

## Background

- Polyolefins are eco-friendly materials that efficiently resist chemical/thermal influences and are non-toxic. They have been around for more than a century in all sorts of manufacturing materials such as fibers for clothing, food/electronic packaging, and industrial products.
- Polyolefins are liable for the 57% portion of plastic waste that is generated per year.

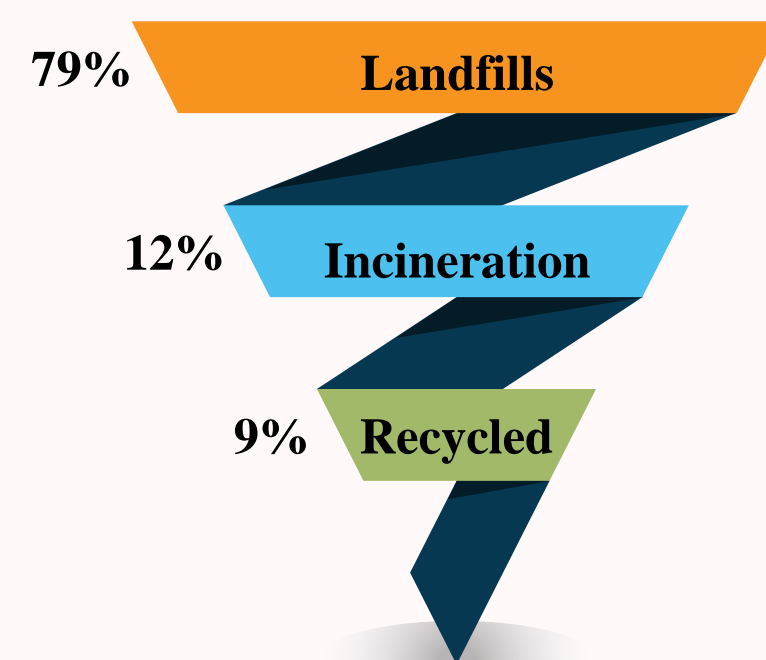


Figure 1. Destination of Plastic Waste.<sup>1</sup>

- There are many places polyolefins end up (Figure 1), but only 9% of the plastics are recycled.

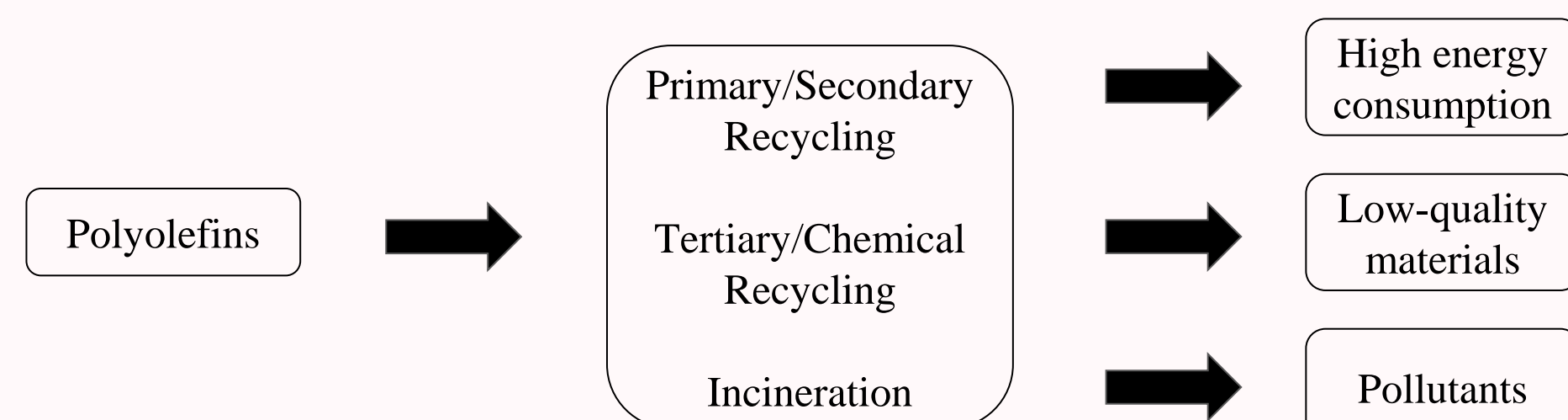


Figure 2. Current Methods of Plastic Degradation and their Drawbacks.<sup>1-5</sup>

- Although heterogeneous catalysts (image created by Emily Podd) are the current standard for hydrogenolysis of polyolefins, homogeneous catalysts are unexplored in this area and have great potential because they can be easily tailor to improve activity and selectivity.

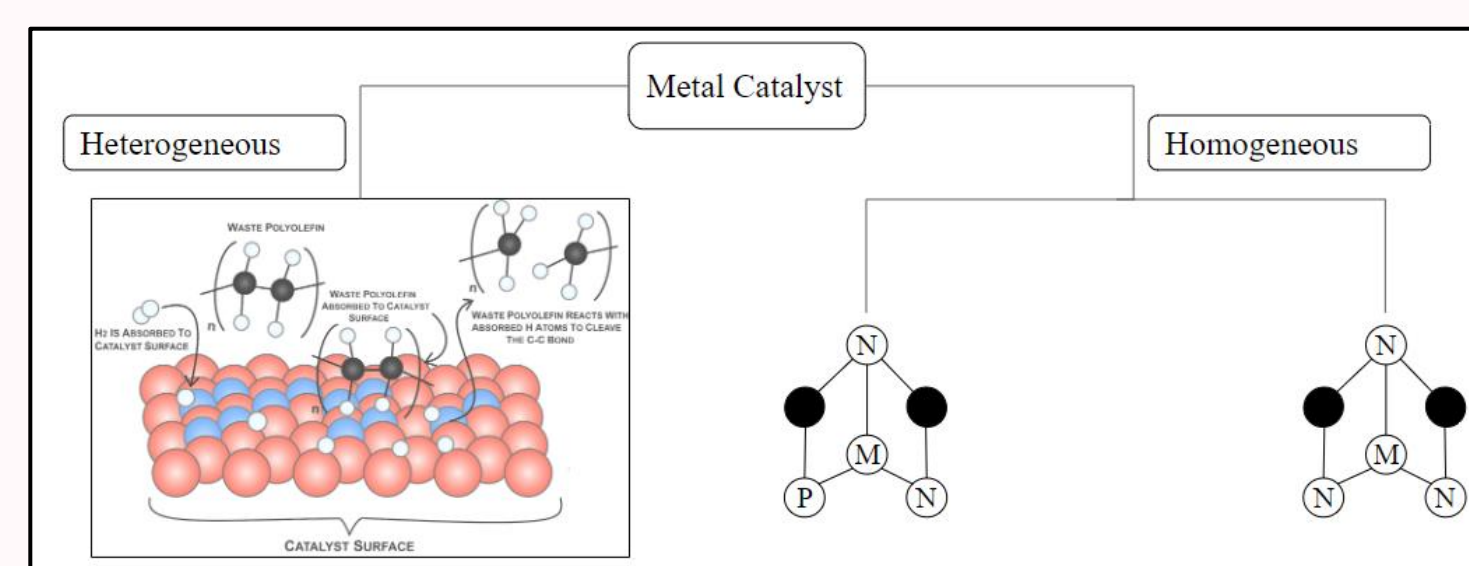
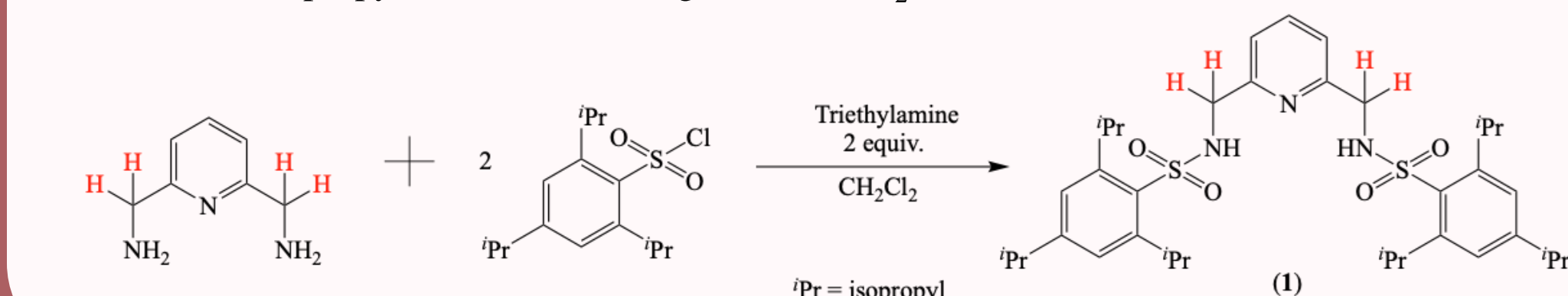


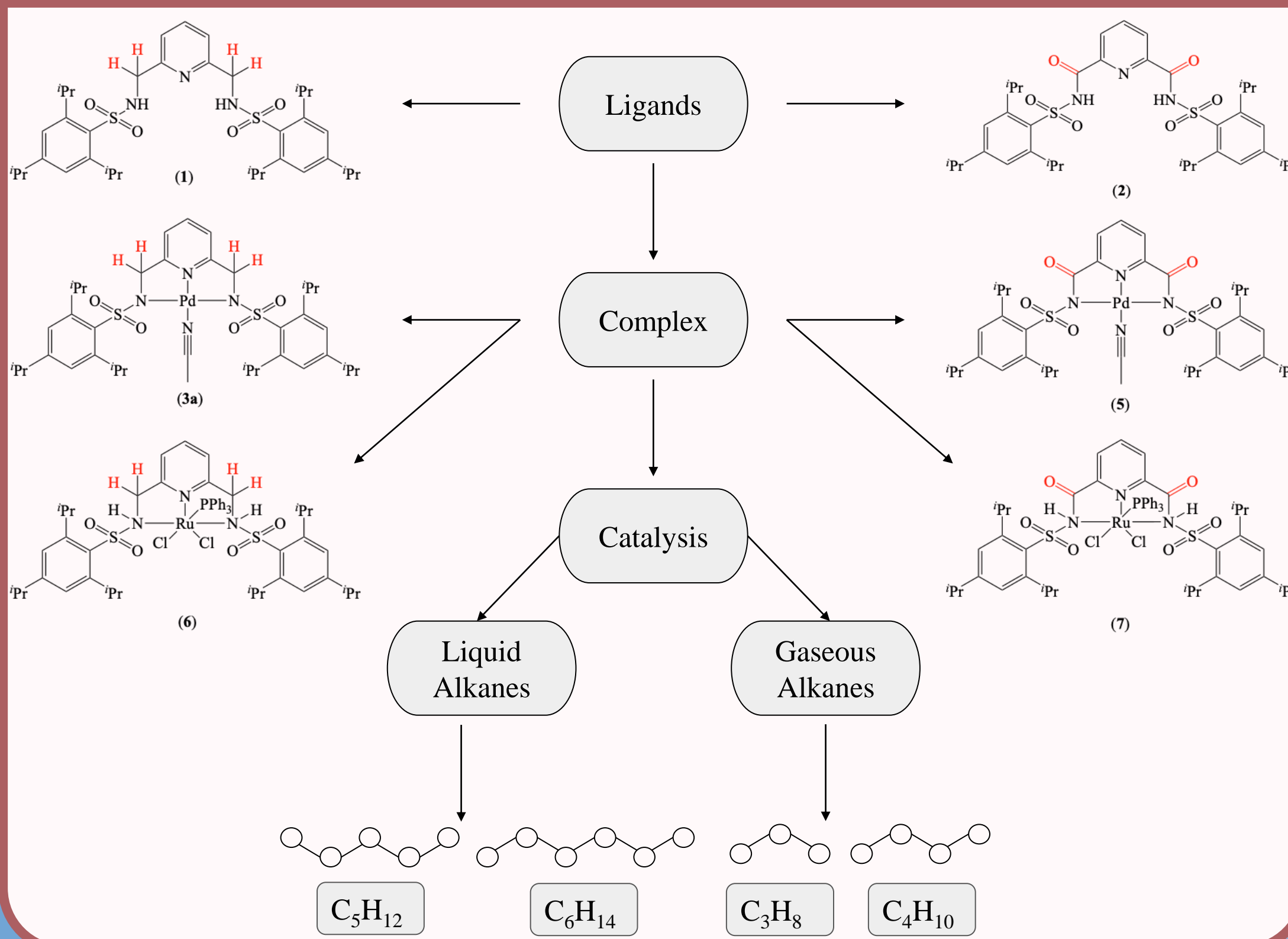
Figure 3. Comparing Heterogeneous and Homogeneous [NNN] Catalysts for Plastic Hydrogenolysis.<sup>6</sup>

- The triisopropyl [NNN] pincer ligand with methylene linkers have been synthesized in the O'Connor lab, which needs to be made into palladium and ruthenium catalysts to examine hydrogenolysis.

Scheme 1. Triisopropyl [NNN] Pincer Ligand with CH<sub>2</sub> Linkers.

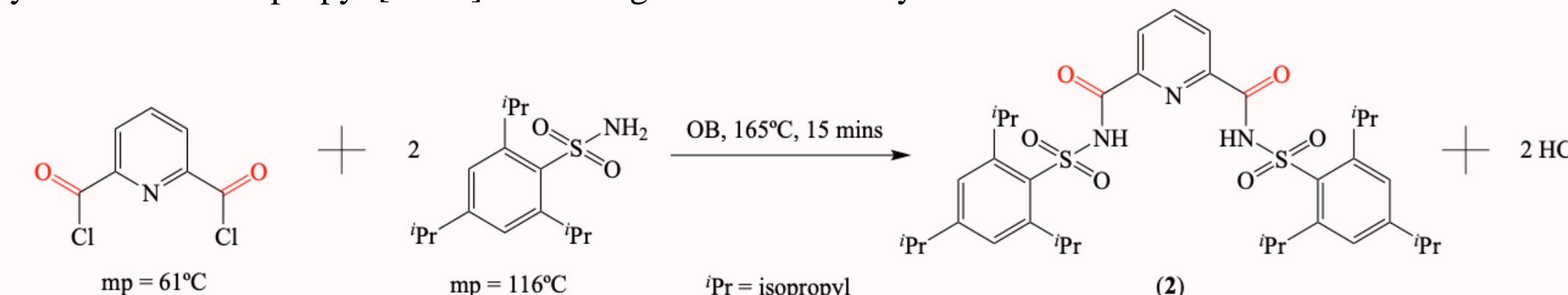


## Objectives



## Synthesizing Triisopropyl [NNN] Pincer Ligand

Scheme 2. Synthesis of Triisopropyl [NNN] Pincer Ligand with Carbonyl Linkers.



- Compound (2) was formed from 2,4,6-triisopropylbenzene sulfonamide and pyridine-2,6-dicarbonyl dichloride in 82%.
- Synthesis was first attempted under microwave conditions but a greener synthesis pathway was identified by removing the addition of the solvent and conducting the reaction neat.
- The target temperature of 165°C was determined based on the melting points of both reagents.

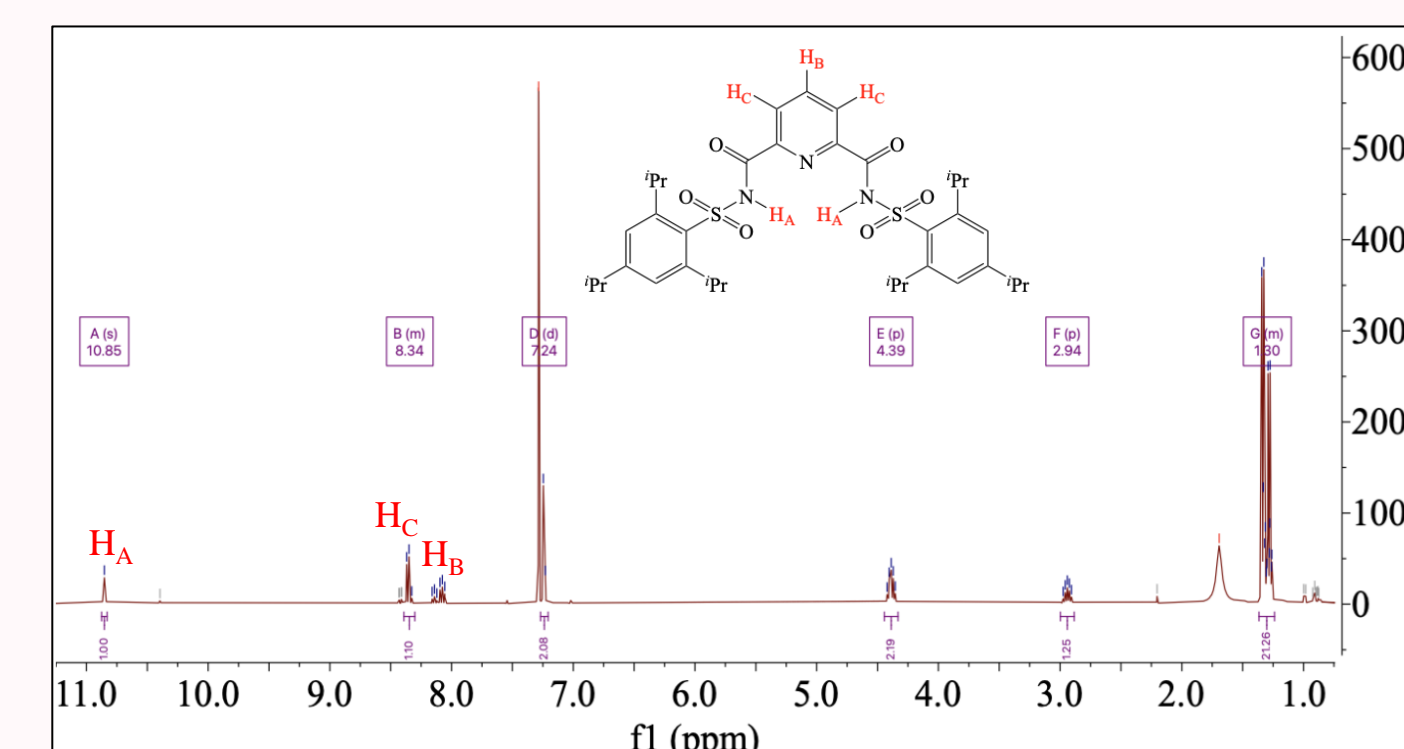
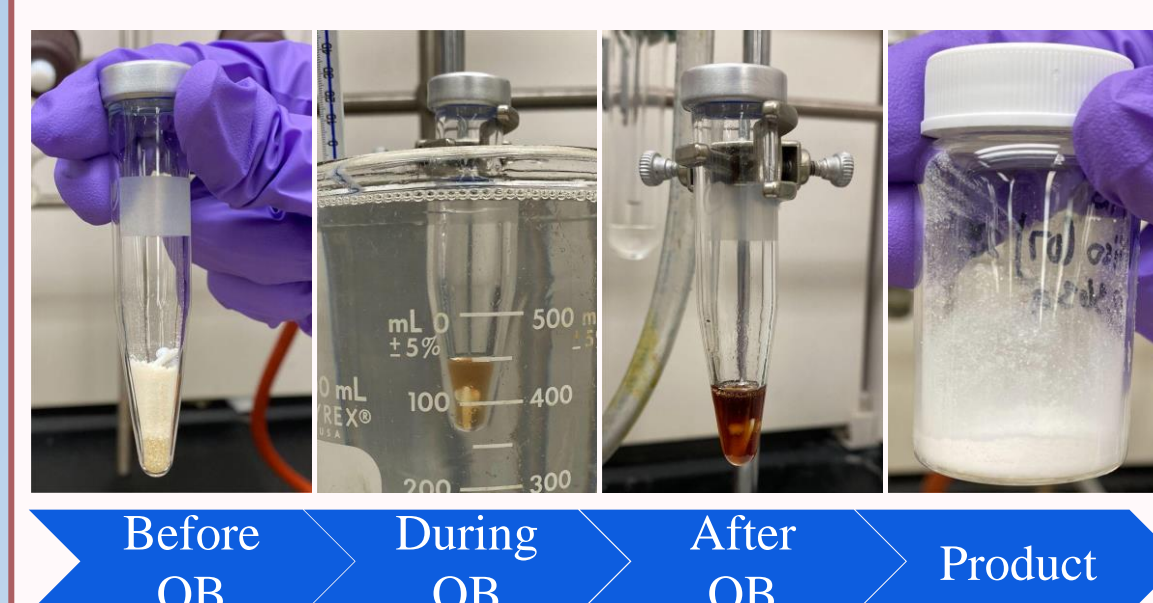
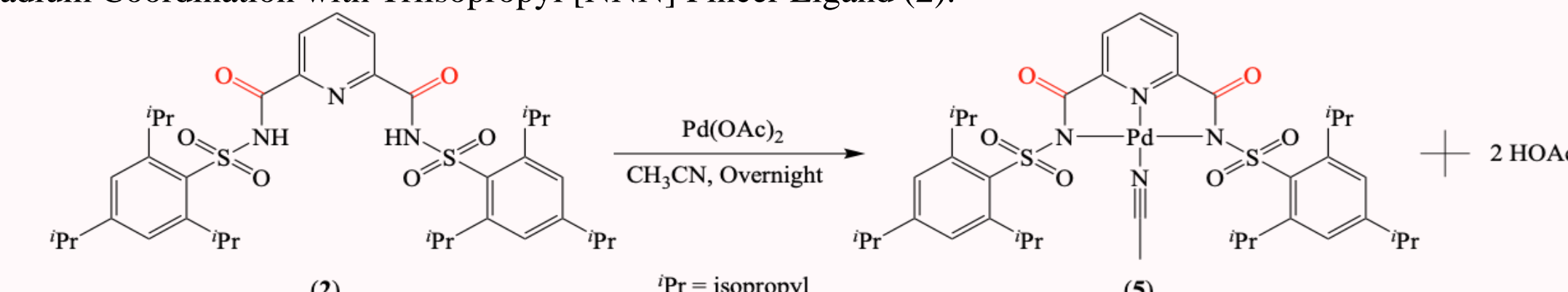


Figure 4. <sup>1</sup>H NMR Spectrum of Compound (2).

- A peak at 10.85 ppm (H<sub>A</sub>, NH peak) confirms formation of the amide bond (Figure 4). The doublet (H<sub>C</sub>) at ~8.30 ppm and a triplet (H<sub>B</sub>) at ~8.00 ppm correspond to the hydrogens located on the pyridine backbone.
- An IR spectrum also confirms formation of compound (2) due to the presence of an NH stretch at ~3200 cm<sup>-1</sup>.

## Palladium Metalation to [NNN] Ligand 2

Scheme 5. Palladium Coordination with Triisopropyl [NNN] Pincer Ligand (2).<sup>7</sup>



- Product (5) was obtained from the filtrate rather than the solid precipitate formed from overnight stirring in CH<sub>3</sub>CN.
- The color of the precipitate was vibrant orange which is not consistent with the literature regarding similar palladium complexes.<sup>7</sup>

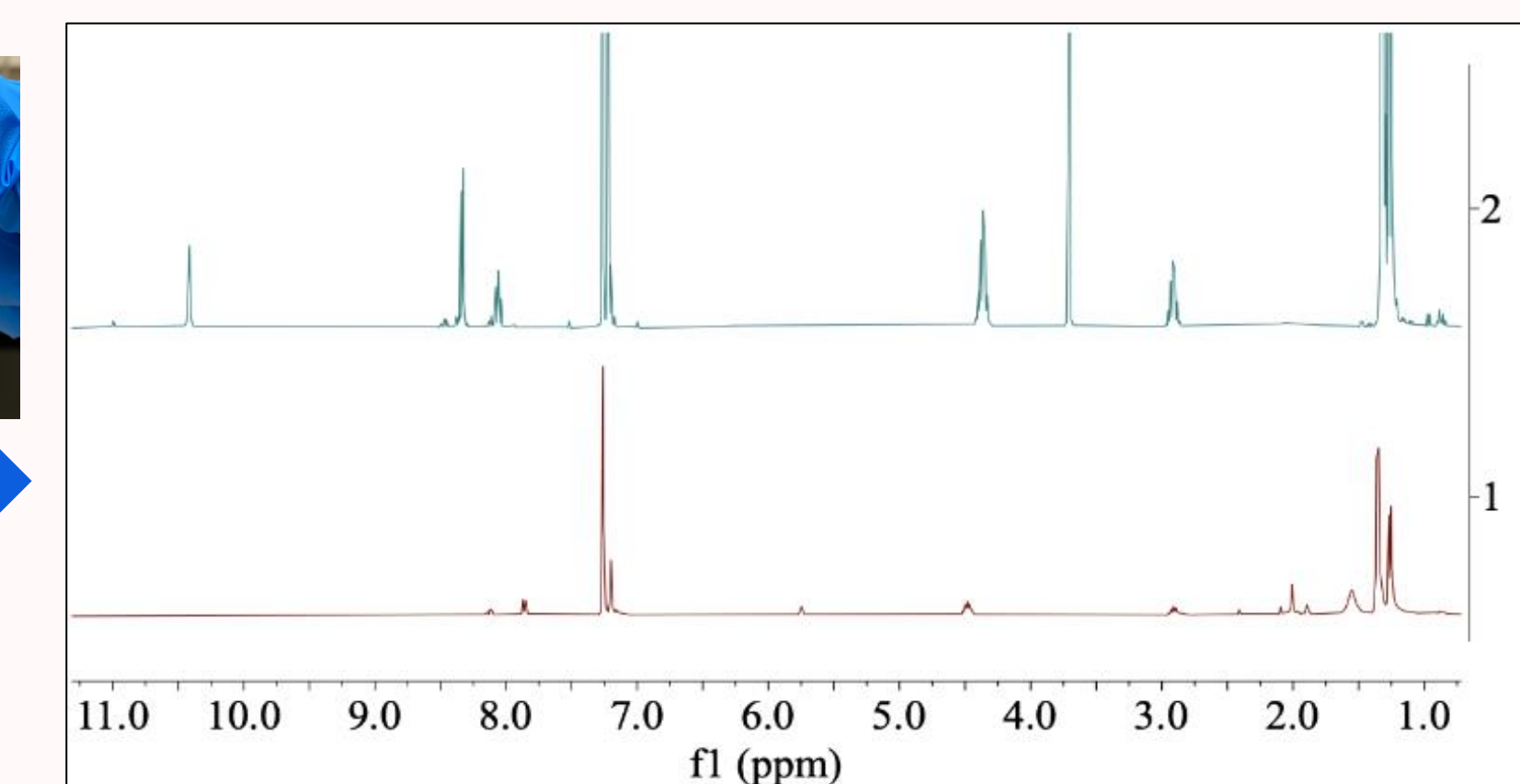
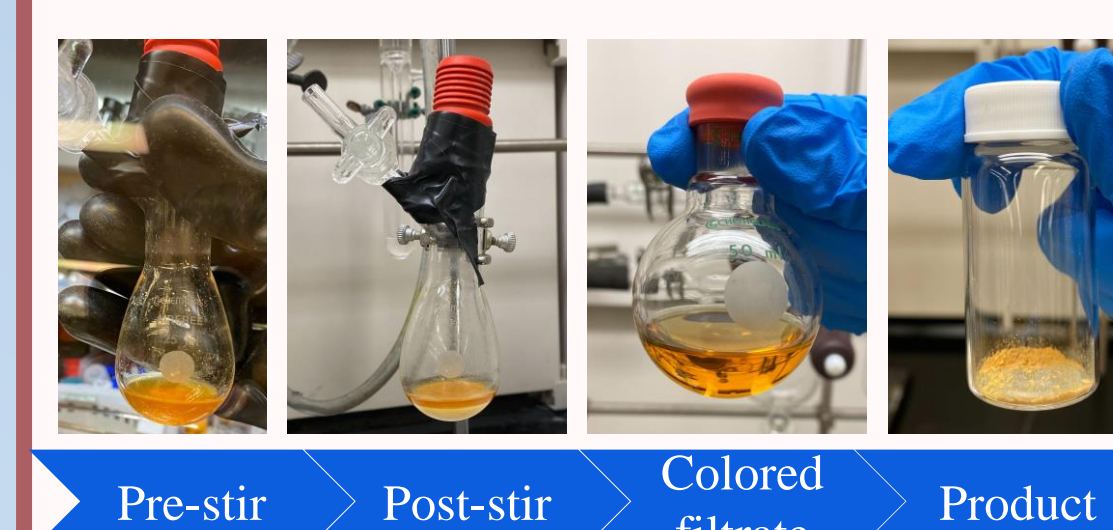


Figure 8. <sup>1</sup>H NMR Spectral Overlay. 1) Compound 2 (top). 2) Complex 5 (bottom).

- Disappearance of the NH peak at 10.7 ppm for compound (2) in the <sup>1</sup>H NMR spectrum (Figure 8) supports that the palladium complex containing the triisopropyl [NNN] (5) ligand formed. The remaining signals shift further confirming formation of the desired product.

## Palladium Metalation to [NNN] Ligand 1

- When the palladium metalation with ligand 1 was conducted at room temperature two unique palladium containing species were obtained as seen in the <sup>1</sup>H spectrum (Figure 5, trace 2). However, when the reaction was heated to 45°C, only one orange complex (3a) was obtained in a yield of 89% (Figure 5, trace 1). This compound lacks an NH group.
- Conducting the reaction at 4°C led to formation of a new complex (3b) that contains an unsymmetrical pyridine backbone and an NH group, assigned to the triplet at 7.5 ppm. The product was assigned through <sup>1</sup>H & <sup>13</sup>C NMR spectral analysis (Figure 5, trace 2).

Scheme 3. Products Obtained when Reaction Conducted Under Different Temperatures.<sup>7</sup>

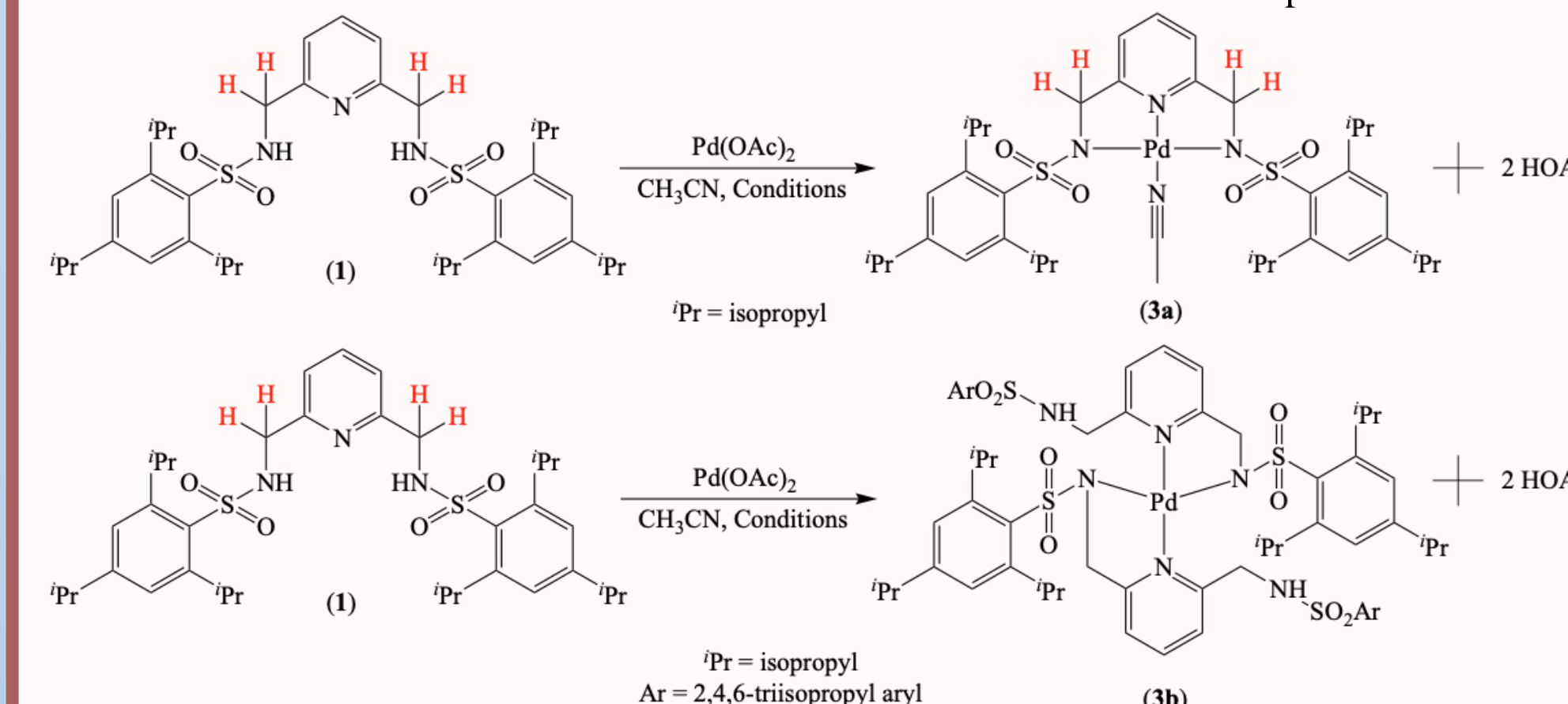


Table 1. Reaction Temperatures, Product Color, and Yield.

Conditions	Product Color	Percent Yield (%)
(mix 3a/3b) 25°C, Overnight	Orange & Yellow	—
(only 3b) 4°C, Overnight	Yellow	35
(only 3a) 45°C, Overnight	Orange	89

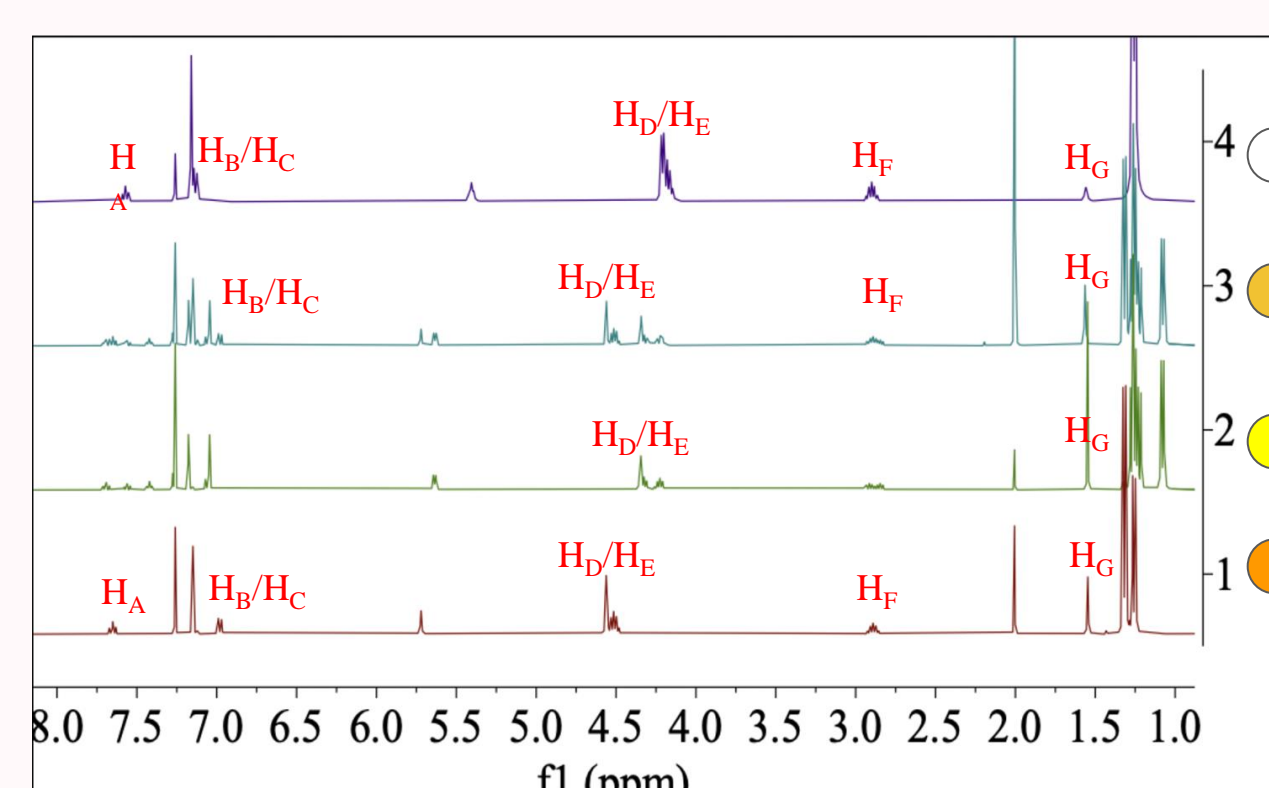


Figure 5. <sup>1</sup>H NMR Spectral Overlay Corresponding with Figure 6. 4) Compound 1, 3) product mixture obtained from 25°C reaction and 45°C, 2) Complex 3b, 1) Complex 3a.

- To further probe the formation of 3a, a palladium starting material with a non-basic anion was used (Scheme 4). The predicted product (4) is symmetric in nature and consistent with the <sup>1</sup>H NMR spectral results shown in Figure 7.
- There is an NH group present assigned as there is a triplet at 6.32 ppm in the <sup>1</sup>H NMR spectrum and the product is symmetric (Figure 7).

Scheme 4. Metalation Using a Different Palladium Starting Material.

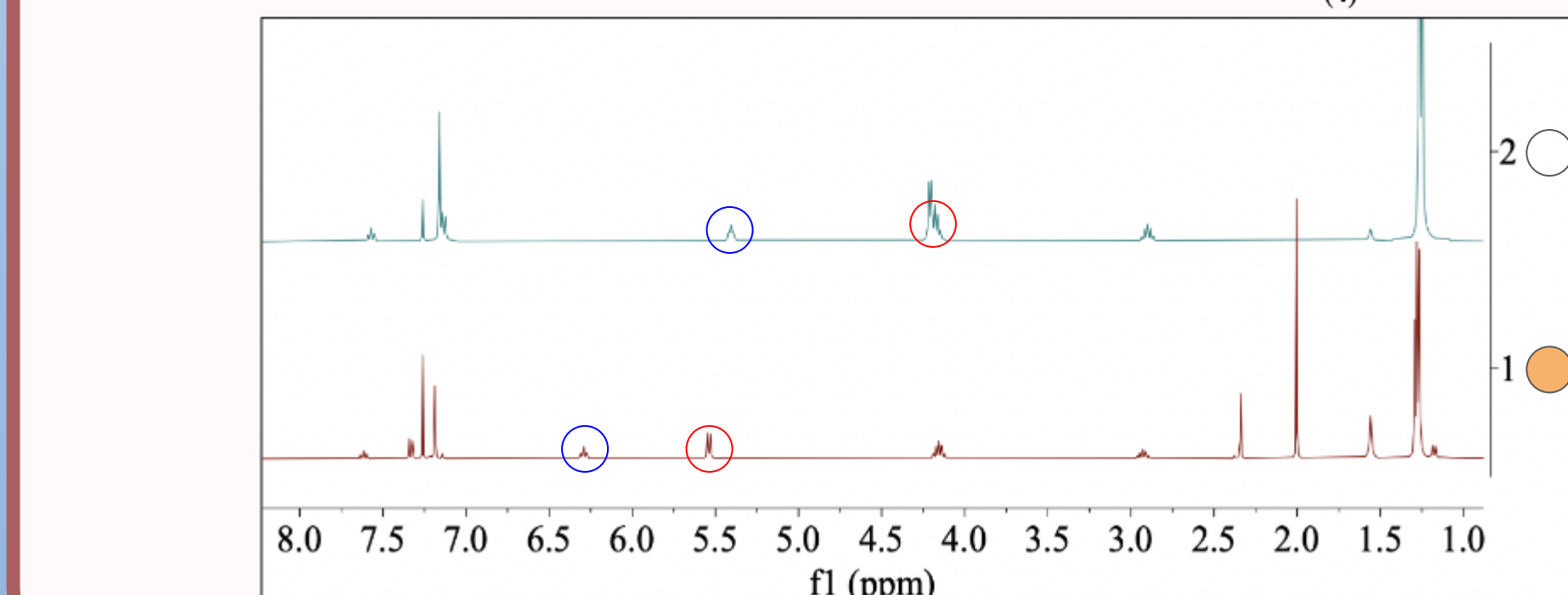
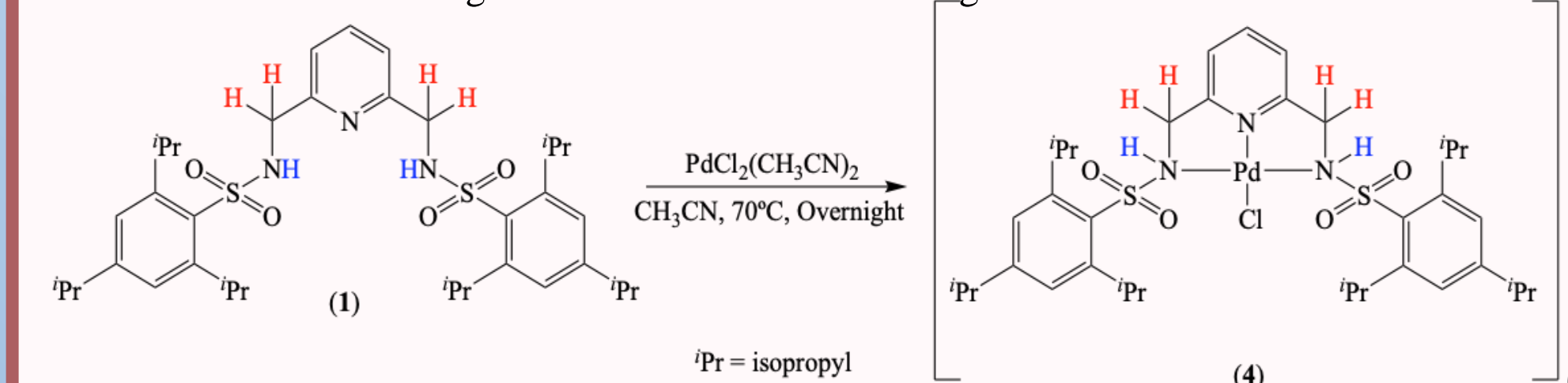


Figure 7. <sup>1</sup>H NMR Spectral Overlay. 2) Compound 1, 1) Complex 4. Circles designate the NH and CH<sub>2</sub> signals.

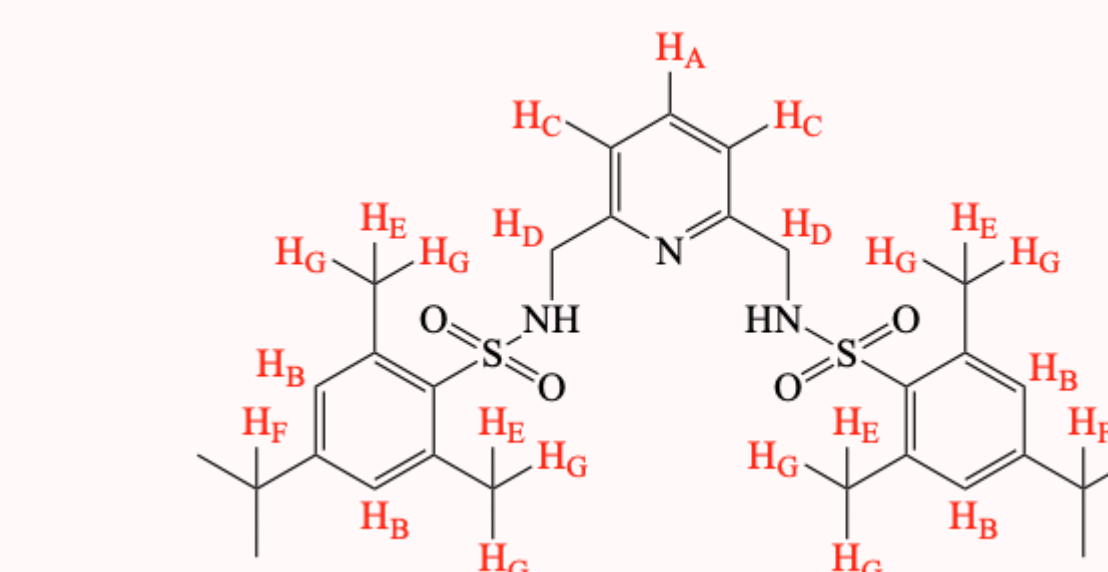
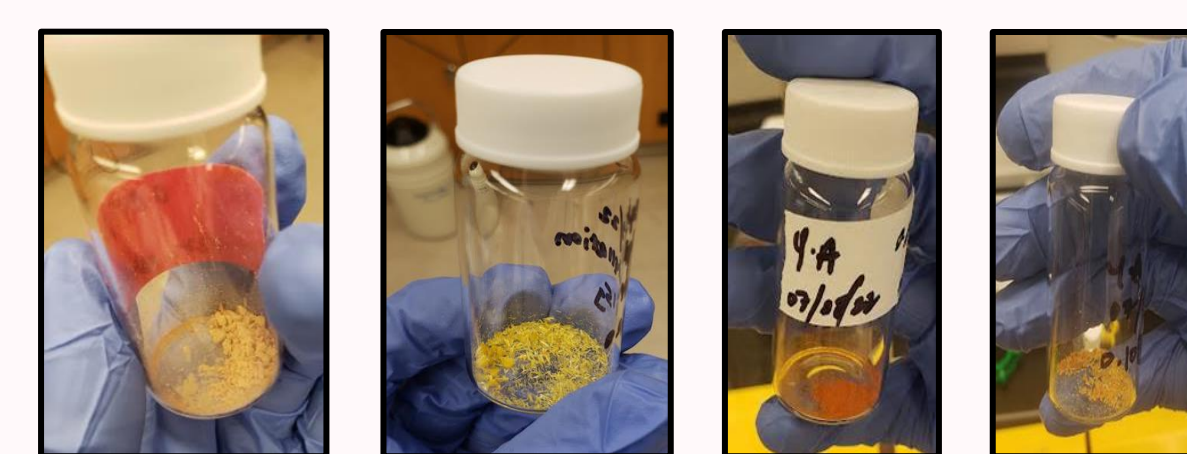


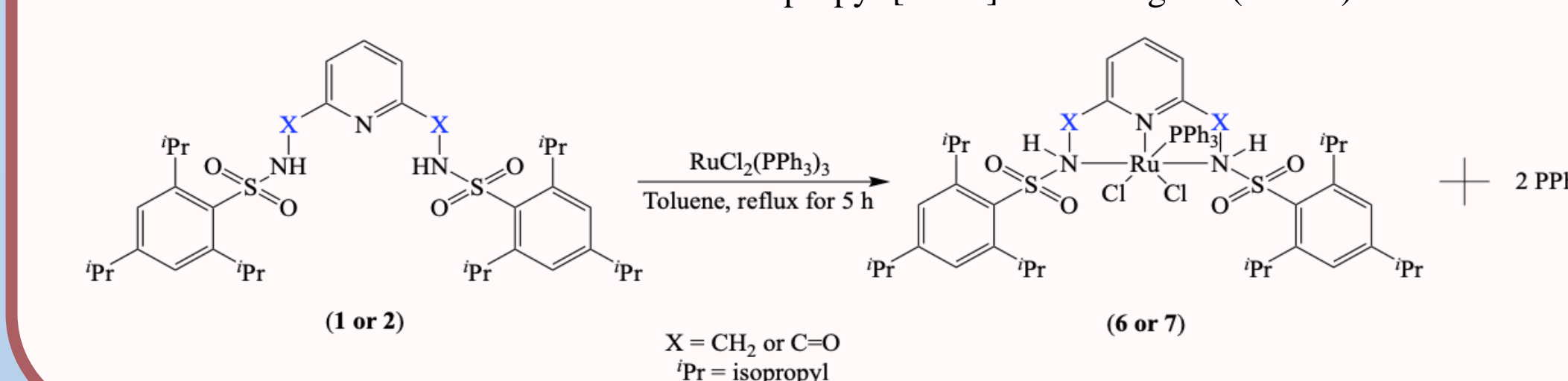
Figure 6. <sup>1</sup>H NMR Predicted Location of Hydrogen Atoms.



## Future Work

- Additional studies need to be complete to determine the ideal conditions necessary to synthesize the coordination complex between triisopropyl [NNN] ligand (1 & 2) and ruthenium.
  - Failed to make the desired ruthenium complex in refluxing toluene (Scheme 6).
    - Loss of NH peak present at ~10.0 ppm.
    - Unreacted ruthenium precursor is also present.
    - Ruthenium complex obtained was not very soluble needed for NMR spectral analysis.
- Crystallize the palladium complexes 3a, 3b, and 5 to confirm structural assignment.
- Once all of the ruthenium and palladium complexes are synthesized, the experiments will shift to incorporating them as catalysts in hydrogenolysis reactions.

Scheme 6. Ruthenium Coordination with Triisopropyl [NNN] Pincer Ligand (1 or 2).<sup>8,9</sup>



## References

- Hou, Q.; Zhen, M.; Qian, H.; Nie, Y.; Bai, X.; Xia, T.; Laiq Ur Rehman, M.; Li, Q.; Ju, M. Upcycling and Catalytic Degradation of Plastic Wastes. *Cell. Rep. Phys. Sci.* **2021**, *2*, 100514.
- Lange, J.-P. Managing Plastic Waste—Sorting, Recycling, Disposal, and Product Redesign. *ACS Sustain. Chem. Eng.* **2021**, *9*, 15722-15738.
- Geyer, R.; Jambeck, J. R.; Law, K. L. Production, Use, and Fate of All Plastics Ever Made. *Sci. Adv.* **2017**, *3*, e1700782.
- Serrano, D. P.; Aguado, J.; Escola, J. M. Developing Advanced Catalysts for the Conversion of Polyolefinic Waste Plastics into Fuels and Chemicals. *ACS Catal.* **2012**, *2*, 1924-1941.
- Ragaert, K.; Delva, L.; Van Geem, K. Mechanical and Chemical Recycling of Solid Plastic Waste. *Waste Manag.* **2017**, *69*, 24-58.
- Rorrer, J. E.; Beckham, G. T.; Román-Leshkov, Y. Conversion of Polyolefin Waste to Liquid Alkanes with Ru-Based Catalysts under Mild Conditions. *JACS Au* **2021**, *1*, 8-12.
- Oloyede, H. O.; Orighomisan Woods, J. A.; Görls, H.; Plass, W.; Esolea, A. O. N-Donor-Stabilized Pd(II) Species Supported by Sulphonamide-Azo Ligands: Ligand Architecture, Solvent Co-Ligands, C-C Coupling. *J. Mol. Struct.* **2020**, *1199*, 127030.
- Gemel, C.; Foltig, K.; Caulton, K. G. New Approach to Ru(II) Pincer Ligand Chemistry. Bis(*tert*-butylaminomethyl)pyridine Coordinated to Ruthenium(II). *Inorg. Chem.* **2000**, *39*, 1593-1597.
- Miecznikowski, J. R.; Caradonna, J. P.; Foley, K. M.; Kwiecien, D. J.; Lisi, G. P.; Martinez, A. An Experiment for Undergraduate Advanced Inorganic Chemistry Students. *J. Chem. Educ.* **2011**, *88*, 657-661.

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