# SLATT UNDERGRADUATE RESEARCH FELLOWSHIP
# FINAL REPORT

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|---|---|
| **SCHOLAR NAME:** | Alexander Hymes |
| **FACULTY ADVISOR:** | Haifeng Gao |
| **PROJECT PERIOD:** | Fall 2020 |
| **PROJECT TITLE:** | |
| **CONNECTION TO ONE OR MORE ENERGY-RELATED RESEARCH AREAS (CHECK ALL THAT APPLY):** | **( x) Energy Conversion and Efficiency ( ) Sustainable and Secure Nuclear<br>( ) Smart Storage and Distribution ( ) Transformation Solar<br>( ) Sustainable Bio/Fossil Fuels ( ) Transformative Wind** |

## MAJOR GOALS AND ACCOMPLISHMENTS

Summarize your research goals and provide a brief statement of your accomplishments (no more than 1-2 sentences). Indicate whether you were able to accomplish your goals by estimating the percentage completed for each one. Use the next page for your written report.

| RESEARCH GOALS | ACTUAL PERFORMANCE AND ACCOMPLISHMENTS | % OF GOAL COMPLETED |
|---|---|---|
| **Prepare Series of Monomers** | Was able to get a good start on preparing monomers that were not commercially available | 50 |
| **Run Polymerization Reactions** | Did not reach | 0 |
| | | |
| | | |
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| | | |

## RESEARCH OUTPUT

Please provide any output that may have resulted from your research project. You may leave any and all categories blank or check with your faculty advisor if you are unsure how to respond.

| CATEGORY | INFORMATION |
|---|---|
| **EXTERNAL PROPOSALS SUBMITTED** | (Sponsor, Project Title, PIs, Submission Date, Proposal Amount) |
| **EXTERNAL AWARDS RECEIVED** | (Sponsor, Project Title, PIs, Award Date, Award Amount) |
| **JOURNAL ARTICLES IN PROCESS OR PUBLISHED** | (Journal Name, Title, Authors, Submission Date, Publication Date, Volume #, Page #s) |
| **BOOKS AND CHAPTERS RELATED TO YOUR RESEARCH** | (Book Title, Chapter Title, Authors, Submission Date, Publication Date, Volume #, Page #s) |
| **PUBLIC PRESENTATIONS YOU MADE ABOUT YOUR RESEARCH** | (Event, Presentation Title, Presentation Date, Location) |
| **AWARDS OR RECOGNITIONS YOU RECEIVED FOR YOUR RESEARCH PROJECT** | (Purpose, Title, Date Received) |
| **INTERNAL COLLABORATIONS FOSTERED** | (Name, Organization, Purpose of Affiliation, and Frequency of Interactions ) |
| **EXTERNAL COLLABORATIONS FOSTERED** | (Name, Organization, Purpose of Affiliation, and Frequency of Interactions) |
| **WEBSITE(S) FEATURING RESEARCH PROJECT** | (URL) |
| **OTHER PRODUCTS AND SERVICES** (e.g., media reports, databases, software, models, curricula, instruments, education programs, outreach for ND Energy and other groups) | (Please describe each item in detail) |

## RESEARCH EXPERIENCE

Please let us know what you thought of your research experience: Did this experience meet your expectations? Were lab personnel helpful and responsive to your needs? What else could have been done to improve your experience or achieve additional results?

**The research experience went well overall. The graduate students in the lab were kind and helpful if I needed things. As I mention in the report, I thought it was difficult to build up significant momentum on the project given that it was in its early stages, I was the only one really focused on it, and I was only able to come in for a limited time each week.**

# FINAL WRITTEN REPORT

(Please use the space below to describe your research project and objectives, any findings and results you can share, and graphs, charts, and other visuals to help us understand what you achieved as a result of this research experience.)

**Introduction:**

The eventual goal of this project is to create a set of new polymers with functional groups varied at specific points to test the effect of these variations on the properties of the resulting material. Before the polymerization can occur though, it is necessary to either create or purchase the target monomers.

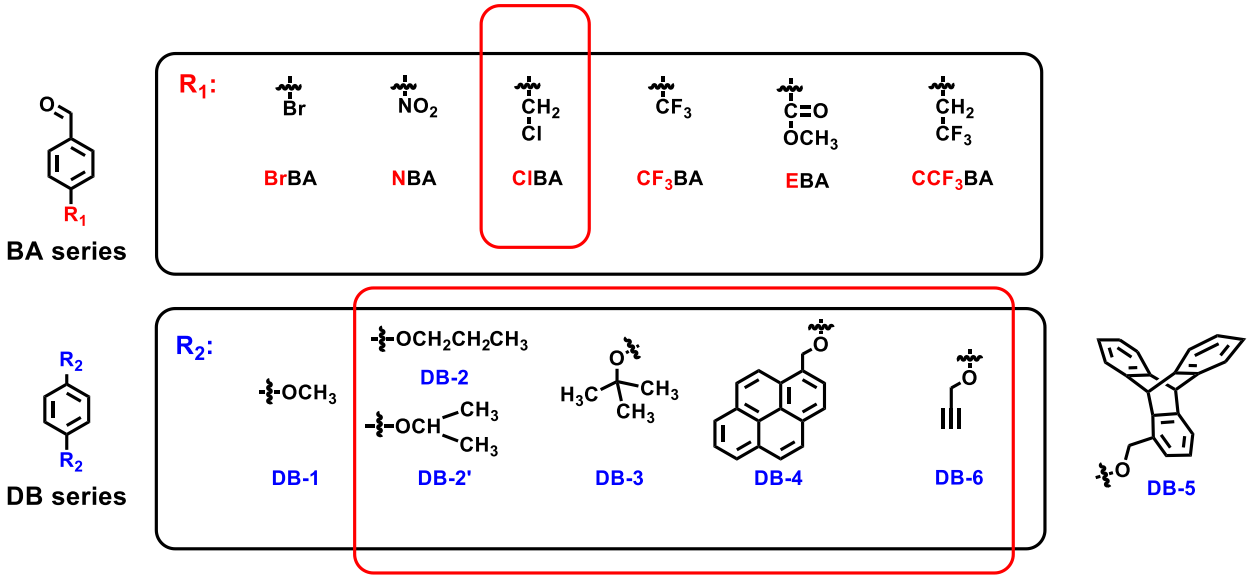



*Figure 1 List of target monomers for project*

Some of these monomers were commercially available at a reasonable price, but others were either unavailable or prohibitively expensive. For the latter group, it was necessary to synthesize them so they could eventually be used in later reactions.

The time in the lab this semester was spent improving procedures for DB-6 and DB-2, and the synthesis DB-2' was attempted once towards the end.

**Experimental:**

*Synthesis of DB-6*

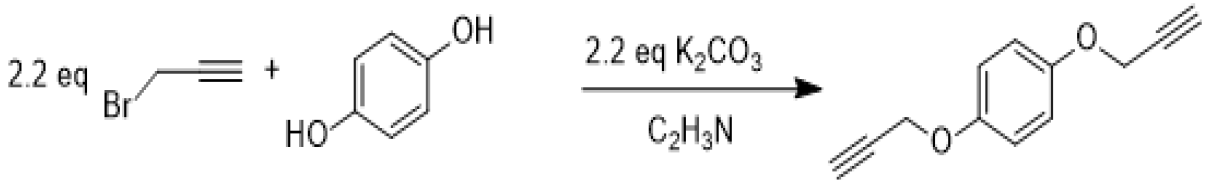



*Figure 2 Reaction of Propargyl Bromide with Hydroquinone to Produce DB-6*

This was the first reaction attempted this semester, and it was run multiple times to try to improve the yield being obtained and overcome problems that came up. The amounts used in each reaction are shown in the table below.

| Experiment | Hydroquinone | Propargyl Bromide | $K_2CO_3$ | Acetonitrile | Time |
|---|---|---|---|---|---|
| AH-01-34 | 1.01 g, 9.21 mmol | 1.51 mL, 19.93 mmol | 2.76 g, 19.99 mmol | 65 mL | 27 h |
| AH-01-35 | 1.00 g, 9.10 mmol | 1.51 mL, 19.93 mmol | 2.77 g, 20.08 mmol | 50 mL | 44 h* |
| AH-01-36 | 1.00 g, 9.09 mmol | 1.51 mL, 19.93 mmol | 2.80 g, 20.22 mmol | 50 mL | 41 h |
| AH-01-37 | 1.01 g, 9.22 mmol | 1.51 mL, 19.93 mmol | 2.78 g, 20.10 mmol | 50 mL | 45 h* |

*Hot plate turned off at some point during reaction

The procedure was mostly based of a procedure used by a past group member. For the most recent version, acetonitrile (50 mL) was added to a three neck round bottom flask. A condenser was added to one opening with a septum and a glass stopper on the others. A flow of nitrogen was added to the septum and allowed to exit through the condenser to a bubbler. $N_2$ was allowed to flow through the system for about 30 minutes while the other reactants were prepared. The hydroquinone was added and allowed to dissolve prior to the subsequent addition of the potassium carbonate. At this point the reaction was added heat, and the propargyl bromide was added. The reaction mixture was left to react while stirring at around 80 °C. The reaction was stopped after 45 h (although hot plate seems to have shut off at some point in the meantime).

The solid was filtered off with vacuum filtration, and the solvents were removed from the filtrate. The resulting residue was dissolved in DCM (50 mL) and washed 3 times with $H_2O$ (50 mL). The organic layer was dried with $MgSO_4$ and filtered through a cotton stopped pipette (will likely use vacuum filtration going forward). Solvents were removed from the filtrate to obtain the crude product.

A column with a slurry packed silica stationary phase and an eluent of 2:1 Hexanes to DCM was run to try to obtain the purified final product. The solvent collected from the column was evaporated to leave behind a white solid. A proton NMR was obtained for the product.

*Synthesis of DB-2*

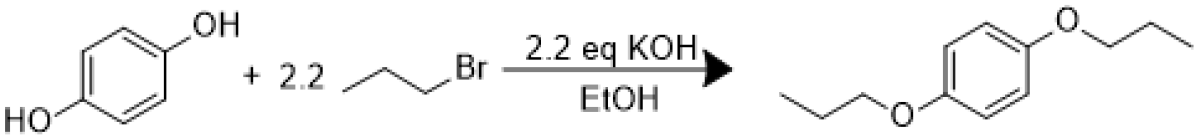



*Figure 3 Reaction of Hydroquinone with 1-Bromopropane to produce DB-2*

This reaction was likewise run multiple times. The relevant data for each run is shown in the table below.

| Experiment | Hydroquinone | 1-Bromopropane | KOH | Ethanol | Time |
|---|---|---|---|---|---|
| AH-01-38 | 1.10 g, 9.96 mmol | 1.82 mL, 20.02 mmol | 1.21 g, 21.63 mmol | 10 mL | 46 h |
| AH-01-39 | 2.00 g, 18.21 mmol | 3.64 mL, 40.04 mmol | 2.29 g, 40.86 mmol | 25 mL | 25 h |
| AH-01-41 | 10.01 g, 0.091 mol | 18.3 mL, 0.20 mol | 11.22 g, 0.20 mol | 100 mL | 27 h |

Attempts were made to improve the procedure and scale up the amount produced with each run until a good method was determined which looked something like what follows (i.e. using vacuum filtration after drying step instead of gravity filtration).

In a round bottom flask, KOH was dissolved in ethanol with stirring. Hydroquinone was then added slowly to the reaction mixture followed by the 1-Bromopropane. After a condenser was attached, the reaction was heated to 70 °C and left to react while stirring. The reaction was stopped 27 h later, and the heat was turned off.

The solid at the bottom of the reaction mixture was filtered off with vacuum filtration, and the solvents were removed from the filtrate. The resulting residue was dissolved in DCM (50 mL) and washed 3 times with $H_2O$ (50 mL) in a separatory funnel. The organic layer was dried with $MgSO_4$, which was subsequently filtered off by vacuum filtration. The solvents were removed from the filtrate to obtain the crude product.

A column with a slurry packed silica stationary phase and an eluent of 2:1 Hexanes to DCM was run to try to obtain the purified final product. The solvent collected from the column was evaporated to leave behind a white solid. A proton NMR was obtained of the product.

*Synthesis of DB-2'*

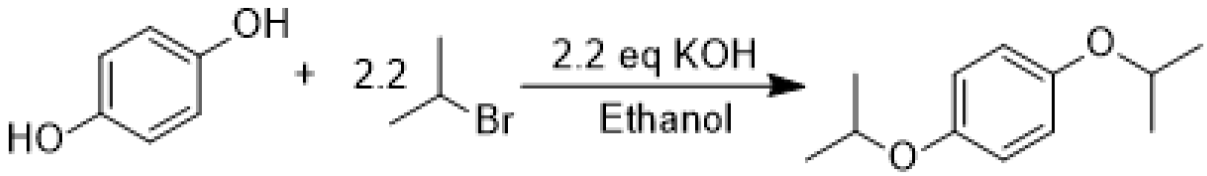



*Figure 4 Reaction of Hydroquinone with 2-Bromopropane to produce DB-2'*

This reaction was only run once toward the end of the semester. The procedure used was based off of what worked for the synthesis of the related compound DB-2. In a round bottom flask, KOH (1.12 g, 19.94 mmol) was dissolved in ethanol (15 mL) with stirring. Hydroquinone (1.06 g, 9.66 mmol) was then added slowly to the reaction mixture followed by the 2-Bromopropane (1.88 mL, 20.02 mmol). After a condenser was attached, the reaction was heated to 60 °C and left to react while stirring. The reaction was stopped 27 h later, but the heat seems to have malfunctioned and turned off at some point during that time.

The solid at the bottom of the reaction mixture was filtered off with vacuum filtration, and the solvents were removed from the filtrate. The resulting residue was dissolved in DCM (50 mL) and washed 3 times with $H_2O$ (50 mL) in a separatory funnel. The organic layer was dried with $MgSO_4$, which was subsequently filtered off by vacuum filtration. The solvents were removed from the filtrate to obtain the crude product.

A column with a slurry packed silica stationary phase and an eluent of 2:1 Hexanes to DCM was run to try to obtain the purified final product. The solvent collected from the column was evaporated to leave behind a yellow oil. A proton NMR was obtained of the product.

**Results/Discussion:**

The yields obtained for each reaction were as follows.

| Reaction | $Mass_{product}$ | Yield |
|---|---|---|
| AH-01-34 | 0.58 g | 33.57 % |
| AH-01-35 | 1.17 g | 69.1 % |
| AH-01-36 | 0.79 g | 46.6 % |
| AH-01-37 | 0.90 g | 52.39 % |
| AH-01-38 | 0.88 g | 45.48 % |
| AH-01-39 | 2.28 g | 64.5 % |
| AH-01-40* | 0.41 g | 21.8 % |
| AH-01-41** | 5.92 g | 33.5 % |

* Product likely not completely pure given NMR results so yield is at best a maximum with the real result and mass probably being smaller
**Value may be inflated by the presence of remaining solvent

The NMRs obtained from each reaction are visible in the appendix. They are grouped by intended product. For DB-6 and DB-2, I was able to get fairly consistent spectral results indicating that I was arriving at the correct end product (though some like AH-01-41 seemed to contain some residual solvent). I only had one opportunity to attempt DB-2', and it did not seem to go well between the low mass/yield and the messy NMR result. Its possible though that the intended product is contained in what was produced since the cluster at 4.43 ppm is actually a group of seven peaks and may represent the protons attached to the tertiary carbon on either side of the ring.

The abnormally low yield on AH-01-41 was likely due to a column that did not run as cleanly as in previous experiments. This could be because the extraction/washing step did not use large enough volumes of solvents to capture all the impurities. It seems like something was missed when trying to scale the reaction up.

**Challenges and Future Plans:**

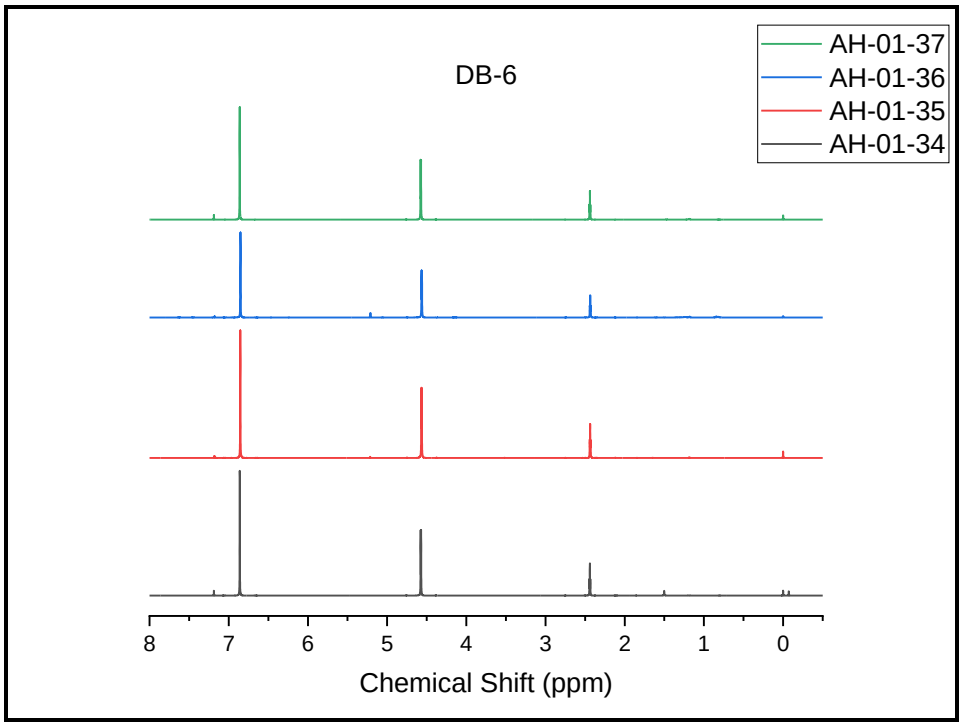
Challenges included equipment issues dealing with inconsistent hot plates, occasionally bumping when making use of the scintillation vial adapter for the rotovap, and the two-week hiatus from in lab work that halted progress toward the beginning of the semester.

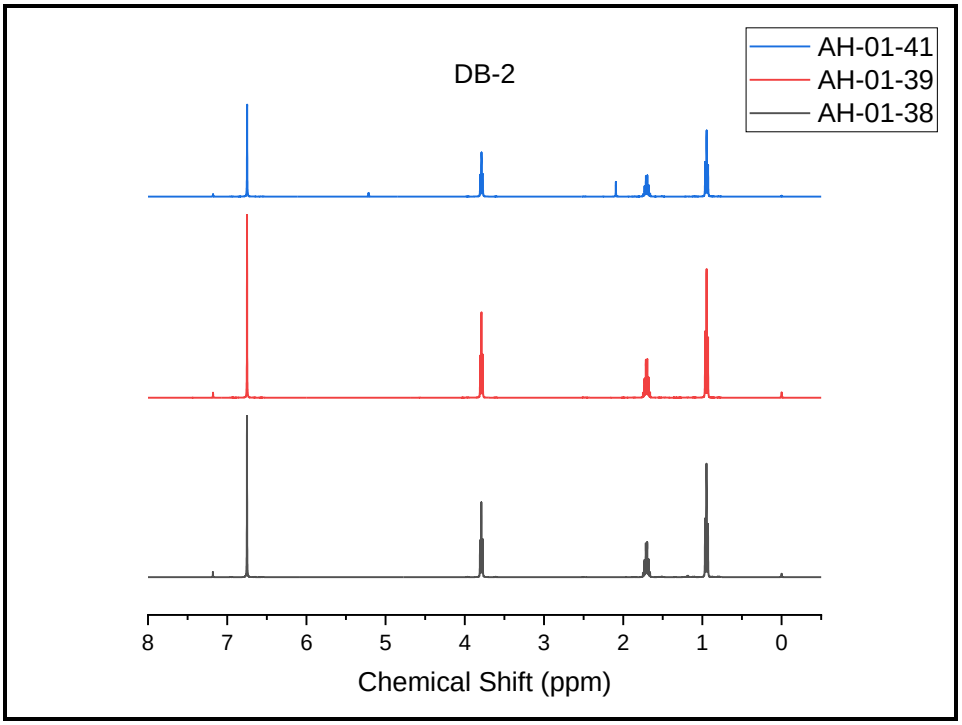
I was somewhat out of practice with regard to my synthesis skills toward the beginning of the semester and so think I may have started out somewhat slowly for this reason. Even so, I was able to become more comfortable working in the lab over time. I also think practicing the technique each time I ran a reaction helped me to become much better at running columns by the end of the semester than I was at the beginning (aside from whatever happened with AH-01-41).

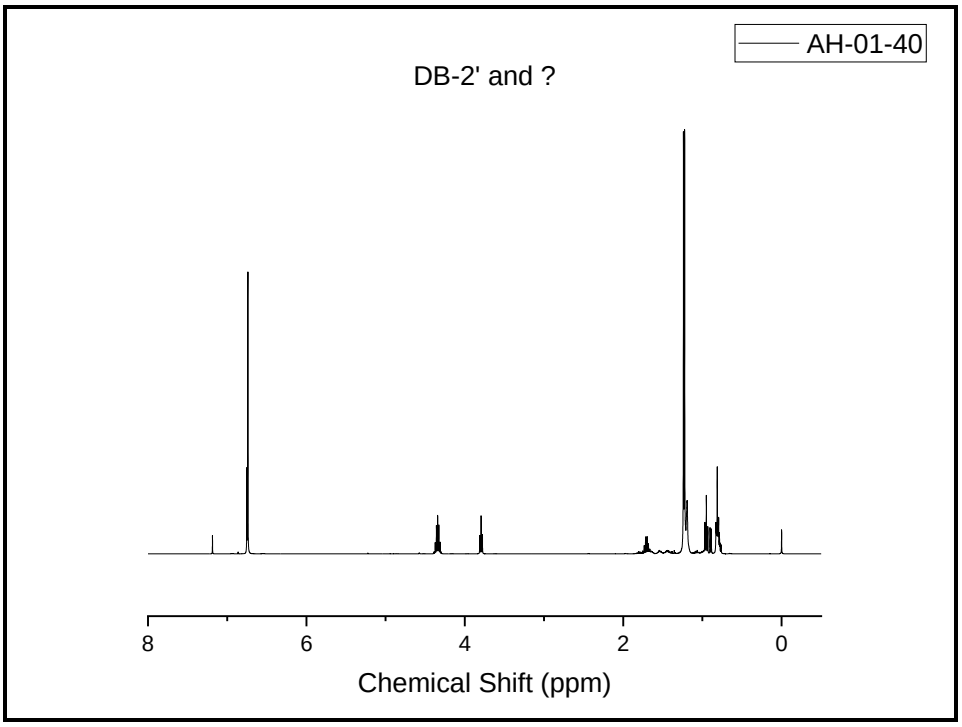
I do feel though that the infrequency with which I came into the lab (twice a week for around four hours at a time) made it difficult to build up and sustain momentum on the project especially with me being the only one working on this portion of it and the reactions often having to be completed over multiple days between the setting them up, running them, and purifying the products.

Future plans include working out what the issue was when I tried to scale up the synthesis of DB-2 in AH-01-41, figuring out how to make the synthesis of DB-2' work, moving on to the other monomers of interest, and getting around to performing some polymerization reactions.

**Appendix:**




DB-2
AH-01-41
AH-01-39
AH-01-38
8
7
6
5
4
3
2
1
0
Chemical Shift (ppm)


AH-01-40
DB-2' and ?
8
6
4
2
0
Chemical Shift (ppm)