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MASTER'S THESIS

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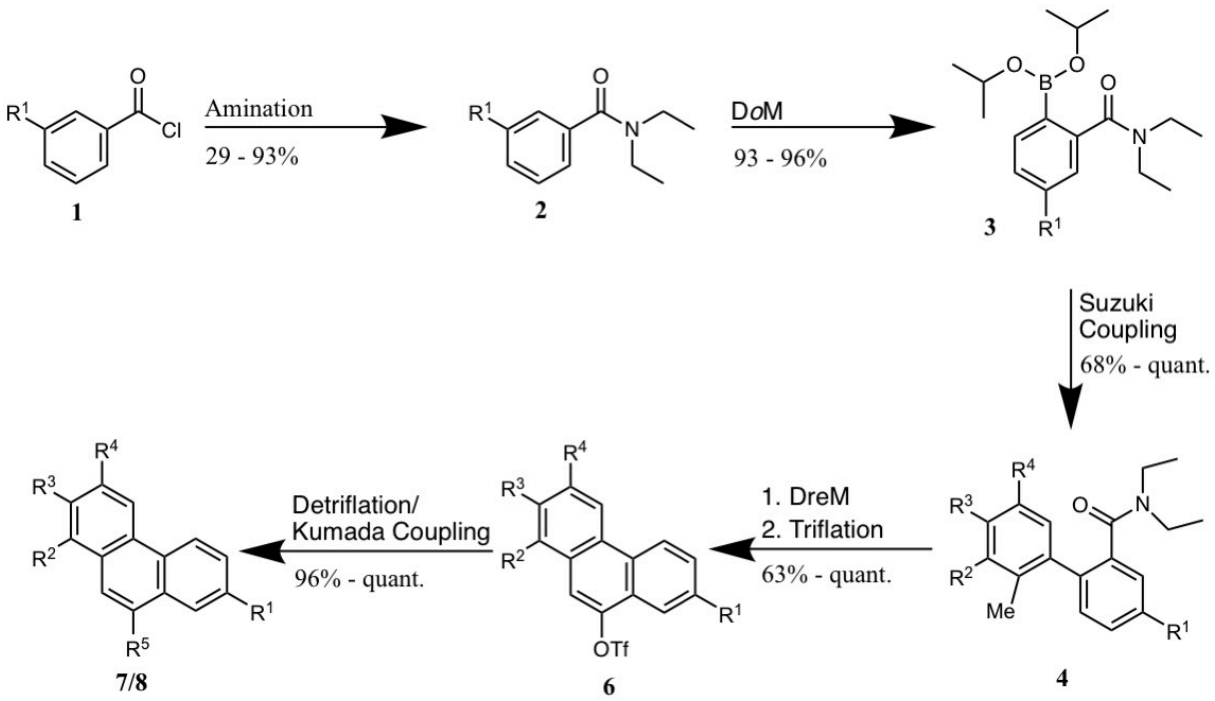
Abstract

This thesis captures the process of synthesizing gram quantities of the compounds 2,3-dimethylphenanthrene (**7a**), 2,7-dimethylphenanthrene (**7b**) and 1,7-dimethylphenanthrene (**7c**) to be used in the EGGTOX project. The EGGTOX project is a fish exposing experiment by Institute of Marine Research.

The **8d** product was made by Kumada coupling, which was an immediate success. The product 1,9-dimethylphenanthrene (**8d**) will be delivered after a request by J. H. Christensen in Section for Environmental Chemistry and Physics at University of Copenhagen, Denmark. Next attempt was to make 2,3,9-trimethylphenanthrene (**8e**), which might have been successfully made, but needs purification to get good analysis of the new compound. Another experiment to make 1-methyl-9-vinylphenanthrene (**8f**) was unsuccessful. The chemical route for the project was a general regiospecific route to produce alkylated phenanthrenes, as shown in the scheme below. The products were made by Directed *ortho* Metalation (D*o*M), Suzuki-Miyaura cross coupling and Directed remote Metalation (DreM). The target molecules were obtained in total yields over 6 steps as listed in the table. The compounds in this thesis made for the EGGTOX project were triflated and deprotected, while the rest went through Kumada Coupling, resulting in a new R group to a specific phenanthrene. Further experiments in adding vinyl group by Kumada Coupling may provide a new way to build substituted PAHs.



Compound	R^1	R^2	R^3	R^4	R^5	Total yield
7a	H	H	Me	Me	H	82%
7b	Me	H	Me	H	H	58%
7c	Me	Me	H	H	H	61%
8d	H	Me	H	H	Me	43%
8e	H	H	Me	Me	Me	n.a.
8f	H	Me	H	H	CH_2=CH	Failed

Selected Abbreviations

δ	Chemical shift measured in ppm from a reference point
app. d	Apparent doublet
app. s	Apparent singlet
aq	Aqueous
BuLi	Butyllithium
CIPE	Complex Induced Proximity Effect
CYPs	Isocytochromes P-450
d	Doublet
dd	Double doublet
DCM	Dichloromethane
DME	1,2-Dimethoxyethane
DMF	Dimethylformamide
DMG	Directed Metalation Group
D*o*M	Directed *ortho* Metalation
DreM	Directed remote Metalation
EtOAc / EA	Ethyl acetate
EtOH	Ethanol
eq.	Equivalent
Hep	*n*-Heptane
h/hr	Hours
Hz	Hertz
IR	Infrared
J	Coupling constant, Hz
LDA	Lithium Diisopropylamide
m	Multiplet
Me	Methyl
MeOH	Methanol
MS	Mass Spectrometry
N.A.	Not available
NMR	Nuclear Magnetic Resonance
PAH	Polycyclic Aromatic Hydrocarbon

r. t.	Room temperature
s	Singlet
t	Triplet
THF	Tetrahydrofuran
TLC	Thin-Layer Chromatography
TMEDA	*N,N,N′,N′*-Tetramethylethylenediamine

Contents

1. Introduction and theory

1.1 Polycyclic Aromatic Hydrocarbons

Polycyclic Aromatic Hydrocarbons (PAHs) has been listed as priority pollutants by The European Community and the U.S. Environmental Protection Agency since they are a threat to all living creatures.[1] Respiratory problems, impair pulmonary function, and bronchitis may be some of the problems atmospheric PAHs can cause.[2] Studies has also been done to confirm PAHs causes both good and bad epigenetic alterations in species. Good as the chemicals can cause stress resistance, while bad since they can cause disease. In Vandegehuchtes study, Zebra fish grew tumors after exposure to 7,12-dimethylbenz(a)anthracene.[3]

Studies have been conducted to get an overview of how contaminated different rivers are. Yuan et. al.'s study of the Yellow River Delta show enlarged petrogenic contamination of parts of the river, which has oil pipeline leakages. The rest of the Yellow River Delta contained PAHs from mostly coal and biomass combustion, vehicular emission and petroleum spills. Fortunately the levels of pollution were not high enough to raise a red flag. Other rivers such as South Carolina marsh and Elizabeth River wetland in USA were badly contaminated.[4,5] Bizerte Lagoon, Tunisia was studied by Barhoumi and his group, this lagoon was not too polluted either. Bizerte Lagoon was compared to the San Francisco Bay,[6] USA and Thau Lagoon,[7] France which was severely polluted, and might have become environmentally damaged.[8]

A large risk assessment by Malaj et. al. concluded that organic pollutions are a continental-scale problem, and needs large-scale integrated solutions as well. When looking at organic compounds the PAHs are harmful. Pesticides often used for controlling pests and weeds has a worse effect on the environment. These chemicals reduce the biodiversity and ecosystem services. The chemicals travel far, and are sources to both acute mortality and chronic long-term effect on fish, invertebrate and algae.[9]

The PAHs can be divided into two categories. The high molecular weight compounds, which is 4-membered rings and heavier. Some of the groups with different membered rings can be seen in figure 1. These PAHs are usually pyrolytic, and comes from wood and coal combustion. The other category are the low molecular weight compounds, being 2- and 3-membered rings, which come from petrogenic sources, like oil spills.[8]

Homocyclic PAHs only contain carbon and hydrogen, and are now well documented, while the heterocyclic PAHs faith are less known. So far some research studies has been carried out on heterocyclic PAHs, and results seem to indicate that PAHs plays a crucial role for some animals, being strongly mutagenic or having genotoxic effects.[10]

The risk assessment looked at the PAHs which is more hydrophobic and likely to find a way into biota. The heterocyclic PAHs on the other hand are more water soluble and can pollute larger areas by traveling further than PAHs.[9,10]

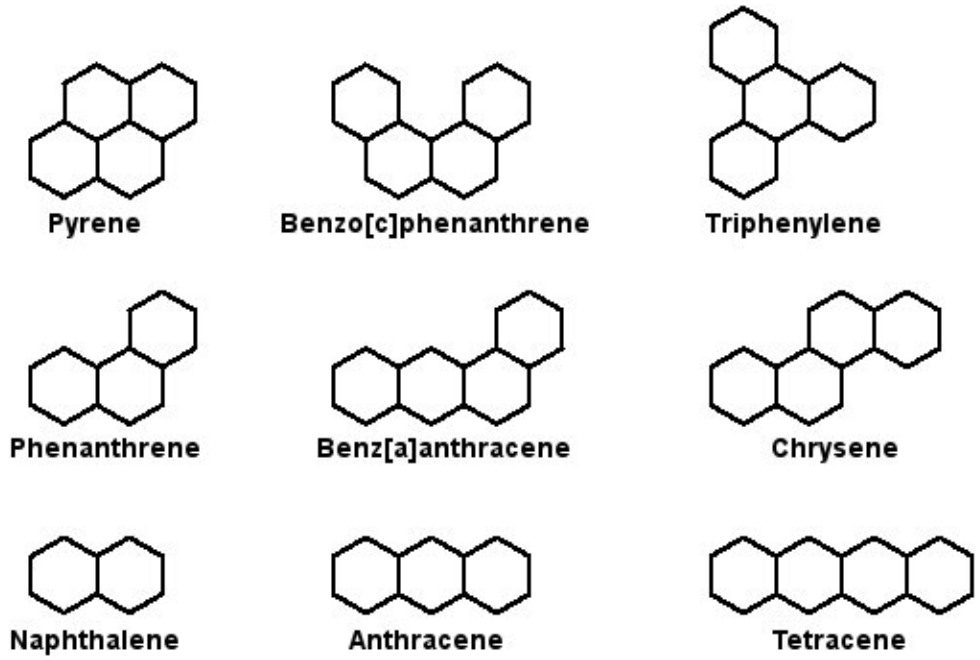


Figure 1. Different PAH groups, aromatic bonds not showing. (Picture from NASA Ames Research Senter.)

1.2 Phenanthrenes and alkylated phenanthrenes

Phenanthrenes have been discovered in many species, forming metabolites. What makes the cancer research more difficult, is that the metabolites formed by oxidation seem to differ between some selected species Jacob have studied[11]. The metabolization can occur at three different sites; the K-region (9,10-position), pre-bay region (1,2-position) and the bay-region (3,4-position).[11] Shou et. al. did an earlier study of the metabolism of phenanthrene by twelve cDNA-expressed isocytochromes P-450 (CYPs), and figured that mice rather resembled humans, than rats.[12] As seen in figure 2, both rat and fish resembles human more than each other, but is dependent of the CYP forms. Although there are different metabolization sites, the phenanthrene still prove to be a carcinogenic threat.[11]

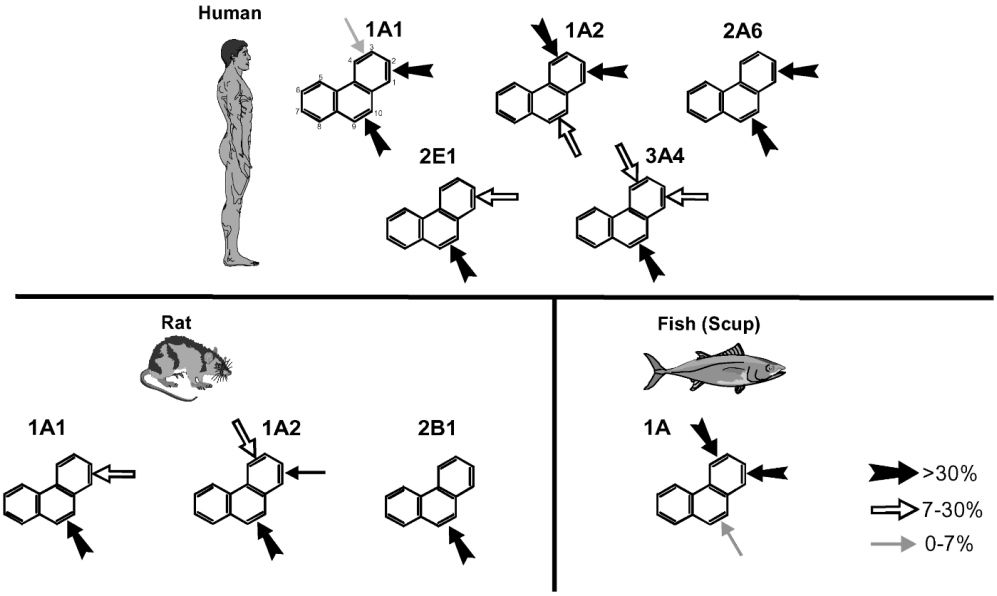


Figure 2. Oxidation of phenanthrene by various human, rat and fish CYP forms[11,13]. (Figure source from Jacob et. al.[11])

A significant and toxic class of PAHs is called alkylated phenanthrenes. This class can be found at aquatic sites, sediment and soil as environmental pollutants.[14] The class have an aromatic ring system, containing of a backbone structure of three rings, substituted by alkyl groups at different positions.[15]

1.3 EGGTOX

1.3.1 Metabolism of PAH's in fish

The RCN-funded project Eggtox led by the Institute of Marine Research in Bergen, aims to unravel the mechanistic effects of crude oil toxicity, observed during early life stages of fish eggs and embryos, as seen in Figure 3. Several studies over the last two decades have shown that the hearts of developing fish (embryos and larvae) are highly susceptible to oil-induced injury, resulting in acute or delayed mortality. Tricyclic PAHs, like phenanthrene, have been potent to induce heart damage in fish embryo by blocking the voltage-gated K^+ channels (ERG) in the heart, causing dangerous arrhythmias and bradycardia.[16] However, the molecular mechanisms and the precise compounds within complex chemical mixtures of crude oil that underlie these effects, are not well understood.

Petrogenic PAHs are characterized by containing large amounts of alkylated isomers and it is claimed that these alkyl-PAHs are more toxic the non-alkylated PAHs.

In this study they investigate the effect of heart development and survival of zebrafish embryo has, when exposed to phenanthrene and its alkylated homologues.

Figure 3 illustrates the exposure of petrogenic PAHs. These are rich in phenanthrenes resulting in two molecular initiating events (MIE) when exposed to embryonic fish. These results in key events (KE) at cellular level, leading further to key events in organ levels, specifically seen in this figure. Impacts on the organs such as cardiorespiratory performance are adverse outcomes (AO) of these pathways. Literature supports the cardiac-based AO or KE indicated in bright orange blocks, while pale orange requires additional quantification. Recent studies suggest the yellow block which is an impaired osmoregulation.[17]

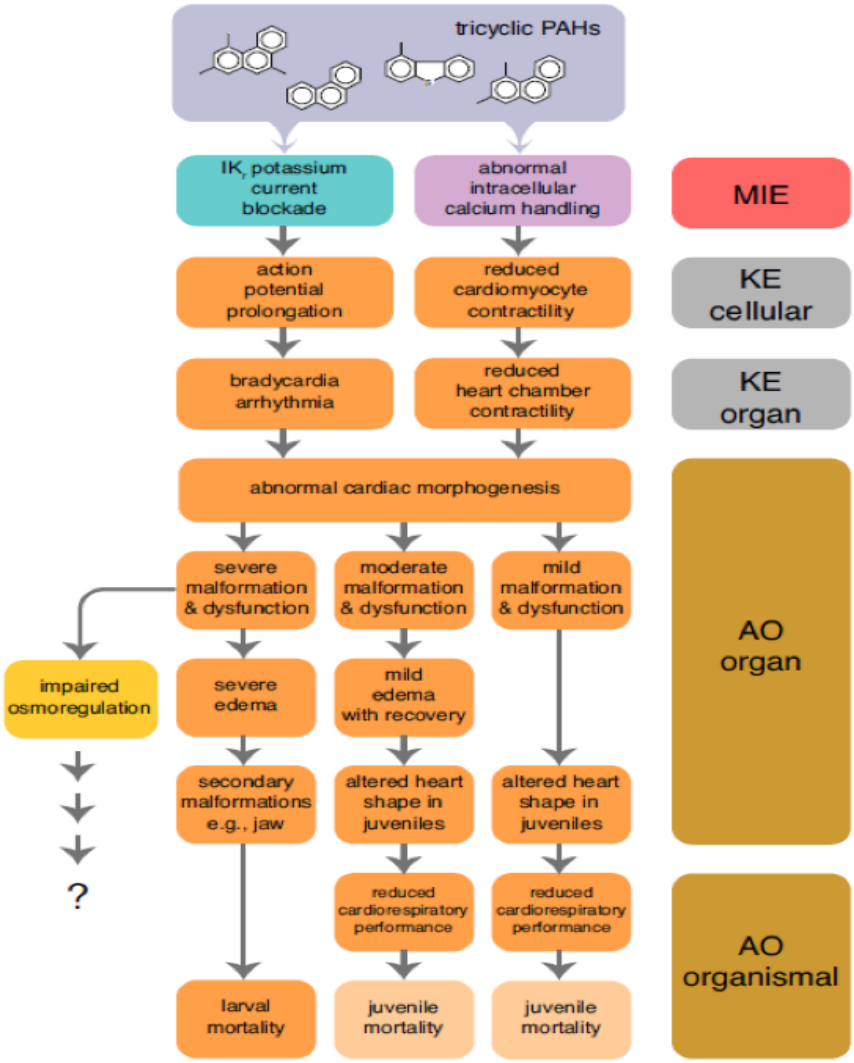


Figure 3. Exposure of petrogenic PAHs in fish embryo. (picture provided by Meier.[18])

1.3.2 Pilot experiments

The first EGGTOX pilot study by Sonnic Meier et. al. on Zebrafish, did not show that C1, C2 or C3 alkylphenanthrene are more toxic than phenanthrene as expected. Phenanthrene was more toxic and generated more bradycardia effects. This may partly be explained by the higher water solubility and bioaccumulation of phenanthrene, compared with the more hydrophobic alkylphenanthrene. The pilot study has not yet been published.

Table 1. Exposure data for single chemicals. (Data provided by Meier.[18])

Compound	Loading of O-ring (MeOH dose mg/ml)	Water concentration (µg/L)
Phenanthrene	10.37	309
1-methylphenanthrene	6.44	96
2-methylphenanthrene	6.63	136
3-methylphenanthrene	6.56	148
4-methylphenanthrene	6.60	135
1,4-dimethylphenanthrene	6.52	40
2,3-dimethylphenanthrene (7a)	6.57	26
2,7-dimethylphenanthrene (7b)	6.64	29
1,7-dimethylphenanthrene (7c)	6.61	78
3,6-dimethylphenanthrene	6.71	20
3- ethylphenanthrene	6.74	20
3-propylphenanthrene	7.06	6
3-isopropylphenanthrene	6.40	6
Retene	7.56	13

One experiment of water exposure of zebrafish embryo (48 h) were done by passive dosing,[19] where the PAHs were dissolved in methanol and thereafter loaded into silicon O-rings (Table 1). The passive dosing provided a stable and controlled water exposure. PAH were measured in the water and the embryo (body burden) by GC-MS.[20]

The survival of zebrafish embryo were calculated after 48 hours.

Figure 4 displays a fairly linear ratio between water concentration and uptake (body burden) for the alkylated phenanthrenes while the more soluble phenanthrene have a lower body burden at high concentrations.

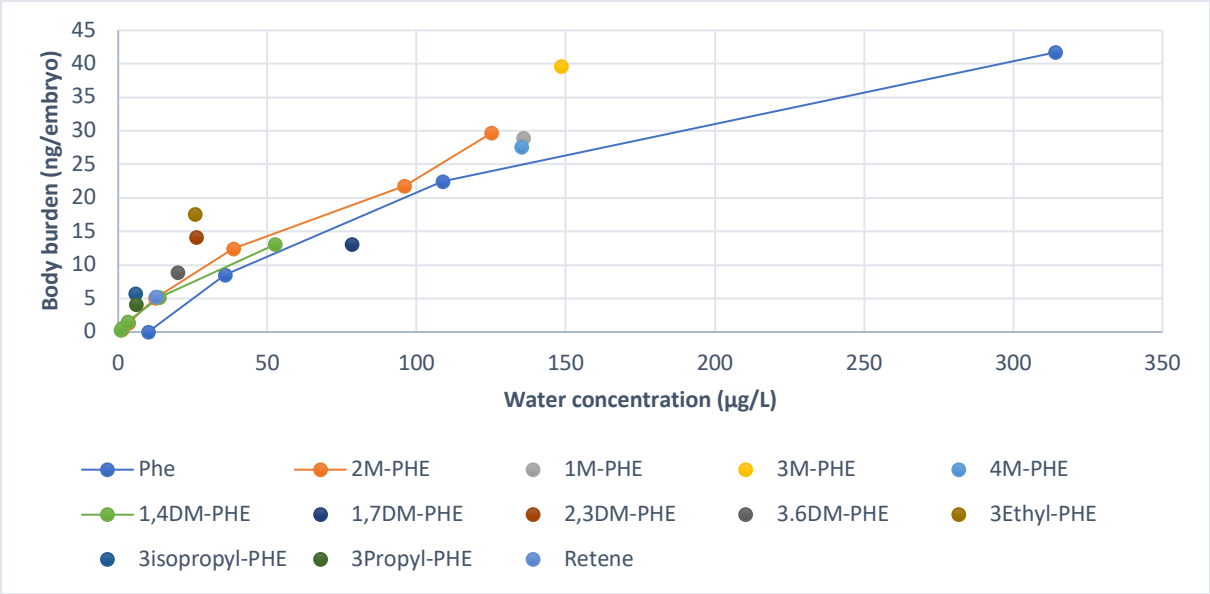


Figure 4. Water concentration (µg/L) and body burden in zebrafish embryo (ng/embryo) after 48 hours exposure for 13 different phenanthrenes. A four-point dose response study were done for phenanthrene, 2-methylphenanthrene and 1,4-dimethylphenanthene the rest of the isomers were only screened at one water concentration. (Figure provided by Meier.[18])

Figure 5 gives the mortality of the zebra fish. Phenanthrene were clearly more toxic than the alkylated compounds. This could be explained by the higher water solubility and water concentration of phenanthrene, but from the body burden, there are not so much more phenanthrene accumulated into the embryo compared with several of the methylphenanthenes. This suggest that phenanthrene are more toxic than its alkylated homologs.[18]

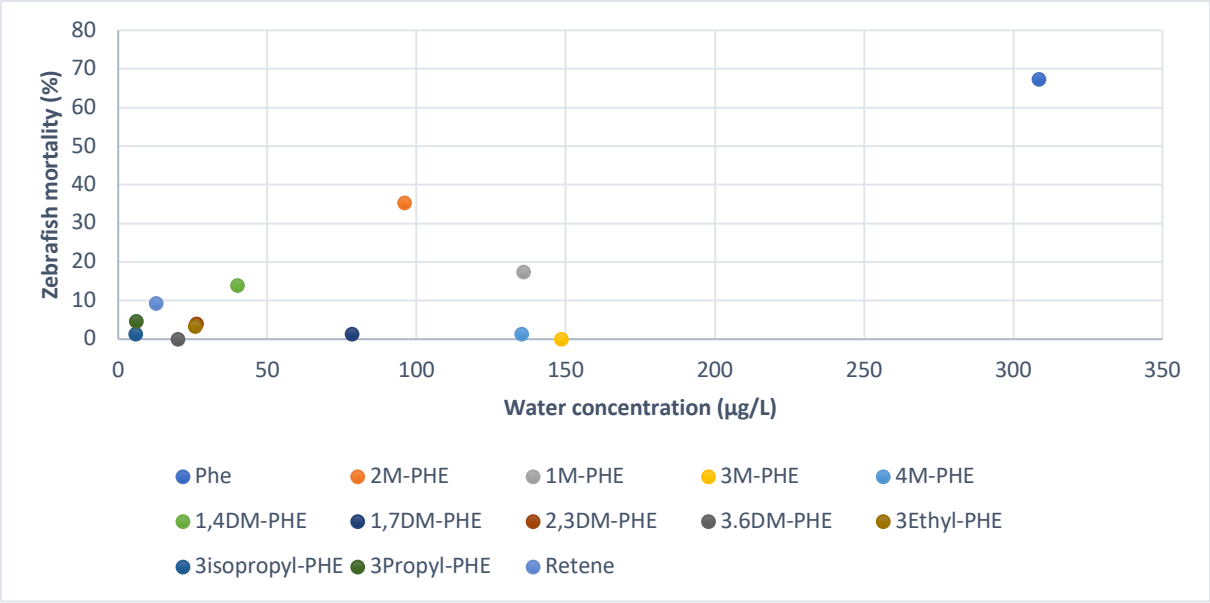


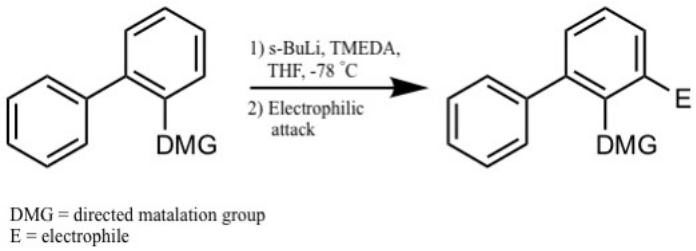
Figure 5: Water concentration (µg/L) and mortality of zebrafish embryo (ng/embryo) after 48 hours exposure for 13 different phenanthrenes. Only results of the highest doses were shown. (Figure provided by Meier.[18])

New studies will be carried out in 2018 on Atlantic haddock, a marine species better suited for the projects purpose. Compounds bolded in table 1 are the thesis products made for this purpose.

1.4 Reactions used to acquire target molecules

1.4.1 Directed *ortho* Metalation

Directed *ortho* Metalation (DoM) reaction is an adaption of electrophilic aromatic substitution. DoM reaction have increased the possibilities of synthesizing aromatic and heteroaromatic molecules.[21,22] In DoM reaction the position *ortho* to a DMG in a benzene gets deprotonated. The deprotonation in DoM happens because of the use of a strong base in the reaction, this base is often an alkyl lithium reagent[21]. By using **2a** or **2b** in DoM reaction, together with s-BuLi and TMEDA in THF at -78 ˚C and after quenching with an electrophile, a C3-substituent is created as seen in figure 6. According to Farmer et. al., by using n-BuLi and THF an exclusive deprotonation at C3 happened and isomerization of the anion to C6. But Farmer et. al. also experimented with Et_2O, in this reaction there was a selective deprotonation at C3, without any occurring isomerization[23]. Isomerization did not happen in the synthesis, suggesting deprotonation did not occur. Tilly et. al. seem to have the answer when explaining that LDA and THF are premixed before adding **2a** or **2b**, the complex induced proximity effect (CIPE) takes place, this effect seem to be stronger than resonance and inductive effect, and creates products **3a** and **3b** without any isomerization.[24-27]

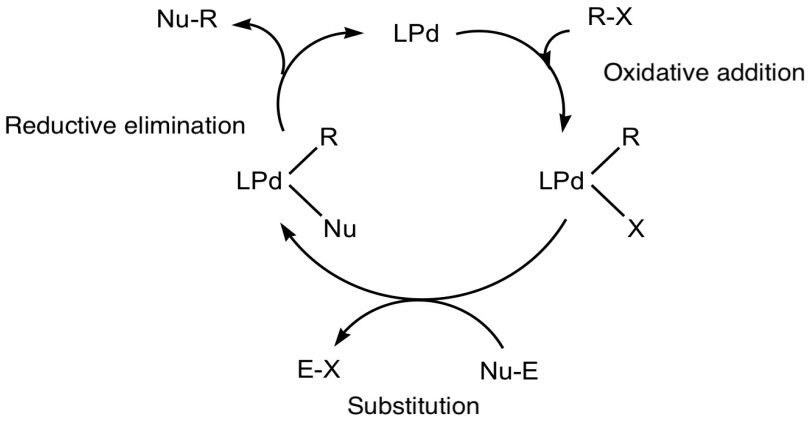


Scheme 1. An illustration of DoM when treated with s-BuLi and TMEDA in THF at -78 ˚C. In the case of **2a** and **2b** the DMG group was $CONEt_2$ and the E was triisoprobyl borate.

Metalation with organometallic compounds was discovered independently in 1939-1940 by Wittig and Fuhrman and Gilman and Bebb.[28,29] Studies of DoM has been conducted by Gilman, then further developed by Hauser with students.[30-32] Later the reaction usage has been expanded by Snieckus.[21,22] PAHs synthesis before DoM contained a great variety of Lewis and Brønsted acid catalyzed S_FAr reactions.[14,33]

1.4.2 Suzuki-Miyaura Cross-Coupling Reaction

The Suzuki-Miyaura Cross-Coupling is a good example of transition metal-catalyzed cross-coupling reactions, which has superseded all other classical methodologies on C-C bond formation, specially the aryl-aryl conjunction.[34,35] It is an organometallic reaction, where boronic acid and an organohalide are coupled by a palladium(0) complex. The reaction is widely used for substituted biphenyls, and a good choice for making the requested phenanthrenes for this thesis. An illustration of the Suzuki coupling can be seen in figure 7. In the reaction a boron ester reacts with a bromo-compound. In the oxidative addition step of Suzuki-Miyaura cross-coupling, the Palladium catalyst reacts with the bromo-compound. Next step is a transmetalation step, where the used base is exchanged with the boron ester. Last step is the reductive elimination step, where the coupled product is eliminated and Palladium(0) is formed.[36,37]



Scheme 2. Schematic mechanism for Suzuki coupling (e = $B(OH)_2$, R = vinyl or aryl, Nu = aryl). Hartwig-Buchwald-coupling (E = H, R = vinyl or aryl, Nu = NR'_2) and Stille-coupling (E = SnR'_3, R = vinyl or aryl, Nu = aryl) are also included in this scheme. (Source of figure from the mail tore.benneche@kjemi.uio.no, for the course KJM5270, Pd-Compendium.)

Palladium chemistry has been known since 1960, starting with the Wacker-process. The use of Palladium has ever since been more developed and broadly used. Compared to other chemicals for coupling, the oxidation number of Palladium is easier to change, while also making a complex to both soft and hard ligands. Palladium tolerates different functional groups, relieving the need for protection groups. Compared to other options Palladium is less sensitive towards

water, acids and oxygen, giving easier conditions to work with. Compared to Platinum, Osmium and Rhodium, Palladium is both cheaper and less toxic.[38]

Some alternatives to Suzuki-Miyaura cross coupling are Stille reaction, Negishi and Hiyama coupling. Stille uses tin, which makes it more toxic, while Hiyama coupling has more limitations.[39-41] Negishi could be an alternative, but is more sensitive to oxygen and water compared to the Suzuki coupling. Hence Suzuki-Miyaura cross coupling seem to be the best solution for this thesis, and has also been used to produce some of the products in this thesis by several other researchers.[14,42,43]

1.4.3 Directed remote Metalation

DreM is a regioselective reaction to make polysubstituted aromatic and heteroaromatic scaffolds. As the name suggest, the reaction is regioselective at remote position, relative to the directing DMG, as seen in figure 6. DreM is an extension of the DoM reaction and a combination of CIPE and kinetically enhanced metalation.[24] Thermodynamic and kinetic factors are important to the metalation regioselectivity in the DreM reaction, but the reaction have a range of factors for the regioselective outcome. Some of the factors in a DreM reaction are base strength and nature, directing metalation groups (DMG) properties, rigidity of reactant skeletons, stability of metalated products and acidity of aromatic hydrogens.[24]

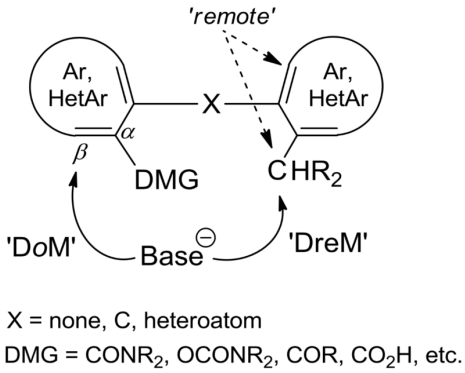


Figure 6. Illustration of a base attacking in D*o*M and Drem reaction. (Figure from Tilly et. al.[24])

1.4.4 Triflation and Detriflation

The OH group in the molecules, in this thesis, is protected with trifluoromethanesulfonic acid (triflate). Illustration of the molecule can be seen in figure 7. The triflate is a strong sulfonic acid used to protect a molecule from oxidation. Triflate is a good leaving and protecting group, but expensive.[43] There are other protecting groups on the market, such as carbamate, but this group may create byproducts which is inseparable from the target molecule, making triflate the perfect candidate.[42]

Another quality of triflate is in an S_N1 reaction, where the triflate as a leaving group is a weak base, which makes a good leaving group compared to methanesulfonic acid. This makes the triflate a good reacting acid when put on a molecule, and a good leaving group when removing it later on.[44]

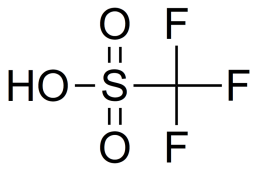
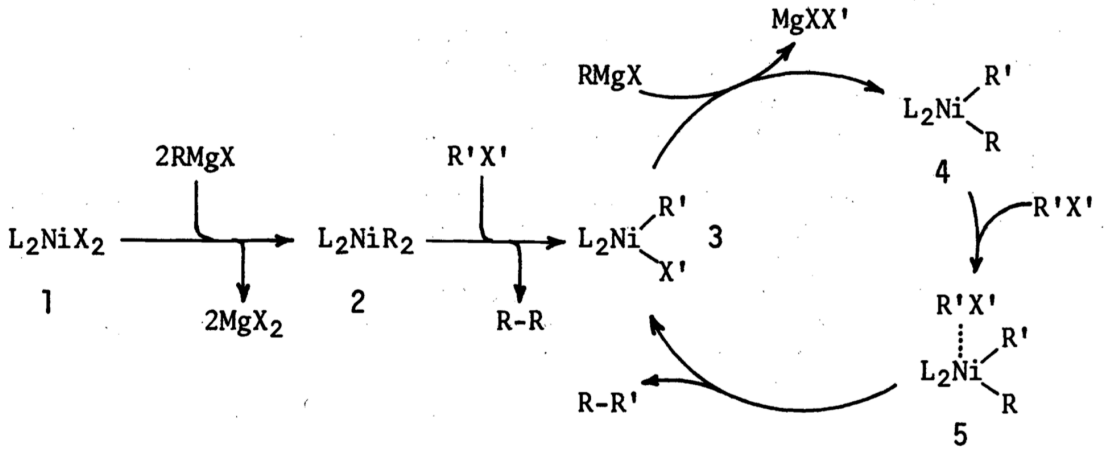


Figure 7. The molecule of trifluoromethanesulfonic acid.

1.4.5 Kumada Coupling

The Kumada coupling was one of the first known catalytic cross-coupling reactions, and is now one of the most important methods for C-C coupling in organic synthesis.[45] It couples C-C bonds usually in the combination of two alkyl, aryl or vinyl groups.[46] The reaction often use nickel or palladium as a transition metal catalyst, like the Suzuki-Miyaura cross coupling, but react organic halides with Grignard reagent.[45] Further development over the 3 last decades have made the procedures between sp-, sp^2 and sp^3-hybridized carbon atoms very efficient.[46,47] Although Kumada have been explored extensively, the aryl halides having no π-electrons, need a different oxidative addition mechanism compared to aryl and vinyl groups. This makes the process of Kumada with aryl halides poorly understood.[48]



Scheme 3. Cycle of Kumada Coupling.[49]

At the scheme 3, is a suggested cycle of Kumada Coupling. It illustrates how a dihalodiphosphinenickel reacts with a Grignard reagent, and forms an intermediate diorganonickel complex. By an organic halide, the diorganonickel complex is subsequently converted to a halo(organo)nickel complex. The halo(organo)nickel complex form a new diorgano complex together with the Grignard reagent, and releases the cross-coupling product from an attack by the organic halide. The attack might happen via the pentacoordinate intermediate, and the original complex gets regenerated, and by this completes the catalytic cycle.[49]

1.5 Aim for the thesis

The aim for the thesis was to make compounds 2,3-dimethylphenanthrene (**7a)**, 2,7-dimethylphenanthrene (**7b)** and 1,7-dimethylphenanthrene (**7c)** in gram scale for the EGGTOX project. Then to make 1,9-dimethylphenanthrene (**8d**) to J. H. Christensen in Section for Environmental Chemistry and Physics at University of Copenhagen, Denmark. Kumada coupling on triflated compounds giving **8d**, and might 2,3,9-trimethylphenanthrene (**8e**) can be a good way of synthesizing new compounds if a vinyl group could be added to the phenanthrene. The products **7a-7c** and **8d** got good total yield, while **8e** needs purification to prove a new compound. 1-methyl-9-vinylphenanthrene (**8f**) has not been successfully made yet. All final molecules has been illustrated in figure 8.
For the EGGTOX part, studies are being conducted on fish eggs and embryos this year. This provides knowledge about fish health when exposed to phenanthrenes. The results from this research will be important information and knowledge for future oil and gas exploration and production activites. The research can give a clearer understanding of the dangers of oil and which phenanthrenes might be a crucial threat to the biota in its environment.

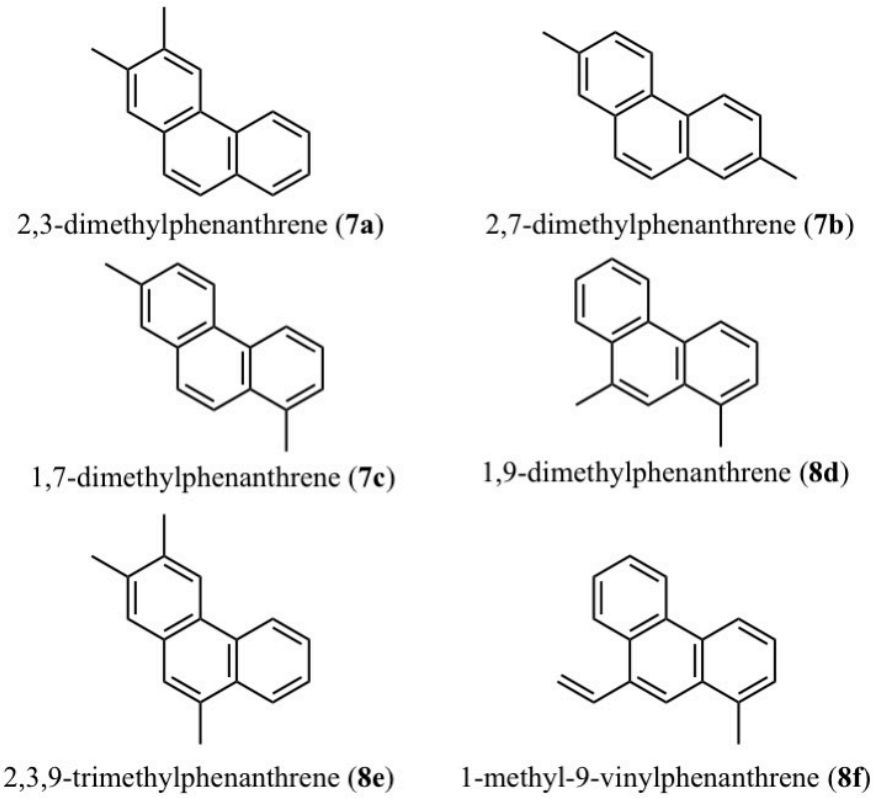


Figure 8. Products made (**7a-c** and **8d**), product might made (**8e**) and product failed to make (**8f**).

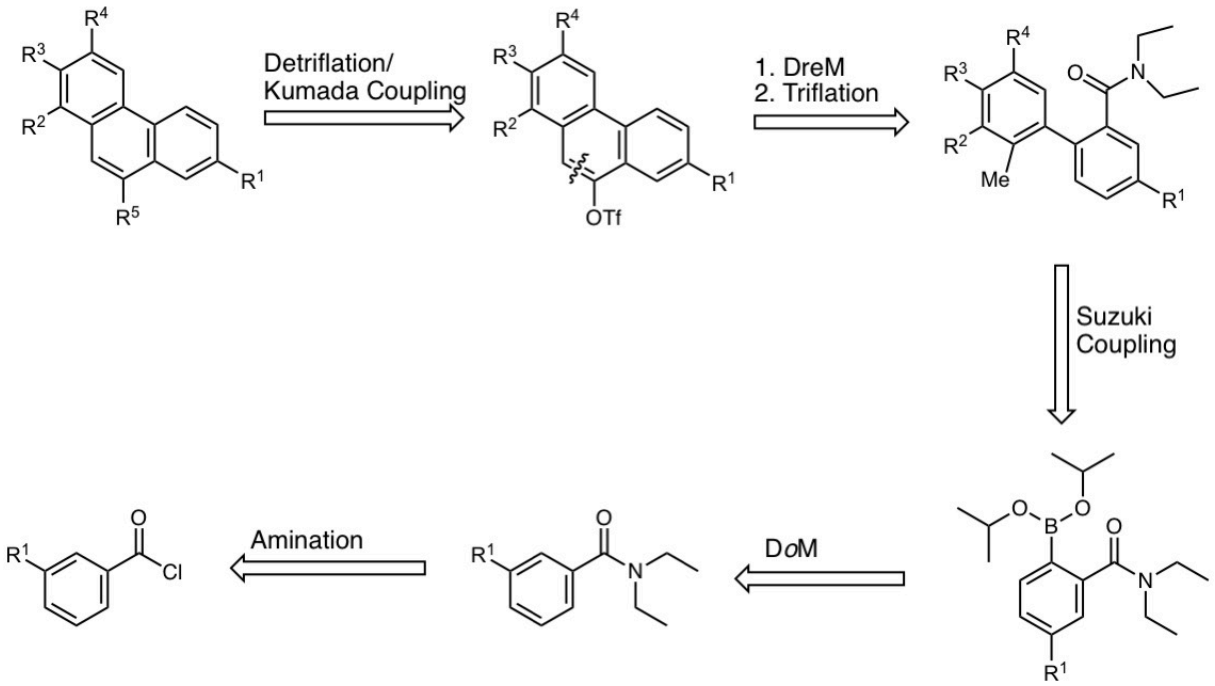
2. Results and discussion

2.1 General

All new compounds were synthesized using standard procedures discussed in the previous chapter. Procedures were similar or exact to previously published literature.

2.2 Synthesis of alkylated phenanthrenes

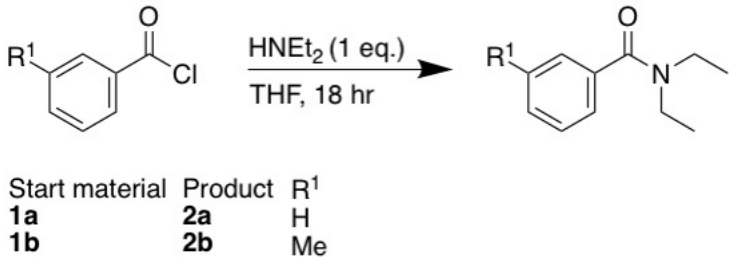
All of the target molecules had the same backbone structure, but had methyl groups at different positions. Four of the compounds were dimethylated, while one compound was trimethylated. Since all the products were similar, the same route of reactions were used. The route used was amination, DoM, Suzuki-Miyaura Cross-Coupling, DreM followed by triflation. The triflated product was then either detriflated or went through Kumada Coupling. Retrosynthesis of the made products can be seen in scheme 4.



Target molecule	R^1	R^2	R^3	R^4	R^5
7a	H	H	Me	Me	H
7b	Me	H	Me	H	H
7c	Me	Me	H	H	H
8d	H	Me	H	H	Me
8e	H	H	Me	Me	Me
8f	H	Me	H	H	CH_2=CH

Scheme 4. Retrosynthesis of disubstituted phenanthrenes with R groups and their corresponding target molecules.

2.3 Amination



Scheme 5: Amination to create amide

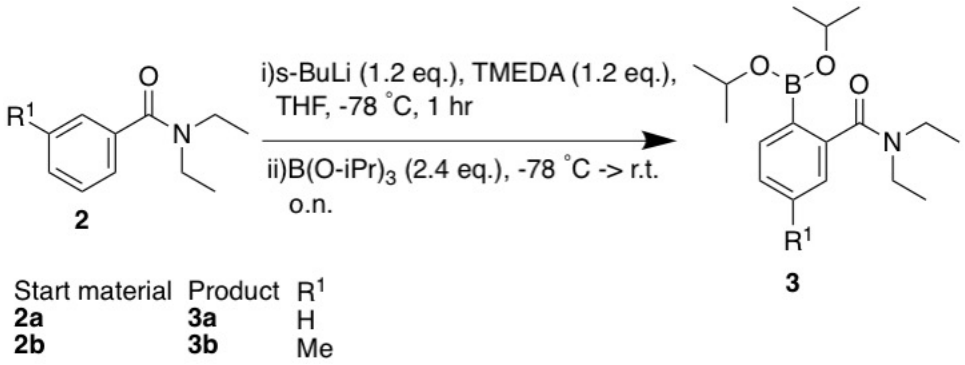
The amide group was synthesized as seen in scheme 5. It was a robust reaction with excellent yield. Product was pure by NMR, without need of further purification.

The one problem to discuss in the procedure were the attempts in the start. An initial attempt to do the reaction at room temperature failed to cause a reaction. 18 hour reflux gained excellent yields as seen in Table 2.

Table 2: Amination reaction and obtained yields.

Start material	R^1	Product	Yield %
1a	H	**2a**	93
1b	Me	**2b**	92

2.4 Directed *ortho* Metalation



Scheme 6: DoM reaction to afford boronate.

The Directed *ortho* Metalation (DoM) reaction with an amide, as seen in scheme 6.

The reaction is quite demanding. First the use of s-BuLi, which is a dangerous, highly reactive base, and second the conditions required for the reaction. The reaction is quite exothermic and have to be kept at -78 °C, but is also very sensitive to both oxygen and water, requiring inert atmosphere then dried conditions.

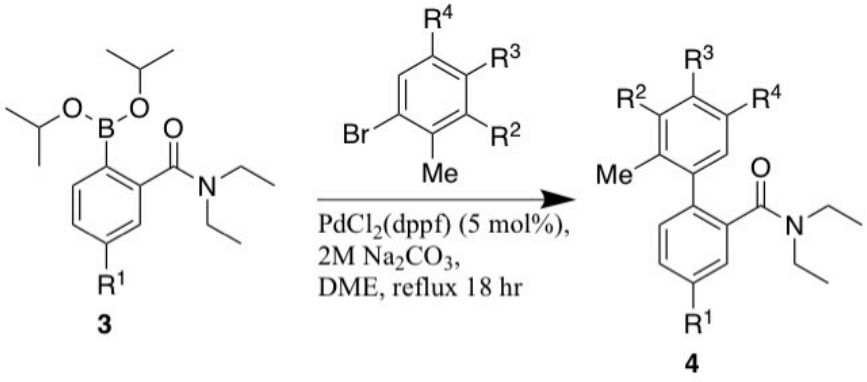
The yields were splendid. One reaction gave 93%, while another gave 96% compound as seen in table 3. Twice the reaction got warmer than it should, because of the lack of dry ice, giving temperatures up to -65 °C, this was inconsequential for the yield. Another factor was the s-BuLi, which started to form a dark brown color and reducing the concentration. In this case the volume of s-BuLi used was raised by 30 – 50% volume, not titration since the bottle was first opened in 2017.

The products of this reaction could not be purified by flash column because they are too polar, this was tested using 3:1 Hep:EA with Rf 0.25, and in the end tried plain EA, without recovering the compound.

Table 3: Yields after DoM reaction.

Starting material	R^1	Product	Yield %
2a	H	**3a**	96
2b	Me	**3b**	93

2.5 Suzuki-Miyaura Cross-Coupling



Start material	Product	R^1	R^2	R^3	R^4
3a	**4a**	H	H	Me	Me
3b	**4b**	Me	H	Me	H
3b	**4c**	Me	Me	H	H
3a	**4d**	H	Me	H	H

Scheme 7: Suzuki coupling to afford biphenyl **4**.

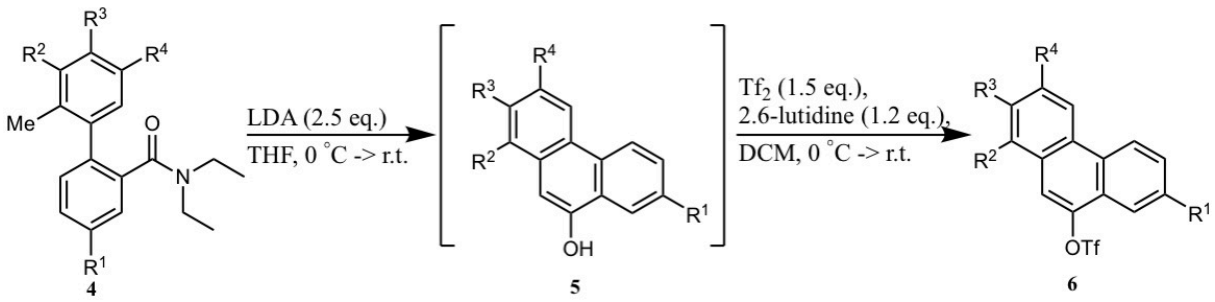
The starting material was mixed with $PdCl_2$(dppf), methylated bromobenzene and Na_2CO_3, followed by an 18 hour reflux time as seen in scheme 7. The reaction gave a brown compound which needed flash column to receive pure product.

The reaction is sensitive to oxygen, so inert atmosphere is required. The procedure is relatively simple and usually give good yields. Another catalyst was tested, $Pd(OAc)_2$, but gave poor results, with only 20% yield for the **4d** product, as seen in table 4 along with yields from $PdCl_2$(dppf).

Table 4: Suzuki Coupling yields.

Start material	**Phenyl bromide**			**Product**	**Yield %**	**Comment**
	R^2	R^3	R^4			
3a	H	Me	Me	**4a**	Quant.	
3b	H	Me	H	**4b**	68	
3b	Me	H	H	**4c**	80	
3a	Me	H	H	**4d**	80	20% with $Pd(OAc)_2$

2.6 Directed remote Metalation and Triflation



Start material	Product	R^1	R^2	R^3	R^4
4a	**6a**	H	H	Me	Me
4b	**6b**	Me	H	Me	H
4c	**6c**	Me	Me	H	H
4d	**6d**	H	Me	H	H

Scheme 8: DreM and triflation of the bifenyls.

Directed remote Metalation (DreM) and triflation reaction can be seen in scheme 8.

The product from the DreM reaction were unstable and required immediately to be concentrated and put in inert atmosphere, before triflating, to prevent oxidation into a ketone.

Yields and NMR have not been taken in this step because of unstable compounds. The crude products were triflated.

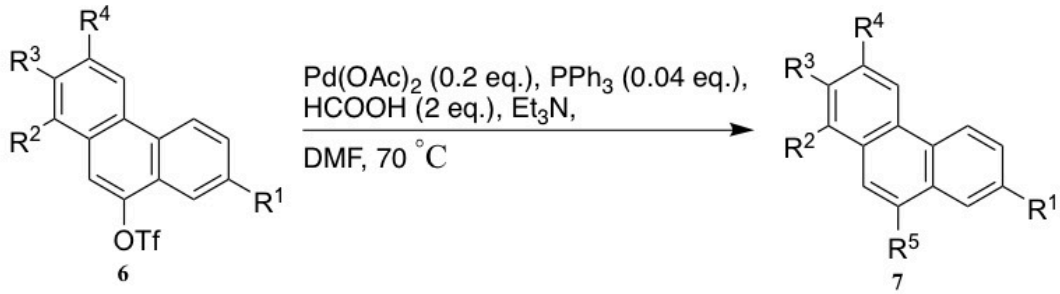
The triflate is a good leaving group, while also giving stable compounds. After the DreM reaction the intermediates have non-isolated alcohols, which would go through air oxidation, creating a ketone, if not triflated,. Substitution or elimination reactions could be smoothly performed, after a backbone of phenanthrene was made by DreM and triflation. The DreM and triflation gave over 90% yields in all cases, except one which gave 63% as seen in Table 5.

Compound **6d** had previously been made by Cai et. al. at a 95% yield, while it was produced at 96% yield in this thesis. The compound in the thesis is more pure than Cai et. al., seen by the melting point. Cai had a melting point of 60 to 61 °C, while the melting point for same compound in the thesis was 70 to 71 °C. The result can differ a little since recrystallization was done in EtOAc in Cai et. al.[14]

Table 5: Yield after DreM and triflating.

Start material	Product	Yields %
4a	**6a**	93
4b	**6b**	Quant.
4c	**6c**	91
4d	**6d**	63

2.7 Detriflation



Start material	Product	R^1	R^2	R^3	R^4
6a	**7a**	H	H	Me	Me
6b	**7b**	Me	H	Me	H
6c	**7c**	Me	Me	H	H

Scheme 9: Removing of triflate to get wanted phenanthrenes.

A good reaction to proceed with a triflated phenanthrene, is to remove the triflate by palladium catalyzed hydrogenolysis. $Pd(OAc)_2$, PPh_3, Et_3N and HCOOH were added to the starting material, then put under inert atmosphere and allowed to reflux for 1 hour, before quenching of the completed reaction, as seen in scheme 9.

The reaction was fast and gave excellent yields of 99% and quant, as seen in Table 6.

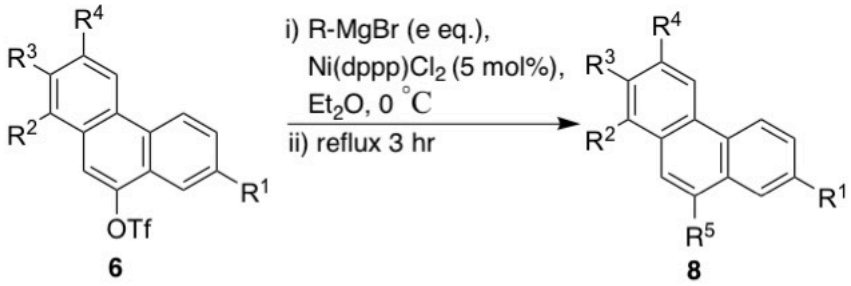
NMR was taken after purification and recrystallization. The spectra's were pure and had clean peaks.

The products **7a-c** has previously been made by same method, the results are correlating, but no 2D NMR was conducted before. Comparing the results: Thomas et. al. previously made **7a** at same purity as this thesis, but he got 73% yield, compared to 99%. Comparing compound **7b**, Thomas got 94% yield and melting point at 101-102 °C, the melting point was same in this thesis, but quant. in yield. **6c** was also made by both, where both gained quant. yield. The difference was purity, where Thomas got 78-80 °C (Recrystallized in EtOH) the compound in this thesis got a better melting point of 82-83 °C (Recrystallized in MeOH).[42]

Table 6: Yields of final phenanthrenes after detriflation.

Start material	Product	Yield %
6a	**7a**	99
6b	**7b**	Quant.
6c	**7c**	Quant.

2.8 Kumada Coupling



Start material	Product	R^1	R^2	R^3	R^4	R^5
6d	**8d**	H	Me	H	H	Me
6a	**8e**	H	H	Me	Me	Me
6d	**8f**	H	Me	H	H	CH_2=CH

Scheme 10: Kumada Coupling to replace the triflate with a wanted R-group.

An exciting turn on the triflated phenanthrenes were the testing of Kumada Coupling with Grignard reagents as illustrated in scheme 10. In inert atmosphere at 0 °C, starting material and Ni(dppp)Cl_2 was added to the Grignard reagent. The reaction were completed after 3 hours of reflux, and quenched by adding methanol slowly afterward. The procedure was built on the procedure of Xia et. al.[50]

By this reaction the **8d** was created at excellent yield and melting point of 89-90 °C (recrystallized in MeOH) when using MeMgBr as seen in Table 7. Because of the success an attempt at making **8e** was conducted. **8e** also seem to be able to make, but flash column has to be done after the thesis. Yet, an ^{1}HNMR was taken to analyse the compound made, seen in figure 9.

1-methyl-9-vinylphenanthrene was attempted to be made with vinylmagnesium bromide, but only gave side products and starting material. The first assumption for the result was that the Grignard reagent did not work. The reagent had crystallized, and only small amounts of brown liquid was in the flask with the solid compound. According to Sigma Aldrich the reagent should have been kept at temperatures above 25 °C to prevent crystallization. It is also mentioned that careful heating could resolve the crystals and make the reagent work again. A newly purchased flask of vinylmagnesium bromide was used in the third attempt of making the 1-methyl-9-vinylphenanthrene structure, but it also seemed unsuccessful. Even when raising the temperature to 68 °C and letting the reflux go over 18 hours.

Table 7: Yield of 1,9-dimethylphenanthrene after Kumada Coupling.

Starting material	Product	Yield %	Comment
6d	**8d**	96	
6a	**8e**	-	Need purification
6d	**8f**	-	No product

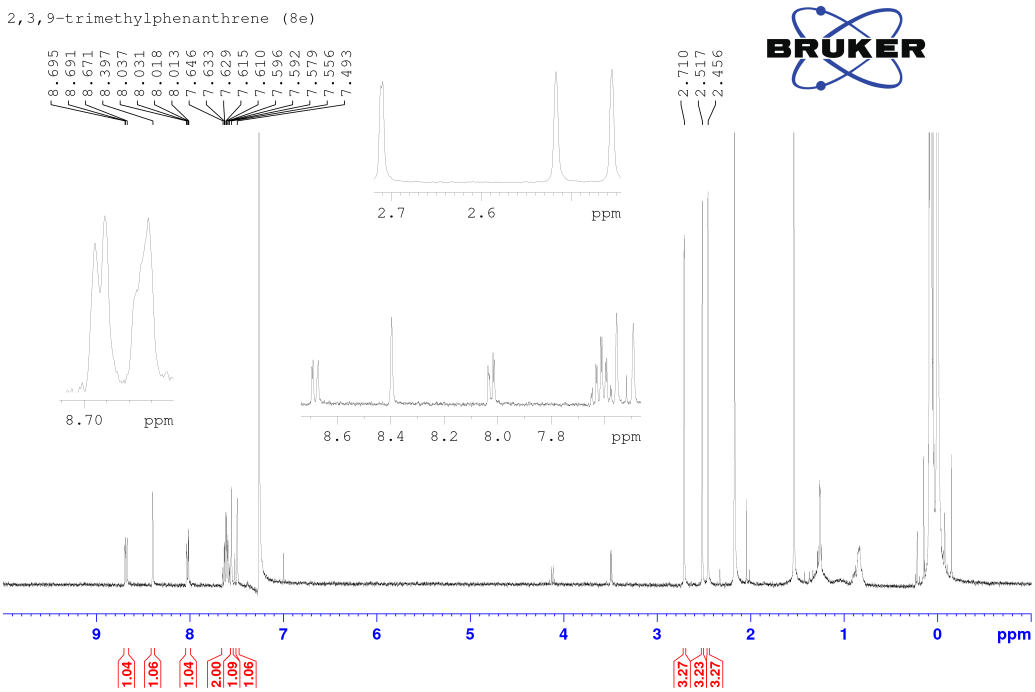


Figure 9. [1]HNMR of the possible **8e** product, not purified.

[1]HNMR of product **8e**: Tops are where they are expected to be. 3 peaks around 2.5 ppm, one having same apparent doublet peak as **8d**. All the 7 protons are found in the aromatic area. The aromatic peaks are also similar to **8d**, for example looking at the multiplets 8.08-8.04 and 8.67-8.70, compared to the peaks in **8d**, which looks almost the same at shifts 8.04-8.09 and 8.72-8.77 ppm. The multiplet at 7.57-7.65 ppm in **8e** is also the same as 7.62-7.69 ppm in **8d**. Since all the right peaks are found and they look quite similar to the same molecule, except for one methyl group, suggest that **8e** is the correct product.

3. Future work

The D*o*M- Suzuki coupling– DreM reaction has become known and tested, but pulling the pathway over to triflate and Kumada coupling to make new compounds seem to be a new way to go. By itself, such as **8d**, it is not really special, but if there is a possibility to add a vinyl group instead of methyl, new possibilities of synthesizing aromatic structures can be tested. By adding vinyl and oxidizing the double bond, new and useful compounds can be synthesized.

Since Kumada coupling seem to have worked on both (**6a**) and (**6d**), it might also work on **(6b)** and **(6c)**. This is another way to produce similar products in a new way or even making compound that have not been synthesized before.

In the Kumada coupling, the MeMgBr is sp^3, while $CH_2CHMgBr$ is sp^2 hybridization, this can be the answer of the vinyl not working, while the methyl group works great. Another catalyst might be the factor to make **8f.**

New experiments could be to react a triflated phenanthrene with (2-bromovinyl)benzene to create styrylphenanthrene, for example 1,9-dimethylstyrylphenanthrene. If example 9-styrylphenanthrene could be made, photochemistry could be attempted to make benzo[g]chrysene. Other methylated phenanthrenes could go through same synthesis and make benzo[g]chrysene with different methyl groups. Another experiments could be to react the vinyl group with an alcohol, then either oxidate to an acid or to do a wittig reaction followed by photoreaction. For these further opportunities more literature search is required.

Ackermann and Althammer has conducted sp^2 hybridized Kumada coupling on both electron-poor and rich aryl tosylates, managing to add new aromates to the start compound. They have used $Pd(dba)_2$ as catalyst and an air-stable preligand, which might be an alternative to try on the vinyl reaction to produce **8f**, or other larger aromates.[51]

4. Conclusions

Results of the compounds made in the thesis compared to when they were made previously shows that these new products were in general both more pure and in better yields than former producers.

As mentioned in the results, both **7a** and **7b** was higher in yield in this thesis than previously reported by Thomas et. al., and **7c** was more pure considered the melting point.[42]

Product **6d** was also slightly better in yield and much purer considered the melting point, compared to Cai et. al., reported in the results part.[14]

8d was successfully made in this thesis, also in good yield and good total yield. It is the first time this compound have been analyzed after synthesizing it. The product **8e** seem according to ^{1}HNMR, not purified, to have been successfully made, which is also the first documentation of this product synthesized.

Several attempts of making phenanthrene containing a vinyl group were conducted, but it seem to be harder to make, and other criteria are be needed to success.

EGGTOX received the requested amount of **6a-c** to start their testing.

5. Spectroscopic analysis and characterization

Analyses for final products and **6d** has been conducted in form of ^{1}HNMR, ^{13}CNMR, COSY, HSQC and HMBC. These analyses have been discussed separately under each table. One problem seem to be constant, the HMBC get to big signal, and coupling of quaternary carbons are because of this often inconclusive. Another common problem in HMBC is that lots of signals are missing, and the phenanthrenes gives a unusual zig-zag coupling from one part of the molecule to the other side.

Data of compound **7a** are provided in table 8.

Data of compound **7b** are provided in table 9. The structure of **7b** is symmetrical.

Data of compound **7c** are provided in table 10.

Data of compound **6d** are provided in table 11. Compound **6d** has been put next to **8d**, making it better to compare them.

Data of compound **8d** are provided in table 12.

2,3-demethylphenanthrene (8a)

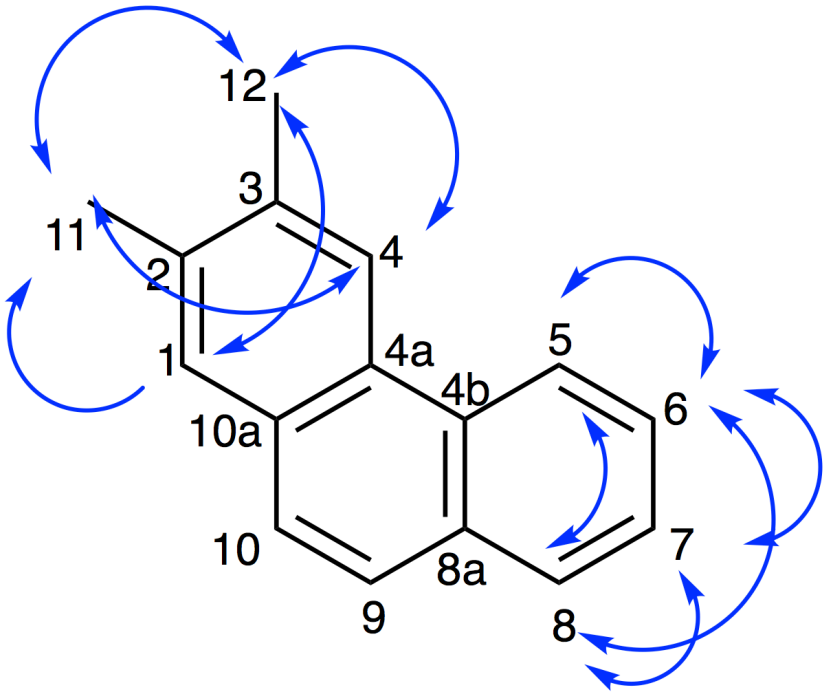


Figure 10. Illustration of **8a** and how COSY couples. Arrows couples between protons on the specific carbons they are pointed on.

Table 8. Product **8a** analyzed by 2D NMR.

Position	∫	δ_H [ppm]	δ_C [ppm]	m	J [Hz]
1	1	7.63	128.6	s	-
2	-	-	135.8/135.9	-	-
3	-	-	135.8/135.9	-	-
4	1	8.43	123.0	s	-
4a	-	-	a	-	-
4b	-	-	a	-	-
5	1	8.65	122.4	d	8.23
6	2	7.58-7.62	126.2	m	2.57, 8.08
7	1	7.52-7.57	126.3	m	-
8	1	7.84-7.87	128.5	m	-
8a	-	-	a	-	-
9/10	2	7.65	126.0	s	-
10a	-	-	a	-	-
11	3	2.53	20.6	s	-
12	3	2.47	20.0	s	-

^{1}HNMR: All peaks can be seen. Two methyl groups at 2.5 ppm and 8 protons in the aromatic area. The peak at 7.64 has overlap with 7.65, so no clear integral was possible to obtain. But it seems like 7.64 is 2 or 3 protons and 7.65 has 1 or 2 protons. The top at 7.65 is taller because of the overlap, than it would be on its own.

^{13}CNMR: As expected, 2 signals at 20 ppm, and 12 signals, where two of the signals have two carbons. The two carbons are taller, and has the shift of 125.96 and 128.62. This is because of the molecule structure being almost symmetrical. The quaternary carbons has lover intensity and higher ppm than other signals in the aromatic area.

COSY: The positions 11 and 12 couples to each other, showing that they the metyl groups are neighbors on the same aromatic ring. Position 1 couples to 11 and weaker to 12. Position 4 couples strongly to 11, and weakly to 12. Position 7 binds strongly to 8, and weakly to 5. Position 6 binds weakly to 8, and strongly to 5. Position 1, 9 and 10 got a big dot, and if they couple to each other is therefore inconclusive. A bit hard to see the coupling between position 6 and 7. The resonation fits nicely to the molecule, and protons seems to be correctly placed. These couplings can be seen in figure 10.

HSQC: All bindings were solid, but the binding of position 7 and 9/10 were unclear, but 126.0 ppm was twice as intense, and had to be 9/10, since they are 2 signals. The quaternary carbons are nicely showing as lower peaks with higher ppm than other aromatic signals.

HMBC: The signals were really bold and oblong, while the carbons are close to each other making it hard to take any real conclusions.

Note[a]: inconclusive peaks.

2,7-dimethylphenanthrene (7b)

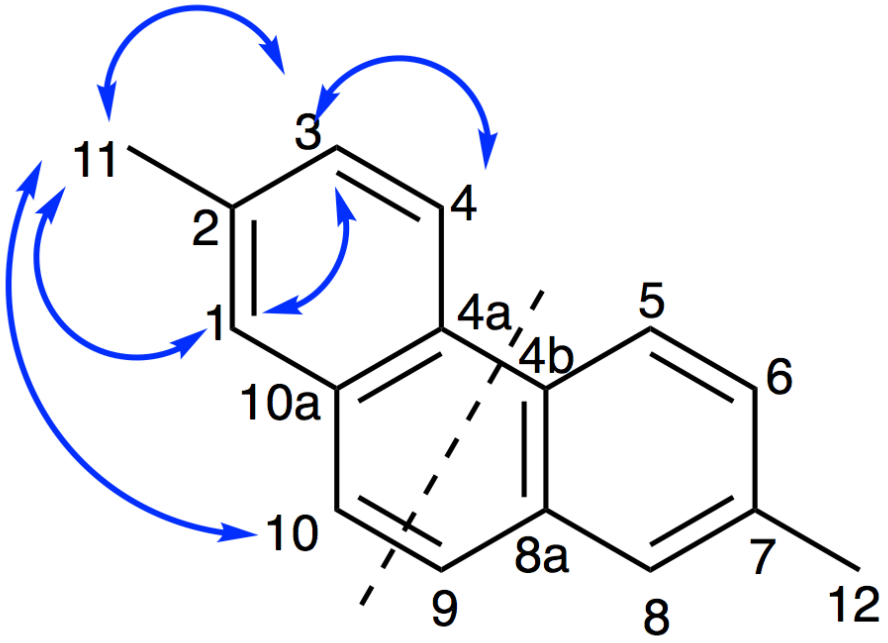


Figure 11. Illustration of **8b** and how COSY couples. Arrows couples between protons on the specific carbons they are pointed on. Since the structure is symmetrical and would be the same on both sides, arrows are only shown on one side.

Table 9. Product **8b** analyzed by 2D NMR.

Position	∫	**δ_H [ppm]**	**δ_C [ppm]**	**m**	**J [Hz]**
1/8	2	7.64	126.7	s	-
2/7	-	-	131.87	-	-
3/6	2	7.45-7.47	128.3	dd	1.68, 8.45
4/5	2	8.52-8.54	122.4	d	8.43
4a/4b	-	-	128.2	-	-
8a/10a	-	-	135.8	-	-
9/10	2	7.65	128.1	s	-
11/12	6	2.55	21.4	s	-

^{1}HNMR: Because of symmetry, only half of the peaks are showing, but with double proton amount. One singlet at 2.55 ppm have both methyl groups, as seen in the integral of 6 protons. In the aromatic area the number of integrals is also correct, with a value of 8 protons. The signals 7.64 and 7.65 have overlap, but looking at their intensity, it seems like they have 2 protons each.

^{13}CNMR: All carbon signals are present, but overlap because of the symmetry. 1 signal for the two methyl groups and 7 signals in the aromatic area for the aromatic carbons.

COSY: Position 4/5 couples to 3/6. Position 1/8 couples to 3/6 and 11/12. Position 11/12 couples to 3/6 and 9/10. These couplings are shown in figure 11.

HSQC: All bindings were good, but carbons 128.1 and 128.3 were close. It looks like the positions have been paired correctly from looking at the HSQC spectra closely. The quaternary carbons are nicely showing as lower peaks with higher ppm than other aromatic signals, except 128.2, which has lower ppm than 128.3, but still lower.

HMBC: Position 4/5 couples to 131.87 and 135.80, and the 11/12 position couples to 135.80. Further information is not possible to say from the spectra. Position 4 are most likely coupling to position 2 and 10a, while 11 is coupling to 10a. This gives 10a the 135.80 ppm peak, while position 2 is 131.87 ppm. 128.21 ppm is the only quaternary position left, and belongs to 4a/4b.

1,7-dimethylphenanthrene

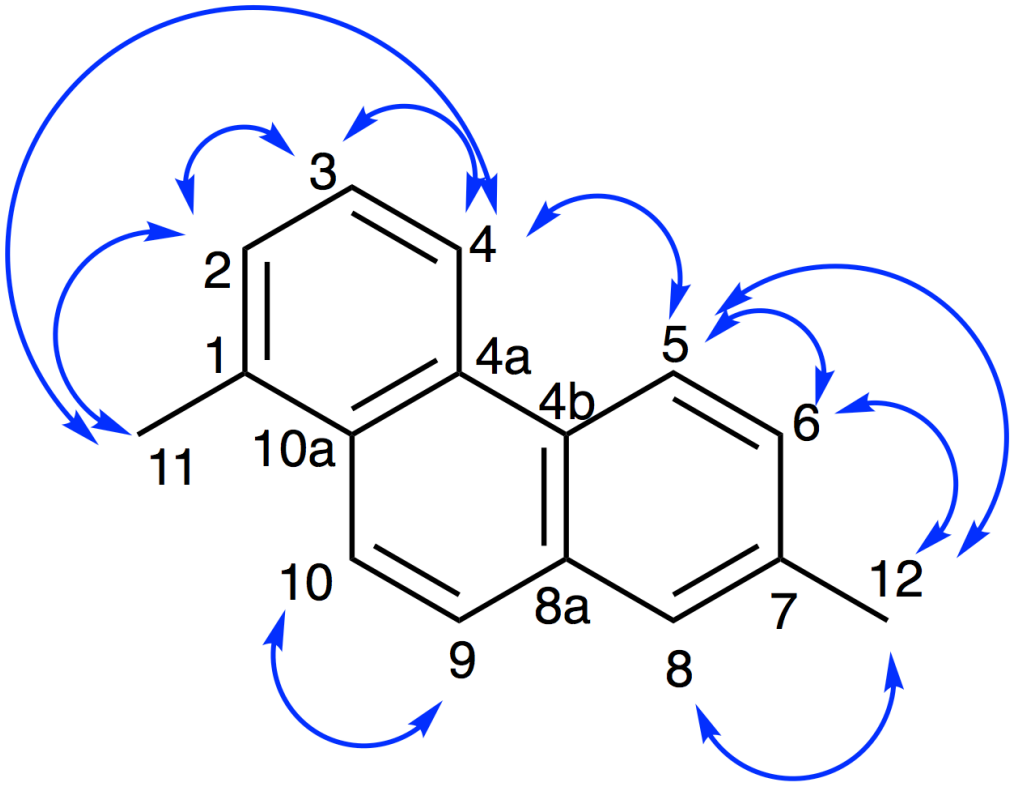


Figure 12. Illustration of **8c** and how COSY couples. Arrows couples between protons on the specific carbons they are pointed on.

Table 10. Product **8c** analyzed by 2D NMR.

Position	∫	δ_H [ppm]	δ_C [ppm]	m	J [Hz]
1	-	-	134.8	-	-
2	1	7.41	127.3	d	7.09
3	1	7.50-7.55	126.1	m	-
4	1	8.55	120.7	d	8.27
4a	-	-	130.4/130.5	-	-
4b	-	-	128.5/131.8	-	-
5	1	8.59	122.9	d	8.52
6	1	7.48	128.4	dd	8.54, 1.71
7	-	-	136.1	-	-
8	1	7.68	128.0	s	-
8a	-	-	128.5/131.8	-	-
9	1	7.72	126.4	d	9.11
10	1	7.93	122.9	d	9.15
10a	-	-	130.4/130.5	-	-
11	3	2.75	19.9	s	-
12	3	2.56	21.4	s	-

^{1}HNMR: All tops are counted for. Doublets 7.72 and 7.93 couples to each other, looking at the shift value. Two tops are to the far right, being methyl groups, while rest is found at the aromatic area.

^{13}CNMR: all expected tops are showing, 2 tops around 20 ppm, being the methyl groups, and the rest at the aromatic area. Quaternary groups having a bit higher shift, and lower intensity compared to other aromatic signals.

COSY: Position 11 couples to 2 and 4. Position 12 couples to 5, 6 and 8. Position 3 couples to 2 and 4. Position 5 couples to 4 and 6. Position 9 couples to position 10. All positions fits nicely, but 11 coupling to 4 is a bit long. This can be seen in figure 12.

HSQC: When zooming on the spectra the couplings are easy to couple. All the bindings between protons and carbons can be seen in table 10.

HMBC: Position 2 couples to 12 and position 8 to 11. Many of the aromatic carbons are close together, but fortunately not many at same place, making it possible to point out 2 possible quaternary carbons per position.

1-methylphenanthren-9-yl trifluoromethanesulfonate (6d)

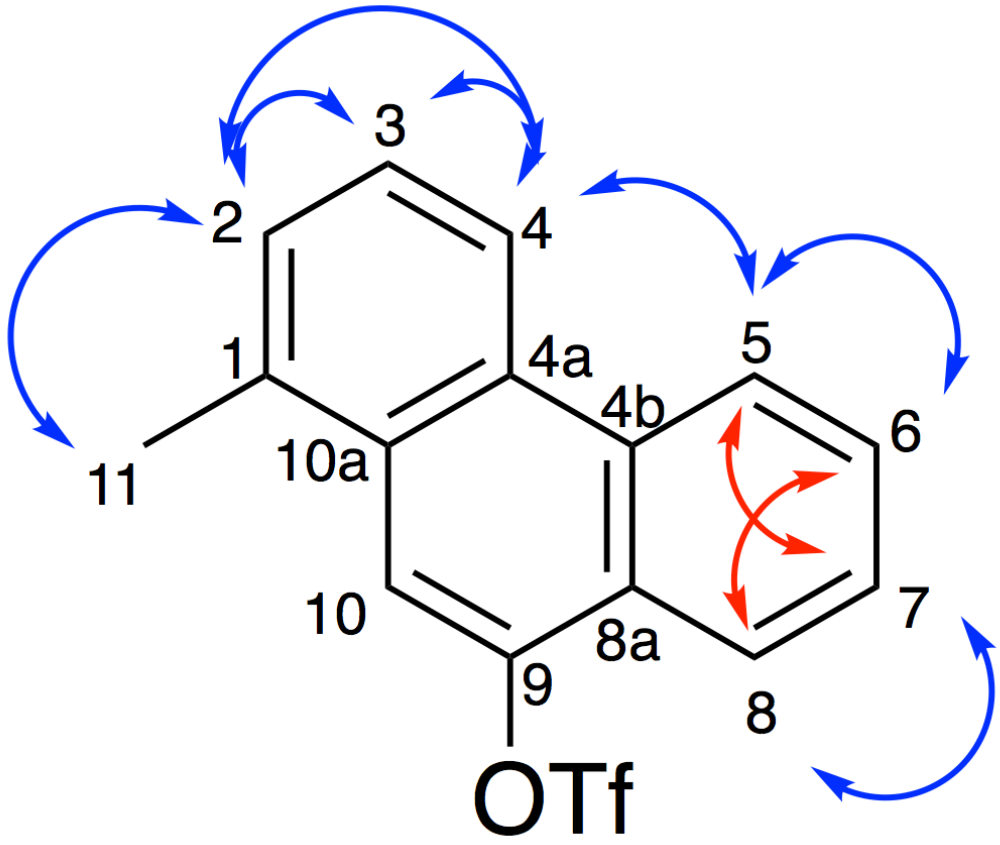


Figure 13. Illustration of **6d** and how COSY couples. Arrows couples between protons on the specific carbons they are pointed on.

Table 11. Product **6d** analyzed by 2D NMR.

Position	∫	δ_H [ppm]	δ_C [ppm]	m	J [Hz]
1	-	-	a	-	-
2	1	7.52	128.8	d	7.05
3	1	7.62	127.5	t	7.33
4	1	8.57	121.0	d	8.49
4a	-	-	a	-	-
4b	-	-	a	-	-
5	1	8.72-8.77	123.3	m	-
6/7	2	7.72-7.80	128.7/128.2	m	-
8	1	8.14-8.18	121.6	m	-
8a	-	-	a	-	-
9	-	-	a	-	-
10	1	7.94	114.4	s	-
10a	-	-	a	-	-
11	3	2.75	19.7	s	-

^{1}HNMR: All Peaks are as expected. One peak at 2.75, being the methyl group, and the 8 aromatic protons in the aromatic area. The doublet at 7.52 and the triplet at 7.62 looks like they couples, same with the multiplet at 814-8.18 and 8.72-8.77 ppm.

^{13}CNMR: All expected peaks are found. Methyl peak at 19.75 and 14 peaks in the aromatic area. The carbon in the triflate is too weak to be seen.

COSY: Position 2 couples to 3, 11 and a weak 4. Position 3 couples to 4. Position 6/7 couples to 5 and 8. Position 4 couples to 5. These couplings can be seen in figure 13. In the figure blue is confirmed, while red is possible, but hard to say since position 6 and 7 have the same shift.

HSQC: The signals are a bold, but have different height in the spectra, making it possible to see what proton bounds to what carbon. The bonded signals can be seen in table 11.

HMBC: There are very inconclusive signals for the quaternary carbons and assigning positions could not be done on this spectra.

Note[a]: inconclusive peaks.

1,9-dimethylphenanthrene

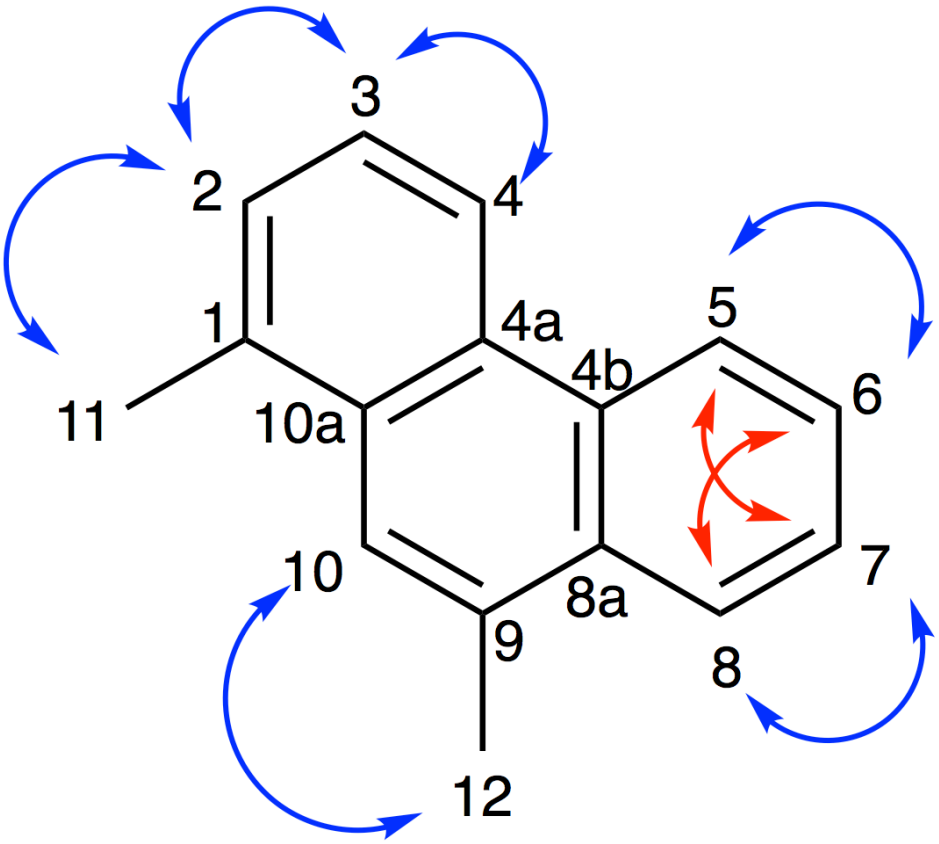


Figure 14. Illustration of **8d** and how COSY couples. Arrows couples between protons on the specific carbons they are pointed on.

Table 12. Product **8d** analyzed by 2D NMR.

Position	∫	**δ_H [ppm]**	**δ_C [ppm]**	**m**	**J [Hz]**
1	-	-	a	-	-
2	1	7.43	127.8	d	7.10
3	1	8.55	120.7	d	8.33
4	1	7.46-7.51	125.4	m	-
4a	-	-	a	-	-
4b	-	-	a	-	-
5	1	8.04-8.09/8.72-8.77	124.6/123.3	m	-
6/7	2	7.62-7.69	126.2/126.4	m	-
8	1	8.04-8.09/8.72-8.77	124.6/123.3	m	-
8a	-	-	a	-	-
9	-	-	a	-	-
10	1	7.79	122.8	s	-
10a	-	-	a	-	-
11	3	2.74	19.9	s	-
12	3	2.78	20.5	app. s	0.97

^{1}HNMR: All peaks are as expected. Two peaks are at 2.7, being the two methyl groups, and 8 protons in the aromatic area. The aromatic area is just like **6d**, only a small movement in the ppm values.
^{13}CNMR: All peaks are present. Two methyl groups at 20.0 ppm, and 14 peaks in the aromatic area. All quaternary peaks have a lower intensity and a bit higher shift than the other peaks in the aromatic area.
COSY: Position 2 couples to 3 and 11. Position 3 couples to 4. Positions 6/7 couples to 5/8. Position 10 couples to 12. The couplings can be seen in figure 14. In the figure blue is confirmed, while red is possible, but hard to say since position 6 and 7, and 5 and 8 is impossible to separate.
HSQC: Very nice signals show the bonds between protons and carbons. The bindings are shown in table 12.
HMBC: There are inconclusive signals for the quaternary carbons and assigning positions could not be done by these results. To show an example of analyzing this HMBC deeply the thought process can be found below. To show how far of the possibility of pointing out the quaternary carbons are.
Note[a]: inconclusive peaks.

HMBC shows lack of some signals, pointing what quaternary carbons are at what positions. Some connections are found in HMBC placing the different quaternary positions at different parts of the molecule. Coupling between position 2 and the quaternary two tops at 130.7, position 11 to 130.7 and 134.1. Position 12 couple to 131.7 or 132.2, but which is not possible to say from this NMR spectra. Position 4 couples to 134.1, and position 10 to 129.7 and 131.7. 8.08 ppm top, at position 5 or 8 couples to 130.7, 131.7 and 132.2, but they are weak. Position 3 couples to 130.7, while ppm 8.75 at position 5 or 8 couples to 131.7 stronger than ppm 8.08 in position 5 or 8. Since positions 2, 11, 3 all couples strongly to the two signals at 130.7 ppm, these signals could be at positions 1, 4a or 10a. Positions 4 and 10 couples to signal 129.7, but since position 4 is far from position 9, it is more likely to be in either 1, 4a, 4b, 8a or 10a. The position 10 couples to 131.7, but other signals are a weak one to ppm 8.75 at position 5 or 8, and for ppm 8.08 at position 5 or 8 and position 12 it is impossible to distinguish between 131.7 and 132.2. This suggest that 131.7 could be any quaternary except for position 1. The position 132.2 do not have any strong signals to any position, only the weak ones already mentioned, so no conclusions can be drawn for this top. Position 4 and 11 couples to top 134.1, while a weak

coupling to position 10 can be observed. This suggest that 134.1 is less likely to be at positions 8a and 9.

The positions possible for the quaternary are then: 129.7 = 1, 4a, 4b, 8a or 10a. 130.7 = any tops. 131.7 = 4a, 4b, 8a, 9 or 10a. 132.2 = no strong couplings. 134.1 = 1, 4a, 4b, 9 or 10a.

ChemDraw suggest 134.1 in position 1, 130.7 in position 4a and 4b, 129.7 in position 8a, 131.7 in position 9 and 132.2 in position 10a. These suggestions, even when weak supports the findings from the 2D NMR.

6. Experimental

6.1 General

Chemicals for the experiments were purchased from Sigma-Aldrich Chemical Company (Oslo, Norway). All chemicals were used without further purification. TMEDA was stored on molecular sieves (4Å). The anhydrous solvents were bought anhydrous.

6.2 Experimental equipment

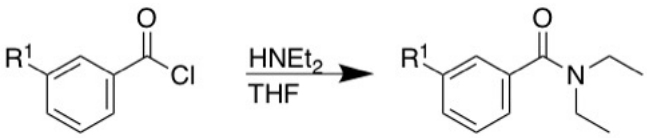
6.2.1 Spectroscopic and spectrometric descriptions

Melting point: Stuart Scientific Melting point apparatus SMP3.
MS: Sendt to Bergen, Mass spectra will be obtained from ESI-TOF instrument.
IR: KBr disks on an Agilent Cary 630 FTIR spectrometer.
NMR: NMR spectra were recorded on Bruker Avance 400 MHz spectrometer with chemical shifts reported in ppm relative to internal TMS ($\delta = 0$) and $CDCl_3$ ($\delta = 77.0$). The multiplicities were recorded as singlet, s; doublet, d; triplet t; double doublet, dd; multiplet, m; apparent, app.

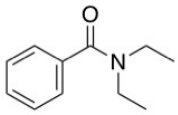
6.2.2 Chromatography

TLC: Merck silica gel 60 F_{254} plates using UV light at 254 nm for detection. n-Heptane and Ethyl acetate were used as solvent in different ratios.
Flash chromatography: Silica gel, particle size 40−60 μm, 60 Å. The eluent composition is given in each case.

6.3 General synthesis of aryl amides



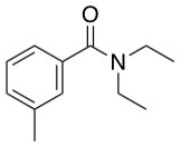
***N*,*N*-diethylbenzamide (2a)**



A 1 L, round-bottom flask with stirrer was charged with benzoyl chloride (15.00 g, 0.1067 mol). The mixture was put under inert atmosphere on an ice bath. Anhydrous THF (300 mL) was added to flask through a syringe. $HNEt_2$ (16.49 mL, 0. 1601 mol) was added dropwise, ice bath was removed and the mixture was allowed reflux 18 h. Diethyl ether (300 mL) was added to the mixture and put into a separation funnel. Mixture was washed with 1 M hydrochloric acid (300 mL), sat. aq. $NaHCO_3$ (300 mL) and brine (100 mL). Diethyl ether (200 mL) were used for extraction of the phases previously used, respectively to retrieve the rest of the compound. Organic phases were combined and dried on $MgSO_4$, filtered and concentrated *in vacuo* to give an oil (17.59 g, 93%), essentially pure based on NMR..

^{1}HNMR (400 MHz, $CDCl_3$) δ: 1.11-1.25 (app. s, J = 55.73 Hz, 6H), 3.26-3.55 (app. s, J = 117.73 Hz, 5H), 7.35-7.41 (m, 5H)
^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.90, 14.22, 39.22, 43.28, 126.28, 128.40, 129.10, 137.30, 171.31.
See appendix 2a.

***N*,*N*-diethyl-3-methylbenzamide (2b)**

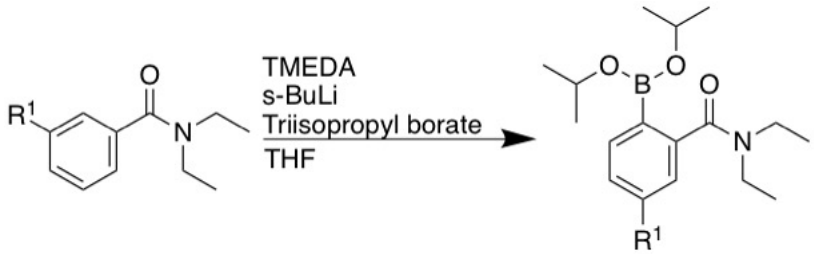


A 1 L, round-bottom flask with stirrer was charged with 3-methylbenzoyl chloride (20.0 g, 0.129 mol). The mixture was put under inert atmosphere on an ice bath. Anhydrous THF (400 mL) was added to flask through a syringe. $HNEt_2$ (20.0 mL, 0.194 mol) was added dropwise, before ice bath was removed and the mixture was allowed reflux 18 h. Diethyl ether (400 mL)

was added to the mixture and put into a separation funnel. The mixture was washed with 1 M hydrochloric acid (400 mL), sat. aq. $NaHCO_3$ (400 mL) and brine (200 mL). Diethyl ether (250 mL) were used for extraction of the phases previously used, respectively to receive the rest of the compound. Organic phases were combined and dried on $MgSO_4$, filtered and concentrated *in vacuo* to give an oil (24.9 g, 92%), essentially pure based on NMR.

^{1}HNMR (400 MHz, $CDCl_3$) δ: 1.10-1.24 (app. s, J = 54.95 Hz, 6H), 3.25-3.54 (app. s, J = 113.90 Hz, 4H), 7.13-7.15 (m, 1H), 7.18-7.20 (m, 2H), 7.25-7.29 (m, 1H).
^{13}C NMR (100 MHz, $CDCl_3$) δ: 12.92, 14.20, 21.38, 39.14, 43.26, 123.15, 126.92, 128.22, 129.77, 137.27, 138.23, 171.50.
See appendix 2b.

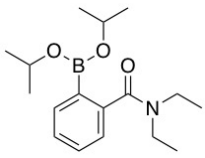
6.4 Directed *ortho* Metalation



General procedure:

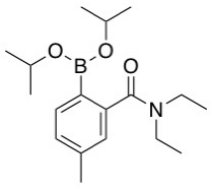
TMEDA was added to a round-bottom flask with stirrer, and degassed. Anhydrous THF was added by syringe to the flask, then cooled to -78 °C. s-BuLi was added dropwise. A solution of starting material in degassed anhydrous THF, was slowly added to the flask 10 minutes later by syringe. The mixture was allowed to react for 1 h, while kept at -78 °C. Triisopropyl borate was added by syringe to the mixture, and the flask was allowed to reach r.t. overnight. The reaction was confirmed completed by TLC analysis and quenched with sat. aq. NH_4Cl. The organic phase was separated and aqueous phase extracted with Diethyl ether (3 X 25 mL per gram stating material). The combined organic phases were washed with brine (25 mL per gram staring material), dried over $MgSO_4$ and concentrated *in vacuo*. Purity of compound was not able to confirm by NMR as explained in results part 2.4.

Diisopropyl (2-(diethylcarbamoyl)phenyl)boronate (3a)



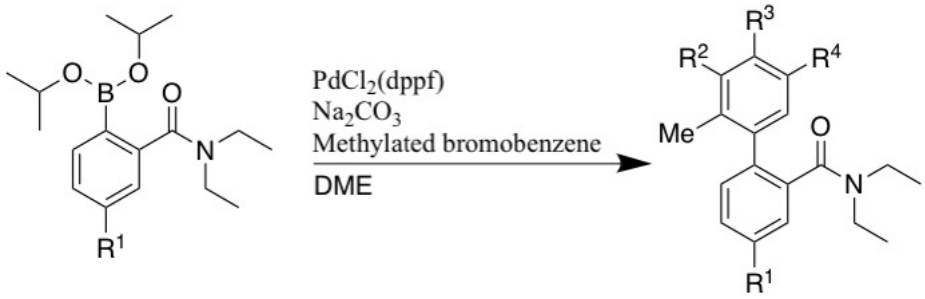
TMEDA (15.83 mL, 125.6 mmol) and anhydrous THF (300 mL) was cooled to -78°C, then added s-BuLi (81.20 mL, 125.6 mmol). **2a** (14.97 g, 84.45 mmol) diluted in anhydrous THF (300 mL) was added 10 minutes later. 1 h later Triisopropyl borate (48.72 mL, 0.2111 mol) was added. Next day mixture was quenched with sat. aq. NH_4Cl (500 mL). Workup done as general procedure to receive a transparent oil (17.56 g, 96%), continued reaction as if 100% completed reaction since NMR was not possible to read. See appendix 3a.

Diisopropyl (2-(diethylcarbamoyl)-4-methylphenyl)boronate (3b)



TMEDA (6.186 mL, 41.26 mmol) and anhydrous THF (150 mL) was cooled to -78°C, then added s-BuLi (31.74 mL, 41.26 mmol). **2b** (6.450 g, 33.01 mmol) diluted in anhydrous THF (150 mL) was added 10 minutes later. 1 h later Triisopropyl borate (19.05 mL, 82.53 mmol) was added. Next day mixture was quenched with sat. aq. NH_4Cl (250 mL). Workup done as general procedure to receive a transparent oil(7.193 g, 93 %)., continued reaction as if 100% completed reaction since NMR was not possible to read. See appendix 3b.

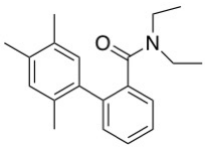
6.5 Suzuki-Miyaura Cross-Coupling Reaction



General procedure:

A mixture of $PdCl_2$(dppf) (5mol%) and a methylated bromobenzene (1eq) was added to a round-bottled flask and degassed. Compounds were diluted in DME and stirred for 15 minutes. A solution of starting material (1.5eq) in degassed anhydrous DME was slowly added to the mixture through a syringe. 2 M aq. Na_2CO_3 (10 mL per gram) was added to the mixture and allowed to reflux with a condenser for 18 h. Complete reaction was confirmed by TLC before removing the heating. Mixture was added to a separation funnel and organic phase was collected into an Erlenmeyer flask. Aquatic phase were extracted 3 times with diethyl ether. Organic phases were combined, washed with brine and dried on $MgSO_4$. The organic phase was concentrated *in vacuo*. Title compound was isolated by flash chromatography.

***N*,*N*-diethyl-2',4',5'-trimethyl-[1,1'-biphenyl]-2-carboxamide (4a)**



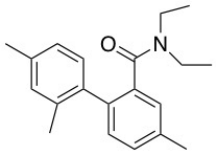
A mixture of $PdCl_2$(dppf) (0.740 g, 0.907 mmol) and a 5-bromo-1,2,4-trimethylbenzene (3.63 g, 18.1 mol) was added to a round-bottled flask. The mixture was added DME (100 mL) and stirred for 15 minutes, before **3a** (2.87 g, 27.2 mmol) in DME (70 mL) was added. After addition of 2 M aq. Na_2CO_3 (100 ml) the mixture was refluxed for 18 hr. The mixture reached r.t. and was extracted, dried and concentrated into a dark brown oil as described in general procedure. The title compound was isolated by flash chromatography (*Rf* = 0.35. n-Hexane/ ethyl acetate = 2/1) as a beige solid (5.440 g, quant.), essentially pure based on NMR.

^{1}HNMR (MHz, $CDCl_3$) δ: 0.59-0.75 (m, 3H), 0.87 (d, *J* = 61.77 Hz, 3H), 0.55 (d, *J* = 31.19 Hz, 3H), 2.29 (s, 3H), 2.40 (s, 3H), 2.55-3.90 (m, 4H), 6.85-7.24 (m, 6H).

^{13}C NMR (MHz, $CDCl_3$) δ: 11.77, 13.70, 17.25, 20.59, 21.12, 22.69, 30.93, 31.88, 37.77, 42.12, 42.49, 124.29, 125.04, 126.25, 126.55, 127.42, 128.96, 129.15, 129.82, 130.73, 136.85, 136.99, 170.34, 206.96.

See appendix 4a.

_N_,_N_-diethyl-2',4,4'-trimethyl-[1,1'-biphenyl]-2-carboxamide (4b)



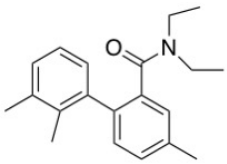
A mixture of $PdCl_2$(dppf) (0.404 g, 0.494 mmol) and a 1-bromo-2,4-dimethylbenzene (1.83g, 9.88 mmol) was added to a round-bottled flask. The mixture was added DME (41.8 mL) and stirred for 15 minutes, before **3b** (3.49 g, 14.8 mmol) in DME (27.9 mL) was added. After addition of 2 M aq. Na_2CO_3 (41.8 ml) the mixture was refluxed for 18 hr. The mixture reached r.t. and was extracted, dried and concentrated into a dark brown oil as described in general procedure. The title compound was isolated by flash chromatography (*Rf* = 0.29. n-Hexane/ ethyl acetate = 2/1) as a yellow oil (1.99 g, 68%), essentially pure based on NMR.

^{1}HNMR (400 MHz, $CDCl_3$) δ: 0.73 (t, *J* = 7.09 Hz, 3H), 0.88 (t, *J* = 7.09 Hz, 3H), 2.18 (s, 3H), 2.31 (s, 3H), 2.39 (s, 3H), 2.77-3.69 (m, 4H), 6.94 (d, *J* = 7.28 Hz, 1H), 7.03 (s, 1H), 7.16 (m, 3H), one top is missing.

^{13}C NMR (100 MHz, $CDCl_3$) δ: 11.82, 13.68, 14.12, 20.18, 21.07, 22.69, 29.02, 31.89, 37.81, 41.27, 125.90, 126.79, 127.20, 128.90, 130.26, 130.78 (2C), 136.95 (2C), 137.04 (2C), 137.15, 170.43.

See appendix 4b.

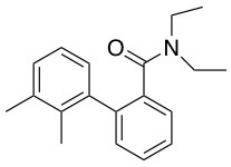
_N_,_N_-diethyl-2',3',4-trimethyl-[1,1'-biphenyl]-2-carboxamide (4c)



A mixture of PdCl(dppf) (0.870 g, 1.66 mmol) and a 1-bromo-2,3-dimethylbenzene (4.11 g, 22.0 mmol) was added to a round-bottled flask. The mixture was added DME (100 mL) and stirred for 15 minutes, before **3b** (7.48 g, 33.1 mmol) in DME (70 mL) was added. After addition of 2 M aq. Na_2CO_3 (100 ml) the mixture was refluxed for 18 hr. The mixture reached r.t. and was extracted, dried and concentrated into a dark brown oil as described in general procedure. The title compound was isolated by flash chromatography (*Rf* = 0.38. n-Hexane/ ethyl acetate = 2/1) as an orange solid (5.22 g, 80%), essentially pure based on NMR.

^{1}HNMR (MHz, $CDCl_3$) δ: 0.72 (t, *J* = 7.02 Hz 3H), 0.89 (m, 3H), 2.15 (s, 3H), 2.19 (s, 3H), 2.23 (s, 3H), 2.61-3.84 (m, 4H), 7.00 (s, 1H), 7.24 (d, *J* = 7.07 Hz, 1H), 7.36 (m, 3H). One H missing.
^{13}C NMR (MHz, $CDCl_3$) δ: 11.62, 13.40, 13.70, 19.11, 19.35, 19.60, 37.93, 42.37, 117.95, 118.40, 127.07, 127.27, 128.07, 130.40, 131.46, 132.25, 135.76, 137.21, 170.25.
See appendix 4c.

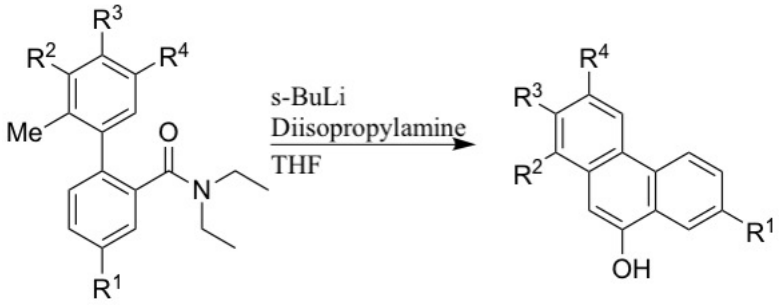
***N*,*N*-diethyl-2',3'-dimethyl-[1,1'-biphenyl]-2-carboxamide (4d)**



A mixture of PdCl(dppf) (0.579 g, 0.709 mmol) and 1-bromo-2,3-dimethylbenzene (2.624 g, 14.18 mmol) was added to a 1 L, round-bottled flask. The mixture was added DME (50 mL) and stirred for 15 minutes, before **3a** (5.001 g, 14.18 mmol) in DME (40 mL) was added. After addition of 2 M aq. Na_2CO_3 50 ml) the mixture was refluxed for 18 hr. The mixture reached r.t. and was extracted, dried and concentrated into a dark brown oil as described in general procedure. The title compound was isolated by flash chromatography (*Rf* = 0.36. n-Hexane/ ethyl acetate = 2/1) as a yellow solid (3.204 g, 80%), essentially pure based on NMR.

^{1}HNMR (MHz, $CDCl_3$) δ: 0.67 (s, 3H), 0.78-1.04 (m, 3H), 2.08 (s, 3H), 2.30 (s, 3H), 2.57-3.91 (m, 4H), 7.01-7.08 (m, 1H), 7.11 (d, *J* = 7.88 Hz, 1H), 7.23 (d, *J* = 6.90 Hz, 1H), 7.33-7.43 (m, 3H). One top missing.
^{13}C NMR (MHz, $CDCl_3$) δ: 11.72, 13.70, 14.12, 17.10, 20.57, 22.70, 29.02, 31.89, 37.84, 42.45, 126.29, 127.21 (3C), 128.39, 129.12 (3C), 136.92, 170.12.
See appendix 4d.

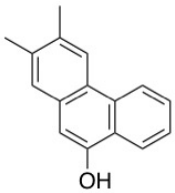
6.6 Directed remote Metalation



General procedure:

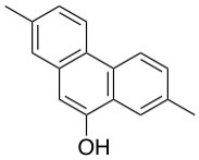
Diisopropylamine (2.5eq) and S-BuLi (2.5eq) added to a degassed round-bottled flask containing a stirrer. Mixture was solved in THF (30 mL per gram starting material), creating LDA. Starting material solved in THF(10 mL per gram starting material) then added to the LDA mixture. Mixture was allowed to react for 30 minutes at r.t. before quenching with sat. aq. NH_4Cl(30 mL per gram starting material). The mixture was put into a separation funnel and organic phase was collected. Extraction of the aquatic phase was done with diethyl ether (3 X 30 mL per gram starting material). All organic phases were combined, washed with brine (30 mL per gram starting material) and dried on $MgSO_4$. Title compounds were concentrated *in vacuo* and stored under inert atmosphere overnight before subjected to triflation without any further characterizations.

2,3-dimethylphenanthren-9-ol (5a)



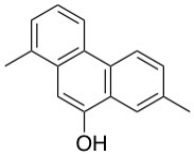
Diisopropylamine (2.960 ml, 21.15 mmol) and S-BuLi (16.27 mL, 21.15 mmol) added to a round-bottled flask, dissolved with THF (70 mL). **4a** (2.570 g, 8.699 mmol) in THF (20 mL) was added to the mixture. Reagents were allowed to react for 30 minutes before quenching with sat. aq. NH_4Cl (70 mL). Workup as described in general procedure and left overnight.

2,7-dimethylphenanthren-9-ol (5b)



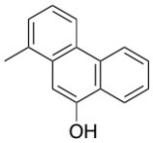
Diisopropylamine (2.354 mL, 16.83 mmol) and S-BuLi (12.95 mL, 16.83 mmol) added to a round-bottled flask, dissolved with THF (70 mL). **4b** (1.989 g, 6.732 mmol) in THF (20 mL) was added to the mixture. Reagents were allowed to react for 30 minutes before quenching with sat. aq. NH_4Cl (70 mL). Workup as described in general procedure and left overnight.

1,7-dimethylphenanthren-9-ol (5c)



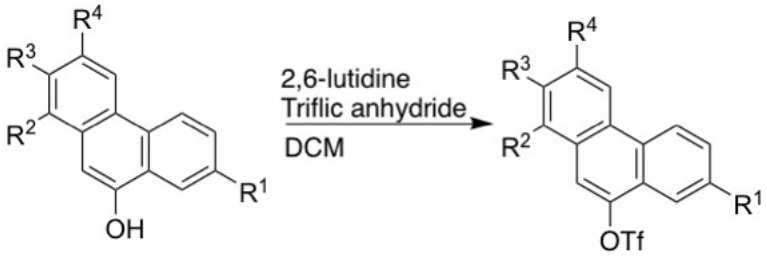
Diisopropylamine (2.960 mL, 21.15 mmol) and S-BuLi (16.27 mL, 21.15 mmol) added to a round-bottled flask, then THF (70 mL) was added. **4c** (2.500 g, 8.462 mmol) in THF (20 mL) was added to the mixture. Reagents were allowed to react for 30 minutes before quenching with sat. aq. NH_4Cl (70 mL). Workup as described in general procedure and left overnight.

1-methylphenanthren-9-ol (5d)



Diisopropylamine (1.850 mL, 13.20 mmol) and S-BuLi (10.15 mL, 13.20 mmol) added to a round-bottled flask, then THF (60 mL) was added. **4d** (1.560 g, 5.280 mmol) in THF (15 mL) was added to the mixture. Reagents were allowed to react for 30 minutes before quenching with sat. aq. NH_4Cl (60 mL). Workup as described in general procedure and left overnight.

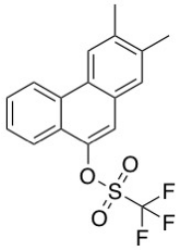
6.7 Triflation



General procedure:

The crude phenols **5a-d** was dried *in vacuo* and dissolved in anhydrous DCM under inert atmosphere. The mixture was cooled on an ice bath and added 2,6-lutidine (1.2eq), then triflic anhydride (1.5eq) was slowly added to the mixture. Reaction was allowed to react for 1 h, then quenched by adding water. Mixture was put into a separation funnel. Organic phase was collected and aquatic phase were extracted 3 times with DCM (50 mL per gram starting material). Organic phases were combined and dried on $MgSO_4$. The mixture was concentrated *in vacuo* before title compound was isolated by flash chromatography. NMR was used to confirm the title compound.

2,3-dimethylphenanthren-9-yl trifluoromethanesulfonate (6a)

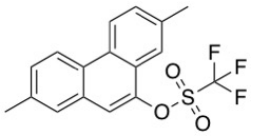


A round-bottled flask with starting material **5a** (directly from DreM) was added anhydrous DCM (150 mL). Cooled down, added 2,6-lutidine (1.180 mL, 10.15 mmol), then triflic anhydride (2.140 mL, 12.69 mmol). Mixture was allowed to react for 1 h, then quenched with water (50 mL). Workup was done according to the general procedure, and purified by flash chromatography (*Rf* = 0.36 . n-Hexane/ ethyl acetate = 3/1) giving a light brown solid (2.526 g, 93%), essentially pure based on NMR.

^{1}HNMR (MHz, $CDCl_3$) δ: 2.47 (S, 3H), 2.54 (S, 3H), 7.65 (d, *J* = 2.78 Hz, 2H), 7.70 (m, 2H), 8.10-8.13 (m, 1H), 8.41 (s, 1H), 8.67 (m, 1H).

^{13}C NMR (MHz, $CDCl_3$) δ: 19.91, 20.65, 117.20, 117.46, 120.39, 121.58, 123.10, 125.13, 127.18, 127.87, 127.94, 128.89, 129.05, 131.54, 137.33, 137.50, 143.75.
See appendix 6a.

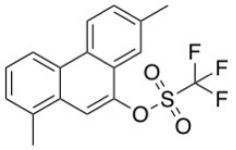
2,7-dimethylphenanthren-9-yl trifluoromethanesulfonate (6b)



A round-bottled flask with starting material **5b** (directly from DreM) was added anhydrous DCM (100 mL). Cooled down and added 2,6-lutidine (0.936 mL, 8.076 mmol), then triflic anhydride (1.699 mL, 10.10 mmol). Mixture was allowed to react for 1 h, then quenched with water (50 mL). Workup was done according to the general procedure, and purified by flash chromatography (*Rf* = 0.60. n-Hexane/ ethyl acetate = 3/1) giving a light orange solid (2.032 g, quant.), essentially pure based on NMR.

^{1}HNMR (MHz, $CDCl_3$) δ: 2.56 (s, 3H), 2.61 (s, 3H), 7.52 (dd, *J* = 8.37, 1.47 Hz, 1H), 7.54 (dd, *J* = 8.52, 1.54 Hz, 1H), 7.65 (s, 1H), 7.68 (s, 1H), 7.89 (s, 1H), 8.52 (d, *J* = 8.61 Hz, 1H), 8.57 (d, *J* = 8.55 Hz, 1H).
^{13}C NMR (MHz, $CDCl_3$) δ: 21.39, 21.80, 117.63, 121.09, 122.50, 122.81, 127.53, 128.53, 129.61, 129.83, 129.91, 130.24, 137.21, 137.43, 144.32.
See appendix 6b.

1,7-dimethylphenanthren-9-yl trifluoromethanesulfonate (6c)



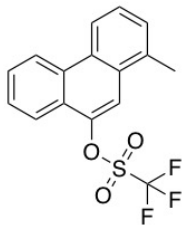
A round-bottled flask with starting material **5c** (directly from DreM) was added anhydrous DCM (150 mL). Cooled down, added 2,6-lutidine (1.180 mL, 10.15 mmol), then triflic anhydride (2.140 mL, 12.69 mmol). Mixture was allowed to react for 1 h, then quenched with water (50 mL). Workup was done according to the general procedure, and purified by flash chromatography (*Rf* = 0.37. n-Hexane/ ethyl acetate = 3/1) giving a brown solid (2.743 g, 91%), essentially pure based on NMR.

^{1}HNMR (MHz, $CDCl_3$) δ: 2.62, 2.74, 7.48 (d, *J* = 7.28 Hz, 1H), 7.57-7.62 (m, 2H), 7.91 (s, 1H), 7.92 (s, 1H), 8.53 (d, *J* = 8.31 Hz, 1H), 8.63 (d, *J* = 8.57, 1H)

^{13}C NMR (MHz, $CDCl_3$) δ: 19.73, 21.80, 114.36, 120.76, 121.01, 123..33, 127.43, 128.34, 130.01, 137.83.

See appendix 6c.

1-methylphenanthren-9-yl trifluoromethanesulfonate (6d)



A round-bottled flask with starting material **5d** (directly from DreM) was added anhydrous DCM (100 mL). Cooled down, added 2,6-lutidine (1.529 mL, 13.20 mmol), then triflic anhydride (1.332 mL, 7.920 mmol). Mixture was allowed to react for 1 h, then quenched with water (50 mL). Workup was done according to the general procedure, and purified by flash chromatography (*Rf* = 0.40. n-Hexane/ ethyl acetate = 3/1) giving a light red solid (1.185 g, 63%), essentially pure based on NMR.

M_p: 70-71 ˚C

HRMS*: sample sent for analysis*

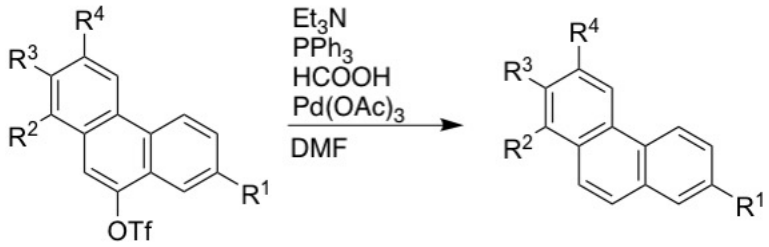
^{1}HNMR (MHz, $CDCl_3$) δ: 2.75 (s, 3H), 7.52 (d, *J* = 7.05 Hz, 1H), 7.62 (t, *J* = 7.33 Hz, 1H), 7.72-7.80 (m, 2H), 7.94 (s, 1H), 8.14-8.18 (m, 1H), 8.57 (d, *J* = 8.49 Hz, 1H), 8.72-8.77 (m, 1H).

^{13}C NMR (MHz, $CDCl_3$) δ: 19.75, 114.43, 120.96, 121.59, 123.39, 125.06, 127.52, 127.68, 128.18, 128.80, 129.53, 129.81, 132.23, 135.51, 144.34.

IR (KBr): 3078, 3034, 2972, 2934, 2871, 1929, 1629, 1604, 1528, 1459, 1417, 1383, 1295, 1246, 1205, 1138, 1043, 1007, 894, 831, 803, 745, 697 cm^{-1}

See appendix 6d.

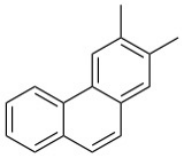
6.8 Detriflation



General procedure:

A round-bottled flask containing the starting material was added a stirrer, $Pd(OAc)_2$ (5 mol%) and PPh_3 (10 mol%). The flask was degassed before adding DMF (60 mL per gram starting material) through a syringe. Et_3N (3 eq.) and HCOOH (2 eq.) was added to the mixture through a syringe before 1 hr reflux. Mixture was cooled down to room temperature and quenched by adding water (60 mL per gram starting material). The mixture was added to a separation funnel. Organic phase was collected and aquatic phase was extracted 3 times with diethyl ether (100 mL per gram starting material). All organic phases were combined, washed with brine and dried on $MgSO_4$ before being concentrated *in vacuo*. Product was isolated by flash chromatography. Confirmation of product was done by NMR.

2,3-dimethylphenanthrene (7a)



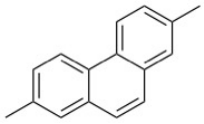
$Pd(OAc)_2$ (0.040 g, 0.178 mmol) and PPh_3 (0.094 g, 0.357 mmol) added to a round-bottled flask containing **6a** (3.16 g, 8.92 mmol). DMF (200 mL) was added, then Et_3N (3.73 ml, 26.8 mmol) and HCOOH (0.673 ml, 17.8 mmol) was added before reflux. Mixture was cooled down and quenched with water (200 mL). Workup was done according to the general procedure, and purified by flash chromatography (*Rf* = 0.36. n-Hexane/ ethyl acetate = 3/1) giving white crystals (1.45 g, 99%), essentially pure based on NMR.

M_p: 77-81˚C

HRMS*: sample sent for analysis*

^{1}HNMR (MHz, $CDCl_3$) δ: 2.47 (s, 3H), 2.53 (s, 3H), 7.52-7.57 (m, 1H), 7.58-7.62 (m, 1H), 7.63 (s, 1H), 7.65 (s, 2H), 7.84-7.87 (m, 1H), 8.43 (s, 1H), 8.65 (d, *J* = 8.23 Hz, 1H).
^{13}C NMR (MHz, $CDCl_3$) δ: 19.94, 20.59, 122.42, 122.95, 125.96, 126.24, 126.37, 128.48, 128.62, 130.04, 130.59, 131.82, 135.83, 135.87.
IR (KBr): 3045, 3012, 2968, 2917, 2858, 1499, 1460, 1446, 1025, 875, 809, 749, 711 cm^{-1}
See appendix 7a.

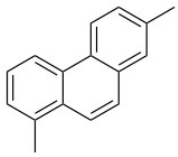
2,7-dimethylphenanthrene (7b)



$Pd(OAc)_2$ (25.3 mg, 0.113 mmol) and PPh_3 (59.1 mg, 0.225 mmol) added to a round-bottled flask containing **6b** (2.00 g, 5.63 mmol). DMF (120 mL) was added, then Et_3N (2.35 mL, 16.9 mmol) and HCOOH (0.425 mL, 11.3 mmol) was added before reflux. Mixture was cooled down and quenched with water (120 mL). Workup was done according to the general procedure, and purified by flash chromatography (*Rf* = 0.47. n-Hexane/ ethyl acetate = 3/1) giving white crystals (1.18 g, quant.), essentially pure based on NMR.

M_p: 101-102 ˚C
HRMS*: sample sent for analysis*
^{1}HNMR (MHz, $CDCl_3$) δ: 2.55 (s, 6H), 7.46 (dd, *J* = 8.42, 1.67 Hz, 2H), 7.64 (s, 2H), 7.65 (s, 2H), 8.53 (d, *J* = 8.47 Hz, 2H).
^{13}C NMR (MHz, $CDCl_3$) δ: 21.44, 122.35, 126.66, 128.07, 128.21, 128.25, 131.87, 135.80.
IR (KBr): 3022, 2911, 2858, 1620, 1476, 1372, 1251, 1038, 890, 873, 815, 797, 710 cm^{-1}
See appendix 7b.

1,7-dimethylphenanthrene (7c)



$Pd(OAc)_2$ (32 mg, 0.14 mmol) and PPh_3 (75 mg, 0.28 mmol) added to a round-bottled flask containing **6c** (2.5 g, 7.1 mmol). DMF (180 mL) was added, then Et_3N (3.0 mL, 7.1 mol) and HCOOH (0.54 mL, 14 mmol) was added before reflux. Mixture was cooled down and quenched

with water (180 mL). Workup was done according to the general procedure, and purified by flash chromatography (*Rf* = 0.30. n-Hexane/ ethyl acetate = 5/1) giving off-white crystals (1.7 g, quant.), essentially pure based on NMR.

M_p: 82-83 ˚C

HRMS*: sample sent for analysis*

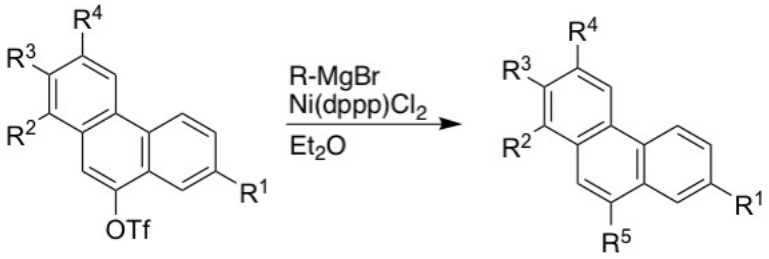
^{1}HNMR (MHz, $CDCl_3$) δ: 2.56 (s, 3H), 2.75 (s, 3H), 7.41 (d, *J* = 7.06, 1H), 7.48 (dd, 8.54, 1.71 Hz, 1H), 7.50-7.55 (m, 1H), 7.68 (s, 1H), 7.72 (d, *J* = 9.11 Hz, 1H), 7.93 (d, *J* = 9.15 Hz, 1H), 8.55 (d, *J* = 8.27 Hz, 1H), 8.59 (d, *J* = 8.52 Hz, 1H).

^{13}C NMR (MHz, $CDCl_3$) δ:19.94, 21.44, 120.67, 122.86, 126.06, 126.43, 127.32, 127.99, 128.36, 128.53, 130.38, 130.47, 131.82, 134.82, 136.14.

IR (KBr): 3019, 2964, 2915, 2860, 1926, 1622, 1600, 1528, 1466, 1438, 1377, 1303, 1250, 1173, 1150, 1034, 964, 881, 829, 811, 791, 756, 710 cm^{-1}

See appendix 7c.

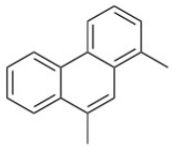
6.9 Kumada coupling



General procedure:

A round-bottled flask with stirrer was filled with starting material and $Ni(dppp)Cl_2$ (5mol%), and degassed. Diethyl ether (15 mL per gram starting material) was added through a syringe and cooled down by ice bath. Mixture was loaded with MeMgBr (3 eq.) or $CH_2CHMgBr$ (3 eq.) through a syringe before allowing reflux for 3 h with condenser. Mixture was put back on ice bath and quenched slowly with methanol (3 mL per gram starting material). The product was isolated by flash chromatography.

1,9-dimethylphenanthrene (8d)



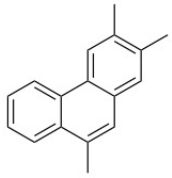
A L round-bottled flask containing **6d** (0.25 g, 0.73 mmol) and $Ni(dppp)Cl_2$ (0.016 g, 0.037 mmol). Diethyl ether (4 mL), then MeMgBr (0.58 mL, 2.2 mmol) was added at 0°C. The mixture was put on reflux for 3 hr, then back on ice bath. Reaction was quenched with methanol (0.60 mL). The title compound was purified by flash chromatography (*Rf* = 0.35. n-Hexane/ ethyl acetate = 60/1) giving white crystals, pure by NMR (0.15 g, 96%), essentially pure based on NMR.

M_p: 89-90 °C

^{1}HNMR (400 MHz, $CDCl_3$) δ: 2.74 (s, 3H), 2.78 (app. s, *J* = 0.97 Hz, 3H), 7.43 (d, *J* = 7.10 Hz, 1H), 7.46-7.51 (m, 1H), 7.62-7.69 (m, 2H), 7.79 (s, 1H), 8.04-8.09 (m, 1H), 8.55 (d, *J* = 8.33 Hz, 1H), 8.72-8.77 (m, 1H).

^{13}C NMR (100 MHz, $CDCl_3$) δ: 19.92, 20.49, 120.68, 122.80, 123.31, 124.60, 125.36, 126.21, 126.36, 127.78, 129.67, 130.69, 130.74, 131.66, 132.22, 134.07.
HRMS*: sample sent for analysis*
IR (KBr): 3064, 3023, 2971, 2863, 1599, 1442, 1409, 1235, 1151, 1035, 874, 806, 756 cm^{-1}
See appendix 8d.

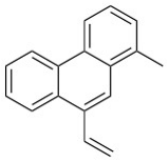
2,3,9-trimethylphenanthrene (8e)



A L round-bottled flask containing **6a** (6 mg, 0.2 mmol) and Ni(dppp)Cl_2 (5.0 mg, 0.009 mmol). Diethyl ether (0.8 mL), then MeMgBr (0.2 mL, 0.6 mmol) was added at 0°C. The mixture was put on reflux for 3 hr, then back on ice bath. Reaction was quenched with methanol (0.2 mL). The title compound seem to be made when looking at ^{1}HNMR, but further workup is needed.

^{1}HNMR (400 MHz, $CDCl_3$) δ: 2.46 (s, 3H), 2.52 (s, 3H), 2.71 (ass. s, *J* = 0.87, 3H), 7.49 (s, 1H), 7.56 (s, 1H), 7.57-7.65 (m, 2H), 8.08-8.04 (m, 1H), 8.40 (s, 1H), 8.67-8.70 (m, 1H).

1-methyl-9-vinylphenanthrene (8f)



A L round-bottled flask containing **6d** (6 mg, 0.2 mmol) and Ni(dppp)Cl_2 (5 mg, 0.009 mmol). Diethyl ether (0.8 mL), then $CH_2CHMgBr$ (0.5 mL, 0.5 mol) was added at 0°C. The mixture was put on reflux for 3 hr, then back on ice bath. Reaction was quenched with methanol (0.2 mL). Reaction did not give any title product.

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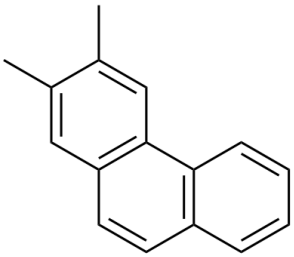
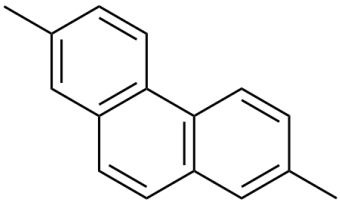
APPENDIX

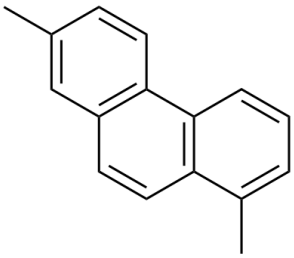
Structures of the final products



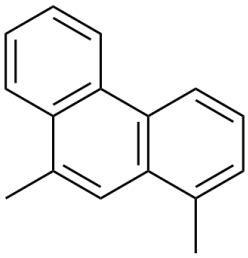
2,3-dimethylphenanthrene (**7a**)



2,7-dimethylphenanthrene (**7b**)

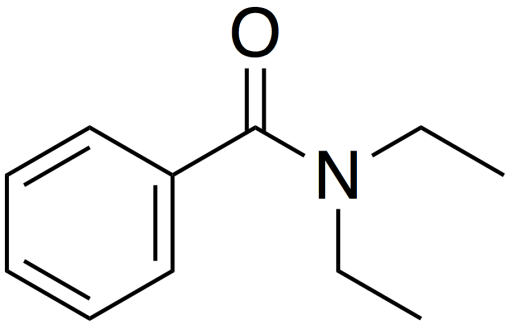


1,7-dimethylphenanthrene (**7c**)



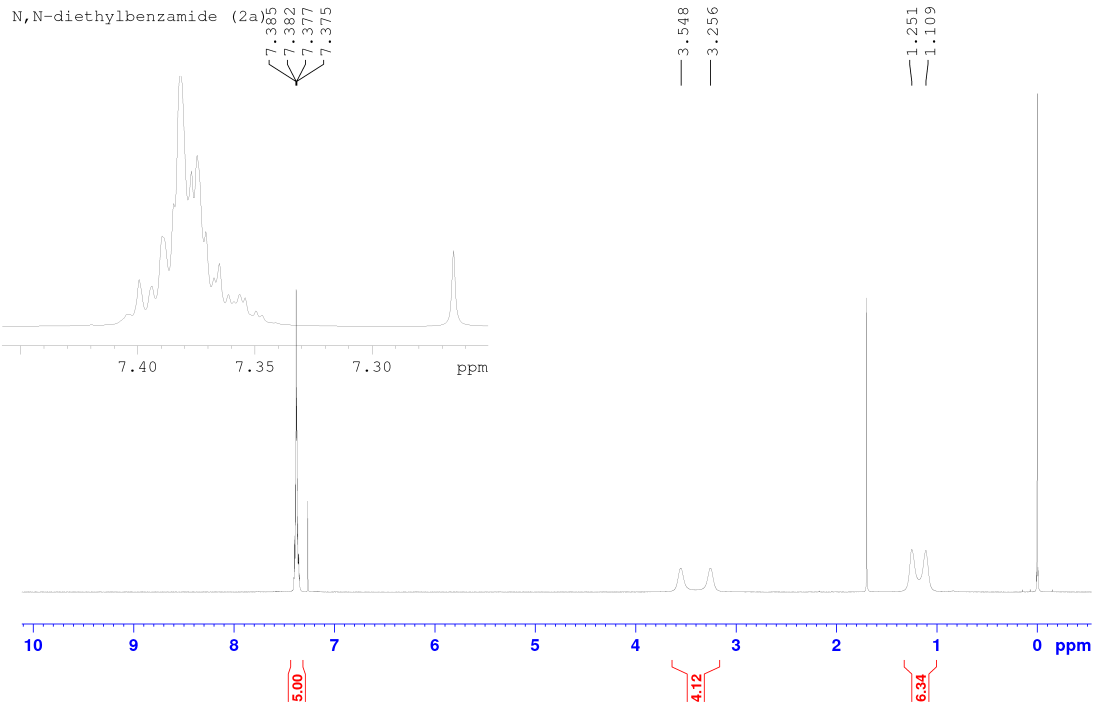
1,9-dimethylphenanthrene (**8d**)

Appendix 2a

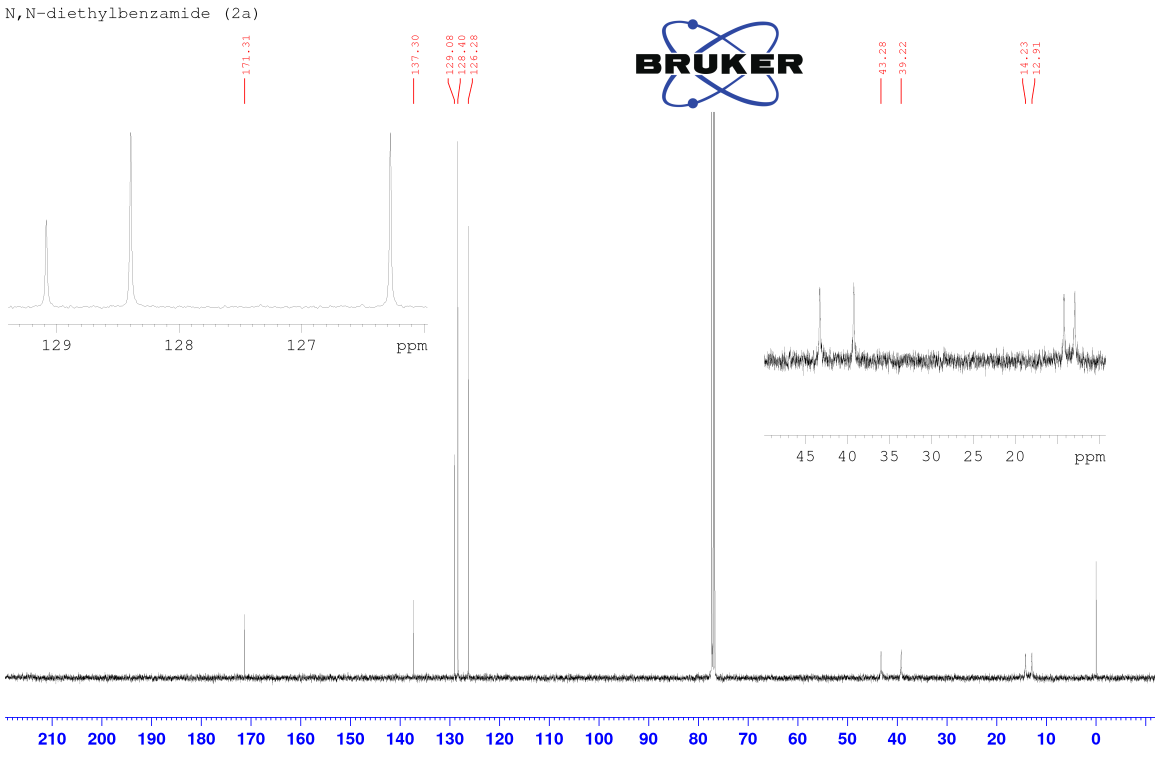


***N*,*N*-diethylbenzamide**

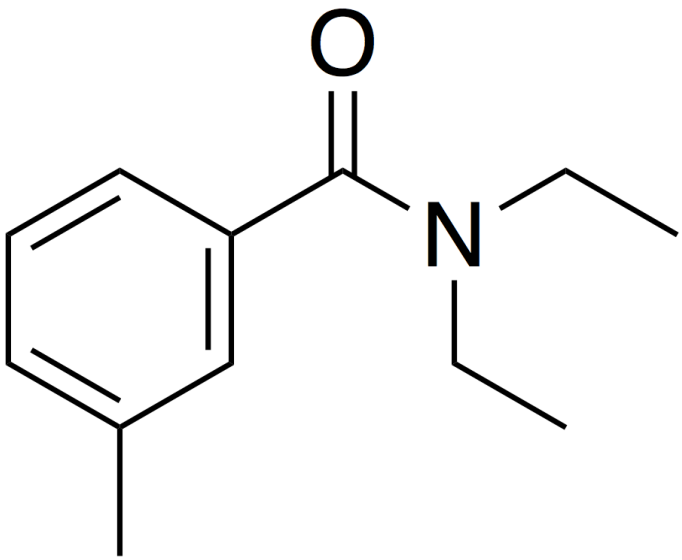
^{1}HNMR:



^{13}CNMR:

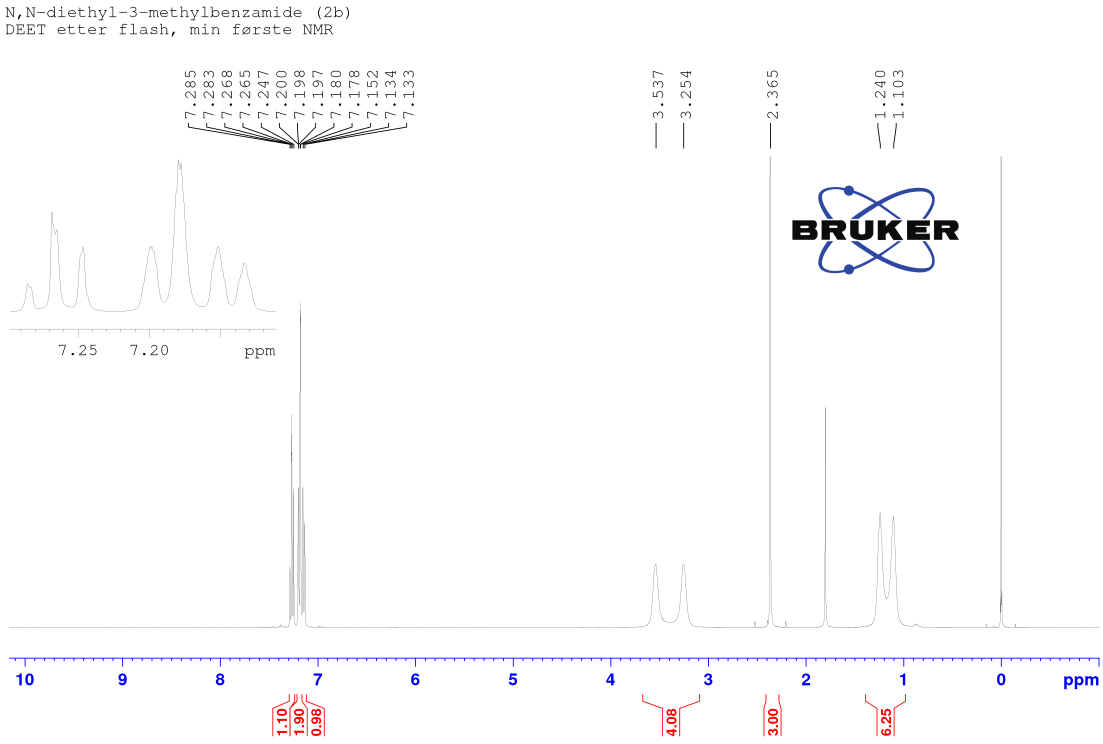

N,N-diethylbenzamide (2a)
171.31
137.30
129.08
128.40
126.28
43.28
39.22
14.23
12.91
BRUKER
129
128
127
ppm
45
40
35
30
25
20
ppm
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

Appendix 2b

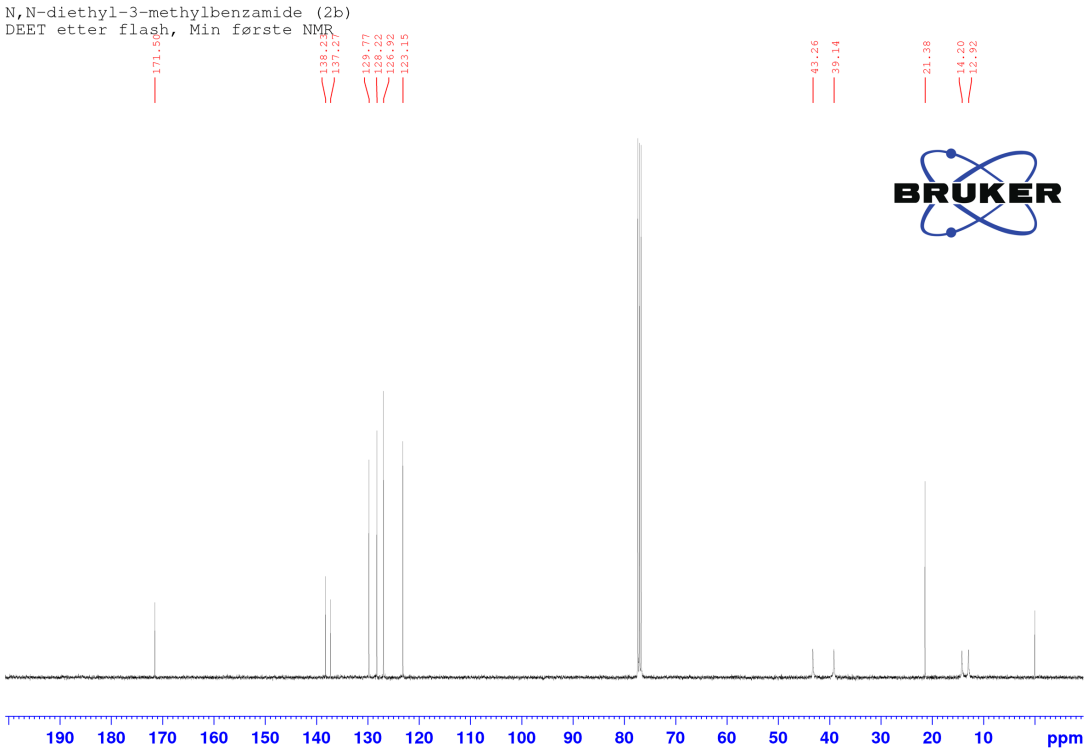


***N*,*N*-diethyl-3-methylbenzamide**

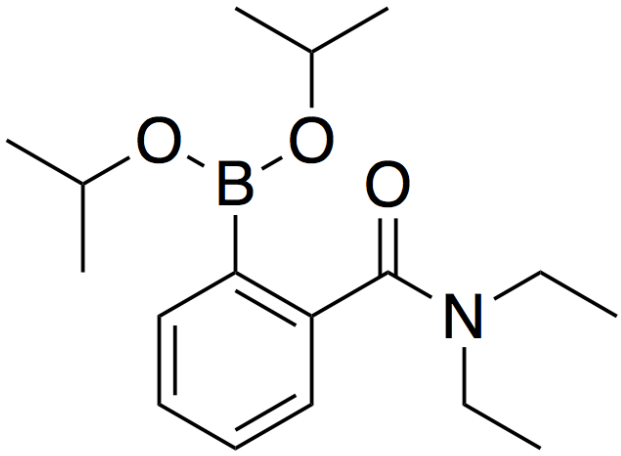
^{1}HNMR:



^{13}CNMR:

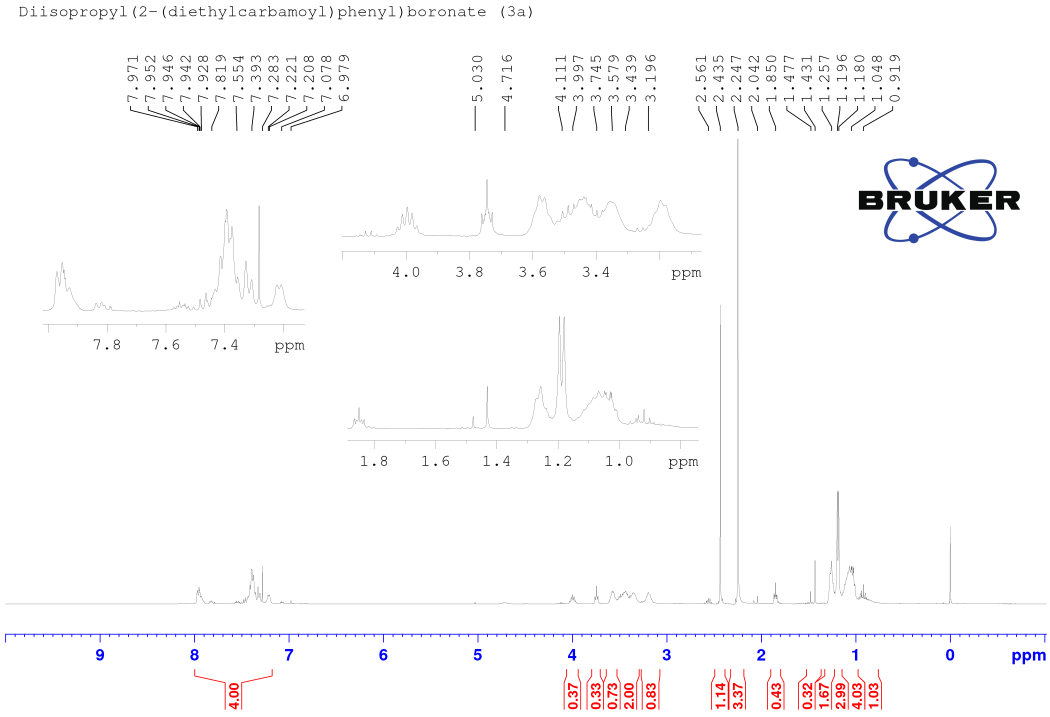

N,N-diethyl-3-methylbenzamide (2b)
DEET etter flash, Min første NMR
171.50
138.23
137.27
129.77
128.22
126.92
123.15
43.26
39.14
21.38
14.20
12.92
BRUKER
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Appendix 3a

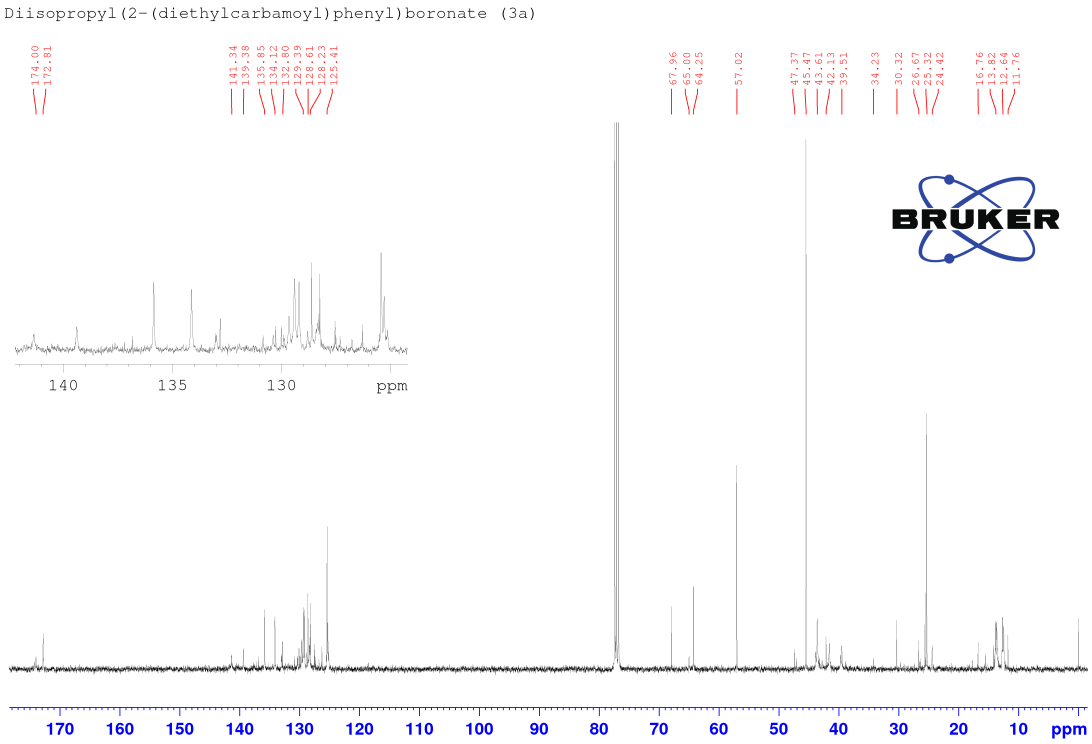


Diisopropyl (2-(diethylcarbamoyl)phenyl)boronate

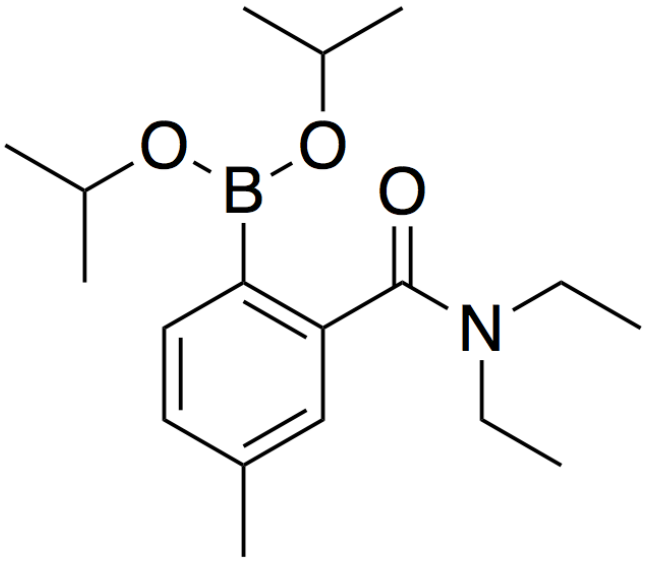
[1]HNMR:



^{13}CNMR:

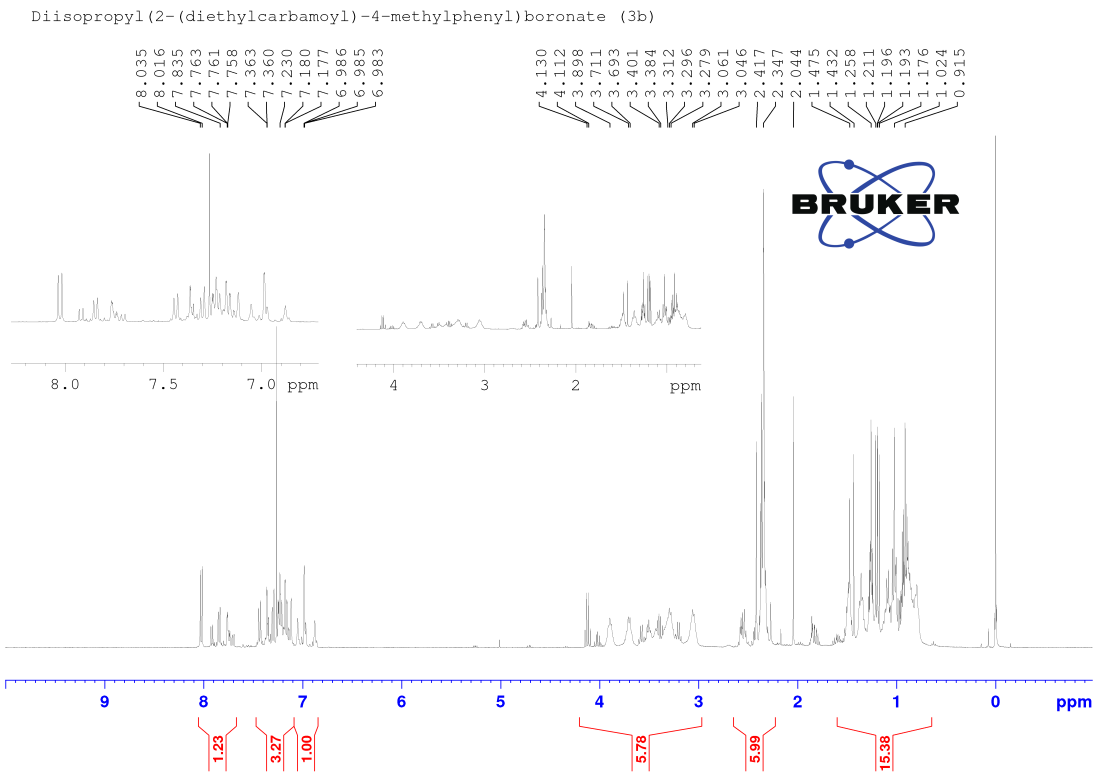

Diisopropyl(2-(diethylcarbamoyl)phenyl)boronate (3a)
174.00
172.81
141.34
139.38
135.85
134.12
132.60
132.39
128.61
128.23
125.41
67.96
65.00
64.25
57.02
47.37
45.47
43.61
42.13
39.51
34.23
30.32
26.67
25.32
24.42
16.76
13.82
12.64
11.76
BRUKER
140
135
130
ppm
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

Appendix 3b

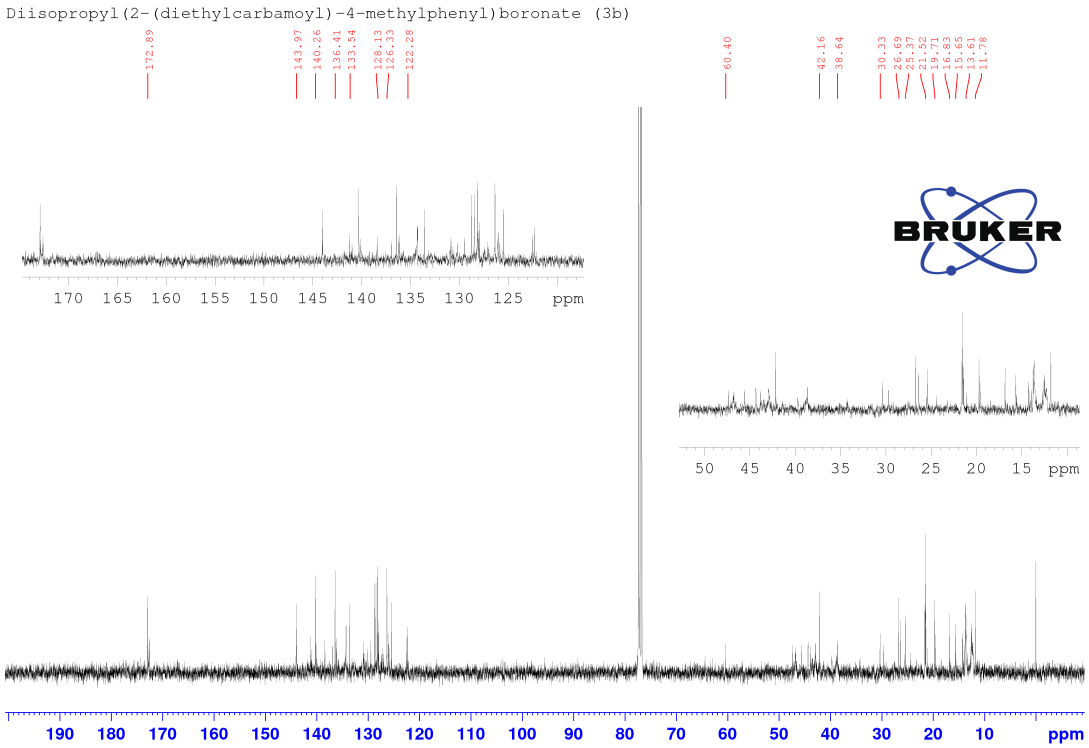


Diisopropyl (2-(diethylcarbamoyl)-4-methylphenyl)boronate

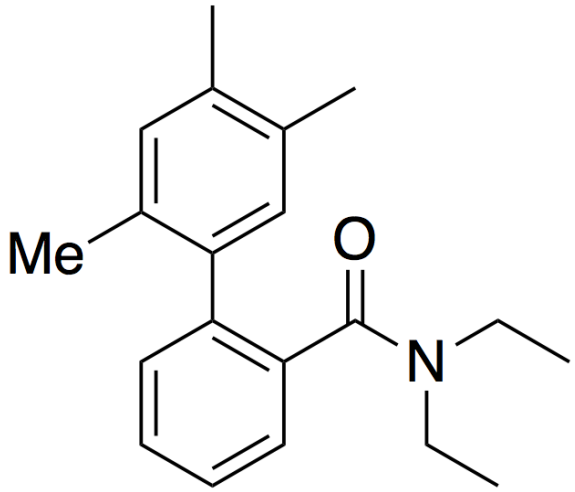
^{1}HNMR:



^{13}CNMR:

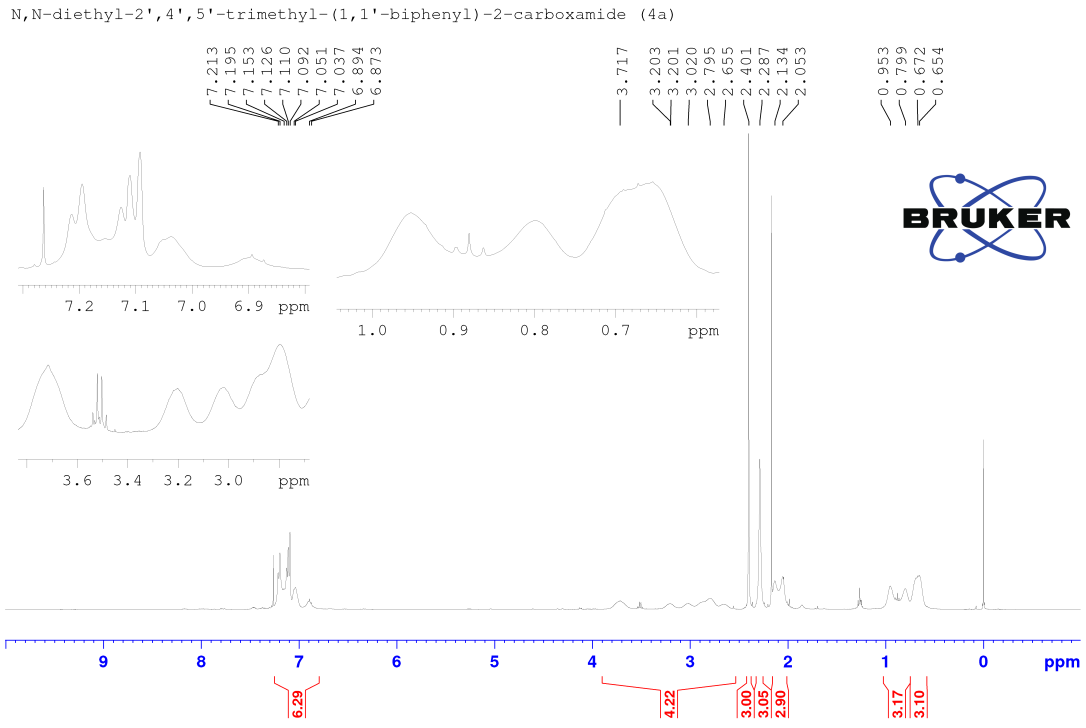

Diisopropyl(2-(diethylcarbamoyl)-4-methylphenyl)boronate (3b)
172.89
143.97
140.26
136.41
133.54
128.13
126.33
122.28
60.40
42.16
38.64
30.33
26.69
25.37
21.52
19.71
16.83
15.65
13.61
11.78
BRUKER
170 165 160 155 150 145 140 135 130 125 ppm
50 45 40 35 30 25 20 15 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Appendix 4a

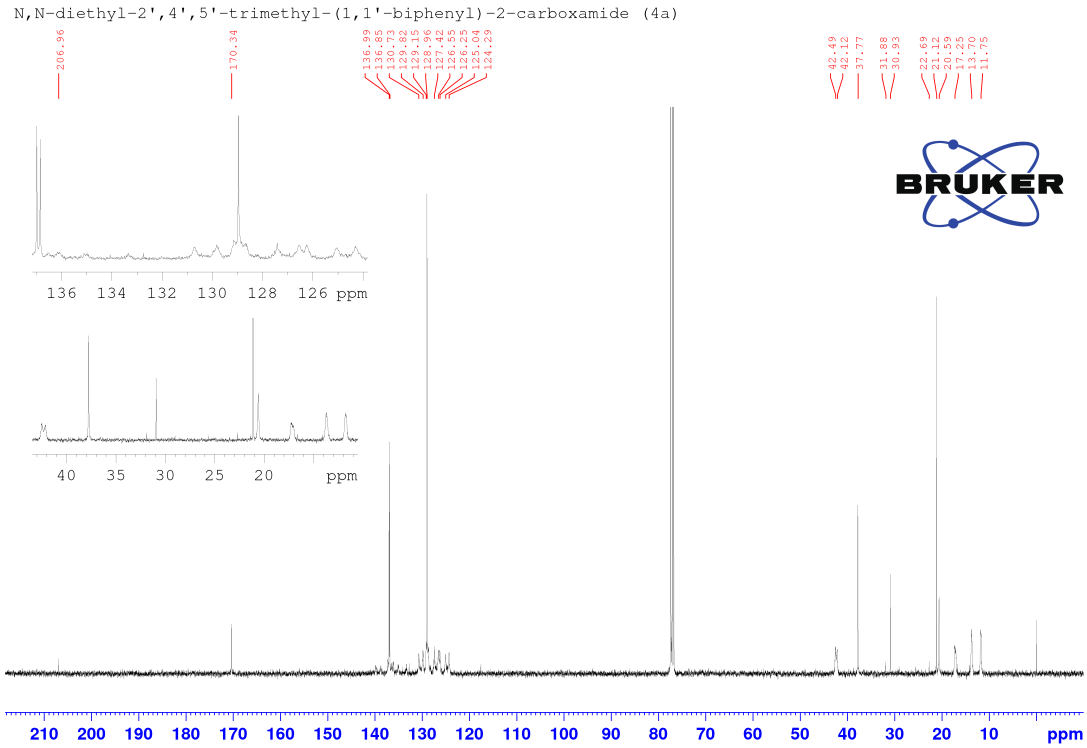


***N*,*N*-diethyl-2',4',5'-trimethyl-[1,1'-biphenyl]-2-carboxamide**

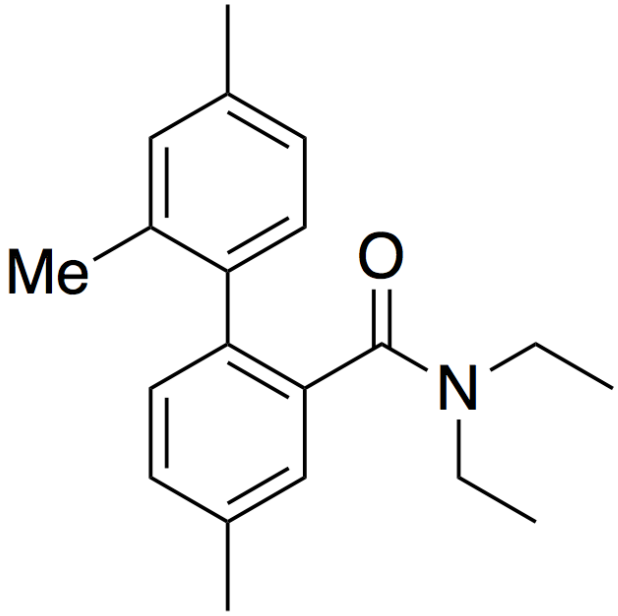
^{1}HNMR:



^{13}CNMR:

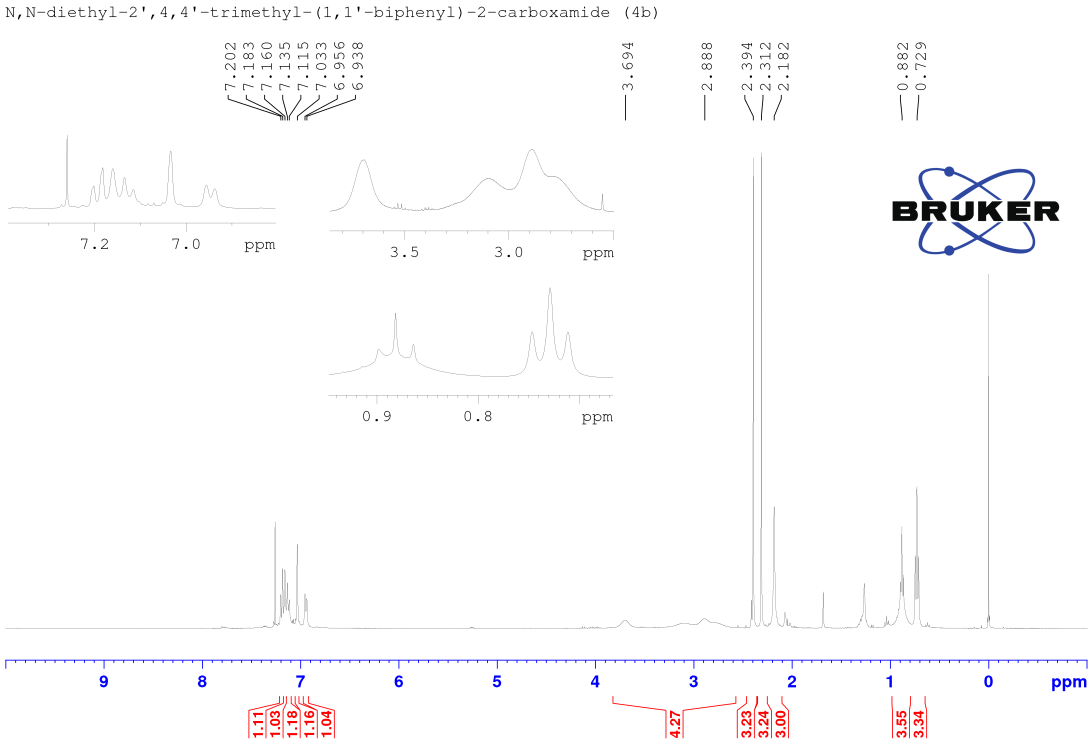

N,N-diethyl-2',4',5'-trimethyl-(1,1'-biphenyl)-2-carboxamide (4a)
206.96
170.34
136.99
136.85
130.73
129.82
129.15
128.62
127.42
126.55
126.25
125.04
124.29
42.49
42.12
37.77
31.88
30.93
22.69
21.12
20.59
13.55
13.30
11.75
BRUKER
136 134 132 130 128 126 ppm
40 35 30 25 20 ppm
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm

Appendix 4b

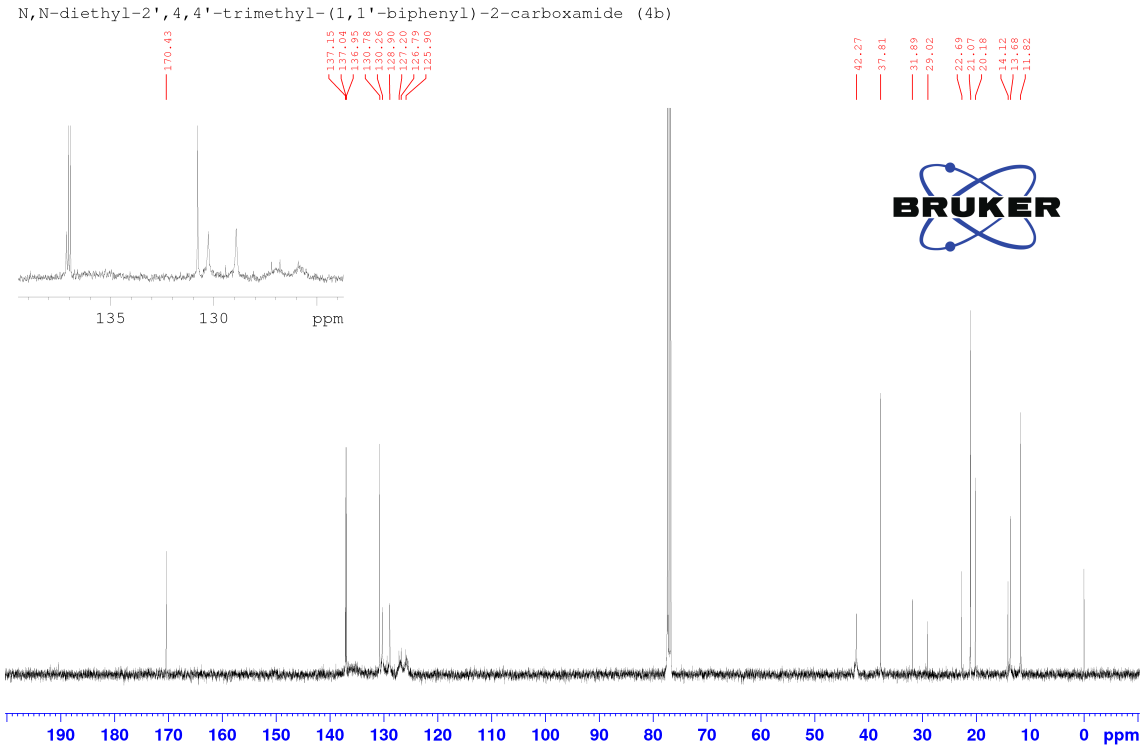


***N*,*N*-diethyl-2',4,4'-trimethyl-[1,1'-biphenyl]-2-carboxamide**

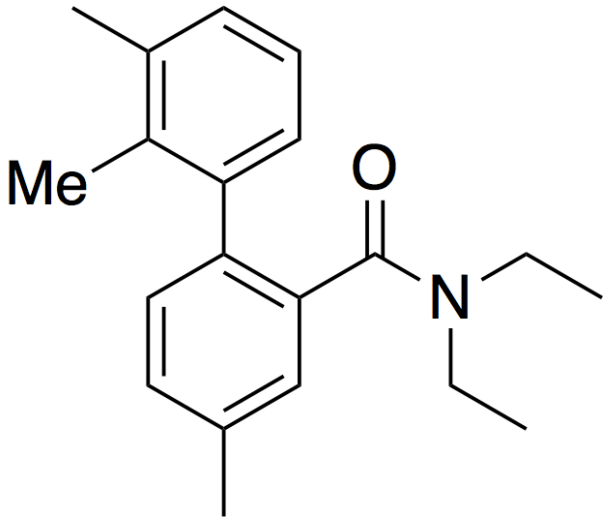
^{1}HNMR:



^{13}CNMR:

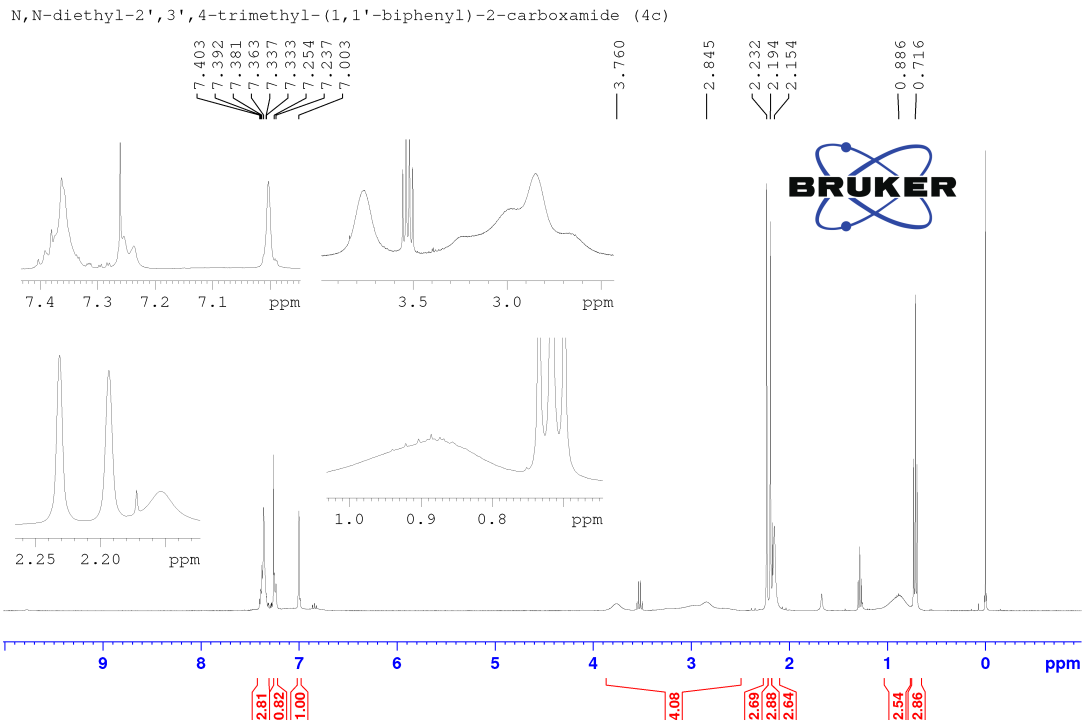

N,N-diethyl-2',4,4'-trimethyl-(1,1'-biphenyl)-2-carboxamide (4b)
170.43
137.15
137.04
136.95
130.78
130.26
128.90
127.20
126.79
125.90
42.27
37.81
31.89
29.02
22.69
21.07
20.18
14.12
13.68
11.82
BRUKER
135
130
ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Appendix 4c

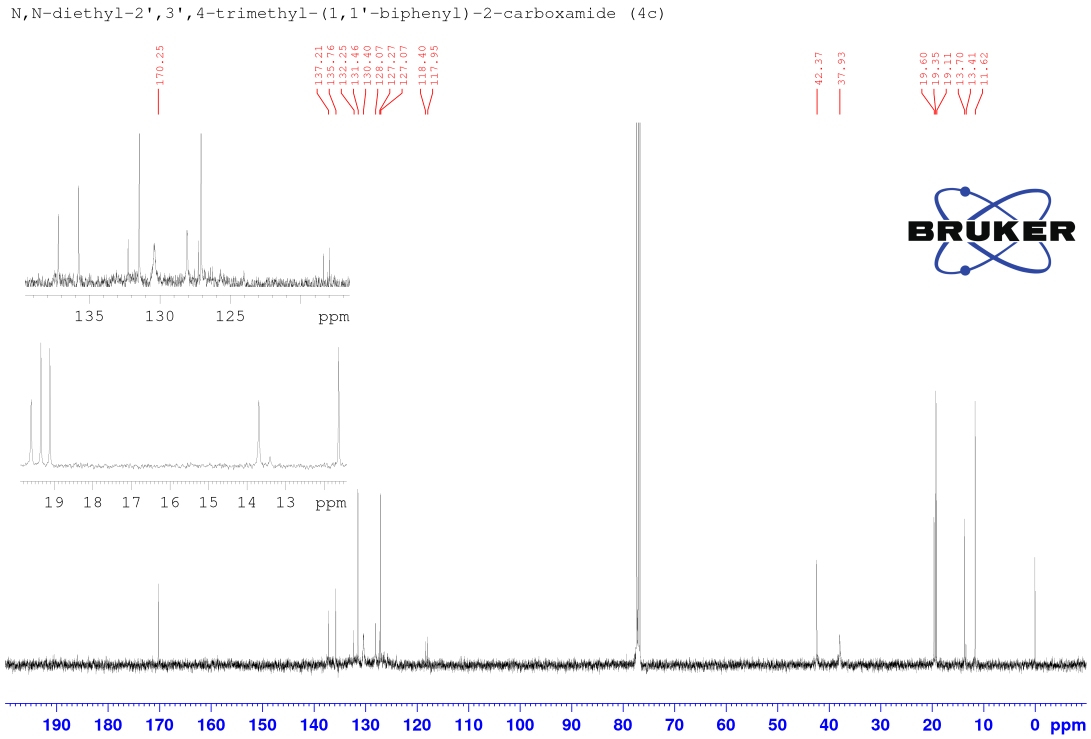


***N*,*N*-diethyl-2',3',4-trimethyl-[1,1'-biphenyl]-2-carboxamide**

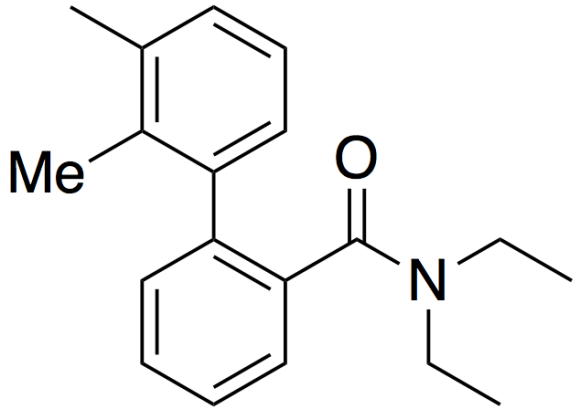
^{1}HNMR:



^{13}CNMR:

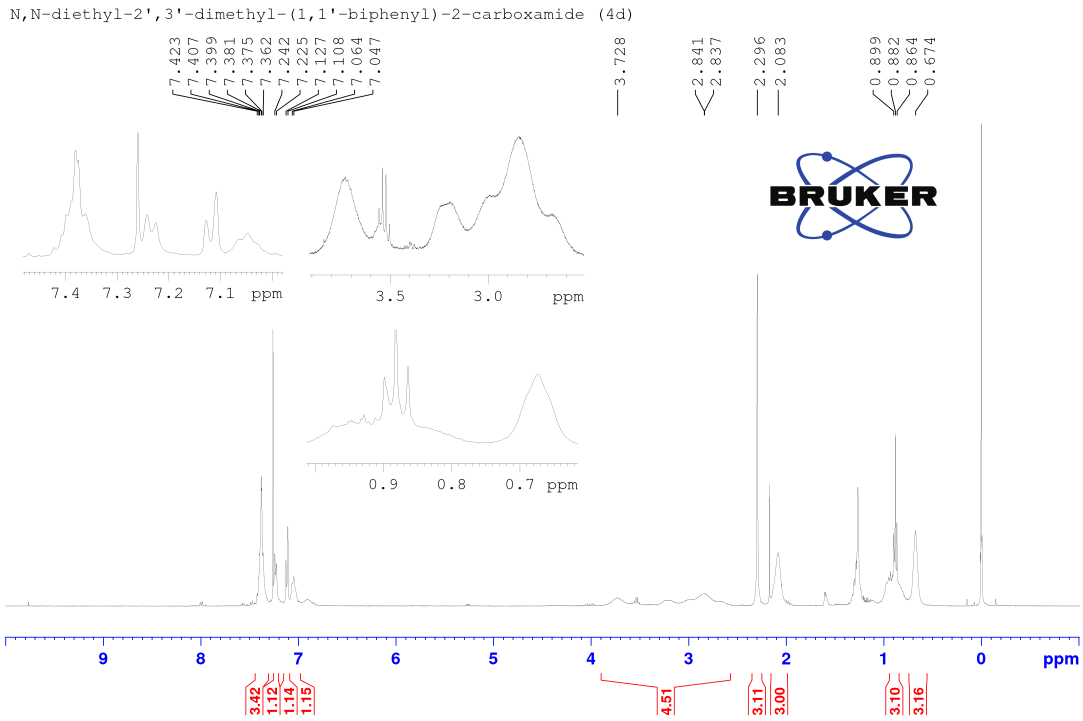

N,N-diethyl-2',3',4-trimethyl-(1,1'-biphenyl)-2-carboxamide (4c)
170.25
137.21
135.76
132.25
131.46
130.40
128.07
127.27
127.07
118.40
117.95
42.37
37.93
19.60
19.35
19.11
13.70
13.41
11.62
BRUKER
135 130 125 ppm
19 18 17 16 15 14 13 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Appendix 4d

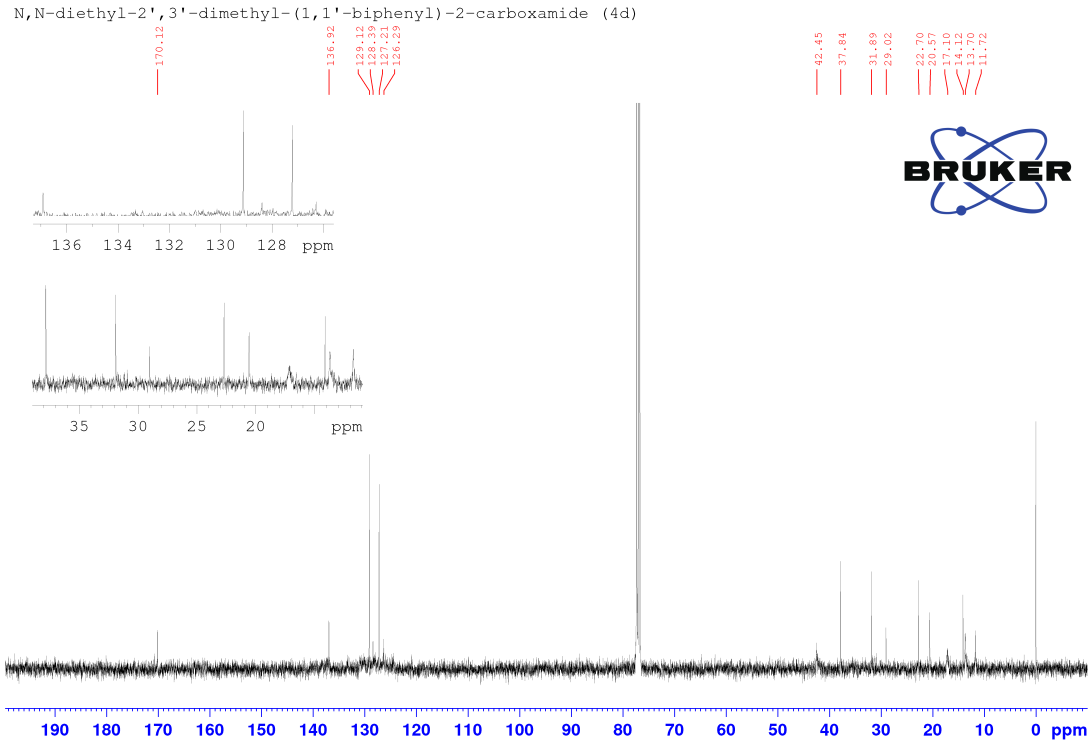


***N*,*N*-diethyl-2',3'-dimethyl-[1,1'-biphenyl]-2-carboxamide**

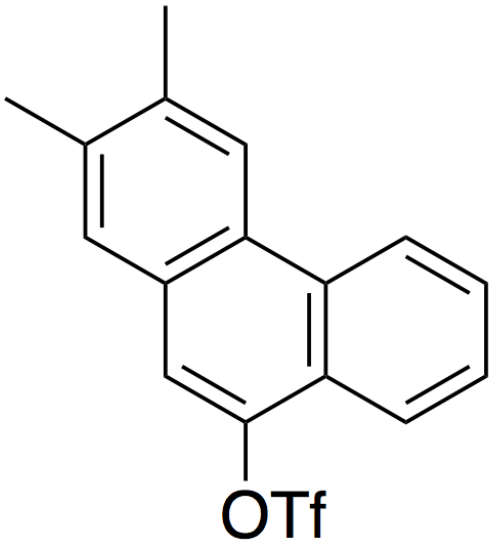
[1]HNMR:



^{13}CNMR:

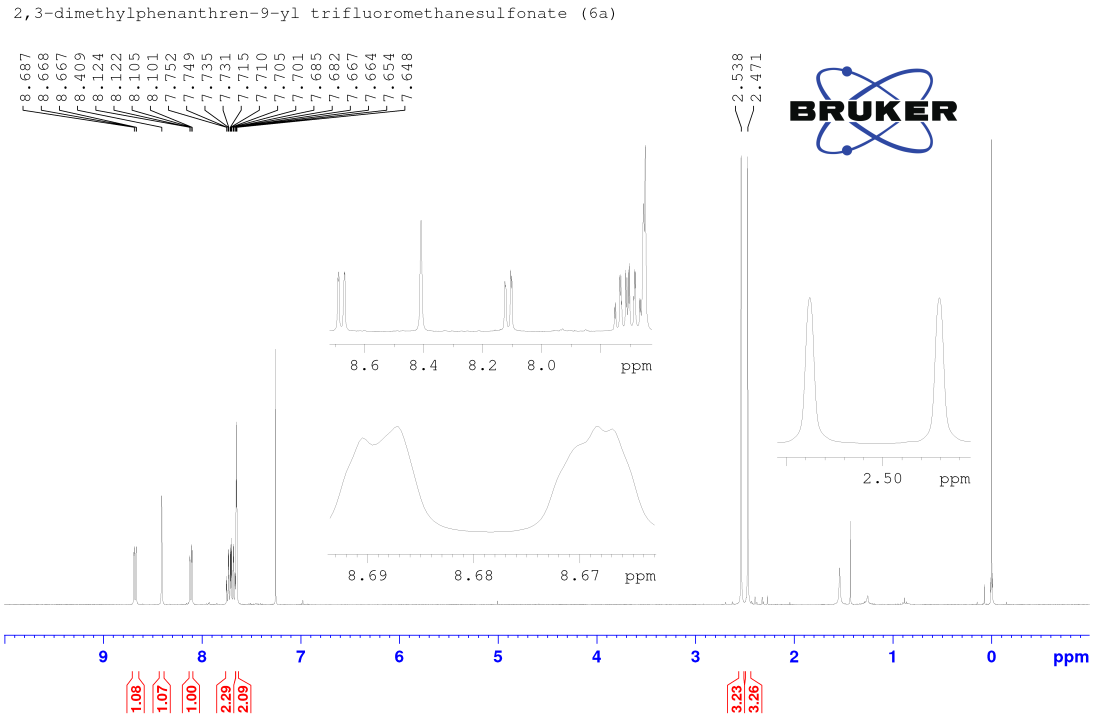

N,N-diethyl-2',3'-dimethyl-(1,1'-biphenyl)-2-carboxamide (4d)
170.12
136.92
129.12
128.39
127.21
126.29
42.45
37.84
31.89
29.02
22.70
20.57
14.10
14.12
13.70
11.72
BRUKER
136 134 132 130 128 ppm
35 30 25 20 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

Appendix 6a

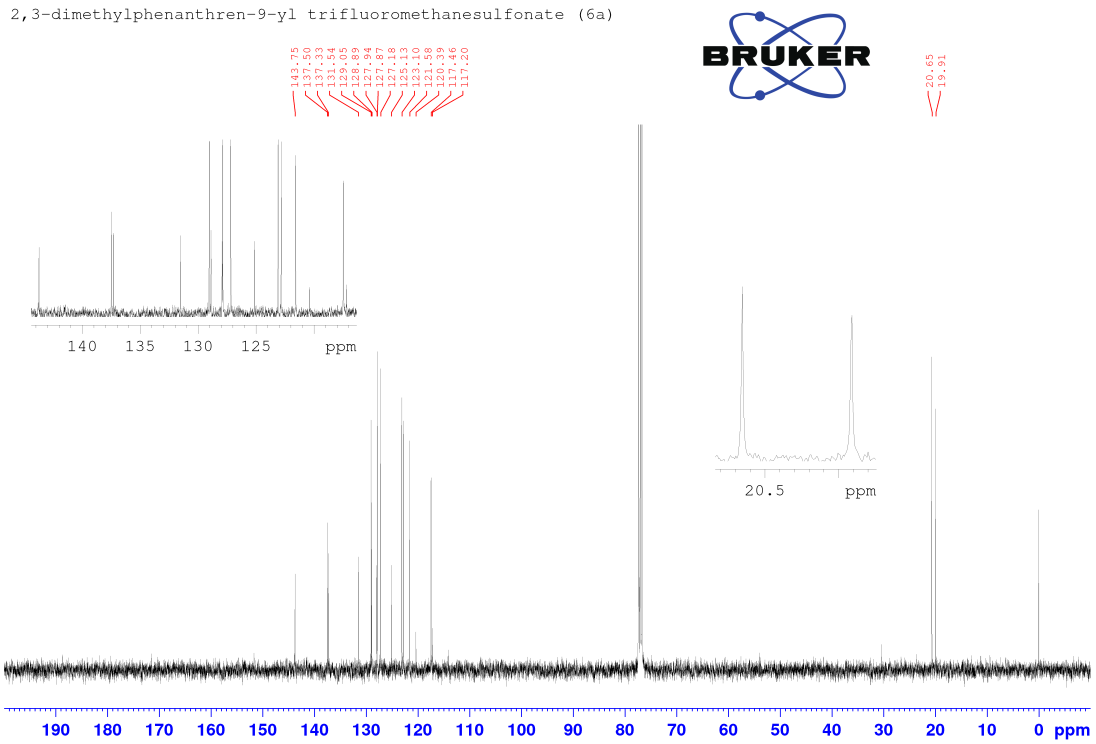


2,3-dimethylphenanthren-9-yl trifluoromethanesulfonate

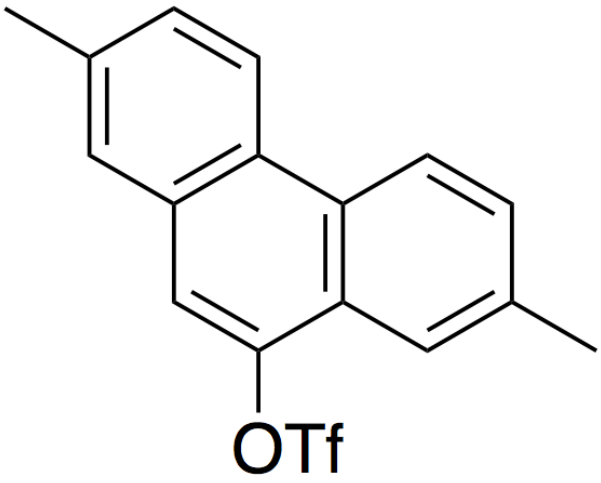
^{1}HNMR:



^{13}CNMR:

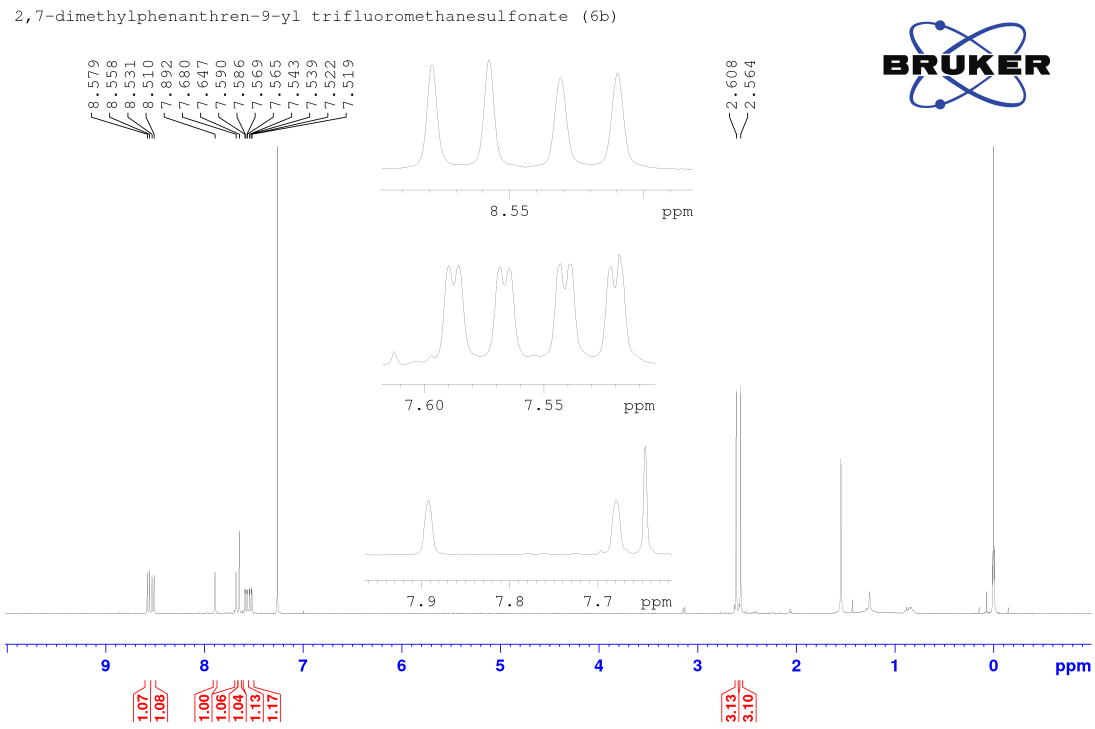

2,3-dimethylphenanthren-9-yl trifluoromethanesulfonate (6a)
BRUKER
143.75
137.50
137.33
131.54
129.05
128.89
127.94
127.37
127.18
126.13
123.10
121.58
120.39
117.46
117.20
20.65
19.91
140
135
130
125
ppm
20.5
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

Appendix 6b

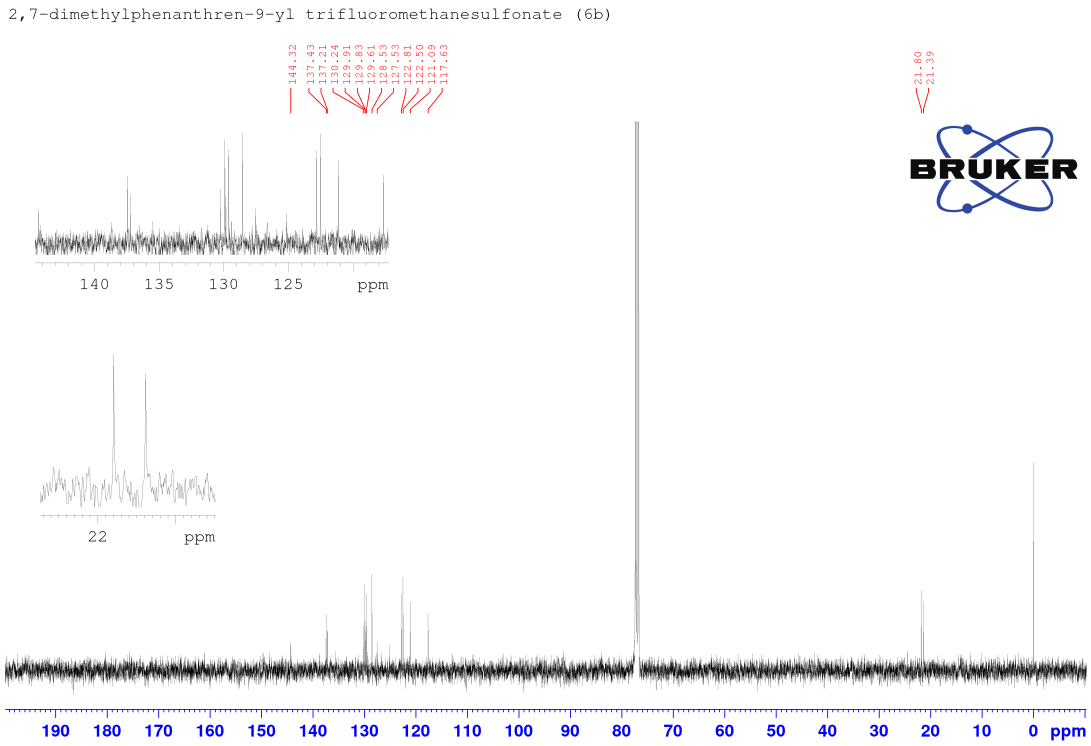


2,7-dimethylphenanthren-9-yl trifluoromethanesulfonate

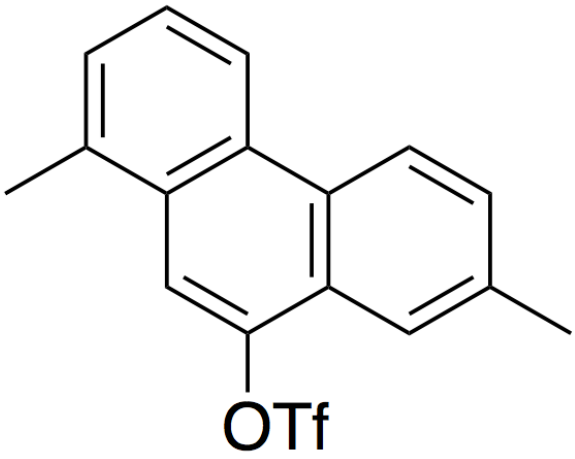
^{1}HNMR:



^{13}CNMR:


2,7-dimethylphenanthren-9-yl trifluoromethanesulfonate (6b)
144.32
137.43
137.21
130.24
129.91
129.83
129.61
128.53
127.53
122.81
122.50
121.09
117.63
21.80
21.39
BRUKER
140
135
130
125
ppm
22
ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

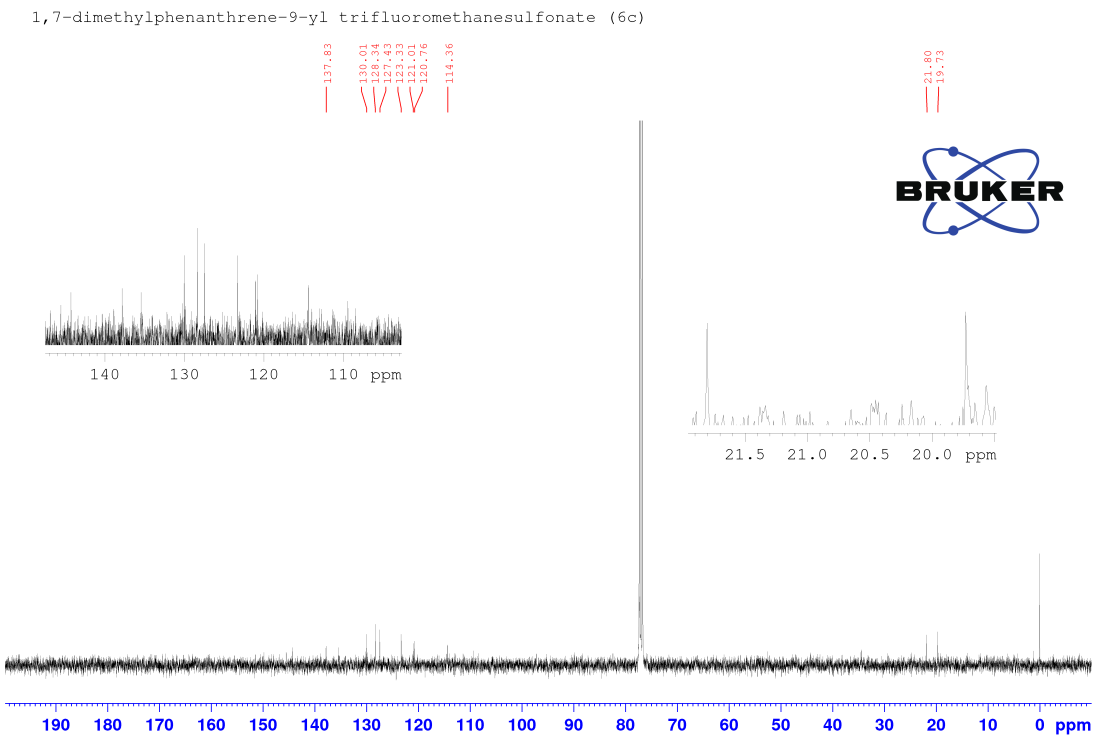
Appendix 6c



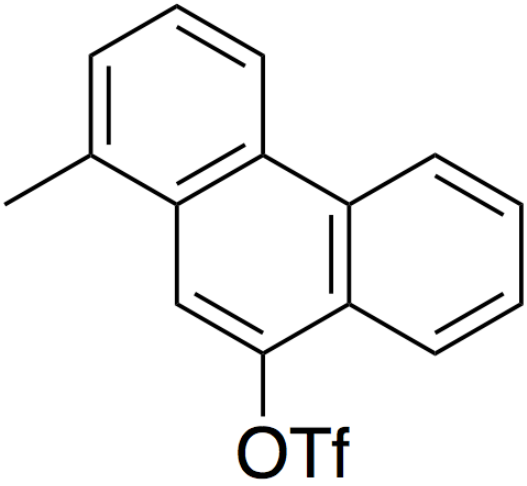
1,7-dimethylphenanthren-9-yl trifluoromethanesulfonate

[1]HNMR:

^{13}CNMR:

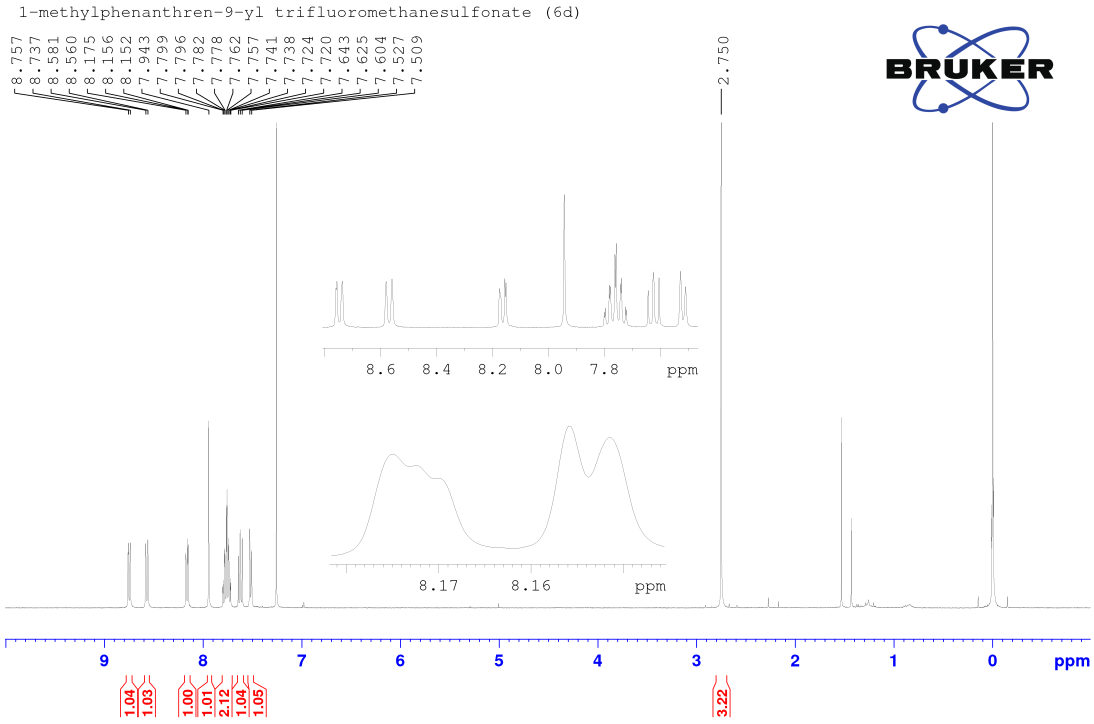

1,7-dimethylphenanthrene-9-yl trifluoromethanesulfonate (6c)
137.83
130.01
128.34
127.43
123.33
121.01
120.76
114.36
21.80
19.73
BRUKER
140
130
120
110 ppm
21.5
21.0
20.5
20.0 ppm
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0 ppm

Appendix 6d

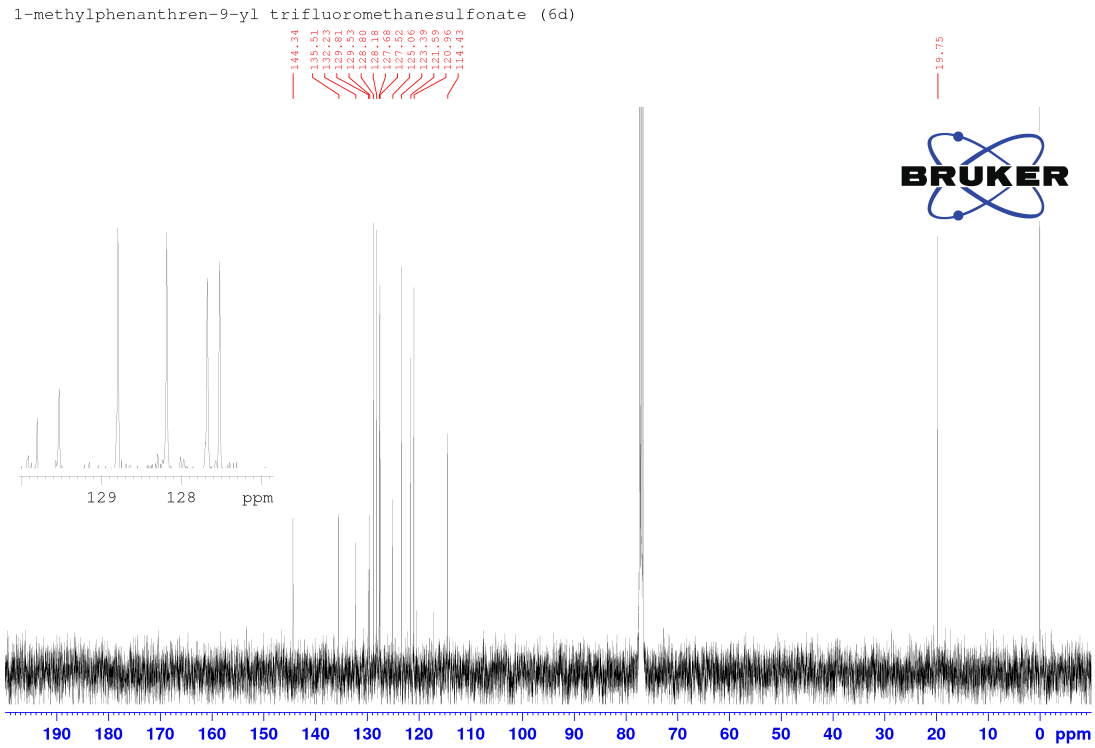


1-methylphenanthren-9-yl trifluoromethanesulfonate

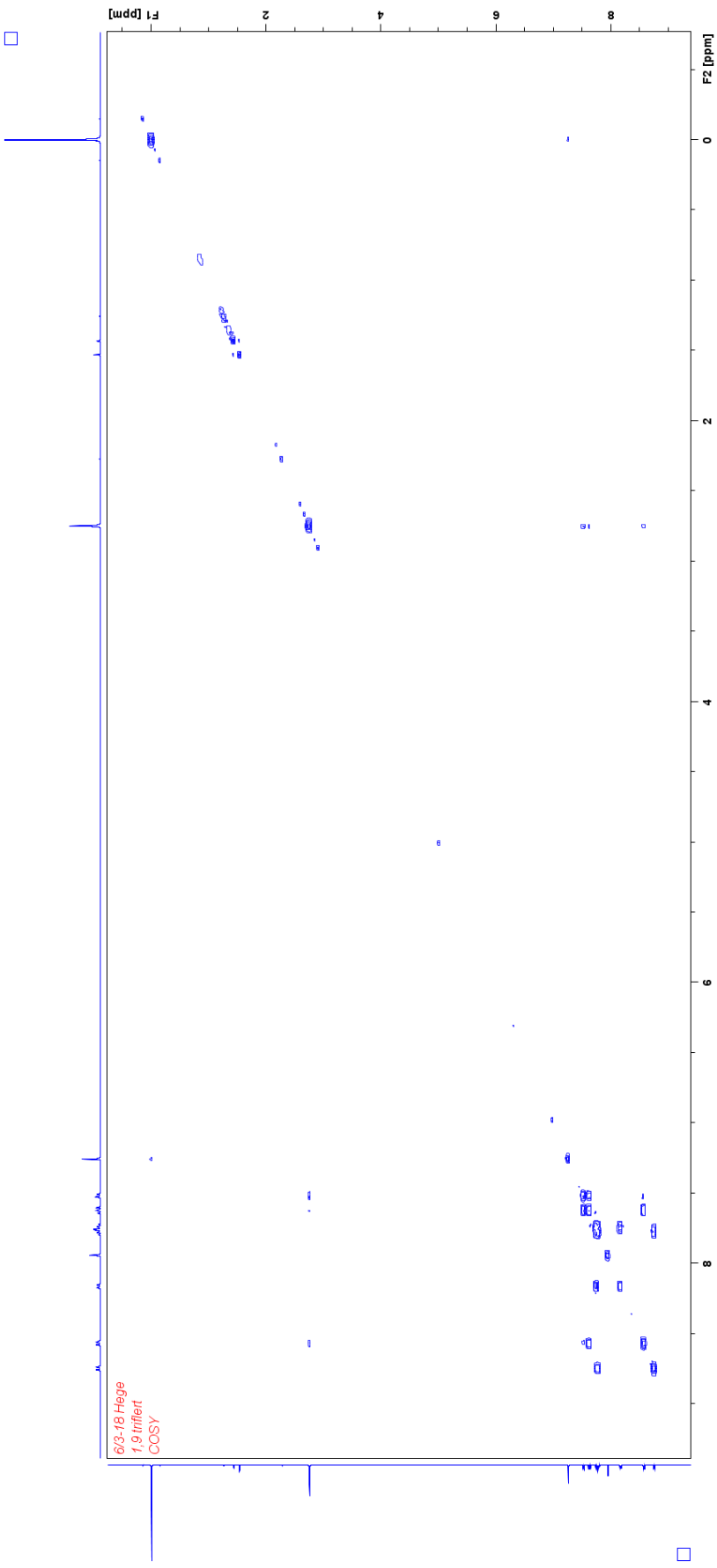
[1]HNMR:



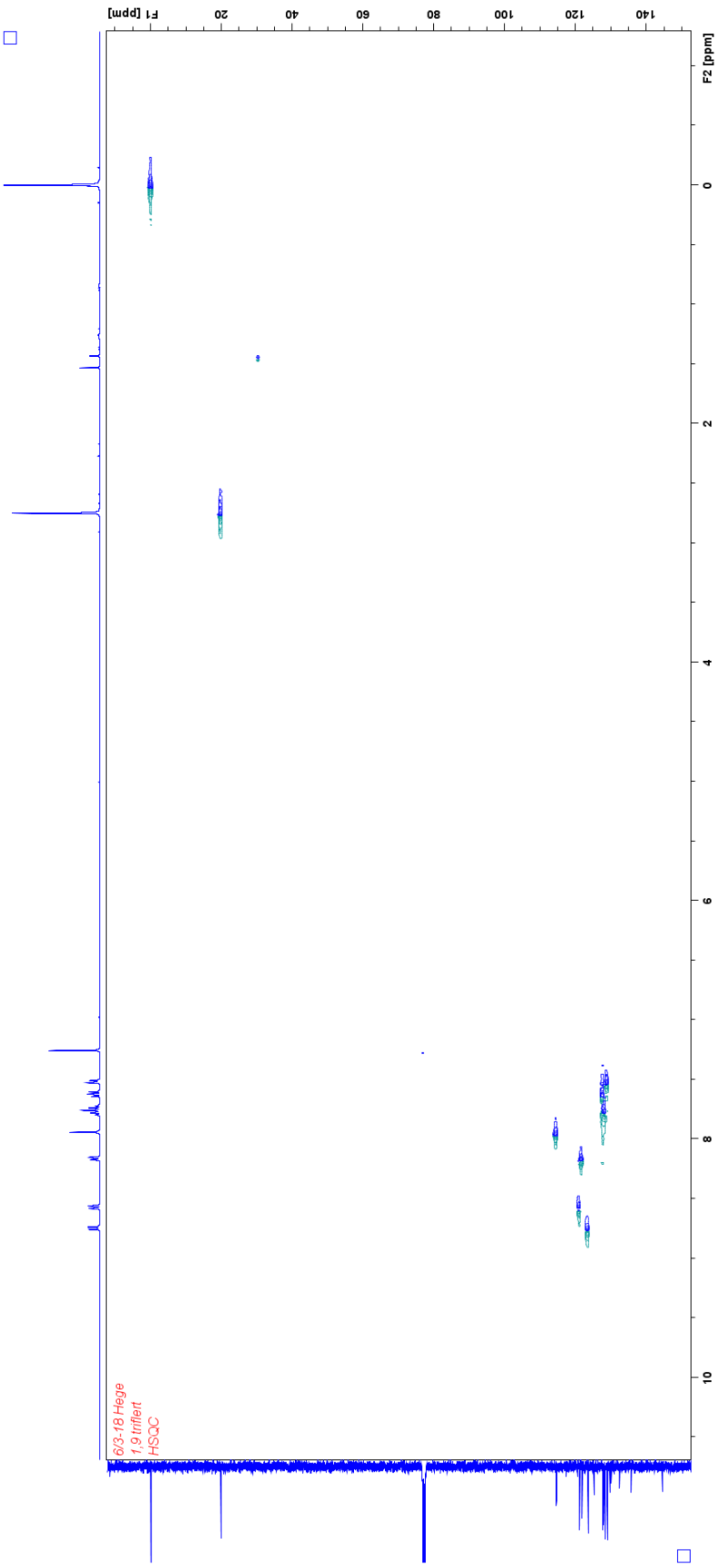
^{13}CNMR:


1-methylphenanthren-9-yl trifluoromethanesulfonate (6d)
144.34
135.51
132.23
129.81
129.53
128.80
128.18
127.68
127.56
125.06
123.39
121.59
120.96
114.43
19.75
BRUKER
129
128
ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

COSY:

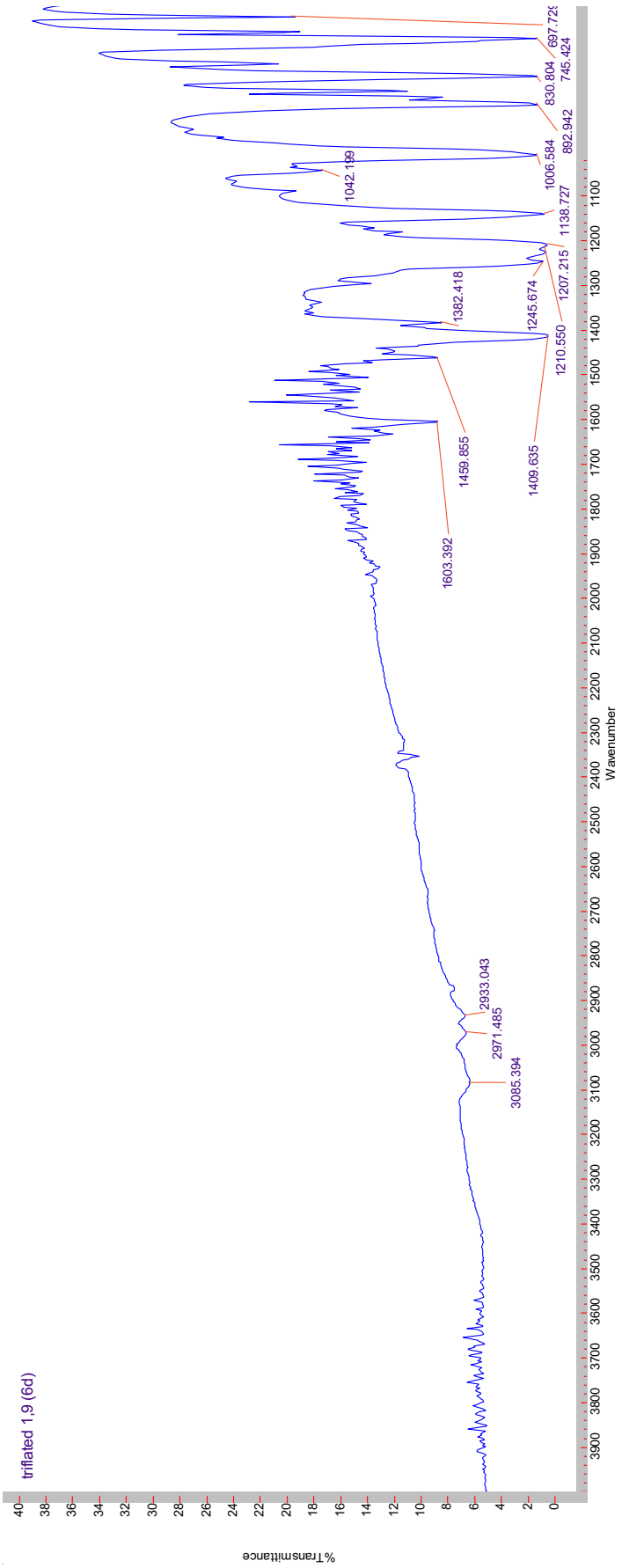


HSQC:

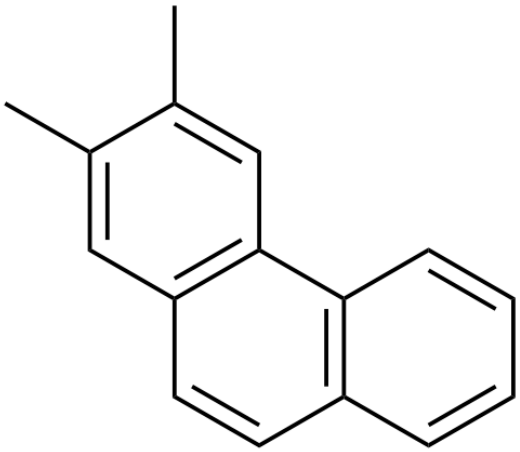

F1 [ppm]
20
40
60
80
100
120
140
F2 [ppm]
0
2
4
6
8
10
6/3-18 Hege
1,9 triflert
HSQC

HMBC:

IR:

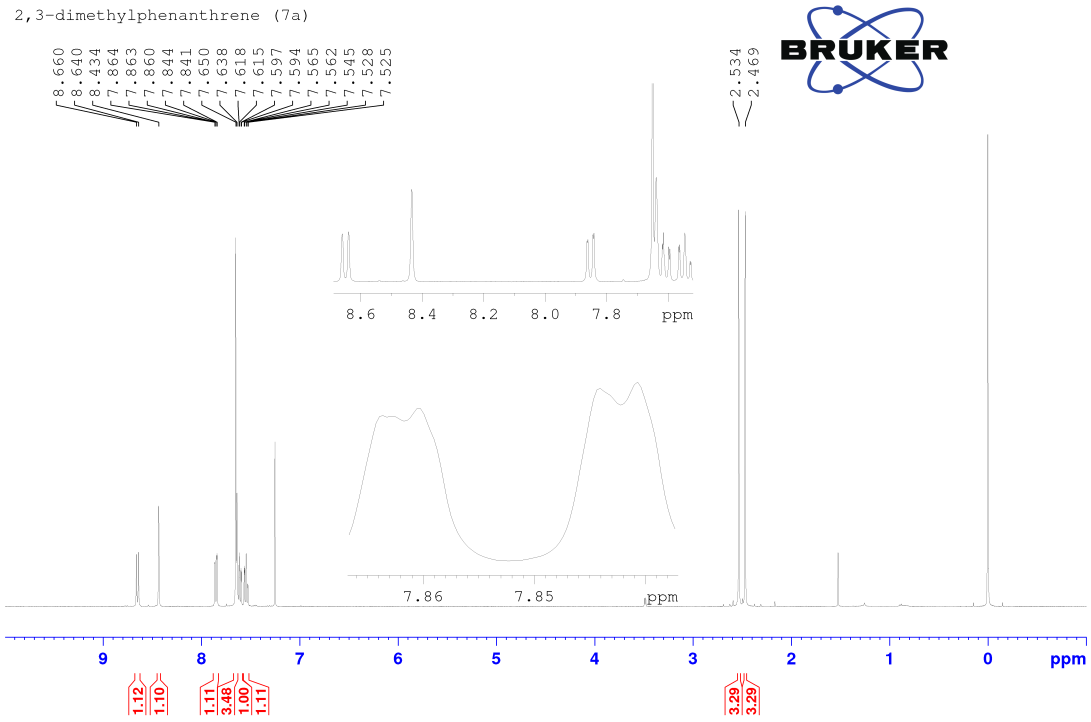

triflated 1,9 (6d)
%Transmittance
Wavenumber
697.725
745.424
830.804
892.942
1006.584
1042.199
1138.727
1207.215
1210.550
1245.674
1382.418
1409.635
1459.855
1603.392
2933.043
2971.485
3085.394

Appendix 7a

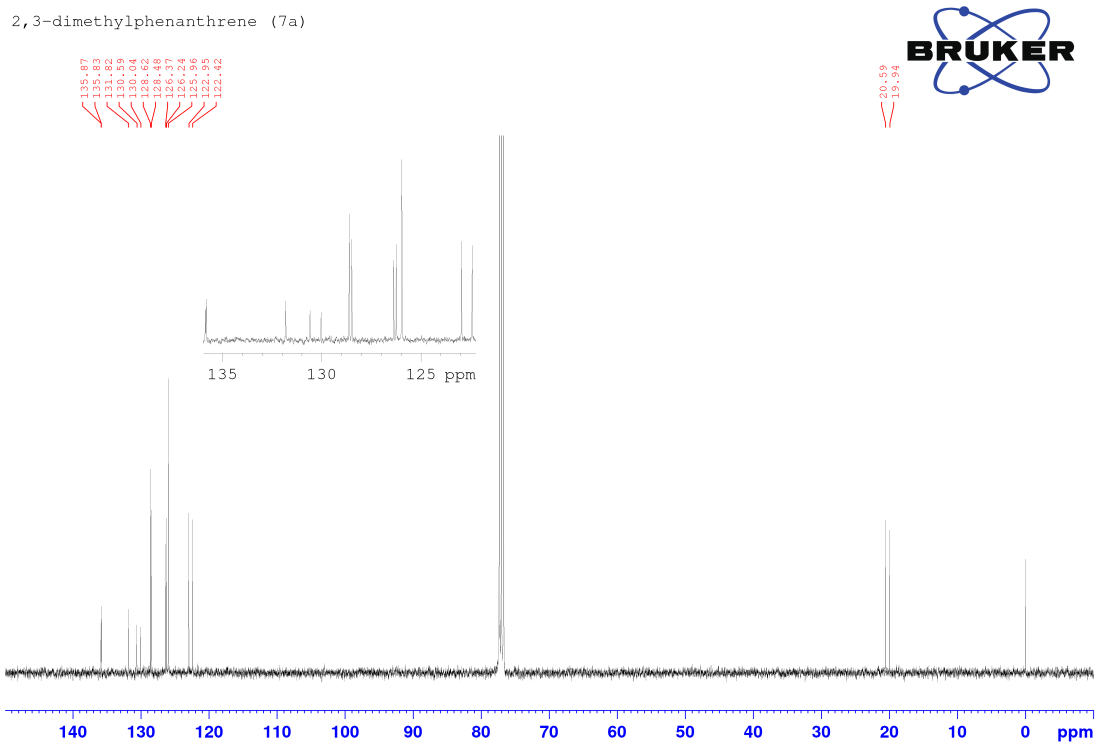


2,3-dimethylphenanthrene

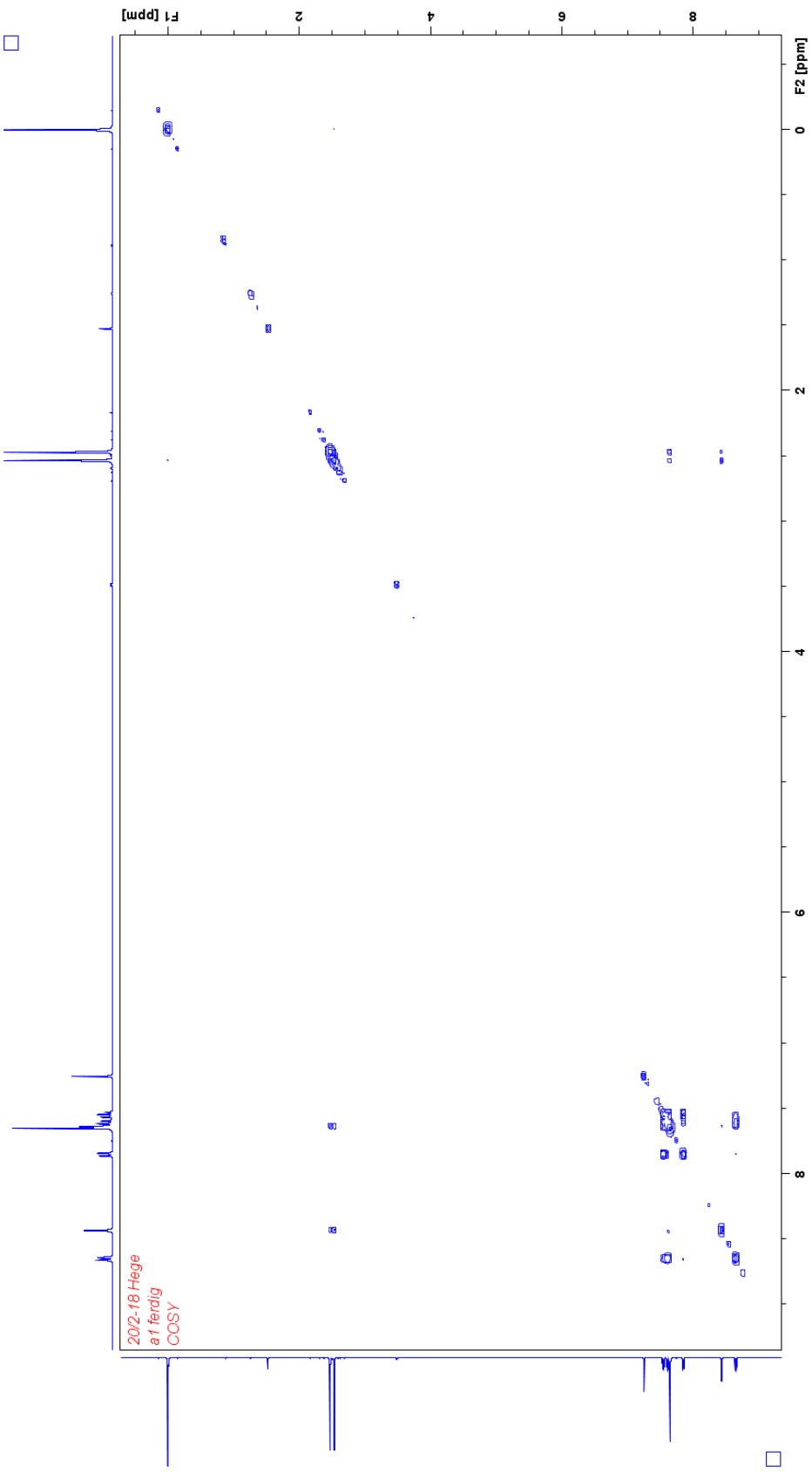
^{1}HNMR:



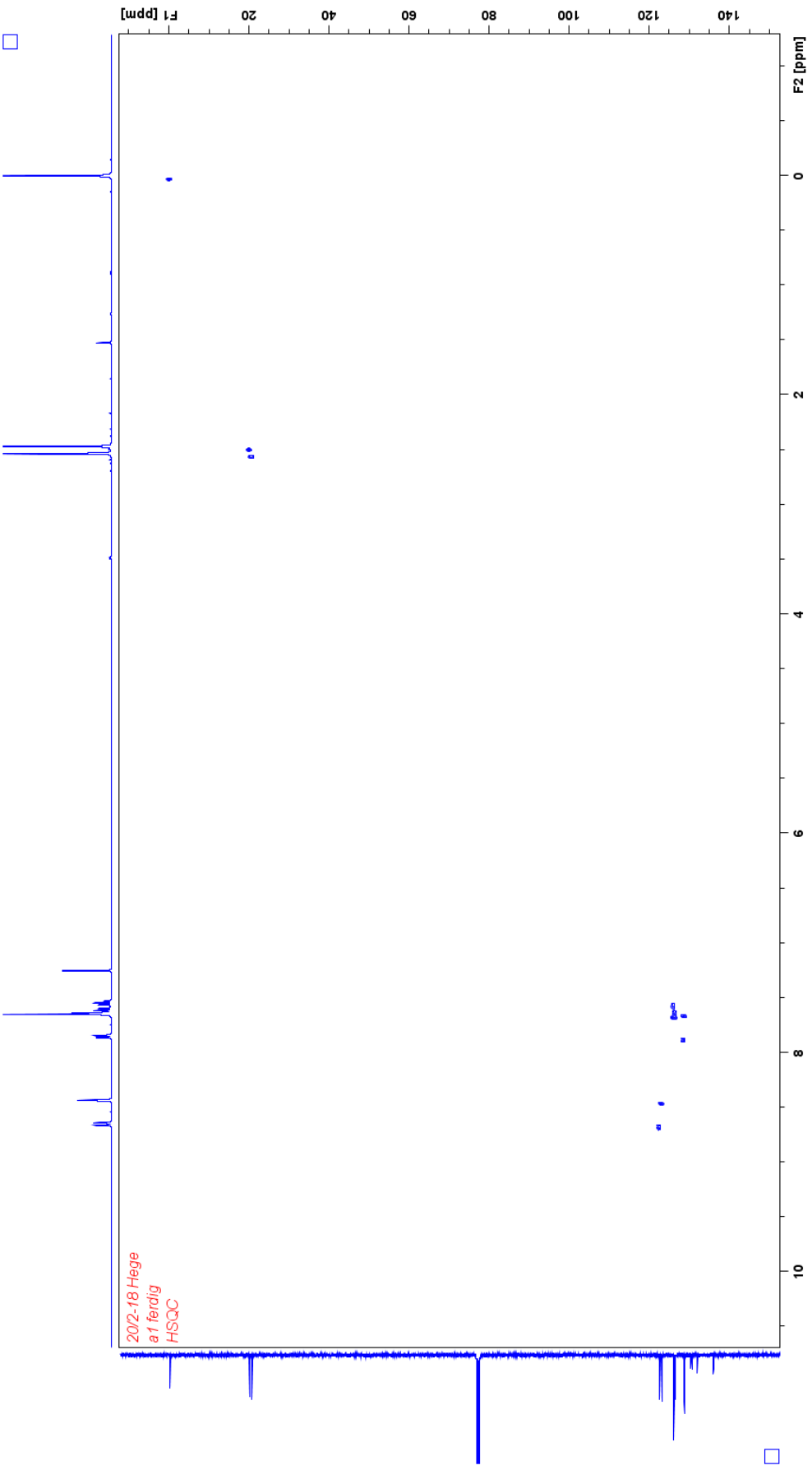
^{13}CNMR:


2,3-dimethylphenanthrene (7a)
135.87
135.83
131.82
130.59
130.04
128.62
128.48
126.37
126.24
125.96
122.95
122.42
20.59
19.94
BRUKER
135
130
125 ppm
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

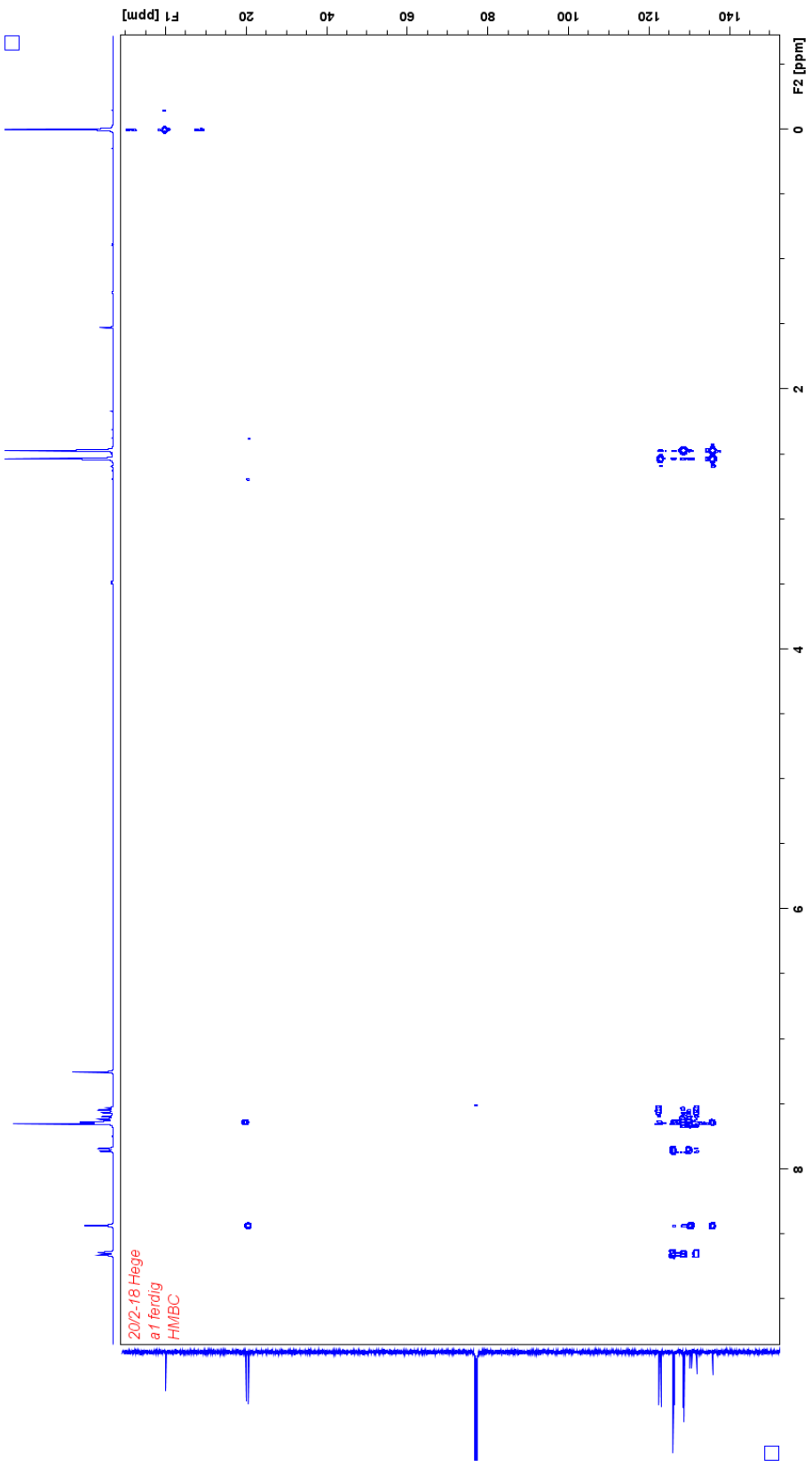
COSY:



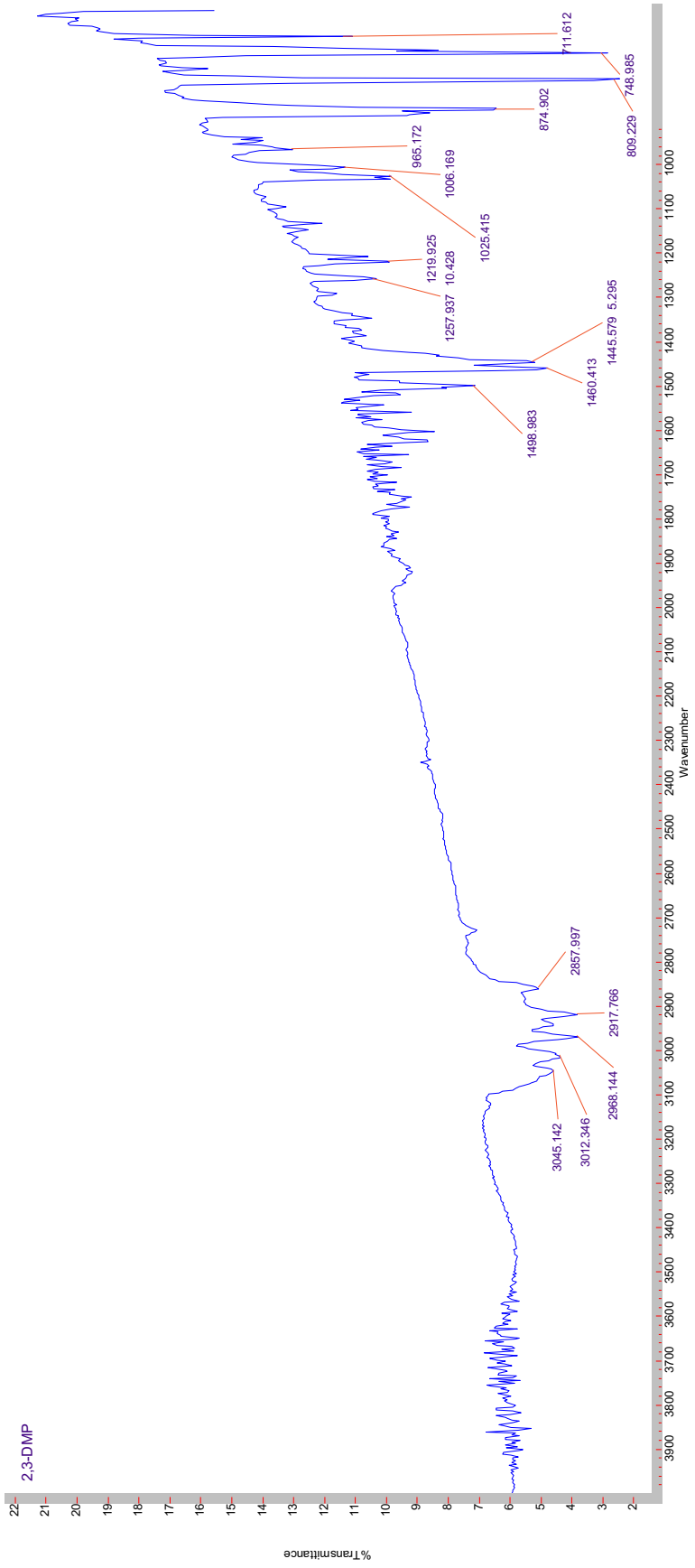
HSQC:


F1 [ppm]
20
40
60
80
100
120
140
F2 [ppm]
0
2
4
6
8
10
2022-18 Hege
a1 ferdig
HSQC

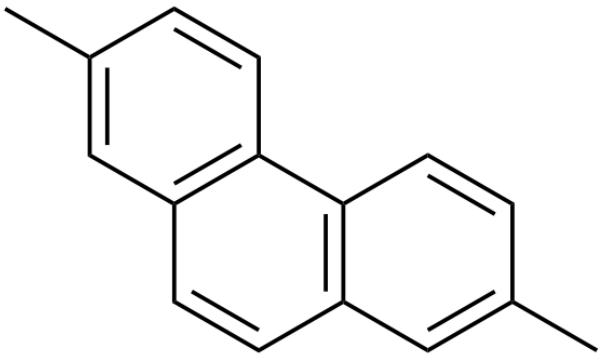
HMBC:


F1 [ppm]
20
40
60
80
100
120
140
F2 [ppm]
0
2
4
6
8
20/2-18 Hege
a1 ferdig
HMBC

IR:

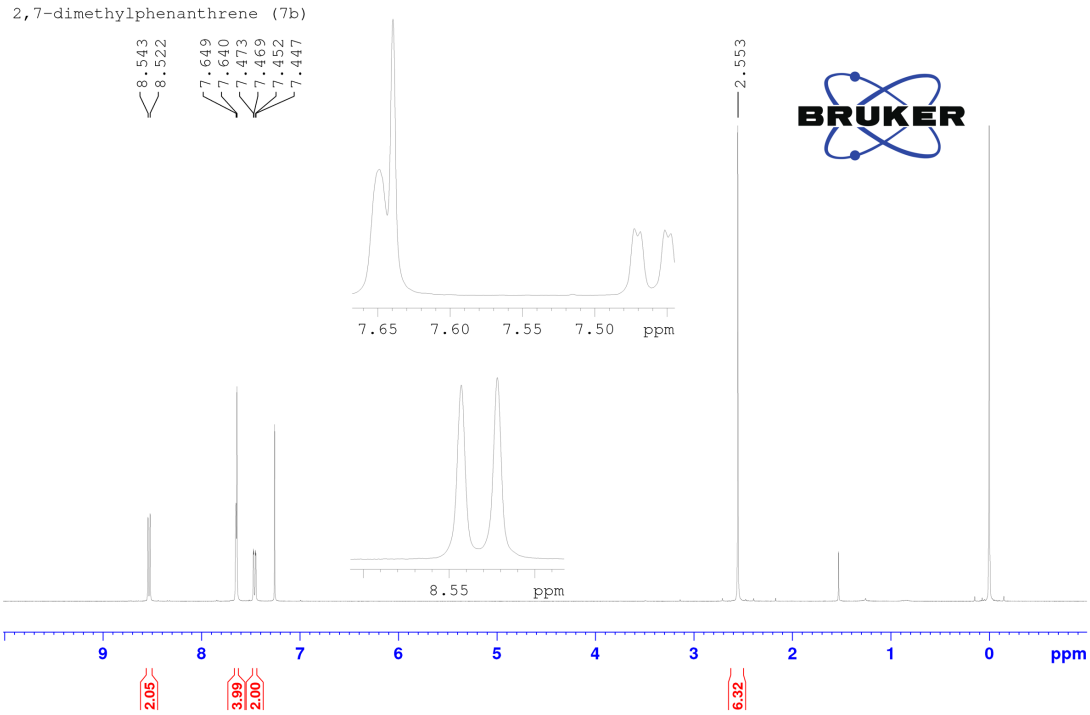

2,3-DMP
%Transmittance
Wavenumber
711.612
748.985
809.229
874.902
965.172
1006.169
1025.415
1219.925
10.428
1257.937
1445.579
5.295
1460.413
1498.983
2857.997
2917.766
2968.144
3012.346
3045.142

Appendix 7b

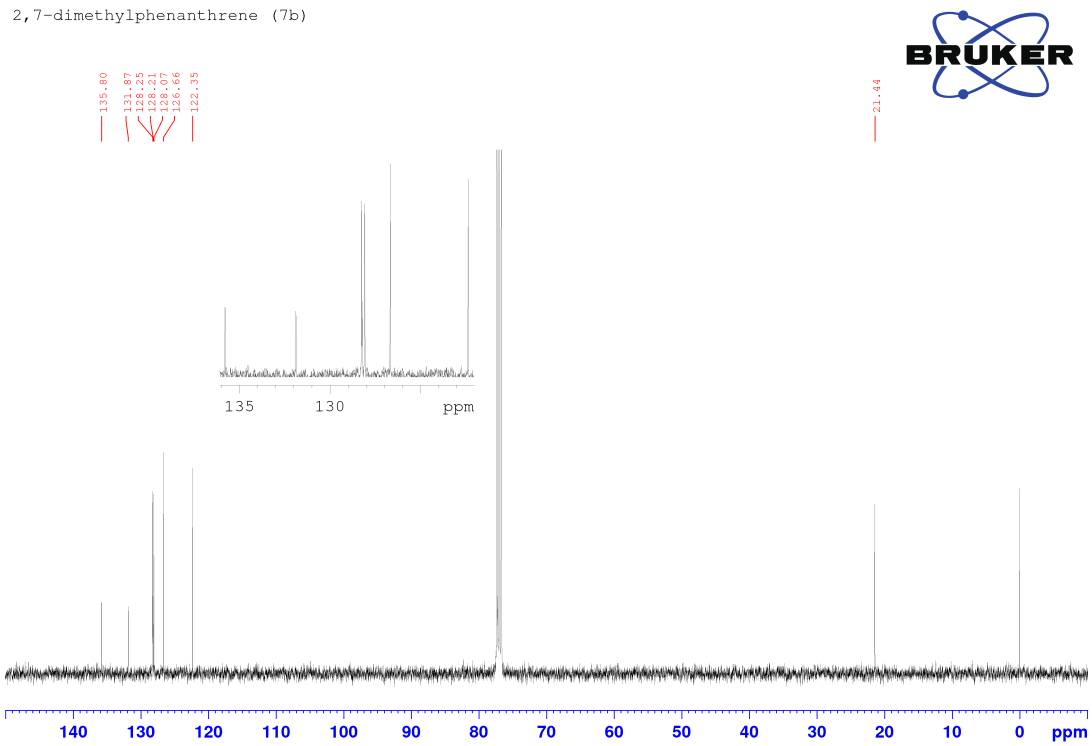


2,7-dimethylphenanthrene

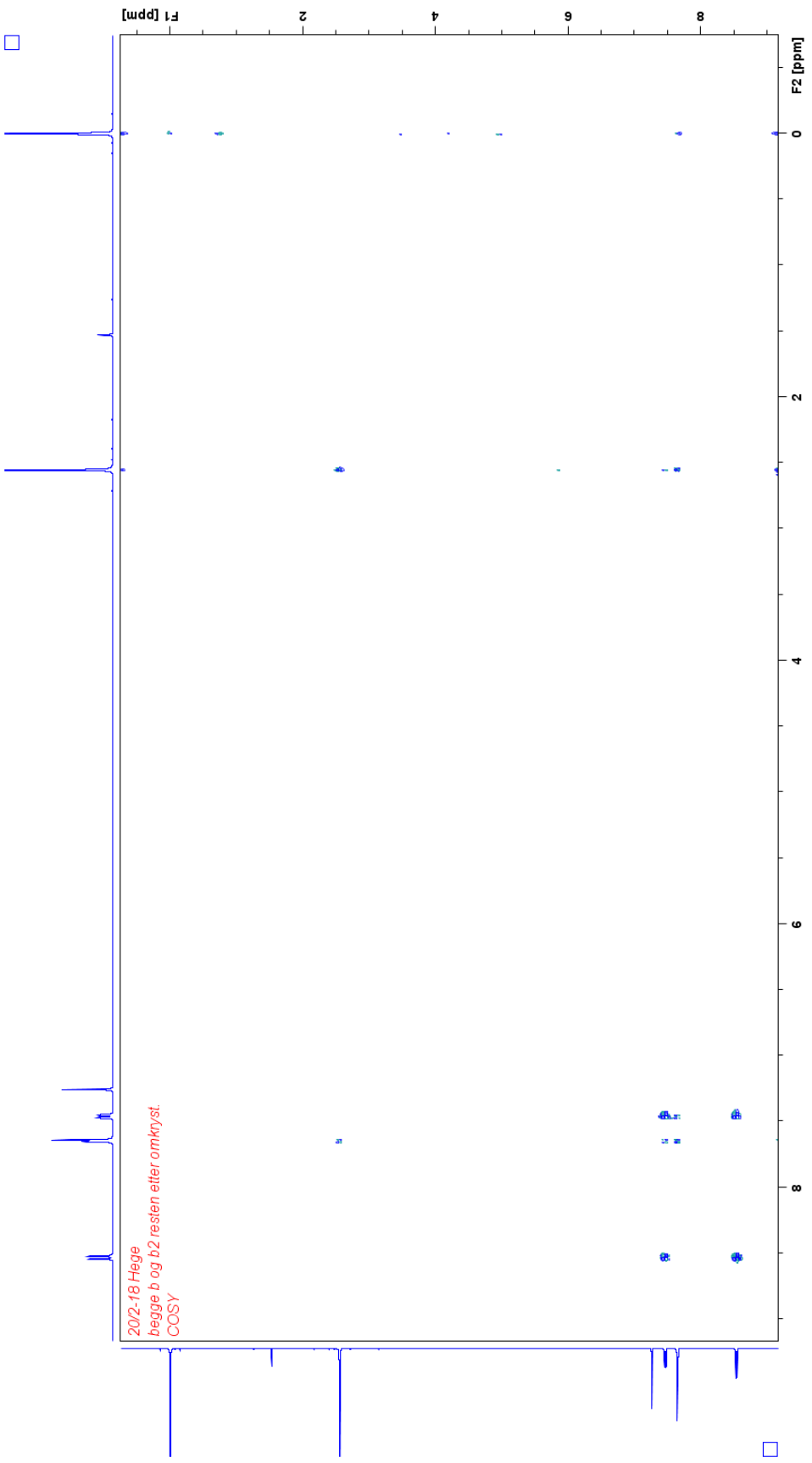
^{1}HNMR:



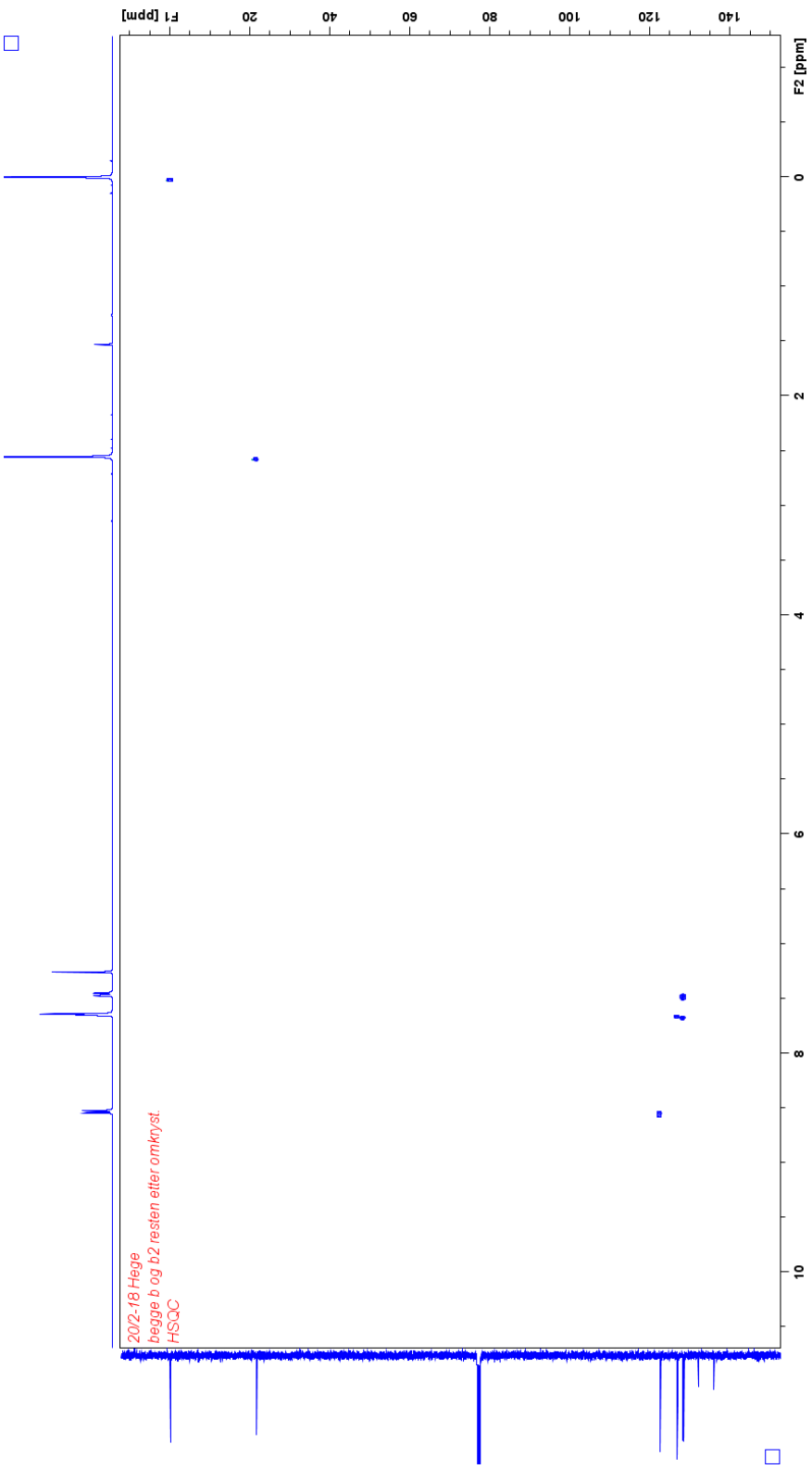
^{13}CNMR:


2,7-dimethylphenanthrene (7b)
135.80
131.87
128.25
128.21
128.07
126.66
122.35
21.44
135
130
ppm
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
ppm

COSY:


F1 [ppm]
F2 [ppm]
20/2-18 Hege
begge b og b2 resten etter omkryst.
COSY

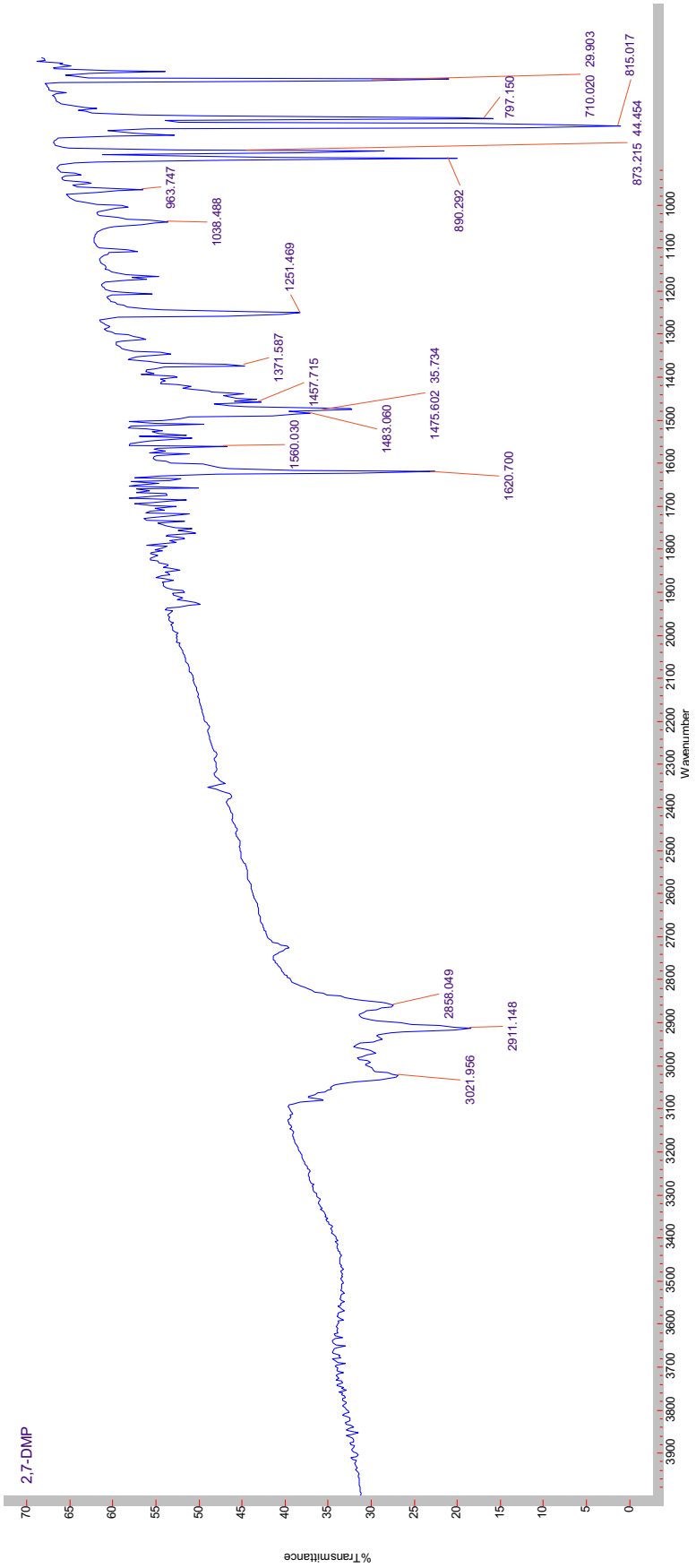
HSQC:


F1 [ppm]
20
40
60
80
100
120
140
F2 [ppm]
0
2
4
6
8
10
20/2-18 Hege
begge b og b2 resten etter omkryst.
HSQC

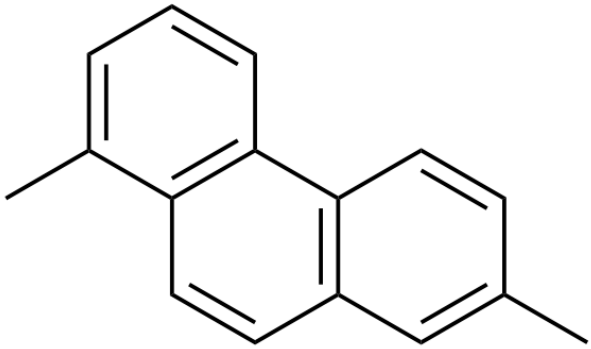
HMBC:


F1 [ppm]
20
40
60
80
100
120
140
F2 [ppm]
0
2
4
6
8
20/2-18 Hege
begge b og b2 resten etter omkryst.
HMBC

IR:

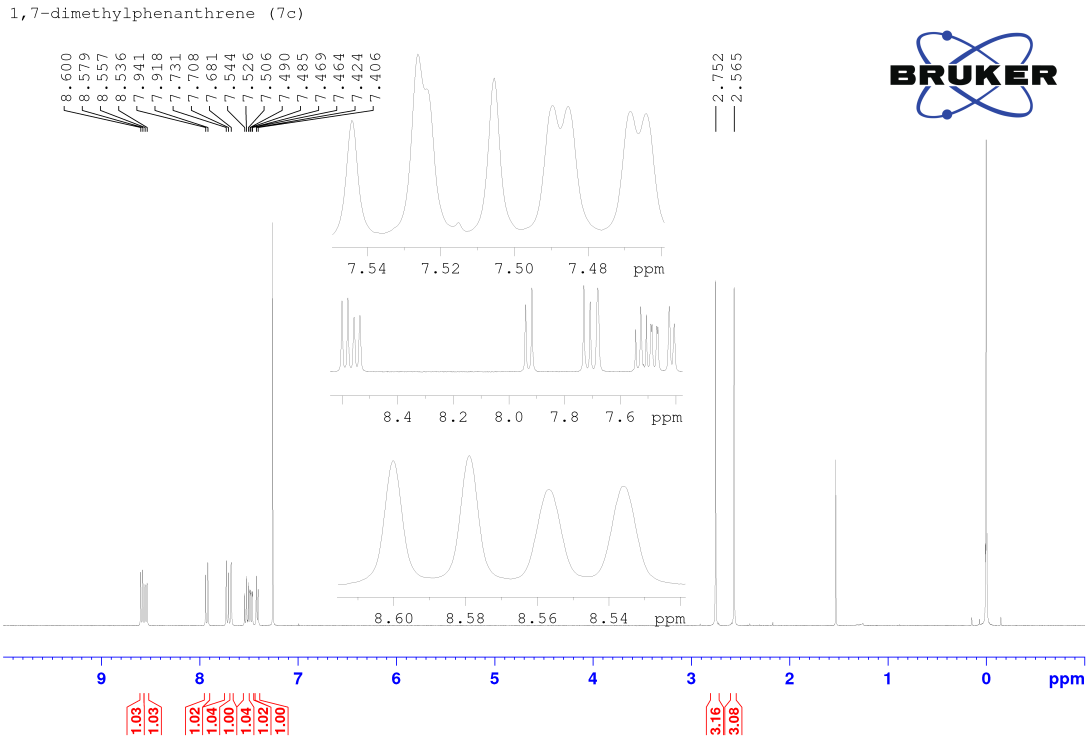

2,7-DMP
%Transmittance
Wavenumber
815.017
29.903
710.020
797.150
44.454
873.215
890.292
963.747
1038.488
1251.469
1371.587
1457.715
35.734
1475.602
1483.060
1560.030
1620.700
2858.049
2911.148
3021.956

Appendix 7c

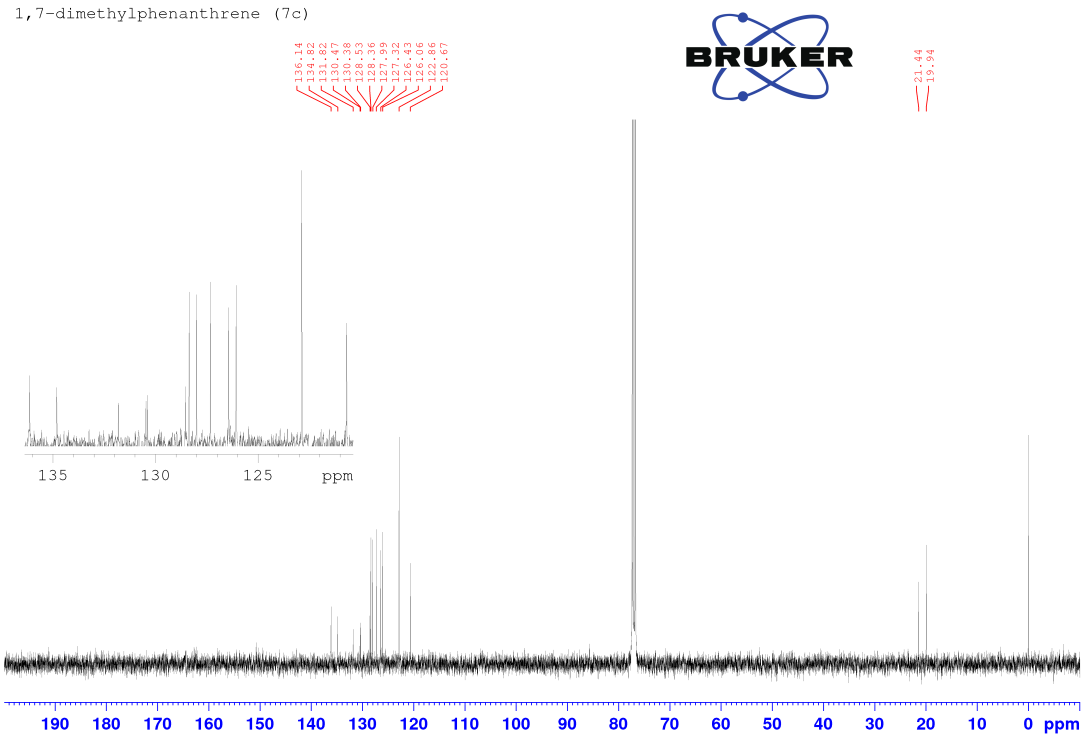


1,7-dimethylphenanthrene

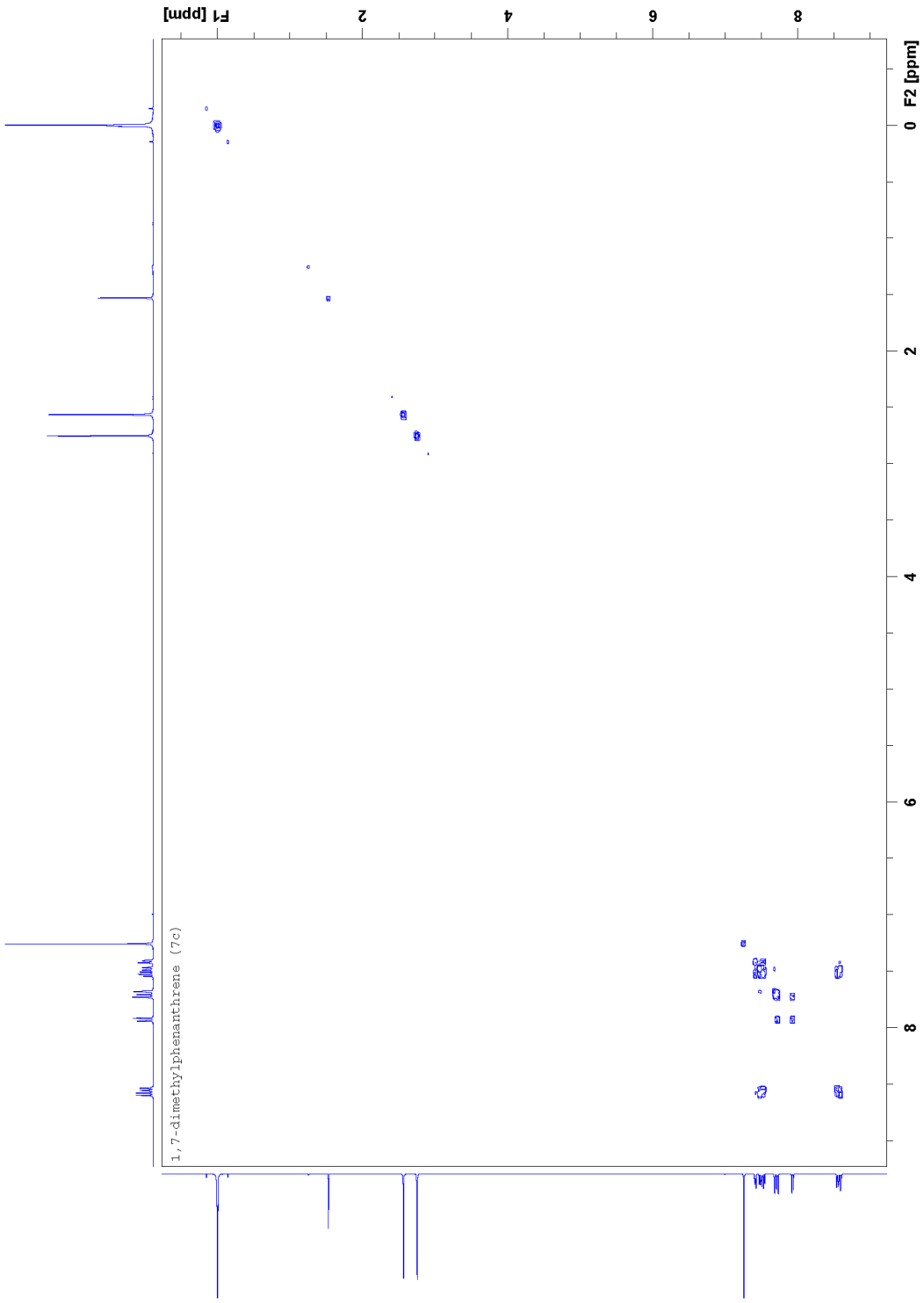
^{1}HNMR:



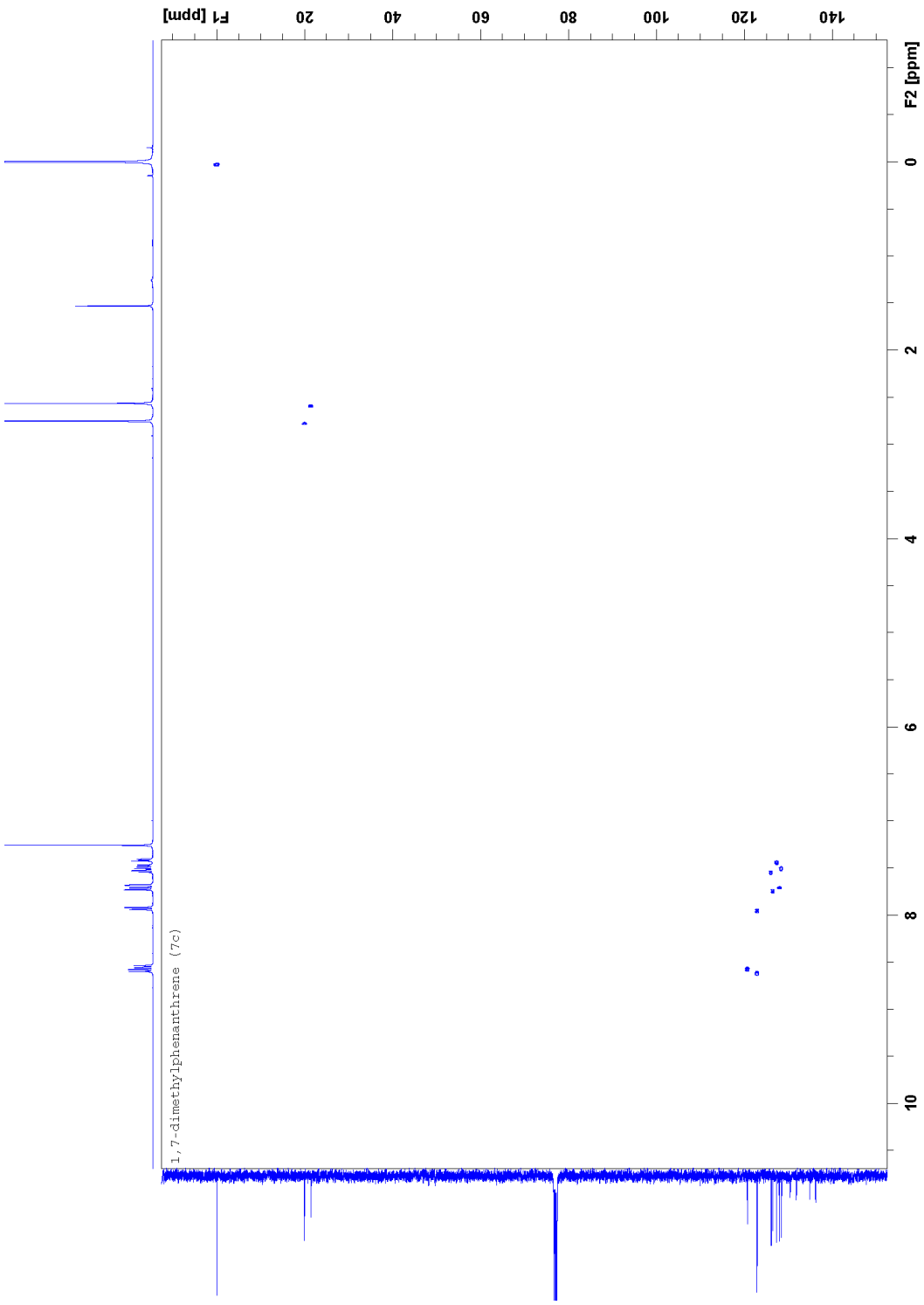
^{13}CNMR:


1,7-dimethylphenanthrene (7c)
136.14
134.82
131.82
130.47
130.38
128.53
128.36
127.99
127.32
126.43
126.06
122.66
120.67
21.44
19.94
135
130
125
ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

COSY:



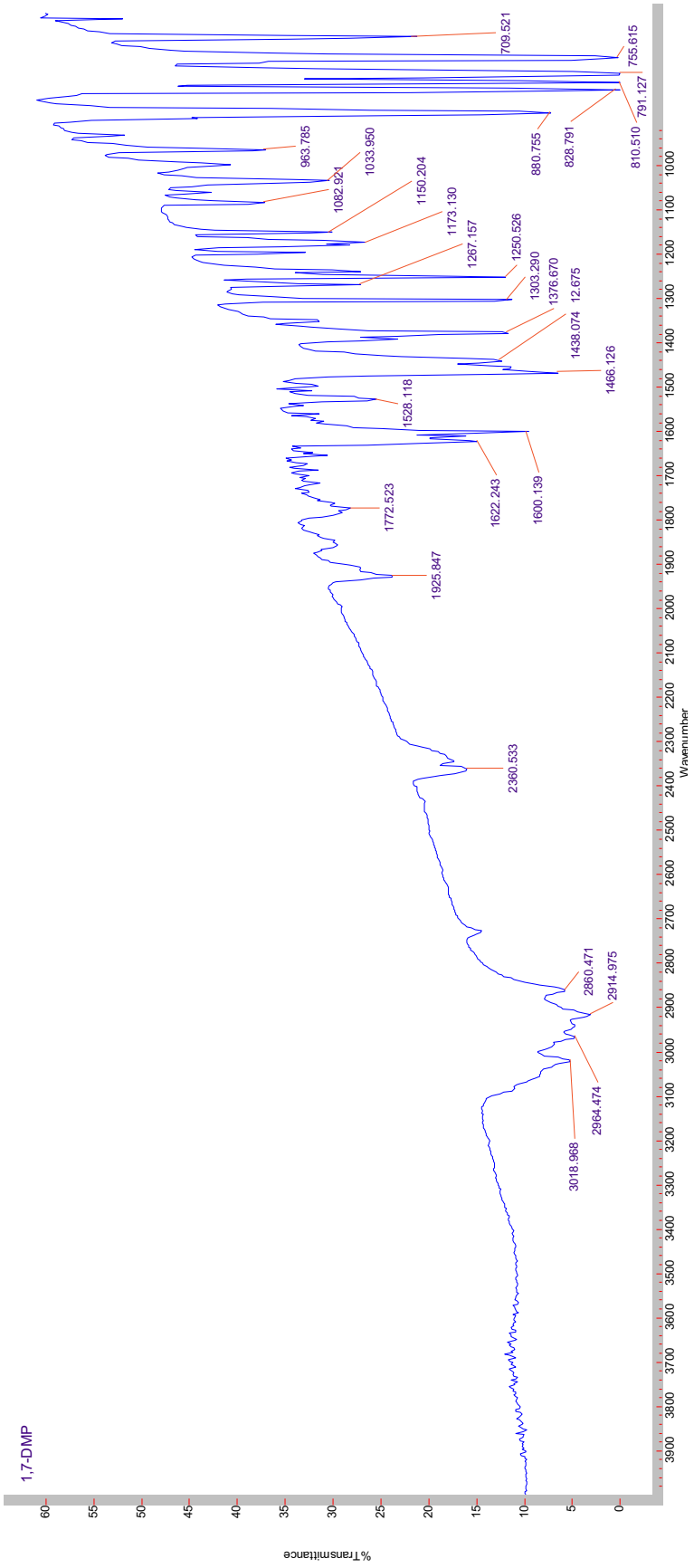
HSQC:


F1 [ppm]
20
40
60
80
100
120
140
F2 [ppm]
0
2
4
6
8
10
1,7-dimethylphenanthrene (7c)

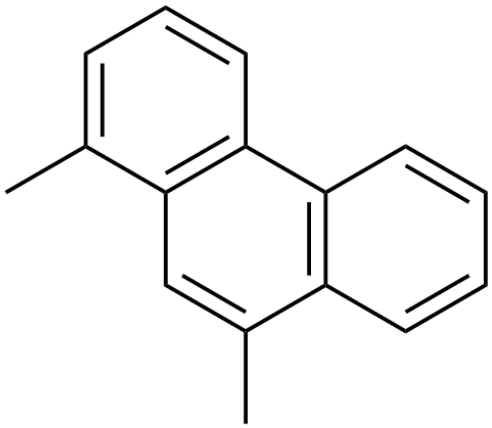
HMBC:


F1 [ppm]
20
40
60
80
100
120
140
F2 [ppm]
0
2
4
6
8
1,7-dimethylphenanthrene (7c)

IR:

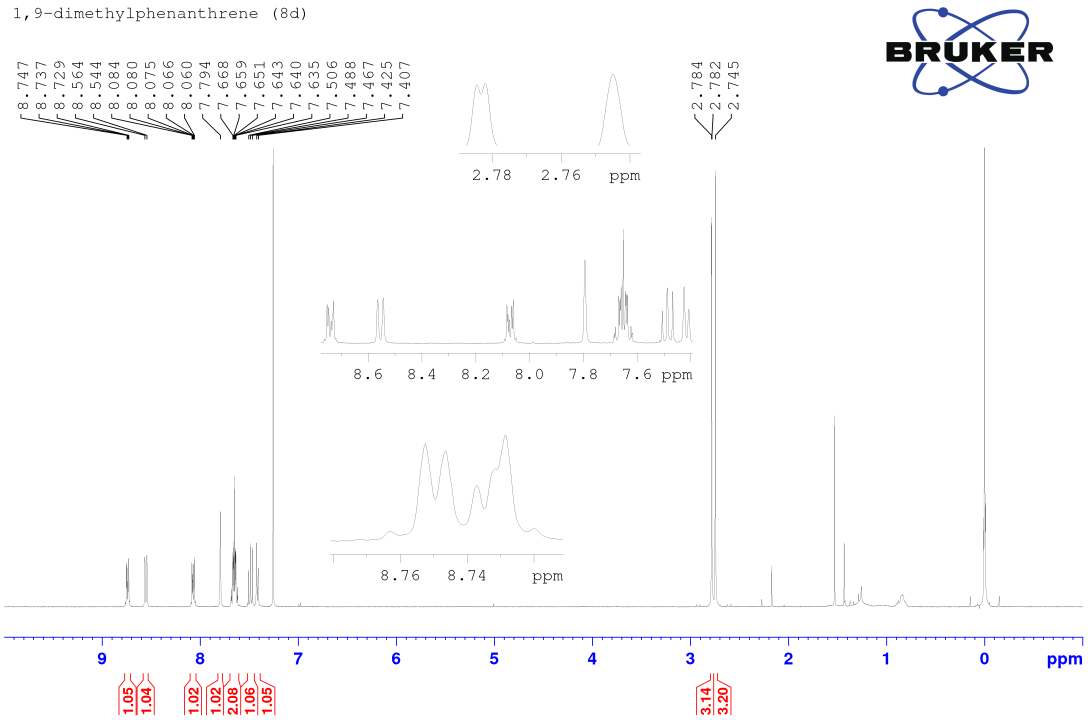

1,7-DMP
%Transmittance
Wavenumber
709.521
755.615
791.127
810.510
828.791
880.755
963.785
1033.950
1082.921
1150.204
1173.130
1267.157
1250.526
1303.290
1376.670
12.675
1438.074
1466.126
1528.118
1622.243
1600.139
1772.523
1925.847
2360.533
2860.471
2914.975
2964.474
3018.968

Appendix 8d

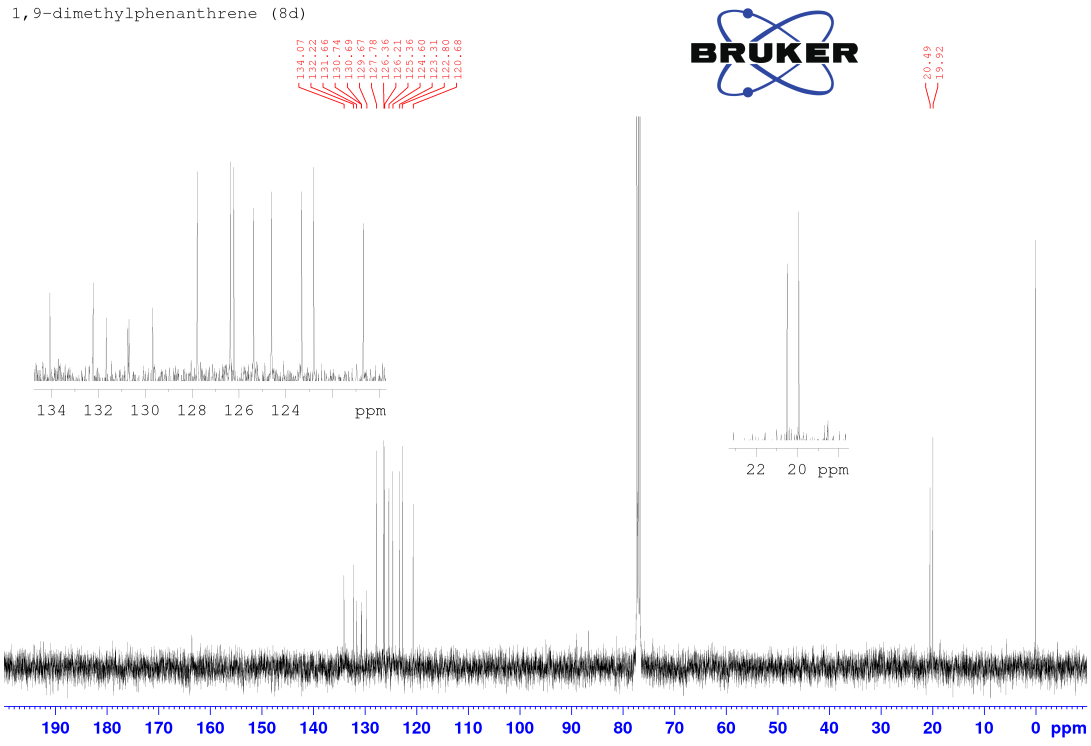


1,9-dimethylphenanthrene

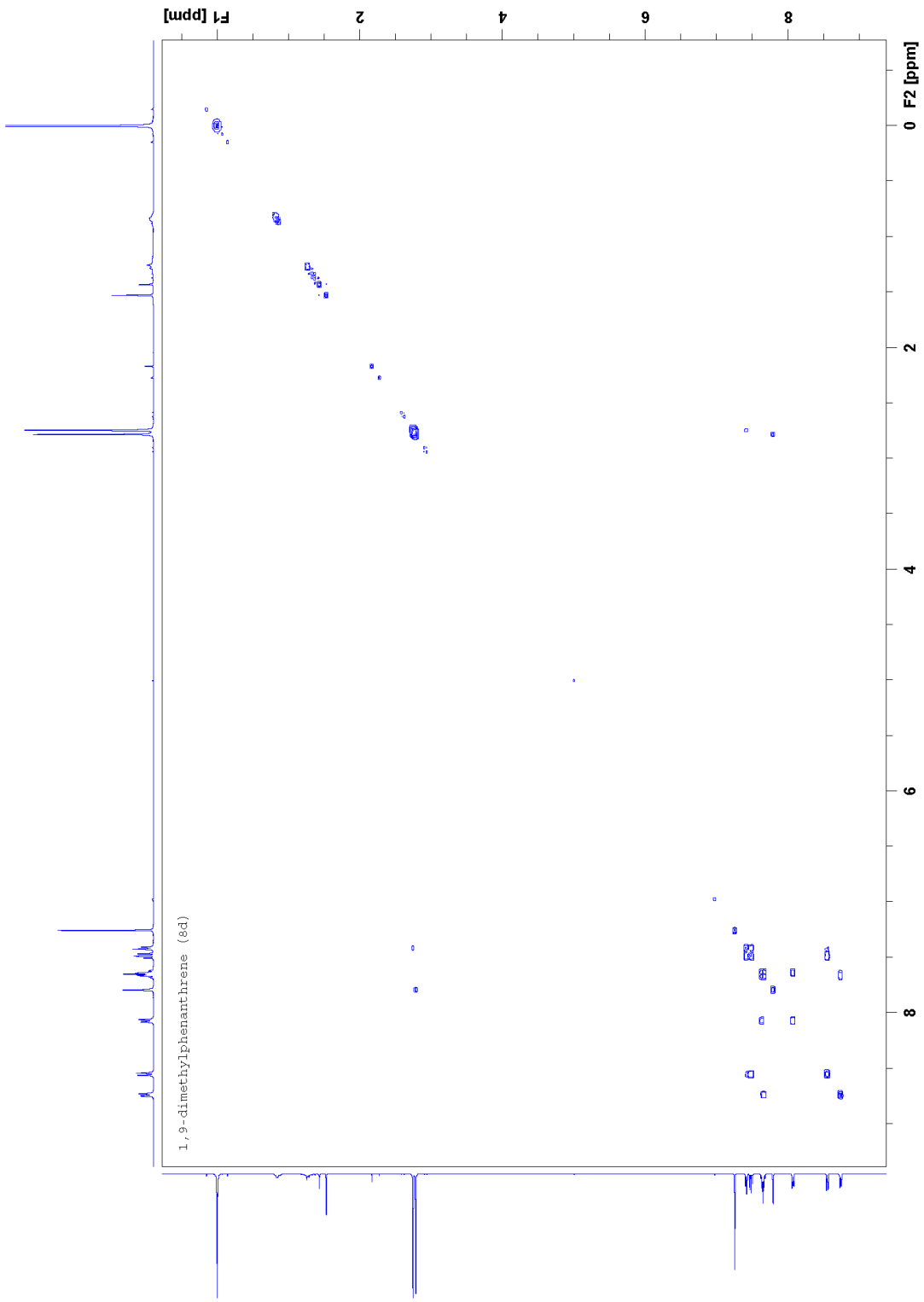
^{1}HNMR:



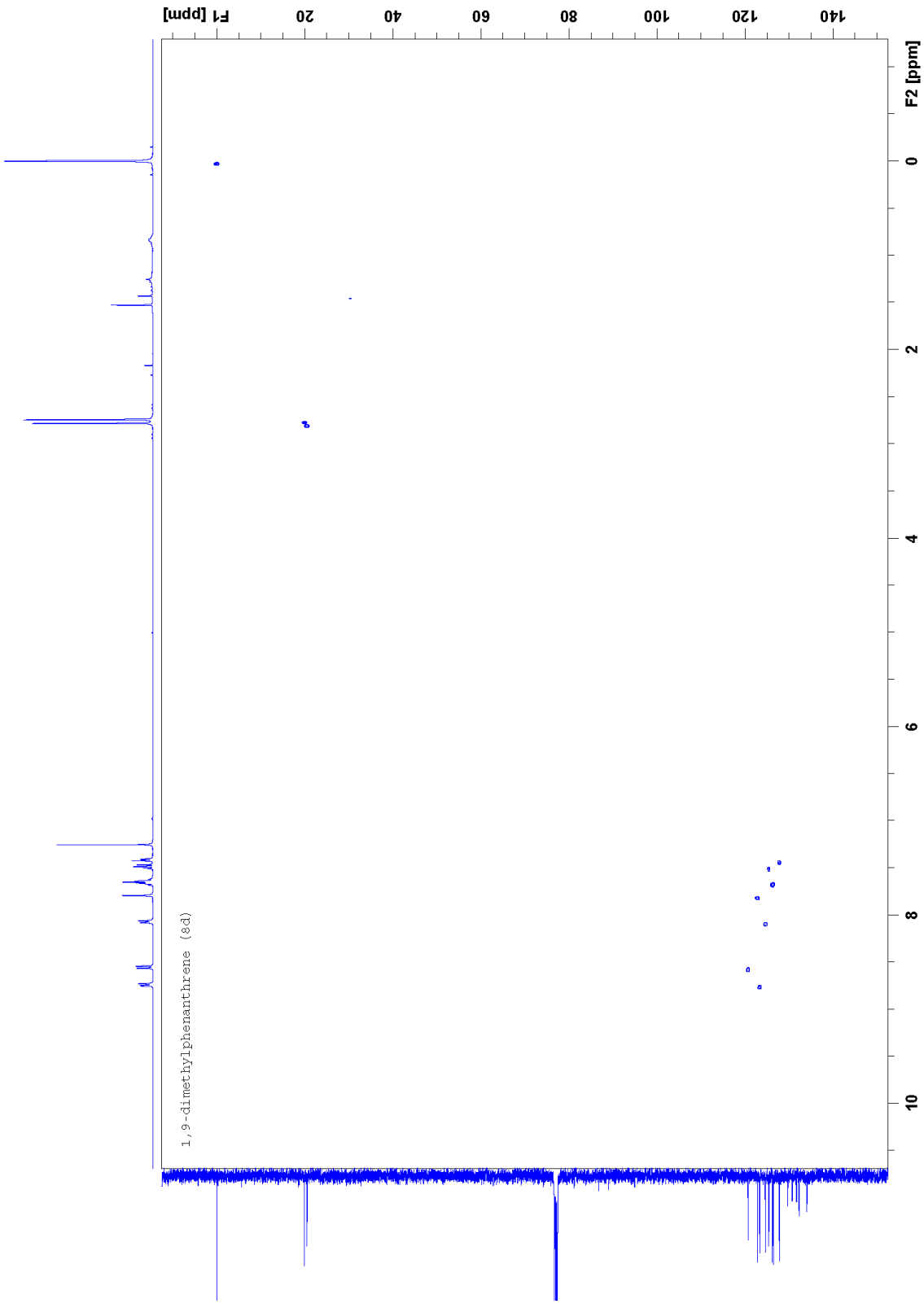
^{13}CNMR:


1,9-dimethylphenanthrene (8d)
134.07
132.22
131.66
131.04
130.64
129.67
127.78
126.36
126.21
125.36
124.60
123.11
122.80
120.68
20.49
19.92
BRUKER
134 132 130 128 126 124 ppm
22 20 ppm
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

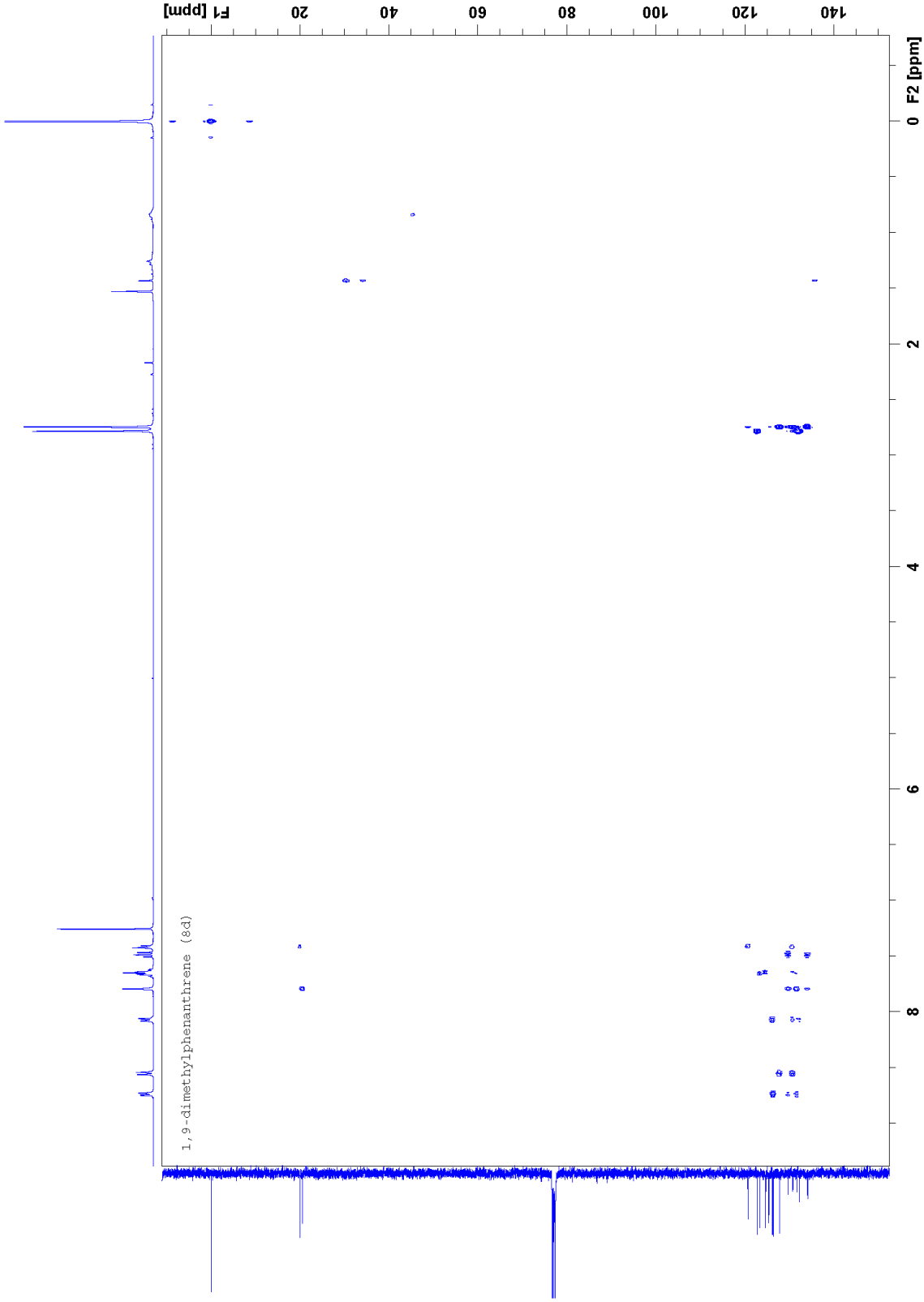
COSY:



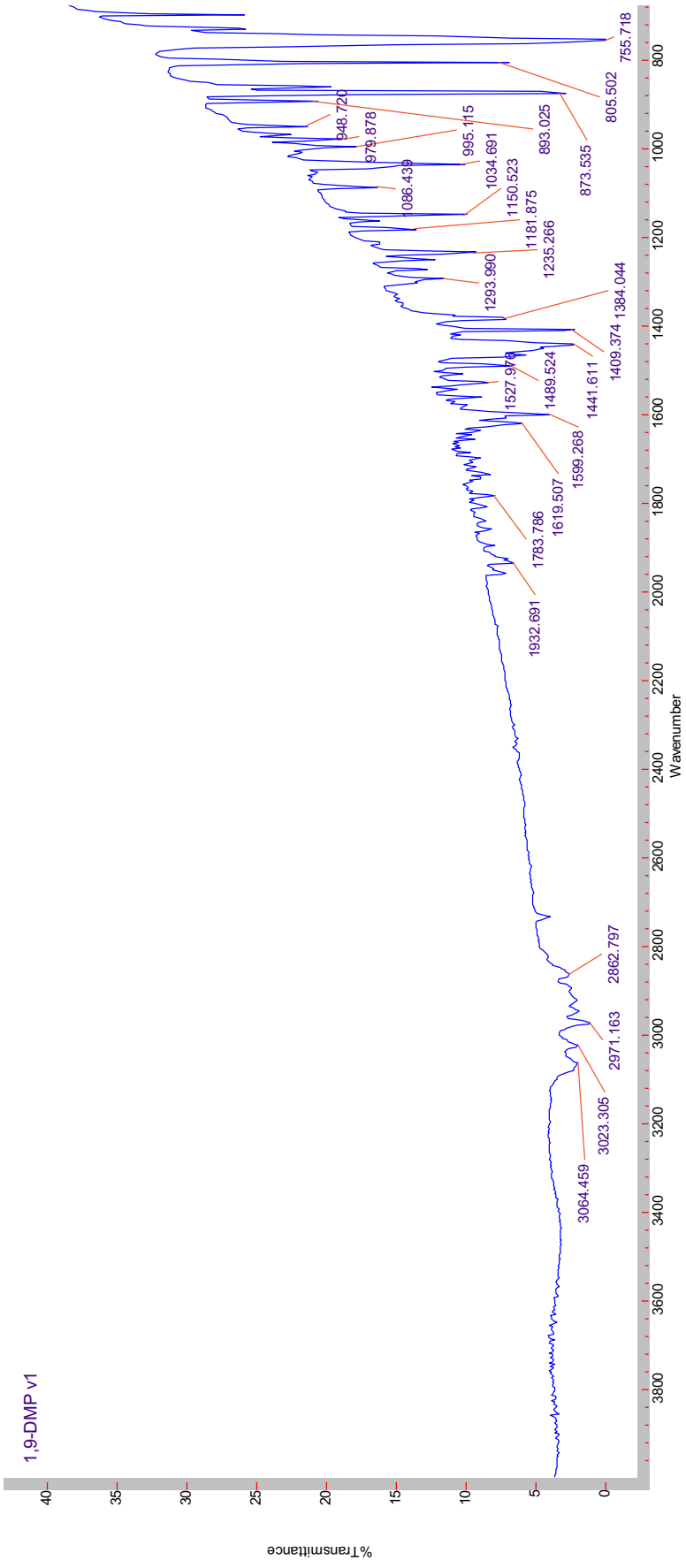
HSQC:


F1 [ppm]
20
40
60
80
100
120
140
F2 [ppm]
0
2
4
6
8
10
1,9-dimethylphenanthrene (8d)

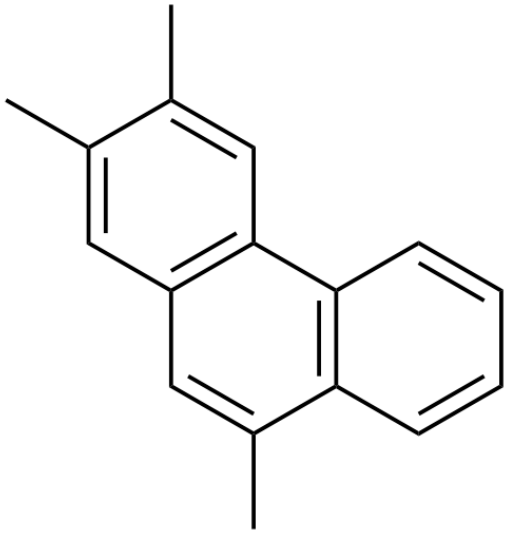
HMBC:


F1 [ppm]
20
40
60
80
100
120
140
F2 [ppm]
0
2
4
6
8
1,9-dimethylphenanthrene (8d)

IR:


1,9-DMP v1
%Transmittance
Wavenumber
755.718
805.502
873.535
893.025
948.720
979.878
995.115
1034.691
1086.439
1150.523
1181.875
1235.266
1293.990
1384.044
1409.374
1441.611
1489.524
1527.978
1599.268
1619.507
1783.786
1932.691
2862.797
2971.163
3023.305
3064.459

Appendix 8e



2,3,9-trimethylphenanthrene

^{1}HNMR: