Electronic Supplementary Information for Dalton Transactions

Supporting Information

for

Simple and Versatile Synthesis of Copper and Silver *N*-Heterocyclic Carbene Complexes in Water or Organic Solvents

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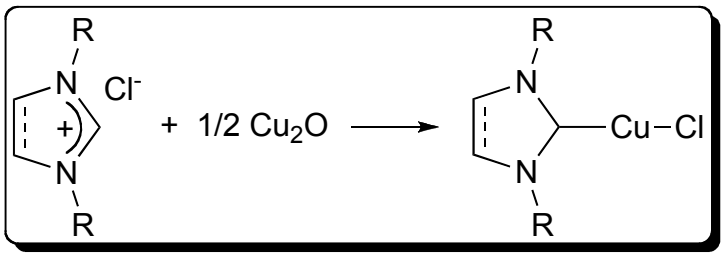
1. General Information

Copper oxide Cu_2O (95%) and silver oxide Ag_2O (99%) were purchased from Strem and Alfa Aesar, respectively. Imidazolium salts (NHC·HCl): IMes·HCl,[1] SIMes·HCl,[2] IPr·HCl[1] and their saturated analogues SIPr·HCl,[3] ICy·HCl[4] and SICy·HCl[5] were prepared according to the literature. Dichloromethane and toluene were dried by a solvent purification system (SPS MBraun). Water was distilled and degassed under Argon prior to use. ^1H and $^{13}C\{^1H\}$ spectra were recorded at 300 and 75 MHz respectively on a Bruker Spectrospin 300 MHz spectrometer operating at 298 K. Proton and carbon chemical shifts were internally referenced to the residual proton resonance in $CDCl_3$ (δ (ppm) 7.26 and 77.16 respectively). Infrared spectra were recorded on a Perkin Elmer Spectrum GX IR spectrometer. High Resolution Mass spectra were recorded at the EPSRC National Mass Spectrometry Service Centre.

2. Synthesis of the copper complexes



2.1. General Procedure in Dichloromethane

Copper oxide (0.217g, 1.52 mmol) and the NHC·HCl (2.34 mmol) were introduced in a glass vial equipped with a magnetic stirring bar. The vial was purged with Argon before the addition of the CH_2Cl_2 (4.8 mL). The reaction mixture was then stirred at room temperature or at 40°C for 24h. An aliquot of the crude reaction mixture was collected to determine the reaction conversion by ^1H NMR in $CDCl_3$. After filtration of the crude reaction mixture through filter paper using CH_2Cl_2 as eluent, the filtrate was dried and washed with water. Subsequent drying under high vacuum afforded a colourless solid.

2.2. General Procedure in Toluene

A glass vial equipped with a magnetic stirring bar was charged with copper oxide (0.217g, 1.52 mmol) and the imidazol(idin)ium chloride (2.34 mmol). The vial was purged with Argon prior to addition of toluene (4.8 mL). The reaction mixture was stirred at reflux for 24h. Then, the reaction conversion was monitored by ^1H NMR in $CDCl_3$. The crude solid was dissolved in CH_2Cl_2 then filtered through filter paper. The

obtained filtrate was dried and washed several times with water, to remove any unreacted imidazolium salt, if necessary. A colourless solid was obtained.

Isolated yields obtained in Toluene

[Cu(IMes)Cl] (0.818 g, 86%)

[Cu(SIMes)Cl] (0.674 g, 71%)

[Cu(IPr)Cl] (0.894 g, 78%)

[Cu(SIPr)Cl] (1.013 g, 88%)

[Cu(ICy)Cl] (0.544 g, 70%)

2.3. General Procedure in Water

Copper oxide (0.217g, 1.52 mmol) and the imidazol(idin)ium chloride (2.34 mmol) were introduced in a glass vial equipped with a magnetic stirring bar. The vial was purged with Argon before the addition of distilled and degassed water (4.8 mL). The reaction mixture was then stirred at reflux for 24h. After removal of the solvent, the reaction conversion was determined by ^{1}H NMR in $CDCl_3$. The crude solid was dissolved in CH_2Cl_2 and filtered. Removal of the solvent, washes with water and drying under vacuum, gave a colourless solid.

Isolated yields obtained in Water

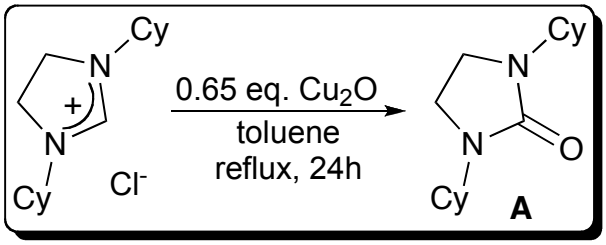
[Cu(IMes)Cl] (0.927 g, 98%)

[Cu(SIMes)Cl] (0.938 g, 99%)

[Cu(IPr)Cl] (1.079 g, 94%)

[Cu(SIPr)Cl] (0.827 g, 72%)

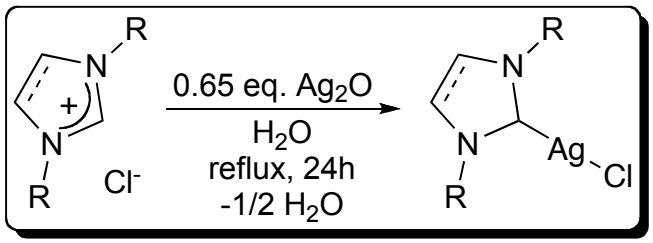
3. Synthesis and characterisation of 1,3-dicyclohexylimidazolidin-2-one (A)



In a glass vial, copper oxide (0.217g, 1.52 mmol) and 1,3-dicyclohexylimidazolinium chloride (0.634g, 2.34 mmol) were dissolved in Argon purged toluene (4.8 mL). The reaction mixture was heated at reflux for 24h. The crude solid obtained after removal of the solvent, was dissolved in CH_2Cl_2, filtered and dried under vacuum. 1,3-

Dicyclohexylimidazolidin-2-one was obtained as a colourless solid in 45% yield (0.263g). ^{1}H NMR ($CDCl_3$, 300 MHz) δ (ppm) 3.64 (m, 2H, CH), 3.18 (s, 4H, NCH_2), 1.73-0.84 (m, 20H, CH_2). $^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 75 MHz) δ (ppm) 160.13 (C=O), 51.35 (CH), 38.48 (NCH_2), 30.15 (CH_2), 25.89 (CH_2). IR (NaCl) $\nu_{C=O}$ 1670 cm^{-1}. HRMS (NSI) $[M+H]^+$ Calcd for $C_{15}H_{27}N_2O$: 251.2118, found: 251.2120.

4. Synthesis of the silver complexes in water



Silver oxide (0.353 g, 1.52 mmol, 0.65 eq.) and the imidazol(idin)ium chloride (2.34 mmol) were introduced in a glass vial containing a stirring bar. Distilled and degassed water (4.8 mL) was added and the reaction mixture was stirred at reflux for 24h in the absence of light. After removal of the solvent by vacuum, the reaction conversion was monitored by ^{1}H NMR in $CDCl_3$. The crude was dissolved in CH_2Cl_2 and filtered. After evaporation of the filtrate, a colourless solid was obtained. The product was washed with water when necessary.

Isolated yields

[Ag(IMes)Cl] (0.966 g, 92%)

[Ag(SIMes)Cl] (0.929 g, 88%)

[Ag(IPr)Cl] (1.081 g, 87%)

[Ag(SIPr)Cl] (0.926 g, 74%)

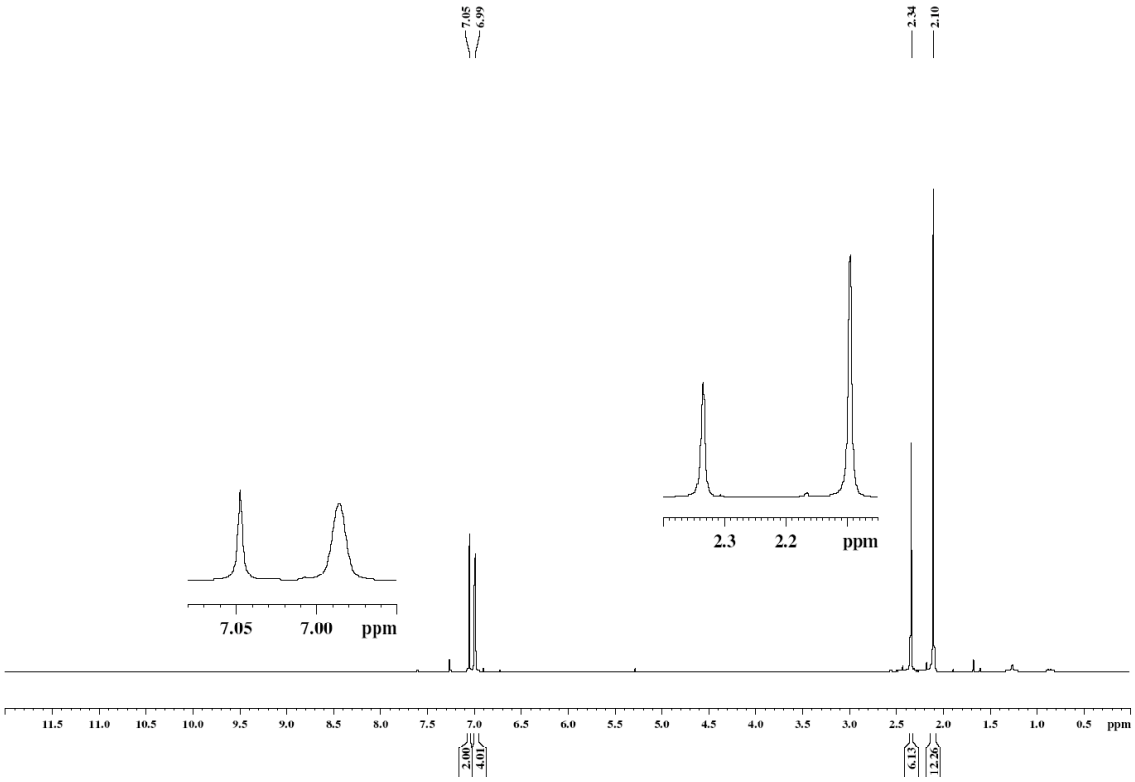
[Ag(ICy)Cl] (0.507 g, 58%)

[Ag(SICy)Cl] (0.399 g, 45%) A mixture of two products was obtained.

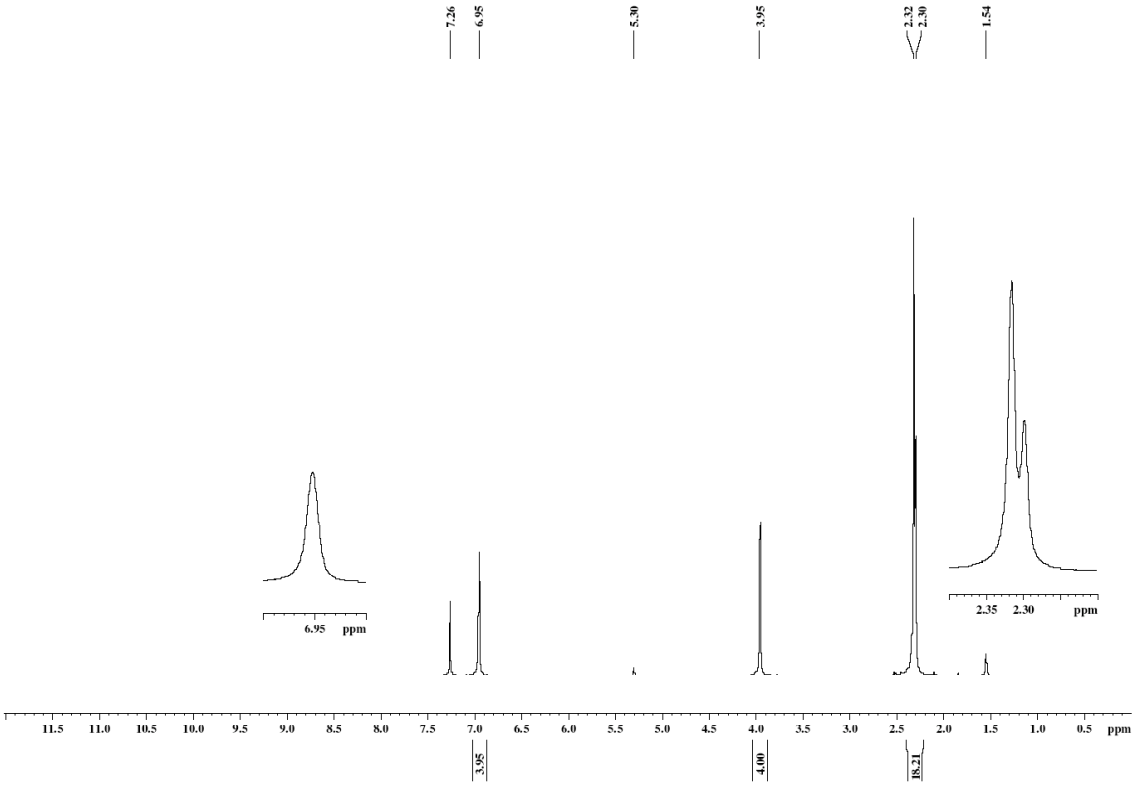
5. NMR spectra

NMR spectra were consistent with previously reported data : [CuCl(IMes)],[6] [CuCl(SIMes)],[7] [CuCl(IPr)],[8] [CuCl(SIPr)],[9] [CuCl(ICy)],[7] [AgCl(IMes)], [AgCl(SIMes)], [AgCl(IPr)], [AgCl(SIPr)] and [AgCl(ICy)].[10]

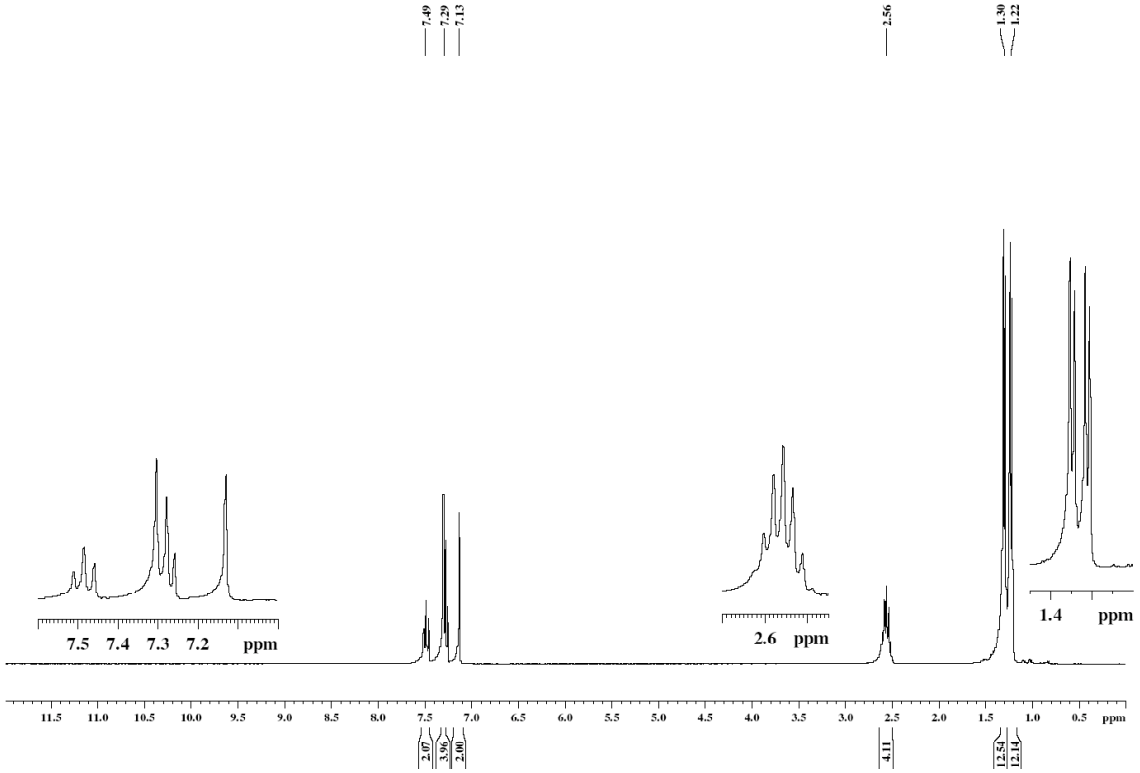
^{1}H NMR ($CDCl_3$) of [CuCl(IMes)]



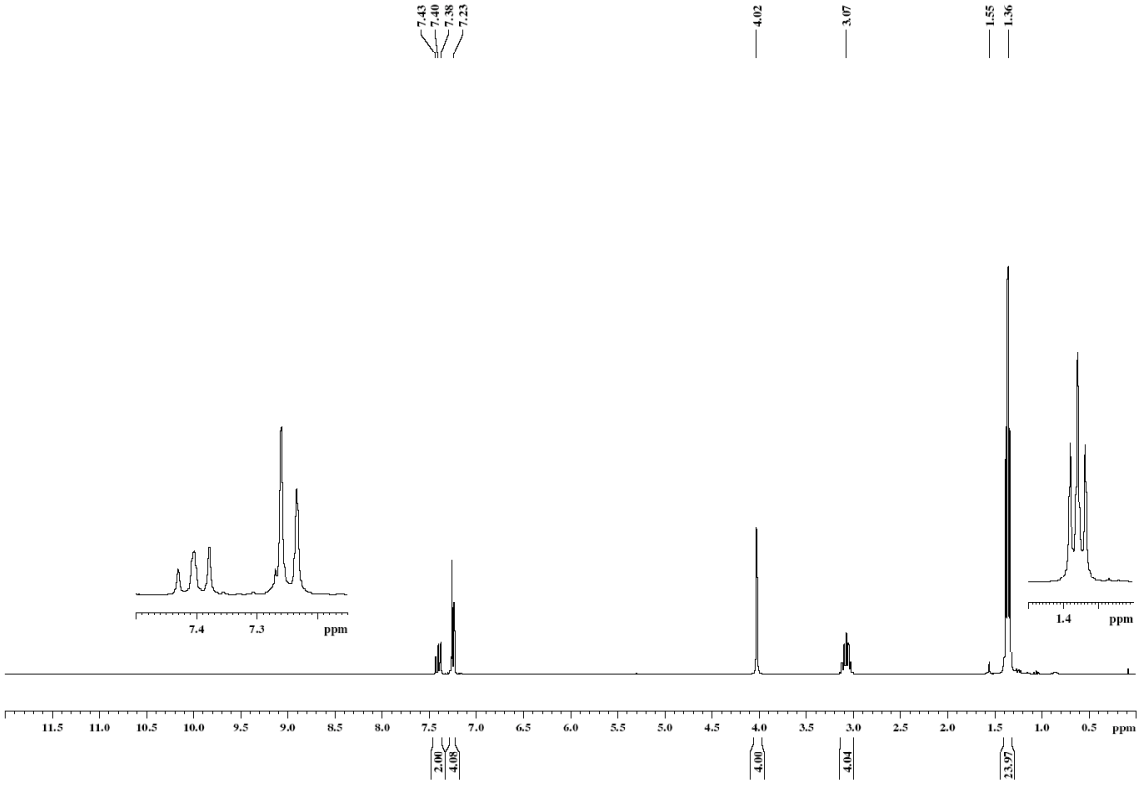
^{1}H NMR ($CDCl_3$) of [CuCl(SIMes)]



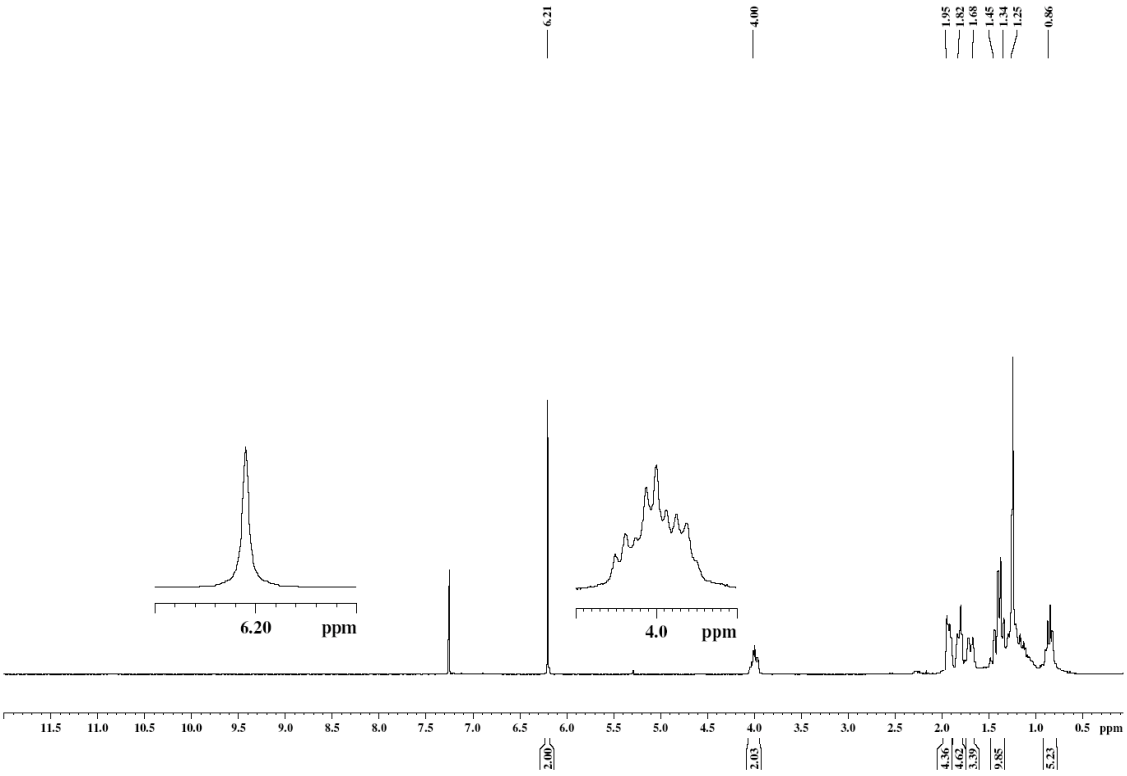
^{1}H NMR ($CDCl_3$) of [CuCl(IPr)]



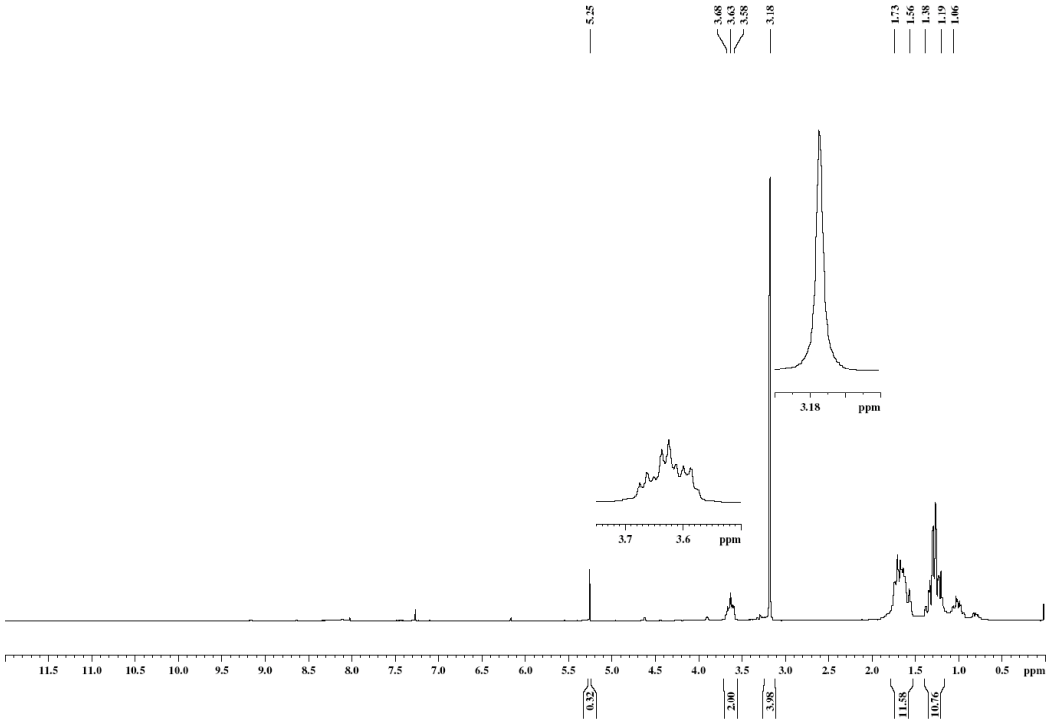
^{1}H NMR ($CDCl_3$) of [CuCl(SIPr)]



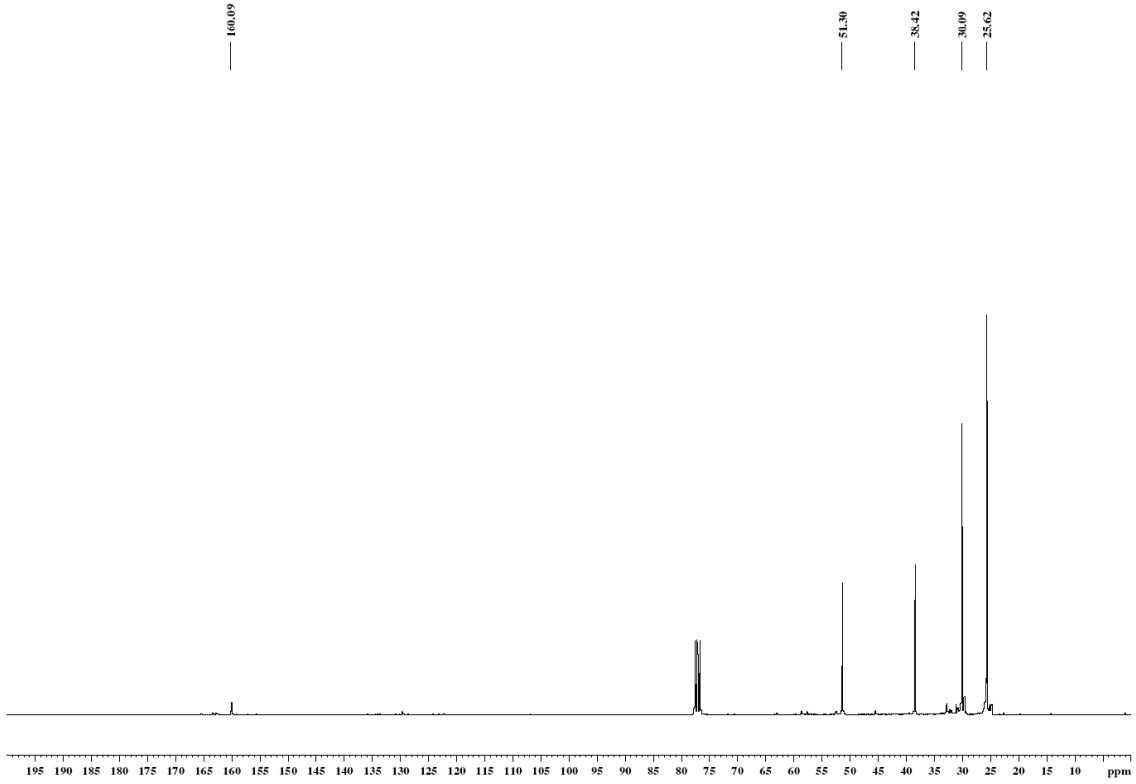
^{1}H NMR ($CDCl_3$) of [CuCl(ICy)]



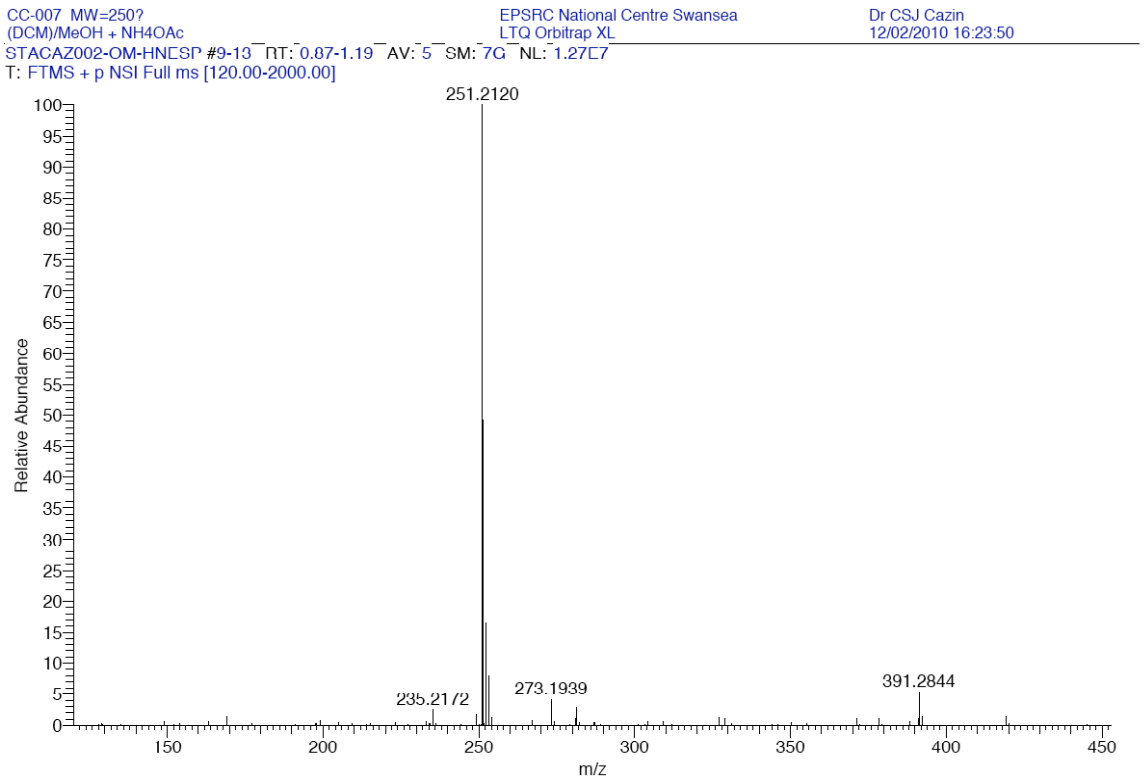
^{1}H NMR ($CDCl_3$) of SICy=O (1,3-dicyclohexylimidazolidin-2-one, A)

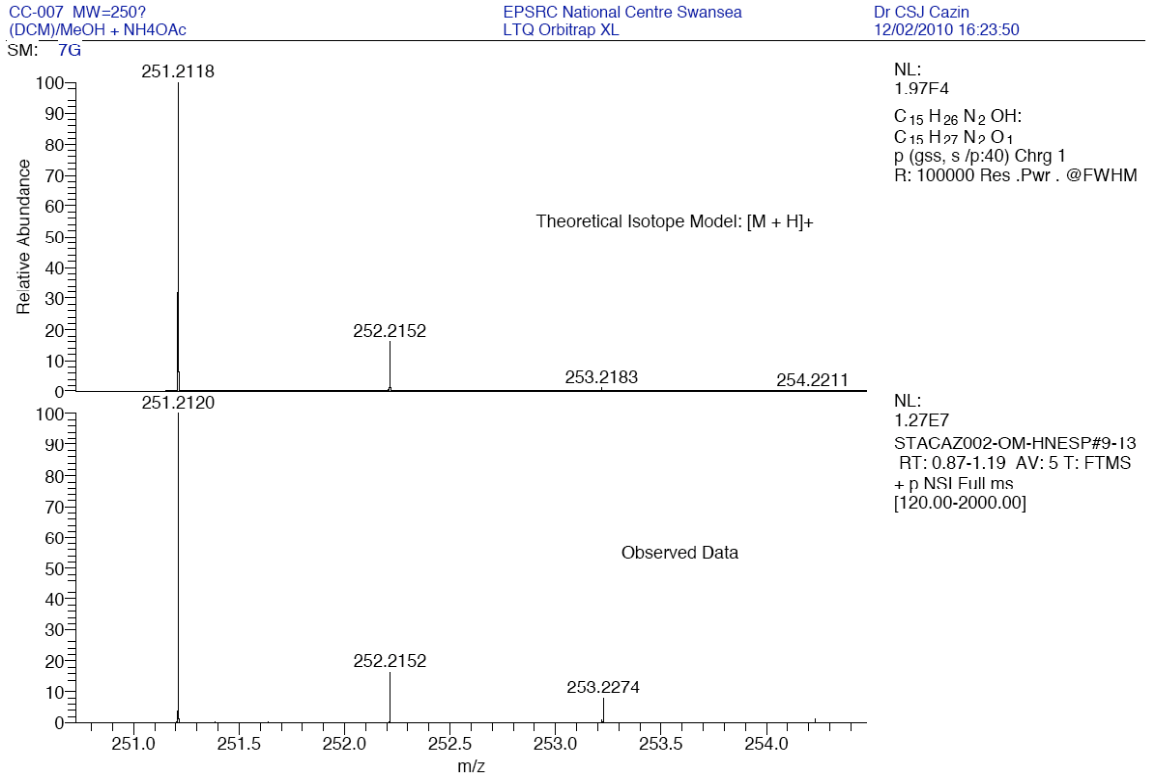


^{13}C-{^{1}H} NMR ($CDCl_3$) of SICy=O (1,3-dicyclohexylimidazolidin-2-one, A)

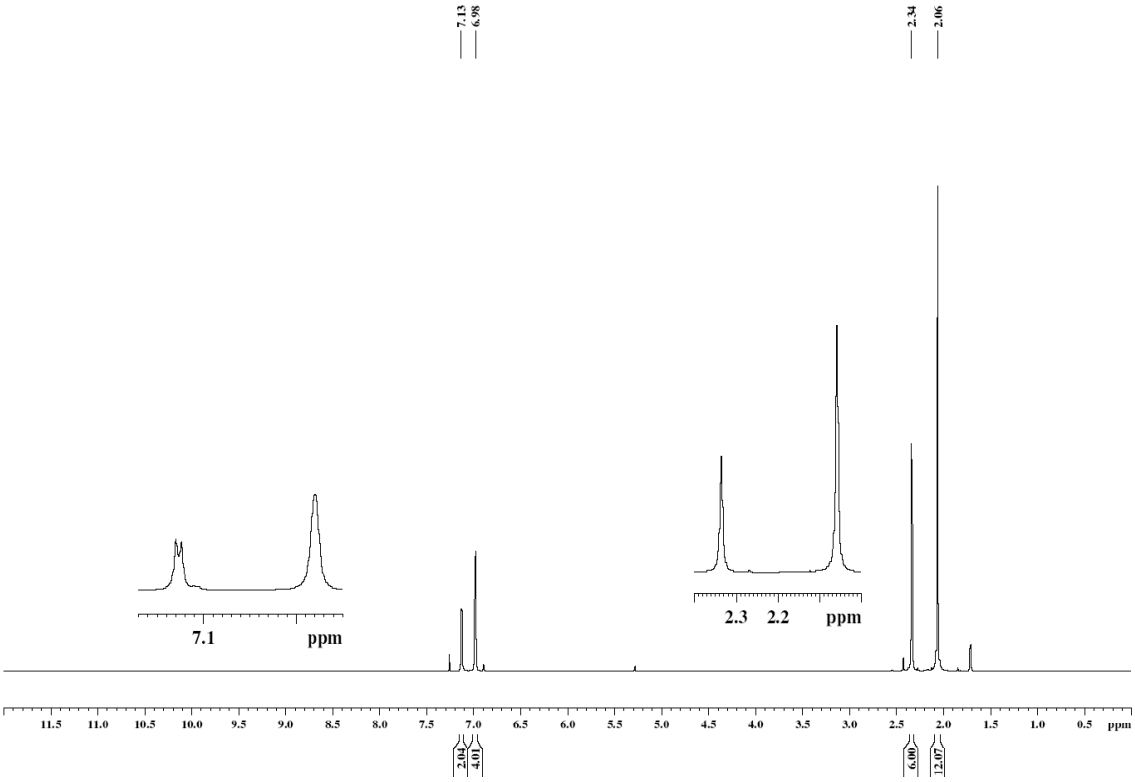


HRMS (NSI) of SICy=O (1,3-dicyclohexylimidazolidin-2-one, A)

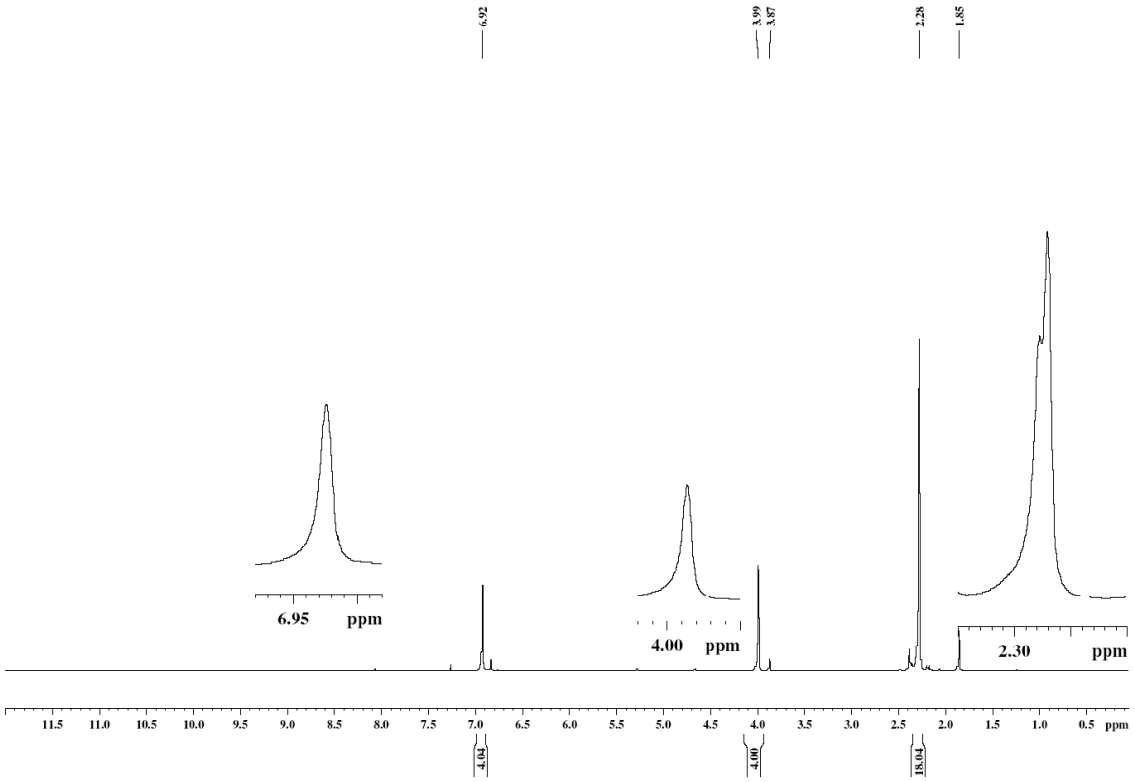




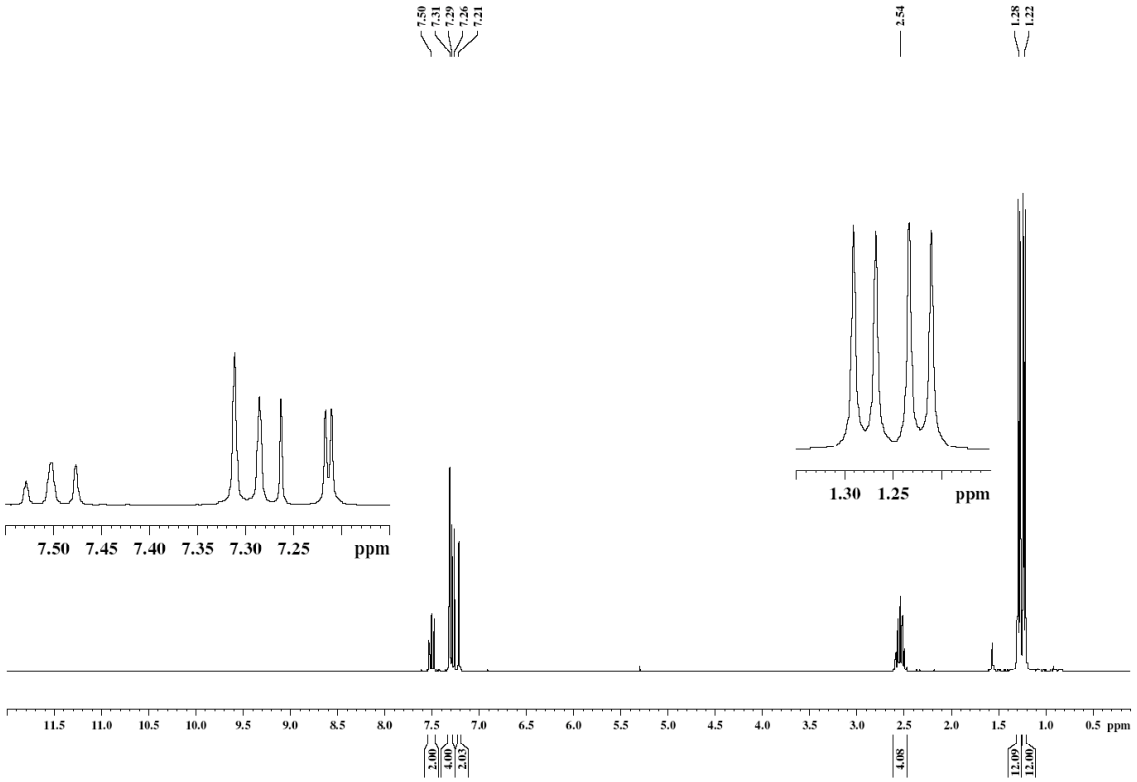
^{1}H NMR ($CDCl_3$) of [AgCl(IMes)]



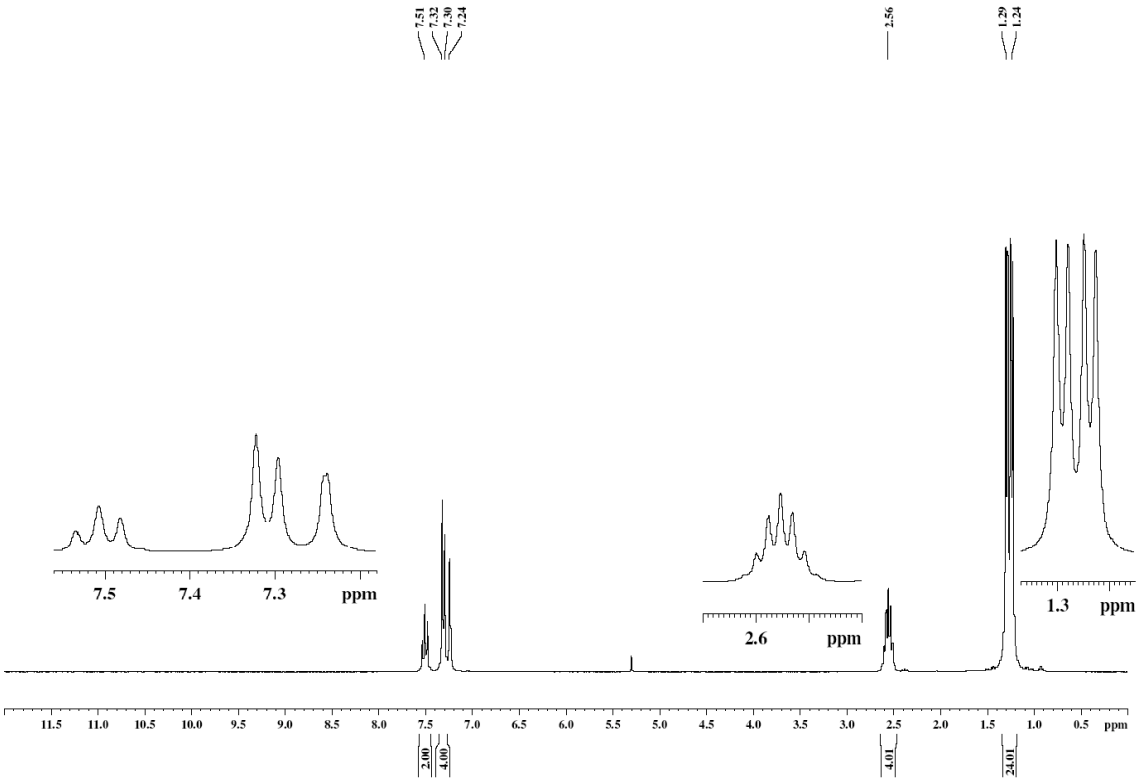
^{1}H NMR ($CDCl_3$) of [AgCl(SIMes)]



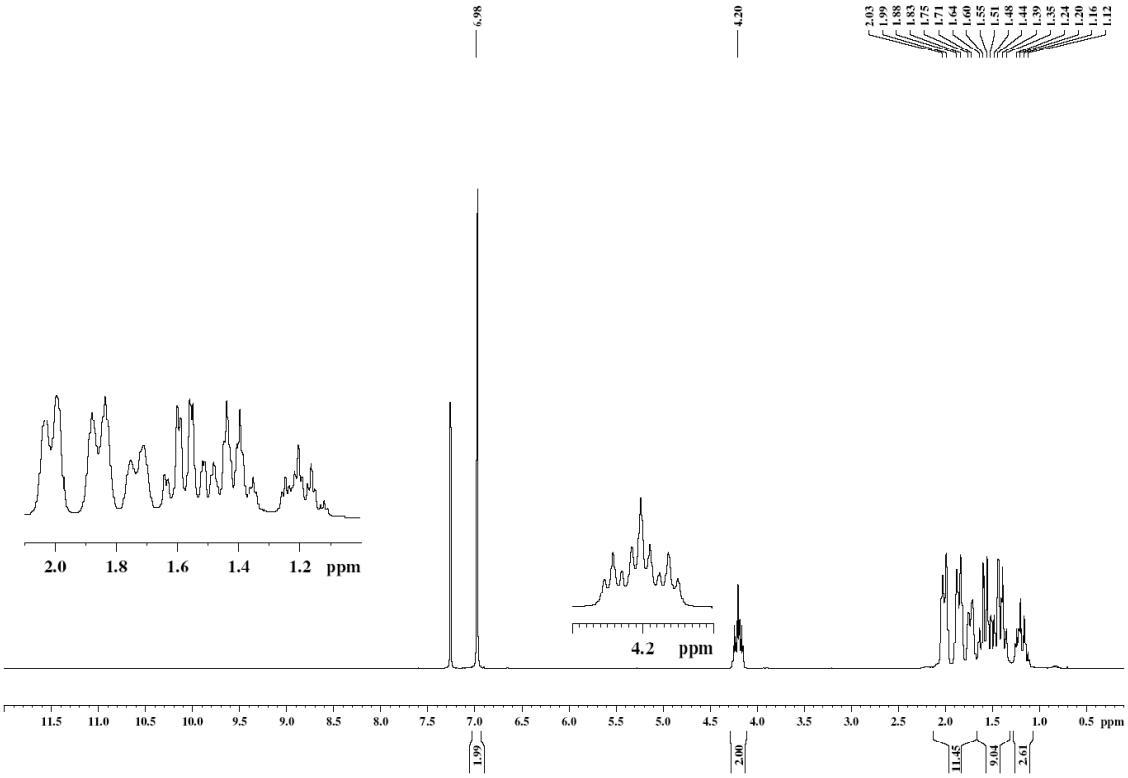
^{1}H NMR ($CDCl_3$) of [AgCl(IPr)]



^{1}H NMR ($CDCl_3$) of [AgCl(SIPr)]



^{1}H NMR ($CDCl_3$) of [AgCl(ICy)]



References

1 S. P. Nolan, U. S. Patent 7109348 B1, 2006.

2 A. J., III. Arduengo, U.S. Patent 5 077 414, 1991.

3 A. J., III. Arduengo, R. Krafczyk and R. Schmutzler, *Tetrahedron* 1999, **55**, 14523.

4 W. A. Herrmann, C. Kocher and L. Goossen, W.O. Patent 97 34 875 A1, 1997.

5 A. Aidouni, S. Bendahou, A. Demonceau and L. Delaude, *J. Comb. Chem.*, 2008, **10**, 886.

6 S. Okamoto, S. Tominaga, N. Saino, K. Kase, K. Shimoda, *J. Organomet. Chem.*, 2004, **23**, 1157.

7 S. Díez González, H. Kaur, F. Kauer Zinn, E. D. Stevens and S. P. Nolan, *J. Org. Lett.*, 2005, **70**, 4784.

8 H. Kaur, F. Kauer Zinn, E. D. Stevens and S. P. Nolan, *Organometallics*, 2004, **23**, 1157.

9 L. A. Goj, E. D. Blue, S. A. Delp, T. B. Gunnoe, T. R. Cundari, A. W. Pierpont, J. L. Petersen and P. D. Boyle, *Inorg. Chem.*, 2006, **45**, 9032.

10 P. de Frémont, N. M. Scott, E. D. Stevens, T. Ramnial, O. C. Lightbody, C. L. B. Macdonald, J. A. C. Clyburne, C. D. Abernethy, S. P. Nolan, *Organometallics*, 2005, **24**, 6301.