

# Synthesis of Salicylaldimine-type Ligands for Use in Ni/X Bimetallic Complexes for Ethylene Polymerization

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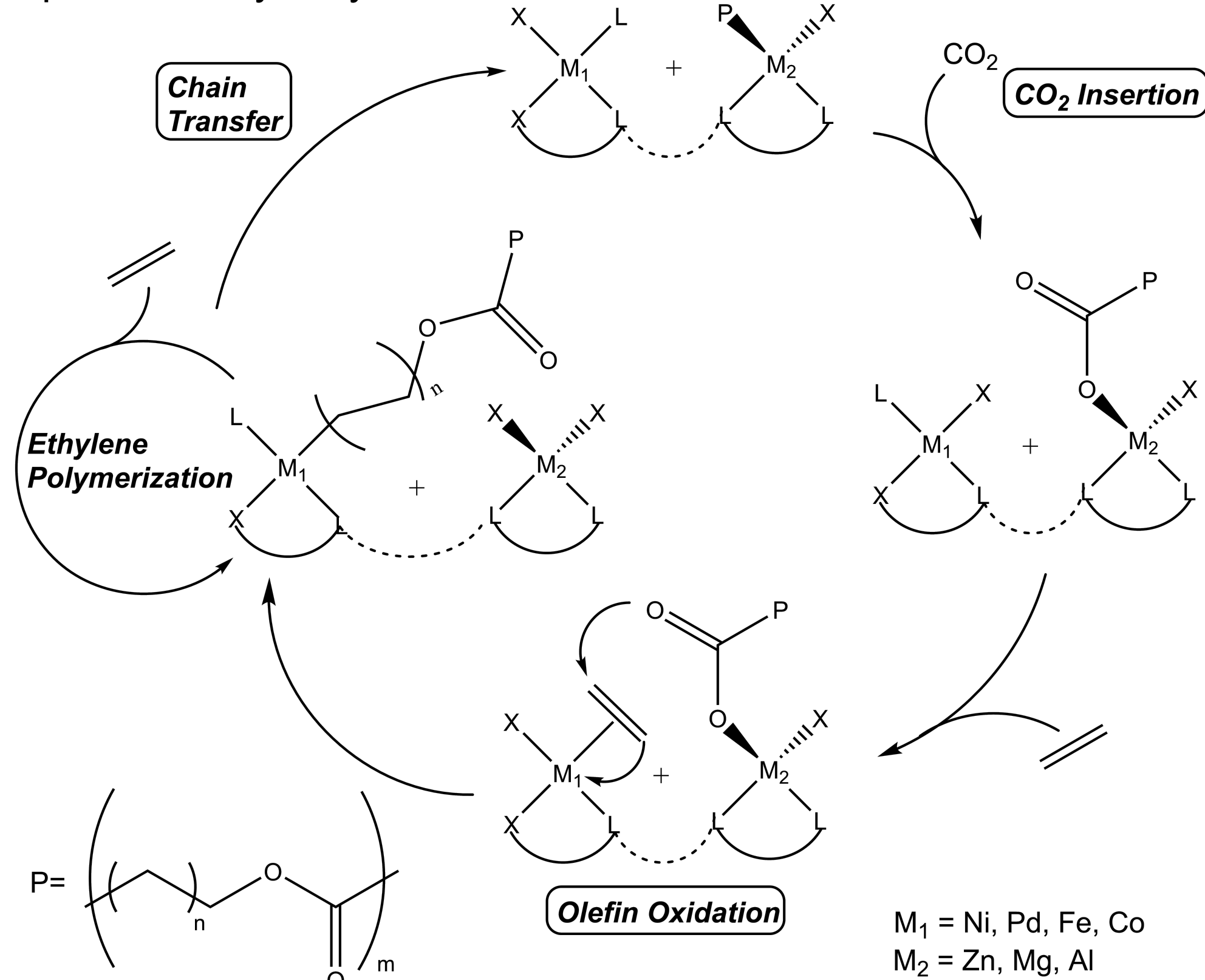
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**Summary:** A sterically-hindered ligand framework for use in bimetallic complexes for homogenous catalytic copolymerization of ethylene and CO<sub>2</sub> was successfully synthesized. Steric bulk is necessary to discourage *bis*-ligation during catalyst synthesis as well as  $\beta$ -hydride elimination during polymerization in order to produce high molecular weight polymers.

## Introduction

Aliphatic polyesters are a biodegradable and potentially sustainable alternative to the petroleum-based polymers, including polyethylene and polypropylene, that currently dominate the market. One approach to their synthesis is the catalytic copolymerization of CO<sub>2</sub> and ethylene through the use of salicylaldimine-type Ni/X bimetallic complexes.

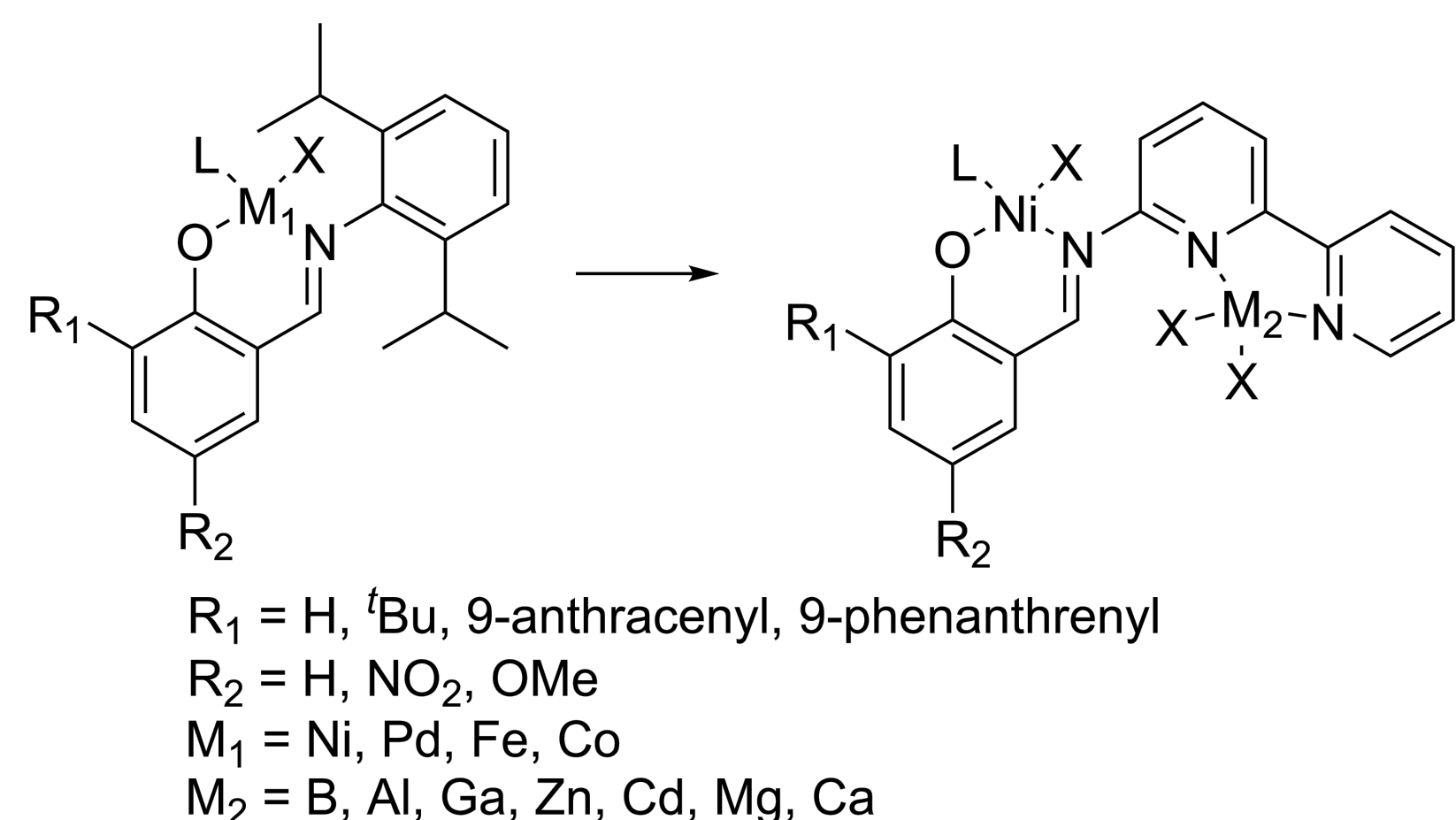
Proposed catalytic cycle:



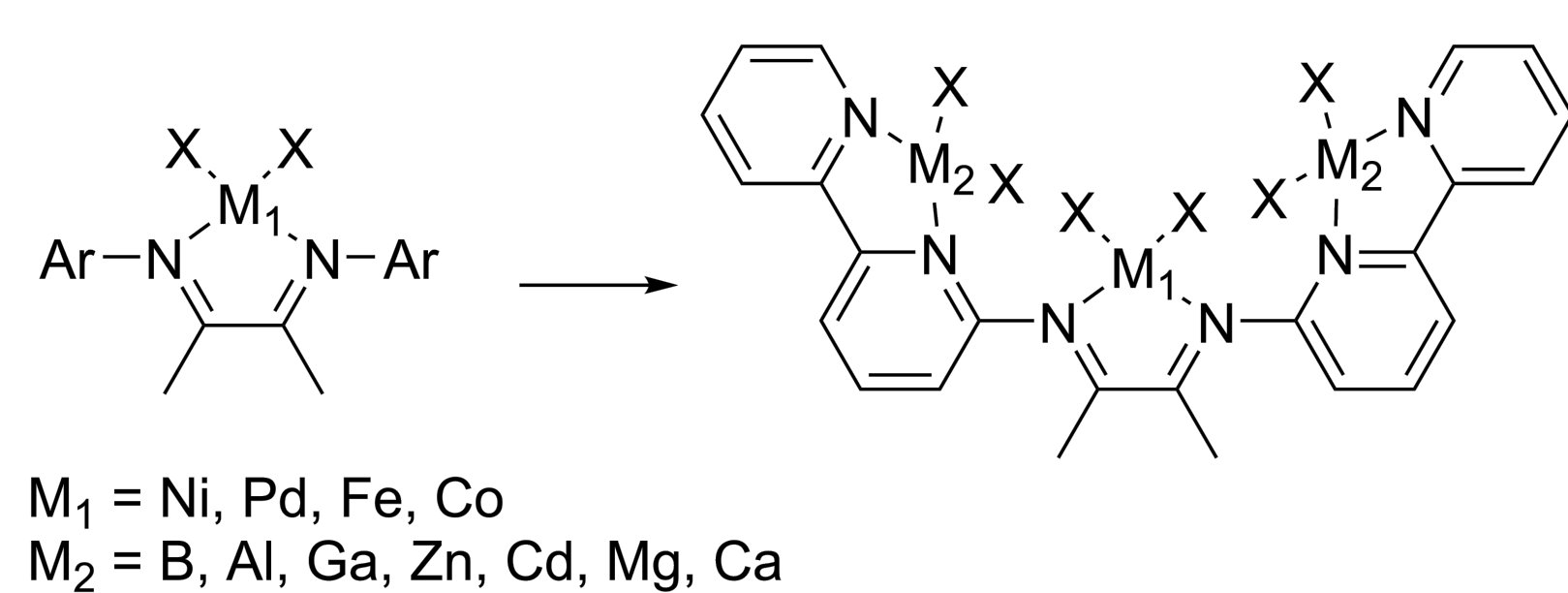
## Proposed Catalyst Systems

Adapt existing ethylene polymerization catalysts for bimetallic catalysis with 2,2'-bipyridine.

**Grubbs's salicylaldimine catalyst<sup>1</sup>:**



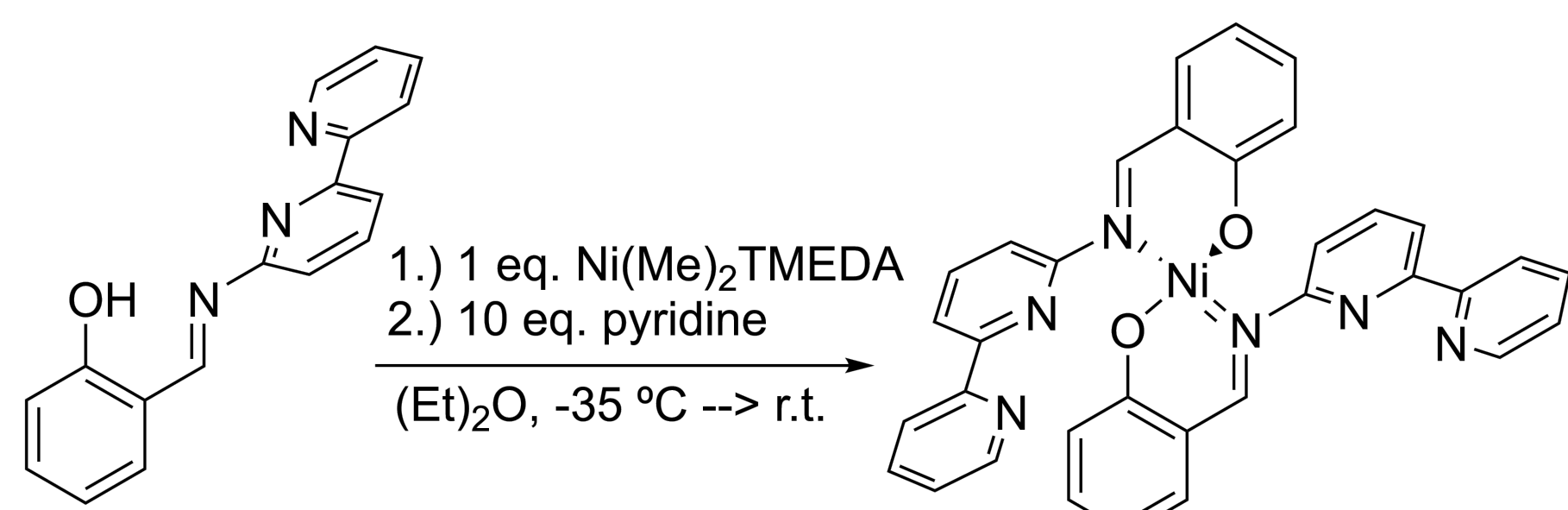
**Brookhart's  $\alpha$ -diimine catalyst<sup>2</sup>:**



So far, only the salicylaldimine-type ligand with  $R_1 = R_2 = \text{H}$  (SAIBPy) has been successfully synthesized.

## Salicylaldimine Challenges

During synthesis of the catalyst, the system undergoes *bis*-ligation, rendering the complex useless:

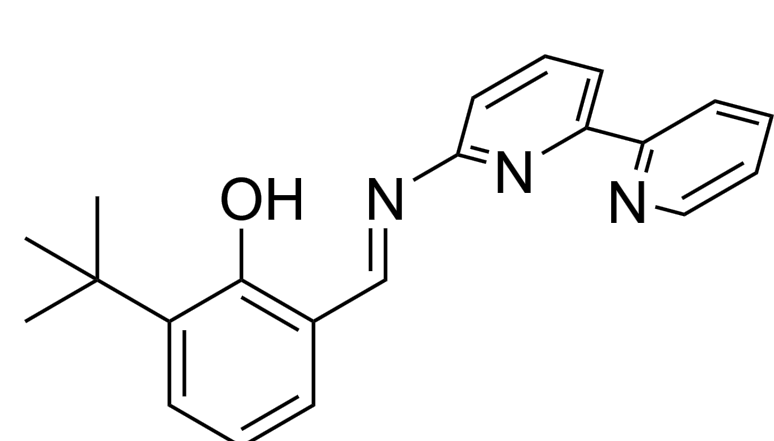


It is thought that this is due to relatively weak Ni-Me bonds, which can be easily displaced by SAIBPy. However, such bonds are desirable for initiating polymerization, so replacing the methyl groups with more strongly coordinating ligands is not ideal.

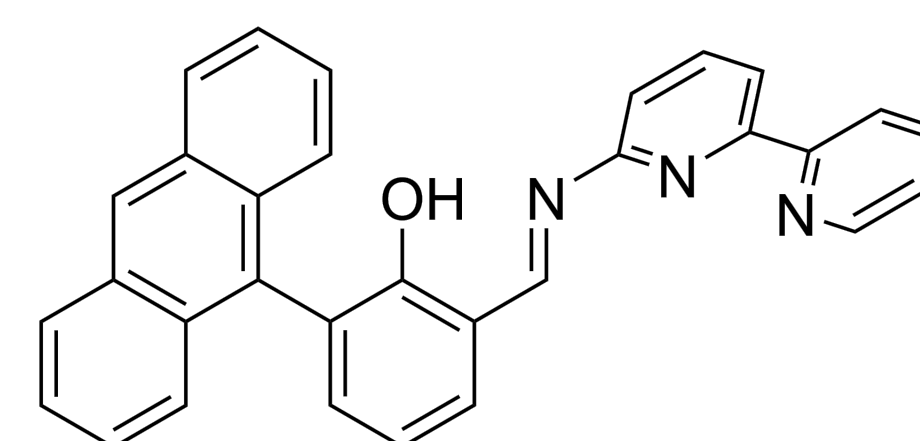
## Introduction of Steric Bulk

To combat the pitfalls of the SAIBPy ligand, it was decided to develop new ligands with large functional groups, such as *tert*-butyl (<sup>t</sup>Bu) and 9-anthracenyl (Anth), near the N,O site:

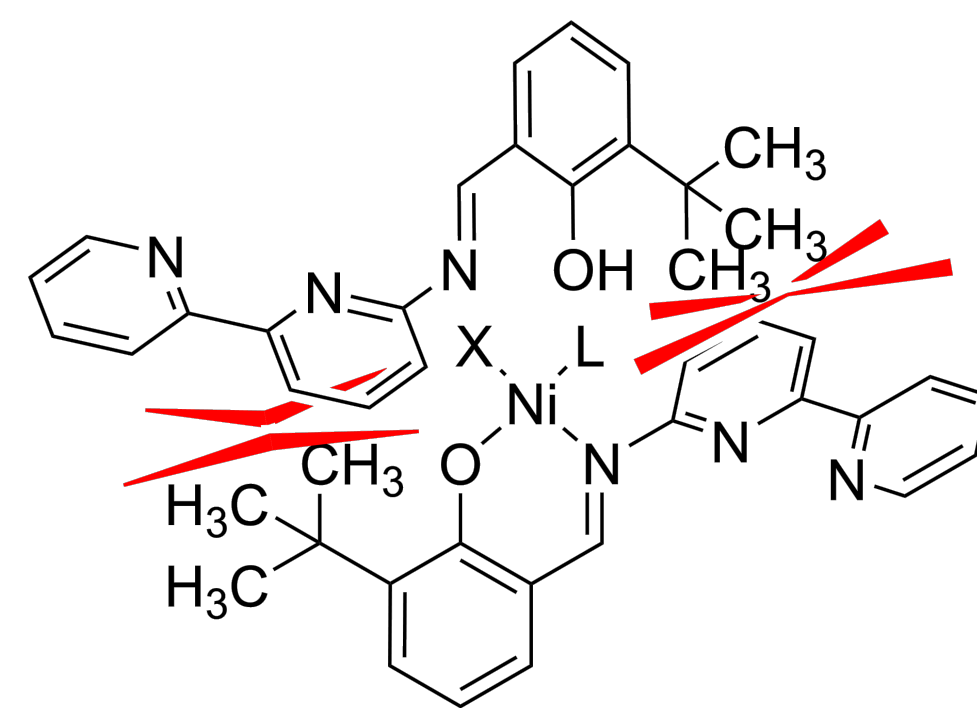
<sup>t</sup>BuSAIBPy:



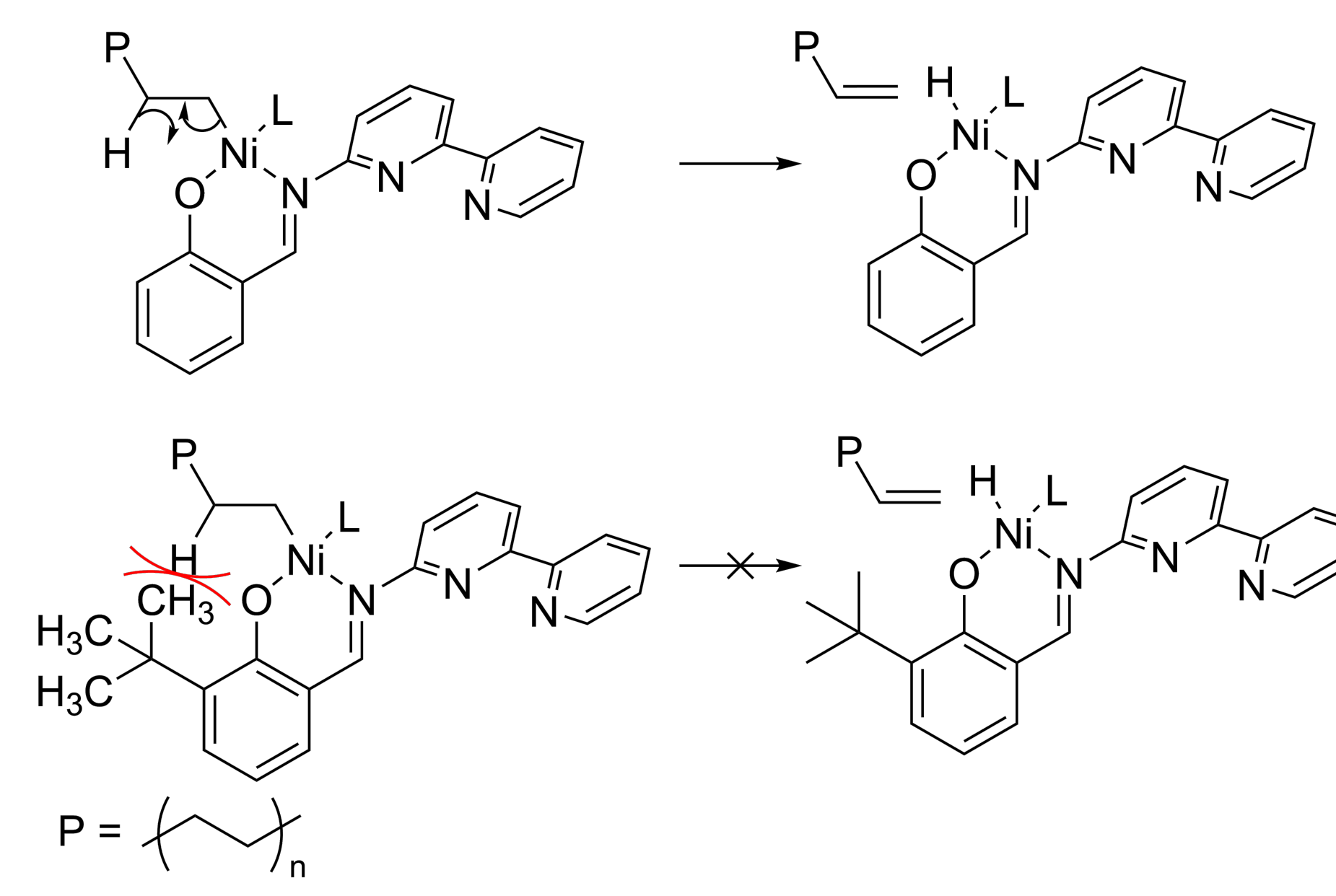
AnthSAIBPy:



These large functional groups will hopefully be sufficiently bulky to discourage the orientation required for *bis*-ligation.

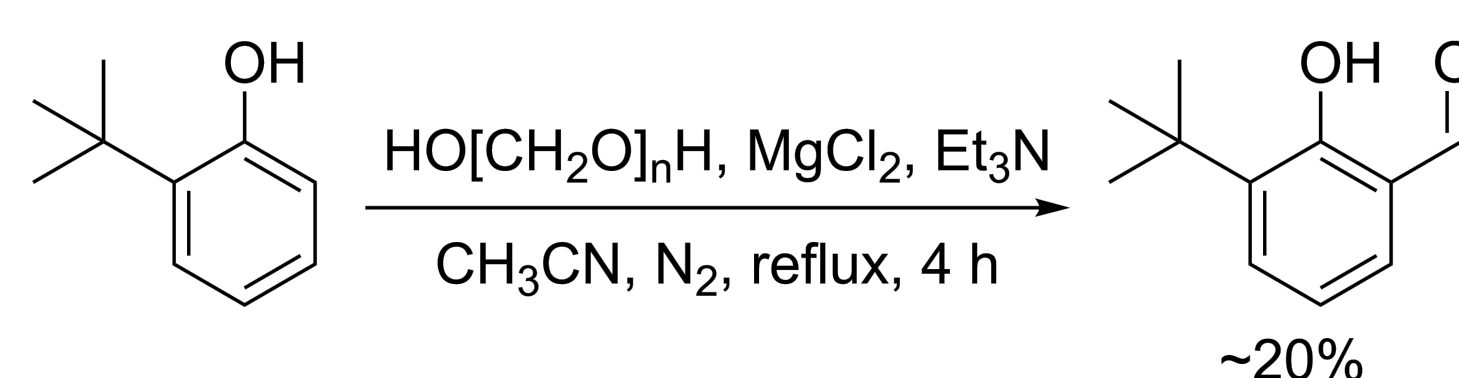


In addition, extra steric bulk has been shown to increase polymer length and decrease branching by discouraging  $\beta$ -hydride elimination<sup>1,2</sup>:

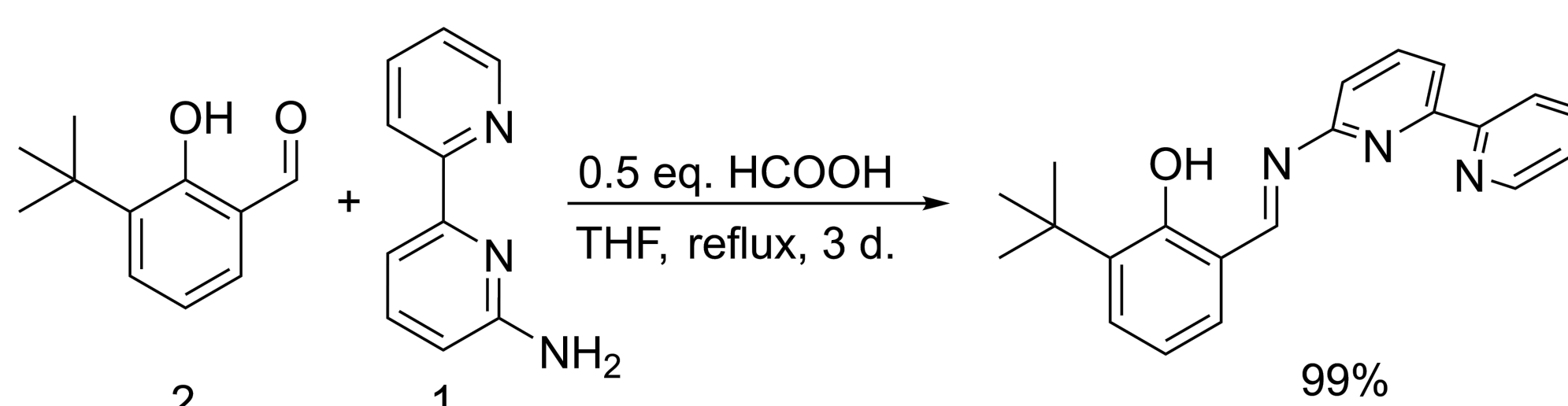


## Progress toward Synthesis

<sup>t</sup>BuSAIBPy has been successfully synthesized in a two-step process:



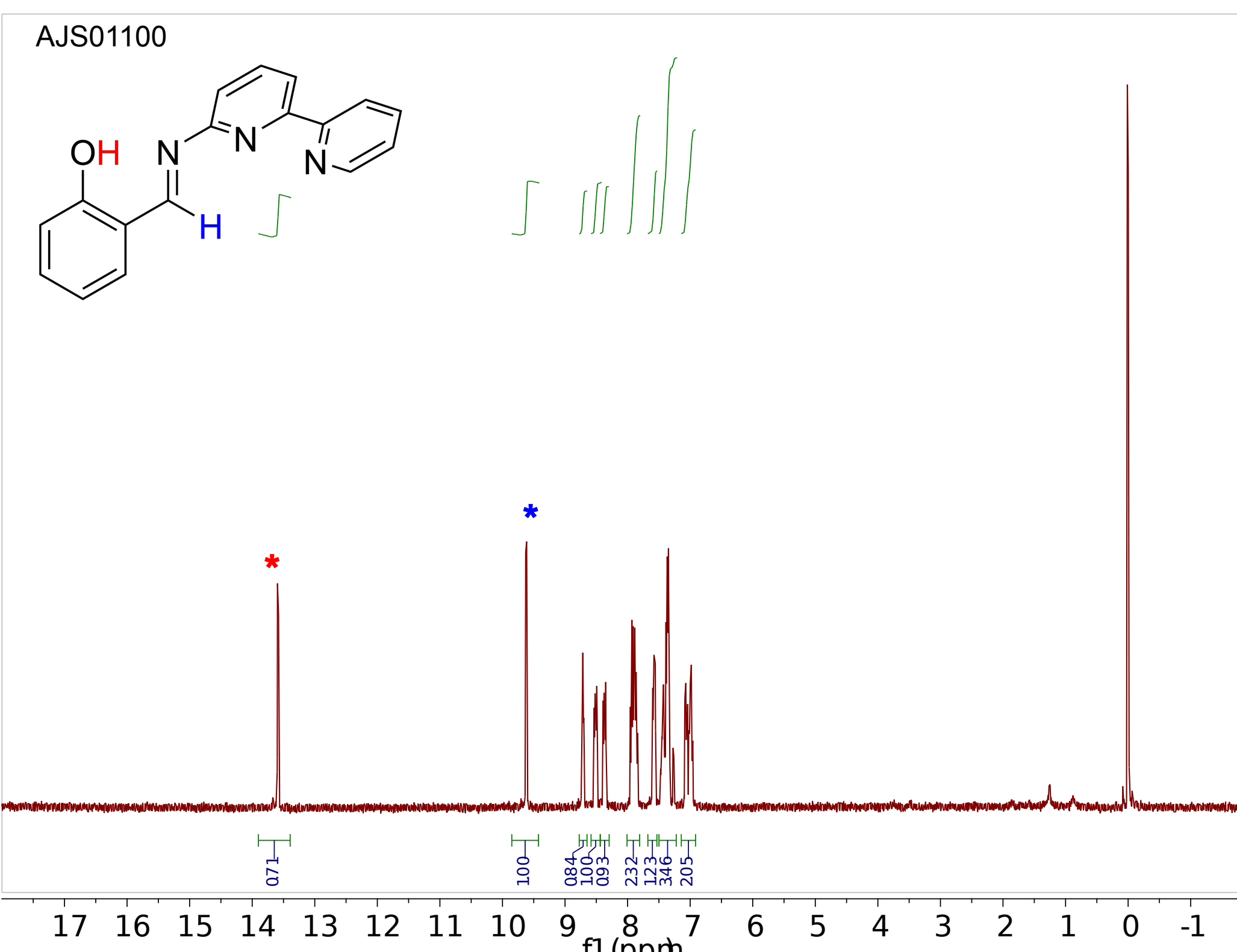
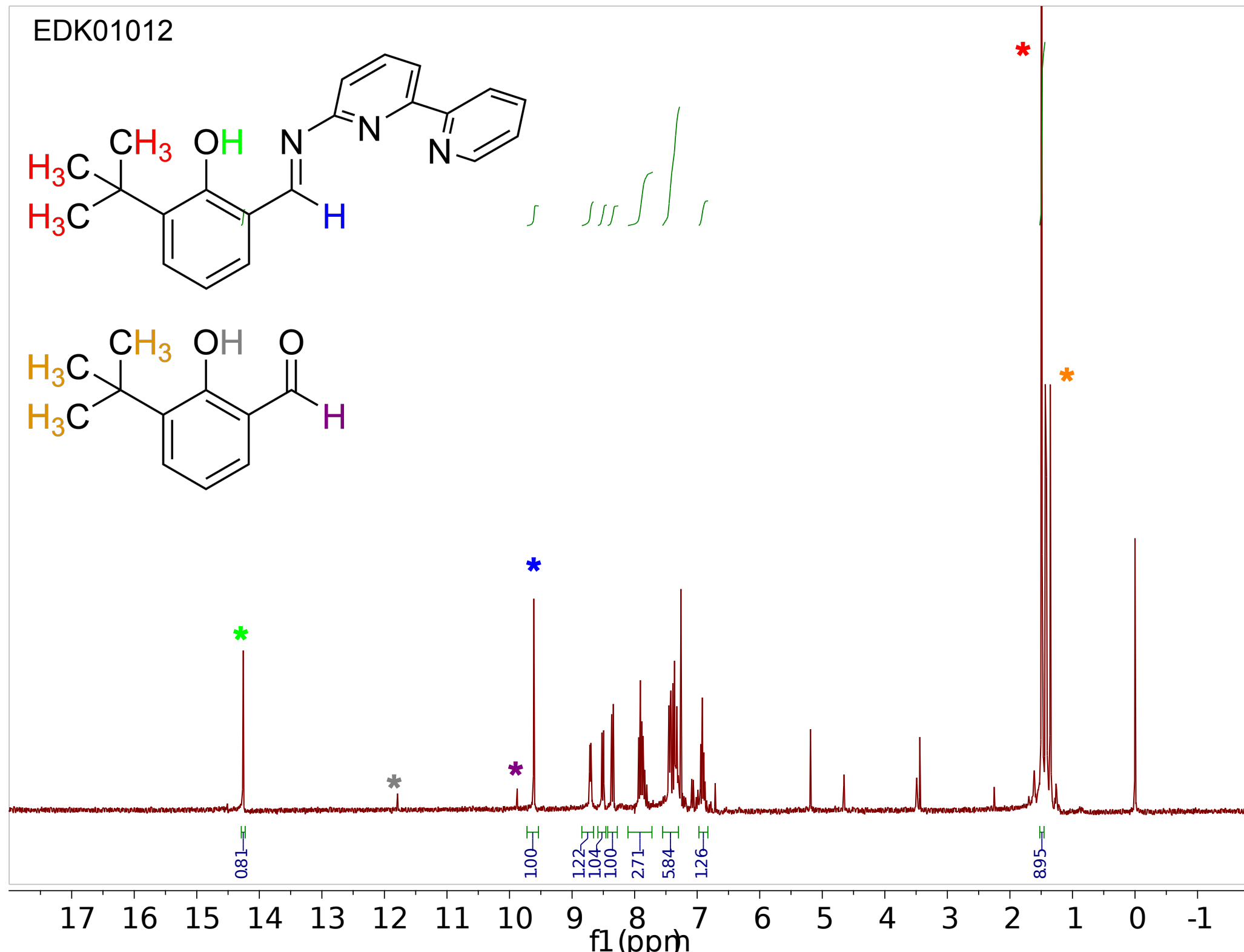
It is hypothesized that low yields in this step can be attributed to hydrated MgCl<sub>2</sub>.



Excess <sup>t</sup>BuSA was necessary for complete conversion of BPy-NH<sub>2</sub>. Synthesis of AnthSAIBPy is still in progress.

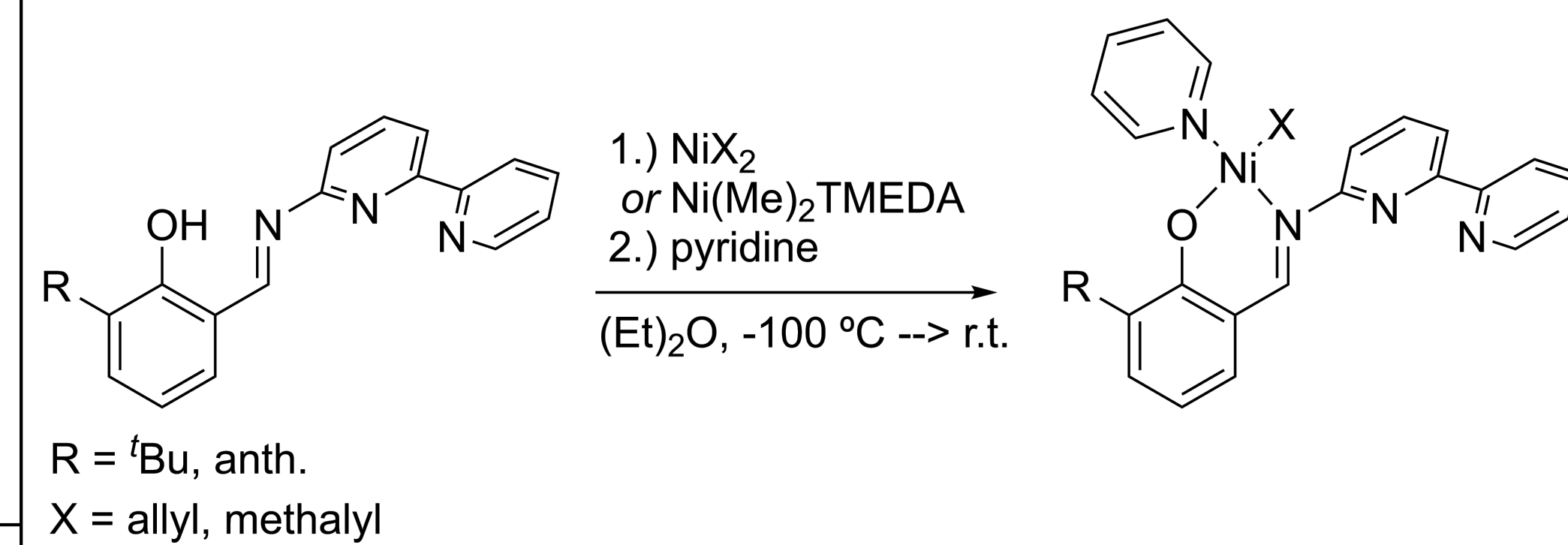
## Characterization

Separation of <sup>t</sup>BuSAIBPy from the remaining <sup>t</sup>BuSA was very difficult, as <sup>t</sup>BuSAIBPy decomposed on silica and alumina and was difficult to crystallize. Partial separation was eventually achieved by allowing the excess <sup>t</sup>BuSA to evaporate off.

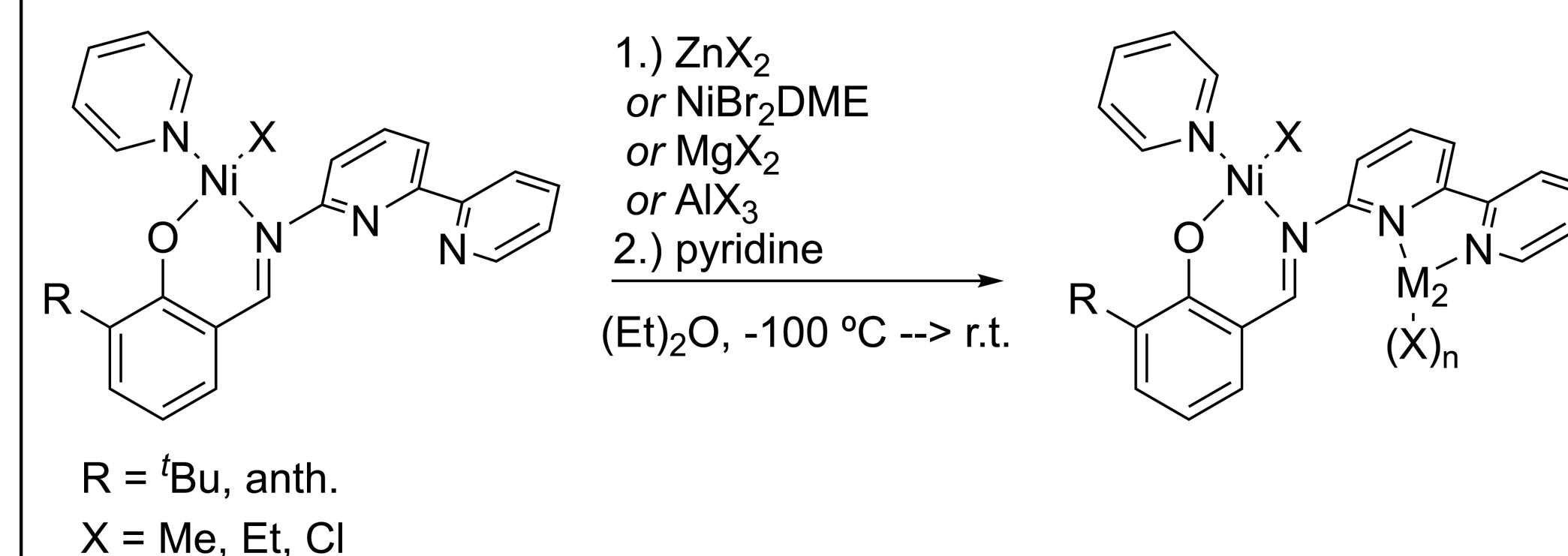


## Future Work

Synthesis of AnthSAIBPy will be completed, and attempts will be made to metallate the O,N pocket of the ligands:



The catalysts will then be tested for their ability to polymerize ethylene. Additionally, the BPy pocket may also be metallated and tested for ethylene polymerization and polymerization with CO<sub>2</sub>:



## References:

- 1.) Wang, C.; Friedrich, S.; Younkin, T.; Li, R.; Grubbs, R.; Bansleben, D.; Day, M. *Organometallics* **1998**, *17*, 3149-3151.
- 2.) Ittel, S.; Johnson, L.; Brookhart, M. *Chem. Rev.* **2000**, *100*, 1169-1204.

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