Supporting Information

Synthesis and Characterisation of Copper(I) Complexes with Relevance to Intramolecular Ullmann *O*, *S*-arylation

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1 Experimental

1.1 General

For reactions that required air-free techniques, all glassware was pre-dried at 120 °C overnight and loaded in a glove-box under nitrogen. The experiments were carried out under a protective atmosphere of N_2. Anhydrous solvents such as dichloromethane, tetrahydrofuran, hexane, and toluene were obtained from a solvent tower using the PureSolv solvent purification system, degassed under N_2, and stored over molecular sieves. Anhydrous DMSO and dioxane were purchased in Sure/Seal™ bottles and used directly from the bottle. Deuterated solvents such as DMSO-d_6 and chloroform-*d* were purchased from Sigma-Aldrich or VWR and dried over 4 Å molecular sieves under N_2 before use. Copper(I) iodide (99.999% trace metals basis, powder) purchased from Sigma-Aldrich was stored in a glove box under N_2. All ligands and aryl halides were purchased from Sigma-Aldrich or VWR and used as received without further purification.

^{1}H and ^{13}C NMR analysis was carried out at room temperature using Bruker AV-400 spectrometers. Chemical shifts (δ) are reported in parts per million (ppm) from tetramethylsilane and are referenced to the residual protonated solvent and carbon resonances of the solvent in ^{1}H and ^{13}C NMR spectra respectively. Coupling constants (*J*) are *J* coupling constant values are given in Hz units. ^{1}H and ^{13}C NMR analysis was performed using MESTRELAB MestReNova software. CHN microanalyses were carried out at the London Metropolitan University, UK. GC-MS analysis was performed on a Micromass Autospec Premier/Agilent HP6890 GC.

1.2 Synthesis of 2-Halogenbenzanilide

Compounds were prepared according to previous publication.[1] 2-halogenaniline (5.0 mmol) was dissolved in dry THF (10 mL) in a round bottom flask at room temperature followed by slow addition of benzoyl chloride (5.0 mmol) and the mixture was stirred at room temperature for 2 h. The solvent was removed by rotary evaporation, yielding the

solid crude product. The solid was redissolved in 20 mL ethyl acetate and washed with distilled water and brine and the organic layer was separated and dried over $MgSO_4$. The pure product was collected by rotary evaporation without any further purification.

2-Chlorobenzanilide (**1a**): white solid (1.14 g, 98%); Melting point: 112 – 115 °C (lit 114 – 116°C); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.59 (dd, *J* = 8.3, 1.5 Hz, 1H), 8.49 (s, 1H), 7.99 – 7.91 (m, 2H), 7.65 – 7.55 (m, 1H), 7.59 – 7.49 (m, 2H), 7.44 (dd, *J* = 8.0, 1.5 Hz, 1H), 7.40 – 7.31 (m, 1H), 7.11 (ddd, *J* = 8.0, 7.4, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.29, 134.75, 134.63, 132.20, 129.03, 128.95, 127.89, 127.10, 124.76, 123.04, 121.52; IR (ATR) ν_{max}/cm^{-1}: 3219 (N-H), 1651 (C=O), 1517 (N-H), 1298 (C-C aromatic), 1057 (C-N), 711 (C-Cl); MS: *m/z* = 232.0 $[M + H]^+$.

2-Bromobenzanilide (**1b**): Light yellow solid (1.32 g, 96%); Melting point: 112 – 113 °C (lit. 111 – 113 °C); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.58 (dd, *J* = 8.2, 1.6 Hz, 1H), 8.50 (s, 1H), 8.01 – 7.86 (m, 2H), 7.65 – 7.45 (m, 4H), 7.39 (ddd, *J* = 8.5, 7.5, 1.5 Hz, 1H), 7.04 (td, *J* = 7.7, 1.6 Hz, 1H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 165.45, 136.03, 134.80, 132.46, 132.41, 129.17, 128.76, 127.31, 125.48, 121.95, 113.94. IR (ATR) ν_{max}/cm^{-1}: 3276 (N-H), 1652 (C=O), 1578 (N-H), 1310 (C-C aromatic), 1028 (C-N), 642 (C-Br); MS: *m/z* = 276.0 $[M + H]^+$.

1.3 Synthesis of 2-Halogenthiobenzanilide

Compounds were prepared according to previous publication.[2] The Lawesson's reagent (4.8 mmol) was added to a solution of 2'-halobenzanilide (4.0 mmol) in dry THF (20 mL). The mixture was refluxed for 6 h at 80 °C followed by evaporation of the solvent under vacuum. The pure product was obtained after purification by flash chromatography (Hexane: EtOAc = 1: 1).

2-Chlorothiobenzanilide (**2a**): Yellow solid (0.81 g, 82%); Melting point: 71 – 73 °C (lit. 69 – 71 °C); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.34 (s, 1H), 8.76 (s, 1H), 7.92 (d, *J* = 7.5 Hz, 2H), 7.62 – 7.33 (m, 28H), 7.32 – 7.20 (m, 5H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 135.77, 131.51, 129.59, 128.77, 127.52, 127.23, 126.94, 126.85,

125.01; IR (ATR) ν_{max}/cm^{-1}: 3195 (NH), 1503 (C-S), 1441 (C=C aromatic), 1058 (C-N), 683 (C-Cl); MS: *m/z* = 248.0 $[M + H]^+$.

2-2-Bromothiobenzanilide (**2b**): Yellow crystalline (1.15 g, 79%); Melting point: 86 – 88 °C (lit. 83 – 85 °C); ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.31 (s, 1H), 8.68 (s, 1H), 7.98 – 7.90 (m, 2H), 7.70 (dd, *J* = 8.1, 1.5 Hz, 1H), 7.62 – 7.37 (m, 4H), 7.20 (td, *J* = 7.7, 1.6 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 136.96, 132.83, 131.52, 128.75, 128.03, 127.88, 126.90, 125.62, 117.76, 76.73. IR (ATR) ν_{max}/cm^{-1}: 3188 (N-H), 1499 (C-S), 1484 (C=C aromatic), 685 (C-Br); MS: *m/z* = 292.0 $[M + H]^+$.

1.4 Synthesis of 1-Benzyl-3-(2-halogenphenyl) Thiourea

Compounds were prepared according to previous publication.[1] 2-Halogenisothiocyanate (5.0 mmol) was slowly added to a solution of benzylamine (5.0 mmol) and triethylamine (5.0 mmol) in DCM (50 mL). The reaction was allowed to run overnight to reach the completion. Solid product was obtained after evaporation of the solvent under vacuum. No further purification was required.

1-Benzyl-3-(2-chlorogenphenyl)-thiourea (**3a**): White solid (1.21 g, 94%); Melting point: 160 – 162°C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 – 7.45 (m, 2H), 7.39 – 7.36 (m, 1H), 7.36 – 7.29 (m, 5H), 7.24 (td, *J* = 7.7, 1.7 Hz, 1H), 4.89 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 128.86, 127.74, 127.01, 110.00 IR (ATR) ν_{max}/cm^{-1}: 3217 (N-H), 3053 (N-H), 1546 (C=S), 1311 (C-C aromatic), 1054 (C-N), 727 (C-Cl); MS: *m/z* = 277.0 $[M + H]^+$.

1-Benzyl-3-(2-bromogenphenyl)-thiourea (**3b**): Pale yellow solid (1.52 g, 95%); Melting point: 156 – 158 °C; ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.68 (dd, J = 8.1, 1.4 Hz, 1H), 7.46 (t, *J* = 4.3 Hz, 1H), 7.37 (dd, *J* = 7.5, 1.4 Hz, 2H), 7.35 – 7.25 (m, 5H), 7.18 (td, *J* = 7.8, 1.7 Hz, 1H), 6.23 (s, 1H), 4.89 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 128.86, 127.91, 127.75, 127.37 IR (ATR) ν_{max}/cm^{-1}: 3216 (N-H), 3050 (N-H), 1546 (C=S), 1336 (C-C aromatic), 693 (C-Br); MS: *m/z* = 321.0 $[M + H]^+$.

1.5 Synthesis of 1-Benzyl-3-(2-halogenphenyl) Urea

Compounds were prepared according to previous publication.[3] Benzyl isocyanate (5.0 mmol) was slowly added to a solution of benzylamine (5.0 mmol) and triethylamine (5.0 mmol) in dichloromethane (10 mL). The reaction was allowed to run overnight to reach the completion. White solid was obtained after evaporation of the solvent under vacuum. No further purification was required.

1-Benzyl-3-(2-chlorogenphenyl)-urea: White solid (1.32 g, 96%); Melting point: 111 – 113°C; ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.04 (s, 1H) 8.17 (dd, J = 8.3, 1.6 Hz, 1H), 8.10 (d, J = 7.5 Hz, 1H), 7.51 – 7.43 (m, 1H), 7.43 – 7.36 (m, 2H), 7.36 – 7.20 (m, 3H), 6.96 (td, J = 7.7, 1.6 Hz, 1H), 4.32 (d, J = 5.7 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) 129.53, 128.85, 127.92, 127.74, 127.34, 122.96, 121.22, 43.32, 40.62, 40.41, 40.21; IR (ATR) ν_{max}/cm^{-1}: 3323 (N-H), 3295 (N-H), 1634 (C=O), 1589 (N-H), 699 (C-Cl); MS: m/z = 261.9 $[M + H]^+$.

1-Benzyl-3-(2-bromogenphenyl)-urea: White solid (1.41 g, 92%); Melting point: 166 – 168 °C (lit. 168 °C); ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.09 (dd, J = 8.3, 1.6 Hz, 1H), 7.93 (s, 1H), 7.59 – 7.50 (m, 2H), 7.42 – 7.29 (m, 5H), 7.28 – 7.17 (m, 1H), 6.96 – 6.85 (m, 1H), 4.32 (d, J = 5.7 Hz, 2H); ^{13}C NMR (101 MHz, DMSO-d_6) δ 132.81, 128.85, 128.43,127.75, 127.34, 123.74, 122.05, 43.35, 40.62, 40.42, 40.21; IR (ATR) ν_{max}/cm^{-1}: 3326 (N-H), 3295 (N-H), 1635 (C=O), 1555 (N-H), 494 (C-Cl); MS: m/z = 305.0 $[M + H]^+$.

1.6 General *O*- and *S*-Arylation Procedure using Cs_2CO_3

A sample vial was charged with Cs_2CO_3 (65 mg, 0.15 mmol) and aryl halides (100 µL, 1 M in DMSO-d_6, 0.1 mmol) followed by addition of CuI solution (50 µL, 0.1 M in DMSO-d_6, 5 mol%), ligand (100 µL, 0.1 M in DMSO-d_6, 10 mol%) and internal standard naphthalene (100 µL, 0.5 M in DMSO-d_6, 0.05 mmol). Another 650 µL of DMSO-d_6 was added to make up the total volume to 1 mL. The reaction was then stirred at 80 °C for 6 h. The mixture was cooled to room temperature and the clear organic layer was

transferred into Young's type NMR tube under an N_2 atmosphere. The conversion and yield were determined by ^{1}H NMR.

2-Phenylbenzoxazole: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.27 (d, *J* = 4.0 Hz, 2H), 7.81-7.78 (m, 1H), 7.60-7.56 (m, 1H), 7.54-7.52 (m, 3H), 7.39-7.33 (m, 2H); ^{13}C NMR (100 MHz, Chloroform-*d*, ppm) δ 163.0, 150.8, 142.1, 131.5, 128.9, 127.6, 127.2, 125.1, 124.6, 120.0, 110.6; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.20 (dd, *J* = 8.0, 1.6 Hz, 2H), 7.85-7.73 (m, 2H), 7.65-7.55 (m, 3H), 7.47-7.36 (m, 2H).

2-Phenylbenzothiazole: ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.11-8.09 (m, 3H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.52-7.49 (m, 4H), 7.38 (t, *J* = 8.0 Hz, 1H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 168.1, 154.2, 135.2, 133.7, 131.1, 129.1, 127.6, 126.4, 125.3, 123.3, 121.7. ^{1}H NMR (400 MHz, DMSO-d_6) δ H 8.28–8.24 (m, 2H), 7.89–7.86 (m, 2H), 7.69–7.65 (m, 3H), 7.48–7.44 (m, 2H).

N-Benzyl-2-aminobenzo[*d*]thiazole: ^{1}H NMR (400 MHz, Chloroform-*d*) δ H 7.60 (dd, *J* = 7.9, 1.2 Hz, 1H), 7.52 (d, *J* = 8.0 Hz, 1H), 7.45-7.26 (m, 6H), 7.11 (t, J = 7.2 Hz, 1H), 6.13 (br s, 1H), 4.66 (s, 2H); ^{13}C NMR (101 MHz, Chloroform-*d*) δ 167.9, 152.3, 137.6, 129.0, 128.0, 127.8, 126.2, 127.0, 121.8, 121.0, 119.0, 49.6; ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.52 (br s, 1H), 7.68 – 7.00 (m, 9H), 4.60 (s, 2H).

1.7 Synthesis of Mesitylcopper(I)

Compounds were prepared according to previous publication.[4] Magnesium turnings (2.48g, 100 mmol) were dried using a heat gun under vacuum in a Schlenk round bottom flask for at least 20 minutes with stirring. The flask was then filled with N_2 and cooled down to room temperature, followed by the addition of 100 mL of pre-dried and degassed THF. 2-Bromomesitylene (15.30 mL, 100 mmol) was added slowly into the magnesium suspension solution at room temperature. Afterward, the mixture was stirring at 0 °C for 2 h to give a grey solution of MgMesBr. Another Schlenk round bottom flask, charged with CuCl (10.90 g, 100 mmol) under N_2 atmosphere, was used to dissolve it in 50 mL of THF. The CuCl solution was cooled down to –78 °C while

being stirred, and the MgMesBr solution was subsequently transferred into it using a PTFE cannula. The obtained green mixture was kept stirring overnight under N_2 atmosphere. Afterward, 60 mL anhydrous dioxane was added to the suspension and allowed to stir for another 30 minutes. A Schlenk tube equipped with a filter stick and a 3 cm layer of pre-dried Celite was flushed with N_2. The suspension was transferred into the filter stick by PTFE cannula (the end on reaction mixture side was equipped with filter paper to avoid the solid blocking the filter stick). The bright yellow filtrate was collected into the Schlenk tube at the end of the filtration. The solvent was evaporated under vacuum to obtain yellow solid which was then redissolved in 50 mL anhydrous toluene. The insoluble impurities were filtered by cannula to obtain bright yellow clear solution which was further concentrated and then placed in the freezer overnight. The pale yellow crystal was collected by removing the solvent using a PTFE cannula and then dried under vacuum to give the pure product. The filtrate was concentrated again and placed in the freezer again overnight to give the product. Pale yellow solid (8.79 g, 48%), ^{1}H NMR (400 MHz, benzene-d_6) δ 6.67 (2 H, s), 6.59 (2 H, s), 2.92 (6 H, s), 2.93 (6 H, s) 2.02 (3 H, s), 1.90 (3 H, s). ^{13}C NMR (101 MHz, benzene-d_6) δ 154.31, 152.50, 141.19, 140.52, 128.96, 126.65, 29.01, 28.77, 20.96, 20.81.

1.8 General Copper(I) Complexes Synthesis Procedure

All copper(I) complexes were prepared and handled under an inert atmosphere of dry N_2 to prevent decomposition. A 4mL vial was charged with mesitylcopper(I) (18 mg, 0.1 mmol) and aryl halides (0.1 mmol) fully dissolved in dry toluene (1.0 mL). The vial was placed inside a larger vial (20 mL) containing dry hexane (500 µL) and left at room temperature. Colourless crystals started to form in the inner vial after 24 h, and were isolated after 72 h.

Cu_4**1a'**$_4$**:** ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.73 (s, 2H), 7.31 (dd, J = 7.9, 1.5 Hz, 1H), 7.26 (t, J = 7.3 Hz, 1H), 7.12 (t, J = 7.5 Hz, 3H), 7.02 (s, 1H), 6.96 (td, J = 7.6, 1.7 Hz, 1H). Elemental analysis: Found 53.18; H 3.16; N 4.71. $C_{52}H_{36}Cl_4Cu_4N_4O_4$ requires 53.07 H 3.08; N 4.76%.

Cu_4**2a'**$_4$: ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.40 (d, J = 8.0 Hz, 1H), 7.30 – 7.16 (m, 6H), 7.13 – 7.05 (m, 1H), 6.93 (d, J = 7.9 Hz, 1H); Elemental analysis: Found C 53.86; H 3.41; N 4.23. $C_{52}H_{36}Cl_4Cu_4N_4S_4$ requires 50.32; H 2.92; N 4.51%. Contains solvent residues in crystal.

Cu_4**2b'**$_4$: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.21 – 8.04 (m, 3H), 7.66 – 7.42 (m, 4H), 7.33 – 7.09 (m, 2H); Elemental analysis: Found C 44.02; H 2.56; N 3.95. $C_{52}H_{36}Br_4Cu_4N_4S_4$ requires C 44.02; H 2.72; N 3.80%.

Cu_4**3a'**$_4$: ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.51 – 6.82 (m, 9H), 4.57 (s, 2H); Elemental analysis: Found C 49.56; H 3.56; N 8.26. $C_{56}H_{48}Cl_4N_8S_4$ requires C 49.70; H 3.28; N 8.28%.

Cu_4**3b'**$_4$: ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.64 (s, 1H), 7.70 (dd, J = 7.9, 1.3 Hz, 1H), 7.47 – 7.12 (m, 6H), 7.04 (td, J = 7.6, 1.2 Hz, 1H), 4.60 (d, J = 5.8 Hz, 2H); Elemental analysis: Found C 43.91; H 3.13; N 7.30. $C_{56}H_{48}Br_4N_8S_4$ requires C 43.82; H 3.15; N 7.30%.

1.9 $Cu_4N_4O_4C_4$ and $Cu_4N_4S_4C_4$ clusters

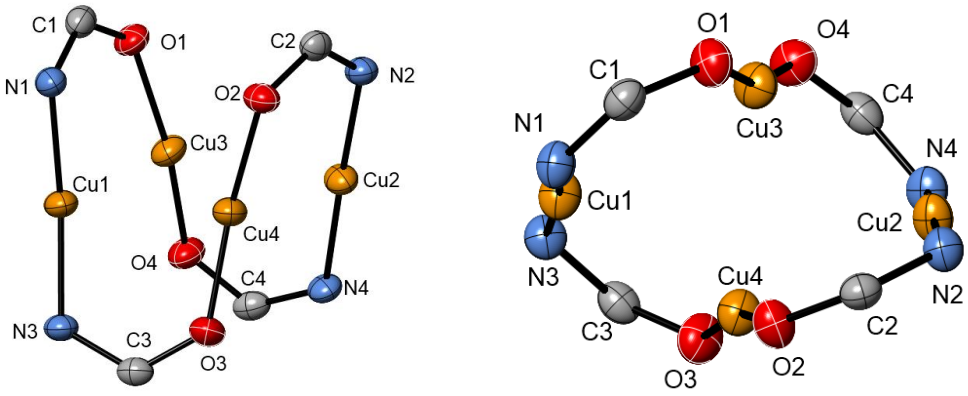

Figure S1.1 Cu_4**1a'**$_4$: $Cu_4N_4O_4C_4$ 16-membered ring.

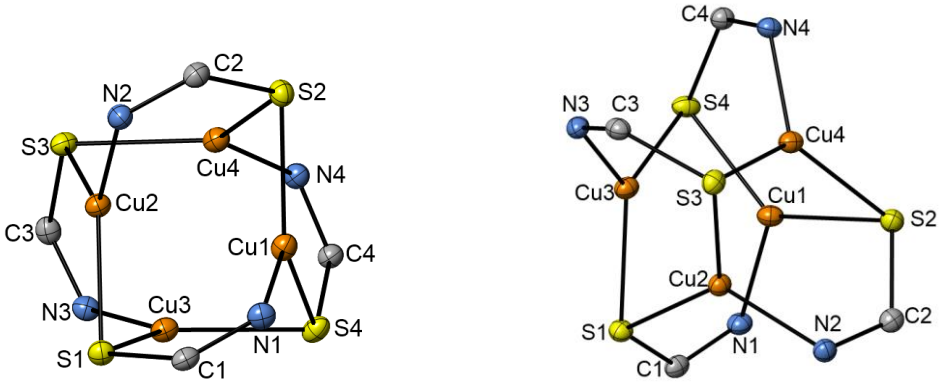

Figure S1.2 Cu_4**2a'**$_4$: $Cu_4N_4S_4C_4$ 16-membered ring.

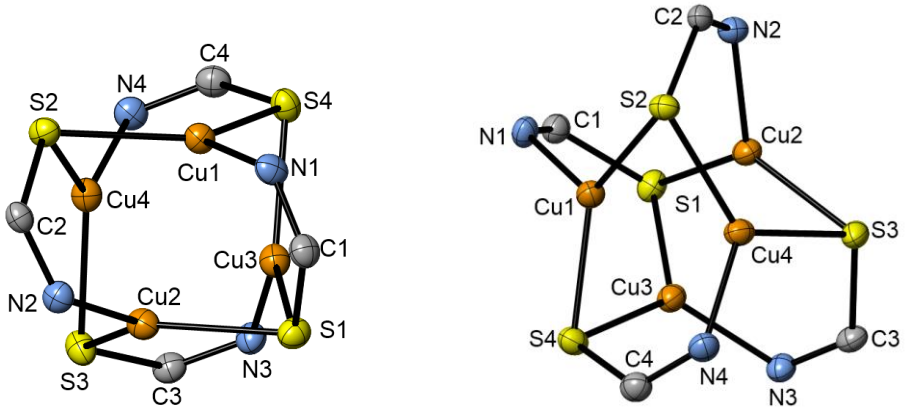

Figure S1.3 Cu_4**2b'**$_4$: $Cu_4N_4S_4C_4$ 16-membered ring.

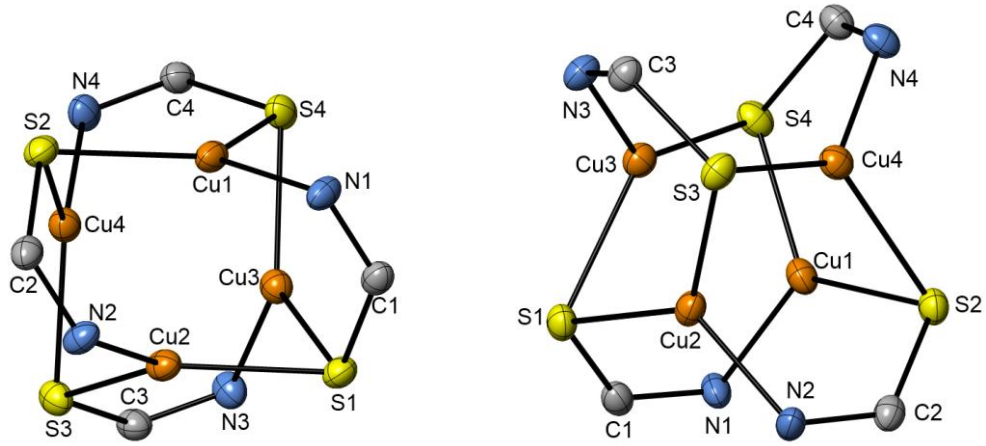

Figure S1.4 Cu_4**3a'**$_4$: $Cu_4N_4S_4C_4$ 16-membered ring.

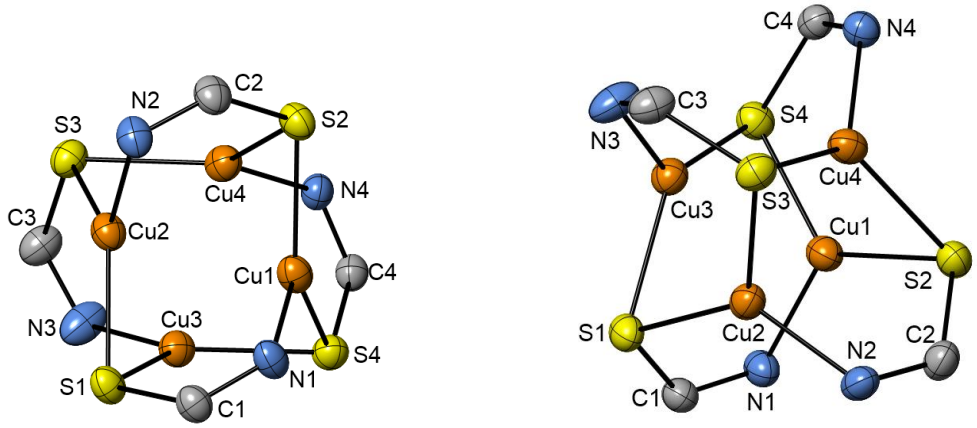

Figure S1.5 Cu_4**3b'**$_4$: $Cu_4N_4S_4C_4$ 16-membered ring.

2 X-ray Crystallographic Data

Table S2.1. Crystal Data, Data Collection and Refinement Parameters for the structures of Cu_4**1a'**$_4$, Cu_4**2a'**$_4$, Cu_4**2b'**$_4$, Cu_4**3a'**$_4$, Cu_4**3b'**$_4$, and **3a**.

data	Cu_4**1a'**$_4$	Cu_4**2a'**$_4$	Cu_4**2b'**$_4$	Cu_4**3a'**$_4$
formula	$C_{52}H_{36}Cl_4Cu_4N_4O_4$	$C_{52}H_{36}Cl_4Cu_4N_4S_4$	$C_{52}H_{36}Br_4Cu_4N_4S_4$	$C_{56}H_{48}Cl_4Cu_4N_8S_4$
solvent	—	C_7H_8·0.5(C_6H_1	1.5(C_7H_8)	0.5(C_7H_8)
formula weight	1176.81	1376.27	1557.09	1403.29
colour, habit	pale yellow	yellow blocks	yellow blocks	colourless thin
temperature / K	173	173	173	173
crystal system	monoclinic	triclinic	triclinic	triclinic
space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
***a* / Å**	9.3512(2)	12.5083(3)	12.7540(6)	10.2309(3)
***b* / Å**	30.6297(7)	14.5425(4)	14.5329(6)	13.7555(5)
***c* / Å**	16.8167(5)	18.2347(4)	18.2953(6)	21.4692(10)
α / deg	90	88.840(2)	88.595(3)	76.317(4)
β / deg	94.298(2)	80.557(2)	80.345(3)	81.511(3)
γ / deg	90	66.647(2)	64.848(4)	80.941(3)
***V* / Å^3**	4803.1(2)	3000.27(14)	3021.9(2)	2879.8(2)
Z	4	2	2	2
***D*$_c$ / g cm^{-3}**	1.627	1.523	1.711	1.618
radiation used	Mo-Kα	Mo-Kα	Mo-Kα	Cu-Kα
μ / mm^{-1}	2.020	1.759	4.214	5.104
no. of unique reflns				
measured (*R*$_{int}$)	9598 (0.0224)	11832 (0.0170)	11868 (0.0188)	10969 (0.0550)
obs, $\|F_o\| > 4\sigma(\|F_o\|)$	7569	9293	9167	8288
completeness (%) [a]	99.0	98.7	98.3	98.1
no. of variables	618	710	718	753
***R*$_1$(obs), *wR*$_2$(all)** [b]	0.0392, 0.0836	0.0377, 0.0884	0.0410, 0.0918	0.0444, 0.1137
CCDC code	2349373	2349374	2349375	2349376

[a] Completeness to 0.84 Å resolution. [b] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma[w(F_o^2)^2]\}^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$.

Table S2.1. ···continued

data	Cu_4**3b'**$_4$	**3a**
formula	$C_{56}H_{48}Br_4Cu_4N_8S_4$	$C_{14}H_{13}ClN_2S$
solvent	$0.5(C_7H_8)$	—
formula weight	1581.13	276.77
colour, habit	colourless	colourless
temperature / K	173	173
crystal system	triclinic	monoclinic
space group	*P*–1 (no. 2)	$P2_1/c$ (no. 14)
***a* / Å**	10.3465(5)	23.3769(16)
***b* / Å**	13.9442(4)	7.4920(4)
***c* / Å**	21.4846(10)	7.6506(5)
α / deg	75.376(4)	90
β / deg	81.788(4)	91.574(6)
γ / deg	81.693(3)	90
***V* / Å^3**	2949.4(2)	1339.43(14)
Z	2	4
***D*$_c$ / g cm^{-3}**	1.780	1.372
radiation used	Cu-Kα	Mo-Kα
μ / mm^{-1}	6.491	0.424
no. of unique reflns		
measured (*R*$_{int}$)	11244 (0.0419)	2676 (0.0260)
obs, $\|F_o\| > 4\sigma(\|F_o\|)$	8496	2110
completeness (%) [a]	98.2	98.8
no. of variables	773	171
***R*$_1$(obs), *wR*$_2$(all)** [b]	0.0465, 0.1169	0.0572, 0.1347
CCDC code	2349377	2349378

Table S2.1 provides a summary of the crystallographic data for the structures of Cu_4**1a'**$_4$, Cu_4**2a'**$_4$, Cu_4**2b'**$_4$, Cu_4**3a'**$_4$, Cu_4**3b'**$_4$, and **3a**. Data were collected using Agilent Xcalibur 3 E (Cu_4**1a'**$_4$, Cu_4**2a'**$_4$, Cu_4**2b'**$_4$ and **3a**) and Xcalibur PX Ultra A (Cu_4**3a'**$_4$ and Cu_4**3b'**$_4$) diffractometers with Mo-Kα and Cu-Kα radiation respectively, and the structures were solved and refined using the OLEX2,[5] SHELXTL[6] and SHELX-2013[7] program systems. CCDC 2349373 to 2349378.

The X-ray crystal structure of Cu_4**1a'**$_4$

The N42-bound chlorophenyl ring in the structure of Cu_4**1a'**$_4$ was found to be disordered. Two orientations were identified of *ca*. 87 and 13% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).

The X-ray crystal structure of Cu_4**2a'**$_4$

The C80-based included toluene solvent molecule in the structure of Cu_4**2a'**$_4$ was found to be disordered. Two orientations were identified of *ca*. 56 and 44% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically).

The X-ray crystal structure of Cu_4**2b'**$_4$

The C80-based included toluene solvent molecule in the structure of Cu_4**2b'**$_4$ was found to be disordered. Two orientations were identified of *ca*. 57 and 43% occupancy, their geometries were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientation were refined anisotropically (those of the minor occupancy orientation were refined isotropically). The C90-based included toluene solvent molecule was found to be disordered across a centre of symmetry, and two unique orientations were identified of *ca*. 25 and 25% occupancy (with two further orientations of the same occupancies being generated by operation of the inversion centre). The geometries of the two unique orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and all of the atoms were refined isotropically.

The X-ray crystal structure of Cu_4**3a'**$_4$

The C80-based included toluene solvent molecule in the structure of Cu_4**3a'**$_4$ was found to be disordered across a centre of symmetry. This was modelled using one complete, 50% occupancy, orientation (with a second 50% occupancy orientation being generated by operation of the inversion centre). The geometry of the unique orientation was optimised and all of the non-hydrogen atoms were refined anisotropically. The N9–, N29–, N49– and N69–H hydrogen atoms were all located from Δ*F* maps and refined freely subject to an N–H distance constraint of 0.90 Å.

The X-ray crystal structure of Cu_4**3b'**$_4$

The N42- and N62-bound bromophenyl rings in the structure of Cu_4**3b'**$_4$ were found to be disordered and two orientations were identified of *ca*. 75 and 25% occupancy in each case. The geometries of each pair of orientations were optimised, the thermal parameters of adjacent atoms were restrained to be similar, and only the non-hydrogen atoms of the major occupancy orientations, and the bromine atoms of the minor occupancy orientations, were refined anisotropically (the remainder were refined isotropically). The C80-based included toluene solvent molecule was found to be disordered across a centre of symmetry. This was modelled using one complete, 50% occupancy, orientation (with a second 50% occupancy orientation being generated by operation of the inversion centre). The geometry of the unique orientation was optimised and all of the non-hydrogen atoms were refined anisotropically. The N9–, N29–, N49– and N69–H hydrogen atoms were all located from Δ*F* maps and refined freely subject to an N–H distance constraint of 0.90 Å.

The X-ray crystal structure of 3a

The N2– and N9–H hydrogen atoms in the structure of 3a were located from Δ*F* maps and refined freely subject to an N–H distance constraint of 0.90 Å.

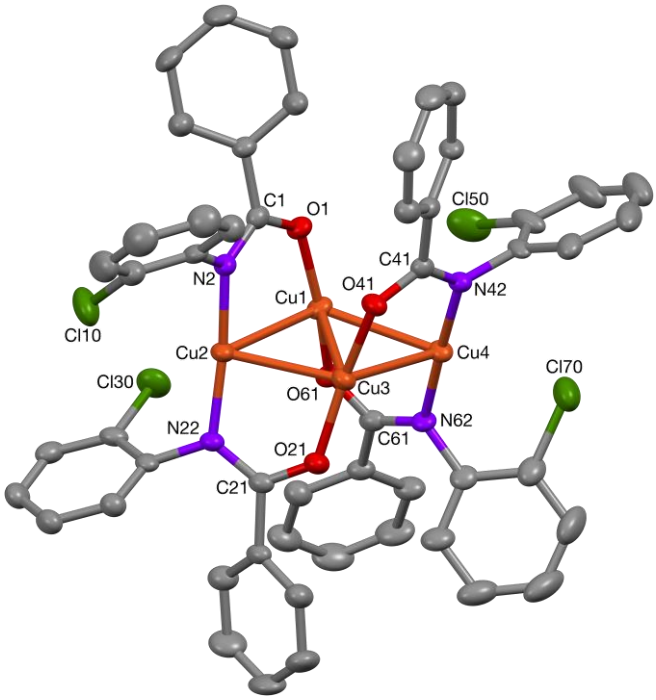

Figure S2.1 The crystal structure of Cu_4**1a'**$_4$ (50% probability ellipsoids).

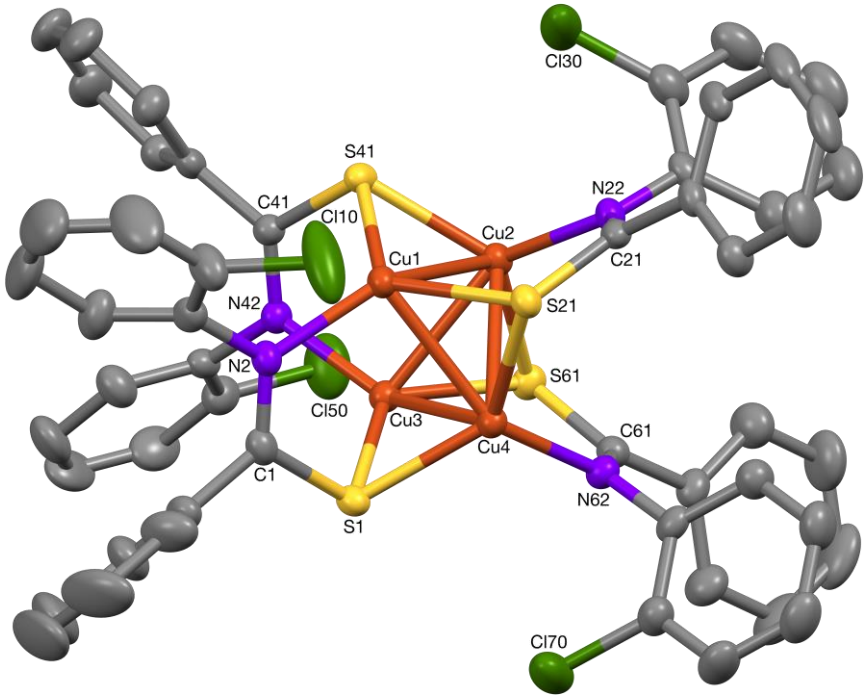

Figure S2.2 The crystal structure of Cu_4**2a'**$_4$ (50% probability ellipsoids).

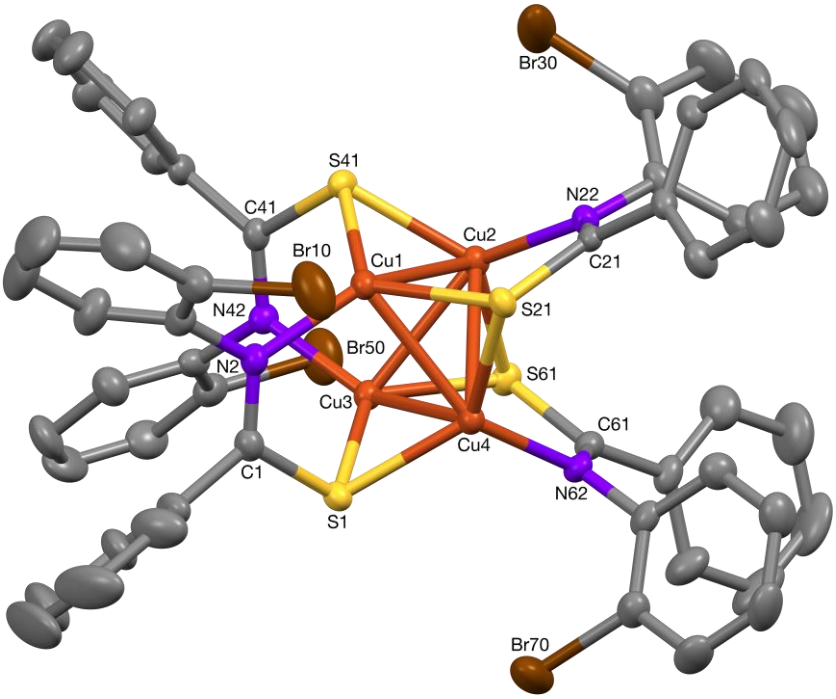

Figure S2.3 The crystal structure of Cu_4**2b'**$_4$ (50% probability ellipsoids).

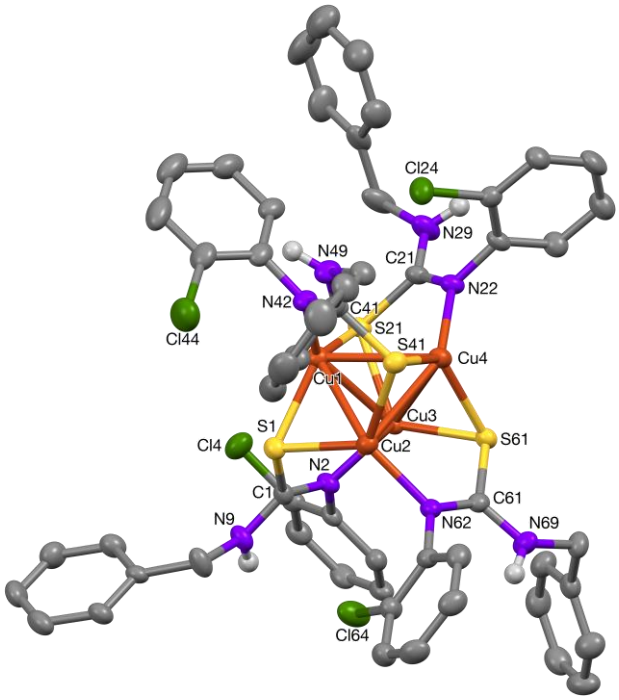

Figure S2.4 The crystal structure of Cu_4**3a'**$_4$ (50% probability ellipsoids).

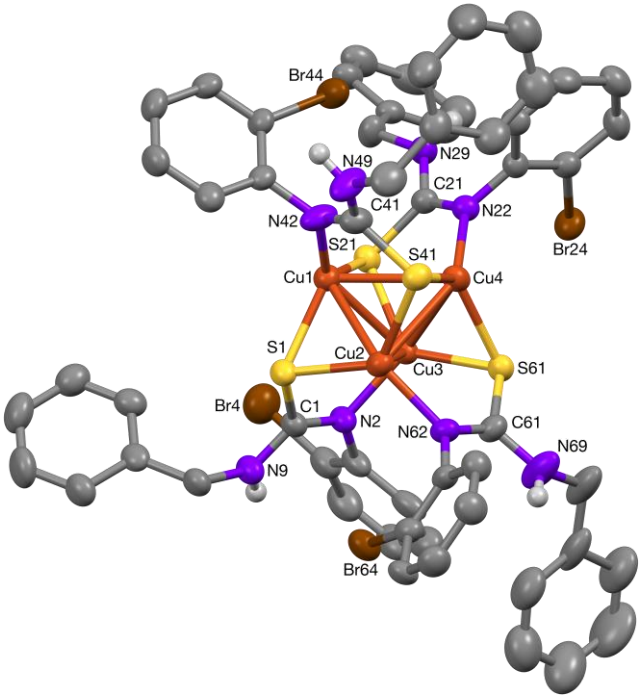

Figure S2.5 The crystal structure of Cu_4**3b'**$_4$ (50% probability ellipsoids).

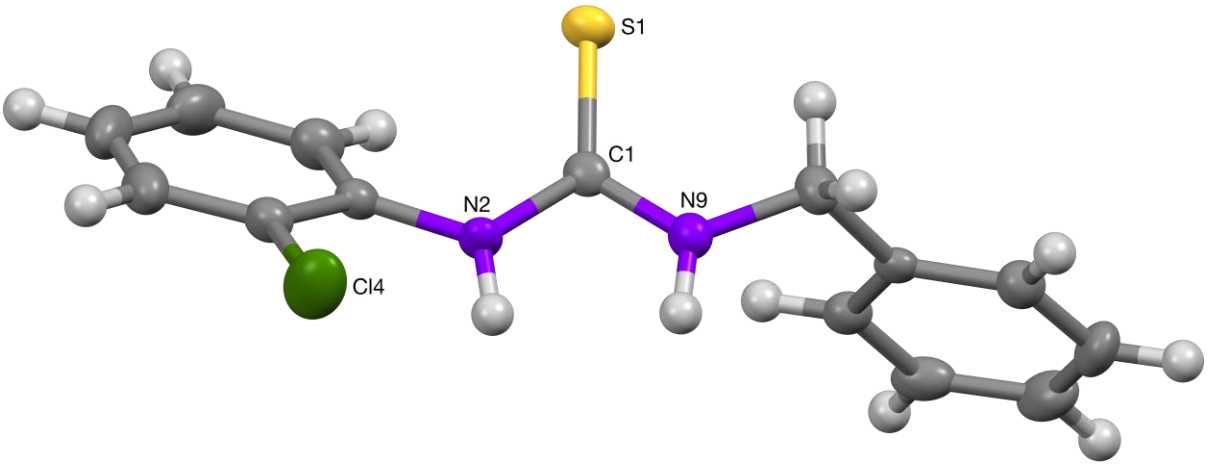

Figure S2.6 The crystal structure of **3a** (50% probability ellipsoids).

3 NMR spectra

Note that the spectra of Cu_4**3a'**$_4$ and Cu_4**3b'**$_4$ contain residual toluene (see SCXRD data Table S2.1)

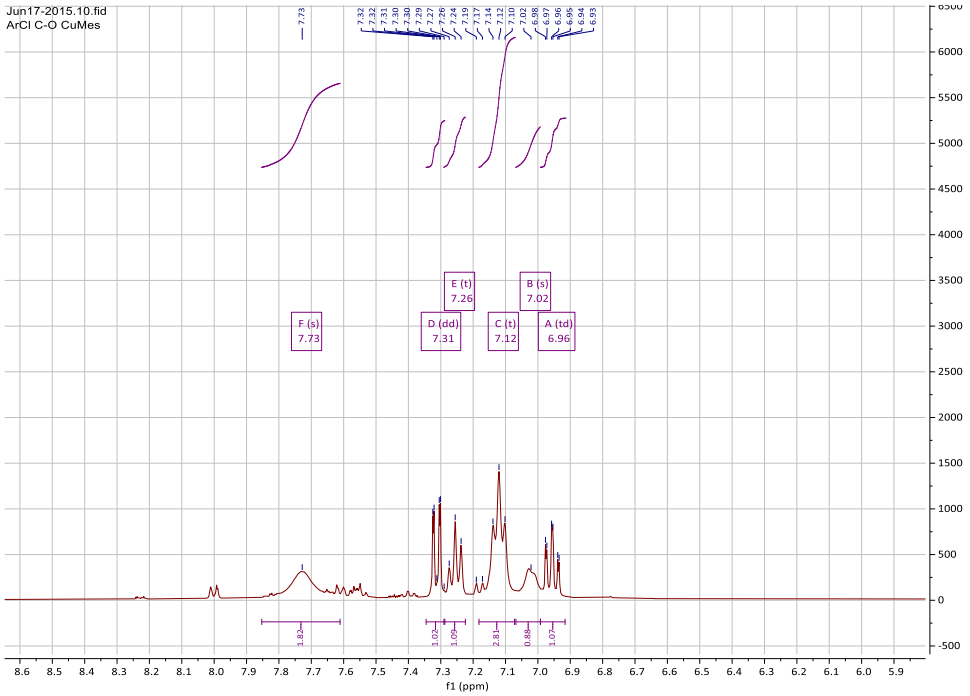

Figure S3.1 ^{1}H NMR of Cu_4**1a'**$_4$

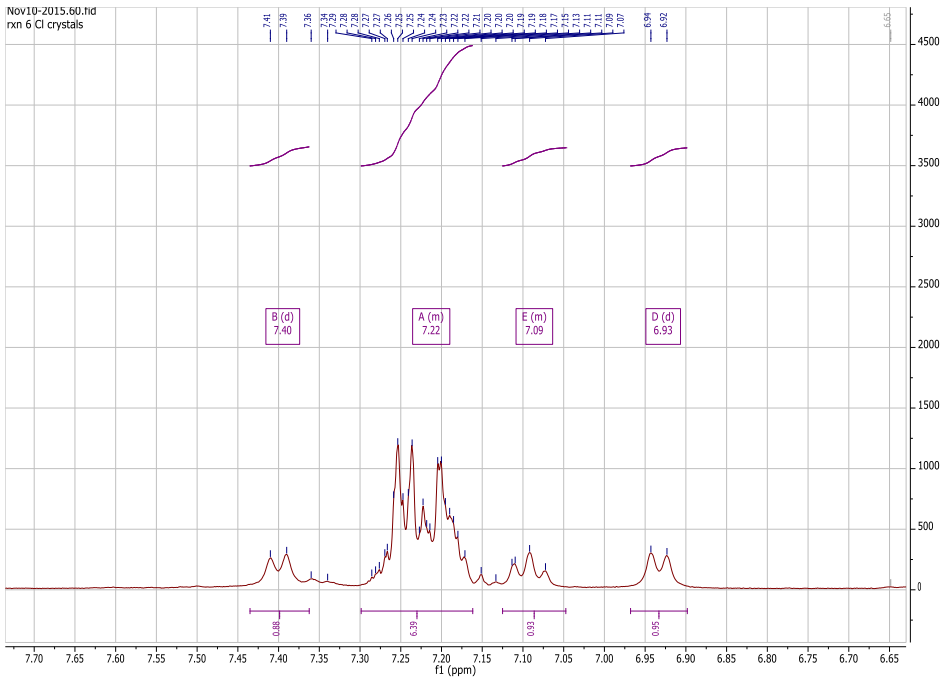

Figure S3.2 ^{1}H NMR of Cu_4**2a'**$_4$

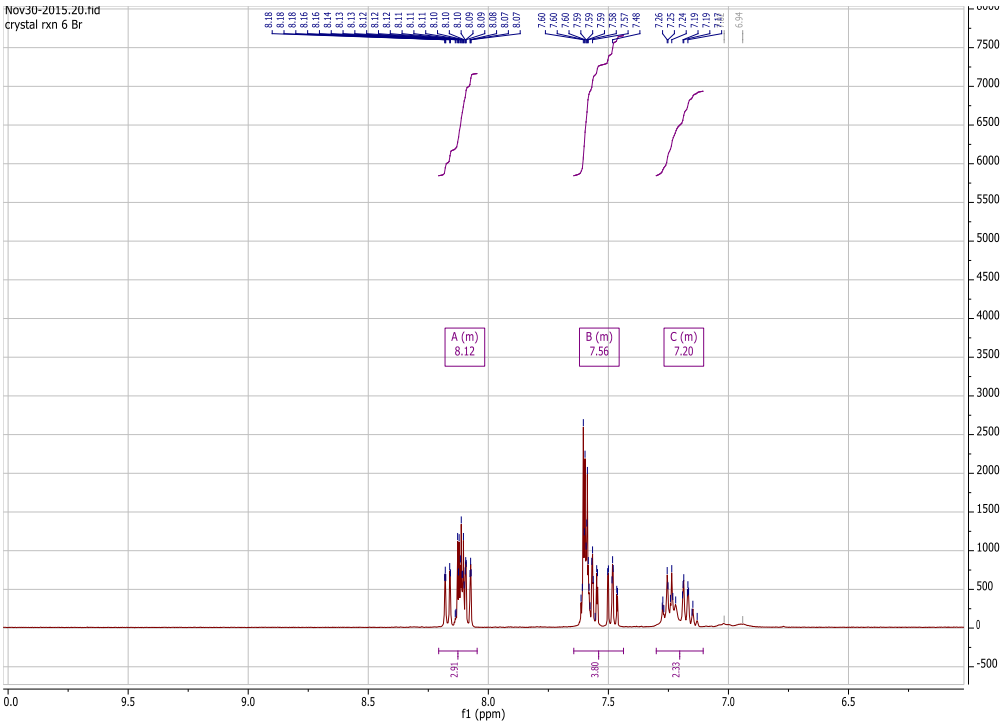

Figure S3.3 ^{1}H NMR of Cu_4**2b'**$_4$

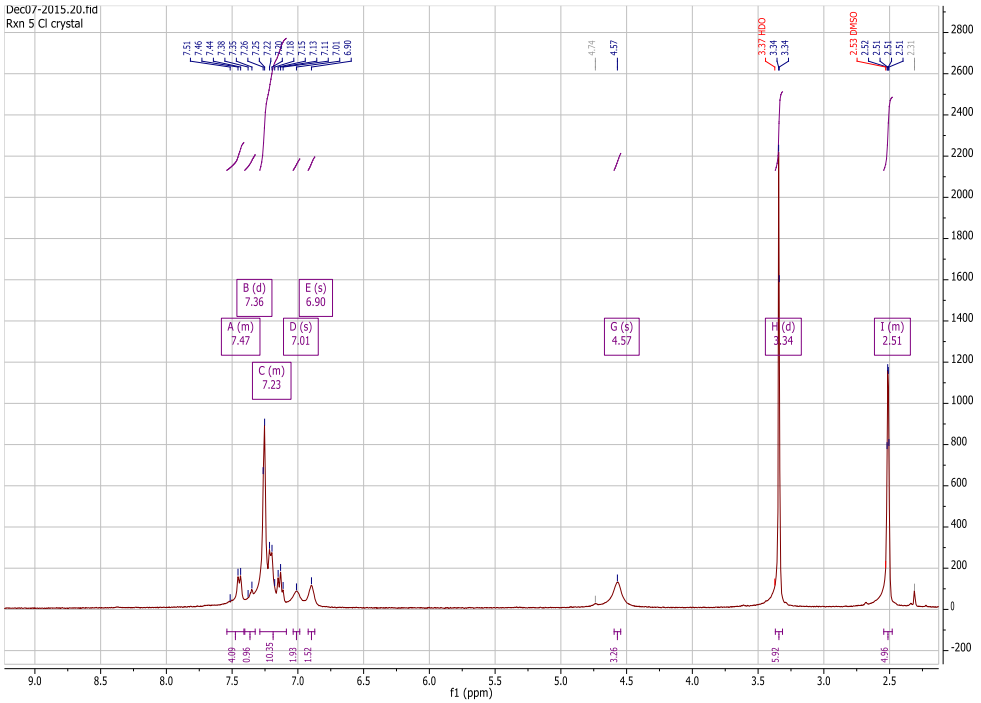

Figure S3.4 ^{1}H NMR of Cu_4**3a'**$_4$

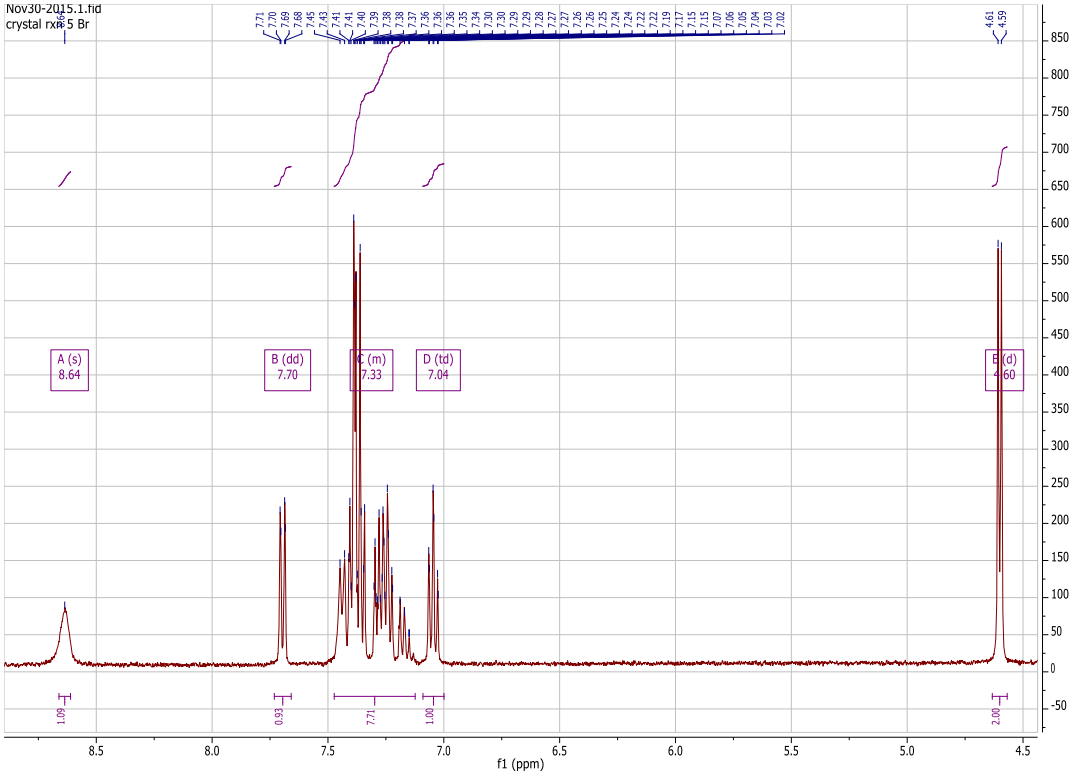

Figure S3.5 ^{1}H NMR of Cu_4**3b'**$_4$

4 References

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