J.S. van Mullem

New derivates of 1,6,7,12-tetra-chloroperylene-9,10-di-carboxylic di-n-butyl mono-imide di-n-butylester

TU Delft

Image from: https://ichemeblog.org/2015/03/

New derivates of 1,6,7,12-tetra-chloroperylene-9,10-di-carboxylic di-n-butyl mono-imide di-n-butylester

By

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in partial fulfilment of the requirements for the degree of

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Preface

Although my master's degree will be chemical engineering, I decided to write my master thesis on the subject of organic chemistry. I always had an affiliation with technology, which is why I decided to pursue the technology track of my bachelor's degree and the subsequent master's in chemical engineering at the Delft University of Technology. On the other hand, during the first year of my bachelor's degree I discovered a strong interest in organic chemistry. Unfortunately, I never had a chance to fit any organic chemistry in my study plan after the first year of my bachelor.

Needless to say, starting this thesis, I had some catching up to do on my theoretical and practical knowledge of organic chemistry. Both the last course and the last experiments I had done in organic chemistry were during the first year of my bachelor's degree. However, jumping into the lab work of this project quickly after I started, I found my skills in organic chemistry were still present somewhere (although very rusty). With the guidance of several people on the lab where I worked, both theoretical and practical, I managed to do all the necessary chemistry of this project and to enjoy my time on the lab.

With this thesis I would like to present to you the result of my time spent in the OMI (organic materials and interfaces) group under the supervision of professor dr. W.F. Jager.

Jesse van Mullem
Delft, April 2019

Contents

Abstract

Synthesis of new perylene-3,4,9,10-tetra-carboxylic acid (PTCA) derivates is a research topic that has rapidly developed during the last decades. Current synthetic efforts are largely focussed on functionalizing the perylene core, via either bay- or ortho-substitution.
The aim of this research project was to synthesize novel perylene mono-imide di-ester derivates by attaching different substituents at the bay-positions.

The first synthetic route that was attempted in this research project was a route via a perylene mono-anhydride mono-imide derivate. The anhydride was attached to this molecule to activate the relevant bay-positions. It was found that the anhydride is not stable enough to withstand the reaction conditions that were used in an attempt to substitute the relevant bay positions.

The next synthetic route that was attempted in this research project was a route via a perylene di-ester mono-imide derivate. Reactions were performed to explore whether the di-ester was able to activate the relevant bay-positions. It was found that at the used reaction conditions, phenol exchange takes place on the bay-positions of the perylene core.

Due to the challenges that arose, the target compounds of this project have not been synthesized. However, three other new PTCA derivates have been synthesized during this project.

Acknowledgements

I would like to thank my supervisor, prof. dr. W.F. Jager, for his guidance during my project and for sharing his vast knowledge of organic chemistry.

I would like to thank the members of my thesis committee, prof. dr. E.J.R. Sudhölter and assoc. prof. dr. R. Eelkema, for taking the time to grade my thesis.

I would like to thank D. Bosma, for sharing his technical know-how, laboratorial tips and tricks, and his good taste in music.

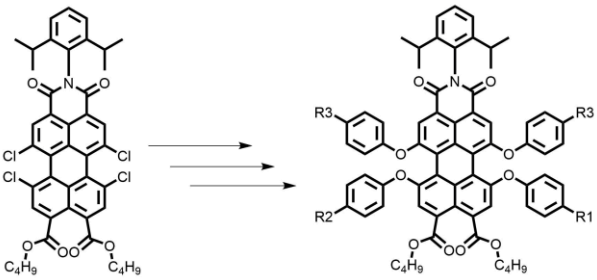
I would like to thank G. Filonenko, PhD., for helping with performing mass spectrometry.

1 Introduction

Perylene tetra-carboxylic acid (PCTA) derivates are a class of organic molecules with a distinct core structure. This structure that can be seen in the left most part of Figure 1. PCTA derivates have been used as high performance pigment in for example the automotive industry [3]. In the last few decades, PCTA derivates have been a recurring topic in research, because of the favorable properties of the molecule and its substituted versions. These properties include thermal stability, photo stability, chemical robustness, strong adsorption in the visible region [4], high electron affinity, high charge carrier mobility [5-7] and high (fluorescence) quantum yields [8].

To employ these favorable properties to the full extent, the perylene core can be functionalized. Functional groups can be attached to the perylene core to tune the properties of the molecule and/or the facilitate in different applications of the molecule (for example, light harvesting antennae can be attached to the perylene core to facilitate in an artificial photosynthesis system). For some applications it could be of interest to maximize the number of functional groups that can be attached. On top of that, it could be of interest to be able to precisely dictate where the functional groups attach to the perylene core (regiospecificity).

In this study, new derivates of the perylene family have been synthesized. The aim of this research was to attach as many distinct substituents to the bay-positions (see Figure 1) of a peri-unsymmetrical PCTA derivate as possible. These substitutions had to take place regiospecific on independent positions, with a clear control over the kind and number of substituents that were attached, to optimally exploit the structural property relationships of substituted perylenes. The number of substituents attached to the perylene core that was envisioned for this project is five, as is shown in Scheme 1.



Scheme 1: Project proposal.

To pose this proposal as a question: Can three different phenol-based substituents be attached to the bay-positions of a tetra-bay-chlorinated perylene core with an imide and a di-ester on the peri-positions?

2 Theory

2.1 History

Perylene derivates occur in nature in some species of lichen [9], a composite algae species that lives among the filaments of certain types of fungi [10].
Perylene-3,4,9,10-tetra-carboxylic di-anhydride (PDA) was synthesized first in 1913 [11]. It has been used as a high performance pigment since the late 1950's, because of its thermal stability, chemical inertness, lightfastness and weatherability [3]. Other important characteristics are strong absorption in the visible region, high fluorescence quantum yield, good electrical conduction (n-type conduction) and their electrochemical stability.

Later, the fluorescent nature of these dyes and the discovery of their high fluorescence quantum yield would lead to other applications. These applications include electron donor–acceptor systems and light-harvesting arrays [12]. On top of that, the listed properties make the molecule a suitable candidate for application in fluorescent probes and battery materials. In such systems, a molecule with tunable electronic and optical properties is highly desirable.
By attaching substituents the perylene core, the electronic and optical properties of the molecule can be tuned [13]. These substitutions can take place on three distinct positions, the "peri-" (3,4,9,10) positions, the "bay-" (1,6,7,12) positions, and the "ortho-" (2,5,8,11) positions (see Figure 1).

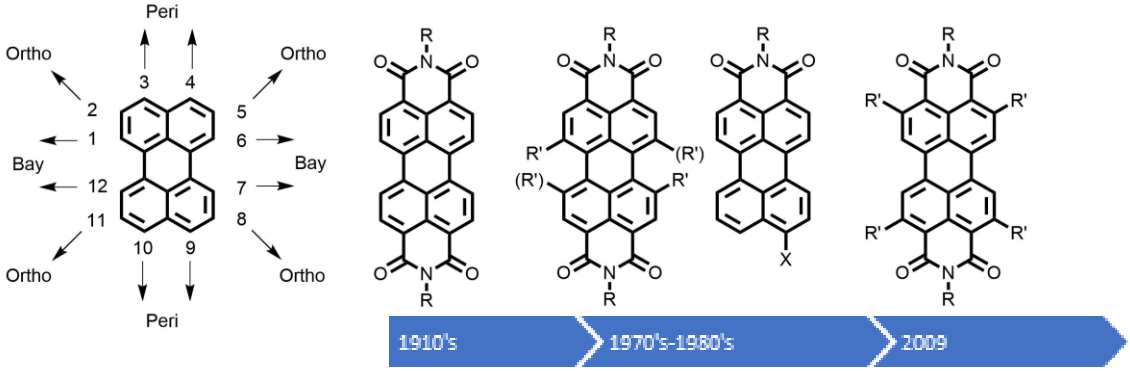


Figure 1: The structure of a perylene core and the development of different substitution positions [1].

2.2 Peri-substituents

Several substituents can be attached to the peri-positions of the perylene core. Three of the most common substituents are the anhydride, the imide and the di-ester (see Figure 2).

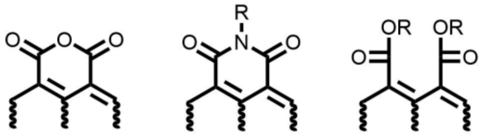


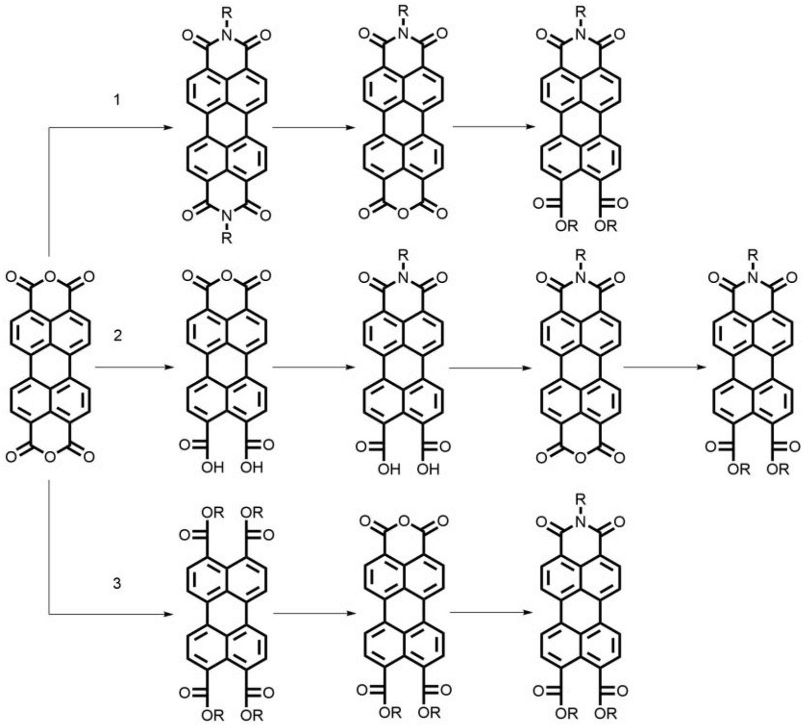
Figure 2: Most commonly encountered peri-substituents for perylenes.

PDA has been used as a starting material for several research projects on perylene peri-substitution. PDA was also the starting material for this project, as can be seen in Appendix D.1.

In this research, a peri-unsymmetrical perylene (a perylene derivate with different substituents on the two peri-positions) derivate is desirable, since peri-asymmetry yields different reactivities of the upper and lower bay-positions (provided the electronic effect of the substituents is sufficiently different). This effect of the peri-substituents on the bay-positions will be explained in section 2.3.4.

A mono-imide di-ester perylene derivate is selected as precursor compound. The reason for this selection will also be provided in section 2.3.4.

Synthesis of the mono-imide di-ester perylene derivate can be done in three ways. The three ways are presented in Scheme 2.



Scheme 2: Three synthesis routes from di-anhydride to imide di-ester.

In this research, route 3 has been chosen. Although routes 1 and 2 are also possible, they have some clear disadvantages:

In the second step of route 1, a strong KOH solution is used to convert an imide into an anhydride. This is quite a blunt method, which is represented by a yield of only 40 % [14]. Due to this low yield, functional group tolerance towards the strong KOH and the availability of a more elegant route (3), route 1 is not used.

Route 2 [15] uses carboxylic acid/carboxylates as intermediates. Due to the poor solubility of these intermediates in organic solvents, chemistry on these molecules is considerably more difficult than on the molecules from route 3.

Route 3 is described in a paper by Sengupta *et al.* [16] for a 1,7-di-bromoperylene and in a paper by Dubey *et al.* [13] for a 1,6,7,12-tetra-chloroperylene. Both these routes are adapted from the procedures described in a paper by Xue *et al.* [17]. Considerable differences in yield between similar steps in the synthesis routes described in the two papers are observed, which can be attributed to the different bay-substituents.

With an overall yield of 60 % from di-anhydride perylene derivate to di-ester mono-imide perylene derivate, the method reported in the paper by Dubey *et al.* [13] is used in this research.

2.3 Bay-substituents

As pointed out by Zhao *et al.* [18], substitution of (the imides at) the peri-positions of the perylene molecule can tune the optical and electrical properties to some degree. However, they also state that direct substitution of the core (the 1, 2, 5, 6, 7, 8, 11, 12 positions) should provide a more versatile means of tuning. The first set of positions available, historically speaking, for direct substitution on the perylene core are the bay-positions (1, 6, 7, 12).

2.3.1 Halogenation

In most research on bay-substitution of perylenes, substitution is preceded by halogenation. Halogenation is usually done via electrophilic aromatic substitution (SE_{Ar}).

Recently, some research appeared on direct substitution (without halogenation). Direct substitution is possible, as can be seen in for example [19]. However, because of the extended development of the routes with halogenation, a route with halogenation is used in this project.

In perylene bay-halogenation, either bromine or chlorine are attached to the perylene molecule. For bromine, a di-, tri- and even tetra-halogenated version exists. Di-brominated perylene can be either 1,6 or 1,7; tri-brominated is 1,6,7 and tetra-brominated is 1,6,7,12. An overview of the different possibilities can be found in a paper by Fan *et al.* [20] and in Figure 3.

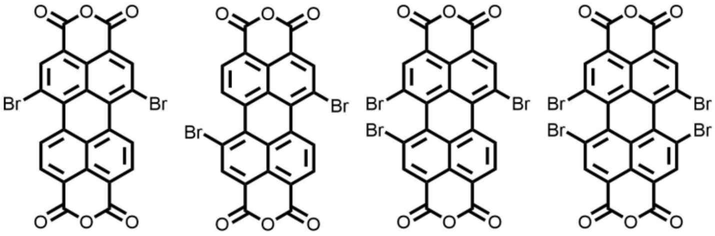


Figure 3: Different bromine substitution configurations on the bay-positions of the perylene core.

For chlorine, the tetra-chlorinated version is the most common. With the chlorination reactions, depending on reaction temperature and time, tri- and penta-chlorinated perylenes are also formed [13]. For an overview, see Figure 4.

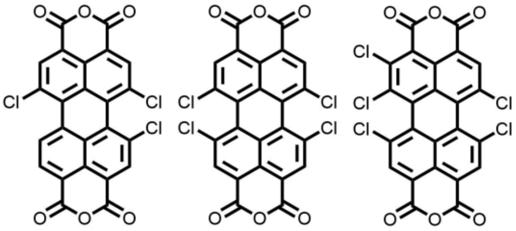


Figure 4: Different chlorine substitution configurations on the bay-positions of the perylene core.

In some rare cases, perylenes are halogenated on both their bay-and ortho-positions at the same time, as can be seen in papers by Kumar *et al.* and Sadrai *et al.* [21, 22] and in Figure 5. As with bay-halogenation, both a chlorinated and a brominated version of an octa-halogenated perylene exist.

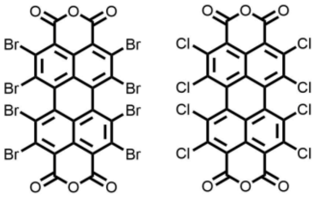


Figure 5: Octa halogenated perylenes.

In this research, tetra-bay-chlorinated perylene is used. A tetra-halogenated perylene is chosen because this provides more available substitution positions than a di- or tri-halogenated perylene.

The chlorine atom, and subsequently the functionalities, will be attached to the bay-positions (and not the ortho-), to keep the complexity of the project appropriate for the time that is available (since bay-substitution is more established compared to ortho-substitution). Chlorine is chosen instead of bromine, because the chlorine atom is less bulky than the bromine atom, due to the lower atom number of chlorine. The result is that the tetra-bay-chlorinated perylene is more susceptible to bay-substitution reactions than tetra-bay-brominated perylene.

Although the substitution on the bay-positions has already been developed in the seventies and eighties of the previous century, substitutions on peri-unsymmetrical perylenes is relatively new. There are several papers on peri-unsymmetrical perylene derivates [17, 23, 24], and starting from 2013, some papers start considering a peri-unsymmetrical perylene core with substitution on the bay-positions [25, 26].

In this research we aim to attach as many different substituents to the bay-positions of the perylene core as possible. In contrast, in previous research, four equal substituents were usually attached to the bay-positions of the perylene.

2.3.2 Substitution

After successful halogenation of the perylene core, substitution of the halogens with other functionalities is usually the next step. This is often done with a simple nucleophilic aromatic substitution (SN_{Ar}), but other methods exist.

Other methods for substitution include Pd complex catalyzed reactions, like Suzuki coupling [27, 28] or Sonogashira coupling [29, 30]. Another metal that is used to catalyze coupling to a halogenated perylene core is copper [31].

However, in this project, SN_{Ar} is used to substitute the halogens with other functionalities, because of the simplicity of the method.

2.3.3 Nucleophilic aromatic substitution

As mentioned before, nucleophilic aromatic substitution is often used to substitute halogens on the bay-positions of the perylene core with other functionalities. A clear advantage of this method compared to the methods discussed above is the ability to sequentially add different functionalities. This sequential substitution is achieved through tuning the reactivity of the bay-positions and controlling the reaction times. This tuning of reactivity can be done by carefully choosing the peri-substituents, as will be explained further in the next section.

2.3.4 Influence of the peri-substituents

Three different peri-substituents will be used during this project, an anhydride, an imide and a di-ester (the three substituents in Figure 2). The order in which these substituents are presented in Figure 2 is also their order of decreasing bay position activation capacity in the SN_{Ar} reactions.

This activation capacity has to do with the substituent's ability to withdraw electrons from the perylene core, leading to an electron deficiency in specific parts of the core. The place of effect of the substituents is visualized in Figure 10 and in Figure 11. The electron deficiency can be measured using the standard reduction potential: the lower the reduction potential of a compound, the higher the electric potential that is needed to reduce the compound. Thus, a perylene core with a high electron density has a lower reduction potential than a perylene core with a low electron density.

In the paper by Sengupta *et al.* [16], the standard reduction potential $E_{1/2\ red}$ is measured for the two compounds in Figure 6. The only difference between those compounds is the substituent attached to the lower peri position. The reduction potential of the imide di-ester is lower than the reduction potential of the di-imide. This means perylene core of the di-imide has a lower electron density/is more electron deficient than the perylene core of the imide di-ester. The more electron deficient the perylene core, the more it is susceptible to SN_{Ar}, indicating the imide has a larger activation capacity in SN_{Ar} than the ester.

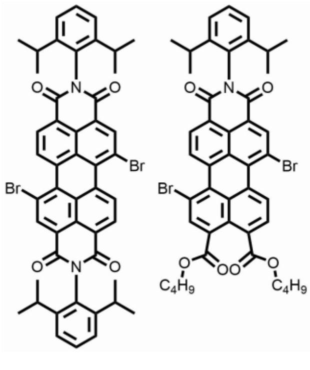


Figure 6: Perylenes with different substituents on the peri positions: di-imide vs imide di-ester.

Unfortunately, no reduction potential data was found in literature for perylene derivates with anhydrides on the peri-positions. However, a more intuitive method to explain the order of activation capacity is the electronegativity of the peri-substituents and the degree to which conjugation is possible in the molecules.
Oxygen is a more electronegative element than nitrogen, which explains why the anhydride has more activation capacity than the imide. However, following this logic, the di-ester should be the most activating substituent, since it has the most oxygen. However, now conjugation comes into play. Because both the anhydride and the imide are cyclic substituents, they are forced into planarity by the configuration of the orbitals of the 5 carbons and the hetero atom that form the ring structure on the peri-position. In Figure 7, the general structure of an anhydride or imide can be seen, with numbers attached to each carbon in the cyclic structure. The X in the figure represent either an oxygen or a nitrogen, not a halogen.

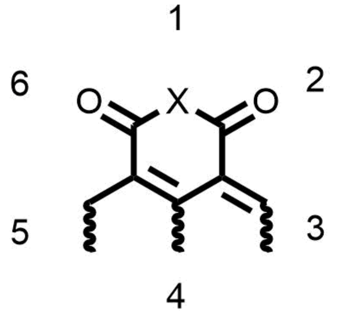


Figure 7: General structure of anhydride or imide on the peri-positions of a perylene core.

The carbons 3, 4 and 5 are forced into planarity by the planar system they are attached to (the perylene core). Carbons 2 and 6 are forced into planarity by their own sp^2 orbital configuration. With all carbons in planarity, the last atom (number 1) is forced into planarity by the 5 carbons in the ring structure.

This planarity effect is only strengthened by the resonance structures, provided in Figure 10 and Figure 11. With double bonds between the carbons 2 and 3 or 5 and 6 in the resonance structures, the electron density in the corresponding π orbitals is higher than it would be without the resonance possibility. This higher electron density makes the sigma bonds between the described carbons more rigid than standard sigma bonds would be.
Both these arguments combined provide the final order of activating capacity (in SN_{Ar}): anhydride > imide > di-ester.

2.3.5 Deactivation

A challenge that rises when attaching more substituents to the perylene core is the deactivation of the core positions. Every group that is attached via SN_{Ar} makes the perylene core less electron deficient (or more electron rich). The stronger the nucleophile, the larger this effect. This in turn makes the subsequent positions on the perylene core less susceptible to nucleophilic attack. The used nucleophiles and their relative nucleophilic strengths will be discussed in section 2.6.1.

This challenge can be used to one’s advantage by carefully choosing the order in which substituents are attached. If the least reactive substituent is attached first, the reaction conditions could be chosen such that, after the first substitution, the subsequent positions are not reactive enough to be attacked by the substituent. This could result in a way to selectively mono-substitute a perylene core with several positions that have near equal reactivity.
An example of mono-substitution on a perylene with two positions that have equal reactivity can be seen in Scheme 10. The result of the reaction in Scheme 10 has been obtained by carefully tuning the reaction time and temperature. It is worth noting that no differentiation can be made between the two lower bay positions (7 and 12). This is both caused and solved by symmetry in the molecule, since due to symmetry, substitution on the 7 or 12 position is structurally equal.

2.4 Ortho-substitution

Substitution on the ortho-positions is relatively new, as pointed out by Li *et al.* [1]. The reactions are either ruthenium [32-35] or iridium [36] catalyzed.

In all articles, the attachment of side groups is non-regiospecific and always done on di-imides (peri-symmetrical).

From Li *et al.* [1]: "Ortho-functionalization creates the possibility to modify the HOMO/LUMO of perylenes without inducing torsion of the perylene core. The exploration of this kind of functionalization is still in its infancy." This quote stems from 2012. Since then, some work has been done on ortho-substitution of perylenes, but this area of research is to this day still an emerging field.

For a recent and complete overview of possible bay-and ortho-substitutions (and some peri-), please refer to an article by Nowak-Król *et al.* [12].

2.5 Preceding work

In work by Dubey *et al.* [25], it has been shown that two different bay-substituents can be added to a peri-unsymmetrical (imide and di-ester) 1,7-di-bromoperylene. These substituents can be added regiospecific and highly efficient. The product of this research is a perylene core with four different substituents (two on the peri-positions and two on the bay-positions).

In this paper, challenges that occur with substitution on a perylene with an imide and a di-ester on its peri-positions are mentioned. A challenge that will be important later in this report is substituent replacement (phenol exchange). A short elaboration on how this effect occurs is provided in section 2.6.1.

In work by Dubey *et al.* [2], it has been shown that two different substituents can be attached to the two lower bay-positions of a peri-unsymmetrical (imide and di-ester) 1,6,7,12-tetra-chloroperylene.

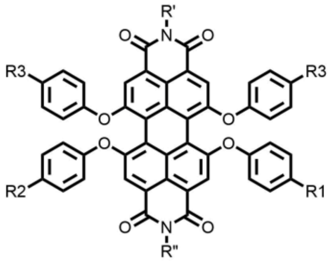


Figure 8: Result of the research done by Dubey et al. *[2].*

On top of that, it has been shown that a total of three different substituents can be attached to the bay-positions of a peri-unsymmetrical (two different types of imide) 1,6,7,12-tetrachloroperylene (two different substituents to the lower bay-positions and one substituent to the two upper bay-positions). This result is represented in Figure 8.

In this research, we aim to repeat this last result (three different substituents) with an imide/di-ester. The important difference between the research described in the paper by Dubey *et al.* [2] and the research in this project, is the activation of the 1 and 6 positions. In the referenced paper, the activation of the 1 and 6 positions is done via an imide, while in this research we aim to activate the positions via an anhydride. This anhydride will be converted to an ester after substituting the 1 and 6 positions, for stability reasons.

It is important to be able to perform the substitutions on an imide/di-ester, because these two substituents are more electronically different than two imides, yielding a larger difference in electron distribution over the perylene core. This could allow for a more precise tuning of electronical properties.

Another advantage of the peri-unsymmetrical perylene core is the difference in reactivity of the 1,6 and 7,12 positions on the core. As discussed in section 2.3.4, the different peri-substituents have different activation capacities. As can be seen in Figure 10 and Figure 11, the substituent on the lower peri-positions influences the reactivity of the 1 and 6 positions, while the substituent on the upper peri-positions influences the reactivity of the 7 and 12 positions.

2.6 This project

2.6.1 Used nucleophiles

Common substitution reactions on the bay-positions include cyanation [37], fluorination [38], amination [18] and phenolation [39, 40]. In the early stages of perylene bay-substitution, all these substitutions were performed on peri-symmetrical perylene derivates, often di-imides.

In this project, phenols are used as nucleophiles. In this section, the three nucleophiles that are used are provided and their relative reactivity is discussed. The three nucleophiles can be seen in Figure 9.

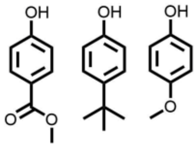


Figure 9: Substituents used.

These nucleophiles are chosen for their easy handling, availability and their easy identification on ^{1}H NMR (they each have a very distinctive (set of) alkyl groups, as can be seen in the ^{1}H NMR spectra in Appendix A.7). They are presented in order of increasing reactivity. The reactivity can be explained using two measurable quantities.

The first quantity is the substituent constant σ from the Hammett equation. For a negatively charged ion (for example phenolate) with a para substituent (aka the three nucleophiles used in this project), the σ_p^- is het relevant parameter to look at. The smaller this constant, the more electron donating the substituent, the higher the electron density on the phenol, thus the more nucleophilic the molecule. The constants are reported in the paper by Hansch *et al.* [41], and from left to right in Figure 9 they are 0.45, -0.20, -0.27 respectively, supporting the claim about the nucleophilic strength of the molecules. Their reactivity is inversely proportional with their deactivation capacity. This deactivation capacity is the extent to which the substituents increase the electron density on the perylene core. As mentioned before, the higher the electron density on the perylene core, the less susceptible the perylene core becomes towards SN_{Ar}.

The second quantity is the pK_a. The lower the pK_a of a phenol derivate, the easier this phenol derivate loses the proton from its hydroxy group, the higher the reactivity of the phenol derivate in SN_{Ar}. In a paper by Hansch *et al.* [42], the pK_a of several phenol derivates has been measured, including the rightmost and leftmost phenol derivates in Figure 9.

The middle phenol in Figure 9 is not mentioned in the paper, but some phenol derivates closely comparable to the middle phenol in Figure 9 have been measured. It can be seen in the paper that the leftmost phenol derivate of Figure 9 has the lowest pK_a, followed by the rightmost phenol and lastly the (phenols closely comparable to the) middle phenol. Thus, based on the pK_a values, the leftmost phenol is the most reactive one, followed in order by the rightmost and lastly the middle phenol. N.B. the gap between the pK_a values of the leftmost and rightmost phenols is much larger than the gap between the rightmost and the middle phenol.

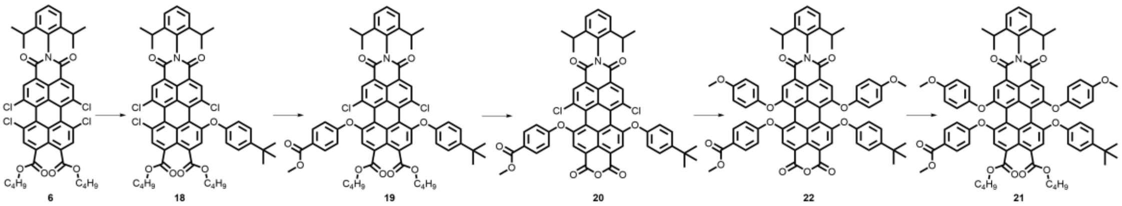
Another relevant property of the nucleophiles is their leaving group ability. This is, just like the deactivation capacity, inversely proportional to their nucleophilic strength, so the worst nucleophile is the best leaving group (the left most phenol in the figure).

2.6.2 Phenol exchange

A challenge that has been touched upon in previous work by Dubey *et al.* [25] is nucleophilic exchange, or in this case phenol exchange. The three characteristics described above (nucleophilic strength, property as leaving group and deactivation capability) all play a role in phenol exchange. If a phenol is attached to the perylene core and an attempt is made to attach a next phenol, phenol exchange could occur. For example, if the new nucleophile is a much stronger nucleophile (and thus a much worse leaving group) than the phenol already attached to the perylene core, the new phenol could do a nucleophilic attack on the position of the old phenol. Now since the old phenol is a better leaving group than the new phenol, the new phenol can eliminate the old phenol.

2.6.3 Envisioned synthesis route

In this project, the aim is to attach as much substituents to the perylene core as possible. The envisioned route can be seen in Scheme 3.



Scheme 3: Envisioned substitution route for research project.

Going through this route step by step, the first substituent that is attached is the 4-tertbutyl phenol. It might seem a logical choice to start with the weakest nucleophile as the first substituent, which is 4-hydroxy methylbenzoate. However, the weakest nucleophile is also the best leaving group. It is expected that 4-hydroxy methylbenzoate might get eliminated, bearing in mind the possibility of phenol exchange described earlier in this chapter.

It is postulated that by attaching 4-tertbutylphenol first, a balance is attained between nucleophilic strength, leaving group ability and deactivation capability. However, reactions could be performed where the first and second substituent in Scheme 3 are inverted, to test if one of the two routes is superior (and if so, which one). Following the explanation above, the second phenol group that is attached is 4-hydroxy methylbenzoate.

In the next step, the esters on the lower peri-positions are replaced by an anhydride. This anhydride has the purpose of activating the 1 and 6 positions of the perylene core. As discussed in section 2.3.4, an anhydride is a better activator than an di-ester.

With the 1 and 6 positions activated, the last phenol can be attached to the perylene core. The strongest nucleophile is saved for last, because the perylene core is most deactivated in this step. On top of that, by saving the strongest nucleophile for last, combined with the activation by the anhydride, it is postulated that the conditions for the last substitution reaction can be kept relatively mild, decreasing the chance of phenol exchange.

The last step is the replacement of the anhydride by a di-ester, to yield a stable final compound that is not a di-imide (because chemistry on di-imides has already been developed in previous research projects).

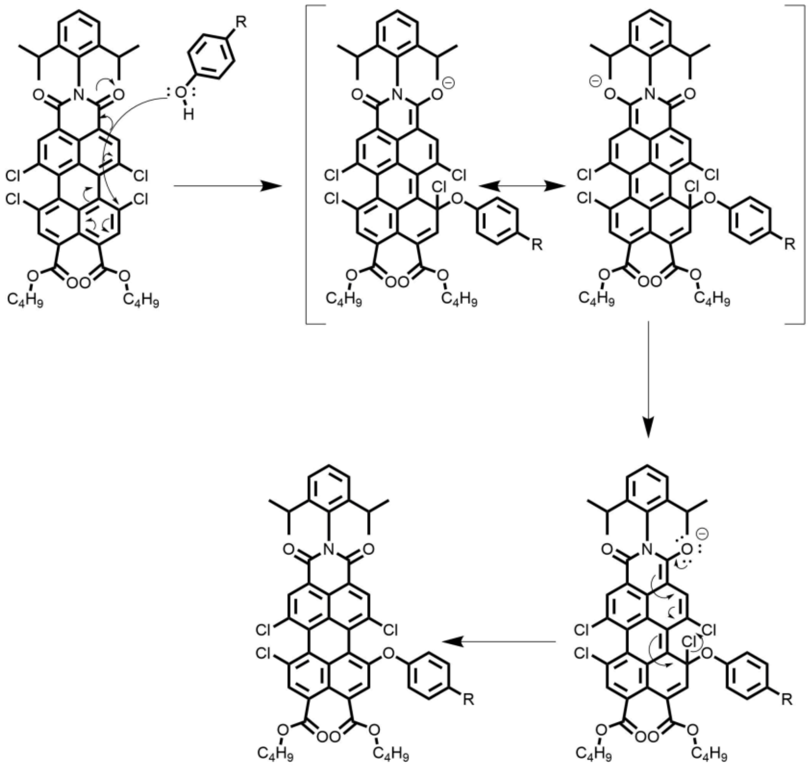


Figure 10: Mechanism of the SN$_{Ar}$ reactions at the imide activated 7 and 12 positions of the perylene core.

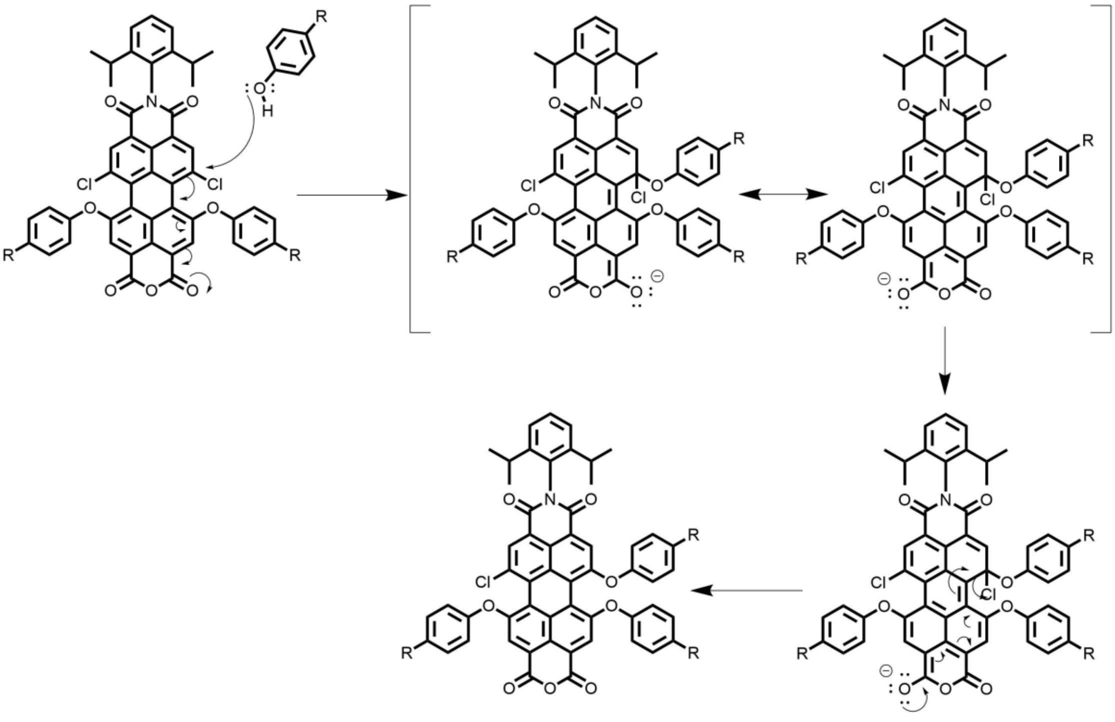


Figure 11: Mechanism of the SN$_{Ar}$ reactions at the anhydride activated 1 and 6 positions of the perylene core.

3 Experimental

3.1 Chemicals and materials

Chemical	**Supplier**	**Catalogue number**	**Purity**
Perylene-3,4,9,10-tetra-carboxylic di-anhydride	Sigma-Aldrich	P11255-100G	97 %
Iodine	Fluka	57655-100G	>99.5 %
Chlorosulfonic acid	Sigma-Aldrich	571024-1KG	99 %
N,N-di-methylformamide	Sigma-Aldrich	227056-1L	99.8 %
1-Butanol	J.T. Baker B.V.	8017-1L	≥99 %
1,8-diazabicyclo[5.4.0]undec-7-ene	Sigma-Aldrich	139009-500G	98 %
1-Bromobutane	Sigma-Aldrich	B59497-500G	99 %
2-Propanol	Sigma-Aldrich	59300-2.5L-M	≥99.8 %
Di-chloromethane	VWR	25629.364-5L	≥99.8 %
Acetonitrile	Merck	1.0003.2500	
p-Toluenesulfonic acid monohydrate	Sigma-Aldrich	402885-500G	≥98.5 %
n-Heptane	Merck	1.04365.1000	
Methanol	VWR	20903.368-5L	
n-Hexane	VWR	24611.297-1L	99 %
2,6-di-isopropyl aniline	TCI	D1755	>90.0 %
Propionic acid	Sigma-Aldrich	81910-1L	>99.5 %
4-Methoxyphenol	Sigma-Aldrich	M18655-100G	99 %
Potassium Carbonate	J.T. Baker B.V.	0205-1KG	
18-Crown-6	Sigma-Aldrich	186651-25G	99 %
Toluene	VWR	28701.364-5L	
Toluene, anhydrous	Alfa Aesar	41464-1L	99.8 %
Caesium carbonate	Sigma-Aldrich	441902-100G	99 %
4-tertbutylphenol	Sigma-Aldrich	B99901-100G	99 %
4-hydroxy methylbenzoate	Sigma-Aldrich	H5501-100G	≥ 99 %

3.2 Procedures

N,N-di-methylformamide will from now on be referred to as DMF, 1,8-diazabicyclo[5.4.0]undec-7-ene as DBU, 2-propanol as IPA, di-chloromethane as DCM, acetonitrile as ACN, n-heptane as heptane and n-hexane as hexane.
^{1}H NMR and ^{13}C NMR spectra are provided in appendix A, the mass spectra are provided in appendix B.

*3.2.1 Synthesis of 7,12-di-4-methoxyphenoxy-N-(2,6-di-isopropylphenyl)-1,6-di-chloroperylene-3,4,9,10-tetra-carboxy mono-imide di-butylester (**7**)*

In a 25 ml round-bottom, a mixture of N-(2,6-di-isopropylphenyl)-1,6,7,12-tetra-chloroperylene-3,4,9,10-tetra-carboxy mono-imide di-butylester (**6**) (0.500 g, 0.610 mmole), 4-methoxyphenol (0.615 g, 4.95 mmole), potassium carbonate (0.845 g, 6.11 mmole) and 18-Crown-6 (1.60 g, 6.05 mmole) in dry toluene (50 ml), was put under argon, heated to 95 °C and stirred for 18 hrs.
The reaction mixture was cooled to room temperature and toluene (100 ml) was added. The organic phase was washed with acidic water several times. The solvent was evaporated. The crude product was dried and chromatographed on silica with a 2:1 DCM:hexane eluent. The final product was obtained with a 53% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.68 (s, 2H), 7.59 (s, 2H), 7.48 (t, J = 8 Hz, 1H), 7.33 (d, J = 8 Hz, 2H), 7.16 (d, J = 8 Hz, 4H), 6.96 (d, J = 8 Hz, 2H), 4.26 (t, J = 6 Hz, 4H), 3.85 (s, 6H), 2.72 (m, J = 7 Hz, 2H), 1.68 (m, J = 7 Hz, 4H), 1.36 (m, J = 8 Hz, 4H), 1.16 (d, J = 8 Hz, 12 H), 0.92 ppm (t, J = 8 Hz, 6 H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.61, 162.96, 157.15, 155.98, 147.06, 145.64, 134.89, 133.79, 133.25, 133.02, 132.54, 130.80, 130.44, 129.67, 124.27, 124.09, 121.74, 120.62, 117.94, 117.75, 115.36, 115.16, 65.72, 55.67, 46.04, 30.38, 29.18, 23.97, 19.13, 13.68, 8.59 ppm. For the ^{1}H NMR spectrum, please refer to appendix A.3, for the ^{13}C NMR spectrum please refer to appendix A.4. MS (electron spray with IPA): $[M]^-$ Calculated for $C_{58}H_{53}Cl_2NO_{10}$, 993.30; found, 993.04. For the mass spectrum, please refer to appendix B.

*3.2.2 Synthesis of 7,12-di-4-methoxyphenoxy-N-(2,6-di-isopropylphenyl)-1,6-di-chloroperylene-3,4,9,10-tetra-carboxy mono-imide mono-anhydride (**8**)*

In a 100 ml round-bottom flask, a mixture of 7,12-di-4-methoxyphenol-N-(2,6-di-isopropyl phenyl)-1,6-di-chloroperylene-3,4,9,10-tetra-carboxy mono-imide di-butylester (**7**) (0.430 g, 0.432 mmole) and p-toluenesulfonic acid (0.246 g, 1.30 mmole), in heptane (40 ml), was stirred under reflux conditions for 6 hrs.
The reaction mixture was cooled to room temperature and the heptane was evaporated under vacuum. The crude product was resuspended in methanol and water was added. The product was filtered with a glass filter and dried. The final product was obtained with a 70% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.76 (s, 2H), 8.16 (s, 2H), 7.50 (t, J = 8 Hz, 1H), 7.35 (d, J = 8 Hz, 2H), 7.18 (d, J = 12 Hz, 4H), 7.01 (d, J = 8 Hz, 4H), 3.88 (s, 6H), 2.73 (m, J = 6 Hz, 2H), 1.17 ppm (d, J = 8 Hz, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 162.63, 159.34, 157.66, 157.24, 146.55, 145.58, 135.36, 133.51, 132.91, 132.61, 130.14, 129.87, 129.78, 129.63, 127.85, 124.47, 124.18, 121.90, 121.69, 120.32, 120.10, 119.41, 119.25, 115.64, 55.74, 29.25, 23.98 ppm.
For the ^{1}H NMR spectrum, please refer to appendix A.3, for the ^{13}C NMR spectrum please refer to appendix A.4. MS (electron spray with IPA): $[M]^-$ Calculated for $C_{50}H_{35}Cl_2NO_9$, 863.17; found, 863.12. Peak at 828.28 is the same molecule with one of the chlorines replaced by a hydrogen. For the mass spectrum, please refer to appendix B.

3.2.3 Synthesis of 1,6-di-tertbutylphenoxy-7,12-di-4-methoxyphenoxy-N-(2,6-di-isopropyl phenyl)perylene-3,4,9,10-tetra-carboxy mono-imide mono-anhydride (**9**)

In a 25 ml round-bottom, a mixture of 7,12-di-4-methoxyphenoxy-N-(2,6-di-isopropylphenyl)-1,6-di-chloroperylene-3,4,9,10-tetra-carboxy mono-imide mono-anhydride (**8**) (0.045 g, 0.046 mmole), 4-tertbutylphenol (0.028 g, 0.184 mmole) and caesium carbonate (0.060 g, 0.184 mmole) in dry DMF (4 ml), was put under argon, heated to 90 °C and stirred for 2 hrs.

The reaction mixture was cooled to room temperature and toluene (20 ml) was added. The organic phase was washed with acidic water several times. The solvent was evaporated. The crude product was dried and chromatographed on silica with a 5 % methanol in DCM eluent. The resulting mixture did not contain the desired product, as indicated by ^{1}H NMR.

3.2.4 Synthesis of 1,6,7,12-tetra-4-methoxyphenoxy-N-(2,6-di-isopropylphenyl)-3,4,9,10-tetra-carboxy mono-imide di-butylester (**15**)

In a 10 ml round-bottom, a mixture of N-(2,6-di-isopropylphenyl)-1,6,7,12-tetrachloroperylene-3,4,9,10-tetra-carboxy mono-imide di-butylester (**6**) (0.50 g, 0.061 mmole), 4-methoxyphenol (0.053 g, 0.427 mmole) and caesium carbonate (0.159 g, 0.488 mmole) in dry DMF (3 mL), was put under argon, heated to 80 °C, stirred for 1 hrs. After 1 h, the temperature was increased by 10 °C each hour. After 5 hrs (T = 120 °C), the reaction was stopped.

The reaction mixture was poured into water. The precipitate was collected by filtration with a glass filter and washed with several portions of water and ethanol. The crude product was dried and chromatographed on silica with DCM eluent. The final product was obtained with a 38 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.14 (s, 2H), 7.56 (s, 2H), 7.40 (t, J = 6 Hz, 1H), 7.25 (t, J = 4 Hz, 2H), 6.93 (d, J = 8 Hz, 8 H), 6.82 (m, J = 4 Hz, 8H), 4.22 (t, J = 6 Hz, 4H), 3.79 (d, J = 8 Hz, 12H), 2.69 (m, J = 7 Hz, 2H), 1.65 (m, J = 7 Hz, 2H (or 5H?)), 1.33 (t, J = 8 Hz, 4H), 1.11 (d, J = 4 Hz, 12H), 0.89 ppm (t, J = 6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.98, 163.50, 154.88, 153.06, 152.88, 147.05, 145.65, 135.35, 133.27, 131.09, 130.87, 129.25, 126.55, 126.42, 123.79, 121.70, 120.46, 120.17, 119.98, 119.33, 119.02, 117.54, 65.33, 34.31, 31.44, 30.38, 29.00, 23.99, 19.07, 13.68 ppm. For the ^{1}H NMR spectrum, please refer to appendix A.5, for the ^{13}C NMR spectrum please refer to appendix A.6. MS (electron spray with IPA): [M]$^-$ Calculated for $C_{72}H_{67}NO_{14}$, 1169.46; found, 1169.20. For the mass spectrum, please refer to appendix B.

3.2.5 Synthesis of 1,6,7,12-tetra-4-tertbutylphenoxy-N-(2,6-di-isopropylphenyl)-3,4,9,10-tetra-carboxy mono-imide di-butylester (**16**)

In a 10 ml round-bottom, a mixture of N-(2,6-di-isopropylphenyl)-1,6,7,12-tetra-chloroperylene-3,4,9,10-tetra-carboxy mono-imide di-butylester (**6**) (0.50 g, 0.061 mmole), 4-tertbutylphenol (0.064 g, 0.427 mmole) and caesium carbonate (0.159 g, 0.488 mmole) in dry DMF (3 mL), was put under argon, heated to 100 °C and stirred for 3 hrs.

The reaction mixture was poured into water. The precipitate was collected by filtration with a glass filter and washed with several portions of water and ethanol. The crude product was dried and chromatographed on silica with DCM eluent. The final product was obtained with a 83 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.24 (s, 2H), 7.66 (s, 2H), 7.41 (t, J = 6 Hz, 1H), 7.24 (m, J = 5 Hz, 8H), 6.84 (d, J = 8 Hz, 8H), 4.22 (t, J = 4 Hz, 4H), 2.71 (m, J = 7 Hz, 2H), 1.64 (m, J = 7 Hz, 4H), 1.34 (m, J = 8 Hz, 4H), 1.28 (d, J = 8 Hz, 36H), 1.11 (d, J = 8 Hz, 12H), 0.88 ppm (t, J = 6 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 168.00, 163.45, 156.47, 155.58, 155.42, 148.81, 148.51, 145.65, 131.05, 129.23, 123.76, 121.66, 121.54, 121.21, 120.88, 119.85, 119.57, 119.08, 118.70, 116.85, 115.10, 114.89, 65.37, 55.68, 55.64, 30.40, 28.99, 23.97, 19.11, 13.67 ppm. For the ^{1}H NMR spectrum, please refer to appendix A.5, for the ^{13}C NMR spectrum please refer to appendix A.6. MS (electron spray with IPA): [M]$^-$ Calculated for $C_{84}H_{91}NO_{10}$, 1273.66; found, 1273.44. For the mass spectrum, please refer to appendix B.

*3.2.6 Synthesis of 7,12-di-4-tertbutylphenoxy-N-(2,6-di-isopropylphenyl)-1,6-dichloroperylene-3,4,9,10-tetra-carboxy mono-imide di-butylester (**11**)*

In a 100 ml round-bottom, a mixture of N-(2,6-di-isopropylphenyl)-1,6,7,12-tetra-chloroperylene-3,4,9,10-tetra-carboxy mono-imide di-butylester (**6**) (0.500 g, 0.610 mmole), 4-tertbutylphenol (0.733 g, 4.88 mmole), potassium carbonate (0.845 g, 6.11 mmole) and 18-Crown-6 (1.60 g, 6.05 mmole) in dry toluene (85 ml), was put under argon, heated to 70 °C and stirred for 5 hrs.

The reaction mixture was cooled to room temperature and toluene (170 ml) was added. The organic phase was washed with acidic water several times. The solvent was evaporated. The crude product was dried and chromatographed on silica with a 1:1 DCM:hexane eluent. The final product was obtained with a 85% yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.66 (s, 2H), 7.68 (s, 2H), 7.48 (t, J = 8 Hz, 1H), 7.43 (d, J = 8 Hz, 4H), 7.33 (d, J = 8 Hz, 2H), 7.14 (d, J = 8 Hz, 4H), 4.26 (m, J = 4 Hz, 4H), 2.7`2 (m, J = 7 Hz, 2H), 1.69 (m, J = 7 Hz, 4H), 1.37 (m, J uncertain due to peak overlap, 4H), 1.35 (s, 18H), 1.16 (d, J = 8 Hz, 12H), 0.92 ppm (t, J = 8 Hz, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.63, 162.94, 155.37, 151.39, 148.36, 145.64, 134.99, 133.93, 133.21, 132.98, 130.74, 130.43, 129.66, 126.93, 124.09, 120.65, 119.74, 118.60, 118.03, 115.90, 65.68, 34.52, 31.42, 30.36, 29.17, 23.97, 19.09, 13.70 ppm. For the ^{1}H NMR spectrum, please refer to appendix A.3, for the ^{13}C NMR spectrum please refer to appendix A.4. MS (electron spray with IPA): $[M]^-$ Calculated for $C_{64}H_{65}Cl_2NO_8$, 1045.41; found, 1045.24. Peak at 933.16 is the perylene derivate with only one tertbutylphenol substituted. For the mass spectrum, please refer to appendix B.

*3.2.7 Synthesis of 1,6-di-4-tertbutylphenoxy-7,12-di-4-methoxyphenoxy-N-(2,6-di-isopropyl phenyl)perylene-3,4,9,10-tetra-carboxy mono-imide di-butylester (**10**)*

In a 25 ml round-bottom, a mixture of 7,12-di-4-methoxyphenoxy-N-(2,6-di-isopropylphenyl)-1,6-dichloroperylene-3,4,9,10-tetra-carboxy mono-imide di-butylester (**7**) (0.045 g, 0.046 mmole), 4-tertbutylphenol (0.055 g, 0.368 mmole) and caesium carbonate (0.120 g, 0.364 mmole) in dry DMF (4 ml), was put under argon, heated to 100 °C and stirred for 12 hrs.

The reaction mixture was cooled to room temperature and toluene (20 ml) was added. The organic phase was washed with acidic water several times. The solvent was evaporated. The crude product was dried and chromatographed on silica with a 2:1 DCM:hexane eluent. The resulting mixture did not contain the desired product, as indicated by ^{1}H NMR.

*3.2.8 Synthesis of 1,6-di-4-methoxyphenoxy-7,12-di-4-tertbutylphenoxy-N-(2,6-di-isopropyl phenyl)perylene-3,4,9,10-tetra-carboxy mono-imide di-butylester (**13**)*

In a 25 ml round-bottom, a mixture of 7,12-di-4-tertbutylphenoxy-N-(2,6-di-isopropylphenyl)-1,6-dichloroperylene-3,4,9,10-tetra-carboxy mono-imide di-butylester (**11**) (0.020 g, 0.019 mmole), 4-methoxyphenol (0.019 g, 0.150 mmole) and caesium carbonate (0.050 g, 0.150 mmole) in dry DMF (2 ml), was put under argon, heated to 100 °C and stirred for 12 hrs.

The reaction mixture was cooled to room temperature and toluene (20 ml) was added. The organic phase was washed with acidic water several times. The solvent was evaporated. The crude product was dried and chromatographed on silica with a 2:1 DCM:hexane eluent. The resulting mixture did not contain the desired product, as indicated by ^{1}H NMR.

*3.2.9 Synthesis of 7-4-hydroxy methylbenzoate-N-(2,6-di-isopropylphenyl)-1,6,12-trichloroperylene-3,4,9,10-tetra-carboxy mono-imide di-butylester (**17**)*

In a 25 ml round-bottom, a mixture of N-(2,6-di-isopropylphenyl)-1,6,7,12-tetra-chloroperylene-3,4,9,10-tetra-carboxy mono-imide di-butylester (**6**) (0.090 g, 0.111 mmole), 4-hydroxy methylbenzoate (0.022 g, 0.132 mmole), potassium carbonate (0.030 g, 0.220 mmole) and 18-Crown-6 (0.088 g, 0.330 mmole) in dry toluene (15 ml), was put under argon, heated to 70 °C and stirred for 14 hrs.

The reaction mixture was cooled to room temperature and toluene (15 ml) was added. The organic phase was washed with acidic water several times. The solvent was evaporated. The crude product was dried and chromatographed on silica with a 2:1 DCM:hexane eluent. The final product was obtained with a 53 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.71 (s, 1H), 8.67 (s, 1H), 8.13 (s, 1H), 8.10 (d, J = 8 Hz, 2H), 7.79 (s, 1H), 7.50 (t, J = 8 Hz, 1H), 7.35 (d, J = 8 Hz, 2H), 7.23 (d, J = 8 Hz, 2H), 4.40 (t, J = 6 Hz, 2H), 4.32 (t, J = 6 Hz, 2H), 3.93 (s, 3H), 2.73 (m, J = 7 Hz, 2H), 1.84 (m, J = 7 Hz, 2H), 1.73 (m, J = 8 Hz, 2H), 1.54 (m, J = 7 Hz, 2H), 1.40 (m, J = 8 Hz, 2H), 1.18 (m, J = 5 Hz, 12H), 1.03 (t, J = 8 Hz, 3H), 0.94 ppm (t, J = 8 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ = 167.04, 166.09, 162.64, 157.87, 153.45, 145.62, 134.93, 134.66, 134.46, 134.32, 133.32, 133.28, 133.20, 132.01, 131.97, 131.72, 131.63, 131.23, 130.25, 130.16, 129.85, 129.40, 126.99, 126.75, 124.19, 124.16, 123.91, 122.26, 121.45, 121.39, 120.88, 119.30, 116.90, 115.74, 66.17, 66.08, 52.25, 30.58, 30.42, 29.22, 24.01, 23.99, 23.97, 19.23, 13.79, 13.70 ppm. For the ^{1}H NMR spectrum, please refer to appendix A.3, for the ^{13}C NMR spectrum please refer to appendix A.4. MS (electron spray with IPA): $[M]^-$ Calculated for $C_{52}H_{46}Cl_3NO_9$, 933.22; found, 935.12. For the mass spectrum, please refer to appendix B.

*3.2.10 Synthesis of 7-4-tertbutylphenoxy-12-4-hydroxy methylbenzoate-N-(2,6-di- isopropyl phenyl)-1,6-di-chloroperylene-3,4,9,10-tetra-carboxy mono-imide di-butylester (**19**)*

In a 25 ml round-bottom, a mixture of 7-4-hydroxy methylbenzoate-N-(2,6-di-isopropylphenyl)-1,6,12-trichloroperylene-3,4,9,10-tetra-carboxy mono-imide di-butylester (**17**) (0.050 g, 0.054 mmole), 4-tertbutylphenol (0.065 g, 0.430 mmole), potassium carbonate (0.075 g, 0.540 mmole) and 18-Crown-6 (0.143 g, 0.540 mmole) in dry toluene (5 ml), was put under argon, heated to 90 °C and stirred for 14 hrs.

The reaction mixture was cooled to room temperature and toluene (10 ml) was added. The organic phase was washed with acidic water several times. The solvent was evaporated. The crude product was dried and chromatographed on silica with a 2:1 DCM:hexane eluent. The final product was obtained with a ~80 % yield. ^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.65 (d, J = 8 Hz, 2H), 8.09 (d, J = 8 Hz, 2H), 7.71 (s, 2H), 7.48 (t, J = 8 Hz, 1H), 7.44 (d, J = 8 Hz, 2H), 7.33 (d, J = 8 Hz, 2H), 7.23 (d, J = 8 Hz, 2H), 7.15 (d, J = 8 Hz, 2H), 4.28 (m, J = 4 Hz, 4H), 3.93 (s, 3H), 2.71 (m, J = 7 Hz, 2H), 1.71 (m, J = 7 Hz, 4H), 1.39 (m, J uncertain due to peak overlap, 4H), 1.36 (s, 9H), 1.16 (d, J = 4 Hz, 12H), 0.92 ppm (t, J = 8 Hz, 6H). ^{13}C NMR (101 MHz, $cdcl_3$) δ = 167.50, 162.82, 158.15, 155.46, 153.53, 151.28, 148.52, 145.60, 133.13, 131.87, 126.99, 126.68, 124.11, 121.07, 119.76, 119.52, 119.18, 117.14, 115.99, 65.92, 60.71, 52.20, 31.41, 30.41, 29.17, 23.96, 19.14, 13.70 ppm. For the ^{1}H NMR spectrum, please refer to appendix A.5, for the ^{13}C NMR spectrum please refer to appendix A.6. MS (electron spray with IPA): $[M]^-$ Calculated for $C_{62}H_{59}Cl_2NO_{10}$, 1047.35; found, 1047.24. For the mass spectrum, please refer to appendix B.

3.2.11 Synthesis of 7-4-tertbutylphenoxy-12-4-hydroxy methylbenzoate-N-(2,6-di- isopropyl phenyl)-1,6-di-4-methoxyphenoxy-perylene-3,4,9,10-tetra-carboxy mono-imide di-butylester (21)

In a 25 ml round-bottom, a mixture of 7-4-tertbutylphenoxy-12-4-hydroxy methylbenzoate-N-(2,6-di-isopropylphenyl)-1,6-di-chloroperylene-3,4,9,10-tetra-carboxy mono-imide di-butylester (**19**) (0.050 g, 0.048 mmole), 4-methoxyphenol (0.047 g, 0.381 mmole), caesium carbonate (0.124 g, 0.381 mmole) in dry DMF (5 ml), was put under argon, heated to 80 °C and stirred for 16 hrs.

The reaction mixture was cooled to room temperature and toluene (45 ml) was added. The organic phase was washed with acidic water several times. The solvent was evaporated. The crude product was dried and chromatographed on silica with a 2:1 DCM:hexane eluent. The resulting mixture did not contain the desired product, as indicated by ^{1}H NMR.

4 Results and discussion

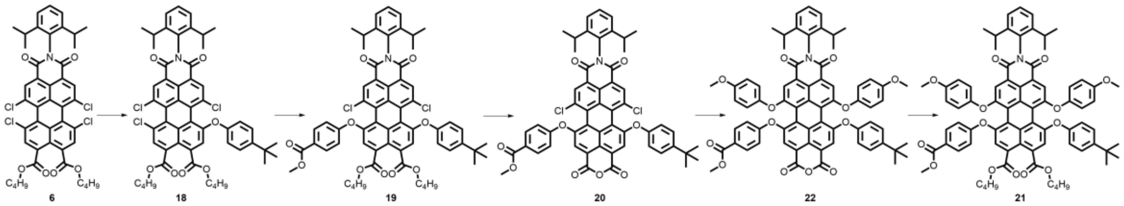
4.1 Precursor synthesis

The precursor for the research project was N-(2,6-di-isopropylphenyl)-1,6,7,12-tetra-chloroperylene-3,4,9,10-tetra-carboxy mono-imide di-butylester (**6**). This perylene derivate was synthesized from commercially available perylene-3,4,9,10-tetra-carboxylic di-anhydride (**1**) as shown in appendix D.1. A detailed description of the synthesis procedures can be found in appendix D.2 and the mechanisms for the reactions can be found in appendix C. Procedures for these reactions where obtained from an article by Dubey *et al.* [13]. The ^{1}H NMR and ^{13}C NMR spectra of compounds **4**, **5** and **6** are provided in appendix A.1.

The ^{1}H NMR and ^{13}C NMR spectra of compound **3** were not recorded in this project, due to solubility issues. These spectra can be found in the article by Dubey *et al.* [13].

4.2 First reaction series

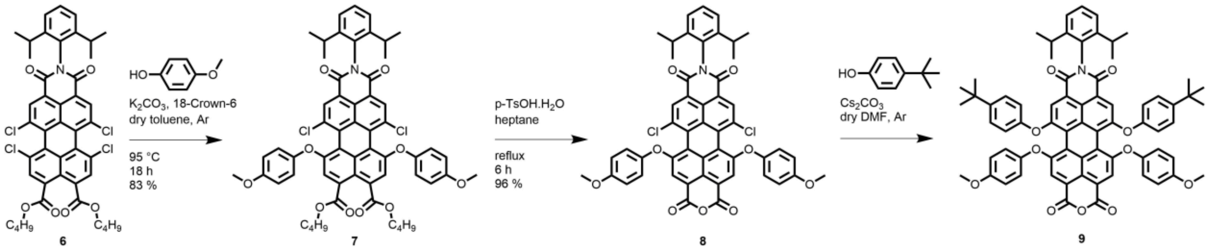
As introduced in section 2.6.3, the envisioned project route was as depicted in Scheme 3 (or repeated below in Scheme 4).



Scheme 4: Envisioned substitution route for research project, repeated.

Before the first bay-substitution reactions were done on the precursor, it was hypothesized that the 1 and 6 positions would not be active enough for nucleophilic aromatic substitution if esters were attached to the 9 and 10 positions. To overcome this challenge, a synthetic route was established with an anhydride intermediate, as can be seen in Scheme 4.

Before the synthetic route in Scheme 4 was performed, a test was done to see whether the step between **20** and **22** was possible, since this step was hypothesized to be the most challenging step in the envisioned synthetic route. This test is depicted in Scheme 5. This hypothesis originated from the novelty of the step between **20** and **22**. All reactions up to **19** have already been performed in previous research, as can be seen in the article by Dubey *et al.* [2]. The question was whether the anhydride would make the 1 and 6 positions of the perylene core active enough for SN_{Ar} and whether the anhydride would remain stable throughout the reaction.



Scheme 5: Test for the anhydride activation.

In the performed test, the first substituent attached to the bay-positions of the perylene core was 4-methoxyphenol, to the 7 and 12 positions. This phenol derivate is the most reactive of the 3 phenols used, and the most deactivating. It was hypothesized that both reactivity and deactivation would not pose a problem for the substitution on the 1 and 6 positions, due to the activation of these positions by the anhydride on the lower peri-positions. This activation was shown before, in Figure 11.

The reaction between **8** and **9** was performed at 90 °C for 2 hours, but the desired product was not isolated from the product mixture. Subsequent attempts were performed at 120 °C for 72 hours in DMF and 90 °C for 24 hours (but in dry toluene as opposed to dry DMF). These attempts represent a “most activating” attempt with high temperature and a highly polar solvent, and a “least activating” attempt with low temperature and a less polar solvent. All attempts yielded comparable results, represented in the TLC in Figure 12. The eluent for this TLC was pure DCM. In this figure, the leftmost dot is the reactant, while the rightmost dot is the reaction product mixture. It is hypothesized that this result indicates that the anhydride is attacked by the nucleophile as opposed to the 1 or 6 positions of the perylene core.

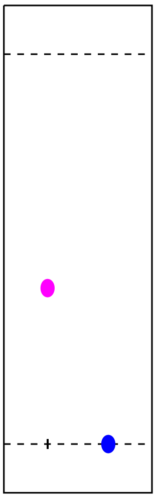


*Figure 12: TLC data from the reaction from **8** to **9**.*

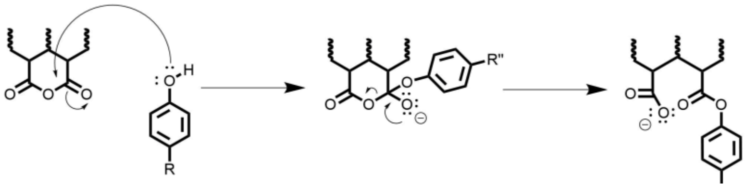
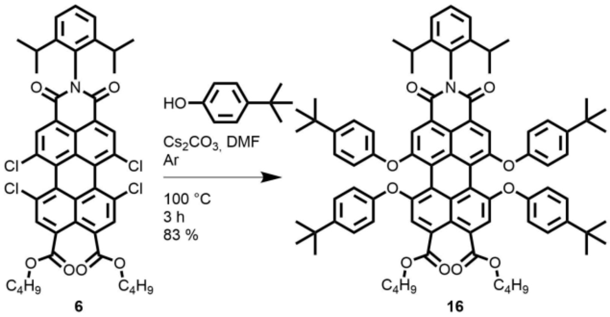


Figure 13: Mechanism of a nucleophilic attack on an anhydride.

To illustrate as to why this is hypothesized, the reactions mechanism for the attack of the anhydride is provided in Figure 13. As can be seen in this figure, when a nucleophile attacks an anhydride, the resulting product is highly polar or even charged, depending on the pH of the environment. This strongly polar group attached to the perylene core would explain why the product stays on the baseline in the depicted TLC. However, further research is needed to verify this hypothesis. It must be mentioned that addition of a strong acid to the product solution did not yield a product that was moving (faster) on TLC. One would expect a strong acid to either re-close the anhydride ring after it has been attacked by a nucleophile or re-establish esters on the opened anhydride. The fact that this does not happen weakens the hypothesis.

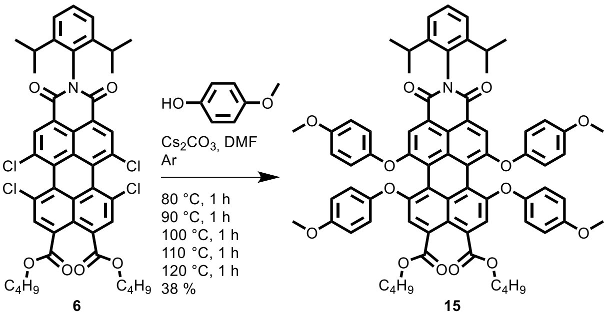
4.3 One step back

To overcome the challenge that arose with the anhydride intermediate the reactions in Scheme 6 and Scheme 7 were performed.



Scheme 6: Reaction towards a tetra-bay-substituted 4-t-butylphenol perylene.

These reactions were performed to test whether the 1 and 6 positions of the perylene core were active enough to be substituted when esters are attached to the lower peri-positions (9, 10) of the perylene core. The substituents that were used in these reactions were the substituents most commonly used during this project (4-tertbutylphenol and 4-methoxyphenol).



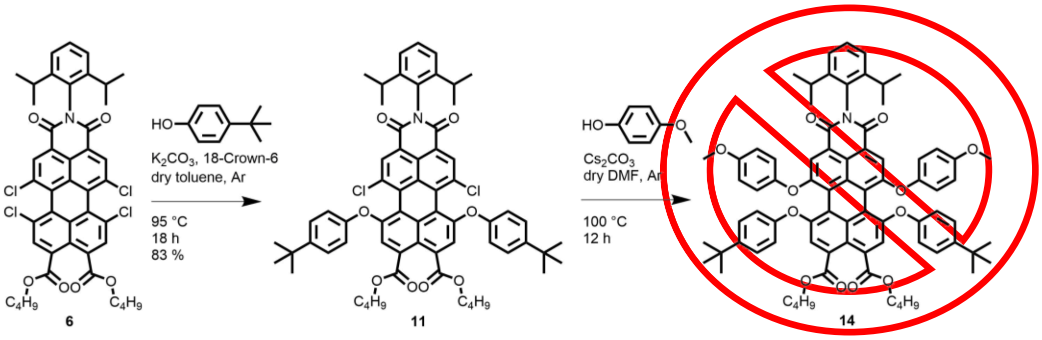
Scheme 7: Reaction towards a tetra-bay-substituted 4-methoxyphenol perylene.

The reaction in Scheme 6 was performed similar to a procedure in a paper by Dubey *et al.* [13]. In this paper, a perylene with imide groups on both the upper and lower peri-positions is substituted with four 4-tertbutylphenol groups.

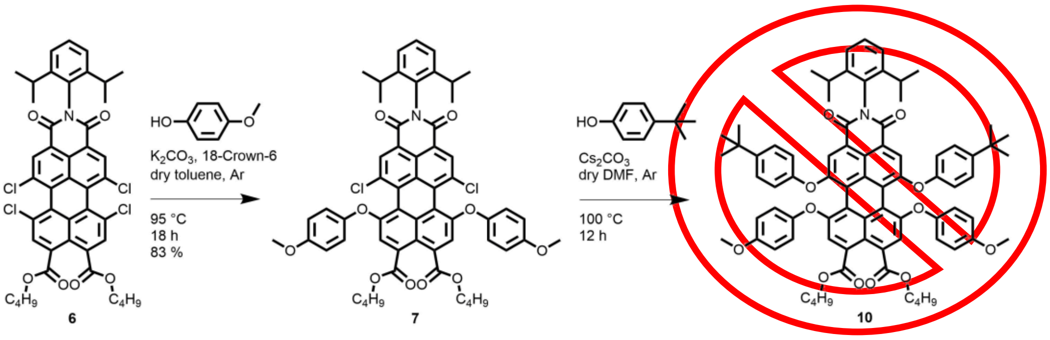
The reaction in Scheme 7 was performed with similar conditions used in the reaction in Scheme 6. However, it was found that to enhance the yield, higher reaction temperatures were needed. The hypothesis is that the reaction could be optimized further. However, since this was not the scope of the project, this optimization was not performed.
Both reactions were successful, as can be seen by the corresponding ^{1}H NMR, ^{13}C NMR and mass spectra in appendices A.5, A.6 and B respectively. Both **15** and **16** have not been synthesized before, which makes these two compounds the first two contributions of this project to the pool of synthesized PTCA derivates.

4.4 Next step

After successful substitution of 4 equal substituents, the next step was to pairwise substitute the 7/12 and 1/6 positions with different phenol substituents. This was done with two different substituents, 4-tertbutylphenol and 4-methoxyphenol. The reaction series was performed twice, with the substituents in different orders. The reaction series can be found in Scheme 8 and Scheme 9.



Scheme 8: Attachment of two different phenol derivates to the perylene core, tertbutyl below and methoxy above.



Scheme 9: Attachment of two different phenol derivates to the perylene core, methoxy below and tertbutyl above.

As can be seen from these figures, both substitutions of the 1 and 6 positions were unsuccessful. For the reaction in Scheme 8, reaction temperatures ranging from 80 °C to 120 °C were attempted. For all reactions temperatures, TLC results were comparable. The desired product was not be isolated, judging by ^{1}H NMR obtained from the different components of the product mixture.

Exactly the same is true for the reaction in Scheme 9.

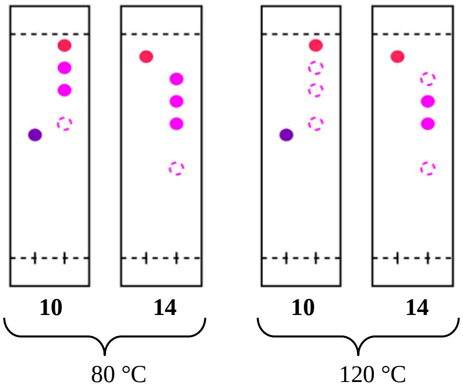


*Figure 14: TLC data from the reactions from **7** to **10** and from **11** to **14**. From left to right: **10** at 80 degrees, **14** at 80 degrees, **10** at 120 degrees, **14** at 120 degrees. Reactant is depicted on the left, product(s) on the right.*

The TLC data of the described reactions can be found in Figure 14, with the compound numbers of the reaction products reported below each TLC. The solvent used for the TLC's is 2:1 DCM:hexane. As with the previous TLC, in each of the TLC's in Figure 14, the left dot is the reactant and the right dot is the product mixture. As expected, the products of the reaction from **7** to **10** have higher R_f values than the reactant, since the phenol derivate that was attached is less polar than the phenol derivate that had already been attached. The products from the reaction from **11** to **14** have lower R_f values than the reactants, which is again in line with the expectation based on the polarity of the second substituent.

During this project, some of the dots in Figure 14 have been identified:

For the TLC's on the reaction towards **10**, the highest dot is 1,6,7,12-tetra-4-tertbutylphenoxy-N-(2,6-di-isopropylphenyl)-3,4,9,10-tetra-carboxy mono-imide di-butylester (**16**) and the second highest dot is a mixture of the two compounds depicted in Figure 19. For the TLC's on the reaction towards **14**, the second lowest dot is 1,6,7,12-tetra-4-methoxyphenoxy-N-(2,6-di-isopropylphenyl)-3,4,9,10-tetra-carboxy mono-imide di-butylester (**15**). Proof on these identifications will be provided in the sections 4.4.2 and 4.4.3.

Procedures for these reactions were adapted from conditions of previous reactions. However, after the first few attempts, a step of pouring the reaction mixture into water directly after the reaction mixture had cooled was introduced as a first purification step. Before this step, any attempt at identifying compounds on ^{1}H NMR were complicated by several extra peaks in the spectrum. These peaks were not predicted from the structure of the molecule and/or the spectra of previous perylene derivates. These peaks were likely from water soluble impurities (for example, residual DMF).

As stated before, for both reactions, the desired product was not isolated. However, ^{1}H NMR results indicate that phenol exchange occurs. This has only been observed for the reactions done at 120 °C, but a side note here is that the reactions at 80 °C were only performed before the step of pouring into water was implemented. This made identification of compounds on ^{1}H NMR virtually impossible. As will be restated in the recommendations in chapter 5, performing this reaction at 80 °C with the step of pouring into water could prove fruitful in a future project. However, due to time constraints, this reaction was not performed during this project.

4.4.1 Complexity of phenol exchange

To explain the complexity of the product mixture obtained after extended phenol exchange in bay-substituted perylenes has occurred, a representation is made in Figure 15 of all phenol exchange outcomes possible for a perylene with two equal substituents on the 7 and 12 positions.

This scheme does take the displacement of the phenol substituents on the 7 and 12 positions to the 1 and 6 positions into account.

4.4.2 4-methoxyphenol as second nucleophile

Figure 16 displays the ^{1}H NMR spectrum taken from one of the fractions obtained from the product mixture that was obtained after the reaction from **11** to **14**. On the TLC's, this is the second lowest dot for the TLC's of the reaction towards **14**. This reaction is displayed in Scheme 8.

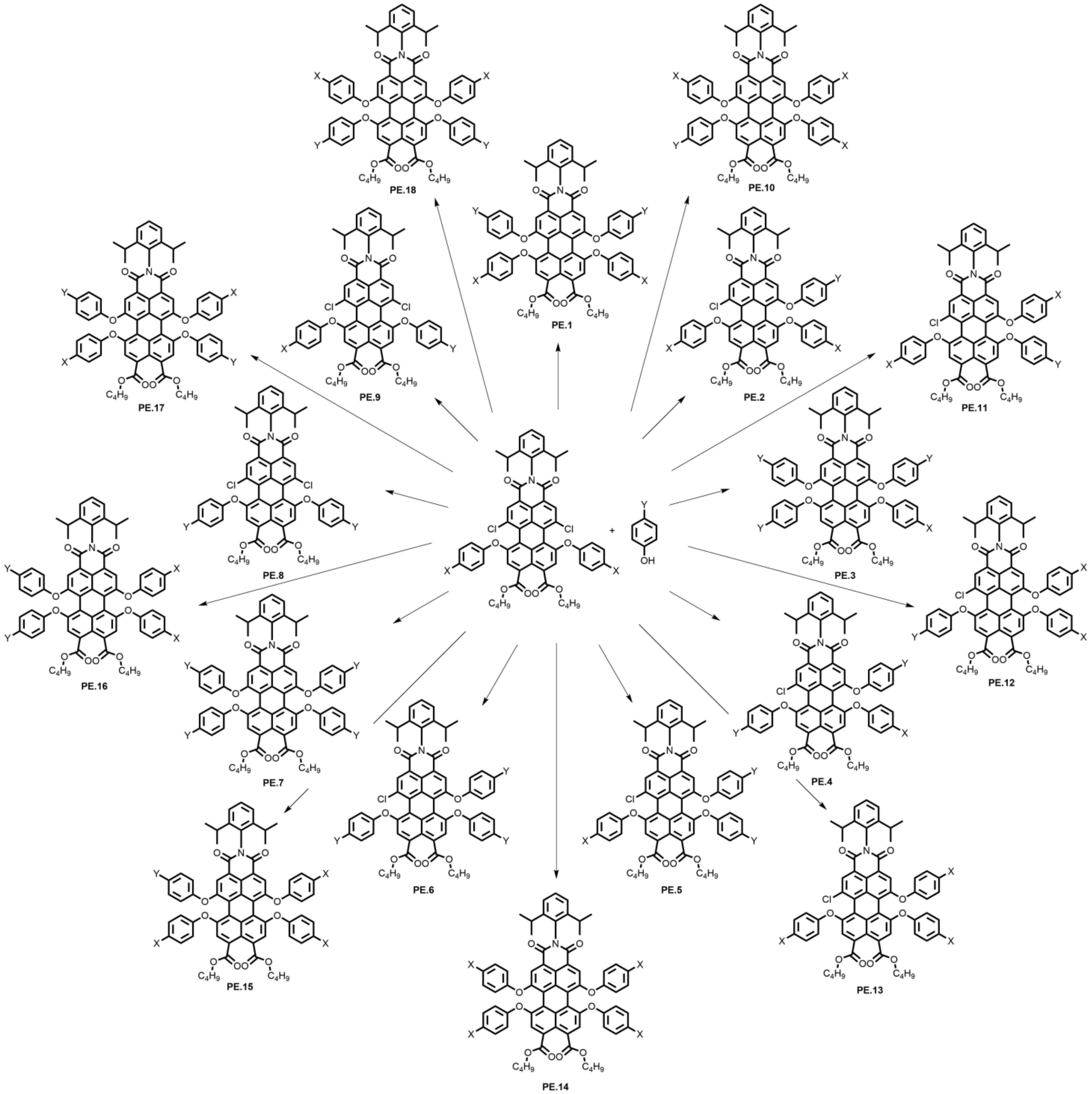


Figure 15: Phenol exchange outcomes of a perylene with equal substituents on the 7 and 12 positions.

As can be observed from the ^{1}H NMR spectrum in Figure 16, quantitative phenol exchange has taken place. The two 4-tertbutylphenoxy groups on the 7 and 12 positions have been exchanged by 4-methoxyphenols, yielding 1,6,7,12-tetra-4-methoxyphenoxy-N-(2,6-di-isopropylphenyl)-3,4,9,10-tetra-carboxy mono-imide di-butyl ester (**15**). This finding is in line with the presented theory on nucleophilic strength and leaving group abilities.

In a fraction of the same product mixture with a higher R_f value, the typical tertbutyl peak (around 1.3 ppm) can be observed (this characteristic peak can be found in the ^{1}H NMR spectrum of 4-tertbutylphenol in appendix A.7). The encounter of this peak indicates that some tertbutyl phenol substituted molecules are still present in the product mixture. It is hypothesized that a more careful approach to the last reaction in Scheme 8, in terms of temperature, might yield the desired product. However, due to time constraints, this was not tested.

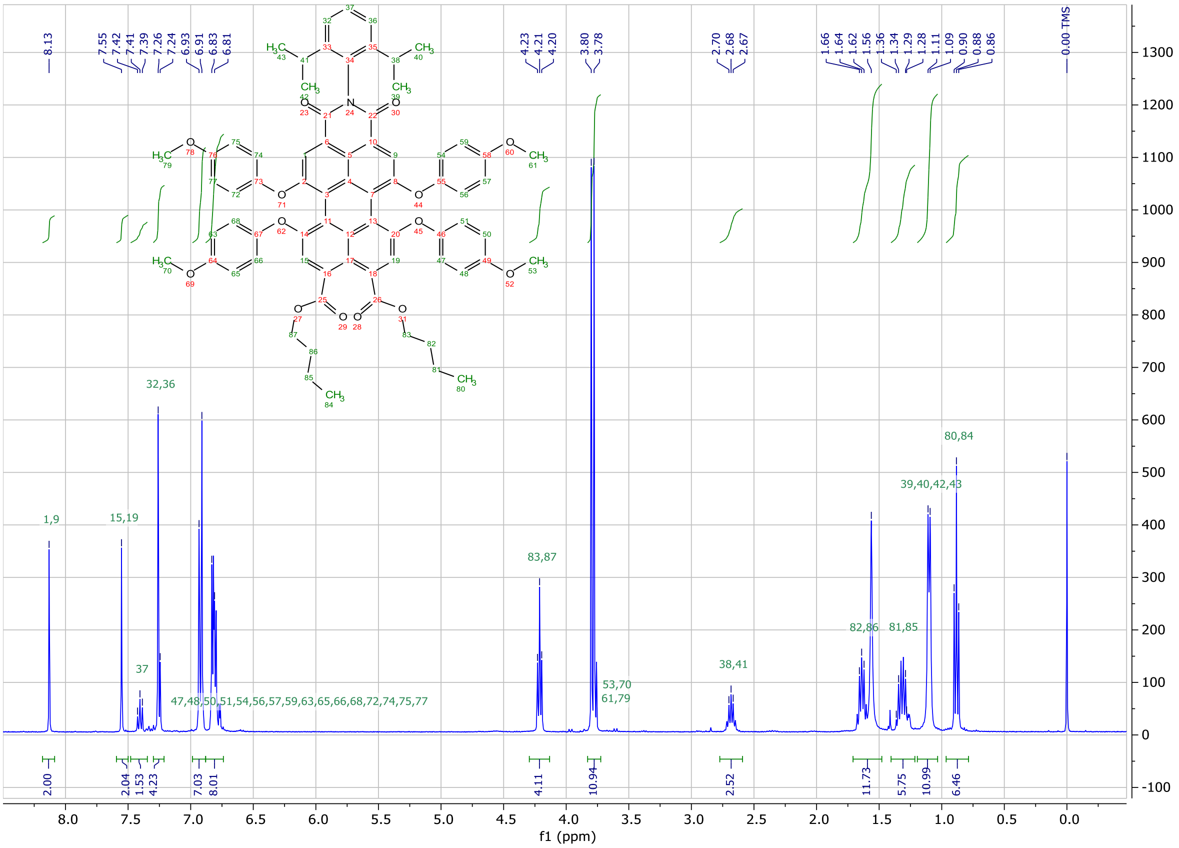


Figure 16: ^{1}H NMR of tetra-4-methoxy substituted perylene, phenol exchange product from the reaction from ***11*** *to* ***14****.*

4.4.3 4-tertbutylphenol as second nucleophile

As with the reaction from **11** to **14**, in the reaction from **7** to **10** displayed in Scheme 9, phenol exchange took place. This goes against the expectation, considering the theory on nucleophilic strength and leaving group ability. However, from the ^{1}H NMR spectrum in Figure 17 it can be observed that phenol exchange goes as far as tetra-4-tertbutylphenol substituted perylene. Other products are formed, as can be seen from the ^{1}H NMR spectrum in figure Figure 22 and Figure 21. A more thorough analysis of this spectrum is provided below.

To draw the conclusion that phenol exchange causes the tetra-4-tertbutylphenol substituted perylene, it must be proven the starting material for the reaction from **7** to **10** does not have any tetra-chlorinated perylene (**6**) present. If this would be the case, the tetra-chlorinated perylene (**6**) could easily be converted to tetra-4-tertbutylphenol substituted perylene (**16**), without the need for phenol exchange.

However, as can be seen from Figure 18, a clear distinction can be made between the two compounds (**6** and **7**) when looking at the aromatic region of the ^{1}H NMR spectrum. From this figure, it can be concluded that the starting material for the reaction in Scheme 9 (compound **7**) was indeed free of tetra-chlorinated perylene (compound **6**).

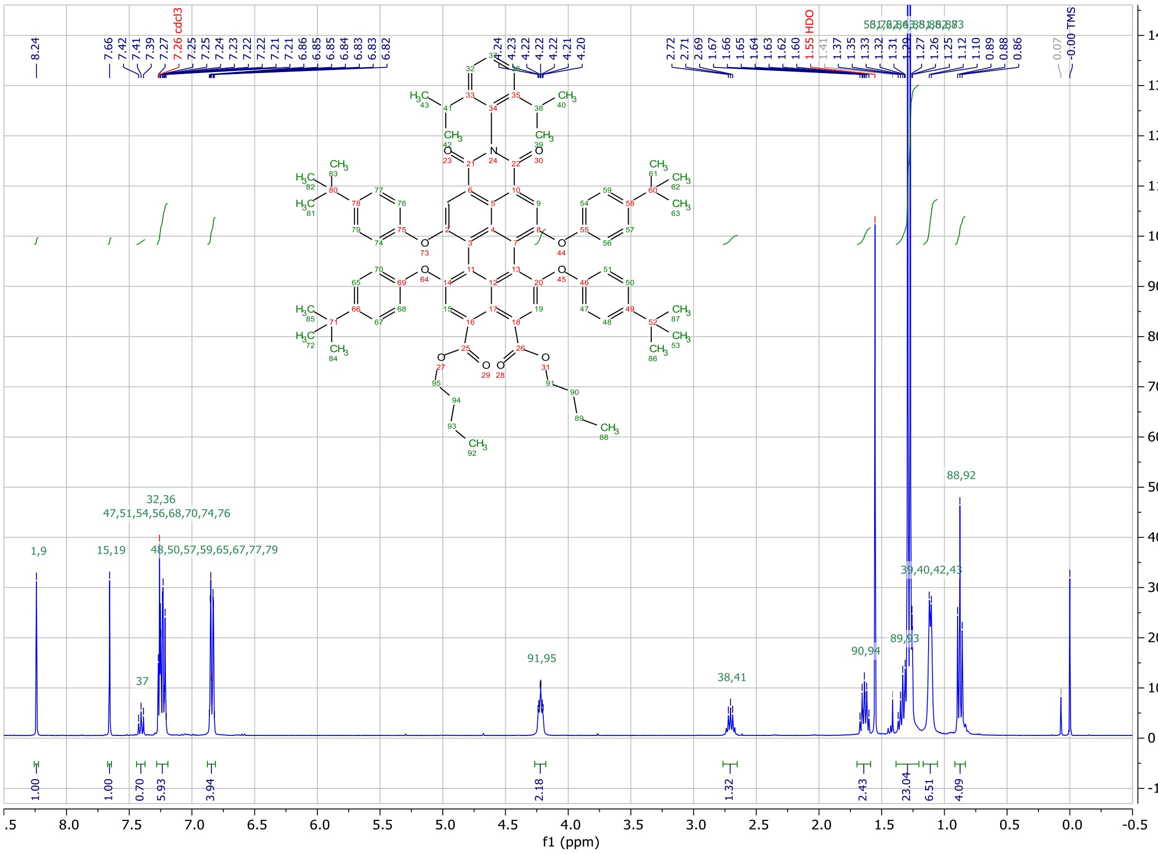


*Figure 17: ^{1}H NMR of tetra-4-tertbutyl substituted perylene, phenol exchange product from the reaction from **7** to **10**.*

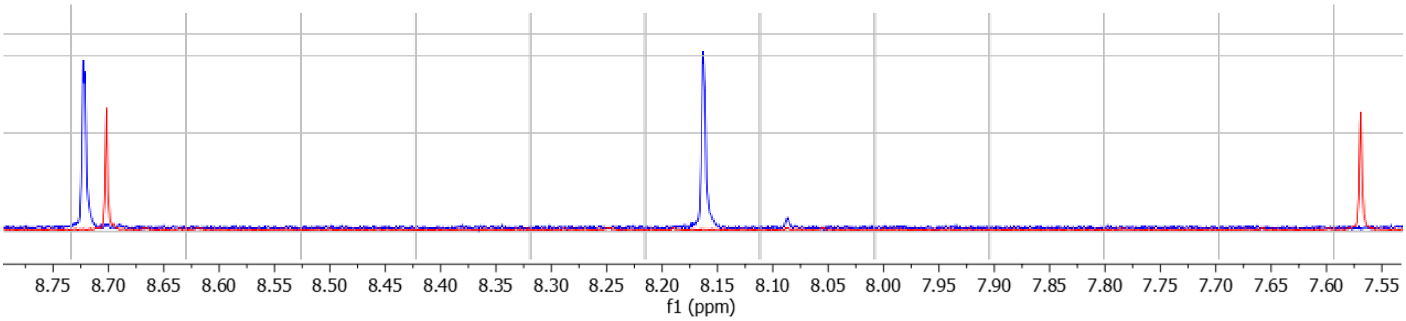
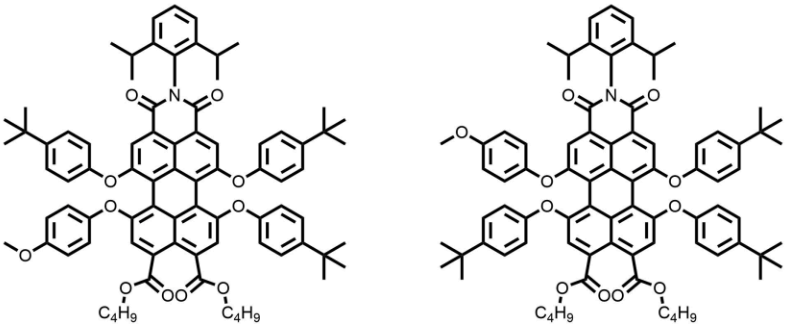


*Figure 18: Aromatic region, with the spectra of N-(2,6-di-isopropylphenyl)-1,6,7,12-tetra-chloroperylene-3,4,9,10-tetra-carboxy mono-imide di-butylester (**6**) in blue and 7,12-di-4-methoxyphenol-N-(2,6-di-isopropyl phenyl)-1,6-di-chloroperylene-3,4,9,10-tetra-carboxy mono-imide di-butylester (**7**) in red.*

It is hypothesized that the ^{1}H NMR spectrum in Figure 22 and Figure 21 (the spectrum is split in the aromatic and the aliphatic regions) is the spectrum of a mixture of the two molecules presented in Figure 19. This hypothesized is confirmed by electron spray mass spectrometry (in IPA). This mass spectrum can be found in Figure 20. On top of that, this hypothesis is backed up by the following four arguments:

- There are eight distinct singlets above 7.5 ppm. Singlets in this region indicate the aromatic protons on the perylene core, as can be seen from previous spectra on perylene derivates. Eight unequal protons on the perylene core could indicate two kinds of perylene derivates with four unequal aromatic protons each. This means that no symmetric perylenes are present in the sample.

- The triplet around 7.4 ppm indicates the aromatic proton on the top of the imide on the peri-position of a perylene core. This triplet in this spectrum looks like two triplets that highly overlap, supporting the hypothesis that two different perylene imides are present in the sample.



28 29

Figure 19: Two of the possible phenol exchange products from a reaction of a 7,12-di-methoxyphenol perylene with 4-tertbutylphenol as second nucleophile.

- The peak around 3.8 ppm is characteristic for a substituted 4-methoxyphenol. Upon integration, this peak indicates that six protons from a methoxy group are present in the sample, indicating that the compounds present in the sample together have two 4-methoxyphenol substituents (three protons per methoxy group).
- The large peak around 1.3 ppm is characteristic for a substituted 4-tertbutylphenol. However, this position on the spectrum is also the position of some of the protons of the esters on the lower peri-positions (9, 10). Upon integration, this peak indicates that 62 protons from the tertbutyl groups and the ester are present. Subtracting the two times four protons from the ester, 54 protons remain. This indicates that the compounds presented in the sample together have six 4-tertbutylphenol substituents (nine protons per tertbutyl group).

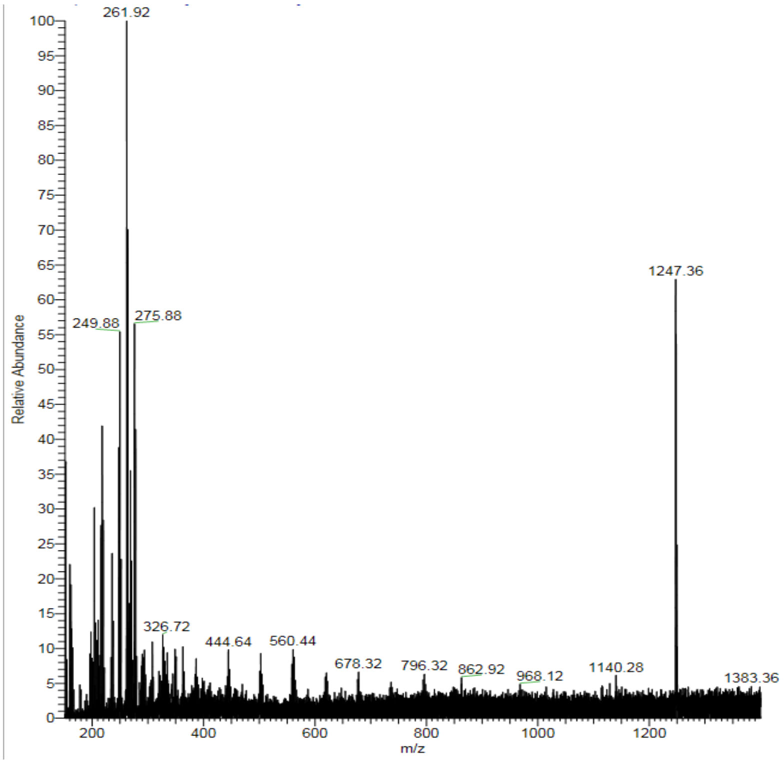


Figure 20: Mass spectrum of the two products present in Figure 19.

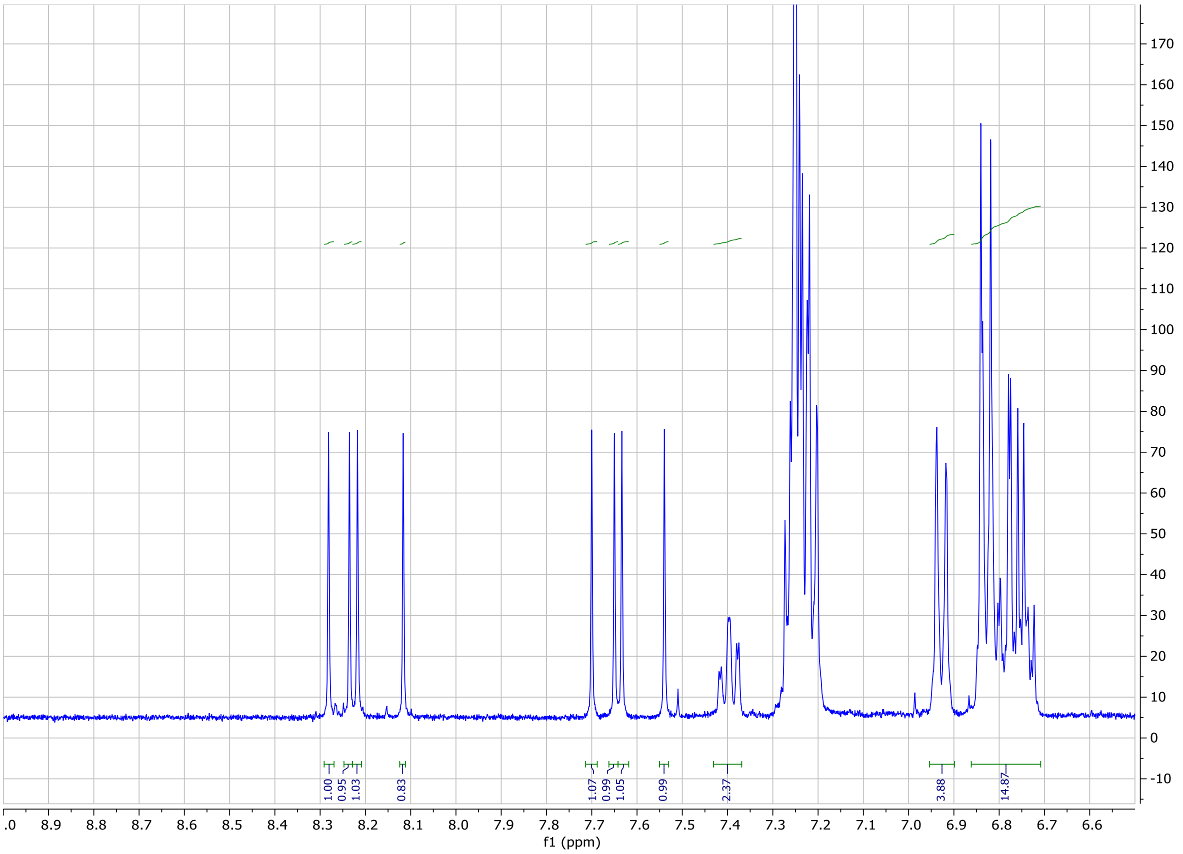


Figure 22: ^{1}H-NMR spectrum of phenol exchange products in Figure 19, aromatic area.

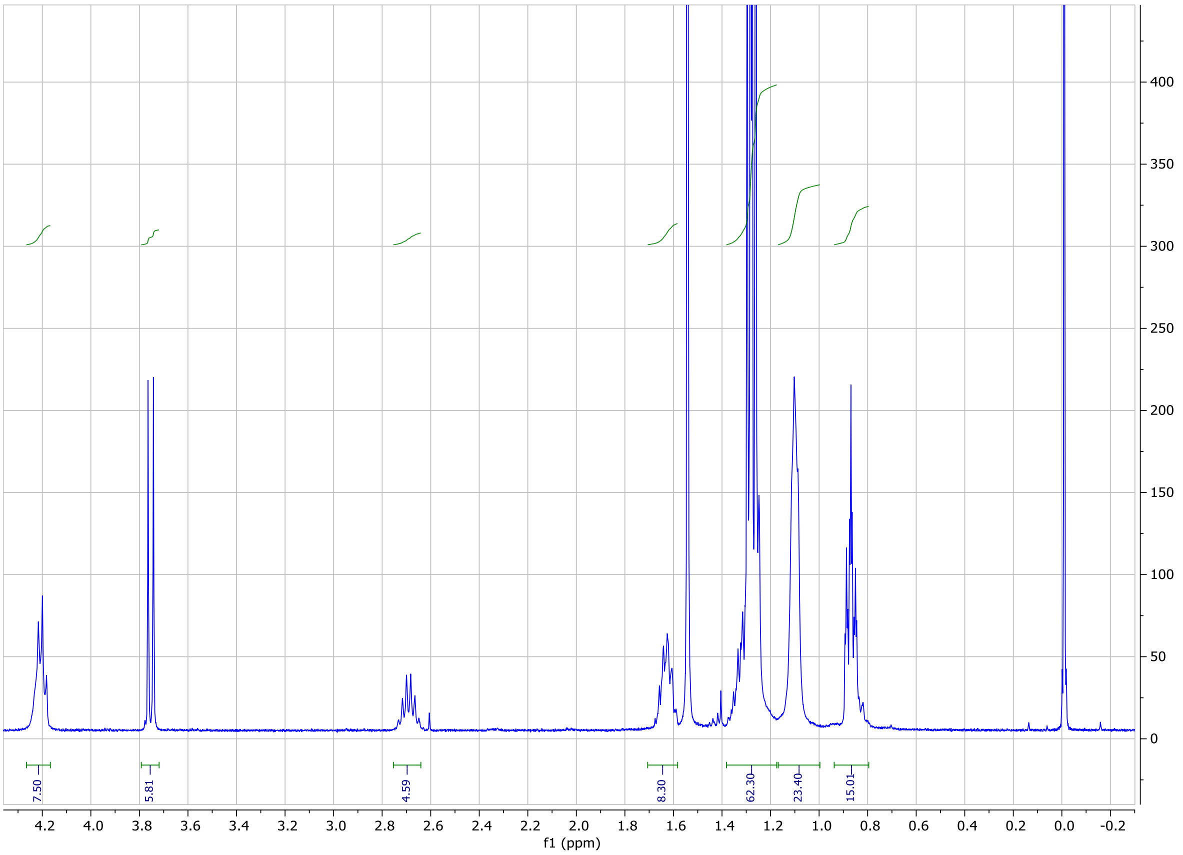


Figure 21: ^{1}H-NMR spectrum of phenol exchange products in Figure 19, aliphatic area.

4.4.4 Conversion at long reaction times

It has been shown that with the reactions in Scheme 8 and Scheme 9, phenol exchange has occurred. It might be expected that full conversion towards tetra-substituted perylene (with a single type of phenol) takes place at long reactions times, provided the temperature is high enough and enough equivalents of phenol substituent are available. This hypothesis has been tested for the reaction in Scheme 8, since it still follows from theory that 4-methoxyphenol is the strongest nucleophile available (provided one can choose from the three nucleophiles provided in Figure 9). As this nucleophile is the strongest, it should have the highest potential to achieve full conversion.

1,6,7,12-tetra-4-methoxyphenoxy-N-(2,6-di-isopropylphenyl)-3,4,9,10-tetra-carboxy mono-imide di-butyl-ester (**15**) was formed, but a yield higher than 38 % could not be obtained. Instead, at long reaction times (+72 hours, with 7 equivalents of phenol derivate and at 120 °C), more polar compounds started to form, judging from TLC (the "more" in "more polar" is in comparison with the rightmost TLC in Figure 14). This TLC can be found in

Concluding this section, the chemistry on perylenes with 2 different bay-substituents is not as trivial as was expected beforehand. More research is needed to explore this complexity.

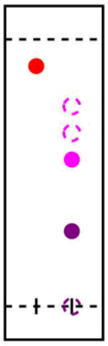
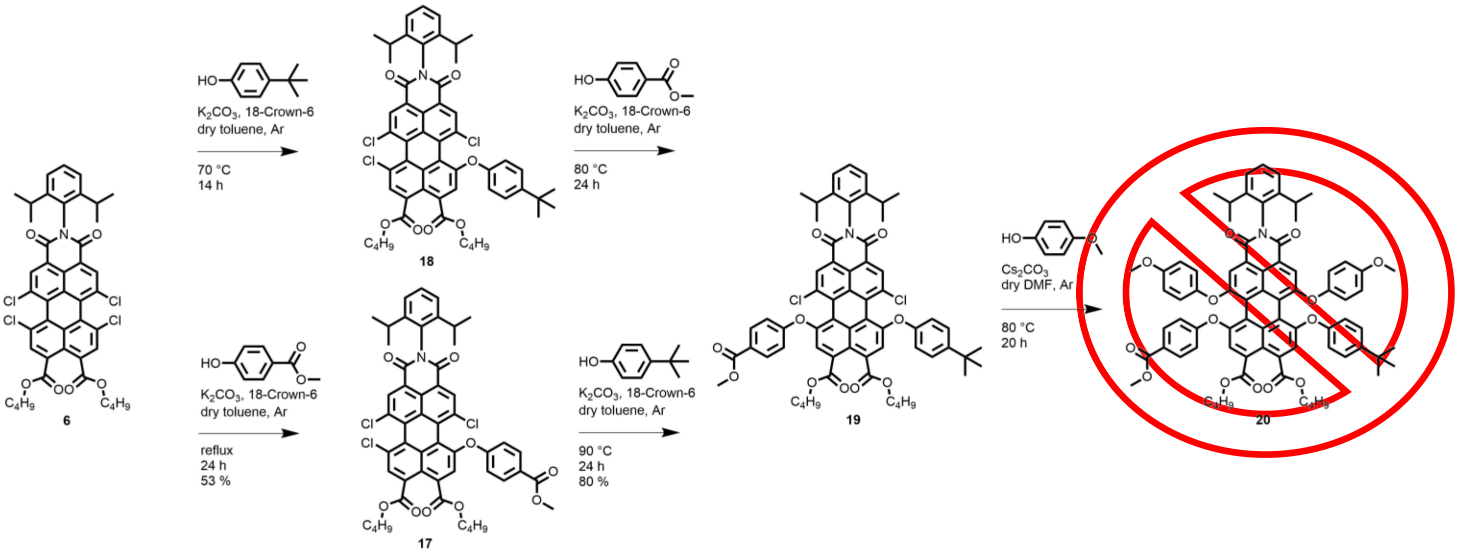


*Figure 23: TLC of long-time experiment of the reaction from **11** to **14**.*

4.5 Final step

Although no success was achieved substituting two different substituents on the bay-positions, a parallel synthetic route was performed towards the original goal compound of the project. This route can be found in Scheme 10. The first two steps in this route were performed via two alternate ways, as can be seen in the figure. Both these routes were successful. However, the lower route in the figure was chosen, since with the upper route, separation of compound **18** from compound **17** turned out to be very difficult (if not impossible). This also made determination of the yield of the upper route very difficult. No procedure, no yields and no spectra, have been recorded for the intermediate compound in the upper route. The ^{1}H NMR, ^{13}C NMR and mass spectra of the intermediate compound of the lower synthetic route can be found in appendices A.3, A.4 and B respectively.



Scheme 10: A reaction series towards the original goal compound of the project.

Procedures for these reactions were adapted from previous reaction procedures. Compound **19** is the third and final novel compound synthesized in this project.

The last step of this synthetic route was unsuccessful, which was expected, considering the failure of comparable steps in the previous synthetic routes.

As with previous attempts to substitute phenol derivates on ester activated 1 and 6 positions of the perylene core, phenol exchange occurred. This exchange goes as far 1,6,7,12-tetra-4-methoxyphenoxy-N-(2,6-di-isopropylphenyl)-3,4,9,10-tetra-carboxy mono-imide di-butylester (**15**), as shown by ^{1}H NMR (Appendix A.9, second set of spectra).

5 Conclusion and recommendations

5.1 Conclusion

In conclusion, the substitution of the bay-positions of 7,12-di-4-methoxyphenoxy-N-(2,6-di-isopropylphenyl)-1,6-di-chloroperylene-3,4,9,10-tetra-carboxy mono-imide mono-anhydride (**8**) is less trivial than expected. No success was attained in attaching five different substituents to the perylene core, specifically three different substituents to the bay-positions.
This can be attributed to a failure of the original project route, seen in Scheme 3. The critical step was the step from **20** to **22**. It turned out that the activation of the 1 and 6 positions by the anhydride was not as straightforward as expected. This was shown by attempting the reaction in Scheme 5. Instead of tetra-substituted perylenes, the reaction in Scheme 5 yielded a mixture of polar compounds, as shown by TLC (Figure 12).
As an alternative, substitutions were attempted on perylene derivates with butylesters attached to the 9 and 10 positions. These routes posed their own challenges, being phenol exchange and the activation of the 1 and 6 positions. It is deemed likely that the route via an ester intermediate will not work. If it would work, it is likely that only very specific substitution pattern and reaction condition combinations will work.

However, it has also been shown that attaching two different substituents on the lower bay-positions poses no challenges. This could mean that, once the challenges for substituting selectively to the upper bay-positions (1, 6) have been addressed, the substitution of three different types of substituents to the bay positions might quickly follow.

Another important result of this research is the initial investigation of the phenol exchange phenomenon. It was found that this exchange is a real threat to selective substitution, when this substitution is performed on a perylene with an imide and a di-ester on the peri-positions. This threat might be avoided by substituting the di-ester with an anhydride, but using an anhydride comes with its own challenges, as was observed during this project.

Although useful insight has been gained during this project, more research is needed to answer the questions raised during this research. Some suggestions for follow-up research are provided below.

5.2 Recommendations

During this research project, the anhydride activated reaction in Scheme 5 was performed. However, this reaction was performed in a strongly polar solvent, with a relatively weak nucleophile. This might have resulted in an attack on the anhydride, instead of on the envisioned bay-positions of the perylene. This reaction could be attempted again, with a less polar solvent and with a stronger nucleophile. The combinations polar solvent/strong nucleophile and less polar solvent/weak nucleophile could also be explored.

With the reactions described in Scheme 8 and Scheme 9, the procedure was altered during the project. The step of pouring the reaction mixture into water after completion of the reaction was introduced as an initial purification step. This step was implemented for attempts on this reaction at 120 °C, but not at lower temperatures. However, it is believed that lower reaction temperatures in this reaction might yield the desired products. On top of that, lowering the reaction temperature could prove an easy way to reduce phenol exchange. Nonetheless, this will not be an easy job, as first attempts at this temperature tuning yielded complex mixtures of perylene derivates.

A third recommendation is to see whether either Suzuki or Sonogashira coupling could be performed on the 1 and 6 positions of a perylene derivate. This would not lead to the original goal of the project, since neither Suzuki nor Sonogashira coupling lend themselves for phenolation. However, it could be used to continue the substitution pathway after compound **19**, and thus further functionalize the perylene core.

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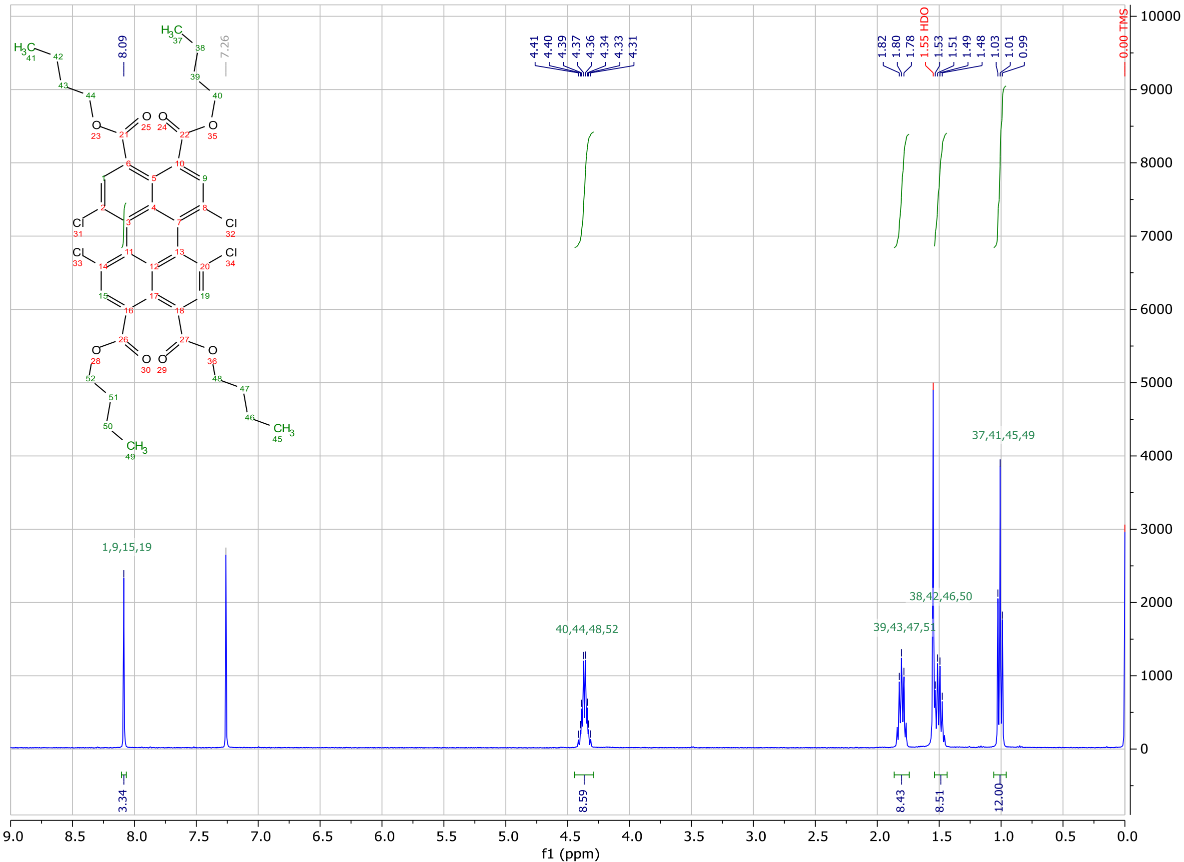
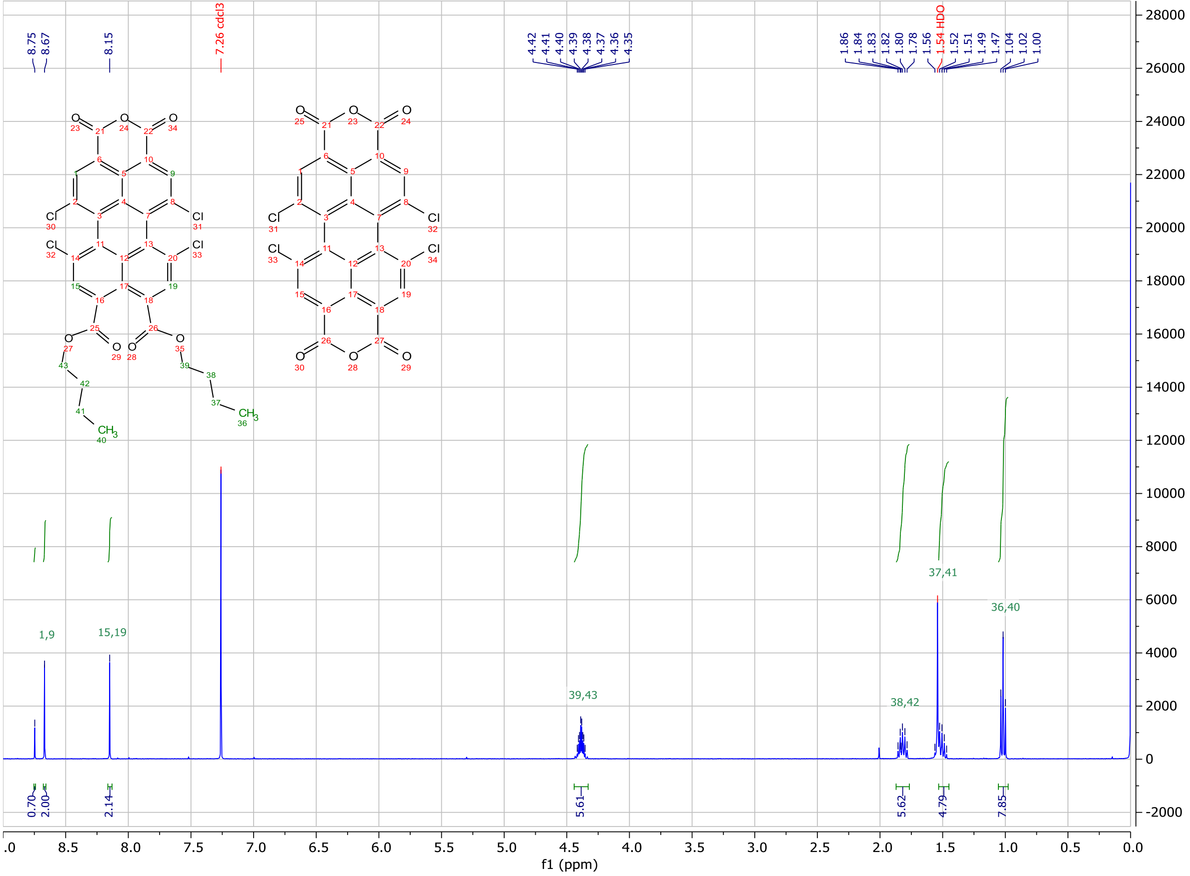
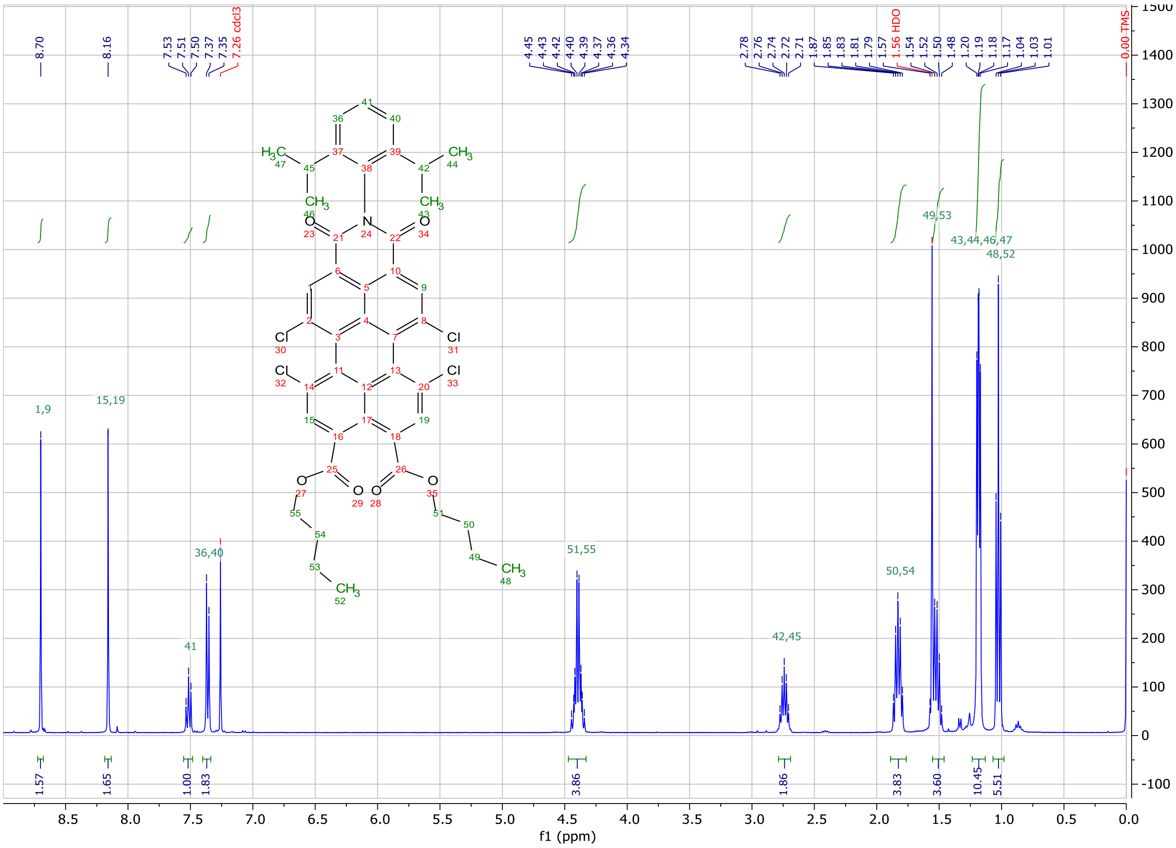
Appendix A.1 - ^{1}H NMR spectra precursor compounds



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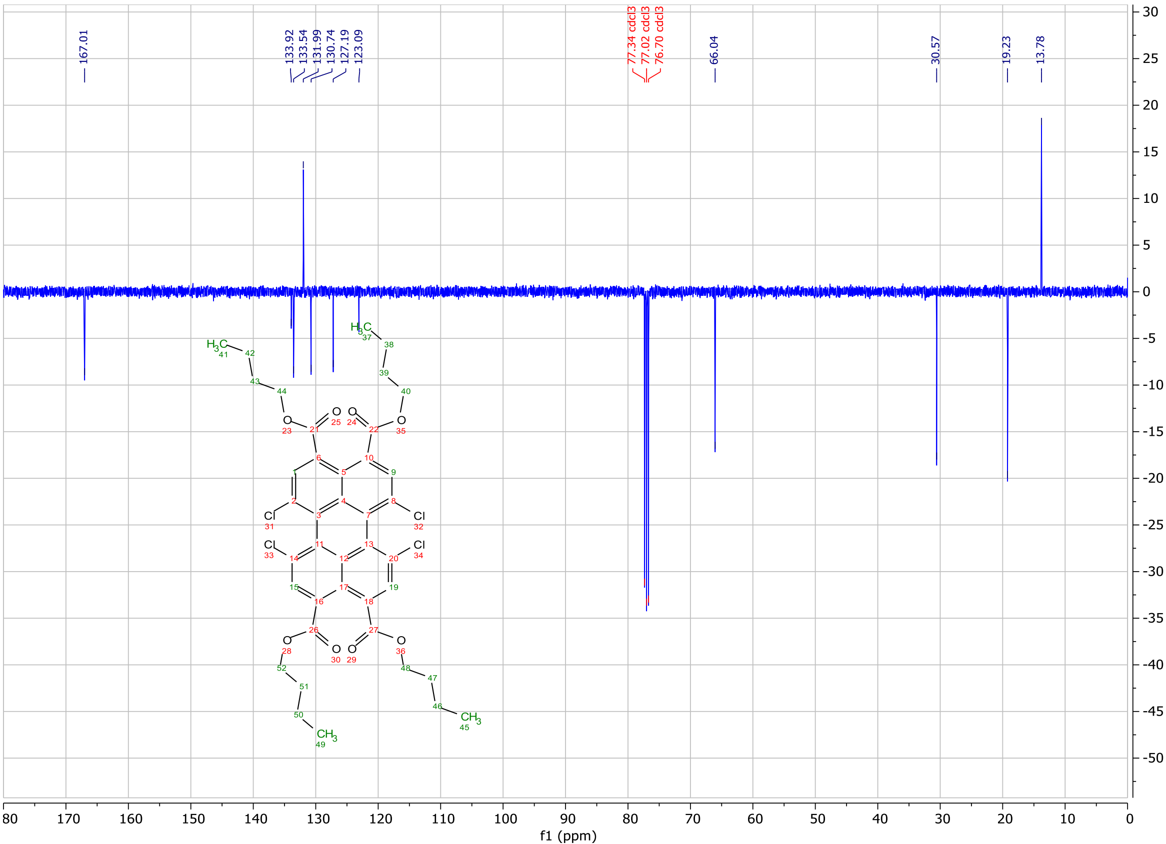
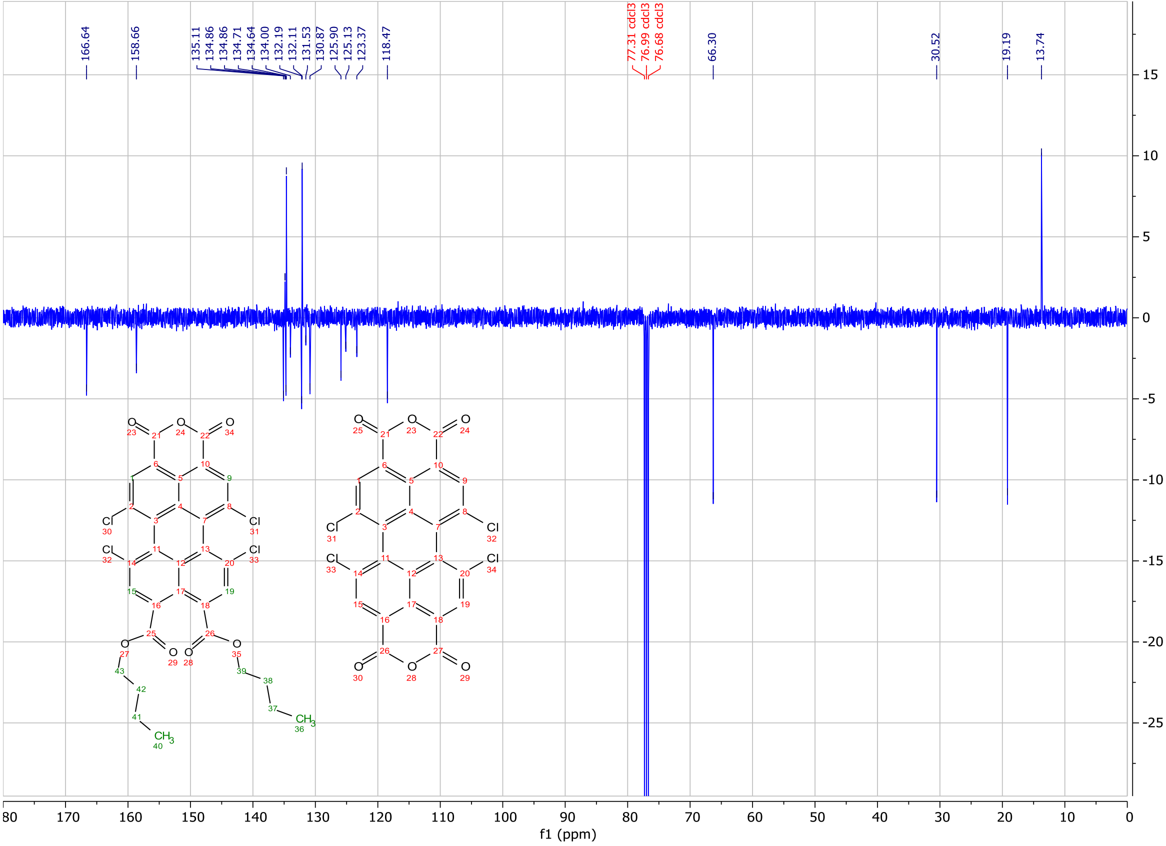
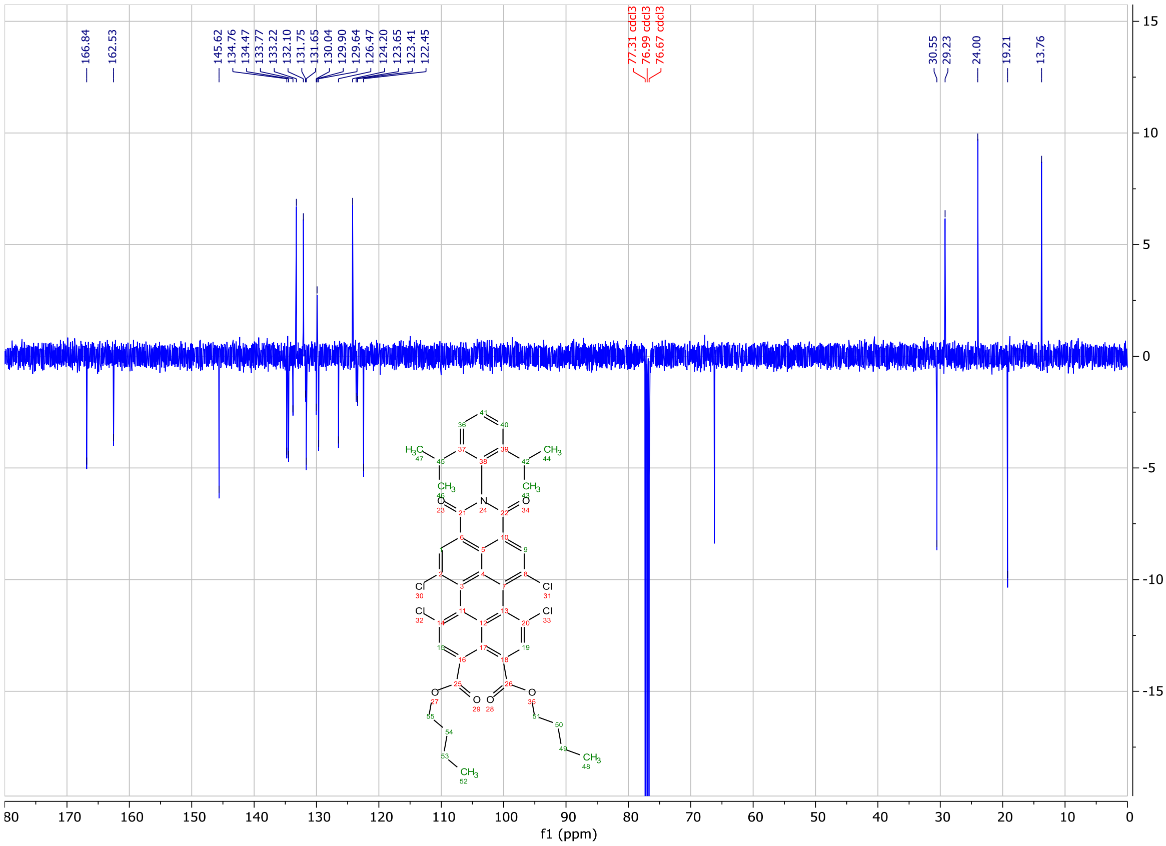
8.16
7.53
7.51
7.50
7.37
7.35
7.26 cdcl3
4.45
4.43
4.42
4.40
4.39
4.37
4.36
4.34
2.78
2.76
2.74
2.72
2.71
1.87
1.85
1.83
1.81
1.79
1.57
1.56 HDO
1.54
1.52
1.50
1.48
1.20
1.19
1.18
1.17
1.04
1.03
1.01
0.00 TMS
1,9
15,19
41
36,40
51,55
42,45
50,54
49,53
43,44,46,47
48,52
1.57
1.65
1.00
1.83
3.86
1.86
3.83
3.60
10.45
5.51
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)
1500
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
H_3C
CH_3
O
N
Cl
O
O
O
O
O

Appendix A.2 - ^{13}C NMR spectra of precursor compounds



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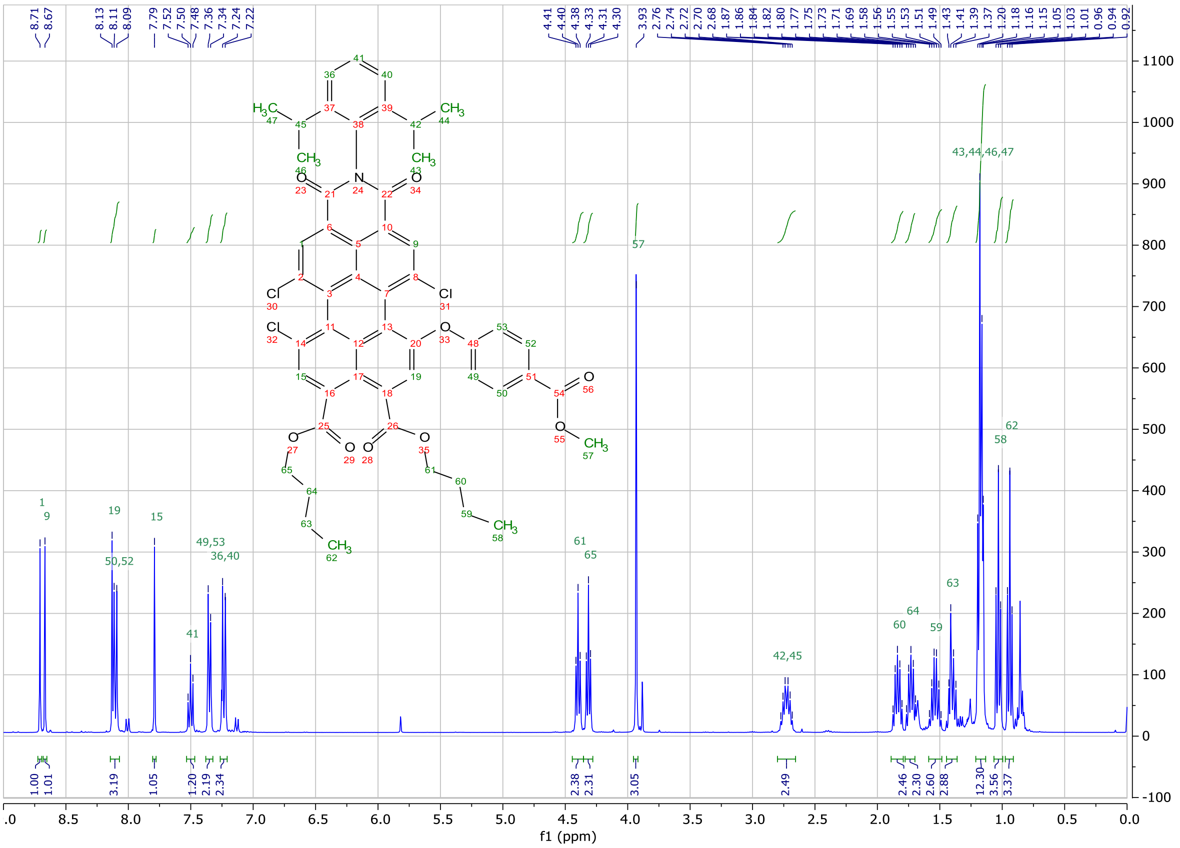
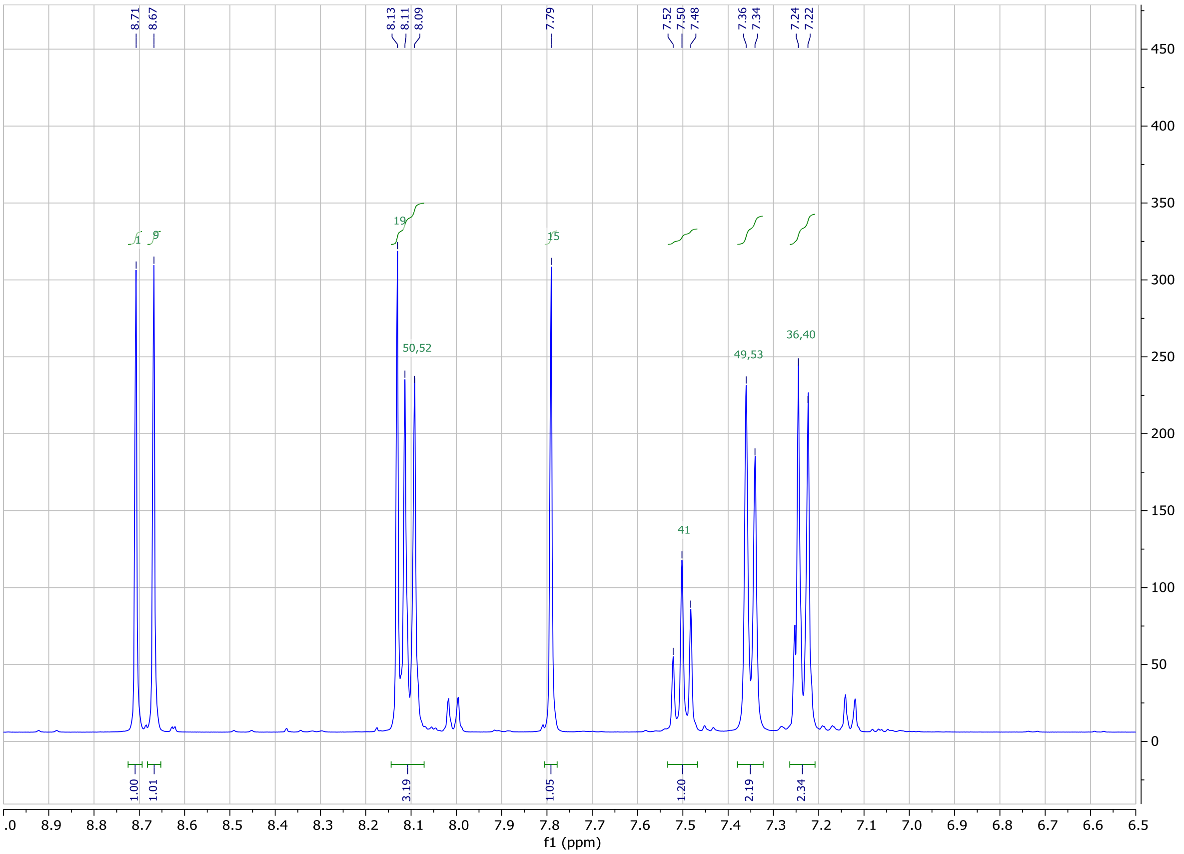
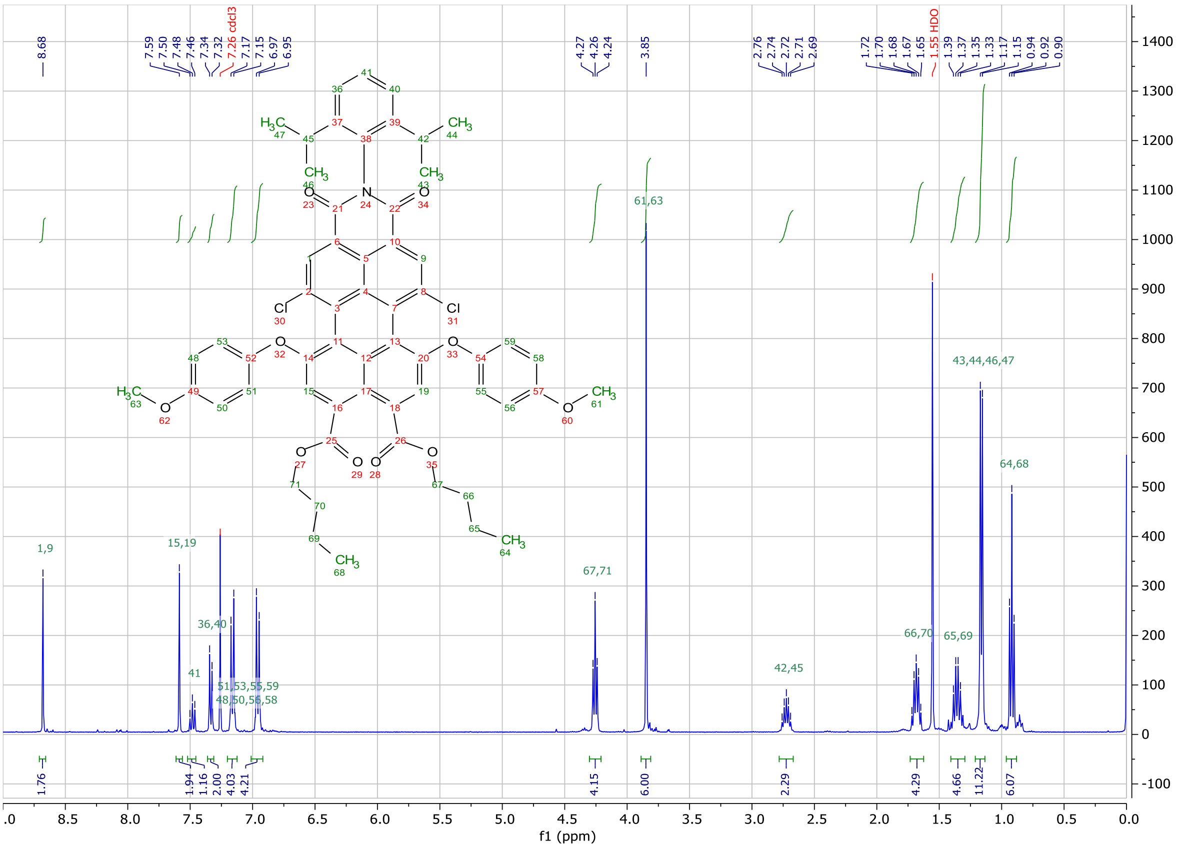
145.62
134.76
134.47
133.77
133.22
132.10
131.75
131.65
130.04
129.90
129.64
126.47
124.20
123.65
123.41
122.45
77.31 cdcl3
76.99 cdcl3
76.67 cdcl3
30.55
29.23
24.00
19.21
13.76
15
10
5
0
-5
-10
-15
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)
H_3C
CH_3
N
O
Cl
Cl
Cl
Cl
O
O
O
O
CH_3
CH_3

Appendix A.3 - ^{1}H NMR spectra of intermediate products

All spectra in this appendix are provided as the full spectra and subsequently a display of the aromatic region of the same spectrum.



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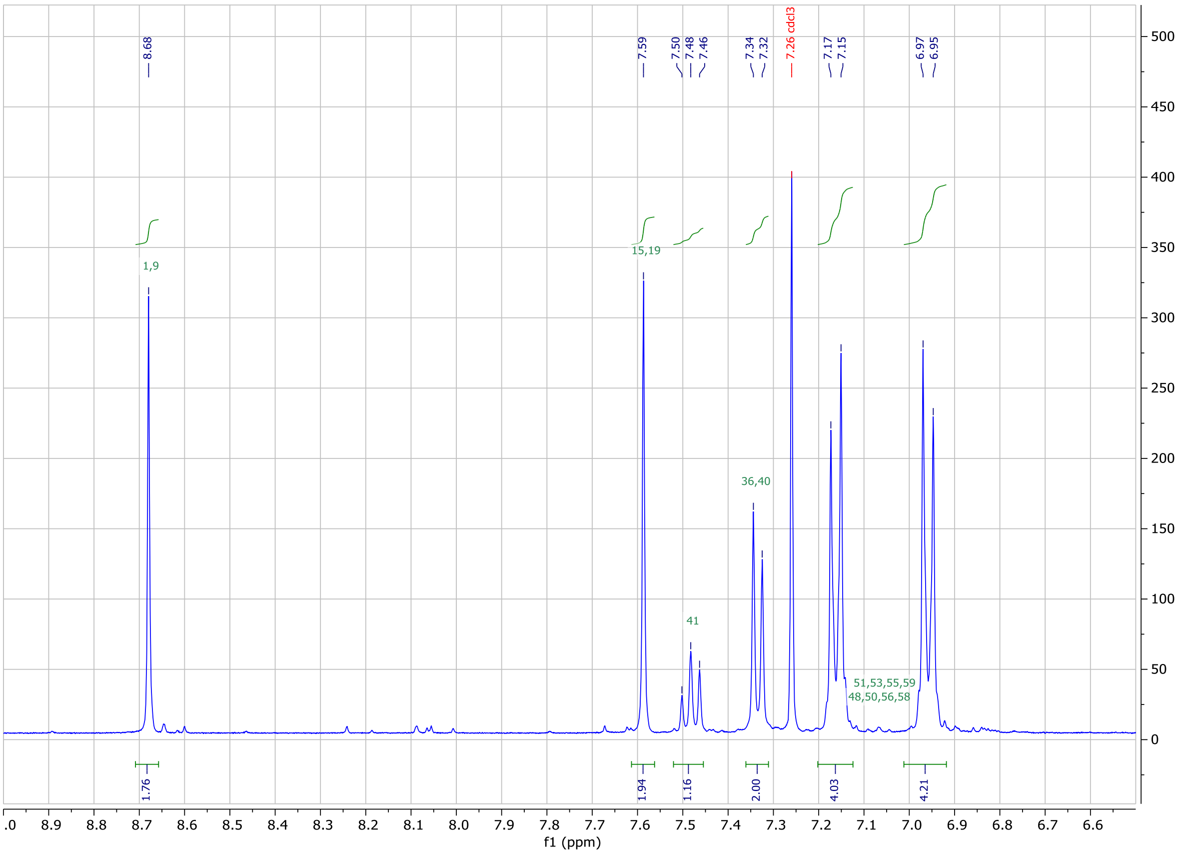
7.50
7.48
7.46
7.34
7.32
7.26 cdcl3
7.17
7.15
6.97
6.95
4.27
4.26
4.24
3.85
2.76
2.74
2.72
2.71
2.69
1.72
1.70
1.68
1.67
1.65
1.55 HDO
1.39
1.37
1.35
1.33
1.17
1.15
0.94
0.92
0.90
1,9
15,19
36,40
41
51,53,55,59
48,50,56,58
67,71
61,63
42,45
66,70
65,69
43,44,46,47
64,68
H_3C
CH_3
Cl
O
N
1.76
1.94
1.16
2.00
4.03
4.21
4.15
6.00
2.29
4.29
4.66
11.22
6.07
f1 (ppm)
1400
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0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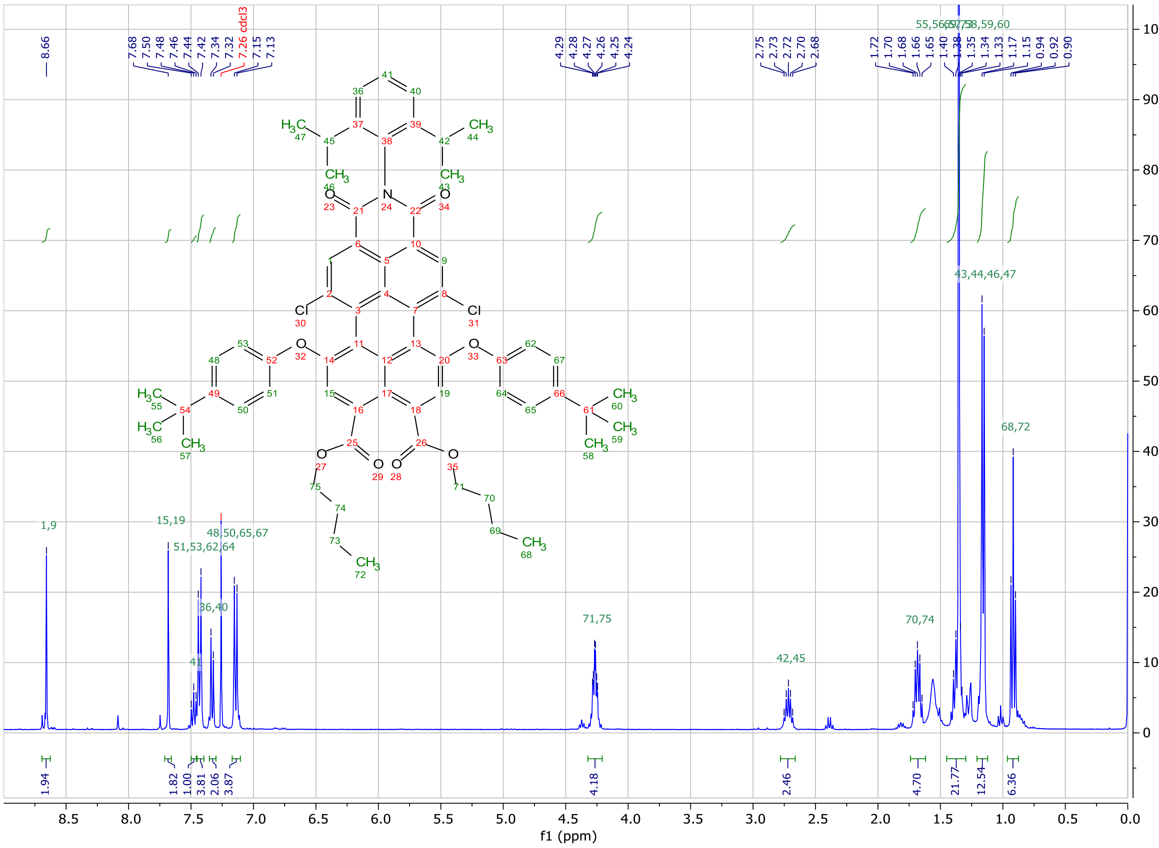
7.59
7.50
7.48
7.46
7.34
7.32
7.26 cdcl3
7.17
7.15
6.97
6.95
1,9
15,19
41
36,40
51,53,55,59
48,50,56,58
1.76
1.94
1.16
2.00
4.03
4.21
f1 (ppm)
500
450
400
350
300
250
200
150
100
50
0
9.0
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6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7.46
7.44
7.42
7.34
7.32
7.26 cdcl3
7.15
7.13
4.29
4.28
4.27
4.26
4.25
4.24
2.75
2.73
2.72
2.70
2.68
1.72
1.70
1.68
1.66
1.65
1.40
1.38
1.35
1.34
1.33
1.17
1.15
0.94
0.92
0.90
55,56,57,58,59,60
43,44,46,47
68,72
1,9
15,19
51,53,62,64
48,50,65,67
36,40
41
71,75
42,45
70,74
1.94
1.82
1.00
3.81
2.06
3.87
4.18
2.46
4.70
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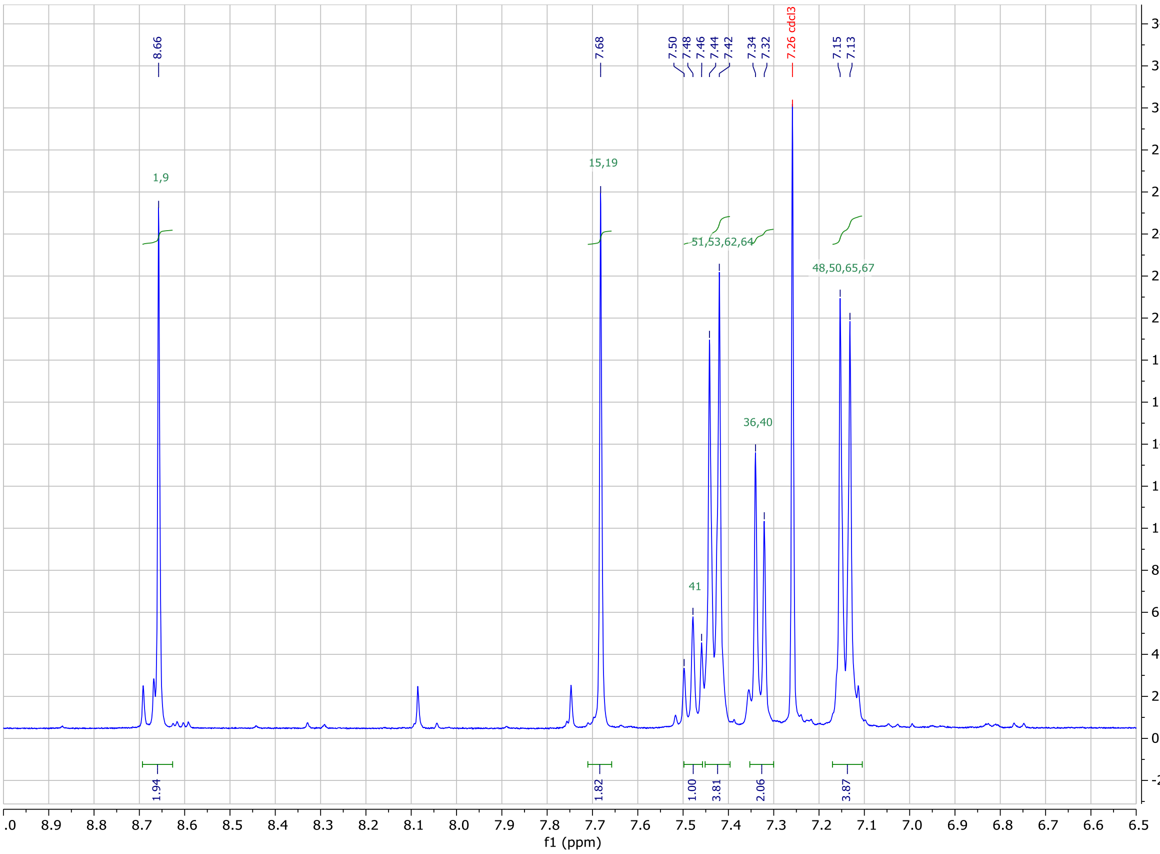
800
700
600
500
400
300
200
100
0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7.68
7.50
7.48
7.46
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7.42
7.34
7.32
7.26 cdcl3
7.15
7.13
1,9
15,19
51,53,62,64
48,50,65,67
36,40
41
1.94
1.82
1.00
3.81
2.06
3.87
f1 (ppm)
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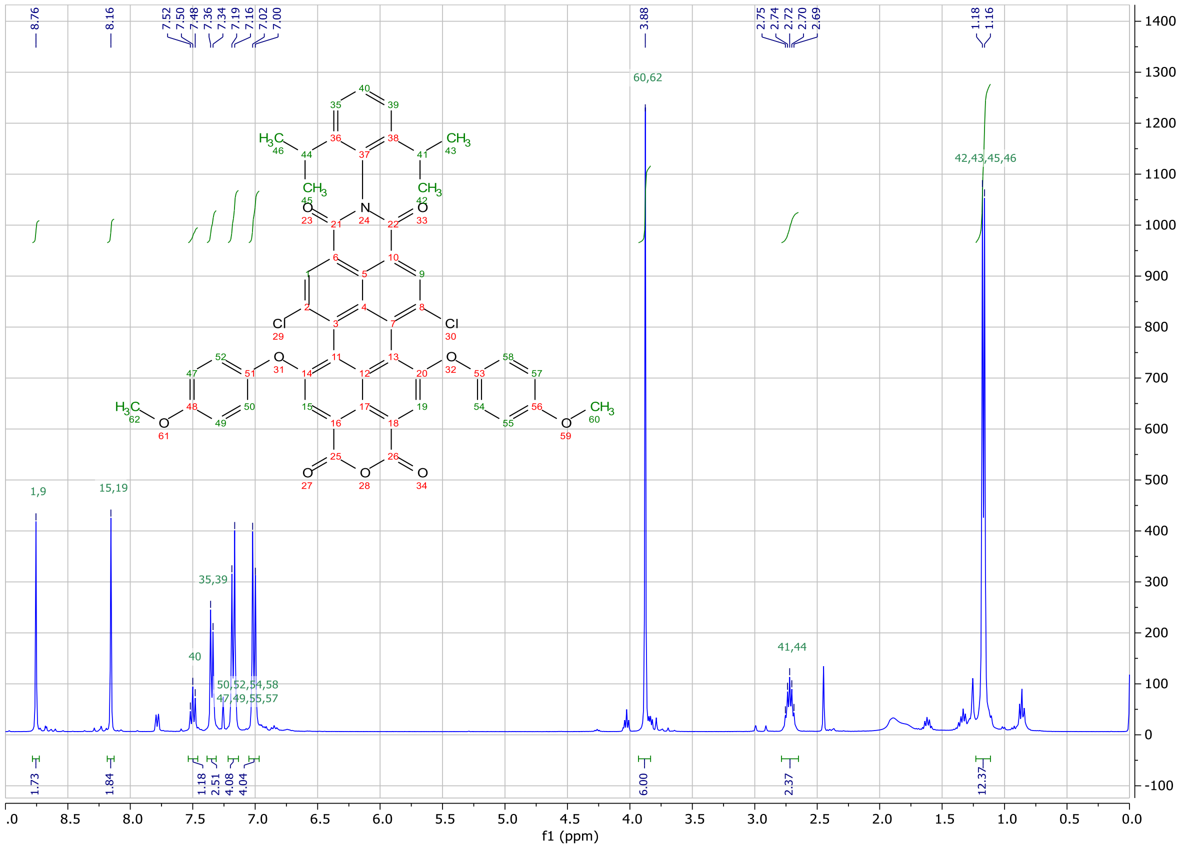
300
280
260
240
220
200
180
160
140
120
100
80
60
40
20
0
-20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8.16
7.52
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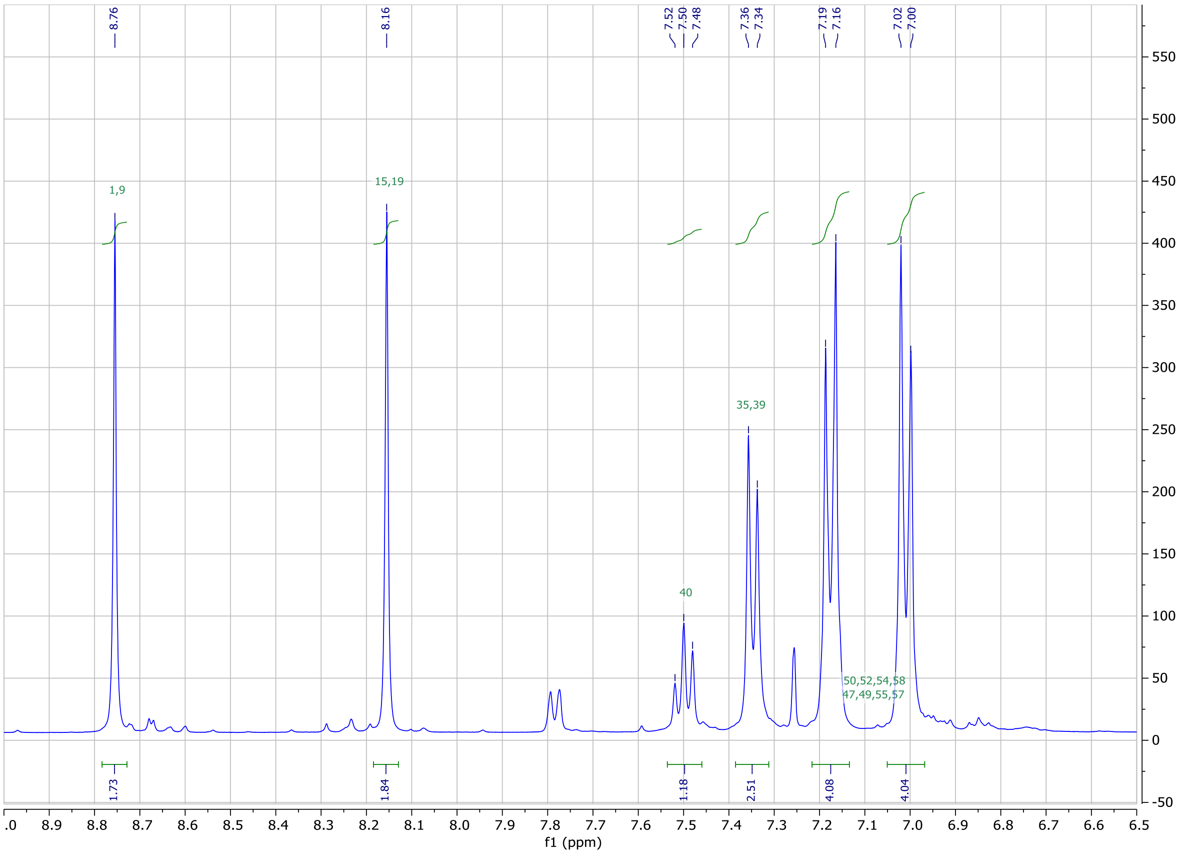
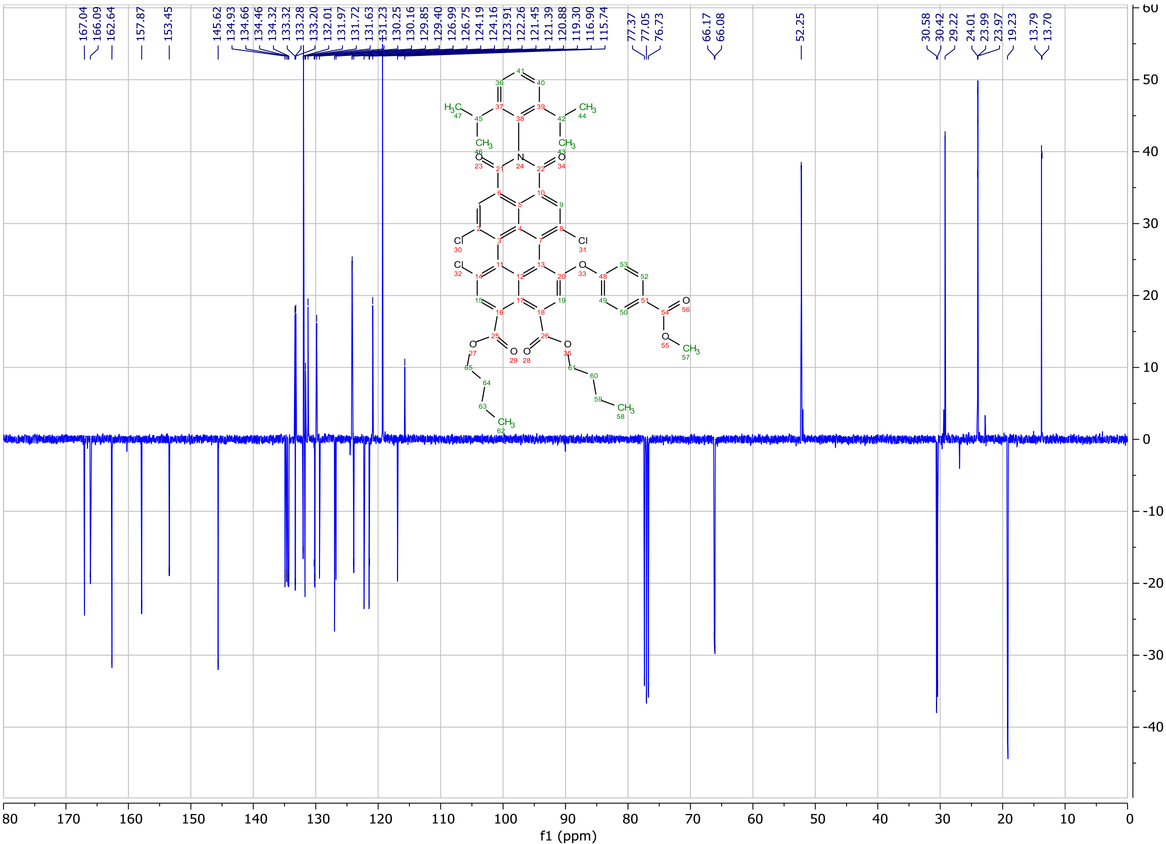
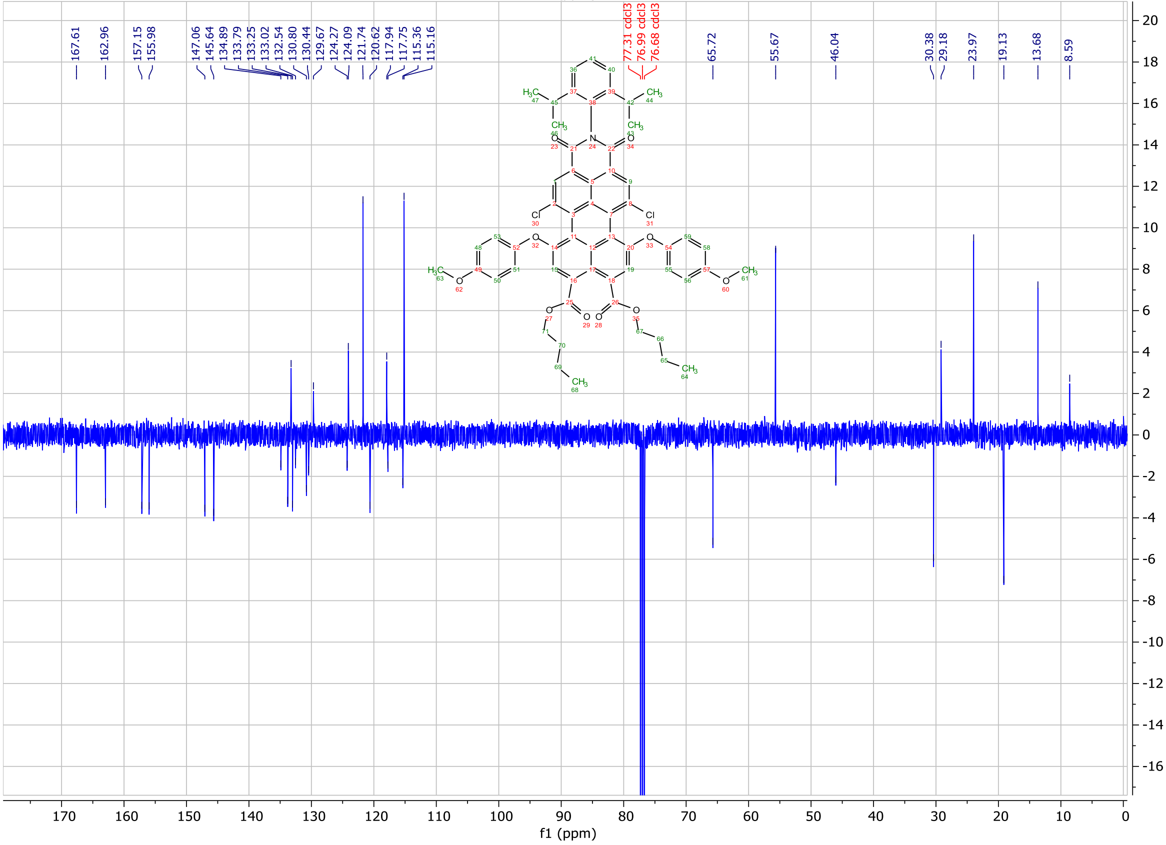
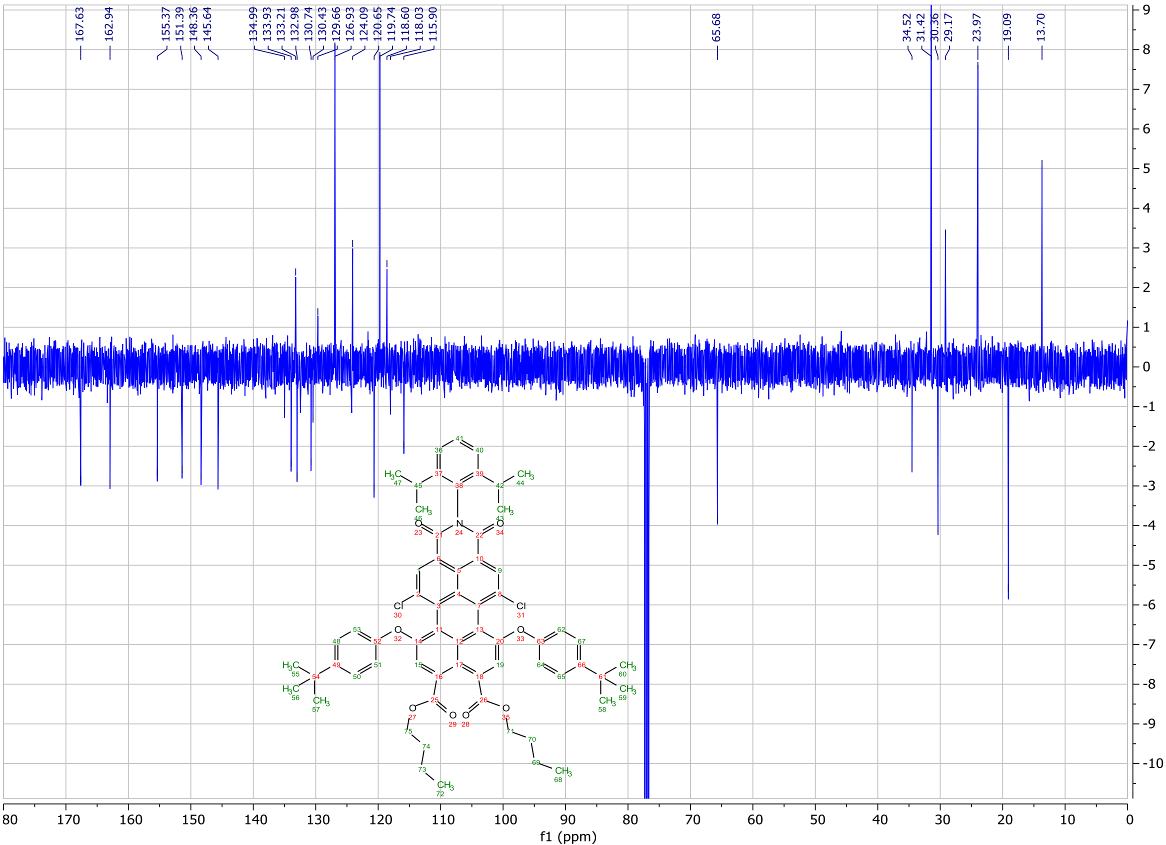
7.48
7.36
7.34
7.19
7.16
7.02
7.00
3.88
2.75
2.74
2.72
2.70
2.69
1.18
1.16
60,62
42,43,45,46
1,9
15,19
35,39
40
50,52,54,58
47,49,55,57
41,44
1.73
1.84
1.18
2.51
4.08
4.04
6.00
2.37
12.37
f1 (ppm)


8.76
8.16
7.52
7.50
7.48
7.36
7.34
7.19
7.16
7.02
7.00
1,9
15,19
35,39
40
50,52,54,58
47,49,55,57
1.73
1.84
1.18
2.51
4.08
4.04
f1 (ppm)

Appendix A.4 - ^{13}C NMR spectra of intermediate products







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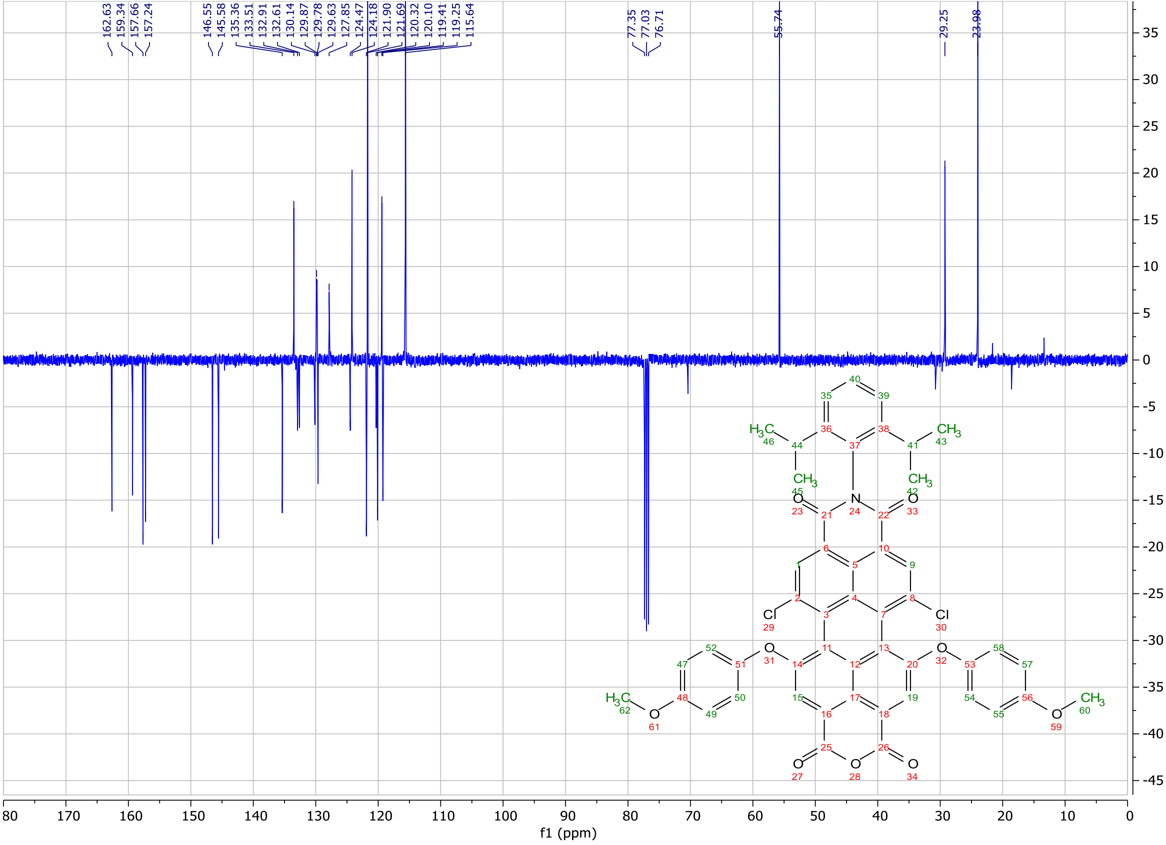
148.36
145.64
134.99
133.93
133.21
132.98
130.74
130.43
129.66
126.93
124.09
120.65
119.74
118.60
118.03
115.90
65.68
34.52
31.42
30.36
29.17
23.97
19.09
13.70
f1 (ppm)



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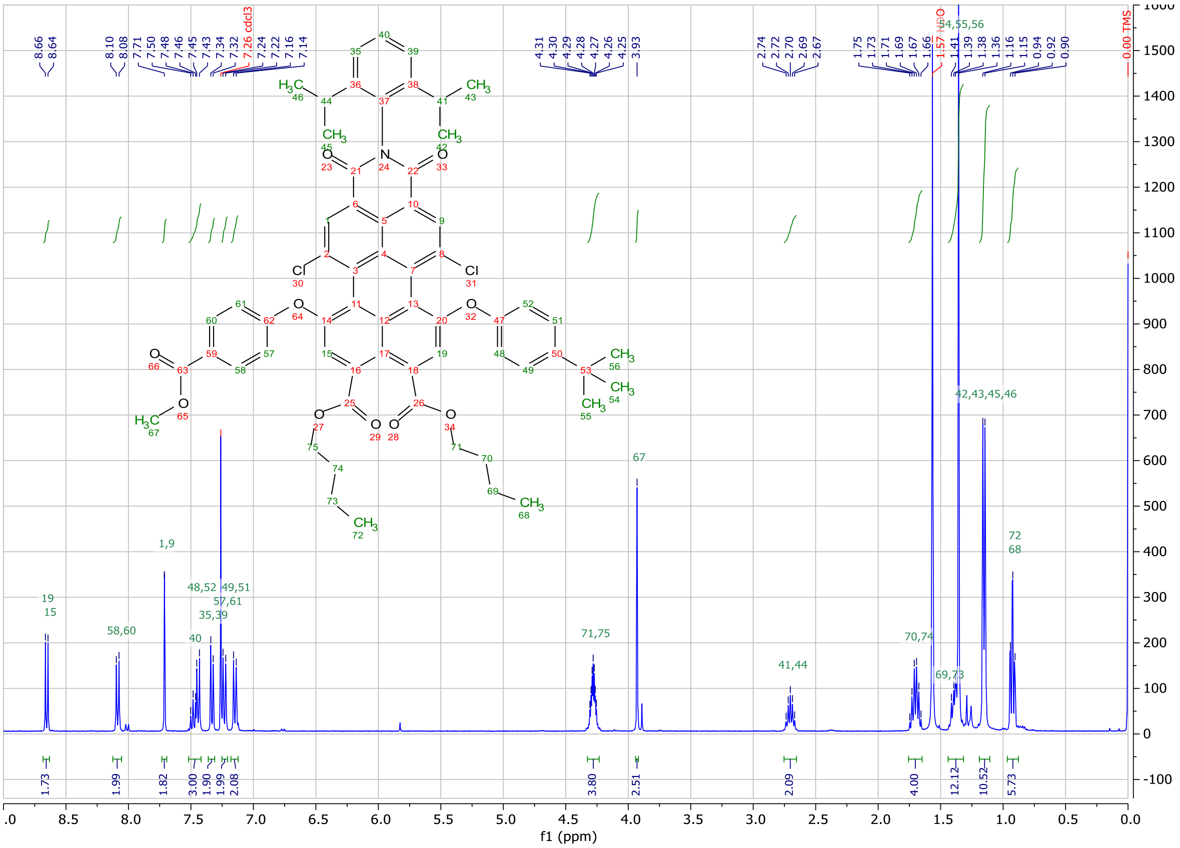
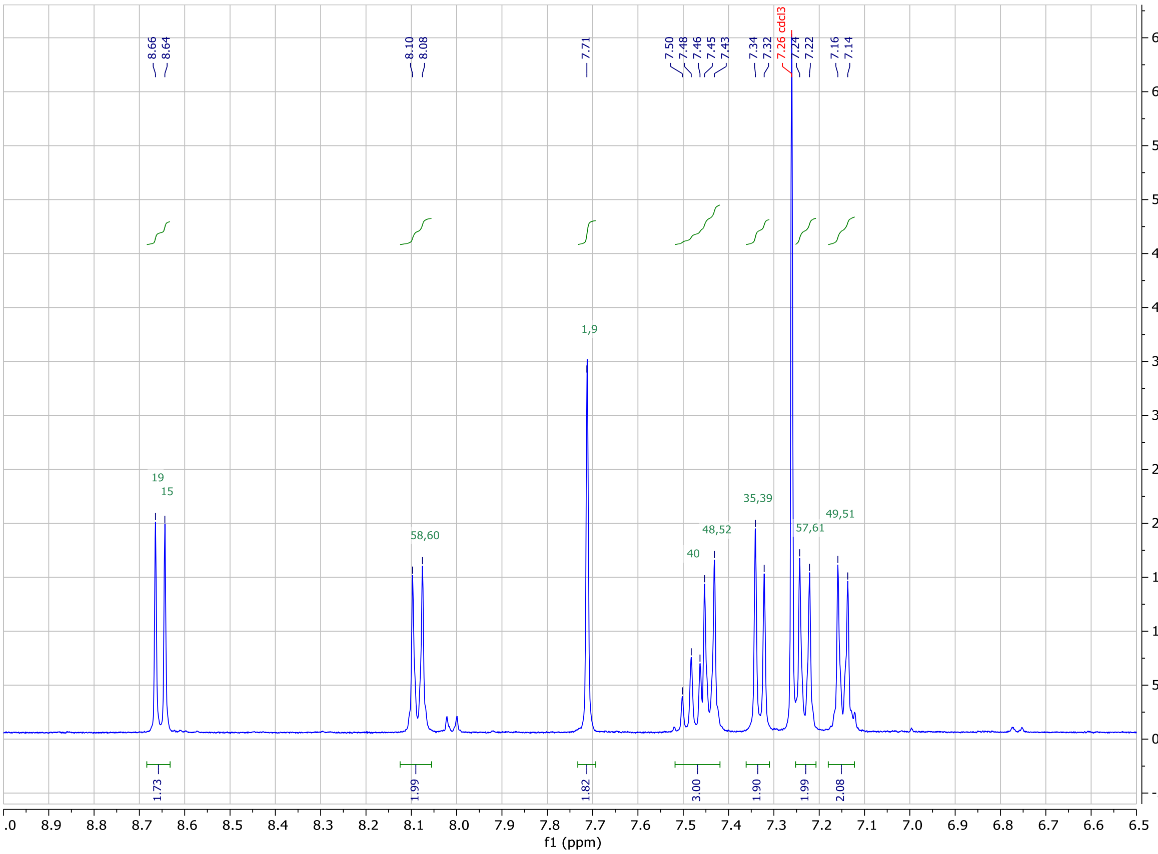
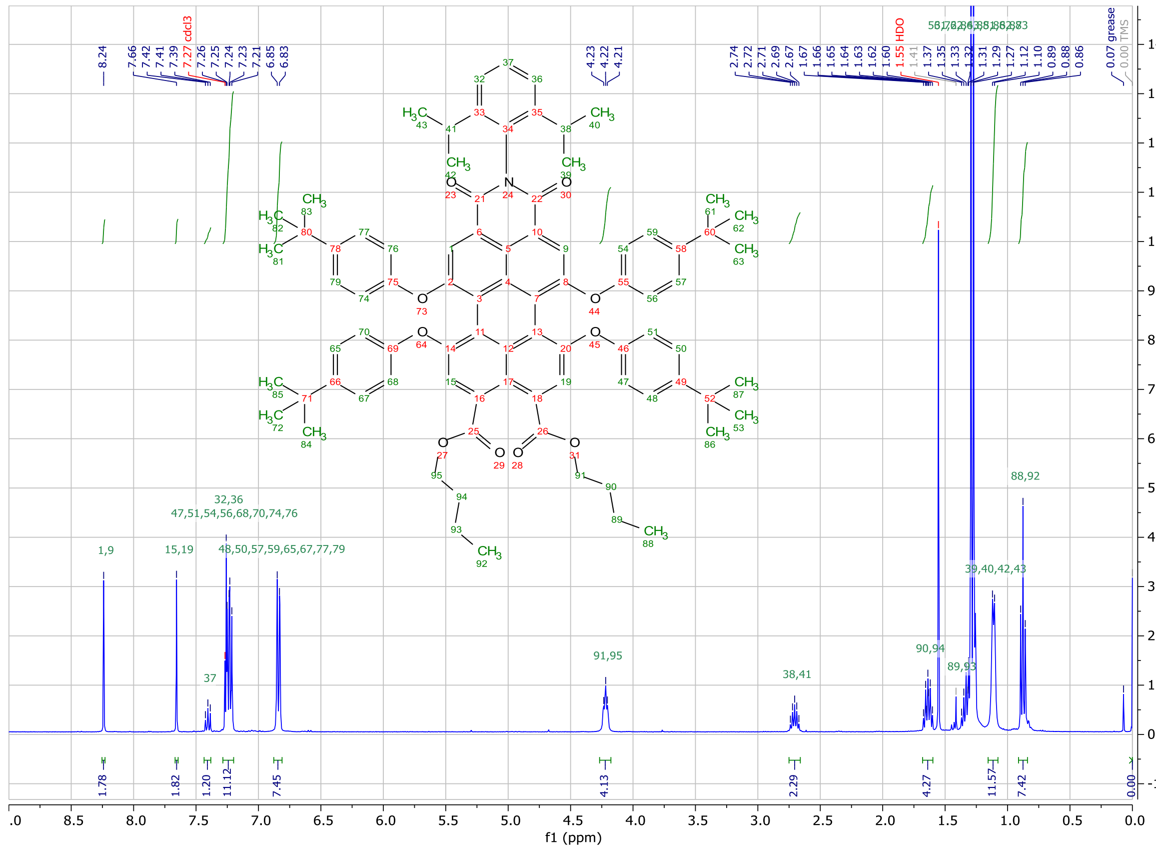
157.66
157.24
146.55
145.58
135.36
133.51
132.91
132.61
130.14
129.87
129.78
129.63
127.85
124.47
124.18
121.90
121.69
120.32
120.10
119.41
119.25
115.64
77.35
77.03
76.71
55.74
29.25
23.98
f1 (ppm)

Appendix A.5 - ^{1}H NMR spectra of final products

All spectra in this appendix are provided as the full spectra and subsequently a display of the aromatic region of the same spectrum.



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7.39
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7.26
7.25
7.24
7.23
7.21
6.85
6.83
4.23
4.22
4.21
2.74
2.72
2.71
2.69
2.67
1.67
1.66
1.65
1.64
1.63
1.62
1.60
1.55 HDO
1.41
1.37
1.35
1.33
1.32
1.31
1.29
1.27
1.12
1.10
0.89
0.88
0.86
0.07 grease
0.00 TMS
1,9
15,19
32,36
47,51,54,56,68,70,74,76
48,50,57,59,65,67,77,79
37
91,95
38,41
90,94
89,93
39,40,42,43
88,92
1.78
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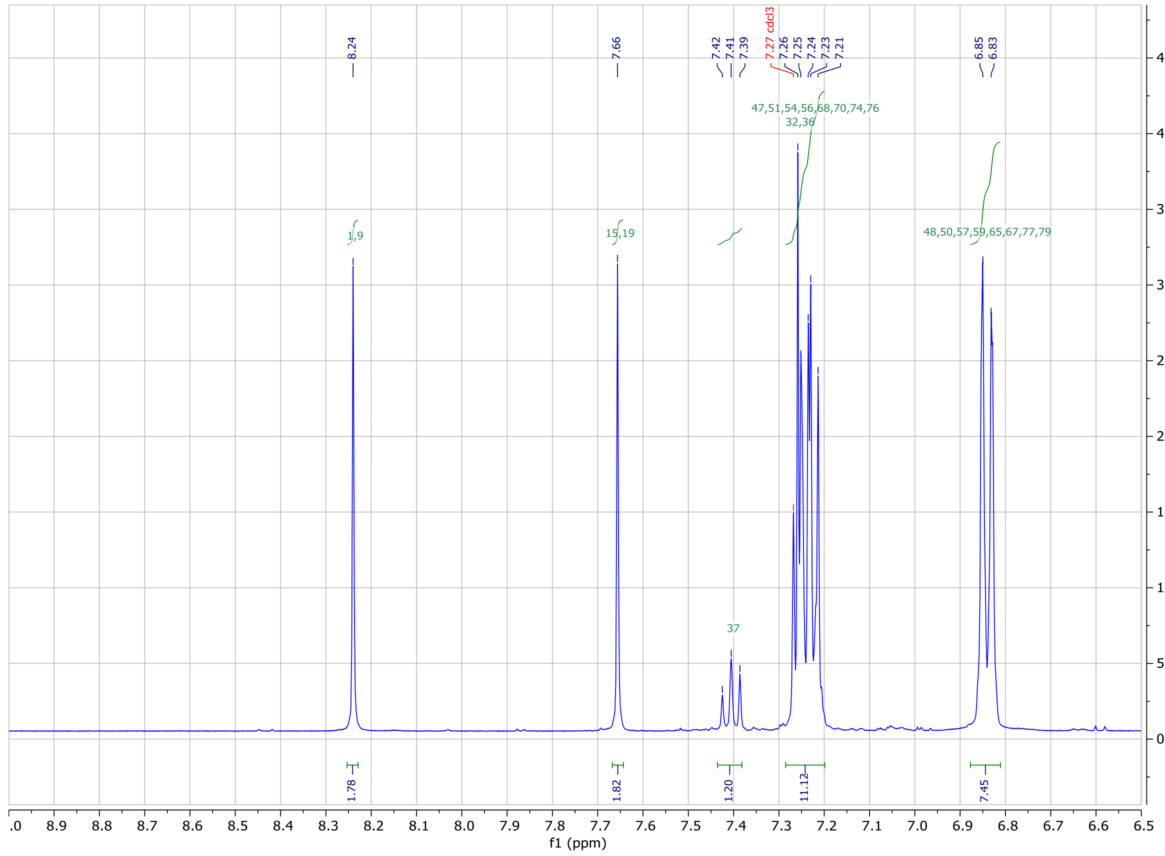
11.12
7.45
4.13
2.29
4.27
11.57
7.42
0.00
f1 (ppm)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7.42
7.41
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7.26
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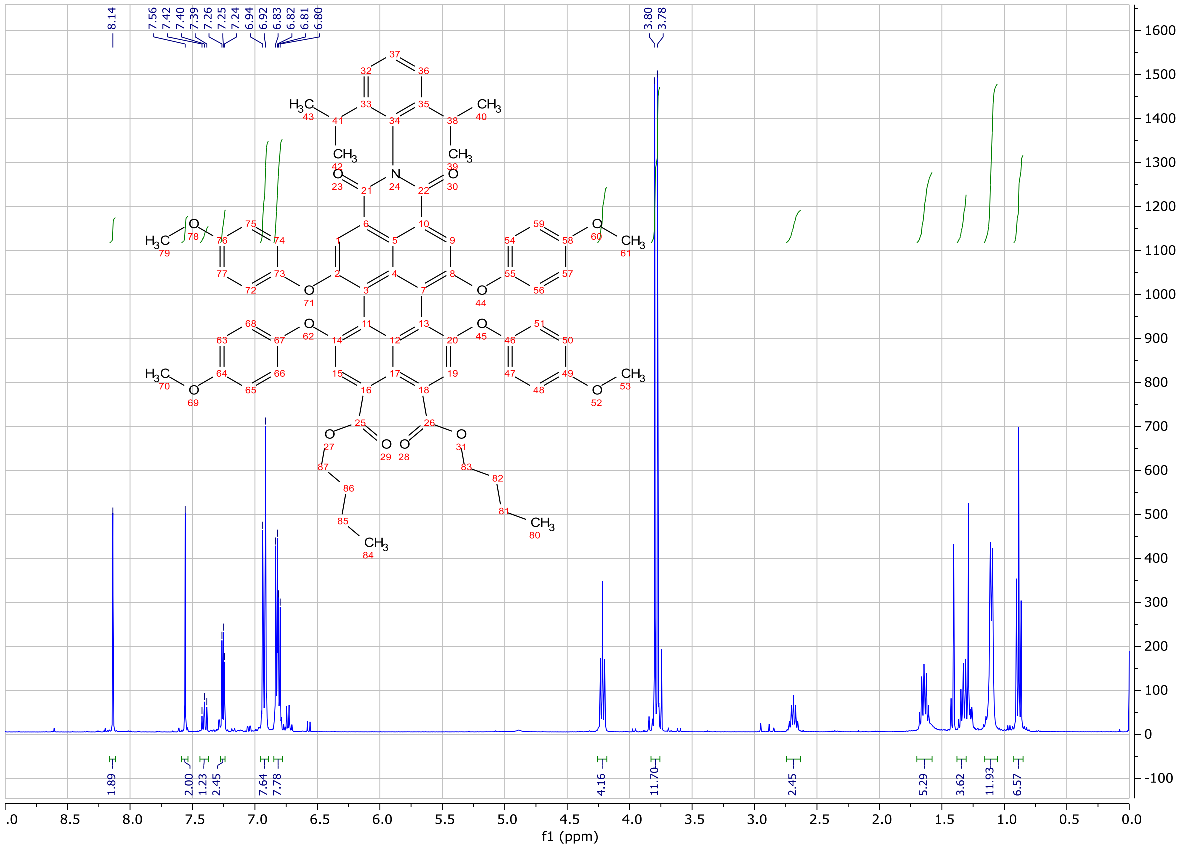
7.24
7.23
7.21
6.85
6.83
1,9
15,19
47,51,54,56,68,70,74,76
32,36
48,50,57,59,65,67,77,79
37
1.78
1.82
1.20
11.12
7.45
f1 (ppm)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7.40
7.39
7.26
7.25
7.24
6.94
6.92
6.83
6.82
6.81
6.80
3.80
3.78
1.89
2.00
1.23
2.45
7.64
7.78
4.16
11.70
2.45
5.29
3.62
11.93
6.57
f1 (ppm)
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1400
1300
1200
1100
1000
900
800
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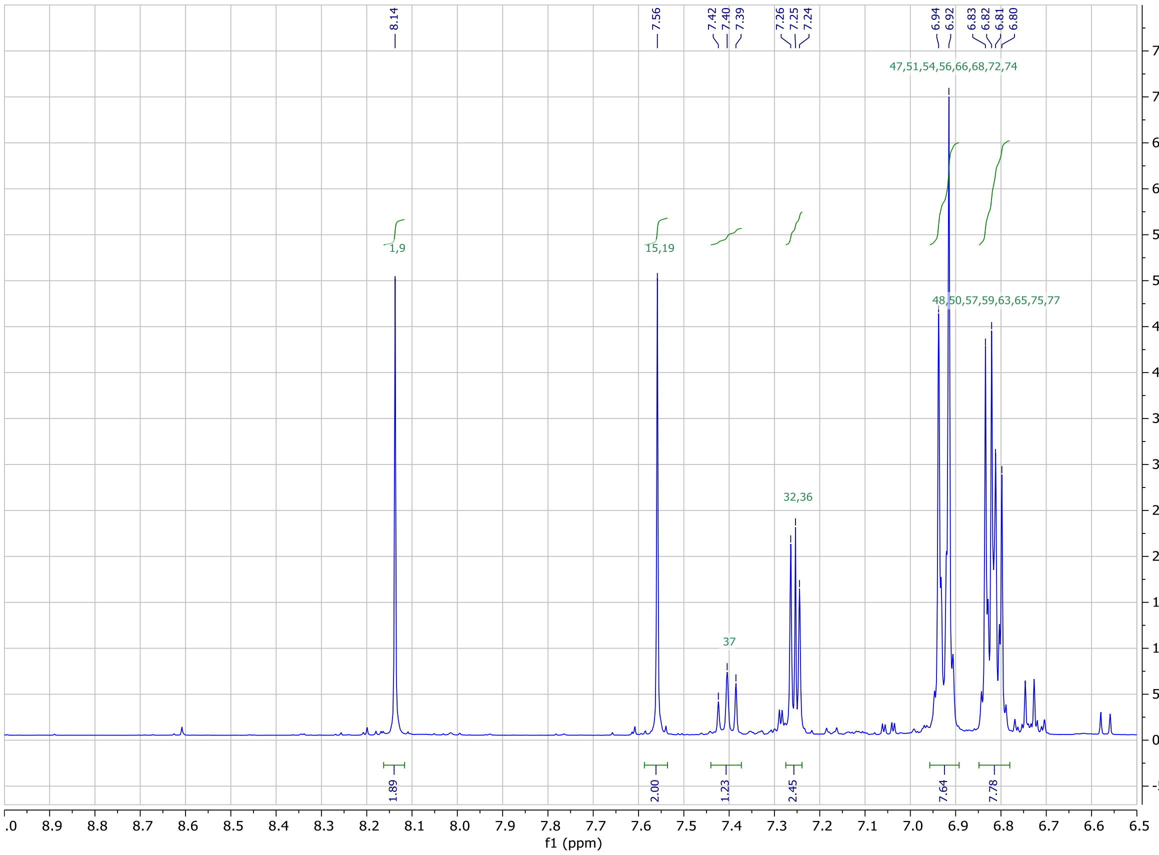
600
500
400
300
200
100
0
-100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7.39
7.26
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7.24
6.94
6.92
6.83
6.82
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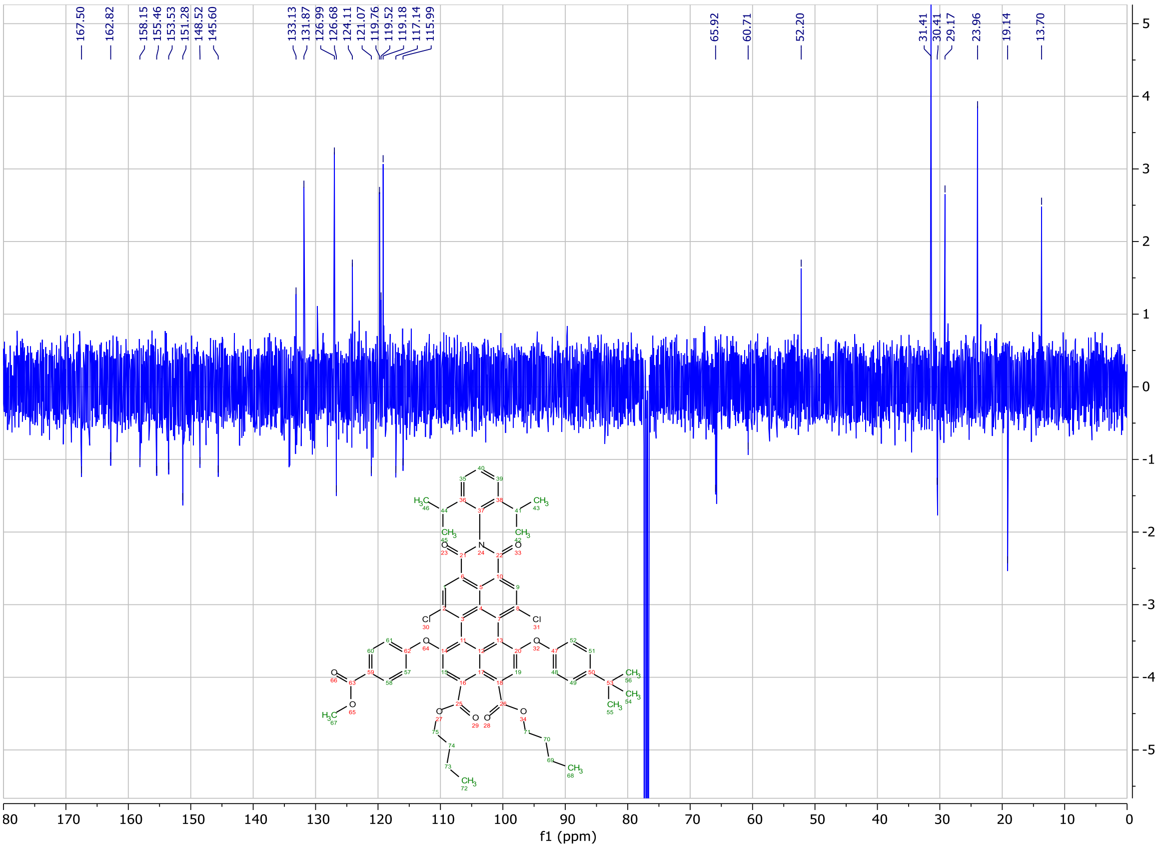
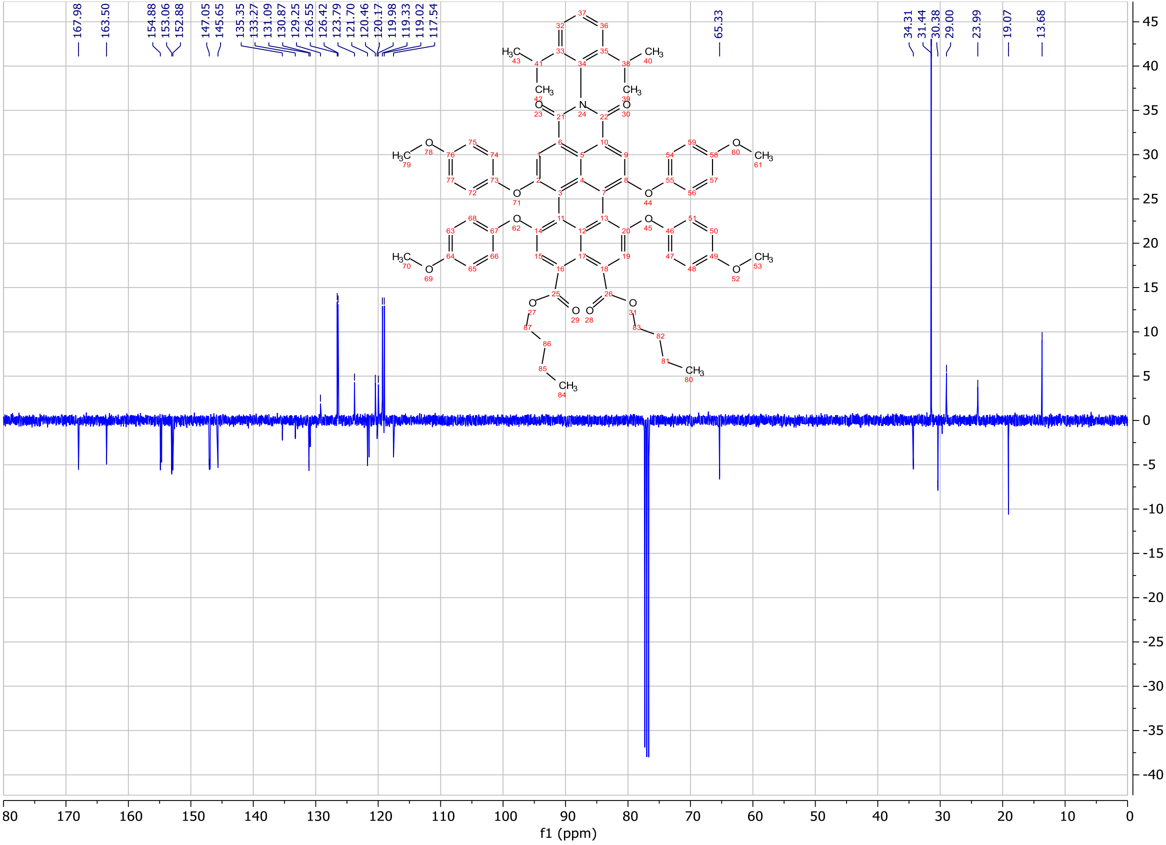
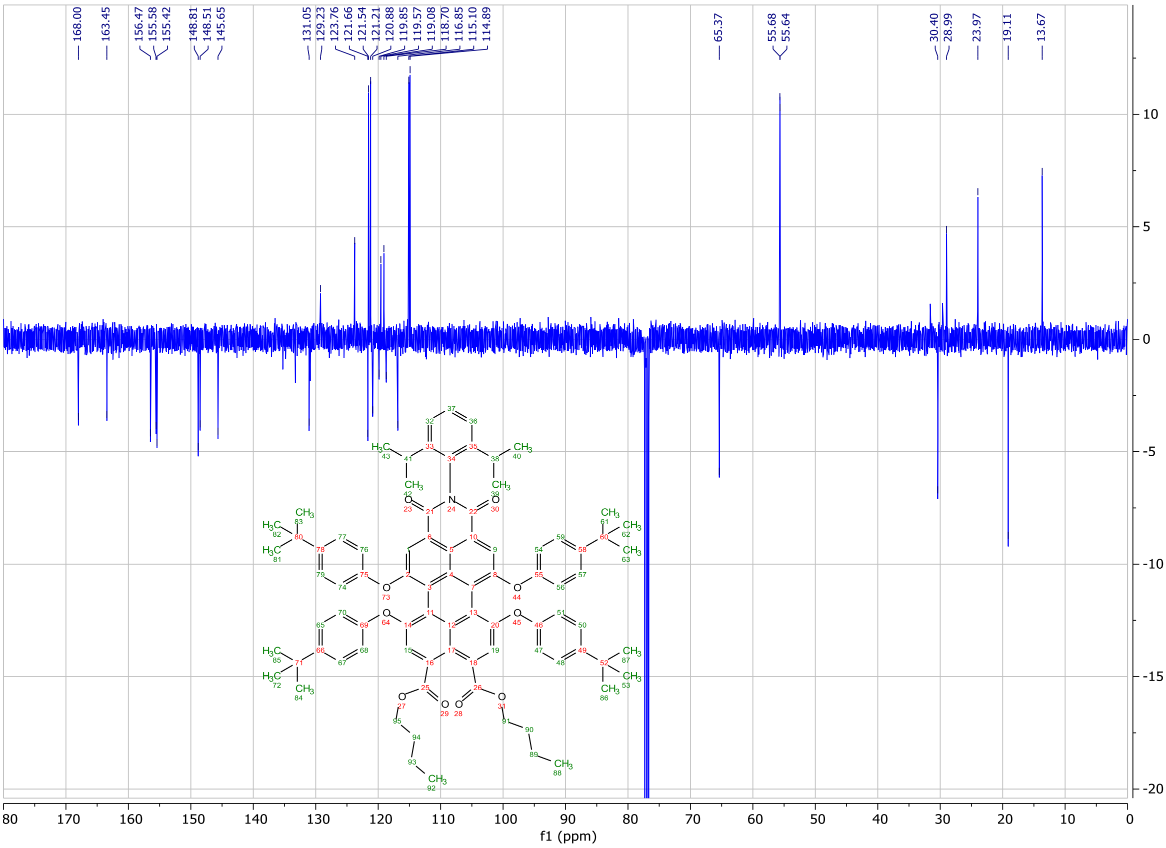
6.80
47,51,54,56,66,68,72,74
1,9
15,19
48,50,57,59,63,65,75,77
32,36
37
1.89
2.00
1.23
2.45
7.64
7.78
f1 (ppm)
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

Appendix A.6 - ^{13}C NMR spectra of final products



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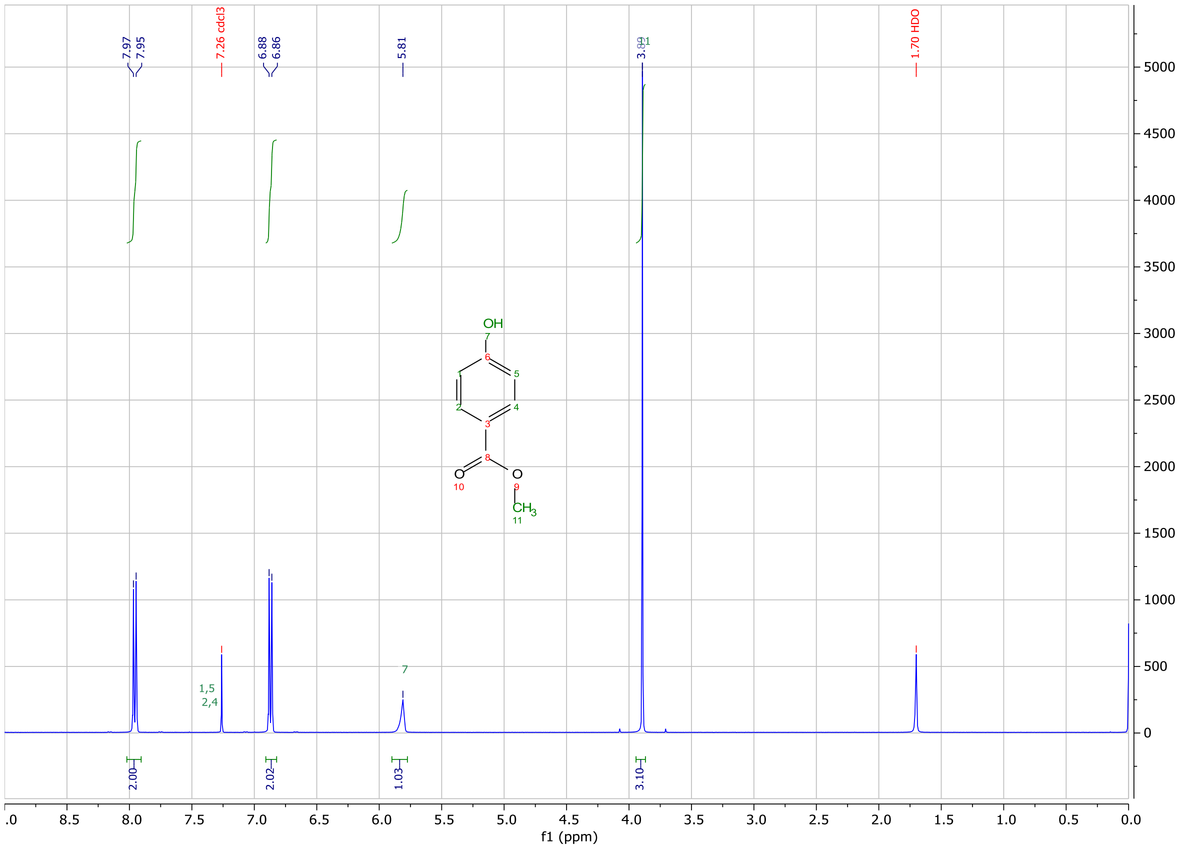
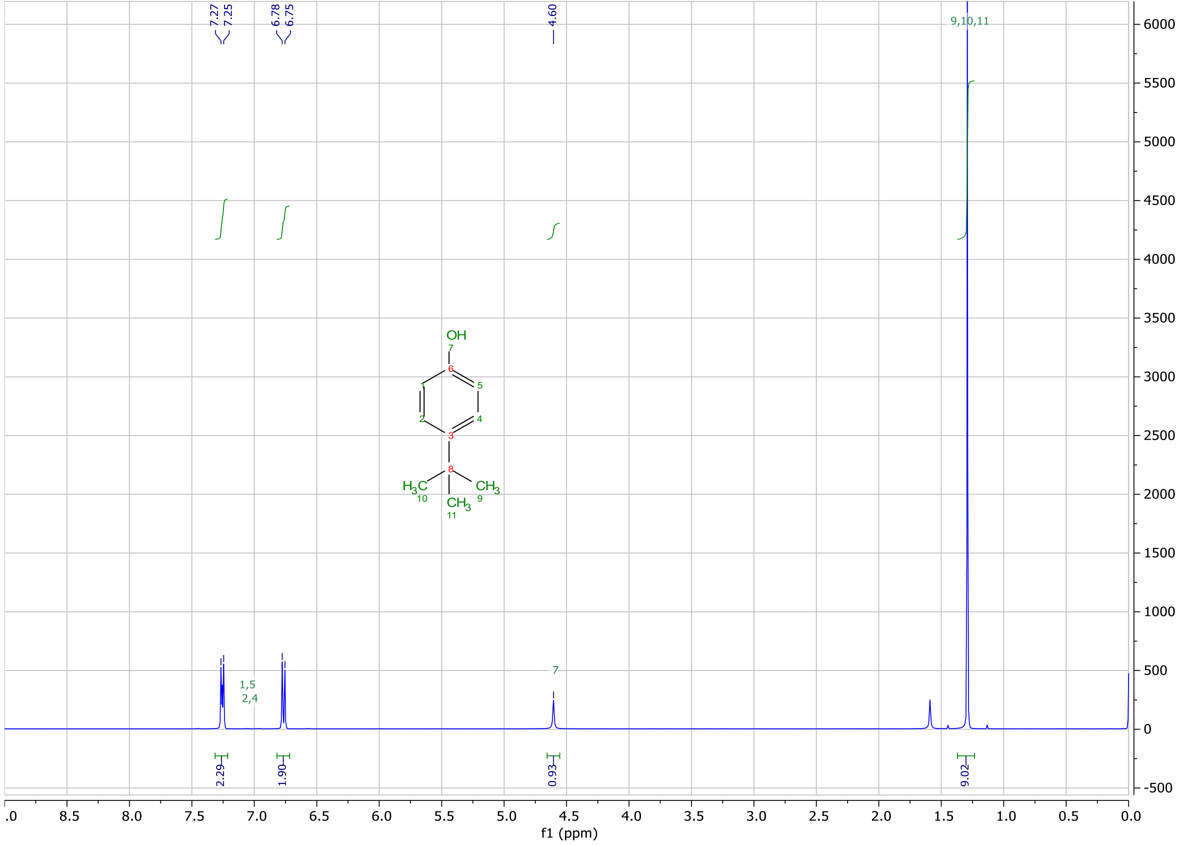
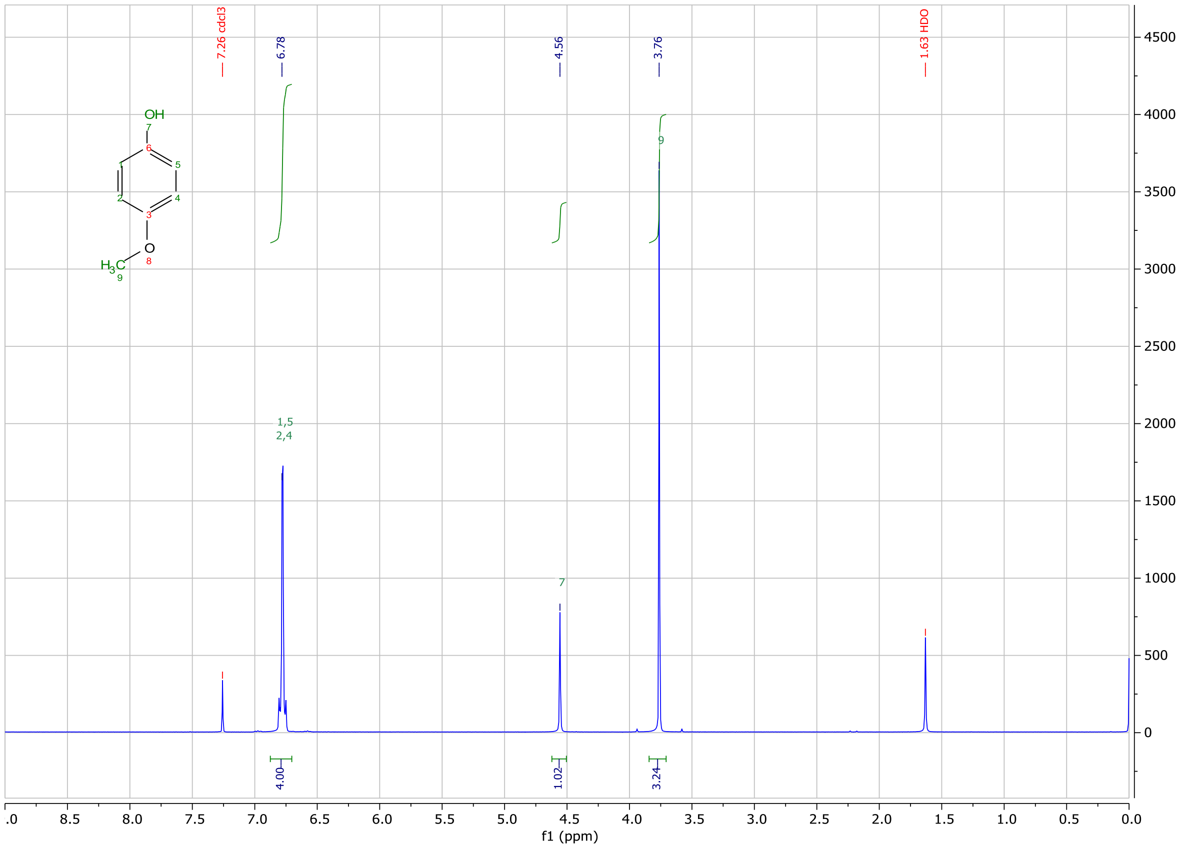
155.58
155.42
148.81
148.51
145.65
131.05
129.23
123.76
121.66
121.54
121.21
120.88
119.85
119.57
119.08
118.70
116.85
115.10
114.89
65.37
55.68
55.64
30.40
28.99
23.97
19.11
13.67
10
5
0
-5
-10
-15
-20
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

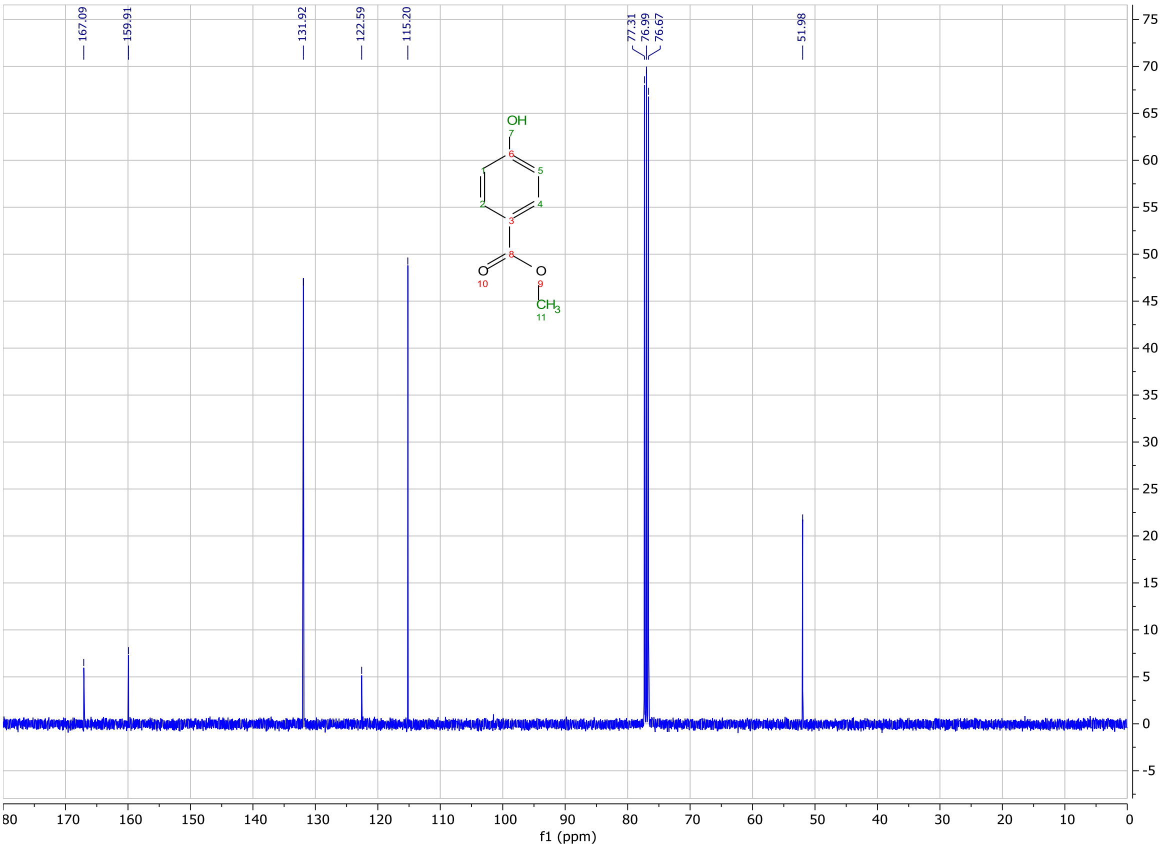
Appendix A.7 - ^{1}H NMR spectra of phenol reactants

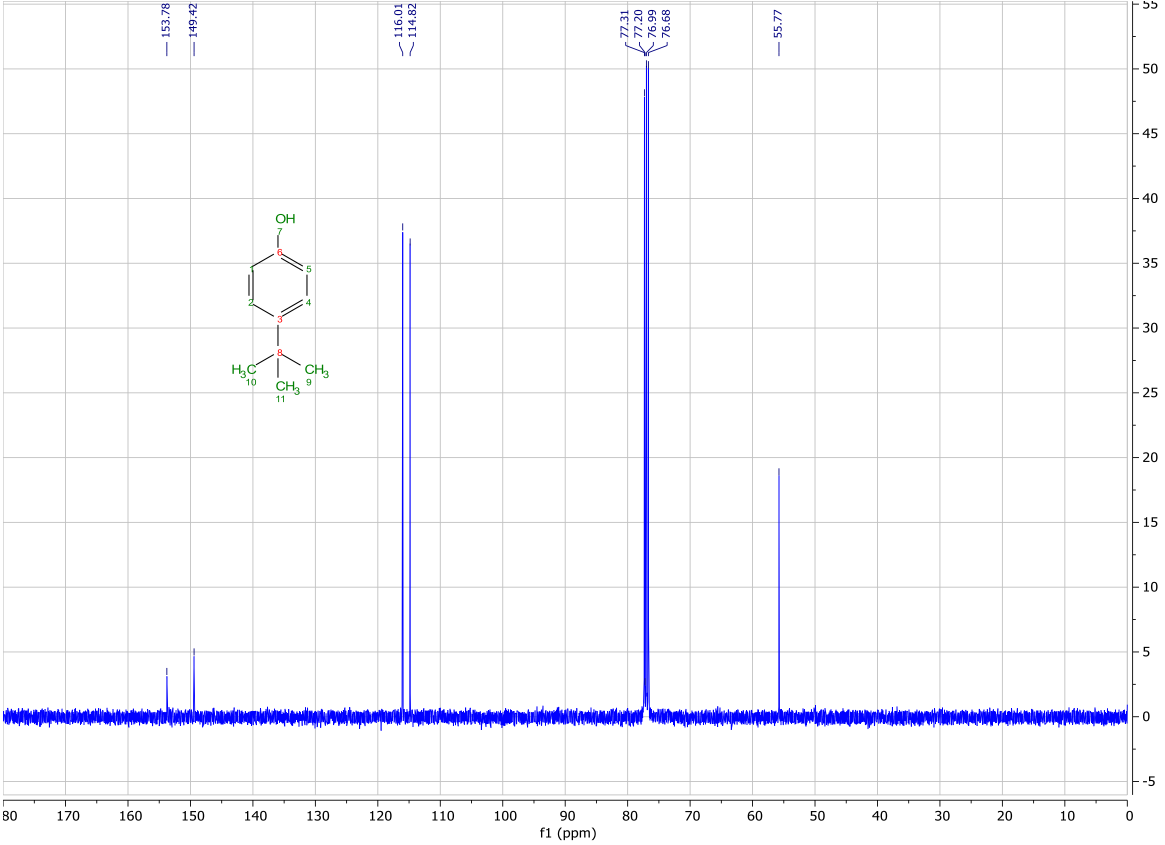


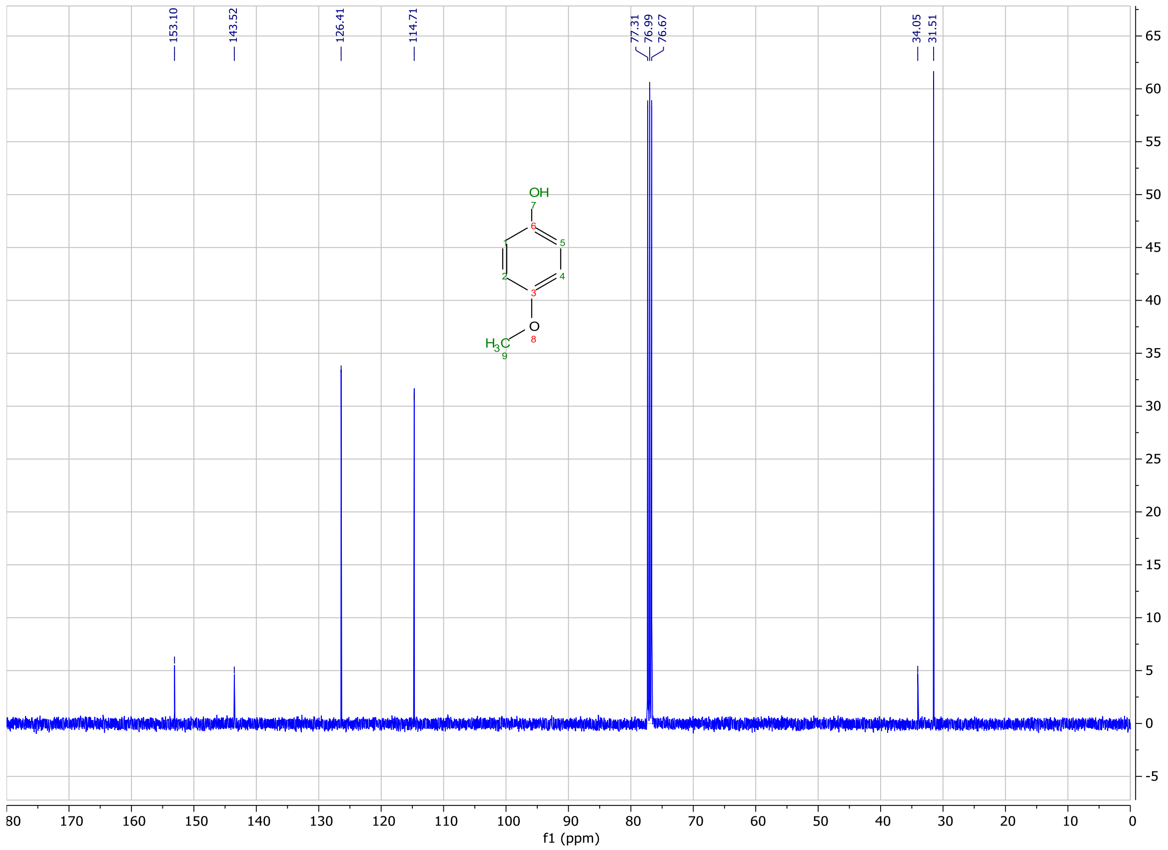



7.26 cdcl3
6.78
4.56
3.76
1.63 HDO
OH
7
6
5
4
3
2
O
8
H3C
9
1,5
2,4
7
9
4.00
1.02
3.24
4500
4000
3500
3000
2500
2000
1500
1000
500
0
.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

Appendix A.8 - ^{13}C NMR spectra of phenol reactants



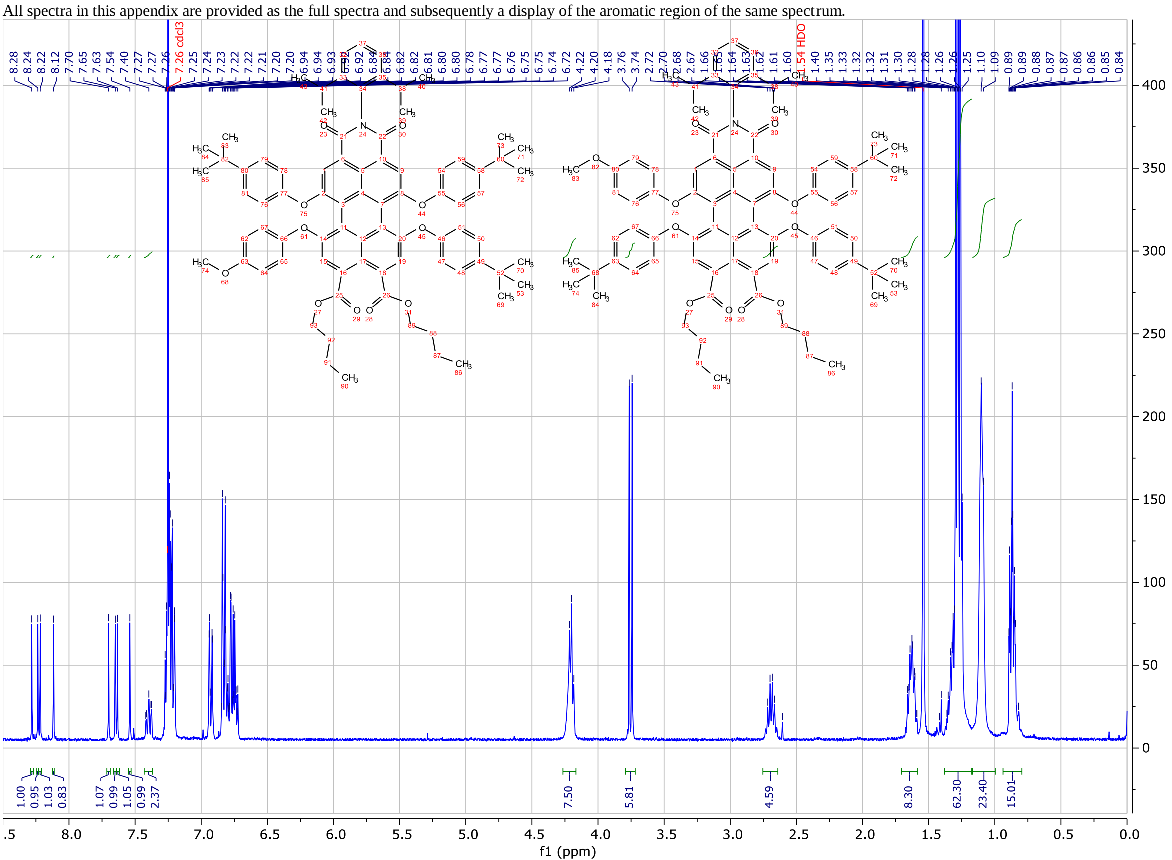


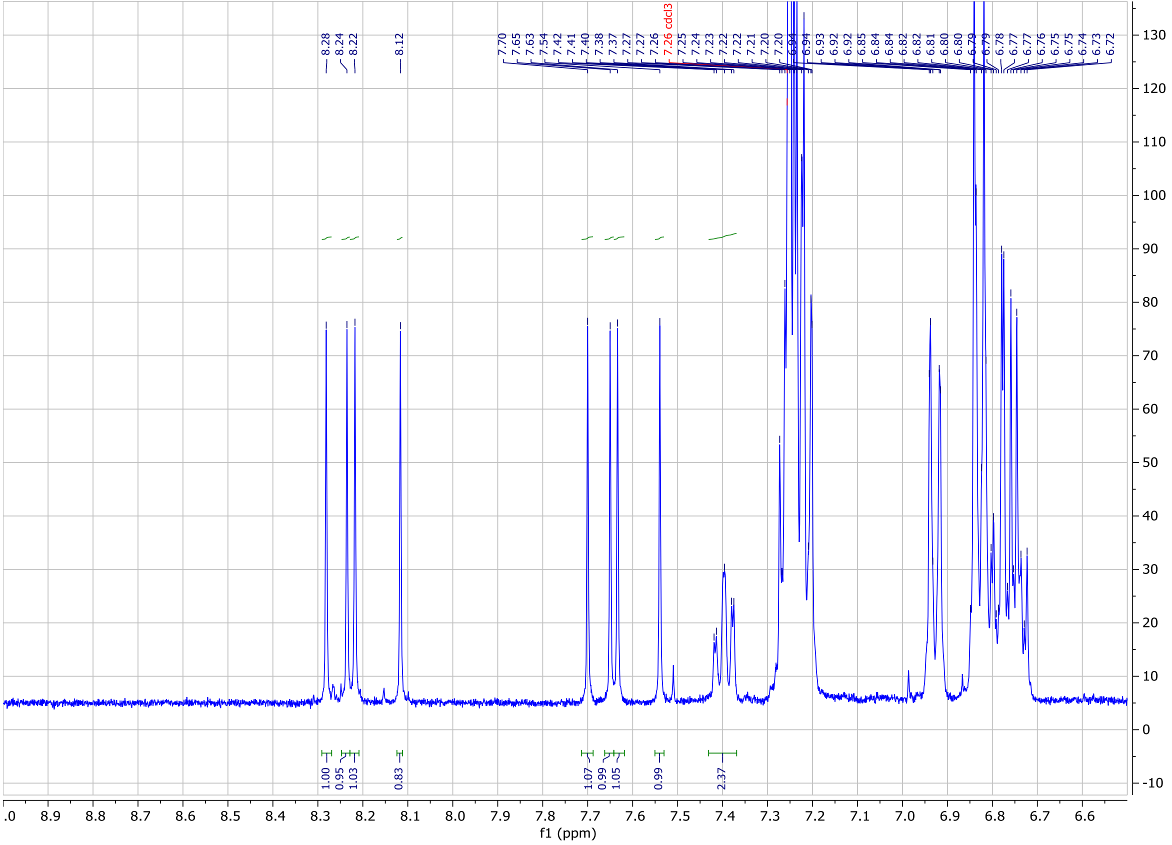


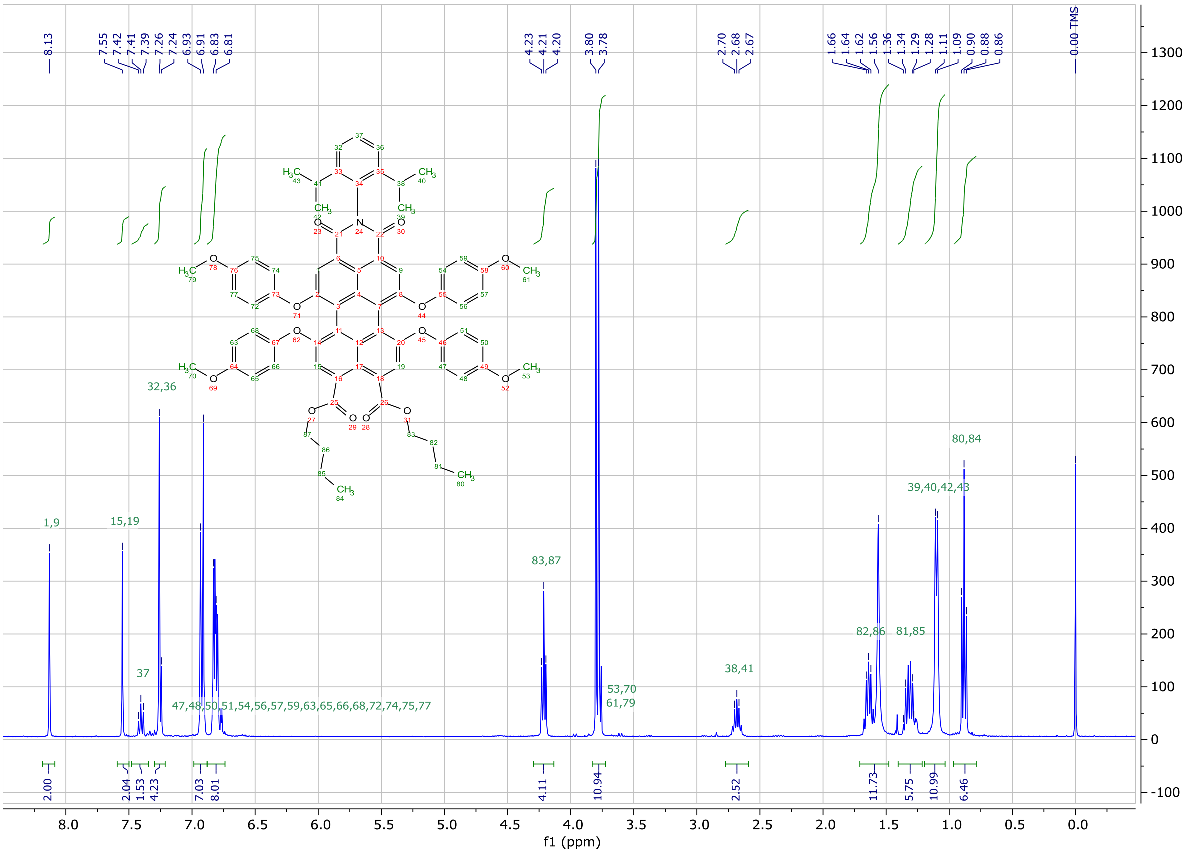
153.10
143.52
126.41
114.71
77.31
76.99
76.67
34.05
31.51
OH
7
6
5
4
3
2
O
8
H_3C
9
65
60
55
50
45
40
35
30
25
20
15
10
5
0
-5
80
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

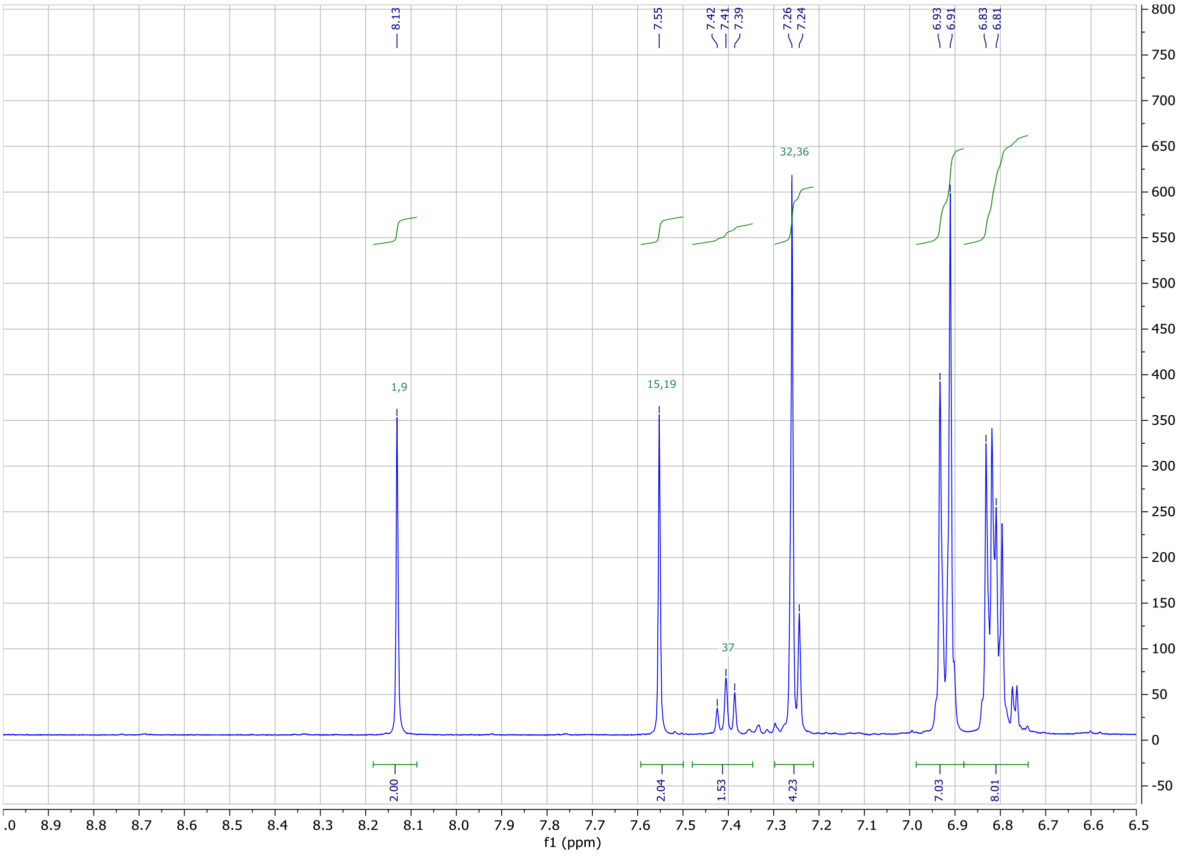
Appendix A.9 - ^{1}H NMR spectra of specific fractions of the phenol exchange product mixtures

All spectra in this appendix are provided as the full spectra and subsequently a display of the aromatic region of the same spectrum.

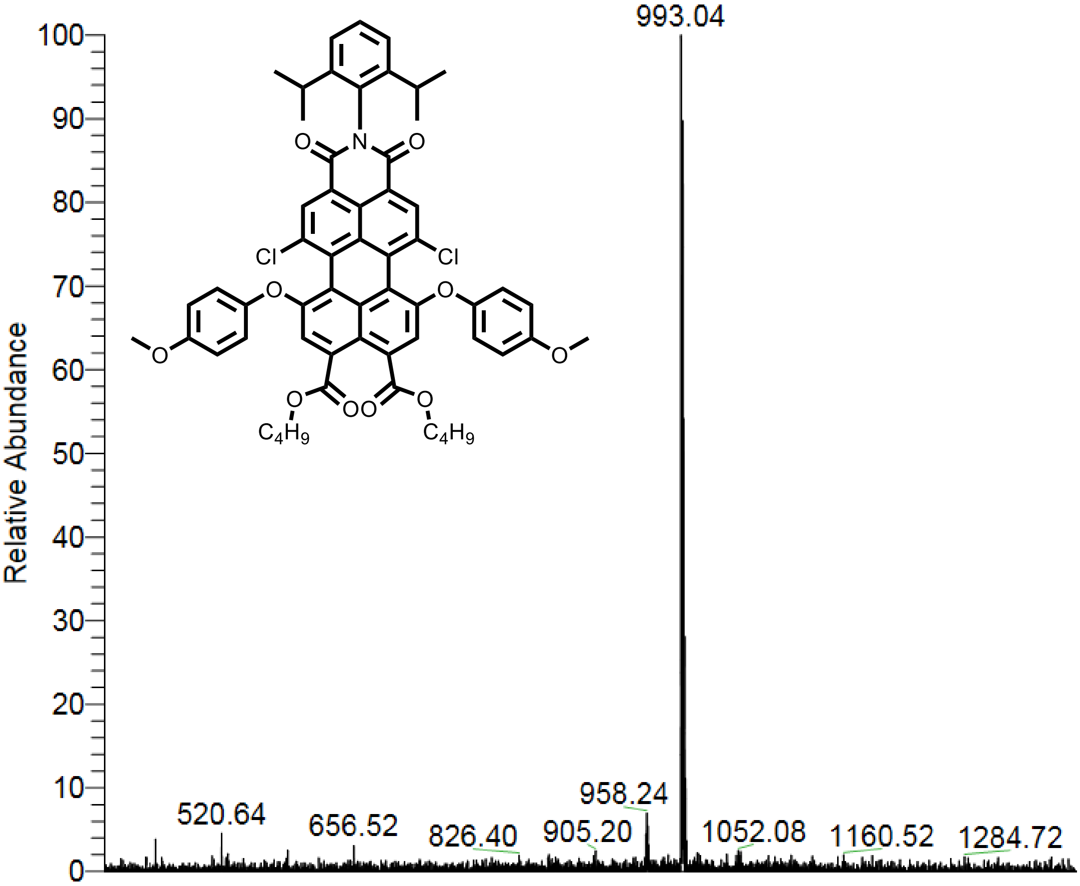


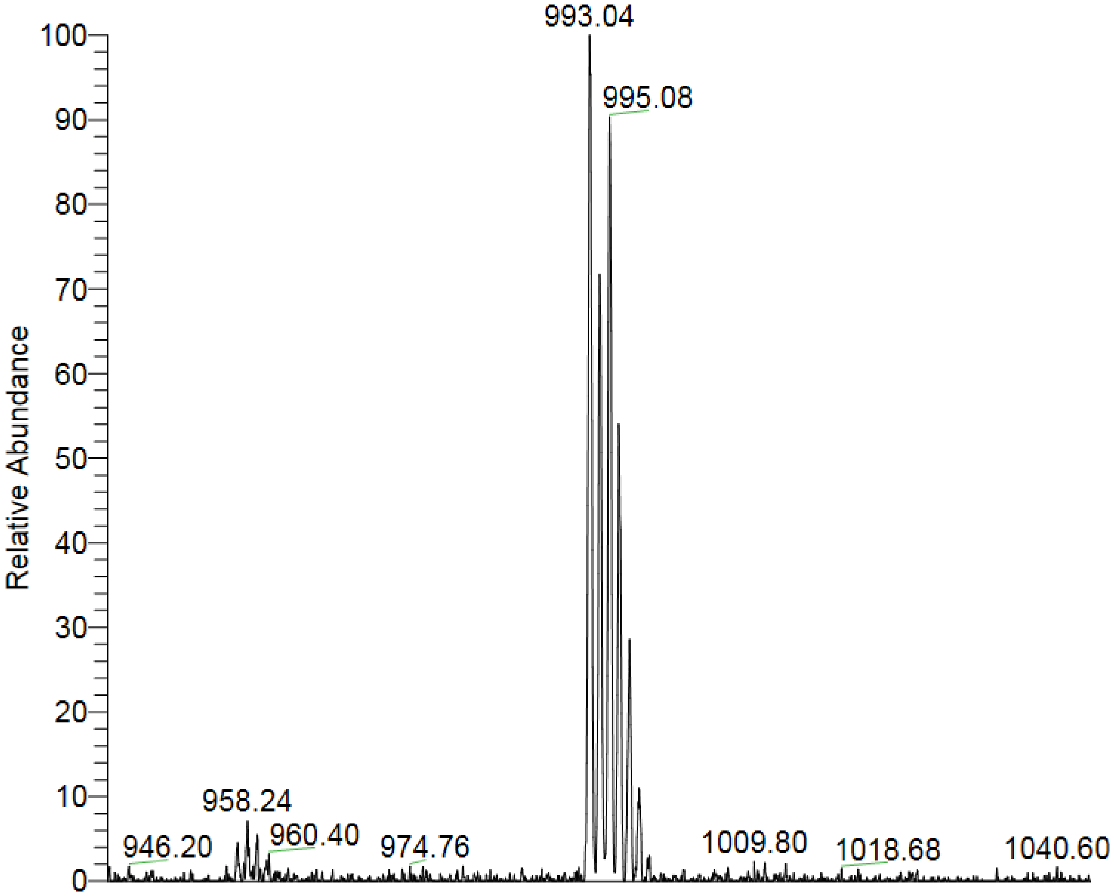


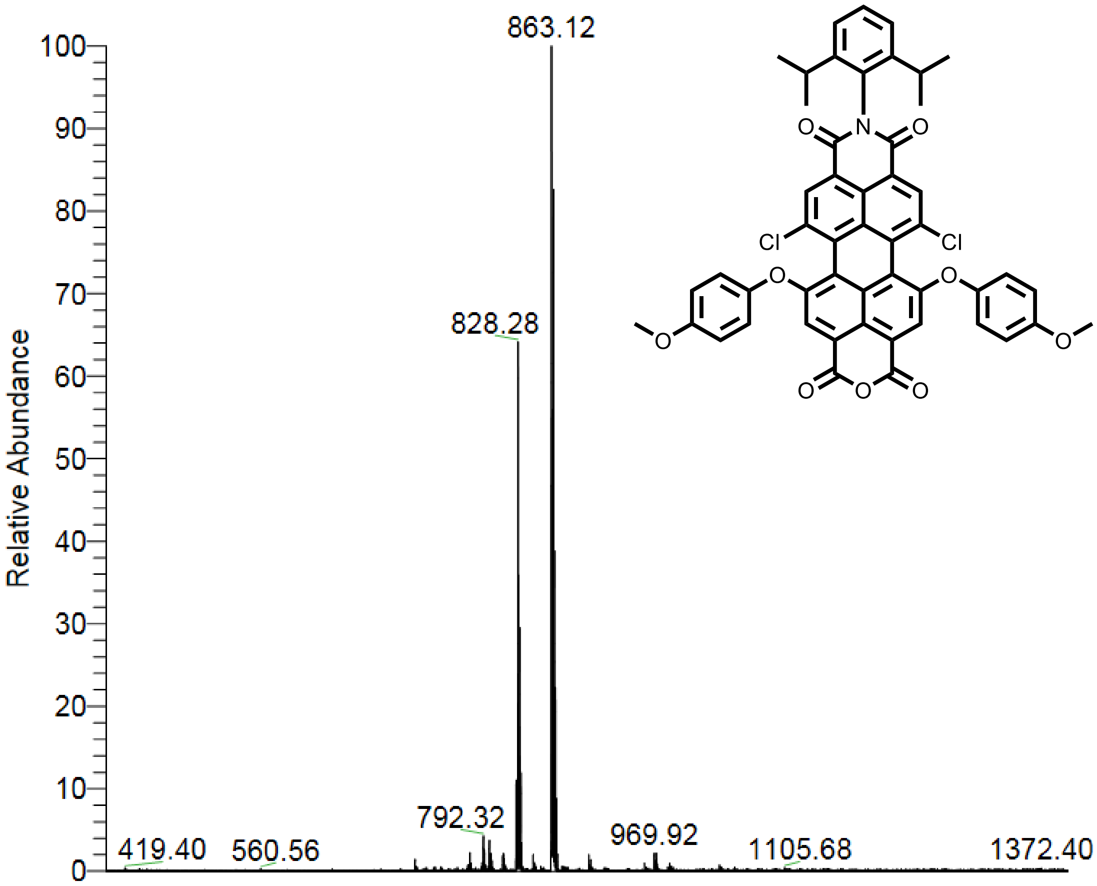

8.13
7.55
7.42
7.41
7.39
7.26
7.24
6.93
6.91
6.83
6.81
4.23
4.21
4.20
3.80
3.78
2.70
2.68
2.67
1.66
1.64
1.62
1.56
1.36
1.34
1.29
1.28
1.11
1.09
0.90
0.88
0.86
0.00 TMS
1,9
15,19
37
32,36
47,48,50,51,54,56,57,59,63,65,66,68,72,74,75,77
83,87
53,70
61,79
38,41
82,86
81,85
39,40,42,43
80,84
2.00
2.04
1.53
4.23
7.03
8.01
4.11
10.94
2.52
11.73
5.75
10.99
6.46
f1 (ppm)
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
1300
1200
1100
1000
900
800
700
600
500
400
300
200
100
0
-100
H_3C
CH_3
O
N

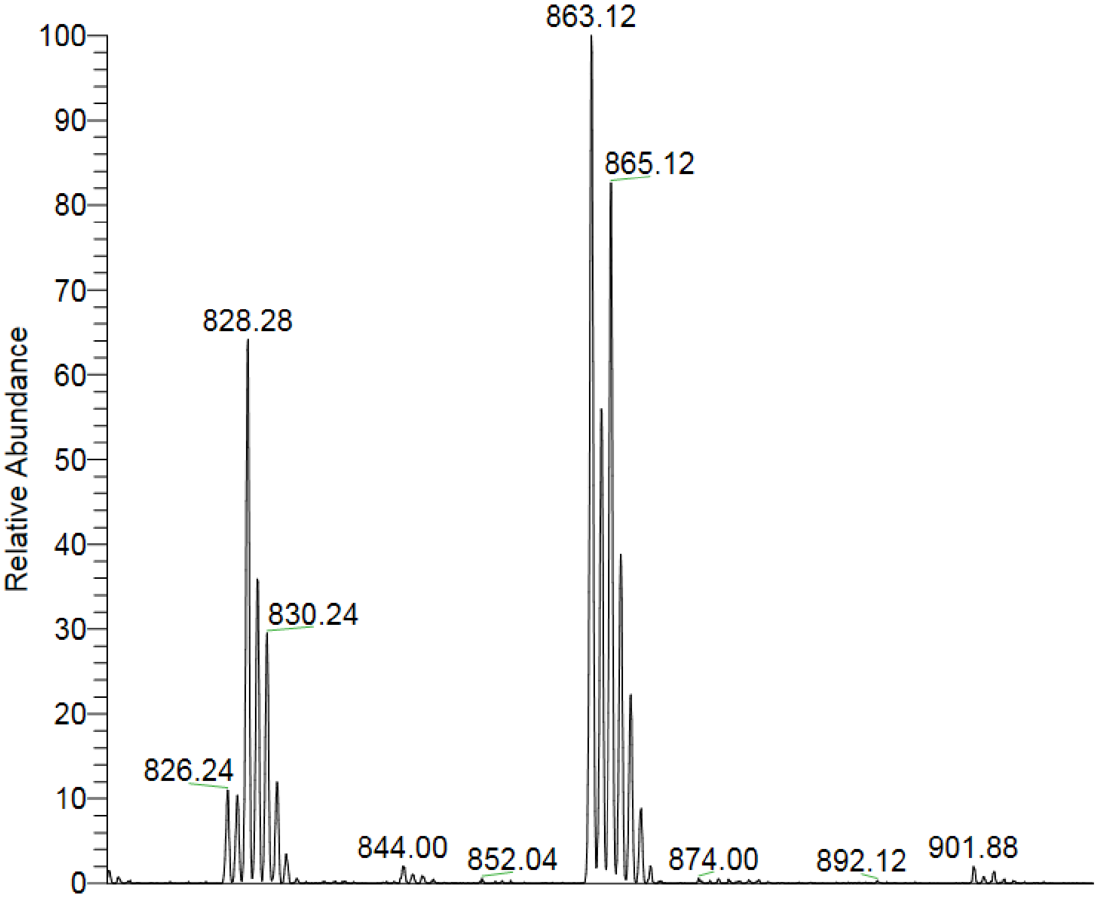

8.13
7.55
7.42
7.41
7.39
7.26
7.24
6.93
6.91
6.83
6.81
1,9
15,19
37
32,36
2.00
2.04
1.53
4.23
7.03
8.01
f1 (ppm)
.0
8.9
8.8
8.7
8.6
8.5
8.4
8.3
8.2
8.1
8.0
7.9
7.8
7.7
7.6
7.5
7.4
7.3
7.2
7.1
7.0
6.9
6.8
6.7
6.6
6.5
800
750
700
650
600
550
500
450
400
350
300
250
200
150
100
50
0
-50

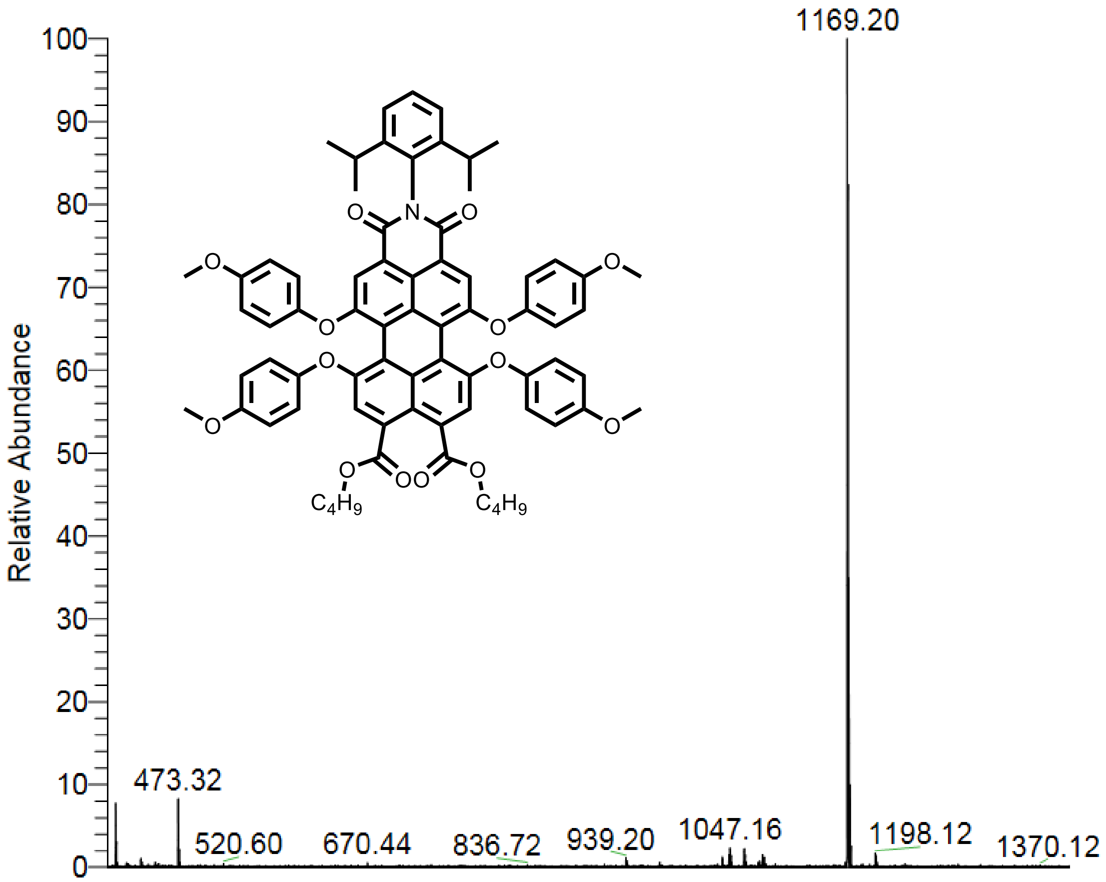
Appendix B - Mass spectra

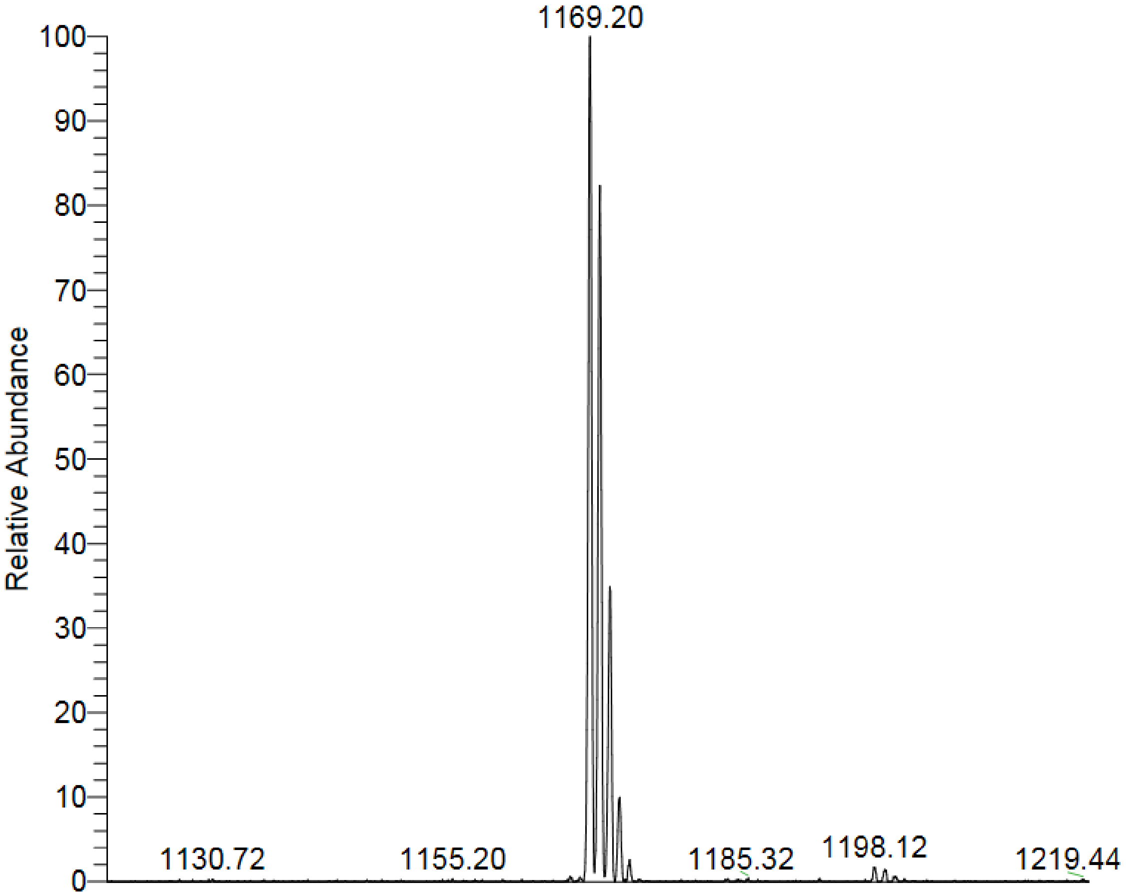


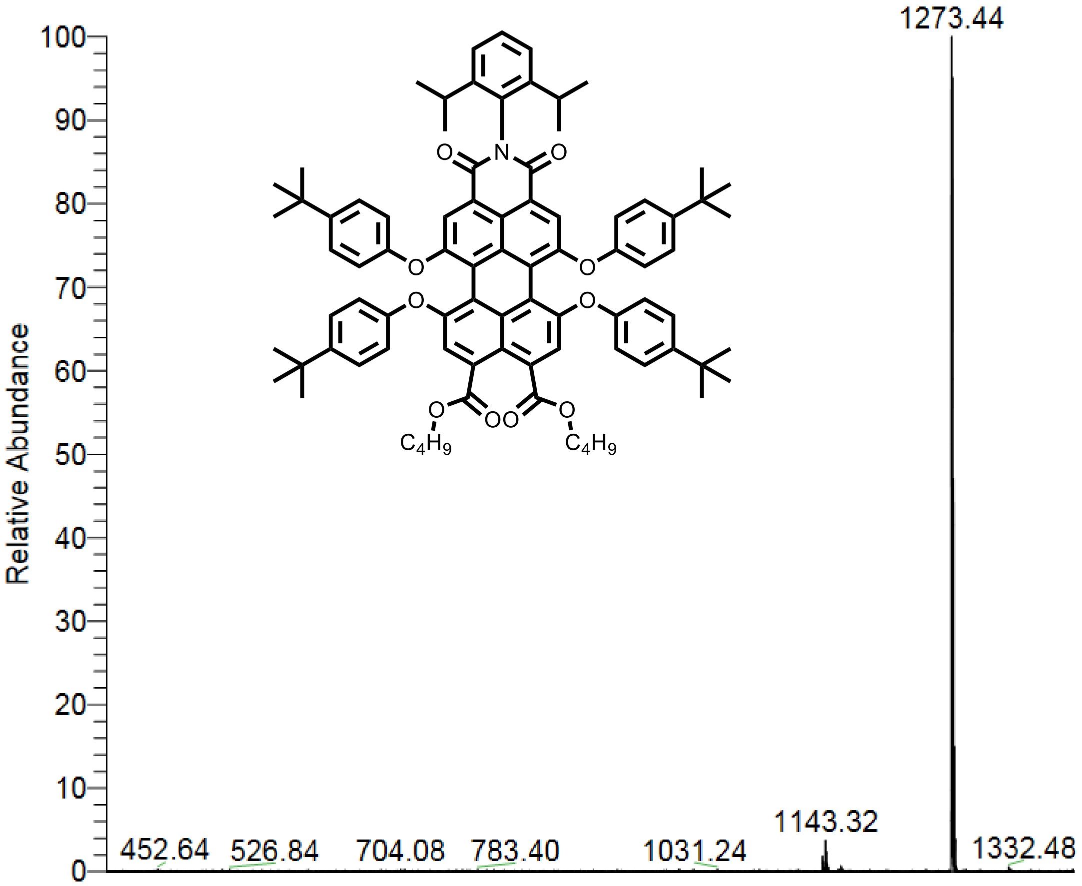


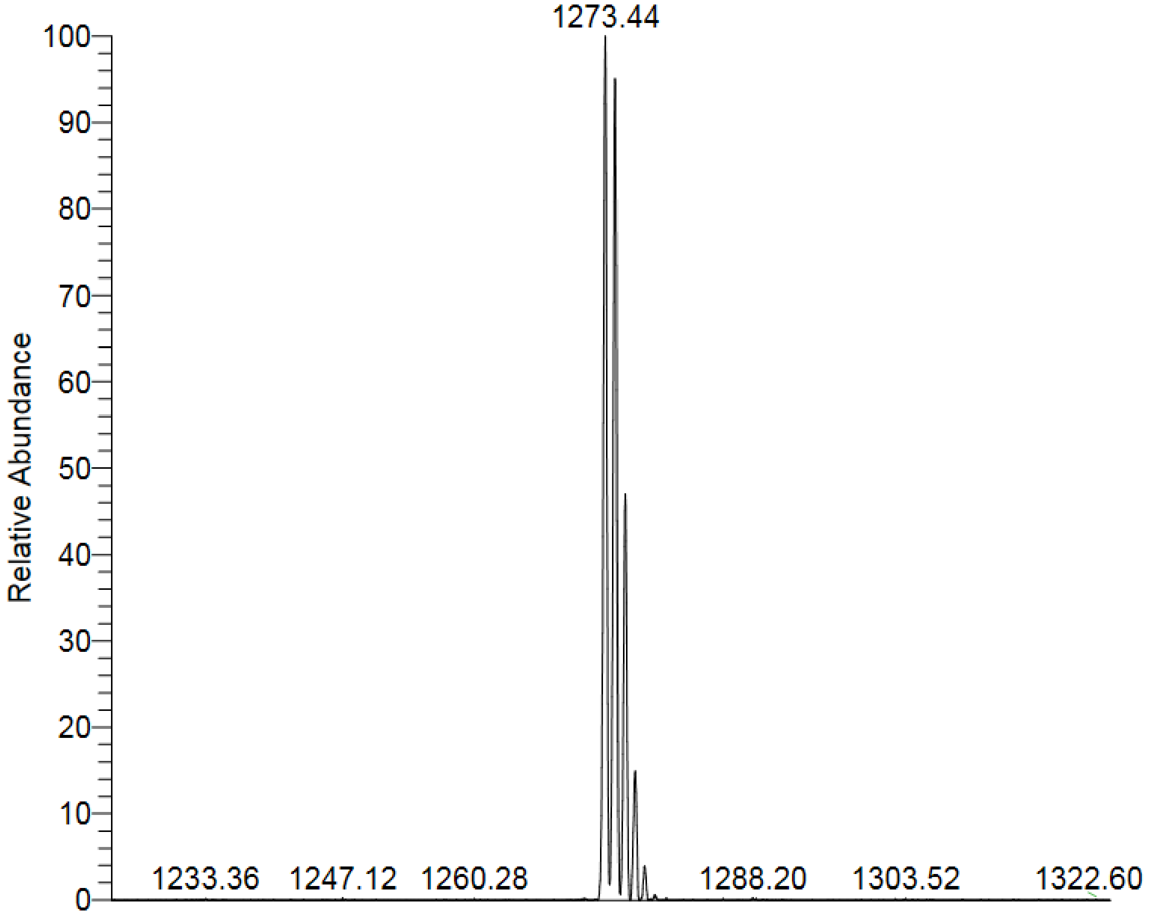

Relative Abundance
0
10
20
30
40
50
60
70
80
90
100
863.12
828.28
792.32
419.40
560.56
969.92
1105.68
1372.40
O
N
O
Cl
Cl
O
O
O
O
O
O
O

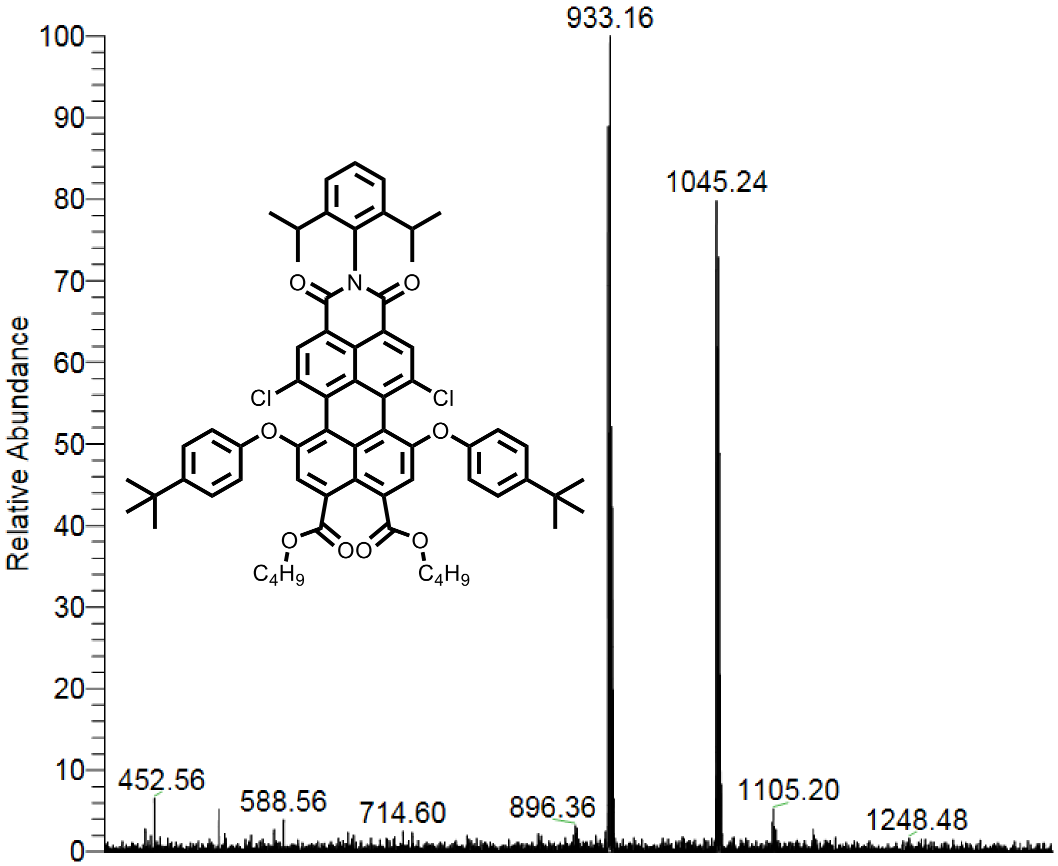

Relative Abundance
0
10
20
30
40
50
60
70
80
90
100
863.12
865.12
828.28
830.24
826.24
844.00
852.04
874.00
892.12
901.88

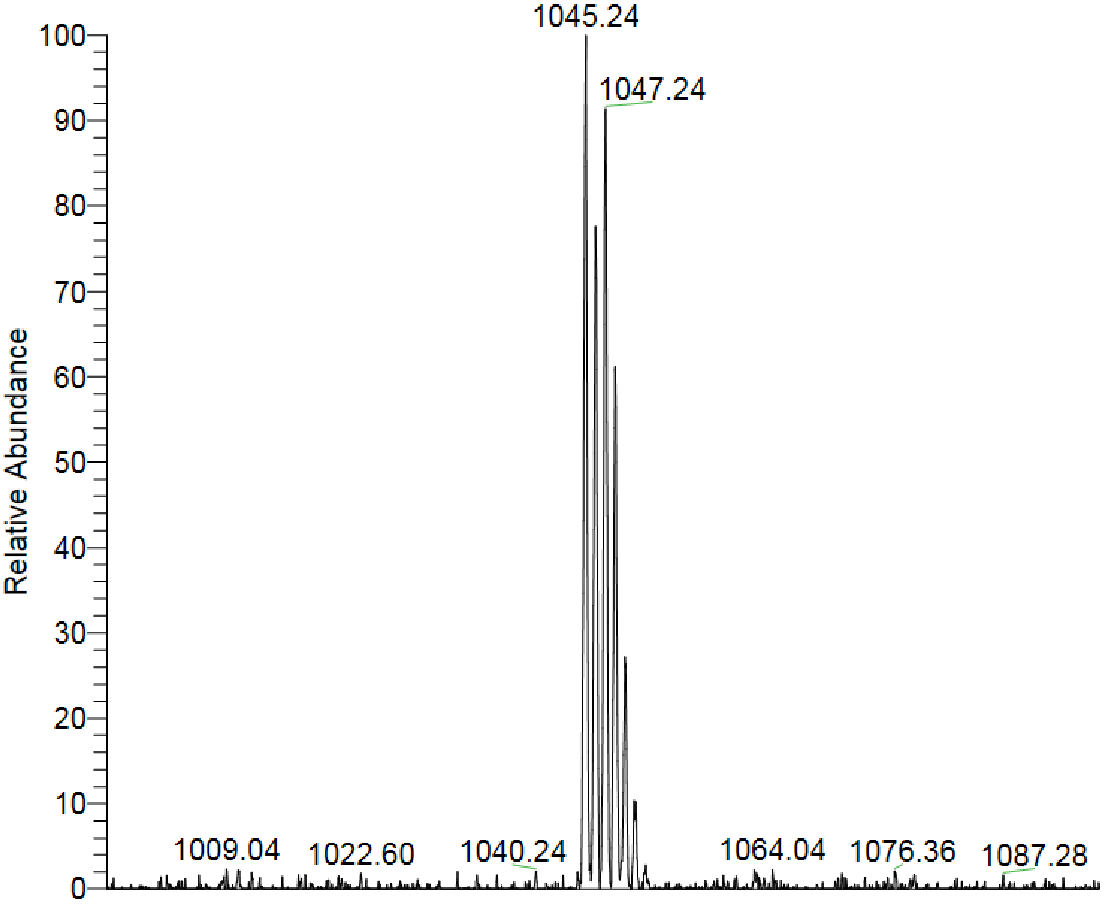

1169.20
100
90
80
70
60
50
40
30
20
10
0
Relative Abundance
473.32
520.60
670.44
836.72
939.20
1047.16
1198.12
1370.12
N
O
O
C4H9
C4H9

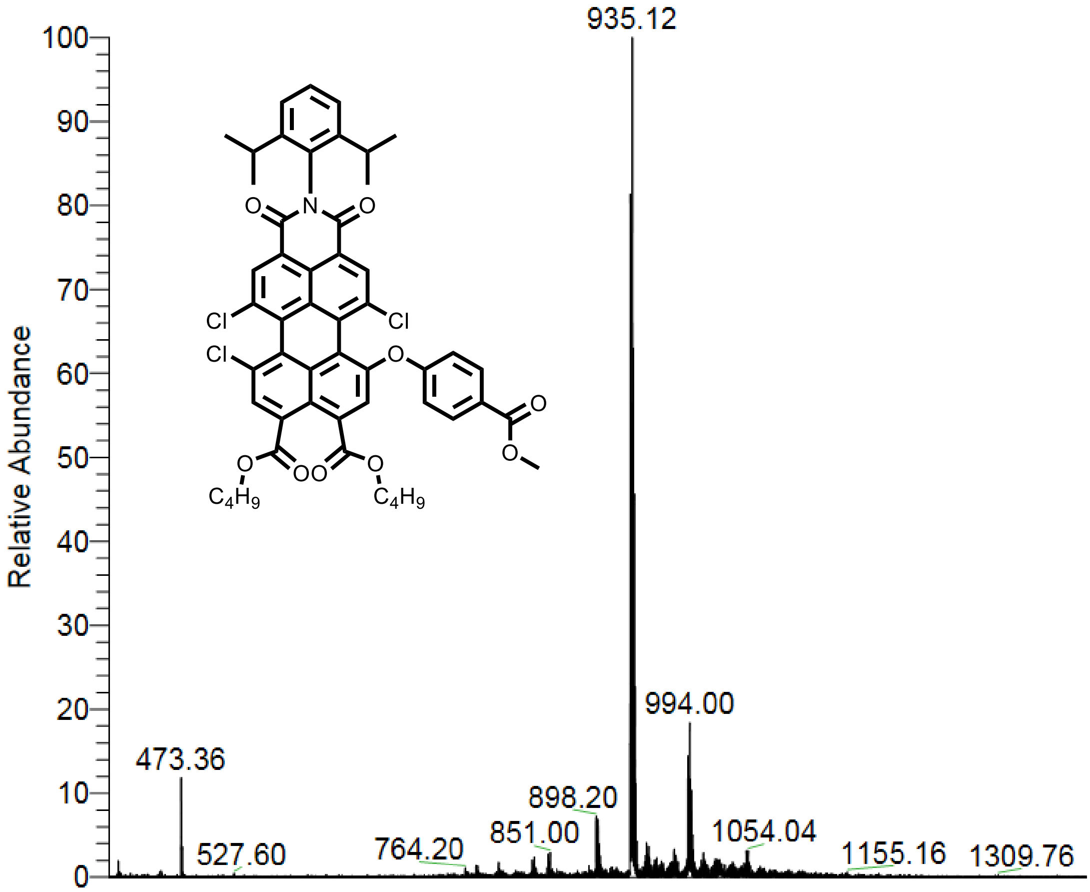

1169.20
100
90
80
70
60
50
40
30
20
10
0
Relative Abundance
1130.72
1155.20
1185.32
1198.12
1219.44

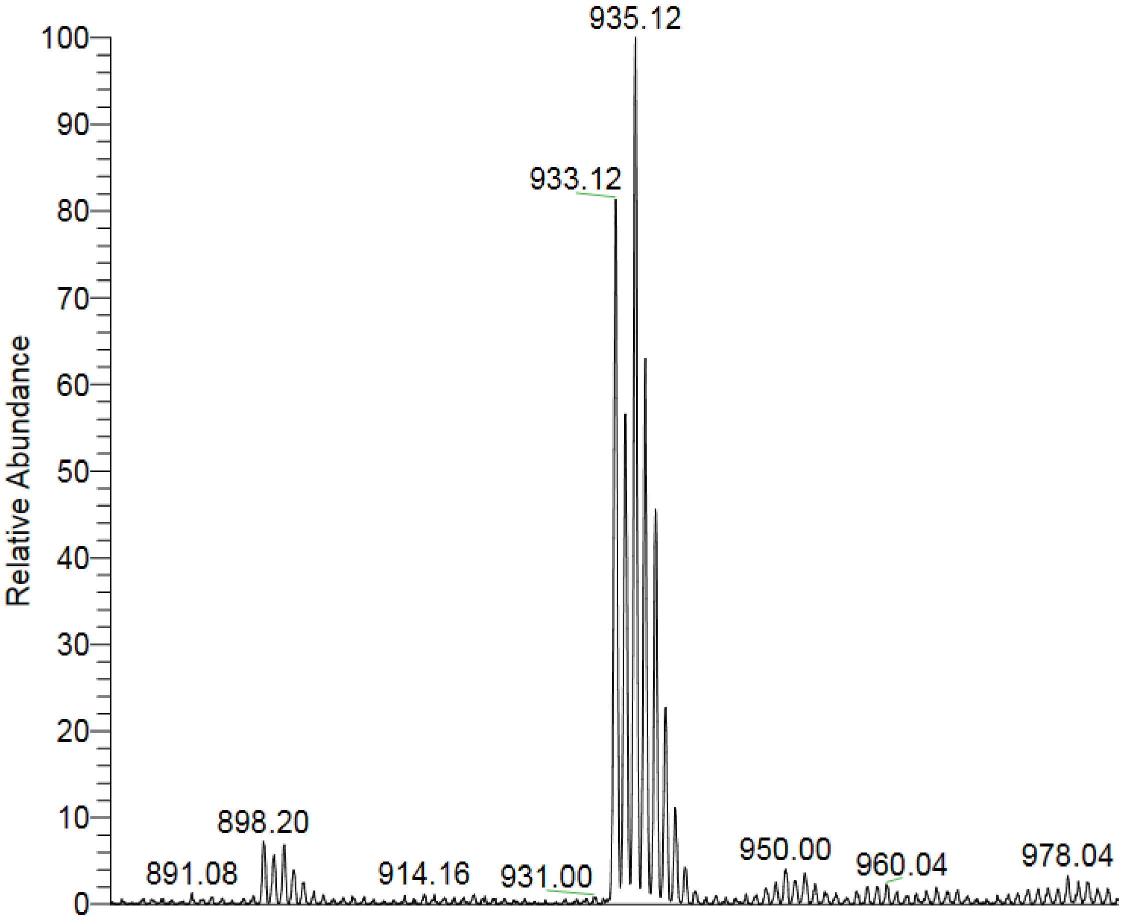

1273.44
100
90
80
70
60
50
40
30
20
10
0
Relative Abundance
452.64
526.84
704.08
783.40
1031.24
1143.32
1332.48
O
N
O
O
O
O
O
O
O
O
O
C_4H_9
C_4H_9

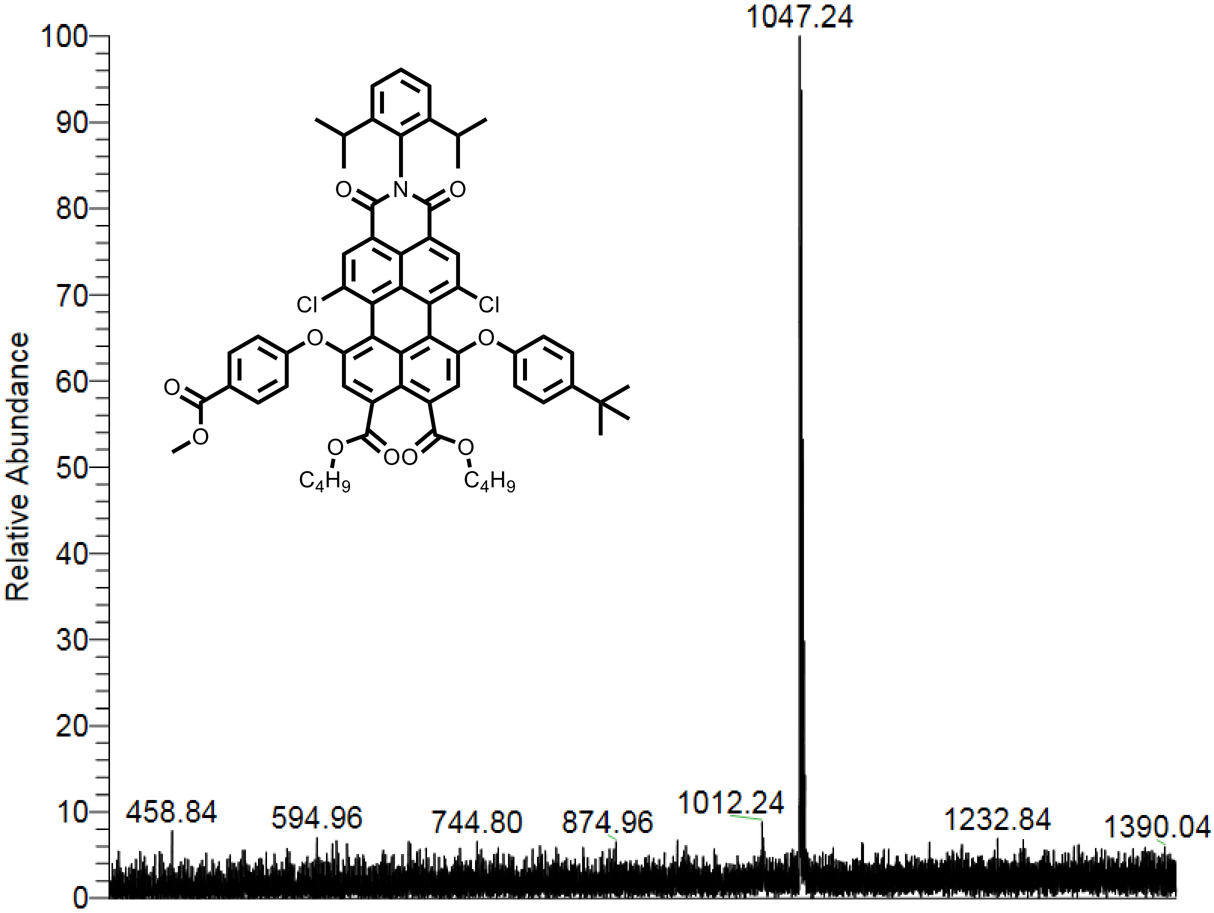

1273.44
100
90
80
70
60
50
40
30
20
10
0
Relative Abundance
1233.36
1247.12
1260.28
1288.20
1303.52
1322.60

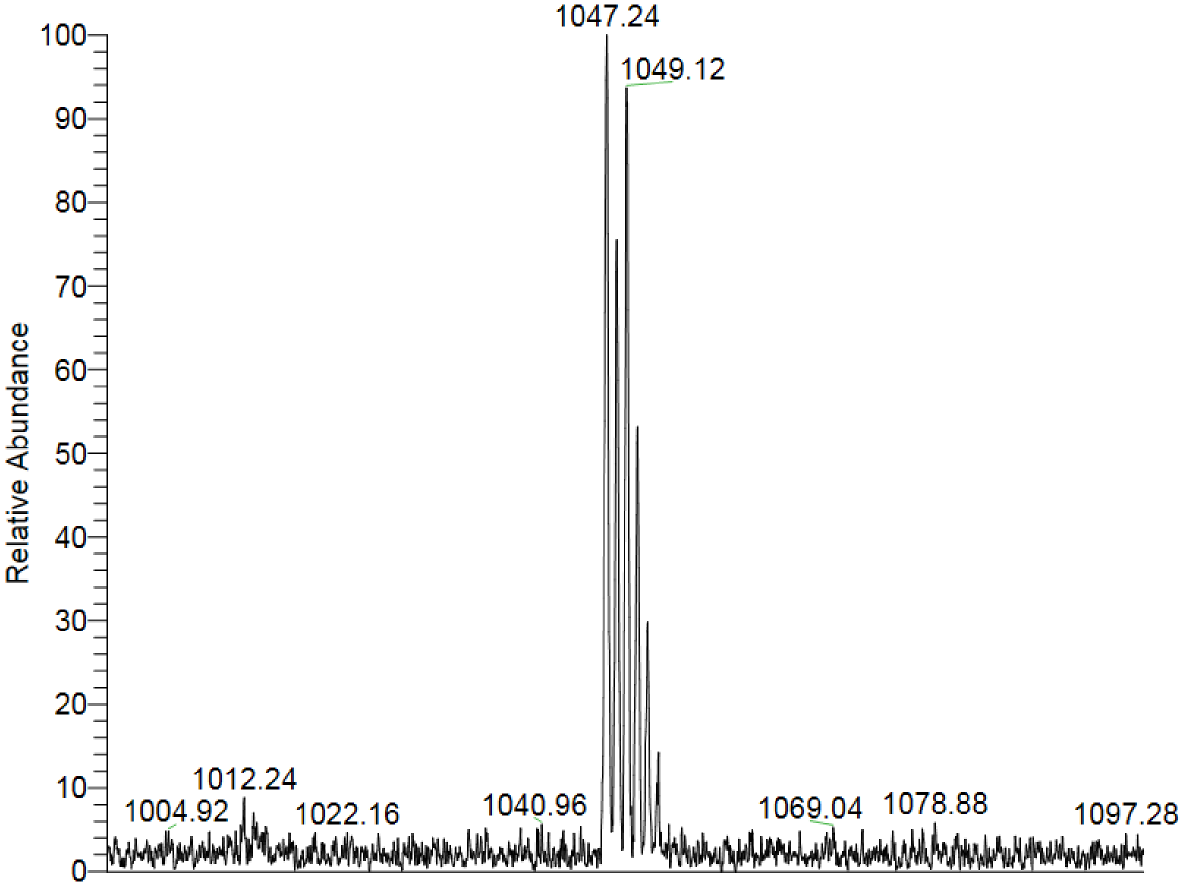

933.16
1045.24
452.56
588.56
714.60
896.36
1105.20
1248.48
Relative Abundance
0
10
20
30
40
50
60
70
80
90
100
N
O
O
Cl
Cl
O
O
O
O
O
O
C_4H_9
C_4H_9


1045.24
1047.24
1009.04
1022.60
1040.24
1064.04
1076.36
1087.28
Relative Abundance
0
10
20
30
40
50
60
70
80
90
100

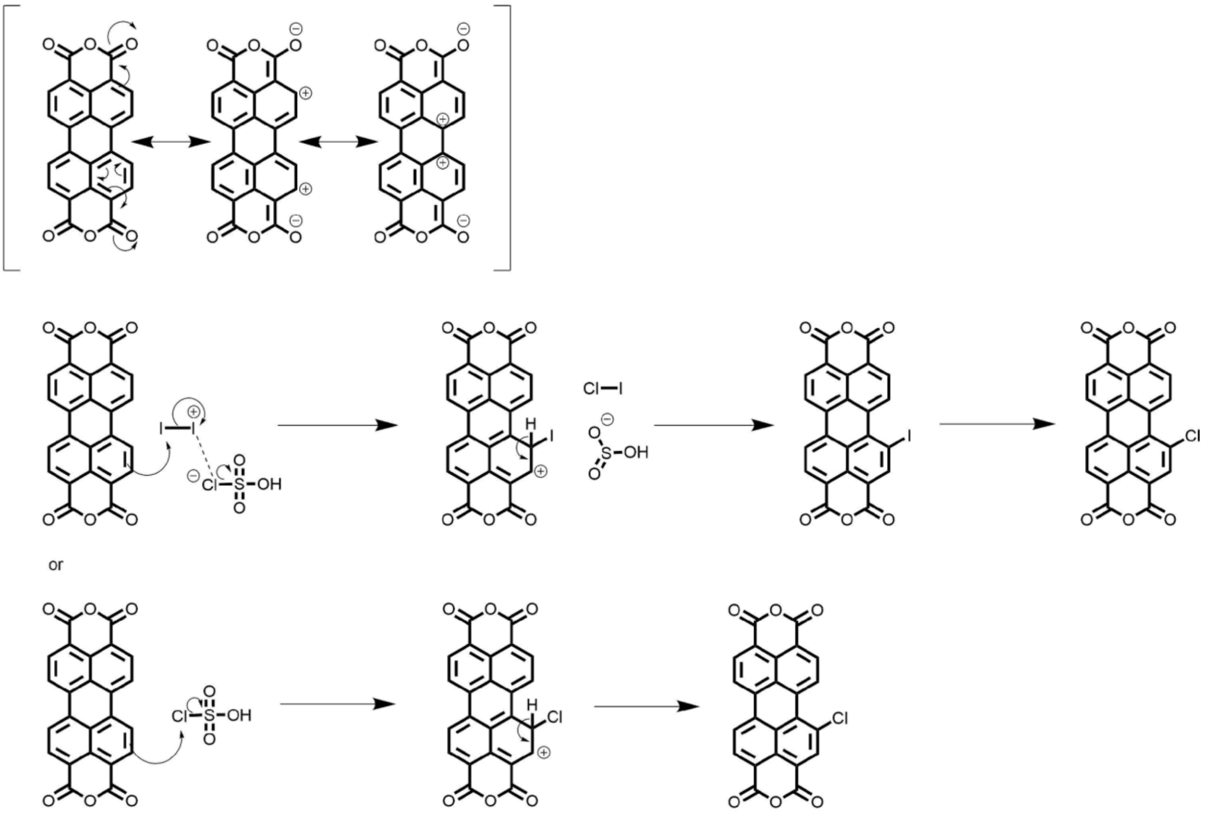

935.12
Relative Abundance
100
90
80
70
60
50
40
30
20
10
0
O
N
O
Cl
Cl
Cl
O
O
O
O
O
O
O
O
C_4H_9
C_4H_9
994.00
473.36
898.20
851.00
1054.04
527.60
764.20
1155.16
1309.76

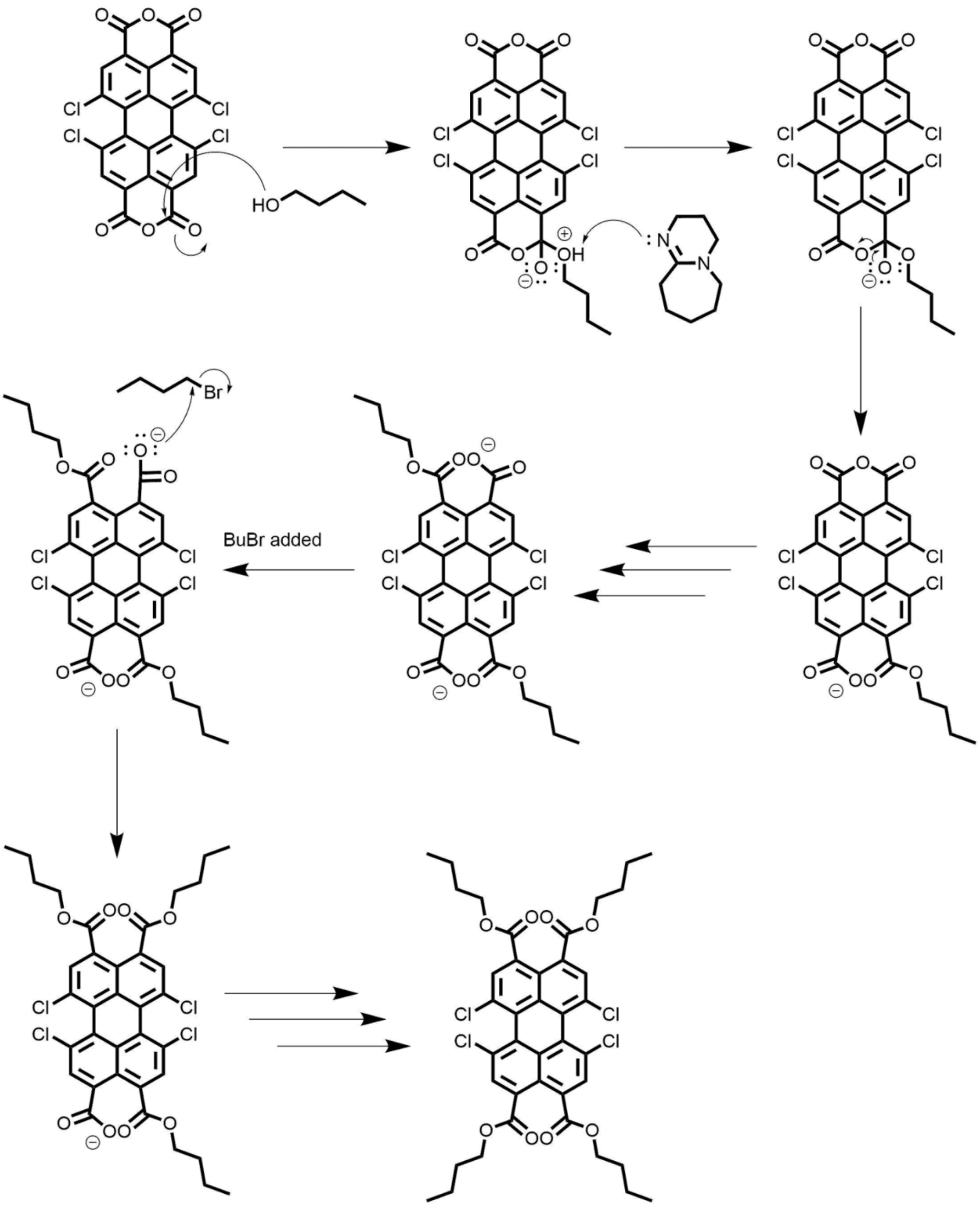

935.12
933.12
Relative Abundance
100
90
80
70
60
50
40
30
20
10
0
898.20
891.08
914.16
931.00
950.00
960.04
978.04

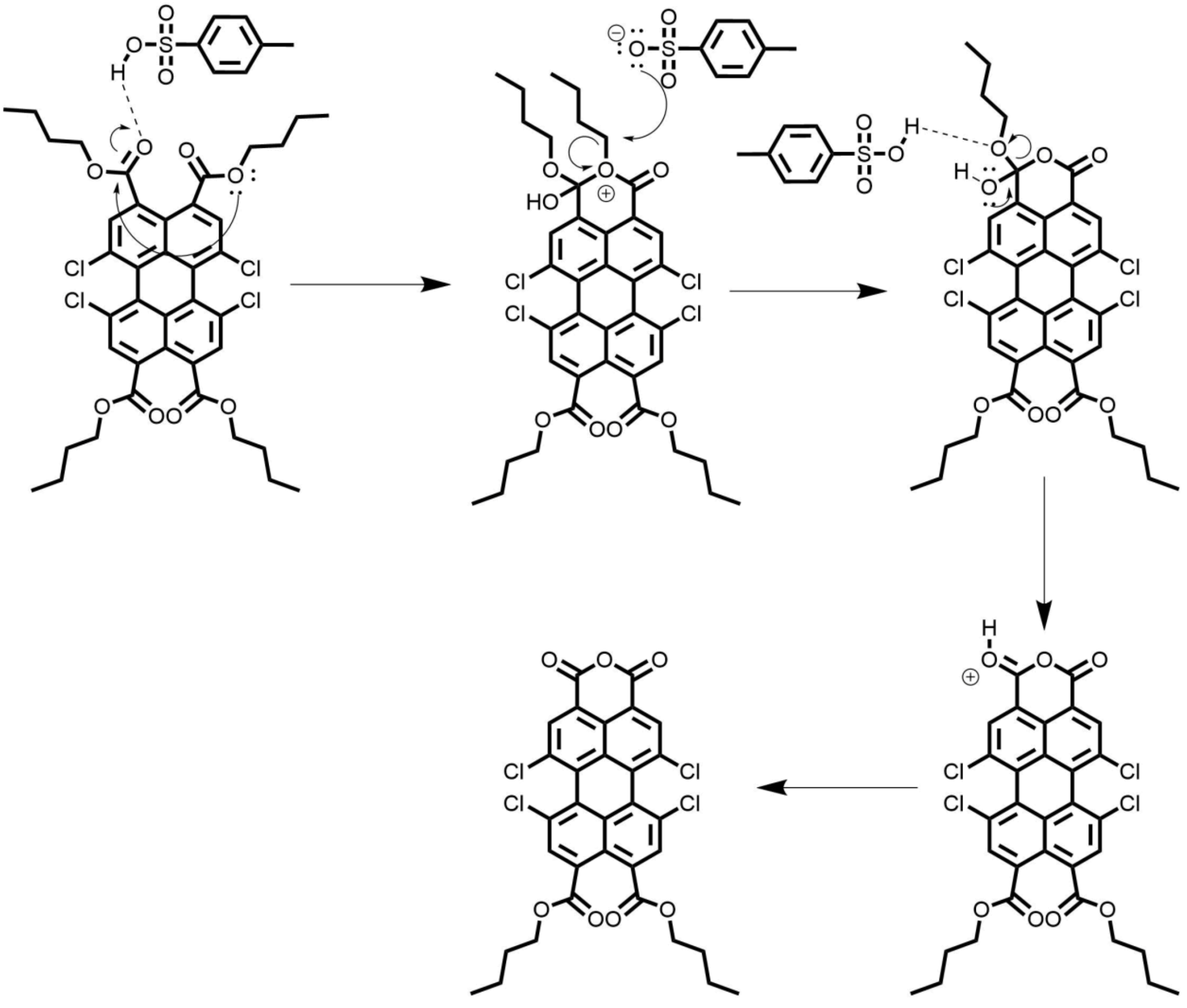

1047.24
100
90
80
70
60
50
40
30
20
10
0
Relative Abundance
458.84
594.96
744.80
874.96
1012.24
1232.84
1390.04
O
N
O
Cl
Cl
O
O
O
O
O
O
O
O
C_4H_9
C_4H_9

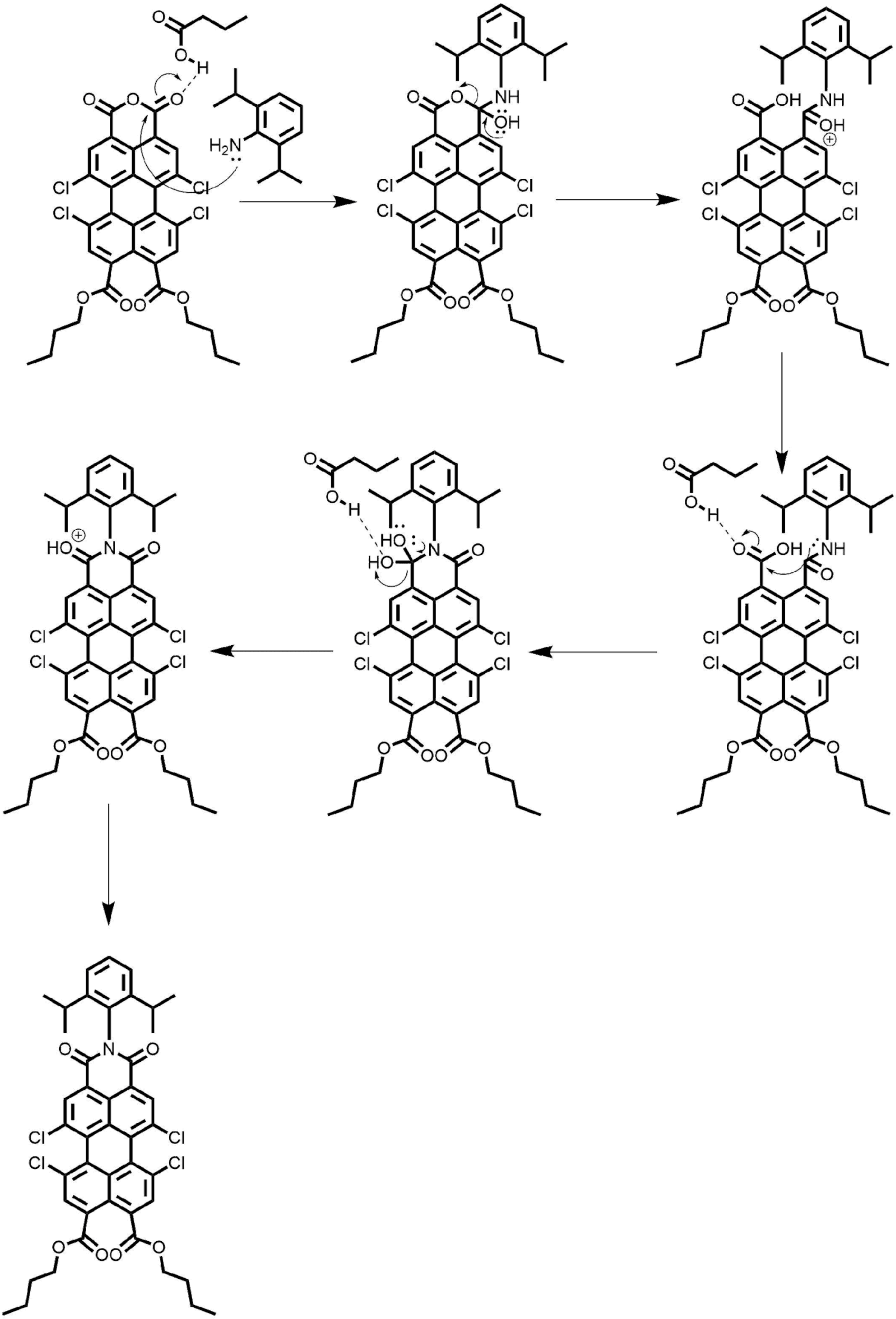

1047.24
1049.12
100
90
80
70
60
50
40
30
20
10
0
Relative Abundance
1004.92
1012.24
1022.16
1040.96
1069.04
1078.88
1097.28

Appendix C - Reaction mechanisms

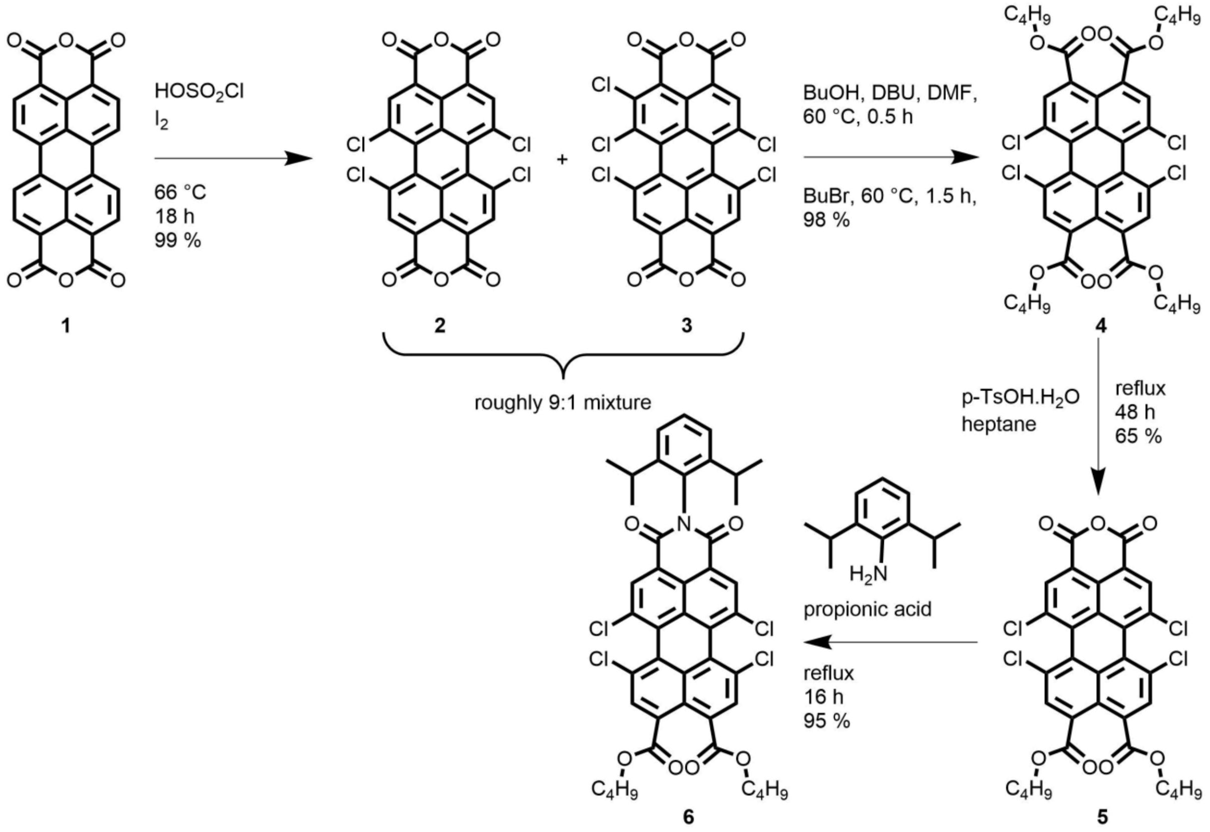



HO
BuBr added
Br
Cl




O
H
H2N
NH
OH
Cl
HO
N

Appendix D.1 - Reaction scheme to precursor



Appendix D.2 - Reaction procedures to precursor

D.2.1 Synthesis of 1,6,7,12-tetra-chloroperylene-3,4,9,10-tetra-carboxy di-anhydride

In a 250 mL round-bottom flask, a mixture of perylene-3,4,9,10-tetra-carboxy di-anhydride (10.0 g, 25.49 mmole) and iodine (1.66 g, 6.54 mmole), in chlorosulfonic acid (60 mL, 707 mmole), was heated to 66 °C and stirred for 18 hrs.

The reaction was poured into an ice-water mixture and the solid was collected by filtration with a glass filter. The solid was washed several times with water. The solid was dried under vacuum at 40 °C. The final product was obtained with a 99% yield.

According to [13] the obtained product is be contaminated with 10% penta chlorinated perylene. No NMR measurements were done due to low solubility of the product and the high risk involved in D_2SO_4 NMR measurements.

D.2.2 Synthesis of 1,6,7,12-tetra-chloroperylene-3,4,9,10-tetra-carboxy tetra-butylester

In a 500 mL round-bottom flask, a mixture of 1,6,7,12-tetrachloroperylene-3,4,9,10-tetra-carboxy di-anhydride, 1,2,6,7,12-pentachloroperylene-3,4,9,10-tetra-carboxy di-anhydride (9:1, 10.0 g, 17.8 mmole), DMF (125 ml), butanol (13.8 ml) and DBU (11.3 ml) was heated to 60 °C and stirred for 30 minutes.

In a separate 250 ml round-bottom flask, bromobutane (16.3 ml) and DMF (75 ml) were mixed. This mixture was added to the reaction vessel and the new mixture was stirred for another 90 minutes at 60 °C.

The reaction was poured into water and the solid was collected by filtration with a glass filter. The solid was washed several times with water and IPA.

To perform recrystallization, the solid was dissolved in 100 ml DCM and 100 ml of ACN was added. After half an hour another 100 ml ACN was added. After again half an hour, the last 100 ml of ACN was added.

The obtained crystals were collected by filtration over a glass filter. The crystals were washed with several portions of ACN. The final product was obtained with a 98% yield. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.086 (s, 4H), 4.365 (m, J = 5.6 Hz, 8H), 1.803 (m, J = 7.2 Hz, 8H), 1.512 (m, J = 7.6 Hz, 8H), 1.007 ppm (t, J = 7.6 Hz, 12H). ^{13}C NMR (101 MHz, $cdcl_3$) δ = 167.01, 133.92, 133.54, 131.99, 130.74, 127.19, 123.09, 66.04, 30.57, 19.23, 13.78 ppm. The ^{1}H NMR and ^{13}C NMR spectra can be found in Appendix A.1 and Appendix A.2 respectively.

D.2.3 Synthesis of 1,6,7,12-tetrachloroperylene-3,4,9,10-tetra-carboxy mono-anhydride di-butylester

In a 250 ml round-bottom flask, a mixture of 1,6,7,12-tetrachloroperylene-3,4,9,10-tetra-carboxy tetra-butylester (5.00 g, 6.33 mmole) and p-toluenesulfonic acid (1.3 g, 6.84 mmole) in heptane (40 ml), was stirred under reflux conditions for 48 hrs.

The reaction mixture was cooled to room temperature and the heptane was evaporated under vacuum. The crude product was washed with several portions of water and methanol respectively.

In a 1 L round-bottom flask, the crude product was collected and dissolved in hexane. The mixture was refluxed for 2 hrs. The obtained solid was collected by filtration with a glass filter.

In a 1 L round-bottom flask, the crude product was collected and dissolved in ACN. The mixture was refluxed for 2 hrs. The resulting solution was left overnight. The resulting crystals were obtained by filtration with a glass filter. The crystals were dried to obtain the final product with a 65% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ = 8.67 (s, 2H), 8.15 (s, 2H), 4.40 (m, J = 4 Hz, 4H), 1.82 (m, J = 6.4 Hz, 4H), 1.52 (m, J = 7.2 Hz, 4H), 1.02 ppm (t, J = 8 Hz, 6H). ^{13}C NMR (101 MHz, $cdcl_3$) δ = 166.64, 158.66, 135.11, 134.86, 134.86, 134.71, 134.64, 134.00, 132.19, 132.11, 131.53, 130.87, 125.90, 125.13, 123.37, 118.47, 66.30, 30.52, 19.19, 13.74 ppm. The ^{1}H NMR and ^{13}C NMR spectra can be found in Appendix A.1 and Appendix A.2 respectively.

D.2.4 Synthesis of N-(2,6-di-isopropylphenyl)-1,6,7,12-tetra-chloroperylene-3,4,9,10 -tetra-carboxy mono-imide di-butylester

In a 50 ml round-bottom, a mixture of 1,6,7,12-tetrachloroperylene-3,4,9,10-tetra-carboxy mono-anhydride di-butylester (0.950 g, 1.16 mmole) and 2,6-di-isopropylaniline, in propionic acid (20 ml), was stirred under reflux conditions for 16 hrs.

The reaction mixture was cooled to room temperature and poured into water. The solid was collected by filtration with a glass filter and washed with several portions of water. The crude product was dried and chromatographed on silica with a 2:1 DCM:hexane eluent. The final product was obtained with a 82% yield.

^{1}H NMR (400 MHz, cdcl$_3$) δ = 8.70 (s, 2H), 8.16 (s, 2H), 7.52 (t, J = 6 Hz, 1H), 7.36 (d, J = 8 Hz, 2H), 4.40 (m, J = 6.3 Hz, 4H), 2.75 (m, J = 7 Hz, 2H), 1.83 (m, J = 6 Hz, 4H), 1.52 (m, J = 7.2 Hz, 4H), 1.19 (m, J = 4 Hz, 12H), 1.03 ppm (t, J = 6 Hz, 6H). ^{13}C NMR (101 MHz, cdcl$_3$) δ = 166.84, 162.53, 145.62, 134.76, 134.47, 133.77, 133.22, 132.10, 131.75, 131.65, 130.04, 129.90, 129.64, 126.47, 124.20, 123.65, 123.41, 122.45, 77.31, 76.99, 76.67, 30.55, 29.23, 24.00, 19.21, 13.76 ppm. The ^{1}H NMR and ^{13}C NMR spectra can be found in Appendix A.1 and Appendix A.2 respectively.