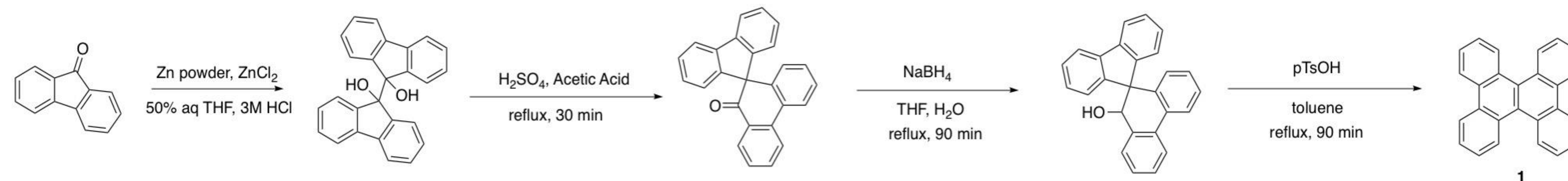


History of Dibenzochrysene

Dibenzochrysene (**1**), DBC, is classified as a small polycyclic aromatic hydrocarbon well known for its nonplanar geometry. This geometry results in a larger gap than expected between its highest occupied molecular orbital and lowest occupied molecular orbital. Additionally, it has a twisted pi system with the ability to influence molecular stacking.¹ This gives the structure unique electronic and optical properties. Electron mobility is one such property, which affects how an electron moves through a metal or semiconductor when attracted by an electric field. A high quantum yield for fluorescence is another attribute, which refers to the efficiency of converting absorbed light to emitted light.² All of these characteristics contribute to the allure and interest chemists have with DBC.

The first synthesis of dibenzochrysene was reported in 1964 by chemist Eric Clar— although with only an 8.1% yield. In 1975, Alder and Whittaker used the Stone Wales rearrangement at 400°C as another synthetic approach. In recent years, there have been many synthetic variations to afford dibenzo[g,p]chrysene but it wasn't until Caitlin Hoffman, a Johnson group alumnus, optimized the synthesis of dibenzochrysene followed in the steps below. This four-step synthesis can be carried out in 88% overall yield. (**Scheme 1**).

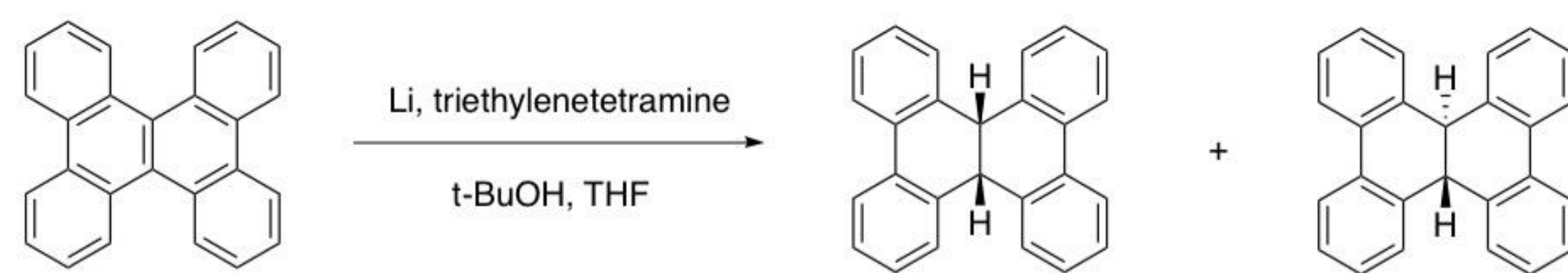


Scheme 1: Hoffman's synthesis of dibenzochrysene

Exploratory Dibenzochrysene Chemistry

DBC provided a palette for many explorative chemical routes. Application of new Birch reduction methods³ as well as photochemical techniques were used for this investigation.

Figure 1 shows the proposed mechanism of the Birch reduction conversion of DBC into two cis/trans stereoisomers. The photodimerization of the structure was another approach, using a 254 nm photoreactor to excite dibenzochrysene. This might result in a [2+2] dimerized product since the exciplex state has two potential pathways to yield either starting material or product (**Scheme 3**). We observed a low yield of Birch reduction. No photoproduct was observed in this exploratory study.



Scheme 2: Birch reduction of dibenzochrysene to afford cis/trans product

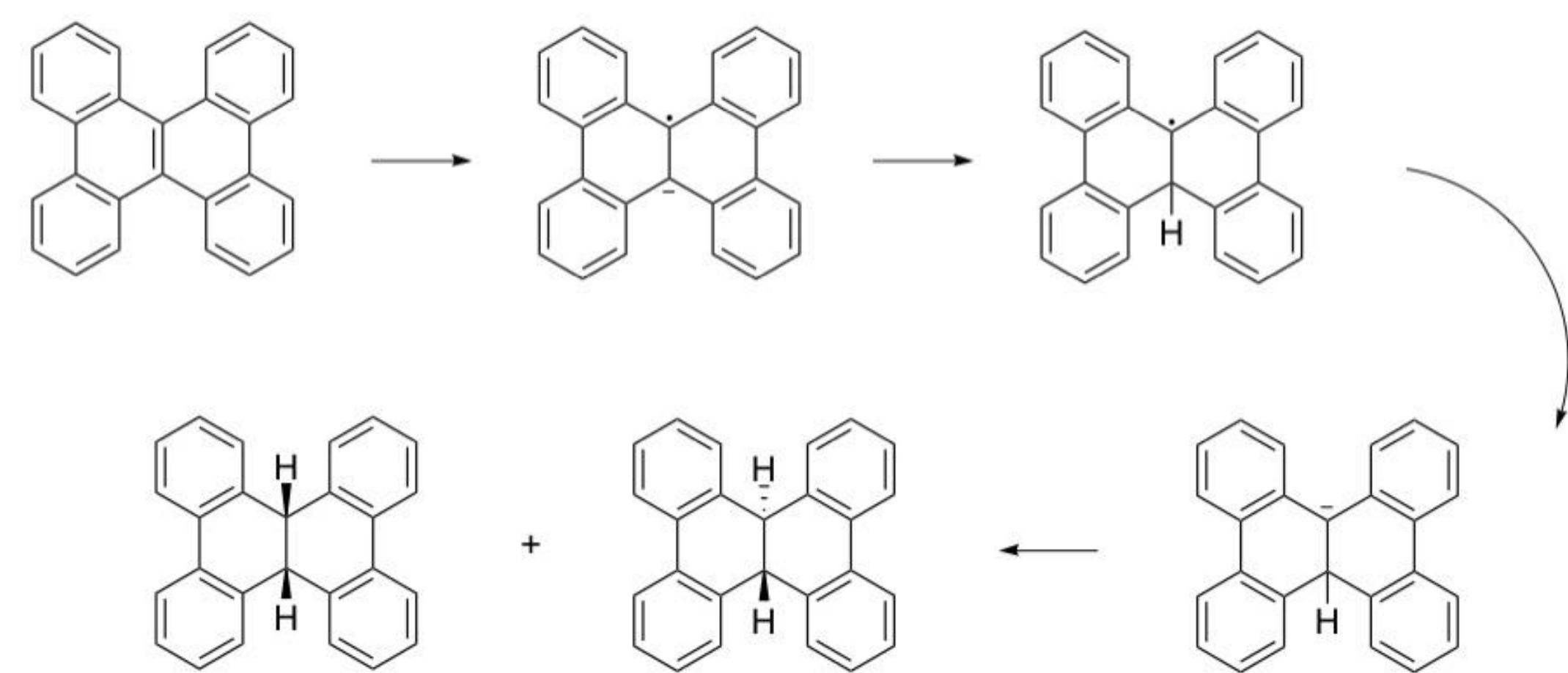
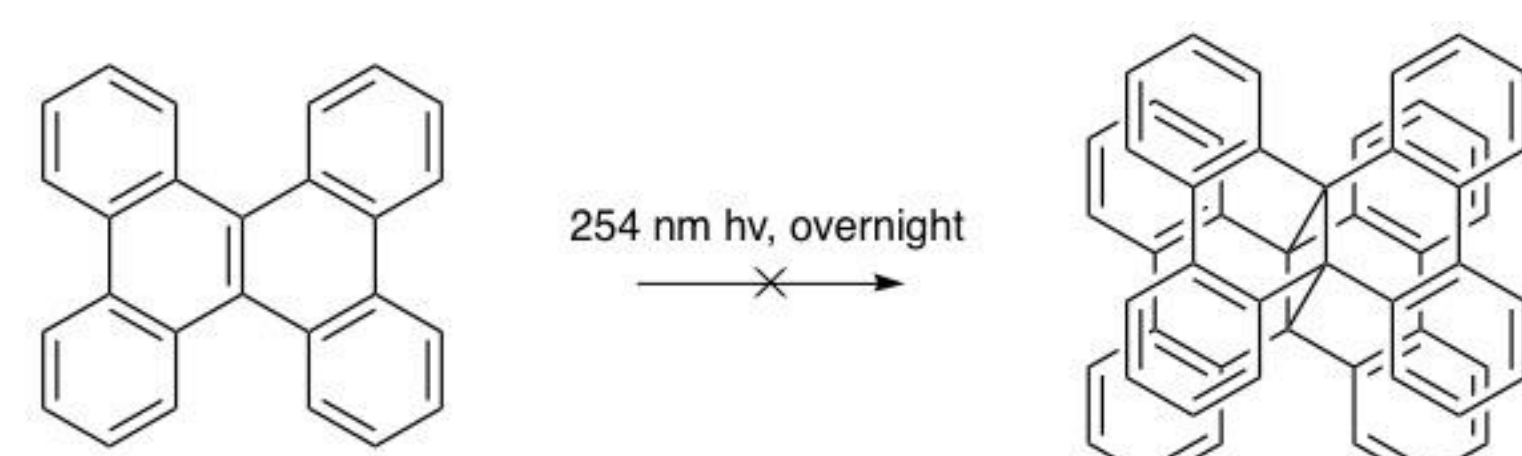


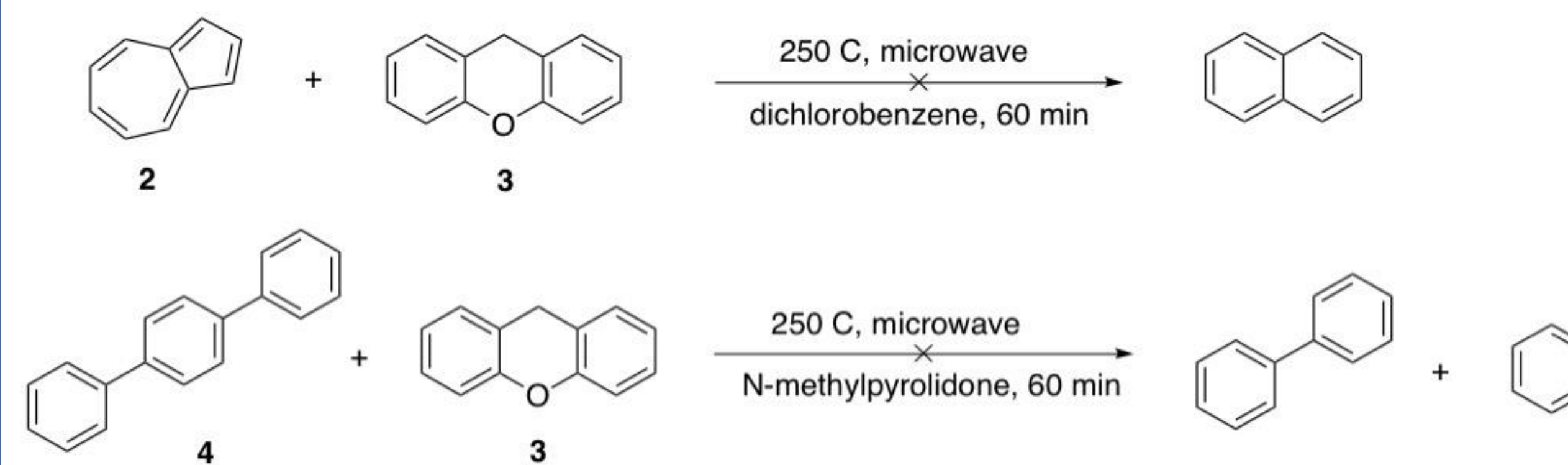
Figure 1: Proposed mechanism for the reduction of dibenzochrysene



Scheme 3: [2+2] dimerization of dibenzochrysene irradiated with 254 nm light

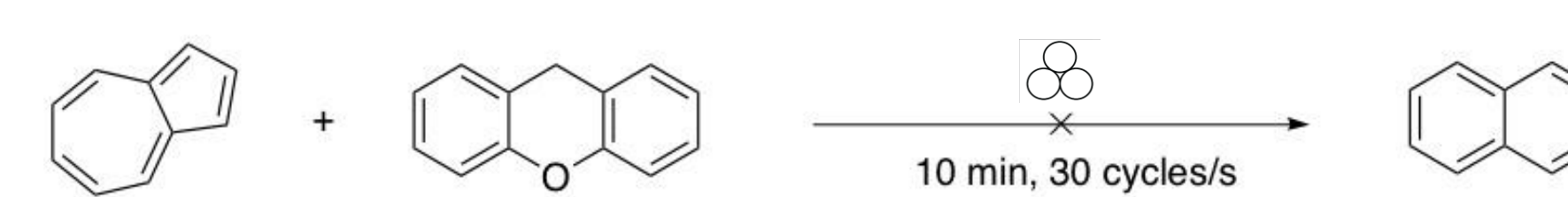
Catalyzed and Reversible Hydrogen Atom Transfer

Many types of chemical reactions proceed by hydrogen atom transfer (HAT).⁴ In this research, we looked at finding potential hydrogen donor substrates to facilitate reversible HAT catalysis which might cause rearrangements of small cyclic structures. Using a microwave reactor, azulene (**2**) and xanthenes (**3**) were heated to 250°C as a preliminary experiment for the potential rearrangement towards naphthalene (**Scheme 4**). Other reactions were run under similar conditions, however with different starting materials and potential hydrogen donors. Terphenyls were also analyzed with this strategy, as HAT can promote aryl-aryl bond cleavage to give phenyl radical and biphenyl products (**Scheme 5**). Neither reaction was successful.



Schemes 4 & 5: Reduction of azulene (**2**) and p-terphenyl (**4**) using xanthenes (**3**) and microwave chemistry

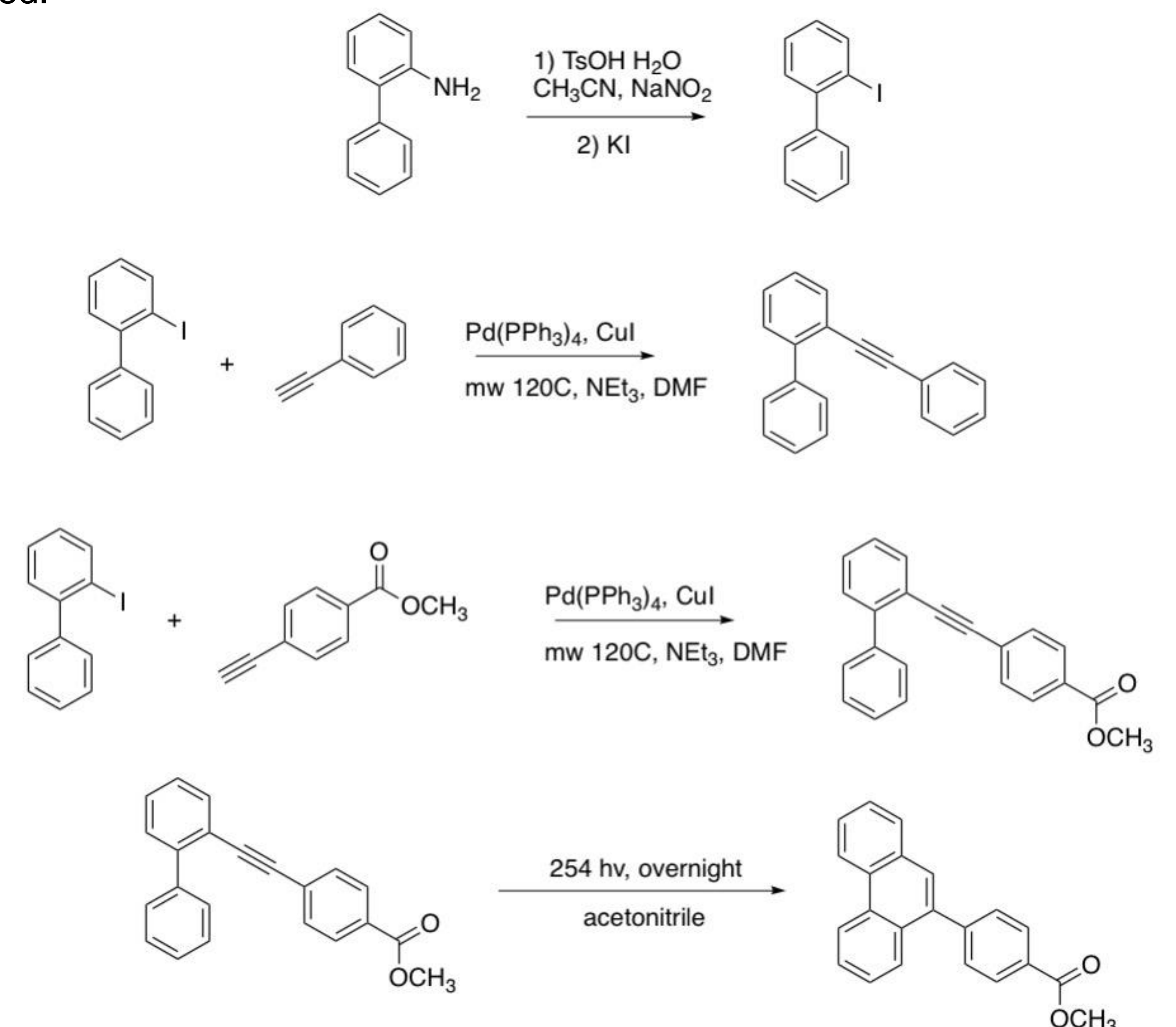
As an effort to try something new, mechanochemistry methods were also attempted using a stainless-steel ball mill (**Scheme 6**). The reaction was run with similar starting materials as the HAT chemistry explored above. Recent findings support mechanochemistry as a practical method for reduction⁵ which is currently being explored.



Scheme 6: Azulene and xanthenes rearrangement using mechanochemistry

Biphenyl Alkyne Chemistry

Our group has discovered that 2-alkynylbiphenyls undergo photocyclization to phenanthrenes. Phenanthrene derivatives have been the target of many synthetic methods and have broad application in material chemistry.⁶ **Scheme 7** depicts the synthetic route to phenanthrene derivatives. The primary objective was to cyclize the alkyne with photochemistry. Phenanthrenes continue to serve in the synthetic approaches for drug design and other medicinal purposes. An efficient cyclization with photochemistry would improve and facilitate their applications. A new carboxyl substituted substrate has been prepared and its photochemistry is being investigated.



Scheme 7: Synthetic approach towards phenanthrenes using photochemistry and biphenyl alkyne precursors

Summary

Overall findings:

- ❖ Our group has developed an efficient and scalable synthesis of dibenzochrysene.
- ❖ Application of a new method for Birch type reduction failed to work with dibenzochrysene. A newer mechanochemistry method is being explored.
- ❖ Dibenzochrysene failed to undergo photodimerization.
- ❖ A new method for hydrogen atom catalyzed reactions was investigated using a microwave reactor. Xanthenes failed to promote reaction.
- ❖ Our group has discovered a new 2-alkynylbiphenyl to phenanthrene photodimerization. A new substrate for the reaction was prepared and is being studied.

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