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N-heterocyclic Carbenes in Catalysts for Ring Opening Polymerizations

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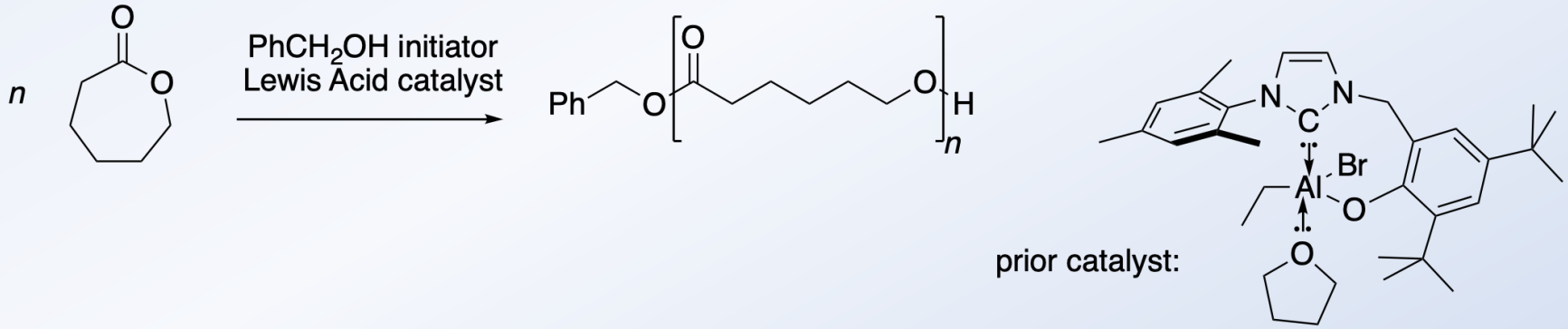
Introduction:

Ring-opening polymerizations, especially those of esters, have been used to make materials with many important uses. These polymerizations begin with a cyclic ester and through the reaction, the ring opens and makes the polymer. One of the useful and sustainable esters is lactide, which is made from corn. Lactide can be used in ring-opening trans-esterification polymerization (ROTEP) to make materials from films for packaging[1] to tissue engineering scaffolds[4]. Since these ROTEPs have so many important applications, there is interest in developing new materials from other plant sources. One of the possible esters is cellulose because it makes up a greater fraction of plant matter. Even though this is a possibility, lactide is currently the most promising plant-based polymer source and is typically used for these reactions.



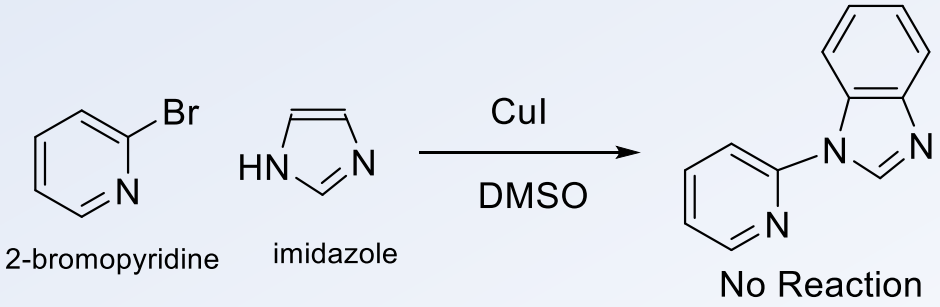
Scheme 1: Ring-opening polymerization of an ester and a catalyst previously developed in the lab.

To polymerize a cyclic ester, this lab has developed an aluminum catalyst. This catalyst works faster than either the tin octoate catalyst or triethylaluminium. It contains a carbene unit, which has been found to promote many useful reactions. Carbene units can be coordinated to transition metals, used as organocatalysts, and coordinated to p-block elements. Attached to a transition metal and used as a catalyst, these carbene units can be used for medicinal and material applications[2]. However, this aluminum catalyst is not effective with lactide which is the most commonly used monomer in ROTEP.

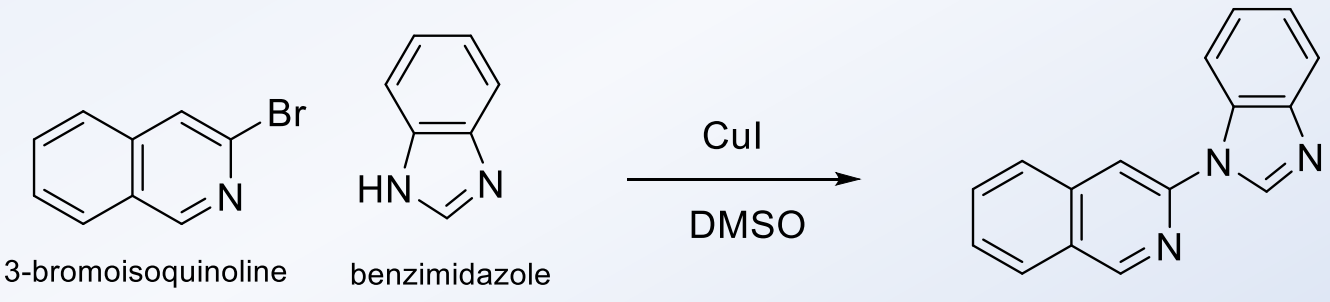
The future goal is to develop an alternative catalyst that also contains a carbene, but with a different side chain. Based on the successful development of nickel complexes containing N-heterocyclic carbene units[3] and the control they provide in the reduction of CO_2 to CO, these units could be used in catalysts to provide control other reactions. Therefore, the catalysts developed in this lab containing a carbene unit will hopefully provide more control in the polymerizations. The catalyst this lab previously developed contained a carbene unit and provided fair control of the polymerization of caprolactone, but an alternative catalyst could potentially work with other monomers. This catalyst would be used to compare with the one previously developed. It could then be used to promote ROTEP reactions with multiple monomers.

Results and Discussions:

There were many attempts at successfully developing a carbene-containing ligand. The attempt in Scheme 2 charged 2-bromopyridine and imidazole in a pressure flask. Based on NMR spectroscopy, there was no reaction, so it was not further developed.



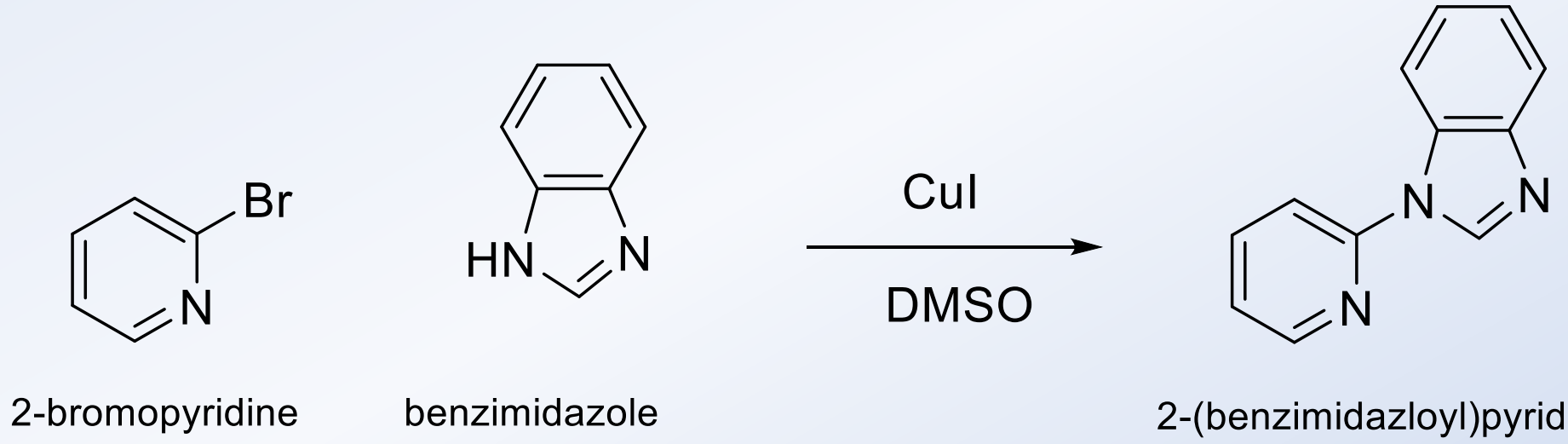
Scheme 2. Attempted synthesis of a ligand from 2-bromopyridine and imidazole.



Scheme 3. Ligand synthesized from 3-bromoisoquinoline and benzimidazole.

Another attempt charged 3-bromoisoquinoline and benzimidazole in an effort to develop the ligand shown in Scheme 3. This had very little yield, so it was also discontinued.

The attempt with the most success was the development of 2-benzimidazloyl pyridine. This attempt charged benzimidazole and 2-bromopyridine to develop the carbene ligand in Scheme 4. Through NMR spectroscopy (Figure 4), it appears that the ligand developed is 2-benzimidazloyl pyridine. The lack of a peak at 12.5 shows that the hydrogen off the nitrogen in benzimidazole is now gone. This corresponds to the final product of 2-benzimidazloyl pyridine.



Scheme 4. Synthesis of 2-(benzimidazloyl)pyridine from 2-bromopyridine and benzimidazole.

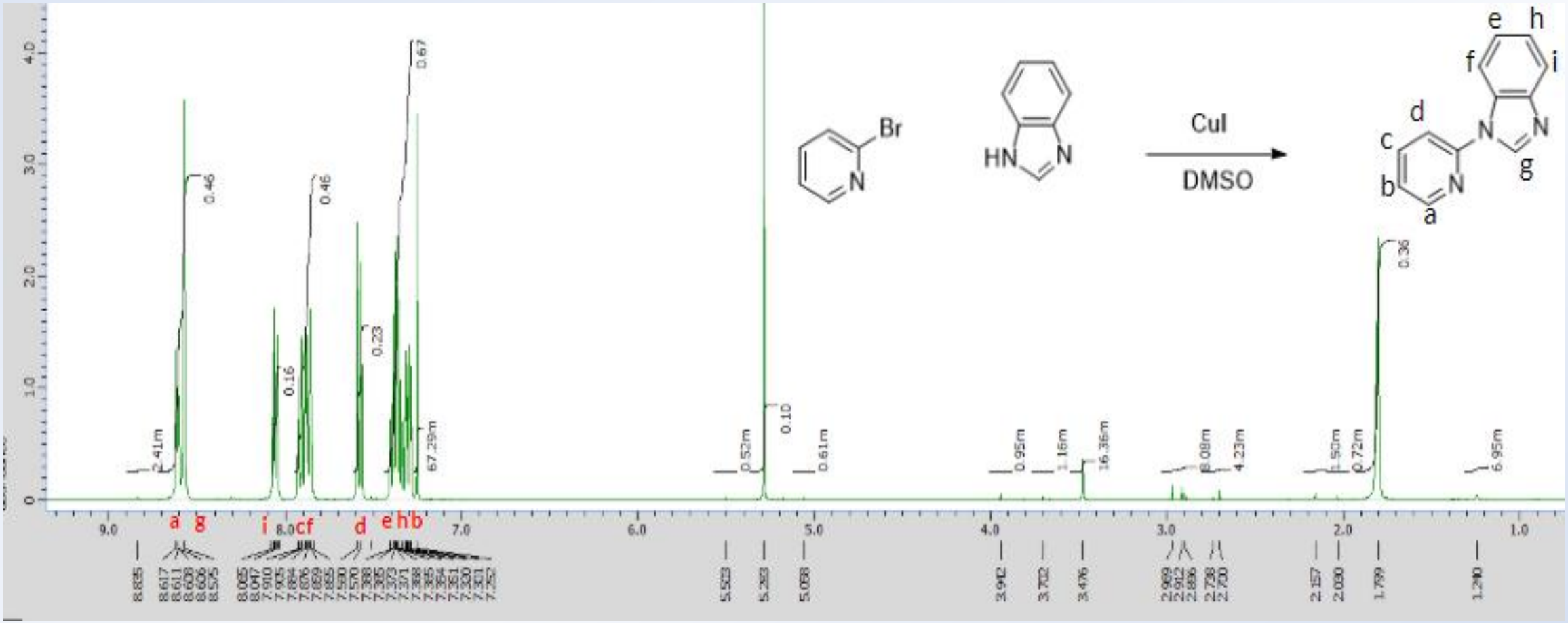
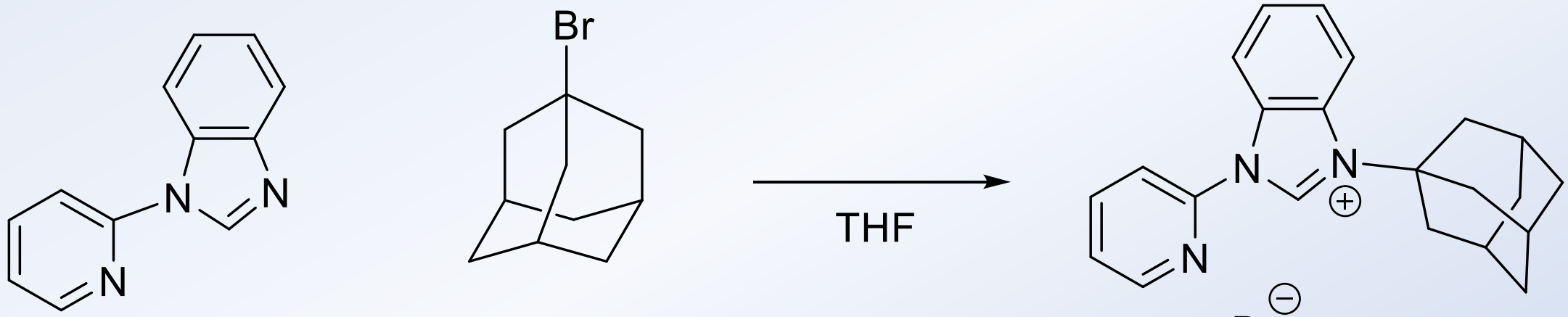


Figure 1. The ^{1}H-NMR spectra of development of 2-benzimidazloyl pyridine from benzimidazole and 2-bromopyridine

Next, the 2-benzimidazloyl pyridine was stirred with 1-bromoadamantane to further develop the ligand into the one that is shown in Scheme 5. This attempt also appears to be successful as the new peaks in the NMR (Figure 2) at 2.3 and 1.7 correspond to those of the adamantyl.



2-(benzimidazloyl)pyridine 1-bromoadamantane

Scheme 5. Synthesis of the ligand that will be coordinated to the metal from 2-(benzimidazloyl)pyridine and 1-bromoadamantane.

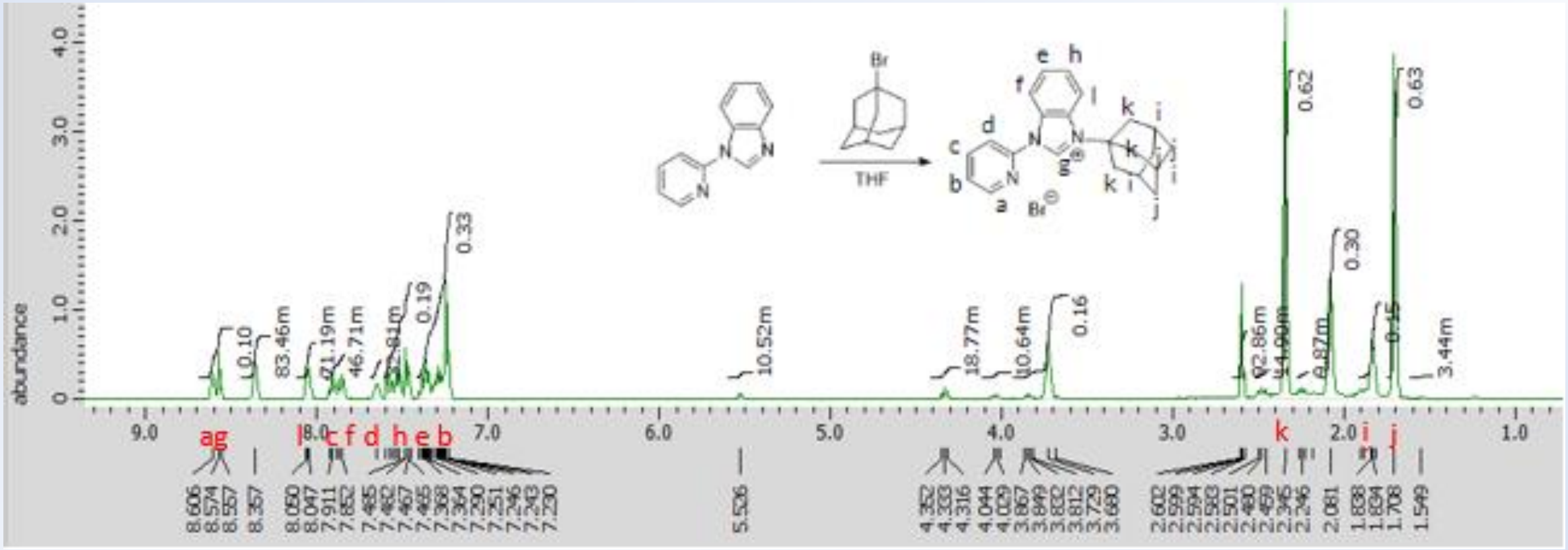


Figure 2. A ^{1}H-NMR spectra of development of the ligand from 2-benzimidazloyl pyridine and 1-bromoadamantane.

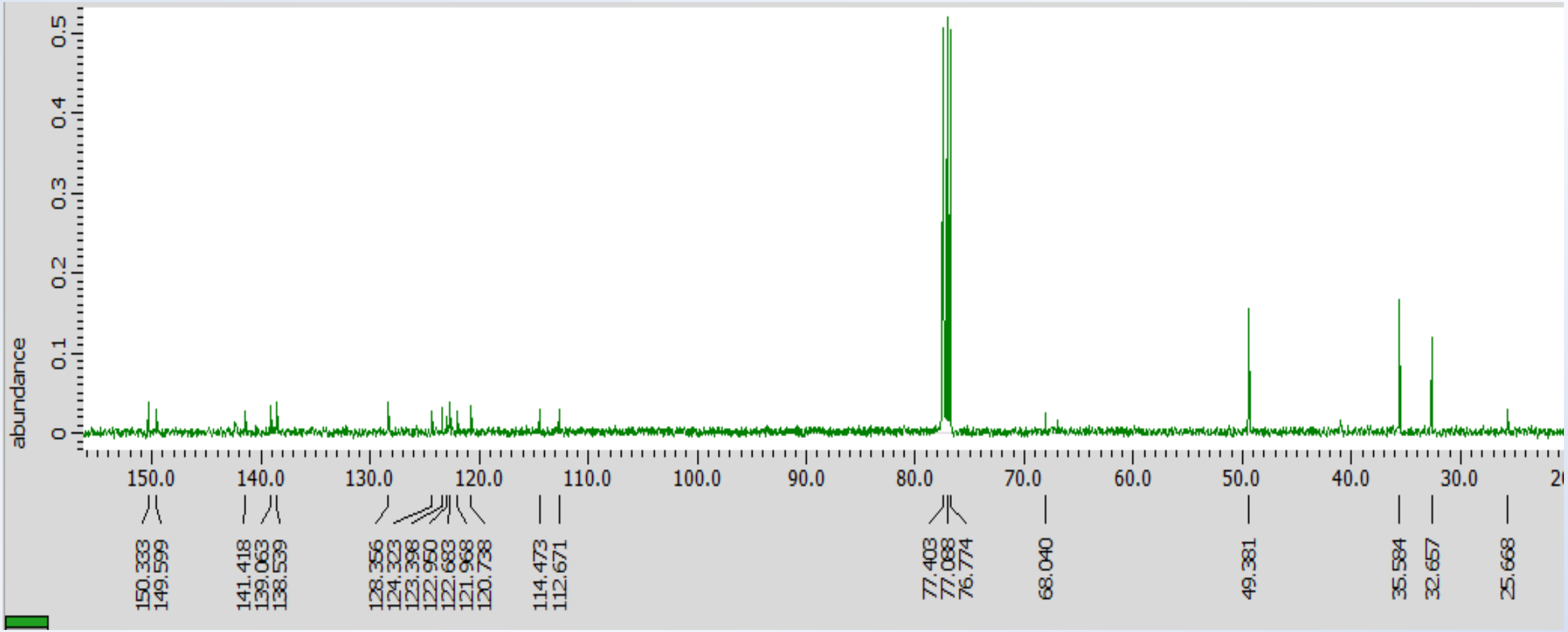


Figure 3. The ^{13}C-NMR spectra of development of the ligand from 2-benzimidazloyl pyridine 1-bromoadamantane.

Experimental

2-Benzimidazloyl pyridine:[3] CuI (0.16g, .86 mmols) was added to a 250 mL round bottom pressure flask in the drybox. The flask was taken out of the box and charged with DMSO (17.5 mL), N-hydroxysuccinimide (0.24g, 2.1 mmols), and NaOMe (1.10g, 20 mmols). It was stirred for 15 minutes. benzimidazole (1.62g, 14 mmols) and 2-bromopyridine (1.4mL, 0.80 mmols) were added to flask. The flask was placed in an oil bath (110 ^{o}C) for 18 hours and then cooled to room temperature. Water (12.5 mL) was added and the mixture was filtered twice to remove solid. The solution was extracted with ethyl acetate (3 x 25 mL). The combined organic layers were washed with water, dried with Na_2SO_4, evaporated *in vacuo* and the resulting yellow oil was purified on a silica gel column. Yield: 0.30g (2.0 mmol, 36%). ^{1}HNMR (400MHz, $CDCl_3$) 8.61 (1H, d), 8.58 (1H, s), 8.05 (1H, d), 7.90 (1H, t), 7.88 (1H, d), 7.57 (1H, d), 7.38 (1H, t), 7.36 (1H, t), 7.30 (1H, t) ppm.

***N*-adamantyl,*N'*-pyridylimidazole**: A 48 mL pressure flask was charged with 2-(benzimidazloyl)pyridine (0.31g, 1.1 mmol), THF (8 mL), and bromoadamantane (.24g, 1.1 mmol). It was stirred in an oil bath (110 ^{o}C) for 24 hours. The mixture was removed from the oil bath and cooled to room temperature. The solvent was evaporated to yield a light brown oil. The substance was then purified through recrystallization from ethanol. Yield: 0.37g (.75 mmol, 68 %). ^{1}HNMR (400MHz, $CDCl_3$) 8.61 (1H, d), 8.56 (1H, s), 8.05 (1H, d), 7.91 (1H, t), 7.89 (1H, d), 7.49 (1H, d), 7.48 (1H, t), 7.36 (1H, t), 7.24 (1H, t), 2.34 (4H, s), 1.83 (2H, d), 1.71 (4H, s) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$) 150, 149, 141, 139, 138, 128,124, 123, 122, 122, 121, 120, 114, 112, 68.0, 49.4, 36.6, 32.7, 25.7 ppm.

Conclusions & Future Work

The development of the ligand from 2-benzimidazloyl pyridine and 1-Bromoadamantane appeared to be successful. Based on the NMRs, the adamantyl appeared to have successfully bonded with the 2-benzimidazloyl pyridine to form the final carbene unit. The next steps are to coordinate this to a transition metal and then run polymerizations.

Acknowledgements:

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