Progress Toward the First Rational Synthesis of a [5.5] Carbon Nanotube

Author: Christopher James Pavlow

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BY CHRISTOPHER JAMES PAVLOW

Boston College Department of Chemistry
Professor Lawrence T. Scott, Research Advisor

Abstract

The purpose of this project was to make progress toward a chemical synthesis of a conductive [5,5] single-walled nanotube (SWNT), specifically a $C_{50}H_{10}$ geodesic cap. The term geodesic cap refers to the smallest fragment of a nanotube that resembles the chirality and structure of a specific nanotube. Beyond synthesizing a specific nanotube, we were also interested in exploring new reactions and compounds to perform indeno-annulation reactions. The interest in these compounds, which contain indeno structures, comes from their resemblance to C_{60} and higher fullerenes, and more specifically the intermediates to our target molecule, the $C_{50}H_{10}$ geodesic cap.

A man who has never gone to school may steal from a freight car;

but if he has a university education he may steal the whole railroad.

- Theodore Roosevelt

Acknowledgements

I would like to take this opportunity to thank the people who helped me while undertaking this project. I thank my mother Yvonne, my father Victor, and my brother Jason, who have always given me constant support no matter what I choose to do. I cannot express in words the appreciation I feel for the sacrifices my parents have made to make my life better every day. I would like to thank my friends, in particular my roommates, who took me in sophomore year and without whom I wouldn't have survived my college career. To Matthew Shinners and especially David Nagib, who pushed me when I needed it and gave me the drive to continue. I thank my girlfriend Kristine for bringing balance and joy to my life, and always being there for me.

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I would also like to thank the Boston College Undergraduate Research grant, the AHANA-Pfizer Scholarship, and the NSF for providing the funding for me to work in this laboratory. Without your generosity, I most certainly could not have accomplished this much.

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CHAPTER I:

INTRODUCTION

1.1. Background

In recent years, the main focus of the Scott group has been on the research of curved polycyclic aromatic hydrocarbons (PAHs) and their derivatives from planar starting materials.[1] PAHs make up a unique branch of organic molecules that have distinguishing chemical and electronic properties[2]. Such properties as rigid geometric structures, delocalized electronic character, and the regioselectivity of their reactions make them a truly unique and interesting molecule for explorative research.

The impetus in the resurgence of interest in PAH chemistry has been driven primarily by the discovery of fullerenes. These were first discovered in 1985 by Kroto, Curl, and Smalley[3] who eventually won the Nobel Prize in chemistry in 1996 for their groundbreaking research. Natural carbon can exist in several forms: the most widespread and familiar are graphite and diamond. Fullerenes represent the third type of carbon allotrope and are cage-like structures in the form of spheres, ellipsoids, or tubes. Research on fullerenes grew at a furious pace in the past decade until buckminsterfullerene, or C_{60}, was the first fullerene that a direct rational synthesis was found for in 2002 by the Scott group[4]. This molecule is not only the prototypical member of the fullerene class, but the synthesis of it has stimulated spectacular dreams of carbon architecture on a nanometer scale[5].

These dreams are becoming more of a reality, as the potential to synthesize pure carbon nanotubes improves every day. Carbon nanotubes are the newest member in the fullerene family, the first having been discovered by Iijima in 1991, observed in very small quantities in the carbon soot resulting from the synthesis of fullerenes[6]. Carbon nanotubes are graphene sheets rolled-up into cylinders with diameters as small as one nanometer. Extensive work in recent years has revealed the intriguing electrical and mechanical properties of these novel molecular scale wires, which look to be the ideal material for building tomorrow's nanoelectronics[7]. Carbon nanotubes have significant potential as building blocks for various practical nanoscale devices such as miniaturized electronic, mechanical, electromechanical, chemical and scanning probe devices and as materials for macroscopic composites. Today, a little more than 10 years after their discovery, nanotubes seem more than ready to make the transition from exotic laboratory wonders to materials that can be utilized in modern technologies.

1.2. Motivation

In order to make this leap and take advantage of certain nanotubes' unique electronic properties, a rational synthesis of specific nanotubes needs to be developed. The ways that nanotubes are currently being made suffer from serious deficiencies as different diameters and lengths, single walled and multiple walled, and a range of chiralities. Clearly, progress in this field would be greatly accelerated by the development of a rational way to make nanotubes.

1.2.1. Properties and Applications[7,8,9,10,11]

Having been the subject of intensive scientific study since they were first discovered in 1991, nanotubes have recently become a subject for engineering as well. Many of the extraordinary properties attributed to nanotubes – among them, superlative resilience, tensile strength and thermal stability – have fed fantastic predictions of microscopic robots, dent-resistant car bodies and earthquake-resistant buildings.

1.2.1.1. Mechanical[12]

Carbon nanotubes have extraordinary properties, both calculated and demonstrated. From a mechanical standpoint, nanotubes are one of the strongest materials known to man, both in tensile strength and elastic modulus. Therefore they are an ideal option for many potential applications. This strength results largely from the covalent sp^2 bonds and that form between the individual carbon atoms, as well as the delocalized electrons in the resulting pi-system. A single nanotube has been calculated to have almost 200 times the tensile strength of high-carbon steel (see Figure 1.1).

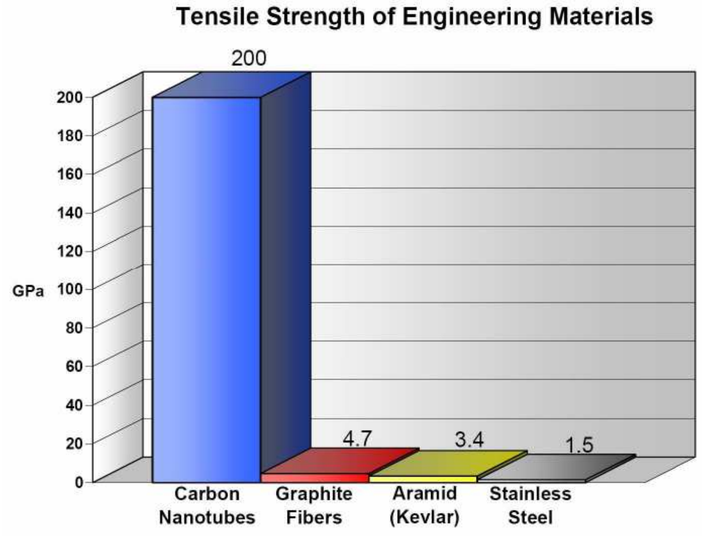


Figure 1.1. Tensile Strength of Engineering Materials

Figure 1.1 clearly shows that nanotubes are much stronger than several other carbon-based engineering materials, such as graphite (another pure carbon allotrope) and Kevlar (a polymer). In 2000 a multi-walled nanotube (MWNT) was tested to have a tensile strength of over 63 GPa[13]. It has been found that carbon nanotubes' elastic modulus is also very high, on the order of 1 TPa[14], which shows their incredible flexibility.

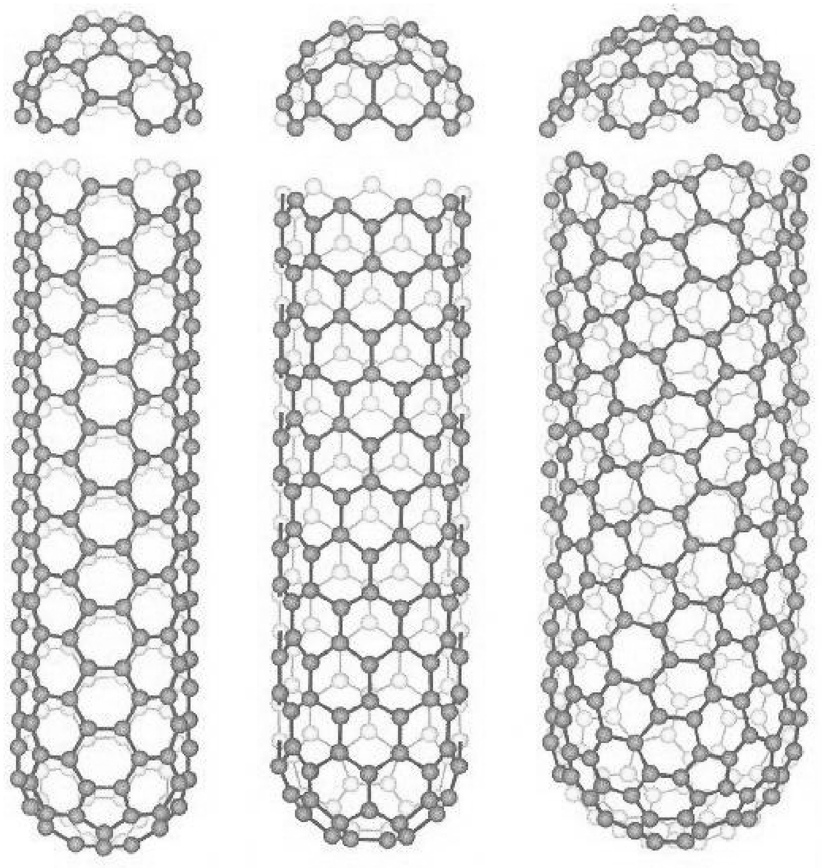
Carbon nanotubes have already been used as composite fibers in polymers and concrete to improve the mechanical properties of the bulk product.[12] Researchers have also found that adding them to polyethylene increases the polymer's elastic modulus by about 30%.[12] Bulk nanotube materials may never achieve a tensile strength similar to that of individual tubes (because of defects), but such composites may yield strengths sufficient for such applications as space elevators, artificial muscles, and ultrahigh-speed flywheels. These mechanical properties, combined with low density (1.33 to 1.40 g/cm^3 compared with 2.70 g/cm^3 for Aluminum[7]) and thermal properties make nanotube composites ideal candidates for next-generation aerospace building materials. Other mechanical applications are also already being used in industry. Paints with incorporated nanotubes are used for anti-radar coating on boats and airplanes.[10] Bullet-proof vests made of nanotube fibers are virtually unbreakable and ultra-light, which give them several advantages over Kevlar vests[15]. Attached to the tip of a scanning probe, microscope, nanotubes can boost the instruments' lateral resolution by a factor of 10 or more, allowing clearer views of proteins and other large molecules[7]. Fuel cell research is another topic of growing importance and interest, as researchers try to utilize the empty space inside nanotubes to store endohedral atoms or molecules (specifically hydrogen[16]).

1.2.1.2. Thermal[17]

All (pure) nanotubes are expected to be very good thermal conductors along the length of the tube; however they are good insulators laterally to the tube axis. This is largely due to a property known as ballistic conduction, which is the allowing of electrons to flow through a material without collisions. Because of these properties, they may prove to be an ideal material for the study of low-dimensional phonon physics, and for thermal management, both on the macro- and micro-scale. In comparison, nanotubes heat transmission has been predicted as high as 6,000 W/m·K at room temperature, whereas nearly pure diamond transmits heat at 3,320 W/m·K[7]. Furthermore, nanotubes are stable up to 2800°C in a vacuum or 750°C in air, and metal wires in microchips melt at 600 to 1000°C.[7]

1.2.1.3. Electrical[18]

They are stronger than steel, but the most important uses for these threadlike macromolecules may be in faster, more efficient and more durable electronic devices. Their electronic properties are arguably the most important, as they seem to be ideally suited for the transport of electrons in one direction. The structure of the nanotube greatly affects it electrical properties.



Arm-Chair
[m.n]
m = n

Zig-Zag
[m.0]
n = 0

Chiral
[m.n]
n ≠ 0,m

Figure 1.2. Types of single wall nanotubes.

As seen in Figure 1.2 (above), single wall nanotubes (SWNTs) can be categorized in three distinct structural classes. Their metallic character can be described by the equation $\mathbf{m - n = 3q}$; where $q \geq 0$ the nanotube is "metallic", otherwise it is a semiconductor[19]. The equation, combined with Figure 1.2 show that all arm-chair SWNTs, one third of zig-zag SWNTs, and some chiral SWNT are considered "metallic". Figure 1.3 (below) demonstrates nanotube naming scheme.

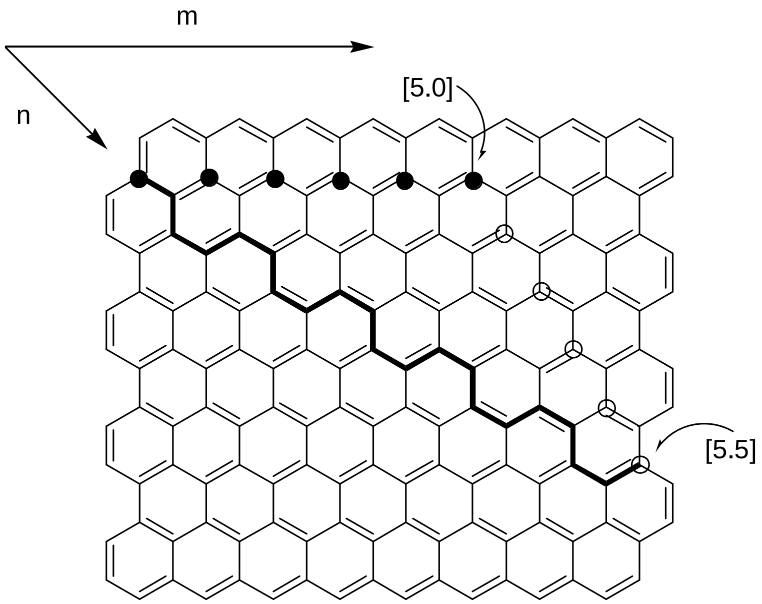


Figure 1.3. Naming scheme for SWNTs.

The applications of the metallic/conductive nanotubes are very significant in the field of nanoelectronics. Due to their long, thin cylindrical shape, the most obvious application is as nanoscale wires. The current carrying capacity of nanotubes is estimated at 1 billion amps per square centimeter, while current copper wires burn out at about 1 million amps per square centimeter.[7] Conductive carbon nanotubes have been used for several years in brushes for commercial electric motors. They replace traditional carbon black, which is mostly impure spherical fullerenes. The nanotubes improve electrical and thermal conductivity, and nanotube-composite motor brushes are better lubricated, cooler-running, less brittle, stronger, and more accurately moldable than conventional motor brushes. Semi-conducting nanotubes change their electrical resistance dramatically when exposed to alkalis, halogens, and other gases at room temperature, which raises hopes for better chemical sensors to be developed.[7] Another use for nanotubes that has already been developed is as extremely fine electron guns, which could be used as miniature cathode ray tubes in thin high-brightness, low-energy, low-weight displays. Nanotubes can activate phosphors at 1 to 3 Volts if electrodes are spaced 1 micron apart. In comparison, Molybdenum tips require fields of 50 to 100 V/µm and have very limited lifetimes.[7] These displays, known as field emission displays (FEDs) make possible the creation of a new generation of flat-panel displays with very low power usage.

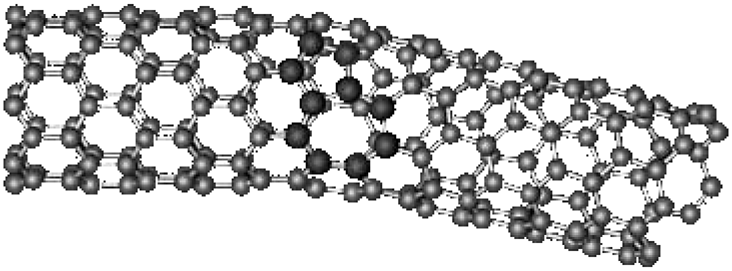


Figure 1.4 The joining of 2 carbon nanotubes with different electrical properties has been proposed.

Yet another possible function is a nanotube formed by joining nanotubes of different diameters (Figure 1.4, above) end to end, which could act as a diode, suggesting the possibility of computer circuits composed entirely out of nanotubes. These diodes could be combined with nanotubes that act as logic gates in computers – that is, in certain conditions they either allow or block electron flow through them.[20]

Long nanotubes could prove to yield a further application. If an electric potential is applied to the ends of a carbon nanotube the nanotube acts as a piezoelectric material, changing its length. This ability allows nanotubes to act as a sort of "muscle" in smart materials.[10]

Their extraordinary properties certainly give rise to many possibilities for future applications, but as with any material, the existence of defects affects their material properties. High levels of defects can lower tensile strength by up to 85%[21]. Defects can also result in a lower conductivity. A well-known form of defect that occurs in carbon nanotubes is the Stone Wales defect, which creates a pentagon and heptagon pair by a rearrangement of the bonds in a naphthalene unit.

1.2.2. Current Methods of Synthesis[22]

As early as 1991, Sumio Iijima had used the carbon arc method to synthesize carbon fibers, and, as he discovered, carbon nanotubes, also. The carbon arc method uses a high voltage over an electrode to ionize a carbon target into a plasma, which then forms PAHs, fullerenes, and other carbon allotropes (such as nanotubes).

In 1996, the Smalley group at Rice University used the laser vaporization technique to produce fullerenes and nanotubes, where a carbon target (typically graphite) is lased in a furnace at 1200°C in the presence of a cobalt-nickel catalyst.[16]

Other techniques have also been developed to synthesize carbon nanotubes, such as the thermal decomposition of hydrocarbons, high pressure carbon monoxide (HiPCO), and chemical vapor deposition (CVD).[22] All of these use a carbon source, a metal catalyst, and a high temperature (>600°C), but the CVD method has shown the most promise in terms of price/unit ratio. Unfortunately, although these methods can produce large quantities of nanotubes, their cost still precludes any large-scale applications.

Furthermore, all of the aforementioned methods generate mixtures of nanotubes. These manufactured mixtures contain nanotubes of a variety of lengths, diameters, chiralities, and defects. Moreover, there is no control as to whether the produced nanotubes will be single- or multiple-walled, or whether they will have the same ring orientation down the entire length of the tube.

In order to circumvent these deficiencies of current nanotube syntheses, our main interest was to explore the possibilities of synthesizing bowl-shaped PAHs, eventually the target molecule $C_{50}H_{10}$. In order to overcome the strain of the fused carbon ring system, Flash Vacuum Pyrolysis (FVP) surfaced as the most viable option in producing buckybowls, and many novel systems have since been created by using this technique.[23] By subjecting suitable precursors to very high temperatures (>900°C) under relatively high vacuum, the molecules are allowed to pass through the very hot part of the system in about one hundredth of a second; long enough to react but not long enough to decompose. Often, this results in rearrangement of the molecular "skeleton" by the loss of hydrogen or hydrogen halides, and formation of new carbon-carbon bonds[24].

FVP has become an important method in the process of synthesizing highly-strained PAHs that were unavailable by conventional synthetic approaches.[25] Probably the most impressive example is the complete synthesis of C_{60} done by the Scott group[26], of which the last step is subjecting the precursor compound to FVP (Figure 1.5, below).

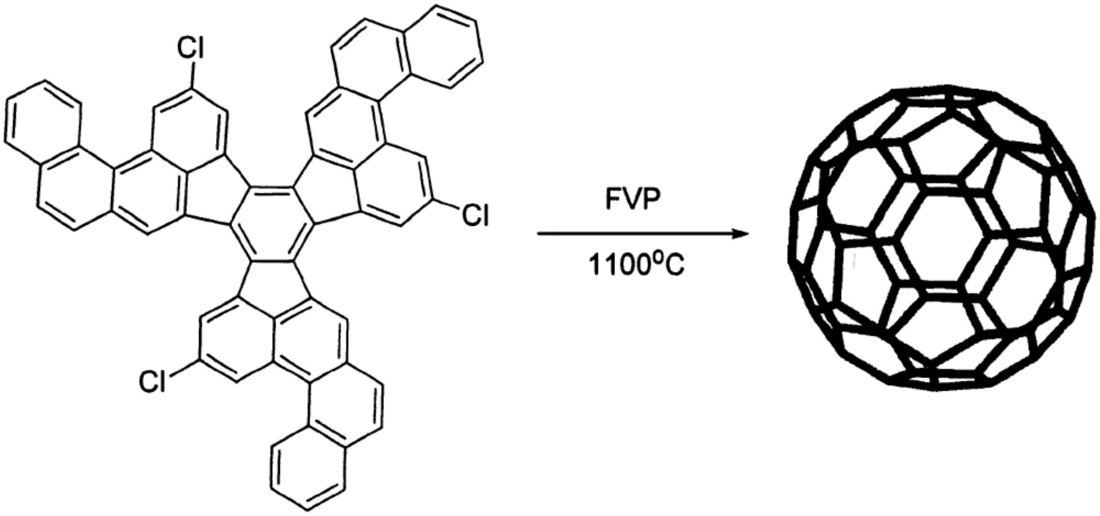


Figure 1.5. Synthesis of C_{60} by FVP

When molecules are subjected to these extremely high temperatures they can be coaxed into abnormal, energetically unfavorable conformations. Here, normally planar aromatic compounds are able to bend and stretch easily, as well as form reactive intermediate species like radicals, carbenes, and benzynes, which in turn form new carbon-carbon bonds.

The yield for bowl-shaped PAHs is typically very low, and decreases as the systems grow in size. Also, as molecules go up in weight, they tend to decrease in volatility, which translates to a smaller chance of bringing the heavier precursors into the hot tube of the pyrolysis setup (Figure 1.6, below), which would allow them to react or decompose prior to vaporization.

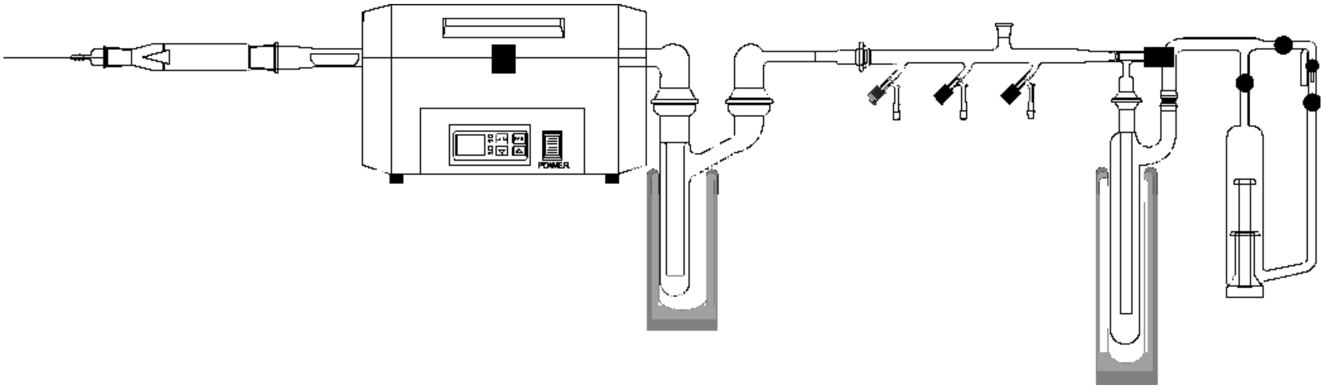


Figure 1.6. Set up of a flash vacuum pyrolysis setup

Furthermore, functional groups are essentially ruled out for FVP, as they are easily disrupted or decomposable at high temperatures. Therefore, FVP is feasible only as one of the latter steps in the synthesis of a buckybowl, in order to generate the $C_{50}H_{10}$ geodesic cap or hydrocarbon intermediate in good yield. Otherwise, FVP is not a realistic option, and non-pyrolytical methods (i.e. solution chemistry) are crucial in a rational synthesis of a carbon nanotube.

1.3. Retrosynthesis of a [5.5] Carbon Nanotube

Because of the aforementioned deficiencies with nanotube synthesis, a pure sample of metallic (or semi-conductive) nanotubes is essentially impossible. Obtained mixtures consist of fullerenes, cones, highly unsaturated PAHs, “onions”, as well as nanotubes of varying lengths, diameters, chiralities, and number of walls. Separation methods have proven lengthy and ultimately are not effective.

In electronic applications it is important for the material to be uniform. In this case, nanotubes would have to be a specific diameter, length, and chirality. The latter is especially important, remembering that the metallic nature of the nanotube depends on its chirality (Figure 1.2). This is why the development of a rational synthesis of specific carbon nanotubes is crucial to the field of future nanoelectronics.

The idea of the geodesic cap is that it is the smallest fragment of a carbon nanotube that “contains” all the information for the structure of a complete, grown nanotube. The geodesic cap is sort of a blueprint or “seed molecule” of which successive reactions can build a specific nanotube off, growing it to a desired length. It has been our hope that after achieving said cap molecule, the nanotube could be extended with repetitive Diels-Alder reactions using acetylene as the dienophile, followed by rearomatization through thermal loss of hydrogen (Figure 1.7, Below).

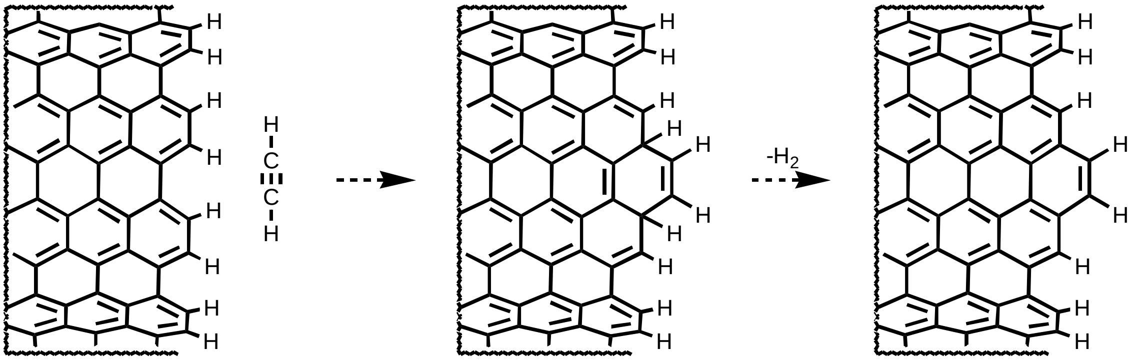


Figure 1.7. Proposed repetitive Diels-Alder extension of a geodesic cap or carbon nanotube

The proposed Diels-Alder extension of the nanotube would only work for nanotubes in the correct configuration, which are armchair nanotubes – those in other conformations would need to utilize a different growth approach. For this reason, we chose as our target the [5.5] SWNT. This fits all the necessary categories to make this a practical and useful goal: being a nanotube in the armchair configuration, it is conductive; the conformation would also allow (seemingly) easy growth out to a full-length nanotube (Figure 1.8, Below).

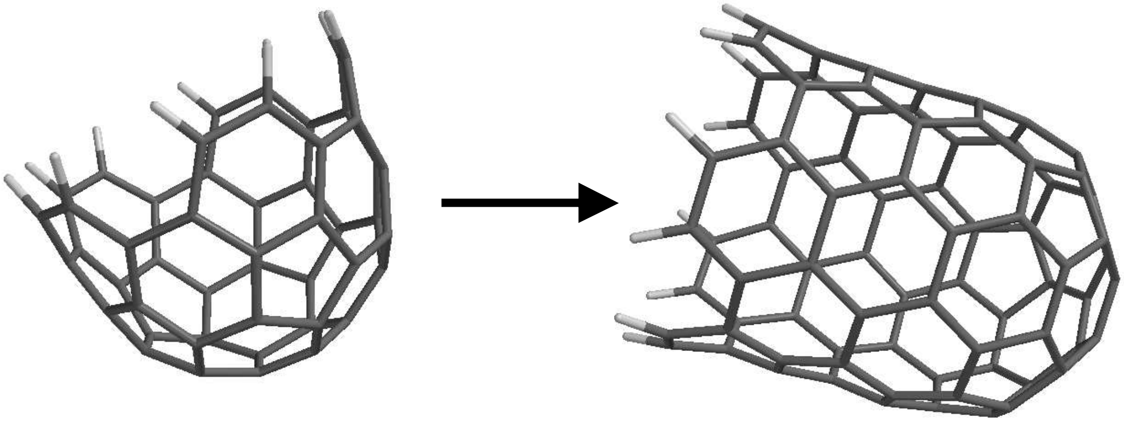


Figure 1.8. Geodesic cap extension

The only problem with the construction of a [5.5] SWNT is that it has the smallest possible diameter for a nanotube (7Å), so the actual construction of the geodesic cap will be difficult in terms of he amount of strain energy that has to be overcome in order to build the compound.

Looking down the central axis of the tube it is easy to observe the specific shape of corannulene, a previously synthesized compound in the Scott group. The main objective of this project is the synthesis of the short buckytube ($C_{50}H_{10}$) using a route which involves the five-fold closure of pentaindenocorannulene which in turn might be derivable from corannulene or derivatives of corannulene. The optimal preference for the five fold closure / formation of the geodesic cap are Müllen-type conditions for new carbon-carbon bond formation in polycyclic arenas, including introducing curves into planar molecules.[27] If these should fail, the alternative would be to subject the molecules to FVP, as mentioned earlier, in order to overcome the high degree of ring strain.

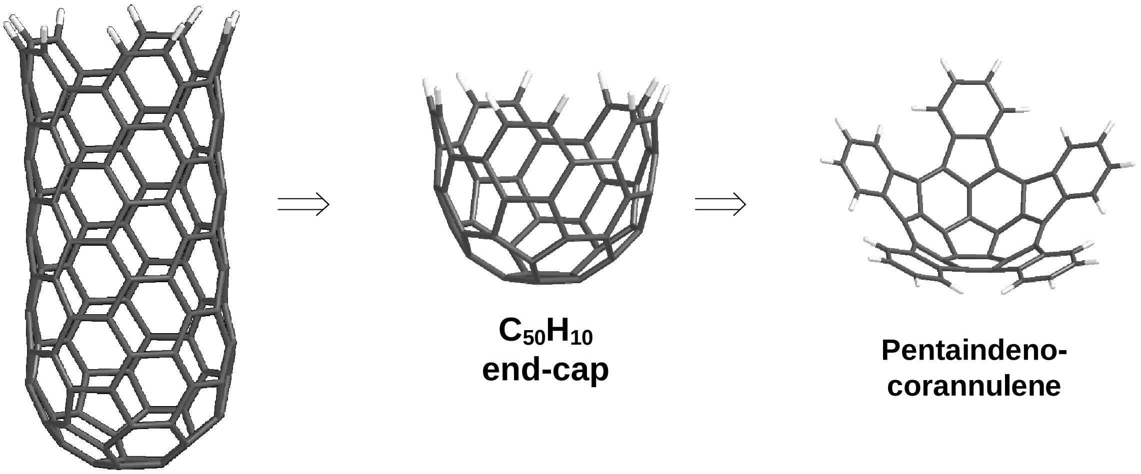


Figure 1.9. Proposed Retrosynthesis of the [5.5] carbon nanotube

As stated earlier, once the buckytube is synthesized, extension to longer nanotubes of desired lengths should be possible by repetitive Diels-Alder reactions using acetylene as a dienophile. This method would allow for production of specific nanotubes of desired length, diameter, and ring orientation.

1.4. Thesis Outline

The ambition behind the research in this thesis is progress toward a rational synthesis of a [5.5] single wall carbon nanotube. The attempted synthesis of a $C_{50}H_{10}$ “buckybowl” or derivative would be the essential cornerstone to the synthesis of a full armchair nanotube.

Chapter 2 presents an approach to a $C_{50}H_{10}$ geodesic cap through an asymmetric route. Here are described improvements in the initial synthesis of a corannulene derivative, the starting material, as well as work toward the extension of the bowl toward the final target.

Chapter 3 describes an alternate approach to a $C_{50}H_{10}$ derivative, using a symmetric route. This chapter shows the synthesis of the key precursor, corannulene, its subsequent halogenation, and the attempted synthesis of the target bowl derivative. Several test reactions are also reported, as well as the attempted synthesis of a peralkoxylated geodesic cap.

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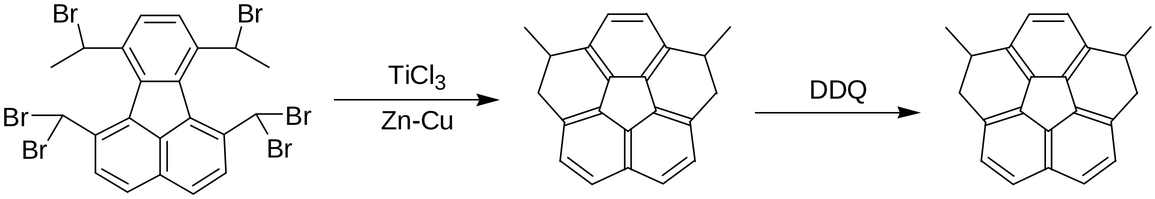
CHAPTER II:

An Asymmetric Route to a $C_{50}H_{10}$ Geodesic Cap

2.1. Motivation

In 1996, the Siegel group reported a non-pyrolytic route to 2,5-dimethylcorannulene through a low-valent titanium reductive coupling of 1,6-bis(dibromomethyl)-7,10-bis(1-bromoethyl)fluoranthene followed by dehydrogenation of the dimethyltetrahydrocorannulene intermediate (Scheme 2.1).[1]

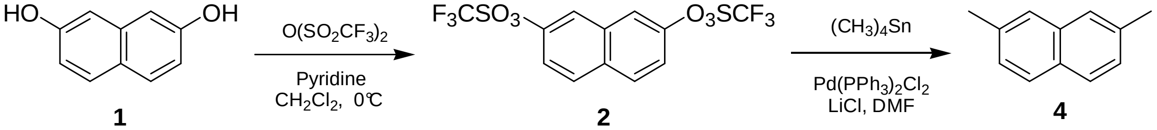


Scheme 2.1

This idea was applied to other compounds, and several different derivatives of corannulene were able to be synthesized using non-pyrolytic methods.[2] This opened new possibilities in the synthesis of the $C_{50}H_{10}$ geodesic cap. Through the research of Mihail Bancu, it was decided that the approach to pentaindenocorannulene was most efficient through the synthesis of 1,2,5,6-tetrabromocorannulene **10** over other bromo-compounds.[3] It was then decided that optimization of this process would go far in obtaining enough precursor compounds to allow more synthetic attempts on the target molecule, the $C_{50}H_{10}$ geodesic cap. The incentive was that unlike other routes to corannulene, this was a non-pyrolytic method, which could eliminate a “bottleneck” which occurred as a low yield in synthetic routes requiring FVP as an essential step.

2.2. Results and Discussion

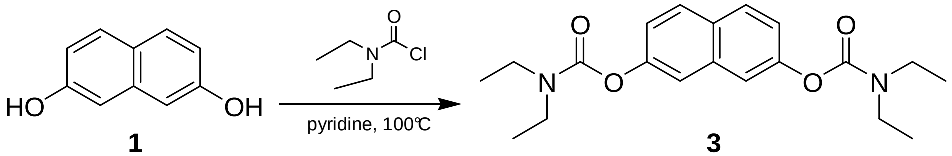
Initially, we chose 2,7-dihydroxynaphthalene as our starting material, it being both relatively inexpensive and readily available. Few synthetic approaches to 2,7-disubstituted naphthalenes had previously been described in literature.[4] Upon my insertion into the laboratory, the initial step was making 2,7-dimethyl naphthalene **4** through the triflate intermediate **2** (Scheme 2.2).



Scheme 2.2

This route was deemed inefficient and expensive. The yield of reacting **1** with triflic anhydride yielded less than 60% of the di-triflate precursor to **4**. The formation of 2,7-dimethylnaphthalene **4** was performed by Stille coupling, using tetramethyl tin in the presence of a palladium catalyst.[5]

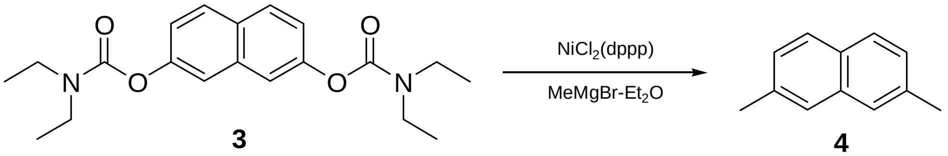
Because of the cost of the reagents needed for this process, low-yielding first step, as well as the desire to avoid the toxic organotin compounds, a different approach was discovered. The low cost of N,N-diethylcarbamoyl chloride (in relation to triflic anhydride) allows the formation of O-carbamates; in our research the synthesis of 2,7-bis(N,N-diethylcarbamoyloxy)naphthalene **3** was formed in almost quantitative yield (Scheme 2.3).[9]



1 **3**

Scheme 2.3

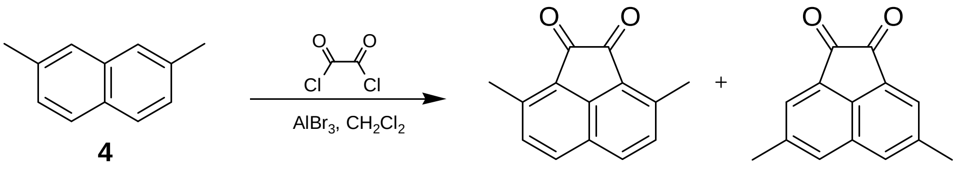
The use of O-carbamates as leaving groups allows for the possibility of incorporating a multitude of diverse substituents using Grignard reagents and relatively inexpensive nickel catalysts.[6] In our research the reaction of 2,7-bis(N,N-diethylcarbamoyloxy)naphthalene **3** with methyl magnesium bromide in the presence of a nickel catalyst gave an 88% yield of 2,7-dimethylnaphthalene **4** (Scheme 2.4).[9]



3 **4**

Scheme 2.4

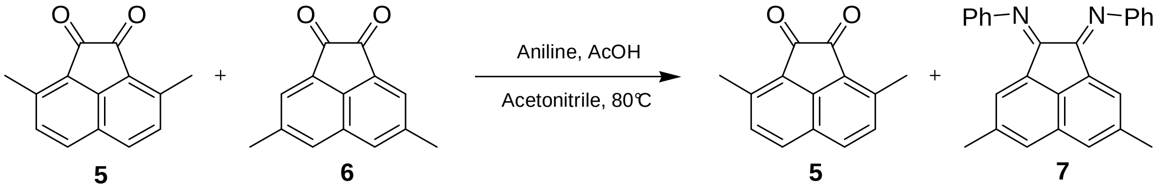
Compound **4** was then subjected to a Friedel-Crafts acylation and reacted with oxalyl chloride in the presence of aluminum bromide in a dry ice/ethylene glycol bath (-15° to -40°C). This reaction gave products of the desired 3,8-dimethylacenaphthequinone **5** and the undesired 4,7-dimethylacenaphtequinone **6** in a mixture (Scheme 2.5).[10]



4 **5** **6**

Scheme 2.5

For a long time this step was (and still is to a certain extent) the bottleneck of this approach, for the reason that the separation of the isomers proves to be difficult. Originally, a combined silica gel column-alumina gel column process was used, using a dichloromethane:hexane eluent to obtain the pure product **5**. However, it was found that the separation was more efficient if the isomer mixture was first reacted with aniline in acetonitrile at 80°C, it produced a mixture of the desired product 3,8-dimethylacenaphthequinone **5** and the (N,N'E,N,N'E)-N,N'-(4,7-dimethylacenaphthylene-1,2-diylidene)dibenzenamine **7** (Scheme 2.6).[11]

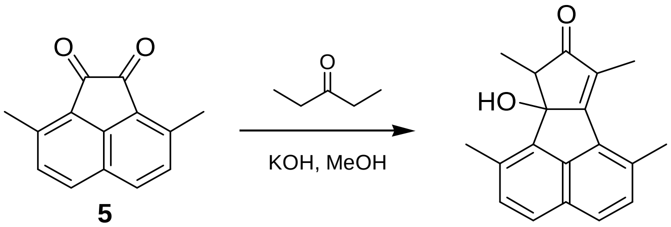


Scheme 2.6

These products were easily separable with silica gel chromatography; however, the chromatography needed to be completed immediately after the reaction was worked up (or the mixture needed to be stored in the refrigerator) due to the fact that the imine compound **7** decomposes back to 4,7-dimethylacenaphthequinone **6** over time at room temperature (noted by reddening of the mixture – probably aniline being re-formed).

The process described in Scheme 2.5 had previously been optimized, and it was found that the reaction was catalyst and temperature dependent. Aluminum chloride worked better than iron trichloride, and aluminum bromide worked better than aluminum chloride. It was important to improve not only the yield but also the ratio of the desired product. A low temperature for the majority of the time, followed by a slow increase to room temperature over the course of an hour, gave the best results. Although a 66% yield of the desired product **5** is obtained for the two-step synthesis and separation, a further optimization of this step would greatly enhance later results.

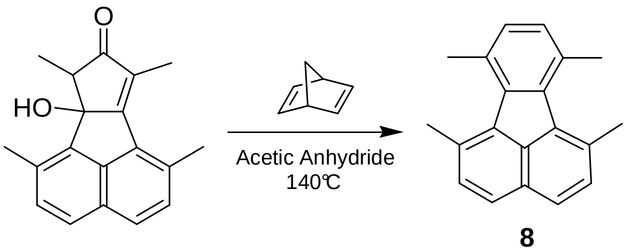
Once the 3,8-dimethylacenaphthequinone **5** was purified, the double aldol condensation was performed at room temperature in methanol with potassium hydroxide (Scheme 2.7). The intermediate product, as a brown, sticky viscous compound was dried under vacuum, and no separation was performed.



5

Scheme 2.7

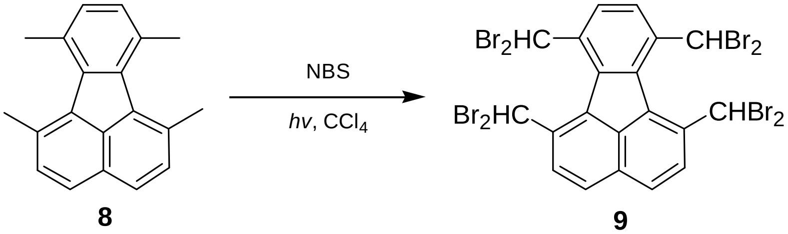
The intermediate product was carried on to the next step, a Diels-Alder-retro-Diels-Alder reaction with norbornadiene (Scheme 2.8).[13] The reaction was performed in a sealed pressure vessel, with acetic anhydride as a solvent. After three days at 140°C and separation using a silica column, the pure product 1,6,7,10-tetramethylfluroanthene **8** was obtained in 60% yield over two steps. This is a significant increase over the <40% yield that was previously reported for this step;[3] the increase is most likely due to the starting material **5** being more pure.



8

Scheme 2.8

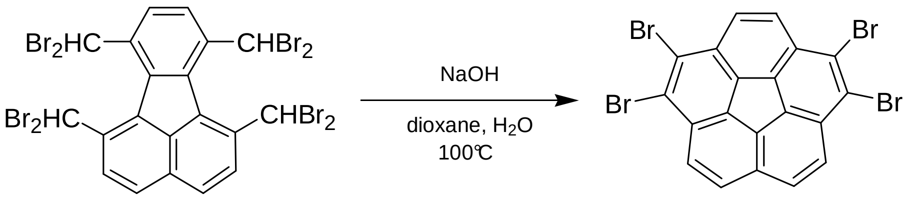
The bromination of compound **8** was done with 10 equivalents of N-bromosuccinimide (NBS) in carbon tetrachloride to form tetrakis(dibromomethyl)fluoranthene **9** (Scheme 2.9).[2] The reaction was initiated with benzoyl peroxide, and the reaction mixture was heated gently under light irradiation. A total of eight bromines were added to the compound: two for each methyl group, as steric crowding prevented a third from being added. The yield for this reaction is about 85%; this is partially due to under-bromination, and partially due to polymerization that occurs over time in solution and in the light. The compound also polymerizes very quickly in basic solutions; however, the solid form of tetrakis(dibromomethyl)fluoranthene **9** is stable at room temperature.



8 **9**

Scheme 2.9

The last step to synthesize the corannulene core is the reaction of compound **9** with sodium hydroxide at reflux in a solution of dioxane and water (Scheme 2.10).[2] The high temperature is necessary to give the molecule enough energy for intramolecular closures to occur – at lower temperatures the formation of polymers is the major outcome. It is for this reason that the addition of sodium hydroxide pellets must occur only after the solution is at reflux. Because of the extreme facility of this particular reaction, it is completed in 15 minutes, and is noted by a color change in the solution from red-brown to grey-white. Since the compound crashes out of solution, a simple filtration is required, and after a wash with water and drying, pure 1,2,5,6-tetrabromocorannulene **10** is obtained in 85% yield.



9 **10**

Scheme 2.10

The group of Rabideau proposes three mechanisms for this reaction.[7] It was determined that the first step must be deprotonation of the dibromomethyl-group, since reflux of **9** in neutral or acidic solutions gave back only starting material. The three suggested mechanisms are nucleophilic substitution, carbene formation with α-elimination of HBr, and a radical mechanism. Currently there is no proof for any of these mechanisms; however, figure 2.1 presents the most probable pathway for the formation of 1,2,5,6-tetrabromocorannulene **10**: the deprotonation of **9** followed by a S_N2 nucleophilic substitution/elimination.

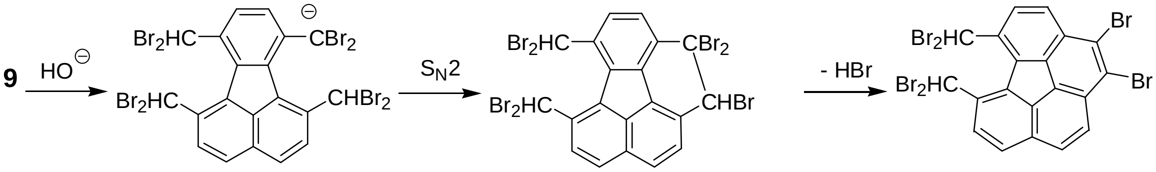
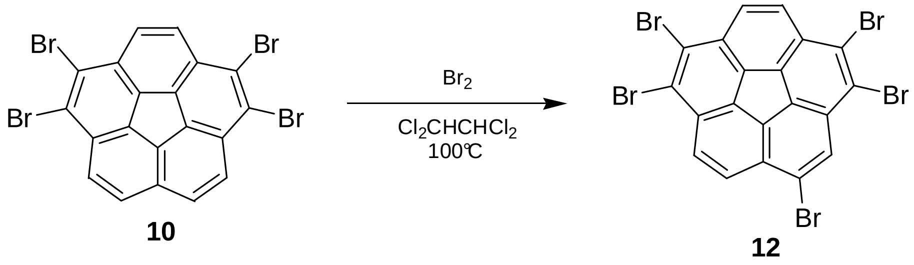


Figure 2.1. The proposed mechanism for the formation of a new carbon-carbon bond.

Since both compounds **10** and **12** (starting material and product, respectively) are very insoluble, subsequent bromination was more difficult than it would have been had the compounds been soluble. Adding catalytic amounts of iron tribromide tends to over-brominate, as does bromination via IBr.[3] Since over-bromination was easier than expected, a route had to be discovered that could brominate compound **10** only once. Following several failed attempts to brominate tetrabromocorannulene, conditions were discovered that provided the product 1,2,5,6,8-pentabromocorannulene **12** in 90% yield (Scheme 2.11). The precursor **10** with elemental bromine was heated at 100° – 120°C. in tetrachloroethane.

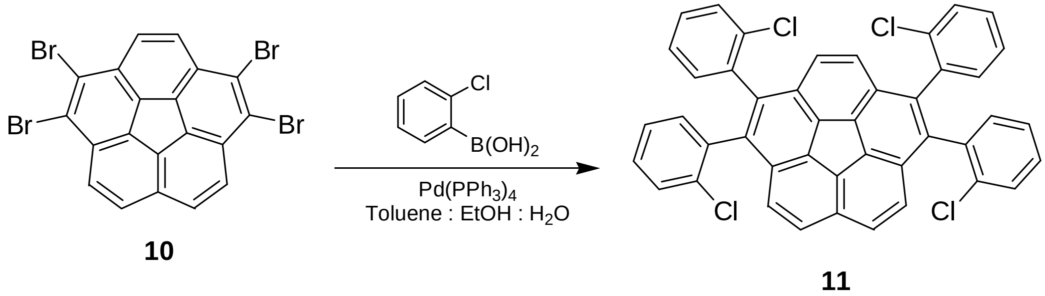


Scheme 2.11

It was found that this reaction was very concentration-dependent. At concentrations greater than 15 mg/mL of **10**, starting material was recovered. At lower concentrations (6-8 mg/mL), a majority of the starting material converted to the desired product. Some starting material and over-brominated products were present in the final mixture.

Tetrabromocorannulene **10** was chosen to be used as a test compound for eventual fivefold indeno-annulation attempts on 1,2,5,6,8-pentabromocorannulene **12**. The goal was to find suitable conditions to make tetra-indenocorannulene so that these conditions could be applied later to form its penta-indeno cousin. Furthermore, since 1,2,5,6-tetrabromocorannulene **10** is symmetric, it was hoped that analyses of the tetra-substituted compound would make those of the penta-substituted compound easier to understand.

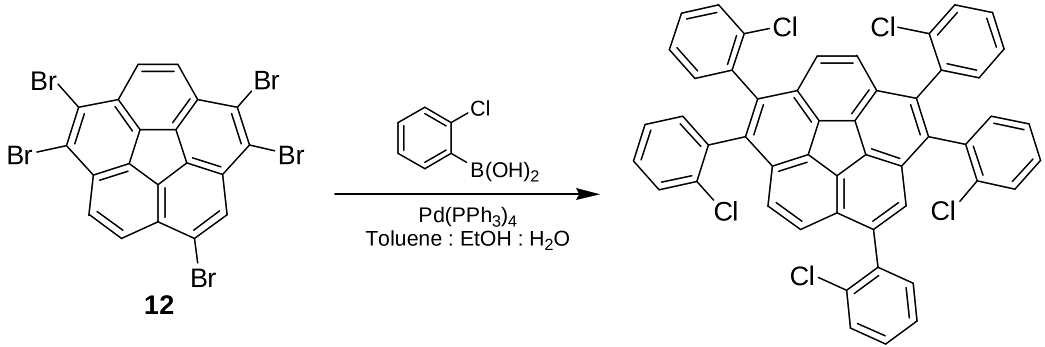
Using conditions previously discovered in the Scott group[3], we were able to synthesize 1,2,5,6-tetrabromocorannulene **10** by an unconventional Suzuki coupling. Since the coupling did not work with standard conditions (in solvents such as DMAc, DMF, and THF), a unique approach was taken. Eventually a combination of solvents toluene:ethanol:water in a ratio of 2:2:1 were discovered to work, in the presence of $Pd(PPh_3)_4$ as a catalyst and potassium carbonate as a base, to form 1,2,5,6-tetrakis(*ortho*-chlorophenyl)corannulene **11** in 74% yield (Scheme 2.12). Separation by column chromatography gave a big yellow band of stereoisomers, which made the NMR a broad series of peaks in the aromatic region. Silica preparative plate chromatography gave different bands, but all were identified by mass spectroscopy to be the same compound (m/z 690.0475). This means that the phenyl rings around corannulene do not rotate readily at room temperature.



Scheme 2.12

The test compounds were further analyzed and experimented with by Mihail Bancu of the Scott group, finding separation of certain stereoisomers, and eventually yielding tetra-indenocorranulene.[3] This gave hope that eventually the synthesis of target molecule penta-indenocorannulene could be achieved.

Seeing that the tetra-substituted test molecules **10** and **11** had successfully given a closely related molecule to the target compound, it was decided to move on to the next step and attempt the synthesis of 1,2,5,6,8-pentakis(*ortho*-chlorophenyl)corannulene **13**. Using the same conditions as synthesis of compound **11**, the desired product **13** was obtained in 91% yield (Scheme 2.13).



12

13

Scheme 2.13

Separation of the crude product by column chromatography gave a big yellow band of stereoisomers, of which further separation was impossible. This is most likely a result of the ability of the *ortho*-chlorophenyl group in the position “8” to rotate easier (due to less steric hindrance) than the other *ortho*-chlorophenyl groups, thereby canceling out the differences in them which made possible the separation of 1,2,5,6-tetrakis(*ortho*-chlorophenyl)corannulene **11**. The MALDI spectra showed only the desired product (Figure 2.2).

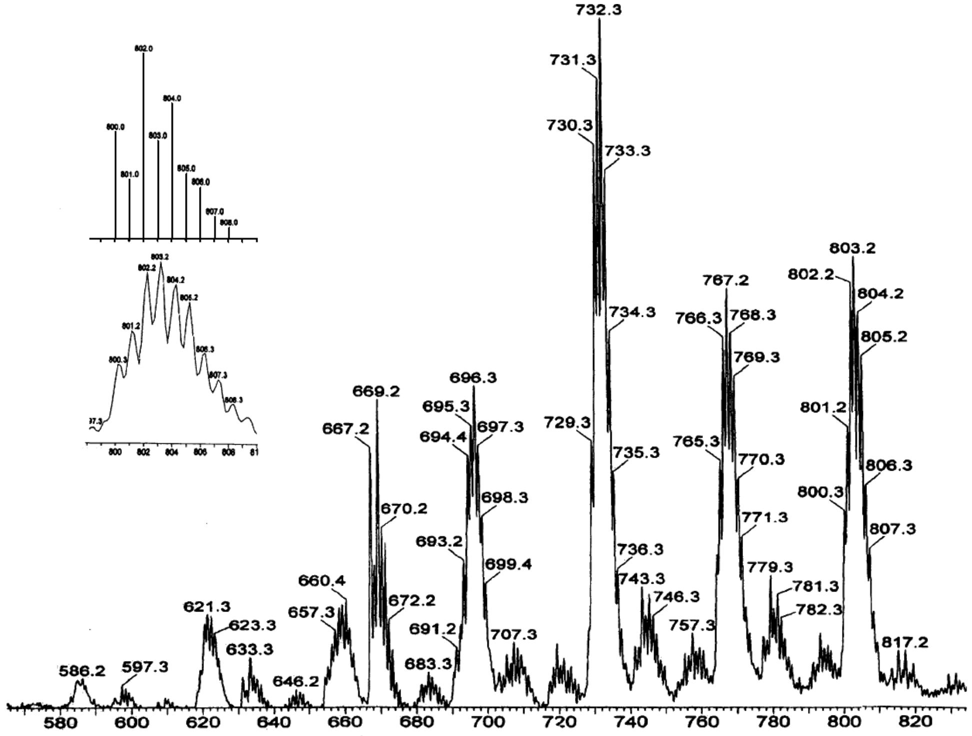
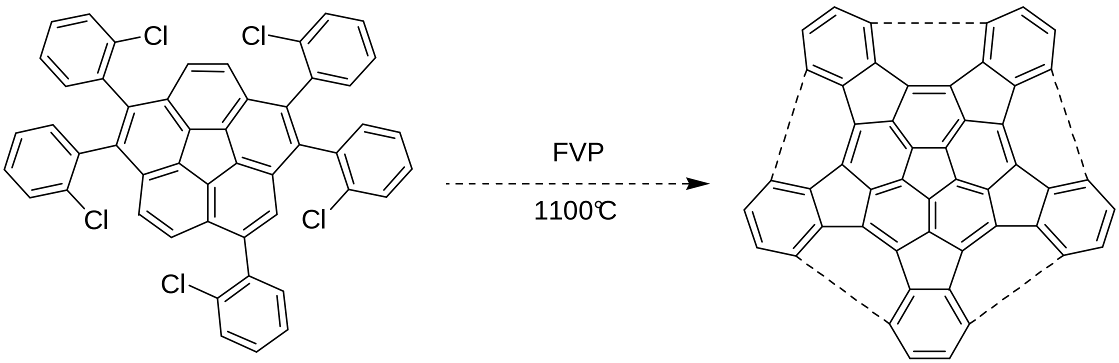


Figure 2.2. MALDI spectrum of 1,2,5,6,8-pentakis(*ortho*-chlorophenyl)corannulene 13

The subsequent obvious step was that of attempting the synthesis of penta-indenocorannulene by FVP (Scheme 2.14). Compound **13** was subjected to FVP at 1100°C, slowly raising the boat temperature so that the entire starting material compound sublimed.



13

Scheme 2.14

The recovered pyrolysate in the trap was very little (5% mass recovery). The MALDI spectra showed that penta-indenocorannulene $C_{50}H_{20}$ was indeed present as a product, along with compounds $C_{50}H_{18}$ $C_{50}H_{16}$, (Figure 2.3).

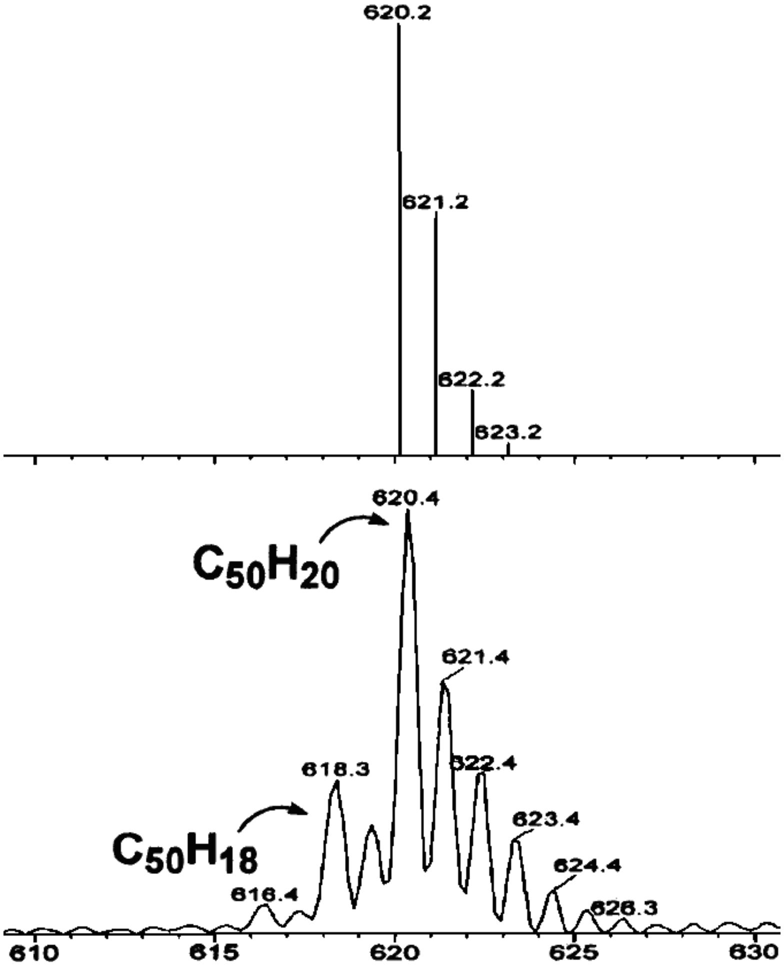


Figure 2.3. MALDI spectra from pyrolysis of 1,2,5,6,8-pentakis(*ortho*-chlorophenyl)corannulene 13

The compounds $C_{50}H_{18}$ and $C_{50}H_{16}$ are formed from penta-indenocorannulene by extra one and two closures, respectively. Because the formation of these has been observed, it is probably possible to synthesize a complete geodesic cap by pyrolysis of the precursor 1,2,5,6,8-pentakis(*ortho*-chlorophenyl)corannulene **13**. Further work is being done to investigate this, especially now that a convenient route to penta-indenocorannulene has been found just recently, replacing the final, pyrolysis step with a closure reaction in a microwave reactor[8]. Since penta-indenocorannulene can be synthesized in larger amounts it is possible to subject that compound to pyrolysis in hopes that it may close all the way.

A side project during the optimization of this process was an attempt at bypassing the Friedel-Crafts acylation bottleneck step (Figure 2.4). This was proposed by using methoxy groups as ortho-directors to the alpha-carbon positions that were directly next to the 2,7-positions, rather than the alpha carbons on the "bottom" of the molecule. After the methoxy groups were added at the 2,7-positions, the synthesis could move on until the bottleneck was bypassed, when they could be removed and the synthesis could continue as normal.

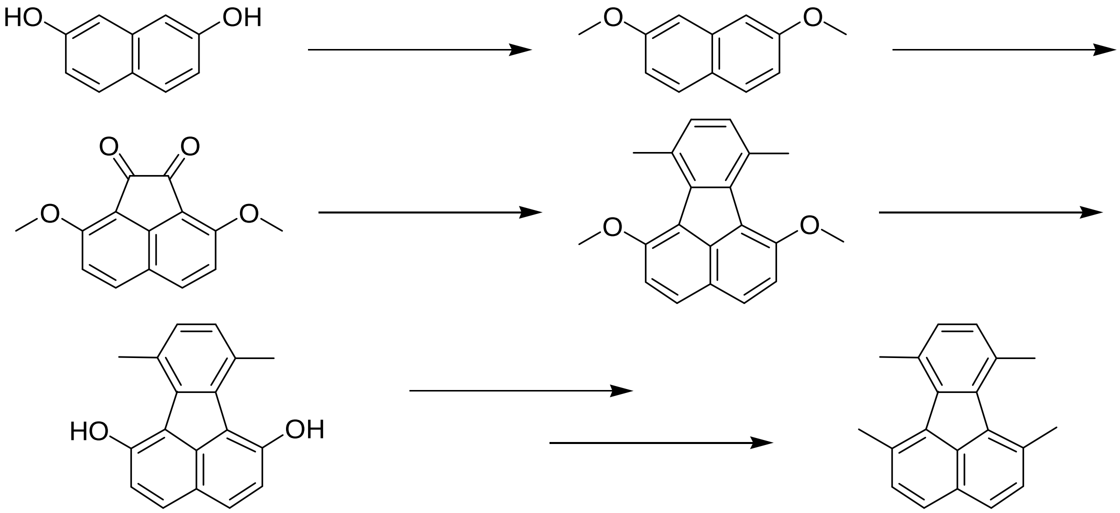
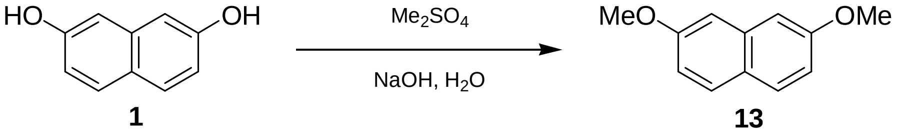


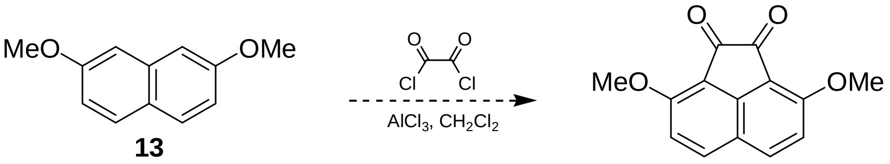
Figure 2.4. Proposed alternate synthetic route to bypass the bottleneck step

The initial step, putting the methoxy groups on, had been done before and worked in almost 90% yield.[17] 2,7-Dihydroxynaphthalene **1** was reacted with sulfuric acid dimethyl ester and sodium hydroxide in water to yield the final product **13** (Scheme 2.15).



Scheme 2.15

We then tried to subject compound **13** to a Friedel-Crafts acylation (Scheme 2.16). We tried using the same conditions as compound **4**, as well as substituting aluminum chloride for aluminum bromide, and trying lower temperatures, to no avail. The product collected was a combination of the desired product (<5% yield) polymers of different lengths, and compounds that had been acylated at only one location. This project was quickly abandoned when the separation using aniline was developed.



Scheme 2.16

2.3. Conclusion

The advantageous gram-scale synthesis of 1,2,5,6-tetrabromocorannulene **10** has been made more efficient, and can serve as a primary route to synthesis of new, curved PAHs. Although my attempts of indeno-annulations via FVP somewhat failed, it has been recently discovered that synthesis of synthetically useful quantities of pentaindenocorannulene is likely possible through microwave reactor chemistry.[8] The successful bromination of 1,2,5,6-tetrabromocorannulene **10** to 1,2,5,6,8-pentabromocorannulene **12** was important because it establishes a way to synthesize new and unique penta-substituted corannulene derivatives. Using **12** we were able to make the 1,2,5,6,8-pentakis(*ortho*-chlorophenyl)corannulene **13** as an intended precursor for pentaindenocorannulene, or our ultimate goal, the $C_{50}H_{10}$ geodesic cap. The FVP of **13** formed the desired product $C_{50}H_{20}$ in trace amounts (as detected by MALDI), and more importantly were observed the closures of one and two sides of the pentaindenocorannulene. Since an efficient way to synthesize a pentaindenocorannulene has recently been found[7], the research to optimize this process has been invaluable.

2.4. Experimental

2.4.1. General

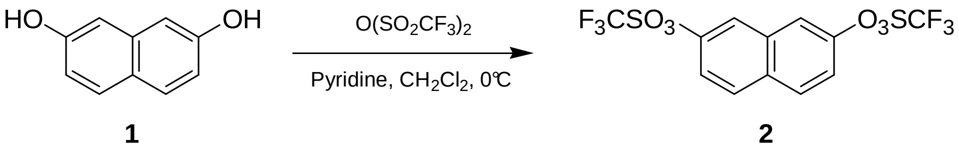
All starting materials and reagents were purchased from Aldrich chemical company or Acros chemical company and used without further purification. All solvents were used as purchased.

Proton and carbon NMR spectra were generated on a Varian 400 (400 MHz for ^{1}H, 100 MHz for ^{13}C) unless otherwise noted. Proton shifts are recorded relative to trimethylsilane (TMS); carbon shifts are recorded relative to deuterated chloroform. MALDI analyses were obtained on a Micromass Tof Spec2E spectrometer.

Baker 60 – 200 mesh silica gel or Aldrich aluminum oxide, activated, neutral, 150 mesh, surface area 155 m^2/g, was used for column chromatography. Preparative thin-layer chromatography was performed on 20 x 20 cm Analteech Unplate Taper plates.

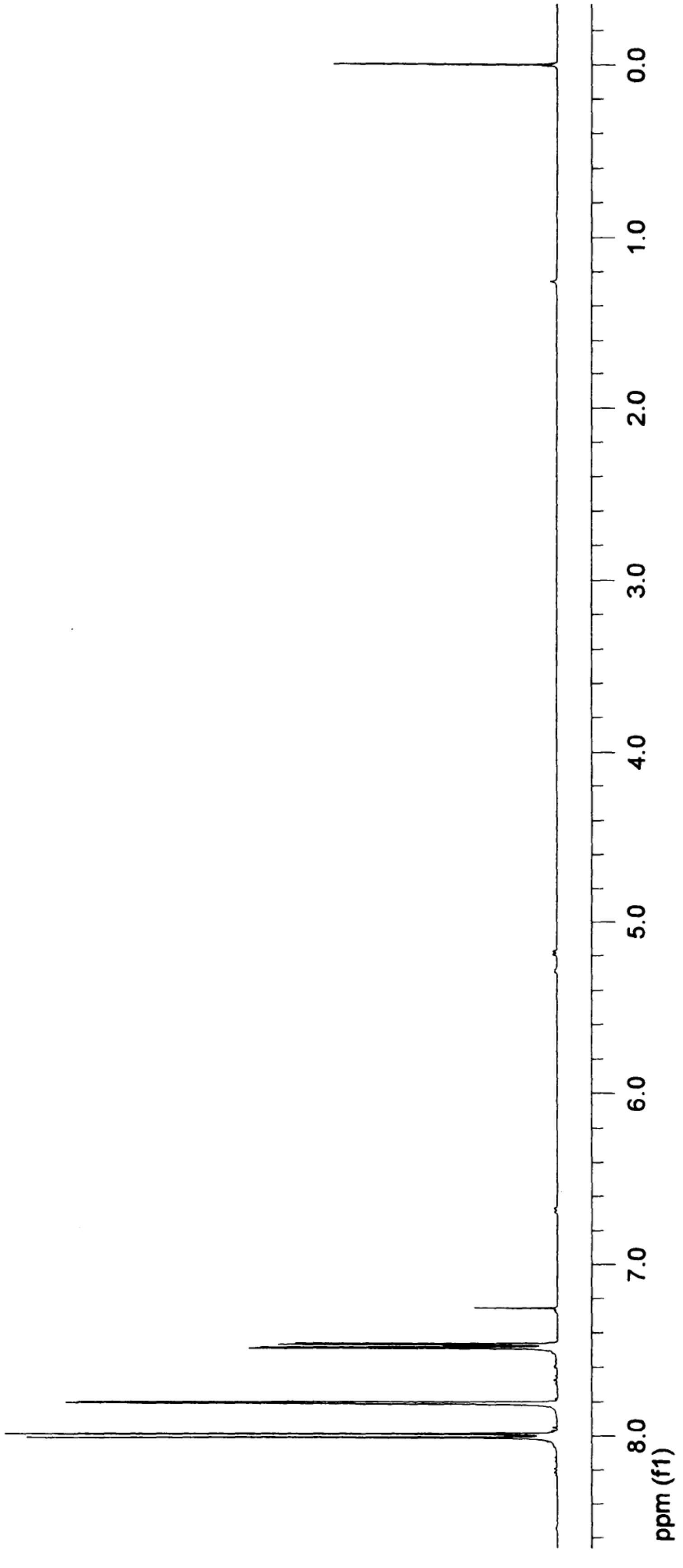
TLC plates were purchased from J. T. Baker. All melting points were determined using a meltemp II Melting Point Apparatus and are reported uncorrected.

2.4.2. 2,7- Bis(trifluoromethanesulfonyloxy)naphthalene 2

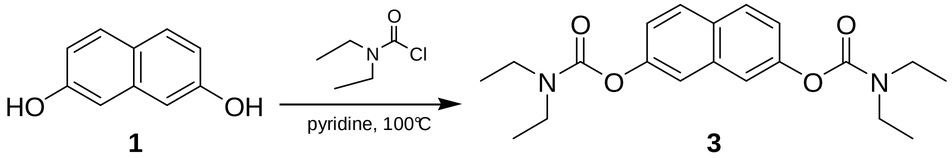


To a solution of 17.75 g (0.11 mol) of 2,7-dihydroxynaphthalene **1** and 75 mL pyridine in 225 mL anhydrous methylene chloride, cooled to 0°C in an ice bath, were added 75 g (0.27 mol) trifluoromethanesulfonic anhydride slowly with a pressure-equalizing dropping funnel.[5] The cooling bath was removed, and the reaction mixture was stirred at room temperature for 4 h. The mixture was then poured into 400 mL water and extracted twice with 200 mL portions of methylene chloride. The organic layers were combined and washed twice with 300 mL 10% aqueous hydrochloric acid, once with water, and once with saturated sodium chloride aqueous solution. The organic layer was separated, dried over magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure. Purification by column chromatography on silica gel with hexane as an eluent followed by recrystallization from hexane (a hot filtration is required) yielded 47 g (59%) of 2,7- bis(trifluoromethanesulfonyloxy)naphthalene **2** as a white solid.

Melting point	62 – 63°C; lit 61.5 – 62.5°C[9]
^{1}H NMR (400 MHz, $CDCl_3$)	δ 8.00 (d, *J* = 9.0 Hz, 2 H); 7.81 (s, 2H); 7.48 (d, *J* = 9.0 Hz. 2H)

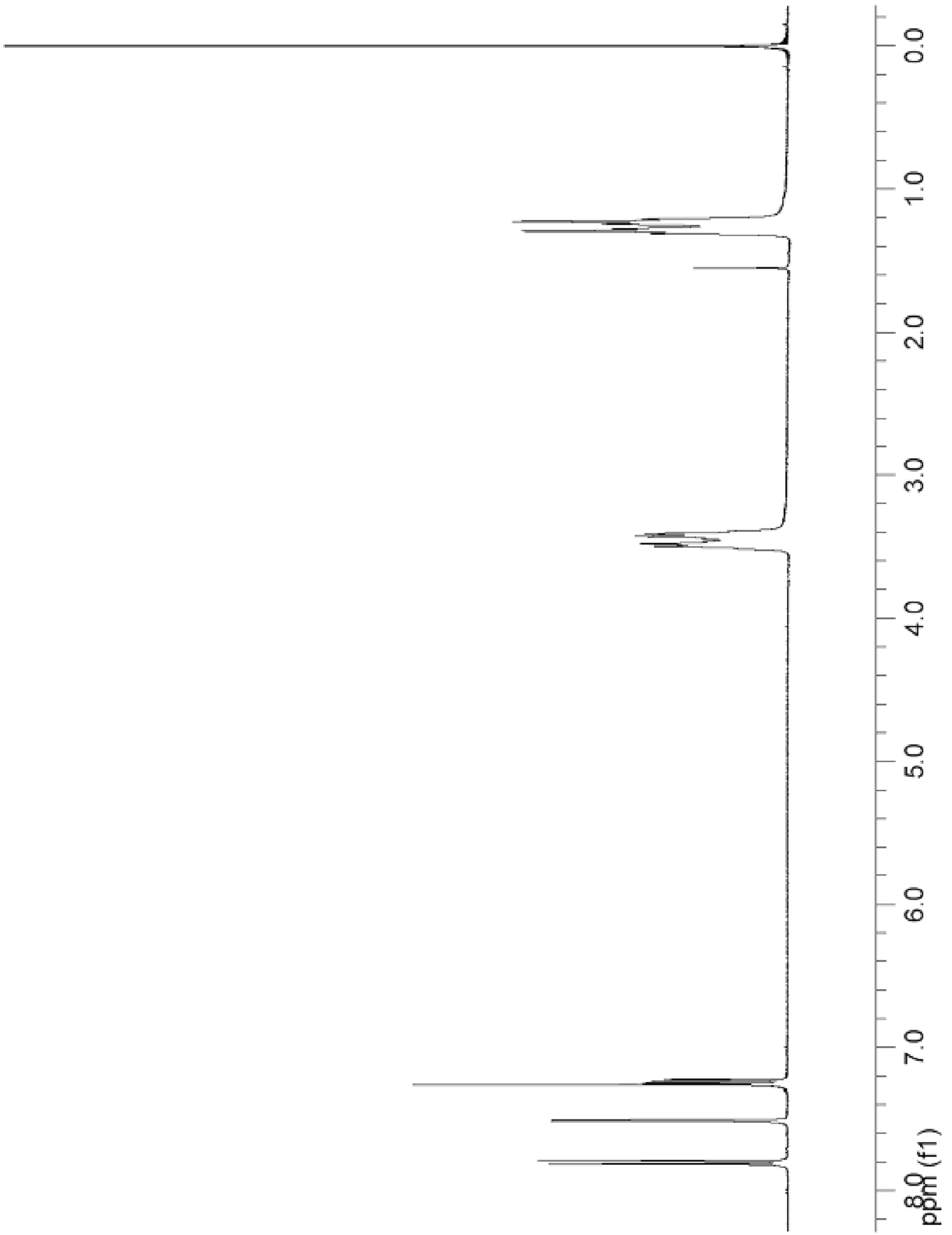

0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (f1)

2.4.3. 2,7-Bis(N,N-diethylcarbamoyloxy)naphthalene 3



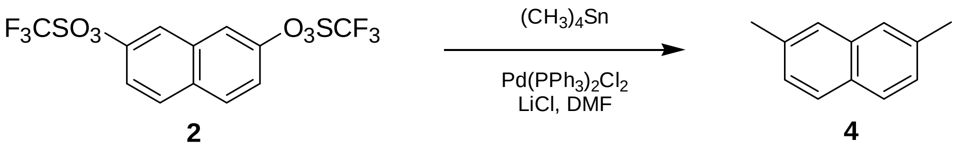
Into a dry 1-L, three-necked, round-bottomed flask, equipped with a mechanical stirrer and a condenser, were added 2,7-dihydroxynaphthalene **1** (50.0 g, 0.312 mol) and pyridine (700 mL) under nitrogen.[10] A dry, pressure-equalizing dropping funnel fitted with a rubber septum was installed and charged with N,N-diethylcarbamoyl chloride (122 mL, 0.906 mol). After the reaction flask is cooled in an ice bath for 30 minutes, N,N-diethylcarbamoyl chloride is added within 10-15 minutes to the vigorously stirred mixture. The ice bath is removed, and the solution is warmed to room temperature. The solution is then heated to 100°C for 2 days. After the flask was cooled in an ice bath, hydrochloric acid (6 M, 300 mL) is poured in over 10 minutes with vigorous stirring. A light-brown solid is formed. The brown mixture is transferred to a 4-L Erlenmeyer flask and more hydrochloric acid (6 M, 500 mL) is added, followed by water (500 mL) to precipitate the compound further. The solid is filtered with a Büchner funnel and washed with water (500 mL). The crude product is dried overnight by vacuum. The purity was found to be sufficient for the next step, obtaining 109.00 g (97.4 % yield) crude product. For purer product a recrystallization was performed by dissolving the compound in boiling ethanol (310 mL), followed by the addition of water (205 mL). The flask was allowed to stand overnight at room temperature. The light-brown crystals were collected by filtration and washed with water, and dried by vacuum to give 99.3 g (88.7 % yield) of pure 2,7-bis(N,N-diethylcarbamoyloxy)naphthalene **3**.

Melting point	89 – 91°C; lit. 89 – 90°C[10]
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.80 (d, *J* = 9.0 Hz, 2H); 7.51 (d, *J* = 2.2 Hz, 2H); 7.24 (dd, *J* = 2.2 Hz, 8.9 Hz, 2H); 3.50-3.41 (m, 8H); 1.29-1.23 (m, 12H)


0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (f1)

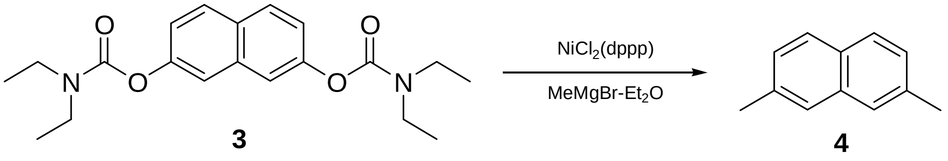
2.4.4. 2,7-Dimethylnaphthalene 4

2.4.4.1. From bis(trifluoromethanesulfonyloxy)naphthalene 2



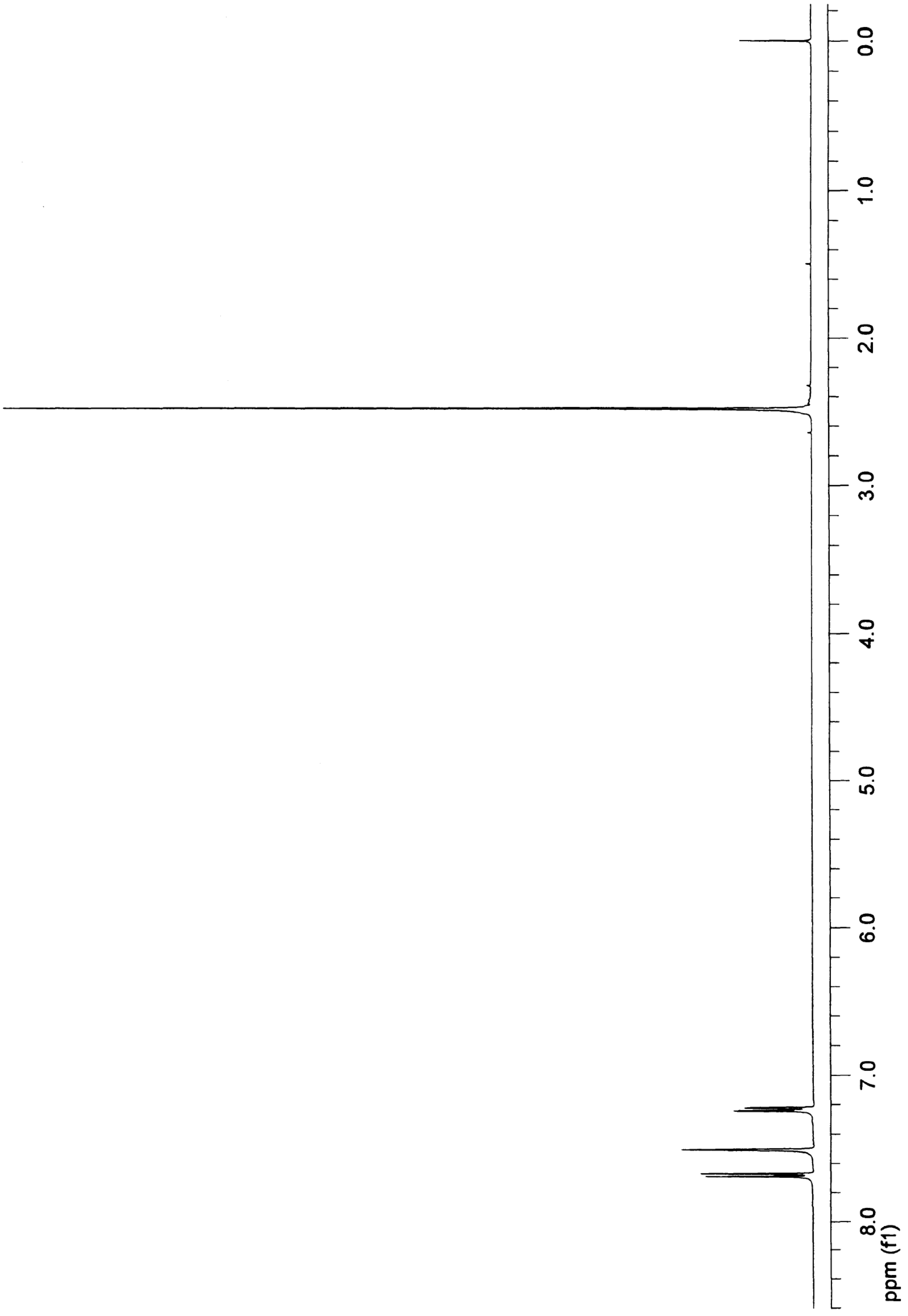
To a solution of 36 g (0.085 mol) bis(trifluoromethanesulfonyloxy)naphthalene **2** in 350 mL anhydrous dimethylformamide were added 21.4 g (0.504 mol) lithium chloride, 2.4 g (3.4 mmol) bis(triphenylphosphine)palladium (II) chloride and 61 g (0.34 mol) tetramethylstannane.[5] The resulting mixture was heated at 100°C under nitrogen for 24 hours, cooled to room temperature, and the black reaction mixture was then diluted with 500 mL 10% aqueous ammonium hydroxide. Extraction with 400 mL diethyl ether was followed by washing of the organic layer with 100 mL portions of 10% aqueous ammonium hydroxide until the aqueous layer was clear. The ether layer was washed twice with water and once with saturated sodium chloride, dried over magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure. The crude product was chromatographed through a short silica column with hexane as an eluent to give 11.5 g (80%) of 2,7-dimethylnaphthalene **4** as a white solid. See section 2.4.4.2 for characterization data.

2.4.4.2. From 2,7-bis(N,N-diethylcarbamoyloxy)naphthalene 3



A 2-L, three-necked, round-bottomed flask is equipped with a mechanical stirrer, a reflux condenser, and a pressure-equalizing dropping funnel.[10] All the glassware were oven-dried before assembly. The flask is charged with 2,7-bis(N,N-diethylcarbamoyloxy)naphthalene **3** (75.0 g, 0.209 mol), the catalyst $NiCl_2(dppp)_2$ (2.04 g, 3.76 mmol, 1.8 mol % relative to 2,7-bis(N,N-diethylcarbamoyloxy)naphthalene) and anhydrous diethyl ether (600 mL) under a flow of nitrogen. A red mixture is obtained. The dropping funnel was charged with an ethereal solution of methylmagnesium bromide (3 M in diethyl ether, 250 mL, 0.750 mol) which was added dropwise over 30 minutes. During the addition, the reaction mixture changes from red to pale brown and to pale green. The mixture is stirred at room temperature to 30°C overnight. The resulting dark brown mixture was cooled in an ice bath, and the dropping funnel is charged with hydrochloric acid (6 M, 350 mL), which is added slowly to the reaction mixture over 30 minutes. The aqueous layer was separated and extracted once with diethyl ether. The combined organic layers were washed with aqueous hydrochloric acid (6 M), distilled water, saturated sodium chloride solution, and dried over anhydrous magnesium sulfate. After filtration and evaporation of the solvent, the compound was dried under reduced pressure to give 33.01 g of crude product, a cream-colored solid. The crude product is recrystallized from boiling ethanol to give fluffy white crystals of 2,7-dimethylnaphthalene **4** (28.7 g, 88 % yield).

Melting point	96-98°C; lit. 95-96°C[10]
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.68 (d, *J* = 8.4 Hz, 2H); 7.51 (s, 2H); 7.23 (d, *J* = 8.4 Hz, 2H); 2.48 (s, 6H)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3.0
4.0
5.0
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7.0
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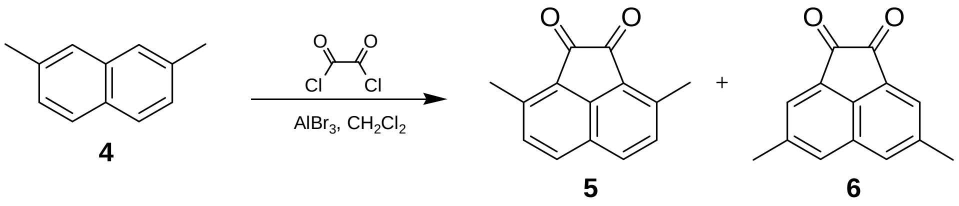
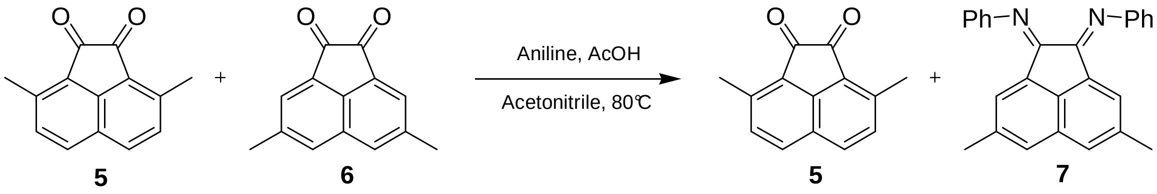
ppm (f1)

2.4.5. 3,8-Dimethylacenaphthenequinone 5 and 4,7-Dimethyacenapthequinone 6



A dry 2-L round-bottomed flask was charged with 1.5 L of anhydrous dichloromethane and cooled to between -15°C and -40°C in a bath of ethylene glycol and dry ice. Under a flow of nitrogen, $AlBr_3$ (100 g, 0.375 mol) was added, and a pressure-equalizing dropping funnel was installed. Separately, a solution was prepared of 2,7-dimethylnaphthalene (27.00 g, 0.173 mol), oxalyl chloride (15.0 mL, 0.174 mol), and anhydrous dichloromethane (200 mL).[11] The dropping funnel was charged with this separately-prepared solution, and it was added dropwise over 30 minutes with vigorous stirring. The mixture was stirred at the same temperature for an additional 4.5 hours, and then slowly brought to room temperature over one hour. The reaction mixture was then quenched by pouring the reaction mixture in 1.5 L of ice water. The resulting organic layer was washed three times with water, once with saturated sodium chloride solution, and then dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a crude product as a yellow powder. A short silica gel plug with dichloromethane as an eluent is used to separate the two isomers from the crude product. The obtained mixture appeared to be a 4:1 ratio of 3,8-dimethylacenaphthenequinone **5** to 4,7-dimethyacenapthequinone **6** as determined by NMR integrals. The isomer mixture yielded 32.43 g (89.3 % yield) of a yellow powder. The mixture was taken on to the next step to be purified.

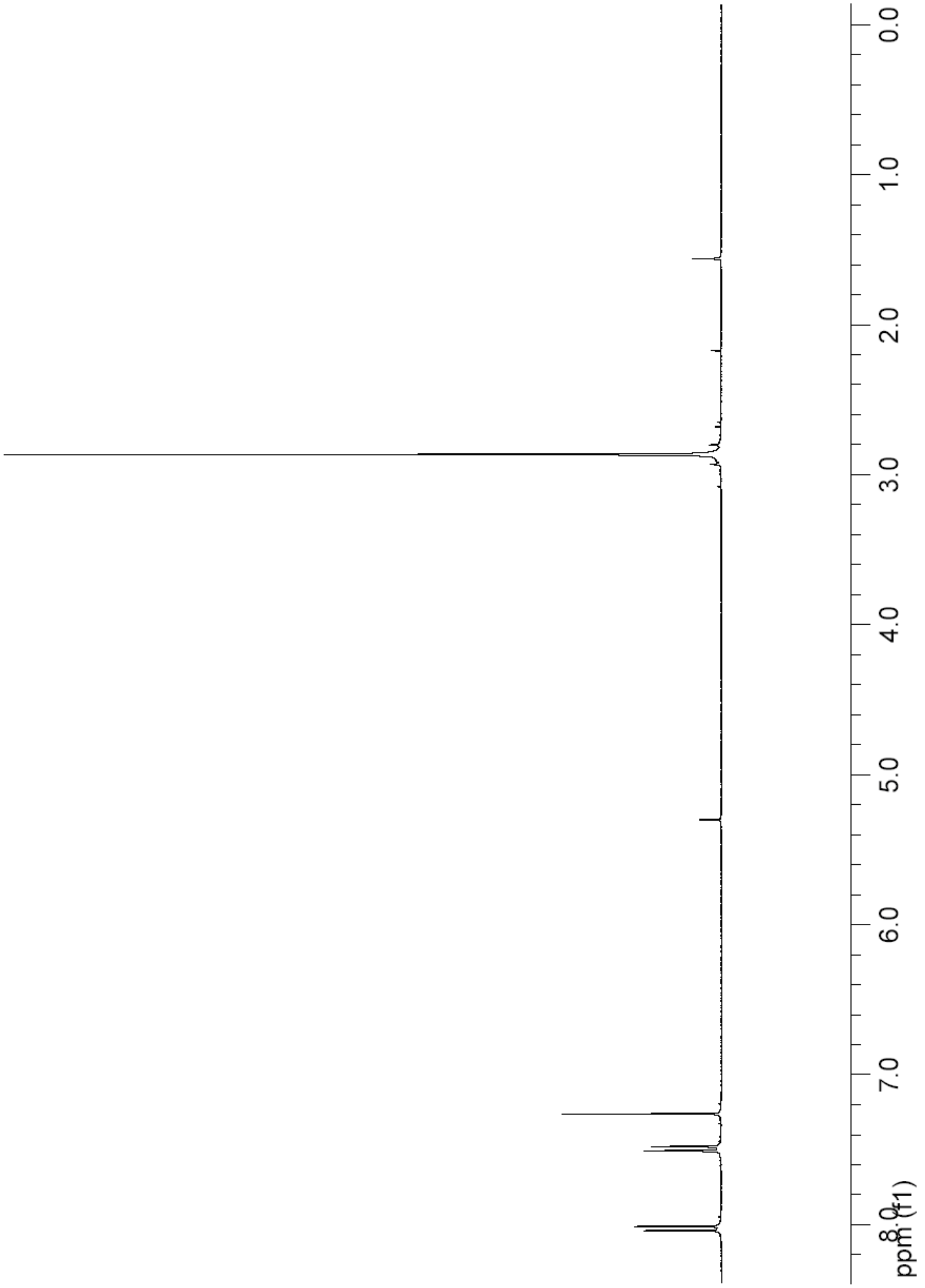
2.4.6. 3,8-Dimethylacenaphthenequinone 5



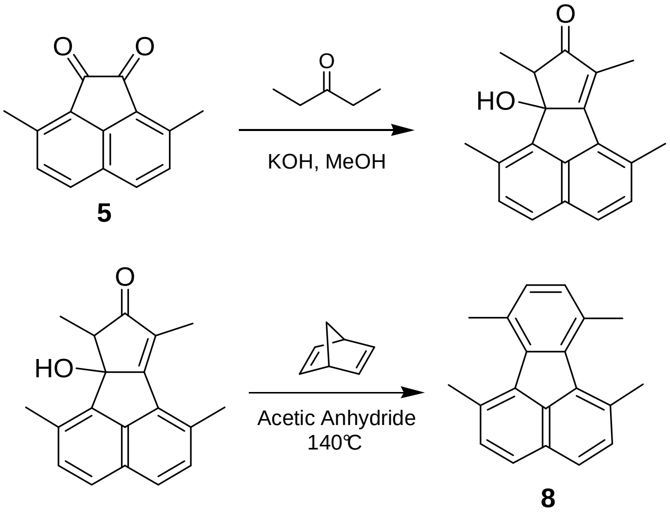
In a 2-L round-bottomed flask was prepared a solution of the dimethylacenaphthequinone isomers (25.30 g, 0.120 mol) and 1 L acetonitrile. A condenser was installed, and the solution was heated under reflux (80°C) for 30 minutes. Then acetic acid was added (161 mL), and the heating was continued until all of the dimethylacenaphthequinone had completely dissolved. To this hot solution aniline (13.2 mL, 0.145 mol) was added directly, and the solution was heated under reflux for an additional 1.5 – 2 hours.[12] The solution was then cooled to room temperature and poured into ice water to precipitate the products. The crude product is a mixture of 3,8-dimethylacenaphthenequinone and (N,N'E,N,N'E)-N,N'-(4,7-dimethylacenaphthylene-1,2-diylidene)dibenzenamine (24.86 g). The quinone is easily separated from the imine using a silica gel column with a 1:1 dichloromethane:hexane solution as the eluent to give the pure product **5** as a yellow solid (18.03 g, 63.6 % yield from **4**, over two steps).

3,8-dimethylacenaphthenequinone **5**

Melting point	206-208°C; lit. 206-207°C[13]
^{1}H NMR (400 MHz, $CDCl_3$)	δ 8.02 (d, *J* = 8.8 Hz, 2H); 7.49 (d, *J* = 8.4 Hz, 2H); 2.87 (s, 6H)


0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (f1)

2.4.7. 1,6,7,10-Tetramethylfluoranthene 8



A 1-L round-bottomed flask was charged with a solution of 3,8-dimethylacenaphthenequinone **5** (13.60 g, 0.065 mol) and 3-pentanone (6.9 mL, 0.065 mol) in methanol (500 mL).[14] Separately was prepared a solution of potassium hydroxide (11 g, 2+ equivalents) in methanol (90 mL), which was added to the flask after the potassium hydroxide had completely dissolved. The solution was stirred at room temperature for 3 hours and then diluted with water (400 mL) and neutralized with 10% hydrochloric acid solution until the pH became acidic. In order to extract the product, the solution was washed with dichloromethane (2 x 250 mL). The resulting organic layer was washed with water (2 x 100 mL), saturated sodium chloride solution (150 mL), and dried over anhydrous magnesium sulfate. After filtration and evaporation of the solvent, the compound was dried under reduced pressure.

The crude, oily intermediate product was transferred to a sealable reaction vessel, and 2,5-norbornadiene (50 mL, 0.494 mol) and acetic anhydride (150 mL) were added to the flask. The vessel was sealed and placed in an oil bath at 140°C for 3 days. The reaction mixture was then cooled to room temperature and diluted with dichloromethane (200 mL). The solution was then neutralized slowly with 10% aqueous sodium hydroxide (250 mL), adding ice constantly to avoid overheating, and washed with water (2 x 200 mL) and saturated sodium chloride solution (200 mL). The organic layer was dried over anhydrous magnesium sulfate and filtered, and the solvent was evaporated to yield a brown solid. The crude product was purified using a silica column with hexane as the eluent to yield 1,6,7,10-tetramethylfluoranthene **8** as a light yellow solid (10.01 g, 59.9% yield for two steps).

Melting point	145 – 147°C*
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.69 (d, *J* = 8.0 Hz, 2H); 7.37 (d, *J* = 8.0 Hz, 2H); 7.12 (s, 2H), 2.85 (s, 6H); 2.76 (s, 6H)

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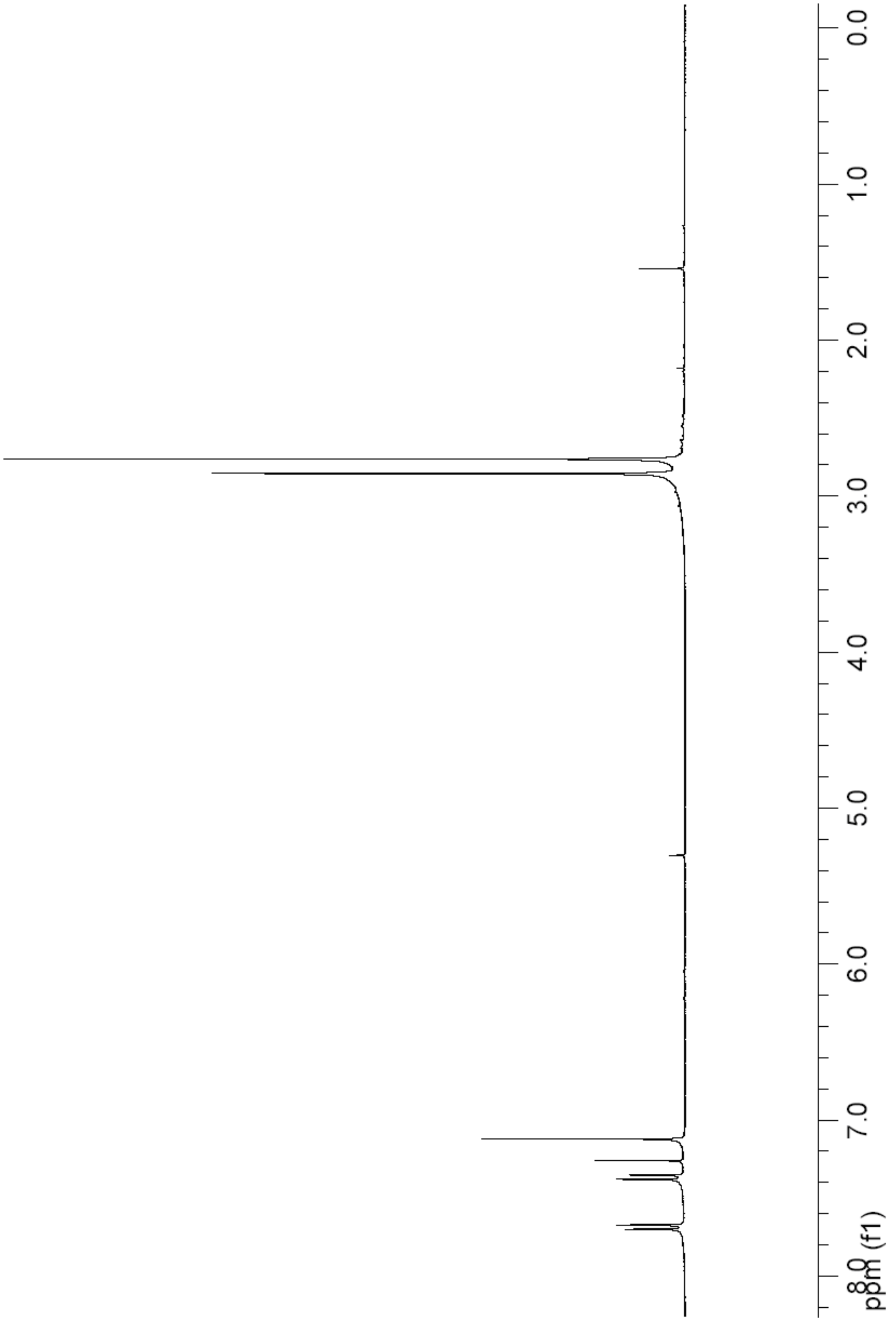
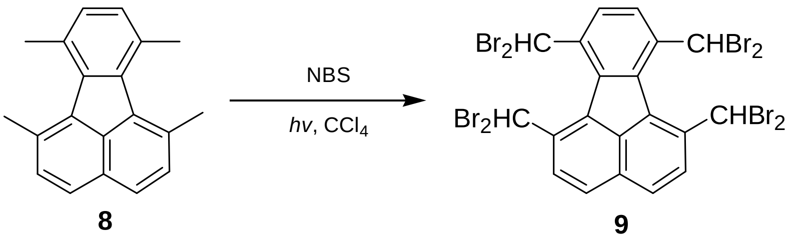
* Literature melting point available from Jay S. Siegel (jss@oci.unizh.ch)


0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (f1)

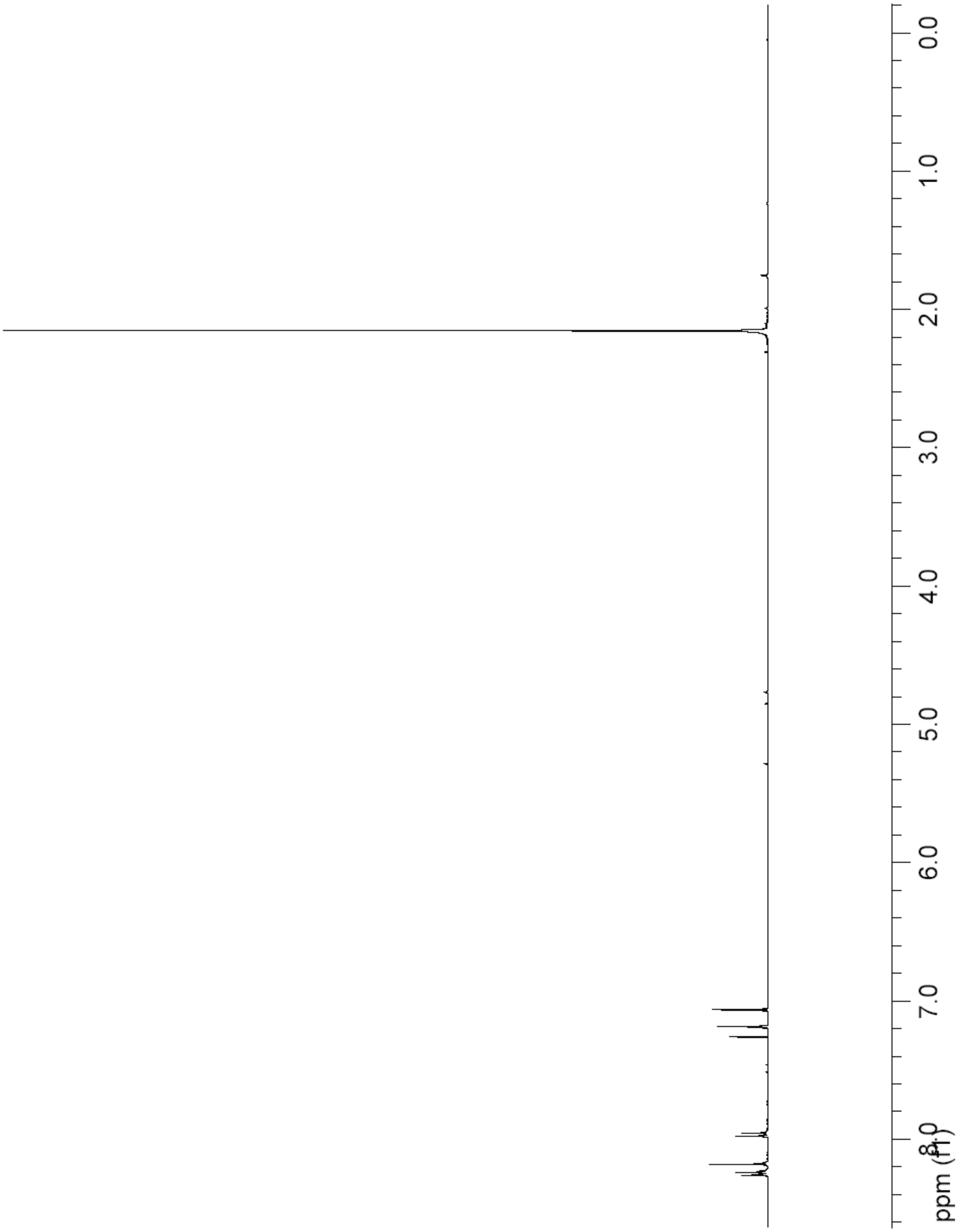
2.4.8. 1,6,7,10-Tetrakis(dibromomethyl)fluoranthene 9



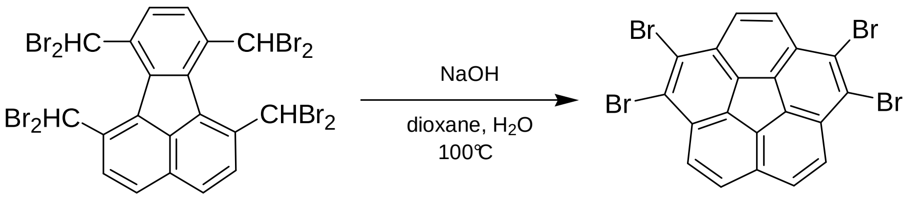
To a 1-L round-bottomed flask equipped with a magnetic stirrer and a condenser were added 1,6,7,10-tetramethylfluoranthene (9.75 g, 0.038 mol), N-bromosuccinimide (69.0 g, 0.39 mol), and benzoyl peroxide (~50 mg) in carbon tetrachloride (500 mL).[2] The reaction mixture was irradiated with incandescent light and refluxed overnight. The reaction mixture was cooled to room temperature, and the carbon tetrachloride was evaporated under reduced pressure. The obtained solid was dissolved in dichloromethane (250 mL) and washed with 10% aqueous sodium thiosulfate (3 x 150 mL), water, (200 mL) saturated sodium chloride solution (200 mL), dried over anhydrous magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure. The obtained crude product was chromatographed on a silica gel column using hexane as an eluent to afford the 1,6,7,10-tetrakis(dibromomethyl)fluoranthene **9** as a yellow solid (28.6 g, 85.2 % yield).

Melting point	266 – 268°C (decomposition observed at 250°C, color changing from yellow to black); lit. 274 – 276°C[15]

^{1}H NMR (400 MHz, $CDCl_3$)	δ 8.25 (d, *J* = 8.8 Hz, 2H); 8.18 (s, 2H); 7.97 (d, *J* = 8.8 Hz, 2H); 7.19 (s, 2H); 7.06 (s, 2H)


0.0
1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (f1)

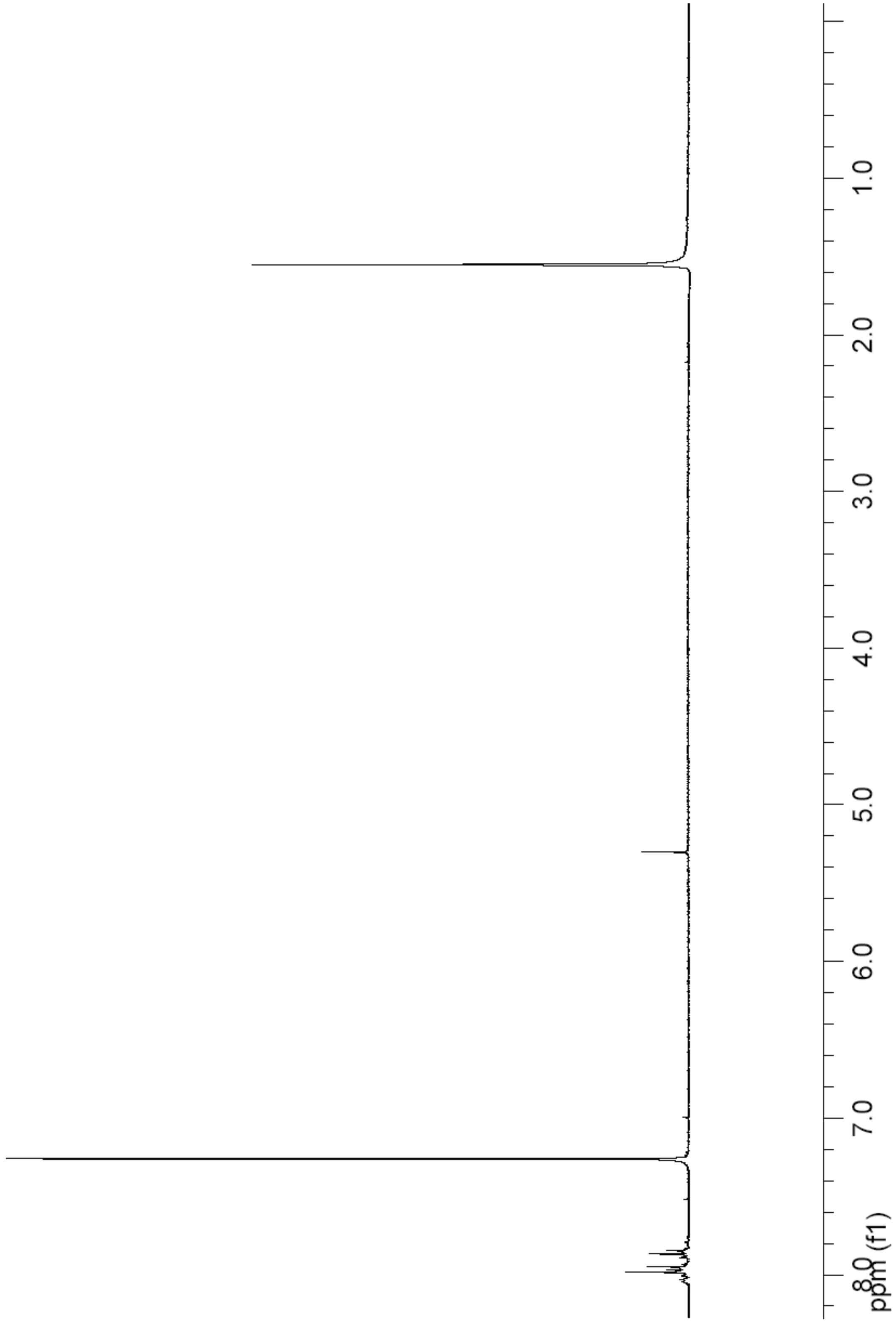
2.4.9. 1,2,5,6-Tetrabromocorannulene 10



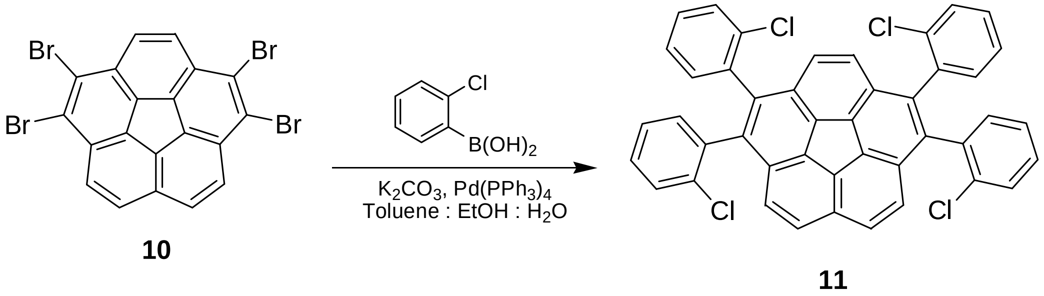
9 **10**

To a 500-mL round-bottomed flask equipped with a condenser was added 1,6,7,10-tetrakis(dibromomethyl)fluoranthene **9** (5.00 g, 5.6 mmol), dioxane (200 mL), and water (80 mL), and the solution was heated to reflux (~100°C). With vigorous stirring, sodium hydroxide pellets (3.0 g, excess) were added to the refluxing solution.[7] The reaction mixture was refluxed for 15 minutes. The solution's original red-brown color faded, eventually becoming gray-white. The reaction mixture was cooled to room temperature, diluted with 200 mL water, and 10% aqueous hydrochloric acid was added until the mixture was acidic. The light yellow precipitate was filtered, washed with water, dichloromethane, and acetone. The product was boiled in 150 mL dichloromethane under vigorous stirring for 1 hour. Filtration of the precipitate gave the pure product **10** as a light yellow solid (2.71 g, 85% yield).

Melting point	340 – 342°C (decomposed); lit. 338-340°C[16]
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.98 (s, 2H); 7.96 (d, *J* = 8.8 Hz, 2H); 7.86 (d, *J* = 8.8 Hz, 2H)


1.0
2.0
3.0
4.0
5.0
6.0
7.0
8.0
ppm (f1)

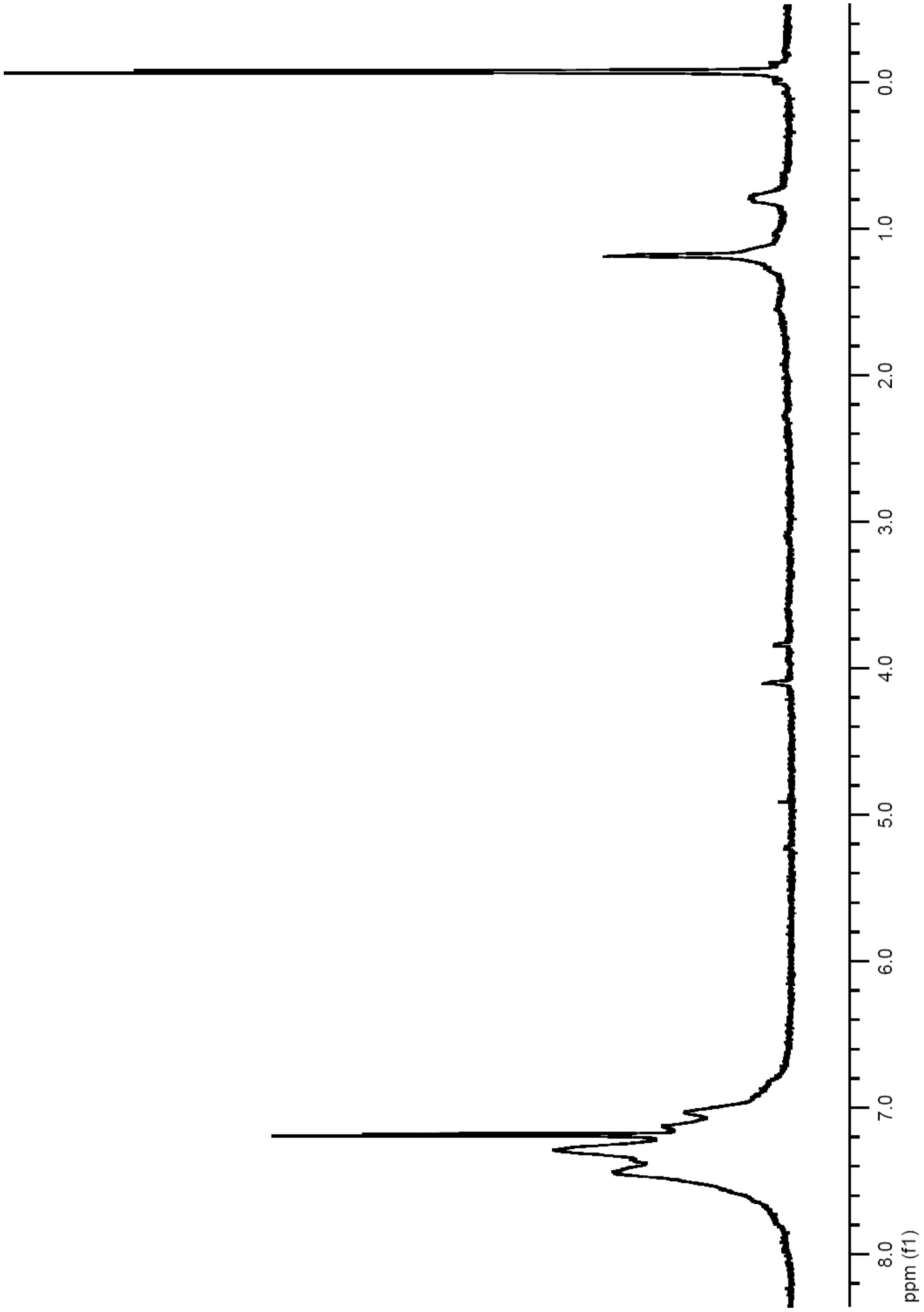
2.4.10. 1,2,5,6-Tetrakis(ortho-chlorophenyl)corannulene 11



To an oven-dried Schlenk flask with a magnetic stirrer were added 1,2,5,6-tetrabromocorannulene **10** (200 mg, 0.360 mmol), 2-chlorophenylboronic acid (266 mg, 1.71 mmol), $Pd(PPh_3)_4$ (165 mg, 0.140 mmol), potassium carbonate (589 mg, 4.27 mmol), and a solvent emulsion composed of 8 mL toluene, 8 mL ethanol, and 4 mL water.[7] The flask was heated at 100°C for 24 hours under nitrogen. The reaction mixture was cooled to room temperature, diluted with 50 mL methylene chloride, and filtered through a silica gel plug. The filtrate was washed once with 10% aqueous hydrochloric acid solution, twice with water, once with saturated sodium chloride solution, dried over magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure. The resulting crude material was chromatographed using a silica gel column and a 1:4 dichloromethane:hexane solution as an eluent to give a mixture of stereoisomer of 1,2,5,6-tetrakis(ortho-chlorophenyl)corannulene **11** as a yellow solid (181 mg, 74% yield).

Mixture of isomers

^{1}H NMR (400 MHz, $CDCl_3$) δ multiple broad signals between 7.68 – 6.85 (m, 22H)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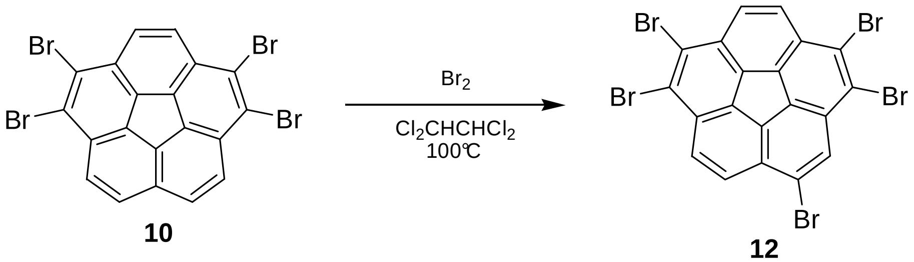
8.0
ppm (f1)

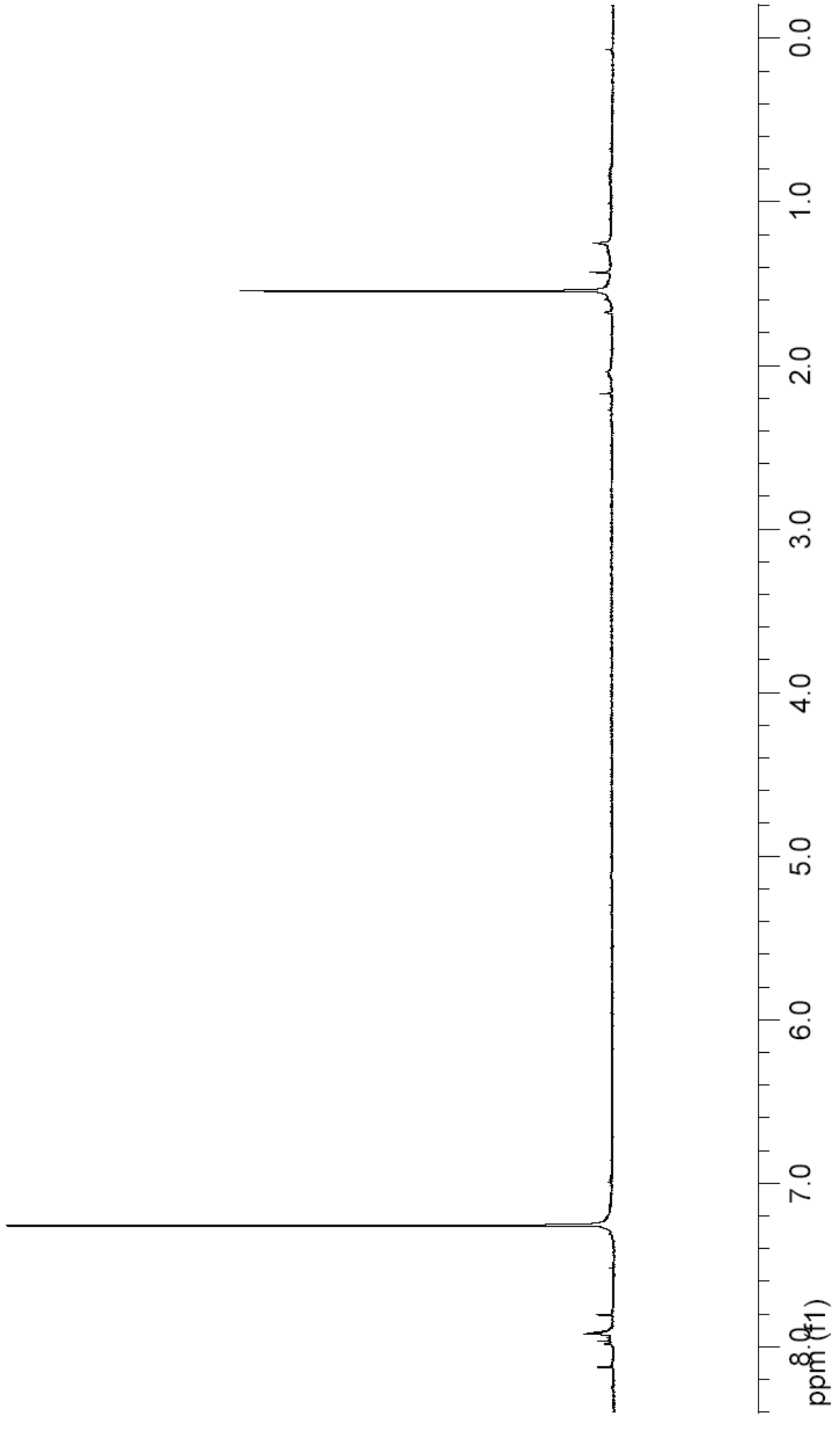
2.4.11. 1,2,5,6,8-Pentabromocorannulene 12



10 **12**

A 300-mL pressure vessel equipped with a magnetic stirrer was charged with 400 mg (0.71 mmol) 1,2,5,6-tetrabromocorannulene **10** and 45 mL 1,1,2,2-tetrachloroethane. The flask was heated at 100°C and stirred vigorously for 30 minutes. A solution of 0.038 mL (0.74 mmol) bromine in 5 mL 1,1,2,2-tetrachloroethane was added to the suspension of 1,2,5,6-tetrabromocorannulene. The flask was closed, and the reaction mixture was stirred for an additional 5 hours at 100°C. The reaction was cooled to room temperature, and the precipitate was separated by vacuum filtration. The precipitate was washed with acetone and dried under reduced pressure. Because some unreacted starting material and over-brominated product are present, a recrystallization from diphenyl ether gave the pure product **12** as yellow-white needle crystals (410 mg, 90% yield).

Melting point	330-332°C (decomposition at 324°C, compound became black)
^{1}H NMR (500 MHz, $CDCl_3$)	δ 8.13 (s, 1H); 7.98 (d, *J* = 8.0 Hz, 1H); 7.96 (d, *J* = 8.0 Hz, 1 H); 7.92 (d, *J* = 8.0 Hz, 1H); 7.81 (d, *J* = 8.0 Hz, 1H)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1.0
2.0
3.0
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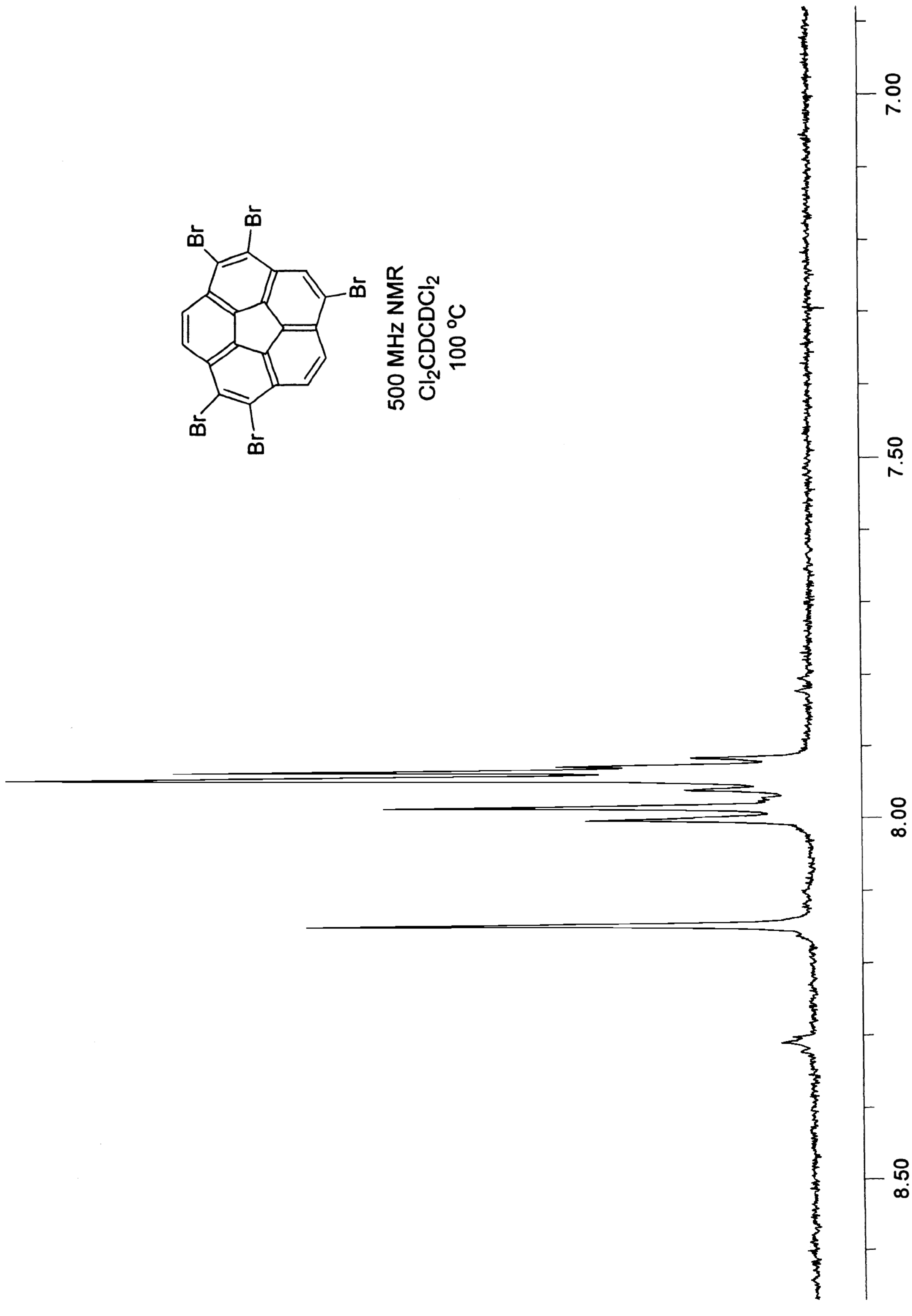
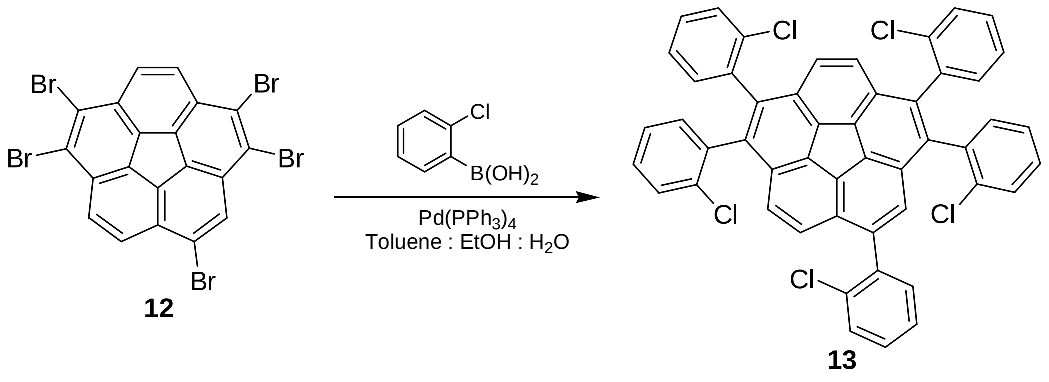
5.0
6.0
7.0
8.0
ppm (t1)



500 MHz NMR
$Cl_2CDCDCl_2$
100 °C

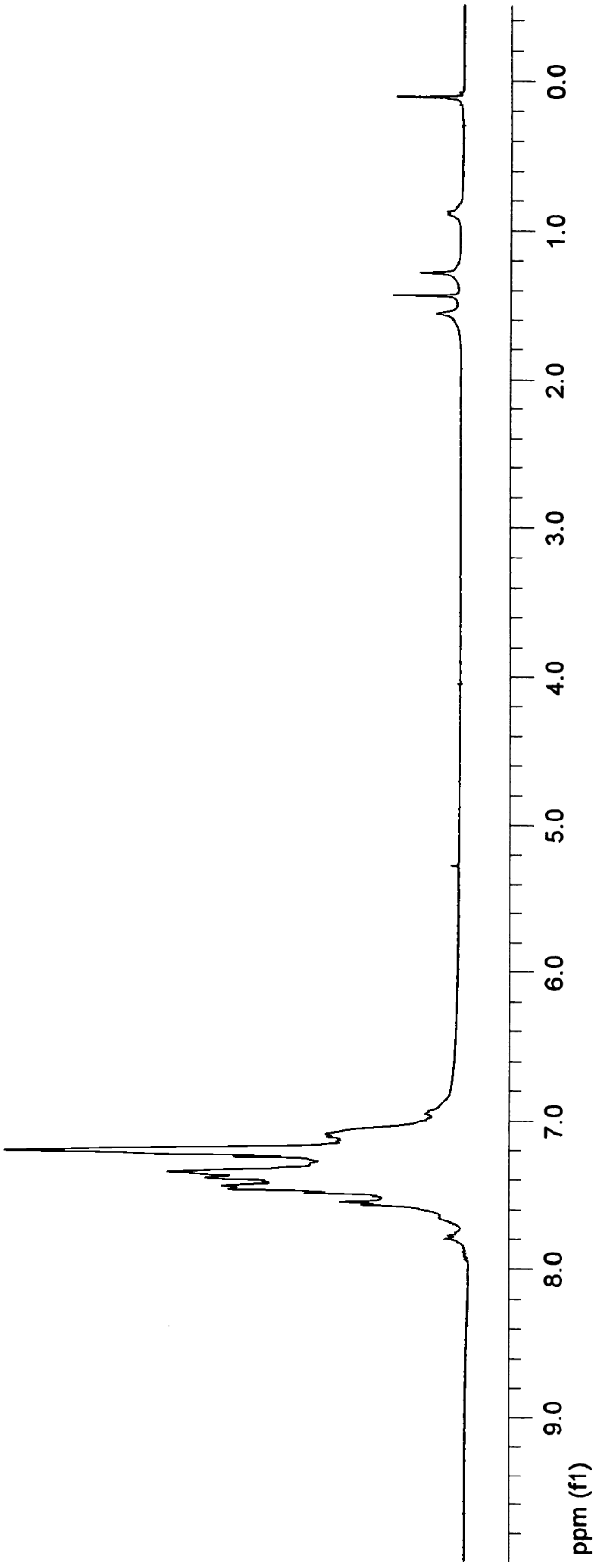
2.4.12. 1,2,5,6,8-pentakis(*ortho*-chlorophenyl)corannulene 13



To an oven-dried Schlenk flask with a magnetic stirrer were added 1,2,5,6,8-pentabromocorannulene **12** (400 mg, 0.620 mmol), 2-chlorophenylboronic acid (576 mg, 3.68 mmol), $Pd(PPh_3)_4$ (356 mg, 0.308 mmol), potassium carbonate (1.27 g, 9.19 mmol), and a solvent emulsion composed of 8 mL toluene, 8 mL ethanol, and 4 mL water. The flask was heated at 100°C for 24 hours under nitrogen. The reaction mixture was cooled to room temperature, diluted with 150 mL methylene chloride, and filtered through a silica gel plug. The filtrate was washed once with 10% aqueous hydrochloric acid solution, twice with water, once with saturated sodium chloride solution, dried over magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure. The resulting crude material was chromatographed using a silica gel column and a 1:5 dichloromethane:hexane solution as an eluent to give a mixture of stereoisomers of 1,2,5,6,8-pentakis(*ortho*-chlorophenyl)corannulene **13** as a yellow solid (455mg, 91.3% yield). All attempts to isolate the isomers using silica gel or alumina preparative separations failed.

Mixture of isomers

^{1}H NMR (400 MHz, $CDCl_3$) δ multiple broad signals between 7.60 – 7.00 (m, 25H)



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3.0
4.0
5.0
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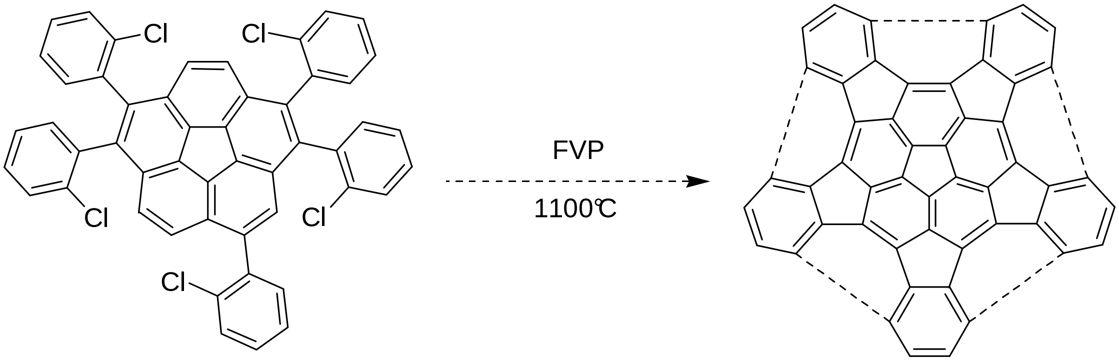
9.0
ppm (f1)

2.4.13. Attempted synthesis of $C_{50}H_{10}$ or Pentaindenocorannulene

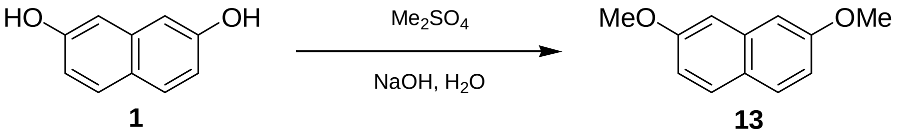


13

Flash vacuum pyrolysis was performed on a 200 mg sample of 1,2,5,6,8-pentakis(ortho-chlorophenyl)corannulene **13** at 1100°C with a steady flow of nitrogen carrier gas (final pressure 0.7-0.9 mm Hg) as previously described†. The temperature of the boat area was raised gradually, and the final temperature reached 230°C over 4 hours. The entire compound from the boat was sublimed and went through the tube. The crude pyrolysate (10 mg, mass recover 5%) was subjected to a silica plug with dichloromethane as an eluent to get rid of the insoluble side products. The filtrate was subject to semi-preparative reversed-phase HPLC with acetonitrile as an eluent. ^{1}H NMR spectra were too complicated to analyze the results due to mixtures of products, so MALDI was utilized. The results showed evidence of pentaindenocorannulene and up two closures toward a $C_{50}H_{10}$ geodesic cap, although all attempts at separation failed due to low solubility.‡

[†] See pages 10-11
[‡] See page 29

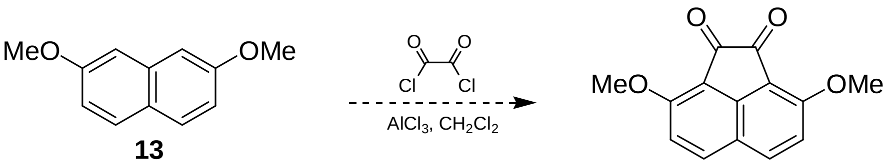
2.4.14. 2,7-Dimethoxynaphthalene 13



To a 1-L round-bottomed flask were added 2,7-dihydroxynaphthalene **1** (50.62 g, 0.316 mol) in 2 M sodium hydroxide solution (415 mL, 0.948 mol).[17] Dimethyl sulfate (138.80 g, 1.10 mol) was carefully added to the resulting, vigorously stirred solution at room temperature. After 1 hour, additional portions of 5 M sodium hydroxide solution (175 mL, 0.875 mol) were added. After 1 more hour at room temperature, the reaction was heated to reflux for 1 hour. The mixture was cooled to room temperature and extracted twice with diethyl ether. The combined ether layers were washed with 5 M sodium hydroxide, once with water, once with saturated sodium chloride solution, dried over magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure. Recrystallization with acetone gave the pure product 2,7-dimethoxynaphthalene **13** as a colorless crystalline solid (52.41 g, 88.1% yield). All spectroscopic data were similar to the reported values.[18]

Melting point	137 – 141°C; lit. 138°C[18]

2.4.15. Attempted synthesis of 3,8-dimethoxyacenaphthenequinone



A dry round-bottomed flask under nitrogen was charged with 50 mL of anhydrous dichloromethane and cooled to between -15°C and -40°C in a bath of ethylene glycol and dry ice. Under a flow of nitrogen, $AlCl_3$ (1.42 g, 10.6 mmol) was added and a pressure-equalizing dropping funnel was installed. Separately a solution was prepared of 2,7-dimethoxynaphthalene (1.00 g, 5.31 mmol), oxalyl chloride (0.46 mL, 5.31 mmol), and anhydrous dichloromethane (10 mL). The dropping funnel was charged with this separately-prepared solution and it was added dropwise over 30 minutes with vigorous stirring. The mixture was stirred at the same temperature for an additional 5 hours, and then slowly brought to room temperature. The reaction mixture was then quenched by pouring the reaction mixture in 100 mL of ice water. The resulting organic layer was washed three times with water, once with saturated sodium chloride solution, and then dried over anhydrous magnesium sulfate. Evaporation of the solvent gave a crude mixture as a yellow-brown sticky solid (0.45 g, 45% mass recovery). Initial silica gel chromatography failed to isolate the desired product before this step was scrapped.§

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§ See page 31

2.5. References

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[5] (a) Adaptation of similar procedure by Echavaren, A. M.; Stille, J. K. *J. Am. Chem. Soc.* **1987**, *109*, 5478. (b) Takeuchi, M.; Tuihiji, T.; Nishimura, J. *J. Org. Chem.*, **1993**, *58*, 7388. (c) Casado, A. L.; Espinet, P.; Gallego, A. M. *J. Am. Chem. Soc.* **2000**, *122*, 11771.

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CHAPTER III:

A Symmetric Route to a $C_{50}H_{10}$ Geodesic Cap Derivative

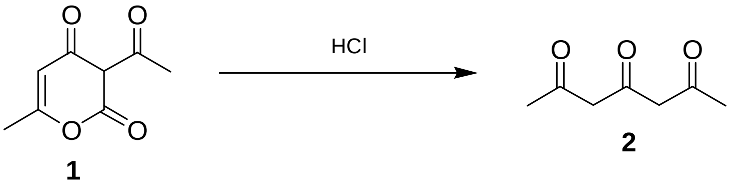
3.1. Motivation

The goal in this chapter is much the same as the previous one: to develop strategies toward a [5.5] SWNT core. We were interested in combining old synthesis (of corannulene) with new ways to perform indeno-annulations around the corannulene core. By indeno-annulations we mean the method of adding to a PAH a new five-membered ring that is fused to a benzene ring (an indeno group). Because all fullerene fragments are composed of five-membered rings surrounded by six-membered rings, the ability to add these basic structures repetitively will prove to be ultimately essential in the synthesis of a [5.5] SWNT. New strategies could not only help us build new PAHs but help extend known compounds.

Lately, much interest in this field of research has been directed at the formation of these indeno-annulated PAHs.[1] Amazingly, not too many formations of PAHs that are fused to these indeno groups have been reported in the literature. Methods which have been “successful” for reactions of this nature often are carried out under harsh conditions, give a mixture of products, or give poor yields.[2] Our goal was to improve upon current strategies of indeno-annulation synthesis, and possibly develop new approaches to creating indeno-annulating PAHs.

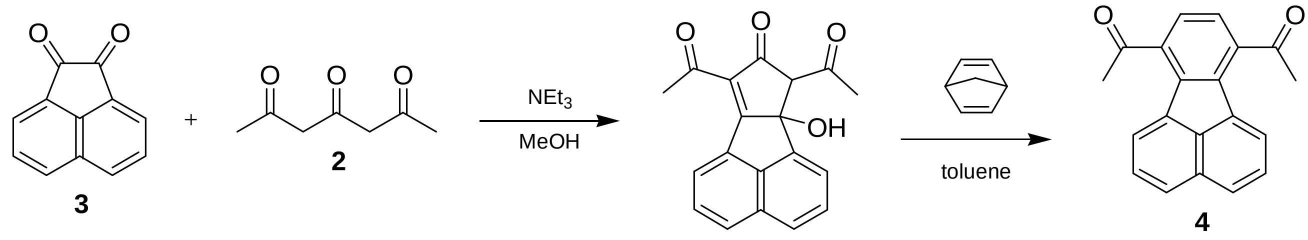
3.2. Results and Discussion

Initially, the synthesis of corannulene developed by the Scott group utilized 2,4,6-heptane trione **2** as one of the starting materials.[3] For some reason the trione became unavailable commercially, so we had to find an efficient way to synthesize it in the laboratory. The optimized procedure allows us to obtain a significant amount (>75 g) of compound **2** in a single run (Scheme 3.1). We used the starting material dehydroacetic acid **1** in a refluxing solution of hydrochloric acid, which forms 2,6-dimethyl-pyran-4-one in quantitative yield.[4] The solution is then basified and a barium hydroxide is used to trap the 2,4,6-heptane trione **2** as its barium salt. Isolation of the salt and treatment in acidic conditions releases the 2,4,6-heptane trione **2**, which is easily extracted by ether and carried on to the next step.



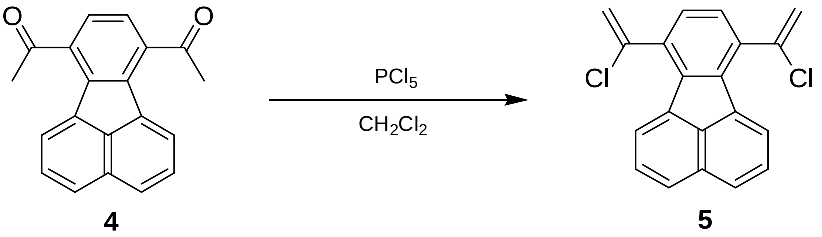
Scheme 3.1

The formation of 7,10-diacetylfluoranthene **4** was a two-step process, the first being a double Knoevanegel condensation with acenaphthequinone, done at room temperature in methanol (Scheme 3.2). The intermediate product was dried under vacuum, and the intermediate was carried on to the next step without further purification. The next step was the Diels-Alder-retro-Diels-Alder reaction with one equivalent of norbornadiene to obtain the desired product **4**.



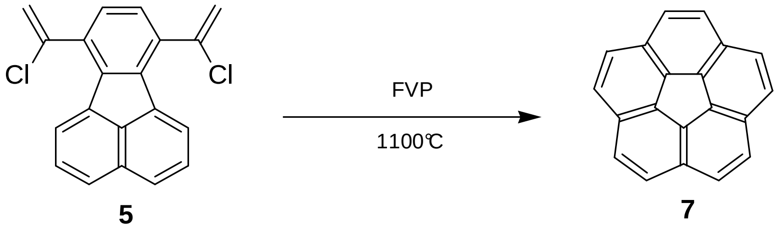
Scheme 3.2

The next step was performed at room temperature with PCl_5 to give 69% of the desired product 7,10-bis(1-chlorovinyl)fluoranthene **5** (Scheme 3.3). This reaction is done over 5 days and can be checked by TLC. If the product is under-chlorinated at the end of this period, more PCl_5 can be added and the reaction continued for a longer period until the reaction goes to completion.



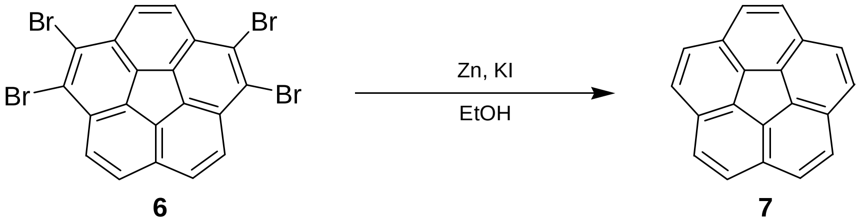
Scheme 3.3

FVP was performed in the next step on compound **5** (Scheme 3.4). The yield of corannulene **7** for this reaction varies between 20-30%, with the yield apparently having an inverse ratio to the amount of compound attempting to be pyrolyzed. The sacrifice of yield is one made for time, however, as FVP is a time-consuming process.



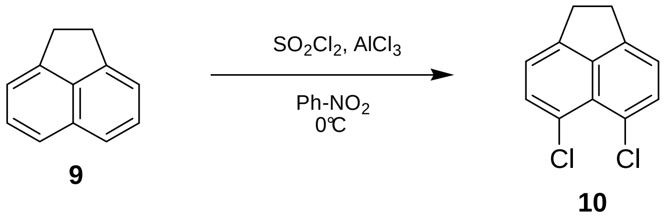
Scheme 3.4

Another way to synthesize corannulene is by the reduction of 1,2,5,6-tetrabromocorannulene **6** with zinc powder (Scheme 3.5).[4] This reaction has two advantages over the pyrolytic way to synthesize corannulene. First, it consistently has good yield (between 85% and 90%). Also, it can be scaled up to a large degree. One disadvantage, however, is that the synthetic process is longer, and the final overall yield for each of the syntheses is not significantly different.



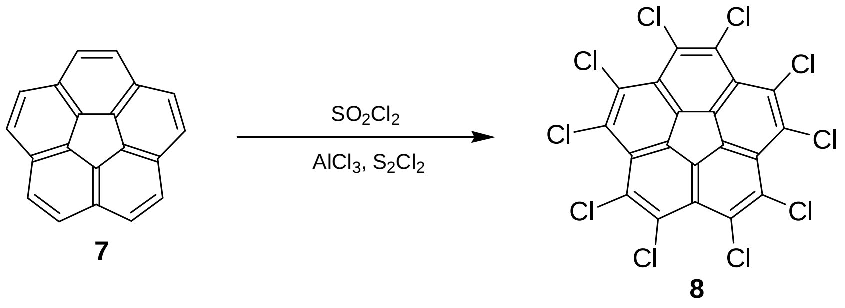
Scheme 3.5

The next step was actually attempting to add an indeno-group onto corannulene. As a test compound we prepared 5,6-dichloroacenaphthene **10** after a modified procedure of the Siegel group (Scheme 3.6).[10] The final product mixture usually contained some 3,5,6-trichloroacenaphthene in it; however, the samples were deemed pure enough to carry on to the next step.



Scheme 3.5

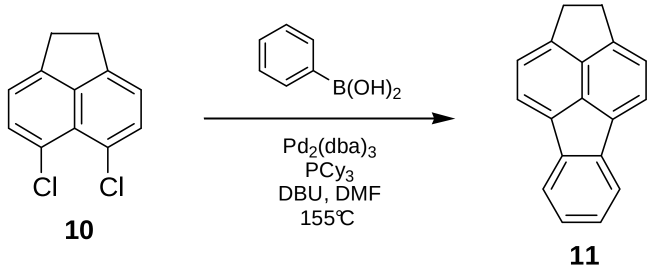
This compound seemed to be an ideal test compound for decachlorocorannulene **8**, which we are able to synthesize in almost gram-scale quantities (Scheme 3.6).[9] Decachlorocorannulene **8** has five pairs of chlorines in *peri* positions, which can be used to extend the compound to larger PAHs if we can find reactions to perform this job, specifically indeno-annulation reactions. The 5,6-dichloroacenaphthene **10** molecule has two chlorines in the *peri* position, and is an obvious fragment of **8**, so the results would hopefully not differ greatly from the test compound **10** to reactions performed on decachlorocorannulene **10**.



Scheme 3.6

The synthesis of decachlorocorannulene **8** is achieved by overchlorination of corannulene by a process developed in the Scott group a few years ago.[9] The second step consists of heating to 160 – 180°C in diphenyl ether for one day, which knocks off extra chlorines and re-aromatizes the corannulene core. The final product **8** is insoluble and is collected by filtration and a wash of dichloromethane and acetone.

The next obvious step was to try an indeno-annulation on the test compound **10**. We initially attempted a combined Suzuki coupling with phenylboronic acid followed by a Heck-type arylation to close the five-membered ring (Scheme 3.7).[11]



Scheme 3.6

Unfortunately, this reaction failed for the most part. The desired product **11** was collected in only 5% yield. The major product, however, was 5-phenylacenaphthene **21** (Figure 3.1).

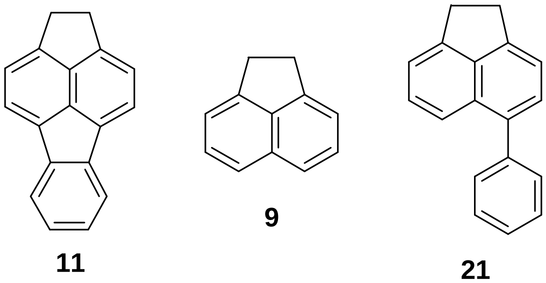
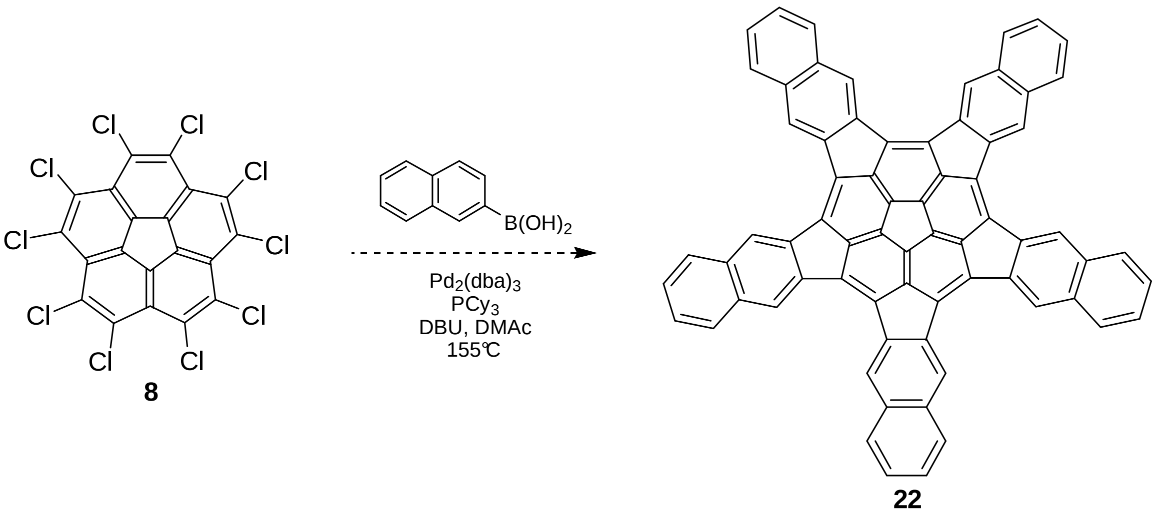


Figure 3.1. Products in the initial indeno-annulation attempt

From these results we can only conclude that the Suzuki coupling worked but the Heck-type arylation did not. Another interesting fact is that none of the compounds discovered in final mixture had any chlorines left on them. From this we can draw the conclusion that the palladium catalyst inserted into the carbon-halogen bond without being able to perform the Heck-type arylation. This is probably because after the oxidative addition of palladium(0) into the aryl halogen bond, the palladium has to coordinate with a double bond. In this instance, the coordination target is a double bond from the benzene ring; however, benzene has a highly delocalized π-system, and the aromatic stabilization most likely plays an important role in this reaction. A similar reaction was performed in the Scott group a few years ago, in which the halogen was on the phenyl ring instead of the acenaphthene.[11] Since naphthalene has a lower aromatic stabilization and the double bonds are more localized, it is probable that the coordination process of palladium is helped by coordinating with a naphthalene system instead of a benzene ring.

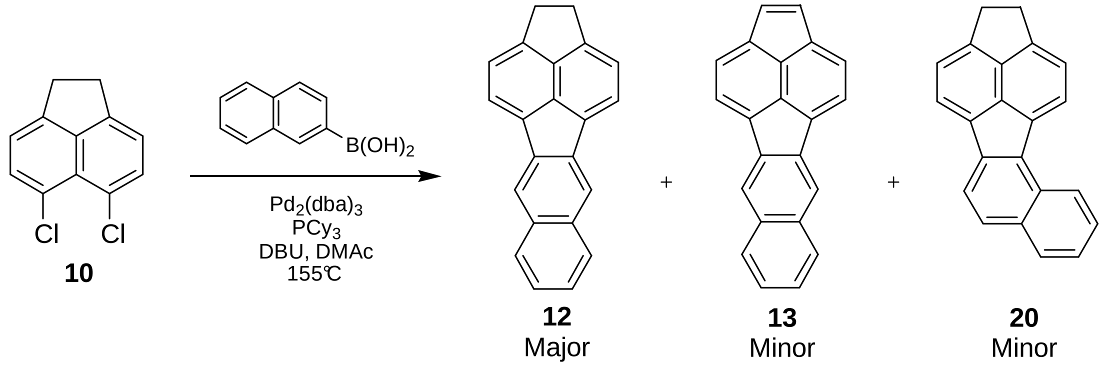
Using this line of reasoning, the next logical step was to attempt the coupling of a naphthalene unit with the test compound **10**. If this worked it would be possible to synthesize a penta-substituted corannulene with benzo-indeno groups attached instead of indeno groups around the outside **22** (Scheme3.7).



Scheme 3.7

Compound **22** looked like a good target because it is actually an extension of pentaindenocorannulene mentioned in chapter 1 (see pages 12-14). The closure of the “arms” would lead to a geodesic cap that is still in armchair formation and can just as easily be extended.

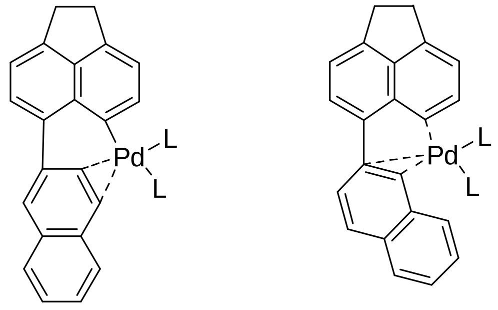
Following this logic, the next obvious step was to try the coupling with a naphthalene structure. For this process, we used the same conditions as the coupling of the benzene group, but replaced phenylboronic acid with 2-naphthylboronic acid (Scheme 3.8).[11]



Scheme 3.8

The main objective was to obtain benzo[k]1,2-dihydrocyclopenta[cd]fluoranthene **12**. On small scale (100 mg), the yield was about 20%, and was a mixture of both the desired compound benzo[k]1,2-dihydrocyclopenta[cd]fluoranthene **12** and benzo[k]cyclopenta[cd]fluoranthene **13** in a 4:1 ratio. On a larger scale (2 g), the yield went up to 25%; however, benzo[j]1,2-dihydrocyclopenta[cd]fluoranthene was then observed in the product mixture (again in a 1:4 ratio with the major product). Compound **13** is not found in the product mixture when scaled up.

We attempt to explain this by presenting possible transition states **A** and **B**, demonstrating that palladium has two choices of where to coordinate with the double bonds for the naphthalene ring. (Figure 3.2). The favored conformation is the exo coordination (**A**) which forms the major product **12**, as opposed to the endo coordination (**B**), which is geometrically more accessable.

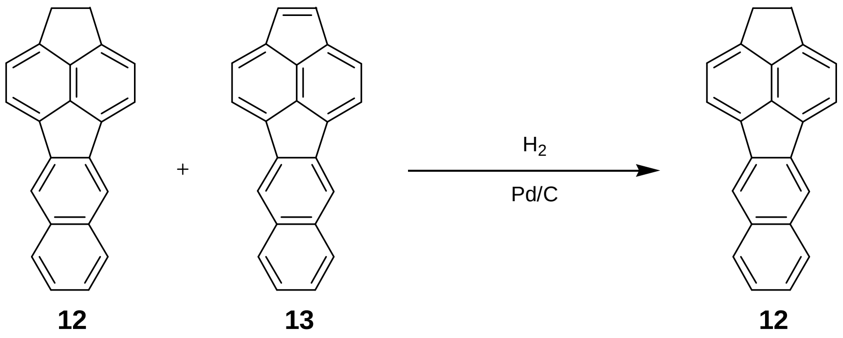


exo
A

endo
B

Figure 3.2. Transition state conformations of benzo[j/k]1,2-dihydrocyclopenta[cd]fluoranthene

On small scale, the oxidized product, benzo[k]cyclopenta[cd]fluoranthene **13**, is inseparable from **12**. This is solved by subjecting a mixture of **12** and **13** to a hydrogenation process, where the reaction mixture is completely converted to the desired product **12** in quantitative yield (Scheme 3.9).

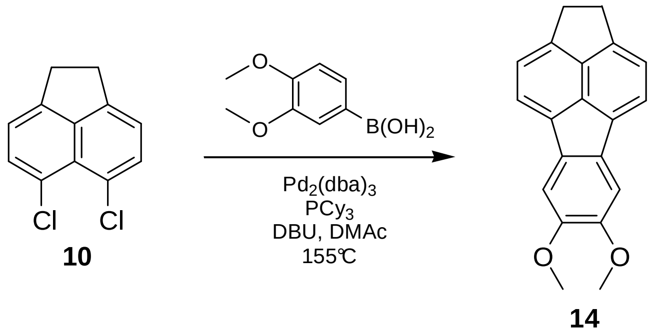


Scheme 3.9

As I stated earlier, the goal of this reaction was to test the possibility of using this reaction to couple five naphthyl groups to decachlorocorannulene **8**. Initial work done in the Scott group showed that the attempted coupling gave none of the desired product (Scheme 3.7).[11] The product mixture was inseparable; and although it appeared that at least one coupling and closure took place, no product was identified with any certainty.

Because of this, I set out to make a compound that was similar to the benzo[k]1,2-dihydrocyclopenta[cd]fluoranthene **12**, had better yield, and was directed so that the 3,4-positions were facing away from the 5-membered ring in the center. The solution that I came up with was using a phenylboronic acid with alkoxy groups at the 3,4-positions. The rationale behind this was that the alkoxy groups are electron-donating back into the benzene ring, so the electron-rich π-system would more easily coordinate with the palladium catalyst. It was our hope that the alkoxy groups would not only act as para-directors but also somewhat sterically hinder the positions ortho to them, so the 3-4 positions are as far away from the five-membered ring as possible.

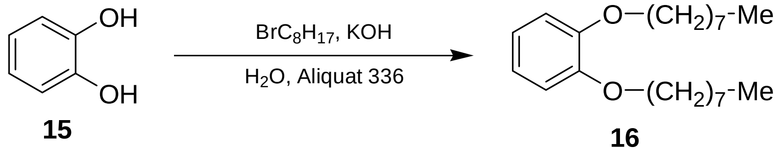
For this reaction, the only commercially available phenylboronic acid with alkoxy groups in the 3,4-positions was 3,4-dimethoxyphenylboronic acid. We used this in the same conditions as the previous two indeno-annulation reactions to get 6,7-dimethoxy-1,2-dihydrocyclopenta[cd]fluoranthene **14** in slightly more than 45% yield (Scheme 3.10).[11] Some of the product mixture consisted of the 5-(3,4-methoxy)phenylacenaphthene and acenaphthene **9**.



Scheme 3.10

The yield was deemed good enough to move on to the next step, and try to add alkoylated indeno groups to decachlorocorannulene **8**. However, when a single dimethoxy-indeno group had been added in the past to corannulene, solubility proved to be a considerable problem, and no separation of products could occur.[11] Therefore, we reasoned that using longer aliphatic chains would significantly increase the solubility and subsequently the yield for the proposed reaction. Since longer alkoxy-phenylboronic acid compounds were not commercially available, we had to synthesize our own. Arbitrarily we chose octyloxy groups to be our aliphatic chains on the phenylboronic acid.

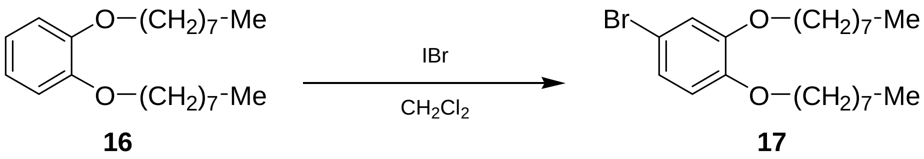
The first step in creating the phenylboronic acid was the addition of the alkoxy chains to catechol (1,2-dihydroxybenzene) **15**. This was done with octyl bromide and potassium hydroxide in water, using Aliquat 336 as a catalyst (Scheme 3.11).[13] The yield was greater than 90%, and the reaction can be scaled up to a large multi-gram scale. The pure product 1,2-bis(octyloxy)benzene **16** was then carried on to the next step.



Scheme 3.11

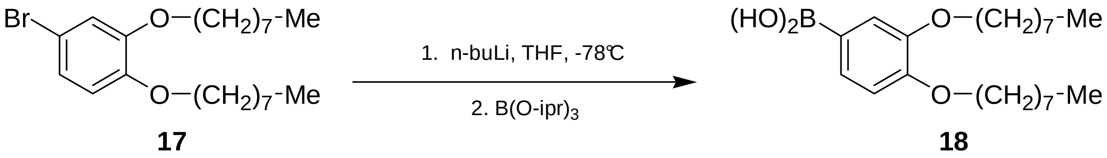
Bromination proved to be more of a problem than originally expected. Initially, we tried to brominate using 1.2 (molecular) equivalents of elemental bromine and iron filings in dichloromethane.[15] This, however, produced more of the di-brominated product than mono-brominated, and separation was difficult.

Next, we tried adding the 1,2-bis(octyloxy)benzene **16** with 1.2 equivalents of IBr in dichloromethane at room temperature for 12 hours (Scheme 3.12).[14] The result was the desired product 4-Bromo-1,2-bis(octyloxy)benzene **17** in 66% yield, which was carried on to the next step.



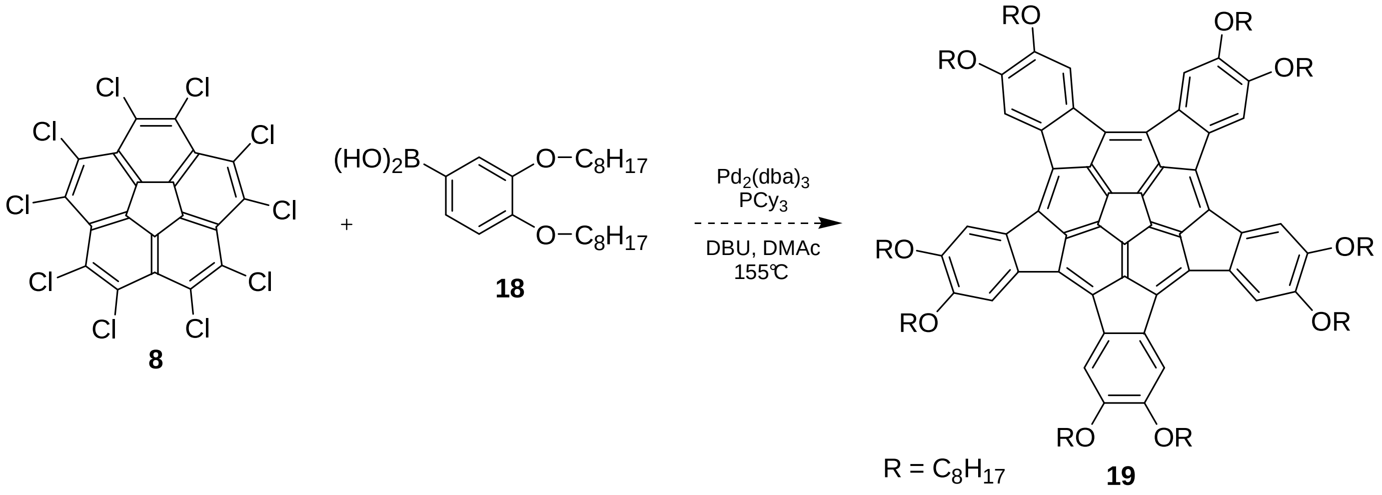
Scheme 3.12

To form the boronic acid was a two-step process (Scheme 3.13).[15] First, compound **17** was mixed with n-butyl lithium in anhydrous THF at -78°C. Then tri-isopropylborate was added, and an acid quench yielded 63% of the desired product 3,4-bis(octyloxy)phenylboronic acid **18**.



Scheme 3.13

Finally we were able to attempt the synthesis of pentakis(3,4-octyloxy)indenocorranulene. Again, the same conditions were used as in the previous reactions, and the mixture was heated at 155°C for 1 day (Scheme 3.14).[11]



Scheme 3.14

The crude product mixture was soluble; unfortunately, it looked like a few couplings and maybe some closures were made, but the NMR was too complicated to identify anything explicitly. This does, however, have much potential to be a viable route to the synthesis of a penta-indenocorannulene derivative.

3.3. Conclusion

In this part of my project I explored a particular route toward the synthesis of a penta-indenocorannulene derivative. In doing so, we explored the unusual reactivity of the *peri*-dichloro conformation of 5,6-dichloroacenaphthene **10**. We saw decent yields for the products benzo[k]1,2-dihydrocyclopentafluoranthene **12** and 6,7-Dimethoxy-1,2-dihydrocyclopenta[cd]fluoranthene **14**, although these could be improved. The attempted synthesis of compound **19** is promising; however, no outstanding conclusions could be made so far, and further progress needs to be made.

3.4. Experimental

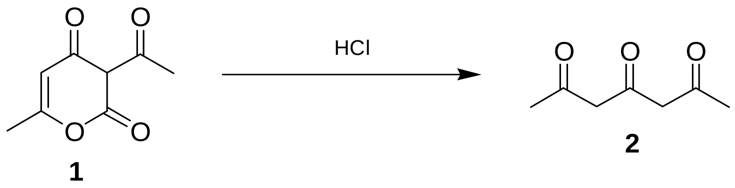
3.4.1. General

All starting materials and reagents were purchased from Aldrich chemical company or Acros chemical company without further purification. All solvents were used as purchased.

Proton and carbon NMR spectra were generated on a Varian 400 (400 MHz for ^{1}H, 100 MHz for ^{13}C) unless otherwise noted. Proton shifts are recorded relative to trimethylsilane (TMS); carbon shifts are recorded relative to deuterated chloroform.

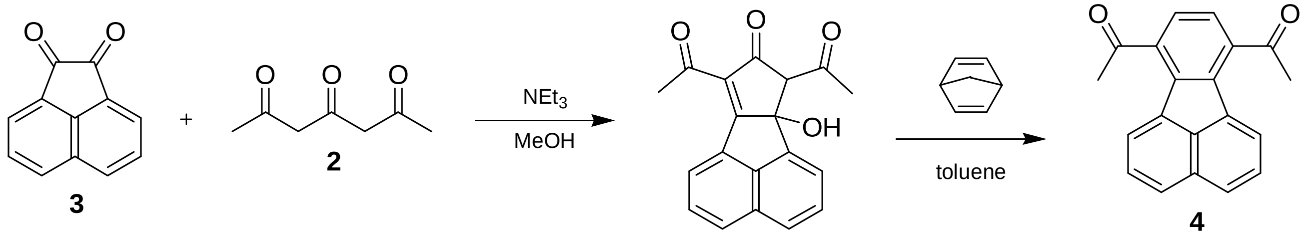
Baker 60 – 200 mesh silica gel or Aldirch almuminum oxide, activated, neutral, 150 mesh, surface area 155 m^2/g, was used for column chromatography. Preparative thin-layer chromatography was performed on 20 x 20 cm Analteech Unplate Taper plates. TLC plates were purchased from J. T. Baker. All melting points were determined using a meltemp II Melting Point Apparatus and are reported uncorrected.

3.4.2. Heptane-2,4,6-trione 2



Into a 1-L round-bottomed flask equipped with a magnetic stirrer and a condenser were added dehydroacetic acid (100 g, 0.543 mol) and concentrated hydrochloric acid (400 mL).[5] The resulting mixture was refluxed 1-2 hours until the entire solid was dissolved and the solution became homogeneous and orange. The solution was then cooled to 0°C using an ice bath, and sodium hydroxide pellets were added slowly until the solution became basic (the color of the solution changed from light yellow to dark yellow). Separately, $Ba(OH)_2{\cdot}8H_2O$ (250 g, excess) was dissolved in 1 L hot water. The two solutions were mixed, stirred for 30 minutes, and the barium salt was separated under vacuum filtration. In a 3-L flask were combined the barium salt, 1 L water, and 1 L diethyl ether. With vigorous stirring, concentrated hydrochloric acid was added dropwise until all of the barium salt was dissolved and the ether layer became yellow. At this point, heptane-2,4,6-trione **2** is in the ether layer. The organic layer was separated, dried over magnesium sulfate, filtered, and the ether was evaporated under reduced pressure, which gave heptane-2,4,6-trione **2** as a colorless liquid (76 g, 90%). The heptane-2,4,6-trione **2** can be stored in the refrigerator for a few days without decomposing. All spectroscopic data were similar to the reported values.[5]

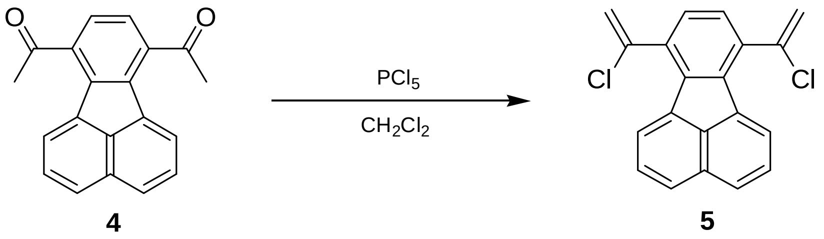
3.4.3. 7,10-Diacetylfluoranthene 4



Into a 2-L round-bottomed flask equipped with a magnetic stirrer were added heptane-2,4,6-trione **2** (71.0 g, 0.499 mol), acenaphthequinone **3** (91.2 g, 0.501 mol), triethylamine (125 mL), and methanol (1.5 L). The reaction mixture was stirred at room temperature for 3 hours, poured over 2 L cold water, and concentrated hydrochloric acid was added slowly until the mixture became acidic. One liter of water was added, and the mixture was allowed to sit for 30 minutes. The precipitate was then filtered, washed with water, and left under vacuum until it was dry. The obtained intermediate compound was used without further separation.

In a 2-L round-bottomed flask equipped with a magnetic stirrer and a condenser were added the intermediate compound (71 g, ~0.234 mol), norbornadiene (50 mL, 0.494 mol), and 500 mL toluene. The reaction mixture was refluxed for 3 days with vigorous stirring. The obtained solution was concentrated under reduced pressure. The recrystallization from the crude reaction mixture using acetone gave the pure 7,10-diacetylfluoranthene **4** as a light yellow solid (86.1 g, 64.8% yield). All spectroscopic data were similar to the reported values.[6]

3.4.4. 7,10-Bis(1-chlorovinyl)fluoranthene 5



Into a 3-L round-bottomed flask equipped with a magnetic stirrer were added 7,10-diacetyl fluoranthene **4** (46.0 g, 0.161 mol), phosphorous pentachloride (140 g, 0.672 mol), and anhydrous methylene chloride (1.5 L). The reaction mixture was stirred vigorously for 5 days.* The reaction mixture was then cooled to 0°C in an ice bath, and ice water was added until the mixture was completely quenched. The organic layer was washed twice with water, once with saturated sodium chloride solution, dried over magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure. The crude product was chromatographed on silica gel using an eluent of 4:1 hexane:methylene chloride to give 7,10-bis(1-chlorovinyl)fluoranthene **5** (35.90 g, 69.1% yield) as a yellow solid. All spectroscopic data were similar to the reported values.[6]

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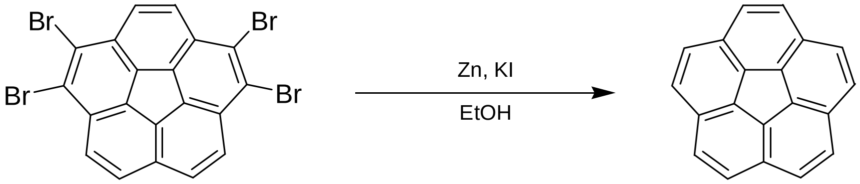
* The reaction can be checked by TLC, and if necessary more PCl_5 can be added and the reaction can be run longer until completion.

3.4.5. Corannulene 7

3.4.5.1. From 1,2,5,6-tetrabromocorranulene 6

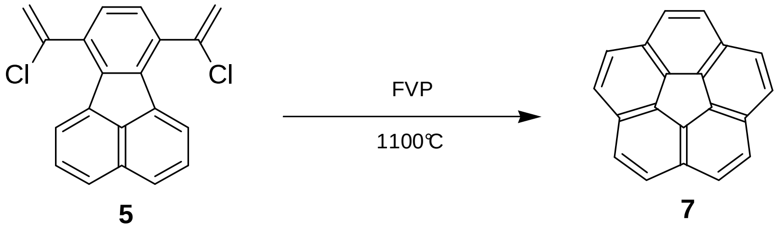


6 **7**

To a 500-mL round-bottomed flask equipped with a magnetic stirrer and a condenser was added aqueous hydrochloric acid solution (5% by mass, 0.20 mL, 0.28 mmol) to a solution mixture of 1,2,5,6-tetrabromocorannulene **6**[†], 10-micron zinc dust (200 mg, 3.06 mmol), and potassium iodide (90.0 mg, 0.542 mmol) in 250 mL ethanol.[7] The reaction mixture was refluxed for 6 hours with vigorous stirring. After evaporation of the solvent, the product was dissolved in methylene chloride and filtered through a silica plug. The filtrate was washed once with water, once with saturated sodium chloride solution, dried over magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure. The pure product **7** was given as a white solid (7.6 mg, 85%).

[†] Made in this step – see page 52.

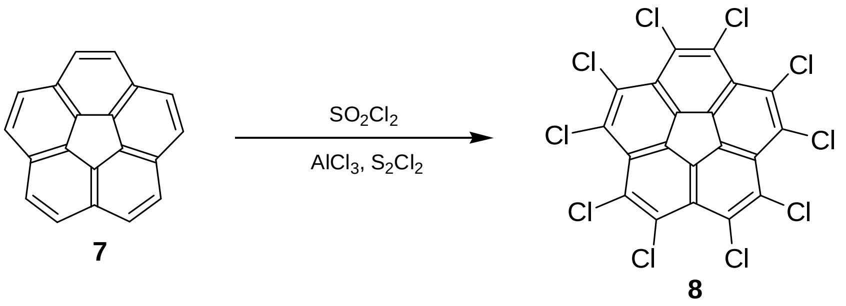
3.4.5.2. From 7,10-Bis(1-chlorovinyl)fluoranthene 5



Flash vacuum pyrolysis was performed on a sample of 7,10-Bis(1-chlorovinyl)fluoranthene (5.00 g, 20.0 mmol) at 1100°C with a steady flow of nitrogen carrier gas (final pressure 1.0 mm Hg) as previously described[8] over a period of 8-10 hours. The temperature of the boat area was raised gradually, and the entire compound from the boat was sublimed and went through the tube. The crude pyrolysate was chromatographed on an alumina column with hexane as an eluent. The yield for this reaction is between 20 and 30%. All spectroscopic data were similar with the reported ones.[6]

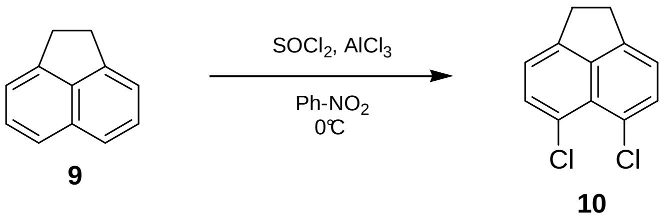
Melting point	265 – 268°C; lit. 268 – 269°C[16]

3.4.6. Decachlorocorannulene 8



Into a 200-mL round-bottomed flask equipped with a magnetic stirrer and a condenser were added anhydrous aluminum chloride (160 mg, 3.45 mmol), sulfur monochloride (0.14 mL, 1.9 mmol), and sulfuryl chloride (25 mL, excess).[9] The resulting mixture was heated to reflux (~70°C) for 2 hours. The mixture was then cooled to room temperature, and 15 mL of sulfuryl chloride and corannulene **7** (430 mg, 1.72 mmol) were added. Upon addition a dark green-black mixture was formed. The resulting mixture was heated gently (~70°C) for about one hour until it was down to one third of its initial solvent volume. It was then refluxed for another 5 hours, keeping the volume constant by periodic additions of sufuryl chloride (approximately 5-10 mL at a time). The reaction was then stirred overnight in the dark at room temperature. At the end of that period the reaction mixture was poured into 125 mL of water, and solid sodium bicarbonate was added until gas evolution ceased. The resulting aqueous mixture was then heated to 90°C for 2 hours, cooled to room temperature, and acidified with excess concentrated hydrochloric acid, which was then extracted with toluene. The combined organic layers were then washed with saturated sodium bicarbonate solution (3 x 100 mL) and saturated sodium chloride solution (3 x 100 mL), dried over magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure. The crude product was partially purified by a short silica gel column using hexane as an eluent. From the column, the yellow band was collected. The resulting solid was heated in 30 mL of phenyl ether at 160 – 180°C for 1 day. The solution was cooled to room temperature and allowed to stand for 2-3 hours. The recrystallized product was collected by vacuum filtration and washed with plenty of methylene chloride to give decachlorocorannulene **8** (620 mg, 60.7% yield) as a yellow solid.

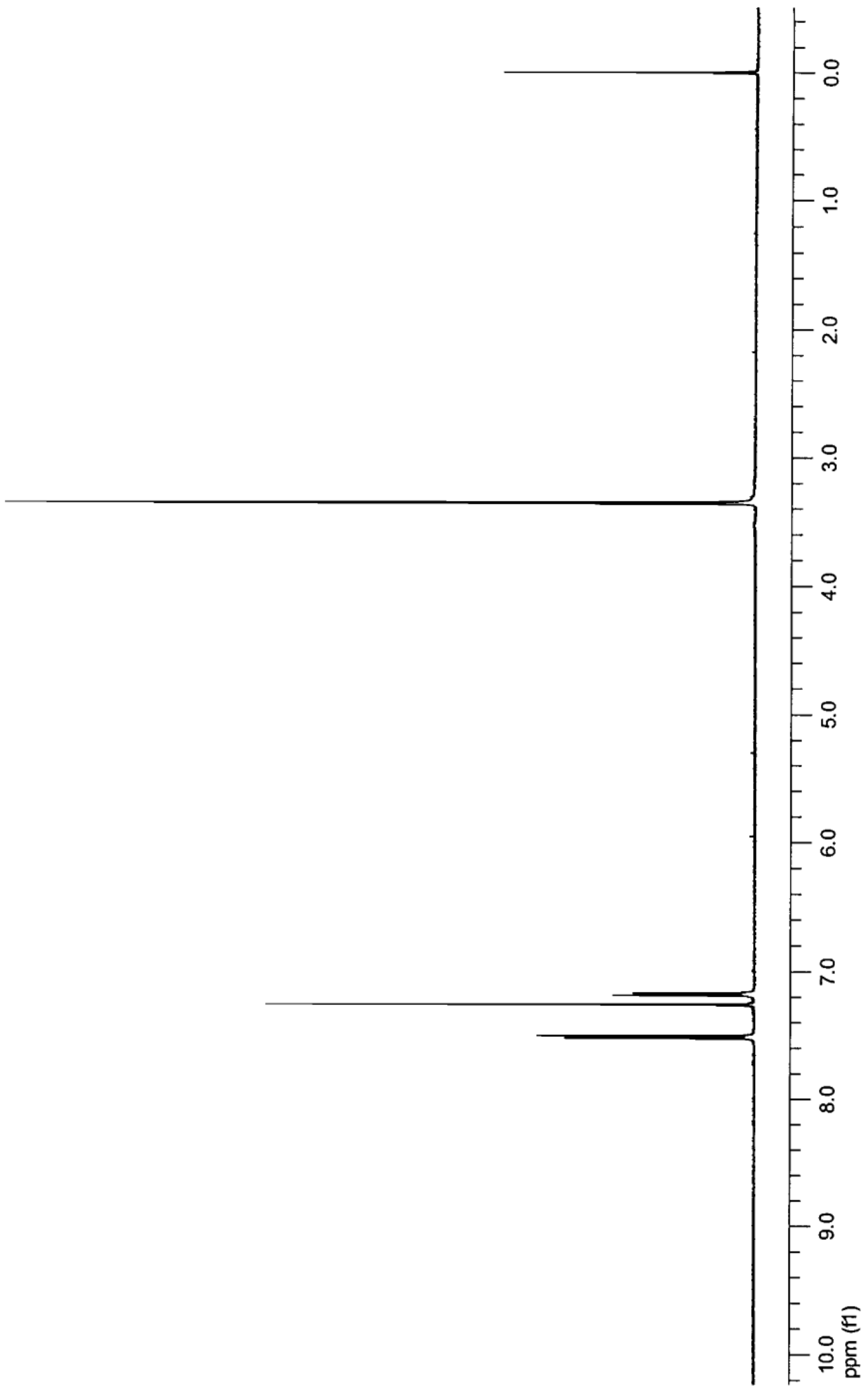
3.4.7. 5,6-dichloroacenaphthene 10



Into a 500-mL round-bottomed flask were added acenaphthene (30 g, 195 mmol) and aluminum chloride (5.5 g, 41.2 mmol) in nitrobenzene (250 mL), and the reaction was cooled to 0°C in an ice bath.[10] A pressure-equalizing dropping funnel was charged with sufuryl chloride (35 mL, 432 mmol), which was added dropwise to the reaction mixture over a period of 1 hour with vigorous stirring, and it was left to stir for an additional 2 hours. The reaction mixture was then poured into 500 mL of a solution of 5:1 methanol:water and cooled to 0°C for 1 hour. The precipitate was collected, washed with methanol, and dried under vacuum to give the product 5,6-dichloroacenaphthene **10** as a yellow solid (27.6g, 63% yield).[‡]

Melting point	173 – 175°C; lit. 167-169°C[10]
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.52 (d, *J* = 7.6 Hz, 2H); 7.18 (d, *J* = 7.2 Hz, 2H); 3.36 (s, 4H)

[‡] Small amounts of tri-chlorinated compound can be present and can be recrystallized from a 2:1 methanol: methylene chloride solution, but generally the product was taken to the next step without further purification.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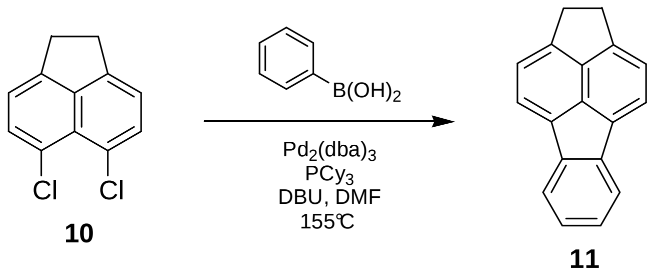
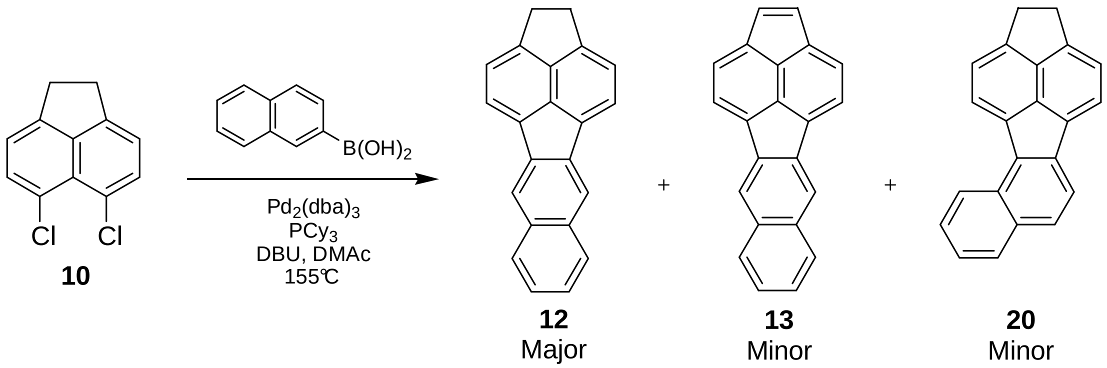
ppm (f1)

3.4.8. 1,2-Dihydrocyclopenta[cd]fluoranthene 11



Into an oven-dried pressure vessel equipped with a magnetic stirrer were added 5,6-dichloroacenaphthalene **10** (20 mg, 0.090 mmol), $Pd_2(dba)_3$ (17 mg, 0.019 mmol), PCy_3 (20 mg, 0.071 mol), and phenyl boronic acid (11 mg, 0.090 mmol) in DBU (0.5 mL) and DMF (2 mL).[11] The resulting mixture was stirred at 155°C for 1 day. The reaction vessel was cooled to room temperature, and the mixture was diluted with methylene chloride (50 mL) and filtered through a short silica plug. The resulting solution was washed with 10% aqueous hydrochloric acid solution (2 x 20 mL), saturated sodium bicarbonate solution (20 mL), water (20 mL), and saturated sodium chloride solution (20 mL). The organic phase was dried over magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure to give the crude product. The obtained mixture was subject to chromatography on silica gel using 9:1 petroleum ether:methylene chloride as an eluent to give 1,2-dihydrocyclopenta[cd]fluoranthene **11** as a white solid (1 mg, 5% yield). All spectroscopic data were similar to the reported values.[12]

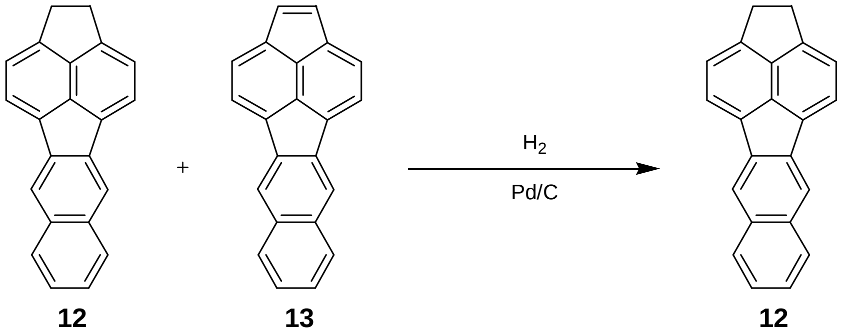
3.4.9. Benzo[k]-1,2-dihydrocyclopenta[cd]fluoranthene 12



In an oven-dried pressure vessel were added 5,6-dimethylacenapthalene **10** (100 mg, 0.448 mmol), 2-naphthylboronic acid (85 mg, 0.494 mmol), $Pd_2(dba)_3$ (82 mg, 0.090 mmol, 20 mol %), and PCy_3 (100 mg, 0.357 mmol, 80 mol %) in DBU (2 mL) and DMAc (8 mL).[11] The resulting mixture was stirred at 155°C for 1 day. The reaction vessel was cooled to room temperature, and the mixture was diluted with methylene chloride (100 mL) and filtered through a short silica plug. The resulting solution was washed with 10% aqueous hydrochloric acid solution (100 mL), saturated sodium bicarbonate solution (100 mL), water (100 mL), and saturated sodium chloride solution (100 mL). The organic phase was dried over magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure to give the crude product. The obtained mixture was subject to preparative chromatography on silica gel using 4:1 hexane:methylene chloride as an eluent to give a combination of benzo[k]-1,2-dihydrocyclopenta[cd]fluoranthene **12** and benzo[k]-1,2-cyclopenta[cd]fluoranthene **13** as a pale yellow mixture (25 mg, 20% yield) in an approximate ratio of 4:1 by NMR integration. All attempts to obtain pure samples of either compound failed. If scaled up to 2 grams, this reaction produces a slightly better yield (between 25-30%) but gives a mixture of benzo[k]-1,2-dihydrocyclopenta[cd]fluoranthene **12** and benzo[j]-1,2-dihydrocyclopenta[cd]fluoranthene **20**. Compound **13** is not observed during scale-up. The mixture is only separable in small amounts by HPLC; large-scale separation was not achieved.

To obtain a pure sample of benzo[k]-1,2-dihydrocyclopenta[cd]fluoranthene **12** the byproduct mixture was hydrogenated to the desired product.

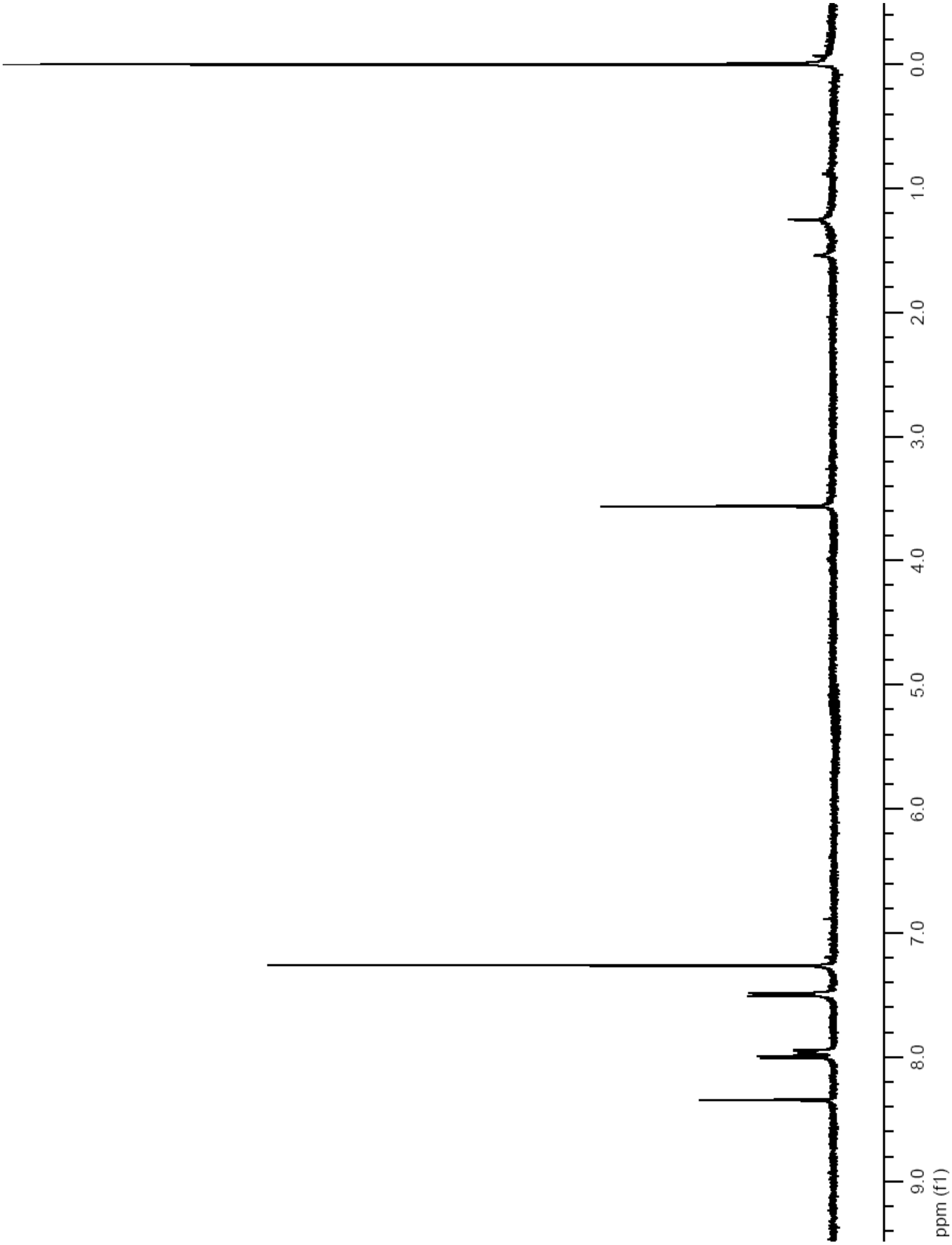
3.4.9.1. Hydrogenation of Benzo[k]-1,2-cyclopenta[cd]fluoranthene 13 to Benzo[k]-1,2-dihydrocyclopenta[cd]fluoranthene 12



In a 100-mL oven-dried round-bottomed flask were added 14 mg of the previously obtained mixture, containing ~3 mg (0.011 mmol) of the unsaturated compound **13** in methylene chloride (3 mL). At room temperature and under agitation were added 10% Pd/C (10 mg, 0.001 mol) as a catalyst. The flask was filled completely with hydrogen gas. A balloon with hydrogen was left connected to the flask for the rest of the reaction.

The reaction mixture was stirred vigorously for 2 hours. After dilution with methylene chloride (10 mL), the contents of the flask were filtered through a small silica plug to retain the catalyst, and the filtrate solution was evaporated under reduced pressure to yield a pale solid (14 mg, 100%). NMR confirmed the solid to be 100% of the desired product, proving the hydrogenation worked in quantitative yield. No further separation was performed.

Melting point	162 – 164°C
^{1}H NMR (400 MHz, $CDCl_3$)	δ 8.35 (s, 2H); 8.00 (d, *J* = 7.0 Hz, 2H); 7.96 (q, *J* = 2.2 Hz, 2H); 7.49 (dd, *J* = 8.1 Hz, 2.0 Hz, 4H); 3.56 (s, 2H)
^{13}C NMR (100 MHz, $CDCl_3$)	δ 145.34; 138.84; 137.21; 133.97; 133.01; 132.56; 128.60; 125.70; 121.09; 121.04; 120.58; 32.35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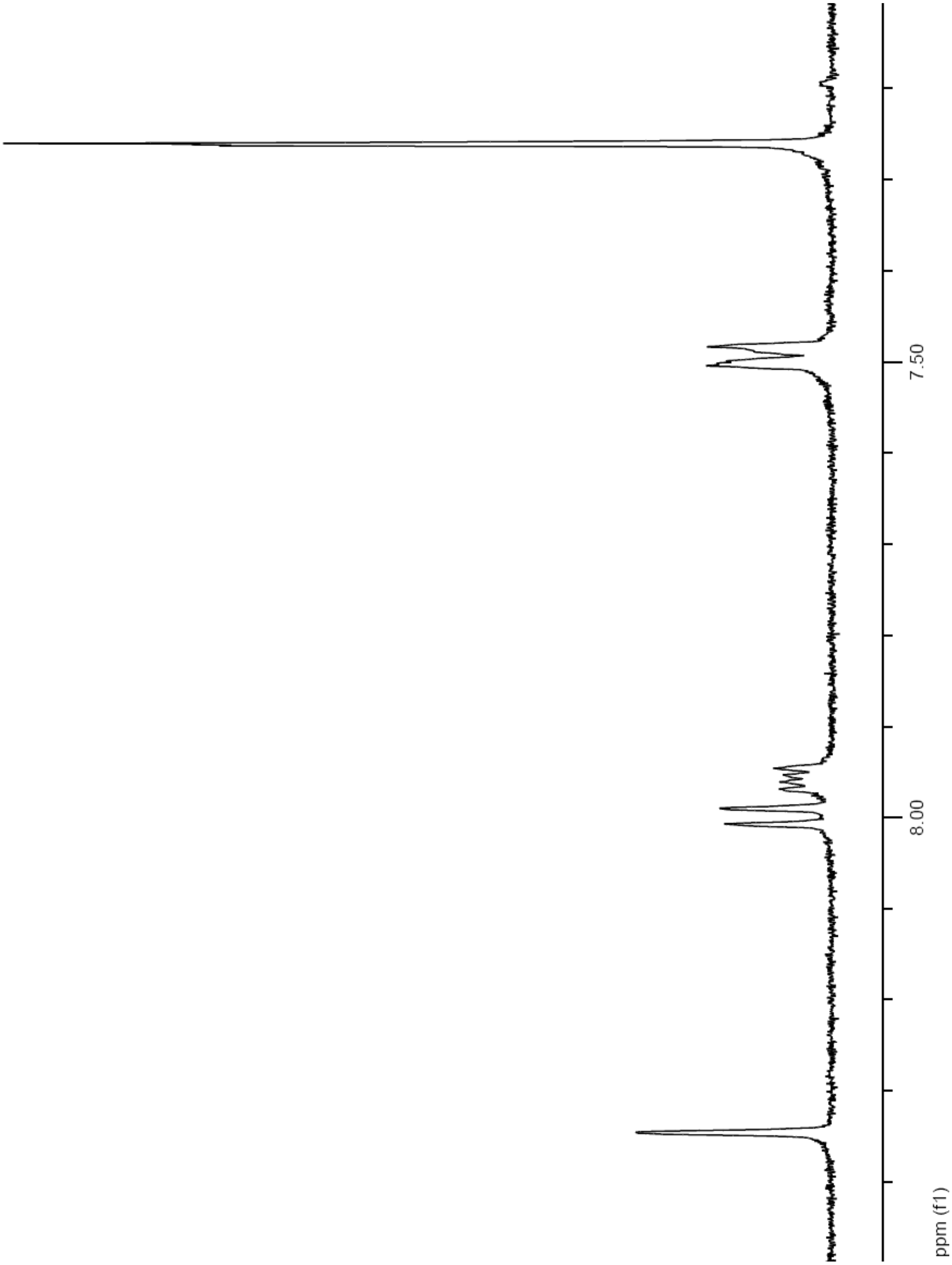
ppm (f1)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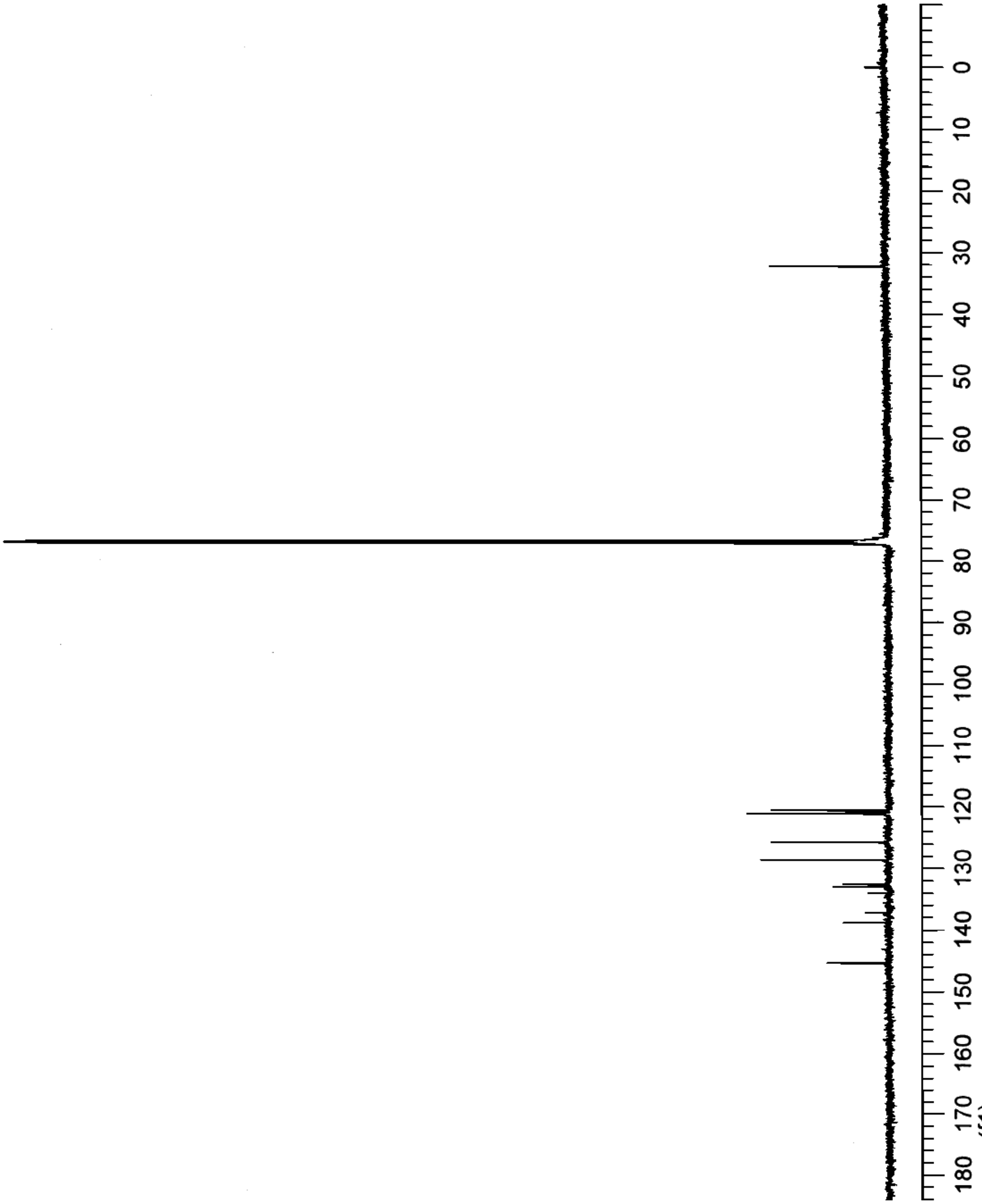
8.00
ppm (f1)

^{13}C NMR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10
20
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40
50
60
70
80
90
100
110
120
130
140
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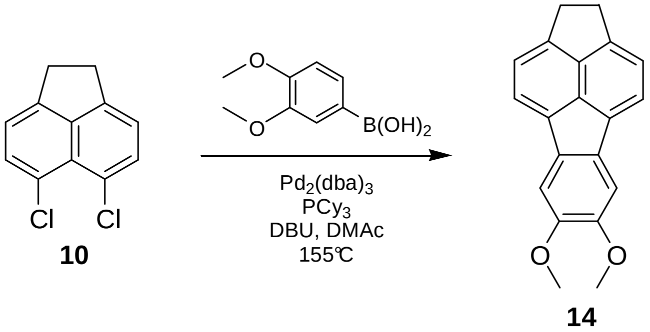
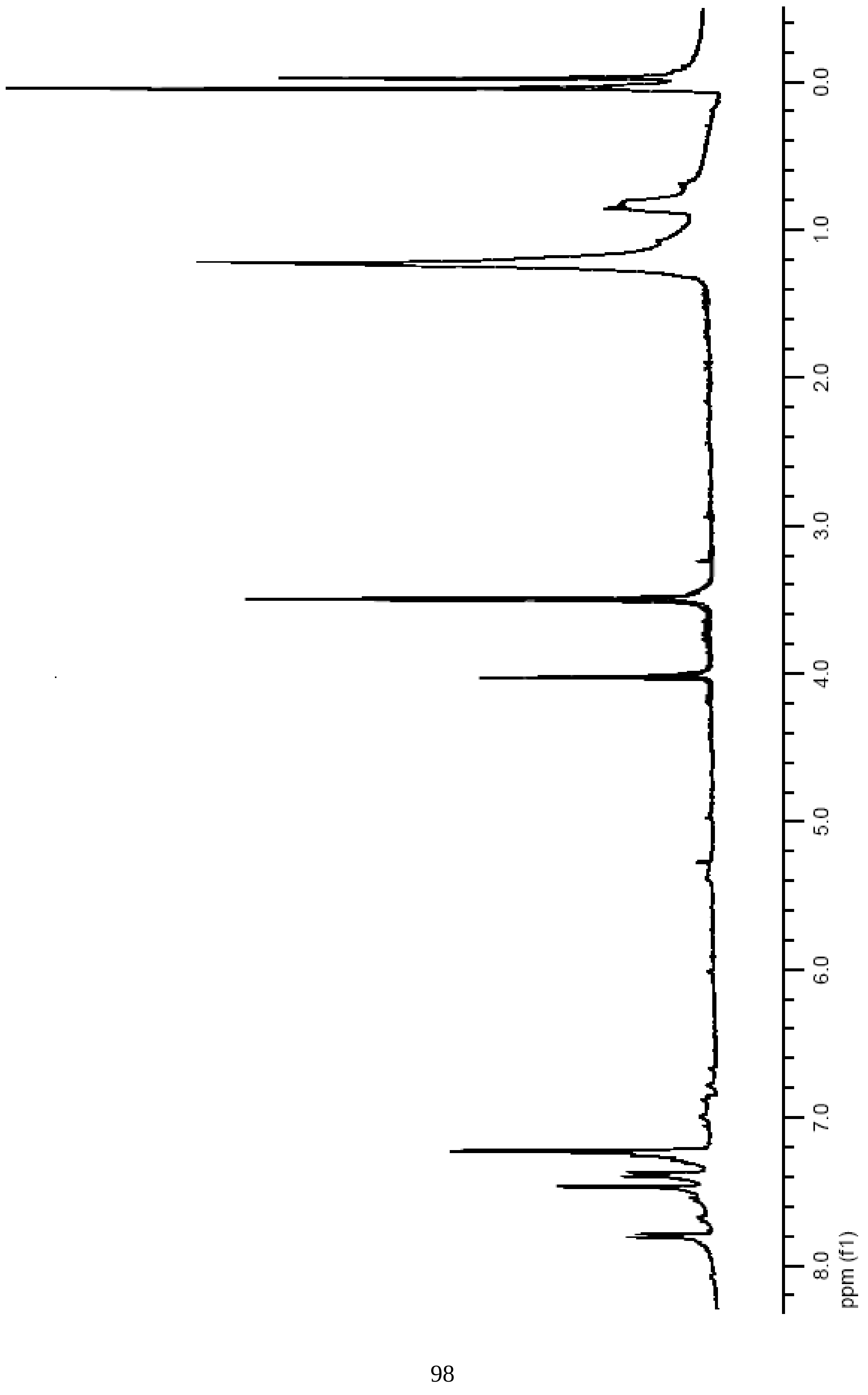
170
180
ppm (f1)

3.4.10. 6,7-Dimethoxy-1,2-dihydrocyclopenta[cd]fluoranthene 14



In an oven-dried pressure vessel were added 5,6-dimethylacenapthalene **10** (100 mg, 0.448 mmol), 3,4-dimethoxyphenylboronic acid (90 mg, 0.493 mmol), $Pd_2(dba)_3$ (82 mg, 0.090 mmol, 20 mol %), and PCy_3 (100 mg, 0.357 mmol, 80 mol %) in DBU (2 mL) and DMAc (8 mL).[11] The resulting mixture was stirred at 155°C for 1 day. The reaction vessel was cooled to room temperature and the mixture was diluted with methylene chloride (100 mL) and filtered through a short silica plug. The resulting solution was washed with 10% aqueous hydrochloric acid solution (100 mL), saturated sodium bicarbonate solution (100 mL), water (100 mL), and saturated sodium chloride solution (100 mL). The organic phase was dried over magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure to give the crude product. The obtained mixture was subject to chromatography on a silica gel column using 5:1 hexane:methylene chloride as an eluent to give 6,7-Dimethoxy-1,2-dihydrocyclopenta[cd]fluoranthene **14** as a yellow solid (59 mg, 46 % yield).

Melting point	212 – 216°C
^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.84 (d, 8.2 Hz, 2H); 7.501 (s, 2 H); 7.43 (d, 7.0 Hz, 2 H); 4.04 (s, 4H); 3.51 (s, 6 H)


8.0
7.0
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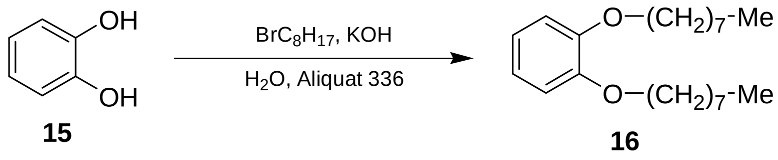
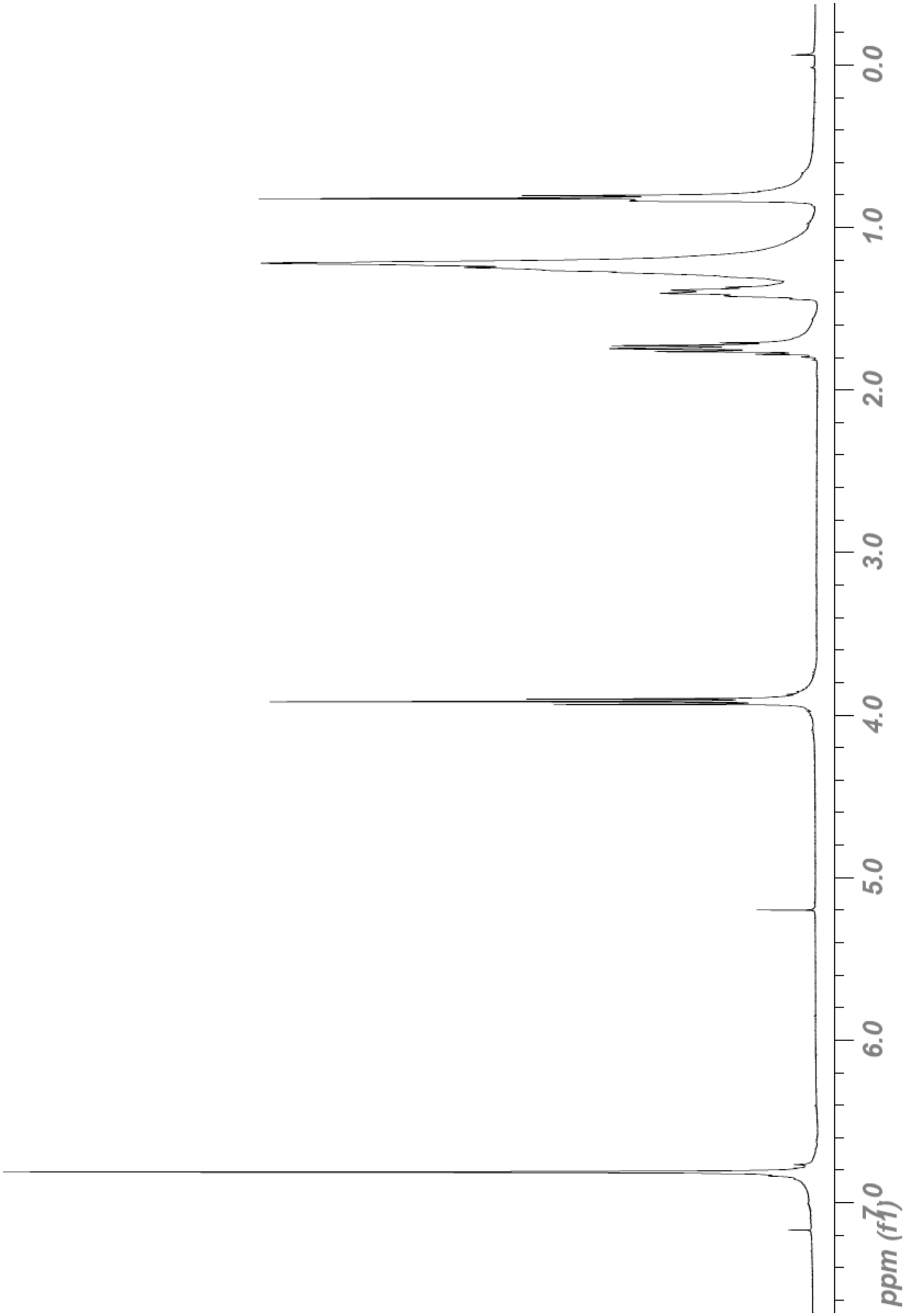
3.4.11. 1,2-Bis(octyloxy)benzene 16



Into a 2-L round-bottomed flask equipped with a magnetic stirrer were added potassium hydroxide (14.10g, 0.250 mol), catechol **15** (11.10 g, 0.100 mol), and Aliquat 336 (0.914 mL, 2 mol %) in water (1.2 L).[13] The mixture was stirred vigorously for 20-30 minutes while it was brought to 60°C. The octyl bromide was then added over 10-15 minutes via pressure-equalizing dropping funnel, and the reaction mixture was stirred for an additional two hours at 60°C. The organic products were collected by extraction with dichloromethane (2 x 300 mL). The organic phase was washed twice with water, once with saturated sodium chloride solution, dried over magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure. The crude product was purified with a short silica column using hexane as an eluent to give 1,2-bis(octyloxy)benzene **16** as a light yellow oil (30.01 g, 89.0% yield).

Melting point	N/A (liquid at room temperature)
^{1}H NMR (400 MHz, $CDCl_3$)	δ 6.90 (m, 4H); 4.00 (t, *J* = 8.1 Hz, 4 H); 1.84 (m, 4H); 1.49 (m, 4H); 1.31 (m, 16H); 0.82 (t, *J* = 8.5Hz, 6H)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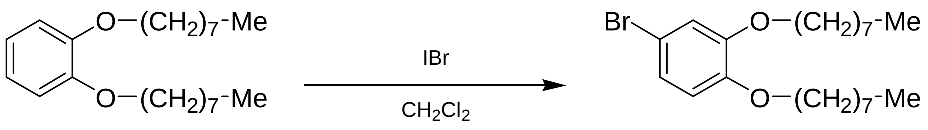
ppm (f1)

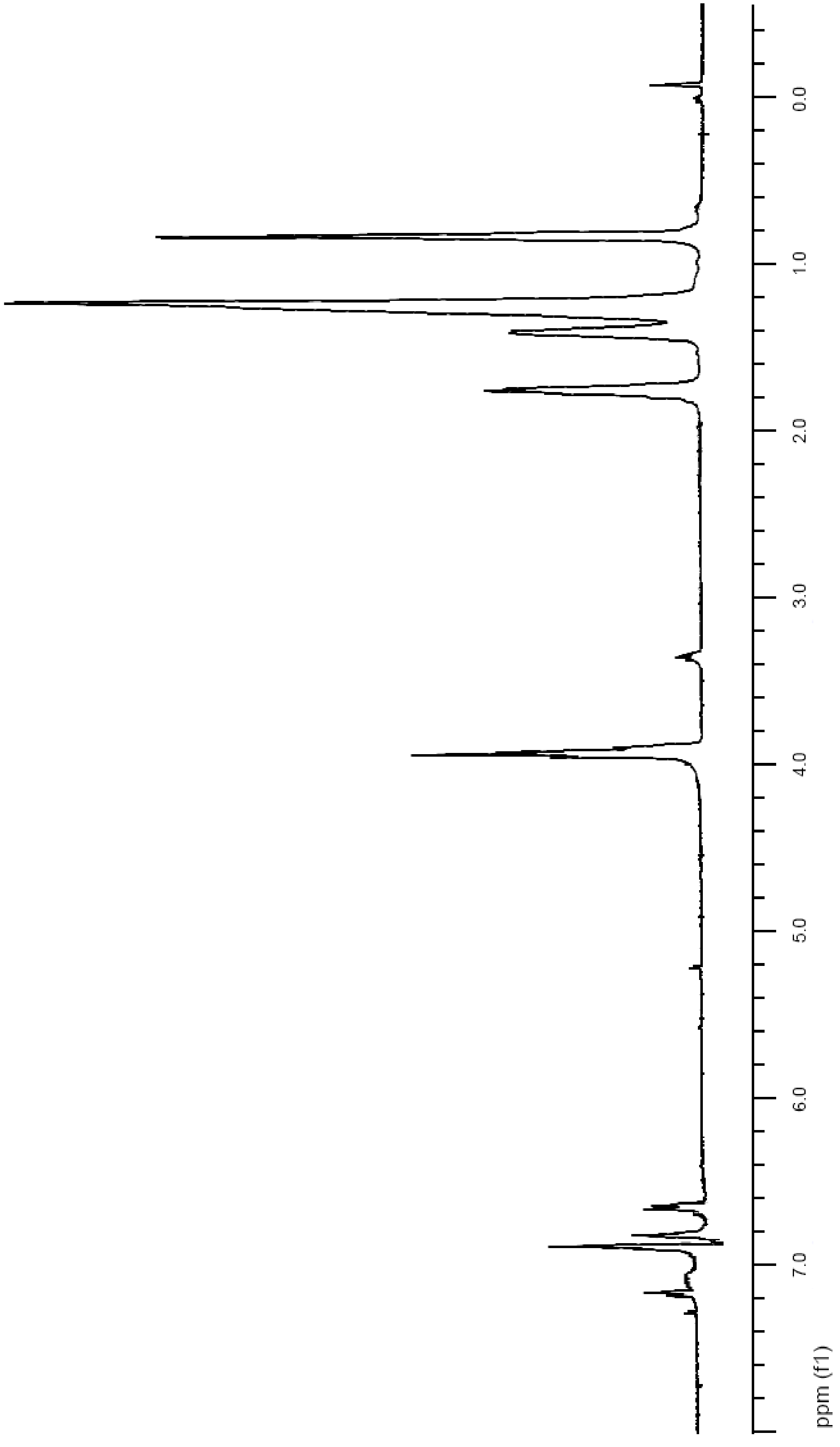
3.4.12. 4-Bromo-1,2-bis(octyloxy)benzene 17



16 **17**

Into a 100-mL oven-dried round-bottomed flask equipped with a magnetic stirrer and pressure-equalizing dropping funnel were added 1,2-bis(octyloxy)benzene **16** (1.00 g, 2.99 mmol) in methylene chloride (25 mL).[14] The dropping funnel was charged with a 1 M solution of iodine monobromide in methylene chloride (3.6 mL, 3.60 mmol) in additional methylene chloride (15 mL), which was added dropwise over 1 hour with vigorous stirring. During this time the reaction mixture changed colors from yellow to brown to green and back to dark brown, and was left to stir for an additional 5 hours. The reaction mixture was quenched by pouring it into 10% aqueous sodium hydroxide solution. The organic phase was washed three times with 10% aqueous sodium thiosulfate solution, once with water, and once with saturated sodium chloride solution. The organic layer was separated, dried over magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure to give 4-bromo-1,2-bis(octyloxy)benzene **17** as a yellow-brown oil (816 mg, 66.1% yield)**.**

^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.18 (d, 1H); 6.90 (s, 1H); 6.74 (d, 1H); 4.00 (m 4H); 1.84 (m, 4H); 1.49 (m, 4H); 1.31 (m, 16H); 0.82 (t, 6H)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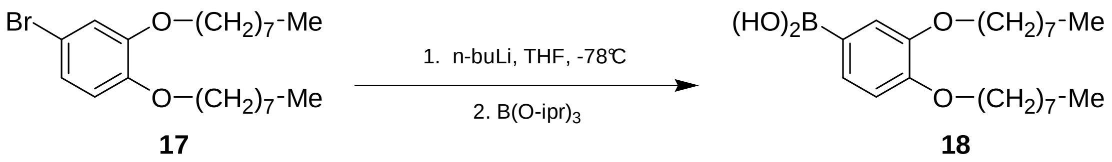
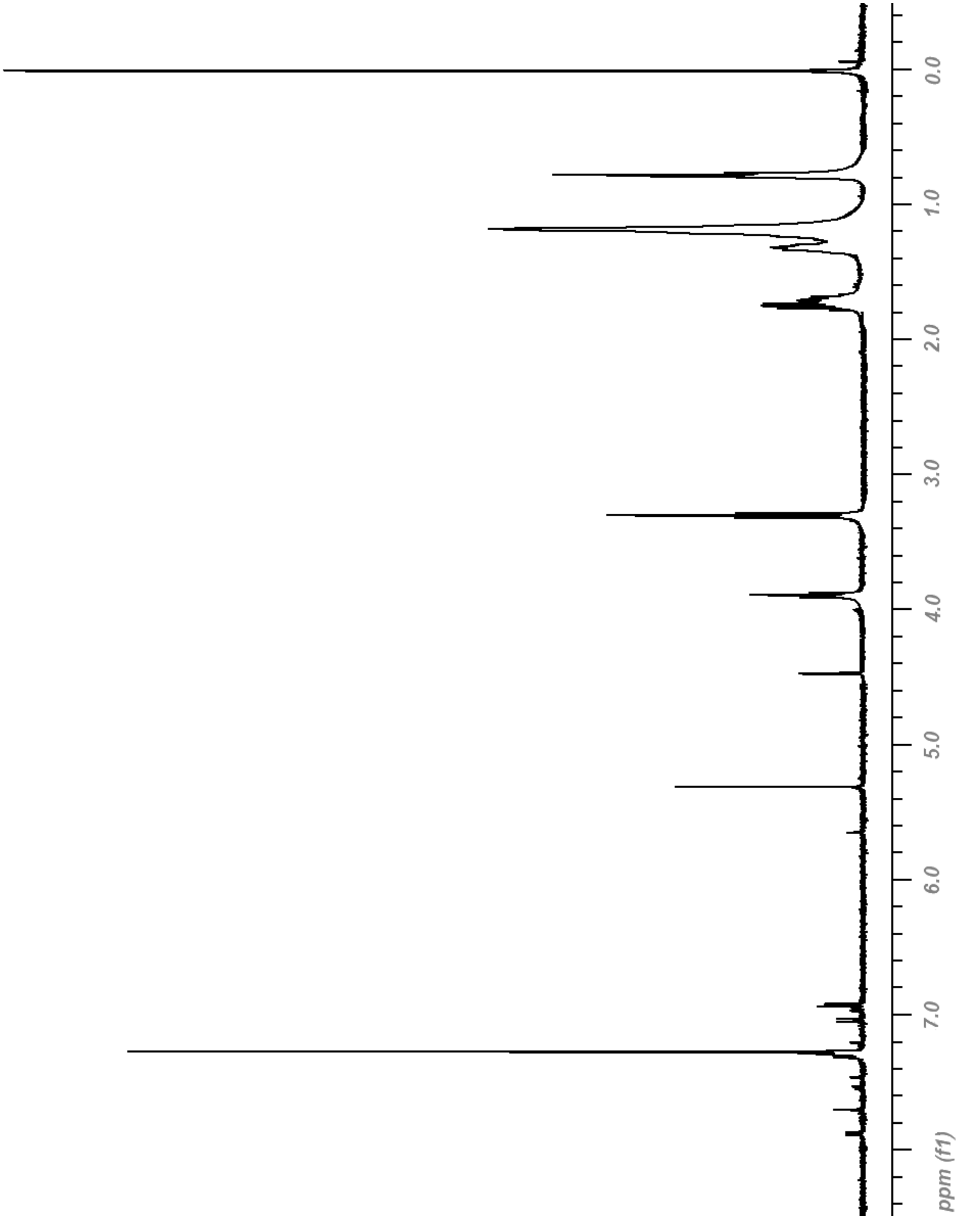
3.4.13. 3,4-Bis(octyloxy)phenylboronic acid 18



Into a 500-mL oven-dried round-bottomed flask was added 4-bromo-1,2-bis(octyloxy)benzene **17** (800 mg, 1.935 mmol) in anhydrous THF (2 mL), and the reaction mixture was cooled to -78°C using a dry ice/acetone bath. [15] To the reaction mixture was syringed n-butyl lithium (1.1 equivalents) in THF. The reaction mixture was stirred vigorously for 10 minutes at -78°C. Tri-isopropyl borate (excess) was added at -78°C and slowly brought to room temperature over 30 minutes. The reaction mixture was poured into 1 M hydrochloric acid to quench it. The organic layer was washed twice with water, once with saturated sodium chloride solution, dried over magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure to give 3,4-bis(octyloxy)phenylboronic acid as a light yellow-brown oil (464 mg, 63.4% yield).

^{1}H NMR (400 MHz, $CDCl_3$)	δ 7.86 (d, 1 H); 7.69 (s, 1 H); 6.91 (d, 1 H); 4,471 (s, 2 H); 3.98 (m 4H); 1.82 (m, 4H); 1.47 (m, 4H); 1.29 (m, 16H); 0.81 (t, 6H)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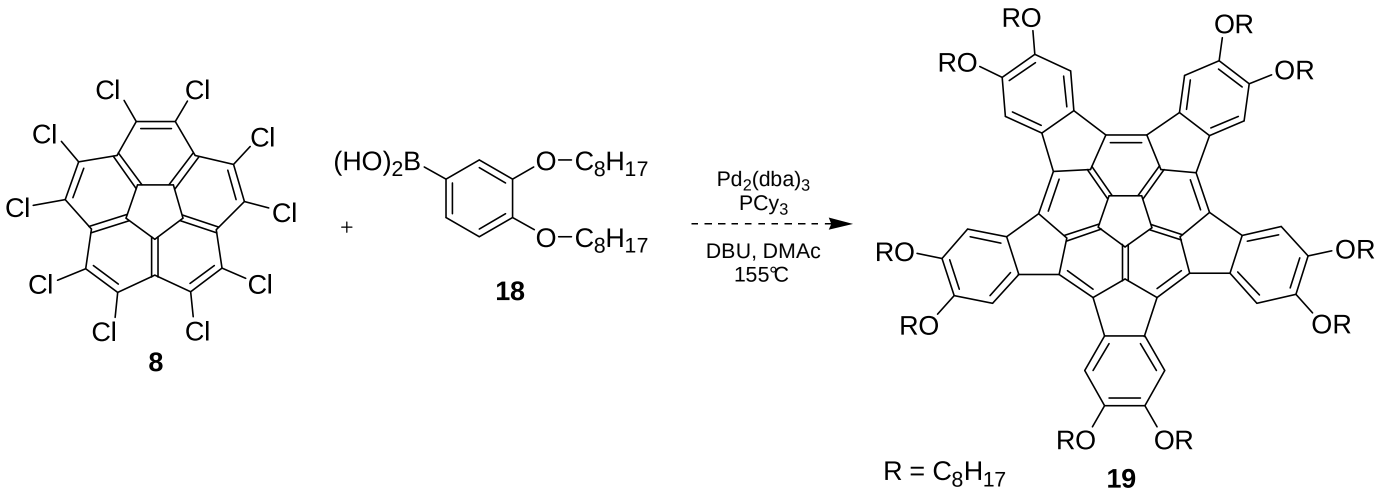
ppm (f1)

3.4.14. Attempted synthesis of pentakis(3,4-dioctyloxy)indenocorannulene



In an oven-dried pressure vessel were added decachlorocorranulene **8** (50 mg, 0.084 mmol), 3,4-bis(octyloxy)phenylboronic acid (35 mg, 0.092 mmol), Pd$_2$(dba)$_3$ (15.5 mg, 0.017 mmol, 20 mol %), and PCy$_3$ (17.7 mg, 0.067 mmol, 80 mol %) in DBU (1 mL) and DMAc (4 mL).[11] The resulting mixture was stirred at 155°C for 1 day. The reaction vessel was cooled to room temperature, and the mixture was diluted with methylene chloride (25 mL) and filtered through a short silica plug. The resulting solution was washed with 10% aqueous hydrochloric acid solution, saturated sodium bicarbonate solution, water, and saturated sodium chloride solution. The organic phase was dried over magnesium sulfate, filtered, and the solvent was evaporated under reduced pressure to give the crude product. The obtained crude mixture was subject to chromatography on a short silica gel column using 4:1 hexane:methylene chloride; however, the separation failed.

3.6. References

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[5] Bethel, J. R.; Maitland, P. *J. Am. Chem. Soc.* **1962**, 3751.

[6] (a) Scott, L. T.; Hashemi, M. M.; Meyer, D. T.; Warren, H. B. *J. Am. Chem. Soc.* **1991**, *113*, 7082. (b) Scott, L. T.; Hashemi, M. M.; Bratcher, M. S. *J. Am. Chem. Soc*. **1992**, *114*, 1920. (c) Scott, L. T.; Cheng, P. C.; Hashemi, M. M.; Bratcher, M. S.; Meyer, D. T. *J. Am. Chem. Soc.* **1997**, *119*, 10963.

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[8] Scott, L. T.; Bratcher, M. S.; Hagen, S. *J. Am. Chem. Soc.* **1996**, *118*, 8734.

[9] (a) first reported by Cheng, P.; Scott, L. T. *In Abstr. of Papers, 208th Nat. Meeting of the Am. Chem. Soc.*; Am. Chem. Soc.; Washington, D. C., **1994**, abstr. no. ORGN-087. (b) Xie, X. Y.; Deng, S. L.; Huang, R. B.; Yu, L. J.; Zeng, L. S. *Chem. Phys. Lett.* **2001**, *343*, 458 and references cited therein. (c) Samdal, S.; Hedberg, L.; Hedberg, K.; Richardson, A. D.; Bancu, M.; Scott, L. T. *J. Phys. Chem. A* **2003**, *107*, 411. (d) Cheng, P. Ph.D. Thesis, Boston College: Chestnut Hill, MA, **1996**.

[10] (a) Adaptation of similar procedure by Sieders, T. J.; Elliot, E. L.; Grube, G. H.; Siegel, J. S. *J. Am. Chem. Soc.* **1999**, *121*, 7804. (b) Ansems, R. B. M.; Ph.D. Thesis, Boston College: Chestnut Hill, MA, **2004**.

[11] Bancu, M.; Ph.D. Thesis, Boston College: Chestnut Hill, MA, **2004**.

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[12] Sarobe, M.; Snoeijer, J. D.; Jenneskens, L. W.; Slagt, M. Q.; Zwikker, J. W. *Tetrahedron Lett.* **1995**, *36*, 8489.

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CHAPTER IV:

Suggestions for Further Research

4.1. Suggestions for Further Research

We are on the verge of fulfilling the quest of making a [5.5] SWNT, $C_{50}H_{10}$ geodesic cap, or geodesic cap derivative, but much work still needs to be done. I suggest the following strategies/approaches to continue my the research presented in this thesis in hopes that more progress will be made and a viable synthetic route will be discovered.

First of all, the synthesis of the test compound (Scheme 3.10, page 75) 6,7-dimethoxy-1,2-dihydrocyclopenta[cd]fluoranthene **14** needs to be optimized. Perhaps heating the mixture at a lower temperature and a longer time (or a higher temperature and shorter time) would help the palladium coordinate to the benzene π-system and encourage more of the second, Heck-type couplings to occur. Other palladium catalysts and ligands could also be explored.

Besides the first step, the synthetic process for the formation of the boronic acid needs to be optimized. Improvement of the of bromination step (Scheme 3.12, page 77) could happen with possible heating of the mixture during bromination, letting it run over longer time, or trying a new bromination procedure. Reginald Mitchell uses N-bromosuccinamide in DMF as a selective brominating reagent, and this looks promising.[1] The coupling step to decabromocorannuelene **8** could be optimized in the same manner as mentioned above for the test compound, although optimization of the test compound should be explored first so that valuable starting material is not wasted.

Once the pentakis(3,4-octyloxy)indenocorannulene 19 is formed (and I am certain that it can be and will), closure should be fairly simple. The Müllen group has used conditions which have formed curved graphene structures[2], and these would be the primary options for the formation of the per-alkoxylated geodesic cap, a jelly-fish looking structure (Figure 3.3).

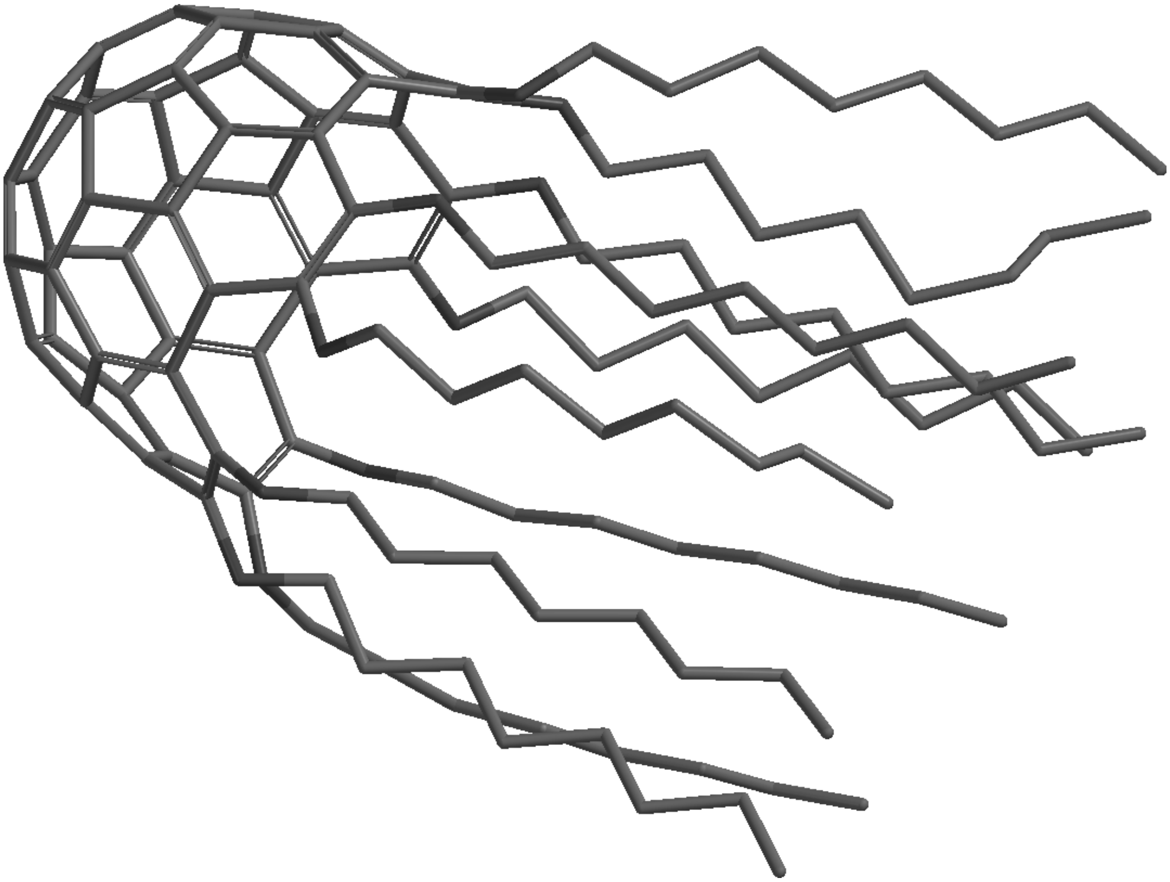

Figure 3.3. A per-alkoxylated C_{50} geodesic cap

4.2. References

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