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Synthesis of Tetraethyl ((2-Amino-1,4-Phenylene)Bis(Methylene)) Bis(Phosphonate): An Intermediate in the Synthesis of Amino-Substituted Conjugated Materials

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SYNTHESIS OF TETRAETHYL ((2-AMINO-1,4-PHENYLENE)BIS(METHYLENE)) BIS(PHOSPHONATE): AN INTERMEDIATE IN THE SYNTHESIS OF AMINO-SUBSTITUTED CONJUGATED MATERIALS

A Thesis

by

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ABSTRACT

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Discussed here are the syntheses of the phosphonate precursors for the Wittig-Horner synthesis of poly-phenylene vinylene (PPV) and distyrylbenzene (DSB) derivatives and their respective distyrylbenzene analogs containing amino moieties. The synthesis of the different compounds was achieved through bromination, Michaelis-Arbuzov reaction, reduction of the nitro group with a commercial cobalt sulfide catalyst and sodium borohydride. Preliminary evidence for the synthesis of amino substituted distyrylbenzene and of nitro/alkoxy substituted poly(p-phenylene vinylene) was obtained. Characterization of the products was performed by ^{1}H-NMR. Preliminary results of the synthesis of a novel amino-substituted distyrylbenzene (DSB) are presented. The luminescence of the new DSB was quenched by addition of acid. The luminescence was restored by addition of a base. This was indirect proof that the amino-substituted DSB was synthesized successfully.

DEDICATION

Para ti, Chaparrita de mi corazón, por amarme como soy.

Para mi bizcocho cachetón (Boris), por existir.

Para el “Pichón mayor”, por sacrificarte por nosotros y enseñarme el valor de trabajo.

Para la “jefa”, por ser capaz de poner al mundo de cabeza con tal de que seamos felices como tú.

Para mis abuelos, por enseñarme que, echándole ganas, todo se puede.

Para mi abuelita, por demostrarme que soy “el Amor de sus amores”.

Para mis suegros, por apoyarme como si fuera su hijo.

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CHAPTER I

INTRODUCTION

Conjugated polymers have delocalized pi-electrons that have been shown to have electrical and photonic properties [1]. There are different types of conjugates polymers. They are classified according to the structure of their backbone and the nature of any heteroatom that is substituted on the main chain.[2] The versatility in the synthesis of these molecules can be observed by the many different substitutions, additions, and other reactions employed in their synthesis. The structure for the conjugated systems reported in the literature varies from linear,[3] kinked,[4] branched,[5] or cruciform.[6]

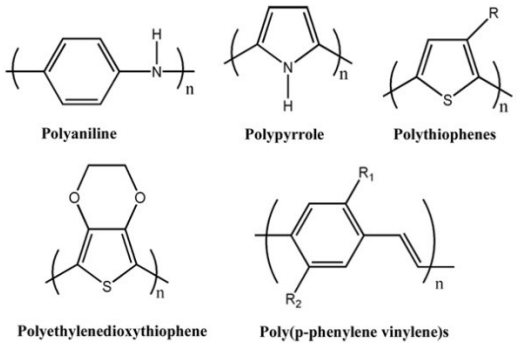


Figure 1.1: Examples of Conjugated Polymers

Conjugated polymers have applications in fields such as biomedical;[7] [8] sensory;[9] chemiluminescence;[10] laser;[11] electroluminescence,[12] in the development of field effect transistors,[13] photovoltaic cells,[14] and light emitting diodes,[1] as indicators of rates in biochemical reactions in living organisms, namely the real-time monitoring of cell apoptosis,[15]

and recently in the development of inkjet systems that are able to print solutions containing conjugated molecules in the development of new organic light emitting diodes (OLEDs).[16] Conjugated compounds can be tuned to specific wavelength emissions by changing the substitution and position of the substituents.[12]

The substitutions made to the benzyne ring are tailored for specific purposes. Some of those substitutions include alkoxy,[17] cyano,[12] on both the alkene[18] or the aromatic ring,[12] phenyl,[19] halide,[20] substituted amines, both charged and uncharged,[21] nitro,[22] and crown groups.[23] The synthesis pathway to create both the poly-p-phenylene vinylene (PPV) and the discrete distyrylbenzene (DSB) molecule with similar substitutions are similar and dependent on whether the reactants used are mono-, di-, or polysubtituted.[24]

The introduction of hydrophilic properties in the conjugated systems is highly desirable because it allows for the use of green solvents (like water) in their processing and applications. Water soluble conjugated polymer (WCPs) are studied for their properties in the fields of diagnosis and cell imaging.[25] These polymers have shown to be sensitive to pH,[26] chemo sensing,[24] electrical charge,[27] and ligands.[28]

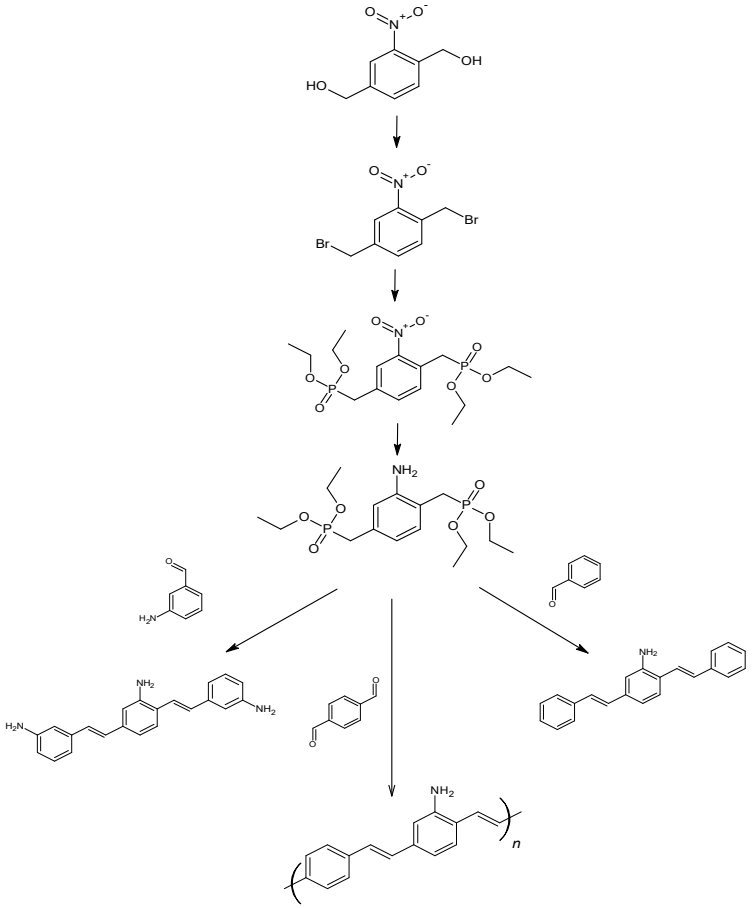
There are various synthetic routes reported in the literature for the synthesis of PPVs or discrete DSBs. Several papers explain in detail the advantages, disadvantages, and challenges that each of the synthetic routes presently used.[29] Of notable mention, however, are the use of phase transfer catalysis systems used by Zhao et al.,[30] the controlled assembly of WCPs by carbon dioxide control,[31] the synthesis and characterization of regioregular PPV by precursors that contain both the aldehyde and the phosphonate moieties in the same aromatic ring by Suzuki et al.,[32] and the one pot synthesis of stilbene via the Wittig and Wittig-Horner-Emmons.[33] The

Wittig-Horner reaction is preferred because it yields a higher content of the *E* isomer and the ability to control the ratio of different moieties in the groups being condensed.

As extensive as the research and development currently are, the synthesis of conjugated systems with an unsubstituted amine (NH_2) directly attached to the aromatic ring has not been reported. The presence of the amino group can make the conjugated material soluble in mild solvents like water, dimethyl sulfoxide, and acetonitrile, among others. It also allows for the binding of the amino groups to proteins which, added to the luminescent properties of the material, makes them excellent candidates for application as dyes in biological systems.

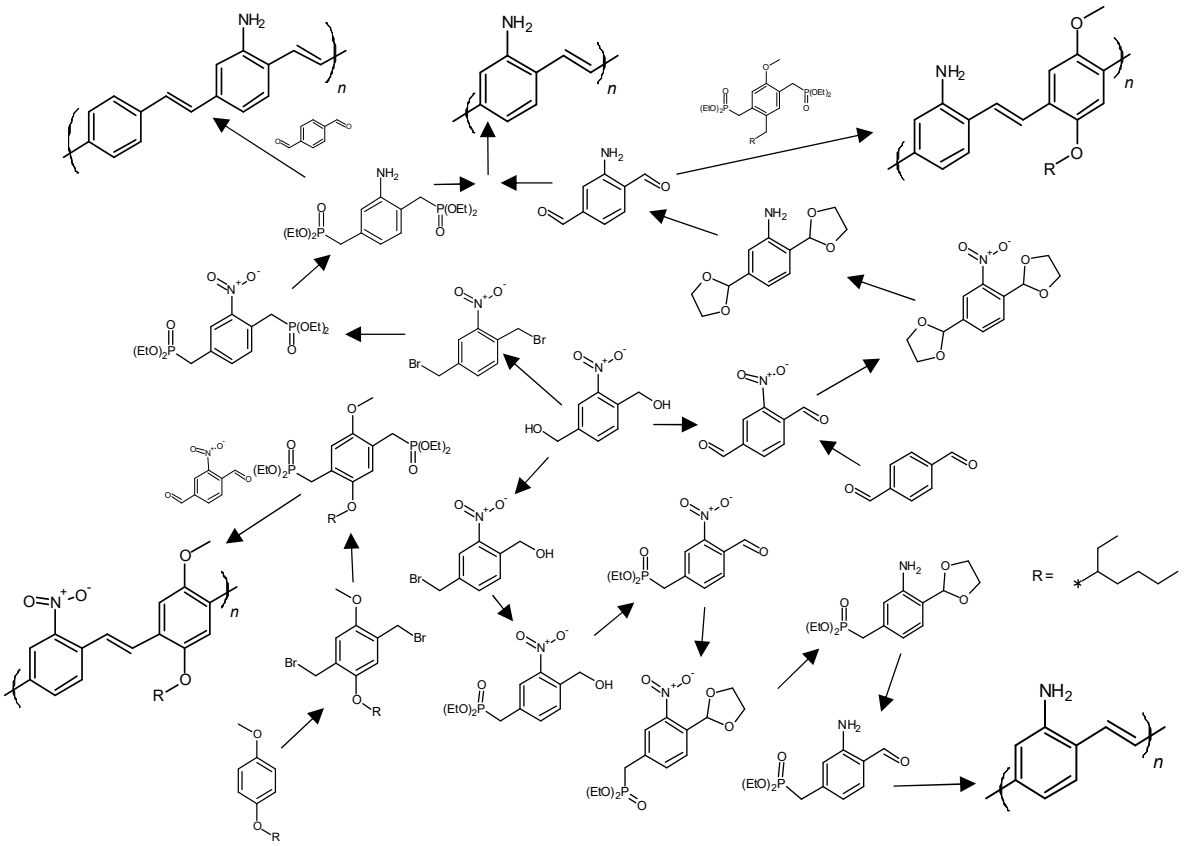
The substitution with nitrogen containing groups in conjugated systems is varied. These include in the addition of cyano groups directly to benzene rings[34] or to the double bond joining them [34], conjugated systems using pyridine,[35] substituted amines,[36] cyclic structures,[36] nitro groups in branched systems,[22] amides,[37] have been developed by different groups.[2] There are no reports in the literature of DSB or PPVs containing the amino group NH_2. However, there are some works reporting amine derivatives. Some of the drawbacks of the reported methods are long reaction times (days)[38] and/or the synthesis requiring eight steps.[39]

In the figure below, we explore the theoretical framework for our proposed synthesis of said compounds.



Scheme 1.1: Theoretical framework for the synthesis of conjugated systems with amino moieties

We propose that the addition of the amino moiety directly on the benzene ring will grant the conjugated compounds solubility in water/organic solvent mixtures. The electron-donating properties of the amino group is expected to increase luminescence. Furthermore, the unencumbered lone pair of electrons in the nitrogen atom can be used in the incorporation or binding to other molecules (by hydrogen or covalent bonding) with relative ease.



Scheme 1.2: Proposed synthesis routes for the development of novel amino-substituted conjugated materials.

CHAPTER II

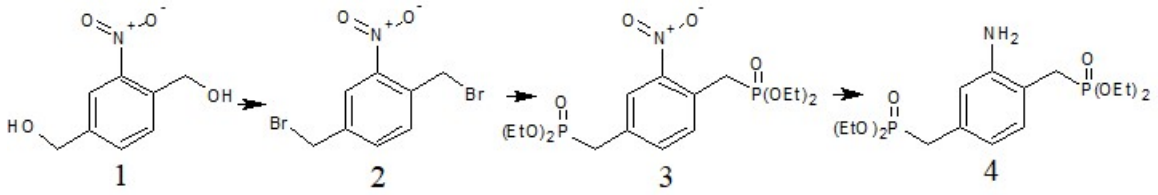
MATERIALS AND METHODS

The chemicals were purchased from TCI Chemicals, Sigma Aldrich, and Fischer Scientific. and were used as received. The progress of the reactions was monitored by thin layer chromatography with different organic solvents as eluents. The products were characterized by ^{1}H-NMR.

Nuclear Magnetic Resonance

The samples were prepared by dissolving 50 mg of each sample in 750 mg of CDCl3 unless specified otherwise. The analysis was performed in a Bruker Ultrashield 600 Plus. The chemical shifts are expressed in ppm.

Chemical Reactions



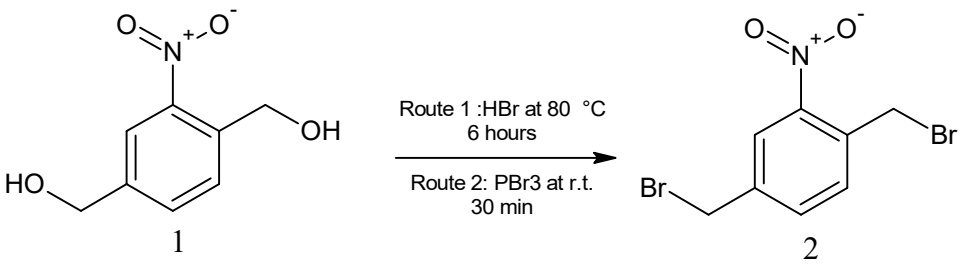
Scheme 2.1: Proposed synthesis route for an amino substituted precursor for the Wittig reaction

1,4-Bis(bromomethyl)-2-nitrobenzene (2)

Route 1: A mixture of 25 mL of hydrobromic acid and 2 grams of 2-nitro-p-xylylene glycol were heated in a round-bottom flask at 80 °C for3 hours. The reaction was followed via thin layer chromatography. After that time, the reaction the TLC plate showed some starting

material left. Another 25 mL of HBr were added. After 2 hours, the TLC plate showed no starting material and only one spot was observable, the reaction was removed from the heat and allowed to cool to room temperature. It was then quenched with cool water. The precipitate formed was filtered and recrystallized from ethanol and 300 mg of activated carbon with water. The product was a pearly white flaky solid.

Route 2: the nitro glycol derivative 1 was dissolved in acetonitrile and 1.1 equivalents of PBr_3 were added dropwise to the solution at room temperature. The precipitate started forming immediately. The reaction was monitored by TLC and was quenched with water. The solid was filtered and washed with a solution of water and acetonitrile. The filtration yielded a white flaky solid.



Scheme 2.2: Synthesis of 1,4-Bis(bromomethyl)-2-nitrobenzene

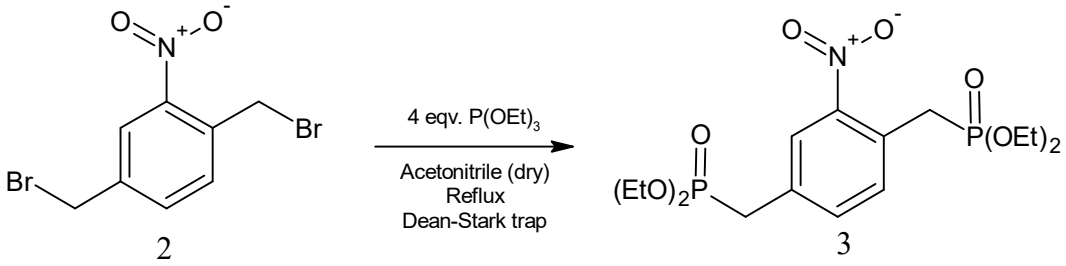
Compound 2 was obtained in 70% yield according to route 1 and in 76% yield using route 2. The product was obtained as an off-white flaky solid; mp: 87-90 °C (route 1); mp: 90-92 °C (route 2) ^{1}H-NMR (600 MHz, $CDCl_3$) δ 4.51 (s, 2H), 4.82 (s, 2H), 7.57 (d, 1H), 7.64 (d, 1H), 8.08 (s, 1H).

Tetraethyl((2-nitro-1,4 phenylene) bis(methylene)) bis(phosphonate) (3)

Route 1: One mmol of the brominated (2) was dissolved in 20 ml of acetonitrile and excess triethyl phosphite ($P(OEt)_3$) the reaction was run under reflux overnight. The solvent was evaporated and the resulting oily residue was purified via column chromatography.

Route 2: One mmol of the brominated (2) was added to a microwave reaction vial and 4 molar equivalents of $P(OEt)_3$ were added. The reaction was carried at 140-150 °C for 10 minutes in a microwave reactor. The resulting oily residue was purified by column chromatography.

Route 3: Two mmol of the brominated (2) were dissolved in acetonitrile (40 ml). Dry 3A molecular sieves were added to the solution (30% by mass). 4 equivalents of triethyl phosphite were added and the reaction mixture was heated to reflux overnight. The TLC plate showed only one spot with acetonitrile as eluent, the reaction was cooled to room temperature. The reaction mixture was filtered, and the solvent was evaporated under reduced pressure. The oily residue obtained was purified by column chromatography. The column was eluted using hexanes, ethyl acetate, and acetonitrile in that order. The acetonitrile fractions were combined and the eluent was evaporated under reduced pressure. The resulting oil was dried in a vacuum oven at room temperature.



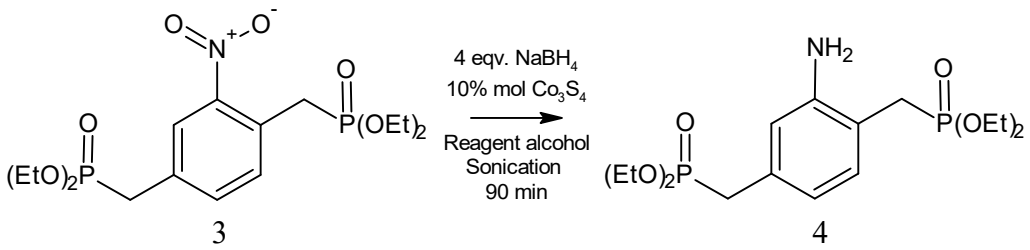
2 3

Scheme 2.3: Synthesis of tetraethyl ((2-nitro-1,4 phenylene) bis(methylene)) bis(phosphonate)

Compound 3 was obtained by Route 3 in 87% yield as a yellow oil. ^{1}H-NMR (600 MHz, $CDCl_3$): δ 1.16 (t, 6H), 1.19 (t, 6H), 3.21 (d, 2H), 3.60 (d, 2H), 3.96 (m, 4H), 4.00 (m,4H), 7.36 (d, 1H), 7.45 (d, 1H), 7.83 (s, 1H).

Tetraethyl ((2-amino-1,4 phenylene) bis(methylene)) bis(phosphonate) (4)

The reduction of nitro phosphonate 3 was carried out following a procedure reported in our group.[40] Accordingly, a mixture of 1 mmol of the (3) was dissolved in a scintillation vial using 8 ml of reagent alcohol. 4 mmol of sodium borohydride were added, followed by 10% mol of Co_3S_4 catalyst. The vial was capped and placed in a sonicator for 90 min. The catalyst was filtered through a celite cake and the solvent evaporated under reduced pressure. The product was extracted with ethyl acetated and water.

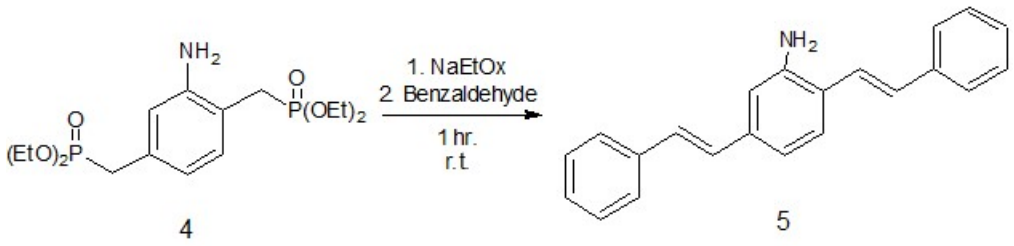


Scheme 2.4: Reduction of Nitro phosphonate compound to yield amino substituted phosphonate

Product 4 was obtained as a yellow oil in 60% yield. ^{1}H-NMR (600 MHz, CD3COCD3): δ 1.22 (m, 12H), 3.03 (d, 2H), 3.10 (d, 2H), 3.94 (m, 8H), 4.85 (s, 2H), 6.16 (d,1H), 6.75 (s,2H), 6.98 (d, 1H).

2,5-bis[(*E*)-2-phenylethenyl]aniline (5)

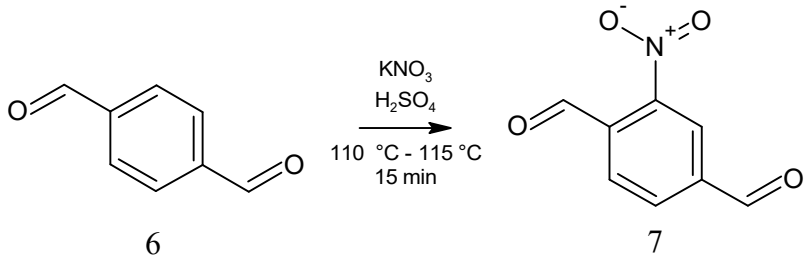
One mmol was dissolved in THF. 1.1 mole equivalents of sodium ethoxide were added. Then 2.2 mole equivalents of benzaldehyde in THF were added slowly. The solution was left to stir for 1 hour. Then the reaction was quenched with water and the product filtered.



Scheme 2.5: Synthesis of novel amino substituted distyrylbenzene (amino DSB)

2-Nitro terephthalaldehyde (7)

The compound was synthesized according to the reference by Low [41]: 1 gr of terephthalaldehyde (6) was placed in a round bottom flask along with 1.5 molar equivalents of potassium nitrate and 15 mL of concentrated sulfuric acid was and heated to 110 °C for 15 min. The reaction was cooled to room temperature and poured over ice water. The solid was filtered and washed with water and a baking soda solution.



Scheme 2.6 Nitration of terephthalaldehyde

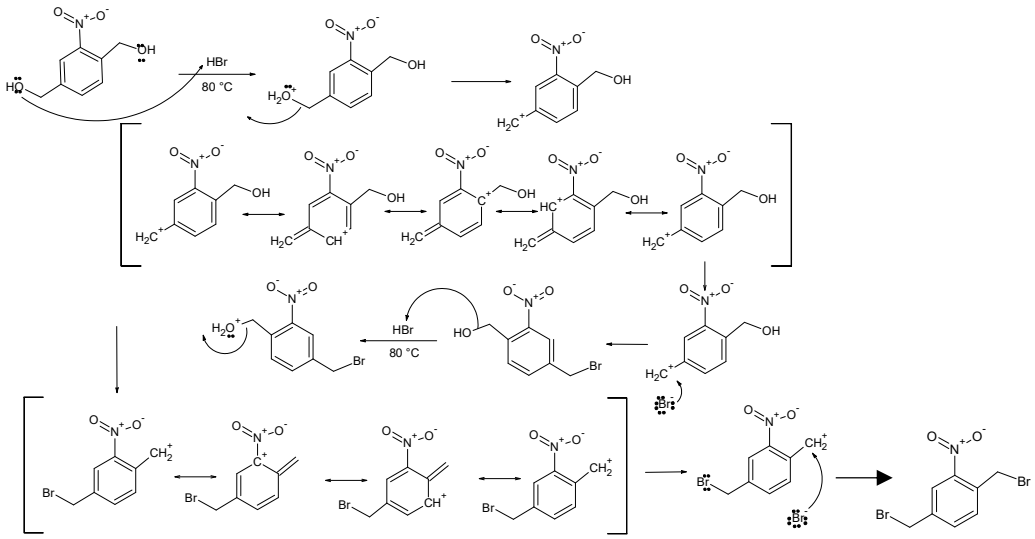
2-nitro-terephtaladehyde was obtained as a yellow solid in 30% yield ^{1}H-NMR (600 MHz, $CDCl_3$): δ 8.11 (d, 1H), 8.30 (d, 1H), 8.62 (s, 1h), 10.19 (s, 1H), 10.47 (s,1H).

CHAPTER III

RESULTS AND DISCUSSION

Synthesis of 1,4-Bis(bromomethyl)-2-nitrobenzene

The Bromination of 1 was successful by either route reported. The product was obtained in 70% yield using route 1. Recrystallization was necessary since the product was obtained as yellow to orange solid following this route. The reaction had to be optimized to maximize yield. At low temperatures or short time, the reaction would not come to completion and the evidence of 2 impurities was shown in the TLC plate (Figure 3.3). These impurities were identified as the respective mono brominated compounds as shown in the proposed mechanism below (Scheme 3.1).



Scheme 3.1 Proposed mechanism of dibrominated compound

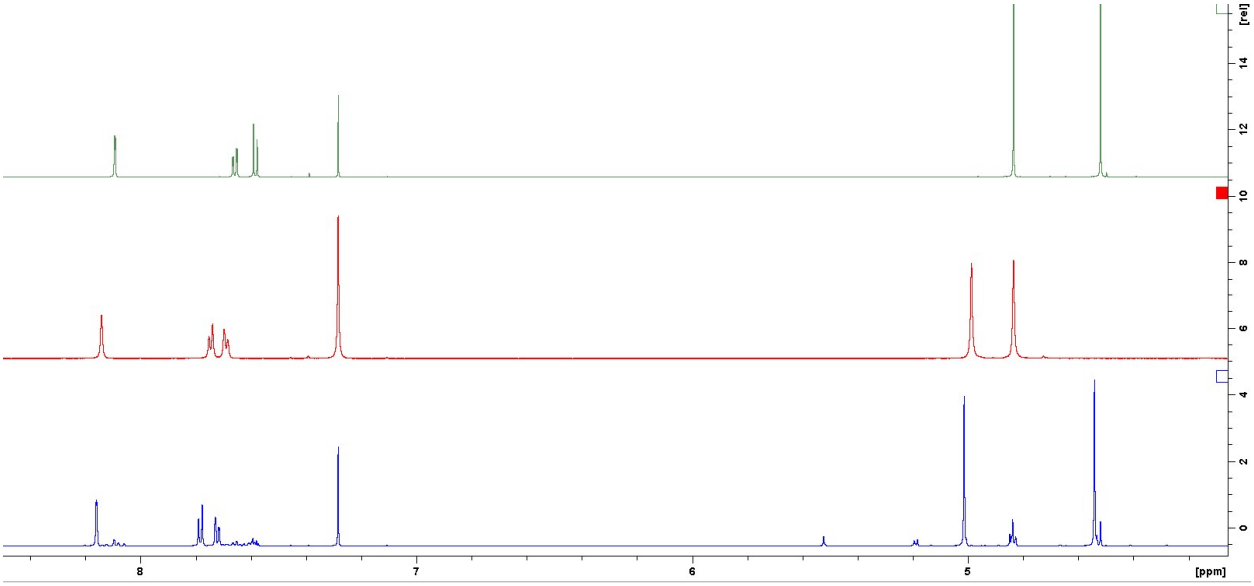


Figure 3.1: Bromination of 1,4-Bis(hydroxymethyl)-2-nitrobenzene: dibrominated (green), starting material (red), and monobrominated impurity (blue)

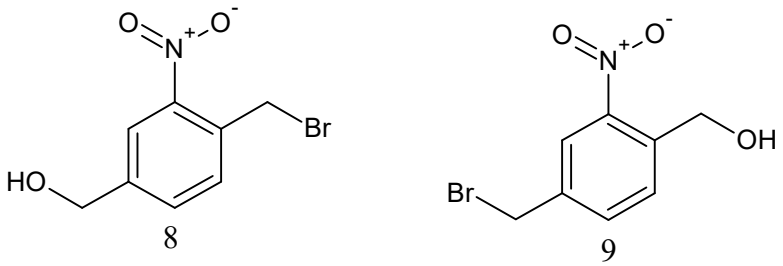


Figure 3.2 Products of the substitution of the alcohol group by bromine at the ortho (Compound 7) and meta (Compound 8) position of (1).

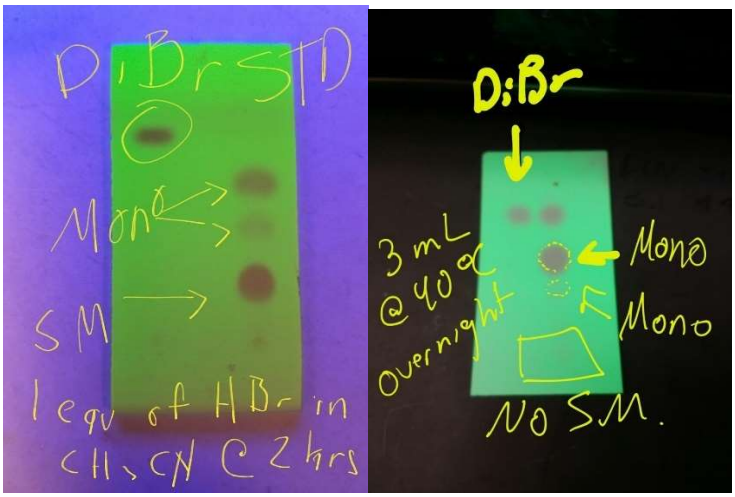


Figure 3.3: TLC of the bromination of 1,4-Bis(hydroxymethyl)-2-nitrobenzene after 2 hours in acetonitrile at room temperature (left), and at 40 °C overnight (right)

Figure 3.3 shows the pictures of TLC for two different reactions. In one (left picture) the reaction conditions were 1 molar equivalent of hydrobromic acid in acetonitrile at room temperature for 2 hours, while the right picture shows the TLC in a reaction of excess hydrobromic acid and allowing the mixture to react overnight at 40 ° C. These results suggest that substitution occurs preferentially on one of the alcohol groups. According to the Scheme 3.1, the substitution a the meta position respect to the nitro group results in more resonance contributors than the substitution on the ortho alcohol. Furthermore, one of the resonance contributors resulting from the substitution on the ortho alcohol places a positive charge on the carbon adjacent to the nitro group, which would be unfavorable. Examination of the ^{1}H-NMR spectra (Figure 3.1) supports this assumption. Note that, in the mono-brominated sample, the signal corresponding to the meta CH_2OH group at 4.83 ppm disappears, while the signal at 5.01 ppm remains, indicating that the CH_2OH group closer to the strong electron-withdrawing nitro group remained unsubstituted (Figure 3.2).

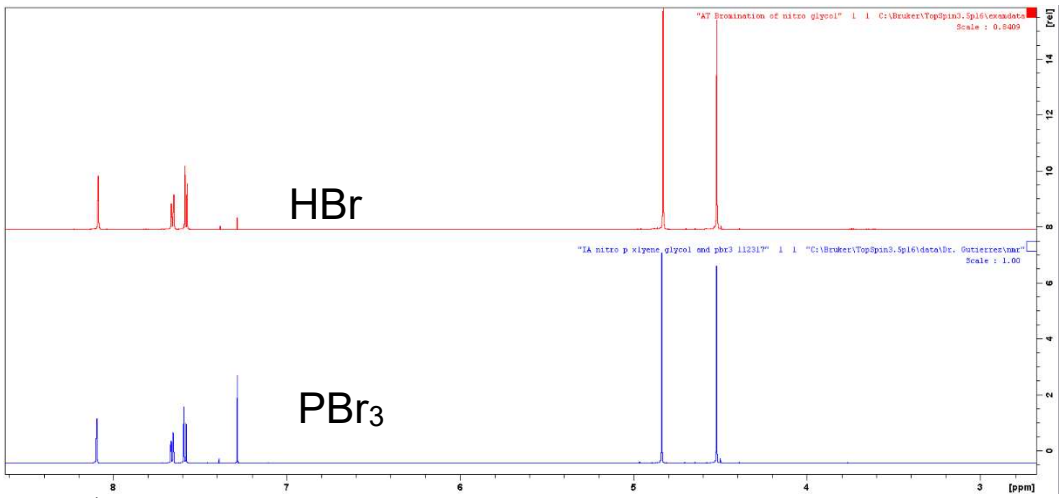


Figure 3.4 ^{1}H-NMR spectra of 1,4-Bis(bromomethyl)-2-nitrobenzene from Routes 1 and 2

The synthesis of the dibrominated compound (2) using route 1 (i.e. reaction with HBr) had several drawbacks. First, the reaction required long reaction times at high temperature using a large of excess of the highly corrosive aqueous hydrobromic acid (HBr). In addition, the resulting product required further purification by crystallization because it was normally obtained as a yellow to orange solid.

The synthesis of the dibrominated compound using PBr_3 (route 2) yielded a product with higher purity as evidenced by the higher and narrower melting point (HBr route: 87-90 °C vs PBr_3 route: 90-92 °C). In addition, the reaction was carried out in only 30 minutes at room temperature. The work-up was also advantageous since the product was isolated by addition of water, which precipitated the product without need of further purification. Figure 3.4 shows the ^{1}H-NMR spectra of the products of both routes and it shows that the signals from both products match perfectly. In figure 3.1, a comparison between the NMR spectra of the glycol (middle) and the dibrominated compound (top) shows the disappearance of the peaks that correspond to the methylene hydrogens in the CH_2OH group and the appearance of two new peaks up field

(CH_2Br). This is consistent with the change in the chemical environment of those protons by the addition of a less electronegative element to the carbon atom to which they are attached.

Synthesis of Tetraethyl((2-nitro-1,4 phenylene) bis(methylene)) bis(phosphonate)

The synthesis of (3) was first attempted by dissolving (2) in acetonitrile with excess triethyl phosphite ($P(OEt)_3$) under reflux overnight. This procedure yielded 64% of compound (3). A synthesis of a solvent-less reaction using 4 equivalents of $P(OEt)_3$ was attempted in a microwave reactor at 150 °C for 10 minutes. This reaction resulted in a 60% yield of a light brown oil. Figure 3.5 and Table 3.1 summarize the expected peaks from ^{1}H-NMR from the successful synthesis of (3). Figure 3.6 shows the ^{1}H-NMR spectrum obtained from the product of the latter reaction after purification by column chromatography.

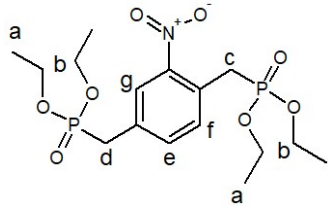


Figure 3.5: Proton signals expected from Compound 3

Protons	Proton type	Region (ppm)	Splitting pattern
a	CH_3	Aliphatic (1-2)	t
b	O-CH_2-CH_3	Aliphatic (3-4)	m
c	P-CH_2-Ar	Aliphatic (3-4)	d
d	P-CH_2-Ar	Aliphatic (3-4)	d
e	Ar-H	Aromatic	d
f	Ar-H	Aromatic	d
g	Ar-H	Aromatic	s

Table 3.1: Expected signals from Compound 3 ^{1}H-NMR spectra

The three signals in the aromatic region confirm the presence of an unsymmetrical tri-substituted benzene ring, the multiplets between 3.9-4.1 ppm suggest the presence of ether

groups, the doublets at 3.1 and 3.6 ppm are typical of the methylene protons adjacent to the phosphorus atom from the phosphonate esters, and the triplets between 1.1-1.2 ppm are consistent with the signal of the terminal methyl groups in the expected phosphonate ester. Note the presence of additional peaks at 1.25 ppm and 4.1 ppm, corresponding to an impurity.

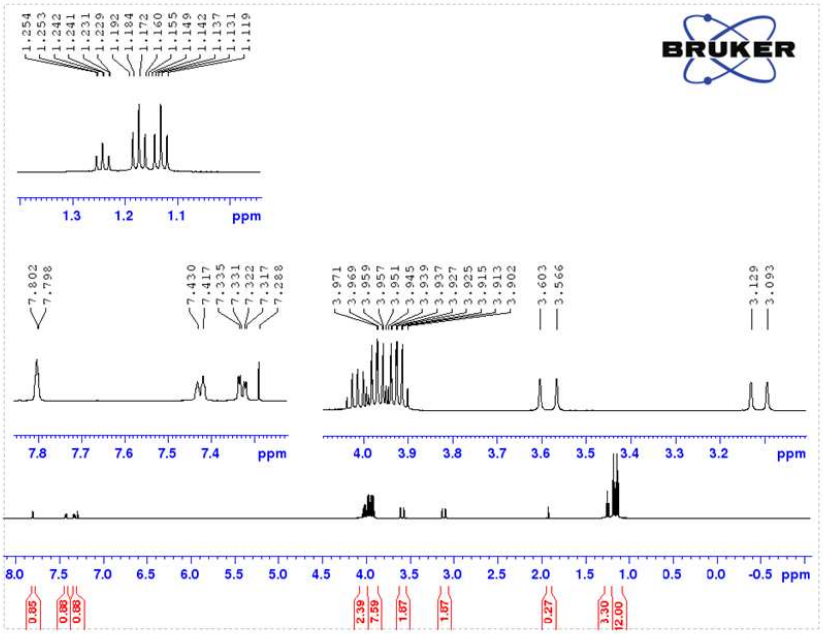


Figure. 3.6: Signals in the NMR spectrum of Nitro phosphonate compound from preliminary reactions

Monophosphonation of (2) was discarded as responsible for the signals at 1.25 ppm and 4.1 ppm. The resulting products of a monophosphonation are shown in Figure 3.7. If either of these compounds were the main product, the ^{1}H-NMR spectra for these molecules would exhibit a singlet peak corresponding to the methylene protons of the alkyl bromide group and a doublet peak of the methylene protons of aryl phosphonate esters. If a mixture of Compounds 9 and 10 were present, the spectrum would also show two doublet signals and two singlet signals in the 3-4 ppm region because the nitro group produces different chemical environments for the methylene protons at the ortho and meta positions. Additionally, this spectrum would display

more than three signals in the aromatic region since the protons in the ring would also be exposed to different chemical environments.

The spectrum shows two peaks in the aryl phosphonate region (3.1 ppm (d) and 3.6 ppm (d)) and three peaks in the aromatic region (7.79 ppm (s), 7.32 ppm (d) and 7.41 ppm (d)). Suggesting that only one type of aromatic compound is present and that the compound was successfully phosphonated at both the ortho and meta positions.

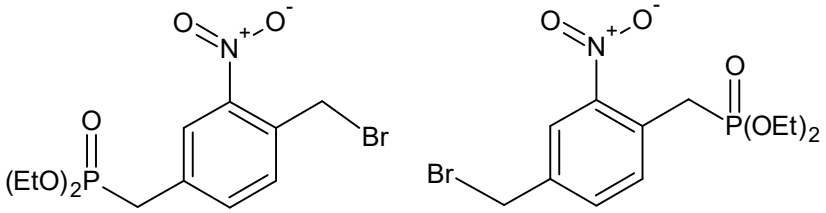
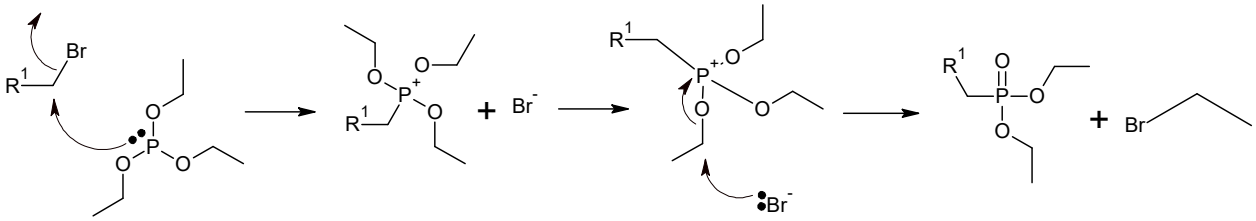
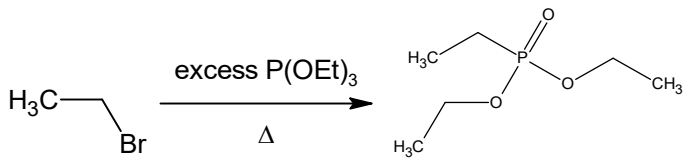


Figure 3.7: Products of the Arbuzov reaction upon mono-substitution of the alkyl bromide group at the meta and ortho positions.

The mechanism shown in Scheme 3.2 shows bromoethane as a byproduct of the Arbuzov reaction. This alkyl bromide can also undergo reaction with excess of $P(OEt)_3$. Since the product of this side reaction would result in a non-aromatic phosphonate ester (Scheme 3.3), we proposed that the signals at 1.25 ppm and 4.1 ppm were the result of the phosphonation of bromoethane.



Scheme 3.2: Mechanism for the Arbuzov reaction.



Scheme 3.3: Reaction of bromoethane with triethyl phosphine.

The removal of bromoethane form the reaction solution would prevent the formation of the corresponding phosphonate ester. Since bromoethane is a low-boiling point liquid and is denser than acetonitrile, we expected that attaching a Dean-Stark trap to the reflux apparatus would result in the removal of this liquid in an efficient manner. The modification was successful. This is evident from the disappearance of the signal at 4.1 ppm and the decrease in the peaks at 1.3 in Figure 3.8. The addition of the Dean-Stark trap and the addition of molecular sieves to the reaction mixture, afforded a significantly cleaner product and an increased yield (from 60% to 87% yield).

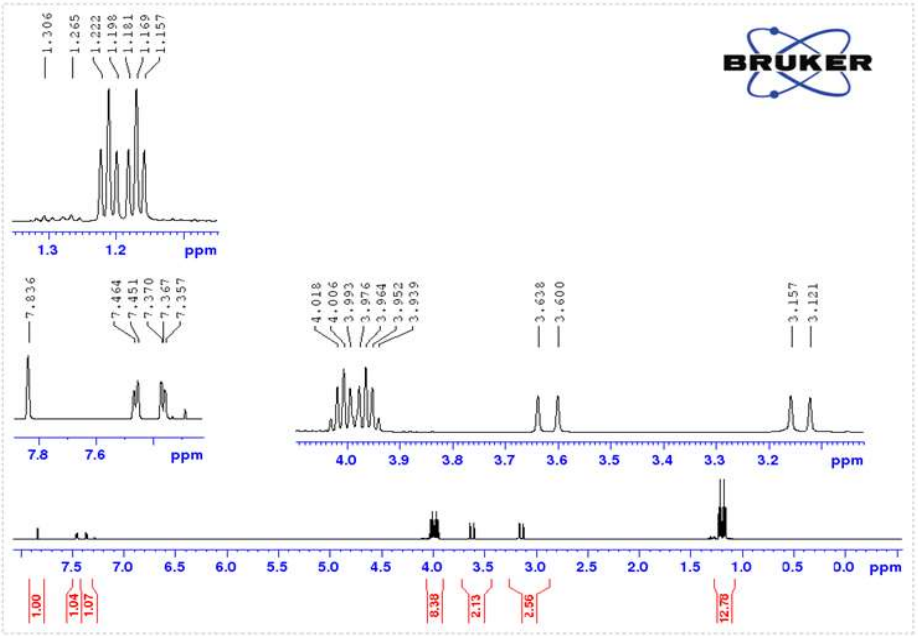


Figure 3.8: ^{1}H-NMR of nitro phosphonate compound synthesis reaction after optimization.

Synthesis of Tetraethyl((2-amino-1,4 phenylene) bis(methylene)) bis(phosphonate)

The reduction of the nitro phosphonate product (Compound 3) was carried out following a procedure developed in our group [40]. Accordingly, the reduction was conducted using the system $Co_3S_4/NaBH_4$ was used. The reduction reaction was optimized. If only 3 molar equivalents of the reducing agent were used, the reaction did not go to completion. Addition of an extra equivalent (4 total) of $NaBH_4$ was necessary to achieve complete reduction of the nitro group to the corresponding amine. Figure 3.9 shows the ^{1}H-NMR of reductions using 3 and 4 equivalents of sodium borohydride, respectively. As seen in Figure 3.8, the aromatic protons of the nitro groups are no longer present when 4 equivalents of the reducing agent. Note also that the aromatic protons in the reduced compound are shifted upfield, as expected by the disappearance of the strong electron withdrawing nitro group (Figure 3.10).

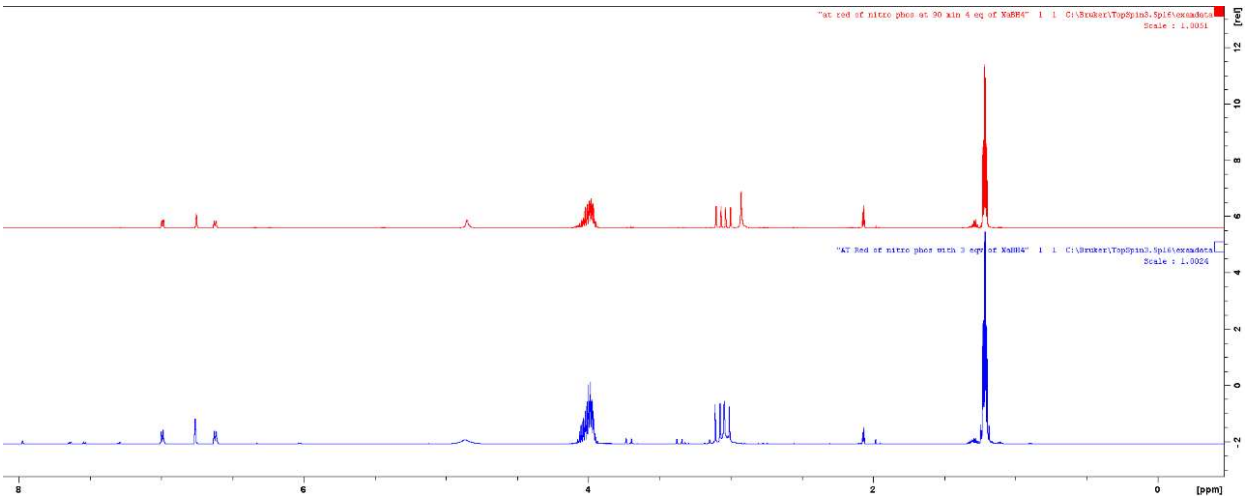


Figure 3.9: Comparison between 3 (blue) and 4 (red) molar equivalents of $NaBH_4$ in the reduction of 3

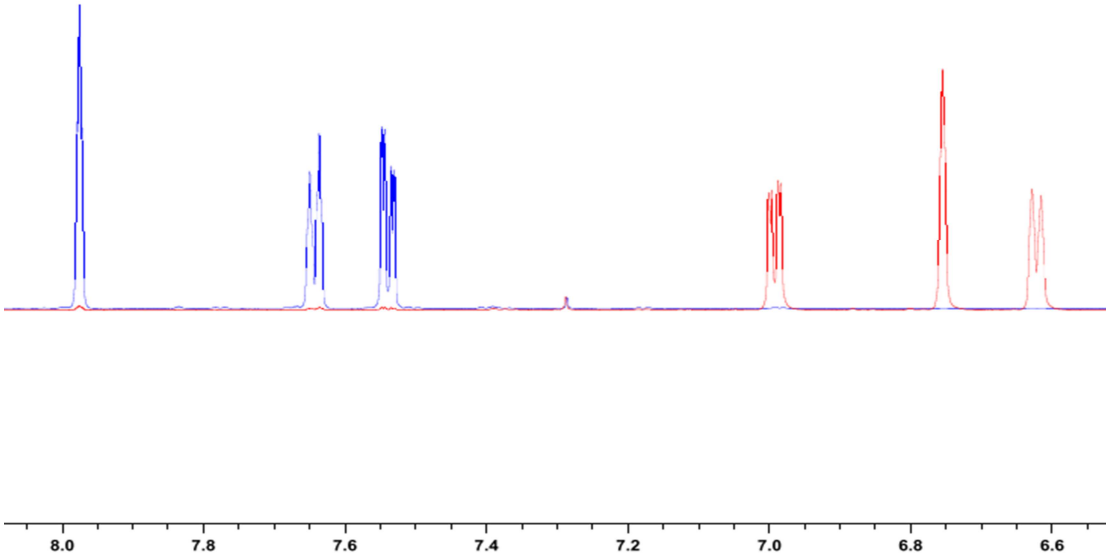


Figure 3.10: Aromatic region for the Nitro (blue) and Amino (red) phosphonate compounds

Furthermore, the aliphatic region underwent a change in the position of the peaks in the spectrum. In the nitro compound, the ether peaks are found as two distinct multiplets. In the amino compound those multiplets combine. A similar effect can be seen in the comparison of spectra between (3) (nitro) and (4) (amino) in Figure 3.11, where the doublet signals of the -CH_2- in between the aromatic ring and the phosphorus (top right) and the terminal -CH_3 (middle), are closer together in (4) than in (3). And lastly, the appearance of a new wide peak 4.8 ppm provides evidence consistent with the addition of new hydrogen atoms to the molecule.

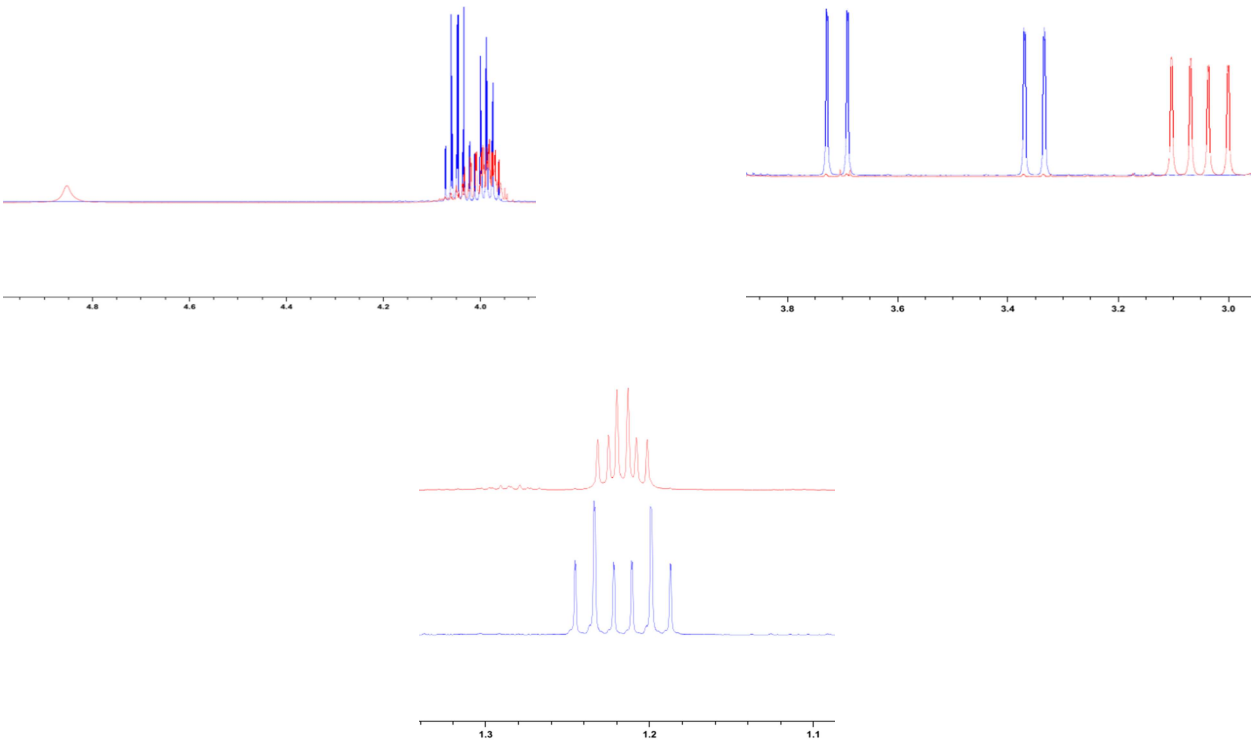
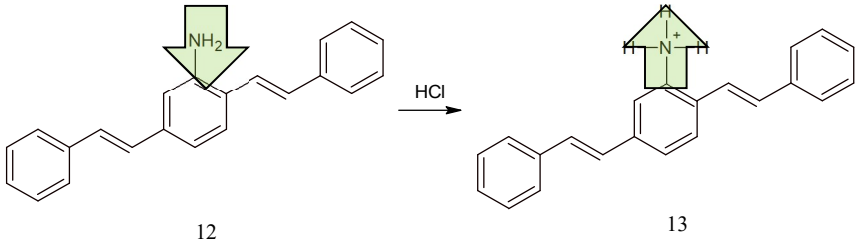


Figure 3.11: Comparison of specific regions in ^{1}H-NMR spectra of nitro and amino phosphonate compounds.

Synthesis of Distyrylbenzene with the Amino Moiety

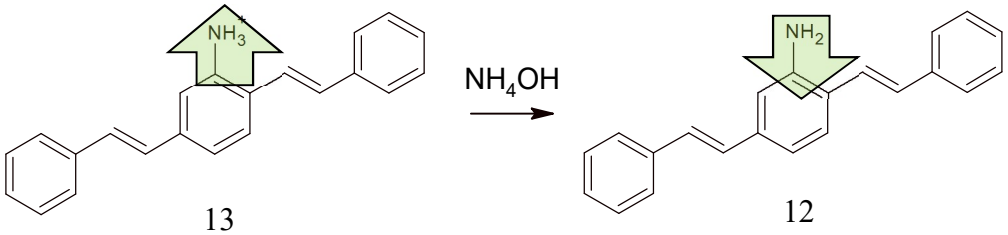
We conducted preliminary experiments in the synthesis of the amino-substituted distyrylbenzene (5). Inside a glove box, a solution of 1 mmol of (4) in 10 mL of anhydrous THF was prepared and added to a three-neck round bottom flask. The same volume and method were used to prepare solutions of 2.2 mmol of sodium ethoxide (NaEtOx) and 2.2 mmol of benzaldehyde. As the phosphonate solution stirred at room temperature, the ethoxide solution was added first. Then the benzaldehyde solution was added slowly to the reaction mixture. After 1 hour, the solution became a deep yellow color. The solid recovered after the coupling reaction was complete exhibited the expected luminescence, especially when it was dissolved in a solution of water/acetonitrile. The presence of the amino group in the DSB was confirmed upon

addition of concentrated hydrochloric acid (HCl). The addition of HCl resulted in quenching of the luminescence, as a result of the protonation of an electron donating group (-NH_2) to an electron withdrawing group (-NH_3^+). As expected, the luminescence was restored after the solution was neutralized with NH_4OH. (Figure 3.13)



Scheme 3.4: Protonation of the amine results in an electron withdrawing substituent

Figure 3.12: Quenching of luminescence after the addition of HCl because of the protonation of the amine group.



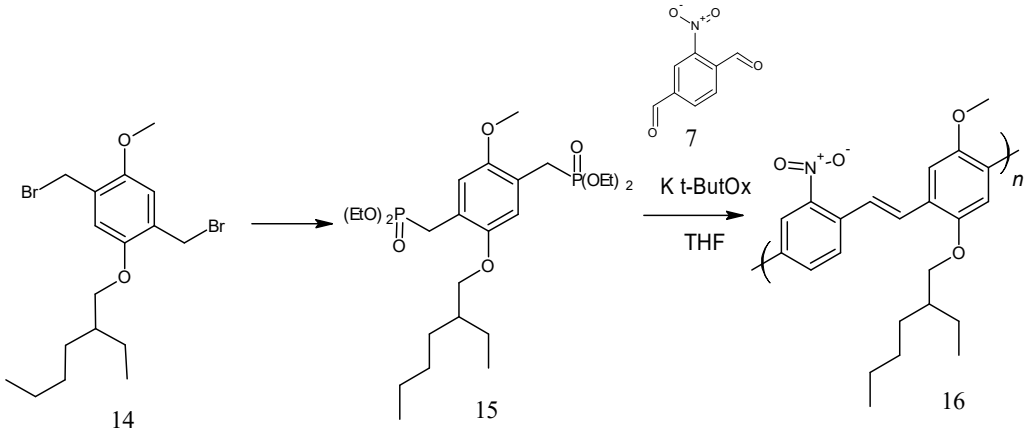
Scheme 3.5 Neutralization of HCl with NH_4OH restores the amino group

Figure 3.13: Progresive reappereance of luminescence upon the addition of NH_4OH

We found that the amino-DSB (12) could be dispersed in a cotton ball. Thus, a cotton ball was soaked in a solution of (12) and dried in a vacuum oven for 1 hour. Figure 3.14 shows that the luminescence is present in the cotton even after the solution has been evaporated. This is indication about the possibility of attaching the novel molecule to fibrous materials.

Figure 3.14: Luminescence observed in cotton ball after beign soaked in solution

Synthesis of 2-Nitroterephthalaldehyde



Scheme 3.6: Proposed route for the synthesis of Nitro/alkoxy substituted PPV.

As seen in Scheme 3.6 the nitration of Compound 6 is critical for the development of a nitro/alkoxy substituted PPV. The nitration was attempted by using the methodology by Low [41] was successful. Figure 3.15 shows a comparison between the terephthalaldehyde and the product of the reaction. The downfield shifts of all the signals are consistent with the addition of an electron withdrawing group to the ring. Furthermore, the addition of a third substituent onto the ring eliminates the symmetry that was present before, resulting in the splitting of the two singlets into five districts signals (3 aromatic and 2 from carbonyl groups). The addition of the nitro group results in three distinct aromatic proton signals (two doublets and a singlet) that are shifted further downfield. Similarly, the signal at 10 ppm, is split and shifted further downfield. Evidence of the signals splitting and the downfield shifts of all the protons suggest that the nitration of terephthalaldehyde was successful.

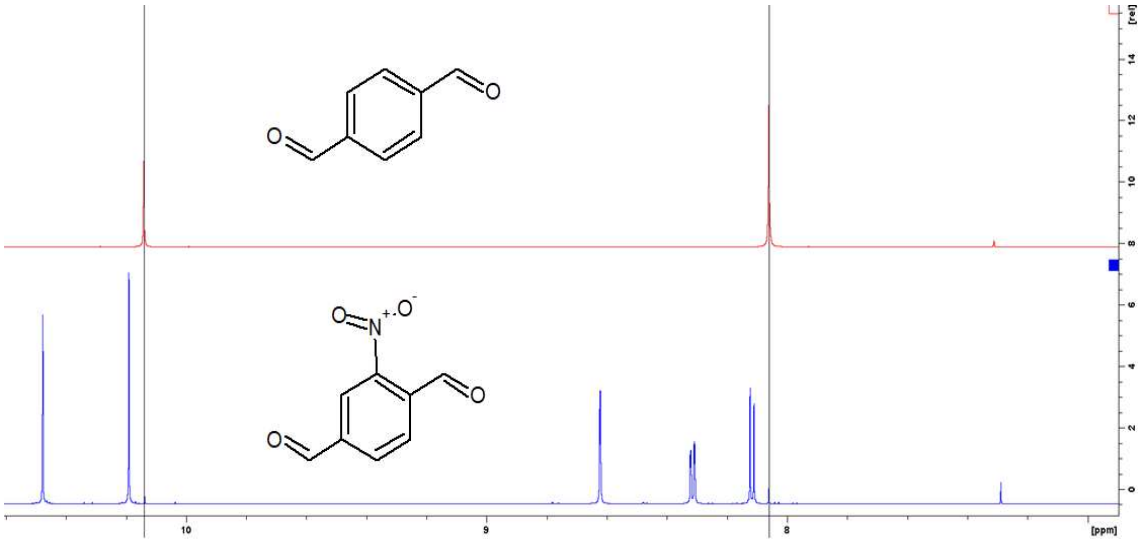


Figure 3.15: Comparison between the 1H-NMR spectra of terphtalaldehyde (red) and the nitration product (blue).

Preliminary experiments were also conducted for the synthesis of the novel nitro/alkoxy PPV. As seen in Figure 3.16, different solutions with the precipitated product were prepared and exposed to UV light. Some of the precipitate is still visible (top), but once more solvent is added the precipitate goes into the solution (bottom). The blue solution on the far left in the bottom picture was prepared by using (3) and (7). Note that the solution is not translucent. The light being produced by the solution is tough to be the result of dispersion instead of emission. Further experimentation and characterization is necessary.

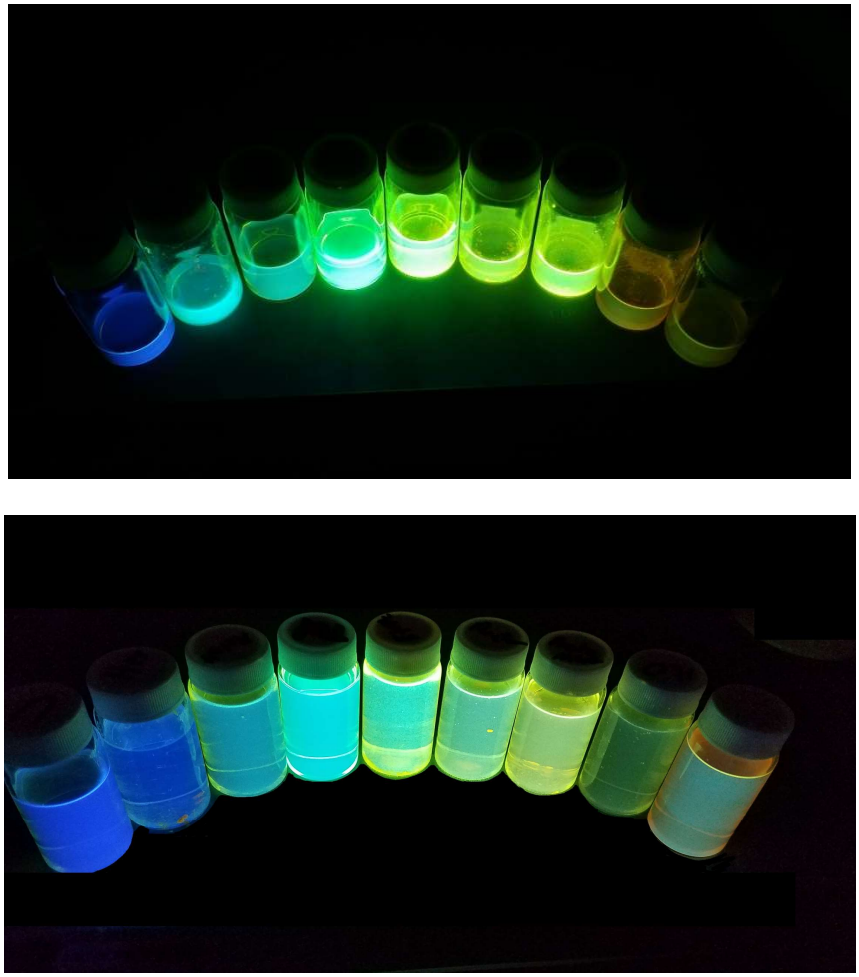


Figure 3.16: Solutions of the product of the coupling reaction of (3) with (7) (far left) and (7) with (15) under UV light

Conclusions

The synthesis of 1,4-Bis(bromomethyl)-2-nitrobenzene was successful using aqueous HBr or PBr_3 as the brominating agents. Bromination with PBr_3 was favored because full conversion was achieved in only 30 minutes at room temperature and the product was obtained in higher purity and yield.

Synthesis of Tetraethyl((2-nitro-1,4 phenylene) bis(methylene)) bis(phosphonate) compound was successful with high purity and high yield. The successful removal of the bromoethane side product via Dean-Stark apparatus and the removal of water via molecular

sieves, produced a dramatic increase in yield when compared to the reaction under reflux (23% increase) or by the microwave assisted synthesis (26%) increase.

The reduction of (3) to the corresponding (name of the compound) was carried out successfully using the system $Co_3S_4/NaBH_4$.

Preliminary evidence for the synthesis of amino substituted distyrylbenzene was obtained as indicated by the disappearance and reappearance of luminescence upon the addition of HCl and NH_4OH respectively. Also, the possibility of doping fibrous materials with the novel molecule was shown by the exhibition of luminescence of cotton fibers after being soaked in the solution containing the compound and dried in an oven for one hour

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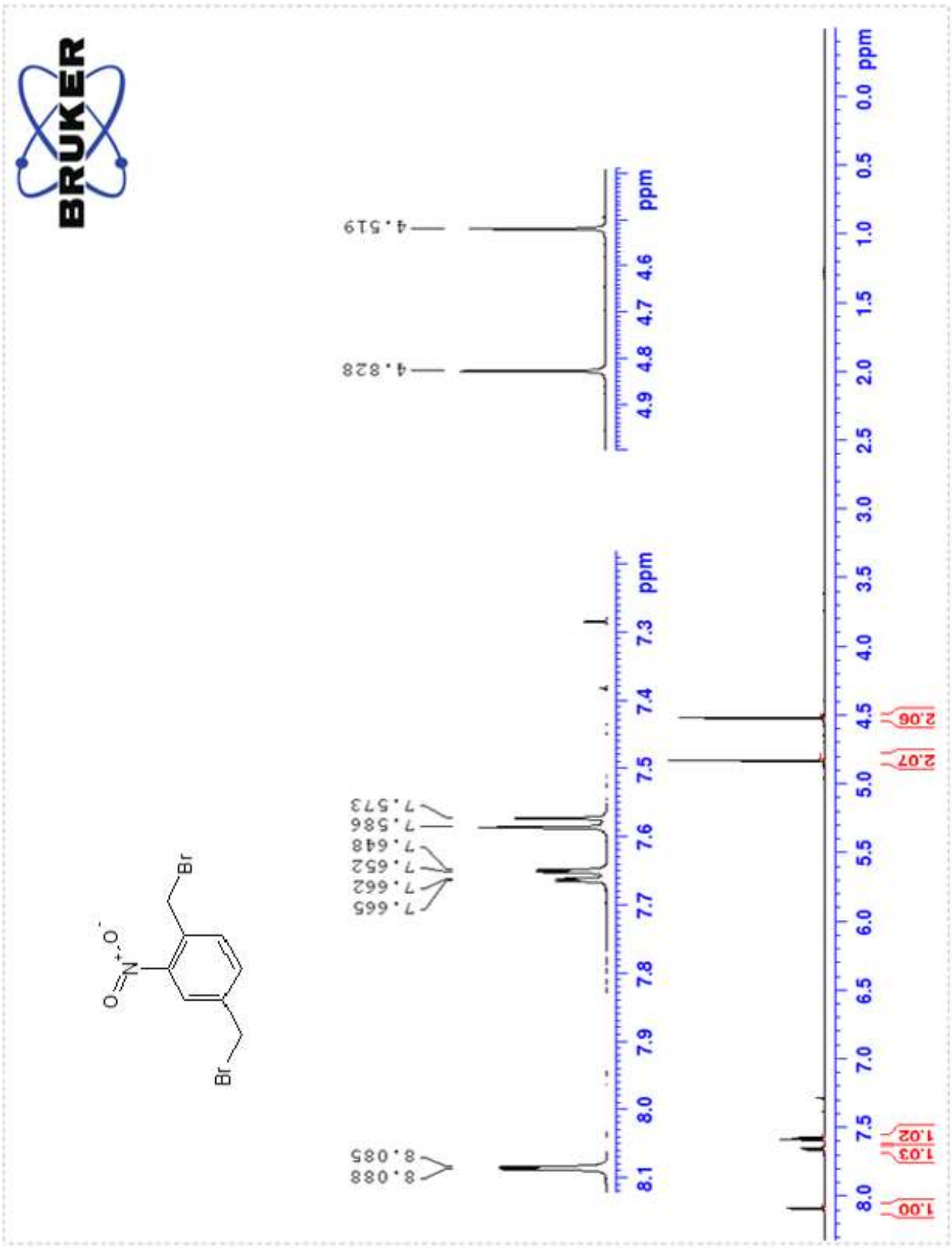
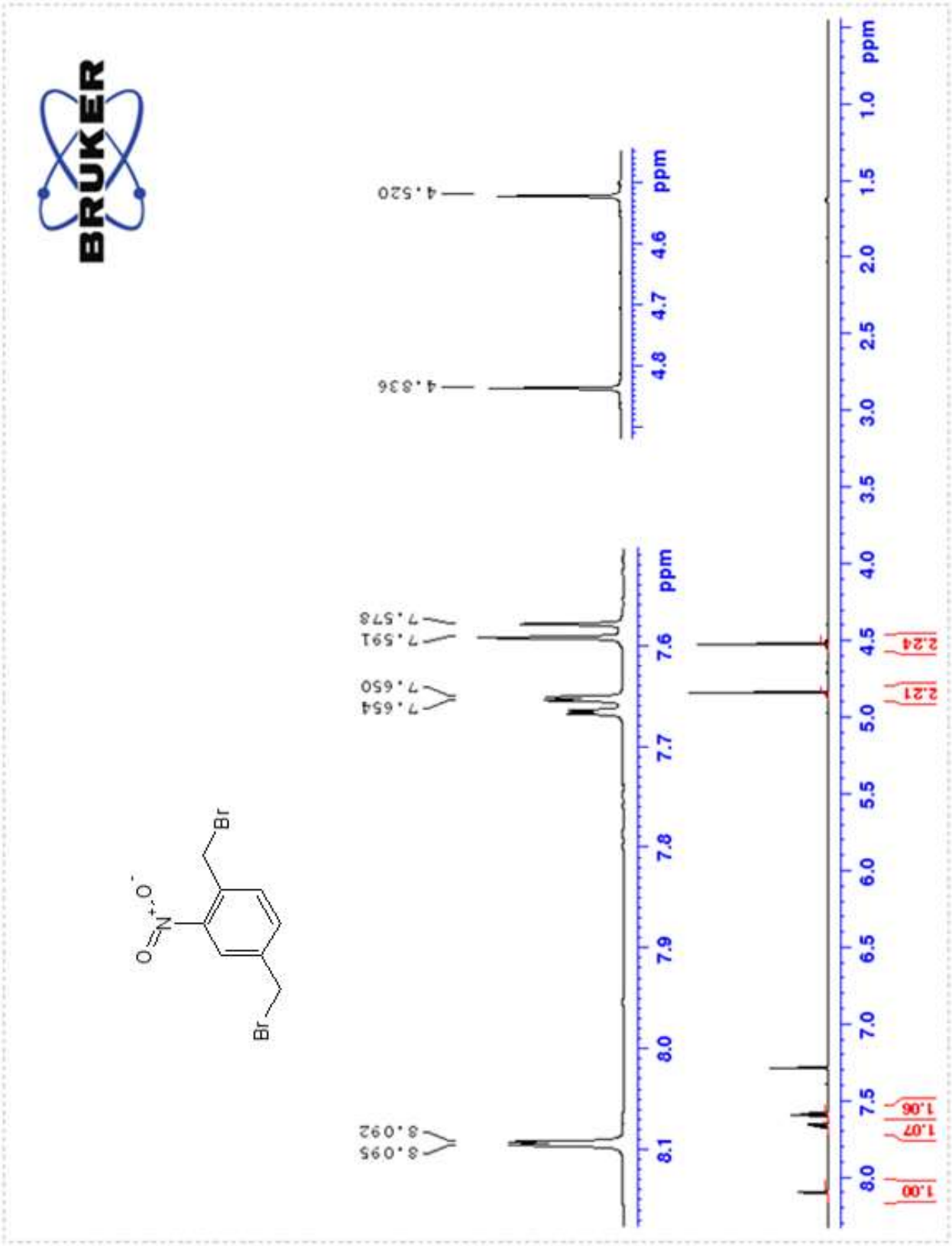
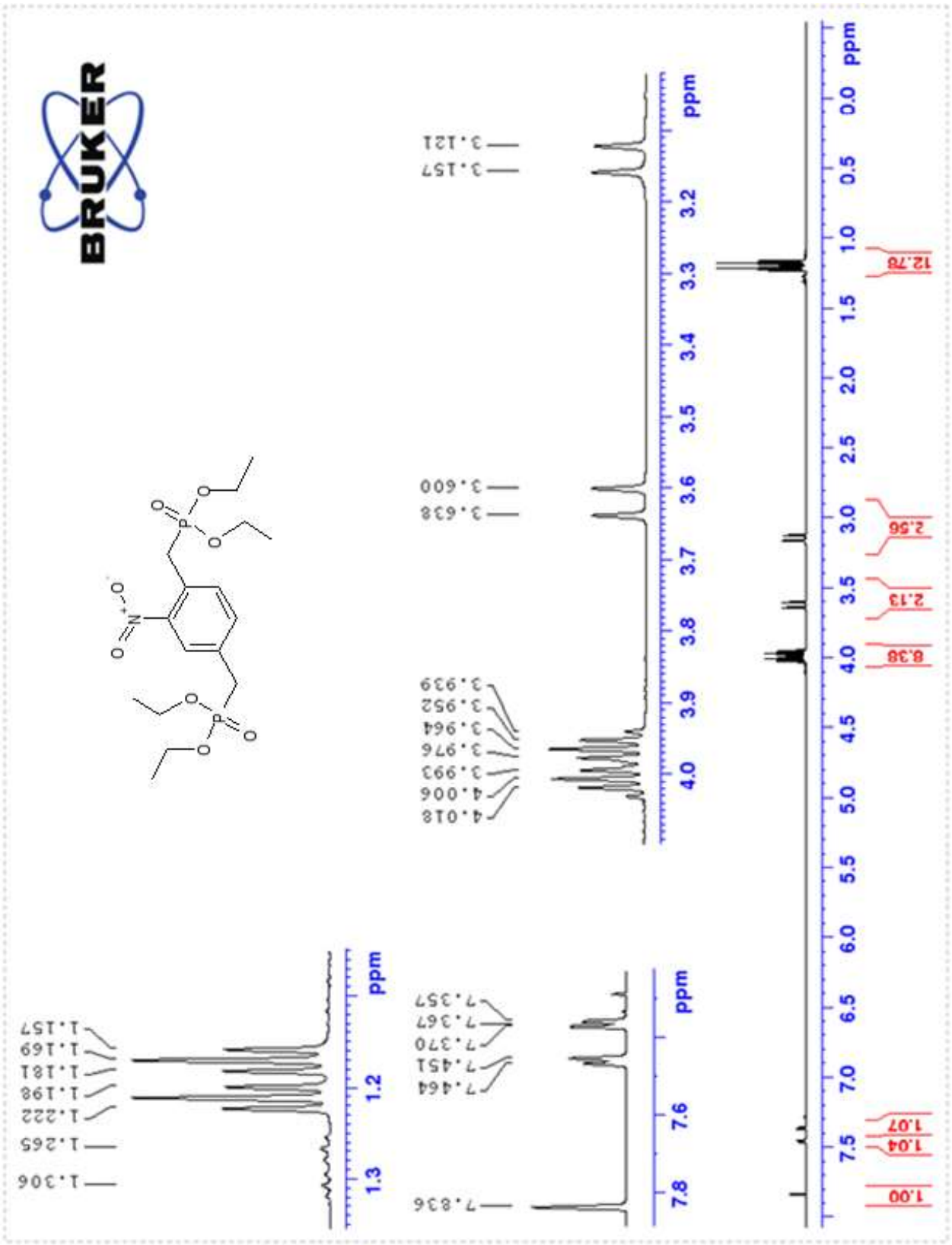
APPENDIX



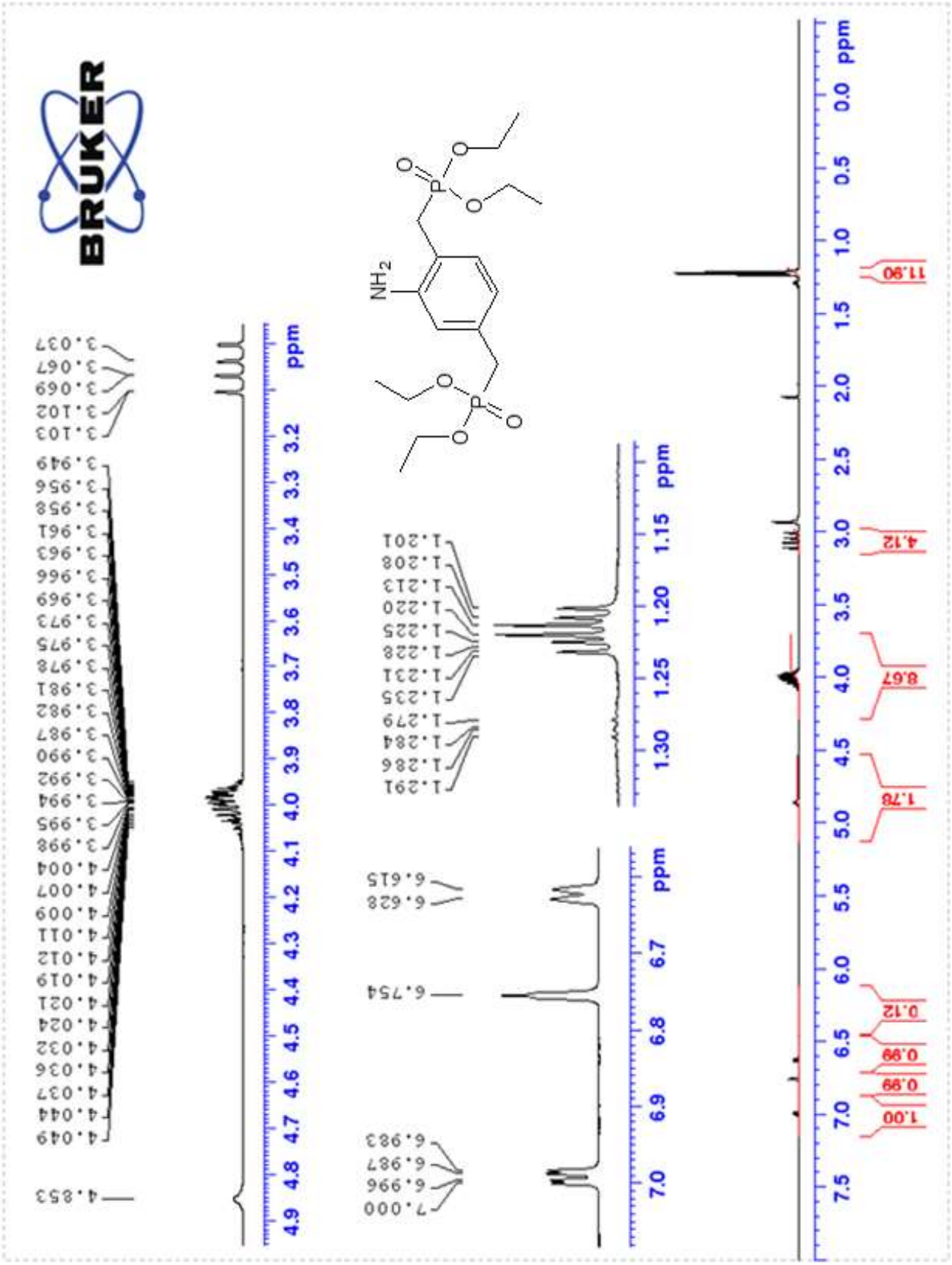
[1]H-NMR 1,4-Bis(bromomethyl)-2-nitrobenzene – HBr route



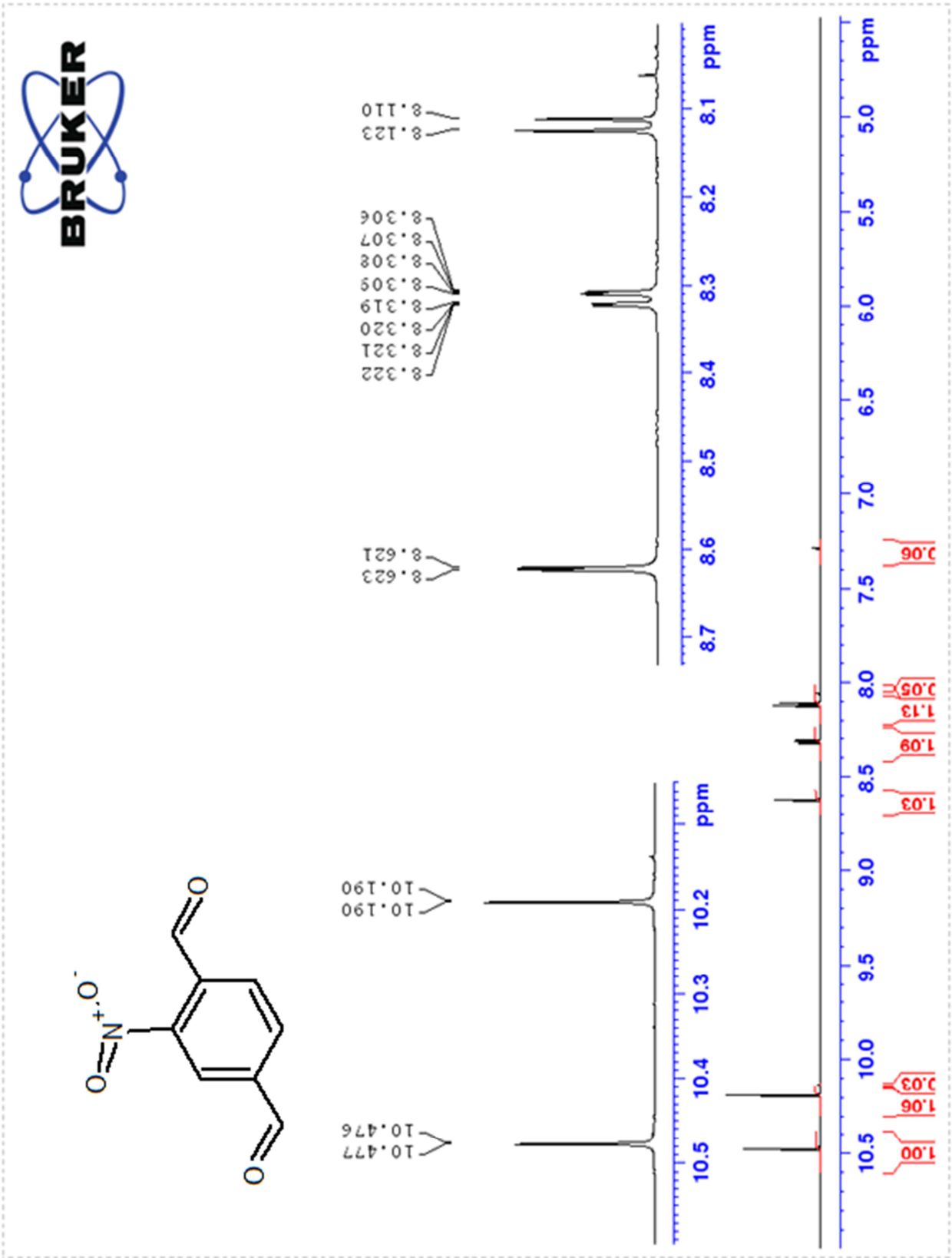
^{1}H-NMR 1,4-Bis(bromomethyl)-2-nitrobenzene - PBr_3 route



[1]H-NMR Tetraethyl((2-nitro-1,4 phenylene) bis(methylene)) bis(phosphonate)



[1]H-NMR Tetraethyl((2-amino-1,4 phenylene) bis(methylene)) bis(phosphonate)



^{1}H-NMR 2-nitroterephtalaldehyde

BIOGRAPHICAL SKETCH

Ariel Ivan Torres Burgueño was born if 1989 in Reynosa Mexico. He graduated from Faith Christian Academy in 2007. He graduated with a double major in Chemistry and Biology from the University of Texas – Pan American in August 2012. After working in an environmental laboratory and as a high school science teacher, Ariel started his graduate studies in August, 2015. He worked under the direction of Dr. Jose Gutierrez. He completed his Master of Science in Chemistry in December 2017. His email address is:

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