Supplementary Information

for

Interplay between anti-anti and syn-anti conformation of thiourea modulating ON-OFF catalysis

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Contents

1. Synthesis

1.1 General information

All chemicals used in this study were procured from commercial suppliers and were utilized without any additional purification steps. Solvents were also employed without further purification unless specifically stated otherwise. Deionized water was acquired via a Millipore milli-Q water purifier.

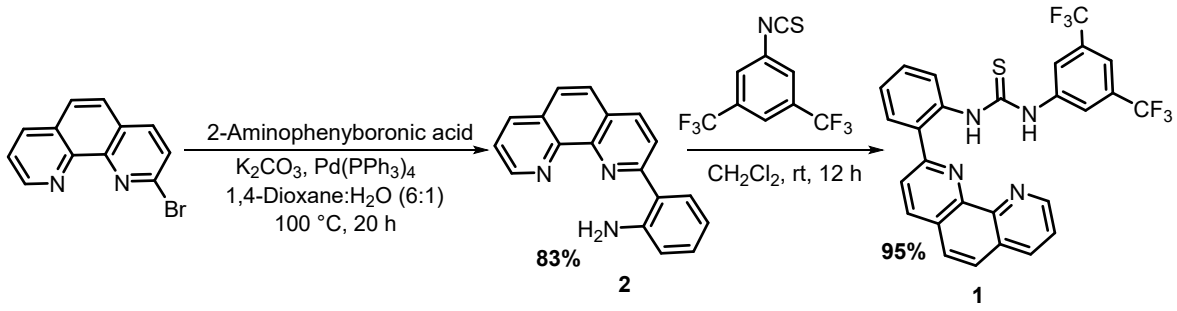
Nuclear Magnetic Resonance (NMR) spectra were obtained using a Bruker Avance 500 MHz spectrometer, and deuterated solvents were used as the lock. The chemical shifts were referenced to the residual protiated fraction of the respective solvents ($CHCl_3$: δ H = 7.26 ppm, $CHDCl_2$: δ H = 5.32 ppm). The following abbreviations were utilized in the ^1H NMR assignments to describe splitting patterns: (s: singlet, d: doublet, t: triplet, dd: doublet of doublets, br: broad singlet, td: triplet of doublets, m: multiplet). The coupling constants were expressed in Hertz (Hz), denoting the number of protons involved, along with the assignment of protons when possible.

High-resolution mass spectra (HRMS) were recorded on a Thermo Scientific™ Q Exactive™ Hybrid Quadrupole-Orbitrap Mass Spectrometer using the electrospray ionization (ESI) technique. The calculated m/z values were obtained from ThermoXCalibur software.

UV–vis spectra were recorded on a Shimadzu UV-3600 Vis-NIR spectrophotometer at room temperature using a quartz cuvette with a path length of 1 mm. For UV–vis analysis, solutions were freshly prepared by dissolving isolated compounds in UV-grade solvents, unless explicitly mentioned otherwise.

All calculations were carried out using the Gaussian 16 program package.[1] Calculations were performed by the density functional theory (DFT) method with restricted B3LYP (Becke's three-parameter hybrid exchange functional and the Lee-Yang-Parr correlation functional) 6 level, employing a basis sets 6-311G(d,p).

1.2 Synthetic Scheme for Switch 1



Scheme S 1: Synthesis of switch **1**.

1.3 Synthesis of 2-(1,10-phenanthroline-2-yl) aniline

2-Bromo-1,10-phenanthroline (1.00 g, 3.86 mmol), 2-aminophenyl boronic acid (529 mg, 3.86 mmol) and K_2CO_3 (1.60 g, 11.6 mmol) were added to a mixture of 1,4-dioxane and water (6:1) and the mixture was then purged with argon gas for two hours. The reaction mixture was heated to 100 °C for 5 minutes, and then Pd $(PPh_3)_4$ (223 mg, 193 µmol) was added. The mixture was further heated at the same temperature for 20 hours. After completion of the reaction, the solvent was removed under reduced pressure, and the residue was extracted with ethyl acetate (3 portions, 50 mL each). The organic layers were combined and dried over $MgSO_4$. The solvent was evaporated under reduced pressure, and the resulting crude product was purified by column chromatography using silica gel as the stationary phase and a mixture of hexane and ethyl acetate in a ratio of 6:4 as the mobile phase. The purified product was obtained as yellow solid, weighing 950 mg.

Yield= 83%

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.13 (d, ^3J=4.5 Hz, 1 H), 8.23- 8.19 (m, 2 H), 8.06 (d, ^3J=8.6 Hz, 1 H), 7.81 (d, ^3J=8.2 Hz, 1 H), 7.74 -7.69 (m, 2 H), 7.58 (dd, ^3J=8.2 Hz, ^4J=4.5 Hz, 1 H), 7.21 (t, ^3J=7.8 Hz, 1 H), 6.85 (d, ^3J=7.8 Hz, 1 H), 6.79 (t, ^3J=7.5 Hz, 1 H), 6.04 (br, 2 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 158.7, 150.2, 148.4, 145.8, 144.3, 136.3, 135.8, 130.4, 129.0, 128.8, 126.0 (2), 125.6, 122.8, 121.0, 120.6, 117.6, 116.7.

HRMS (ESI) m/z: $[M + H]^+$; Calculated ($C_{18}H_{13}N_3$ +H): 272.1182, Found: 272.1179.

1.4 Synthesis of the molecular switch 1

Under an inert atmosphere, 2-(1,10-phenanthroline-2-yl) aniline (**2**) (100 mg, 0.37 mmol) was dissolved in dry DCM (5 mL), 1-isothiocyanato-3,5-bis(trifluoromethyl)benzene (1.34 mL, 0.732 mmol) was added to this solution, and the mixture was stirred at room temperature overnight. The reaction mixture was then extracted with DCM (3 portions, 50 mL each), and

the combined organic layer was dried over $MgSO_4$. The solvent was evaporated under reduced pressure, and the resulting crude product was purified by column chromatography using a mixture of DCM and hexane in a 1:1 ratio as the eluent. The purified product was obtained as yellow solid, weighing 190 mg.

Yield= 95%

^{1}H NMR (500 MHz, $CDCl_3$) δ 16.60 (s, 1 H), 10.92 (s, 1 H), 9.38 (d, ^3J=8.6 Hz, 1 H), 8.75-8.74 (m, 1 H), 8.35 (d, ^3J= 8.6 Hz, 2 H), 8.24 (d, ^3J= 9 Hz, 1 H), 8.04 (s, 2 H), 8.02 (d, ^3J= 8 Hz, 1 H), 7.84 (s, 2 H), 7.68 (s, 1 H), 7.63 (dd, ^3J=8 Hz, ^4J=4.4 Hz 1 H), 7.51 (t, ^3J= 7.8 Hz 1 H), 7.23 (t, ^3J= 7.8 Hz, 1 H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 179.5, 157.1, 150.0, 145.0, 142.4, 141.4, 141.0, 137.6, 137.5, 131.7, 131.4, 130.5, 129.8, 128.1, 126.9, 126.5, 125.4, 124.3, 123.6, 123.5, 123.3, 123.0, 122.1, 121.0.

HRMS (ESI) m/z: $[M]^+$ Calculated ($C_{26}H_{16}N_4F_6S$ +H): 543.1073, Found: 543.1072

1.5 Synthesis of Copper complex [Cu (1)(3)]PF_6

Switch **1** (3 mg, 5.50 µmol), dimesityl phenanthroline **3** (2.29 mg, 5.50 µmol), and [(Cu $(CH_3CN)_4)PF_6$] (2.05 mg, 5.50 µmol) were dissolved in CD_2Cl_2 in NMR tube at room temperature to obtain [Cu (**1**)(**3**)]PF_6 in quantitative yield. The color of the complex turns red upon the addition of Cu salt.

^{1}H NMR (500 MHz, CD_2Cl_2) δ 8.63 (d, ^3J= 8.4 Hz, 3 H), 8.46 (d, ^3J= 8.0 Hz, 1 H), 8.41 (d, ^3J= 8.0 Hz, 1 H), 8.21 (s, 2 H), 8.11 (br, 1 H), 7.92- 7.87 (m, 5 H), 7.76- 7.78 (m, 1 H), 7.70 (d, ^3J= 8.0 Hz, 2 H), 7.61 (s, 1 H), 7.31 (br, 1 H), 7.23 (d, ^3J= 6.2 Hz, 1 H), 6.95- 6.98 (m, 1 H), 6.83 (d, ^3J= 8.0 Hz, 1 H), 6.27 (s, 2 H), 6.13 (s, 2 H), 5.72- 5.75 (m, 1 H)

HRMS (ESI) m/z: $[M]^+$ Calculated ($C_{57}H_{44}N_6F_6SCu$): 1021.2543, Found: 1021.2537

2. Characterization

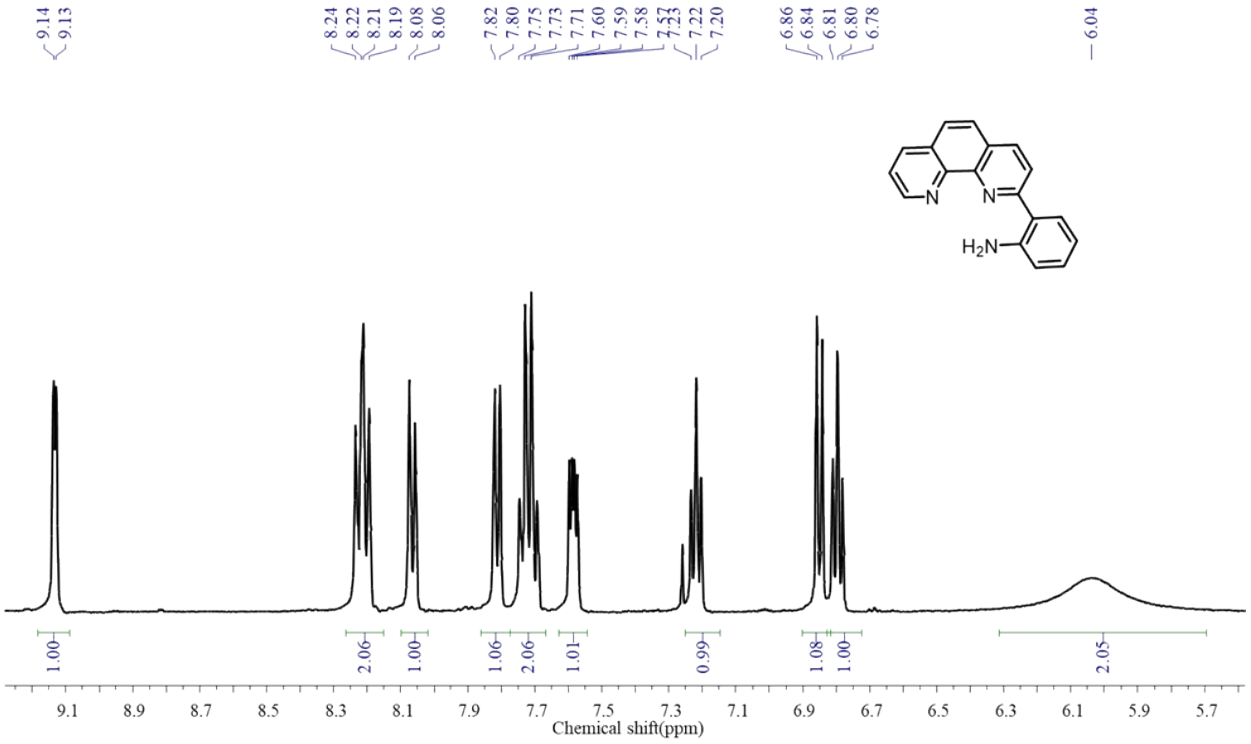


Figure S 1: Partial ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of compound **2**.

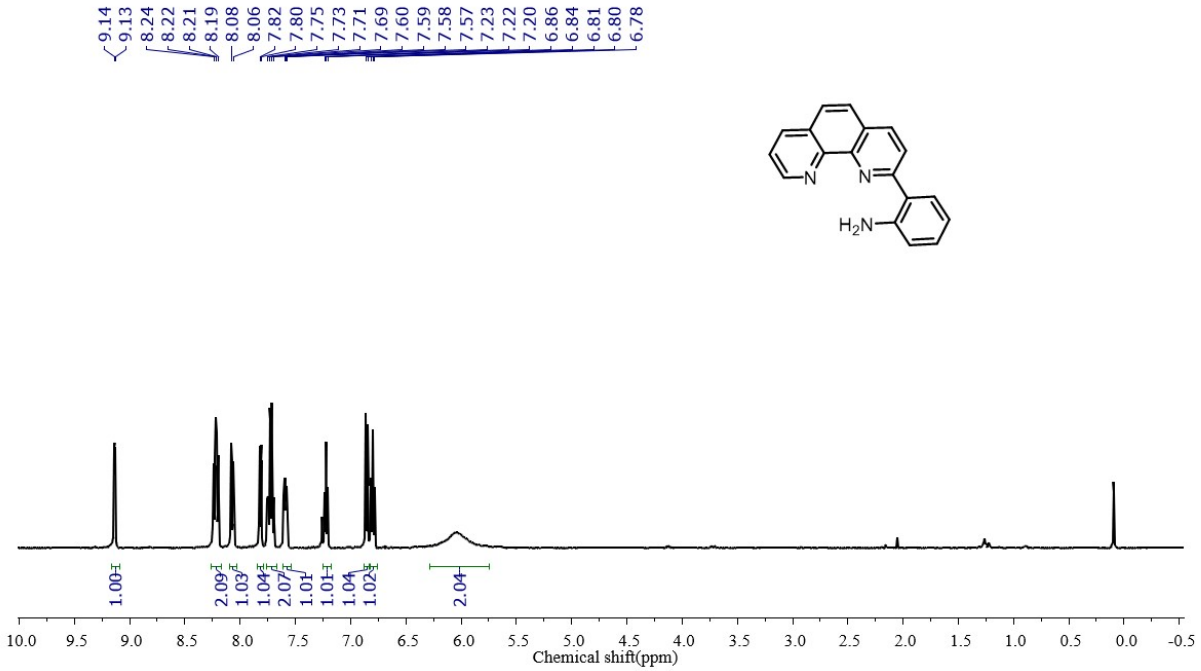


Figure S 2: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of compound **2**.

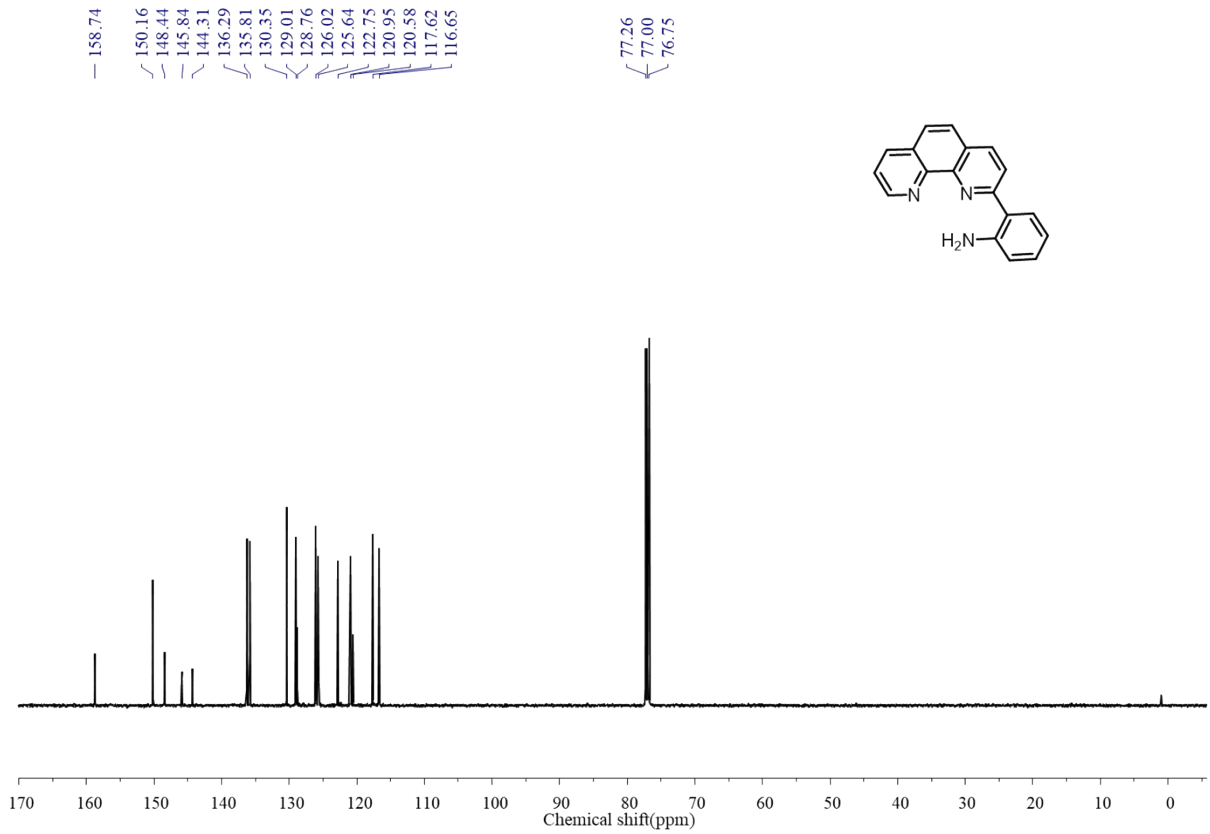


Figure S 3: ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) spectrum of compound **2**.

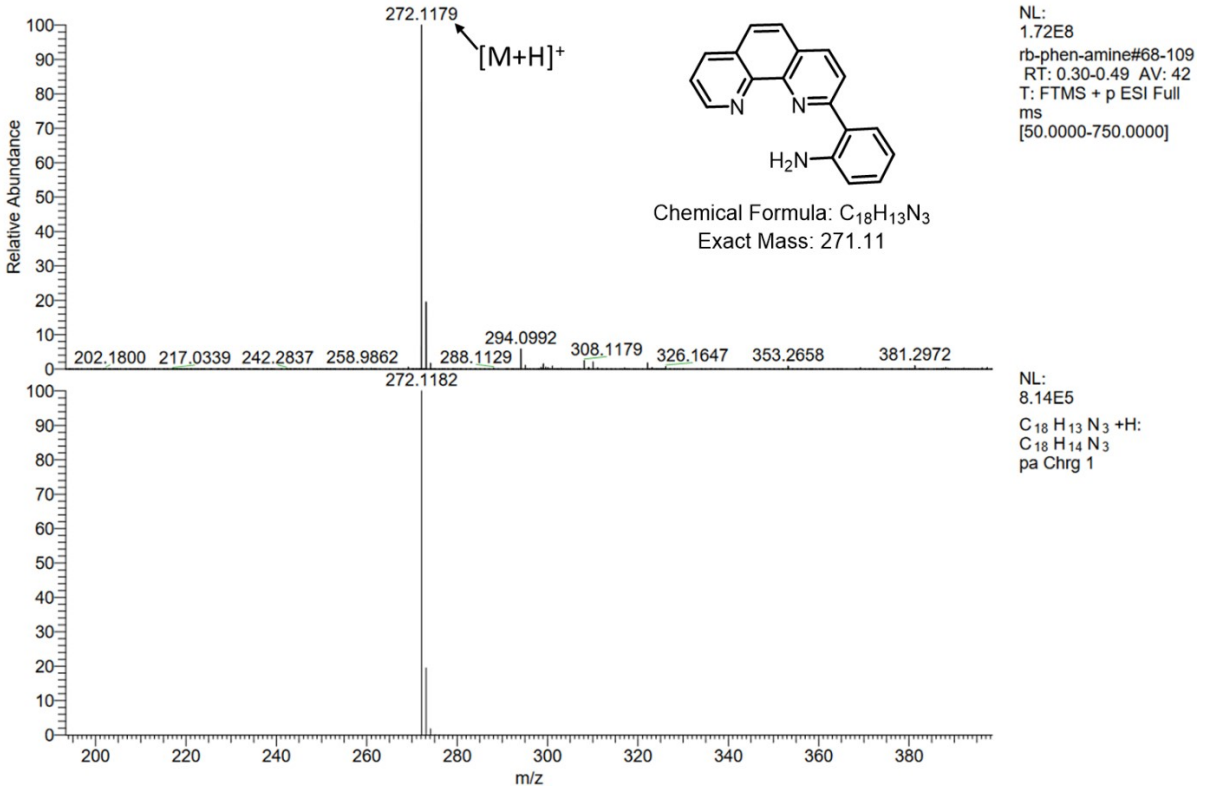


Figure S 4: High-Resolution Mass Spectrum (HRMS) of a) experimental and b) theoretical of compound **2**

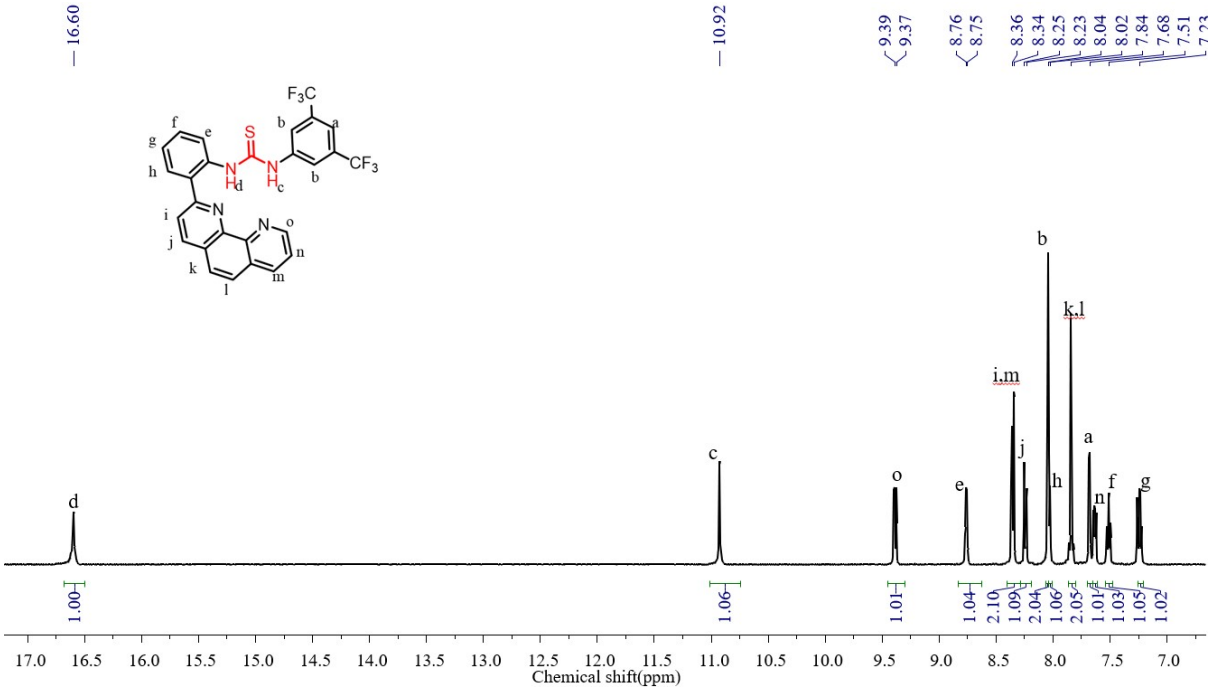


Figure S 5: Partial ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of compound **1**.

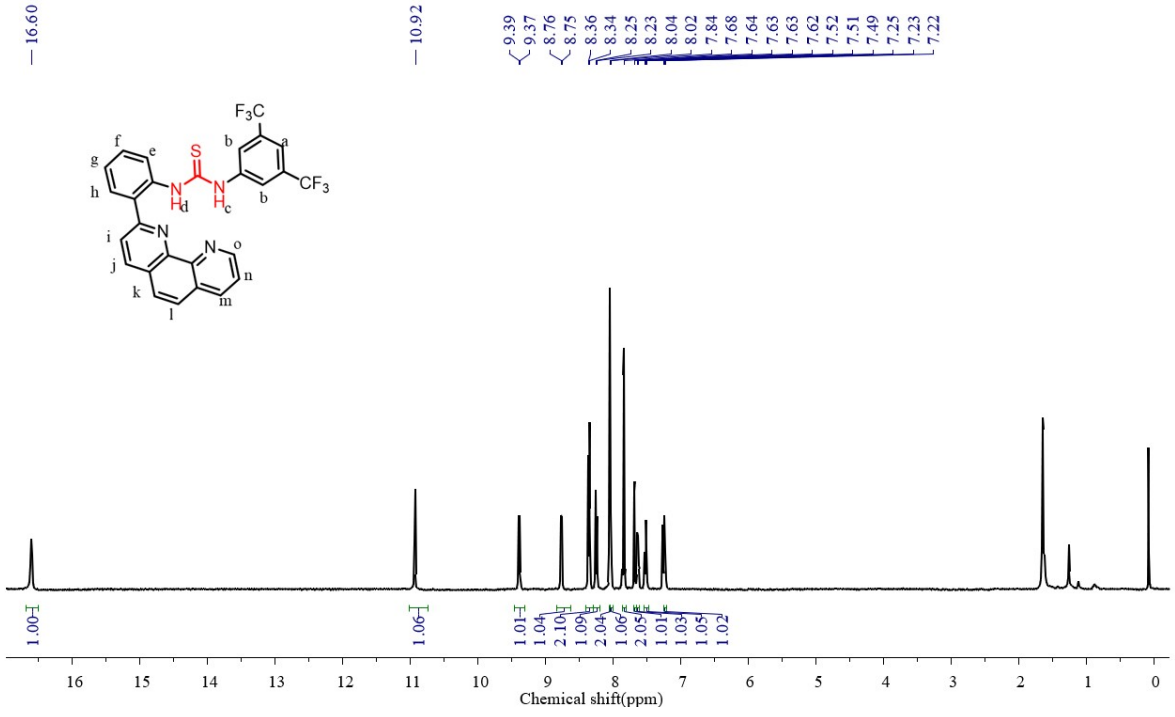


Figure S 6: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of compound **1**.

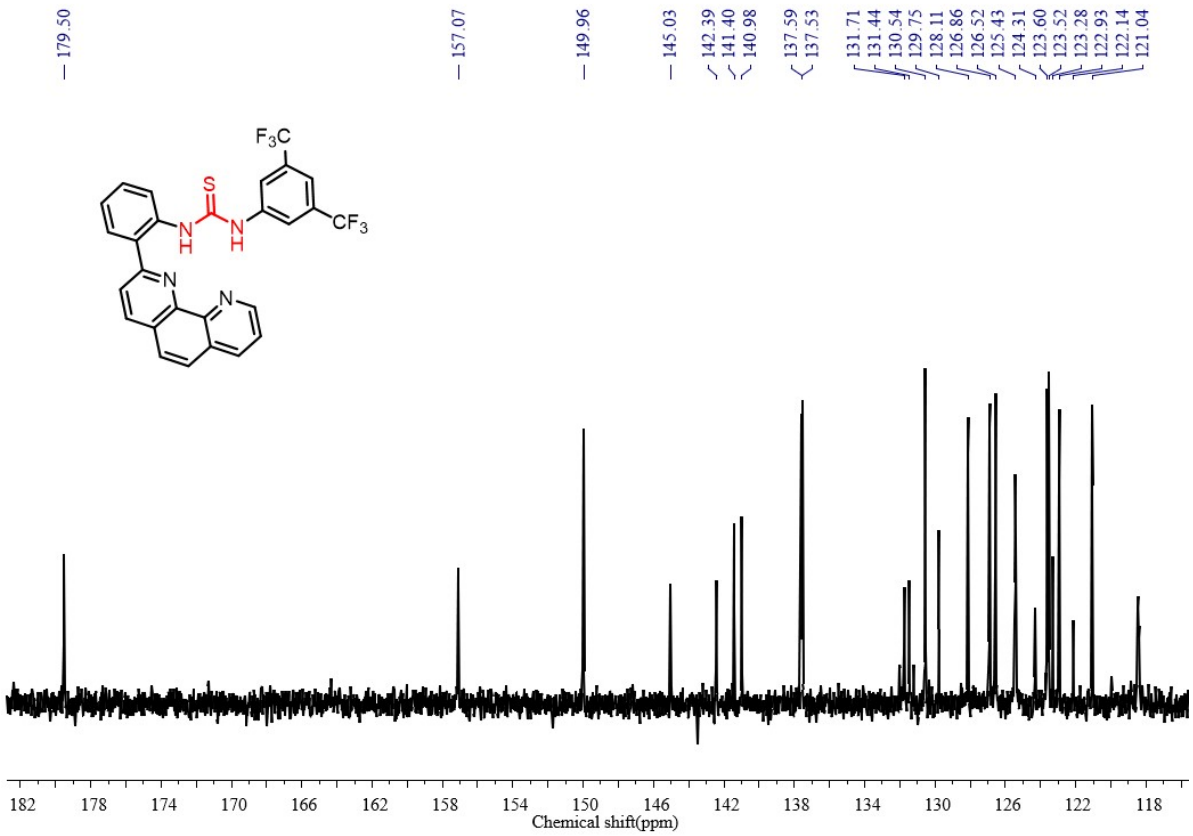


Figure S 7: Partial ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) spectrum of compound **1**.

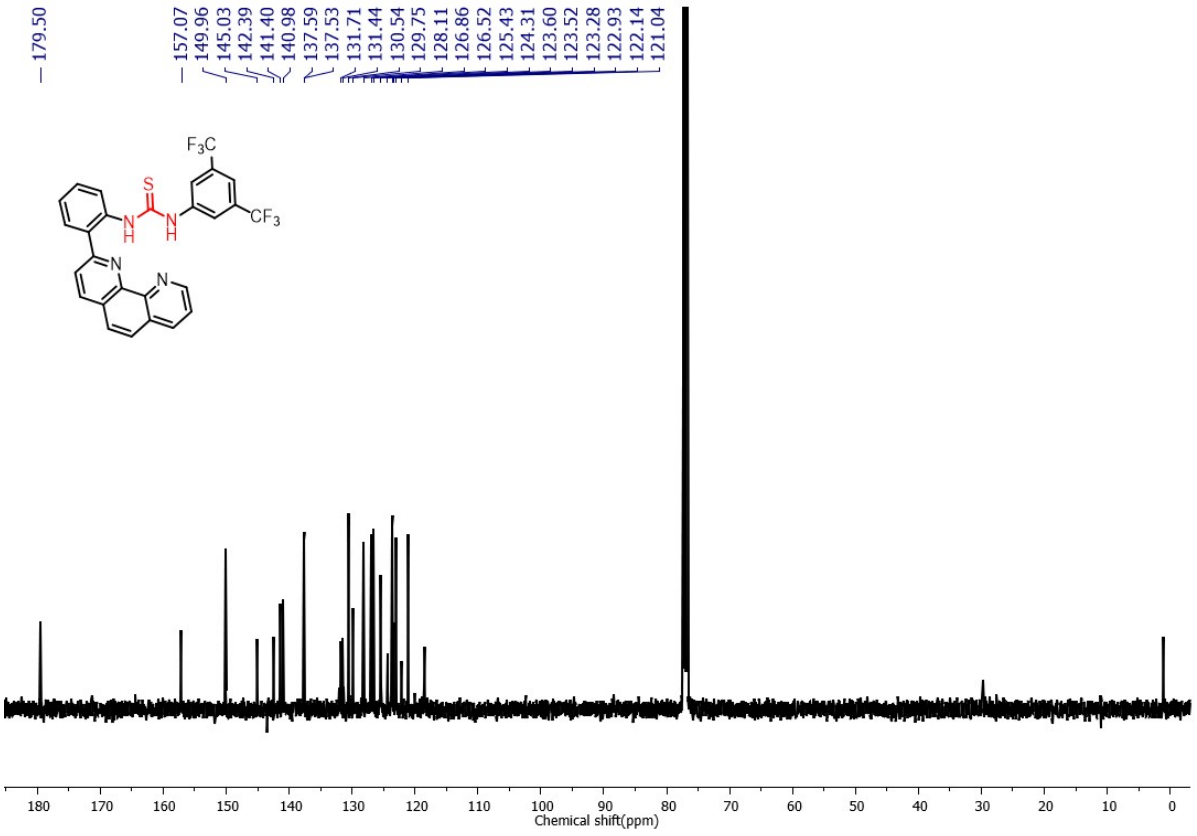


Figure S 8: ^{13}C NMR (126 MHz, $CDCl_3$, 298 K) spectrum of compound **1**.

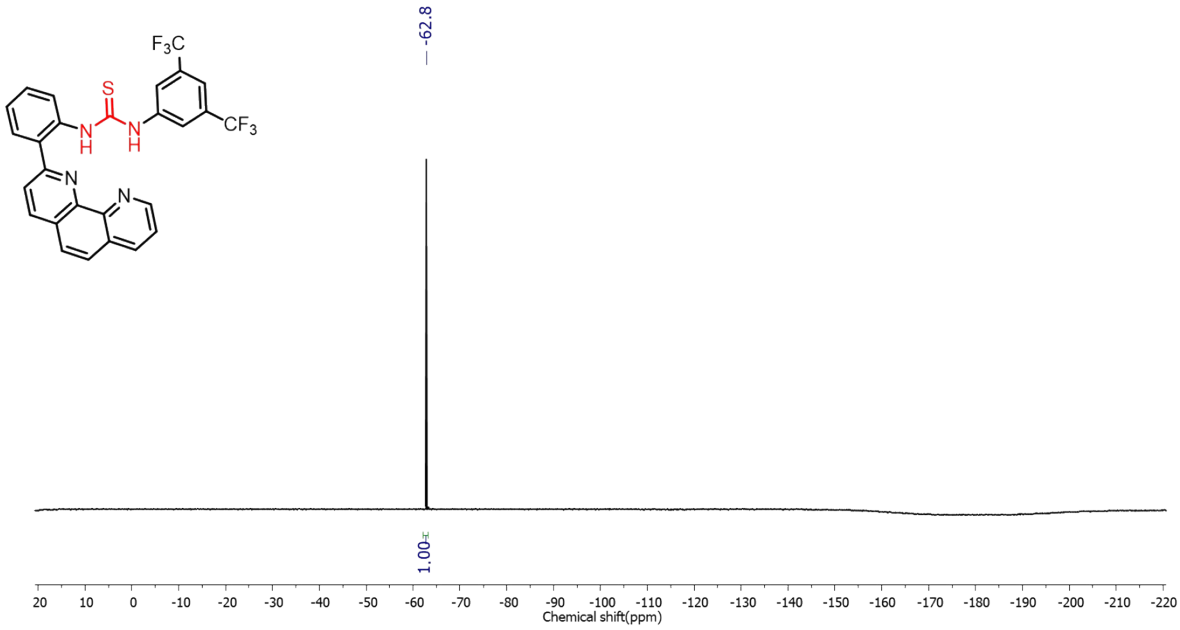


Figure S 9: ^{19}F NMR (471 MHz, 298 K) spectrum of compound **1.**

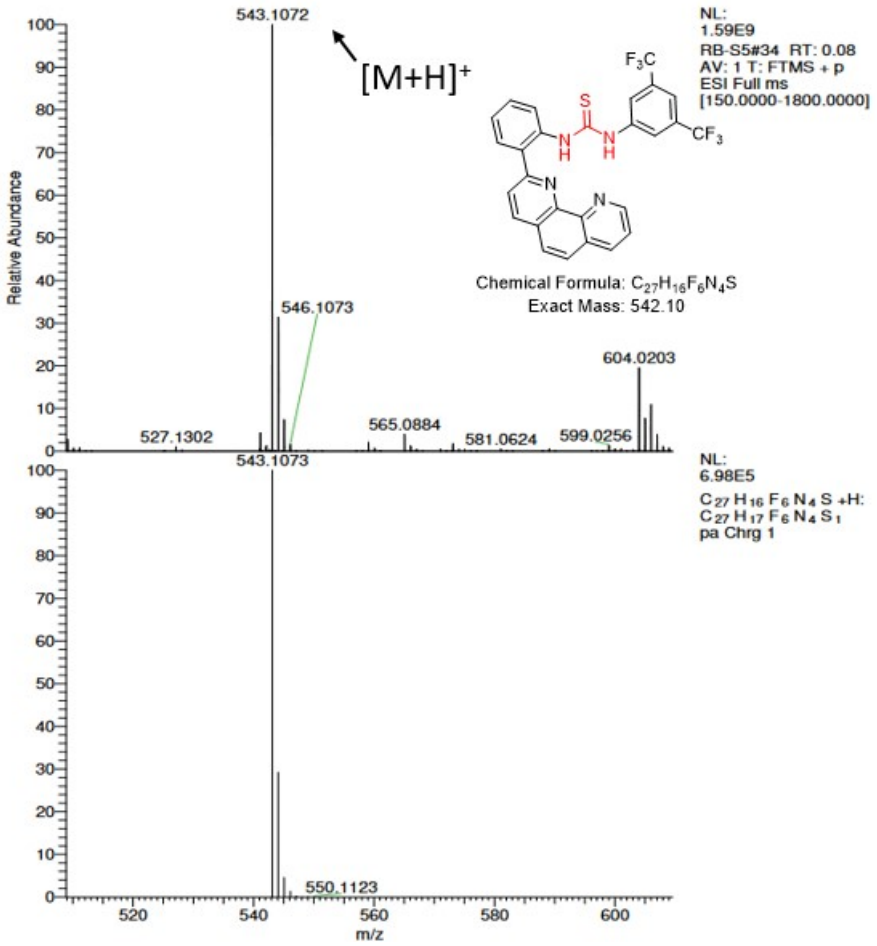


Figure S 10: High-Resolution Mass Spectrum (HRMS) of a) experimental and b) theoretical of compound **1**.

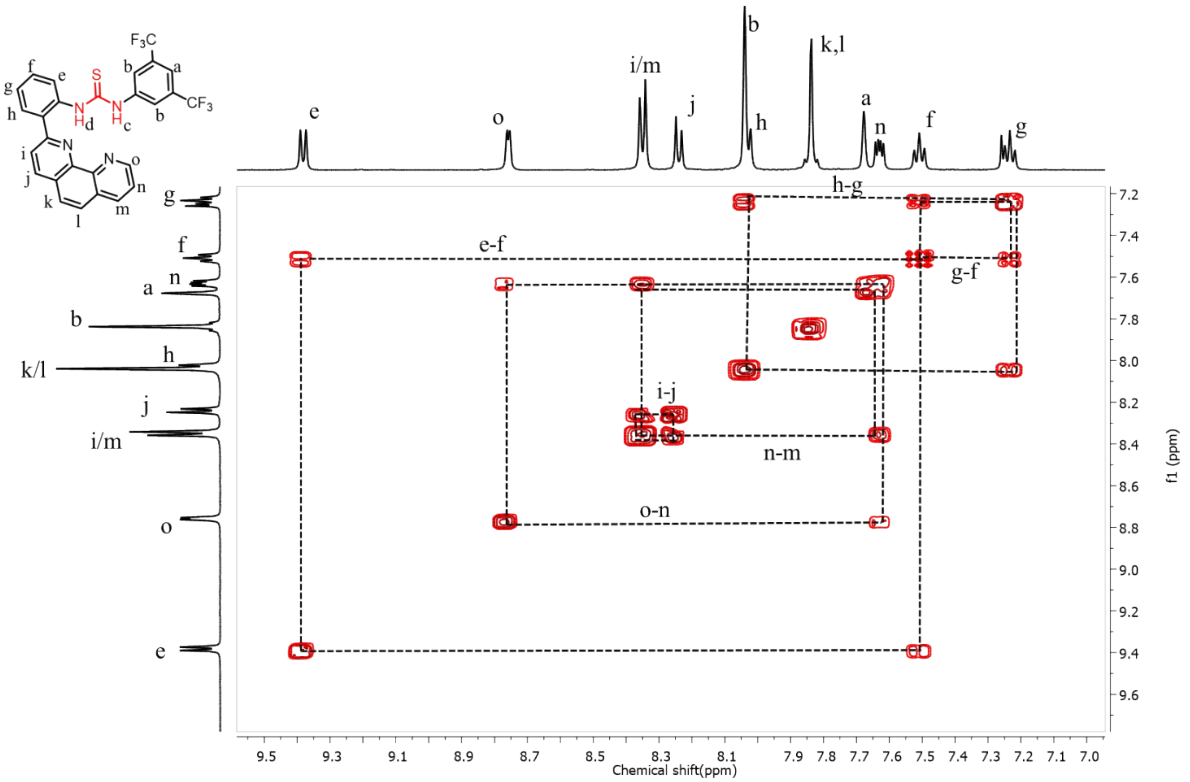


Figure S 11: Partial ^{1}H-^{1}H COSY (500 MHz, $CDCl_3$, 298 K) spectrum of compound **1**.

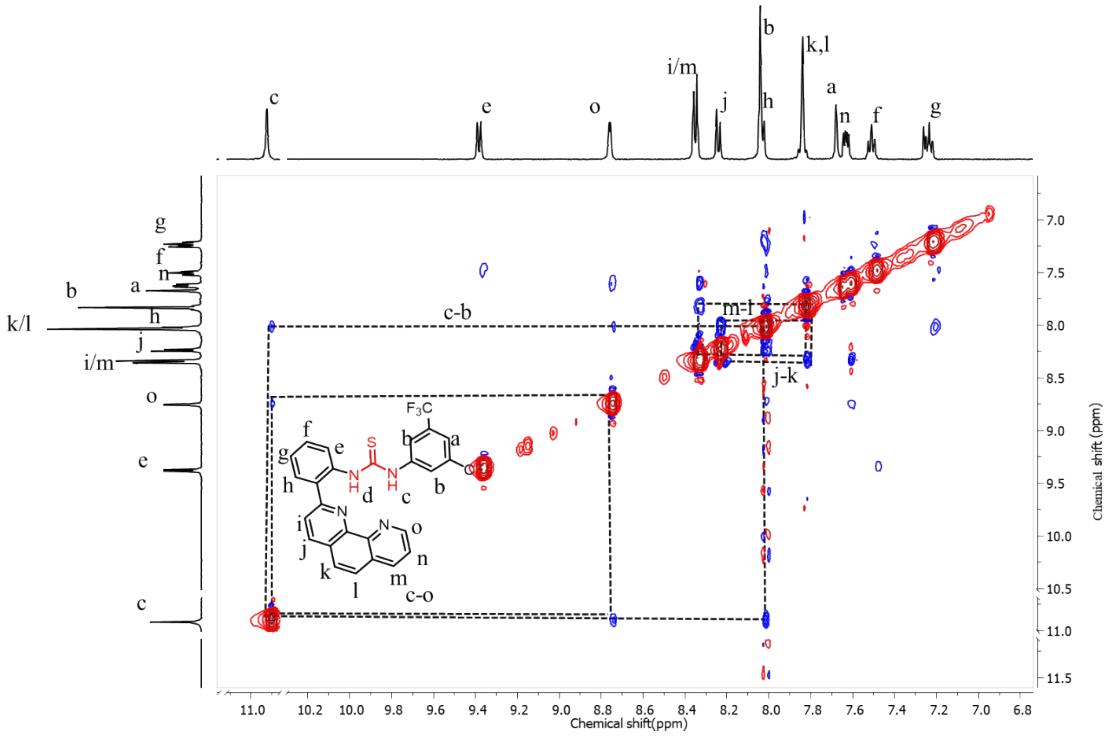


Figure S 12: Partial ^{1}H-^{1}H NOESY (500 MHz, $CDCl_3$, 298 K) spectrum of compound **1**.

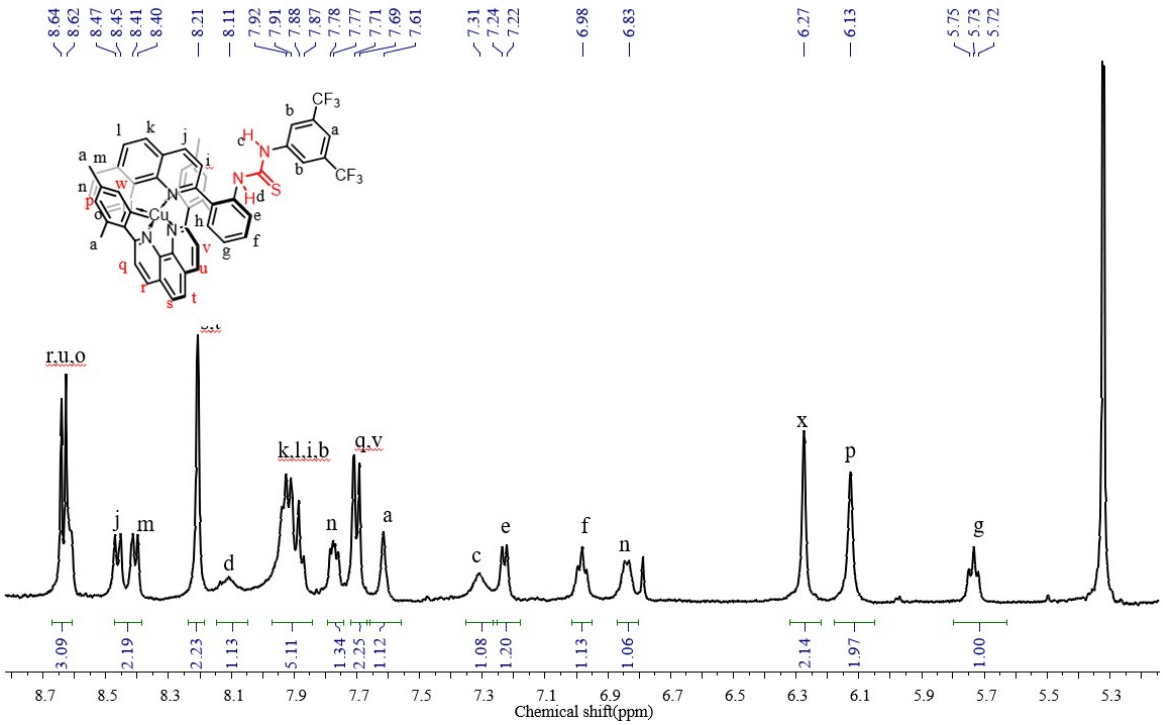


Figure S 13: Partial ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of [Cu (**1**)(**3**)]PF_6

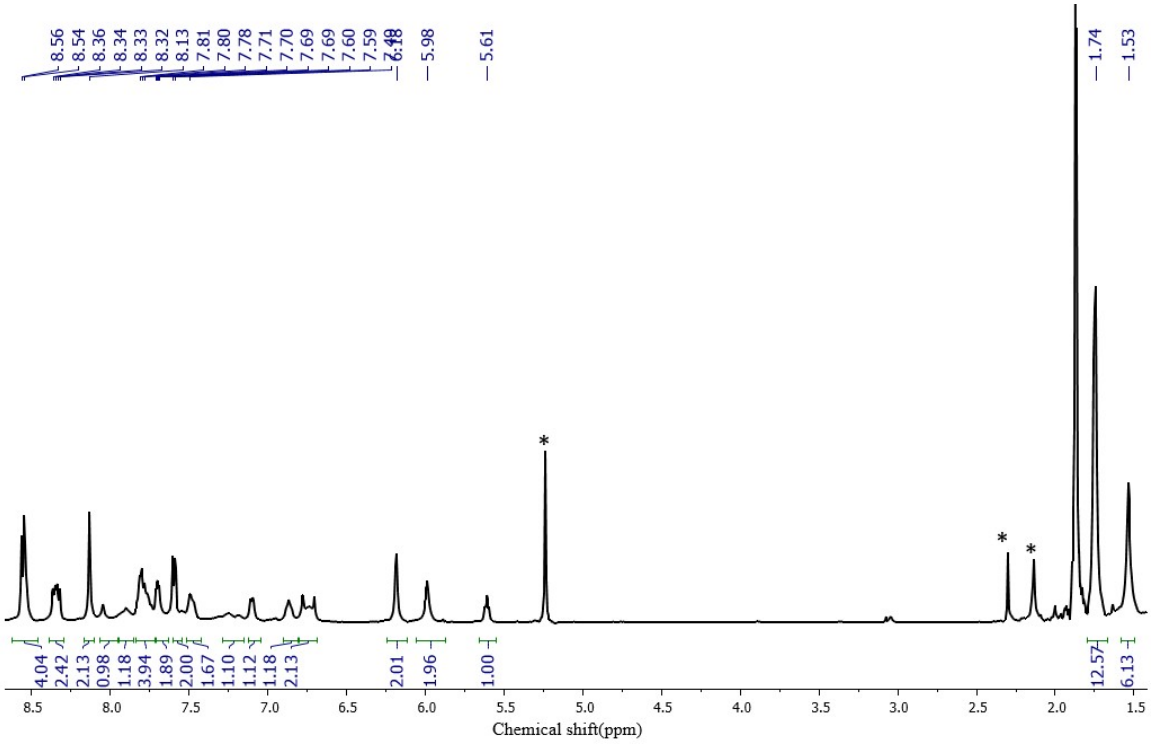


Figure S 14: ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectrum of [Cu (**1**)(**3**)]PF_6.

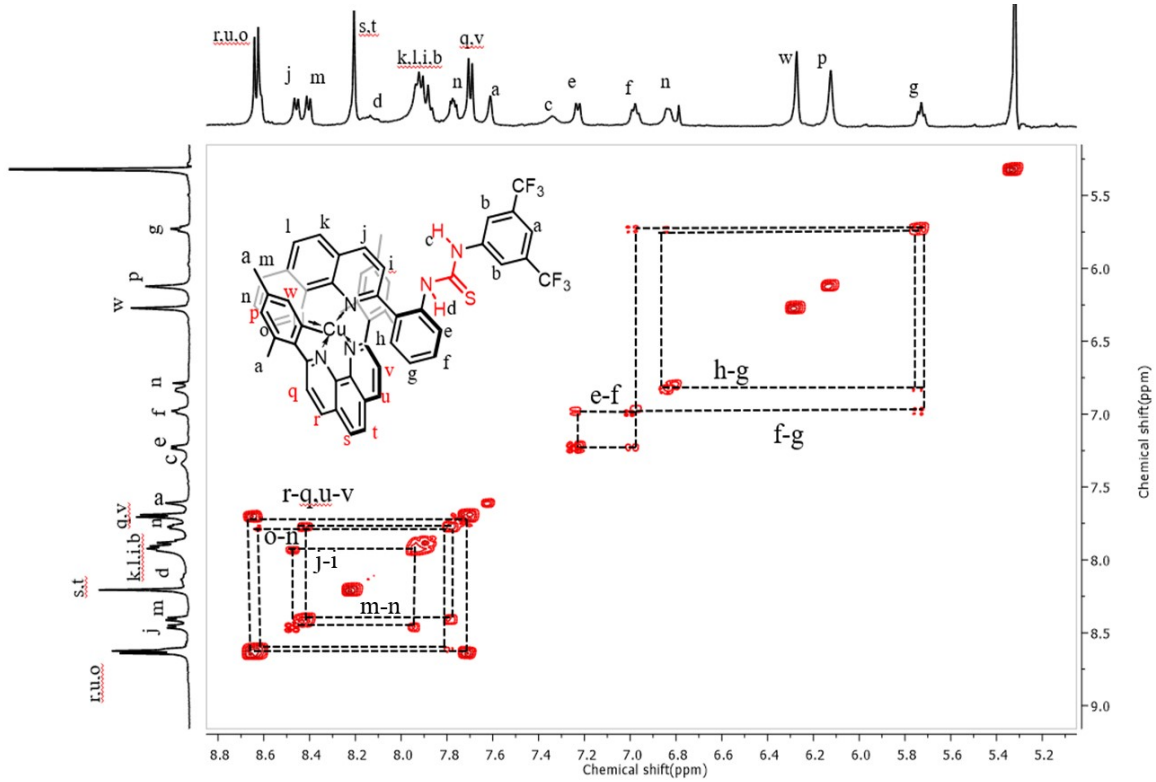


Figure S 15: Partial ^{1}H-^{1}H COSY (500 MHz, CD_2Cl_2, 298 K) spectrum of **[**Cu (**1**)(**3**)]PF_6.

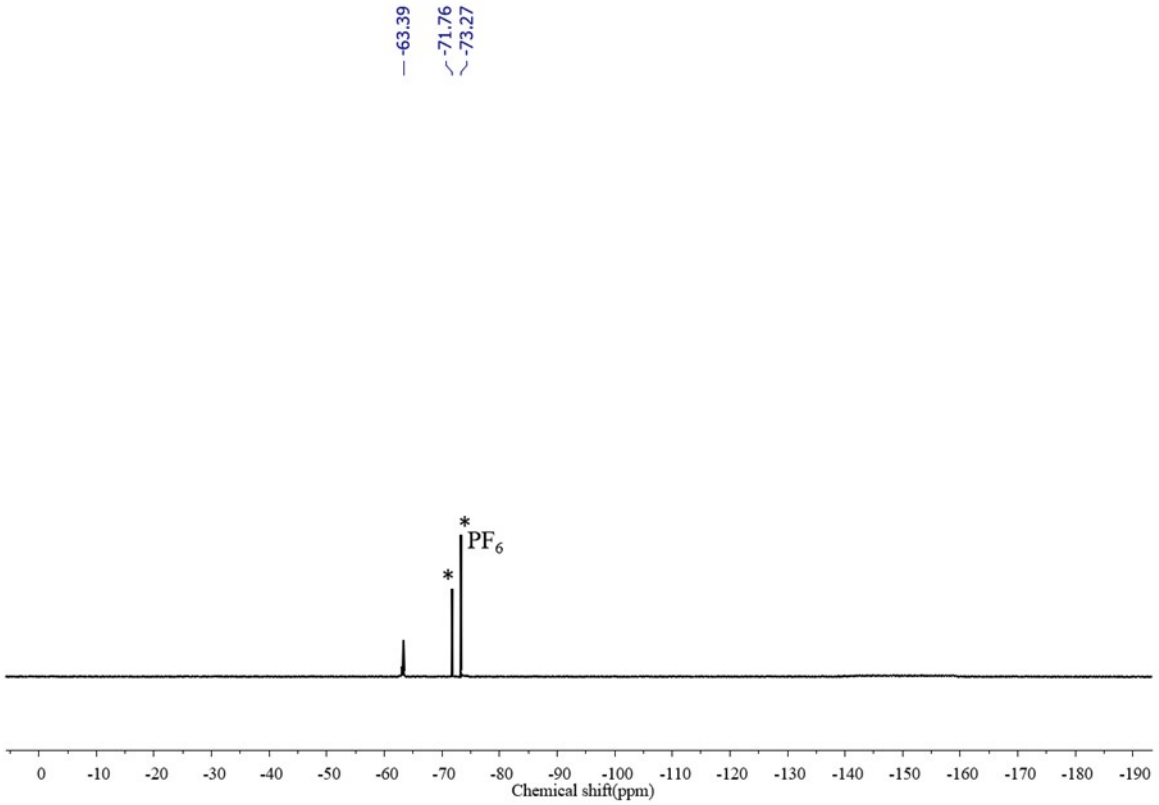


Figure S 16: ^{19}F (471 MHz, CD_2Cl_2, 298 K) NMR spectrum of [Cu (**1**)(**3**)]PF_6.

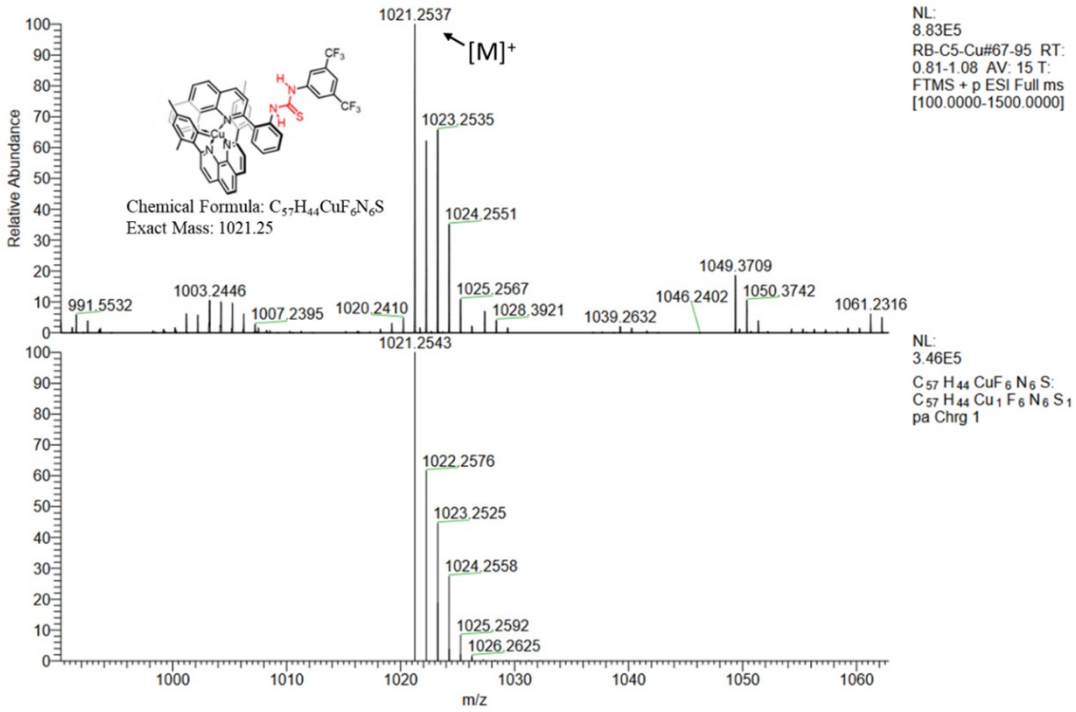


Figure S 17: High-Resolution Mass Spectrum (HRMS) a) experimental and b) theoretical of [Cu (**1**)(**3**)]PF_6.

3. D_2O exchange studies

Sample was taken in an NMR tube and dissolved in deuteriated ($CDCl_3$ for **1** and CD_2Cl_2 for [Cu (**1**)(**3**)]PF_6) solvent and added 100 µL of D_2O. It was shaken well and the ^1H NMR was measured.

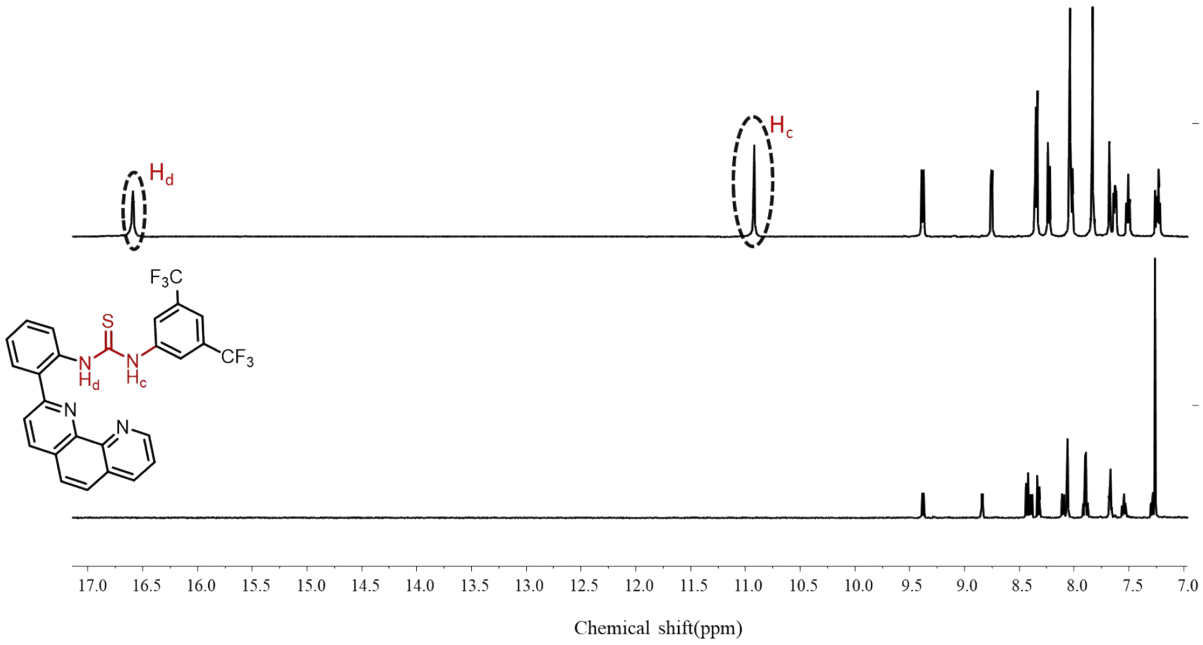


Figure S 18: Partial ^1H NMR (500 MHz, $CDCl_3$, 298 K) spectra of a) **1**; b) after shaking with D_2O

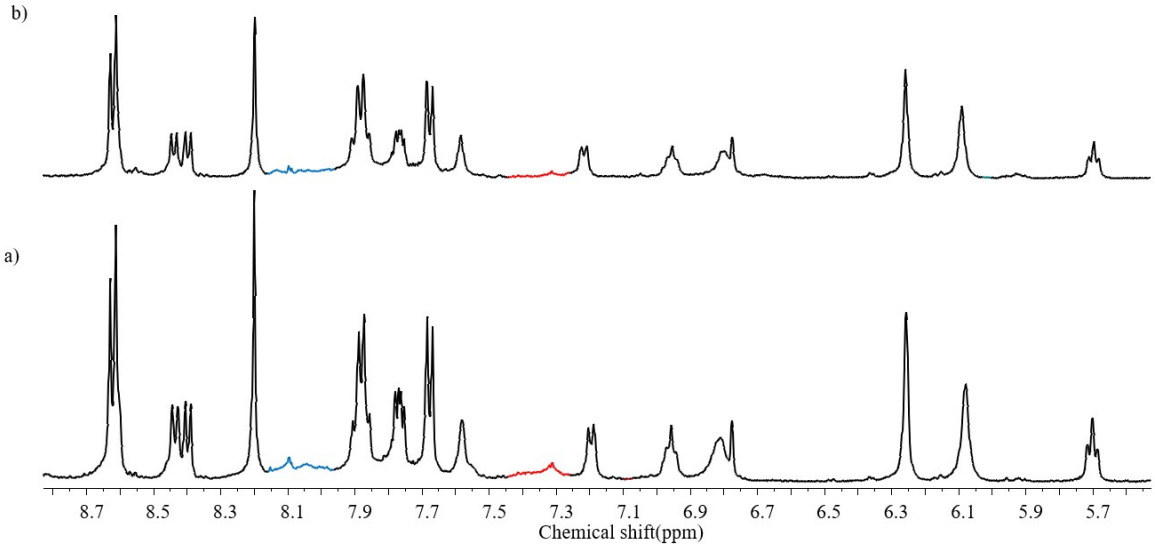
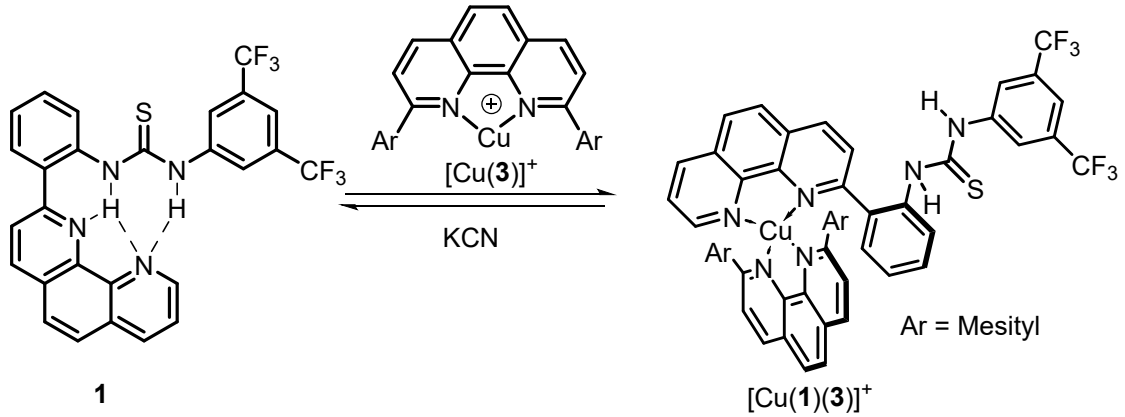


Figure S 19: Partial ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) of a) [Cu (**1**)(**3**)]PF_6; **b)** after shaking with D_2O.

4. Metal induced reversible switching



Scheme S 2: Schematic representation of reversible switching between two states of switch **1**.

1, **3** and [$Cu(CH_3CN)_4PF_6$] (1: 1: 1) were dissolved in 0.5 mL of CD_2Cl_2 and ^{1}H NMR was measured. 1 equivalent of KCN was added to the mixture. The solution was shaken well, colour turned pale yellow and ^{1}H NMR was measured. Upon addition of one more equivalent of [$Cu(CH_3CN)_4(PF_6)$] to the same mixture, red colour appears. The same procedure was continued for three times without observing any noticeable decomposition.

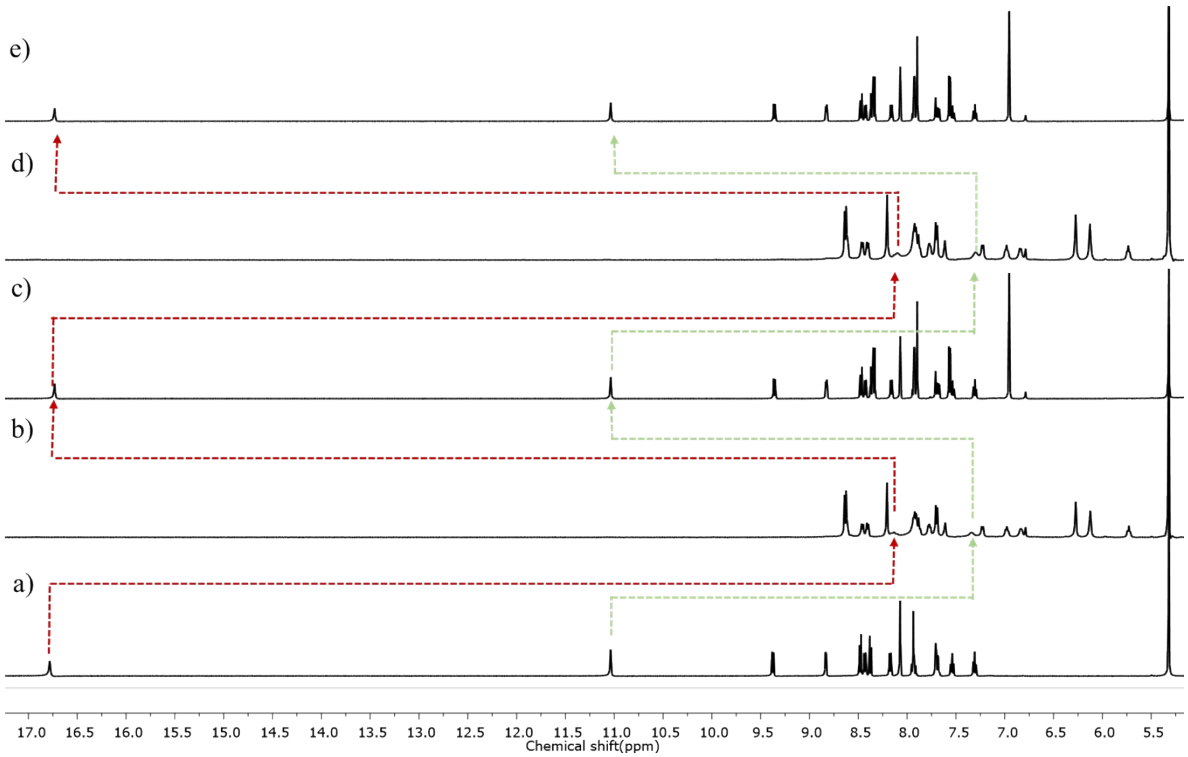


Figure S 20: Partial ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectra of a) **1** (10 mM), b) after addition of one equivalent of $[Cu(CH_3CN)_4PF_6]$ and **3**; c) after addition of excess aqueous KCN to Cu complex followed by removal of water; d) after addition of $[Cu(CH_3CN)_4PF_6]$ to c; e) after addition of excess aqueous KCN to d and removal of water.

5. Concentration dependent ^{1}H NMR

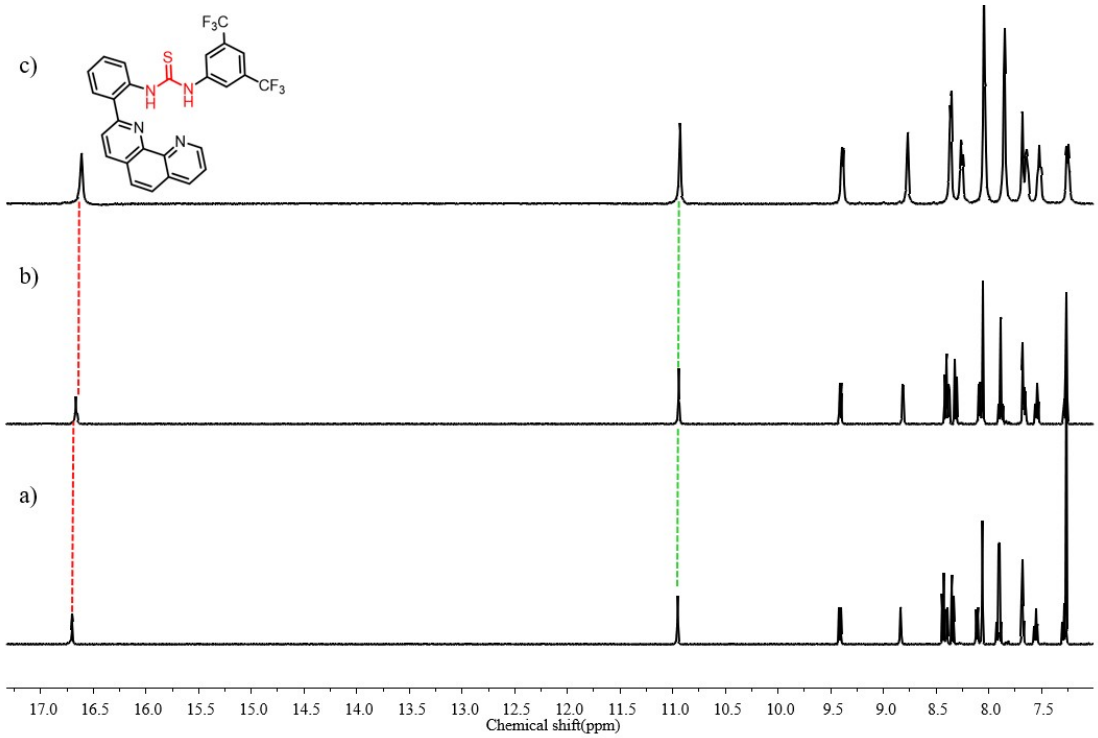


Figure S 21: Partial ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectra of **1** at a) 11 mM**,** b) 22 mM**,** c) 33 mM concentration.

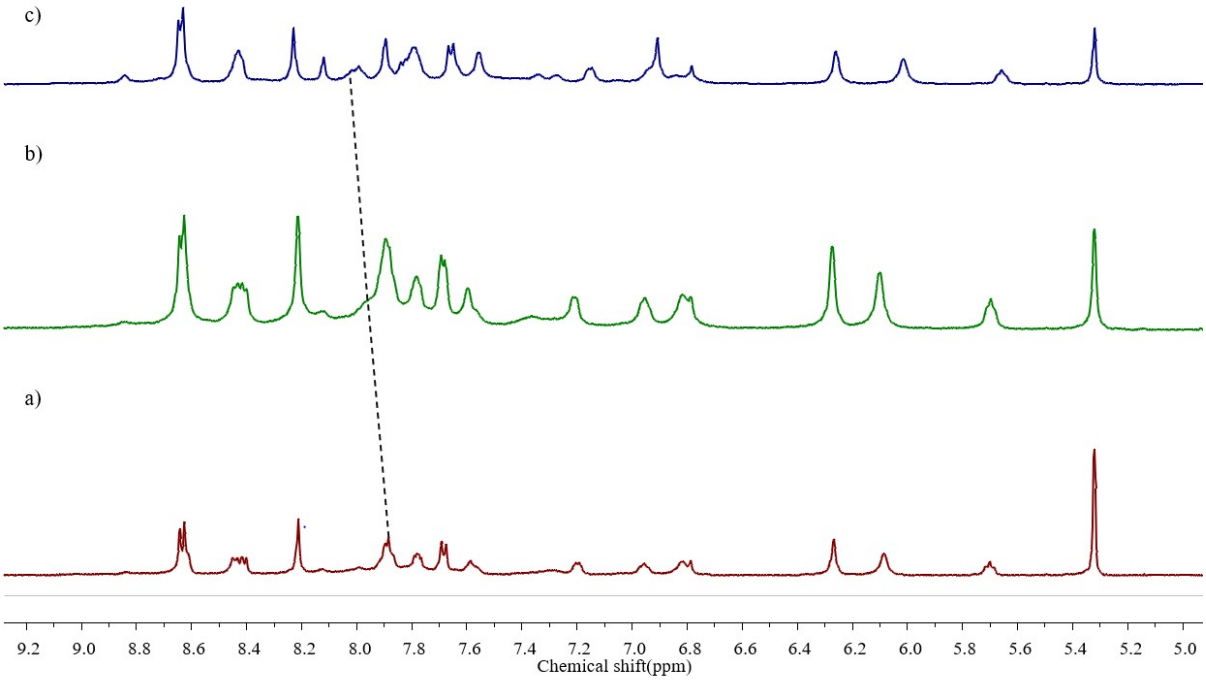


Figure S 22: Partial ^{1}H NMR (500 MHz, CD_2Cl_2, 298 K) spectra of [Cu(**1**)(**3**)]PF_6 at a) 11 mM**,** b) 22 mM**,** c) 33 mM concentration.

6. Comparison of UV-Visible spectra of 1 & [Cu (1)(3)] PF_6

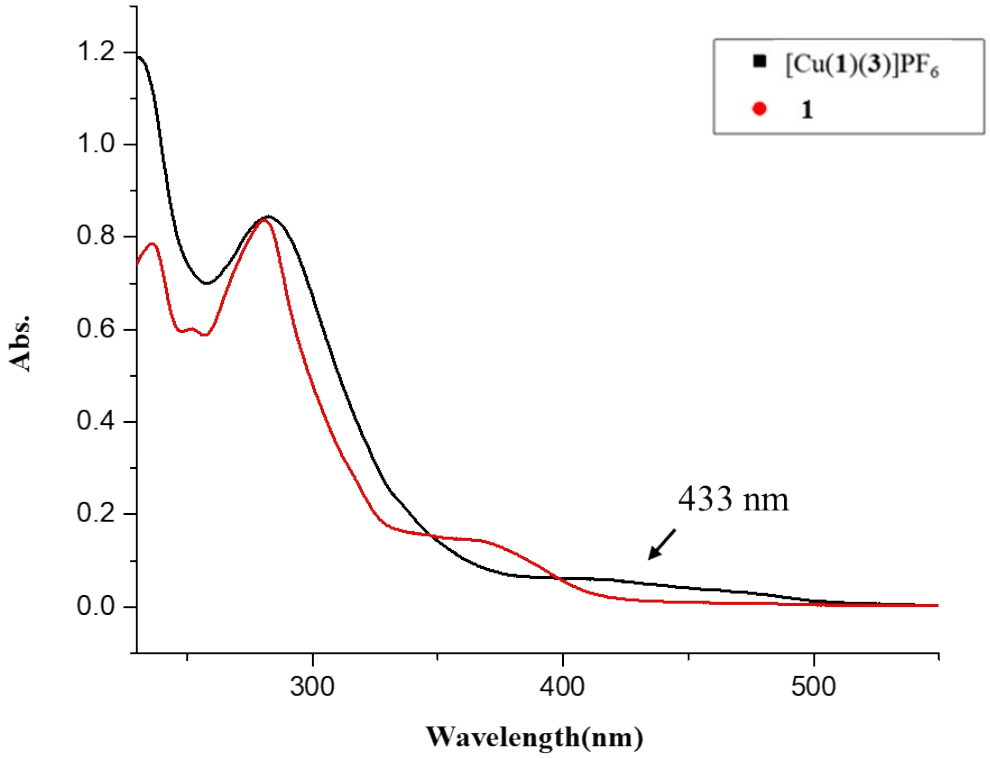


Figure S 23: UV-Visible spectra (CH_2Cl_2, 5 × 10^{-5} M, 298 K) of **1** & [Cu (**1**)(**3**)] PF_6

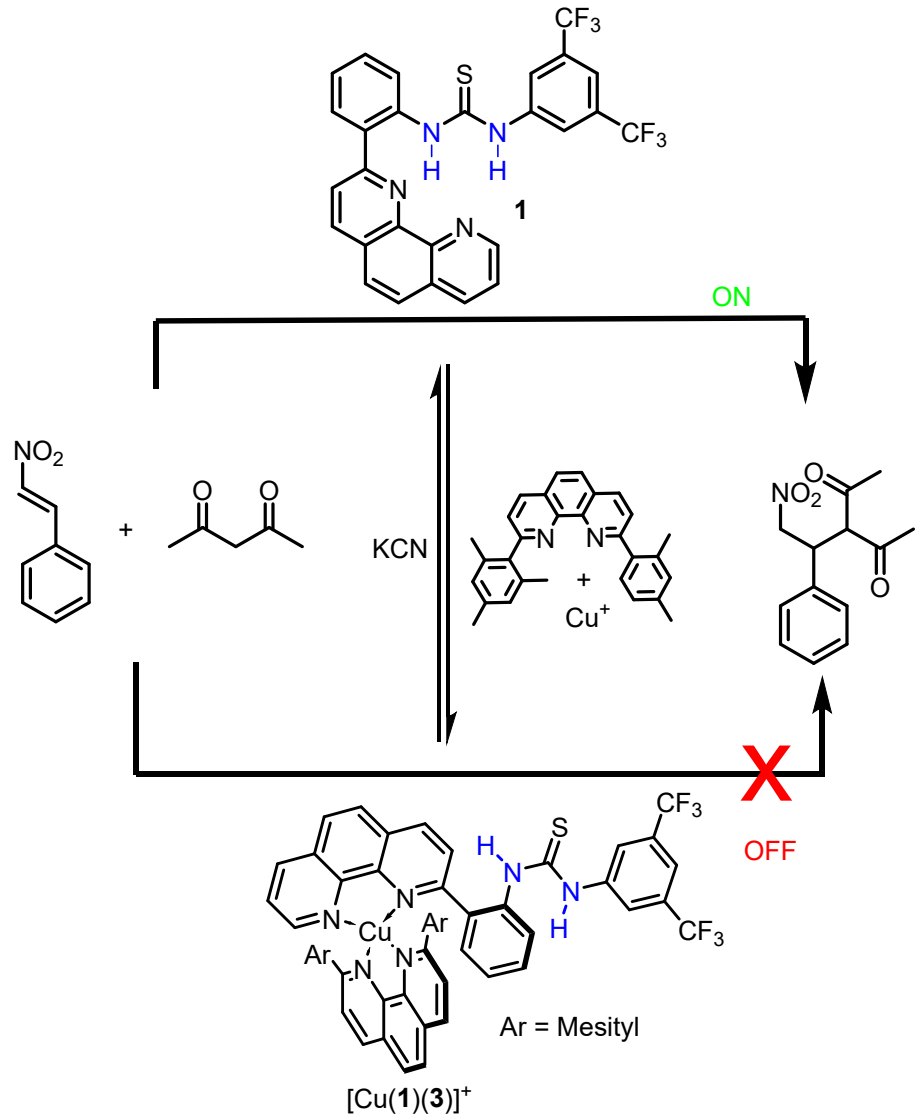
7. Catalytic studies

1 (5.24 mg, 9.70 µmol), [Cu $(CH_3CN)_4PF_6$] (3.62 mg, 9.70 µmol) and **3** (4.04 mg, 9.70 µmol) were dissolved in distilled 1,2-dichloromethane, stirred for one minute and dried under vacuum and used directly for catalytic studies.

7.1 Model reactions

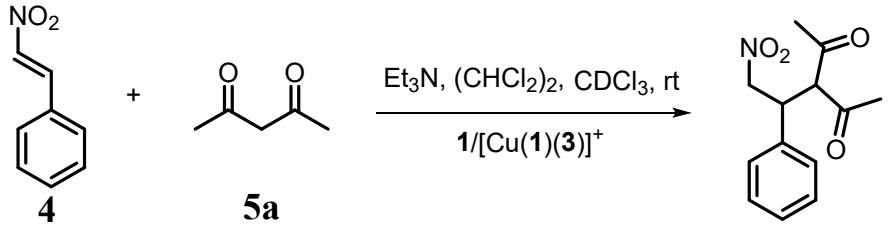
7.1.2 General procedure for model catalytic reactions

Beta-nitrostyrene (5 mg, 33.5 µmol), activemethylene compound (**5a**/**5b**/**5c**/**5d**/**5e**) (335 µmol), tetrachloroethelene (1.59 µL, 33.5 µmol), triethylamine (0.47 µL, 3.35 µmol) and **1** (1.82 mg, 3.35 µmol) were dissolved in $CDCl_3$ (0.5 mL) in an NMR tube and monitored the reaction by measuring ^{1}H NMR at room temperature at specified time.



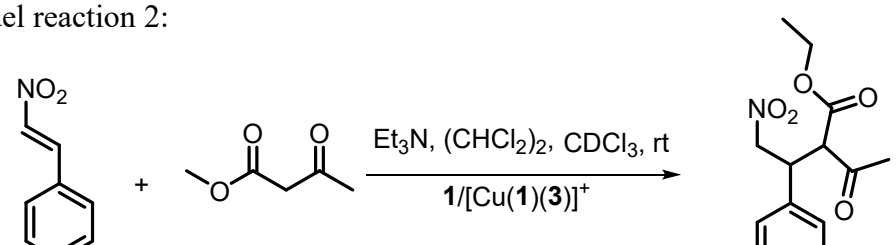
Scheme S 3: Schematic representation of Cu^{+} induced ON/OFF catalysis.

Model reaction 1:



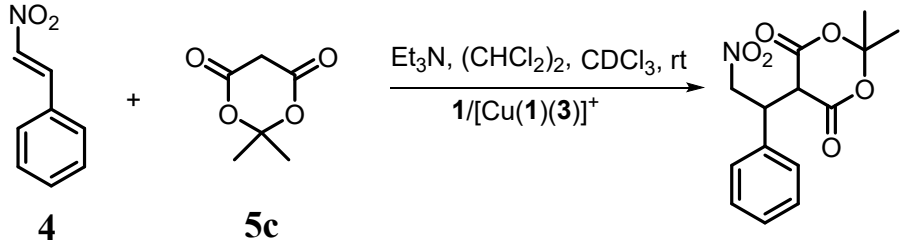
4 **5a** **6**

Model reaction 2:



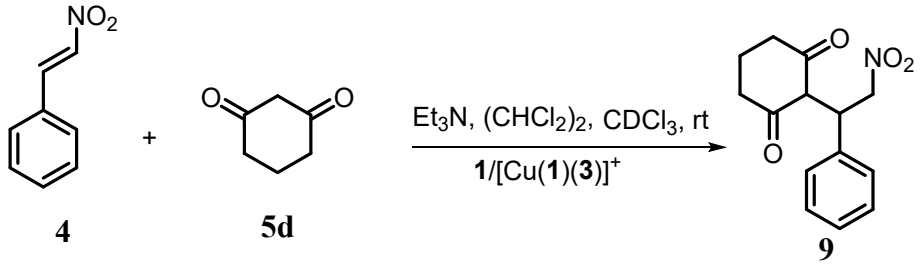
4 **5b** **7**

Model reaction 3:



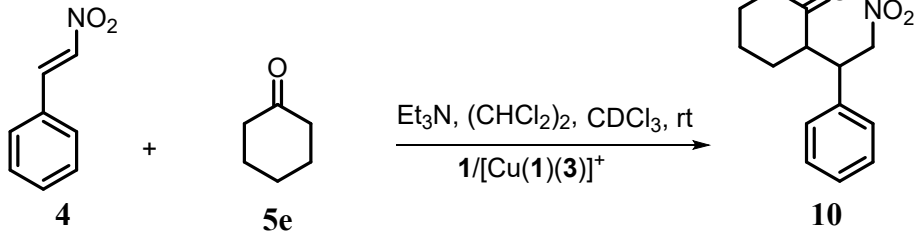
4 **5c** **8**

Model reaction 4:



4 **5d** **9**

Model reaction 5:



4 **5e** **10**

Scheme S 4: Model reactions used in ON/OFF catalysis

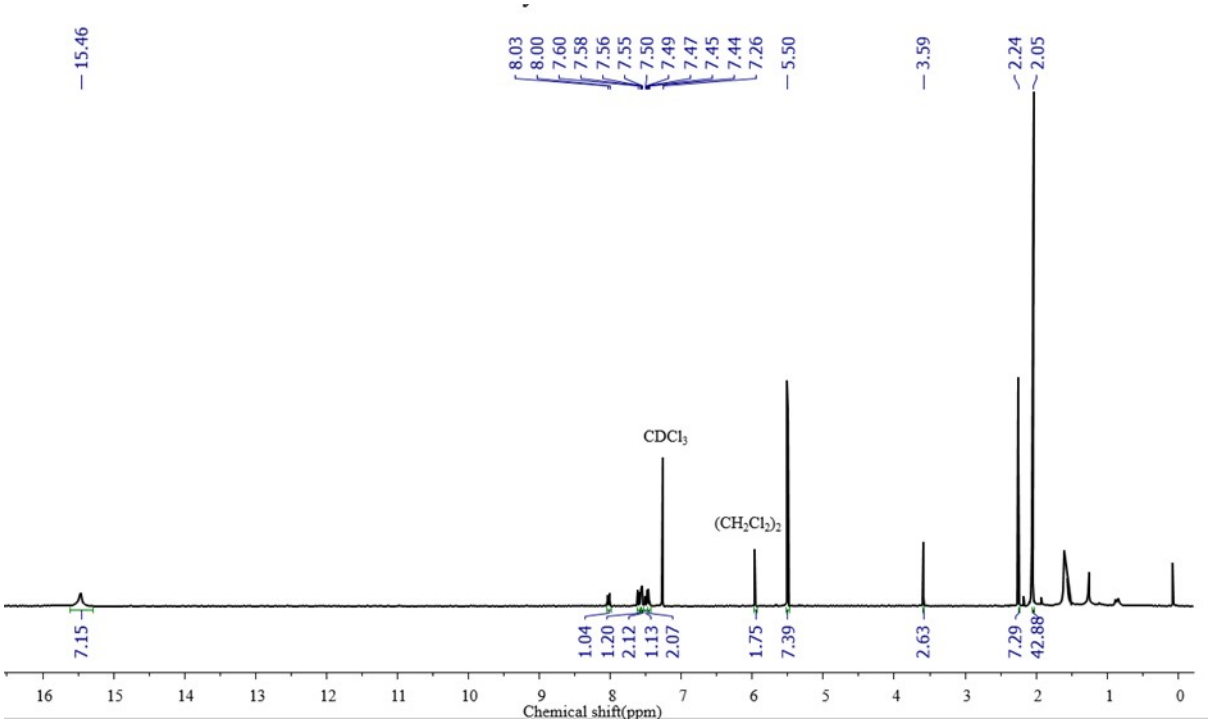


Figure S 24: ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectrum of model catalytic reaction 1 in the absence of switch **1**.

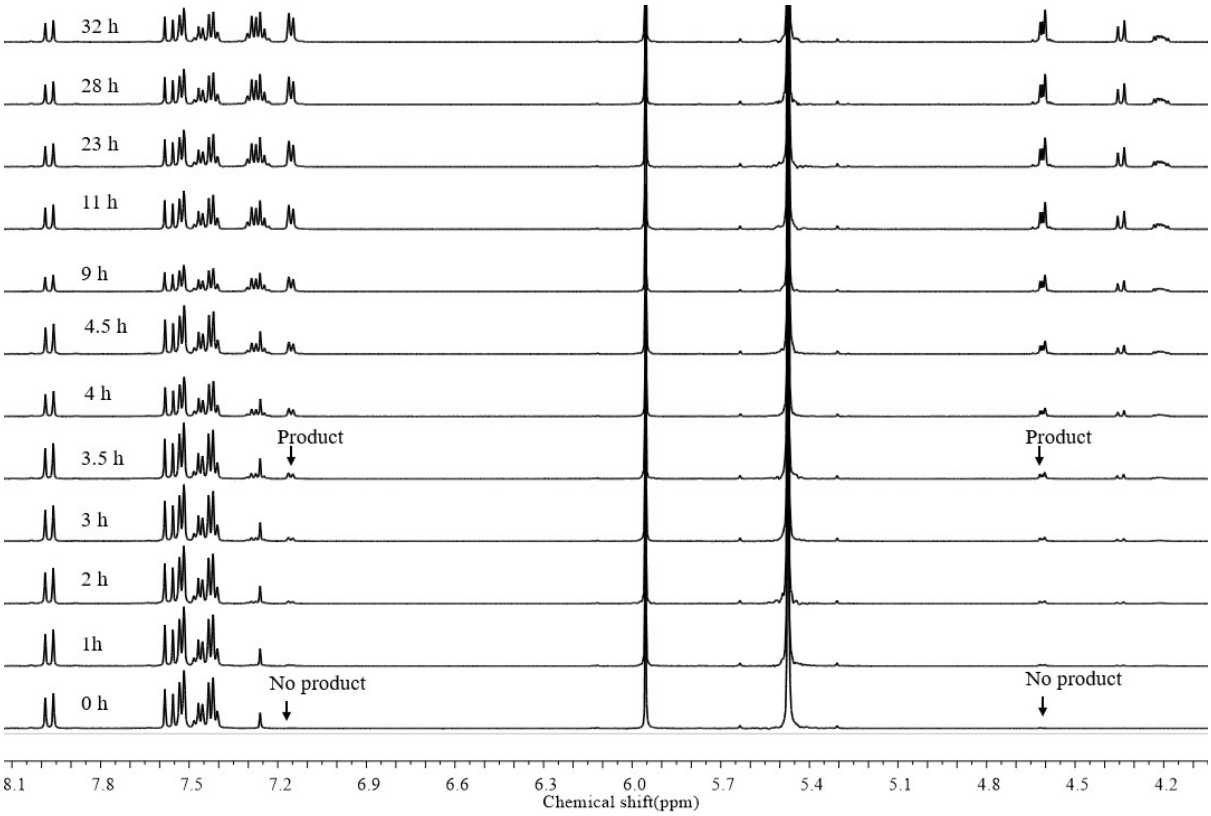


Figure S 25: Time profile ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectra of model reaction 1 in the presence of 5 mol% switch **1**.

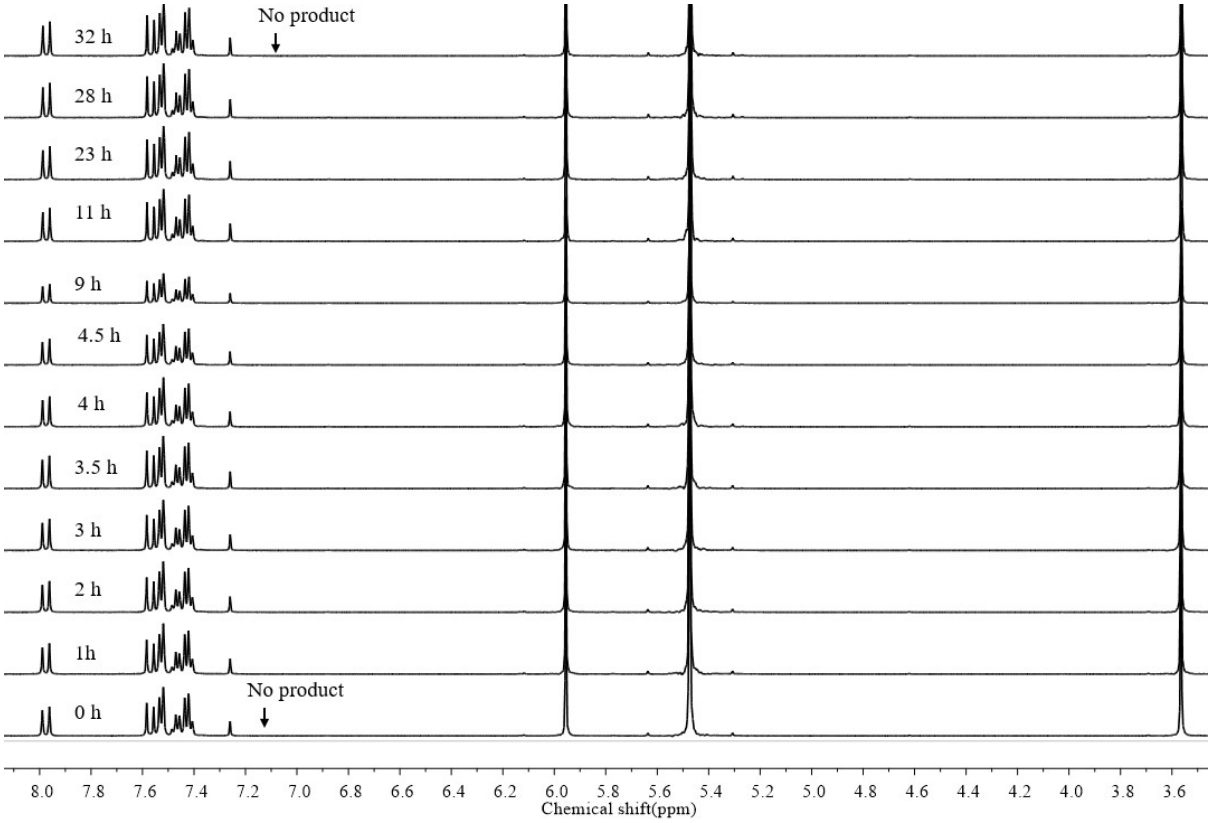


Figure S 26: Time profile ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectra of model reactions in the presence of [Cu (**1**)(**3**)]PF_6.

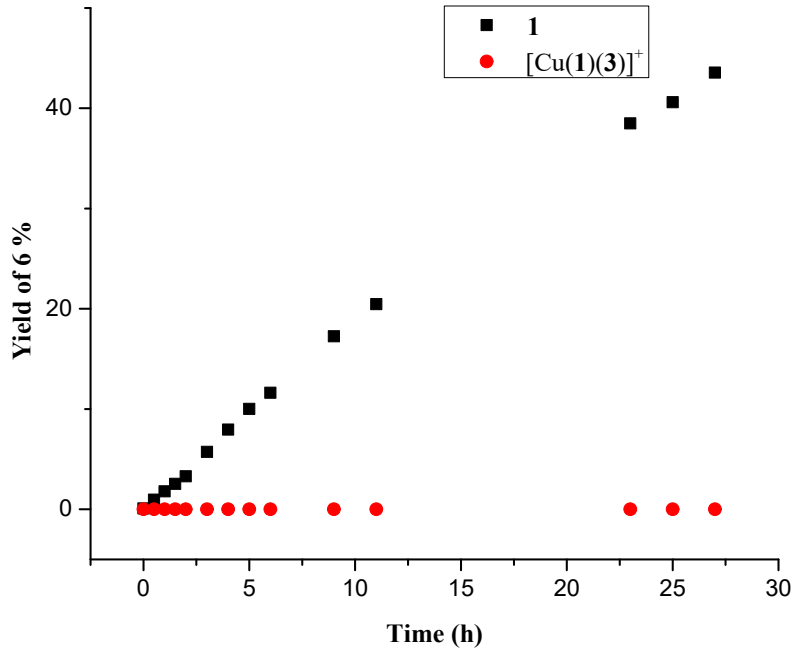


Figure S 27: Comparison for the product formation with switch **1** (5 mol%) (black) and with [Cu (**1**)(**3**)]PF_6 (red) (5 mol%).

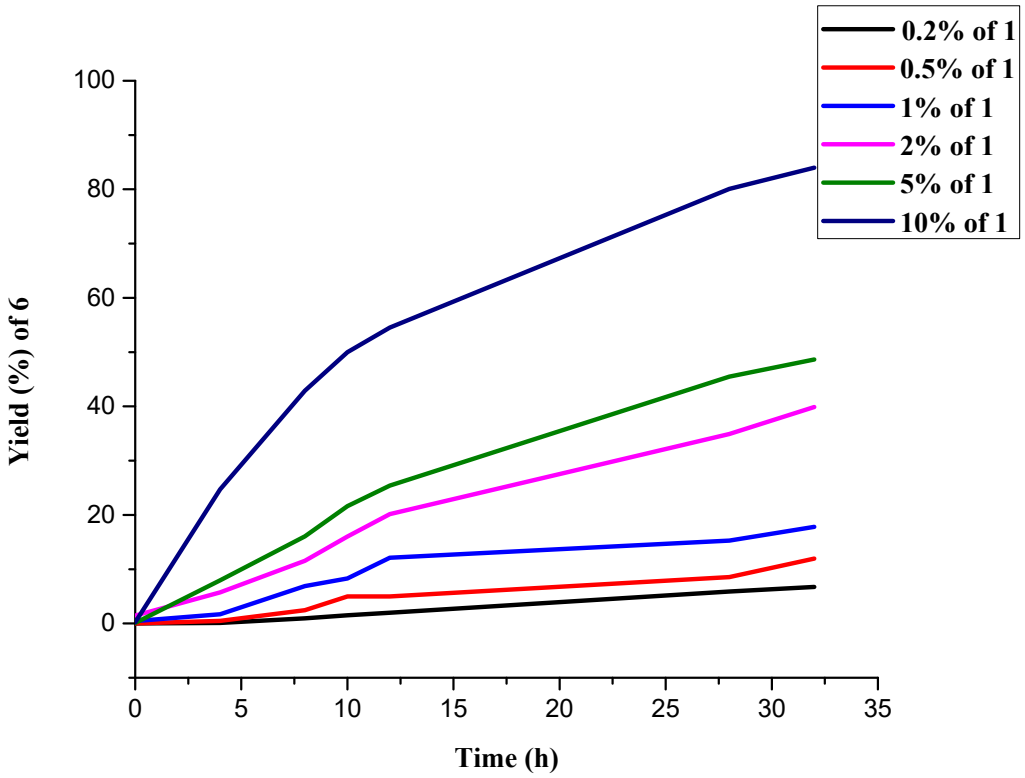


Figure S 28: Comparison for the product formation with different mol% of switch **1**.

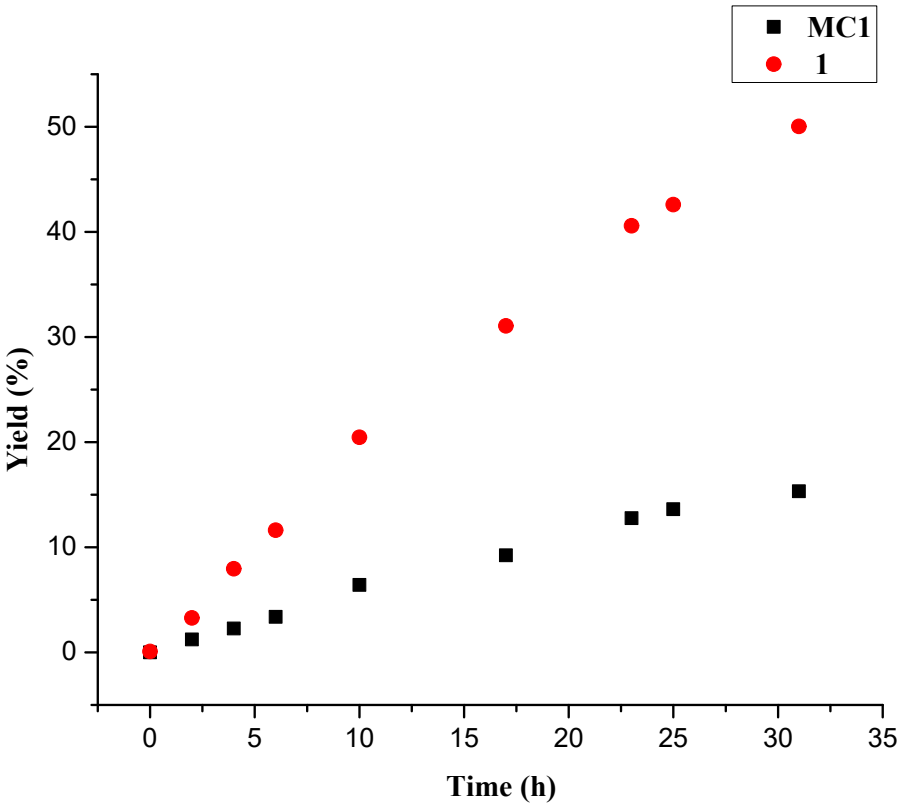


Figure S 29: Comparison for the product formation for model reaction 1 with the switch **1** (5 mol%) (red) and with (5 mol%) model catalyst1 (**1a**) (black).

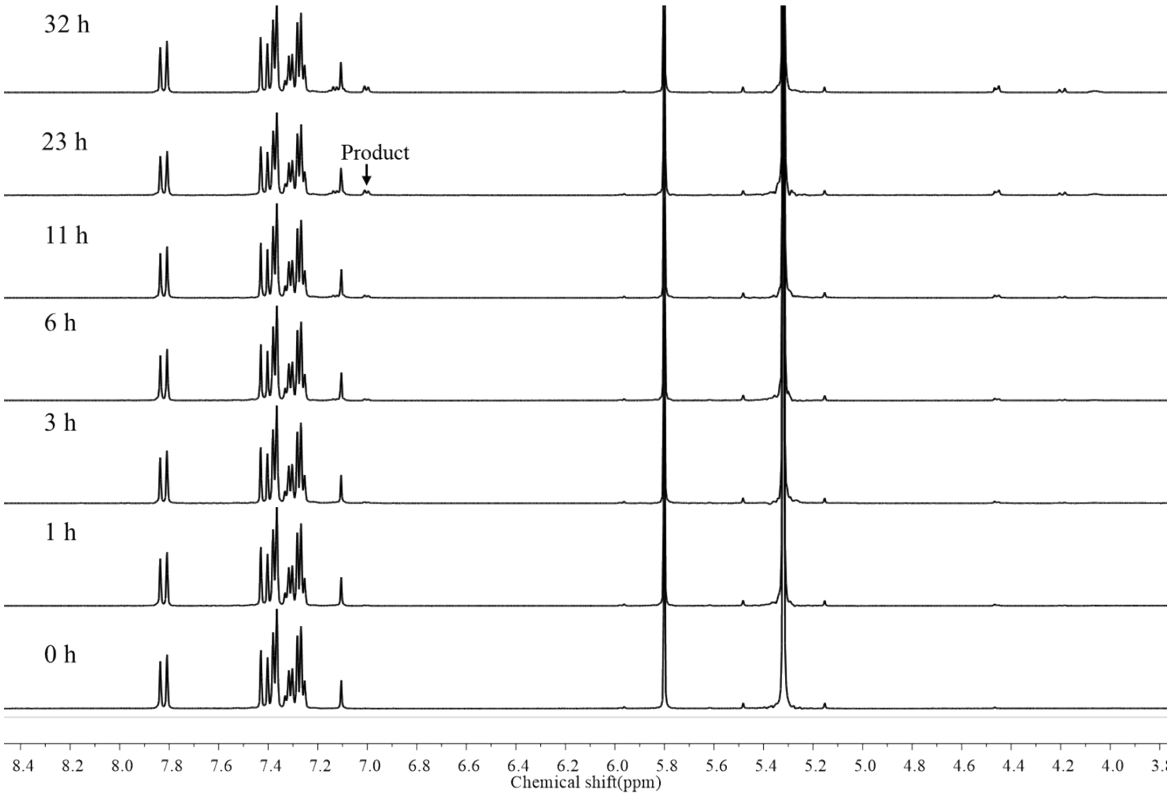
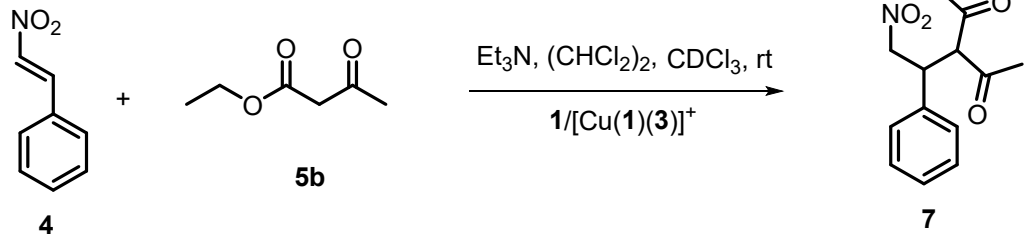


Figure S 30: Time profile ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectra of model reaction 1 in the presence of 5 mol% **1a**.

Model reaction 2



4 **5b** **7**

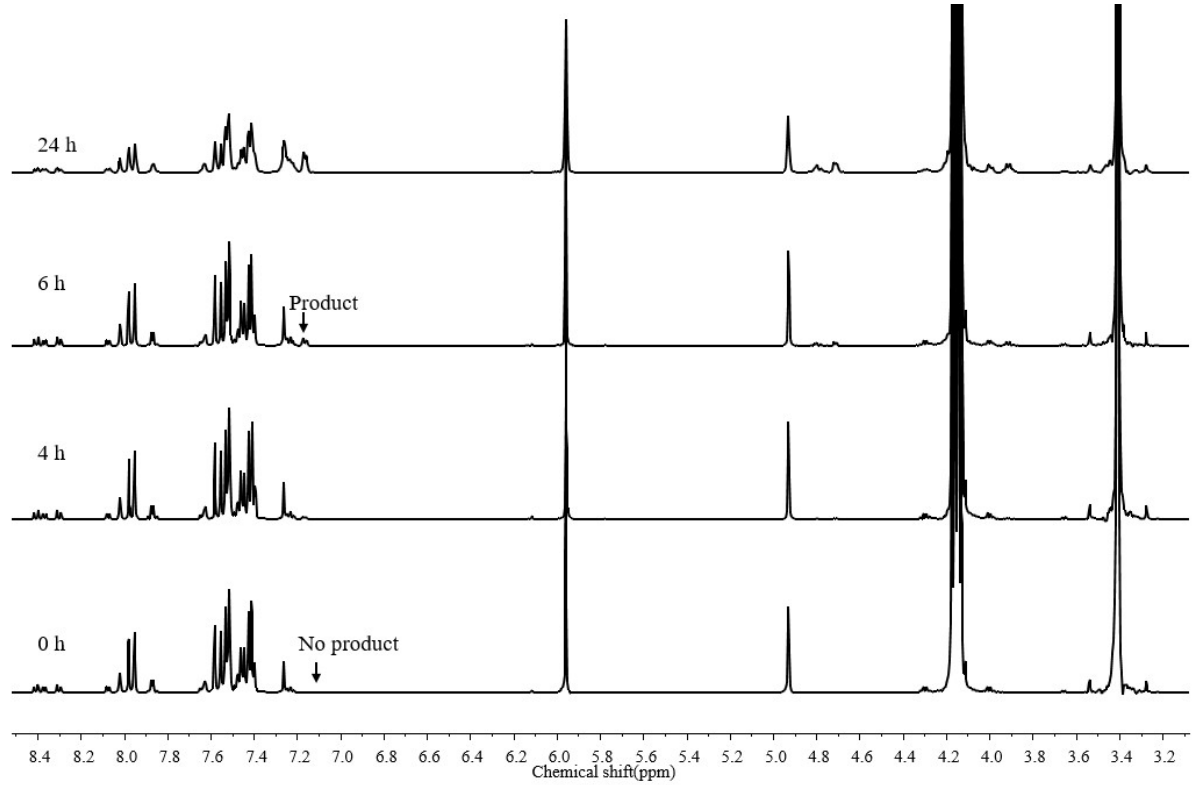


Figure S 31: Time profile ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectra of model reaction 2 in the presence of one mol% **1**.

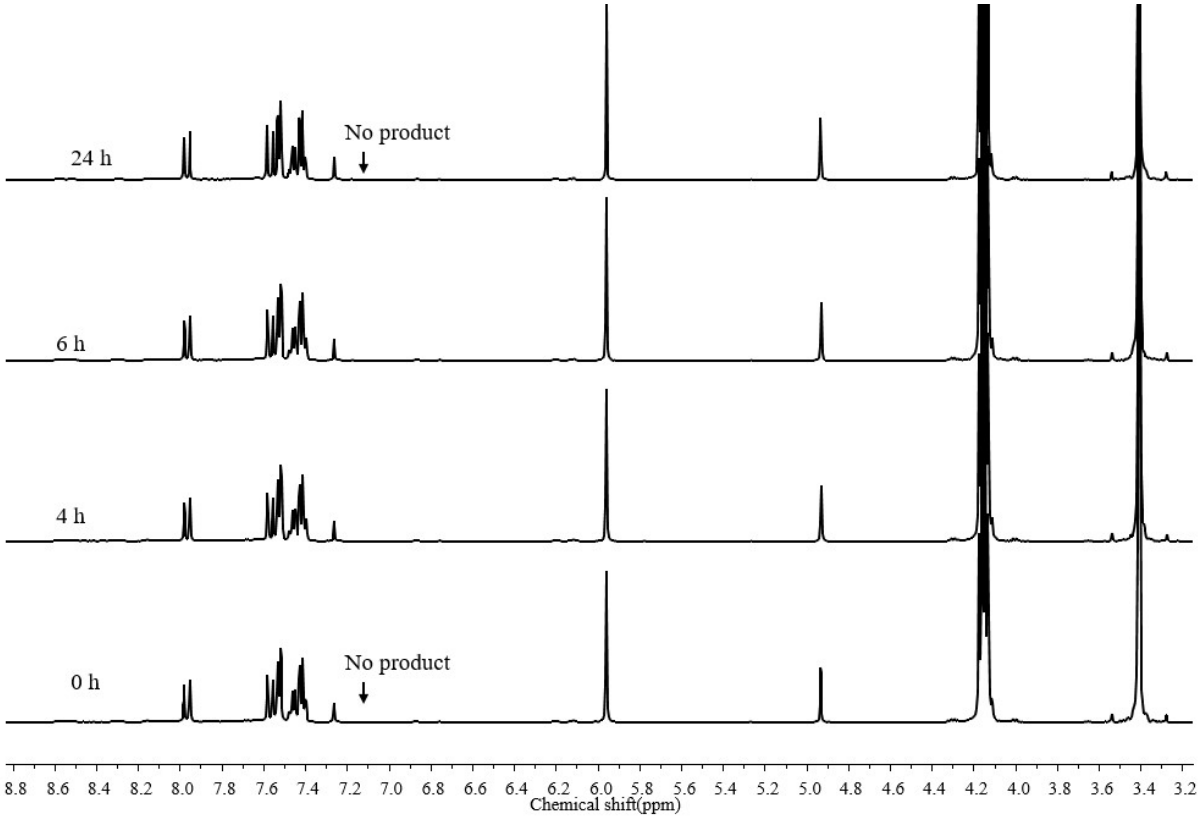


Figure S 32: Time profile ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectra of model reaction 2 in the presence of one mol% [Cu(**1**)(**3**)]PF_6.

Model reaction 3:

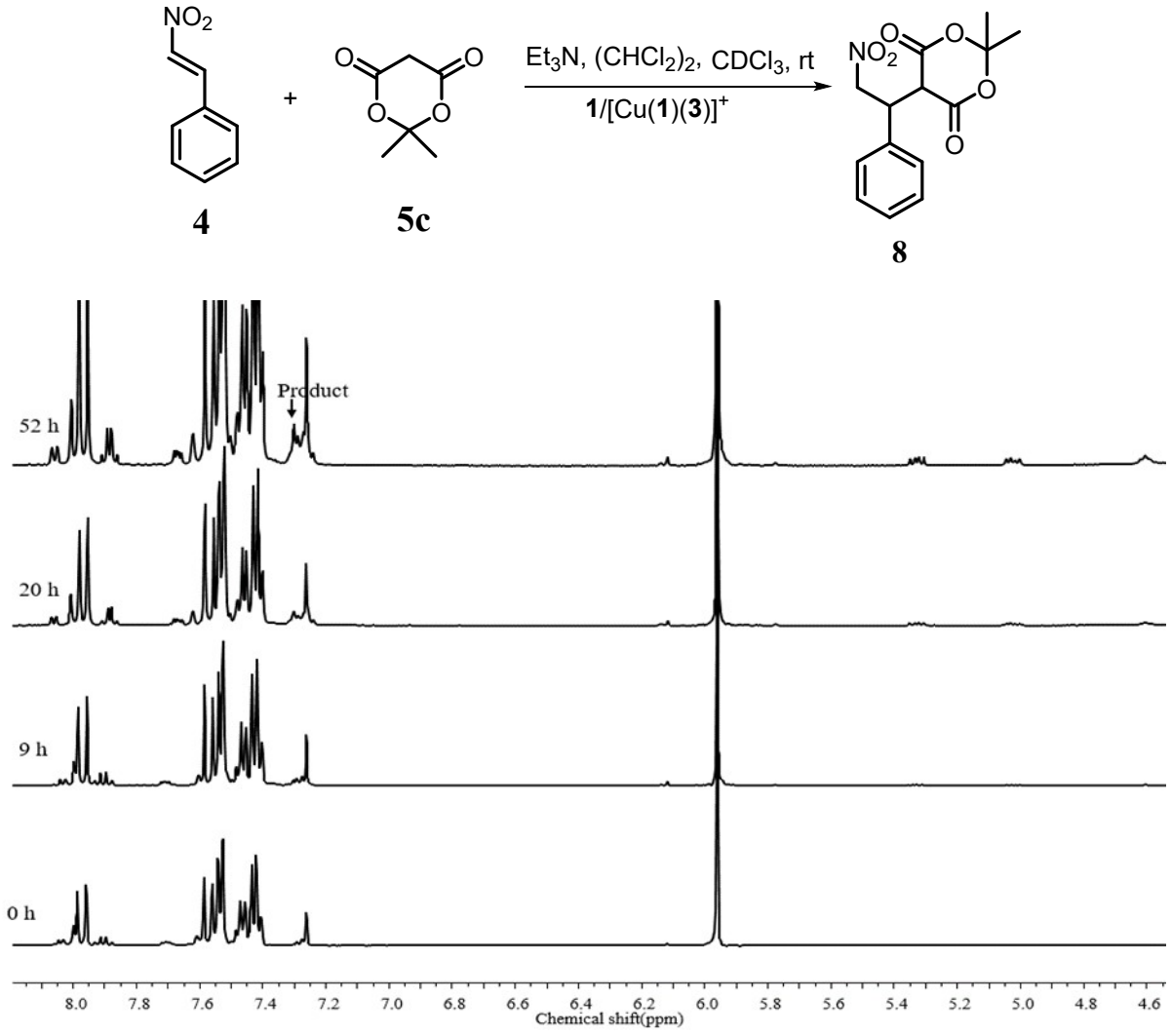


Figure S 33: Time profile ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectra of model reaction 3 in the presence of one mol% **1**.

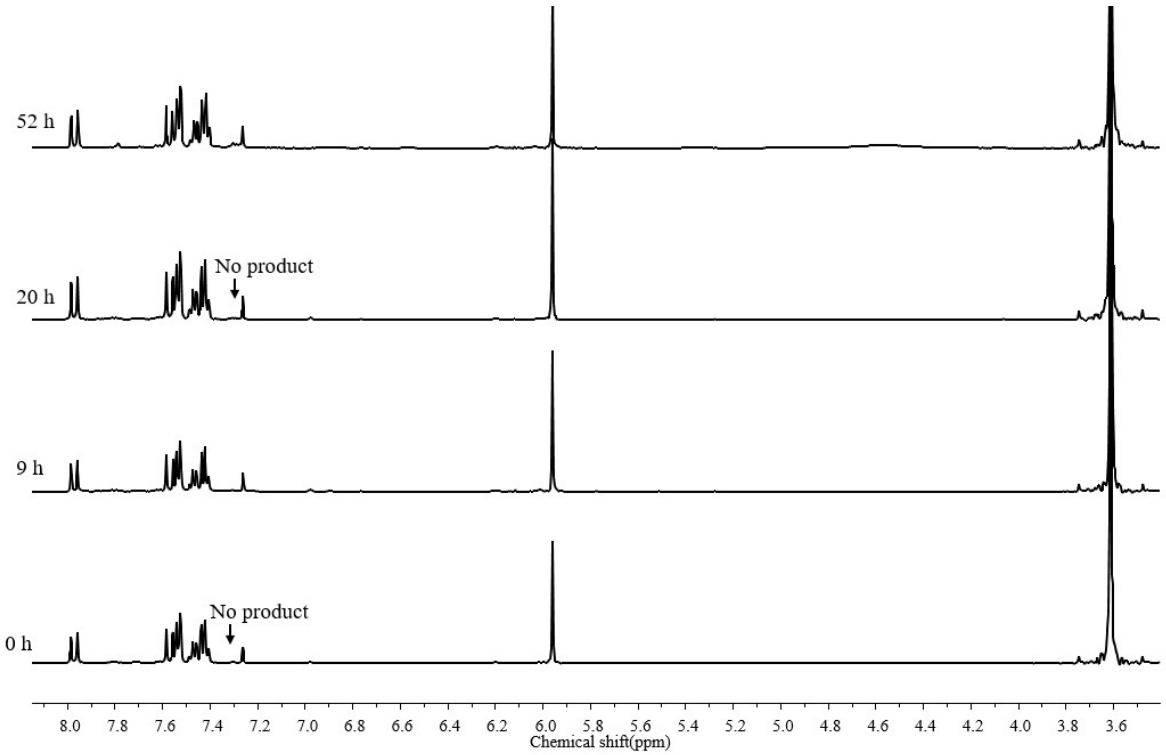
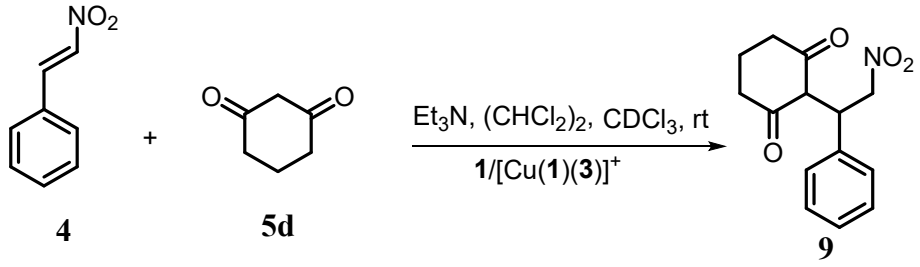


Figure S 34: Time profile ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectra of model reaction 3 in the presence of one mol% [Cu (**1**)(**3**)]PF_6.

Model reaction 4:



4 **5d** **9**

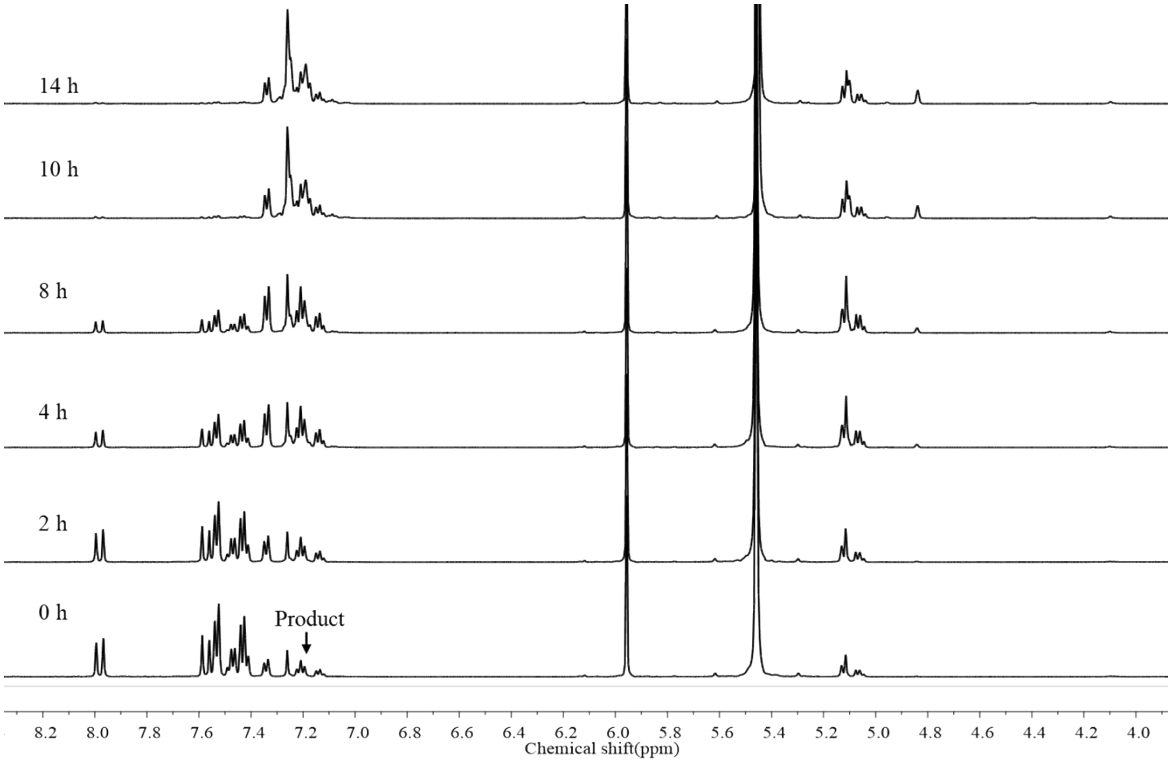


Figure S 35: Time profile ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectra of model reaction 4 in the presence of one mol% **1**.

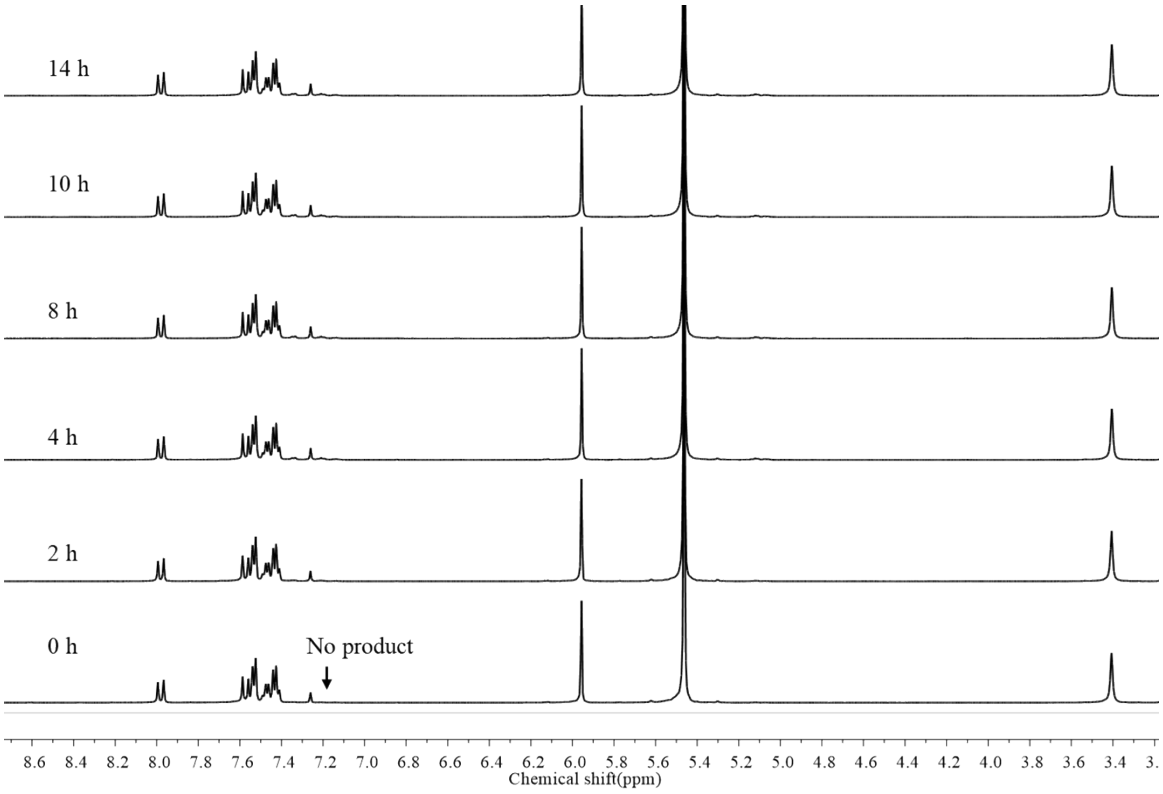
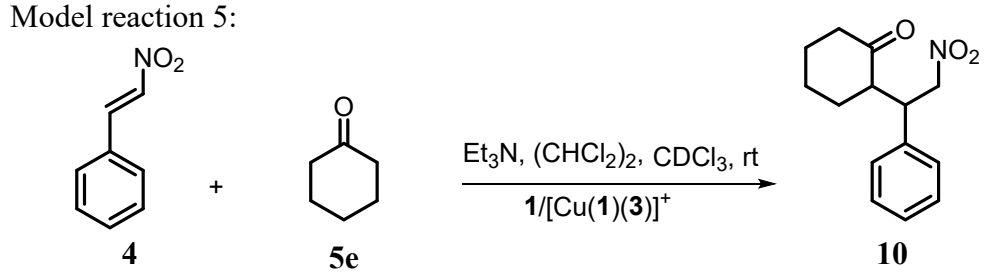


Figure S 36: Time profile ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectra of model reaction 4 in the presence of one mol% [Cu (**1**)(**3**)]PF_6.

Model reaction 5:



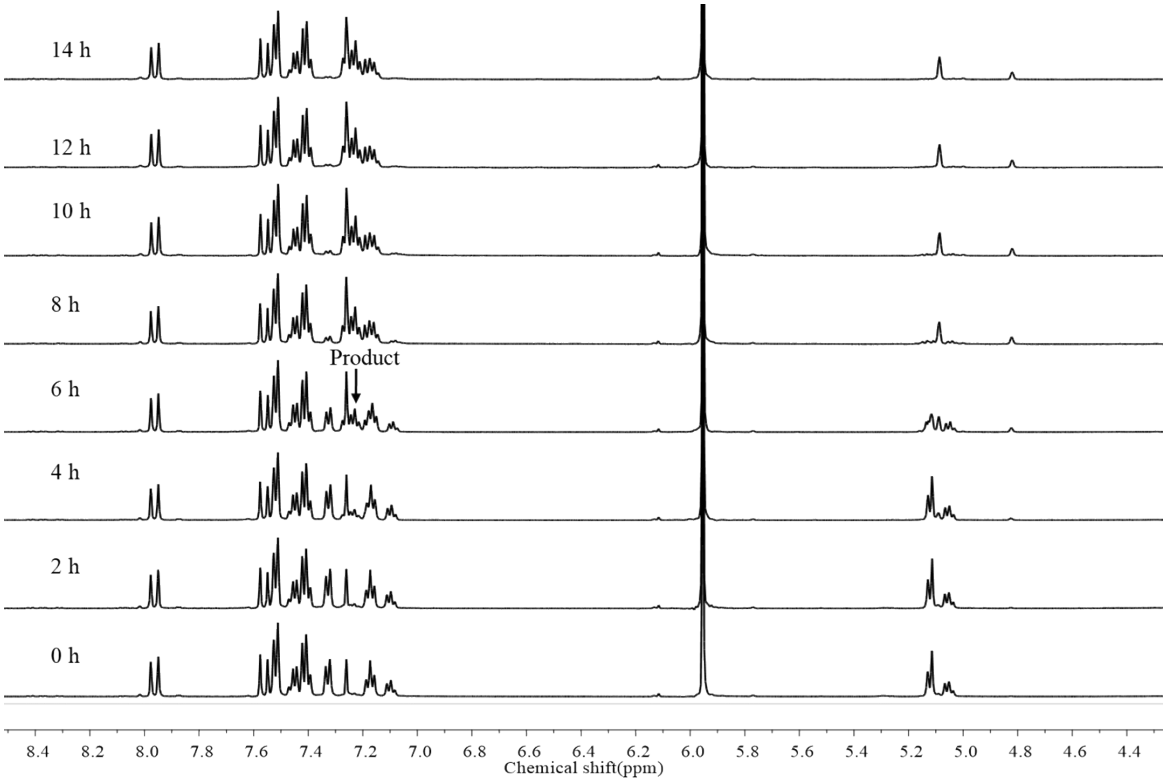


Figure S 37: Time profile ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectra of model reaction 5 in the presence of one mol% **1**.

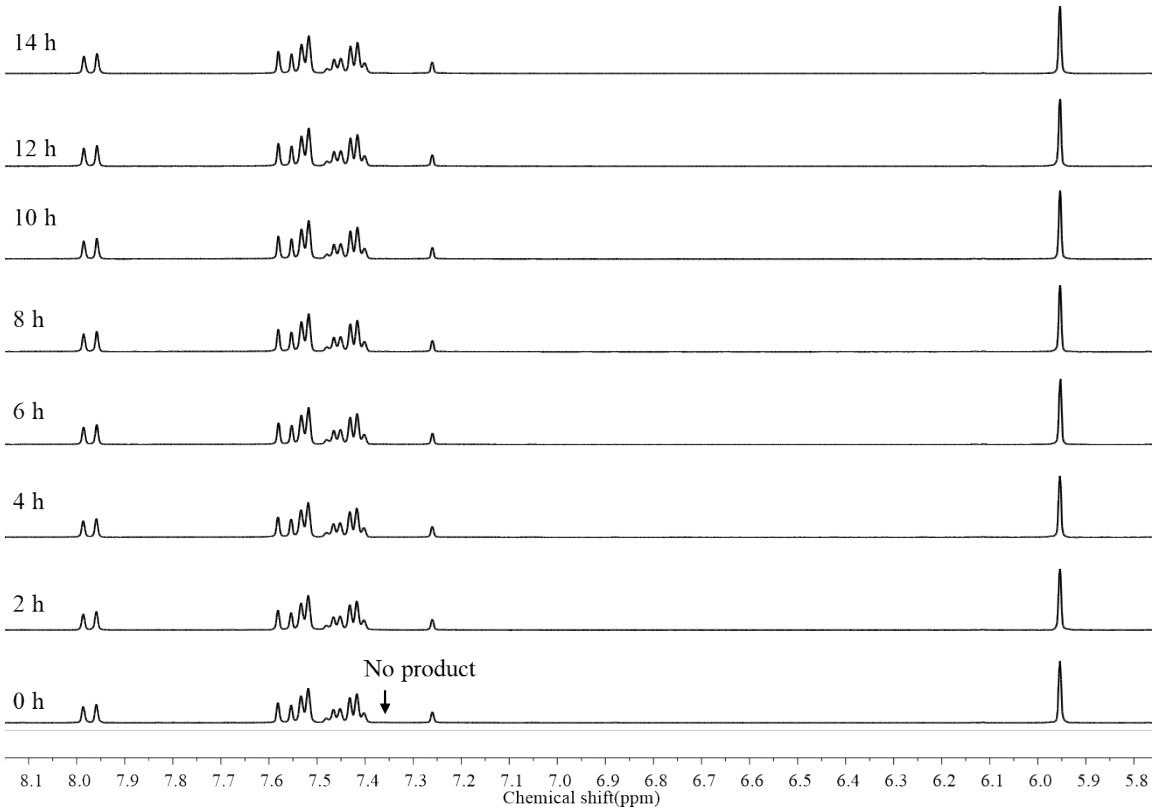
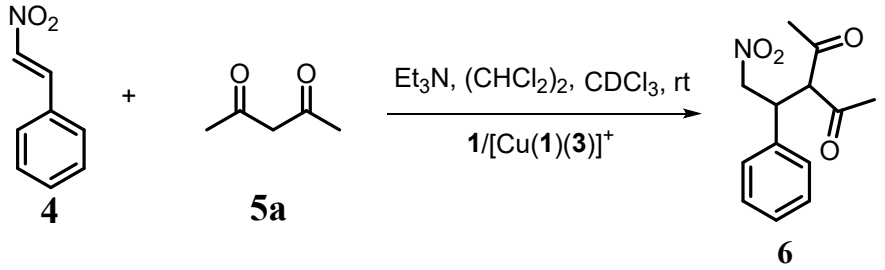


Figure S 38: Time profile ^{1}H NMR (500 MHz, $CDCl_3$, 298 K) spectra of model reaction 5 in the presence of one mol% [Cu (**1**)(**3**)]PF_6.

7.2 In situ changes in the yield of the reaction by alternating switching between two states

Model reaction 1:



4 **5a** **6**

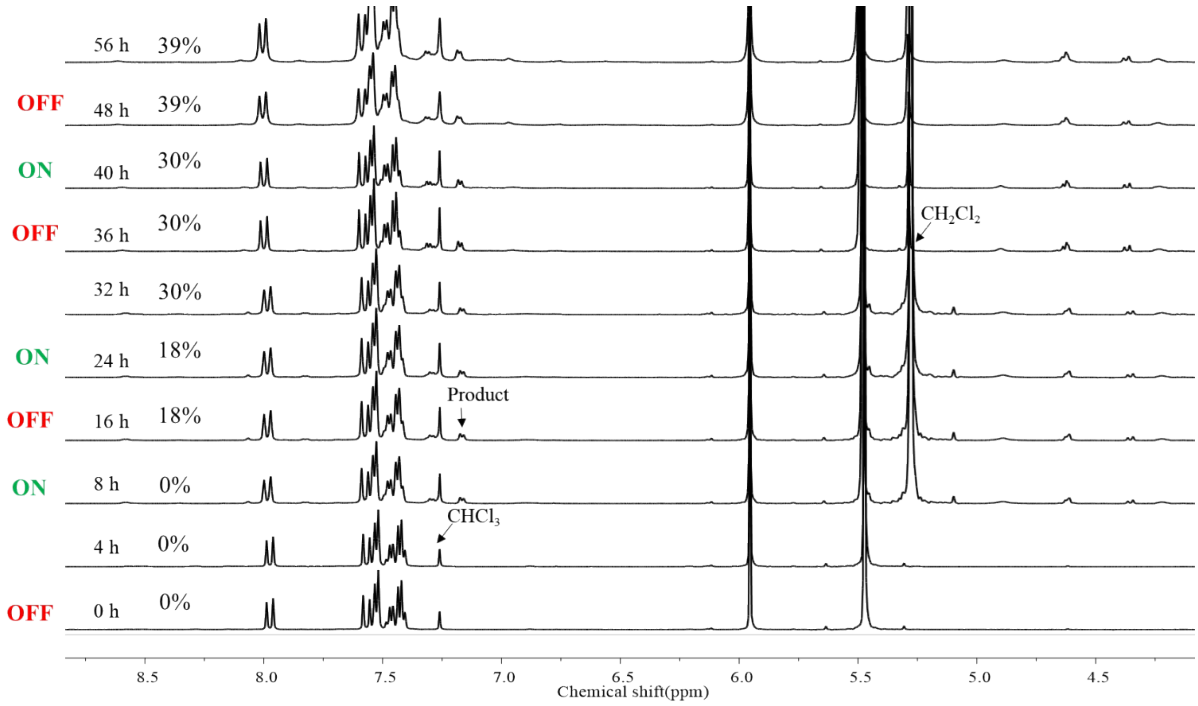


Figure S 39: Evolution of ^{1}H NMR for the catalytic reaction 1 with 5 mol% [Cu (**1**)(**3**)]PF_6 (0 to 8h, OFF state); upon addition of excess aqueous KCN to [Cu (**1**)(**3**)]PF_6 followed by drying and keeping the reaction for 8 h (8 h to 16 h, ON state); further addition of one equivalent of $[Cu(CH_3CN)_4]PF_6$ to the above mixture (16 h to 24 h, OFF state); again washing with aqueous KCN followed by drying and keeping the reaction for 8 h (24 h to 32 h, ON state); addition of one equivalent of one equivalent of $[Cu(CH_3CN)_4]PF_6$ (32 h to 40 h, OFF state); again washing with aqueous KCN followed by drying and keeping the reaction for 8 h (40 h to 48 h, ON state); further OFF state was generated by addition of one equivalent of $[Cu(CH_3CN)_4]PF_6$ (48 h to 56 h, OFF state). In each successive ON cycle conversion decreases due to loss of some amounts of catalyst during work-up and drying after treatment with aqueous KCN.

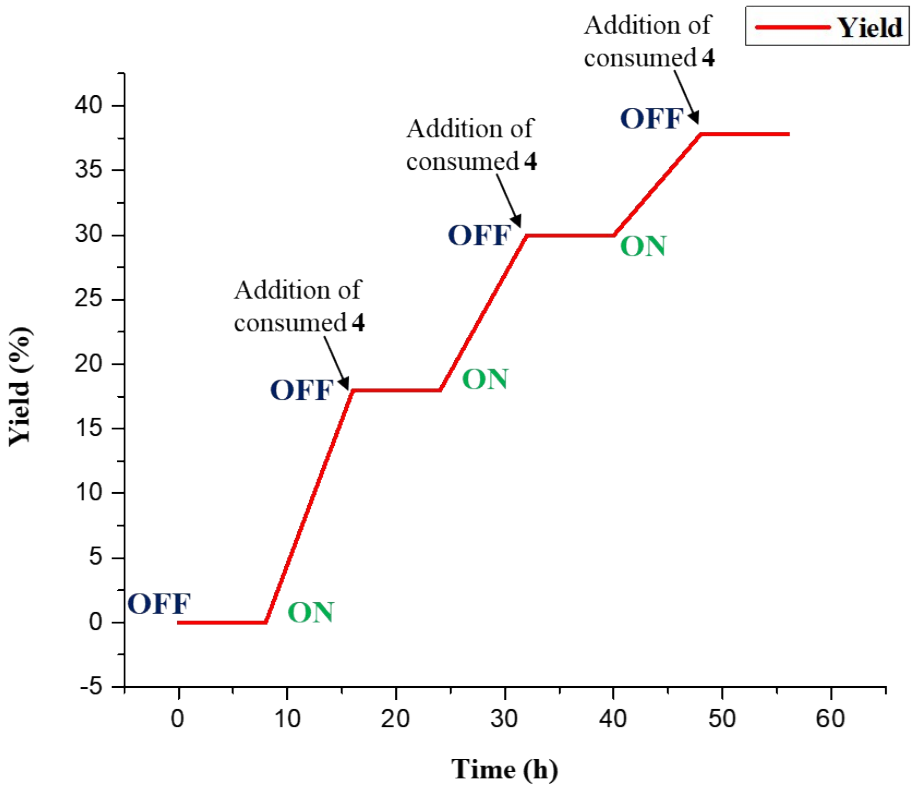


Figure S 40: Graph showing changes in the yield on OFF-ON-OFF switching

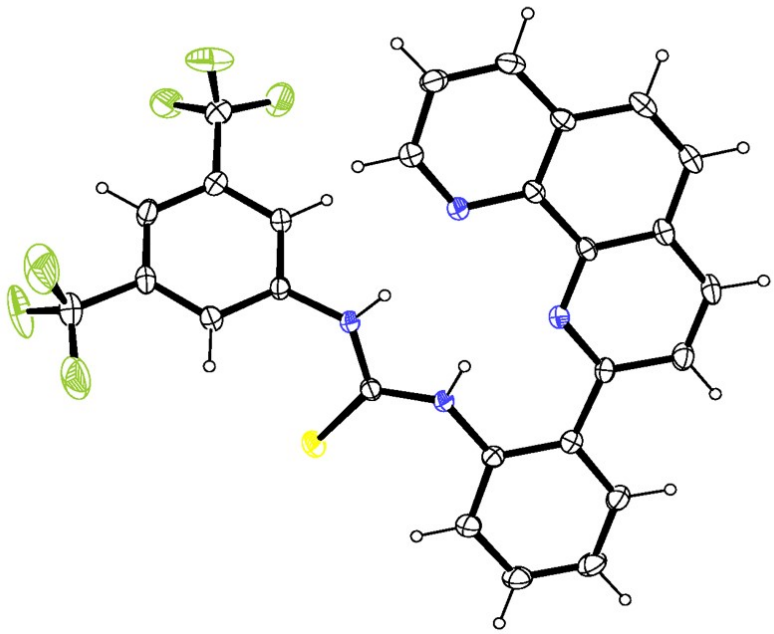


Figure S 41: Single crystal XRD structure for **1**(anti-anti conformation)

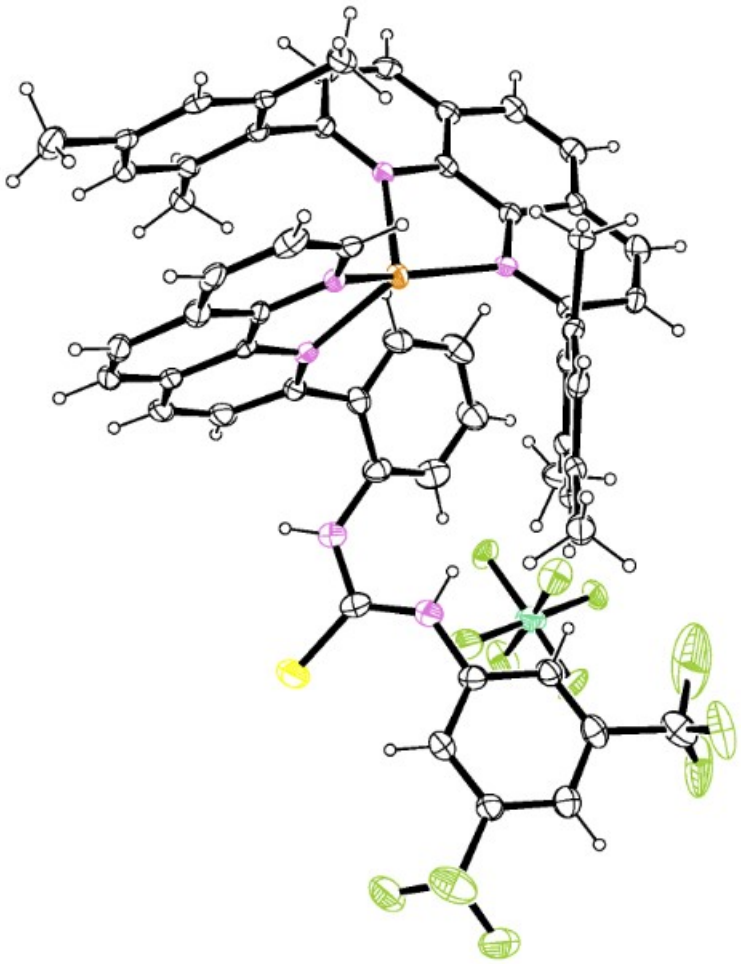


Figure S 42: Single crystal XRD structure for [Cu (**1**)(**3**)] $^{+}$ (syn-anti conformation)

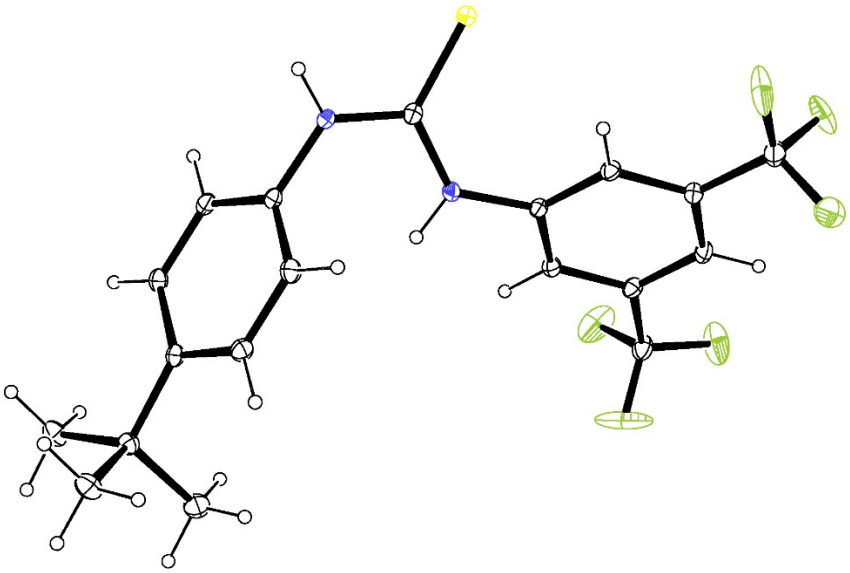


Figure S 43: Single crystal XRD structure for **1a** (syn-anti conformation).

9. Geometry optimised structures of [Cu(**1**)(**3**)]$^{+}$:

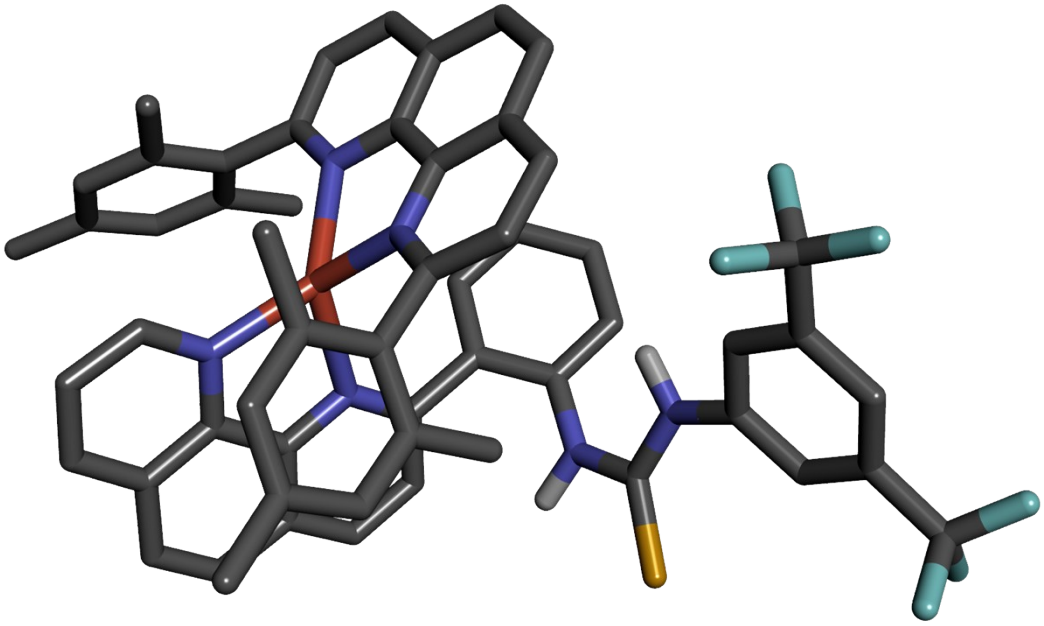


Figure S1: Geometry optimized structure of syn-anti conformation of [Cu (**1**)(**3**)]$^{+}$ at 6-311G(d, p) basis set on C,H,N,F,S and the LANL2DZ ECP basis set on Cu.

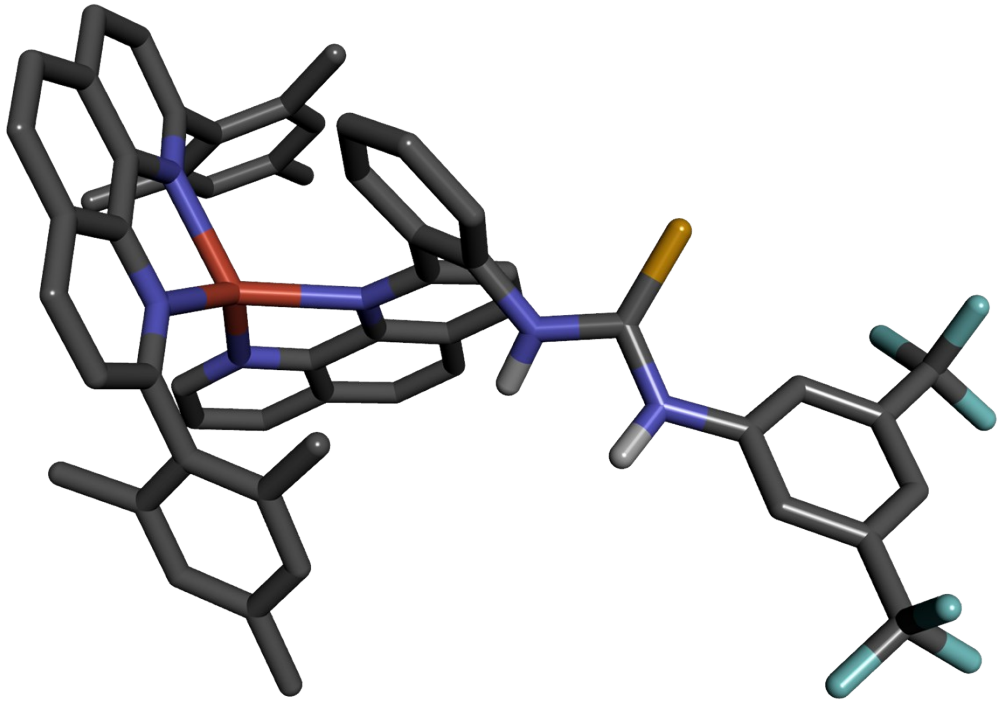


Figure S2: Geometry optimized structure of anti-anti conformation of [Cu (**1**)(**3**)] $^{+}$at 6-311G(d, p) basis set on C,H,N,F,S and the LANL2DZ ECP basis set on Cu.

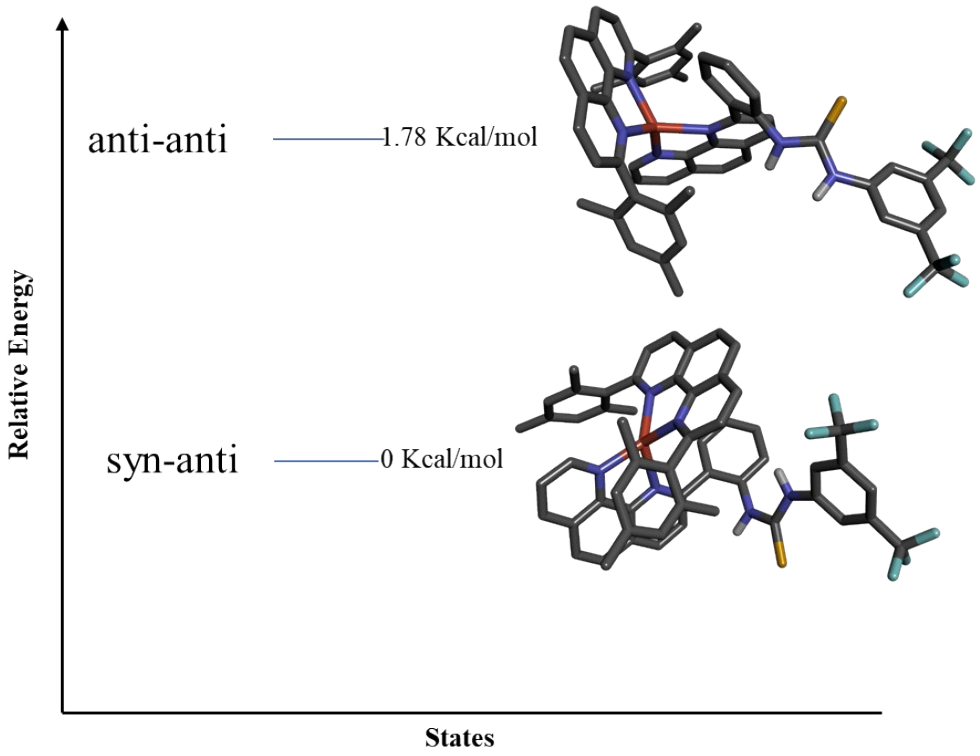


Figure S3: Relative energies of 6-311G (d, p)-optimized geometries of different configuration of [Cu (**1**)(**3**)] $^{+}$. It was found that the syn-anti is more stable compare to anti-anti.

Table S1. Crystal data and structure refinement for **1**.

Identification code	shelx	
Empirical formula	C_{27} H_{16} F_6 N_4 S	
Formula weight	542.50	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.1911(17) Å	a= 81.801(7)°.
	b = 9.8765(19) Å	b= 74.954(6)°.
	c = 13.755(3) Å	g = 79.844(6)°.
Volume	1180.8(4) $Å^3$	
Z	2	
Density (calculated)	1.526 Mg/m^3	
Absorption coefficient	0.210 mm^{-1}	
F(000)	552	
Crystal size	0.095 x 0.068 x 0.048 mm^3	

Theta range for data collection	2.457 to 24.997°.
Index ranges	-12<=h<=12, -13<=k<=13, -18<=l<=18
Reflections collected	4157
Independent reflections	4157 [R(int) = 0.0498]
Completeness to theta = 24.997°	99.9 %
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4157 / 30 / 398
Goodness-of-fit on F^2	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0405, wR2 = 0.1010
R indices (all data)	R1 = 0.0658, wR2 = 0.1107
Extinction coefficient	n/a
Largest diff. peak and hole	0.167 and -0.177 e.$Å^{-3}$

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for rb55. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	4553(2)	4305(2)	3542(1)	40(1)
C(2)	3419(2)	3812(2)	5404(1)	39(1)
C(3)	2256(2)	4926(2)	5566(2)	54(1)
C(4)	1146(2)	4957(3)	6452(2)	62(1)
C(5)	1184(2)	3900(3)	7207(2)	64(1)
C(6)	2344(2)	2816(2)	7075(2)	51(1)
C(7)	3508(2)	2721(2)	6189(1)	39(1)
C(8)	4733(2)	1510(2)	6114(1)	38(1)
C(9)	4728(2)	407(2)	6890(2)	53(1)
C(10)	5848(2)	-689(2)	6774(2)	54(1)
C(11)	7016(2)	-763(2)	5893(1)	42(1)
C(12)	6981(2)	370(2)	5157(1)	35(1)
C(13)	8183(2)	375(2)	4239(1)	36(1)
C(14)	9297(2)	1471(2)	2717(2)	50(1)
C(15)	10511(2)	398(2)	2532(2)	52(1)
C(16)	10534(2)	-717(2)	3230(2)	50(1)
C(17)	9362(2)	-757(2)	4119(1)	40(1)

C(18)	9327(2)	-1902(2)	4881(2)	50(1)
C(19)	8202(2)	-1906(2)	5729(2)	50(1)
C(20)	6278(2)	4050(2)	1838(1)	40(1)
C(21)	6319(2)	5381(2)	1357(2)	46(1)
C(22)	6863(2)	5572(2)	321(2)	50(1)
C(23)	7047(4)	7002(3)	-185(2)	74(1)
C(24)	7340(2)	4471(2)	-254(2)	56(1)
C(25)	7312(2)	3142(2)	231(2)	52(1)
C(26)	7869(4)	1930(3)	-368(2)	74(1)
C(27)	6782(2)	2943(2)	1269(1)	46(1)
N(1)	4530(2)	3735(2)	4499(1)	41(1)
N(2)	5840(2)	3767(2)	2898(1)	45(1)
N(3)	8148(2)	1478(2)	3525(1)	42(1)
N(4)	5856(2)	1466(2)	5279(1)	36(1)
S(1)	3203(1)	5440(1)	3142(1)	60(1)
F(1)	7466(11)	2115(7)	-1222(4)	107(3)
F(2)	9370(7)	1689(8)	-621(7)	125(3)
F(3)	7430(10)	788(7)	108(5)	110(3)
F(4)	6445(13)	7353(10)	-928(8)	127(4)
F(5)	8525(10)	7114(12)	-533(10)	154(4)
F(6)	6536(17)	7982(6)	452(5)	142(4)
F(3')	6895(15)	1640(20)	-811(18)	174(8)
F(4')	7260(30)	7040(20)	-1190(12)	156(8)
F(1')	9040(30)	2060(20)	-1083(16)	179(8)
F(5')	8136(19)	7431(15)	-87(15)	115(6)
F(6')	5842(12)	7864(10)	72(15)	118(5)
F(2')	8250(40)	852(17)	181(12)	190(9)

Table S3. Bond lengths [Å] and angles [°] for **1**.

C(1)-N(1)	1.352(2)
C(1)-N(2)	1.354(2)
C(1)-S(1)	1.6682(18)
C(2)-C(3)	1.391(3)
C(2)-N(1)	1.393(2)
C(2)-C(7)	1.420(2)
C(3)-C(4)	1.371(3)
C(4)-C(5)	1.366(3)
C(5)-C(6)	1.366(3)
C(6)-C(7)	1.400(3)
C(7)-C(8)	1.487(3)
C(8)-N(4)	1.330(2)
C(8)-C(9)	1.412(2)
C(9)-C(10)	1.352(3)
C(10)-C(11)	1.396(3)
C(11)-C(12)	1.400(2)
C(11)-C(19)	1.423(3)
C(12)-N(4)	1.355(2)
C(12)-C(13)	1.447(2)
C(13)-N(3)	1.360(2)
C(13)-C(17)	1.408(2)
C(14)-N(3)	1.320(2)
C(14)-C(15)	1.395(3)
C(15)-C(16)	1.355(3)
C(16)-C(17)	1.405(3)
C(17)-C(18)	1.427(3)
C(18)-C(19)	1.343(3)
C(20)-C(27)	1.379(3)
C(20)-C(21)	1.387(2)
C(20)-N(2)	1.409(2)
C(21)-C(22)	1.381(3)
C(22)-C(24)	1.377(3)
C(22)-C(23)	1.500(3)
C(23)-F(5')	1.198(10)
C(23)-F(4)	1.263(8)
C(23)-F(6')	1.275(9)

C(23)-F(5)	1.337(9)
C(23)-F(6)	1.339(6)
C(23)-F(4')	1.341(16)
C(24)-C(25)	1.386(3)
C(25)-C(27)	1.382(3)
C(25)-C(26)	1.490(3)
C(26)-F(2')	1.266(16)
C(26)-F(1')	1.267(11)
C(26)-F(3')	1.294(11)
C(26)-F(3)	1.295(7)
C(26)-F(1)	1.301(6)
C(26)-F(2)	1.319(7)

N(1)-C(1)-N(2)	109.98(15)
N(1)-C(1)-S(1)	127.58(14)
N(2)-C(1)-S(1)	122.36(14)
C(3)-C(2)-N(1)	122.22(17)
C(3)-C(2)-C(7)	119.54(17)
N(1)-C(2)-C(7)	118.23(16)
C(4)-C(3)-C(2)	121.1(2)
C(5)-C(4)-C(3)	120.3(2)
C(4)-C(5)-C(6)	119.5(2)
C(5)-C(6)-C(7)	123.1(2)
C(6)-C(7)-C(2)	116.42(17)
C(6)-C(7)-C(8)	119.49(17)
C(2)-C(7)-C(8)	124.08(16)
N(4)-C(8)-C(9)	119.47(17)
N(4)-C(8)-C(7)	118.37(15)
C(9)-C(8)-C(7)	122.16(17)
C(10)-C(9)-C(8)	119.92(19)
C(9)-C(10)-C(11)	121.30(18)
C(10)-C(11)-C(12)	116.35(17)
C(10)-C(11)-C(19)	123.33(18)
C(12)-C(11)-C(19)	120.32(18)
N(4)-C(12)-C(11)	122.03(17)
N(4)-C(12)-C(13)	118.85(15)
C(11)-C(12)-C(13)	119.12(16)
N(3)-C(13)-C(17)	122.19(17)

N(3)-C(13)-C(12)	119.02(15)
C(17)-C(13)-C(12)	118.79(16)
N(3)-C(14)-C(15)	124.62(19)
C(16)-C(15)-C(14)	118.34(19)
C(15)-C(16)-C(17)	119.77(18)
C(16)-C(17)-C(13)	117.82(17)
C(16)-C(17)-C(18)	122.24(17)
C(13)-C(17)-C(18)	119.94(18)
C(19)-C(18)-C(17)	120.98(18)
C(18)-C(19)-C(11)	120.81(18)
C(27)-C(20)-C(21)	119.21(17)
C(27)-C(20)-N(2)	117.81(17)
C(21)-C(20)-N(2)	122.83(18)
C(22)-C(21)-C(20)	119.50(19)
C(24)-C(22)-C(21)	121.56(19)
C(24)-C(22)-C(23)	119.0(2)
C(21)-C(22)-C(23)	119.3(2)
F(5')-C(23)-F(6')	110.8(9)
F(4)-C(23)-F(5)	106.6(6)
F(4)-C(23)-F(6)	108.0(6)
F(5)-C(23)-F(6)	103.4(6)
F(5')-C(23)-F(4')	103.9(10)
F(6')-C(23)-F(4')	103.8(8)
F(5')-C(23)-C(22)	114.5(6)
F(4)-C(23)-C(22)	114.8(5)
F(6')-C(23)-C(22)	112.2(4)
F(5)-C(23)-C(22)	110.0(5)
F(6)-C(23)-C(22)	113.3(3)
F(4')-C(23)-C(22)	110.9(9)
C(22)-C(24)-C(25)	118.72(19)
C(27)-C(25)-C(24)	120.0(2)
C(27)-C(25)-C(26)	120.1(2)
C(24)-C(25)-C(26)	119.9(2)
F(2')-C(26)-F(1')	105.0(11)
F(2')-C(26)-F(3')	107.4(10)
F(1')-C(26)-F(3')	103.7(9)
F(3)-C(26)-F(1)	107.2(5)
F(3)-C(26)-F(2)	106.0(6)

F(1)-C(26)-F(2)	105.0(4)
F(2')-C(26)-C(25)	111.2(8)
F(1')-C(26)-C(25)	114.5(6)
F(3')-C(26)-C(25)	114.3(6)
F(3)-C(26)-C(25)	113.9(4)
F(1)-C(26)-C(25)	112.9(3)
F(2)-C(26)-C(25)	111.2(4)
C(20)-C(27)-C(25)	120.96(18)
C(1)-N(1)-C(2)	132.74(15)
C(1)-N(2)-C(20)	127.99(15)
C(14)-N(3)-C(13)	117.24(16)
C(8)-N(4)-C(12)	120.91(15)

Table S4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1**. The anisotropic displacement factor exponent takes the form: $-2p^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	45(1)	35(1)	39(1)	1(1)	-12(1)	-5(1)
C(2)	37(1)	41(1)	37(1)	-5(1)	-9(1)	-5(1)
C(3)	53(1)	54(1)	49(1)	-7(1)	-11(1)	6(1)
C(4)	47(1)	67(2)	63(2)	-16(1)	-7(1)	10(1)
C(5)	50(1)	78(2)	51(1)	-13(1)	7(1)	-3(1)
C(6)	50(1)	60(1)	39(1)	-1(1)	-5(1)	-10(1)
C(7)	38(1)	44(1)	37(1)	-4(1)	-10(1)	-10(1)
C(8)	41(1)	44(1)	33(1)	3(1)	-14(1)	-13(1)
C(9)	48(1)	61(2)	44(1)	12(1)	-7(1)	-11(1)
C(10)	59(1)	50(1)	51(1)	22(1)	-20(1)	-14(1)
C(11)	44(1)	39(1)	47(1)	7(1)	-22(1)	-11(1)
C(12)	39(1)	33(1)	39(1)	1(1)	-20(1)	-6(1)
C(13)	41(1)	32(1)	40(1)	-3(1)	-18(1)	-5(1)
C(14)	50(1)	49(1)	45(1)	-1(1)	-10(1)	-1(1)
C(15)	49(1)	57(1)	47(1)	-14(1)	-5(1)	-1(1)
C(16)	50(1)	44(1)	58(1)	-19(1)	-17(1)	7(1)
C(17)	44(1)	34(1)	49(1)	-10(1)	-22(1)	0(1)
C(18)	55(1)	32(1)	69(2)	-4(1)	-30(1)	3(1)

C(19)	58(1)	34(1)	64(2)	10(1)	-29(1)	-7(1)
C(20)	44(1)	42(1)	33(1)	4(1)	-10(1)	-4(1)
C(21)	53(1)	40(1)	46(1)	2(1)	-16(1)	-7(1)
C(22)	54(1)	49(1)	45(1)	13(1)	-14(1)	-14(1)
C(23)	88(2)	64(2)	65(2)	20(2)	-16(2)	-24(2)
C(24)	61(1)	63(2)	37(1)	10(1)	-3(1)	-13(1)
C(25)	57(1)	55(1)	40(1)	-3(1)	-5(1)	-7(1)
C(26)	96(2)	67(2)	49(2)	-9(2)	-6(2)	2(2)
C(27)	52(1)	42(1)	41(1)	6(1)	-9(1)	-7(1)
N(1)	39(1)	43(1)	33(1)	2(1)	-8(1)	5(1)
N(2)	50(1)	46(1)	31(1)	4(1)	-10(1)	8(1)
N(3)	42(1)	42(1)	39(1)	2(1)	-9(1)	0(1)
N(4)	39(1)	37(1)	34(1)	1(1)	-12(1)	-6(1)
S(1)	57(1)	59(1)	54(1)	9(1)	-18(1)	11(1)
F(1)	167(6)	98(3)	53(2)	-28(2)	-40(3)	31(4)
F(2)	80(3)	128(5)	151(7)	-59(5)	-8(4)	35(3)
F(3)	200(6)	52(3)	65(3)	-16(2)	9(3)	-36(4)
F(4)	186(7)	97(5)	128(9)	70(6)	-109(6)	-57(5)
F(5)	106(4)	130(6)	195(8)	68(5)	-2(5)	-59(3)
F(6)	266(12)	56(2)	100(3)	14(2)	-29(5)	-52(4)
F(3')	147(7)	218(15)	194(17)	-141(13)	-26(9)	-49(8)
F(4')	290(20)	110(9)	66(5)	49(5)	-38(10)	-72(12)
F(1')	210(19)	146(11)	137(11)	-84(8)	115(10)	-90(11)
F(5')	118(10)	82(6)	176(13)	49(8)	-87(10)	-72(7)
F(6')	116(6)	45(4)	163(13)	28(6)	-11(6)	4(4)
F(2')	320(20)	96(9)	114(8)	-49(7)	-37(13)	74(12)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **1**.

	x	y	z	U(eq)
H(3)	2230	5679	5054	64
H(4)	347	5716	6541	74
H(5)	411	3918	7818	76
H(6)	2360	2094	7610	61
H(9)	3938	435	7493	64

H(10)	5839	-1423	7302	65
H(14)	9297	2252	2226	59
H(15)	11303	447	1932	63
H(16)	11339	-1469	3119	61
H(18)	10112	-2673	4788	60
H(19)	8198	-2681	6225	60
H(21)	5975	6155	1738	55
H(24)	7681	4620	-969	67
H(27)	6766	2029	1596	55
H(1)	5387	3212	4562	49
H(2)	6481	3167	3176	54

Table S6. Torsion angles [°] for **1**.

N(1)-C(2)-C(3)-C(4)	177.82(19)
C(7)-C(2)-C(3)-C(4)	-3.5(3)
C(2)-C(3)-C(4)-C(5)	1.6(4)
C(3)-C(4)-C(5)-C(6)	0.5(4)
C(4)-C(5)-C(6)-C(7)	-0.6(4)
C(5)-C(6)-C(7)-C(2)	-1.2(3)
C(5)-C(6)-C(7)-C(8)	179.5(2)
C(3)-C(2)-C(7)-C(6)	3.2(3)
N(1)-C(2)-C(7)-C(6)	-178.04(16)
C(3)-C(2)-C(7)-C(8)	-177.60(18)
N(1)-C(2)-C(7)-C(8)	1.2(3)
C(6)-C(7)-C(8)-N(4)	-177.68(17)
C(2)-C(7)-C(8)-N(4)	3.1(3)
C(6)-C(7)-C(8)-C(9)	3.1(3)
C(2)-C(7)-C(8)-C(9)	-176.09(18)
N(4)-C(8)-C(9)-C(10)	-0.9(3)
C(7)-C(8)-C(9)-C(10)	178.33(19)
C(8)-C(9)-C(10)-C(11)	-0.4(3)
C(9)-C(10)-C(11)-C(12)	1.6(3)
C(9)-C(10)-C(11)-C(19)	-178.8(2)
C(10)-C(11)-C(12)-N(4)	-1.6(3)
C(19)-C(11)-C(12)-N(4)	178.81(17)
C(10)-C(11)-C(12)-C(13)	178.31(16)
C(19)-C(11)-C(12)-C(13)	-1.3(3)

N(4)-C(12)-C(13)-N(3)	0.0(2)
C(11)-C(12)-C(13)-N(3)	-179.90(15)
N(4)-C(12)-C(13)-C(17)	179.24(16)
C(11)-C(12)-C(13)-C(17)	-0.7(3)
N(3)-C(14)-C(15)-C(16)	-0.6(3)
C(14)-C(15)-C(16)-C(17)	-0.9(3)
C(15)-C(16)-C(17)-C(13)	1.0(3)
C(15)-C(16)-C(17)-C(18)	-179.86(19)
N(3)-C(13)-C(17)-C(16)	0.5(3)
C(12)-C(13)-C(17)-C(16)	-178.70(16)
N(3)-C(13)-C(17)-C(18)	-178.69(17)
C(12)-C(13)-C(17)-C(18)	2.1(3)
C(16)-C(17)-C(18)-C(19)	179.22(18)
C(13)-C(17)-C(18)-C(19)	-1.6(3)
C(17)-C(18)-C(19)-C(11)	-0.4(3)
C(10)-C(11)-C(19)-C(18)	-177.73(19)
C(12)-C(11)-C(19)-C(18)	1.8(3)
C(27)-C(20)-C(21)-C(22)	0.0(3)
N(2)-C(20)-C(21)-C(22)	175.47(17)
C(20)-C(21)-C(22)-C(24)	1.3(3)
C(20)-C(21)-C(22)-C(23)	-174.1(2)
C(24)-C(22)-C(23)-F(5')	-99.4(13)
C(21)-C(22)-C(23)-F(5')	76.2(13)
C(24)-C(22)-C(23)-F(4)	55.0(7)
C(21)-C(22)-C(23)-F(4)	-129.4(7)
C(24)-C(22)-C(23)-F(6')	133.3(12)
C(21)-C(22)-C(23)-F(6')	-51.1(13)
C(24)-C(22)-C(23)-F(5)	-65.1(8)
C(21)-C(22)-C(23)-F(5)	110.5(7)
C(24)-C(22)-C(23)-F(6)	179.7(8)
C(21)-C(22)-C(23)-F(6)	-4.7(9)
C(24)-C(22)-C(23)-F(4')	17.8(13)
C(21)-C(22)-C(23)-F(4')	-166.6(13)
C(21)-C(22)-C(24)-C(25)	-2.0(3)
C(23)-C(22)-C(24)-C(25)	173.5(2)
C(22)-C(24)-C(25)-C(27)	1.3(3)
C(22)-C(24)-C(25)-C(26)	-178.0(2)
C(27)-C(25)-C(26)-F(2')	-21.6(18)

C(24)-C(25)-C(26)-F(2')	157.7(17)
C(27)-C(25)-C(26)-F(1')	-140.4(17)
C(24)-C(25)-C(26)-F(1')	38.9(17)
C(27)-C(25)-C(26)-F(3')	100.2(14)
C(24)-C(25)-C(26)-F(3')	-80.5(14)
C(27)-C(25)-C(26)-F(3)	17.8(6)
C(24)-C(25)-C(26)-F(3)	-162.9(5)
C(27)-C(25)-C(26)-F(1)	140.4(6)
C(24)-C(25)-C(26)-F(1)	-40.3(7)
C(27)-C(25)-C(26)-F(2)	-101.8(5)
C(24)-C(25)-C(26)-F(2)	77.5(5)
C(21)-C(20)-C(27)-C(25)	-0.6(3)
N(2)-C(20)-C(27)-C(25)	-176.32(17)
C(24)-C(25)-C(27)-C(20)	-0.1(3)
C(26)-C(25)-C(27)-C(20)	179.2(2)
N(2)-C(1)-N(1)-C(2)	-171.88(18)
S(1)-C(1)-N(1)-C(2)	4.9(3)
C(3)-C(2)-N(1)-C(1)	-24.8(3)
C(7)-C(2)-N(1)-C(1)	156.46(19)
N(1)-C(1)-N(2)-C(20)	177.89(18)
S(1)-C(1)-N(2)-C(20)	0.9(3)
C(27)-C(20)-N(2)-C(1)	-131.7(2)
C(21)-C(20)-N(2)-C(1)	52.8(3)
C(15)-C(14)-N(3)-C(13)	2.0(3)
C(17)-C(13)-N(3)-C(14)	-2.0(3)
C(12)-C(13)-N(3)-C(14)	177.26(16)
C(9)-C(8)-N(4)-C(12)	1.0(3)
C(7)-C(8)-N(4)-C(12)	-178.28(15)
C(11)-C(12)-N(4)-C(8)	0.3(3)
C(13)-C(12)-N(4)-C(8)	-179.60(15)

Table S7. Hydrogen bonds for **1** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(3)-H(3)...S(1)	0.95	2.58	3.209(2)	124.0

N(1)-H(1)...N(4)	0.88	1.90	2.586(2)	133.7
N(2)-H(2)...N(3)	0.88	2.15	3.010(2)	166.3
C(3)-H(3)...S(1)	0.95	2.58	3.209(2)	124.0
N(1)-H(1)...N(4)	0.88	1.90	2.586(2)	133.7
N(2)-H(2)...N(3)	0.88	2.15	3.010(2)	166.3

Table S8. Crystal data and structure refinement for [Cu(**1**)(**3**)]PF_6.

Identification code	shelx	
Empirical formula	C_{57} H_{44} Cu F_6 N_4 S	
Formula weight	1172.03	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 12.904(3) Å	□= 80.438(8)°.
	b = 14.672(3) Å	□= 84.213(8)°.
	c = 14.907(3) Å	□ = 66.335(7)°.
Volume	2547.2(9) $Å^3$	
Z	2	
Density (calculated)	1.528 Mg/m^3	
Absorption coefficient	0.613 mm^{-1}	
F(000)	1196	
Crystal size	0.085 x 0.042 x 0.030 mm^3	
Theta range for data collection	1.530 to 25.000°.	
Index ranges	-15<=h<=15, -17<=k<=17, -17<=l<=17	
Reflections collected	66133	
Independent reflections	6868 [R(int) = 0.2516]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.982 and 0.950	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6868 / 6 / 773	
Goodness-of-fit on F^2	1.030	
Final R indices [I>2sigma(I)]	R1 = 0.0842, wR2 = 0.1789	
R indices (all data)	R1 = 0.2389, wR2 = 0.2602	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.564 and -0.432 $e.Å^{-3}$	

Table S9. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3)
for [Cu(**1**)(**3**)]PF_6. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5517(7)	7790(7)	-819(7)	46(2)
C(2)	5098(9)	8507(9)	-1585(7)	60(3)
C(3)	4354(8)	9448(8)	-1440(9)	62(3)
C(4)	4033(8)	9662(7)	-554(8)	53(3)
C(5)	3244(9)	10639(8)	-372(10)	67(3)
C(6)	2946(9)	10805(8)	482(10)	69(4)
C(7)	3398(8)	10060(7)	1240(9)	54(3)
C(8)	4198(7)	9097(7)	1084(8)	44(2)
C(9)	4486(7)	8904(6)	159(7)	42(2)
C(10)	3132(8)	10237(8)	2135(10)	65(3)
C(11)	3681(8)	9509(8)	2826(8)	63(3)
C(12)	4526(7)	8584(7)	2622(7)	48(2)
C(13)	3359(7)	6481(6)	1363(6)	37(2)
C(14)	2756(8)	5916(7)	1763(6)	47(2)
C(15)	3293(9)	5050(7)	2331(7)	56(3)
C(16)	4417(8)	4735(7)	2492(6)	45(2)
C(17)	4987(8)	5334(6)	2077(6)	39(2)
C(18)	6171(7)	5050(6)	2174(6)	38(2)
C(19)	6787(8)	4115(6)	2691(6)	42(2)
C(20)	6191(9)	3529(7)	3132(6)	51(3)
C(21)	5080(9)	3825(7)	3030(7)	54(3)
C(22)	7953(8)	3850(7)	2727(6)	52(3)
C(23)	8439(8)	4463(7)	2252(6)	46(2)
C(24)	7793(8)	5371(7)	1732(6)	44(2)
C(25)	8339(7)	5997(6)	1168(7)	40(2)
C(26)	8465(7)	5975(6)	242(6)	38(2)
C(27)	9055(7)	6507(6)	-282(7)	45(2)
C(28)	9494(7)	7057(6)	102(8)	49(3)
C(29)	9374(7)	7060(7)	1020(8)	54(3)
C(30)	8806(8)	6542(7)	1573(7)	48(2)

C(31)	8672(9)	6566(8)	2588(7)	71(3)
C(32)	8056(7)	5339(6)	-210(6)	46(2)
C(33)	10120(8)	7620(7)	-489(7)	66(3)
C(34)	2837(7)	7389(6)	679(6)	37(2)
C(35)	2071(7)	8308(6)	954(6)	39(2)
C(36)	1608(7)	9121(6)	297(7)	43(2)
C(37)	1846(7)	9082(7)	-613(7)	42(2)
C(38)	2591(7)	8167(7)	-864(6)	44(2)
C(39)	3102(7)	7326(6)	-239(6)	37(2)
C(40)	3911(8)	6356(7)	-546(6)	54(3)
C(41)	1332(8)	9972(7)	-1322(7)	62(3)
C(42)	1785(8)	8392(7)	1931(6)	53(3)
C(43)	5182(8)	7844(7)	3368(7)	53(3)
C(44)	5204(9)	6894(8)	3475(7)	62(3)
C(45)	5842(10)	6143(8)	4167(8)	74(3)
C(46)	6397(10)	6389(9)	4738(8)	76(3)
C(47)	6343(10)	7349(10)	4664(7)	76(3)
C(48)	5775(9)	8069(8)	3987(7)	58(3)
C(49)	6542(10)	9399(8)	4011(7)	68(3)
C(50)	8678(9)	8750(8)	3963(7)	55(3)
C(51)	9585(9)	7859(7)	4207(7)	57(3)
C(52)	10612(10)	7847(8)	4251(7)	64(3)
C(53)	10804(9)	8739(8)	4068(7)	62(3)
C(54)	9900(9)	9628(8)	3813(7)	58(3)
C(55)	8838(9)	9654(7)	3756(6)	57(3)
C(56)	10079(11)	10590(9)	3556(9)	68(3)
C(57)	11663(17)	6886(11)	4476(14)	85(5)
Cu(1)	5547(1)	6997(1)	1176(1)	47(1)
F(1)	10252(7)	10792(5)	2669(5)	105(2)
F(2)	10976(7)	10561(5)	3941(6)	115(3)
F(3)	9204(6)	11364(5)	3803(5)	103(2)
F(11)	7711(6)	8082(5)	6217(5)	105(2)
F(12)	8867(5)	5908(4)	7364(4)	79(2)
N(1)	5237(6)	7954(5)	29(5)	42(2)
N(2)	4734(6)	8374(5)	1767(6)	45(2)
N(3)	6673(6)	5669(5)	1717(4)	36(2)
N(4)	4435(6)	6213(5)	1515(5)	36(2)
N(5)	5699(7)	9096(6)	3936(6)	71(3)

N(6)	7614(8)	8713(6)	3905(6)	69(3)
S(1)	6191(3)	10588(2)	4166(3)	94(1)
Cl(1)	8292(3)	6997(2)	6782(2)	77(1)
F(4)	11300(30)	6150(40)	4580(40)	240(30)
F(5)	12040(30)	6780(30)	5200(20)	179(19)
F(6)	12360(20)	6660(20)	3847(17)	125(11)
F(7)	8535(14)	6597(13)	5814(9)	92(7)
F(8)	9429(12)	7119(14)	6690(18)	98(10)
F(9)	7980(20)	7466(10)	7695(10)	101(10)
F(10)	7096(9)	6942(10)	6797(14)	68(6)
F(4')	11350(30)	6240(30)	5150(20)	94(10)
F(5')	11750(60)	6260(30)	3890(30)	160(20)
F(6')	12520(30)	6980(20)	4710(60)	160(30)
F(7')	7820(40)	6400(20)	6275(19)	131(16)
F(8')	9440(30)	6650(20)	6160(20)	146(16)
F(9')	8890(30)	7423(14)	7397(19)	72(8)
F(10')	7270(20)	7187(18)	7540(20)	113(15)

Table S10. Bond lengths [Å] and angles [°] for [Cu(**1**)(**3**)]PF_6.

C(1)-N(1)	1.313(11)
C(1)-C(2)	1.405(12)
C(2)-C(3)	1.366(13)
C(3)-C(4)	1.392(14)
C(4)-C(9)	1.386(12)
C(4)-C(5)	1.438(14)
C(5)-C(6)	1.325(14)
C(6)-C(7)	1.423(14)
C(7)-C(10)	1.384(14)
C(7)-C(8)	1.416(12)
C(8)-N(2)	1.354(11)
C(8)-C(9)	1.436(13)
C(9)-N(1)	1.373(10)
C(10)-C(11)	1.371(14)
C(11)-C(12)	1.417(13)
C(12)-N(2)	1.336(11)
C(12)-C(43)	1.478(13)

C(13)-N(4)	1.315(10)
C(13)-C(14)	1.382(11)
C(13)-C(34)	1.495(11)
C(14)-C(15)	1.366(12)
C(15)-C(16)	1.367(12)
C(16)-C(17)	1.394(11)
C(16)-C(21)	1.423(12)
C(17)-N(4)	1.377(10)
C(17)-C(18)	1.429(11)
C(18)-N(3)	1.373(10)
C(18)-C(19)	1.416(11)
C(19)-C(22)	1.400(12)
C(19)-C(20)	1.415(11)
C(20)-C(21)	1.338(12)
C(22)-C(23)	1.362(11)
C(23)-C(24)	1.402(12)
C(24)-N(3)	1.333(10)
C(24)-C(25)	1.480(12)
C(25)-C(26)	1.379(11)
C(25)-C(30)	1.411(12)
C(26)-C(27)	1.397(11)
C(26)-C(32)	1.510(11)
C(27)-C(28)	1.374(12)
C(28)-C(29)	1.361(13)
C(28)-C(33)	1.504(12)
C(29)-C(30)	1.383(13)
C(30)-C(31)	1.509(13)
C(34)-C(39)	1.386(11)
C(34)-C(35)	1.413(11)
C(35)-C(36)	1.377(11)
C(35)-C(42)	1.479(12)
C(36)-C(37)	1.366(12)
C(37)-C(38)	1.387(12)
C(37)-C(41)	1.501(12)
C(38)-C(39)	1.384(11)
C(39)-C(40)	1.501(11)
C(43)-C(44)	1.366(12)
C(43)-C(48)	1.411(13)

C(44)-C(45)	1.421(14)
C(45)-C(46)	1.342(14)
C(46)-C(47)	1.368(14)
C(47)-C(48)	1.358(14)
C(48)-N(5)	1.460(12)
C(49)-N(5)	1.350(12)
C(49)-N(6)	1.357(12)
C(49)-S(1)	1.668(11)
C(50)-C(51)	1.383(13)
C(50)-C(55)	1.404(12)
C(50)-N(6)	1.407(12)
C(51)-C(52)	1.327(13)
C(52)-C(53)	1.405(13)
C(52)-C(57)	1.530(18)
C(53)-C(54)	1.382(13)
C(54)-C(55)	1.366(13)
C(54)-C(56)	1.502(14)
C(56)-F(3)	1.314(12)
C(56)-F(1)	1.322(12)
C(56)-F(2)	1.326(12)
C(57)-F(5)	1.19(2)
C(57)-F(6)	1.22(2)
C(57)-F(6')	1.25(4)
C(57)-F(4)	1.33(5)
C(57)-F(5')	1.33(4)
C(57)-F(4')	1.40(4)
Cu(1)-N(1)	1.986(7)
Cu(1)-N(3)	2.000(7)
Cu(1)-N(4)	2.149(6)
Cu(1)-N(2)	2.160(7)
F(11)-Cl(1)	1.590(6)
F(12)-Cl(1)	1.604(6)
Cl(1)-F(8)	1.538(11)
Cl(1)-F(7')	1.563(16)
Cl(1)-F(9)	1.570(14)
Cl(1)-F(10)	1.576(10)
Cl(1)-F(9')	1.600(17)
Cl(1)-F(7)	1.602(12)

Cl(1)-F(10')	1.607(19)
Cl(1)-F(8')	1.61(2)

N(1)-C(1)-C(2)	124.8(10)
C(3)-C(2)-C(1)	117.7(10)
C(2)-C(3)-C(4)	119.8(10)
C(9)-C(4)-C(3)	118.4(10)
C(9)-C(4)-C(5)	120.1(11)
C(3)-C(4)-C(5)	121.5(11)
C(6)-C(5)-C(4)	119.5(11)
C(5)-C(6)-C(7)	122.8(11)
C(10)-C(7)-C(8)	117.5(10)
C(10)-C(7)-C(6)	123.3(11)
C(8)-C(7)-C(6)	119.1(11)
N(2)-C(8)-C(7)	122.7(10)
N(2)-C(8)-C(9)	119.1(8)
C(7)-C(8)-C(9)	118.1(9)
N(1)-C(9)-C(4)	122.8(10)
N(1)-C(9)-C(8)	116.9(8)
C(4)-C(9)-C(8)	120.3(9)
C(11)-C(10)-C(7)	119.8(10)
C(10)-C(11)-C(12)	119.9(11)
N(2)-C(12)-C(11)	120.9(10)
N(2)-C(12)-C(43)	119.9(8)
C(11)-C(12)-C(43)	119.2(10)
N(4)-C(13)-C(14)	122.0(8)
N(4)-C(13)-C(34)	116.7(7)
C(14)-C(13)-C(34)	121.2(8)
C(15)-C(14)-C(13)	119.1(8)
C(14)-C(15)-C(16)	120.7(8)
C(15)-C(16)-C(17)	118.1(9)
C(15)-C(16)-C(21)	125.7(9)
C(17)-C(16)-C(21)	116.1(9)
N(4)-C(17)-C(16)	120.8(8)
N(4)-C(17)-C(18)	116.8(7)
C(16)-C(17)-C(18)	122.3(8)
N(3)-C(18)-C(19)	122.9(8)
N(3)-C(18)-C(17)	118.4(8)

C(19)-C(18)-C(17)	118.5(8)
C(22)-C(19)-C(20)	125.2(8)
C(22)-C(19)-C(18)	116.3(8)
C(20)-C(19)-C(18)	118.5(8)
C(21)-C(20)-C(19)	121.0(9)
C(20)-C(21)-C(16)	123.4(9)
C(23)-C(22)-C(19)	119.9(9)
C(22)-C(23)-C(24)	121.5(9)
N(3)-C(24)-C(23)	120.2(8)
N(3)-C(24)-C(25)	118.8(8)
C(23)-C(24)-C(25)	121.0(8)
C(26)-C(25)-C(30)	120.2(8)
C(26)-C(25)-C(24)	118.7(8)
C(30)-C(25)-C(24)	121.0(9)
C(25)-C(26)-C(27)	118.7(8)
C(25)-C(26)-C(32)	121.9(8)
C(27)-C(26)-C(32)	119.3(8)
C(28)-C(27)-C(26)	121.6(9)
C(29)-C(28)-C(27)	118.9(9)
C(29)-C(28)-C(33)	121.3(9)
C(27)-C(28)-C(33)	119.8(10)
C(28)-C(29)-C(30)	122.0(9)
C(29)-C(30)-C(25)	118.5(9)
C(29)-C(30)-C(31)	121.1(9)
C(25)-C(30)-C(31)	120.3(9)
C(39)-C(34)-C(35)	119.6(8)
C(39)-C(34)-C(13)	119.5(8)
C(35)-C(34)-C(13)	120.9(8)
C(36)-C(35)-C(34)	118.7(8)
C(36)-C(35)-C(42)	121.0(8)
C(34)-C(35)-C(42)	120.3(8)
C(37)-C(36)-C(35)	123.2(9)
C(36)-C(37)-C(38)	116.9(9)
C(36)-C(37)-C(41)	122.6(9)
C(38)-C(37)-C(41)	120.5(9)
C(39)-C(38)-C(37)	122.9(9)
C(38)-C(39)-C(34)	118.7(8)
C(38)-C(39)-C(40)	120.8(9)

C(34)-C(39)-C(40)	120.4(8)
C(44)-C(43)-C(48)	118.1(10)
C(44)-C(43)-C(12)	118.3(9)
C(48)-C(43)-C(12)	123.6(9)
C(43)-C(44)-C(45)	120.9(10)
C(46)-C(45)-C(44)	118.9(10)
C(45)-C(46)-C(47)	120.8(11)
C(48)-C(47)-C(46)	121.2(11)
C(47)-C(48)-C(43)	119.9(10)
C(47)-C(48)-N(5)	120.4(10)
C(43)-C(48)-N(5)	119.5(10)
N(5)-C(49)-N(6)	116.4(9)
N(5)-C(49)-S(1)	118.1(9)
N(6)-C(49)-S(1)	125.4(8)
C(51)-C(50)-C(55)	120.0(10)
C(51)-C(50)-N(6)	118.1(9)
C(55)-C(50)-N(6)	121.8(10)
C(52)-C(51)-C(50)	120.7(10)
C(51)-C(52)-C(53)	121.1(10)
C(51)-C(52)-C(57)	123.6(12)
C(53)-C(52)-C(57)	115.4(12)
C(54)-C(53)-C(52)	118.3(10)
C(55)-C(54)-C(53)	121.5(10)
C(55)-C(54)-C(56)	118.3(10)
C(53)-C(54)-C(56)	120.1(10)
C(54)-C(55)-C(50)	118.4(10)
F(3)-C(56)-F(1)	107.0(10)
F(3)-C(56)-F(2)	107.1(10)
F(1)-C(56)-F(2)	106.0(10)
F(3)-C(56)-C(54)	111.8(10)
F(1)-C(56)-C(54)	112.6(9)
F(2)-C(56)-C(54)	112.0(10)
F(5)-C(57)-F(6)	116(3)
F(5)-C(57)-F(4)	102(3)
F(6)-C(57)-F(4)	101(3)
F(6')-C(57)-F(5')	122(4)
F(6')-C(57)-F(4')	109(3)
F(5')-C(57)-F(4')	87(4)

F(5)-C(57)-C(52)	115.4(18)
F(6)-C(57)-C(52)	114.9(16)
F(6')-C(57)-C(52)	117.6(19)
F(4)-C(57)-C(52)	105(2)
F(5')-C(57)-C(52)	108(2)
F(4')-C(57)-C(52)	108.4(19)
N(1)-Cu(1)-N(3)	141.5(3)
N(1)-Cu(1)-N(4)	115.8(3)
N(3)-Cu(1)-N(4)	81.3(3)
N(1)-Cu(1)-N(2)	81.8(3)
N(3)-Cu(1)-N(2)	129.0(3)
N(4)-Cu(1)-N(2)	105.4(3)
C(1)-N(1)-C(9)	116.5(8)
C(1)-N(1)-Cu(1)	130.2(6)
C(9)-N(1)-Cu(1)	112.7(6)
C(12)-N(2)-C(8)	118.9(8)
C(12)-N(2)-Cu(1)	133.7(7)
C(8)-N(2)-Cu(1)	106.4(6)
C(24)-N(3)-C(18)	119.1(7)
C(24)-N(3)-Cu(1)	128.0(6)
C(18)-N(3)-Cu(1)	112.7(5)
C(13)-N(4)-C(17)	119.3(7)
C(13)-N(4)-Cu(1)	131.6(6)
C(17)-N(4)-Cu(1)	108.6(5)
C(49)-N(5)-C(48)	127.8(9)
C(49)-N(6)-C(50)	132.1(9)
F(8)-Cl(1)-F(9)	91.1(11)
F(8)-Cl(1)-F(10)	174.9(7)
F(9)-Cl(1)-F(10)	91.0(10)
F(8)-Cl(1)-F(11)	89.8(5)
F(7')-Cl(1)-F(11)	99.1(10)
F(9)-Cl(1)-F(11)	90.4(6)
F(10)-Cl(1)-F(11)	85.6(5)
F(7')-Cl(1)-F(9')	170.2(13)
F(11)-Cl(1)-F(9')	90.7(7)
F(8)-Cl(1)-F(7)	90.4(11)
F(9)-Cl(1)-F(7)	175.5(8)
F(10)-Cl(1)-F(7)	87.1(8)

F(11)-Cl(1)-F(7)	85.4(7)
F(8)-Cl(1)-F(12)	90.5(5)
F(7')-Cl(1)-F(12)	81.3(10)
F(9)-Cl(1)-F(12)	88.9(6)
F(10)-Cl(1)-F(12)	94.1(5)
F(11)-Cl(1)-F(12)	179.2(5)
F(9')-Cl(1)-F(12)	89.0(7)
F(7)-Cl(1)-F(12)	95.4(7)
F(7')-Cl(1)-F(10')	91.5(17)
F(11)-Cl(1)-F(10')	93.5(8)
F(9')-Cl(1)-F(10')	88.6(15)
F(12)-Cl(1)-F(10')	85.7(8)
F(7')-Cl(1)-F(8')	90.0(17)
F(11)-Cl(1)-F(8')	96.2(11)
F(9')-Cl(1)-F(8')	88.3(14)
F(12)-Cl(1)-F(8')	84.6(11)
F(10')-Cl(1)-F(8')	169.9(15)

Table S11. Anisotropic displacement parameters ($Å^2 x\ 10^3$)for [Cu(**1**)(**3**)]PF_6. The anisotropic
displacement factor exponent takes the form: $-2\pi^2[h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	36(6)	51(6)	62(7)	-16(6)	-4(5)	-24(5)
C(2)	58(7)	82(8)	50(7)	20(6)	-16(6)	-46(7)
C(3)	42(6)	47(7)	101(10)	30(7)	-32(7)	-29(6)
C(4)	42(6)	46(7)	74(8)	7(6)	-6(6)	-23(5)
C(5)	40(7)	36(7)	125(12)	15(7)	-23(7)	-19(6)
C(6)	37(7)	32(6)	140(12)	-9(8)	-16(8)	-14(5)
C(7)	30(6)	41(6)	99(9)	-18(7)	-7(6)	-16(5)
C(8)	20(5)	37(6)	78(8)	-8(6)	-8(5)	-15(4)
C(9)	27(5)	26(5)	72(8)	11(5)	-9(5)	-15(4)
C(10)	35(6)	50(7)	118(11)	-34(8)	6(7)	-20(6)
C(11)	46(7)	60(7)	96(9)	-30(7)	9(7)	-29(6)

C(12)	32(6)	46(6)	67(8)	-19(6)	4(5)	-15(5)
C(13)	32(5)	40(5)	39(6)	-9(4)	-5(4)	-10(4)
C(14)	36(6)	61(7)	55(7)	-15(5)	1(5)	-29(5)
C(15)	63(8)	55(7)	67(8)	-10(6)	4(6)	-41(6)
C(16)	50(6)	38(6)	48(6)	-8(5)	5(5)	-21(5)
C(17)	48(6)	31(5)	38(6)	-11(4)	8(5)	-16(5)
C(18)	40(6)	33(5)	43(6)	-4(4)	-1(5)	-16(5)
C(19)	45(6)	27(5)	49(6)	-1(4)	-8(5)	-11(5)
C(20)	68(8)	38(6)	46(6)	5(5)	-1(6)	-24(6)
C(21)	64(7)	40(6)	55(7)	-8(5)	9(6)	-20(6)
C(22)	61(7)	38(6)	49(7)	12(5)	-7(5)	-16(5)
C(23)	35(5)	41(6)	54(6)	-4(5)	-6(5)	-7(5)
C(24)	38(6)	44(6)	52(6)	-10(5)	-4(5)	-15(5)
C(25)	34(5)	26(5)	53(7)	-3(4)	1(5)	-7(4)
C(26)	31(5)	34(5)	48(7)	-1(4)	-10(5)	-11(4)
C(27)	31(5)	39(5)	57(7)	1(5)	-2(5)	-8(5)
C(28)	36(6)	25(5)	83(9)	-7(5)	-11(6)	-7(4)
C(29)	32(6)	37(6)	93(9)	-23(6)	-7(6)	-8(5)
C(30)	46(6)	42(6)	53(7)	-15(5)	-6(5)	-10(5)
C(31)	81(8)	76(8)	71(8)	-27(6)	2(7)	-41(7)
C(32)	45(6)	42(5)	56(6)	-10(5)	-3(5)	-21(5)
C(33)	47(6)	46(6)	102(9)	-2(6)	5(6)	-21(5)
C(34)	36(5)	41(6)	42(6)	-5(5)	-7(5)	-21(5)
C(35)	35(5)	41(6)	45(6)	-13(5)	3(5)	-16(5)
C(36)	34(5)	35(5)	60(7)	-5(5)	-7(5)	-14(4)
C(37)	35(5)	40(6)	58(7)	0(5)	-11(5)	-23(5)
C(38)	39(6)	56(7)	50(6)	-7(5)	-6(5)	-32(5)
C(39)	30(5)	36(5)	52(7)	-13(5)	-5(5)	-18(4)
C(40)	58(7)	50(6)	57(7)	-16(5)	3(5)	-24(5)
C(41)	44(6)	66(7)	72(8)	6(6)	-10(6)	-21(5)
C(42)	44(6)	49(6)	66(8)	-11(5)	-4(5)	-17(5)
C(43)	49(6)	51(7)	54(7)	-21(6)	9(5)	-13(5)
C(44)	76(8)	65(7)	54(7)	-25(6)	-5(6)	-29(6)
C(45)	105(10)	60(8)	61(8)	-20(7)	8(7)	-33(7)
C(46)	99(10)	67(8)	61(8)	-10(6)	-15(7)	-29(7)
C(47)	90(9)	104(10)	48(8)	-13(7)	-6(7)	-50(8)
C(48)	56(7)	73(8)	54(7)	-23(6)	3(6)	-30(6)
C(49)	65(8)	76(8)	74(8)	-16(6)	-15(7)	-35(7)

C(50)	62(7)	56(7)	54(7)	-8(5)	-7(6)	-29(6)
C(51)	64(8)	44(6)	62(7)	-1(5)	-12(6)	-19(6)
C(52)	71(8)	52(7)	56(7)	-12(6)	17(6)	-15(6)
C(53)	64(7)	61(7)	55(7)	-10(6)	1(6)	-18(6)
C(54)	54(7)	54(7)	69(8)	-12(6)	5(6)	-25(6)
C(55)	64(7)	43(6)	60(7)	-7(5)	2(6)	-18(6)
C(56)	70(9)	58(8)	72(9)	-20(7)	6(7)	-20(7)
C(57)	124(16)	63(10)	63(12)	4(9)	-1(12)	-39(10)
Cu(1)	42(1)	32(1)	62(1)	-2(1)	-5(1)	-13(1)
F(1)	168(8)	94(5)	74(5)	-13(4)	15(5)	-78(5)
F(2)	111(6)	102(6)	155(7)	0(5)	-33(6)	-66(5)
F(3)	107(6)	63(5)	140(7)	-23(4)	27(5)	-38(4)
F(11)	124(6)	77(5)	121(6)	45(4)	-63(5)	-56(4)
F(12)	81(4)	38(3)	107(5)	7(3)	-10(4)	-17(3)
N(1)	32(4)	36(5)	59(6)	-4(4)	-6(4)	-15(4)
N(2)	32(4)	50(5)	57(6)	-16(5)	-6(4)	-15(4)
N(3)	43(5)	33(4)	35(4)	-4(3)	-6(4)	-18(4)
N(4)	35(4)	32(4)	42(5)	-8(4)	0(4)	-14(4)
N(5)	61(6)	63(6)	97(8)	-21(5)	-11(5)	-27(5)
N(6)	63(6)	61(6)	90(7)	-25(5)	-1(5)	-27(5)
S(1)	78(2)	67(2)	148(3)	-42(2)	15(2)	-35(2)
Cl(1)	83(2)	71(2)	86(2)	-3(2)	-13(2)	-41(2)
F(4)	170(30)	180(30)	250(60)	110(40)	-30(40)	10(20)
F(5)	130(30)	200(30)	110(18)	-85(17)	-74(18)	80(20)
F(6)	128(17)	81(17)	72(14)	17(12)	31(13)	38(12)
F(7)	90(12)	128(13)	52(9)	-23(8)	-6(8)	-33(9)
F(8)	48(10)	96(13)	140(20)	53(13)	-38(12)	-42(10)
F(9)	150(20)	75(9)	60(10)	-24(7)	-39(14)	-12(12)
F(10)	39(7)	74(9)	86(13)	9(8)	9(7)	-28(6)
F(4')	84(17)	98(17)	56(17)	52(15)	-25(14)	-8(13)
F(5')	270(60)	60(20)	110(30)	-30(20)	-10(30)	-10(20)
F(6')	38(15)	82(16)	360(70)	-20(30)	-40(30)	-18(13)
F(7')	240(40)	160(20)	90(20)	-5(17)	-30(20)	-170(30)
F(8')	180(40)	180(30)	90(20)	-79(18)	110(20)	-100(20)
F(9')	88(19)	58(11)	95(19)	-22(11)	-21(15)	-45(13)
F(10')	76(18)	97(18)	110(30)	0(17)	58(19)	3(13)

Table S12. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for [Cu(**1**)(**3**)]PF_6.

	x	y	z	U(eq)
H(1)	6042	7139	-921	55
H(2)	5325	8344	-2184	72
H(3)	4058	9954	-1942	75
H(5)	2938	11162	-860	80
H(6)	2409	11449	592	82
H(10)	2571	10861	2270	78
H(11)	3495	9625	3442	76
H(14)	1978	6127	1644	56
H(15)	2882	4662	2617	67
H(20)	6586	2916	3506	62
H(21)	4714	3405	3332	64
H(22)	8406	3243	3082	63
H(23)	9233	4271	2273	56
H(27)	9155	6487	-920	54
H(29)	9690	7430	1288	65
H(31A)	8710	7183	2720	107
H(31B)	9281	5982	2893	107
H(31C)	7939	6547	2808	107
H(32A)	8468	4628	20	69
H(32B)	8191	5451	-870	69
H(32C)	7244	5526	-73	69
H(33A)	9732	8340	-446	98
H(33B)	10142	7510	-1122	98
H(33C)	10895	7379	-283	98
H(36)	1098	9738	486	51
H(38)	2757	8115	-1494	53
H(40A)	4629	6127	-242	81
H(40B)	4046	6460	-1207	81
H(40C)	3586	5847	-390	81
H(41A)	979	10582	-1030	93

H(41B)	757	9880	-1637	93
H(41C)	1923	10036	-1764	93
H(42A)	1429	9103	2014	79
H(42B)	2478	8064	2277	79
H(42C)	1260	8066	2151	79
H(44)	4787	6732	3081	75
H(45)	5874	5477	4224	89
H(46)	6832	5891	5198	91
H(47)	6711	7515	5095	92
H(51)	9472	7249	4344	69
H(53)	11536	8731	4118	75
H(55)	8224	10270	3579	69
H(5A)	5023	9575	3846	85
H(6A)	7651	8137	3775	83

Table S13. Torsion angles [°] for [Cu(**1**)(**3**)]PF_6.

N(1)-C(1)-C(2)-C(3)	0.8(13)
C(1)-C(2)-C(3)-C(4)	-0.5(13)
C(2)-C(3)-C(4)-C(9)	0.1(13)
C(2)-C(3)-C(4)-C(5)	-179.4(8)
C(9)-C(4)-C(5)-C(6)	-0.7(14)
C(3)-C(4)-C(5)-C(6)	178.9(9)
C(4)-C(5)-C(6)-C(7)	1.6(15)
C(5)-C(6)-C(7)-C(10)	177.0(10)
C(5)-C(6)-C(7)-C(8)	-0.1(14)
C(10)-C(7)-C(8)-N(2)	-2.8(12)
C(6)-C(7)-C(8)-N(2)	174.5(8)
C(10)-C(7)-C(8)-C(9)	-179.7(8)
C(6)-C(7)-C(8)-C(9)	-2.4(12)
C(3)-C(4)-C(9)-N(1)	0.0(13)
C(5)-C(4)-C(9)-N(1)	179.6(8)
C(3)-C(4)-C(9)-C(8)	178.6(8)
C(5)-C(4)-C(9)-C(8)	-1.8(12)
N(2)-C(8)-C(9)-N(1)	5.0(11)
C(7)-C(8)-C(9)-N(1)	-178.0(7)
N(2)-C(8)-C(9)-C(4)	-173.7(7)

C(7)-C(8)-C(9)-C(4)	3.3(11)
C(8)-C(7)-C(10)-C(11)	3.2(13)
C(6)-C(7)-C(10)-C(11)	-173.9(9)
C(7)-C(10)-C(11)-C(12)	0.7(14)
C(10)-C(11)-C(12)-N(2)	-5.6(13)
C(10)-C(11)-C(12)-C(43)	174.5(8)
N(4)-C(13)-C(14)-C(15)	-0.3(13)
C(34)-C(13)-C(14)-C(15)	175.0(8)
C(13)-C(14)-C(15)-C(16)	-1.0(14)
C(14)-C(15)-C(16)-C(17)	1.4(14)
C(14)-C(15)-C(16)-C(21)	-176.6(9)
C(15)-C(16)-C(17)-N(4)	-0.6(13)
C(21)-C(16)-C(17)-N(4)	177.6(8)
C(15)-C(16)-C(17)-C(18)	-177.4(8)
C(21)-C(16)-C(17)-C(18)	0.8(13)
N(4)-C(17)-C(18)-N(3)	0.8(11)
C(16)-C(17)-C(18)-N(3)	177.8(8)
N(4)-C(17)-C(18)-C(19)	-175.4(7)
C(16)-C(17)-C(18)-C(19)	1.6(13)
N(3)-C(18)-C(19)-C(22)	0.9(13)
C(17)-C(18)-C(19)-C(22)	176.9(8)
N(3)-C(18)-C(19)-C(20)	-179.5(8)
C(17)-C(18)-C(19)-C(20)	-3.5(12)
C(22)-C(19)-C(20)-C(21)	-177.3(9)
C(18)-C(19)-C(20)-C(21)	3.1(14)
C(19)-C(20)-C(21)-C(16)	-0.7(15)
C(15)-C(16)-C(21)-C(20)	176.8(10)
C(17)-C(16)-C(21)-C(20)	-1.3(14)
C(20)-C(19)-C(22)-C(23)	178.1(9)
C(18)-C(19)-C(22)-C(23)	-2.4(13)
C(19)-C(22)-C(23)-C(24)	1.0(14)
C(22)-C(23)-C(24)-N(3)	2.2(14)
C(22)-C(23)-C(24)-C(25)	-175.8(9)
N(3)-C(24)-C(25)-C(26)	-75.5(11)
C(23)-C(24)-C(25)-C(26)	102.5(10)
N(3)-C(24)-C(25)-C(30)	109.7(10)
C(23)-C(24)-C(25)-C(30)	-72.3(11)
C(30)-C(25)-C(26)-C(27)	-0.4(12)

C(24)-C(25)-C(26)-C(27)	-175.2(8)
C(30)-C(25)-C(26)-C(32)	175.3(8)
C(24)-C(25)-C(26)-C(32)	0.5(12)
C(25)-C(26)-C(27)-C(28)	-0.9(12)
C(32)-C(26)-C(27)-C(28)	-176.7(8)
C(26)-C(27)-C(28)-C(29)	1.7(13)
C(26)-C(27)-C(28)-C(33)	-179.8(8)
C(27)-C(28)-C(29)-C(30)	-1.2(14)
C(33)-C(28)-C(29)-C(30)	-179.7(8)
C(28)-C(29)-C(30)-C(25)	-0.1(13)
C(28)-C(29)-C(30)-C(31)	-179.3(9)
C(26)-C(25)-C(30)-C(29)	0.9(13)
C(24)-C(25)-C(30)-C(29)	175.6(8)
C(26)-C(25)-C(30)-C(31)	-179.8(8)
C(24)-C(25)-C(30)-C(31)	-5.2(13)
N(4)-C(13)-C(34)-C(39)	73.7(10)
C(14)-C(13)-C(34)-C(39)	-101.9(10)
N(4)-C(13)-C(34)-C(35)	-107.0(9)
C(14)-C(13)-C(34)-C(35)	77.5(11)
C(39)-C(34)-C(35)-C(36)	-0.2(12)
C(13)-C(34)-C(35)-C(36)	-179.6(7)
C(39)-C(34)-C(35)-C(42)	-179.5(7)
C(13)-C(34)-C(35)-C(42)	1.1(12)
C(34)-C(35)-C(36)-C(37)	0.6(12)
C(42)-C(35)-C(36)-C(37)	179.8(8)
C(35)-C(36)-C(37)-C(38)	0.2(12)
C(35)-C(36)-C(37)-C(41)	179.7(8)
C(36)-C(37)-C(38)-C(39)	-1.4(12)
C(41)-C(37)-C(38)-C(39)	179.1(7)
C(37)-C(38)-C(39)-C(34)	1.8(12)
C(37)-C(38)-C(39)-C(40)	-179.4(7)
C(35)-C(34)-C(39)-C(38)	-0.9(11)
C(13)-C(34)-C(39)-C(38)	178.5(7)
C(35)-C(34)-C(39)-C(40)	-179.8(7)
C(13)-C(34)-C(39)-C(40)	-0.4(11)
N(2)-C(12)-C(43)-C(44)	-55.0(13)
C(11)-C(12)-C(43)-C(44)	125.0(10)
N(2)-C(12)-C(43)-C(48)	126.0(10)

C(11)-C(12)-C(43)-C(48)	-54.0(13)
C(48)-C(43)-C(44)-C(45)	-2.4(15)
C(12)-C(43)-C(44)-C(45)	178.5(9)
C(43)-C(44)-C(45)-C(46)	2.2(17)
C(44)-C(45)-C(46)-C(47)	0.7(18)
C(45)-C(46)-C(47)-C(48)	-3.3(19)
C(46)-C(47)-C(48)-C(43)	2.9(17)
C(46)-C(47)-C(48)-N(5)	178.2(10)
C(44)-C(43)-C(48)-C(47)	-0.1(15)
C(12)-C(43)-C(48)-C(47)	178.9(10)
C(44)-C(43)-C(48)-N(5)	-175.4(9)
C(12)-C(43)-C(48)-N(5)	3.7(15)
C(55)-C(50)-C(51)-C(52)	0.2(15)
N(6)-C(50)-C(51)-C(52)	178.4(9)
C(50)-C(51)-C(52)-C(53)	1.2(16)
C(50)-C(51)-C(52)-C(57)	-177.3(12)
C(51)-C(52)-C(53)-C(54)	-1.9(16)
C(57)-C(52)-C(53)-C(54)	176.7(12)
C(52)-C(53)-C(54)-C(55)	1.3(16)
C(52)-C(53)-C(54)-C(56)	-176.2(10)
C(53)-C(54)-C(55)-C(50)	0.1(15)
C(56)-C(54)-C(55)-C(50)	177.6(9)
C(51)-C(50)-C(55)-C(54)	-0.8(15)
N(6)-C(50)-C(55)-C(54)	-178.9(9)
C(55)-C(54)-C(56)-F(3)	36.6(15)
C(53)-C(54)-C(56)-F(3)	-145.8(11)
C(55)-C(54)-C(56)-F(1)	-83.8(13)
C(53)-C(54)-C(56)-F(1)	93.8(13)
C(55)-C(54)-C(56)-F(2)	156.8(10)
C(53)-C(54)-C(56)-F(2)	-25.6(15)
C(51)-C(52)-C(57)-F(5)	-110(4)
C(53)-C(52)-C(57)-F(5)	72(4)
C(51)-C(52)-C(57)-F(6)	112(3)
C(53)-C(52)-C(57)-F(6)	-67(3)
C(51)-C(52)-C(57)-F(6')	-163(4)
C(53)-C(52)-C(57)-F(6')	18(5)
C(51)-C(52)-C(57)-F(4)	2(4)
C(53)-C(52)-C(57)-F(4)	-177(4)

C(51)-C(52)-C(57)-F(5')	55(5)
C(53)-C(52)-C(57)-F(5')	-124(4)
C(51)-C(52)-C(57)-F(4')	-39(3)
C(53)-C(52)-C(57)-F(4')	143(2)
C(2)-C(1)-N(1)-C(9)	-0.6(12)
C(2)-C(1)-N(1)-Cu(1)	169.3(6)
C(4)-C(9)-N(1)-C(1)	0.3(11)
C(8)-C(9)-N(1)-C(1)	-178.4(7)
C(4)-C(9)-N(1)-Cu(1)	-171.5(6)
C(8)-C(9)-N(1)-Cu(1)	9.9(9)
C(11)-C(12)-N(2)-C(8)	6.0(12)
C(43)-C(12)-N(2)-C(8)	-174.0(8)
C(11)-C(12)-N(2)-Cu(1)	-160.2(6)
C(43)-C(12)-N(2)-Cu(1)	19.8(13)
C(7)-C(8)-N(2)-C(12)	-1.9(12)
C(9)-C(8)-N(2)-C(12)	175.0(7)
C(7)-C(8)-N(2)-Cu(1)	167.7(6)
C(9)-C(8)-N(2)-Cu(1)	-15.4(8)
C(23)-C(24)-N(3)-C(18)	-3.7(12)
C(25)-C(24)-N(3)-C(18)	174.4(7)
C(23)-C(24)-N(3)-Cu(1)	171.1(6)
C(25)-C(24)-N(3)-Cu(1)	-10.9(12)
C(19)-C(18)-N(3)-C(24)	2.2(12)
C(17)-C(18)-N(3)-C(24)	-173.8(8)
C(19)-C(18)-N(3)-Cu(1)	-173.4(7)
C(17)-C(18)-N(3)-Cu(1)	10.6(9)
C(14)-C(13)-N(4)-C(17)	1.2(12)
C(34)-C(13)-N(4)-C(17)	-174.3(7)
C(14)-C(13)-N(4)-Cu(1)	-169.9(6)
C(34)-C(13)-N(4)-Cu(1)	14.7(11)
C(16)-C(17)-N(4)-C(13)	-0.7(12)
C(18)-C(17)-N(4)-C(13)	176.3(7)
C(16)-C(17)-N(4)-Cu(1)	172.2(6)
C(18)-C(17)-N(4)-Cu(1)	-10.8(9)
N(6)-C(49)-N(5)-C(48)	17.1(16)
S(1)-C(49)-N(5)-C(48)	-166.2(8)
C(47)-C(48)-N(5)-C(49)	46.9(16)
C(43)-C(48)-N(5)-C(49)	-137.9(11)

N(5)-C(49)-N(6)-C(50)	-177.8(10)
S(1)-C(49)-N(6)-C(50)	5.8(18)
C(51)-C(50)-N(6)-C(49)	152.7(11)
C(55)-C(50)-N(6)-C(49)	-29.2(17)

Table S14. Hydrogen bonds for [Cu(**1**)(**3**)]PF_6 [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(2)-H(2)...F(10'^b)#1	0.95	2.44	3.01(2)	118.4
C(23)-H(23)...F(12)#2	0.95	2.47	3.390(11)	164.4
C(23)-H(23)...F(8^a)#2	0.95	2.49	3.158(14)	127.6
C(47)-H(47)...F(7^a)	0.95	2.45	3.162(19)	131.9
C(47)-H(47)...F(10^a)	0.95	2.57	3.31(2)	134.6
C(47)-H(47)...F(7'^b)	0.95	2.34	3.00(3)	126.2
C(51)-H(51)...F(7^a)	0.95	2.62	3.30(2)	128.7
C(55)-H(55)...S(1)	0.95	2.56	3.165(11)	121.9

Symmetry transformations used to generate equivalent atoms:
#1 x,y,z-1 #2 -x+2,-y+1,-z+1

Table S15. Crystal data and structure refinement for **1a**.

Identification code	shelx	
Empirical formula	C19 H18 F6 N2 S	
Formula weight	420.41	
Temperature	140(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 8.3638(13) Å	α= 90°.
	b = 28.079(4) Å	β= 103.956(5)°.
	c = 8.3943(13) Å	γ = 90°.
Volume	1913.2(5) $Å^3$	
Z	4	
Density (calculated)	1.460 Mg/m^3	

Absorption coefficient	0.232 mm^{-1}
F(000)	864
Crystal size	0.068 x 0.048 x 0.035 mm^3
Theta range for data collection	2.509 to 24.995°.
Index ranges	-9<=h<=9, -33<=k<=33, -9<=l<=9
Reflections collected	42523
Independent reflections	3345 [R(int) = 0.0546]
Completeness to theta = 24.995°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.992 and 0.984
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3345 / 126 / 311
Goodness-of-fit on F^2	1.118
Final R indices [I>2sigma(I)]	R1 = 0.0440, wR2 = 0.0873
R indices (all data)	R1 = 0.0584, wR2 = 0.0949
Extinction coefficient	n/a
Largest diff. peak and hole	0.446 and -0.322 e.$Å^{-3}$

Table S16. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **1a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	4370(3)	4248(1)	8680(3)	23(1)
C(2)	6302(3)	4482(1)	6996(3)	23(1)
C(3)	7990(3)	4536(1)	7479(3)	25(1)
C(4)	8948(3)	4434(1)	6387(3)	24(1)
C(5)	8260(3)	4271(1)	4805(3)	22(1)
C(6)	6548(3)	4234(1)	4329(3)	28(1)
C(7)	5581(3)	4342(1)	5402(3)	29(1)
C(8)	9291(3)	4115(1)	3619(3)	26(1)
C(9)	9118(3)	3573(1)	3394(3)	40(1)
C(10)	8683(3)	4359(1)	1950(3)	35(1)
C(11)	11119(3)	4232(1)	4266(3)	34(1)
C(12)	3493(3)	3393(1)	8305(3)	22(1)
C(13)	4279(3)	2956(1)	8364(3)	24(1)
C(14)	3440(3)	2540(1)	8533(3)	26(1)
C(15)	1825(3)	2554(1)	8654(3)	27(1)
C(16)	1046(3)	2993(1)	8580(3)	24(1)
C(17)	1858(3)	3413(1)	8393(3)	24(1)
C(18)	-721(3)	3008(1)	8653(3)	35(1)
C(19)	4311(3)	2070(1)	8589(3)	35(1)
N(1)	5312(2)	4570(1)	8139(2)	26(1)
N(2)	4384(2)	3802(1)	8039(2)	26(1)
S(1)	3311(1)	4394(1)	10075(1)	27(1)
F(1)	3550(5)	1723(1)	9197(9)	89(2)
F(2)	5774(5)	2078(1)	9734(6)	76(2)
F(3)	4639(9)	1946(2)	7284(5)	102(3)
F(4)	-1336(6)	3429(1)	8686(10)	92(2)
F(5)	-921(5)	2796(2)	10051(5)	69(1)
F(6)	-1669(4)	2754(2)	7531(6)	83(2)
F(1')	4899(14)	1903(3)	9895(7)	72(3)
F(2')	5434(11)	2082(3)	7724(13)	69(3)
F(3')	3260(6)	1739(2)	7654(12)	59(2)
F(4')	-1321(9)	2641(2)	9033(18)	86(3)
F(5')	-1039(11)	3350(3)	9522(12)	78(3)

F(6')	-1696(8)	3137(5)	7153(8)	88(3)

Table S17. Bond lengths [Å] and angles [°] for **1a**.

C(1)-N(1)	1.348(3)
C(1)-N(2)	1.364(3)
C(1)-S(1)	1.681(2)
C(2)-C(3)	1.380(3)
C(2)-C(7)	1.385(3)
C(2)-N(1)	1.432(3)
C(3)-C(4)	1.385(3)
C(4)-C(5)	1.391(3)
C(5)-C(6)	1.394(3)
C(5)-C(8)	1.530(3)
C(6)-C(7)	1.382(3)
C(8)-C(11)	1.530(3)
C(8)-C(10)	1.532(3)
C(8)-C(9)	1.536(3)
C(12)-C(13)	1.388(3)
C(12)-C(17)	1.389(3)
C(12)-N(2)	1.415(3)
C(13)-C(14)	1.388(3)
C(14)-C(15)	1.380(3)
C(14)-C(19)	1.500(3)
C(15)-C(16)	1.389(3)
C(16)-C(17)	1.387(3)
C(16)-C(18)	1.494(3)
C(18)-F(4')	1.221(6)
C(18)-F(5')	1.274(7)
C(18)-F(4)	1.294(4)
C(18)-F(6)	1.289(4)
C(18)-F(5)	1.361(4)
C(18)-F(6')	1.373(7)
C(19)-F(1')	1.186(6)
C(19)-F(3)	1.242(5)
C(19)-F(2')	1.320(8)
C(19)-F(1)	1.332(4)
C(19)-F(2)	1.362(4)

C(19)-F(3')	1.387(5)

N(1)-C(1)-N(2)	114.94(19)
N(1)-C(1)-S(1)	121.33(17)
N(2)-C(1)-S(1)	123.71(17)
C(3)-C(2)-C(7)	119.4(2)
C(3)-C(2)-N(1)	120.0(2)
C(7)-C(2)-N(1)	120.6(2)
C(2)-C(3)-C(4)	119.8(2)
C(3)-C(4)-C(5)	121.8(2)
C(4)-C(5)-C(6)	117.3(2)
C(4)-C(5)-C(8)	123.1(2)
C(6)-C(5)-C(8)	119.6(2)
C(7)-C(6)-C(5)	121.3(2)
C(6)-C(7)-C(2)	120.3(2)
C(5)-C(8)-C(11)	112.30(19)
C(5)-C(8)-C(10)	110.65(19)
C(11)-C(8)-C(10)	108.14(19)
C(5)-C(8)-C(9)	108.21(19)
C(11)-C(8)-C(9)	108.2(2)
C(10)-C(8)-C(9)	109.3(2)
C(13)-C(12)-C(17)	119.8(2)
C(13)-C(12)-N(2)	117.4(2)
C(17)-C(12)-N(2)	122.6(2)
C(14)-C(13)-C(12)	120.1(2)
C(15)-C(14)-C(13)	120.7(2)
C(15)-C(14)-C(19)	120.0(2)
C(13)-C(14)-C(19)	119.3(2)
C(14)-C(15)-C(16)	118.7(2)
C(17)-C(16)-C(15)	121.4(2)
C(17)-C(16)-C(18)	119.9(2)
C(15)-C(16)-C(18)	118.7(2)
C(16)-C(17)-C(12)	119.2(2)
F(4')-C(18)-F(5')	109.4(6)
F(4)-C(18)-F(6)	110.1(4)
F(4)-C(18)-F(5)	104.4(4)
F(6)-C(18)-F(5)	101.9(3)
F(4')-C(18)-F(6')	105.8(6)

F(5')-C(18)-F(6')	99.5(5)
F(4')-C(18)-C(16)	117.4(4)
F(5')-C(18)-C(16)	112.9(5)
F(4)-C(18)-C(16)	115.3(3)
F(6)-C(18)-C(16)	113.3(2)
F(5)-C(18)-C(16)	110.6(3)
F(6')-C(18)-C(16)	110.2(3)
F(1')-C(19)-F(2')	109.1(6)
F(3)-C(19)-F(1)	111.0(4)
F(3)-C(19)-F(2)	105.9(4)
F(1)-C(19)-F(2)	99.9(3)
F(1')-C(19)-F(3')	108.8(5)
F(2')-C(19)-F(3')	98.2(5)
F(1')-C(19)-C(14)	117.9(4)
F(3)-C(19)-C(14)	115.4(3)
F(2')-C(19)-C(14)	111.4(4)
F(1)-C(19)-C(14)	112.5(2)
F(2)-C(19)-C(14)	110.8(2)
F(3')-C(19)-C(14)	109.6(3)
C(1)-N(1)-C(2)	126.04(18)
C(1)-N(2)-C(12)	128.86(19)

Table S18. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for **1a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2 a^{*2} U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
C(1)	21(1)	21(1)	26(1)	1(1)	4(1)	-1(1)
C(2)	27(1)	17(1)	28(1)	1(1)	10(1)	-3(1)
C(3)	29(1)	21(1)	22(1)	1(1)	3(1)	-6(1)
C(4)	20(1)	25(1)	27(1)	4(1)	3(1)	-2(1)
C(5)	23(1)	18(1)	25(1)	5(1)	5(1)	-1(1)
C(6)	27(1)	32(1)	24(1)	-3(1)	3(1)	-4(1)
C(7)	21(1)	33(1)	33(1)	-2(1)	6(1)	-4(1)
C(8)	26(1)	26(1)	26(1)	2(1)	7(1)	1(1)
C(9)	45(2)	29(1)	48(2)	-3(1)	19(1)	4(1)
C(10)	33(1)	46(2)	28(1)	5(1)	9(1)	4(1)
C(11)	26(1)	45(2)	33(1)	5(1)	11(1)	3(1)

C(12)	25(1)	20(1)	23(1)	-2(1)	7(1)	-4(1)
C(13)	21(1)	25(1)	28(1)	-2(1)	6(1)	-1(1)
C(14)	27(1)	20(1)	29(1)	-2(1)	6(1)	0(1)
C(15)	28(1)	22(1)	30(1)	1(1)	7(1)	-7(1)
C(16)	23(1)	25(1)	26(1)	-1(1)	7(1)	-3(1)
C(17)	25(1)	18(1)	28(1)	-1(1)	6(1)	0(1)
C(18)	29(1)	29(1)	50(2)	-2(1)	14(1)	-4(1)
C(19)	32(1)	24(1)	48(2)	1(1)	9(1)	-1(1)
N(1)	32(1)	17(1)	33(1)	-5(1)	16(1)	-6(1)
N(2)	28(1)	19(1)	36(1)	-3(1)	17(1)	-4(1)
S(1)	29(1)	24(1)	31(1)	-5(1)	13(1)	-6(1)
F(1)	70(3)	26(2)	190(6)	40(2)	69(3)	15(2)
F(2)	50(2)	45(2)	112(4)	-10(2)	-21(2)	21(2)
F(3)	201(8)	69(4)	32(2)	-1(2)	21(3)	84(4)
F(4)	38(2)	36(2)	218(7)	43(3)	61(4)	14(2)
F(5)	43(2)	116(4)	59(2)	21(2)	32(2)	0(2)
F(6)	24(2)	149(5)	75(3)	-63(3)	8(2)	-22(2)
F(1')	128(7)	57(5)	26(3)	12(3)	6(4)	50(5)
F(2')	75(5)	30(3)	128(8)	11(4)	73(5)	21(3)
F(3')	45(3)	22(3)	107(6)	-27(3)	14(4)	-2(2)
F(4')	51(4)	45(4)	172(8)	44(5)	48(5)	-3(3)
F(5')	56(4)	98(5)	90(4)	-67(4)	36(3)	-3(4)
F(6')	24(3)	185(10)	52(4)	27(6)	3(3)	15(5)

Table S19. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^{2}x 10^3) for **1a**.

	x	y	z	U(eq)
H(3)	8493	4644	8556	30
H(4)	10108	4477	6728	29
H(6)	6037	4133	3247	34
H(7)	4416	4321	5045	35
H(9A)	9792	3465	2658	59
H(9B)	7961	3492	2918	59
H(9C)	9490	3416	4462	59
H(10A)	8742	4705	2097	53

H(10B)	7541	4265	1467	53
H(10C)	9379	4263	1219	53
H(11A)	11251	4576	4461	51
H(11B)	11724	4135	3456	51
H(11C)	11552	4061	5297	51
H(13)	5394	2941	8290	29
H(15)	1257	2270	8786	32
H(17)	1301	3710	8325	28
H(1)	5319	4862	8524	31
H(2)	5037	3763	7369	31

Table S20. Torsion angles [°] for **1a**.

C(7)-C(2)-C(3)-C(4)	-2.5(3)
N(1)-C(2)-C(3)-C(4)	177.7(2)
C(2)-C(3)-C(4)-C(5)	-0.7(3)
C(3)-C(4)-C(5)-C(6)	2.8(3)
C(3)-C(4)-C(5)-C(8)	-174.7(2)
C(4)-C(5)-C(6)-C(7)	-1.8(3)
C(8)-C(5)-C(6)-C(7)	175.8(2)
C(5)-C(6)-C(7)-C(2)	-1.3(4)
C(3)-C(2)-C(7)-C(6)	3.4(3)
N(1)-C(2)-C(7)-C(6)	-176.7(2)
C(4)-C(5)-C(8)-C(11)	-8.9(3)
C(6)-C(5)-C(8)-C(11)	173.6(2)
C(4)-C(5)-C(8)-C(10)	-129.9(2)
C(6)-C(5)-C(8)-C(10)	52.7(3)
C(4)-C(5)-C(8)-C(9)	110.4(2)
C(6)-C(5)-C(8)-C(9)	-67.0(3)
C(17)-C(12)-C(13)-C(14)	-0.8(3)
N(2)-C(12)-C(13)-C(14)	-176.5(2)
C(12)-C(13)-C(14)-C(15)	-0.5(3)
C(12)-C(13)-C(14)-C(19)	179.8(2)
C(13)-C(14)-C(15)-C(16)	1.0(3)
C(19)-C(14)-C(15)-C(16)	-179.3(2)
C(14)-C(15)-C(16)-C(17)	-0.2(3)
C(14)-C(15)-C(16)-C(18)	177.9(2)
C(15)-C(16)-C(17)-C(12)	-1.1(3)

C(18)-C(16)-C(17)-C(12)	-179.1(2)
C(13)-C(12)-C(17)-C(16)	1.6(3)
N(2)-C(12)-C(17)-C(16)	177.0(2)
C(17)-C(16)-C(18)-F(4')	-170.6(8)
C(15)-C(16)-C(18)-F(4')	11.3(9)
C(17)-C(16)-C(18)-F(5')	-42.0(7)
C(15)-C(16)-C(18)-F(5')	140.0(6)
C(17)-C(16)-C(18)-F(4)	-6.3(5)
C(15)-C(16)-C(18)-F(4)	175.7(4)
C(17)-C(16)-C(18)-F(6)	121.9(5)
C(15)-C(16)-C(18)-F(6)	-56.2(5)
C(17)-C(16)-C(18)-F(5)	-124.4(3)
C(15)-C(16)-C(18)-F(5)	57.5(4)
C(17)-C(16)-C(18)-F(6')	68.3(7)
C(15)-C(16)-C(18)-F(6')	-109.7(7)
C(15)-C(14)-C(19)-F(1')	-82.9(8)
C(13)-C(14)-C(19)-F(1')	96.8(8)
C(15)-C(14)-C(19)-F(3)	111.6(5)
C(13)-C(14)-C(19)-F(3)	-68.7(5)
C(15)-C(14)-C(19)-F(2')	149.9(5)
C(13)-C(14)-C(19)-F(2')	-30.4(6)
C(15)-C(14)-C(19)-F(1)	-17.1(5)
C(13)-C(14)-C(19)-F(1)	162.6(4)
C(15)-C(14)-C(19)-F(2)	-128.1(3)
C(13)-C(14)-C(19)-F(2)	51.7(4)
C(15)-C(14)-C(19)-F(3')	42.3(6)
C(13)-C(14)-C(19)-F(3')	-138.0(5)
N(2)-C(1)-N(1)-C(2)	-0.6(3)
S(1)-C(1)-N(1)-C(2)	177.96(18)
C(3)-C(2)-N(1)-C(1)	-117.3(2)
C(7)-C(2)-N(1)-C(1)	62.9(3)
N(1)-C(1)-N(2)-C(12)	-177.5(2)
S(1)-C(1)-N(2)-C(12)	4.0(3)
C(13)-C(12)-N(2)-C(1)	-143.8(2)
C(17)-C(12)-N(2)-C(1)	40.6(4)

Table S21. Hydrogen bonds for **1a** [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(17)-H(17)...S(1)	0.95	2.74	3.199(2)	110.8
N(1)-H(1)...S(1)#1	0.88	2.53	3.3478(19)	154.3
C(17)-H(17)...S(1)	0.95	2.74	3.199(2)	110.8
N(1)-H(1)...S(1)#1	0.88	2.53	3.3478(19)	154.3

Symmetry transformations used to generate equivalent atoms:

#1 -x+1,-y+1,-z+2

Table S22: Coordinates of syn-anti conformation of $[Cu(1)(3)]^+$ in Figure S36.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	4.103278	1.535796	2.031218
2	1	0	4.106536	0.671246	2.683292
3	6	0	4.844781	2.677400	2.367174
4	1	0	5.422223	2.691786	3.282658
5	6	0	4.816931	3.759653	1.517671
6	1	0	5.376539	4.660749	1.742207
7	6	0	4.046777	3.696286	0.338337
8	6	0	3.973286	4.788135	-0.585347
9	1	0	4.531506	5.691081	-0.366385
10	6	0	3.221124	4.694071	-1.710999
11	1	0	3.166427	5.519935	-2.410869
12	6	0	2.480889	3.503467	-2.002254
13	6	0	2.520403	2.397864	-1.116228
14	6	0	3.328805	2.501391	0.081000
15	6	0	1.704300	3.370154	-3.168704

16	1	0	1.667995	4.180433	-3.888171
17	6	0	1.014588	2.203997	-3.388660
18	1	0	0.455483	2.064363	-4.306148
19	6	0	1.077157	1.154372	-2.442298
20	6	0	3.792097	-2.817248	-0.407252
21	6	0	3.820261	-4.200944	-0.699575
22	1	0	4.722180	-4.629844	-1.117440
23	6	0	2.721433	-4.983229	-0.433079
24	1	0	2.732266	-6.045939	-0.649956
25	6	0	1.580630	-4.403911	0.160903
26	6	0	1.625537	-3.014246	0.421571
27	6	0	0.507665	-2.388812	1.095240
28	6	0	-0.606092	-3.176655	1.468075
29	6	0	-0.633933	-4.571826	1.143586
30	1	0	-1.505441	-5.151652	1.425338
31	6	0	0.418606	-5.161897	0.518186
32	1	0	0.402424	-6.222147	0.292645
33	6	0	-1.642796	-2.532380	2.176776
34	1	0	-2.525088	-3.091186	2.468676
35	6	0	-1.510974	-1.205050	2.514785
36	1	0	-2.278777	-0.701227	3.087864
37	6	0	-0.355099	-0.488660	2.127347
38	6	0	-0.148022	0.916893	2.596334
39	6	0	0.645611	1.138342	3.739072
40	6	0	0.811477	2.445932	4.196945
41	1	0	1.416292	2.616604	5.082366
42	6	0	0.212363	3.534803	3.560653
43	6	0	-0.570222	3.286252	2.432925
44	1	0	-1.047555	4.117150	1.922921
45	6	0	-0.769640	1.994248	1.942615
46	6	0	-1.648898	1.775984	0.736007

47	1	0	-1.920164	2.722231	0.267627
48	1	0	-2.581796	1.272770	1.008680
49	1	0	-1.149287	1.158665	-0.014541
50	6	0	1.288682	-0.006213	4.489395
51	1	0	0.537551	-0.689358	4.898195
52	1	0	1.883115	0.364846	5.325446
53	1	0	1.940736	-0.602031	3.844896
54	6	0	0.373034	4.934091	4.101968
55	1	0	0.284463	5.681710	3.310990
56	1	0	1.340632	5.065693	4.591358
57	1	0	-0.400410	5.153005	4.845655
58	6	0	5.022199	-1.987102	-0.593480
59	6	0	5.493919	-1.637616	-1.868876
60	6	0	6.666413	-0.878230	-1.971135
61	1	0	7.023590	-0.604588	-2.959388
62	6	0	7.389881	-0.478942	-0.853463
63	6	0	6.917167	-0.866793	0.405584
64	1	0	7.484832	-0.594586	1.290328
65	6	0	5.753916	-1.613480	0.559333
66	6	0	5.334960	-2.063009	1.941371
67	1	0	4.329891	-1.720424	2.198294
68	1	0	6.029809	-1.688887	2.694600
69	1	0	5.324854	-3.154893	2.018096
70	6	0	8.663257	0.319505	-0.983254
71	1	0	8.851152	0.607486	-2.018762
72	1	0	9.524992	-0.258340	-0.635437
73	1	0	8.622196	1.231306	-0.380482
74	6	0	4.795342	-2.033234	-3.151550
75	1	0	5.505035	-2.485154	-3.849356
76	1	0	4.372827	-1.156806	-3.653013
77	1	0	3.988852	-2.748626	-2.994447

78	6	0	0.350807	-0.115193	-2.731847
79	6	0	1.085814	-1.302099	-2.793798
80	1	0	2.141137	-1.260396	-2.564131
81	6	0	0.499109	-2.508944	-3.157047
82	1	0	1.096491	-3.411000	-3.205103
83	6	0	-0.851206	-2.538774	-3.490205
84	1	0	-1.317793	-3.461928	-3.812838
85	6	0	-1.605228	-1.371586	-3.442974
86	1	0	-2.643894	-1.388433	-3.748025
87	6	0	-1.030209	-0.155802	-3.044531
88	6	0	-3.087102	1.205205	-2.451901
89	6	0	-4.780456	-0.019801	-1.041947
90	6	0	-4.731074	-0.883046	0.053693
91	1	0	-3.798927	-1.372037	0.311728
92	6	0	-5.868686	-1.118363	0.819769
93	6	0	-7.072213	-0.498289	0.507231
94	1	0	-7.959053	-0.682632	1.096911
95	6	0	-7.116353	0.354034	-0.595539
96	6	0	-5.990331	0.598025	-1.375155
97	1	0	-6.050792	1.253534	-2.229190
98	6	0	-8.408316	1.062935	-0.927376
99	6	0	-5.744016	-2.021323	2.016121
100	29	0	2.210309	-0.165510	0.359259
101	9	0	-8.507851	2.230072	-0.257845
102	9	0	-9.481323	0.319434	-0.590882
103	9	0	-8.502529	1.345784	-2.240293
104	7	0	3.370822	1.443013	0.927958
105	7	0	1.827700	1.248541	-1.340920
106	7	0	0.600545	-1.067336	1.396920
107	7	0	2.701599	-2.243970	0.109141
108	7	0	-1.825376	1.014239	-2.980279

109	1	0	-1.431036	1.883685	-3.304874
110	7	0	-3.588705	0.123000	-1.783542
111	1	0	-2.928866	-0.627916	-1.627602
112	16	0	-3.821765	2.695558	-2.621000
113	9	0	-4.992857	-1.446496	2.993750
114	9	0	-5.110591	-3.181541	1.700946
115	9	0	-6.925933	-2.339097	2.556932

Table S23: Coordinates of anti-anti conformation of [Cu(1)(3)]$^+$ in Figure S37

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	3.972381	0.694409	3.001263
2	1	0	4.725724	-0.069902	2.855442
3	6	0	4.035539	1.544369	4.114931
4	1	0	4.838316	1.431033	4.832356
5	6	0	3.068182	2.512077	4.265171
6	1	0	3.085971	3.192918	5.108910
7	6	0	2.037012	2.617402	3.309583
8	6	0	1.000392	3.600335	3.405474
9	1	0	1.018706	4.294683	4.237656
10	6	0	0.014478	3.659585	2.473810
11	1	0	-0.770060	4.404236	2.545974
12	6	0	-0.023444	2.734568	1.381651
13	6	0	0.986211	1.752365	1.240994
14	6	0	2.047096	1.704796	2.224470
15	6	0	-1.047925	2.752520	0.413668
16	1	0	-1.821054	3.511482	0.461855
17	6	0	-1.057201	1.806320	-0.578970

18	1	0	-1.826982	1.803031	-1.340359
19	6	0	-0.030287	0.831528	-0.632853
20	6	0	4.909372	1.034424	-1.790022
21	6	0	5.712024	0.985527	-2.952886
22	1	0	6.154293	1.901481	-3.323586
23	6	0	5.935704	-0.214905	-3.582616
24	1	0	6.553932	-0.268733	-4.472095
25	6	0	5.372195	-1.394306	-3.053082
26	6	0	4.569669	-1.265134	-1.893848
27	6	0	3.990649	-2.453507	-1.302741
28	6	0	4.253852	-3.713424	-1.891507
29	6	0	5.057409	-3.799711	-3.073801
30	1	0	5.234925	-4.776695	-3.508601
31	6	0	5.593666	-2.684487	-3.633786
32	1	0	6.207254	-2.753366	-4.524801
33	6	0	3.706341	-4.849850	-1.261950
34	1	0	3.886021	-5.833733	-1.681231
35	6	0	2.966841	-4.697965	-0.113931
36	1	0	2.555332	-5.555388	0.403215
37	6	0	2.743015	-3.408030	0.415667
38	6	0	1.980214	-3.252474	1.692100
39	6	0	2.684551	-3.085144	2.900310
40	6	0	1.962836	-2.969271	4.088282
41	1	0	2.505963	-2.847940	5.020488
42	6	0	0.567912	-3.024503	4.114976
43	6	0	-0.102758	-3.218562	2.907481
44	1	0	-1.186301	-3.290593	2.910436
45	6	0	0.577334	-3.342663	1.693984
46	6	0	-0.196754	-3.598175	0.421332
47	1	0	-1.266727	-3.454797	0.584609
48	1	0	-0.063348	-4.626412	0.070246

49	1	0	0.116906	-2.939950	-0.391488
50	6	0	4.195899	-3.095394	2.938576
51	1	0	4.588914	-4.090200	2.704082
52	1	0	4.560674	-2.826918	3.931131
53	1	0	4.630257	-2.404903	2.212249
54	6	0	-0.187990	-2.872746	5.412018
55	1	0	-1.183403	-3.316541	5.348932
56	1	0	-0.313843	-1.815784	5.670345
57	1	0	0.342713	-3.348120	6.239931
58	6	0	4.744825	2.332329	-1.064617
59	6	0	3.878694	3.327680	-1.554848
60	6	0	3.782372	4.534991	-0.860052
61	1	0	3.106109	5.298200	-1.232516
62	6	0	4.536098	4.792929	0.285376
63	6	0	5.406354	3.799029	0.734945
64	1	0	6.016703	3.986055	1.613020
65	6	0	5.530555	2.573455	0.079254
66	6	0	6.538748	1.560023	0.571446
67	1	0	6.085556	0.581164	0.741966
68	1	0	6.998291	1.892579	1.503237
69	1	0	7.342779	1.416447	-0.157764
70	6	0	4.446379	6.125075	0.988432
71	1	0	5.126539	6.851641	0.531636
72	1	0	4.719945	6.040713	2.042226
73	1	0	3.438531	6.541765	0.928447
74	6	0	3.073631	3.135498	-2.820032
75	1	0	2.355511	3.946542	-2.947119
76	1	0	2.517238	2.196212	-2.820682
77	1	0	3.715797	3.127529	-3.706486
78	6	0	-0.078762	-0.185933	-1.718226
79	6	0	1.039332	-0.400433	-2.533610

80	1	0	1.949199	0.140511	-2.315827
81	6	0	0.982813	-1.258219	-3.624229
82	1	0	1.853461	-1.387685	-4.256012
83	6	0	-0.199914	-1.938514	-3.909764
84	1	0	-0.256617	-2.606663	-4.760734
85	6	0	-1.308570	-1.770160	-3.091265
86	1	0	-2.223838	-2.314559	-3.284145
87	6	0	-1.259206	-0.898582	-2.002574
88	6	0	-3.640165	-0.363232	-1.476203
89	6	0	-5.901504	-0.250474	-0.363274
90	6	0	-6.802549	-1.162958	0.187528
91	1	0	-6.472823	-2.159500	0.457741
92	6	0	-8.128347	-0.797283	0.400854
93	6	0	-8.576654	0.473325	0.057426
94	1	0	-9.604520	0.759471	0.230510
95	6	0	-7.670804	1.377799	-0.492007
96	6	0	-6.339865	1.032225	-0.699816
97	1	0	-5.652832	1.754287	-1.111616
98	6	0	-8.140700	2.752466	-0.900111
99	6	0	-9.088487	-1.816966	0.959427
100	29	0	2.859626	-0.311080	0.305242
101	9	0	-7.164586	3.675928	-0.754597
102	9	0	-9.194496	3.159461	-0.166237
103	9	0	-8.519626	2.780053	-2.193408
104	7	0	3.018004	0.768869	2.082126
105	7	0	0.984413	0.831876	0.237859
106	7	0	3.230668	-2.317430	-0.182129
107	7	0	4.337759	-0.066491	-1.295410
108	7	0	-2.383704	-0.819437	-1.130762
109	1	0	-2.188486	-0.914960	-0.142983
110	7	0	-4.550553	-0.650683	-0.481972

111	1	0	-4.298701	-1.423666	0.119205
112	16	0	-3.968014	0.433266	-2.899270
113	9	0	-8.484156	-2.622367	1.862464
114	9	0	-9.577265	-2.616933	-0.011327
115	9	0	-10.138889	-1.239151	1.569067

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