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Unexpected Outcomes during the Attempted Iodination of Biphenol

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Unexpected Outcomes during the Attempted Iodination of Biphenol

By
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A thesis submitted to the faculty of The University of Mississippi in partial fulfillment of
the requirements of the Sally McDonnell Barksdale Honors College

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Reader: Professor Jason Ritchie

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First, I would like to thank my thesis advisor, Dr. Mattern, for guiding me through the many problems during this project. I would also like to thank Trey Vaughn for teaching me all the necessary laboratory techniques. Lastly, I would like to thank my parents for supporting me throughout my degree.

Abstract

The goal of this research was to create a new procedure to iodinate 4,4-biphenol using a ball miller. Iodination of 4,4-biphenol was first attempted in solution using electrophilic aromatic substitution. Several attempts were made to iodinate 4,4-biphenol, but the general insolubility of crude products inhibited progress. Interestingly, NMR analysis of the aqueous ammonia product suggested that 4,4-biphenol dimerized or polymerized with itself to make an ether. The exact mechanism by which the ether dimer was created is unknown, but the reaction may have occurred using a radical mechanism. Though the original goal of the project is left unmet, a future inquiry into the ether dimer could prove just as fascinating.

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Introduction.

Ball milling is a relatively underutilized technique in organic chemistry. It uses a ball mill to “mill”, or grind, its contents; this can be used to induce chemical reactions between solid reactants. The instrument is primarily a rotatable or vibrating cylindrical tube that holds steel balls. During use, ball mills are set to rotate below critical speed for efficiency. At critical speed, the steel balls inside the tube cease to mill and are pressed against the tube’s walls as shown below in Illustration 1. As a result, many mills are set to rotate at approximately 70-80% of critical speed.¹ A mill’s critical speed is calculated using the formula: $N_c = 76.6(D^{0.5})$, where D is the inside diameter in feet and N_c is the critical speed in revolutions per minute. In addition to critical speed, efficient mills should have a ball filling of 20% - 40% inside the cylinder.¹

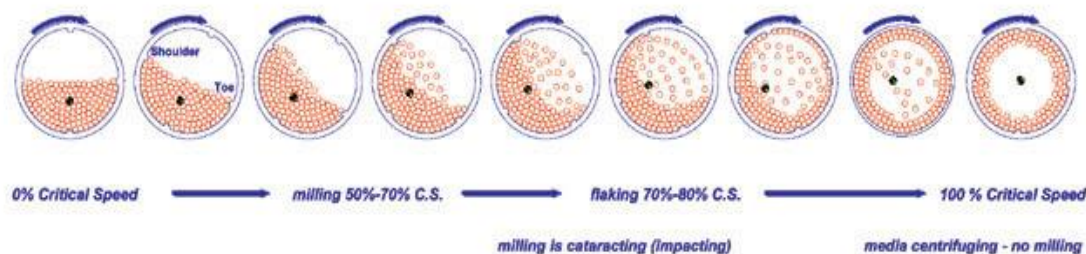
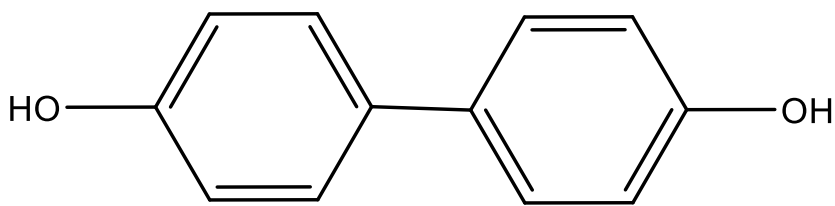


Illustration 1.⁷

One of the main attractions of the ball mill is its “greener” approach to chemistry. Because the ball mill functions without solvent, costs and waste involving solvents can be entirely cut out. Solvent waste is a topic of concern as many organic solvents such as benzene, CCl_4 , DCM, and toluene are classified

as carcinogens or neurotoxins.² Therefore, it is of utmost importance to reduce exposure to hazardous chemicals where possible.

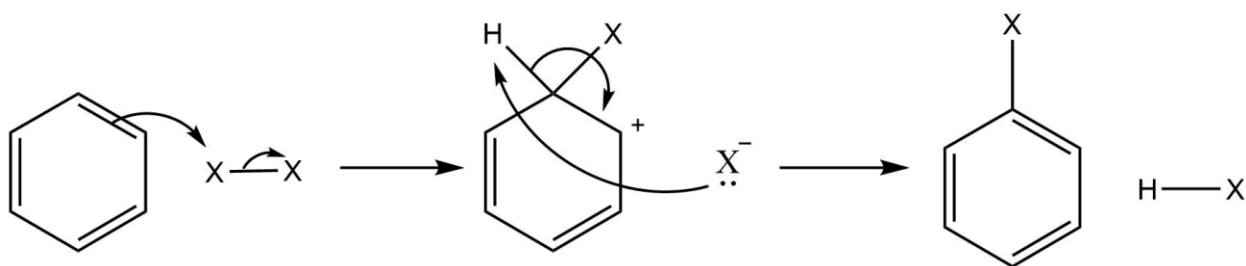
The original goal of this research was to synthesize polyiodinated 4,4-biphenol, shown in Structure 1., through use of a ball mill. Little study has been done on the synthesis of iodinated 4,4-biphenol, and no study has been done on the ball mill synthesis of iodinated biphenol. Electrophilic Aromatic Substitution (EAS) is a commonly used method to halogenate aromatic compounds. 4,4-Biphenol has both strong aromaticity and two -OH activating groups making it ideal for EAS.



Structure 1. Shown in the structure of 4,4-biphenol.

EAS is a substitution reaction in which an aromatic hydrogen is replaced by an electrophile. Electrophiles are species that are electron deficient and accept electrons, much like Lewis acids. The mechanism occurs in two steps: electrophilic attack and proton loss. During EAS, electrophilic attack is the rate determining step of the reaction as the attack will result in an unfavorable loss of aromaticity and the gain of a carbocation. The resulting arenium ion, while relatively stabilized by resonance, still contains a carbocation that can be further stabilized with the second step: proton loss. A base is used to deprotonate the newly substituted carbon, restoring the arene's neutral charge and aromaticity.

Due to its simplicity, EAS is a commonly used method to halogenate aromatic compounds.



Chlorine and bromine are readily used as electrophiles in halogenations. As the halogen with the smallest electrophilicity, iodine reacts slowly, if at all, under normal conditions. After the electrophilic attack on iodine, the reaction creates hydrogen iodide, a strong reducing agent. The hydrogen iodide then regenerates iodine and the arene, reversing the previous electrophilic attack. To solve this problem, strong oxidants such as iodic acid are used to convert hydrogen iodide back into iodine. According to Le-Chatelier's principle, the increase in reactant concentration will cause the equilibrium of the reaction to shift toward products. In addition to oxidizing agents, activating groups on the arene can be used to increase the reaction rate of iodination.

We began this project by attempting iodinations in solution to serve as reference points for reactions in the ball miller. However, the solution reactions took unexpected turns, and all the work ended up being in solution.

Experimental Procedures.

1. Procedure for the attempted polyiodination of 4,4-biphenol without triethylamine

Biphenol (1 mmol) was dissolved in methanol (7.4 mL). Iodine (4.4 mmol) was added into the dissolved methanol and stirred using a stir bar. The mixture was monitored by thin layer chromatography and heated under reflux for approximately 24 hours. The solution was filtered by vacuum filtration. Solid collected on the filter paper was washed using aqueous sodium sulfite (4 mL), DCM (4 mL), and methanol. The solid was dissolved in deuterated methanol and analyzed by H-NMR. For C-NMR, the solid was dissolved in deuterated DMSO.

2. Procedure for the attempted polyiodination of 4,4-biphenol using triethylamine

Biphenol (1 mmol) and iodine (4.4 mmol) were dissolved in methanol (7.4 mL) and mixed using a stir bar. Triethylamine (1 mL) was slowly dripped into the solution. The mixture was monitored by thin layer chromatography until completion. After completion, aqueous sodium sulfite was added until dark-orange color of iodine subsided. The solid was collected by vacuum filtration. The solid was dissolved in deuterated DMSO and analyzed by H-NMR and C-NMR.

3. Procedure for the attempted diiodination of 4,4-biphenol using KOH

Biphenol (1 mmol) was dissolved in methanol (5 mL) and KOH (2 mmol) was dissolved in methanol (20 mL). The two were mixed together in a flask using

a stir bar. Iodine (1.9 mmol) was dissolved in methanol (5 mL) and slowly dripped into the biphenol-KOH solution. The reaction was monitored by thin layer chromatography until completion. The solid was collected by vacuum filtration. Then, the solid was dissolved in deuterated DMSO and analyzed by H-NMR and C-NMR.

4. Procedure for the triiodination of phenol using Sharma's method with sodium sulfite⁵.

A round bottom flask (100 mL) was charged with phenol (3 mmol) and acetic acid (10 mL). A solution of potassium triiodide and sodium sulfite, preliminarily prepared by adding iodine (3 mmol) and sodium sulfite (3 mmol) to a solution of potassium iodide (3 mmol) in water (3 mL), was quickly added into the flask. Soon after, a solution of sodium periodate (3 mmol) in water (5 mL) was added and sulfuric acid (0.5 mL) was rapidly added using a pressure equalizing funnel. The mixture was stirred 24 hours using a stir bar and monitored by TLC until completion. After completion, the mixture was poured into ice-cold water and filtered by vacuum filtration. The solid was washed with deionized water (5 mL) twice. The crude solid was dissolved in deuterated DMSO and analyzed by H-NMR. The crude solid was also analyzed by melting point analysis.

5. Procedure for the triiodination of phenol using Sharma's method without sodium sulfite⁵.

A round bottom flask (100 mL) was charged with phenol (3 mmol) and acetic acid (10 mL). A solution of potassium triiodide, preliminarily prepared by adding iodine (3 mmol) to a solution of potassium iodide (3 mmol) in water (3 mL), was quickly added into the flask. Soon after, a solution of sodium periodate (3 mmol) in water (5 mL) was added and sulfuric acid (0.5 mL) was rapidly added using a pressure equalizing funnel. The mixture was stirred 24 hours using a stir bar and monitored by TLC until completion. After completion, the mixture was poured into ice-cold water and filtered by vacuum filtration. The solid was washed with deionized water (5 mL) twice. The crude solid was dissolved in deuterated DMSO and analyzed by H-NMR. The crude solid was also analyzed by melting point analysis.

6. Procedure for the triiodination of phenol using aqueous ammonia⁶.

Phenol (2.83 mmol) was dissolved in 30% aqueous ammonia (20 mL). A solution of iodine (8.51 mmol) in potassium iodide (17.1 mmol) was gradually added into the phenol solution, whereupon the addition was stopped. The mixture was filtered by vacuum filtration and washed with water (10 mL) and analyzed by melting point analysis and H-NMR in deuterated chloroform and DMSO.

7. Procedure for the attempted iodination of 4,4-biphenol using aqueous ammonia

4,4-Biphenol (3 mmol) was dissolved in aqueous ammonia (20 mL). A solution of iodine (3 mmol) in potassium iodide (3 mmol) was gradually added into the biphenol solution until iodine color persisted. The mixture was filtered by vacuum filtration and washed with water (10 mL) and methanol (10 mL). The solid was dissolved in deuterated DMSO and analyzed by H-NMR and C-NMR. A mass spectrum of the solid was also taken.

8. Procedure for the attempted iodination of 4,4-biphenol using Sharma's method without sodium sulfite

A round bottom flask (100 mL) was charged with biphenol (3 mmol) and acetic acid (10 mL). A solution of potassium triiodide, preliminarily prepared by adding iodine (3 mmol) to a solution of potassium iodide (3 mmol) in water (3 mL), was quickly added into the flask. Soon after, a solution of sodium periodate (3 mmol) in water (5 mL) was added and sulfuric acid (0.5 mL) was rapidly added using a pressure equalizing funnel. The mixture was stirred 24 hours using a stir bar and monitored by TLC until completion. After completion, the mixture was poured into ice-cold water and filtered by vacuum filtration. The solid was washed with deionized water (5 mL) twice.

9. Attempted Iodination of 4-phenylphenol using Sharma et al.'s method without sodium sulfite

A round bottom flask (100 mL) was charged with 4-phenylphenol (3 mmol) and acetic acid (10 mL). A solution of potassium triiodide, preliminarily prepared by adding iodine (3 mmol) to a solution of potassium iodide (3 mmol) in water (3 mL), was quickly added into the flask. Soon after, a solution of sodium periodate (3 mmol) in water (5 mL) was added and sulfuric acid (0.5 mL) was rapidly added using a pressure equalizing funnel. The mixture was stirred 24 hours using a stir bar and monitored by TLC until completion. After completion, the mixture was poured into ice-cold water and filtered by vacuum filtration. The solid was washed with deionized water (5 mL) twice.

Results and Discussion.

1. Attempted Polyiodination of 4,4-biphenol without triethylamine

While thin layer chromatography showed that all biphenol had reacted, the iodination of biphenol did not occur. NMR analysis of pure 4,4-biphenol resulted in the following NMR data: ^1H (500 MHz, DMSO- d_6): δ /ppm 6.80 (d, 4H), 7.37 (d, 4H), and 9.38 (s, 2H); ^{13}C (500 MHz, DMSO- d_6): δ /ppm 116.0, 127.0, 132.0, and 156.0. NMR analysis of the crude product resulted in the following NMR data: ^1H (500 MHz, MeOH- d_4): δ /ppm 6.81 (d, 1.23H), 6.97-6.98 (d, 0.46H), 7.35 (d, 1.05H), 7.43-7.46 (d, 0.76H), and 7.83 (s, 0.11H); ^{13}C (500 MHz, DMSO- d_6): δ /ppm 115.6, 127.0, 131.2, and 156.2. The absence of ^{13}C signals around 85 ppm indicates that no aromatic iodination occurred. Though the H-NMR of the crude product seemed to have some contamination and is clearly different from starting material, comparison between the NMRs of 4,4-biphenol and the crude product show significant similarity in the C-NMRs.

As discussed in the introduction above, the electrophilic aromatic substitution of iodine is difficult without the assistance of an oxidant or further activation. This experiment was used to test if the increased resonance and hydroxyl activating groups were enough to induce iodination. Unfortunately, it was not enough, so further experiments enlisted the aid of oxidants or bases.

2. Attempted Polyiodination of 4,4-biphenol using triethylamine

Unlike previously, this reaction called for the use of a base to further activate the biphenol rings by deprotonating the -OH groups. The resulting

biphenoxide should encourage the attack on iodine, the electrophile, by the aromatic rings. A complication, however, arose with triethylamine and iodine. Triethylamine and iodine were found to react quickly and violently together. Spectroscopic studies on the reaction reported that the reaction produces I⁻ along with making an Et₃N-I⁺ intermediate.⁴ It is possible that this reaction interfered with the iodination of biphenol. The NMR data of the crude product was: ¹H (500 MHz, DMSO-d₆): δ/ppm 6.78(d, 4H), 6.93 (s, 1H), 7.35-7.37 (d, 2H), 7.39-7.41 (d, 1.5H), 7.45 (s, 1.5H), 7.82 (s, 0.01H), and 9.36 (s, 1H); ¹³C (500 MHz, DMSO-d₆): δ/ppm 115.6, 126.9, 127.1, 129.2, and 156.2. Regardless, the crude NMRs lacked the ChemDraw predicted ~87.0 carbon peaks, suggesting that no iodination took place. There was a single peak at 7.82 ppm where ChemDraw predicts ~7.80 ppm peaks, but the small size of the peak leaves doubt on its reliability. And as in the reaction without triethylamine, the material obtained does not seem to be starting material. The peculiar reaction between iodine and triethylamine indicated a different base needed to be used to avoid any unwanted interactions.

3. Attempted Diiodination of 4,4-biphenol using KOH

To avoid any odd interactions with iodine and triethylamine, the experiment was repeated with a different base, KOH. In addition, only 1.9 equivalence of iodine was used compared to the 4.4 equivalence in the two previous experiments. This was done in hopes to avoid the solubility problems characteristic of polyiodinated compounds. The crude product proved to be

incredibly insoluble in common NMR solvents such as DMSO-d₆, MeOH-d₄, CDCl₃ and 5% KOH in D₂O. Due to its insolubility, it was thought that an IR would reveal some information on the identity of the product. Comparison of an IR spectrum of the starting material 4,4-biphenol and the product showed the likely presence of hydroxyl groups in both, and possible differences in the fingerprint region around 1300 cm⁻¹. Any carbon-iodine shifts would be located below 600 cm⁻¹, far too low for detection using the current instrument. The failure of the previous few experiments resulted in an investigation on different procedures for iodination.

4. Triiodination of phenol using Sharma et al.'s method with sodium sulfite

Because the iodination of biphenol proved to be more difficult than previously expected, there was a need to find other iodination procedures to model the biphenol iodination after. Luckily, a few studies have been done on iodinating phenol, an almost identical compound to biphenol. A study by Sharma et al. offered two methods to triiodinate phenol: one method with sodium sulfite and one method without sodium sulfite.⁵ In both procedures, however, an oxidant, sulfuric acid, was used to prevent the reversal of the halogenation. For this project, the procedure with sodium sulfite was successful in creating 2,4,6-triiodophenol, as indicated by NMR. NMR analysis of the crude product yielded the NMR data: ¹H (500 MHz, CDCl₃): δ/ppm 7.93 (s, 2H) and 5.75 (s, 1H). These peaks match the reported peaks by Sharma et al. In addition, melting point analysis of the product also matched the literature value of 159-160°C. The total isolated yield was 84%.

5. *Triiodination of phenol using Sharma et al.'s method without sodium sulfite*

Sharma et al.'s procedure without sodium sulfite is, as the title says, the exact same but without sodium sulfite. It was also successful in creating 2,4,6-triiodophenol. Analysis of the product by NMR and melting point analysis gave the data: ^1H (500 MHz, CDCl_3): δ /ppm 7.93 (s, 1.95H) and 5.75 (s, 1H); 159-160°C. These values are identical to those from the procedure with sodium sulfite. The only difference between the two was that the total isolated yield of this procedure was 80%, 4% lower than the reaction with sodium sulfite.

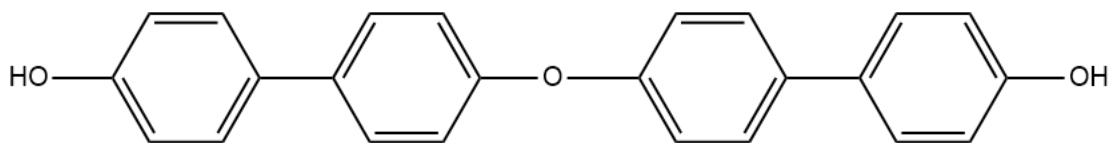
6. *Triiodination of phenol using aqueous ammonia*

Another procedure, using aqueous ammonia, was found to quantitatively produce 2,4,6-triiodophenol. After recrystallization from acetic acid, the total isolated yield using this method was 94%. NMR analysis and melting point analysis were identical to the previous two procedures. With two proven iodination procedures available, both were used in attempts to iodinate 4,4-biphenol.

7. *Attempted Iodination of 4,4-biphenol using aqueous ammonia*

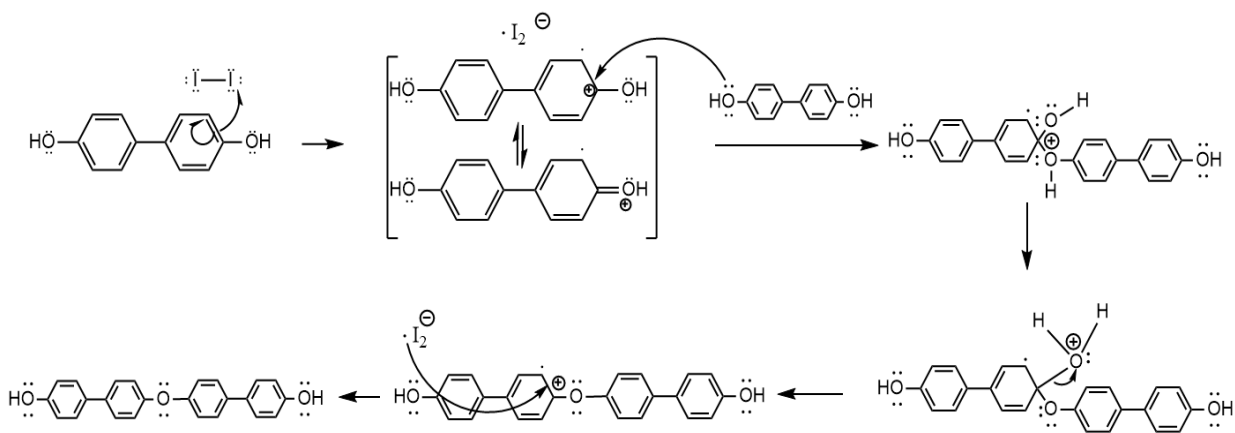
As the simplest of the three procedures, the aqueous ammonia method was the first to be used on biphenol. Analysis of the crude product yielded the NMR data: ^1H (500 MHz, DMSO-d_6): δ /ppm 6.77 (d, 0.98H), 6.91-6.93 (d, 1.71H), 7.37-7.39 (d, 4.28H), 8.31 (s, 0.04H), 9.22 (s, 1H), and 9.36 (s, 0.42H); ^{13}C ^1H (500 MHz, DMSO-d_6) 115.6, 116.2, 126.1, 127.1, 129.2, 131.1, 153.5,

and 156.2. In accordance with the general tone of this thesis, the iodination failed as the product lacked proton and carbon iodine peaks indicative of iodination. However, a new product had clearly formed. One possibility is that the biphenol may have dimerized or polymerized with itself. The C-NMR of the crude product roughly matches the ChemDraw predicted peaks of an ether dimer shown in Figure 3. A theoretical biphenol ether dimer has predicted C-NMR peaks of 116.4, 118.0, 128.8, 130.0, 133.4, 133.9, 155.9, and 157.4 ppm. Both the predicted and experimental spectra contain eight carbon peaks; their chemical shifts agree within ~1-2 ppm. A DEPT-Q spectrum of the product gave similar results. The product H-NMR is more puzzling. ChemDraw predicted four doublet peaks at 6.83, 7.27, 7.42, and 7.78 ppm for the ether dimer. The product NMR only contains three doublets. However, it is possible that the fourth doublet is hidden inside the 7.37-7.39 doublet. There was also some suspicion on the identity of the two peaks around 9.30 ppm. To confirm that the peaks were from the hydroxyl groups, a D₂O shake was done. As expected, the two peaks disappeared after D₂O was added to the NMR solution. Finally, an ESI mass spectrum was taken of the product. The predicted masses of the ether dimer were 354.1, 355.1, and 356.1 m/z. Both the positive and negative modes of the ESI mass spectrometer did not detect compounds of similar masses. Further polymerized versions of 4,4-biphenol were also not present in the mass spectra.



Structure 2. Shown is the structure of a biphenol ether dimer.

A possible mechanism for the formation of the ether dimer is shown below in Mechanism 1. The reaction begins with the creation of biphenol and iodine radicals. Though odd, the strong resonance helps to stabilize the radical. The reaction also forms a carbocation, making a site open to nucleophilic attack by another biphenol's hydroxyl group. Afterwards, the ether's hydrogen is removed and placed onto the adjacent -OH group which immediately leaves as water. Then, the iodine radical and dimer radical react together to restore aromaticity. Since the reaction procedure failed, Sharma's method was used next.



Mechanism 1. Shown is the proposed mechanism for the creation of an ether dimer from 4,4'-biphenol.

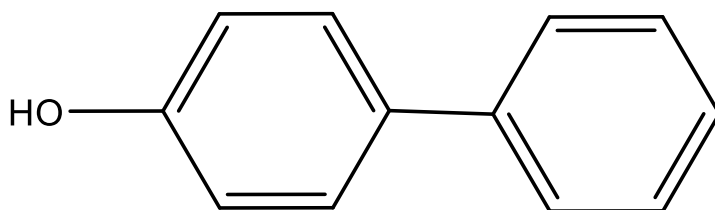
8. Attempted Iodination of 4,4-biphenol using Sharma et al.'s method without sodium sulfite

Like in Experiment 3, the diiodination of 4,4-biphenol, the product proved to be insoluble in most common NMR solvents such as DMSO-d₆, MeOH-d₄, CDCl₃ and 5% KOH in D₂O. The product was also analyzed by ESI mass spectrometry, but there were no relevant peaks. This may be due to the product's insolubility preventing the products from being vaporized for ionization. Again, it is possible that biphenol polymerized with itself, reducing its solubility. As in Experiment 3, an IR spectrum was taken of the product. The fingerprint region of the product also contained differences to the fingerprint of 4,4-biphenol around 1300 cm⁻¹. Because of the possible polymerization, a new compound 4-phenylphenol was introduced.

9. Attempted Iodination of 4-phenylphenol using Sharma et al.'s method without sodium sulfite

To control the possible polymerization, a different compound, shown in **Figure 3.**, with only one alcohol group was used. This would make any further polymerization impossible past an ether dimer. NMR analysis resulted in the following shifts: ¹H (400 MHz, DMSO-d₆): δ/ppm 7.15-7.17 (d, 0.12H), 7.32 (s, 0.40H), 7.41 (s, 1H), 7.58-7.60 (d, 0.60H), 7.66-7.68 (d, 0.23H), and 7.99-8.02 (d, 0.12H); ¹³C (300 MHz, DMSO-d₆): δ/ppm 117.7, 127.0, 127.1, 129.0, 129.1, 130.5, 130.7, 131.0, 140.5, 151.3 and 152.7. The iodination likely did not occur as the H-NMR lacks an 8.0 ppm peak and the C-NMR lacks the characteristic

carbon-iodine peak at 83 ppm for the mono-iodo product.⁸ A 4-phenylphenol ether dimer is also unlikely. NMR data of the ether dimer is: ¹H NMR (500 MHz, CDCl₃) δ/ppm 7.59 (m, 8H), 7.45 (m, 4H), 7.35 (m, 2H), 7.14 (m, 4H); ¹³C NMR (125 MHz, CDCl₃) δ/ppm 157.0, 140.8, 136.7, 129.0, 128.7, 127.3, 127.1, 119.4.⁹ Both the H-NMR and C-NMR of the product have little in common with the literature NMRs.



Structure 3. Shown is the structure of 4-phenylphenol, the new compound with only one alcohol group.

Conclusions.

In summary, the project failed to meet its original goal. Many of the reactions formed products with severely reduced solubility, making the products difficult to analyze at best. Other experiments did not react at all, with just starting material in the crude product. While the goal of creating a procedure to iodinate 4,4-biphenol through use of a ball miller was left unmet, efforts to do so resulted in discovering other reactions to explore. The possible polymerization of biphenol and its perplexing mechanism of formation would be one direction future researchers may do. The most obvious, however, is continuing to find a method of iodination for biphenol. Its activating alcohol groups and aromatic rings should make it prime for electrophilic aromatic substitution. Once a reliable reaction has been found, finishing the iodination with a ball miller will be in sight.

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Supporting Information.

1. Attempted Polyiodination of 4,4-biphenol

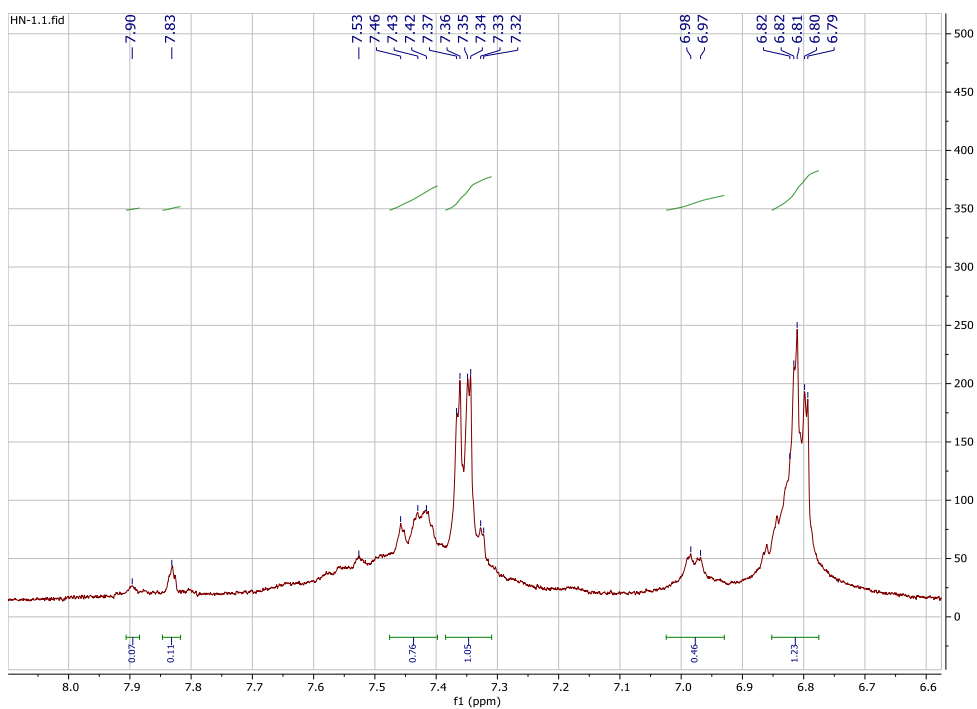


Figure 1. H-NMR in MeOH-d₄.

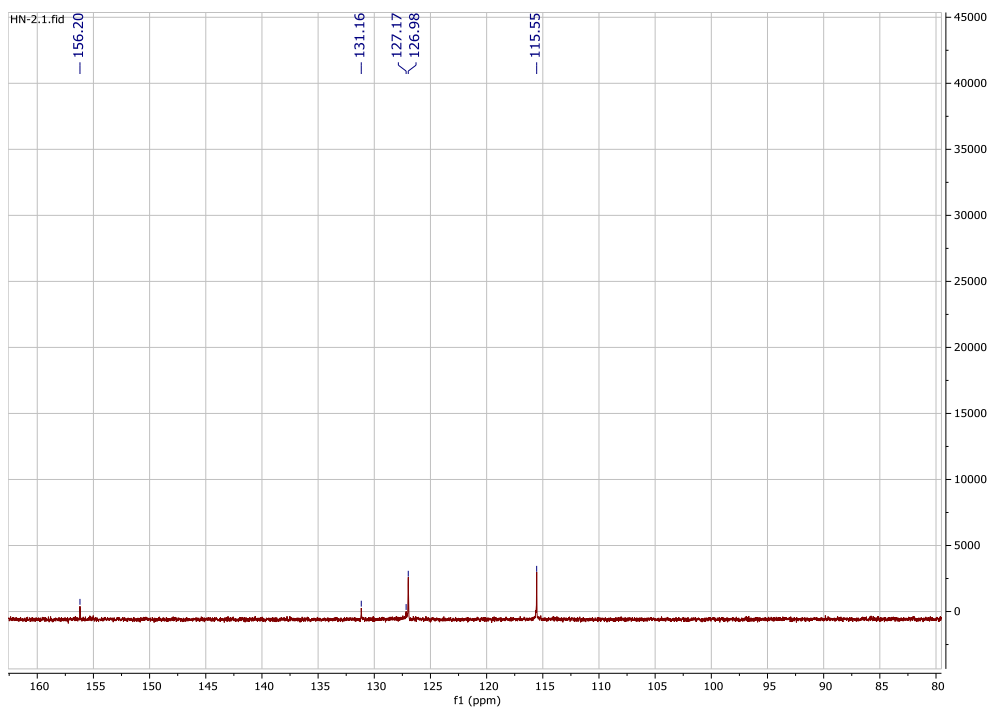


Figure 2. C-NMR in DMSO-d₆.

2. Attempted Polyiodination of 4,4-biphenol using triethylamine

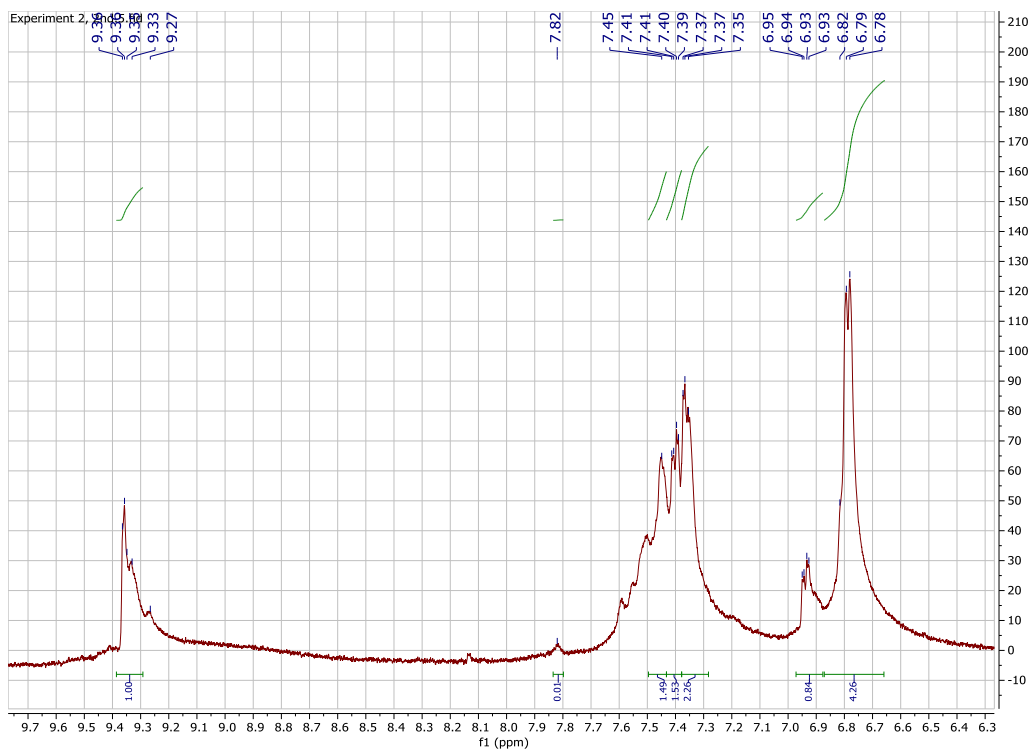


Figure 3. $^1\text{H-NMR}$ in DMSO-d_6 .

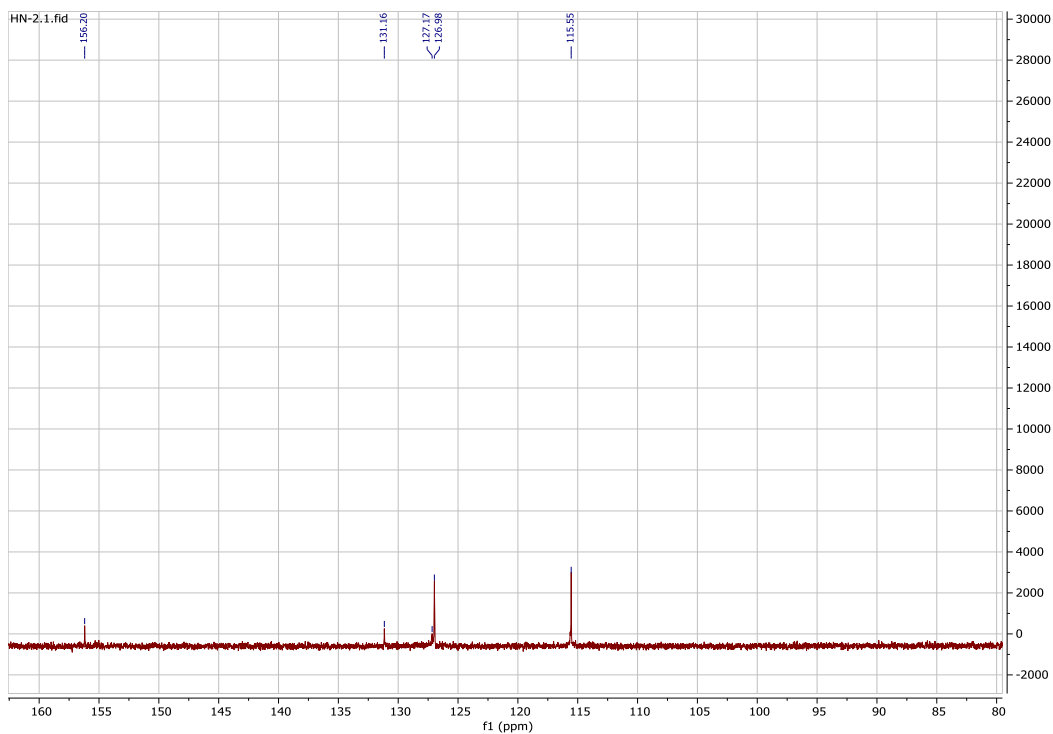


Figure 4. $^{13}\text{C-NMR}$ in DMSO-d_6 .

3. Attempted Diiodination of 4,4-biphenol using KOH

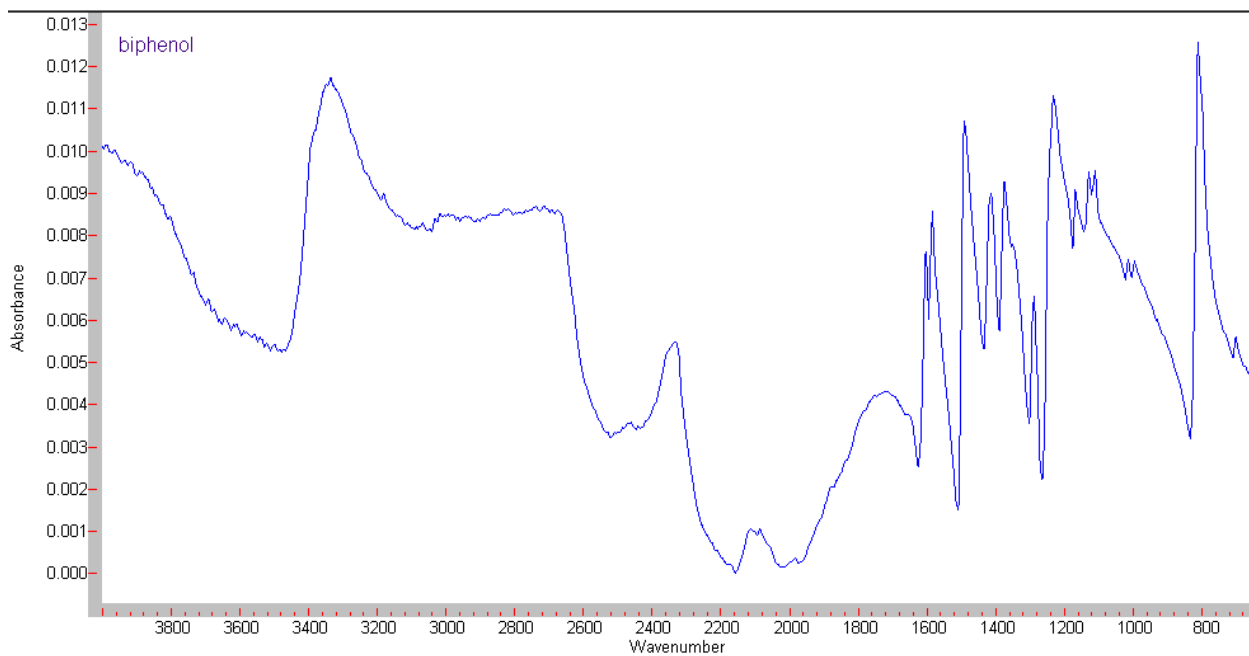


Figure 5. ATR-FTIR of 4,4-biphenol.

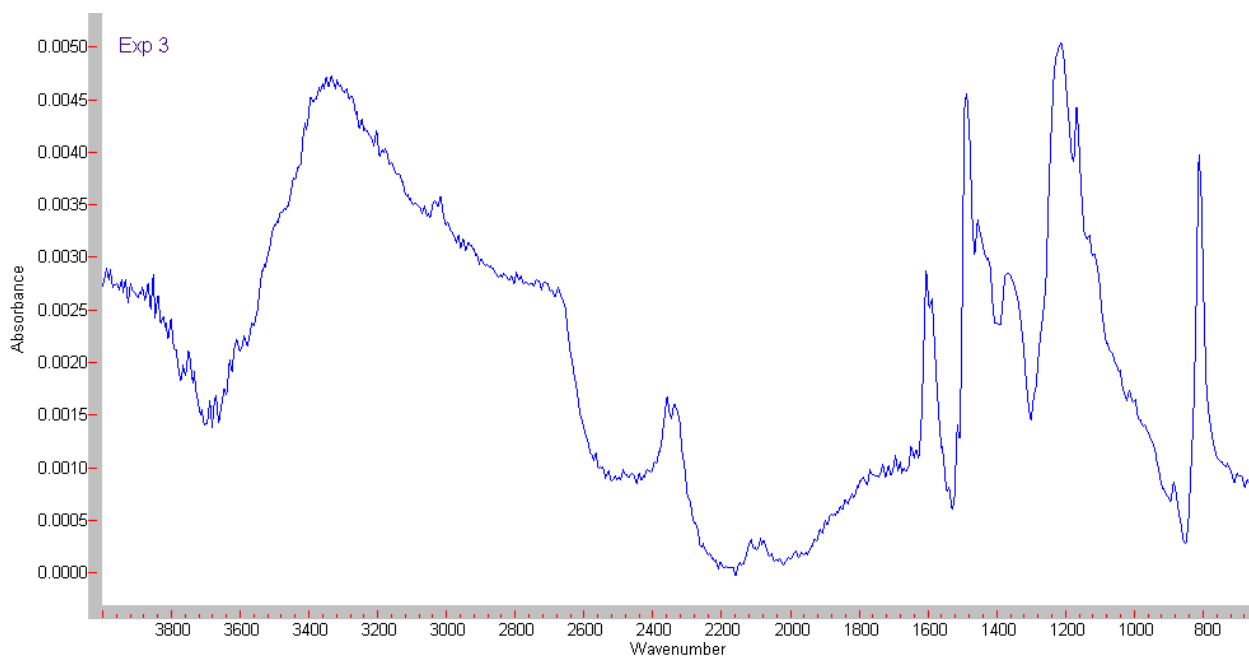


Figure 6. ATR-FTIR of product.

4. Triiodination of phenol using Sharma et al.'s method with sodium sulfite

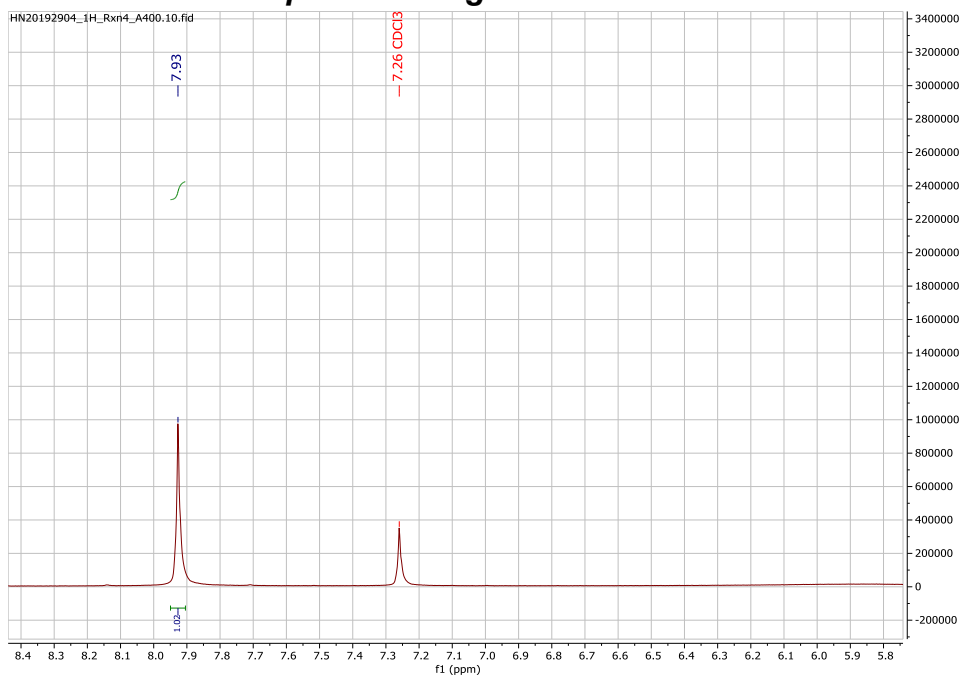


Figure 7. H-NMR in CDCl₃.

5. Triiodination of phenol using Sharma et al.'s method without sodium sulfite

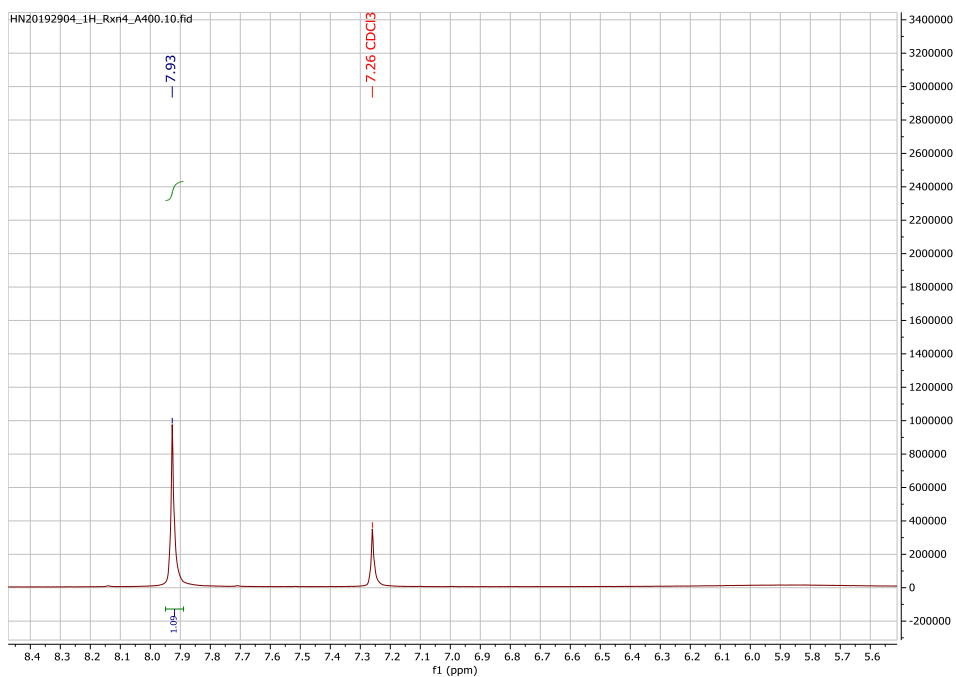


Figure 8. H-NMR in CDCl₃.

6. Triiodination of phenol using aqueous ammonia

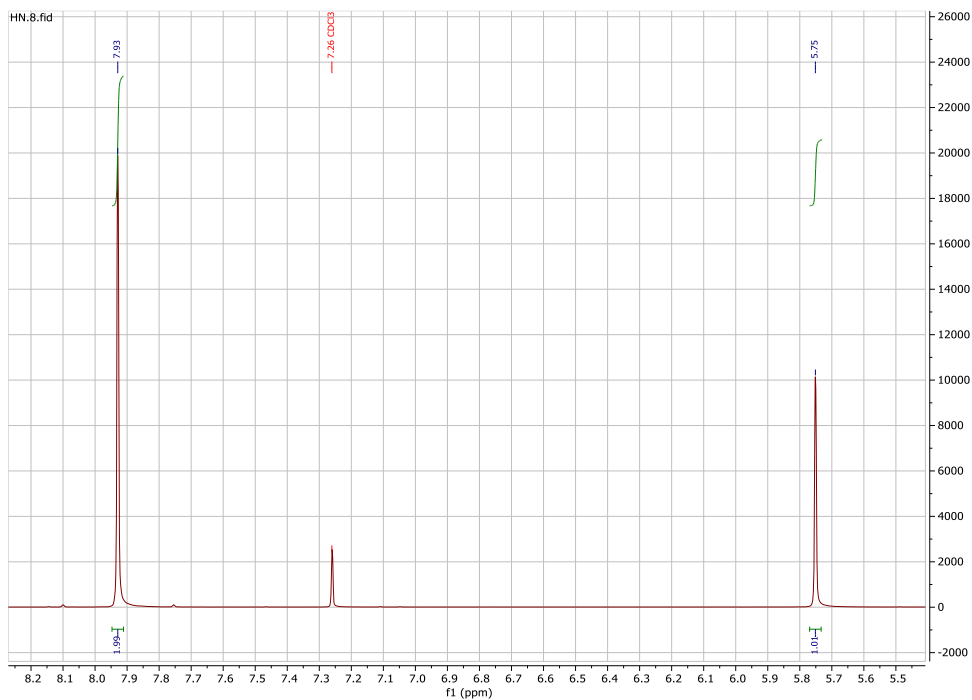


Figure 9. H-NMR in DMSO-d₆.

7. Attempted Iodination of 4,4-biphenol using aqueous ammonia

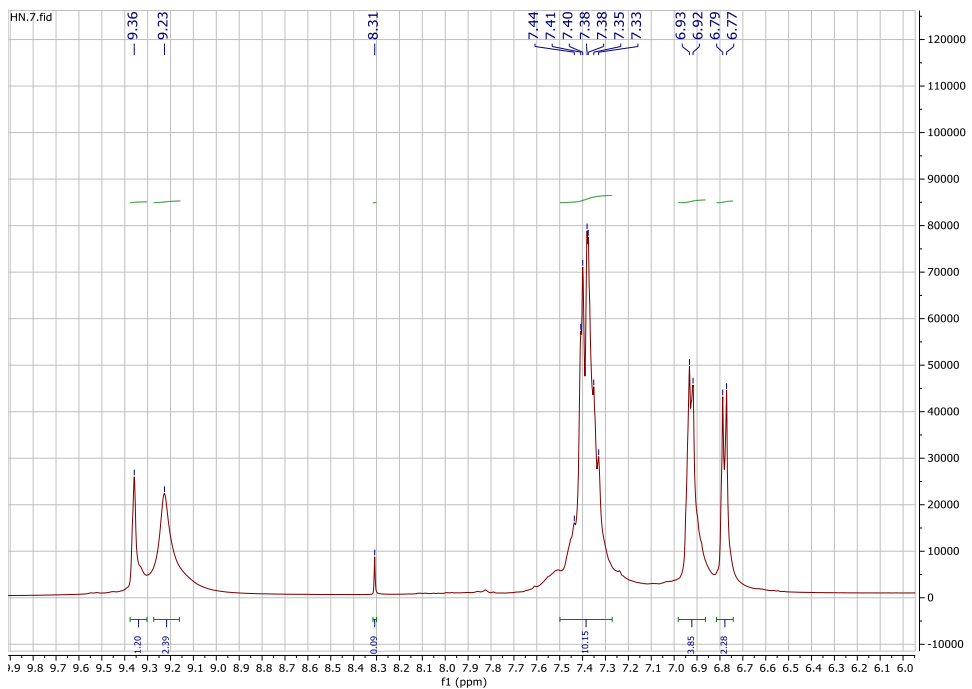


Figure 10. H-NMR in DMSO-d₆.

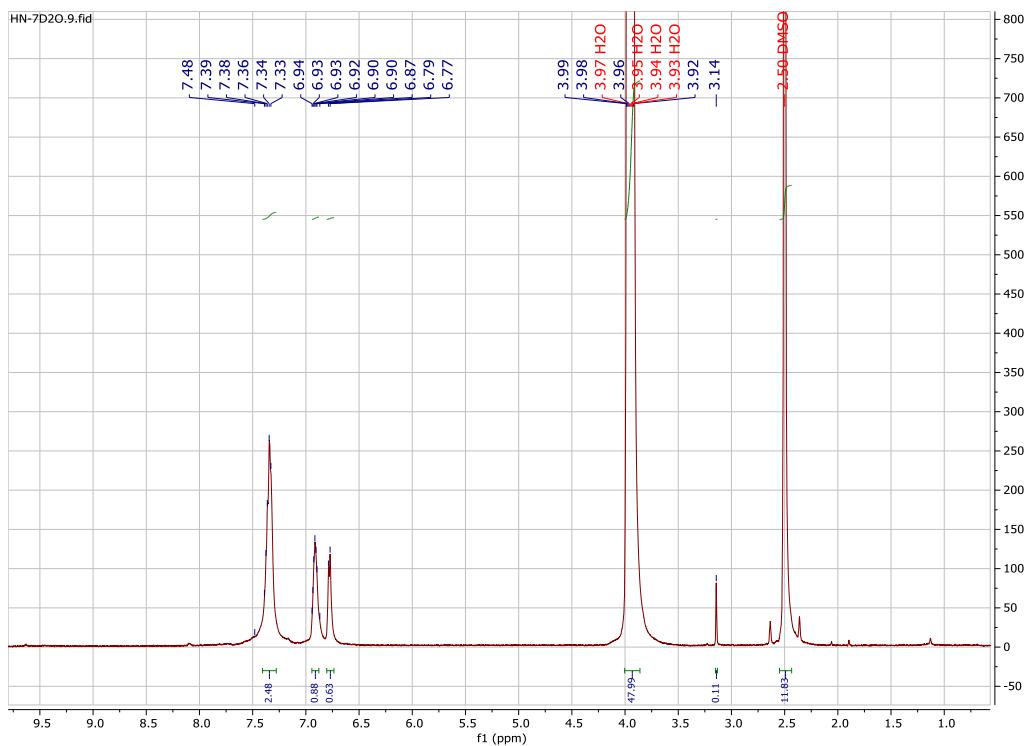


Figure 11. H-NMR in DMSO-d₆ with D₂O shake.

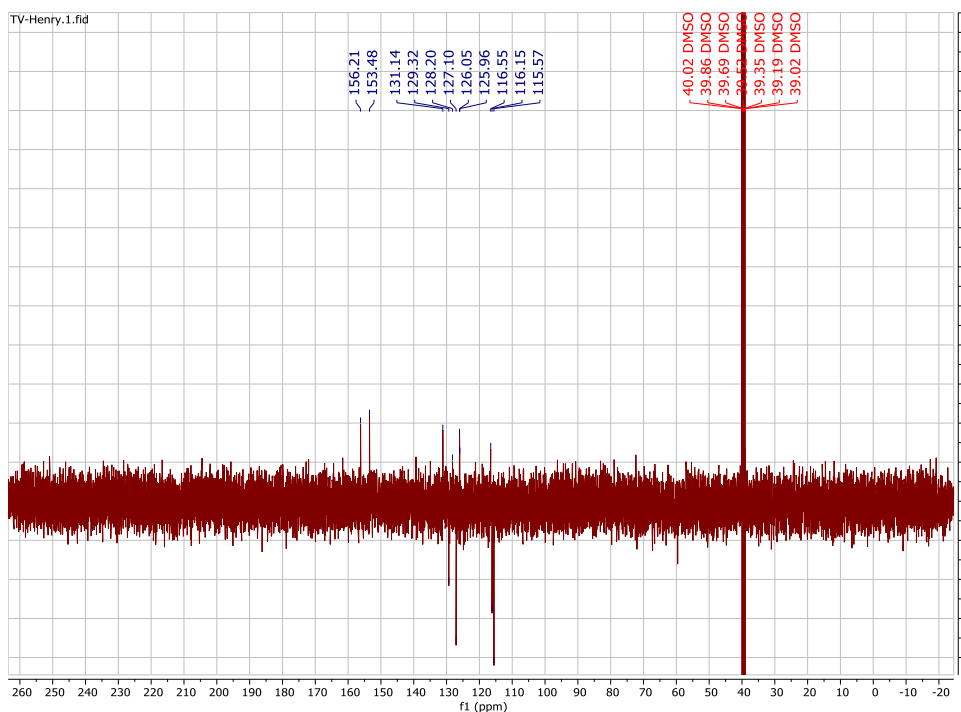


Figure 12. DEPT-Q in DMSO-d₆.

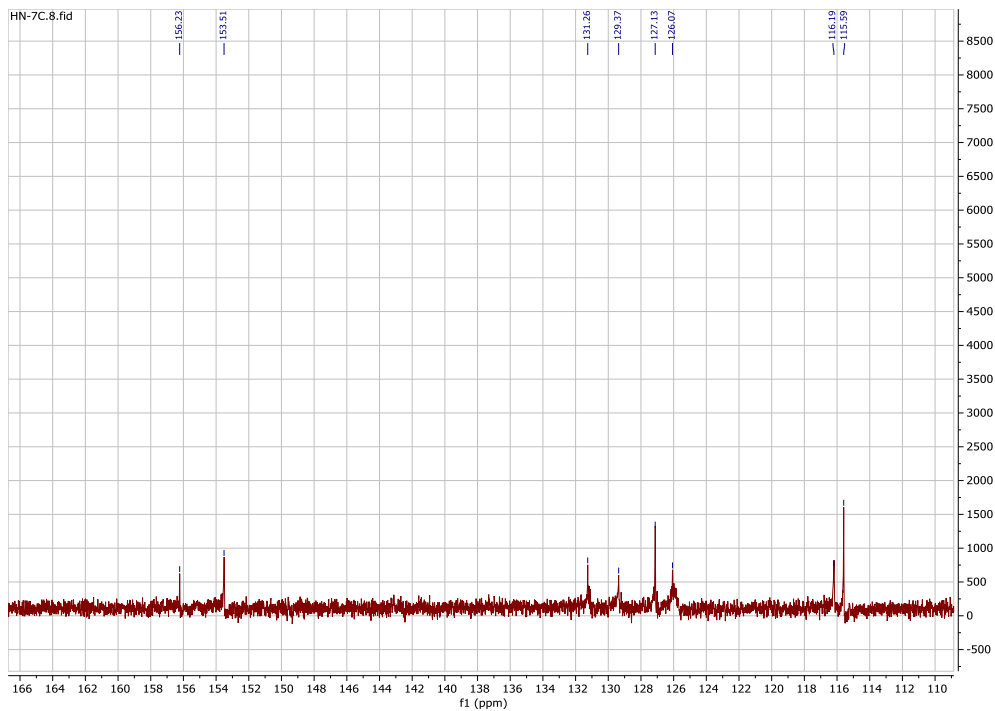


Figure 13. C-NMR in DMSO-d₆.

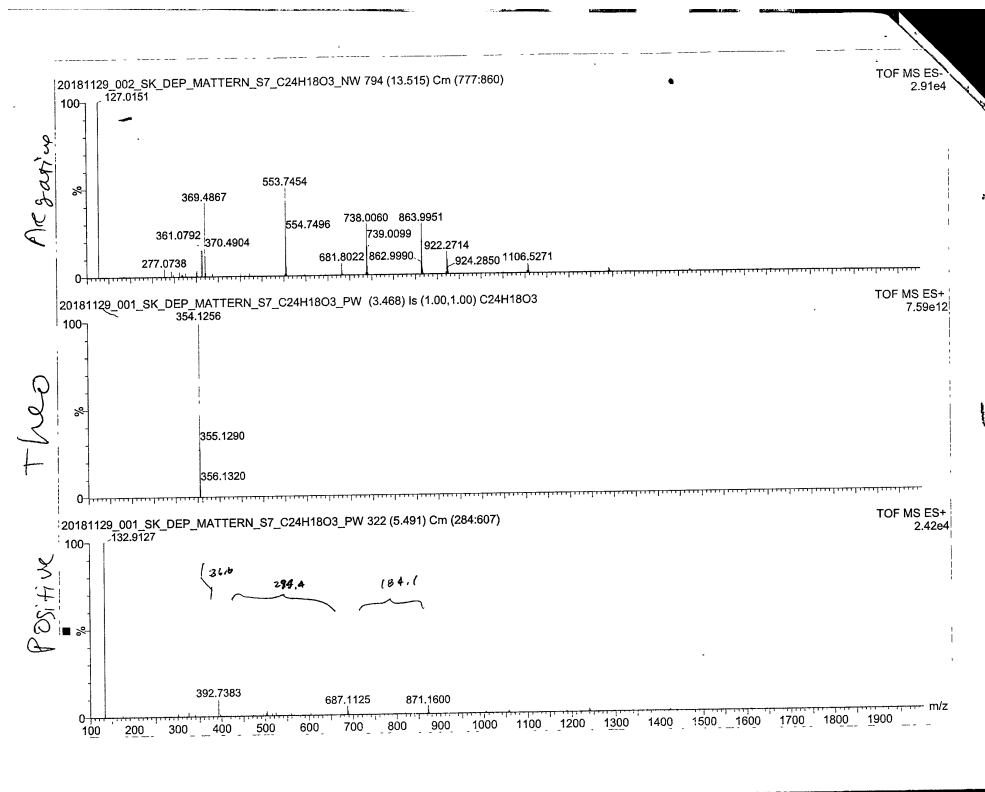


Figure 14. ESI Mass Spectrum.

8. Attempted Iodination of 4,4-biphenol using Sharma et al.'s method without sodium sulfite

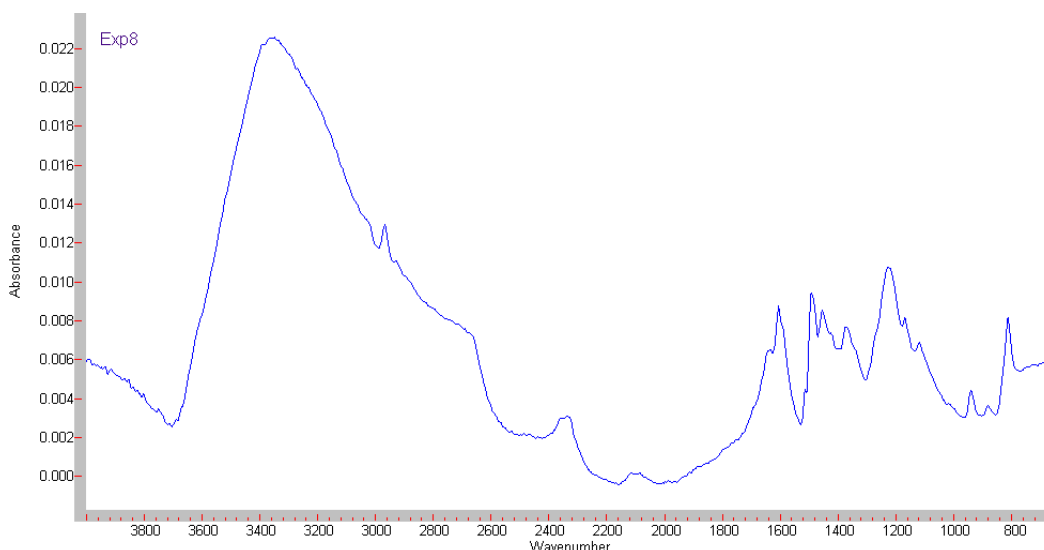


Figure 15. ATR-FTIR of product.

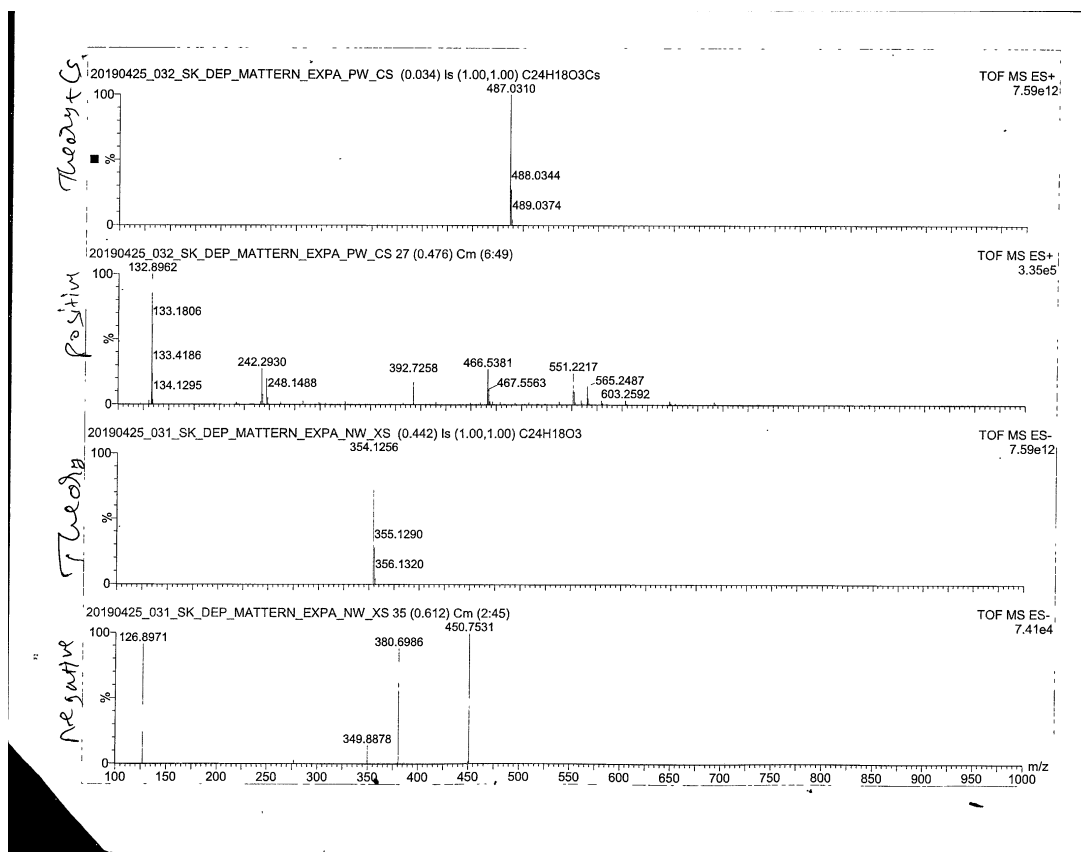


Figure 16. ESI Mass Spectrum.

9. Attempted Iodination of 4-phenylphenol using Sharma et al's method without sodium sulfite

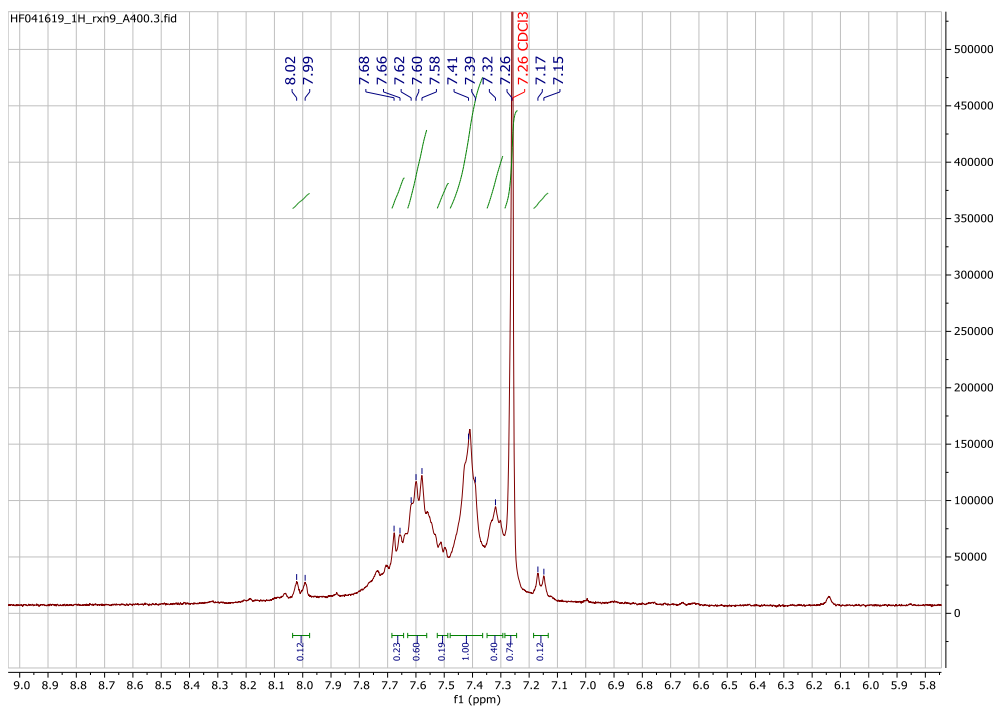


Figure 17. H-NMR in CDCl₃.

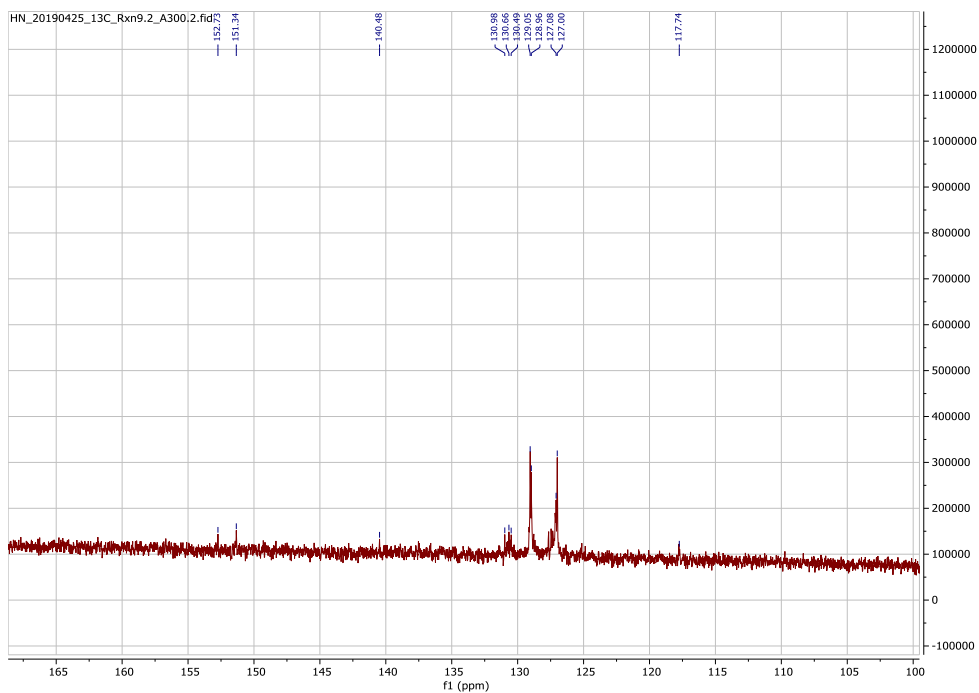


Figure 18. C-NMR in CDCl₃.