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Synthesis of a key building block for a metal-like carbon-based compound

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SYNTHESIS OF A KEY BUILDING BLOCK FOR A METAL-LIKE CARBON-BASED
COMPOUND

By

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SYNTHESIS OF A KEY BUILDING BLOCK FOR A METAL-LIKE CARBON-BASED COMPOUND

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SYNTHESIS OF A KEY BUILDING BLOCK FOR A METAL-LIKE CARBON-BASED COMPOUND

Background

Organic compounds can be radicals where there is a free unpaired electron present, such as methyl and ethyl groups, ($\cdot\text{CH}_3$) and ($\cdot\text{C}_2\text{H}_5$), respectively (Walling, 2018). With respect to organic radicals, Moses Gomberg was the first to report a free radical compound in the 1900s at the University of Michigan (fig.1) (Moses Gomberg, 2022; Gomberg, 1924).

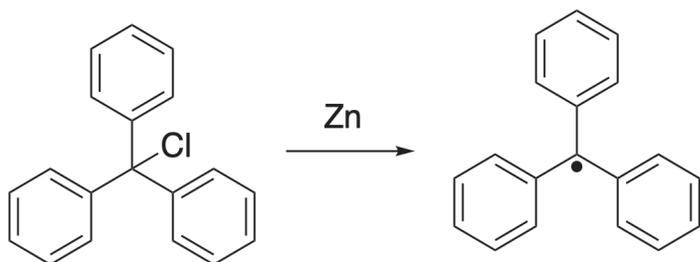


Figure 1: First free radical compound by Moses Gomberg.

In figure 1, the triphenylchloromethane was reacted with zinc to synthesize triphenylmethyl radical compound that has trivalent carbon and the black dot represents the free unpaired electron. The radical compound he discovered was unstable as it dimerized and reacted easily with oxygen. There is also a biradical compound having two free unpaired electrons (Abe, 2013). Oxygen (O_2) and Ozone (O_3) are some examples of biradical compounds as they have two unpaired electrons (Kemsley, 2017; Braïda et al., 2017). Biradicals have interesting properties; they are very reactive and unstable. They are very air-sensitive and water-sensitive as well. These

can be made stable by adding bulky aromatic groups around the compound due to steric hindrance (Frey et al., 2002).

In 2016, my research professor made a stable biradical compound, Diindenoanthracene (DIAn) which has bulky aromatic and silicon groups attached to make it stable (fig. 2) (Rudebusch, et al., 2016).

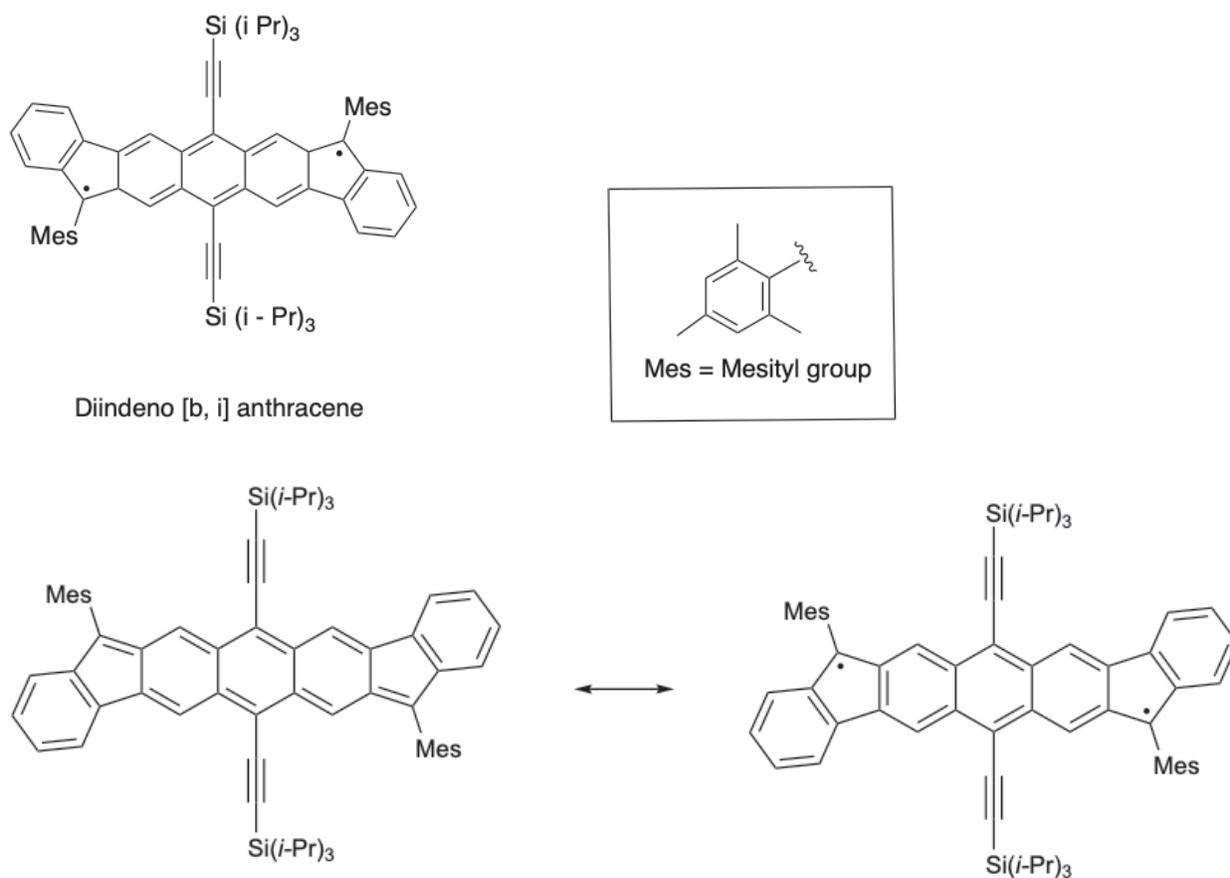
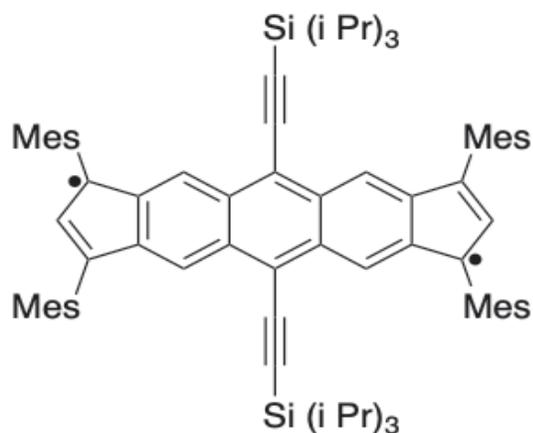


Figure 2: Structure of Diindeno [b, i] anthracene (DIAn)

There are radicals or biradicals which have the ability to transfer or accept electrons that give them metal-like properties (Chen et al., 2021). These are the electronically-charged radicals or radical ions. They can be used in organic electronics, such as rechargeable batteries.

Goals

My goal is to synthesize the key building blocks that are required for the synthesis of our final compound dicyclopentaanthracene (DCA) (fig. 3). These key building blocks are Weinreb Amide and cinnamoyl anthracene, shown in figure 4.



dicyclopentaanthracene DCA

Figure 3: The structure of our final compound

dicyclopentaanthracene (DCA)

DIAn, shown in figure 1 is similar to the final compound, dicyclopentaanthracene (DCA) which I plan to synthesize, except that DIAn has an extra two benzene rings at the ends. This final DCA compound has not been made yet and so by synthesizing it, we will be able to learn more about its unique properties. They can be used to make materials for organic electronics due to their carbon-based structures. Hence, my research time was spent synthesizing our desired key building blocks compounds for the ultimate DCA synthesis.

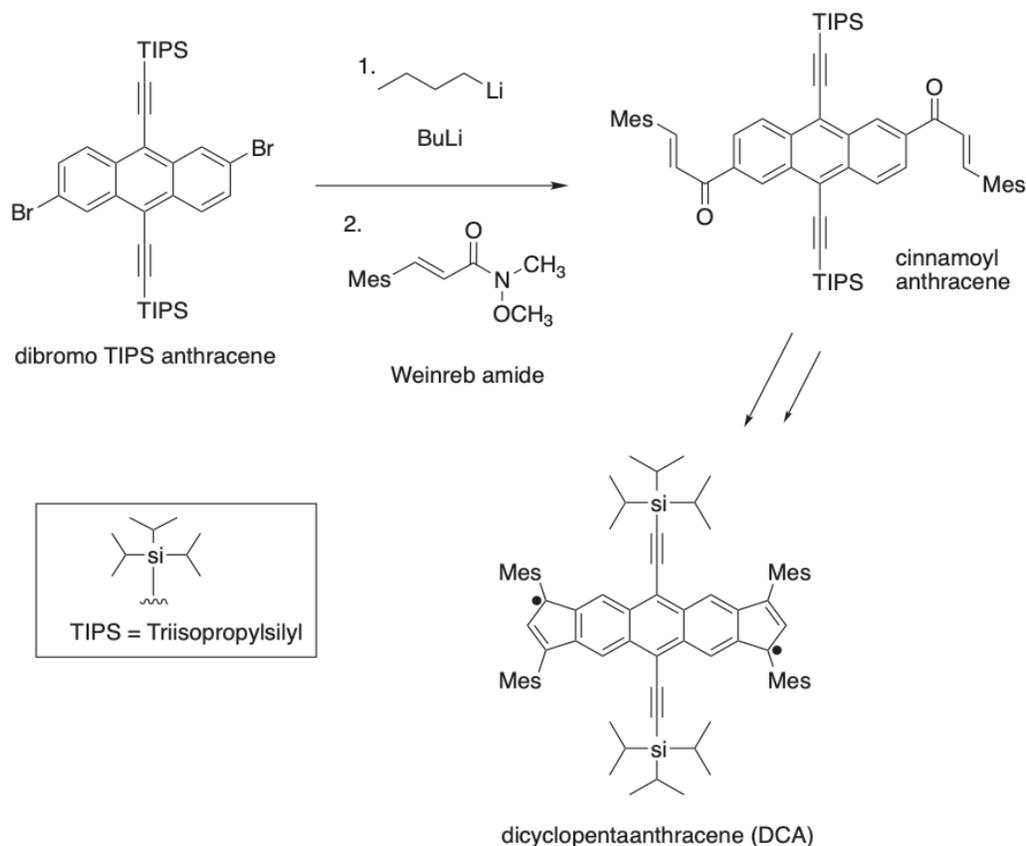


Figure 4: Overall reaction mechanism to synthesize our final compound DCA.

Methodology

I used an air-free organic synthesis as these organic compounds are air and water-sensitive. For that, I used a high vacuum and inert nitrogen gas. For further analysis, I took NMR (Nuclear Magnetic Resonance), where we can observe the position and number of proton peaks in the spectrum of our desired products. I also calculated the percent yield of each reaction and their crude mass. We have a 3-hour lab meeting every two days a week where we conduct these reaction syntheses, purifications, and analyses. We have a 1-hour group meeting on Fridays where we discuss the progress of our project.

Results and Discussion

All the reaction syntheses were air and water sensitive so to tackle these problems, high vacuum and nitrogen gas were used to carry out these syntheses. I synthesized dibromo TIPS anthracene, shown in figure 3 - Overall reaction scheme for final compound DCA. I synthesized it with a two-step process: I used 2,6 - dibromo - 9,10 - anthraquinone with nBuLi to make an intermediate product and then reacted with SnCl₂ and toluene to synthesize dibromo TIPS anthracene (fig.5).

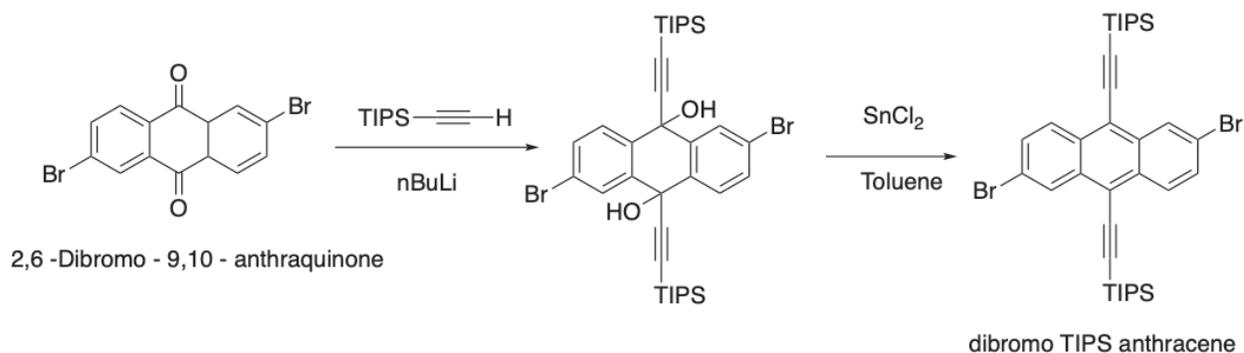


Figure 5: Reaction mechanism to synthesize dibromo TIPS anthracene

There were a lot of impurities seen from the bench-top NMR readings (fig.6). Therefore, we decided to take other steps to make the desired Dibromo TIPS anthracene with a good yield.

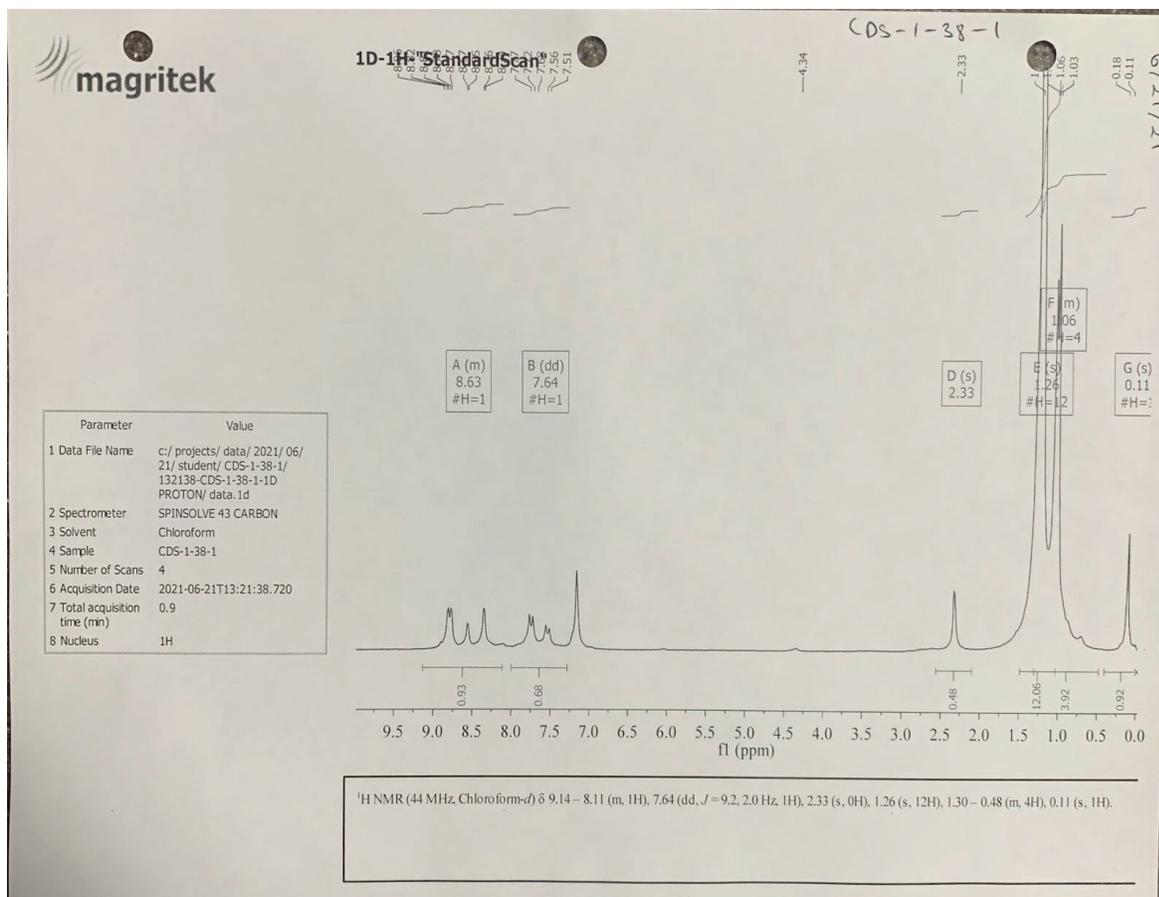


Figure 6: Bench-top NMR readings of Dibromo TIPS anthracene.

Then I synthesized Weinreb amide through these steps: Horner-Wadsworth-Emmons reaction (HWE), saponification, and acid chloride synthesis (fig. 7). The HWE reaction combines an aromatic aldehyde with triethyl phosphonoacetate and sodium hydride to form an ester. The yield for this reaction was quantitatively determined. Here, the reaction mechanism is the nucleophilic addition of phosphonate carbanion onto the carbon of aldehyde.

Secondly, the saponification reaction involved the ester with an excess strong base, potassium hydroxide (KOH), and ethanol as a solvent to synthesize carboxylic acid or trimethyl cinnamic acid. The yield for this reaction was 76%. The reaction mechanism is that the hydroxide anion of KOH reacts with the carbonyl group of the ester to make carboxylic acid. Then, acid chloride

synthesis was performed where there is a nucleophilic reaction of carboxylic acid and acyl chloride (COCl_2).

Lastly, I synthesized Weinreb amide by reacting acid chloride with pyridine as a solvent. The reaction mechanism for this reaction is also a nucleophilic substitution. The yield acquired for this reaction synthesis was 86%.

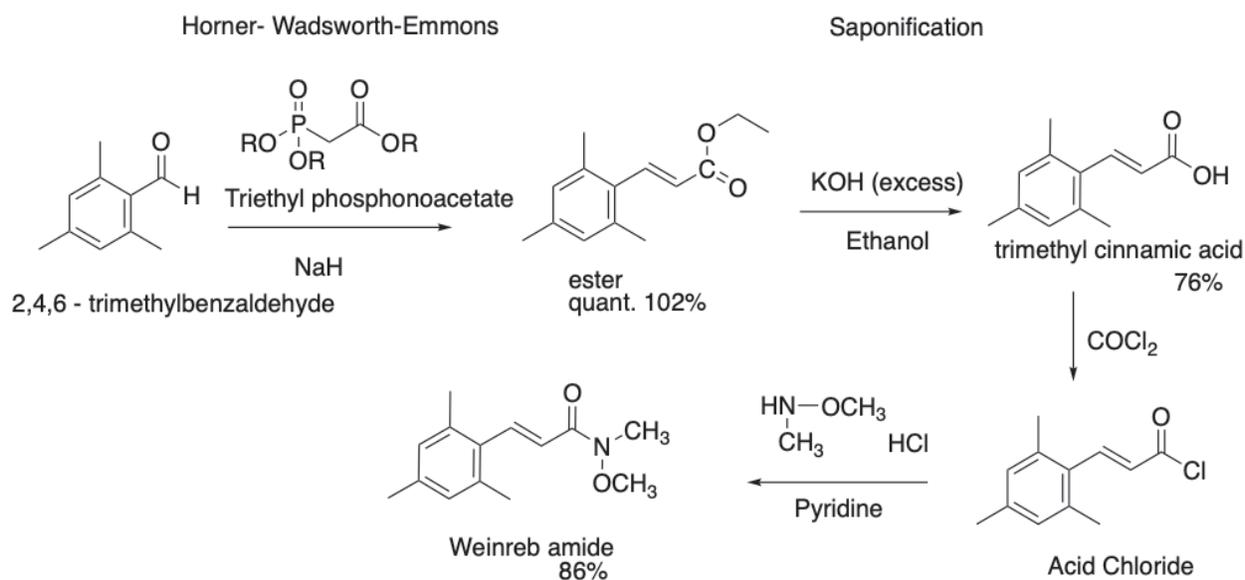


Figure 7: Overall scheme of Weinreb Amide synthesis.

I analyzed the reaction mixtures by finding the crude mass, taking NMR (Nuclear Magnetic Resonance) or TLC (Thin-layer Chromatography) for each of these four reaction mechanisms. The overall reaction yield of Weinreb amide was 65% and a crude mass of 2.036g. The NMR results also proved that I made the desired product by looking at the number of proton peaks of the molecule and the position of those peaks (fig.8). The position of proton peaks of this molecule is shown with the arrow in figure 8.

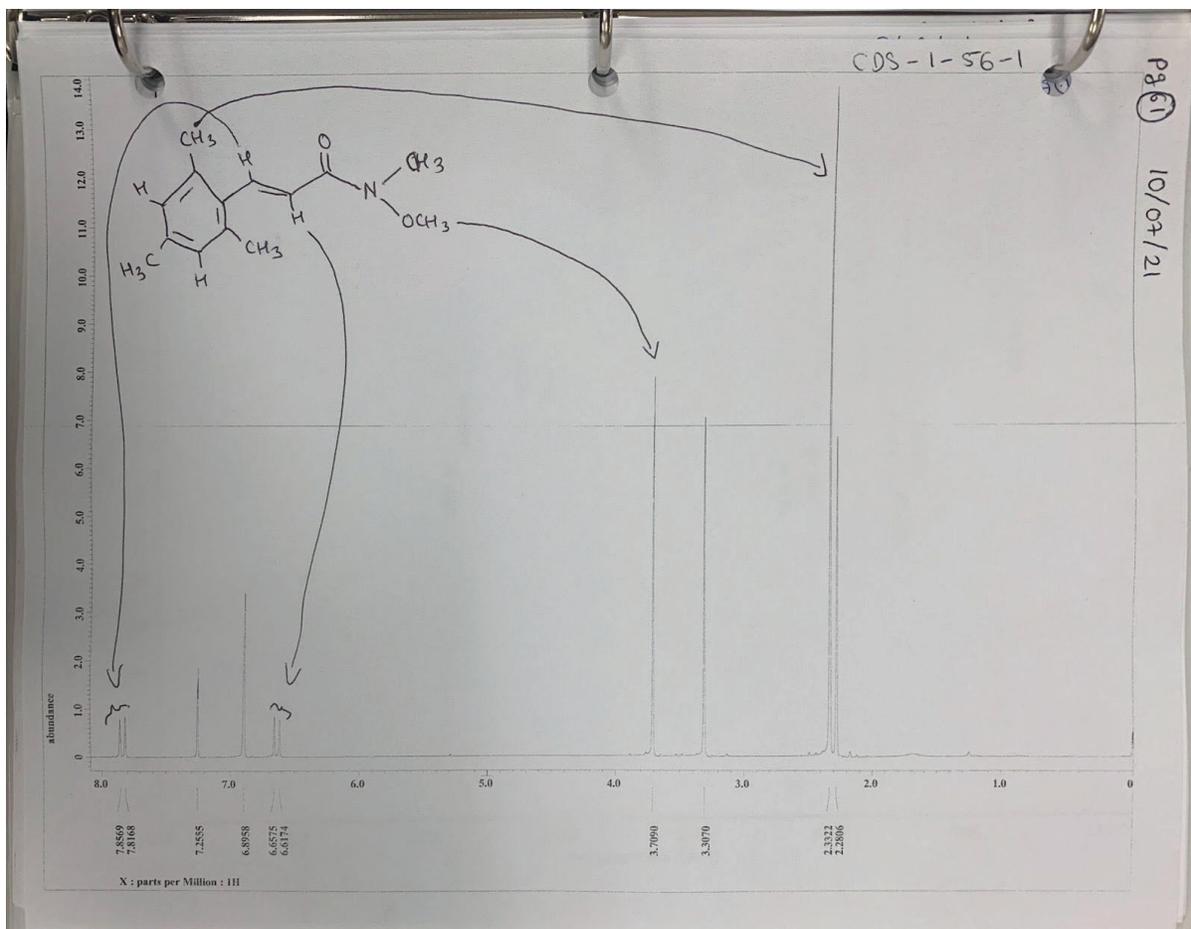


Figure 8: NMR readings of Weinreb Amide where the arrows show the position of their respective proton peaks

After making a good amount of Weinreb amide, I then attempted a synthesis of cinnamoyl anthracene. I did a small-scale initial test reaction with bromobenzene, Weinreb amide, and BuLi to form a Weinreb ketone (fig.9). This test reaction was done to see if this water-sensitive reaction with BuLi could be carried out in a good yield before we moved to the more precious dibromoanthracene compound.

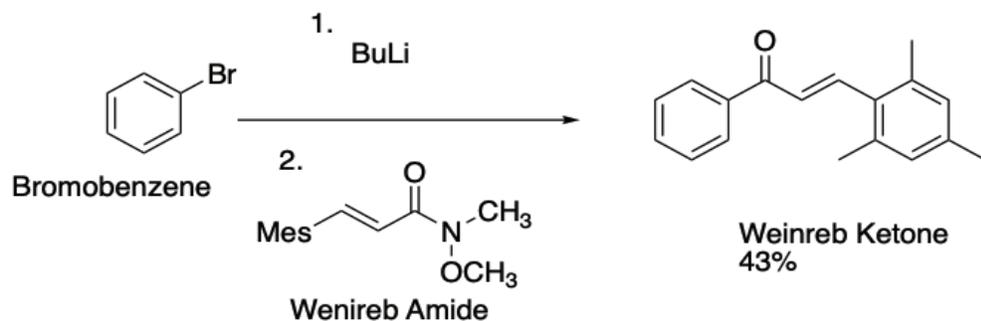


Figure 9: Initial test - Reaction mechanism of Weinreb ketone with BuLi

The percent yield of this initial test was 43% and 0.094g. The column chromatography, followed by the TLC spots with 10% ethyl acetate and NMR readings (fig. 10) of this first test resulted in a Weinreb ketone product.

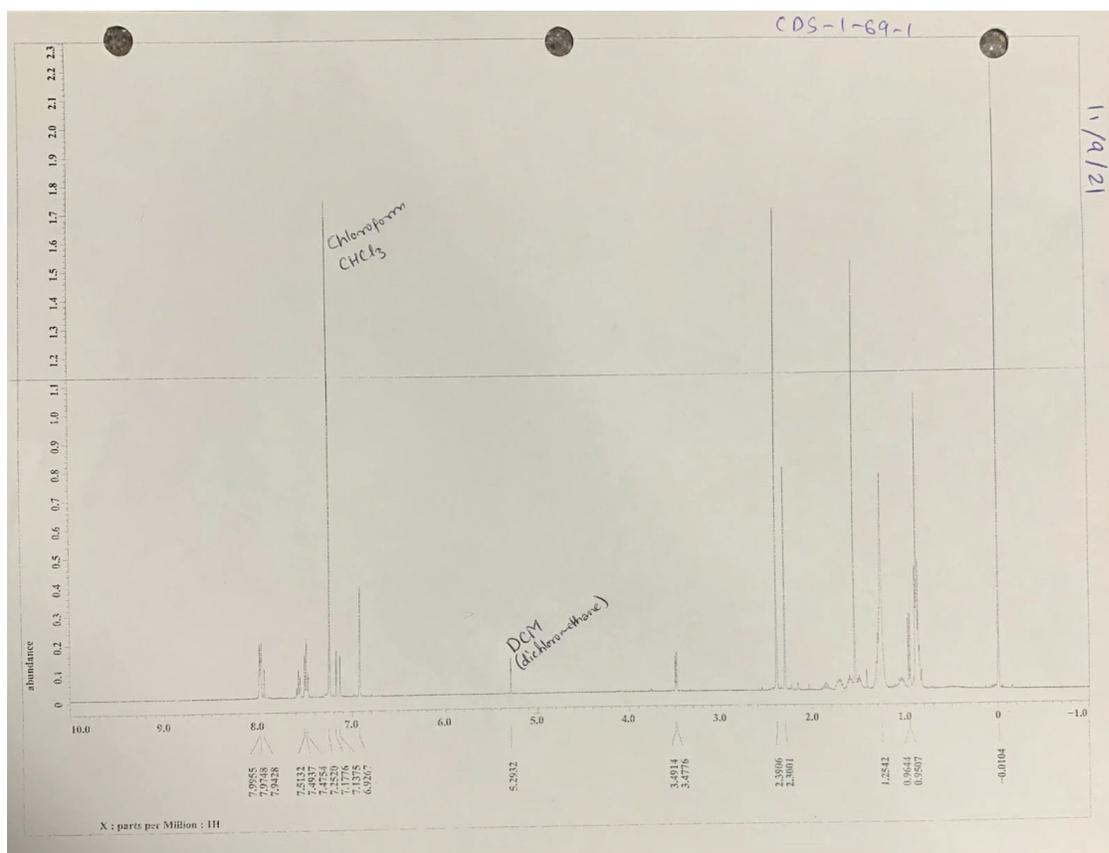


Figure 10: NMR readings of Weinreb ketone.

Since the percent yield of my first test was only 43%, I also attempted the reaction using an *in situ* formed Grignard reagent (R-Mg-X) to see if this route was more effective than with BuLi (fig. 11).

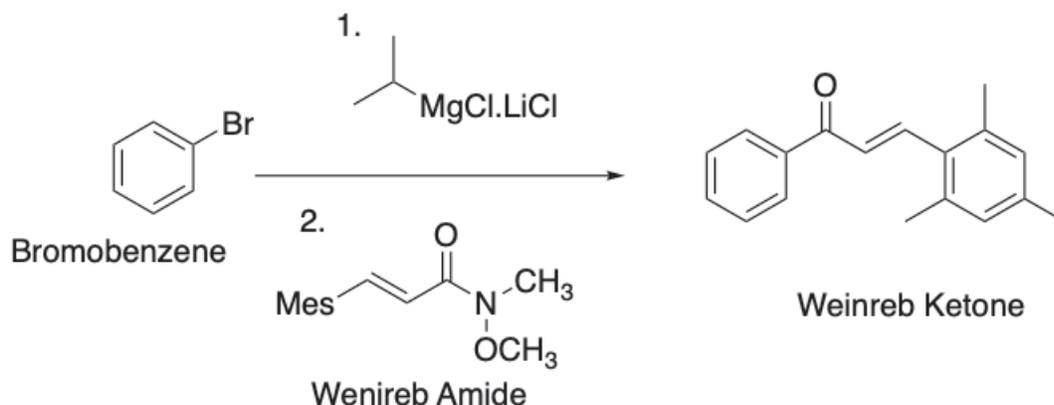


Figure 11: Second test - Reaction mechanism of Weinreb ketone with Grignard reagent

The crude mass from this second test was 0.515g. This second test reaction was unsuccessful. I did the TLC spot with the authentic Weinreb ketone made in the initial test. It showed that there was no presence of the authentic product in the reaction mixture. So, we did not take any further NMR readings and decided to take the initial test with BuLi and try to take it in a different route to produce a greater yield than before.

Conclusion and Future Work

In conclusion, I used air-free and water-sensitive reaction synthesis to make desired products. I have been doing this research synthesis since the start of the Winter 2021 semester with a 3-hour lab meeting every two days a week. I was successful in synthesizing Weinreb Amide with an overall yield of 65%. Since this is ongoing research, I still have to synthesize the cinnamoyl

anthracene to be able to build our final compound, DCA. Therefore, my future work is to synthesize the final compound, dicyclopentaanthracene DCA.

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