# The Effects of Substituents on Concerted Proton Electron Transfer in Base Appended Racial Cations

Francesca Marie Claire S. Simpson

Candidate for the degree

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Ian Rhile, Ph.D.

Michele Cramer, M.S.

Julia Heberle, Ph.D.

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Street Address: 483 BRIDGE ST

City, State, Zip Code: COLLEGEVILLE, PA 19426

# The Effects of Substituents on Concerted Proton-Electron Transfer in Base-Appended Radical Cations



Francesca Marie Claire S. Simpson

Department of Chemistry and Biochemistry

Albright College

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**Introduction:**

Proton and electron transfer are important in many chemical reactions. Proton transfer is accomplished by transferring a hydrogen atom that has lost its electron which leaves just the proton in the nucleus. Electron transfer is when one electron is transferred. In some reactions involving both electron and proton transfer, the electron will be transferred first, followed by the proton, or vice versa.[2] Concerted proton electron transfer, or CPET, is a reaction for which an electron and a proton are transferred to and from differing places on a molecule in one mechanistic step.[1] Chemical reactions will undergo the mechanism which requires the least amount of free energy. Molecules undergo CPET when the intermediates for the stepwise mechanism are higher in energy than the CPET barrier.[1]

The molecules that were studied in this work are base-appended radical cations. A radical cation is a molecule that has a positive charge on one of its atoms and an unpaired electron. These molecules tend to gain electrons. When a base is attached to a radical cation, it becomes a great model system for CPET. The base accepts the proton while the radical cation accepts the electron, which means that the accepting sites are spatially separated; this is necessary for CPET.[3]



Changes to the structure of a molecule can potentially change the reaction that it undergoes. Further separating the two accepting sites could change the concerted mechanism into a stepwise mechanism or it could slow the reaction. Another change is that substituents, or side groups, can be added to the molecule. Changing the substituents could change the bond strengths or change how readily the molecule can accept the electron or proton.

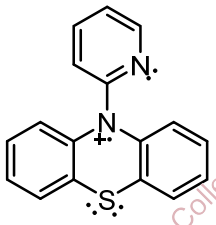
To characterize the molecular structure for the thermodynamics of the proton and electron gain, one can use the cyclic voltammetry and acid-base titration. Cyclic voltammetry is

used to find the reduction potential, or the measure of the tendency for a compound to gain an electron. A more positive reduction potential corresponds to a greater the tendency to gain electrons. Acid-base titration is used to find the p$K_a$, which is a measurement of how acidic the compound is. The smaller the number is, the more acidic the compound is, which means that the molecule is more likely to donate a proton. Its conjugate base will be less basic and less likely to gain a proton. With the reduction potential and the p$K_a$, the bond dissociation free energy (BDFE) can be calculated using the equation shown below.[4]

$$\text{BDFE} = 23.06E^{\circ} + 1.37\text{p}K_a + 54.90$$

The formula provides the BDFE in kcal/mol, and it is the amount of energy needed to break the bond in one mole of the compound, in this case the N–H bond of the product of CPET. The compound being more oxidizing or more basic will increase the bond strength.

There are several systems that were explored and compared to the parent compound10-(pyrid-2-yl)-10*H*-phenothiazine which can be seen below:

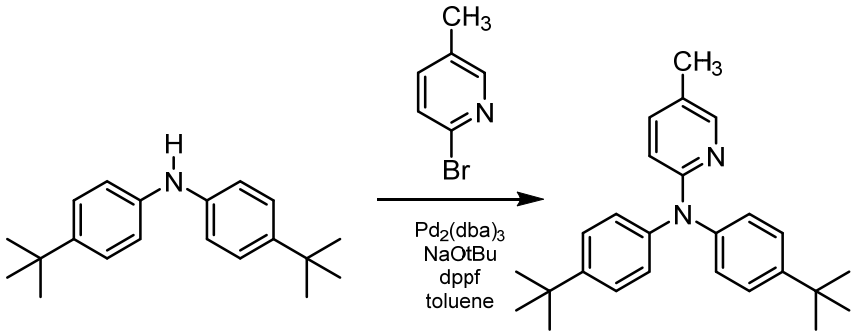




In one system, the sulfur atom was removed to see how delocalization of electrons affects the compound. In another system, chlorine as a substituent is added to test how changing the radical cation will affect the system. Then a system with both a methoxy group and a trifluoromethyl was used to determine if the effects of substituents on the base and radical cation are additive on the same system. A system with a methylene spacer and a trifluoromethyl group was developed

to determine the effect of separating the base from the cation. The last system that was investigated is one that has a methylene space but the sulfur atom has been removed. This was studied to see how separating the base and cation effect a system that has delocalized electron density.

**Experimental:**




**Scheme 1. Preparation of *N,N*-di-(4-*tert*-butylphenyl)-*N*-(2-pyridyl)amine**

**Procedure for the Preparation of *N,N*-di-(4-*tert*-butylphenyl)-*N*-(2-pyridyl)amine.[7,8]**

In a round bottom flask, 1.5649 g bis(*t*-butylphenyl)amine (5.560 mmol), 1.411 g sodium *tert*-butoxide (14.683 mmol), 38.6 mg BINAP (2,2'-bis(diphenylphosphino)-1,1'-binaphthyl, 0.062 mmol), 1.7589 g 2-bromo-5-methylpyridine (10.225 mmol), and 47.3 mg $Pd_2(dba)_3$ (0.052 mmol; dba = dibenzylideneacetone) were added to 25 mL of dry toluene. The reaction mixture was put under nitrogen and stirred at 70 °C for 24 h. An additional 40.1 mg $Pd_2(dba)_3$ (0.044 mmol) and 33.8 mg BINAP (0.054 mmol) were added. The reaction was monitored by TLC until completion. The reaction mixture was cooled to room temperature before being filtered through Celite and washed with ethyl acetate, and the solvent was removed under reduced pressure. The

crude product was subjected to column chromatography. The column was eluted with 20/1 to 10/1 to 6/1 to 2/1 v/v hexanes/toluene, and the eluent was removed under reduced pressure to yield an impure product. A second column eluted with 1/1 v/v hexanes/ethyl acetate separated the product. The solid was recrystallized using hexanes to isolate 0.6669 g of a solid (32.19%). $^{1}$H NMR (400 MHz, $CDCl_3$): δ 8.061 (s, 1H), 7.252-7.305 (t, 4H), 7.051-7.072 (d, 4H), 6.659-6.681 (d, 1H), 2.216 (s, 3H), 1.551 (s,1H), 1.303 (s, 18H) ppm; mp 121.1-122.4 °C.

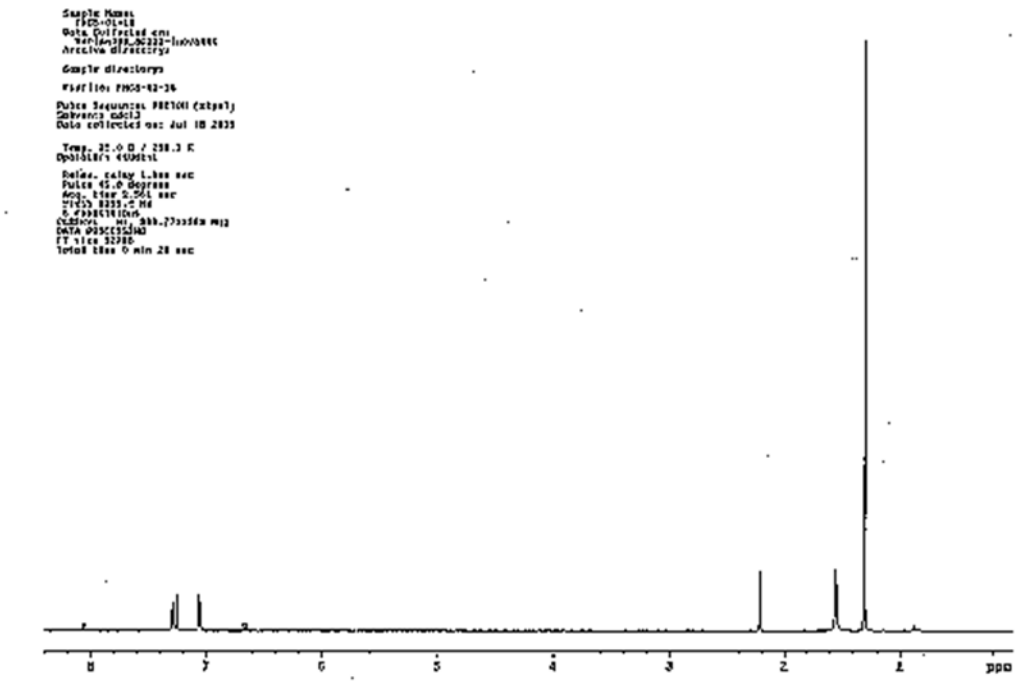


**Figure 1. $^{1}$H NMR spectrum of *N,N*-di-(4-*tert*-butylphenyl)-*N*-(2-pyridyl)amine.**

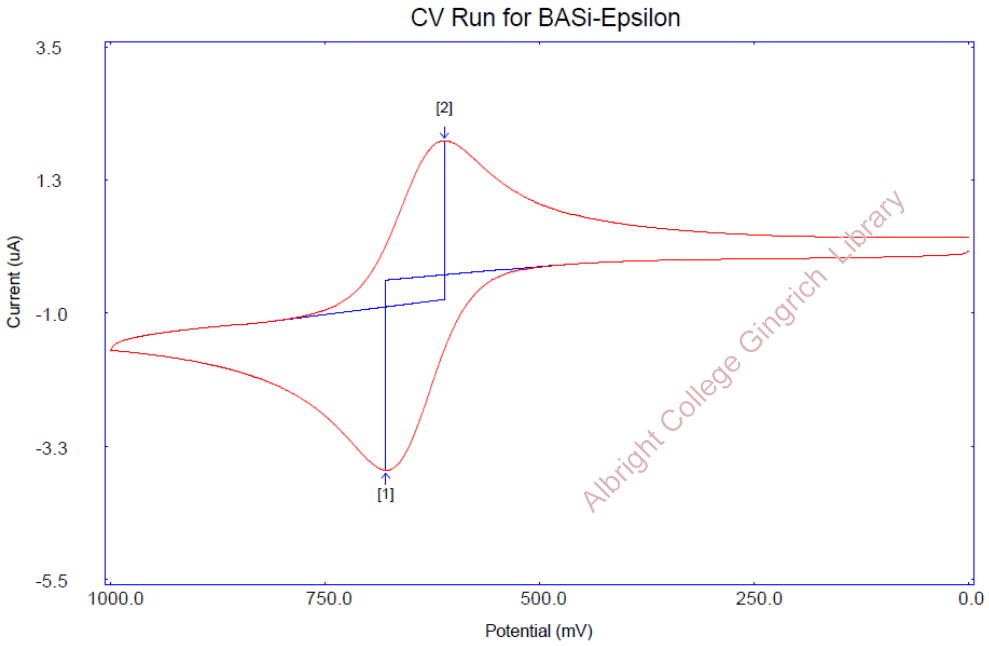



**Figure 2. Cyclic voltammogram for *N,N*-di-(4-*tert*-butylphenyl)-*N*-(2-pyridyl)amine.**

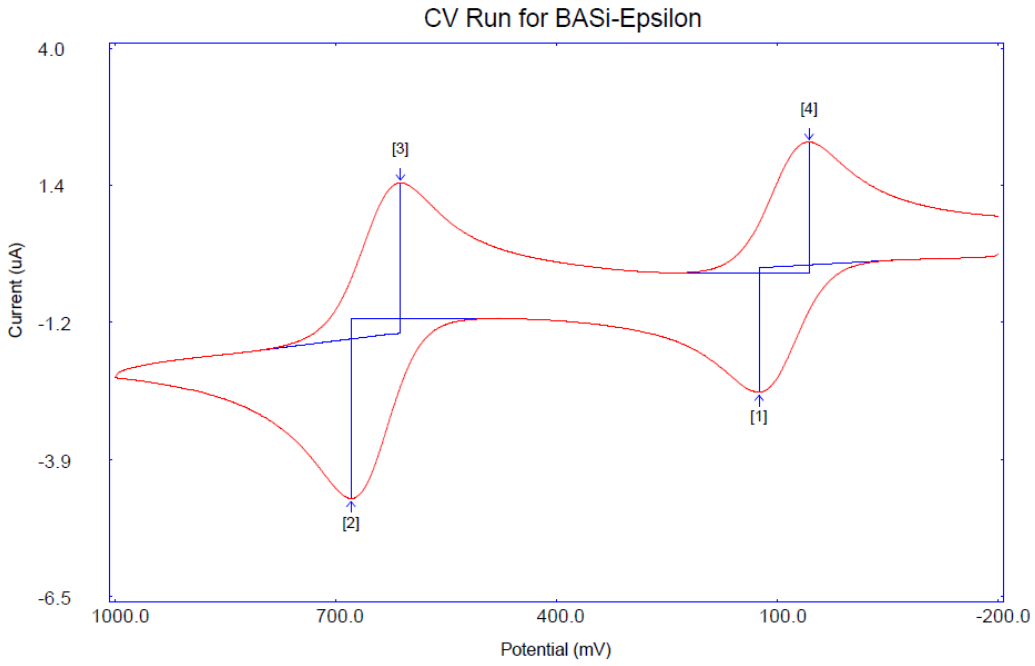



**Figure 3. Cyclic voltammogram for *N,N*-di-(4-*tert*-butylphenyl)-*N*-(2-pyridyl)amine with ferrocene internal standard.**

**Cyclic Voltammetry.** The galvanostat-potentiostat was setup with three electrodes: A platinum wire electrode (auxiliary), a platinum disc electrode (working), and an $Ag/AgNO_3$ electrode (reference). 0.9686 g tetra-*n*-butylammonium hexafluorophosphate ($NBu_4PF_6$: 2.5 mmol) was dissolved in 25 mL of acetonitrile to make the electrolyte solution (0.1 M). *N,N*-Di-(4-*tert*-butylphenyl)-*N*-(2-pyridyl)amine was added to the electrolyte solution and the cyclic voltammogram was obtained. Then, ferrocene was added to the solution as an internal standard (0 V). A reduction potential of 0.55 V was obtained versus the ferrocenium-ferrocene couple.



**Acid-Base Titration.[5] General Procedure.** The appropriate indicator was dissolved in 20.00 mL acetonitrile. 1.00 ml of the solution was diluted to 15.00 mL. 3.00 mL of the solution was

syringed into a cuvette. A measured amount of purified radical cation precursor was dissolved in 4.00 mL of acetonitrile to obtain a second solution. The UV-vis spectrometer was blanked using a cuvette of acetonitrile. A spectrum was taken of the solution, and the absorbance at the $\lambda_{max}$ was measured. 50 µL of the second solution was added to the indicator at a time and the spectrum was taken after each addition. The absorbance was recorded at the $\lambda_{max}$. More than 15 additions were done. The spectrum of the acetonitrile was taken as a baseline.

***Attempt 1:*** 8.6 mg of thymol blue was used for the first solution and 13.4 mg of the purified material was used in the second solution. The indicator was entirely deprotonated by the compound.

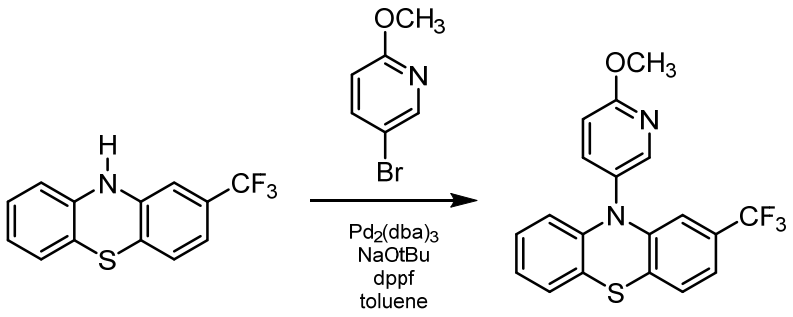
***Attempt 2:*** 4.5 mg of *p*-nitrophenol was used for the first solution and 13.5 mg of the purified product was used in the second solution. The indicator was not deprotonated at all.

***Attempt 3:*** 3.7 mg of bromophenol blue was used in the first solution and 13.5 mg of the purified product was used in the second solution. The results were inconclusive due to the indicator being diprotic.

***Attempt 4:*** 8.7 mg of 2,4-dinitrophenol was used in the first solution and 13.4 mg of the purified product was used in the second solution. The p$K_a$ was determined to be 13.1.



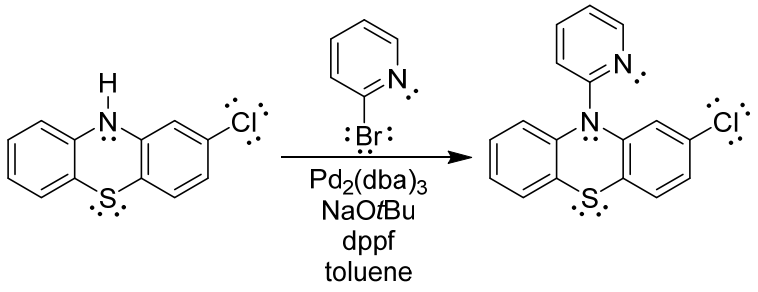
**Procedure for the Preparation of the Radical Cation.** 2.1 mg of purified solid (0.006 mmol) and 2.3 mg tris(4-bromophenyl)aminium hexachloroantimonate (0.003 mmol) were put into separate vials which were then filled with 10.0 mL of acetonitrile. The vials were then combined. A UV-vis was taken of the radical cation. The $\lambda_{max}$ was determined to be 490 nm.




**Scheme 2. Preparation of 2-trifluoromethyl-10-(4-methoxypyrid-3-yl)-10*H*-phenothiazine**

**Procedure for the Attempted Preparation of 2-trifluoromethyl-10-(4-methoxypyrid-3-yl)-10*H*-phenothiazine.[7,8]**

In a round bottom flask, 2.4804 g 2-(trifluoromethyl)phenothiazine (9.281 mmol), 1.3967 g sodium *tert*-butoxide (14.534 mmol), 36.0 mg DPPF (1,1'-bis(diphenylphosphino)ferrocene, 0.065 mmol), 1.35 mL 5-bromo-2-methoxypyridine (1.9616 g, 10.433 mmol), and 49.6 mg $Pd_2(dba)_3$ (0.054 mmol) were added to 25 mL of dry toluene. The reaction mixture was put under nitrogen and refluxed for 24 h. Additional 39.9 mg $Pd_2(dba)_3$ (0.044 mmol) and 31.1 mg DPPF (0.056 mmol) were added as well as 7.4 mg 2,8,9-tributyl-2,5,8,9-tetraaza-1-phosphabicyclo[3.3.3]undecane (0.022 mmol). The reaction was monitored by TLC until completion. The reaction mixture was cooled to room temperature before being filtered through Celite washed with ethyl acetate, and the solvent was removed under reduced pressure. The crude was subjected to column chromatography (3/1 v/v hexanes/toluene, then 1/1 v/v hexanes/toluene). The TLC plates showed that one of the reagents was being separated with the product. The solvent was removed under reduced pressure and a $^1$H NMR was taken. TLC results concluded that while there was product, it was mixed with starting material.




**Scheme 3. Preparation of 2-chloro-10-(pyrid-2-yl)-10*H*-phenothiazine**

**Procedure for the Preparation of 2-chloro-10-(pyrid-2-yl)-10*H*-phenothiazine.[7,8]**

In a round bottom flask, 2.1249 g 2-chlorophenothiazine (9.092 mmol), 1.3987 g sodium *tert*-butoxide (14.554 mmol), 32.6 mg DPPF (0.059 mmol), 1.6731 g 2-bromopyridine (10.589 mmol), and 40.3 mg $Pd_2(dba)_3$ (0.044 mmol) were added to 25 mL of dry toluene. The reaction mixture was put under nitrogen and refluxed for 24h. Additional 38.2 mg $Pd_2(dba)_3$ (0.041 mmol) and 30.7 mg DPPF (0.055 mmol) were added. The reaction was monitored by TLC until completion. The reaction mixture was cooled to room temperature before being filtered through Celite washed with ethyl acetate, and the solvent was removed under reduced pressure. The crude was subjected to column chromatography (3/1 v/v hexanes/toluene, then 1/1 v/v hexanes/toluene). The solid was recrystallized using ethanol to isolate 0.890 g of a solid (31.50%). $^1$H NMR (400 MHz, $CDCl_3$): 8.350-3.375 (dd), 7.59 9 (d), 7.565 (d), 7.551 (d), 7.534 (d), 7.385 (d), 7.358 (d), 7.348 (d), 7.322 (d), 7.259 (t), 7.237 (d), 7.225 (s), 7.211 (d), 7.152 (d), 7.126 (d), 7.102 (d), 7.077 (d), 7.010 (s), 6.965-6.990 (m), 6.949 (s); mp 103.67-106.50 °C.

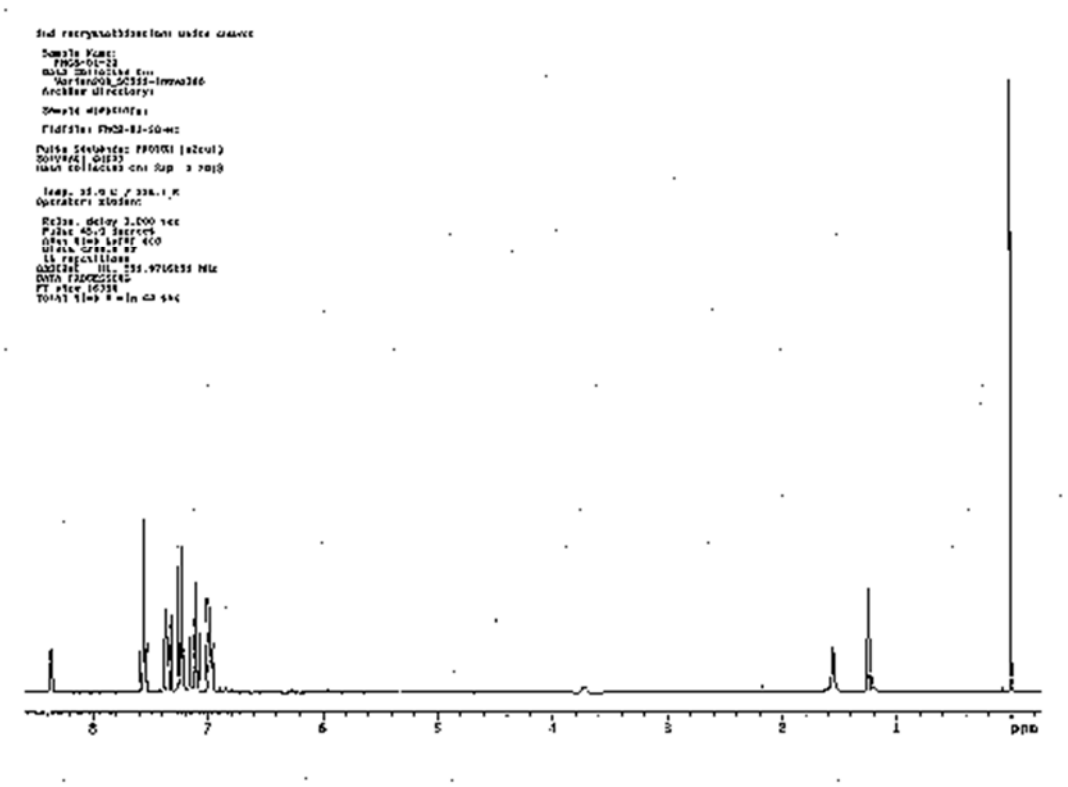



**Figure 4. $^{1}$H NMR spectrum of 2-chloro-10-(pyrid-2-yl)-10*H*-phenothiazine.**

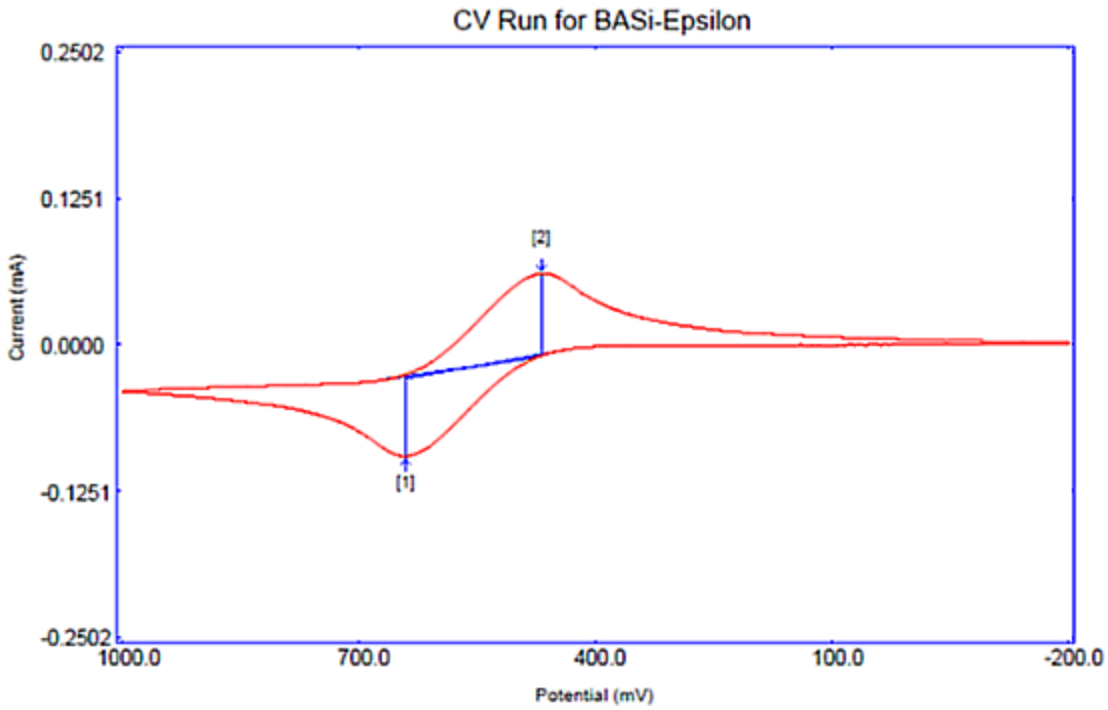



**Figure 5. Cyclic voltammogram for 2-chloro-10-(pyrid-2-yl)-10*H*-phenothiazine.**

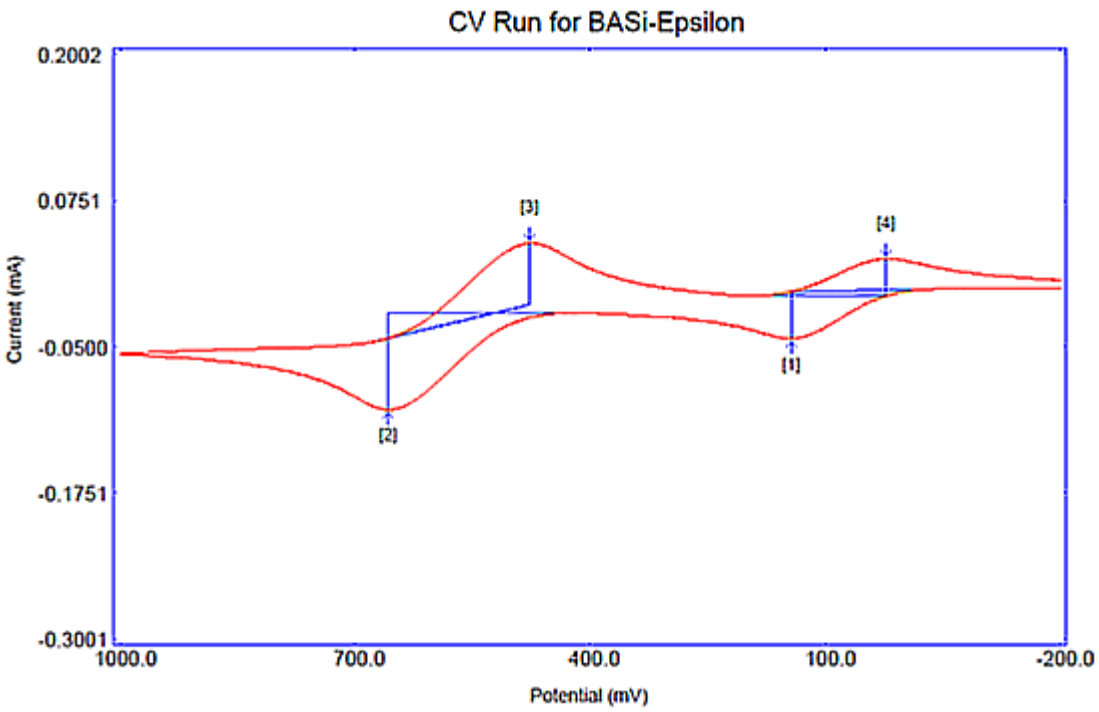



**Figure 6. Cyclic voltammogram for 2-chloro-10-(pyrid-2-yl)-10*H*-phenothiazine with ferrocene internal standard**

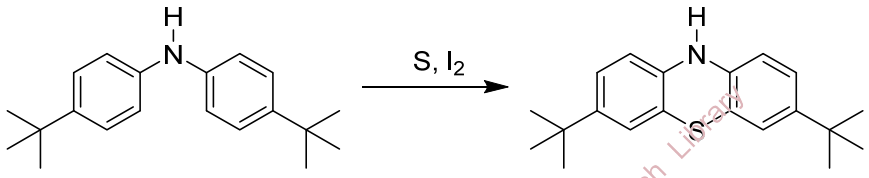
**Cyclic Voltammetry.** The galvanostat-potentiostat was setup with three electrodes: A platinum wire electrode (auxiliary), a platinum disc electrode (working), and an $Ag/AgNO_3$ electrode (reference). 0.9686 g tetra-*n*-butylammonium hexafluorophosphate ($NBu_4PF_6$: 2.5 mmol) was prepared in 25 mL of acetonitrile (0.1 M) to create the electrolyte solution. 10-(2-Pyridinyl-methyl)-2-trifluoromethyl-10*H*-phenothiazine was added to the electrolyte solution. Then, ferrocene was added to the solution as an internal standard (0 V). A reduction potential of 485 mV was obtained versus ferrocene.



**Acid-Base Titration.** The indicator was dissolved in 20.00 mL acetonitrile. 1.00 ml of the dilute solution was taken and then diluted to 15.00 mL. 3.00 mL of the solution was syringed into a

cuvette. A second solution was mixed in a vial using the purified material and 4.00 mL of acetonitrile. The UV-vis spectrometer was blanked using a cuvette of acetonitrile. A spectrum was taken of the solution cuvette at 395 nm, the $\lambda_{max}$ for the compound.[5] 50 µL of the second solution was added to the indicator at a time and the spectrum was taken after each addition. The absorbance was recorded at the $\lambda_{max}$ for more than 15 additions. The spectrum of the acetonitrile was taken as a baseline at the $\lambda_{max}$. 8.7 mg of thymol blue was used for the first solution and 13.8 mg of the purified material was used in the second solution. A p$K_a$ of 10.6 was determined.

**Procedure for the Preparation of the Radical Cation.** 2.1 mg of purified solid (0.0068 mmol) and 2.3 mg tris(4-bromophenyl)aminium hexachloroantimonate (0.003 mmol) were put into separate vials which were then filled with 10 mL of acetonitrile. The vials were then combined. A UV-vis was taken of the radical cation. The $\lambda_{max}$ was determined to be 528 nm.

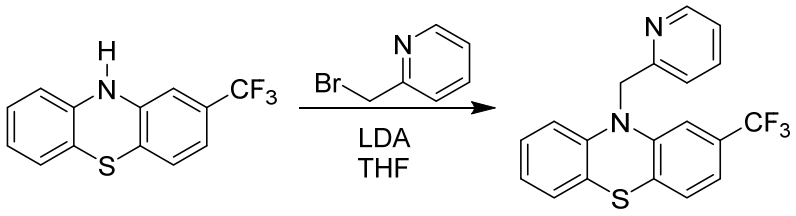



**Scheme 4. Preparation of 3,7-bis(1,1-dimethylethyl)-10 *H*-phenothiazine**



**Procedure for the attempted preparation of 3,7-bis(1,1-dimethylethyl)-10*H*-phenothiazine.** In a round bottom flask, 0.9218 g bis(4-*tert*-butylphenyl)amine (12.60 mmol), 0.4566 g sulfur (14.24 mmol), and 0.1467 g iodine (0.58 mmol) were added to 50 mL of 1,2-dichlorobenzene. The reaction mixture was placed under nitrogen and refluxed for 24 h. The reaction was monitored by TLC until completion. A simple distillation was done on the reaction mixture with

the temperature fluctuating between 170-179 °C. Another TLC was done on the distilled reaction solution. A GC-MS spectrum was taken of the reaction solution. The spectrum indicated a complex reaction mixture with no prominent peak that belonging to the desired product, leading to the conclusion that separation of the product, if present, would be difficult.




**Scheme 5. Preparation of 10-(2-pyridinylmethyl)-2-trifluoromethyl-10*H*-phenothiazine.**

**Procedure for the Preparation of 10-(2-pyridinylmethyl)-2-trifluoromethyl-10-*H*-phenothiazine.[10,11]**

In a three-neck round bottom flask, 2.25 mL previously distilled diisopropylamine, 10 mL 1.6 M butyllithium in hexane, 1.0012 g 2-trifluoromethyl-10*H*-phenothiazine (3.75 mmol), and 1.5534 g 2-(bromomethyl)pyridine hydrobromide (6.14 mmol), were added to 20 mL THF. The reaction mixture was stirred overnight under nitrogen. The reaction was monitored by TLC. The reaction mixture was then transferred to a separatory funnel and diluted with ethyl acetate. The organic layer was extracted with deionize water and brine. The organic layer was transferred to a flask and dried using magnesium sulfate. The drying agent was filtered off and the solvent was removed from the reaction mixture under pressure. The crude was subjected to column chromatography. The solvent 15/1/2 v/v hexanes/ethyl acetate/toluene was used but was switched to 49/31/20 v/v hexanes/ethyl acetate/ toluene halfway through the chromatography to draw off more product. The solvent was removed under reduced pressure and a $^1$H NMR was

taken. Various crystallization techniques were attempted, but the compound remained a dark red oil. $^1$H NMR (400 MHz, $CDCl_3$): 8.633 (dd), 8.620 (dd), 7.606 (d), 7.587 (d), 7.568 (d), 7.288 (s), 7.268 (s), 7.252 (s), 7.202 (s), 7.190 (s), 7.170 (s), 7.092-7.123 (m), 7.047 (d), 7.028 (dd), 7.008 (d), 6.933 (d), 6.915 (d), 6.896 (d), 6.833 (s), 6.691 (d), 6.671 (d), 1.565 (s, 3H) p

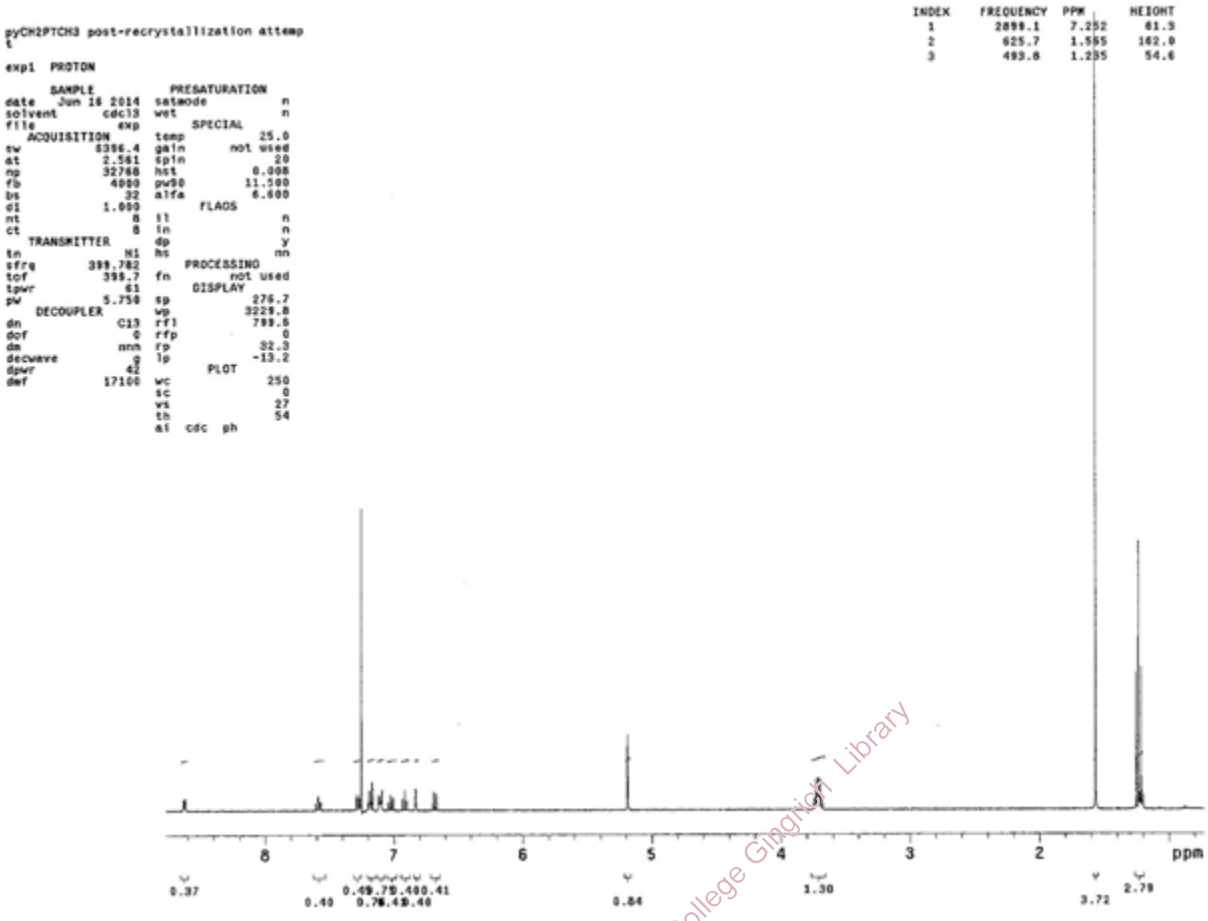





**Figure 7. $^1$H NMR spectrum of 10-(2-pyridinylmethyl)-2-trifluoromethyl-10*H*-phenothiazine.**

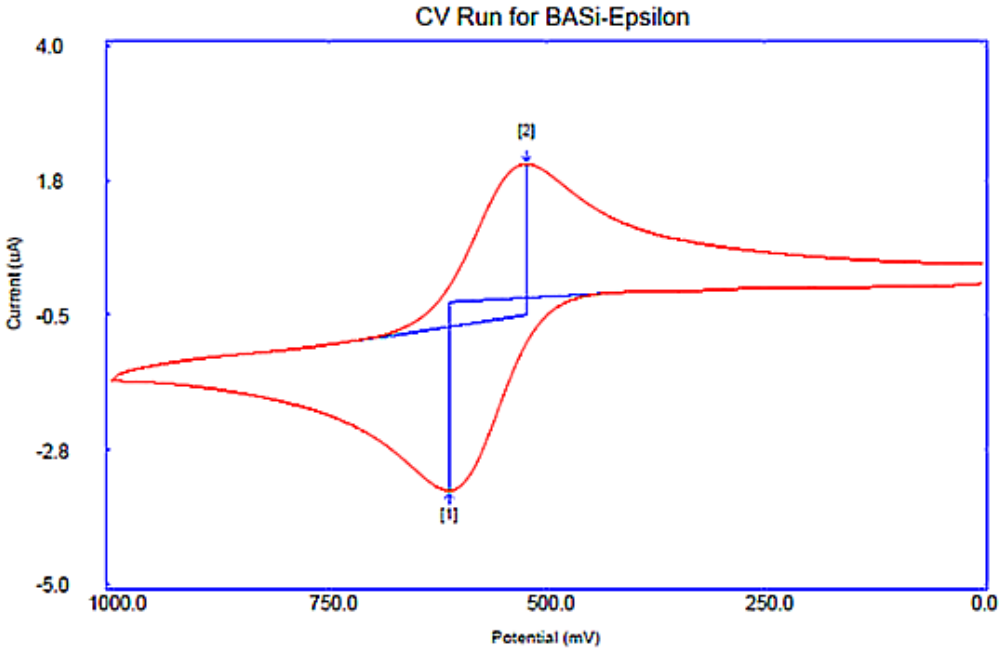



**Figure 8. Cyclic voltammogram for 10-(2-pyridinylmethyl)-2-trifluoromethyl-10*H*-phenothiazine.**

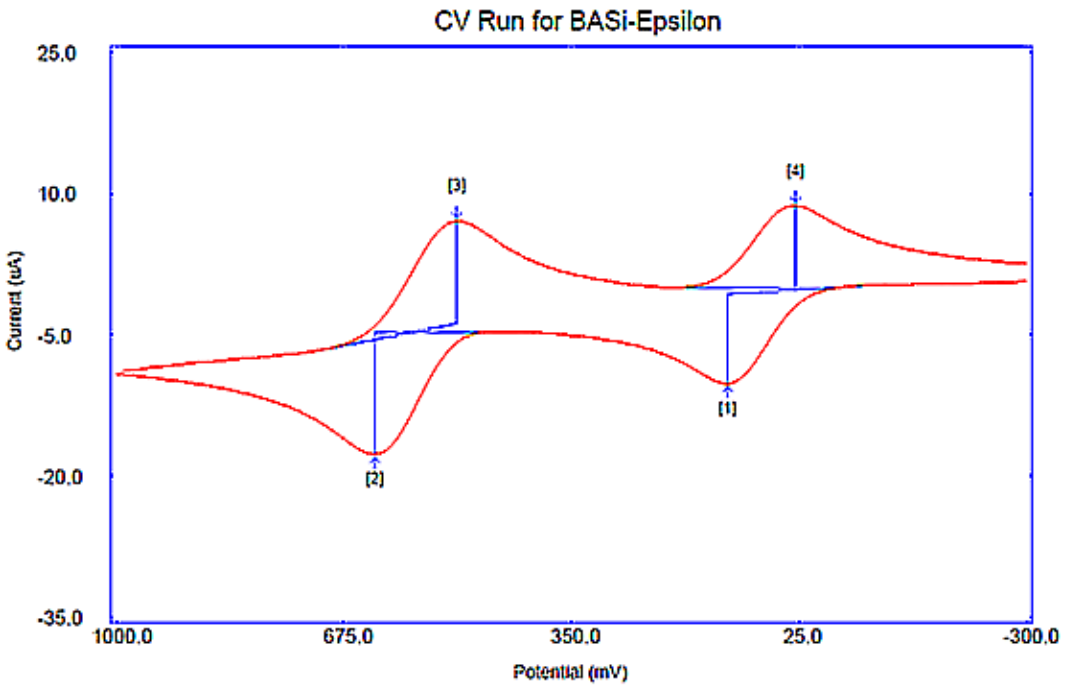
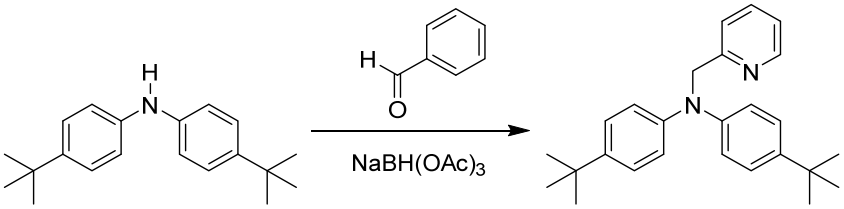



**Figure 9. Cyclic voltammogram for 10-(2-pyridinylmethyl)-2-trifluoromethyl-10*H*-phenothiazine with ferrocene internal standard.**

**Cyclic Voltammetry.** The galvanostat-potentiostat was setup with three electrodes: A platinum wire electrode (auxiliary), a platinum disc electrode (working), and an $Ag/AgNO_3$ electrode (reference). 0.9686 g tetra-*n*-butylammonium hexafluorophosphate ($NBu_4PF_6$: 2.5 mmol) was prepared in 25 mL of acetonitrile (0.1 M) to generate the electrolyte solution. 10-(2-pyridinyl-methyl)-2-trifluoromethyl-10*H*-phenothiazine was added to the electrolyte solution. Then, ferrocene was added to the solution as an internal standard (0 V). A reduction potential of 494 mV was obtained versus ferrocenium-ferrocene.




**Scheme 6. Preparation of di-(4-*tert*-butylphenyl)-2-pyridylmethylamine.**

**Procedure for the Preparation of di-(4-*tert*-butylphenyl)-2-pyridylmethylamine.[10]**

20 mL 1,2-dichloroethane (25.120 g, 253.840 mmol), 0.740 mL pyridine-2-carboxaldehyde (0.833 g, 7.779 mmol), 1.137 g (4-tert-butylphenyl) amine (5.05 mmol), 1.40 mL glacial acetic acid (1.469 g, 24.256 mmol), and 2.384 g sodium triacetoxyborohydride (11.25 mmol) were combined in a round bottom flask. The reaction mixture was left to stir under nitrogen for 24 h. The reaction was quenched using 33 mL saturated sodium bicarbonate. Extraction was done using three washings of 75 mL ethyl acetate, keeping the top organic layer. The organic layers were dried using magnesium sulfate, the drying agent was filtered off, and the solvent was removed under pressure. Column chromatography was done on the crude using 1/1 v/v/hexanes/ ethyl acetate and then switching to 49/31/20 v/v hexanes/toluene/ ethyl acetate. A $^1$H NMR was taken and recrystallization was done using hexanes to yield 0.313 g of a solid (16.65 % yield). The reduction potential was attempted to be found using cyclic voltammetry but the reduction wave was diminished.

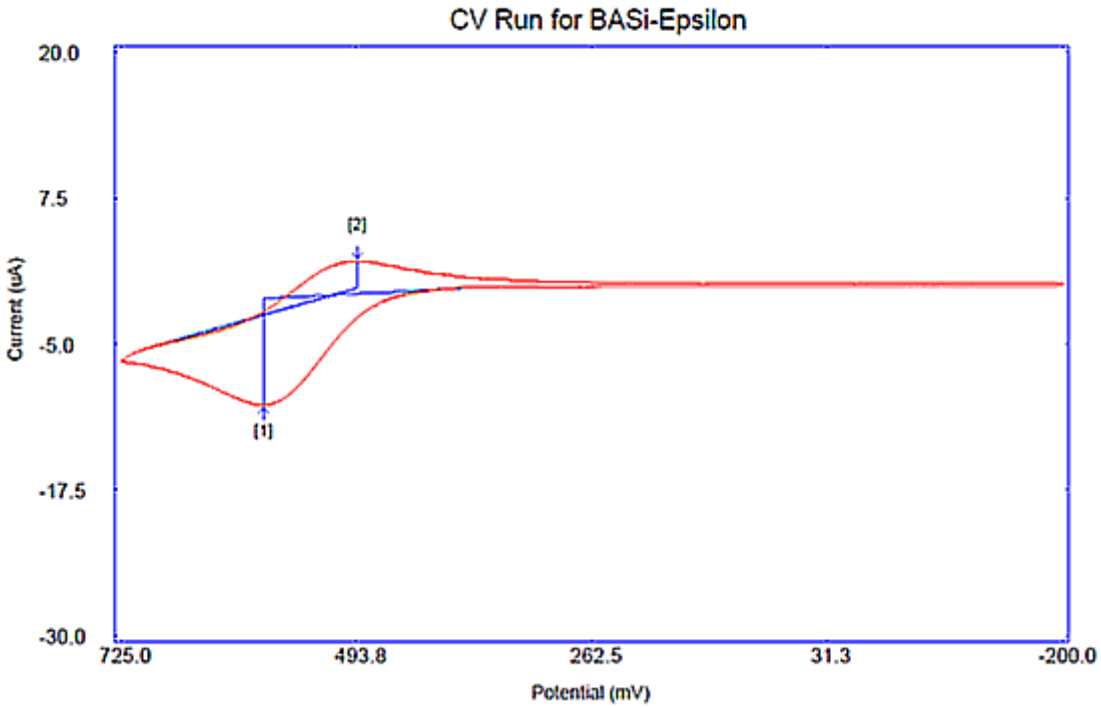



**Figure 10. Cyclic voltammogram for di-(4-*tert*-butylphenyl)-2-pyridylmethylamine.**

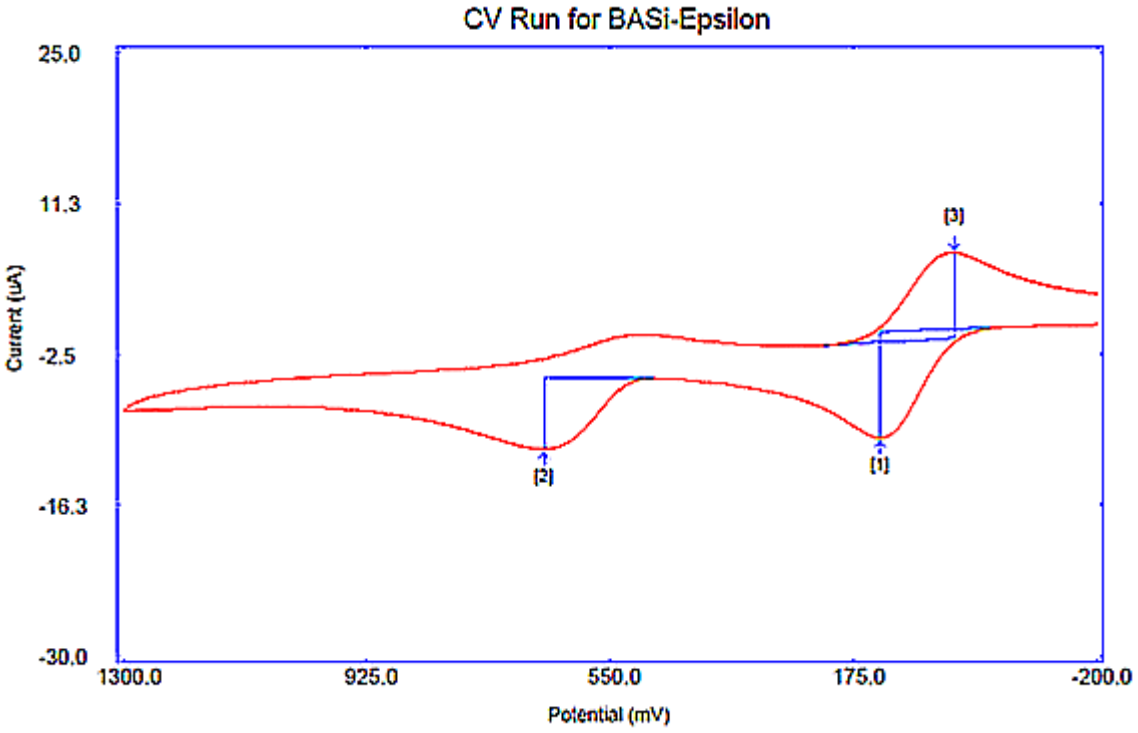
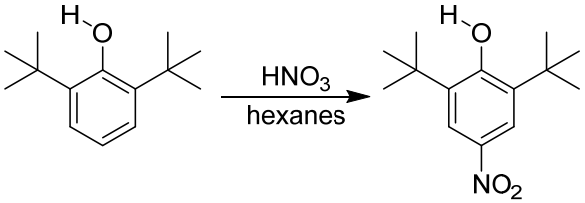



**Figure 11. Cyclic voltammogram for di-(4-*tert*-butylphenyl)-2-pyridylmethylamine with ferrocene internal standard.**




**Scheme 7. Preparation of 4-nitro-2,6-di-*tert*-butylphenol**



**Procedure for the Preparation of 4-nitro-2,6-di-*tert*-butylphenol.[9]**

In an Erlenmeyer flask, 1.5454 g 2,6-di-*tert*-butylphenol (7.49 mmol) was added to 4.5 mL hexanes. About 1.5 mL of concentrated nitric acid was added dropwise. The acidic solution was

diluted using ice. The reaction was filtered using ice water and recrystallization performed using ethanol.

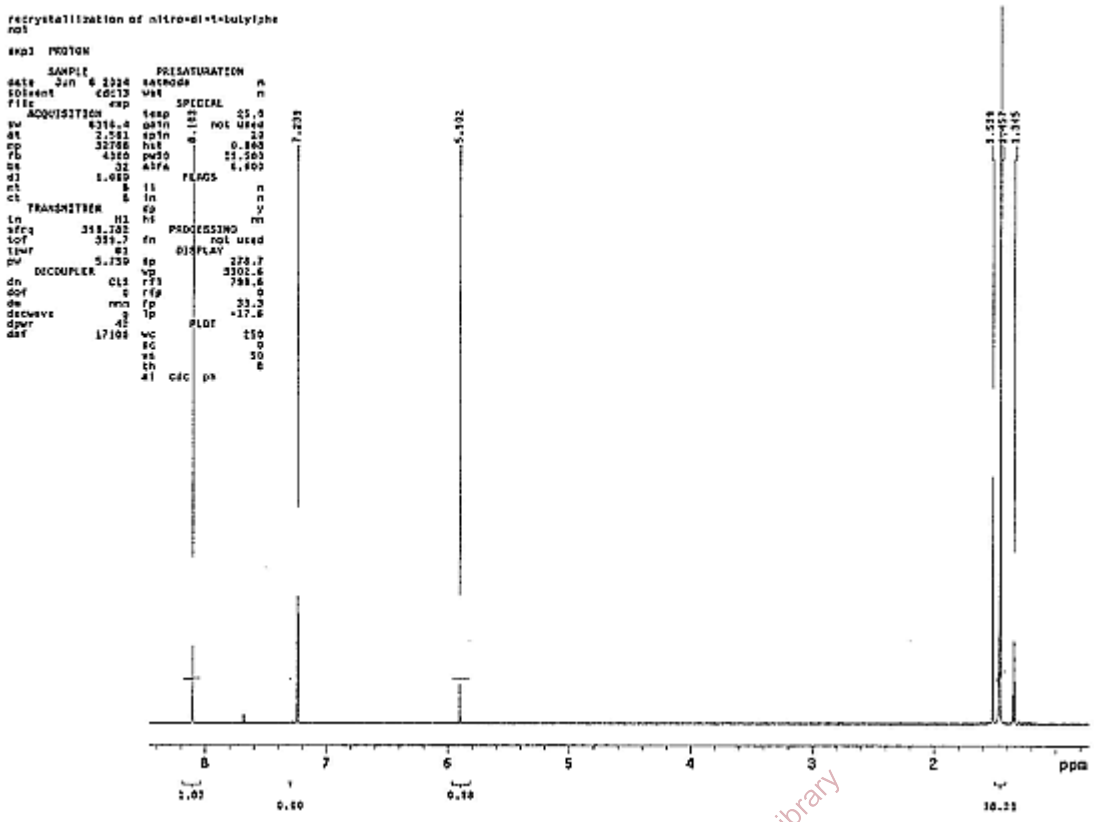



**Figure 12. $^{1}$H NMR spectrum of 4-nitro-2,6-di-*tert*-butylphenol.**

**Discussion:**

*N*,*N*-Di-(4-*tert*-butylphenyl)-N-(2-pyridyl)amine was the first compound that was synthesized. This compound was synthesized to be compared to 10-(pyrid-2-yl)-10*H*-phenothiazine. It was hypothesized that removing the sulfur bond between the two phenyl rings would make a more reactive molecule due to the electron density then being more localized and that the reduction potential would increase due to the lack of the electron donating group. The reduction potential was determined to be 0.55 V and the p$K_a$ was determined to be 13.1. The BDFE was then calculated to be 85.5 kcal/mol. The parent compound, 10-(pyrid-2-yl)-10*H*-phenothiazine, had a reduction potential of 0.39 V and a p$K_a$ of 10.9, which yields a BDFE of 78.8 kcal/mol. This shows that the removal of the sulfur did increase the reduction potential; however, the basicity increased as well.

The next compound that was synthesized was 2-trifluoromethyl-10-(4-methoxypyrid-3-yl)-10*H*-phenothiazine. Past research concluded the having a methoxy group on the 10-(pyrid-2-yl)-10*H*-phenothiazine decreased the BDFE while having the trifluoromethyl group alone increased the BDFE After performing the Buchwald-Hartwig amination and analyzing the product by TLC, it was found that there was too little product and it was mixed with a large amount of starting material.



The third compound to be synthesized was 2-chloro-10-(pyrid-2-yl)-10*H*-phenothiazine. This compound was synthesized with the hypothesis that the chlorine group would make the compound more oxidizing in comparison to 10-(pyrid-2-yl)-10*H*-phenothiazine. The experimental reduction potential was 0.49 V and the p$K_a$ was determined to be 10.6. The reduction potential of 10-(pyrid-2-yl)-10*H*-phenothiazine is 0.39 V which means that the

chlorine group did make the radical cation more oxidizing. The goal compound was also slightly more acidic in comparison to 10-(pyrid-2-yl)-10*H*-phenothiazine which had a p$K_a$ of 10.9 though the change is relatively small. The bond strength of the goal compound was determined to be 80.6 kcal/mol, was also larger than the base compound which had strength of 78.8 kcal/mol.

The fourth synthesis was of 3,7-bis(1,1-dimethylethyl)-10*H*-phenothiazine. The compound was attempted to be synthesized to compare it to *N*,*N*-di-(4-*tert*-butylphenyl)-*N*-(2-pyridyl)amine. Data on both compounds would allow us a better understanding on how a phenothiazine and a diarylamine compare to each other. What was hypothesized was that the aminium system would react inherently faster as the CPET reaction requires overlap which is more effective in the aminium. This hypothesis was largely based on the electron density being more localized on one ring in the diphenyl system, thus increasing the reactivity. This synthesis was shown to have not succeeded through mass spectrometry. When the crude reaction mixture was analyzed, there were more peaks than what was expected and none of the peaks that were present corresponded to the intended product. 3,7-Bis(1,1-dimethylethyl)-10*H*-phenothiazine was



The next synthesis was 10-(2-pyridinylmethyl)-2-trifluoromethyl-10*H*-phenothiazine. This compound was synthesized to be compared to 2-(trifluoromethyl)-10-(pyridin-2-yl)-10*H*-phenothiazine, synthesized by Evan Walker, and 10-(2-pyridinylmethyl)-10*H*-phenothiazine, synthesized by Andy Riegel. These structures can be seen below in Figure 13.

**Figure 13. Structures of 2-(trifluoromethyl)-10-(pyridin-2-yl)-10H-phenothiazine and 10-(2-pyridinylmethyl)-10*H*-phenothiazine**

Previous research concluded that adding a methylene spacer insulated the radical cation and the base systems. The trifluoromethyl group increased both the reduction potential and the p$K_a$ relative to the 10*H*-(pyridin-2-yl)-10*H*-phenothiazine. By using both a methylene spacer and a trifluoromethyl group, it was hypothesized that the reduction potential will be increased due to the trifluoromethyl group but the p$K_a$ will be changed to a lesser degree due to the insulating effects of the methylene spacer. The reduction potential for this compound was determined to be 0.49 V. The trifluoromethyl substituted compound had a reduction potential of 0.56 while the 10-(pyrid-2-yl)-10*H*-phenothiazine compound had a reduction potential of 0.39 V. The goal product with the methylene spacer as well as the trifluoromethyl group did increase the reduction potential by 10 mV, but the radical cation is not as oxidizing as the compound with trifluoromethyl group alone. The product was a dark oil which prevented the p$K_a$ from being determined. If the p$K_a$ had been obtained, then the acidity of the compound could be compared along with the BDFE.



The next compound was di-(4-*tert*-butylphenyl)-2-pyridylmethylamine. This compound was made after 10-(2-pyridinylmethyl)-10*H*-phenothiazine was not synthesized successfully. The compound was synthesized without a hypothesis on how it would change the reduction

potential or the p$K_a$ in comparison to 10-(2-pyridinylmethyl)-10*H*-phenothiazine. The p$K_a$ was not found and when cyclic voltammetry was done on the sample, the reduction wave was found to diminish which meant that the radical cation was too unstable, undergoing intramolecular reaction or reaction with the solvent.

A hydrogen atom donor, 4-nitro-2,6-di-*tert*-butylphenol, was synthesized to act as a hydrogen atom donor with the radical cations. When kinetics data was attempted to be measured, it was determined that the radical cation was reacted too fast for the rapid scan instrument to measure the kinetics; 4-nitro-2,6-di-*tert*-butylphenol was synthesized to slow down the reaction.. When the radical cation is generated, the hydrogen from the hydroxyl group is expected to be transferred to the ring system. Adding the nitro group to the compound increases the bond strength of the O–H bond so that it takes more energy to abstract it.

Bond strengths were determined for two of the three synthesized compounds. Using the figure below the relative BDFE for the two compounds can be compared to other compounds that have been synthesized by other students under Dr. Rhile.

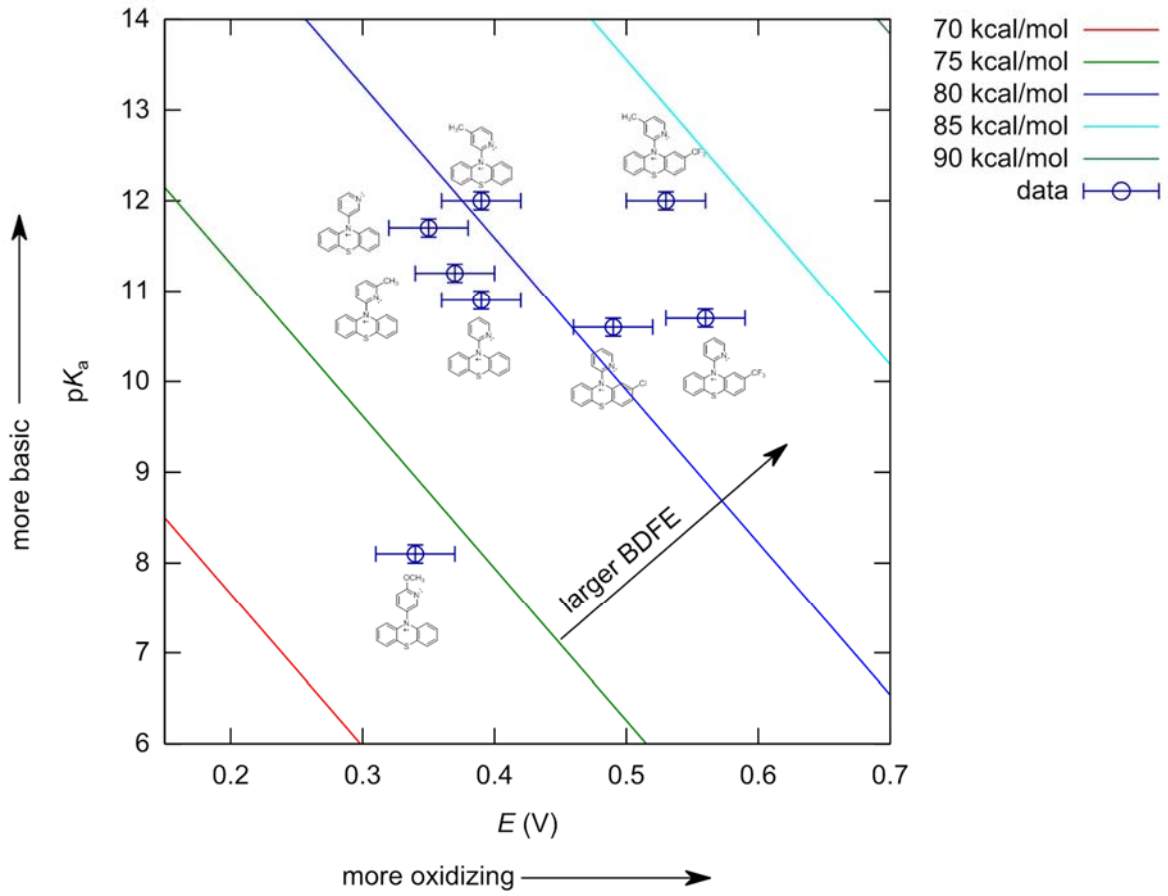



**Figure 14. Graph of Compound Result.[6]**

*N*,*N*-Di-(4-*tert*-butylphenyl)-*N*-(2-pyridyl)amine has a BDFE of 85.5 kcal/mol. From the graph, it can be seen that this compound has the highest bond strength of the compounds that have been synthesized. As hypothesized, the compound is more reactive due to the removal of the sulfur, decreasing its electron density. With a reduction potential of 0.55 V and a p$K_a$ of 13.1, it is more basic and oxidizing than the other compounds. The second compound, 2-chloro-10-(pyrid-2-yl)-10*H*-phenothiazine, has a BDFE of 80.6 kcal/mol. It has a higher BDFE than the unsubstituted compound. The basicity of the compound is normal but it is slightly more oxidizing than the rest of the compounds.

**Conclusion:**

Table 1 is a summary of the three compounds that were synthesized. The di-4-*tert*-butylphenyl compound has a higher BDFE than the other compounds and is also more oxidizing and basic. When compared to the parent compound, the removal of the sulfur drastically increased the oxidizing ability and the basicity. The chlorine compound had a similar BDFE compared to the previously synthesized compound but was more oxidizing. When compared to the parent compound, 10-(pyrid-2-yl)-10*H*-phenothiazine, the chlorine group increased the reduction potential without affecting the basicity. It also increased the overall bond strength. The last compound, 10-(2-pyridinylmethyl)-2-trifluoromethyl-10*H*-phenothiazine, the methylene space and the trifluoromethyl increased the reduction potential, but its p$K_a$ could not be determined due to the fact that the product is a dark color. The product has to be colorless in order to perform acid-base titration with it in conjunction with the diode array.

**Table 1. Summary of results.**



| Compound | Reduction Potential (V) | p$K_a$ | BDFE (kcal/mol) |
|---|---|---|---|
| Parent Compound: 10-(pyrid-2-yl)-10*H*-phenothiazine | 0.39 | 10.9 | 78.8 |
| *N*,*N*-di-(4-*tert*-butylphenyl)-*N*-(2-pyridyl)amine | 0.55 | 13.1 | 85.5 |
| 2-chloro-10-(pyrid-2-yl)-10*H*-phenothiazine | 0.49 | 10.9 | 80.6 |
| 10-(2-pyridinylmethyl)-2-trifluoromethyl-10*H*-phenothiazine | 0.49 | - | - |

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