz, 1H), 6.56 (dd, *J* = 8.6, 0.8 Hz, 1H), 6.42 (dd, *J* = 5.9, 2.9 Hz, 1H), 5.68 (s, 1H), 3.80 (s, 3H), 2.47 (q, *J* = 10.1 Hz, 1H), 2.37 – 2.29 (m, 2H), 1.83 (ddd, *J* = 11.1, 8.7, 2.6 Hz, 1H), 1.69 (q, *J* = 9.4 Hz, 1H), 1.51 – 1.46 (m, 1H), 1.45 – 1.38 (m, 2H), 1.23 (s, 3H). **13C NMR** (151 MHz, CDCl₃): δ = 158.4, 142.1, 134.1, 133.4, 131.4, 130.4, 128.9, 127.5, 121.7, 120.7, 113.4, 107.8, 74.5, 73.7, 55.2, 41.9, 29.9, 29.3, 22.7, 22.6, 21.7. **HRMS** (ESI): calcd for C₂₃H₂₃BrNaO₂ [M+Na]⁺ 433.0774, found 433.0762.

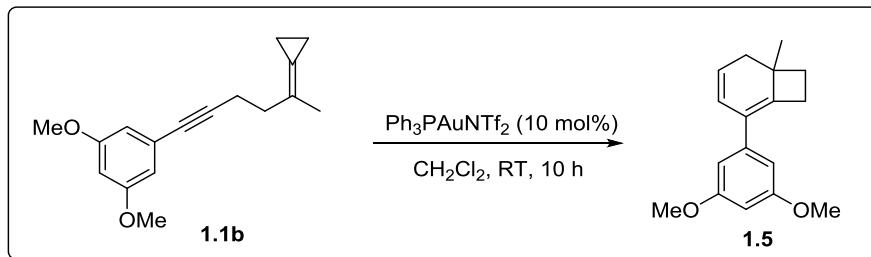
1.8.5 Isolation of di-gold vinyl 1.7



In an oven dried vial, enyne **1.1b** (2 mg, 0.0078 mmol), 4-bromobenzaldehyde (14 mg, 0.078 mmol) and 2,6-di-*tert*-butylpyridine (polymer bound, 1.8 mmol/g loading; 43 mg, 0.078 mmol) were dissolved in 1 mL anhydrous CH₂Cl₂. Activated molecular sieves (~60 mg) were added. The solution was cooled to -78 °C. Ph₃PAuNTf₂ (11.5 mg, 0.0156 mmol) was added to the solution. The mixture was stirred and allowed to warm to room temperature. The solution was passed through a glass plug of cotton to remove the resin base, and the solvent was evaporated under reduced pressure. The resulting residue was washed with 2 mL anhydrous diethyl ether at -78 °C to remove excess aldehyde (**7** is slightly soluble in ether). The ether was discarded, and the residual solvent was removed under reduced pressure. The washing process was repeated 4 times, and resulted in an orange oil (4 mg, 0.0024 mmol, 31%). Protodemetallated product **1.4k** and [(Ph₃P)₂Au]⁺[NTf₂]⁻ were always observed as impurities. Continuous washing with ether removed **1.4k**, but increased the [(Ph₃P)₂Au]⁺[NTf₂]⁻ impurity.

¹H NMR (600 MHz, CDCl₃): δ = 8.03 (d, *J* = 2.2, 1H), 7.59 – 7.35 (m, 30H), 6.80 (d, *J* = 8.4, 2H), 6.55 (d, *J* = 2.2, 1H), 6.49 (d, *J* = 8.3, 2H), 5.98 (s, 1H), 3.49 (s, 3H), 3.36 (s, 3H), 3.13 – 3.08 (m 1H), 2.68 – 2.58 (m, 2H), 1.84 – 1.71 (m, 3H), 1.53 – 1.48 (m, 1H), 1.45 – 1.40 (m, 1H), 1.28 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃): δ = 159.9, 156.9, 140.7, 134.1, 133.9, 133.8, 133.7, 133.6, 133.0, 132.5, 132.2, 130.6, 130.1, 129.7, 129.4, 129.4, 128.8, 128.4, 127.6, 127.2, 126.9, 121.0, 117.5, 103.0, 101.1, 74.2, 72.6, 55.4, 55.1, 34.9, 32.5, 29.7, 28.7, 22.9, 21.8. **³¹P NMR** (243 MHz, CDCl₃): δ = 38.5 (1P), 33.6 (1P). **HRMS** (ESI): calcd for C₆₀H₅₄O₃P₂Au₂Br₁ [M]⁺ 1357.2063, found 1357.2055. Note: ¹H, ¹³C and ³¹P NMR contain the [(Ph₃P)₂Au]⁺[NTf₂]⁻ impurity.

1.8.6 Isolation of cycloisomer 1.5



In an oven dried vial, enyne **1.1b** (10 mg, 0.039 mmol) was dissolved in 1 mL anhydrous CH_2Cl_2 . $\text{Ph}_3\text{PAuNTf}_2$ (2.9 mg, 0.00039 mmol) was added, and the mixture was stirred for 10 hours. Upon evaporation of the solvent under reduced pressure, the residue was purified by silica gel column chromatography (Hexanes: ethyl acetate 10:1) to afford the cycloisomer **1.5** in pure form (8.2 mg, 82% yield). **1H NMR** (600 MHz, CDCl_3) δ = 6.43 (d, J = 2.3, 2H), 6.34 (t, J = 2.3, 1H), 6.24 (dd, J = 9.7, 3.5, 1H), 5.82 (ddd, J = 8.9, 6.4, 1.8, 1H), 3.79 (s, 6H), 3.28 (dt, J = 17.6, 9.1, 1H), 2.92 – 2.81 (m, 1H), 2.31 (dt, J = 16.7, 3.0, 1H), 2.02 (dd, J = 16.6, 6.4, 1H), 1.96 (td, J = 9.9, 3.1, 1H), 1.86 (q, J = 8.8, 1H), 1.25 (s, 3H). **13C NMR** (151 MHz, CDCl_3) δ = 160.8, 143.9, 140.0, 126.0, 125.3, 124.1, 104.5, 98.7, 55.4, 40.7, 35.4, 34.5, 31.0, 20.8. **HRMS** (ESI): calcd for $\text{C}_{17}\text{H}_{20}\text{O}_2$ [M+H]⁺ 257.1536, found 257.1536.

1.8.7 Experimental procedure for acid/base experiments

Reactions with acid

$[\text{Ph}_2\text{NH}_2][\text{BF}_4]$ was synthesized according to a literature procedure.⁵⁹ In an oven dried vial, enyne **1.1b** (6 mg, 0.023 mmol), $[\text{Ph}_2\text{NH}_2][\text{BF}_4]$ (6 mg, 0.023 mmol), and propionaldehyde (8.5 μL , 0.117 mmol) were dissolved in 0.5 mL anhydrous CH_2Cl_2 . $\text{Ph}_3\text{PAuNTf}_2$ (1.7 mg, 0.0023 mmol) was added, and the mixture was stirred for 1 hour. The solution was pushed through a short plug of silica gel, eluting with CH_2Cl_2 , and analyzed by GCMS. This reaction was repeated with 5 equivalents of acid.

Reactions with base

In an oven dried vial, enyne **1.1b** (6 mg, 0.023 mmol), N-methyldiphenylamine (4.1 μ L, 0.023 mmol), and propionaldehyde (8.5 μ L, 0.117 mmol) were dissolved in 0.5 mL anhydrous CH₂Cl₂. Ph₃PAuNTf₂ (1.7 mg, 0.0023 mmol) was added, and the mixture was stirred for 1 hour. The solution was pushed through a short plug of silica gel, eluting with CH₂Cl₂, and analyzed by GCMS. This reaction was repeated with 5 equivalents of base.

1.8.8 Experimental procedure for competition experiments

In an NMR tube, enyne **1.1b** (8 mg, 0.031 mmol), p-CF₃-benzaldehyde (21 μ L, 0.155 mmol), and benzaldehyde (16 μ L, 0.155 mmol) were dissolved in 0.5 mL CD₂Cl₂. The reaction was cooled to -78 °C in a dry ice/acetone bath. Ph₃PAuNTf₂ (2.3 mg, 0.0031 mmol) was added, and the reaction was transferred to a cryobath set at -35 °C for 12 hours. The resulting mixture was analyzed by ¹H NMR. The reaction was repeated with p-anisaldehyde (19 μ L, 0.155 mmol) in place of benzaldehyde.

1.8.9 NMR spectra of new compounds

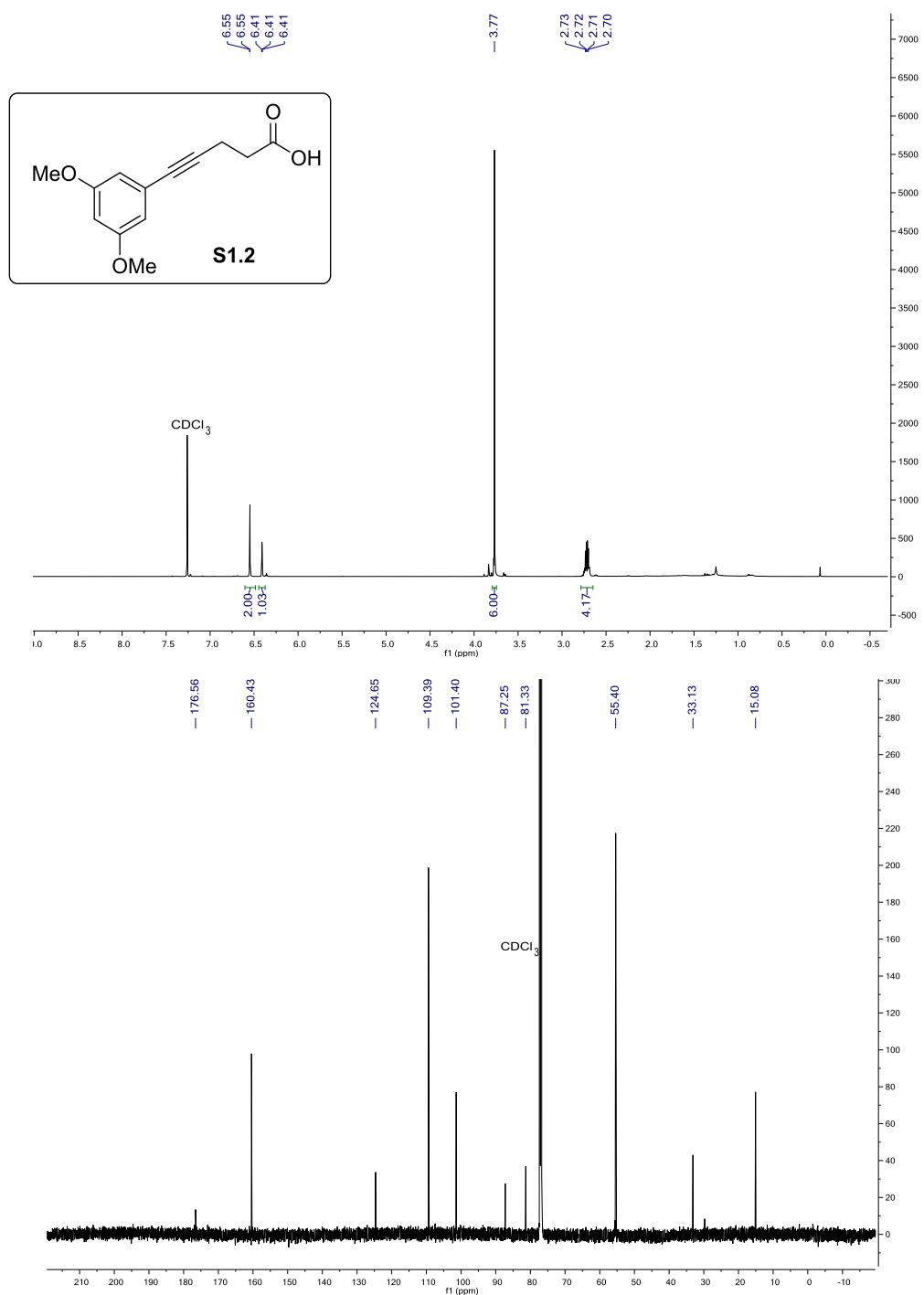


Figure 1.7. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **S1.2** in CDCl₃ at 25 °C.

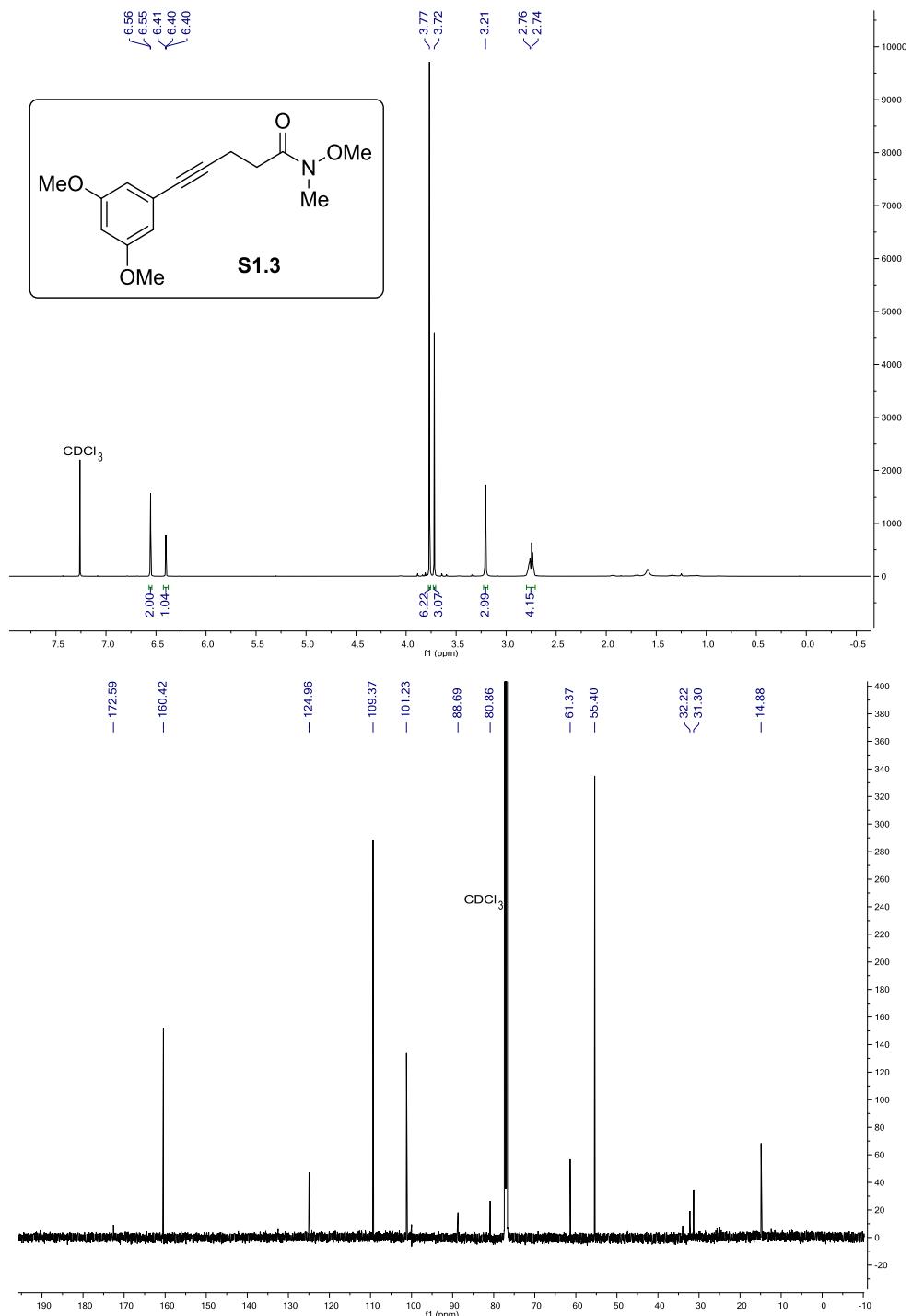


Figure 1.8. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **S1.3** in CDCl_3 at 25 °C.

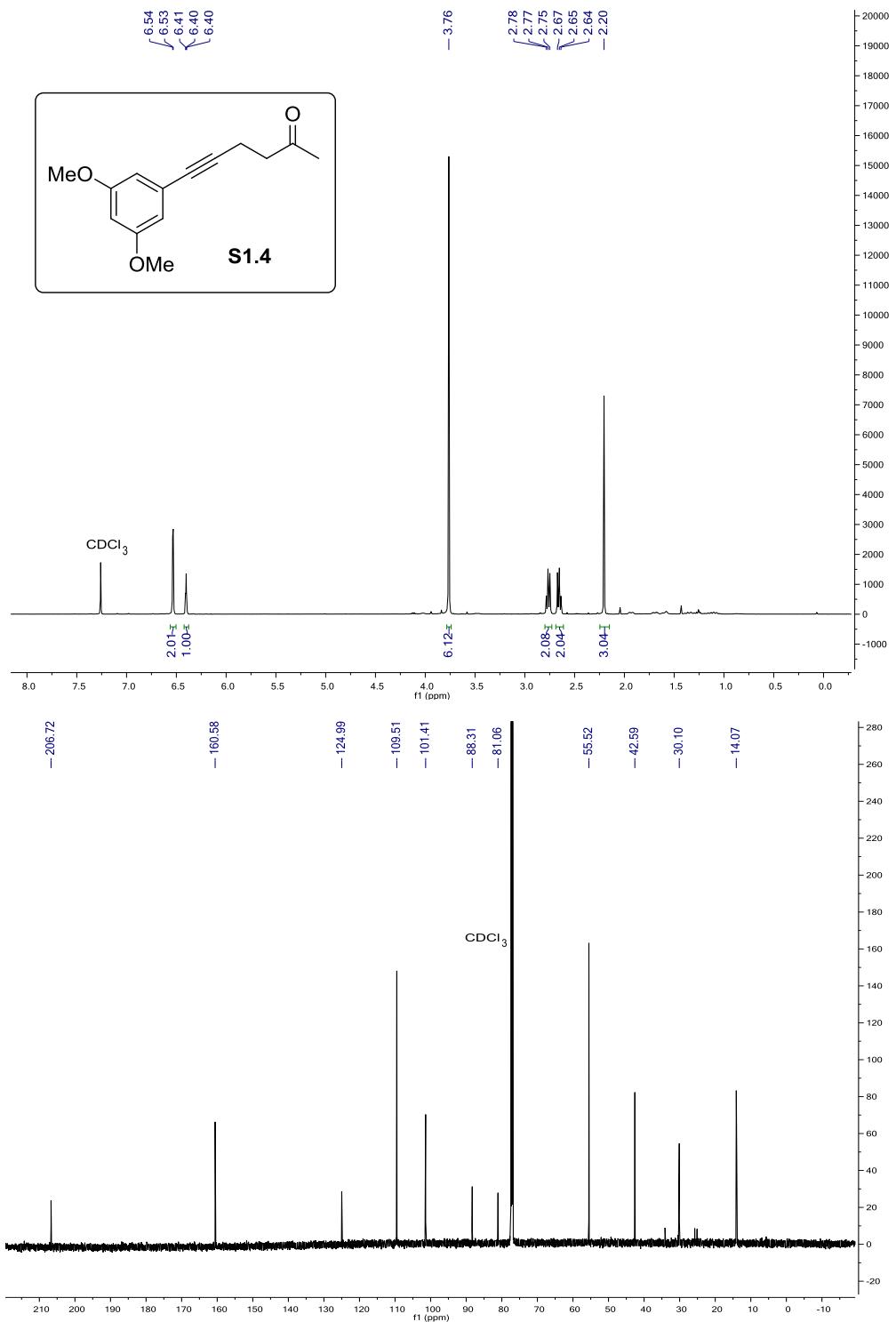


Figure 1.9. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **S1.4** in CDCl_3 at 25 °C.

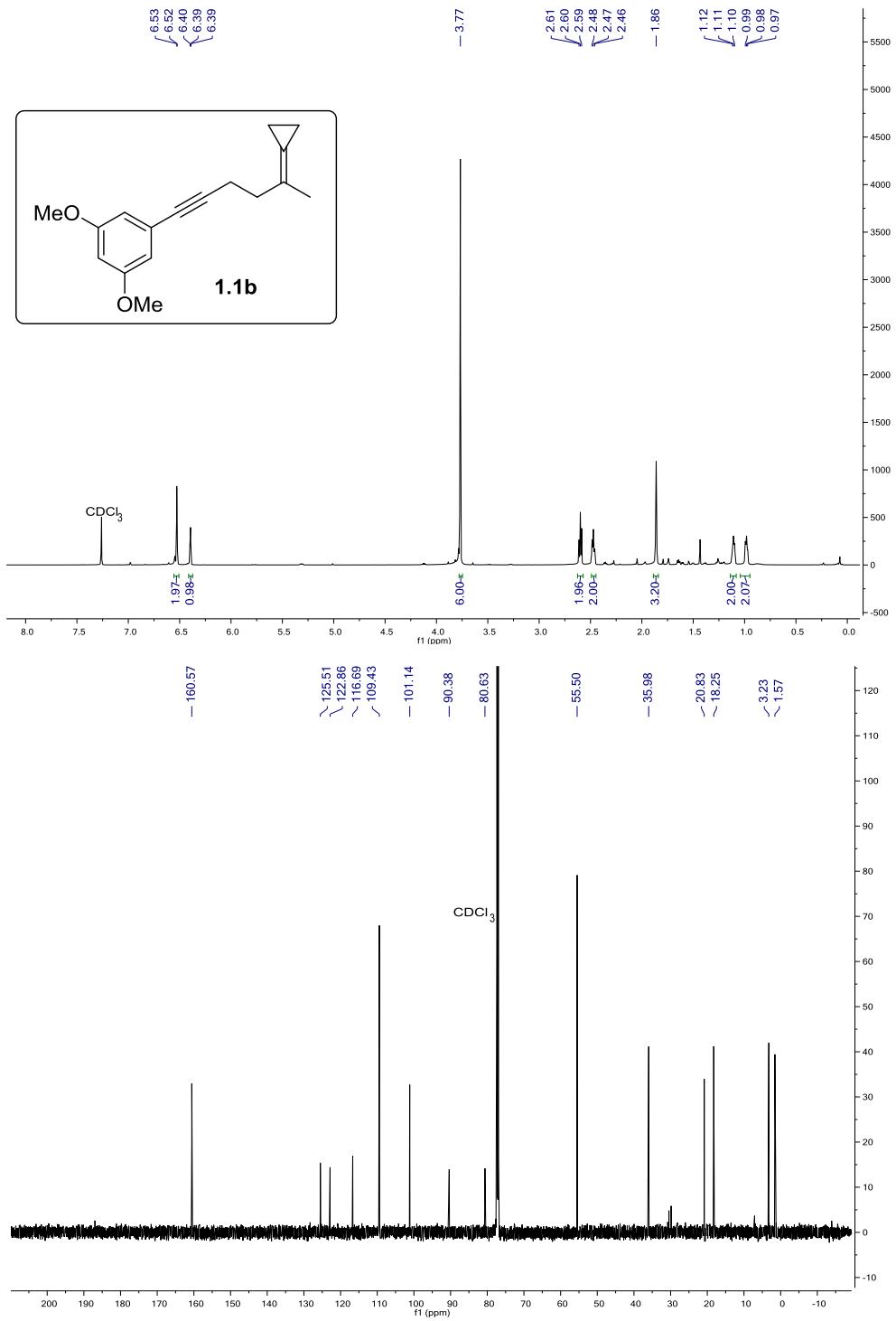


Figure 1.10. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **1.1b** in CDCl_3 at 25 °C.

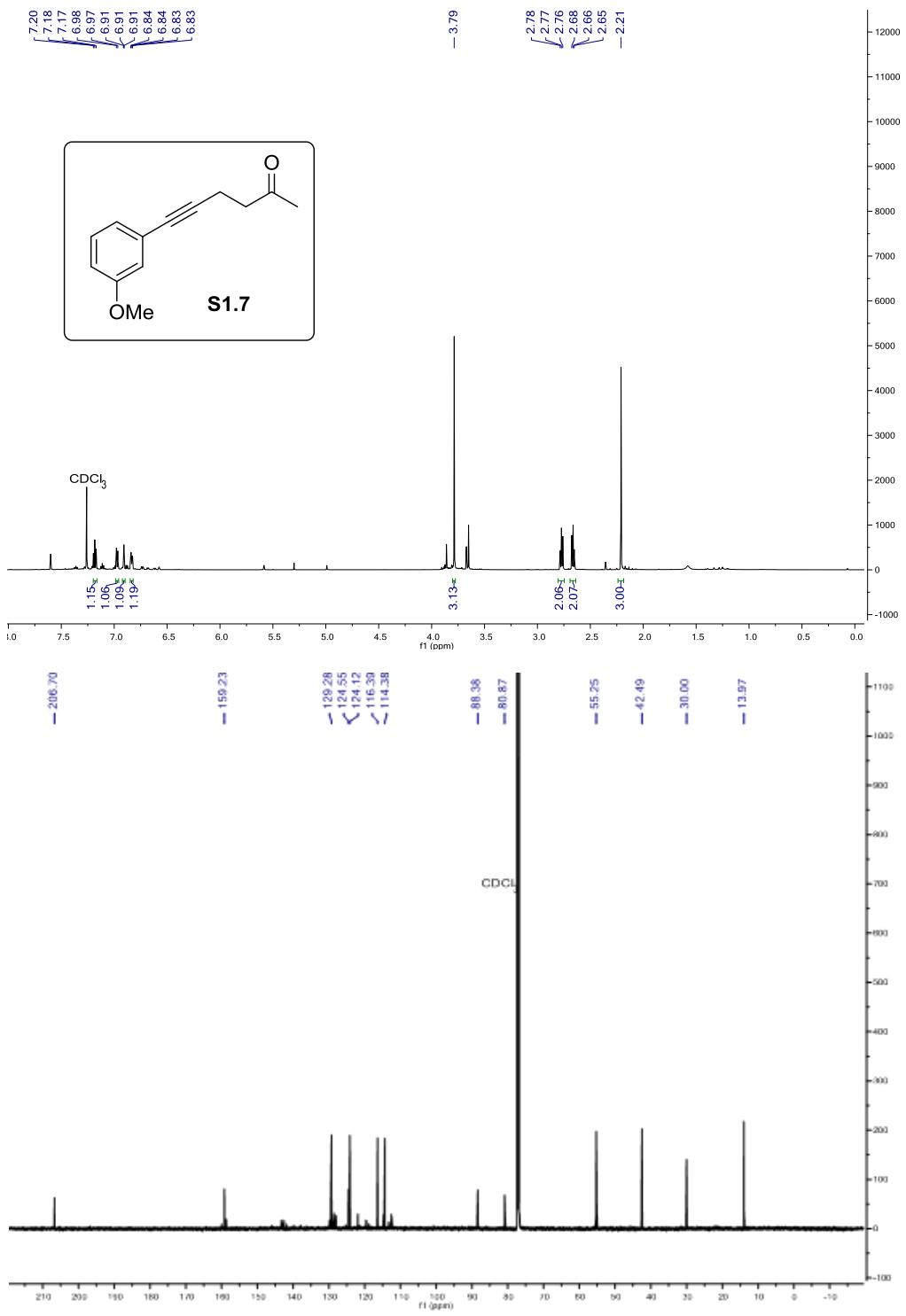


Figure 1.11. ¹H and ¹³C{¹H} NMR of S1.7 in CDCl₃ at 25 °C.

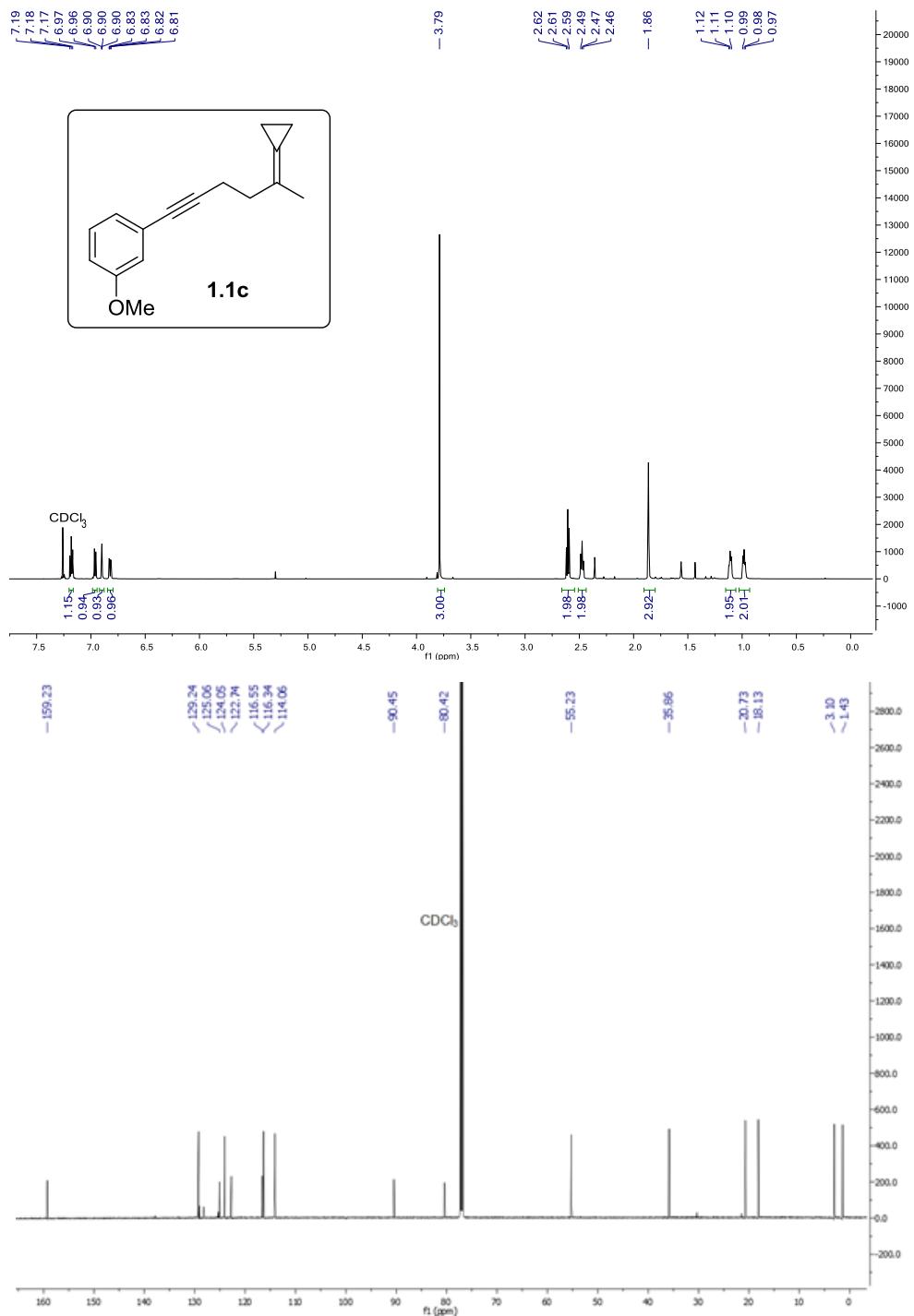


Figure 1.12. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **1.1c** in CDCl_3 at 25 °C.

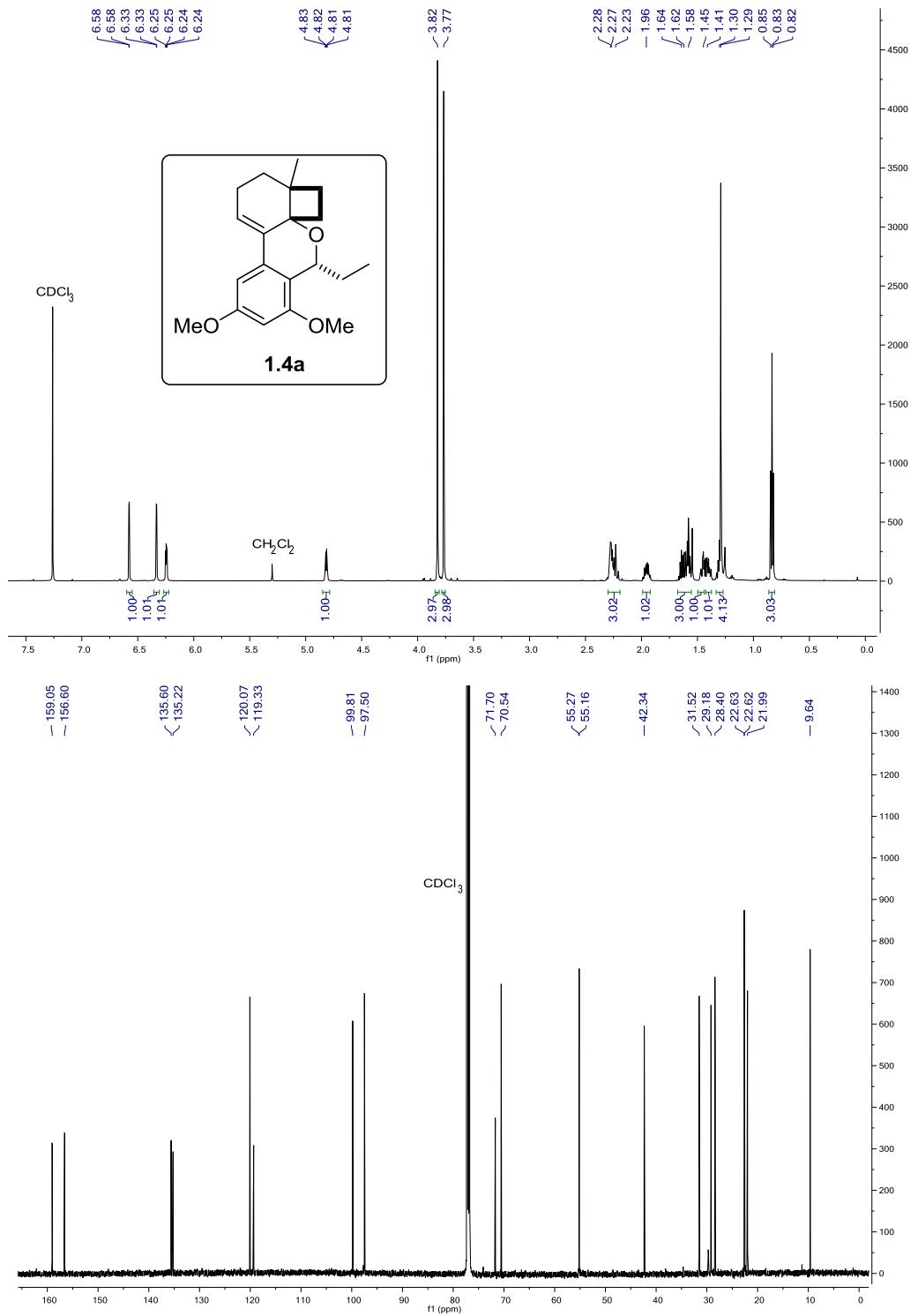


Figure 1.13. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **1.4a** in CDCl_3 at 25 °C.

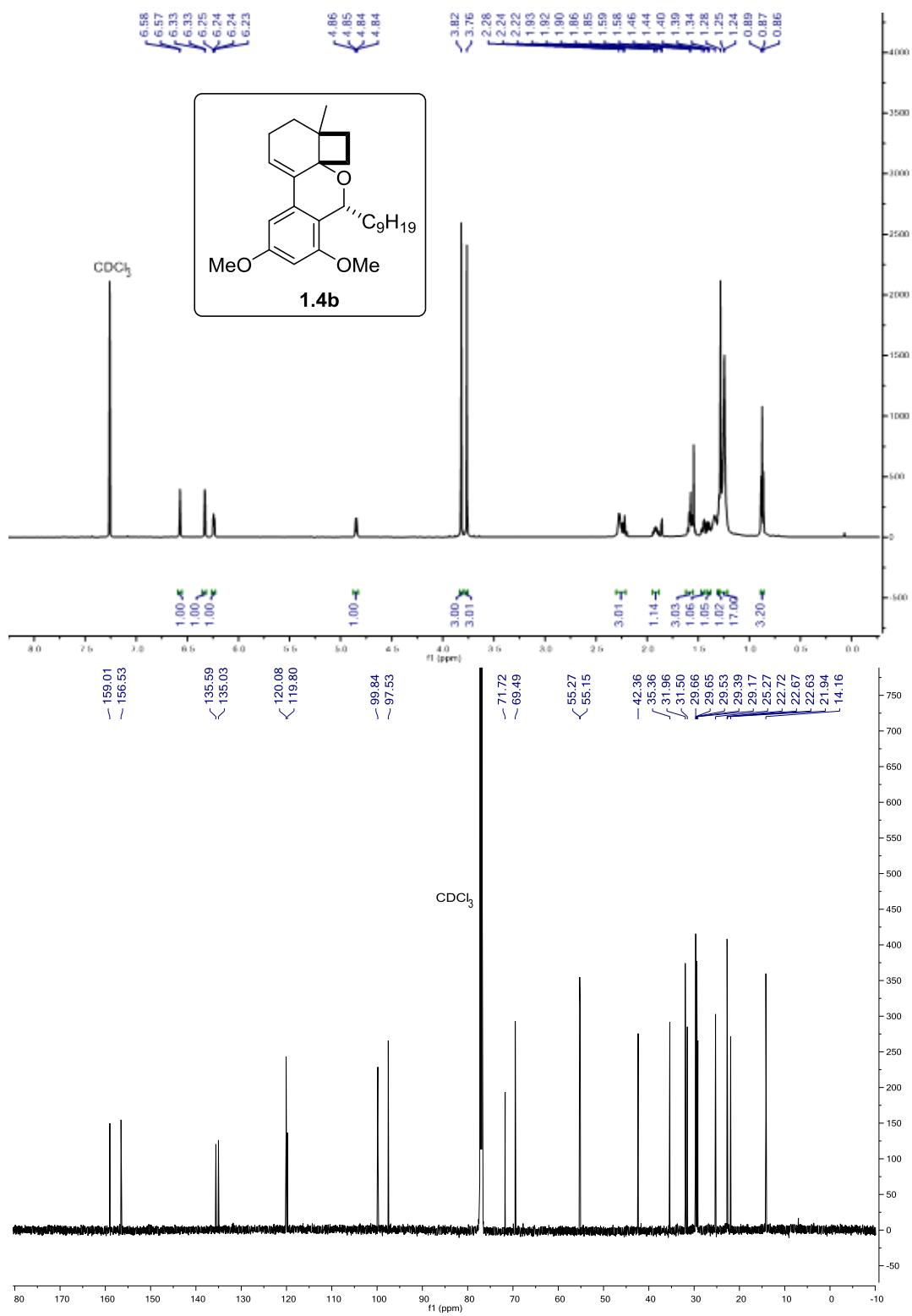


Figure 1.14. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **1.4b** in CDCl_3 at 25 °C.

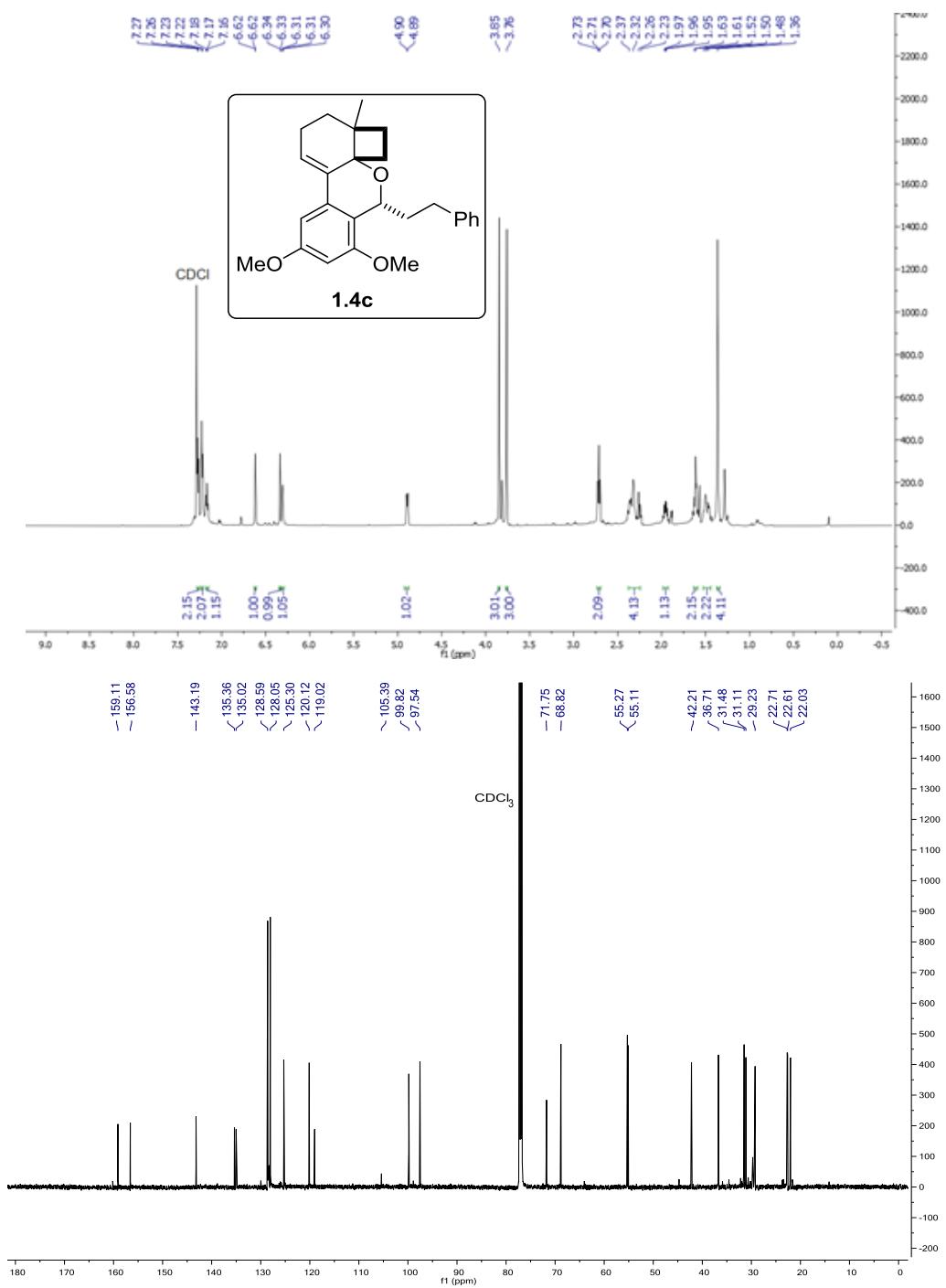


Figure 1.15. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **1.4c** in CDCl_3 at 25 °C.

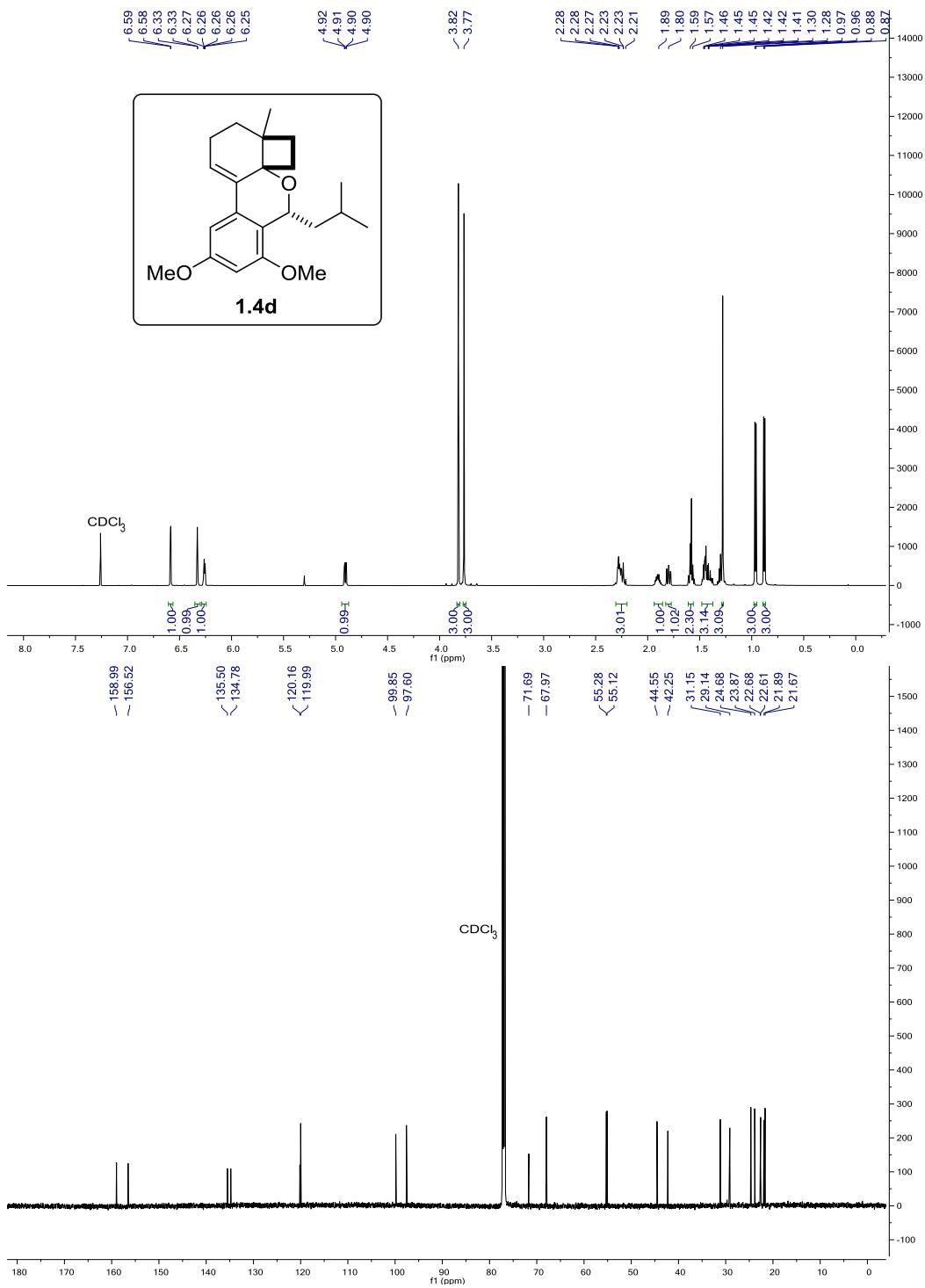


Figure 1.16. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **1.4d** in CDCl_3 at 25 °C.

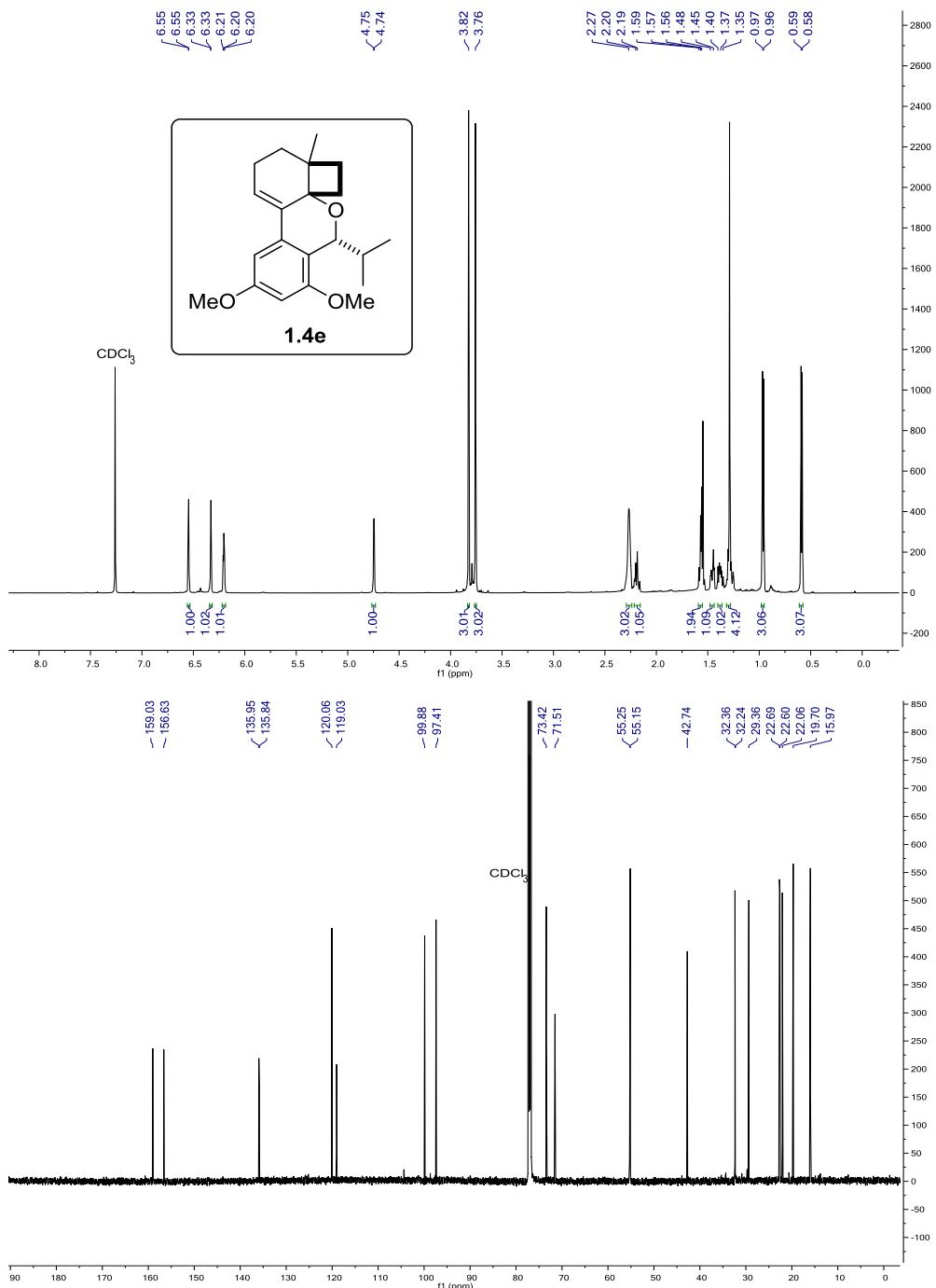


Figure 1.17. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **1.4e** in CDCl_3 at 25 °C.

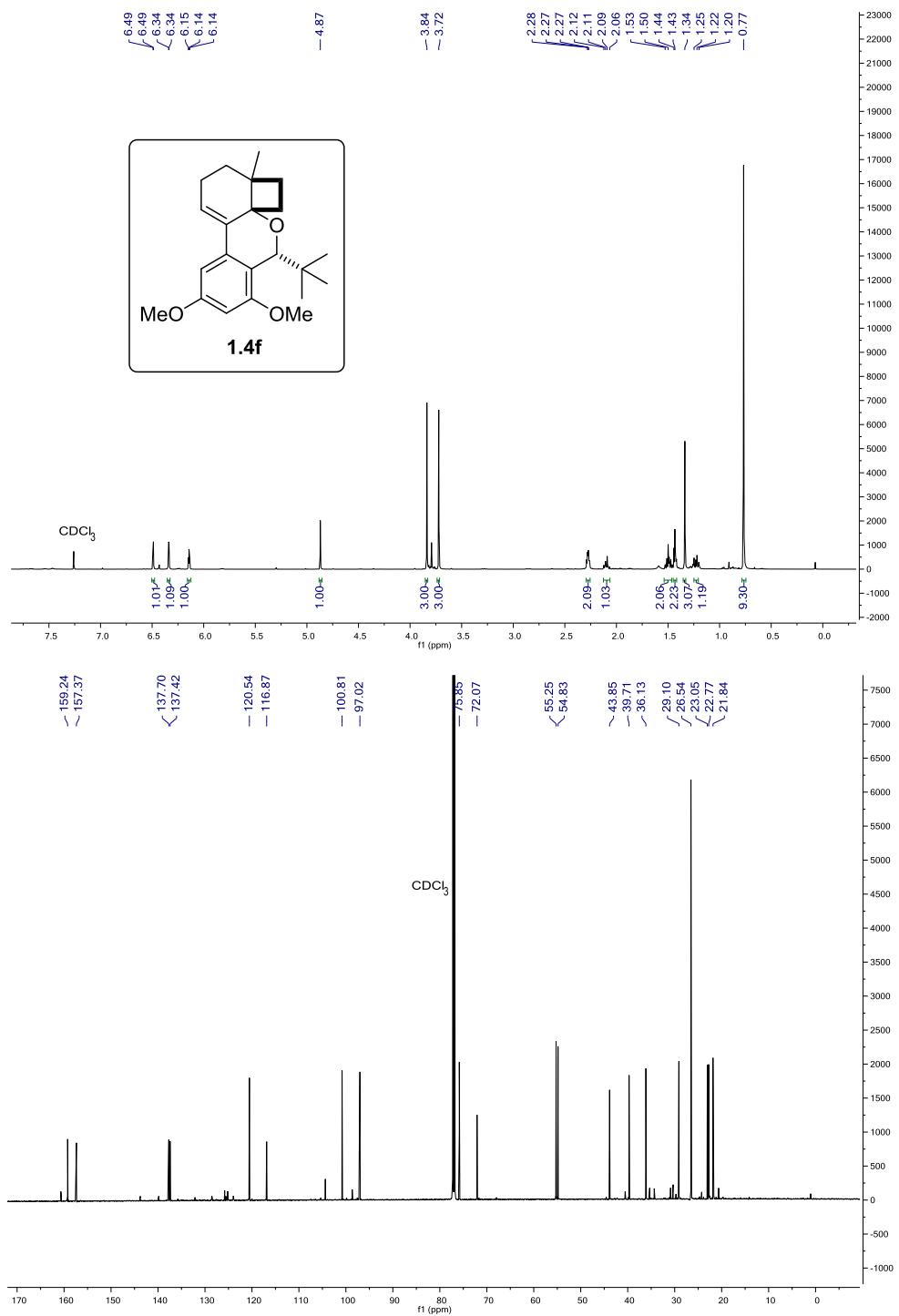


Figure 1.18. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **1.4f** in CDCl_3 at 25 °C.

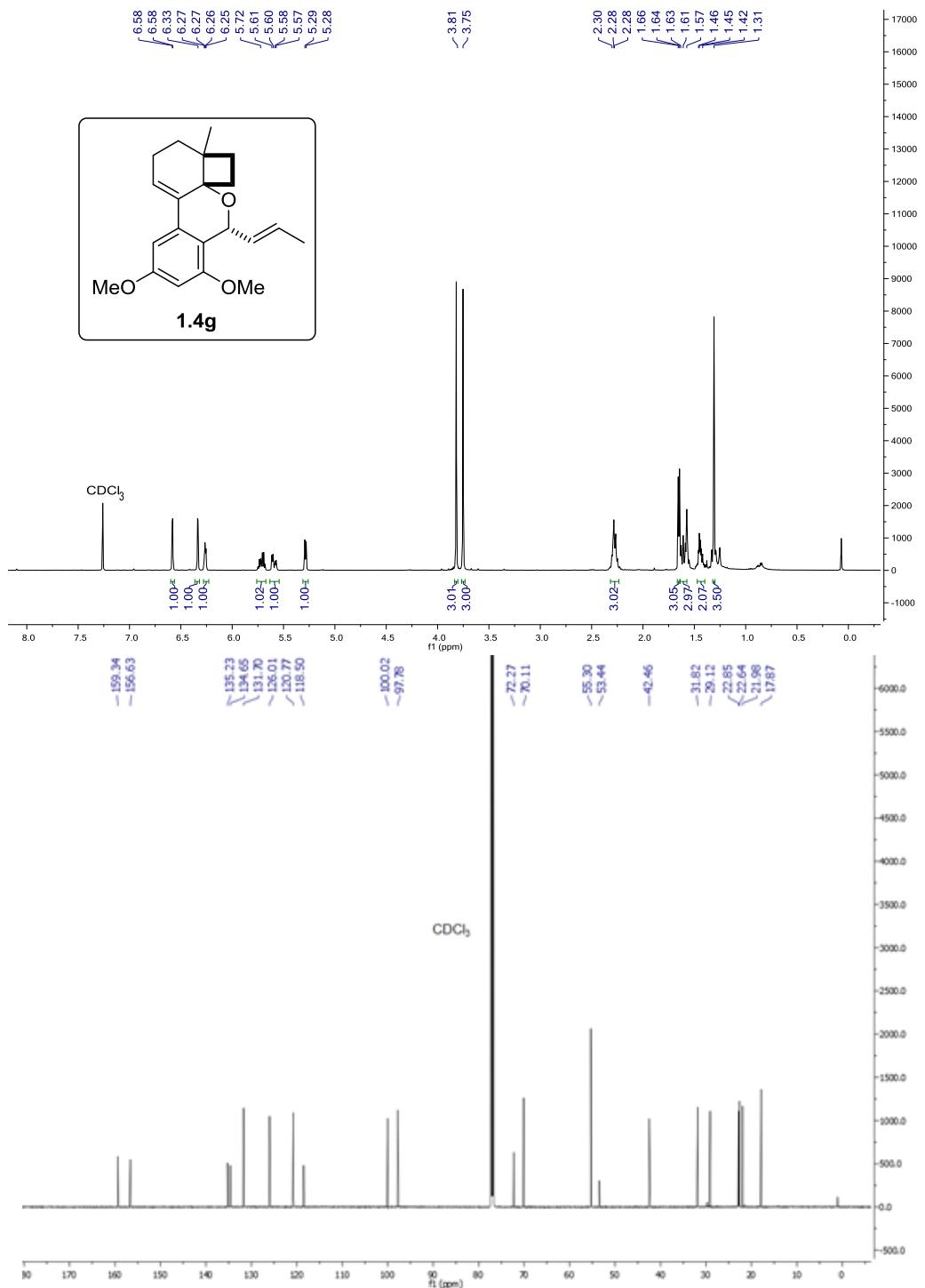


Figure 1.19. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **1.4g** in CDCl_3 at 25 °C.

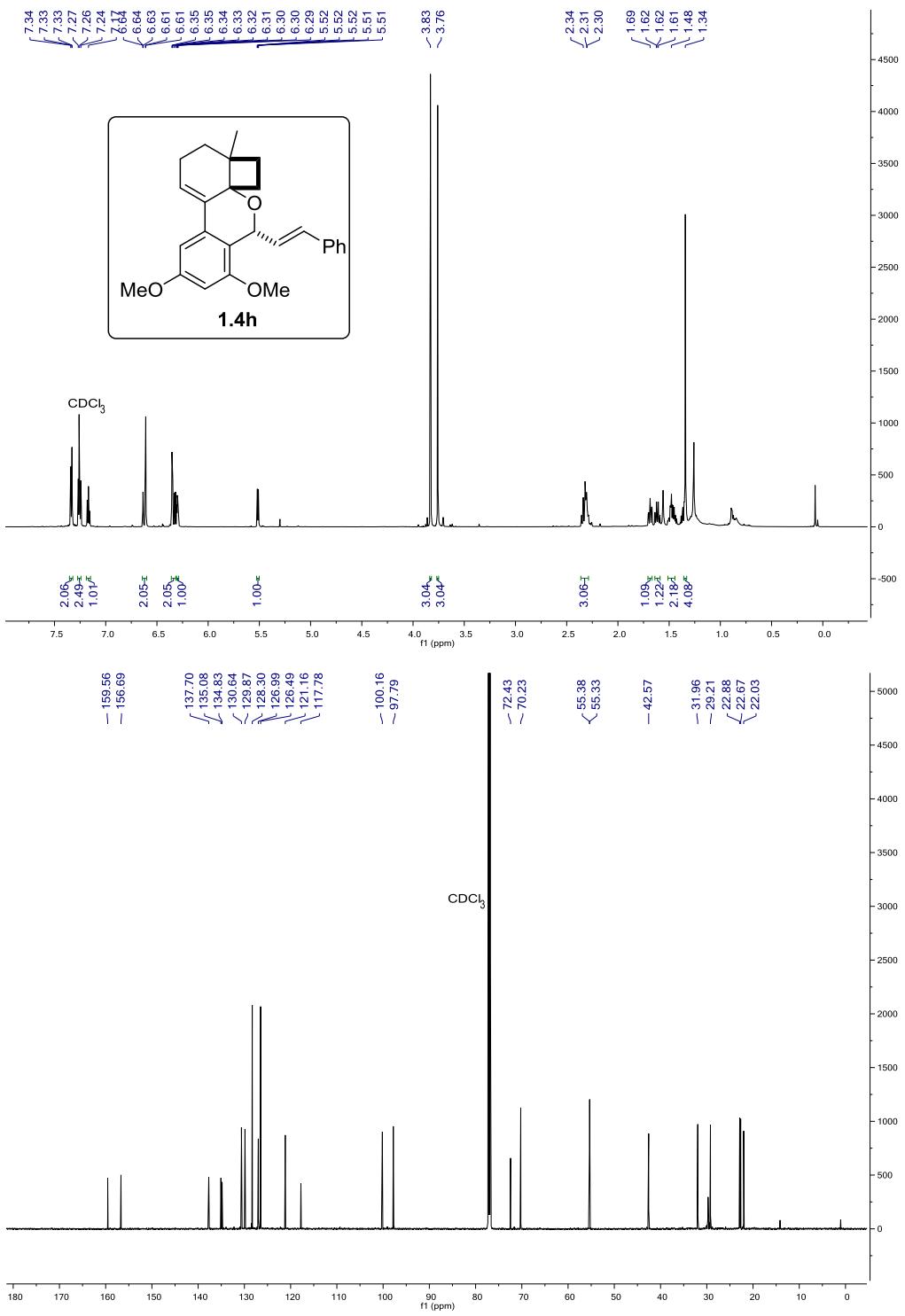


Figure 1.20. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **1.4h** in CDCl_3 at 25 °C.

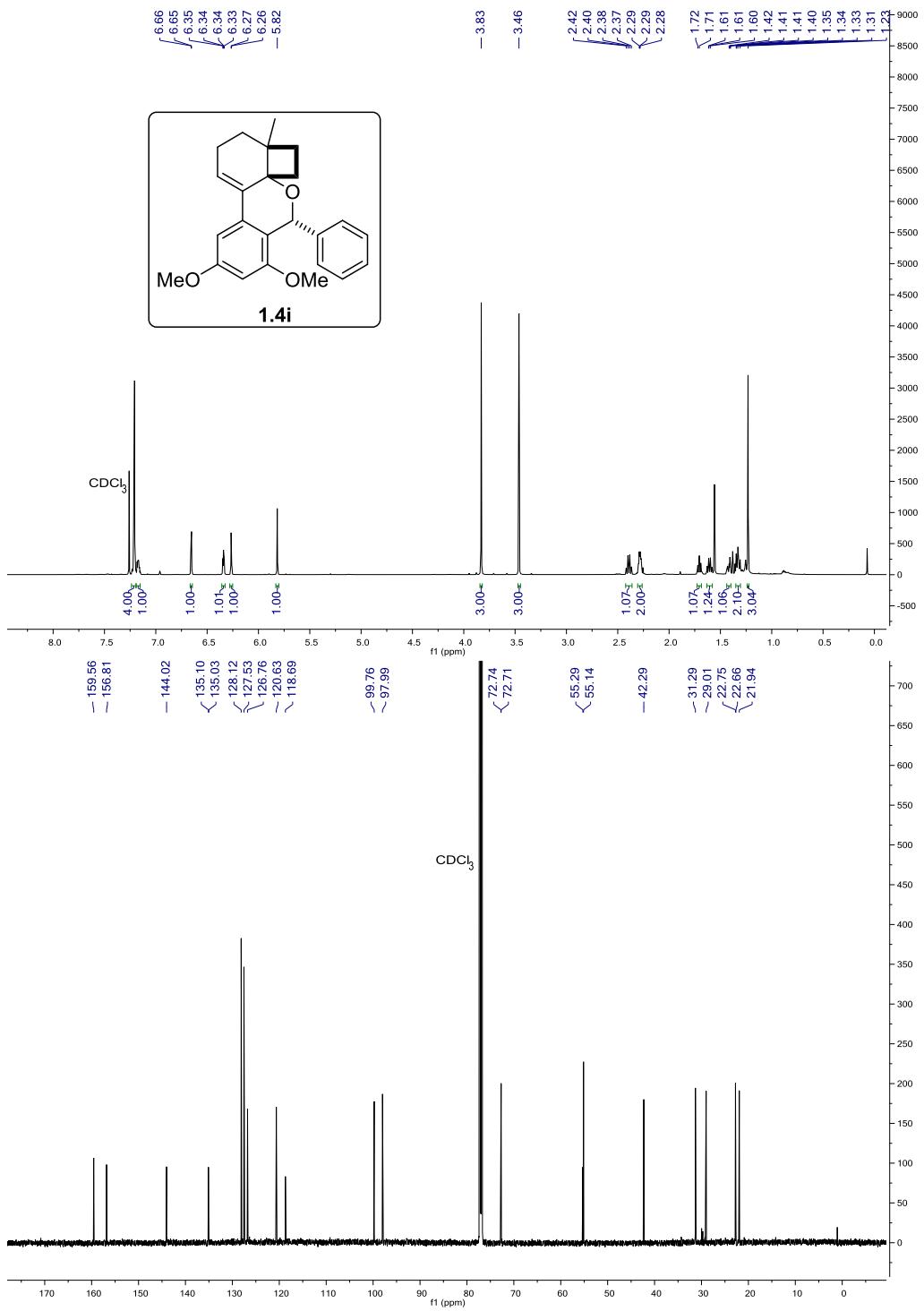
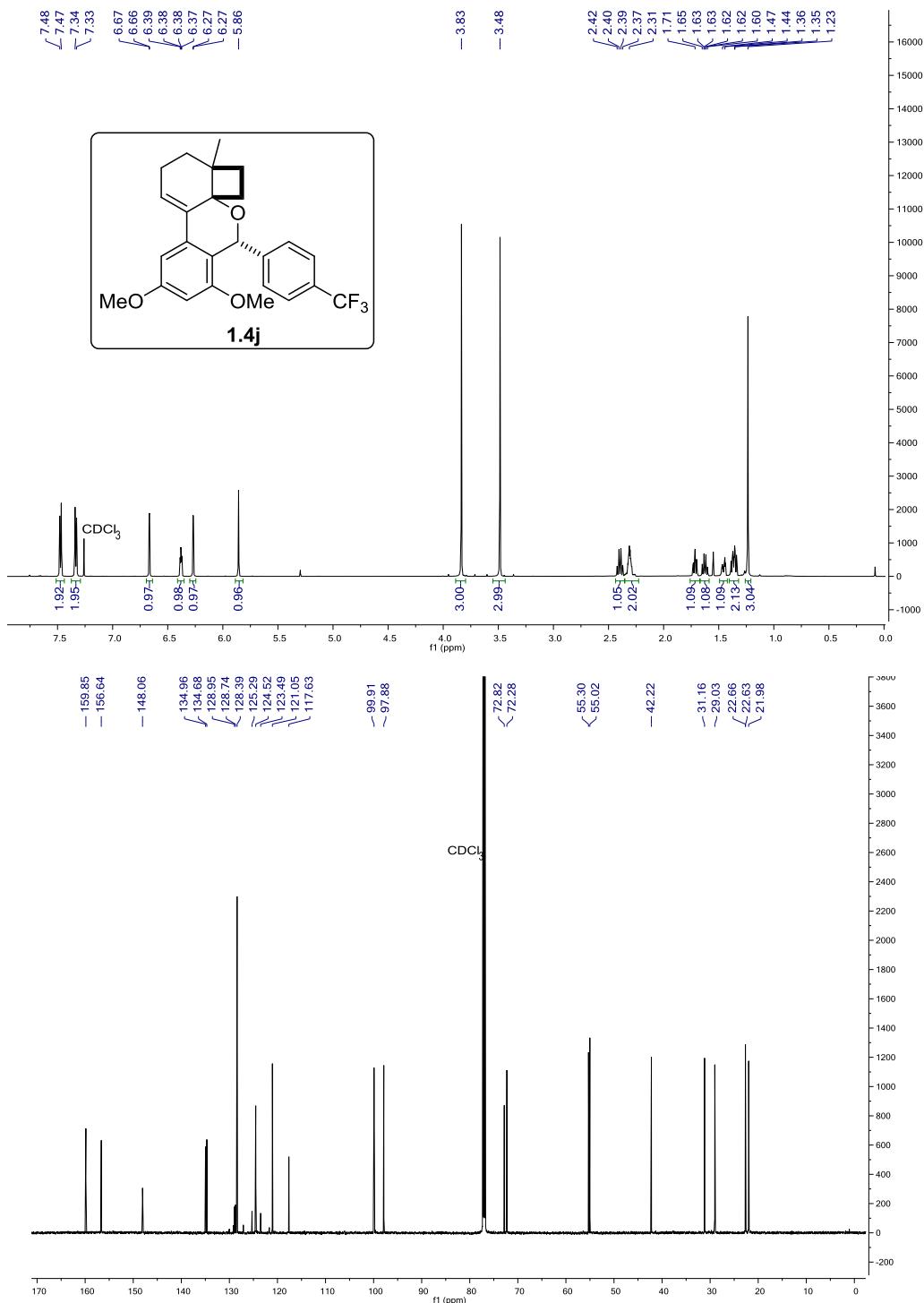


Figure 1.21. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **1.4i** in CDCl_3 at 25 °C.



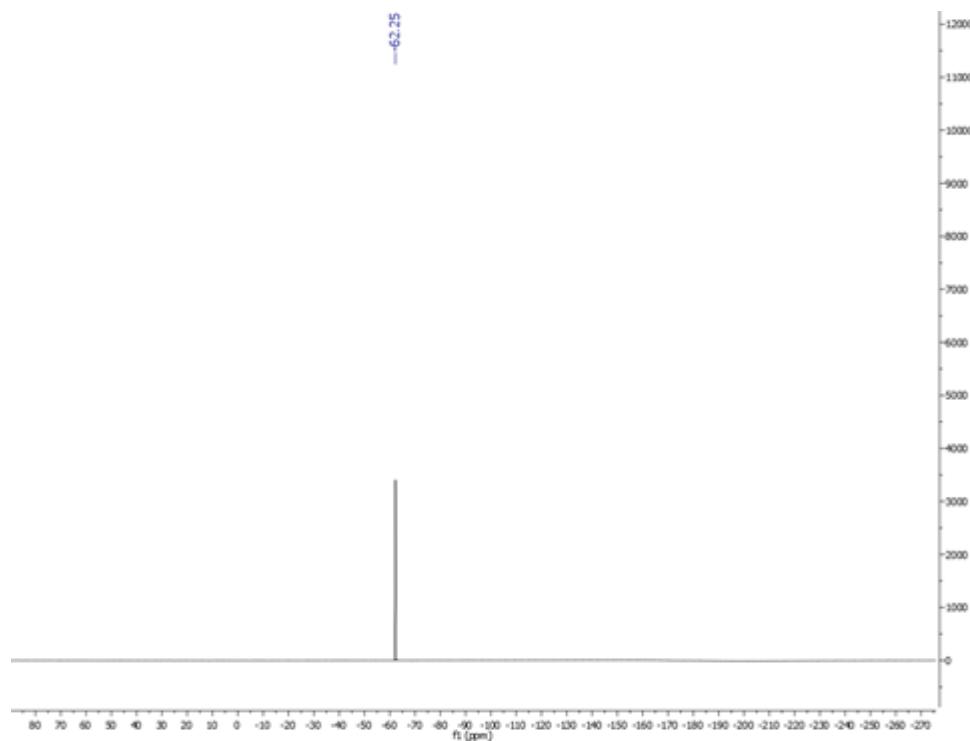
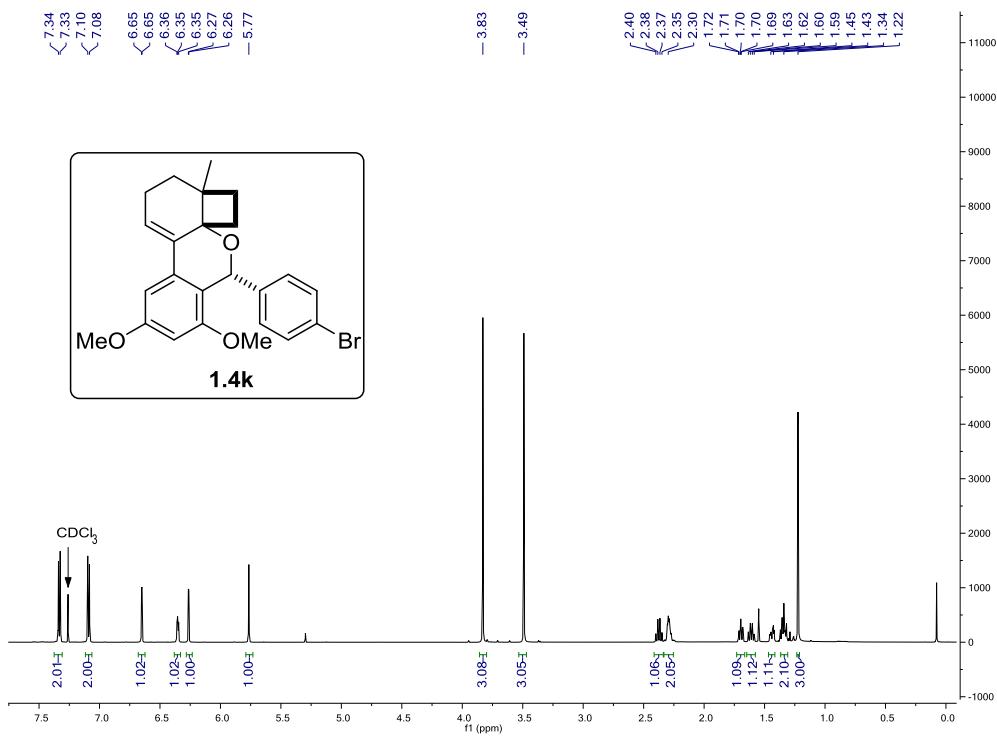


Figure 1.22. ¹H, ¹³C{¹H}, and ¹⁹F{¹H} NMR of **1.4j** in CDCl₃ at 25 °C.



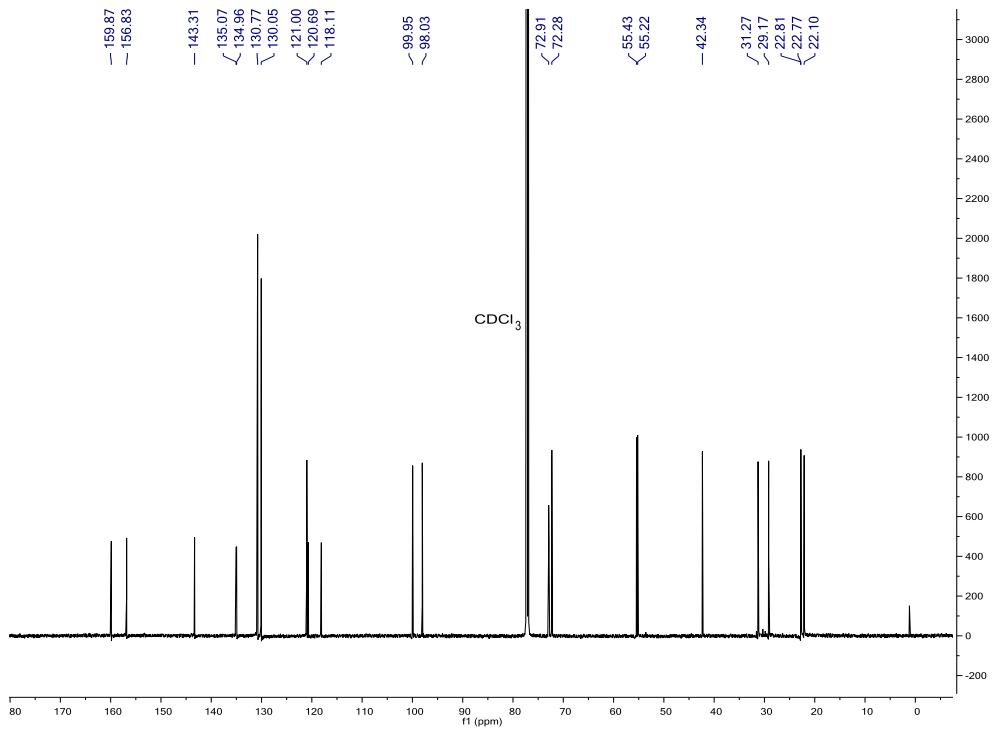
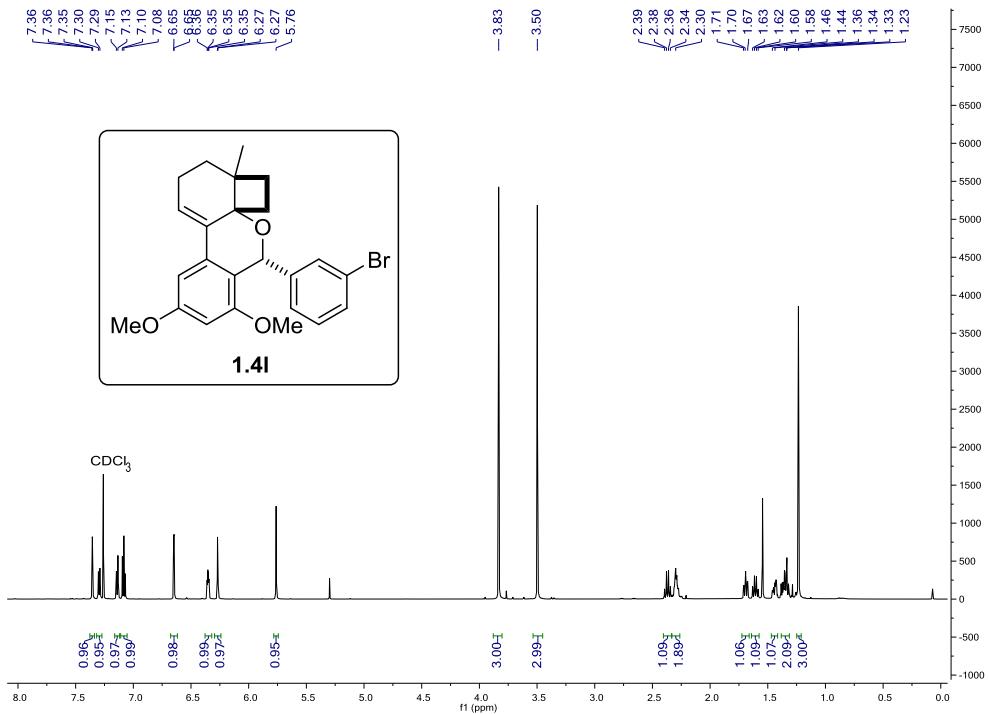


Figure 1.23. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **1.4k** in CDCl_3 at 25 °C.



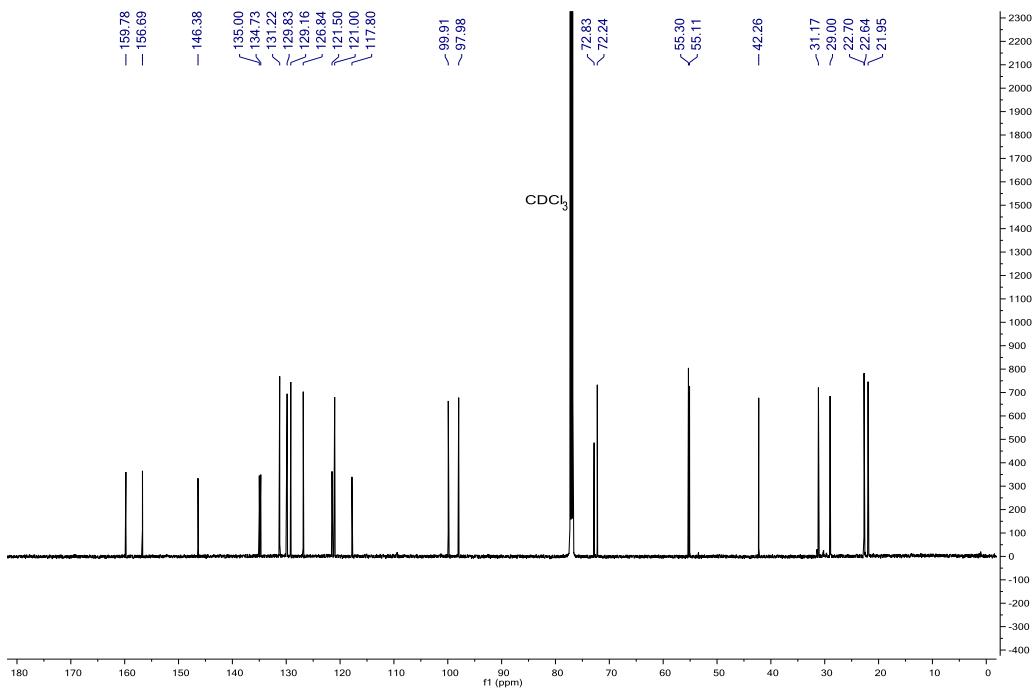
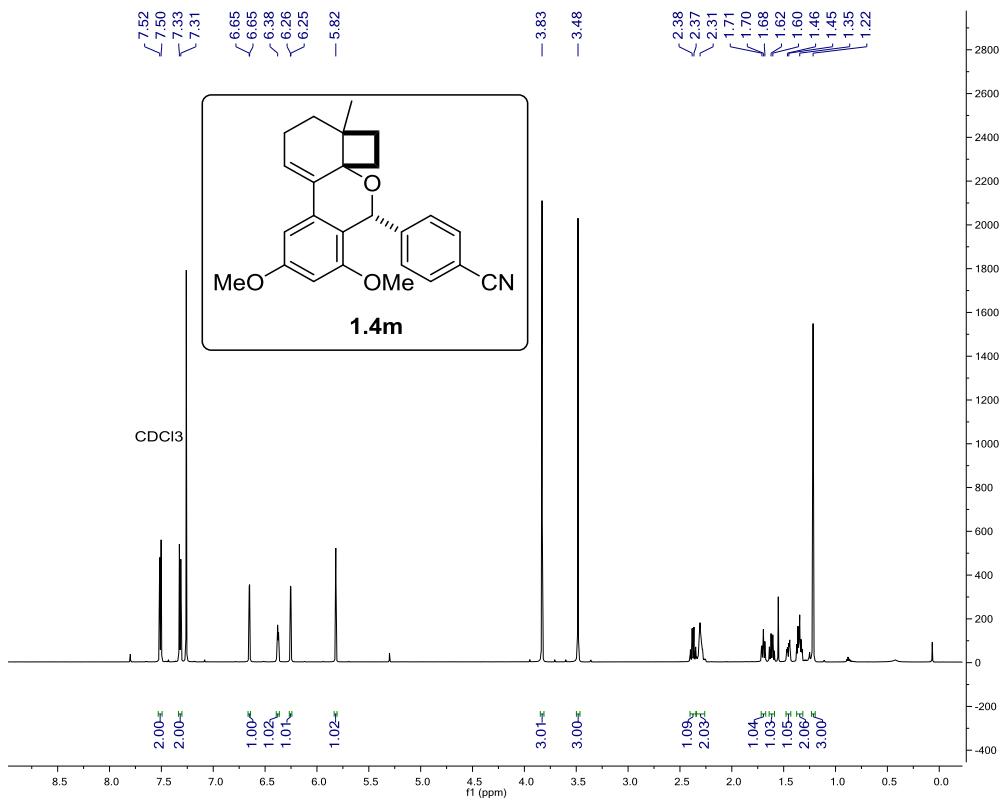


Figure 1.24. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **1.4l** in CDCl_3 at 25°C .



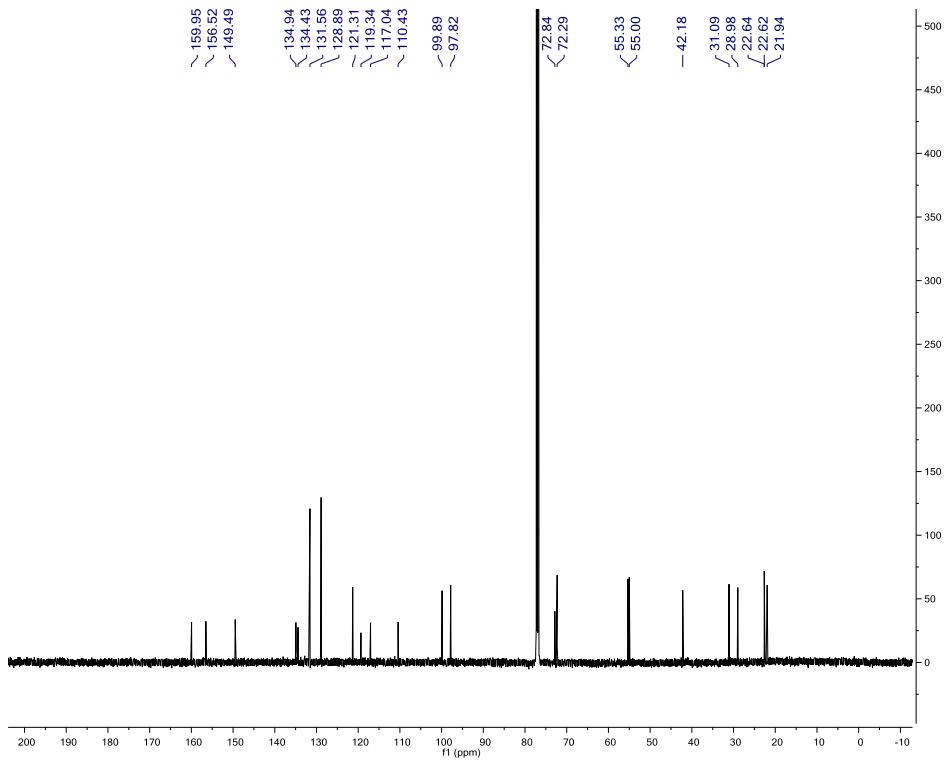
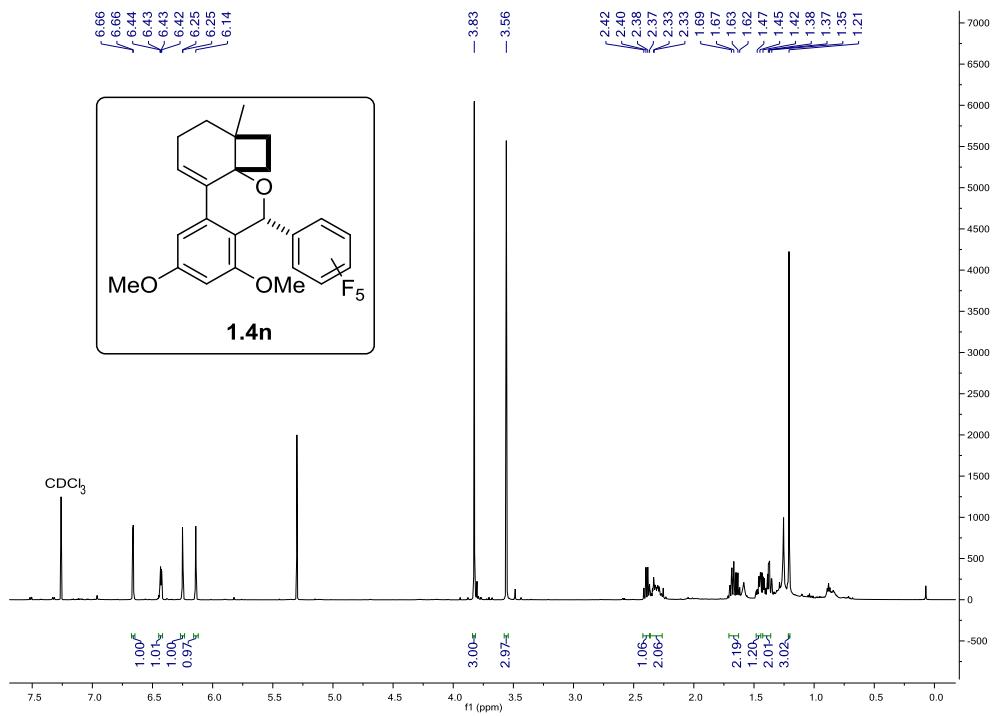


Figure 1.25. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **1.4m** in CDCl_3 at 25°C .



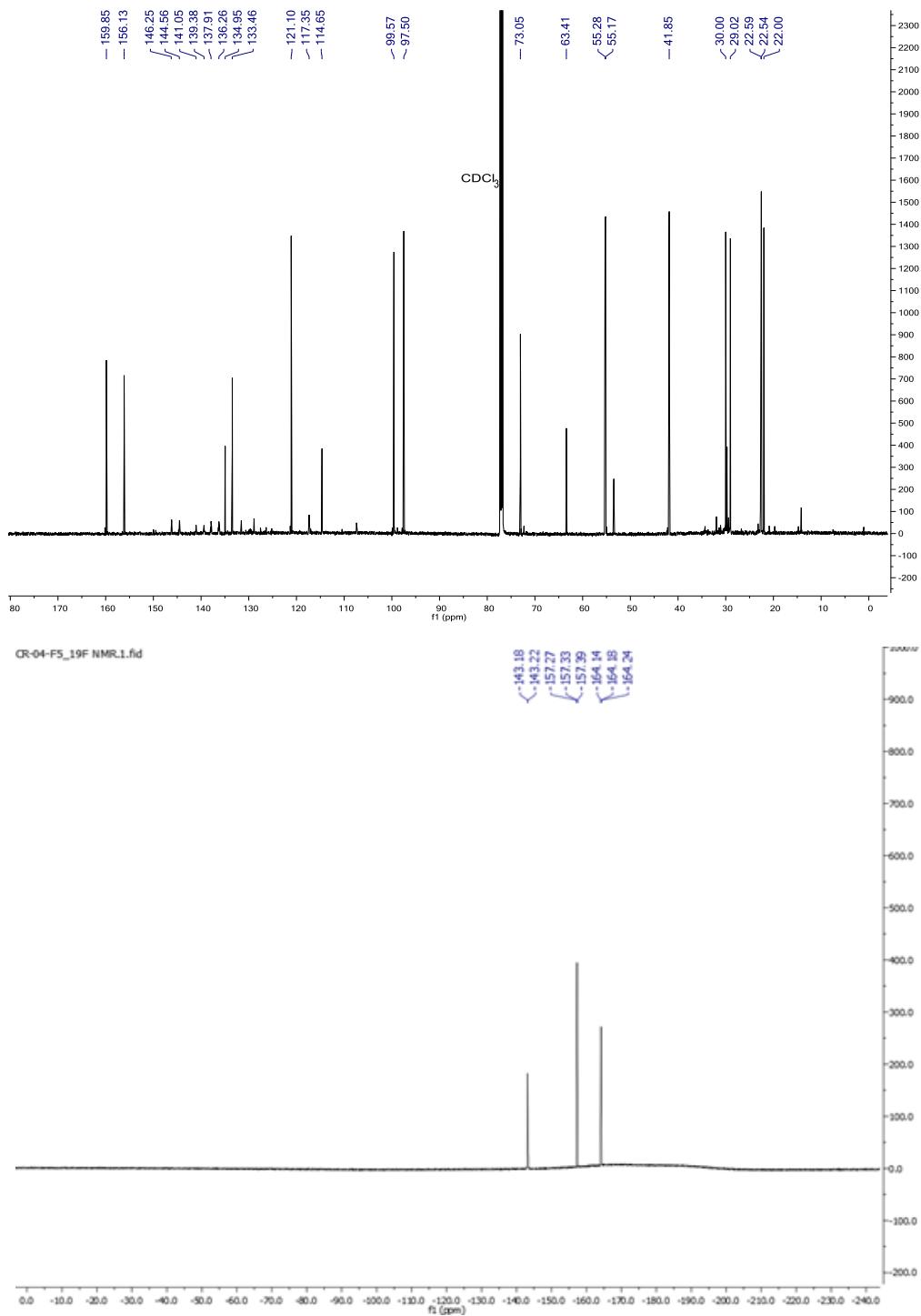


Figure 1.26. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR of **1.4n** in CDCl₃ at 25 °C.

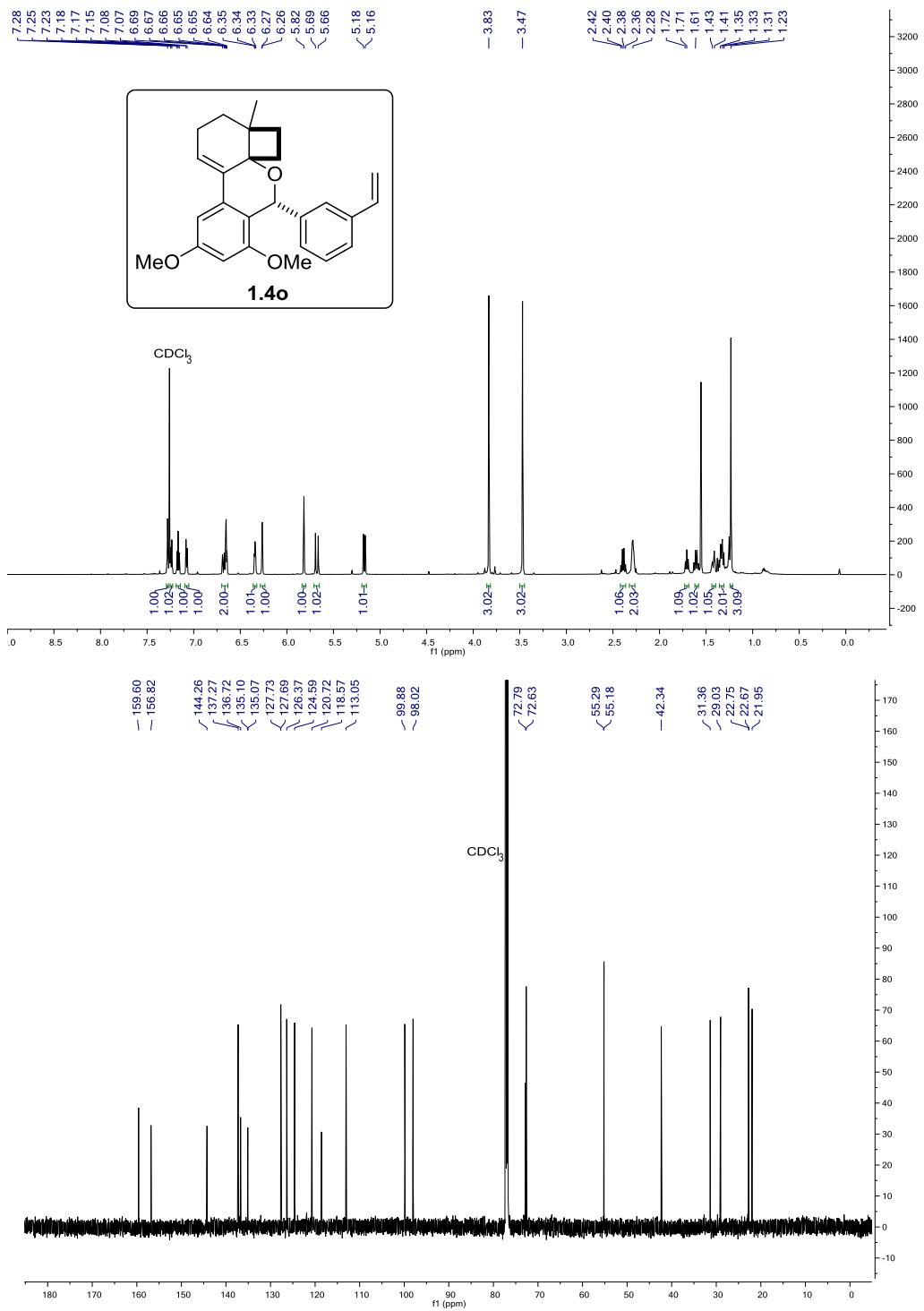


Figure 1.27. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **1.4o** in CDCl_3 at 25 °C.

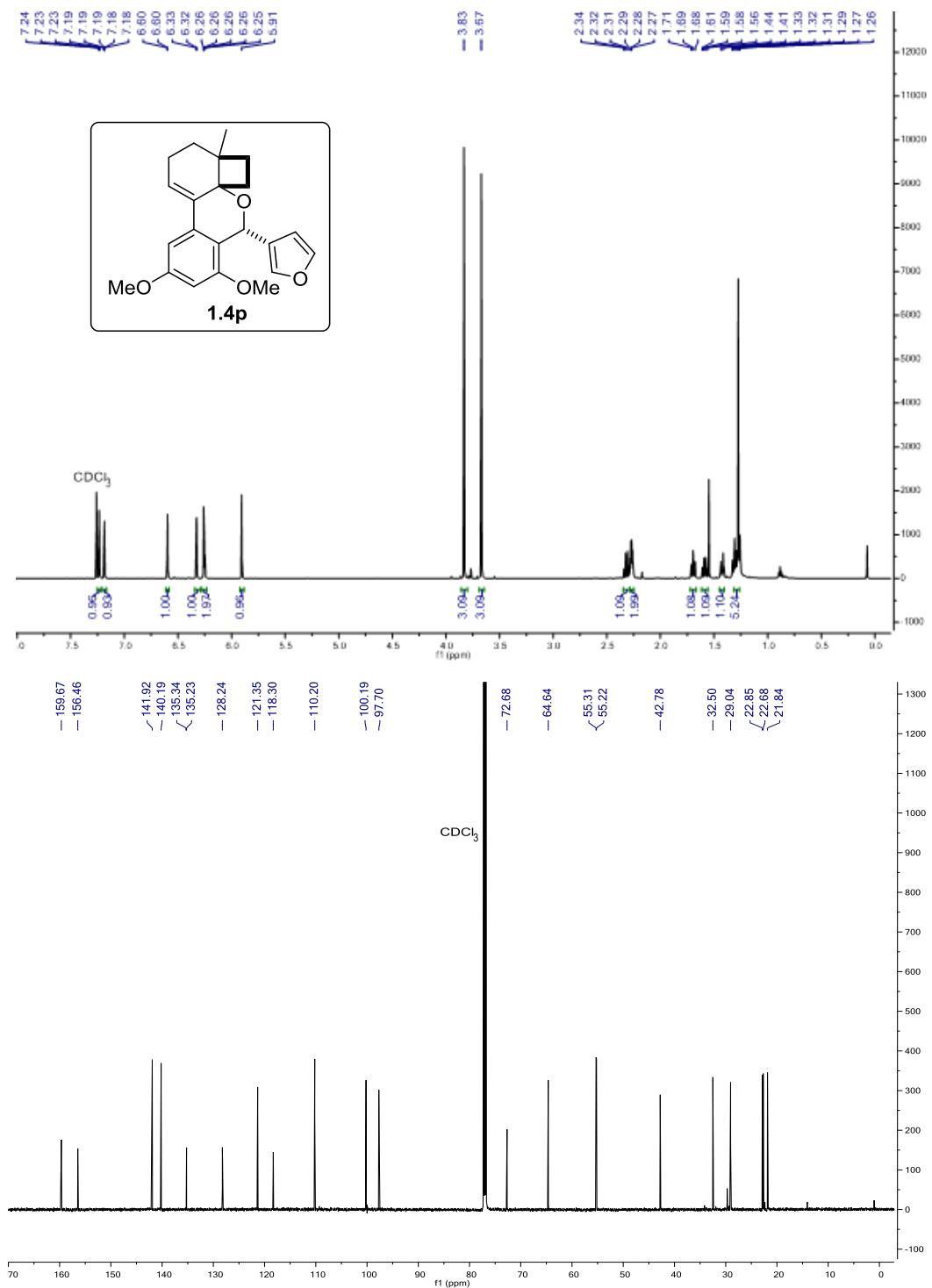


Figure 1.28. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **1.4p** in CDCl_3 at 25 °C.

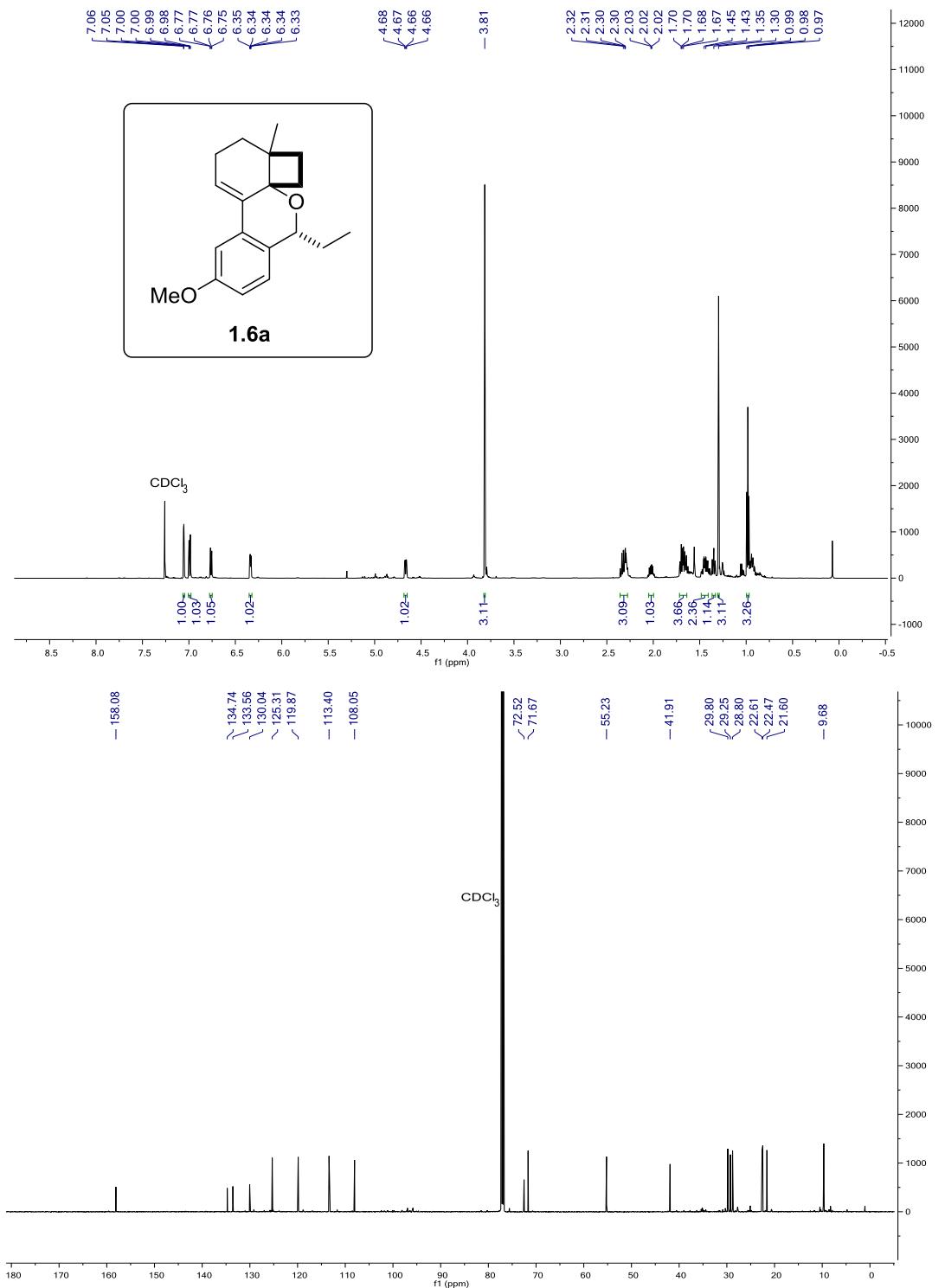


Figure 1.29. ¹H and ¹³C{¹H} NMR of **1.6a** in CDCl₃ at 25 °C.

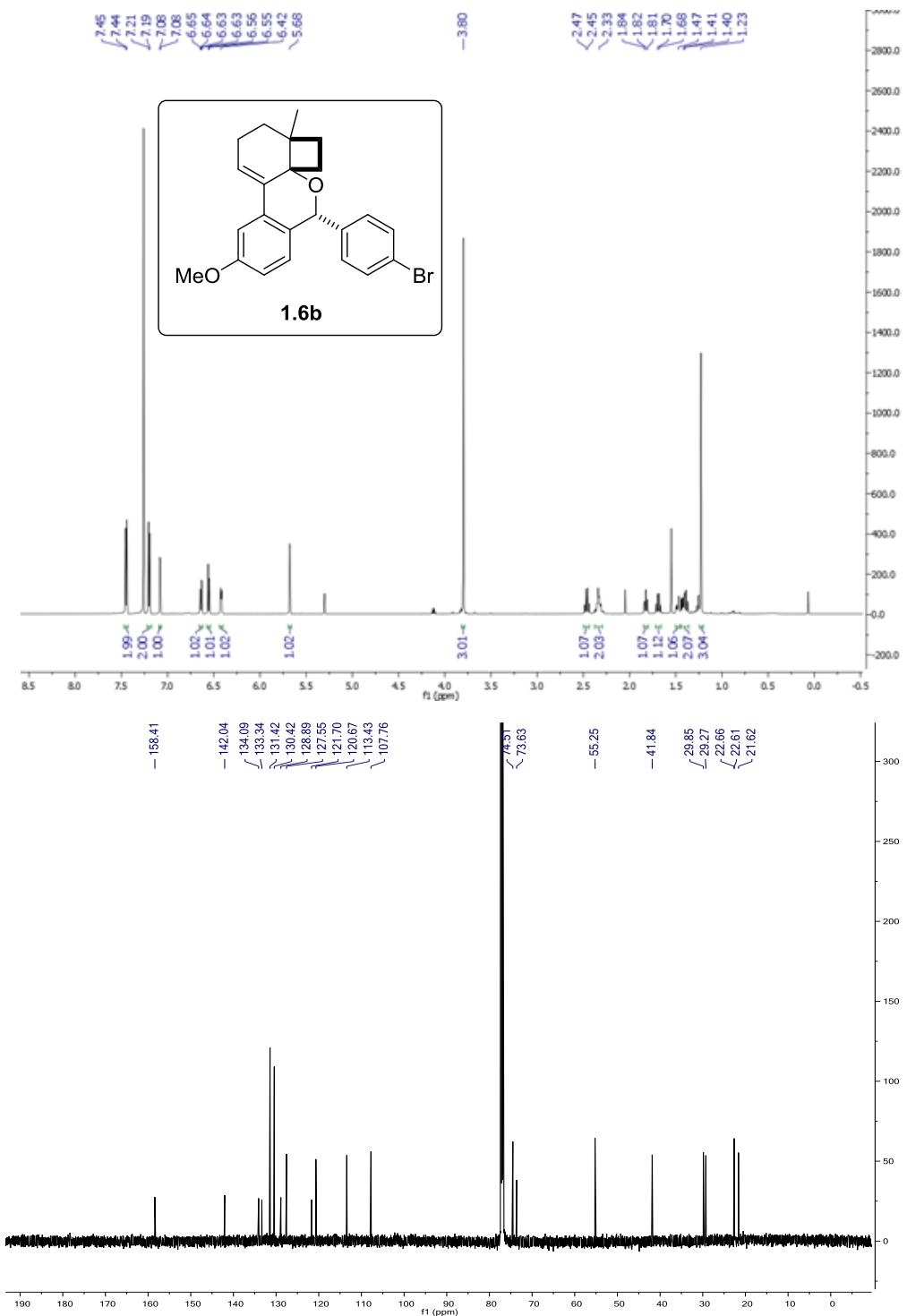
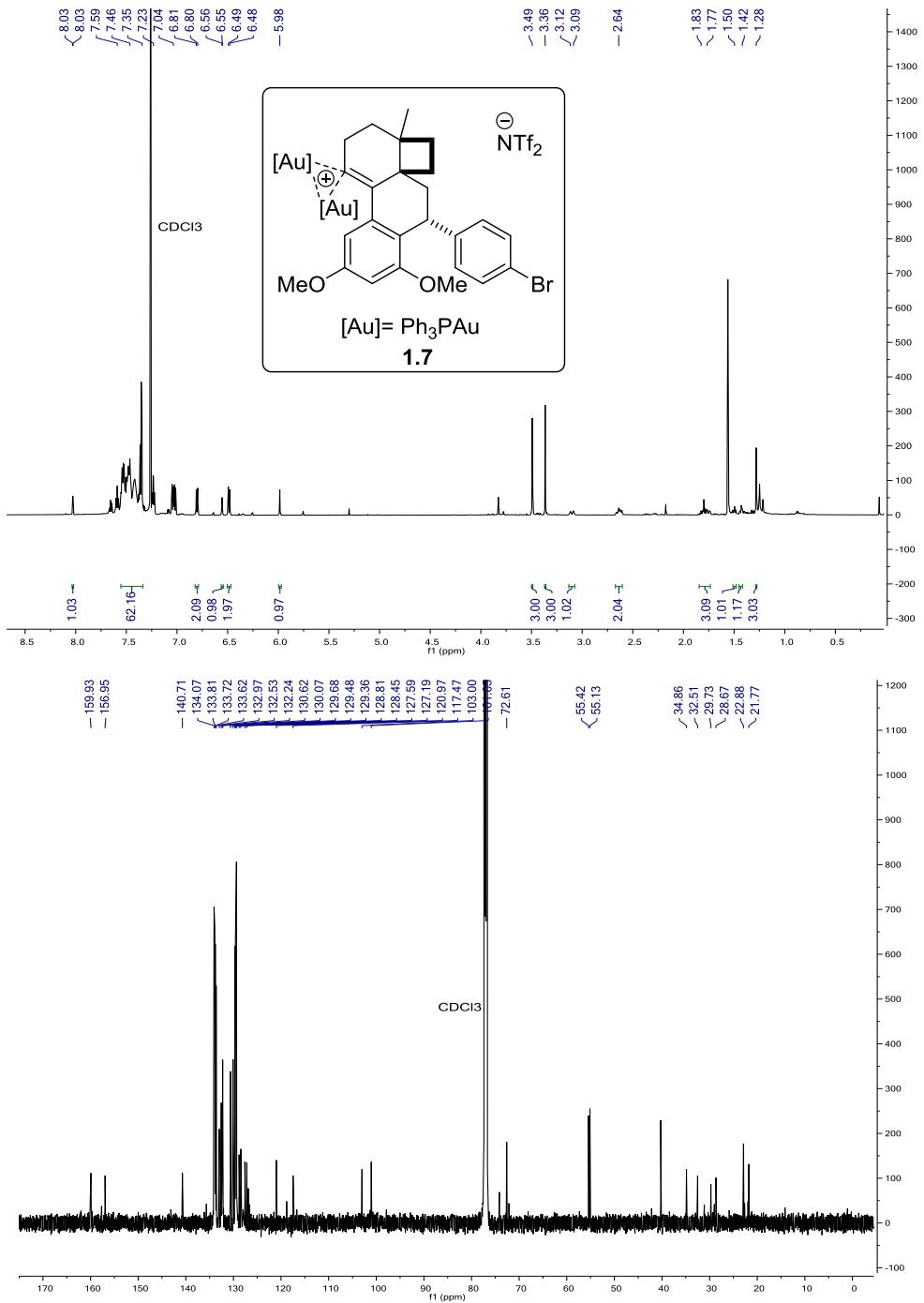


Figure 1.30. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **1.6b** in CDCl_3 at 25 °C.



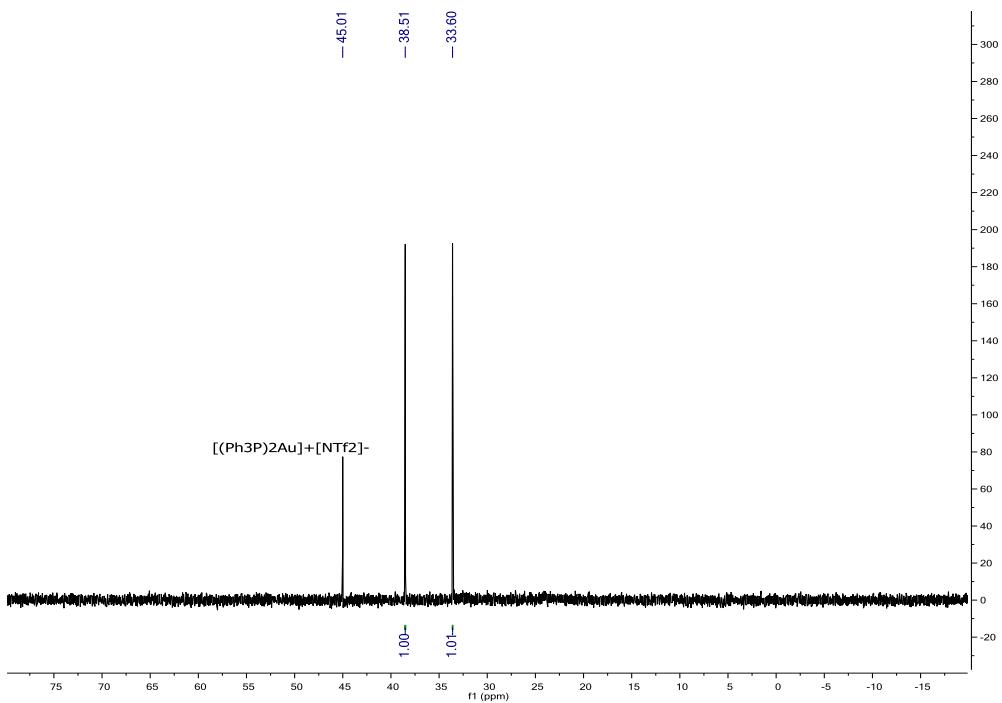
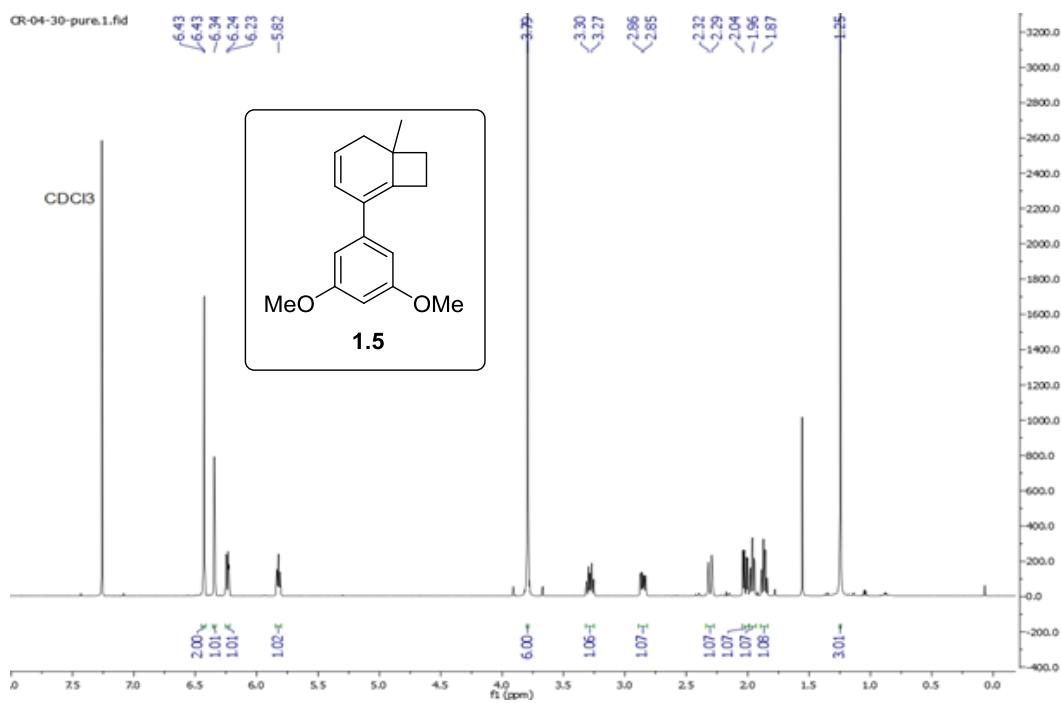


Figure 1.31. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{31}\text{P}\{^1\text{H}\}$ NMR of **1.7** in CDCl_3 at 25°C



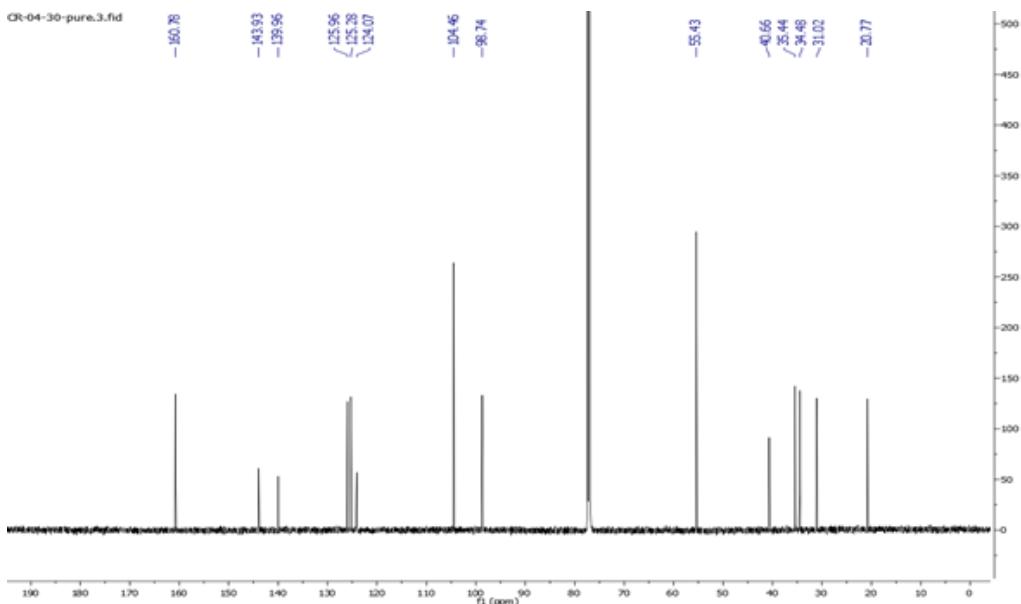
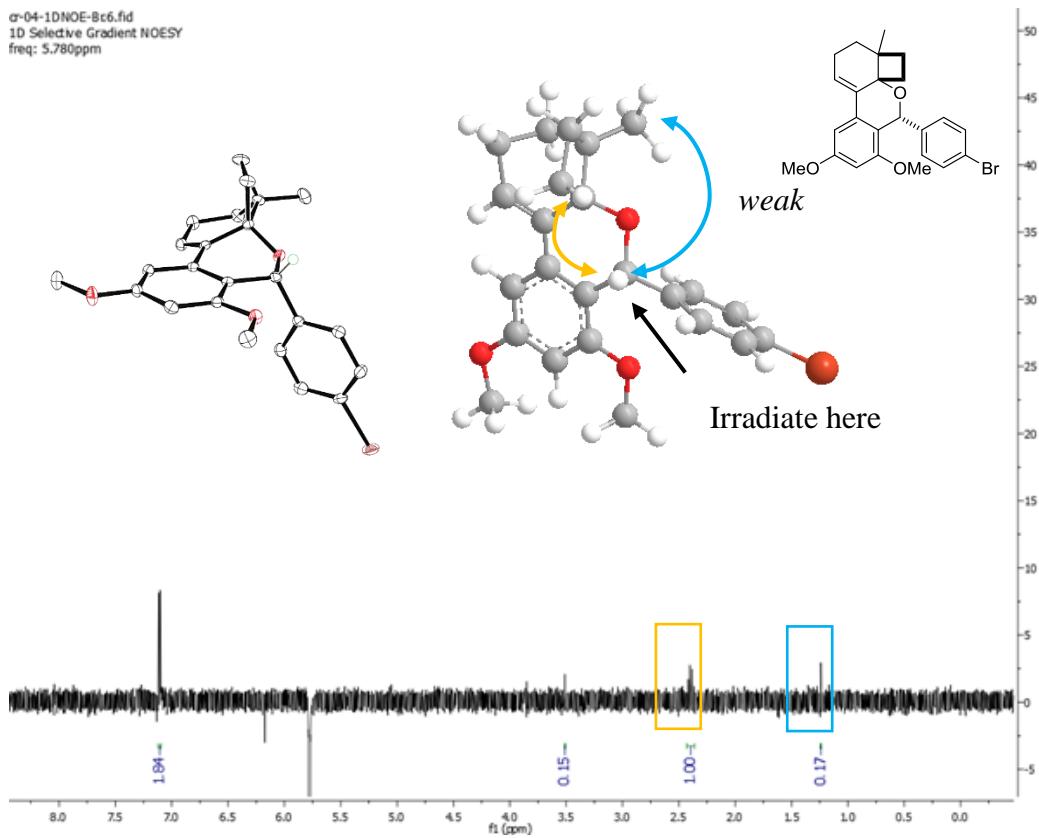


Figure 1.32. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **1.5** in CDCl_3 at 25°C .

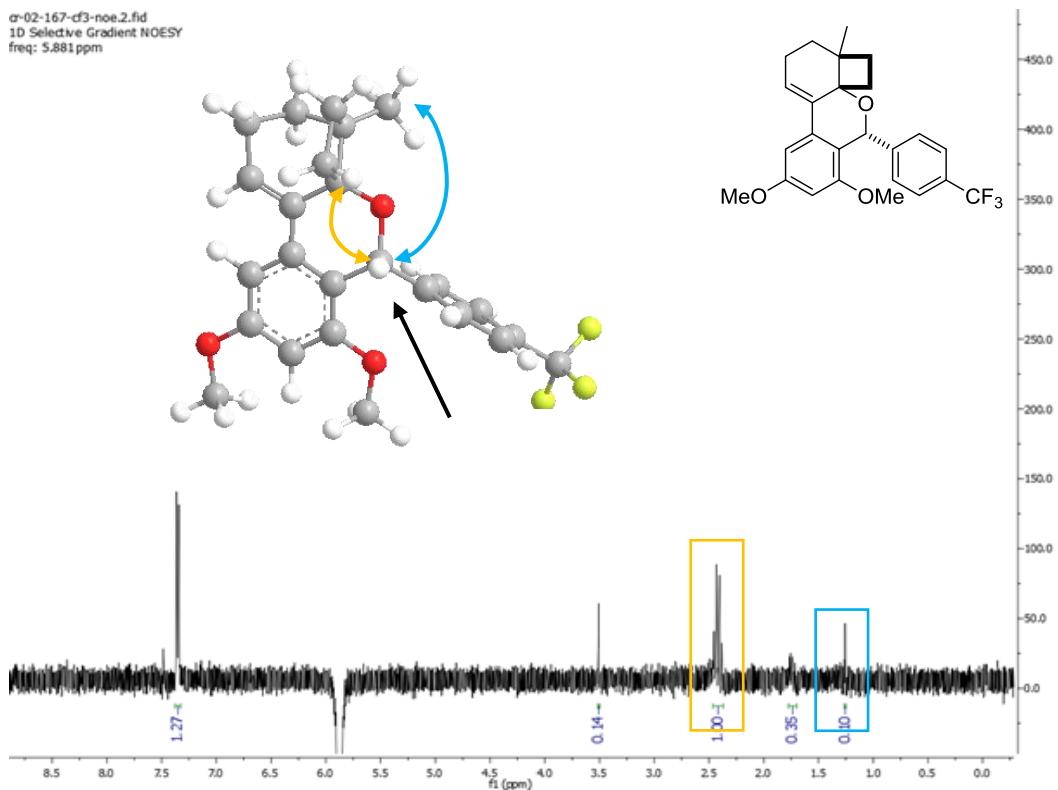
1.8.10 Gradient 1D NOESY stereochemical assignment

Stereochemistry of **1.4k** confirmed via X-ray structure.



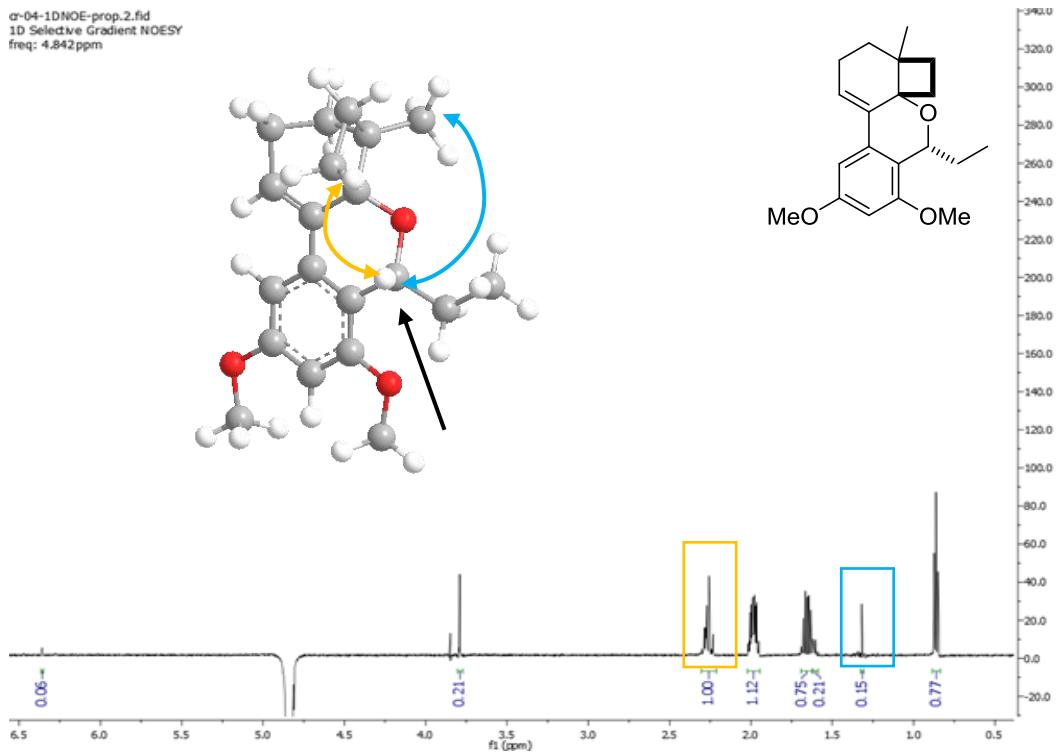
Stereochemical assignment of 1.4j

cr-02-167-cf3-noe.2.fid
1D Selective Gradient NOESY
freq: 5.881 ppm

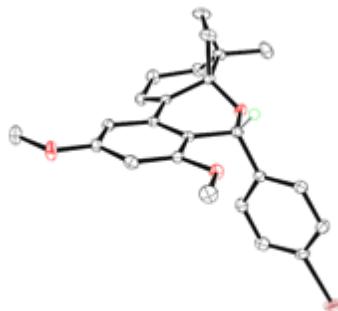


Stereochemical assignment of 1.4a.

cr-04-1DNOE-prop.2.fid
1D Selective Gradient NOESY
freq: 4.842 ppm



1.8.11 Single Crystal X-ray diffraction analysis



ORTEP representation of the solid state molecular structure of **1.4k**; ellipsoids drawn at 50% probability, only one enantiomer of the asymmetric unit, and the majority of hydrogen atoms are omitted for clarity.

Table 1.4. Single crystal X-ray diffraction analysis of **1.4k**.

Empirical formula	2(C ₂₄ H ₂₅ BrO ₃)	D _{calcd} (Mg m ⁻³)	1.437
F _w	441.37	Radiation	Cu K α
Colour, habit	Colourless, block	Absorption coeff. (μ) (mm ⁻¹)	2.92
Crystal dimensions (mm)	0.21 x 0.17 x 0.11	Absorption correction	Numerical
			SADABS
			2014/5
Crystal system	Triclinic	F(000)	912
Space group	P-1	θ_{\min} to θ_{\max} (°)	3.1 to 70.1
Z	2	Measured reflections	20859
a (Å)	11.9878(6)	Independent reflections	7453
b (Å)	13.1429(7)	Data/restraints/parameters	7453/0/511
c (Å)	14.8309(8)	Maximum shift/error	0.004
		(R _{int} =0.021)	

α (°)	72.229(2)	Goodness-of-fit on F^2	1.05
β (°)	86.297(2)	Final R indices ($I > 2\sigma(I)$)	$R_1 = 0.026$
			$wR_2 = 0.066$
γ (°)	66.705(2)	R indices (all data)	$R_1 = 0.028$
			$wR_2 = 0.067$
Collection ranges	$h = -9 \rightarrow 14$ $k = -14 \rightarrow 16$ $l = -18 \rightarrow 18$	absolute structure parameter	N/A
Temperature (K)	100	Extinction coefficient	N/A
Volume (Å³)	2039.57 (19)	Largest diff. peak and hole (e Å⁻³)	0.36 and -0.42

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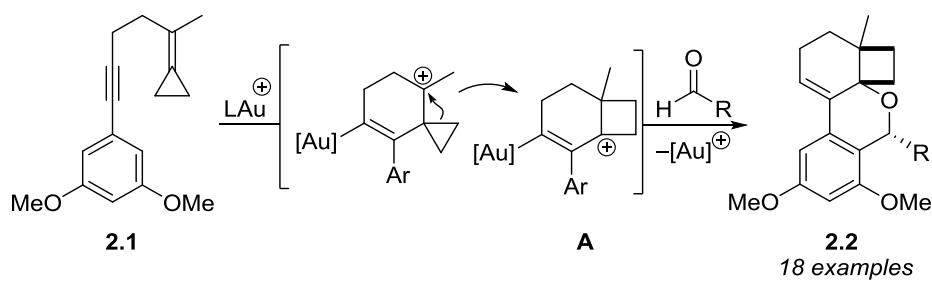
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Chapter 2: Expanding the Scope of the Intermolecular Addition of Aldehydes to Enynes

2.1 Introduction: addition of aldehydes to cyclopropylidene-bearing 1,5-enynes

The use of electrophilic gold(I) complexes for the addition of nucleophiles to enynes has enabled the development of novel molecular scaffolds.^{1,2} Reported in Chapter 1 is a diastereoselective, gold-catalyzed cascading cycloisomerization of alkylidene cyclopropane bearing 1,5-enynes that terminated in a cyclo-addition of aldehydes (Scheme 2.1).³ The key reaction intermediate was auro-allyl cation **A**, which could be trapped by aldehydes to form an oxocarbenium ion, poised to undergo a Friedel-Crafts annulation. A diverse array of aldehydes was incorporated into the products providing access to 18 different derivatives. A mechanistic study revealed the catalyst rests as an off-cycle di-gold vinyl intermediate, which was also isolated and characterized.



Scheme 2.1. Intermolecular addition of aldehydes to 1,5-enynes.

The following studies elaborate on the utility of this reaction: chiral catalysts were screened to develop an enantioselective variant, a model gold vinyl substrate was developed to investigate alternative turnover pathways to protodemetallation, and nucleophiles other than aldehydes were screened to develop more diverse heterocyclic products.

2.2 Enantioselective catalysis

2.2.1 Background

Despite the vast number of gold catalyzed reactions developed, enantioselective gold catalysis remains a challenge.^{4–7} The difficulty in achieving high enantioselectivities stems from the fact that gold(I) complexes prefer a linear coordination mode (Figure 2.1).⁴ This geometric limitation places the substrate and the chiral ligand on opposite sides of the metal center, limiting the proximity of the substrate to the ligand-centered chirality. Additionally, many gold-catalyzed reactions proceed through outer-sphere attack of nucleophiles on the coordinated π -bond, bypassing any metal-nucleophile interactions and limiting the extent of chirality transfer from the ligand.⁵

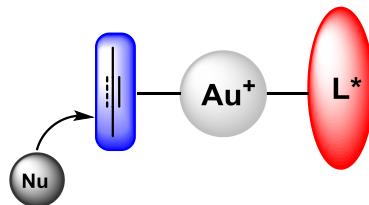
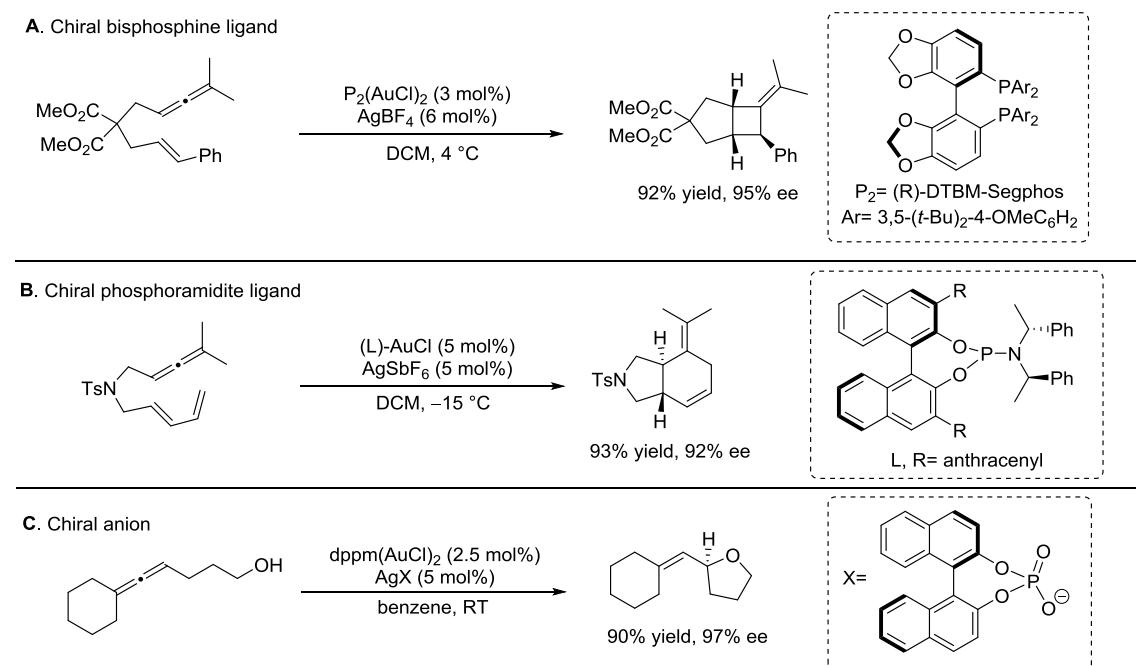


Figure 2.1. Linear coordination mode of gold(I).

The two most common approaches to developing enantioselective gold(I) transformations involve the use of either chiral ligands or chiral anions (Scheme 2.2).⁵ Bimetallic gold complexes with axially chiral bisphosphines have been used extensively due to the commercial availability of chiral bisphosphines, allowing variation in both the steric and electronic properties of the ligands. An asymmetric [2+2] cycloaddition of eneallenes was developed by the Toste group to afford alkylidene cyclobutanes in high enantioselectivities (Scheme 2.2, A).⁸ Monodentate phosphoramidite ligands have recently been applied in enantioselective gold catalysis.⁴ One of the first uses of a chiral phosphoramidite ligand in gold catalysis was reported by Mascareñas and co-workers in 2009 with the intramolecular [4+2] cycloaddition of allenedienes (Scheme 2.2,

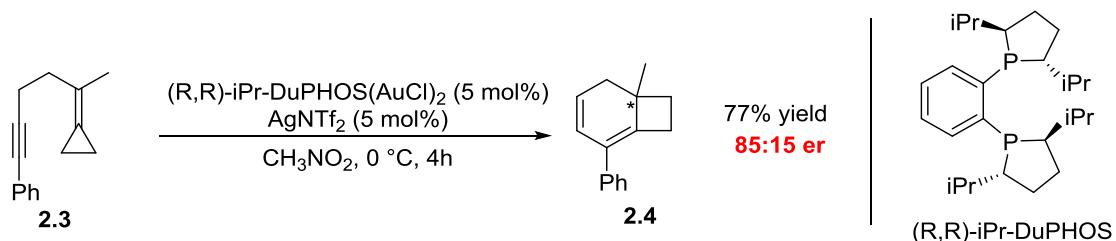
B).⁹ The chirality of the amine moiety on the ligand was shown to control the absolute stereochemical outcome of the bicyclic product. Alternatively, the use of chiral anions with achiral gold complexes can provide high enantioselectivities.⁵ This approach overcomes the limitations of the linear coordination geometry of the ligand by providing an outer-sphere source of chirality that is still associated with the metal center.¹⁰ The first use of chiral anions in gold catalysis was reported by the Toste group in 2007 in the intramolecular hydroalkoxylation of hydroxy allenes (Scheme 2.2, C).¹⁰ When chiral phosphines were screened, poor enantioselectivities were obtained. By using an achiral ligand with a chiral anion in a non-polar solvent, high enantioselectivities were obtained, demonstrating that the chirality transfer was dependent on the formation of a tight ion pair.



Scheme 2.2. Common approaches to enantioselective gold catalysis.

Recent work in the Gagné lab has focused on developing an enantioselective cycloisomerization of cyclopropylidene bearing 1,5-enynes.¹¹ Through a chiral ligand screen and

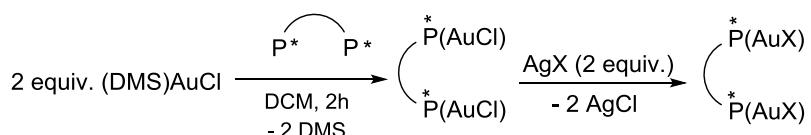
reaction optimization, the (R,R)-*i*-Pr-DuPHOS dinuclear gold complex, in combination with the silver bistriflimide salt, provided promising enantioselectivities, with enantiomeric ratios as high as 85:15 (Scheme 2.3). Because our catalytic system is based upon the same initial enyne activation, we sought to develop an enantioselective variant of our aldehyde trapping reaction.



Scheme 2.3. Enantioselective cycloisomerization of 1,5-enynes.

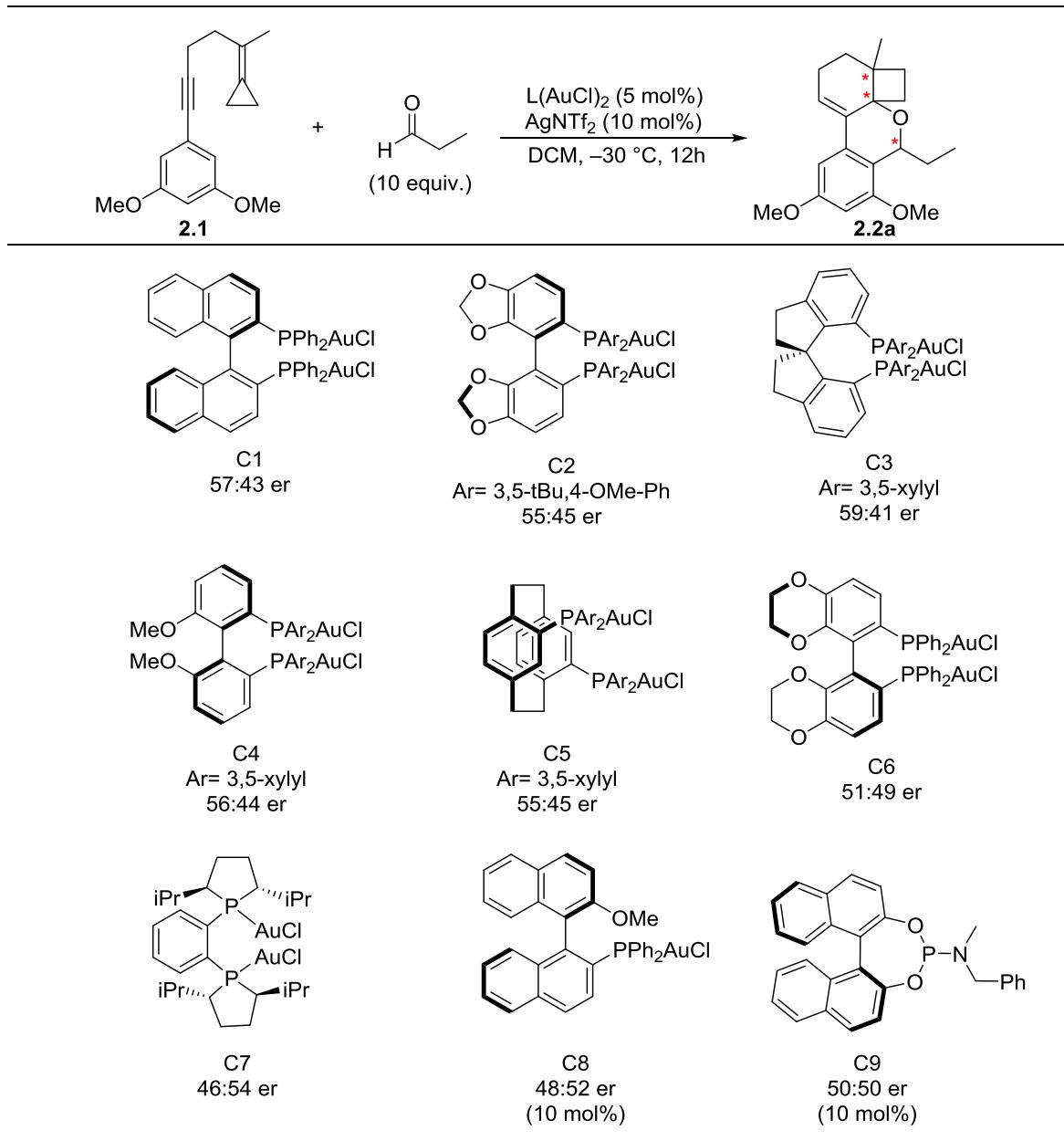
2.2.2 Results and discussion

Our initial approach to developing an enantioselective reaction was to screen a library of dinuclear gold complexes with chiral ligands. The gold chloride complexes were synthesized by stirring the chiral ligand with (DMS)AuCl precursor in DCM (Au:P ratio of 1:1, Scheme 2.4). The gold chloride complexes were activated in-situ with silver salts prior to the introduction of the substrate. As shown in Table 2.1, we began by looking at the reaction of enyne **2.1** with excess propionaldehyde in the presence of our chiral gold catalyst to furnish the aldehyde trapped product **2.2a**.



Scheme 2.4. Synthesis and activation of chiral gold complexes.

Table 2.1. Chiral gold complex screen.^a



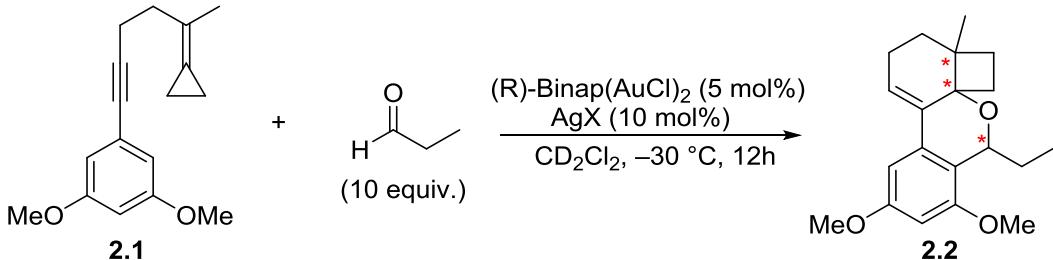
^aReaction conditions: L(AuCl)_2 (0.0015 mmol) was added to a vial equipped with a stir bar. AgNTf_2 (0.003 mmol) was added, followed by 0.25 mL DCM. The mixture was stirred at RT for 30 minutes, then transferred to a solution of **2.1** (0.03 mmol) and propionaldehyde (0.3 mmol) in 0.25 mL DCM, precooled to -78°C . This vial was sealed and placed in a cryo bath set to -30°C . After stirring for 12 hours, the solution was removed from the bath, concentrated, and analyzed by NMR and chiral GC.

The conversions to **2.2a** using complexes C1–C9 were all >90% to a single diastereomer of product as determined by ^1H NMR spectroscopy. Enantiomers could be separated by chiral

GC (stationary phase: β -Cyclosil). This moderate ligand screen revealed that phosphine-type ligands gave enantioselectivities that were poor—the axially chiral bisphosphines and monodentate phosphines gave relatively similar enantioselectivities, while the chiral phosphoramide gave a racemic mix. Complexes **C1** and **C3** gave the highest enantioselectivities of those screened, with enantiomeric ratios of 57:43 and 59:41, respectively. Due to the ready availability of the (R)-Binap ligand (**C1**) compared to the (R)-xylyl-SDP ligand (**C3**), we proceeded with the optimization studies using **C1**.

In the next round of optimization, silver salts were screened in combination with the (R)-Binap(AuCl)₂ complex (Table 2.2). Both the size and coordinating nature of the counter anion in gold catalysis has been shown to impact both the kinetics and selectivity of the reaction.¹² While most of the silver salts gave similar results, the AgSbF₆ salt performed the best, with an enantiomeric ratio of 67:33 (entry 4). When we reduced the amount of silver by half to account for a 2:1 Au:Ag ratio, such that only one gold center had been activated, a drop in the enantiomeric ratio was observed (entry 5). In some examples in the literature, this strategy has been shown to increase enantioselectivities.¹² Further optimizations including lowering the temperature and screening other solvents resulted in decreased yields of **2.2a** and lower enantioselectivities. The outcome of screening these conditions showed that the best enantioselectivities for the cyclo-addition of aldehydes were 67:33 (34% *ee*) through the combination of (R)-Binap(AuCl)₂ and AgSbF₆ (2 equiv.) in DCM.

Table 2.2. Silver screen.



Entry	Silver Salt	Yield (NMR)	Enantiomeric ratio
1	AgNTf ₂ (10 mol%)	>95%	57:43
2	AgBF ₄ (10 mol%)	90%	56:44
3	AgPF ₆ (10 mol%)	65%	57:43
4	AgSbF ₆ (10 mol%)	>95%	67:33
5	AgSbF ₆ (5 mol%)	>95%	58:42

2.3 Intercepting protodemetallation with halonium sources

2.3.1 Background

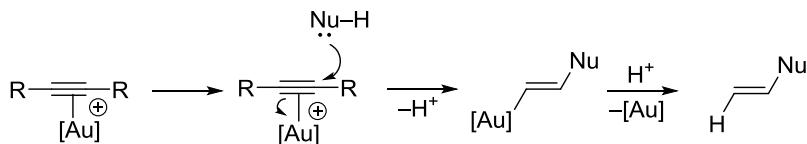


Figure 2.2. Gold activation of alkynes.

The accepted mechanism for gold-catalyzed activation of alkynes begins with gold coordination to the alkyne, activating the alkyne for nucleophilic attack by either inter- or intramolecular nucleophiles (Figure 2.2).¹³ As a result, a gold vinyl intermediate is formed which is then typically protodemetallated to furnish the product and regenerate the catalyst. To further diversify the products obtained in gold catalyzed reactions, several groups have reported the

trapping of gold vinyl intermediates with N-halosuccinimides^{14–17} or electrophilic fluorine sources (Figure 2.3).^{18–20}

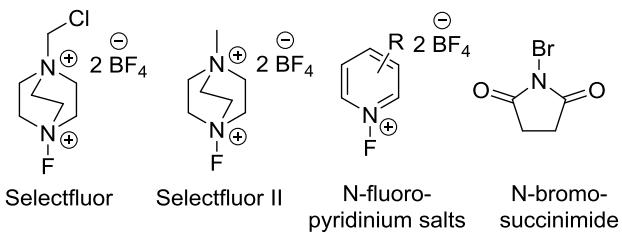
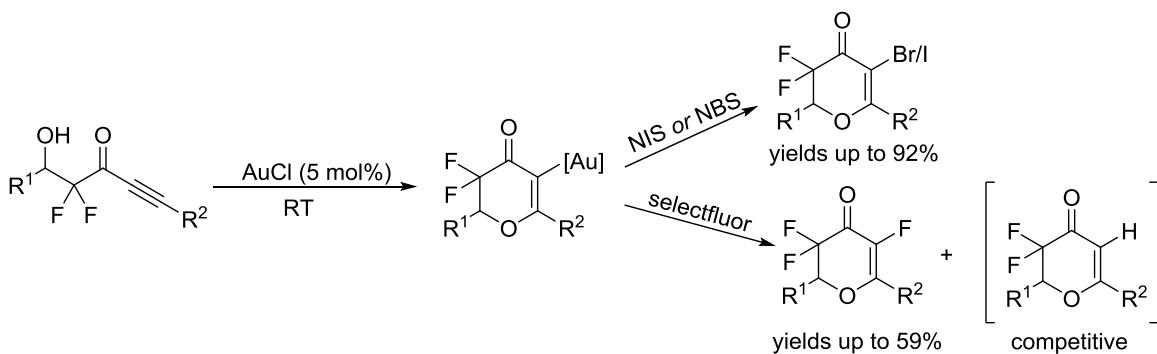


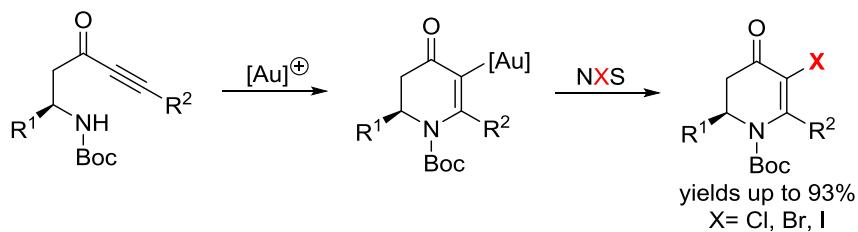
Figure 2.3. Common electrophilic halogen sources.

An example of the first gold-mediated C–F bond formation using fluoronium sources is shown in Scheme 2.5.¹⁸ In this example, gold catalyzes a 6-*endo-dig* cyclization of the β -hydroxy- α,α -difluoropyrone to afford a transient gold vinyl that is intercepted with the electrophilic fluorine source selectfluor. They also demonstrated successful bromination and iodination through using the corresponding N-halosuccinimide sources. As shown in Scheme 2.5, only moderate yields of the fluorine-intercepted products were obtained, as protodeuaration was increasingly competitive under the reaction conditions. Control experiments demonstrated that the gold-carbon bond in the intermediate undergoes fluorination, as no reaction occurs when the protodemetalated product is treated with selectfluor either with or without AuCl present.



Scheme 2.5. Gold-mediated halogenation of pyranones.

More recently, the Gouault group reported a one-step halopyridone synthesis based on the gold-catalyzed cyclization and halogenation of β -amino-ynones (Scheme 2.6).¹⁷ The halogenated products were further functionalized by subjecting the vinyl halides to a variety of different palladium-catalyzed cross coupling reactions, allowing for the formation of 5 different derivatives in high yields. To probe the mechanism, a series of control experiments were conducted. Under the optimized reaction conditions, the reaction is complete in under 10 minutes. However, if the protodemettalated product is treated with NIS in the absence of gold, the halogenation proceeds, albeit in longer reaction times and lower yields. In summary, the one-pot procedure afforded the halogenated products in a more rapid and efficient process.

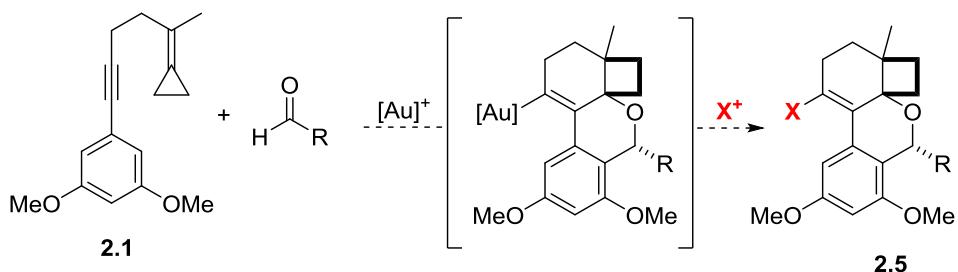


Scheme 2.6. Gold-catalyzed halocyclization.

2.3.2 Results and discussion

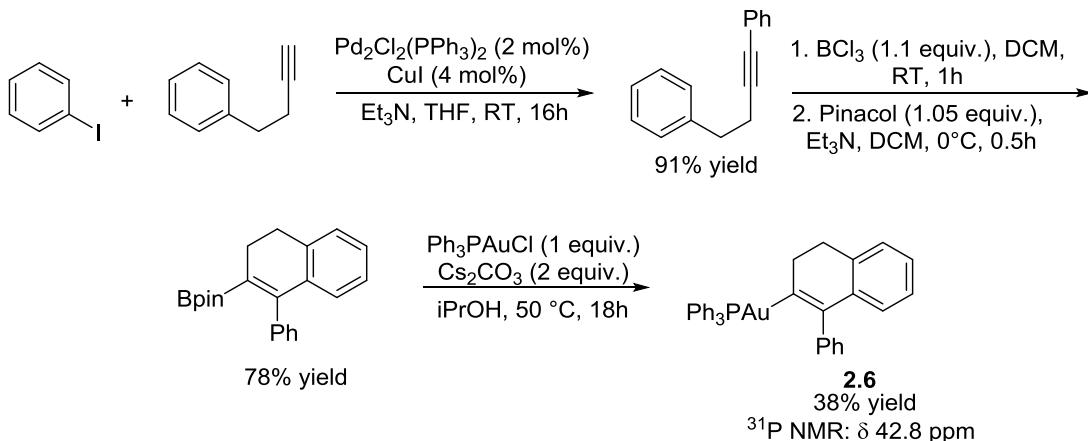
This work aims to develop a methodology to intercept the gold vinyl intermediate in our cycloaddition reaction with electrophilic halogen sources to generate more highly functionalized products that provide a handle for downstream product modification (Scheme 2.7). We started by performing stoichiometric reactions with isolated mono-gold vinyl intermediates. We had synthesized various batches of the di-gold vinyl in our previous mechanistic studies of the reaction (Chapter 1). Due to the sensitivity of the di-gold compound, purity ranged from ~80-95% (mass balance is protodemettalated product). We converted our di-gold vinyl to the mono-gold vinyl by passing the di-gold through a short alumina plug eluting with DCM (^{31}P NMR δ

=42.1 ppm).²¹ Despite our best efforts, all samples were contaminated with protodemetallated product, which would further complicate our analysis. So that we could more conveniently address the key problem of the gold vinyl reactivity, we developed a model gold vinyl complex to initiate our study.



Scheme 2.7. Proposed reactivity pathway.

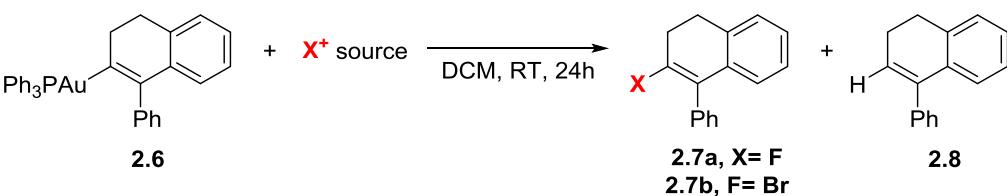
The synthesis of the model gold vinyl compound is detailed in Scheme 2.8. This gold vinyl was designed as it has a relatively similar steric and electronic profile to that of our gold vinyl. The first step of the synthesis involves a Sonogashira cross coupling to afford the phenyl substituted alkyne in high yields.²² This step is followed by the synthesis of the boronate ester via a borylative cyclization of the alkyne using BCl_3 .²³ The final step in the synthesis is the transmetallation of the boronic ester with Ph_3PAuCl to afford our gold vinyl compound in a 27% overall yield.²⁴ Using this route, we were able to begin our studies with a clean, well-defined model complex that had a characteristic ${}^{31}\text{P}$ NMR shift of 42.8 ppm.



Scheme 2.8. Synthesis of model gold vinyl compound **2.6**.

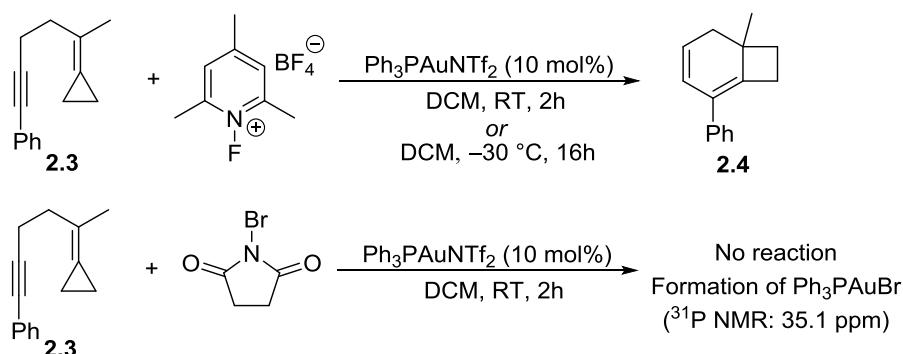
With our gold vinyl in hand, we began looking at stoichiometric reactions with electrophilic halogen sources (Table 2.3). These reactions were set up by dissolving gold vinyl **2.6** in CD₂Cl₂ in an NMR tube, followed by the addition of two equivalents of the halonium source. The reactions were monitored by ¹H NMR, ³¹P NMR and GC-MS.

Table 2.3. Stoichiometric reactivity with halogen sources.



Entry	X ⁺ Source	Outcome (ratio 2.7 : 2.8)
1	selectfluor	NR, trace protodemetallation
2	selectfluor II	NR, trace protodemetallation
3	1-fluoro-2,4,6-trimethylpyridinium BF ₄	7 : 1 (full conversion of 2.6)
4	N-bromosuccinimide	Full conversion to 2.7b

Selectfluor and the second generation derivative selectfluor II were unreactive, with only trace protodemetallation observed. The N-fluoropyridinium salt (entry 3) provided fluorinated derivative **2.7b** as the major product with only a minor amount of protodemetallated product formed. With NBS, within 2 hours full conversion to the brominated product was observed. With the identification of two electrophilic halogen sources as compatible reagents in our stoichiometric model system, we looked to apply this methodology to our catalytic reaction. To simplify our reaction, we looked first at the cycloisomerization reaction, omitting the aldehyde addition step until the reaction was fully optimized (Scheme 2.9).



Scheme 2.9. Catalytic reactivity with enyne **2.3**.

We first looked at the addition of the 1-fluoro-2,4,6-trimethylpyridinium salt to the enyne in the presence of a catalytic amount of $\text{Ph}_3\text{PAuNTf}_2$. Within two hours, full conversion to the protodemetallated product **2.4** was observed. In an attempt to slow down the reaction to allow for incorporation of fluorine, we ran the reaction at -30°C . To our surprise, the protodemetallated product was the sole product formed. Other N-fluoropyridinium salts (N-fluoropyridinium, 2,6-dichloro-N-fluoropyridinium) were screening for reactivity, but did not provide the fluorinated product. With NBS as the electrophile, monitoring the reaction *in situ* by ^1H NMR revealed that no reaction occurs. Through ^{31}P NMR analysis, the singlet at 30.7 ppm for the $\text{Ph}_3\text{PAuNTf}_2$ catalyst had disappeared and a new shift at 35.7 ppm emerged, consistent with the formation of

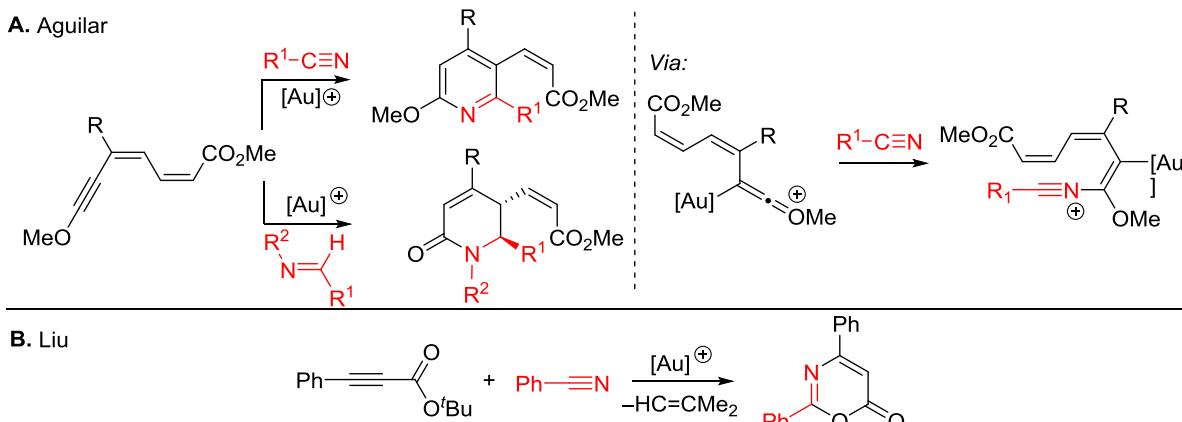
Ph_3PAuBr .²⁵ From this experiment, it was clear that NBS deactivates our catalyst and is the reason why our catalytic reaction is unsuccessful.

2.4 Moving beyond aldehydes: trapping with other unsaturated nucleophiles

2.4.1 Introduction

The key step in our gold catalyzed cycloaddition of aldehydes to 1,5-enynes was the generation of an auro-allyl carbocation. Under the right conditions, this cation could be trapped regioselectively by aldehydes to form an oxocarbenium ion that undergoes a subsequent Friedel-Crafts annulation to generate a novel polycyclic molecular scaffold. While there are several examples of the intermolecular addition of aldehydes or ketones^{14,26–30} to cationic gold intermediates, the use of other unsaturated nucleophiles like nitriles^{31–34} or imines³⁵ is limited.

Aguilar and co-workers have reported a gold-catalyzed intermolecular heterodehydro-Diels–Alder reaction between dienynes and nitriles³¹ or imines³⁵ to furnish tetrasubstituted pyridines or dihydropyridinones (Scheme 2.10, A). While the electronic nature of the dienyne was crucial for the success of the reaction, a large scope of both imines and nitriles with different steric and electronic profiles were well-incorporated. Similarly, Liu reported the gold-catalyzed [4+2] cycloaddition of *tert*-butyl propiolates with nitriles (Scheme 2.10, B).³⁴ This method was also expanded to include the addition of various ketones and aldehydes to further diversify the products.



Scheme 2.10. Addition of nitriles and imines to gold intermediates.

As shown above, most examples are limited by the requirement of specific functional groups on the substrate to facilitate a successful cycloaddition. To expand upon the current methodologies, this work probed the use of unsaturated nucleophiles as cation traps to generate more diverse heterocyclic products with our enyne **2.1**. (Figure 2.4). We proposed that imines, nitriles and ketones could behave in a similar manner to aldehydes, trapping key intermediate **A**, followed by the subsequent Friedel-Crafts reaction.

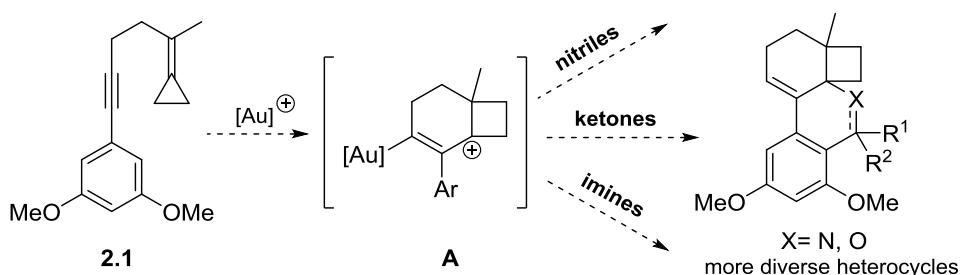
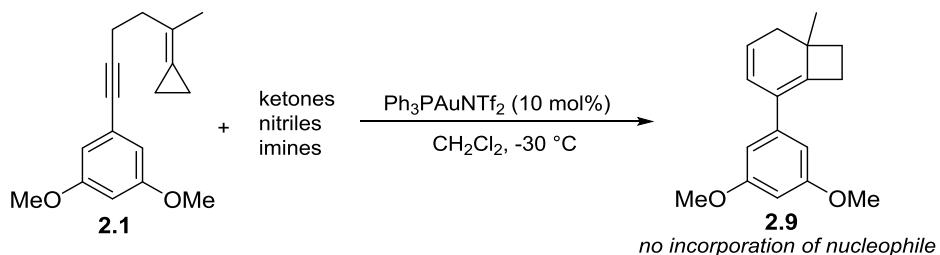


Figure 2.4. The proposed use of other nucleophiles as cation traps.

2.4.2 Gold-catalyzed addition of unsaturated nucleophiles to 1,5-enynes

Initially, we looked at ketones as nucleophiles, running the reaction under the previously optimized conditions with aldehydes. Acetone was chosen first, as it was the simplest and smallest ketone. To our surprise, only the cycloisomerized product was obtained (Scheme 2.11).

Despite running the reaction in neat acetone, only the cycloisomerized product **2.9** was returned. Acetophenone was also screened to assess the reactivity of aromatic ketones, however only **2.9** was obtained. We proposed that this lack of reactivity could be due to the increased steric hindrance of the methyl group versus the smaller hydrogen substituent in the case of aldehydes. With aldehydes, we obtain the product as a single diastereomer, confirming this reaction is very sensitive to sterics.



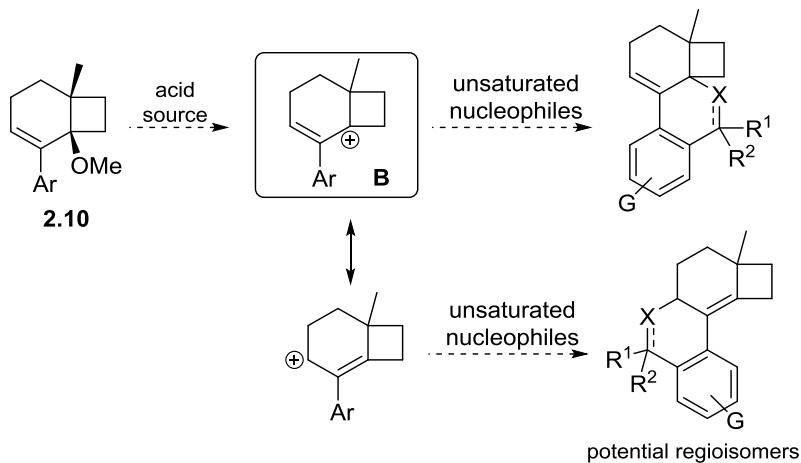
Scheme 2.11. Reactivity of **2.1** with nucleophiles

We next examined nitriles and imines. First, the reaction was run in deuterated acetonitrile which returned the cycloisomerized product. The reaction of **2.1** with gold in DCM with 20 equivalents of benzonitrile also returned cycloisomer **2.9**. Two imines were synthesized through the condensation of benzaldehyde with either methylamine or aniline. With the N-Ph imine, only **2.9** was returned. With the N-Me imine, no reaction was observed, likely due to the increased basicity of the imine and likely coordination to gold.

2.4.3 In-situ generation of tertiary carbocation for nucleophile incorporation

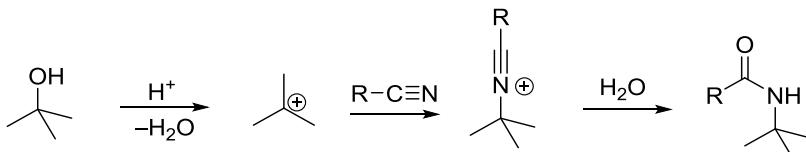
It was apparent that ketones, imines and nitriles were either uncompetitive with cycloisomerization or incompatible with gold. Therefore, we looked to alternative methods to generating more diverse heterocycles. From the mechanistic study with the cycloisomerization chemistry, we knew that methanol could efficiently trap the auro-allyl cation, generating [4.2.0] bicyclomethoxy product **2.10** in high yields.¹¹ We rationalized that we could use either **2.10** or

the related alcohol in combination with a Lewis or Brønsted acid to eliminate the ether to generate tertiary carbocation **B** (Scheme 2.12).



Scheme 2.12. Proposed reactivity of key carbocation **B**.

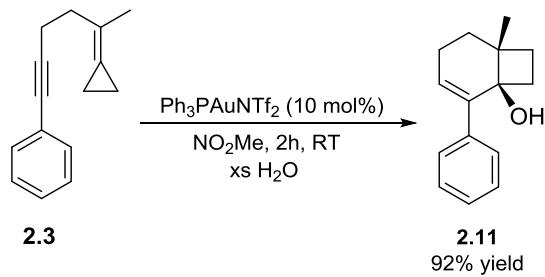
This proposed reactivity draws parallels to the Ritter reaction (Scheme 2.13).³⁶ In the classic Ritter reaction, a carbocation is generated through the protonation of an alkene or alcohol with a strong acid. This cation is then trapped by a nitrile to form a nitrilium intermediate which is then hydrolyzed to form an amide. Several Ritter-type reactions have been developed catalytically with both Lewis and Brønsted acids.³⁶



Scheme 2.13. Ritter reaction.

To begin, we synthesized water trapped product **2.11** by stirring phenyl substituted enyne **2.3** with gold catalyst Ph₃PAuNTf₂ in NO₂Me with excess water (Scheme 2.14). Product **2.11** was obtained as a single diastereomer in high yields. We first screened a variety of Lewis acids with alcohol **2.11** and 10 equivalents of propionaldehyde (Table 2.4). The reactions were

monitored by GC-MS to identify the major products formed. With Bi(OTf)₃ (entry 1), the reaction was scaled up, and all products were isolated and analyzed by NMR to confirm the identity of the products. For the aldehyde incorporated product, the structural analysis of the product did not match up with the anticipated aldehyde incorporated product. Although we did an extensive NMR analysis, the identity of the product remains unconfirmed. For this reaction, Bi(OTf)₃ was the best catalyst, however, significant amounts of side products were observed (**P1**, **P2**).



Scheme 2.14. Synthesis of water-trapped product.

Table 2.4. Lewis acid screen with **2.11**.

2.11

Lewis acid (10-15 mol%)
DCM, RT

P1 + P2 + aldehyde incorporated + SM

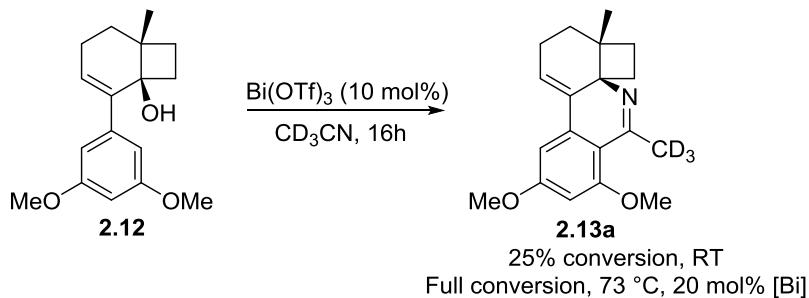
P1 **P2** **P3** **2.11**

Entry	Lewis Acid	Time	Outcome			
			P1	P2	P3	2.11
1 ^b	Bi(OTf) ₃	4h	X	X	X ^c	
2	Yb(OTf) ₃	16h				X
3	Sc(OTf) ₃	16h				X
4	Fe(OTf) ₃	16h	X	X	X	
5	Cu(OTf) ₂	16h	X			X
6	In(OTf) ₃	2h	X			
7	Al(OTf) ₃	16h	X	X	X	X
8	Zn(OTf) ₂	16h				X

^aProduct mixtures were analyzed by GCMS. ^bReaction was scaled up and products were isolated by column chromatography to confirm product identity. ^cMajor product.

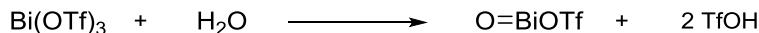
We were curious to see if the anticipated Friedel-Crafts type products formed with the more electron rich, methoxy-substituted arene. Tertiary alcohol **2.12** was synthesized in high yields and screened for reactivity with nitriles with Bi(OTf)₃ as catalyst (Scheme 2.15). When **2.12** was treated with 10 mol% Bi(OTf)₃ in deuterated acetonitrile, after 16 hours, partial conversion to nitrile-trapped product **2.13a** was observed. Through analysis by NMR spectroscopy, the structure of **2.13a** mapped very similarly to the aldehyde-trapped products

previously obtained. Through reaction optimization, full conversion to **2.13a** was observed by increasing the catalyst loading to 20 mol% and heating the reaction to reflux overnight.



Scheme 2.15. Nitrile trapping with **2.12**.

As we began scaling the reaction up and screening other nitriles, several reproducibility issues were encountered. By increasing the catalyst loading, greater conversions were observed, suggesting the catalyst may be deactivating. Also, if rigorously dry conditions were used, low conversions of **2.13a** were obtained. These results suggested that $\text{Bi}(\text{OTf})_3$ may be generating HOTf in-situ and that the reaction is in fact Brønsted acid catalyzed (Equation 2.1).³⁷ Upon looking through the literature, there is debate on the role of Bi(III) salts in catalysis, with several authors proposing their role is to generate Brønsted acids in situ.^{37–40}



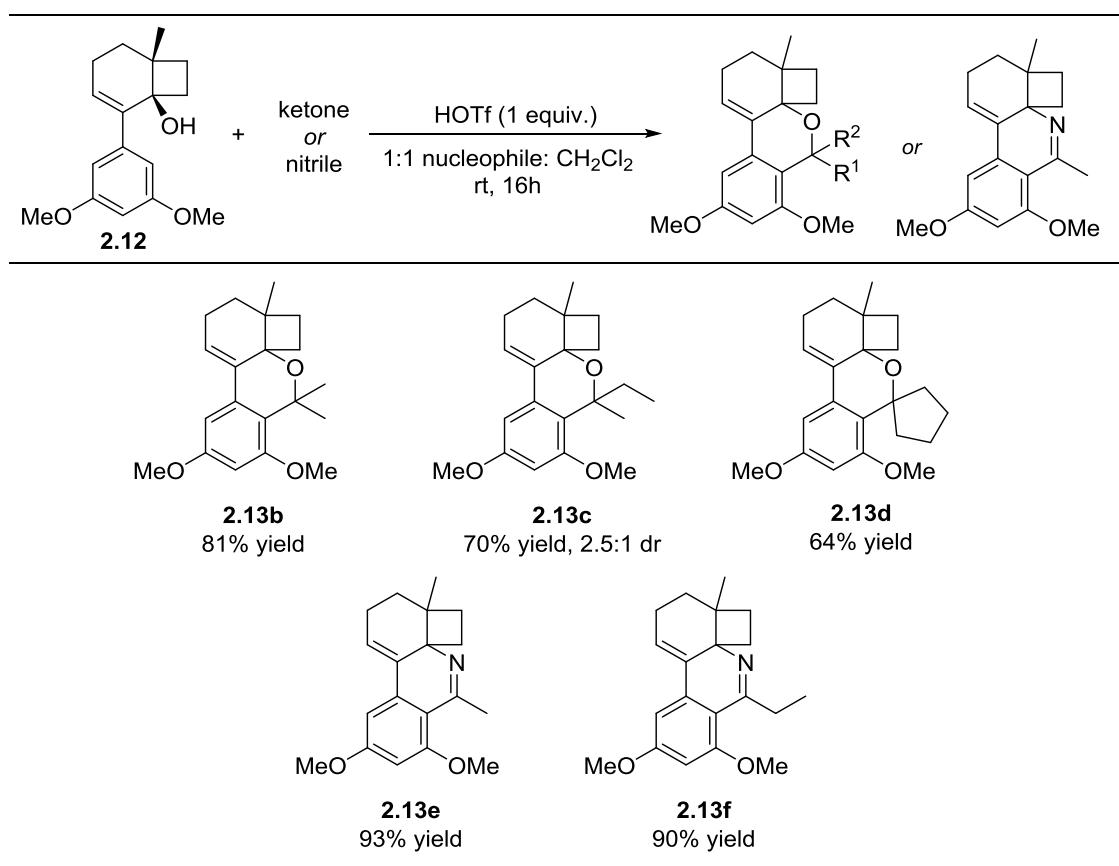
Equation 2.1. Proposed hydrolysis of $\text{Bi}(\text{OTf})_3$.

With this notion, we screened HOTf as a catalyst for this transformation. At room temperature, with catalyst loadings of 2 mol%, less than 10% conversion to **2.13a** was observed. Increasing the loading to 10 mol% afforded 80% conversion to **2.13a**. Heating this reaction did not lead to higher conversions. Although this reaction should be catalytic in acid, we ultimately found that using a full equivalent of HOTf lead to full conversion to **2.13a** with high

reproducibility. To avoid running these reactions in neat nucleophile, we found that using a 1:1 mixture of nucleophile to DCM gave very similar results.

With these optimized conditions in hand, we began to screen other nitriles and ketones with **2.12** (Table 2.5). Generally, small aliphatic ketones worked well with our system. Ketone incorporated products were obtained in high yields and could be purified by silica gel column chromatography. In the case of 2-butanone, two diastereomers of **2.13c** were obtained in a 2.5:1 ratio. Ketones with aromatic substituents, such as acetophenone or benzophenone, resulted in complex mixtures.

Table 2.5. Reactivity of **2.12** with ketones and nitriles.



Moving to nitriles was more challenging in terms of purification. With low boiling point nitriles, the excess nitrile could be removed en vacuo, however this was more difficult with higher boiling point nitriles such as benzonitrile. The cyclic imine products were also unstable on silica gel or alumina, so the separation of the products from unreacted starting material was a challenge. Despite these challenges, compounds **2.13e** and **2.13f** were obtained cleanly from acetonitrile and propionitrile, respectively. Trimethylacetonitrile and benzonitrile were also screened but resulted in lower conversions to the desired products and their purification remained a challenge. We also screened imines under these reaction conditions, however no imine incorporated products were detected.

2.5 Conclusion

In summary, we expanded the diversity of the products obtained from our gold-catalyzed addition of aldehydes to 1,5-enynes. Developing an enantioselective reaction proved a challenge, as the highest enantiomeric ratios obtained were 67:33. Although our model gold-vinyl complex underwent electrophilic halogenation, the catalytic functionalization reactions with our enyne could not outcompete protodemetallation. When expanding the scope of unsaturated trapping nucleophiles, we found that ketones and nitriles could not be incorporated into our scaffold. Through the development of an alternate reaction pathway, we found that protonolysis of the bicyclo [4.2.0] hydroxy compound could generate the key tertiary allyl carbocation to allow for the incorporation of these nucleophiles.

2.6 Experimental section

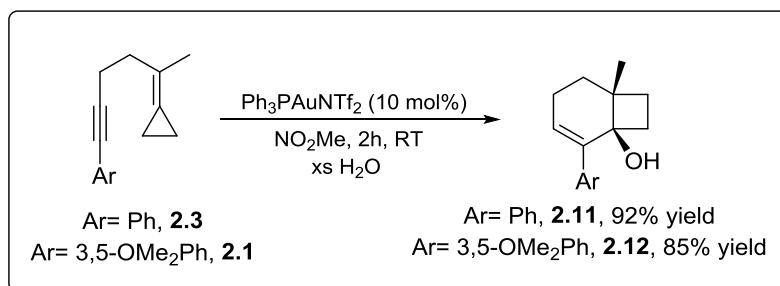
2.6.1 General Methods

Unless otherwise noted, all commercially available reagents were used without further purification. Anhydrous DCM was passed through a column on alumina.⁴¹ Column

chromatography was performed on SilaFlash P60 40-63 µm (230-400 mesh). TLC was performed on SiliCycle Silica Gel 60 F254 plates and was visualized using either a UV lamp or KMnO₄ stain. NMR spectra were recorded on a Bruker Avance 400, 500 or 600 MHz spectrometer. All deuterated solvents were purchased from Cambridge Isotopes Laboratories, Inc. and stored over activated molecular sieves. The residual solvent protons or carbons were used as internal standards. ¹H NMR data are presented as follows: chemical shift in ppm (δ) downfield from tetramethylsilane (multiplicity, coupling constant, integration). The following abbreviations are used in reporting NMR data: s, singlet; d, doublet; t, triplet; q, quartet; dd, doublet of doublets; dt, doublet of triplets; ddd, doublet of doublet of doublets; m, multiplet. Enynes **2.1**³ and **2.3**,¹¹ as well as Ph₃PAuNTf₂⁴² were synthesized following literature procedures.

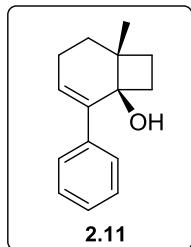
2.6.2 Preparation of starting materials and products

Synthesis of the [4.2.0]bicyclo alcohols, **2.11** and **2.12**



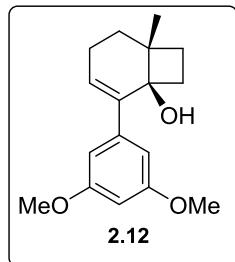
To a scintillation vial was added enyne (0.41 mmol), nitromethane (2 mL) and water (300 µL). The contents were mixed with vigorous stirring. Ph₃PAuNTf₂ (0.041 mmol) was added. The vial was stirred for 2 hours, then concentrated. After crude NMR, the alcohols were purified by silica gel chromatography, with 6:1 hexanes/ethyl acetate as eluent.

Synthesis of compound 2.11.



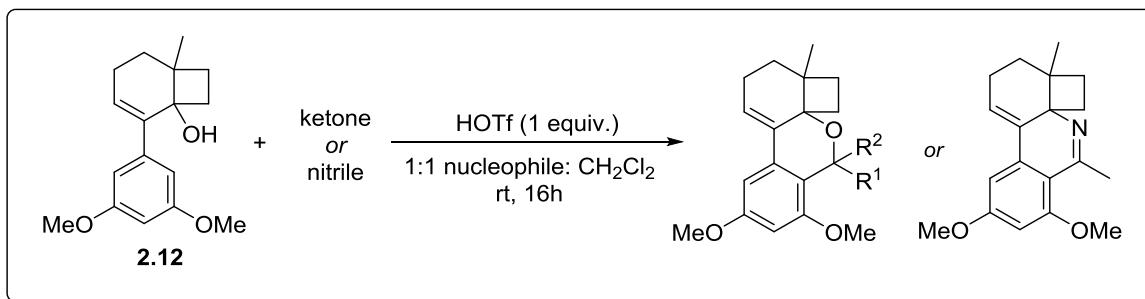
The product was obtained as a white solid in 92% yield. **¹H NMR** (600 MHz, CDCl₃) δ 7.55 – 7.43 (m, 2H), 7.36 – 7.29 (m, 2H), 7.26 – 7.24 (m, 1H), 6.21 – 6.16 (m, 1H), 2.56 – 2.44 (m, 2H), 2.28 (tddd, *J* = 24.3, 11.6, 5.9, 2.7 Hz, 2H), 1.73 (s (br), 1H), 1.67 (dt, *J* = 11.0, 9.2 Hz, 1H), 1.52 (dddd, *J* = 13.7, 6.2, 2.8, 0.8 Hz, 1H), 1.50 – 1.32 (m, 2H), 1.29 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ = 140.8, 139.5, 128.2, 127.9, 127.7, 127.0, 72.9, 44.4, 36.4, 29.2, 23.2, 23.0, 22.3.

Synthesis of compound 2.12.



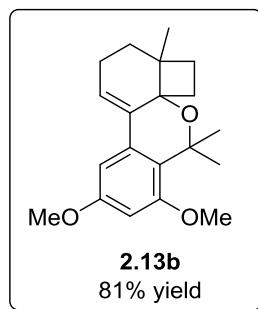
The product was obtained as a clear colorless oil in 85% yield. **¹H NMR** (600 MHz, CDCl₃) δ 6.60 (d, *J* = 2.3 Hz, 2H), 6.38 (t, *J* = 2.3 Hz, 1H), 6.18 – 6.14 (m, 1H), 3.79 (s, 6H), 2.55 – 2.39 (m, 2H), 2.35 – 2.18 (m, 2H), 1.83 (s (br), 1H), 1.66 (dt, *J* = 11.0, 9.2 Hz, 1H), 1.54 – 1.47 (m, 1H), 1.43 – 1.34 (m, 2H), 1.28 (s, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ = 160.4, 141.8, 141.0, 128.1, 106.0, 99.0, 72.8, 55.3, 44.2, 36.4, 29.3, 23.1, 22.9, 22.4.

General procedure for the synthesis of ketone and nitrile trapped products **2.13b – 2.13f**



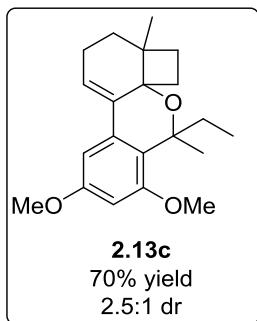
To a 1-dram vial was added enyne **2.12** (0.05 mmol) and DCM (0.3 mL). The appropriate ketone or nitrile was added (0.3 mL), and the contents were stirred. TfOH (1 equiv., 0.05 mmol) was added. The reaction was stirred for 16 hours and concentrated. For ketone-incorporated products **2.13b**, **2.13c**, and **2.13d**, the products were purified by silica gel column chromatography. Nitrile-incorporated products **2.13e** and **2.13f** were analyzed as is.

Synthesis of **2.13b.**



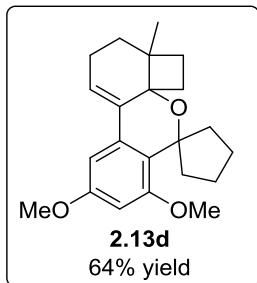
The product was isolated as a clear colorless oil in 81% yield. **$^1\text{H NMR}$** (600 MHz, CDCl_3) δ 6.64 (d, $J = 2.5$ Hz, 1H), 6.40 (d, $J = 2.4$ Hz, 1H), 6.23 (t, $J = 4.3$ Hz, 1H), 3.85 (s, 3H), 3.80 (s, 3H), 2.50 (q, $J = 10.3$ Hz, 1H), 2.30 (q, $J = 6.1$ Hz, 2H), 1.77 (ddd, $J = 10.7, 8.5, 2.0$ Hz, 1H), 1.65 (s, 3H), 1.64 – 1.60 (m, 1H), 1.48 (s, 3H), 1.40 (t, $J = 6.9$ Hz, 2H), 1.33 (s, 3H), 1.27 (ddd, $J = 11.8, 8.7, 2.0$ Hz, 1H). **$^{13}\text{C NMR}$** (151 MHz, CDCl_3) δ = 158.6, 156.7, 135.9, 134.2, 123.5, 120.1, 100.0, 98.5, 74.4, 70.3, 55.2, 55.1, 42.8, 33.9, 29.6, 28.8, 28.5, 22.6, 22.5, 22.3.

Synthesis of 2.13c.



Compound **2.13c** was obtained as a mixture of 2.5 : 1 mixture of diastereomers in a 70% overall yield. The crude NMR is provided with the NMR spectra. The major diastereomer was separated and analyzed by NMR. **¹H NMR** (600 MHz, CDCl₃) δ 6.60 (d, *J* = 2.5 Hz, 1H), 6.36 (d, *J* = 2.4 Hz, 1H), 6.20 – 6.15 (m, 1H), 3.83 (s, 3H), 3.75 (s, 3H), 2.48 – 2.41 (m, 1H), 2.26 (dt, *J* = 8.5, 3.9 Hz, 2H), 2.00 (dq, *J* = 13.4, 7.3 Hz, 1H), 1.73 (ddd, *J* = 10.7, 8.5, 2.0 Hz, 1H), 1.68 (dt, *J* = 13.4, 7.3 Hz, 1H), 1.63 – 1.59 (m, 1H), 1.58 (s, 3H), 1.42 – 1.34 (m, 2H), 1.28 (s, 3H), 1.25 (td, *J* = 9.7, 2.0 Hz, 2H), 0.55 (t, *J* = 7.3 Hz, 3H). **¹³C NMR** (151 MHz, CDCl₃) δ = 158.6, 156.7, 136.2, 135.6, 121.9, 120.0, 100.0, 98.4, 70.2, 55.2, 55.2, 43.0, 34.2, 34.2, 28.8, 27.8, 22.7, 22.6, 22.4, 8.4.

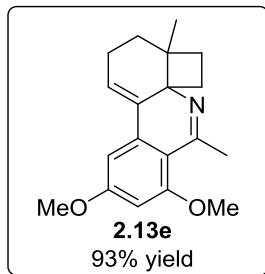
Synthesis of 2.13d.



Compound **2.13d** was isolated in 64% yield as a colorless oil. **¹H NMR** (600 MHz, CDCl₃) δ 6.62 (d, *J* = 2.4 Hz, 1H), 6.37 (d, *J* = 2.4 Hz, 1H), 6.19 (t, *J* = 4.3 Hz, 1H), 3.83 (s, 3H), 3.76 (s, 3H), 2.53 (q, *J* = 10.2 Hz, 1H), 2.32 – 2.14 (m, 4H), 2.05 – 1.98 (m, 1H), 1.92 – 1.81 (m,

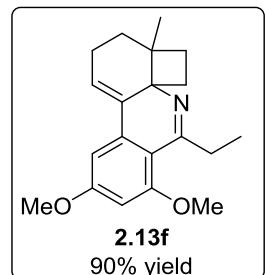
1H), 1.82 – 1.66 (m, 2H), 1.61 (td, J = 10.6, 10.1, 8.4 Hz, 3H), 1.42 – 1.34 (m, 2H), 1.28 (s, 3H), 1.27 – 1.21 (m, 2H). **^{13}C NMR** (151 MHz, CDCl_3) δ = 158.7, 156.7, 136.1, 135.2, 121.4, 120.1, 100.0, 98.5, 84.3, 70.5, 55.2, 55.1, 43.0, 41.1, 38.6, 33.1, 28.6, 25.6, 25.1, 22.7, 22.4, 22.4.

Synthesis of 2.13e.



The product **2.13e** was obtained as a pale yellow oil in 93% yield. The product contains trace impurities due to the sensitivity of the product to column chromatography. **^1H NMR** (600 MHz, CDCl_3) δ 6.77 (d, J = 2.2 Hz, 1H), 6.70 (dd, J = 6.2, 2.4 Hz, 1H), 6.45 (d, J = 2.2 Hz, 1H), 3.98 (s, 3H), 3.95 (s, 3H), 2.92 (s, 3H), 2.53 (dtd, J = 19.2, 5.4, 2.8 Hz, 1H), 2.44 (q, J = 10.4 Hz, 1H), 2.40 – 2.29 (m, 1H), 2.04 (ddd, J = 11.5, 8.8, 2.8 Hz, 1H), 1.71 (s, 3H), 1.68 (m, 1H), 1.62 (ddd, J = 14.2, 6.7, 1.8 Hz, 1H), 1.54 (ddd, J = 11.6, 9.9, 2.8 Hz, 1H), 1.37 (ddd, J = 14.1, 11.2, 5.5 Hz, 1H). **^{13}C NMR** (151 MHz, CDCl_3) δ = 174.1, 168.2, 163.8, 140.4, 132.8, 130.0, 107.6, 102.5, 98.2, 57.0, 56.3, 56.1, 42.6, 33.1, 28.4, 24.8, 23.2, 23.1, 23.0.

Synthesis of 2.13f.



The product **2.13f** was obtained as a pale yellow oil in 90% yield. The product contains trace impurities due to the sensitivity of the product to column chromatography. **¹H NMR** (600 MHz, CD₂Cl₂) δ 6.83 (d, *J* = 2.2 Hz, 1H), 6.75 (dd, *J* = 6.2, 2.3 Hz, 1H), 6.49 (d, *J* = 2.2 Hz, 1H), 3.98 (s, 3H), 3.97 (s, 3H), 3.44 (dq, *J* = 14.9, 7.5 Hz, 1H), 3.21 (dq, *J* = 14.1, 7.2 Hz, 1H), 2.60 – 2.50 (m, 1H), 2.44 – 2.28 (m, 2H), 2.06 (ddd, *J* = 11.4, 8.6, 2.6 Hz, 1H), 1.81 – 1.70 (m, 1H), 1.67 (s, 3H), 1.66 – 1.58 (m, 1H), 1.56 – 1.45 (m, 1H), 1.38 (ddd, *J* = 14.1, 11.3, 5.7 Hz, 1H), 1.25 (t, *J* = 7.8 Hz, 3H). **¹³C NMR** (151 MHz, CD₂Cl₂) δ = 178.5, 168.4, 163.5, 140.8, 132.8, 129.9, 106.6, 103.0, 98.2, 56.6, 56.4, 56.2, 42.3, 33.0, 30.1, 28.2, 23.1, 23.0, 22.7, 12.1.

2.6.3 NMR spectra of new compounds

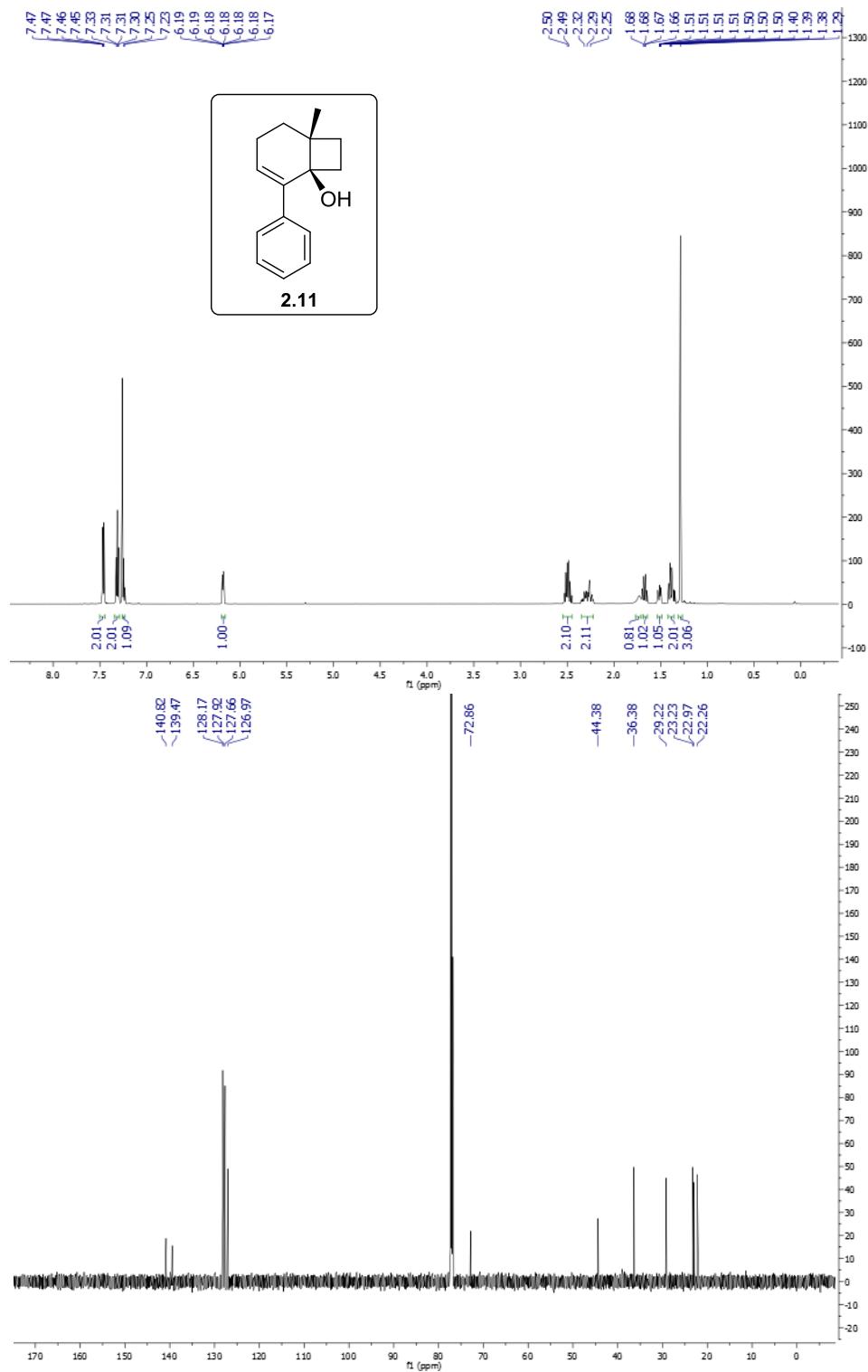


Figure 2.5. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of 2.11 in CDCl_3 at 25 °C

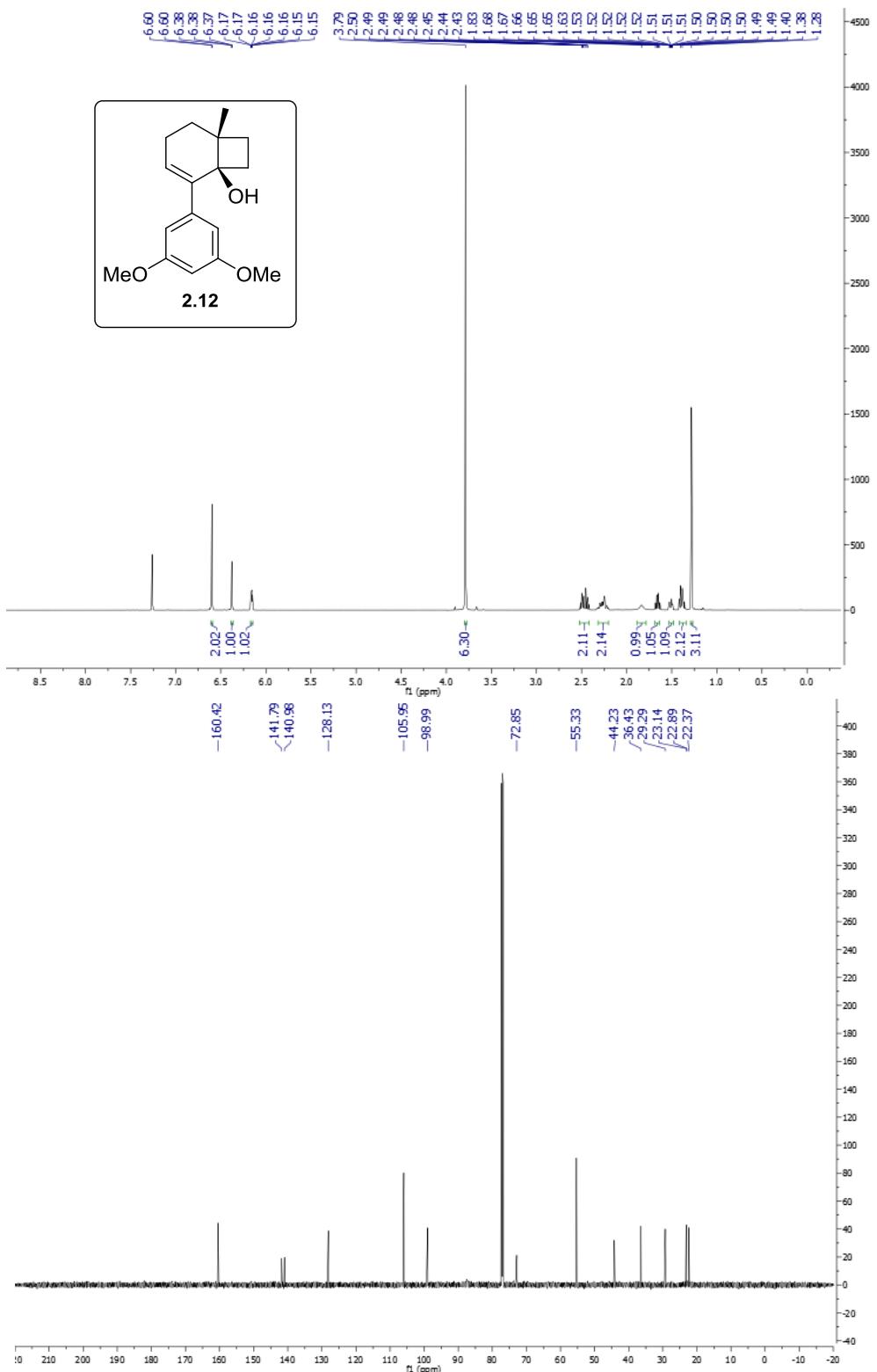


Figure 2.6. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **2.12** in CDCl_3 at 25 °C.

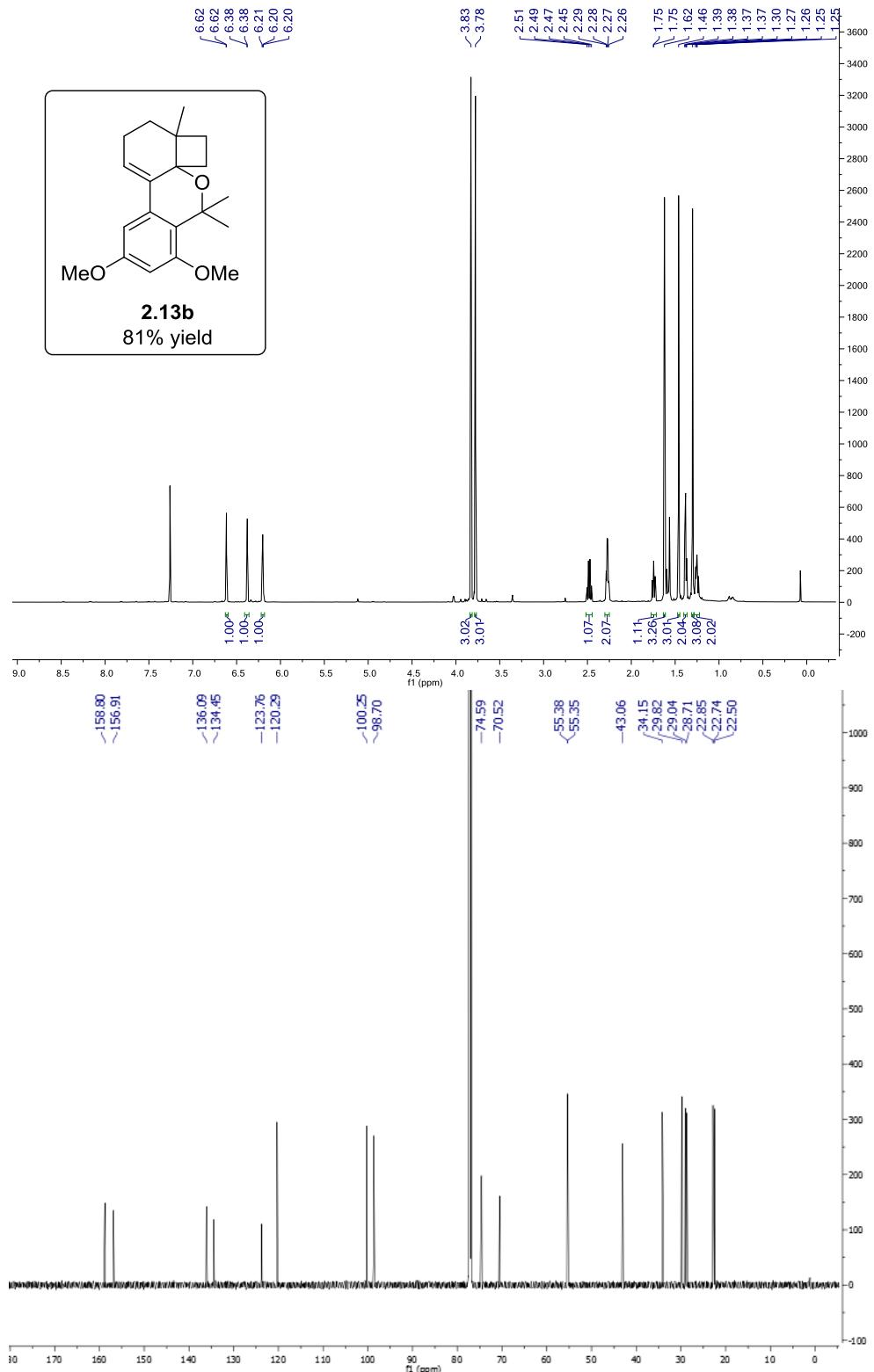


Figure 2.7. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **2.13b** in CDCl₃ at 25 °C.

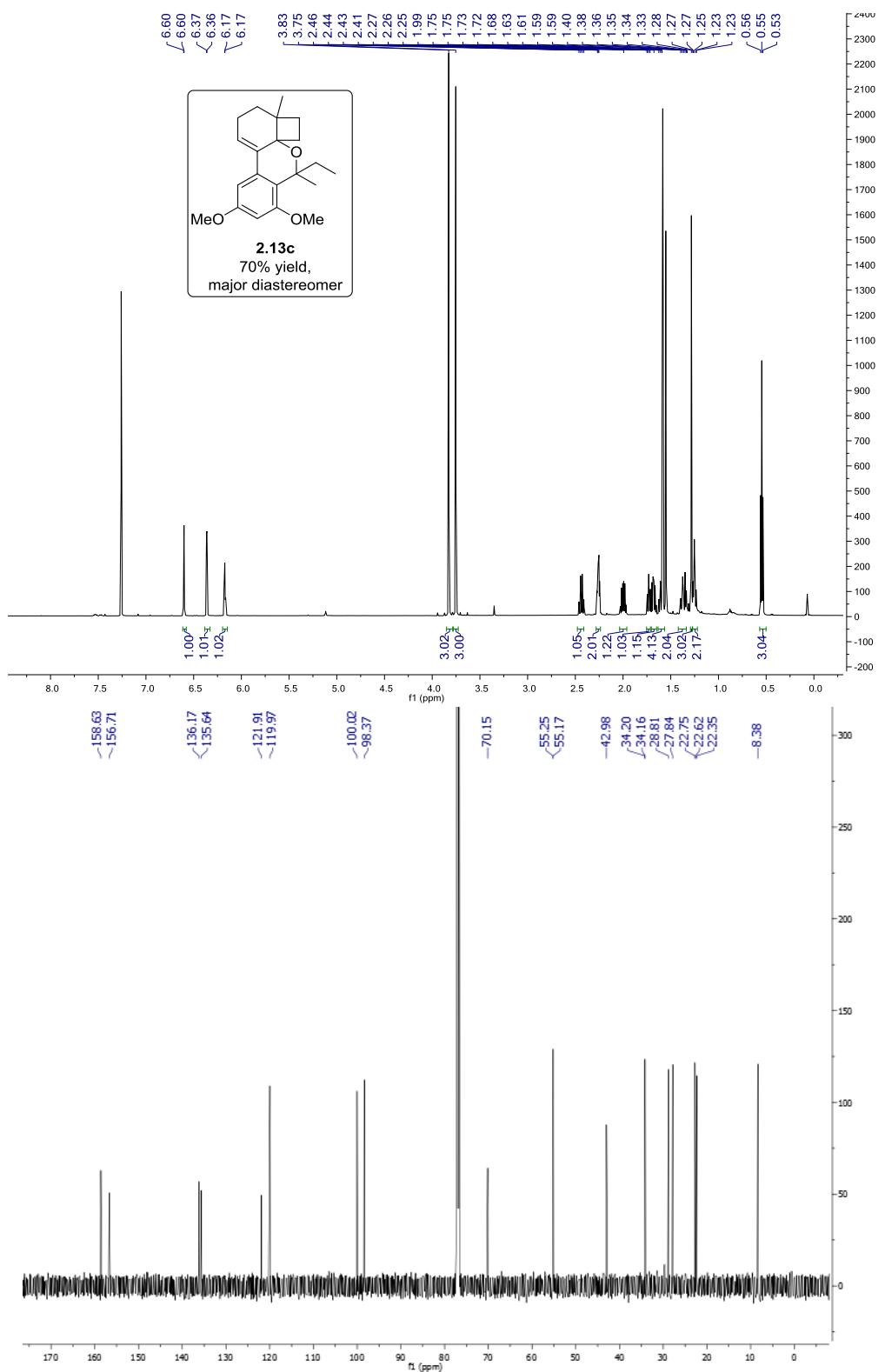


Figure 2.8. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of the major diastereomer of **2.13c** in CDCl_3 at 25 °C.

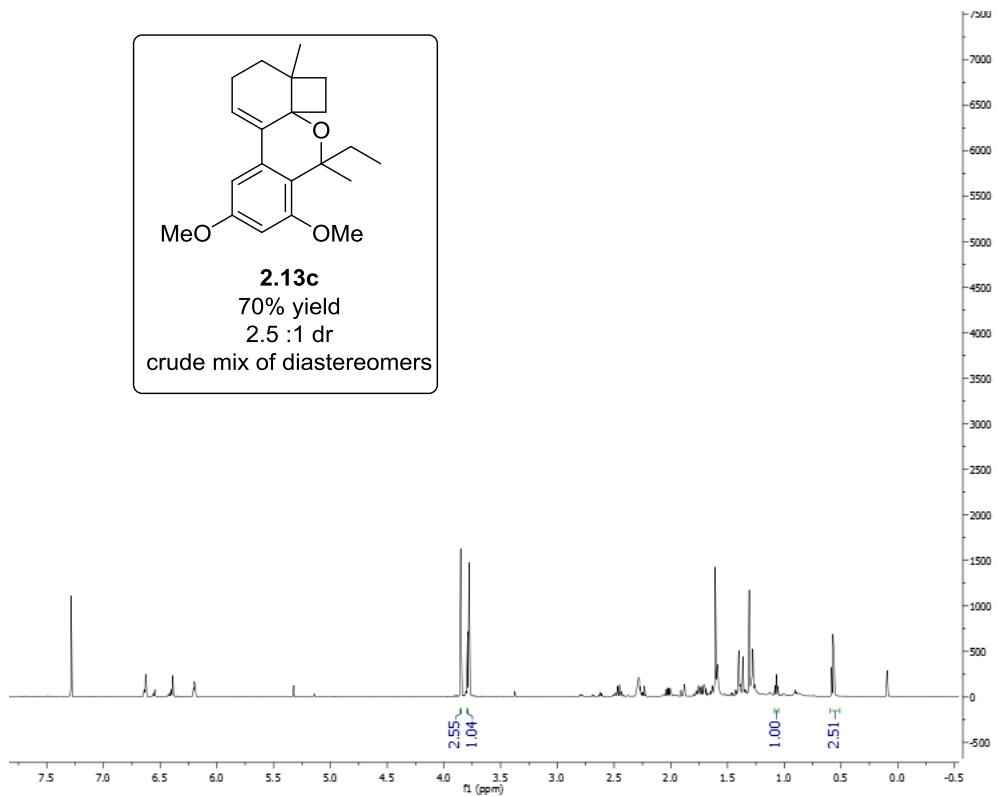


Figure 2.9 Crude ^1H of **2.13c** in CDCl_3 at 25 °C.

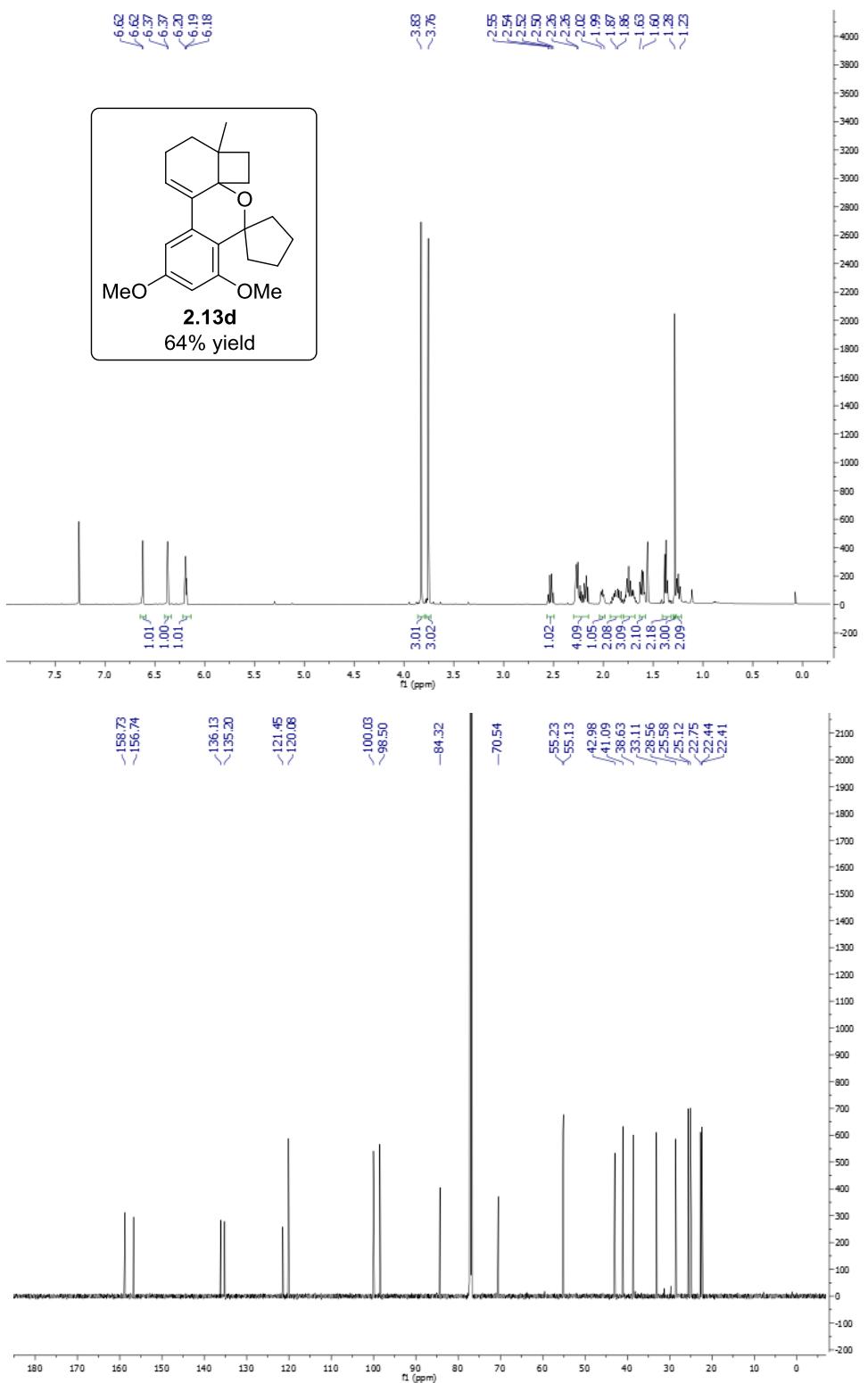


Figure 2.10. ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **2.13d** in CDCl_3 at 25°C .

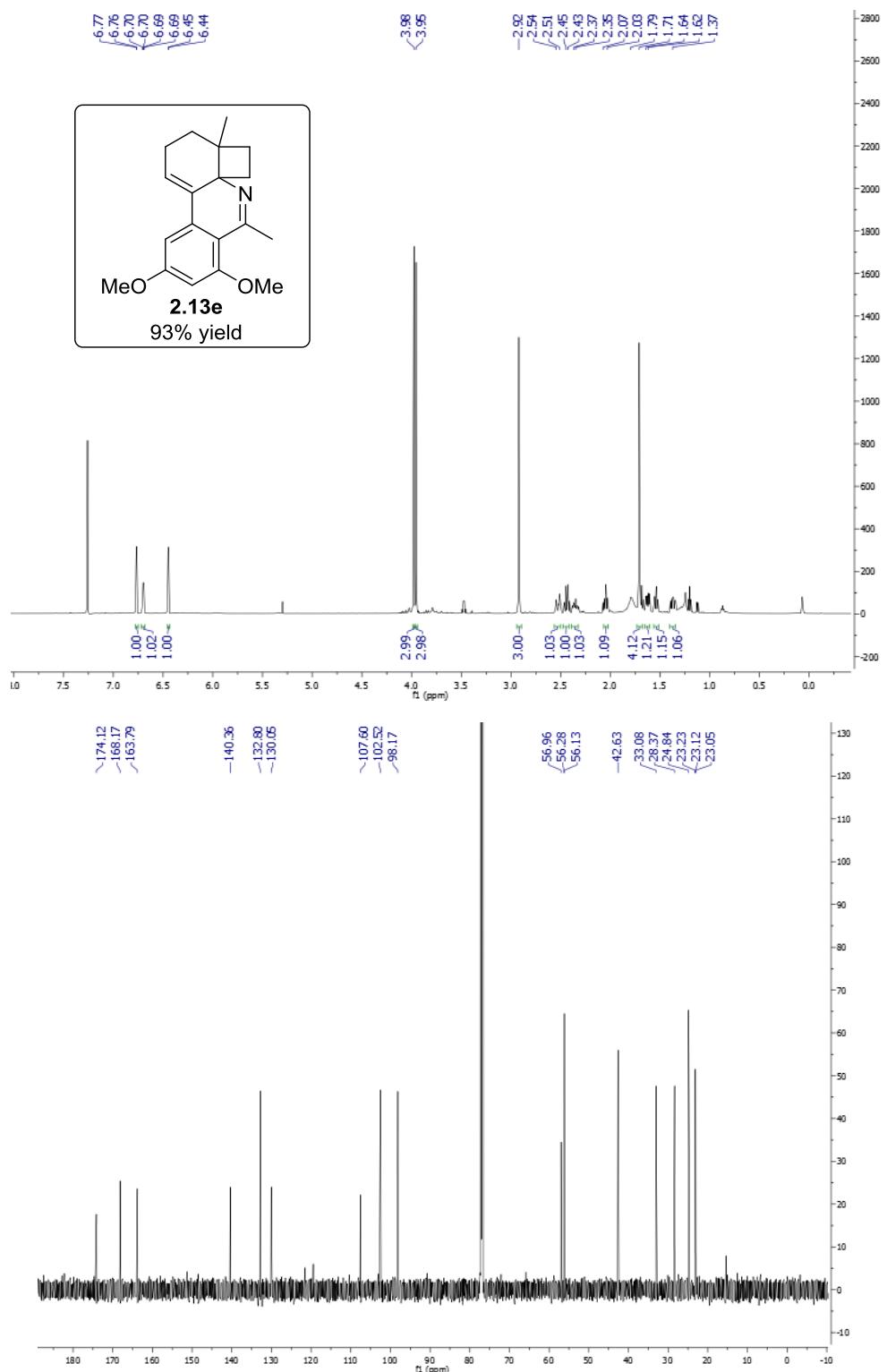


Figure 2.11 ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR of **2.13e** in CDCl_3 at 25 °C.

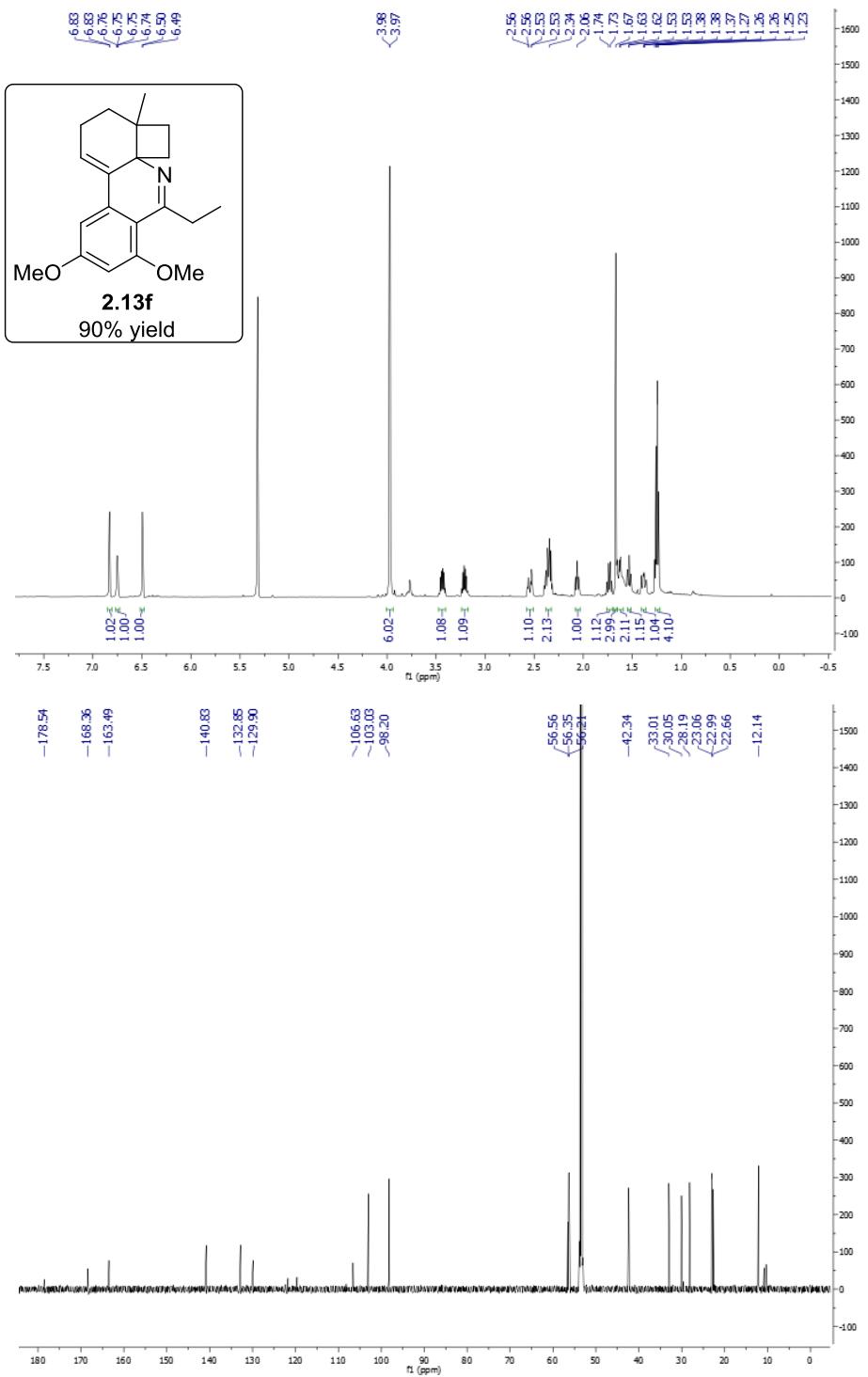


Figure 2.12. ^1H and $^{13}\text{C}\{\text{H}\}$ NMR of **2.13f** in CDCl_3 at 25 °C.

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Chapter 3: Computed thermodynamic stabilities of silylum Lewis base adducts

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3.1 Introduction

3.1.1 Silylum ions in catalysis

The use of silylum ions (“ R_3Si^+ ”) to activate Lewis bases for catalysis has proven to be of great importance in many synthetic applications.² The pronounced electrophilicity of the silylum ion requires stabilization by a Lewis base or solvent molecule as the free silylum ion has only been found to exist in situations with extreme steric congestion (Figure 3.1).^{3,4} One of the first reports of an isolated and fully characterized silylum ion that did not exhibit interaction with the anion is shown in Figure 3.1.^{5,6} Although it was initially proposed to be a naked silylum ion, in-depth analysis of the crystal structure revealed a Si–C interaction with the toluene solvent (Si–C bond length 2.18 Å). A few years later, the first “free” silylum ion was reported by Lambert and co-workers (**B**).^{7,8} The free silylum character was confirmed through X-ray analysis and NMR spectroscopy, with an unprecedented downfield ^{29}Si NMR chemical shift of 225.5 ppm. Compound **B** is the only truly “free” silylum ion reported to date. Other approaches, such as incorporating bulky aryl groups to shield the electron deficient silylum, reveal the stabilization of Si through a weak Si–C interaction (**C**, Si–C bond length 2.13 Å).⁹ The high Lewis acidity of the silylum ion can be attributed to the combination of an empty *p*-orbital on silicon, as well as an inefficient hyperconjugative stabilization of the electron deficient silicon cation.⁴

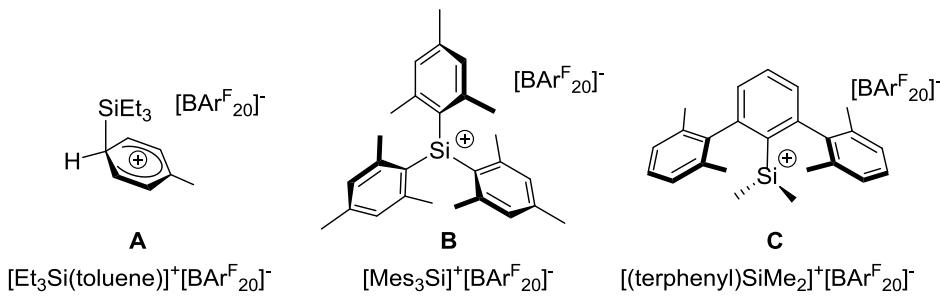


Figure 3.1. Isolated silylum ions.

While there are several methodologies for generating silylum ions *in situ*,¹⁰ a common and mild method is through the activation of a hydrosilane with the perfluoroaryl borane catalyst $\text{B}(\text{C}_6\text{F}_5)_3$ (BCF). The BCF catalyst heterolytically activates the silane once a Lewis base is added to a transiently formed BCF-silane adduct.^{11,12} The resulting stabilized silylum and borohydride ion pair can then act together to activate substrates for reduction (e.g. see Figure 3.2 for the phosphine variant¹³ on ethers). The combination of BCF and silane is effective in a number of reductions,^{14,15} including the reduction of bio-mass derived sugars,^{16–19} ethers,²⁰ and imines,^{21–23} as highlighted in Scheme 3.1). Okuda has shown that Ph_3B can also activate silanes for amide reductions, though this appears to proceed by a different mechanism.²⁴

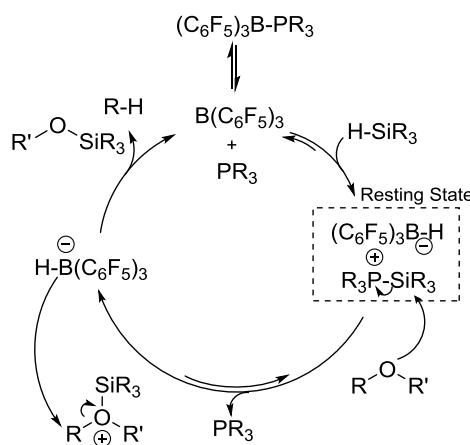
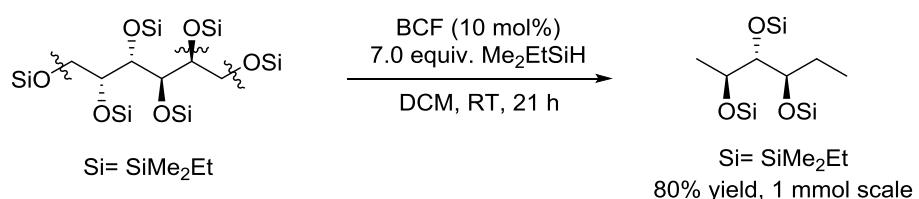
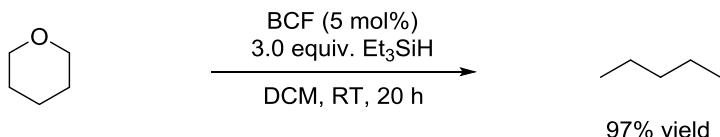


Figure 3.2. Phosphine-modified catalytic cycle for the BCF-catalyzed reduction of ethers.

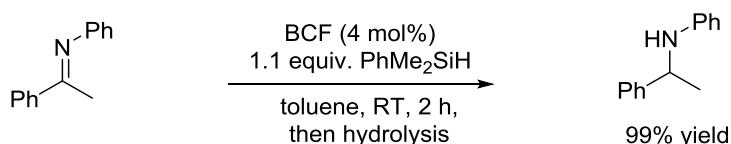
Reduction of bio-mass derived sugars, Gagné



Reduction of ethers, Gevorgyan/Yamamoto



Reduction of imines, Klankermayer

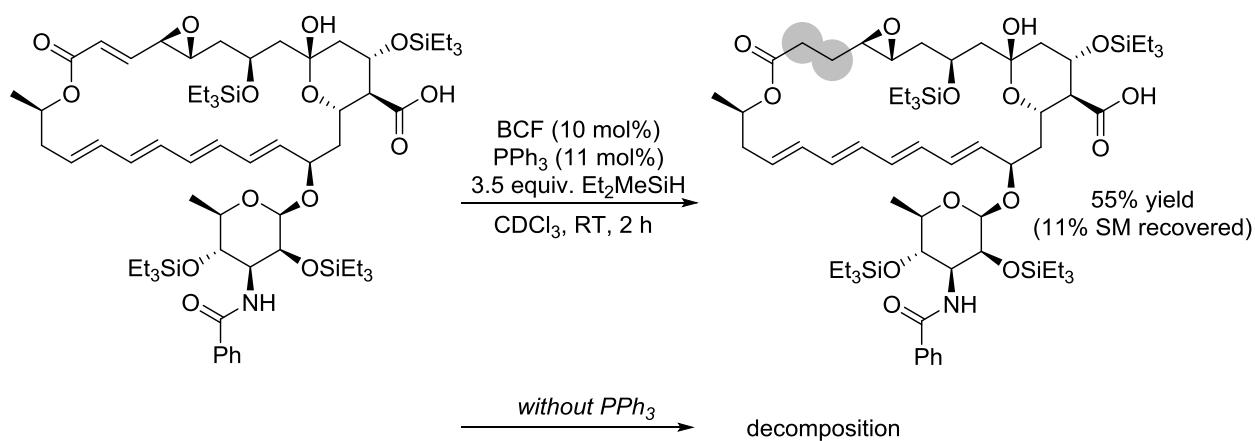


Scheme 3.1. BCF catalyzed reductions

3.1.2 Combination of BCF and silane for chemoselective reductions

Most recently, our group demonstrated that this methodology could also provide highly chemoselective transformations on complex natural products.²⁵ Through careful selection of Lewis acid catalyst and silane, the selective modification of diverse, densely functionalized molecules was achieved. Important for sensitive compounds was the realization that the addition of a phosphine Lewis base attenuates the reactivity of the system (through the formation of a silyl-phosphonium ion), and seemingly acts as a silylium ion carrier that delivers silylium to the various Lewis basic sites in the molecule. In the case of natamycin, BCF was shown to decompose the natural product, requiring catalytic PPh₃ as an additive to achieve reductions (Scheme 3.2). This report was followed by an experimental and theoretical study on the role of phosphines as silylium ion carriers and thermodynamic driver for catalyst speciation into the [R₃Si–PR₃⁺][H–BCF[–]] ion pair (Figure 3.2).¹³ Various combinations of phosphines and silanes

were screened with BCF to study the extent of speciation in systems with different steric and electronic parameters. With these studies in mind, we aimed to compute the “silaphilicity” of various Lewis bases, including phosphines, amines and oxygenated groups as a way to further understand how inherent Lewis base preferences might correlate with chemoselectivity in complex molecules.



Scheme 3.2. Chemoselective reduction of natamycin.

3.1.3 Research objective

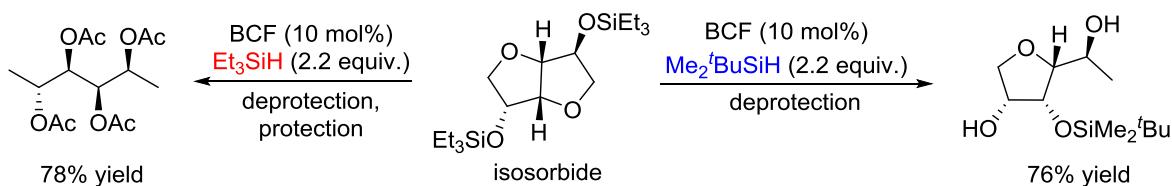
Herein we report a computational investigation on the thermodynamic stability of Lewis base silylium adducts as a function of silane and Lewis base. These studies delineate optimum coordination geometries in addition to revealing comparative strengths of the Lewis bases that would be competing to coordinate a silylium ion in a complex molecule.

3.2 Results and discussion

3.2.1 Variation of silane

The reactivity and selectivity in the reduction of ethers and biomass-derived sugars is sensitive to the reducing silane. While steric bulk in the substrate can play a role in determining regioselectivity, it is the steric and electronic properties of the silane that impart the largest

impact over chemoselectivity. For example, in the reduction of Et₃Si-protected isosorbide, the use of Et₃SiH as reductant affords the tetraol product (Scheme 3.3).¹⁷ Alternatively, the bulkier Me₂^tBuSiH only ring opens one of the THF rings to afford the cyclic THF product. We therefore began our study by computing ΔG for silylum exchange between triphenylphosphine and 2-methyltetrahydrofuran (2-Me-THF) as a function of silane (Table 3.1).



Scheme 3.3. Silane-dependent reduction of isosorbide.

The results in Table 3.1 follow the trend that silylum-transfer from R₃Si–PPh₃⁺ to 2-Me-THF becomes increasingly less favorable as the size of the R₃Si increases, presumably due to the short Si–O in the products (c.f. Si–P). The Et₃Si⁺ group exhibits the lowest Gibbs free energy for transfer to 2-Me-THF at +2.5 kcal/mol, followed by Me₃Si⁺ at 3.1 kcal/mol. While it is somewhat unexpected that the free energy of Et₃Si⁺ is lower than that of Me₃Si⁺, the calculated Si–P and Si–O bond lengths are longer (by 0.01 Å), which would alleviate steric congestion in the 2-Me-THF adduct (especially). The free energies for Me₂EtSi⁺ and Me₂PhSi⁺ transfer were calculated to be +4.6 and +4.1 kcal/mol, respectively. Of the five R₃Si's calculated, Ph₃Si⁺ is the least favorable at +8.5 kcal/mol.

Experimentally, bulkier silanes are less prone to ionization upon reacting with a combination of phosphine and BCF.¹³ Those same studies demonstrated that triphenylsilane is only partially speciated by the combination of BCF and a triarylphosphine, while even bulkier silanes such as tri-*iso*-propylsilane are completely unreactive. To simplify the model and reduce computational costs, the following calculations were done using “Me₃Si⁺”.

Table 3.1. Effect of substituents on free energy of transfer to 2-Me-THF.

R_3Si^+	$\text{R}_3\text{Si}-\overset{\oplus}{\text{PPh}}_3$	2-Me-THF	$\xrightleftharpoons[\text{CH}_2\text{Cl}_2]{}$	PPh_3	SiR_3 -O-alkyl cation
	ΔG^a				Si-P bond length ^c
Me_3Si^+	3.1	0.0			2.333
Me_2EtSi^+	4.6	1.5			2.331
Et_3Si^+	2.5	-0.6			2.343
Me_2PhSi^+	4.1	1.0			2.333
Ph_3Si^+	8.5	5.4			2.337
Me_3Si^+	3.1	0.0			2.333

^aFree energy reported in kcal/mol. ^b ΔG_{ref} normalized to the free energy of Me_3SiH .

^cBond lengths reported in Ångströms. ^d $\Delta \text{C}-\text{O}$ reflects the change in bond length between C_1-O and C_4-O of the silyloxonium. $\Delta \text{C}-\text{O}$ for the free 2-Me-THF is 0.006 Å.

3.2.2 Variation of phosphine

We next aimed to study how the phosphine basicity and steric profile affects the thermodynamics of silylium transfer; experimentally both features play a crucial role in ionizing the silane with BCF. Phosphines such as PPh_3 make a stable and insoluble adduct with BCF, which provides little free BCF and phosphine to allow for silylium ion generation. Bulkier phosphines such as tri(*o*-tolyl)phosphine don't ionize bulkier silanes such as Et_3SiH , though the smaller Me_2EtSiH does efficiently heterolyze to give the silylphosphonium/ borohydride ion pair.¹³

The propensity to transfer Me_3Si^+ from triphenylphosphine to a broad array of phosphine Lewis bases is collected in Table 3.2. These calculations reveal the general trend that smaller, electron-rich phosphines are better able to stabilize a silylium ion relative to larger, electron

deficient phosphines. The balance of steric and electronic factors is rather nuanced as demonstrated by trimesitylphosphine and di-*tert*-butyl(*o*-biphenyl)phosphine forming poor silyl-phosphoniums, while P'Bu₃ and PCy₃ are actually more stabilizing than PPh₃.

Table 3.2. Steric and electrons perturbations of phosphine Lewis base acceptor.

Phosphine	ΔG (kcal/mol)	Si–P bond length (\AA) ^a	$\Delta \text{Si–P}$ (\AA) ^b
P'Bu ₃	-6.0	2.357	0.024
P(<i>p</i> -tol) ₃	-3.9	2.330	0.003
PCy ₃	-3.3	2.351	0.018
P(<i>o</i> -tol) ₃	-2.2	2.367	0.035
PPh ₂ (<i>p</i> -tol)	-1.7	2.332	-0.001
PPh ₂ <i>i</i> Pr	-1.3	2.329	-0.004
PPh ₂ (<i>o</i> -biphenyl)	1.4	2.346	0.013
P(<i>p</i> -F-Ph) ₃	2.3	2.336	0.003
P(1-naphthyl) ₃	3.3	2.380	0.047
PPh ₂ (C ₆ F ₅)	6.1	2.359	0.026
P(<i>p</i> -CF ₃ -Ph) ₃	6.2	2.344	0.011
P('Bu) ₂ (<i>o</i> -biphenyl)	10.8	2.400	0.067
P(mesityl) ₃	11.1	2.412	0.079

^aThe calculated Si–P bond length of Me₃Si–PPh₃⁺ is 2.333 \AA . ^b Δ Si–P measures

the difference in bond length between the silyl-phosphonium and Me₃Si–PPh₃⁺.

These computational studies correlate well to experimental results previously reported using triethylsilane.¹³ For example, when $[\text{Et}_3\text{Si}-\text{PPh}_2(o\text{-biphenyl})^+][\text{H}-\text{BCF}^-]$ (in the presence of 5 equivalents of free $\text{PPh}_2(o\text{-biphenyl})$) is treated with 5 equivalents of $\text{PPh}_2(p\text{-tol})$, silylium transfer to the less sterically hindered phosphine occurs quantitatively. Computationally, the transfer of Me_3Si^+ from $\text{PPh}_2(o\text{-biphenyl})$ to $\text{PPh}_2(p\text{-tol})$ is thermodynamically favorable by 3 kcal/mol.

3.2.3 Variation of heteroatom Lewis base silylium acceptors

To begin comparing heteroatom-stabilizers of silylium, the thermodynamics of silylium transfer from $\text{Me}_3\text{Si}-\text{PPh}_3^+$ to simple ethers was studied. These calculations were designed to reveal how sterics affected the ether's ability to stabilize a silylium ion (Table 3.3). The transfer of silylium from the reference $\text{Me}_3\text{Si}-\text{PPh}_3^+$ to the simplest ether, dimethylether, is disfavored by +7.5 kcal/mol. The corresponding ethyl ether increases slightly (0.2 kcal/mol), while bulkier groups are even more destabilizing (+1.5 and +4.7 kcal/mol for ${}^i\text{Pr}$ and ${}^t\text{Bu}$, respectively). Dimethoxyethane reports on how inductive deactivation of a $\beta\text{-OMe}$ group lowers O-basicity (+9.9 vs. MeOEt at +7.7 kcal/mol). Despite increasing charge delocalization to the more substituted carbons (as reflected by $\Delta C-\text{O}$), it is clear that sterics dominate the thermodynamics, and this would be enhanced for larger R_3Si^+ groups.

Table 3.3. Effect of substitution on methyl ether silylum acceptors.

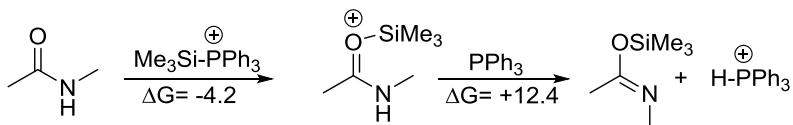
Ether	ΔG^a	$\Delta\Delta G_{ref}^{a,b}$	$\Delta C-O^{c,d}$	$\Delta Si-O^{c,e}$
Me ₂ O	7.5	–	0.000	0.000
MeOEt	7.7	0.2	0.021	-0.011
MeO <i>i</i> Pr	9.0	1.5	0.050	-0.012
MeO <i>t</i> Bu	12.2	4.7	0.079	-0.001
(MeOCH ₂) ₂	9.9	2.4	0.002	-0.005

^aFree energy reported in kcal/mol. ^b ΔG_{ref} normalized to the free energy of Me₂O. ^cBond lengths reported in Å. ^d $\Delta C-O$ reflects the change in bond length between R–O and H₃C–O of the silyloxonium. ^e $\Delta Si-O$ reflects the change in bond length between O–Si of the silyl oxonium and O–Si of Me₂O–SiMe₃⁺.

The stability of a collection of Lewis bases/functional groups commonly encountered in complex structures was assessed relative to PPh₃, the Lewis base added to inhibit decomposition in our work on natamycin (vide infra). The tested groups include amines, ethers, epoxides, and carbonyls (Figure 3.3). Thermodynamic data on where silylum preferentially rests could provide insights into the chemoselectivity that is observed when reactive groups compete in complex natural products, sugars and other simpler substrates.

A limited number of substrates were more stabilizing than PPh₃, including aliphatic amines and amides, as well as triphenylarsine. DABCO has the most negative ΔG (-9.5 kcal/mol) and benefits from a reduced steric profile and the high basicity of the pre-pyramidalized nitrogen. Tertiary amides, including N,N-dimethylacetamide and N-acetylpyrrolidine, are more

stabilizing than a secondary amide. We considered the possibility that the O-silylum adduct of a secondary amide might also be deprotonated by the PPh_3 , however this reaction is computed to be disfavored by 12.4 kcal/mol in CH_2Cl_2 (Scheme 3.4).



Scheme 3.4. Potential reactivity pathway for N-methylacetamide.

The majority of the calculated functional groups were less stabilizing than PPh_3 . Cyclic and acyclic ketones follow the trend that the enones are lower in energy than their saturated counterparts—2-cyclohexenone is 3.4 kcal/mol more stabilizing than cyclohexanone, 3-penten-2-one is 4.0 kcal/mol lower than 2-pentanone, and methyl crotonate is 2.0 kcal/mol more stabilizing than methyl butyrate. The conjugated alkene thus provides 2-4 kcal/mol of extra stabilization. When an inductive electron withdrawing group is near the enoate, a predictable reduction in stabilization is observed (3.1 kcal/mol). This array is present in natamycin (vide infra). Recent reactivity initiated by Me_3Si^+ transfer to acetal ethers is also included in the ranking.¹⁰

A comparison of the cyclic ethers was also informative. THF is 1.1 kcal/mol lower in energy than the 2-Me-THF, and it is 5.5 kcal/mol more stable than tetrahydrothiophene.²⁶ Tetrahydropyran (THP) is 4.2 kcal/mol lower in energy than 1,4-dioxane and is also lower in energy than isochroman, chromane, and 4H-chromene (2.2, 9.2 and 15.0 kcal/mol, respectively). Each of these latter cases reduces O-basicity through conjugation or inductive effects. While most substrates followed reasonable trends, several cases stood out. The cis and trans 2,5-Me₂-THF optimizations revealed that silylum transfer to the cis-Me₂-THF is more favorable than the trans-

Me2-THF (by 3.7 kcal/mol). In the optimized geometries, the methyl groups of the cis-THF allow Me3Si+ to occupy a position more distal from the methyl groups while in the trans case it is forced to reside between them causing the Si–O bond length to lengthen (Scheme 3.5).

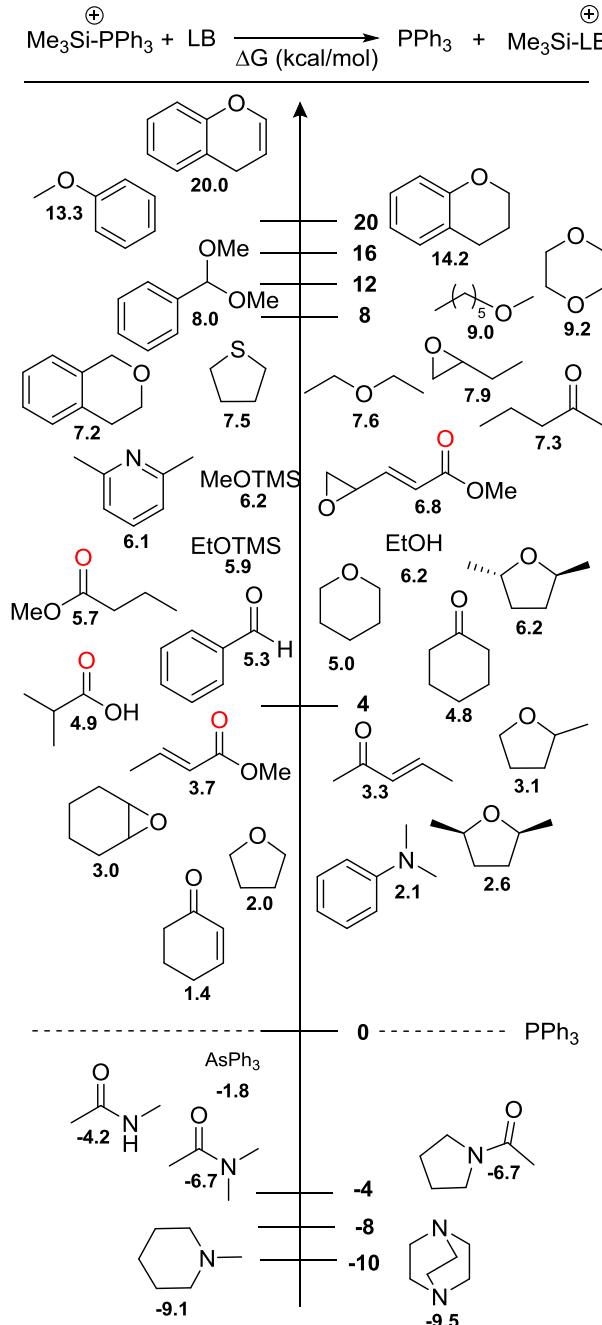
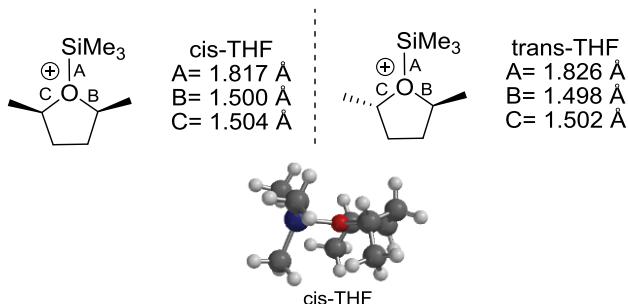


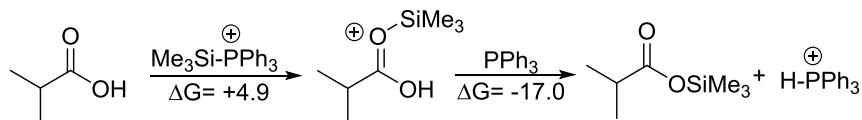
Figure 3.3. Thermodynamic Lewis base stabilities of various substrates. The numbers in bold indicate the Gibbs free energy (kcal/mol) for the transfer of Me3Si+ from Me3Si-PPh3 to the

Lewis base. The heterolysis of $\text{Me}_3\text{Si}-\text{PPh}_3^+$ to PPh_3 and Lewis base free Me_3Si^+ is endergonic by 24.0 kcal/mol.



Scheme 3.5. Bond lengths for the cis and trans 2,5-Me₂-THF silylum ions.

For carboxylic acids, the product of O-silylation is expected to be quite acidic. The viability of PPh_3 , a weak base, to deprotonate the intermediate is supported by the large negative free energy change for the follow-up deprotonation (Scheme 3.6). An exogenous Lewis base could therefore also function as a Brønsted base under catalytic conditions.



Scheme 3.6. Potential reactivity pathway for isobutyric acid.

A number of biomass-derived sugar molecules were also examined. To best mimic experiments demonstrating selective deoxygenation of these structures, the free alcohols on the sugar were protected with Me_3Si groups (Figure 3.4). In the case of isosorbide, there are two diastereomeric ethereal sites, with transfer of Me_3Si^+ to O-1 being more favorable by 2.0 kcal/mol. Transfer to isomannide (+3.2 kcal/mol), a diastereomer of isosorbide, is more favorable than both isomers of isosorbide. Experimentally, the reductive pathways of isosorbide

and isomannide are highly dependent on the sterics of the reducing silane, as shown in Scheme 3.3.¹⁷

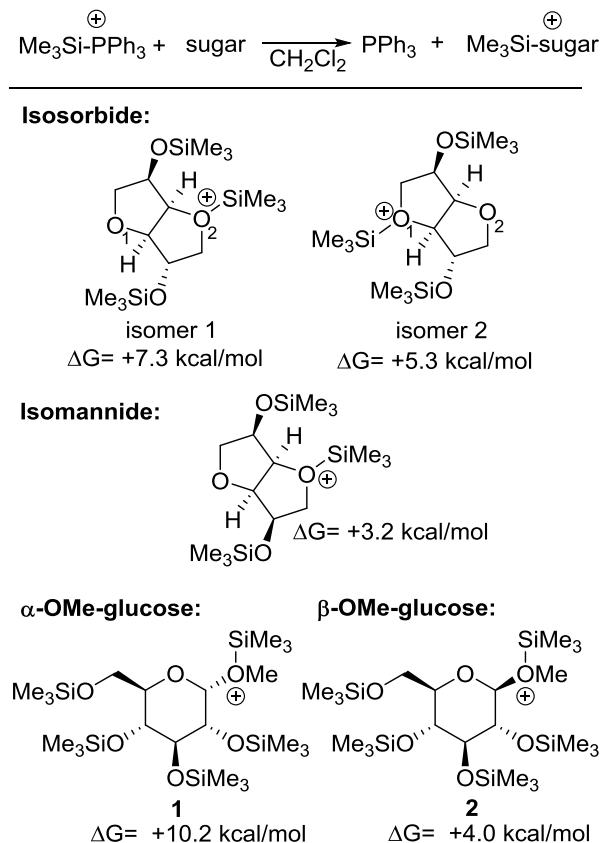


Figure 3.4. Silylium Lewis base adducts of bio-mass derived sugar substrates.

The stability of the alpha- and beta- anomers of per-silyl protected methylglucose were also studied. To begin, the belt of Me_3Si -protecting groups is geared and well-organized around the sugar, and the α -anomer is 3.7 kcal/mol more stable than the β -form (Figure 3.5). These stabilities, however, are inverted in the silyloxonium ion, where the β -anomer is now 2.4 kcal/mol more stable than the α (Figure 3.5). This is in agreement with experimental observations as β -OMe-glucose is considerably more reactive than α -OMe-glucose.²⁷ The mechanism of demethoxylation has been proposed to occur via a common oxocarbenium intermediate.^{27,28} As shown in Figure 3.5, generation of this species is calculated to be downhill

(-0.6 kcal/mol) for the α -silyloxonium, and slightly uphill by 1.8 kcal/mol for the β -silyloxonium ion. In hindered gluco-disaccharides the α -linkage is more reactive than the β -disaccharide.¹⁹

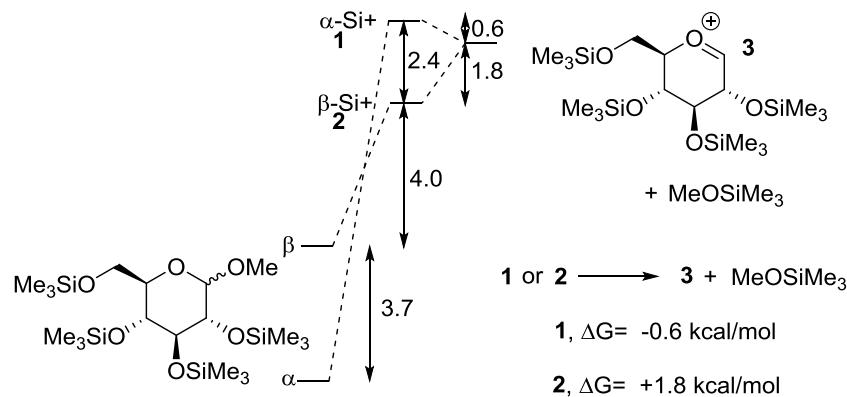


Figure 3.5. Free energy diagram for the demethylation of α - and β -OMe-glucose. Each horizontal line represents the energy of the most stable energy minimized conformer.

3.2.4 Rationalization of reactivity in complex natural products

Our small molecule model systems can be used to begin rationalizing the reactivity observed with the complex natural product natamycin. A rank ordering of the reactivity of the functional groups in natamycin was experimentally determined via the stepwise addition of one equivalent of silane in combination with catalytic amounts of fluoroarylborane and triphenylphosphine (Figure 3.6).²⁵ The reaction was monitored by *in situ* NMR spectroscopy. The most reactive site is the carboxylic acid, which undergoes dehydrosilation to form the silyl ester ($\uparrow H_2$). While the initial silylium transfer to model isobutyric acid is uphill by +4.9 kcal/mol, the subsequent acid-base chemistry to form silyl ester and $H-PPh_3^+$ is favored by -12.1 kcal/mol.

Thus, while the amide in natamycin is likely more basic, a rapid and favorable deprotonation apparently enhances acid silylation reactivity. The resulting phosphonium acid/borohydride would recombine to form H₂ (observed), though it is also conceivable that the

acid directly reacts with borohydride to give H₂ without the intervention of PPh₃. Traces of H-PPh₃⁺ is observed by ³¹P NMR, though its kinetic role is difficult to ascertain.

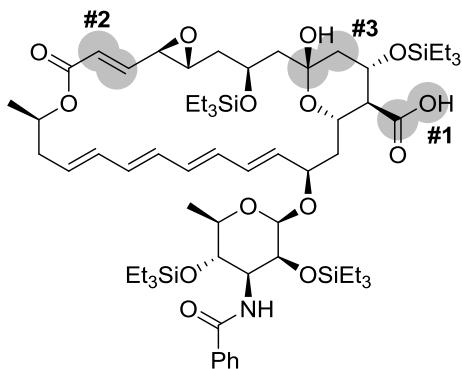


Figure 3.6. Reactivity hierarchy observed experimentally with natamycin (using B(3,5-(CF₃)₂C₆H₃)₃ and Me₂EtSiH).

The second most reactive site in natamycin under these conditions was the enoate, which is conjugatively reduced to a silyl ketene acetal (hydrolyzed upon workup). Computationally, an electronically deactivated enoate should be comparable to cyclic ethers, though the experimental data clearly show that the latter sp³-electrophiles are kinetically disadvantaged. While these thermodynamic measures of silylium activation suggest that SiMe₃⁺ should predominantly bind to the amide, the reducing agent generated in situ (H-BAr^{F₃-}) is apparently insufficiently nucleophilic to reduce the activated amide. In contrast, the conjugate hydride of the less electrophilic mixed fluoroaryl/alkyl Lewis acids (BAr^{F₂(R)}) are likely more nucleophilic and are capable of amide reductions, i.e. H-BAr^{F₂(R)-} vs H-BAr^{F₃-}. Continuing this trend to Ph₃B, Okuda has shown that this much less Lewis acidic borane can reduce amides with silane.²⁴ Based on the calculations of Heiden, Ph₃B-H⁻ should be 19 kcal/mol more hydridic than (C₆F₅)₂BR-H⁻, which in turn is 10 kcal/mol more hydridic than BCF-H⁻.²⁹ These calculations therefore imply that chemoselectivity is a consequence of both silylium ion Lewis base preference and the

nucleophilicity of the ion-pair reductant. The lactol is the third most reactive site, resulting in elimination at ambient temperatures and reduction at reduced temperatures (0 °C).

Monitoring of catalytic reductions by ^{19}F NMR spectroscopy clearly shows that the BAr^{F}_3 catalyst rests as the borohydride ion, whose ion pair is presumably a silylum–Lewis base adduct. The location of the SiMe_2Et^+ group under these conditions is murky as broad signals are observed in both the ^{31}P and ^1H NMR spectra. Our working hypothesis is that the silylum ion exchanges between multiple Lewis basic functional groups, but that it predominantly exists on PPh_3 and the amide, both of which are unreactive under the reaction conditions. The PPh_3 can thus be considered a carrier of SiR_3^+ and is able to transfer this activating group to multiple positions, some of which are more reactive to reduction than others. A second role for the PPh_3 in these experiments is to ensure that the concentration of BCF remains low by driving the formation of $\text{H}-\text{BCF}^-$ -containing ion pairs. In this form the fluoroaryl borane is not electrophilic and does not decompose the sensitive natural product.

3.3 Conclusions

In summary, we have compared the relative thermodynamic stabilities of several Lewis bases relevant to catalysis. Through these calculations we are able to understand the balance between sterics and basicity in the transfer of silylum to various Lewis basic sites to both simple and more complex substrates. These results also provide a better appreciation for which processes account for thermodynamic vs. kinetic control. In the cases where experiment and theory do not agree, it can be rationalized that kinetics, rather than thermodynamics, are the key factors at play. Additional studies involving transition state calculations could provide additional support. These calculations will help rationalize and guide future experiments.

3.4 Acknowledgements

We thank the Department of Energy (Basic Energy Science, DE-FG02-05ER15630) for support.

3.5 Experimental Section

3.5.1 Computational Methods

All calculations were performed using the Gaussian 09³⁰ software package, revision E.01. The ωB97X-D³¹ functional was used in conjunction with the 6-31G+**³² basis set. Geometry optimizations were performed using standard gradient methods. Final geometry optimizations and frequency calculations were performed without symmetry constraints. The conductor-like polarizable continuum (CPCM)³³ solvation model was used with solvent parameters for dichloromethane. All free energy calculations were obtained by taking into account vibrational zero-point energies, thermal motions, and entropy contributions at standard conditions (298 K, 1 M).

3.5.2 Basis set comparison

Table 3.4. Calculations for the splitting of trimethylsilane with BCF and PPh₃.^a

BCF + PPh ₃ + HSiMe ₃	$\xrightarrow{\text{CH}_2\text{Cl}_2}$	Me ₃ Si-PPh ₃ ⁺ + H-BCF ⁻	
Basis set	Time (h) ^b	ΔG (kcal/mol)	$\Delta\Delta G$ (kcal/mol) ^c
6-31G	13.2	-5.52	-2.91
6-31G*	39.6	2.29	4.91
6-31+G*	226.3	-3.12	-0.51
6-31+G**	191.8	-2.61	--
6-311+G*	326.8	-3.17	-0.55
6-311+G**	341.3	-2.48	0.13
6-311++G**	425.8	-2.56	0.05

^aAll calculations were run using the ω B97X-D functional using the CPCM solvation mode with solvent parameters for dichloromethane. ^bThe time listed represents the amount of time for all calculations in the reaction scheme to converge. To make for a fair comparison, the calculations were performed starting from the same structure for each molecule. ^c $\Delta\Delta G$ represents the difference in Gibbs free energy between the other basis set relative to 6-31+G** which was chosen for the study.

To determine the best basis set for the scope of this study, several basis sets were screened using the ω B97X-D functional. We aimed to strike a balance between minimized energy and computational cost. Assuming the 6-311++G** basis set gives the most accurate energy for the reaction shown in Table 3.4, we compared the Gibbs free energies of seven

different basis sets. For our study, we chose 6-31+G** as our basis set as the value for the test calculation comes close to that of the 6-311++G** basis set in less than half the computational time.

3.5.3 Table of summarized energies

Table 3.5. Relevant energies of all optimized coordinates.

Compound	Absolute E (a.u.)	Zero Point E (a.u.)	G (a.u.)
Me ₃ Si–PPh ₃ ⁺	-1445.191	-1444.799	-1444.852
PPh ₃	-1036.094	-1035.818	-1035.863
2-Me-THF	-271.712	-271.566	-271.596
Me ₃ Si–2-Me-THF ⁺	-680.803	-680.541	-680.580
Me ₂ EtSi–PPh ₃ ⁺	-1484.494	-1484.072	-1484.129
Me ₂ EtSi–2-Me-THF ⁺	-720.105	-719.813	-719.854
Et ₃ Si–PPh ₃ ⁺	-1563.097	-1562.616	-1562.674
Et ₃ Si–2-Me-THF ⁺	-798.709	-798.359	-798.403
Me ₂ PhSi–PPh ₃ ⁺	-1636.872	-1636.424	-1636.482
Me ₂ PhSi–2-Me-THF ⁺	-872.480	-872.163	-872.209
Ph ₃ Si–PPh ₃ ⁺	-2020.232	-2019.674	-2019.741
Ph ₃ Si–2-Me-THF ⁺	-1255.834	-1255.407	-1255.460

P ^t Bu ₃	-814.788	-814.415	-814.456
Me ₃ Si-P ^t Bu ₃ ⁺	-1223.898	-1223.407	-1223.454
P(<i>p</i> -tol) ₃	-1154.024	-1153.664	-1153.716
Me ₃ Si-P(<i>p</i> -tol) ₃ ⁺	-1563.125	-1562.650	-1562.711
PCy ₃	-1047.016	-1046.527	-1046.573
Me ₃ Si-PCy ₃ ⁺	-1456.121	-1455.514	-1455.567
P(<i>o</i> -tol) ₃	-1154.008	-1153.647	-1153.695
Me ₃ Si-P(<i>o</i> -tol) ₃ ⁺	-1563.107	-1562.630	-1562.687
PPh ₂ (<i>p</i> -tol)	-1075.404	-1075.099	-1075.147
Me ₃ Si-PPh ₂ (<i>p</i> -tol) ⁺	-1484.502	-1484.082	-1484.138
PPh ₂ <i>i</i> -Pr	-923.027	-922.746	-922.790
Me ₃ Si-PPh ₂ <i>i</i> -Pr ⁺	-1332.126	-1331.730	-1331.780
PPh ₂ (<i>o</i> -biphenyl)	-1267.086	-1266.728	-1266.781
Me ₃ Si-PPh ₂ (<i>o</i> -biphenyl) ⁺	-1676.184	-1675.709	-1675.768
P(<i>p</i> -F-Ph) ₃	-1333.739	-1333.487	-1333.537
Me ₃ Si-P(<i>p</i> -F-Ph) ₃ ⁺	-1742.832	-1742.464	-1742.522
P(1-naphthyl) ₃	-1496.887	-1496.468	-1496.522

$\text{Me}_3\text{Si}-\text{P}(1\text{-naphthyl})_3^+$	-1905.981	-1905.445	-1905.506
$\text{PPh}_2(\text{C}_6\text{F}_5)$	-1532.126	-1531.890	-1531.941
$\text{Me}_3\text{Si}-\text{PPh}_2(\text{C}_6\text{F}_5)^+$	-1941.211	-1940.860	-1940.920
$\text{P}(p\text{-CF}_3\text{-Ph})_3$	-2047.008	-2046.717	-2046.782
$\text{Me}_3\text{Si}-\text{P}(p\text{-CF}_3\text{-Ph})_3^+$	-2456.093	-2455.687	-2455.760
$\text{P}({}^t\text{Bu})_2(o\text{-biphenyl})$	-1119.553	-1119.131	-1119.180
$\text{Me}_3\text{Si}-\text{P}({}^t\text{Bu})_2(o\text{-biphenyl})^+$	-1528.639	-1528.098	-1528.152
$\text{P}(\text{mesityl})_3$	-1389.863	-1389.334	-1389.394
$\text{Me}_3\text{Si}-\text{P}(\text{mesityl})_3^+$	-1798.950	-1798.302	-1798.365
Me_2O	-154.991	-154.910	-154.936
$\text{Me}_3\text{Si}-\text{OMe}_2^+$	-564.072	-563.875	-563.913
MeOEt	-194.301	-194.192	-194.220
$\text{Me}_3\text{Si}-\text{OMeEt}^+$	-603.384	-603.158	-603.197
$\text{MeO}i\text{Pr}$	-233.611	-233.474	-233.504
$\text{Me}_3\text{Si}-\text{OMe}i\text{Pr}^+$	-642.692	-642.439	-642.478
$\text{MeO}t\text{Bu}$	-272.920	-272.754	-272.786
$\text{Me}_3\text{Si}-\text{OMe}t\text{Bu}^+$	-681.999	-681.716	-681.755

(MeOCH ₂) ₂	-308.788	-308.645	-308.677
Me ₃ Si-(MeOCH ₂) ₂ ⁺	-717.866	-717.608	-717.650
1,2-epoxybutane	-232.373	-232.258	-232.286
Me ₃ Si-1,2-epoxy-	-641.457	-641.226	-641.265
butane ⁺			
Anisole	-346.680	-346.545	-346.576
Me ₃ Si-anisole ⁺	-755.752	-755.503	-755.544
2-pentanone	-271.727	-271.584	-271.617
Me ₃ Si-2-pentanone ⁺	-680.812	-680.554	-680.596
Cyclohexenone	-308.596	-308.468	-308.498
Me ₃ Si-cyclohexenone ⁺	-717.687	-717.444	-717.484
Cyclohexeneoxide	-309.786	-309.633	-309.622
Me ₃ Si-	-718.873	-718.606	-718.646
cyclohexeneoxide ⁺			
AsPh ₃	-2928.587	-2928.311	-2928.357
Me ₃ Si-AsPh ₃ ⁺	-3337.685	-3337.293	-3337.349
Cyclohexanone	-309.828	-309.676	-309.706
Me ₃ Si-cyclohexanone ⁺	-718.913	-718.646	-718.687

Dabco	-345.260	-345.074	-345.105
Me ₃ Si–Dabco ⁺	-754.373	-754.070	-754.109
Cis-2,5-Me ₂ -THF	-311.025	-310.851	-310.883
Me ₃ Si–Cis-2,5-Me ₂ -	-720.117	-719.827	-719.867
THF ⁺			
trans-2,5-Me ₂ -THF	-311.025	-310.851	-310.883
Me ₃ Si–trans-2,5-Me ₂ -	-720.111	-719.821	-719.862
THF ⁺			
Dioxane	-307.591	-307.467	-307.496
Me ₃ Si–dioxane ⁺	-716.671	-716.432	-716.470
3-penten-2-one	-270.493	-270.375	-270.408
Me ₃ Si–3-penten-2-one ⁺	-679.583	-679.350	-679.392
Methylbutyrate	-346.939	-346.790	-346.824
Me ₃ Si–methylbutyrate ⁺	-756.022	-755.758	-755.801
Et ₂ O	-233.612	-233.475	-233.504
Me ₃ Si–OEt ₂ ⁺	-642.695	-642.441	-642.481
EtOH	-155.011	-154.931	-154.956
Me ₃ Si–ethanol ⁺	-564.093	-563.897	-563.935

Hexylmethylether	-351.525	-351.302	-351.339
Me ₃ Si-	-760.609	-760.268	-760.314
hexylmethylether ⁺			
H-PPh ₃ ⁺	-1036.527	-1036.239	-1036.286
Imine	-657.118	-656.914	-656.954
iPrCOOH	-307.645	-307.525	-307.556
Me ₃ Si-iPrCOOH ⁺	-716.730	-716.495	-716.537
iPrCOO-SiMe ₃	-716.322	-716.100	-716.142
Lutidine	-326.841	-326.696	-326.728
Me ₃ Si-lutidine ⁺	-735.931	-735.667	-735.707
Methylcrotonate	-345.705	-345.850	-345.613
Me ₃ Si-methylcrotonate ⁺	-754.790	-754.551	-754.596
Methyl-(E)-3-(oxiran-2-yl)acrylate	-458.957	-458.821	-458.856
Me ₃ Si-Methyl-(E)-3-(oxiran-2-yl)acrylate ⁺	-868.039	-867.788	-867.834
MeOSiMe ₃	-524.371	-524.217	-524.251
Me ₃ Si-MeOSiMe ₃ ⁺	-933.458	-933.187	-933.230

EtOSiMe ₃	-563.682	-563.498	-563.535
Me ₃ Si–EtOSiMe ₃ ⁺	-972.770	-972.470	-972.514
N-Me-acetamide	-248.476	-248.373	-248.403
Me ₃ Si–N-Me-	-657.574	-657.355	-675.396
acetamide ⁺			
N-Me-piperidine	-291.153	-290.964	-290.995
Me ₃ Si–N-Me-	-700.265	-699.959	-699.998
piperidine ⁺			
N,N-dimethylaniline	-366.123	-365.947	-365.981
Me ₃ Si–N,N,-	-775.217	-774.925	-774.966
dimethylaniline ⁺			
THF	-232.400	-232.282	-232.311
Me ₃ Si–THF ⁺	-641.490	-641.257	-641.296
Tetrahydropyran	-271.713	-271.566	-271.594
Me ₃ Si–tetrahydropyran ⁺	-680.800	-680.536	-680.575
Tetrahydrothiophene	-555.388	-555.274	-555.302
Me ₃ Si–	-964.471	-964.241	-964.279
tetrahydrothiophene ⁺			

4H-chromene	-422.862	-422.714	-422.747
Me ₃ Si–4H-chromene ⁺	-831.925	-831.663	-831.704
Chroman	-424.096	-423.925	-423.957
Me ₃ Si–chroman ⁺	-833.168	-832.881	-832.923
Isochroman	-424.089	-423.918	-423.950
Me ₃ Si–isochroman ⁺	-833.172	-832.885	-832.927
N,N-dimethylacetamide	-287.770	-287.638	-287.669
Me ₃ Si–N,N-dimethylacetamide ⁺	-696.873	-696.626	-696.669
N-acetyl-pyrrolidine	-365.181	-365.012	-365.044
Me ₃ Si–N-acetyl-pyrrolidine ⁺	-774.287	-774.001	-774.044
Benzaldehyde	-345.480	-345.369	-345.399
Me ₃ Si–Benzaldehyde ⁺	-754.564	-754.338	-754.380
Benzaldehyde	-500.480	-500.285	-500.323
dimethylacetal			
Me ₃ Si–Benzaldehyde	-909.563	-909.252	-909.299
dimethylacetal ⁺			

Isosorbide	-1352.743	-1352.372	-1352.429
Me ₃ Si-isosorbide ⁺	-1761.832	-1761.344	-1761.406
Isomer1			
Me ₃ Si-isosorbide ⁺	-1761.833	-1761.345	-1761.410
Isomer2			
Isomannide	-1761.832	-1761.343	-1761.404
Me ₃ Si-isomannide ⁺	-1352.741	-1352.368	-1352.420
Alpha-Me-glucose	-2361.018	-2360.382	-2360.462
Me ₃ Si-Alpha-Me-	-2270.102	-2769.350	-2769.434
glucose ⁺			
Beta-Me-glucose	-2361.017	-2360.380	-2360.456
Me ₃ Si-Beta-Me-	-2770.107	-2769.354	-2769.438
glucose ⁺			
Glucose-oxocarbenium ⁺	-2245.700	-2245.108	-2245.184
Me ₃ Si ⁺	-409.015	-408.904	-408.935

3.6 Associated content

APPENDIX A: OPTIMIZED COORDINATES AND GIBBS FREE ENERGIES.

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Chapter 4: Towards a controlled Kumada catalyst-transfer polycondensation of a fluorine-incorporated donor-acceptor conjugated monomer

4.1 Introduction

4.1.1 π -Conjugated polymers

The design and synthesis of π -conjugated polymers has long been of interest to scientists for their applicability as semiconductors in organic electric materials, such as organic light emitting diodes, transistors and photovoltaic cells.¹ The unique electronic properties of π -conjugated polymers arises from the chain of overlapping p-orbitals, creating a system of delocalized π -electrons along the conjugated polymer backbone. The conductivity arises from the transport of charge either along the conjugated backbone or through neighboring stacked polymer chains. In the simplest π -system such as ethylene, the difference between the π bonding and π antibonding orbitals is quite large.² In a polymer, however, as the conjugation length increases, the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) decreases, leading to the development of continuous valence bands and conduction bands (Figure 4.1).² The difference between these energy levels is referred to as the band gap (E_g) of the polymer, and it can be finely tuned by modifying the polymer structure.

The structural features of the monomer unit impart unique properties on the resulting polymer, including redox activity, optical absorption and emission, and charge transporting capabilities.¹ The main variations in monomer backbone include the repeat unit, side chain and

substituents (Figure 4.2). Aromatic hydrocarbons and fused aromatics with heteroatoms such as sulfur, nitrogen and oxygen are common monomer units.³ Due to the π -stacking nature and the conjugated backbone, alkyl or ether based side chains are often incorporated into the monomer unit to allow for better solubility of the resulting polymer.¹ The positioning of these side-chains requires careful thought, as the steric hindrance between neighboring alkyl chains has been shown to strongly impact the energy levels of the polymer.⁴ The incorporation of electron donating or withdrawing substituents can elevate or lower the energy levels of the resulting polymer.³ The variation of these three key structural features allows for the fine tuning of band gap, solubility and other electronic parameters.

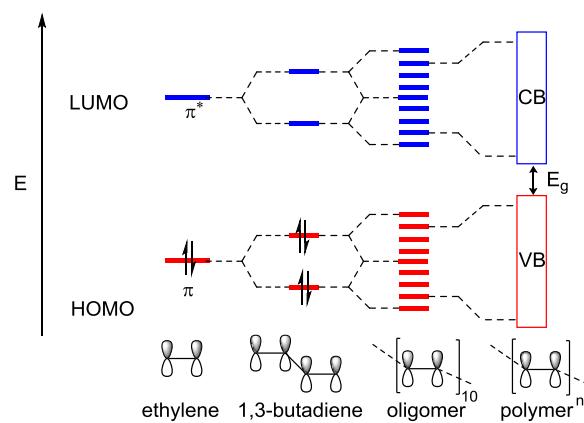


Figure 4.1. Comparison of band gap in conjugated systems.

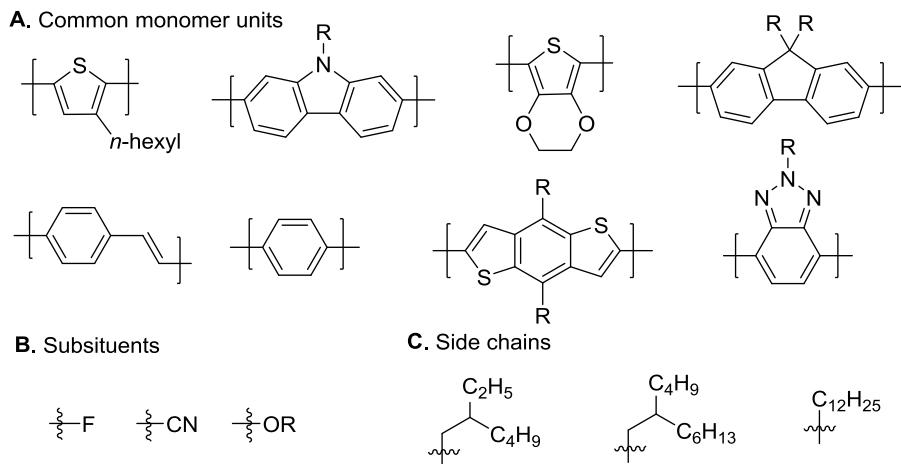


Figure 4.2. Common structural features of conjugated polymers.

Conjugated polymers are traditionally synthesized through transition metal catalyzed step-growth polycondensations.⁵ In a step growth reaction, polymer chains grow through the reaction of any two molecular species—monomers can react with monomers, oligomers or polymers. Because there is no control over which species react with which, step growth methods have a low degree of control over the molecular weight and dispersity of the polymer, leading to irreproducible polymer properties among different batches.⁶ Another limitation is that high molecular weights can only be achieved at high conversions of monomer (Figure 4.3). Alternatively, chain-growth polymerizations overcome these limitations through the sequential addition of single monomer units to the active end of a growing polymer chain.⁶ Key features of chain-growth polymerizations include the formation of high molecular weight polymers at relatively low monomer conversions and a steady increase in monomer consumption throughout the course of the reaction.⁷ A living polymerization is a subclass of chain-growth polymerizations in which no termination or chain transfer reactions occur during the polymerization. Thus, the molecular weight of the polymer increases linearly with conversion of

monomer, allowing for precise control over monomer sequence, composition and molecular weight.

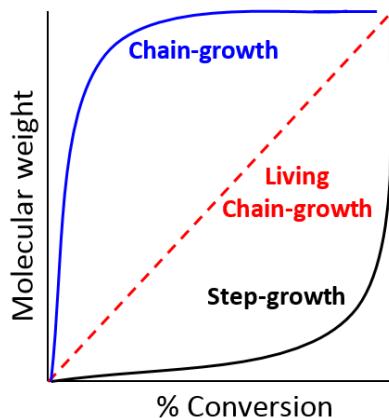
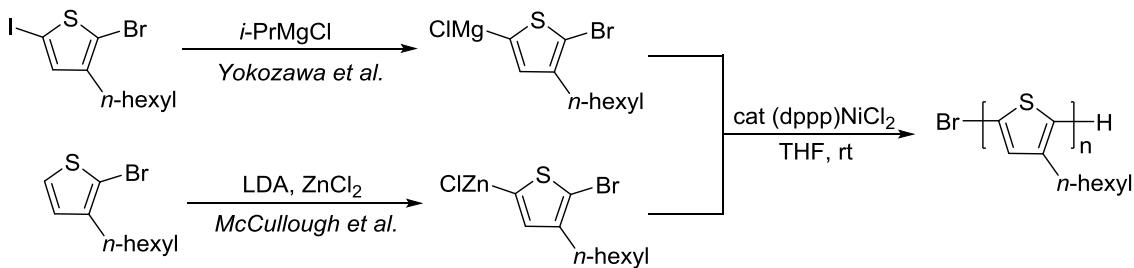


Figure 4.3. Step-growth vs. chain-growth and living chain-growth polymerization

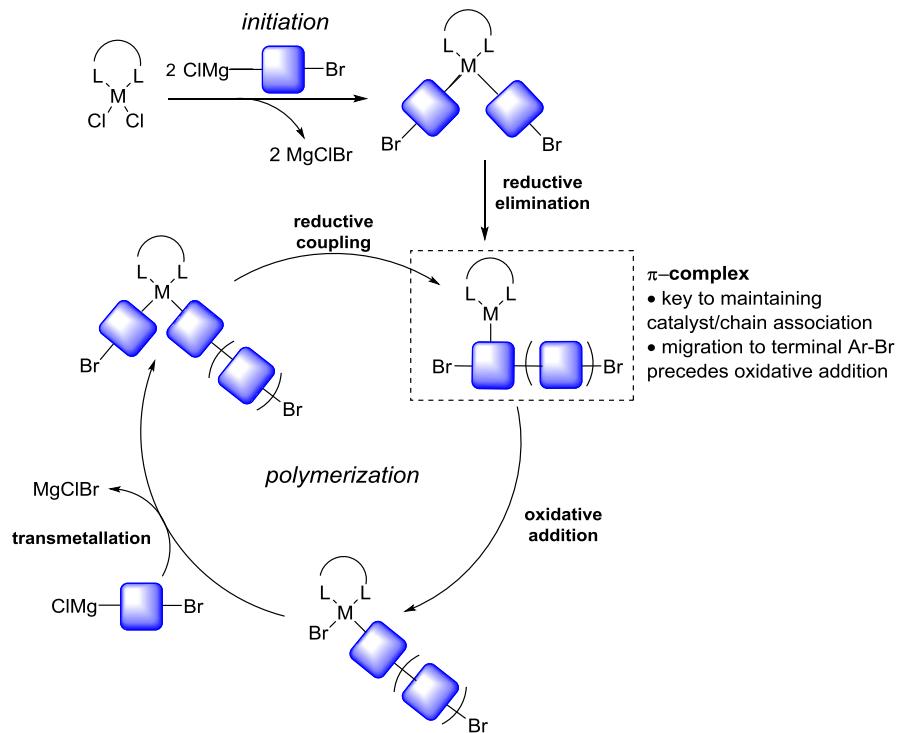
4.1.2 Catalyst transfer polycondensation

The development of living, chain-growth polymerization methods for the synthesis of conjugated polymers gained traction in 2004 when both Yokozawa⁸ and McCullough⁹ independently identified a Ni-catalyzed living chain-growth mechanism for the synthesis of poly(3-hexylthiophene) (P3HT) (Scheme 4.1). While the Ni-catalyzed Grignard polymerization was first reported in 1980, the reaction was long believed to enchain monomer by a step-growth mechanism.¹⁰ Both Yokozawa and McCullough performed a number of mechanistic and kinetic studies to prove the living chain-growth mechanism, which is now referred to as catalyst transfer polycondensation (CTP). The key evidence supporting this mechanism included (a) the dependence of molecular weight on catalyst loading, (b) the linear correlation between molecular weight and monomer conversion, and (c) the successful synthesis of block copolymers with sequential monomer addition.



Scheme 4.1. Discovery of living chain-growth mechanism for synthesis of P3HT.

The proposed mechanism for a chain-growth Kumada CTP is shown in Figure 4.4.¹⁰ The reaction begins with an initiation step with the metal pre-catalyst to generate the bis(aryl) metal complex. Reductive elimination, or rather, reductive coupling, leads to the formation of a metal π -association complex, which enables the subsequent intramolecular oxidative addition after migration of the metal to the terminus. Transmetallation with an equivalent of activated monomer reforms a bis(aryl) metal complex, which then undergoes a reductive coupling to afford the metal π -association complex. The formation of the metal π -association complex is key to the living mechanism, as it enables the catalyst to stay associated to the growing polymer chain, and ensures one equivalent of monomer is added per cycle.¹¹ McNeil has carried out several mechanistic studies in support of this cycle, however no direct spectroscopic evidence for a Ni- π complex has yet been reported.¹²⁻¹⁴



4.1.3 Donor-acceptor conjugated polymers

Alternating donor-acceptor (D-A) conjugated polymers are composed of alternating electron-rich and electron-poor monomer units. Incorporating both donor and acceptor units enables fine tuning of the band gaps and energy levels of conjugated polymers.^{15,16} Because the donor unit is primarily responsible for the HOMO energy levels, and the acceptor determines the LUMO levels, the relative band gap of the resulting polymer can be estimated through careful choice of each monomer unit (Figure 4.5).³ D-A conjugated polymers are typically synthesized via step-growth methods which result in polymers with high dispersities and variable molecular weights.⁵ There are limited reports in the literature of the synthesis of D-A conjugated polymers through living chain-growth mechanisms. Thus, the field would benefit from the development and identification of living chain growth methods for the synthesis of these industrially relevant polymers.

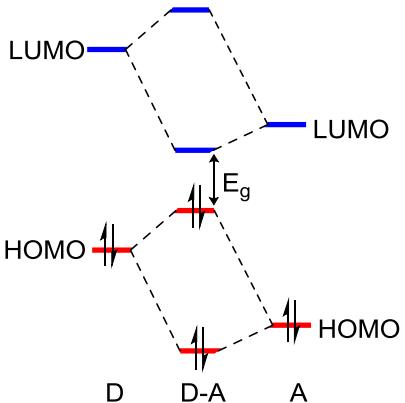
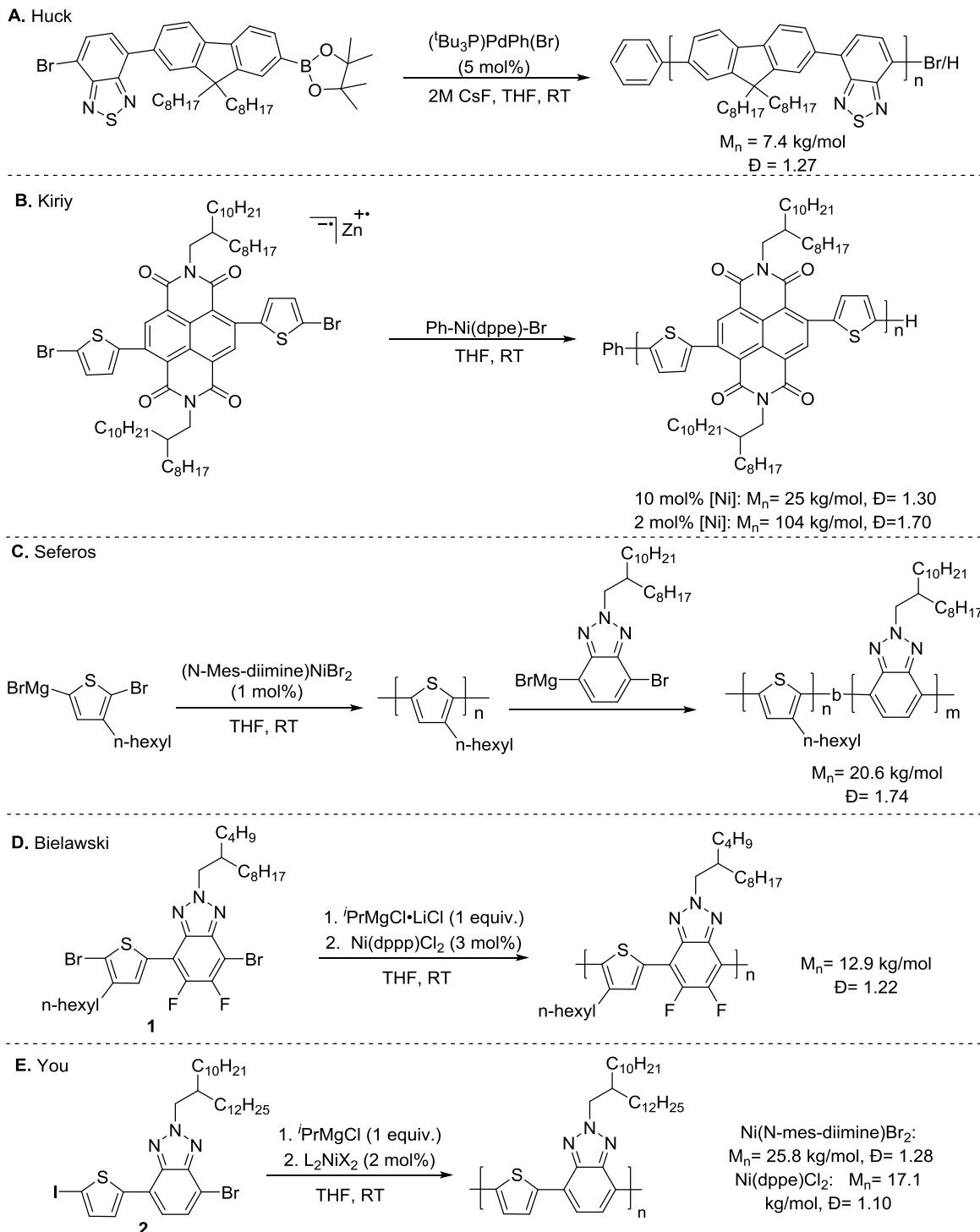


Figure 4.5. Frontier molecular orbital interactions of D-A units.

Examples of D-A conjugated polymers that have been synthesized through CTP methods are shown in Scheme 4.2. In 2011, Huck and co-workers reported the first chain-growth polymerization of a D-A monomer (**A**, Scheme 4.2).¹⁷ The asymmetric AB monomer, composed of a fluorene linked to a benzothiadiazole, was designed to undergo a Pd-catalyzed Suzuki polycondensation, affording polymers with modest molecular weights and low dispersities. The same year, Kiriy and co-workers reported that the Ni-catalyzed polymerization of the unusual naphthalene diimide radical-anion monomer provided high molecular weight polymers (**B**).¹⁸ In 2014, after identifying that Ni(diimine) catalysts could polymerize electron-deficient monomers through chain growth mechanisms,¹⁹ Seferos reported the controlled synthesis of conjugated D-A block copolymers through a Ni-catalyzed Kumada CTP (**C**).²⁰ Block copolymers composed of P3HT and poly(benzotriazole) blocks were synthesized independent of monomer order.



Scheme 4.2. D-A conjugated polymers.

More recently, in 2015, the Bielawski group reported the first Kumada CTP of alternating D-A conjugated monomers (**D**).²¹ Pre-monomer **1** was composed of a 3-hexyl-thiophene unit

linked to a fluorinated benzotriazole moiety. Through the Grignard metathesis with $i\text{PrMgCl}\bullet\text{LiCl}$, polymers were synthesized with molecular weights up to 12.9 kg/mol and relatively low dispersities. Kinetics and block-copolymer synthesis with P3HT provided reactivity consistent with a living mechanism. Concurrently, the You group was developing similar D-A monomer precursor **2** that linked a thiophene to a benzotriazole (**E**).²² Different molecular weights and dispersities were obtained depending on the choice of Ni catalyst. Further, kinetics and the synthesis of homo-block and di-block copolymers with P3HT supported a living mechanism.

With these reports in mind, we set out to develop a living chain-growth Kumada CTP of D-A conjugated pre-monomer **3** (Figure 4.6). While this monomer may be similar to that of Bielawski, there are several differences. Our monomer incorporates an unsubstituted thiophene moiety, while Bielawski's incorporates a *n*-hexyl chain on the thiophene unit. Studies have shown that the position and length of alkyl side chains on the conjugated backbone can disrupt the planarity of the conjugated system, and in turn affect the polymer electronics.^{3,4,23} While it cannot be predicted whether the omission of the alkyl side-chain will have a positive or negative effect on polymer device efficiency, it is clear that the resulting polymers will likely have different properties. The formation of the Grignard is also in different positions between the two systems— we incorporate the Grignard on the thiophene donor unit, while Bielawski forms the Grignard at the benzotriazole acceptor unit. Thus, mechanistically, our transmetallation, chain walking and subsequent oxidative addition take place at opposite sites on the monomer compared to Bielawski.

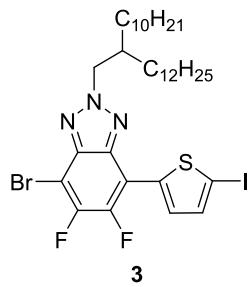


Figure 4.6. Our D-A conjugated monomer precursor.

It is also important to note the significance of incorporating fluorine substituents into the monomer backbone. Several studies have analyzed the fluorine effect that is observed when comparing fluorinated polymers with their non-fluorinated counterparts.^{24–26} It is clear from these studies that incorporating fluorine substituents on the monomer unit enhances key parameters of device output in polymer solar cells, resulting in better device efficiency. The study of fluorine-incorporated **3** will complement the studies on the similar monomers reported by Bielawski (**1**) and You (**2**).

4.2 Results and discussion

4.2.1 Monomer synthesis and Grignard metathesis

Monomer precursor **3** was synthesized in 7 total steps, resulting in a 17% overall yield (Figure 4.7). Compound **4**, a known compound in the literature,²⁷ was prepared in a total of 3 steps, resulting in a 65% overall yield. The solubilizing alkyl side chain was incorporated into the benzotriazole unit through a Mitsonobu reaction using the corresponding alcohol. Metallation with LDA, followed by quenching of the lithiated benzotriazole with NIS, afforded compound **6** in a 64% yield. The next step was the Pd-catalyzed Stille coupling with 2-tri-*n*-butyl(stannyll)thiophene to install the thiophene unit. The final step in the synthesis was the iodination of the thiophene with NIS to afford pre-monomer **3**. We strategically installed the

iodine substituent at the thiophene end of the monomer, taking advantage of the selectivity of iodine over bromine for the magnesium-halogen exchange.^{28,29}

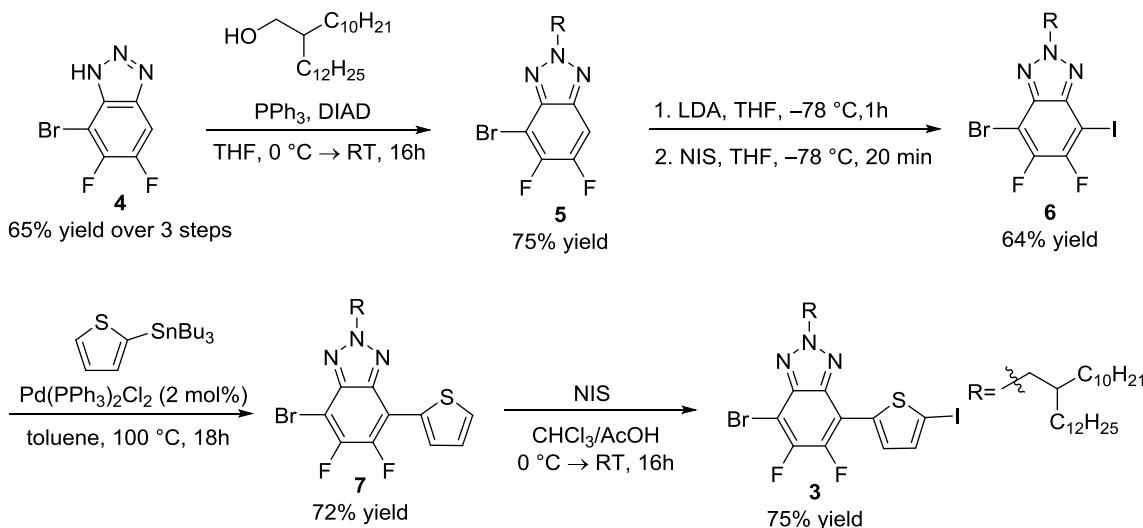
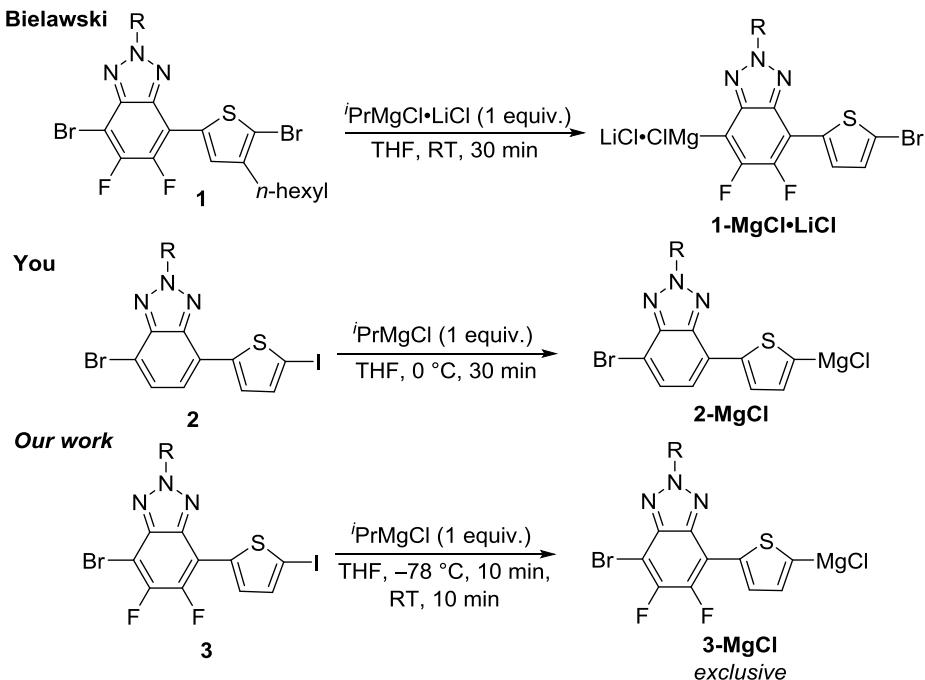


Figure 4.7. Synthesis of monomer precursor **3**.

With monomer in hand, we began looking at the Grignard metathesis reaction. You and co-workers prepared **2-MgCl** by reacting **2** with 1 equivalent of $^i\text{PrMgCl}$ at $0\text{ }^\circ\text{C}$ for 30 minutes (Scheme 4.3). Upon testing those reaction conditions and quenching with methanol-d₄ to determine the site of Grignard formation, we expected to observe deuterium incorporation at the thiophene. Instead, while some deuterated product was obtained, we observed a significant amount of water-quenched monomer, either through adventitious water or through other means. We also tested the use of the turbo Grignard ($^i\text{PrMgCl}\bullet\text{LiCl}$) used by Bielawski, but we observed mixtures of Grignard formation at both the benzotriazole and thiophene sites (at Br and I). Optimizing the reaction conditions using $^i\text{PrMgCl}$ as the Grignard reagent provided the means to obtain exclusive formation of the Grignard at the thiophene site (Scheme 4.3). The key experimental factor was lowering the temperature to obtain the necessary kinetic selectivity.



Scheme 4.3. Selective Grignard formation.

4.2.2 Initial reactivity

Nickel bisphosphine complexes are among the most popular for the CTP of electron-rich monomers.¹⁰ We began screening the commercially available (dppp)NiCl₂ and (dppe)NiCl₂ complexes as pre-catalysts due to their success in the polymerizations of similar monomers **1** and **2**. Polymerizations were set up by transferring the bright yellow solution of **3-MgCl** (in THF) to a flame-dried Schlenk flask containing metal complex (pre-loaded in a glovebox) in THF at RT. The reactions were stirred for 30 minutes before quenching with ~1 mL of 5 M HCl_(aq) and precipitating with methanol. Upon filtration, the molecular weight and dispersity of the polymer was determined by gel permeation chromatography (GPC) in THF at 25 °C. With both Ni bisphosphine complexes, at 2 mol% loading in THF (0.025M in monomer), the polymerization solution turned a yellow-orange color within 1 minute of adding the Grignard. While we were expecting the color to change to a deep red or purple color (consistent with You's observations),

the solution remained light orange. No solid material was obtained upon quenching the reaction with 5 M HCl_(aq) after 30 minutes. ¹H NMR analysis of the concentrated solution revealed the majority of material was quenched monomer.

We next looked at the nickel diimine catalyst that was also used to polymerize **2**. In 2013, Seferos and co-workers demonstrated that a series of Ni(diimine) complexes could polymerize electron deficient monomers in a controlled manner via Kumada CTP.¹⁹ Through catalyst design and DFT studies, they proved that as the calculated strength of the Ni π-association complex increases, the dispersity of the resulting polymer decreases, leading to a more controlled polymerization (Figure 4.8). Thus, having a strong Ni π-association complex will limit unwanted chain-transfer and termination reactions. Seferos also used these Ni(diimine) complexes to synthesize π-conjugated block co-polymers composed of electron-rich and electron-poor (D-A) monomers (Scheme 4.2, C).²⁰ This literature precedence was encouraging for our polymerization of **3**.

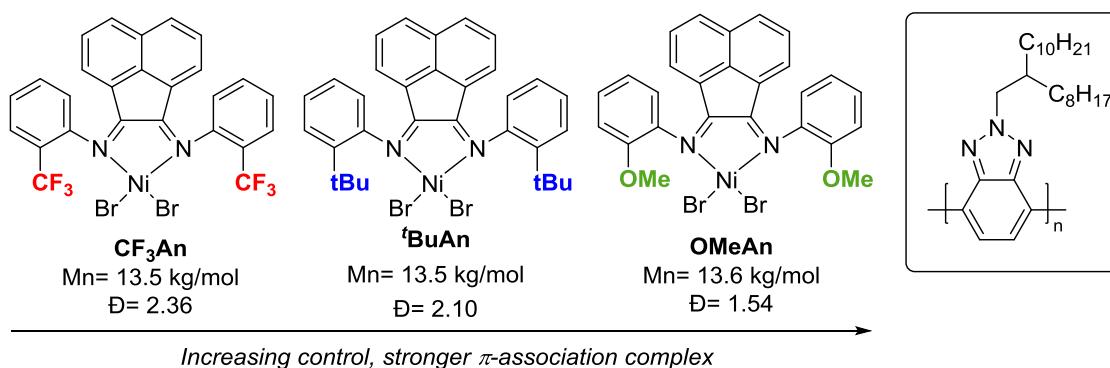
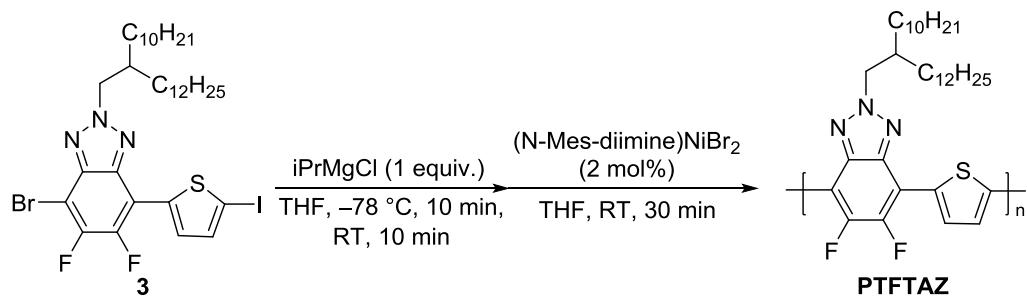


Figure 4.8. Ni(diimine) complexes.

We initially screened the (N-Mes-diimine)NiBr₂ complex due to its success with the polymerization of **2** (Scheme 4.4). At 2 mol% loading in THF, upon the addition of **3-MgCl** to the catalyst solution we noticed a rapid color change from yellow to red to deep purple within 1

minute. Upon completion of the reaction, the isolated polymer appeared black in color, however in THF it formed a deep purple solution. Encouragingly, PTFTAZ with a M_n of 18.2 kg/mol and a very narrow D of 1.09 was obtained (theoretical molecular weight at 2 mol% = 28.6 kg/mol). Because Seferos had great success with the **OMeAn** Ni diimine complex, we also synthesized and screened this complex. Unfortunately, throughout the polymerization, the solution remained orange, and the resulting solid had a M_n of 4.6 kg/mol and D of 1.07. The lack of deepening of the color signaled that n was small and no polymer would be forthcoming.



Scheme 4.4. Polymerization of **3**.

Because the mesityl diimine complex looked promising for the polymerization of **3**, a catalyst loading screen was next performed (Table 4.1). One of the key characteristics of a living chain-growth polymerization is the control over molecular weight of the polymer through the alteration of monomer/catalyst ratio. Decreasing the catalyst loading to 1 mol% resulted in a mix of polymer and oligomers—a small amount of high molecular weight polymer was obtained, however the majority of material had a M_n of 3.6 kg/mol and D of 1.05. Doubling the standard catalyst loading to 4 mol% resulted in a polymer with nearly the same M_n and D obtained at 2 mol%. Similarly, at 10 mol% loading lead to a decrease in M_n to 13.9 kg/mol with a D of 1.06. These results suggest our polymerization is not proceeding through a living chain-growth

mechanism, as we would expect more significant changes to the M_n with decreased catalyst loadings.

Table 4.1. Catalyst loading screen of **3-MgCl** with (N-Mes-diimine)NiBr₂.

Entry	Catalyst loading	M_n (kg/mol)	\bar{D}	Yield
1	1 mol%	18.2 ^a	1.04	82%
2	2 mol%	19.5	1.07	86%
3	4 mol%	18.9	1.08	69%
4	10 mol%	13.9	1.06	80%

^aMinor peak by GPC—major peak: M_n : 3.6 kg/mol, \bar{D} = 1.05.

Another characteristic of a living mechanism is the ability to synthesize di-block copolymers through the sequential addition of monomer. We attempted the synthesis of a homo-block copolymer with **3-MgCl** as another test for a living chain growth polymerization. An aliquot of the first block of polymer revealed a M_n of 20.7 kg/mol and \bar{D} of 1.06. After adding the second batch of **3-MgCl** and quenching, the bulk polymer had a M_n of 21.4 kg/mol and \bar{D} of 1.06. These results do not align with a living chain growth mechanism, as the second batch of monomer was not incorporated into the polymer chain.

We considered the possibility that the solubility of the polymer may be playing a role in the lack of control over the polymerization. If an increase in polymer molecular weight lead to a material that was less soluble in the solvent, it could dissociate from the metal and crash out of solution. This theory would explain the consistent molecular weights of 18 kg/mol that were obtained at 1, 2, and 4 mol% loadings. To test this theory, we performed a solvent screen.

Although THF is the most common solvent for Kumada CTP,¹⁰ we screened the ethereal solvents diethyl ether (Et₂O), dioxane, and methyl *tert*-butyl ether (MTBE).

The results from the ethereal solvent screen are shown in Table 4.2. Dioxane provides similar molecular weights to that of THF, albeit with higher dispersities. MTBE resulted in unreasonably high M_n values of 38.7 kg/mol and D of 1.57. With Et₂O, an increase in M_n of 25.2 kg/mol and D of 1.37 was observed. It is important to note that in all 3 cases, the GPC trace was bimodal. It is likely that a disproportionation and chain-coupling pathway is occurring, which would explain the bimodal behavior and unexpected increases in molecular weight.¹⁰ Although we were able to obtain high molecular weight polymers with very low dispersities, we looked to screen alternate metal complexes that would better support a living chain growth mechanism for the polymerization of monomer **3**.

Table 4.2. Solvent screen for the polymerization of **3-MgCl** with (N-Mes-diimine)NiBr₂.^a

Entry	Solvent ^b	M _n (kg/mol)	D	Yield
1	Dioxane	22.8	1.21	83%
2	MTBE	38.7	1.57	66%
3	Et ₂ O	25.2	1.37	62%

^aReaction conditions: 2 mol% catalyst loading, 0.025M. ^bGrignard reagent prepared in THF, accounting for ~5% of the solvent composition.

4.2.3 Ligand screen

McNeil and co-workers studied the influence of ligand electronic properties on the control over the chain-growth polymerization of an electron-rich monomer.³⁰ A variety of dppe analogues were screened, varying the electron-rich and electron-poor aryl substituents on the phosphine. The catalyst with the most electron-donating aryl groups on the phosphine (p-OMe-

Ph) provided the most controlled polymerization when compared to dppe. Thus, electron-rich ligands are proposed to promote Ni(0) π -complex formation by donating electron density from the metal to the arene LUMO.¹⁰ With these studies in mind, we looked to N-heterocyclic carbene (NHC) ligated Ni precatalysts for the polymerization of **3**, as they are stronger σ -donors than phosphines.³¹ Although phosphines are the most popular ligands for CTP, there have been a handful of reports that successfully make use of NHC ligands for living polymerizations.³¹⁻³⁴

Under the standard polymerization conditions (THF, 0.025M, RT), we screened two (NHC)Ni complexes for the polymerization of **3** (Figure 4.9). At 2 mol% catalyst loading, we found that the commercially available IPr(PPh₃)NiCl₂ complex only afforded oligomers of **PTFTAZ**, with M_n of 3.7 kg/mol and increased D of 1.64. With the IPrNi(acac)₂ complex, at either 2 or 5 mol% loading, upon quenching and precipitating the reaction, no solid material was obtained.

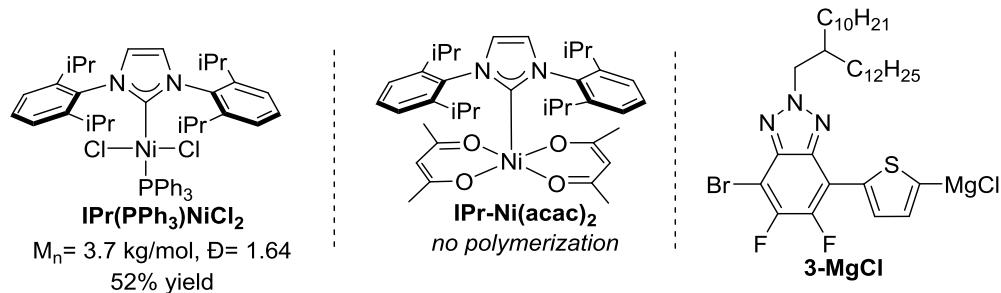
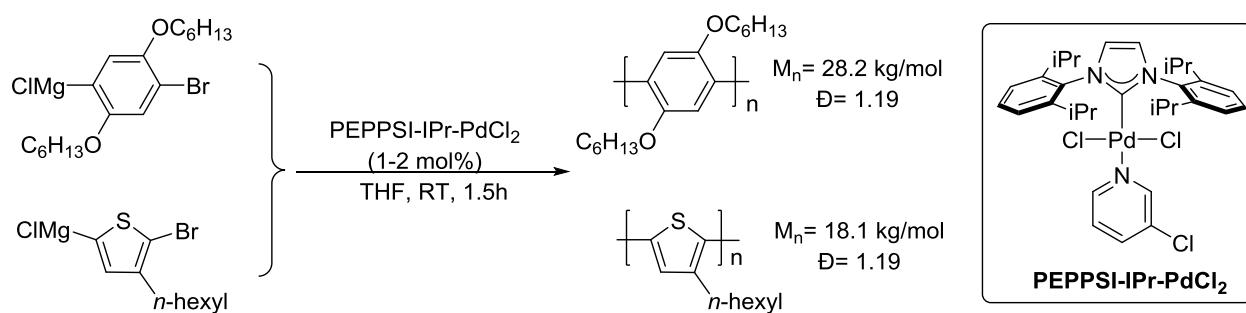


Figure 4.9. Polymerization of **3** with (NHC)Ni complexes.

4.2.4 The switch to palladium

While nickel remains the most popular metal for CTP, the use of palladium complexes has increased significantly.¹⁰ The most common Pd precatalysts include ligands with bulky monodentate phosphines, such as PCy₃ or P^tBu₃, or NHCs.¹¹ In 2012, McNeil and co-workers discovered that the PEPPSI-IPr-PdCl₂ complex could facilitate the living, chain-growth

polymerization of electron-rich monomers (Scheme 4.5). Although the catalyst appeared to be moderately unstable upon full consumption of monomer, block co-polymerizations and kinetic studies confirmed the living nature when electron-rich monomers were polymerized. Another advantage to this system is that the PEPPSI-IPr-PdCl₂ precatalyst is also commercially available and air and moisture stable.



Scheme 4.5. Living chain growth polymerization using NHC-Pd pre-catalysts.

We began our studies using the Pd precatalyst described above using the standard polymerization conditions. The same rapid sequence of color changes were observed upon adding **3-MgCl** to [Pd]. The resulting polymer had a M_n of 22.2 kg/mol and D of 1.23, although the GPC trace was bimodal. We also screened other monomer concentrations (Table 4.3), but ultimately found 0.025 M was optimal.

Table 4.3. Concentration screen for the polymerization of **3** with PEPPSI-IPr-PdCl₂.

Concentration ^a	M _n (kg/mol)	D	Bimodal? ^b
0.01 M	11.8	1.21	no
0.025 M	22.2	1.23	yes
0.05 M	16.7	1.17	yes

^aConcentration of monomer in THF. ^bBimodal GPC trace

To gain insight into the rate of the polymerization, the reaction was quenched after 5 minutes. The resulting polymer had a M_n 22.4 kg/mol and D of 1.26, suggesting the reaction was complete in just 5 minutes. To slow the reaction down to allow for a kinetic analysis, the polymerization temperature was held constant at 0 °C over the course of four hours. The polymer was obtained in 22% yield, with a M_n of 8.0 kg/mol and D of 1.11. The filtrate of the solution contained a significant amount of quenched monomer. Thus, cooling the solution was not a feasible route to allow for kinetic determinations.

It is possible that our polymer is forming aggregates in solution at room temperature which gives rise to the bimodal GPC trace,³⁵ so the sample was sent to China for analysis by GPC in 1,2,4-trichlorobenzene at 160 °C. Analysis of this sample in a THF GPC at room temperature provided a M_n of 22.2 kg/mol and D of 1.23 (bimodal, Figure 4.10). The results obtained in the high temperature GPC on the same polymer sample gave a M_n of 24.4 kg/mol and D of 1.22, but importantly, the GPC showed a unimodal trace (Figure 4.11). Thus, it is very likely that the bimodal GPC trace is due to the formation of aggregates in solution at room temperature, as opposed to bimodal peaks due to the formation of higher molecular weight polymers through chain coupling or catalyst disproportionation. This also confirms the molecular weights obtained by GPC at room temperature in THF are reliable, despite the aggregation that might be occurring.

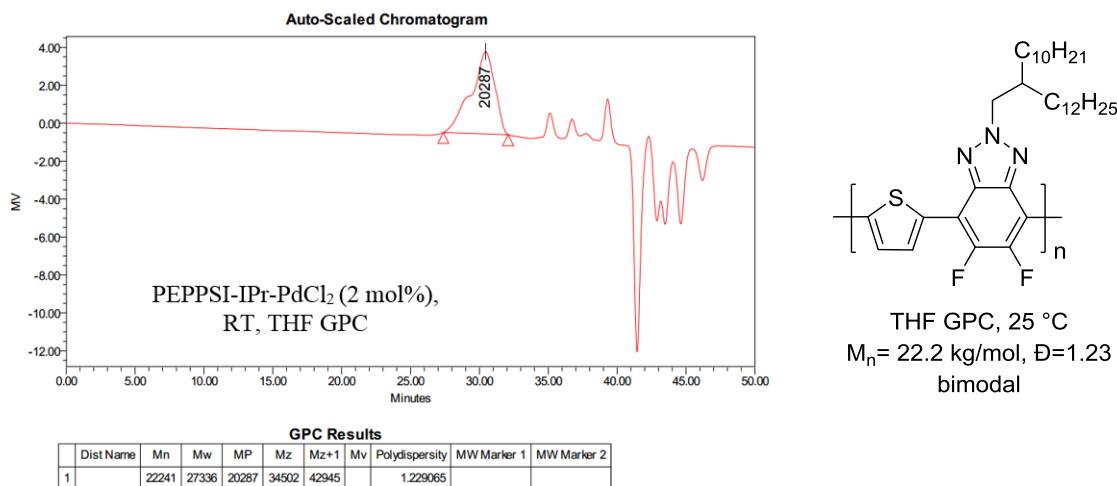


Figure 4.10. Room temperature GPC trace.

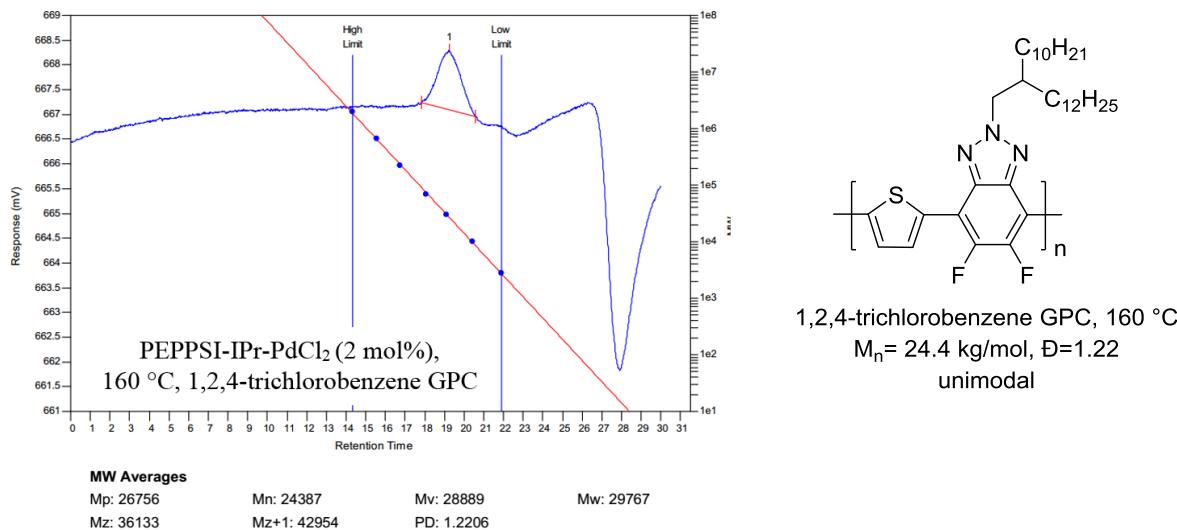


Figure 4.11. High temperature GPC trace.

4.3 Catalyst loading study and block co-polymer synthesis

To test for the living nature of the polymerization, we next performed catalyst loading screens with PEPPSI-IPr-PdCl₂ in THF (RT, 0.025M) (Figure 4.12). Across the range of catalyst loadings, the dispersities ranged from 1.10 to 1.36. Encouragingly, the molecular weight of the polymer increased with decreased catalyst loading in a linear fashion (as expected). However,

the molecular weight increase is less than what is expected for a living polymerization. If this polymerization was in fact living, we would expect a doubling of molecular weight for each halving of catalyst loading. It is also important to note that at 1% catalyst loading, the molecular weight is almost the same as at 2 mol% loading.

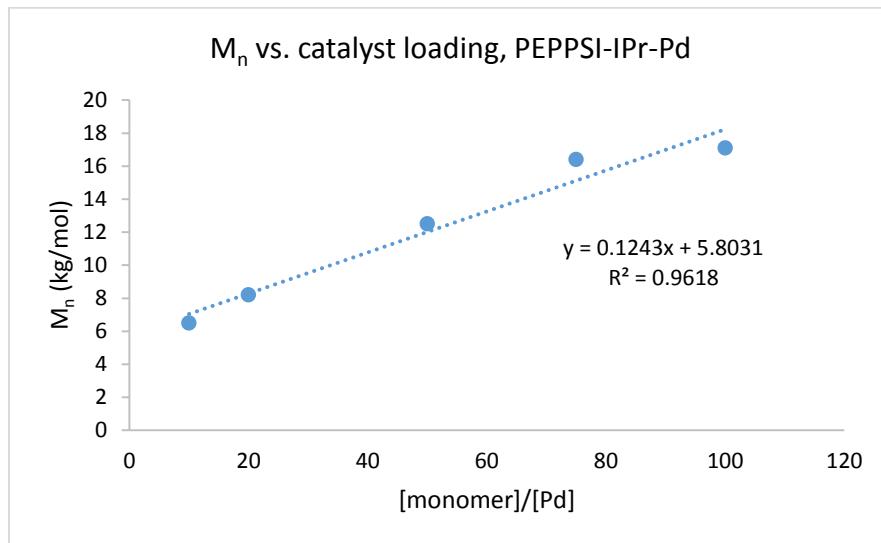


Figure 4.12. Catalyst loading screen.

Another hallmark of a living chain growth polymerization is the ability to synthesize block co-polymers through the sequential addition of monomer. We conducted chain extension studies with our monomer and 2-Br-5-I-3-hexylthiophene (**8**), a common monomer incorporated into π -conjugated block copolymers.²⁰⁻²² The study by McNeil showed that the PEPPSI-IPr-PdCl₂ precatalyst is well-suited for the controlled, living synthesis of P3HT.³¹ To begin, we polymerized monomer **3** first at 4 mol% catalyst loading. Removing an aliquot after 30 minutes revealed a polymer with a molecular weight of 13.7 kg/mol and low dispersity of 1.07. The second batch of monomer, 2-Br-5-MgCl-3-hexylthiophene (**8**), was added to the polymerization solution and stirred for 1 hour. The resulting diblock copolymer had a M_n of 25.9 kg/mol and D

of 1.39 (Figure 4.13). Although the dispersity increased with the addition of the second block, the results support a controlled mechanism and provide support that the catalyst is still active.

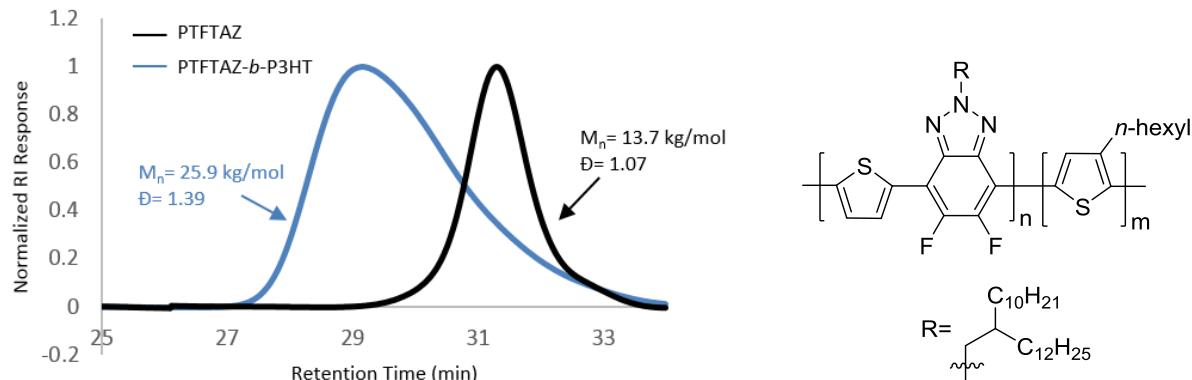
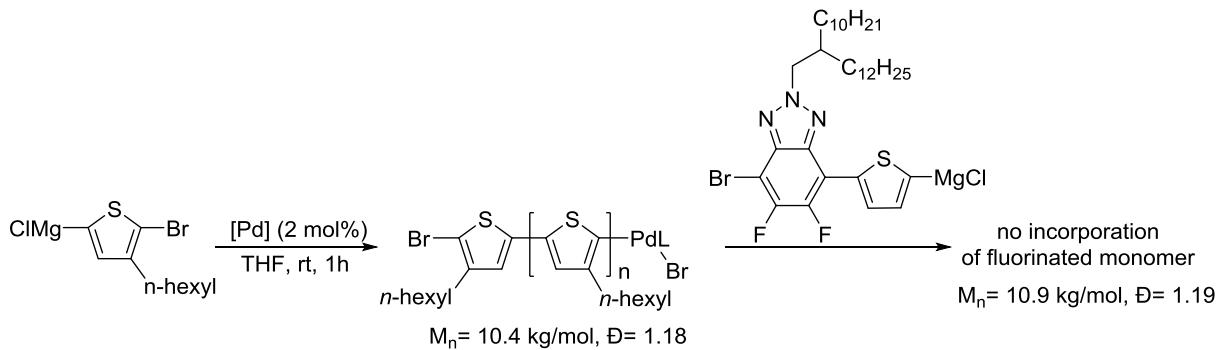


Figure 4.13. GPC trace of block copolymer

To test this further, we attempted to switch the order of the block polymerization, as the order of block addition should not matter in a living mechanism. Beginning with thiophene monomer **8**, the first polymer block had M_n of 10.4 kg/mol and D of 1.18 (Scheme 4.6). Addition of the second batch of **3-MgCl** resulted in a bulk polymer with a M_n of 10.9 kg/mol and D of 1.19. It is clear that monomer **3** was not incorporated into the polymer chain. There are several possibilities for this lack of incorporation of **3**. McNeil alluded to catalyst stability issues with PEPPSI-IPr-PdCl₂ once full monomer conversion was achieved.³¹ It could be that the thiophene monomer was fully consumed, resulting in an unstable catalyst that then decomposes before the second block was added. A possible way to test this is to add the second batch of monomer after a shorter time period to ensure the catalyst is still active. It is known that the chain-growth polymerization for electron-poor monomers is more challenging than for electron-rich monomers.¹⁰ Since **3** is more challenging monomer, it must be polymerized first to synthesize block copolymers.



Scheme 4.6. Reversed order of block copolymerization.

4.4 Summary

In summary, we have developed the donor-acceptor monomer **3** composed of an electron-rich thiophene unit and an electron-deficient fluorinated benzotriazole unit. Several Ni complexes were screened for the polymerization reaction to identify a catalyst capable of providing a living, chain growth mechanism. The switch to the PEPPSI-IPr-PdCl₂ precatalyst allowed for somewhat more control over the polymerization. Molecular weights up to 22 kg/mol and low dispersities (1.23) were obtained. Catalyst loading screens revealed that the molecular weights increase with decreased catalyst loadings, however not to the extent that would be expected for a true living mechanism. Chain extension studies also support the controlled nature of the polymerization, as the block copolymer PTFTAZ-*b*-PT was successfully synthesized. While we cannot say this polymerization follows a true living, chain growth mechanism, we identified a new D-A polymer and worked towards expanding the current methodologies to develop alternating D-A monomers.

4.5 Acknowledgements

We would like to thank Dr. Philippa Payne for her work in developing the initial monomer synthesis, as well as Dr. Qianqian Zhang, Prof. Wei You and Prof. Maurice Brookhart

for helpful discussions. We would also like to thank the Liebfarth group for the training and use of their GPC instrument.

4.6 Experimental Section

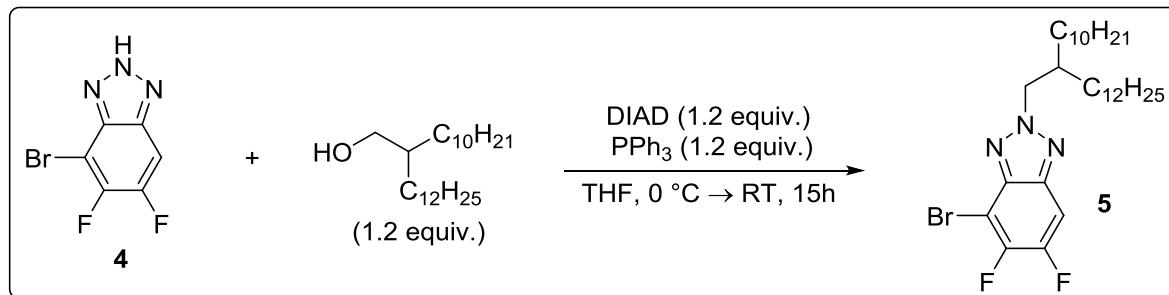
4.6.1 General methods

Unless otherwise stated, all commercially available reagents were used as received. Tetrahydrofuran (anhydrous, 99%, stabilized, Acros Organics) was purchased from Fisher Scientific and freeze-pump-thawed three times and stored over activated 3 Å sieves before use. Column chromatography was performed using SilaFlash P60 40-63 µm (230-400 mesh). Thin layer chromatography (TLC) was performed on SiliCycle Silica Gel 60 F254 plates and was visualized with either UV light or KMnO₄ stain. NMR spectra were recorded on a Bruker Avance 400 or 600 MHz spectrometer. All deuterated solvents were used as received from Cambridge Isotope Laboratories, Inc. The residual solvent protons (¹H) or the solvent carbons (¹³C) were used as internal standards. GPC was performed on a Waters Alliance 2695 liquid chromatograph and Waters 2414 refractive index detector at room temperature with THF as eluent (flow rate: 1 mL/min). High temperature GPC measurements were measured on a Polymer Laboratories PL-GPC 220 instrument, using 1,2,4-trichlorobenzene as the eluent at 160 °C. The obtained molecular weight is relative to polystyrene standards. The mass spectrometer used in these studies was purchased with the support of the National Science Foundation under Grant No. CHE-1726291. Samples were analyzed with a Q Exactive HF-X (ThermoFisher, Bremen, Germany) mass spectrometer operating in positive ion mode with an electrospray ionization source by Mike Peruzzi. Molecular formula assignments were determined with Molecular Formula Calculator (v 1.2.3). The following compounds were synthesized according to literature

procedures: 4-bromo-5,6-difluoro-2H-benzo[d][1,2,3]triazole (**4**),²⁷ IPr(Ni)(acac)₂,³⁶ (N-Mes-diimine)NiBr₂,³⁷ and (N-(2-OMe-Ph)diimine)NiBr₂ (**OMeAn**).¹⁹

4.6.2 Preparation of starting materials

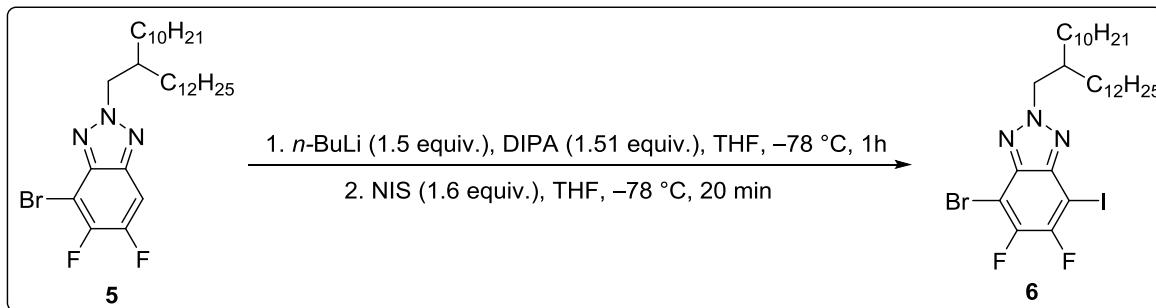
Synthesis of compound **5**



A flame-dried Schlenk flask was charged with 4-bromo-5,6-difluoro-2H-benzo[d][1,2,3]triazole (Compound **4**, 5.56 g, 23.7 mmol, 1 equiv.) and THF (80 mL). 2-decyltetradecan-1-ol (12.0 mL, 28.5 mmol, 1.2 equiv.) was added by syringe, followed by PPh₃ (7.47 g, 28.5 mmol, 1.2 equiv.). The mixture was cooled to 0 °C and DIAD (5.61 mL, 28.5 mmol, 1.2 equiv.) was added by syringe pump over 30 minutes. The resulting solution was allowed to warm to room temperature overnight. The reaction was quenched with water, then diluted with ethyl acetate. The organics were washed with water and brine and dried over Na₂SO₄. After filtration, the solution was concentrated *en vacuo*. The crude product was purified by silica gel chromatography using hexane/dichloromethane (5:1) as eluent. Compound **5** was obtained as a colorless oil (10.12 g, 75% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.57 (dd, *J* = 8.9, 6.6 Hz, 1H), 4.61 (d, *J* = 7.1 Hz, 2H), 2.29 – 2.23 (m, 1H), 1.36 – 1.20 (m, 40H), 0.87 (t, *J* = 7.0 Hz, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 151.4 (dd, *J* = 252.8, 17.7 Hz), 149.1 (dd, *J* = 250.4, 18.7 Hz), 140.3 (d, *J* = 4.6 Hz), 138.7 (d, *J* = 12.2 Hz), 102.9 (d, *J* = 21.2 Hz), 96.9 (d, *J* = 21.9 Hz), 61.0, 39.2, 32.1, 32.1, 31.3, 31.2, 29.9, 29.9, 29.8, 29.8, 29.8, 29.7, 29.7, 29.6, 29.5, 29.5,

26.2, 26.1, 22.8, 14.3. **¹⁹F NMR** (376 MHz, CDCl₃) δ -128.92 (d, *J* = 19.9 Hz, 1F), -131.66 (d, *J* = 19.9 Hz, 1F). **HRMS** (ESI): calcd for C₃₀H₅₀BrF₂N₃ [M+H]⁺ 570.32344, found 570.32365.

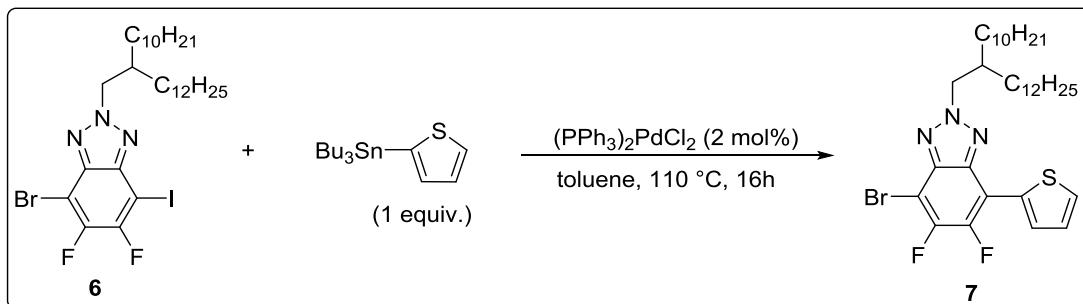
Synthesis of Compound 6



To a flame-dried Schlenk flask was added **5** (2.37 g, 4.16 mmol, 1 equiv.). THF (40 mL) was added and the solution was cooled to -78 °C. To a separate flame-dried Schlenk flask was added diisopropyl amine (0.88 mL, 6.28 mmol, 1.51 equiv.) and THF (13 mL). This solution was cooled to -78 °C and *n*-BuLi (2.5M in hexanes, 2.5 mL, 6.24 mmol, 1.5 equiv.) was added. The resulting mixture was stirred for 1 minute, then cannula transferred dropwise to the solution of triazole in THF. The resulting solution was stirred at -78 °C for 1 hour. N-iodosuccinimide (1.50 g, 6.65 mmol, 1.6 equiv.) in THF (5 mL) was added dropwise via cannula to this solution and allowed to stir for 20 minutes at -78 °C. The reaction was quenched with water (1 mL) at -78 °C. The solution was warmed to room temperature and diluted with hexanes. The organics were washed with water, then brine, dried over MgSO₄, filtered and concentrated. The crude product was purified by silica gel chromatography using hexanes/chloroform (2:1) as eluent to afford the desired product as a pale yellow oil (2.54 g, 88% yield). **¹H NMR** (600 MHz, CDCl₃) δ 4.64 (d, *J* = 7.3 Hz, 2H), 2.32 – 2.26 (m, 1H), 1.33 – 1.20 (m, 40H), 0.87 (t, *J* = 7.0 Hz, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ 152.2 (dd, *J* = 250.0, 18.2 Hz), 148.6 (dd, *J* = 253.5, 20.3 Hz), 141.4 (d, *J* = 7.0 Hz), 138.3 (d, *J* = 4.5 Hz), 97.4 (d, *J* = 23.4 Hz), 67.2 (d, *J* = 28.0 Hz), 61.2, 39.1, 32.1, 32.1,

31.2, 29.9, 29.8, 29.8, 29.7, 29.6, 29.5, 29.5, 26.2, 26.1, 22.9, 14.3. **¹⁹F NMR** (376 MHz, CDCl₃) δ -114.04 (d, *J* = 22.4 Hz, 1F), -126.54 (d, *J* = 22.5 Hz, 1F). **HRMS** (ESI): calcd for C₃₀H₄₉BrF₂IN₃ [M+H]⁺ 696.55628, found 696.22032.

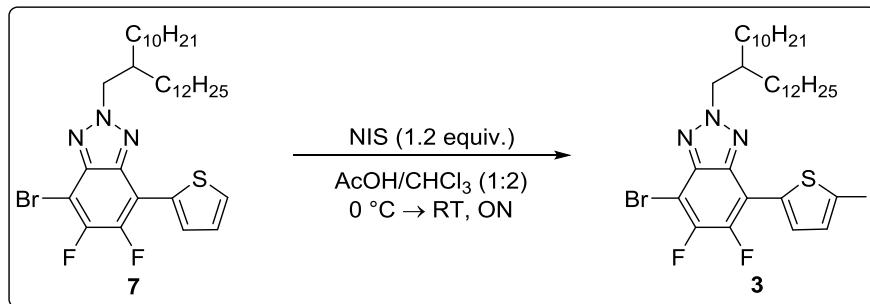
Synthesis of Compound 7



A flame-dried Schlenk flask was charged with **6** (2.54 g, 3.64 mmol, 1 equiv.), toluene (40 mL), and 2-(tributyltin)thiophene (1.15 mL, 3.64 mmol, 1 equiv.). Pd(PPh₃)₂Cl₂ (51 mg, 0.073 mmol, 2 mol%) was added in one portion. The flask was fitted with a water-cooled condenser fitted with a nitrogen inlet. The reaction mixture was heated to reflux and stirred for 16h under a nitrogen atmosphere. The reaction mixture was cooled to room temperature and diluted with ethyl acetate. The reaction mixture was extracted with water (3 x 20 mL), and the organics were washed with brine, dried over MgSO₄, filtered and concentrated. The crude product was purified by silica gel chromatography using hexanes/dichloromethane (10:1) as eluent to afford the desired product as a pale yellow oil (1.64 g, 69% yield). **¹H NMR** (600 MHz, CDCl₃) δ 8.29 (d, *J* = 3.5 Hz, 1H), 7.57 (d, *J* = 5.1 Hz, 1H), 7.24 (t, *J* = 4.3 Hz, 1H), 4.68 (d, *J* = 6.9 Hz, 1H), 2.33 – 2.26 (m, 1H), 1.33 – 1.20 (m, 40H), 0.87 (td, *J* = 7.1, 2.1 Hz, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ 149.6 (dd, *J* = 248.8, 19.0 Hz), 146.8 (dd, *J* = 255.4, 18.6 Hz), 139.8 (d, *J* = 5.5 Hz), 137.0 (d, *J* = 8.7 Hz), 131.7 (d, *J* = 4.1 Hz), 130.6 (d, *J* = 5.7 Hz), 128.6 (d, *J* = 7.6 Hz), 127.5, 111.7 (d, *J* = 13.3 Hz), 94.0 (d, *J* = 23.1 Hz), 60.8, 39.2, 32.1, 32.1, 31.4, 30.0, 29.8, 29.8, 29.7, 29.5, 29.5, 26.2, 22.9, 22.8, 14.3. **¹⁹F NMR** (376 MHz, CDCl₃) δ -128.8 (d, *J* = 18.6

Hz, 1F), -132.3 (d, J = 18.5 Hz, 1F). **HRMS** (ESI): calcd for $C_{34}H_{52}BrF_2SN_3$ [M+H]⁺ 652.31116, found 652.31103.

Synthesis of Monomer 3

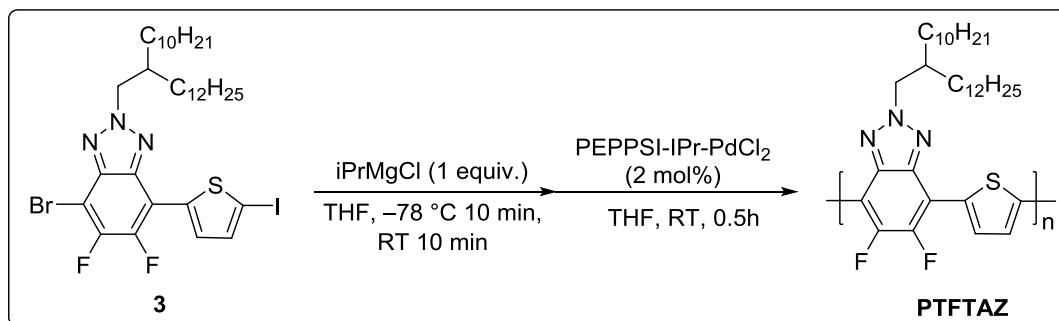


To a round bottom flask was added **7** (1.64 g, 2.52 mmol, 1 equiv.), chloroform (50 mL) and acetic acid (25 mL). The solution was cooled to 0 °C in an ice bath. N-iodosuccinimide (0.679 g, 3.02 mmol, 1.2 equiv.) was added portion-wise over the course of 5 minutes. The resulting solution was allowed to warm to room temperature overnight. The solution was diluted with hexanes and washed with water (3 x 20 mL). The organics were washed with brine, dried over MgSO₄, filtered and concentrated. The crude product was purified by silica gel chromatography using hexanes/toluene (2:1) as eluent. To the resulting oil was added pentane (2 mL) and the solution was stored in the freezer to afford a pale yellow solid. The excess pentane was pipetted off, and the solid was dried under high vacuum (1.31 g, 67% yield). **¹H NMR** (600 MHz, CDCl₃) δ 7.91 (d, J = 4.0 Hz, 1H), 7.37 (dd, J = 4.0, 1.4 Hz, 1H), 4.67 (d, J = 6.9 Hz, 2H), 2.31 – 2.25 (m, 1H), 1.34 – 1.20 (s, 6H), 0.87 (td, J = 7.1, 1.5 Hz, 6H). **¹³C NMR** (151 MHz, CDCl₃) δ 149.4 (dd, J = 249.4, 19.0 Hz), 146.9 (dd, J = 256.0, 18.8 Hz), 139.7 (d, J = 5.4 Hz), 137.8 (dd, J = 5.9, 3.1 Hz), 137.5, 136.6 (d, J = 8.4 Hz), 131.8 (d, J = 7.0 Hz), 110.7 (d, J = 13.0 Hz), 94.6 (d, J = 23.1 Hz), 78.5 (d, J = 8.7 Hz), 60.8, 39.2, 32.1, 31.4, 30.0, 29.8, 29.8, 29.8, 29.7, 29.5, 29.5, 26.2, 22.9, 14.3. **¹⁹F NMR** (376 MHz, CDCl₃) δ -128.7 (d, J = 18.8 Hz, 1F), -

131.9 (d, $J = 18.8$ Hz, 1F). **HRMS** (ESI): calcd for $C_{34}H_{52}BrF_2SIN_3$ [M+H]⁺ 778.20781, found 778.20738.

4.6.3 Polymerization reactions

Representative polymerization procedure

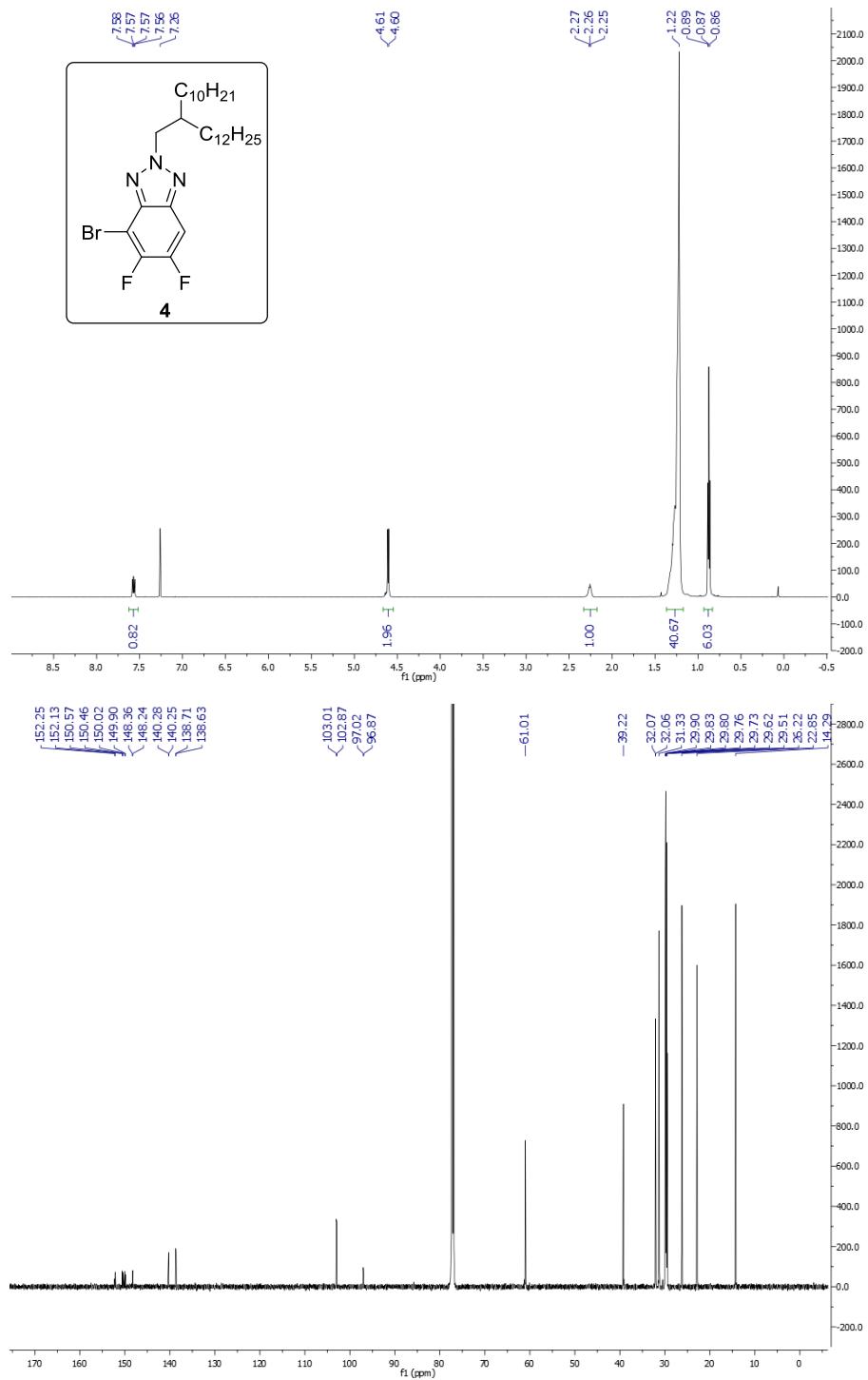


The Grignard reagent was titrated with salicylaldehyde phenylhydrazone prior to use.³⁸ In the glovebox, an oven-dried Schlenk flask was charged with monomer (100 mg, 0.128 mmol, 1 equiv.) and stir bar and fitted with a rubber septum. The flask was removed from the glovebox and anhydrous THF (3 mL) was added. The solution was cooled to -78 °C in a dry ice/acetone bath. $iPrMgCl$ (0.128 mmol, 1 equiv., 0.4M in THF) was added, and the reaction mixture stirred at -78 °C for 10 minutes. The Schlenk flask was placed in a room temperature water bath and stirred for an additional 10 minutes. This solution was transferred to an oven-dried Schlenk flask preloaded in the glovebox with PEPPSI-IPr-PdCl₂ (1.8 mg, 0.0026 mmol, 0.02 equiv.) in THF (2 mL). The solution was stirred at room temperature for 30 minutes. Aqueous 5 M HCl was added, followed by methanol. The precipitate was collected by vacuum filtration, washed with methanol, and dried under high vacuum. The polymer was analyzed by GPC.

Representative block copolymerization procedure (PTFTAZ-*b*-PT**)**

The Grignard reagent was titrated with salicylaldehyde phenylhydrazone prior to use.³⁸ In the glovebox, an oven-dried Schlenk flask was charged with monomer (80 mg, 0.102 mmol, 1 equiv.) and stir bar. The flask was removed from the glovebox and anhydrous THF (2 mL) was added. The solution was cooled to -78 °C in a dry ice/acetone bath. ⁱPrMgCl (0.102 mmol, 1 equiv., 0.4M in THF) was added, and the reaction mixture stirred at -78 °C for 10 minutes. The Schlenk flask was placed in a room temperature water bath and stirred for an additional 10 minutes. This solution was transferred to an oven-dried Schlenk flask preloaded in the glovebox with PEPPSI-IPr-PdCl₂ (1.4 mg, 0.002 mmol, 0.02 equiv.) in THF (2.7 mL). The solution was stirred at room temperature for 30 minutes. An aliquot (~0.2 mL) was removed and quenched with 5 M HCl_(aq) before analysis by GPC. A solution of 2-bromo-5-chloromagnesium-3-hexyl-thiophene (0.204 mmol) in THF (1 mL) was added by syringe to the polymerization solution. After 1 hour, the solution was quenched with 5 M HCl_(aq) and precipitated with MeOH. The resulting solid was isolated by vacuum filtration and analyzed by GPC.

4.6.4 NMR spectra of new compounds



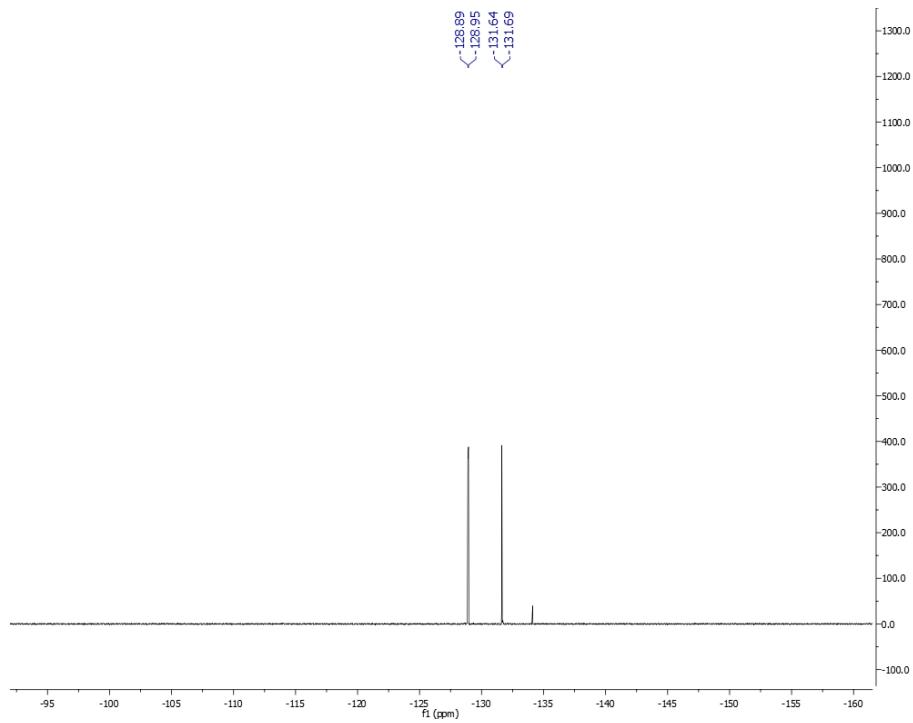
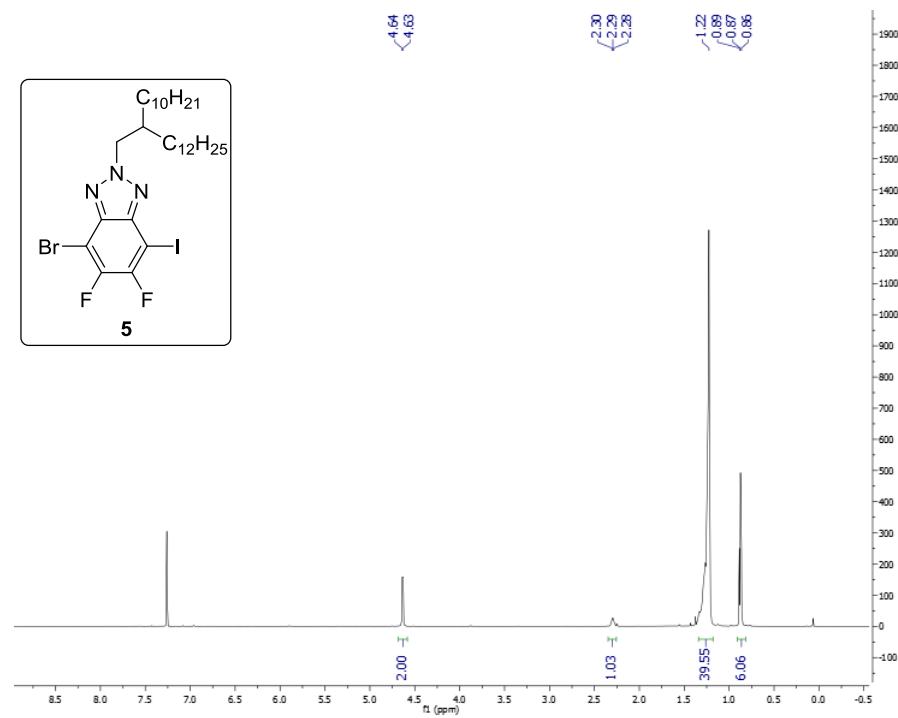


Figure 4.14. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR of **4** in CDCl_3 .



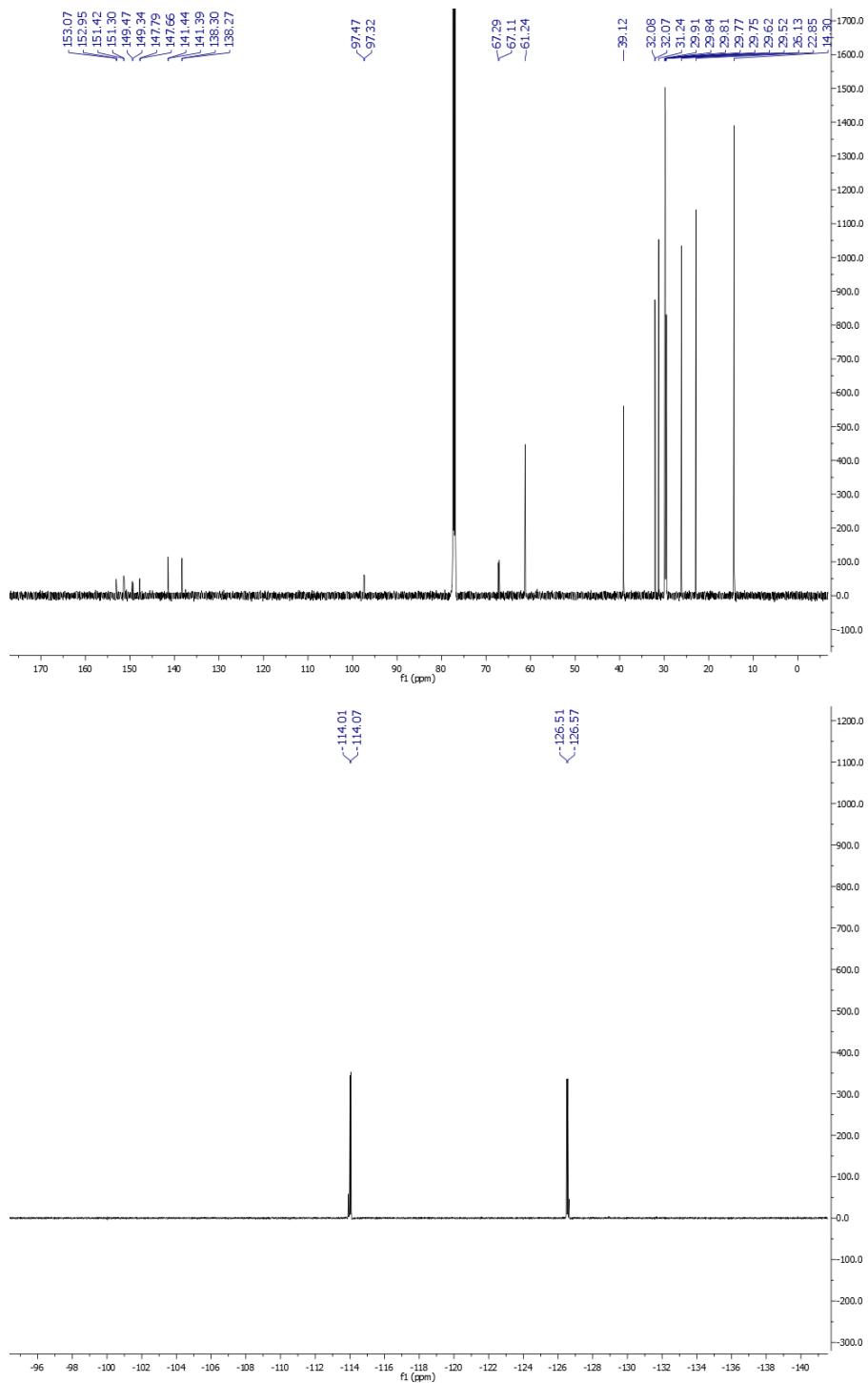
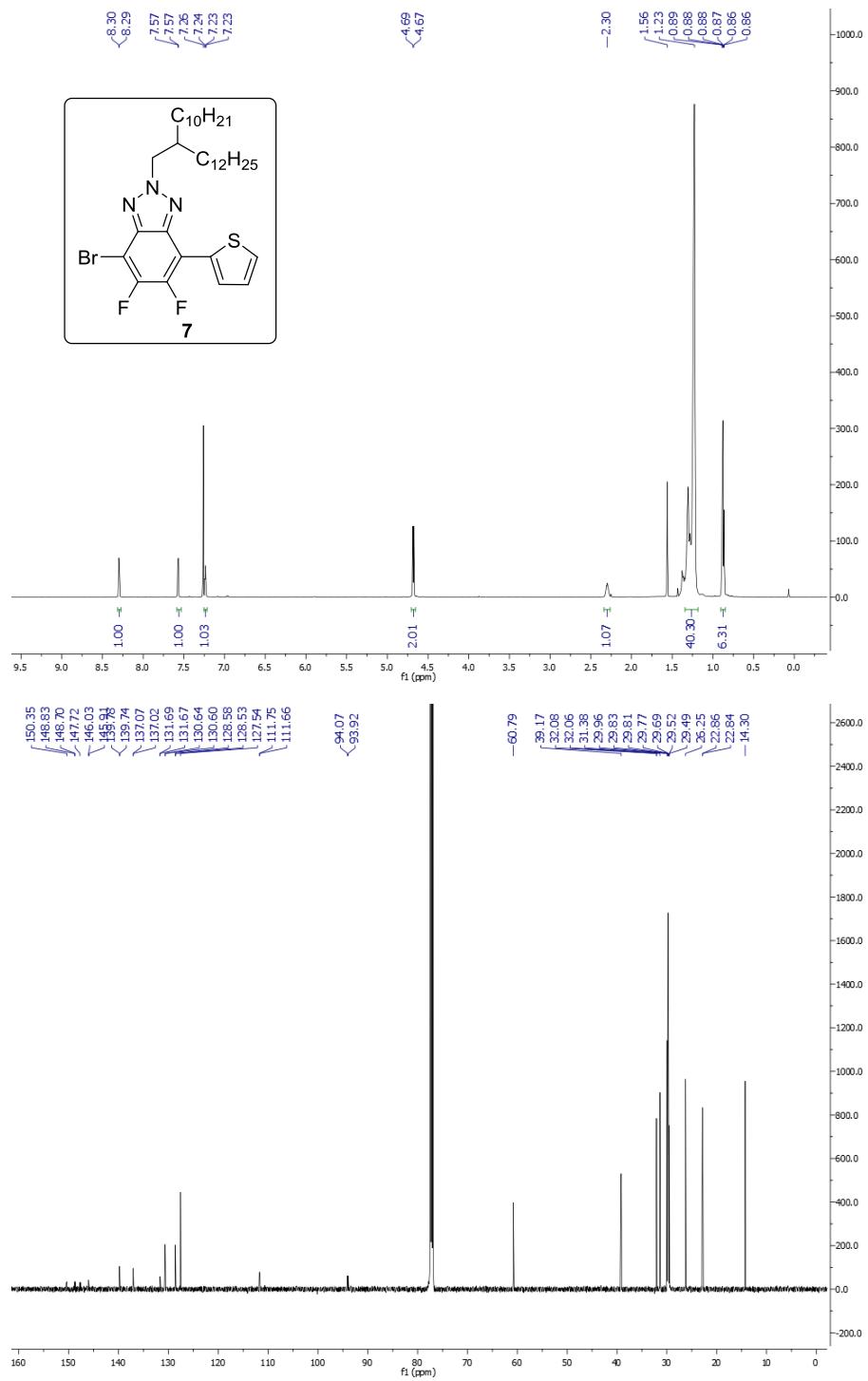


Figure 4.15. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR of **5** in CDCl_3 .



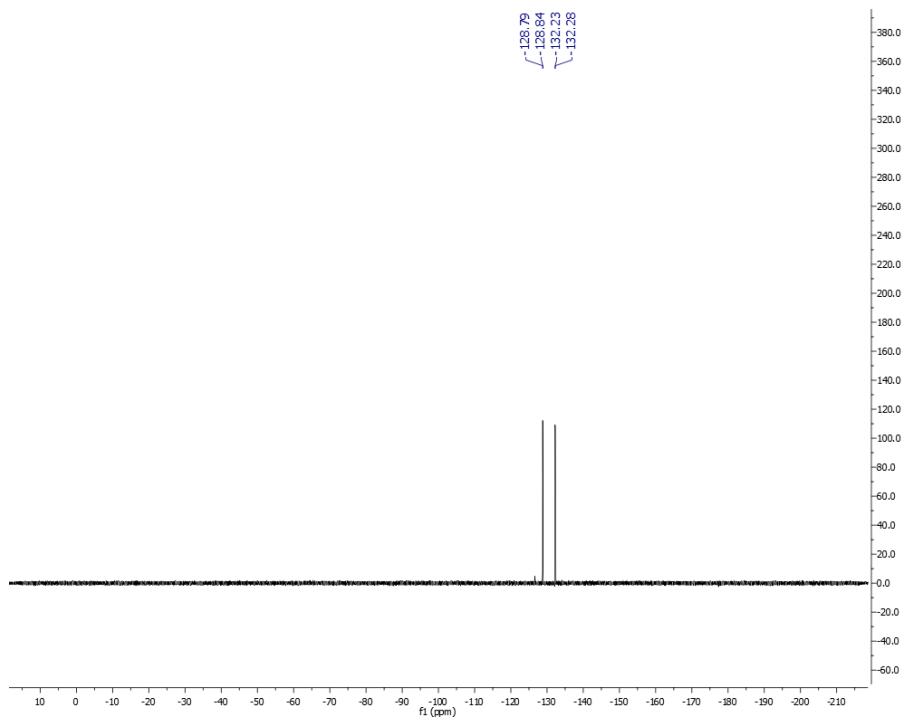
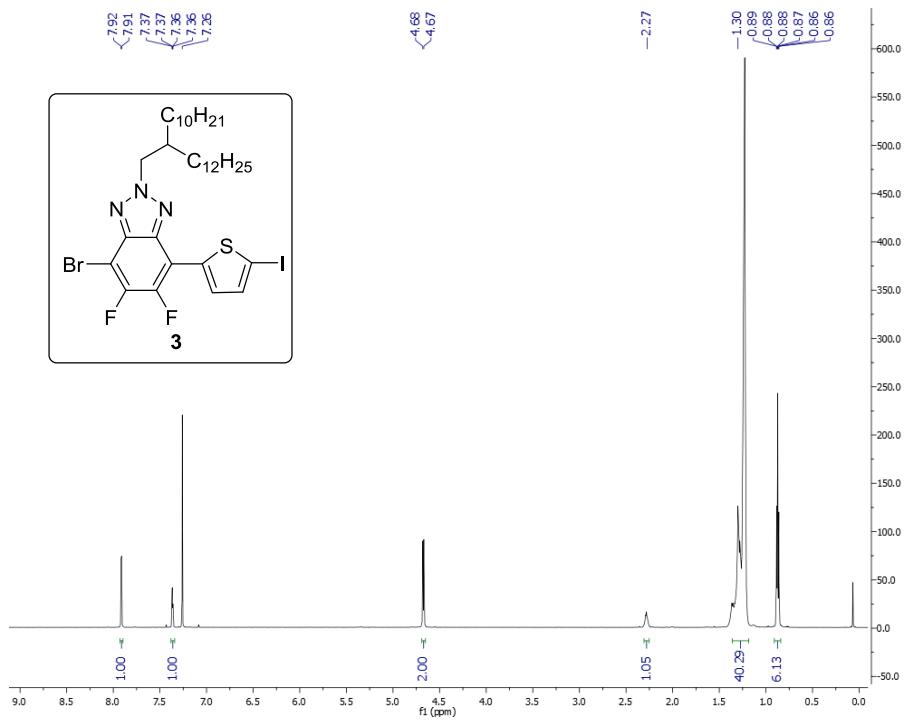


Figure 4.16. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR of **7** in CDCl_3 .



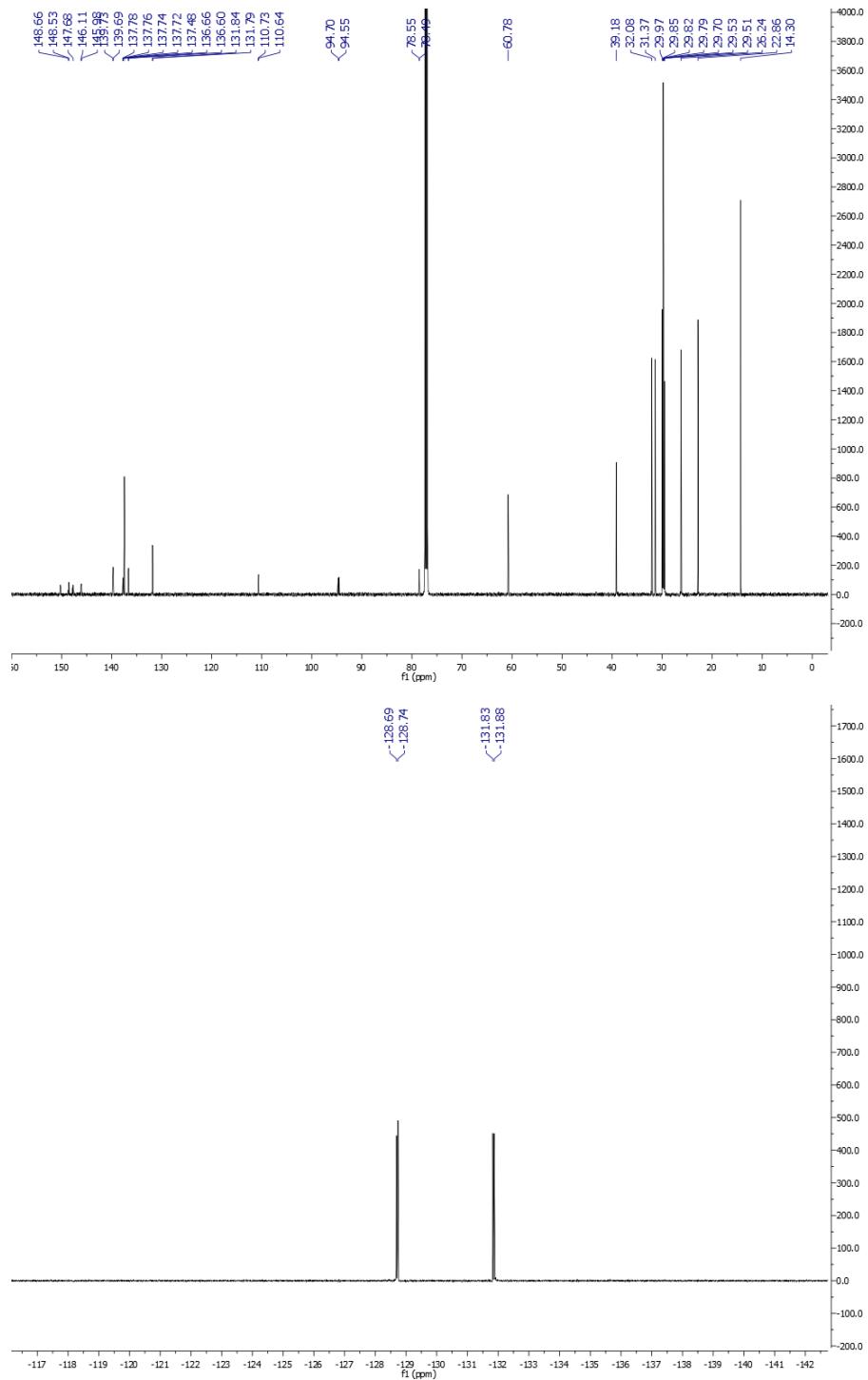


Figure 4.17. ^1H , $^{13}\text{C}\{^1\text{H}\}$, and $^{19}\text{F}\{^1\text{H}\}$ NMR of **3** in CDCl_3 .

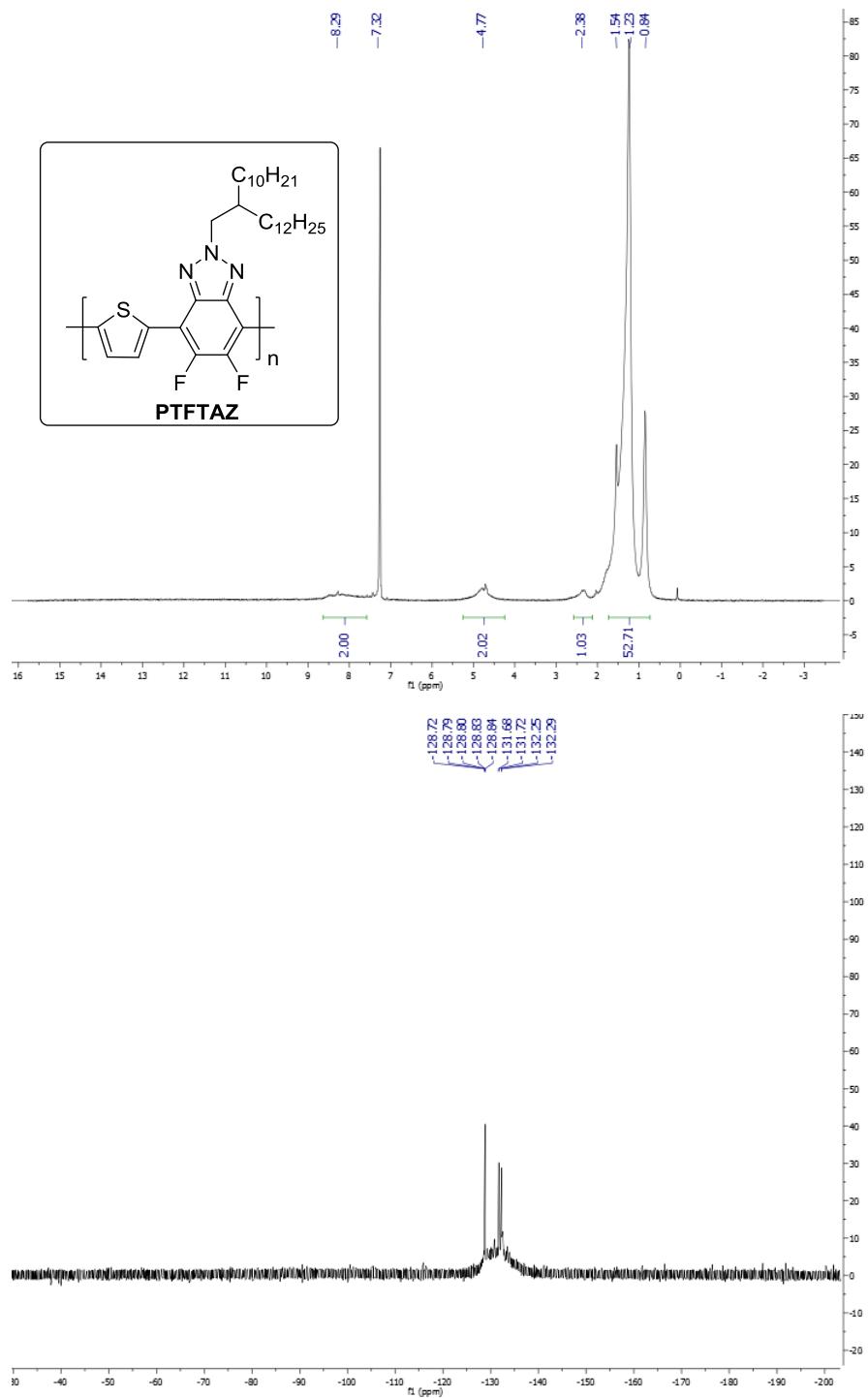
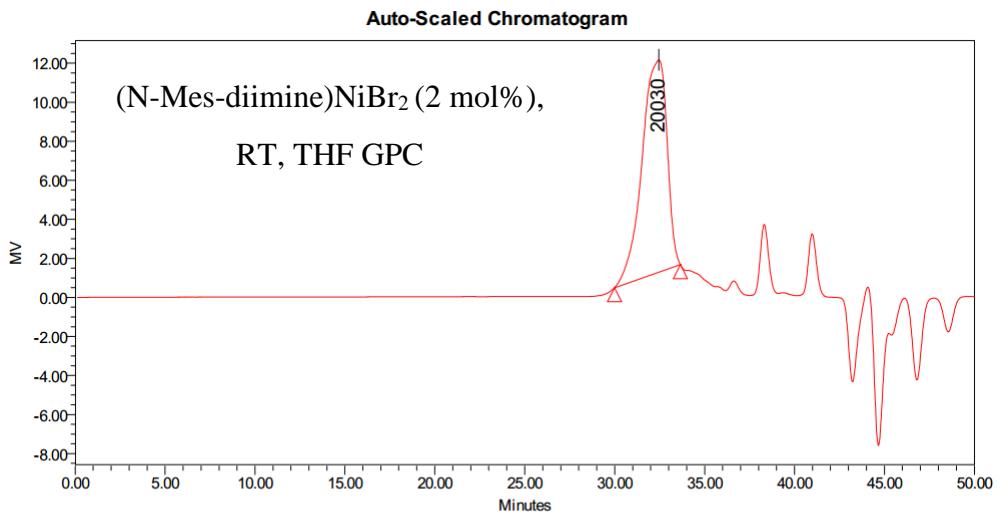
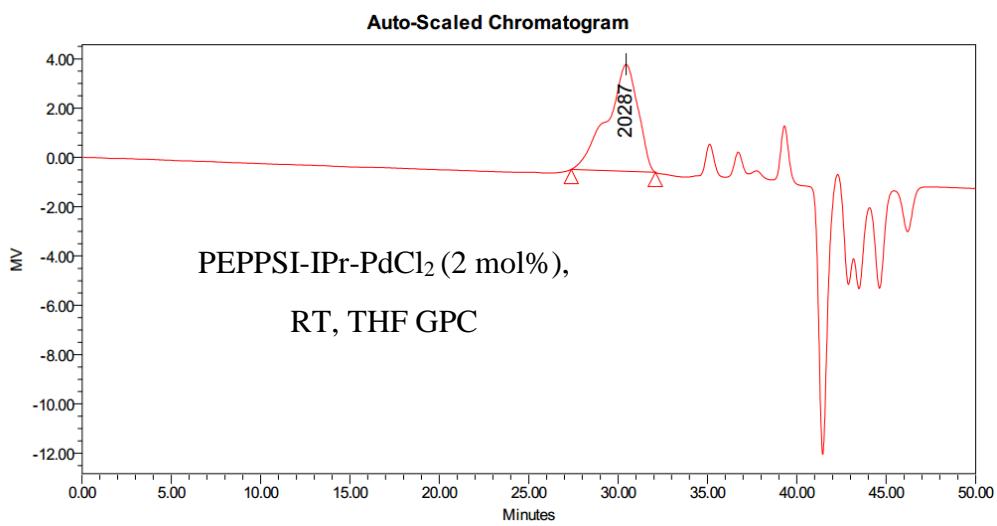


Figure 4.18. ^1H and $^{19}\text{F}\{^1\text{H}\}$ NMR of PTFTAZ in CDCl_3 .

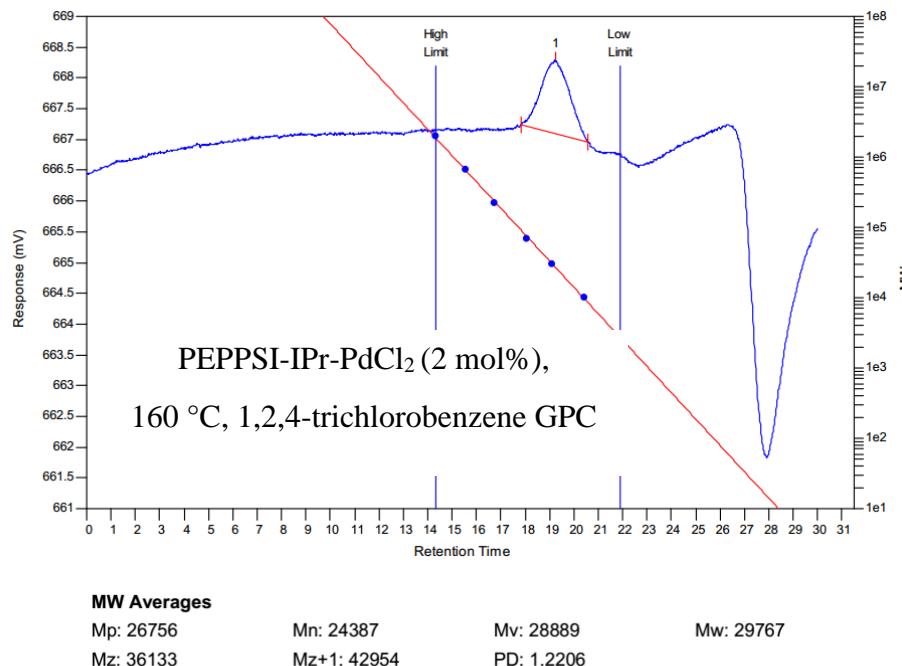
4.6.5 Representative GPC traces



	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		22336	24316	20030	26725	29561		1.088647		



	Dist Name	Mn	Mw	MP	Mz	Mz+1	Mv	Polydispersity	MW Marker 1	MW Marker 2
1		22241	27336	20287	34502	42945		1.229065		



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APPENDIX A. OPTIMIZED COORDINATES AND GIBBS FREE ENERGIES

47

Me₃Si–PPh₃⁺. Gibbs free energy: -1444.851922

P	-0.00050700	0.00965100	0.17536700
C	1.58420200	0.60322300	-0.47449900
C	1.62732200	1.52091700	-1.52798000
C	2.77434700	0.10698100	0.07264700
C	2.85776600	1.93876300	-2.02955700
H	0.71084900	1.91095500	-1.95841000
C	3.99877600	0.52622900	-0.43564600
H	2.75569800	-0.61399200	0.88437700
C	4.04064000	1.44289000	-1.48603300
H	2.88852500	2.65257900	-2.84557000
H	4.91758800	0.13702600	-0.01077000
H	4.99654600	1.77109400	-1.88056400
C	-1.30921000	1.08433800	-0.47158800
C	-1.43856100	2.37676800	0.05292600
C	-2.16662200	0.65082500	-1.48647000
C	-2.42279700	3.22823300	-0.43559100
H	-0.76899600	2.73008000	0.83146200
C	-3.15200100	1.50921400	-1.96960300
H	-2.06894700	-0.34622500	-1.90297100
C	-3.28181500	2.79294500	-1.44490000
H	-2.52084700	4.22756700	-0.02580700
H	-3.81805200	1.17111800	-2.75603300
H	-4.05173100	3.45766700	-1.82235900
C	-0.27571900	-1.66806000	-0.45540700
C	0.59956500	-2.24067100	-1.38169900
C	-1.38338300	-2.39253800	0.00443500

C	0.36636300	-3.53420800	-1.84364000
H	1.45910100	-1.68774300	-1.74531000
C	-1.61142400	-3.68139000	-0.46403700
H	-2.07754200	-1.95536000	0.71604700
C	-0.73498500	-4.25335900	-1.38665600
H	1.04802500	-3.97592300	-2.56240700
H	-2.47164600	-4.23753600	-0.10777500
H	-0.91252700	-5.26043300	-1.74903300
Si	-0.01181200	0.00755900	2.50877900
C	0.72018300	-1.64059800	2.99706800
H	0.62490100	-1.74745900	4.08323300
H	0.18971300	-2.47404900	2.52807700
H	1.78155300	-1.71770900	2.74585600
C	-1.80892000	0.18772300	2.98800400
H	-1.86310400	0.28355800	4.07811300
H	-2.25866200	1.08224600	2.54844700
H	-2.40626800	-0.68145400	2.69956300
C	1.03328700	1.46804400	3.02524600
H	1.16759100	1.42138200	4.11165000
H	2.02327600	1.44974600	2.56187000
H	0.55450400	2.42226600	2.78942300

34

PPh₃. Gibbs free energy: -1035.86317

P	-0.05237900	-0.04147700	-1.25474200
C	0.56823600	1.51906600	-0.49374000
C	1.43682000	1.56641700	0.60205500
C	0.13004700	2.72402400	-1.05946400
C	1.85230500	2.79108000	1.12417700

H	1.79208900	0.64557000	1.05446200
C	0.53332900	3.94768100	-0.53013400
H	-0.53616900	2.70659800	-1.91867700
C	1.39850200	3.98347700	0.56333300
H	2.52898700	2.81111300	1.97301300
H	0.17868200	4.87144800	-0.97653700
H	1.72093300	4.93552100	0.97321700
C	1.02104200	-1.30351600	-0.44798700
C	2.26784200	-1.54664200	-1.04014900
C	0.67140700	-2.01846300	0.70265800
C	3.15430700	-2.46545400	-0.48409300
H	2.55061500	-1.00987900	-1.94251900
C	1.55288300	-2.94942900	1.25232200
H	-0.29055500	-1.85036100	1.17731200
C	2.79665800	-3.17170600	0.66431500
H	4.11898500	-2.63576600	-0.95176500
H	1.26704500	-3.49704500	2.14521900
H	3.48254200	-3.89454400	1.09498000
C	-1.65577500	-0.27661500	-0.37729700
C	-2.02182800	0.41934800	0.78013700
C	-2.55226100	-1.20943100	-0.91549000
C	-3.25415400	0.18426000	1.38814700
H	-1.34362700	1.14883400	1.21216600
C	-3.77866600	-1.45456200	-0.30148700
H	-2.29020400	-1.74886700	-1.82246800
C	-4.13343100	-0.75472200	0.85148700
H	-3.52479700	0.73355600	2.28469100
H	-4.46052300	-2.18349900	-0.72834400

H -5.09263400 -0.93646800 1.32598900

16

2-Me-THF. Gibbs free energy: -271.596066

C 1.35061200 -0.83310900 -0.20690500

O -0.01015200 -1.13983400 0.11512900

C -0.74117200 0.06260800 0.40649100

C 0.12452400 1.19690900 -0.14022000

C 1.53712300 0.65665500 0.08563200

H 2.00829400 -1.47313000 0.38914000

H 1.51934400 -1.05228200 -1.26902300

H -0.81807000 0.15902300 1.50062800

H -0.06993500 1.33353200 -1.21094900

H -0.06638700 2.14499800 0.36828900

H 2.28813600 1.11576400 -0.56126500

H 1.84044300 0.80955700 1.12653100

C -2.13287400 -0.03881900 -0.18761700

H -2.66723600 -0.90129100 0.22060100

H -2.70793500 0.86284000 0.04633900

H -2.07471400 -0.14579700 -1.27560500

29

Me₃Si–2-Me-THF⁺. Gibbs free energy: -680.579885

C 1.05464100 -1.43260900 -0.55170300

O 0.36055000 -0.23151500 -0.04403400

C 1.35391900 0.81085500 0.40304100

C 2.69595100 0.12639300 0.16467000

C 2.38665700 -1.36990300 0.16128400

H 0.44274100 -2.29447000 -0.29629800

H 1.13795100 -1.32148500 -1.63439300

H	1.14713800	0.93754500	1.46712500
H	3.10144200	0.43406100	-0.80412000
H	3.40933500	0.40926500	0.93987500
H	3.14379800	-1.95244800	-0.36542100
H	2.28814400	-1.75808600	1.17826600
C	1.15675800	2.09214500	-0.37264100
H	0.20062100	2.57391200	-0.16101000
H	1.94741100	2.78741100	-0.07700500
H	1.24284400	1.91034600	-1.44703900
Si	-1.44609900	-0.05000700	0.04132200
C	-1.93485600	0.73178100	-1.57041800
H	-3.02771600	0.77871600	-1.62894800
H	-1.54678900	1.74798900	-1.67434300
H	-1.57870200	0.13316300	-2.41431400
C	-2.07394100	-1.78672300	0.24151600
H	-1.61731900	-2.29172600	1.09767500
H	-3.15190700	-1.72516000	0.42941700
H	-1.93251800	-2.39409800	-0.65645700
C	-1.71430700	0.99114500	1.55669000
H	-1.31700000	2.00491300	1.46608700
H	-2.79488700	1.07606200	1.71667600
H	-1.28252300	0.51780800	2.44334800

50

Me₂EtSi-PPh₃⁺. Gibbs free energy: -1484.128609

P	-0.00440300	-0.00789300	0.17802000
C	1.57869600	0.59329600	-0.46948300
C	1.62068700	1.54467200	-1.49237300
C	2.76945700	0.07330400	0.05427700

C	2.85064900	1.97263900	-1.98700100
H	0.70405600	1.95307600	-1.90513400
C	3.99303200	0.50296500	-0.44685000
H	2.75179600	-0.67350500	0.84245100
C	4.03391800	1.45370100	-1.46666200
H	2.88054400	2.71223200	-2.77969400
H	4.91208900	0.09573800	-0.03975500
H	4.98929200	1.79020400	-1.85545700
C	-1.31873900	1.06407600	-0.46160200
C	-1.48331900	2.33856600	0.09522500
C	-2.14321500	0.64631300	-1.51029600
C	-2.46827700	3.18827700	-0.39496500
H	-0.84264300	2.67929100	0.90286100
C	-3.12955600	1.50245600	-1.99496800
H	-2.01969800	-0.33750800	-1.95080900
C	-3.29325400	2.76903700	-1.43864100
H	-2.59295600	4.17373000	0.04032000
H	-3.76961800	1.17631500	-2.80760200
H	-4.06366800	3.43230900	-1.81760900
C	-0.27740300	-1.68192600	-0.46329700
C	0.59392800	-2.24532600	-1.39880900
C	-1.38378700	-2.41017800	-0.00645600
C	0.35837000	-3.53399200	-1.87298300
H	1.45182300	-1.68879500	-1.76073900
C	-1.61417500	-3.69411200	-0.48720600
H	-2.07529900	-1.97944300	0.71172700
C	-0.74163000	-4.25710500	-1.41907500
H	1.03686600	-3.96847600	-2.59911400

H	-2.47338800	-4.25349700	-0.13357400
H	-0.92133700	-5.26012700	-1.79147300
Si	0.00438600	-0.01514100	2.50942700
C	0.72513800	-1.67006000	2.99614100
H	0.61942500	-1.78758700	4.08011700
H	0.19530200	-2.49800200	2.51661600
H	1.78836200	-1.74910600	2.75288500
C	-1.78530300	0.17355600	3.01580300
H	-1.82796200	0.24415500	4.10832700
H	-2.23489500	1.07959900	2.60085300
H	-2.39190300	-0.68546800	2.71618000
C	1.07868000	1.44023500	3.01313400
H	2.07019100	1.32506400	2.56120700
H	0.66141100	2.36873000	2.60682700
C	1.20784100	1.55203700	4.54264400
H	1.65868600	0.65334700	4.97483400
H	1.84278000	2.40080000	4.81180800
H	0.23505800	1.70329100	5.02042500

32

Me₂EtSi–2-Me-THF⁺. Gibbs free energy: -719.854163

C	1.09638300	-1.40691800	-0.74308500
O	0.62423200	-0.06939100	-0.31595800
C	1.79157500	0.75208100	0.18335200
C	2.97330700	-0.20404100	0.05176400
C	2.35707500	-1.60235200	0.06678300
H	0.30267500	-2.12380400	-0.53787900
H	1.27491600	-1.33878900	-1.81677500
H	1.56275400	0.95713200	1.23156100

H	3.48931900	-0.02604400	-0.89656100
H	3.68373500	-0.04521500	0.86422300
H	3.00710500	-2.35311800	-0.38464700
H	2.11042400	-1.91636700	1.08494700
C	1.89617000	2.01336000	-0.63843100
H	1.03448400	2.66832600	-0.50768600
H	2.78789800	2.55639400	-0.31206900
H	2.00981900	1.76999300	-1.69775700
Si	-1.06983100	0.09444500	0.33362500
C	-1.29473100	1.90110200	0.69616700
H	-2.27534000	2.01540100	1.17220300
H	-0.55037300	2.29433900	1.39384300
H	-1.29541700	2.50535400	-0.21478600
C	-2.12072100	-0.51990300	-1.07821000
H	-1.94028800	-1.58787600	-1.24381300
H	-1.80888600	-0.00079500	-1.99214700
C	-1.08802500	-0.97111000	1.85750200
H	-0.34647900	-0.63518200	2.58854800
H	-2.07460300	-0.89720900	2.32785400
H	-0.90631500	-2.02589600	1.63255500
C	-3.62063500	-0.28146600	-0.82110700
H	-4.21526100	-0.65128700	-1.66044800
H	-3.96466600	-0.79998200	0.07935500
H	-3.84411300	0.78299100	-0.70201300

56

Et3Si-PPh3+. Gibbs free energy: -1562.674398

P	0.02187900	-0.14425800	0.17781400
C	1.55827700	0.56406300	-0.47625400

C	1.53207000	1.57039800	-1.44497500
C	2.78302400	0.07441800	-0.00437800
C	2.72995500	2.08393600	-1.93766000
H	0.58853000	1.95567800	-1.81745000
C	3.97405900	0.58926400	-0.50325700
H	2.81560400	-0.71378200	0.74239000
C	3.94721700	1.59588100	-1.46862700
H	2.70825900	2.86523100	-2.68956500
H	4.91985000	0.20568600	-0.13631400
H	4.87685300	2.00001600	-1.85535800
C	-1.36158300	0.88582100	-0.38729500
C	-1.58530700	2.12112000	0.23338700
C	-2.18978200	0.47048000	-1.43444900
C	-2.63504900	2.93013200	-0.18623500
H	-0.94059000	2.46463900	1.03583700
C	-3.24128400	1.28483400	-1.84799800
H	-2.02241600	-0.48167300	-1.92625800
C	-3.46606200	2.51006700	-1.22443700
H	-2.80331900	3.88564900	0.29827000
H	-3.88426800	0.95833500	-2.65816500
H	-4.28788800	3.14021800	-1.54783300
C	-0.18233700	-1.79178500	-0.56011200
C	0.74820600	-2.28359800	-1.47926400
C	-1.29120100	-2.56966900	-0.20486700
C	0.56999500	-3.54926900	-2.03439500
H	1.60826000	-1.68997900	-1.76903000
C	-1.46563300	-3.82840800	-0.76633100
H	-2.02201300	-2.20161100	0.50655700

C	-0.53308400	-4.32104200	-1.67944200
H	1.29505100	-3.92628300	-2.74753800
H	-2.32730300	-4.42505100	-0.48716000
H	-0.66908400	-5.30517500	-2.11535400
Si	0.12371500	-0.11979300	2.51870900
C	0.98949300	-1.67281500	3.12949600
H	0.92726400	-1.57342500	4.22285000
C	-1.62505200	0.13607500	3.16418300
H	-1.52957200	-0.01528200	4.24837200
H	-1.86258200	1.19884500	3.03522600
C	1.18395900	1.38692800	2.90974300
H	2.17523500	1.25738100	2.46172400
H	0.75456000	2.28273100	2.44700800
C	1.31941900	1.60685300	4.42748900
H	1.79590900	0.75236000	4.91775300
H	1.93422400	2.48781000	4.63232100
H	0.34641600	1.76715300	4.90213900
C	-2.77825700	-0.71868700	2.62719500
H	-2.97052500	-0.51007300	1.56957200
H	-2.58450800	-1.78933900	2.74066800
H	-3.70203800	-0.49639000	3.16844000
H	2.05644100	-1.57552600	2.89383700
C	0.48119200	-3.05827000	2.71232600
H	-0.59090000	-3.17578700	2.89583200
H	0.66039300	-3.24724300	1.65146200
H	0.99866000	-3.83749200	3.27919900

C	1.40659900	-0.84168000	-1.43603700
O	0.77516800	0.10579100	-0.48864700
C	1.84018300	0.81273500	0.32008200
C	3.13648400	0.18941500	-0.19001100
C	2.73017800	-1.15936800	-0.78012600
H	0.73847100	-1.69376900	-1.54931800
H	1.50672500	-0.31074500	-2.38337500
H	1.63951300	0.53056900	1.35548600
H	3.57180600	0.82820700	-0.96444600
H	3.85843100	0.09661800	0.62271100
H	3.45208000	-1.53287900	-1.50776100
H	2.59910000	-1.91512300	-0.00070100
C	1.73482100	2.30275000	0.10542700
H	0.83006000	2.72713300	0.53988700
H	2.59400600	2.77369100	0.59172400
H	1.77197800	2.53781100	-0.96146700
Si	-0.92344000	-0.24624600	0.08666400
C	-1.42041700	1.19012300	1.17058500
H	-2.21262000	0.78994300	1.81833200
H	-0.60866600	1.45456200	1.85784000
C	-1.89704600	-0.34287100	-1.50148600
H	-1.46801600	-1.09320600	-2.17403300
H	-1.81212100	0.62205300	-2.01523200
C	-0.78907900	-1.86368500	1.00788400
H	-1.82015200	-2.12406900	1.28405800
H	-0.46502000	-2.65342300	0.31942900
C	-3.37793600	-0.67625600	-1.23686500
H	-3.94150900	-0.67799100	-2.17345800

H -3.49221300 -1.66430300 -0.78099400
 H -3.85005500 0.05374200 -0.57148600
 C 0.09552600 -1.84926100 2.26396400
 H 0.03579800 -2.80685000 2.78790800
 H 1.14855600 -1.68327800 2.01643400
 H -0.21079800 -1.06896500 2.96760200
 C -1.94150000 2.43063800 0.42704100
 H -2.85699900 2.20432300 -0.12667000
 H -2.17325400 3.23219300 1.13323700
 H -1.21515800 2.81964200 -0.29258000

54

Me2PhSi-PPh3⁺. Gibbs free energy: -1636.48249

P -0.06537800 -0.04757600 0.20344100
 C 1.56675200 0.53331000 -0.33639500
 C 1.74058300 1.79463700 -0.90853100
 C 2.67851200 -0.27734900 -0.06993000
 C 3.02481300 2.24659400 -1.20509200
 H 0.88690900 2.42800600 -1.12436100
 C 3.95641800 0.18106000 -0.36759100
 H 2.55175000 -1.26598900 0.36179800
 C 4.13039200 1.44611300 -0.92988900
 H 3.15747000 3.22633800 -1.65105200
 H 4.81484700 -0.44826300 -0.15920100
 H 5.12894800 1.80472400 -1.15652800
 C -1.35456100 1.03334300 -0.47342800
 C -1.51460800 2.32311000 0.05087600
 C -2.19762600 0.58349200 -1.49467000
 C -2.50880800 3.15657800 -0.44979000

H	-0.86474400	2.68658600	0.84066800
C	-3.19179500	1.42463200	-1.98880500
H	-2.08586600	-0.41455000	-1.90517300
C	-3.34899100	2.70720400	-1.46768400
H	-2.62774700	4.15385700	-0.04029900
H	-3.84575900	1.07315200	-2.77953100
H	-4.12655500	3.35784500	-1.85391300
C	-0.30286300	-1.71243400	-0.46879900
C	0.33918800	-2.09120900	-1.65341400
C	-1.16893200	-2.60416000	0.17370000
C	0.11792200	-3.35816100	-2.18436000
H	1.00847100	-1.40524900	-2.16219200
C	-1.38591400	-3.86938300	-0.36329400
H	-1.68358600	-2.32039900	1.08554100
C	-0.74102800	-4.24679800	-1.53980800
H	0.61762800	-3.64918700	-3.10186400
H	-2.05544100	-4.55826700	0.13993200
H	-0.90803500	-5.23469900	-1.95588300
Si	-0.08437900	0.01189900	2.53561500
C	0.99917400	-1.41519500	3.05629700
H	0.92341900	-1.52534300	4.14319600
H	0.68381100	-2.35555700	2.59532300
H	2.05009600	-1.23982400	2.81018200
C	-1.87098800	-0.11231500	3.06051500
H	-1.93996300	0.11509000	4.12972400
H	-2.50678700	0.59418600	2.51905200
H	-2.27078800	-1.11864800	2.91184900
C	0.65575500	1.68498600	2.91863900

C	2.02523600	1.93135300	2.72774100
C	-0.14932500	2.73650900	3.38596600
C	2.56934900	3.18767100	2.98010800
H	2.68194200	1.14263900	2.37079900
C	0.39263200	3.99447100	3.64128500
H	-1.21236400	2.58167000	3.54990200
C	1.75188400	4.22228500	3.43336100
H	3.62902200	3.35883400	2.82056300
H	-0.24657600	4.79478600	4.00004100
H	2.17500600	5.20293300	3.62641900

36

Me₂PhSi-2-Me-THF⁺. Gibbs free energy: -872.208859

C	0.89712800	-1.49114200	-0.81904200
O	1.24648600	-0.24092200	-0.10963900
C	2.65254000	-0.30596800	0.42939400
C	3.10969000	-1.70110300	0.01575700
C	1.82260200	-2.50100200	-0.17973200
H	-0.16327500	-1.66726700	-0.65334500
H	1.10184200	-1.32495100	-1.87831200
H	2.52770600	-0.22365500	1.51053600
H	3.66722900	-1.64258600	-0.92416400
H	3.76397700	-2.12772800	0.77739400
H	1.96360000	-3.36985600	-0.82407400
H	1.41259900	-2.83537400	0.77692600
C	3.48348400	0.82171900	-0.13671700
H	3.15388900	1.80356300	0.20775400
H	4.51348100	0.68251200	0.20337400
H	3.47524500	0.79690100	-1.22958600

Si	0.11276800	1.16732000	0.09467700
C	0.43343500	2.26202900	-1.36870600
H	-0.32444100	3.05121400	-1.40845900
H	1.41456300	2.73860000	-1.29879500
H	0.38974100	1.69977600	-2.30623800
C	0.57214300	1.85920700	1.75514800
H	1.55907000	2.32783700	1.76236200
H	-0.16220300	2.63001700	2.01200800
H	0.54065800	1.09567300	2.53753100
C	-1.56147100	0.36407500	0.06981400
C	-2.05515500	-0.29389400	1.20864400
C	-2.35936600	0.39174700	-1.08491800
C	-3.30298200	-0.91093800	1.19131900
H	-1.46504400	-0.33052100	2.12052800
C	-3.60864500	-0.22449500	-1.10467200
H	-2.00783800	0.89432600	-1.98186700
C	-4.07941500	-0.87772400	0.03307200
H	-3.67081200	-1.41458100	2.07932700
H	-4.21248400	-0.19505200	-2.00586800
H	-5.05206800	-1.35901300	0.01843500

68

Ph₃Si–PPh₃⁺. Gibbs free energy: -2019.740903

P	0.05716200	-0.04158600	0.25324400
C	1.68272700	0.41733800	-0.40778600
C	1.80188200	1.43685900	-1.35689700
C	2.82987600	-0.23374600	0.06917400
C	3.06245900	1.80800800	-1.81867200
H	0.92190200	1.94394000	-1.73729700

C	4.08369000	0.14343800	-0.39805800
H	2.75295500	-1.03135600	0.80093600
C	4.20158700	1.16715500	-1.33796000
H	3.15009400	2.59955300	-2.55494800
H	4.96772800	-0.36110200	-0.02367600
H	5.18180200	1.46247100	-1.69733800
C	-1.18505500	1.09934300	-0.41261200
C	-1.19521900	2.43217100	0.02348700
C	-2.13005700	0.66066300	-1.34430000
C	-2.15413700	3.31199400	-0.46543100
H	-0.45983900	2.78939700	0.73737100
C	-3.08762500	1.54922400	-1.82772500
H	-2.12583600	-0.36557700	-1.69509300
C	-3.10349700	2.87018200	-1.38697400
H	-2.15955700	4.34133700	-0.12366800
H	-3.82029800	1.20509900	-2.54955000
H	-3.85314900	3.55856100	-1.76281700
C	-0.35160200	-1.72926400	-0.27185000
C	0.53595900	-2.47978700	-1.04771700
C	-1.55318600	-2.30201900	0.17096200
C	0.22969400	-3.80124200	-1.36495100
H	1.46342500	-2.04596700	-1.40485200
C	-1.85021600	-3.62104200	-0.15084400
H	-2.25756600	-1.72671200	0.76314000
C	-0.95609000	-4.37389800	-0.91189800
H	0.92164800	-4.38157000	-1.96557600
H	-2.77851400	-4.06044300	0.19769100
H	-1.18585100	-5.40633100	-1.15342000

Si	0.07464900	0.02994100	2.58895400
C	0.50937600	1.79586300	3.00148400
C	1.69076600	2.38510300	2.51735200
C	-0.36191800	2.58067900	3.77189200
C	1.98139100	3.71990400	2.78179100
H	2.39070500	1.80585800	1.92118600
C	-0.06906100	3.91635300	4.04107400
H	-1.27950100	2.15272300	4.16522800
C	1.09882600	4.48831900	3.54086900
H	2.89416200	4.16009200	2.39380600
H	-0.75367900	4.50948500	4.63853900
H	1.32220500	5.53093300	3.74311000
C	-1.66406600	-0.46409300	3.04720500
C	-2.76541900	0.30649500	2.63382000
C	-1.90845300	-1.65428300	3.74859600
C	-4.06683100	-0.10999600	2.89698300
H	-2.61524400	1.23809600	2.09489400
C	-3.21126500	-2.07158400	4.01365100
H	-1.08070600	-2.26929600	4.08884500
C	-4.29108200	-1.30438800	3.58166500
H	-4.90418200	0.49533800	2.56548400
H	-3.38120800	-2.99847600	4.55169400
H	-5.30602000	-1.63333400	3.78059600
C	1.38446900	-1.21472900	3.05302300
C	1.27374800	-2.56556100	2.67761100
C	2.53600100	-0.80568400	3.74302200
C	2.28655300	-3.47301200	2.97251700
H	0.39549000	-2.92013400	2.14501900

C	3.54999100	-1.71432900	4.03958100
H	2.65184300	0.23035300	4.04775400
C	3.42839700	-3.04669800	3.65070000
H	2.18389900	-4.51095300	2.67321400
H	4.43494200	-1.38005600	4.57119300
H	4.21945500	-3.75392400	3.87849000

50

Ph₃Si–2-Me-THF⁺. Gibbs free energy: -1255.460198

C	-1.11448300	-0.27742500	2.49777800
O	-0.22646600	0.41842800	1.53755300
C	0.14936400	1.78578700	2.07778900
C	-0.72245300	1.91065800	3.32615300
C	-1.83410500	0.87187700	3.16173700
H	-1.74272300	-0.95626800	1.92438000
H	-0.46938400	-0.83379100	3.17974800
H	-0.15649600	2.47620600	1.29127800
H	-0.12711300	1.68804000	4.21655400
H	-1.10976300	2.92628700	3.41829000
H	-2.26868800	0.57065000	4.11578800
H	-2.63337400	1.24069400	2.51323600
C	1.63647400	1.83136400	2.32605900
H	2.20936700	1.72412800	1.40376100
H	1.87472500	2.80615600	2.76137400
H	1.93664100	1.05731200	3.03719800
Si	-0.00424600	-0.14569900	-0.16549500
C	-1.71039000	-0.70566400	-0.64768600
C	-2.82475100	0.13904900	-0.50024400
C	-1.91170100	-1.98755000	-1.18075100

C	-4.09481500	-0.28012200	-0.88277000
H	-2.71378100	1.13071700	-0.06902800
C	-3.18251400	-2.40657100	-1.57103400
H	-1.07672600	-2.67403200	-1.28782600
C	-4.27344100	-1.55322900	-1.42439500
H	-4.94305200	0.38502600	-0.75853000
H	-3.31943900	-3.40000500	-1.98537400
H	-5.26350500	-1.88045000	-1.72543900
C	0.63212400	1.32921800	-1.09674000
C	2.01527700	1.48589500	-1.28660100
C	-0.23202600	2.28766900	-1.65154700
C	2.52033200	2.57745100	-1.98801600
H	2.70726200	0.74707700	-0.89042000
C	0.27134500	3.38155900	-2.34952800
H	-1.30753000	2.18371400	-1.54765700
C	1.64803200	3.52845100	-2.51498500
H	3.59117800	2.68429000	-2.12572800
H	-0.41016500	4.11489800	-2.76794300
H	2.04057500	4.38052200	-3.06063500
C	1.25724100	-1.50092500	-0.03668800
C	1.84607200	-1.87131700	1.18015400
C	1.66372000	-2.16565800	-1.20641000
C	2.80535300	-2.88056200	1.23174000
H	1.56966300	-1.36752600	2.10091900
C	2.61977600	-3.17600500	-1.15678900
H	1.23951400	-1.89303400	-2.16999100
C	3.19073100	-3.53512300	0.06389600
H	3.25310500	-3.15142100	2.18228700

H 2.92131500 -3.67930700 -2.06952200
H 3.93861000 -4.32047700 0.10306500

40

P'Bu₃. Gibbs free energy: -814.455735

P -0.00014400 0.00016200 0.70509400
C 1.44859900 1.05506800 0.00844600
C 2.68889100 0.76568500 0.88333100
C 1.81961500 0.84949200 -1.46899500
C 1.14342300 2.54988500 0.22470000
H 2.47214800 0.93122800 1.94351700
H 3.07071100 -0.24808900 0.77080200
H 3.49531100 1.45092800 0.59349400
H 0.97869500 1.03796300 -2.13947800
H 2.62208100 1.54855400 -1.73799000
H 2.19185700 -0.15746800 -1.66791300
H 2.05285800 3.12479100 0.01267600
H 0.36460100 2.92695200 -0.43977200
H 0.85631500 2.76122100 1.25978300
C -1.63768600 0.72714600 0.00833700
C -2.01176300 1.94123700 0.88727200
C -1.64286800 1.15583500 -1.46772500
C -2.77902500 -0.28651700 0.21725300
H -2.06721800 1.66156000 1.94420200
H -1.31790600 2.77561300 0.79494000
H -3.00113800 2.30606300 0.58424100
H -1.37444000 0.33824000 -2.13997900
H -2.65170800 1.49182600 -1.73992800
H -0.96485700 1.98941800 -1.66148100

H	-3.73164200	0.21546000	0.00950500
H	-2.71683500	-1.14318700	-0.45544300
H	-2.81874600	-0.65122300	1.24867800
C	0.18856700	-1.78141500	0.00868400
C	-0.67855500	-2.71095300	0.88693600
C	-0.17604500	-2.00216900	-1.46844200
C	1.63696000	-2.26288900	0.22113100
H	-0.42664000	-2.60111800	1.94666700
H	-1.74843300	-2.54024500	0.77492300
H	-0.48399400	-3.75235500	0.60162500
H	0.40148800	-1.36250700	-2.13908600
H	0.03762100	-3.04465500	-1.73763100
H	-1.23607700	-1.83062500	-1.66616700
H	1.67776700	-3.33980100	0.01884600
H	2.34830000	-1.78355700	-0.45325900
H	1.97135700	-2.10983800	1.25225300

53

Me₃Si-P'Bu₃⁺. Gibbs free energy: -1223.45397

P	0.27588100	-0.00032900	0.00016100
C	0.87363900	-1.14685400	1.40928300
C	0.69507800	-2.62869900	1.02645100
C	2.35369100	-0.91446000	1.76312500
C	0.01639000	-0.91327200	2.67009200
H	-0.32816100	-2.87035300	0.73460800
H	1.37699200	-2.95239900	0.24027300
H	0.92497700	-3.22403700	1.91561200
H	2.53119800	0.06157600	2.21539700
H	2.64005900	-1.66806500	2.50382600

H	3.02063600	-1.03000100	0.90823000
H	0.42177400	-1.54439300	3.46715200
H	0.03428200	0.11298200	3.03141900
H	-1.02245600	-1.21519500	2.52310300
C	0.87042300	1.79400800	0.28925300
C	0.68610900	2.20388200	1.76324500
C	2.35172700	1.98835400	-0.08357800
C	0.01297100	2.76838900	-0.54453500
H	-0.33742200	2.06831800	2.11587400
H	1.36779900	1.68852500	2.43961400
H	0.91177400	3.27246600	1.83443900
H	2.53516700	1.88427300	-1.15332000
H	2.63089500	3.01060000	0.19158600
H	3.01922500	1.31322600	0.45292200
H	0.41531400	3.77473600	-0.39151700
H	0.03462300	2.57221900	-1.61475900
H	-1.02692400	2.78873500	-0.21269100
C	0.87566600	-0.64586700	-1.69669000
C	0.69447700	0.42685400	-2.78775900
C	2.35715900	-1.06392900	-1.67291400
C	0.02217500	-1.85654400	-2.12704800
H	-0.32939200	0.79847200	-2.85168900
H	1.37376100	1.27148500	-2.67392100
H	0.92646100	-0.04299900	-3.74866500
H	2.53746100	-1.94276400	-1.05318300
H	2.64405500	-1.32843100	-2.69581500
H	3.02153500	-0.26377700	-1.34484000
H	0.42930400	-2.22761900	-3.07284200

H 0.04226500 -2.68427700 -1.42096000
 H -1.01760500 -1.58128200 -2.31489300
 Si -2.08149500 -0.00271800 -0.00145300
 C -2.70979700 1.05230400 1.41611800
 H -3.79664500 0.90782200 1.43634100
 H -2.32174800 0.75368500 2.39205800
 H -2.52635100 2.11996100 1.27481700
 C -2.70513900 0.69889900 -1.62521900
 H -2.52224100 0.04106000 -2.47800400
 H -3.79179900 0.79315700 -1.51215400
 H -2.31169300 1.69157800 -1.85347900
 C -2.70638400 -1.75915700 0.20240600
 H -3.79445300 -1.70395000 0.07721600
 H -2.32485800 -2.45088200 -0.55138300
 H -2.51419700 -2.17491100 1.19417500

43

P(*p*-tol)₃. Gibbs free energy: -1153.715656

P -0.01940300 -0.01086300 1.45826200
 C -1.63654200 -0.34465200 0.64485700
 C -1.79173100 -1.09238800 -0.52673400
 C -2.78255600 0.19722600 1.24033700
 C -3.05296300 -1.28315800 -1.08718900
 H -0.92351800 -1.52824000 -1.01221100
 C -4.03949700 0.01373100 0.67127300
 H -2.69324500 0.77324300 2.15842100
 C -4.19708100 -0.73369000 -0.50074800
 H -3.14690900 -1.86468800 -2.00085700
 H -4.91193700 0.45234200 1.14872600

C	1.09055700	-1.23112100	0.63938400
C	1.25331800	-2.47852100	1.25533800
C	1.77509800	-0.99046900	-0.55618600
C	2.06215000	-3.45737200	0.68547100
H	0.74230200	-2.68890100	2.19186100
C	2.59104700	-1.96970000	-1.11909000
H	1.67170800	-0.03255500	-1.05751800
C	2.74921000	-3.21784500	-0.50981400
H	2.16879800	-4.41879800	1.18129900
H	3.11001800	-1.75921300	-2.05076800
C	0.50216800	1.56042900	0.65125200
C	-0.11315200	2.12049500	-0.47253300
C	1.60385000	2.22633700	1.20336200
C	0.36714000	3.30467100	-1.02953400
H	-0.97012500	1.63003800	-0.92490500
C	2.08813500	3.40121600	0.63668200
H	2.09621000	1.81816500	2.08297700
C	1.47480500	3.96356500	-0.48821800
H	-0.12578900	3.71890600	-1.90544800
H	2.95147000	3.89176500	1.07881800
C	-5.56272100	-0.96721100	-1.09458900
H	-5.50437700	-1.11515500	-2.17612800
H	-6.02220500	-1.86312900	-0.66262100
H	-6.23188200	-0.12585400	-0.89558900
C	3.65859200	-4.26530400	-1.09993500
H	3.82372000	-4.09366700	-2.16661700
H	4.63581100	-4.25031500	-0.60510400
H	3.24148800	-5.26808100	-0.97182700

C	1.97371900	5.25813400	-1.07768600
H	1.47483300	6.11349900	-0.60874400
H	3.04891300	5.37811000	-0.92042600
H	1.77445500	5.30924700	-2.15147800

56

Me3Si-P(p-tol)3^+. Gibbs free energy: -1562.710617

P	-0.00951500	0.00831100	0.43169100
C	0.54801500	-1.60158700	-0.17895700
C	1.50232500	-1.69472900	-1.19599700
C	-0.01368700	-2.77118200	0.34630100
C	1.88362000	-2.94248000	-1.67724600
H	1.94635300	-0.79932800	-1.61886000
C	0.37387800	-4.01171100	-0.14424400
H	-0.76671100	-2.72458500	1.12741800
C	1.32976400	-4.11859100	-1.16128200
H	2.62384700	-3.00057800	-2.46970000
H	-0.07462100	-4.90976800	0.26963800
C	1.13066900	1.26757600	-0.19215700
C	2.40976800	1.37377600	0.37070500
C	0.76985700	2.11362800	-1.24230100
C	3.30738000	2.31363800	-0.11442300
H	2.71809500	0.71549200	1.17765000
C	1.67957800	3.05381200	-1.71999500
H	-0.21363700	2.04229400	-1.69525900
C	2.95655400	3.17123300	-1.16626400
H	4.29574700	2.38473600	0.32993200
H	1.38670800	3.70478600	-2.53824200
C	-1.64993600	0.33371500	-0.26204900

C	-2.20405200	-0.50807000	-1.22752400
C	-2.37264800	1.45404300	0.17174400
C	-3.46511100	-0.23132700	-1.75019200
H	-1.66108100	-1.37955000	-1.57818400
C	-3.62599100	1.72083600	-0.35925200
H	-1.95894200	2.13031500	0.91416500
C	-4.19469000	0.88179000	-1.32783400
H	-3.88297400	-0.89596900	-2.50026400
H	-4.17357500	2.59392400	-0.01664700
C	1.77056300	-5.46411800	-1.67241500
H	1.99276200	-5.42566900	-2.74181900
H	2.68129600	-5.78632900	-1.15652700
H	1.00459500	-6.22449500	-1.50312800
C	3.93779500	4.19512000	-1.67125300
H	3.58153300	4.67173000	-2.58683900
H	4.09583100	4.97599800	-0.92025800
H	4.90947000	3.73590600	-1.87412600
C	-5.55762100	1.18602300	-1.88963000
H	-6.30809000	1.20799300	-1.09363000
H	-5.56556600	2.16812600	-2.37218900
H	-5.86176500	0.43991700	-2.62650600
Si	-0.08634500	0.03970400	2.76003900
C	0.12992400	1.83379500	3.23728900
H	0.20299800	1.89295400	4.32885200
H	1.04411600	2.25919900	2.81415100
H	-0.71775800	2.45019800	2.92536400
C	1.32380300	-1.04713400	3.33042100
H	1.23834100	-1.17571400	4.41504100

H	1.28745000	-2.03764000	2.86887200
H	2.29999900	-0.60061600	3.12261000
C	-1.76750200	-0.64335700	3.20837400
H	-1.90447300	-0.53161600	4.28958800
H	-2.57388000	-0.10004500	2.70772300
H	-1.86247900	-1.70591100	2.96805100

52

PCy₃. Gibbs free energy: -1046.572961

P	-0.35311500	0.01269100	0.31545800
C	-1.70640100	-0.74502900	-0.77712800
C	-2.40522500	-1.95413100	-0.12307600
C	-2.80390500	0.25272900	-1.19424100
H	-1.21090600	-1.08515100	-1.69522000
C	-3.27002700	-1.55336700	1.07729500
H	-1.69133400	-2.73222600	0.16218900
H	-3.05373300	-2.40814500	-0.88606100
C	-3.67253600	0.70129600	-0.01487600
H	-2.38328500	1.11114000	-1.72374700
H	-3.44617300	-0.26087500	-1.92392600
C	-4.31472800	-0.50274400	0.68364000
H	-2.62923500	-1.15092100	1.87229300
H	-3.76521600	-2.44031300	1.48811200
H	-4.44876300	1.39029100	-0.36674900
H	-3.05860400	1.25648300	0.70619600
H	-4.87480200	-0.17553100	1.56679600
H	-5.04149700	-0.96290800	-0.00087800
C	0.72037400	-1.52737700	0.53926900
C	1.08301900	-2.44110300	-0.64960700

C	1.90997800	-1.38979100	1.51994400
H	-0.02918500	-2.08068000	1.11989300
C	2.43969100	-2.15199700	-1.29324200
H	0.29685900	-2.43053100	-1.41000000
H	1.11394900	-3.47120600	-0.26450300
C	3.28617400	-1.17103700	0.88184700
H	1.70291300	-0.60480800	2.25684400
H	1.96427200	-2.33120200	2.08480800
C	3.55880000	-2.16642300	-0.24881100
H	2.41576200	-1.18426800	-1.80724800
H	2.63815300	-2.90491400	-2.06459500
H	4.05250500	-1.27151300	1.65924300
H	3.37794700	-0.15275400	0.49743800
H	4.52383800	-1.94725500	-0.71932900
H	3.63498000	-3.17900700	0.17268000
C	0.33561100	1.27226400	-0.91870500
C	-0.38512800	2.62869600	-0.70294200
C	1.84820600	1.53509900	-0.87908200
H	0.08763900	0.90460900	-1.92339800
C	0.07768600	3.37794700	0.55163900
H	-1.46976700	2.50482800	-0.65743500
H	-0.18134900	3.25289600	-1.58487100
C	2.31248800	2.24046500	0.39819500
H	2.40209400	0.61019400	-1.03420200
H	2.09045300	2.18217900	-1.73484500
C	1.59357600	3.57892400	0.57240200
H	-0.22078400	2.81027100	1.44220500
H	-0.43610800	4.34440100	0.60483500

H	3.39789900	2.38924400	0.36371000
H	2.10655500	1.60681500	1.27111700
H	1.90119200	4.06082500	1.50712200
H	1.88454200	4.25314900	-0.24547300

65

Me₃Si-PCy₃⁺. Gibbs free energy: -1455.566893

P	-0.25011600	-0.06081900	0.40462600
C	-1.64528500	-1.11786900	-0.30015000
C	-2.21073300	-2.20296300	0.64005700
C	-2.80655200	-0.41703300	-1.03112400
H	-1.07719300	-1.63190300	-1.08192100
C	-3.34766500	-1.72371400	1.54527200
H	-1.42721200	-2.68092100	1.23553200
H	-2.59938800	-2.99148700	-0.01622900
C	-3.90680400	0.10123100	-0.10831600
H	-2.45209000	0.36239400	-1.70797400
H	-3.24155300	-1.18716300	-1.68134100
C	-4.46257800	-1.02654200	0.76371600
H	-2.96167400	-1.03615000	2.30331500
H	-3.74741300	-2.58336500	2.09227000
H	-4.70522000	0.54243200	-0.71309900
H	-3.52268200	0.90414300	0.53083200
H	-5.21620600	-0.63775900	1.45622200
H	-4.96792800	-1.75887900	0.12048800
C	1.06613600	-1.38689400	0.63763800
C	1.44974000	-2.25812300	-0.57810700
C	2.33434500	-1.02663600	1.43918700
H	0.47762500	-2.03203300	1.30116900

C	2.59227500	-1.70452600	-1.42976000
H	0.58985000	-2.49306600	-1.20916200
H	1.77228300	-3.21751800	-0.15335800
C	3.49658800	-0.47527300	0.61377000
H	2.10946100	-0.35340800	2.26695800
H	2.66104900	-1.96650400	1.90238000
C	3.82512600	-1.37607000	-0.58116600
H	2.25635100	-0.82270000	-1.98471800
H	2.85497200	-2.45165500	-2.18539600
H	4.37317200	-0.39396800	1.26465100
H	3.27692900	0.54282400	0.28087800
H	4.59723200	-0.91023300	-1.20180300
H	4.24795700	-2.31665500	-0.20341700
C	0.00706300	1.20061500	-0.95684200
C	-0.99646800	2.37868700	-0.86638800
C	1.41730500	1.74934600	-1.22603100
H	-0.26235400	0.59661800	-1.83224900
C	-0.54107700	3.55009300	0.00857300
H	-1.98333400	2.04857600	-0.53426300
H	-1.12965600	2.74003200	-1.89362000
C	1.86206100	2.86565200	-0.28504500
H	2.15116900	0.94809600	-1.25201400
H	1.38214300	2.15502900	-2.24562200
C	0.87207100	4.02946000	-0.31955500
H	-0.58244200	3.26921400	1.06457200
H	-1.26092900	4.36622300	-0.10981100
H	2.85973500	3.20446600	-0.58226000
H	1.95821500	2.48780400	0.73976500

H	1.17413200	4.81053700	0.38545900
H	0.88329400	4.48007400	-1.32056100
Si	-0.58135800	0.75924000	2.58292300
C	-0.49786900	-0.77287300	3.66504500
H	0.52078500	-1.16448800	3.73357700
H	-0.80192600	-0.46968000	4.67350800
H	-1.15901800	-1.58370100	3.35277000
C	-2.22114400	1.65439300	2.74344400
H	-3.08043600	0.98269300	2.78176100
H	-2.17910000	2.19241200	3.69779000
H	-2.39263600	2.39543900	1.95924200
C	0.79059200	1.93252900	3.10082600
H	0.70276700	2.92426200	2.65361700
H	0.66836700	2.05032400	4.18474300
H	1.80191600	1.56072800	2.92648900

43

P(*o*-tol)₃. Gibbs free energy: -1153.69451

P	-0.04857100	-0.03248400	-0.92309100
C	0.68801800	1.55365900	-0.33233100
C	1.61827200	1.79025000	0.70258700
C	0.24291300	2.63833800	-1.10588300
C	2.04879000	3.10625700	0.91576400
C	0.65896500	3.94179400	-0.85873700
H	-0.45478700	2.45331700	-1.91948800
C	1.57833200	4.17537900	0.15929300
H	2.76696800	3.29609400	1.70905200
H	0.28206700	4.75849400	-1.46601500
H	1.93270300	5.18111200	0.36275800

C	0.99359100	-1.41322500	-0.27997800
C	2.14191000	-1.58511100	-1.07058000
C	0.78016100	-2.28390700	0.81010800
C	3.09837300	-2.55250800	-0.78452500
H	2.29315500	-0.93321000	-1.92804900
C	1.74001500	-3.27292600	1.06267600
C	2.89094900	-3.40877600	0.29231200
H	3.98443700	-2.64322000	-1.40455300
H	1.58250900	-3.94750700	1.90011400
H	3.61530000	-4.18099800	0.53173600
C	-1.73838600	-0.19150000	-0.19931400
C	-2.32277200	0.47630700	0.89828900
C	-2.51517900	-1.10640400	-0.92897100
C	-3.65352400	0.17988300	1.22023700
C	-3.82585700	-1.40812900	-0.57640100
H	-2.07515400	-1.59874300	-1.79309400
C	-4.40136500	-0.75312400	0.50779400
H	-4.10977400	0.68856900	2.06534700
H	-4.39265600	-2.13227500	-1.15270500
H	-5.42767300	-0.95898100	0.79548900
C	-1.59402600	1.47262900	1.76510200
H	-0.66162400	1.06068700	2.15972600
H	-1.33353100	2.38037600	1.21406900
H	-2.21683000	1.75912200	2.61572800
C	2.15955800	0.71844500	1.61608200
H	1.35845700	0.12714700	2.06666400
H	2.80896900	0.01854300	1.08300900
H	2.73695800	1.17006000	2.42595900

C	-0.40210600	-2.19930600	1.74373200
H	-0.49551600	-1.20563900	2.19057100
H	-1.34545400	-2.40720400	1.23210900
H	-0.29087700	-2.92025800	2.55685800

56

Me₃Si-P(*o*-tol)₃⁺. Gibbs free energy: -1562.6866

P	0.00861100	-0.01798500	0.02420800
C	1.61960400	0.65536700	-0.50111600
C	1.84188900	1.56489200	-1.55541900
C	2.70241700	0.16199100	0.24245400
C	3.16355000	1.96439400	-1.78955900
C	4.00417800	0.56066300	-0.02364000
H	2.53686400	-0.56612900	1.02974800
C	4.23158800	1.48089900	-1.04253100
H	3.35626800	2.66713500	-2.59451000
H	4.82508400	0.15876900	0.55950200
H	5.23981800	1.81490500	-1.26406100
C	-1.36530700	1.04217800	-0.53552000
C	-1.43143200	2.26515500	0.14924600
C	-2.29468100	0.75175200	-1.55486700
C	-2.40552600	3.20766000	-0.14433900
H	-0.69489000	2.50449100	0.90948000
C	-3.27881900	1.71348600	-1.81708500
C	-3.34385000	2.92077900	-1.13110600
H	-2.42885200	4.14984300	0.39160400
H	-4.00636100	1.50834200	-2.59642600
H	-4.11956100	3.63866900	-1.37578400
C	-0.19986900	-1.75043200	-0.50324900

C	0.48941900	-2.39083800	-1.55372500
C	-1.16866700	-2.45134100	0.23096300
C	0.18420000	-3.73584600	-1.79591900
C	-1.46331900	-3.77905900	-0.04199800
H	-1.72475500	-1.95216900	1.01750000
C	-0.77073800	-4.42770900	-1.05959600
H	0.70499100	-4.24730900	-2.59966900
H	-2.22170500	-4.29619300	0.53507000
H	-0.97664100	-5.46857500	-1.28597500
Si	-0.03412300	0.01597100	2.39023100
C	0.76125200	-1.56998900	2.98487400
H	0.57126600	-1.63801100	4.06227900
H	0.33754900	-2.45911900	2.51217200
H	1.84469200	-1.58014000	2.84101800
C	-1.83352400	0.13212100	2.89085500
H	-1.85475300	0.32004400	3.97054800
H	-2.34942900	0.95863200	2.39564400
H	-2.39111500	-0.78956900	2.70662300
C	0.93368300	1.52075500	2.93926500
H	1.11801200	1.40499900	4.01353900
H	1.90196000	1.60682500	2.44044200
H	0.38261200	2.45410800	2.79933000
C	-2.27764800	-0.48912800	-2.41319800
H	-1.30149800	-0.65043300	-2.87881400
H	-2.52144800	-1.38916100	-1.84376200
H	-3.01062600	-0.39138500	-3.21570000
C	1.49361500	-1.72393800	-2.46055100
H	1.10021200	-0.80307100	-2.89893400

H	2.41717800	-1.46905200	-1.93510700
H	1.74946700	-2.39376100	-3.28312900
C	0.77314500	2.10138600	-2.47546700
H	0.12463500	1.31084300	-2.86075000
H	0.13144200	2.83143300	-1.97512200
H	1.23714400	2.59199100	-3.33266000

37

PPh₂(*p*-tol). Gibbs free energy: -1075.14702

P	-0.02484900	-0.01583600	1.45494800
C	-1.64209400	-0.34581900	0.63558800
C	-1.79589500	-1.13651200	-0.50830900
C	-2.78033700	0.23415300	1.21194100
C	-3.05761200	-1.33396100	-1.06853800
H	-0.92878900	-1.60076200	-0.96815400
C	-4.03951400	0.04776600	0.64630200
H	-2.68184800	0.83805700	2.11078800
C	-4.18076400	-0.73979800	-0.49609000
H	-3.16063600	-1.95068700	-1.95609100
H	-4.91000300	0.50860900	1.10267900
C	1.09033800	-1.22881100	0.63461100
C	1.26822400	-2.47085800	1.25688900
C	1.76125300	-0.99005000	-0.56928300
C	2.07909600	-3.44704600	0.68525900
H	0.76740000	-2.67920600	2.19924000
C	2.57938600	-1.96635700	-1.13351300
H	1.64576300	-0.03617500	-1.07569000
C	2.75274500	-3.20959700	-0.51790000
H	2.19746600	-4.40471300	1.18559400

H 3.08815500 -1.75785200 -2.07118100
 C 0.49839000 1.55979400 0.65316700
 C -0.12659500 2.12847100 -0.46175300
 C 1.60710000 2.21168000 1.20997400
 C 0.35391900 3.31682900 -1.01269600
 H -0.98943200 1.64354700 -0.90844500
 C 2.09554200 3.39063700 0.65308200
 H 2.09670400 1.79057900 2.08478200
 C 1.46740900 3.94747300 -0.46093500
 H -0.14071400 3.74595000 -1.87872300
 H 2.96038000 3.87762200 1.09275100
 C 3.66437800 -4.25368400 -1.11032800
 H 3.82217600 -4.08448000 -2.17847400
 H 4.64431200 -4.23125000 -0.62125200
 H 3.25371500 -5.25834800 -0.97648200
 H -5.16161000 -0.89303700 -0.93512900
 H 1.84245900 4.86928700 -0.89446800

50

Me3Si-PPh2(p-tol)+. Gibbs free energy: -1484.138497

P -0.01198100 0.00553400 0.42698200
 C 0.55053000 -1.60519500 -0.18724200
 C 1.51827400 -1.69290900 -1.19179200
 C -0.02029900 -2.77071600 0.33963900
 C 1.91086200 -2.94270100 -1.66556900
 H 1.96465300 -0.79571400 -1.60771500
 C 0.37464600 -4.01451200 -0.13994400
 H -0.78041900 -2.71677400 1.11313100
 C 1.34127500 -4.10084600 -1.14186000

H	2.66204500	-3.00756300	-2.44520700
H	-0.07146700	-4.91416900	0.26967600
C	1.12777800	1.27060600	-0.19666900
C	2.41189600	1.36012700	0.35576600
C	0.74514600	2.13744600	-1.22375400
C	3.30541700	2.31394900	-0.11825600
H	2.72633600	0.68250000	1.14389600
C	1.64547500	3.09163900	-1.69273700
H	-0.24585900	2.07061500	-1.66025100
C	2.92101500	3.18166600	-1.14077000
H	4.29833200	2.38128400	0.31280000
H	1.34626000	3.76451400	-2.48906400
C	-1.65284100	0.32768700	-0.26483000
C	-2.20336800	-0.50672400	-1.23980000
C	-2.38018400	1.43938200	0.18148500
C	-3.46505400	-0.22983500	-1.75848100
H	-1.65816500	-1.37341100	-1.59860400
C	-3.63525400	1.70675100	-0.34681000
H	-1.97080400	2.10839400	0.93279200
C	-4.19890500	0.87747500	-1.32553600
H	-3.88206700	-0.88982600	-2.51318400
H	-4.18731500	2.57187900	0.00811000
C	-5.55124500	1.19054600	-1.90728500
H	-6.23737200	1.55454800	-1.13810600
H	-5.46486100	1.97355900	-2.66816800
H	-5.99414400	0.31142600	-2.38039900
Si	-0.08115700	0.03231800	2.75806800
C	0.14172900	1.82522500	3.23472900

H	0.21568600	1.88293700	4.32631900
H	1.05747800	2.24750500	2.81183500
H	-0.70376900	2.44519000	2.92416800
C	1.32768800	-1.05983700	3.32015100
H	1.24697500	-1.18630500	4.40541400
H	1.28442500	-2.05106600	2.86087800
H	2.30475100	-0.61791600	3.10711300
C	-1.76241700	-0.64828700	3.20831600
H	-1.89475000	-0.53917300	4.29039300
H	-2.56991400	-0.10229600	2.71261900
H	-1.86028800	-1.71005600	2.96587100
H	3.61884700	3.92750700	-1.50664600
H	1.64960200	-5.07206600	-1.51448300

33

PPh₂i-Pr. Gibbs free energy: -922.7895

P	-0.00429900	-0.04645300	1.46143100
C	-1.65923200	-0.31935800	0.68972200
C	-1.88252300	-0.97941800	-0.52534500
C	-2.76654600	0.19130300	1.38122100
C	-3.17185900	-1.11803000	-1.03696700
H	-1.05261500	-1.39491200	-1.08821900
C	-4.05536900	0.06587800	0.86647600
H	-2.61897500	0.69350900	2.33419400
C	-4.26140000	-0.59148300	-0.34543000
H	-3.32262500	-1.63391500	-1.98026900
H	-4.89814200	0.47467400	1.41521400
C	0.51280100	1.53221000	0.65205000
C	0.25666700	1.82839200	-0.69300800

C	1.24154100	2.45211900	1.41428200
C	0.72600800	3.00965000	-1.26219300
H	-0.31703600	1.13651700	-1.30346000
C	1.71627100	3.63488300	0.84632700
H	1.44266400	2.24209500	2.46152000
C	1.45967500	3.91467400	-0.49384300
H	0.52059300	3.22337600	-2.30671000
H	2.28376300	4.33484700	1.45175600
H	-5.26442100	-0.69809400	-0.74661400
H	1.82691000	4.83412500	-0.93913700
C	1.10571100	-1.25958200	0.56855400
C	0.75015200	-2.69621300	0.96569000
C	2.57073500	-0.95005700	0.89610500
H	0.96918600	-1.13501600	-0.51284600
H	-0.29141300	-2.94430100	0.74139300
H	1.38840300	-3.40295200	0.42466200
H	0.91112200	-2.85258000	2.03834400
H	2.85849200	0.05436500	0.57236600
H	2.75943500	-1.02963600	1.97293100
H	3.22375300	-1.66758300	0.38804800

46

Me₃Si–PPh₂*i*-Pr⁺. Gibbs free energy: -1331.780338

P	0.02488200	0.26468500	0.38437500
C	-1.45391100	-0.76068200	0.12777300
C	-2.43242500	-0.93004000	1.11119400
C	-1.60721600	-1.38421900	-1.11836300
C	-3.55849300	-1.70657100	0.84384000
H	-2.33261200	-0.47413800	2.08933500

C	-2.73199100	-2.15802300	-1.37827900
H	-0.84151100	-1.28804500	-1.88211900
C	-3.71187800	-2.31588100	-0.39836100
H	-4.31337500	-1.83397100	1.61222600
H	-2.84118600	-2.63946100	-2.34397300
C	1.45148600	-0.81122700	0.06876200
C	1.38034000	-2.17129700	0.39272600
C	2.64019400	-0.27817100	-0.44103500
C	2.49188800	-2.98715800	0.20542000
H	0.46221100	-2.59695900	0.78557700
C	3.74835900	-1.09961400	-0.62698200
H	2.71807900	0.77417300	-0.69296800
C	3.67430000	-2.45323600	-0.30499200
H	2.43101800	-4.04106200	0.45457300
H	4.66543300	-0.68063400	-1.02655800
H	-4.59121300	-2.91753500	-0.60281500
H	4.53764900	-3.09322300	-0.45377300
C	0.09303400	0.80459200	2.15353000
C	-0.90417000	1.93440600	2.44386300
C	1.51903100	1.20220100	2.55333300
H	-0.18651400	-0.09077400	2.72188000
H	-1.91724900	1.72057500	2.09488800
H	-0.95136600	2.09353700	3.52424600
H	-0.57777700	2.87357100	1.98814100
H	2.22447300	0.37632600	2.44217600
H	1.88446800	2.05291000	1.96986600
H	1.51125100	1.50161400	3.60493600
Si	-0.10541800	2.04168700	-1.11586700

C	1.11240400	3.36057700	-0.58981900
H	1.02432800	4.18736100	-1.30382900
H	0.89683500	3.75872900	0.40494500
H	2.15031600	3.01773300	-0.61149900
C	-1.88460200	2.60073600	-0.99872400
H	-2.05969000	3.34347000	-1.78497800
H	-2.57934700	1.77071000	-1.15794000
H	-2.10984000	3.06876000	-0.03734900
C	0.30035700	1.31802600	-2.79158600
H	-0.48567300	0.64475700	-3.14358700
H	0.36964400	2.14724300	-3.50466600
H	1.25403800	0.78391700	-2.80403300

44

PPh₂(*o*-biphenyl). Gibbs free energy: -1266.781078

P	-0.45016200	0.00777000	-0.80191100
C	-0.23869900	1.58063600	0.13367200
C	-0.22923500	1.66085900	1.53091300
C	-0.05988000	2.75189700	-0.61069700
C	-0.04441500	2.88549800	2.16873800
H	-0.35851000	0.76054900	2.12489300
C	0.11800800	3.97950600	0.02493600
H	-0.04799500	2.70306400	-1.69665000
C	0.12942800	4.04775800	1.41729900
H	-0.03600500	2.93261100	3.25339000
H	0.25883000	4.87917000	-0.56589300
H	0.27680400	5.00116600	1.91481700
C	0.05016900	-1.25289000	0.45772600
C	1.41813700	-1.56909200	0.58942500

C	-0.88002800	-1.94242200	1.24468900
C	1.81226500	-2.55691800	1.49701500
C	-0.47558200	-2.92360300	2.14697700
H	-1.93710800	-1.71548100	1.15008000
C	0.87554600	-3.23357600	2.27401600
H	2.86882100	-2.79022100	1.59340800
H	-1.21624400	-3.44275300	2.74707000
H	1.20091400	-3.99697000	2.97351600
C	-2.28409400	-0.18452100	-0.82124200
C	-3.16832600	0.58479700	-0.05671300
C	-2.81141500	-1.15465400	-1.68477800
C	-4.54509700	0.38295600	-0.14818300
H	-2.78595800	1.34602400	0.61584700
C	-4.18540800	-1.36666700	-1.76701600
H	-2.14186700	-1.75255800	-2.29835500
C	-5.05660900	-0.59446400	-0.99961100
H	-5.21685600	0.99075500	0.45010700
H	-4.57490700	-2.12514300	-2.43879600
H	-6.12858200	-0.74999400	-1.07000700
C	2.47049400	-0.87865800	-0.21619300
C	3.06795300	-1.53062700	-1.30065400
C	2.89263000	0.41334700	0.11350600
C	4.05412200	-0.89549600	-2.05278700
H	2.75072500	-2.53733200	-1.55816000
C	3.87831900	1.04975200	-0.63830000
H	2.44297000	0.92405500	0.95936900
C	4.45840400	0.39901100	-1.72611800
H	4.50344800	-1.40932500	-2.89692800

H 4.19012000 2.05565400 -0.37445500

H 5.22370100 0.89560100 -2.31431500

57

Me₃Si-PPh₂(*o*-biphenyl)⁺. Gibbs free energy: -1675.767643

P 0.61684100 0.02061400 0.06160200

C 0.43753700 1.64953200 -0.71387700

C 0.29939500 1.74332500 -2.10329500

C 0.48133700 2.81032500 0.06472200

C 0.19001500 2.99297200 -2.70451200

H 0.26583300 0.84662300 -2.71446700

C 0.37212900 4.05771200 -0.54328100

H 0.60843600 2.75696800 1.14093700

C 0.22203100 4.14914600 -1.92558400

H 0.07520000 3.06295500 -3.78072900

H 0.40238100 4.95550600 0.06443100

H 0.12978900 5.12185600 -2.39698000

C -0.13171300 -1.23064300 -1.03753400

C -1.52015200 -1.47576400 -1.08274800

C 0.73200000 -1.97376300 -1.85536100

C -1.98359900 -2.49538000 -1.92284600

C 0.24502800 -2.96916300 -2.69360800

H 1.79823800 -1.78063800 -1.83984300

C -1.11879300 -3.24014500 -2.71666900

H -3.05095000 -2.68800000 -1.96256600

H 0.93139800 -3.53035800 -3.31789900

H -1.51285700 -4.01959000 -3.36012400

C 2.40283900 -0.33508900 0.11908800

C 3.34039400 0.62263800 -0.27195900

C	2.83490000	-1.56477200	0.63539700
C	4.70221800	0.35133100	-0.14552400
H	3.02078300	1.57772500	-0.67473100
C	4.19328100	-1.82916900	0.75720500
H	2.11723700	-2.32455700	0.93021300
C	5.12910000	-0.86909500	0.36952800
H	5.42644700	1.09804100	-0.45255700
H	4.52113600	-2.78310800	1.15594500
H	6.18955600	-1.07484400	0.46999100
C	-2.55701000	-0.71131900	-0.32844700
C	-3.40143200	-1.38952700	0.56051200
C	-2.80697800	0.63893900	-0.59996500
C	-4.46471800	-0.73081600	1.17139800
H	-3.23031600	-2.44257000	0.76409100
C	-3.87368400	1.29699500	0.00942500
H	-2.19204300	1.17150700	-1.31687100
C	-4.70549800	0.61500500	0.89427000
H	-5.10805100	-1.27102700	1.85815400
H	-4.05723100	2.34231800	-0.21650000
H	-5.53832500	1.12703100	1.36505800
Si	-0.03613500	-0.05511900	2.31376100
C	-0.36212400	-1.86844400	2.63230700
H	0.56839100	-2.43813100	2.70154500
H	-0.88098400	-1.95768600	3.59301500
H	-0.99582400	-2.32129500	1.86598400
C	1.48508500	0.56403000	3.21224500
H	1.72058900	1.60469800	2.97099000
H	1.27527500	0.51048700	4.28672400

H	2.36716800	-0.04760800	3.00727200
C	-1.50510200	1.04880000	2.62062000
H	-1.42938700	2.01472900	2.11614900
H	-2.43766400	0.57164200	2.31699400
H	-1.54987700	1.23381300	3.70005500

34

P(*p*-F-Ph)₃. Gibbs free energy: -1333.536838

P	0.07264100	0.03480500	1.44101100
C	1.67836100	-0.16884600	0.56199700
C	2.02493000	0.51430100	-0.60873600
C	2.60240100	-1.06544000	1.11607500
C	3.25858100	0.30716700	-1.22260200
H	1.33094800	1.21863700	-1.05561900
C	3.83425400	-1.29717300	0.51113600
H	2.36067400	-1.59555500	2.03338900
C	4.13379200	-0.59993900	-0.64889200
H	3.53509200	0.83407500	-2.12887100
H	4.55149100	-1.99367500	0.93026200
C	-0.63407700	1.52244800	0.61595300
C	-0.38867500	2.76574600	1.21279500
C	-1.38969800	1.48040300	-0.56189900
C	-0.86378700	3.94520000	0.64538900
H	0.18077600	2.82038700	2.13653200
C	-1.88220200	2.64726600	-1.14094800
H	-1.59897200	0.52937900	-1.04147800
C	-1.60291500	3.85566000	-0.52315000
H	-0.67731700	4.91067800	1.10153900
H	-2.46697500	2.62350700	-2.05361700

C -0.94176900 -1.31217000 0.69828900
 C -0.56127100 -2.06772500 -0.41594300
 C -2.17593300 -1.58312000 1.30494800
 C -1.39188000 -3.06590900 -0.92275900
 H 0.39102200 -1.88393400 -0.90301200
 C -3.02586900 -2.56541600 0.80629600
 H -2.48545100 -1.01809300 2.18015100
 C -2.60919600 -3.28786100 -0.30110500
 H -1.10402700 -3.65702900 -1.78490500
 H -3.98393900 -2.77506800 1.26803700
 F 5.33305000 -0.81022700 -1.24066400
 F -2.07722900 4.99432000 -1.08044500
 F -3.42252000 -4.25342500 -0.79025400

47

Me3Si-P(p-F-Ph)3⁺. Gibbs free energy: -1742.521915

P -0.00202200 -0.00905100 0.39098700
 C 0.81721900 -1.48442200 -0.26543900
 C 1.73342100 -1.38749800 -1.31789500
 C 0.51758100 -2.73730800 0.28628200
 C 2.35143700 -2.52953000 -1.81530200
 H 1.97149800 -0.42533600 -1.75824200
 C 1.12638200 -3.88497000 -0.20307300
 H -0.20156700 -2.83504900 1.09333600
 C 2.03485200 -3.75189400 -1.24384700
 H 3.06662700 -2.47569500 -2.62738300
 H 0.90964500 -4.86137900 0.21317800
 C 0.88364500 1.44304000 -0.23146100
 C 2.15843500 1.72235000 0.27989600

C	0.32509400	2.27752300	-1.20437300
C	2.87250600	2.82314100	-0.17225300
H	2.61367300	1.07927500	1.02636500
C	1.02958800	3.38589300	-1.66332000
H	-0.65804000	2.07286200	-1.61403300
C	2.28659600	3.63304100	-1.13516000
H	3.85932600	3.05306400	0.21103400
H	0.61492200	4.04603000	-2.41580000
C	-1.69445900	0.03462900	-0.25244000
C	-2.11935200	-0.87565100	-1.22511000
C	-2.58777700	0.99472900	0.24265800
C	-3.42505300	-0.83236000	-1.70248000
H	-1.43962200	-1.62383400	-1.61807600
C	-3.89218400	1.05038400	-0.22886800
H	-2.27479600	1.71676800	0.99025200
C	-4.28165600	0.12991000	-1.19218900
H	-3.77317500	-1.53081100	-2.45406200
H	-4.59623700	1.78669900	0.13972300
F	2.63405900	-4.85860300	-1.71791000
F	2.97040400	4.70452100	-1.57499700
F	-5.54597900	0.17483100	-1.64858300
Si	-0.01465300	-0.01769500	2.72739400
C	-1.51612000	-1.02089800	3.20611600
H	-1.66175000	-0.91776700	4.28703900
H	-2.42234600	-0.66386000	2.70910800
H	-1.39216000	-2.08487500	2.98748100
C	1.59979300	-0.80971500	3.23393400
H	1.57867600	-0.95290300	4.32000300

H	1.74194500	-1.78865400	2.76820700
H	2.46311000	-0.18146200	2.99898300
C	-0.14029100	1.78207300	3.21050400
H	0.01287700	1.85397000	4.29293200
H	0.62389600	2.39250200	2.72149500
H	-1.12310700	2.20530400	2.98680200

52

P(1-naphthyl)₃. Gibbs free energy: -1496.522113

P	0.12963700	-0.74349000	0.12147700
C	0.53949400	0.05558500	-1.48797600
C	-0.16851500	1.24995600	-1.85801300
C	1.45383000	-0.48314600	-2.36655000
C	-1.11926600	1.87692000	-1.00525900
C	0.09967300	1.85325700	-3.12133100
C	1.70657200	0.11170000	-3.62611700
H	1.99976300	-1.38163700	-2.09653800
C	-1.76315800	3.02945100	-1.38250400
H	-1.34322100	1.43625900	-0.03877500
C	-0.58292000	3.04581000	-3.48553800
C	1.04708400	1.25419400	-3.99499500
H	2.43215000	-0.34324700	-4.29279700
C	-1.49273800	3.62469300	-2.63707100
H	-2.48539200	3.48692800	-0.71383800
H	-0.36855400	3.49444900	-4.45160500
H	1.24039700	1.71893700	-4.95773000
H	-2.00605300	4.53676500	-2.92419700
C	1.05877000	0.30217600	1.32423300
C	0.80844600	0.12710900	2.72789200

C	1.94878700	1.27126100	0.91568200
C	-0.08903300	-0.85328400	3.23595000
C	1.49527800	0.95608800	3.66311100
C	2.61992200	2.09874700	1.84676600
H	2.14949200	1.41070600	-0.14170200
C	-0.29208000	-1.00053300	4.58609600
H	-0.62935400	-1.49261800	2.54460900
C	1.26534600	0.77996000	5.05469200
C	2.40111300	1.94321900	3.19001100
H	3.31395800	2.85117300	1.48629400
C	0.39312800	-0.17627500	5.50965500
H	-0.98586900	-1.75280200	4.94777700
H	1.79731100	1.41888900	5.75417500
H	2.91771300	2.57071300	3.91095700
H	0.22554200	-0.30357900	6.57428800
C	1.13803600	-2.28706600	0.08464000
C	0.63326900	-3.42726300	-0.62974000
C	2.32096700	-2.40202000	0.78206300
C	-0.56945900	-3.39169000	-1.38907600
C	1.37057600	-4.64741100	-0.59817900
C	3.04418800	-3.61788700	0.81808900
H	2.71877500	-1.54767800	1.31982000
C	-1.01379600	-4.49807200	-2.07064800
H	-1.14886900	-2.47436900	-1.42981600
C	0.88498100	-5.77646300	-1.31193100
C	2.58027700	-4.71615000	0.14423100
H	3.97074800	-3.66866700	1.38089100
C	-0.27970800	-5.70699600	-2.03371600

H -1.93652700 -4.44590500 -2.63982000
 H 1.45589400 -6.70026400 -1.27626900
 H 3.13006700 -5.65296100 0.16559400
 H -0.64146700 -6.57538000 -2.57483900

65

Me3Si-P(1-naphthyl)3^+. Gibbs free energy: -1905.505543

P 0.27412700 -0.44818600 0.08555100
 C 0.59511400 0.13096200 -1.61429700
 C 0.03783800 1.35608300 -2.11256000
 C 1.36096900 -0.66562400 -2.44013000
 C -0.68421400 2.27664700 -1.30914100
 C 0.24035100 1.68030200 -3.48535000
 C 1.57695800 -0.32059400 -3.79171600
 H 1.80427500 -1.58108900 -2.06530400
 C -1.21554700 3.42449500 -1.84251000
 H -0.80045900 2.09550300 -0.24710800
 C -0.32334900 2.87340700 -4.01166600
 C 1.01349200 0.81695000 -4.30581000
 H 2.18100700 -0.97028700 -4.41487100
 C -1.04409100 3.72446100 -3.21321100
 H -1.76518900 4.10843200 -1.20431600
 H -0.16750800 3.10075000 -5.06200100
 H 1.15928500 1.07883400 -5.34953000
 H -1.47127700 4.63246700 -3.62498200
 C 1.17036000 0.65144300 1.23046500
 C 1.03593000 0.51418000 2.65285300
 C 1.94888300 1.66040700 0.70325900
 C 0.33065700 -0.54729800 3.27792300

C	1.66723400	1.48096700	3.48744500
C	2.58991300	2.59868700	1.54146900
H	2.07383400	1.75743200	-0.36926900
C	0.21808500	-0.62135800	4.64386900
H	-0.10314600	-1.33896200	2.67815400
C	1.52992600	1.38279200	4.89800200
C	2.43607300	2.52054100	2.90011700
H	3.19078700	3.38359000	1.09621200
C	0.81485600	0.36014800	5.46752200
H	-0.32393800	-1.44660100	5.09376100
H	2.01019800	2.13254700	5.51969400
H	2.91090500	3.24952900	3.55007500
H	0.71657100	0.29182700	6.54551200
C	0.99794600	-2.11527700	0.23591300
C	0.41971300	-3.24323100	-0.43687500
C	2.10418700	-2.28269600	1.04223700
C	-0.65815300	-3.14419300	-1.35527100
C	0.97694900	-4.53202200	-0.19435000
C	2.66242600	-3.56152200	1.25635800
H	2.56005300	-1.43131400	1.53504900
C	-1.18386500	-4.25882300	-1.95955100
H	-1.06259800	-2.17308100	-1.61620200
C	0.40983200	-5.66896300	-0.82990100
C	2.09938200	-4.66163000	0.66596400
H	3.52957600	-3.66023500	1.89951000
C	-0.65229800	-5.54029700	-1.68820900
H	-2.00580700	-4.15286200	-2.65987200
H	0.84141000	-6.64499400	-0.62930500

H	2.51418800	-5.65028300	0.83843800
H	-1.07760100	-6.41432600	-2.16948400
Si	-2.05204700	-0.46283700	0.58642400
C	-2.39274200	1.04878500	1.63817000
H	-3.32831300	0.85127800	2.17432200
H	-1.61778800	1.24065200	2.38423500
H	-2.54120400	1.94993800	1.03856700
C	-2.97241200	-0.40075300	-1.04402200
H	-3.95164900	0.04670900	-0.83871500
H	-2.48143000	0.21522500	-1.80111100
H	-3.14200800	-1.39965300	-1.45380700
C	-2.41120100	-2.04338900	1.52582300
H	-2.24928800	-1.92241900	2.59972500
H	-3.47335800	-2.26602000	1.37194000
H	-1.83900600	-2.90484800	1.17351400

34

PPh₂(C₆F₅). Gibbs free energy: -1531.94085

P	-0.82990300	0.18780100	-1.24479100
C	-1.65651000	1.49877500	-0.25755600
C	-1.15442300	2.05477600	0.92311900
C	-2.87107600	1.97904700	-0.76761000
C	-1.85605700	3.06095700	1.58514000
H	-0.21089900	1.71532200	1.33658800
C	-3.57957200	2.97355300	-0.09821800
H	-3.26923300	1.57167200	-1.69365700
C	-3.07119600	3.51880900	1.08008400
H	-1.44998100	3.48536600	2.49784400
H	-4.52075500	3.33031200	-0.50420600

H -3.61607600 4.30174500 1.59791400
 C 0.84796600 0.09220400 -0.46428300
 C 1.92907100 0.60676800 -1.18135700
 C 1.15582600 -0.48908600 0.76758000
 C 3.23762400 0.54315700 -0.72257500
 C 2.45479900 -0.57487300 1.24936100
 C 3.50109300 -0.05524700 0.50045000
 C -1.60748500 -1.36779900 -0.63732900
 C -2.66432200 -1.40445900 0.27610800
 C -1.14458000 -2.56785400 -1.19184000
 C -3.23767800 -2.62201800 0.63951600
 H -3.03713600 -0.48588400 0.71837800
 C -1.70557700 -3.78500500 -0.81403100
 H -0.33742700 -2.55587900 -1.92044000
 C -2.75683100 -3.81453800 0.10188600
 H -4.05573900 -2.63721400 1.35295100
 H -1.32781000 -4.70774700 -1.24306100
 H -3.20187400 -4.76133900 0.39090500
 F 1.73273300 1.19686900 -2.36648200
 F 4.23820300 1.04907800 -1.44540100
 F 4.74816100 -0.12524100 0.95630700
 F 0.19395300 -0.97727600 1.55685400
 F 2.70350800 -1.13858200 2.43294300

47

Me3Si-PPh2(C6F5)+. Gibbs free energy: -1940.919959

P 0.71532200 -0.10336600 -0.18042900
 C 1.27767600 -1.21814300 1.12991100
 C 0.42352700 -1.63755300 2.15295200

C	2.60568100	-1.66370000	1.09383600
C	0.89838000	-2.50551700	3.13320200
H	-0.60497900	-1.29500900	2.19654600
C	3.07243700	-2.52570700	2.07888000
H	3.28512900	-1.33675400	0.31255800
C	2.21758200	-2.95013000	3.09602500
H	0.23277600	-2.83214200	3.92456900
H	4.10098700	-2.86791800	2.04861100
H	2.58155800	-3.62902400	3.85981900
C	-1.08749500	0.08770000	0.02532300
C	-1.92908700	-0.92544400	-0.43790900
C	-1.70503200	1.18538700	0.63220700
C	-3.30826400	-0.85620000	-0.34667700
C	-3.08722500	1.28017900	0.73138300
C	-3.89042000	0.26104400	0.23898100
C	1.49197600	1.51750300	0.04488000
C	2.26791600	1.79126100	1.17298700
C	1.31370200	2.49096200	-0.94512800
C	2.86273100	3.04316100	1.30867100
H	2.40569100	1.04280000	1.94594500
C	1.90553500	3.73941700	-0.79852800
H	0.70807900	2.29019500	-1.82397100
C	2.68151000	4.01502800	0.32758000
H	3.46395200	3.25753800	2.18550100
H	1.76344600	4.49467300	-1.56368700
H	3.14593900	4.98905200	0.43904300
F	-1.39438600	-2.02442600	-0.97922800
F	-4.06805800	-1.84495600	-0.80411800

F	-5.20703300	0.34729600	0.33762500
F	-0.99693800	2.17925600	1.15948300
F	-3.64258400	2.34025900	1.30901300
Si	1.30147400	-0.92364300	-2.31345300
C	1.48735700	-2.77073600	-2.13988200
H	1.82358100	-3.15809000	-3.10854300
H	2.24364700	-3.03365900	-1.39580100
H	0.55167200	-3.26918400	-1.88098100
C	2.93402200	-0.08292700	-2.65771400
H	3.32557100	-0.50304400	-3.59125900
H	2.82369600	0.99552800	-2.79190100
H	3.67905800	-0.26156300	-1.87749400
C	-0.05485800	-0.37246000	-3.47172700
H	0.26124600	-0.61737100	-4.49200900
H	-0.99980500	-0.88666000	-3.28256400
H	-0.22661900	0.70652400	-3.43009700

43

P(*p*-CF₃-Ph)₃. Gibbs free energy: -2046.781507

P	-0.00747400	0.03033700	-1.85805300
C	1.63210400	-0.16787900	-1.03692300
C	1.83301600	-0.88535900	0.14690200
C	2.72980800	0.44782000	-1.64994900
C	3.10047600	-0.98120800	0.71152800
H	0.99903400	-1.37279400	0.64108900
C	3.99865900	0.36461200	-1.08682300
H	2.59706600	0.99714100	-2.57752400
C	4.17990300	-0.35034300	0.09568800
H	3.24077900	-1.53676900	1.63217300

H	4.83916200	0.85007000	-1.57023400
C	-0.98115100	-1.30794200	-1.04447400
C	-0.87916800	-2.58963100	-1.59999000
C	-1.79434700	-1.11981600	0.07682800
C	-1.55339100	-3.66586600	-1.03582100
H	-0.26362200	-2.75424600	-2.47983500
C	-2.48232500	-2.19041700	0.64061600
H	-1.89228800	-0.13721200	0.52621600
C	-2.35378800	-3.46240200	0.08778900
H	-1.45664500	-4.65378200	-1.47229600
H	-3.10482400	-2.03097300	1.51402300
C	-0.67077800	1.53342900	-1.02116700
C	-0.08489000	2.13452600	0.09693100
C	-1.83251800	2.09806900	-1.56283900
C	-0.64999500	3.27097700	0.66774900
H	0.81580100	1.71862300	0.53562600
C	-2.40991700	3.22563400	-0.99078900
H	-2.29612000	1.65326800	-2.43881800
C	-1.81481800	3.81040300	0.12632300
H	-0.18589000	3.72568400	1.53597200
H	-3.31323500	3.64722300	-1.41718700
C	-2.39577100	5.06693600	0.71242700
C	5.55838800	-0.49706800	0.67807600
C	-3.12498800	-4.61338900	0.67141100
F	-3.72621200	5.15870200	0.51869800
F	-1.85070900	6.17698400	0.15950200
F	-2.18355600	5.16043200	2.04050300
F	6.35035300	0.55693700	0.39863300

F	5.53859500	-0.63073900	2.01902500
F	6.19245900	-1.59164700	0.19379900
F	-2.48520600	-5.79009600	0.51813400
F	-4.33622600	-4.75781700	0.08214300
F	-3.35859800	-4.46073500	1.98986100

56

Me₃Si-P(*p*-CF₃-Ph)₃⁺. Gibbs free energy: -2455.760363

P	-0.01825700	0.02528800	0.93231700
C	1.07703900	1.31376600	0.27103600
C	0.67412400	2.13079500	-0.78921700
C	2.34991100	1.46250800	0.82939400
C	1.54408200	3.09429400	-1.28418200
H	-0.30773600	2.02042500	-1.23578300
C	3.22043500	2.42486900	0.33166900
H	2.68271400	0.82692200	1.64348200
C	2.81127600	3.23766300	-0.72153700
H	1.23174000	3.72827400	-2.10675100
H	4.20599200	2.53750400	0.76654200
C	-1.67721300	0.29547600	0.24399600
C	-2.41674500	1.40439100	0.67617400
C	-2.21454400	-0.58203700	-0.69703900
C	-3.68520200	1.63088600	0.16433800
H	-2.00998100	2.10291700	1.40015200
C	-3.49082100	-0.35618500	-1.20687400
H	-1.65265300	-1.44215800	-1.04301700
C	-4.21827300	0.74596300	-0.77472600
H	-4.25426300	2.49145000	0.49806500
H	-3.90542000	-1.04012600	-1.93730900

C	0.58142900	-1.57255900	0.31124600
C	1.52313700	-1.63280400	-0.71830800
C	0.06539000	-2.75108900	0.86089800
C	1.94496000	-2.86783500	-1.19804500
H	1.93038200	-0.72787600	-1.15524900
C	0.48453600	-3.98411800	0.37873600
H	-0.67442500	-2.72329700	1.65401600
C	1.42236900	-4.03663200	-0.65060800
H	2.67405700	-2.91128100	-1.99870900
H	0.07727700	-4.89396600	0.80338900
Si	-0.06987900	0.07230700	3.27511200
C	1.38032400	-0.97111000	3.81666900
H	1.31159300	-1.09975100	4.90262300
H	1.37133900	-1.96437300	3.36027700
H	2.33930200	-0.49362400	3.59871800
C	0.10581000	1.87687800	3.71855200
H	0.17474700	1.94867800	4.80977500
H	1.01326700	2.31682800	3.29638100
H	-0.75347200	2.47309800	3.40031200
C	-1.73038200	-0.65131700	3.72510400
H	-1.85867400	-0.54477700	4.80798900
H	-2.55405200	-0.12348400	3.23659400
H	-1.80479700	-1.71523600	3.48496800
C	1.91442200	-5.37258500	-1.14917300
C	3.73106500	4.29436000	-1.27969700
C	-5.60374000	1.01257400	-1.30673600
F	1.00518800	-6.34744100	-0.97112200
F	3.03426300	-5.75761800	-0.49935300

F 2.21625900 -5.34255100 -2.45995300
 F 4.92984700 4.30937900 -0.67528900
 F 3.95118000 4.11074000 -2.59788200
 F 3.20194300 5.52840100 -1.14543300
 F -5.68233500 2.22519100 -1.89310300
 F -6.52124600 1.00324100 -0.31717400
 F -5.99306200 0.10568300 -2.21689000

48

P('Bu)₂(*o*-biphenyl). Gibbs free energy: -1119.180476

P 0.54313800 0.86217000 -0.06196300
 C 0.32036400 1.79764500 1.57746400
 C 0.83455800 0.82081000 2.65243500
 C 1.24397700 3.02648600 1.55447900
 C -1.09761500 2.23297000 1.97062000
 H 0.22055500 -0.08503400 2.69822700
 H 1.87074700 0.52115800 2.46614200
 H 0.78956800 1.30408900 3.63614200
 H 0.87688800 3.80302300 0.87741100
 H 1.29394300 3.46435200 2.55869900
 H 2.26379300 2.76270500 1.25359400
 H -1.05138900 2.77293400 2.92490300
 H -1.55483100 2.89981500 1.23685100
 H -1.75762600 1.37369200 2.11436500
 C 0.08422600 1.96646600 -1.54524800
 C -1.01258600 3.02651900 -1.37452100
 C 1.38921700 2.68505100 -1.94657500
 C -0.30157000 1.01875000 -2.69529900
 H -1.98221400 2.59677500 -1.11412600

H	-0.75004400	3.76985400	-0.61771900
H	-1.14118900	3.55986000	-2.32489800
H	2.19174000	1.96825500	-2.14683800
H	1.21856500	3.26780700	-2.86022700
H	1.73728300	3.37612700	-1.17369000
H	-0.36218800	1.58858500	-3.63034400
H	0.44618700	0.22953400	-2.83507700
H	-1.27070700	0.54160600	-2.52673800
C	-0.80504900	-0.40964400	0.03554900
C	-0.45123000	-1.76458500	0.20418500
C	-2.17097300	-0.09125400	-0.01625300
C	-1.45312600	-2.73474900	0.34462100
C	0.96726200	-2.23701100	0.22457900
C	-3.15998600	-1.06098100	0.10405100
H	-2.47508600	0.93958100	-0.14915800
C	-2.79964500	-2.39294700	0.29557000
H	-1.16286900	-3.77253700	0.48139100
C	1.67754600	-2.39039200	-0.97050700
C	1.58639200	-2.58371900	1.42774600
H	-4.20626700	-0.77581300	0.05427800
H	-3.56043100	-3.16036300	0.39830700
C	2.98706000	-2.86342000	-0.96159500
H	1.19918000	-2.13177200	-1.91082000
C	2.89981000	-3.05273300	1.44024800
H	1.04181600	-2.47477500	2.36119800
C	3.60434400	-3.19172900	0.24588700
H	3.52509000	-2.97629900	-1.89782600
H	3.37125900	-3.30897700	2.38407400

H 4.62595000 -3.55887500 0.25442200

61

Me₃Si-P('Bu)₂(*o*-biphenyl)⁺. Gibbs free energy: -1528.152075

P -0.81597600 -0.29329000 0.13025100

C -0.95509900 -0.68286800 1.98030800

C -1.52824900 -2.08887900 2.21862100

C 0.41319800 -0.56342200 2.65853200

C -1.90360800 0.35138600 2.61161900

H -2.48858900 -2.24593300 1.72568800

H -0.84151400 -2.87875000 1.91198000

H -1.69286200 -2.20352500 3.29464000

H 1.15164500 -1.24833600 2.23906500

H 0.79628700 0.45801800 2.59857200

H 0.29234800 -0.80941300 3.71842400

H -1.89335600 0.20348100 3.69599200

H -1.59078700 1.38170800 2.42035300

H -2.93676800 0.22209200 2.28055200

C -0.11494100 -1.72880500 -0.89381000

C 0.29553800 -1.16036600 -2.26275700

C 1.07317500 -2.43697600 -0.22256100

C -1.20622400 -2.79002300 -1.13372100

H -0.55725100 -0.76653100 -2.81616200

H 1.04088400 -0.37418800 -2.18485300

H 0.72885300 -1.97329900 -2.85393600

H 0.77247700 -2.97613400 0.67744900

H 1.45934200 -3.17697200 -0.93093300

H 1.88907800 -1.76651500 0.02973500

H -0.74714300 -3.60312700 -1.70454000

H	-1.59619800	-3.22234400	-0.21125300
H	-2.03731700	-2.41492000	-1.73232400
Si	-3.03292100	0.10010600	-0.70046200
C	-3.85063200	1.68239500	-0.09223500
H	-3.56765400	2.55623300	-0.68471400
H	-4.92226600	1.51412700	-0.25577100
H	-3.71731700	1.90720500	0.96756800
C	-2.93444000	0.21049800	-2.56645900
H	-2.74495800	-0.74259900	-3.06426500
H	-3.91615300	0.56803900	-2.89932100
H	-2.19035200	0.94172600	-2.89530300
C	-4.12972700	-1.30169500	-0.10606400
H	-5.07296800	-1.18142000	-0.65291900
H	-3.76431700	-2.31052300	-0.29500500
H	-4.36119000	-1.20005100	0.95808300
C	0.18414700	1.27513500	-0.00517600
C	1.58688100	1.48576400	-0.09954500
C	-0.63489100	2.41495200	0.05586500
C	2.05805500	2.80530700	-0.16451200
C	2.69598100	0.47731500	-0.12854600
C	-0.14399700	3.71290900	0.00837500
H	-1.70093900	2.30008800	0.15560200
C	1.22182100	3.91301800	-0.11599100
H	3.12988500	2.95253700	-0.24897600
C	3.28348400	0.03093600	1.05938700
C	3.28230400	0.10810000	-1.34408800
H	-0.83412000	4.54767700	0.06149700
H	1.63978800	4.91246300	-0.16910800

C	4.36438700	-0.84750500	1.03136700
H	2.90180900	0.37665300	2.01238400
C	4.36037000	-0.77235400	-1.37581800
H	2.89943800	0.51787100	-2.27339600
C	4.89206200	-1.26969800	-0.18718600
H	4.79707700	-1.19578000	1.96362500
H	4.79028200	-1.06100200	-2.32942600
H	5.72779900	-1.96145200	-0.20992400

61

P(mesityl)₃. Gibbs free energy: -1389.393624

P	0.02086100	-0.00579600	0.98038200
C	-1.68706800	-0.37253900	0.39122500
C	-2.06039800	-1.27799400	-0.62830100
C	-2.70473900	0.27797200	1.13108900
C	-3.41691800	-1.52635100	-0.85528000
C	-4.04663100	0.01058800	0.85323200
C	-4.42754400	-0.90094700	-0.12774900
H	-3.69270400	-2.22234400	-1.64476600
H	-4.81369600	0.53205700	1.42158600
C	1.17833800	-1.29308700	0.34647000
C	1.12506800	-2.51758600	1.06001000
C	2.14188300	-1.14248000	-0.67460300
C	2.02334400	-3.53968800	0.75502600
C	3.03502900	-2.18935100	-0.92856300
C	3.00065600	-3.39165800	-0.22783200
H	1.95664100	-4.47810300	1.30136100
H	3.77262600	-2.06199600	-1.71815000
C	0.53569500	1.65280600	0.36071800

C	-0.09955600	2.42091400	-0.64118500
C	1.62602200	2.22023200	1.06585700
C	0.34371800	3.72502500	-0.88192500
C	2.04419200	3.51951000	0.77420300
C	1.40529900	4.29923300	-0.18689100
H	-0.15085900	4.30596200	-1.65762000
H	2.89250700	3.93197700	1.31598200
C	-5.87869300	-1.21247300	-0.38928300
H	-6.06099900	-1.38569100	-1.45366200
H	-6.18225400	-2.11845700	0.14702000
H	-6.52742000	-0.39790400	-0.05647500
C	3.99038100	-4.49319400	-0.50874000
H	4.46388400	-4.36365100	-1.48545600
H	4.78288400	-4.50247800	0.24750600
H	3.50706400	-5.47422900	-0.48717600
C	1.83397700	5.71898800	-0.45523300
H	1.27374600	6.41632300	0.17754400
H	2.89700600	5.86149300	-0.24281600
H	1.64971000	5.99819100	-1.49628100
C	2.39847500	1.44549900	2.10776400
H	1.73932800	1.06859500	2.89644000
H	2.89947400	0.57476400	1.66957500
H	3.16378800	2.07666600	2.56524200
C	-1.21145500	1.91039300	-1.52664700
H	-0.98332500	0.92372300	-1.93686500
H	-2.16070000	1.81830200	-0.99156300
H	-1.36212200	2.59587300	-2.36393400
C	2.24834000	0.07236400	-1.56537200

H 1.27141600 0.39221500 -1.93524700
 H 2.68551600 0.93027700 -1.04632700
 H 2.87785600 -0.15444800 -2.42922500
 C 0.08137800 -2.78390400 2.11911600
 H 0.07580000 -2.00070700 2.88363500
 H -0.92555100 -2.81353300 1.68707100
 H 0.26370500 -3.74522500 2.60505400
 C -1.07985500 -1.97155200 -1.54367900
 H -0.32980100 -1.27935200 -1.93346800
 H -0.53645400 -2.77412600 -1.03675100
 H -1.60880900 -2.40857000 -2.39391200
 C -2.39711700 1.31111700 2.18953400
 H -1.70428800 0.92383100 2.94322700
 H -1.92686500 2.20003700 1.75356900
 H -3.31365500 1.63103400 2.69056600

74

Me3Si-P(mesityl)3+. Gibbs free energy: -1798.364771

P 0.01379900 -0.00847800 0.96397600
 C -1.71265900 -0.36345900 0.43423300
 C -2.04016500 -1.34741700 -0.53242200
 C -2.75197900 0.36248900 1.06051200
 C -3.38532100 -1.65713700 -0.73525300
 C -4.07856300 0.01378300 0.81091600
 C -4.42032700 -1.01893300 -0.05521000
 H -3.63267800 -2.41340500 -1.47532600
 H -4.86439900 0.58448000 1.29966100
 C 1.17865900 -1.31382700 0.39276300
 C 1.08421900 -2.58766200 0.99931700

C	2.18067300	-1.08409100	-0.58355400
C	2.05403100	-3.55057600	0.72502400
C	3.12789900	-2.08330100	-0.81092000
C	3.10914600	-3.30845200	-0.14799900
H	1.96280000	-4.52504900	1.19834400
H	3.89638700	-1.90217600	-1.55772400
C	0.55117200	1.66319900	0.41292300
C	-0.16381900	2.42889600	-0.54312800
C	1.70413500	2.21388600	1.01657900
C	0.21838500	3.75368700	-0.75091600
C	2.04379100	3.54250700	0.76191600
C	1.29262200	4.34549500	-0.08838100
H	-0.33441900	4.34000000	-1.48027800
H	2.93503500	3.94795500	1.23437700
C	-5.85577400	-1.41406200	-0.27059800
H	-5.99990200	-1.87021200	-1.25295800
H	-6.16295900	-2.14623100	0.48385900
H	-6.52234800	-0.55227100	-0.18417200
C	4.17471200	-4.34349600	-0.38623600
H	4.63862800	-4.21981300	-1.36771700
H	4.96308700	-4.25371800	0.36884300
H	3.76554300	-5.35456800	-0.31673400
C	1.63785900	5.79267600	-0.31152600
H	1.03059100	6.43060100	0.33960000
H	2.68869800	5.99038400	-0.08729600
H	1.43899900	6.09155600	-1.34388600
C	2.67092200	1.43509600	1.87710500
H	2.54626300	0.35462000	1.81347300

H	3.69205700	1.64759600	1.54997700
H	2.60398500	1.73542200	2.92630500
C	-1.26830300	1.91322100	-1.43809900
H	-1.07716600	0.90054800	-1.79629000
H	-2.24276500	1.90647800	-0.94402300
H	-1.34677800	2.56093900	-2.31318700
C	2.27137200	0.12882800	-1.48225200
H	1.29436700	0.45224300	-1.84623300
H	2.73705600	0.98629000	-0.99134000
H	2.87753300	-0.12063200	-2.35517600
C	-0.05579200	-3.03428000	1.88486500
H	-0.94451800	-2.40766900	1.81720200
H	-0.36537700	-4.03911400	1.58594300
H	0.25149200	-3.09783800	2.93241400
C	-1.05725400	-2.04770900	-1.44323700
H	-0.28226400	-1.37554600	-1.81538700
H	-0.55529300	-2.88700900	-0.95623000
H	-1.59227100	-2.44166600	-2.30915500
C	-2.54273800	1.57033200	1.94396200
H	-1.55413800	2.01965800	1.85502600
H	-3.25995700	2.34543500	1.66248900
H	-2.72768400	1.33451500	2.99556500
Si	0.04329900	-0.02005500	3.37577900
C	1.59268200	-0.93075100	3.93749500
H	2.33111000	-0.22210000	4.32010000
H	1.31332000	-1.60321800	4.75537900
H	2.07399400	-1.53159500	3.16224300
C	0.06563900	1.76698100	3.96913500

H	-0.90783100	2.04240800	4.38195100
H	0.80756300	1.84936600	4.77029600
H	0.32417500	2.49834900	3.19978100
C	-1.50795000	-0.90649500	3.97007900
H	-1.25666600	-1.90107700	4.34617300
H	-1.93367100	-0.33045700	4.79830400
H	-2.28325300	-1.02097800	3.20865100

9

Me₂O. Gibbs free energy: -154.935743

O	0.72547000	-1.06192000	-0.40419400
C	1.70333000	-0.10030500	-0.73586000
H	2.63112800	-0.57942600	-1.08005700
H	1.91241400	0.47810600	0.16556700
H	1.34466500	0.57723000	-1.52403800
C	0.38632600	-1.88069700	-1.50210400
H	-0.36738100	-2.59190500	-1.16034500
H	-0.02723100	-1.28631500	-2.32946400
H	1.26255900	-2.43313700	-1.87075800

22

Me₃Si–OMe₂⁺. Gibbs free energy: -563.912567

O	0.47195100	-0.60735600	-0.98810300
C	1.82957400	-0.18617900	-0.65724400
H	2.25513500	-0.89075000	0.05839600
H	1.76618100	0.81374700	-0.23624900
Si	-0.91845600	-0.05828300	0.10699800
C	-2.42938600	-0.63988800	-0.79744100
H	-2.57133500	-1.72173000	-0.73336100
H	-3.29637800	-0.16624100	-0.32340900

H -2.42133600 -0.33502700 -1.84790200
 C -0.58518100 -0.91555700 1.71789400
 H 0.37788500 -0.62168600 2.14498600
 H -1.36559600 -0.63470100 2.43349800
 H -0.60842400 -2.00354800 1.60808700
 C -0.71681500 1.78583500 0.13258800
 H 0.10334500 2.11587700 0.77528100
 H -0.57229900 2.18954400 -0.87359000
 H -1.64092700 2.21573600 0.53469900
 H 2.39798500 -0.16734400 -1.58549800
 C 0.43231200 -1.92126200 -1.62220500
 H -0.57603300 -2.06988100 -1.99780900
 H 1.14107500 -1.90141000 -2.44817300
 H 0.70281100 -2.68063700 -0.88739700

12

MeOEt. Gibbs free energy: -194.220131

O 0.73498500 -1.04640800 -0.40249300
 C 1.71649800 -0.08288900 -0.74136300
 H 2.62110900 -0.59113300 -1.11022900
 H 1.34164900 0.55670800 -1.55569600
 C 0.39039000 -1.87339700 -1.49209100
 H -0.36286000 -2.58104700 -1.14185500
 H -0.02632900 -1.28621600 -2.32296600
 H 1.26368900 -2.43071100 -1.86031300
 C 2.03592400 0.74824700 0.48447500
 H 2.79380100 1.49822900 0.24076300
 H 1.14215500 1.26568500 0.84490300
 H 2.42171100 0.11674700 1.28994000

Me₃Si–OMeEt⁺. Gibbs free energy: -603.196623

O	0.81139900	-1.13332100	-0.12289000
C	2.21113600	-0.66040400	-0.12451900
H	2.69282800	-1.20701400	0.68353400
H	2.62461900	-1.00351800	-1.07344800
C	0.07763800	-0.86939800	-1.35349000
H	-0.85813100	-1.42097700	-1.29704700
H	-0.11002400	0.19988900	-1.44489500
H	0.67833900	-1.24222300	-2.18139800
C	2.30764800	0.83653400	0.05013500
H	3.36726300	1.10519900	0.06156100
H	1.83450500	1.37856600	-0.77119300
H	1.86832200	1.16134400	0.99639100
Si	-0.15441200	-1.43424400	1.41696800
C	-1.29417600	0.02653900	1.52609100
H	-1.85936100	-0.04344200	2.46197300
H	-0.74162600	0.97038500	1.53817500
H	-2.01541000	0.04948700	0.70443200
C	-0.98820200	-3.05611700	1.07665000
H	-0.25964800	-3.81873100	0.78800000
H	-1.47929700	-3.38897400	1.99775900
H	-1.75616500	-2.98612500	0.30188300
C	1.12861300	-1.51330300	2.75355500
H	0.59859300	-1.71469200	3.69158000
H	1.84210400	-2.32732600	2.59954100
H	1.67087400	-0.57265400	2.88153600

MeO*i*Pr. Gibbs free energy: -233.503718

O 0.66265800 -0.99753400 -0.46694800
C 1.65448200 -0.02837800 -0.80038400
H 2.54860000 -0.56189400 -1.16233200
C 0.43253900 -1.97037200 -1.46323200
H -0.24074900 -2.71506500 -1.03470600
H -0.04003200 -1.54524200 -2.35781400
H 1.36941300 -2.46353300 -1.75944900
C 1.99771100 0.70160200 0.48816000
H 2.78533200 1.43926000 0.30955900
H 1.11630100 1.22460900 0.87396900
H 2.34569700 -0.00250700 1.24873300
C 1.17417900 0.93095900 -1.88701500
H 0.96425400 0.41446400 -2.82758200
H 0.26431100 1.44537300 -1.56004000
H 1.94379400 1.68246300 -2.08774600

28

Me₃Si-OMe*i*Pr⁺. Gibbs free energy: -642.478167

O 0.77447500 -1.05268100 -0.36736600
C 1.79461400 0.02897900 -0.62468600
H 2.02283800 -0.11649600 -1.68120900
C 0.28320500 -1.65826900 -1.60087400
H -0.45265900 -2.41247200 -1.33525300
H -0.17021800 -0.88334400 -2.21947700
H 1.13042400 -2.12758400 -2.09824700
C 3.03305000 -0.25387900 0.19574500
H 3.82780700 0.40564800 -0.16281600
H 2.88596000 -0.05216100 1.25700100

H	3.35893300	-1.28736300	0.06189600
C	1.16513300	1.39043200	-0.42362100
H	0.25682900	1.50193900	-1.02018100
H	0.93757300	1.58999100	0.62601800
H	1.88163900	2.14605300	-0.75557100
Si	-0.28374000	-1.24864000	1.12658500
C	0.67951600	-0.63865000	2.59048800
H	0.94439900	0.41949900	2.54871200
H	0.01691900	-0.77341100	3.45425500
H	1.57777200	-1.23462900	2.76896800
C	-1.80895500	-0.26191400	0.74097500
H	-2.54908500	-0.44232900	1.52836100
H	-1.60423500	0.81143100	0.70929500
H	-2.25787100	-0.56210700	-0.21051500
C	-0.55496600	-3.08619000	1.20776500
H	0.38028000	-3.63444800	1.06204100
H	-0.92453300	-3.31844800	2.21275300
H	-1.29840800	-3.44939200	0.49388000

18

MeOtBu. Gibbs free energy: -272.785926

O	1.18053700	-1.34873500	-0.54432700
C	1.84542600	-0.07895200	-0.66962500
C	0.29183100	-1.72119900	-1.57641200
H	-0.06107200	-2.72484800	-1.33180300
H	-0.57553400	-1.05208300	-1.63579100
H	0.78130000	-1.75590500	-2.55768700
C	2.61029200	0.06427800	0.64414000
H	3.17462300	1.00126900	0.65893800

H	1.91576700	0.06267600	1.48956300
H	3.31238500	-0.76581900	0.76792200
C	0.83344800	1.06196500	-0.81840900
H	0.32277200	1.03368300	-1.78547200
H	0.08240100	1.01306900	-0.02365600
H	1.34867600	2.02431300	-0.74625700
C	2.82224300	-0.09468700	-1.85036000
H	3.39948900	0.83480700	-1.86808700
H	3.51991600	-0.93265000	-1.75677400
H	2.30388200	-0.17702900	-2.81014500

31

Me3Si-OMe. Gibbs free energy: -681.755246

O	0.88580900	-1.05008000	-0.39790000
C	1.84344000	0.12992400	-0.66410100
C	0.31615100	-1.65959100	-1.60026600
H	0.24189800	-2.72805800	-1.42259500
H	-0.65956600	-1.21858600	-1.80354800
H	0.99029900	-1.48403500	-2.43081400
C	2.31960300	0.64331100	0.68313100
H	2.98225100	1.48935300	0.48792300
H	1.50741000	1.01791500	1.30767100
H	2.89317100	-0.11005000	1.22459200
C	1.06467000	1.19121300	-1.42414800
H	0.70009100	0.82931100	-2.38760700
H	0.22081400	1.56121700	-0.83751900
H	1.73774300	2.02936600	-1.62132000
Si	-0.10770600	-1.32774300	1.14071700
C	1.08249500	-1.62580000	2.53771300

H 1.42875000 -0.71219000 3.02319300
 H 0.55097600 -2.22545200 3.28514300
 H 1.94843800 -2.20611900 2.20617100
 C -1.22403800 0.15188700 1.29331600
 H -1.95303400 -0.06294200 2.08287900
 H -0.70521500 1.07451100 1.56314100
 H -1.78211600 0.31891300 0.36711100
 C -1.07287600 -2.87737400 0.78250400
 H -0.42937500 -3.73915500 0.58456400
 H -1.63321500 -3.09362300 1.70009200
 H -1.79815000 -2.77017300 -0.02723800
 C 3.02461000 -0.43411800 -1.44332000
 H 3.80590500 0.32929100 -1.46290000
 H 3.42571100 -1.32105100 -0.94764100
 H 2.78917500 -0.67177000 -2.48176400

16

(MeOCH₂)₂. Gibbs free energy: -308.677374

O 0.74595200 -1.03375200 -0.40409800
 C 1.72352000 -0.07665100 -0.74711500
 H 2.63942400 -0.57021200 -1.10561900
 H 1.35633500 0.58316800 -1.54762200
 C 0.39701100 -1.86461600 -1.49107800
 H -0.35673600 -2.56808900 -1.13447900
 H -0.02017200 -1.27812500 -2.32142500
 H 1.26892500 -2.42431200 -1.85716600
 C 2.02933800 0.73971500 0.49476200
 H 1.11343400 1.23327500 0.85326600
 H 2.39652200 0.07989500 1.29526900

O	3.00690600	1.69681600	0.15174500
C	3.35584700	2.52767900	1.23872500
H	4.10959400	3.23115200	0.88212600
H	2.48393200	3.08737500	1.60481300
H	3.77303000	1.94118900	2.06907200

29

Me₃Si-(MeOCH₂)₂⁺. Gibbs free energy: -717.650333

O	0.80345200	-0.94572600	0.08032000
C	1.17054000	0.41379300	-0.30961000
H	1.40522800	0.38621000	-1.37424000
H	0.29514200	1.04146200	-0.15559600
C	1.42007000	-2.00089500	-0.71659200
H	1.28266900	-2.93926200	-0.18411000
H	0.92685300	-2.02780700	-1.68761200
H	2.48251400	-1.78256000	-0.80923500
C	2.35583900	0.87925600	0.51915800
H	2.08451800	0.92262100	1.58476100
H	3.19901900	0.18063200	0.41284100
O	2.68401000	2.15149600	0.02857400
C	3.77721400	2.74108400	0.71050700
H	3.94725200	3.71600600	0.25375000
H	3.55141200	2.87278600	1.77645300
H	4.68171400	2.12807200	0.60704200
Si	-0.44226500	-1.38005400	1.37418100
C	-1.14778900	0.25713500	1.88231400
H	-1.85877100	0.05995600	2.69281800
H	-0.39285800	0.94581200	2.27171100
H	-1.70001800	0.74198400	1.07285500

C 0.57770800 -2.21979200 2.67587400
 H 1.33570500 -1.54400800 3.08188000
 H -0.08228900 -2.52236200 3.49619300
 H 1.07193600 -3.11979200 2.29969900
 C -1.62413600 -2.48068000 0.46233400
 H -2.45718200 -2.72406000 1.13084800
 H -2.03298600 -1.97806400 -0.41875200
 H -1.16386900 -3.42281600 0.15268300.

13

1,2-epoxybutane. Gibbs free energy: -232.286417

C -2.40485300 0.81201800 -0.10539300
 C -1.01820000 0.58089200 -0.51412200
 H -3.07887400 1.36486600 -0.75551700
 H -2.87679600 0.11607100 0.58570600
 C -0.21538400 -0.59722300 -0.02823000
 H -0.70104200 1.00086200 -1.47002400
 C 1.26312000 -0.25389200 0.15755800
 H -0.64389400 -0.95523600 0.91469900
 H -0.32377600 -1.40686800 -0.75997800
 H 1.82632100 -1.12664900 0.49942200
 H 1.70891800 0.08768400 -0.78270200
 H 1.38731000 0.54105100 0.89941000
 O -1.33870700 1.58557000 0.45794400

26

$\text{Me}_3\text{Si}-1,2\text{-epoxybutane}^+$. Gibbs free energy: -641.265193

C -2.13738700 0.83714700 -1.50859300
 C -1.02839100 0.95187700 -0.56311600
 H -2.07135600 1.32261400 -2.47615200

H	-2.84016800	0.01687500	-1.41721700
C	-0.78596900	-0.03069400	0.53866800
H	-0.19035900	1.57603800	-0.86529000
C	-0.23082400	0.62727500	1.80109400
H	-1.71323500	-0.57067700	0.75141400
H	-0.07064400	-0.76018800	0.14138900
H	-0.02050200	-0.13108000	2.55802600
H	0.69920600	1.16446300	1.59228300
H	-0.95084900	1.33389200	2.22332700
O	-2.26922300	1.77367000	-0.37768600
Si	-2.43959300	3.59589600	-0.45666800
C	-4.25784300	3.77321300	-0.76311600
H	-4.50882200	4.83740700	-0.82609600
H	-4.55340800	3.30264600	-1.70529100
H	-4.83862400	3.33270000	0.05178100
C	-1.84616400	4.07879800	1.23095000
H	-0.78627900	3.84575300	1.36812600
H	-1.97168200	5.15929600	1.35884900
H	-2.42503700	3.57761900	2.01186900
C	-1.35316800	4.15956000	-1.85440600
H	-1.45259400	5.24834200	-1.93160000
H	-0.29576600	3.94157800	-1.68014600
H	-1.65338100	3.73967600	-2.81846400

16

Anisole. Gibbs free energy: -346.576098

C	-2.53858600	-1.37058600	0.12654600
C	-1.15826700	-1.48845100	0.31471300
C	-0.31201800	-0.43007600	0.01216300

C -0.83918300 0.76860600 -0.48562700
 C -2.21683200 0.89659300 -0.67959000
 C -3.05477900 -0.17846800 -0.36983500
 H -3.19863000 -2.19781800 0.36563600
 H -0.73772800 -2.41155200 0.70177300
 H 0.76060900 -0.51135800 0.15557100
 H -2.64838400 1.81217600 -1.06589800
 H -4.12418600 -0.06983300 -0.52263900
 O 0.06662600 1.74851700 -0.74859000
 C -0.40977300 2.98809500 -1.24711500
 H 0.47012600 3.61755500 -1.37377500
 H -0.90849000 2.86120300 -2.21439200
 H -1.09734200 3.46252500 -0.53803700

29

Me3Si-anisole+. Gibbs free energy: -755.543649

C -1.06700900 -2.30381000 0.65361300
 C -0.65474400 -1.34082300 1.57352300
 C -0.36868900 -0.04372600 1.15073200
 C -0.50586100 0.24005500 -0.19796300
 C -0.91822000 -0.68906900 -1.13761500
 C -1.20054200 -1.98005000 -0.69634900
 H -1.28538800 -3.31143300 0.99028800
 H -0.55226800 -1.59350600 2.62292500
 H -0.05001300 0.71875400 1.85291100
 H -1.01032000 -0.40964100 -2.18122900
 H -1.52251800 -2.73005000 -1.41004200
 O -0.20435000 1.55450400 -0.66209600
 C -1.28318400 2.53052500 -0.47489400

H	-0.97960600	3.43886800	-0.98890000
H	-2.17614100	2.10898600	-0.93181000
H	-1.41733300	2.70169500	0.59230300
Si	1.56508600	2.06268500	-0.92365500
C	1.42060500	3.37116500	-2.23002300
H	1.06142200	4.32470800	-1.83402800
H	2.42047200	3.54194000	-2.64433200
H	0.77103800	3.05196400	-3.05001500
C	2.34365200	0.47964800	-1.48772300
H	3.40009600	0.68033000	-1.69831100
H	2.29552800	-0.29987800	-0.72305200
H	1.87964200	0.10819400	-2.40548400
C	2.10783600	2.68040300	0.73872800
H	3.09318200	3.14769300	0.63461100
H	1.42066300	3.43835500	1.12700000
H	2.19504400	1.87067500	1.46813700

16

2-pentanone. Gibbs free energy: -271.616831

C	0.79015000	0.88019200	0.09040500
O	-0.00091100	-0.04900400	0.11725300
C	0.32014300	2.31475700	0.08712500
H	-0.74206000	2.37073200	0.32790000
H	0.90076000	2.91711700	0.79165400
H	0.48445900	2.73878500	-0.90977000
C	2.28732300	0.66384600	0.04565800
C	2.72849300	-0.78818600	-0.09459800
H	2.68771100	1.27812400	-0.77253200
C	4.25015200	-0.92440700	-0.12554600

H	2.31840000	-1.37127000	0.73654700
H	4.70027200	-0.53380700	0.79371000
H	4.54824000	-1.97208200	-0.22662100
H	4.67909600	-0.37134800	-0.96834800
H	2.70102300	1.10674700	0.96298200
H	2.29822300	-1.21019200	-1.00943300

29

Me₃Si–2-pentanone⁺. Gibbs free energy: -680.596455

C	0.83472900	0.90938000	0.01234800
O	0.06436400	-0.08229300	0.03350700
C	0.32437000	2.30121500	-0.05353200
H	-0.59377600	2.42652400	0.52161600
H	1.08092800	3.01132900	0.27883000
H	0.09965900	2.51382200	-1.10667000
C	2.29399400	0.65498100	0.02230100
C	2.72503100	-0.80461600	-0.06436300
H	2.72075000	1.26271800	-0.78878000
C	4.24671600	-0.93853300	-0.06051200
H	2.29864100	-1.35747600	0.77826300
H	4.53844600	-1.98997300	-0.12220100
H	4.69191000	-0.41573800	-0.91314200
H	4.67892600	-0.52161500	0.85482900
Si	-1.72970800	-0.34589200	0.04454900
C	-2.23189800	0.11305900	1.77310400
H	-2.10707800	1.17984900	1.97783100
H	-3.29123200	-0.12989500	1.90977200
H	-1.65693400	-0.45690300	2.50848800
C	-2.43780400	0.71549300	-1.30763900

H -1.87932500 0.59763500 -2.24119000
H -3.46502600 0.38215400 -1.49314300
H -2.47634200 1.77583700 -1.04648100
C -1.78393300 -2.16160500 -0.32256400
H -1.24843100 -2.73352200 0.44049800
H -2.82407000 -2.50312800 -0.33894500
H -1.33987200 -2.37609600 -1.29891300
H 2.66907500 1.13321800 0.94037700
H 2.31295900 -1.24944800 -0.97573900

15

Cyclohexenone. Gibbs free energy: -308.497558

C -3.25335900 -0.81927000 -1.21595400
C -1.72839000 -0.87484800 -1.11868000
C -1.13711600 0.48053000 -0.86534400
C -1.83186700 1.50905200 -0.35261000
C -3.23864000 1.36163400 0.06386300
C -3.84887700 -0.01921200 -0.05585400
H -0.08599300 0.62283100 -1.10692300
H -1.42035700 -1.54298100 -0.30117700
H -1.29504900 -1.29701000 -2.03080200
H -3.53319100 -0.34321300 -2.16320400
H -3.67247800 -1.82907300 -1.22800100
H -1.37586800 2.48212600 -0.19530100
H -3.64536400 -0.53297600 0.89480700
H -4.93323400 0.08567600 -0.14054900
O -3.86789700 2.30677400 0.52864700

28

Me₃Si-cyclohexenone⁺. Gibbs free energy: -717.484112

C	-3.46029700	-0.79391900	-1.11006500
C	-1.97734900	-1.02952200	-1.38919600
C	-1.17941200	0.22056900	-1.26868200
C	-1.58216500	1.31523900	-0.57790700
C	-2.80851400	1.27109300	0.15710100
C	-3.64919900	0.03911500	0.15688800
H	-0.20503800	0.24727200	-1.74952000
H	-1.55167500	-1.74979100	-0.67289100
H	-1.81779700	-1.46741300	-2.37825800
H	-3.90902700	-0.26911600	-1.95991900
H	-3.98345000	-1.74562700	-1.00230300
H	-0.95928000	2.19992300	-0.53250100
H	-3.33283900	-0.53142500	1.04386900
H	-4.69001200	0.32461100	0.32251400
O	-3.21445800	2.23289100	0.88323900
Si	-2.58331000	3.85405300	1.30933500
C	-2.48611200	4.80084800	-0.28979400
H	-2.27192200	5.85100800	-0.06295600
H	-1.70105900	4.43865800	-0.95874100
H	-3.44255800	4.76221500	-0.81972300
C	-0.95444100	3.55933200	2.15978000
H	-1.05837100	2.81117100	2.95142700
H	-0.16611300	3.23689100	1.47456600
H	-0.62850900	4.49610100	2.62484600
C	-3.92066900	4.44990700	2.44828700
H	-3.67723300	5.45421600	2.81023400
H	-4.88390200	4.49866900	1.93224300
H	-4.02009000	3.79040300	3.31539400

17

Cyclohexeneoxide. Gibbs free energy: -309.662423

C -3.23922700 -0.37642200 -0.98305100
C -1.70478900 -0.36152500 -0.97550200
C -1.12076500 1.03015200 -0.82647800
C -1.95854400 2.17583500 -0.44112100
C -3.43800600 2.00631500 -0.19447700
C -3.82326800 0.55039500 0.08468300
H -1.32521300 -0.97454600 -0.14889100
H -1.32044500 -0.80725800 -1.89853500
H -3.59999900 -0.04927700 -1.96728800
H -3.59635400 -1.40118900 -0.83967200
H -1.64112900 3.17240400 -0.74805600
H -3.74241900 2.65850900 0.63215900
H -3.96258500 2.36289500 -1.09039700
H -3.45469600 0.25290200 1.07350700
H -4.91403000 0.46201200 0.10901300
H -0.20771900 1.23115600 -1.38528400
O -1.08004700 1.56361900 0.50934500

30

Me₃Si–cyclohexeneoxide⁺. Gibbs free energy: -718.646463

C -3.36269400 0.03531300 -1.36875800
C -2.01058800 -0.48965100 -0.86641700
C -1.10393200 0.60357400 -0.36264600
C -1.59432800 1.96976800 -0.13431500
C -3.02522400 2.33351000 -0.39458500
C -3.94358500 1.10847700 -0.44586900
H -2.14456000 -1.21020200 -0.05252700

H	-1.48111700	-1.01684200	-1.66450300
H	-3.23400300	0.46054500	-2.37130100
H	-4.05722900	-0.80285300	-1.46507700
H	-0.86345300	2.77338200	-0.12320200
H	-3.34999200	3.05786700	0.35782300
H	-3.03133700	2.85198300	-1.36108500
H	-4.08351100	0.70318700	0.56249900
H	-4.92761400	1.42123600	-0.80394700
H	-0.03348400	0.47084900	-0.48768800
O	-1.42788200	1.05196900	1.02906300
Si	-0.30860200	1.22146800	2.45187700
C	1.25201300	1.99140900	1.79928500
H	1.08857800	3.00241800	1.41556100
H	1.96650500	2.06715800	2.62665800
H	1.72247900	1.38486000	1.01988200
C	-1.31640700	2.31813400	3.55485800
H	-0.78578700	2.48321200	4.49826000
H	-1.48822200	3.29292800	3.08854800
H	-2.28284900	1.85977400	3.78225100
C	-0.13645700	-0.54704600	2.98143400
H	-1.11277300	-0.98814900	3.20071300
H	0.35559600	-1.14535500	2.20876900
H	0.47381600	-0.60022600	3.88909300

34

AsPh₃. Gibbs free energy: -2928.357134

As	0.14972600	-0.06685900	-1.18563600
C	0.95355900	1.45011800	-0.27266100
C	1.60475500	1.36746800	0.95930700

C	0.87938100	2.68818100	-0.91864600
C	2.15899600	2.50497200	1.54529500
H	1.68044500	0.41214200	1.47015000
C	1.42790000	3.82826500	-0.33516200
H	0.38881200	2.76835500	-1.88572000
C	2.06785200	3.73783600	0.90090600
H	2.65925700	2.42745900	2.50572700
H	1.35918700	4.78415800	-0.84513200
H	2.50009400	4.62365000	1.35574100
C	0.89467400	-1.52934900	-0.14341200
C	2.09205600	-2.08178800	-0.60854300
C	0.30656500	-2.05911300	1.00670900
C	2.70242100	-3.13290900	0.07215600
H	2.55560400	-1.69003500	-1.51068800
C	0.91231100	-3.11333700	1.68990500
H	-0.62748100	-1.64748900	1.37812600
C	2.11270800	-3.64967000	1.22551800
H	3.63247700	-3.55167700	-0.29961800
H	0.44716500	-3.51470100	2.58511400
H	2.58279100	-4.47234500	1.75537000
C	-1.64942500	0.00144800	-0.45259100
C	-2.62260100	-0.77134800	-1.09409700
C	-2.01965600	0.78138700	0.64420100
C	-3.93844400	-0.78122700	-0.63644200
H	-2.35438100	-1.37320500	-1.95924200
C	-3.33651100	0.77840000	1.10309600
H	-1.27903200	1.39459600	1.14914700
C	-4.29722800	-0.00566900	0.46598500

H -4.68280200 -1.38854700 -1.14216600
 H -3.61127900 1.38739300 1.95900500
 H -5.32262000 -0.00736600 0.82251200

47

Me3Si-AsPh3+. Gibbs free energy: -3337.348791

As 0.14654600 -0.06186600 -1.03360700
 C 1.01156200 1.47239900 -0.29626200
 C 1.81571300 1.36400100 0.83779100
 C 0.82554500 2.71260000 -0.91106100
 C 2.42939800 2.50049800 1.35969400
 H 1.96602800 0.40182500 1.31719900
 C 1.43570300 3.84663100 -0.38569800
 H 0.19963800 2.80738100 -1.79322500
 C 2.23952000 3.73863000 0.74894900
 H 3.05339100 2.41789400 2.24311100
 H 1.28681800 4.80963700 -0.86186100
 H 2.71871300 4.62206700 1.15764400
 C 0.90087900 -1.59380200 -0.18007100
 C 2.10507900 -2.11389400 -0.65847000
 C 0.26427500 -2.18402100 0.91175800
 C 2.67544800 -3.22326700 -0.04288700
 H 2.60881200 -1.66166000 -1.50701100
 C 0.83730300 -3.29463300 1.52687700
 H -0.67308800 -1.78376600 1.28550400
 C 2.03943400 -3.81345300 1.04880400
 H 3.60969700 -3.62769100 -0.41703800
 H 0.34489700 -3.75338700 2.37756900
 H 2.48132600 -4.68174600 1.52625200

C	-1.68657300	0.02129400	-0.50276200
C	-2.58908400	-0.88764400	-1.06015900
C	-2.12331200	0.96661000	0.42434100
C	-3.92786300	-0.85480200	-0.68482600
H	-2.25793300	-1.63074600	-1.77943200
C	-3.46604600	1.00058300	0.79484400
H	-1.42581100	1.67504700	0.85986000
C	-4.36576200	0.09196700	0.24132900
H	-4.62708700	-1.56398300	-1.11449700
H	-3.80657600	1.73542500	1.51634400
H	-5.41128700	0.12199200	0.52977400
Si	0.37033400	-0.14861600	-3.43131600
C	0.08774800	-1.94324800	-3.86299200
H	0.32190400	-2.09190500	-4.92265200
H	0.72579800	-2.60951500	-3.27555200
H	-0.95478700	-2.23392700	-3.70685900
C	-0.96903900	0.99488200	-4.05133100
H	-0.74678200	2.04304800	-3.83388600
H	-1.04771300	0.88681200	-5.13844400
H	-1.94124600	0.74756100	-3.61490900
C	2.10543200	0.45671600	-3.76286900
H	2.23351500	0.58324700	-4.84324500
H	2.29235200	1.42202600	-3.28361100
H	2.86064400	-0.25400100	-3.41672400

17

Cyclohexanone. Gibbs free energy: -309.706092

C	-0.39931100	-0.26426700	-0.98912300
C	0.30095300	0.10249700	0.32086800

C	-0.12121300	1.49483000	0.79442000
C	-1.64730300	1.59596300	0.96256900
C	-2.38479800	1.12824300	-0.27281900
C	-1.92973800	-0.19466300	-0.84831900
H	0.36168700	1.74301400	1.74432700
H	0.04893800	-0.63889700	1.09092300
H	1.38679000	0.06673200	0.18612600
H	-0.07827200	0.42751200	-1.77807500
H	-0.11442900	-1.26986500	-1.31301000
H	-1.95982500	0.93802000	1.78567600
H	-2.25867200	-0.97462100	-0.14729700
H	-2.43696800	-0.36303000	-1.80125400
O	-3.30014100	1.77027100	-0.76488100
H	-1.96624200	2.61245600	1.20489800
H	0.21081600	2.24280600	0.06351400

30

Me₃Si–cyclohexanone⁺. Gibbs free energy: -718.687165

C	-0.73981600	-0.41447200	-0.98689700
C	0.36832900	0.06113200	-0.04889300
C	0.14506900	1.51324800	0.36853100
C	-1.23254300	1.70609400	1.04023300
C	-2.32136600	1.11108300	0.22236400
C	-2.13249200	-0.24841800	-0.34302600
H	0.91025800	1.84343000	1.07429400
H	0.40105800	-0.57959000	0.84121800
H	1.33742300	-0.03198000	-0.54675900
H	-0.70868800	0.15476400	-1.92242100
H	-0.60959000	-1.46747000	-1.24604000

H -1.24738600 1.15384200 1.99113000
 H -2.20924000 -0.93462100 0.51355600
 H -2.94772700 -0.47511300 -1.03120500
 O -3.41146600 1.69335600 -0.00666000
 Si -4.14173500 3.28819600 0.46594700
 C -3.04826100 4.58170900 -0.30085900
 H -3.55562300 5.54962900 -0.22264200
 H -2.07810000 4.67628100 0.19341500
 H -2.88464300 4.37535200 -1.36260400
 C -4.19854600 3.27010700 2.32371500
 H -4.65711400 2.34765700 2.69191400
 H -3.21263500 3.38173800 2.78209100
 H -4.81917400 4.10834100 2.65900800
 C -5.79959300 3.13098900 -0.34701200
 H -6.38123100 4.04155200 -0.16962100
 H -5.69458000 2.99901600 -1.42770900
 H -6.35926100 2.28348400 0.05862100
 H -1.42735800 2.75439000 1.26519800
 H 0.20666600 2.16940500 -0.50673300

20

Dabco. Gibbs free energy: -345.104723

C 1.19516200 0.77570100 -0.69421800
 C 1.19516200 -0.78253400 -0.68644400
 H 1.18729900 1.16876800 -1.71608400
 H 2.08154200 1.17640100 -0.19184400
 H 1.19989300 -1.18592300 -1.70428500
 H 2.07553100 -1.17795500 -0.16948000
 C -1.19516200 0.78253400 -0.68644400

H -2.07553100 1.17795500 -0.16948000
 H -1.19989300 1.18592300 -1.70428500
 C -1.19516200 -0.77570100 -0.69421800
 H -2.08154200 -1.17640100 -0.19184400
 H -1.18729900 -1.16876800 -1.71608400
 C -0.00668100 -0.77886800 1.38074900
 H -0.89679200 -1.16961600 1.88439900
 H 0.87064500 -1.18486900 1.89469700
 C 0.00668100 0.77886800 1.38074900
 H -0.87064500 1.18486900 1.89469700
 H 0.89679200 1.16961600 1.88439900
 N -0.00369700 -1.28398900 0.00029700
 N 0.00369700 1.28398900 0.00029700

33

Me3Si-Dabco+. Gibbs free energy: -754.108643

C -2.19326500 1.05646600 0.88067300
 C -0.65954700 0.93436300 1.05841400
 H -2.45641500 2.02286600 0.44444100
 H -2.68443500 0.98152200 1.85315400
 H -0.15788000 1.89790700 0.95351400
 H -0.39563100 0.50816800 2.02720500
 C -2.19195000 0.23431900 -1.35505800
 H -2.45541100 -0.62548200 -1.97529600
 H -2.68229000 1.11462700 -1.77620100
 C -0.65859800 0.44906700 -1.33633900
 H -0.15588700 -0.12307400 -2.11794700
 H -0.39581700 1.50163200 -1.44993200
 C -0.65891400 -1.38252500 0.28144000

H	-0.39336100	-2.00770100	-0.57196600
H	-0.15798100	-1.77241800	1.16903100
C	-2.19267500	-1.29106500	0.47441900
H	-2.68226700	-2.09561100	-0.07841400
H	-2.45736400	-1.39853300	1.52880400
N	-0.12397800	0.00023700	0.00151200
N	-2.69171900	-0.00020600	-0.00011500
Si	1.79003100	-0.00004400	-0.00019200
C	2.28961600	1.61705800	-0.77763800
H	3.37354500	1.72067000	-0.65751800
H	2.07027300	1.64680200	-1.84819300
H	1.82558000	2.48275200	-0.29665000
C	2.28758000	-1.48155700	-1.01317300
H	3.37169700	-1.43154600	-1.16213400
H	2.06534800	-2.42344600	-0.50447500
H	1.82330000	-1.49569000	-2.00332800
C	2.29509400	-0.13626800	1.78708500
H	3.37947700	-0.28963500	1.81251100
H	2.07624800	0.77474100	2.35047900
H	1.83466200	-0.98730400	2.29688200

19

Cis-2,5-Me₂-THF. Gibbs free energy: -310.882615

C	-1.18580600	0.17061900	0.48035800
O	0.07321300	0.86414700	0.51167500
C	1.15586800	-0.05843800	0.35424600
C	0.55256800	-1.21073100	-0.44250400
C	-0.85163800	-1.30015700	0.15753700
H	-1.64519100	0.25662500	1.47315000

H 1.45790000 -0.42495900 1.34912900
 H 0.50966900 -0.94219000 -1.50480700
 H 1.12482200 -2.13634600 -0.34304100
 H -1.58400300 -1.74410400 -0.52173300
 H -0.83400600 -1.89909300 1.07342700
 C -2.08629600 0.83270900 -0.55110900
 H -3.08374900 0.38234600 -0.52758500
 H -2.18603500 1.90259400 -0.34655700
 H -1.66991300 0.70837500 -1.55660700
 C 2.32532800 0.65045800 -0.29840700
 H 2.66091900 1.49325800 0.31261100
 H 3.16403200 -0.04268900 -0.41589400
 H 2.03971400 1.02624000 -1.28621900

32

Me3Si-Cis-2,5-Me2-THF+. Gibbs free energy: -719.867308

C 1.14484100 1.24371800 -0.21885900
 O 0.27974400 0.02259500 -0.11942200
 C 1.08238800 -1.24008700 -0.27663000
 C 2.51280300 -0.72627800 -0.30138800
 C 2.40243600 0.68708000 -0.86743400
 H 0.60961200 1.92571600 -0.87742500
 H 0.78576100 -1.63563000 -1.25067600
 H 2.92743200 -0.71571500 0.71095700
 H 3.13735500 -1.37588300 -0.91644300
 H 3.27036600 1.30390700 -0.62871700
 H 2.28265400 0.65958400 -1.95338000
 C 1.32194400 1.83306900 1.16340000
 H 1.90678000 2.75260800 1.07771300

H	0.35998300	2.08871700	1.61402900
H	1.84872200	1.14437100	1.82843800
C	0.77354500	-2.20591900	0.84343700
H	-0.23872600	-2.61034000	0.78812600
H	1.46723800	-3.04691200	0.75756300
H	0.92462500	-1.73233600	1.81683500
Si	-1.53619100	0.06494500	-0.09480000
C	-2.04077300	-1.26089100	-1.29493200
H	-1.80022900	-2.27115100	-0.95434500
H	-3.12803800	-1.20495600	-1.41840100
H	-1.58598300	-1.09883200	-2.27667800
C	-1.97458300	1.77292400	-0.68080200
H	-3.06860800	1.83897000	-0.68649900
H	-1.60516000	2.56012500	-0.01781700
H	-1.62736900	1.96460400	-1.69988600
C	-2.02009900	-0.23373900	1.67419400
H	-1.50397600	0.45906000	2.34538800
H	-3.09696000	-0.05996100	1.77711400
H	-1.81177200	-1.25519700	2.00075900

19

trans-2,5-Me₂-THF. Gibbs free energy: -310.882825

C	1.10702300	-0.12504700	-0.41885300
O	0.00003000	-0.93960300	0.00006300
C	-1.10701000	-0.12510600	0.41885700
C	-0.76246000	1.29309700	-0.04027400
C	0.76242600	1.29313400	0.04030100
H	1.14737500	-0.15339000	-1.51817800
H	-1.14745000	-0.15345200	1.51818300

H	-1.09300600	1.44280600	-1.07522700
H	-1.23560500	2.05478300	0.58417200
H	1.23548900	2.05483200	-0.58419600
H	1.09301000	1.44286900	1.07523300
C	2.39941100	-0.68659400	0.14342800
H	2.55778700	-1.71473900	-0.19428100
H	3.24874200	-0.08208300	-0.19133000
H	2.37405900	-0.67767500	1.23802900
C	-2.39940700	-0.68660500	-0.14349600
H	-2.55788400	-1.71474000	0.19418400
H	-3.24868700	-0.08200500	0.19122400
H	-2.37397400	-0.67766000	-1.23809400

32

Me₃Si–trans-2,5-Me₂-THF⁺. Gibbs free energy: -719.86168

C	1.20323600	1.08620700	0.46422000
O	0.32718100	0.01238100	-0.10495700
C	1.18734400	-1.19436100	-0.34957600
C	2.58795200	-0.60070000	-0.56311800
C	2.43714200	0.91530000	-0.39740000
H	1.38746600	0.78562300	1.49991800
H	0.77797300	-1.63376000	-1.25758800
H	3.27095900	-1.00474500	0.18781700
H	2.97684600	-0.86305500	-1.54738200
H	3.30696900	1.37083300	0.07867700
H	2.27283800	1.40638100	-1.36080800
C	0.55862300	2.44752800	0.40895500
H	-0.32124300	2.52512400	1.05004800
H	1.29669000	3.16117900	0.78502600

H	0.30357600	2.73028800	-0.61434500
C	1.10487600	-2.14313600	0.82786300
H	0.09882500	-2.53463800	0.98704600
H	1.76494600	-2.99088700	0.62446300
H	1.44972600	-1.65999600	1.74607300
Si	-1.49621500	-0.07791100	-0.07309300
C	-1.92496100	-0.10141800	1.73410400
H	-1.61242700	0.81538700	2.24217500
H	-3.01131000	-0.18922500	1.84245500
H	-1.46406000	-0.95386400	2.24118500
C	-1.88831500	-1.64544900	-0.99500200
H	-2.98144600	-1.72269400	-1.02391600
H	-1.53953200	-1.59775200	-2.03094400
H	-1.50904300	-2.55777300	-0.53102900
C	-2.13922800	1.38551100	-1.02286400
H	-1.58301500	1.53133900	-1.95333000
H	-3.17801400	1.15972800	-1.29040900
H	-2.13717500	2.31733200	-0.45526800

14

Dioxane: Gibbs free energy: -307.495603

C	-4.43416400	0.63680000	-1.26697300
C	-2.50230400	1.95243000	-1.26339400
C	-2.57763400	2.05816600	0.25110100
C	-4.50949300	0.74253600	0.24752200
H	-1.46305200	1.94874400	-1.59977800
H	-5.03451900	1.43640000	-1.72689400
H	-4.81190500	-0.33016800	-1.60691400
H	-1.97727800	1.25856600	0.71102100

H	-2.19989200	3.02513500	0.59104200
H	-3.98808100	-0.11030900	0.70810600
H	-5.54874500	0.74622300	0.58390600
H	-3.02371600	2.80527500	-1.72397900
O	-3.92430700	1.95828300	0.69389500
O	-3.08749000	0.73668300	-1.70976800

27

Me₃Si–dioxane⁺. Gibbs free energy: -716.469714

C	-4.13972800	0.00754800	-0.93702300
C	-2.29043500	1.35774600	-1.39597400
C	-2.59602600	2.25939800	-0.21815200
C	-4.52400000	0.85462600	0.25777200
H	-1.20977100	1.31317300	-1.53969000
H	-4.67118800	0.35070000	-1.83506300
H	-4.41505400	-1.02963700	-0.73924000
H	-2.11865700	1.91937400	0.70256700
H	-2.32866000	3.29700000	-0.41365300
H	-4.04502700	0.51577500	1.17817500
H	-5.60102500	0.91344600	0.39402900
H	-2.75479200	1.75621200	-2.30875000
O	-4.04396000	2.22788700	0.03746700
Si	-5.08556600	3.72409700	-0.23173300
C	-4.97180000	4.02599300	-2.05869800
H	-5.54445500	4.92749500	-2.30317000
H	-3.94132700	4.19261900	-2.38560800
H	-5.39406500	3.19206300	-2.62633900
C	-6.76243500	3.21331300	0.37115100
H	-6.74296000	2.85548800	1.40442200

H	-7.39849000	4.10565200	0.34374800
H	-7.22970600	2.45992900	-0.26871100
C	-4.24606500	4.99720200	0.82576400
H	-4.89235600	5.88069200	0.87308000
H	-4.09915900	4.63091100	1.84566000
H	-3.28324700	5.31779400	0.41902500
O	-2.74058900	0.03986000	-1.14870600

14

3-penten-2-one. Gibbs free energy: -270.408009

C	-1.08426100	0.14472000	0.00050500
O	-1.26483600	1.35733200	0.00035800
C	-2.24156000	-0.82228300	-0.00057500
H	-2.18527000	-1.46725000	-0.88416400
H	-2.18071900	-1.47665400	0.87566800
H	-3.19009000	-0.28494000	0.00440800
C	0.27215300	-0.45661300	0.00100600
C	1.38107300	0.29441200	-0.00052000
H	0.33675500	-1.54294000	0.00245700
C	2.77809900	-0.23000200	-0.00018800
H	1.25882900	1.37723000	-0.00220400
H	3.31901500	0.13640300	-0.87957900
H	3.32000700	0.14036000	0.87692400
H	2.80713700	-1.32227100	0.00226900

27

Me₃Si-3-penten-2one⁺. Gibbs free energy: -679.391541

C	0.85941200	0.88921800	0.00290600
O	0.07053300	-0.11060500	-0.01545100
C	0.32931800	2.27864400	-0.00489600

H	-0.51728000	2.37916400	0.67745700
H	1.10122100	3.00064000	0.25598500
H	-0.02814400	2.50132700	-1.01738500
C	2.27310500	0.65145800	0.00302800
C	2.78195300	-0.60242700	-0.00881000
H	2.92275400	1.51977700	0.01475900
C	4.22585800	-0.92712200	-0.00828000
H	2.08618000	-1.43962300	-0.01728800
H	4.45756700	-1.55129500	0.86229700
H	4.46137300	-1.53576900	-0.88879300
H	4.85766600	-0.03798600	0.00092800
Si	-1.69836600	-0.35804200	0.00519400
C	-2.20240000	-0.00950200	1.76142200
H	-2.07775300	1.04273100	2.03199700
H	-3.26151000	-0.26075700	1.88410600
H	-1.62575700	-0.62225600	2.46024300
C	-2.44749300	0.78006700	-1.26312700
H	-1.90585600	0.73312900	-2.21282700
H	-3.47452500	0.44788000	-1.45167700
H	-2.49256400	1.81987600	-0.92946400
C	-1.79176800	-2.14975600	-0.46863200
H	-1.24780900	-2.77475600	0.24548200
H	-2.83723400	-2.47493100	-0.48040300
H	-1.37337000	-2.31320200	-1.46619900

17

Methylbutyrate. Gibbs free energy: -346.823658

C	-0.75981700	2.15606200	-0.88017100
O	-0.04110900	2.55004600	-1.77726600

C -1.04061200 0.71247300 -0.54703400
 C -0.49014100 -0.27619200 -1.56997300
 H -0.60934400 0.52305100 0.44421100
 C -0.77582300 -1.72236100 -1.16869400
 H -0.93360400 -0.06757500 -2.54957900
 H -0.38672200 -2.42070500 -1.91513300
 H -0.30880400 -1.96280700 -0.20745900
 H -1.85226200 -1.90002800 -1.07087500
 C -1.18214400 4.38744500 -0.24139900
 H -1.49254900 4.68322400 -1.24533300
 H -1.79307100 4.88605700 0.50857800
 H -0.12761100 4.63050000 -0.09676600
 O -1.39965300 2.98442700 -0.04399200
 H -2.12374700 0.59602000 -0.42909700
 H 0.58860900 -0.12452500 -1.67776800

30

Me3Si-methylbutyrate^+. Gibbs free energy: -755.800841

C 0.15345800 1.74909000 -0.67012100
 O 1.19463900 1.47676100 -1.32843700
 C -1.02518400 0.84203600 -0.73052100
 C -0.89441400 -0.29464300 -1.74329700
 H -1.17352600 0.44718400 0.28421400
 C -2.14326900 -1.17347500 -1.74527100
 H -0.73247400 0.12914700 -2.73895600
 H -2.04432200 -1.97361000 -2.48289100
 H -2.30412500 -1.63545800 -0.76595900
 H -3.03677700 -0.59317500 -1.99729500
 C -0.96563500 3.24874800 0.83215300

H	-1.25619400	2.45719400	1.52153700
H	-0.61069400	4.11867300	1.37641800
H	-1.78287800	3.52081400	0.16498900
O	0.17604500	2.82369300	0.04334400
H	-1.90918400	1.45623300	-0.94134900
H	-0.01240400	-0.89532200	-1.50354800
Si	2.75320300	2.38322700	-1.45459100
C	2.30673000	4.02507000	-2.20274100
H	1.68637500	4.62396600	-1.53099600
H	3.22714400	4.58396700	-2.40422200
H	1.77924000	3.89396000	-3.15212100
C	3.69642000	1.25820800	-2.58892300
H	3.83050700	0.26939800	-2.14078300
H	3.18519500	1.14337100	-3.54903400
H	4.68786500	1.68211500	-2.77997900
C	3.43250500	2.46575400	0.27347500
H	4.43481300	2.90638300	0.23733200
H	2.81215800	3.08727100	0.92425300
H	3.52007500	1.46776100	0.71295000

15

Et₂O. Gibbs free energy: -233.504207

C	0.00000000	2.38240700	0.40661000
C	0.00000000	1.17994100	-0.51504100
H	-0.88827400	2.38049100	1.04530700
H	0.88827400	2.38049100	1.04530700
H	0.00000000	3.30553100	-0.18061700
H	0.88793800	1.19205000	-1.16655400
H	-0.88793800	1.19205000	-1.16655400

O	0.00000000	0.00000000	0.26842400
C	0.00000000	-1.17994100	-0.51504100
C	0.00000000	-2.38240700	0.40661000
H	0.88793800	-1.19205000	-1.16655400
H	-0.88793800	-1.19205000	-1.16655400
H	0.00000000	-3.30553100	-0.18061700
H	0.88827400	-2.38049100	1.04530700
H	-0.88827400	-2.38049100	1.04530700

28

Me₃Si–OEt₂⁺. Gibbs free energy: -642.48091

C	-1.64895900	1.93239500	-0.41326900
C	-1.26777800	1.16804200	0.83386100
H	-0.77270100	2.28163600	-0.96379200
H	-2.27050100	1.33415400	-1.08133900
H	-2.22005800	2.81298900	-0.10684800
H	-2.13894700	0.84274800	1.40267000
H	-0.61828200	1.74242900	1.49341400
O	-0.52280500	-0.06840700	0.52130900
C	-1.28127900	-1.33022500	0.62374100
C	-2.36935500	-1.43281900	-0.41819800
H	-1.66355800	-1.36330300	1.64505100
H	-0.53541300	-2.11459900	0.50654200
H	-2.82192900	-2.42413000	-0.33203200
H	-3.15862500	-0.69403000	-0.26410200
H	-1.96402800	-1.32550700	-1.42689600
Si	1.19560300	-0.06087200	-0.11329300
C	1.00264200	-0.28809800	-1.94507500
H	0.43191600	0.52729300	-2.39771600

H 1.99363400 -0.31065500 -2.41109200
 H 0.50591500 -1.23533700 -2.17575300
 C 1.86773500 1.58354100 0.42389800
 H 1.86099700 1.68706600 1.51267800
 H 2.91292900 1.62320600 0.09647300
 H 1.35437400 2.43845000 -0.02210000
 C 2.01487900 -1.48548300 0.75340200
 H 1.80931300 -1.47543100 1.82766700
 H 1.73488000 -2.45887400 0.34262400
 H 3.09678000 -1.37277100 0.62001700

9

EtOH. Gibbs free energy: -154.956083

C -2.51905900 0.69095900 -0.00003000
 C -1.00415000 0.70972000 -0.00001000
 H -2.90892300 1.71321600 -0.00001200
 H -2.89940200 0.17773000 -0.88832300
 H -2.89942400 0.17769000 0.88822900
 H -0.63123900 1.23678100 -0.88814800
 H -0.63126200 1.23674200 0.88816000
 O -0.53975800 -0.63931000 -0.00003500
 H 0.42200200 -0.63487900 -0.00002200

22

Me₃Si–ethanol⁺. Gibbs free energy: -563.934993

C -2.33831500 0.70586600 0.35393400
 C -1.00267500 0.64311300 -0.34103200
 H -2.76926200 1.69562800 0.18303900
 H -3.03327200 -0.03645600 -0.04761300
 H -2.22587600 0.55509600 1.42936100

H	-1.06928100	0.77220800	-1.42153500
H	-0.28936100	1.35461900	0.07266700
O	-0.38382500	-0.68180300	-0.10324000
H	-0.93944200	-1.40136200	-0.43880300
Si	1.43372600	-0.97712200	-0.00816300
C	2.09943200	-0.22605500	-1.56732400
H	1.92969400	0.85392800	-1.60473400
H	3.18082500	-0.39429000	-1.61208100
H	1.64881900	-0.68633400	-2.45130500
C	1.89283700	-0.09108100	1.55366100
H	1.32818600	-0.47708900	2.40662400
H	2.95827800	-0.25471700	1.74833300
H	1.73440100	0.98853900	1.47961600
C	1.48342300	-2.82776900	0.07646500
H	1.09253400	-3.28958900	-0.83476400
H	2.52620300	-3.14330500	0.18801400
H	0.92590100	-3.20487900	0.93849000

24

Hexylmethylether. Gibbs free energy: -351.339336

C	2.94307100	3.31051800	0.00000000
C	1.50710900	2.78755800	0.00000000
H	2.97144000	4.40460400	0.00000000
H	3.48671000	2.96060700	0.88469000
H	3.48671000	2.96060700	-0.88469000
C	1.43154200	1.26080600	0.00000000
H	0.97550100	3.17512300	0.87881200
H	0.97550100	3.17512300	-0.87881200
C	0.00000000	0.72464100	0.00000000

H	1.96354000	0.87225500	-0.87952200
H	1.96354000	0.87225500	0.87952200
H	-0.53075100	1.11317200	0.87994000
H	-0.53075100	1.11317200	-0.87994000
C	-0.06201800	-0.80290200	0.00000000
C	-1.48786100	-1.32330400	0.00000000
H	0.45852000	-1.19549200	0.88220500
H	0.45852000	-1.19549200	-0.88220500
H	-2.02870500	-0.95882800	0.88867500
H	-2.02870500	-0.95882800	-0.88867500
O	-1.46742900	-2.73857200	0.00000000
C	-2.76182800	-3.29920400	0.00000000
H	-2.64725300	-4.38451200	0.00000000
H	-3.32723400	-2.99692900	0.89322700
H	-3.32723400	-2.99692900	-0.89322700

37

Me₃Si–hexylmethylether⁺. Gibbs free energy: -760.313752

C	5.81281400	-0.61423200	-0.51376100
C	4.71219300	-0.00486100	0.35322700
H	6.79304000	-0.51744700	-0.03751900
H	5.62857400	-1.67976500	-0.68963000
H	5.86351900	-0.11866100	-1.48947500
C	3.32673400	-0.11930600	-0.28291700
H	4.70047300	-0.49952500	1.33283700
H	4.93515900	1.05302400	0.54201800
C	2.22191400	0.48146200	0.58593000
H	3.33362200	0.38177700	-1.26027400
H	3.10270500	-1.17718100	-0.47587600

H	2.20572600	-0.02983900	1.55711600
H	2.44850100	1.53615100	0.78779000
C	0.84187500	0.37592500	-0.06966600
C	-0.22307200	0.93612700	0.85011900
H	0.62643600	-0.67460800	-0.29514600
H	0.84406300	0.92065000	-1.02014100
H	-0.33651400	0.35530900	1.76495000
H	-0.03392000	1.97696800	1.11797500
O	-1.55914200	0.93749400	0.22182000
C	-1.84247200	2.11837100	-0.58363500
H	-2.83101200	1.99141500	-1.01879500
H	-1.83397400	2.98000700	0.08206400
H	-1.09014000	2.20604400	-1.36681900
Si	-2.53393900	-0.59832300	-0.04411400
C	-1.85847000	-1.77519900	1.22035500
H	-2.42064200	-2.71094900	1.12350000
H	-0.80224900	-2.01154400	1.06825800
H	-2.00404700	-1.40655000	2.23951300
C	-4.27587400	-0.05784700	0.29863600
H	-4.67411500	0.61698300	-0.46348700
H	-4.91141700	-0.95043800	0.31091000
H	-4.35352500	0.42432900	1.27714500
C	-2.19088500	-1.05617500	-1.80997200
H	-2.49752700	-0.26663900	-2.50217500
H	-1.13115500	-1.27133300	-1.97224300
H	-2.76184700	-1.95719400	-2.05934500

P	-0.03020800	-0.02892900	-0.88320200
C	0.59624600	1.57995600	-0.38508600
C	1.57460500	1.67833100	0.60865600
C	0.05492500	2.73097800	-0.97225800
C	2.01044400	2.93650700	1.01607000
H	1.99598200	0.78693200	1.06225500
C	0.49847700	3.98125600	-0.55776500
H	-0.70719100	2.65817200	-1.74245800
C	1.47394800	4.08313000	0.43499200
H	2.76943300	3.01737900	1.78624300
H	0.08359100	4.87529300	-1.00987600
H	1.81754000	5.06124200	0.75500200
C	1.06261300	-1.34239000	-0.32994500
C	2.28808200	-1.53009200	-0.98174500
C	0.70824100	-2.13230900	0.76785500
C	3.15971100	-2.51223100	-0.52561000
H	2.56442500	-0.91675500	-1.83429800
C	1.58980000	-3.11224600	1.21610000
H	-0.24397700	-1.98929800	1.26872400
C	2.81081600	-3.30025100	0.57202400
H	4.10959800	-2.66298500	-1.02643100
H	1.31967000	-3.72816000	2.06678700
H	3.49494900	-4.06504900	0.92419900
C	-1.69983600	-0.27758600	-0.27126800
C	-2.14630500	0.43500400	0.84620500
C	-2.52390800	-1.22283400	-0.89463700
C	-3.42409000	0.19460700	1.34271200
H	-1.50898100	1.17188000	1.32483200

C -3.79940400 -1.45245500 -0.39098800
 H -2.17804400 -1.77552700 -1.76297100
 C -4.24674200 -0.74564100 0.72564500
 H -3.77572900 0.74365400 2.20909100
 H -4.44427200 -2.17982600 -0.87159000
 H -5.24288300 -0.92719300 1.11510200
 H -0.07666000 -0.06756800 -2.28102400

24

Imine. Gibbs free energy: -656.954123

C -0.98208800 0.78832900 0.19999400
 O -1.64976800 -0.32016100 0.56880000
 N 0.20496300 0.70024100 -0.25387700
 C -1.77718600 2.05086000 0.39570700
 H -1.32553800 2.65975700 1.18578600
 H -1.77547700 2.65060300 -0.51905700
 H -2.80520600 1.81972000 0.67275500
 C 0.88385300 1.92938300 -0.63359800
 H 0.88187000 2.68118900 0.16687800
 H 1.92450400 1.70261300 -0.87517200
 H 0.42867700 2.38845700 -1.52152900
 Si -1.01658300 -1.91822000 0.47978500
 C 0.48650900 -2.09324100 1.58117500
 H 1.36109900 -1.60564800 1.14417700
 H 0.29814300 -1.65027400 2.56490900
 H 0.71362500 -3.15519000 1.72854200
 C -0.67075500 -2.38133500 -1.29999700
 H -0.47392300 -3.45705200 -1.37100700
 H -1.53485000 -2.15529700 -1.93376500

H 0.19585300 -1.84156500 -1.68934600
C -2.44247200 -2.92483800 1.15662700
H -3.35563000 -2.75829900 0.57600300
H -2.20427800 -3.99335300 1.11317000
H -2.64761400 -2.66679000 2.20079500

14

iPrCOOH. Gibbs free energy: -307.555966

C -1.42621900 1.07666800 -0.45056000
C -0.61558500 -0.22277300 -0.41303900
H -0.63536700 -0.68143000 -1.40505800
H -0.97173500 1.82341100 -1.10738700
H -2.42951000 0.86298500 -0.82777600
H -1.55617100 1.51784400 0.54542300
C -1.19867500 -1.22696900 0.59645200
H -0.64787600 -2.17078900 0.58099300
H -1.17328200 -0.82524200 1.61459000
H -2.24186900 -1.43285100 0.34218400
C 0.86133900 -0.01931200 -0.11396200
O 1.19503300 0.90727700 0.80365100
H 0.41898600 1.37763300 1.13420600
O 1.74392500 -0.67193200 -0.62746600

27

Me₃Si-iPrCOOH⁺. Gibbs free energy: -716.5369

C 3.48960100 -0.67226700 -0.23586100
C 2.33821400 0.31203700 -0.43567900
H 2.25282800 0.56538400 -1.49930100
H 3.35375000 -1.59791500 -0.80340200
H 4.40978300 -0.21085700 -0.59843900

H	3.64795000	-0.90485500	0.82326300
C	2.54288700	1.62238600	0.35048700
H	1.73124900	2.32874500	0.16917400
H	2.61453200	1.42510200	1.42339700
H	3.47879200	2.07771700	0.02176100
C	0.99458800	-0.25922500	-0.09260500
O	0.83764800	-1.42800100	0.44286900
H	1.67812000	-1.88949200	0.59375300
O	-0.03870200	0.41752600	-0.32282200
Si	-1.79040800	0.04980800	-0.01129900
C	-2.16123600	-1.44415800	-1.05096100
H	-3.23134400	-1.66636300	-0.97672300
H	-1.92805200	-1.26066500	-2.10376000
H	-1.60917600	-2.32453100	-0.71181900
C	-1.91503400	-0.21427100	1.82316600
H	-1.39214500	-1.11948600	2.14194200
H	-1.51363000	0.64187300	2.37299000
H	-2.97181400	-0.32193900	2.09070300
C	-2.56322200	1.62322500	-0.61465900
H	-2.19320000	2.48490200	-0.05169100
H	-2.35960000	1.78243800	-1.67734900
H	-3.64868500	1.57007400	-0.48000500

26

iPrCOO-SiMe₃. Gibbs free energy: -716.142184

C	-2.33954000	-1.14802900	0.41153900
C	-1.10950200	-0.73911100	-0.40877200
H	-1.27058800	-1.00795400	-1.45648300
H	-3.24425800	-0.64489800	0.05748100

H	-2.49555300	-2.22717100	0.32418800
H	-2.19798600	-0.90556400	1.46864700
C	0.15929100	-1.43598700	0.09968400
H	1.04024100	-1.14017700	-0.47796900
H	0.33801900	-1.19683100	1.15204600
H	0.04196200	-2.51973800	0.00908800
C	-0.93293800	0.76643100	-0.39912200
O	-0.74607000	1.27210900	0.81753400
O	-0.95699100	1.45775700	-1.40442800
Si	-0.52669900	2.96357700	1.13768400
C	-2.06163700	3.88293100	0.59958200
H	-2.95277000	3.47166700	1.08457900
H	-1.97956500	4.93865500	0.88067300
H	-2.19680100	3.82397100	-0.48357500
C	1.01785900	3.55039300	0.26573900
H	1.21857900	4.59538500	0.52662400
H	1.88617400	2.95424700	0.56461300
H	0.90430700	3.48111900	-0.81935500
C	-0.32557200	2.98174400	2.99439000
H	0.54573800	2.39455400	3.30160900
H	-0.18536700	4.00818100	3.35011600
H	-1.21085400	2.56930600	3.48869800

17

Lutidine. Gibbs free energy: -326.728259

C	1.15759400	0.26677100	-0.00615100
C	1.19845700	-1.12989600	-0.00850100
C	0.00000000	-1.83471800	0.00000000
C	-1.19845700	-1.12989600	0.00850100

C	-1.15759400	0.26677100	0.00615100
N	0.00000000	0.94372900	0.00000000
H	0.00000000	-2.92043700	0.00000000
H	2.15162500	-1.64786800	-0.01529100
H	-2.15162500	-1.64786800	0.01529100
C	-2.41647700	1.09177000	-0.00386600
H	-2.51595000	1.61585200	-0.95990100
H	-3.30419200	0.47232100	0.14165300
H	-2.38101200	1.84914800	0.78383800
C	2.41647700	1.09177000	0.00386600
H	2.38101200	1.84914700	-0.78383800
H	2.51595000	1.61585300	0.95990100
H	3.30419200	0.47232100	-0.14165300

30

Me₃Si-lutidine⁺. Gibbs free energy: -735.707285

C	-1.07369100	-1.18831000	0.07287300
C	-2.44661000	-1.19393700	-0.12720200
C	-3.13906300	-0.00252900	-0.26935600
C	-2.44460100	1.18618000	-0.11930500
C	-1.07137000	1.17581200	0.07989000
N	-0.37916700	-0.00678800	0.08535700
H	-4.20942500	-0.00104300	-0.44160300
H	-2.96366300	-2.14524600	-0.15012700
H	-2.95890100	2.13919800	-0.13585400
C	-0.38659100	2.48567000	0.34479200
H	-0.06720100	2.96677800	-0.58174500
H	-1.10079400	3.15131900	0.83122400
H	0.47291600	2.38573200	1.00659300

C	-0.38984700	-2.49859700	0.33527300
H	-0.00136000	-2.94462500	-0.58190400
H	0.42078900	-2.40684400	1.05870500
H	-1.12367600	-3.19023900	0.75057900
Si	1.54128400	0.00578500	-0.04461900
C	2.05810300	1.46784800	-1.09329100
H	1.37801500	1.63383500	-1.93446900
H	2.18213300	2.40243300	-0.54599600
H	3.03220900	1.20182900	-1.51696900
C	2.14438700	0.05049000	1.71741300
H	1.81479300	-0.82862900	2.27857900
H	3.23959200	0.05487100	1.71103800
H	1.80659800	0.94249900	2.25178200
C	2.12940900	-1.49353400	-0.99637300
H	2.20525600	-2.41096100	-0.41325400
H	1.52916300	-1.68238400	-1.89143000
H	3.13900000	-1.23655900	-1.33626900

15

Methylcrotonate. Gibbs free energy: -345.612744

C	0.67053400	0.70271600	0.17827600
O	0.60402600	1.91105500	0.32325100
C	-0.47473100	-0.21835600	0.03542300
C	-1.73277800	0.23397100	0.06543300
H	-0.24826600	-1.27272400	-0.09294700
C	-2.95100800	-0.61843900	-0.06424300
H	-1.88921600	1.30356700	0.19822300
H	-3.57939500	-0.51589800	0.82708100
H	-3.55635200	-0.28660300	-0.91473100

H	-2.70140700	-1.67337000	-0.19994300
C	3.02491100	0.82293800	0.26315600
H	3.03724300	1.33547300	1.22713100
H	3.84857900	0.11464800	0.19883800
H	3.08797900	1.55756700	-0.54198200
O	1.83443600	0.03782700	0.13080900

28

Me₃Si–methylcrotonate⁺. Gibbs free energy: -754.595585

C	0.79300100	0.44485500	-0.01770600
O	-0.06510000	-0.49512100	0.00621300
C	2.20431500	0.14758900	-0.03443200
C	2.63055800	-1.13071600	-0.02422700
H	2.90759000	0.97045300	-0.05395400
C	4.05543600	-1.54034200	-0.03734700
H	1.88804800	-1.92572100	-0.00431700
H	4.26610900	-2.15070300	0.84774200
H	4.24207900	-2.18302000	-0.90459600
H	4.73765800	-0.68934200	-0.06161800
C	1.16783600	2.82303400	-0.05262100
H	1.76510000	2.82381900	-0.96421500
H	0.47402800	3.65868100	-0.05322600
H	1.79095300	2.84655900	0.84125300
O	0.31777000	1.65010500	-0.02582900
Si	-1.85321700	-0.40435900	0.03354300
C	-2.29905500	0.49497600	1.59953000
H	-2.01923600	1.55060600	1.55380100
H	-3.38238800	0.43546100	1.75013900
H	-1.81426600	0.03698800	2.46691400

C -2.34834000 0.46490400 -1.53459200
 H -1.88039700 -0.00241900 -2.40629100
 H -3.43431500 0.39202500 -1.65744300
 H -2.07800200 1.52375700 -1.51321100
 C -2.27420600 -2.21268900 0.05730800
 H -1.85604700 -2.70199800 0.94189800
 H -3.36175300 -2.33832000 0.08181800
 H -1.89364700 -2.71726400 -0.83561800

17

Methyl-(E)-3-(oxiran-2-yl)acrylate. Gibbs free energy: -458.856373

C 0.64164800 0.57840200 0.17004600
 O 0.47917100 1.73911300 -0.15769100
 C -0.46294400 -0.29977500 0.63115400
 C -1.71172200 0.17542700 0.68911600
 H -0.25721000 -1.32412400 0.91966600
 C -2.86630900 -0.63911400 1.11100300
 H -1.91395400 1.20691800 0.40716100
 H -2.64620200 -1.61830100 1.53222100
 C 2.18215500 -1.27662800 0.46824700
 H 1.64369800 -1.97883900 -0.17205600
 H 3.25222000 -1.38801900 0.30409100
 H 1.95669000 -1.46196500 1.52083500
 O 1.88561100 0.07847500 0.10965000
 C -4.18475800 -0.43750800 0.48605400
 H -4.29794900 0.31655000 -0.28959100
 H -4.87716800 -1.27475500 0.44957800
 O -3.91086500 0.07058400 1.78646000

30

Me₃Si-Methyl-(E)-3-(oxiran-2-yl)acrylate⁺. Gibbs free E: -867.834248

C	1.11573100	0.09540700	0.33040900
O	1.62639600	1.10432300	-0.24926900
C	-0.28252600	-0.22072500	0.14150700
C	-1.04764500	0.55413300	-0.64857400
H	-0.69321300	-1.08488600	0.64789900
C	-2.46644700	0.28431100	-0.90999800
H	-0.62087400	1.42568200	-1.14021300
H	-2.96067900	-0.44914400	-0.27744800
C	1.46334800	-1.78228000	1.79600000
H	1.09903900	-2.52703500	1.08919000
H	2.35479000	-2.14321100	2.30044300
H	0.70112600	-1.50221800	2.52229200
O	1.90718900	-0.60343000	1.07784800
C	-2.99579400	0.50585500	-2.27326700
H	-2.32954100	0.85850700	-3.05679700
H	-3.84524100	-0.09428700	-2.58810700
O	-3.25122200	1.43244000	-1.23196300
Si	3.30363200	1.73980700	-0.18259600
C	3.15965000	3.16847100	-1.35944000
H	4.12456500	3.68040500	-1.43633700
H	2.87738900	2.82665700	-2.35966700
H	2.41693200	3.89310700	-1.01334000
C	4.40390600	0.36948000	-0.79159400
H	4.04844400	-0.02577700	-1.74792200
H	5.41305800	0.76665000	-0.94570700
H	4.46600700	-0.44996200	-0.07121300
C	3.57968300	2.23345000	1.58874800

H 4.55643100 2.72111800 1.67783500
H 2.81737000 2.94383600 1.92186800
H 3.57170800 1.36711100 2.25552800

18

MeOSiMe₃. Gibbs free energy: -524.251478

O 0.54167800 -0.83575200 -0.71575500
C 1.87647300 -0.57774100 -0.32141700
H 2.53944300 -1.20284400 -0.92478800
H 2.04078500 -0.81916400 0.73675600
Si -0.76303500 -0.09428400 0.04902300
C -2.26762100 -0.66150000 -0.90590400
H -2.37529600 -1.74998800 -0.85775100
H -3.17591500 -0.21289500 -0.48918400
H -2.19644800 -0.37002200 -1.95876200
C -0.84400200 -0.64917600 1.84145500
H 0.05827400 -0.36267200 2.39259900
H -1.70074700 -0.18452300 2.34239400
H -0.95837100 -1.73582300 1.91357900
C -0.56193500 1.77145500 -0.02663600
H 0.32073300 2.10325900 0.53078800
H -0.46287600 2.11819200 -1.06066300
H -1.43652700 2.26295400 0.41400300
H 2.14587000 0.47340300 -0.48577200

31

Me₃Si-MeOSiMe₃⁺. Gibbs free energy: -933.23013

O 0.03018600 0.24296400 0.49471700
C 0.08438400 1.58626000 1.08070800
H 0.57553300 1.51698000 2.04811800

H	-0.93372600	1.94390200	1.21829100
Si	-1.58119300	-0.18672400	-0.22910700
C	-1.45774600	-1.93073600	-0.85460200
H	-1.35265200	-2.65464800	-0.04321900
H	-2.41166800	-2.13375500	-1.35598900
H	-0.66720700	-2.09095200	-1.59099000
C	-2.78129000	-0.04811900	1.18514100
H	-3.02713900	0.98429100	1.44589100
H	-3.71215400	-0.54470100	0.89022800
H	-2.39781100	-0.55666700	2.07472500
C	-1.81052400	1.06738000	-1.58160500
H	-1.82699900	2.09168100	-1.19855300
H	-1.01976800	0.98798200	-2.33363900
H	-2.76916500	0.88304400	-2.07818700
Si	1.62987000	-0.57631900	0.17855500
C	2.86312900	0.33939800	1.22687200
H	2.64560100	0.25009400	2.29505400
H	3.83418700	-0.13780300	1.05037900
H	2.96478100	1.39574000	0.96684700
C	1.43112400	-2.33472500	0.74873500
H	0.82931100	-2.39126000	1.66072600
H	0.99298800	-2.98692600	-0.00862300
H	2.42902400	-2.72023400	0.98534000
C	1.91755500	-0.34440900	-1.64355100
H	2.89796200	-0.76169200	-1.89822800
H	1.17262700	-0.85317800	-2.26087100
H	1.92566900	0.71732900	-1.90786000
H	0.62240100	2.24915400	0.40391500

21

EtOSiMe₃. Gibbs free energy: -563.534775

O	0.57457800	-0.64272500	-0.80600900
C	1.86903500	-0.82368300	-0.25214800
C	2.60886900	0.48658500	-0.02205100
H	2.42758300	-1.44488500	-0.95961300
H	1.79907200	-1.38456200	0.69015900
H	3.63556200	0.28442300	0.29940200
H	2.64376500	1.07519000	-0.94377100
H	2.12686600	1.08842600	0.75486000
Si	-0.73655600	0.02487300	0.01129000
C	-2.25268300	-0.70326000	-0.81074100
H	-2.29026100	-1.78946000	-0.67944500
H	-3.16460600	-0.27518900	-0.38012700
H	-2.25388200	-0.48810300	-1.88461000
C	-0.64678900	-0.44093300	1.82872500
H	0.23320100	-0.00544300	2.31451100
H	-1.53400000	-0.06873900	2.35280800
H	-0.60689600	-1.52740600	1.96107800
C	-0.74908800	1.89440400	-0.17528800
H	0.11253400	2.35890000	0.31470900
H	-0.73204100	2.17837900	-1.23301500
H	-1.65780200	2.31336700	0.27208800

34

Me₃Si-EtOSiMe₃⁺. Gibbs free energy: -972.51417

O	0.00169400	0.36829100	0.26278600
C	-0.01697900	1.76768100	0.75843300
C	-0.38958100	2.74148300	-0.33424200

H	0.98166100	1.96516400	1.14824900
H	-0.70909700	1.78836000	1.59845400
H	-0.33053300	3.75249800	0.07786500
H	0.29711900	2.67400200	-1.17999500
H	-1.40865900	2.58652100	-0.69462800
Si	-1.59524500	-0.45535900	-0.03051400
C	-1.42211600	-2.19579000	0.60635000
H	-0.79299400	-2.24904400	1.49987600
H	-2.42415100	-2.53571200	0.89102900
H	-1.03796200	-2.88839500	-0.14448900
C	-2.84324500	0.48310800	0.98229600
H	-2.96510100	1.53072600	0.69782900
H	-3.80640500	-0.01334700	0.81523300
H	-2.62858300	0.42293100	2.05333500
C	-1.87717200	-0.32222200	-1.86320600
H	-1.98737000	0.71880800	-2.17892600
H	-1.06550900	-0.77341900	-2.43998500
H	-2.80228700	-0.85173300	-2.11632100
Si	1.67035200	-0.29678500	-0.00707700
C	2.38846800	-0.45220700	1.70065600
H	1.75311900	-1.07475000	2.33753800
H	3.36628400	-0.93977600	1.62034800
H	2.53911400	0.51305100	2.19152400
C	1.50789100	-1.93759600	-0.86494100
H	1.23795300	-2.74365000	-0.18037100
H	0.81478000	-1.93159400	-1.70947200
H	2.50231000	-2.16373000	-1.26749100
C	2.52404000	0.95223400	-1.09000000

H 3.53449900 0.57829500 -1.28991900
H 2.01302300 1.06134900 -2.05113000
H 2.62589400 1.93698000 -0.62663500

12

N-Me-acetamide. Gibbs free energy: -248.403202

C -0.95027000 0.84135200 0.07588500
O -1.44762700 -0.28383700 -0.03612400
N 0.35871000 1.01549200 0.35342400
C -1.78130800 2.09353800 -0.08922300
H -1.20609900 3.01567300 0.01472700
H -2.25082300 2.07482500 -1.07545600
H -2.57727700 2.08534800 0.65924600
C 1.26302400 -0.10329200 0.54241200
H 1.29482600 -0.73183700 -0.35184400
H 2.26120200 0.28714200 0.73882200
H 0.94767800 -0.72157300 1.38767000
H 0.72149200 1.95135600 0.43938400

25

Me₃Si-N-Me-acetamide⁺. Gibbs free energy: -657.395714

C -0.96924700 0.78713300 -0.11600300
O -1.43460800 -0.41378800 -0.15022800
N 0.33117000 0.90901700 -0.18424800
C -1.84971600 1.98109900 0.02637200
H -2.02847500 2.15603600 1.09239800
H -1.39154500 2.87276000 -0.39869500
H -2.80764000 1.80682800 -0.46125100
C 1.08300400 2.16232100 -0.15197600
H 0.79327200 2.75982900 0.71298300

H 2.13823500 1.91307100 -0.06831300
 H 0.92223700 2.72860500 -1.07134600
 Si -3.05554100 -1.11776600 -0.06946400
 C -3.89897000 -0.68454100 -1.67279500
 H -4.10206700 0.38526600 -1.77448300
 H -3.29757200 -1.00715700 -2.52794400
 H -4.85994800 -1.20840100 -1.72008400
 C -3.88827200 -0.41907500 1.44361600
 H -4.79879400 -0.99606500 1.63909200
 H -3.24309900 -0.50464500 2.32339600
 H -4.18057300 0.62736200 1.32196100
 C -2.65059800 -2.92352100 0.08141700
 H -2.09297300 -3.12732500 1.00021900
 H -3.57685700 -3.50698100 0.10858900
 H -2.05808100 -3.26574200 -0.77216800
 H 0.85027100 0.04209600 -0.26979200

20

N-Me-piperidine. Gibbs free energy: -290.994701

C -1.83445800 -1.04454200 -1.16133100
 C -0.30234300 -1.05530600 -1.13349400
 C 0.24587400 0.37566100 -1.15944200
 C -0.39281400 1.21143500 -0.04077000
 C -2.38277100 -0.14601400 -0.04290200
 H 1.33463100 0.37563800 -1.03458200
 H 0.03598200 -1.55052800 -0.21209200
 H 0.09609000 -1.63719300 -1.97160400
 H -2.18340000 -0.68158600 -2.13665200
 H -2.23269300 -2.05816900 -1.03970100

H	-0.07844200	0.79945000	0.92839300
H	-0.03930300	2.24744000	-0.08128400
H	-2.11880300	-0.59038300	0.92686900
H	-3.47610800	-0.09583000	-0.08807500
H	0.03881900	0.83442200	-2.13469100
N	-1.85720600	1.22105500	-0.05915500
C	-2.41241900	2.03401300	-1.13291800
H	-3.50116000	2.07459200	-1.02781600
H	-2.02599500	3.05432900	-1.04762100
H	-2.18622000	1.67259900	-2.14970100

33

Me₃Si-N-Me-piperidine⁺. Gibbs free energy: -699.997892

C	-1.77701300	-1.05242000	-1.03952500
C	-0.25256800	-0.95772000	-1.10162000
C	0.18847600	0.50238300	-1.20442700
C	-0.41713400	1.35903700	-0.09666400
C	-2.32425900	-0.19514700	0.09450900
H	1.27464100	0.58786400	-1.10994500
H	0.17437300	-1.40508000	-0.19527600
H	0.13042800	-1.52676500	-1.95245000
H	-2.22471500	-0.76501500	-1.99649400
H	-2.09374100	-2.08095300	-0.84581500
H	-0.02447300	1.03963600	0.87306400
H	-0.16899000	2.41183400	-0.23842400
H	-1.92752200	-0.561114300	1.04429300
H	-3.41452500	-0.23471900	0.13933300
H	-0.06649000	0.91018100	-2.18777900
N	-1.92462900	1.25923000	-0.01076300

C	-2.55590500	1.89074900	-1.21069400
H	-3.63050700	1.71407100	-1.18620300
H	-2.35728400	2.96279000	-1.20133200
H	-2.14836100	1.46674500	-2.12573300
Si	-2.53159200	2.19943100	1.55586400
C	-1.65022800	3.84136700	1.54003400
H	-2.09998000	4.45935100	2.32510800
H	-0.58549800	3.74147200	1.76707500
H	-1.76114900	4.38329800	0.59665700
C	-4.37656500	2.36773700	1.36283500
H	-4.87427000	1.41256400	1.17313400
H	-4.76967400	2.75726700	2.30858200
H	-4.65073400	3.07458900	0.57552100
C	-2.05872500	1.15717100	3.02615000
H	-2.22632400	1.76726500	3.92083200
H	-2.67615500	0.25988600	3.11966000
H	-1.00485800	0.86521300	3.02634400

20

N,N-dimethylaniline. Gibbs free energy: -365.980647

N	-1.56974000	-0.00002700	-0.17248500
C	-2.28549800	-1.23975800	0.06809200
H	-3.35492400	-1.06059800	-0.04420900
H	-2.00484600	-2.00243300	-0.66448400
H	-2.10505000	-1.64515200	1.07535100
C	-2.28568300	1.23969900	0.06745800
H	-2.00276400	2.00280700	-0.66374600
H	-3.35486000	1.06104300	-0.04790700
H	-2.10772300	1.64431000	1.07553000

C	-0.18633700	0.00008500	-0.07876600
C	0.54697400	1.20641500	-0.03590200
C	0.54695500	-1.20638100	-0.03623000
C	1.93758800	1.19669800	0.01846900
H	0.03671300	2.16164900	-0.04571700
C	1.93746800	-1.19673700	0.01809900
H	0.03647600	-2.16150300	-0.04648400
C	2.65167500	0.00000800	0.04309200
H	2.46533100	2.14578600	0.04732200
H	2.46529500	-2.14578400	0.04666600
H	3.73568500	-0.00010500	0.08920500

33

Me₃Si-N,N,-dimethylaniline⁺. Gibbs free energy: -774.966081

N	0.48150500	0.65197700	-0.66381100
C	0.77239900	0.40713300	-2.11754700
H	1.80344800	0.69430400	-2.31886000
H	0.64684600	-0.64136600	-2.36850000
H	0.09411200	1.01536700	-2.71751800
C	0.79343000	2.09689400	-0.40432400
H	0.79574200	2.30823600	0.66327300
H	1.78133100	2.31036700	-0.80677300
H	0.05285500	2.71942500	-0.90822800
C	-0.93082900	0.31770400	-0.33565200
C	-1.66800000	1.12086700	0.53346500
C	-1.50422300	-0.83879300	-0.86588700
C	-2.97452200	0.76686800	0.86286600
H	-1.25516500	2.01985300	0.97014600
C	-2.80981300	-1.18320700	-0.52930500

H	-0.95872300	-1.48723200	-1.53842900
C	-3.55152100	-0.38337200	0.33497100
H	-3.53805200	1.40287900	1.53664700
H	-3.24288600	-2.08293900	-0.95238100
H	-4.57052000	-0.65186400	0.59125300
Si	1.64023600	-0.43501800	0.46231300
C	0.97825500	-0.22387700	2.18743000
H	-0.00921600	-0.67837700	2.30078900
H	1.66733400	-0.73852300	2.86646400
H	0.92582100	0.82088200	2.50500800
C	3.34550200	0.27771500	0.22730900
H	3.45037800	1.27141800	0.66999200
H	4.04656000	-0.38824200	0.74276400
H	3.65116600	0.31945400	-0.82192000
C	1.51308400	-2.18887900	-0.14507400
H	2.23203300	-2.77130300	0.44281900
H	0.52547900	-2.62333000	0.02530200
H	1.78506000	-2.30691300	-1.19705900

13

THF. Gibbs free energy: -232.310676

C	1.12808200	0.47306800	0.16394000
O	-0.00483400	1.20061400	-0.29489000
C	-1.13650700	0.46194100	0.15038500
C	-0.76725400	-1.01877900	-0.04175300
C	0.78108700	-1.00627400	-0.05985100
H	1.99880100	0.81670000	-0.39759200
H	1.29122000	0.67895700	1.23272200
H	-1.32496700	0.68206100	1.21191900

H	-1.99981500	0.78485100	-0.43451400
H	-1.17010600	-1.63639700	0.76447700
H	-1.16549400	-1.39993900	-0.98517900
H	1.21475300	-1.64162600	0.71603500
H	1.16183500	-1.34926000	-1.02508000

26

Me₃Si-THF⁺. Gibbs free energy: -641.296209

C	1.27624500	-1.20386400	-0.22174900
O	0.45576800	0.03340700	-0.21402100
C	1.29670900	1.22730900	0.04272100
C	2.70100500	0.71568900	-0.20373300
C	2.63113300	-0.73725800	0.27447500
H	0.78593500	-1.92785700	0.42802800
H	1.28507900	-1.55303500	-1.25442900
H	0.96244300	1.99898300	-0.64760600
H	1.12691500	1.52469400	1.07932500
H	2.94263100	0.76571600	-1.26849000
H	3.43276800	1.30507200	0.35007300
H	3.43055400	-1.35452800	-0.13711000
H	2.67602700	-0.78852700	1.36536300
Si	-1.34653900	-0.00106400	0.02493700
C	-1.87276300	1.69720100	-0.50610400
H	-2.96680800	1.74293600	-0.47340900
H	-1.49069700	2.47620000	0.15946700
H	-1.55924300	1.91385200	-1.53132300
C	-1.56951000	-0.35034600	1.83521300
H	-2.64013600	-0.40198800	2.06080400
H	-1.12211800	-1.30611500	2.12328100

H	-1.13374800	0.44184700	2.45090200
C	-1.87893400	-1.37130100	-1.10726900
H	-2.97324200	-1.41909300	-1.10805300
H	-1.54841500	-1.18883100	-2.13376700
H	-1.50586700	-2.34626700	-0.78133700

16

Tetrahydropyran. Gibbs free energy: -271.594208

C	-4.10133100	-0.00164400	-1.23270900
C	-2.57012700	-0.02115200	-1.26184900
C	-2.02932600	1.41184800	-1.23123100
C	-2.64874500	2.18561000	-0.07159400
C	-4.59585500	0.85531000	-0.07162400
H	-0.93868900	1.41801100	-1.12776400
H	-2.19841400	-0.56627000	-0.38333600
H	-2.20575600	-0.55291200	-2.14647700
H	-4.48656600	0.41615500	-2.17112100
H	-4.50669300	-1.01448900	-1.13240100
H	-2.32048300	1.75019300	0.88706300
H	-2.35273300	3.23730100	-0.08847000
H	-4.30958200	0.39069600	0.88668200
H	-5.68311200	0.96218500	-0.08783400
H	-2.27379200	1.92223500	-2.17106500
O	-4.06920200	2.17467000	-0.12841800

29

Me₃Si–tetrahydropyran⁺. Gibbs free energy: -680.575023

C	-4.32672800	0.05958000	-0.98501900
C	-2.90656100	0.08321200	-1.55701800
C	-2.42489600	1.52418600	-1.74501000

C	-2.56728700	2.32040700	-0.46401800
C	-4.41105800	0.88321500	0.28241900
H	-1.37005600	1.55092600	-2.03424300
H	-2.22960300	-0.44424800	-0.87406800
H	-2.87733600	-0.44660300	-2.51207800
H	-5.04411300	0.44550200	-1.71782600
H	-4.63158900	-0.96179900	-0.73815800
H	-1.96669800	1.91922200	0.35557500
H	-2.33482300	3.37716800	-0.59014100
H	-3.74348400	0.51860200	1.06692400
H	-5.41920500	0.96746300	0.67953400
H	-2.99367000	2.01565000	-2.54162500
O	-3.96459900	2.26226700	0.00636400
Si	-5.04397000	3.73232800	-0.15301700
C	-4.86497000	4.24188400	-1.93034100
H	-5.49421600	5.12200000	-2.10281300
H	-3.83824300	4.51650300	-2.18856700
H	-5.20102700	3.44982000	-2.60571200
C	-6.74185300	3.12505400	0.28239400
H	-6.80756100	2.74777700	1.30656800
H	-7.41730900	3.98521400	0.20719300
H	-7.10518100	2.36260700	-0.41243000
C	-4.31582800	4.91732800	1.07503500
H	-4.88256800	5.85419800	1.04418100
H	-4.38048200	4.51242500	2.08891800
H	-3.27065600	5.15488500	0.85790400

C	0.05391700	-1.33954400	0.13640800
C	0.05348000	1.33964500	-0.13673200
C	-1.28006500	0.71357700	0.27455900
C	-1.28001800	-0.71379800	-0.27437100
H	0.34490700	-2.16966400	-0.50957400
H	0.02131800	-1.69372400	1.16972200
H	0.34470500	2.16994100	0.50890400
H	0.02083900	1.69323500	-1.17023100
H	-1.35886600	0.68912400	1.36739300
H	-2.11857000	1.30177200	-0.11007500
H	-2.11821900	-1.30225600	0.11049000
H	-1.35915000	-0.68932400	-1.36718400
S	1.30869700	0.00010100	0.00008600

26

Me₃Si–tetrahydrothiophene⁺. Gibbs free energy: -964.279144

C	1.47570000	1.36969300	-0.10904100
C	1.44313000	-1.32460100	-0.47333900
C	2.36699200	-0.80758000	0.62842700
C	2.75996300	0.62122400	0.25266700
H	1.63040700	2.21458600	-0.77859400
H	0.92930800	1.70192900	0.77505300
H	0.77002900	-2.12233500	-0.15700600
H	1.99083600	-1.65157800	-1.35759700
H	1.84969800	-0.81828500	1.59214800
H	3.23965700	-1.45964700	0.70891600
H	3.26049800	1.13471500	1.07670300
H	3.44038700	0.61440300	-0.60401500
S	0.44511200	0.13272900	-1.01646900

Si	-1.48855600	-0.00540300	0.16811000
C	-2.21130900	1.69280300	-0.07050600
H	-2.37605500	1.91218500	-1.12898300
H	-3.18036400	1.73087300	0.43886400
H	-1.57857000	2.47452700	0.35944800
C	-2.39572900	-1.37376700	-0.70711300
H	-1.87274500	-2.33091000	-0.62651400
H	-3.37842900	-1.49135300	-0.23731100
H	-2.55044900	-1.14221400	-1.76438200
C	-1.03153200	-0.40330800	1.92902400
H	-1.95945000	-0.42979400	2.51188600
H	-0.55748000	-1.38437500	2.02100500
H	-0.38256700	0.35247600	2.37962900

18

4H-chromene. Gibbs free energy: -422.746599

C	-3.61273600	-0.60064200	-0.04612800
C	-2.26015500	-0.89762800	-0.22761100
C	-1.28742900	0.10146300	-0.22877900
C	-1.66218500	1.42689800	-0.04504400
C	-3.00752500	1.75105900	0.13987900
C	-3.96329900	0.74020100	0.13736200
C	-4.66155000	-1.69106800	-0.04640800
H	-0.24844200	-0.17567000	-0.37399500
H	-0.90494300	2.20408800	-0.04545400
H	-3.30720400	2.78370800	0.28530000
H	-5.01235600	0.98607500	0.28179600
H	-5.40069600	-1.49865000	-0.83487000
C	-4.02853400	-3.03788100	-0.24508800

H -4.65498100 -3.92278200 -0.25859600
 C -2.71781200 -3.19670000 -0.40798400
 H -2.23120500 -4.15276000 -0.55378700
 O -1.79899900 -2.18016400 -0.41422600
 H -5.22068300 -1.67022800 0.89787700

31

Me₃Si-4H-chromene⁺. Gibbs free energy: -831.703501

C -3.01911500 -0.31914500 -0.28430400
 C -2.29638900 -0.77944900 -1.37534900
 C -1.86455000 0.02132300 -2.41771100
 C -2.12407300 1.38656600 -2.33395000
 C -2.81881800 1.89957800 -1.23910800
 C -3.27657400 1.05152400 -0.23401700
 C -3.55182400 -1.30086600 0.73101900
 H -1.34992800 -0.40632100 -3.26932600
 H -1.79203100 2.04325400 -3.13004200
 H -3.02172900 2.96307700 -1.17733800
 H -3.84695800 1.45012300 0.59906600
 H -4.49022600 -0.93126500 1.14968100
 C -3.76311800 -2.64176000 0.08595300
 H -4.54697100 -3.30111700 0.44056000
 C -3.04026100 -3.03820700 -0.94681100
 H -3.11135900 -3.94871800 -1.52230700
 O -1.99669200 -2.18161000 -1.44128800
 Si -0.24174400 -2.74481900 -0.99614800
 C 0.86206100 -1.77514700 -2.12048200
 H 0.84722700 -0.70379000 -1.90867700
 H 1.88251400 -2.13697200 -1.94706700

H 0.62575700 -1.94465300 -3.17424900
C -0.12431800 -2.30150700 0.79920000
H 0.88365800 -2.54807600 1.15032700
H -0.27914800 -1.23091800 0.96257800
H -0.83641200 -2.87091600 1.40280200
C -0.31815500 -4.55498900 -1.38138600
H 0.69778100 -4.95386500 -1.28135100
H -0.96147100 -5.10924900 -0.69397700
H -0.64450200 -4.73463400 -2.40976300
H -2.85604100 -1.40195600 1.57381000

20

Chroman. Gibbs free energy: -423.956906

C -3.62439300 -0.61558000 0.11476300
C -2.29107000 -0.96058800 -0.14806200
C -1.33047400 0.02484700 -0.39488300
C -1.68866800 1.36705300 -0.37136500
C -3.00914900 1.73359400 -0.10171700
C -3.95711900 0.74271800 0.13306700
C -4.66414900 -1.68773500 0.35160500
H -0.30945700 -0.28090300 -0.60022900
H -0.93662600 2.12643800 -0.56185700
H -3.29578300 2.78003900 -0.08108100
H -4.99045300 1.01874700 0.32970000
H -5.60150800 -1.40966500 -0.13984700
C -4.16488700 -3.03967900 -0.15610400
H -4.79545600 -3.85339400 0.21325600
H -4.18902500 -3.07191800 -1.25128000
C -2.73753000 -3.25254100 0.31667400

H -2.32715200 -4.20265500 -0.02802500
 H -2.68743700 -3.22482000 1.41379200
 O -1.85682500 -2.25372300 -0.20580900
 H -4.87974200 -1.75861700 1.42521300

33

Me3Si-chroman+. Gibbs free energy: -832.923016

C -3.32166000 -0.66294000 -0.36235400
 C -2.01733700 -0.83860800 0.08427400
 C -1.12181400 0.19971800 0.29113300
 C -1.52903100 1.49215300 -0.02013200
 C -2.81790200 1.71380500 -0.50538000
 C -3.70178700 0.65124400 -0.65625500
 C -4.31588000 -1.79985100 -0.44927400
 H -0.13725000 0.00407400 0.69766600
 H -0.84382400 2.31945500 0.12643900
 H -3.13983400 2.72055500 -0.74880100
 H -4.71339600 0.83289900 -1.00737400
 H -4.75238900 -1.83191800 -1.45111500
 C -3.71967000 -3.16690000 -0.08956400
 H -4.48844300 -3.82514500 0.32266600
 H -3.32240400 -3.66882300 -0.97702900
 C -2.61582600 -3.02338000 0.93154200
 H -2.12801100 -3.95884100 1.19192100
 H -2.92568400 -2.50525200 1.84008700
 O -1.55370600 -2.16477600 0.34946700
 Si -0.29939000 -2.86179700 -0.85997500
 C -0.93603800 -2.31761500 -2.51485400
 H -0.24472000 -2.68586700 -3.28110800

H -1.92661700 -2.72592100 -2.73253500
 H -0.97805800 -1.22807100 -2.59569700
 C 1.30924500 -2.09498600 -0.34784100
 H 2.11511000 -2.68849900 -0.79456100
 H 1.41683600 -1.06795000 -0.70394000
 H 1.44062300 -2.11943900 0.73754000
 C -0.36122300 -4.69034400 -0.55432200
 H 0.36888700 -5.14084900 -1.23699900
 H -0.05864400 -4.94969000 0.46410700
 H -1.33214400 -5.14160400 -0.77276000
 H -5.13523200 -1.56675600 0.23902400

20

Isochroman. Gibbs free energy: -423.949914

C -3.60001000 -0.57194200 0.09746600
 C -2.26161000 -0.91008400 -0.13232800
 C -1.32007800 0.09613900 -0.36510700
 C -1.69739800 1.43537800 -0.36703300
 C -3.03095400 1.77723600 -0.13497700
 C -3.97046500 0.77706000 0.09459600
 C -4.61551600 -1.66232700 0.35643700
 H -0.28141600 -0.17259400 -0.54298400
 H -0.95648700 2.20852900 -0.54514300
 H -3.33567100 2.81928200 -0.13552200
 H -5.01055200 1.03983200 0.27153900
 H -5.55622500 -1.43751200 -0.15747600
 C -4.08661900 -3.01534600 -0.10058400
 H -4.71186900 -3.83088600 0.26754100
 H -4.05753700 -3.06981800 -1.19987700

C	-1.83672500	-2.36374400	-0.16595700
H	-1.65493200	-2.66606400	-1.21040900
H	-0.90405700	-2.50191900	0.38680200
O	-2.78337600	-3.23493500	0.42060000
H	-4.83856300	-1.70803400	1.42923800

33

Me₃Si-isochroman⁺. Gibbs free energy: -832.927239

C	-3.13099100	-0.99031100	1.60123300
C	-1.93762800	-1.17173900	0.89550900
C	-0.73412900	-0.68067500	1.40704500
C	-0.71232900	-0.00345400	2.62070500
C	-1.89867500	0.17793500	3.33248800
C	-3.09490100	-0.31587000	2.82472700
C	-4.43758200	-1.54601700	1.07766900
H	0.18948900	-0.83426200	0.85585000
H	0.22528100	0.37510500	3.01365700
H	-1.88965100	0.70175600	4.28261100
H	-4.01902300	-0.17634300	3.37862200
H	-5.23435100	-0.80241000	1.17418300
C	-4.34296500	-1.93986300	-0.37899100
H	-5.16404700	-2.56792900	-0.71510700
H	-4.25206300	-1.08168000	-1.04665100
C	-1.92489500	-1.87488500	-0.43676500
H	-1.94233300	-1.18299400	-1.28219000
H	-1.06090700	-2.53090200	-0.54666700
O	-3.11021600	-2.71926300	-0.59074100
Si	-2.96742000	-4.52071000	-0.20178900
C	-2.16437000	-4.57007100	1.47131900

H -2.04949500 -5.61906200 1.76612000
 H -1.16957500 -4.11582700 1.47068200
 H -2.77562400 -4.07165900 2.22896800
 C -1.91967500 -5.14070100 -1.60004700
 H -1.78272900 -6.22067600 -1.47855600
 H -2.40964200 -4.96521000 -2.56169200
 H -0.92696100 -4.68330900 -1.62029100
 C -4.72147600 -5.12022600 -0.23555400
 H -5.20079100 -4.94506200 -1.20263700
 H -4.69166700 -6.20397000 -0.07508700
 H -5.33585100 -4.69026200 0.56004300
 H -4.74307700 -2.40944300 1.68049400

15

N,N-dimethylacetamide. Gibbs free energy: -287.669423

C -1.00726100 0.84669100 0.16022800
 O -1.59511900 -0.23631300 0.27323200
 N 0.34381800 0.92430400 0.04744700
 C -1.78784200 2.14551200 0.15344900
 H -1.53717300 2.76337200 1.02095300
 H -1.58722700 2.73159400 -0.74760600
 H -2.84840500 1.90088700 0.19256900
 C 1.07015400 2.16537800 -0.17237700
 H 0.54315200 3.01752000 0.25298400
 H 2.04273800 2.09414100 0.32069900
 H 1.23617100 2.34499700 -1.24135800
 C 1.14032000 -0.28817300 -0.04697500
 H 0.49653900 -1.15281200 0.09945000
 H 1.61590400 -0.35421300 -1.03216600

H 1.92223500 -0.28245700 0.71871400

28

Me₃Si-N,N-dimethylacetamide⁺. Gibbs free energy: -696.668878

C -0.21288200 0.45148200 0.20668500

O -0.23742800 -0.79264300 -0.13716800

N 0.51218200 1.26822800 -0.51723600

C -0.96540100 0.94358600 1.40109000

H -0.28541600 1.00245200 2.25697800

H -1.39232400 1.93112500 1.22856100

H -1.77118300 0.25593100 1.64874800

C 0.63582300 2.69292000 -0.18861600

H 0.75933400 2.83590100 0.88379300

H 1.52309800 3.07500400 -0.69032800

H -0.23941800 3.24175100 -0.54411400

C 1.23108400 0.81963700 -1.71243200

H 2.30517900 0.88956700 -1.52879100

H 0.96360500 -0.20579700 -1.94893000

H 0.96086500 1.47508200 -2.54208600

Si -0.99427500 -2.25741800 0.47889400

C -0.51902300 -2.41978100 2.27360200

H 0.55515700 -2.26271000 2.41149600

H -1.06064500 -1.72389700 2.91996800

H -0.75383500 -3.43580100 2.60937300

C -0.20770000 -3.54397300 -0.60606200

H -0.62248000 -4.52968900 -0.37080200

H -0.40075700 -3.33824300 -1.66311400

H 0.87433100 -3.58365000 -0.44959700

C -2.82659600 -2.08016400 0.19039500

H -3.03360100 -1.83769500 -0.85627800
H -3.31347800 -3.03538100 0.41610800
H -3.28826400 -1.31709800 0.82338000

19

N-acetyl-pyrrolidine. Gibbs free energy: -365.04442

C -1.90525400 0.95986600 0.16227400
C -2.26318600 3.16184300 -0.82106100
C -1.96419700 3.30483700 0.67277800
C -2.36996700 1.94057600 1.24087900
H -2.51865900 0.05811300 0.09979600
H -0.86465700 0.64988100 0.31634900
H -1.62009300 3.79134200 -1.44061300
H -3.30862700 3.41291400 -1.04106300
H -0.89210600 3.47058400 0.82271900
H -2.50444200 4.14023600 1.12251400
H -1.91733000 1.73000800 2.21186400
H -3.45807500 1.88721100 1.35299000
N -2.01618900 1.73756300 -1.07534700
C -1.90683800 1.15651400 -2.28622900
O -1.68222000 -0.05675600 -2.40512800
C -2.06445800 2.05705700 -3.49181200
H -2.99070500 2.63665700 -3.43993300
H -1.23262000 2.76587100 -3.55317700
H -2.07199300 1.44147700 -4.39062900

32

Me₃Si-N-acetyl-pyrrolidine⁺. Gibbs free energy: -774.043998

C -2.05936000 1.98297200 0.82640500
C -2.02938400 3.54976800 -1.05968900

C	-1.92140900	4.31167500	0.26126800
C	-2.55487900	3.35565200	1.27622000
H	-2.74441300	1.16477900	1.04969200
H	-1.07663000	1.74217200	1.24236100
H	-1.23526600	3.79579300	-1.76489500
H	-3.00115700	3.70534600	-1.53795000
H	-0.86911200	4.48575000	0.50506200
H	-2.42561600	5.27719800	0.20659800
H	-2.26441600	3.57028000	2.30535900
H	-3.64622400	3.40091800	1.21064100
N	-1.92556000	2.13500200	-0.63811100
C	-1.72056800	1.12293700	-1.43353500
O	-1.60665400	-0.03875600	-0.87459000
Si	-1.34438000	-1.67807700	-1.45312900
C	-1.09046800	-2.58101300	0.15061800
H	-0.92557900	-3.64587600	-0.04354000
H	-0.21738100	-2.19286600	0.68350400
H	-1.96660800	-2.48465800	0.79863300
C	0.17330700	-1.66481800	-2.53471700
H	0.46693800	-2.70092500	-2.73641000
H	0.00247700	-1.17597100	-3.49771600
H	1.01170700	-1.17098900	-2.03389800
C	-2.89878800	-2.18903600	-2.34585900
H	-2.85186700	-3.26461700	-2.54908600
H	-3.78327400	-2.00174400	-1.72968300
H	-3.02682800	-1.67813900	-3.30449300
C	-1.59166000	1.30214300	-2.90970400
H	-2.13187800	2.18065300	-3.25877200

H -0.53254300 1.41990300 -3.16003000
H -1.97541800 0.42485200 -3.42953700

14

Benzaldehyde. Gibbs free energy: -345.399467

C -0.32843800 -1.39166000 0.00167400
C 1.06576500 -1.38845600 0.00224300
C 1.75210800 -0.17703100 0.00181000
C 1.04437500 1.02911100 0.00078900
C -0.35644900 1.02135000 0.00022100
C -1.03947800 -0.18806300 0.00067200
H -0.86520300 -2.33510900 0.00201900
H 1.61301500 -2.32517100 0.00302400
H 2.83904600 -0.16436400 0.00226700
H -0.89218400 1.96522200 -0.00056600
H -2.12449600 -0.19960300 0.00023700
C 1.79884400 2.29905900 0.00032500
O 1.29198400 3.40672100 -0.00065300
H 2.90054500 2.19094100 0.00087600

27

Me₃Si–Benzaldehyde⁺. Gibbs free energy: -754.379844

C -0.43026400 -1.22261500 0.09573300
C 0.78682700 -1.31045600 -0.58207900
C 1.58384500 -0.18254700 -0.70172400
C 1.15465800 1.03490100 -0.13701500
C -0.07646200 1.11635500 0.54767200
C -0.86270500 -0.01521900 0.65933300
H -1.05386800 -2.10583000 0.18765000
H 1.10587100 -2.25230600 -1.01264200

H	2.53284800	-0.23322500	-1.22645600
H	-0.39239200	2.06087900	0.97647400
H	-1.81205500	0.03021500	1.18025700
C	1.99771600	2.17220500	-0.28681500
O	1.69462700	3.30200400	0.18521000
H	2.94088800	2.06410900	-0.83113400
Si	2.60669300	4.85791000	0.09068300
C	1.27450200	6.04126900	-0.42300200
H	1.69928700	7.04572300	-0.52244000
H	0.84345600	5.75771000	-1.38739000
H	0.47590600	6.08135300	0.32297400
C	3.93652100	4.59652300	-1.18265500
H	4.67085500	3.84407900	-0.88055800
H	3.52201700	4.32488000	-2.15824600
H	4.47268400	5.54400900	-1.30672200
C	3.22507500	5.06940900	1.82730300
H	3.74014000	6.03177200	1.91575600
H	2.39848400	5.06078700	2.54348000
H	3.93237800	4.27921800	2.09494300

23

Benzaldehyde dimethylacetal. Gibbs free energy: -500.322804

C	-0.48381100	-1.12231800	-0.03760200
C	0.25214100	-0.84128500	1.11577200
C	1.02977400	0.31068000	1.18397800
C	1.07452200	1.19307500	0.10153900
C	0.34142100	0.90835100	-1.04887200
C	-0.43873300	-0.24677800	-1.11985800
H	-1.08622100	-2.02383700	-0.09152100

H	0.22143600	-1.52477000	1.95864300
H	1.61023600	0.52821100	2.07526700
H	0.37969300	1.59005600	-1.89476100
H	-1.00412200	-0.46258800	-2.02102600
C	1.92357600	2.44372200	0.17956200
O	1.36095500	3.29825100	1.12254700
H	1.95762900	2.93869900	-0.80929300
C	1.95131400	4.59115200	1.15496600
H	1.91770800	5.05688200	0.16149500
H	1.35899900	5.18580000	1.85074300
H	2.98834500	4.54533200	1.49935000
O	3.24850300	2.16612900	0.58574700
C	4.01722700	1.50471600	-0.40182000
H	4.05471600	2.08857600	-1.33160200
H	5.02549200	1.40205100	0.00012500
H	3.61391200	0.50842300	-0.62291800

36

Me₃Si–Benzaldehyde dimethylacetal⁺. Gibbs free energy: -909.298812

C	0.60977500	-0.90888400	1.88999800
C	0.98507000	0.18436500	2.67081200
C	1.33242600	1.38916500	2.06721500
C	1.30970000	1.49874500	0.67468400
C	0.91732900	0.40896100	-0.10491900
C	0.57056800	-0.79498500	0.50149300
H	0.34054600	-1.84653800	2.36496400
H	1.00566800	0.09858800	3.75202900
H	1.61335200	2.24223000	2.67544200
H	0.86878400	0.49853100	-1.18652100

H	0.26426800	-1.63799200	-0.10853200
C	1.72002200	2.76273200	-0.01256400
O	1.50802500	3.85690100	0.74232200
H	1.32532300	2.84832300	-1.02742400
C	1.66362800	5.11293700	0.06886800
H	1.03285000	5.14243200	-0.82457700
H	1.34366900	5.87441700	0.77666300
H	2.71042700	5.27203800	-0.20313300
O	3.25003700	2.69772400	-0.31011700
C	4.09320900	2.65707900	0.87780000
H	3.67658000	3.35673300	1.59960500
H	4.11375400	1.64249800	1.27549400
H	5.08562900	2.98744200	0.57944000
Si	3.97803900	2.11856900	-1.88290800
C	4.37448800	0.32997100	-1.58281500
H	3.48138600	-0.24063100	-1.31267100
H	4.79040000	-0.10191800	-2.49944100
H	5.12000000	0.21076400	-0.79120000
C	2.66549400	2.42402100	-3.16127400
H	3.12658400	2.21872700	-4.13446700
H	1.79820800	1.76502600	-3.07259300
H	2.33146700	3.46561300	-3.17468000
C	5.46038500	3.21794900	-2.09798700
H	6.28895600	2.94227700	-1.44037300
H	5.81255900	3.11716100	-3.13048900
H	5.20520300	4.26865800	-1.93171000

C	-0.70961800	1.17550500	-0.03222200
C	0.12940700	2.43885900	0.12123000
C	-0.80036900	3.26623500	1.03608300
C	-2.19230300	2.87627500	0.52155100
C	-1.81453700	5.21362500	0.26561800
C	-2.54598800	4.04148500	-0.40350200
H	-0.59878500	0.52245300	0.84448900
H	-2.47402200	5.68666700	1.00598100
H	-2.10281100	3.83410500	-1.38397100
H	-0.63705400	2.98030800	2.07981900
H	-2.94310600	2.79388000	1.31506000
O	-0.66436700	4.66605400	0.91082900
O	-2.06502200	1.62525700	-0.13995400
H	-0.45716400	0.61481300	-0.93415300
H	1.09680100	2.23726700	0.59662200
H	-1.47919100	5.96949800	-0.44952300
O	0.27405300	3.09843800	-1.11177200
O	-3.93658100	4.23138900	-0.50532400
Si	-4.65627800	5.17792900	-1.70574200
Si	1.66578800	3.07380100	-2.05784000
C	2.02404600	1.31482700	-2.60635700
H	2.90492000	1.28804900	-3.25767500
H	2.22516100	0.66377800	-1.74820700
H	1.17820300	0.89606300	-3.16176500
C	1.24668600	4.17865900	-3.50598600
H	1.04335700	5.20033400	-3.16899400
H	2.07506900	4.21425000	-4.22159900
H	0.36001500	3.80787900	-4.03058600

C	3.10942100	3.74172500	-1.06260700
H	4.00917100	3.78956800	-1.68630300
H	2.89760700	4.74990000	-0.69187100
H	3.33788400	3.10242900	-0.20300000
C	-6.44994900	4.65121600	-1.71463400
H	-6.90371700	4.80023300	-0.72927400
H	-7.01931400	5.24135000	-2.44087900
H	-6.54858600	3.59391500	-1.98028200
C	-4.49762000	6.99509900	-1.26238200
H	-4.92710500	7.19431100	-0.27502500
H	-3.45174200	7.31961100	-1.25295600
H	-5.03129400	7.61197000	-1.99433900
C	-3.81473500	4.84146800	-3.34919800
H	-2.78384400	5.21192400	-3.35951000
H	-3.79647600	3.76989900	-3.57452300
H	-4.35606700	5.34854100	-4.15573500

57

Me₃Si-isosorbide⁺ Isomer1. Gibbs free energy: -1761.40644

C	-0.63950800	1.37122200	-0.25536000
C	0.22961500	2.58291000	0.08186300
C	-0.69608300	3.26547300	1.10563100
C	-2.09578500	2.99555700	0.54783800
C	-1.75548200	5.37275700	0.53859800
C	-2.44177000	4.26069600	-0.24807000
H	-0.52201800	0.58977400	0.50653900
H	-2.38175500	5.72670700	1.35960800
H	-1.96473000	4.16291000	-1.23050300
H	-0.54381200	2.90527400	2.12188100

H	-2.84458600	2.83502100	1.32954500
O	-0.57057100	4.71940700	1.12027200
O	-1.99012600	1.84483400	-0.26421400
H	-0.41163200	0.95570300	-1.23658600
H	1.18509700	2.28030600	0.52353400
H	-1.40143900	6.19807600	-0.07729200
O	0.39276700	3.45533900	-1.00016500
O	-3.81606600	4.48890800	-0.33511700
Si	-4.54091300	4.90153900	-1.81971100
Si	1.61657300	3.38393600	-2.17237700
C	1.60567800	1.71499500	-3.02175300
H	2.36312700	1.70201700	-3.81327300
H	1.84376800	0.90340800	-2.32588300
H	0.63448700	1.50679300	-3.48228900
C	1.16439100	4.76285800	-3.34670400
H	1.12742500	5.73129100	-2.83790100
H	1.90307400	4.83359100	-4.15207200
H	0.18481400	4.57828400	-3.79950000
C	3.27217500	3.66439900	-1.33861900
H	4.07091400	3.62883800	-2.08767200
H	3.32320100	4.63993100	-0.84433400
H	3.48844600	2.88764800	-0.59660100
C	-6.33406500	5.18853100	-1.39418200
H	-6.43932900	5.99367300	-0.66022100
H	-6.89732800	5.46876200	-2.29062400
H	-6.78642700	4.28255400	-0.97865300
C	-3.70102500	6.44843200	-2.46639600
H	-3.77760500	7.26753600	-1.74354600

H	-2.63973400	6.27258800	-2.67558500
H	-4.17061400	6.77541400	-3.40042000
C	-4.30935700	3.47922600	-3.01651200
H	-3.24889200	3.28276000	-3.20786600
H	-4.76020900	2.56208200	-2.62414400
H	-4.78401600	3.70941500	-3.97659700
Si	0.79983500	5.70215600	1.82917000
C	1.31396100	6.78642800	0.41403700
H	0.60446100	7.59831300	0.23200700
H	2.28580200	7.23676500	0.64190800
H	1.41860500	6.19742000	-0.50108400
C	-0.00998700	6.57896700	3.24893700
H	0.73923300	7.18451100	3.77026100
H	-0.80461000	7.25197600	2.91430100
H	-0.42721000	5.86496400	3.96515800
C	2.05639800	4.43426500	2.33064600
H	2.85067000	4.96614300	2.86723200
H	1.65261900	3.68042400	3.01191400
H	2.51835800	3.94093900	1.47243700

57

Me₃Si-isosorbide⁺ Isomer2. Gibbs free energy: -1761.409565

C	-0.97268100	0.84444800	-0.32591500
C	-0.07819900	2.04459600	-0.11187700
C	-0.96371500	2.93453500	0.79438900
C	-2.35593200	2.77195000	0.18821600
C	-1.50057600	4.97429300	-0.19567500
C	-2.47968200	3.93942000	-0.79039500
H	-1.00421400	0.17230300	0.53384900

H	-2.05744000	5.75655300	0.32931600
H	-2.11521600	3.59700800	-1.76537000
H	-0.90678000	2.58994100	1.82978100
H	-3.16864800	2.75838600	0.91482400
O	-0.66183500	4.29999500	0.74805300
O	-2.31943300	1.45718200	-0.47751200
H	-0.76004300	0.31176900	-1.24916700
H	0.84672900	1.74740600	0.39433600
H	-0.87533500	5.42941100	-0.96891100
O	0.13960200	2.67960100	-1.33719800
O	-3.79675200	4.40722700	-0.86959600
Si	-4.34815200	5.39991900	-2.13462600
Si	1.62917700	3.26727700	-1.90071000
C	2.75486700	1.80572700	-2.22728800
H	3.71307200	2.14838700	-2.63327800
H	2.96521300	1.24957900	-1.30714100
H	2.30658200	1.11652000	-2.95027000
C	1.16218500	4.16964000	-3.46750000
H	0.44426600	4.96930700	-3.25727500
H	2.04563800	4.62080600	-3.93123000
H	0.70983800	3.48510800	-4.19223000
C	2.38496800	4.40510100	-0.62172300
H	3.33824000	4.80087400	-0.98947400
H	1.72088400	5.24625400	-0.40263900
H	2.58093800	3.87795900	0.31800800
C	-6.20445500	5.20086300	-2.10243200
H	-6.60532300	5.42448300	-1.10858000
H	-6.67320800	5.88465800	-2.81801500

H	-6.49470700	4.17925400	-2.36803200
C	-3.83175600	7.16946700	-1.79981600
H	-4.20859300	7.51370100	-0.83118100
H	-2.74184900	7.27881800	-1.80357900
H	-4.23322500	7.83285300	-2.57404200
C	-3.59744500	4.79489400	-3.74294900
H	-2.51598200	4.96438900	-3.78132300
H	-3.78398000	3.72706600	-3.89777400
H	-4.04505100	5.33754300	-4.58283500
Si	-3.81590100	0.40445700	-0.64411300
C	-4.28862800	0.02254800	1.11078300
H	-4.67835100	0.90026100	1.63372900
H	-5.07742000	-0.73745500	1.10458600
H	-3.44315300	-0.38037600	1.67638700
C	-3.17773000	-1.04752000	-1.60632300
H	-2.47654000	-1.66041500	-1.03373600
H	-4.03605400	-1.67853300	-1.86287500
H	-2.70569100	-0.73525100	-2.54230800
C	-4.99828000	1.48684100	-1.56663500
H	-4.62796700	1.69848100	-2.57386300
H	-5.95797000	0.96634500	-1.65496200
H	-5.16192300	2.43618000	-1.05058100

44

Isomannide. Gibbs free energy: -1352.41992

C	-1.56087600	1.31002600	0.35167400
C	-0.21359600	2.00157900	0.16333700
C	-0.48156700	3.32642300	0.91875700
C	-2.01338400	3.51243100	0.82681400

C	-0.86154700	5.48762700	0.23912200
C	-2.19066600	4.78129500	-0.04247500
H	-1.60562500	0.82140300	1.33609300
H	-0.91753800	6.04240100	1.18748000
H	-0.14944300	3.22664600	1.95937400
H	-2.45409400	3.68786700	1.81584000
O	0.12153400	4.46024400	0.33155900
O	-2.55115800	2.33332700	0.26833500
H	-1.75818300	0.57275300	-0.42800200
H	0.59018400	1.42942400	0.64226400
H	-0.56741600	6.17150600	-0.55851300
O	0.04472800	2.17333100	-1.20313300
H	-3.03690600	5.38406300	0.31143900
O	-2.34059900	4.44215200	-1.39202400
Si	-3.05570900	5.40582500	-2.56755200
Si	1.49347900	2.68610200	-1.89509000
C	-2.97622100	4.36603700	-4.11942400
H	-3.44219300	4.88878100	-4.96163800
H	-1.93714300	4.14857800	-4.38782700
H	-3.49782000	3.41415800	-3.97712800
C	-4.82775800	5.78039600	-2.07344500
H	-5.32508800	6.36602300	-2.85467300
H	-5.39454700	4.85477300	-1.92877200
H	-4.87525900	6.35909100	-1.14455600
C	-2.09888300	7.00814300	-2.77900700
H	-1.04462100	6.80932200	-3.00071700
H	-2.51587800	7.58965000	-3.60899100
H	-2.15047900	7.63017400	-1.87858300

C	2.84047900	2.76694600	-0.59085900
H	3.01015400	1.79122900	-0.12278100
H	3.78199100	3.08255000	-1.05420900
H	2.58548800	3.48959300	0.18993800
C	1.27821000	4.33772200	-2.75447700
H	2.18407200	4.58886500	-3.31831600
H	0.44049300	4.30519300	-3.45931600
H	1.08537100	5.13162700	-2.02849600
C	1.91152500	1.38592100	-3.18415500
H	1.11290900	1.30594100	-3.92983600
H	2.83774500	1.64479300	-3.70978000
H	2.04575200	0.40212400	-2.72189900

57

Me₃Si-isomannide⁺. Gibbs free energy: -1761.403626

C	-1.71768600	1.24960300	0.14434100
C	-0.38855600	1.97046200	0.06590400
C	-0.67839200	3.25099000	0.89566200
C	-2.18064800	3.53518000	0.71835300
C	-0.91061300	5.44850000	0.24904900
C	-2.24795200	4.81257000	-0.14835800
H	-1.87034500	0.73310600	1.09401400
H	-1.02016600	6.00023900	1.19256100
H	-0.43476900	3.07313500	1.94829900
H	-2.70261100	3.65680800	1.66746300
O	0.01158300	4.37573900	0.41454600
O	-2.70903700	2.34204000	0.07005300
H	-1.89380300	0.59230200	-0.70493500
H	0.38598800	1.36527000	0.55062900

H	-0.52265400	6.12000800	-0.51604300
O	-0.09021300	2.23391200	-1.26484400
H	-3.08209200	5.45149400	0.16599900
O	-2.33859100	4.46972000	-1.49845900
Si	-2.79279600	5.52207200	-2.74902000
Si	1.40777700	2.72656600	-1.89035400
C	-2.56475400	4.51557500	-4.30757500
H	-2.62277000	5.17149200	-5.18303800
H	-1.59068300	4.01726900	-4.32282800
H	-3.33959300	3.75036100	-4.41556100
C	-4.58413900	6.02603300	-2.51732600
H	-4.86667700	6.73624300	-3.30250200
H	-5.25869900	5.16652200	-2.58793500
H	-4.75147400	6.52306700	-1.55528200
C	-1.71355800	7.05461500	-2.75748100
H	-0.65299100	6.80955500	-2.87279200
H	-2.00413100	7.69008100	-3.60178200
H	-1.83857100	7.64700600	-1.84476400
C	2.70997300	2.63116600	-0.54595000
H	2.82681400	1.61307700	-0.15942900
H	3.67740500	2.94292200	-0.95507500
H	2.46517400	3.29731800	0.28706300
C	1.27356600	4.45344600	-2.59799800
H	2.16687600	4.68598400	-3.18867600
H	0.40419300	4.53695000	-3.25710800
H	1.18002100	5.19924500	-1.80499300
C	1.77121900	1.51300700	-3.27121800
H	0.97516200	1.52758100	-4.02348100

H	2.71164700	1.76884400	-3.77184700
H	1.85823600	0.49201300	-2.88512500
Si	-4.46720500	1.98850400	-0.30019800
C	-4.44684000	1.66414300	-2.12357300
H	-3.89514200	0.75246400	-2.36989200
H	-5.47260500	1.54596700	-2.48821500
H	-3.98610000	2.50625800	-2.64434800
C	-4.83425000	0.50565900	0.75586900
H	-4.64648100	0.71039200	1.81405000
H	-5.89580500	0.25856400	0.64454200
H	-4.25753900	-0.37360500	0.45514900
C	-5.36281700	3.52089900	0.23389000
H	-6.43346900	3.34312700	0.08272600
H	-5.21261600	3.74184300	1.29424300
H	-5.08797400	4.39309600	-0.36183200

75

Alpha-Me-glucose. Gibbs free energy: -2360.461538

C	-2.91621100	0.22328400	-1.07011600
C	-1.48126500	0.78846300	-0.98886200
C	-1.45095800	2.31166300	-0.76748000
C	-2.39450300	2.67165700	0.37619600
C	-3.82208400	0.79709400	0.03241600
H	-0.43562400	2.58801400	-0.45438300
H	-0.97900700	0.58977300	-1.94175300
H	-2.83293400	-0.86299700	-0.91576900
H	-4.85975100	0.63177800	-0.26933400
O	-3.70319200	2.21190200	0.11230900
C	-3.59483500	0.10340600	1.38092100

H	-3.92052700	-0.94080000	1.27331600
H	-2.52804200	0.08636200	1.62650800
O	-4.34384600	0.75590400	2.38273900
O	-3.50052500	0.51315600	-2.31989200
O	-0.82820600	0.11806800	0.07042300
O	-1.79278600	2.95740000	-1.96091100
Si	-3.90158500	0.68580300	4.00505400
Si	0.83089200	0.14651300	0.38395400
Si	-3.38362300	-0.46795500	-3.68194900
Si	-1.13899300	4.39141200	-2.54959800
C	-2.07077300	1.07521400	4.18678200
H	-1.43931600	0.30933100	3.72348900
H	-1.81883200	2.04301100	3.74057800
H	-1.80803800	1.12009200	5.24980000
C	-4.95735400	1.98104900	4.84364000
H	-6.02224700	1.77274300	4.69775800
H	-4.75993300	2.00437300	5.92075300
H	-4.74544500	2.97513400	4.43630400
C	-4.24491100	-1.03389600	4.67367200
H	-3.98618100	-1.09890100	5.73631800
H	-5.30412000	-1.28986300	4.56512700
H	-3.65597000	-1.78683200	4.13812200
C	-4.22583100	-2.10892100	-3.33195200
H	-5.28459700	-1.96120500	-3.09497200
H	-4.16063000	-2.76630900	-4.20613100
H	-3.75714100	-2.62984000	-2.48973400
C	-4.26456100	0.49514100	-5.01986400
H	-3.78273600	1.46606800	-5.17557400

H	-4.24185700	-0.05189800	-5.96862400
H	-5.31167700	0.67120100	-4.75353200
C	-1.58798400	-0.77039900	-4.14622600
H	-1.06002300	0.17325300	-4.32141200
H	-1.05369600	-1.32561900	-3.36712800
H	-1.53909100	-1.36164400	-5.06792100
C	-0.74858800	4.04719200	-4.35125300
H	-0.36035800	4.94385800	-4.84696600
H	0.00156100	3.25419700	-4.44215000
H	-1.64877800	3.72727400	-4.88731900
C	-2.40394000	5.76571500	-2.41387900
H	-3.33224200	5.49187500	-2.92670300
H	-2.63737500	5.96356400	-1.36369100
H	-2.02343100	6.68664000	-2.87018100
C	0.42015400	4.81909000	-1.59461300
H	0.85897700	5.73593100	-2.00397300
H	0.20338700	4.99277500	-0.53551600
H	1.17583700	4.02894900	-1.66810200
C	1.21905000	1.51612900	1.60904000
H	0.51821300	1.48292300	2.45056100
H	2.23161700	1.39262100	2.00964200
H	1.15733600	2.51098700	1.15589300
C	1.74290600	0.40987800	-1.23409800
H	2.82481000	0.39980800	-1.06331700
H	1.50623100	-0.37912700	-1.95597600
H	1.48780400	1.37311300	-1.68995900
C	1.20161600	-1.52000800	1.14623300
H	0.92816800	-2.33094500	0.46370400

H	2.26840800	-1.61137400	1.37740100
H	0.64171900	-1.65215200	2.07823400
H	-2.01972500	2.20854400	1.30519200
O	-2.42875400	4.04876300	0.51741300
C	-3.10359300	4.49347100	1.68410900
H	-2.65176000	4.05704300	2.58448700
H	-2.99239700	5.57783300	1.71578900
H	-4.16553100	4.23260100	1.65129200

88

Me₃Si–Alpha-Me-glucose⁺. Gibbs free energy: -2769.434103

C	0.84365100	-1.50693000	-0.33734500
C	0.95061800	-0.41712700	0.74373200
C	0.65015400	0.99614400	0.20470100
C	-0.70033600	0.89243800	-0.50182400
C	-0.44594300	-1.37480500	-1.16500600
H	0.53420700	1.64926200	1.08214400
H	1.97173200	-0.44028700	1.14741600
H	0.78609500	-2.46038500	0.20803400
H	-0.28465900	-1.87579900	-2.12170300
O	-0.69405700	-0.00896600	-1.54423100
C	-1.66101200	-2.00796600	-0.49205600
H	-1.41468100	-3.05852100	-0.28678300
H	-1.85323100	-1.53047700	0.47666000
O	-2.77253800	-1.93041900	-1.35478500
O	1.96861500	-1.46619600	-1.18206100
O	-0.02864500	-0.67969100	1.72249700
O	1.59584800	1.50301500	-0.68236000
Si	-4.33427600	-1.77863900	-0.73313100

Si	0.24277400	-0.94752400	3.36965600
Si	2.95008900	-2.83301800	-1.36800400
Si	3.12156500	2.13707300	-0.30573700
C	-4.44273100	-0.15451900	0.20473600
H	-3.74081700	-0.13910100	1.04663000
H	-4.22029100	0.68869600	-0.45784200
H	-5.44728700	-0.00773300	0.61583500
C	-5.45478200	-1.79234800	-2.22626100
H	-5.37993200	-2.74439700	-2.76128200
H	-6.49840600	-1.65303200	-1.92500500
H	-5.19077900	-0.98740100	-2.91971100
C	-4.67589000	-3.20448700	0.43630800
H	-5.68119900	-3.12148200	0.86347400
H	-4.60237200	-4.16706600	-0.08017900
H	-3.96073200	-3.20786700	1.26659400
C	1.89033400	-4.26278100	-1.96399300
H	1.41215500	-4.02568700	-2.92022500
H	2.50883300	-5.15561100	-2.10773900
H	1.10573400	-4.52004100	-1.24400700
C	4.23678500	-2.36590900	-2.63779800
H	4.94360700	-1.63122000	-2.24177400
H	4.80360600	-3.25463500	-2.93623200
H	3.76826900	-1.94652500	-3.53390600
C	3.71896800	-3.24365700	0.29353900
H	4.28424900	-2.39158100	0.68616100
H	2.95881600	-3.51550500	1.03381500
H	4.40725500	-4.09077300	0.19920700
C	4.43380100	0.89519000	-0.77819000

H	5.43190100	1.30241600	-0.58236000
H	4.32090900	-0.03492800	-0.21344000
H	4.36450200	0.65472300	-1.84341400
C	3.27384200	3.68699300	-1.34015500
H	3.10497200	3.46344200	-2.39882000
H	2.54921400	4.44622100	-1.03103400
H	4.27691400	4.11599100	-1.24167300
C	3.20178800	2.50507800	1.53221200
H	4.13535900	3.03636500	1.74781200
H	2.37680800	3.13379200	1.88342800
H	3.20929500	1.58295100	2.12311800
C	0.73040900	0.66833400	4.18374500
H	-0.05549800	1.42216400	4.06638500
H	0.89585200	0.51888400	5.25646900
H	1.65539000	1.07173100	3.75960500
C	1.60194400	-2.22300200	3.55550300
H	1.78566900	-2.42830100	4.61572900
H	1.32518900	-3.16501400	3.07059200
H	2.54483800	-1.87640600	3.11847300
C	-1.41261100	-1.55735500	3.98063500
H	-1.69192700	-2.49127200	3.48213300
H	-1.38847100	-1.73938200	5.06014700
H	-2.19186300	-0.81465500	3.77893700
H	-1.49207900	0.68409600	0.22269600
O	-1.07760800	2.17253600	-1.10360700
Si	-1.71493100	3.57740600	-0.10590500
C	-2.29894100	2.81164900	1.48063000
H	-2.66276400	3.63250300	2.10949600

H	-3.13322700	2.12345500	1.32235000
H	-1.51163200	2.29876400	2.03910600
C	-3.09182500	4.24639000	-1.15332400
H	-3.64233700	4.98525400	-0.56049100
H	-2.73892900	4.74482500	-2.05954100
H	-3.79056700	3.45302800	-1.43369800
C	-0.24309500	4.69128800	0.08276800
H	0.13892100	5.03609500	-0.88196100
H	-0.53810200	5.57417100	0.66023600
H	0.56710600	4.19318100	0.62256800
C	-0.62391800	2.42893400	-2.48194100
H	-1.23541800	1.82728100	-3.14786400
H	-0.78471200	3.48994500	-2.65829500
H	0.43124000	2.18013200	-2.53988800

75

Beta-Me-glucose. Gibbs free energy: -2360.455616

C	-2.65239900	0.45968900	-0.96878200
C	-1.41292700	1.35796100	-0.80257500
C	-1.78535800	2.83050900	-0.57664400
C	-2.94376300	3.01776200	0.42267600
C	-3.68472200	0.72520400	0.13085000
H	-0.89777000	3.31665700	-0.14845300
H	-0.82322700	1.31494200	-1.72762100
H	-2.31989500	-0.58322300	-0.87342100
H	-3.38181800	4.00858900	0.23929800
H	-4.62653800	0.27794100	-0.19987500
O	-3.99133000	2.11799000	0.23317700
C	-3.31753100	0.08295700	1.46615900

H	-3.07241300	-0.97155000	1.27131600
H	-2.43323200	0.56728700	1.88688900
O	-4.42233000	0.16071300	2.34894900
O	-3.27221400	0.67127800	-2.21750500
O	-0.66560600	0.91460500	0.30904900
O	-2.16171200	3.42832900	-1.79763500
O	-2.50424200	2.94000300	1.76187400
C	-1.97111700	4.14453700	2.27083500
H	-2.69091700	4.96843200	2.16915800
H	-1.76785600	3.97455100	3.32916300
H	-1.03470100	4.42759100	1.77221300
Si	-4.18228500	-0.02036900	4.00511200
Si	0.68997400	-0.07910600	0.22826900
Si	-2.91033700	-0.15717500	-3.63407100
Si	-1.14482500	4.48034800	-2.63131500
C	-3.12389300	1.38261700	4.66379100
H	-2.15217400	1.41735900	4.16051300
H	-3.61400000	2.34848600	4.50587800
H	-2.94849900	1.25353000	5.73785700
C	-5.89698400	0.01507900	4.75290100
H	-6.52106000	-0.78776300	4.34721900
H	-5.84209000	-0.11344800	5.83949100
H	-6.39137300	0.97059800	4.54943900
C	-3.32261300	-1.66058800	4.32431700
H	-3.17780300	-1.81664700	5.39907300
H	-3.91184400	-2.49780800	3.93523500
H	-2.33617600	-1.68911300	3.84797400
C	-2.96323800	-2.00534300	-3.30590400

H	-3.93752000	-2.30694200	-2.90733800
H	-2.79122600	-2.55456900	-4.23831200
H	-2.19274300	-2.31797700	-2.59267300
C	-4.23760600	0.38030500	-4.83502400
H	-4.19716400	1.46330700	-4.99237800
H	-4.10101300	-0.10898300	-5.80546900
H	-5.23387000	0.12561300	-4.45988300
C	-1.21440600	0.31763800	-4.29041600
H	-1.14221700	1.40056300	-4.43540400
H	-0.40283800	0.00641000	-3.62386900
H	-1.04586000	-0.16331400	-5.26085600
C	-1.97871200	4.73441400	-4.28410900
H	-1.37750800	5.38916200	-4.92397900
H	-2.11064200	3.77899300	-4.80257900
H	-2.96465200	5.19319200	-4.15780500
C	-0.99660900	6.07883000	-1.66011100
H	-1.97793000	6.54485600	-1.52320000
H	-0.56313000	5.89973400	-0.66962700
H	-0.34903700	6.79176000	-2.18238200
C	0.55279900	3.69850200	-2.81561100
H	1.22034500	4.36996800	-3.36687100
H	1.01026500	3.50571700	-1.83892400
H	0.50418000	2.75011000	-3.36061900
C	2.05199400	0.81060300	-0.70488800
H	2.28493100	1.77129800	-0.23373000
H	2.96598000	0.20625000	-0.71671300
H	1.76757000	1.00184900	-1.74541200
C	0.27275300	-1.68869200	-0.64482500

H 1.13705300 -2.36207500 -0.61925600
 H -0.56707900 -2.19988700 -0.16191600
 H 0.01845800 -1.52541200 -1.69783100
 C 1.13090000 -0.37205300 2.02025400
 H 0.30468600 -0.86701500 2.54172100
 H 2.01845900 -1.00784900 2.10584700
 H 1.33790300 0.57466800 2.52957400

88

Me3Si-Beta-Me-glucose+. Gibbs free energy: -2769.437814

C -2.72214600 0.33708900 -0.76742400
 C -1.34851300 1.02951700 -0.69523500
 C -1.51983000 2.55278400 -0.48131900
 C -2.84877700 2.82177900 0.21881300
 C -3.51809700 0.57709900 0.52913300
 H -0.70671400 2.85312400 0.19013200
 H -0.82565000 0.89791400 -1.64974600
 H -2.57774000 -0.74378000 -0.89195900
 H -3.63847400 3.00086800 -0.51844500
 H -4.58231700 0.60602400 0.26478300
 O -3.17928200 1.84125000 1.12724500
 C -3.29099500 -0.47806400 1.59470300
 H -3.53113000 -1.45929900 1.16282400
 H -2.22977500 -0.47153300 1.87039400
 O -4.12057200 -0.21175100 2.70310800
 O -3.46111600 0.87968600 -1.83794200
 O -0.60859100 0.51070200 0.38357900
 O -1.51414800 3.29036800 -1.67420700
 O -2.73941000 4.04858400 1.01327600

C	-3.52920700	5.16285600	0.49133900
H	-4.58674100	4.95106200	0.64908600
H	-3.21920600	6.05418900	1.02849600
H	-3.29101300	5.26115200	-0.56579100
Si	-3.71303700	-0.78049300	4.24164600
Si	0.51077600	-0.75352600	0.29592100
Si	-3.39762900	0.34871600	-3.44490700
Si	-0.19530100	4.24894200	-2.13972600
C	-2.12998800	0.05123900	4.81435300
H	-1.32083500	-0.06503100	4.08560600
H	-2.28612100	1.12179400	4.97948400
H	-1.79198100	-0.39123100	5.75798200
C	-5.15894900	-0.29653400	5.32065700
H	-6.07900000	-0.79177200	4.99477500
H	-4.97168400	-0.57619800	6.36288700
H	-5.32092400	0.78607700	5.28560300
C	-3.46600300	-2.63751200	4.15659500
H	-3.26378300	-3.04569000	5.15281500
H	-4.35808800	-3.13400800	3.76064100
H	-2.61798100	-2.89622900	3.51256000
C	-3.88636900	-1.46059300	-3.48984000
H	-4.88034900	-1.61008100	-3.05581300
H	-3.90741700	-1.82292000	-4.52357100
H	-3.17501900	-2.08424200	-2.93721300
C	-4.63256900	1.44798500	-4.31305500
H	-4.34040500	2.49964800	-4.22463700
H	-4.69172800	1.20004000	-5.37806000
H	-5.63099800	1.33163300	-3.87957300

C	-1.67794400	0.56941000	-4.16321500
H	-1.30970400	1.58518600	-3.98672800
H	-0.95745500	-0.14035100	-3.74173100
H	-1.70911100	0.40062600	-5.24569700
C	-0.71197900	4.96331800	-3.78373400
H	0.04838900	5.65674900	-4.15810900
H	-0.84758700	4.17336000	-4.52953100
H	-1.65512800	5.51106900	-3.68932300
C	0.06788500	5.57450600	-0.83791800
H	-0.81803200	6.20901700	-0.73015500
H	0.30086600	5.14088400	0.14068600
H	0.90857100	6.21802600	-1.11961300
C	1.31706000	3.15240000	-2.26749400
H	2.19863300	3.73583600	-2.55419600
H	1.53471900	2.67191200	-1.30752500
H	1.17130700	2.36643200	-3.01643800
C	2.04325200	-0.16818500	-0.60612500
H	2.49651000	0.69131800	-0.10177000
H	2.78784100	-0.97105800	-0.64355300
H	1.81421400	0.12070700	-1.63750000
C	-0.24354500	-2.21429500	-0.60754400
H	0.47785000	-3.03845800	-0.63913100
H	-1.14547400	-2.57853500	-0.10430600
H	-0.50021100	-1.96522700	-1.64335900
C	0.84689800	-1.15170900	2.08997800
H	-0.04557300	-1.56898000	2.56876300
H	1.65100800	-1.88958500	2.18033300
H	1.14452800	-0.25298800	2.64028500

Si	-2.27281800	3.96927100	2.82084000
C	-3.78834500	3.38463800	3.71388900
H	-3.63535900	3.50856500	4.79193200
H	-4.66315400	3.97885900	3.43144400
H	-3.98808100	2.33360300	3.49334400
C	-1.83913400	5.74436500	3.16782000
H	-2.71081100	6.39900400	3.24710500
H	-1.32808000	5.76126600	4.13763200
H	-1.14508300	6.14957300	2.42493200
C	-0.77892800	2.87217300	2.88844800
H	-0.94407800	1.89566200	2.42841900
H	0.08390900	3.35136000	2.41583100
H	-0.53566600	2.72025100	3.94654500

70

Glucose-oxocarbenium⁺. Gibbs free energy: -2245.183604

C	-2.71380700	0.34383300	-0.97544100
C	-1.59783100	1.40100800	-0.91251900
C	-2.24453000	2.80427200	-0.97285300
C	-3.66524800	2.84152700	-0.50629000
C	-3.72180400	0.53156200	0.15036800
H	-1.71677500	3.41621700	-0.21616500
H	-0.97018100	1.31076700	-1.80514100
H	-2.28334400	-0.65791500	-0.85588300
H	-4.22816900	3.76669400	-0.63045900
H	-4.60467300	-0.07778600	-0.04263800
O	-4.29712400	1.91242000	0.03779200
C	-3.25860800	0.32712100	1.57880400
H	-2.73245600	-0.63837900	1.59416300

H	-2.53715500	1.10107600	1.85856800
O	-4.37715500	0.31959800	2.42507100
O	-3.41874300	0.49130200	-2.17580700
O	-0.86652900	1.29072600	0.27384700
O	-2.26047200	3.38374000	-2.23790400
Si	-4.17480700	0.11895500	4.10013900
Si	0.53328700	0.35054400	0.51890100
Si	-3.02054300	-0.24716600	-3.65899900
Si	-1.11899800	4.55921100	-2.74360300
C	-3.03845600	1.46962000	4.73457400
H	-2.03841900	1.39779500	4.29317500
H	-3.44179600	2.46346200	4.51474700
H	-2.92457900	1.38238500	5.82065600
C	-5.89720400	0.25468600	4.80443200
H	-6.55621500	-0.50986500	4.38097300
H	-5.87234400	0.11587800	5.89059500
H	-6.33190200	1.23771000	4.59800400
C	-3.41332500	-1.56541400	4.41521600
H	-3.29093300	-1.72685700	5.49186600
H	-4.04852000	-2.36595700	4.02237300
H	-2.42319800	-1.65660300	3.95550400
C	-2.82654300	-2.08589400	-3.36274500
H	-3.73139900	-2.51346100	-2.91916600
H	-2.64293800	-2.59480700	-4.31541100
H	-1.98061200	-2.31109600	-2.70419900
C	-4.47792800	0.15999700	-4.74844400
H	-4.58704000	1.24267700	-4.86752200
H	-4.34226000	-0.27882000	-5.74265000

H	-5.40598500	-0.23634600	-4.32488300
C	-1.43436000	0.48735300	-4.33726700
H	-1.47618300	1.58070400	-4.30644000
H	-0.54835500	0.15633500	-3.78476700
H	-1.30189300	0.18219400	-5.38120400
C	-1.53168500	4.82947200	-4.53967400
H	-0.85393400	5.57377200	-4.97106400
H	-1.42683900	3.90423000	-5.11462100
H	-2.55639900	5.19535700	-4.65645500
C	-1.36192600	6.09328800	-1.70228500
H	-2.36699800	6.50520300	-1.83757100
H	-1.21170500	5.89296500	-0.63593200
H	-0.63788800	6.86080200	-1.99660100
C	0.58288300	3.82866800	-2.48306900
H	1.35198900	4.53412500	-2.81512000
H	0.76789600	3.61635500	-1.42471800
H	0.70954100	2.89969600	-3.04908800
C	2.01440900	1.25166200	-0.18212300
H	2.12631900	2.24270100	0.26927500
H	2.92646300	0.68076400	0.02506200
H	1.93716800	1.37347100	-1.26728300
C	0.33418800	-1.30632500	-0.33569600
H	1.26014300	-1.88082800	-0.22186000
H	-0.47935700	-1.90221900	0.09068500
H	0.15814300	-1.18921600	-1.41075000
C	0.61787100	0.18893200	2.37606000
H	-0.25340400	-0.34714700	2.76606800
H	1.51553900	-0.36380100	2.67247700

H 0.65518400 1.17441600 2.85140600

13

Me₃Si⁺. Gibbs free energy: -408.934892

Si 0.16595600 0.87225200 0.00416600

C 0.92830600 1.17933400 -1.63264700

H 1.42073800 2.15700600 -1.64180000

H 1.70909600 0.42513800 -1.79623200

H 0.20031600 1.11680300 -2.44310200

C 1.10869400 1.23121100 1.53269800

H 0.68750500 2.13529100 1.99174500

H 0.98579300 0.41852700 2.25545300

H 2.16765200 1.40137600 1.33106800

C -1.53385700 0.19775100 0.10502000

H -1.54879800 -0.79230000 -0.36729300

H -1.88744600 0.11338700 1.13371300

H -2.21370400 0.83366500 -0.47278800