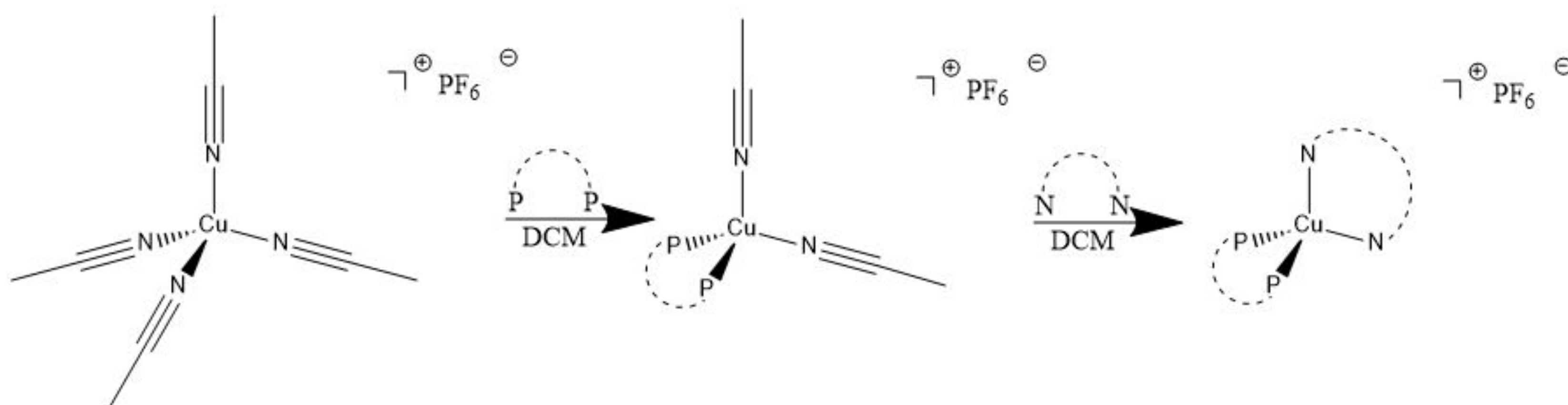


Introduction

Much of the technology we use on a daily basis emits light from a screen in order to relay information. This light comes from the electron movement, relaxation and subsequent photon emission during metal-ligand charge transfer (MLCT) in a metal-centered photosensitizer.¹ The photon emitted by a photosensitizer is characteristic to the structure of the discrete complex, and can be adjusted by decorating a desired metal center with various functionalized organic ligands.²

Late-transition metals such as Ru and Ir provide excellent electronic frameworks for such complexes. However, the natural abundance of some of these metals is low enough to raise both economic and environmental concerns. Whereas, Cu [specifically Cu(I)] is both plentiful in nature and has potential to form photoemissive organometallic complexes.³ This project serves to highlight the design, synthesis and characterization of a small library of Cu(I)-centered coordinated compounds for electrochemical analysis in the prospect of use in light-emitting electrochemical cells (LEEC's).

Synthesis



Scheme 1: Synthesis of a four-coordinate Cu(I)-centered photosensitizer from tetrakis acetonitrile copper(I) hexafluorophosphate

Two different sets of ligands are used to coordinate about a Cu(I) center: two electron donating diphosphine ligands of varying molecular rigidity ('parent' ligands) as well as four electron accepting diimine ligands of varying functionalizations ('sister' ligands). A desired parent ligand is first reacted with tetrakis acetonitrile copper(I) hexafluorophosphate in dichloromethane for ~15 minutes. After this time, the desired sister ligand is added to the solution and stirred for another ~15 minutes. The resulting mixture is then poured into diethyl ether as to crash out the solid before vacuum filtration. The final product is allowed to dry until a fine powdery consistency is achieved.

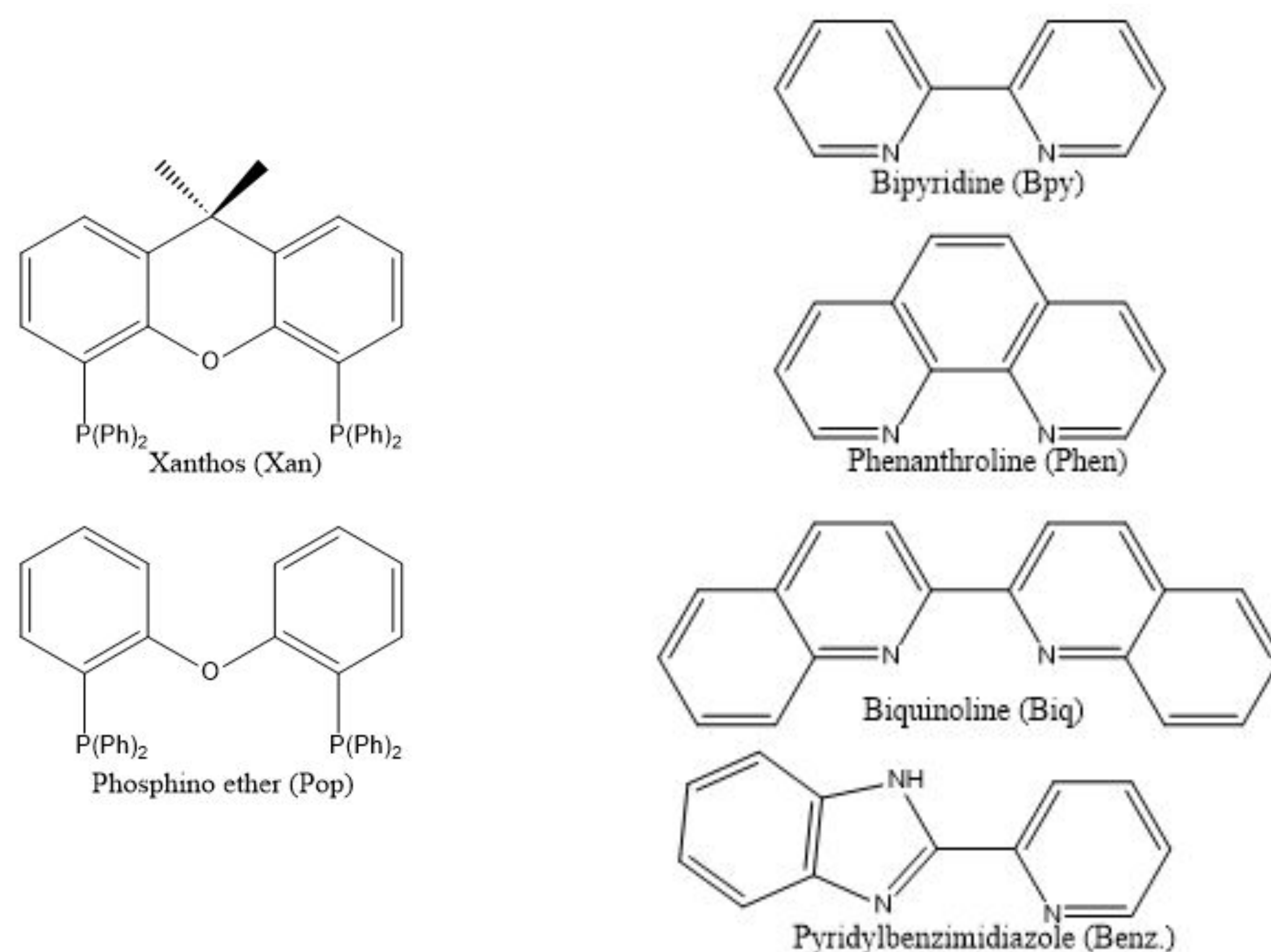


Figure 1: Electron donating bidentate diphosphine ligands ('parents', left), electron withdrawing bidentate diimine ligands ('sisters', right)

Results and Discussion

The proposed structures of the complexes were confirmed using ¹H NMR spectroscopy. In general, major chemical shifts of concern to our group occur in the aromatic region (between 7-9 ppm). This is mainly due to the plethora of hydrogens connected to the carbon atoms within the extended π -conjugation systems of both the diphosphine and diimine ligands. Compounds containing the Xanth. parent ligand possess at least one upfield peak indicative of the presence of the rigid C(CH₃)₂ backbone. For most of the compounds in our library, overall molecular symmetry is a major contributor to the low number of intense, significant peaks.

Cyclic voltammetry was carried out on the complexes to determine the redox potentials corresponding to the electron transfer resulting in MLCT. These values were verified by examining the samples and later examining upon spiking with ferrocene, a well known reference, to analyze reductive and oxidative couples. Reductive couples correspond to the electron accepting capability of the lowest unoccupied molecular orbital (LUMO) of the diimine ligand, while oxidative couples are characteristic of the electron donating abilities of the highest occupied molecular orbital (HOMO) of the diphosphine ligand. A silver/silver chloride pseudo-reference electrode is used in conjunction with a 0.1 M electrolyte solution of tetra-n-butylammonium hexafluorophosphate in dichloromethane under argon gas. Sublimed ferrocene is then added to the system before degassing and retaking the scans, as a form of pseudo-reference referencing since the Fc/Fc⁺ couple is well-studied.

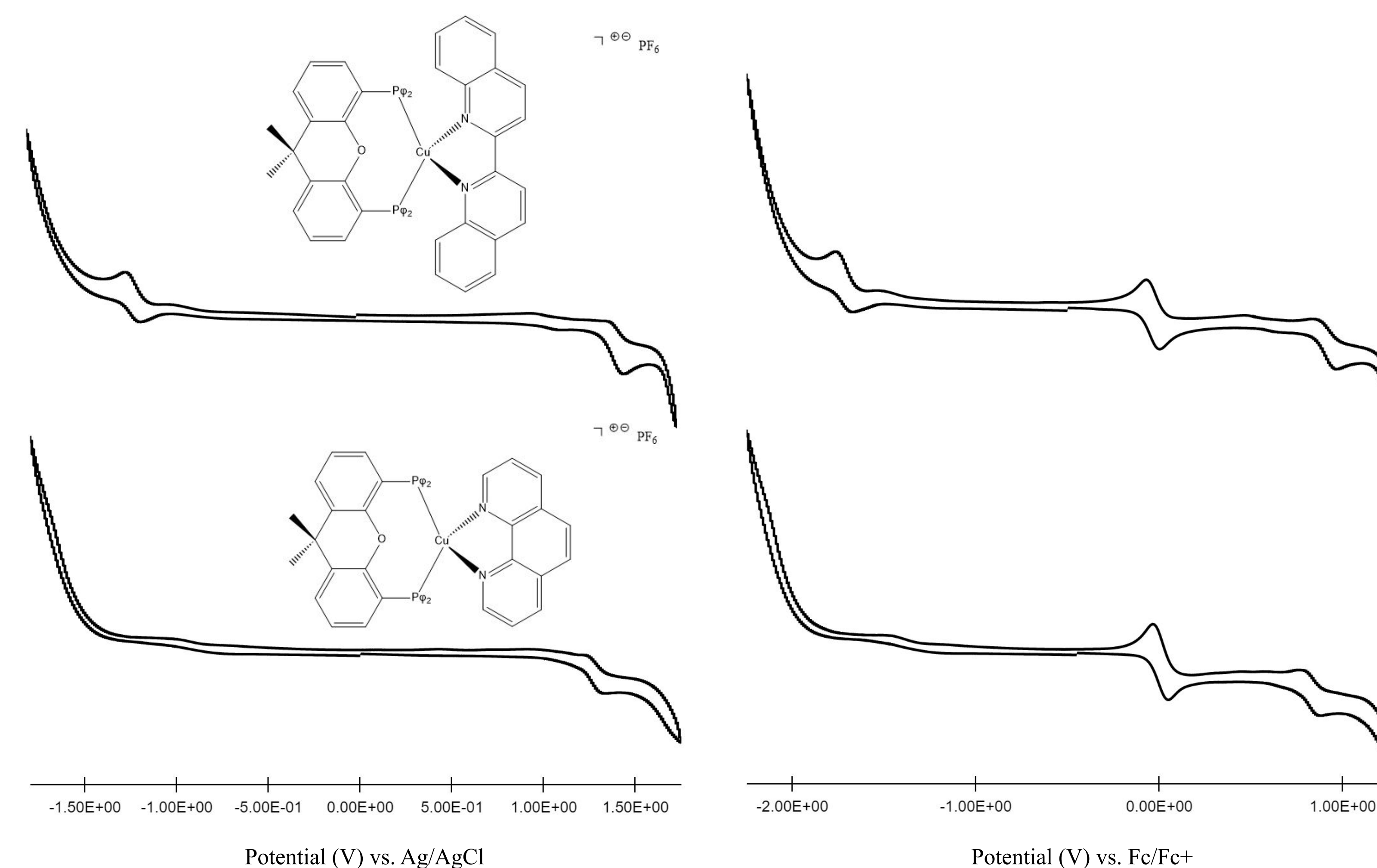


Figure 2: Cyclic voltammograms taken against Ag/AgCl pseudo-reference in 0.1 M [NBu₄]PF₆ in DCM under Ar gas for Xanth./biq. (top) and Xanth./phen. (bottom), scanned at 50 mV/s

Figure 3: Cyclic voltammograms taken against Fc/Fc⁺ reference in 0.1 M [NBu₄]PF₆ in DCM under Ar gas for Xanth./biq. (top) and Xanth./phen. (bottom), scanned at 50 mV/s

Conclusions and Future Work

Copper(I)-centered photosensitizers have plenty of potential for use in LEEC's. They can be produced with relative ease and quickness on the benchtop scale and can show desirable emissions depending on the ligands chosen for coordination when interacting with UV light. During this interaction, it is likely that the initial tetrahedral geometry at the copper center temporarily distorts to a pseudo-square planar geometry due to a quasi-oxidation of the Cu(I) to Cu(II) upon excitation. Once the UV light source is removed, relaxation of the excited state returns the Cu(I) center to its ground state geometry. It is of interest to further investigate how the differences in molecular rigidity of the parent ligands impact the excited state distortion of the Cu complexes. Likewise, the electronic properties of the sister ligands have a subsequent effect on the electronic structure of the complex and the resulting photon emitted upon MLCT.

Full structural analysis including ¹³C, ¹⁹F and ³¹P NMR spectroscopies as well as single crystal X-ray diffraction is yet to be conducted on this library. In addition, UV-Visible spectroscopy can be implemented to further explore the photophysical properties of these complexes. Further electrochemical analysis including square wave voltammetry will be used to determine the rate of electron transfer during the excited state. Future collaboration with materials scientists to incorporate these compounds into LEEC's is anticipated upon the verification of structures and functions.

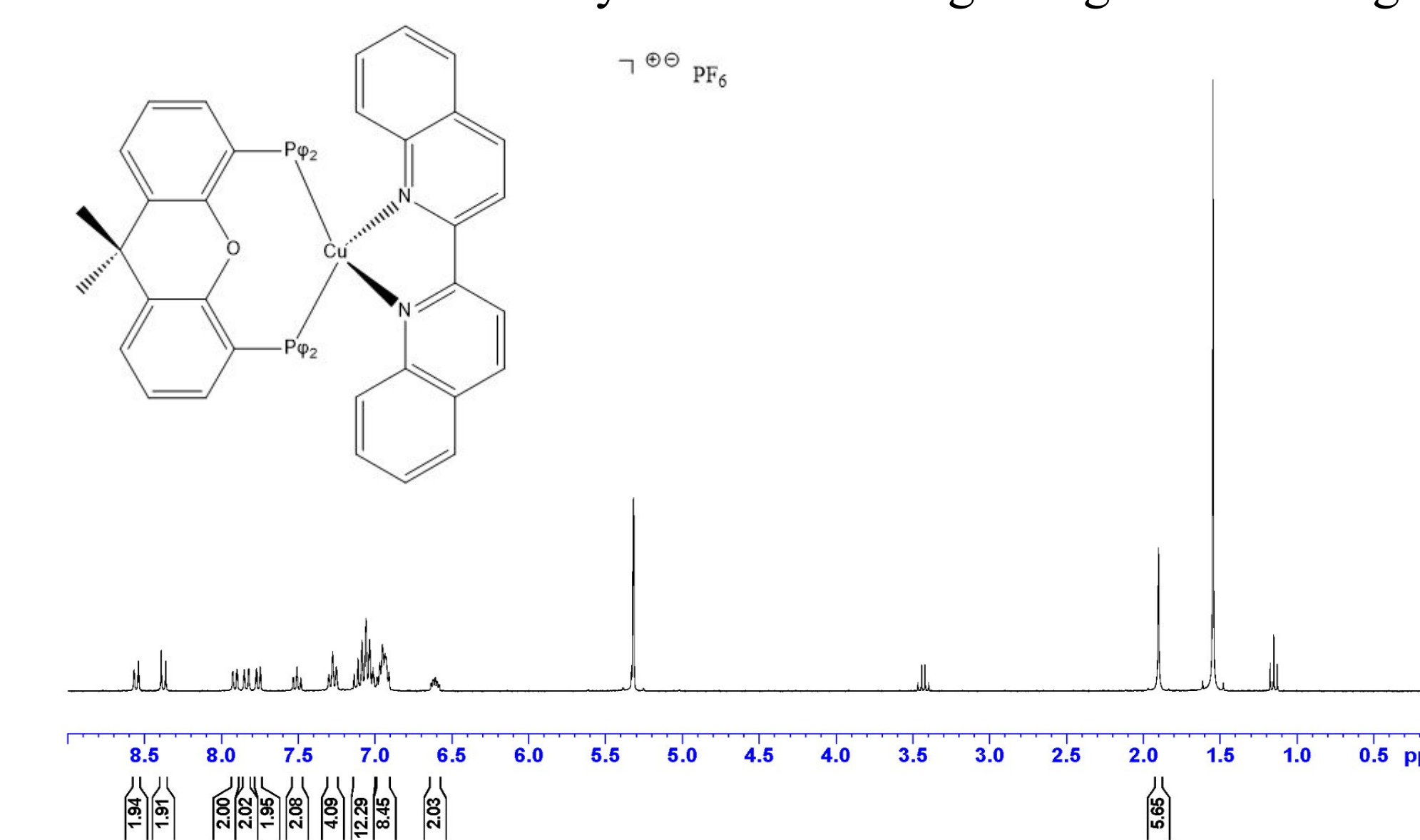


Figure 4: ¹H NMR spectra obtained for Xanth./biq. in d-DCM at 300 MHz

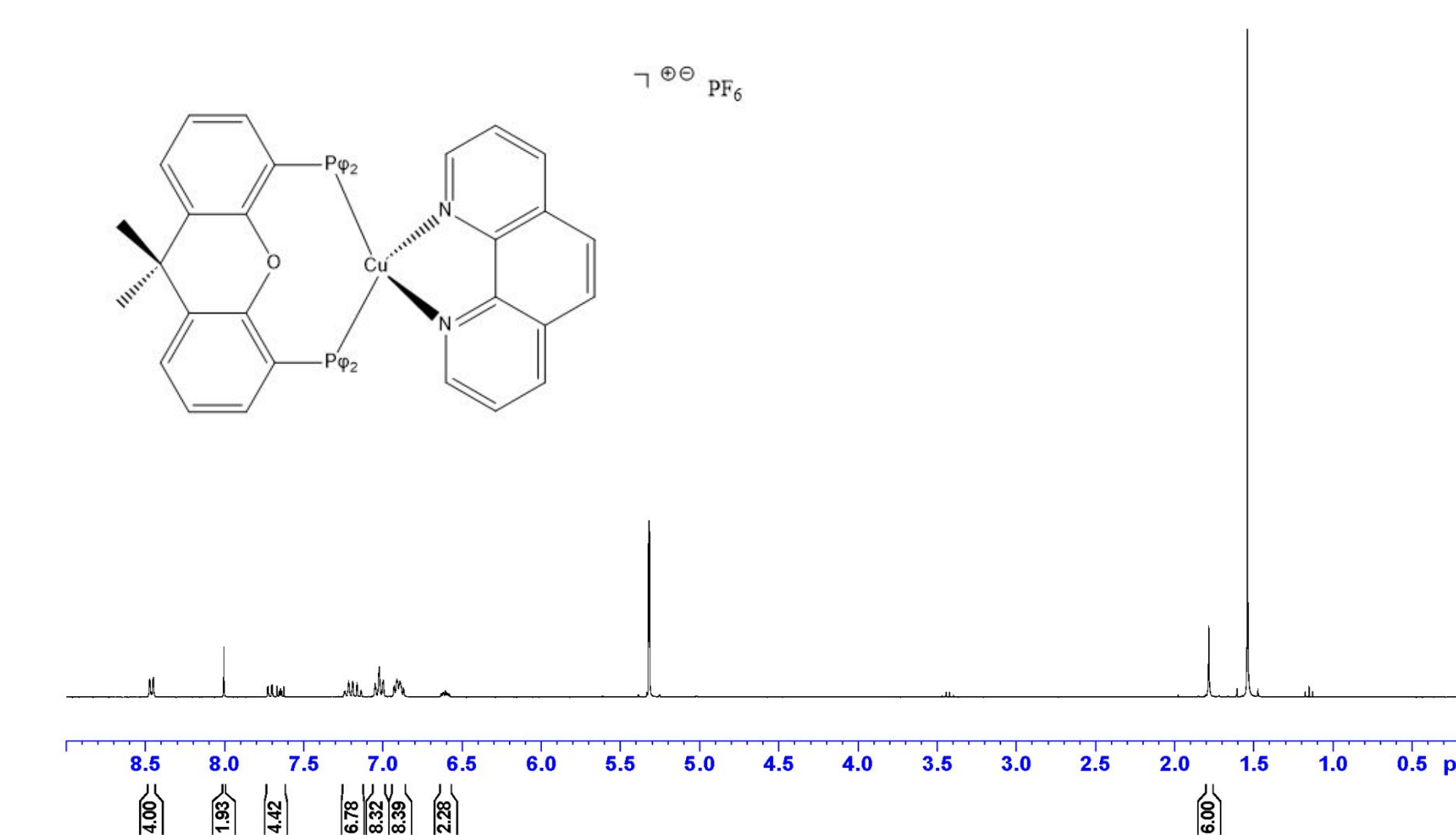


Figure 5: ¹H NMR spectra obtained for Xanth./phen in d-DCM at 300 MHz

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