



Progress Towards the Synthesis of 2,2'-bipyridine-4,4'-bis(propargylmethoxy) for Use in Photoredox Catalysis

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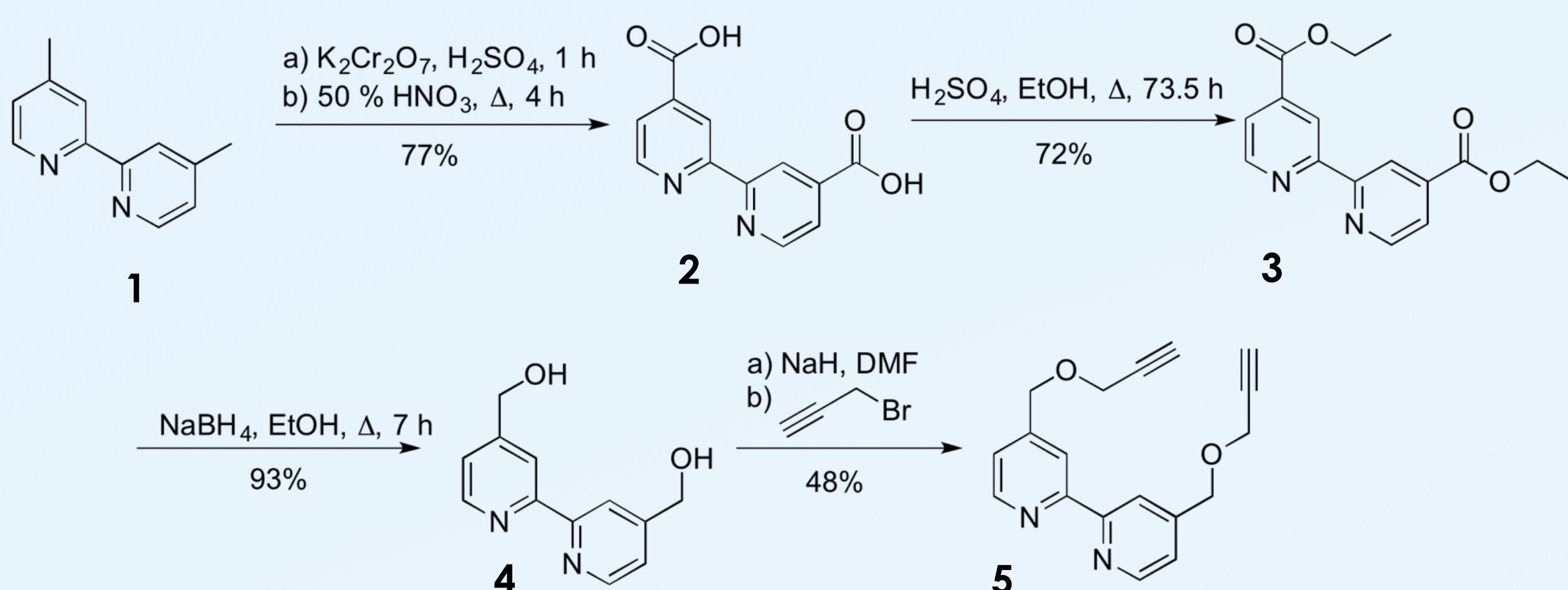


Introduction:

Photosensitizers have become increasingly important in photoredox catalysis. The role of photosensitizers in redox catalysis is to donate electrons to a catalyst through the LUMO, which resides on a pi-acid ligand.³ Transition metal photosensitizers, particularly Ru(bipy)₃²⁺ derivatives, are widely utilized for the aforementioned reactions as they can undergo single-electron transfer to a catalyst upon the photoreductive quench of Ru(bipy)₃²⁺.⁴ The following synthesis of 2,2'-bipyridine-4,4'-bis(propargylmethoxy) (**5**), when complexed to a metal, acts as an electron donor that can be used as part of the formation of hydrogen gas.¹ This work utilizes polymer folding by an external cross-linker through CuAAC reactions that also function as a photosensitizer for the catalysis of H₂.⁵

Experimental Design:

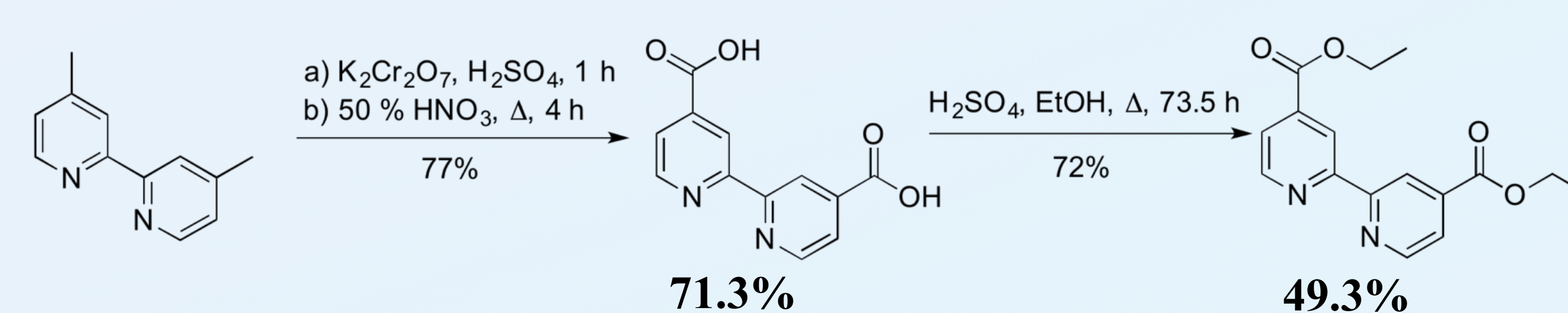
A multistep synthesis was performed starting with 2,2'-bipyridine-4,4'-dimethyl (**1**) to yield 2,2'-bipyridine-4,4'-dicarboxylic acid (**2**). A Fischer esterification of which resulted is the ester substituted 2,2'-bipyridine-4,4'-dicarboxylate (**3**),² that when combined with sodium borohydride, underwent the reaction to produce 2,2'-bipyridine-4,4'-bis(hydroxymethyl) (**4**). This product then undergoes substitution to form the final product, 2,2'-bipyridine-4,4'-bis(propargylmethoxy) (**5**). The product formed is a vital element in the synthesis of the Rubipy complex shown in **scheme 3**. Each product obtained was analyzed by ¹H NMR to verify purity.



Scheme 1. Proposed Synthetic Route to 2,2'-bipyridine-4,4'-bis(propargylmethoxy) (**5**)

Results and Discussion:

The Fischer esterification product of 2,2'-bipyridine-4,4'-dicarboxylate (**3**) was successfully synthesized, according to ¹H NMR analysis (**Figure 2**). However, the synthesis of 2,2'-bipyridine-4,4'-bis(hydroxymethyl) (**4**) resulted in an unsuccessful product formation, evident by residual starting material of (**3**). Due to insufficient product collection of the Fischer esterification reaction, there was a deficient amount of reactant to continue on with the ester reduction. Thus, further synthesis is required to analyze the complete reaction.



Scheme 2. Completed Experimental Work Toward Synthesis

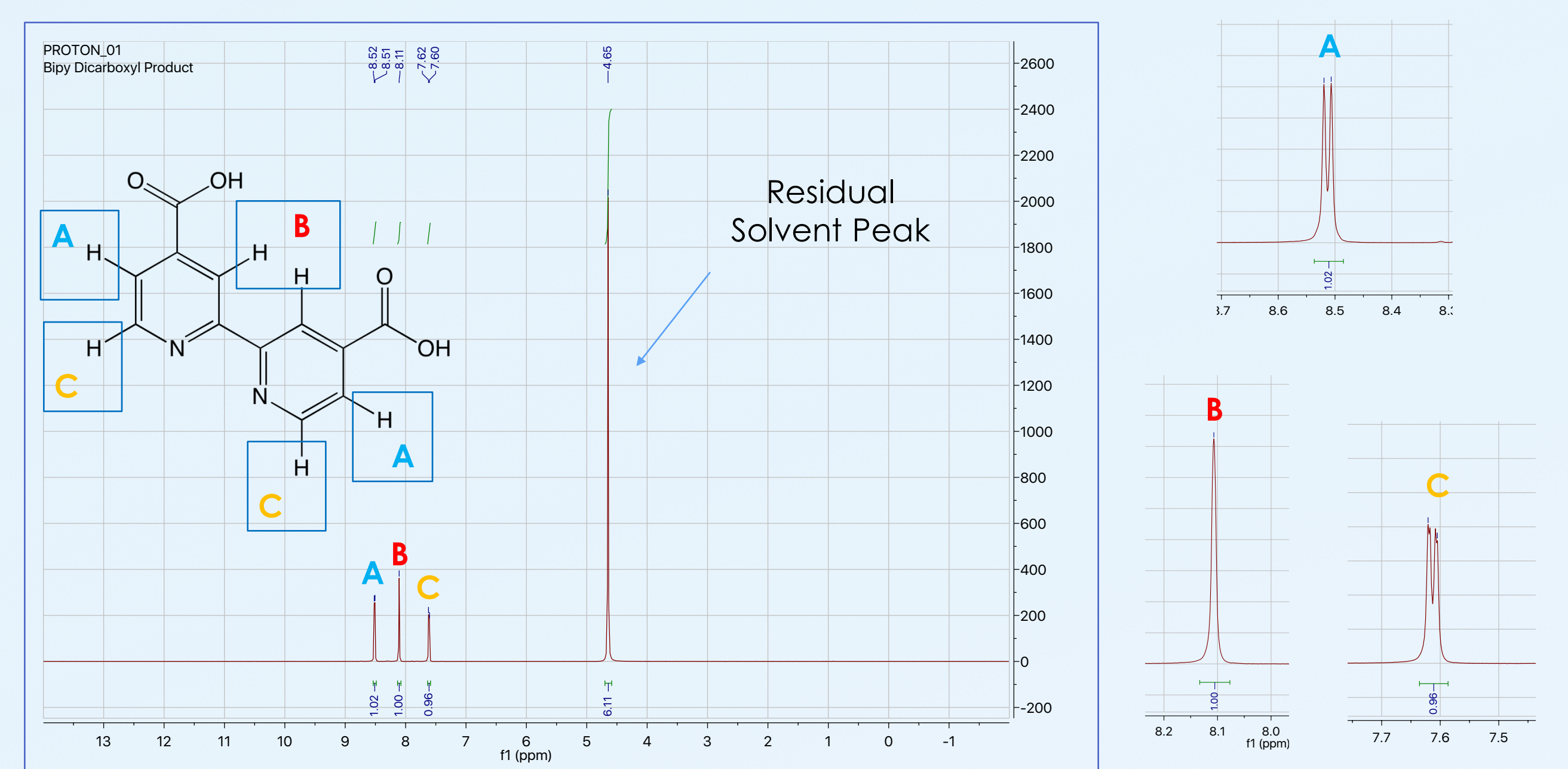


Figure 1. ¹H NMR Spectra of Purified **2**.

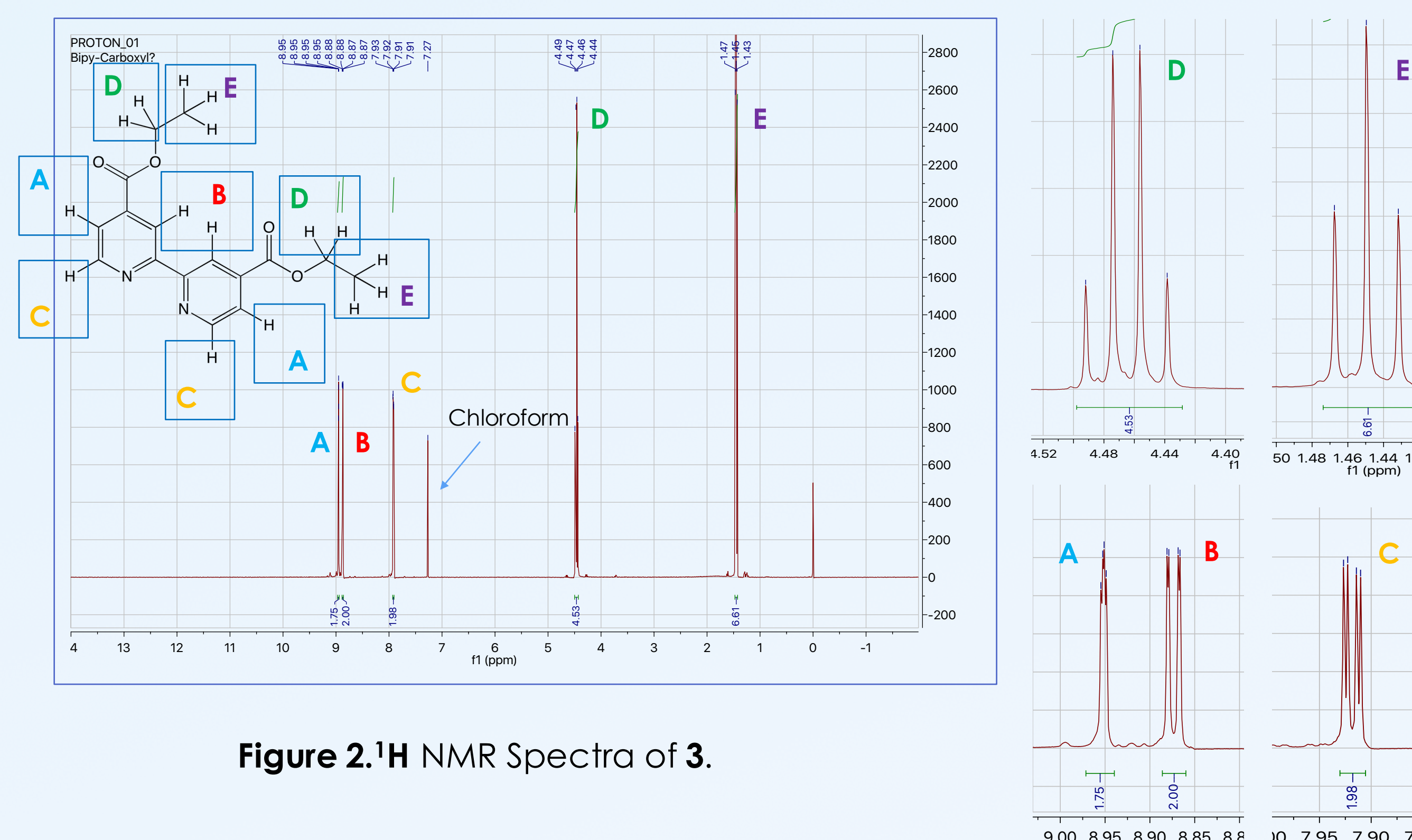
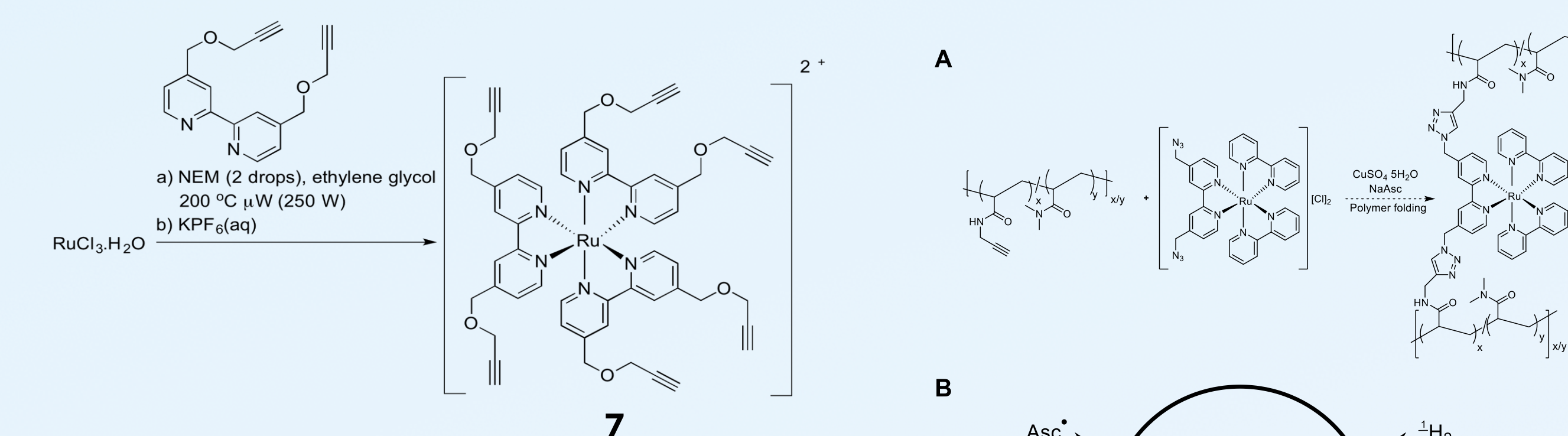


Figure 2. ¹H NMR Spectra of **3**.

Future Work:

The reactions performed in **Scheme 1** show the multi-step synthesis of 2,2'-bipyridine-4,4'-bis(propargylmethoxy) from 2,2'-bipyridine-4,4'-dimethyl. First, the completion of the synthesis of (**4**) and (**5**) is required. The formation of this ligand (**5**) can be used in the future synthesis of a tris-Rubipy complex (**7**, **scheme 3**), which has the ability to crosslink with polymers, causing them to fold.⁵ This Rubipy complex will become a photosensitizer for photocatalysis, and can be used in combination with other sections of this project to produce H₂.



Scheme 3. Synthesis and design of Ru(II) photosensitizer, and further synthesis of a polymer DYAD system.

Conclusions:

According to ¹H NMR analysis, the synthesis of the 2,2'-bipyridine-4,4'-dicarboxylic acid (**2**) and 2,2'-bipyridine-4,4'-dicarboxylate (**3**) were successful. Despite the large solvent contamination in the synthesis of (**2**), the formation of the correct product in the next reaction suggests success. The formation of 2,2'-bipyridine-4,4'-bis(hydroxymethyl) (**4**) was unsuccessful, likely due to the evaporation of the solvent during reflux. The formation of the final product (**5**) requires further studies.

Acknowledgments:

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