Winter 2016

SYNTHESIS OF POLYCYCLIC AROMATIC HYDROCARBONS: STUDIES OF ARYNE CYCLOADDITION, ACID-CATALYZED REARRANGEMENT, AND COUPLING PATHWAYS

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BY

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THESIS

Submitted to the University of New Hampshire

in Partial Fulfillment of

the Requirements for the Degree of

Master of Science

in

Chemistry

December 2016

This thesis has been examined and approved in partial fulfillment of the requirements for the degree of a Master of Science in Chemistry by:

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On December 12, 2016

Original approval signatures are on file with the University of New Hampshire Graduate School.

DEDICATION

To my parents,

who have supported me from start to finish.

ACKNOWLEDGEMENTS

I would like to thank my advisor, Richard Johnson, for his support during my graduate career. I was surprised everyday by the immense amount of chemical knowledge he has, and I'm grateful to say that I'm taking some of it with me. I would also like to thank my committee members for their guidance.

Cindi and Peg, thank you for all your help with everything. I don't think any of us would make it through without everything you both do. I also want to thank Pat, for all her help with instrumentation and for just being a great person to talk to.

To past and present Johnson group members, thank you for your support, all of your suggestions, and all of the epic lab jam sessions.

A massive thank you goes to my family. My parents, Steve and Sue, have been my biggest support system through all of the highs, lows, and everything in-between. I could not have done this without them. My sisters, Danielle and Emily, and Dan supported me throughout this process as well and helped me keep my sanity. Thank you all so much for always telling me I can do this, even when I thought I couldn't.

Another thank you goes to the National Science Foundation for funding, which made this research possible.

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ABSTRACT

SYNTHESIS OF POLYCYCLIC AROMATIC HYDROCARBONS: STUDIES OF ARYNE CYCLOADDITION, ACID-CATALYZED REARRANGEMENT, AND COUPLING PATHWAYS

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Caitlin L. Hoffman

University of New Hampshire, December 2016

Various synthetic routes towards polycyclic aromatic hydrocarbons dibenzo[*g,p*]chrysene (DBC), chrysene, zethrene, and their derivatives were studied. All of these compounds are not readily available and the literature lacks facile, efficient, and scalable syntheses. Microwave flash pyrolysis (MFP) was used for the synthesis of benzyne and phenanthryne, both of which have the ability to undergo a Diels-Alder reaction at the bay region of polycyclic aromatic hydrocarbons. Phthalic anhydride was used as a benzyne precursor and 9,10-dicarboxyphenanthrene anhydride as a phenanthryne precursor. DBC was observed after the MFP of biphenyl and 9,10-dicarboxyphenanthrene anhydride, signifying phenanthryne generation. Fluoride-induced elimination and Grignard pathways were also explored for phenanthryne formation, but no indication of phenanthryne was seen. DBC was efficiently prepared *via* a synthetic sequence that is the functional equivalent of the Stone-Wales rearrangement. This sequence is referred to as the pinacol-pinacolone Stone-Wales sequence, which provides DBC in high yield under mild reaction conditions. This is one of the most efficient and scalable syntheses of DBC with all of the steps providing high yields in short reaction times. Calculations for the rearrangement steps using density functional theory (DFT) further support the conclusion of a very efficient synthetic pathway. The same conditions were not successful for the synthesis of chrysene, however treatment of 1-indanopinacol with

polyphosphoric acid (PPA) did provide chrysene, suggesting an alternative mechanism from the pinacol-pinacolone Stone-Wales route. For the synthesis of zethrene, the pinacol-pinacolone Stone-Wales sequence was applied to 1-acenaphthenopinacol, but like 1-indanopinacol, no pinacolone structure was observed. Treatment of 1-acenaphthenopinacol with PPA in a microwave reactor generated a small amount of zethrene. This suggests that the reaction between aromatic pinacols and PPA is an alternative and simple route towards polycyclic aromatic hydrocarbons. Other pathways for zethrene synthesis were also studied. Although further work needs to be completed to optimize the syntheses of chrysene and zethrene, these reactions show promise as mild, simple pathways towards these compounds.

General Introduction

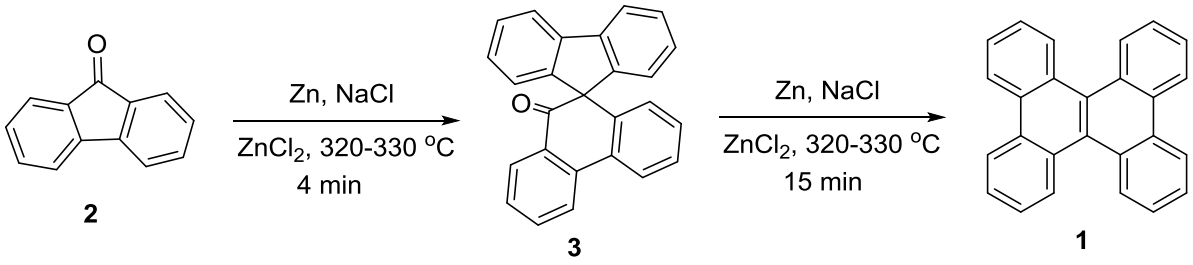
This thesis consists of three separate chapters: (I) cycloaddition chemistry: synthetic routes using aryne precursors, (II) pinacol-pinacolone Stone-Wales sequence, (III) progress towards zethrene. Each chapter is self-contained with its own introduction, results and discussion, and conclusion.

Dibenzo[g,p]chrysene: A History Lesson

Background

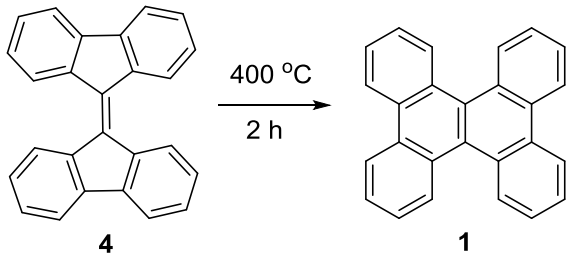
In the field of polycyclic aromatic chemistry, dibenzo[*g,p*]chrysenes are of interest due to their optical and electronic properties which arise from a nonplanar geometry. Dibenzo[g,p]chrysene (DBC, **1**) is one of the smallest nonplanar polycyclic aromatic hydrocarbons (PAHs). Its twisted conformation enhances solubility; this has attracted attention from the field of materials science.[1-3]

In 1964, Clar[4] reported the synthesis of **1**, however the yield was only 8.1%, concluding this reaction pathway was not an efficient route (Scheme 1). The reaction involves treatment of 9-fluorenone (**2**) with a zinc melt to yield the spiroketone (**3**), which after treatment with a second zinc melt provides **1**.



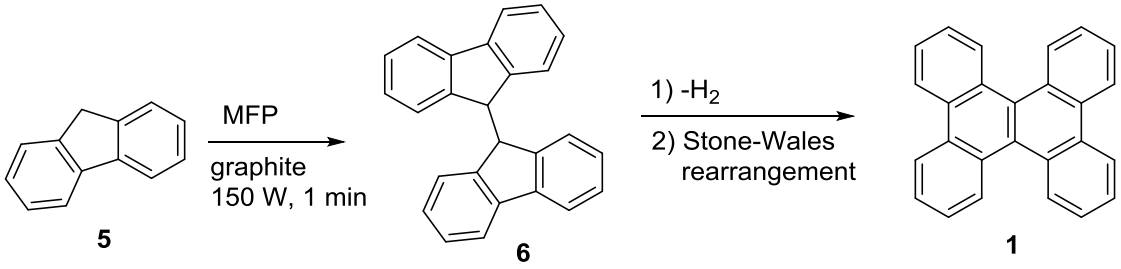
Scheme 1. Clar's synthesis of **1**.[4]

In 1975, Alder and Whittaker[5] reported the thermal Stone-Wales rearrangement of bifluorenylidene (**4**) at 400 °C to afford **1** (Scheme 2). This synthetic pathway required high temperature and was conducted only on a small scale.



Scheme 2. Thermal Stone-Wales rearrangement of **4**.[5]

In more recent years, there have been reports of DBC synthesis by intramolecular oxidative carbon-carbon bond formation,[6-8] metal catalysis,[9-10] and super acid conditions.[11-13] None of these routes are suitable for a large scale, efficient preparation. Previous research in our group has explored a cationic Stone-Wales pathway,[12] as well as a radical pathway towards **1**.[12, 14] The proposed radical pathway involves the use of microwave flash pyrolysis (MFP) with fluorene (**5**), generating 9,9'-bifluorene (**6**) which, after the loss of two hydrogens, can undergo a rearrangement to afford **1** (Scheme 3). The cationic Stone-Wales route involves the treatment of **4** with trifluoromethanesulfonic acid (TfOH) to give a product mixture containing **1**. Although there are many synthetic routes towards **1**, the literature lacks a facile, efficient, and scalable route which affords a high yield of this simple structure.



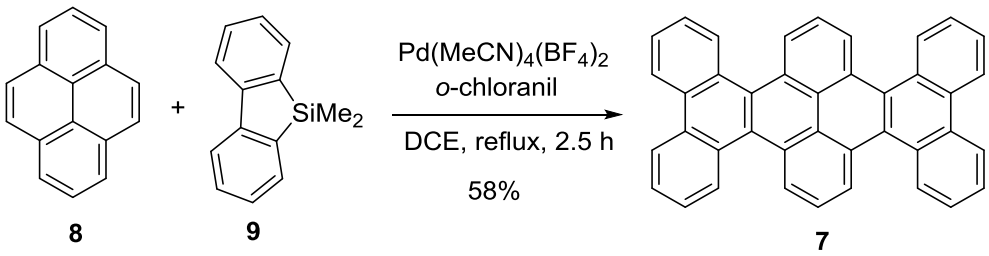
Scheme 3. Proposed radical pathway towards **1**.[14]

Route Towards Dibenzochrysenes: Origin of The Research

Exploring alternative pathways towards **1** that require mild reaction conditions, while producing high yields would make **1** more readily available and more affordable. By avoiding syntheses involving expensive reagents, long reaction times, high temperatures, and multiple

steps, more research can be done investigating the applications of **1**. A similar synthetic route might then be applied to prepare other larger or more elusive PAHs.

Discovering an efficient pathway towards **1** could lead to the synthesis of an array of dibenzochrysene homologues. Extension along the bay region of **1** creates a *π*-extended PAH which can adopt a twisted conformation. The synthesis of unsubstituted hexabenzo[a,c,fg,j,l,op]tetracene (**7**) has been very recently reported by Itami *et.al*.[15] *via* a palladium catalyzed annulative *π*-extension reaction from pyrene (**8**) and dibenzosilole (**9**) in refluxing 1,2-dichloroethane (DCE) (Scheme 4). Analysis using X-ray crystallography revealed a helically twisted structure.



Scheme 4. Synthesis of helically twisted **7**.[15]

Further extension along the bay region should enhance the helical structure. Density functional theory (DFT) calculations done in our group at the M052x/6-31G(d) level of theory reveal that a helical structure is preferred over other nonplanar conformations (Figure 1). The staggered conformation is 2.4 kcal/mol higher in energy than the helical, while the zigzag conformation is 3.2 kcal/mol higher in energy than the helical. Although these energy differences are not very large, they do show preference for the helical structure and this is further supported by the report[15] of helically twisted **7**. In these helical structures, a full 360 ^{o} turn is completed every six units.

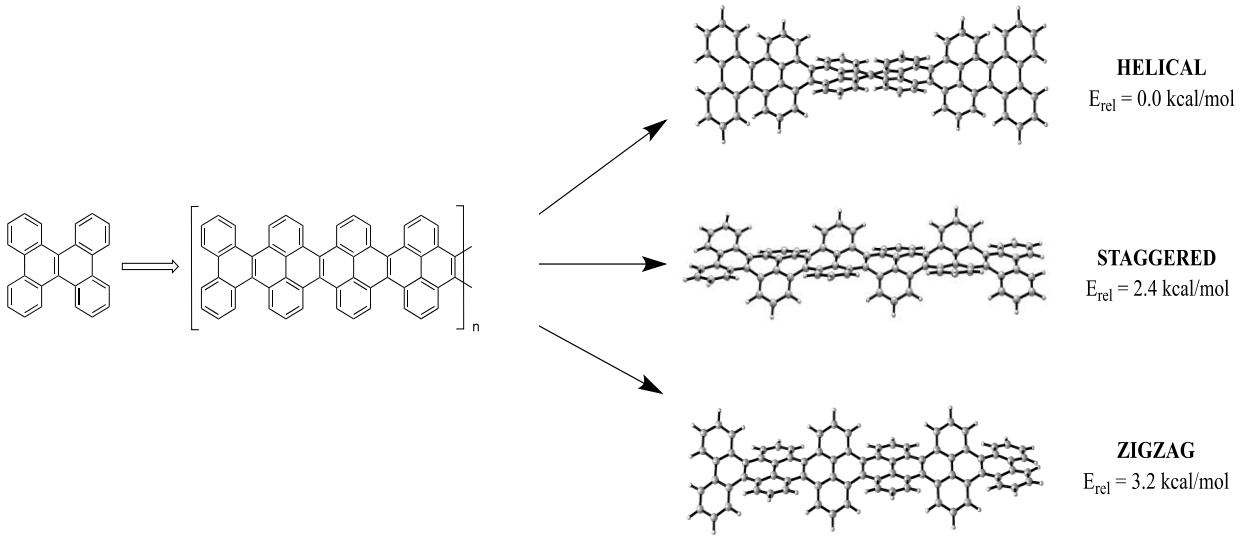


Figure 1. Twisted conformations of π-extended dibenzo[g,p]chrysene.

Major goals of this research were to develop a short, efficient, low cost synthetic route towards **1** and to investigate possible pathways to extend **1** along the bay region to form larger homologues, as shown in Figure 1.

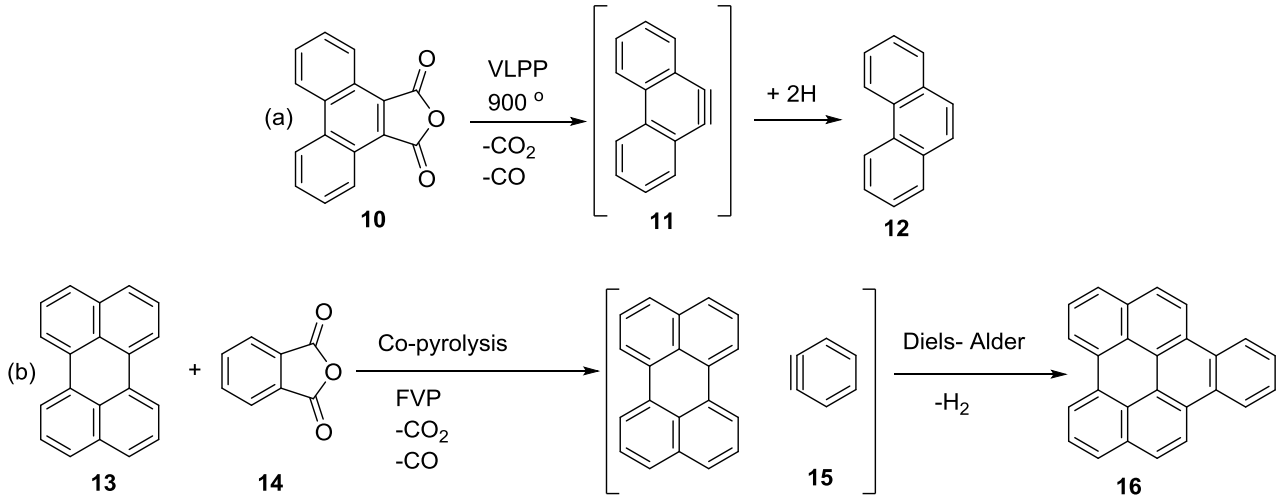
Chapter I. Cycloaddition Chemistry: Synthetic Routes Using Aryne Precursors

Introduction

Aryne Synthesis *via* Pyrolysis

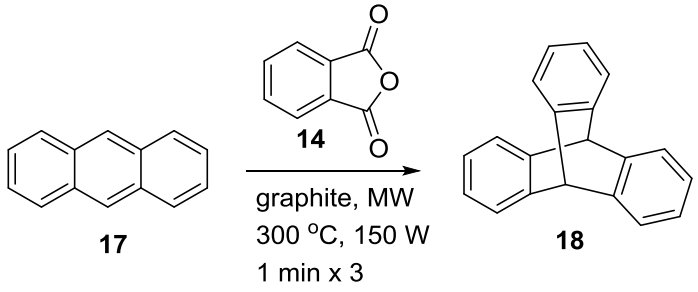
Aryne chemistry has been widely studied for the use in cycloaddition reactions. Aryne species are highly reactive, so they are not isolable and are typically generated *in situ*. There are numerous routes for aryne generation;[16-17] however, many of them require harsh reaction conditions like extreme temperatures. Some of the most commonly reported pathways for aryne synthesis involve pyrolysis. Pyrolysis reactions typically involve the loss of carbon monoxide and carbon dioxide from anhydride precursors.[18]

Pyrolysis of anhydrides is one common route to benzynes. In 1980, Straetmans and Grutzmacher[19] reported the very low pressure pyrolysis (VLPP) of 9,10-dicarboxyphenanthrene anhydride (**10**), which generates phenanthryne (**11**) *in situ* as a precursor to phenanthrene (**12**) (Scheme 5a). In a similar way, Scott and Fort[20] report the flash vacuum co-pyrolysis (FVP) of perylene (**13**) and phthalic anhydride (**14**), where **14** acts as a benzyne (**15**) precursor. A Diels-Alder reaction with **13** at the bay region yields aromatic compound **16** (Scheme 5b).



Scheme 5. (a) Generation of phenanthryne *via* VLPP.[19] (b) FVP of phthalic anhydride and perylene.[20]

MFP offers another route for aryne generation. Our techniques followed earlier work by Laporterie who developed a method where graphite is used to transmit thermal energy to the compounds in the reaction mixture, without being reactive itself.[21] This application was further reviewed by Besson.[22] Our research group developed an MFP procedure[23] using graphite or carbon nanotubes, which generates **15**. One of the examples involves the reaction of anthracene (**17**) with **14**. Benzyne is generated by the loss of carbon monoxide and carbon dioxide from **14**, and can undergo a Diels-Alder reaction with **17**, to form trypticene (**18**) (Scheme 6).[23]

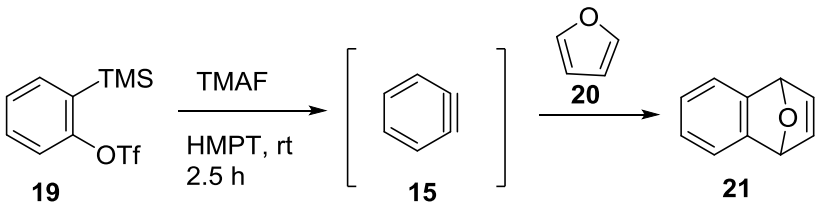


Scheme 6. Synthesis of trypticene *via* MFP.[23]

Pyrolysis is a useful pathway towards aryne formation, however it requires harsh reaction conditions. There are many alternative routes which don't involve extreme temperatures, pressures, or power. Examples include fluoride induced elimination, formation in aprotic media solution, lithium-halogen exchange, and many others.[16-17]

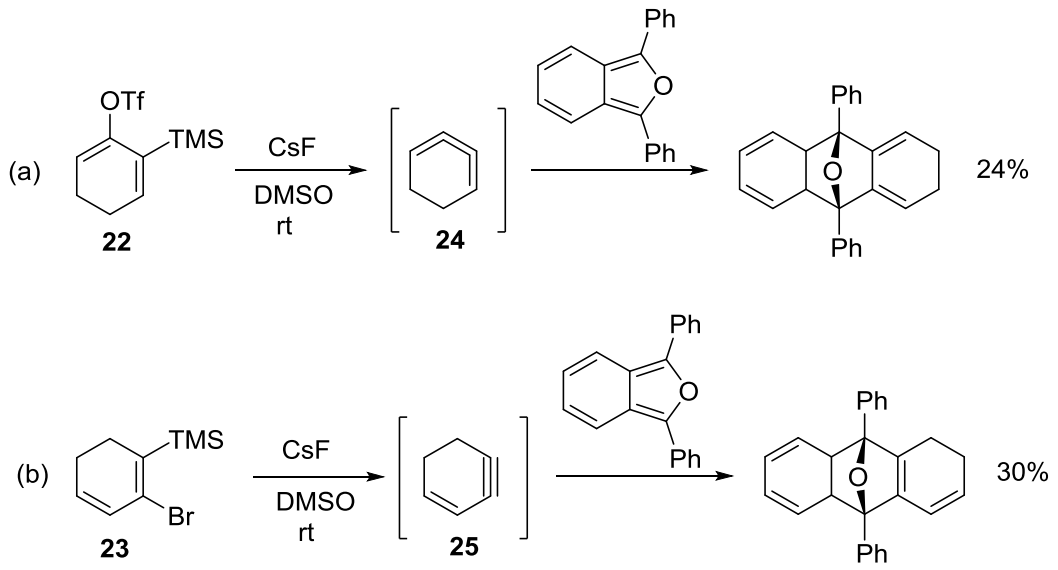
Fluoride Induced Elimination Pathway Towards Aryne Synthesis

The fluoride-induced elimination of organosilanes to yield cumulenes,[24] strained alkenes, and enynes[25] has been reported previously. Utilizing these more mild reaction conditions, aryne generation has been reported using this technique. Kobayashi *et. al*.[26] reported the formation of **15** *via* the fluoride-induced desilylation and triflate elimination of *o*-trimethylsilylphenyl triflate (**19**) at room temperature using various fluoride sources. Commonly used fluoride sources are tetramethylammonium fluoride (TMAF), potassium fluoride (KF), cesium fluoride (CsF), tetrabutylammonium fluoride (TBAF), and a KF/18-crown-6 combination. Due to the fact **15** is not isolable, its formation was investigated by introducing furan (**20**) as a trapping agent. This can undergo a Diels-Alder reaction with **15** to form adduct **21** (Scheme 7).



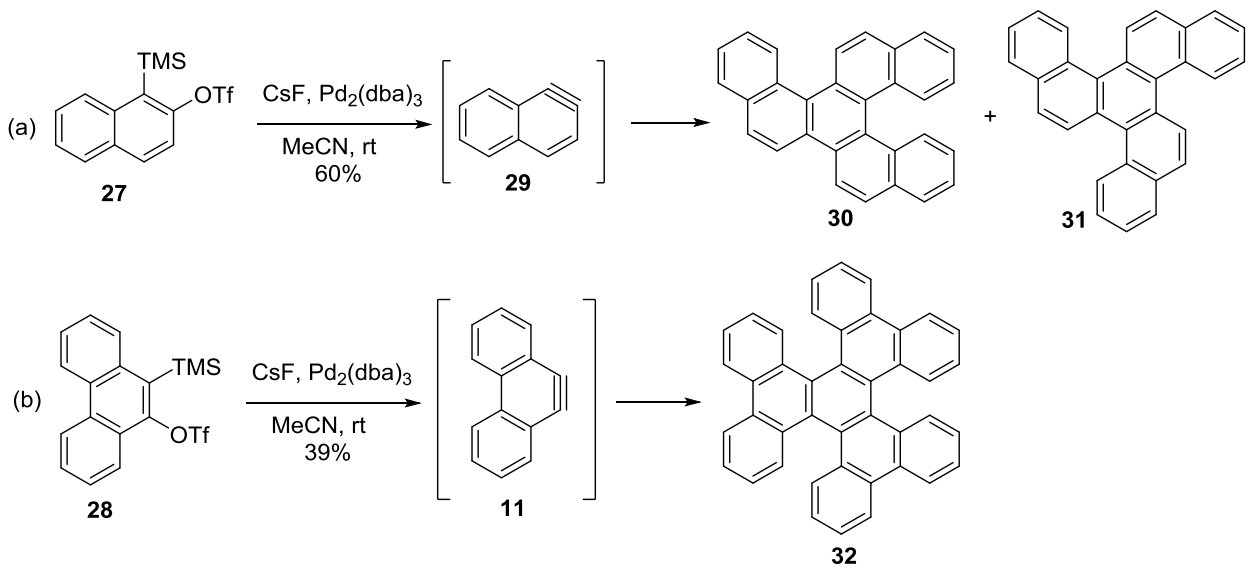
Scheme 7. Benzyne formation and reaction with **20**.[26]

Shakespeare and Johnson[25] reported the fluoride-induced elimination of dienes **22** and **23** for the synthesis of 1,2,3-cyclohexatriene (**24**) and cyclohexen-3-yne (**25**), respectively (Scheme 8). Both reactions used CsF as a fluoride source and proceeded at room temperature, using furan derivatives as trapping agents. In the case of **22**, the fluoride attacks the silicon and the triflate group leaves, where in the case of **23**, a halide is used as the leaving group.



Scheme 8. Synthesis of **24** and **25** *via* fluoride-induced elimination.[25]

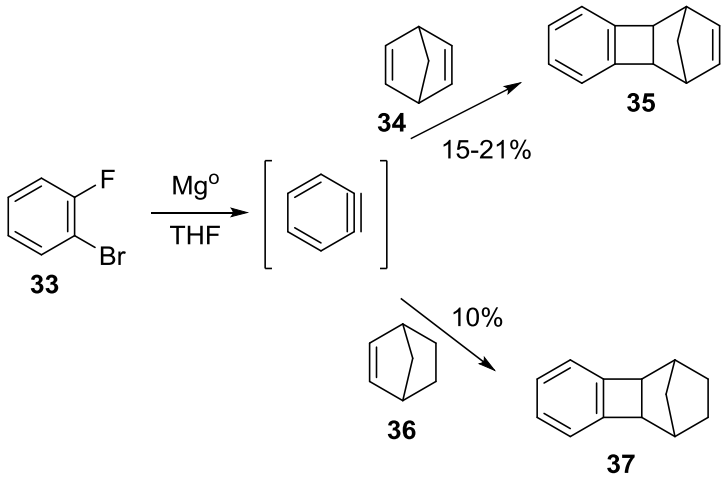
In more recent work, Castedo *et. al*. utilized these fluoride elimination conditions for the synthesis of several arynes. They report that **19** will react with CsF to form **15**, which in the presence of a palladium catalyst undergoes cyclotrimerization, forming triphenylene (**26**).[27] A similar report involves generating **15** *in situ* which can undergo a co-cyclization in the presence of an alkyne to form phenanthrene and naphthalene derivatives.[28] In 1999, Castedo *et. al.*[29] reported the fluoride-induced elimination of triflates **27** and **28** to generate naphthalyne (**29**) and **11** respectively, followed by cyclotrimerization to their triphenylene derivatives **30**, **31**, and **32** (Scheme 9). Given the results of these reactions, it can be said the fluoride-induced elimination pathway is a useful route towards strained and/or reactive intermediates.



Scheme 9. Cyclotrimerization of arynes.[29]

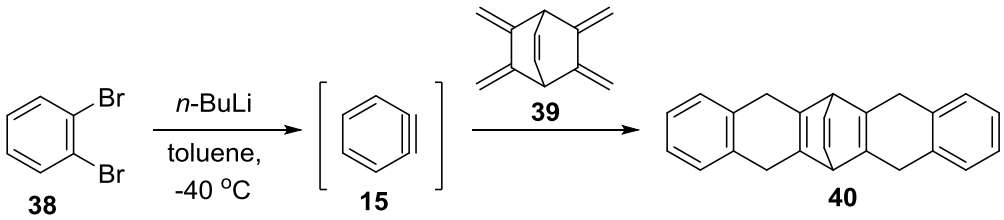
Aryne Formation Using Dihaloarenes

Dihaloarenes have been reported to act as aryne precursors *via* a reaction with metals. When compared to the fluoride-induced elimination pathway, this route commonly requires higher temperatures. There have been many reports of using metals such as lithium,[30-32] magnesium,[33-34] nickel,[35] along with several others. In an early example, Wittig[33] reported using *o*-fluorobromobenzene (**33**) in the presence of magnesium in tetrahydrofuran (THF) as a benzyne precursor (Scheme 10). The formation of **15** was confirmed because in the presence of bicyclo[2.2.1]heptadiene (**34**), the cycloaddition product **35** was observed in 15-21% yield. Wittig applied these conditions to other dienes such as **20** and **17**, again observing the Diels-Alder product from **15**.[36-39] Following this work, Simmons[34] used Wittig's conditions for benzyne formation in the presence of bicyclo[2.2.1]heptene (**36**) and observed cycloaddition product **37** in 10% yield (Scheme 10).



Scheme 10. Benzyne reaction with **34** and **36**.[33-34]

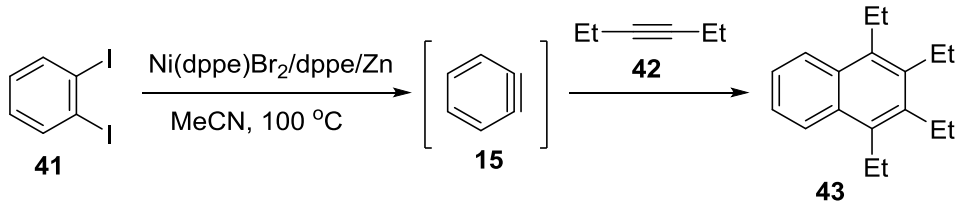
Another commonly used approach for metal promoted aryne generation involves treatment of a dibromo-substituted arene with *n*-butyllithium (*n*-BuLi). As one example, Müllen and Herwig[30] demonstrated that treatment of 1,2-dibromobenzene (**38**) with *n*-BuLi generates **15** which can react with tetraene **39**, to form pentacene precursor **40** in moderate yield (Scheme 11). These conditions were also applied to form a nonacene precursor in 58% yield.



Scheme 11. Synthesis of a pentacene precursor *via* benzyne generation.[30]

It has also been reported that nickel is able to generate arynes from *o*-dihaloarenes and catalyze cycloaddition reactions. Cheng and Hsieh[35] reported a nickel-catalyzed cycloaddition of **15** with various alkynes and nitriles. The synthesis involves using 1,2-diiodobenzene (**41**) as the benzyne precursor. Treatment of **41** and diethylacetylene (**42**) with dibromo[1,2-bis(diphenylphosphino)ethane]nickel(II) (Ni(dppe)Br_2), bis(diphenylphosphino)ethane (dppe), and zinc powder, yields 1,2,3,4-tetraethylnaphthalene (**43**) in high yield (Scheme 12). Synthesis

of many substituted naphthalenes, phenanthridines, and even triphenylenes were reported using this method. These results prove dihaloarenes are useful precursors to aryne generation when treated with a nickel catalyst, providing good to high yields of cycloaddition products. However, even with the report of the reaction conditions being efficient, the aryne precursors are not always readily available.



Scheme 12. Tetraethylnaphthalene synthesis using nickel-catalyzed cycloaddition chemistry.[35]

Research Objective

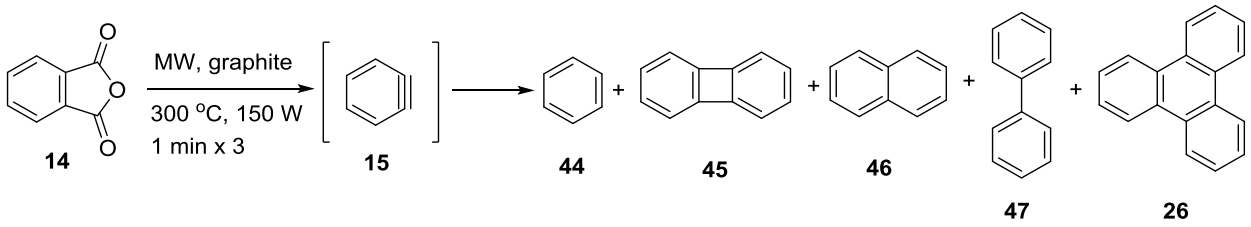
One goal of this project was to explore various reaction conditions, such as microwave flash pyrolysis (MFP), with different aryne precursors to generate PAHs. Using MFP to generate arynes *in situ*, one could potentially produce a wide variety of PAHs in one step with short reaction times. Another goal of this research was to investigate alternative phenanthryne precursors for cycloaddition chemistry. These precursors could be subjected to pyrolysis, fluoride-induced elimination, or metal-catalyzed aryne formation conditions to test their efficiency.

Results and Discussion

Aryne Generation Using Microwave Flash Pyrolysis (MFP)

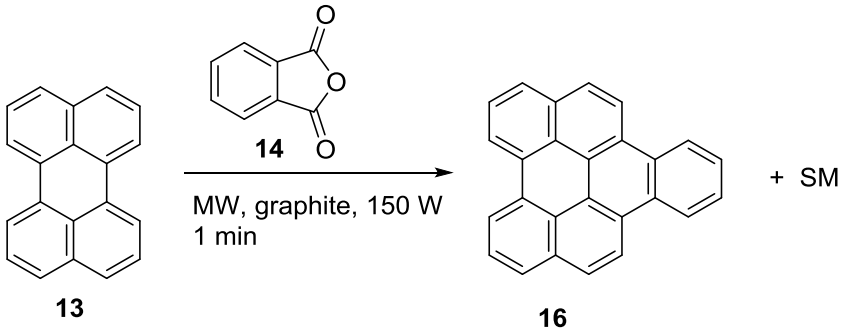
The technique of MFP for benzyne formation was previously studied in our group.[14, 23] The use of **14** as a benzyne precursor is commonly reported in the literature because of its ability to lose CO_2 and CO under pyrolysis conditions.[18] Previous work in our group reports MFP of **14** which affords a product mixture of starting material, benzene (**44**), biphenylene (**45**),

naphthalene (**46**), biphenyl (**47**), and **26**, all derived in one or more steps from **15** (Scheme 13). Using MFP conditions, the ability of **15** and **11** to undergo Diels-Alder cycloaddition at the bay region of various PAHs was investigated.



Scheme 13. MFP of **14**.[23]

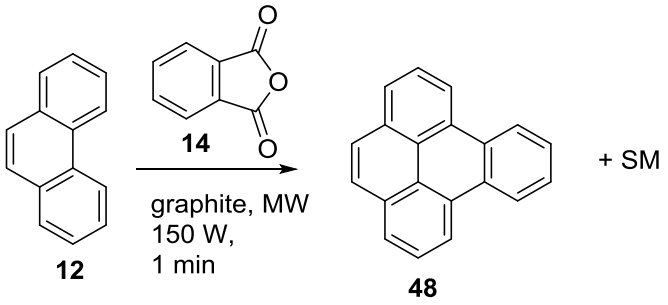
Although the addition of **15** to **13** has been previously reported,[20, 40-41] the MFP approach offers greater simplicity. Using the MFP conditions developed by our group, **14** and **13** were reacted in a quartz tube at 150 W for 1 minute. Using graphite as a thermal sensitizer, a 2:1 ratio of reactant **13** to the cycloaddition product **16** was observed *via* ^{1}H NMR (Scheme 14). The reaction was repeated at 300 W in an attempt to increase the conversion to product. The maximum pressure threshold, or safe point, of the CEM microwave was reached after 30 seconds, so the reaction was automatically shut down. The same 2:1 reactant:product ratio was observed.



Scheme 14. MFP of **13** with **14**.

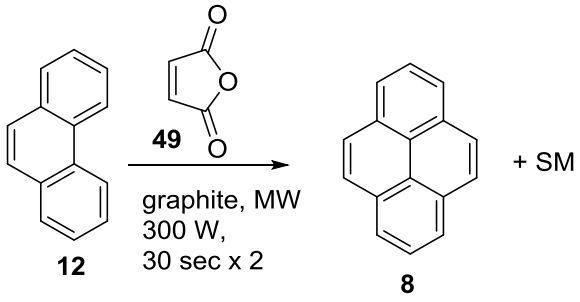
This result led us to explore a similar addition to phenanthrene (**12**). The same conditions were applied to the reaction between **12** and **14** (Scheme 15). It was observed there

was only about a 5% yield of the cycloaddition product **48**. The amount of **14** was increased in hopes of forming more desired product; however this did not improve the conversion.



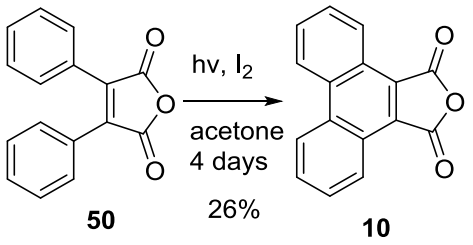
Scheme 15. MFP of **12** with **14**.

This reaction was repeated using maleic anhydride (**49**) to determine if it could add to the bay region of **12** to afford **8** under MFP conditions; however only approximately 2% conversion to product was observed (Scheme 16). This reaction presumably proceeds by initial cycloaddition of **49** to the bay region of **12**.



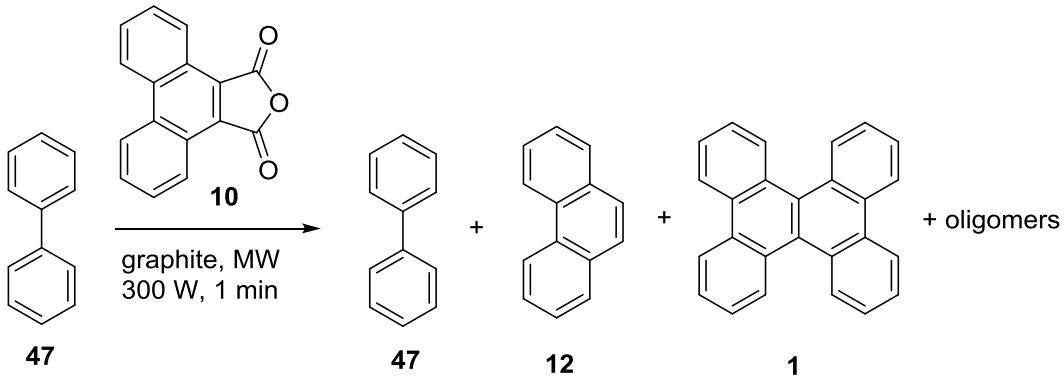
Scheme 16. MFP of **12** with **49**.

In an attempt to further explore aryne addition to the bay region of PAHs using MFP, alternative aryne precursors were investigated. Anhydride **10** was synthesized as a phenanthryne precursor using a method reported by Fields *et. al*.[42] The reaction proceeds through an oxidative photochemical cyclization of diphenylmaleic anhydride (**50**) in the presence of iodine in acetone (Scheme 17).



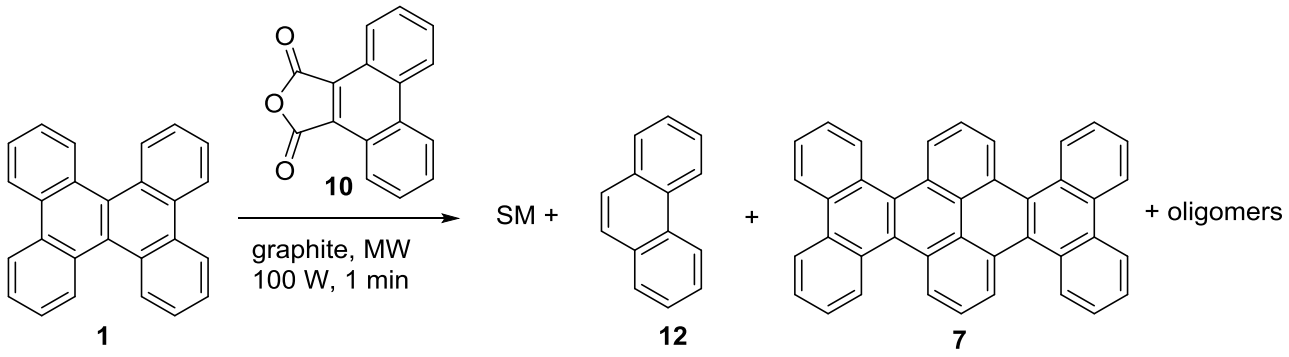
Scheme 17. Photochemical cyclization of **50**.

With **10** in hand, MFP was used to determine if it had the ability to act as a phenanthryne precursor to add to various PAHs. To explore this possibility, a reaction between **47** and **10** in the MW at 300 W for 1 minute was completed (Scheme 18). Analysis *via* ^{1}H NMR indicates the product mixture contains mostly **12**, starting material **47**, and NMR resonances which correspond to **1**, in a 5:2:1 ratio respectively. There was also indication of oligomerization in the NMR baseline.



Scheme 18. MFP of **10** in the presence of **47**.

To determine whether MFP could be used to synthesize larger PAHs *via* aryne addition to the bay region, a reaction between commercially available **1** and **10** was completed (Scheme 19). In this reaction, mostly **1** and **12** were observed, but a small amount of cycloaddition product **7** was detected. Analysis by ^{1}H NMR shows a 20:1.5:1 ratio of **1** to **12** to **7**. This indicates the generation of **11** and suggests that after optimization, these reaction conditions could serve as a route to **7**.



Scheme 19. MFP of **1** and **10**.

9-(Dibromomethylidene)fluorene: A Potential Phenanthryne Precursor

Phenanthryne precursors have received little attention. Some previously reported compounds which act as phenanthryne precursors are 10-trimethylsilylphenanthryl 9-trifluoromethanesulfonate (**28**),[29] **10**,[19] triazole **51**,[43] and 9-bromophenanthrene (**52**)[44-46] (Figure 2). All of these precursors have the basic skeleton of **11** which can be formed by elimination of leaving groups.

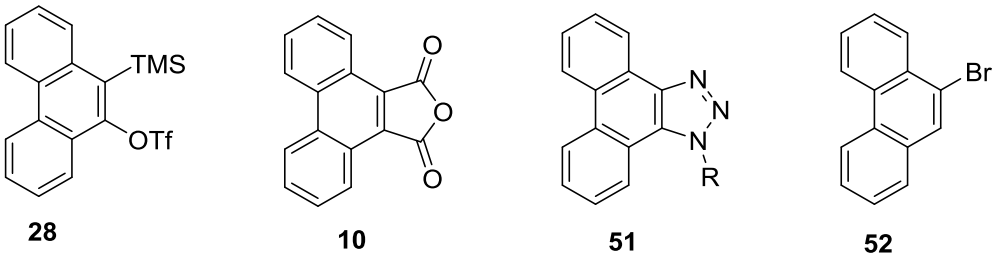


Figure 2. Phenanthryne precursors.

An alternative way to form an aryne is through rearrangement of a carbene. Thermal interconversion of vinylidene **53** and **15** is well known (Figure 3).[47] With this in mind, it was predicted that a fluorene derivative could potentially rearrange to generate **11**.

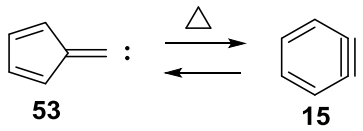


Figure 3. Interconversion of **53** to benzyne.

The rearrangement of carbene **54** was studied computationally in Gaussian 09[48] with DFT at the B3LYP/6-31+G(d,p) level of theory (Figure 4). The calculations for the free-energies of the carbene rearrangement show a transition state barrier of 10.9 kcal/mol. Due to the fact this barrier is not very high, a facile rearrangement of **54** might provide an efficient route to **11**.

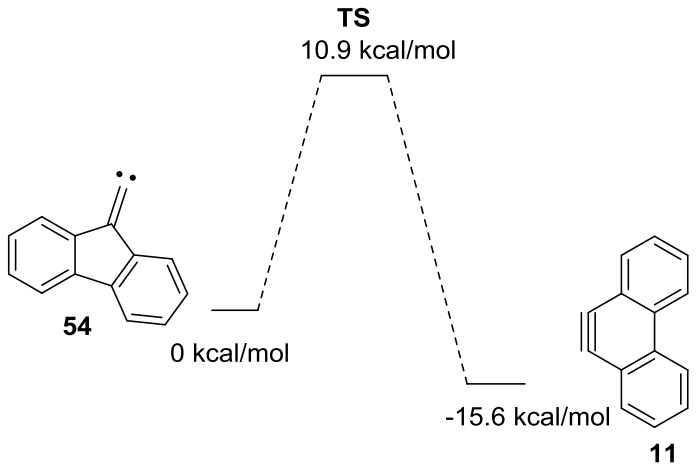
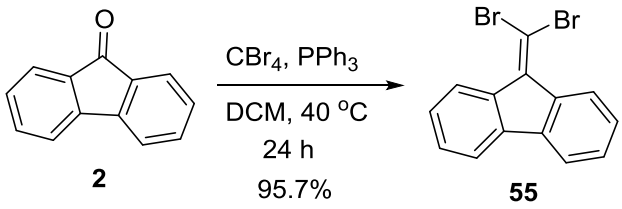


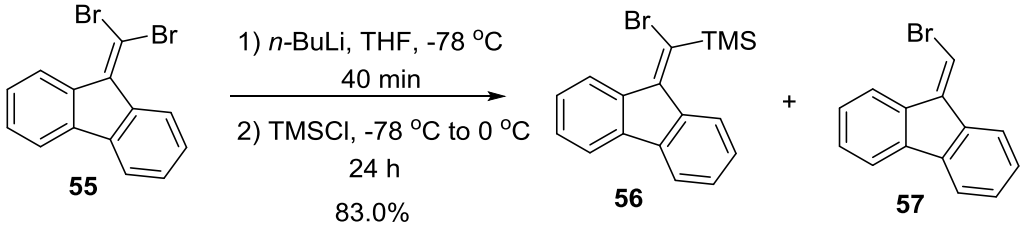
Figure 4. Free-energies of carbene rearrangement (B3LYP/6-31+G(d,p)).

9-(Dibromomethylidene)fluorene (**55**) was synthesized using dibromoolefination conditions to act as a potential phenanthryne precursor. The reaction involves the treatment of 9-fluorenone (**2**) with carbon tetrabromide (CBr_4) and triphenylphosphine (PPh_3) in DCM (Scheme 20).[49] This compound can act as a precursor to carbene **54**, which can theoretically rearrange to **11**. There was also the question of whether **55** itself could act as phenanthryne precursor, or if it would require a transformation into one of the more common silyl-substituted precursors.



Scheme 20. Dibromoolefination of 9-fluorenone (**2**).

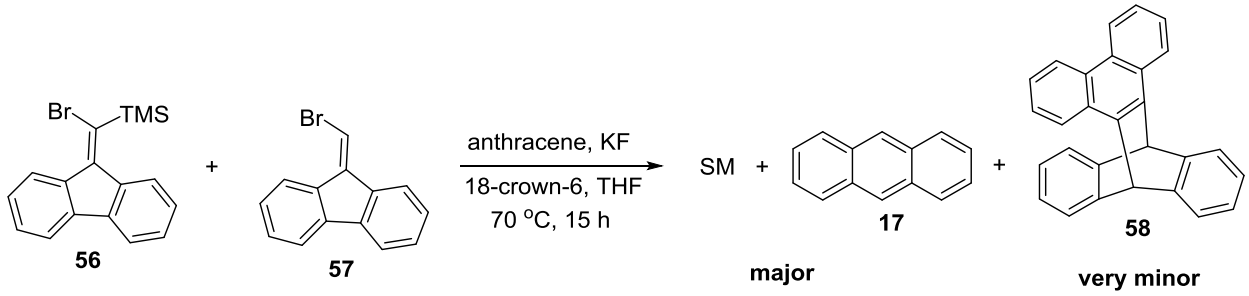
The first route to generating **11** involved treatment of **55** with *n*-BuLi in the presence of trimethylsilyl chloride (TMSCl) to afford **56**, which has not been previously reported (Scheme 21). It was identified *via* ^{1}H NMR through correlation with predicted chemical shifts calculated in Spartan 08.[50] The replacement of a bromine with a TMS group provides a substituent that can easily undergo nucleophilic attack by a fluoride. Isolation of pure **56** proved difficult because separation of the crude product mixture containing **56** by column chromatography was challenging. Analysis of column fractions *via* ^{1}H NMR indicated the presence of **56**, but also resonances which correspond to the reported NMR[51] of the monobromo-compound **57** in a 1.5:1 ratio, respectively. In attempt to get a better yield, the equivalents of *n*-BuLi were increased and various temperatures were used, however only mixtures of **56** and **57** were obtained.



Scheme 21. Silylation of **55**.

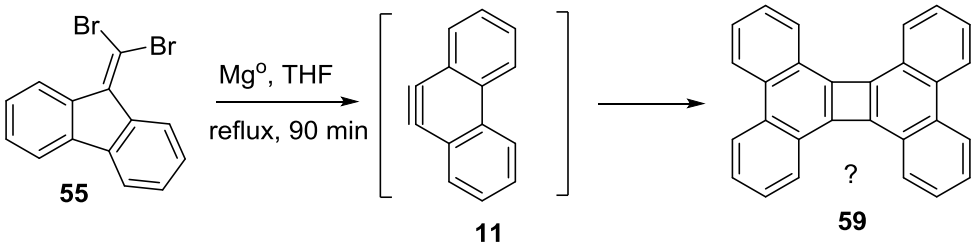
The crude reaction mixture of **56** and **57** was utilized to determine if a fluoride-induced elimination pathway could lead to **11**. Although **56** was not pure, the goal was to investigate if any conversion to **11** occurred to react with a trapping agent. Fluoride sources tested were CsF, TBAF, and KF with 18-crown-6. In these experiments, KF provided the most promising results. The crude mixture was heated in THF in the presence of KF and 18-crown-6, with **17**

as a trapping agent (Scheme 22). Analysis *via* ^{1}H NMR displayed **56**, **57**, **17**, and very minor peaks within the baseline which correspond to the predicted resonances calculated using DFT at B3LYP/6-31G* level for the desired product **58**. The yield was too low to deem this reaction efficient in phenanthryne generation. Variations of temperature, concentration, time, and order of addition were explored, but no major improvements were observed. Further purification of **56** could lead to enhanced reactivity, however with the results obtained, the fluoride-induced elimination of crude **56** is not a promising route for phenanthryne generation.



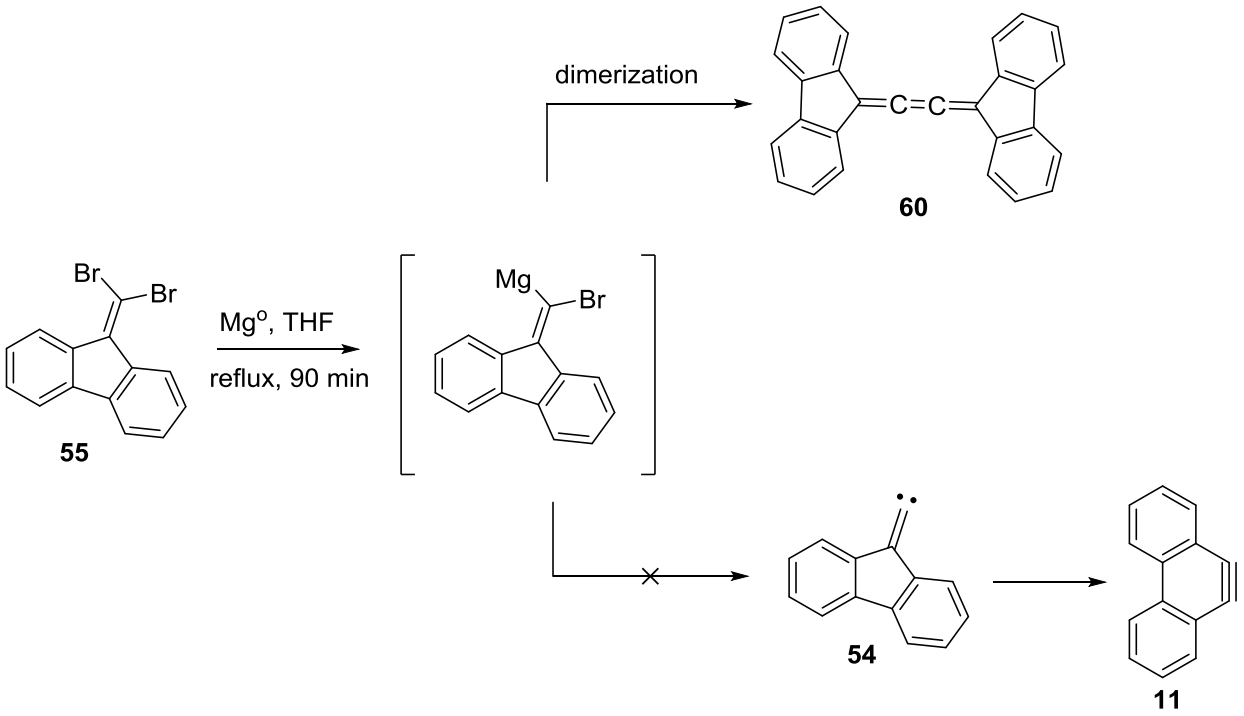
Scheme 22. Fluoride-induced elimination of **56** and **57** mixture.

Direct use of **55** as a phenanthryne precursor was investigated. Previous reports of using magnesium in the presence of dihaloarenes to generate arynes have been efficient,[33-34] so similar conditions were applied to **55**. This Grignard type reaction could produce a carbenoid which could rearrange to **11**. A stirring suspension of magnesium in refluxing THF was treated with **55**. After 90 minutes, workup afforded a bright red solid which was highly insoluble (Scheme 23). The proposed structure of the product was biphenylene derivative **59** due to its intense color, insolubility, mass spectrometry (MS) results, and calculated ^{1}H NMR spectrum obtained from DFT using B3LYP/6-31G(d). Attempts at obtaining a ^{13}C NMR were unsuccessful due to the compound's low solubility.



Scheme 23. Grignard reaction of **55**.

Tetrabenzobiphenylene (**59**) has been reported to be unstable,[43] so to prove this was the compound isolated, further analysis was done. The ^{1}H NMR chemical shifts corresponded to the calculated spectrum, along with the MS value of 352.1 m/z. A UV/vis analysis displayed a spectrum which did not match the predicted maximum absorbance values of 335 m and 419 m, but instead showed them as more red shifted. This discredited the proposed structure, therefore other possibilities were explored. The red substance was identified as cumulene **60** which has been described previously.[24, 52] This compound has the same mass value and a similar ^{1}H NMR splitting pattern to **59**. The previously reported ^{1}H NMR of **60** is an exact match to the isolated product, and it is described as a red, very insoluble solid.[24, 52] With these results, it can be concluded the Grignard route for phenanthryne formation is not efficient due to rapid dimerization of the carbenoid intermediate (Scheme 24).



Scheme 24. Synthesis of cumulene **60**.

Conclusions

Microwave flash pyrolysis provides a general route for aryne generation. The Diels-Alder reaction between arynes and the bay region of various PAHs can be applied to the synthesis of larger PAH derivatives. Phthalic anhydride (**14**) was utilized as a benzyne precursor, while the anhydride **10** was utilized as a phenanthryne precursor. MFP reactions of biphenyl (**47**) and dibenzo[*g,p*]chrysene (**1**) with 9,10-dicarboxyphenanthrene anhydride (**10**) displayed compounds **1** and **7**, respectively. This signifies MFP conditions are useful for aryne generation. Further optimization of these reactions could lead to higher conversion to Diels-Alder products, serving as a useful route to polycyclic aromatics. In search of a precursor which generates phenanthryne under more mild conditions, the attempted synthesis of **56** was done, which has the potential to be used in fluoride-induced elimination, however the reaction requires further optimization and purification. An alternative precursor for fluoride-induced elimination could be explored if the bromine of **56** was replaced with a triflate. TMS/triflate substituted

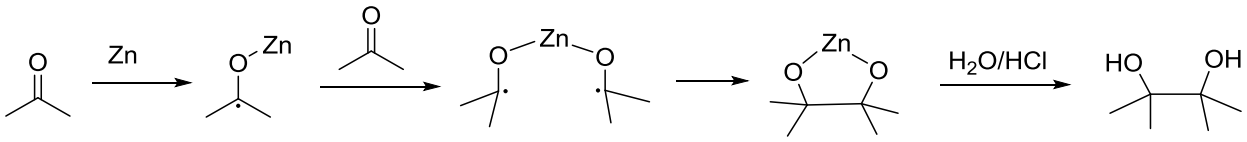
arenes have proven to be efficient in aryne generation. It was discovered that under Grignard conditions, **55** does not generate phenanthryne, but instead the carbenoid dimerizes to form a cumulene (**60**). Alternative phenanthryne precursors might be investigated.

Chapter II. Pinacol-Pinacolone Stone-Wales Sequence

Introduction

Pinacol Coupling and Pinacol Rearrangement

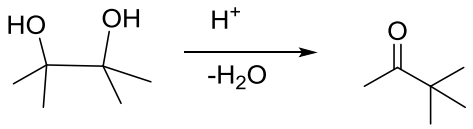
Pinacol coupling has been widely studied by researchers since 1859 when Fittig described the coupling of acetone using sodium.[53-54] The reaction involves forming a carbon-carbon bond between carbonyl compounds to generate 1,2-diols. The commonly accepted mechanism proceeds through radical-radical coupling (Scheme 25). The efficiency of the coupling depends on reaction conditions, such as what type of metal is used, temperature, time, and concentration. Commonly used metals are zinc,[55-58] aluminum,[59-60] and magnesium[61-63] due to their low cost and efficiency. Other metals like titanium are highly efficient, but expensive and potentially lead to olefination.[64-66] Pinacol coupling *via* photochemistry is also well known.[67-68] Certain pinacol coupling methods require anhydrous and inert reaction conditions because reagents needed are moisture and air sensitive. Recently, a focus has been placed on improving the pinacol reaction by utilizing low cost metals, as well as aqueous media which has economical and environmental advantages.[61, 69-71] These 1,2-diols are useful precursors in a variety of other reactions involving ring expansions and rearrangements.



Scheme 25. General pinacol coupling mechanism.

Using a classic carbocation rearrangement approach, pinacolone synthesis is achieved by the acid-catalyzed loss of water and a 1,2-shift within a pinacol (Scheme 26). Pinacolone formation can be catalyzed using acids such as H_2SO_4,[72-75] AcOH,[76-77] *p*-TsOH,[76, 78] and there have also been reports of using solid state chemistry in the presence of a Lewis acid like

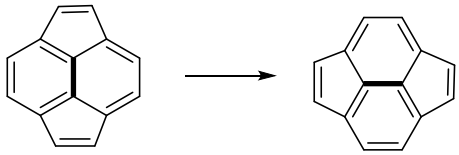
$AlCl_3$.[78-79] The rearrangement is of interest in cyclic systems because instead of an alkyl group migration, the carbon of the ring migrates, leading to a ring expanded product. This is useful for the synthesis of compounds such as spiroketones.



Scheme 26. Pinacol-pinacolone rearrangement.

Stone-Wales Rearrangement of Polycyclic Aromatic Hydrocarbons

Alder and Whittaker reported the thermal rearrangement of **4** to **1** (Scheme 2) *via* a radical pathway in 1975.[5] In 1986, Stone and Wales[80] proposed the isomerization of fullerene molecules *via* a similar 1,2-carbon rotation of 90°. This is an uncommon thermal rearrangement which transposes a two carbon fragment. The best studied example studied in the literature is the rearrangement of pyracyclene (**61**) (Figure 5).[80]



61

Figure 5. Stone-Wales rearrangement of pyracyclene (**61**).

The Stone-Wales rearrangement has been used to hypothetically describe fullerene synthesis,[81-83] isomerization,[84-89] as well as possible graphene precursor formation.[90-94] The exact mechanism of this reaction is still under scrutiny, however several different pathways have been proposed. Stone and Wales[80] suggested the concerted reaction would involve a 4 electron process to reach the transition state, which is a forbidden transformation according to orbital symmetry (Figure 6a).[95] Scuseria *et. al*. described a stepwise carbene, or sp^3, mechanism, but calculations concluded the energy barriers were similar to the concerted pathway (Figure 6b).[96-97] More recently, Karney *et.al*.[98] reported a computational study that

suggests compounds that do not contain a pyracyclene moiety are more likely to follow the carbene mechanism, while those which do contain a pyracyclene moiety follow a stepwise mechanism by means of a cyclobutyl intermediate. Although the computational results displayed lower energy barriers than what was previously reported, they are still high. In search of lower energy barrier pathways, investigators have discovered this rearrangement can occur under radical-catalyzed[99-101] and cationic conditions.[5, 12]

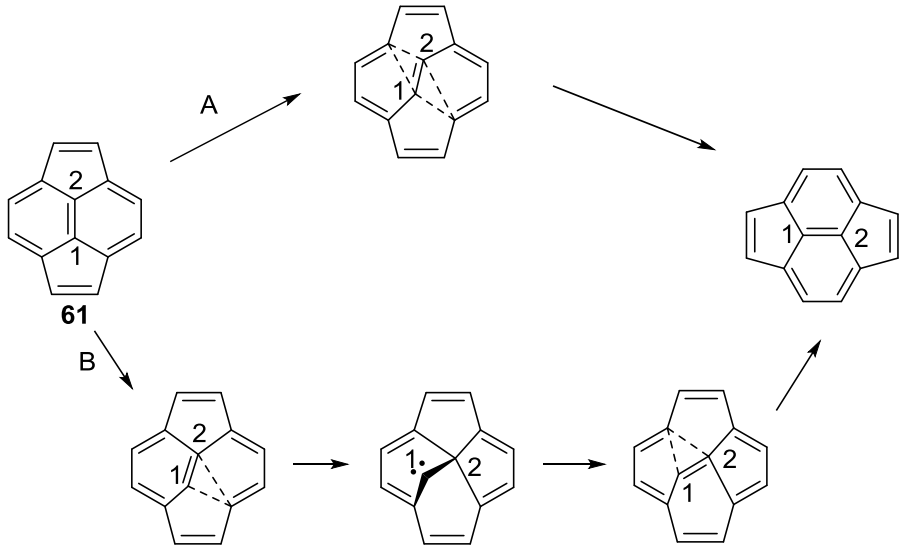


Figure 6. (A) Concerted and (B) stepwise Stone-Wales rearrangement pathways.

Previous work by Cahill[12] supported a cationic pathway for the Stone-Wales rearrangement of **4** to **1**. This was first investigated with DFT using the B3LYP/6-31+G(d,p) level of theory (Figure 7). It was found that the highest transition state barrier was 24.2 kcal/mol above the initial cation **62**, which is much lower than the 43.8 kcal/mol barrier for the radical-catalyzed pathway calculated by Alder and Harvey for the same transformation.[100] This indicates the cationic pathway is plausible.

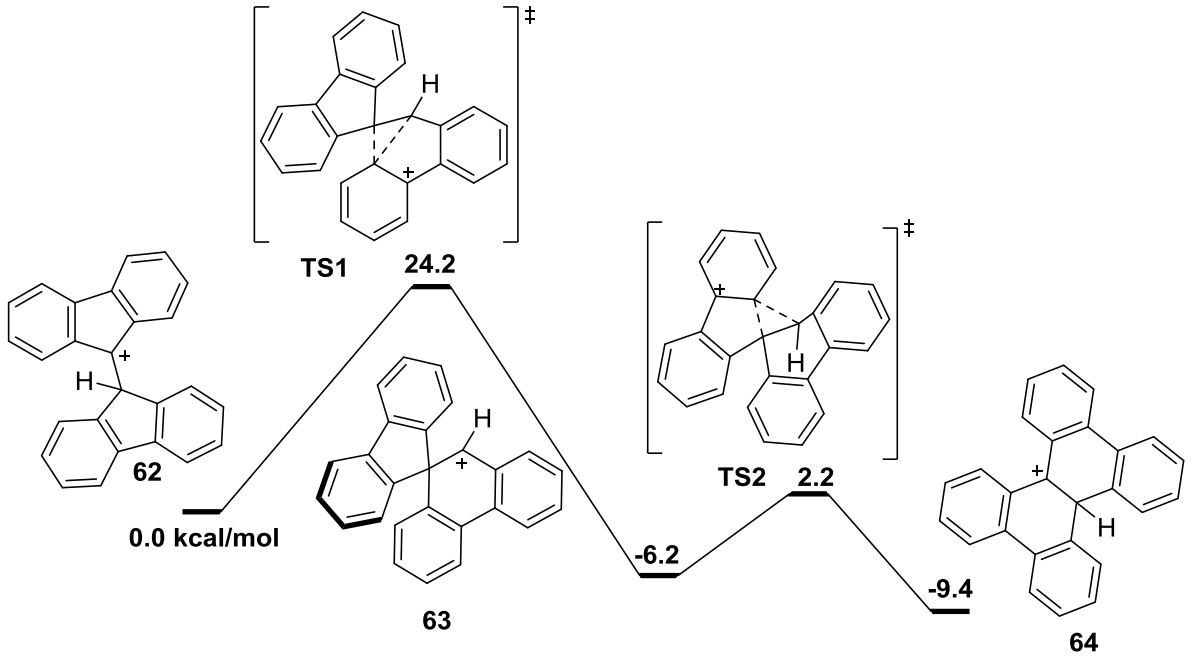
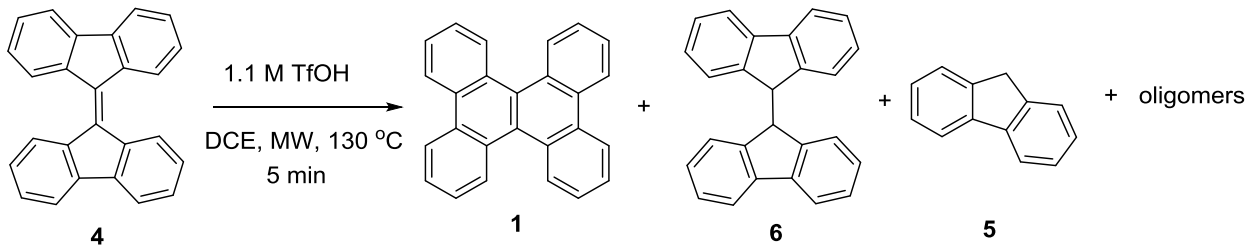


Figure 7. Cationic Stone-Wales rearrangement towards DBC.[12]

When **4** was treated with TfOH in DCE and heated in the microwave, Cahill reported a 30% yield of **1** (Scheme 27). This proves the cationic Stone-Wales rearrangement is feasible, however it is not an efficient route towards **1**.



Scheme 27. Cationic Stone-Wales rearrangement of **4**.[12]

Research Objective

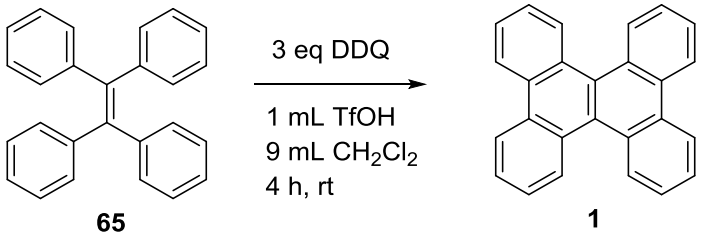
While the pinacol-pinacolone reaction and the Stone-Wales rearrangement have been widely studied, utilizing the three reactions together as a stepwise approach to polycyclic aromatic hydrocarbons has only been explored a few times.[102-103] One goal of this research was

to utilize acid-catalyzed rearrangements under mild conditions to efficiently synthesize **1**. It was observed that the pinacol-pinacolone Stone-Wales (PPSW) sequence was a scalable and efficient route towards **1**. This synthetic route could then be applied to synthesize other PAHs from aromatic ketones.

Results and Discussion

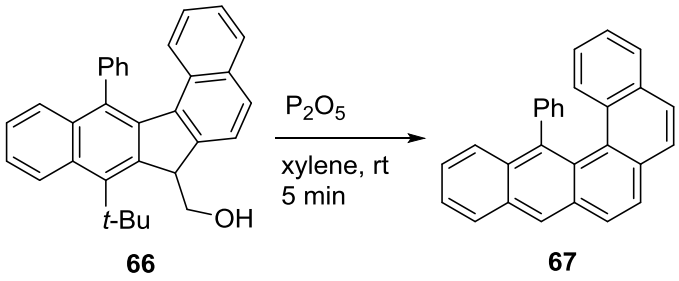
Synthesis of Dibenzo[g,p]chrysene

Synthesis of **1** from **4** was previously studied in our group by Cahill[12] using a cationic pathway under superacid conditions.[104] The cationic oxidative cyclization of tetraphenylethylene (**65**) to **1** was also studied. Using 3 equivalents of 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and 1.3 M TfOH in room temperature DCE for 4 hours, conversion to **1** was observed in a 58% yield (Scheme 28). Although this reaction reported a higher yield than the cationic Stone-Wales route, the yield could still be improved, as well as exploring a more scalable synthetic route.



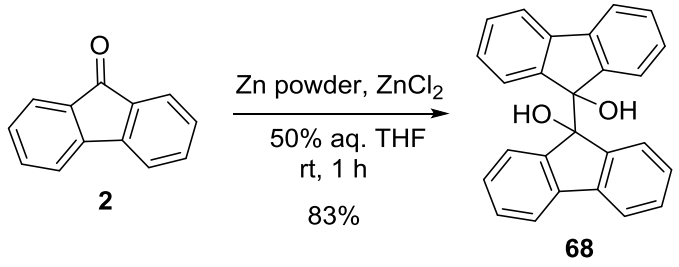
Scheme 28. Cationic oxidative cyclization of **65**.[12]

In search of a more efficient acid-catalyzed route towards **1**, it has been reported that 9-fluorenyl alcohols can rearrange to PAHs under acidic conditions. Brown and Bluestein have reported the rearrangement of 9-fluorenylmethanol to **12** in high yield using Wagner-Meerwein rearrangement conditions.[105] Yang *et. al.* expanded this reaction to include benzofluorene methanols which rearrange to phenanthrene derivatives using phosphorus pentoxide (P_2O_5) in xylene (Scheme 29).[106]



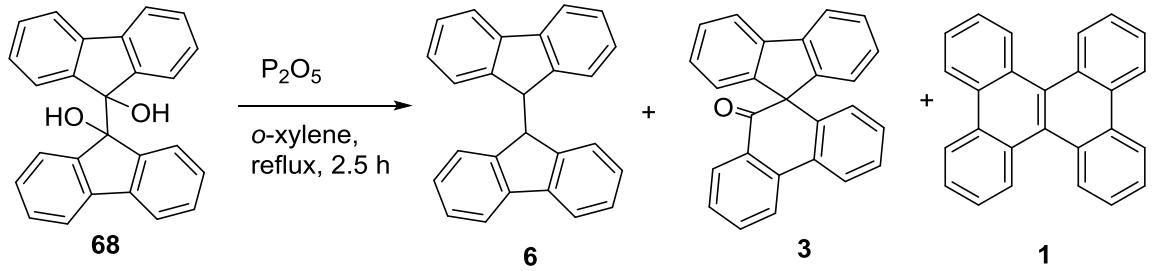
Scheme 29. Wagner-Meerwein rearrangement of a fluorenyl alcohol (**66**).[106]

We explored the synthesis of **1** starting from a pinacol precursor. Homocoupling of **2** using zinc powder and zinc chloride ($ZnCl_2$)[107] led to the formation of 9, 9'-bifluorenyl-9, 9'-diol (**68**) (Scheme 30).



Scheme 30. Pinacol coupling of **2**.

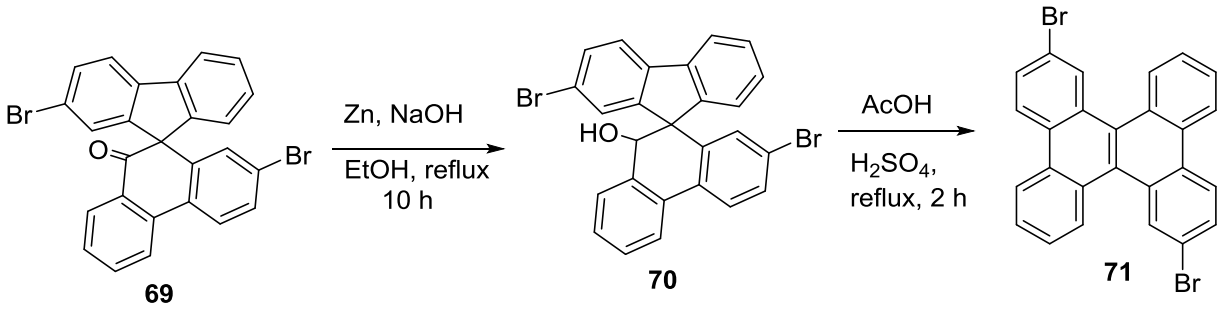
Reaction of **68** with P_2O_5 led to a mixture of products (Scheme 31). Dehydration and pinacol rearrangement were observed. This mixture also included the expected ketone from pinacol rearrangement, along with small amounts of **1**.



Scheme 31. Wagner-Meerwein rearrangement of **68**.

Sōda *et. al.* reported the synthesis of a DBC derivative from the pinacolone after reduction to the spirofused alcohol, followed by rearrangement (Scheme 32).[108] Using this

technique, the pinacolone **3** could be isolated to explore if rearrangement to the parent DBC would occur.



Scheme 32. Synthesis of dibromo-substituted DBC.[102]

Free-energy calculations of this rearrangement pathway were investigated with DFT at B3LYP/6-31+G(d,p) level of theory. As shown in Figure 8, the barrier for the transition state is 7.9 kcal/mol, indicating a facile rearrangement.

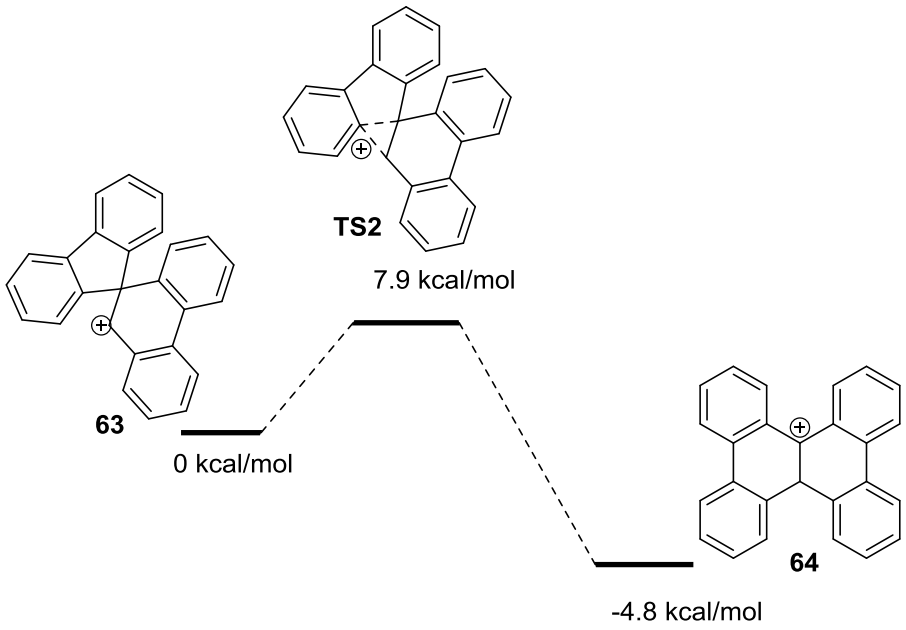
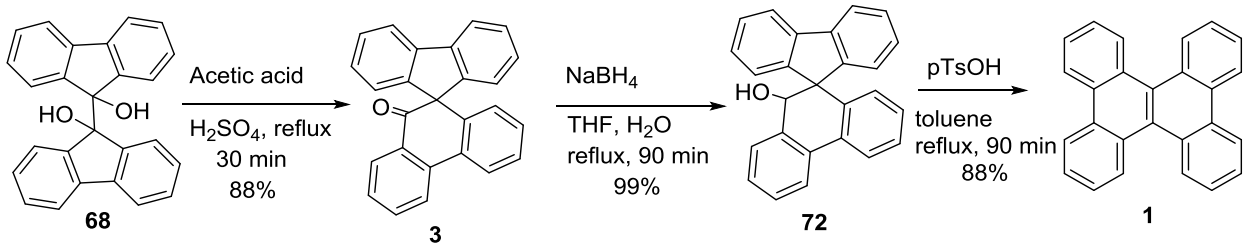


Figure 8. Free –energies of the cationic rearrangement towards DBC (B3LYP/6-31+G(d,p)).

This combined approach yielded an efficient and scalable route to **1** as shown in Scheme 33. All of the synthetic steps give high yields, do not require harsh reaction conditions,

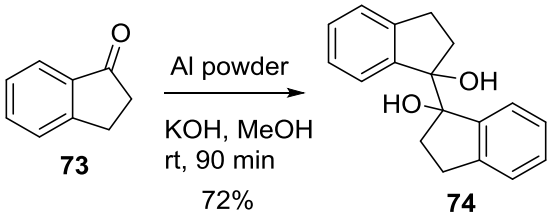
and can be scaled up, making this the most efficient pathway to **1**, with an overall yield of 64%. In the largest scale reaction to date, 4 g of pinacol **68** yielded 2 g of DBC (**1**).



Scheme 33. Pinacol-pinacolone Stone-Wales route towards **1**.

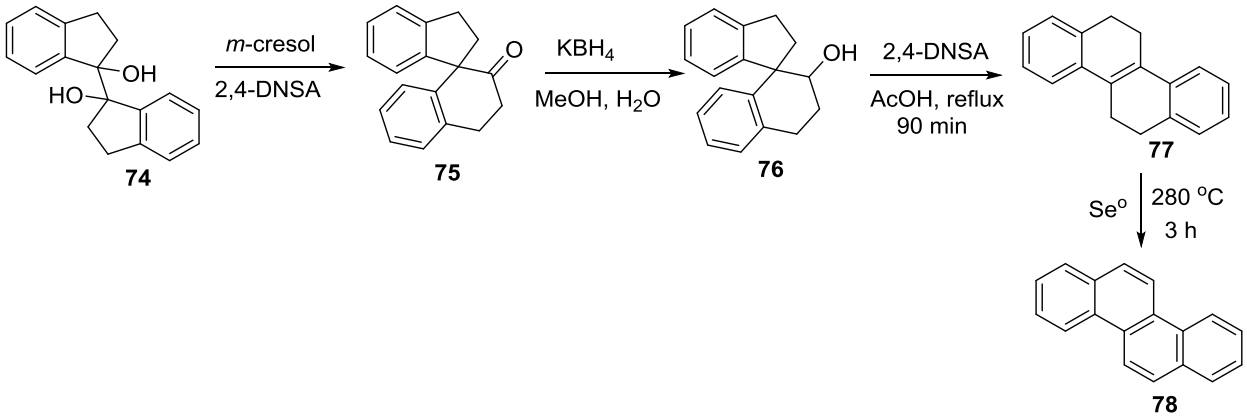
Progress Towards Polycyclic Aromatic Hydrocarbons *via* PPSW Pathway

With these results in hand, the next question was whether the same pinacol-pinacolone Stone-Wales sequence would yield other polycyclic aromatics. Following the same approach, these conditions were applied to 1-indanone (**73**). The pinacol was not successfully isolated using the conditions for the coupling of **2**, so another variation of the pinacol reaction was used.[60] In the presence of aluminum powder, potassium hydroxide (KOH), and methanol (MeOH), 1-indanopinacol (**74**) was isolated in a 72% yield (Scheme 34).



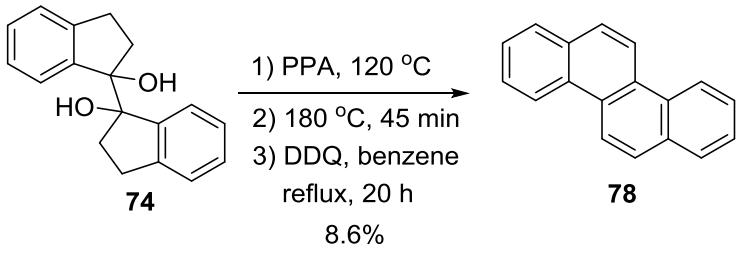
Scheme 34. Synthesis of 1-indanopinacol (**74**).

Ourisson *et. al*.[103] previously studied the rearrangement of **74** *via* treatment with *m*-cresol and 2,4-dinitrosulfonic acid (2,4-DNSA) to yield pinacolone **75** (Scheme 35). It should be noted that these are quite unusual reaction conditions. The pinacolone **75** was reduced and the spirofused alcohol **76** was treated with acid at reflux to afford tetrahydrochrysene (**77**). Dehydrogenation with selenium yields chrysene (**78**).



Scheme 35. Synthesis of chrysene from pinacol **74**.[103]

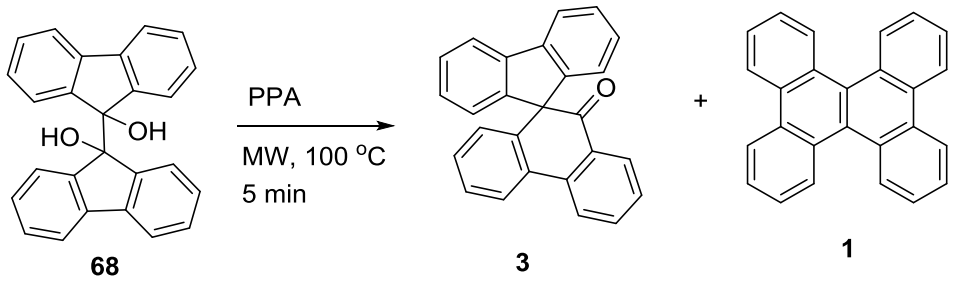
Attempts to synthesize **75** using acetic acid (AcOH) and sulfuric acid (H_2SO_4) were not successful. Cyclization of aromatic alcohols using polyphosphoric acid (PPA) has been studied in our group. Using this approach, **74** was added to PPA and placed in a CEM microwave (MW) at 100 ^oC for 5 minutes. After a work up and characterization *via* ^1H NMR, both **75** and chrysene (**78**) were observed. With these results, the next step was to determine if the reaction could be completed on a larger scale without the MW and to provide a higher conversion to **78**. As shown in Scheme 36, **74** can rearrange to **78** in about a 10% yield. An oxidation with DDQ is needed because after purification of the reaction, the column fraction containing **78** also contains the tetra- and dihydro-derivatives. The yield of **78** could be improved by transforming **75** to **78** using the PPSW conditions.



Scheme 36. Rearrangement of **74** using PPA.

To further explore if these conditions could be applied to other pinacol cyclizations, the reaction was also completed with **68** (Scheme 37). Similar results were observed, where **3** and

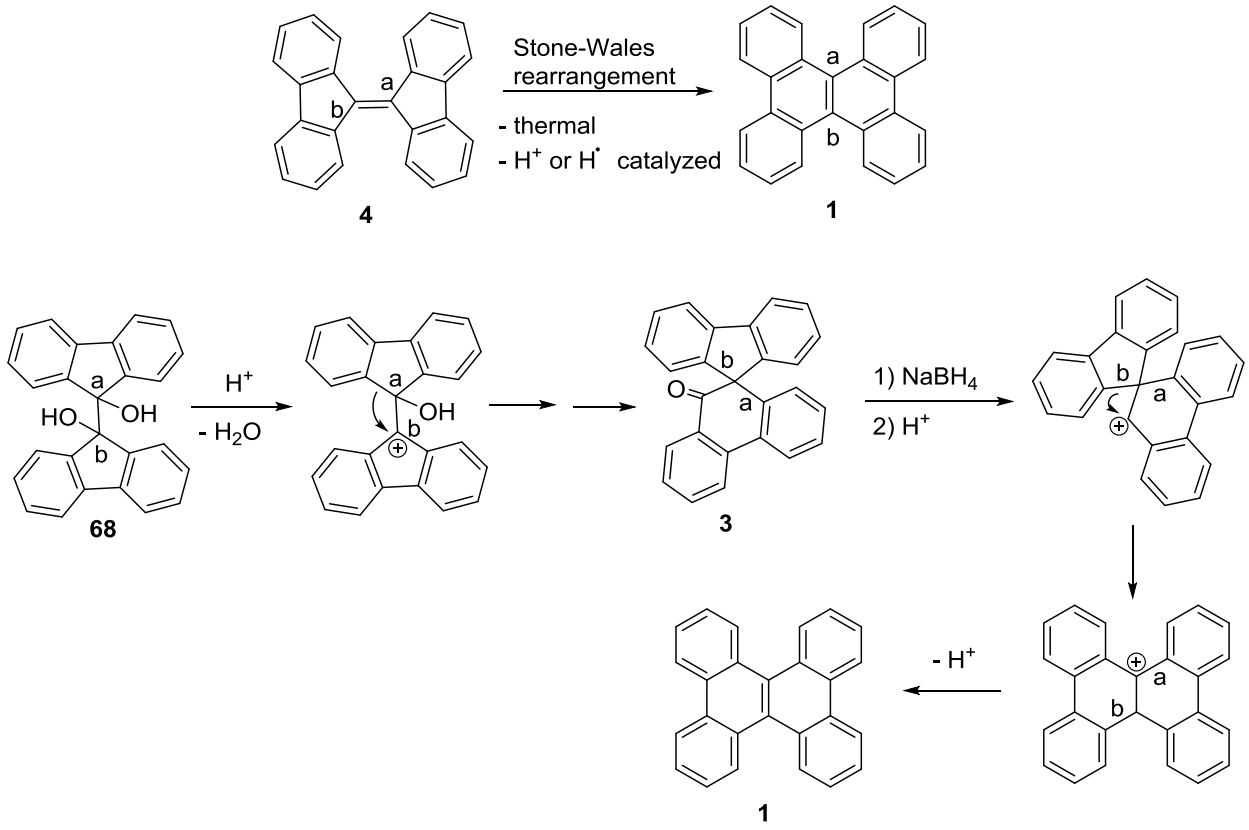
1 were isolated in a 2:1 ratio respectively. Although this is an interesting result and is another way to synthesize **1**, the pinacol-pinacolone Stone-Wales sequence is a more efficient route for this pinacol.



68 **3** **1**

Scheme 37. PPA reaction with **68**.

Scheme 38 summarizes the strategy that developed in this work. The Stone-Wales rearrangement can be thermal, or hydrogen radical catalyzed, as shown by Alder[5], or cationic, as shown by Cahill.[12] A synthetically efficient, but more complex route starts with a pinacol and proceeds by two consecutive aryl group migrations to cationic centers. This sequence can be accomplished in one step (Scheme 37), but affords low yields. A stepwise pathway (Scheme 33) is longer, but higher yields are obtained. This provides a scalable and efficient synthesis of **1**. We have shown that a similar route yields chrysene (**78**) beginning from 1-indanone (**73**).



Scheme 38. Comparison of Stone-Wales and pinacol-pinacolone Stone-Wales sequence.

Conclusions

The acid-catalyzed rearrangement of pinacols can be used as a facile and efficient route to synthesize certain PAHs which typically are expensive or difficult to isolate. In particular, the pinacol-pinacolone Stone-Wales sequence can be applied to synthesize **1** in high yield without harsh reaction conditions. Another pathway involves the rearrangement of pinacols using PPA, which can generate their pinacolone, as well as an aromatic hydrocarbon derivative, as seen with chrysene (**78**). These reaction conditions are still under investigation to optimize the yield. Alternatively, the pinacolone could be easily separated, submitted to the conditions in the last two steps of the PPSW sequence, and produce the PAH. Applying these pathways to various aromatic ketones is under investigation to generate a variety of PAHs.

Chapter III. Progress Towards Zethrene

Introduction

Synthesis of Zethrene and Zethrene Derivatives

Zethrene (**79**) is a PAH which gets its name from the fact its structure appears as a z-shape. Zethrenes are of interest due to their potential diradical character and for applications in non-linear optics, organic semiconductors, and near-infrared dyes.[109-111] The center rings lack aromaticity, with fixed double bonds as in **79**. The diradical character (**79a**) suggests applications in organic electronics; however this substance is reported to be oxygen sensitive. Expanding along the m- or n-axis of **79** generates larger homologues such as heptazethrene (**80**) and 1,2:9,10-dibenzooctazethrene (**81**), which are also of interest (Figure 9).

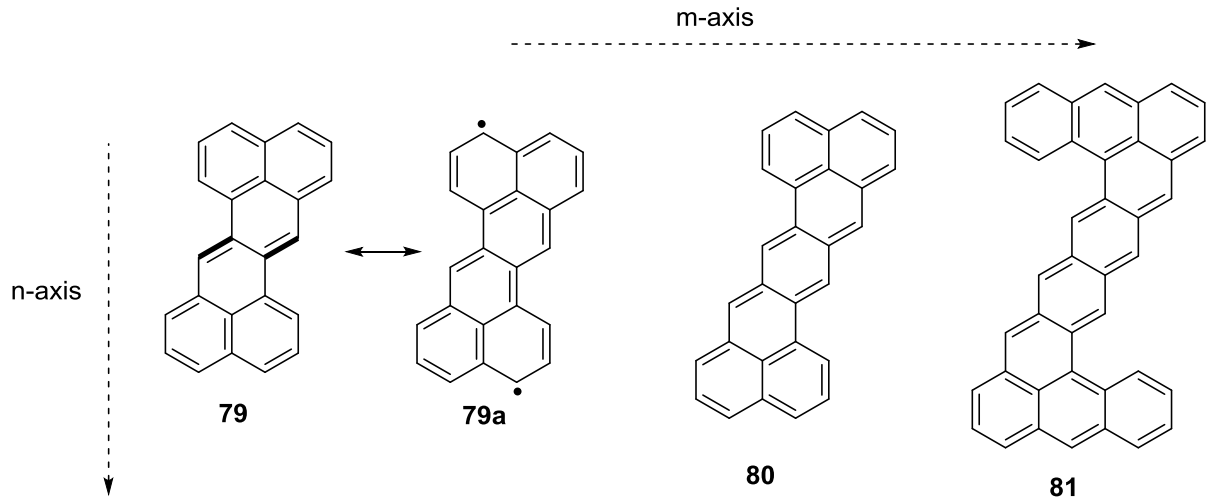
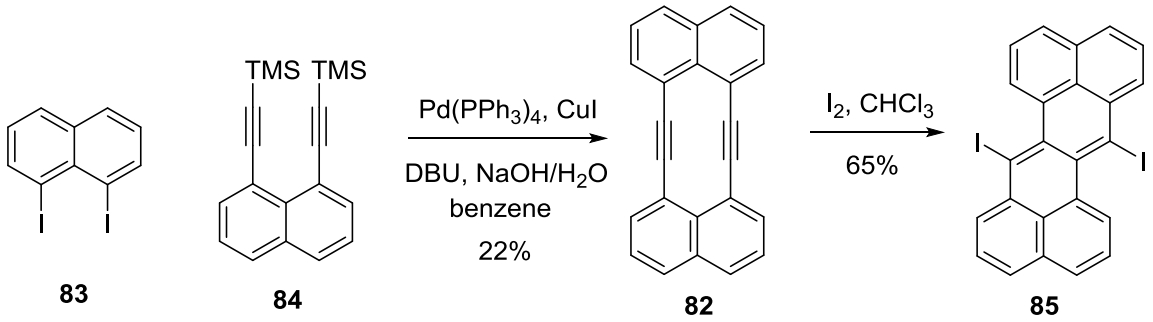


Figure 9. Extension of **79**.

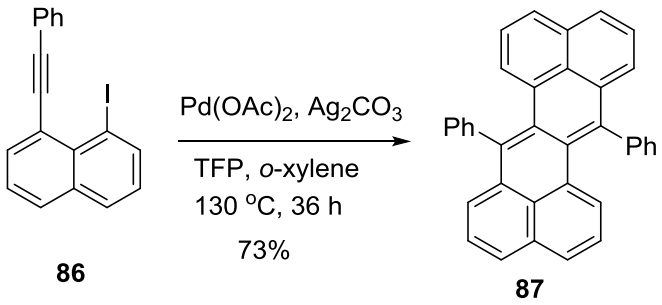
Zethrene was first synthesized by Clar in 1955.[112] More convenient cross-coupling routes were reported by Ipaktschi *et. al*.[113] in 1968 and again by Sondheimer and Mitchell[114] in 1970 while both were attempting to synthesize tetradehydrodinaphtho[10]annulene (**82**). Annulene **82** is not stable and it undergoes transannular cyclization to **79** after hydrogen abstraction by an intermediate diradical. In 2009, coupling of 1,8-diiodonaphthalene (**83**) and

1,8-bis(trimethylsilylethynyl)naphthalene (**84**) produced **82** as a pure compound which was characterized by Tobe *et. al*.[111] After treatment with iodine, this undergoes transannular cyclization to zethrene derivative **85** (Scheme 39). The majority of zethrene syntheses in the literature involve substitution at the bay region or *peri*-position because it enhances the stability, as well as solubility. With this being said, reports of the synthesis of the parent zethrene **79** are scarce.



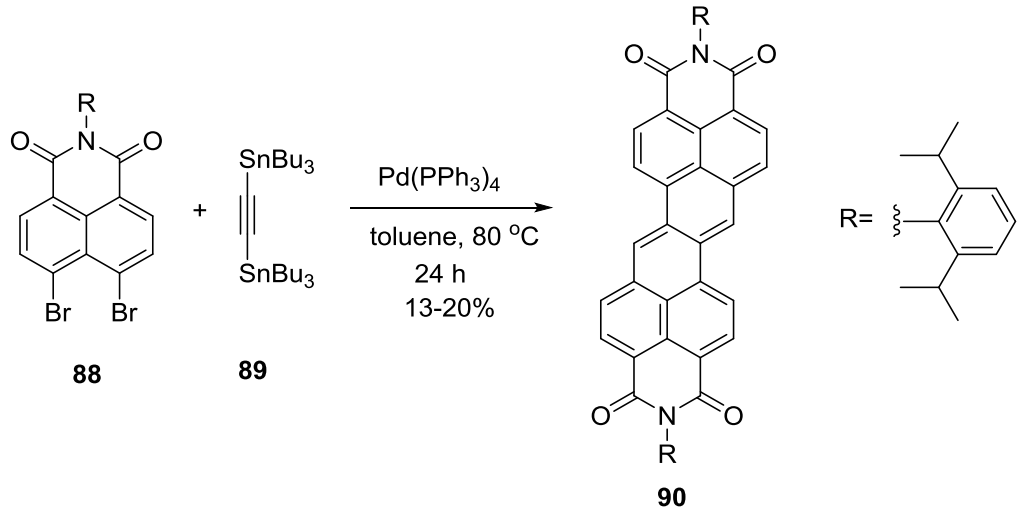
Scheme 39. Synthesis of zethrene derivative **85**.[111]

In 2010, Wu *et. al*.[115] reported a metal-catalyzed annulation of halonaphthalenes to afford zethrene derivatives. The reaction involves treatment of 1-iodo-8-(phenylethynyl)naphthalene (**86**) with $Pd(OAc)_2$, Ag_2CO_3, and ligand tri-(2-furyl)phosphine (TFP) in *o*-xylene to form phenyl-substituted zethrene **87** in 73% yield (Scheme 40). These conditions were applied to various other iodoarenes to synthesize a collection of substituted zethrenes.[115]



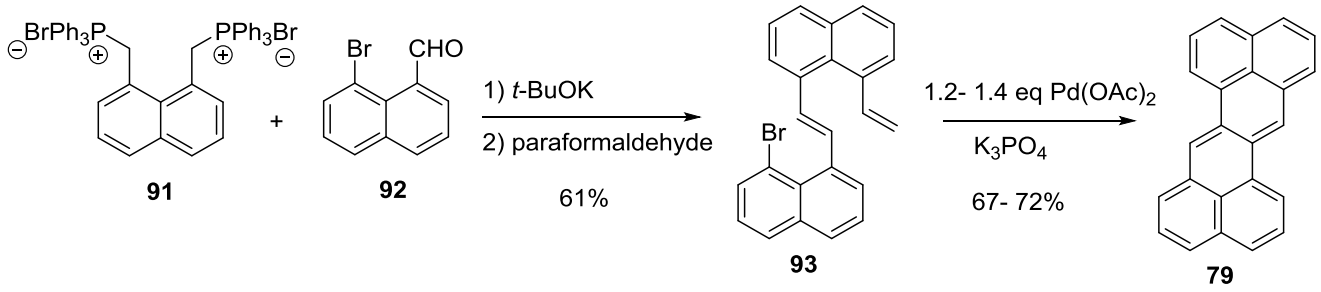
Scheme 40. Metal-catalyzed annulation to afford zethrene derivatives.[115]

Another route towards zethrene derivatives was developed by Wu and Sun.[116] This Stille cross-coupling of dihaloarene **88** and bis(tri-*n*-butylstannyl)acetylene (**89**) to form an annulene which undergoes transannular cyclization to afford dicarboximide-substituted zethrene **90** (Scheme 41). Substitution at the *peri*-position makes **90** a stable compound with interesting photophysical properties.



Scheme 41. Stille cross-coupling route for zethrene synthesis.[116]

Parent zethrene **79** was prepared by Miao *et. al*.[117] using a Wittig-Heck pathway. The bis(triphenylphosphonium) salt **91** undergoes a Wittig reaction with 8-bromo-1-naphthaldehyde (**92**) to yield dinaphthyl-derivative **94**, which under Heck reaction conditions is treated with $Pd(OAc)_2$ to generate **79** in 67-72% yield (Scheme 42). Applying the Heck conditions from Scheme 42 to **83** and 1,8-divinylnaphthalene, **79** was isolated in only a 10% yield. This same reaction failed with more typical Heck conditions which involve only a catalytic amount of palladium catalyst. It was concluded that more than one equivalent of $Pd(OAc)_2$ is required to isolate an acceptable yield of **79** for this reaction pathway.



Scheme 42. Synthesis of **79** *via* a Wittig-Heck approach.[117]

Experimental and computational studies provide conflicting information on the biradical character of zethrenes. Early theoretical calculations predict **79** and its substituted derivatives to be closed-shell.[118-120] More recently, Wu *et. al*.[121] report an experimental study which concludes **79** actually possesses singlet open-shell biradical character. The study reports analysis *via* X-ray crystallography shows bond shortening and a slight enhancement in aromaticity of the center rings, along with electron spin resonance measurements showing signals characteristic of compounds with singlet open-shell biradical character. The electrochemical and photophysical properties were also studied to further confirm the biradical character. Analysis of substituted zethrenes and *π*-extended derivatives has also been reported.

Factors which influence if a zethrene derivative is open- or closed-shell are ring substituents and the extended *π*-conjugation. Substitution at the bay region of **79** reportedly favors a closed-shell compound.[121] By contrast, vertical or horizontal *π*-extension enhances the singlet open-shell biradical character of the molecule.[119-124] These extended zethrenes have larger biradical character because aromaticity is being reestablished in the biradical resonance form (Figure 10). In general, extending along the m- or n-axis of zethrene creates an increase in biradical character, but this decreases the kinetic stability.

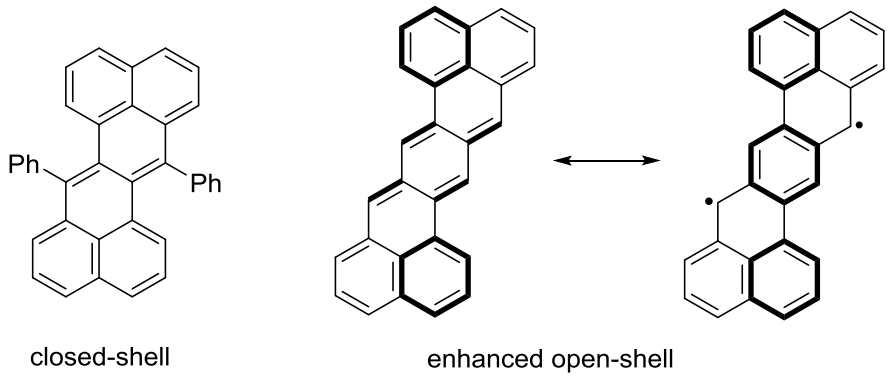
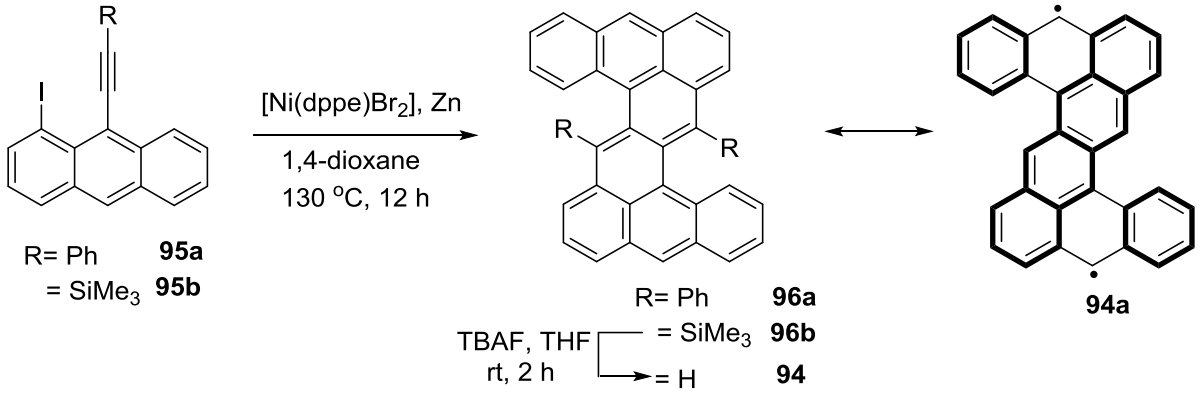


Figure 10. Open- versus closed-shell zethrenes.

Dibenzozethrene **94** exemplifies the impact substituents and *π*-extension have on the biradical properties of a molecule. The biradical resonance form **94a** contains three sextets, while parent **94** contains two. The synthesis involves the nickel-catalyzed cyclodimerization of ethynyl-iodoanthracene analogs **95a** and **95b** (Scheme 43).[121] The phenyl and TMS-substituted dibenzozethrenes (**96a** and **96b**) display closed-shell character, while unsubstituted **94** is believed to be singlet open-shell. Computational studies support these conclusions.



Scheme 43. Synthesis of dibenzozethrene derivatives.[121]

Computational analysis can predict electronic character using biradical character indices as well as the relative energies of open and closed-shell compounds. Wu *et. al.*[121] demonstrated using DFT at the CAM-B3LYP/6-31G** level, the open-shell biradical form of **94** is lower in energy than the closed-shell, which signifies the open-shell is more stable. The same

is observed with **79**, however the difference is not as great. The biradical character indices display the same trend, supporting the conclusion that **79** and **94** are singlet open-shell biradicals. Open-shell biradical character would make these compounds candidates for two-photon absorption (TPA) which is very useful for nonlinear optical materials, near-infrared dyes, and organic photovotalics.

Research Objective

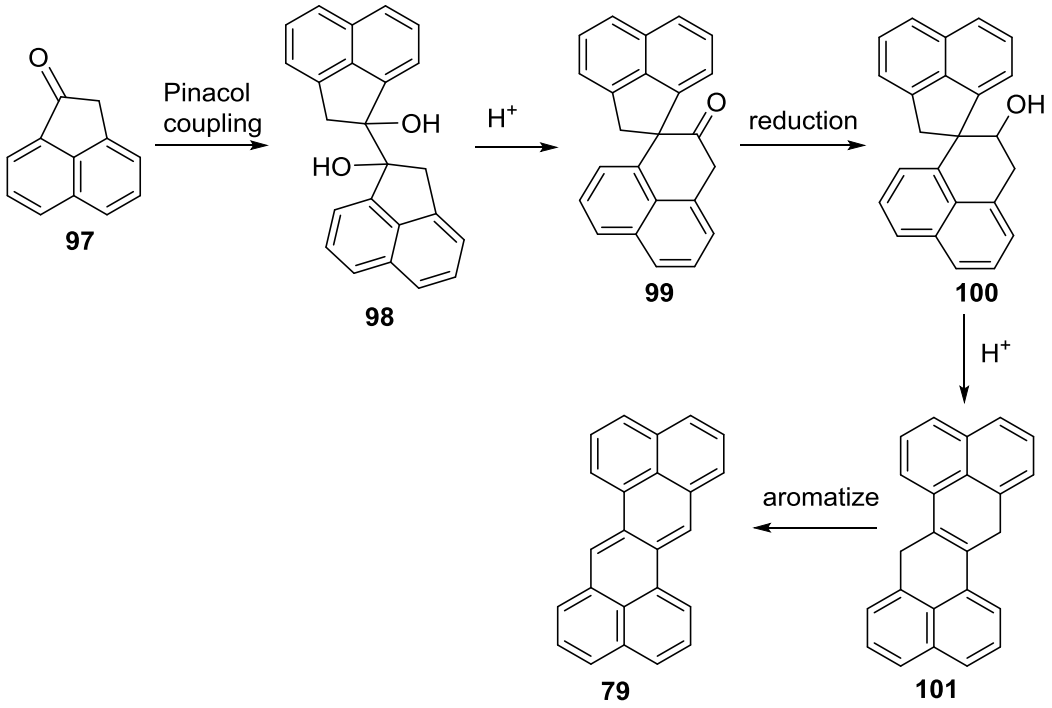
There have been various reports of the successful synthesis of substituted zethrenes, however isolation of parent zethrene **79** has proven to be difficult. Also, although zethrene derivatives can be obtained in moderate yields, the syntheses are typically long because of the requirement to prepare 1,10-disubstituted naphthalenes. The goal of this research was to develop a facile, efficient, low cost synthetic pathway towards **79**. This would make **79** more readily available for studies in the field of nonlinear optics and near-infrared dyes. Once optimized, the synthesis could be applied to generate larger homologues of **79**, which have not received as much attention in the literature.

Results and Discussion

A Pinacol Precursor to Zethrene

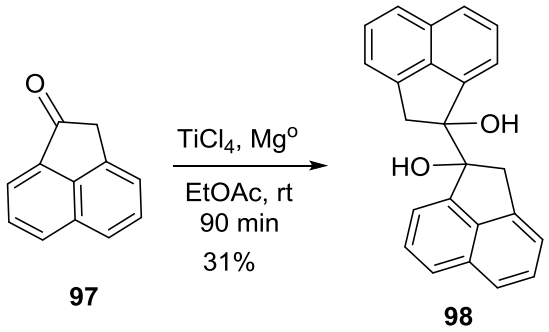
The synthesis of **79** has proven to be difficult and has not been as widely reported as its substituted homologues. In an attempt to avoid the use of metal catalysts or long synthetic procedures, alternative routes towards **79** were explored. Another aspect to avoid from previously reported syntheses is using **82** as an intermediate. The synthesis of **82** is not efficient and the compound itself is not very stable, so developing a synthesis without it is desired. The first step in most reported syntheses of **79** and its derivatives involves various coupling reactions of naphthalene compounds using metal catalysis, however there are other coupling reactions that have not yet been investigated.

Following our successful synthesis of dibenzo[*g,p*]chrysene (**1**) *via* the pinacol-pinacolone Stone-Wales sequence, the same process can provide a plausible route to **79**. The synthesis would involve the pinacol coupling reaction of readily available 1-acenaphthenone (**97**), followed by a pinacol rearrangement, reduction, and acid-catalyzed rearrangement to **101**, followed by aromatization (Scheme 44).



Scheme 44. Proposed synthetic pathway towards **79**.

Efficient pinacol coupling of **97** proved to be elusive. The previous conditions used for **2** and **73** were unsuccessful, as were various other methods such as Mg/MgI_2,[125] sonication,[62] and photochemical coupling.[126] Applying pinacol coupling conditions reported by Li *et. al*.[127] using titanium(IV) chloride ($TiCl_4$) and Mg, the pinacol **98** was successfully isolated in a 31% yield (Scheme 45).



97 **98**

Scheme 45. Pinacol coupling of **97**.

To determine if the pinacol-pinacolone Stone-Wales sequence was feasible for **98**, calculations for the pinacol rearrangement were completed. The computations were done with DFT at the B3LYP/6-31+G(d,p) level. The calculations show the free-energies, where the barrier for the transition state is 17.5 kcal/mol (Figure 11). This barrier is not high; however this is larger than what was observed for the rearrangement of **68** which underwent a facile rearrangement. This suggested that **98** may not rearrange to its pinacolone **99** as readily as **68**.

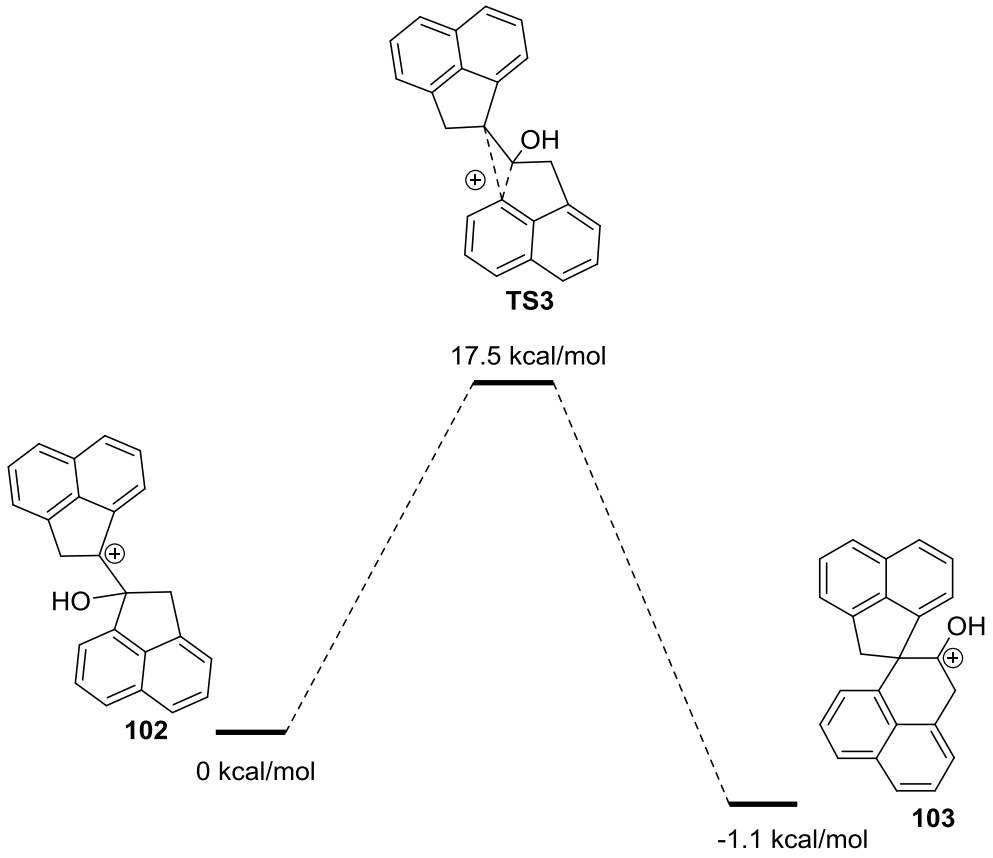
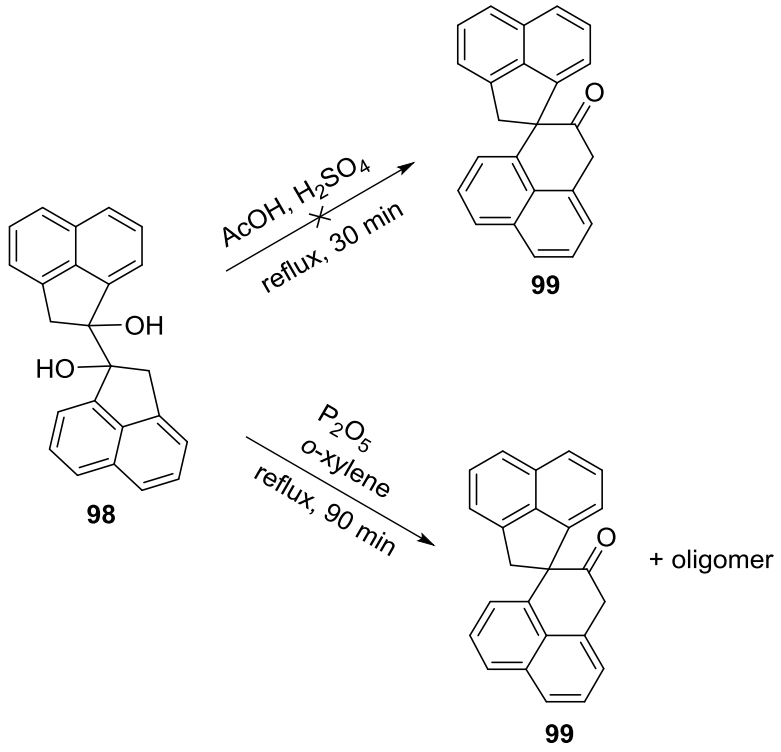


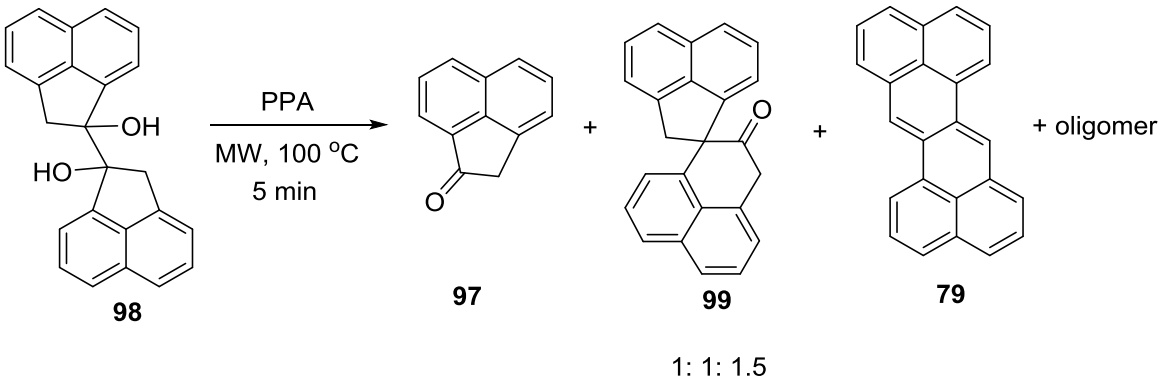
Figure 11. Free-energies of the cationic rearrangement of **98**.

The next step was the synthesis of **99**. Typical conditions using AcOH and H_2SO_4 were applied for pinacol rearrangement of **98**, however the desired product was not observed and instead a very dark, insoluble solid was isolated (Scheme 46). The Wagner-Meerwein rearrangement conditions with P_2O_5 were applied and **98** was observed in ^{1}H NMR, but purification by column chromatography was unsuccessful because of oligomerization (Scheme 46). Attempts to alter both reaction routes in Scheme 46 for the formation of **99** did not provide any improvements in isolating pure product. Although the pinacol-pinacolone Stone-Wales was very successful for the synthesis of **1**, the conditions need to be altered and optimized for synthesis of **79** by improving the pinacol coupling of **97** and the pinacol rearrangement of **98**.



Scheme 46. Pinacol rearrangement of **98**.

As this project neared completion, polyphosphoric acid catalyzed reactions were further explored in our research group. PPA cyclization of **74** to **78** was observed. Pinacol **98** was treated with PPA in the MW at 100 ^{o}C for 5 minutes (Scheme 47). Analysis *via* ^{1}H NMR displayed **97**, **99**, and peaks which correspond to **79** in a 1:1:1.5 ratio respectively, however many impurities were also observed. The presence of **79** within the ^{1}H NMR was identified by comparing to the reported spectrum.[115] The reaction was run on a small scale and the yield was so low that the crude product mixture was not submitted to further purification. Further optimization of these reaction conditions could lead to a simple route towards **79**.



Scheme 47. Microwave PPA reaction with **98**.

Route Towards Zethrene: An Acylation Approach

Previously reported syntheses of **79** involve coupling of substituted naphthalenes. There have not been reports of coupling naphthalene (**46**) with some type of linker. It was predicted that acylation of **46** could lead to a precursor to **79**. The acylated compound **104** could undergo acid-catalyzed cyclization to enedione **105**, followed by reduction to dihydrozethrene **101**, and lastly aromatization leading to **79** (Figure 12).

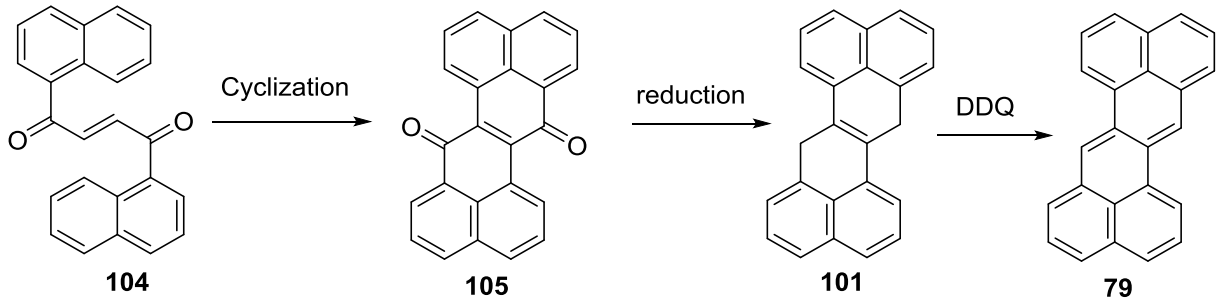
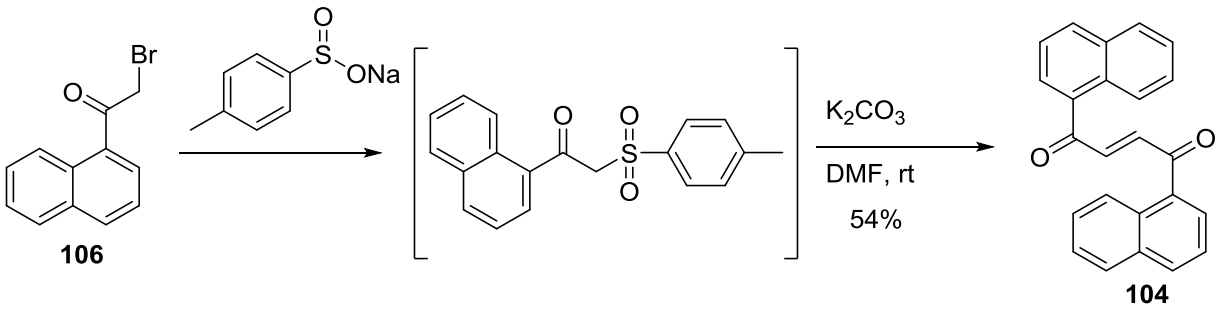


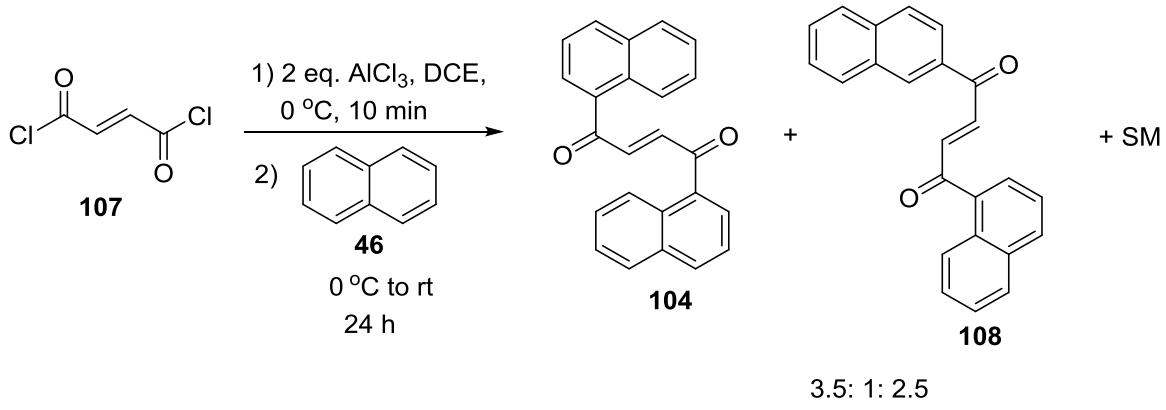
Figure 12. General proposed route towards **79.**

The Friedel-Crafts reaction is one of the most common acylation pathways. Kong *et. al*.[128] reported the sodium sulfinate mediated coupling of 2-bromo-1'-acetonaphthone (**106**) to generate acylated compound **104** in a 54% yield (Scheme 48). Due to the fact **106** is expensive and the sodium sulfinate mediated route only gave a moderate yield**,** the Friedel-Crafts acylation pathway was first investigated for synthesis of **104**.



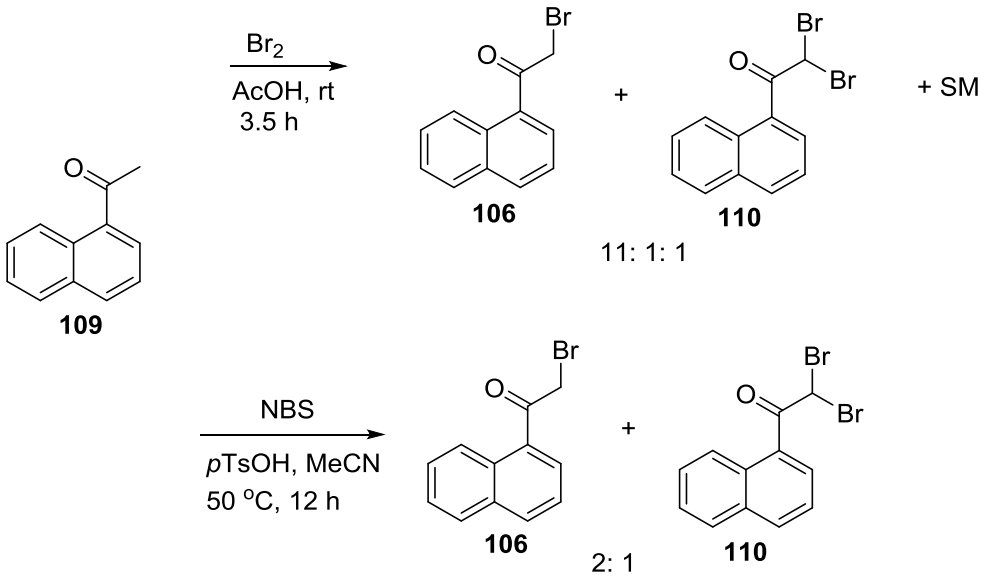
Scheme 48. Sodium sulfinate mediated route towards **104**.[128]

In order to synthesize **104** using a Friedel-Crafts approach, an acyl chloride needed to be chosen. Fumaryl chloride (**107**) contains two acyl chloride moieties, allowing for the reaction to occur for two naphthalene units at once. Naphthalene **46** and **107** were treated with aluminum chloride ($AlCl_3$) in DCE to yield a crude reaction mixture containing starting material, 1,1-isomer **104**, and a substance believed to be the 1,2-isomer **108**. This was tentatively identified by comparison to the predicted ^1H NMR using Spartan '08. This may be formed from isomerization of **104** (Scheme 49). Various other Lewis acids, temperatures, reaction times, and orders of addition were tested, however the conditions in Scheme 49 provided the best results. The issue with this reaction is the synthesis of the two isomers of the acylated compound. Both are observed under all reaction conditions and did not separate *via* column chromatography. A cyclization of the isomer mixture was attempted using iron (III) chloride ($FeCl_3$), however mostly starting material was recovered.



Scheme 49. Friedel-Crafts acylation of **46**.

Going back to Kong's synthesis of **104**, the sodium sulfinate mediated approach was investigated. The first route involved bromination of 1-acetonaphthone (**109**) using liquid bromine (Br_2) in AcOH or Et_2O,[129] however a mixture of **106**, the dibromoketone **110**, and starting material were observed in a 11:1:1 ratio respectively (Scheme 50). Separation of the starting material from the brominated compounds was not difficult, but isolating pure **106** from **110** was unsuccessful. Another route involved bromination using *N*-bromosuccinimide and *p*TsOH in acetonitrile (MeCN),[130] where **106** and **110** were observed in a 2:1 ratio *via* ^{1}H NMR (Scheme 50). Again, obtaining a pure sample of **106** proved elusive. Altering the reaction conditions of both routes did not improve the conversion to **106**.



Scheme 50. Attempted bromination routes of **109**.

The bromination pathways require optimization before proceeding to the sodium sulfinate mediated coupling. Attempts of submitting the crude mixtures to the coupling conditions only provided complex product mixtures. This reaction route does show promise due to the reported synthesis of **104**, however more work needs to be done.

Conclusions

In this research, two routes were explored for the synthesis of the elusive hydrocarbon zethrene (**79**). The first route involved our pinacol-pinacolone Stone-Wales method. To start, the pinacol coupling of 1-acenaphthenone was studied. This proceeded in only modest (31%) yield. The anticipated pinacol rearrangement (Scheme 46) was inefficient as the pinacolone was difficult to isolate. In search of an alternative approach, a brief investigation of the cyclization of **98** in PPA provided a low yield of **79**; this route needs to be further explored. The second route involved formation of an acylated naphthalene compound which would undergo cyclization. This began with a Friedel-Crafts acylation of naphthalene (**46**) with fumaryl chloride (**107**) to provide a mixture of acylated naphthalenes **104** and **108**, where **108** may be due to

isomerization of **104**. The separation of isomers by chromatography proved inefficient. Another acylation pathway used a sodium sulfinate mediated coupling of α-bromoketone **106** to acylated compound **104**, which was previously isolated in a 54% yield.[128] Several approaches to isolate **106** proved unsuccessful because both mono- and dibromination occurred. The bromination conditions need to be optimized and applied to the synthesis of enedione **104**, which can potentially be cyclized (Figure 12).[131] Once optimized, these conditions can potentially be applied to the synthesis of larger zethrene homologues.

Chapter IV. Experimental

General Experimental Section

Solvents

Anhydrous solvents [diethyl ether, dichloromethane (DCM), tetrahydrofuran (THF), toluene, and dimethylformamide (DMF)], passed through drying agent with nitrogen pressure, were obtained from an Innovative Technology, Inc. Solvent Delivery System prior to use and stored over 4 Å molecular sieves. Other solvents, including 1,2-dichloroethane (DCE), hexanes, ethyl acetate, benzene, and methanol were purchased from EMD Serono, Inc. or Pharmco-AAPER.

Reagents

All reagents were received from commercial sources and were used as received unless otherwise noted. Reagents were obtained from the following sources: Fisher Scientific (Acros), Alfa Aesar, TCI America, Sigma-Aldrich, and Cambridge Isotope Laboratories. *Note:* Many of the polycyclic aromatic hydrocarbons used here have some level of carcinogenicity. All reactions were carefully conducted in a hood to limit exposure.

Reactions

Glassware and magnetic stir bars were dried in an oven at 75 ^{o}C prior to use. Sigma-Aldrich natural rubber septa were used. Unless otherwise noted, nitrogen gas was introduced to the reaction vessel through a Tygon® tube with a needle or glass inlet adapter. Henke Sass Wolf Norm-ject® plastic syringes were used for volumetric addition of reagents with oven-dried Popper & Sons needles, Precision Glide sterile needles, or Sterican® sterile needles unless otherwise noted.

Chromatography

Flash column chromatography was performed with Silicycle SiliaFlash P60 Flash Silica Gel or with a Teledyne Isco CombiFlash Rf 200 purification system. Purifications using CombiFlash Rf used RediSep® pre-packed silica gel columns (20-70 μm particle size). Preparative chromatography was completed with Analtech Uniplate Silica Gel GF 100 micron UV 254 glass-backed plates. Thin Layer Chromatography (TLC) analysis used Whatman polyester-backed Silica Gel, 60 Å, 250 μm thickness, on flexible plates with a fluorescent indicator. Mobile phases were prepared per-use as described in the detailed experimental section.

Instrumentation

Nuclear Magnetic Resonance (NMR) spectra were measured on a Varian Mercury Plus 400 FT-NMR operating at 400 MHz for ^{1}H and 100 MHz for ^{13}C spectroscopy. Deuterated solvents for NMR analysis were purchased from Cambridge Isotope Laboratory and stored over 4 Å molecular sieves. All ^{1}H resonances were reported relative to an internal standard tetramethylsilane (TMS, δ 0 ppm), unless otherwise noted. Microwave-assisted reactions were conducted in a CEM Discover single-mode microwave reactor in capped 10 mL or 35 mL vessels. Matrix assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on a Shimadzu Kratos Axima-CFR running in reflection mode.

Detailed Experimental Section

Chapter I

General Procedure for MFP.

The substrate (0.05 g) and phthalic anhydride (**14**) (0.034 g, 0.23 mmol) were combined with graphite (ca. 0.25 g) in a quartz tube. Glass wool was placed above the mixture and the quartz tube was inserted into a Pyrex tube where it was purged with nitrogen and capped. The

reaction mixture was heated in a MW reactor at a constant power. Reaction time was typically 30 s to 1 min, but depended on how fast the reaction mixture reached the MW temperature limit (300 ^{o}C). The crude product mixture was extracted with $CDCl_3$ and filtered through a small silica plug before being characterized by ^{1}H NMR.

Microwave Flash Pyrolysis of Perylene (13) and Phthalic Anhydride (14).

Compound **13** (54 mg, 0.21 mmol) and **14** (34 mg, 0.23 mmol) were mixed with graphite (0.25 g) and reacted following the general MFP procedure at 150 W for 1 minute. Analysis *via* ^{1}H NMR indicated **13** and 1,12-phenyleneperylene (**16**) in a 2:1 ratio. The crude product was concentrated under vacuum to a yellow solid (34 mg, 63% recovery).

Microwave Flash Pyrolysis of Phenanthrene (12) and Phthalic Anhydride (14).

Compound **12** (51 mg, 0.28 mmol) and **14** (51 mg, 0.34 mmol) were mixed with graphite (0.25 g) and reacted following the general MFP procedure at 150 W for 50 s. Analysis *via* ^{1}H NMR indicated **12** (95%) and benzo[*e*]pyrene (5%). The crude product was concentrated under vacuum to a light yellow solid (26 mg, 51% recovery).

Microwave Flash Pyrolysis of Phenanthrene (12) and Maleic Anhydride (49).

Compound **12** (52 mg, 0.28 mmol) and maleic anhydride (56 mg, 0.56 mmol) were mixed with graphite (0.24 g) and reacted following the general MFP procedure at 300 W for 30 s. The reaction vessel was allowed to cool and again, the general MFP procedure was followed at 300 W for 30 s. Analysis *via* ^{1}H NMR indicated **12** (98%) and pyrene (**8**, 2%). The crude product was concentrated under vacuum to a light yellow solid (17 mg, 33% recovery).

Photochemical Reaction of Diphenylmaleic Anhydride (50).[42]

Diphenylmaleic anhydride **(50)** (1.01 g, 3.9 mmol) and iodine (4.1 mg, 15.9 mmol) were dissolved in acetone (60 mL) in a Pyrex tube. The tube was inserted into a photochemical reactor with 300 nm lamps for 4 days. A yellow solid precipitated which was collected *via*

vacuum filtration (0.251 g, 26% yield). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.13 – 9.07 (m, 2H), 8.89 – 8.83 (m, 2H), 8.07 – 7.93 (m, 4H).

Microwave Flash Pyrolysis of Biphenyl (47) and 9,10-Dicarboxyphenanthrene Anhydride (10).

Compound **47** (0.301 g, 1.9 mmol) and 9,10-dicarboxyphenanthrene anhydride (**10**) (0.105 g, 4.2 mmol) were mixed with graphite (0.29 g) and reacted following the general MFP procedure at 300 W for 1 minute. Analysis *via* ^{1}H NMR indicated **47**, phenanthrene (**12**), and dibenzo[*g,p*]chrysene (**1**) in a 2:5:1 ratio respectively. The crude product was concentrated under vacuum to an off-white solid (0.01 g, 3.5 % recovery).

Microwave Flash Pyrolysis of Dibenzo[*g,p*]chrysene (1) and 9,10-Dicarboxyphenanthrene Anhydride (10).

Compound **1** (20 mg, 0.061 mmol) and **10** (23 mg, 0.091 mmol) were mixed with graphite (0.12 g) and reacted following the general MFP procedure at 100 W for 1 minute. Analysis *via* ^{1}H NMR indicated **1**, phenanthrene (**12**), and hexabenzo[a,c,fg,j,l,op]tetracene (**7**) in a 20:1.5:1 ratio respectively. The crude product was concentrated under vacuum to an off-white solid (12 mg, 60% recovery). The crude product was analyzed by MALDI-TOF-MS, confirming the presence of hexabenzotetracene (**7**, *m/z* = 501.4), as well as DBC (**1**, *m/z* = 328.5) and higher oligomers (*m/z* = 627.2).

Dibromoolefination of 9-Fluorenone (2).

9-Fluorenone (**2**) (1.05 g, 5.8 mmol) and carbon tetrabromide (3.41 g, 10.2 mmol) were added to an oven dried 250 mL round bottom flask. Dry dichloromethane (50 mL) was added. Triphenylphosphine (5.36 g, 20.4 mmol) was added portionwise and the reaction was stirred at room temperature for 24 hours. Hexanes (100 mL) was added and the mixture was filtered through a silica pad and concentrated to a yellow solid. The crude product was purified *via*

CombiFlash with hexanes to yield **55** as a light yellow solid (1.82 g, m.p. 119-121 ^{o}C, *lit*. 122-123 ^{o}C, 96% yield). ^{1}H NMR (400MHz, $CDCl_3$) δ 8.62 (d, 2H), 7.69 (d, 2H), 7.42 (t, 2H), 7.30 (td, 2H).

Silylation of 9-(Dibromomethylidene)fluorene (55).

Compound **55** (0.801 g, 2.4 mmol) was added to an oven dried 250 mL round bottom flask and purged with nitrogen. Anhydrous THF (80 mL) was added *via* syringe. The flask placed in a dry ice bath (-78 ^{o}C) and 2.5 M *n*-BuLi in hexanes (1.0 mL, 2.5 mmol) was added slowly *via* syringe. After stirring under nitrogen for 40 minutes, TMSCl (1.2 mL, 9.5 mmol) was added slowly *via* syringe and the solution was stirred at room temperature for 24 hours. Sat. aq. $NaHCO_3$ (80 mL) was added and reaction extracted with ethyl acetate (3 x 30 mL). The combined extracts were dried over Na_2SO_4 and concentrated to an orange solid. The crude product was purified *via* column chromatography using silica and hexanes as an eluent to yield a yellow solid (0.182 g). Analysis *via* ^{1}H NMR indicated desired product **56** by correlation with predicted chemical shifts, however **57** was also present in a 1.5:1 ratio. Compound **57** was identified from the reported ^{1}H NMR.[51]

Fluoride-Induced Elimination for Phenanthryne Formation.

Potassium fluoride (0.075 g, 1.25 mmol), 18-crown-6 (0.341 g, 1.25 mmol), and anthracene (0.095 g, 0.52 mmol) were added to an oven dried 25 mL round bottom flask which was purged with nitrogen. Anhydrous THF (2 mL) was added *via* syringe and the flask placed in ice bath. The crude mixture of **56** and **57** (0.182 g) was dissolved in anhydrous THF (0.5 mL) and added to the flask *via* syringe. The solution was stirred at room temperature for 15 hours. Water (15 mL) was added to the reaction which was then extracted with dichloromethane (3 x 15 mL). The combined extracts were dried over Na_2SO_4 and concentrated to a yellow residue (0.440 g). Analysis *via* ^{1}H NMR displayed starting material with very minor peaks which correspond to the predicted chemical shifts of Diels-Alder product **58** in the baseline.

Grignard Reaction of 9-(Dibromomethylidene)fluorene.

Magnesium turnings (44 mg, 1.7 mmol) ground with a mortar and pestle were transferred to an oven dried 25 mL two-neck round bottom flask and purged with nitrogen. Anhydrous THF (2 mL) was added and the solution was brought to reflux. 9-(Dibromomethylidene)fluorene (**55**) (0.513 g, 1.49 mmol) dissolved in anhydrous THF (2 mL) was added dropwise *via* an addition funnel and the reaction was stirred at reflux for 90 minutes. After cooling to room temperature, 10% aq. HCl (10 mL) was added and the reaction was extracted with dichloromethane (4 x 20 mL). The combined extracts were dried over Na_2SO_4 and concentrated to yield **60** as a red solid (0.364 g, 69% yield). The product was analyzed by MALDI-TOF-MS, which showed *m/z* = 352.1. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.84 (m, 4 H), 7.72-7.70 (m, 4H), 7.42-7.36 (8 H).

Chapter II

Synthesis of 9,9'-Bifluorenyl-9,9'-diol (68).

9-Fluorenone (**2**) (1.03 g, 5.70 mmol) and 50% aq. THF (10 mL) were added to a 250 mL round bottom flask, followed by zinc chloride (1.07 g, 7.80 mmol). The reaction flask was placed into a water bath and zinc powder (5.0 g, 0.076 mol) was added portionwise over 5 minutes. The reaction was stirred for 1 hour under nitrogen. 3M HCl (5 mL) was added and the reaction stirred for 20 minutes, where it was then filtered to remove the residual zinc, which was rinsed with toluene, followed by water. The filtrate was extracted with toluene (4 x 10 mL) and the combined organics were dried over $MgSO_4$. The solution was filtered and concentrated to yield a white solid (0.82 g, m.p. 180-183 ^{o}C, *lit*. 190-192 ^{o}C, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39-7.37 (m, 5H), 7.27-7.26 (m, 6H), 7.07 (m, 5H), 3.16 (s, 2H).

Pinacol Rearrangement to Form Spiro[9*H*-fluorene-9,9'(10'*H*)-phenanthren]-10'-one (3).

9,9'-Bifluorenyl-9,9'-diol **68** (0.79 g, 0.0022 mol) was put in a 250 mL round bottom flask. Concentrated sulfuric acid (0.1 mL) and acetic acid (10 mL) were added to the reaction flask.

The solution was stirred at reflux for 30 minutes. After cooling to room temperature, a white solid formed which was isolated by vacuum filtration (0.66 g, m.p. 248-252 ^{o}C, *lit* 256-258 ^{o}C, 88% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.20 (d, 1H), 8.10 (d, 1H), 7.99 (dd, 1H), 7.82-7.75 (m, 3H), 7.45 (td, 1H), 7.41-7.34 (m, 3H), 7.18 (td, 2H), 7.10-7.02 (m, 3H), 6.62 (dd, 1H).

Synthesis of Spiro[9*H*-fluorene-9,9'(10'*H*)-phenanthren]-10'-ol (72).

Compound **3** (0.94 g, 2.6 mmol) was dissolved in THF (15 mL) and water (0.5 mL) in a 50 mL round bottom flask. Sodium borohydride (0.22 g, 5.8 mmol) was added slowly. The solution was stirred at reflux under nitrogen for 90 minutes. After cooling to room temperature, water was added (15 mL) and the solution was stirred for 5 minutes. The reaction was extracted with dichloromethane (3 x 10 mL) and the combined extracts were dried over Na_2SO_4 and concentrated to a white solid (0.87 g, m.p. 164-167 ^{o}C, *lit*. 174-175 ^{o}C,[132] 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (td, 2H), 7.79 (dt, 1H), 7.74 (dt, 1H), 7.53-7.49 (m, 2H), 7.44-7.19 (m, 7H), 7.02 (dtd, 2H), 6.80 (d, 1H), 6.67 (dd, 1H), 5.31 (d, 1H).

Synthesis of Dibenzochrysene (1).

Compound **72** (1.97 g, 5.7 mmol) and toluene (50 mL) were added to a 250 mL round bottom flask. *p*-Toluenesulfonic acid (2.98 g, 17.3 mmol) was added to the reaction mixture, and it was stirred at reflux under nitrogen for 90 minutes. After cooling to room temperature, water (5 mL) was added, and the reaction solution was extracted with toluene (4 x 15 mL). The combined extracts were dried over Na_2SO_4. The crude product showed very minor impurities and was recrystallized in ethanol to yield a white solid (1.38 g, m.p. 216-217 ^{o}C, *lit*. 218 ^{o}C, 74% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.73 – 8.67 (m, 8H), 7.66 (dddd, 8H).

Pinacol Coupling of 1-Indanone (73).

1-Indanone (**73**) (0.51 g, 3.8 mmol), potassium hydroxide (1.91 g, 34.0 mmol), and methanol (10 mL) were added to a 25 mL round bottom flask. The solution was stirred while aluminum

powder (0.31 g, 11.5 mmol) was added slowly. The flask was placed in a water bath where it stirred under nitrogen for 20 hours. The solution was filtered to remove excess aluminum and water (25 mL) was added to the filtrate. A solid formed which was filtered off and the filtrate was extracted with dichloromethane (3 x 15 mL). The combined extracts were dried over $MgSO_4$ and concentrated to a white solid (0.36 g, m.p. 139-142 ^oC, *lit*. 154-156 ^oC, 72% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 7.82-7.80 (m, 1H), 7.31-7.21 (m, 6H), 7.14-7.12 (d, 1H), 3.09-3.01 (m, 2H), 2.98 (s, 2H), 1.97-1.93 (td, 4H).

Reaction of 1-Indanopinacol (74) in PPA.

PPA (18 mL) were added to an oven dried 100 mL round bottom flask. The flask was heated in an sand bath to 120 ^oC with stirring. Pinacol **74** (1.20 g, 4.5 mmol) was added to the flask and the reaction was heated to 180 ^oC under nitrogen. After 45 minutes, the reaction was cooled to room temperature, quenched with sat. aq. $NaHCO_3$, and extracted with ethyl acetate (5 x 40 mL). The combined extracts were dried over Na_2SO_4. The crude material was purified *via* CombiFlash with 100% hexanes to yield a light yellow/orange solid (0.903 g). Analysis *via* ^1H NMR displays a mixture of chrysene (**78**), dihydrochrysene, and tetrahydrochrysene in a 1:3.5:2 ratio, respectively.

The crude mixture (0.091 g) was dissolved in benzene (5.5 mL) and purged with nitrogen. 2,3-Dichloro-5,6-dicyano-1,4-benzoquinone (DDQ, 0.17 g, 0.78 mmol) was added and the mixture was stirred at reflux for 20 h. The reaction mixture was concentrated under vacuum and filtered through a silica plug with hexanes to yield chrysene (**78**) as an off-white solid (0.086 g, 8.4% overall yield). ^1H NMR (400 MHz, $CDCl_3$) δ 8.80-8.78 (d, 2H), 8.74-8.7 (d, 2H), 8.02-7.98 (dd, 4H), 7.73-7.69 (t, 2H), 7.66-7.62 (t, 2H).

Reaction of 9,9'-Bifluorenyl-9,9'-diol (68) in PPA.

Pinacol **68** (0.104 g, 0.29 mmol) and PPA (4 mL) were added to an oven dried 35 mL quartz MW tube. The viscous mixture was stirred with a glass stir rod to evenly disperse solid and the

quartz tube was placed in a Pyrex tube. The reaction vessel was purged with nitrogen, capped, and heated in the MW reactor at 100 ^{o}C for 5 minutes. Once cool, the reaction was quenched with sat. aq. $NaHCO_3$ and extracted with ethyl acetate (4 x 15 mL). The combined extracts were dried over Na_2SO_4 and concentrated to a tan solid (0.067 g). Analysis *via* ^{1}H NMR displayed a mixture of pinacolone (**3**) and dibenzo[*g,p*]chrysene (**1**) in a 2:1 ratio.

Chapter III

Synthesis of Acenaphthenopinacol (98).

An oven dried 50 mL 2-neck round bottom flask was charged with dry ethyl acetate (7 mL) and titanium tetrachloride (0.4 mL, 3.7 mmol). The flask was placed in an ice water bath and magnesium turnings (0.23 g, 8.9 mmol) were added. The flask was purged with nitrogen and allowed to warm to room temperature. 1-Acenaphthenone (**97**) (0.25 g, 1.5 mmol) dissolved in dry ethyl acetate (1 mL) was added *via* syringe. After 90 minutes, 10% aq. potassium carbonate (15 mL) was added to quench. A solid formed which was filtered off and the filtrate was extracted with ethyl acetate (3 x 15 mL). The combined organics were washed with sat. aq. $NaHCO_3$ and brine respectively and dried over $MgSO_4$. The crude material was purified *via* CombiFlash with 10% EtOAc:hexanes to yield a white solid (0.079 g, 31% yield). ^{1}H NMR(400 MHz, $CDCl_3$) δ 7.98-7.96 (d, 2H), 7.82-7.80 (d, 2H), 7.67-7.65 (d, 2H), 7.62-7.58 (t, 2H), 7.43-7.40 (dd, 2H), 7.06-7.04 (d, 2H), 3.48 (s, 2H), 3.13-3.03 (d, 2H), 2.92-2.87 (d, 2H).

Reaction of Acenaphthenopinacol (98) in PPA.

Pinacol **98** (0.068 g, 0.201 mmol) and PPA (2.1 mL) were added to an oven dried 35 mL quartz MW tube. The viscous mixture was stirred with a glass stir rod to evenly disperse solid and the quartz tube was placed in a Pyrex tube. The reaction vessel was purged with nitrogen, capped, and heated in the MW reactor at 100 ^{o}C for 5 minutes. Once cool, the reaction was quenched with sat. aq. $NaHCO_3$ and extracted with ethyl acetate (3 x 20 mL). The combined organics

were dried over Na_2SO_4 and concentrated to a dark orange/red solid (0.036 g). Analysis *via* ^1H NMR displayed a mixture of 1-acenaphthenone (**97**), pinacolone **99**, and zethrene (**79**) in a 1:1:1.5 ratio, as well as oligomers.

Friedel-Crafts Acylation of Naphthalene.

Aluminum chloride (1.03 g, 7.6 mmol) and DCE (50 mL) added to oven dried 250 mL round bottom flask. The flask was purged with nitrogen and placed in an ice bath. Fumaryl chloride (**107**) (0.45 mL, 4.2 mmol) was added *via* syringe and the solution was stirred for 10 min. Naphthalene (**46**) (1.07 g, 8.2 mmol) was added and the reaction was stirred at room temperature for 24 hours. Water (150 mL) was added and the mixture was diluted with DCE (50 mL). The organics were washed with 2 M HCl (2 x 25 mL), dried over Na_2SO_4, and concentrated to dark brown residue. The crude material was purified *via* CombiFlash with 5% EtOAc:hexanes to yield a pale yellow solid (0.15 g). Analysis *via* ^1H NMR indicated the 1,1'-isomer (**104**) and 1,2'-isomer (**108**) in a 3.5:1 ratio respectively.

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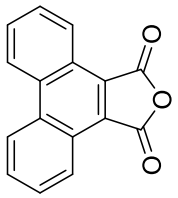
Appendices

Appendix A: Spectra



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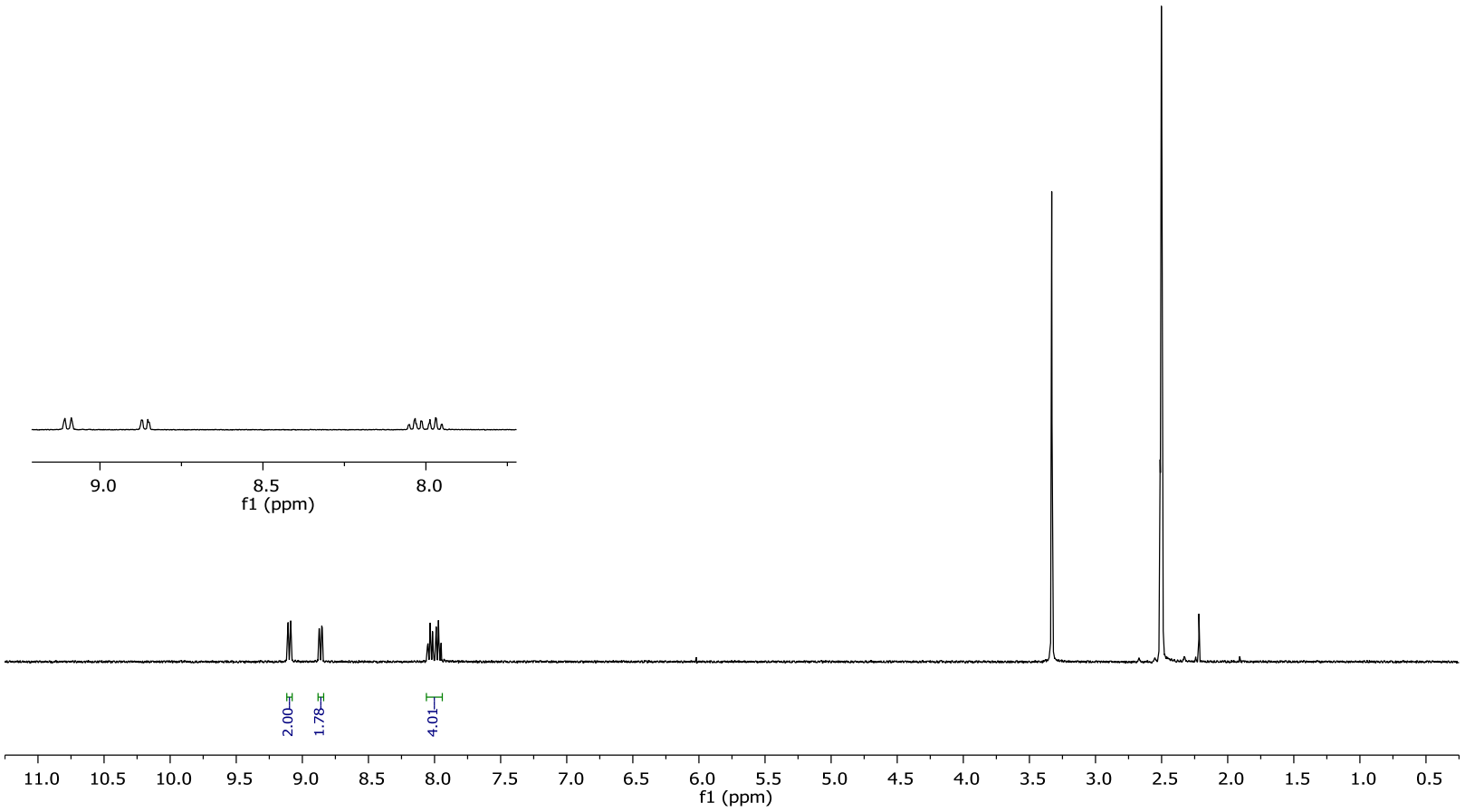
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8.5
8.0
7.5
7.0
6.5
6.0
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4.0
3.5
3.0
2.5
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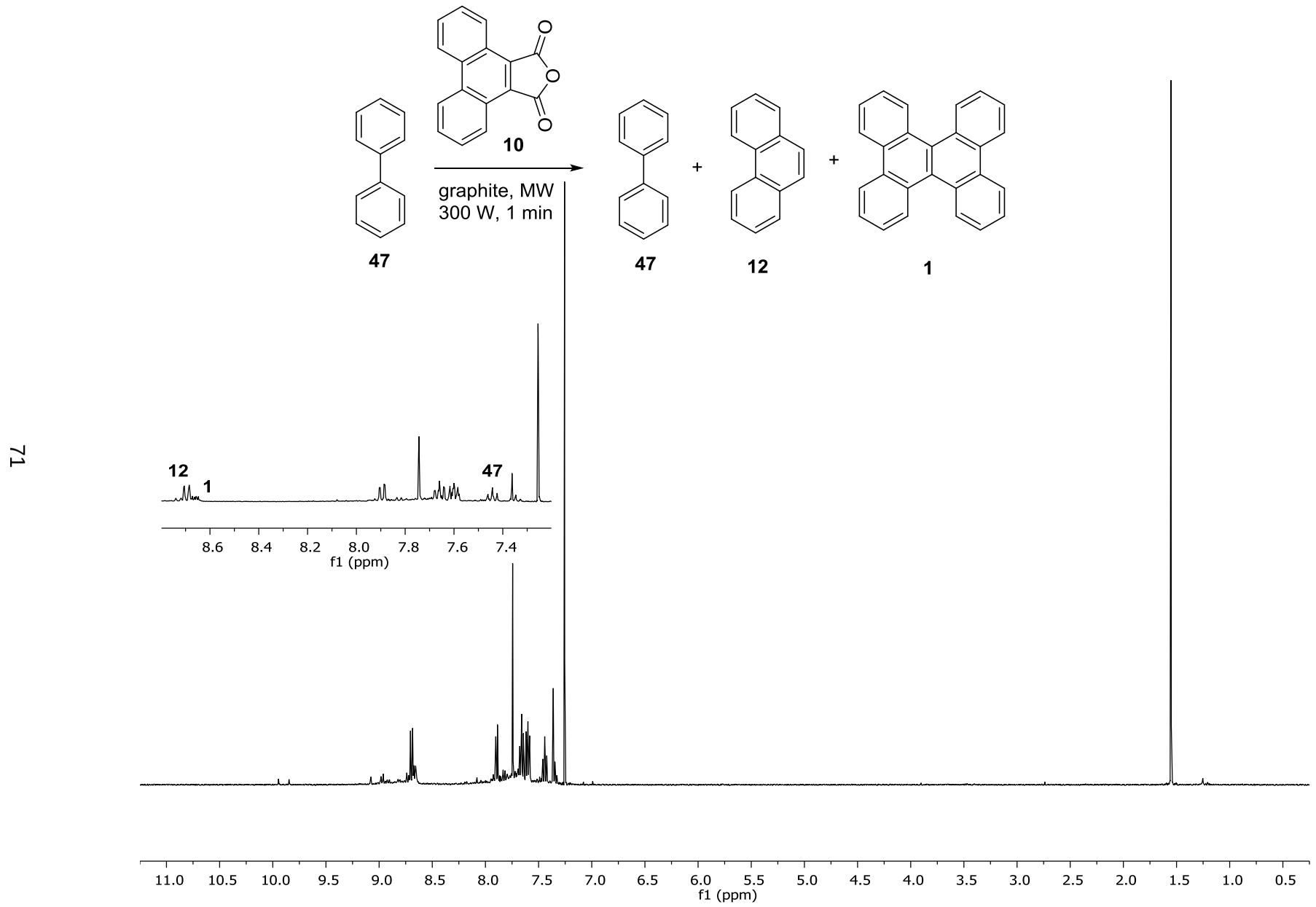
1.5
1.0
0.5
f1 (ppm)


47
10
graphite, MW
300 W, 1 min
47
12
1
12
1
47
8.6
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8.2
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7.8
7.6
7.4
f1 (ppm)
11.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
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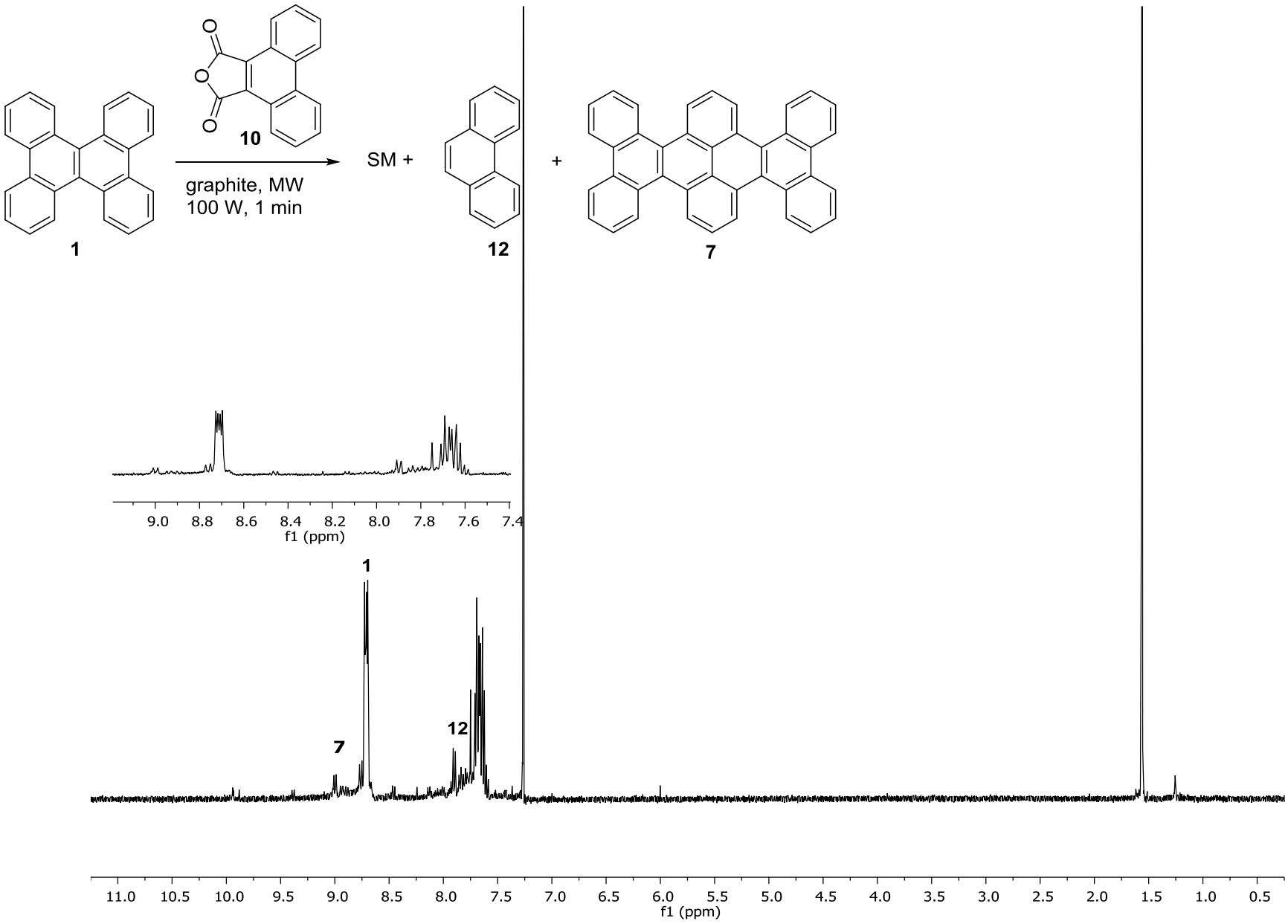
0.5
f1 (ppm)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graphite, MW
100 W, 1 min
SM +
+
1
12
7
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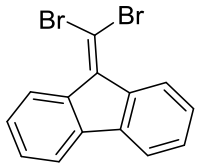
f1 (ppm)
1
7
12
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)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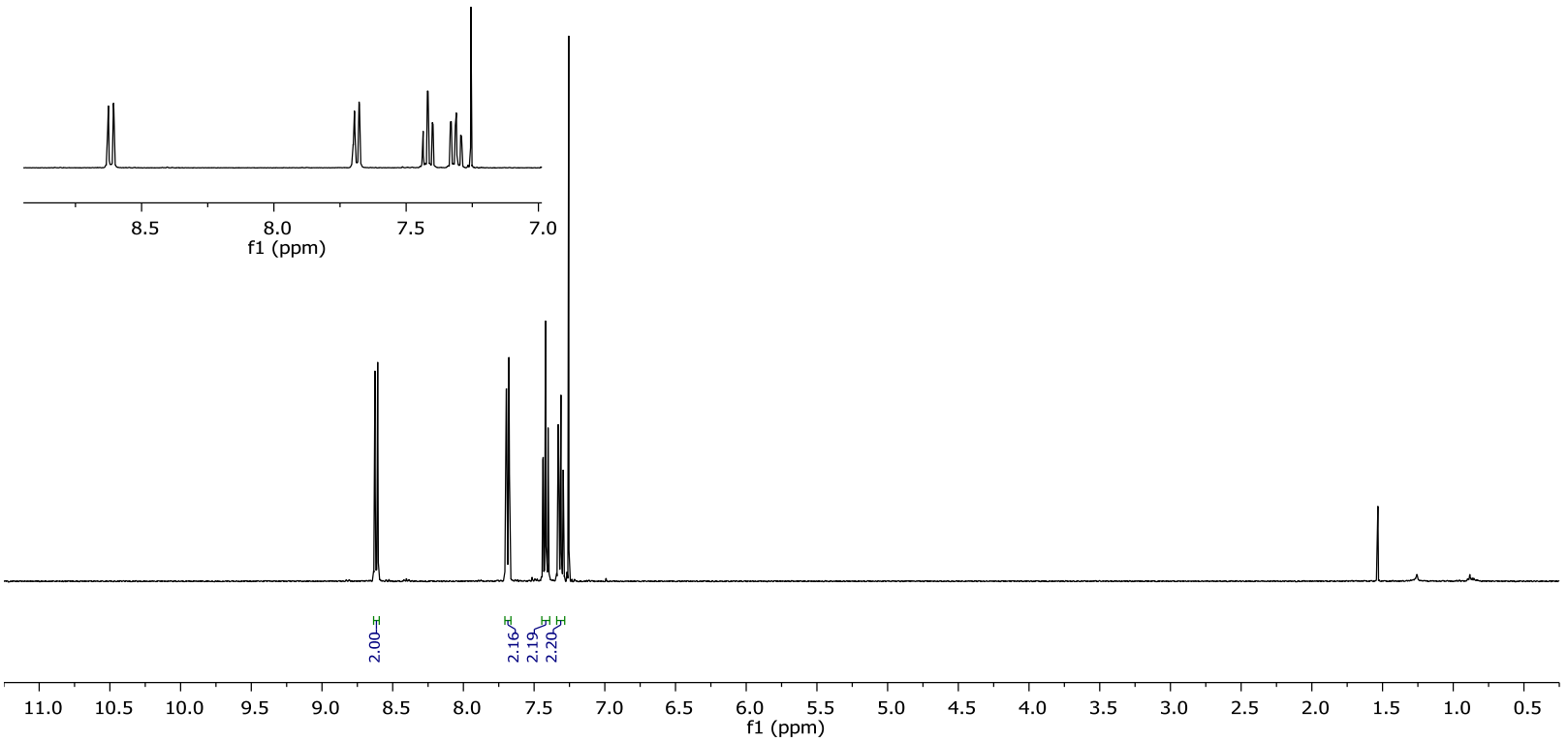
Br

55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5.5
5.0
4.5
4.0
3.5
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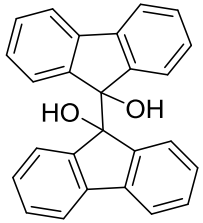
4.00
f1 (ppm)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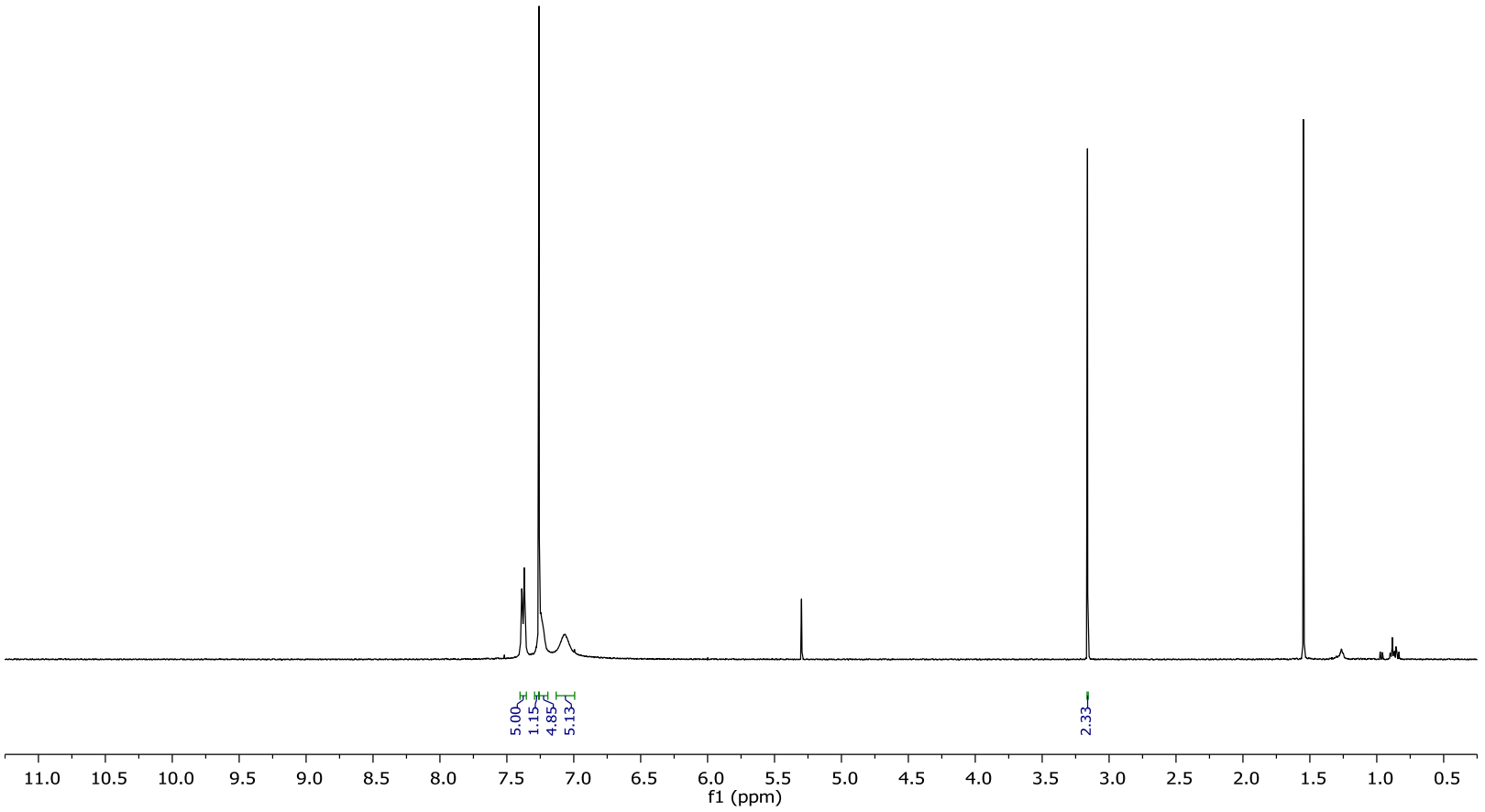
OH

68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7.0
6.5
6.0
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3.5
3.0
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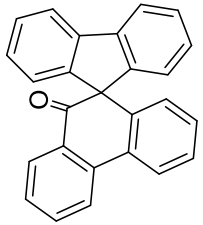
0.5
f1 (ppm)


O

3

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0.89
11.0
10.5
10.0
9.5
9.0
8.5
8.0
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7.0
6.5
6.0
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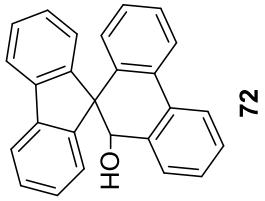
f1 (ppm)



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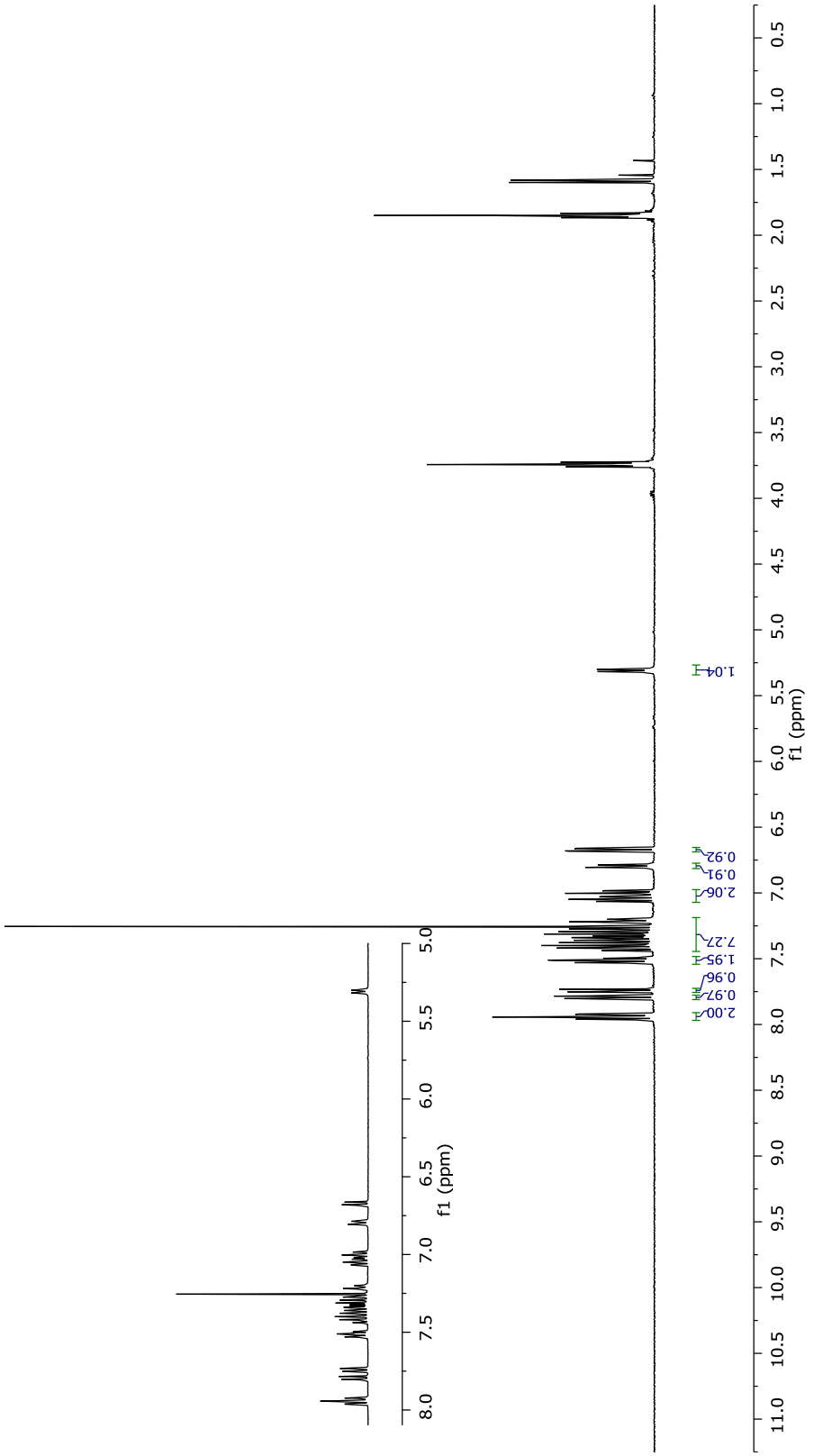

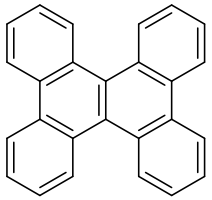

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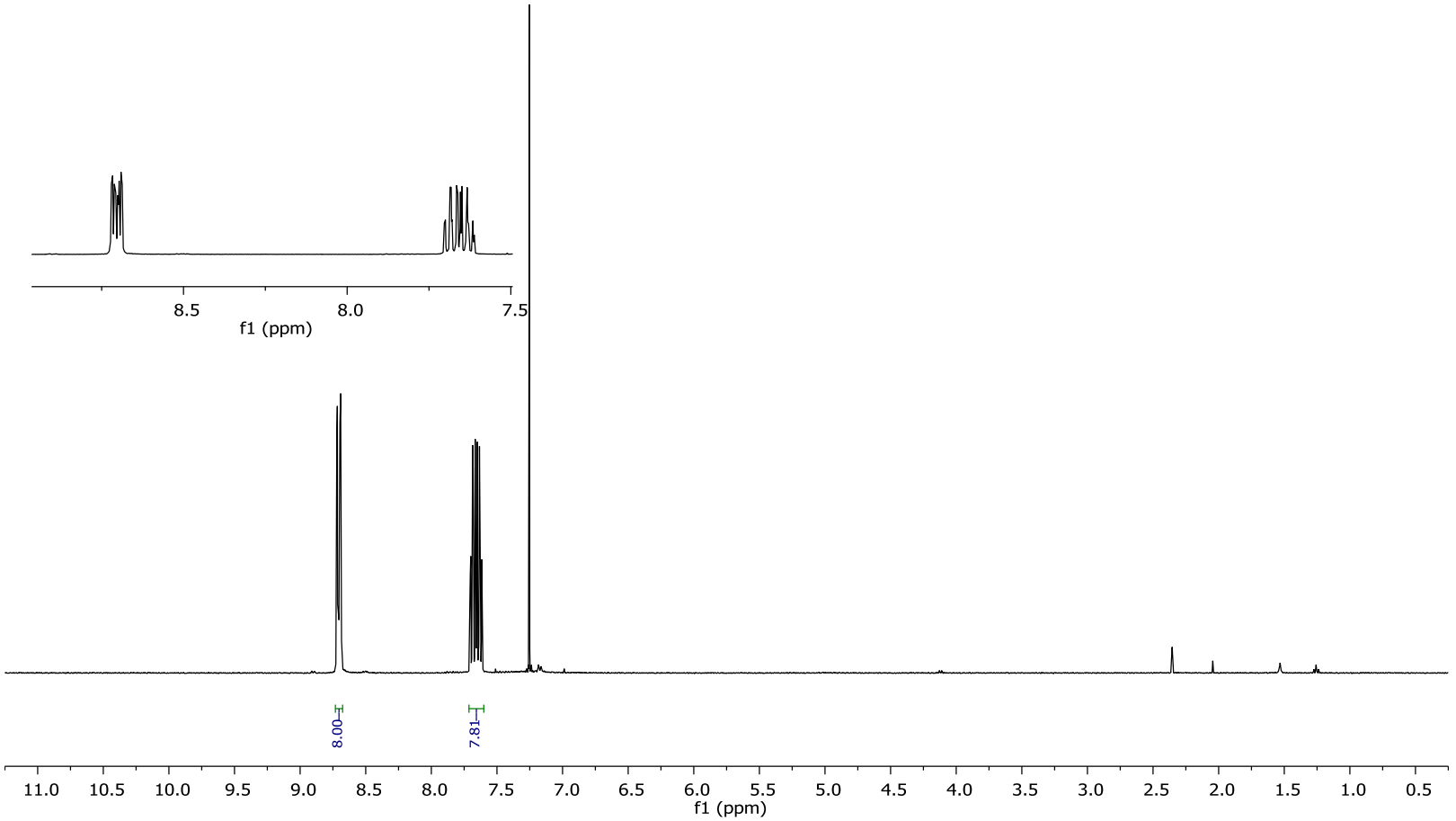
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6.0
5.5
5.0
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3.5
3.0
2.5
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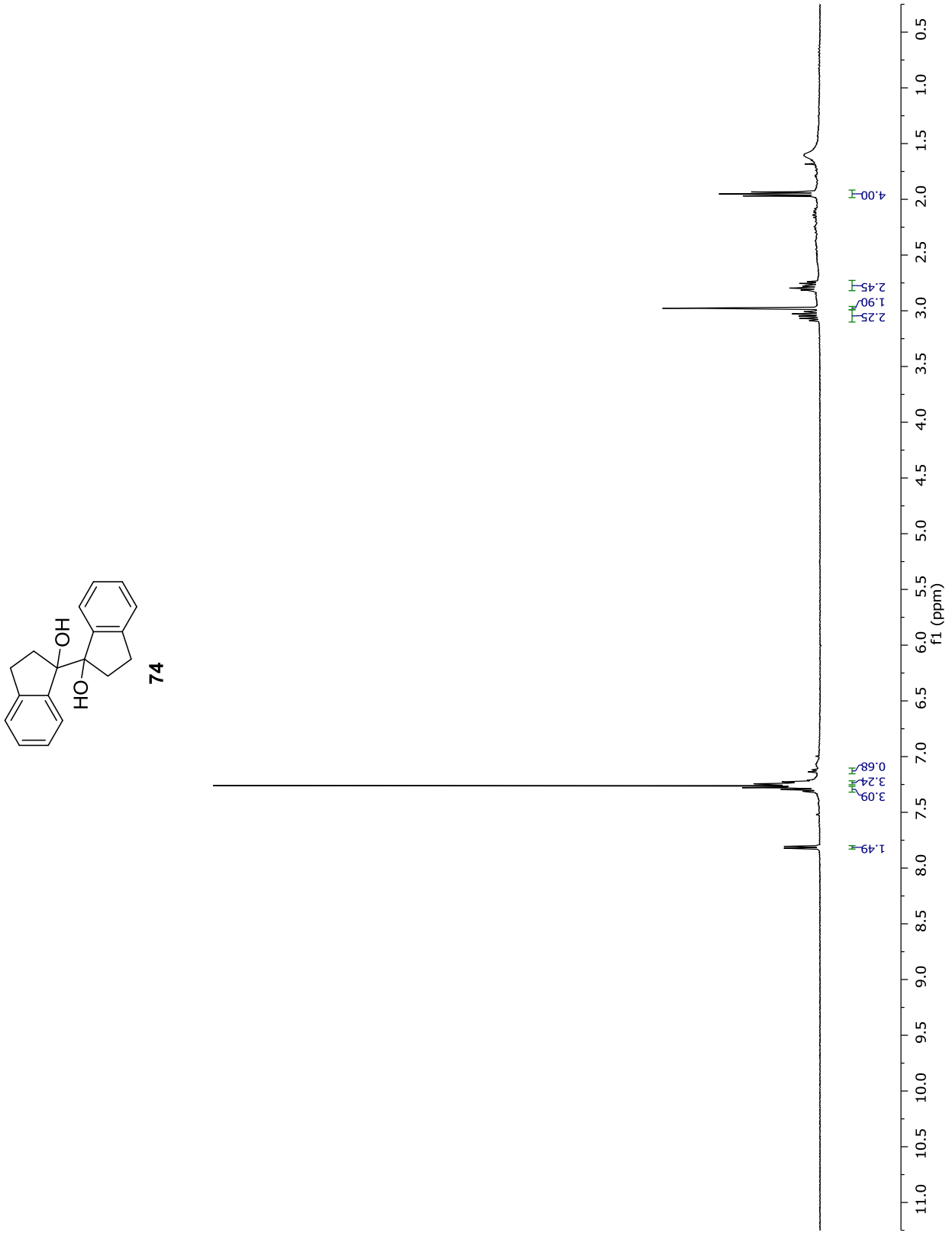
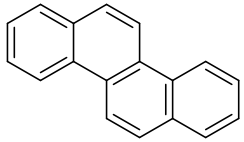
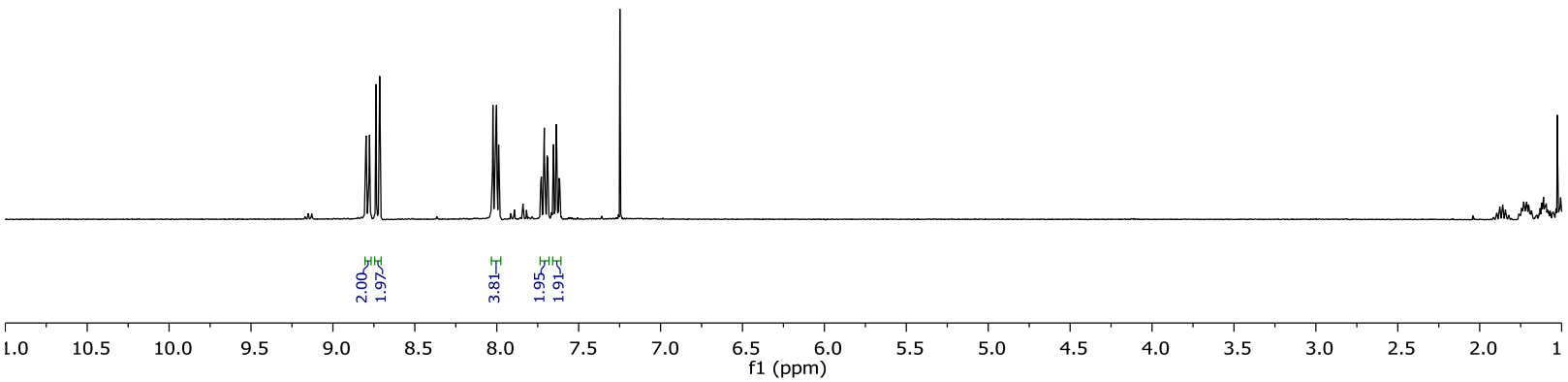
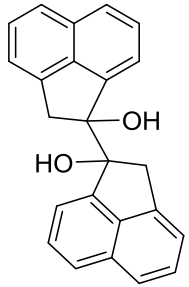
1.5
1.0
0.5
f1 (ppm)


OH
HO
74
4.00
2.45
1.90
2.25
3.09
3.24
0.68
1.49
f1 (ppm)



78


2.00
1.97
3.81
1.95
1.91
1.0
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1
f1 (ppm)


OH
HO

98

8.2
8.0
7.8
7.6
7.4
7.2
7.0
6.8
f1 (ppm)
2.00
2.21
2.33
2.48
2.27
1.94
2.00
2.22
1.93
10.5
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
f1 (ppm)