

University of Arkansas, Fayetteville

ScholarWorks@UARK

---

Chemistry & Biochemistry Undergraduate  
Honors Theses

Chemistry & Biochemistry

---

5-2016

## Improving Photocatalytic Activity by Appending a Quinone to Ruthenium Polypyridyl Complex

Amy N. James

*University of Arkansas, Fayetteville*

Follow this and additional works at: <https://scholarworks.uark.edu/chbcuht>



Part of the [Organic Chemistry Commons](#)

---

### Citation

James, A. N. (2016). Improving Photocatalytic Activity by Appending a Quinone to Ruthenium Polypyridyl Complex. *Chemistry & Biochemistry Undergraduate Honors Theses* Retrieved from <https://scholarworks.uark.edu/chbcuht/17>

This Thesis is brought to you for free and open access by the Chemistry & Biochemistry at ScholarWorks@UARK. It has been accepted for inclusion in Chemistry & Biochemistry Undergraduate Honors Theses by an authorized administrator of ScholarWorks@UARK. For more information, please contact [scholar@uark.edu](mailto:scholar@uark.edu).

# **Improving Photocatalytic Activity by Appending a Quinone to Ruthenium Polypyridyl Complex**

---

A thesis submitted in partial fulfillment of the  
requirements for the degree of Bachelors of  
Science of Biochemistry

**By: Amy Nicole James**

2016

Chemistry

J. William Fulbright College of Arts and Sciences

**The University of Arkansas**

## Acknowledgements

I would like to recognize and thank the Arkansas Department of Higher Education for selecting me as a recipient of the Student Undergraduate Research Grant. Most importantly to my undergraduate research experience, I would like to personally thank Dr. Nan Zheng and Theresa Nguyen for their teaching, guidance, and assistance throughout the duration of this thesis research. Only with the help and patience of these mentors has it been possible for me to learn all that I have during my research experience. In addition, I would also like to thank Dr. Neil Allison, Dr. Fran Hagstrom, and Dr. Cory Mixdorf for volunteering their time to review and critique my thesis as members of my thesis committee.

## Table of Contents

I. Introduction .....	3
II. Experimental Plan .....	7
III. Results .....	10
IV. Future Work.....	13
V. Conclusions .....	14
VI. Experimental Data.....	15
VII. Reference .....	17
VIII. Appendix .....	22

## **Improving Photocatalytic Activity by Appending a Quinone to Ruthenium Polypyridyl Complex**

### **Introduction:**

Photochemistry is an upcoming and fascinating field of study that has made significant progress, but also has a great potential for future work. Photochemistry, incorporating green chemistry, is a quickly developing field inspired by the need for renewable and sustainable resources that are environmentally friendly. By utilizing light as a natural energy source, many reaction processes in chemistry can be viewed with a new perspective. While ultra-violet light is one of the most powerful energy wavelengths, it is not always ideal for use in the chemistry laboratory because it is a safety hazard and requires specialized and expensive apparatuses. Common laboratory glassware is not permeable by the UV spectrum, and these photochemical reactions require specific equipment which often must utilize quartz instead of glass. However, visible light can permeate glassware and does not require a high energy light source. In fact, fluorescent bulbs, standard household bulbs, or sunlight can all be utilized to achieve the conversion of visible light energy to chemical energy in visible light photochemistry.<sup>16</sup> Visible light catalysis also offers an advantage over UV light catalysis by being able to be photoexcited with less energy. This allows for selectively photoexciting the catalyst without causing organic reactants to reach the excited state. The latter photoexcitation often leads to more side reactions and thus hinder the desired reaction. The desire for safer and more feasible techniques in photochemistry is what has driven the work towards harnessing the energy from visible light, which is not only safe, simple to use, and environmentally sustainable, but also more abundant than ultra-violet light.

Photocatalysts such as ruthenium or iridium polypyridyl complexes have been found capable of successfully utilizing visible light to engage organic molecules in redox chemistry. Ruthenium polypyridyl complex is a specifically noteworthy photocatalyst due to its electrochemical properties. Its absorption spectrum is a broad range centered at 450 nm, which allows it to reach the photoexcited state with a variety of visible light wavelengths.<sup>16</sup> The absorption band also relates to metal to ligand charge transfer to create the photoexcited state with a high quantum yield.<sup>13</sup> One benefit of this excited state is that it is electrochemically stable, even at high temperatures, and acidic or basic reaction conditions. This specific MLCT state is of particular interest to chemists due to its ability to act as an electron donor or as an electron acceptor in redox reactions as well as an energy transfer agent (Figure 1).<sup>16</sup> The effectiveness of the MLCT state in participating in the three different cycles is the foundation of photoredox chemistry. The MLCT

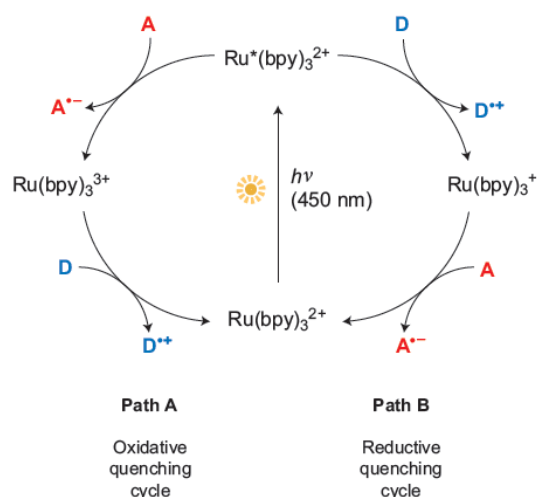


Figure 1: Oxidative and reductive quenching cycles in Ru(bpy)<sub>3</sub><sup>2+</sup> photochemistry<sup>16</sup>

state has the capability to generate radical ions from stable, closed shell compounds. This is commonly done by using an electron donor to reduce the excited state of the polypyridyl complex, and then accomplishing efficient single-electron transfer to a poor electron acceptor. As portrayed in Figure 1, this mechanism allows for the reductive potential to be utilized while also regenerating the initial state of the catalytic cycle. Path A of Figure 1 represents the oxidative quenching cycle, where an electron acceptor oxidizes the ruthenium complex. The oxidized ruthenium complex can then react with a reductant to regenerate the photocatalyst. The

ruthenium complex is also able to alter an acceptor molecule by electronic energy transfer.<sup>15</sup>

After entering the triplet state, the ruthenium complex is able to transfer the energy absorbed from visible light to excite another molecule. When the ruthenium complex transfers its energy, it regenerates the ground state of the photocatalyst.

Visible light photochemistry is environmentally friendly and is considered to be a major type of green chemistry.<sup>14</sup> It provides a number of benefits over other classes of organic reactions. One benefit of photocatalysis is the oxidative generation of reactive intermediates such as amine radical cations. An example of this benefit to synthetic application is a tin-free reductive dehalogenation method, which has many advantages compared to traditional radical chemistry.<sup>12</sup> Utilizing photoredox for dehalogenation improves the chemoselectivity and also provides an environmentally friendly method, which avoids toxicity and difficult purification. The amine reductive quencher used for this dehalogenation method has provided insight for the formation of amine radical cations. This has allowed for iminium intermediate generation using photocatalysis, which has biological relevance as well as benefits for pharmaceutical synthesis.<sup>3</sup> This photocatalytic process has also been used for the functionalization of amines.<sup>14</sup> The reductive and oxidative utility of the ruthenium polypyridyl complex photocatalytic cycles allows for a diversity of reactions and benefits in synthetic chemistry.

Another valuable synthetic attribute of photocatalysts is their use for forming carbon-carbon bonds in intramolecular reactions. One example of this synthetically relevant work is the improvement of Diels-Alder reaction conditions to eliminate the need of high loading of the oxidant or photosensitizer and of high-intensity lamps.<sup>8</sup> In order to successfully conduct photocatalyzed [4+2] cycloadditions, ligand modifications of the ruthenium complex were utilized and this allowed electronically mismatched reactions to occur under photocatalytic

conditions. Cycloadditions using the ruthenium photocatalyst have continued to be improved, and the [3+2] cycloaddition of cyclopropylamines not only allows for mild reaction conditions, but also reduces chemical waste by using an amine group as a sacrificial donor and as the substrate.<sup>9</sup> Modifications of the ruthenium polypyridyl complex are not only useful for synthesis, but light activated complexes are even being studied in antitumor drug delivery, known as photodynamic theory.<sup>5</sup>

By proceeding through a catalytic cycle (Figure 1), the ruthenium center is photoexcited by visible light. In this excitation process, the photocatalyst absorbs photons from visible light and is able to reach the photoexcited state. Photon

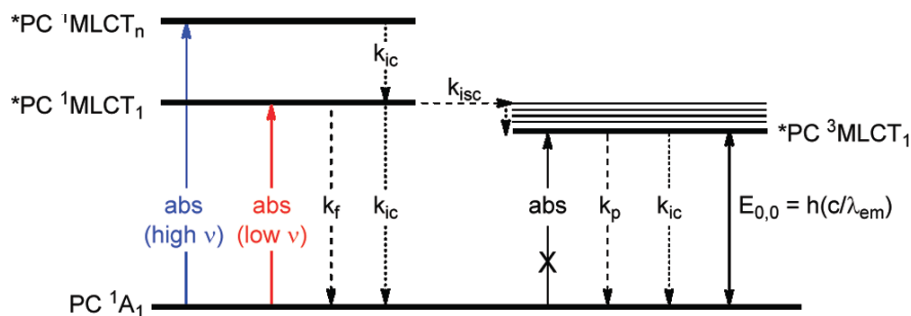


Figure 2: Generalized Jablonski diagram of photocatalysts.  $k_f$ ,  $k_{ic}$ ,  $k_{isc}$ , and  $k_p$  are the rate constants for fluorescence, internal conversion, intersystem crossing, and phosphorescence, respectively and  $\lambda_{em}$  is the maximum emission wavelength of the photocatalyst.<sup>14</sup>

absorption is what allows for the chemical potential of photocatalysts, and as can be seen in Figure 2, the energy is related to the wavelength absorbed. Following excitation, the complex relaxes to the lowest spin-allowed metal-to-ligand-charge-transfer (MLCT) state. From this state, intersystem crossing occurs ( $k_{isc}$ , Figure 2) to reach the triplet state. Intersystem crossing is possible in the ruthenium polypyridyl complex due to a similarity in energy levels of the metal and the bipyridine ligand. Internal conversion then allows the complex to reside in a long lifetime first triplet excited state.<sup>14</sup> Once the triplet state is achieved, spin-forbidden symmetry causes the electrons to be held in the excited for an extended period of time, which must relax through the process of phosphorescence. Therefore, the process of phosphorescence allows for a

longer relaxation time than fluorescence.<sup>15</sup> While the electrons are in the excited state, the ruthenium complex can act as a reducer or an oxidizer to catalyze redox chemistry in organic molecules. Additionally, the excited ruthenium complex can transfer energy to organic molecules via the energy transfer cycle.

The catalytic energy of ruthenium complexes is stored as a form of charge separation in the metal-to-ligand-charge-transfer (MLCT) photoexcited state.<sup>17</sup> The lifetime of the charge separation is prolonged by a facile intersystem crossing in ruthenium polypyridyl complexes. Various ligands have been tested with the ruthenium complex and have been found to improve photoactivity due to altering the reduction potential of the complex ground state. For example, electron donating ligands attached to the ruthenium complex will enhance the reductive process, therefore lowering the reduction potential (Figure 3).<sup>14</sup> Electron withdrawing groups decrease the electron density of the ligand and increase the oxidative power of the complex. Also by extending the distance between charges, this can increase

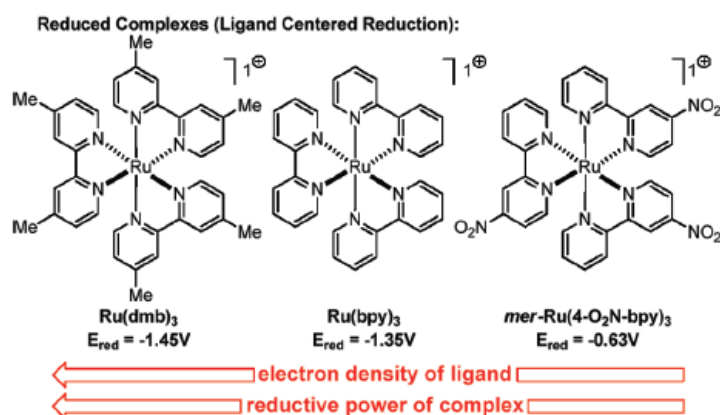


Figure 3: Ligand effects on ground-state redox properties of catalysts

the energy stored in charge-separated excited states.<sup>11</sup> Through ligand alteration, the transferred electron from the ruthenium metal can be delocalized over a larger ligand-based system. This delocalization is able to reduce vibrational overlap with the ground state and decrease the amount of non-radiative decay, therefore prolonging the lifetime of the MLCT excited state.<sup>10</sup> In order to further prolong the lifetime of the photoexcited state, a unique appendage attached to the bipyridyl ligand will be studied. The experimental design, including a Quinone appendage, has



the possibility of further increasing the lifetime of MLCT between the ruthenium metal center and the ligand.

### Experimental Plan:

First of all, the addition of a Quinone appendage has possible benefits of creating a greater distance between the charges, prolonging lifetime, and reducing the amount of chemical waste by avoiding the use of sacrificial electron donors. The Quinone is also able to serve as a more distant electron sink for the MLCT.

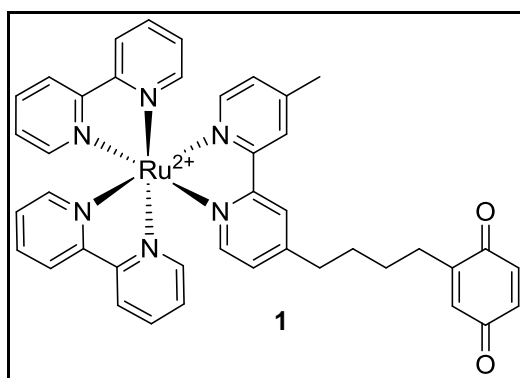


Figure 4: The targeted Ruthenium Polypyridyl Complex with Quinone Appendage

An increased distance between the charge transfers has the ability to prolong the catalyst lifetime and keep the electrons in the excited state longer. The excited state of the original ruthenium polypyridyl complex has a limited lifetime of 200 nanoseconds. Therefore, an extension of this time would be beneficial to promote photochemical reactions. The design of the Quinone appendaged photocatalyst is to create a second, additional charge separation. The Ruthenium center reduces the original bipyridine ligand, and then the Quinone is able to accept

this electron for a second charge transfer to occur. The Ruthenium center has a positive charge, and the negative charge on the Quinone creates an increased charge separation for the MLCT.

Scheme 1: Synthesis of 3-(2,5-dimethoxyphenyl)propanal

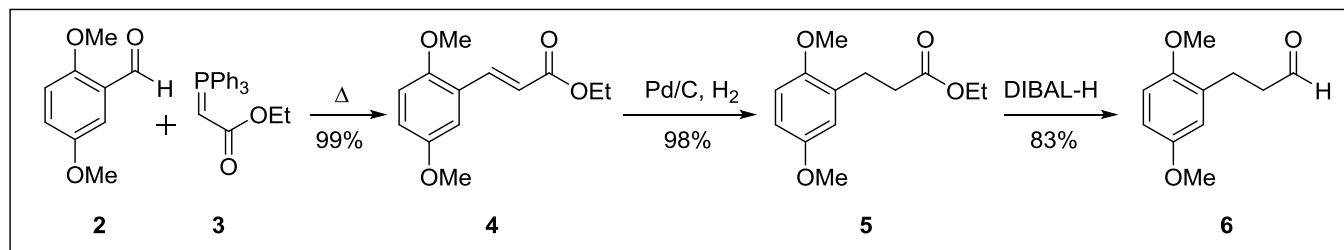


Figure made by Amy James

Scheme 2: Synthesis of Phosphonate Reactant

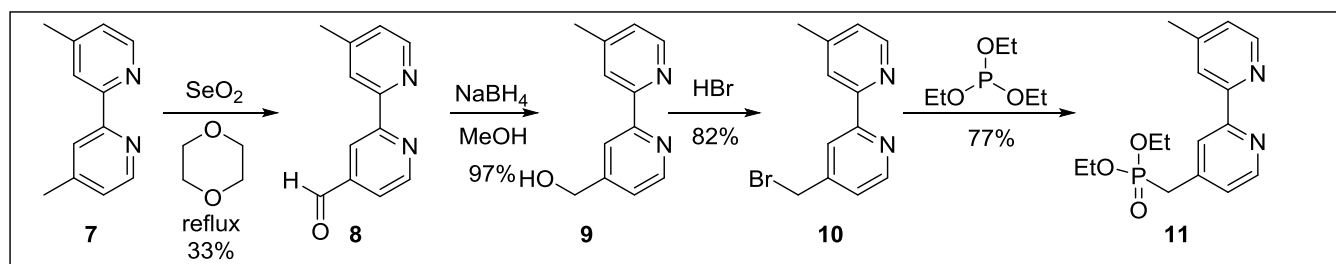


Figure made by Amy James

Scheme 3: Synthesis of Quinone Appendage and Ruthenium Catalyst

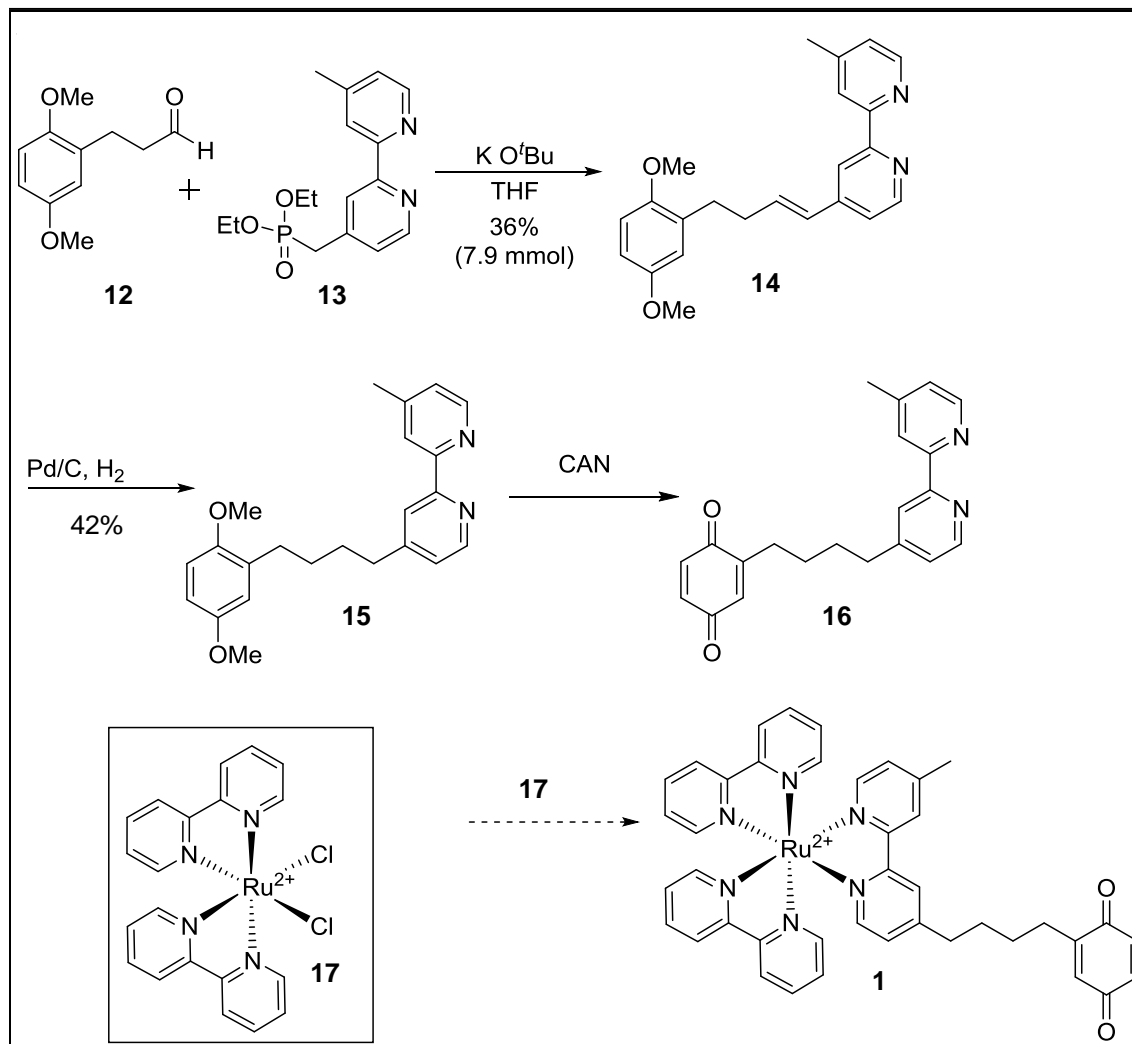


Figure made by Amy James

Retrosynthetically, the bipyridyl ligand with the Quinone appendage **1** is envisioned to be synthesized by a Horner-Wadsworth-Emmons (HWE) reaction, revealing two reactants: 3-(2,5-dimethoxyphenyl)propanal **6** and phosphonate **11**. Scheme 1 details the synthesis of **6** while Scheme 2 describes the synthesis of **11**. Scheme 3 focuses on the union of **6** and **11** via the HWE

reaction and subsequent hydrogenation to give the desired ligand, which will be converted to the targeted ruthenium complex by substitution of the two chlorides on ruthenium complex **17**.

The product will be purified using column chromatography and then analyzed by NMR to decipher if the synthesis is successful. After the structure of the ruthenium complex with the Quinone appendage is confirmed, it will be tested for catalytic activity under visible light in comparison to the original ruthenium polypyridyl complex. The [3+2] annulation of cyclopropylaniline and styrene developed in our group will be used as a model reaction.<sup>9</sup>

## Results:

Several synthetic steps must be successfully completed in order to produce the targeted ruthenium complex. The first step of Scheme 1 was where this project began and was completed with 99% yield. The reaction solvent used was toluene. Then, the ester (**4**) underwent hydrogenation using 10% Palladium on Carbon in methanol. A hydrogen balloon was used and the reaction ran for 12 hours. After the product was filtered over a celite pad and through column chromatography, the percent yield was 99%.<sup>2</sup> DIBAL was utilized next to reduce the ester group. The solution of starting material in dichloromethane (DCM) was cooled to -78 °C and DIBAL-H was added dropwise. After stirring for 30 minutes, methanol was added and the reaction was warmed to room temperature. After extraction with CHCl<sub>3</sub>, washing with HCl, and drying with brine and Na<sub>2</sub>SO<sub>4</sub>, solvent was removed. The remaining oil product was transferred to a silica gel column and eluted. Purification was completed following the previously published procedure and the percent yield was 83%.<sup>4</sup>

The second scheme was also completed in order to obtain the other reactant for the final catalysis synthesis. 4,4'-Dimethyl-2,2'-bipyridine underwent oxidation with selenium dioxide in dioxane.<sup>1</sup> The aldehyde was isolated in 33% yield. Rather than continuing with the proposed scheme due to the reduced amount of material, alcohol **9** prepared by a former student was used to complete the synthesis of **11**. This compound was dissolved in 48% HBr. Following the conditions according to a literature procedure,<sup>7</sup> 4-bromomethyl-4'-methyl-2,2'-bipyridine was afforded in 82% yield. The brominated product was then treated with triethylphosphite in chloroform under nitrogen for 24 hours. The conditions were similar to the published procedure,<sup>6</sup> and gave phosphonate **11** in 77% yield.

The final scheme for combining aldehyde **6** and phosphonate **11** was attempted next. A small scale of 0.5 mmol was tested first before subjecting all of the materials. After deciphering the NMR to confirm a successful reaction, there was not enough product from Scheme 2 to react with all of the product from Scheme 1 and the amount of the product would have been too small to continue. Therefore, the original product that I had made in step **8** was also reduced using sodium borohydride to provide alcohol **9** in 98% yield. The rest of Scheme 2 was successfully completed with this additional product. The HWE reaction between aldehyde **6** and phosphonate **11** was performed on a 7.9 mmol scale, and alkene **14** was obtained in 37% yield.

The original scheme did not require reduction of alkene **14**. When NMR was analyzed however, it appeared that this product was present as a mixture of cis/trans isomers. Due to the similarity in the isomers' structures, the isolation of the trans isomer from the mixture proved to be challenging. This is when the additional reaction, reducing the alkene, was attempted so that both isomers were converted to one single compound. This was initially done under the same reaction conditions as shown for synthesizing **5** (Scheme 1). The alkene in a solution of methanol

underwent hydrogenation using 10% Palladium on Carbon for 12 hours. A hydrogen balloon was used. The reaction did not go to completion as observed by thin layer chromatography (TLC). When the reduced product was attempted to be separated from the starting material and impurities using column chromatography, the structures with only a difference between a single bond and a double bond were too similar to be separated by this purification method. In order to form more products, the same reaction was repeated with a Parr hydrogenator to allow for a higher H<sub>2</sub> pressure to be applied. NMR analysis of this second reaction attempt showed that both cis/trans isomers were converted to the alkane. The NMR from the first reaction attempt of compound **15** can be seen in the Appendix for comparison with the second trial, where the isomer peaks are no longer present. Purification was attempted once again using a 5:1 hexane to ethyl acetate solvent in alumina gel column chromatography. Even though the separation was better than the original procedure, it was still difficult to isolate the pure compound. Product **15** was collected in 42% yield. The rest of the product was recovered, but remained in mixed fractions based on TLC analysis and was not used for further reactions. This new structure was characterized by <sup>1</sup>H NMR, DEPT, and <sup>13</sup>C NMR to ensure that the correct product was formed.

For the cerium ammonium nitrate (CAN) oxidation to form the Quinone, a small scale of 0.1 mmol was first completed to ensure success of the reaction before subjecting all of the material. Acetonitrile and water were added to a vial containing 0.1 mmol of **15**. CAN was added and a stir bar was used to stir the solution for 10 minutes. The reaction was worked up using water and dichloromethane (DCM). After the organic layer was collected, the aqueous phase was extracted with DCM three times and the organic layer was collected each time. The combined organic phases were washed with brine and dried over sodium sulfate. Rotary evaporation was used to remove solvent, and the residual was analyzed by NMR. The small scale formation of

product **16** was found to be successful. The full amount of material **15** was then subjected to the same reaction conditions on a 1.2 mmol scale. Based on NMR analysis, the methoxy groups were reduced and the Quinone was indeed synthesized.

### Future Work:

In previously studied photochemical reactions, it is necessary to utilize sacrificial amines in order to reduce the photoexcited state of  $Ru^{II+}$  to regenerate the catalyst.<sup>16</sup> By altering the ruthenium complex to contain the DABCO ring, the complex can function solely without the required use of an external amine as a sacrificial electron donor.

Scheme 4: Synthesis of DABCO appendage

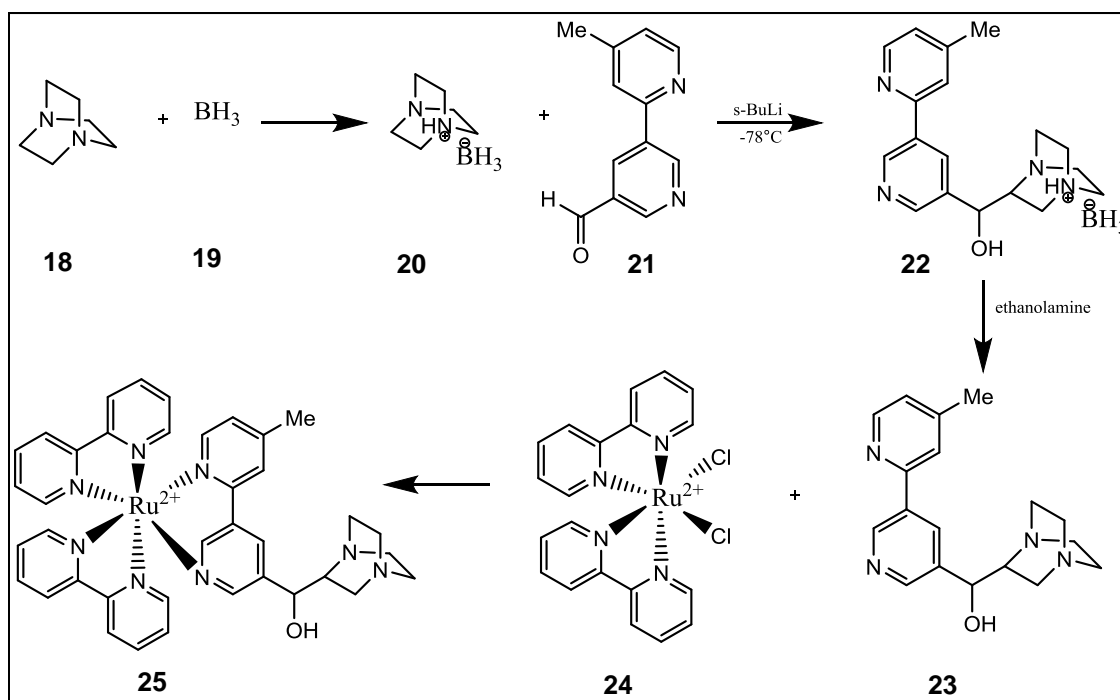


Figure made by Amy James

Scheme 4 can be used to synthesize the DABCO appendage to the ruthenium polypyridyl complex. The ruthenium polypyridyl complex incorporating the DABCO ring may also be tested as a photo-catalyst to catalyze the [3+2] annulation of cyclopropylanilines and alkynes previously developed in our group. The product should then be purified using column chromatography and its structure will be confirmed by NMR.

### Conclusions:

Based on characterization of  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and DEPT, it can be concluded that the completion of Schemes 1 and 2 has been successful. The combination of previously developed procedures to produce the reactants for creating a new photocatalyst has been shown to be possible based on the proposed synthetic route. The products of Schemes 1 and 2 were also used to synthesize new compounds **14**, **15**, and **16**. Products **14** and **15** were successfully characterized by  $^1\text{H}$  NMR,  $^{13}\text{C}$  NMR, and DEPT, and the desired structure was formed based on the proposed procedure.

The accomplished synthetic schemes that have been proven to be successful are a significant contribution to the formation of the targeted photocatalyst. With the majority of the synthesis completed, the final synthesis of the ruthenium polypyridyl complex with a Quinone appendage can be fulfilled in simply one more reaction. Once this unique photocatalyst is generated, it can be tested for photocatalytic efficiency in photochemical reactions, such as [3+2] annulation of cyclopropylaniline and styrene.

By contributing to the development of a new photocatalyst, advancements in photochemistry continue to be pursued. With each new photocatalyst containing its



individualized electrochemical properties, the possibility for new reactions and benefits arise. Stronger, and more diverse photocatalysts allow for existing reactions that are environmentally harmful, or difficult to complete to be replaced with simplistic methods that only require visible light as a source of energy. Not only are current reactions improved, but new synthesis becomes possible too. Visible light photochemistry with its sustainable and user-friendly methods opens the door to industrial scale synthesis of reactions that are too complex, expensive, or harmful to be produced currently at this level. The final synthesis of a Quinone appendage to ruthenium polypyridyl complex has the potential to be a new and effective photocatalyst, and should be completed and tested for its photocatalytic activity in order to contribute to the development of photochemical reactions. If successful, this new strategy to improve photocatalyst's performance can be applied to a large number of the existing ruthenium polypyridyl complexes.

**Experimental Data:**

**4**  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  7.95 (dd,  $J = 16.1, 0.5$  Hz, 1H), 7.02 (dt,  $J = 3.1, 0.5$  Hz, 1H), 6.89 (dd,  $J = 9.0, 3.0$  Hz, 1H), 6.87 – 6.81 (m, 1H), 6.47 (d,  $J = 16.1$  Hz, 1H), 4.24 (q,  $J = 7.1$  Hz, 2H), 3.82 (s, 3H), 3.77 (d,  $J = 0.6$  Hz, 4H), 1.32 (t,  $J = 7.1$  Hz, 3H).

**4**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  167.57, 153.68, 153.01, 139.95, 124.20, 119.20, 117.25, 113.43, 112.63, 77.55, 60.60, 56.28, 55.98, 14.58.

**5**  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  6.73 – 6.69 (m, 3H), 4.11 (dd,  $J = 7.2, 0.4$  Hz, 2H), 3.77 – 3.73 (m, 6H), 2.89 (dd,  $J = 8.7, 7.0$  Hz, 3H), 2.63 – 2.57 (m, 2H), 1.22 (dt,  $J = 7.1, 0.4$  Hz, 3H).

**5**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  173.51, 153.58, 151.96, 130.28, 116.51, 111.68, 111.27, 60.51, 55.98, 55.89, 34.48, 26.46, 14.47.

**6**  $^1\text{H}$  NMR (300 MHz, Chloroform-*d*)  $\delta$  9.80 (t,  $J = 1.6$  Hz, 1H), 6.82 – 6.66 (m, 3H), 3.80 – 3.71 (m, 6H), 2.92 (t,  $J = 7.5$  Hz, 2H), 2.75 – 2.68 (m, 2H).

**6**  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  202.51, 153.59, 151.76, 129.95, 116.57, 111.62, 111.24, 55.85, 44.02, 23.83.

**8**  $^1\text{H}$  NMR (300 MHz, Chloroform-*d*)  $\delta$  10.19 (d,  $J = 0.6$  Hz, 1H), 8.96 – 8.88 (m, 1H), 8.83 (dd,  $J = 1.7, 0.9$  Hz, 1H), 8.58 (d,  $J = 4.9$  Hz, 1H), 8.28 (td,  $J = 1.4, 0.7$  Hz, 1H), 7.73 (dd,  $J = 4.9, 1.6$  Hz, 1H), 2.47 (s, 3H).

**9**  $^1\text{H}$  NMR (300 MHz, Chloroform-*d*)  $\delta$  8.56 (dd,  $J = 4.9, 0.8$  Hz, 1H), 8.48 (d,  $J = 5.0$  Hz, 1H), 8.29 (dd,  $J = 1.9, 1.0$  Hz, 1H), 8.20 – 8.11 (m, 1H), 7.31 – 7.22 (m, 1H), 7.16 – 7.05 (m, 1H), 4.74 (s, 2H), 3.91 (s, 1H), 2.41 (s, 3H).

**10**  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.75 – 8.57 (m, 1H), 8.55 (dt,  $J = 5.4, 1.4$  Hz, 1H), 8.47 – 8.32 (m, 1H), 8.31 – 8.10 (m, 1H), 7.41 – 7.06 (m, 2H), 4.48 (d,  $J = 4.8$  Hz, 2H), 2.45 (q,  $J = 1.1$  Hz, 3H).

**11**  $^1\text{H}$  NMR (300 MHz, Chloroform-*d*)  $\delta$  8.60 (dt,  $J = 5.0, 0.8$  Hz, 1H), 8.52 (dd,  $J = 5.0, 0.9$  Hz, 1H), 8.31 (ddd,  $J = 2.7, 1.7, 0.8$  Hz, 1H), 8.21 (dd,  $J = 1.7, 1.0$  Hz, 1H), 7.34 – 7.28 (m, 1H), 7.12 (ddt,  $J = 4.9, 1.6, 0.8$  Hz, 1H), 4.11 – 4.02 (m, 4H), 3.22 (d,  $J = 22.2$  Hz, 2H), 2.43 (d,  $J = 0.8$  Hz, 3H), 1.25 (t,  $J = 7.1$  Hz, 6H).

**11**  $^{13}\text{C}$  NMR (75 MHz,  $\text{CDCl}_3$ )  $\delta$  155.73, 149.35, 149.14, 148.29, 142.38, 124.99, 124.96, 122.64, 122.14, 62.61, 62.52, 34.67, 32.86, 21.35, 16.56, 16.49.

**14**  $^1\text{H}$  NMR (300 MHz, Chloroform-*d*)  $\delta$  8.61 – 8.50 (m, 2H), 8.37 – 8.25 (m, 1H), 8.22 (dp,  $J = 2.4, 0.8$  Hz, 1H), 7.21 (dd,  $J = 5.1, 1.8$  Hz, 1H), 7.17 (dd,  $J = 5.1, 1.7$  Hz, 1H), 7.13 (ddd,  $J = 5.1, 1.8, 0.9$  Hz, 1H), 6.95 (d,  $J = 2.8$  Hz, 1H), 6.77 – 6.68 (m, 3H), 6.43 (dt,  $J = 15.8, 1.4$  Hz, 1H), 6.22 (dt,  $J = 15.9, 6.8$  Hz, 1H), 3.80 – 3.74 (m, 6H), 2.88 (dd,  $J = 9.1, 6.5$  Hz, 1H), 2.63 (ddd,  $J = 8.4, 6.7, 1.7$  Hz, 1H), 2.43 (s, 3H).

**15**  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.56 (ddd,  $J = 5.0, 3.1, 0.8$  Hz, 2H), 8.25 (dd,  $J = 1.7, 0.8$  Hz, 2H), 7.15 (dtd,  $J = 5.1, 1.8, 1.0$  Hz, 2H), 6.78 (d,  $J = 8.6$  Hz, 1H), 6.74 – 6.67 (m, 2H), 3.78 (d,  $J = 5.1$  Hz, 6H), 2.79 – 2.69 (m, 2H), 2.71 – 2.60 (m, 2H), 2.46 (t,  $J = 0.8$  Hz, 3H), 1.85 – 1.73 (m, 2H), 1.68 (td,  $J = 8.5, 6.9$  Hz, 2H).

**15**  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ )  $\delta$  156.12, 156.10, 153.40, 152.74, 151.74, 148.96, 148.93, 148.09, 131.97, 124.60, 123.97, 122.00, 121.36, 116.26, 111.17, 110.75, 55.89, 55.64, 35.35, 30.22, 30.07, 29.48, 21.19.

**16**  $^1\text{H}$  NMR (400 MHz, Chloroform-*d*)  $\delta$  8.61 (dd,  $J = 9.3, 5.1$  Hz, 2H), 8.37 (s, 2H), 7.23 (s, 2H), 6.87 – 6.54 (m, 3H), 2.80 (td,  $J = 7.6, 3.3$  Hz, 2H), 2.52 (d,  $J = 4.5$  Hz, 5H), 1.83 (h,  $J = 7.2$  Hz, 2H), 1.68 – 1.59 (m, 2H).

**References:**

1. Aldridge, W. Steven, et al. "Synthesis and characterization of oligoproline-based molecular assemblies for light harvesting." *The Journal of organic chemistry* 71.14 (2006): 5186-5190.
2. Bang, Hyun Bae, et al. "High yield total syntheses of XH-14 derivatives using Sonogashira coupling reaction." *Arkivoc* 2 (2009): 112-125.
3. Freeman, David B., et al. "Functionally diverse nucleophilic trapping of iminium intermediates generated utilizing visible light." *Organic letters* 14.1 (2011): 94-97.
4. Gangjee, Aleem, Jie Yang, and Sherry F. Queener. "Novel non-classical C9-methyl-5-substituted-2, 4-diaminopyrrolo [2, 3-d] pyrimidines as potential inhibitors of dihydrofolate reductase and as anti-opportunistic agents." *Bioorganic & medicinal chemistry* 14.24 (2006): 8341-8351.
5. Garner, Robert N., Lauren E. Joyce, and Claudia Turro. "Effect of Electronic Structure on the Photoinduced Ligand Exchange of Ru (II) Polypyridine Complexes." *Inorganic chemistry* 50.10 (2011): 4384-4391.

6. Gu, Jing, Jin Chen, and Russell H. Schmehl. "Using Intramolecular Energy Transfer to Transform non-Photoactive, Visible-Light-Absorbing Chromophores into Sensitizers for Photoredox Reactions." *Journal of the American Chemical Society* 132.21 (2010): 7338-7346.
7. Kodama, Koichi, Akinori Kobayashi, and Takuji Hirose. "Synthesis and spectral properties of ruthenium (II) complexes based on 2, 2'-bipyridines modified by a perylene chromophore." *Tetrahedron Letters* 54.40 (2013): 5514-5517.
8. Lin, Shishi, et al. "Radical Cation Diels–Alder Cycloadditions by Visible Light Photocatalysis." *Journal of the American Chemical Society* 133.48 (2011): 19350-19353.
9. Maity, Soumitra, et al. "Intermolecular [3+ 2] Cycloaddition of Cyclopropylamines with Olefins by Visible-Light Photocatalysis." *Angewandte Chemie International Edition* 51.1 (2012): 222-226.
10. Meylemans, Heather A., and Niels H. Damrauer. "Controlling Electron Transfer through the Manipulation of Structure and Ligand-Based Torsional Motions: A Computational Exploration of Ruthenium Donor– Acceptor Systems using Density Functional Theory." *Inorganic chemistry* 48.23 (2009): 11161-11175.

11. Meylemans, Heather A., et al. "Exploiting Conformational Dynamics To Facilitate Formation and Trapping of Electron-Transfer Photoproducts in Metal Complexes." *Journal of the American Chemical Society* 132.33 (2010): 11464-11466.
12. Narayanam, Jagan MR, Joseph W. Tucker, and Corey RJ Stephenson. "Electron-transfer photoredox catalysis: development of a tin-free reductive dehalogenation reaction." *Journal of the American Chemical Society* 131.25 (2009): 8756-8757.
13. Sun, Yujie, et al. "Effect of Ligands with Extended  $\pi$ -System on the Photophysical Properties of Ru (II) Complexes†." *The Journal of Physical Chemistry B* 114.45 (2010): 14664-14670.
14. Tucker, Joseph W., and Corey RJ Stephenson. "Shining light on photoredox catalysis: theory and synthetic applications." *The Journal of organic chemistry* 77.4 (2012): 1617-1622.
15. Wardle, Brian. *Principles and applications of photochemistry*. John Wiley & Sons, 2009.

16. Yoon, Tehshik P., Michael A. Ischay, and Juana Du. "Visible light photocatalysis as a greener approach to photochemical synthesis." *Nature chemistry* 2.7 (2010): 527-532.

17. Zeitler, Kirsten. "Photoredox catalysis with visible light." *Angewandte Chemie International Edition* 48.52 (2009): 9785-9789.

## Appendix:

