

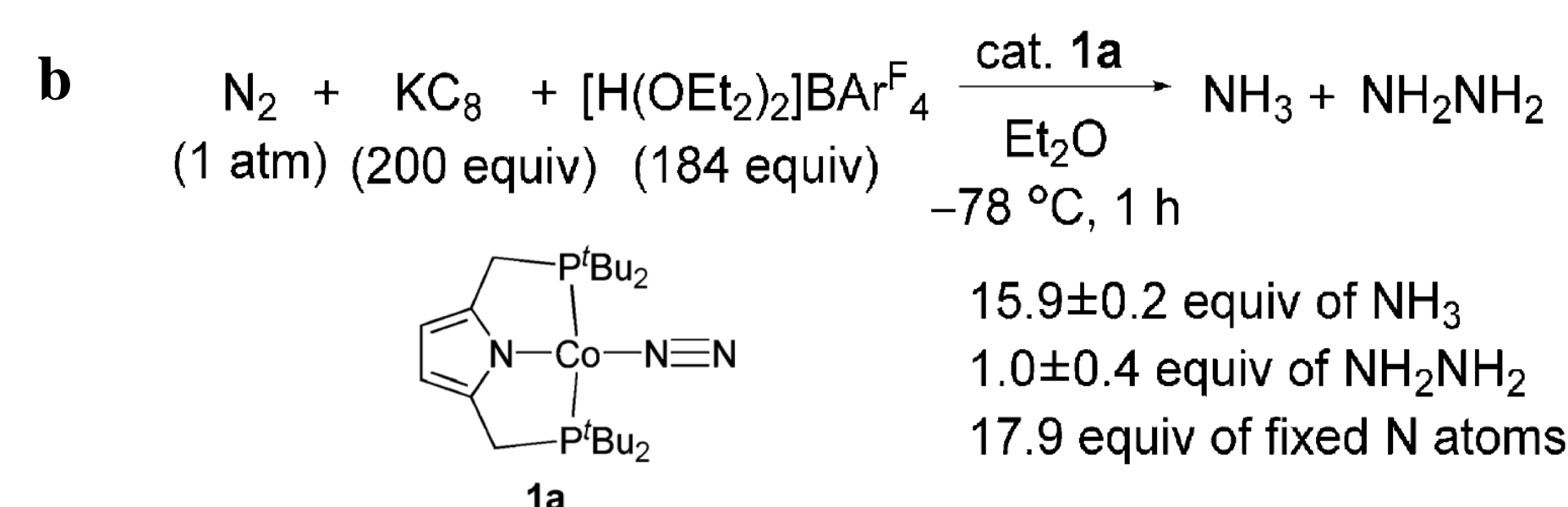
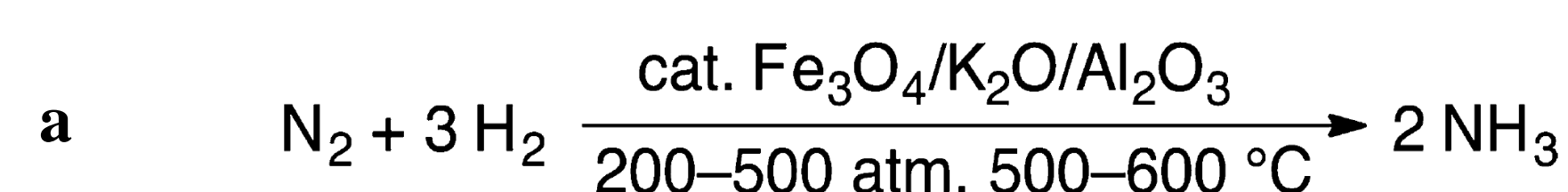
Overview: Synthesis of PNP-Pincer Ligands for Potential use in Nitrogen Fixation

Developed over a century ago to enable the large scale production of fertilizers, the Haber-Bosch nitrogen fixation process remains essential today as ammonia is a vital component of dyes, resins, and explosives (**Fig 1a**).^{1,2} However, similar to biological systems, synthetic nitrogen fixation is an energy-intensive process, requiring a highly active catalyst and high temperatures and pressures.³

An expanding area of research is the finding of an environmentally sustainable, and cost-efficient nitrogen fixation process to supplement the Haber-Bosch. Catalysts for nitrogen fixation, specifically various transition-metal dinitrogen complexes, have been developed but they lack the efficiency of the Haber-Bosch and require large excess of strong reducing agents and exotic proton sources (**Fig 1b**).^{3,4} **The goal of this project was to explore how PNP-pincer ligand design can enable the use of milder reducing agents and minimize key side-reactions for the cobalt-PNP dinitrogen complex catalyzed nitrogen fixation process.**

Two PNP-pincer ligands based on work of the Ozerov group, an anionic *N*-donor **2** and neutral *N*-donor **3**, were successfully synthesized and characterized via ³¹P and ¹H NMR.⁵ **2** was successfully complexed first with palladium **4** to demonstrate its ability to form a complex, and then with cobalt **5** and were characterized by NMR and FT-IR respectively (**Spectra 1-2**). After trying three reducing agents, **5** was still unable to be reduced to form **6**, as shown by the absence of an N₂-Co peak (2016 cm⁻¹) in the FT-IR (**Spectra 3**).⁴ However, comparison ¹H NMR showed that the complex was reduced but undesired side products were produced (**Spectra 2**). If this project was to be continued, modifications would be made to the ligands to prevent undesired side reactions in the reduction step. The cobalt-dinitrogen complex synthesized would then be tested for nitrogen fixation capabilities.

Figure 1. (a) Haber-Bosch Process³ **(b)** Sample cobalt-PNP dinitrogen complex for N₂ fixation⁴



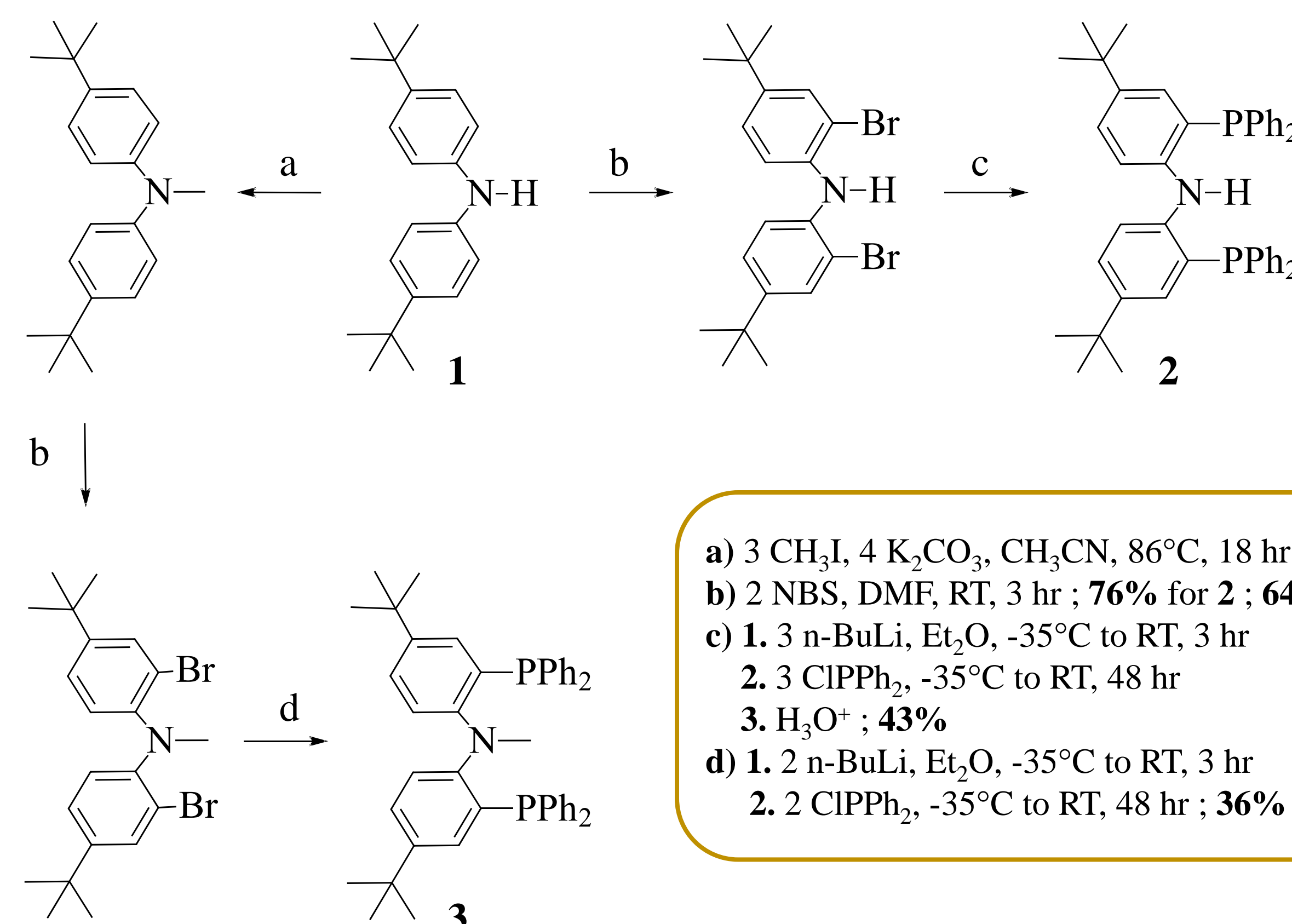
References and Acknowledgements

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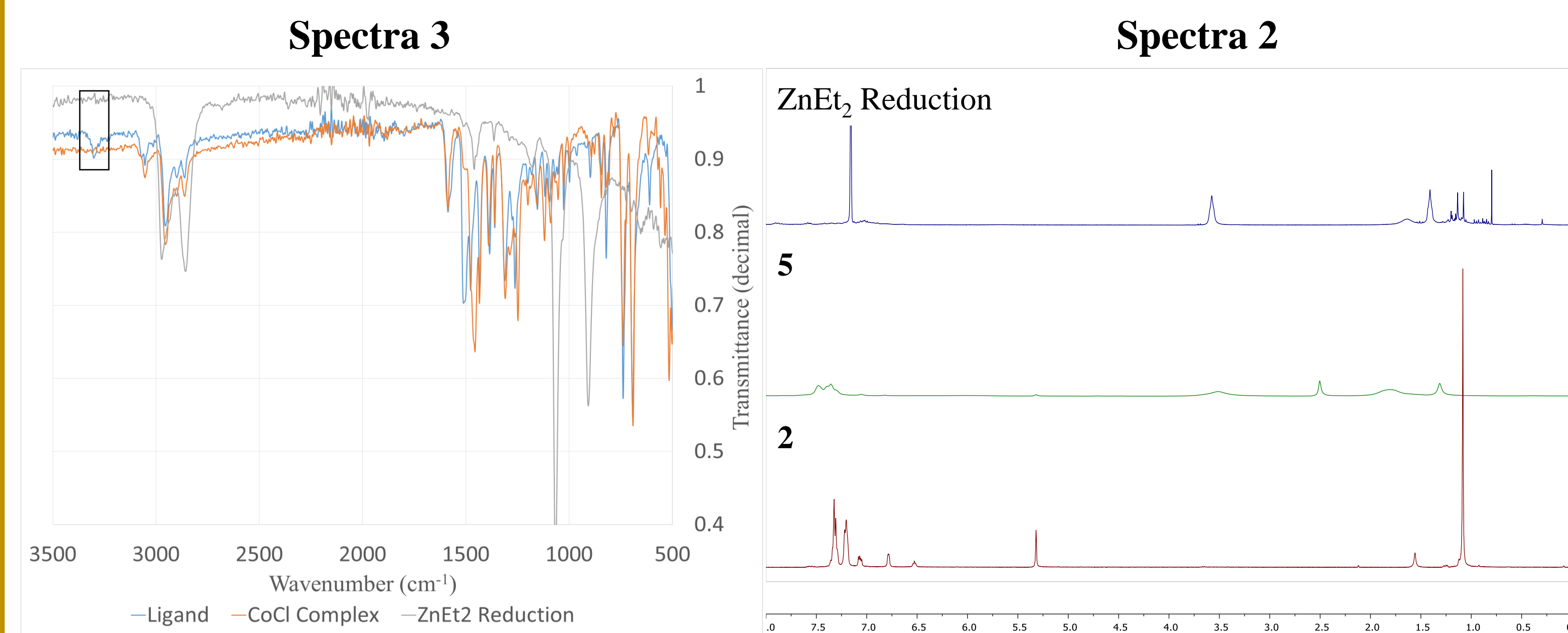
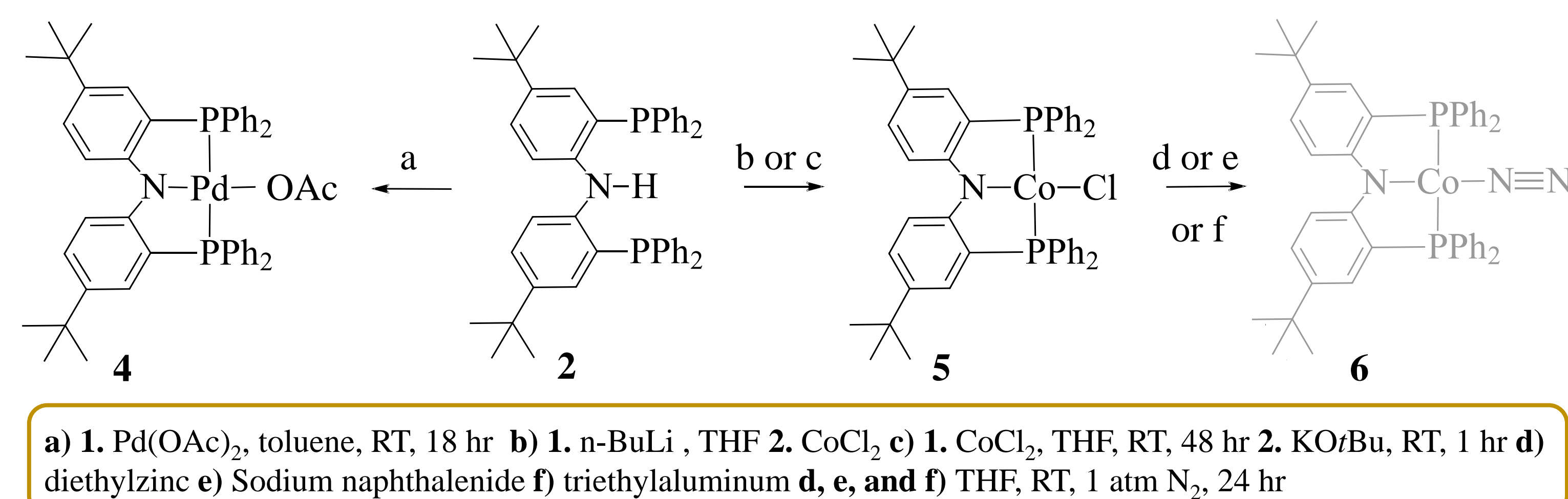
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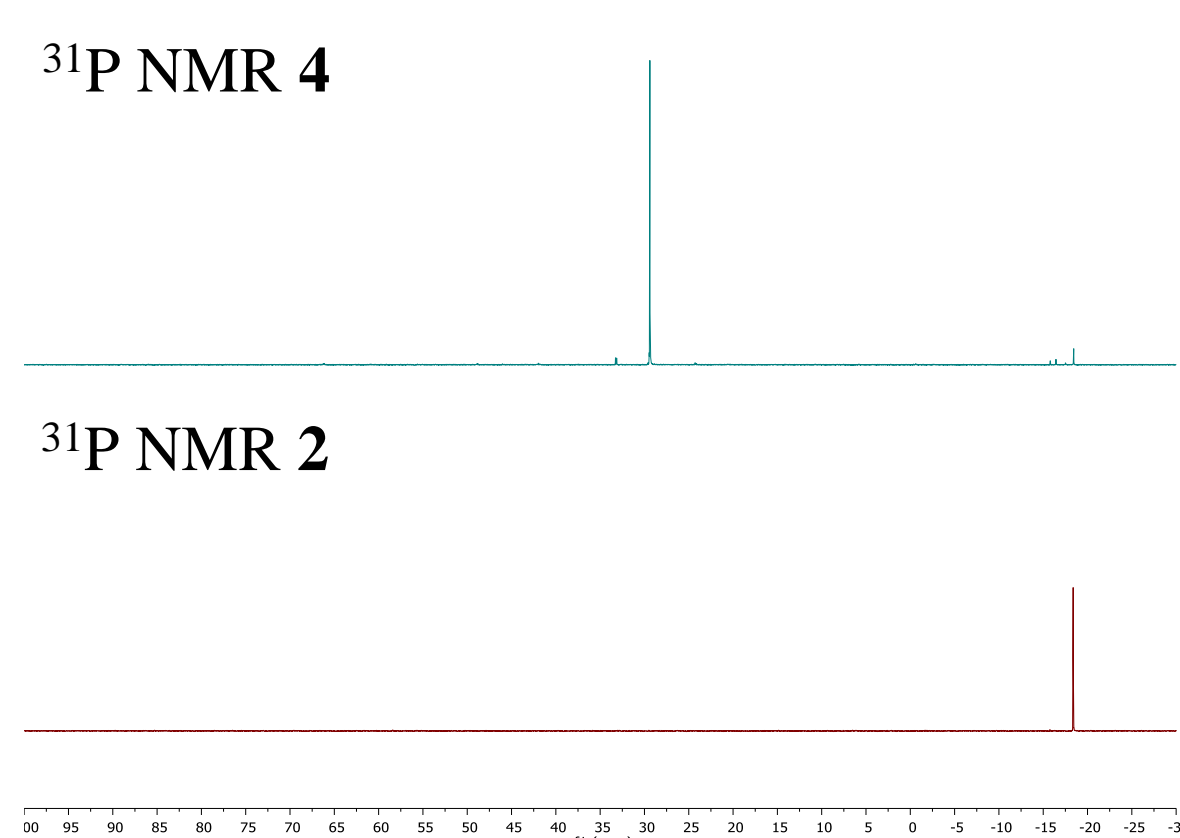
Target PNP-Pincer Ligand Synthesis



Complex Synthesis, Reduction and Selected Characterization



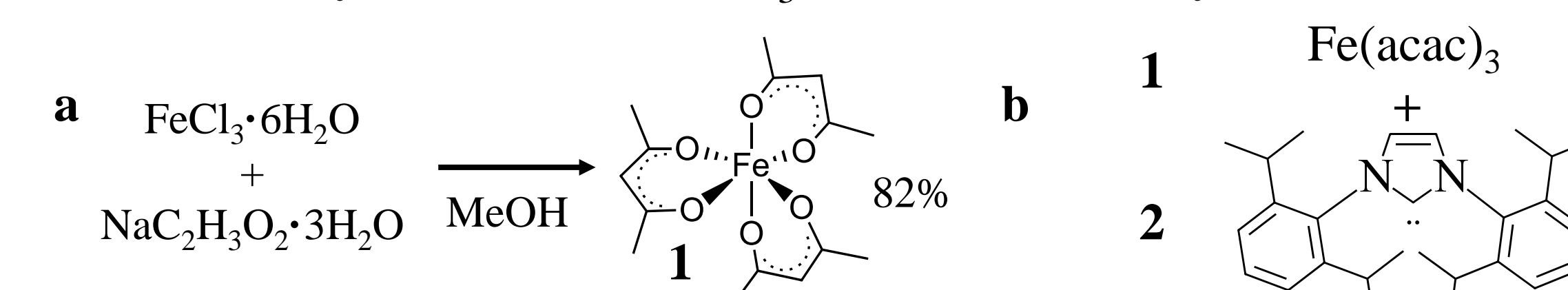
Spectra 1



Overview: Exploring Iron-NHC Complexes as Catalysts for Organic Reactions

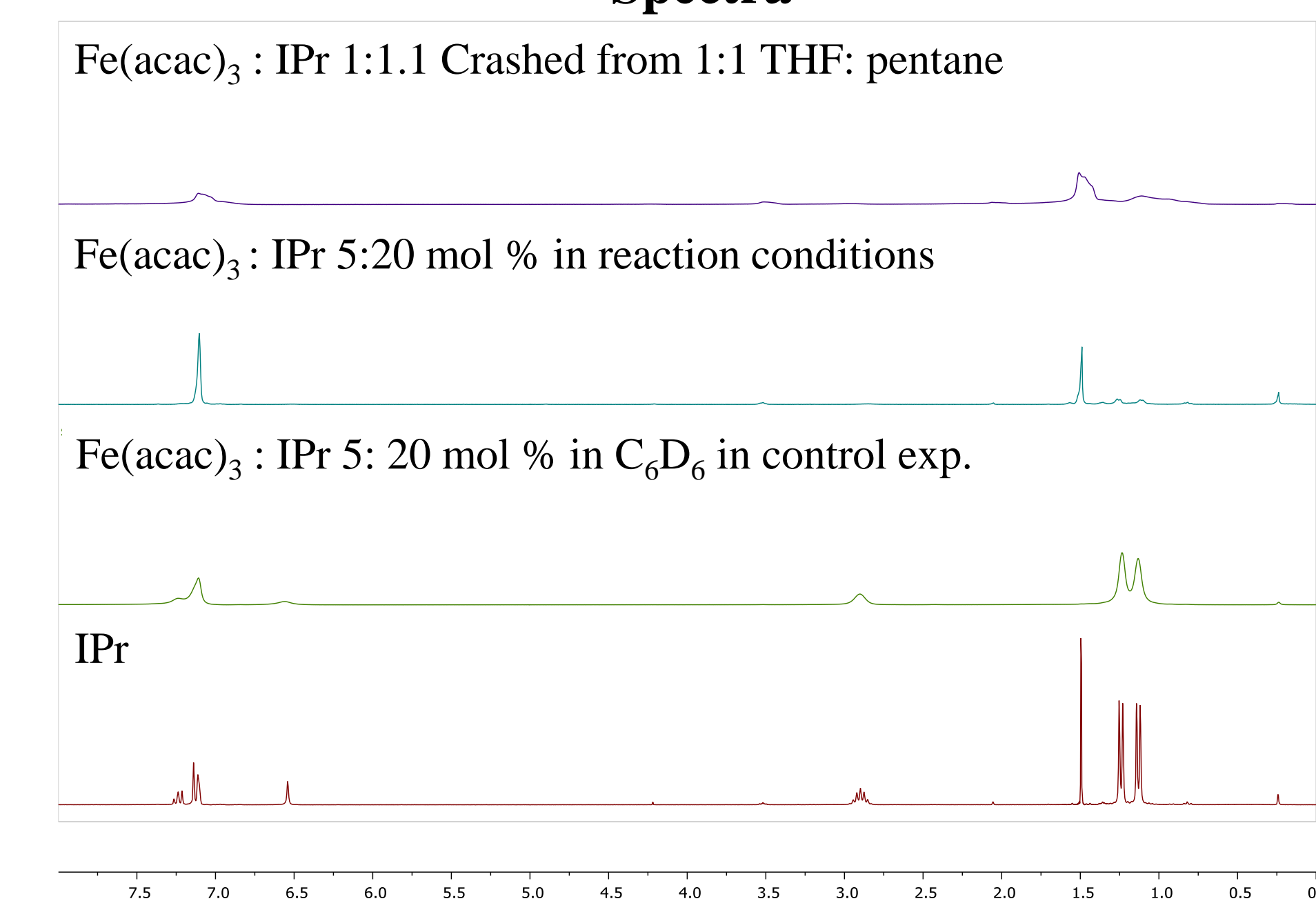
Iron complexes are attractive as potential catalysts given their existence in a variety of oxidation states, cost of the metal, and often air and moisture stability. There are several different classes of ligands that may be used to construct iron complexes, but our interest lies with the use of *N*-heterocyclic carbene (NHC) ligands. To our knowledge, no iron-NHC complexes have been reported that catalyze Michael and aza-Michael reactions. Given the widespread use of these addition reactions in the synthesis of biologically active molecules we sought to expand the type of iron-based catalysts available.¹⁻³ Catalyst **A** has been selected for two reasons: (1) simple *in-situ* synthesis from Fe(acac)₃ and commercially available IPr and (2) demonstrated catalytic ability for the cross coupling of aryl Grignards (**Scheme 1**).³

Scheme 1. (a) Synthesis of Fe(acac)₃ **(b)** *in-situ* catalyst **A**



Initially, the stability of **1** and **2** in various solvents (C₆D₆, CH₃CN, CDCl₃) was monitored by ¹H NMR to determine optimal reaction conditions. However, the ¹H NMR spectra did not suggest the formation of **A** in C₆D₆, but that the presence of the Fe(acac)₃ seemed to decompose the IPr (**Spectra 1-2**).

Spectra



Two papers report the use of the iron-IPr *in-situ* complex catalyzing Grignard reactions; but evidence to support the formation and/or isolation is absent.^{3,4} A search of the literature reveals no iron-acac-NHC complexes nor anything similar to the acac binding motif. Attempts to isolate **A** in the reported reaction conditions show the degradation of IPr (**Spectra 3-4**). Future work on this project includes determining both the origin of the degradation of IPr and a closer examination of the reported Grignard reactions to determine the active catalyst.

References and Acknowledgements

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