Universitetet i Stavanger

DET TEKNISK-NATURVITENSKAPELIGE FAKULTET

MASTEROPPGAVE

Studieprogram/spesialisering: Organisk kjemi	Høst 3 semester 2013 Vår 4 semester 2014 Åpen
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Fagansvarlig: Kåre B. Jørgensen Veileder(e): Kåre B. Jørgensen	
Tittel på masteroppgaven: Regiospesifikk syntese av disubstituerte fenantrener. Engelsk tittel: Regiospecific synthesis of disubstituted phenanthrenes.	
Studiepoeng: 60 p	
Emneord: Organisk kjemi, Polycyclic aromatic hydrocarbons (PAH), Phenanthrenes, Directed ortho-Metalation (DoM), Directed remote-Metalation (DreM), Suzuki coupling.	Sidetall: 53 + vedlegg/annet: 38 Stavanger, 16.06.2014 dato/år

Preface

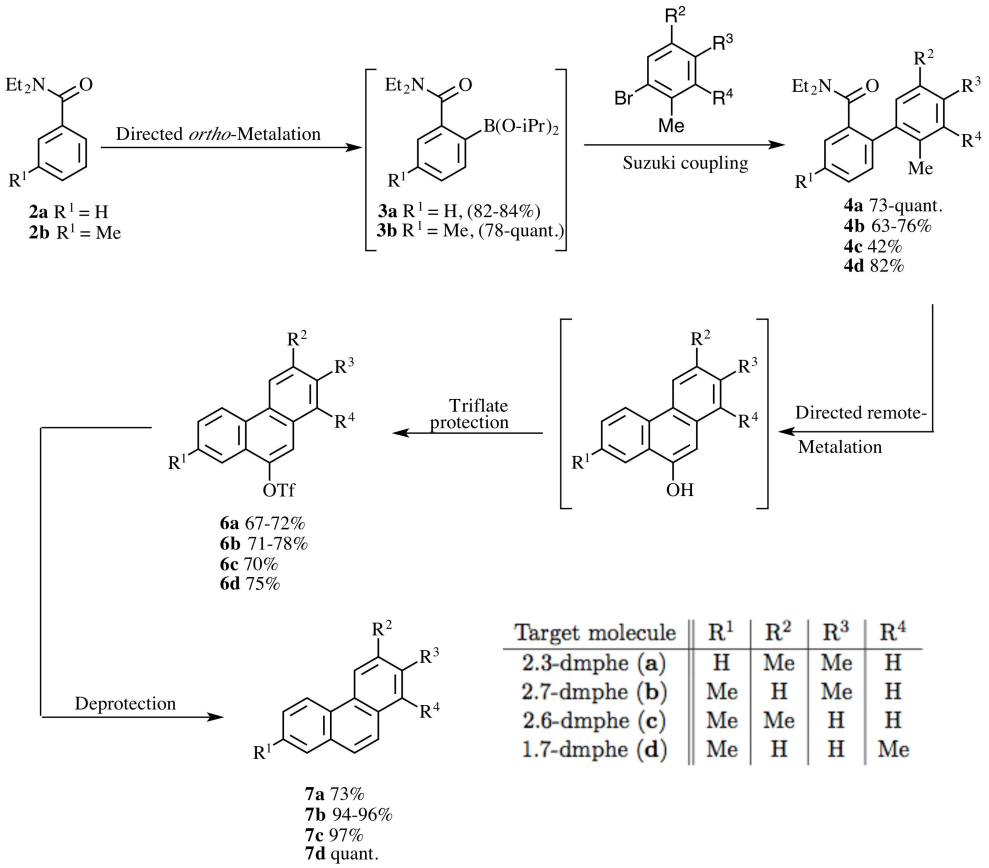
This last year has been both exciting and educational. In regard to that I would like to thank my supervisor Kåre B. Jørgensen and co-supervisor Marianne Lorentzen for all the inspirational help and support. This would not have been possible without you! I've would also like to thank Magne Sydnes for all the good humour. I really would like to thank my supervisor for the chance to experience the organic chemistry wintermeeting which was very educational in many ways.

A special thanks to my family who always have supported and believed in me. A huge thanks to all my friends who have been there and supported me through this process.

Enjoy!

Abstract

As the Norwegian oil fields mature, the wells produce more water. This produced water containing a diverse mixture of dissolved PAHs is eventually released to the environment. A major part of these discharges are alkylated PAHs, but due to lack of pure compounds the effect of alkylated PAHs have been scarcely studied. Studies on the metabolism of monomethylated phenanthrenes by the benthic invertebrate Nereis diversicolor gave different product distributions depending on the position of the substituent. Now various dimethylated phenanthrenes are needed for further environmental studies. In this thesis a selection of dimethylated phenanthrenes has been prepared using a combination of Directed ortho-Metalation (DoM), Suzuki-Miyaura cross coupling, and Directed remote-Metalation (DreM). 2,7-, 2,3-, 1,7- and 2-6-dimethyl-9-phenanthrol have been made into the corresponding phenanthrenes by a simple Pd-catalyzed hydrogenolysis of the triflate protected alcohol. The single isomers resulting from this route provides the dimethylphenanthrenes in high purity and in gram quantities, as shown in the figure below:



Target molecule	R^1	R^2	R^3	R^4
2.3-dmphe (**a**)	H	Me	Me	H
2.7-dmphe (**b**)	Me	H	Me	H
2.6-dmphe (**c**)	Me	Me	H	H
1.7-dmphe (**d**)	Me	H	H	Me

The regioselectivity of the Directed *ortho*-Metalation (DoM) on chrysene-2-yl N,N-diethylcarbamate was further explored, however, no results was afforded.

Contents

1 Abbreviations

δ	Chemical shift measured in ppm from a reference point
aq	Aqueous
BSD	Blue Sack Disease
BuLi	Buthyllithium
CIPE	Complex Induced Proximity Effect
CYP-450	Cytochrome P-450
d	Doublet
DCM	Dichloromethane
DIPA	Diisopropylamine
DME	Dimethoxyethane
DMF	Dimethylformamide
DMG	Directed Metalation Group
Dmphe	Dimethylophenanthrene
DNA	Deoxyribonucleic Acid
DoM	Directed *ortho*-Metalation
DreM	Direceted remote-Metalation
eq.	equivalent
GJIC	Gap Junctional Intercellular Communication
h	Hours
HHS	the American Health and Human Services
IR	Infrared
J	coupling constant, Hz
LDA	Lithium Diisopropylamide
LiTMP	Lithium Tetramethylpiperidide
m	Multiplet
MS	Mass Spectrometry
mCPBA	meta-Chloroperoxybenzoic Acid
NMR	Nuclear Magnetic Resonance
PAH	Polycyclic Aromatic Hydrocarbon
r. t.	Room Temperature
s	Singlet
S. M.	Starting Material
THF	Tetrahydrofuran
TLC	Thin-Layer Chromatography
TMEDA	Tetramethylethylenediamine
Uridine 5'-diphospho-glucuronosyltransferase	UDP-glucuronyltransferase

2 Introduction

2.1 Polycyclic aromatic hydrocarbons (PAHs)

Polycyclic aromatic hydrocarbons, often shortened to PAHs, are a group of molecules that consist of two or more benzene rings fused together. Depending on their origin [1], PAHs have been divided into two subgroups, the petrogenic group, and the pyrogenic group. Petrogenic PAHs are found naturally in oil, while the pyrogenic PAHs is made by incomplete combustion of organic molecules, such as cigarette smoke or forest fires. They are found naturally in oil [2], but can also be formed by the incomplete burning of coal, oil, gas, wood, garbage or other organic substances [3]. The burning of sigarettes [4] and barbecued meat [5] have shown to be a source of various PAHs. Polycyclic aromatic hydrocarbons are an enormous group that contains a huge amount of various molecules, some of which are categorized as the most unhealthy [6] are presented in Figure 1 below.

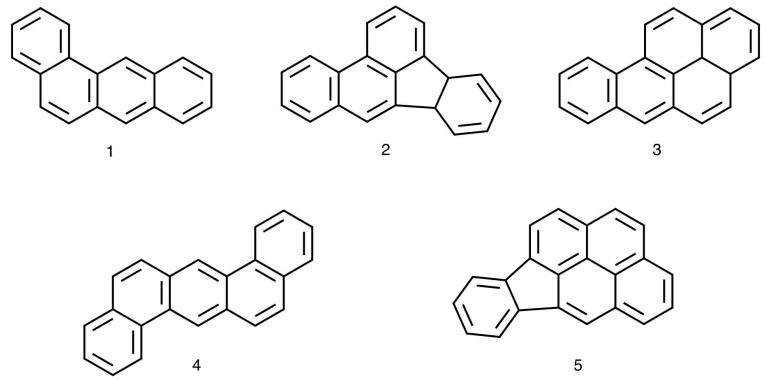


Figure 1: Known animal carcinogens, classified by the American Health and Human Services. 1) benzo(a)anthracene, 2) benzo(b)fluoranthene, 3) benzo(a)pyrene, 4) dibenz(a,h)anthracene, 5) indeno(1,2,3-c,d)pyrene.

2.2 The importance of PAH studies

PAHs are found throughout the environment, both naturally occuring from oil, but also as an effect of industrial combustion, forest fires, and car exhaust. Since this is the case, the importance of knowing its effects on the environment is significant. The five PAHs presented in figure 1 are classified by HHS as animal carcinogens. People, as well as other living beings, are exposed to PAHs on a daily basis [6]. This exposure happens at home, outside, or at the workplace, mostly by PAHs attached to particles in the air, or by vapors.

Polycyclic aromatic hydrocarbons are normally not found in the environment as individuals, but as a group of several PAHs. Being found as mixtures, makes it hard to do studies on the individual compunds, making it hard to single out the most toxic compund.

Sir Percival Pott, a medical doctor, observed in 1775 a higher number of patients with scrotal cancer among chimney sweepers [7], drawing the comparison that this was all connected. The conclusion was that the soot they were exposed to contained chemicals of a carcinogenic nature. This observation was the start of the chemical carcinogens field and expecially the carcinogenesis of PAHs. As years have passed, more knowledge on this field have been obtained. Today it is known that it is practically impossible to avoid exposure of PAHs.

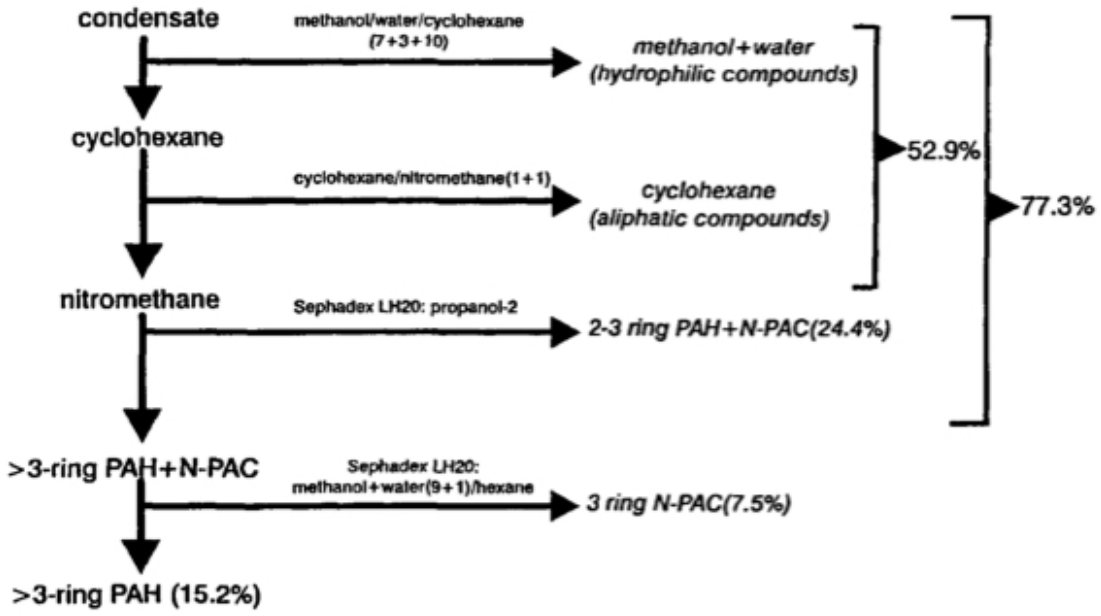


Figure 2: Fractions of hard-coal combustion exhaust. Picture taken from reference [8]

Experiments done with vehicle exhaust and hard-coal combustion effluents show that the PAHs that are found in this mix in most cases are the chemicals that have carcinogenic effects [8]. Fractions of hard-coal combustion exhaust are found in Figure 2. When mice where tested with this mixture by skin application, the carcinogenic effects are mostly found in the PAH fraction that contains more than three rings.

2.3 Metabolism of PAHs

It is not the PAHs themselves that are toxic, but their metabolites [9]. PAHs require metabolic activation [8]. The nonsubstituted ringsystem is first oxidized by cytochrome P-450 that creates an epoxide. From here a number of possibilities are present, Figure 3 shows most of them. The epoxide can directly undergo a glutathion-S-epoxide transferase [10] and creates the phase II metabolite. After dipeptidase and acetylation the product, a mercapturic acid, can be excreted. This is a way of detoxifying the PAH. Other way of detoxification is to isomerize the epoxide and create the phenol. The phenol can undergo sulfotranserfase [11] and create another phase II metabolite that can be excreated. The most critical pathway is the work of epoxide hydrases to create trans-diols. These trans-diols can be excreated through UDP-glucuronyltransferase [12] creating clucuronic acids.

The trans-diol can be oxidized a second time by P-450 and create the vicinal diol-epoxide. If this vicinal diol-epoxide is hydrolyzed it can be excreated in the same way as mentioned above by UDP-glucuronyltransferase. This diol-epoxide can covalently bind to DNA [13] and can form DNA-adducts. If these adducts are not repaired they can create mutant DNA, that can end up causing cancer.

Many theories have been made in attempts to explain the carcinogenic nature of some PAHs and the non-carcinogenic nature of others. Theories such as bay-region, fjord-region, di-region-, C1-transfer-, one electron oxidation-activation, etc, [14]. None of these theories fully explains the problem without having several exeptions to the rule. The favoured theories are the bay and/or fjord-region. Figure 4 explains the idea of bay- and fjord-regions.

Down regulation of gap junctional intercellular communication (GJIC) is the reason for uncontrolled cellular growth which leads to the development of tumors [15, 16]. Cancer cells have shown to have dysfunctional or inhibited GJIC [17], this supports the idea that GJIC activity have a direct link to carcinogenesis. A monomethyl isomer of anthracene with a bay-like structure has shown to inhibit GJIC [18]. Anthracene itself or monomethyl isomers with no bay-like region has proved to not inhibit GJIC. Weiss et al. [19] further studied the effects of Bay- and fjord-regions on GJIC. They further proved that PAHs with bay- and fjord-regions, e.g. phenanthrene and fluoranthene, inhibited GJIC. It is also worth mentioning that naphtalene which has no bay-regions partially inhibited GJIC, the same was the case for 2-methylnaphtalene.

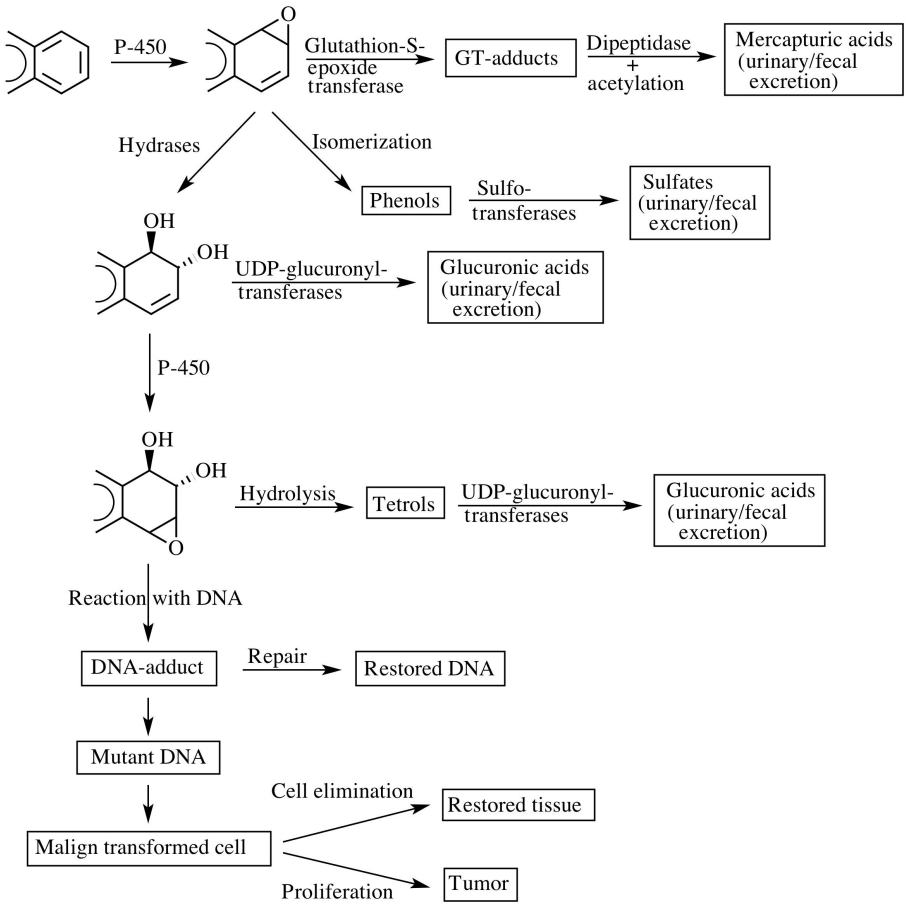


Figure 3: Metabolism of nonsubstituted PAHs [8].

To complicate matters further different animals have different analogues or isoforms of these Cytochrome P-450 that oxidize the PAHs in various positions [20]. Nonsubstituted phenanthrene can be oxidized at three different sites, at the 1,2-position, the bay region (3,4-position) and at what is known as the K-region (9,10-position). A number of Cytochrome P450 are expressed in humans, as well as in other species. Jacob et al. [21] showed that these isoforms, although not exclusively, have prefered sites they attack. hCYP1A1 oxidize phenanthrene mainly on the 1,2- and 9,10-position, whereas hCYP1A2 oxidize mainly at the 1,2- and 3,4-position. Rat CYP1A1 and CYP1A2 prefer the K-region, meaning that homologues in different species have different preferences [21, 22]. Figure 5 shows the prefered oxidation sites for some CYP450 isoforms in humans, rat and fish.

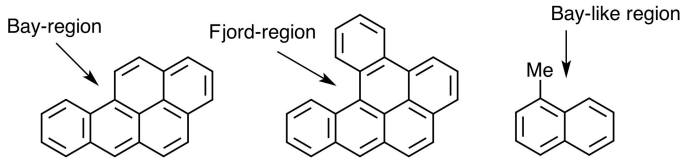


Figure 4: Explenation of Bay- and Fjord-region.

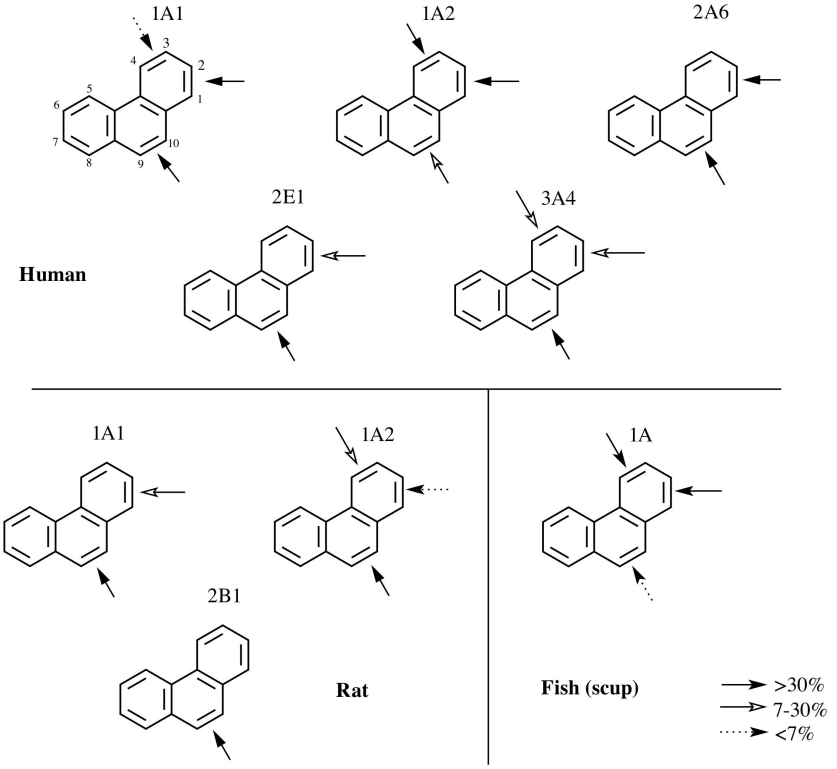


Figure 5: Various CYP-450 and their prefered oxidation sites [21, 22].

2.4 Substituted PAHs

Most fate and effect studies done on crude oil PAHs focus on the nonsubstituted molecules, even though as much as 98% of the crude oil contains alkylsubstituted PAHs [23]. Making knowledge of the toxicity and persistency of these molecules scarce. Its also worth mentioning that the toxicity and persistency doesnt always relate to the PAHs themselves, but often their metabolites [8]. A study done at Roskilde University shows how different 1-methylpyrene metabolites are from the nonsubstituted pyrene [24]. The study showed that insted of the previously mentioned ring oxidation to a vicinal diol-epoxide, a carboxylic acid was formed as the main metabolite on the methyl group as phase I metabolite. Phase II metabolites 1-methylpyrene glucuronide and 1-carbonylpyrene glycine were also identified.

Other studies on methyl substituted phenanthrenes and other K-region derivaties have shown that this methyl group has an effect, and can completely change the metabolic pathway [25, 26]. LaVoie *et al.* [25, 26] proved that substituents that inhibits the formation of 9,10-dihydrodiol was found to be mutagenic in S. typhimurium. 1- and 9-methylphenanthrene were both strongly mutagenic, whereas the rest of the monosubstituted phenanthrenes were not. Among the disubstituted tested 1,4-dimethylphenanthrene was the only one that showed mutagenic ability, 2,7-, 3,6-, and 4,5-dimethylphenanthrene showed no mutagenic effect and were at the same level as nonsubstituted phenanthrene. This supports the idea that substituted phenanthrenes are more toxic than nonsubstituted [27]. The main metabolite found in the mutagenic substituted phenanthrenes were 1,2- or 7,8-dihydrodiols which are necesarry for the formation of bay-region vicinal diol-epoxides.

Rhodes *et al.* [28] studied the effects of dimethylated and alkylated PAHs on embryonic development of Japanese medaka. This study showed that out of the tested compounds, unsubstituted PAHs showed an increase in blue sack disease (BSD) compared to dimethylated PAHs. However, no trends were found between nonsubstituted and dimethylated PAHs in other sublethal endpoints.

In this thesis the synthesis of four dimethyl substituted phenanthrenes will be described. These target molecules, shown in Figure 6, will be sent for biological testing and help aid in the understanding of substituted PAHs.

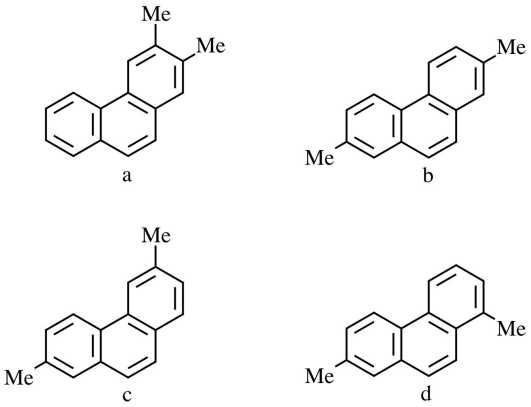


Figure 6: Target molecules. a) 2,3-dimethylphenanthrene, b) 2,7-dimethylphenanthrene, c) 2,6-dimethylphenanthrene and c) 1,7-dimethylphenanthrene.

3 PAH synthesis

3.1 Many possible routes.

Today a number of alternatives exist for making or synthesizing PAHs. The Pschorr synthesis was developed in the late 19th century [29, 30] and was for a long period of time the way of making simple phenanthrenes. Another well known way of making nonsubstituted- as well as several substituted-PAHs is the ring closure of stilbenes with the oxidative photochemical Mallory reaction [31, 32, 33]. The stilbenes can be made with several different reactions, with the Wittig reaction [34, 35] as the most common. The problem with these routes is the lack of regioselective control, Figure 7. Oxidative coupling with mCPBA [36] is similar to the Mallory reaction, but have a restriction to substituents. Other alternative ways to make PAHs and alkyl substituted PAHs include palladium catalyzed pericyclic reactions [37, 38].

With the Suzuki-Miyaura cross-coupling [39, 40, 41] reaction came a good way of making biphenyls that could be ring closed into PAHs. A number of these reactions exist and are being used in PAH synthesis. Ring closing of an ortho-alkyne with $PtCl_2$ [42, 43], or by an iron-catalyzed [4+2] benzannulation between alkyne and biaryl or 2-alkenyphenyl grignard reagent [44] are two examples.

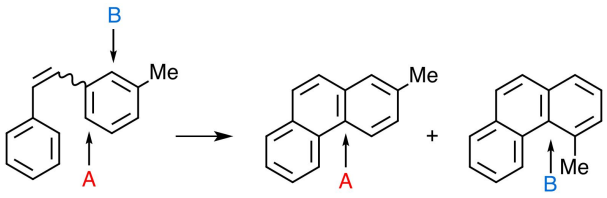


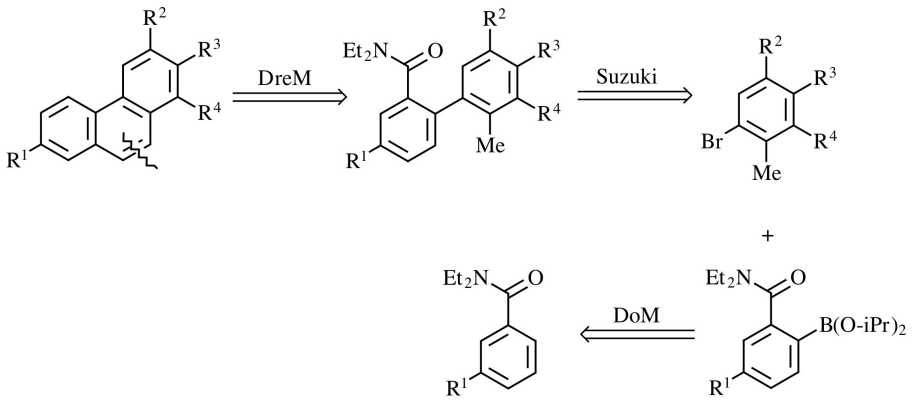
Figure 7: Regioselective problems accour with oxidative photoreaction.

3.2 Synthesis of di-methylphenanthrenes.

Snieckus group developed a method which incorporates the previously mentioned Suzuki coupling with variations of metalations to synthesize a variety of PAHs in a regioselective manner [45]. The target molecules mentioned in chapter 1.4 have methyl groups in four specific postitions. The choosen synthetic route was therefor the prefered way of making these dimethylated phenanthrenes.

Metalation with organometallic compounds was first discovered independantly around 1940 by Henry Gilman [46] and Georg Wittig [47]. Gilman et al. showed that the addition of n-buthyllithium (n-BuLi) to a molecule with a directed metalation group (DMG) could be quenched with electrophiles to yield products in a regioselective way. More is mentioned on the mechanism in chapter 2.3.

Another way of closing the ring on a biphenyl that was not mentioned in chapter 2.1 is the Directed remote Metalation (DreM) reaction. More on that reaction can be found in chapter 2.3. The biphenyl can be made as previously mentioned by a Suzuki cross-coupling. Commercially available bromo-compounds will be cross-coupled with borate esters made from the DoM reaction. A closer look on the retrosynthesis of the target molecules is present in Figure 8.



Target molecule	R^1	R^2	R^3	R^4
2.3-dmphe (**a**)	H	Me	Me	H
2.7-dmphe (**b**)	Me	H	Me	H
2.6-dmphe (**c**)	Me	Me	H	H
1.7-dmphe (**d**)	Me	H	H	Me

Figure 8: Retrosynthesis of disubstituted phenanthrenes with R-groups and their corresponding target molecules. Dimethylphenanthrene is shortened to dmphe.

3.3 Directed ortho- and remote- Metalation.

If N,N-diethyl 2-biphenyl carboxamide is treated with s-BuLi/TMEDA (1.1 eq.) in THF at -78 °C followed by an in situ quench with an electrophile it affords a C3-substituent [48] (DoM reaction), Figure 9. If instead the carboxamide is treated with LDA (1.1 eq.) at 0 °C, the observed product is the fluorenone [49], ergo a cyclization has taken place (DreM reaction).

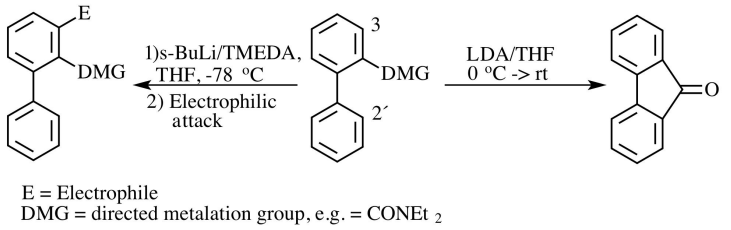


Figure 9: Treated with s-BuLi/TMEDA in THF at -78 °C and quenched with an electrophile affords a different product than when treated with LDA at 0 °C.

Mortier *et al.* [50] proposed the mechanism found in Figure 10. It was proved by the same group that carboxamide **a** does not undergo deprotonation at -78 °C [49]. When LDA and the electrophile in THF is premixed before the addition of molecule **a**, compound **c** is the sole product formed. Product **c** was also formed as the only product when **a** was treated with s-BuLi/TMEDA in thf and the electrophile was added after the reaction had been left to warm to room temperature. From these experiments it is clear that the *ortho.*-lithiated compound **b** does not undergo selfcondensation to product **f** and is stable up to room temperature and is not in an equilibrium with **d**. ($K_2 > K_3$). This propose the idea that the C3 proton has a higher kinetic over thermodynamic acidity than the C2' proton in **a**. This also shows that the quenching of **b** to make **c** is faster than the equilibrium to **d** since **c** was formed exclusively. Compound **f** would have been formed had this not been the case.

However, when **a** was treated with LDA at -20 °C and attempted quenched with an electrophile, fluorenone **f** was formed. This gives way for the idea that K_3 creates the remote-lithiated compound **d** slowly, but that this rapidly undergoes ring closing in the irreversible step K_4. Several other studies supported this, showing that K_4 is greater than K_{-3}

In the middle of Figure 10 is Complex C, also known as the complex induced proximity effect (CIPE) [51, 52]. Both the ortho-lithiated molecule **b** and the remote-lithiated compound **d** are thought to be formed through this pre-lithiation complex. It is believed that this complex brings the reactive groups close together before the metalation takes place. It is suggested that CIPE has an effect that is greater than resonance and inductive effect since it metalates β-hydrogens rather than more thermodynamically acidic α-hydrogens. This can be exploited when doing metalations on molecules with more acidic hydrogens, e.g. if the biphenyl in Figure 10 had a methyl group.

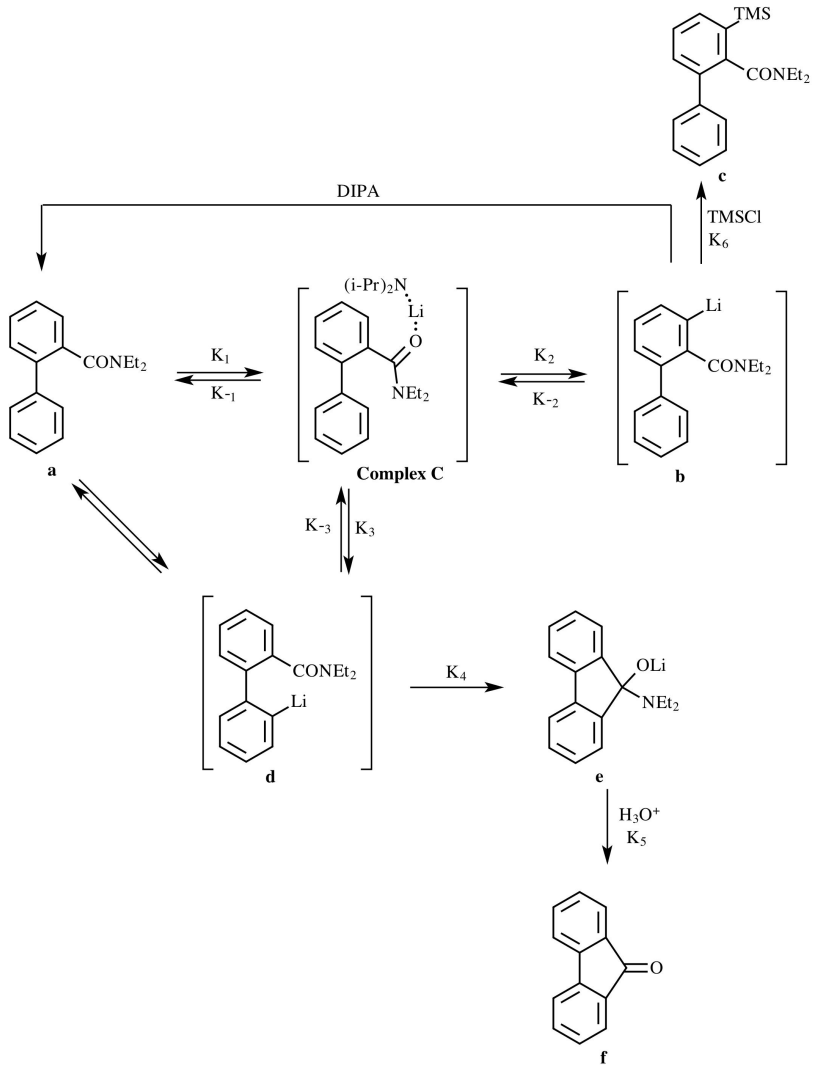


Figure 10: Proposed mechanism of the DoM and DreM reaction [50].

3.4 Biphenyl synthesis.

Many ways to synthesize biphenyls are known. With Suzuki-Miyaura cross-coupling as the most prominent one. The Suzuki-coupling was the prefered biphenyl formation in this synthetic route and will therefore be described in more detail below. To obtain the biphenyl system the boron ester was reacted with a halide, in this case a bromo-compound, in a Suzuki-Miyaura cross-coupling. Reacting the bromo-compound with the Palladium catalyst is know as the oxidative addition step [53, 54]. The two other steps involved are the transmetalation [55], where the base that was added undergoes an exchange with the boron ester, and the reductive elimination step [56]. During this elimination step the product is released by the palldim catalyst which returnes to Pd°. All steps are presented in the catalytic cycle in Figure 11.

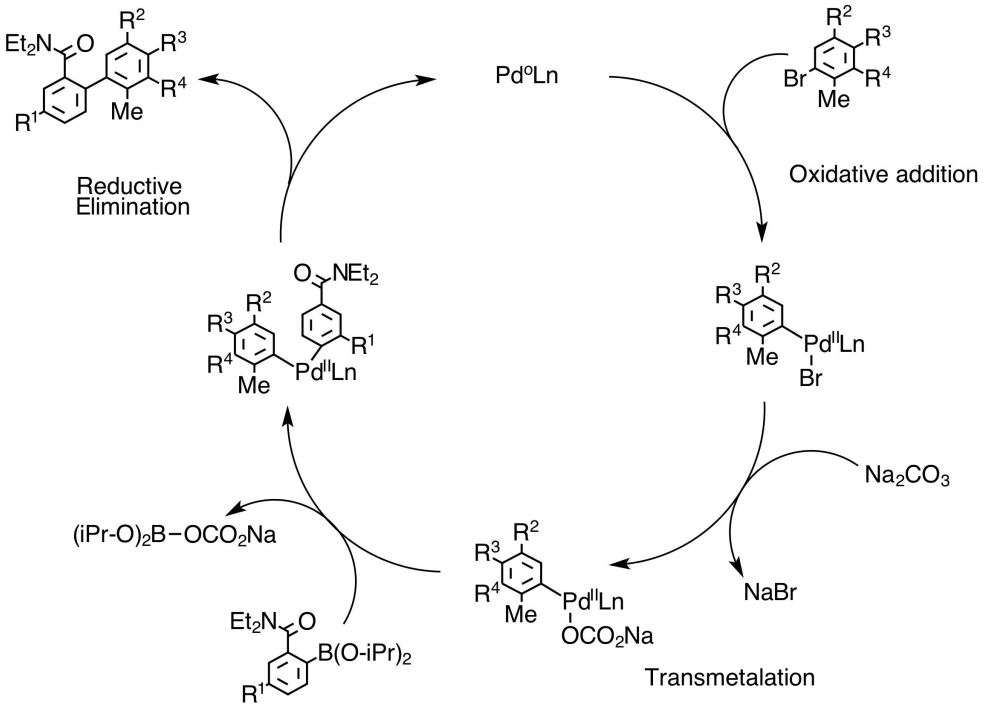


Figure 11: Suzuki-Miyaura cross-coupling.

Other carbon-carbon formation alternatives exist. Instead of the Suzuki cross-coupling, the Hiyama coupling [57] is an alternative. Compared to the Suzuki coupling this reaction has a lot more limitations. More interesting is the Stille reaction [58], that in many ways is similar to the Suzuki coupling. The Stille reaction is a palladium catalyzed coupling of organotin compounds with halides. The drawback of this reaction is the use of tin compounds, as tin compounds are often known to be very toxic [59]. Another way of making nonsymmetrical biphenyls is the nikkel or palladium catalyzed Negishi coupling [60], which includes the coupling of a halide with an organozinc compound.

3.5 Deprotection of vinyl triflates.

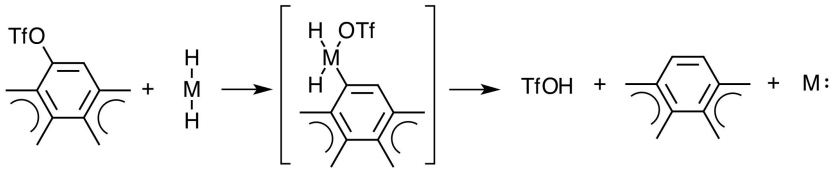


Figure 12: General mechanism of deprotection of vinyl triflates.

Protection of the phenantrols were necessary for two reasons. First because the alcohol group needs to be removed, second because the phenantrols are air sensetive and often oxidizes if not protected. The alcohol group was protected to the corresponding triflate [61] and removed by a palladium catalyzed reaction. The Pd(0) complex is inserted between the carbon-oxygen bond in a reaction where formic acid in the prescence of triethylamine acts as the reducing agent [62, 63]. For this reaction to be able to take place, hydrogen will have to be inserted into the metal (Pd-catalyst) to form the reducing agent MH_2 (PdH_2) [64, 65], where M is the metal. As the mechanism in Figure 12 shows, Pd-catalyst attaches between the carbon-oxygen bond, goes through an intermediate, and ends up reducing the product.

3.6 Photocyclization of stilbenes under oxidative conditions.

Stilbenes can undergo intramolecular ringclosing under UV irradiation. Under oxidative conditions that ring closing results in an aromatic ring [31, 32, 33]. The first step of the mechanism presented below in figure 13 is the excitation of the stilbene which makes the dihydrophenanthrene intermediate. Trans stilbene isomerize since only the cis-stilbenes can be ring closed [66]. The three membered ring with the hydrogens in trans position [67] is made, no oxidant is needed up to this point. In the presence of an oxidant, in this thesis iodine, the three membered ring is oxidized to phenanthrene.

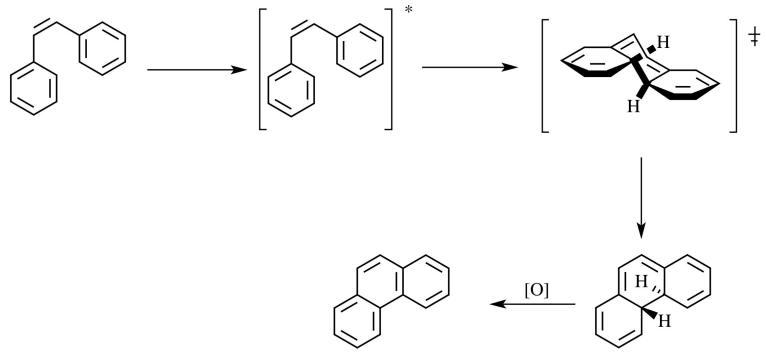


Figure 13: Mechanism of the oxidative photocyclization of stilbenes.

4 Results and Discussion

4.1 Synthesis of Dimethylphenanthrenes.

Given the structure of the four target molecules, a general way of synthesizing all of them were applied [45]. From the retrosynthetic analysis in Figure 14, its clear that all target molecules have the same backbone structure. The only difference is the position of the two methyl groups. As previously described in the introduction, starting from the biphenyl, a ring closing was done by Directed remote Metalation. This reaction affords the alcohol which is protected right away with a triflate group. A simple deprotection of the triflate group later affords the phenanthrene.

The biphenyl could be obtained by a Suzuki-Miyaura cross-coupling between commercially available bromo-reagents and borate esters made with Direct *ortho.*-Metalation from N,N-diethylbenzamide and N,N-diethyl-3-methylbenzamide.

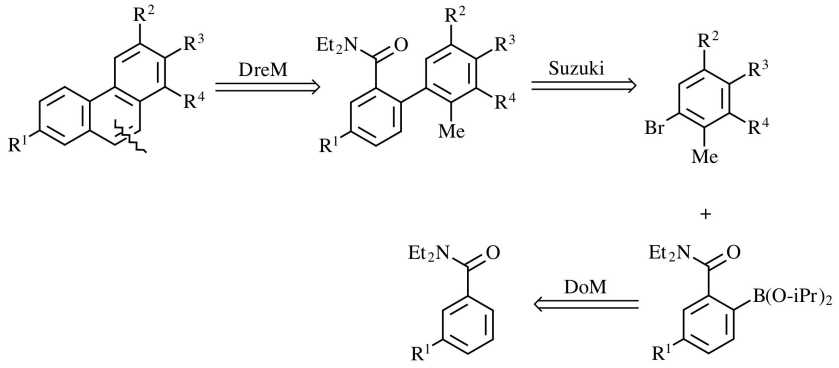


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Figure 14: Retrosynthesis of dimethylphenanthrenes.

4.2 Dom and Suzuki.

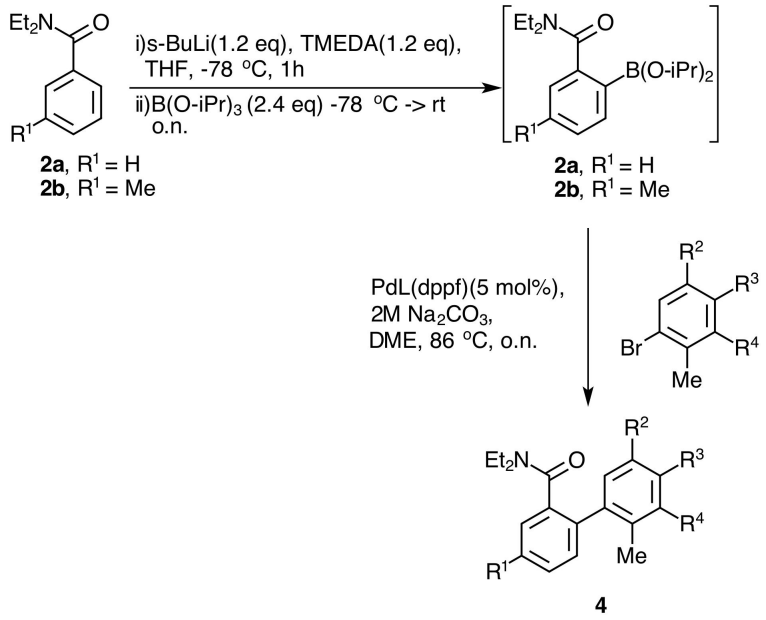


Figure 15: DoM and Suzuki coupling to afford bipheyl **4**.

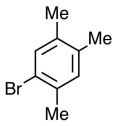
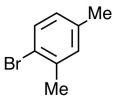
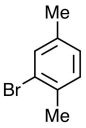
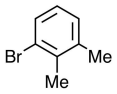
Starting molecule N,N-diethylbenzamide (**2a**) was made from commercially available benzoylchloride, while the other starting molecule N,N-diethyl-3-methylbenzamide (**2b**) was commercially available. Both molecules where dissolved in THF and added dropwise to a solution of s-BuLi and TMEDA in THF at -78 °C. After an hour of stirring 3-isopropylborate was added according to general procedure [45], in what is known as the Directed *ortho.*-Metalation, Figure 15. Insted of trimethyl borate used by Snieckus group, triisopropyl borate was used. Triisopropyl is a more stable alternative to trimethyl borate and more sterically demanding. Because of symmetri in **2a** there was no concern to where the electrophile would attack. With **2b** however, only an electrophile attack in the sixth position was of interest. Crude products **3a** and **3b** were both coupled with specific bromo compound without further purification. A number of standard DoM reactions were carried out, yields of these reactions are presented in Table 1.

Table 1: DoM reactions and the obtained yields.

	Temp (°C)	R^1	Crude product	Yield %	Comment
2a	-78	H	**3a**	82-84	-
2b	-93	Me	**3b**	71	-
2b	-98	Me	**3b**	3	Attempted to directly put on the pinacol.
2b	-78	Me	**3b**	78-quant.	-

Compounds **3** were cross coupled with a variety of bromo compounds in a Suzuki-Miyaura cross-coupling. A mixture of the prefered catalyst and the halide was dissolved in DME at room temperature for 15 minutes before a solution of **3** dissolved in DME was added to the mixture, quickly followed by the addition of a 2M sodium carbonat-solution. This was the standard for alle Suzuki coupling, the only variables where the catalyst and the number of equivalents used of crude products **3**. Table 2 displays all the obtained yields from the different reactions.

Table 2: Yields of Suzuki-coupling of various compounds. The prefered catalyst was $PdCl_2$(dppf).

Entry	Borate	Equiv.					Product	Yield %
1	**3a**	1	1 eq.				**4a**	65
2	**3a**	1.2	1 eq.				**4a**	73-quant.
3	**3b**	1.2		1 eq.			**4b**	53-54
4	**3b**	2		1 eq.			**4b**	63-76
5	**3b**	2			1 eq.		**4c**	42
6[a]	**3b**	2				1 eq.	**4d**	82

[a] Pd(dppf) was used as the catalyst.

When only 1.2 equivalents of **3b** were used in the cross coupling the yields were significantly lower than with 2 equivalents, whereas **4c** is the exception. The same was the case for cross couplings featuring **3a**, 1.2 equivalents were a whole lot better than 1 equivalent.

Before going with 2 eq. of **3b** the DoM reaction was highlighted as the cause for the low yields, where insufficient boronation or electrophilic attack in the second position insted of the sixth position were pointed out as the problem. The first attempt to solve this problem was to lower the temperature for the reaction in case the problem was that

the methyl group was attacked instead of the aromativ ring. As Table 1 shows, lowering the temperature only correspond with even lower yields. At -98 °C it was attempted to directly put on a pinacol protected borate ester in hope that this would be possible to purify by flash column chromatography, unfortnunately that reaction did not prove to work.

The idea of protecting the borate ester with a pinacol was preserved, however instead of direcly putting the group on, the idea was to protect after the DoM reaction. After several attemps it was proved that it was difficult to isolate the product, and the idea was soon abandoned. NMR spectroscopy shows that the only isolated compound after flash column purification is the starting compound **2b**.

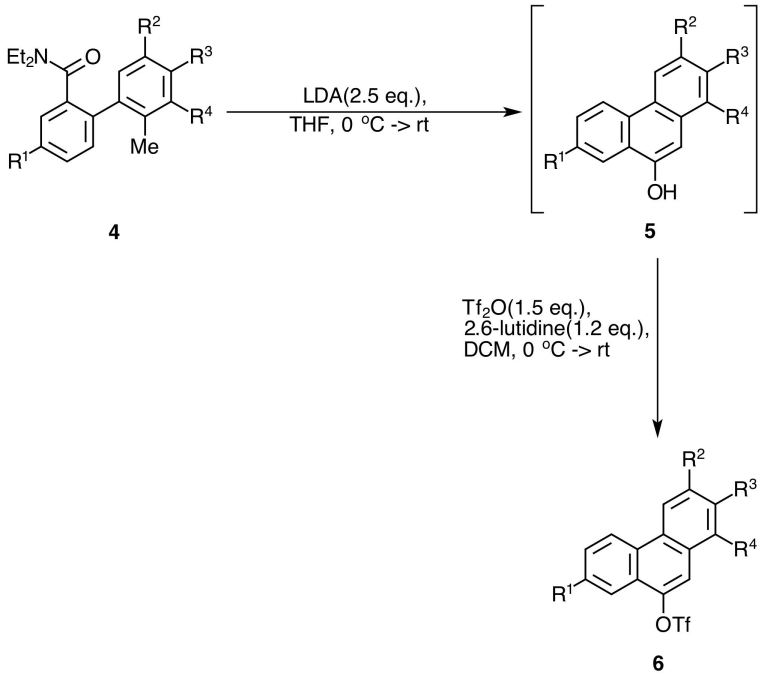
A very exciting alternative to the borate ester has been developed the last couple of years, and looks to be very promising. The problem with the borate esters as mentioned is the lack of ability to isolate them. The promising MIDA boronates [68, 69] is proved to be very stable and can easily be purified on a flash column. It has also proved to afford high yields in cross coupling reactions [69]. The main issue is the price as they are very expensive, but might be the solution in the future.

To fully identify compounds **4a-d**, both proton- and ^{13}C-nmr spectroscopy was used. In the proton-spectrum for all four compounds it is easy to identify the expected signals presented in Table 3. All four compounds were expected to have an aromatic region (6H), three methyl groups on the aromatic rings (9H), one CH_2 top from the diethyl amide (4H) and one top from the CH_3 group on the diethyl amide.

Table 3: Proton-nmr of compounds **4a-d**.

Comopund	Aromatic region	3x Methyl	-CH_2	-CH_3
4a	7.00-7.40 (6H)	2.16 (3H), 2.20 (3H) and 2.24 (3H)	2.64-3.85 (4H)	0.65-1.00 (6H)
4b	6.93-7.21 (6H)	2.18 (3H), 3.31 (3H) and 2.39 (3H)	2.89-3.70 (4H)	0.70-0.88 (6H)
4c	7.00-7.21 (6H)	2.17 (3H), 2.28 (3H) and 2.40 (3H)	2.82-3.75 (4H)	0.67-0.92 (6H)
4d	6.91-7.2 (6H)	2.07 (3H), 2.29 (3H) and 2.40 (3H)	2.81-3.72 (4H)	0.67-0.95 (6H)

4.3 DreM and Protection.



4 **5** **6**

Figure 16: DreM of biphenyls and Protection of alcohols.

Compounds **4a-d** were dissolved in THF and underwent ring closing by addition to a stirred solution of lithium diisopropylamide (LDA) in THF at 0 °C. LDA was made *in situ*. by adding n-BuLi to DIPA (diisopropylamine). All reaction were followed by TLC, and proved to take 30 minutes. Compound **5**, in Figure 16, is written as an intermediate, this is because these alcohols undergoes rapid air oxidation and to avoid this they are at no point isolated, but rather protected by a triflate group. After workup of **5**, the compounds were dissolved in DCM, added 2,6-lutidine and stirred at 0 °C for five minutes before triflicanhydride was added. **6a-d** were isolated by flash chromatography, yields are presented in Table 4.

Table 4: DreM and Protection yields.

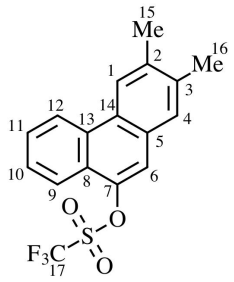
Entry	S. M.	Product	Yield %	Melting point (°C)
1	**4a**	**6a**	67-72	98-99
2	**4b**	**6b**	71-78	138-139
3	**4c**	**6c**	70	83.5-84
4	**4d**	**6d**	75	87-88

The two step reaction gave good yields for all four compounds, the yields were also very similar at around 70%. Those yields were comperable to those yields previously achived by Snieckus groups [45]. In Snieckus group the phenantrols were isolated, which was not the case in this thesis. Experience with air oxidation of the phenantrols let to the plan to not isolate them, but rather protect them straight away. The idea to save a step and still get a high yield was also tempting.

All compounds were fully identified by NMR, IR and melting point. The melting point of **6b** (138-139 °C) was identical to the already mentioned Snieckus paper [45]. The melting point of **6d** was 13 degrees higher to the one previously mentioned in Snieckus paper [45], but the prefered solvent was ethyl acetate, where textbf6d in this thesis was recrystilized in ethanol.

Table 5 shows assigned NMR shifts (δ), splitting pattern and coupling constants, J, for compound **6a**. As shown in Table 5 this was the case for all four molecules. The experimental data that was found on **6b** and **6d** [45], both compare to the results in Table 7. No experimental data was found on neither **6a** or **6c**.

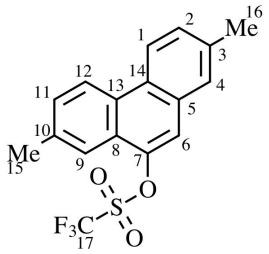
Table 5: NMR Shifts for compound **6a**.



Position	δH [ppm]	#H	Split. pat.	J [Hz]	δC
1	8.39	1	s		121.8
2					137.5
3					137.7
4, 6, 10-11	7.64-7.75	4	m		127.4, 116.8, 129.0, 129.2
5					128.0
7					143.9
8					125.3
9	8.10	1	d	7.5	123.0
12	8.65	1	d	7.5	123.3
13					131.7
14					121.1
15	2.53	3	s		20.1
16	2.46	3	s		20.9
17					117.7

Table 6 shows assigned NMR shifts (δ), splitting pattern and coupling constants, J, for compound **6b**. The experimental data presented in the table compares well to the results from Snieckus groups [45].

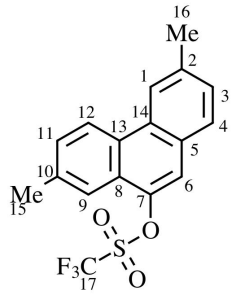
Table 6: NMR Shifts for compound **6b**.



Position	δH [ppm]	#H	Split. pat.	J [Hz]	δC
1, 12	8.49-8.57	2	m		122.7, 123.0
2, 11	7.51-7.58	2	m		127.7, 128.7
3					137.4
4, 9	7.64-7.67	2	m		129.8, 130.1
5					130.4
6	7.88	1	s		117.8
7					144.5
8					125.3
10					137.6
13					130.0
14					122.7
15	2.55	3	s		21.6
16	2.60	3	s		22.0
17					121.3

Table 7 shows assigned NMR shifts (δ), splitting pattern and coupling constants, J, for compound **6c**.

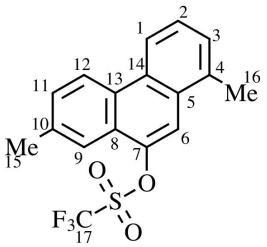
Table 7: NMR Shifts for compound **6c**.



Position	δH [ppm]	#H	Split. pat.	J [Hz]	δC
1	8.40	1	s		121.2
2					137.9
3	7.42	1	d	8.1	129.2
4	7.75	1	d	8.1	125.8
5					129.9
6	7.65	1	s		116.9
7					143.8
8					123.1
9	7.88	1	s		128.1
10					138.0
11	7.54	1	d	8.4	129.0
12	8.55	1	d	8.7	122.5
13					129.6
14					121.1
15	2.60	3	s		22.4
16	2.61	3	s		22.0
17					117.9

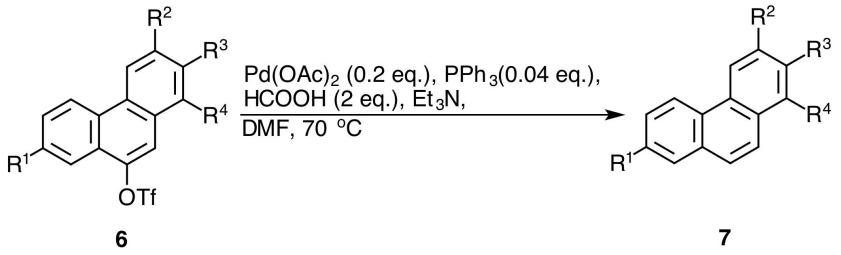
Table 8 shows assigned NMR shifts (δ), splitting pattern and coupling constants, J, for compound **6d**. The experimental data presented in the table compares well to the results from Snieckus groups [45].

Table 8: NMR Shifts for compound **6d**.



Position	δH [ppm]	#H	Split. pat.	J [Hz]	δC
1	8.50	1	d	8.4	119.7
2, 9	7.90-7.92	2	m		128.5
3	7.46	1	d	6.9	127.6
4					135.6
5					130.4
6, 11	7.57-7.62	2	m		117.0
7					147.6
8					123.5
10					138.0
12	8.60	1	d	8.4	121.2
13					130.2
14					120.9
15	2.61	3	s		22.0
16	2.73	3	s		19.9
17					114.6

4.4 Deprotection.



6 **7**

Figure 17: Deprotection of phenantrols to the corresponding phenanthrene.

The phenanthrols **6a**, **6b**, **6c** and **6d** were all deprotected by a palladium catalyzed hydrogenolysis. As displayed in Figure 17, the phenantrols were dissolved in DMF, added the catalyst and the ligand, formic acid and triethyl amine. The reaction mixture was heated to 70 °C and stirred until the reaction was complete. Normal workup and flash column purification afforded **7a-d** in high yields, as shown in Table 9.

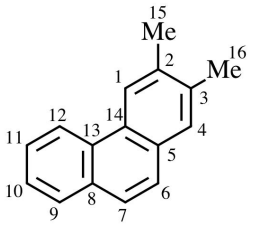
Table 9: Deprotection yields for compounds **7a-d**.

Entry	S. M.	Product	Yield %)
1	**6a**	**7a**	73
2	**6b**	**7b**	94-96
3	**6c**	**7c**	97
4	**6d**	**7d**	quant.

Except for the deprotection of compund **6a**, the reaction gave yields well over 90%. To successfully determine the formation of the right compunds melting points and nmr was measured for each compound, as well as IR.

Table 10 shows assigned NMR shifts (δ), splitting pattern and coupling constants, J, for compound **7a**.

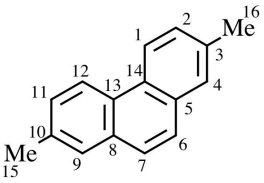
Table 10: NMR Shifts for compound **7a**.



Position	δH [ppm]	#H	Split. pat.	J [Hz]	δC
1	8.42	1	s		122.6
2					136.1
3					136.0
4, 6, 7, 10, 11	7.51-7.64	5	m		126.2, 126.4, 126.6
5					130.2
8					132.0
9	7.84	1	d	7.8	128.8
12	8.62	1	d	8.4	123.2
13					130.8
14					128.7
15	2.45	3	s		20.2
16	2.51	3	s		20.8

Table 11 shows assigned NMR shifts (δ), splitting pattern and coupling constants, J, for compound **7b**. Because of perfect symmetri in the molecule, only half of the signals show. The NMR analysis compares well to the results from Snieckus groups [45].

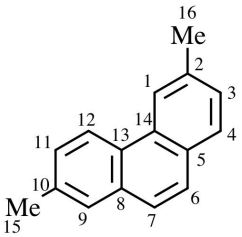
Table 11: NMR Shifts for compound **7b**.



Position	δH [ppm]	#H	Split. pat.	J [Hz]	δC
1, 12	8.52	2	d	8.4	122.3
2, 11	7.45	2	dd	8.4, 1.8	126.6
3, 10					135.8
4, 6, 7, 9	7.64	4	br		128.0, 128.1
5, 8					131.8
13, 14					128.2
15, 16	2.55	6	s		21.4

Table 12 shows assigned NMR shifts (δ), splitting pattern and coupling constants, J, for compound **7c**.

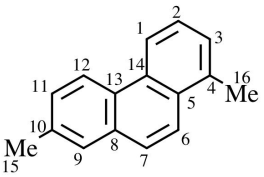
Table 12: NMR Shifts for compound **7c**.



Position	δH [ppm]	#H	Split. pat.	J [Hz]	δC
1	8.46	1	s		122.4
2					136.3
3	7.41	1	dd	8.1, 1.8	126.9
4	7.78	1	d	8.1	128.0
5					130.6
6, 7, 9	7.61-7.69	3	m		128.3
8					132.5
10					136.4
11	7.47	1	dd	8.4, 1.8	125.9
12	8.57	1	d	8.4	122.7
13					128.6
14					129.8
15	2.58	3	s		21.7
16	2.64	3	s		22.3

Table 13 shows assigned NMR shifts (δ), splitting pattern and coupling constants, J, for compound **7d**. The NMR analysis compares well to the results from Snieckus groups [45].

Table 13: NMR Shifts for compound **7d**.



Position	δH [ppm]	#H	Split. pat.	J [Hz]	δC
1	7.90	1	d	9.3	120.9
2, 11	7.65-7.70	2	m		126.3, 126.6
3, 6, 7	7.38-7.53	3	m		123.1, 127.5, 128.2
4					135.0
5					130.6
8					132.0
9, 12	8.50-8.57	2	m		123.1, 128.6
10					136.3
13					128.7
14					130.7
15	2.54	3	s		21.7
16	2.72	3	s		20.2

2.6-dimethylphenanthrene (**7c**) was a liquid at room temperature and therefore no melting point was measured. Snieckus group have previously measured the melting point of 1.7-dimethylphenanthrene (**7d**) to 83-84 °C, which is significantly higher than 70 °C. The NMR shows some impurities that might explain why the melting point is significantly lower that previously reported [45]. The compound underwent flash column chromatography twice in hope that it would solve the problem and remove the impurities. Nmr spectroscopy of **7d** corresponds well with the formerly reported spectrum. The measured nmr of 2.7-dimethylphenanthrene (**7b**) compares well to the one reported by Snieckus group [45], the melting point was also identical.

2.6- and 2.3-dimethylphenanthrene has previously not been reported and only predicted nmr spectrums could be found. 2.6-dimethylphenanthrene (**7c**) which was a liquied at room temperature had a reported melting point of 33-34 °C [70, 71, 72]. Some small impurities might explain why **7c** was not a solid, the proton nmr revealed some small impurities in the aliphatic region. The top in the proton nmr at 1.5 is due to water in the solvent. The reported melting point of 2.3-dimethylphenanthrene **7a** was 79-80 °C [73] which is 7-8 degrees lower than the measured melting point (86-87 °C).

Total yields of the four synthesis are very good when considering that it was done

on production scale. The total yield of the synthesis of 2.3-dimethylphenanthrene **7a** was 34% which was the lowest of the four target molecules. The synthesis of 2.7-dimethylphenanthrene **7b** gave a lot higher yield, a total of 40%. The synthesis of 2.6-dimethylphenanthrene **7c** took a blow in the Suzuki coupling, but still managed a total yield of 24% which was close to **7a**. The total yield of target molecule **7d** was by far the best at 61%.

4.5 Total synthesis of 2- and 4-methoxychrysene

A DoM reaction on compound **3b** with triisopropyl borate, as used in chapter 4.2, could possibly yield two products. Even thought it was impossible to see if both products had made in the NMR of crude product **3b**, only a single product was found after the Suzuki coupling. Previous work done on DoM reactions with a variety of electrophiles gave poor regioselectivity when using s-BuLi/TMEDA as the base [74]. To further investigate this DoM regioselectivity, 2- and 4-methoxychrysene was made.

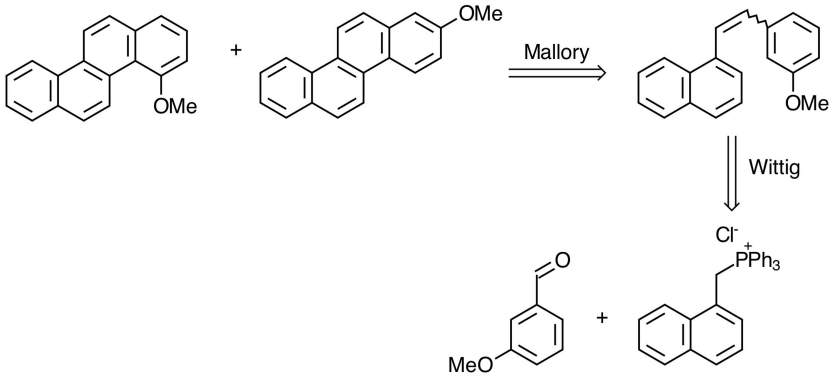


Figure 18: Retrosynthesis of 2- and 4-methoxychrysene.

As the retrosynthesis in Figure 18 shows 2- and 4-methoxychrysene can be synthesized by first doing a wittig reaction with the phosphonium salt and the commercially available aldehyde. Ringclosing can be achieved by a photoreaction (Mallory reaction) on the stilbene, which in this case will afford the two wanted products.

Figure 19 features the Wittig reaction mechanism. The Wittig salt is deprotonated by a base, in this thesis NaOH was the preferred base, and stabilized by resonance. The resonance structure then attacks as a nucleophile to the carbonyl and forms a betain. The negative charged oxygen atom attacks the positive phosphorus atom creating a four membered ring. This ring decomposes to triphenyl phosphine oxide and the alkene (stilbene).

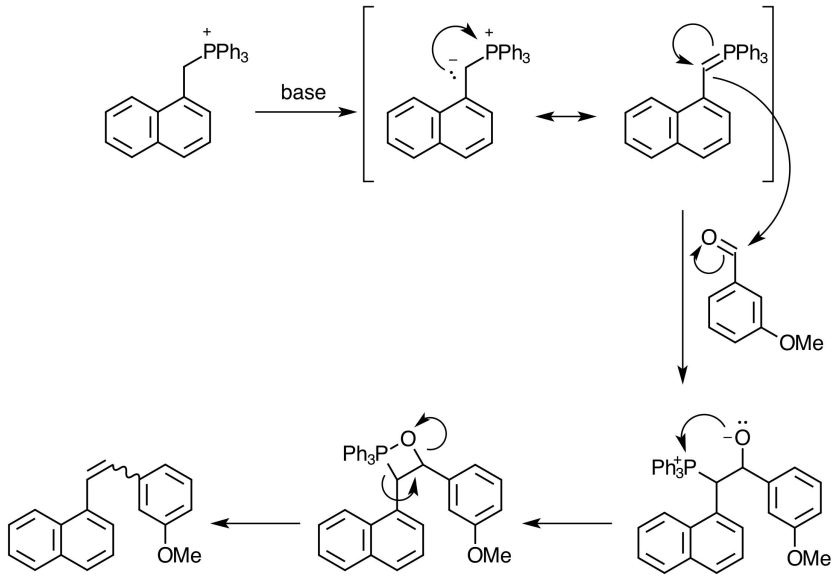


Figure 19: Wittig reaction mechanism.

Benzaldehyde (**8**) was reacted with the naphtylphosphonium salt (**9**) by adding both reagents to a roundbottom flask, disolving them in DCM and adding 50% NaOH and stirring the reaction for three days, as Figure 20 shows. The stilbene product (**10**) was afforded at quantitative yield. All experimental data was identical to litterature [74].

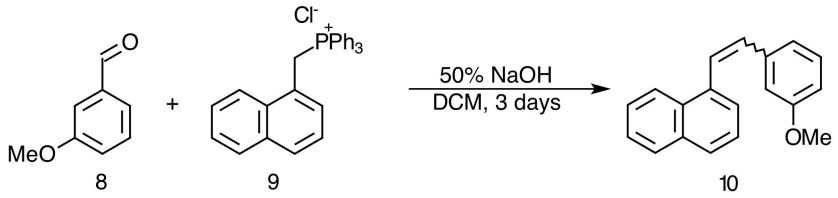


Figure 20: Wittig reaction.

Because of isomerization of the double bond under irradiation stilbene **10** can undergo a ring closing by stilbene photocyclization (Mallory method) under oxidative conditions which will afford both 2- and 4-methoxychrysene. Since the photoreaction setup could only handle about three grams of stilbene at a time. While 8.88 g needed to undergo ringclosing, the reaction was done in three turns. Where the reaction mixtures where added together and isolated by recrystalization and flash column chromatography.

As Figure 21 describes, stilbene **10** was disolved in toluene, added epoxybutane and iodine and left under uv-irridiation for four hours. Normal workup featured washing with sodium thiosulphate to get rid of the excess iodine, extracted with ethyl acetate and dried with $MgSO_4$. The first product, 2-methoxychrysene (**11a**) was isolated by recrystalization from acetone to afford 3.23 gram (37%) as white powder. The second

product, 4-methoxychrysene (**11b**) was isolated by flash column chromatography which was difficult since both products are very similar, but 2.66 grams of pure **11b** (30%) was isolated as a white powder. All experimental data are identical to litterature [74].

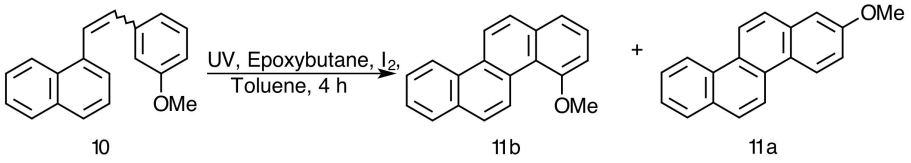


Figure 21: Stilbene photocyclization.

4.6 Chrysene-2- and chrysene-4-yl N,N-diethylcarbamate

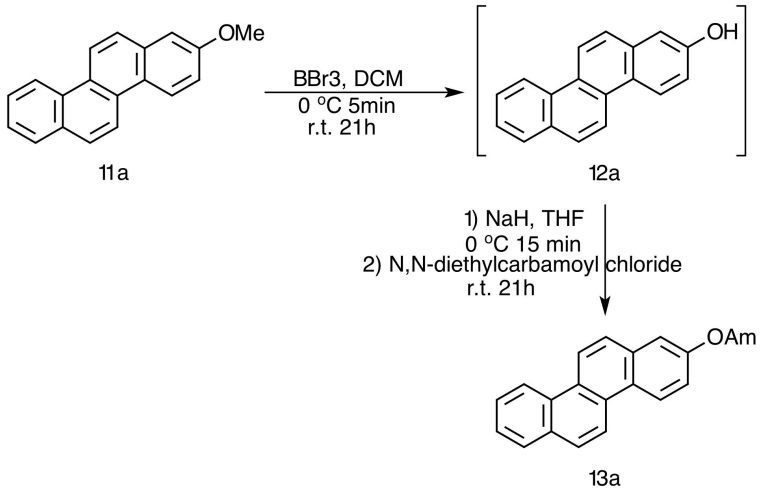


Figure 22: Synthesis of chrysene-2-yl N,N-diethylcarbamate (**13a**).

To be able to perform Directed *ortho*-Metalation reactions on the compound it needed a good directed metalation group (DMG). This group was made by first deprotecting the methoxy group with BBr_3 in DCM, as shown in Figure 22. Alcohol **12a** was never isolated, just worked up and dried before deprotonated with NaH in THF. After the reaction had stirred at 0 °C for 15 minutes, it was heated to room temperature before N,N-diethylcarbamoyl chloride was added, the reaction was then left to stirr overnight. Carbamate **13a** was isolated by flash column chromatography after normal workup to afford the product as a white powder (75%). All experimental data was identical to litterature [74].

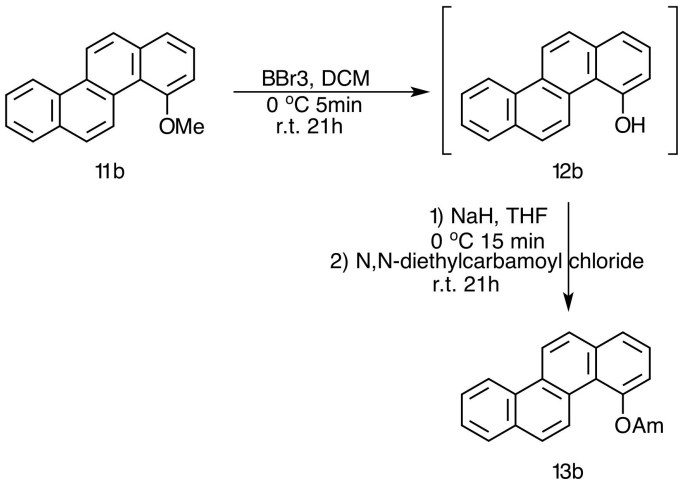


Figure 23: Synthesis of chrysene-4-yl N,N-diethylcarbamate (**13b**).

Figure 23 shows that carbamate **13b** was attempted to be synthesized in the same way as **13a**. According to TLC, compund **12b** was formed at high yields. The problem, however, was attaching the carbamoyl to the chrysene. Two attempts were done, first one with 1.5 equivalents of the base NaH, which was according to litterature procedure [74], this afforded (33%) of product **13b** after flash column chromatography. The rest was recovered starting material of compound **12b**. Attempt two featured 2 equivalents of NaH, but the reaction only affordet starting material after being left to stirr for two days, followed by TLC. All experimental data was identical to litterature [74].

4.7 Directed ortho-Metalations on chrysene-2-yl N,N-diethylcarbamate (13a)

Previous DoM reactions on **13a** using s-BuLi/TMEDA as base affords two products, making the reaction not very regioselective, Figure 24. However, resent development has shown promising results with the use of the more steric hindered LiTMP as base [75]. Where s-BuLi/TMEDA makes both the 1- and 3-substituted product, LiTMP only yields the 3-substituted product.

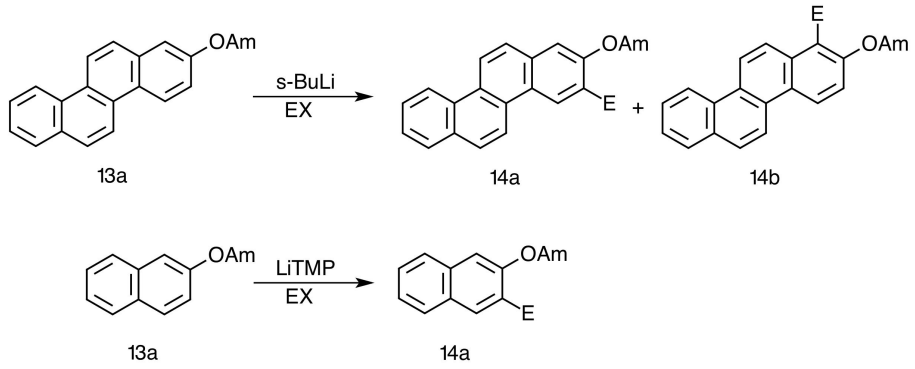


Figure 24: S-BuLi vs LiTMP in selectivity. The top reaction shows previous work with s-BuLi on chrysene-2-yl N,N-diethylcarbamate while the bottom reaction shows resent work with LiTMP to better the regioselectivity on O-naphtyl 2-carbamate [75].

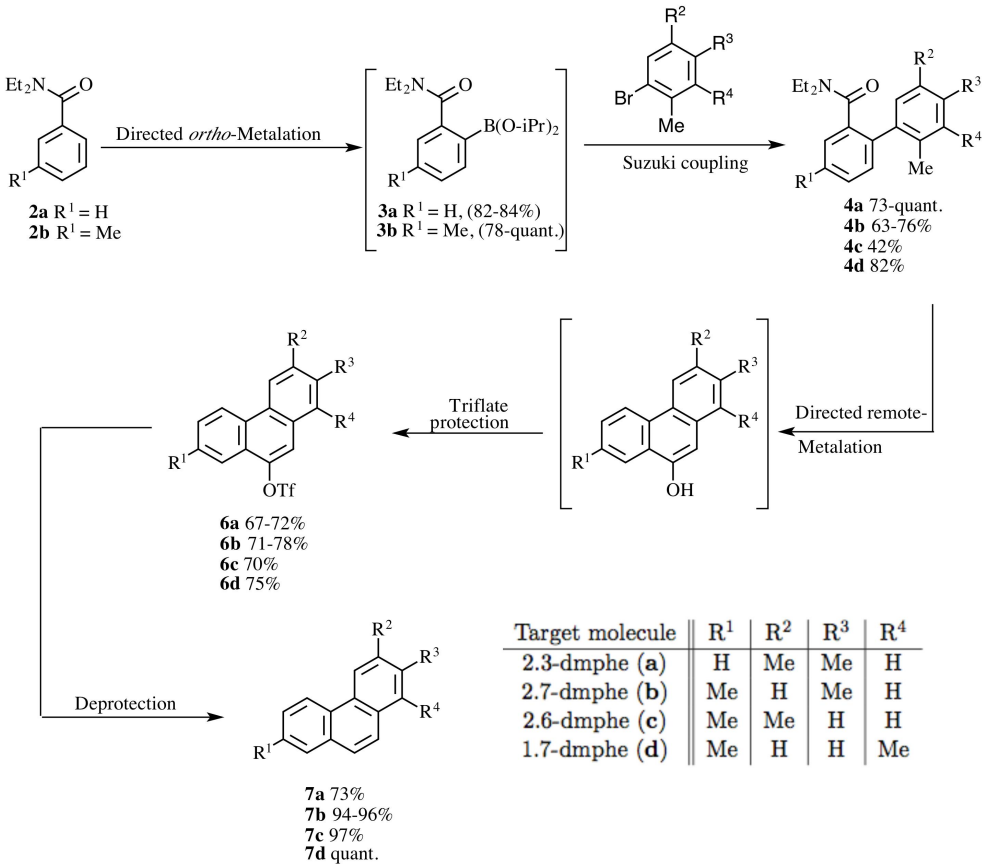
Several attempts where done to further explore this, unfortnunately no results where obtained. After numerous attempt with LiTMP as base without results, s-BuLi/TMEDA along with following litterature procedure was tried. The hope was to get some idea to why no reaction occured, but when attempts following litterature procedure failed, more questions where raised than answered. Table 14 shows all of the failed reactions.

Table 14: Attempted Directed ortho-Metalations on **13a**.

Reagent	E^+	Base	Yield %	Comment
TMSCl	TMS^+	LiTMP	-	-
I_2	I^+	LiTMP	-	-
I_2	I^+	s-BuLi/TMEDA	-	-
I_2	I^+	s-BuLi/TMEDA	-	**13a** left on vacuum for half a day due to suspected hygroscopic effect

5 Conclusion

A selection of dimethylated phenanthrenes has been prepared using a combination of Directed ortho-Metalation (DoM), Suzuki-Miyaura cross coupling, and Directed remote-Metalation (DreM). 2,7-, 2,3-, 1,7- and 2-6-dimethyl-9-phenanthrol have been made into the corresponding phenanthrenes by a simple Pd-catalyzed hydrogenolysis of the triflate protected alcohol. The single isomers resulting from this route provides the dimethylphenanthrenes in high purity and in gram quantities, as shown in the Figure 25 below:



Target molecule	R^1	R^2	R^3	R^4
2.3-dmphe (**a**)	H	Me	Me	H
2.7-dmphe (**b**)	Me	H	Me	H
2.6-dmphe (**c**)	Me	Me	H	H
1.7-dmphe (**d**)	Me	H	H	Me

Figure 25: Total synthesis of dimethylsubstituted phenanthrenes and the afforded yields.

The regioselectivity of the Directed *ortho*-Metalation (DoM) on chrysene-2-yl N,N-diethylcarbamate was further explored, however, no results was afforded.

6 Experimental

6.1 General

The reactions were followed by TLC on silica plate (60, F_{254}. The plates were analyzed under ultraviolet-light (254 nm, Uvltec, CV-006). The compounds that were purified were purified by flash column chromatography on silica gel (40-63 μm, 60). The stilbenes were ring closed in a photoreactor (Photochemical Reactor Ltd. 400 W, Mercury lamp). All the melting points were measured in capilary tubes on a Bibb SMP3 melting point apparatus. NMR-spectroscopy were performed on Varian Mercury 300 MHz. Infrared spectroscopy were perfromed on a PerkinElmer, FT-IR spectrometer. Mass spectrometry (MS) will be done at a later time.

6.2 Bis(propan-2-yl)[2-(diethylcarbamoyl)phenyl]boronate (3a)

A solution of N,N-diethylbenzamide (5.48 g, 30.92 mmol) in anhydrous THF (100 ml) was added dropwise to a solution of s-BuLi (41.22 ml of a 0.9 M solution, 37.10 mmol), and TMEDA (5.56 ml, 37.10 mmol) in anhydrous THF (100 ml) at -78 °C. After the resulting mixture had stirred for 1 h at -78 °C it was treated with triisopropyl borate (17.84 ml, 77.30 mmol), the mixture was warmed to room temperature overnight and quenced with satd. Aq. NH_4Cl solution (150 ml). The reaction mixture was extracted with diethylether (3x150 ml), dried over $MgSO_4$, filtred and concentrated *in vacuo*. to give 7.75 g (82%) of **3a** as a brown oil.

6.3 N,N-diethyl-2-(2,4,5-trimethylphenyl)benzamide (4a)

All solutions were degassed prior to use. A mixture of $PdCl_2$(dppf) (0.86 g, 1.05 mmol) and 5-bromo-1,2,4-trimethylbenzene (4.17 g, 20.94 mmol) in DME (60 ml) was stirred at room temperature for 15 min before **3a** (7.75 g, 25.39 mmol) in DME (40 ml) was added, followed by the addition of 2M sodium carbonate-solution (60 ml). The mixture was heated at reflux for 18 hours, cooled and extracted with diethylether (3x150 ml), dried with magnesiumsulphate and concentrated *in vacuo*. The crude product was purified by flash chromatography (petroleum ether: ethyl acetate, 5:1) to afford 4.53 g (73%) of **4a** as a brown oil. IR (KBr): 1633 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.65-1 (m, 9H), 2.16-2.24 (m, 9H), 2.64-3.85 (br d, 4H), 7.18-7.40 (m, 6H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$) δ: 11.61, 13.68, 19.10, 19.34, 19.59, 37.87, 42.34, 127.05, 128.06, 130.39, 131.44, 135.75, 137.18, 170.22.

6.4 2,3-dimethylphenanthryl-6-triflourmethanesulfonate (6a)

A stirred mixture of diisopropylamine (5.08 ml, 36.26 mmol), n-BuLi (25.00 ml, 1.45 M, 36.26 mmol) in THF (85 ml) at 0 °C was added **4a** (4.28 g, 14.48 mmol). The mixture

was stirred at room temperature for 30 min before being quenced with satd. aq. NH_4Cl (150 ml), extracted with diethylether (3x200 ml) dried with magnesiumsulphate and concentrated *in vacuo*.

A solution of 2,3-dimethyl-6-phenanthrol (14.48 mmol) and 2,6-lutidine (2.14 ml, 18.40 mmol) in DCM (50 ml) was stirred at 0 °C for 5 min before the addition of triflicanhydride (3.87 ml, 23.00 mmol). The resulting mixture was stirred at room temperature for 1 hour, added 50 ml water, seperated by DCM (3x100 ml), dried on $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash chromatography (petroleumether: ethyl acetate, 6:1) to give 3.46 g (67%) of the product as white powder. Mp = 98-99 °C (ethanol). IR (KBr): 1414, 1218, 1143 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.46 (s, 3H), 2.53 (s, 3H), 7.64-7.75 (m, 4H), 8.10 (d, J = 7.5 Hz, 1H), 8.39 (s, 1H), 8.65 (d, J = 7.5 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 20.1, 20.9, 116.8, 117.7, 121.1, 121.8, 123.0, 123.3, 125.3, 127.4, 128.0, 129.0, 129.2, 131.7, 137.5, 137.7, 143.9

6.5 2,3-dimethylphenanthrene (7a)

6a (3.433 g, 9.69 mmol) was stirred at 70 °C in a flask with $Pd(OAc)_2$ (0.04 g, 0.19 mmol), PPh_3 (0.101 g, 0.38 mmol), Et_3N (4.06 ml, 29.08 mmol), and HCO_2H (0.73 ml, 19.39 mmol) in DMF (190 ml) for 30 min, cooled to room temperature and treated with water (190 ml). The solution was extracted with Et_2O (3x200 ml), the combined organic layers was dried with $MgSO_4$ and concentrated *in vacuo*. The crude product was purified with flash cromatography (petroleumether: ethyl acetate, 8:1) to afford **7a** (1.463 g, 73%) as colorless crystals. Mp = 86-87 °C (ethanol). IR (KBr): 2967 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.45 (s, 3H), 2.51 (s, 3H), 7.51-7.64 (m, 5H), 7.84 (d, J = 7.8 Hz, 1H), 8.42 (s, 1H), 8.62 (d, J = 8.4 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 20.2, 20.8, 122.6, 123.2, 126.2, 126.4, 126.6, 128.7, 128.8, 130.2, 130.8, 132.2, 136.0, 136.1

6.6 Bis(propan-2-yl)[2-(diethylcarbamoyl)-4-methylphenyl]boronate (3b)

A solution of N,N-diethyl-3-methylbenzamide (5.25 g, 27.46 mmol) in anhydrous THF (80 ml) was added dropwise to a solution of s-BuLi (62.20 ml of a 0.53 M solution, 32.94 mmol), and TMEDA (4.94 ml, 32.94 mmol) in anhydrous THF (80 ml) at -78 °C. After the resulting mixture had stirred for 1 h at -78 °C it was treated with 3-isopropylborate (15.72 g, 68.62 mmol), the mixture was warmed to room temperature overnight and quenced with satd. Aq. NH_4Cl solution (15 ml). The reaction mixture was extracted with diethylether (3x150 ml), dried over $MgSO_4$, filtred and concentrated *in vacuo* to give 8.82 g (quant.) of **3b** as a brown oil.

6.7 2-(2,4-dimethylphenyl)-N,N-diethyl-5-methylbenzamide (4b)

All solutions were degassed prior to use. A mixture of $PdCl_2$(dppf) (0.58 g, 0.71 mmol) and 4-bromo-m-xylene (2.62 g, 14.17 mmol) in DME (60 ml) was stirred at room temperature for 15 min before **3b** (8.82 g, 27.62 mmol) in DME (40 ml) was added, followed by the addition of 2M sodium carbonate-solution (60 ml). The mixture was heated at reflux for 18 hours, cooled and extracted with diethylether (3x150 ml). Dried with magnesiumsulphate and concentrated *in vacuo*. The crude product was purified by flash chromatography (petroleum ether: ethyl acetate, 5:1) to afford 2.64 g (63%) of **4b** as a brown oil. IR (KBr): 1682 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.70-0.88 (m, 6H), 2.18 (s, 3H), 2.31 (s, 3H), 2.39 (s, 3H), 2.89-3.70 (br, 4H), 6.93-7.21 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 11.78, 13.65, 20.16, 21.05, 37.75, 42.16, 128.85, 130.19, 130.23, 130.74, 136.93, 137.01, 170.39.

6.8 2,7-dimethylphenanthryl-9-triflourmethanesulfonate (6b)

A stirred mixture of diisopropylamine (2.97 ml, 21.21 mmol), n-BuLi (18.61 ml, 1.14 M, 21.21 mmol) in THF (60 ml) at 0 °C was added **4b** (2.50 g, 8.48 mmol). The mixture was stirred at room temperature for 30 min before being quenced with satd. aq. NH_4Cl (120 ml), extracted with diethylether (3x150 ml) dried with magnesiumsulphate and concentrated *in vacuo*. A solution of 2,7-dimethyl-9-phenanthrol (8.48 mmol) and 2,6-lutidine (1.20 ml, 10.20 mmol) in DCM (130 ml) was stirred at 0 °C for 5 min before the addition of triflicanhydride (2.14 ml, 12.73 mmol). The resulting mixture was stirred at room temperature for 1 hour, added 50 ml water, seperated by DCM (3x100 ml), dried on $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash chromatography (petroleumether: ethyl acetate, 6:1) to give 2.15 g (71%) of the product as white powder. Melting point 138-139 °C (Hexane). IR (KBr) (cm^{-1}): 1430, 1223, 1139. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.56 (s, 3H), 2.60 (s, 3H), 7.51-7.58 (m, 2H), 7.64-7.67 (m, 2H), 7.88 (s, 1H), 8.49-8.57 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 21.6, 22.0, 117.8, 121.3, 122.7, 123.0, 125.3, 127.7, 128.7, 129.8, 130.0, 130.1, 130.4, 137.4, 137.6, 144.5.

6.9 2,7-dimethylphenanthrene (7b)

6b (2.12 g, 5.98 mmol) was stirred at 70 °C in a flask with $Pd(OAc)_2$ (0.02 g, 0.12 mmol), PPh_3 (0.06 g, 0.24 mmol), Et_3N (2.50 ml, 18.01 mmol), and HCO_2H (0.45 ml, 12.01 mmol) in DMF (120 ml) for 30 min, cooled to room temperature and treated with water (120 ml). The solution was extracted with Et_2O (3x200 ml), the combined organic layers was dried with $MgSO_4$ and concentrated *in vacuo*. The crude product was purified with flash cromatography (petroleumether: ethyl acetate, 8:1) to afford 1.17 g of **7b** (94%) as colorless crystals. Mp 101-102 °C (ethanol). IR (KBr): 2910 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.55 (s, 6H), 7.44 (dd, J = 8.41, 1.8 Hz, 2H), 7.64 (br, 4H),

8.52 (d, J = 8.41 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 21.4, 122.3, 126.6, 128.0, 128.1, 128.2, 131.8, 135.8.

6.10 2-(2,5-dimethylphenyl)-N,N-diethyl-5-methylbenzamide (4c)

All solutions were degassed prior to use. A mixture of $PdCl_2$(dppf) (0.48 mg, 0.59 mmol) and 2-bromo-p-xylene (2.18 g, 11.78 mmol) in DME (60 ml) was stirred at room temperature for 15 min before **3b** (7.57 g, 23.56 mmol) in DME (40 ml) was added, followed by the addition of 2M sodium carbonate-solution (60 ml). The mixture was heated at reflux for 18 hours, cooled and extracted with diethylether (3x150 ml). Dried with magnesiumsulphate and concentrated *in vacuo*. The crude product was purified by flash chromatography (petroleum ether: ethyl acetate, 5:1) to afford 1.476 g (42%) of **4c** as a brown oil. IR (KBr): 1630 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 0.67-0.92 (m, 6H), 2.17 (s, 3H), 2.28 (s, 3H), 2.40 (s, 3H), 2.82-3.75 (br, 4H), 7.00-7.21 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 11.75, 13.76, 19.85, 20.95, 21.20, 37.89, 42.41, 128.21, 128.96, 130.10, 137.11, 170.40.

6.11 2,6-dimethylphenanthryl-9-triflourmethanesulfonate (6c)

A stirred mixture of diisopropylamine (1.55 ml, 11.10 mmol), n-BuLi (10.80 ml, 11.10 mmol) in THF (35 ml) at 0 °C was added **4c** (1.312 g, 4.44 mmol). The mixture was stirred at room temperature for 30 min before being quenced with satd. aq. NH_4Cl (40 ml), extracted with diethylether (3x40 ml) dried with magnesiumsulphate and concentrated *in vacuo*. A solution of 2,6-dimethyl-9-phenanthrol (4.44 mmol) and 2,6-lutidine (0.63 ml, 5.32 mmol) in DCM (70 ml) was stirred at 0 °C for 5 min before the addition of triflicanhydride (1.12 ml, 6.67 mmol). The resulting mixture was stirred at room temperature for 1 hour, added 10 ml water, seperated by DCM (3x30 ml), dried on $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash chromatography (petroleumether: ethyl acetate, 6:1) to give 1.10 g (70%) of the product as yellow solid. Melting point 83.5-84 °C (EtOH). IR (KBr) (cm^{-1}): 1416, 1204, 1141. ^{1}H NMR (300 MHz, $CDCl_3$) δ: 2.59 (d, 6H), 7.42 (d, J = 8.11 Hz, 1H), 7.53 (d, J = 8.41 Hz, 1H), 7.65 (s, 1H), 7.74 (d, J = 8.11 Hz, 1H), 7.88 (s, 1H), 8.38 (s, 1H), 8.54 (d, J = 8.71 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 22.0, 22.4, 116.9, 117.9, 121.1, 121.2, 122.5, 123.1, 125.8, 128.1, 129.0, 129.2, 129.6, 129.9, 137.9, 138.0, 143.8.

6.12 2,6-dimethylphenanthrene (7c)

6c (1.01 g, 2.85 mmol) was stirred at 70 °C in a flask with $Pd(OAc)_2$ (0.01 g, 0.06 mmol), PPh_3 (0.03 g, 0.11 mmol), Et_3N (1.20 ml, 8.56 mmol), and HCO_2H (0.23 ml, 5.71 mmol) in DMF (30 ml) for 2 hours, cooled to room temperature and treated with water (30 ml). The solution was extracted with Et_2O (3x30 ml), the combined organic layers was

dried with MgSO4 and concentrated *in vacuo*. The crude product was purified with flash cromatography (petroleumether: ethyl acetate, 8:1) to afford **7c** (574 mg, 97%) as a brown liquid. IR (KBr): 2920 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.58 (s, 3H), 2.65 (s, 3H), 7.41 (dd, J = 8.11, 1.80 Hz, 1H), 7.47 (dd, J = 8.41, 1.80 Hz, 1H), 7.61-7.69 (m, 3H), 7.78 (d, J = 8.11 Hz, 1H), 8.46 (s, 1H), 8.57 (d, J = 8.41 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 21.7, 22.3, 122.4, 122.7, 125.9, 126.9, 128.0, 128.3, 128.6, 129.8, 130.6, 132.5, 136.3, 136.4.

6.13 2-(2,3-dimethylphenyl)-N,N-diethyl-5-methylbenzamide (4d)

All solutions were degassed prior to use. A mixture of Pd(dppf) (0.38 g, 0.53 mmol) and 3-bromo-o-xylene (1.96 g, 10.57 mmol) in DME (60 ml) was stirred at room temperature for 15 min before **3b** (6.79 g, 21.14 mmol) in DME (40 ml) was added, followed by the addition of 2M sodium carbonate-solution (60 ml). The mixture was heated at reflux for 18 hours, cooled and extracted with diethylether (3x150 ml). Dried with magnesiumsulphate and concentrated *in vacuo*. The crude product was purified by flash chromatography (petroleum ether: ethyl acetate, 5:1) to afford 2.59 g (82%) of **4d** as a brown oil. IR (KBr): 1630 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 0.67-0.95 (m, 6H), 2.07 (s, 3H), 2.29 (s, 3H), 2.40 (s, 3H), 2.81-3.72 (br, 4H), 6.91-7.22 (m, 6H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 11.83, 13.77, 17.31, 20.67, 21.18, 37.82, 42.56, 129.01, 136.89, 137.03, 170.37.

6.14 1,7-dimethylphenanthryl-9-triflourmethanesulfonate (6d)

A stirred mixture of diisopropylamine (2.63 ml, 18.84 mmol), n-BuLi (16.25 ml, 18.84 mmol) in THF (60 ml) at 0 °C was added **4d** (2.22 g, 7.53 mmol). The mixture was stirred at room temperature for 30 min before being quenced with satd. aq. NH_4Cl (60 ml), extracted with diethylether (3x60 ml) dried with magnesiumsulphate and concentrated *in vacuo*. A solution of 1,7-dimethyl-9-phenanthrol (7.53 mmol) and 2,6-lutidine (1.07 ml, 9.04 mmol) in DCM (120 ml) was stirred at 0 °C for 5 min before the addition of triflicanhydride (1.90 ml, 11.31 mmol). The resulting mixture was stirred at room temperature for 1 hour, added 20 ml water, seperated by DCM (3x60 ml), dried on $MgSO_4$, and concentrated *in vacuo*. The crude product was purified by flash chromatography (petroleumether: ethyl acetate, 6:1) to give 1.99 g (75%) of the product as white powder. Mp = 87-88 °C (EtOH). IR (KBr): 1419, 1207, 1136 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.62 (s, 3H), 2.73 (s, 3H), 7.46 (d, J = 6.91 Hz, 1H), 7.57-7.62 (m, 2H), 7.90-7.92 (m, 2H), 8.50 (d, J = 8.41 Hz, 1H), 8.60 (d, J = 8.41 Hz, 1H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 19.9, 22.0, 114.6, 117.0, 119.7, 120.9, 121.2, 123.5, 127.6, 128.5, 130.2, 130.4, 135.6, 138.0, 147.6.

6.15 1,7-dimethylphenanthrene (7d)

6d (2.00 g, 5.66 mmol) was stirred at 70 °C in a flask with $Pd(OAc)_2$ (0.02 g, 0.11 mmol), PPh_3 (0.06 g, 0.22 mmol), Et_3N (2.37 ml, 16.99 mmol), and HCO_2H (0.46 ml, 11.33 mmol) in DMF (60 ml) for 2 hours, cooled to room temperature and treated with water (60 ml). The solution was extracted with Et_2O (3x60 ml), the combined organic layers was dried with $MgSO_4$ and concentrated *in vacuo*. The crude product was purified with flash cromatography (petroleumether: ethyl acetate, 8:1) to afford **7d** (1.33 g, quant.) as a yellow solid. Mp = 70 °C (hexane). IR (KBr): 2933 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ: 2.54 (s, 3H), 2.72 (s, 3H), 7.38-7.53 (m, 3H), 7.65-7.70 (m, 2H), 7.90 (d, J = 9.31 Hz, 1H), 8.50-8.57 (m, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$) δ: 20.2, 21.7, 120.9, 123.1, 126.3, 126.6, 127.5, 128.2, 128.6, 128.7, 130.6, 130.7, 132.0, 135.0, 136.3.

6.16 1-[(Z/E)-2-(3-methoxyphenyl)ethenyl]naphtalene (10)

3-methoxybenzaldehyde (**8**) (4.62 g, 33.93 mmol) and (naphthalen-1-ylmethyl)triphenylphosphanium chloride (**9**) (20.87 g, 47.54 mmol) was dissolved in DCM (380 ml) and added NaOH (50%, 47.5 ml) before being stirred for three days at room temperature. The reaction was then quenched with water (0.5L) and extracted with DCM (3x0.5L), dried with magnesium sulphate and concentrated in vacuo. This affordet 8.83 g (quant.) product **10** as white powder. All experimental data was identical to litterature [71].

6.17 2- and 4-methoxychrysene (11a and 11b)

This reaction was done with three seperate reactions since the photoreactor only could handle a maximum of three grams. **10** (8.82 g, 33.88 mmol) was dissolved in degassed toluene (3.6L), and added epoxybutane (43.74 ml, 0.51 mol) and iodine (9.55g, 37.57 mmol). The reaction mixture was stirred under inert atmosphere and reacted with ultraviolet irridation for four hours. Half of the volume was then evaporated before being washed with sodium thiosulphate (900 ml), extracted with EtOAc (3x900 ml), dried over $MgSO_4$ and concentrated *in vacuo*. 2-methoxychrysene was isolated by recrystillization with acetone to afford 3.23 g (37%) of product **11a** as a white powder. 4-methoxychrysene was isolated by flash column chromatography (Petroleum ether:EtOAc, 19:1) to afford 2.66 g (30%) of product **11b** as a white powder. All experimental data was identical to litterature [71].

6.18 Chrysene-2-yl N,N-diethylcarbamate (13a)

11a (0.99 g, 3.85 mmol) was dissolved in DCM (40 ml) and added BBr_3 (5.77 ml, 5.77 mmol) at 0 °C and stirred at room temperature for 21 hours. The reaction was quenched with water (20 ml) and concentrated in vacuo before extracted with EtOAc (3x40 ml), dried over $MgSO_4$ and concentrated *in vacuo*.

12a (3.85 mmol) in THF (18 ml) was added to a suspension of NaH (0.23 g, 5.77 mmol) in THF (12 ml) at 0 °C. After 15 minutes the reaction was heated to room temperature before N,N-diethylcarbamoyl chloride (0.45 ml, 3.94 mmol) was added. The reaction mixture was stirred for 21 hours before being quenched with saturated ammonium chloride (25 ml) and concentrated *in vacuo*. It was then extracted with EtOAc (3x40 ml), dried over $MgSO_4$ and concentrated in vacuo. **13a** was isolated by flash column chromatography (petroleum ether:EtOAc, 3:1 with 10% DCM) to afford 0.99 g (75%) as a white powder. All experimental data was identical to litterature [71].

6.19 Chrysene-4-yl N,N-diethylcarbamate (13b)

11b (1.03 g, 3.98 mmol) was dissolved in DCM (40 ml) and added BBr_3 (5.98 ml, 5.98 mmol) at 0 °C and stirred at room temperature for 21 hours. The reaction was quenched with water (20 ml) and concentrated in vacuo before extracted with EtOAc (3x40 ml), dried over $MgSO_4$ and concentrated *in vacuo*.

12b (3.98 mmol) in THF (18 ml) was added to a suspension of NaH (0.24 g, 5.98 mmol) in THF (12 ml) at 0 °C. After 15 minutes the reaction was heated to room temperature before N,N-diethylcarbamoyl chloride (0.53 ml, 4.18 mmol) was added. The reaction mixture was stirred for 21 hours before being quenched with saturated ammonium chloride (25 ml) and concentrated in vacuo. It was then extracted with EtOAc (3x40 ml), dried over $MgSO_4$ and concentrated *in vacuo*. **13b** was isolated by flash column chromatography (petroleum ether:EtOAc, 3:1 with 10% DCM) to afford 0.44 g (33%) as a white powder. All experimental data was identical to litterature [71].

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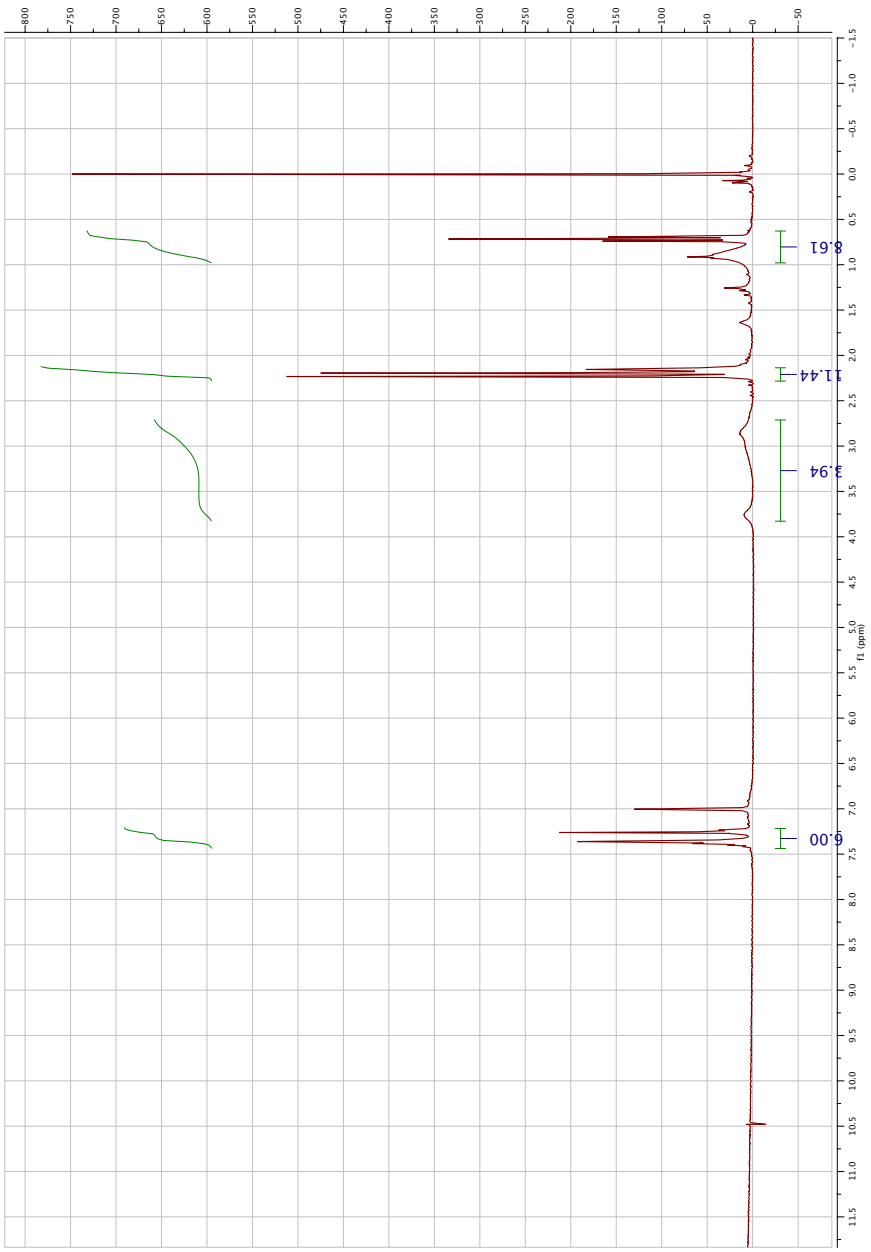

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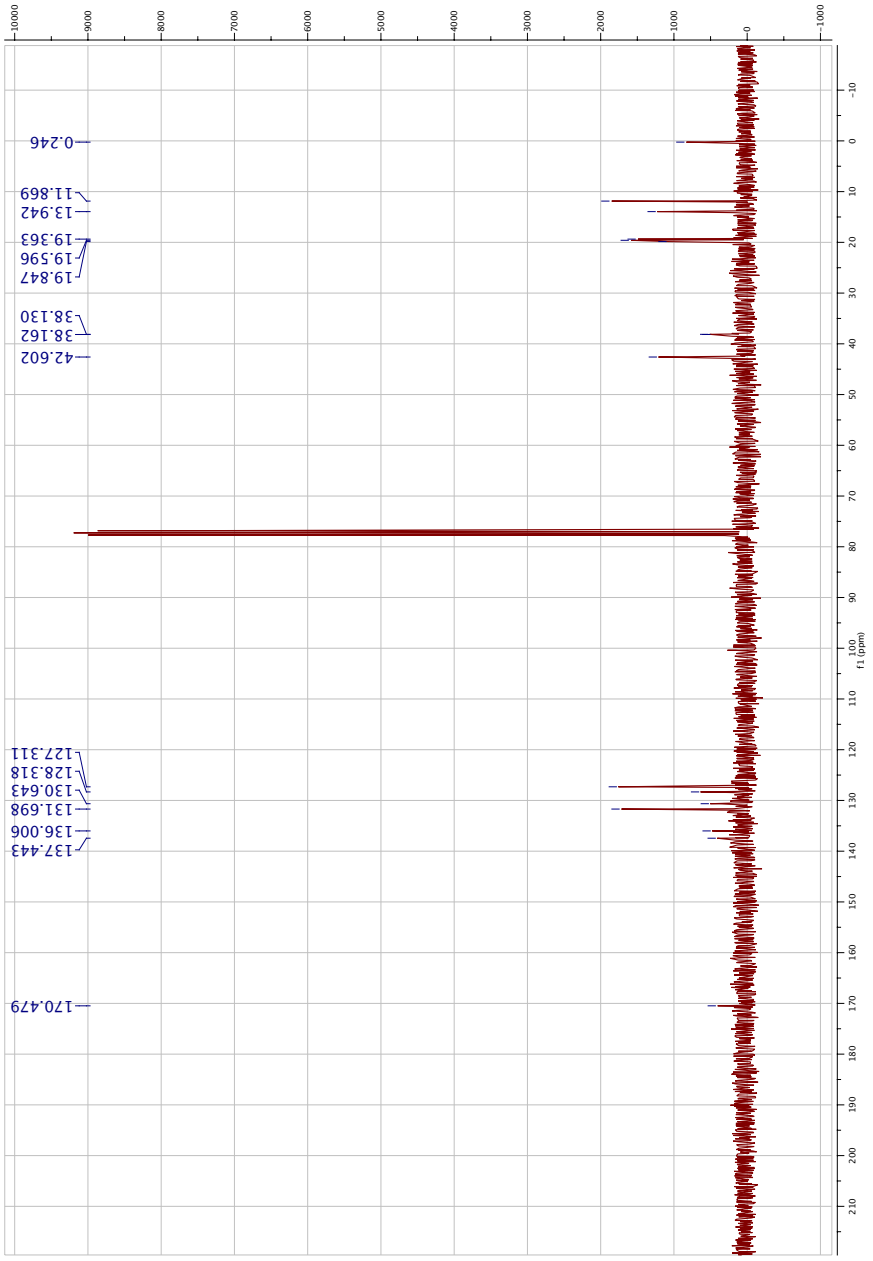
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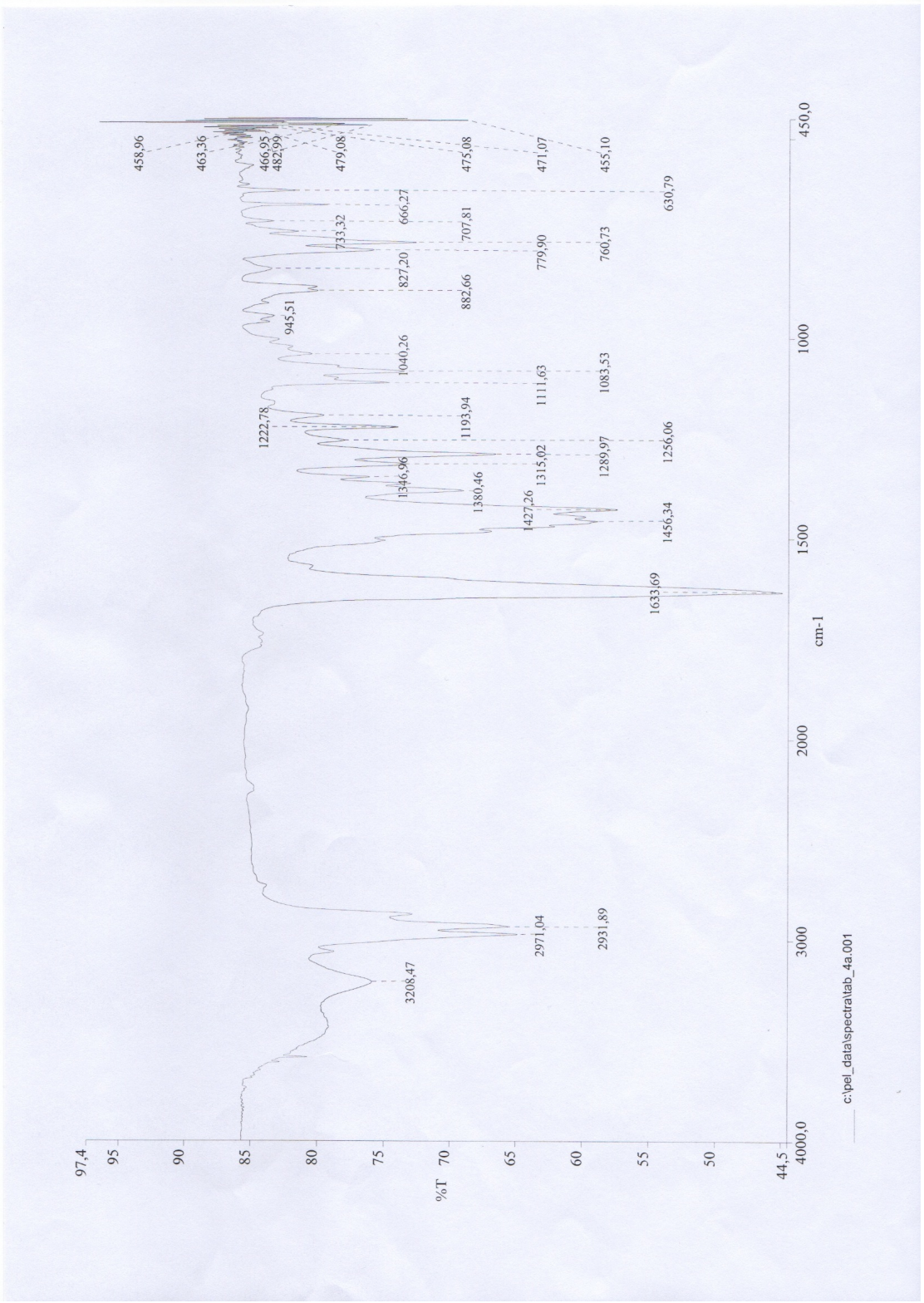
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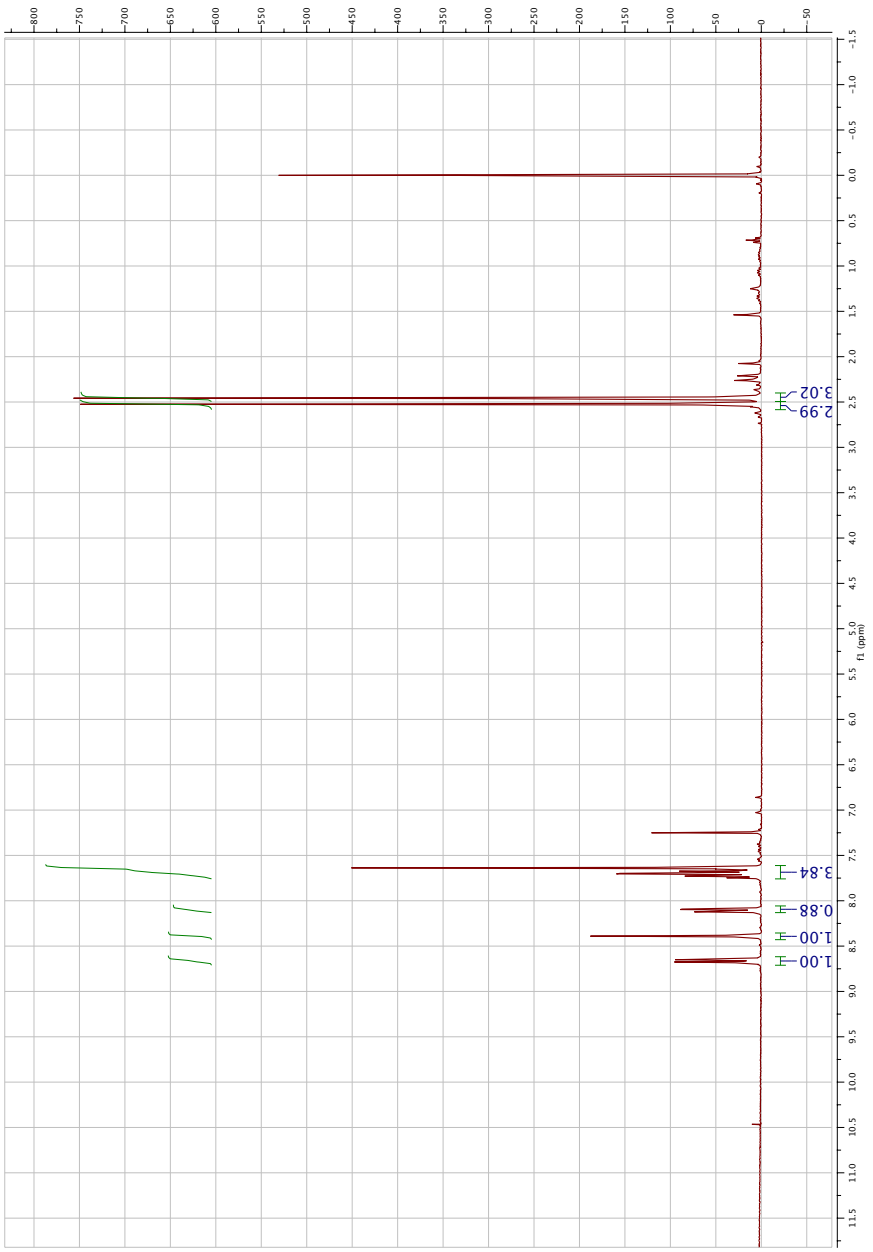

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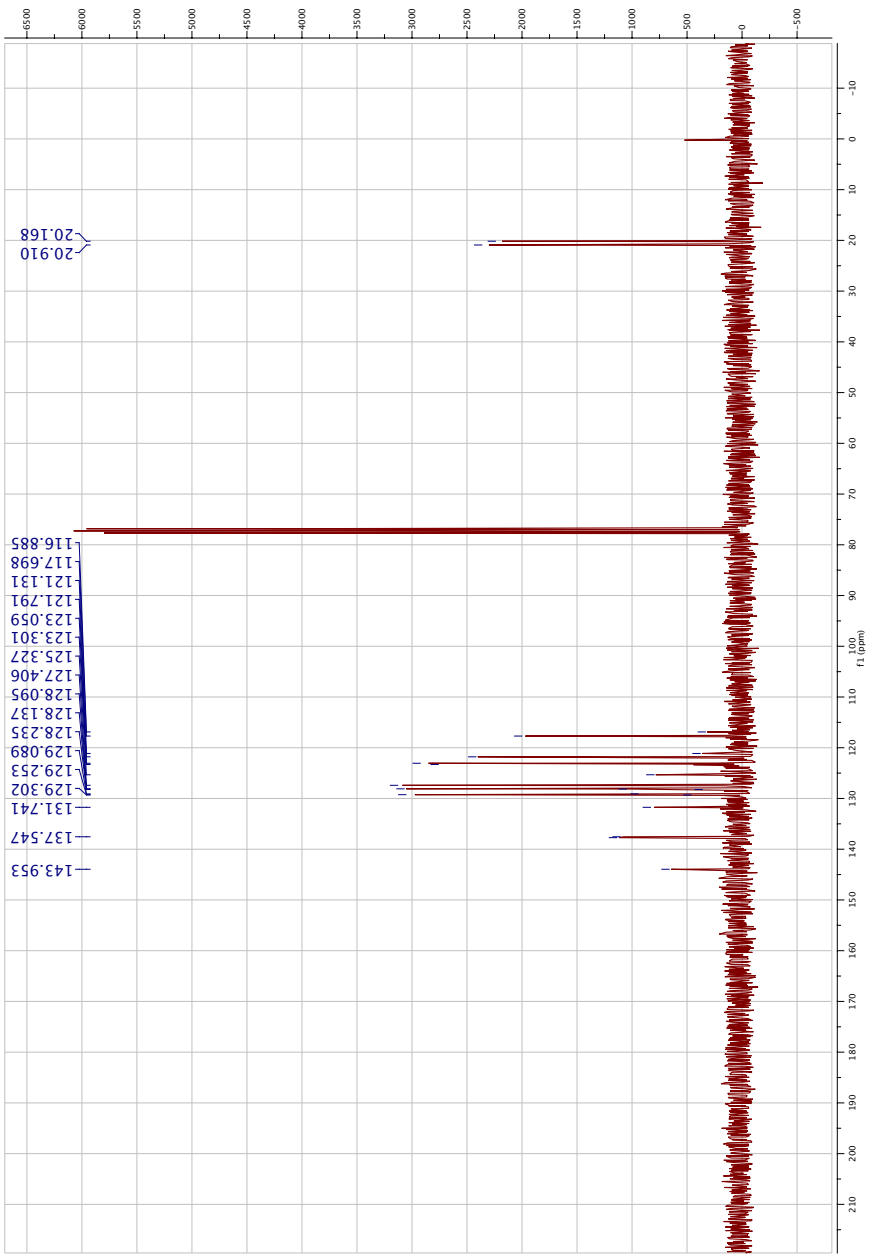
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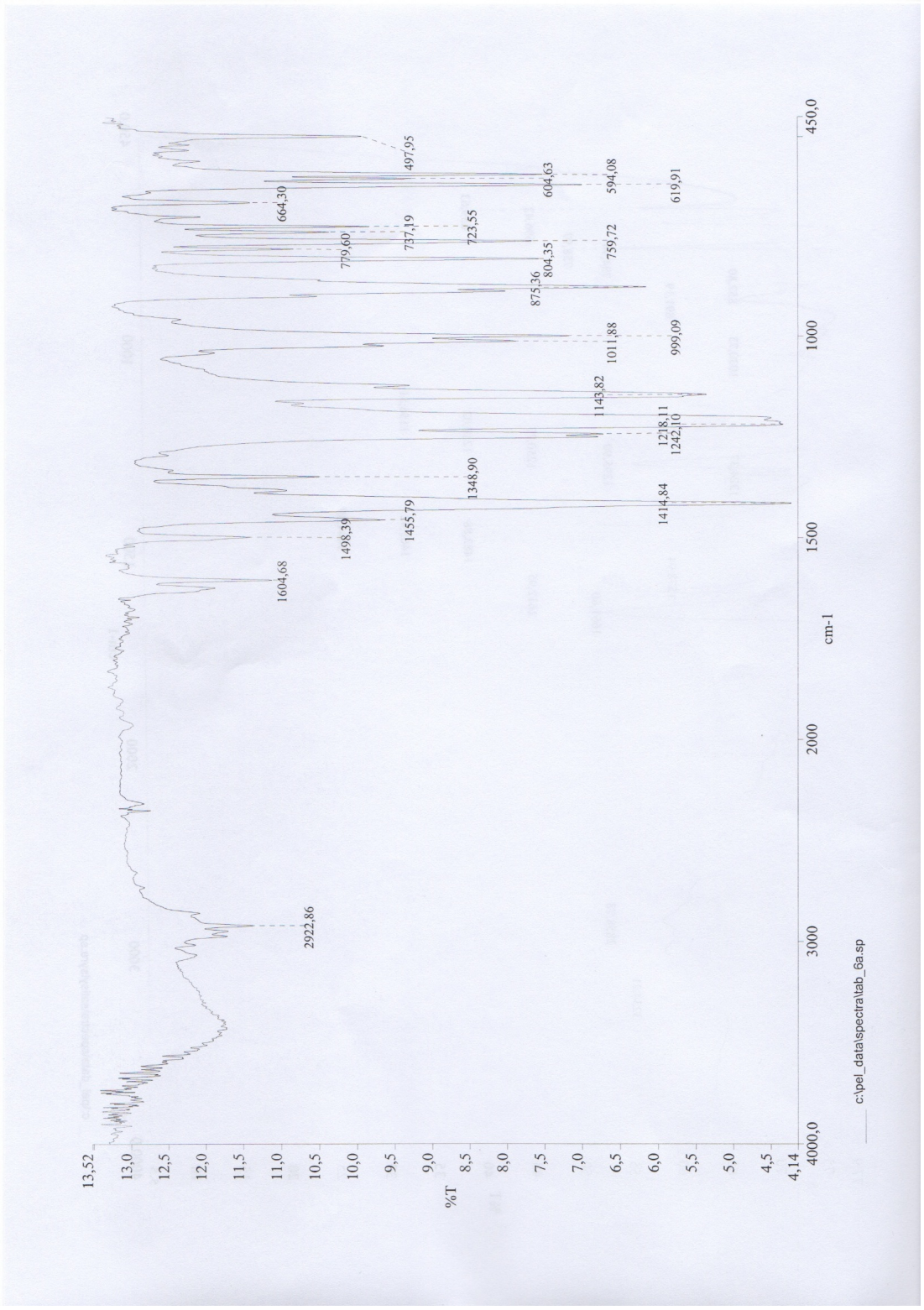
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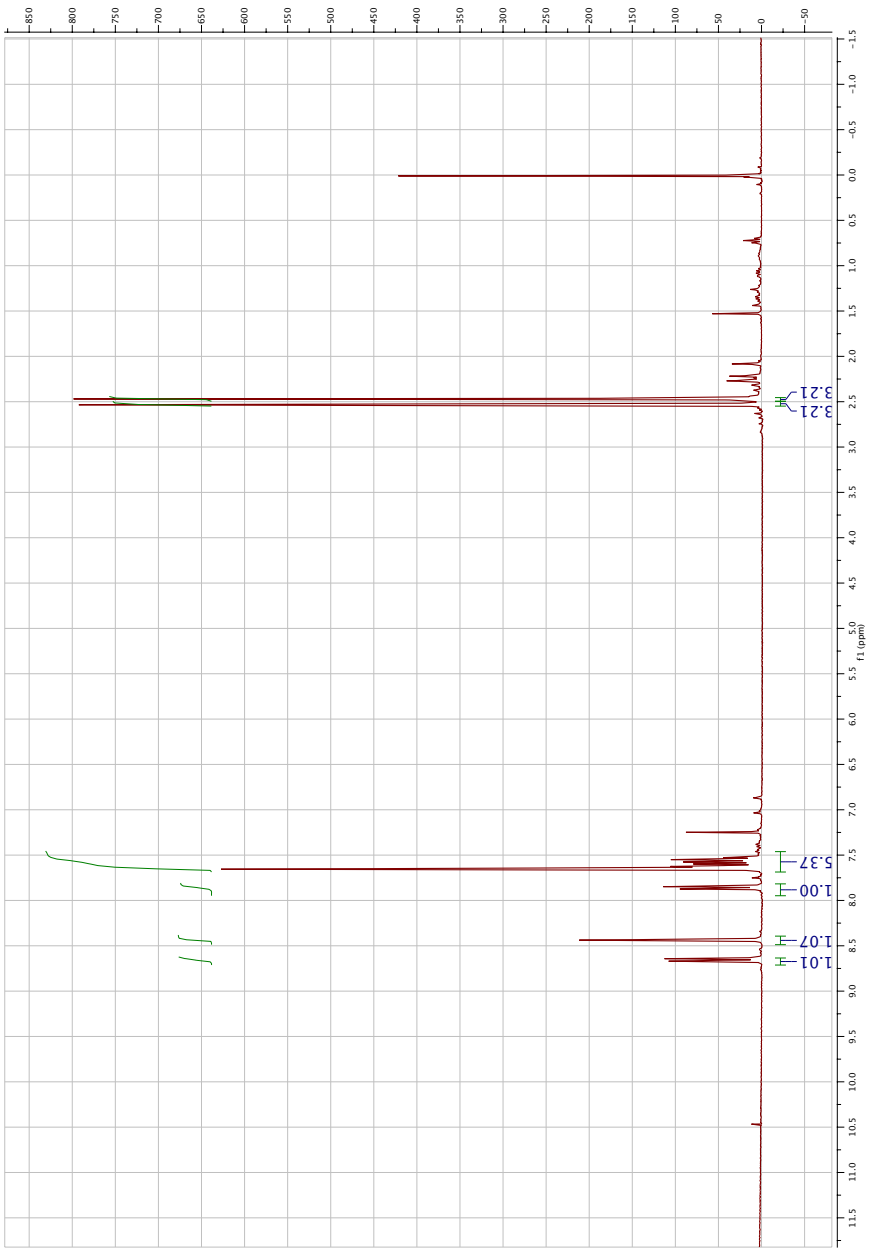

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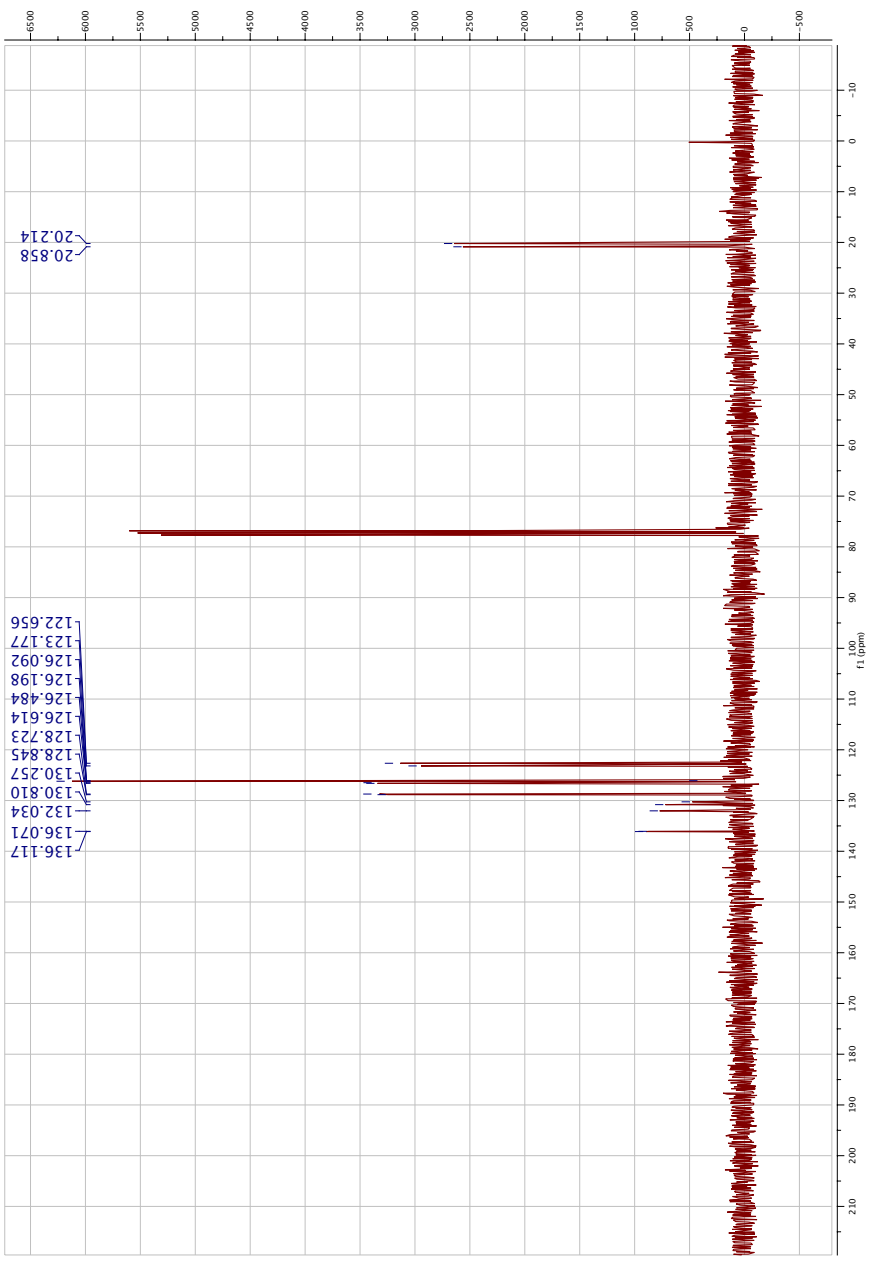
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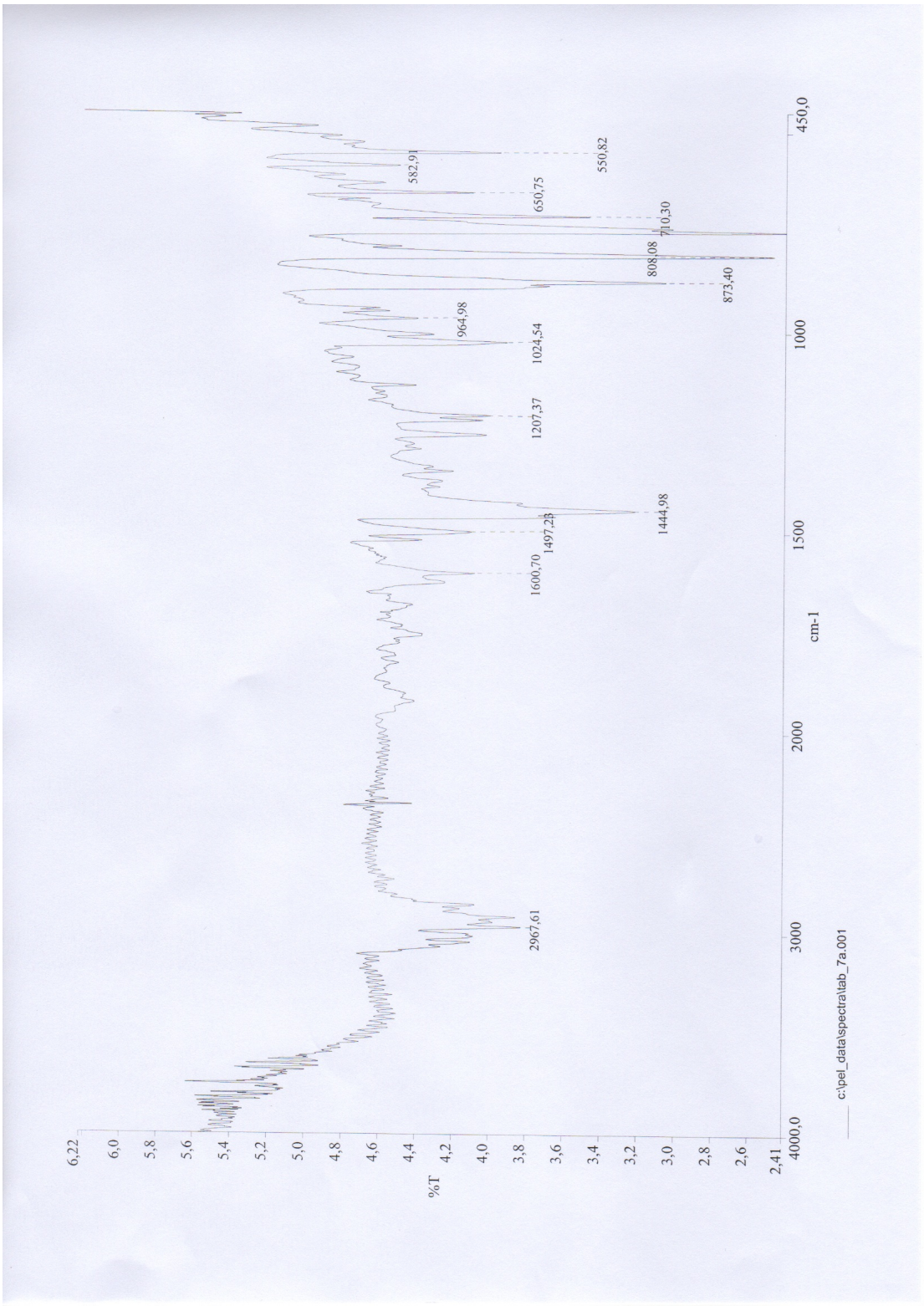
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D 4b

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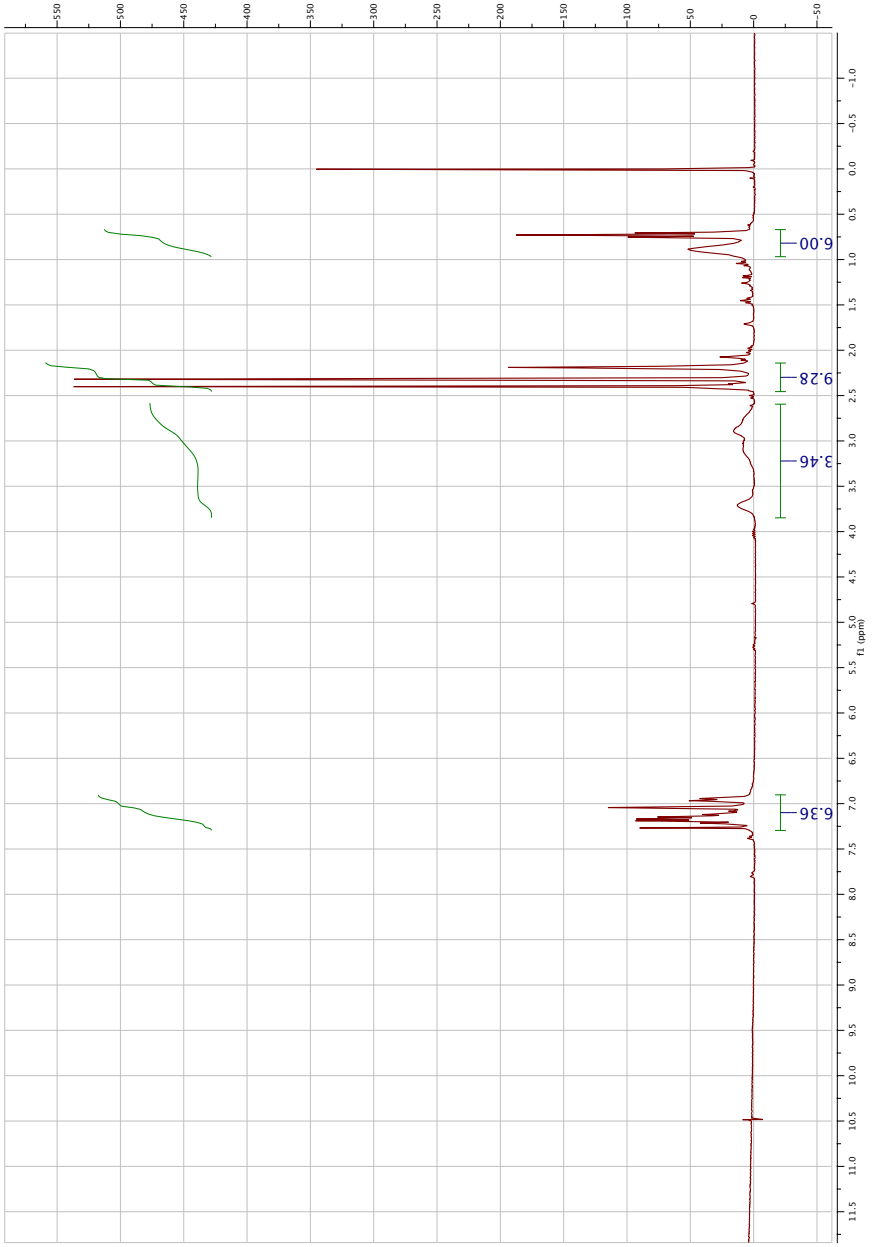

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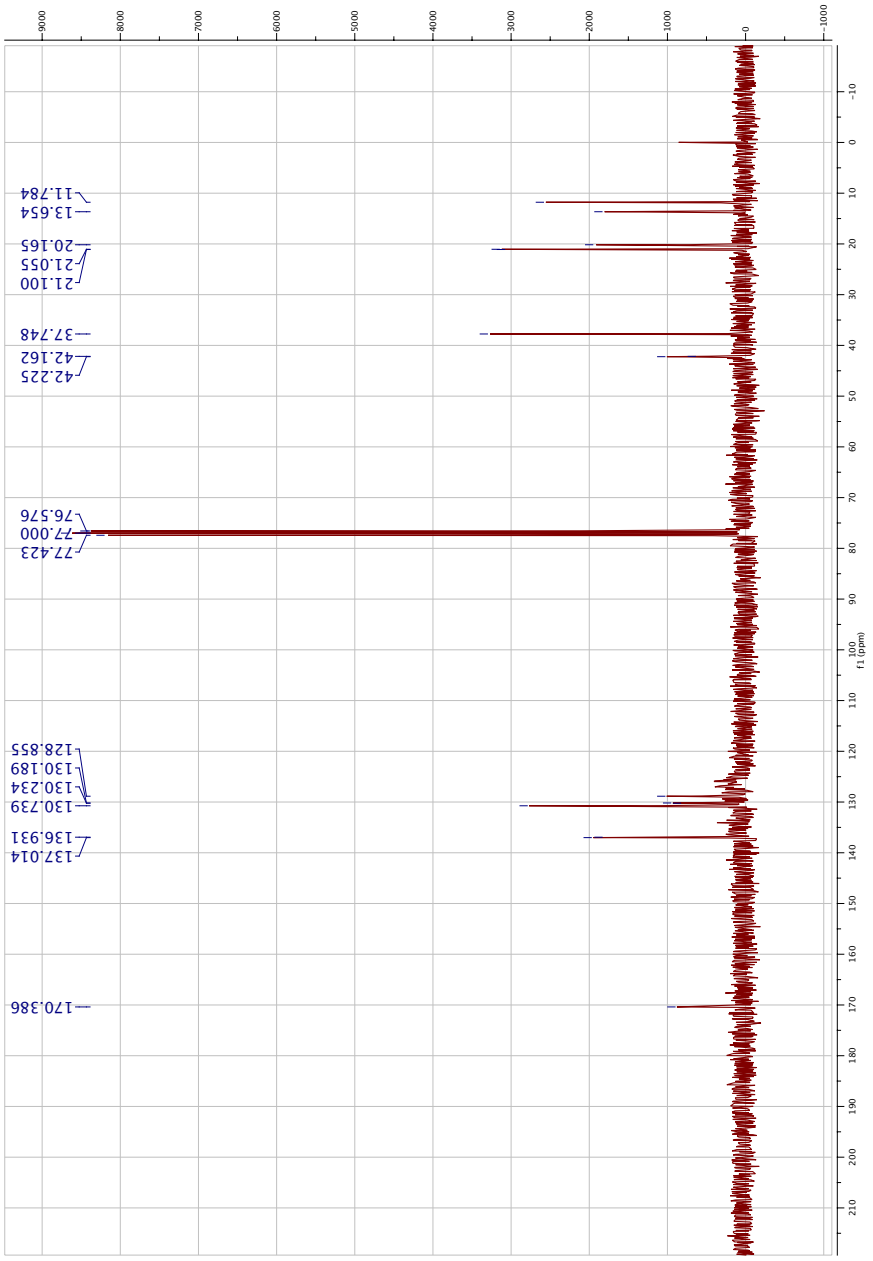
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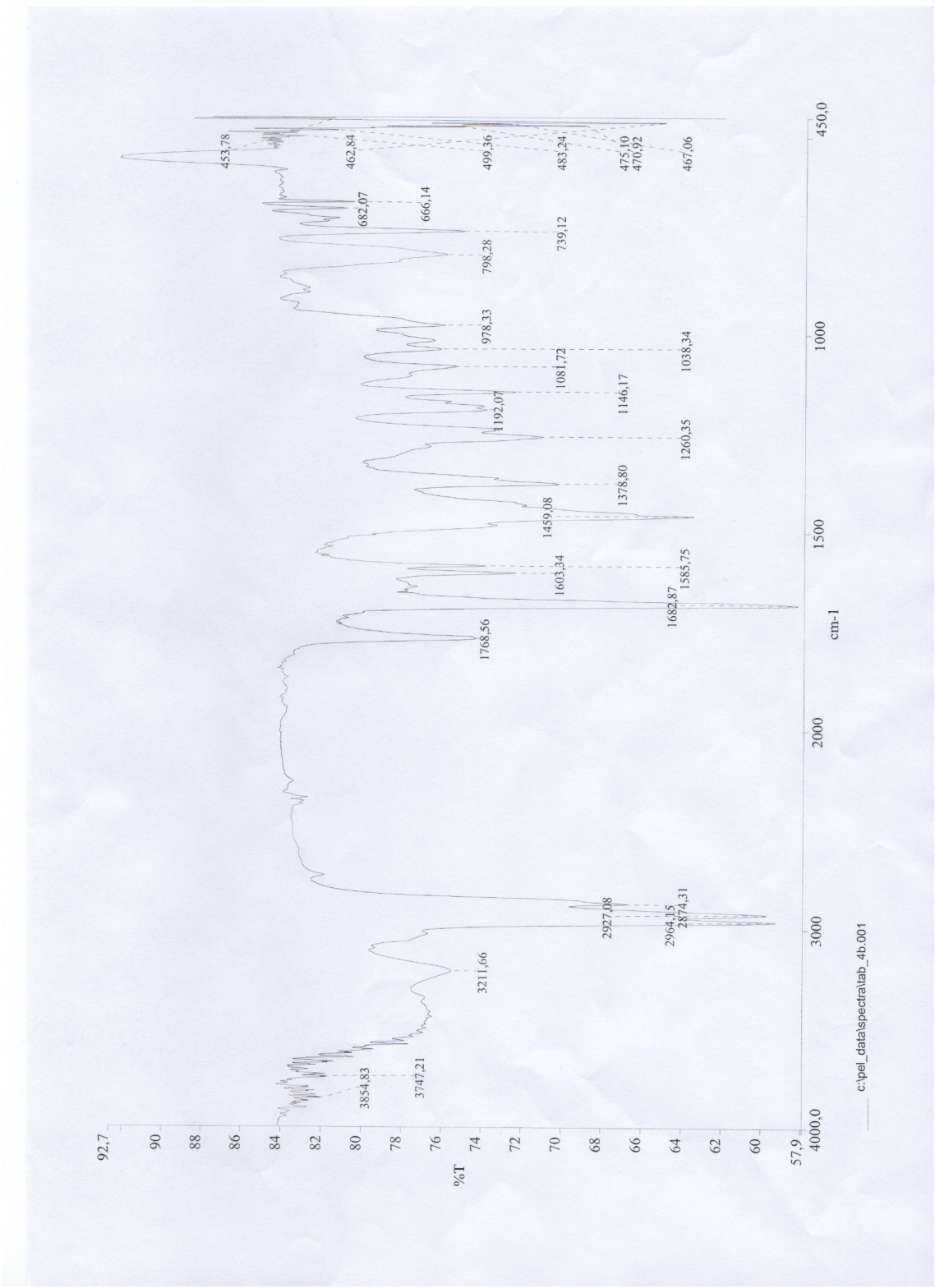
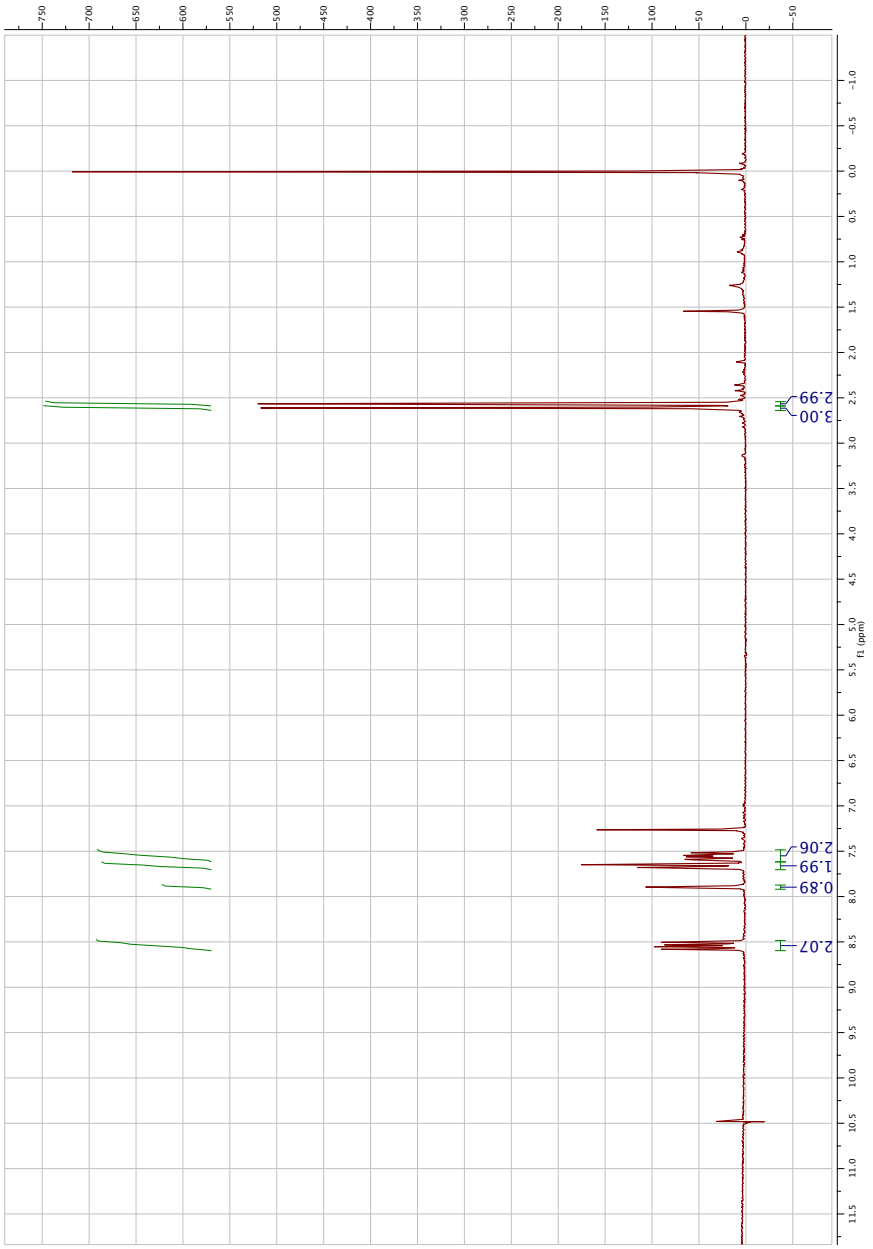
136.931
137.014
170.386
f1 (ppm)

D.3 4b IR.

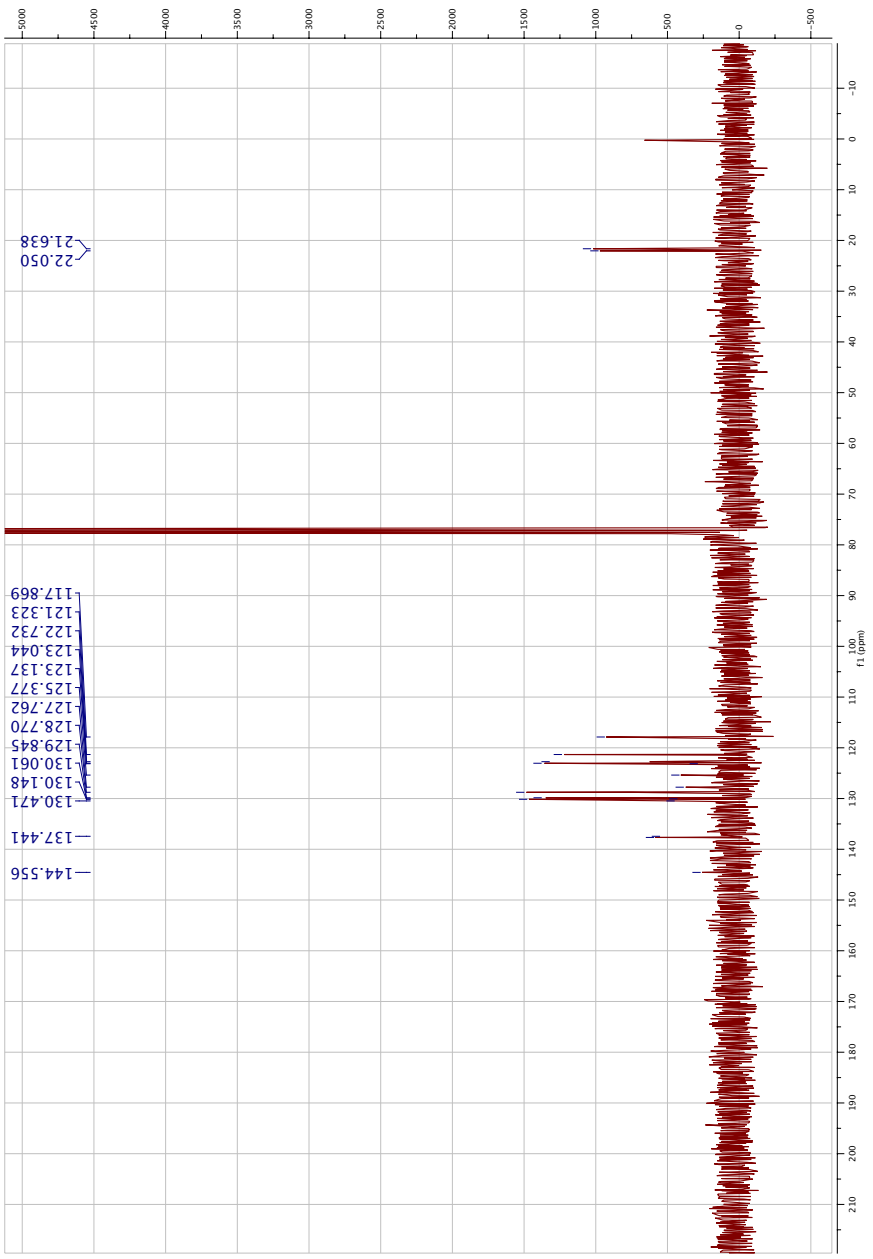

453,78
462,84
499,36
483,24
475,10
470,92
467,06
682,07
666,14
798,28
739,12
978,33
1081,72
1038,34
1192,07
1146,17
1260,35
1378,80
1459,08
1603,34
1585,75
1682,87
1768,56
2927,08
2964,15
2874,31
3211,66
3747,21
3854,83
%T
cm-1
c:\pel_data\spectra\tab_4b.001

E 6b

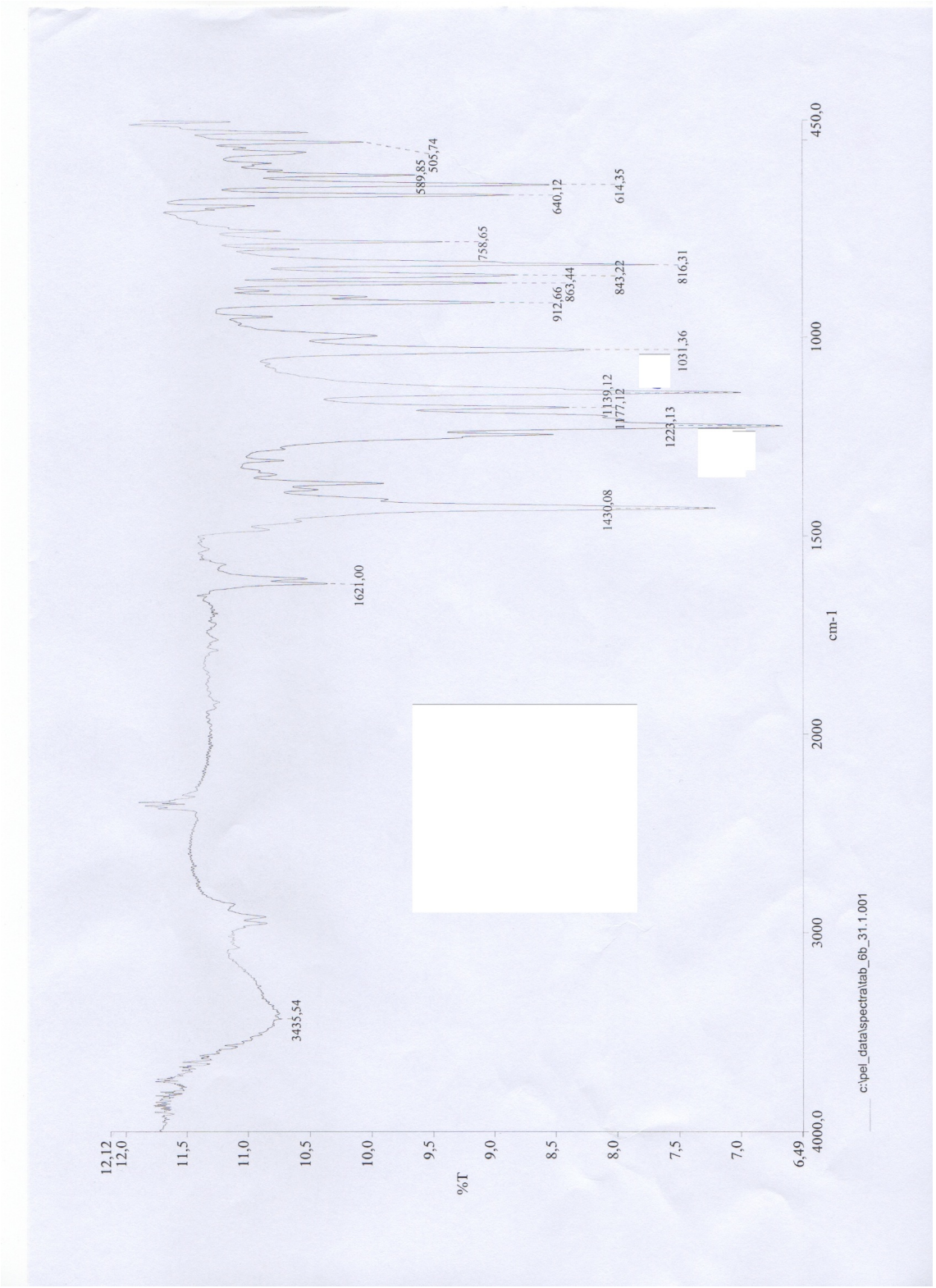
E.1 6b proton-nmr.



E.2 6b C13-nmr.

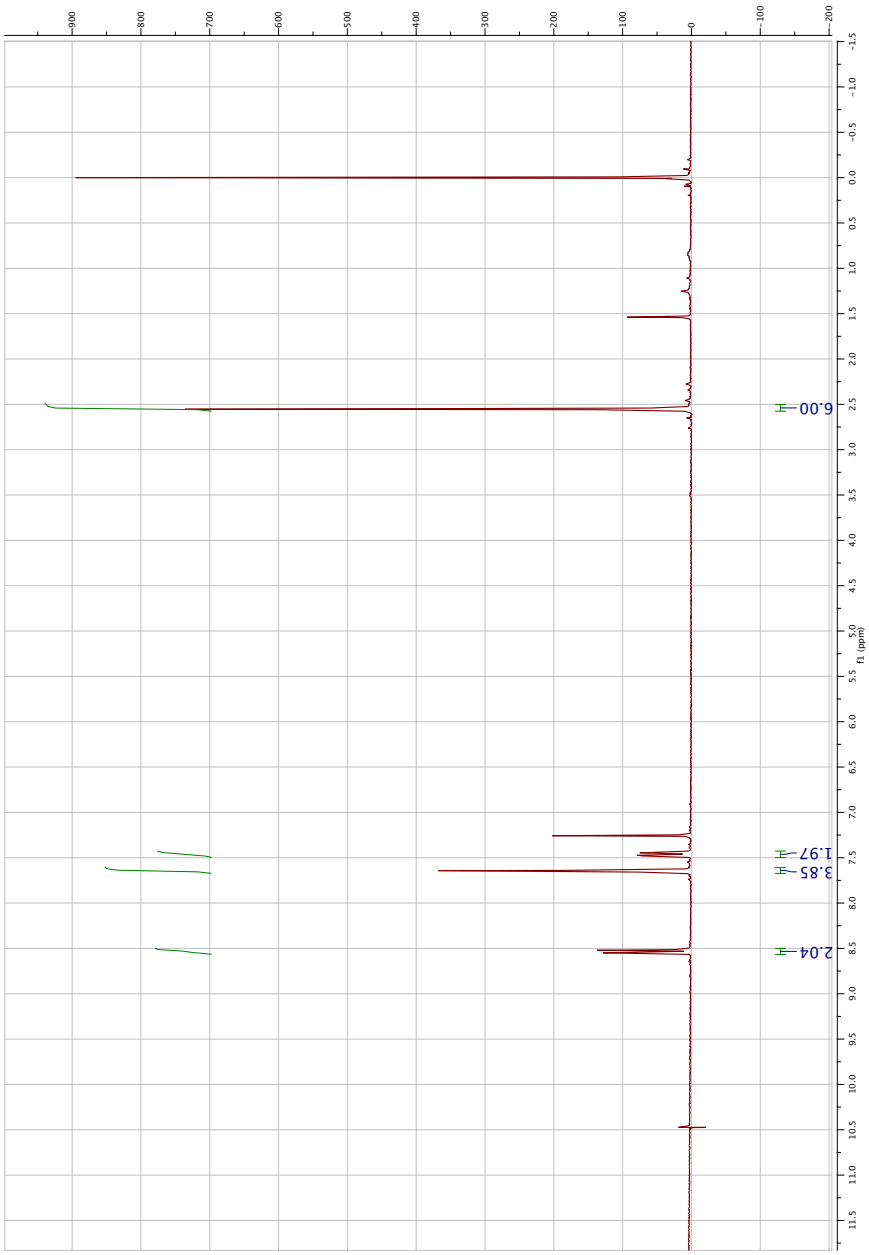

22.050
21.638
117.869
121.323
122.732
123.044
123.137
125.377
127.762
128.770
129.845
130.061
130.148
130.471
137.441
144.556
f1 (ppm)

E.3 6b IR.

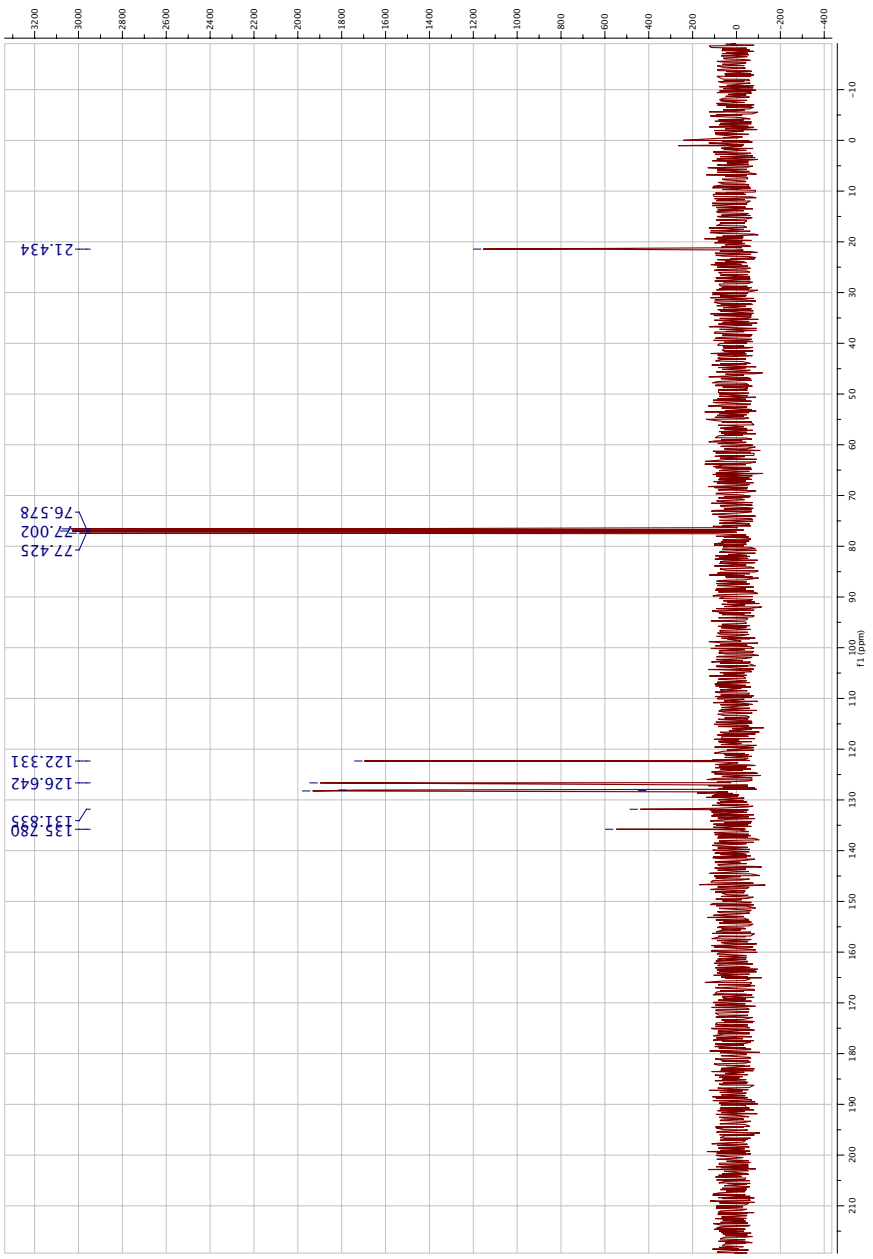

3435,54
1621,00
1430,08
1223,13
1177,12
1139,12
1031,36
912,66
863,44
843,22
816,31
758,65
640,12
614,35
589,85
505,74
%T
cm-1
4000,0
3000
2000
1500
1000
450,0
12,12
12,0
11,5
11,0
10,5
10,0
9,5
9,0
8,5
8,0
7,5
7,0
6,49
c:\pel_data\spectra\tab_6b_31.1.001

F 7b

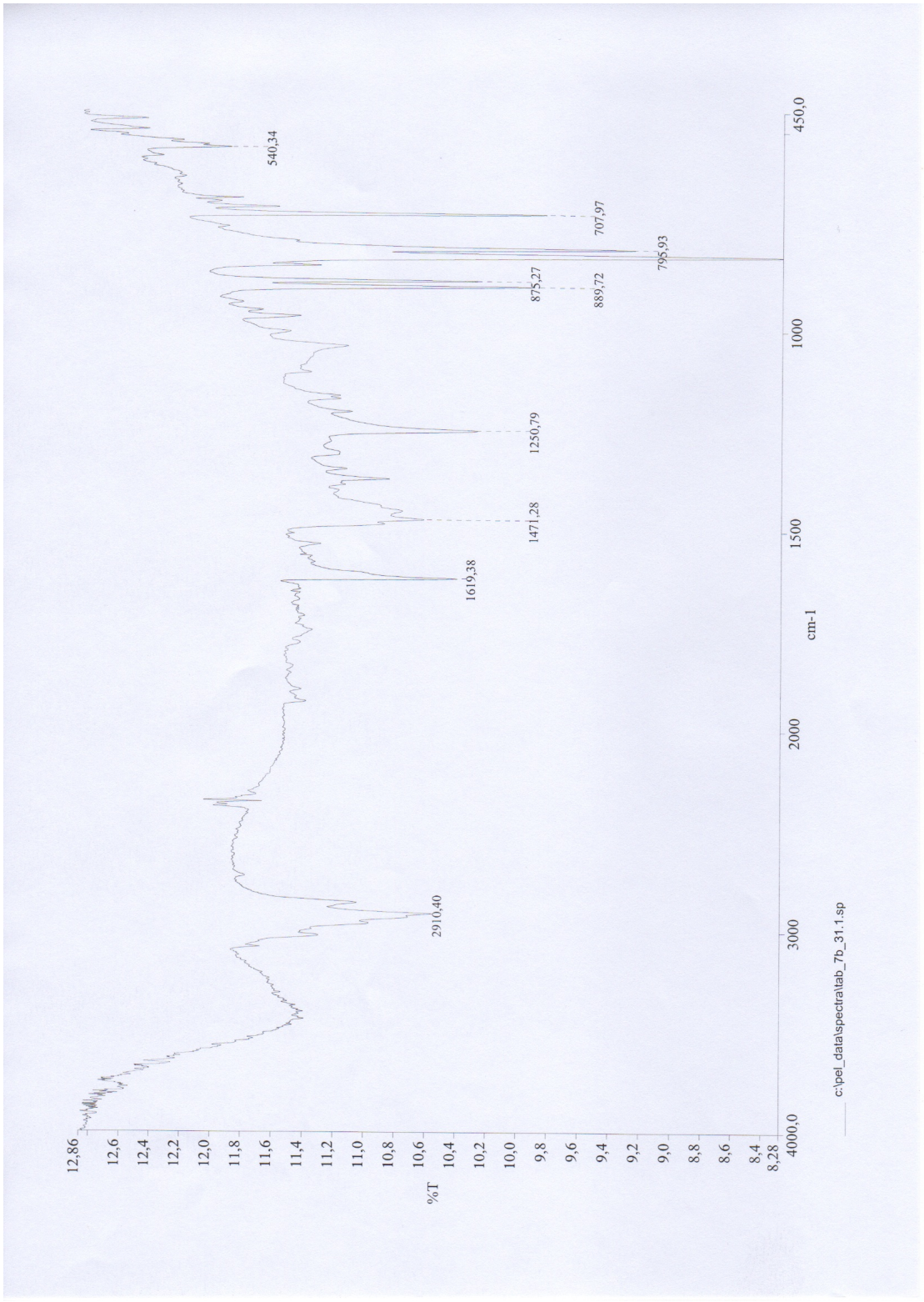
F.1 7b Proton-nmr.



F.2 7b C13-nmr.



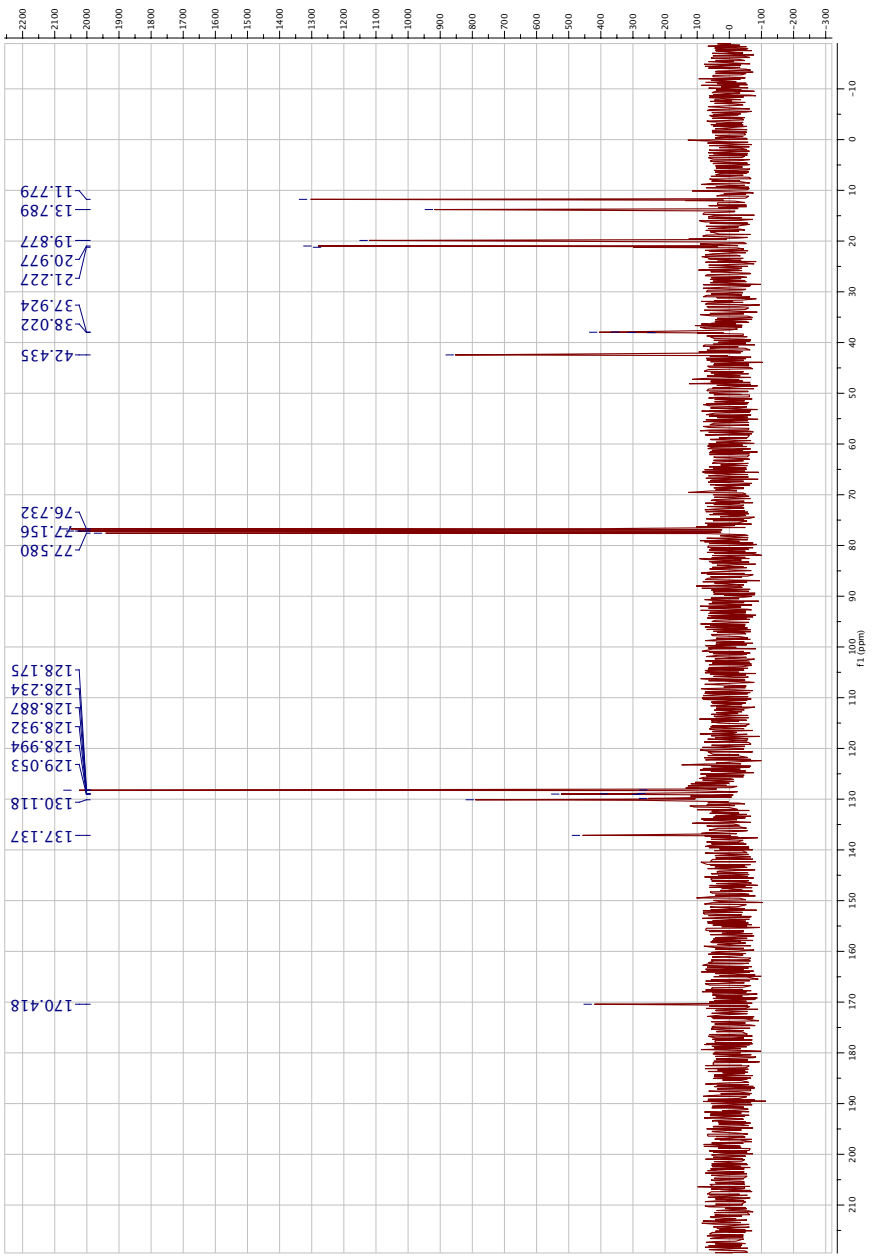
F.3 7b IR.


540,34
707,97
795,93
875,27
889,72
1250,79
1471,28
1619,38
2910,40
%T
cm-1
4000,0
3000
2000
1500
1000
450,0
12,86
12,6
12,4
12,2
12,0
11,8
11,6
11,4
11,2
11,0
10,8
10,6
10,4
10,2
10,0
9,8
9,6
9,4
9,2
9,0
8,8
8,6
8,4
8,28
c:\pel_data\spectra\tab_7b_31.1.sp

G 4c

G.1 4c proton-nmr.

G.2 4c C13-nmr.

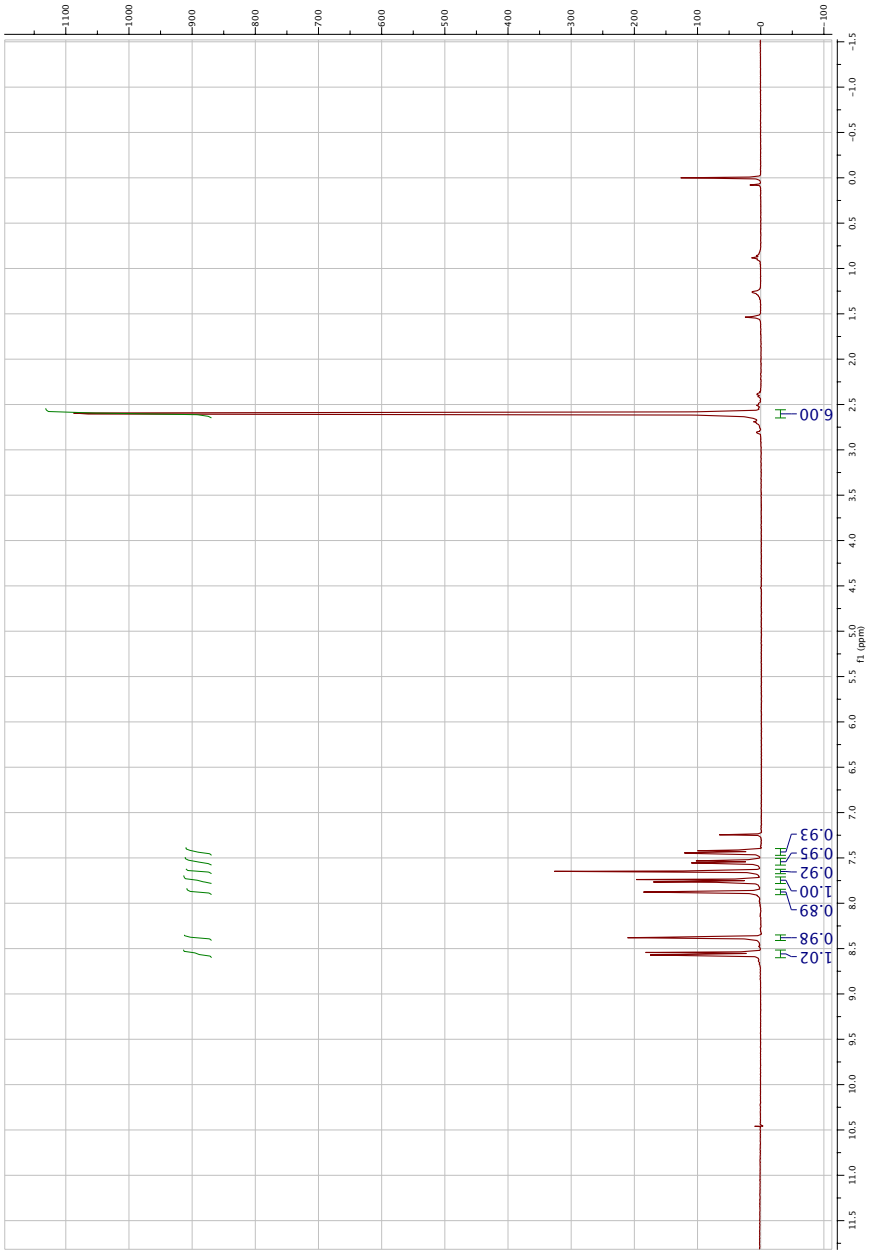

11.779
13.789
19.877
20.977
21.227
37.924
38.022
42.435
76.732
77.156
77.580
128.175
128.234
128.887
128.932
128.994
129.053
130.118
137.137
170.418
f1 (ppm)

G.3 4c IR.

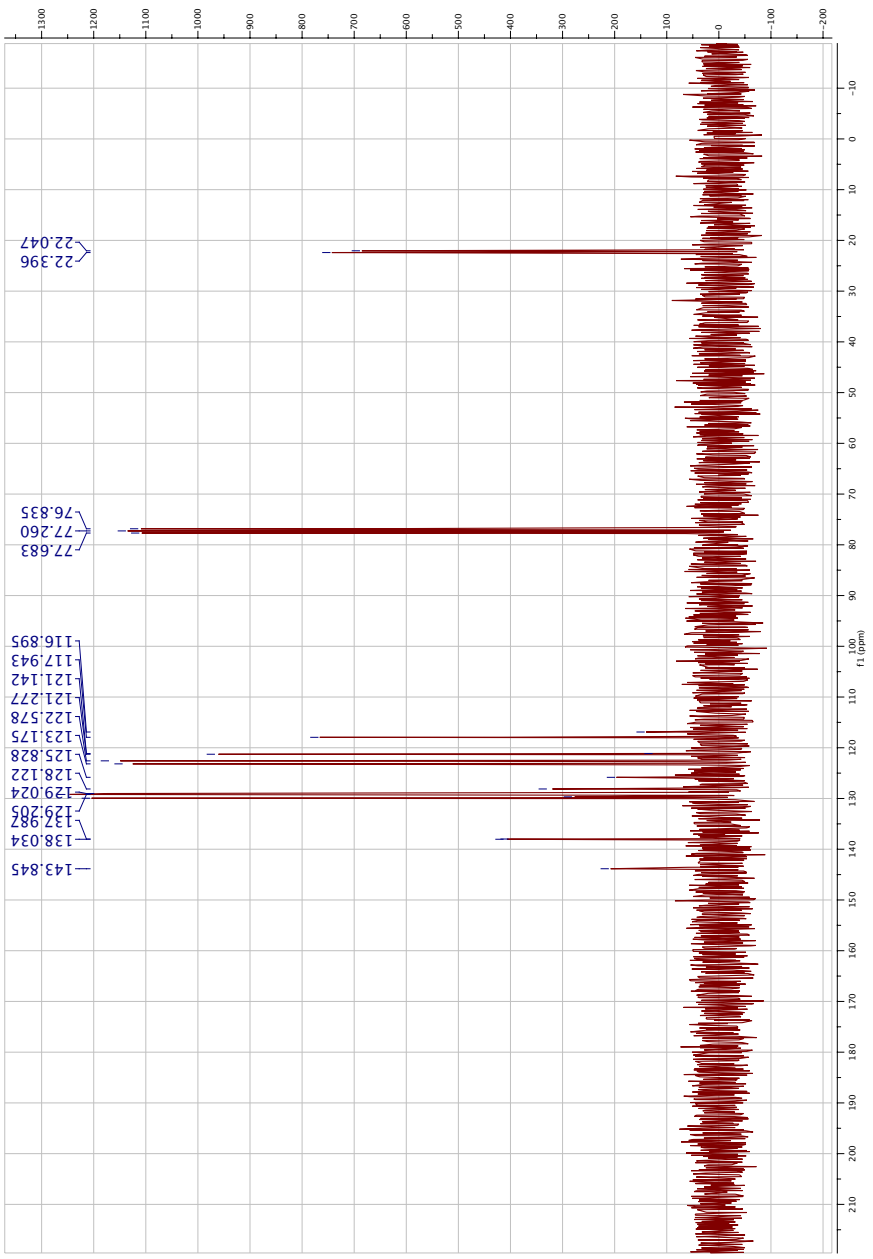

%T
cm-1
c:\pel_data\spectra\tab_4c.001
3236,86
2929,83
2871,43
2972,31
2733,88
2237,95
1910,44
1630,90
1458,87
1435,37
1473,26
1380,01
1362,93
1346,77
1314,71
1293,11
1256,68
1219,94
1184,25
1166,80
1135,37
1089,05
1069,57
1035,15
976,89
946,56
920,02
888,58
872,49
826,17
811,85
784,45
757,91
730,66
666,03
640,30
602,52
585,86
573,85
544,91
499,25
479,03
455,12
458,87
463,42
467,03
471,06
483,20

H 6c

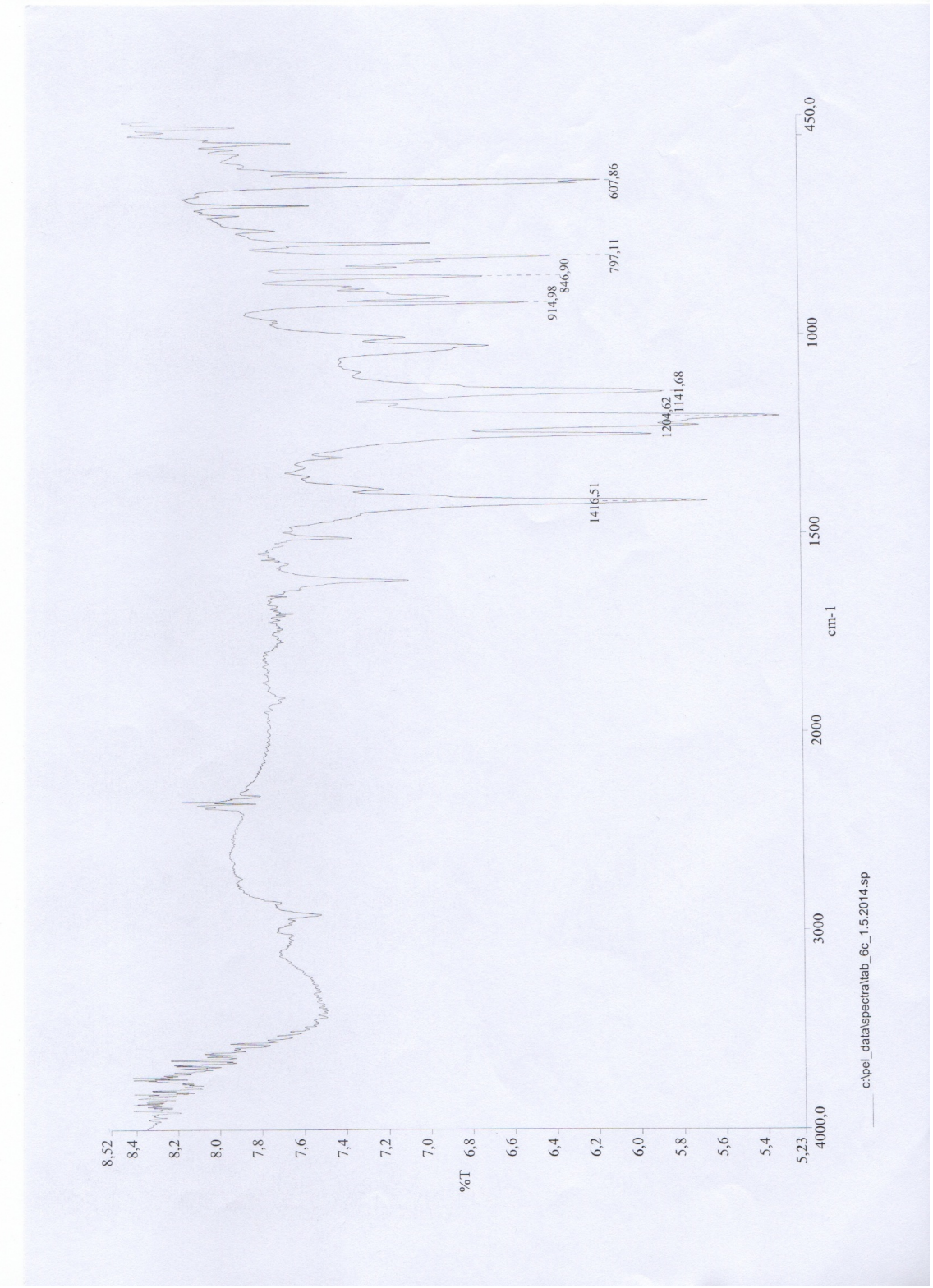
H.1 6c proton-nmr.



H.2 6c C13-nmr.

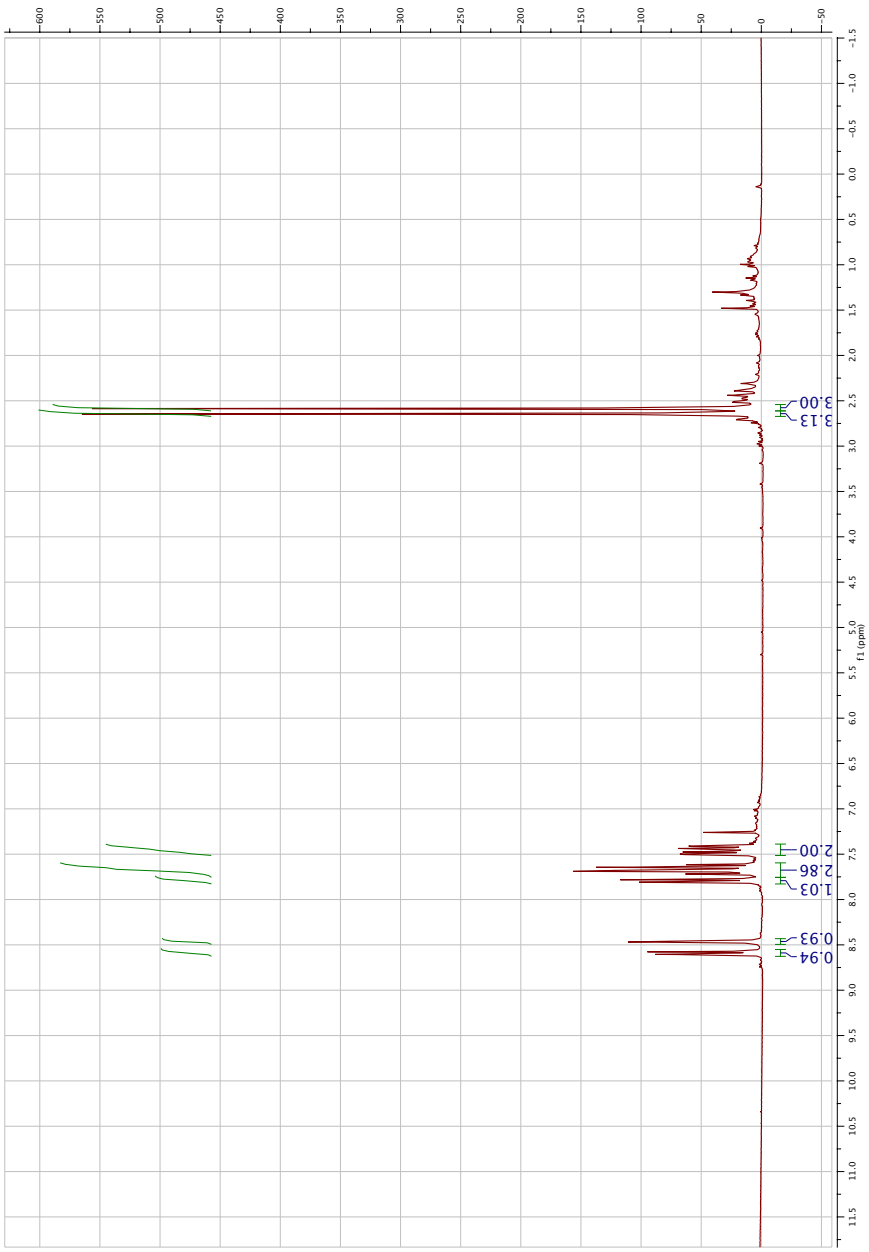

22.396
22.047
77.683
77.260
76.835
116.895
117.943
121.142
121.277
122.578
123.175
125.828
128.122
129.024
129.205
132.982
138.034
143.845
f1 (ppm)

H.3 6c IR.

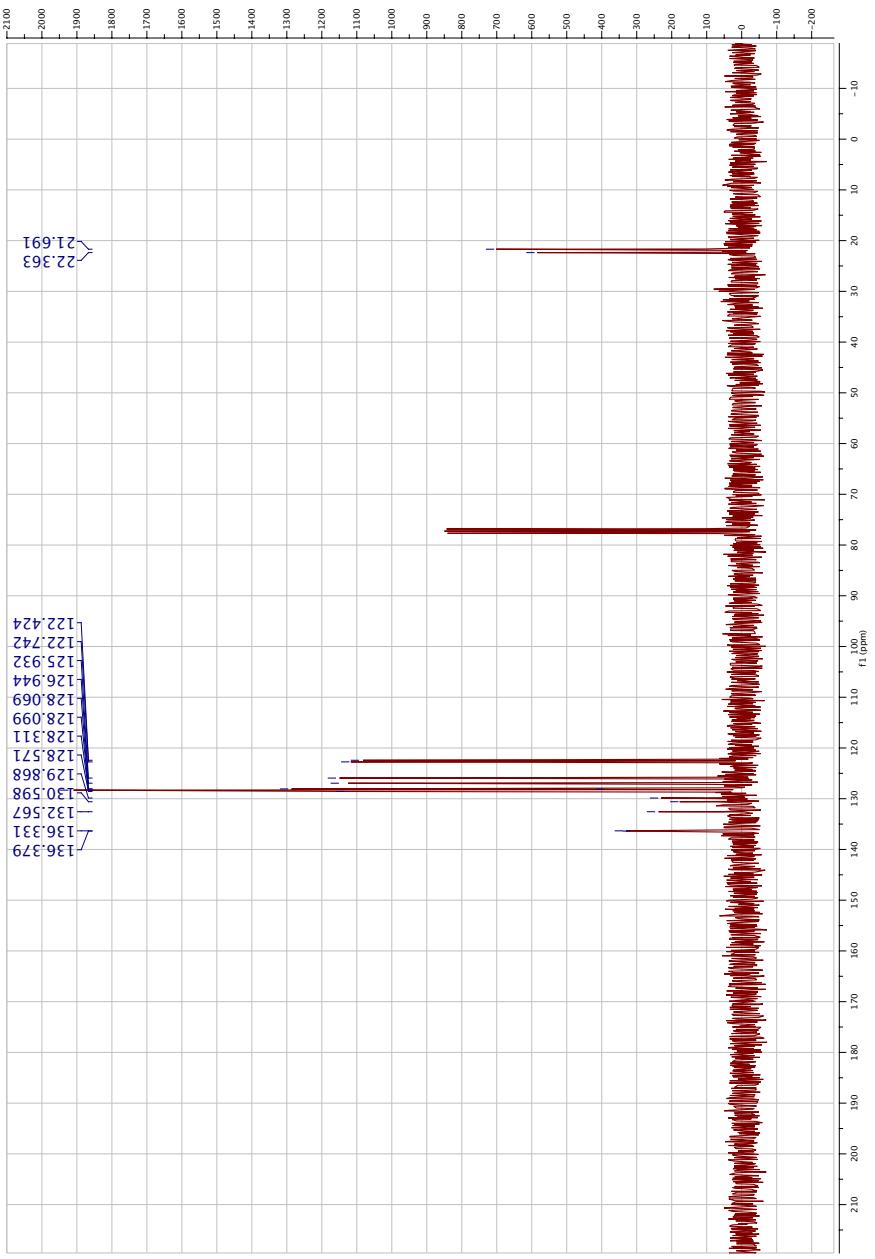

8,52
8,4
8,2
8,0
7,8
7,6
7,4
7,2
7,0
6,8
6,6
6,4
6,2
6,0
5,8
5,6
5,4
5,23
%T
4000,0
3000
2000
1500
1000
450,0
cm-1
1416,51
1204,62
1141,68
914,98
846,90
797,11
607,86
c:\pel_data\spectra\tab_6c_1.5.2014.sp

I 7c

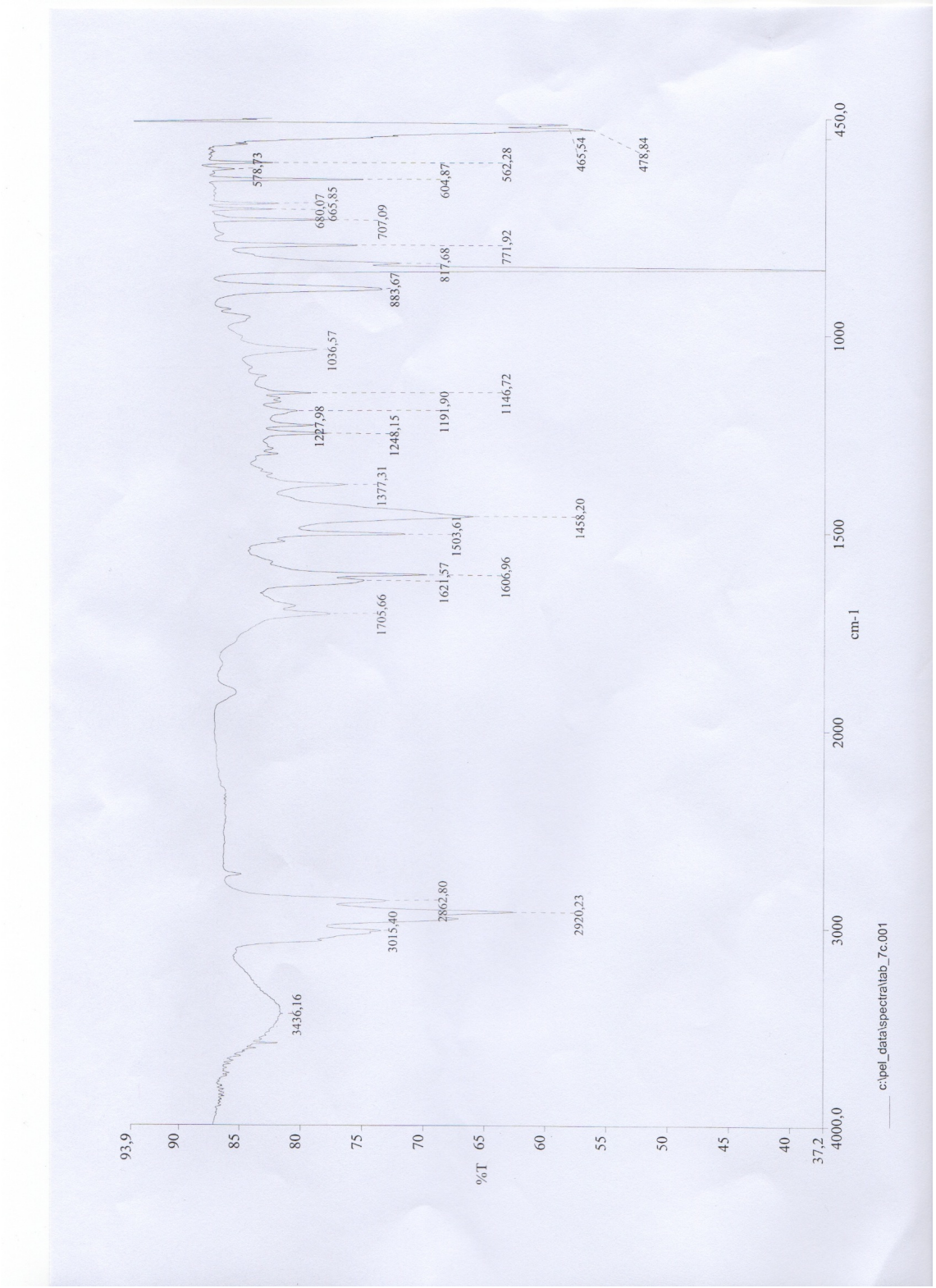
I.1 7c Proton-nmr.



I.2 7c C13-nmr.

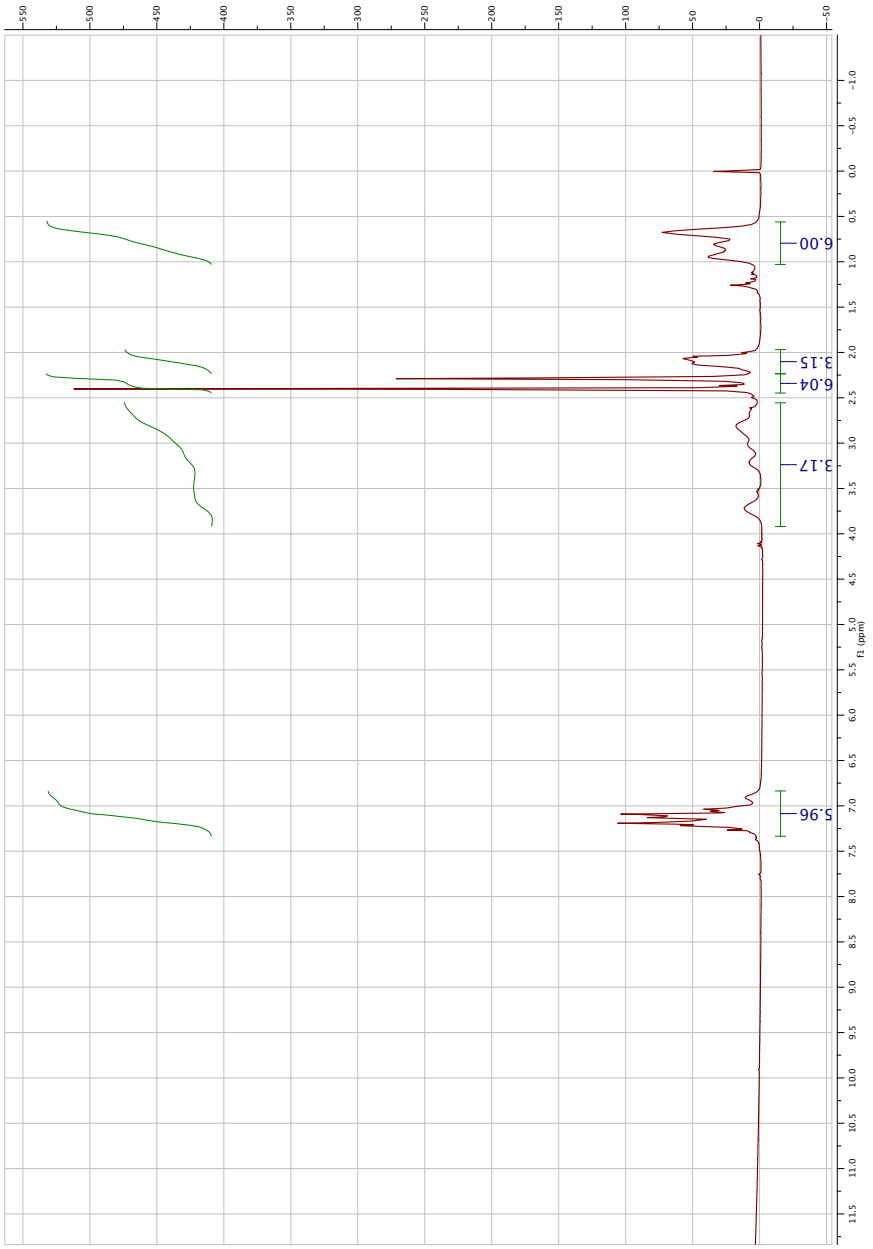

22.363
21.691
122.424
122.742
125.932
126.944
128.069
128.099
128.311
128.571
129.868
130.598
132.567
136.331
136.379
f1 (ppm)

I.3 7c IR.

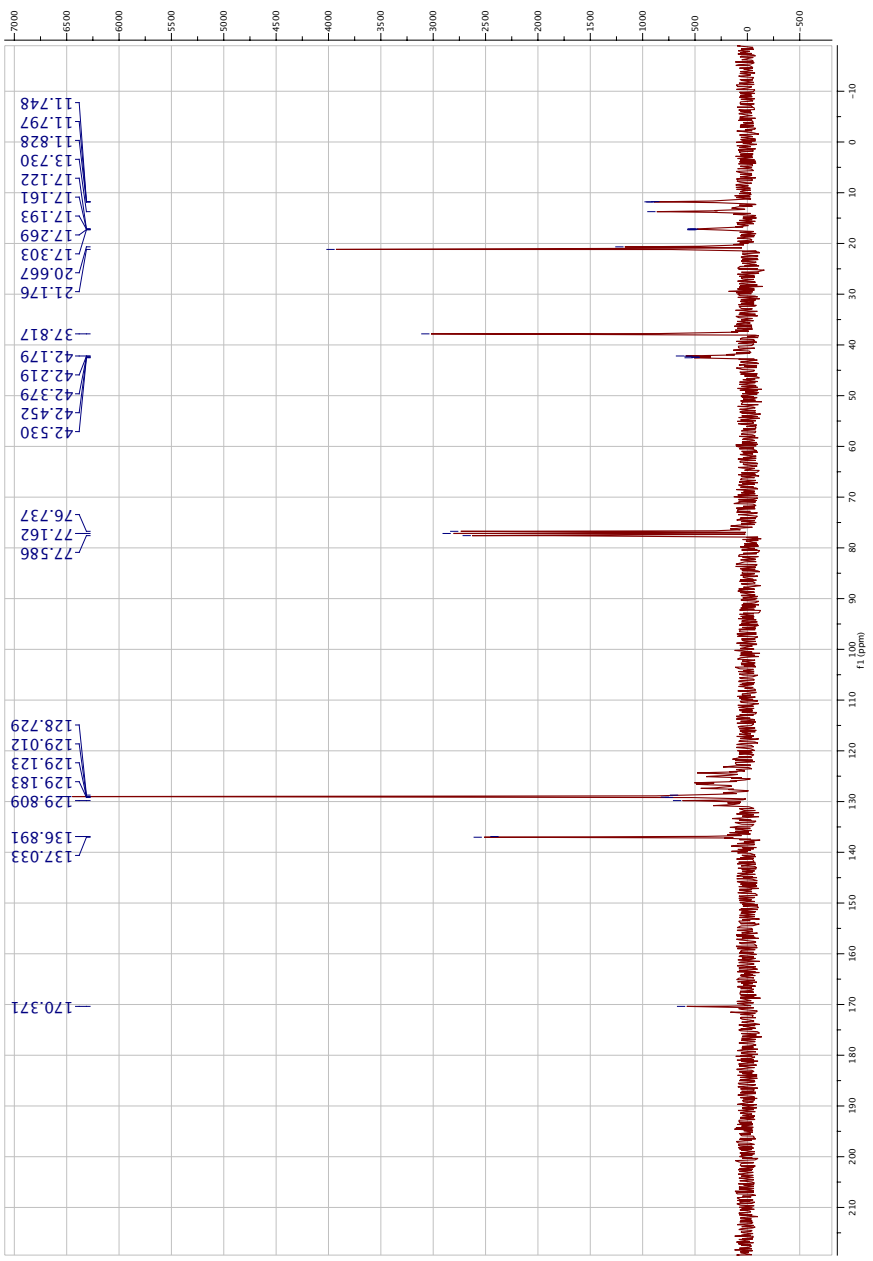

93,9
90
85
80
75
70
65
60
55
50
45
40
37,2
%T
4000,0
3000
2000
1500
1000
450,0
cm-1
3436,16
3015,40
2862,80
2920,23
1705,66
1621,57
1606,96
1503,61
1458,20
1377,31
1248,15
1227,98
1191,90
1146,72
1036,57
883,67
817,68
771,92
707,09
680,07
665,85
604,87
578,73
562,28
478,84
465,54
c:\pel_data\spectra\tab_7c.001

J 4d

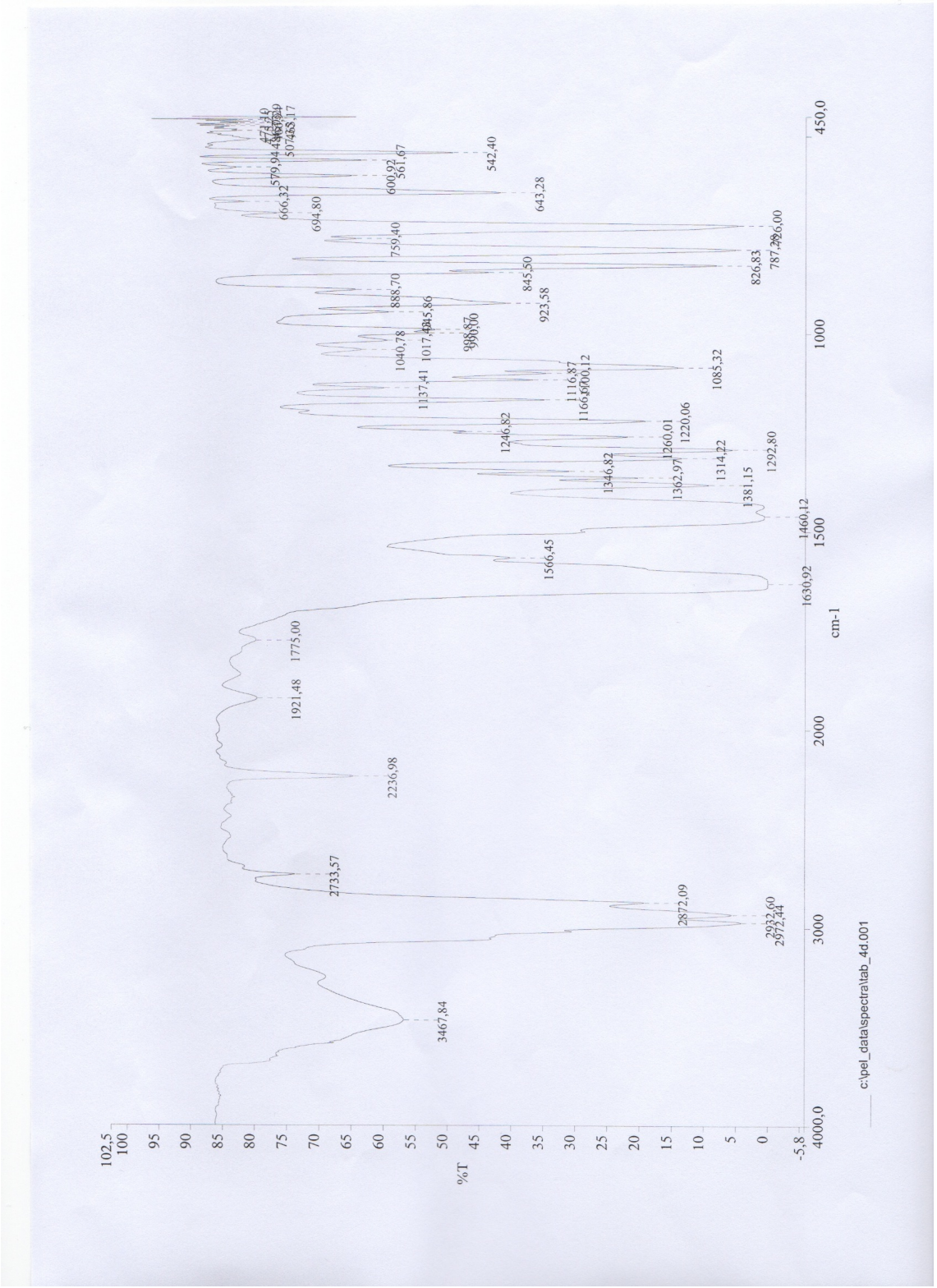
J.1 4d proton-nmr.



J.2 4d C13-nmr.

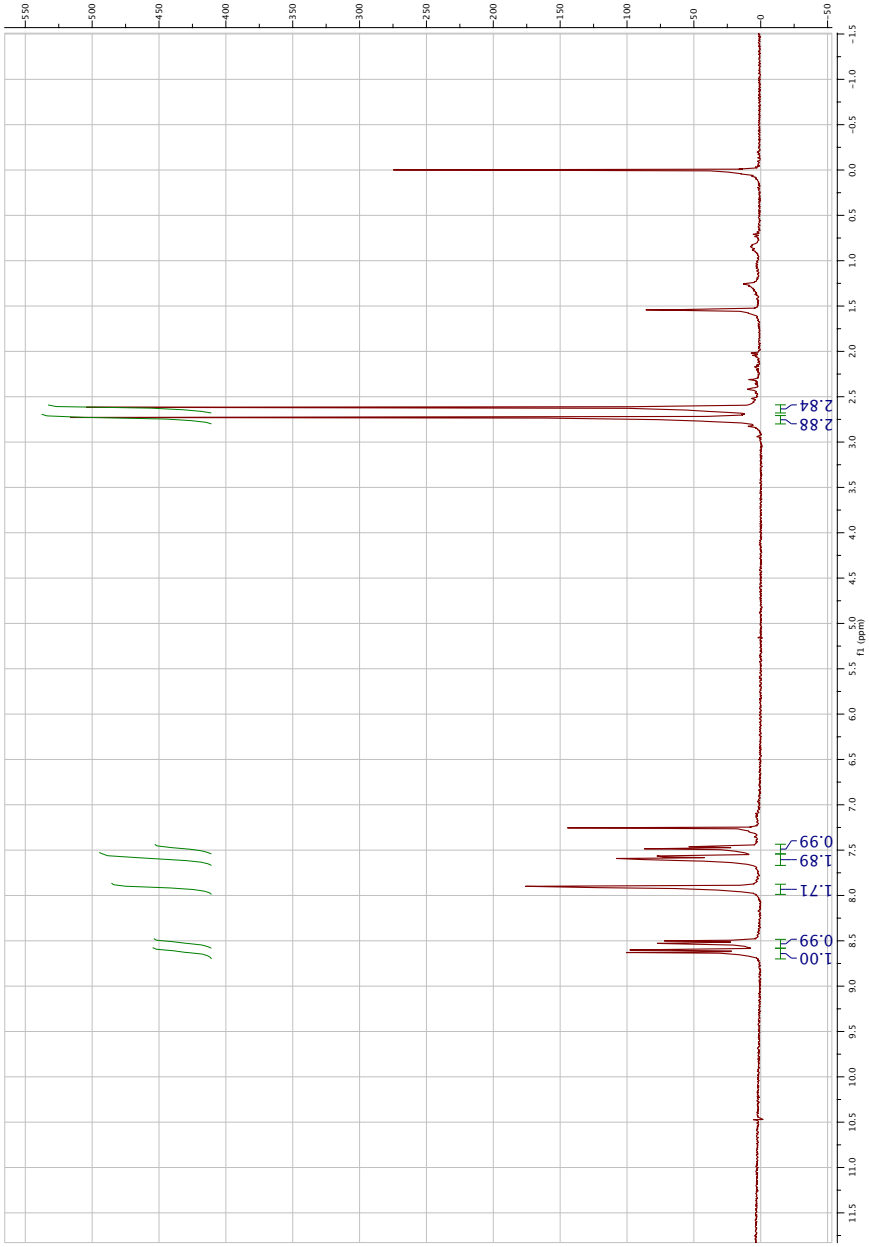

11.748
11.797
11.828
13.730
17.122
17.161
17.193
17.269
17.303
20.667
21.176
37.817
42.179
42.219
42.379
42.452
42.530
76.737
77.162
77.586
128.729
129.012
129.123
129.183
129.809
136.891
137.033
170.371
f1 (ppm)

J.3 4d IR.

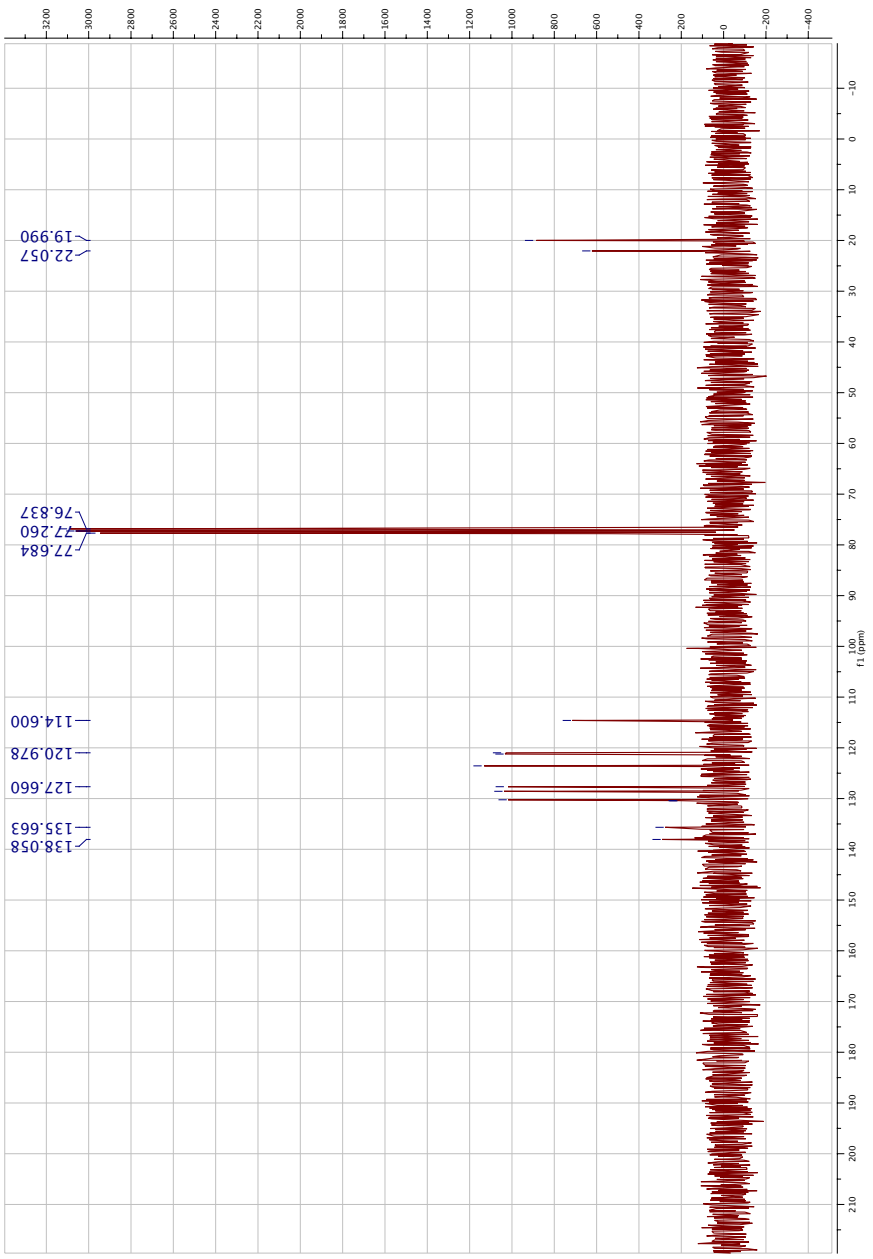

%T
cm-1
c:\pel_data\spectra\tab_4d.001
3467,84
2933,60
2872,09
2733,57
2236,98
1921,48
1775,00
1630,92
1566,45
1460,12
1381,15
1362,97
1346,82
1314,22
1292,80
1260,01
1246,82
1220,06
1166,87
1137,41
1085,32
1040,78
1017,41
990,06
923,58
888,70
845,50
826,83
787,29
759,40
694,80
666,32
643,28
600,92
542,40
507,63
4000,0
3000
2000
1500
1000
450,0

K 6d

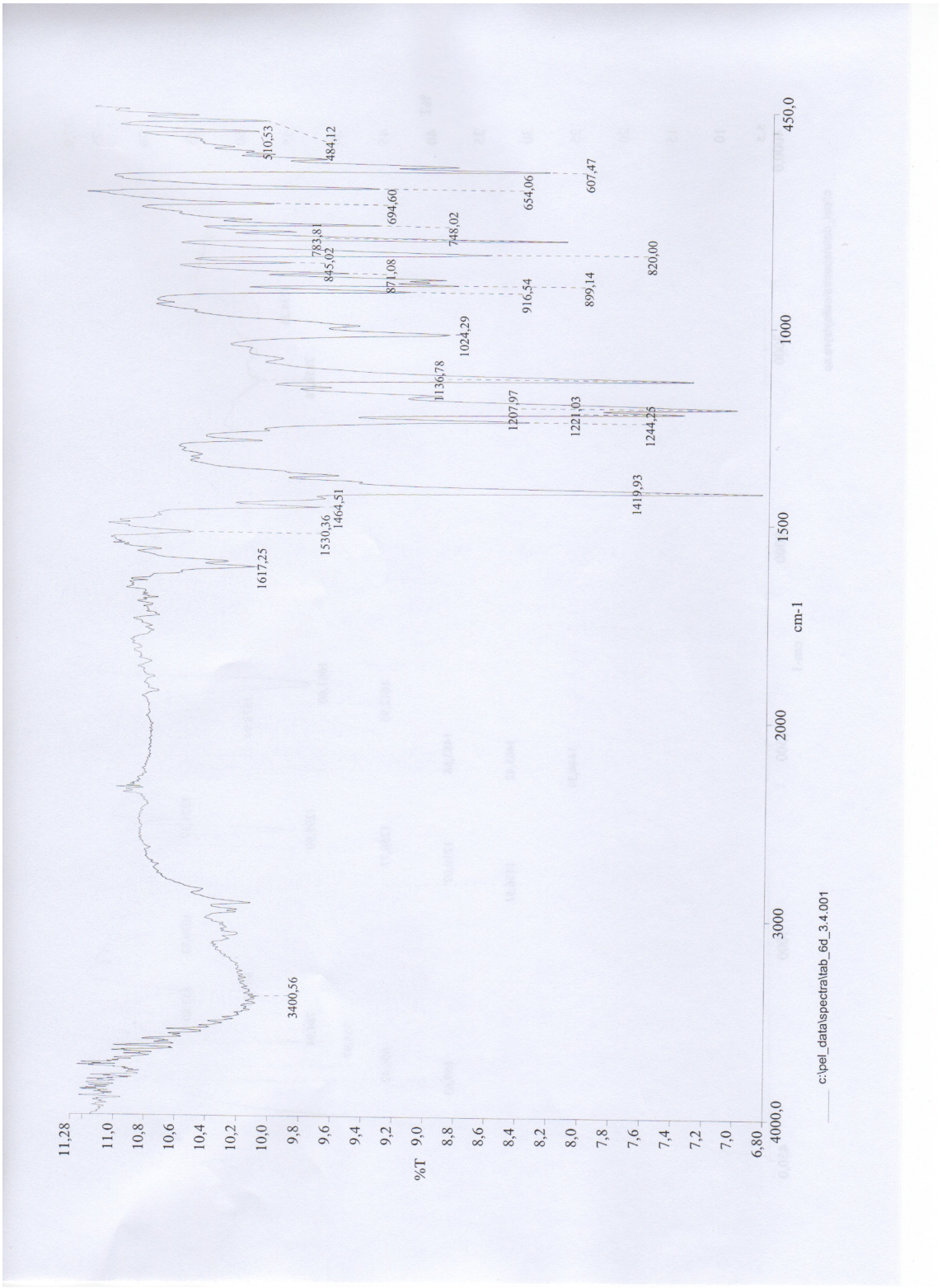
K.1 6d proton-nmr.



K.2 6d C13-nmr.

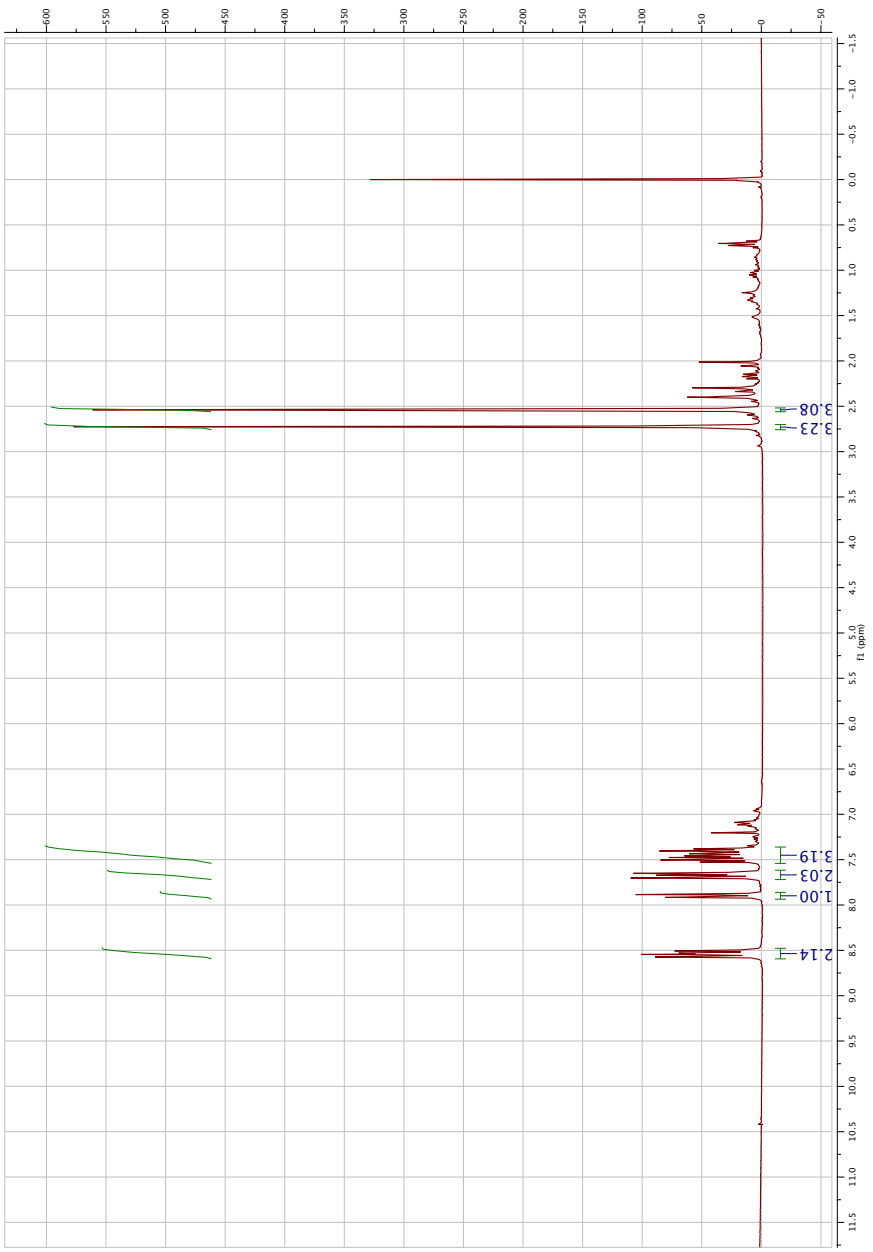

19.990
22.057
76.837
77.260
77.684
114.600
120.978
127.660
135.663
138.058
f1 (ppm)

K.3 6d IR.

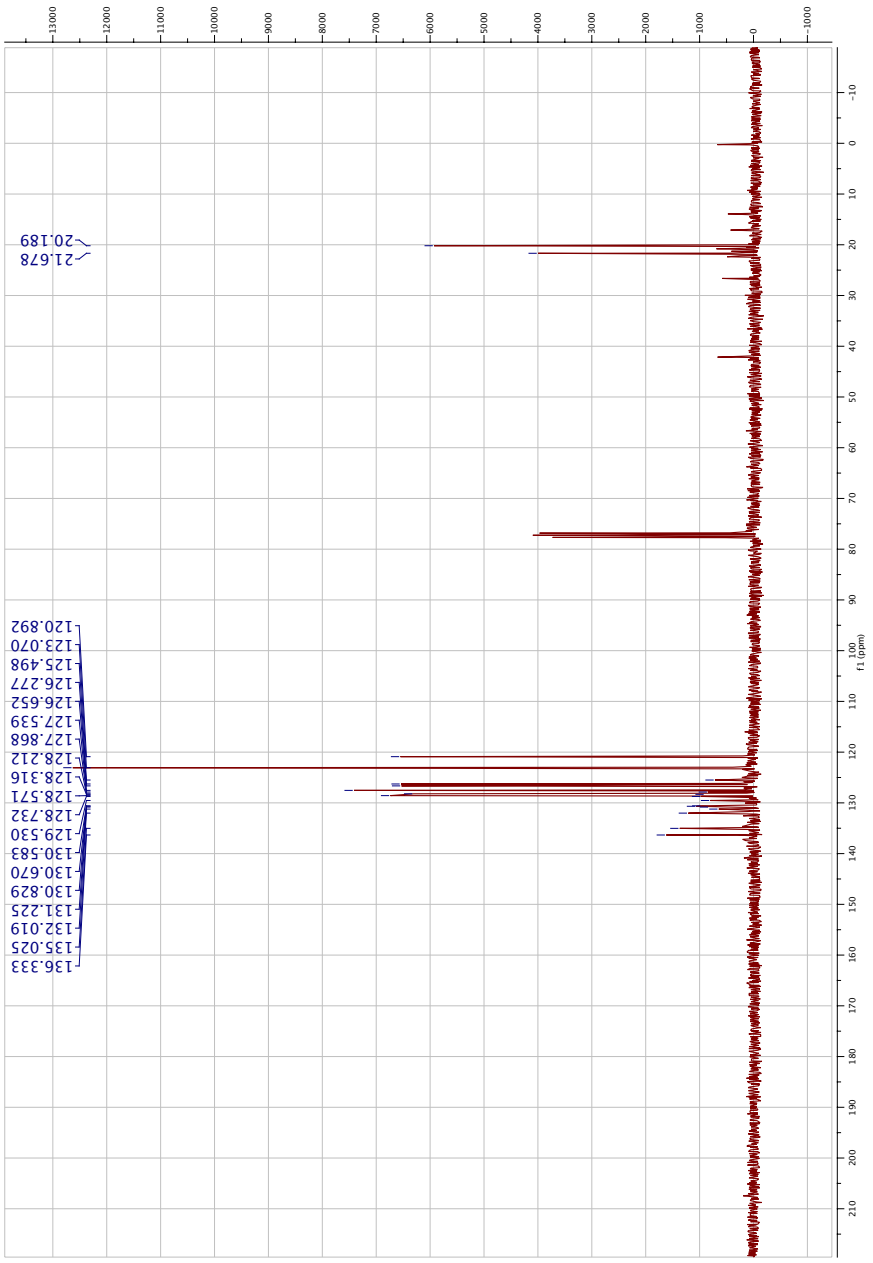

%T
cm-1
3400,56
1617,25
1530,36
1464,51
1419,93
1244,25
1221,03
1207,97
1136,78
1024,29
916,54
899,14
871,08
845,02
783,81
748,02
694,60
654,06
607,47
510,53
484,12
820,00
c:\pel_data\spectra\tab_6d_3.4.001

L 7d

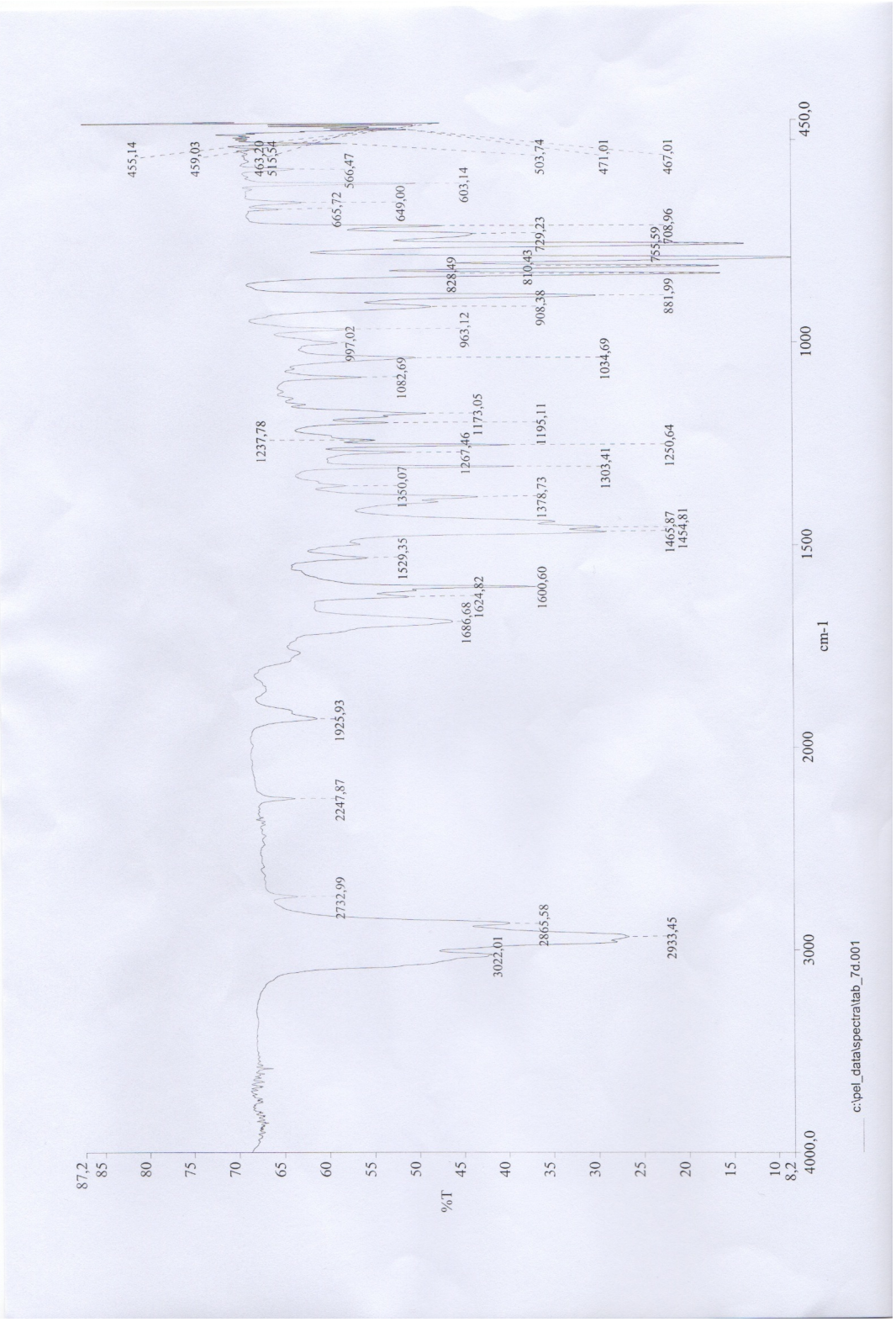
L.1 7d Proton-nmr.



L.2 7d C13-nmr.


21.678
20.189
120.892
123.070
125.498
126.277
126.652
127.539
127.868
128.212
128.316
128.571
128.732
129.530
130.583
130.670
130.829
131.225
132.019
135.025
136.333
f1 (ppm)

L.3 7d IR.


%T
cm-1
c:\pel_data\spectraltab_7d.001
455,14
459,03
463,20
515,54
566,47
603,14
649,00
665,72
729,23
755,59
810,43
828,49
881,99
908,38
963,12
997,02
1034,69
1082,69
1173,05
1195,11
1237,78
1250,64
1267,46
1303,41
1350,07
1378,73
1454,81
1465,87
1529,35
1600,60
1624,82
1686,68
1925,93
2247,87
2732,99
2865,58
2933,45
3022,01
471,01
503,74
708,96
881,99
467,01