

TOWARDS THE SYNTHESIS OF A SWALLOWTAILED PERYLENE MONOIMIDE

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ABSTRACT

This project was initiated in conjunction with Dr. Justin Youngblood from the University of North Texas. The goal was to synthesize a molecule to be used in solar cell testing. The target molecule involved combining donor and acceptor groups to make a combination that would be able to transfer electricity in a unilateral direction to increase efficiency in solar cells. My project involved the donor portion, a perylene monoimide donor with a long alkyl “swallowtail” to impart solubility. While the final molecule was not synthesized, the proposed procedure for making such a molecule was improved upon. A perylene tetracarboxylic dianhydride was decarboxylated using an autoclave, and an amine synthesis procedure was attempted. Future research into this molecule will be greatly assisted by the findings of this project, and potential alterations are discussed.

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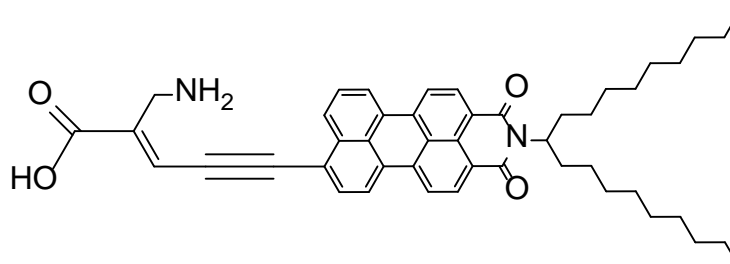
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INTRODUCTION

Dr. Justin Youngblood from University of North Texas has designed three molecules that he believes could be used in solar cells to increase efficiency of solar technology. The molecule attempted in this research project was a derivative of a perylene molecule.



Perylene



Target Molecule

The base of the target molecule was created by decarboxylating perylene-3,4:9,10-tetracarboxylic dianhydride (1) to create perylene-3,4-dicarboxylic anhydride (2). This process was a reaction that had previously been accomplished, albeit in low yield and with a tedious isolation procedure, by the Langhals group.^[1] Regiocontrolled partial decarboxylation is still an unsolved subject area, but they were able to create a procedure that is only a one-step reaction. The procedural details were slightly unclear in

their writings however, and further notation was made once the procedure was replicated.

The main properties of carboxylated perylenes are that they are highly insoluble and are good conductors of electricity. These properties are caused by the pi stacking that forms among the aromatic rings of this molecule. Pi stacking refers to attractive, noncovalent interactions between aromatic rings. Solubility is increased with addition of a long alkyl chain to one side of a carboxylated perylene, and the imide group can act as an acceptor molecule.

EXPERIMENTAL PROCEDURES

Perylene-3,4-dicarboxylic Anhydride (2)

Perylene-3,4:9,10-tetracarboxylic dianhydride (2.00 g, 5.1 mmol), diisopropylethylamine (2.63 g, 20.4 mmol), zinc acetate dehydrate (1.49 g, 6.8 mmol) and imidazole (16 g, .24 mol) were combined and then heated in a steel autoclave at 170°C for 3.5 hours. The still hot mixture was then dispersed in hot ethanol (240 ml). 2 N HCl was added (450 ml) and the solid was collected by vacuum filtration. After drying at 110°C in a drying oven, the solid (0.55 g) was washed with hot, super-concentrated aqueous K₂CO₃ solution (50 ml), and the aqueous layer was subsequently discarded. The residue was extracted with six portions of hot 2 N K₂CO₃ solutions (250 ml). The combined aqueous phases were extracted with chloroform, acidified with 2 N HCl (150 ml) and the precipitate was collected by vacuum filtration. After drying at 110°C in a drying oven, the product (0.62 g) was treated with 1-butanol at 100°C, washed with deionized water, and dried again at 110°C in a drying oven to give final product (0.188 g). This is a 7.2% yield.

10-Nonadecanoxime (5)

A solution of 1.00 g (3.54 mmol) of 10-nonadecanone in 10 mL of ethanol and 5 mL of pyridine was treated with 0.50 g (7.2 mmol) of hydroxylamine hydrochloride and then heated on a steam bath for 2 h. The resulting mixture was concentrated by rotary evaporation and the residue was partitioned between 5% HCl (aq)

and hexanes. The organic layer was dried over MgSO_4 and concentrated by rotary evaporation to yield 0.84 g (2.8 mmol, 80% yield) of 10-nonadecanone oxime as an oil. $^1\text{H-NMR}$ (CDCl_3) δ 0.88 (t, 8.6H), 1.26 (m, 32.H), 1.50 (t, 5.3H), 2.16 (t, 2.4H), 2.32 (t, 2.3H),

Benzyloxime of 10-Nonadecanone

The oxime (0.59 g, 2 mmol) was mixed with KOH (0.112 g, 2.4 mmol) in ethanol (2 ml) and stirred at room temperature for 15 minutes. Benzyl bromide (0.3 ml, 2.4 mmol) was added to ethanol (2 ml) and solution was added dropwise. The reaction mixture was heated under reflux for 7 hours with stirring. A black solid formed upon cooling and hexanes were added. The mixture was vacuum filtered to remove KBr particles, and the solid was discarded. The filtrate was concentrated by rotary evaporation and ethanol (4 ml) was added to the residue and heated to completely dissolve the crude product. The solution was allowed to cool to room temperature and crystallize. The resulting solid was broken up using cold ethanol and vacuum filtered to give the benzyloxime 0.224 g. M.P. 42-44°C, $^1\text{H-NMR}$ (CDCl_3) δ 0.88 (t, 6.0H), 1.27 (m, 30H), 1.57 (8.9H), 3.72 (d, 1.4H), 6.04 (broad, 8.1H)

10-Nonadecanamine (from oxime)

The oxime was dissolved in 25 mL of toluene. About 10 mL was distilled off to dry the system, which was then flushed with N_2 . Four mL of 70% sodium bis(2-ethoxyethoxy)aluminum hydride (RedAl) in toluene were added over 5 min. There was immediate gas evolution which subsided as more RedAl was added. The system was

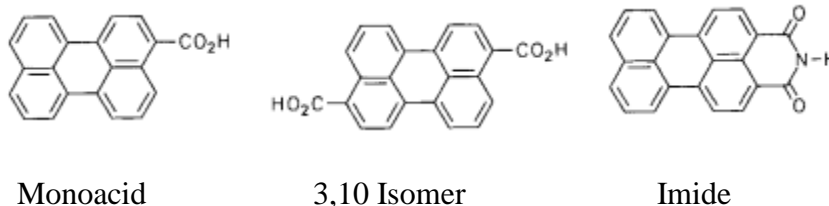
refluxed for 2 h. The resulting mixture was carefully added, with stirring, to 20 mL of 5% HCl; then 7 mL of conc HCl was added to dissolve aluminum salts and render the mixture acidic to litmus. The solution was extracted with hexanes and the organic layer was washed with 5% NaOH, dried, and concentrated by rotary evaporation to yield 0.81 g. $^1\text{H-NMR}$ (CDCl_3) δ 0.88 (t, 6.0H), 1.26 (m, 23H), 1.62 (t, 2.7H), 3.04 (m, .56H), 4.67 (m, .07H)

10-Nonadecanamine (from benzyloxime)

The benzyloxime (0.14g, 0.36 mmol) was dissolved in 2.2 mL of dried toluene. The mixture was then flushed with N_2 . 0.6 mL of 70% sodium bis(2-ethoxyethoxy)aluminum hydride (RedAl) in toluene were added over 1 min. There was immediate gas evolution which subsided as more RedAl was added. The system was refluxed for 2 h. The resulting mixture was carefully added, with stirring, to 3 mL of 5% HCl; then 1 mL of conc HCl was added to dissolve aluminum salts and render the mixture acidic to litmus. The solution was extracted with hexanes and the organic layer was washed with 5% NaOH, dried, and concentrated by rotary evaporation to yield 0.10 g. $^1\text{H-NMR}$ (CDCl_3) δ 0.88 (t, 6.3H), 1.27 (m, 25H), 1.4 (m, 6.3H), 2.3 (s, 1.0H), 3.57 (s, 0.84H), 4.87 (s, .73H), 7.2 (m, 1.9H)

RESULTS

The decarboxylation reaction may be an entropy controlled reaction, and thus high temperatures were used. According to the Gibbs Free Energy equation, $\Delta G = \Delta H - T\Delta S$, so higher temperatures would lower the entropy required for the reaction to proceed. A Parr Pressure Reactor (autoclave) was used to reach the increased temperatures needed for this synthesis. Multiple products are formed by this reaction, but they were separated by the workup procedure. The other products formed from the partial decarboxylation reaction are a monoacid, a 3,10 isomer, and an imide.

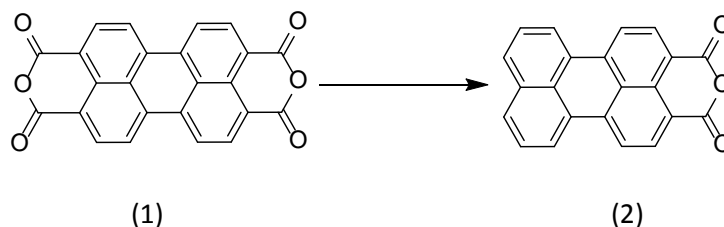


Using a sterically hindered noncondensing amine, diisopropylethylamine, increases production of (2) while decreasing the imide byproduct. The insolubility of even the partially decarboxylated perylene was used to separate the desired product from the other products formed. Zinc acetate was used to improve isolation of (2) from the monoacid derivative by catalyzing the reaction. The reaction was attempted multiple times before the product was formed.

When the mixture was not allowed to cool after heating in the autoclave, more product was formed because of the solubility issues of the perylene derivatives. When the solid was treated with 6 portions of K₂CO₃ the mixture was allowed to dissolve before

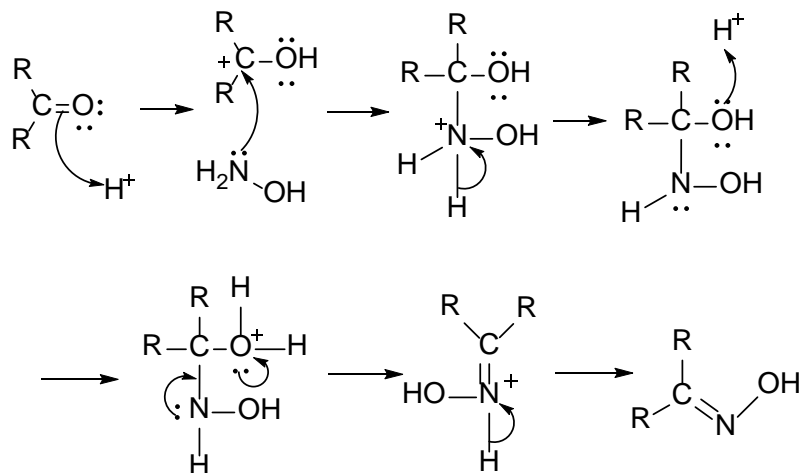
filtration occurred for each portion. This maximized the amount of product that was able to be extracted. The literature reaction gave a 25% yield, but only a 7.2% yield was attained. A significant portion of product lost was most likely due to the use of multiple filter papers after the extraction process. The filter paper may have been too porous for each paper to hold more. Another explanation could be that the product was difficult to filter because of how tightly the molecules were stacking, therefore preventing large amounts of the mixture to be filtered. Since the product is insoluble, an NMR was unable to be attained. The IR Spectrum for this product^{A-2} was different from the starting material^{A-1}, but a known IR Spectrum was not available for comparison. The R_f value using a TLC plate with silica gel using chloroform/acetic acid 10:1 ratio was 0.7. The literature value was 0.78, and there was significant moving of the product as compared to the starting material, which did not travel. The TLC also did not show that there was any starting material or other molecules remaining so the reaction was assumed to have gone to completion.

Unfortunately this reaction has an unknown mechanism so rational ways to optimize this reaction are limited. Compound (2) is still extremely insoluble after isolation; a swallowtail amine is needed to increase solubility so that a handle may be attached.

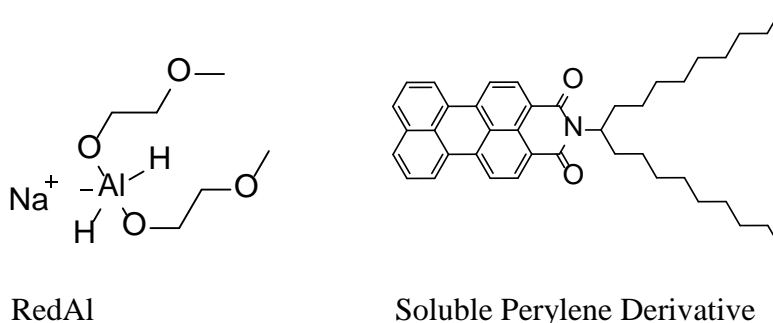


10-Nonadecanone^{A-3} (**3**) was used to attempt to synthesize 10-nonadecanamine (**4**), which is the swallowtail that would be used to increase solubility of (2). The initial

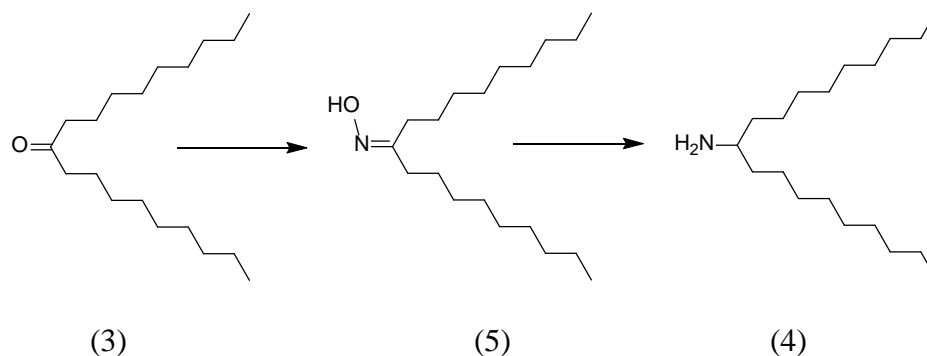
procedure used called for a 2 step reaction process that would convert the ketone into an oxime before reduction occurred to convert it into the final amine. The general electron-pushing mechanism for this type of reaction is shown below. Pyridine was used as a base to collect the released hydrogen ion in the last step.



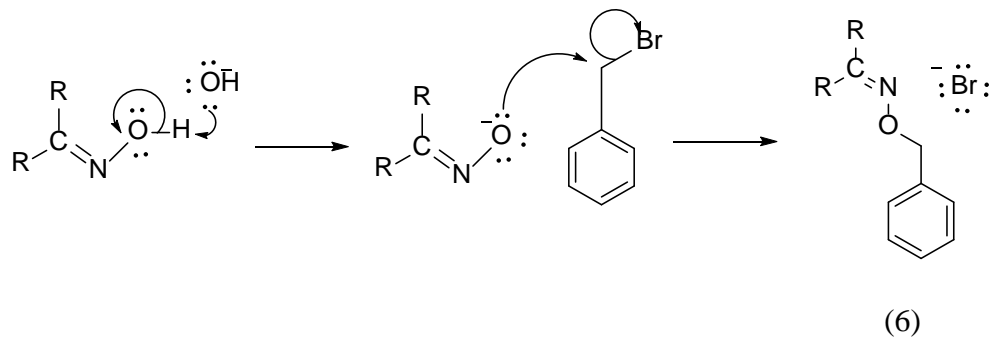
The second step called for the reduction of 10-nonadecanoxime^{A-4,5} (**5**) by sodium bis(2-methoxyethoxy)aluminum hydride (RedAl) to produce (**4**). This was a reaction that has been previously studied, and RedAl was the reagent with best results for such a long alkyl group. The reaction has also been successfully accomplished in the Mattern group.^[2] The long alkyl group of 9 carbons on each side was used to maximize solubility of the final perylene.^[2] The length of 9 carbons has been previously shown to allow for maximum solubility.^[3] The difficulty of this reaction however is that the long chains could cause problems with reduction, which was the case.



The reaction was carried out under nitrogen gas to keep the mixture as dry as possible under reflux; water would quench the reagent. Initially the procedure called for toluene to be added then distilled off to dry the system. However, when previously-dried toluene was used, the results seemed to improve. The toluene was dried over a period of a week using molecular sieves that were activated from prolonged exposure to heat in a drying oven. A new bottle of RedAl was used after multiple attempts, and the oxime present decreased more. Eventually a setup was designed that allowed as minimal exposure to air as possible, but the desired product was still not formed. Unfortunately this reaction did not go to completion, and an unknown product was formed so another way to reduce the oxime was explored.



One possible explanation is that (5) is reacting with adjacent molecules to form unwanted reactions during reduction. Specifically, the oxide OH could be interfering with the hydride reduction. Therefore a reaction to protect (5) was proposed. Compound (5) was converted into a benzyloxime^{A-12} (6) and then reduction was tried again.^[4]



When the reduction was attempted without the benzyl group added to protect, the oxime peaks on the HNMR disappeared, but the new peaks did not match the known literature values. There were unexpected peaks at 7.2 and 2.3, but those peaks are assumed to be credited to residual toluene that was not roto-vapped off. There was also an unknown peak at 4.7, but the integration values were 0.1 or less every attempt^{A-6,7,8,9,10,11}. The other expected values were slightly off on each reaction that was tested. The product formed was an oil.

After reduction of the benzyloxime, the product formed was a solid, crystalline compound instead of an oil as expected. The HNMR shifts of this compound^{A-13} showed two triplets around 7.2 with an integration value of 1.87 and two other peaks at 4.8 and 4.6, but the total integration value for these peaks are 0.73. These could be from a benzyloxyl group. If this was the case, then 1/3 of the swallowtail would be associated with the benzyloxyl. Using a TLC of chloroform as the developing solvent showed that the product was pure, but it is unknown if the product was pure after reduction was attempted.

CONCLUSIONS

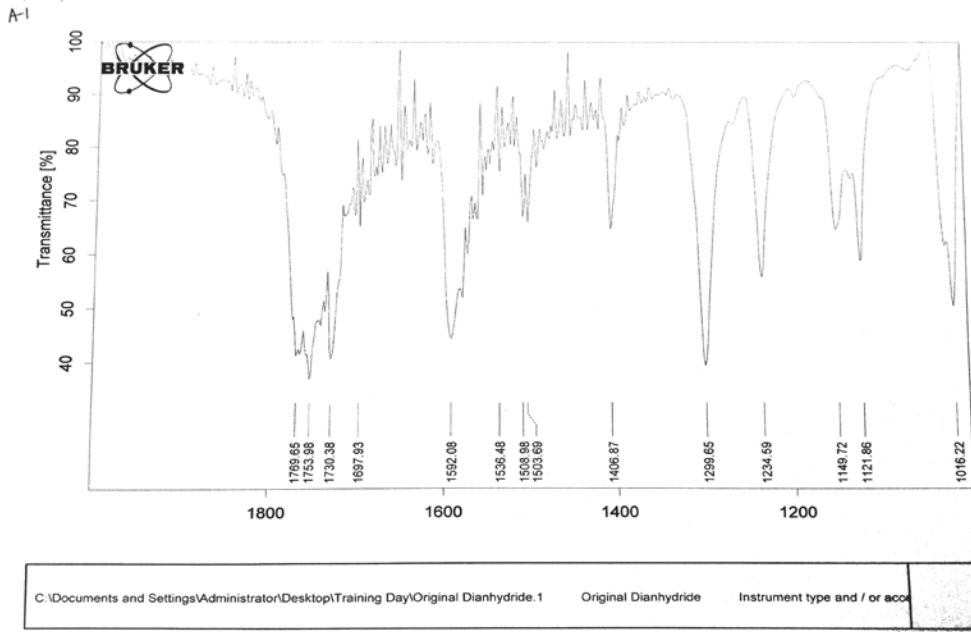
The formation of the partially decarboxylated perylene was most likely a success, but this is hard to confirm until a swallowtail is added so that further tests can be run. The oxime was formed, but further reduction to the amine was unsuccessful. Further investigation should be done with a 7 chained tail. This will decrease the solubility of the perylene derivative, but the alkyl groups would be less likely to interfere with the reduction process. Once the final target compound is made with the shorter swallowtail, it may be soluble enough for the purposes needed. Once a suitable amine is made, there are plethora previous procedures for substituting the amine onto a carboxylated perylene, and the reaction should work just as well for a partially decarboxylated perylene. The new benzyloxime could be a mechanism for converting oximes into amines, but unfortunately it did not work with this oxime reduction. The products that were formed from the reduction of the benzyloxime and the oxime are unknown, but there is significant evidence to support that new compounds were made.

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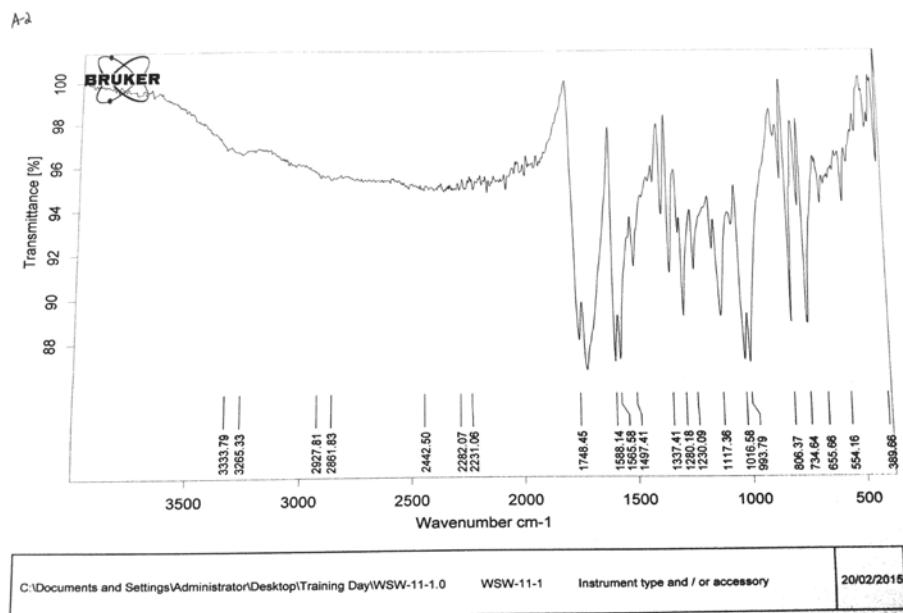
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APPENDIX

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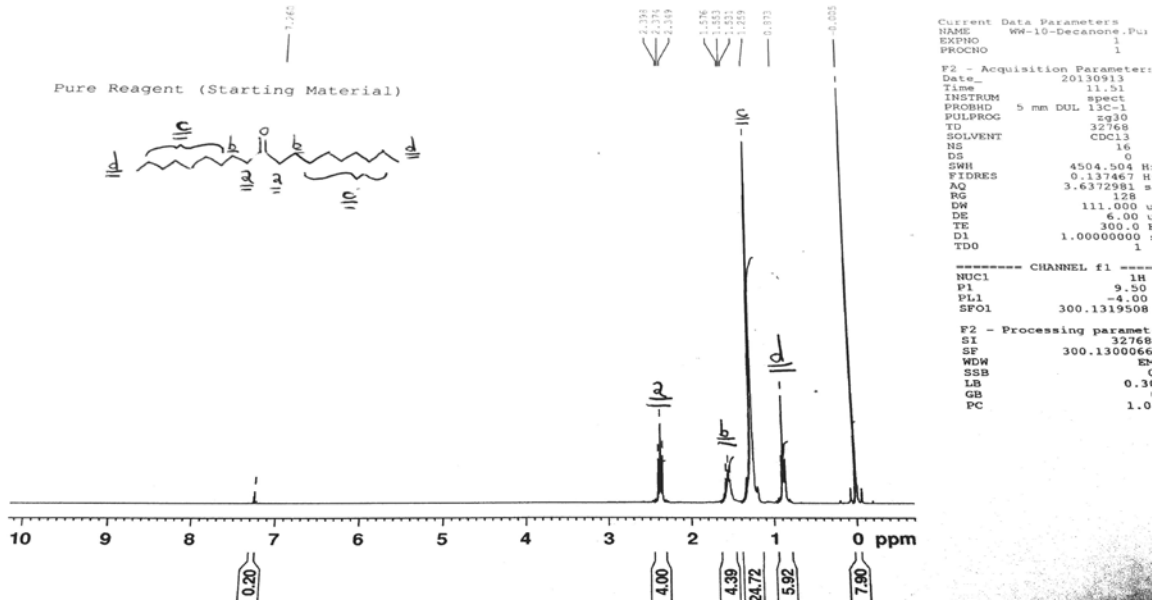


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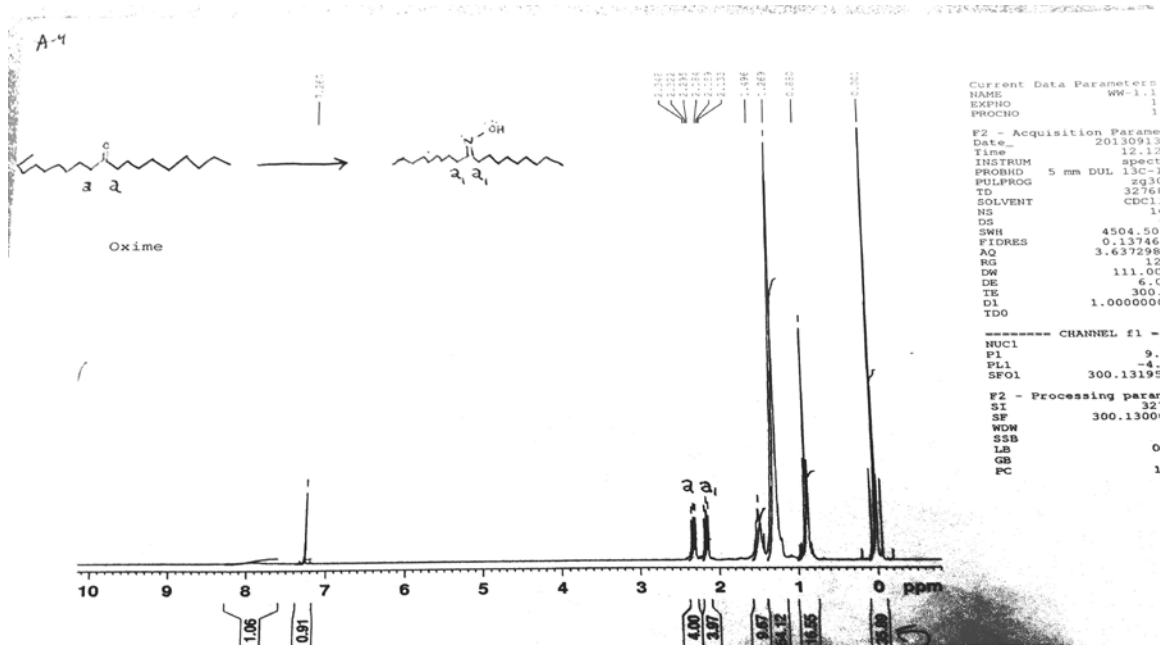


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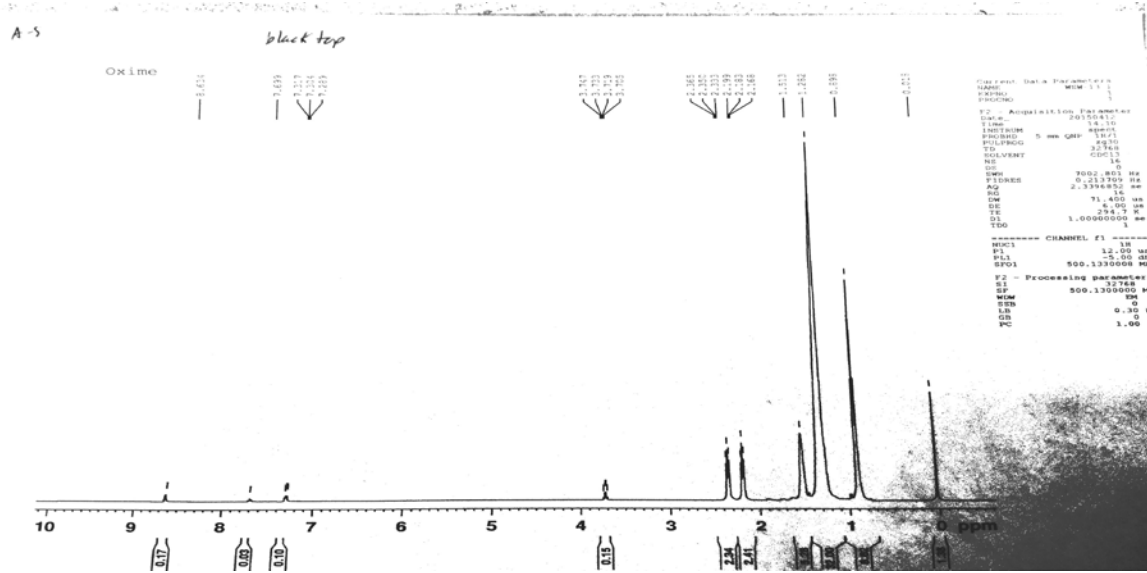
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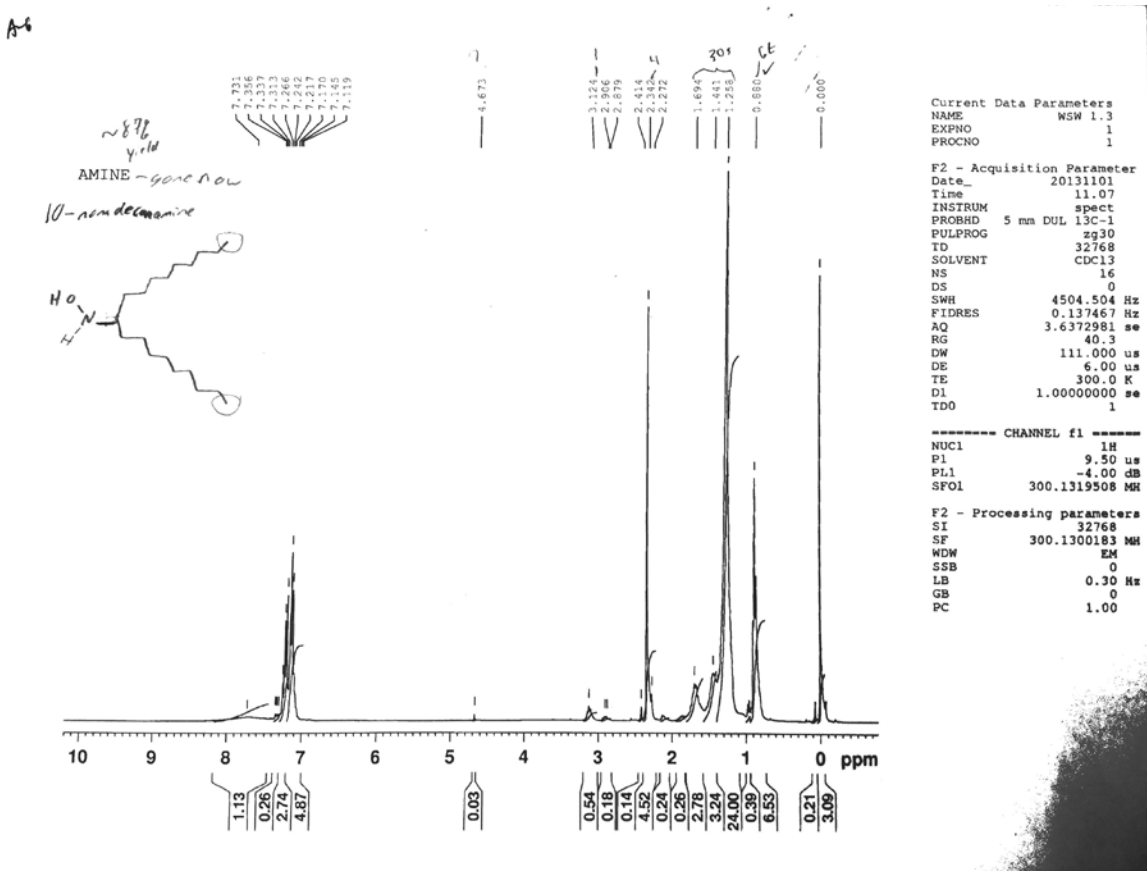
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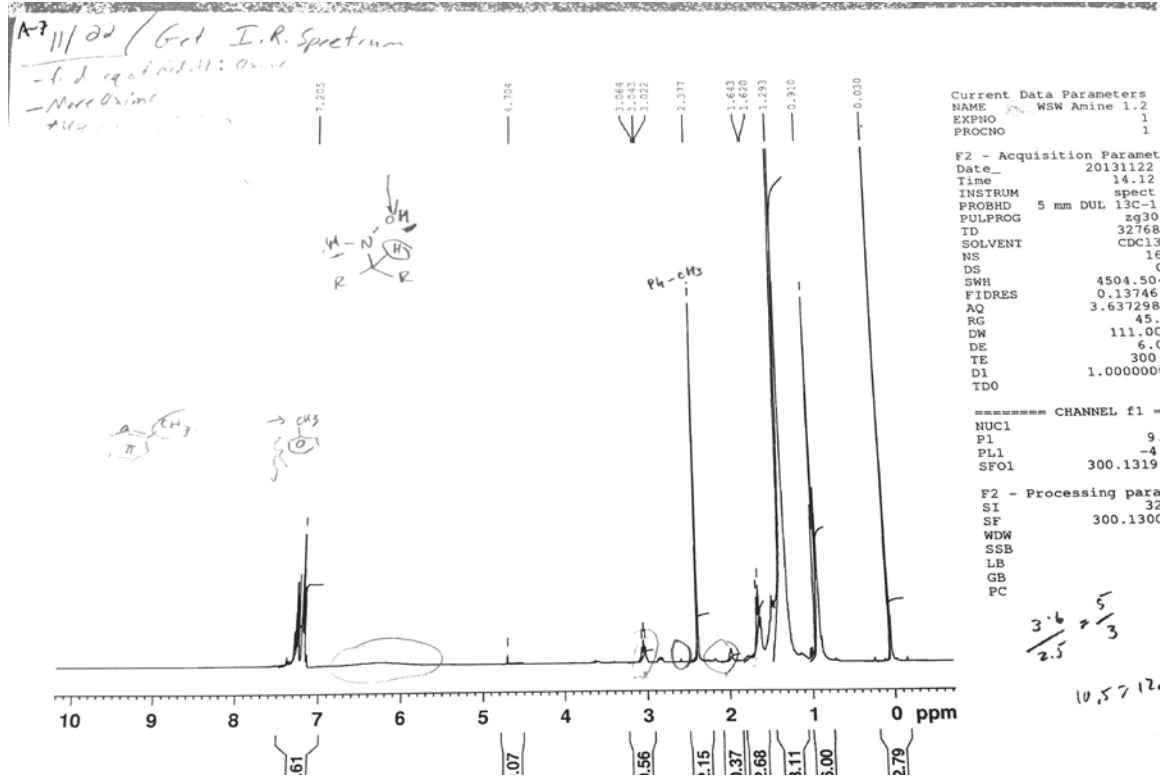
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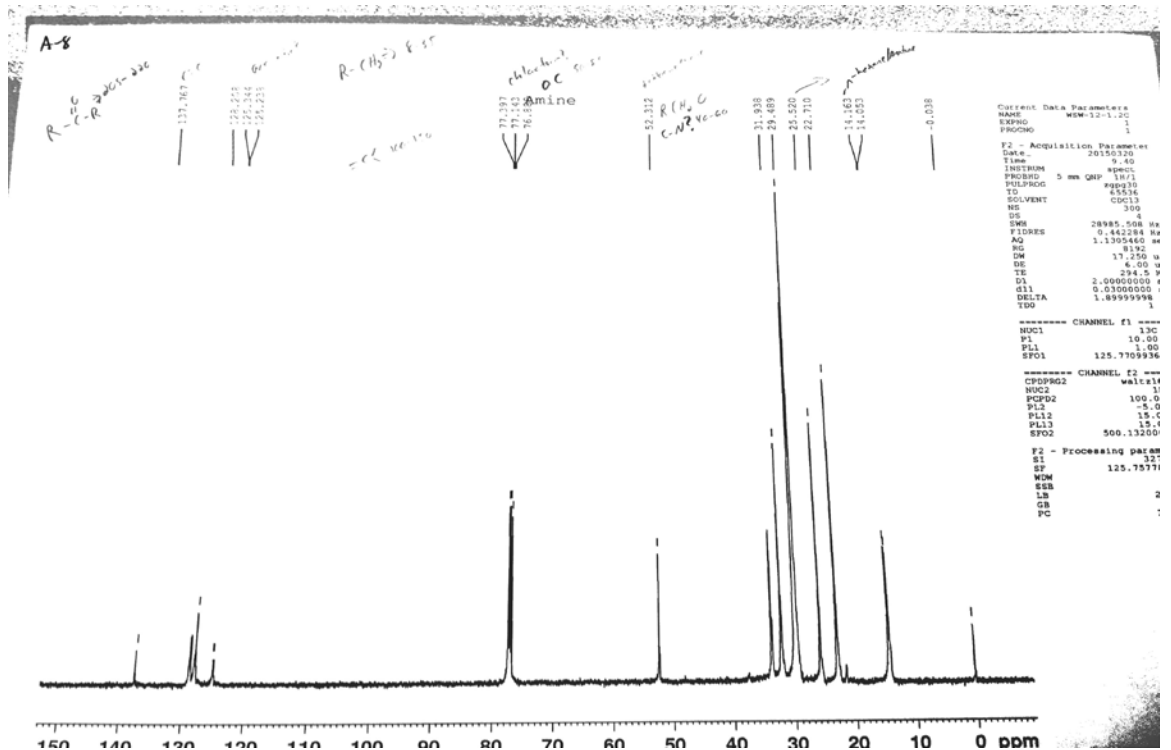
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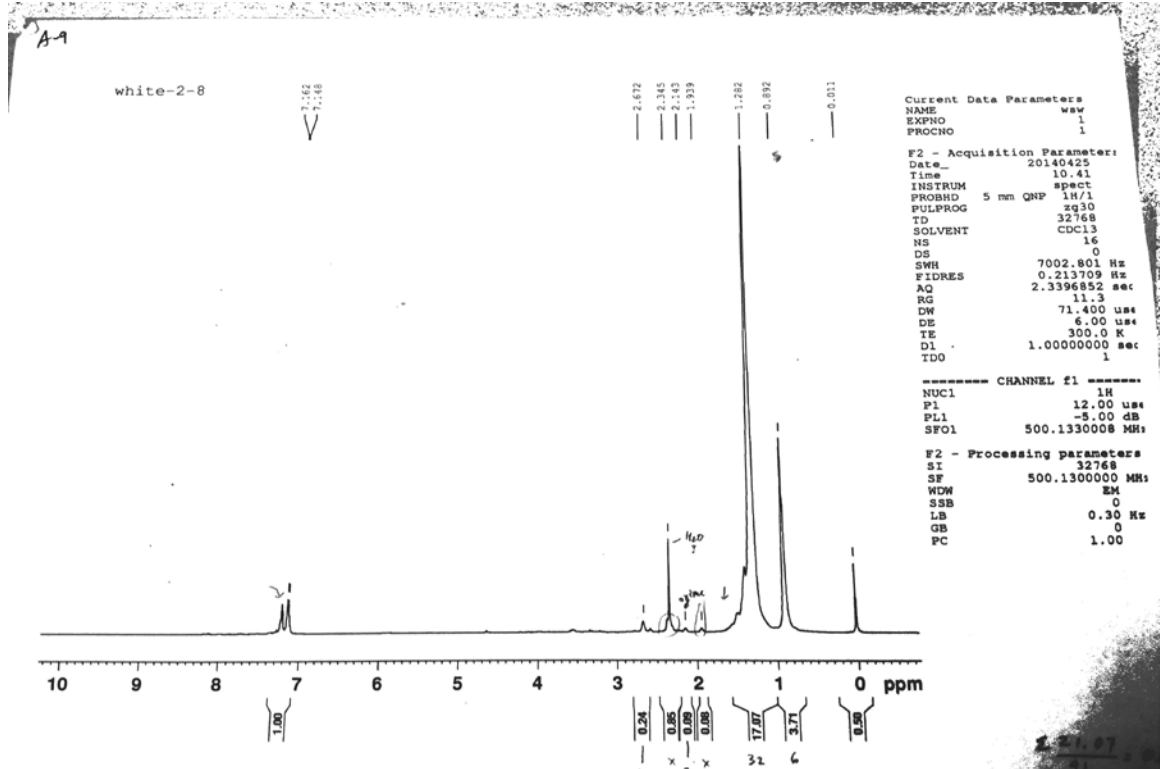
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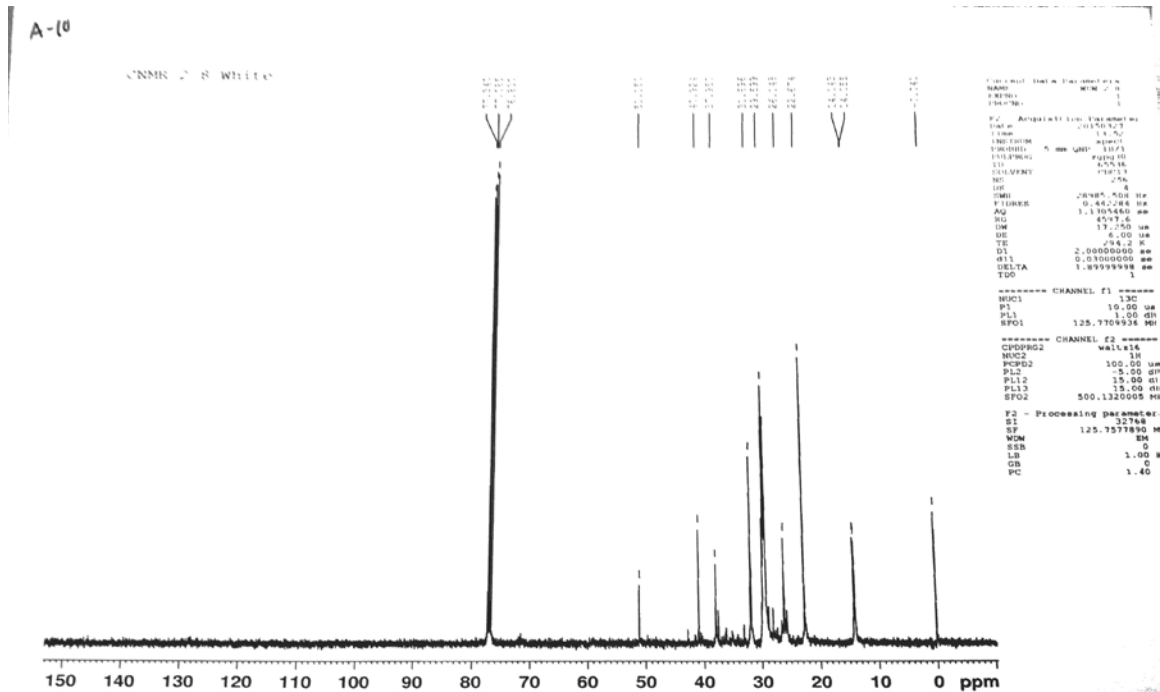
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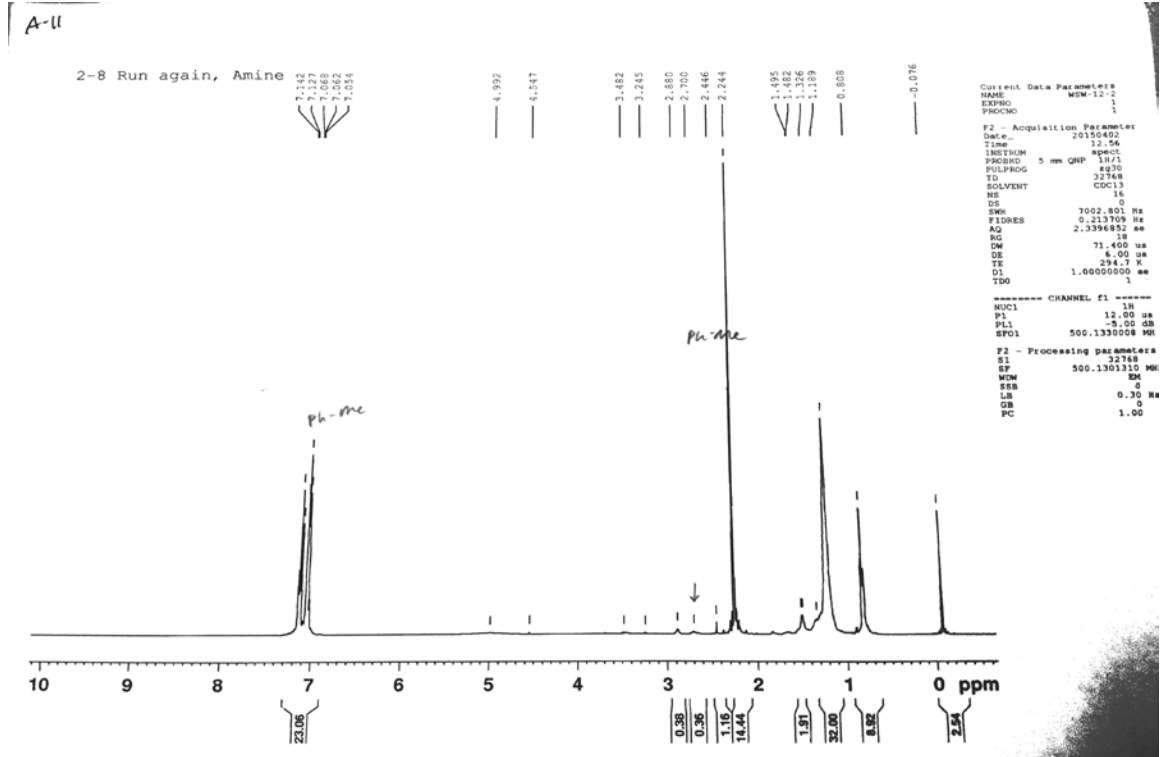
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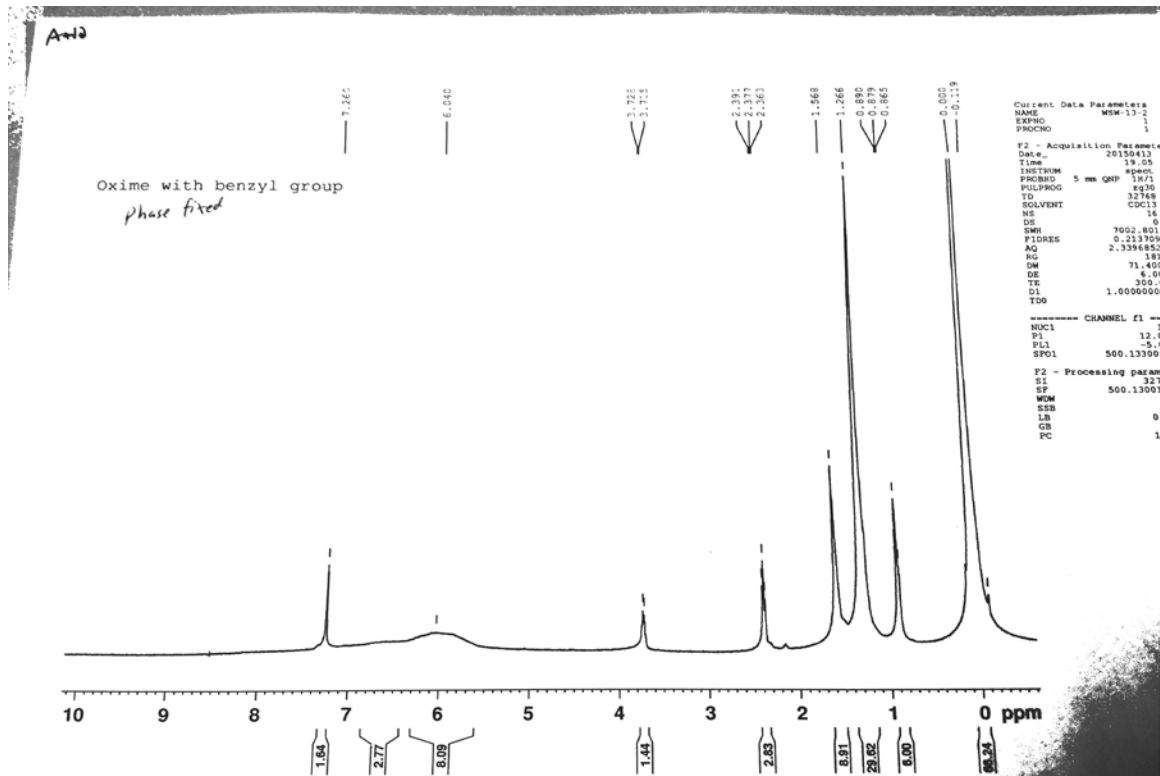
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A-12



A-13

