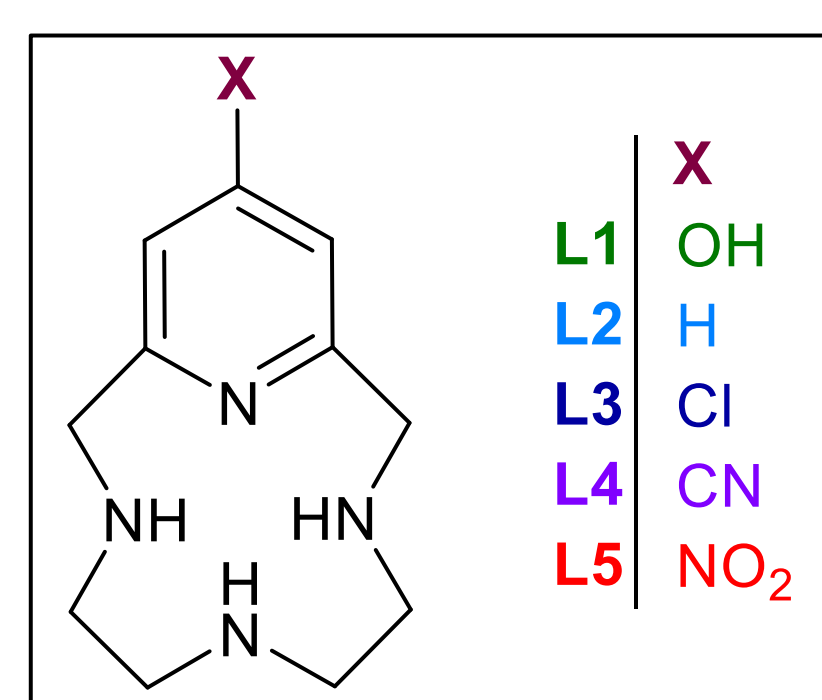
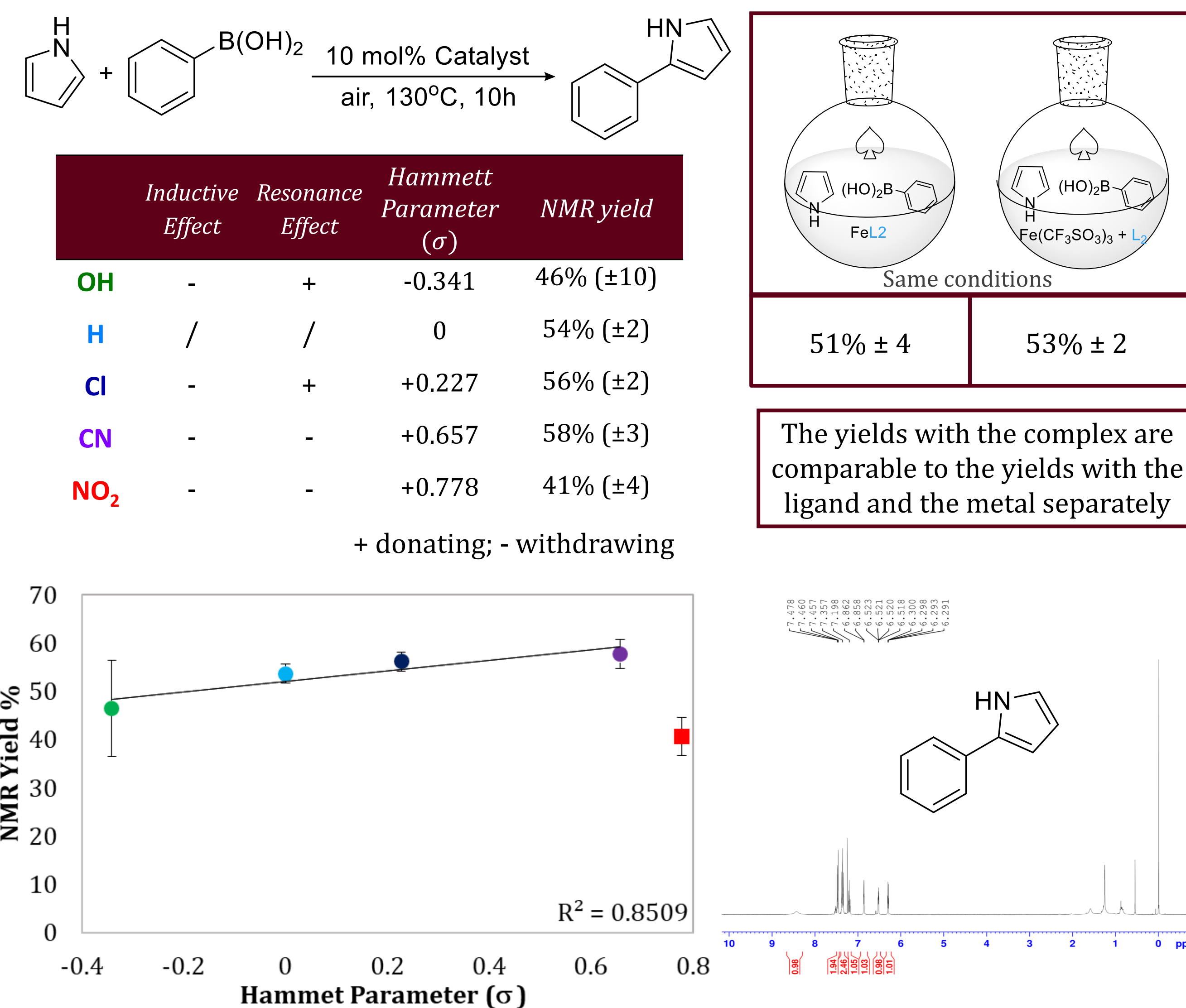


ABSTRACT

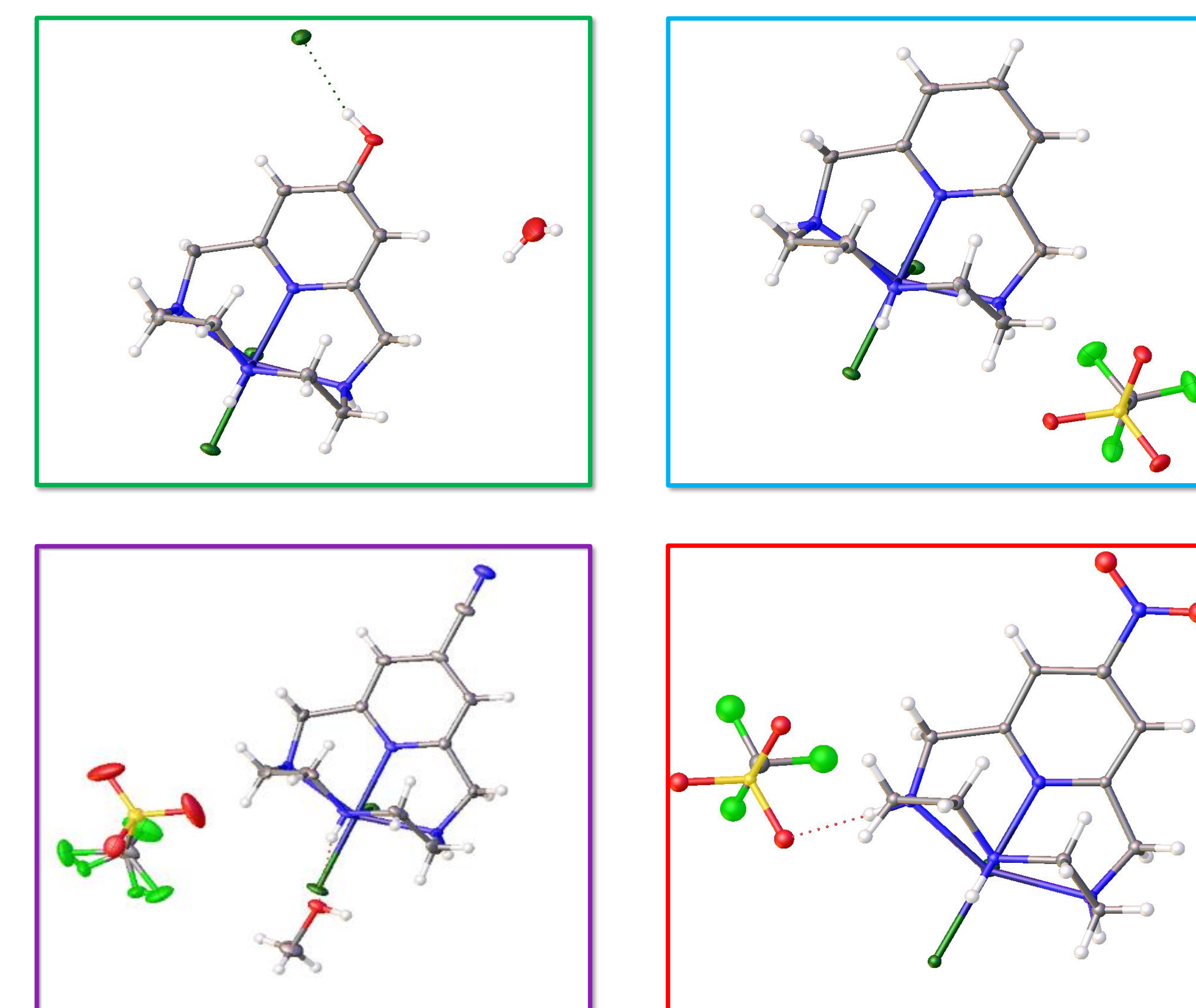
The use of macrocyclic pyridinophanes is of increasing interest in the fields of bioinorganic modeling, catalysis, and imaging. However, a full study of the electronic effects imparted by substitution to the pyridyl moiety and the subsequent impact on the metal center have not been explored. In this study five tetra-aza macrocyclic ligands were explored, three of which were synthesized, metalated with Fe(III) and characterized for the first time. The pyridyl functional groups studied include: **A**) 4-hydroxyl (**L1**), **B**) 4-H (**L2**), **C**) 4-chloro (**L3**), **D**) 4-nitrile (**L4**) and **E**) 4-nitro (**L5**) modified pyridyl on a pycen base structure. Analysis of the resulting iron (III) complexes indicate six-coordinate metal centers based on X-ray diffraction analysis. Electrochemistry and C-C coupling catalytic results allow us to understand the effect of the electronics and the donor ability of each ligand.



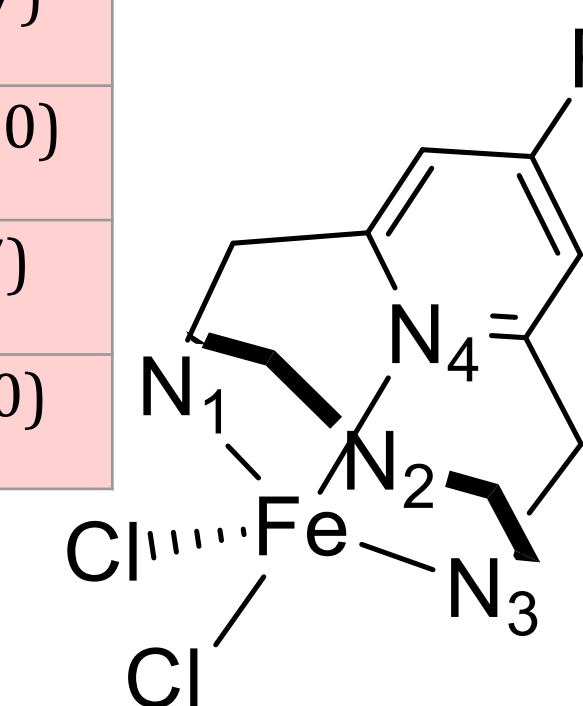
C-C COUPLING REACTION



SINGLE CRYSTAL X-RAY DIFFRACTION

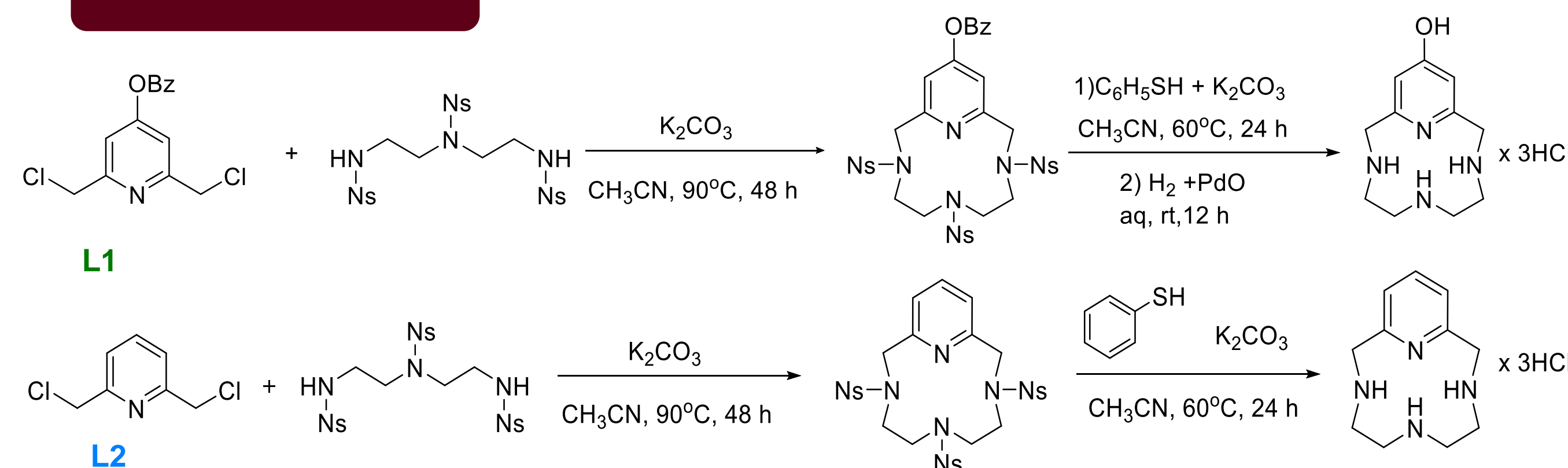


Bond Angles (°)/Lengths (Å)	Fe ^{III} L1	Fe ^{III} L2	Fe ^{III} L4	Fe ^{III} L5
Cl(1) Fe Cl(2)	92.06 (3)	98.37 (14)	92.83 (3)	99.95 (13)
N(4) Fe N(2)	87.23 (8)	85.21 (4)	85.94 (14)	84.4 (4)
N(3) Fe N(1)	148.45 (8)	147.08 (5)	147.32 (15)	147.1 (4)
Fe-N(1)	2.178 (2)	2.178 (11)	2.170 (3)	2.169 (7)
Fe-N(2)	2.156 (2)	2.197 (12)	2.157 (4)	2.191 (10)
Fe-N(3)	2.175 (2)	2.158 (11)	2.170 (3)	2.169 (7)
Fe-N(4)	2.065 (2)	2.114 (11)	2.105 (4)	2.116 (10)

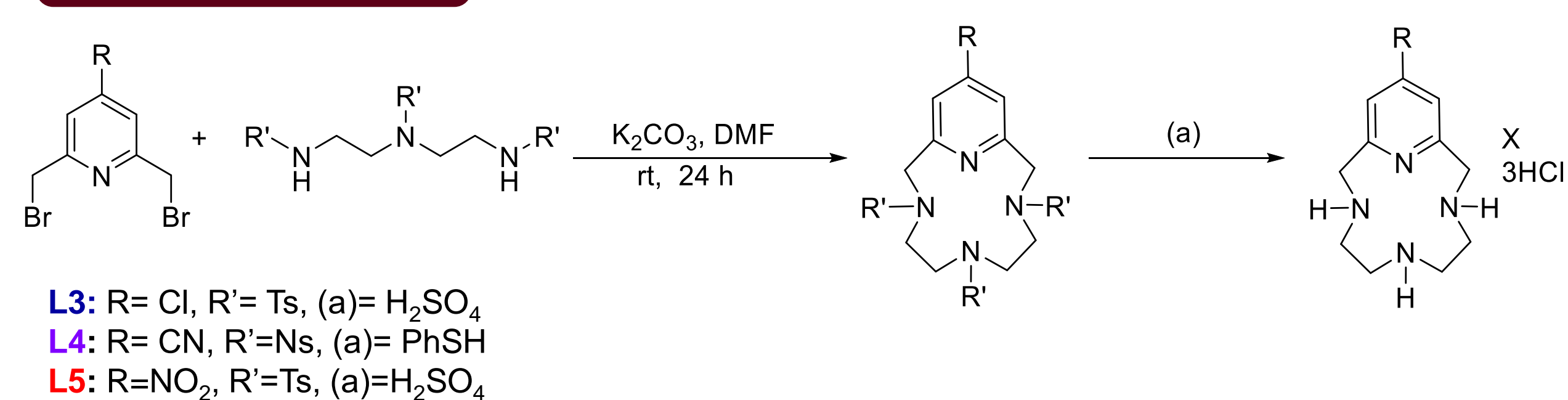


SYNTHESIS

Generation 1



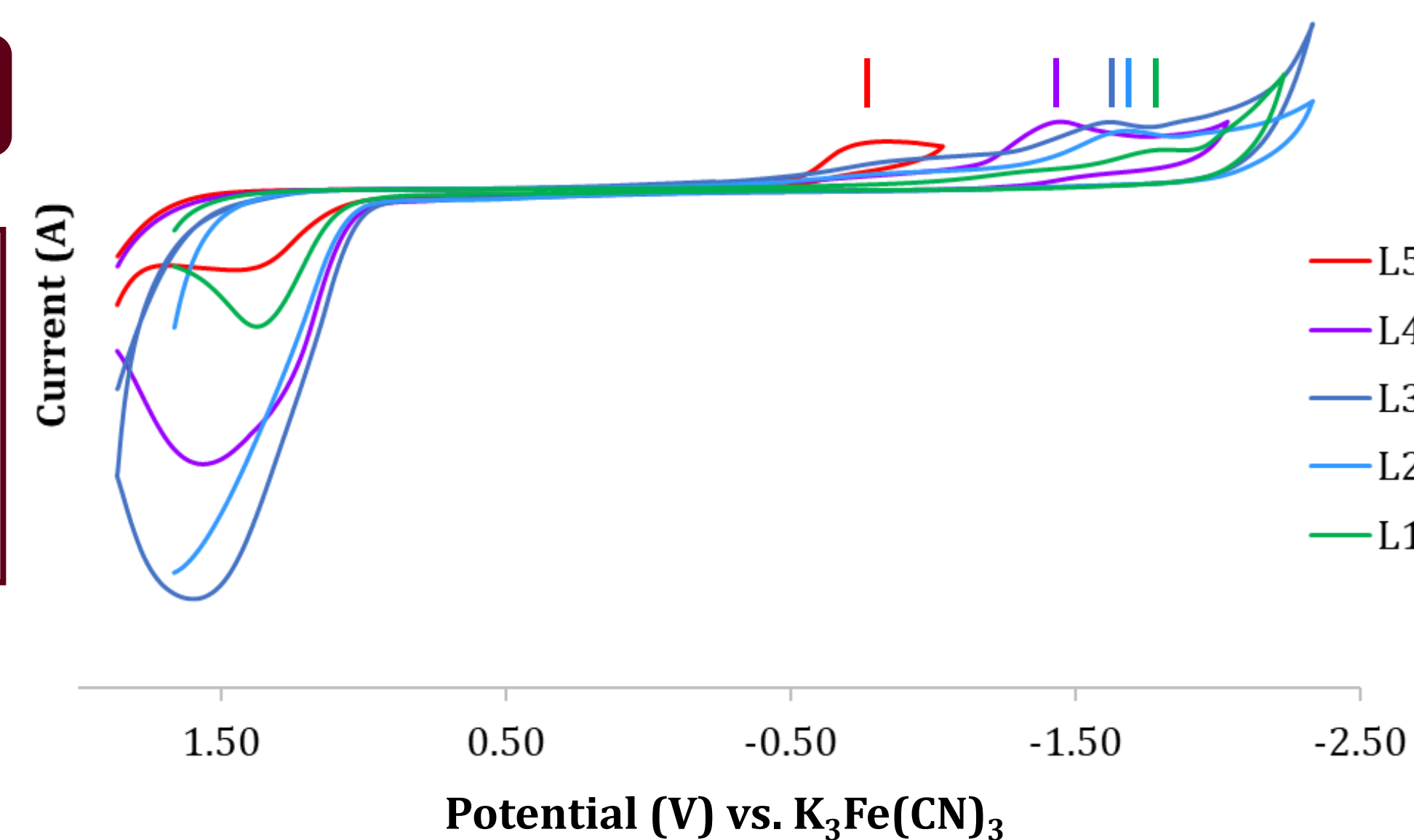
Generation 2



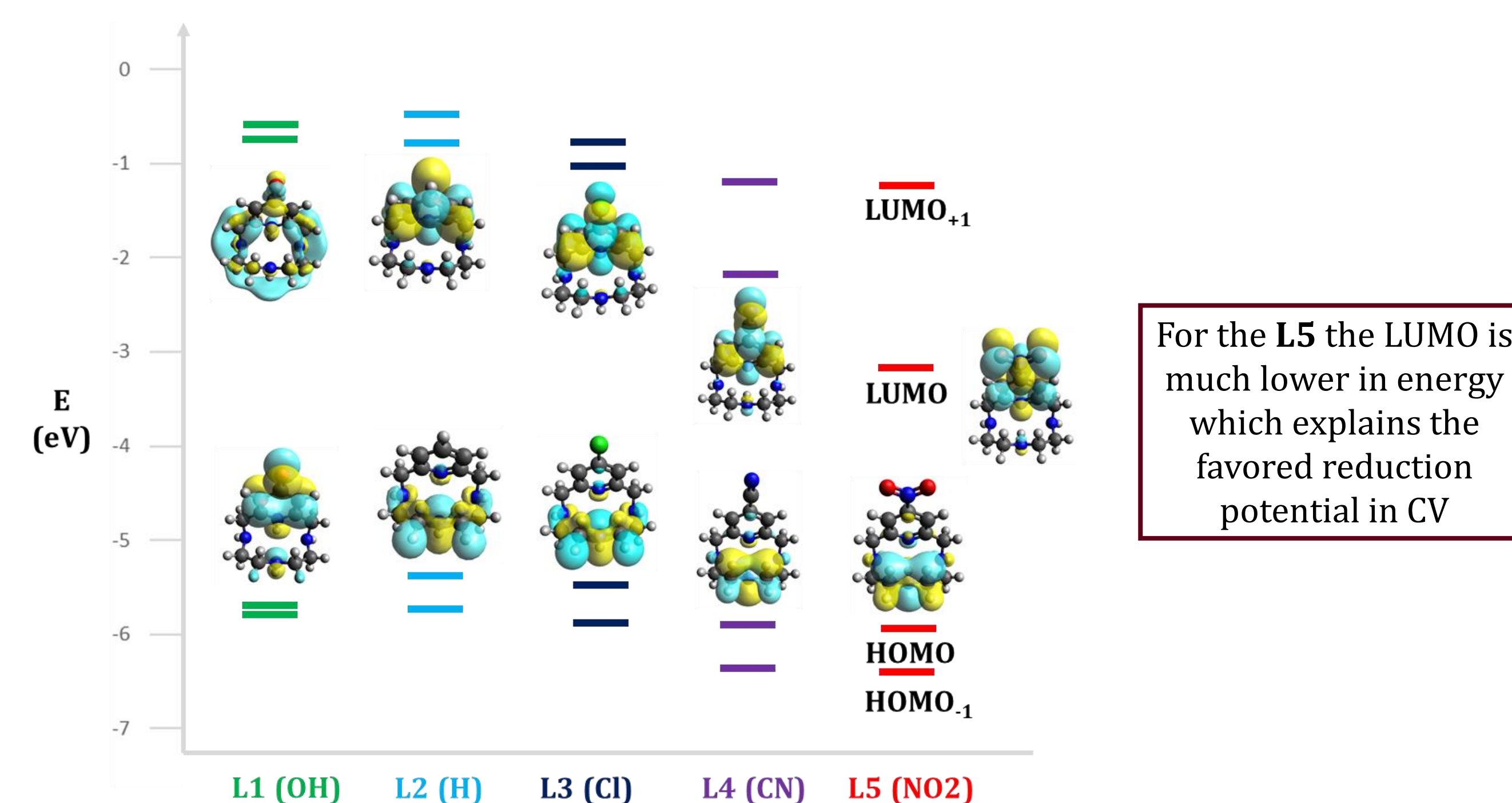
CV AND DFT STUDY FOR LIGANDS

Cyclic Voltammetry

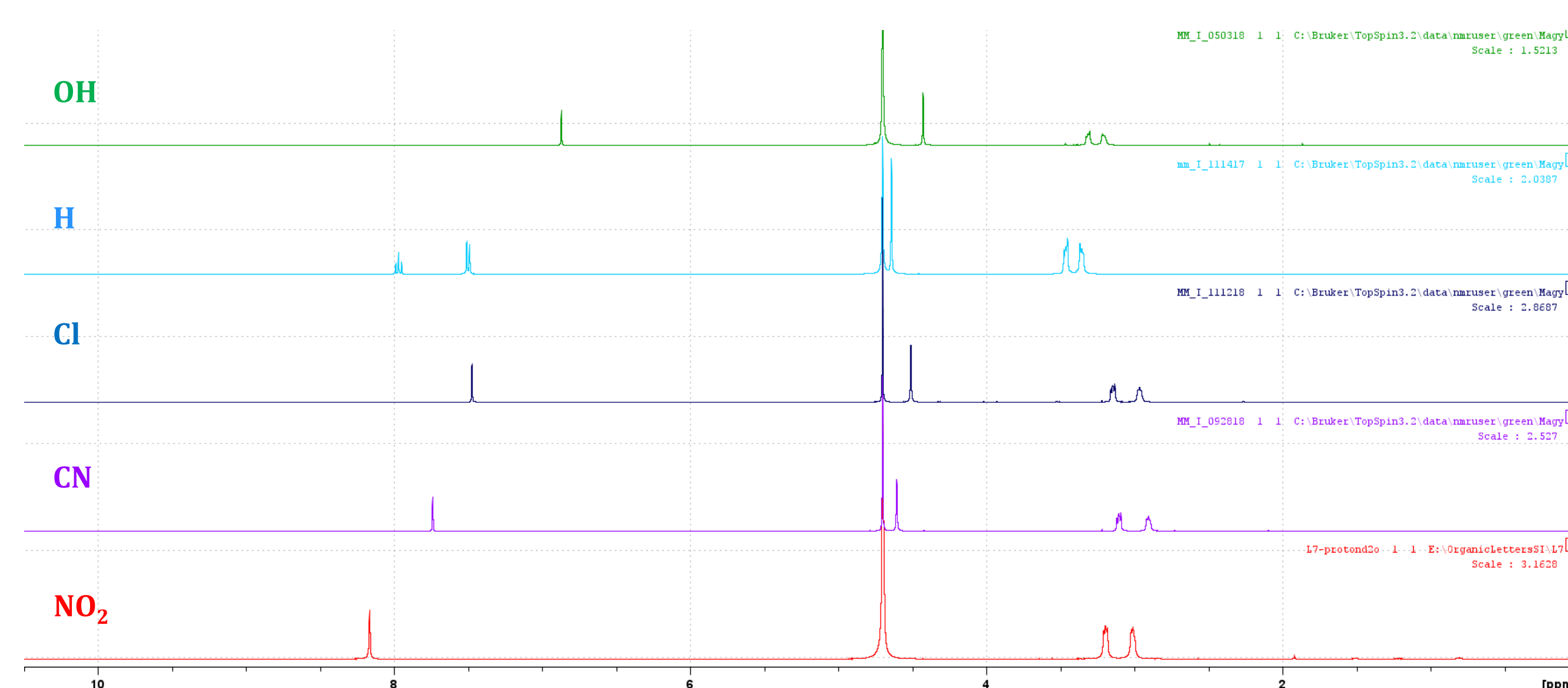
The reduction of the **L5** falls within the redox window of iron activity with the C-C coupling reaction (400 → -800 mV)¹



Theoretical



CHARACTERIZATION (¹H-NMR)



CONCLUSIONS

- Successful synthesis, purification, and characterization of **L1-L5**.
- The catalytic yields were dependent on ligand substitution.
- The redox activity of the ligands is dependent on the functional groups and correlate to the hammett parameters and DFT studies.
- Crystal structures of **Fe^{III}L1**, **Fe^{III}L2**, **Fe^{III}L4**, and **Fe^{III}L5** validate Fe^{III}-ligand binding.
- The nitro substituted ligand did not follow the trend observed and it is attributed to its redox activity.

Acknowledgements:

Green Research Group,
Instrumentation provided by Texas Christian University, College of Science & Engineering,
Department of Chemistry & Biochemistry.

¹ Brewer, m. S.; Wilson, c. K.; Jones, G. D.; Reinheimer, W. E.; Archibald, J. S.; Prior, J. T.; Ayala, A. M.; Foster, L. A.; Hubin, J. T.; Green, K. N., Increase of Direct C-C Coupling Reaction Yield by Identifying Structural and Electronic Properties of High-Spin Iron Tetraazamacrocyclic Complexes. *Inorg. Chem.* **2018**, *57*, 8890-8902