

Investigating the Synthesis of Imidazolium-Based NHC Ligands



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Introduction

N-heterocyclic carbenes (NHCs) are a convincing choice for building ligands in transition metal complexes. In general, carbenes are neutral compounds containing a divalent carbon atom possessing a lone pair in an sp^2 hybridized orbital available for coordination. A contributing factor to the NHCs' efficacy is that they are stabilized through electronics and are effective sigma donors, forming strong bonds with transition metals. This stabilization is attributed to the two nitrogen atoms 'pulling' electron density away from the usually reactive carbene carbon. Supplementally, the lone pairs of electrons on the nitrogen atoms can delocalize and 'push' into the vacant p orbital of the carbene center, thus stabilizing the singlet carbene. Imidazolium can serve as a backbone for NHCs allowing for nearly infinitely diverse functionalization options, namely, variation of the N-substituents. The N-substituents can vary with respect to the electronics and sterics, impacting the donor properties of the ligand. Several proposed substituent groups can be seen in **Figure 1**.

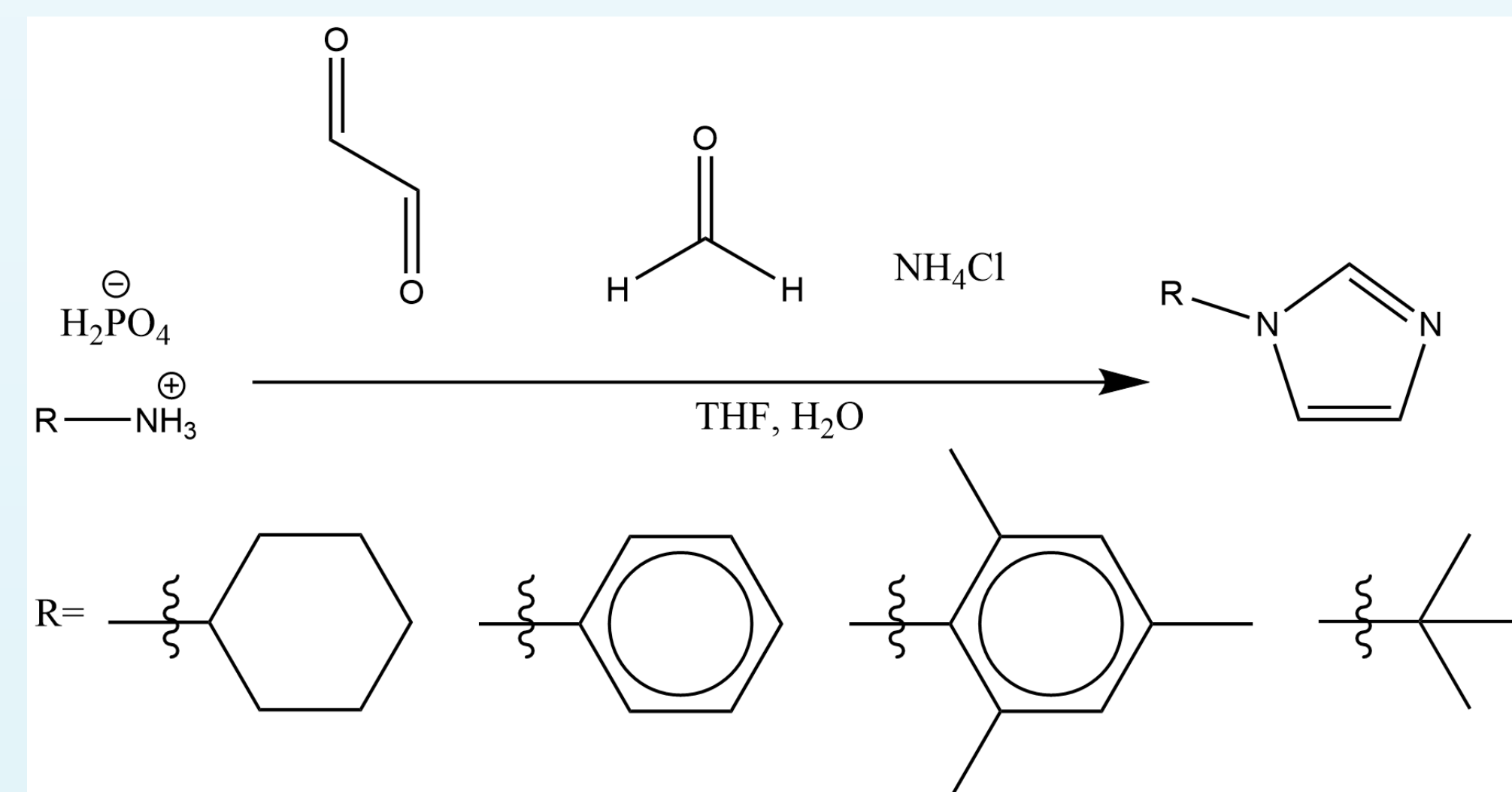


Figure 1: Proposed R groups for imidazolium backbone NHC ligands

This allows many variations of imidazolium-based ligands to be synthesized for coordination with transition metals. These ligand precursors will be used to synthesize a bimetallic complex to study metallophilic interactions, which are unusual, attractive interactions between closed-shell metal atoms. This type of interaction is thought to be the driving force behind some forms of chemical luminescence.

Design and Rationale

Imidazolium-based ligands were selected for this project because of the diversity of N-substituents that can be investigated. The relative ease of a one-pot synthesis renders this ligand class quite attractive, as multiple derivatives can be synthesized in a short time.

Design and Rationale

As these ligands would facilitate on/off metallophilic interactions within a bimetallic species, the sterics of the N-substituted R groups were considered. The addition of varying the sterics is hypothesized to modulate the photophysical properties of the final bimetallic species. The pyridyl arm with a carbon spacer allows for flexibility within the ligand and is advantageous in facilitating on/off metallophilic interactions. The reaction pathway for this addition can be seen in **Figure 2**

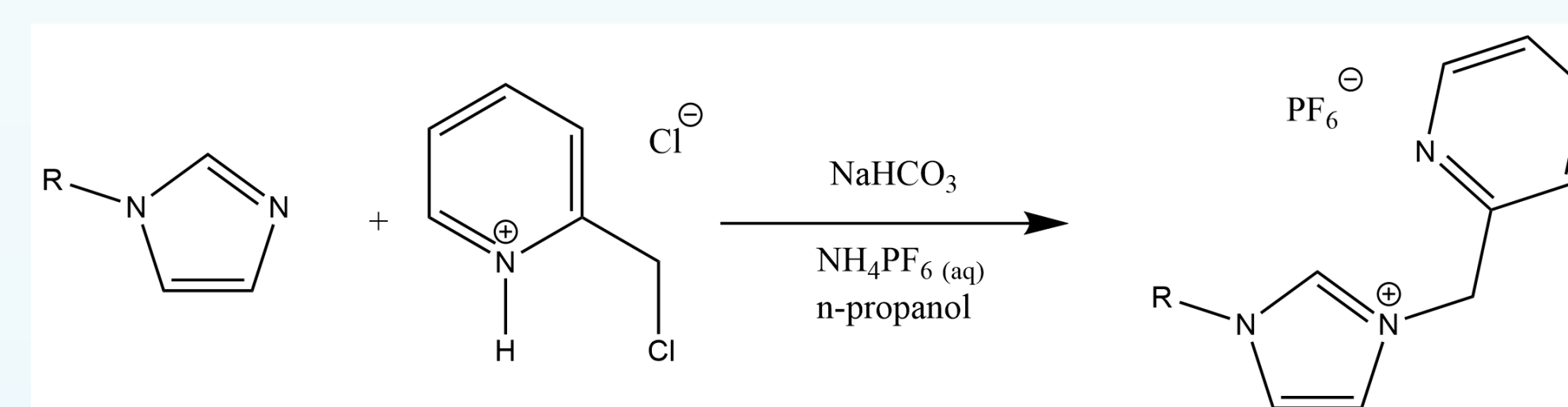


Figure 2: Proposed addition of pyridyl arm onto imidazolium backbone

The interaction between the overall cation charge of the species, and counteranions can affect the luminescent properties of the final species through electrostatic interactions.

Results and Discussion

Multiple variations of the imidazolium precursor ligand were synthesized, with varying success. During the synthesis of the precursors, two methods were explored. The first route involved initial isolation of an ammonium phosphate salt, followed by the similar reaction conditions as established by the Debus-Radziszewski imidazole synthesis. The 1-mesitylimidazole and 1-cyclohexylimidazole species were synthesized using this multi-step method. Fortunately, a one-pot imidazolium ligand synthesis has been reported in the literature. This reaction methodology was employed with aniline, resulting in 1-phenylimidazole. As an example of a successful imidazole precursor synthesis, the NMR for 1-mesitylimidazole is presented in **Figure 3**. Using 2-picolylchloride hydrochloride, a pendant pyridyl arm was added as another substituent of 1-mesitylimidazole and 1-methylimidazole. After analyzing the NMR, which can be seen in Figure 4, it was determined that the 1-methyl-3-(2-picolyl) Imidazolium hexafluorophosphate synthesis was the most successful. The final structure and NMR can be seen in **Figure 4**.

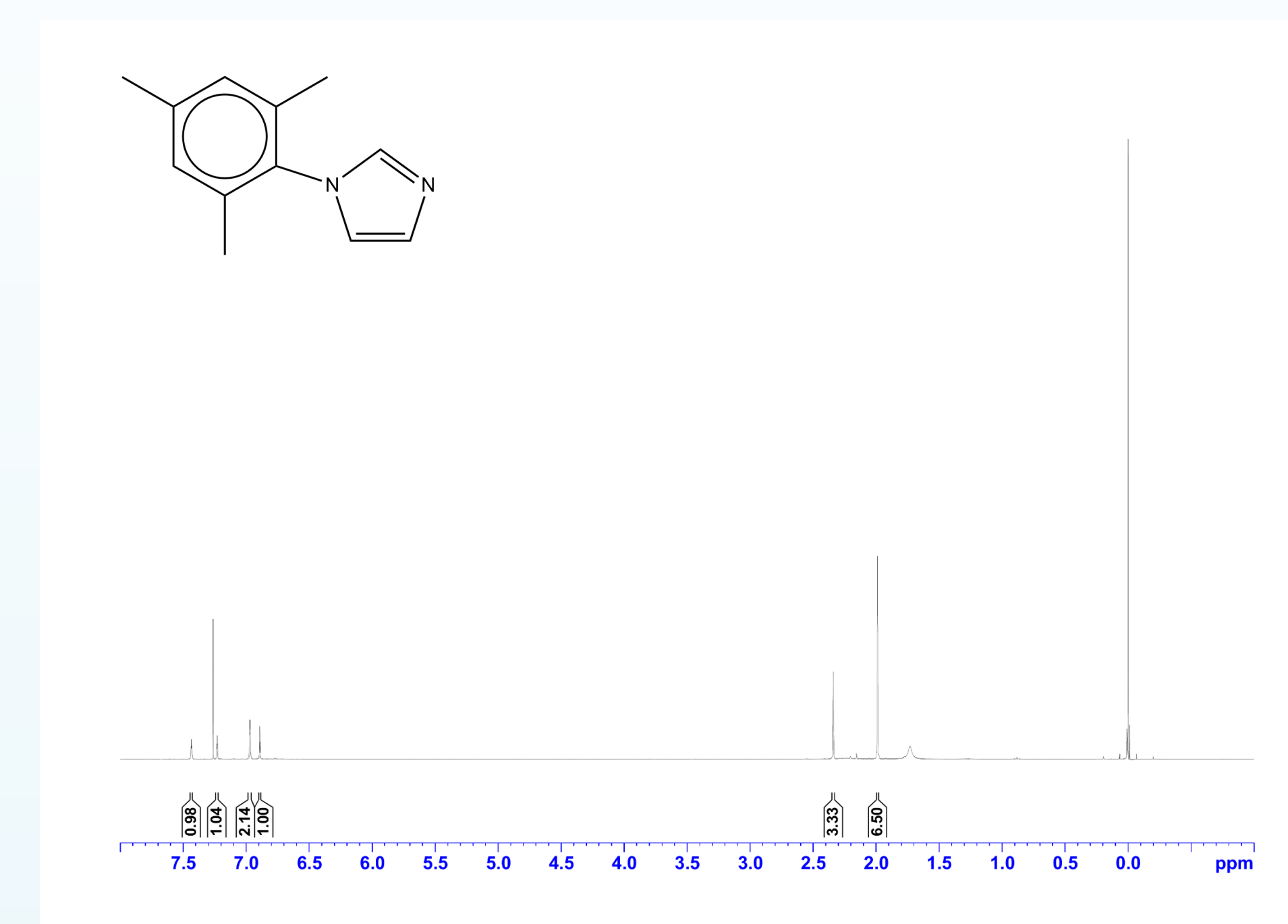


Figure 3: Structure and NMR of 1-mesitylimidazole

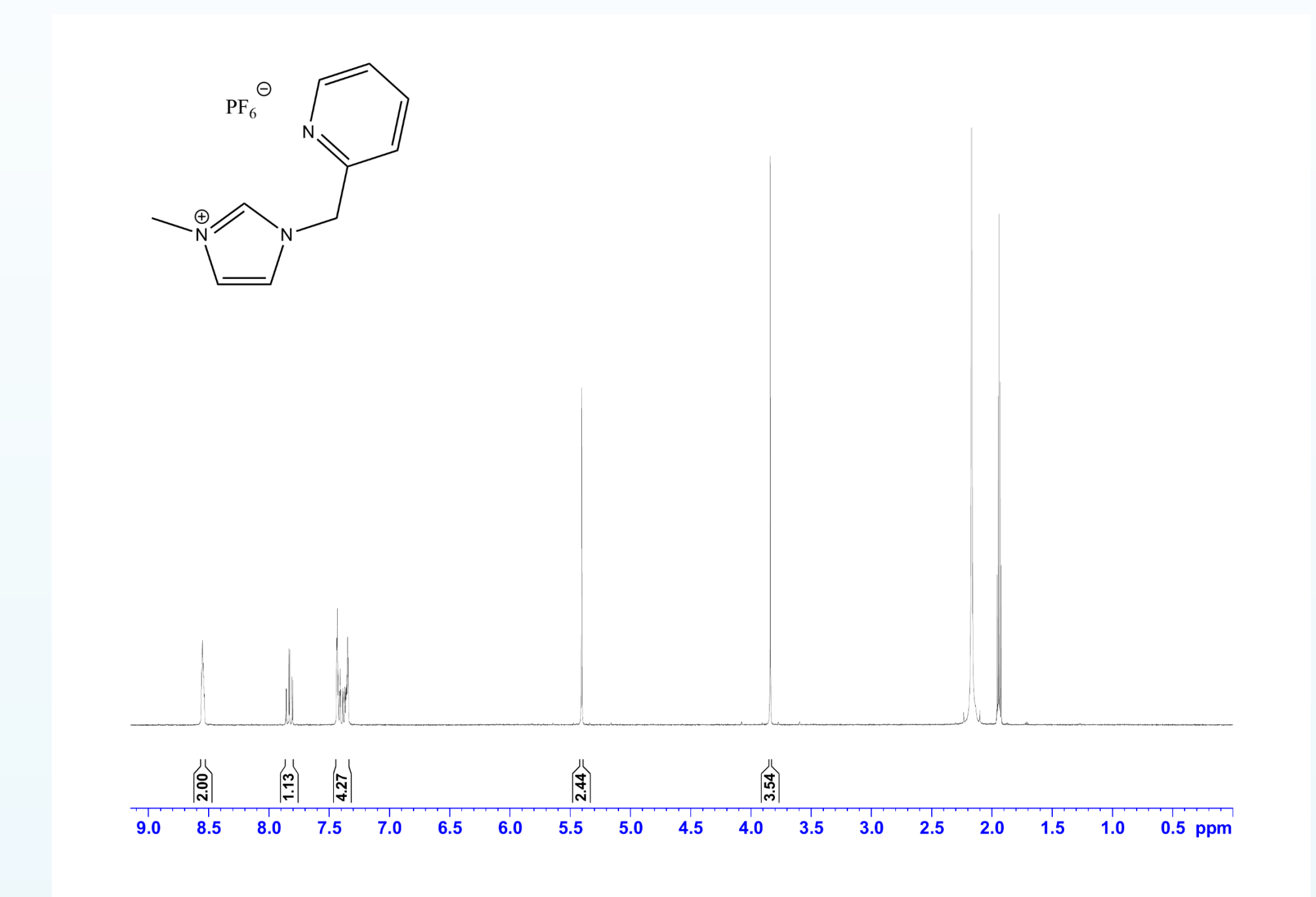
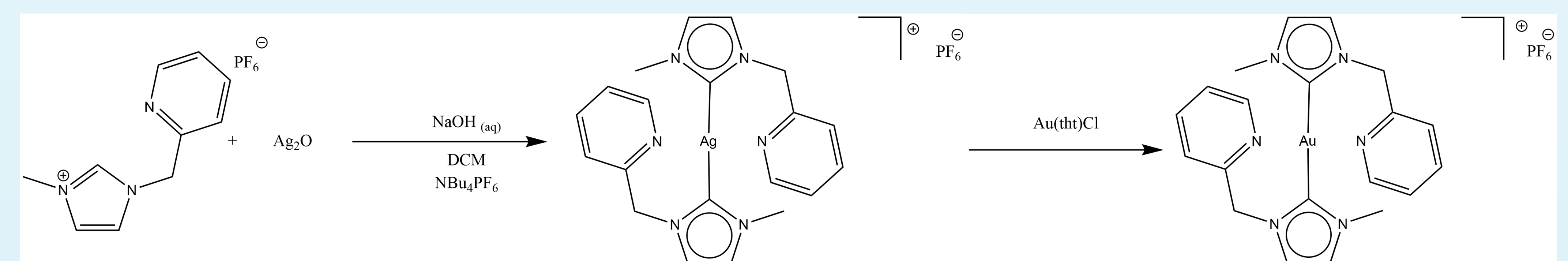


Figure 4: Structure and NMR of 1-Methyl-3-(2-picolyl) Imidazolium hexafluorophosphate

Conclusions and Future Work

The synthesis of multiple imidazolium-based ligands was explored, and the steric implications of varying N-substituents were investigated. As the ligand built with a methyl substituent was the most successful, it may be prudent to construct other ligands using substituents with similar sterics. Moving forward, this methylimidazole-based ligand will be used in a 4:1 ratio to generate a monometallic silver(I) complex containing two NHCs. This silver species will undergo a transmetalation reaction with Au(tht)Cl, yielding the monometallic gold species. Once the Au species is characterized, an equivalent of copper(I) will be added to generate a heterobimetallic species. The resulting bimetallic species will be used to investigate on/off metallophilic interactions and the photophysical properties of these unusual interactions.



References

1. Tolomeu, H. V.; Fraga, C. A. M. Imidazole: Synthesis, Functionalization and Physicochemical Properties of a Privileged Structure in Medicinal Chemistry. *Molecules* **2023**, *28* (2), 838.
2. Smith, C. A.; Narouz, M. R.; Lummis, P. A.; Singh, I.; Nazemi, A.; Li, C.-H.; Crudden, C. M. N-Heterocyclic Carbenes in Materials Chemistry. *Chem. Rev.* **2019**, *119* (8), 4986–5056
3. Vinh Huynh, H. *The Organometallic Chemistry of N-heterocyclic Carbenes*.

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