

Metalation of Pyrrole-Based NNN-Pincer Ligands with Heteroaromatic Donor Substituents

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Introduction:

There are 12 principles of green chemistry that have been developed, and the idea of atom economy,¹ producing less waste and overall more efficient and safe reactions are important principles that guide the direction of this research.²

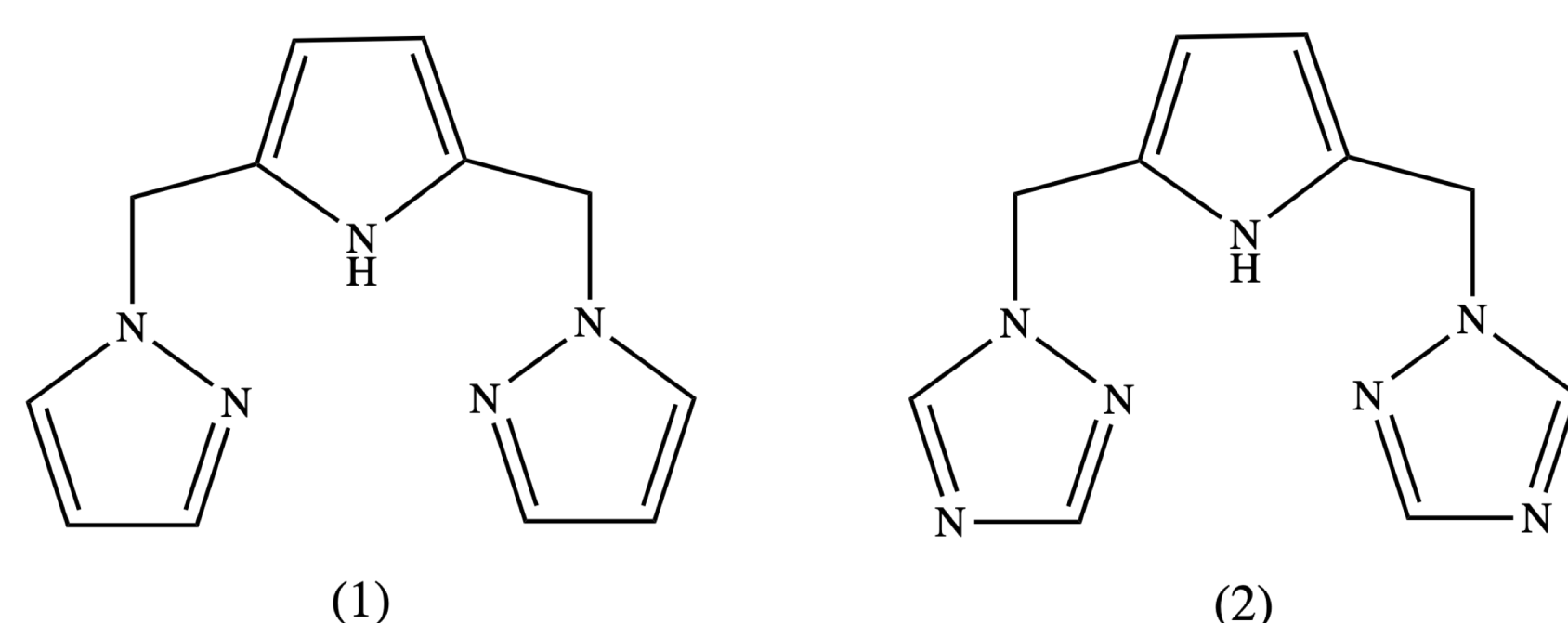


Figure 1: The two NNN-pincer ligands used for this project: 2,5-bis((1H-pyrazol-1-yl)methyl)-1H-pyrrole **(1)** and 2,5-bis((1H-1,2,4-triazol-1-yl)methyl)-1H-pyrrole **(2)**.

Pincer complexes are a sub-set of coordination compounds that contain a pincer ligand bound to a transition metal. Such organometallic complexes have proven to be effective catalysts in a variety of reactions. The NNN pincer ligands used in this research are hypothesized to be redox-active, which has been demonstrated by structurally similar NNNN tetradentate complexes.³

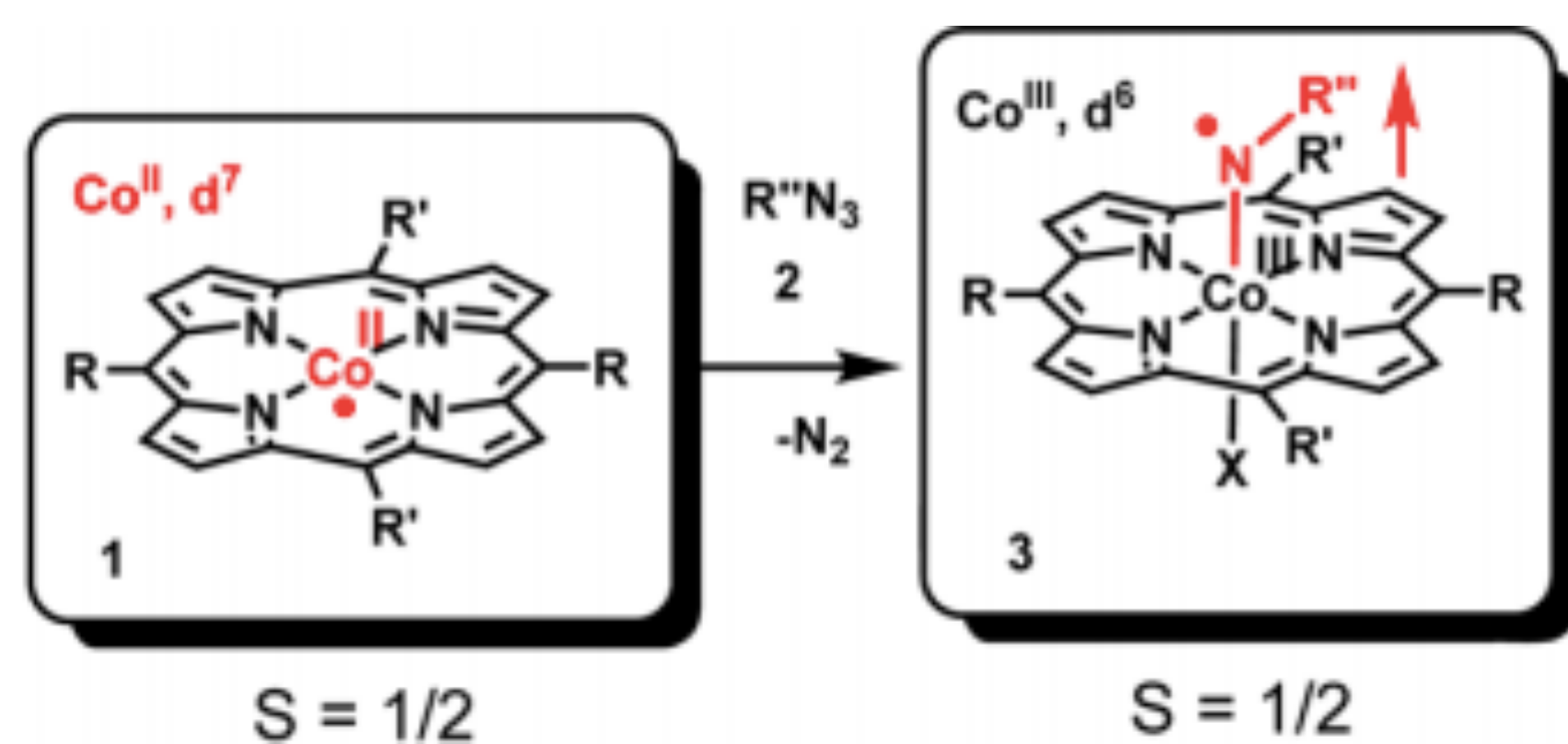


Figure 2: Example of a metal complex with redox-active NNNN ligand performing a nitrene transfer reaction.³

With structural similarities of these NNN ligands to porphyrins, it has been theorized that complexes containing these ligands would be suitable to perform proton coupled electron transfer (PCET) events.^{4,5} These type of reactions occur in biological systems, including the processes of photosynthesis and respiration.⁶

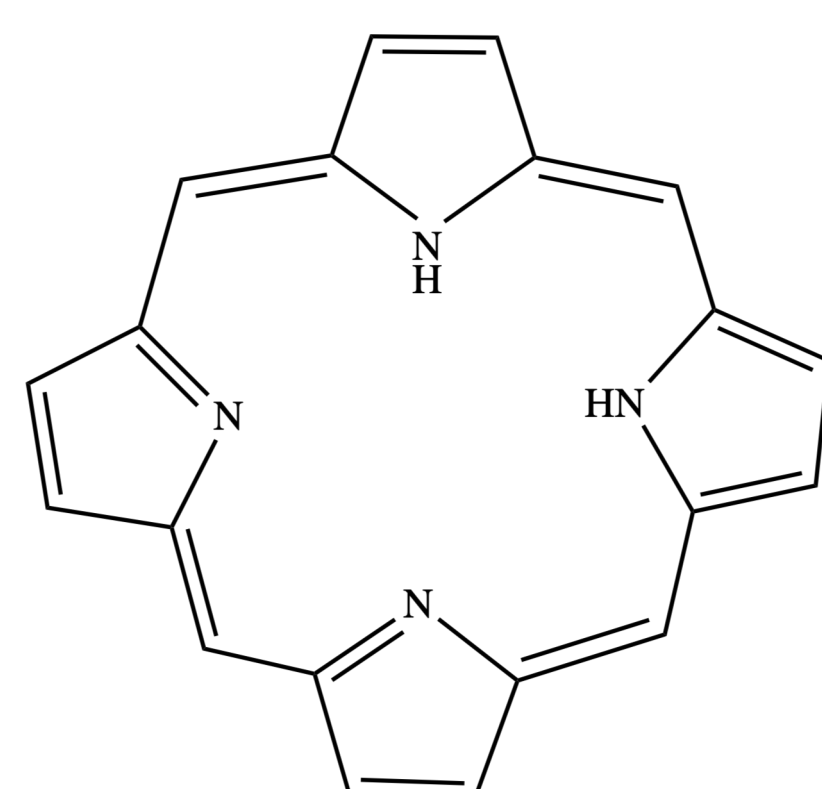
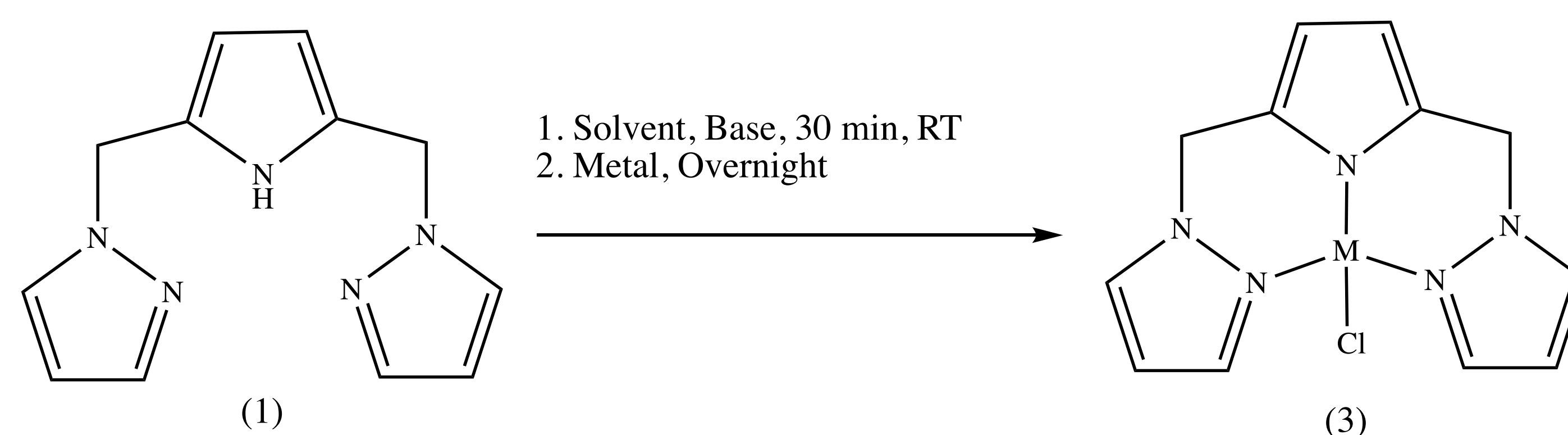


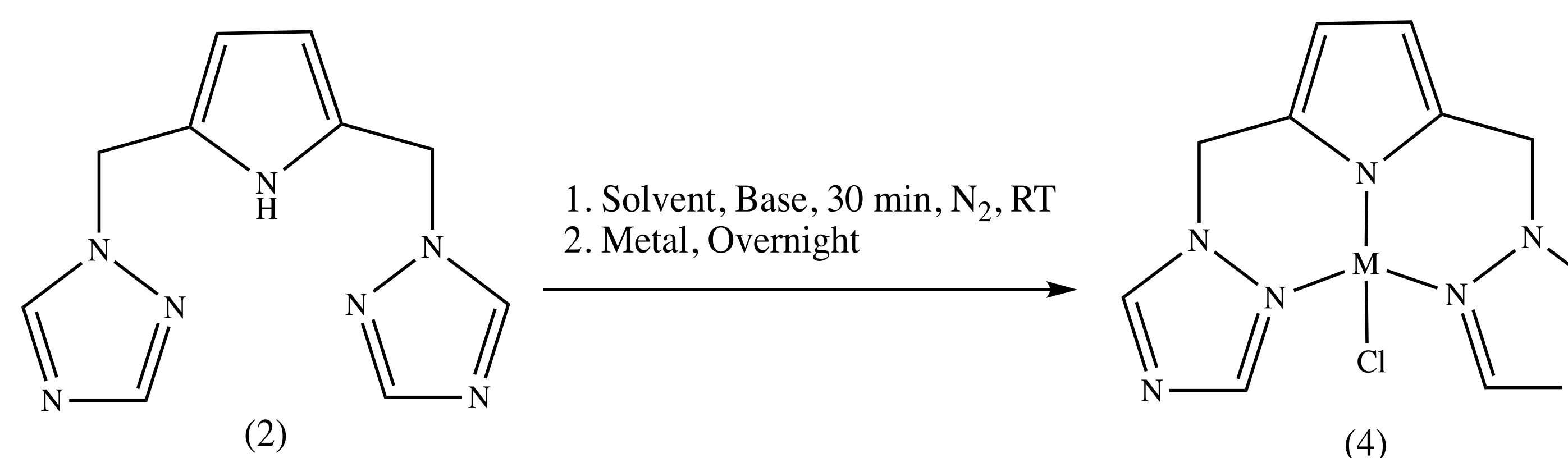
Figure 3: The structure of porphyrin is shown, and has binding sites that are very similar to those in the NNN-pincer ligands shown in **(1)** and **(2)**.

Metalation:

Metalation reactions were attempted with both **(1)** and **(2)** using a modified protocol reported by Lin.⁴ Protocol varied in atmosphere, base, solvent, and metal precursor.



Scheme 1: General reaction scheme for metalation of **(1)**.



Scheme 2: General reaction scheme for metalation of **(2)**.

Table 1: Varied reaction conditions in metalation reactions of **(1)** and **(2)**.

Solvents	Bases	Metal Precursors	Atmosphere
ACN, DCM, MeOH, THF	NEt ₃ , NaOtBu, KOtBu, NaH	PdCl ₂ , Ni(DME)Cl ₂ , CuI, CuCl ₂	N ₂ , air

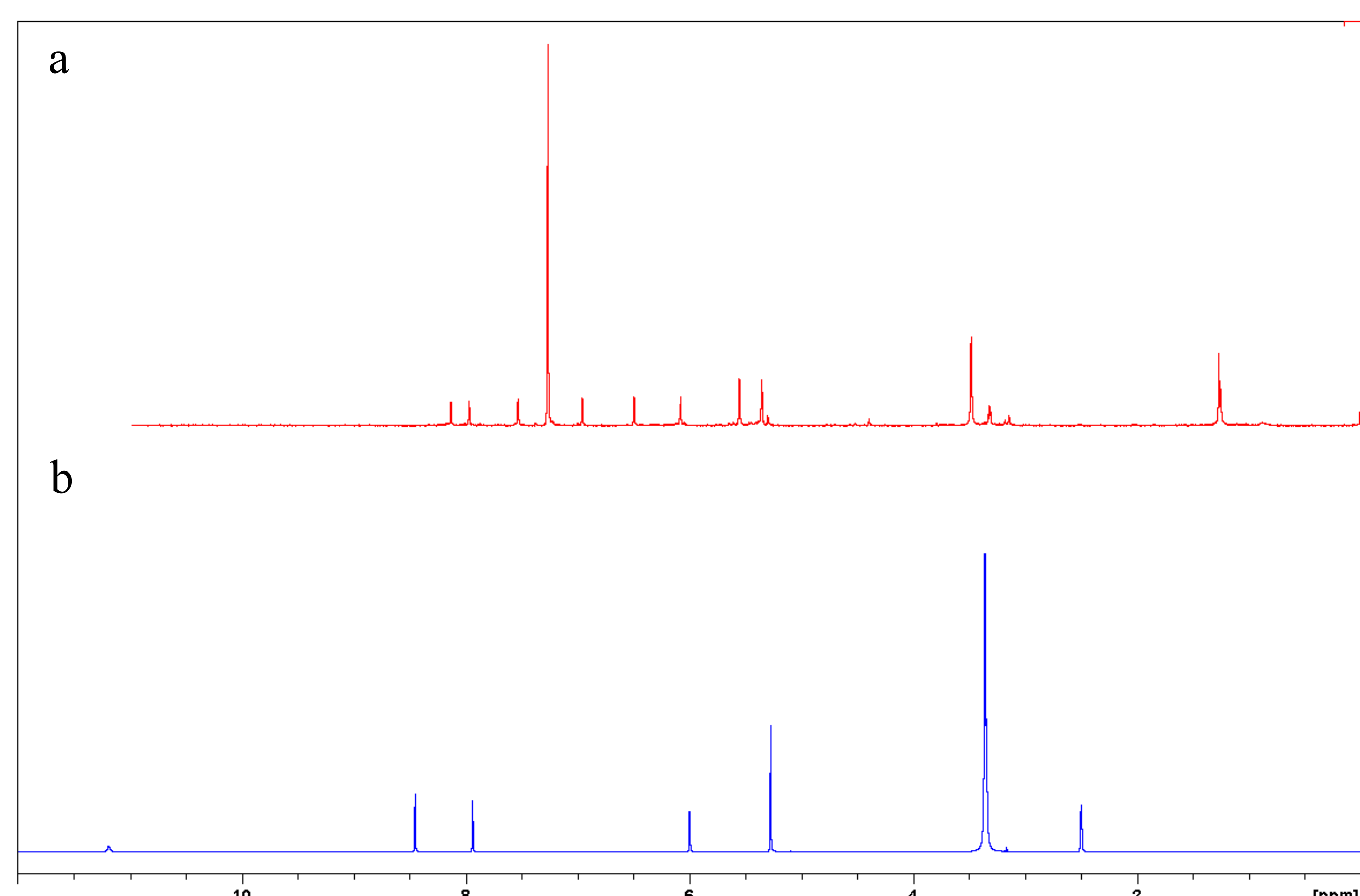


Figure 4a: ¹H NMR spectrum (400 MHz, CDCl₃) of reaction mixture resulting from the combination of **(2)** with PdCl₂ and KOtBu in MeOH under an N₂ atmosphere.

Figure 4b: ¹H NMR spectrum (400 MHz, DMSO-d₆) of free ligand, **(2)**. The pyrrole hydrogen is at a chemical shift of about 11.2 ppm.

Conclusions:

- Metalation reactions to palladium and nickel with **(1)** have not been successful thus far.
- Metalation reactions to palladium and nickel with **(2)** have been mostly unsuccessful. However, through ¹H-NMR analysis, it appears the combination of PdCl₂ with KOtBu in MeOH in a nitrogen atmosphere shows an unexpected product. The peaks on the spectrum provide evidence for the creation of what appears to be an asymmetric molecule.

Future directions:

- Continuing trials and attempting to find optimum metalation conditions.
- Once optimum conditions are found and complex is created, experiments can be conducted to test catalytic ability.

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