


8-2012

Part I - A Study of the Formation of Carbenes by Elimination of α -Bromosilanes and Application toward the Synthesis of Transition Metal Complexed Quinone Methide Analogs. Part II - Development of Novel 7-Membered Ring Carbene Ligands for Palladium Catalyzed Cross Coupling Reactions.

Christian Michael Loeschel
University of Arkansas, Fayetteville

Follow this and additional works at: <http://scholarworks.uark.edu/etd>

 Part of the [Biochemistry Commons](#), [Inorganic Chemistry Commons](#), and the [Organic Chemistry Commons](#)

Recommended Citation

Loeschel, Christian Michael, "Part I - A Study of the Formation of Carbenes by Elimination of α -Bromosilanes and Application toward the Synthesis of Transition Metal Complexed Quinone Methide Analogs. Part II - Development of Novel 7-Membered Ring Carbene Ligands for Palladium Catalyzed Cross Coupling Reactions." (2012). *Theses and Dissertations*. 437.
<http://scholarworks.uark.edu/etd/437>

PART I - A STUDY OF THE FORMATION OF CARBENES BY ELIMINATION OF α -
BROMOSILANES AND APPLICATION TOWARD THE SYNTHESIS OF TRANSITION
METAL COMPLEXED QUINONE METHIDE ANALOGS

PART II - DEVELOPMENT OF NOVEL 7-MEMBERED RING CARBENE LIGANDS FOR
PALLADIUM CATALYZED CROSS COUPLING REACTIONS

PART I - A STUDY OF THE FORMATION OF CARBENES BY ELIMINATION OF α -
BROMOSILANES AND APPLICATION TOWARD THE SYNTHESIS OF TRANSITION
METAL COMPLEXED QUINONE METHIDE ANALOGS

PART II - DEVELOPMENT OF NOVEL 7-MEMBERED RING CARBENE LIGANDS FOR
PALLADIUM CATALYZED CROSS COUPLING REACTIONS

A dissertation submitted in partial fulfillment
of the requirements for the degree of
Doctor of Philosophy in Chemistry

By

Christian Michael Loeschel
University of Arkansas
Bachelor of Science in Chemistry, 2005

August 2012
University of Arkansas

ABSTRACT

In part I, we wish to report our approaches toward transition metal complexed *ortho*-quinone methide analogs. *ortho*-Quinone Methides are a class of highly reactive compounds with a wide range of chemical and biological applications. Previously, a stable iron complexed benzannulated 5-membered ring quinone methide analog was reported by Allison and Neal²⁷. Herein, we report our approaches to improve the reactivity of that system by removing benzannulation as well as changing the metal from iron to manganese and rhenium.

Furthermore, a methodological study on generating carbenes under mild conditions by elimination of α -halosilanes and its application towards metal complexed quinone methide analogs will be included.

In part II, we report our attempts toward steric and electronic control of palladium-catalyzed cross coupling reactions by means of 7-membered ring carbene ligands. Cycloheptatrienyliene has recently emerged as an efficient catalyst ligand for both C-C and C-N bond forming reactions.⁵⁶ Our efforts will focus on fine-tuning both the electronic environment of the metal center by benzannulation of the cycloheptatrienyliene ligand and the steric environment by addition of substituents to the ligand.

This dissertation is approved for recommendation
to the Graduate Council

Dissertation Director

Dr. Neil T. Allison

Dissertation Committee

Dr. Bill Durham

Dr. Robert Gawley

Dr. Matthias McIntosh

DISSERTATION DUPLICATION RELEASE

I hereby authorize the University of Arkansas Libraries to duplicate this dissertation when needed for research and scholarship.

Agreed

Christian Michael Loeschel

Refused

Christian Michael Loeschel

ACKNOWLEDGEMENTS

Let me start with an obvious disclaimer: the list of people who have made this dissertation possible is far too long for me to thank them all. I have dreaded and put off writing these acknowledgements solely because I am afraid of leaving out anyone who has helped me along the way. So, to those who may have been inadvertently left out, I am grateful to every last one of you for all that you have done for me – none of this would have been possible without the support, advice, input and encouragement I have received over the years from countless sources.

First and foremost I want to thank my parents. To my father Rudolf – a mere thank you feels woefully inadequate in light of everything you have done for me. I would have been thoroughly lost without your emotional (not to mention financial) support; on too many occasions to count, our long conversations were the push to get back in the lab when yet another reaction did not work as intended. To my mother Angelika – throughout my childhood, you have tried to instill in me a love of knowledge and a desire to excel in all my endeavors. I hope this dissertation is at least a small testament to your success. And to Lynne – you have opened up your home to me and treated me like a son; through these years of being away from my family, having you close meant that I really wasn't.

Dr. Allison, your enthusiasm for chemistry has been truly inspiring. Most of all, I want to thank you for your patience with me. Over the years, so many of your great ideas have been placed into what must seem to be sadly inept hands. The fact that you have always taken the time to sit down with me and guide me through this learning process amidst a frenzy of other obligations has meant a lot to me. A great debt of gratitude is also owed to the rest of my committee – Drs. Durham, Gawley, and McIntosh. I greatly appreciate that your doors have always been open to me and that I could count on your invaluable input.

Without Marv Leister, I would have found myself hopelessly stuck too many times to remember – thank you for not retiring before I graduate. Thanks are also owed to Aaron Beuterbaugh for doing far more than his fair share of maintaining our lab, all while teaching me so many handy techniques as well as a thing or two about which way to hold a screwdriver. To Beng, who apparently lives in the research building, because there has never been a time of night that I wasn't able to walk over to his lab and have an enthusiastic conversation about anything related to chemistry or soccer.

Lastly, I want to thank everyone in my personal life who has had to put up with my endless ramblings about my research or my teaching. Particularly, I want to thank Jason for always being up for a run and Courtney for your unquestioning and unconditional support, motivation and sarcasm.

TABLE OF CONTENTS

PART I - A STUDY OF THE FORMATION OF CARBENES BY ELIMINATION OF α -BROMOSILANES AND APPLICATION TOWARD THE SYNTHESIS OF TRANSITION METAL COMPLEXED QUINONE METHIDE ANALOGS	1
INTRODUCTION	2
Metal-Assisted Cyclization of η^5 -Pentadienyl Ligands and Hydroxyferrocenes	8
Quinone Methides	3
Transition Metal-Complexed Quinone Methides	6
π -Allylic Cyclic Ketones	12
π -Allylic 5-Membered Ring Ketones from Vinyl Allenes	13
Vinyl Allenes from Carbene-Carbene Rearrangements	17
Carbenes by Elimination of α -Halosilanes	18
RESULTS AND DISCUSSIONS	22
Attempted Synthesis of Rhenium and Manganese oQM Analogs	22
Attempted Synthesis of Vinyl Allenes	25
Ionic Liquids as Solvents for Carbene Generation	33
Conclusion	37
EXPERIMENTAL SECTION	38
General Remarks	38
1-(2-bromophenyl)-2-butynyl acetate (22)	39
1-Bromo-2-(3-methyl-1,2-butadienyl)-benzene (23)	40
Manganesepentacarbonyl bromide	41
(η^1 -(2-Methyl-1,2-butadienyl)benzene)pentacarbonylmanganese (41a)	41
Rheniumpentacarbonyl bromide	42
(η^1 -(2-Methyl-1,2-butadienyl)benzene)pentacarbonylrhenium (41b)	42

(1,1-Diphenylmethyl)trimethylsilane (44).....	43
(1-Bromo-1,1-diphenylmethyl)trimethylsilane (43).....	43
Tetraphenylethylene (45).....	44
Benzhydryl Methyl Ether (47).....	44
<i>trans</i> -Dimethyl-3,3-diphenylcyclopropane-1,2-dicarboxylate (50).....	45
(1-Bromo-1-phenylmethyl)trimethylsilane (48).....	45
<i>trans</i> -Stilbene (49).....	46
Benzyl Methyl Ether (51).....	46
<i>trans</i> -Dimethyl-3-phenylcyclopropane-1,2-dicarboxylate (50).....	47
Benzyl- <i>tert</i> -butyldimethylsilane (56).....	47
(1-Bromo-1-phenylmethyl)- <i>tert</i> -butyldimethylsilane (55).....	48
Representative Procedure for Generating Carbenes in Ionic Liquids.....	48
PART II - DEVELOPMENT OF NOVEL 7-MEMBERED RING CARBENE LIGANDS FOR PALLADIUM CATALYZED CROSS COUPLING REACTIONS.....	49
INTRODUCTION	50
Types of Ligands.....	51
Ligands for Palladium-Catalyzed Coupling Reactions.....	52
Phosphine Ligands in Palladium-Catalyzed Cross-Coupling Reactions	53
N-Heterocyclic Carbenes as Ligands in Palladium-Catalyzed Cross-Coupling Reactions ..	56
Cycloheptatrienylidenes as Strong Donor Ligands in Organometallic Complexes.....	62
RESULTS AND DISCUSSIONS.....	66
Benzodiazepines	66
Cycloheptatrienylidene Ligands	71
Conclusion	77

EXPERIMENTAL	77
General Remarks	77
1,3-Diphenylpropynone (87).....	78
2,4-Diphenyl-3 <i>H</i> -benzo[1,4]diazepine (88).....	79
3-Bromo-2,4-diphenyl-3 <i>H</i> -benzo[1,4]diazepine (89).....	79
Lithium-Halogen Exchange Experiment on 89.	80
(η^5 -Cyclopentadienyldicarbonyl)(3-(2,4-Diphenyl-3 <i>H</i> -benzo[1,4]diazepinyl)Iron (85).	80
(<i>E</i>)- <i>N,N</i> -Diethylbuta-1,3-dien-1-amine (91).	81
2,7-Diphenyltropone (92).	81
7-Oxo-7 <i>H</i> -benzocycloheptene-6,8-dicarboxylic acid dimethyl ester (97).	82
4,5-Benzotropone (95).	82
4,5-Benzobromotropylium Bromide (100, 101).	83
4,5-Benzobromotropylium Tetrafluoroborate (102).	84
Attempted Synthesis of Di- μ -Bromobis(4,5-benzocycloheptatrienyli- dibromopalladium(II) (99).	84

PART I - A STUDY OF THE FORMATION OF CARBENES BY ELIMINATION OF α -
BROMOSILANES AND APPLICATION TOWARD THE SYNTHESIS OF TRANSITION
METAL COMPLEXED QUINONE METHIDE ANALOGS

INTRODUCTION

Herein, we report the study of a synthetic approach to carbenes through fluoride-promoted elimination of α -halosilanes. This methodology was studied for potential application in the synthesis of metal-complexed five-membered quinone methide analogs of the type shown in Figure 1 through cyclization of vinyl allenes. In this study, we will describe mechanistic studies and model systems that establish carbene intermediacy.

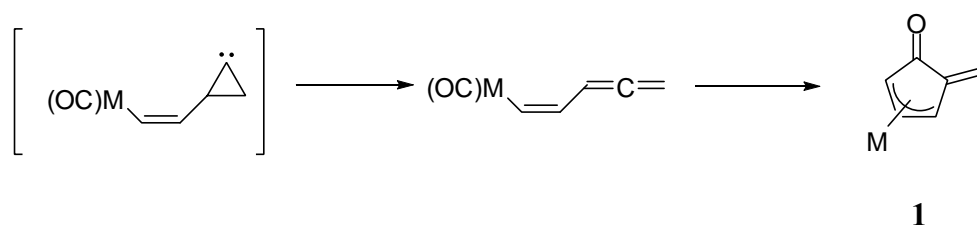


Figure 1. Proposed Synthesis of Metal-stabilized Quinone Methide Analog **1**.

Quinone methides are highly reactive organic compounds with a wide range of applications.¹⁻³ They have proven to be particularly useful in organic synthesis, where their reactivity mimics that of α,β -unsaturated ketones; however, a challenge is presented by their very high reactivity, which is driven by aromatization of the benzene ring, thereby making it very difficult to isolate simple quinone methides. We describe our approaches towards transition metal complexed five-membered ring analogs of quinone methides (Figure 1); we envision these complexes to show similar reactivity to organic quinone methides, but to exhibit a decreased drive towards aromaticity due to coordination to a transition metal, which disrupts delocalization of the π -electrons.¹ Thus, these quinone methide analogs may provide access to a structurally interesting class of compounds known as hydroxymetallocenes as shown in Figure 2.

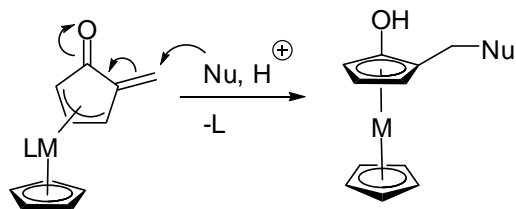


Figure 2. Proposed Synthesis of Substituted Hydroxymetalloenes

A key step in the proposed synthesis of **1** is the generation of a cyclopropyl carbene under mild conditions; thus, we report mechanistic studies on the fluoride-promoted elimination of α -halosilanes, a methodology that we hope will allow generation of carbenes at ambient temperature without the use of unstable and potentially explosive intermediates such as organic diazo-compounds or strongly basic conditions, which are typically employed in the synthesis of carbenes.

Quinone Methides

Quinone methides (QMs) are a class of six-membered diene ring ketones bearing an exocyclic methylene. There are three constitutionally isomeric QMs shown in Figure 3.

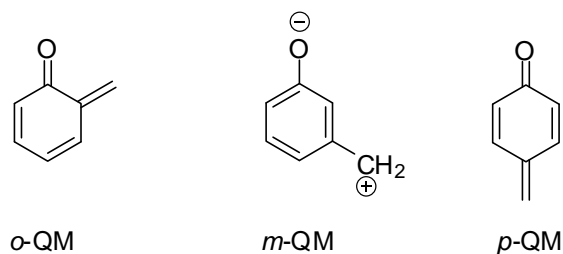


Figure 3. Constitutional Isomers of QM.

QMs are highly reactive organic moieties with a large number of biological uses such as DNA cross-linking,⁵ industrial applications in wood treatment,² as well as synthetic applications in complex molecule synthesis.³

o-QM was first isolated by Gardner *et al.*⁴ It readily polymerizes, and reacts rapidly with nucleophiles at the exocyclic methylene position, providing access to a number of cresol derivatives, shown in Figure 4.

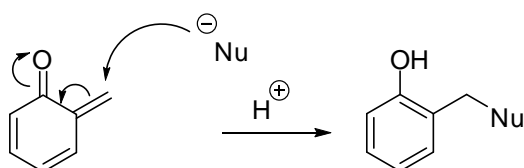


Figure 4. Formation of Cresols from *o*-QMs.

This ability to act as an electrophile can be used to cross-link DNA strands, as shown by Rokita *et al.*⁵ Due to their ability to alkylate DNA strands,⁶ a large subclass of anti-tumor agents based on QMs have been developed, including taxodione, taxodone,⁷ anthracyclines,⁸ and mytomylicins.⁹ Both anthracyclines and mytomylicins form QM intermediates *in situ* from the *p*-quinone, whereas the QM moiety is already in place in taxodone and taxodione.

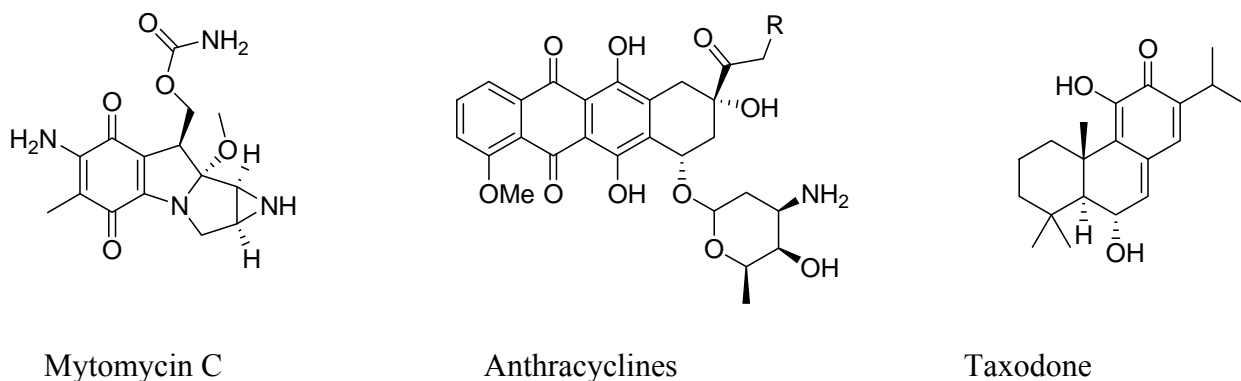
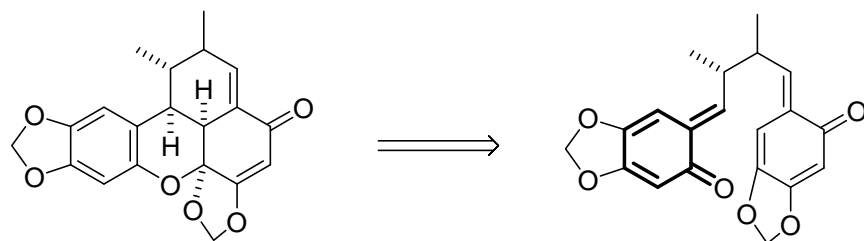
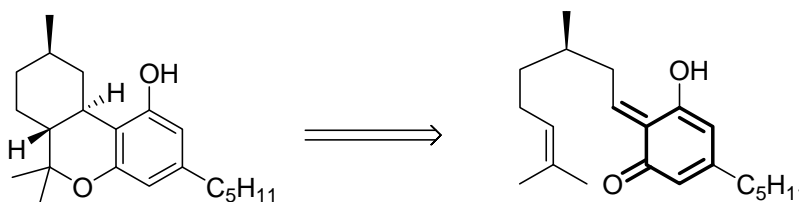


Figure 5. Examples of QM Antitumor Agents

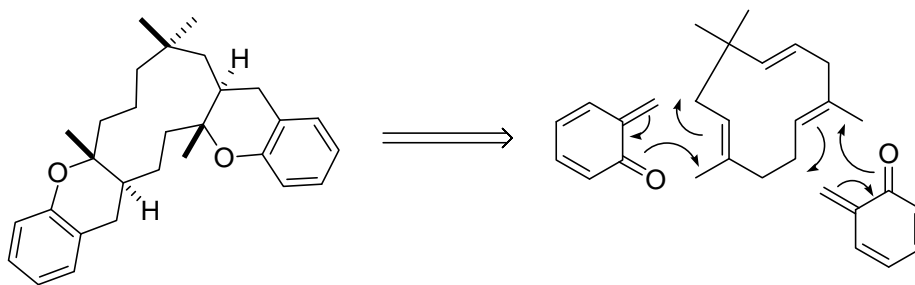
Another synthetically important role of *o*-QMs is their ability to act as dienes as well as dienophiles in [4+2]-cycloaddition reactions. This mode of reactivity has been showcased in the syntheses of carpanone,¹⁰ hexahydrocannabinol,¹¹ as well as lucidene and alboatrin.¹²



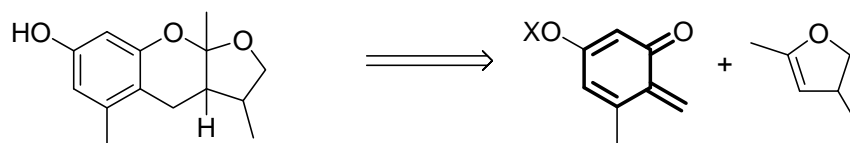
carpanone



(-)-hexahydrocannabinol



(±)-lucidene



(±)-alboatrin

Figure 6. Examples of natural product syntheses involving *o*-QM intermediates.

In general, *o*-QMs have reactivity that is similar to that of α,β -unsaturated ketones; however, reactions of *o*-QM derivatives are comparably much more facile due to aromatization of the product.

Transition Metal-Complexed Quinone Methides

As previously discussed, QMs are highly reactive to both nucleophiles and electrophiles and polymerize rapidly due to formation of aromatic phenol derivatives. As a result, isolation is usually difficult and examples of isolated organic QMs are rare.^{4,13} One strategy to stabilize this highly reactive class of compounds is through transition metal- π interactions. This can be achieved through coordination of the exocyclic methylene position as in compounds **2**¹⁴ and **3**.¹⁵

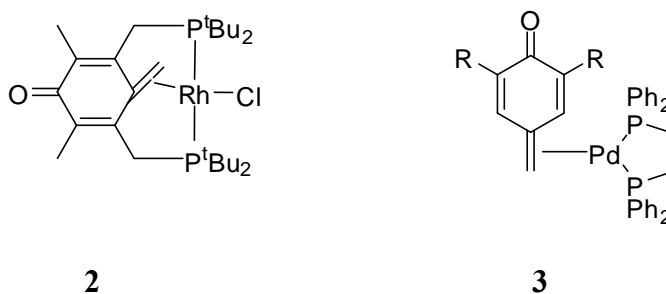


Figure 7. Metal-Complexed *p*-QMs.

The QM moiety in **2** is part of a PCP-type pincer ligand and is thus very strongly coordinated and essentially inert. Complex **3** on the other hand is solely coordinated through the exocyclic methylene. The complex is thermally stable, showing no signs of decomposition either in solution as well as in the solid state after storage under nitrogen atmosphere for a month. Even

after heating under reflux in aqueous methanol, **3** was recovered unchanged and no release of QM was observed. Controlled release of the QM moiety was achieved through ligand exchange with soft ligands - addition of dibenzylideneacetone led to immediate dissociation of QM, and somewhat slower release was observed upon addition of diphenylacetylene, whereas no free QM was detected upon addition of hard ligands such as pyridine or acetonitrile.

Amouri *et al.*¹⁶ have prepared several transition-metal complexed *o*-QM complexes, shown in Figure 8. These complexes are thermally stable, and notably do not exhibit any migration of the MCp* fragment to other double bonds.

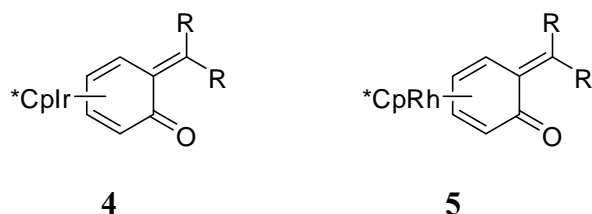
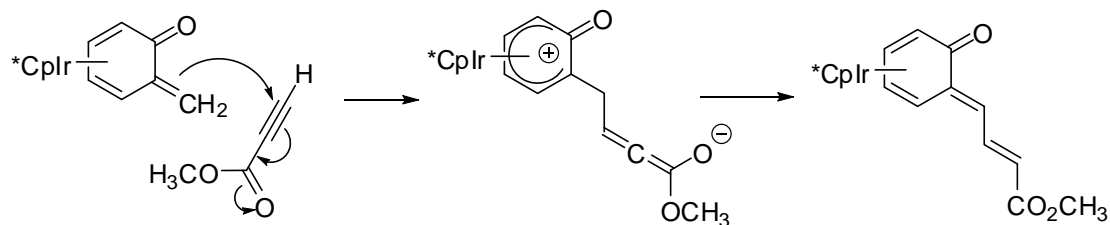


Figure 8. *o*-QM Complexes of Iridium and Rhodium.

Surprisingly, the exocyclic methylene of these complexed *o*-QMs exhibits nucleophilic character, as shown in Scheme 1. This is further confirmed by DFT calculations by Grotjahn *et al.*¹⁷ suggesting a partial negative charge on the exocyclic methylene of **4** and **5** when R is hydrogen; when R is methyl, however, natural bond order analysis suggested a partial positive charge, indicating that the substitution pattern of the QM moiety is highly relevant to the observed reactivity.

Scheme 1. Conjugate Addition of Ir-Complexed QM to an Electrophilic Alkyne.



Metal-Assisted Cyclization of η^5 -Pentadienyl Ligands and Hydroxyferrocenes

Transition metals can bind with the pentadienyl ligand in three different ways - in the monohapto form **6**, where the pentadienyl ligand is a simple alkyl group, or by incorporation of either one or both of the alkenes, giving rise to the trihapto form **7** (comparable to an allyl group), and the pentahapto form **8**. Due to the additional olefin attachment, the pentadienyl ligand is a better chelating ligand than the allyl ligand, thus imparting higher thermal stability.¹⁸

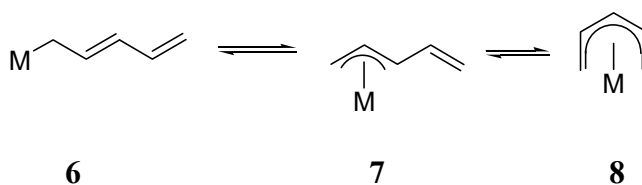
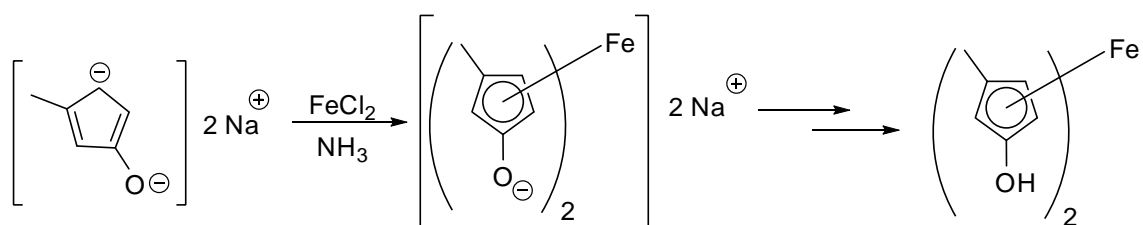


Figure 9. Hapticities of metal-pentadienyl complexes.

These metal-bound pentadienyl systems can undergo thermal electrocyclic ring closure, as shown by Kirss,¹⁹ as well as photolytic ring closure, as demonstrated by Stone *et al.*²⁰

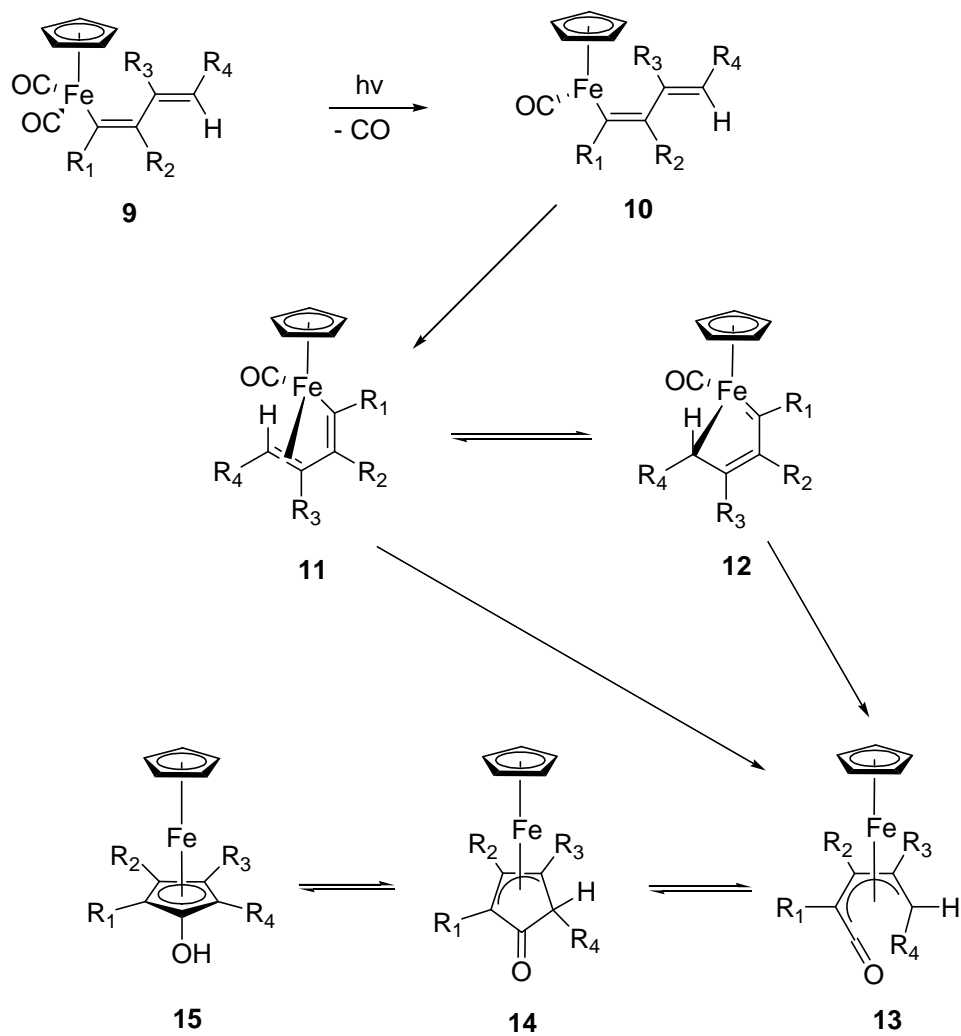
Further functionalization of the resulting cyclopentadienyl systems provides access to hydroxyferrocenes, an organometallic structural analog to phenol. Benson *et al.* first synthesized ferrocene derivatives bearing a hydroxyl group on the cyclopentadienyl ligand by treatment of ferrocene derivatives bearing a hydroxyl group on the cyclopentadienyl ligand by treatment of iron (II) chloride with disodium hydroxycyclopentadiene, followed treatment with benzoyl chloride and subsequent alkaline hydrolysis of the resulting dibenzoate,²¹ as shown in Scheme 2.

Scheme 2. Synthesis of Methylhydroxyferrocene.

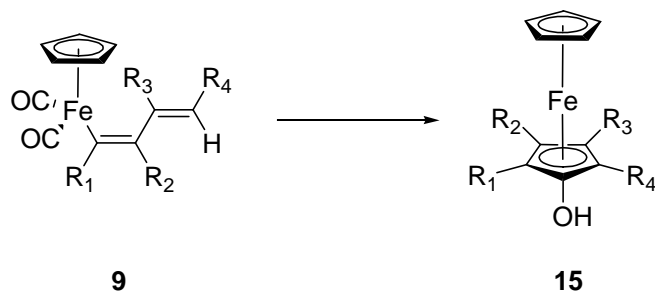


More recently, Allison *et al.* published the synthesis of hydroxyferrocenes *via* rapid electrocyclic ring closure of iron pentadienyl complexes.^{22,23} These pentadienyl complexes were accessed *via* photochemical loss of carbonyl from (η^1 -butadienyl) cyclopentadienyl dicarbonyl iron to give **11** and **12**, followed by either an alkyl migration/CO insertion from **11** or CO-carbene ligand coupling^{23,24} to the pentadienyl complex **13**, as shown in Scheme 3. This complex then underwent electrocyclic ring closure to form hydroxyferrocene **15**.²⁵

Scheme 3. Electrocyclic Ring Closure of a (η^1 -Butadienyl)iron Complex.



This pathway provides a high yielding and versatile approach to hydroxyferrocenes. A number of derivatives have been prepared in near quantitative yields, as shown in Table 1.

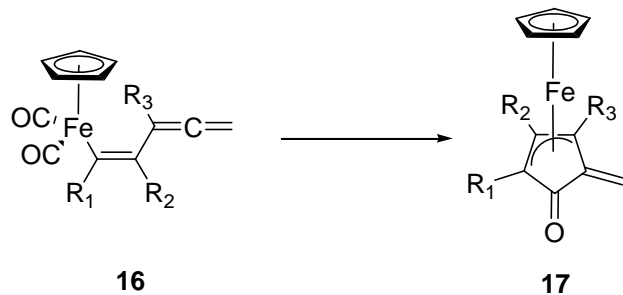


R₁	R₂	R₃	R₄	% Yield
H	H	H	CH ₃	95
H	H	H	Ph	95
Ph	H	H	Ph	99
-CH ₂ CH ₂ CH ₂ -		H	H	99
-CH ₂ CH ₂ CH ₂ -		H	Ph	99
-CH ₂ CH ₂ CH ₂ CH ₂ -		H	H	99
-CH ₂ CH ₂ CH ₂ CH ₂ -		H	Ph	99

Table 1. Cyclization of various Fp-butadienes.

Given the apparent flexibility in substitution of the butadiene moiety, one can imagine that cyclization of a corresponding vinyl allene would lead to compound **17**, a metal complexed *ortho*-quinone methide analog comparable to **1**.

Scheme 4. Route to *o*-Quinone Methide Analog **17**.



It is our hope that derivatives of **17** will mimic the reactivity of quinone methides and allow control of the reactivity via the transition metal and its ligands.

π -Allylic Cyclic Ketones

There are examples in the literature of cyclizations of metal complexed allenes to give π -allylic cyclic ketones.²⁶ Welker *et al.* reported the synthesis of molybdenum alkylidene cyclobutanoyl complex from an allenyl tosylate as shown in Figure **11**.

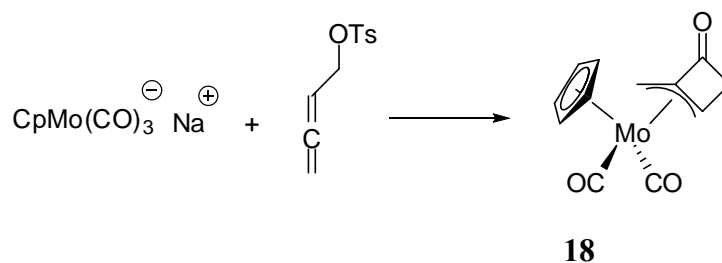


Figure 11. Synthesis of Molybdenum Alkylidene Complex **18**.

This reaction is thought to proceed via an S_N2 -reaction of the metal anion with the allenyl tosylate, followed by an alkyl migration and subsequent alkene insertion to give **18** (Figure **12**).

change in the partial charge present at that position; benzannulation of the cyclopentenone is likely to decrease the driving force towards aromaticity upon reaction of the QM analog with nucleophiles; and the choice of transition metal may inhibit reactivity.

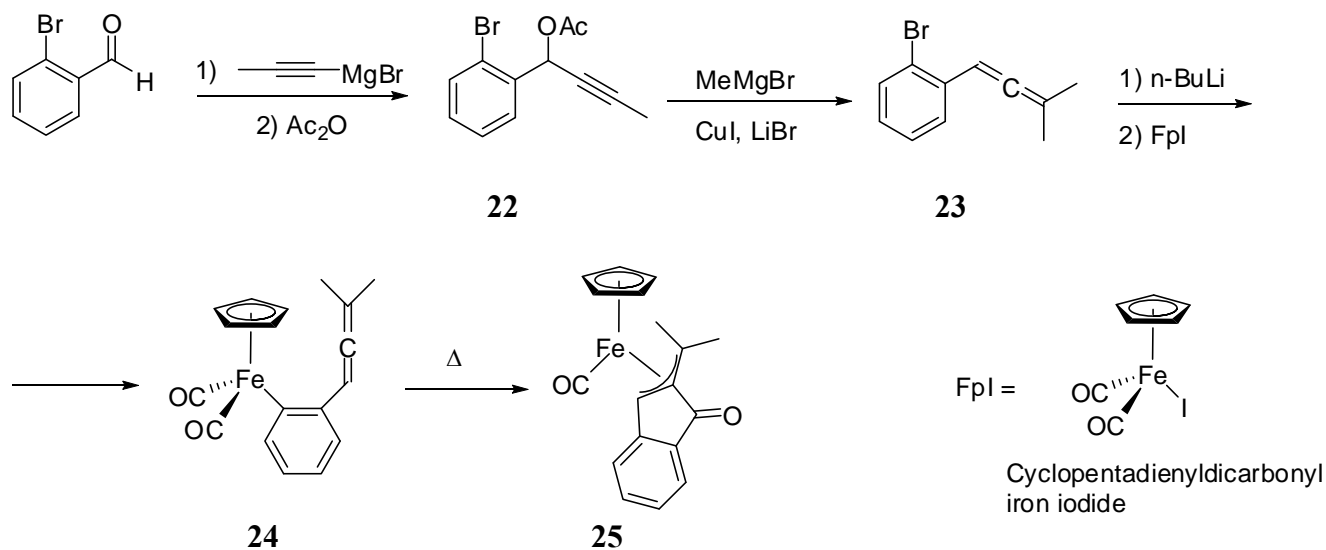


Figure 14. Synthesis of Iron-Complexed QM Analog **25**.

In an attempt to remove the stabilization imparted to the QM analog by benzannulation of the vinyl allene, bromocyclopentyl allene **26** was prepared and treated with FpI as before.²⁸ However, the desired σ -complex **27** was not isolated.

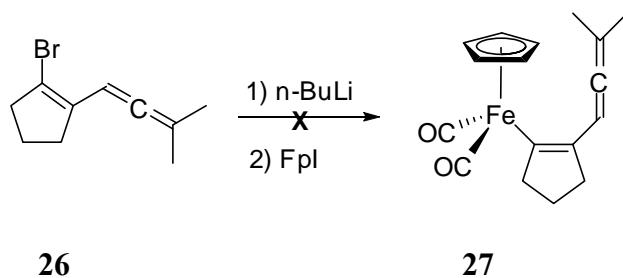


Figure 15. Attempted Synthesis of **27**.

In order to understand this in the light of the previously discussed butadiene chemistry (Scheme 2), one has to consider the three possible pathways towards the desired σ -complexes - an associative S_N2 pathway, a dissociative S_N1 pathway,²⁹ or an attack of a metal carbonyl with subsequent alkyl migration, as discussed in Figure 16.

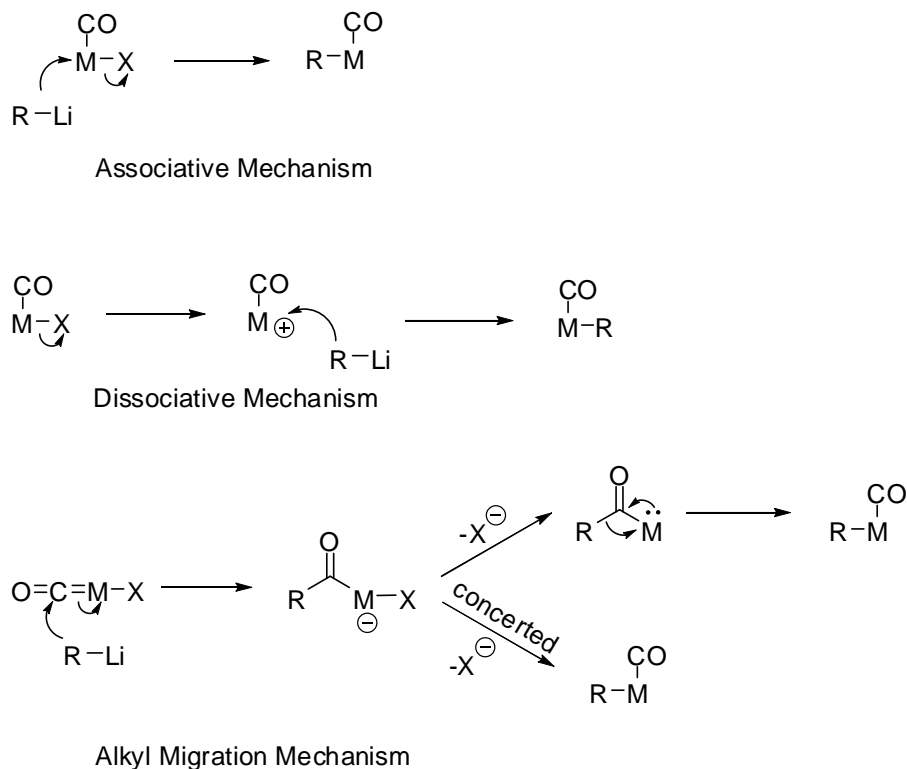
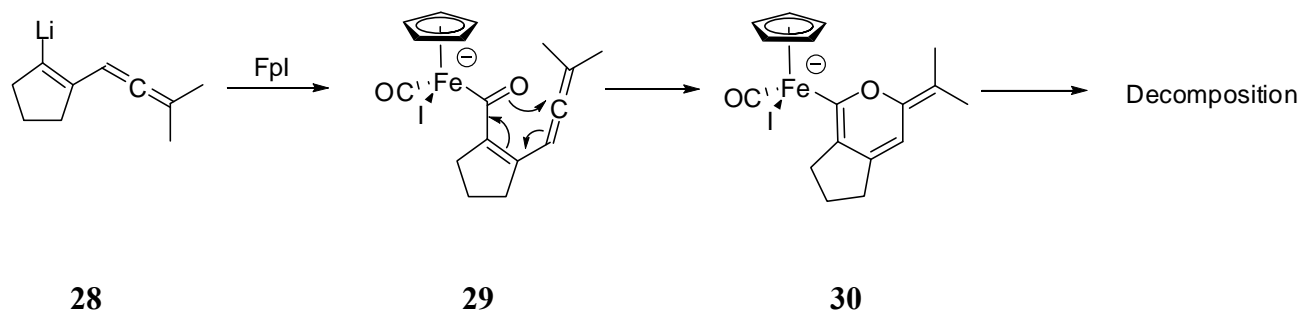


Figure 16. Nucleophilic Substitution Mechanisms for Metal Carbonyl Halides.

In previous work in the Allison group²² (Table 1), FpI was treated with several substituted lithiobutadienes, including two where the butadiene moiety was annulated with a 5-membered ring, resulting in excellent yields of the desired hydroxyferrocenes. Thus, if the formation of **27** went through a direct substitution mechanism, one would expect successful formation of the desired σ -complex analogously to entries 4 and 5 in Table 1. If the substitution

occurs through initial attack of a carbonyl ligand, an undesired electrocyclic ring closure of acyl complex **29** to form **30** may be taking place (Scheme 5).

Scheme 5. Possible Electrocyclic Ring Closure of Acyl Complex **29**.



While **30** was never isolated, computational studies³⁰ on model systems utilizing the GAMESS 6-21G basis set at a B3LYP level of theory revealed that while this cyclization is slightly disfavored for the model butadiene system, the cyclization of the model vinyl allene system is favored by nearly 20 kcal/mol; the results of these calculations are shown in Figure 17.

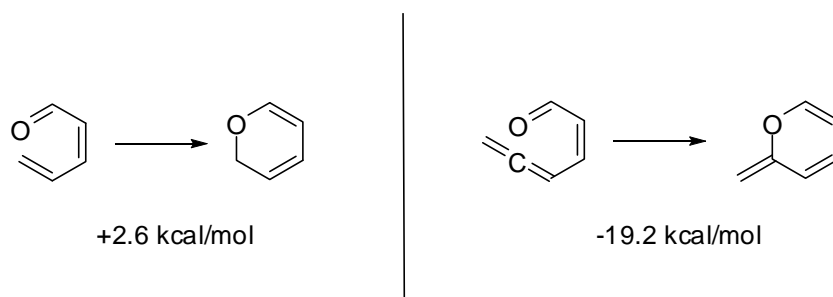


Figure 17. Cyclization of Acyl Butadiene and Acyl Vinylallene.

Vinyl Allenes from Carbene-Carbene Rearrangements

To circumvent the above mentioned undesired electrocyclic ring closure, the vinyl allene moiety would have to be generated after the formation of the desired metal σ -complex.

Skatteboel³¹ and Brinker³² have demonstrated that vinyl cyclopropylidenes can rearrange to give vinyl allenenes, as shown in Figure 18.

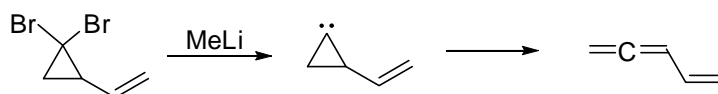


Figure 18. Vinyl Allene from Carbene-carbene Rearrangement.

By attaching a vinyl cyclopropane to FpI and subsequently generating the vinyl allene by carbene-allene rearrangement, formation of σ -complex **33** can occur without the undesired pyran formation shown in Scheme 5.³³ With this in hand, synthesis of **34** was proposed as outlined in Figure 19.

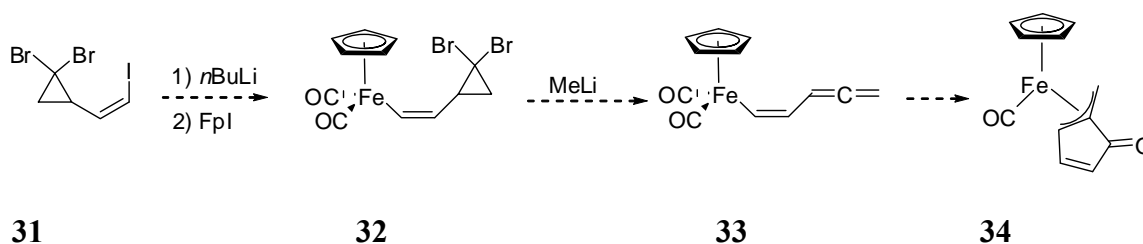


Figure 19. Proposed Synthesis of Vinyl Allene σ -Complex **33**.

Unfortunately, in previous attempts in our group,³³ **32** was never isolated, presumably due to preferred lithium-halogen exchange on the cyclopropyl dibromide over the vinyl iodide.

Thus, alternate mild pathways to generate cyclopropyl carbenes using alternative synthons would be desirable.

Carbenes by Elimination of α -Halosilanes

There are a few examples in the literature of reactions that appear to generate carbenes by elimination of α -halosilanes. Hoffmann and Reiffen showed that trimethylsilyltropylium tetrafluoroborate dimerizes or undergoes cyclopropanation upon treatment with fluoride.³⁴ More recently, Cunico and Zhang observed cyclopropanation when trichloromethyl trimethyl silane was treated with cesium fluoride in the presence of an electron-deficient alkene.³⁵ These examples are summarized in Figure 20.

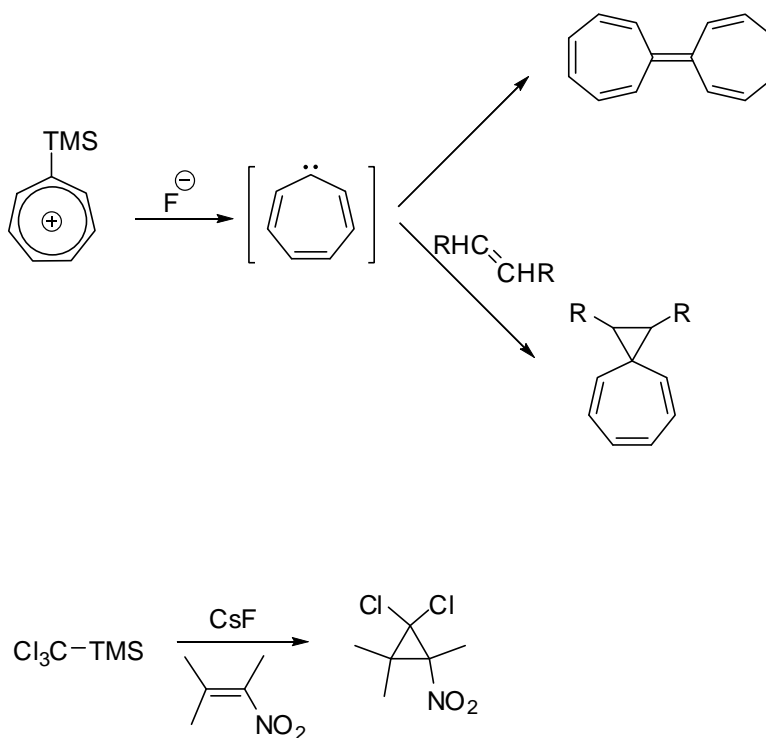


Figure 20. Examples of Carbenes from α -Halosilanes.

There are also examples of eliminations of benzylic α -halosilanes and subsequent cyclopropanation, dimerization, and cycloaddition reactions; however, in these cases there is some debate about carbene intermediacy. Beak *et al.*³⁶ proposes that cyclization of **34** upon treatment with cesium fluoride to give isobenzofuran **36** is consistent with intermediacy of the benzylic carbene **35** (Figure 21).

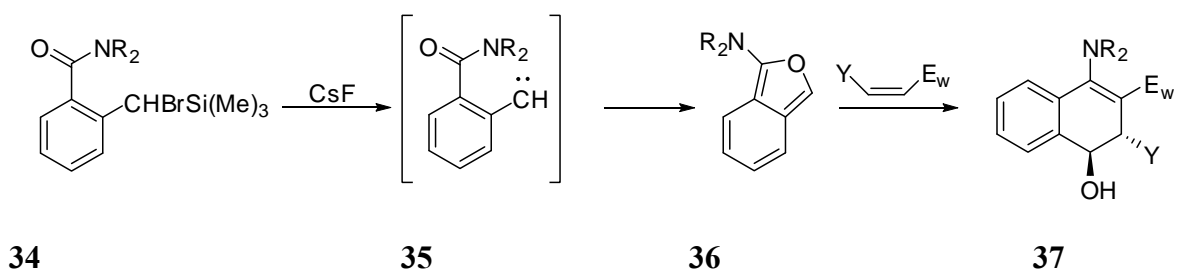
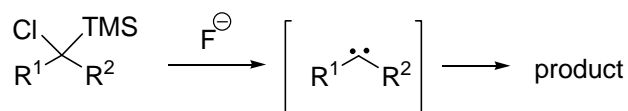


Figure 21. Synthesis of Isobenzofurans by Trapping of Benzylic Carbenes.

Kessar *et al.* argue against carbene intermediacy.³⁷ While they successfully observed dimerization, epoxidation and cyclopropanation reactions (shown in table 2), they did not observe intramolecular trapping of a benzylic carbene by an ancillary carboxymethyl group, as suggested by Beak.³⁶



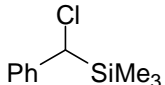
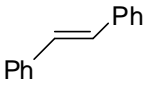
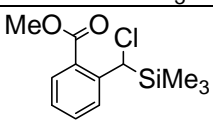
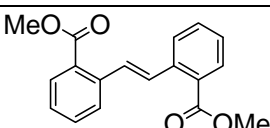
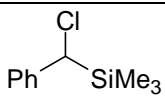
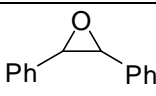
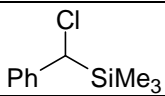
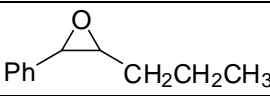
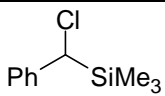
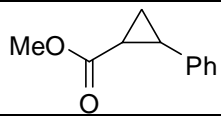
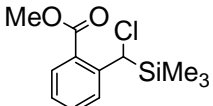
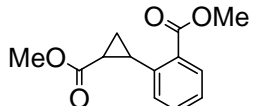
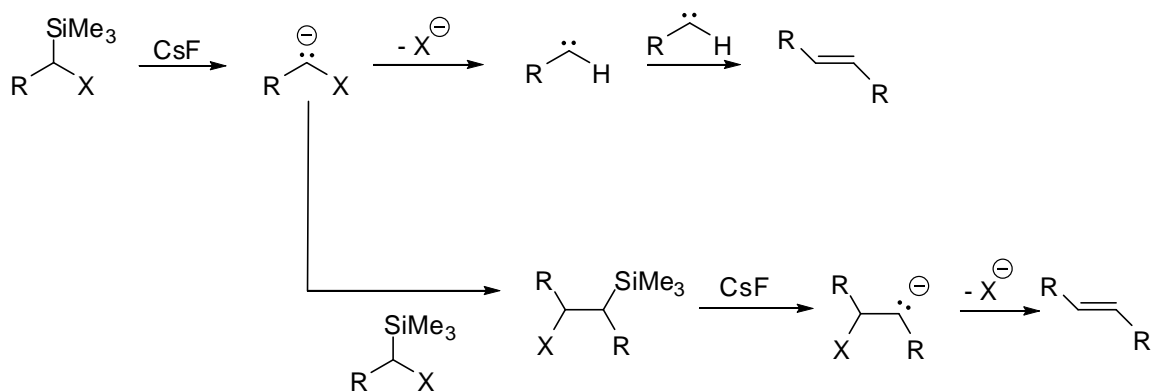
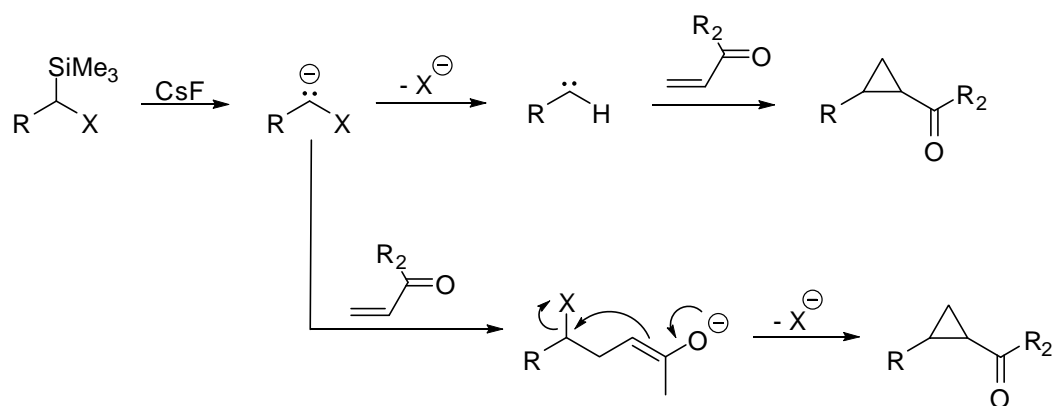
Reactant	Additive	Product	Yield
			89%
			76%
	C ₆ H ₅ CHO		87%
	CH ₃ CH ₂ CH ₂ CHO		60%
	CH ₂ =CHCO ₂ Me		59%
	CH ₂ =CHCO ₂ Me		54%

Table 2. Synthesis of Stilbenes, Epoxides, and Cyclopropanes.

Instead of carbenes being formed, Kessar suggests a stepwise mechanism of anion generation through desilylation, followed by nucleophilic attack of a halide and subsequent elimination to account for the dimerization products; similarly, Kessar proposes cycloaddition of a benzylic anion onto an alkene to form the observed cyclopropanes and epoxides. These mechanisms are summarized in Figure 22.



Dimerization Mechanisms



Cyclopropanation Mechanisms

Figure 22. Potential Dimerization and Cyclopropanation Mechanisms.

In summary, we set out to mimic the reactivity of organic quinone methides with 5-membered ring transition metal complexes such as **1**. Iron complex **25** (which was previously synthesized in our group) did not exhibit the expected reactivity; thus, we plan to increase the drive towards aromaticity by removing benzannulation. In order to accomplish this, we hope to use fluoride-promoted elimination of α -halosilanes to generate vinyl cyclopropyl carbenes, which we then envision to undergo a carbene-allene rearrangement followed by metal-assisted cyclization to give the title compound.

RESULTS AND DISCUSSIONS

Attempted Synthesis of Rhenium and Manganese *o*-QM Analogs

One goal of complexed quinone methide analog chemistry is to control the reactivity of the quinone methide moiety. In the case of iron complex **25**, this was accomplished since it is unreactive towards nucleophilic substitution at the exocyclic methylene position. In an attempt to further study transition metal control of this ligand, our approach was to synthesize manganese and rhenium analogs of **25**.

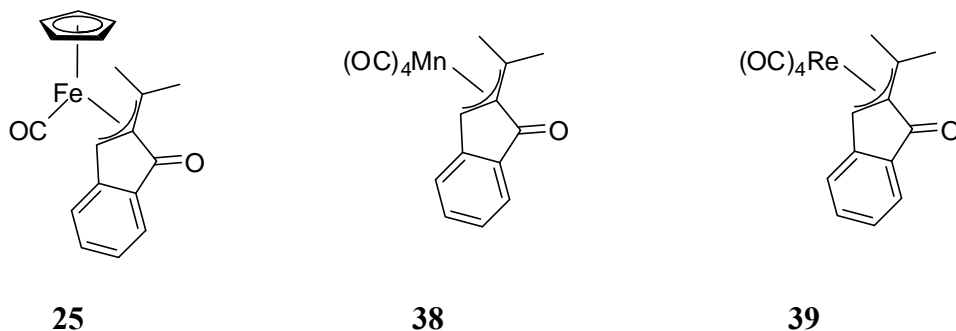
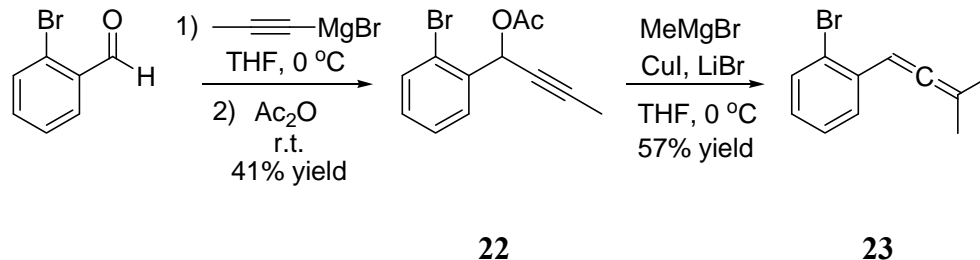


Figure 23. Manganese and Rhenium Analogs of **25**.

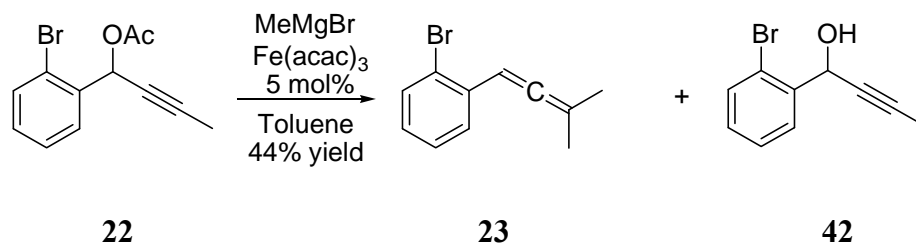
Synthesis of the corresponding Mn and Re σ -complexes **41** was successful as shown in Scheme 8. *o*-Bromobenzaldehyde was treated with propynylmagnesium bromide to give propargyl acetate **22**, which was further reacted with methylmagnesium bromide, cuprous iodide and lithium bromide to give benzylic allene **23** in 57% yield. The two terminal methyl groups on the allene had a ¹H chemical shift of 1.82 (d, 6H, *J* = 2.9 Hz) and a ¹³C chemical shift of 20.8. The benzylic hydrogen has an absorption of 6.39 (sep, 1H, *J* = 2.9 Hz), the sp² allene carbons have shifts of 92.0 and 100.2, whereas the central carbon of the allene has a resonance of 204.8.

Scheme 6. Synthesis of Allene **23** from Bromobenzaldehyde.



Alternatively, **23** can be synthesized from acetate **22** by reaction of the acetate with methylmagnesium bromide and catalytic tris(acetylacetonato)iron(III) in 44% yield,³⁸ however, formation of significant amounts of benzylic propargyl alcohol **42** could not be avoided (Scheme 7).

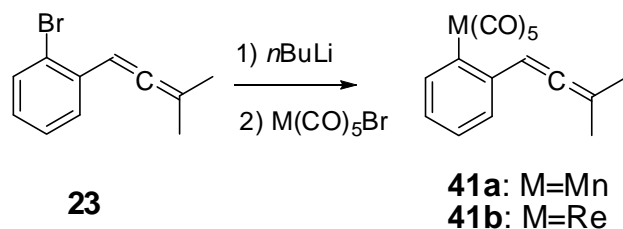
Scheme 7. Formation of Allene **23** with catalytic $\text{Fe}(\text{acac})_3$.



Lithium-halogen exchange of the bromide on **23** with butyllithium followed by quench with the respective metal pentacarbonyl bromide (prepared by literature methods)³⁹ provided the desired σ -complexes **41a** and **41b**. For both allene σ -complexes, the septet corresponding to the benzylic allene proton shifted upfield by about 0.4 ppm - to 5.970 ppm for manganese complex **41a** and 5.975 ppm for rhenium complex **41b**. The terminal methyl protons did not move significantly as expected, with chemical shifts of 1.812 ppm for **41a** and 1.813 ppm for **41b**. The upfield shift of the benzylic position while maintaining the long-range coupling to the terminal

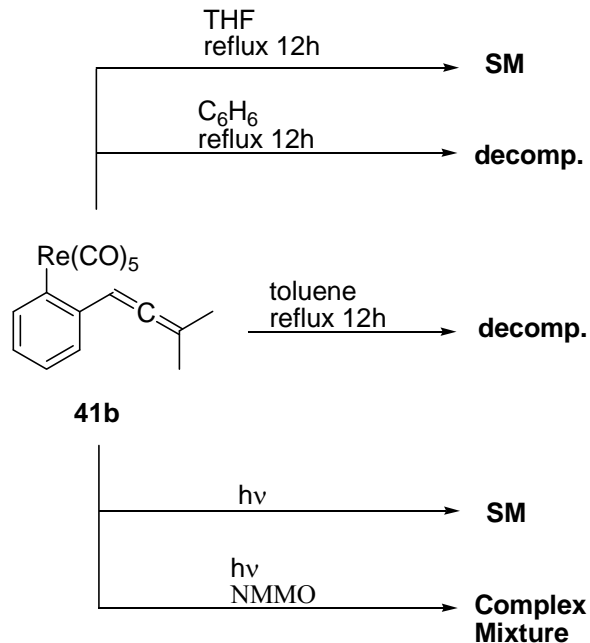
methyl protons indicates that carbonyl insertion has not yet occurred, since coordination of the metal to the allene would be expected to affect the terminal methyl protons as well as the splitting across the allene.

Scheme 8. Synthesis of Manganese and Rhenium σ -Complexes.



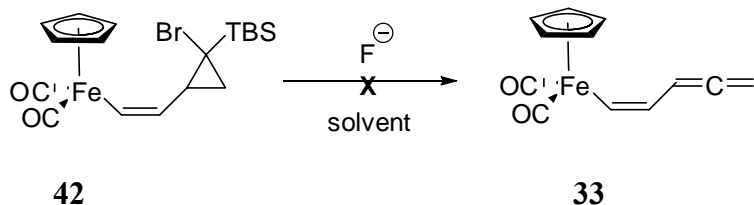
Unfortunately, carbonyl insertion and cyclization to the desired π -allyl complexes **38** and **39** was not accomplished. Manganese complex **41a** rapidly decomposed even under rigorously inert atmosphere; however, new peaks in the $^1\text{H-NMR}$ around 3.5 ppm and ^{13}C signals of 65.8 and 68.0 are consistent with formation of a manganese π -allyl complex. Cyclization of Rhenium complex **41b** to **39** was unsuccessful. When **41b** was refluxed for 12 hours in THF, only starting material was isolated; reflux in higher-boiling solvents such as benzene or toluene lead to decomposition. Neither ambient light photolysis nor irradiation with a broad spectrum UV lamp lead to **39**. Lastly, photolysis in the presence of *N*-methylmorpholine-*N*-oxide - a reagent known to remove carbonyl ligands by oxidation and subsequent loss of CO_2 ⁴⁰ - lead to a complex mixture of products with a proton NMR signal consistent with formation of a π -allyl complex; however, the mixture decomposed upon attempted purification by silica gel chromatography.

Scheme 7. Cyclization Attempts of 41b to 39.



Attempted Synthesis of Vinyl Allenes

A parallel study to generate quinone methide analogs was pursued by Beuterbaugh and Allison.³³ Since they found that the preparation of dibromocyclopropyl complex **32** to yield the corresponding cyclopropyl carbene and subsequently vinyl allene complex **33** was unsuccessful, it was thought that elimination of α -halosilanes may be an alternate way of generating vinyl cyclopropyl carbenes under mild conditions. In their hands, as shown in table **3**, this approach resulted only in apparent protonolysis of the silyl group.³³

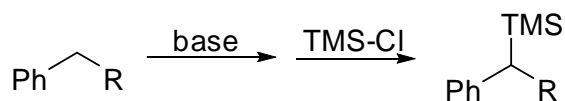


Compound	Fluoride	Solvent	Temperature	33 Observed
42	TBAF	THF	r.t.	no
42	TASF	THF	-78 °C	no
42	TASF	THF	0 °C	no
42	TASF	THF	r.t.	no
42	TASF	CH ₃ CN	r.t.	no

Table 3. Attempted Synthesis of Allene **33** from **42**.

In order to investigate why allene complex **33** was not isolated, we decided to study model systems containing the α -brosilyl motif for the crucial α -elimination step. Observation of protonolysis of the cyclopropyl silanes even under rigorously anhydrous reaction conditions lead us to the assumption that formation of the anion upon desilylation is thought to be the rate determining step; thus, stabilization of that anion was initially targeted as an approach to successfully generate carbenes. As an initial model system, (bromodiphenylmethyl)-trimethylsilane **43** was synthesized from diphenylmethane. Silylation of diphenylmethane proved to be challenging initially. Treatment with *n*-BuLi in THF at -78 °C for 2 hours, followed by quenching with chlorotrimethylsilane only gave 3% of the desired product **44**. When 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (DMPU), which has been shown to improve kinetic basicity of butyllithiums,⁴¹ was used as an additive in 3 equivalents under the same conditions, the yield improved to 10%. When the experiment was repeated at -10 °C and 0 °C,

the yield improved to 66% and 92%, respectively; there was no significant improvement when DMPU or *N,N,N',N'*-tetramethylethylenediamine (TMEDA) additives were employed at these higher temperatures. The same trends were observed for silylation of toluene; however, the yields were much lower, prompting us to purchase benzyltrimethylsilane instead. These results are summarized in Table 4.

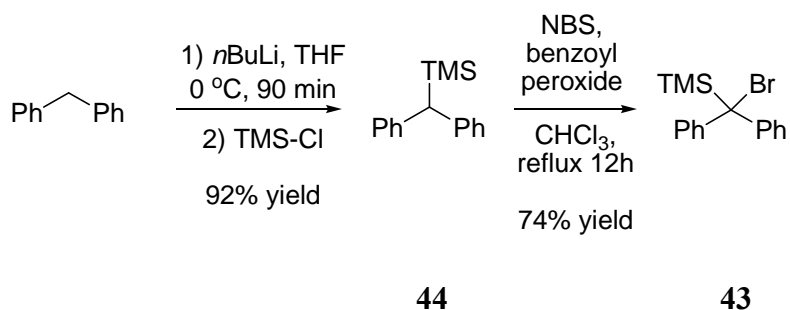


Compound	Base	Additive	Temperature (°C)	Yield
Toluene	<i>n</i> BuLi	-	-78	trace
Toluene	<i>s</i> BuLi	-	-78	3%
Toluene	<i>s</i> BuLi	TMEDA (3 eq)	-78	5%
Toluene	<i>s</i> BuLi	TMEDA (3 eq)	-10	23%
Toluene	<i>s</i> BuLi	-	-10	26%
Diphenylmethane	<i>n</i> BuLi	-	-78	3%
Diphenylmethane	<i>n</i> BuLi	DMPU (3 eq)	-78	10%
Diphenylmethane	<i>n</i> BuLi	-	-10	66%
Diphenylmethane	<i>n</i> BuLi	DMPU (3 eq)	-10	60%
Diphenylmethane	<i>n</i> BuLi	-	0	92%
Diphenylmethane	<i>n</i> BuLi	DMPU (3 eq)	0	86%
Diphenylmethane	<i>n</i> BuLi	TMEDA (3 eq)	0	88%

Table 4. Silylation of Toluene and Diphenylmethane.

Ultimately, diphenylmethane was treated with *n*-butyllithium at 0 °C for 90 minutes, followed by quench with chlorotrimethylsilane to give **44** in 92% yield. The resulting (diphenylmethyl)trimethylsilane was then brominated with NBS to obtain the desired model **43** in 74% yield as shown in Scheme 10.

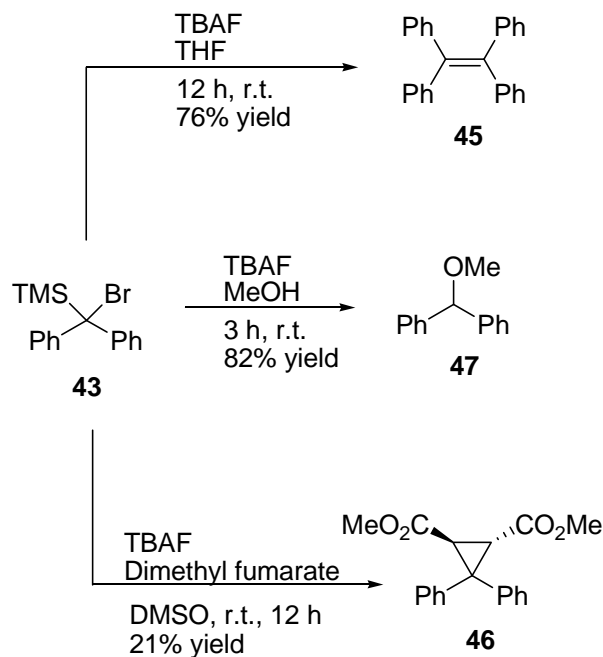
Scheme 10. Synthesis of (Bromodiphenylmethyl)trimethylsilane **43**.



When compound **43** was then treated with TBAF in DMSO at room temperature, dimerization to tetraphenylethylene was observed by comparison to known spectra (Scheme 11). This reaction could have occurred by a simple carbene-carbene dimerization, or, as previously discussed in Figure 20, through a stepwise mechanism of desilylation, nucleophilic substitution and β -elimination. Furthermore, **43** was reacted with TBAF in the presence of dimethyl fumarate to afford cyclopropanation. The desired *trans*-cyclopropane **46** was isolated in 21% yield and identified by comparison to previously published data; the absence of the *cis*-cyclopropane points to a carbene mechanism. Lastly, **43** was treated with TBAF in methanol to see whether the proposed carbene would undergo O-H insertion. The resulting benzhydryl methyl ether **47** was formed in 82% yield. Again, two mechanisms could be at play - carbene O-H insertion, or an S_{N}^1 -type mechanism, initiated by formation of a dibenzylic carbocation upon loss of bromide,

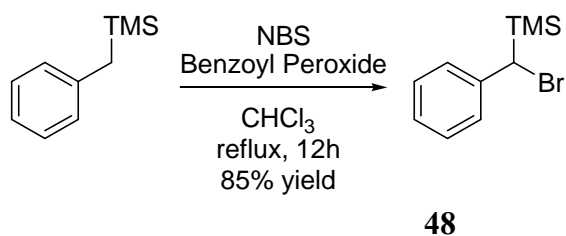
followed by nucleophilic attack of methanol and subsequent desilylation with TBAF. These results are summarized in Scheme 11.

Scheme 11. Trapping of Diphenylcarbene.



The benzylic α -bromosilane **48** was generated by free radical bromination. Benzyltrimethylsilane was refluxed with *N*-bromosuccinimide in chloroform, using benzoyl peroxide as a radical initiator, giving **48** in 53% yield (Scheme 12).

Scheme 12. Bromination of Benzyltrimethylsilane.



When **48** was reacted with TBAF in DMSO, the resulting carbene dimerized to *trans*-stilbene **49** in 49% yield. It appears that a solvent with a high dielectric constant is essential for this reaction, as previously noted by Kessar *et al.*³⁷ As previously discussed, this dimerization could proceed through a carbene intermediate, or follow an ionic mechanism, as shown in figure **20**.

When the same carbene was trapped with dimethyl fumarate, the corresponding *trans*-cyclopropane **50** was formed in 23% yield. The NMR matched previously published spectra⁴² for *trans*-dimethyl 3-phenylcyclopropane-1,2-dicarboxylate. While a stepwise mechanism such as the one shown in Figure **24** may be involved, the absence of any *cis* product strongly suggests a carbene mechanism.

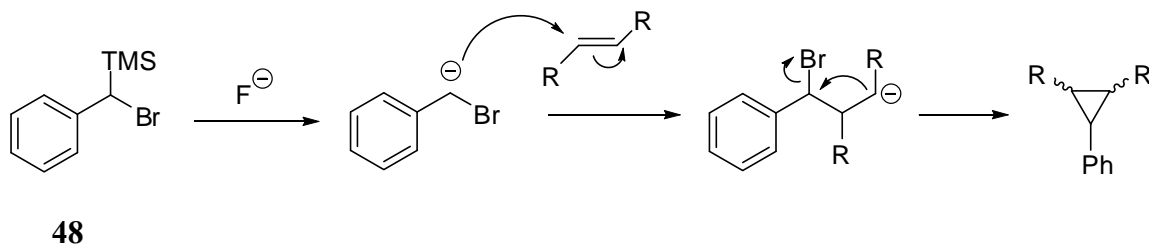


Figure 24. Alternate Stepwise Cyclopropanation Mechanism.

Generation of the carbene intermediate in methanol resulted in O-H insertion, generating benzyl methyl ether **51** in 88% yield; proton and carbon NMR data matched previously published spectra.⁴³ Even though O-H insertion is a well documented reaction pathway of carbenes,⁴⁴ there is again the possibility for an alternate mechanism to form **51**. Dissociation of bromine would generate a benzylic carbocation which would be trapped by methanol, yielding silyl ether **52**; desilylation of **52** with TBAF would then lead to benzyl methyl ether **51**, as illustrated in figure 25.

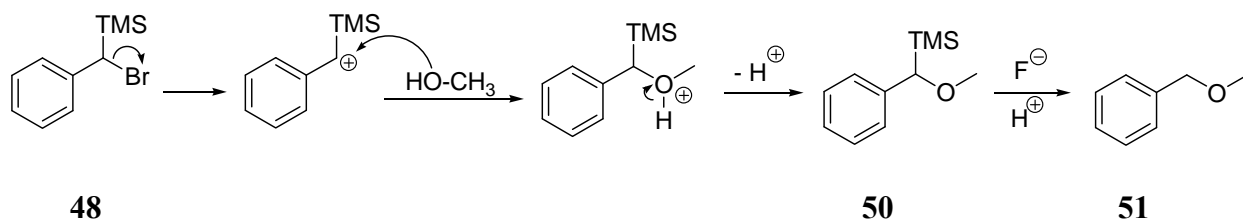
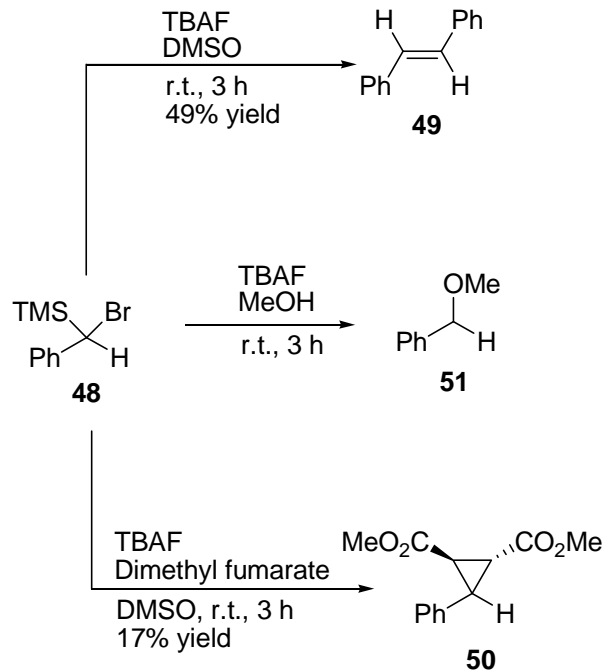


Figure 25. Alternate Pathway to Benzyl Methyl Ether.

Scheme 13. Trapping of Phenylcarbene.



In an effort to elucidate the mechanism, **48** was treated with TBAF in a solution of benzyl bromide. Only stilbene was isolated, consistent with α -elimination to a carbene followed by carbene-carbene dimerization. No evidence of formation of 1-bromo-1,2-diphenylethane (**53**), which would be formed as illustrated in Figure **26**, was found.

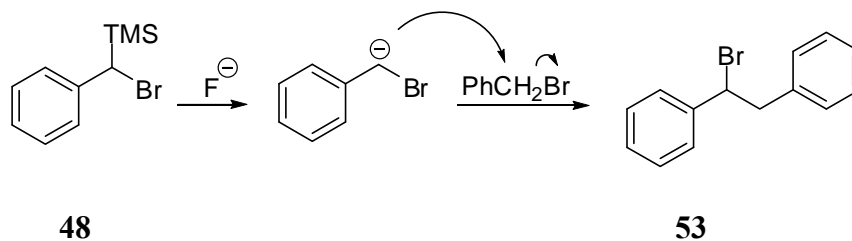
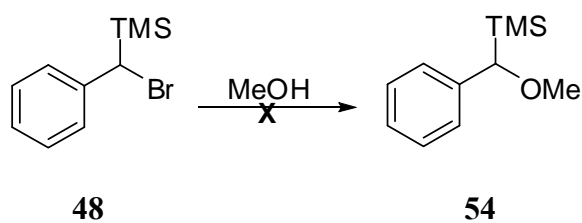


Figure 26. Proposed Formation of **53**.

Also, as illustrated in Figure 25, O-H insertion could occur by a substitution mechanism. In order to rule this out, **48** was allowed to stir in methanol without addition of a fluoride source. The substitution mechanism would then presumably result in formation of silyl ether **54** (Scheme 14). Aliquots were taken at 15 minutes, 1 hour, and 3 hours and analyzed by GCMS and ¹H-NMR; **54** was not isolated, strongly suggesting O-H insertion of a benzylic carbene.

Scheme 14. O-H insertion Control Experiment.



Ionic Liquids as Solvents for Carbene Generation

It appears that stabilization of the anion resulting from desilylation is crucial to formation of the reactive carbene species, as illustrated by the successful generation of mono- and dibenzylic carbenes from **43** and **48**, while reaction of cyclopropyl α -bromosilanes resulted only in protodesilylation. Use of high dielectric solvents such as DMSO was shown to assist in carbene generation;³⁷ ionic liquids⁴⁵ such as 1-butyl-3-methylimidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium *n*-octylsulfate or 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl) imide are a highly polar solvent that may improve stabilization for polar intermediates (Figure 27).

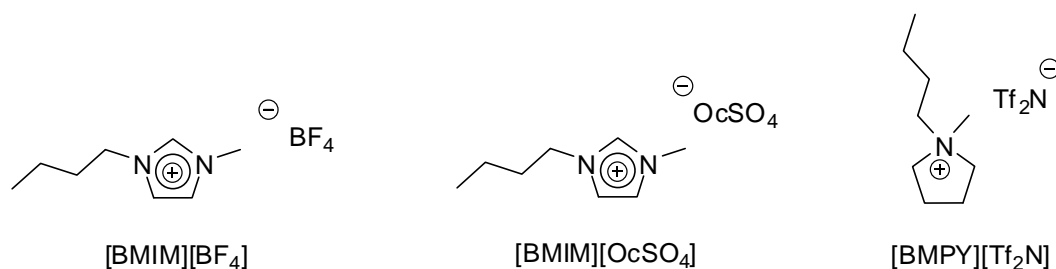
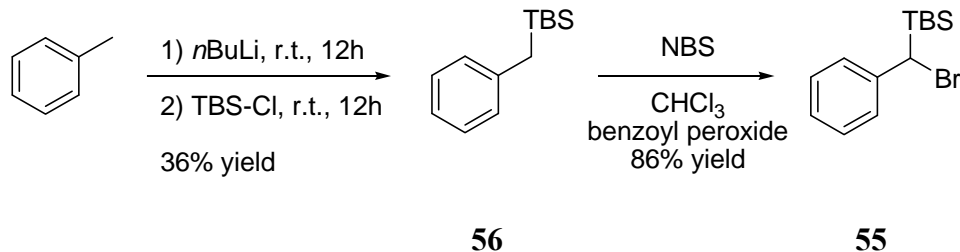


Figure 27. Some Examples of Ionic Liquids.

In particular, solvatochromic measurements have revealed that ionic liquids in general possess significantly higher polarities than traditional organic solvents.⁴⁶ Their highly ordered structure affects solvation in a much more complex way than by the traditional solubility principles. Some studies suggest that the three-dimensional structure of the salts contain holes in which solute molecules may be accommodated with little regard to polarity.⁴⁷ Ionic liquids have been demonstrated to cause a notable change in reactivity compared to traditional solvents. Wasserscheid *et al.* have shown that carbon-halogen bond cleavage in the 9-chloroanthracene radical anion accelerates significantly due to ion pairing between the cation of the ionic liquid and the small leaving ion.⁴⁸

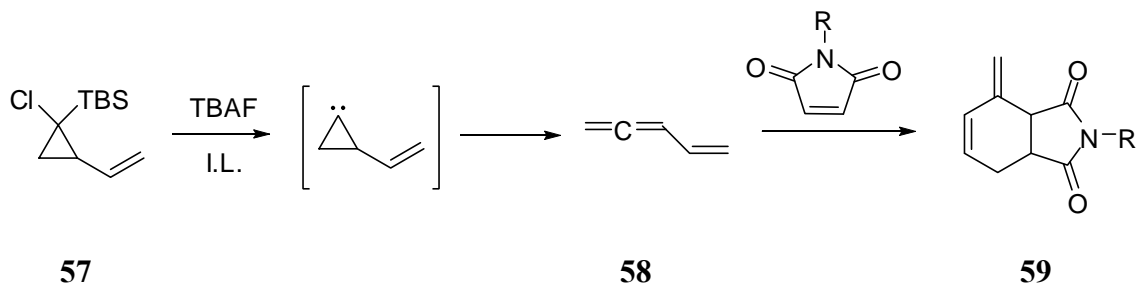
With this information in hand, we decided to investigate generation of carbenes by elimination α -bromosilanes in ionic liquids; the additional stabilizing interaction between the ionic liquid and the anion generated by desilylation was thought to allow us to expand the scope of this reaction to aliphatic and cyclopropyl carbenes. Bromosilanes were treated with different fluoride sources in ionic liquid solutions; **55** was prepared by lithiation of toluene at room temperature followed by quench with *tert*-butyldimethylsilyl chloride and subsequent NBS bromination (Scheme 15).

Scheme 15. Synthesis of (1-Bromo-1-phenylmethyl)-*tert*-butyldimethylsilane.



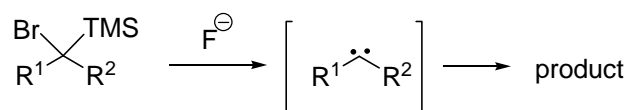
Vinyl cyclopropane **57** was provided by Aaron Beuterbaugh. It was envisioned that generation of the cyclopropyl carbene would lead to vinyl allene **58**, which could then be directly observed or trapped by a suitable dienophile as illustrated in Scheme 16.

Scheme 16. Attempted Generation of Vinylcyclopropyl Carbene.



Solubilizing of all organic reagents as well as the fluoride sources in the selected ionic liquids proved challenging. Only starting material was observed when cesium fluoride was used as the fluoride source since the solubility of CsF in any of the ionic liquids used was negligible. Some success was achieved when using TBAF as a fluoride source, but the desired products were only isolated in trace amounts, presumably due to both low solubility as well as intrinsically lower diffusion in ionic liquids as a result of their viscosity.⁴⁹ When the cyclopropyl

carbene precursor **57** was treated with TBAF in [BMIM][BF₄], no evidence of a carbene-allene rearrangement was observed. These results are summarized in Table 5.



S.M.	Solvent	Additive	Fluoride	Product	Yield
48	[BMIM][BF ₄]	-	CsF	S.M.	-
48	[BMIM][BF ₄]	-	TBAF	49	trace
48	[BMIM][OcSO ₄]	-	CsF	S.M.	-
55	[BMIM][BF ₄]	-	TBAF	49	trace
55	[BMIM][BF ₄]	dimethyl fumarate	TBAF	50	trace
57	[BMIM][BF ₄]	-	TBAF	Complex mixture	-
57	[BMIM][BF ₄]	4-Phenylazo- maleinanil	TBAF	Complex mixture	-

Table 5. Attempts to Generate Carbenes in Ionic Liquid Solvents.

Conclusion

Manganese and Rhenium sigma complexes **41a** and **41b** have been synthesized. While cyclization to the desired π -allyl quinone methide analog complexes was not achieved, **41a** and **41b** represent key intermediates in the further study of these systems. Furthermore, a study of generating carbenes under mild conditions by elimination of α -halosilanes was performed with the intent to apply this methodology to the synthesis of more reactive iron-complexed 5-membered ring quinone methide analogs. Evidence for carbene intermediacy was found for mono- and dibenzylic systems **43** and **48**.

EXPERIMENTAL SECTION

General Remarks

All solvents used in air-sensitive reactions were degassed by slowly bubbling nitrogen through them prior to use. Tetrahydrofuran and diethyl ether were purified using a Solv-Tek solvent purification system. The solvents were stored in a Solv-Tek solvent keg and passed through an alumina column. Dimethylsulfoxide was stored over 4Å molecular sieves for at least 24 hours before use. Hexane was distilled to remove high-boiling impurities and stabilizers. *N*-Bromosuccinimide was recrystallized from boiling water and dried *in vacuo*. Cuprous iodide was heated under reflux in aqueous potassium iodide for 45 minutes; upon addition of crushed ice, a white precipitate formed. The precipitated CuI was collected by vacuum filtration and sequentially washed with cold water, acetone, and diethyl ether. Lithium bromide was purified by sequential heating to 120 °C and grinding in a mortar until no more clumping was observed; dry LiBr is then stored in a dessicator.

¹H-NMR and ¹³C-NMR spectra were acquired on a Bruker 400 UltraShield instrument using 5 mm diameter sample tubes. Deuterated solvents were purified by passing through a short alumina column and storing over 4Å molecular sieves. All spectra were recorded at ambient temperature. All NMR data are reported in the following manner: δ for the chemical shift in ppm relative to TMS, with residual deuterated solvent used as internal standard. Coupling constants are reported in Hz. Multiplicities are abbreviated as follows: s for singlet, d for doublet, t for triplet, sep for septet, dd for doublet of doublets, dt for doublet of triplets, and m for higher order and/or complex multiplets.

Mass spectral data was acquired using an Agilent Technologies 6890N Network GC System coupled with a 5973 inert Mass Selective Detector. Electron impact (EI) or chemical ionization (CI) (methane) were both employed.

Infrared spectra were acquired on a Perkin Elmer Spectrum 100 FTIR using either thin film on NaCl or KBr plates or NaCl solution cells.

1-(2-Bromophenyl)-2-butynyl acetate (22).²⁷

2-Bromobenzaldehyde (5.195 g, 28.05mmol) was added to an oven dried Schlenk tube containing a stir bar under nitrogen atmosphere. The flask was placed in an ice bath at 0 °C. Dry THF (100 mL) and propynylmagnesium bromide (84.2 mL, 42.1 mmol) was added and the solution was allowed to stir for 1.5 hours. Acetic anhydride (5.3 mL, 56.1 mmol) was added and the reaction was allowed to stir for another hour at room temperature. The product was extracted with ether and washed with de-ionized water. The ether layer was dried over magnesium sulfate and concentrated *in vacuo*. The acetate was purified by silica gel chromatography, eluting with 10:1 hexanes:ether. After concentrating on a rotary evaporator, 3.05 g (11.5 mmol, 41%) of a yellow solid was obtained, matching previously published data.²⁷ M.p. 50-53 °C. ¹H NMR (CDCl₃) □ 7.78 (dd, 1H, J = 1.7, 7.73 Hz), 7.58 (dd, 1H, J = 1.2, 7.95 Hz), 7.37 (td, 1H, J = 1.2, 7.6 Hz), 7.22 (td, 1H, J = 1.7, 7.7 Hz), 6.65 (q, 1H, J = 2.2 Hz), 2.12 (s, 3H), 1.91 (d, 3H, J = 2.2 Hz). IR (film) 2238cm⁻¹ (C≡C), 1744cm⁻¹ (C=O).

1-Bromo-2-(3-methyl-1,2-butadienyl)-benzene (23).²⁷

(a) Cuprous iodide (31.05 g, 110.5 mmol), and lithium bromide (9.6 g, 110.5 mmol) were added to an oven dried Schlenk tube containing a stir bar. A nitrogen atmosphere was established in the flask and then the flask was placed in an ice bath at 0 °C. Dry THF (300 mL) was added to the flask and the solution allowed to stir for 1 hour. Methylmagnesium bromide (37 mL, 111 mmol) was added and the solution was allowed to stir for an additional 1 hour. Acetate **22** (5.882 g, 22.02 mmol) was placed in a small round bottom flask under nitrogen atmosphere. Dry THF (75 mL) was added to the acetate and the solution transferred dropwise via cannula to the Schlenk flask and allowed to stir at room temperature overnight. Diethyl Ether (100 mL) and saturated ammonium chloride (100 mL) were added to the flask and the resulting solution was filtered. The solution was then transferred to a separatory funnel and the ether layer was washed with ammonium chloride solution until the aqueous layer was no longer blue. The ether layer was then washed with de-ionized water and dried over magnesium sulfate then concentrated *in vacuo*. Purification of the allene was performed on a small plug of silica gel eluting with pentane, yielding a colorless oil (2.79g, 12.55 mmol, 57%).

(b) To a Schlenk flask containing a magnetic stir bar under nitrogen atmosphere was added tris(acetylacetonato)iron(III) (9.8 mg, 0.028 mmol). The flask was cooled to -10 °C in a salt/ice bath before adding **22** (0.151g, 0.56 mmol) in 14 mL toluene. Methylmagnesium bromide (0.29 mL, 3 M in diethyl ether, 0.87 mmol) was added dropwise and the solution turned dark brown. After 5 minutes, 10 mL saturated aqueous ammonium chloride solution and 10 mL diethyl ether was added and the solution was transferred to a separatory funnel. The ether layer was washed with water and the aqueous layer was backwashed with diethyl ether. The combined organic layers were dried over magnesium sulfate, the solvent removed *in vacuo* and the crude allene

was purified over silica, eluting with pentane (0.055g, 0.24 mmol, 44%) to give a colorless oil, which matched previously published spectral data.²⁷

¹H NMR (CD₂Cl₂) 7.51 (dd, 1H, *J* = 1.2, 8.0 Hz), 7.41 (dd, 1H, *J* = 1.7, 7.8 Hz), 7.24 (td, 1H, *J* = 1.2, 7.5 Hz), 7.03 (td, 1H, *J* = 1.7, 7.6 Hz), 6.39 (sep, 1H, *J* = 2.9 Hz), 1.82 (d, 6H, *J* = 2.9 Hz).

Appendix 1. ¹³C NMR (CD₂Cl₂) 204.8 (C), 135.8 (C), 133.4 (CH), 129.0 (CH), 128.3(CH), 127.9 (CH), 122.6 (C), 100.2 (C), 92.0 (CH), 20.8 (CH₃ x 2). Appendix 2. IR (film) 1952 cm⁻¹ (C=C=C).

Manganesepentacarbonyl bromide.³⁹

In a round-bottom flask containing a magnetic stir bar, dimanganesedecacarbonyl (3.0 g, 7.7 mmol) was dissolved in 75 mL dichloromethane; bromine was added (0.6 mL, 11.6 mmol) and the solution stirred for 90 minutes. The volatiles were then removed *in vacuo*, leaving behind crude manganesepentacarbonyl bromide as an orange powder. The powder was redissolved in 175 mL dichloromethane and filtered to remove any remaining solids. 80 mL hexanes was added and the volume was slowly reduced to 30 mL on a rotary evaporator, at which point manganesepentacarbonyl bromide precipitated. The pure product was then filtered off, the resulting orange crystals dried *in vacuo* overnight and stored for future use in the refrigerator in the glove box.

(η^1 -(2-Methyl-1,2-butadienyl)benzene)pentacarbonylmanganese (41a).

Allene **23** (0.358 g, 1.608 mmol) was dissolved in 5 mL THF and added to a Schlenk flask charged with nitrogen and containing a magnetic stir bar. The solution was placed in a dry

ice/acetone bath and cooled to -78 °C before adding *n*-butyllithium (0.71 mL, 2.7 M in THF, 1.91 mmol) dropwise and stirring for 2 hours. In a separate round-bottom flask containing a nitrogen atmosphere, manganesepentacarbonyl bromide was dissolved in 5 mL THF and cooled to -78 °C. The solution was transferred to the Schlenk flask dropwise via cannula and stirred for 3 hours. 2 g silica gel was added to the mixture and the solvent was removed by rotary evaporator under strict exclusion of air. The σ -complex coated on silica gel is purified over silica gel, eluting with pentane to give **41a** as yellow crystals (0.168 g, 0.499 mmol, 31%) which decomposed rapidly. ¹H-NMR 7.1-7.4 (m, br), 5.9 (s, br), 3.7 (s, br), 3.4 (s, br), 2.3 (s, br), 1.8 (s, br). Appendix 3.

Rheniumpentacarbonyl bromide.³⁹

Dirheniumdeca carbonyl (0.898 g, 1.3 mmol) was placed in a round-bottom flask along with a magnetic stir bar and 60 mL hexanes. Bromine (0.2 g, 1.25 mmol) was added dropwise and the cloudy solution stirred for 12 hours, after which time the solution turned white. The solvent and excess bromine were removed *in vacuo* and the resulting crude white product recrystallized by dissolving in warm acetone, adding 2 volumes of methanol and cooling in the freezer to give rheniumpentacarbonyl bromide as a white solid (0.832 g, 0.975 mmol, 75%).

(η^1 -(2-Methyl-1,2-butadienyl)benzene)pentacarbonylrhenium (41b).

In a Schlenk flask containing a magnetic stir bar under nitrogen atmosphere, allene **23** (0.165g, 0.74 mmol) was dissolved in 12 mL THF and cooled to -78 °C in a dry ice/acetone bath. *n*-Butyllithium (0.3 mL, 2.72 M in THF, 0.8 mmol) was added dropwise and the reaction mixture was allowed to stir for 30 minutes. In a separate round bottom flask under nitrogen atmosphere,

Rheniumpentacarbonyl bromide (0.301 g, 0.7 mmol) was dissolved in 20 mL THF and added to the Schlenk flask containing the allene/*n*BuLi mixture *via* canula. This solution was stirred for 1 hour while maintaining -78 °C before adding 0.5 g silica gel, removing the solvent on a rotary evaporator and chromatographing over silica gel, eluting with pentane. ¹H-NMR 7.1-7.42 (m, 4H), 5.98 (sep, 1H, J = 2.7 Hz), 1.82 (d, 6H, J = 2.7 Hz). Appendix 4.

(1,1-Diphenylmethyl)trimethylsilane (44).

In an oven-dried Schlenk flask containing a magnetic stir bar, a nitrogen atmosphere was created. Diphenylmethane (2.0 g, 12.8 mmol) was added in 30 mL THF. The flask was placed in an ice bath and cooled to 0 °C before adding *n*BuLi (6.3 mL, 2.2 M in THF, 14 mmol) dropwise and stirring for 90 minutes. Chlorotrimethylsilane (1.5 g, 14 mmol) was dissolved in 10 mL THF and added dropwise to the solution. The reaction mixture was removed from the ice bath and allowed to stir for 1 hour before diluting with 50 mL de-ionized water and 50 mL diethyl ether and transferring to a separatory funnel. The ether layer was washed with brine, dried with magnesium sulfate and the solvent removed on a rotary evaporator. The resulting clear solid (1.69 g, 11.8 mmol, 92%) was used without further purification. Spectral data matched previously published data.⁵⁰ ¹H-NMR (CDCl₃) 7.05-7.3 (m, 10H), 3.49 (s, 1H), -0.05 (s, 9H). Appendix 5. ¹³C-NMR (CDCl₃) 130.1, 128.2, 127, 30, -0.2. Appendix 6

(1-Bromo-1,1-diphenylmethyl)trimethylsilane (43).

In a round-bottom flask fitted with a magnetic stir bar and a reflux condenser, **44** (0.34 g, 1.42 mmol) was dissolved in 10 mL chloroform. *N*-Bromosuccinimide (0.422 g, 2.4 mmol) and

benzoyl peroxide (0.05 g, 0.2 mmol) were added and the solution heated to reflux for 12 hours. The reaction mixture was allowed to cool to room temperature and filtered, then the solvent was removed *in vacuo* to give **43** (0.43 g, 1.36 mmol, 96%), which was used without further purification. The ¹H-NMR matched previously published data.⁵¹ ¹H-NMR (CDCl₃) 7.39-7.41 (m, 3H), 7.27-7.29 (m, 6H), 0.25 (s, 9H). Appendix 7.

Tetraphenylethylene (45).

(1-Bromo-1,1-diphenylmethyl)trimethylsilane (**43**) (0.51 g, 1.6 mmol) was stirred in a Schlenk flask in 5 mL THF under nitrogen atmosphere. TBAF (1.6 mL, 1 M in THF, 1.6 mmol) was added dropwise and the solution turned brown. After stirring for 12 hours, 15 mL diethyl ether and 15 mL de-ionized water were added and the organic layer washed with water three times and then dried over magnesium sulfate. The solvent was removed on a rotary evaporator and the resulting solid purified over silica gel, eluting with hexanes to give tetraphenylethylene (0.202 g, 0.61 mmol, 76%), which was identified by comparison to an authentic sample.

Benzhydryl Methyl Ether (47).

In a round-bottom flask containing a magnetic stir bar, **43** (0.251g, 0.79 mmol) was dissolved in 5 mL of methanol. TBAF (1 mL, 1 M in THF, 1 mmol) was added and the solution was stirred at room temperature for 3 hours. 10 mL diethyl ether and 10 mL de-ionized water were added and the reaction mixture was transferred to a separatory funnel. The organic layer was washed with three 10 mL portions of de-ionized water, then dried over magnesium sulfate. The solvent was removed *in vacuo* to give the crude benzhydryl methyl ether as a colorless oil

that was not purified further (0.128 g, 0.64 mmol, 82%). The $^1\text{H-NMR}$ matched previously published data.⁵² $^1\text{H-NMR}$ (CDCl_3): 7.16-7.34 (m, 10H), 5.29 (s, 1H), 3.33 (s, 3H); $^{13}\text{C-NMR}$ (CDCl_3): 142.0, 128.3, 127.3, 126.8, 85.3, 56.8 ppm.

***trans*-Dimethyl-3,3-diphenylcyclopropane-1,2-dicarboxylate (50).**

In a round-bottom flask, dimethylfumarate (0.288 g, 2.0 mmol) and TBAF (2 mL, 1 M in THF, 2.0 mmol) were dissolved in 6 mL DMSO before adding **43** (0.2 g, 0.55 mmol) in 12 mL DMSO *via* syringe pump over 12 hours. Diethyl ether (20 mL) and saturated aqueous sodium bicarbonate (20 mL) were added to the reaction mixture and transferred to a separatory funnel. The aqueous layer was drained off and the organic layer washed with water before drying over magnesium sulfate to give a mix of **50** and tetraphenylethylene. The crude product was purified by chromatography over silica gel to give **50** (0.035g, 0.115 mmol, 21%) and the spectra matched previously published data.⁵³

(1-Bromo-1-phenylmethyl)trimethylsilane (48).

A round bottom flask containing a magnetic stir bar was fitted with a reflux condenser. To the flask were added 60 mL chloroform, benzyl trimethylsilane (2.0 g, 0.012 mol), *N*-bromosuccinimide (2.67 g, 0.015 mol) and benzoyl peroxide (0.1 g, 0.4 mmol) and the mixture was heated to reflux for 24 hours. The solvent was removed on a rotary evaporator and the resulting mixture was filtered to remove solids and give **48** as a yellow oil (2.47g, 0.010 mmol, 85% yield) matched previously published spectral data³⁷ and was used without further purification. $^1\text{H-NMR}$ (CDCl_3): 7.31 (m, 5H), 4.39 (s, 1H), 0.31 (s, 9H).

***trans*-Stilbene (49).**

In a vial containing a magnetic stir bar, **48** (0.30 g, 1.24 mmol) was dissolved in 6 mL DMSO before adding TBAF (2 mL, 1M in THF, 2 mmol) and stirring for 3 hours. The mixture was transferred to a separatory funnel and 10 mL diethyl ether and 10 mL de-ionized water were added. The aqueous layer was removed and the organic layer washed with three 10 mL portions of de-ionized water before drying the organic layer over magnesium sulfate. *trans*-Stilbene (0.79 g, 0.61 mmol, 49%) was characterized by comparison to an authentic sample purchased from Alfa Aesar. ¹H-NMR (CDCl₃): 7.15-7.65 (m, 10H), 7.05 (s, 2H); ¹³C-NMR (CDCl₃): 137.4, 129, 128.2, 127; EI-MS: 180, 165, 91, 65.

Benzyl Methyl Ether (51).

In a vial containing a magnetic stir bar, **48** (0.23 g, 0.94 mmol) was dissolved in 5 mL methanol. TBAF (1 mL, 1M in THF, 1 mmol) was added and the mixture was allowed to stir for 3 hours. The solution was then transferred to a separatory funnel, 10 mL diethyl ether and 10 mL de-ionized water were added and the organic layer was washed with three 10 mL portions of de-ionized water. After drying over magnesium sulfate and removal of the solvent, the product was identified by comparison to an authentic sample obtained from Alfa Aesar. ¹H-NMR (CDCl₃): 7.33-7.35 (m, 5H), 4.45 (s, 2H), 3.35 (s, 3H).

***trans*-Dimethyl-3-phenylcyclopropane-1,2-dicarboxylate (50).**

To a vial containing a magnetic stir bar was added 5 mL DMSO and TBAF (1 mL, 1 M in THF, 1 mmol). **48** (0.20 g, 0.82 mmol) was dissolved in 5 mL DMSO and to the stirring solution dropwise. The reaction mixture was then stirred for 3 hours before transferring to a separatory funnel and adding 10 mL diethyl ether and 10 mL de-ionized water. The organic layer was washed with brine and dried over magnesium sulfate before removing the solvent *in vacuo* and purifying the crude residue by silica gel chromatography, eluting with 9:1 hexanes:diethyl ether (0.033g, 0.14 mmol, 17% yield). The NMR spectra matched previously published data.⁵³ ¹H-NMR (CDCl₃): 7.3 (m, 5H), 3.8 (s, 3H), 3.5 (s, 3H), 3.10 (dd, 1H, J = 6.4 Hz), 2.85 (dd, 1H, J = 4.8 Hz), 2.63 (dd, 1H, J = 4.8 Hz); ¹³C-NMR (CDCl₃): 172, 168.8, 134, 128.8, 128.1, 127, 52.3, 51.9, 32.7, 29.8, 25.8; EI-MS: 234, 203, 175, 115, 114, 91, 77, 59.

Benzyl-*tert*-butyldimethylsilane (56).

In a Schlenk flask containing a magnetic stir bar, 10 mL toluene was stirred under nitrogen atmosphere at room temperature. *n*-Butyllithium (3.7 mL, 2.7M in THF, 10 mmol) was added and the solution was allowed to stir for 12 hours. *tert*-Butyldimethylsilyl chloride (1.50 g, 10 mmol) was added and the reaction mixture was allowed to stir for an additional 12 hours before adding 10 mL de-ionized water and transferring to a separatory funnel. The organic layer was washed with brine, dried over magnesium sulfate and concentrated *in vacuo* to give crude benzyl-*tert*-butyldimethylsilane, which was purified by flash chromatography over silica gel, eluting with hexanes (0.74 g, 3.6 mmol, 36%). The ¹H-NMR matched previously published

data.⁵⁴ ¹H-NMR (CDCl₃): 7.17-7.30 (m, 2H), 6.93-7.11 (m, 3H), 2.15 (s, 2H), 0.91 (s, 9H), 0.03 (s, 6H).

(1-Bromo-1-phenylmethyl)-*tert*-butyldimethylsilane (55).

In a round bottom flask fitted with a reflux condenser and a magnetic stir bar, **52** (0.74 g, 3.6 mmol) was dissolved in 10 mL chloroform and stirred before adding *N*-bromosuccinimide (0.71 g, 4.0 mmol) and benzoyl peroxide (0.1 g, 0.4 mmol). The reaction mixture was refluxed for 12 hours, filtered and concentrated *in vacuo* before purification by flash chromatography over silica gel, eluting with hexanes to give **55** as a slightly yellow oil (0.883 g, 3.1 mmol, 86%) which matched previously published data.⁵⁵ ¹H-NMR (CDCl₃): 7.28 (m, 5H), 4.37 (s, 1H), 1.0 (s, 9H), 0.31 (s, 6H).

Representative Procedure for Generating Carbenes in Ionic Liquids.

To a vial containing a magnetic stir bar and 5 mL of an ionic liquid was added TBAF (1.2 molar equivalents) dropwise while stirring, followed by addition of α -bromosilane (1 molar equivalent) and dimethyl fumarate (1.2 molar equivalent). The mixture was stirred for 48 hours before transferring to a separatory funnel and extracting three times with 6 mL portions of diethyl ether. The combined ether layers were washed with 10 mL de-ionized water and dried over magnesium sulfate to give the crude product.

PART II - DEVELOPMENT OF NOVEL 7-MEMBERED RING CARBENE LIGANDS FOR
PALLADIUM CATALYZED CROSS COUPLING REACTIONS

INTRODUCTION

Herein, we describe the attempted synthesis of novel palladium benzocycloheptatrienyliene **60** complex, a benzannulated derivative of previously published complex **61**.⁵⁶ This complex may offer electronic tunability of the carbon-metal double bond through benzannulation, as well as steric tunability through substitution at positions adjacent to the carbene carbon, thereby allowing fine-tuning of catalytic systems. Bulky ligands in palladium catalyzed cross-coupling reactions can promote ligand dissociation to form the catalytically active low-valent palladium species;⁶² furthermore, steric bulk around the metal center allows control of relative rates of initiation and propagation in polymerization catalysts.⁵⁷ Tightly bound ligands such as N-heterocyclic carbenes promote stability of metal complexes.⁵⁸ The present approach would allow us to combine the flexibility offered by traditional phosphine ligands with the benefits of having a tightly bound ligand such as N-heterocyclic carbenes, in particular for use in palladium catalyzed cross-coupling reactions.

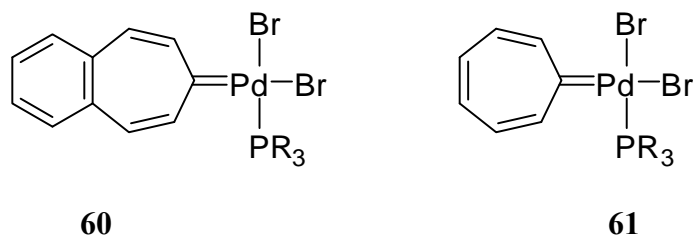


Figure 28. Palladium Cycloheptatrienyliene Complexes.

It has been demonstrated that the use of bulky ligands can significantly improve stability of metal complexes, particularly for complexes with open coordination sites. Schrock *et al.* demonstrated that the judicious use of bulky ligands in tuning ring-opening metathesis

polymerization not only makes for more stable metal complexes, but also provides a means of effectively controlling the rates of initiation, propagation and termination within the catalytic cycle:⁵⁹ if the ligands are too bulky, initiation is slow relative to propagation, if the ligands are too small, chain termination and chain transfer becomes too fast; both of those scenarios lead to high variability in the polydispersity of the target polymer. Additionally, Herrmann and coworkers have shown that the combination of tightly bound ligands such as N-heterocyclic carbenes with more labile ligands such as phosphines allows access to complexes that exhibit improved stability as well as facile activation and entry into the catalytic cycle for palladium catalyzed cross-coupling reactions.⁵⁶

Types of Ligands

Most ligands can form the M-L σ bond in one of three ways: by coordination of a lone pair (classical Werner coordination,⁶⁰ such as phosphine or amine complexes; singlet carbenes also belong to this family), by donation from a π bond (such as in complexes of ethylene), or lastly by coordination of a σ bond to the metal (as seen in complexes of molecular hydrogen). Typically, the binding ability is lone pair donor $>$ π -donor $>$ σ donor.⁶¹ In all three cases, there is also a significant backbonding component from the d_{π} -orbital of the metal - for Werner and π -complexes, the π^* orbital of the ligand acts as the acceptor, whereas in σ -complexes, back donation is accepted by the σ^* -orbital of the ligand. This is illustrated in Figure 29. These ligands largely serve the purpose of imparting some electronic or steric property to the complex, thus aiding its reactivity.

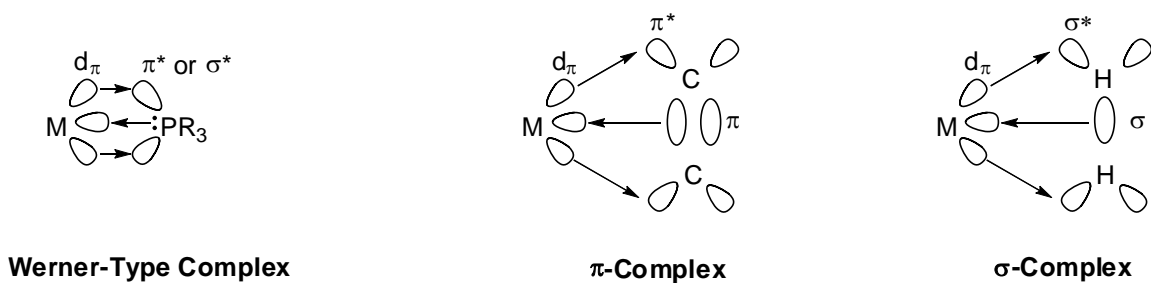


Figure 29. Examples of Types of Metal-Ligand Complexes.

Ligands for Palladium-Catalyzed Coupling Reactions

Palladium cross-coupling reactions are an immensely important tool to form carbon-carbon and carbon-nitrogen bonds by such processes as the Suzuki-Miyaura reaction,⁶² the Heck reaction,⁶³ and aryl amination reactions.⁶⁴ These reactions typically proceed through a Pd(0)/Pd(II) pathway, where an aryl halide is oxidatively added to a palladium(0) center, followed by a transmetalation step, resulting in a palladium(II) species bearing the two moieties to be coupled. Lastly, a reductive elimination step releases the product and regenerates the active palladium(0) catalyst. A general catalytic cycle is presented in Figure 30.

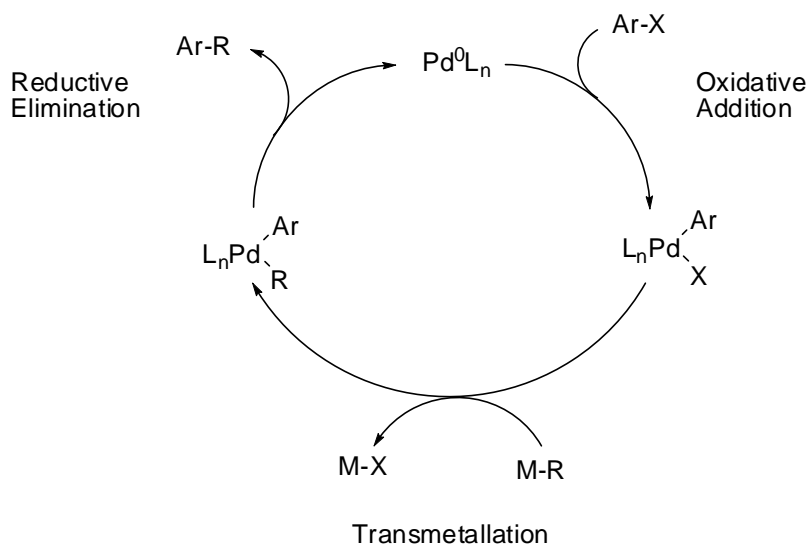


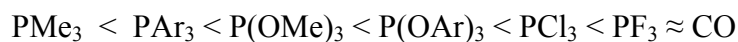
Figure 30. A General Catalytic Cycle for Palladium-Catalyzed Coupling Reactions.

Oxidative addition of the aryl halide is generally thought to be the rate-limiting step, with aryl iodides reacting the fastest, followed by aryl bromides, and lastly aryl chlorides.

Phosphine Ligands in Palladium-Catalyzed Cross-Coupling Reactions

The bulk of palladium-catalyzed cross-coupling reactions are done using tertiary phosphine ligands of the type PR_3 , with tetrakis-triphenylphosphine palladium being by far the most prevalent pre-catalyst for these types of reactions. The steric and electronic properties of these phosphine ligands can be systematically and predictably altered by changing the substituent. In contrast to carbonyl ligands, which are generally thought to utilize the π^* orbital for back bonding, the σ^* orbital of phosphine ligands is believed to act as the acceptor.⁶⁵ The π -acidity is ultimately highly dependent upon the nature of R, with alkyl phosphines being the weakest acceptors and trifluorophosphines being the strongest acceptors, roughly comparable to carbonyl ligands.

The order of increasing π -acid character is:⁶⁵



This trend shows that phosphine ligands possess significant electronic tunability. Additionally, by varying the size of R, phosphines show great variability in steric parameters. With complexes of smaller ligands such as PMe_3 or CO, the number of bound ligands is dictated by achieving 18 electron complexes. In contrast, bulkier phosphine ligands tend to form low-coordinate complexes,⁶⁶ favoring the binding of small, weakly coordinating ligands. Altering ligand donation effects can significantly change properties of organometallic complexes; one outcome is perturbation of oxidative addition/reductive elimination equilibria, as shown by Crabtree *et al.*⁶⁷ Tolman⁶⁸ illustrated the variability in both sterics and electronics of phosphine ligands by graphing the cone angle Θ (an indicator of steric bulk, obtained by measuring the apex angle of a cylindrical cone centered 2.28 Å below the P atom and just touching the outside of the Van der Waals radii of the outermost atoms of the model, Figure 31) against the amount of backbonding of simultaneously coordinated CO ligands in LNi(CO)_3 complexes, as monitored by infrared spectroscopy (the stronger donor phosphines increase electron density on Ni, thus increasing the back bonding to CO and consequently lowering $\nu(\text{CO})$). Figure 32 illustrates Tolman's results.

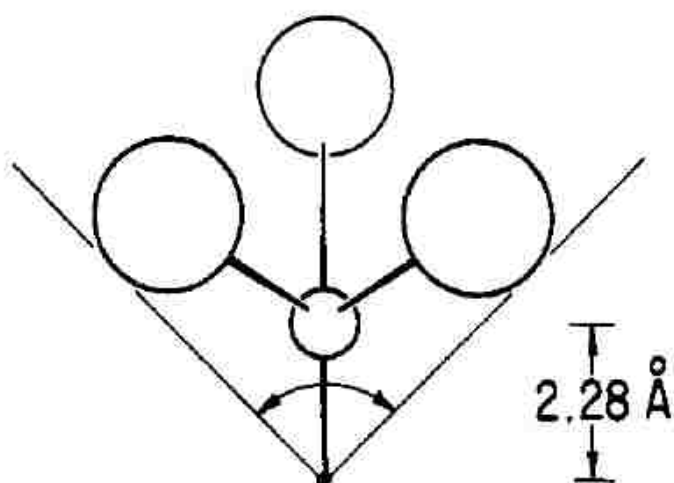


Figure 31. Measurement of Cone Angles of Phosphine Ligands.⁶⁸

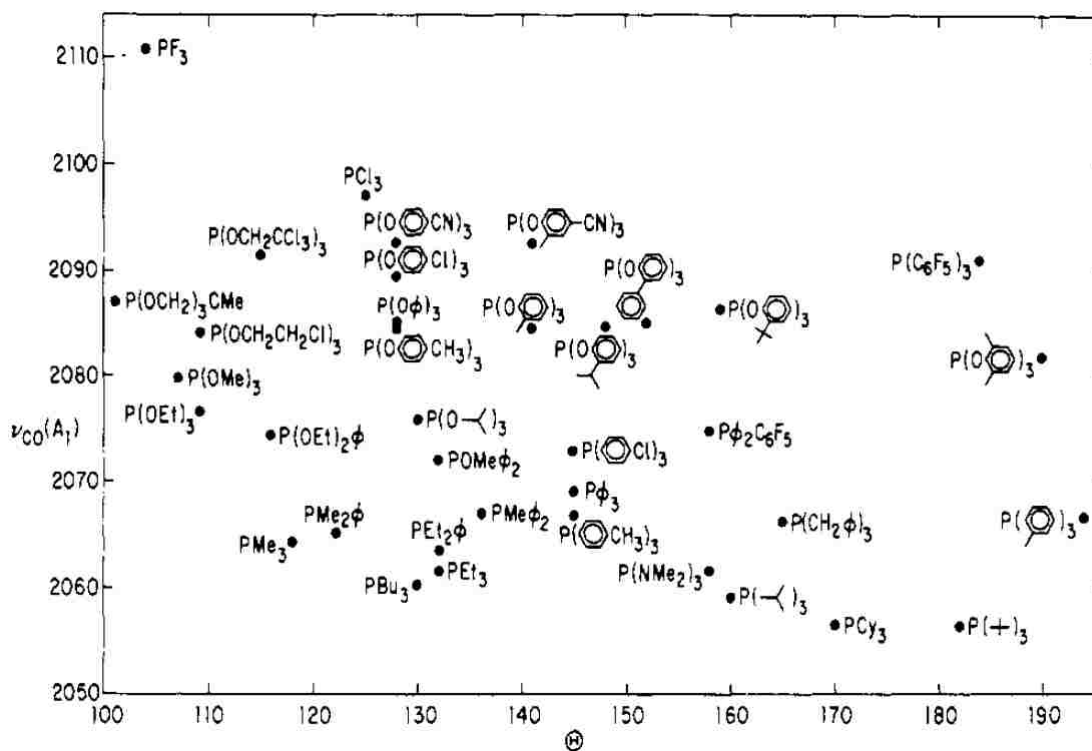


Figure 32. Steric and Electronic Map of Phosphine Ligands.⁶⁸

N-Heterocyclic Carbenes as Ligands in Palladium-Catalyzed Cross-Coupling Reactions

In the early 1960s, Wanzlick discovered that carbenes could be significantly stabilized by amino-substituents.⁶⁹ This discovery ultimately led to the isolation of the first crystalline carbene by Arduengo *et al.*⁷⁰ 1,3-Di-1-adamantylimidazol-2-ylidene (Figure 33) was prepared by deprotonation of 1,3-di-1-adamantylimidazolium chloride with sodium hydride and proved kinetically and thermodynamically stable enough to be isolated and characterized.

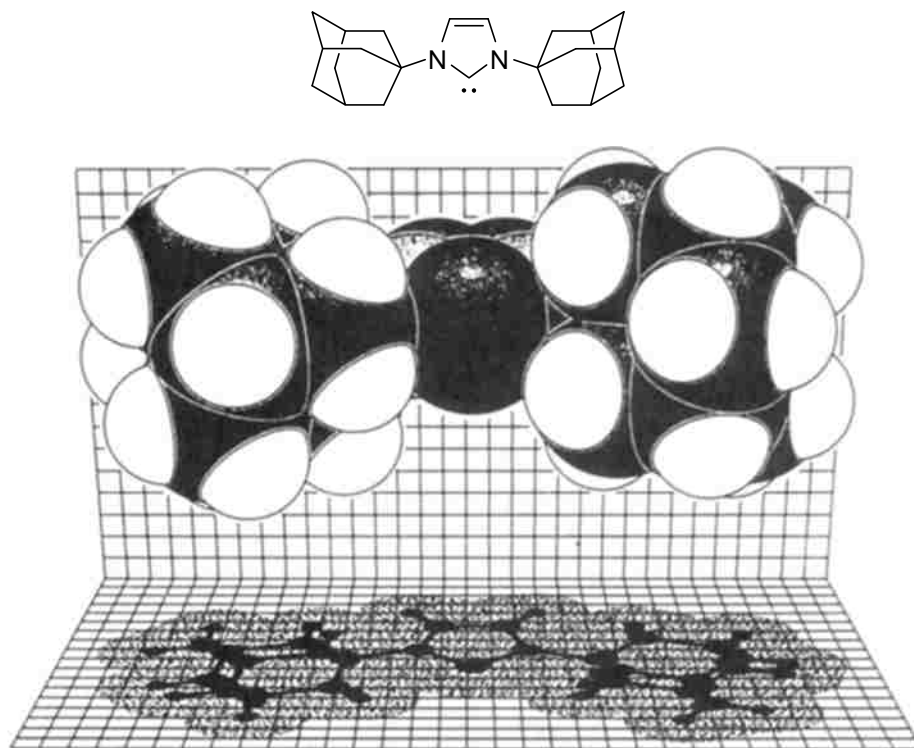


Figure 33. Space-Filling KANVAS Drawing of 1,3-Di-1-adamantylimidazol-2-ylidene.

These N-heterocyclic carbenes (NHCs) were found to be very useful ligands in organometallic chemistry. In 1968, Wanzlick reported mercury carbene complex **62**,⁷¹ and Öfele published the synthesis of chromium carbene complex **63**.⁷²

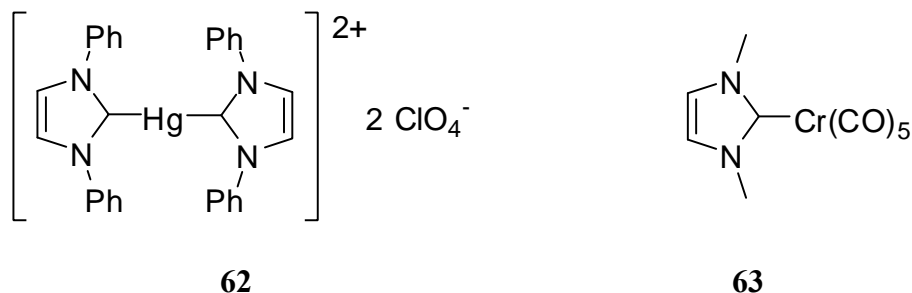


Figure 34. Early NHC-Metal Complexes.

Unlike traditional carbene ligands, NHCs are usually spectator ligands in catalytic processes. They are considered to be electronically similar to trialkylphosphines;⁷³ however, unlike phosphine ligands, NHCs are strongly coordinating ligands that undergo little to no dissociation from the metal. The exact character of the metal-carbon bond in NHCs seems to depend on the nature of the complex. Compounds **64** and **65** have Pt-C bond lengths that are generally comparable to a typical Pt-C single bond (~ 2.08 Å) - 2.009 Å (**64**) and 2.023 Å (**65**),⁷³ thus implying no significant $d_{\pi} \rightarrow p_{\pi}$ backbonding. Furthermore, synthesis of stable beryllium compound **66**⁷⁴ points to a M-L single bond, since beryllium has no p-electrons to back donate. *Ab initio* studies of several model beryllium complexes analogous to **66** further confirm this view.⁷⁵ Complex **67**⁷⁶ on the other hand shows a large discrepancy between the Ru-C_{sp2}(aryl) bond (2.006 Å) and the Ru-C_{sp2}(carbene) bond (1.908 Å), indicating significant metal-carbon double bond character.

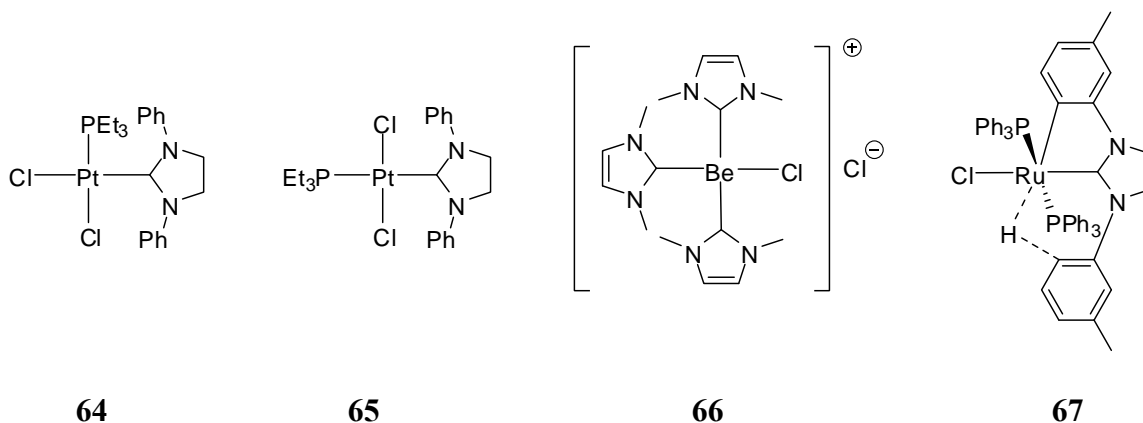


Figure 35. Examples of NHC Complexes.

The NHC ligand behaves differently from traditional alkylidenes, as evidenced by complexes bearing both types of ligand. This is most prominently illustrated by the second generation Grubbs' metathesis catalyst **68**,⁷⁷ as well as Herrmann's metathesis catalyst **69**.⁷⁸ the alkylidene ligand is a crucial actor ligand in the catalytic cycle, whereas the NHC ligand is purely a spectator ligand.

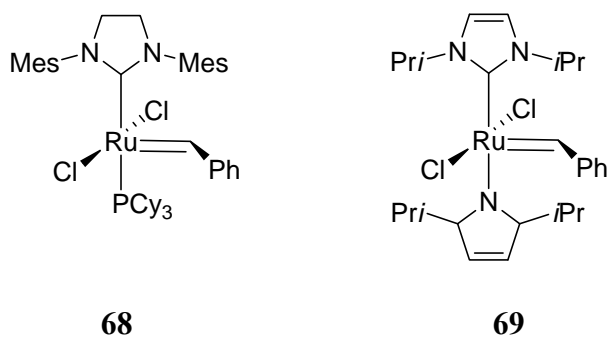


Figure 36. Examples of Metathesis Catalysts Containing NHC and Alkylidene Ligands.

Various palladium complexes of N-heterocyclic carbenes have been prepared and used in numerous catalytic applications. Complex **70** has been shown to be an active catalyst for Suzuki

and Heck coupling reactions,⁷⁹ and complexes **71** and **72** exhibit excellent activity as catalysts for Suzuki, Heck, Sonogashira and Stille reactions.⁸⁰

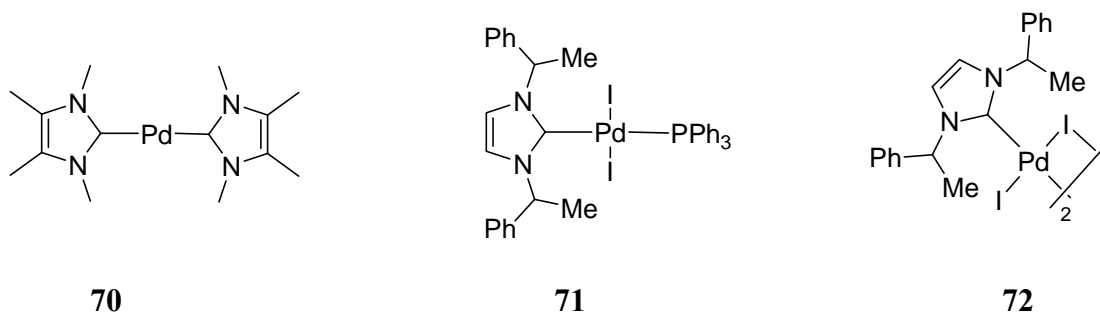


Figure 37. Examples of Catalytically Active Pd-NHC Complexes.

The Pd(II) complexes **71** and **72** are much more stable than their Pd(0) counterpart **70**; in order to enter the archetypical Pd(0) - Pd(II) catalytic cycle, **71** and **72** reductively eliminate I₂. In the case of **72**, this is followed by dissociation of the phosphine ligand to give the catalytically active 12-electron Pd(0) species **73**. **72** forms **73** directly upon loss of I₂.

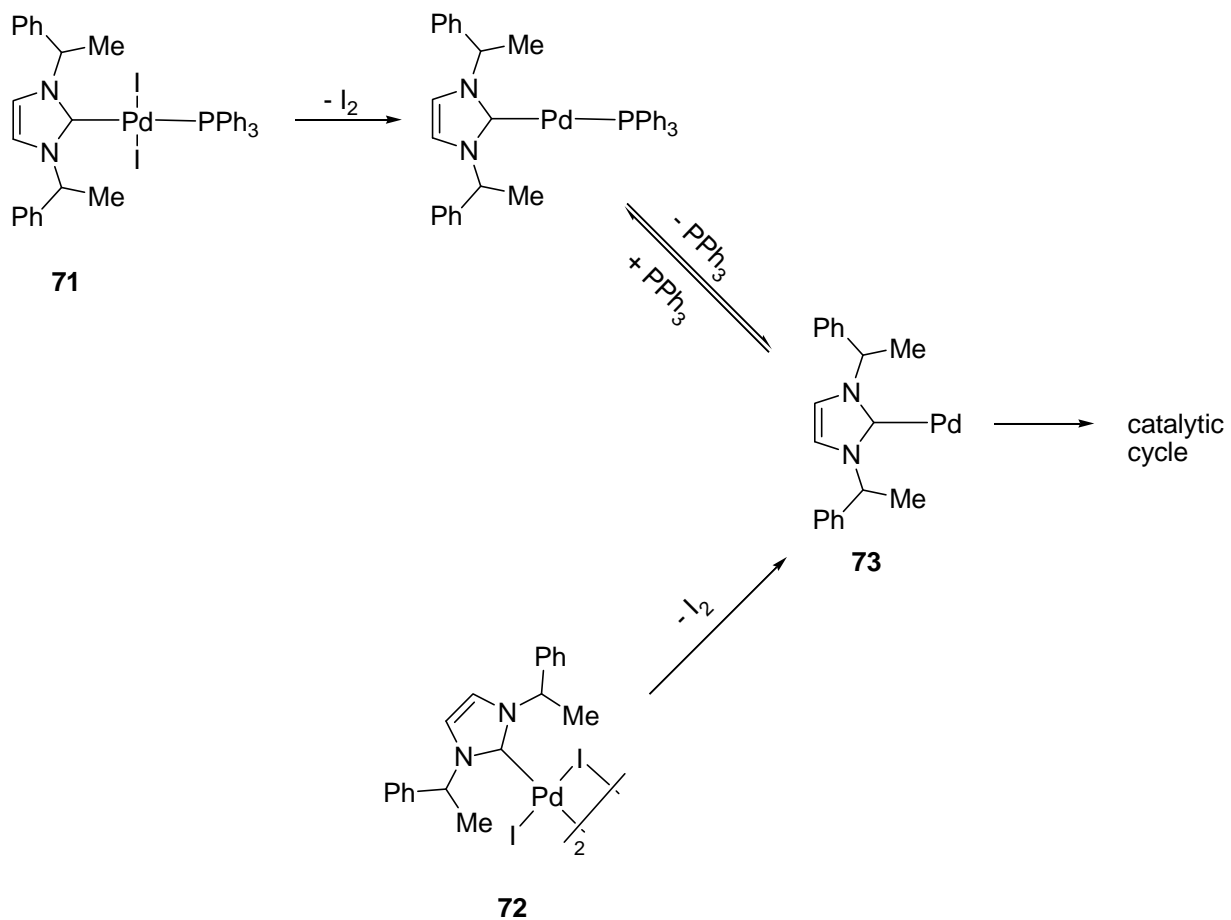
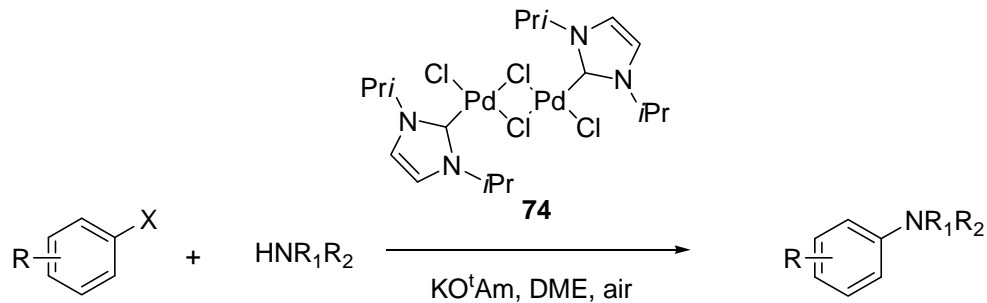


Figure 38. Formation of Catalytically Active Pd(0) Complex **73**.

Ultimately, **72** was preferable due to markedly increased stability compared to **70** as well as **71**; significant precipitation of palladium black was observed after prolonged exposure to the reaction conditions for both **70** and **71**, whereas **72** showed no signs of decomposition. Nolan *et al.* report that an aryl amination catalyzed by **74** can be performed in reagent grade solvent (without the need to exclude water) in air without any notable effect on the yield of the reaction.⁵⁸

Scheme 16. Aryl Amination Catalyzed by **74**.



Recently, efforts have been made to study the effects of altering the ring size of NHC ligands. While changing the size of the amine substituents on the NHC provides a convenient way of fine-tuning the steric environment of the resulting metal complexes, changing the size of the ring brings the N-bound ligands closer to the metal center (larger NHC rings) or farther away (smaller NHC rings). Grubbs *et al.*⁸¹ published the synthesis of 4-membered ring NHC **75** shown in Figure 39.

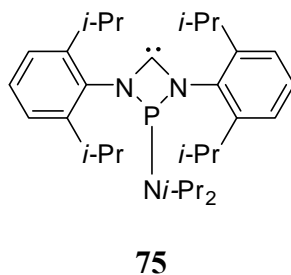


Figure 39. Example of a 4-Membered Ring NHC

Cycloheptatrienylienes as Strong Donor Ligands in Organometallic Complexes

Cycloheptatrienyliene (CHT) is an organic carbocyclic carbene that can be thought of as three energetically similar forms: the singlet carbene form **76**, the triplet carbene form **77**, and the cycloheptatetraene form **78**⁸² (Figure 40).

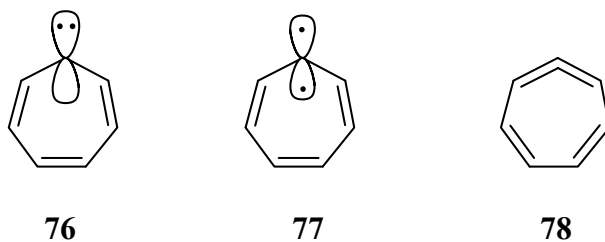


Figure 40. Forms of CHT.

Originally, the singlet state was thought to be the ground state configuration - this allowed for an aromatic cyclic fragment with an exocyclic lone pair; this assignment is also in agreement with the apparent nucleophilicity and relatively low reactivity of CHT.⁸³ Later studies⁸⁴ introduced the idea that the triplet carbene of CHT is either the ground state, or at least lies within several kcal per mole of the singlet carbene; this is illustrated by an intense triplet in the ESR spectrum of CHT generated by matrix irradiation of diazocycloheptatriene at 574 nm and 21 K (Figure 41).

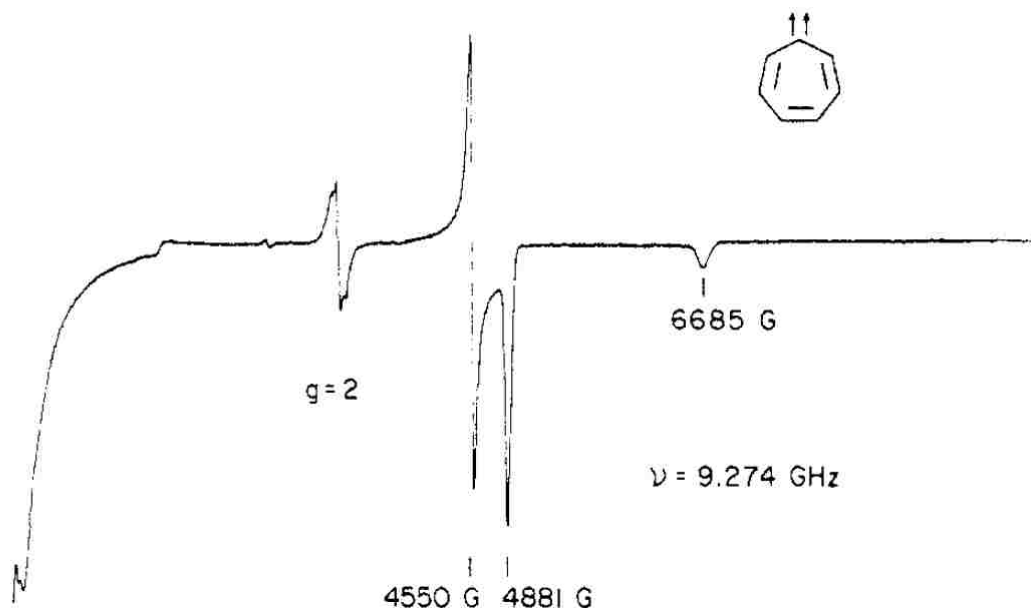


Figure 41. ESR Spectrum of Matrix-Irradiated Diazocycloheptatriene.

Waali investigated the interconversion of singlet CHT **76** and cycloheptatetraene **78**⁸⁵ by use of the semiempirical MNDO technique.⁸⁶ It was found that the nonplanar cycloheptatetraene is more stable than the planar singlet CHT by about 23 kcal/mol. The barrier of interconversion between **76** and **78** is relatively high; this is due to the fact that isomerization from the carbene to the cumulene is only allowed if the carbene electron pair is in the σ orbital.

Finally, calculations by Schaefer *et al.*⁸⁷ revealed that the singlet is in fact the true planar ground state when taking into account d-orbitals; however, the difference is only 6.7 kcal/mol, as predicted by McMahon and Chapman. When considering the calculated geometries, the singlet and triplet states are well separated geometrically, with the carbene carbon bond angles differing by 13.8° and bond lengths differing by as much as 0.045 Å. Thus, it appears that the singlet, triplet and allene isomers of CHT are all relatively close in energy, but separated by relatively

high barriers of inversion; this explains the experimental observations of unique properties of each of them.

It is worth noting that both the rearrangement chemistry of CHT and its apparent nucleophilicity can be attributed to the cycloheptatetraene isomer as well as the singlet carbene.^{88,89}

The inherent nucleophilicity of CHT makes it a strong donor ligand that binds tightly to metal centers. Iron,⁹⁰ ruthenium,⁹¹ tungsten,⁹⁰ rhodium,⁹² platinum⁹³ and palladium complexes of CHT have been isolated. Some examples are shown in Figure 42.

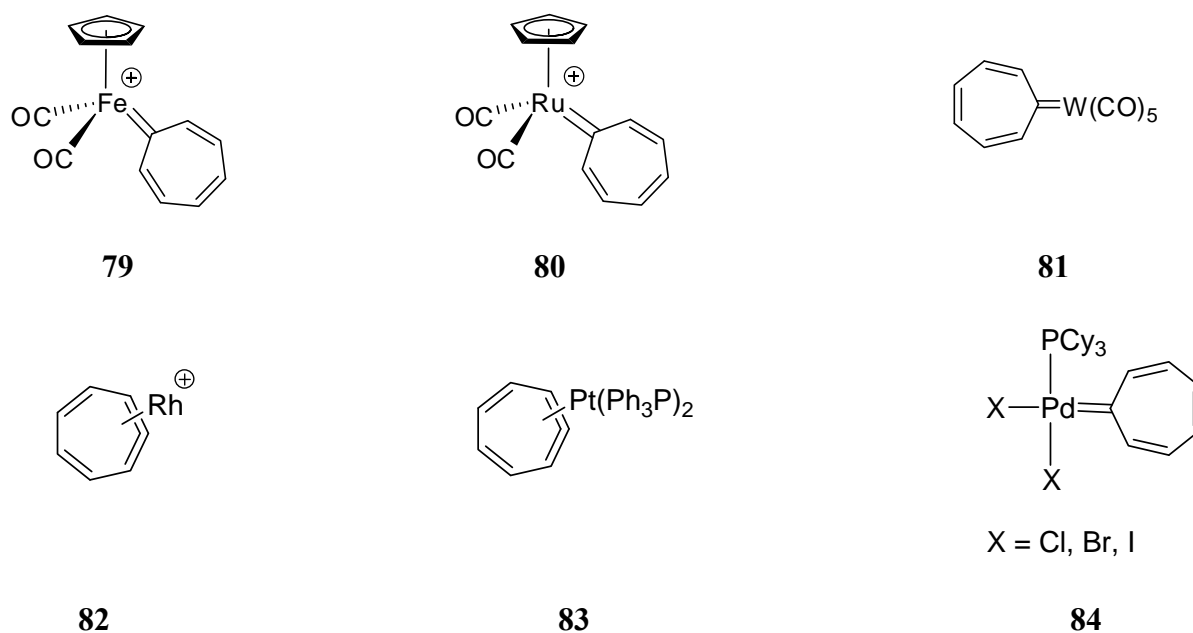
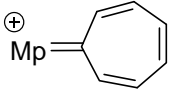
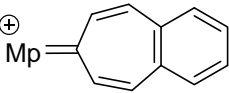
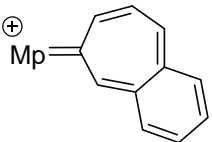


Figure 42. Transition Metal Complexes of CHT.

Ultimately, it appears that the mode of coordination of the CHT ligand appears to depend on the metal - with iron, ruthenium, tungsten and palladium, the ligand binds as the carbene, whereas platinum and rhodium coordinate to the allene moiety of cycloheptatetraene.

Of the above complexes, **84** stands out as a highly efficient catalyst for numerous C-C coupling reactions. The chlorine derivative of **84** greatly outperforms the highly active NHC analog in Heck and Suzuki coupling reactions, and its bromine derivative has been shown to be an efficient catalyst for Hartwig-Buchwald aminations⁵⁶. To date, no efforts have been made to investigate sterically and electronically modified CHT ligands; however, work by Jones *et al.*^{91,94} suggests that benzannulation of the CHT ring in different positions can significantly alter the nature of the metal-carbene carbon bond. Upon benzannulation, considerable changes are observed in ¹³C-shift of the carbene carbon, indicating a significant change in the metal-carbene carbon bond, likely due to perturbation of the aromaticity; benzannulation in the 4,5-position appears to increase the amount of positive charge on the ligand, thus shifting the carbene carbon downfield. Benzannulation in the 1,2-position leads to a more metal-centered positive charge, as seen by the upfield shift of the carbene carbon relative to the parent CHT complex. This leads us to believe that benzannulation is a viable route toward electronic tuning of CHT ligands in palladium catalyzed cross coupling reactions.

Table 6. ^{13}C -NMR Shifts of Carbene Carbons of CHT Complexes of Ru and Fe.⁹¹

Type	Fe	Ru
	242.3 ppm	223.6 ppm
	265.9 ppm	244.7 ppm
	201.0 ppm	186.6 ppm

Mp = Dicarbonyl(η^5 -cyclopentadienyl)-Metal

In summary, our goal is to design a class of ligands for palladium-catalyzed coupling reactions that combines access to steric and electronic tunability with the apparent stability imparted upon palladium catalysts by the use of N-heterocyclic carbene ligands.

RESULTS AND DISCUSSIONS

Benzodiazepines

Our initial attempts to access more tunable carbene ligands focused on the synthesis of 7-membered ring NHCs. Preliminary calculations comparing a typical 5-membered NHC and a 7-membered NHC at a DFT-B3LYP/6-31gd level of theory revealed that the frontier molecular orbitals of both systems were largely analogous (Figure 43).

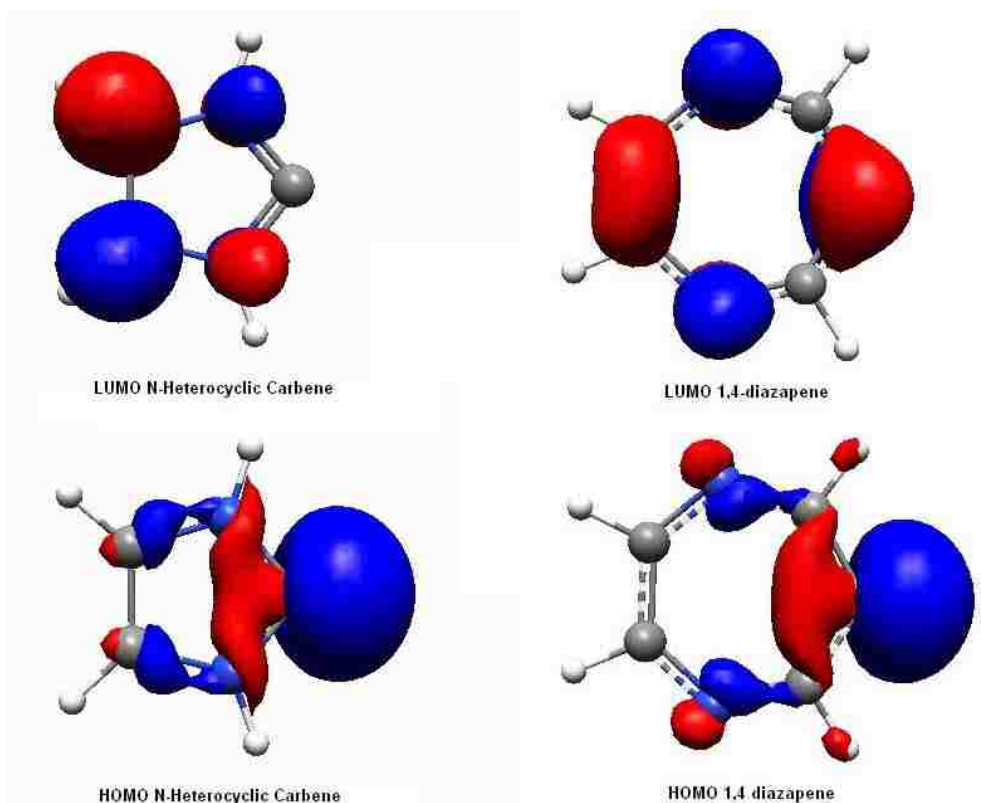
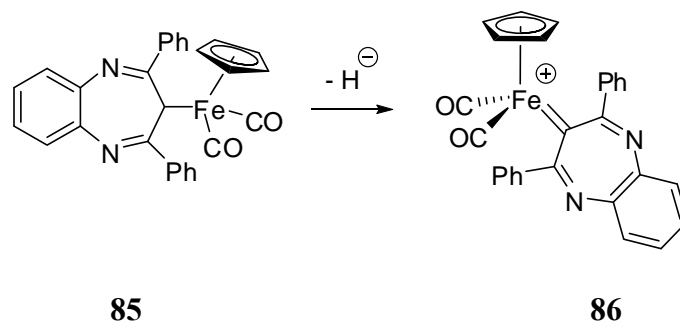


Figure 43. Frontier Molecular Orbitals of 5- and 7-Membered NHCs.

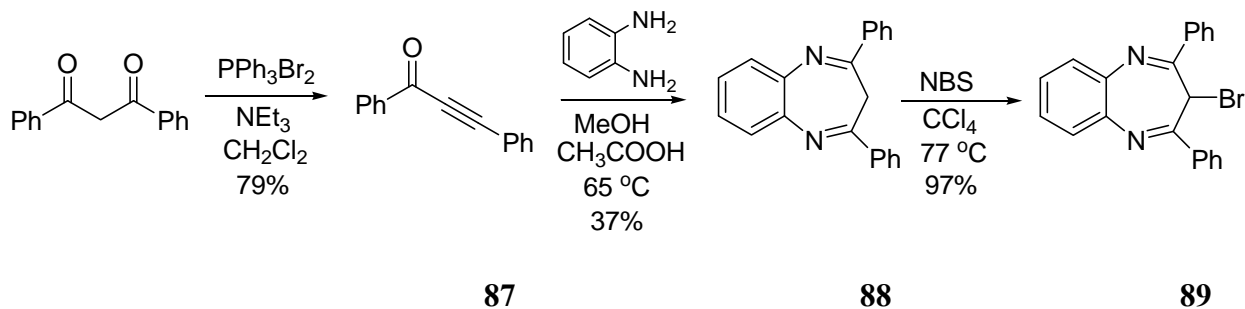
We envisioned synthesis of a metal-diazepine complex similarly to previously discussed iron,⁹⁰ ruthenium⁹¹ and tungsten⁸⁸ complexes of cycloheptatrienyliidene by hydride abstraction of the corresponding metal σ -complex, as shown in Scheme 17.

Scheme 17. Proposed Synthesis of Benzodiazepine Carbene Complex **86**.



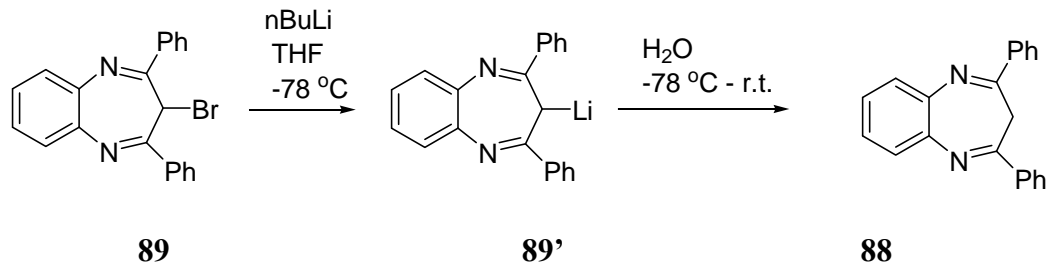
The synthesis of ligand **89** proved to be more challenging than originally thought; even though direct condensation of phenylenediamine with dibenzoylmethane is well documented,⁹⁵ we were unable to reproduce these results. Ultimately, **89** was prepared by condensing phenylenediamine with 1,3-diphenylpropynone,⁹⁶ which was synthesized by reaction of dibenzoylmethane with triphenylphosphine dibromide and triethylamine.⁹⁷ The resulting diazepine **88** then underwent free radical bromination to give **89** (Scheme 18). The NMR and infrared spectra of bromobenzodiazepine **89** matched previously published data,⁹⁸ with proton peaks at 7.02 (singlet, H-3), 7.48 (m, ArH), 7.7 (dd, ArH) and 7.92 (m, ArH) as well a characteristic C=N stretch at 1580 cm⁻¹.

Scheme 18. Synthesis of Benzodiazepine Ligand **89**.



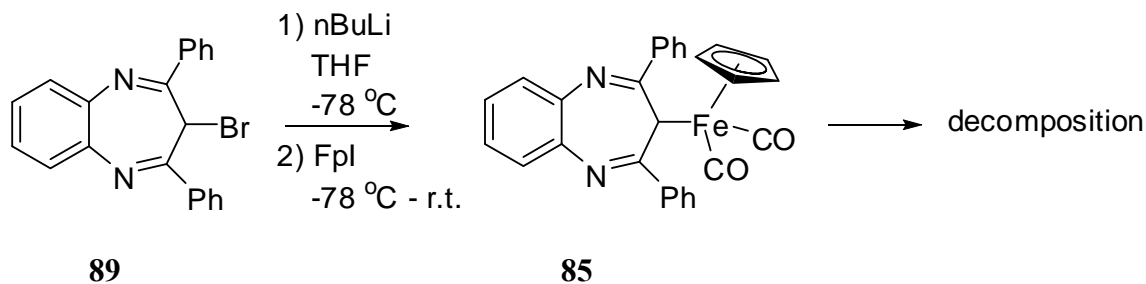
To confirm that lithium-halogen exchange occurs rather than nucleophilic attack of the imine moiety, bromobenzodiazepine **89** was treated with *n*-butyllithium followed by quench with water, regenerating **88** quantitatively.

Scheme 19. Lithium-Halogen Exchange on **89**.



Having confirmed that lithium-halogen exchange proceeds smoothly, **89'** was quenched with cyclopentadienylcarbonyliron iodide (FpI) to make **85**. NMR analysis of **85** after initial purification indicated formation of the desired σ -complex; particularly, a singlet at 5.33 ppm is consistent with the cyclopentadienyl ligand on **85**. The compound, however, decomposed in solution overnight.

Scheme 20. Synthesis of σ -Complex **85**.



A further concern is the question of hydride abstraction from σ -complex **85** to form the desired carbene complex **86**. DFT-B3LYP/6-31gd calculations revealed that for cycloheptatriene, removal of a hydride to give the corresponding tropylium ion with triphenylcarbenium hexafluorophosphate is thermodynamically favored by 12 kcal/mol. A comparison of the tropylium ion with the corresponding diazepine ion revealed that the

tropylium ion is 19.2 kcal/mol more stable than the diazepine ion, presumably due to the electronegativity of nitrogen. This indicates that hydride removal from the parent diazepine is thermodynamically disfavored by 7.2 kcal/mol. While complexation of the diazepine ligand with cyclopentadienyldicarbonyl iron appears to make hydride abstraction more favorable, it would still be energetically uphill by 3.0 kcal/mol (Figure 44).

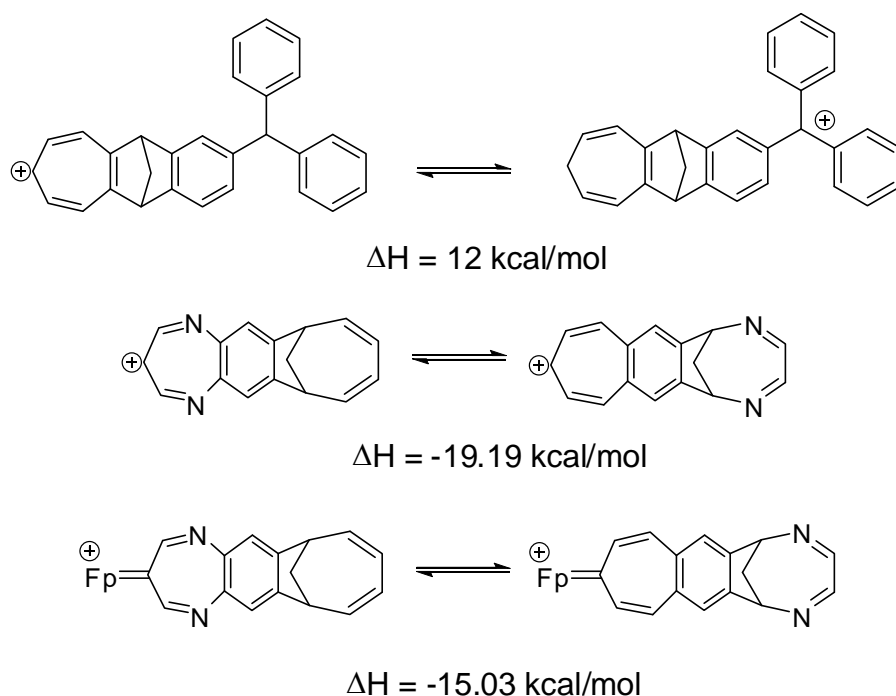
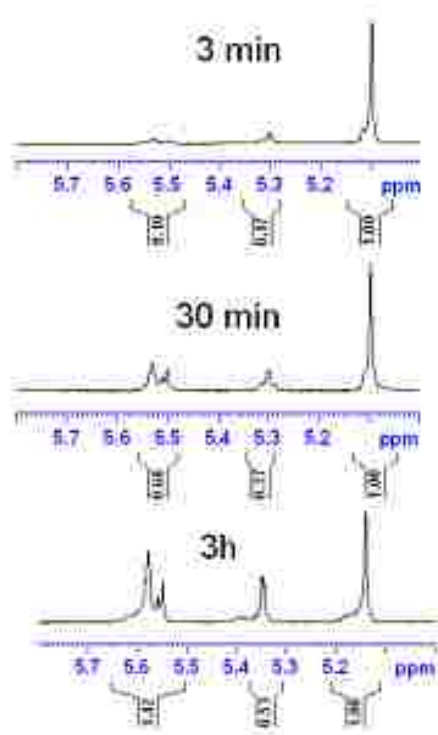
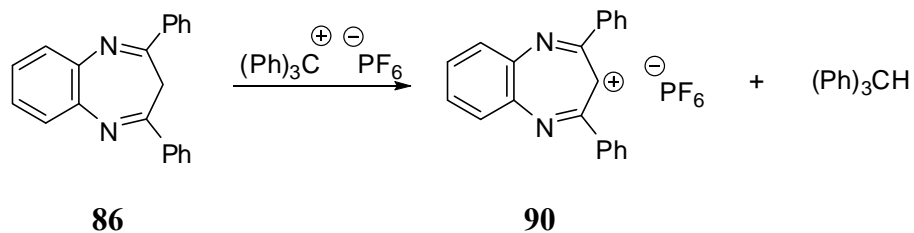


Figure 44. Comparison of Tropylium and Diazepine Ions.

Experimentally, uncomplexed benzodiazepine **86** was treated with triphenylcarbenium hexafluorophosphate in a J Young Valve NMR tube in deuterodichloromethane. Over the next 3 hours, an ^1H -NMR signal at 5.3 ppm consistent with triphenylmethane was observed (Figure 45); this was confirmed by addition of an authentic sample of triphenylmethane to the NMR tube. This indicated successful hydride abstraction. Unfortunately, the cationic diazepine salt could not be isolated.

Figure 45. Hydride Abstraction from benzodiazepine **86**.



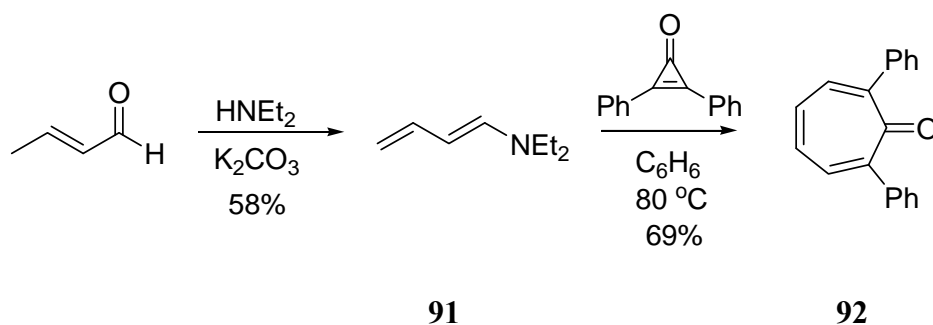
Considering the instability of σ -complex **85** and the computationally indicated difficulty in hydride abstraction to form **86**, we decided to pursue carbocyclic carbene ligands.

Cycloheptatrienyldene Ligands

As previously discussed, cycloheptatrienyldene (CHT) has been demonstrated to be an excellent ligand for palladium catalyzed C-C and C-N bond forming reactions.⁵⁶ First, we chose

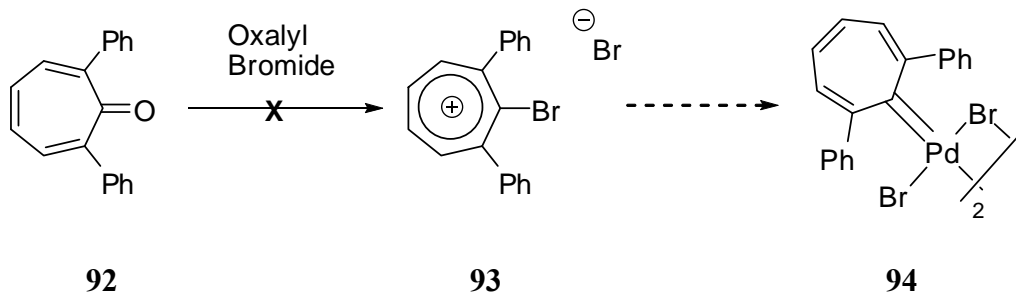
to investigate the effect of substitution of the CHT ligand in the 2 and 7 positions. To accomplish this, 2,7-diphenyltropone⁹⁹ **92** was synthesized as shown in Scheme 21.

Scheme 21. Synthesis of 2,7-Diphenyltropone.



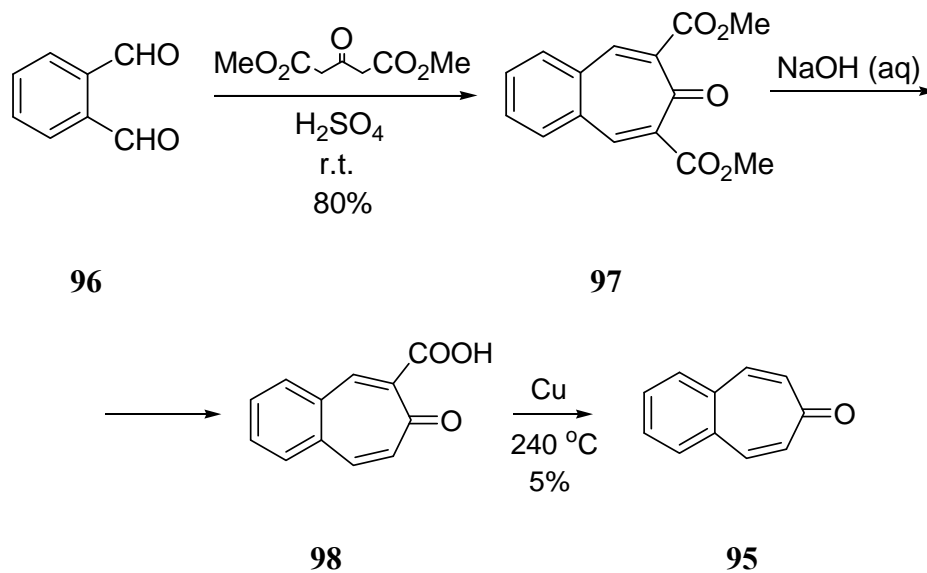
Crotonaldehyde was reacted with diethyl amine in the presence of potassium carbonate to form dienamine **91** in 58% yield. This enamine then underwent cycloaddition and subsequent ring expansion with diphenylcyclopropenone to give 2,7-diphenyltropone **92** in 80% yield; the tropone signals appear as a 4H multiplet at 7.51-7.62 ppm, the *o*- and *m*-phenyl protons give rise to an 8H multiplet at 7.32-7.43 ppm, and the *p*-phenyl protons appear as a 2H multiplet at 6.98-7.10 ppm. With **92** in hand, we set out to make the corresponding tropylium bromide to treat with palladium black to make the desired palladium carbene complex **94** as shown in Scheme 22; unfortunately, treatment of **92** with oxalyl bromide did not produce the desired tropylium salt **93**.

Scheme 22. Attempted Synthesis of Palladium Carbene Complex **94**.



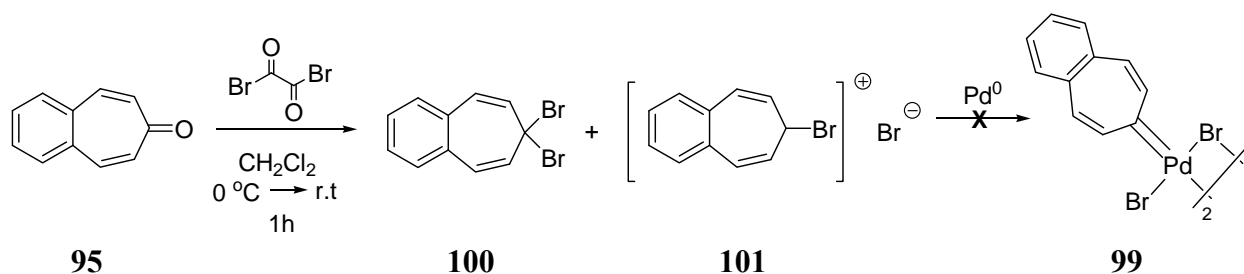
With synthesis of **94** unsuccessful, we chose to investigate the electronic and steric tunability of CHT by benzannulation of the 4,5-position, with complex **60** being the target. 4,5-Benzotropone (**95**) was synthesized by condensation of *o*-phthalaldehyde (**96**) with dimethyl 1,3-acetonedicarboxylate under acidic conditions, followed by basic hydrolysis of **97** and subsequent copper-mediated decarboxylation¹⁰⁰ as shown in scheme **23**.

Scheme 23. Synthesis of 4,5-Benzotropone.



When **95** was subsequently treated with oxalyl bromide, the corresponding bromobenzotropylium bromide was formed as indicated by NMR analysis and the intense red color of the resulting solid; however, treatment with palladium black or Pd₂(dba)₃ analogous to Herrmann's procedure⁵⁶ for formation of **62** did not yield the desired dinuclear palladium CHT complex **99**. Closer inspection of the NMR spectrum revealed that unlike the parent tropone, reaction of 4,5-benzotropone with oxalyl bromide does not lead to only the ionic bromotropylium bromide, but rather a mixture of covalent **100** and ionic **101** in what appears to be a 5:1 ratio by NMR integration. **100** gives rise to a multiplet from 7.39-7.52 ppm (4H, ArH), as well as doublets at 6.68 ppm (1H, J = 12 Hz) and 6.58 ppm (1H, J = 12 Hz) for the cycloheptatriene double bond protons. Signals for **101** appear collectively further downfield, consistent with ionic character; the aryl protons appear as 1H multiplets at 8.16-8.19 ppm and 8.30-8.43 ppm, and the tropylium protons appear as 1H doublets at 8.415 ppm (J = 12 Hz) and 8.735 ppm (J = 12 Hz).

Scheme 24. Treatment of 4,5-Benzotropone with Oxalyl Bromide.



The ionic character of the bromotropylium fragment appears to be crucial for the initial insertion of palladium into the carbon-bromine bond. In order to convert **100** and **101** to the bromobenzotropylium salt, a mix of the two was reacted with silver tetrafluoroborate. The ¹H-

NMR of the resulting bromobenzotropylium tetrafluoroborate ion **102** revealed signals far downfield of the covalently bonded bromide **100** as well as of the bromobenzotropylium bromide **101** (due to the less coordinating counterion); the tropylium protons of **102** appeared as doublets at 9.41 ppm ($J = 12$ Hz) and 9.10 ppm ($J = 12$ Hz), whereas the benzene protons gave rise to multiplets at 8.87 ppm and 8.68 ppm. When this highly reactive salt was treated with a source of Pd(0) in the presence of sodium bromide, **99** was not isolated (Scheme 25). These attempts are summarized in Table 7.

Scheme 25. Attempted Synthesis of **99** via Bromo-4,5-benzotropylium Tetrafluoroborate.

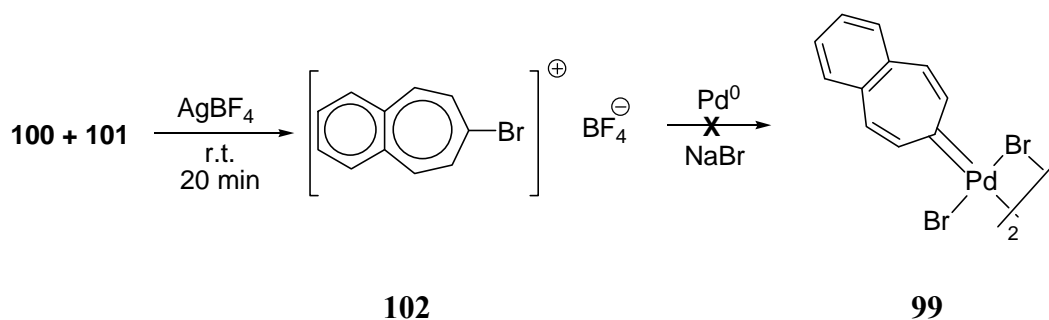


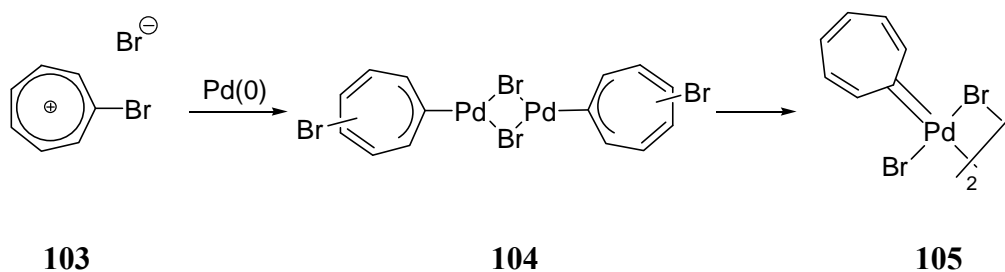
Table 7. Attempted Synthesis of **99**.

S.M.	Pd Source	Additive	Temperature	Solvent	Time	99 observed?
100/101	Pd black	-	-10 °C	DCM	6h	no
100/101	Pd ₂ (dba) ₃	-	-78 °C → r.t.	THF	12h	no
102	Pd ₂ (dba) ₃	-	-78 °C → r.t.	THF	12h	no
102	Pd ₂ (dba) ₃	NaBr	-78 °C → r.t.	THF	12h	no

Failure to synthesize **99** from **102** may be due to a number of reasons. Herrmann *et al.*⁵⁶ have shown that formation of **61** proceeds through insertion of palladium into the C-Br bond,

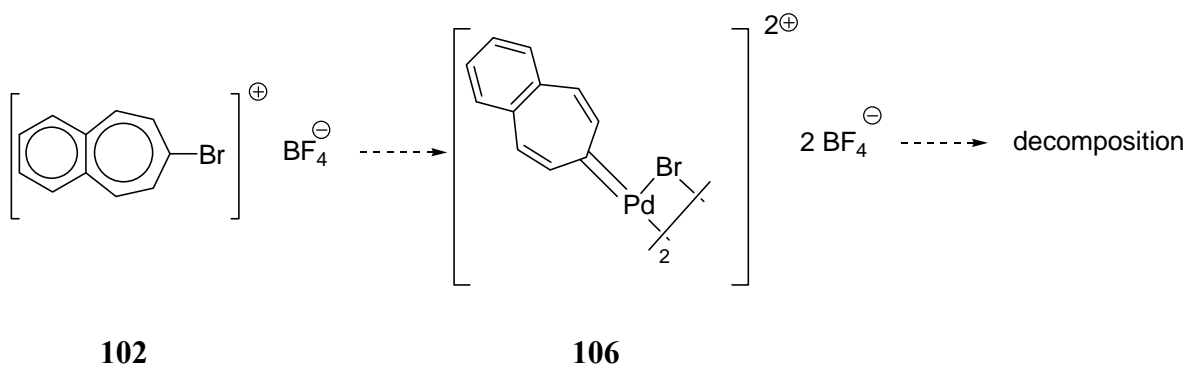
leading to dimeric palladium allyl complex **104**, which quickly rearranges to give the desired carbene complex **105** (Scheme 26). This work was successfully reproduced in our hands.

Scheme 26. Formation of Palladium Carbene Complex **104**.



With a tetrafluoroborate counterion, cationic palladium complex **106** would be formed, which is believed to be quite unstable and, if formed, would like decomposes rather quickly (Scheme 27).

Scheme 27. Proposed Formation of **106**.



To circumvent formation and subsequent decomposition of **106**, sodium bromide was added along with the palladium(0) precursor; however, it is possible that **102** in the presence of

sodium bromide simply reforms **100** and **101**. As illustrated in Scheme **24**, **100** and **101** also do not produce the desired carbene complex **99** when treated with palladium(0).

Conclusion

Precursors for 7-membered ring carbene ligands **89**, **92** and **95** have successfully been synthesized and the approaches towards formation of palladium carbene complexes have been described. Even though the desired carbene complexes were not formed, we believe **89**, **92** and **95** to be key intermediates in future exploration of steric and electronic control of cycloheptatrienyliene ligands.

EXPERIMENTAL

General Remarks

Reagents were used as purchased unless otherwise noted. Hexane was distilled prior to use. Tetrahydrofuran and diethyl ether were purified by passing through a Solv-Tek solvent purification column packed with alumina. Methylene Chloride was distilled over CaH₂ and stored over 4Å molecular sieves. Benzene, acetonitrile, and dimethyl sulfoxide were stored over 4Å molecular sieves for at least 24 hours before use. N-Bromosuccinimide was recrystallized from boiling water and dried *in vacuo* for 24 hours.

^1H -NMR and ^{13}C -NMR were acquired on a Bruker 400 UltraShield instrument using 5mm diameter sample tubes. Deuterated solvents used were purified by passing through a short alumina column and storing over 4Å molecular sieves. All spectra were recorded at ambient temperature. All NMR data are reported in the following manner: δ for the chemical shift in ppm relative to TMS, with residual undeuterated solvent used as internal standard. Coupling constants are reported in Hz. Multiplicities are abbreviated as follows: s for singlet, d for doublet, t for triplet, sep for septet, dd for doublet of doublets, dt for doublet of triplets, and m for higher order and/or complex multiplets.

Mass spectral data were acquired using an Agilent Technologies 6890N Network GC System coupled with a 5973 inert Mass Selective Detector. Electron impact (EI) or chemical ionization (CI) (methane) were both employed.

Infrared spectra were acquired on a Perkin Elmer Spectrum 100 FTIR using either thin film on NaCl or KBr plates or NaCl solution cells.

1,3-Diphenylpropynone (87).

In a Schlenk flask containing a magnetic stir bar, a nitrogen atmosphere was established and 15 mL dichloromethane was added to the flask. Dibenzoylmethane (3.06 g, 13.6 mmol), triphenylphosphine dibromide (6.01 g, 14.2 mmol) and triethylamine (8 mL, 56 mmol) were added and the solution turned yellow. After 30 minutes, the reaction mixture had turned brown. 10 mL de-ionized water was added and the mixture was transferred to a separatory funnel. The organic layer was washed with three 10 mL portions of de-ionized water, dried over magnesium sulfate and the solvent was removed *in vacuo*. Purification over silica gel eluting with 9:1 hexanes/ethyl acetate gave diphenylpropynone as an orange oil (2.27 g, 10.68 mmol, 79%)

matching previously published NMR and IR data.⁹⁷ ¹H-NMR (CDCl₃): 8.20 (dd, 2H, J = 8.0, 1.6 Hz), 7.63 (d, 2H, J = 8.0 Hz), 7.57 (t, 1H, J = 8.0 Hz), 7.34 - 7.48 (m, 5H); Appendix 8. ¹³C-NMR (CDCl₃): 178.2, 137.0, 134.4, 133.3, 131.1, 129.8, 129.0, 128.9, 120.2, 93.4, 87.2; IR (film) 3057 cm⁻¹, 2199 cm⁻¹, 1640 cm⁻¹.

2,4-Diphenyl-3H-benzo[1,4]diazepine (88).

In a round-bottom flask fitted with a reflux condenser and containing a magnetic stir bar, 1,3-diphenylpropynone **87** (2.2 g, 10.7 mmol) was dissolved in 20 mL methanol. *o*-Phenylenediamine (1.76 g, 16.3 mmol) was added in 20 mL methanol and the solution was stirred for 5 minutes before adding 4 mL acetic acid and heating the reaction mixture to reflux for 15 minutes. The flask was then allowed to cool to room temperature and placed in the freezer overnight; the resulting white crystals were collected by vacuum filtration (1.19 g, 4.0 mmol, 37.6%, m.p. 139-141 °C). The ¹H-NMR matched previously published data.⁹⁸ ¹H-NMR (CDCl₃): 7.97-8.01 (m, 4H), 7.62 (dd, 2H, J = 6.1, 3.5 Hz), 7.40-7.44 (m, 6H), 7.36 (dd, 2H, 6.1, 3.5 Hz) 3.74 (br s, 2H); Appendix 9. IR (film): 1580 cm⁻¹

3-Bromo-2,4-diphenyl-3H-benzo[1,4]diazepine (89).

To a round bottom flask fitted with a reflux condenser and containing a magnetic stir bar was added 30 mL carbon tetrachloride, benzodiazepine **88** (0.45 g, 1.53 mmol), *N*-bromosuccinimide (0.29 g, 1.65 mmol), and benzoyl peroxide (0.02 g, 0.08 mmol). The reaction mixture was heated to reflux for 16 hours before adding 0.5 g silica gel and removing the solvent *in vacuo*. The crude product coated on silica gel was transferred onto a short silica gel column

and flashed with 8/2 hexanes/diethyl ether to obtain **89** as a yellow oil (0.558 g, 1.49 mmol, 97%). The ¹H-NMR spectrum matched previously published data.⁹⁸ ¹H-NMR (CDCl₃): 7.91-7.94 (m, 4H), 7.71 (dd, 2H, 6.1, 3.5 Hz), 7.46-7.50 (m, 8H), 7.02 (s, 1H); Appendix 10. IR (film): 1580 cm⁻¹.

Lithium-Halogen Exchange Experiment on 89.

1,3-Diphenylpropynone (**87**) (0.213 g, 0.577 mmol) was placed in a Schlenk flask and a nitrogen atmosphere was established. 12 mL THF was added and the solution was cooled to -78 °C before adding *n*-butyllithium (1.3 mL, 1.6 M in hexane, 0.8 mmol). The solution was stirred for 15 minutes and turned a dark violet color. 5 mL de-ionized water was added and the reaction mixture turned reddish brown. The mixture was transferred to a separatory funnel, 10 mL diethyl ether was added, extracted, and the organic layer was washed with three 10 mL portions of de-ionized water before drying over magnesium sulfate. The ¹H-NMR of the crude product matched that of **88** (0.165 g, 0.56 mmol, 98%).

(η^5 -Cyclopentadienyldicarbonyl)(3-(2,4-Diphenyl-3*H*-benzo[1,4]diazepinyl)Iron (85**).**

In a Schlenk flask containing a magnetic stir bar, nitrogen atmosphere was established. 10 mL tetrahydrofuran and bromodiazepine **89** (0.16 g, 0.43 mmol) were added and the solution cooled to -78 °C in a dry ice/acetone bath. *n*-Butyllithium (0.4 mL, 1.6M in THF, 0.64 mmol) was added and the reaction mixture stirred for 30 minutes before adding cyclopentadienyldicarbonyliron iodide (0.18 g, 0.6 mmol) and stirring for an additional 30 minutes at -78 °C. The mixture was allowed to warm to room temperature and an aliquot was taken and filtered through

a plug of grade III alumina. ¹H-NMR (CDCl₃): 7.972-7.996 (m, 2H), 7.601-7.639 (m, 1H), 7.428-7.446 (m, 3H), 7.321-7.370 (m, 4H), 7.149-7.244 (m, 3H), 5.330 (s, 1H). Appendix 11. The remaining reaction mixture was chromatographed over grade III alumina, eluting with pentane, resulting in a complex mixture of products.

(E)-N,N-Diethylbuta-1,3-dien-1-amine (91).

In a round bottom flask containing a magnetic stir bar, a nitrogen atmosphere was established and the flask was cooled to -10 °C in an ice/water bath. To the flask were added 10 mL benzene, diethylamine (15 g, 0.2 mol) - distilled freshly from potassium hydroxide, crotonaldehyde (6.5 g, 0.09 mol), potassium carbonate (4.6 g, 0.033 mol) before removing the icebath and stirring at room temperature overnight. The reaction mixture was decanted, phenanthrenequinone (0.055 g, 0.26 mmol) was added to the liquid and **91** was obtained by vacuum distillation (6.542 g, 0.052 mol, 58%). The ¹H-NMR spectrum matched previously published data.⁹⁹

2,7-Diphenyltropone (92).

A round bottom flask was fitted with a reflux condenser and a magnetic stir bar before establishing a nitrogen atmosphere. To this flask was added diphenylcyclopropenone (0.247 g, 1.25 mmol) in 3 mL benzene and **91** (0.162 g, 1.27 mmol) in 2 mL benzene and the reaction mixture was refluxed for 12 hours. The solution was then transferred to a separatory funnel and 10 mL diethyl ether and 10 mL de-ionized water was added and the aqueous layer drained. The organic layer was washed with 1M hydrochloric acid, dried over magnesium sulfate and the

solvent removed on a rotary evaporator. The crude product was recrystallized from absolute ethanol to give 2,7-diphenyltropone **92** (0.223 g, 0.86 mmol, 69%). The ¹H-NMR matched previously published data.⁹⁹ ¹H-NMR (CDCl₃): 7.51-7.62 (m, 4H), 7.32-7.43 (m, 8H), 6.98-7.10 (m, 2H). Appendix 12.

7-Oxo-7H-benzocycloheptene-6,8-dicarboxylic acid dimethyl ester (97).

In a 100 mL round bottom flask, *ortho*-phthalaldehyde (1.0 g, 7.46 mmol) was dissolved in 30 mL concentrated sulfuric acid and the solution cooled to 0 °C before adding dimethyl-3-oxopentanedioate (1.36 g, 7.5 mmol). The yellow solution was warmed to room temperature and stirred for 1 hour. The resulting brown solution was poured over ice and filtered. The precipitate was washed with water until pH 7 (4 washes) and dried *in vacuo*, yielding **97** as off-white crystals (1.63 g, 5.98 mmol, 80%), which was used without further purification. The ¹H-NMR matched previously published data.¹⁰⁰ ¹H-NMR (CDCl₃) 8.20 (s, 2H), 7.80-7.81 (m, 2H), 7.67-7.69 (m, 2H), 3.94 (s, 6H). Appendix 13.

4,5-Benzotropone (95).

In a round bottom flask fitted with a reflux condenser and a magnetic stir bar, **97** (1.63 g, 5.98 mmol) was stirred along with 70 mL de-ionized water and sodium hydroxide (3.6 g, .09 mol). The suspension was heated to reflux for 8 hours, then was cooled to room temperature before pouring over crushed ice and acidifying to pH 1 with 6 M hydrochloric acid. The resulting precipitate is collected by vacuum filtration, washed with cold water and dried *in vacuo* for 1 hour. The solid was then transferred to a round bottom flask fitted with a reflux condenser and a

magnetic stir bar and refluxed in 10 mL *n*-butanol for 2 hours. The solution was then concentrated *in vacuo* until a precipitate was observed when cold. This precipitate was collected by vacuum filtration, washed with ice-cold butanol and dried *in vacuo* for 1 hour. The brown solid was then transferred to a mortar and ground with copper (2.0 g, 31.5 mmol), and the mixture placed in a sublimator with the cold finger cooled with a dry ice/acetone mixture. The sublimator was placed in a sand bath and heated to 250 °C at 2 mmHg. The sublimated 4,5-Benzotropone was rinsed off the cold finger with chloroform. The solution was dried over magnesium sulfate and the solvent removed on a rotary evaporator to give **95** (0.071 g, 0.3 mmol, 5%) as a yellow, low-melting solid. The NMR spectra matched previously published data.¹⁰⁰ ¹H-NMR (CDCl₃) 7.687-7.701 (m, 2H), 7.590-7.613 (m, 2H), 7.477 (d, 2H, 12 Hz), 6.817 (d, 2H, 12 Hz). Appendix 14. ¹³C-NMR (CDCl₃): 188.4, 141.5, 136.0, 135.0, 134.0, 130.5. Appendix 15.

4,5-Benzobromotropylium Bromide (100, 101).¹⁰⁰

In a Schlenk flask fitted containing a magnetic stir bar, a nitrogen atmosphere was established. 4,5-Benzotropone (0.11 g, 0.69 mmol) was added in 4 mL dichloromethane and solution was cooled to 0 °C before adding oxalyl bromide (0.1 mL, 1.04 mmol). The reaction mixture was removed from the ice bath and allowed to stir for 1 hour, at which point evolution of CO and CO₂ had stopped. An aliquot was taken from the solution and placed in a J-Young Valve NMR tube and the solvent was removed under vacuum to give **100** and **101**, a deep red solid, as a mixture of covalent and ionic isomers. Appendix 16.

4,5-Benzobromotropylium Tetrafluoroborate (102).

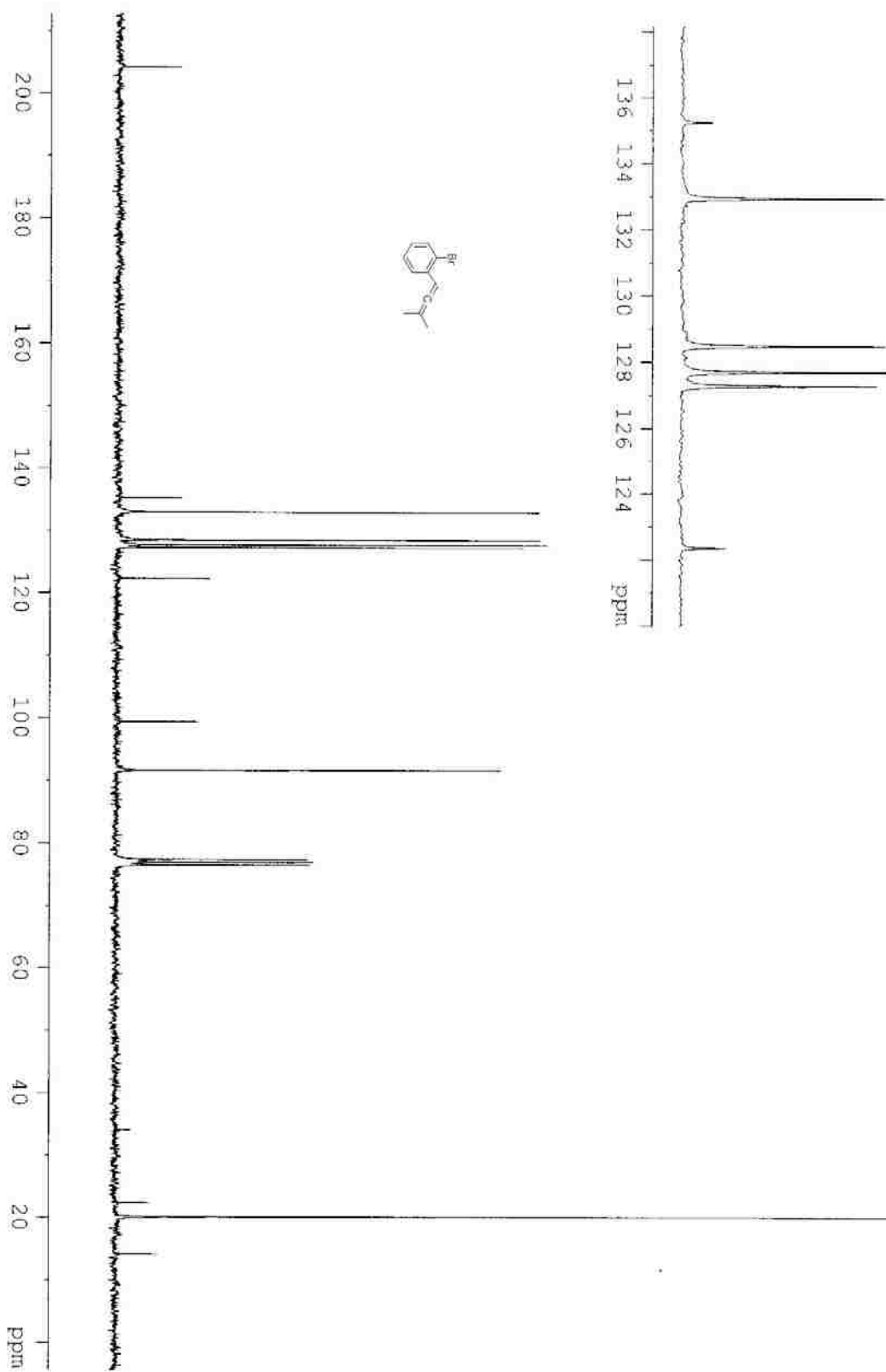
In an aluminum foil-wrapped Schlenk flask in a glove box, a mixture of **100** and **101** (0.208 g, 0.69 mmol) was dissolved in 4 mL dichloromethane and stirred at room temperature before adding silver tetrafluoroborate (0.136 g, 0.7 mmol); the reaction mixture was continued to stir for 20 minutes before removing the voluminous silver bromide precipitate by filtration. An aliquot of the supernatant was transferred to a J-Young Valve NMR tube and the solvent was removed *in vacuo* to give **102** as a brown solid. The product quickly decomposed even under strictly inert atmosphere, thus allowing for only a crude $^1\text{H-NMR}$ to be obtained. $^1\text{H-NMR}$ (CD_2Cl_2): 9.415 (2H, d, $J = 12$ Hz), 9.10 (2H, d, $J = 12$ Hz), 8.86-8.88 (2H, m), 8.67-8.69 (2H, m). Appendix 17.

Attempted Synthesis of Di- μ -Bromobis(4,5-benzocycloheptatrienylydene)-dibromopalladium(II) (99).

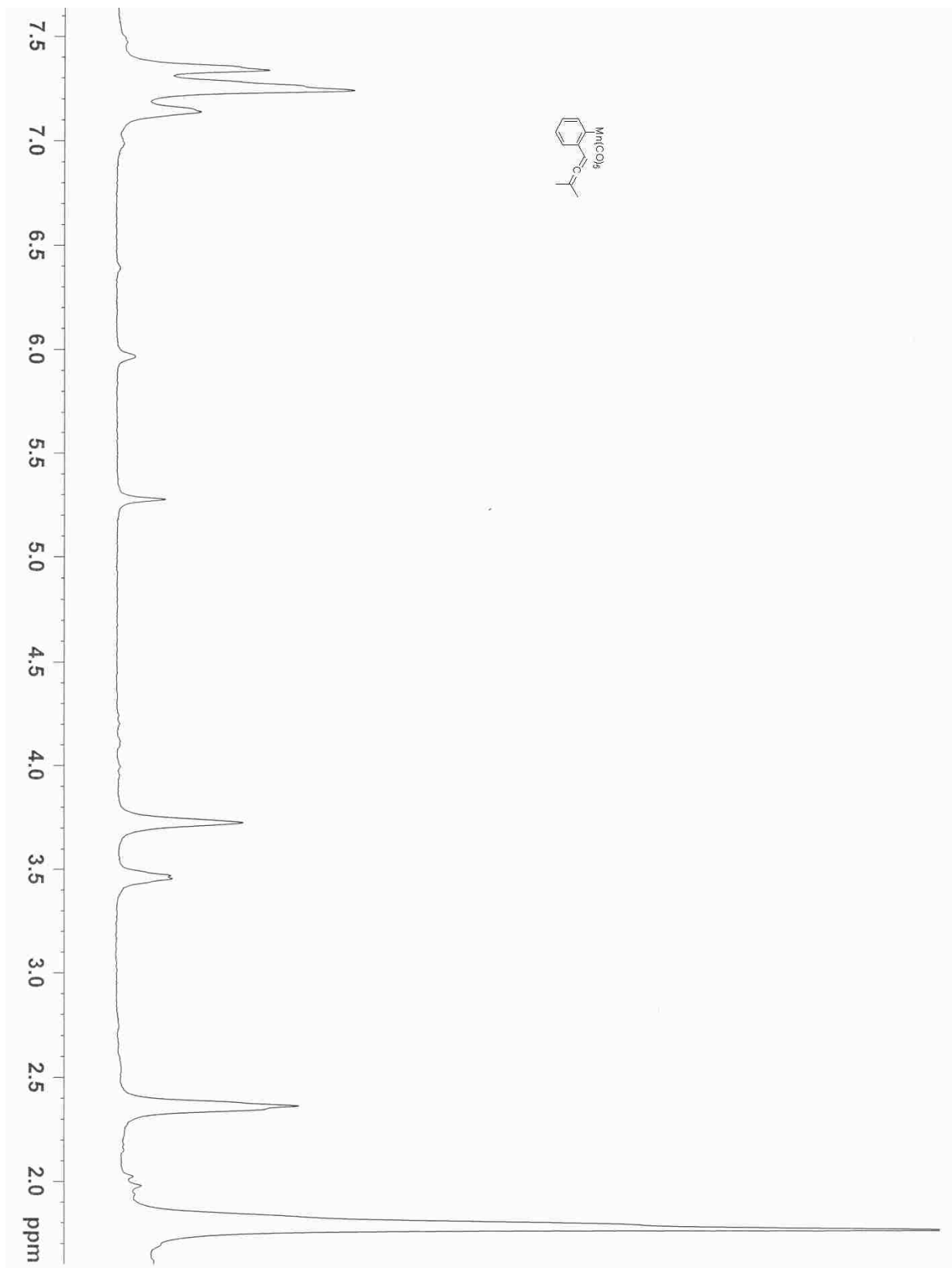
In a Schlenk flask fitted containing a magnetic stir bar, a nitrogen atmosphere was established. 4,5-Benzotropone (0.11 g, 0.69 mmol) was added in 6 mL dichloromethane and solution was cooled to 0 °C before adding oxalyl bromide (0.1 mL, 1.04 mmol). The reaction mixture was removed from the ice bath and allowed to stir for 1 hour, at which point evolution of CO and CO₂ had stopped. Volatiles were removed *in vacuo* and the red solid was redissolved in 6 mL dichloromethane. The Schlenk flask was transferred to the glove box, wrapped in aluminum foil and silver tetrafluoroborate (0.14 g, 0.73 mmol) was added. The mixture was stirred for 15 minutes at room temperature, the precipitate removed by vacuum filtration and the solvent removed *in vacuo* before redissolving the 4,5-benzobromotropylium tetrafluoroborate in 4 mL tetrahydrofuran. The Schlenk flask was again removed from the glove box and placed in a

dry ice/acetone bath before adding tris(dibenzylideneacetone)dipalladium(0) (0.29 g, 0.32 mmol) and sodium bromide (0.153 g, 1.5 mmol) in 8 mL THF (precooled to -78 °C). The solution was slowly warmed to room temperature overnight and an aliquot was removed via syringe and placed in a J-Young Valve NMR tube, where the solvent was removed *in vacuo*. The crude NMR revealed only peaks consistent with dibenzylideneacetone. ¹H-NMR (CDCl₃): 7.75 (d, 2H, J = 16 Hz), 7.603-7.636 (m, 4H), 7.389-7.448 (m, 5H), 7.10 (d, 2H, J = 16). ¹³C-NMR (CDCl₃): 188.99, 143.30, 134.79, 130.48, 128.95, 128.37, 125.43.

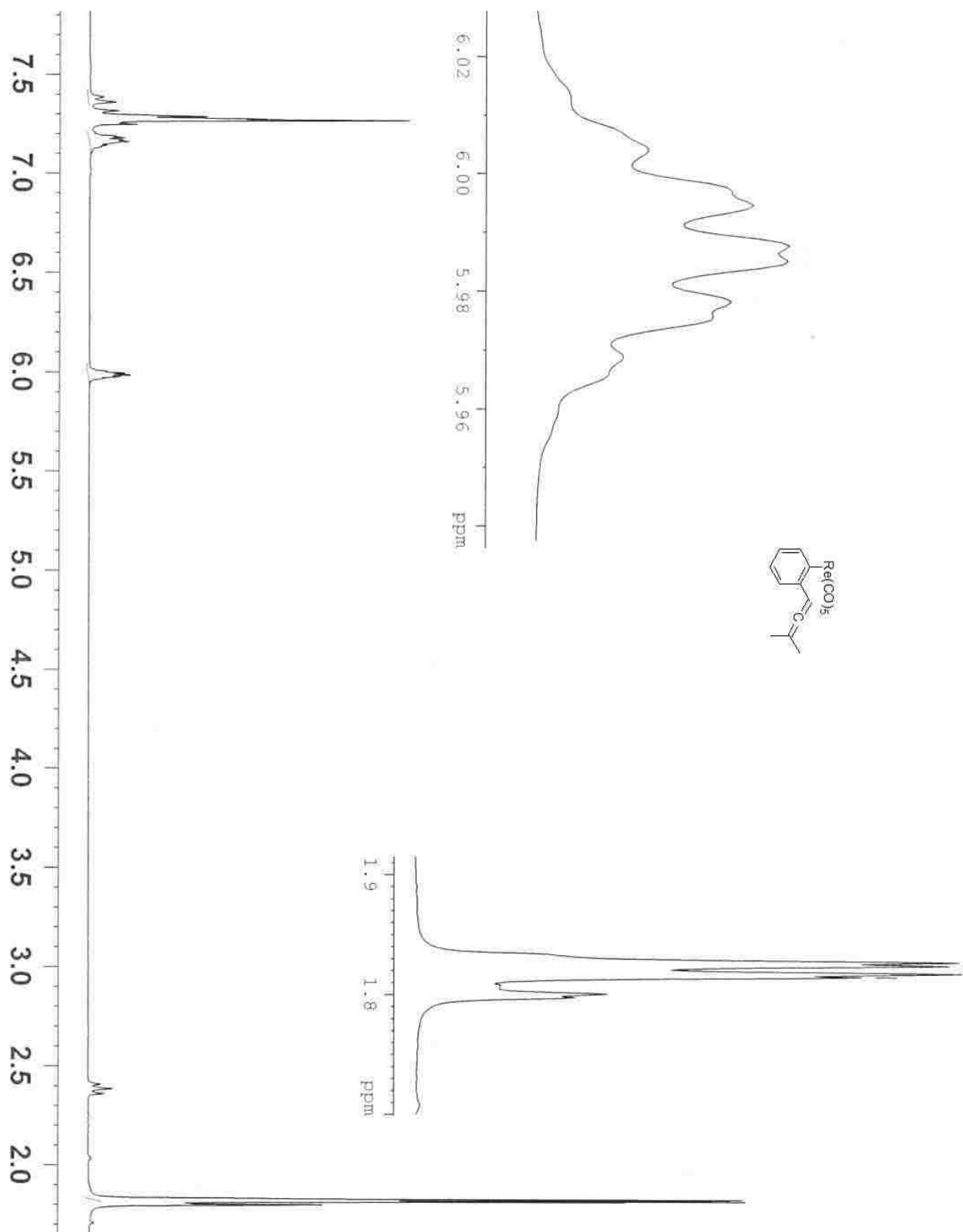
Appendix 2: 1-Bromo-2-(3-methyl-1,2-butadienyl)-benzene (23), ^{13}C -NMR.



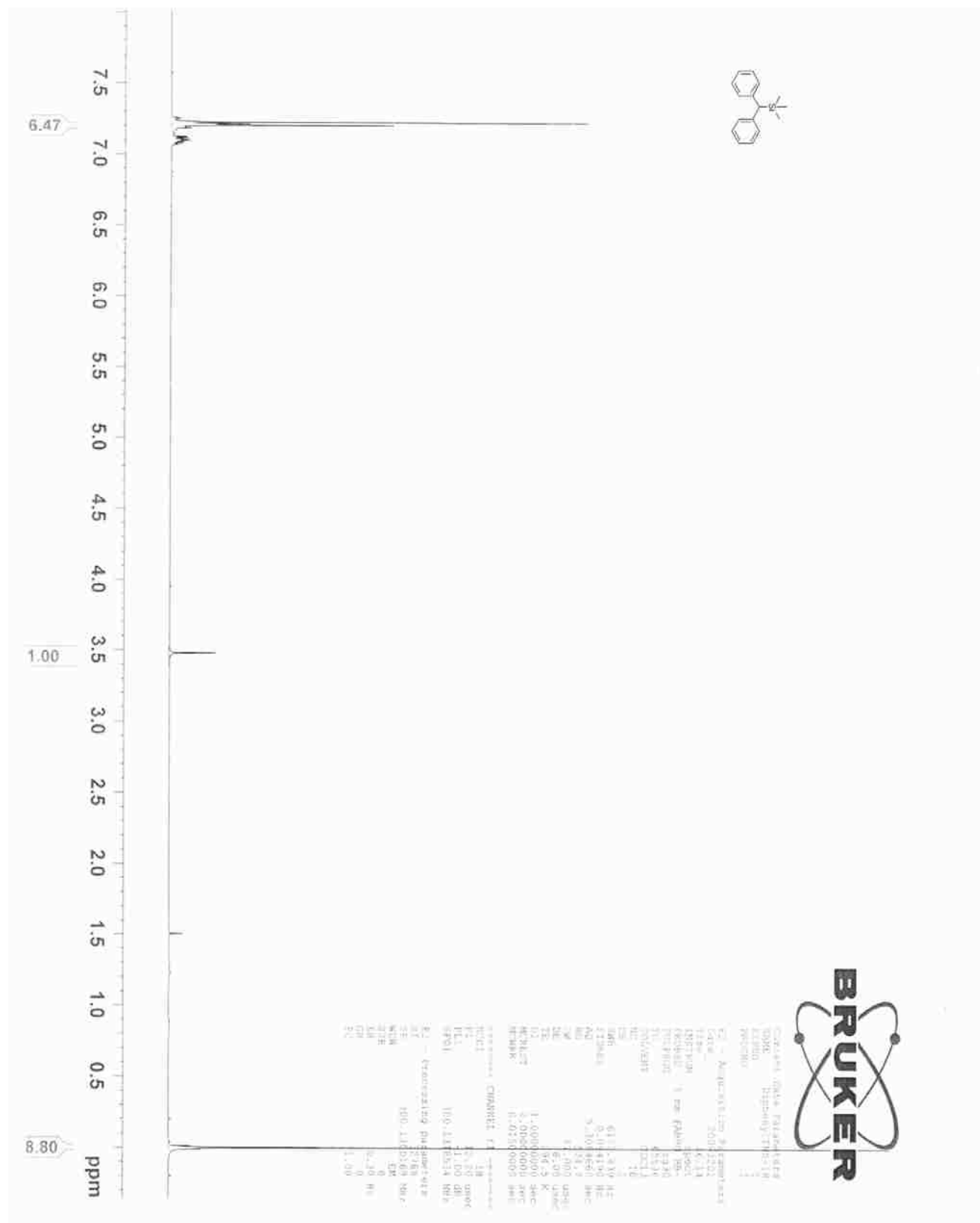
Appendix 3: (η^1 -(2-Methyl-1,2-butadienyl)benzene)pentacarbonylmanganese (41a).



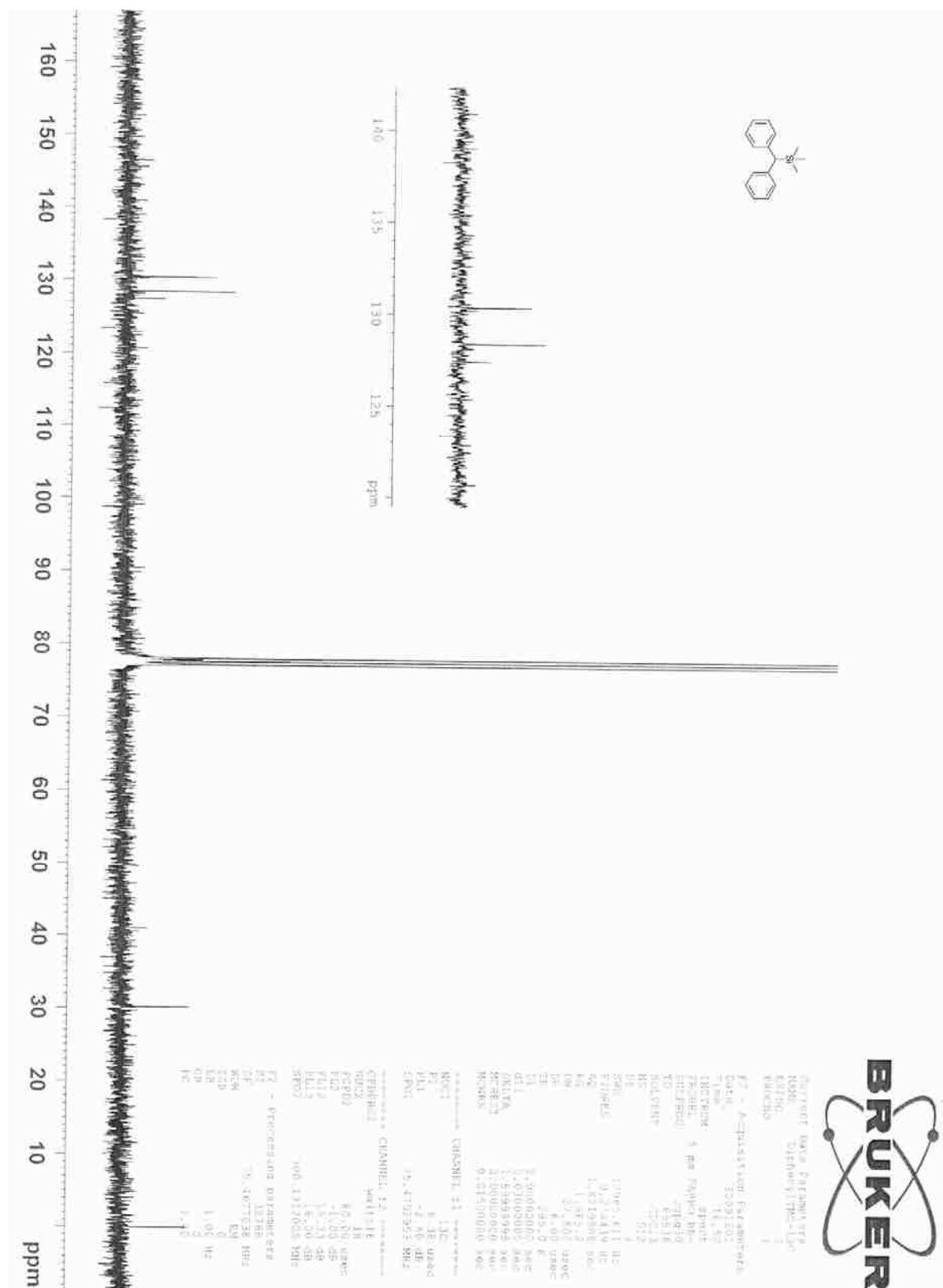
Appendix 4: (η^1 -(2-Methyl-1,2-butadienyl)benzene)pentacarbonylrhenium (41b).



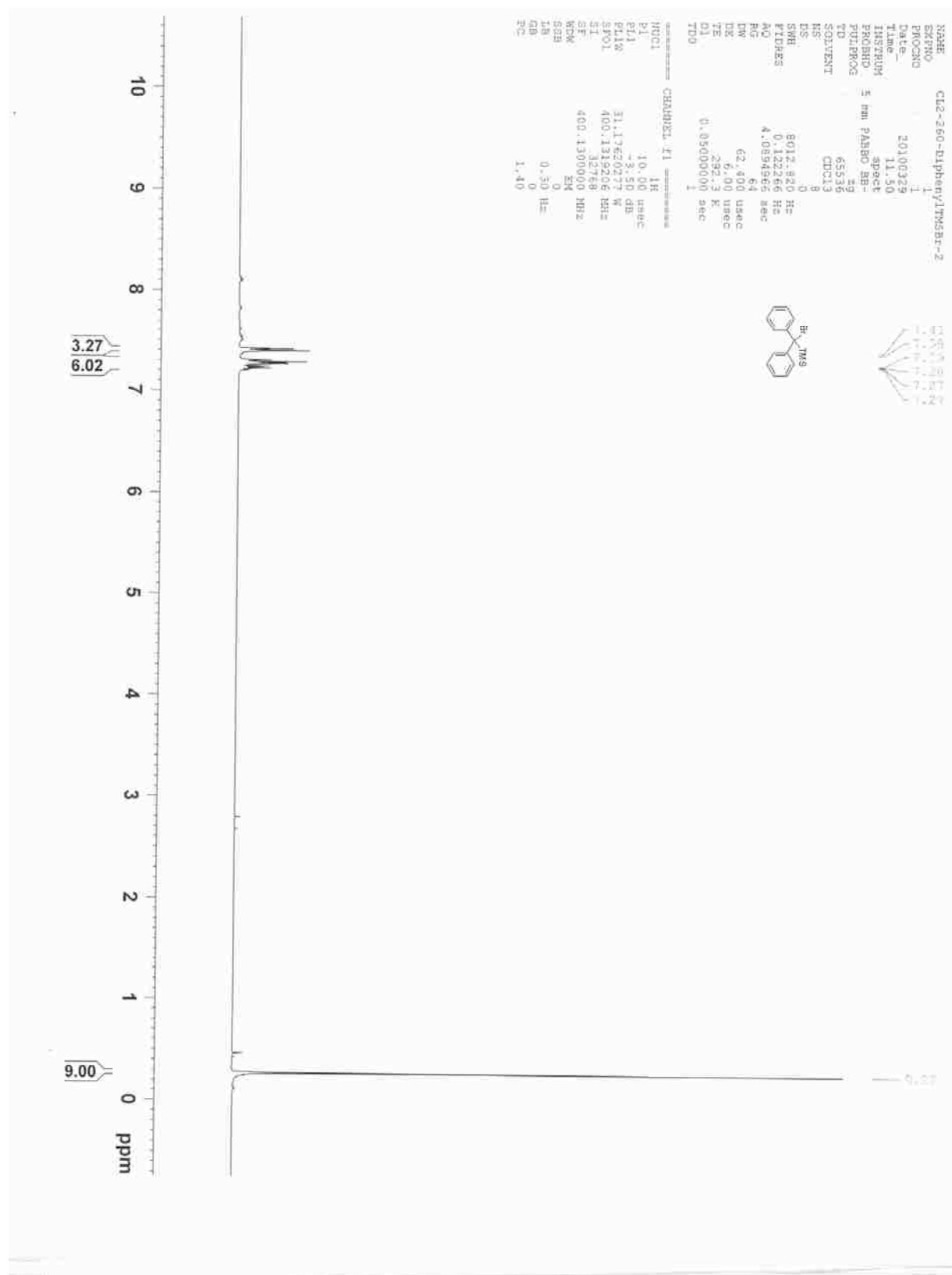
Appendix 5: (1,1-Diphenylmethyl)trimethylsilane (44), ¹H-NMR.



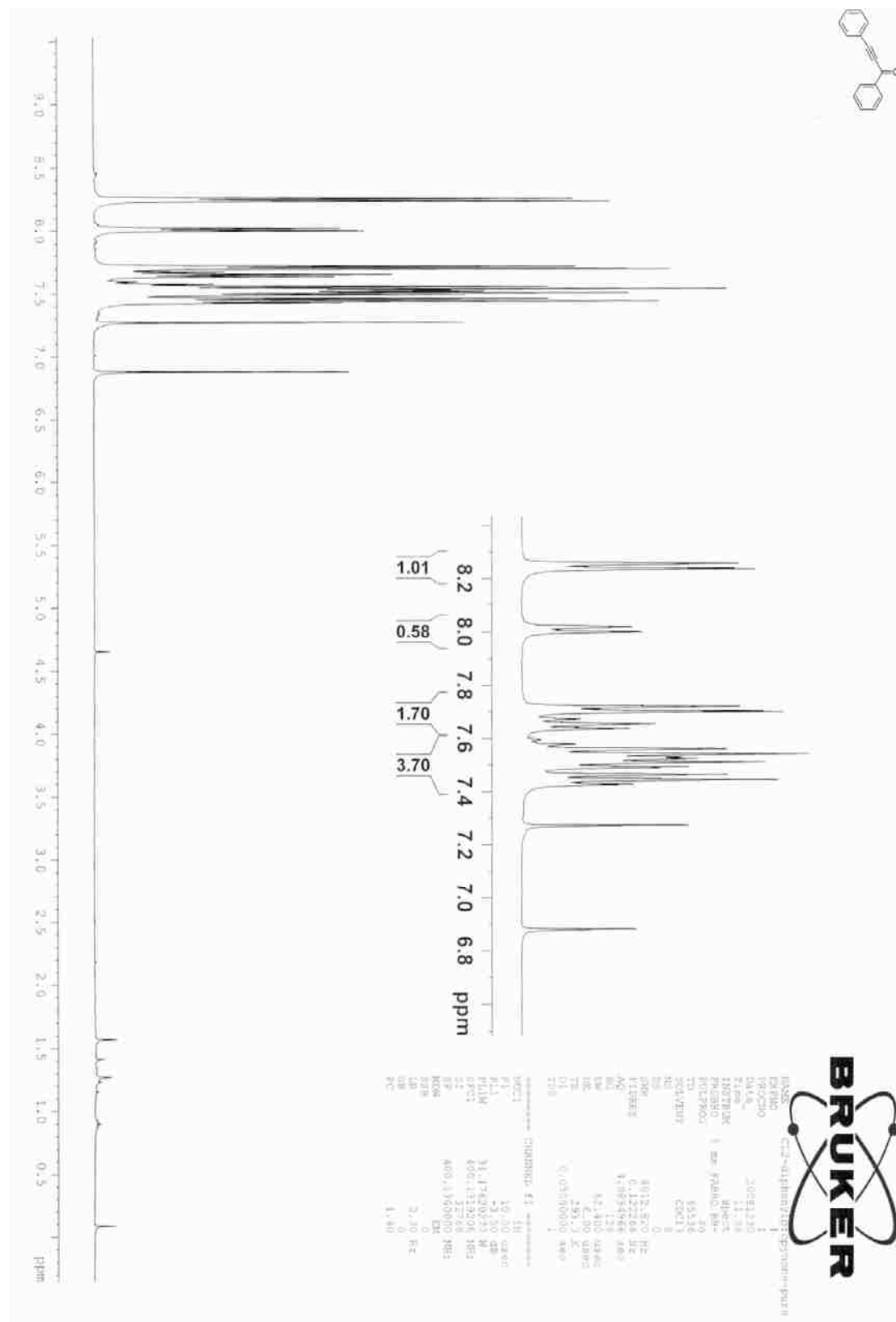
Appendix 6: (1,1-Diphenylmethyl)trimethylsilane (44), ¹³C-NMR.



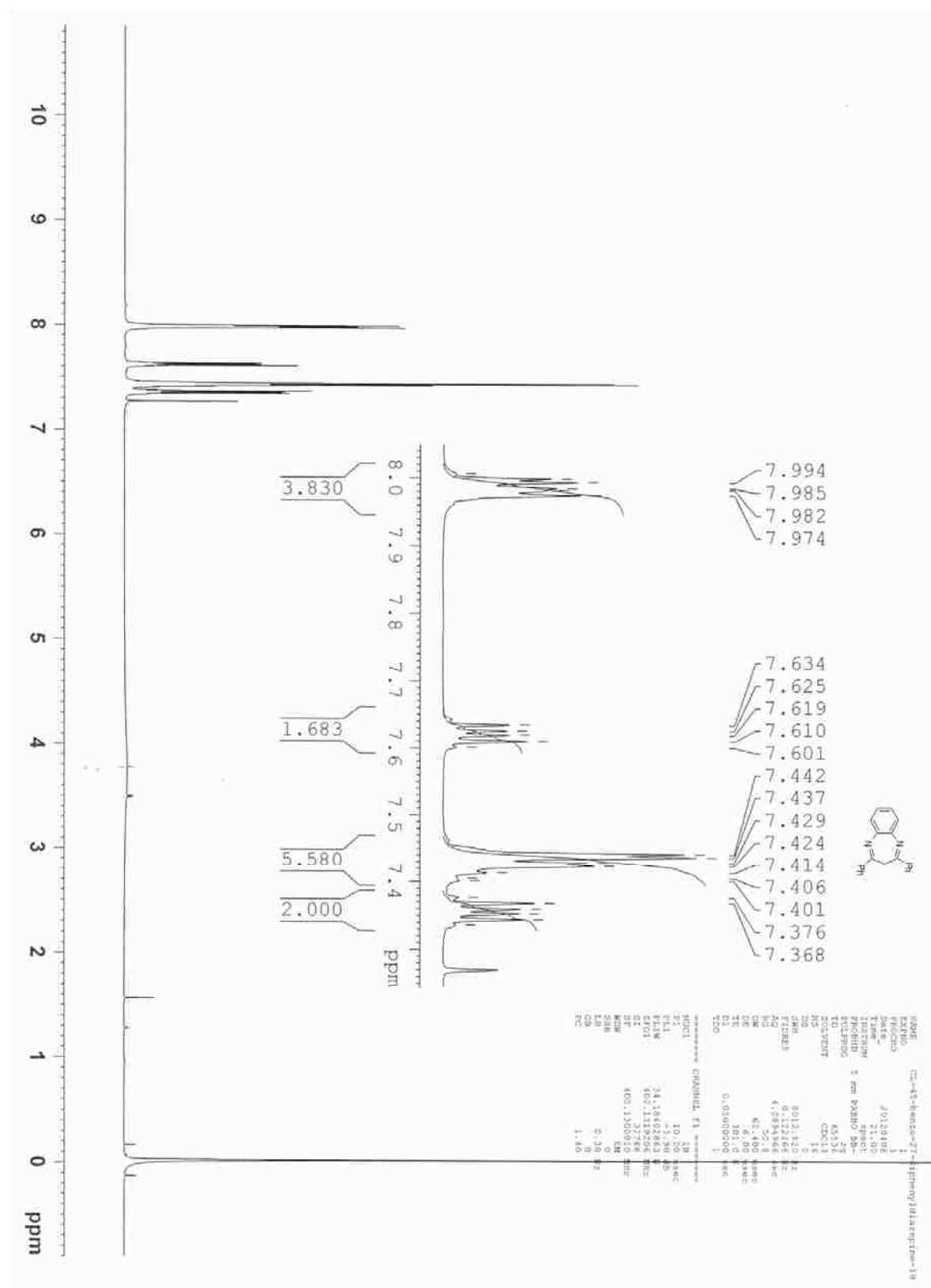
Appendix 7: (1-Bromo-1,1-diphenylmethyl)trimethylsilane (43).



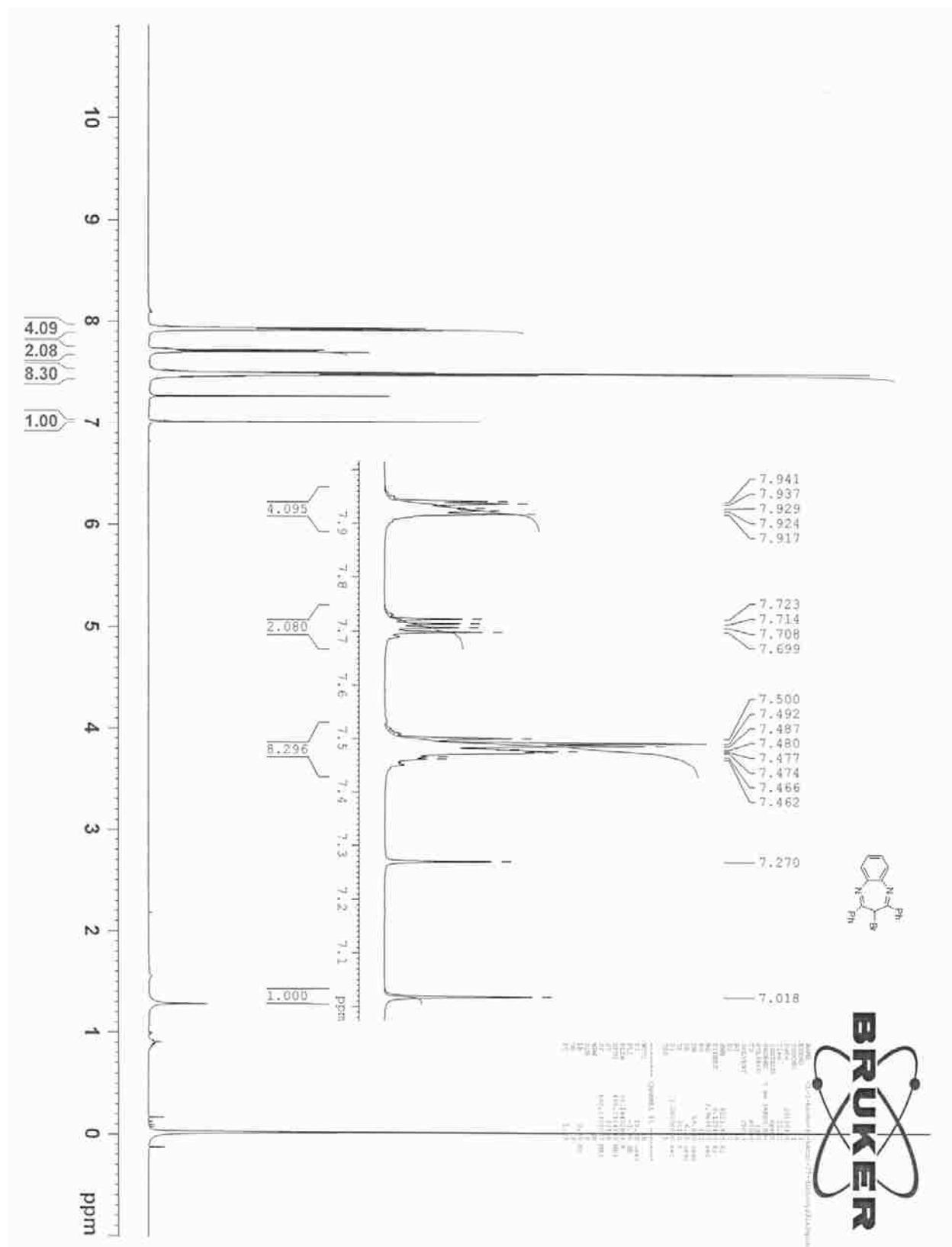
Appendix 8: 1,3-Diphenylpropynone (87)



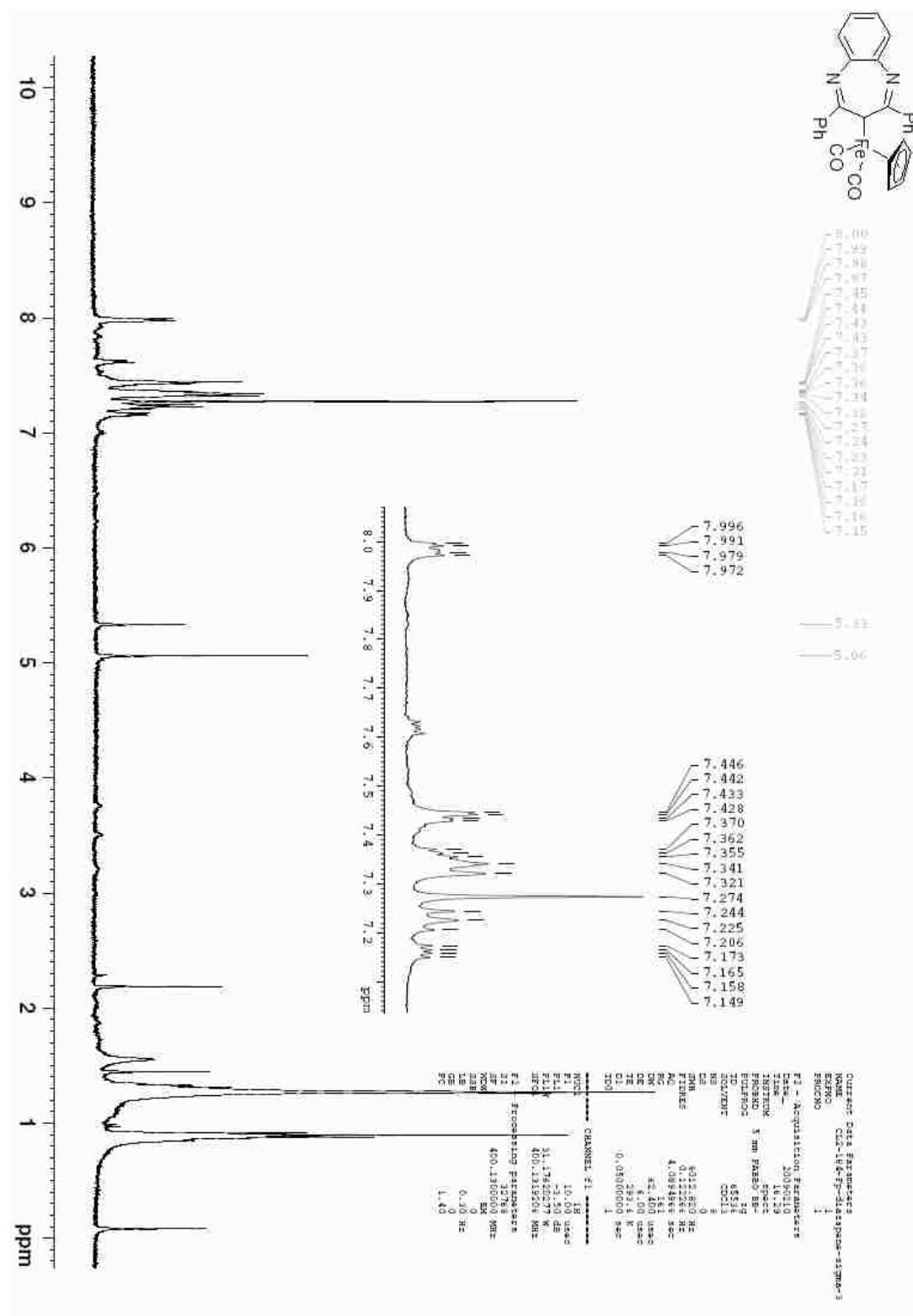
Appendix 9: 2,4-Diphenyl-3H-benzo[1,4]diazepine (88).



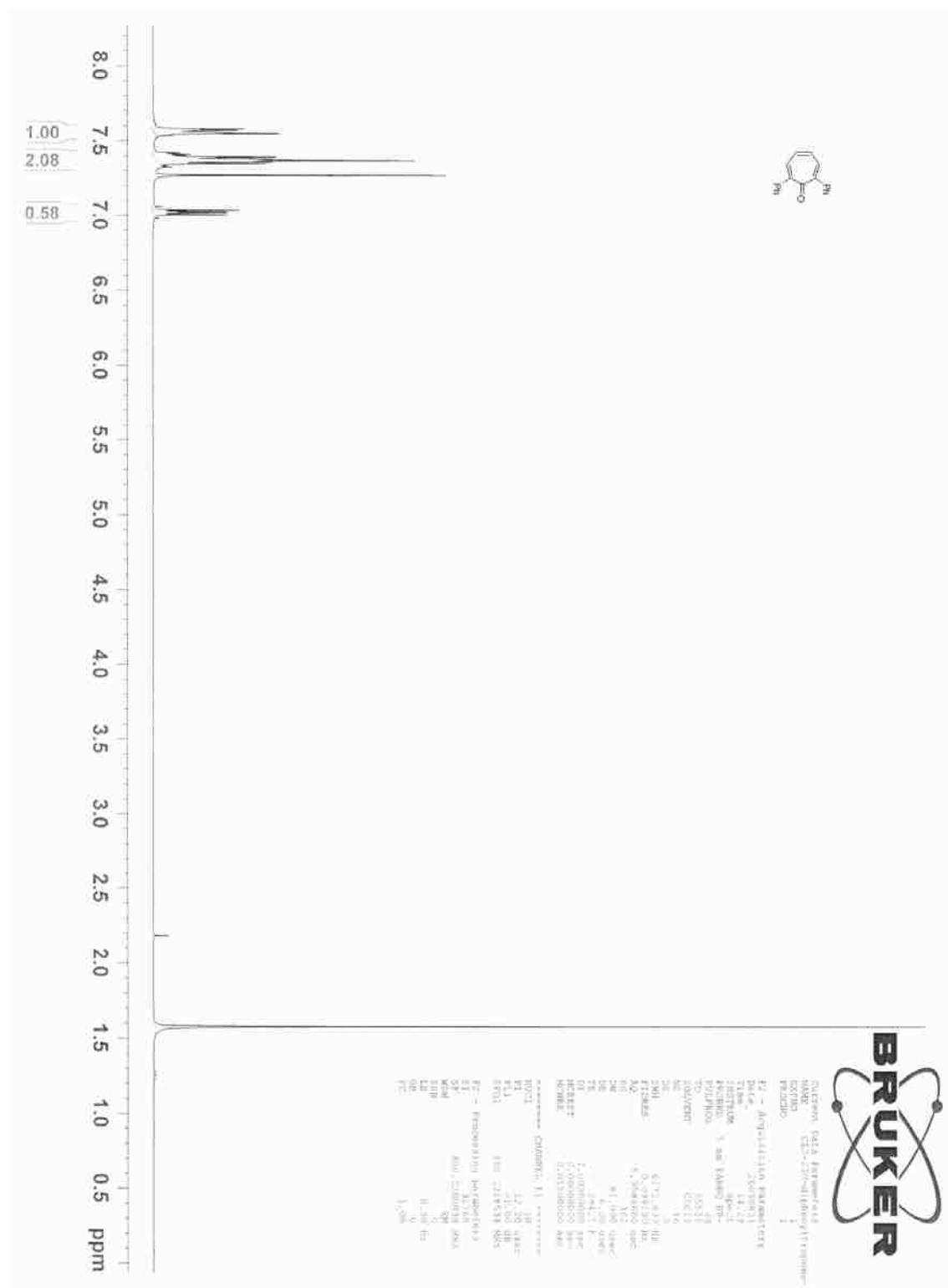
Appendix 10: 3-Bromo-2,4-diphenyl-3H-benzo[1,4]diazepine (89).



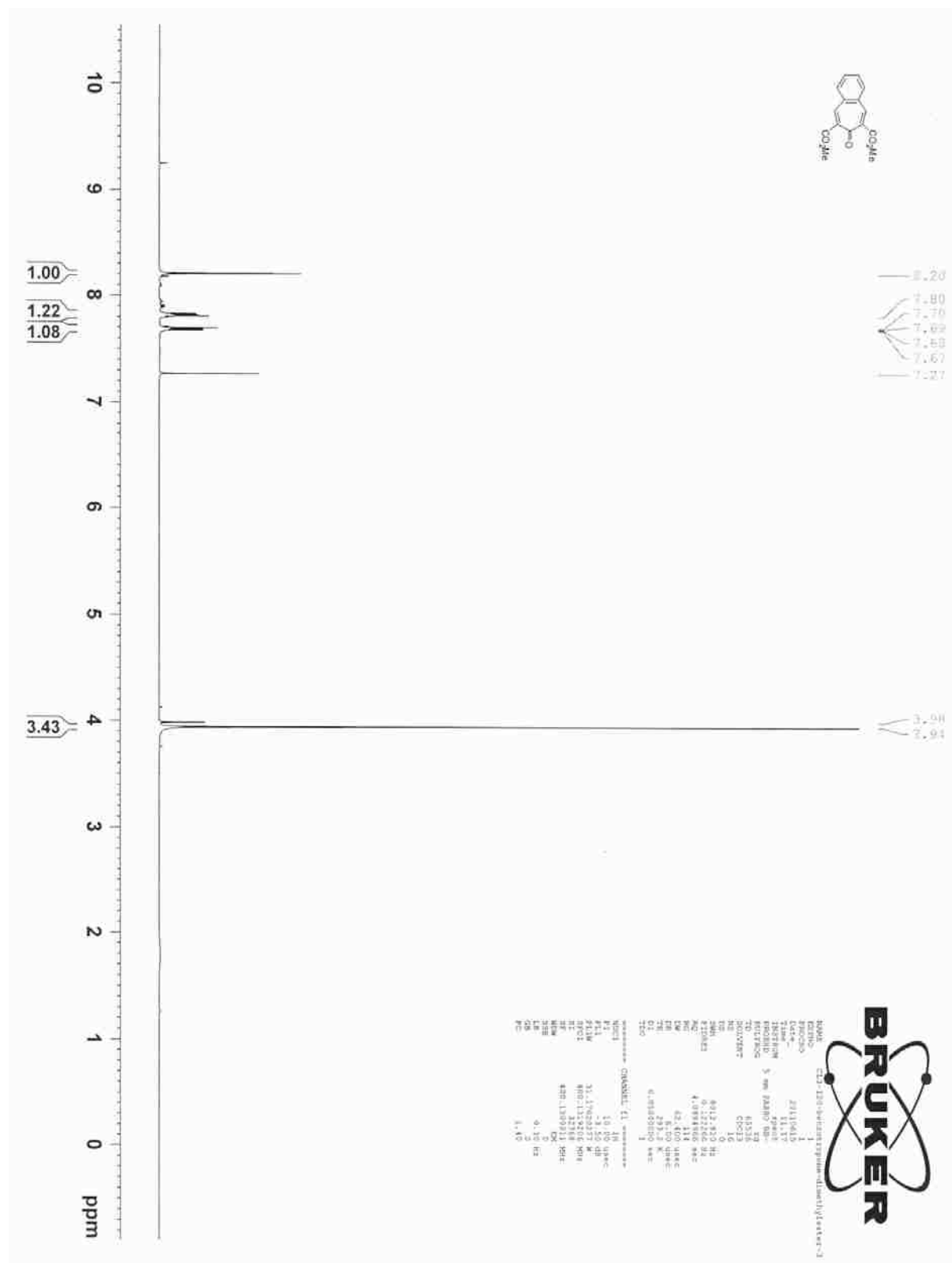
Appendix 11: (η^5 -Cyclopentadienyldicarbonyl)(3-(2,4-Diphenyl-3*H*-benzo[1,4]diazepinyl)Iron
(85).



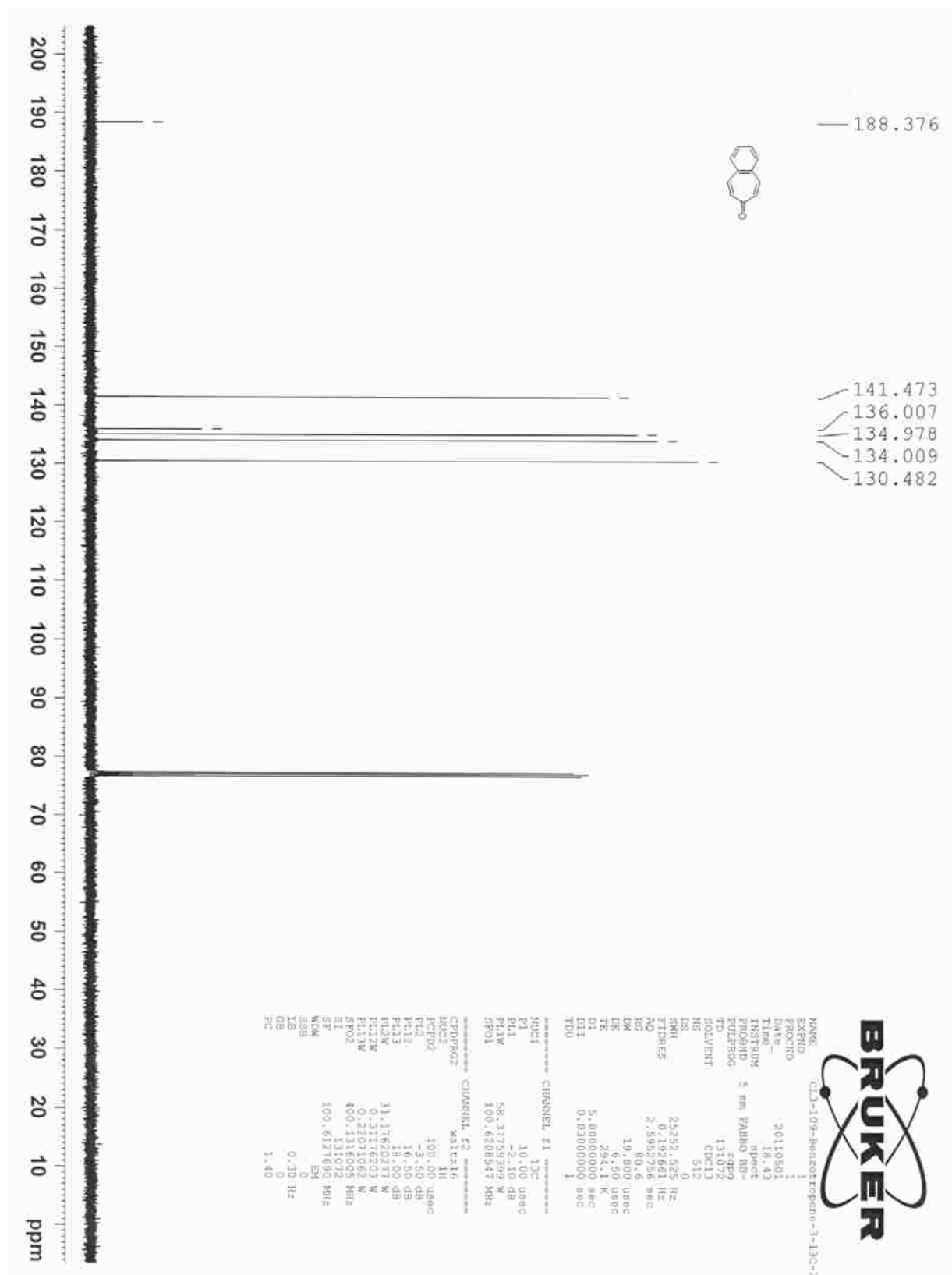
Appendix 12: 2,7-Diphenyltropone (92).



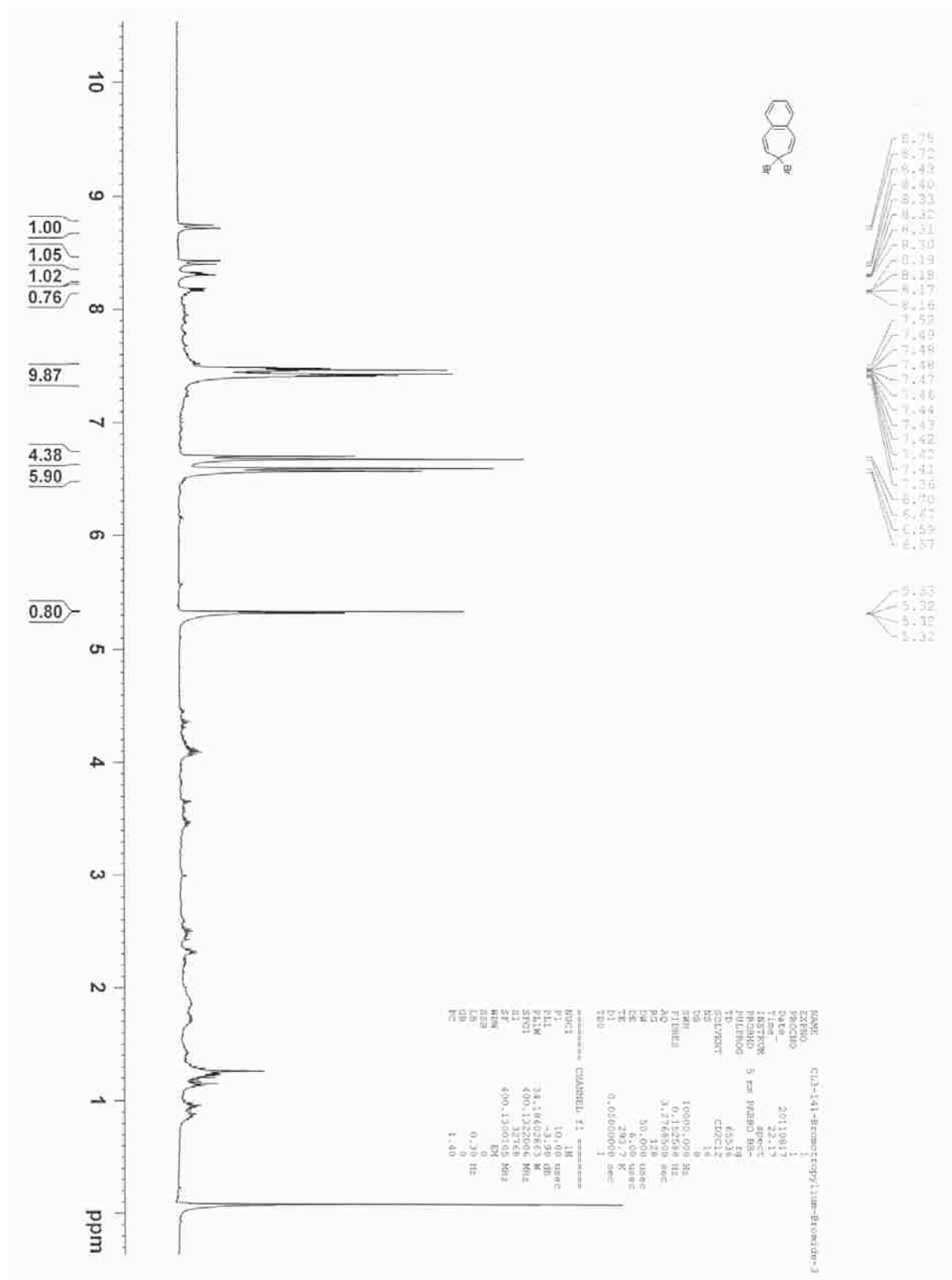
Appendix 13: 7-Oxo-7H-benzocycloheptene-6,8-dicarboxylic acid dimethyl ester (97).



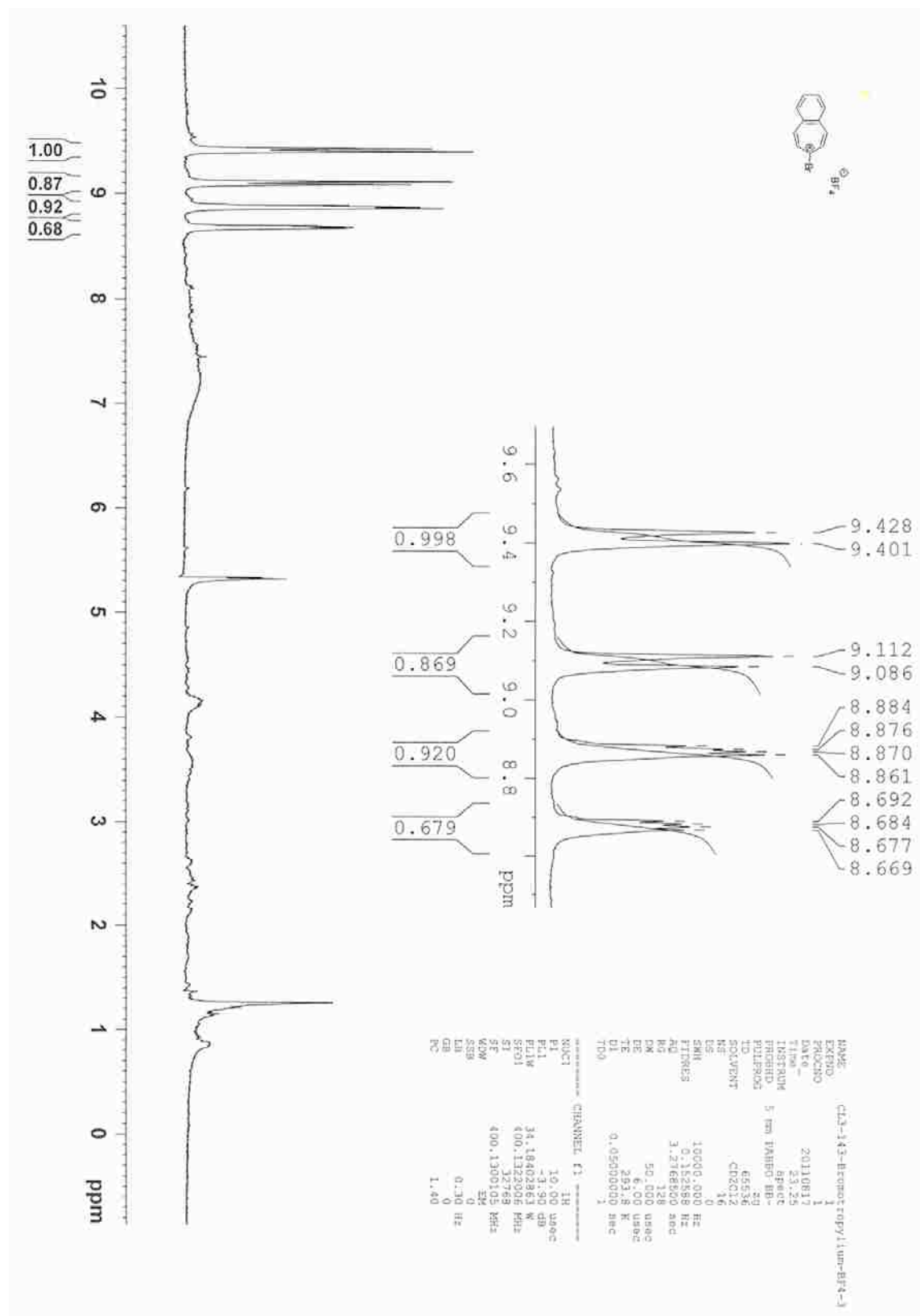
Appendix 15: Appendix 15: 4,5-Benzotropone (95), ¹³C-NMR.



Appendix 16: 4,5-Benzobromotropylium Bromide (100, 101).



Appendix 17: 4,5-Benzobromotropylium Tetrafluoroborate (102).



-
- ¹ *Organometallic Chemistry of Arene Ruthenium and Osmium Complexes* Le Bozec, H.; Touchard, D.; Dixneuf, P. H. *Adv. Organomet. Chem.* **1989**, *29*, 163-247.
- ² (a) *Lignin-based Concrete Modifiers* Bremner, T.; Zhor, J.; Goyal, G. C.; Lora, J. H. *PCT Int. Appl.* **1997**, WO 9713733 A1 19970417. (b) *Phenol-Formaldehyde Resins. V. Hardening Reactions of p-Methylol Groups* Hultsch, K. *Ber. Dtsch. Chem. Ges.* **1941**, *74B*, 1533-1538.
- ³ *o-Quinone Methide Chemistry* Schleigh, W. R. *Org. Chem. Bull.* **1971**, *43*, 1-3.
- ⁴ *o-Quinone Methide* Gardner, P. D.; Sarrafizadeh, R. H.; Brandon, R. L. *J. Am. Chem. Soc.* **1959**, *81*, 5515.
- ⁵ *Immortalizing a Transient Electrophile for DNA Cross-Linking* Wang, H.; Wahi, M. S.; Rokita, S. E. *Angew. Chem., Int. Ed.* **2008**, *47*, 1291-1293.
- ⁶ *Naturally Occuring Quinone Methides as Potential Bioreductive Alkylating Agents* Moore, H. W.; Czerniak, R. *Med. Res. Rev.* **1981**, *1(3)*, 249-280.
- ⁷ *Taxodione and Taxodone: Two Novel Diterpenoid Tumor Inhibitors* Kupchan, S. A.; Karim, A.; Marcks, C. *J. Am. Chem. Soc.* **68**, *90*, 5923-5924.
- ⁸ (a) *Synthesis and Chemistry of a Quinone Methide Model for Anthracycline Antitumor Antibiotics* Angle, S. R.; Yang, W. *J. Am. Chem. Soc.* **1990**, *112*, 4524-4528. (b) *Synthesis and Chemistry of Quinone Methide Models for the Anthracycline Antitumor Antibiotics* Angle, S. R.; Rainier, J. D.; Woytowicz, C. *J. Org. Chem.* **1997**, *62*, 5884-5892.
- ⁹ *Reductive Metabolism and Alkylating Activity of Mitomycin C Induced by Rat Liver Microsomes* Tomasz, M.; Lipman, R. *Biochemistry* **1981**, *20(17)*, 5056-5061.
- ¹⁰ *The Total Synthesis of Carpanone* Steffens, J. J.; Chipman, D. M. *J. Am. Chem. Soc.* **1971**, *93*, 6696-6698.
- ¹¹ *An Efficient Desyllilation Method for the Generation of o-Quinone Methides: Application to the Synthesis of (+) and (-)-Hexahydrocannabinol* Marino, J. P.; Dax, S. L. *J. Org. Chem.* **1984**, *49*, 3671-3672.
- ¹² *A New and Efficient Method for o-Quinone Methide Intermediate Generation: Application to the Biomimetic Synthesis of the Benzopyran Derived Natural Products (±)-lucidene and (±)-alboatrin* Rodriguez, R.; Moses, J. E.; Adlington, R. M.; Baldwin, J. E. *Org. Biomol. Chem.* **2005**, *3*, 3488-3495.
- ¹³ *Novel Dimeric Products from 10-Methyleneanthrone* Starnes, Jr. W. H. *J. Org. Chem.* **1970**, *35(6)*, 1974-1978.

-
- ¹⁴ (a) *Metal-Stabilized Quinone and Thioquinone Methides* Vigalok, A.; Milstein, D. *J. Am. Chem. Soc.* **1997**, *119*, 7873-7874. (b) *Methylene Arenium Cations via Quinone Methides and Xylelenes Stabilized by Metal Complexation* Vigalok, A.; Shimon, L. J. W.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 477-483.
- ¹⁵ *Metal-Mediated Generation, Stabilization and Controlled Release of a Biologically Relevant, Simple Para Quinone Methide: BHT-QM* Rabin, O.; Vigalok, A.; Milstein, D. *J. Am. Chem. Soc.* **1998**, *120*, 7119-7120.
- ¹⁶ (a) *General Synthesis, First Crystal Structure, and Reactivity of Stable o-Quinone Methide Complexes of Cp*Ir* Amouri, H.; Besace, Y.; Le Bras, J.; Vaissermann, J. *J. Am. Chem. Soc.* **1998**, *120*, 6171-6172. (b) *Stable o-Quinone Methide Complexes of Iridium: Synthesis, Structure and Reversed Reactivity Imparted by Metal Complexation* Amouri, H.; Vaissermann, J.; Rager, M. N.; Grotjahn, D. B. *Organometallics* **2000**, *19*, 1740-1748. (c) *Rhodium-Stabilized o-Quinone Methides: Synthesis, Structure, and Comparative Study with their Iridium Congeners* Amouri, H.; Vaissermann, J.; Rager, M. N.; Grotjahn, D. B. *Organometallics* **2000**, *19*, 5143-5148.
- ¹⁷ *Reversal of Reactivity in Diene-Complexed o-Quinone Methide Complexes: Insights and Explanations from ab Initio Density Functional Theory Calculations* Lev, D. A.; Grotjahn, D. B.; Amouri, H. *Organometallics* **2005**, *24*, 4232-4240.
- ¹⁸ *Metal Pentadienyl Chemistry* Ernst, R. D. *Acc. Chem. Res.* **1985**, *18*, 56-62
- ¹⁹ *Electrocyclic Reactions of Open Metallocenes: Carbon-Carbon Bond Formation during Thermolysis of bis(2,4-dimethyl-1,3-pentadienyl)ruthenium and -osmium* Kirss, R.U. *Organometallics* **1992**, *11*(2), 497-499.
- ²⁰ *Insertion Reactions of Hexafluorobut-2-yne, Tetrafluoroethylene, and Hexafluoroacetone with η^5 -Cyclopentadienyl-iron, -ruthenium, -palladium, and -molybdenum Complexes; Molecular and Crystal Structures of $[\text{Fe}_2(\text{CO})\{\text{C}_4(\text{CF}_3)_4\text{CO}\}(\eta^5\text{-C}_5\text{H}_5)_2]$ and $[\text{Fe}\{\text{COCF}_2\text{C}_3\text{H}_5\}(\eta^5\text{-C}_5\text{H}_5)]$* Davidson, J. L.; Green, M.; Stone, F. G. A.; Welch, A. J. *J. Chem. Soc., Dalton Trans.*(1972-1999), **1976**, *20*, 2044-2053.
- ²¹ *Hydroxymetallocenes* Benson, R. E.; Lindsey, Jr., R. V. *J. Am. Chem. Soc.* **1957**, *79*, 5471-5474.
- ²² *Photochemical Conversion of (η^1 -Butadienyl)iron Complexes to Hydroxyferrocenes* Yongskulrote, W.; Bramlett, J. M.; Mike, C. A.; Durham, B.; Allison, N.T. *Organometallics* **1989**, *8*, 556-558.
- ²³ *Complexes. Synthesis and Electrocyclic Ring Closure of ($\eta^5\text{-C}_5\text{H}_5$)Fe(pentadienoyl) Complexes to Hydroxyferrocenes* Dawson, D. P.; Yongskulrote, W.; Bramlett, J. M.; Wright, J. B.; Durham, B.; Allison, N. T. *Organometallics* **1994**, *13*, 3873-3880.
- ²⁴ *Transition Metal-mediated Cycloaddition Reactions of Alkynes in Organic Synthesis* Schore, N. E. *Chem. Rev. (Washington, DC, U.S.)* **1988**, *88*(7), 1081-1119.

-
- ²⁵ *Frontier Molecular Orbital Control of Stereochemistry in Organometallic Electrocyclic Reactions* Pinhas, A. R.; Carpenter, B. K. *J. Chem. Soc., Chem. Commun.* **1980**, *1*, 17-19.
- ²⁶ (a) *Addition of Aromatic C-H Bonds to Terminal Metal-Carbonyl Groups. A New Method for Cyclocarbonylation of Aromatic Groups* Wu, Y.-R.; Lin, G.-H.; Madhushaw, R. J.; Horng, K.-M.; Hu, C.-C.; Li, C.-L.; Liao, F.-L.; Wang, S.-L.; Liu, R.-S. *Organometallics* **1999**, *18*, 3566-3568. (b) *Preparation and Subsequent Reaction Chemistry of Cyclopentadienyl Molybdenum Dicarbonyl η^3 -2-Alkylidene Cyclobutanonyl Complexes* Vinson, N. A.; Day, C. S.; Welker, M. E. *Organometallics* **2000**, *19*, 4356-4358. (c) *Preparation and Characterization of Molybdenum Tris(pyrazolyl)borate Dicarbonyl η^3 -Dienyl Complexes* Lantero, D. R.; Glenn, A. G.; Day, C. S.; Welker, M. E. *Organometallics* **2003**, *22*, 1998-2000.
- ²⁷ Neal, S. R. (2006) *A Study of the Synthesis and Chemistry of Iron Complexed Aromatic Annulated 5-Membered Quinone Methide Analogs* Masters of Science Thesis. University of Arkansas.
- ²⁸ Dietz, D. (2006) *The Study of the Cyclization Mechanism of Non-Aromatic Annulated Trienyl Iron Complexes in the Formation of o-Quinone Methide Analogs*. Bachelor Honors Thesis, University of Arkansas.
- ²⁹ *Early Kinetic Studies on CO Substitution Reactions of Metal Carbonyls* Basolo, F. J. *Organomet. Chem.* **1990**, *383(1-3)*, 579-586.
- ³⁰ PQSMol version 1.0 Beta; Parallel Quantum Solutions; 2013 Green Acres Road, Suite A, Fayetteville, AR 72703
- ³¹ *Chemistry of gem-Dihalocyclopropanes. VI. A Novel Synthesis of Cyclopentadienes and Fulvenes* Skatteboel, L. *Tetrahedron* **1967**, *23(3)*, 1107-1117.
- ³² *Temperature Dependence of Carbene-carbene Rearrangements. A New Method for the Generation of Carbenes* Brinker, U. H.; Ritzer, J. *J. Am. Chem. Soc.* **1981**, *103(8)*, 2116-2119.
- ³³ Beuterbaugh, A. M. (2011) *The Synthesis of Transition Metal 5- and 6-Membered Quinone Methide Analogs* Doctoral Dissertation, University of Arkansas.
- ³⁴ *Carbene Reactions. XIII. Cycloheptatrienylidene from Trimethylsilyltropylium Tetrafluoroborate* Reiffen, M.; Hoffmann, R. W. *Tetrahedron Lett.* **1978**, *13*, 1107-1110.
- ³⁵ *Conversion of Nitroalkenes into β -(Trichloromethyl)nitroalkanes* Cunico, R. F.; Zhang, C. P. *Synth. Commun.* **1991**, *21(21)*, 2189-2195.
- ³⁶ *1-(Dialkylamino)isobenzofurans: Generation and Use for Annulation of Aromatic Rings* Chen, C.-W.; Beak, P. J. *Org. Chem.* **1986**, *51*, 3325-3334.

-
- ³⁷ *Fluoride Ion Promoted Reactions of α -Halo Silanes: Synthesis of Stilbenes, Epoxides, Cyclopropanes, Benzazepines, and Phthalidylisoquinolines* Kessar, S. V.; Singh, P.; Kaur, N. P.; Chawla, U.; Shukla, K.; Aggarwal, P.; Venugopal, D. *J. Org. Chem.* **1991**, *56*(12), 3908-3912.
- ³⁸ *Iron Catalyzed Cross-Coupling Reactions: Efficient Synthesis of 2,3-Allenol Derivatives* Fürstner, A.; Mendez, M. *Angew. Chem., Int. Ed.* **2003**, *42*, 5355-5357.
- ³⁹ (a) *Pentacarbonylmanganese halides. Pentacarbonylbromomanganese, $MnBr(CO)_5$* Quick, M. H.; Angelici, R. J. *Inorg. Synth.* **1979**, *19*, 160-161. (b) *Pentacarbonylrhenium halides* Schmidt, S. P.; Trogler, W. C.; Basolo, F. *Inorg. Synth.* **1990**, *28*, 160-165.
- ⁴⁰ (a) *Reactions of Iron Pentacarbonyl with Compounds Containing the N-O Linkage.* Alper, H.; Edward, J. T. *Can. J. Chem.* **1970**, *48*(10), 1543-1549. (b) *Intermediate Compound in the Decomplexation of a Tricarbonyl Iron Complex using Trimethylamine Oxide* Eekhof, J. H.; Hogeveen, H.; Kellogg, R. M. *J. Chem. Soc., Chem Comm.* **1976**, *16*, 657.
- ⁴¹ *Ureas and Amides as Dipolar Aprotic Solvents in Highly Basic Media. The Dependence of Kinetic Basicity on Solvent Composition* Kankaanpera, A.; Scharlin, P.; Kuusisto, I.; Kallio, R.; Bernoulli, E. *J. Chem. Soc. Perkin Trans. 1* **1999**, *2*, 169-174.
- ⁴² (a) *Reactions of Stabilized Sulfur Ylides with α,β -Unsaturated Alkoxychromiumcarbene Complexes* Alcaide, B.; Casarrubios, L.; Dominguez, G.; Retamosa, A.; Sierra, M. A. *Tetrahedron* **1996**, *52*(41), 13215-13226. (b) *Cyclopropane Formation by Electroreductive Coupling of Activated Olefins and gem-Polyhalo Compounds* Leonel, E.; Paugam, J. P.; Condon-Gueugnot, S.; Nedelec, J.-Y. *Tetrahedron* **1998**, *54*(13), 3207-3218.
- ⁴³ *Direct Benzylic Alkylation via Ni-Catalyzed Selective Benzylic sp^3 C-O Activation* Guan, B.-T.; Sun, Z.-P.; Wang, Y.; Zhao, K.-Q.; Shi, Z.-J. *J. Am. Chem. Soc.* **2008**, *130*(11), 3268-3269.
- ⁴⁴ *Copper-Catalyzed Carbene Insertion into O-H Bonds: High Selective Conversion of Alcohols into Ethers* Morilla, M. E.; Molina, M. J.; Diaz-Requejo, M. M.; Belderrain, T. R.; Nicasio, C. M.; Trofimenko, S.; Perez, P. J. *Organometallics* **2003**, *22*(14), 2914-2918.
- ⁴⁵ For a review, see *Ionic Liquids in Synthesis*, Wasserscheid, P., Welton, T., Ed; Wiley-VCH: Weinheim, 2008.
- ⁴⁶ *Ionic Liquids in Biphasic Ethylene Polymerisation* Wilkes, J. S. *J. Mol. Catal. A.* **2004**, *214*, 11-17.
- ⁴⁷ *The Heck Reaction in Ionic Liquids: A Multiphasic Catalyst System* Carmichael, A. J.; Earle, M. J.; Holbrey, J. D.; McCormac, P. B.; Seddon, K. R. *Org. Lett.* **1999**, *1*(7), 997-1000.
- ⁴⁸ *1-n-Butyl-3-Methylimidazolium ([BMIM]) Octylsulfate - An Even 'Greener' Ionic Liquid* Wasserscheid, P.; Van Hal, R.; Bossmann, A. *Green Chem.* **2002**, *4*, 400-404.

-
- ⁴⁹ *Advanced Organic Chemistry* March, J., 4th edn., Wiley, Chichester, **1992**.
- ⁵⁰ *Synthesis of N- and p-(Diphenylmethyl)anilines. ESR Study of their Photofragmentation*, Siskos, M. G.; Garas, S. K.; Zarkadis, A. K.; Bokaris, E. P. *Chem. Ber.* **1992**, *125(11)*, 2477-2481.
- ⁵¹ *Thermal Rearrangement of α -Substituted Silanes*, Bassindale, A. R.; Brook, A. G.; Jones, P. F.; Lennon, J. M. *Can. J. Chem.* **1975**, *53(3)*, 332-337.
- ⁵² *Photolysis of Tetraarylmethanes and 3-(Triarylmethyl)pyridines*, Shi, M.; Okamoto, Y.; Takamuku, S. *Bull. Chem. Soc. Jpn.* **1990**, *63(9)*, 2731-2733.
- ⁵³ *Cyclopropane Formation by Copper-Catalyzed Indirect Electroreductive Coupling of Activated Olefins and Activated α,α,α -Trichloro or gem-Dichloro Compounds* Sengamy, S.; Leonel, E.; Paugam, J. P.; Nedelec, J.-Y. *Synthesis* **2002**, *4*, 533-537.
- ⁵⁴ *Synthesis and Structural Characterization of Some Novel Trialkylsilyl-Substituted Lithium Benzyl Complexes [Li(tmeda)][CHRSiMe₂R'] (R=Ph, 3,5-Me₂C₆H₃; R = Me, tBu, Ph)* Schumann, H.; Freckmann, D. M. M.; Dechert, S. Z. *Anorg. Allg. Chem.* **2008**, *634(8)*, 1334-1338.
- ⁵⁵ *Silicon Effects. III. Rates and Products for Solvolysis of α -(Pentamethyldisilanyl)benzyl Halides and 1,1,2,2-Tetramethyl-1,2-Disilaindan-3-yl Chloride. Structure and Stability of α -(Pentamethyldisilanyl)benzyl Cation in Solution* Shimizu, N.; Kinoshita, C.; Osajima, E.; Hayakawa, F.; Tsuno, Y. *Bull. Chem. Soc. Jpn.* **1991**, *64(11)*, 3280-3288.
- ⁵⁶ (a) *A Carbocyclic Carbene as an Efficient Ligand for C-C Coupling Reactions* Herrmann, W. A.; Öfele, K.; Schneider, S. K.; Herdtweck, E.; Hoffmann, S. D. *Angew. Chem., Int. Ed.* **2006**, *45(23)*, 3859-3862. (b) *Carbocyclic Carbene Ligands in Palladium-Catalyzed C-N Coupling Reactions* Taubmann, C.; Tosh, E.; Öfele, K.; Herdtweck, E.; Herrmann, W. A. *J. Organomet. Chem.* **2008**, *693*, 2231-2236.
- ⁵⁷ Odian, G. *Principles of Polymerization*, Wiley: New York; **1981**.
- ⁵⁸ *An Air-Stable Palladium/N-Heterocyclic Carbene Complex and its Reactivity in Aryl Amination* Viciu, M. S.; Kissling, R. M.; Stevens, E. D.; Nolan, S. P. *Org. Lett.* **2002**, *4(13)*, 2229-2231.
- ⁵⁹ *Living Ring-Opening Metathesis Polymerization Catalyzed by Well-Characterized Transition-Metal Alkylidene Complexes* Schrock, R. R. *Acc. Chem. Res.* **1990**, *23(5)*, 158-165.
- ⁶⁰ *1:6-Dichlorotetramminocobalt Salts (Chloropraseo-salt)* Werner, A.; Klein, A. Z. *Anorg. Chem.* **1897**, *14*, 21-27
- ⁶¹ Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; Wiley: New York, **2001**.

-
- ⁶² (a) *Palladium-Catalyzed Cross-Coupling Reactions of Organoboron Compounds* Miyaura, N.; Suzuki, A. *Chem. Rev.* **1995**, *95*(7), 2457-2483. (b) *Recent Advances in the Cross-Coupling Reactions of Organoboron Derivatives with Organic Electrophiles, 1995-1998* Suzuki, A. *J. Organomet. Chem.* **1999**, *576*(1-2), 147-168. (c) Suzuki, A. *Metal-Catalyzed Cross-Coupling Reactions*, Wiley-VCH, Weinheim **1998**, pp. 49-97.
- ⁶³ (a) *Coordination Chemistry and Mechanism of Metal-Catalyzed CC Coupling Reactions. 9. Metal Complexes of N-Heterocyclizing Carbenes - A New Structural Principle for Catalysts in Homogeneous Catalysis* Herrmann, W. A.; Elison, M.; Fischer, J.; Koecher, C.; Artus, G. R. J. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*(21), 2371-2374 (b) *Variations on a Theme: Recent Developments on the Mechanism of the Heck Reaction and their Implications for Synthesis* Crisp, G. T. *Chem. Soc. Rev.* **1998**, *27*(6), 427-436. (c) *Application of Palladacycles in Heck Type Reactions* Herrmann, W. A.; Bohm, V. P. W.; Resisinger, C.-P. *J. Organomet. Chem.* **1999**, *576*(1-2), 23-41.
- ⁶⁴ (a) *Rational Development of Practical Catalysts for Aromatic Carbon-Nitrogen Bond Formation* Wolfe, J. P.; Wagaw, S.; Marcoux, J.-F.; Buchwald, S. L. *Acc. Chem. Res.* **1998**, *31*(12), 805-818. (b) *Carbon-Heteroatom Bond-Forming Reductive Eliminations of Amines, Ethers, and Sulfides* Hartwig, J. F. *Acc. Chem. Res.* **1998**, *31*(12), 852-860.
- ⁶⁵ *Metal-Phosphine Bonding Revisited. σ -Basicity, π -Acidity, and the Role of Phosphorous d Orbitals in Zerovalent Metal-Phosphine Complexes* Pacchioni, G.; Bagus, P. S. *Inorg. Chem. (Washington, DC, U.S.)* **1992**, *31*(21), 4391-4398.
- ⁶⁶ *Tert-Butyl is Superior to Phenyl as an Agostic Donor to 14-Electron Ir(III)* Cooper, A. C.; Streib, W. E.; Eisenstein, O.; Caulton, K. G. *J. Am. Chem. Soc.* **1997**, *119*(38), 9069-9070.
- ⁶⁷ *Stretched H₂ Complexes: Structural Control in $\text{ReH}_7\{\text{P}(\text{C}_6\text{H}_4\text{-}p\text{-}X)_3\}_2$ ($X=\text{CH}_3, \text{H}, \text{F}, \text{CF}_3, \text{OMe}$) Complexes by Electronic Ligand Effects* Michos, D.; Luo, X.-L.; Howard, A. K.; Crabtree, R. H. *Inorg. Chem. (Washington, DC, U.S.)* **1992**, *31*(19), 3914-3916.
- ⁶⁸ *Steric Effects of Phosphorous Ligands in Organometallic and Homogeneous Catalysis* Tolman, C. A. *Chem. Rev. (Washington, DC, U.S.)* **1977**, *77*, 313-348.
- ⁶⁹ *Nucleophilic Carbene Chemistry. Preparation of 2,2'-bis(1,3-Diphenylimidazolidine)* Wanzlick, H. W.; Kleiner, H. J. *Angew. Chem.* **1961**, *73*, 493.
- ⁷⁰ *A Stable Crystalline Carbene* Arduengo, A. J. III; Harlow, R. L.; Kline, M. *J. Am. Chem. Soc.* **1991**, *113*(1), 361-363.
- ⁷¹ *Direkt-Synthese eines Quecksilbersalz-Carben-Komplexes* Wanzlick, H.-W.; Schönherr, H.-J. *Angew. Chem.* **1968**, *4*, 154.

-
- ⁷² *1,3-Dimethyl-4-imidazoline-2-pentacarbonylchromium, a New Transition Metal-Carbene Complex* Öfele, K. *J. Organomet. Chem.* **1968**, *12(3)*, 42-43.
- ⁷³ *trans/cis-Isomerism and Isomerization of Palladium(II) and Platinum(II) Carbene Complexes. Crystal and Molecular Structures of cis- and trans-PtCl₂[C(NPhCH₂)₂]PEt₃* Cardin, D. J.; Cetinkaya, B.; Cetinkaya, E.; Lappert, M. F.; Manojlovic-Muir, L. J.; Muir, K. W. *J. Organomet. Chem.* **1972**, *44(2)*, C59-C62.
- ⁷⁴ *Synthesis and Structure of an Ionic Beryllium-“Carbene” Complex* Herrmann, W. A.; Runte, O.; Artus, G. *J. Organomet. Chem.* **1995**, *501*, C1-C4.
- ⁷⁵ *Carbenes as Pure Donor Ligands: Theoretical Study of Beryllium-Carbene Complexes* Froehlich, N.; Pidun, U.; Stahl, M. Frenking, G. *Organometallics* **1997**, *16(3)*, 442-448.
- ⁷⁶ *The Coordination Chemistry of Electron-Rich Alkenes (Enetetramines)* Lappert, M. F. *J. Organomet. Chem.* **1988**, *358*, 185-213.
- ⁷⁷ *Highly Efficient Ring-Opening Metathesis Polymerization (ROMP) Using New Ruthenium Catalysts Containing N-Heterocyclic Carbene Ligands* Bielawski, C. W.; Grubbs, R. H. *Angew. Chem., Int. Ed.* **2000**, *39(16)*, 2903-2906.
- ⁷⁸ *A Novel Class of Ruthenium Catalysts for Olefin Metathesis* Weskamp, T.; Schattenmann, W. C.; Spiegler, M.; Herrmann, W. A. *Angew. Chem., Int. Ed.* **1998**, *37(18)*, 2490-2493.
- ⁷⁹ *Zerovalent Palladium and Nickel Complexes of Heterocyclic Carbenes: Oxidative Addition of Organic Halids, Carbon-Carbon Coupling Processes, and the Heck Reaction* McGuinness, D. S.; Cavell, K. J.; Skeltyon, B. W.; White, A. H. *Organometallics* **1999**, *18(9)*, 1596-1605.
- ⁸⁰ *Synthesis, Structure and Catalytic Application of Palladium(II) Complexes Bearing N-Heterocyclic Carbenes and Phosphines* Herrmann, W. A.; Böhm, V. P. W.; Gstöttmayr, C. W. K.; Grosche, M.; Reisinger, C.-P.; Weskamp, T. *J. Organomet. Chem.* **2001**, *617*, 616-628.
- ⁸¹ *A Stable 4-Membered N-Heterocyclic Carbene* Despagnet-Ayoub, E.; Grubbs, R. H. *J. Am. Chem. Soc.* **2004**, *126*, 10198-10199.
- ⁸² *Cycloheptatrienyliidene: Structure and Role in Carbene-Carbene Rearrangements* Jones, W. M. *Angew. Chem., Int. Ed. Engl.* **1972**, *11(4)*, 325-326.
- ⁸³ *Cycloheptatrienyliidene* Jones, W. M.; Ennis, C. L. *J. Am. Chem. Soc.* **1969**, *91*, 6391-6397.
- ⁸⁴ *Triplet Ground-State Cycloheptatrienyliidene* McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1986**, *108*, 1713-1714.
- ⁸⁵ *The Cycloheptatrienyliidene-Cycloheptatetraene Problem. A MNDO Investigation* Waali, W. E. *J. Am. Chem. Soc.* **1981**, *103*, 3604-3606.

-
- ⁸⁶ *Ground States of Molecules. 38. The MNDO Method. Approximations and Parameters* Dewar, M. J. S.; Thiel, W. *J. Am. Chem. Soc.* **1977**, *99*(15), 4899-4907.
- ⁸⁷ *Cycloheptatrienyliidene Singlet-Triplet Energetics: Theory Responds* Janssen, C. L.; Schaefer, H. F. III *J. Am. Chem. Soc.* **1987**, *109*, 5030-5031.
- ⁸⁸ *Ground States of Molecules. 43. A MINDO/3 Study of the Rearrangement of Phenylcarbene to Cycloheptatrienylcarbene* Dewar, M. J. S.; Landman, D. *J. Am. Chem. Soc.* **1977**, *99*(19), 6179-6182.
- ⁸⁹ Waali, E. E.; Wenslaff, J. B.; Rehrauer, L. F. American Chemical Society - Chemical Society of Japan Chemical Congress, Honolulu, April 1979.
- ⁹⁰ *Synthesis of Transition Metal Complexes of Cycloheptatrienyliidene* Allison, N. T.; Kawada, Y.; Jones, W. M. *J. Am. Chem. Soc.* **1978**, *100*(16), 5224-5226.
- ⁹¹ *Dicarbonyl(η^5 -cyclopentadienyl)ruthenium Complexes of Cycloheptatrienyliidene and two isomeric Benzocycloheptatrienyliidenes* Lisko, J. R.; Jones, W. M. *Organometallics* **1986**, *5*(9), 1890-1896.
- ⁹² *Hydrogenation of the Rhodium Complex $RhC_7H_6^+$ in the Gas Phase* Jacobson, D. B.; Freiser, B. S. *J. Am. Chem. Soc.* **1984**, *106*(4), 1159-1160.
- ⁹³ *Platinum Complexes of Cycloheptatrienyliidene and Cycloheptatetraene* Lu, Z.; Jones, W. M.; Winchester, W. R. *Organometallics* **1993**, *12*(4), 1344-1350.
- ⁹⁴ *Synthesis and Crystal Structure of Cycloheptatrienyliidene Complexes of Iron* Riley, P. E.; Davis, R. E.; Allison, N. T.; Jones, W. M. *J. Am. Chem. Soc.* **1980**, *102*(7), 2458-2460.
- ⁹⁵ (a) *Seven Membered Heterocyclic Compounds. I. 1,5-Diazepines and Derivatives of 3,6-Diaza-4,5-benzotropone* Barltrop, J. A.; Richards, C.G.; Russell, D. M.; Ryback, G. *J. Chem. Soc.* **1959**, 1132. (b) *Synthesis of 3-Carboxylic Derivatives of 1,5-Benzodiazepines* Mansour, O.; Szymonski, B.; Thomasson, F.; Morand, J. M.; Cussac, M. *J. Heterocycl. Chem.* **2001**, *38*(3), 641-643.
- ⁹⁶ *3H-1,5-Benzodiazepines from Ethynyl Ketones and Phenylenediamine* Ried, W.; Teubner, R. *Liebigs Ann.* **1978**, *5*, 741-744.
- ⁹⁷ *Reaction of Tertiary Phosphines on α -Halocarbonyl Compounds. Model Experiment on the Perkow Reaction.* Hoffmann, H.; Diehr, H. J. *Tetrahedron Lett.* **1962**, 583-586.
- ⁹⁸ *Synthesis of 3-Carboxylic Derivatives of 1,5-Benzodiazepines* Mansour, O.; Szymonski, B.; Thomasson, F.; Morand, J. M.; Cussac, M. *J. Heterocycl. Chem.* **2001**, *38*, 641-643.

⁹⁹ *Cycloaddition Reaction of Diphenylcyclopropanone with Enamines*, Ciabattoni, J.; Berchtold, G.A. *J. Org. Chem.* **1966**, *31*(5), 1336-1339.

¹⁰⁰ *Tropyliumionen und Tropilidene - V. Synthese und Ambiente Reaktivität von 7-Chlor- und 7-Brombenzocycloheptenyliumkationen*. Föhlich, B.; Fischer, C.; Widmann, E.; Wolf, E. *Tetrahedron* **1977**, *34*, 533-539.