

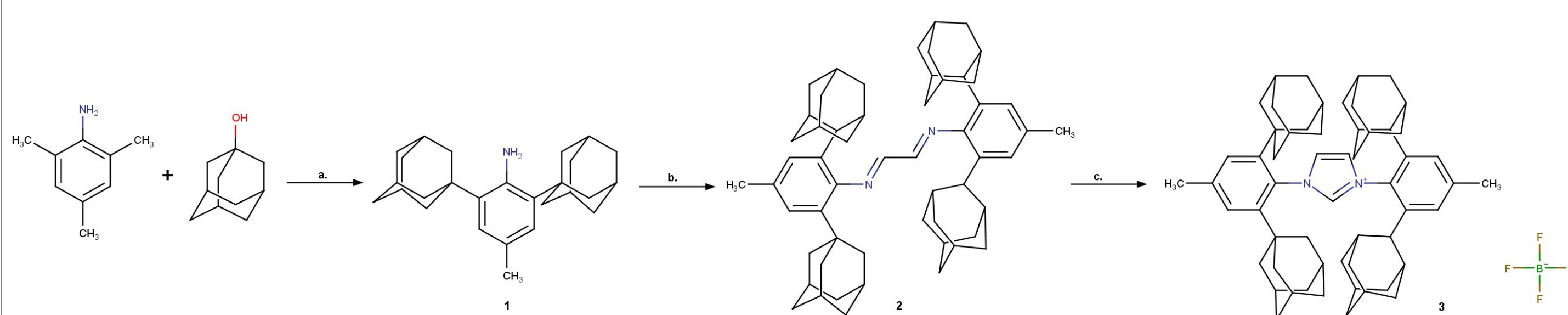
## ABSTRACT

Sterically hindered *N*-heterocyclic carbenes (NHCs) have shown impressive flexibility despite their extreme steric demands. NHCs are strong electron donors, perfect for use in catalysis. So far, research on substituents on carbene ligands has mostly been two-dimensional, flexible structures. This experiment targets the synthesis of an imidazolium salt NHC with three-dimensional substituents. Adamantane was chosen as a bulky, three-dimensional substituent. The imidazolium salt was synthesized in three steps, beginning with *p*-toluidine and 1-adamantanol. The resulting imidazolium salt was coordinated to silver and copper. A novel NHC-ligand possessing large, adamantyl based substituents has been prepared. Herein are reported its synthesis and subsequent attempts to form transition metal coordination complexes.

## METHODOLOGY

- Ligand **3** synthesized in three steps seen below
- Each step was characterized by IR, GC-MS (if possible, and <sup>1</sup>H NMR (if possible)
- Ligand **3** optimized via WebMO for buried volume calculations with SambVca

### Scheme 1. Synthesis of novel adamantyl-substituted NHC (**3**)



Legend: (a) ZnCl<sub>2</sub>, HCl, 200 °C; (b) glyoxal, CHCl<sub>2</sub>; (c) paraformaldehyde, HBF<sub>4</sub>, toluene, 160 °C. (Ad = adamantyl)

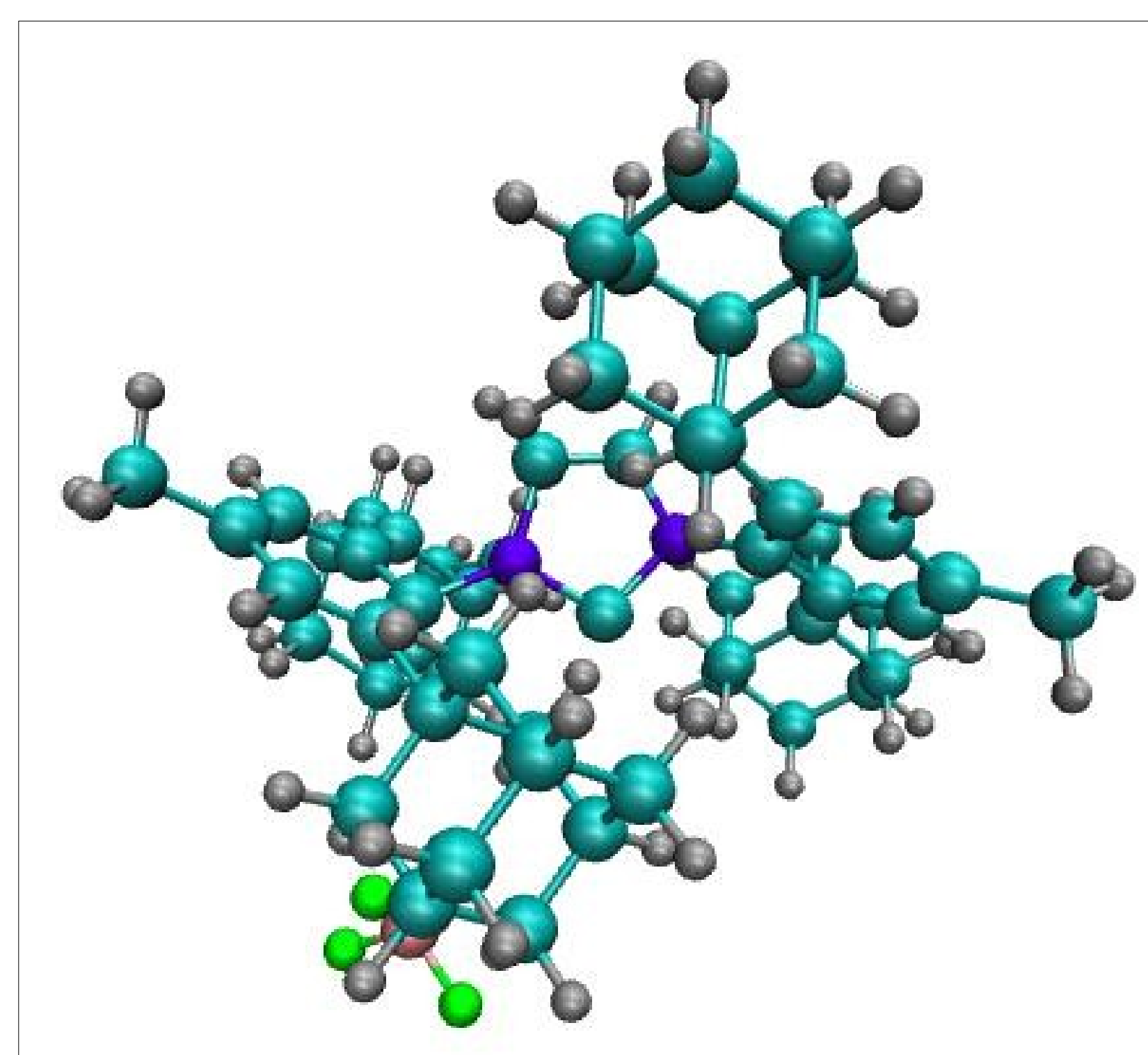


Figure 1. 3-D model of ligand **3**

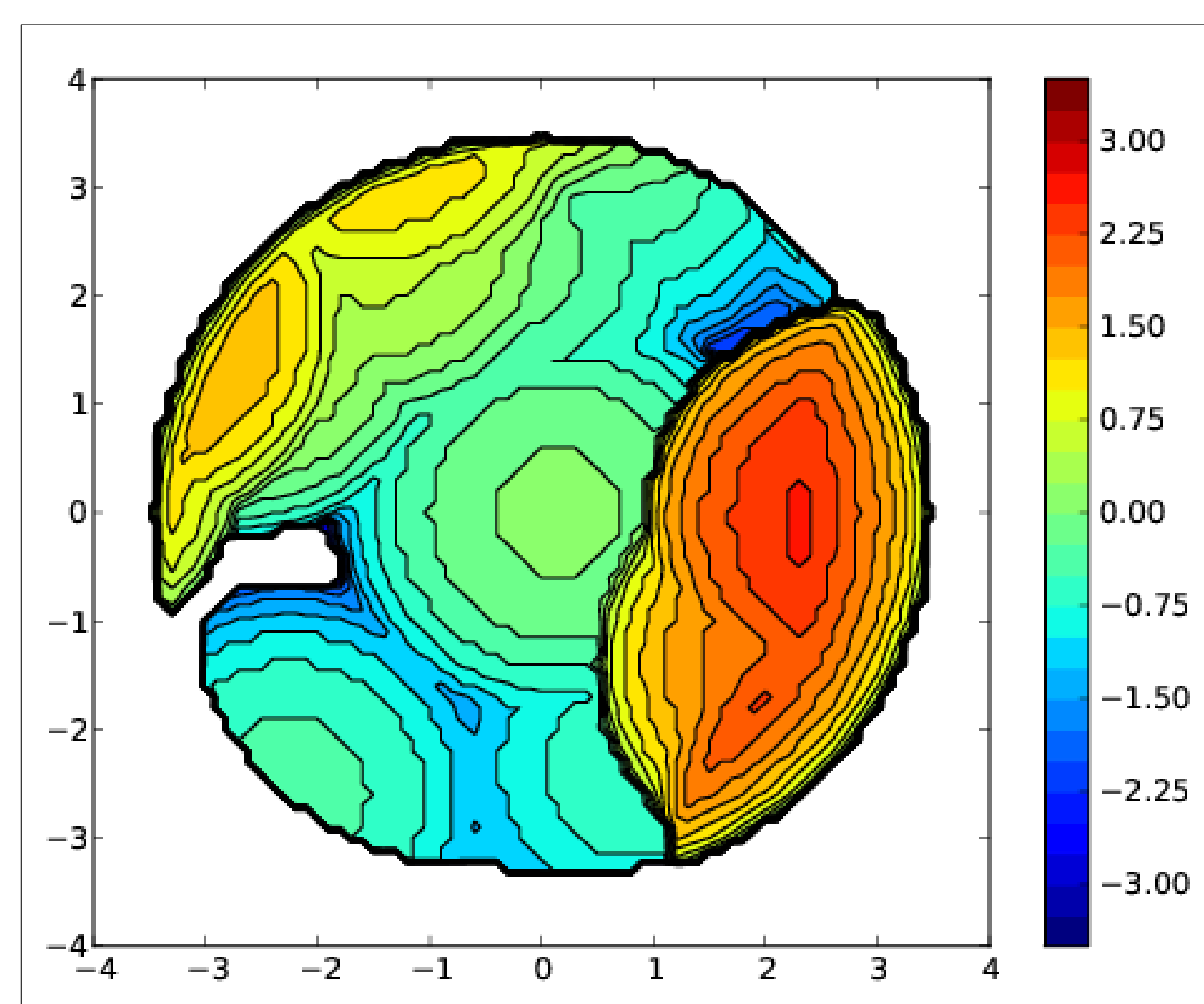


Figure 3. Steric map of the copper complex (Figure 3), demonstrating high steric stress and flexibility

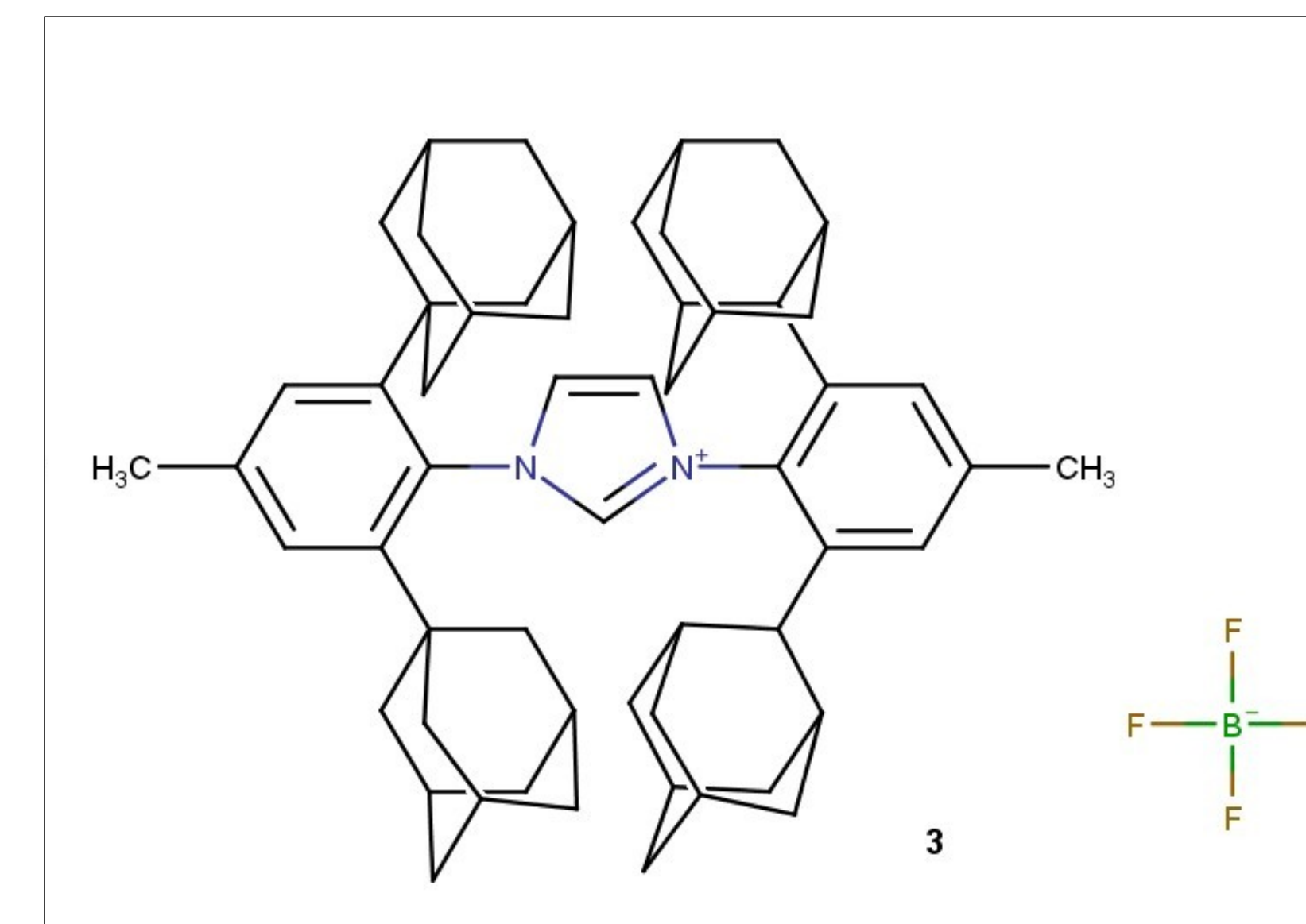


Figure 2. 2-D model of ligand **3**

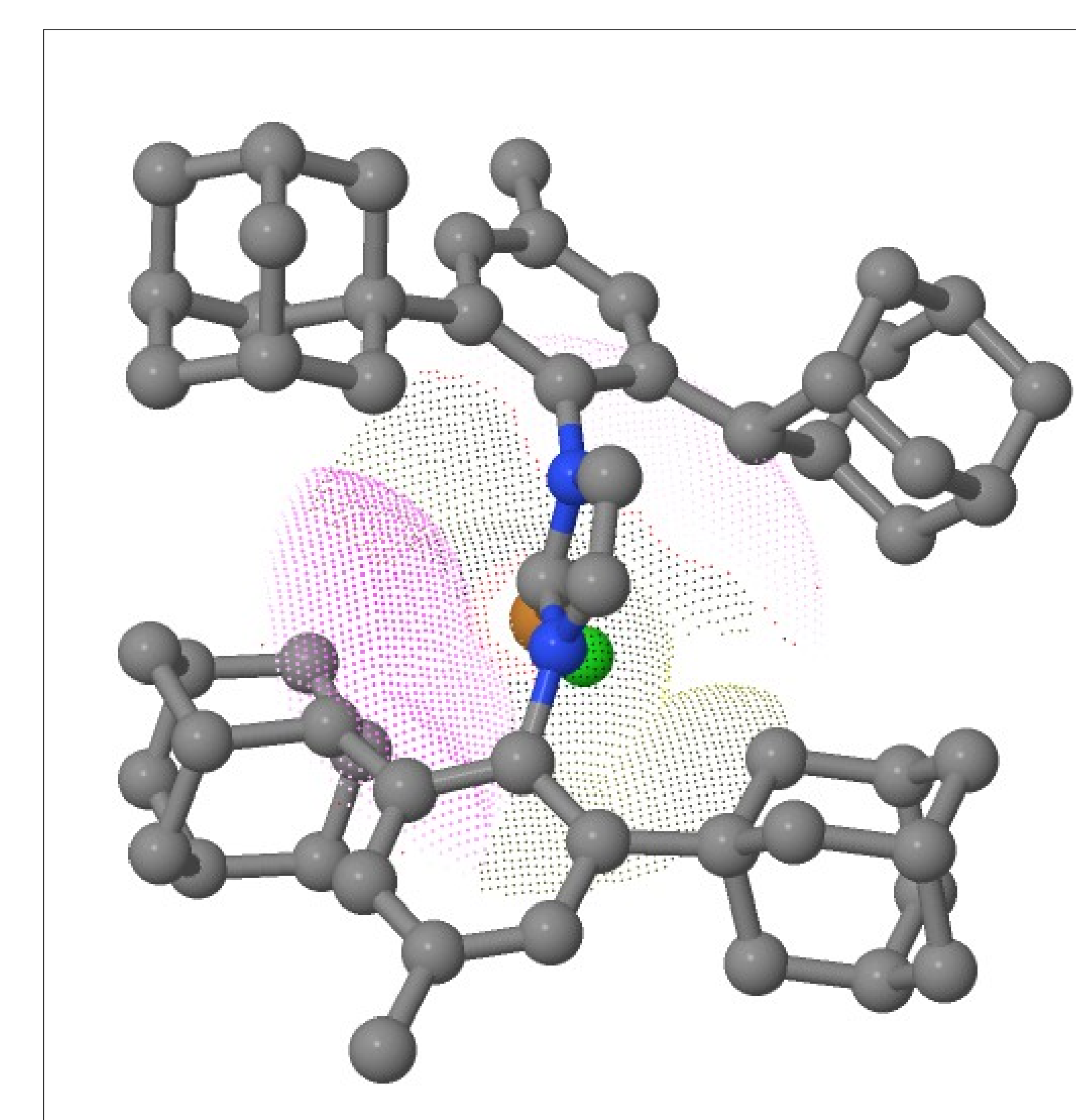


Figure 4. Model of ligand **3** copper complex demonstrating the coordination pocket

## DATA AND RESULTS

423-imidazolium-methanol5 #238 RT: 4.54 AV: 1 NL: 8.68E2  
T + c Full ms [50.00-800.00]

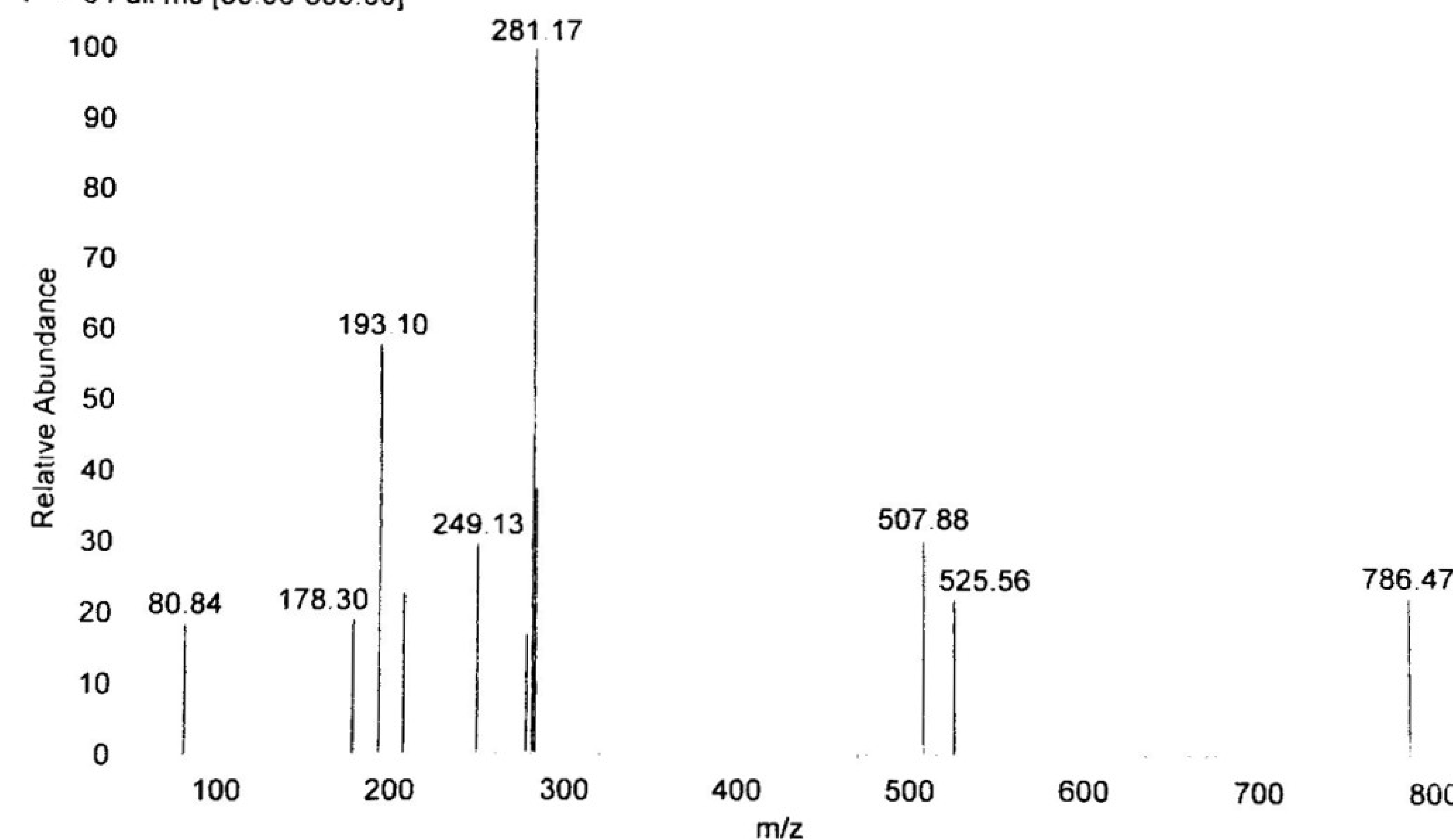


Figure 5. Mass spectrum of ligand **3** showing an *m/z* consistent with mass of the ligand without BF<sub>4</sub><sup>-</sup> (~786 g/mol)

## DATA AND RESULTS

% V Free	% V Buried	% V Tot/V Ex
45.1	54.9	99.9

Figure 6. Table of % V given by SambVca

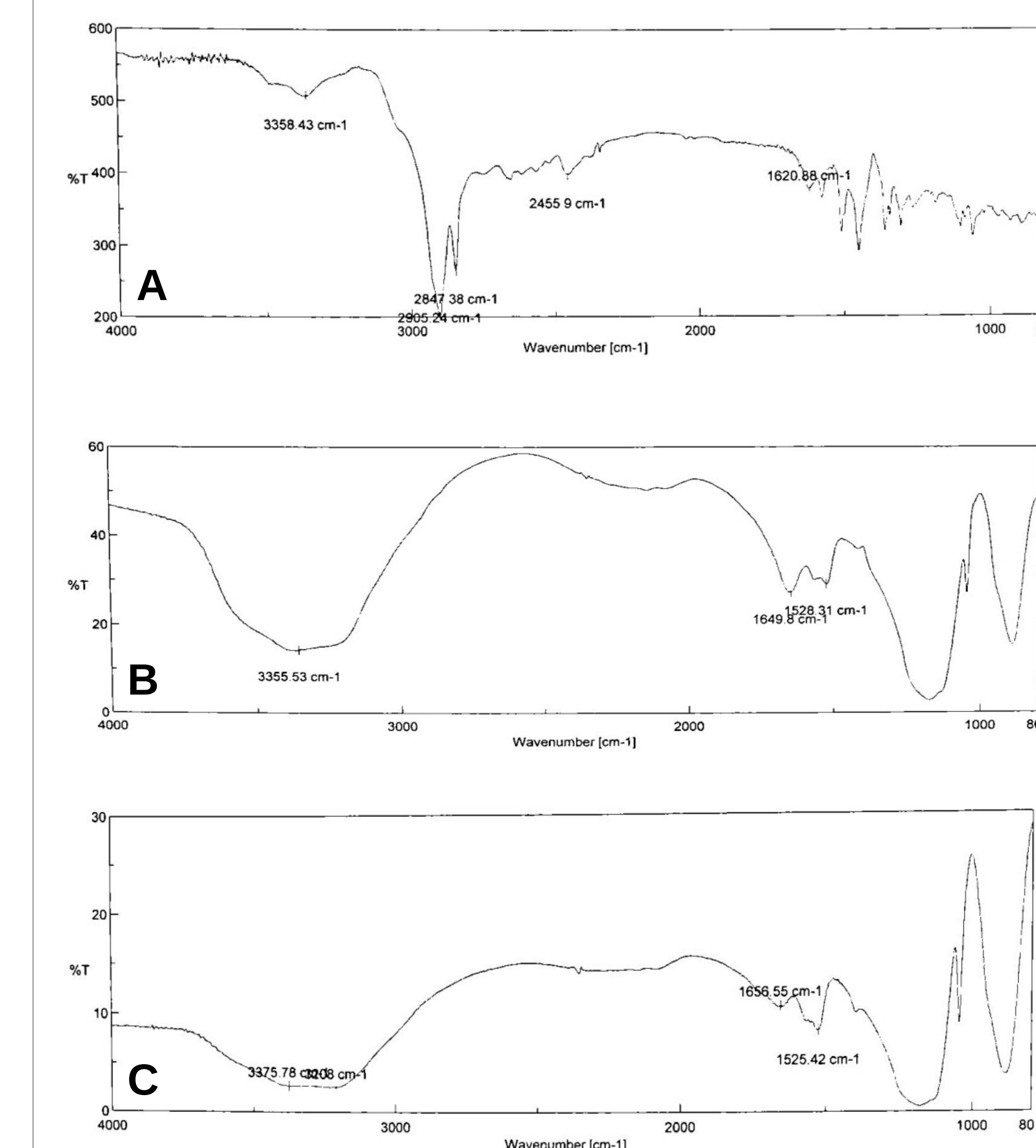


Figure 7. Infrared spectra of the aniline (A), diazadiene (B), and imidazolium salt (C)

## CONCLUSIONS

- A novel *N*-heterocyclic carbene with steric bulk and flexibility was synthesized
- Buried volume calculations for copper complex suggest it could be effective as a catalyst
- If this research were to continue, the solubility of ligand **3** needs exploration

## ACKNOWLEDGMENTS

I would like to thank the Saint Vincent College Chemistry Department, especially Dr. Vohs for being my research advisor.

A special thank you to Dr. Kevin Range at Lock Haven University for running the WebMO calculations from the LHU server.