Synthesis of Phenazine and Quinone Containing Organic Monomers Suitable for Linear and Branched Two-Dimensional Polymers

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Abstract

Covalent organic frameworks (COFs) are a relatively new type of porous crystalline materials created through covalent bonding of organic building blocks. The use of COFs for the creation of organic polymer-based batteries has recently sparked interest in the attempts to find non-metal-based compounds for sustainable energy storage. To be eligible for use as energy storage in organic batteries, the monomers that make up the framework have to be redox active. Thus, monomers with functional groups such ketones are often found in the framework. The framework also has to be electrically conductive. Studies have shown electrical conductivity in polymers containing phenazine and phenazine derivatives; due to this, there is an interest in finding different phenazine derivatives which are able to store and release a large quantity of electrons. In this project, the interest was in finding synthesis pathways for quinone and/or phenazine containing two-dimensional monomers and linkers suitable for linear and branched two-dimensional organo-based polymers. 2,3,7,8-Tetraaminophenazine **1** and pyrene-4,5,9,10-tetraone **3** were both able to be synthesised. **1** was obtained in a high yield with no purification needed before being used for further synthesis while **3** was obtained in a low yield and needed to be purified by column chromatography. It is unclear if 2,3,6,7,10,11-hexaketotriphenylene **2** and 2,3,7,8-tetraaminophenazine-4,5,9,10-tetraone **4** were able to be synthesised or not. The ^{1}H NMR spectrum obtained of **2** does agree with the one found in the literature. However, peaks in the obtained ^{13}C NMR spectrum do not correspond to the chemical environments present on **2**. Due to the very low solubility of **2**, no conclusive solution NMR spectrum could be obtained and direct infusion MS yielded no relevant *m/z* values. However, since the molecule shows potential to be used for organo-based energy storage, there is an interest to further try to characterise the formed powder by solid-state measurements.

List of abbreviations

ACN	Acetonitrile
COF	Covalent Organic Framework
DCM	Dichloromethane
DMSO	Dimethylsulfoxide
DMSO-d_6	Deuterated dimethylsulfoxide
DDQ	2,3-Dichloro-5,6-dicyano-p-benzoquinone
eqv.	equivalent
NMR	Nuclear Magnetic Resonance
MS	Mass spectroscopy
m/z	*mass/charge*
RAOF	Redox Active Organic Framework

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1. Introduction

Redox active organic frameworks (RAOFs) are a type of porous crystalline materials which are assembled from either redox active organic monomers or metal nodes held together with so-called *linkers* – organic molecules which are able to form bonds with the organic monomers or metal nodes and sit in between them, thus linking them together and enabling the formation of a polymer. Depending on the structure of the redox active organic monomers and linkers, the formed RAOF may take on either a two- or three-dimensional structure, with the two-dimensional frameworks often containing monomers of aromatic nature, leading to the formation of pores due to the flat polymers stacking upon each other (Figure 1), enabling π-π interactions, which stabilise the framework. Covalent organic frameworks (COFs) – a term coined by Yaghi and co-workers in 2005[1] – are a relatively new type of porous crystalline materials created through covalent bonding of purely organic building blocks.[2] Because of their high porosity – which often gives the framework a low density – and large surface areas, COFs have found their way into fields previously dominated by metal containing materials such as gas and ion filtrations, electrochemical catalysis, batteries and more.[3]

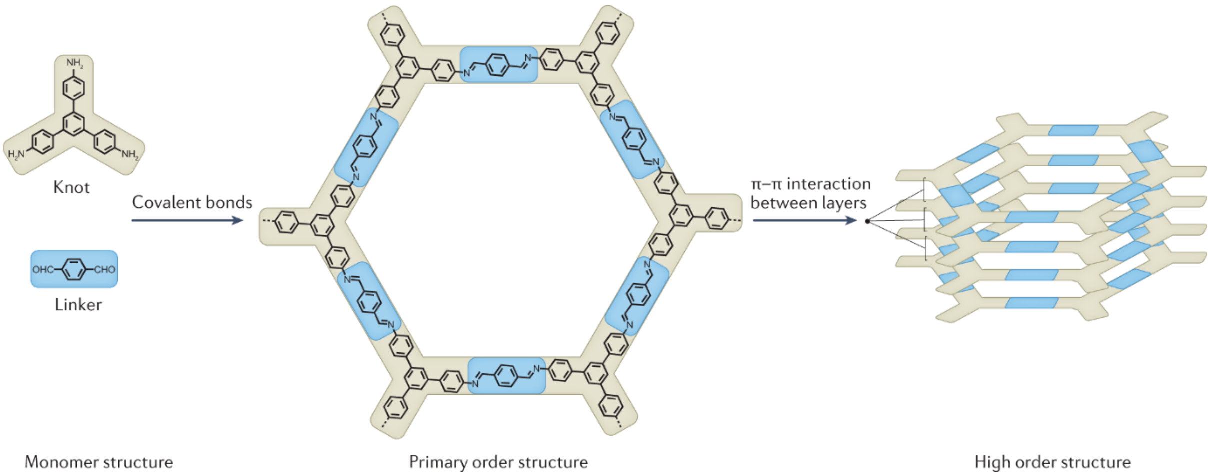


Figure 1. Illustration of two-dimensional stacking (reproduced with permission from Tan et *al.*[4])

The use of COFs for the creation of organic polymer-based batteries has recently sparked interest in the attempts to find non-metal-based compounds for sustainable energy storage. Since being introduced in 2005, many successful attempts have been made to find combinations of organic monomers and linkers that make suitable candidates for future non-metal-based energy storage. An example of a successful combination comes from DeBlase et *al.* who in 2013 presented a β-ketoenamine-linked two-dimensional COF which showed reversible reduction/oxidation of its anthraquinone subunits.[5] A more recent example is the work done by Shi et *al.*, who in a recent publication reported a COF based electrode with triquinoxalinylene and benzoquinone in the covalent framework.[6]

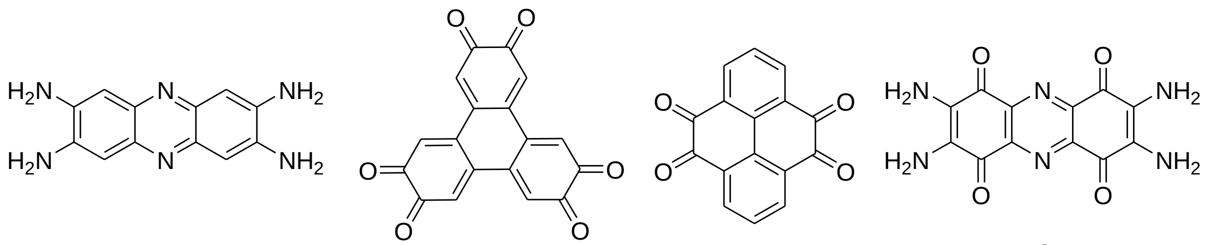
For the COF to be eligible for use as energy storage in organic batteries, the monomers that make up the framework have to be redox active, thus monomers with functional groups such ketones are often found in the framework since the reduction/oxidation of the ketone/alcohol from is reversible, permitting both the storage and release of electrons from the framework. When considering the eligibility of a COF for energy storage, one need to consider the number of redox active functional groups present on each individual monomer since the amount of redox active functional groups present on the monomers composing the organic framework limits the number of electrons which may be stored along the polymer chains. However, when considering energy storage, the volume of the framework also has to be taken into consideration since a battery consists of a limited space. As previously mentioned, depending on the monomers and linkers used, the COF may take on either a two- or three-dimensional structure with the two-dimensional structure being more volume efficient since it allows the flat polymers to stack upon each other, thus minimising dead space. Therefore, monomers and linkers of an aromatic nature and monomers with multiple sites of redox active functional groups are preferred.

Even when the polymers contain redox active functional groups that can store and release electrons, the formed COF is not automatically electrically conductive upon formation. To create a current – or an electron *flow* – the electrons have to be able to move from the anode to the cathode. For COFs, solutions to the low (or absence of) conductivity have consisted of the addition of a conductive material to the formed COF such as carbon or by synthesising the COF as a thin film which allows for electron hopping.[7] A third – and also the preferred – solution is to design COFs which are conductive upon formation. However, this approach limits the design of the COF since not all redox active organic monomers are conductive. Studies have shown conductivity in polymers containing, for instance, phenazine and phenazine derivatives without the need for the addition of a conductive material or use of thin films.[8-10] Due to this, there is an interest in finding different phenazine derivatives which are able to store and release a large quantity of electrons and, when coupled with linkers, will yield a conducting polymer suitable for organo-based energy storage.

In this project, the interest was in finding synthesis pathways for quinone and/or phenazine containing two-dimensional monomers and linkers suitable for linear and branched organo-based polymers. The goal was to find synthesis pathways for two-dimensional organic redox active monomers and linkers which stem from cheap starting material, have very good to quantitative yields and required little to no purification before they could be used for the formation of a polymer.

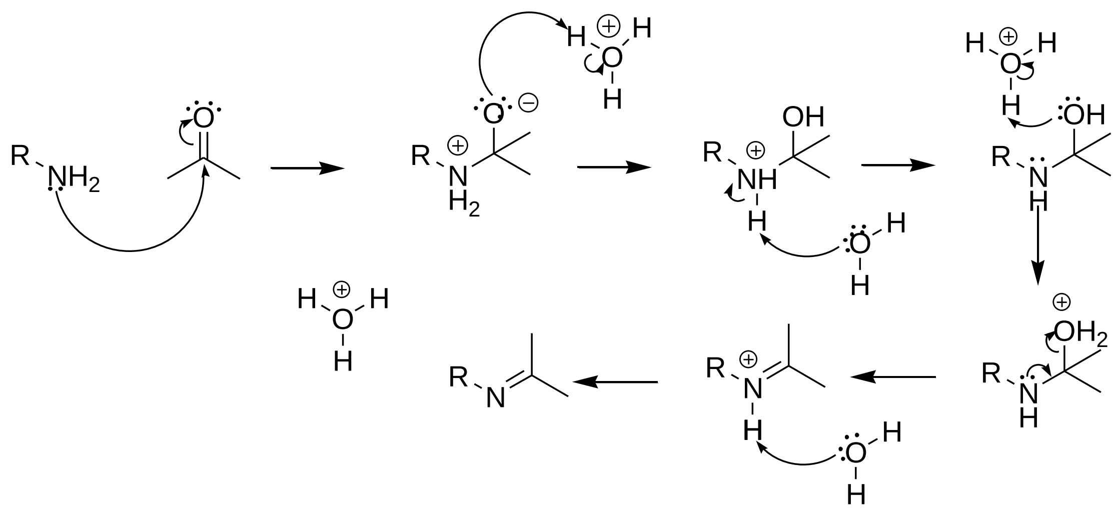
2. Results and discussion

At the end of the project, the synthesis of four molecules (Figure 2) had been attempted to be synthesised with varying results. COFs may be, as previously mentioned, built up of redox active organic monomers coupled together with organic linkers. Polymer formation is often achieved via an acid catalysed reaction between a primary amine and a ketone (Scheme 1), hence the attempted molecules all have either primary amines or ketones at the perimeter of their carbon skeleton. During the project, the focus was split evenly between finding synthesis pathways for both monomers and linkers since a combination of the two are needed to form a polymer. Molecules **1** and **4** are two-dimensional redox active organic monomers that may be used as the energy storage component of the polymer since the reduction and oxidation of their ketone and phenazine functional groups is reversible, thus allowing for both the uptake and release of electrons. The synthesis pathways for both molecules were found in the literature and were able to be followed apart from minor changes during the workup for 1 and to the reaction conditions for **4**. Molecules **2** and **3** are, like molecules **1** and **4**, two-dimensional and contain redox active ketones which may be used for energy storage. However, these two molecules were designed to act as the framework's linkers, yielding either a branched or linear two-dimensional polymer by reaction between their quinones and the monomer's amine groups (Scheme 1). The synthesis pathway used for the formation of **2** was composed of reaction procedures reported in three different publications all done by different authors. The synthesis pathway used for **3** could be found in a multitude of publications with the one used and reported in this project being a summary of three different publications which all report a different scale of the reaction. However, the work up reported in this project is different from the one in the literature.



1 2 3 4

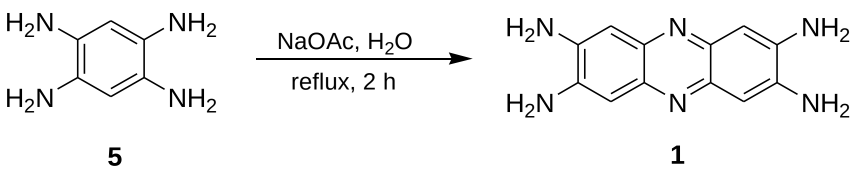
Figure 2. Illustrations of the four desired molecules



Scheme 1. Reaction mechanism of a nucleophilic attack by a primary amine on a ketone

2.1 Synthesis of 2,3,7,8-tetraaminophenazine (1)

Since phenazine derivatives with two amino groups sitting in a trans position have been shown to be electrically conductive in combinations with different linkers by Vitaku et *al.*,[8] there was an interest to see if a derivative in the form of a tetraamine would display similar behaviour. According to an article by Gajiwala and Zand,[11] 2,3,7,8-tetraaminophenazine **1** is able to be synthesised from 1,2,4,5-tetraaminobenzene·4HCl **5** in a solution of sodium acetate and deionised water by what is believed – however *not* proven – to be a nucleophilic attack in which ammonia is eliminated. When refluxing 1,2,4,5-tetraaminobenzene·4HCl with sodium acetate (Scheme 2) in our lab, **1** precipitated as a fine powder that evenly dispersed in solution upon allowing the reaction mixture to cool to room temperature. When trying to vacuum filter the product, the fine crystals became embedded in the filter paper and were difficult to remove which resulted in a poor yield; thus, centrifugation and freeze drying were preferred over vacuum filtration when collecting the product. A problem that arose when centrifugating the sample was that the pellet formed was very fragile and redispersed into solution when the solvent was removed by decanting or pipetting. When increasing the scale of the reaction from 200 mg to 1 g, less product was observed to redisperse into solution when removing the supernatant, something which is thought to be due to the larger amount of product being able to form a less fragile plug after centrifugation. Apart from a larger scale, a less fragile plug was also observed when the solution was cooled to 0 ^{o}C before the solvent was removed by either decanting or pipetting. ^{1}H NMR of the product before removal of the solvent showed no trace of sodium acetate in the spectrum likely due to its solubility in DMSO being poor, something which was observed when attempting to dissolve sodium acetate in DMSO-d_6 to obtain a reference of sodium acetate in the same solvent as the one used to dissolve **1**. It therefore may be necessary to use D_2O and DMSO-d_6 as solvents (one sample each) to determine both the molecular identity of the formed product and if traces of sodium acetate are present.

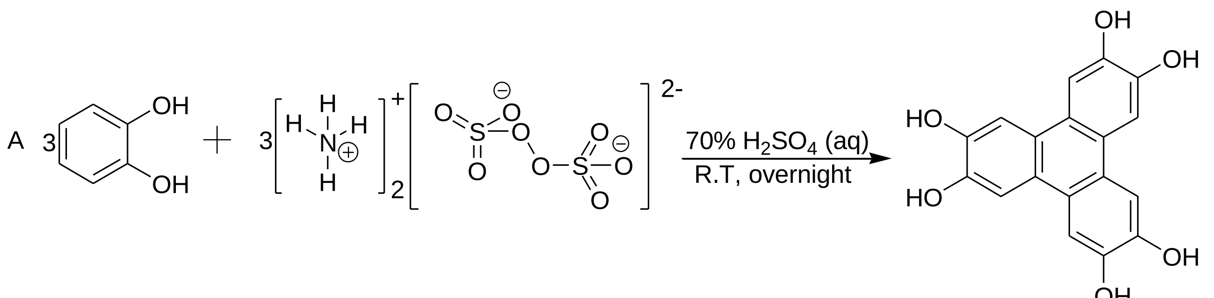


Scheme 2. Synthesis pathway for the formation of **1**

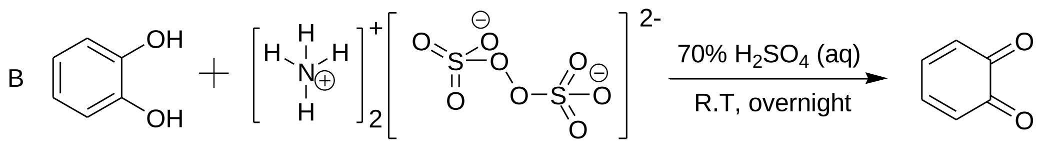
2.2 Synthesis of 2,3,6,7,10,11-hexaketotriphenylene (2)

2,3,6,7,10,11-hexaketotriphenylene **2** is a molecule which have previously been used to synthesise graphitic frameworks for use as metal-free catalysts in which it acted as a linker, yielding a branched two-dimensional framework.[12] Since it has been shown to be useful in frameworks designed for metal-free catalysis, the question arose whether it can be used for frameworks designed for non-metal-based energy storage as well. Since the addition of functional groups to phenylene is not completely stereoselective, synthesis during this project was preferred to be done with starting material which contain functional groups in the correct positions from which the phenylene derivative may be formed.

The synthesis of **2** was attempted in three steps starting from 1,2-dimethoxybenzene **10**. At first, an attempt to synthesise the molecule in two steps was made starting from 1,2-dihydroxybenzene **6** and using ammonium persulphate **7** as the oxidation agent (Scheme 3).[13] However, the two-step synthesis was not successful, possibly due to the ammonium persulfate oxidising the more easily oxidisable hydroxide groups instead of the ring carbons leading to the formation of benzene-1,2-dione instead **9** of 2,3,6,7,10,11-hexahydroxytriphenylene **8**. Since methoxides can be deprotected to form hydroxides, the reported three step synthesis was tested where 2,3,6,7,10,11-hexamethoxytriphenylene **10** is formed from **9** whereafter the methoxides are deprotected by reaction with boron tribromide to form hydroxide groups which can then be further oxidised to ketones by reaction with 2,3-dichloro-5,6-dicyano-p-benzoquinone (DDQ) to yield **2** (Scheme 4).

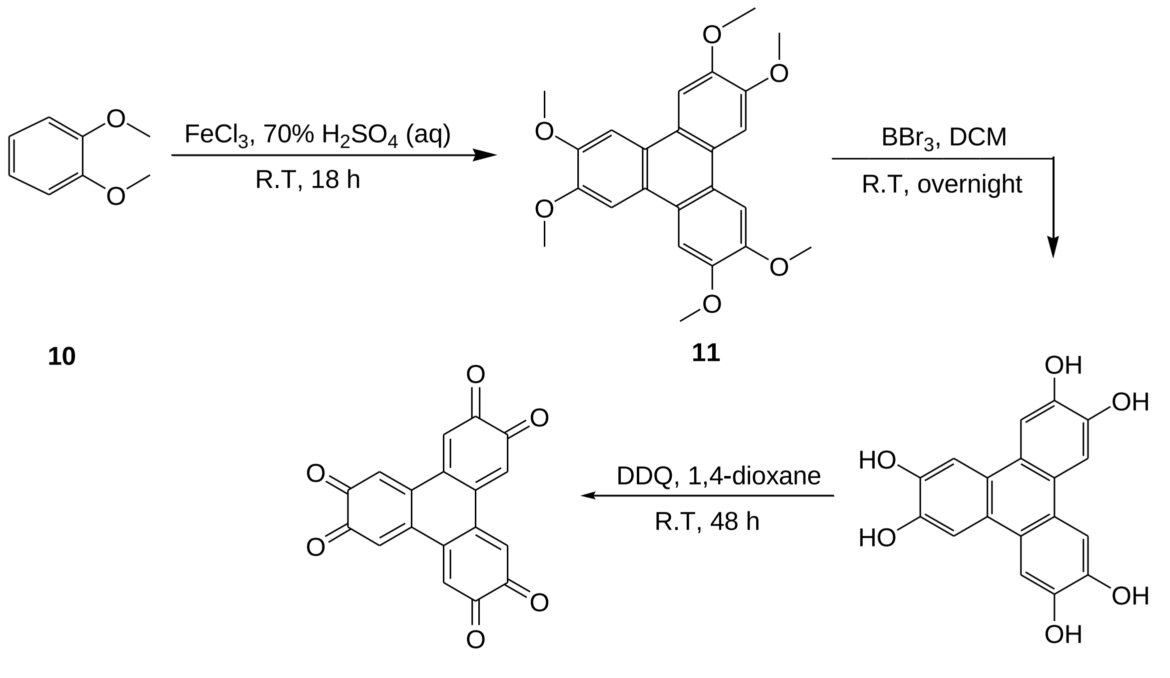


6 **7** **8**



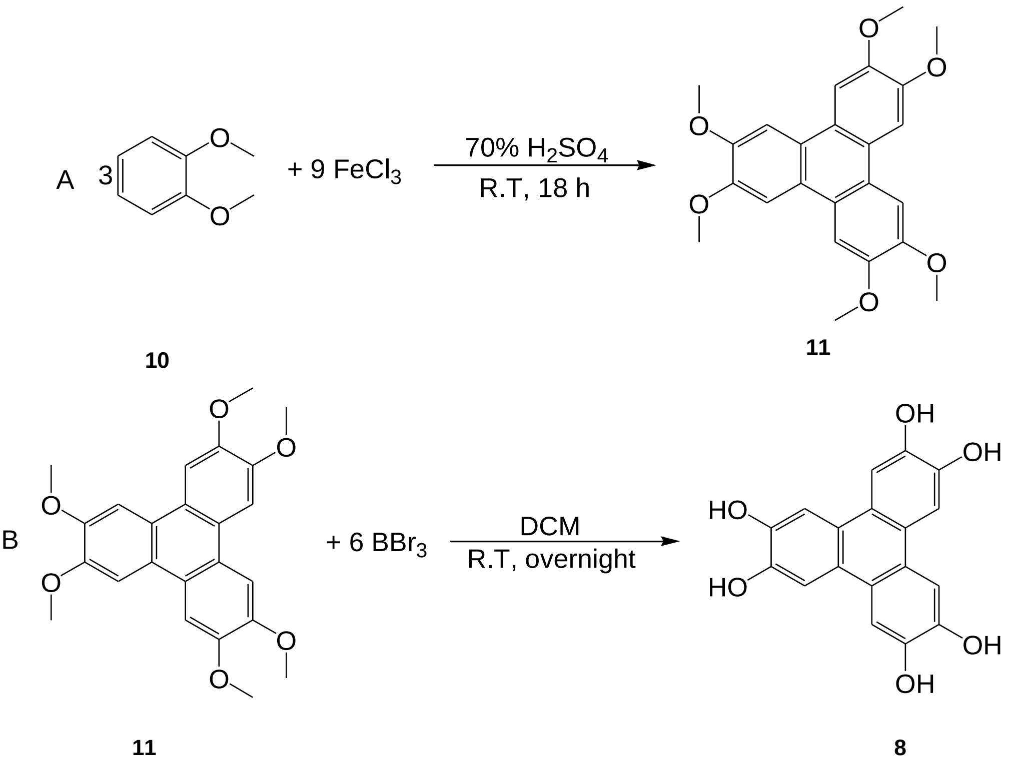
6 **7** **9**

Scheme 3. (A) Attempted reaction, (B) Proposed reaction



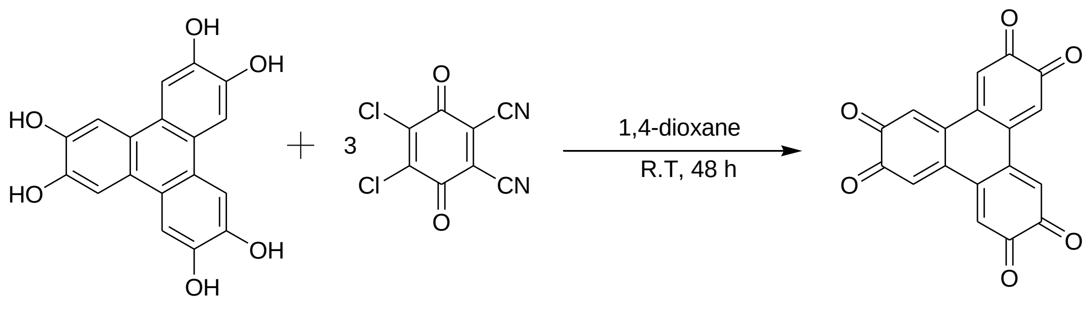
Scheme 4. Attempted synthesis pathway for **2** starting from 1,2-dimethoxybenzene

The first and second step of the synthesis pathway – formation of **11** and **8** according to synthesis pathways reported by Mattmer and co-workers and Ito and co-workers respectively (Scheme 5) – both gave products that either were or could be directly used for synthesis without further purification.[14-15] While the first step gave **11** in a yield of 90%, only 19% of **11** was converted to **8** in the second step. When poured onto water, **8** precipitated as a dark purple powder and was collected by vacuum filtration and the filter paper dried in the oven (100 ^{o}C) to remove excess water. When taken out of the oven, the collected powder had turned black and was difficult to collect due to the powder becoming stuck in the filter paper. The product was attempted to be extracted from the filter paper by sonication in acetone which was then evaporated under reduced pressure, however, the filter paper remained a dark colour indicating that product remained embedded. ^{1}H NMR spectroscopy of the dried product showed peaks corresponding to the desired product, indicating its formation, but also peaks present in the region between 0-2 ppm. These peaks are thought to be originating from the extraction of the filter paper which is why it is stated in the reported experimental procedure that the product could be used directly for further synthesis after collection. When repeating the attempted synthesis, instead of collection by vacuum filtration, the product was extracted with ethyl acetate after being poured onto ice and obtained by evaporation of the organic phase under reduced pressure. Depending on the particle size of the crystals formed from the product and the scale of the reaction, either collection method is possible.



Scheme 5. (A) Synthesis of **11**, (B) Synthesis of **8**

The third step of the synthesis pathway – formation of **2** by oxidation of **8** with DDQ (Scheme 6) – turned out to be a less straightforward reaction than initially thought. Several attempts to synthesise **2** by another student yielded inconclusive results. It is reported in the literature that only ^{1}H NMR data, and not ^{13}C NMR data, can be obtained due to the short lifetime of **2**.[16] While following the reported procedure, both ^{1}H and ^{13}C NMR spectra was obtained for the formed powder. When analysing the ^{1}H NMR data, a peak can be found at 6.68 ppm which agrees with the spectrum reported in the literature. However, the signals in the ^{13}C NMR spectrum do not correlate to the ppm values associated with the chemical environments present on the molecule. The peak found at 170.2 ppm in the ^{13}C NMR spectrum indicate the presence of either a carboxylic acid or ester group which is not consistent with the quinones present on **2**. Peaks found at 66.4 and 59.8 ppm indicate that the carbon skeleton is of an alkane nature which is contradictive of the double bonds found on **2**. Thus, the formation of **2** could not be confirmed.



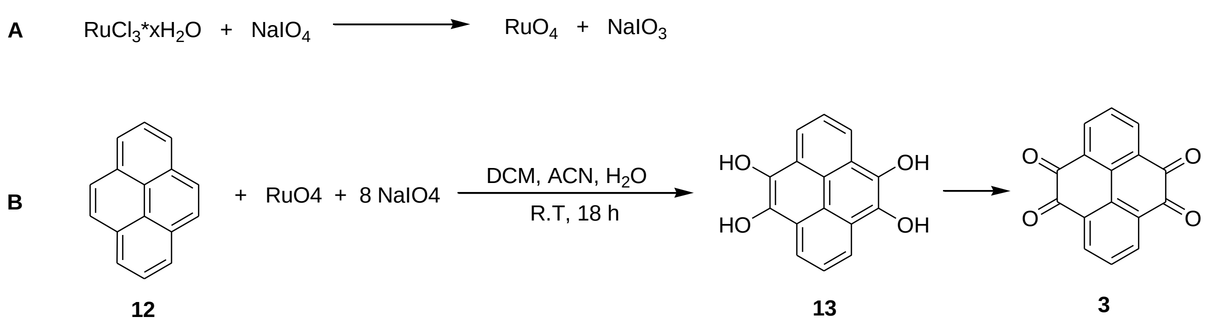
8 **2**

Scheme 6. Attempted synthesis pathway for **2**

2.3 Synthesis of pyrene-4,5,9,10-tetraone (3)

In a study published by Peng et *al.*, pyrene-4,5,9,10-tetraone **3** was used to synthesise a high-performance organic cathode material in rechargeable aluminium ion batteries by coupling with tetraaminobenzoquinone.[17] Cyclic voltammetry measurements done in the study found reversible redox processes in the polymer containing **3** when it was coupled between an aluminium anode and molybdenum cathode, indicating that the polymer is electrically conductive. Due to this finding and other publications on the same subject, there is an interest to see if electrical conductivity can be achieved in polymers present in metal-free batteries containing **3**.

When synthesising **3** by oxidation of pyrene with RuO_4 (which is formed *in-situ* from $RuCl_3 \cdot xH_2O$ and $NaIO_4$) (Scheme 7), many difficulties were encountered, starting with the work-up. According to the literature, the reaction mixture is to be poured onto water, the organic phase collected and the aqueous phase extracted with dichloromethane (DCM) whereafter the organic fractions are combined and evaporated, yielding the crude product.[17-19] However, when the reaction mixture was poured onto water, instead of two phases, an emulsion – likely due to the addition of acetonitrile (ACN) at the beginning of the reaction – was formed which made it impossible to separate the organic phase from the aqueous phase and thus difficult to collect the crude product. To hinder the emulsion from forming, the reaction mixture was heated under reduced pressure to remove all three solvents and the solids were then sonicated in DCM since the inorganic salts used and formed during the reaction are not soluble in the organic solvent. However, further purification was still needed since not only the product but also unreacted starting material as well as organic-based side products such as the reported pyrene-4,5-dione and perhaps metal-organic complexes between **2** and Ru are soluble.



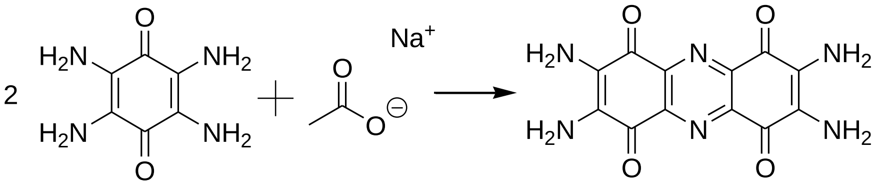
Scheme 7. (A) Formation of *in-situ* RuO_4 from $RuCl_3*xH_2O$ and $NaIO_4$ (B) Proposed reaction pathway for the formation of **3**

The yield of **3** reported in this project – 47% – was the highest yield achieved during the conducted attempts to make the desired molecule. When attempting to scale the reaction to make 1 g of product, the yield instantly decreased to 16%. Since the highest yield achieved was from a scale of 300 mg, 900 mg of the molecule was attempted to be made by synthesising the molecule in three 300 mg batches which were then pooled before being purified by column chromatography. The thought behind the multiple batch synthesis was to see whether the decrease in yield came from the column chromatography, the increased scale of the reaction or because of faulty result from the first attempt since it has been reported in the literature that an increased scale of the reaction brings with a more complicated purification which is thought to lead to a lower yield.[18] The attempt where multiple small scale reactions were pooled together before purification resulted in the yield of **3** dropping further to 13%. Since the two repeats of the reaction both gave low yields in the same range, it is suspected that the high yield achieved during the first attempt most likely originates from an error made during the synthesis or purification. A likely cause would be the presence of silica in the sample when weighed, leftover from the column chromatography used to purify the sample. Since the solvent used for the ^{1}H NMR of **3** was DMSO-d_6, the protons present on silica's alcohol groups would likely exchange with the deuterium present on DMSO-d_6 and thus not be able to be seen in the obtained spectrum.

In the literature, the formation of pyrene-4,5-dione reported at both room temperature and under reflux, and once with acetonitrile being exchanged for tetrahydrofuran to lower the reaction time.[17-19] Since the only difference in reaction conditions and set up between the synthesis of the dione and tetraone of pyrene is the equivalence of sodium periodate used to reoxidise ruthenium trichloride, four batches made up of different combinations of room temp vs. reflux and acetonitrile vs. tetrahydrofuran (Table A1) were set up and tested to see which reaction conditions gave the highest yield. Based on crude ^{1}H NMR of each individual batch, it was determined that the reaction that had been done at room temp and with acetonitrile gave the highest amount of **13** since the crude ^{1}H NMR showed the least amounts of traces of unreacted pyrene and pyrene-4,5-dione.

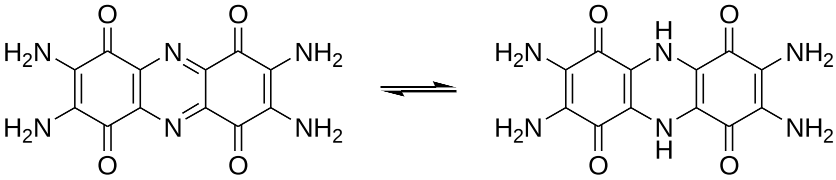
2.4 Synthesis of 2,3,7,8-tetraaminophenazine-1,4,6,9-tetraone (4)

According to a study published by Li et *al.*,[20] 2,3,7,8-tetraaminophenazine-1,4,6,9-tetraone **4** is able to be synthesised in the same manner as **1** by exchanging 1,2,4,5-tetraaminobenzene·4HCl **5** for 1,2,4,5-tetraaminobenzoquinone·4HCl **14** (Scheme 8). In the publication by Li et *al.*, they claim that solution NMR spectroscopy of **4** is able to be done in DMSO-d_6 at 25 ^{o}C and a ^{1}H NMR spectrum in which the product is shown to resonate at 6 ppm is provided. However, according to Dincă et *al.*,[21] the reduced analogue of the molecule (Scheme 9) is insoluble and requires solid-state NMR to be measured. When dissolving the black powder obtained at the end of the synthesis in hot DMSO-d_6, at first, only peaks correlating to the starting material can be seen in the ^{1}H and ^{13}C NMR spectra, indicating that no product had formed. However, after further inspection of the ^{13}C NMR spectrum, some peaks correlating to the desired product can be seen just above the noise level. Since the obtained spectrum contains peaks correlating to the starting material, and since the solubility of the starting material compared to the product in DMSO-d_6 is much greater which causes the peaks correlating to the starting material to overpower the peaks correlating to the product, the obtained spectrum were deemed not to hold enough proof to confirm that the desired product had formed. However, the signals believed to be originating from the desired product does open up interest to further try and characterise the formed powder by solid-state measurements.



14 **4**

Scheme 8. Attempted synthesis pathway for the formation of **4**



4a **4b**

Scheme 9. Oxidised **4a** vs. reduced **4b** form of **4**

3. Methods and materials

Below, information regarding the reagents and solvents used during the project is presented as well as information about the machines used to obtain the presented ^{1}H and ^{13}C NMR data. The method used for each synthesis, including amounts and equivalences of reactants and reagents, is described and visual observations presented. All provided schemes and Figure 2 were drawn in ChemDraw Pro 8.0.

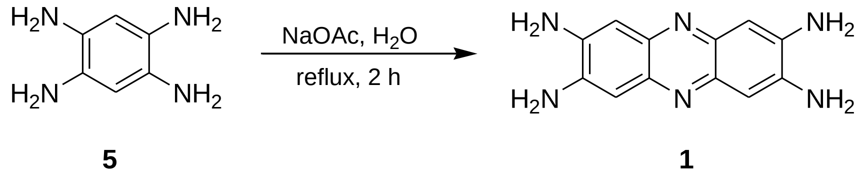
3.1 Chemicals

The reagents and solvents used during this study were bought from commercial sources and used without further purification.

3.2 Instrumentation

Solution ^{1}H NMR spectroscopy was performed on either a Varian NMR 400 MHz spectrometer DD2 or a Bruker NMR 500 MHz spectrometer Avance Neo. Solution ^{13}C NMR spectroscopy was performed on a Bruker NMR 500 MHz spectrometer Avance Neo.

3.3 Synthesis of 2,3,7,8-tetraaminophenazine (1)



Scheme 1. Attempted synthesis pathway for **1**

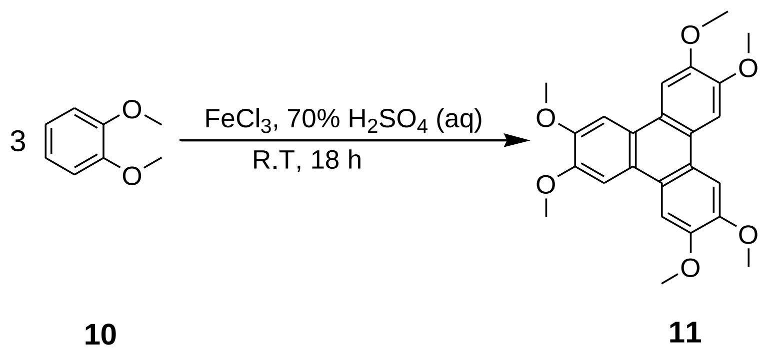
1 was synthesised in one step starting from 1,2,4,5-tetraaminobenzene·4HCl similarly to a previously reported procedure.[11] 1,2,4,5-tetraaminobenzene (0.217g, 0.765 mmol, 2 eqv.) and sodium acetate (0.171 g, 2.08 mmol, 6 eqv.) were dissolved in deionised water (3 mL, 0.25 M **5**, 0.7 M NaOAc) and refluxed for two hours under a stream of air. The solution instantly turned dark purple when water was added to the starting material. After the reflux was stopped, the solution was allowed to cool to room temperature before it was centrifuged (10 000 rpm, 5 min) due to the product forming very small crystals which are dispersed throughout the solvent and not possible collect by vacuum filtration. The solution was then cooled to 0 ^{o}C and as much as possible of the supernatant removed by pipetting before the sample was freeze dried overnight to remove any remaining water which gave 0.075 g of the desired product (yield 82%). No further purification was done.

^{1}H NMR (DMSO-d$_6$, 400 MHz, 25 ^{o}C): 6.92 (s, 4 H, aromatic protons), 6.11 (s, 8 H, amine protons)

3.4 Synthesis of 2,3,6,7,10,11-hexaketotriphenylene (2)

2 was attempted to be synthesised in three steps starting from 1,2-dimethoxybenzene **10**.

3.4.1 Synthesis of 2,3,6,7,10,11-hexamethoxytriphenylene from 1,2-dimethoxybenzene

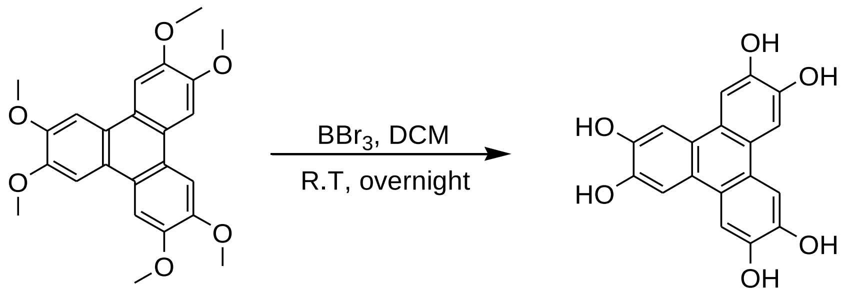


Scheme 2. Attempted synthesis pathway for **2**, first step

11 was synthesised according to a synthesis pathway previously reported in the literature.[14] Anhydrous $FeCl_3$ (1.06 g, 6.51 mmol, 6 eqv.) was dissolved at 0^{o}C in sulphuric acid (70%, 13 M, 4 mL, 1.6 M $FeCl_3$, 0.68 M 1,2-dimethoxybenzene). Thereafter 1,2-dimethoxybenzene **10** (0.350 mL, 2.75 mmol, 3 eqv.) was added dropwise. The solution was allowed to come to room temperature and was left to stir overnight. At first, the solution exhibited a green colour with a black oil on top but was observed to shift to a dark blue or almost black colour after left to stir overnight. The solution was then poured over ice (20 g), filtered using vacuum filtration and washed with ice-cold water, ice-cold ethanol and room temp toluene before the precipitate was dried under vacuum. Upon drying, the precipitate changed colour from dark blue to lavender. The reaction gave 0.394 g (yield 91%) of the desired product.

^{1}H NMR (DMSO-d$_6$, 400 MHz, 25 ^{o}C): δ 7.98 (s, 6 H, ring protons), 4.03 (s, 18 H, methoxide protons)

3.4.2 Synthesis of 2,3,6,7,10,11-hexahydroxytriphenylene from 2,3,6,7,10,11-hexamethoxytriphenylene



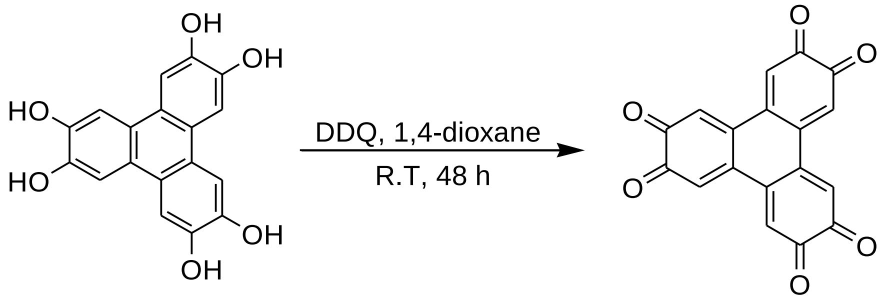
11 **8**

Scheme 3. Attempted synthesis pathway for **2**, second step

The synthesis of **8** was done according to a previously reported reaction with some minor changes.[15] **11** (0.251 g, 0.618 mmol, 1 eqv.) was dissolved in DCM (4 mL, 0.15 M **11**, 1.2 M BBr_3) and cooled to 0 ^{o}C in an ice bath. BBr_3 (0.45 mL, 4.74 mmol, 8 eqv.) was then slowly added dropwise to the solution during a 20 min period after which the solution was allowed to warm to room temperature and stir overnight. Upon addition of boron tribromide, the solution instantly turned from purple to black but later changed to a brown-ish red colour after the addition was complete. The solution was then poured over ice and vigorously stirred until the ice had melted which gave a dark purple precipitate which was filtered off using vacuum filtration and the filter paper dried in the oven (100 ^{o}C). Instead of vacuum filtration, the precipitate may be extracted with ethyl acetate, yielding a purple solution which can be evaporated while heated under reduced pressure. The reaction gave 38.8 mg (yield 19%) of the desired product.

^{1}H NMR (DMSO-d$_6$, 400 MHz, 25 ^{o}C): δ 9.26 (s, 6 H, hydroxy protons) ,7.60 (s, 6 H, aromatic protons)

3.4.3 Synthesis of 2,3,6,7,10,11-hexaketotriphenylene from 2,3,6,7,10,11-hexahydroxytriphenylene



8 **2**

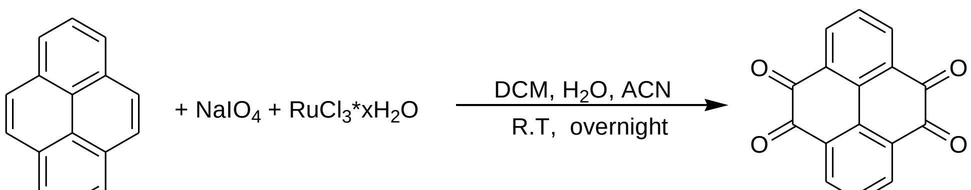
Scheme 4. Attempted synthesis pathway for **2**, third step

2 was attempted to be synthesised according to a procedure by Talapaneni et *al*.[12] **8** (0.216 g, 0.667 mmol, 1 eqv.) was dissolved in 1,4-dioxane (5 mL, 0.38 m **8**, 0.13 M DDQ) whereafter DDQ (0.435 g, 1.92 mmol, 3 eqv.) was added while stirring and the reaction mixture was left to stir over the weekend at room temp. The reaction mixture was then extracted with ethyl acetate and deionised water which gave a black precipitate that was suspended in the organic phase. The suspended precipitate was filtered off using vacuum filtration and the collected solids were washed with ethyl acetate to remove any unreacted DDQ before it was dried under vacuum which gave 0.156 g in the form of a black powder. No further purification was done. Both ^{1}H and ^{13}C NMR spectra of the powder was able to be obtained, however, no ^{13}C NMR spectra is available in the literature, thus, only the ^{1}H NMR was able to be compared against a reference.

^{1}H NMR (DMSO-d$_6$, 500 MHz): δ 6.68 (s, 4 H)

^{13}C NMR (DMSO-d$_6$, 500 MHz): δ 170.2, 66.4, 59.8

3.5 Synthesis of pyrene-4,5,9,10-tetraone (3)



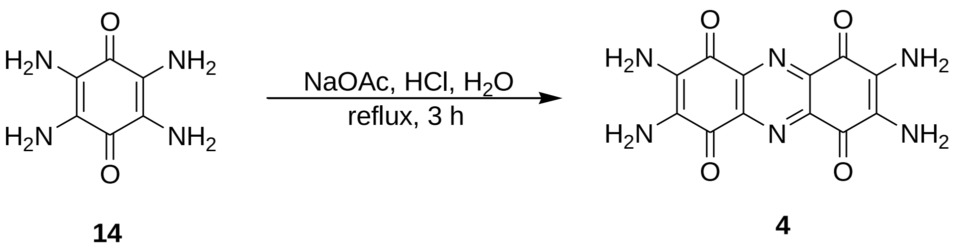
12 **3**

Scheme 5. Attempted synthesis pathway for **3**

The synthesis of **3** was done similarly to procedures published by Walsh et. *al.* and Hu et. *al.* with changes during the work-up.[17-19] Pyrene **12** (0.243 g, 1.20 mmol, 1 eqv.) and $RuCl_3{\cdot}xH_2O$ (0.03 g, 0.115 mmol, $\frac{1}{10}$ eqv.) were dissolved in DCM (4 mL), ACN (4 mL) and deionised water (5 mL) whereafter $NaIO_4$ (1.96 g, 9.61 mmol, 8 eqv.) was added in batches, allowing the $NaIO_4$ to fully dissolve between additions. The dark green solution was left stirring overnight at room temperature. At first, the solution had a black colour which later turned dark green upon addition of $NaIO_4$. Upon complete addition of $NaIO_4$, a dark grey precipitate was observed which resulted in the solution turning into a slurry. After completion of the reaction all solvents were removed under reduced pressure. The solids were then sonicated in DCM (20 mL) for 10 min, filtrated using vacuum filtration and washed with DCM until the filtrate ran clear. Evaporated filtrate under reduced pressure while heating to yield crude product. Purification by column chromatography (width 2 cm × height 15 cm, CH_2Cl_2) gave 148 mg of the desired product (yield 47%) as an orange powder.

^{1}H NMR (DMSO-d$_6$, 400 MHz, 25 °C): δ 8.31 (d, J = 7.7 Hz, 4 H), 7.74 (t, J = 7.7 Hz, 2 H)

3.6 Synthesis of 2,3,7,8-tetraaminophenazine-1,4,6,9-tetraone (4)



Scheme 6. Attempted synthesis pathway for **4**

An attempt to synthesise **4** was made according to a procedure found in Li et *al*.[20] 2,3,5,6-tetraaminobenzoquinone (0.224 g, 1.33 mmol, 2 eqv.) was dissolved in deionised water (10 mL, 0.13 M **4**, 0.4 M NaOAc) which contained 5.5 mmol of concentrated HCl (four equivalents of HCl for every molecule of **4**). The solution was stirred for 15 min whereafter sodium acetate (0.328 g, 4.00 mmol, 3 eqv.) was added and the solution was refluxed under a stream of air for 2.5 hours. The solution was allowed to warm to room temp, centrifuged (10 000 rpm, 10 min) and as much of the supernatant as possible removed by pipetting before the sample was freeze dried to remove any remaining water which gave 0.197 g in the form of a black powder. No ^{1}H or ^{13}C NMR spectra could be obtained due to poor solubility of the product and direct injection MS showed no relevant *m/z* values. Thus, the identity of the formed product was not able to obtained.

4. Conclusion

Out of the four desired molecules, only **1** was able to be synthesised in high yield with little to no purification needed before being used for further synthesis. The collection of the formed product by centrifugation is facilitated by a larger scale synthesis since the plug formed is observed to become less porous when the scale is increased, leading to less product loss during removal of the supernatant by manual pipetting. **3** was able to be synthesised. However, the obtained yield remained continuously low over multiple attempts and purification via column chromatography is needed since multiple side products are formed such as diones and perhaps metal-organic complexes between **3** and Ru. This, paired with a low solubility in dichloromethane – leading to large amounts having to be used during synthesis and purification

– deems the synthesis not adequate to be used for production of **3** aimed for further use within the research group. Instead, it is recommended that the molecule is bought commercially if it is to be used as starting material. It is unclear if **2** and **4** were able to be synthesised or not. The ^{1}H NMR spectrum obtained of **2** does agree with the one found in the literature, however, peaks in the obtained ^{13}C NMR spectrum does not correspond to the chemical environments present on **2**. Due to the very low solubility of **4**, no conclusive solution NMR data could be obtained and direct infusion MS yielded no relevant *m/z* values. However, since the molecule shows potential to be used for organo-based energy storage, there is an interest to further try to characterise the formed powder by solid-state measurements.

5. References

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6. Appendix

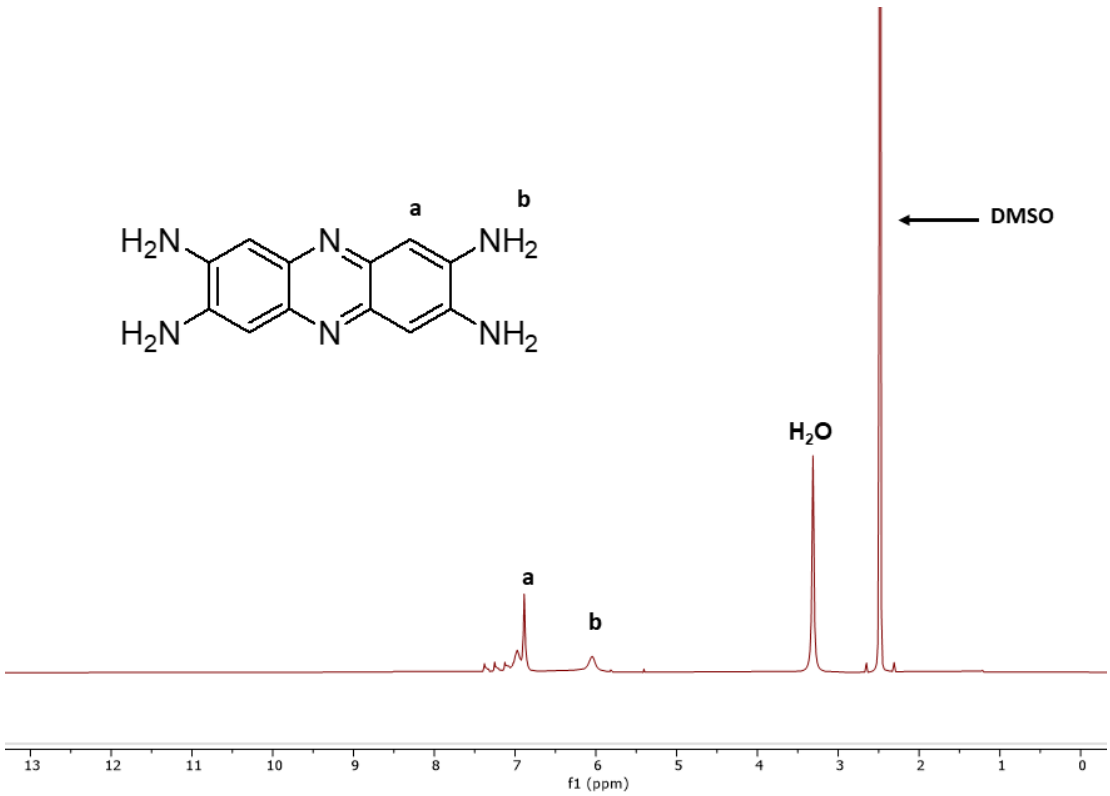

Figure A1. [1]H NMR of 2,3,7,8-tetraaminophenazine (400 MHz, DMSO-d6, 25 °C)

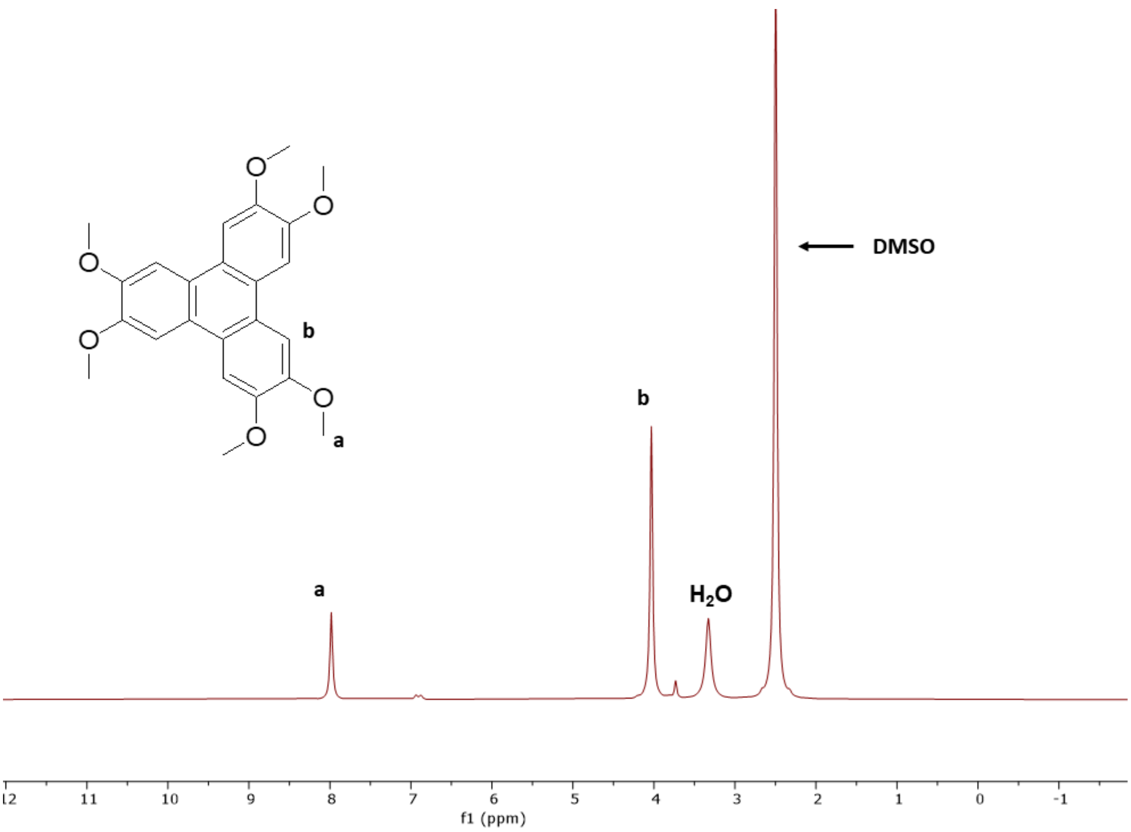

Figure A2. [1]H NMR of 2,3,6,8,10,11-hexamethoxytriphenylene (400 MHz, DMSO-d6, 25 °C)

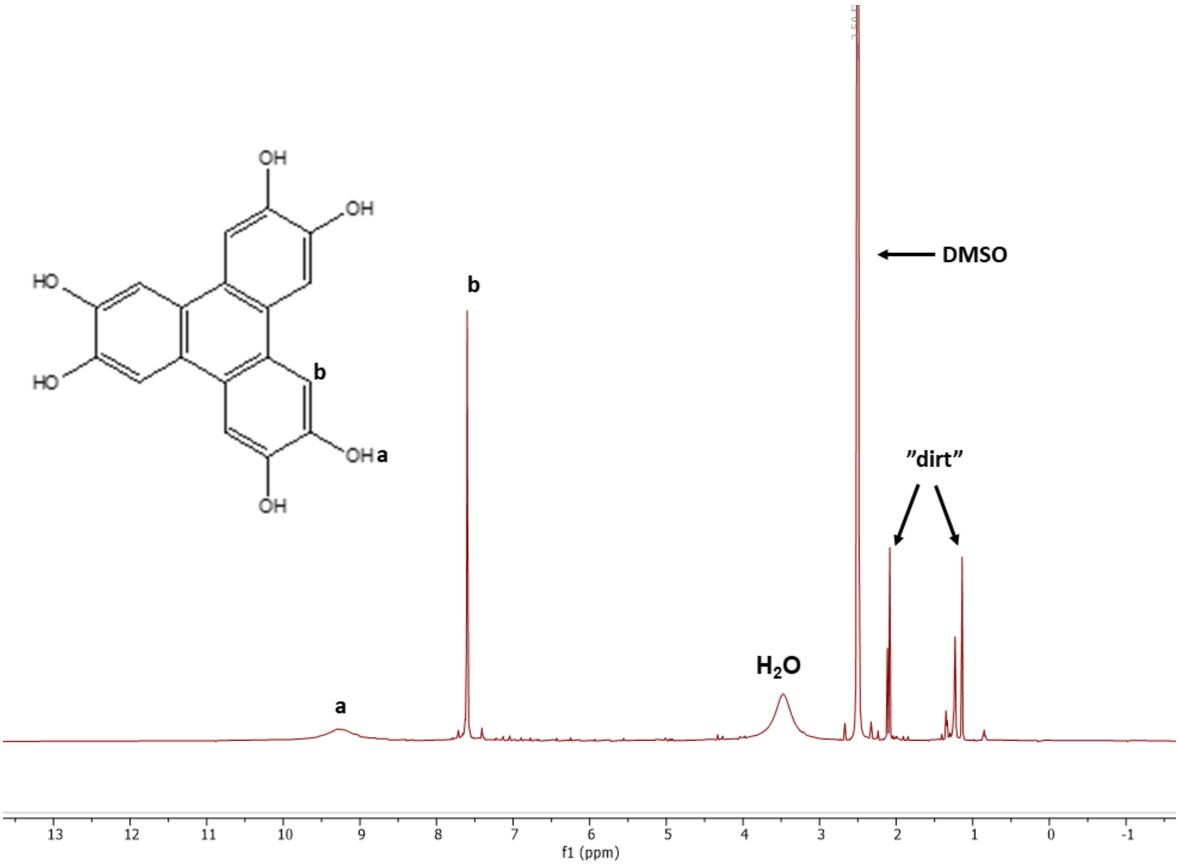

Figure A3. ^{1}H NMR of 2,3,6,8,10,11-hexahydroxytriphenylene (400 MHz, DMSO-d_6, 25 °C)

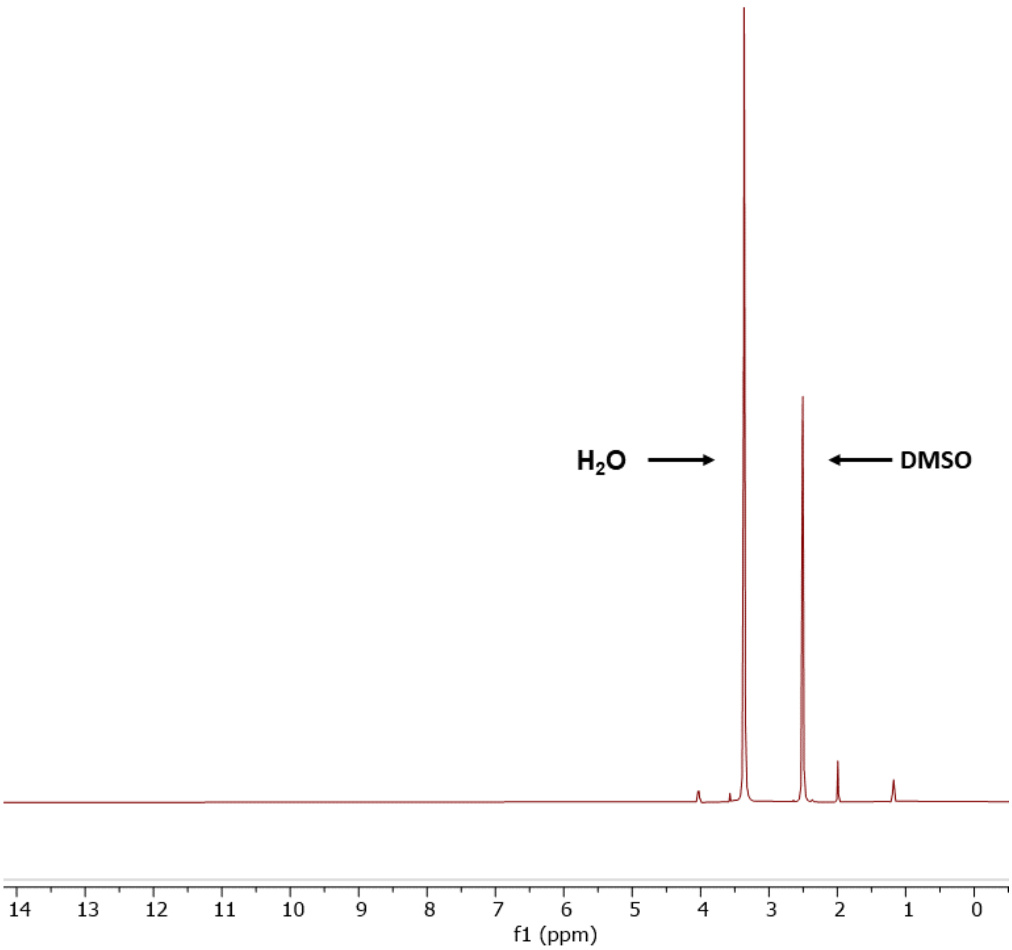

Figure A4. ^1H NMR of obtained powder from attempted synthesis of 2,3,6,8,10,11-hexaketotriphenylene (500 MHz, DMSO-d_6, 25 ^oC)

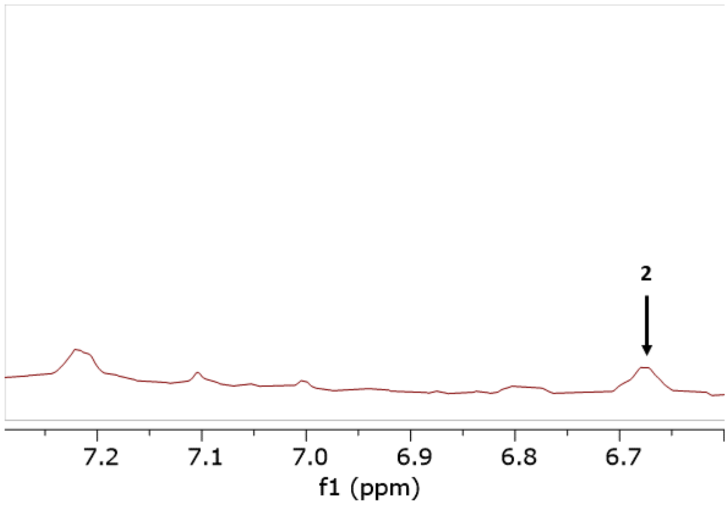

Figure A5. Extraction of ^1H NMR spectra from Figure A4

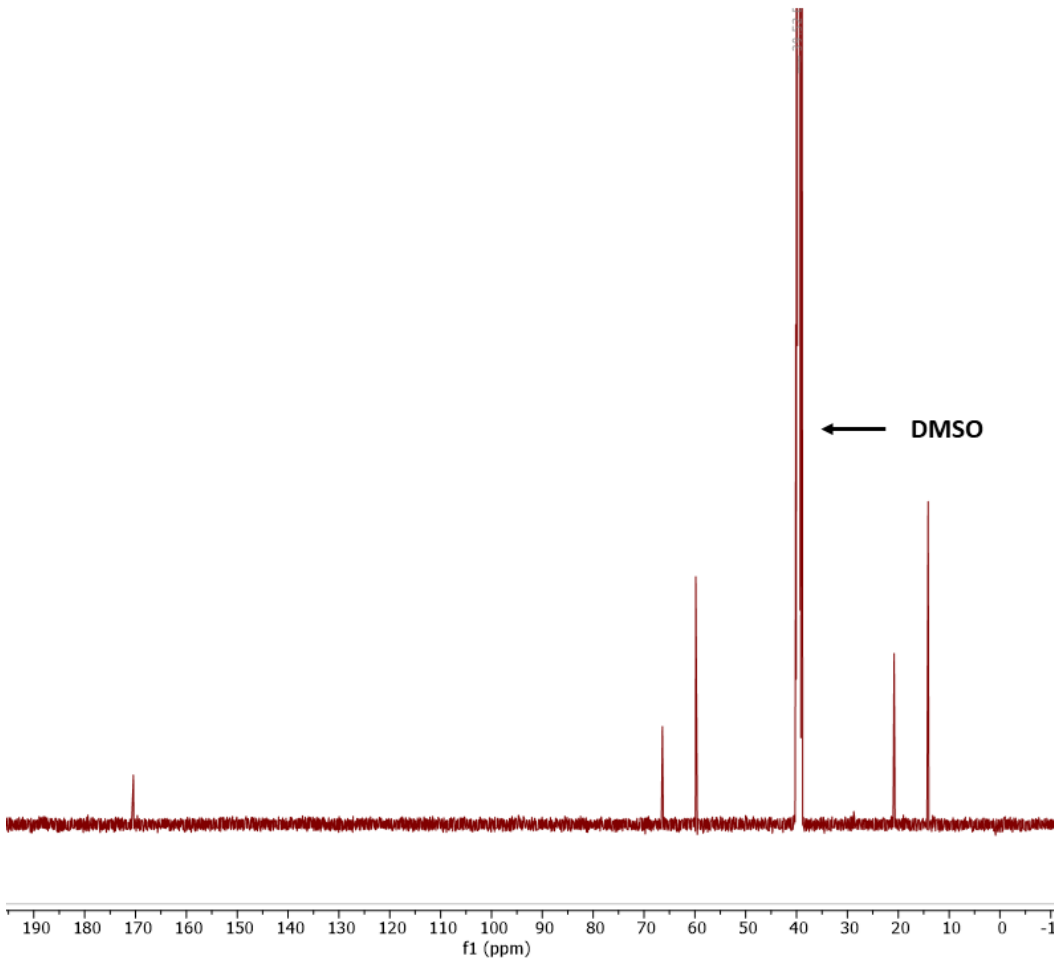

Figure A6. ^{13}C NMR of obtained powder from attempted synthesis of 2,3,6,8,10,11-hexaketotriphenylene (500 MHz, DMSO-d_6, 25 ^oC)

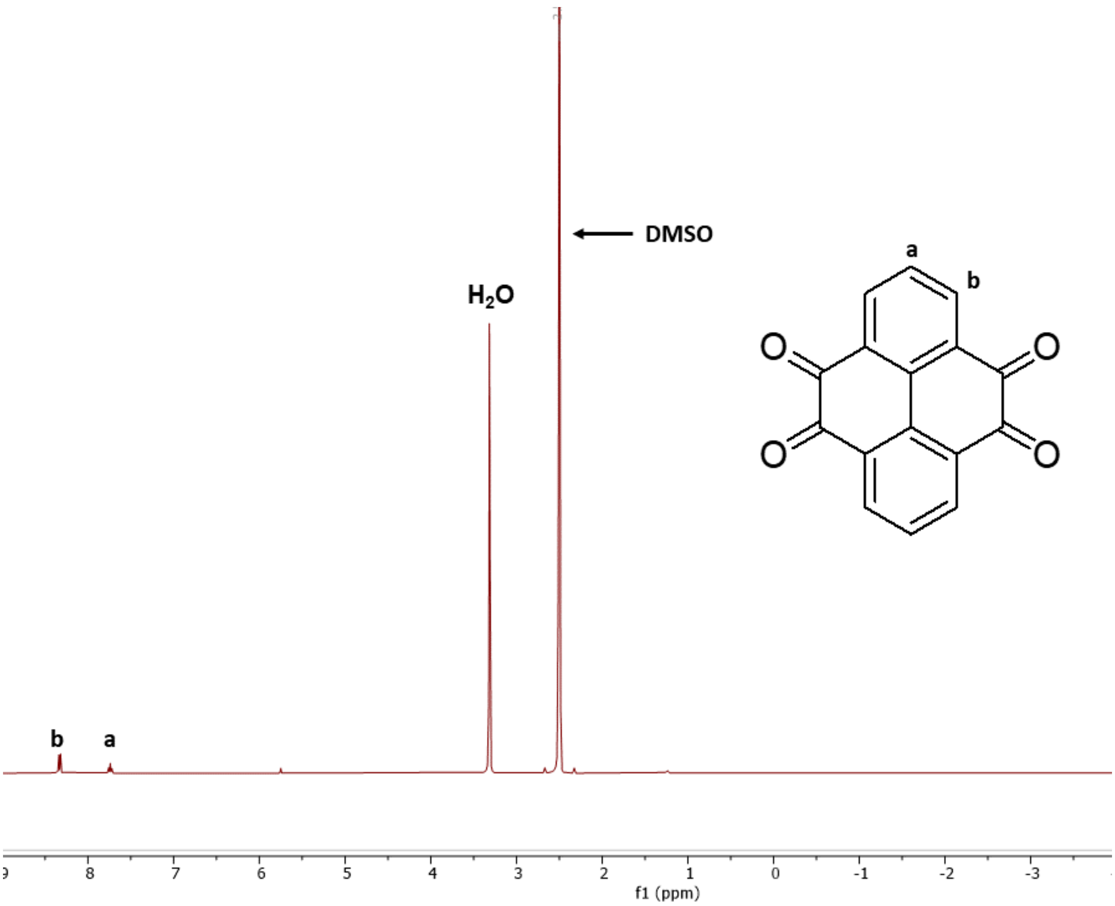

Figure A7. ^1H NMR of pyrene-4,5,9,10-tetraone (400 MHz, DMSO-d_6, 25 ^oC)

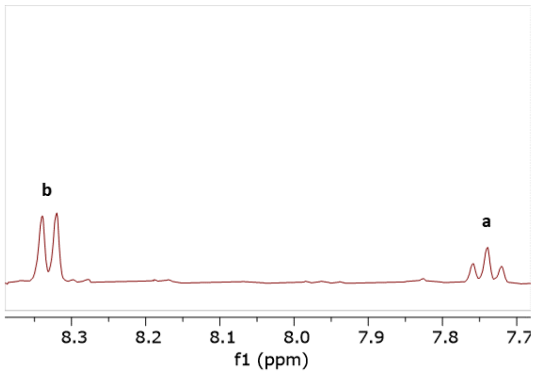

Figure A8. Extraction of ^1H NMR spectra from Fig. A7

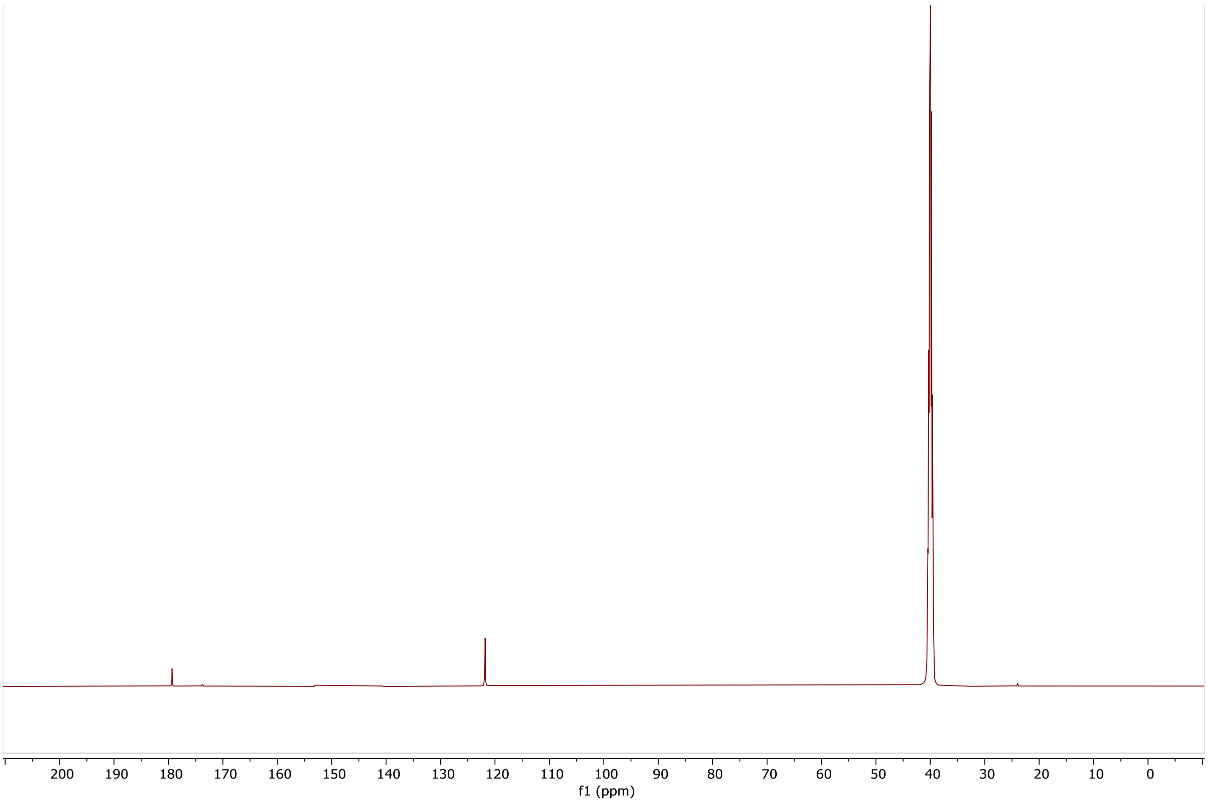

Figure A9. ^{13}C NMR spectra of obtained powder from attempted synthesis of 2,3,7,8-tetraaminophenazine-1,4,6,9-tetraone (500 MHz, DMSO-d_6, 25 °C)

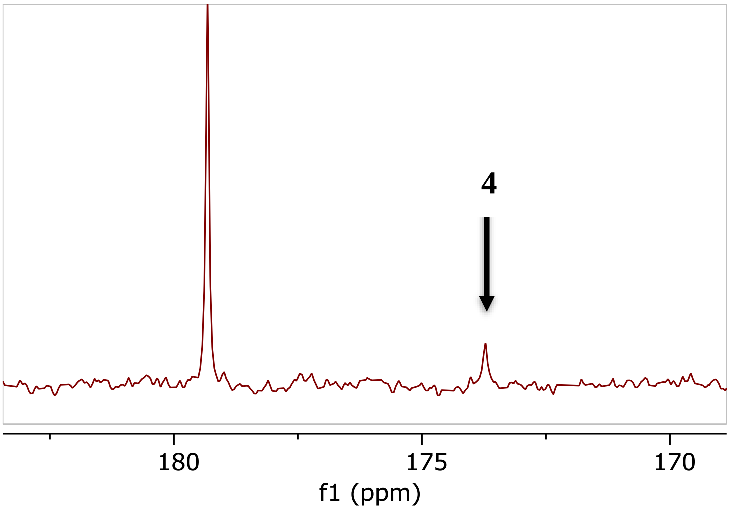

Figure A10. Extraction of ^{13}C NMR spectra from Fig. A9

Table A1. Combinations of room temp vs. reflux and acetonitrile vs. tetrahydrofuran

Batch 1	Reflux + acetonitrile
Batch 2	Room temp + acetonitrile
Batch 3	Reflux + tetrahydrofuran
Batch 4	Room temp + tetrahydrofuran