Electronic Supplementary Material (ESI) for Dalton Transactions

Supporting Information For:

Complexes of Cu(I) supported by a tris(ketimine) tripod

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Experimental

General. All reactions and subsequent manipulations were performed under anaerobic and anhydrous conditions either under high vacuum or an atmosphere of nitrogen. Hexanes, diethyl ether, THF and toluene were dried by passage over activated molecular sieves using a Vacuum Atmospheres solvent purification system, while C_6D_6 and THF_{d8} were dried over activated 4Å molecular sieves for 24 h. $[Cu(MeCN)_4][PF_6]$ was synthesized by oxidation of Cu metal with $[NO][PF_6]$ in MeCN.[1] All other reagents were purchased from commercial suppliers and used as received.

^{19}F NMR spectra were recorded on a Varian UNITY INOVA 400 MHz spectrometer, while ^{1}H NMR and ^{13}C NMR spectra were recorded on a Varian UNITY INOVA 500 MHz spectrometer. ^{1}H NMR and $^{13}C\{^{1}H\}$ NMR spectra are referenced to external $SiMe_4$ using the residual protio solvent peaks as internal standards. $^{19}F\{^{1}H\}$ NMR spectra are referenced to $CFCl_3$ in $CDCl_3$. IR spectra were recorded on a Mattson Genesis FTIR spectrometer using CaF_2 plates for solution-phase experiments. Elemental analyses were performed by the Microanalytical Laboratory at UC Berkeley. ESI MS analyses were performed on the Micromass (Waters) QTOF2 mass spectrometer with electrospray ionization source. Samples were diluted in methanol and infused directly into the electrospray interface at 5 μL/minute via a Harvard Apparatus syringe pump.

Cyclic Voltammetry Measurements. CV experiments were performed with a CH Instruments 600c Potentiostat, and the data were processed using CHI software (version 6.29). All experiments were performed under inert atmosphere using a 20 mL glass vial as the cell. The working electrode consisted of a platinum disk embedded in glass (2 mm diameter), the counter electrode was a platinum wire, and the reference electrode

consisted of AgCl plated on Ag wire. Solutions employed during CV studies were typically 1.0 mM in the metal complex and 0.1 M in $[Bu_4N][PF_6]$. All potentials are reported versus the Fc/Fc^+ couple. For all trials, $i_{p,a}/i_{p,c}$= 1 for the $[Cp_2Fe]^{0/+}$ couple, while $i_{p,c,}$ increased linearly with the square root of the scan rate (i.e., √v).

X-ray Crystallography. Data for **1**, **2**·C_7H_8**,** **3**·$7CH_3CN$**,** **4**·$1.5CH_2Cl_2$, and **5**·$4CH_2Cl_2$ were collected on a Bruker KAPPA APEX II diffractometer equipped with an APEX II CCD detector using a TRIUMPH monochromater with a Mo Kα X-ray source (α = 0.71073 Å). The crystals of **1**, **2**·C_7H_8**,** **3**·$7CH_3CN$**,** **4**·$1.5CH_2Cl_2$, and **5**·$4CH_2Cl_2$ were mounted on a cryoloop under Paratone-N oil, and all data were collected at 100(2) K using an Oxford nitrogen gas cryostream system. Frame exposures of 10 seconds were used for **1**, **2**·C_7H_8**,** **4**·$1.5CH_2Cl_2$, and **5**·$4CH_2Cl_2$, while exposures of 2 seconds were used for **3**·$7CH_3CN$. Data collection and cell parameter determination were conducted using the SMART program.[2] Integration of the data frames and final cell parameter refinement were performed using SAINT software.[3] Absorption correction was carried out using the multi-scan method SADABS,[4] Subsequent calculations were carried out using SHELXTL.[5] Structure determination was done using direct or Patterson methods and difference Fourier techniques. All hydrogen atom positions were idealized, and rode on the atom of attachment. Structure solution, refinement, graphics, and creation of publication materials were performed using SHELXTL.[5]

Preparation of $N(ArCNHPh)_3$ (1). Tris(2-benzylnitrile)amine[6] (270 mg, 0.84 mmol) was added to a Schlenk flask fitted with septum and suspended in Et_2O (5 mL). Phenyllithium in Et_2O (1.31 ml, 2.6 mmol, 2.0 M) was injected dropwise. After 24 hours the ethereal slurry of tris(2-benzylnitrile)amine was consumed, resulting in the formation

of a red solution. Methanol (1 ml) was injected into the reaction flask, resulting in formation of a yellow solution. The volatiles were removed *in vacuo* to provide a yellow solid. This was extracted into chloroform (15 ml), dried over anhydrous magnesium sulfate, filtered through a medium porosity frit, and dried in vacuo. Colourless crystals were grown from a dichloromethane solution layered with hexanes (378 mg, 80% yield) ^{1}H NMR (CD_2Cl_2, 500 MHz, 25 °C): δ 6.68 (m, 3H, N(*Ar*CNHPh)$_3$), δ 6.73 (m, 6H, N(*Ar*CNHPh)$_3$), 6.91 (m, 3H, N(*Ar*CNHPh)$_3$, 7.16 (t, J = 7.6 Hz, 6H, N(ArCNH*Ph*)$_3$, 7.27 (t, J = 7.3 Hz, 3H, N(ArCNH*Ph*)$_3$, 7.52 (dd, J = 8.5 Hz, J = 1.3 Hz, 6H, N(ArCNH*Ph*)$_3$), 10.31 (s, 3H, N(ArCN*H*Ph)$_3$). ^{13}C{^{1}H} NMR (THF-d_8, 125 MHz, 25 °C): δ 123.52 (N(*Ar*CNHPh)$_3$), 125.19 (N(*Ar*CNHPh)$_3$), 128.11 (N(ArCNH*Ph*)$_3$), 128.36 (N(ArCNH*Ph*)$_3$), 130.01 (N(ArCNH*Ph*)$_3$, 130.27 (N(ArCNH*Ph*)$_3$), 131.67 (N(*Ar*CNHPh)$_3$), 133.74 (N(*Ar*CNHPh)$_3$), 138.86 (N(*Ar*CNHPh)$_3$), 146.60 (N(*Ar*CNHPh)$_3$), 171.14 (N(Ar*C*NHPh)$_3$). HRMS (ESI) Calcd m/z 555.2543 $(M\text{-}H)^+$; Found 555.2523. Anal Calcd for $C_{39}H_{30}N_4$: C, 84.45, H, 5.45, N, 10.10. Found: C, 84.06, H, 5.32, N, 9.92.

Preparation of [N(ArCNHPh)$_3$Cu][CuCl$_2$] (2). To a solution of **1** (22.5 mg, 40.5 μmol) in THF (1 mL) was added a slurry of CuCl (4.0 mg 40.5 μmol) in THF (1 mL). This resulted in immediate formation of an orange solution. After stirring for 2 h the volatiles were removed in vacuo and the resulting orange solid dissolved in THF-d_8. The ^{1}H NMR spectrum indicated the presence of a 1:1 mixture of free scaffold and Cu coordination complex by integration of imine resonances. ^{1}H NMR (C_4D_8O, 500 MHz, 25 °C): δ 6.82 (bs, N(*Ar*CNHPh)$_3$), 7.06 (bs, N(*Ar*CNHPh)$_3$), 7.21 (bs, N(*Ar*CNHPh)$_3$, 7.31 (bs,

N(ArCNH*Ph*)$_3$, 7.36 (bs, N(ArCNH*Ph*)$_3$, 7.47 (bs, N(ArCNH*Ph*)$_3$), 9.92 (bs, 3H, N(ArCN*H*Ph)$_3$).

Alternative preparation of [N(ArCNHPh)$_3$Cu][CuCl$_2$] (2). A solution of **1** (120.4 mg, 217 μmol) in CH_2Cl_2 (2 mL) was added dropwise to a CuCl slurry (43.5 mg 439 μmol) in CH_2Cl_2 (1 mL). This resulted in immediate formation of an orange solution. After stirring for 2 h the solution was filtered through a Celite column (2 cm × 0.5 cm) supported on glass wool. The volatiles were removed in vacuo to give an orange powder (160 mg, 97% yield). Crystals suitable for X-ray crystallography were grown by slowly cooling a hot toluene solution of [N(Ph(CNH)Ph)$_3$Cu][CuCl$_2$]. ^{1}H NMR (THF-d_8, 500 MHz, 25 °C): δ 6.89 (t, *J* = 9.5 Hz, 3H, N(*Ar*CNHPh)$_3$), 7.04 (d, *J* = 7.6 Hz, 3H, N(*Ar*CNHPh)$_3$), 7.23 (t, *J* = 7.5 Hz, 3H, N(*Ar*CNHPh)$_3$), 7.31 (m, 9H, N(ArCNH*Ph*)$_3$), 7.36 (t, *J* = 7.3 Hz, 3H, N(*Ar*CNHPh)$_3$), 7.47 (d, *J* = 7.6 Hz, 6H, N(ArCNH*Ph*)$_3$), 10.13 (s, 3H, N(ArCN*H*Ph)$_3$). ^{13}C{^{1}H} NMR (THF-d_8, 125 MHz, 25 °C): δ 123.53 (s, N(*Ar*CNHPh)$_3$), 125.20 (s, N(*Ar*CNHPh)$_3$), 128.13 (s, N(ArCNH*Ph*)$_3$), 128.38 (s, N(ArCNH*Ph*)$_3$), 130.01 (s, N(ArCNH*Ph*)$_3$), 130.29 (s, N(ArCNH*Ph*)$_3$), 131.68 (s, N(*Ar*CNHPh)$_3$), 133.80 (s, N(*Ar*CNHPh)$_3$), 138.87 (s, N(*Ar*CNHPh)$_3$), 146.62 (s, N(*Ar*CNHPh)$_3$), 171.15 (s, N(Ar*C*NHPh)$_3$). Anal Calcd for $C_{39}H_{30}N_4Cu_2Cl_2$: C, 62.23, H, 4.02, N, 7.44. Found: C, 62.20, H, 4.02, N, 7.06.

Preparation of [N(ArCNHPh)$_3$Cu]$_2$[CuI$_3$] (3). To a vial containing CuI (4.8 mg, 25.2 μmol) was added dropwise a CD_2Cl_2 (1 mL) solution of **1** (14.6 mg, 26.3 μmol). A ^{1}H NMR spectrum of this solution indicated the formation of a 1:2 mixture of free scaffold and copper coordination complex, respectively, by integration of imine resonances. ^{1}H NMR (CD_2Cl_2, 500 MHz, 25 °C): δ 6.86 (dt, *J* = 8.5 Hz, *J* = 1.2 Hz, 6H, N(*Ar*CNHPh)$_3$),

7.06 (dd, J = 7.8 Hz, J = 2.6 Hz, 6H, N(*Ar*CNHPh)$_3$), 7.15 (dt 6H, J = 8.8 Hz, J = 1.6 Hz N(*Ar*CNHPh)$_3$), 7.29 (dd, 6H, J = 8.2 Hz, J = 1.0 Hz, N(*Ar*CNHPh)$_3$, 7.32 (t, 12H, J = 7.3 Hz, N(ArCNH*Ph*)$_3$), 7.42 (t, J = 8.5 Hz, 12H, N(ArCNH*Ph*)$_3$), 7.52 (d, 6H, N(ArCNH*Ph*)$_3$), 9.22 (s, 6H, N(ArCN*H*Ph)$_3$).

Alternate Preparation of [N(ArCNHPh)$_3$Cu]$_2$[CuI$_3$] (3). A solution of **1** (106.4 mg, 191 μmol) in CH_2Cl_2 (2 mL) was added dropwise to a CuI slurry (55.0 mg 288 μmol) in CH_2Cl_2 (1 mL). This resulted in immediate formation of an orange solution. After stirring for 2 h the solution was filtered through a Celite column (2 cm × 0.5 cm) supported on glass wool. The volatiles were removed in vacuo to give an orange powder (132 mg, 82% yield). Crystals suitable for X-ray crystallography were grown from slow cooling of an acetonitrile solution, yielding a compound with the formulation [N(Ph(CNH)Ph)$_3$Cu]$_2$[CuI$_3$]. ^{1}H NMR (CD_2Cl_2, 500 MHz, 25 °C): δ 6.85 (dt, J = 8.5 Hz, J = 1.2 Hz, 3H, N(*Ar*CNHPh)$_3$), 7.04 (dd, J = 7.8 Hz, J = 2.6 Hz, 3H, N(*Ar*CNHPh)$_3$), 7.15 (dt, 3H, J = 8.8 Hz, J = 1.6 Hz, N(*Ar*CNHPh)$_3$), 7.27 (dd, 3H, J = 8.2 Hz, J = 1.0 Hz, N(*Ar*CNHPh)$_3$), 7.32 (dt, 6H, J = 7.3 Hz, J = 1.5 Hz, N(ArCNH*Ph*)$_3$), 7.40 (dt, J = 8.5 Hz, J = 1.1 Hz, 6H, N(ArCNH*Ph*)$_3$), 7.41 (s, 3H, N(ArCNH*Ph*)$_3$), 9.37 (s, 3H, N(ArCN*H*Ph)$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz, 25 °C): δ 123.38 (s, N(*Ar*CNHPh)$_3$), 124.89 (s, N(*Ar*CNHPh)$_3$), 128.22 (s, N(ArCNH*Ph*)$_3$), 128.40 (s, N(ArCNH*Ph*)$_3$), 129.15 (s, N(ArCNH*Ph*)$_3$), 130.65 (s, N(ArCNH*Ph*)$_3$), 131.60 (s, N(*Ar*CNHPh)$_3$), 134.04 (s, N(*Ar*CNHPh)$_3$), 138.64 (s, N(*Ar*CNHPh)$_3$), 146.51 (s, N(*Ar*CNHPh)$_3$), 171.48 (s, N(Ar*C*NHPh)$_3$). Anal Calcd for $C_{78}H_{60}N_8Cu_3I_3$: C, 55.74, H, 3.60, N, 6.67. Found: C, 52.22, H, 3.77, N, 6.08.

Preparation of [N(ArCNHPh)$_3$Cu][OTf] (4). A solution of **1** (109.7 mg, 197 μmol) in CH_2Cl_2 (2 mL) was added dropwise to a [Cu(CH_3CN)$_4$][OTf] slurry (74.5 mg 197 μmol) in CH_2Cl_2 (1 mL). This resulted in immediate formation of an orange solution. After stirring for 2 h the solution was filtered through a Celite column (2 cm × 0.5 cm) supported on glass wool. The volatiles were removed in vacuo to give an orange powder (148 mg, 80% yield). ^{1}H NMR (C_6D_6, 500 MHz, 25 °C): δ 6.33 (t, *J* = 7.6 Hz, 3H, N(ArCNH*Ph*)$_3$), 6.67 (t, *J* = 8.3 Hz, 3H, N(*Ar*CNHPh)$_3$), 6.71 (d, *J* = 6.4 Hz, 3H, N(*Ar*CNHPh)$_3$), 6.87 (t, *J* = 8.4 Hz, 6H, N(ArCNH*Ph*)$_3$), 6.91 (d, *J* = 8.4 Hz, 3H, N(*Ar*CNHPh)$_3$), 6.96 (t, *J* = 6.4 Hz, 3H, N(*Ar*CNHPh)$_3$), 7.09 (d, *J* = 7.4 Hz, 6H, N(ArCNH*Ph*)$_3$), 9.59 (s, 3H, N(ArCN*H*Ph)$_3$). ^{13}C{^{1}H} NMR (CD_2Cl_2, 125 MHz, 25 °C): δ 124.46 (s, N(*Ar*CNHPh)$_3$), 125.45 (s, N(*Ar*CNHPh)$_3$), 127.89 (s, N(ArCNH*Ph*)$_3$), 128.78 (s, N(ArCNH*Ph*)$_3$), 129. 41 (s, N(ArCNH*Ph*)$_3$), 131.33 (s, N(ArCNH*Ph*)$_3$), 132.42 (s, N(*Ar*CNHPh)$_3$), 134.27 (s, N(*Ar*CNHPh)$_3$), 138.41 (s, N(*Ar*CNHPh)$_3$), 146.52 (s, N(*Ar*CNHPh)$_3$), 173.50 (s, N(Ar*C*NHPh)$_3$). ^{19}F NMR (CD_2Cl_2, 376 MHz, 25 °C): -78.80 (s). Anal Calcd for $C_{40}H_{30}N_4CuSO_3F_3$: C, 62.61, H, 3.94, N, 7.30. Found: C, 62.43, H, 4.06, N, 7.14.

Preparation of [N(ArCNHPh)$_3$Cu][PF$_6$] (5). A solution of **1** (82.0 mg, 148 μmol) in CH_2Cl_2 (1 mL) was added dropwise to a [Cu(CH_3CN)$_4$][PF_6] slurry (48.0 mg 148 μmol) in CH_2Cl_2 (1 mL). This resulted in immediate formation of an orange solution. After stirring for 2 h the volatiles were removed in vacuo, and the resulting orange solid was dissolved in toluene (3 mL) and filtered through a Celite column (2 cm × 0.5 cm) supported on glass wool. The supernatant was then pumped to dryness to give an orange powder (91 mg, 80% yield). ^{1}H NMR (CD_2Cl_2, 500 MHz, 25 °C): δ 7.06 (t, *J* = 6.7 Hz,

3H, N(*Ar*CNHPh)$_3$), 7.14 (dd, *J* = 7.7 Hz, *J* = 1.4 Hz, 3H, N(*Ar*CNHPh)$_3$), 7.33 (m 9H, N(ArCNH*Ph*)$_3$), 7.38 (m, 3H, N(*Ar*CNHPh)$_3$), 7.44 (t, *J* = 7.6 Hz, 6H, N(ArCNH*Ph*)$_3$), 7.53 (t, *J* = 7.4 Hz, 3H, N(*Ar*CNHPh)$_3$), 9.16 (s, 3H, N(ArCN*H*Ph)$_3$). $^{13}C\{^1H\}$ NMR (CD_2Cl_2, 125 MHz, 25 °C): δ 124.76 (s, N(*Ar*CNHPh)$_3$), 125.63 (s, N(*Ar*CNHPh)$_3$), 127.84 (s, N(ArCNH*Ph*)$_3$), 128.89 (s, N(ArCNH*Ph*)$_3$), 129.35 (s, N(ArCNH*Ph*)$_3$), 131.61 (s, N(*Ar*CNHPh)$_3$), 132.70 (s, N(ArCNH*Ph*)$_3$), 134.36 (s, N(*Ar*CNHPh)$_3$), 138.27 (s, N(*Ar*CNHPh)$_3$), 146.53 (s, N(*Ar*CNHPh)$_3$);, 174.35 (s, N(Ar*C*NHPh)$_3$). ^{19}F NMR (CD_2Cl_2, 376 MHz, 25 °C): -73.45 (d, *J* = 115.05 Hz). Anal Calcd for $C_{39}H_{30}N_4CuPF_6$: C, 61.38, H, 3.96, N, 7.34. Found: C, 61.17, H, 4.14, N, 7.14.

Preparation of [N(ArCNHPh)$_3$Cu(CO)][PF$_6$] (6). A 50 ml Schlenk tube was charged with **5** (50.0 mg, 54.8 μmol), dissolved in dichloromethane (5 ml), and sealed with a rubber septa. An IR spectrum of this solution was recorded. A gaseous mixture of carbon monoxide (10%) in argon was then bubbled through the solution for 5 minutes. No colour change was observed. An IR spectrum of this solution was recorded, and a CO stretch was observed at ν_{CO} = 2086 cm^{-1}. The solution was then placed under vacuum for several minutes, and an IR spectrum was rerecorded. This revealed the disappearance of the CO stretch, indicating that the CO ligand is quite labile (see Fig. S23).

Reaction of [N(ArCNHPh)$_3$Cu][OTF] (4) with Oxygen. A sample of **1** (10 mg, 20 μmol) and [Cu(MeCN)$_4$][OTf] (8 mg, 20 μmol) was dissolved in CD_2Cl_2 and a ^1H NMR spectrum collected in a sealed J-young NMR tube. An atmosphere of O_2 was then introduced into the NMR tube, and the sample monitored over the course of 24 hrs (see Figs. S24, S25). The resonances associated with **4** were broadened, however no new

resonances were observed, suggesting that complex **4** does not react with O_2. Additionally, no colour change was observed.

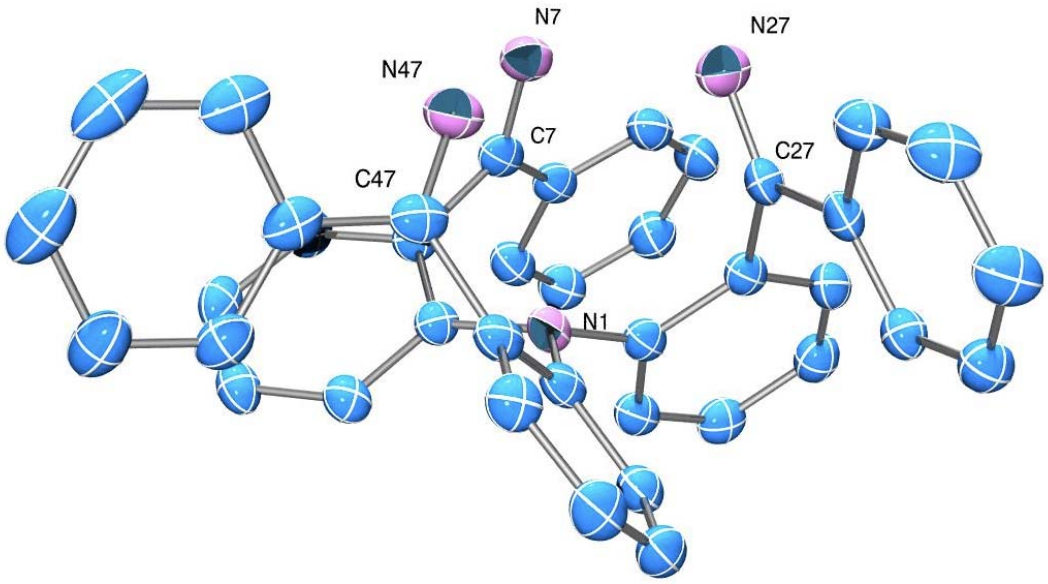

Fig. S1 Solid state molecular structure of $N(ArCNHPh)_3$ (**1**). Hydrogen atoms omitted for clarity.

Crystal data for **1**: $C_{39}H_{30}N_4$, M = 554.67, monoclinic, space group *C2/c*, a = 14.0041(7) Å, b = 11.7778(6) Å, c = 34.924(2) Å, α = 90°, β = 91.959(3)°, γ = 90°, V = 5756.9(5) Å^3, Z = 8, T = 100(2) K, λ = 0.71073 Å, R_{int} = 0.0218; a total of 13170 reflections collected in the range 2.26 < θ < 26.73 of which 5951 were unique. GOF = 1.099, R_1 = 0.0403 [for 4638 reflections with $I > 2\sigma(I)$] and wR_2 = 0.0747 (for all data).

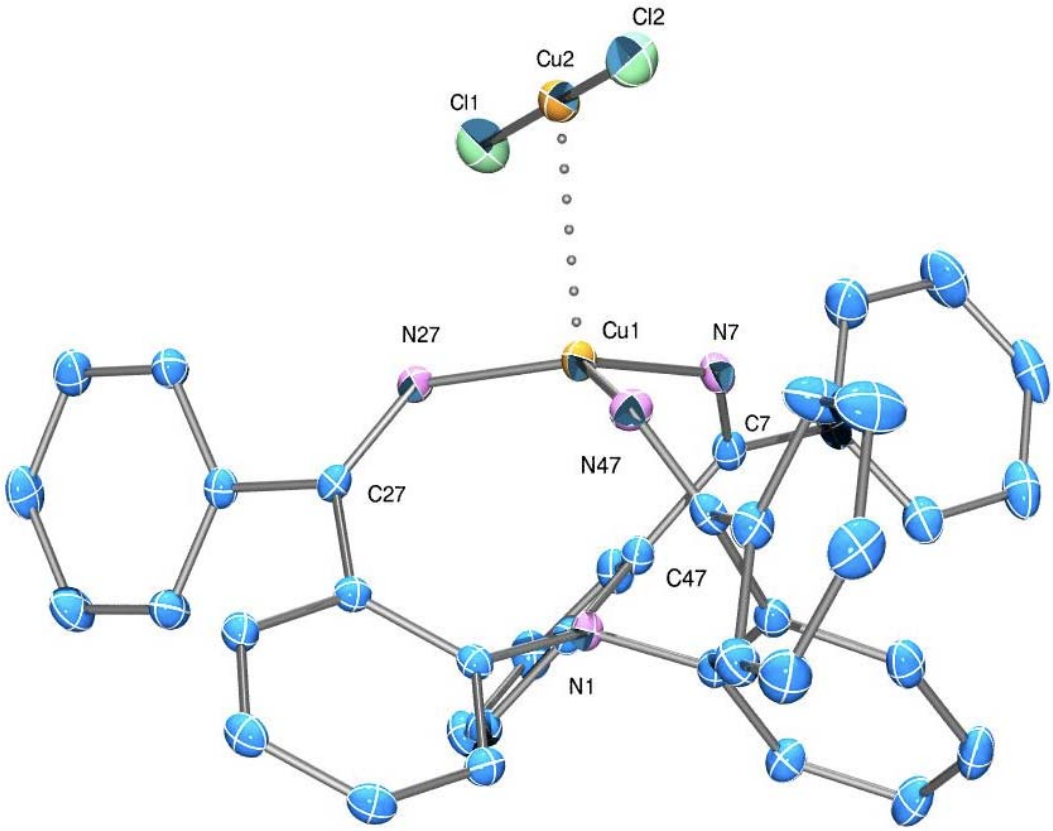

Fig. S2 Solid state molecular structure of $[N(ArCNHPh)_3Cu][CuCl_2]$ **(2)** Hydrogen atoms and toluene solvate omitted for clarity.

Crystal data for **2**·C_7H_8: $C_{46}H_{38}Cl_2Cu_2N_4$, M = 844.78, triclinic, space group *P-1*, a = 9.800(3) Å, b = 13.950(4) Å, c = 14.453(4) Å, α = 101.020(9)°, β = 97.408(9)°, γ = 94.634(11)°, V = 1911.9(9) Å^3, Z = 2, T = 100(2) K, λ = 0.71073 Å, R_{int} = 0.0335; a total of 23930 reflections collected in the range $1.45 < \theta < 26.73$, of which 8137 were unique. GOF = 1.026, R_1 = 0.0256 [for 7543 reflections with $I > 2\sigma(I)$] and wR_2 = 0.0729 (for all data).

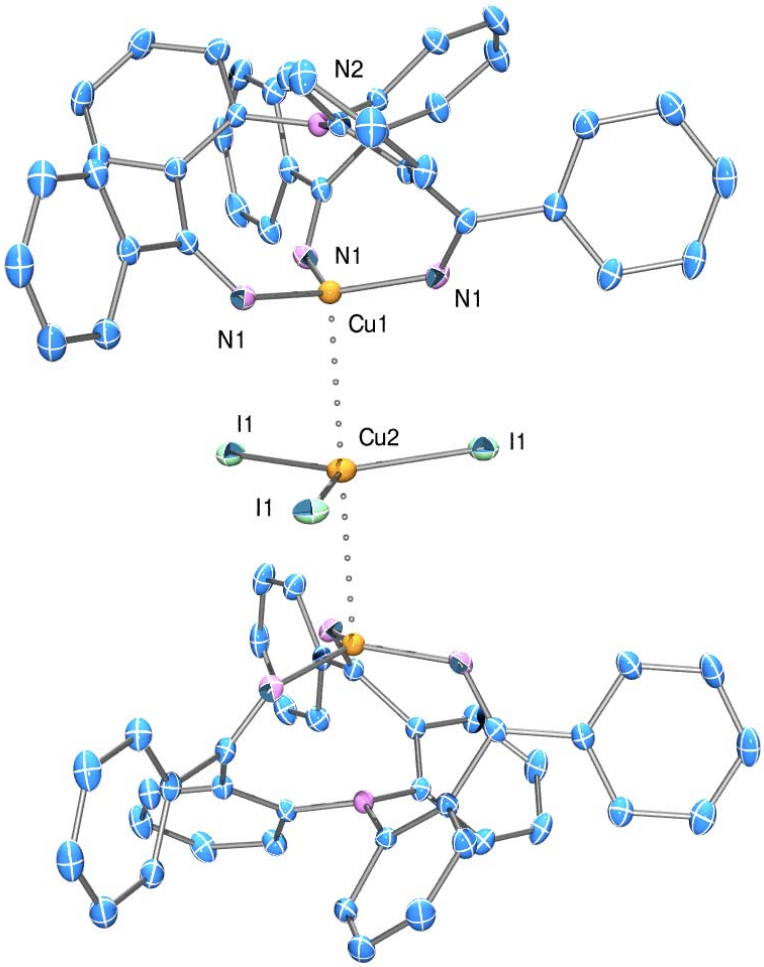

Fig. S3 Solid state molecular structure of $[N(ArCNHPh)_3Cu]_2[CuI_3]$ **(3)**. Hydrogen atoms and acetonitrile solvate molecules omitted for clarity.

The Cu2 nuclei for **3** is found in a distorted trigonal pyramidal coordination environment with N1-Cu1-N1 bond angles of 118.19(2)°. The solid state structure reveals a Cu2-N1 distance of 1.9304(16) Å, consistent with those exhibited by complex **2**. Cu2 resides 0.2621(15) Å out of the plane defined by the three ketimine nitrogen. The Cu2-Cu3 bond distance (2.9190(4) Å) is greater than the sum of the covalent radii[7] and the Cu3-I1 bond distance (2.5892(2) Å) is consistent with that for other compounds with the CuI_3^{2-} dianion (2.546(2),[8] 2.606(1)[9] Å).

Crystal data for **3**·7MeCN: $C_{92}H_{81}N_{15}Cu_3I_3$, M = 1968.04, hexagonal, space group *P6(3)/m*, a = 16.9356(8) Å, b = 16.9356(8) Å, c = 17.9643(8) Å, α = 90°, β = 90°, γ = 120°, V = 4462.1(4) Å^3, Z = 2, T = 100(2) K, λ = 0.71073 Å, R_{int} = 0.0369; a total of 26538 reflections collected in the range $1.39 < \theta < 35.19$, of which 6797 were unique. GOF = 1.020, R_1 = 0.0363 [for 4969 reflections with $I > 2\sigma(I)$] and wR_2 = 0.0997 (for all data).

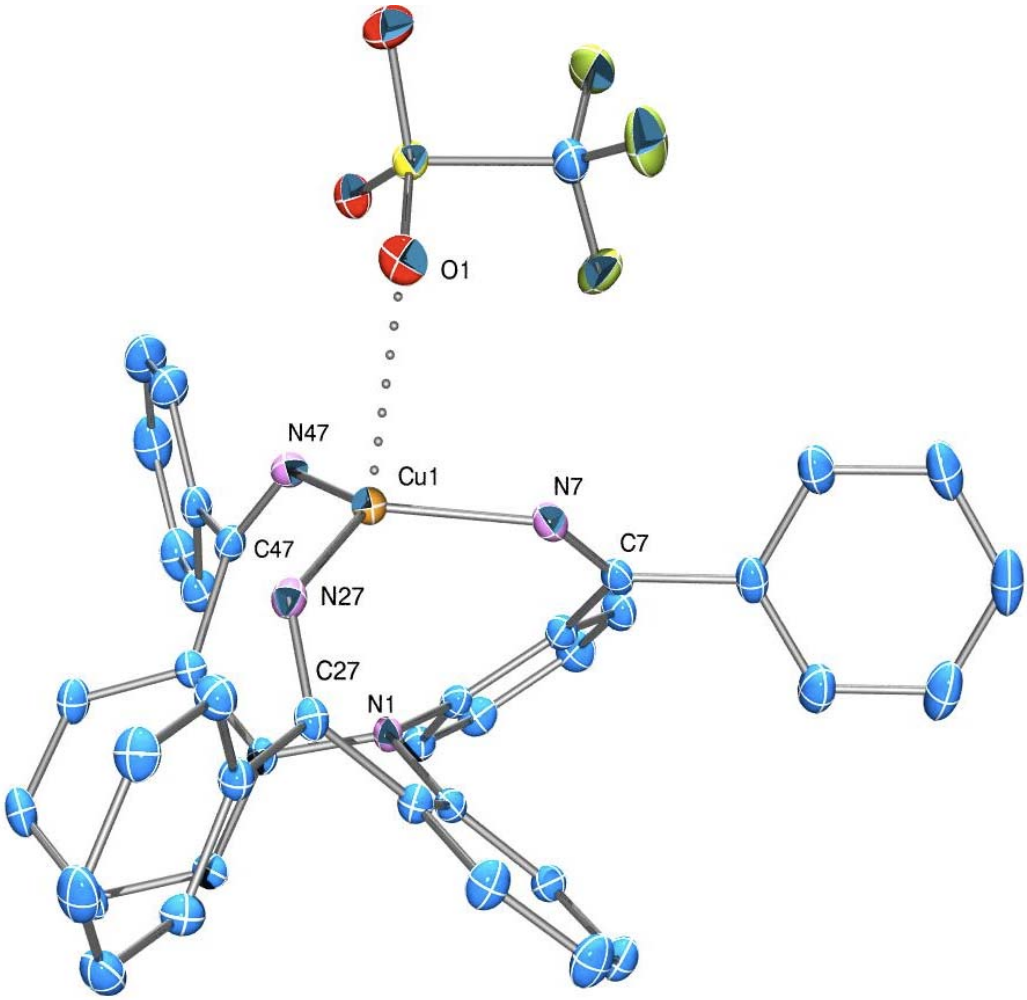

Fig. S4 Solid state molecular structure of [N(ArCNHPh)$_3$Cu][OTf] **(4)**. Hydrogen atoms and methylene chloride solvate molecules omitted for clarity.

Crystal data for **4**·1.5CH_2Cl_2: $C_{41.5}H_{33}N_4Cl_3CuF_3O_3S$: M = 894.67, monoclinic, space group *C2/c*, a = 18.3059(5) Å, b = 17.9205(5) Å, c = 24.6247(7) Å, α = 90°, β = 104.0330(10)°, γ = 90°, V = 7837.1(4) Å^3, Z = 8, T = 100(2) K, λ = 0.71073 Å, R_{int} = 0.0181; a total of 30855 reflections collected in the range 2.14 < θ < 28.28, of which 9698 were unique. GOF = 1.016, R_1 = 0.0395 [for 8467 reflections with $I > 2\sigma(I)$] and wR_2 = 0.1034 (for all data).

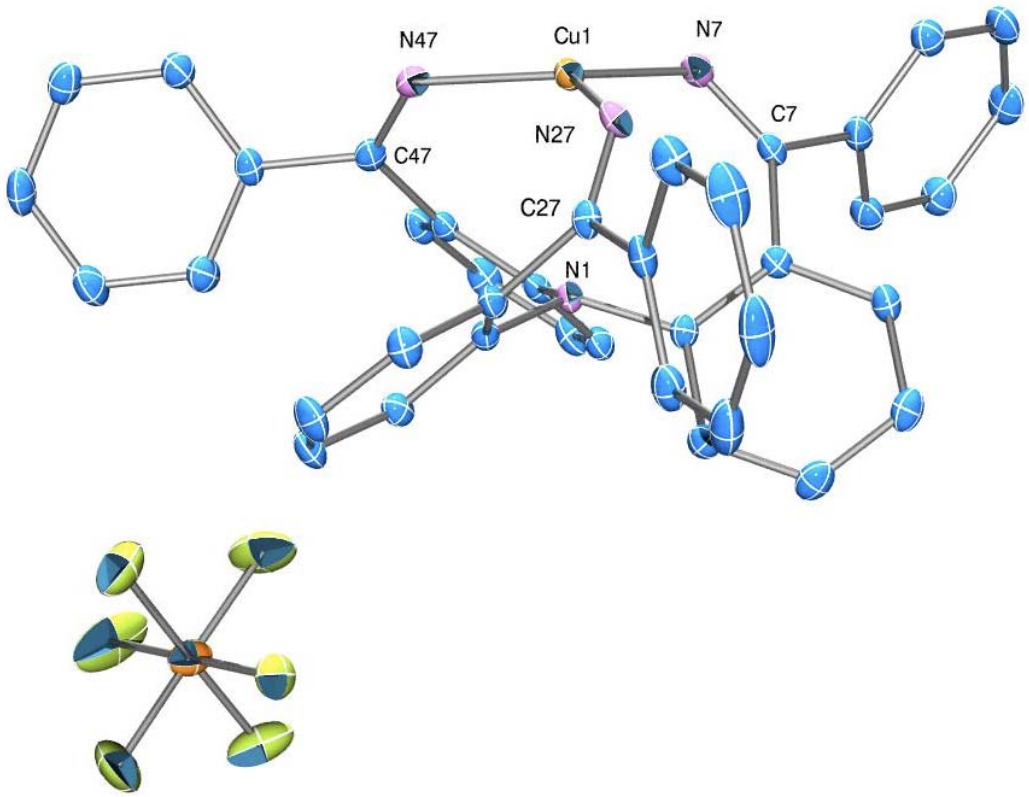

Fig. S5 Solid state molecular structure of $[N(ArCNHPh)_3Cu][PF_6]$ **(5)**. Hydrogen atoms and methylene chloride solvate molecules omitted for clarity.

Crystal data for **5**·$4CH_2Cl_2$: $C_{43}H_{38}N_4CuCl_8F_6P$: M = 1102.88, triclinic, space group *P-1*, a = 12.7642(6) Å, b = 13.1378(6) Å, c = 16.1379(7) Å, α = 107.663°, β = 91.273(3)°, γ = 113.713(2)°, V = 2328.44(18) Å^3, Z = 2, T = 100(2) K, λ = 0.71073 Å, R_{int} = 0.0305; a total of 27387 reflections collected in the range 1.77 < θ < 28.28, of which 11511 were unique. GOF = 1.187, R_1 = 0.0472 [for 8860 reflections with $I > 2\sigma(I)$] and wR_2 = 0.0953 (for all data).

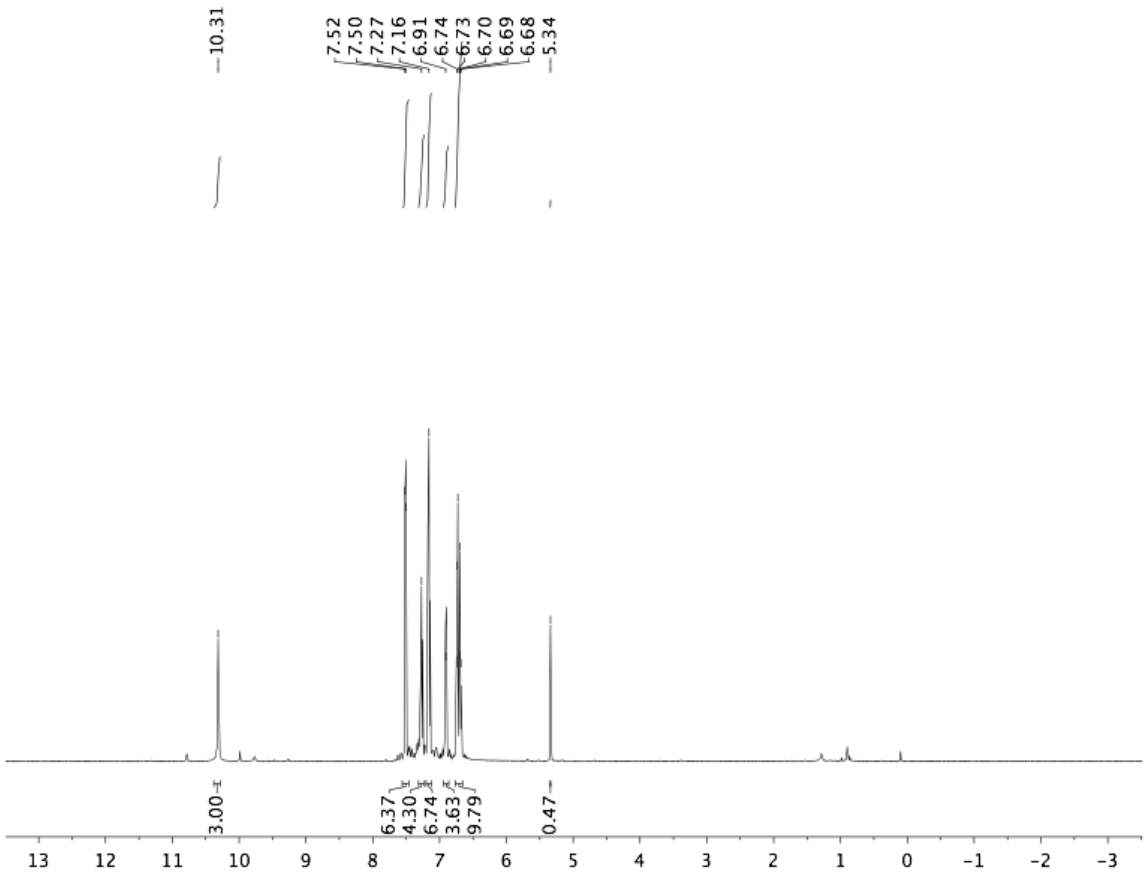

Figure S6. ^{1}H NMR spectrum of N(ArCNHPh)$_3$ (**1**) in CD_2Cl_2.

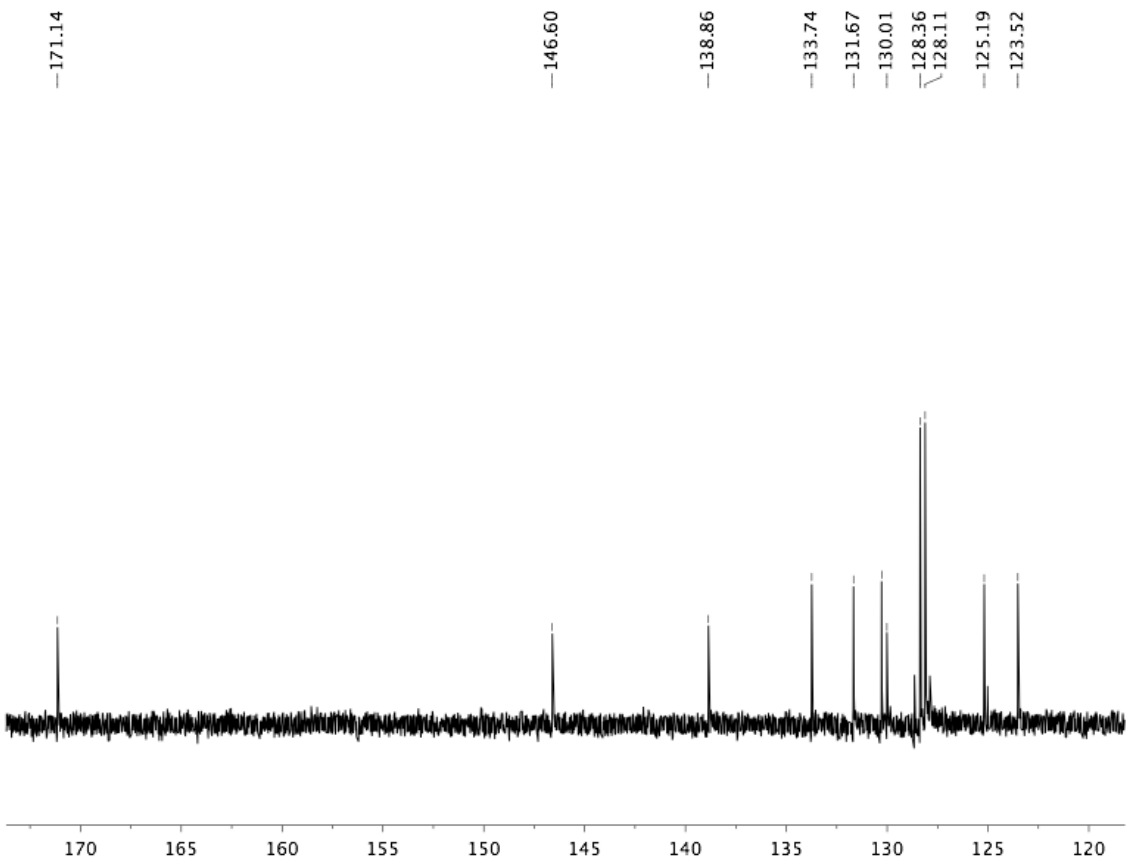

Figure S7. $^{13}C\{^{1}H\}$ NMR spectrum of $N(ArCNHPh)_3$ (**1**) in THF-d_8.

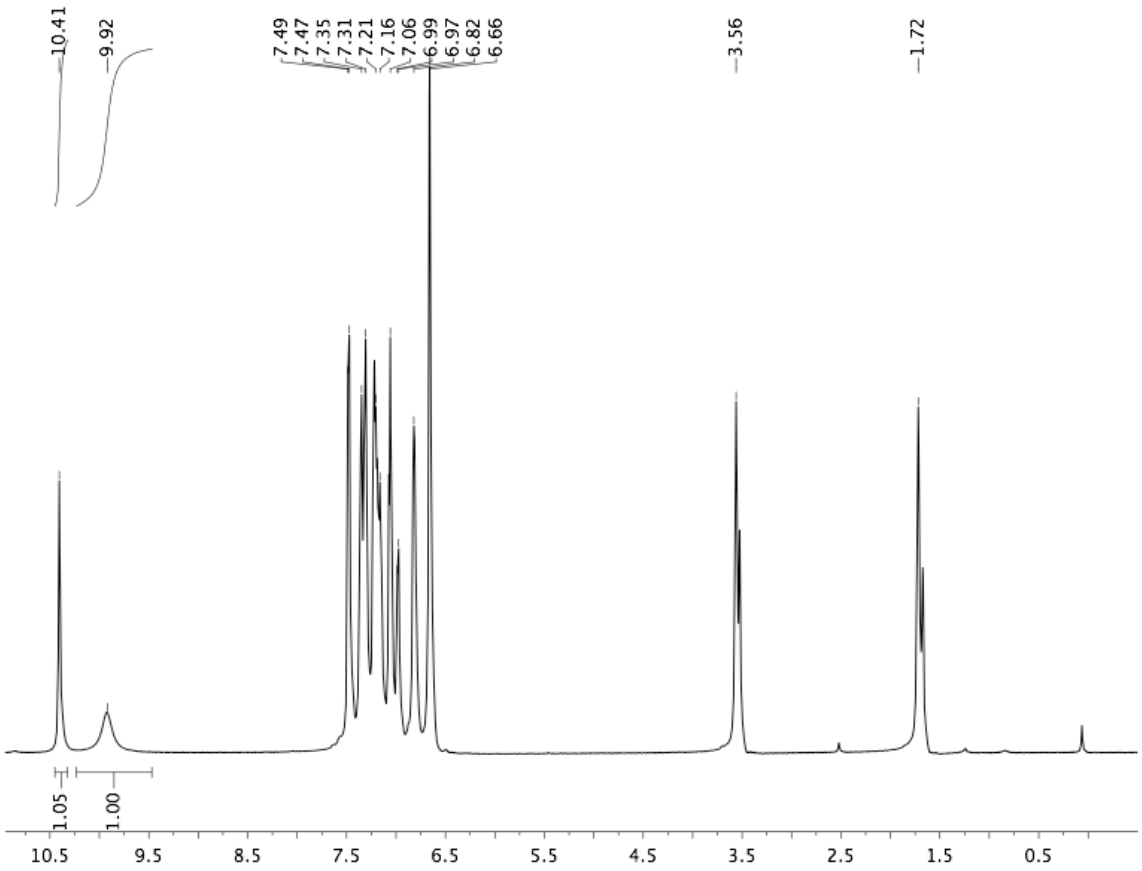

Figure S8. ^{1}H NMR spectrum of the equimolar combination of N(ArCNHPh)$_3$ (**1**) with CuCl in THF-d_8. The resonance at 10.41 ppm is assigned to the imine protons of the free scaffold N(ArCNHPh)$_3$, while the resonance at 9.92 ppm is assigned to [N(ArCNHPh)$_3$Cu][CuCl$_2$] (**2**).

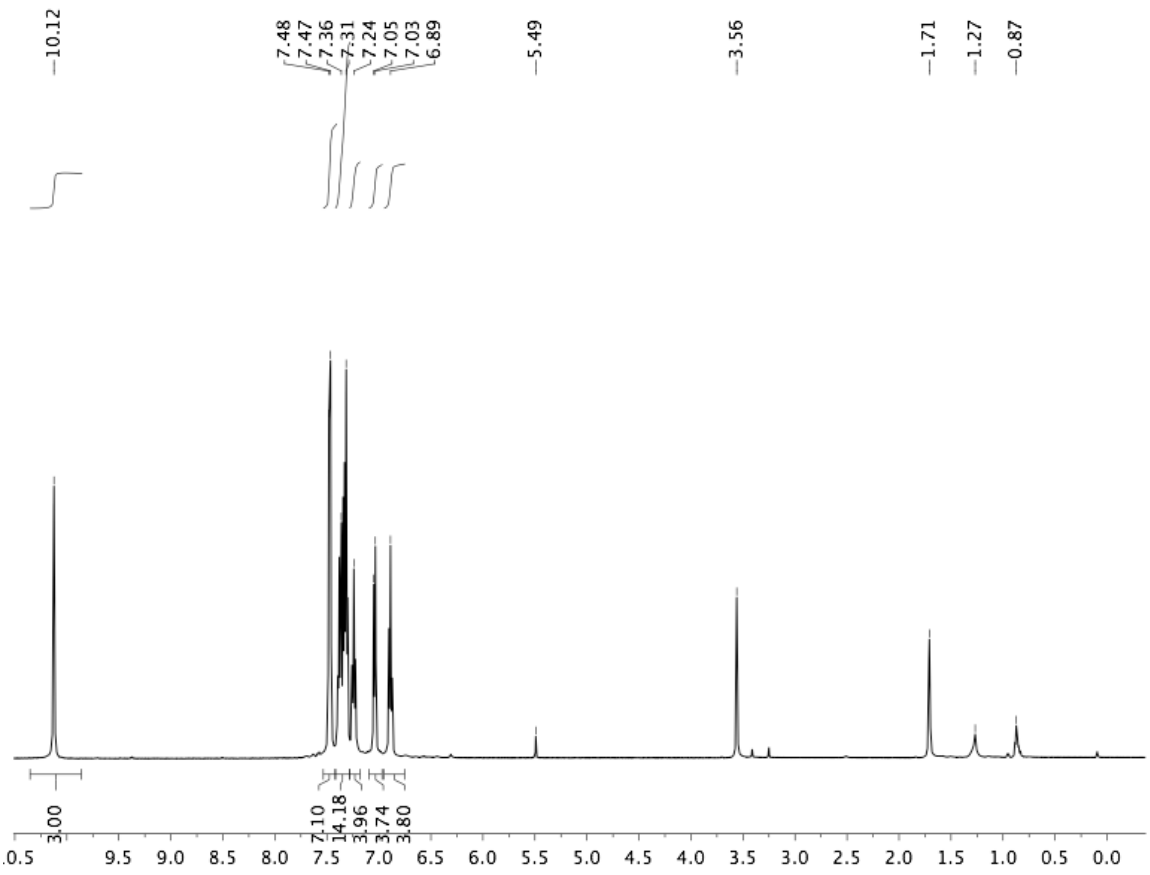

Figure S9. ^{1}H NMR spectrum of $[N(ArCNHPh)_3Cu][CuCl_2]$ (**2**) in THF-d_8.

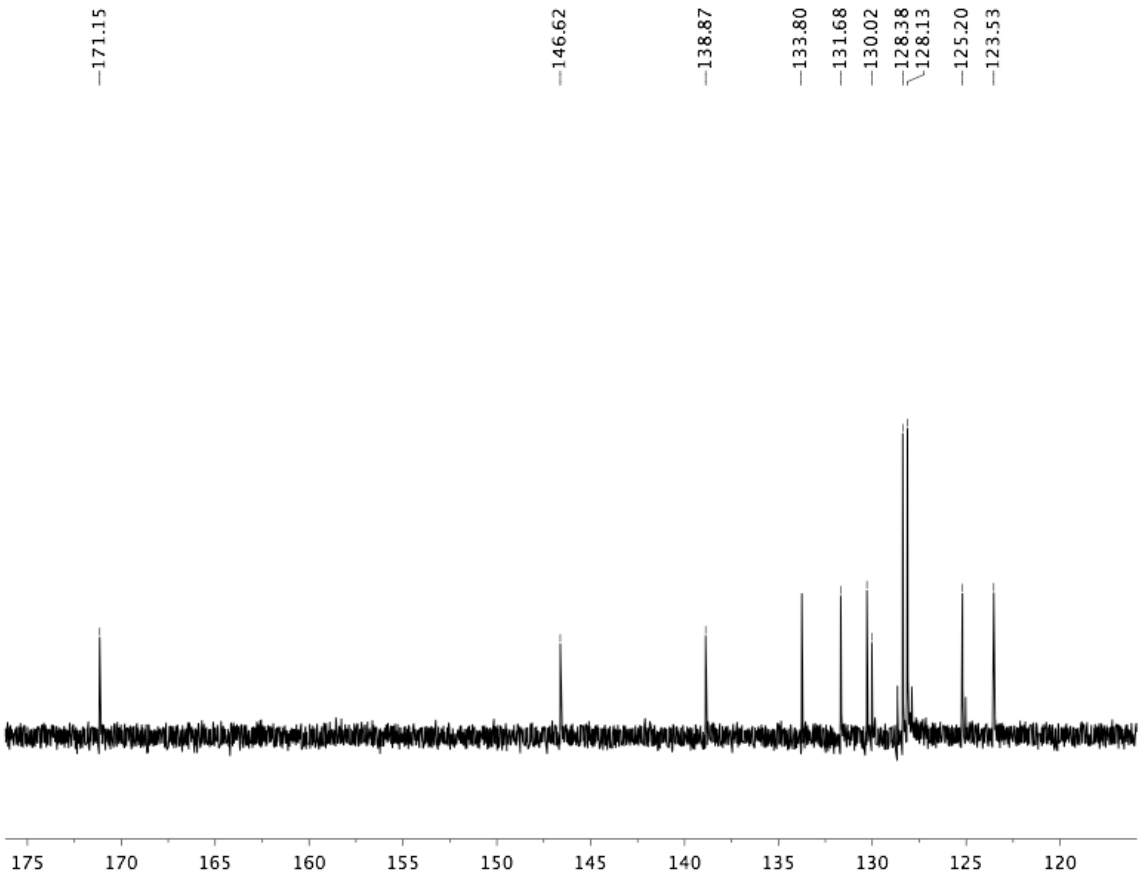

Figure S10. $^{13}C\{^{1}H\}$ NMR spectrum of $[N(ArCNHPh)_3Cu][CuCl_2]$ (**2**) in THF-d_8.

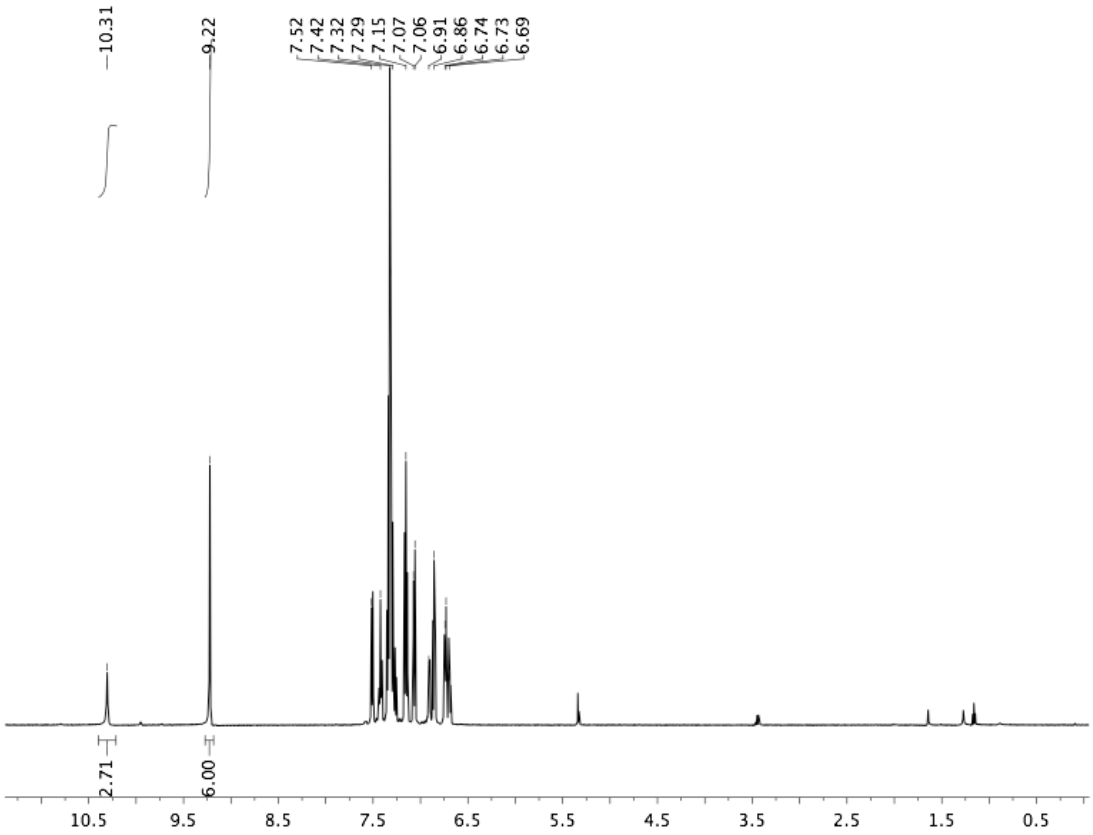

Figure S11. ^{1}H NMR spectrum of the equimolar combination of N(ArCNHPh)$_3$ (**1**) with CuI in CD_2Cl_2. The resonance at 10.31 ppm is assigned to the imine protons of the free scaffold N(ArCNHPh)$_3$, while the resonance at 9.22 ppm is assigned to [N(ArCNHPh)$_3$Cu]$_2$[CuI$_3$] (**3**).

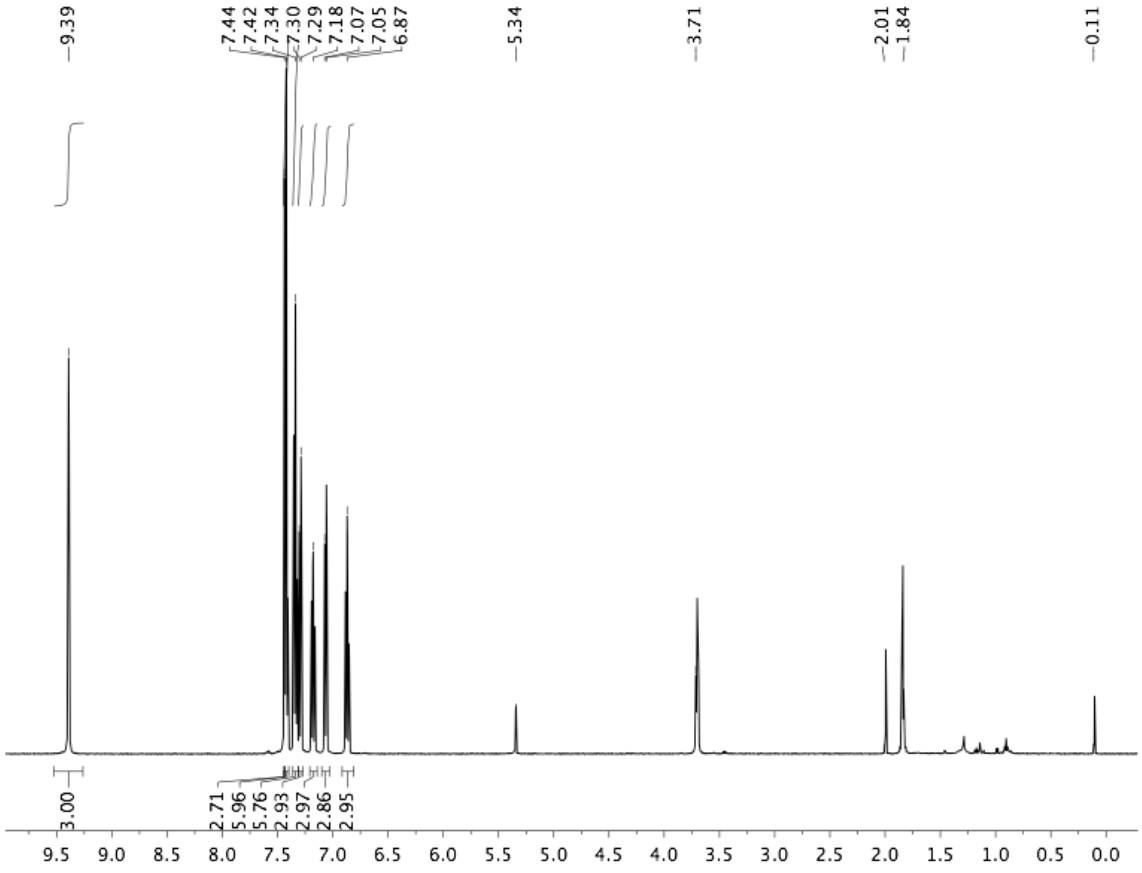

Figure S12. ^{1}H NMR spectrum of $[N(ArCNHPh)_3Cu]_2[CuI_3]$ (**3**) in CD_2Cl_2.

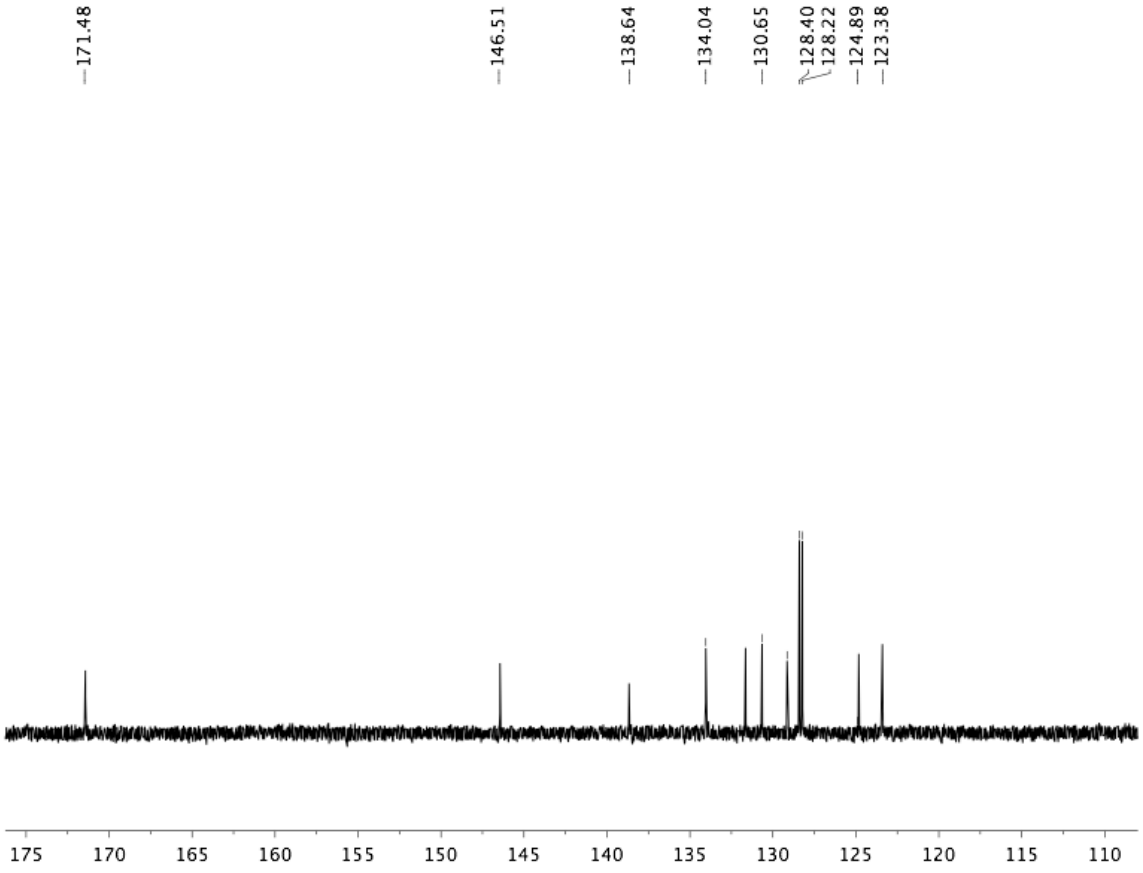

Figure S13. $^{13}C\{^{1}H\}$ NMR spectrum of $[N(ArCNHPh)_3Cu]_2[CuI_3]$ (**3**) in CD_2Cl_2.

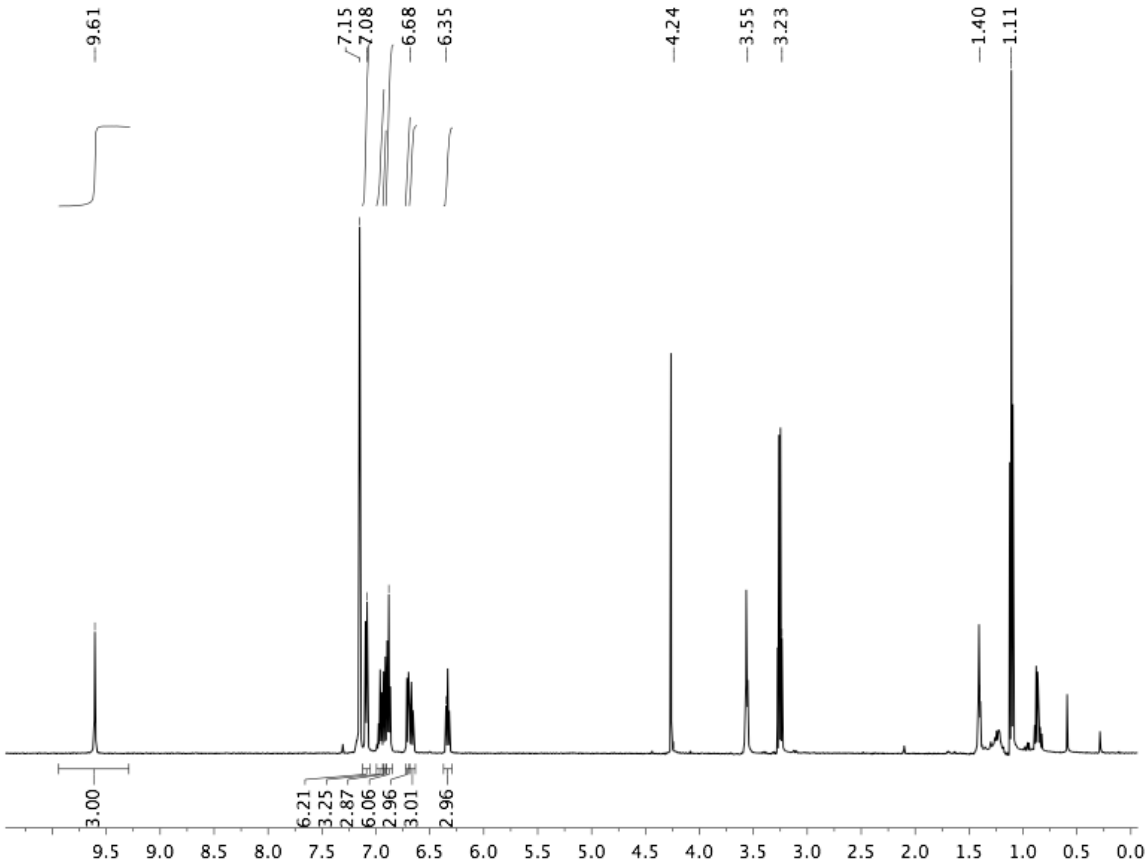

Figure S14. ^{1}H NMR spectrum of [N(ArCNHPh)$_3$Cu][OTf] (**4**) in C_6D_6. Residual CH_2Cl_2 is observed at 4.24 ppm, THF at 3.55 ppm and 1.40 ppm, and diethyl ether at 3.23 and 1.11 ppm.

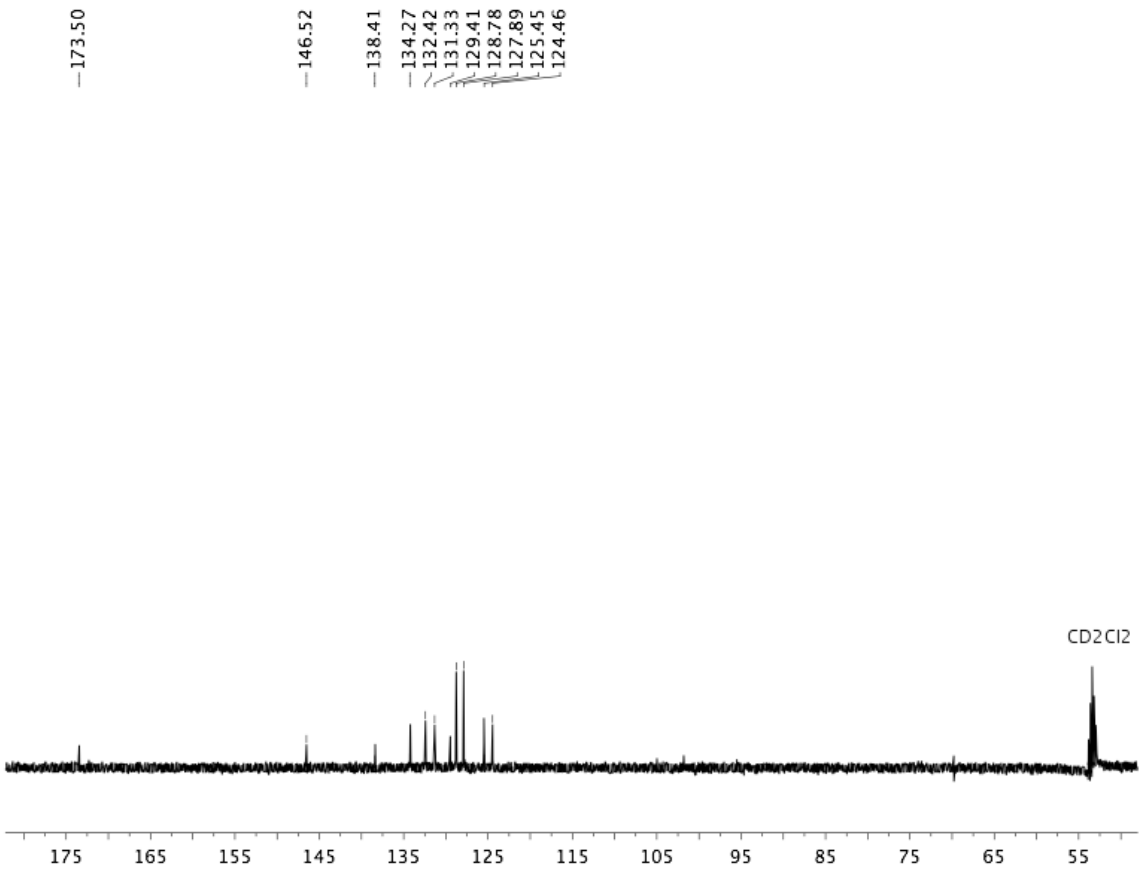

Figure S15. $^{13}C\{^{1}H\}$ NMR spectrum of $[N(ArCNHPh)_3Cu][OTf]$ (**4**) in CD_2Cl_2

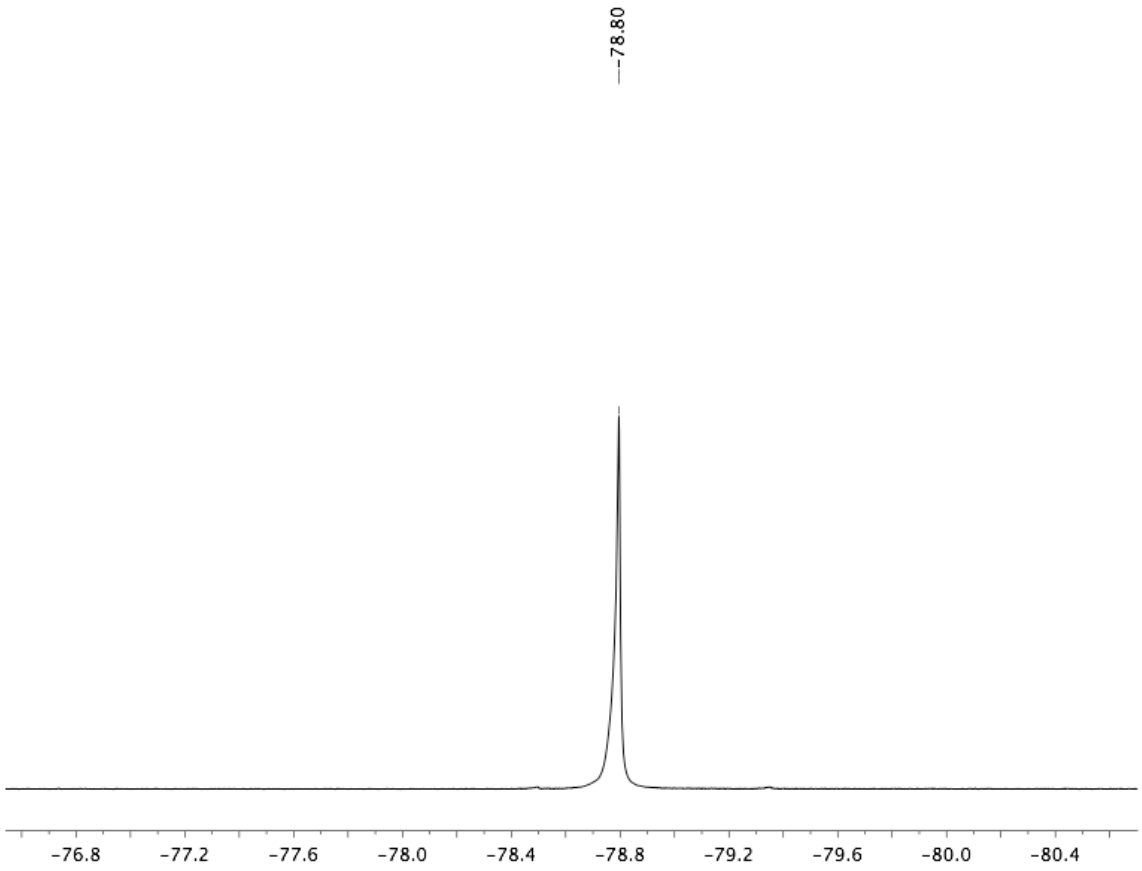

Figure S16. ^{19}F NMR spectrum of $[N(ArCNHPh)_3Cu][OTf]$ (**4**) in CD_2Cl_2

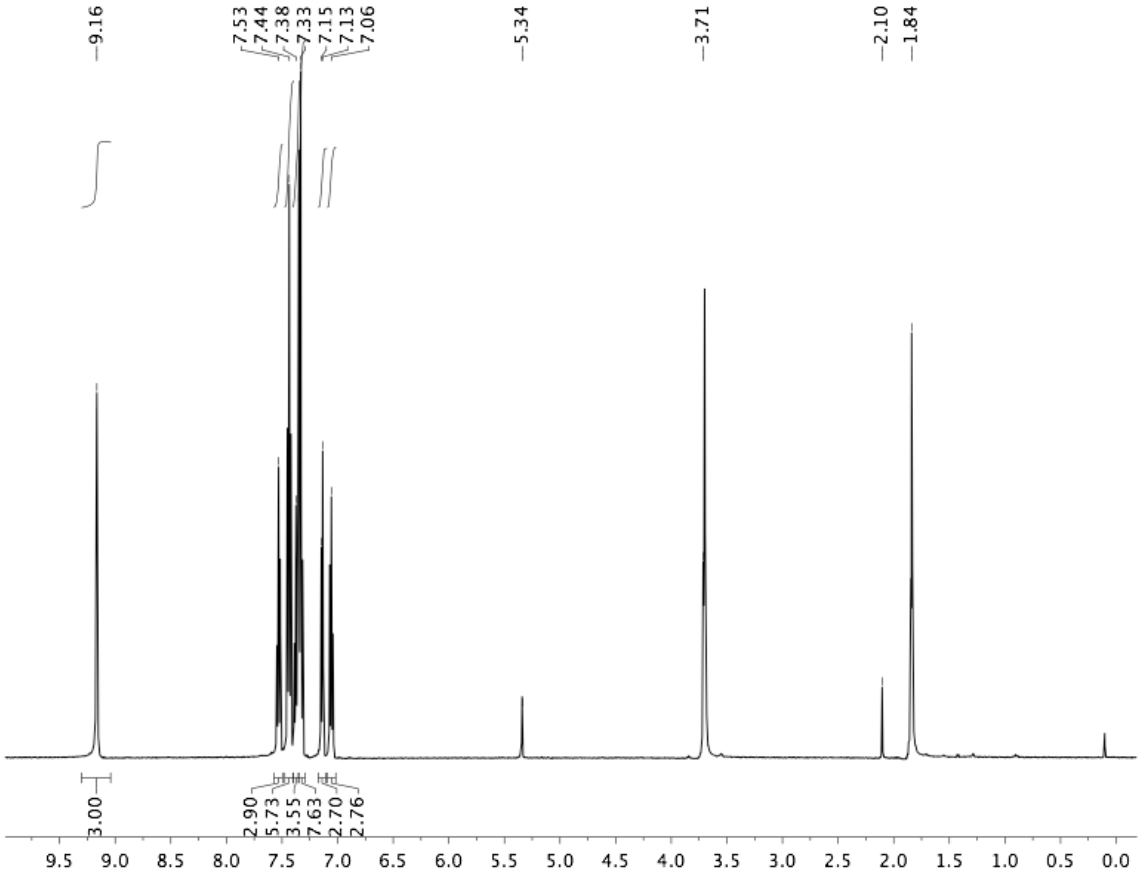

Figure S17. ^{1}H NMR spectrum of $[N(ArCNHPh)_3Cu][PF_6]$ (**5**) in CD_2Cl_2. Residual THF is observed at 3.71 ppm and 1.84 ppm and toluene at 2.10 ppm.

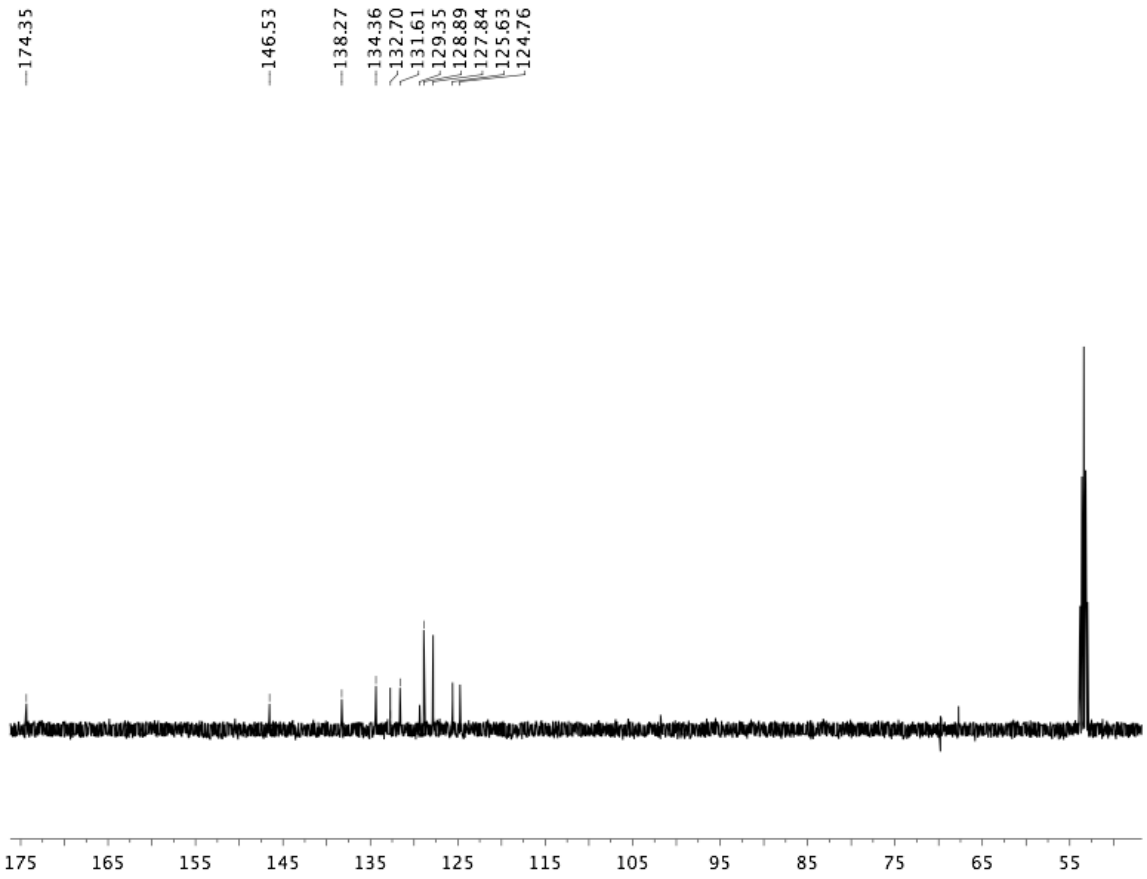

Figure S18. $^{13}C\{^{1}H\}$ NMR spectrum of $[N(ArCNHPh)_3Cu][PF_6]$ (**5**) in CD_2Cl_2.

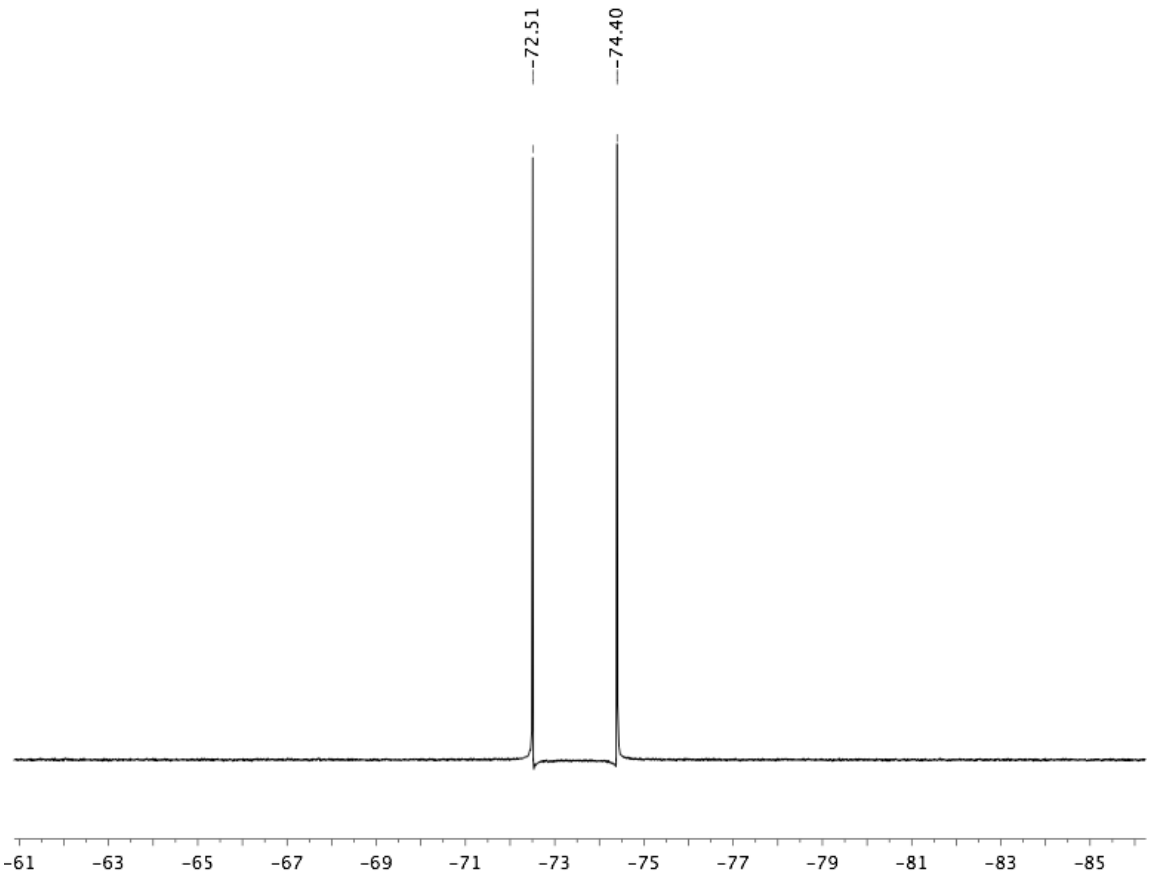

Figure S19. ^{19}F NMR spectrum of $[N(ArCNHPh)_3Cu][PF_6]$ (**5**) in CD_2Cl_2.

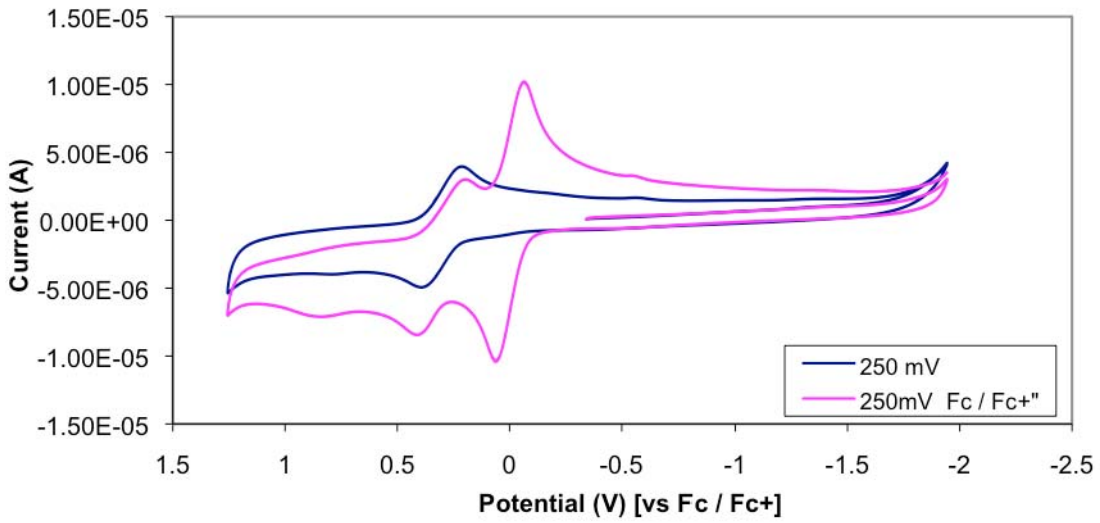

Figure S20. Complete cyclic voltammogram of a 0.66 mM solution of $[N(ArCNHPh)_3Cu][OTf]$ (**4**) (250 mV/s, vs. Fc/Fc^+) measured in CH_2Cl_2 with 0.1 M $[NBu_4][PF_6]$ as supporting electrolyte. The feature centred at 0.28 V is assignable to the Cu^I/Cu^{II} couple.

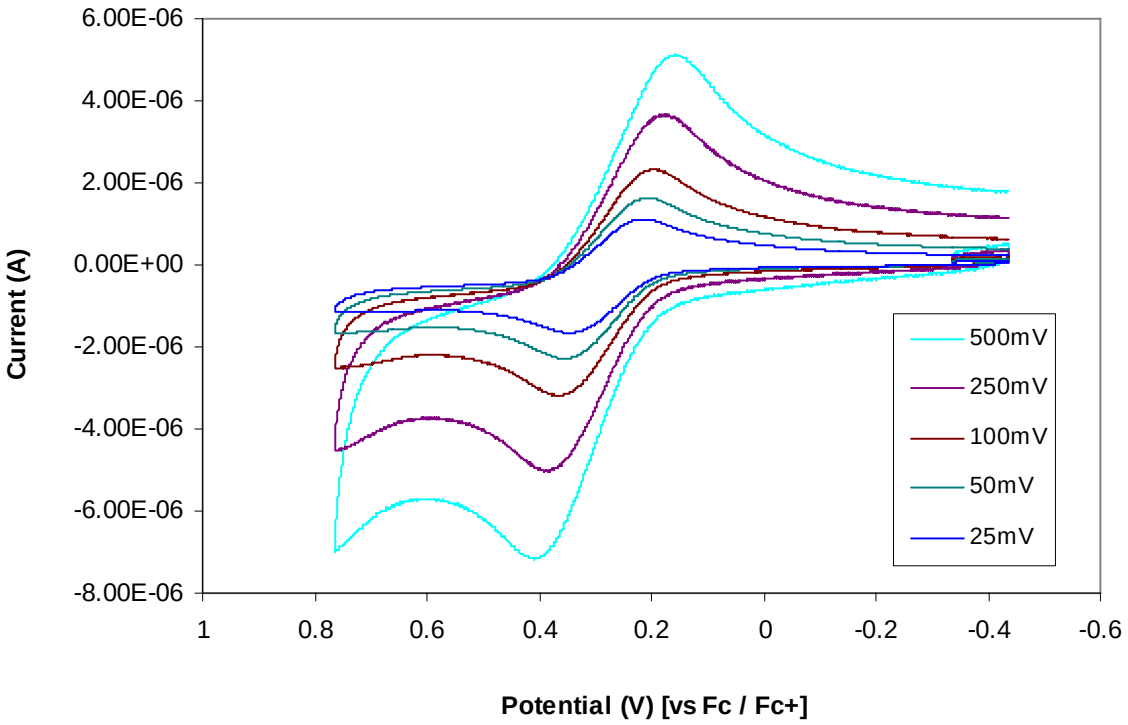

Figure S21. Partial cyclic voltammogram of a 0.66 mM solution of [N(ArCNHPh)$_3$Cu][OTf] (**4**) (vs. Fc/Fc$^+$). Measured in CH_2Cl_2 with 0.1 M [NBu_4][PF_6] as supporting electrolyte.

Table S1. Electrochemical parameters for [N(ArCNHPh)$_3$Cu][OTf] (**4**) in CH_2Cl_2 (vs. Fc/Fc$^+$, [NBu_4][PF_6] as supporting electrolyte).

Oxidation feature	Scan rate, mV/s	$E_{p,a}$, V	$E_{p,c}$, V	$\Delta E_p{}^a$	$i_{p,c}/i_{p,a}$
	25	0.361	0.202	0.159	1.01
	50	0.368	0.195	0.173	0.989
	100	0.375	0.181	0.194	0.943
	250	0.400	0.164	0.236	0.833
	500	0.420	0.147	0.273	0.695

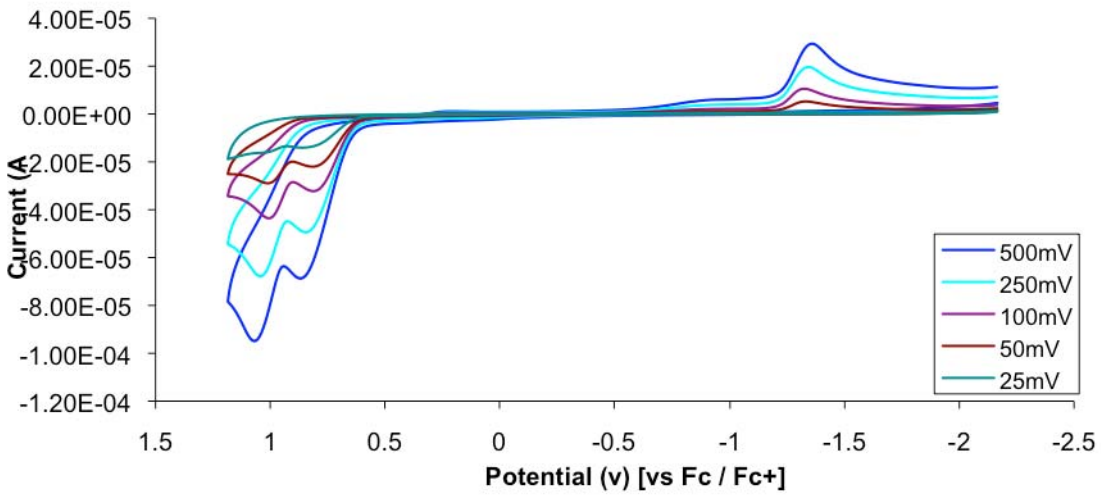

Figure S22. Complete cyclic voltammogram of a 3.4 mM solution of $N(ArCNHPh)_3$ (**1**) (vs. Fc/Fc^+) measured in CH_2Cl_2 with 0.1 M $[NBu_4][PF_6]$ as supporting electrolyte. The irreversible features at 0.832 V and 1.032 V are assignable to ligand centered oxidations, while the feature centred at -1.353 V is assignable to the reduction of an oxidation product.

Table S2. Electrochemical parameters for $N(ArCNHPh)_3$ (**1**) in CH_2Cl_2 (vs. Fc/Fc^+, $[NBu_4][PF_6]$ as supporting electrolyte).

Reduction feature 1	Scan rate, mV/s	$E_{p,c}$, V
	25	-1.356
	50	-1.348
	100	-1.336
	250	-1.353
	500	-1.369
Oxidation feature 1	Scan rate, mV/s	$E_{p,a}$, V
	25	0.843
	50	0.800
	100	0.798
	250	0.832
	500	0.857
Oxidation feature 2	Scan rate, mV/s	$E_{p,a}$, V
	25	1.013
	50	0.997
	100	0.993
	250	1.032
	500	1.055

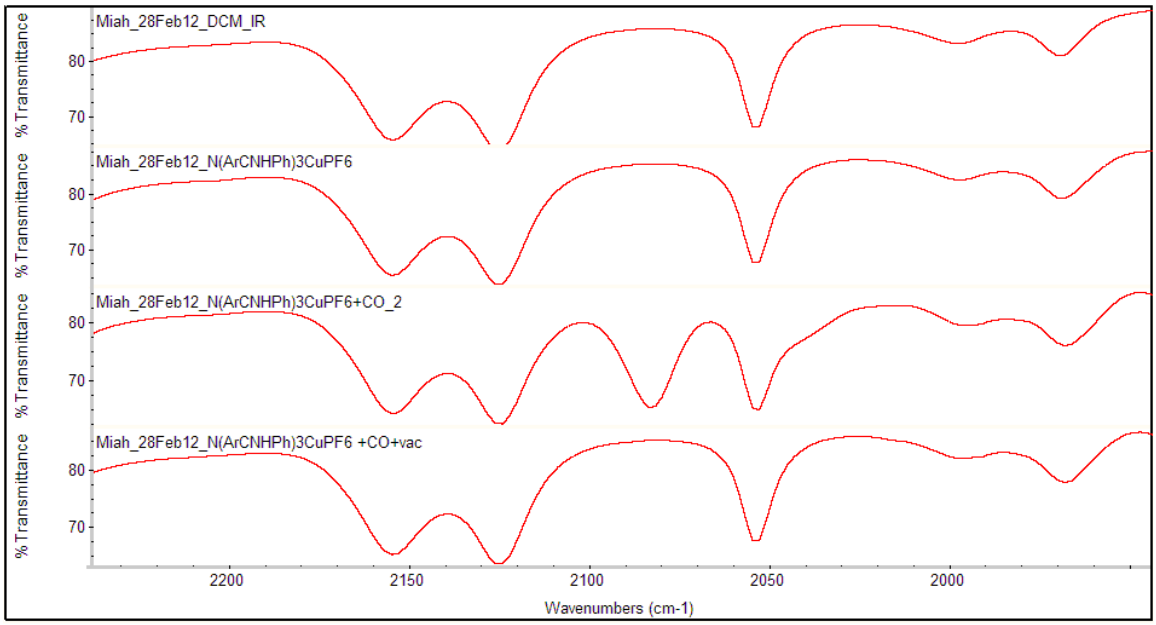

Figure S23. IR spectrum of dichloromethane (Top); complex **5** prior to addition of CO (2^{nd} from Top); complex **5** after addition of CO (2^{nd} from bottom); and complex **5** after the sample had been placed under vacuum for several minutes (Bottom). The absorption at 2086 cm^{-1} has been assigned to ν_{CO} stretch of CO bound to Cu^{I}.

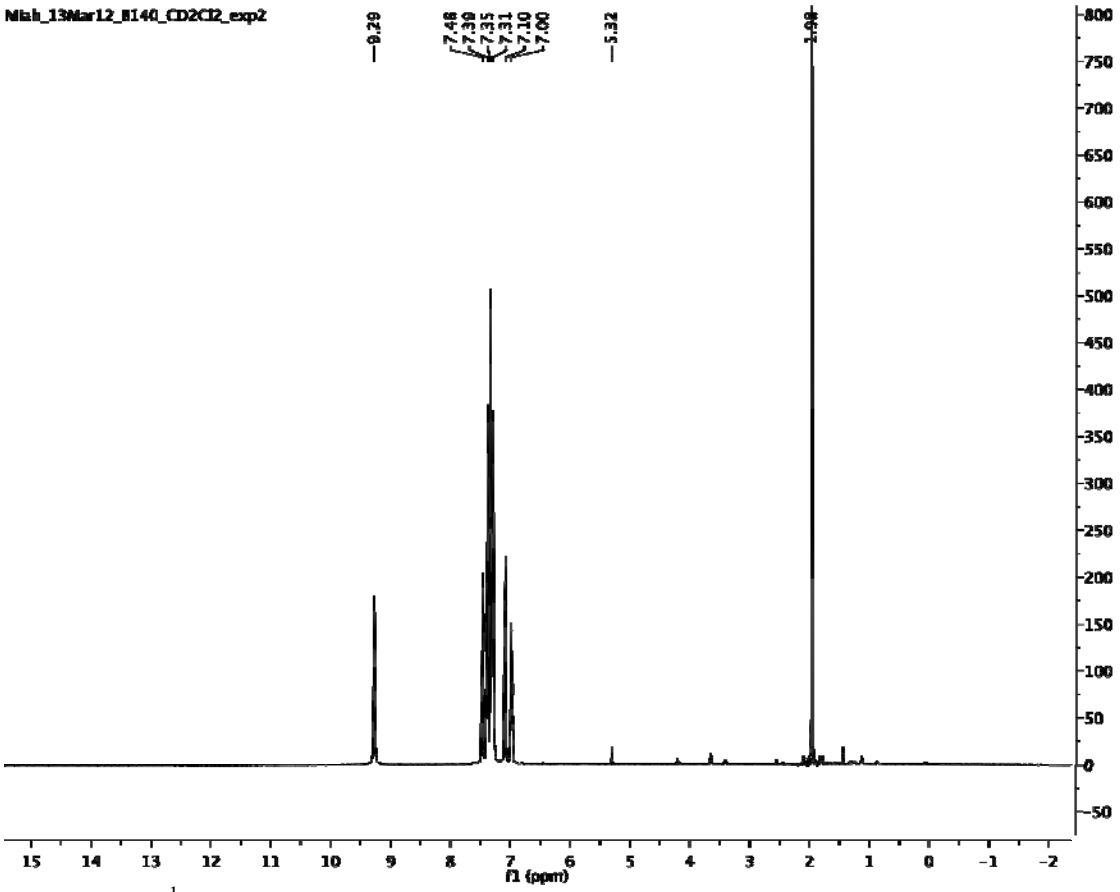

Figure S24. ^{1}H NMR spectrum of [N(ArCNHPh)$_3$Cu][OTf] (**4**) generated in situ from [Cu(MeCN)$_4$][OTf] and **1** in CD_2Cl_2 in a sealed J-young tube prior to introduction of an atmosphere of O_2. The resonance at 1.98 ppm is assignable to MeCN.

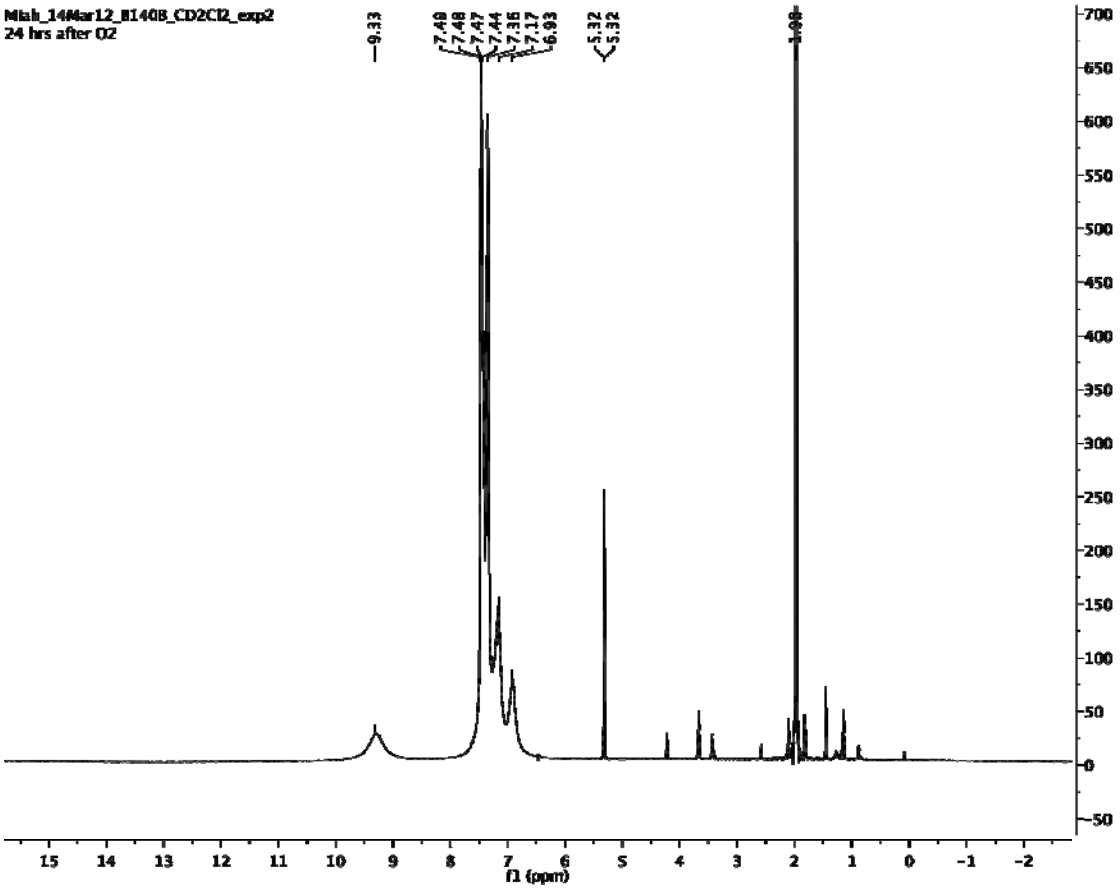

Figure S25. ^{1}H NMR spectrum of [N(ArCNHPh)$_3$Cu][OTf] (**4**) in CD_2Cl_2 in a sealed J-young tube 24 hr after introduction of an atmosphere of O_2.

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