Electronic Supporting Information
for

Monomer-dimer nanoswitch that mimics the working principle of the SARS-CoV 3CLpro enzyme controls copper-catalysed cyclopropanation

Soumen De, Susnata Pramanik and Michael Schmittel*

Center of Micro and Nanochemistry and Engineering, Organische Chemie I, Universität Siegen, Adolf-Reichwein-Str. 2, D-57068 Siegen, Germany,
E-mail: schmittel@chemie.uni-siegen.de
Fax: (+49) 271-740-3270

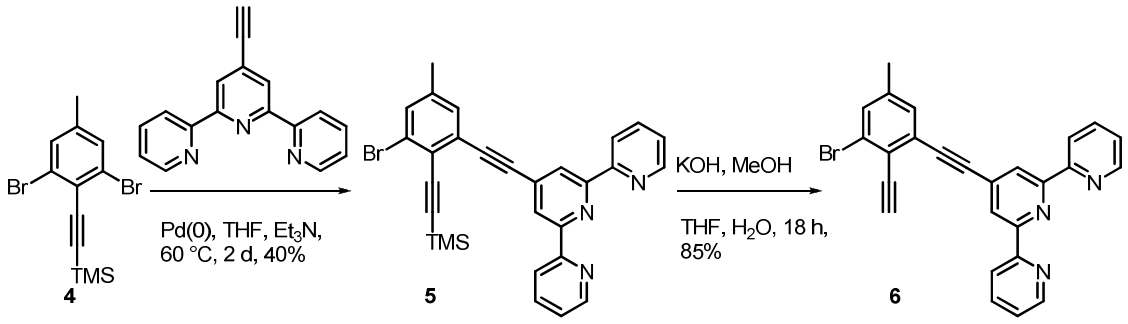
Table of Contents

Synthesis

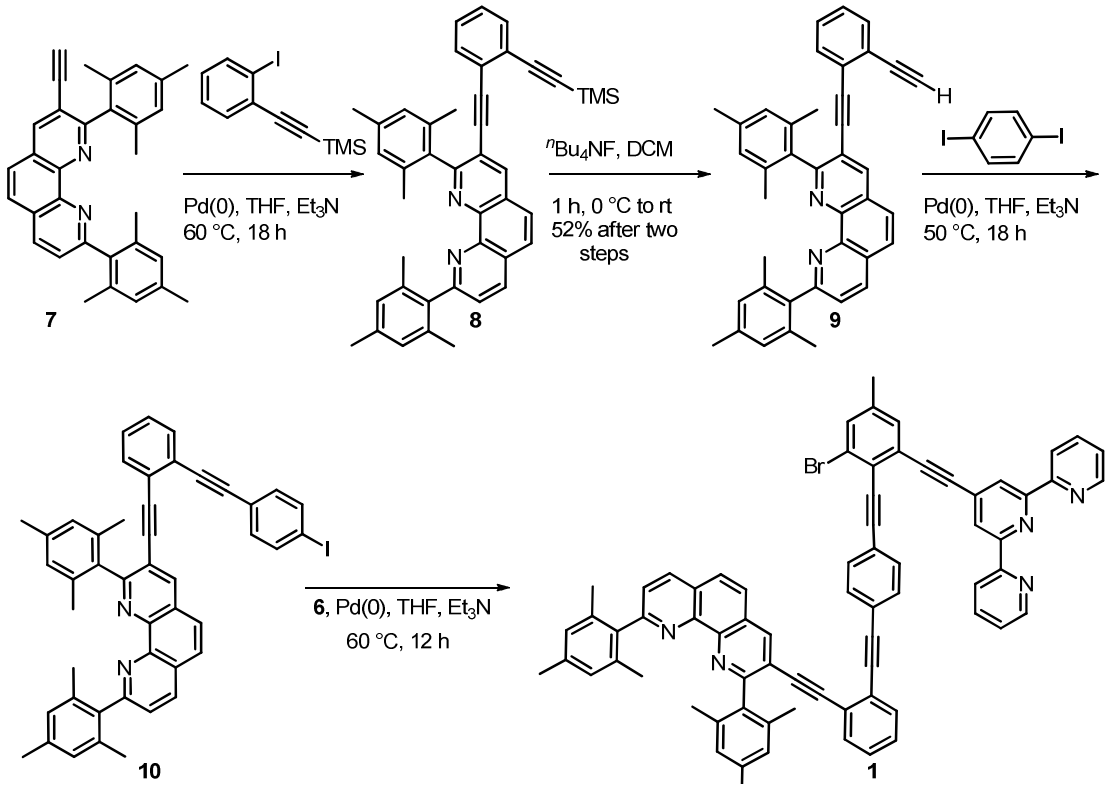
General information

All commercially available reagents were used without further purification and all solvents were distilled prior to use for column chromatography. We used silica gel 60 as stationary phase in thin-layer and column chromatography. The 400 MHz ^{1}H NMR spectra were recorded using the deuterated solvent as the lock and residual solvent as the internal reference. In ^{1}H NMR assignments, first, the chemical shift (in ppm) is given, followed, in brackets, by the multiplicity of the signal (s: singlet, d: doublet, t: triplet, dd: doublet of doublets, ddd: doublet of doublet of doublets, td: triplet of doublets, m: multiplet, bs: broad singlet), the value of the coupling constants in Hertz (Hz), the number of protons implied, and finally the assignment of the proton where ever possible. In the experimental section, numbering of the carbon atoms of the molecular formulae is only used for the assignments of the NMR signals and is not in accordance with IUPAC nomenclature rules. Anhydrous tetrahydrofuran (THF) was distilled over potassium and triethyl amine was dried over calcium hydride. The melting points of solid compounds were not further corrected. IR spectra were recorded on a Perkin-Elmer FT-IR 1750. Electrospray ionisation mass spectra (ESI-MS) were recorded on a Thermo-Quest LCQ Deca. Microanalyses were performed on a Euro elemental analyser from EuroVector.

Synthetic schemes



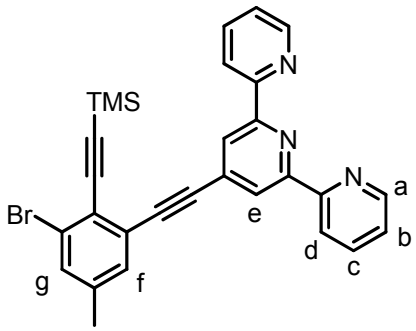
Scheme S1: Synthesis of building block **6.**



Scheme S2: Synthesis of nanoswitch **1.**

Preparative procedures

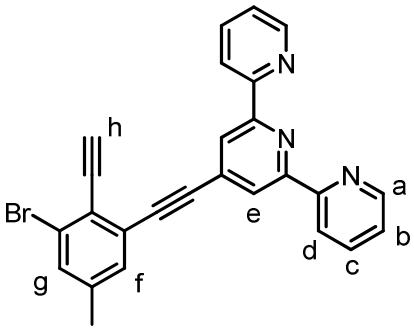
4-((3-Bromo-5-methyl-2-(trimethylsilylethynyl)phenyl)ethynyl)-[2,2';6',2"]terpyridine (**5**)**:**



To a deaerated solution of (2,6-dibromo-4-methylphenyl-ethynyl)trimethylsilane (2.26 g, 6.53 mmol) and 4-ethynyl-[2,2';6',2"]terpyridine (840 mg, 3.26 mmol) in a mixture of dry THF (50 mL) and dry triethylamine (30 mL) was added $Pd(PPh_3)_4$ (375 mg, 325 µmol). The mixture was stirred at 65 °C under argon for 12 h. Then the reaction mixture was cooled to room temperature and the solvents were evaporated under reduced pressure. The residue was dissolved in DCM (50 mL), washed with water, brine, and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude residue was purified by chromatography on silica gel with DCM as mobile phase to furnish the pure product as white solid (R_f = 0.55 in 50% DCM in hexane on neutral alumina).

Yield: 1.05 g (2.01 mmol, 31% yield). **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 0.35 (s, 9 H, Si$\underline{Me}_3$), 2.34 (s, 3 H, C$\underline{H}_3$), 7.32-7.36 (m, 3 H, b-, f/g-H), 7.43 (s, 1 H, g/f-H), 7.86 (td, ^3J = 8.0 Hz, ^4J = 2.0 Hz, 2 H, c-H), 8.60-8.63 (m, 4 H, d, e-H), 8.70 (ddd, ^3J = 4.4 Hz, ^4J = 2.0 Hz, ^5J = 0.8 Hz, 2 H, a-H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = –0.2, 21.0, 91.6, 91.8, 101.4, 104.1, 121.1, 123.0, 124.0, 125.1, 125.8, 126.6, 131.5, 133.0, 133.6, 136.8, 139.4, 149.1, 156.2 (2 C) ppm. **ESI-MS:** *m/z* (%) = 524.1 (100) [**5**•H]$^+$; Calcd: *m/z* = 523.9.

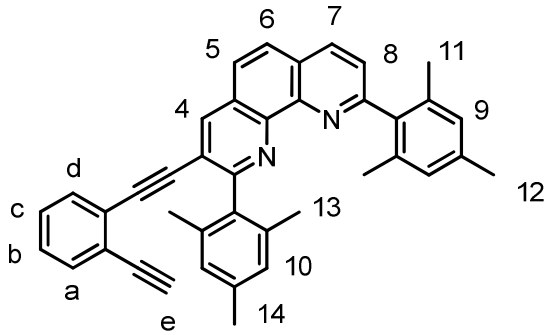
4-(3-Bromo-5-methyl-2-ethynylphenyl-ethynyl)-[2,2';6',2"]terpyridine (**6**)**:**



Terpyridine **11** (700 mg, 1.34 mmol) was dissolved in a mixture of methanol (30 mL) and THF (40 mL) in a 250 mL round-bottom flask, then 1 N aqueous KOH (10 mL, 10.0 mmol) was added slowly. After stirring for 12 h at room temperature, the solution was extracted with DCM (150 mL). After the organic layer had been dried over Na_2SO_4, the solvent was removed under reduced pressure to afford the pure product as a white solid.

Yield: 500 mg (1.11 mmol, 83%). **MP**: 126 °C. **IR (KBr)**: $\tilde{\nu}$ = 3288, 3054, 3009, 2952, 2920, 2862, 2211, 1583, 1463, 1389, 1264, 1201, 1114, 992, 884, 855, 798, 736, 661, 627, 544 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$)**: δ = 2.36 (s, 3 H, C$\underline{H}_3$), 3.71 (s, 1 H, h-H), 7.35-7.38 (m, 3 H, b-, f/g-H), 7.45 (s, 1 H, g/f-H), 7.88 (td, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 2 H, c-H), 8.58 (s, 2 H, e-H), 8.59-8.61 (m, 2 H, d-H), 8.72 (ddd, ^3J = 4.8 Hz, ^4J = 1.6 Hz, ^5J = 0.8 Hz, 2 H, a-H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 21.0, 91.4, 91.6, 121.3, 122.9, 123.5, 123.8, 124.0, 125.7, 127.2, 128.4, 128.6, 131.9, 132.9, 133.6, 136.9, 139.9, 149.2, 156.6 ppm. **ESI-MS**: *m/z* (%) = 450.1 (100) [**6**•H]$^+$; Calcd: *m/z* = 499.9. **Elemental analysis**: $C_{26}H_{16}BrN_3$•0.5EtOAc; Calcd: C, 68.02; H, 4.08; N, 8.50. Found: C, 68.15; H, 3.75; N, 8.17.

3-(2-Ethynylphenyl-ethynyl)-2,9-dimesityl[1,10]-phenanthroline (**9**):

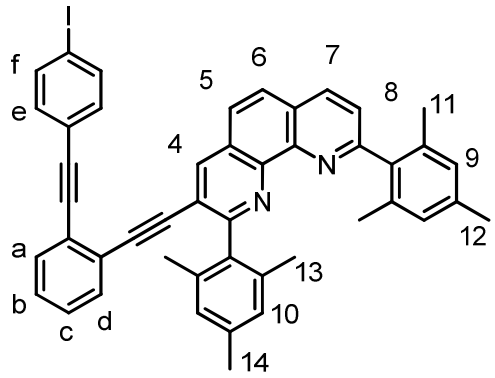


Compounds **7** (420 mg, 953 µmol) and (2-iodophenyl-ethynyl)trimethylsilane (372 mg, 1.24 mmol) were put into a round bottom flask under nitrogen. To the mixture, dry THF (20 mL) and dry Et_3N (20 mL) were added and subjected to a freeze-pump-thaw process for degassing. After addition of $Pd(PPh_3)_4$ (110 mg, 93 µmol) the mixture was heated to 60 °C for 18 h. The solution was cooled and the solvents were removed under reduced pressure. The residue was dissolved in DCM and washed with water. The crude mixture was passed rapidly through silica gel using 10% ethyl acetate in hexane. The mixture collected after column filtration was reacted with $^{n}Bu_4NF$ (662 mg, 2.14 mmol) at 0 °C in DCM and then stirred for additional 1 h at rt. The organic layer was washed with water for several times to remove $^{n}Bu_4NF$ and after removal of the solvents, purified by column chromatography using 6% ethyl acetate in hexane (R_f = 0.3 in 10% ethyl acetate in hexane).

Yield: 52% (496 mg, 268 µmol). **MP**: decomposed above 190°C. **IR (KBr)**: $\tilde{\nu}$ = 2999, 2953, 2916, 2856, 2728, 2399, 2279, 2213, 2107, 1925, 1814, 1731, 1613, 1580, 1534, 1503, 1471, 1456, 1372, 1289, 1241, 1162, 1148, 1105, 1031, 992, 923, 886, 848, 757, 720, 640, 614, 586 cm^{-1}. **^{1}H NMR (400 MHz, $CDCl_3$):** δ = 2.03 (s, 6 H, 11/13-H), 2.05 (s, 6 H, 13/11-H), 2.13 (s, 3 H, 12/14-H), 2.24 (s, 3 H, 14/12-H), 3.12 (s, 1 H, e-H), 6.82 (s, 2 H, 9/10-H), 6.84 (s, 2 H, 10/9-H), 6.99-7.03 (m, 1 H, d-H), 7.13-7.18 (m, 2 H, b-, c-H), 7.35-7.39 (m, 1 H, a-H), 7.49 (d, ^3J = 8.0 Hz, 1 H, 8-H), 7.75 (d, ^3J = 8.8 Hz, 1 H, 5/6-H), 7.79 (d, ^3J = 8.8 Hz, 1 H, 6/5-H), 8.20 (d, ^3J = 8.0 Hz, 1 H, 7-H), 8.44 (s, 1 H, 4-H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$):** δ = 20.2, 20.6, 21.1, 21.2, 81.3, 81.6, 90.9, 92.9, 119.8, 124.1, 125.2, 125.6, 125.9, 126.7, 126.9, 127.5, 128.0, 128.1, 128.4, 128.5, 132.4, 132.4, 135.8, 136.2, 136.3, 137.0, 137.1, 137.5, 137.9, 139.4, 145.0, 145.9, 160.4, 161.6

ppm. **ESI-MS:** *m/z* (%) = 541.5 (100) $[\mathbf{9}\bullet H]^+$; Calcd: *m/z* = 541.3. **Elemental analysis:** $C_{40}H_{32}N_2\bullet 0.2Et_2O$; Calcd: C, 88.21; H, 6.17; N, 5.04. Found: C, 88.26; H, 6.06; N, 5.07.

3-(4-Iodophenylethynyl)phen-2-ylethynyl)-2,9-dimesityl[1,10]-phenanthroline (**10**)

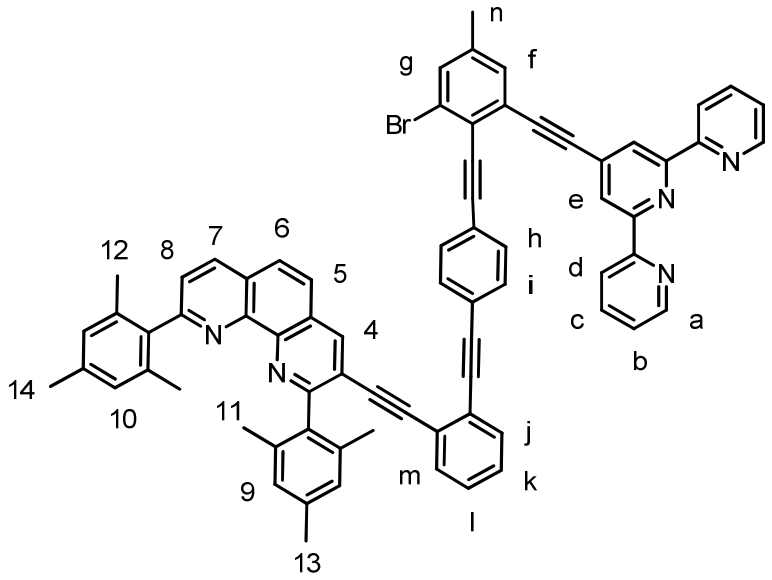


In a round bottom flask, compound **9** (200 mg, 370 µmol) and 1,4-diiodobenzene (1.60 g, 3.70 mmol) were placed under nitrogen atmosphere. The compounds were dissolved by adding dry THF (20 mL) and dry Et_3N (20 mL) followed by removal of oxygen by a freeze-pump-thaw protocol, then $Pd(PPh_3)_4$ (43 mg, 37 µmol) was added. The reaction mixture was stirred at 50 °C for 18 h. The organic solvents were evaporated under reduced pressure and the residue dissolved in DCM. The organic layer was washed with water and dried over Na_2SO_4. Finally, the product was purified by column chromatography (R_f = 0.35 in 10% ethyl acetate in hexane) using 6% ethyl acetate in hexane as eluent.

Yield: 65% (178 mg, 241 µmol). **MP**: decomposed above 225 °C. **IR (KBr)**: $\tilde{\nu}$ = 3002, 2952, 2916, 2856, 2730, 2358, 2330, 2213, 1926, 1902, 1724, 1614, 1583, 1535, 1487, 1458, 1391, 1296, 1241, 1148, 1106, 1059, 1032, 1004, 917, 887, 849, 820, 758, 705, 639, 615, 583 cm^{-1}. **^{1}H NMR (400 MHz, CD_2Cl_2):** δ = 2.07 (s, 12 H, 11-, 13-H), 2.35 (s, 3 H, 12/14-H), 2.37 (s, 3 H, 14/12-H), 6.96 (s, 2 H, 9/10-H), 6.97 (s, 2 H, 10/9-H), 7.04 (dd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1 H, d-H), 7.26 (td, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1 H, c-H), 7.31 (td, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1 H, b-H), 7.35 (d, ^3J = 8.8 Hz, 2 H, e-H), 7.53 (dd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1 H, a-H), 7.58 (d, ^3J = 8.0 Hz, 1 H, 8-H), 7.78 (d, ^3J = 8.8 Hz, 2 H, f-H), 7.80 (d, ^3J = 8.8 Hz, 1 H, 5/6-H), 7.92 (d, ^3J = 8.8 Hz, 1 H, 6/5-H), 8.33 (d, ^3J = 8.0 Hz, 1 H, 7-H), 8.49 (s, 1 H, 4-H) ppm. **^{13}C NMR (100 MHz, CD_2Cl_2):** δ = 20.0, 20.4, 21.1,

21.2, 89.6, 91.2, 92.8, 93.4, 94.8, 119.9, 123.0, 125.2, 125.5, 125.9, 127.1, 127.4, 128.0, 128.2, 128.5 (2 C), 128.7, 128.8, 132.1, 132.7, 133.4, 136.0, 136.2, 136.3, 137.3, 137.7, 137.8, 138.0, 138.4, 139.3, 145.5, 146.4, 160.9, 161.8 ppm. **ESI-MS**: *m/z* (%) = 743.4 (100) $[\mathbf{10}\bullet H]^+$; Calcd: *m/z* = 743.2. **Elemental analysis**: $C_{46}H_{35}IN_2\bullet 0.33DCM$; Calcd: C, 72.18; H, 4.66; N, 3.63. Found: C, 72.50; H, 4.50; N, 3.76.

Nanoswitch **1:**

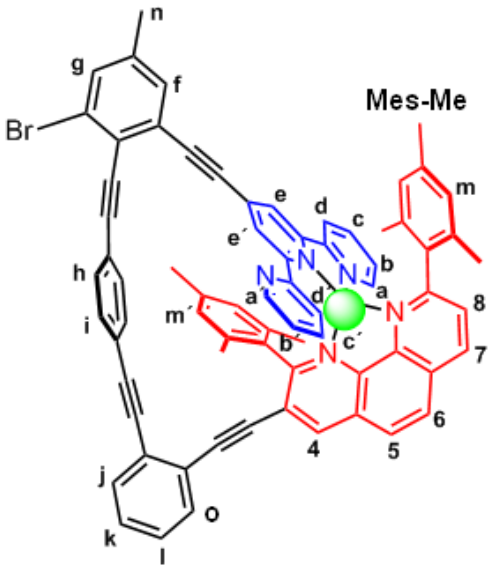


Phenanthroline **10** (210 mg, 283 μmol) and terpyridine **6** (128 mg, 284 μmol) were placed in a flask under argon atmosphere. Now 30 mL of dry THF and 30 mL of dry TEA were added. After the solution had been deaerated for 1 h by purging with argon, $Pd(PPh_3)_4$ (50.0 mg, 43.3 μmol) was added. The reaction was heated at 65 °C for 18 h, then the solvents were removed in vacuum. The residue was dissolved in DCM and washed with water. The organic layer was dried over Na_2SO_4. The resulting solid obtained after evaporating the solvents was chromatographed over silica gel (10% EtOAc in DCM) to furnish ligand **1** as an white solid (R_f = 0.7 in DCM on neutral alumina). The ligand obtained after column chromatography was furthermore purified over Bio-Beads S-X8 using toluene as eluent. The middle fraction was the target compound.

Yield: 130 mg (122 μmol, 43%). **MP**: Decomposition > 200 °C. **IR (KBr)**: $\tilde{\nu}$ = 3053, 2919, 2854, 2209, 1714, 1586, 1460, 1389, 1254, 994, 847, 793, 749, 618, 543 cm^{-1}. **^{1}H**

NMR (400 MHz, $CDCl_3$): δ = 2.05 (s, 6 H, 11/12-H), 2.06 (s, 6 H, 12/11-H), 2.33 (s, 3 H, 13/14-H), 2.37 (s, 3 H, 14/13-H), 2.41 (s, 3 H, n-H), 6.95 (s, 2 H, 9/10-H), 6.97 (s, 2 H, 9/10-H), 6.98-7.00 (m, 1 H, l-H), 7.24-7.29 (m, 3 H, m-, b-H), 7.33 (dt, ^3J = 7.6 Hz, ^4J = 1.6 Hz 1 H, j-H), 7.48-7.50 (m, 2 H, 8-, f-H), 7.51 (d, ^3J = 8.8 Hz, 1 H, 6/5-H), 7.55-7.57 (m, 2 H, k-, g-H), 7.61 (d, ^3J = 8.8 Hz, 1 H, 5/6-H), 7.68 (d, ^3J = 8.4 Hz, 2 H, i-H), 7.73 (td, ^3J = 7.6 Hz, ^4J = 2.0 Hz, 2 H, c-H), 8.85 (d, ^3J = 8.4 Hz, 2 H, h-H), 8.13 (d, ^3J = 8.0 Hz, 1 H, 7-H), 8.31 (s, 1 H, 4-H), 8.45 (ddd, ^3J = 7.6 Hz, ^4J = 1.2 Hz, ^5J = 1.2 Hz, 2 H, d-H), 8.68 (ddd, ^3J = 8.4 Hz, ^4J = 2.0 Hz, ^5J = 1.2 Hz, 2 H, a-H), 8.70 (s, 2 H, e-H) ppm. **^{13}C NMR (100 MHz, $CDCl_3$)**: δ = 20.1, 20.5, 21.1 (2C), 21.2, 89.3, 90.3, 91.1, 91.9, 92.0, 93.4, 93.6, 97.6, 119.8, 121.1, 122.9, 123.3, 123.5, 124.1, 124.9, 125.0, 125.2, 125.5, 125.6, 125.7, 126.5, 126.7, 126.8, 127.5, 128.0, 128.2, 128.3, 128.5, 131.6, 131.8 (2C), 132.0, 132.4, 132.9, 133.8, 136.0, 136.1 (2C), 136.7, 137.0 (2C), 137.4, 137.6, 137.7, 139.0, 139.7, 144.6, 145.6, 149.0, 155.5, 160.3, 161.5 ppm. **ESI-MS:** *m/z* (%) = 1065.9 (100) [**1**•H]$^+$; calcd. *m/z* = 1065.3. **Elemental analysis:** $C_{72}H_{50}N_5Br$·0.33DCM; Calcd: C, 79.46; H, 4.67; N, 6.41. Found: C, 79.25; H, 4.42; N, 6.38.

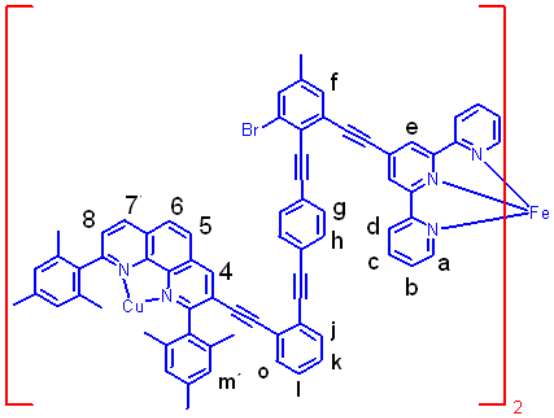
Complex [Cu(**1**)]$^+$



Switch **1** (2.57 mg, 2.41 μmol) and $[Cu(CH_3CN)_4]PF_6$ (0.899 mg, 2.41 μmol) were placed into an NMR tube and dissolved in CD_2Cl_2. The mixture was heated to 40 °C for few seconds affording a reddish solution. The NMR was recorded without purification.

Yield: Quantitative. **MP**: Above 300 °C. **^{1}H NMR (400 MHz, CD_2Cl_2)**: δ = 1.05 (s, 3 H, Mes-Me), 1.09 (s, 3 H, Mes-Me), 1.63 (s, 3 H, Mes-Me), 1.82 (s, 3 H, Mes-Me), 1.88 (s, 6 H, Mes-Me), 2.43 (s, 3 H, n-H), 4.48 (s, 1 H, m´-H), 5.89 (s, 1 H, m´-H), 6.28 (s, 1 H, m-H), 6.43 (s, 1 H, m-H), 6.67 (d, ^3J = 4.8 Hz, 1 H, a´-H), 6.78 (ddd, ^3J = 7.6 Hz, ^3J = 4.8 Hz, ^4J = 1.2 Hz, 1 H, b´-H), 7.28 (d, ^3J = 8.4 Hz, 2 H, h/i-H), 7.30-7.39 (m, 4 H, b-, c´-, k-, l-H), 7.43-7.45 (m, 2 H, e´-, j/o-H), 7.58 (d, ^3J = 8.4 Hz, 2 H, i/h-H), 7.60-7.62 (m, 2 H, e-, o/j-H), 7.64 (d, ^3J = 7.6 Hz, 1 H, d´-H), 7.76 (d, ^3J = 7.6 Hz, 1 H, d-H), 7.78 (d, ^3J = 8.4 Hz, 1 H, 8-H), 7.85 (d, ^4J = 1.2 Hz, 1 H, f/g-H), 7.87 (td, ^3J = 7.6 Hz, ^4J = 1.2 Hz 1 H, c-H), 8.03 (d, ^4J = 1.2 Hz, 1 H, g/f-H), 8.15 (d, ^3J = 4.8 Hz, 1 H, a-H), 8.18 (d, ^3J = 8.8 Hz, 1 H, 5/6-H), 8.24 (d, ^3J = 8.8 Hz, 1 H, 6/5-H), 8.65 (d, ^3J = 8.4 Hz, 1 H, 7-H), 8.81 (s, 1 H, 4-H) ppm. **^{13}C NMR (100 MHz, CD_2Cl_2)**: δ = 18.6, 19.9, 20.0, 20.5, 20.7, 21.2, 21.2, 88.5, 89.0, 89.1, 89.6, 92.0, 93.6, 94.5, 96.9, 116.9, 120.9, 122.7, 123.0, 123.1, 123.2, 123.9, 124.3, 124.6, 124.6, 124.7, 124.9, 125.9, 126.5, 126.8, 126.9, 127.0, 127.2, 127.4, 127.6, 127.7, 127.8, 127.9, 128.6, 128.9, 129.5, 131.3, 131.7, 132.4, 132.5, 132.9, 134.0, 134.5, 134.7, 135.0, 135.0, 136.4, 136.6, 137.0, 137.1, 137.4, 137.4, 138.3, 141.0, 141.0, 142.9, 144.4, 147.1, 148.1, 150.6, 152.7, 153.7, 153.8, 159.5, 159.9 ppm. **ESI-MS:** *m/z* (%) = 1128.1 (100) $[Cu(\mathbf{1})]^+$; calcd. *m/z* = 1128.3. **Elemental analysis:** $C_{72}H_{50}BrCuF_6N_5P$·0.5DCM; Calcd: C, 66.16; H, 3.91; N, 5.32. Found: C, 66.19; H, 4.11; N, 5.07.

Dimeric complex $[Fe(Cu(\mathbf{1}))_2]^{4+}$



Switch **1** (2.58 mg, 2.42 µmol) and $[Cu(CH_3CN)_4]PF_6$ (903 µg, 2.42 µmol) were put into an NMR tube, dissolved in CD_2Cl_2 and heated to 40 °C for a few seconds affording a reddish solution. A solution of $Fe(ClO_4)_2 \cdot 6H_2O$ (439 µg, 1.21 µmol) in CD_3CN was added to the mixture and after that the mixture was heated for about 5 min at 40 °C affording a deep violet solution. The NMR was recorded without further purification.

Yield: Quantitative. **MP**: Above 300 °C. **^{1}H NMR (400 MHz, CD_2Cl_2: CD_3CN** = 3: 1**)**: δ = 1.32 (s, 6 H, Mes-Me), 1.76 (s, 18 H, Mes-Me), 2.32 (s, 6 H, Mes-Me), 2.33 (s, 6 H, Mes-Me), 2.47 (s, 6 H, n-H), 6.90 (d, ^3J = 7.6 Hz, 2 H, o-H), 6.95 (s, 4 H, m´-H), 6.96 (s, 4 H, m´-H), 7.07-7.10 (m, 8 H, a-, b-H), 7.21-7.25 (m, 2 H, l-H), 7.28-7.32 (m, 2 H, k-H), 7.45 (d, ^3J = 7.6 Hz, 2 H, j-H), 7.66-7.71 (m, 8 H, f-, g/h-H), 7.78 (d, ^3J = 8.0 Hz, 2 H, 8-H), 7.80-7.85 (m, 2 H, c-H), 7.92 (d, ^3J = 8.4 Hz, 4 H, g/h-H), 8.04 (d, ^3J = 8.8 Hz, 2 H, 6-H), 8.07 (d, ^3J = 8.8 Hz, 2 H, 5-H), 8.15 (d, ^3J = 7.6 Hz, 4 H, d-H), 8.58 (d, ^3J = 8.0 Hz, 2 H, 7-H), 8.70 (s, 2 H, 4-H), 8.80 (s, 4 H, e-H) ppm. **^{13}C NMR (100 MHz, CD_2Cl_2: CD_3CN** = 3: 1**)**: δ = 19.6, 19.9, 21.0, 21.1, 21.1, 89.3, 89.4, 90.3, 90.8, 93.2, 95.2, 97.1, 97.6, 122.3, 123.4, 123.9, 124.2, 124.5, 124.9, 125.2, 125.3, 125.6, 125.7, 126.5, 126.9, 127.6, 127.8, 128.1, 128.2, 128.2, 128.3, 128.8, 129.4, 132.2, 132.3, 132.3, 132.7, 132.9, 132.9, 135.2, 135.7, 135.9, 136.2, 137.1, 138.2, 138.9, 138.9, 139.1, 140.0, 141.2, 142.2, 143.4, 153.1, 157.2, 160.1, 160.3, 161.5 ppm. **ESI-MS**: *m/z* (%) = 1128.1 (100) $[Fe(Cu(\mathbf{1}))_2]^{4+}$; calcd. *m/z* = 1128.3. **Elemental analysis:** $C_{144}H_{100}Br_2Cl_2Cu_2F_{12}FeN_{10}O_8P_2 \cdot 3CH_2Cl_2 \cdot CH_3CN$; Calcd: C, 57.77; H, 3.55; N, 4.97. Found: C, 57.47; H, 3.52; N, 5.32.

NMR spectra of the synthetic precursors

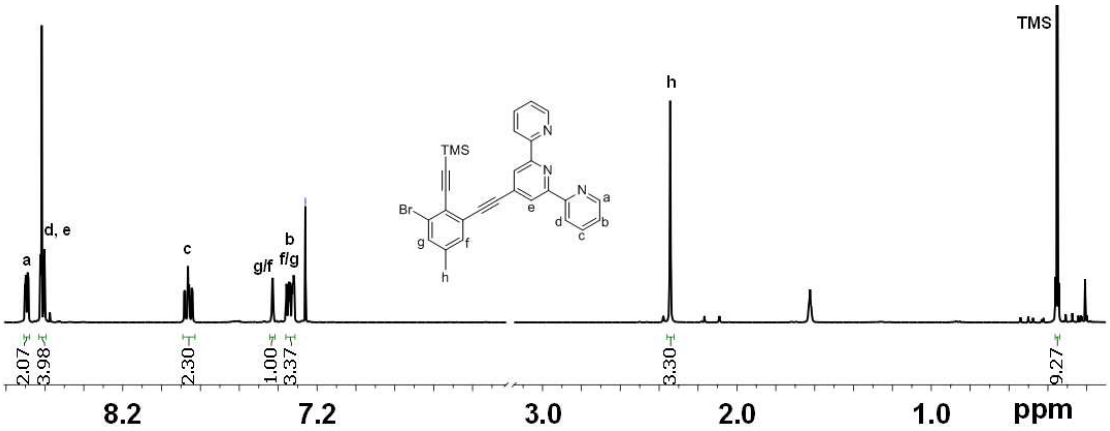


Figure S1: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **5.**

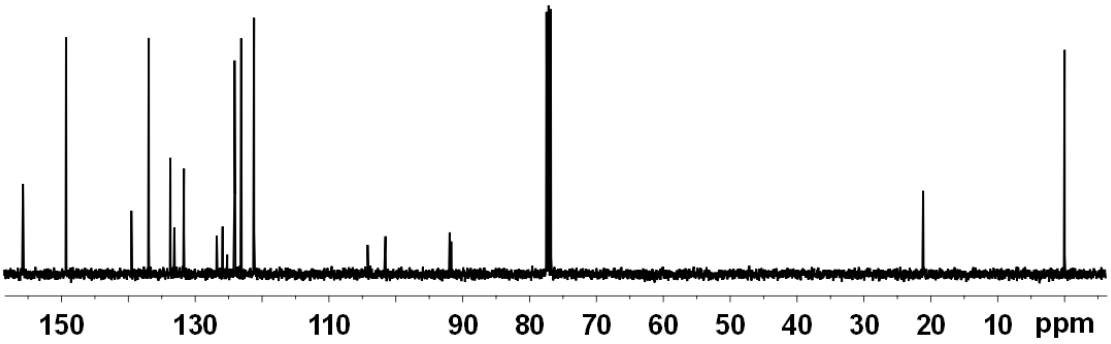


Figure S2: ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of compound **5.**

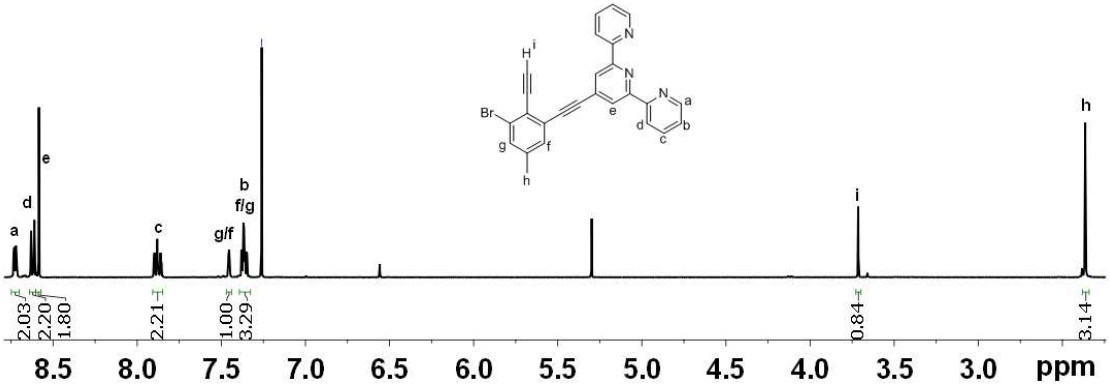


Figure S3: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **6.**

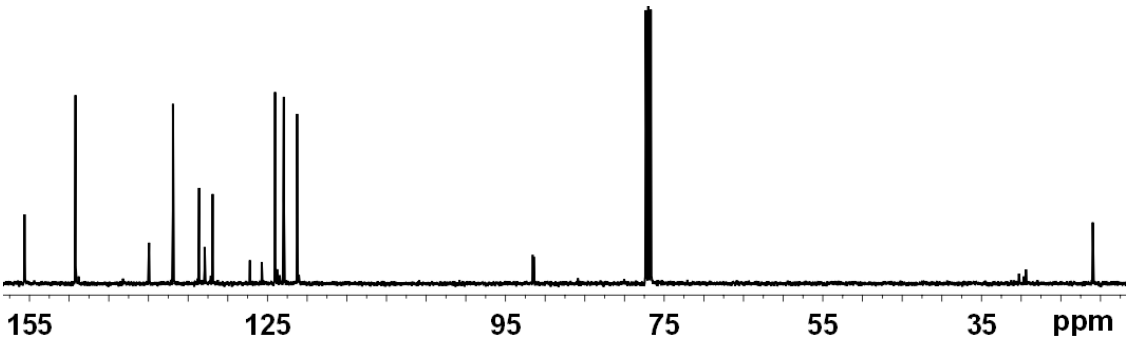


Figure S4: ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of compound **6.**

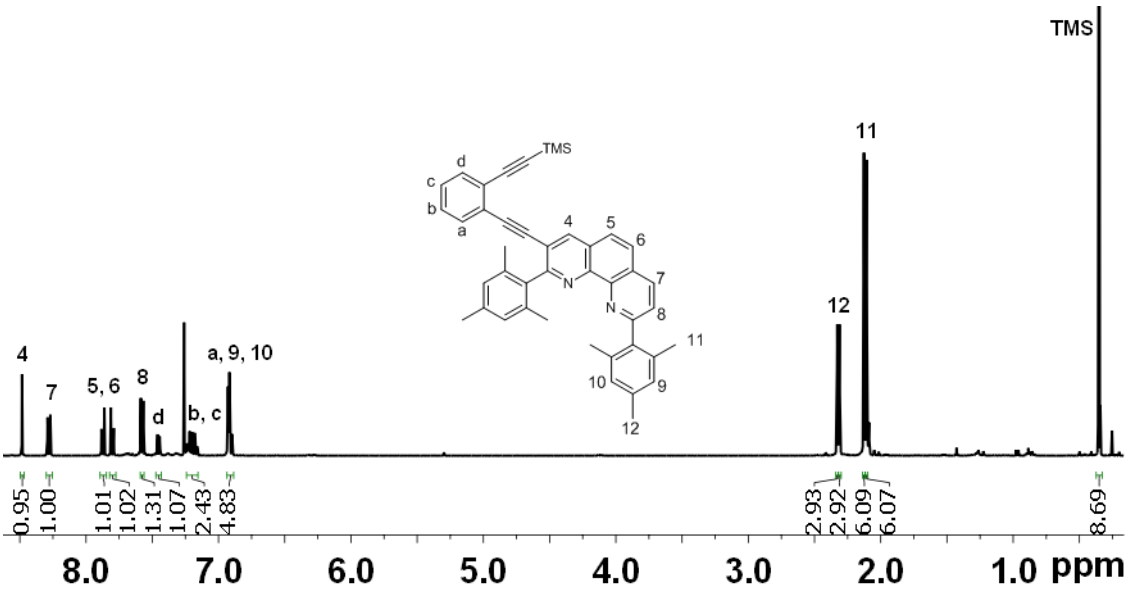


Figure S5: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **8.**

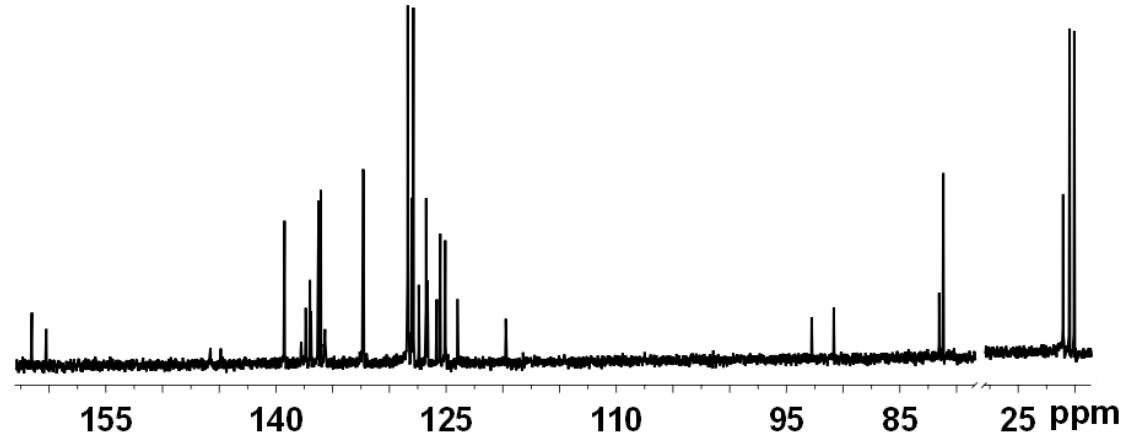


Figure S6: ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of compound **8.**

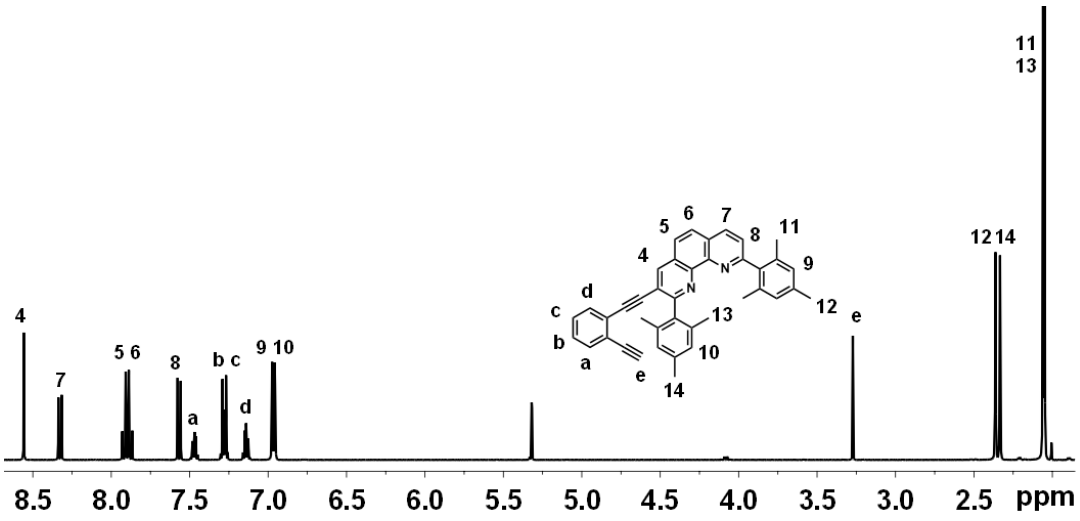


Figure S7: ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) of compound **9.**

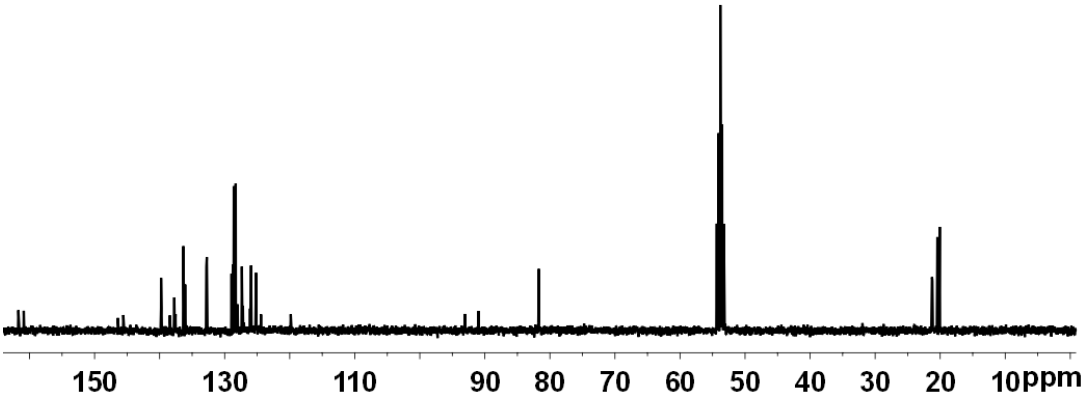


Figure S8: ^{13}C NMR spectrum (100 MHz, $CDCl_3$, 298 K) of compound **9**.

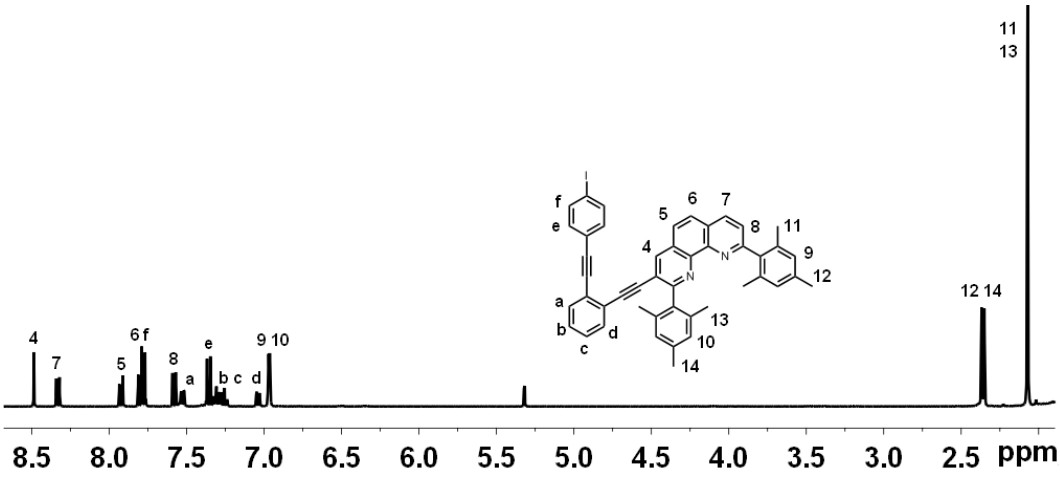


Figure S9: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of compound **10**.

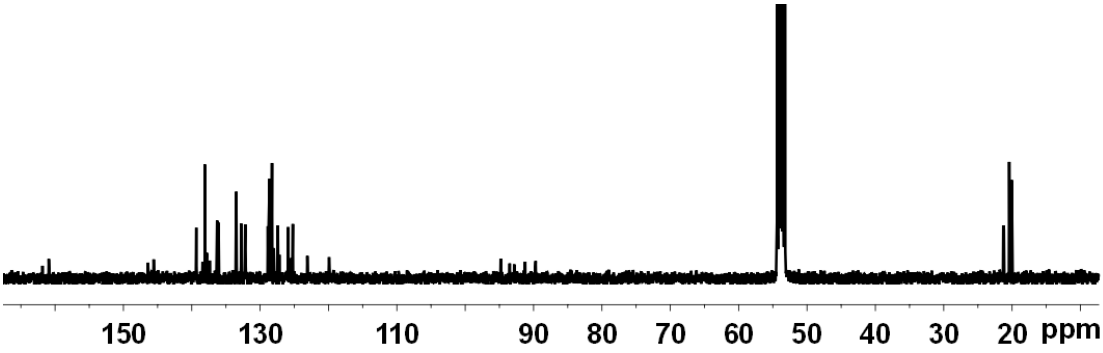


Figure S 10: ^{13}C NMR spectrum (100 MHz, CD_2Cl_2, 298 K) of compound **10**.

NMR spectra of nanoswitch 1 and its complexes

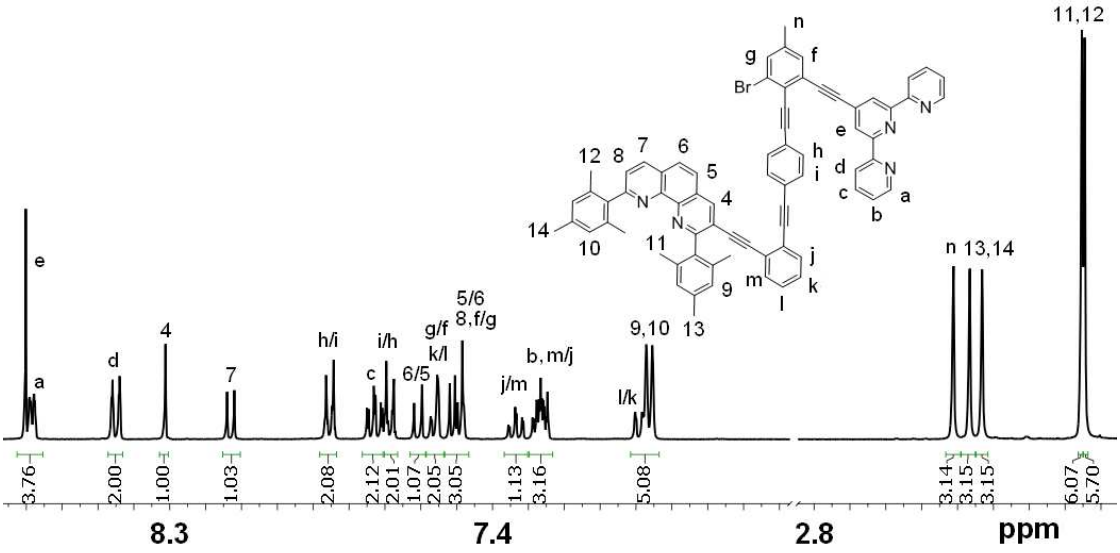


Figure S11: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of nanoswitch **1**.

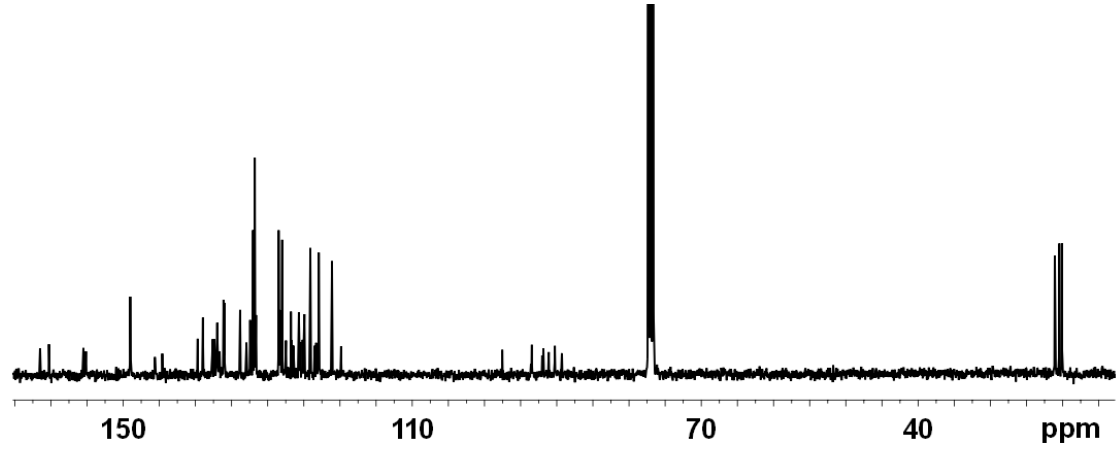


Figure S12: ^{13}C NMR spectrum (100 MHz, CD_2Cl_2, 298 K) of nanoswitch **1**.

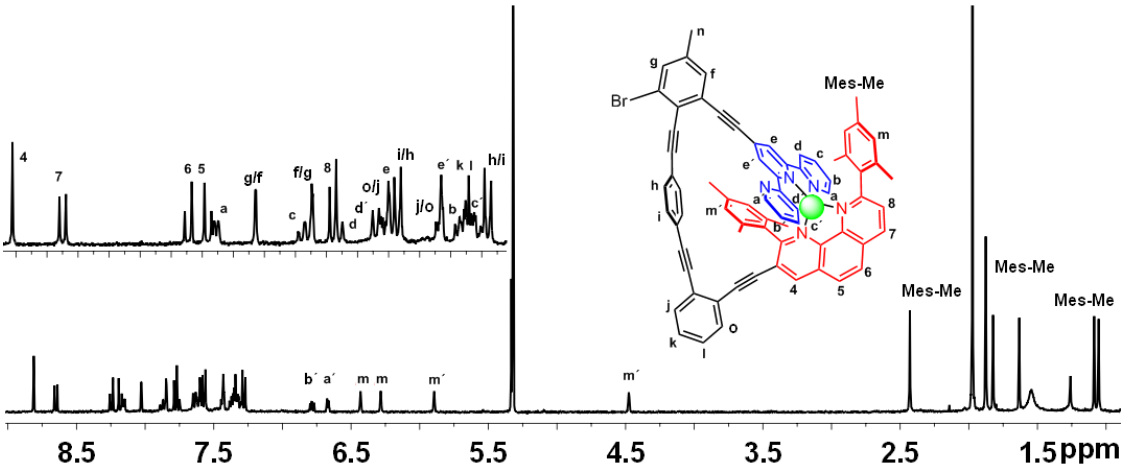


Figure S13: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of complex $[Cu(\mathbf{1})]^{+}$.

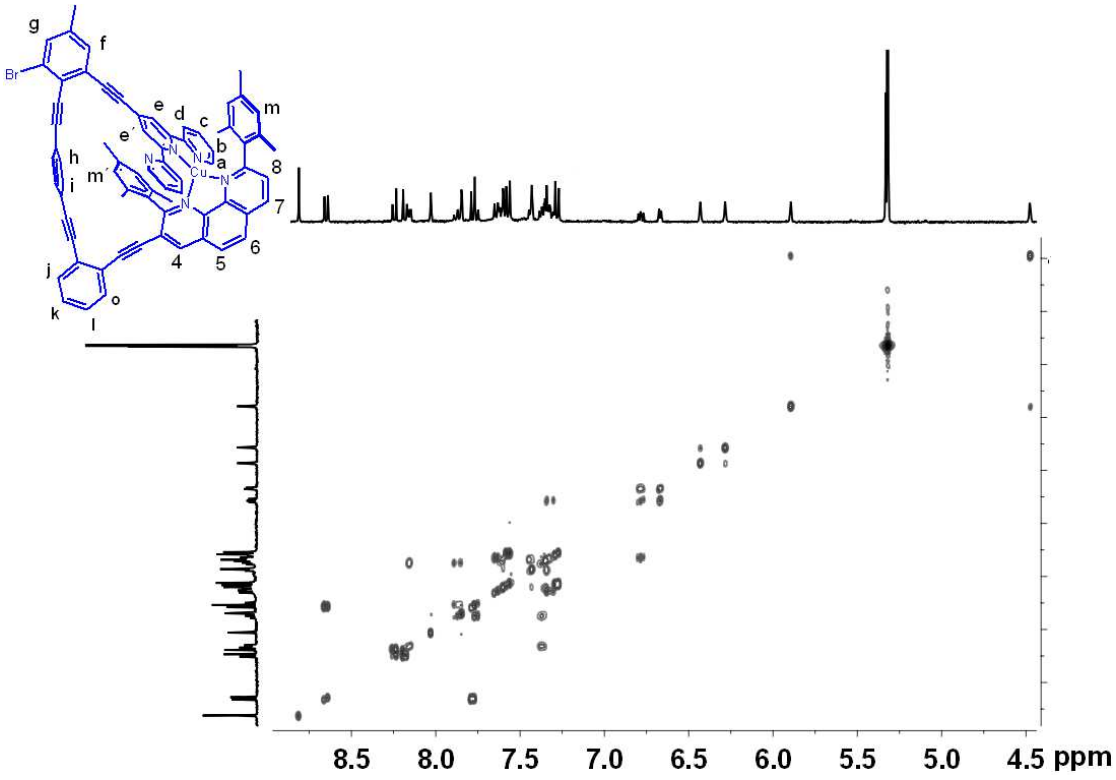


Figure S14: ^{1}H-^{1}H COSY spectrum (400 MHz, CD_2Cl_2, 298 K) of complex [Cu(**1**)]$^{+}$.

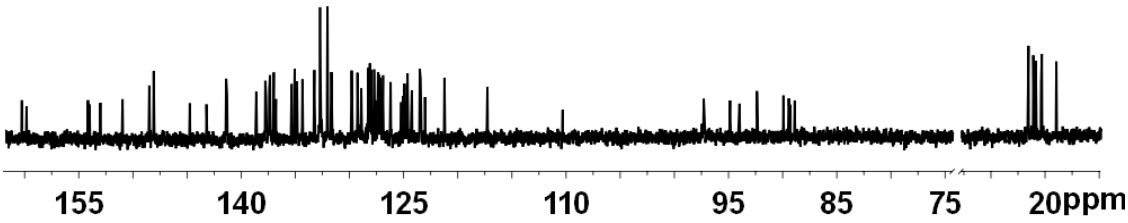


Figure S15: ^{13}C NMR spectrum (100 MHz, CD_2Cl_2, 298 K) of complex [Cu(**1**)]$^{+}$.

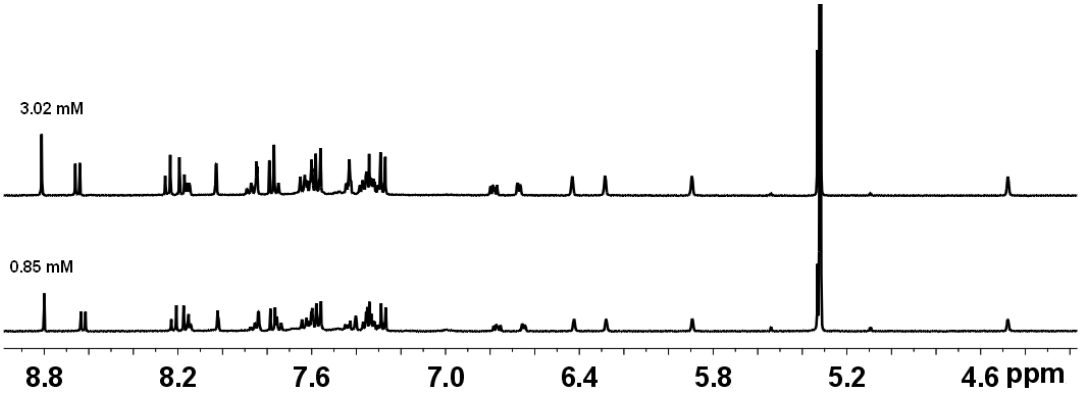


Figure S16: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of complex [Cu(**1**)]$^{+}$ at two different concentrations.

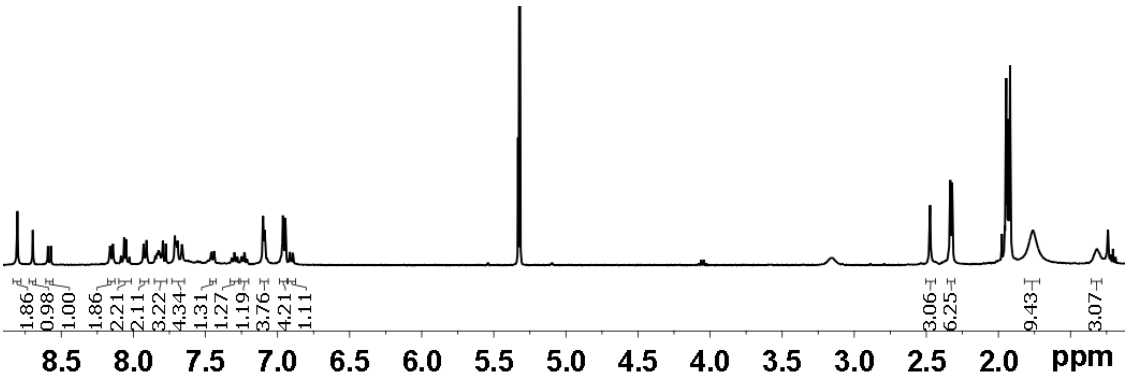


Figure S17: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2: CD_3CN = 3: 1, 298 K) of complex $[Fe(Cu(\mathbf{1}))_2]^{4+}$.

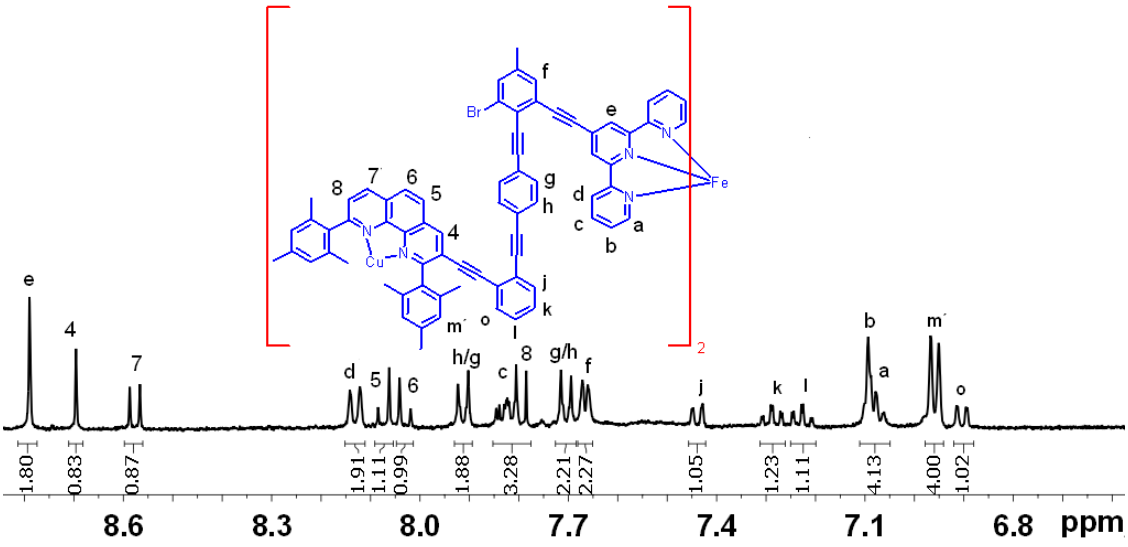


Figure S18: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2: CD_3CN = 3: 1, 298 K) of complex $[Fe(Cu(\mathbf{1}))_2]^{4+}$. Aromatic region is expanded.

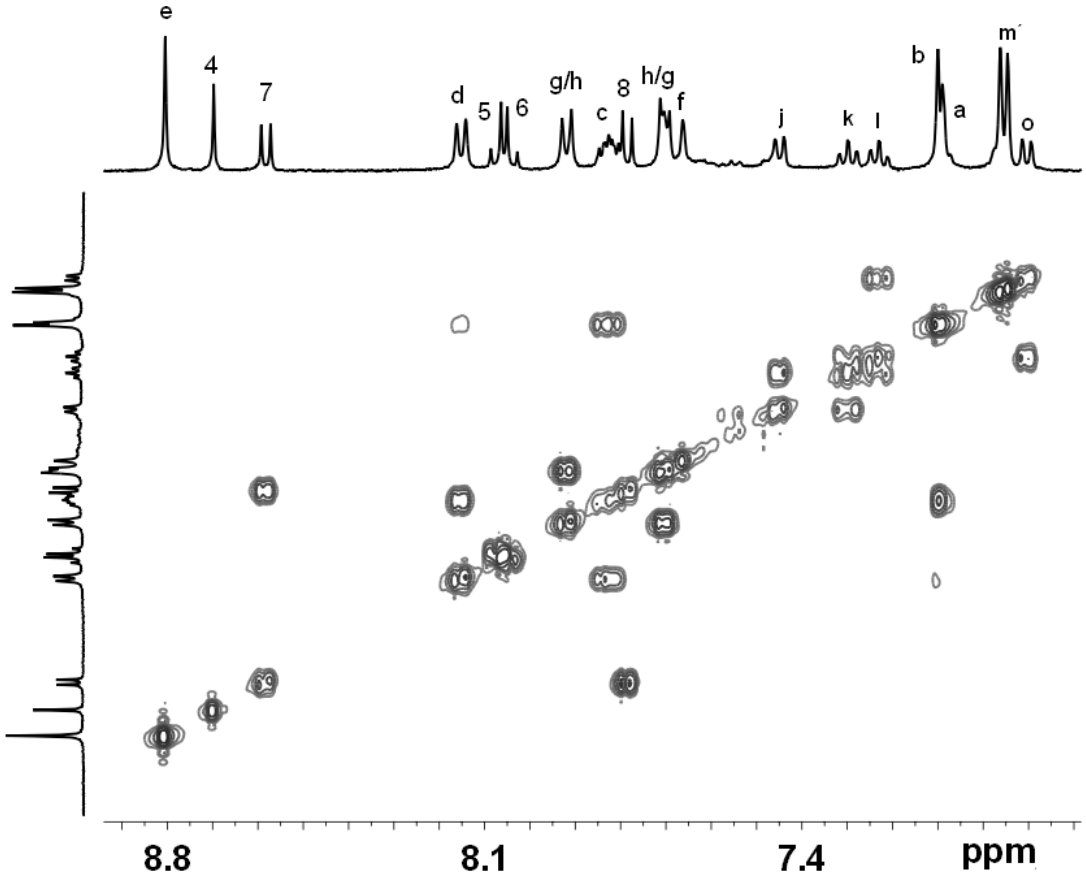


Figure S19: ^{1}H-^{1}H COSY spectrum (400 MHz, CD_2Cl_2: CD_3CN = 3: 1, 298 K) of complex $[Fe(Cu(\mathbf{1}))_2]^{4+}$. Aromatic region is expanded.

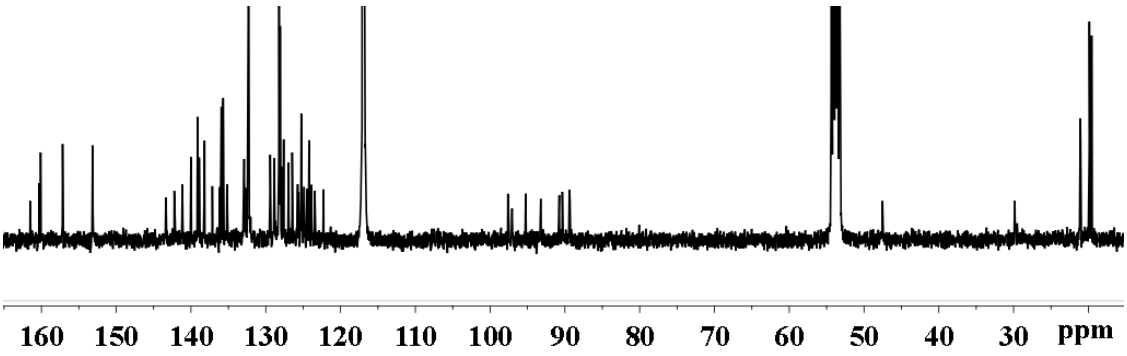


Figure S20: ^{13}C NMR spectrum (100 MHz, CD_2Cl_2: CD_3CN = 3: 1, 298 K) of complex $[Fe(Cu(\mathbf{1}))_2]^{4+}$.

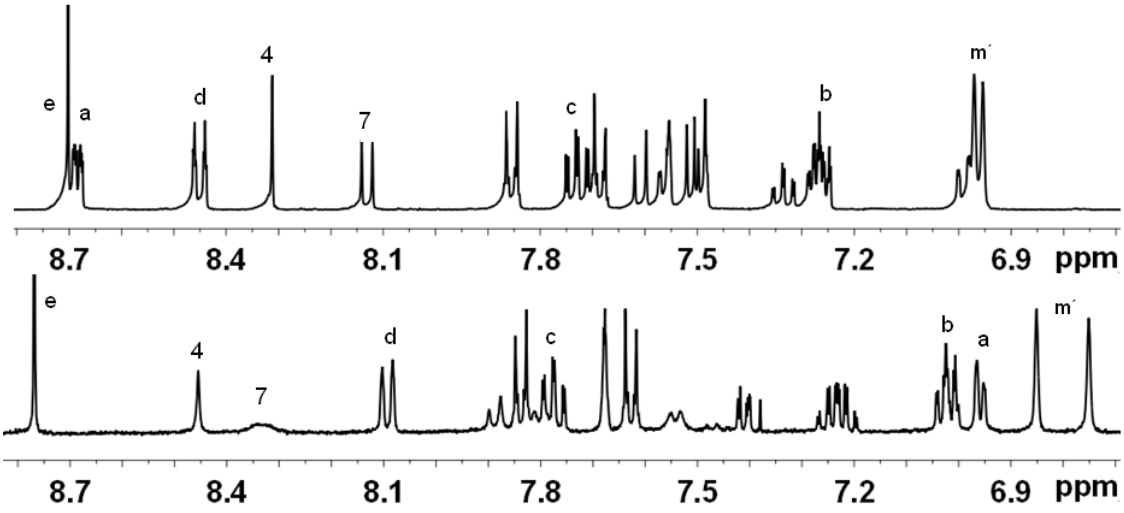


Figure S21: Partial ^{1}H NMR spectrum (400 MHz, 298 K) of (top) nanoswitch **1** in CD_2Cl_2, (bottom) after addition of 0.5 equiv. of Fe^{2+} to nanoswitch **1** in CD_2Cl_2: CD_3CN = 3: 1 (v/v). The upfield shifts of protons a-, b-, d-H and downfield shifts of c-, e-H are indicative of the formation of $[Fe(\mathbf{1})_2]^{2+}$.

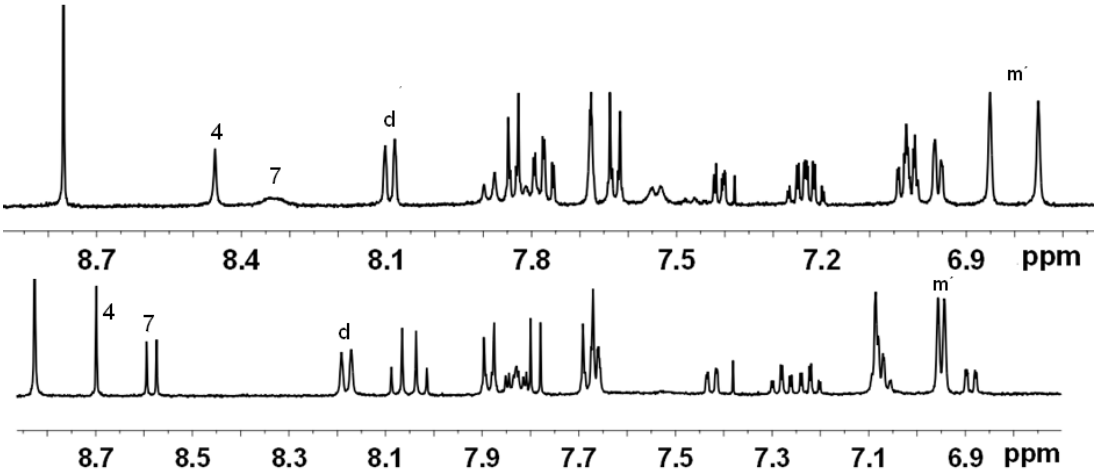


Figure S22: Partial ^{1}H NMR spectrum (400 MHz, CD_2Cl_2: CD_3CN = 3: 1, 298 K) of (top) $[Fe(\mathbf{1})_2]^{2+}$, (bottom) after addition of 2.0 equiv. of Cu^{+} to $[Fe(\mathbf{1})_2]^{2+}$. The downfield shifts of protons 4-, 7- and m'-H of the phenanthroline ligand suggest the formation of $[Fe(Cu(\mathbf{1}))_2]^{4+}$, where Cu^{+} occupies the phenanthroline cavity and Fe^{2+} is octahedrally coordinated by two terpyridines.

NMR spectra of model complexes

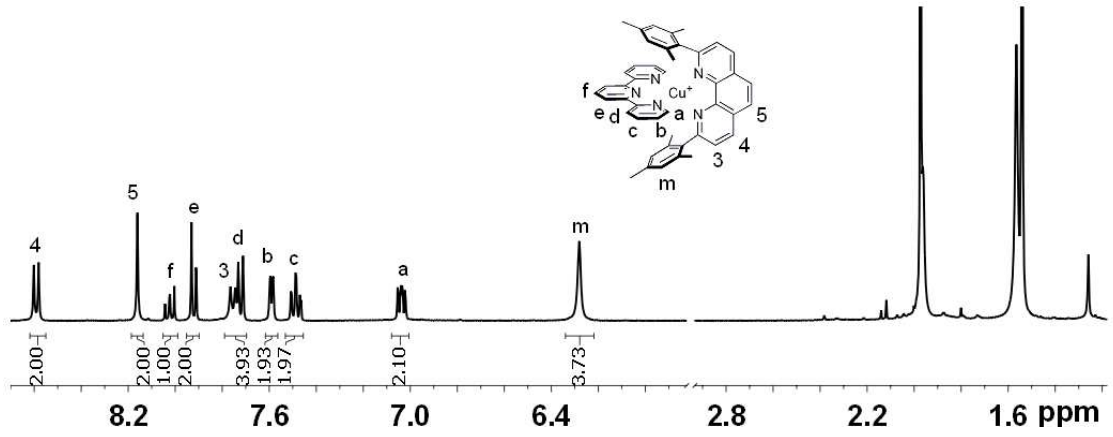


Figure S23: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of complex [Cu(**2**)(**3**)]$^{+}$.

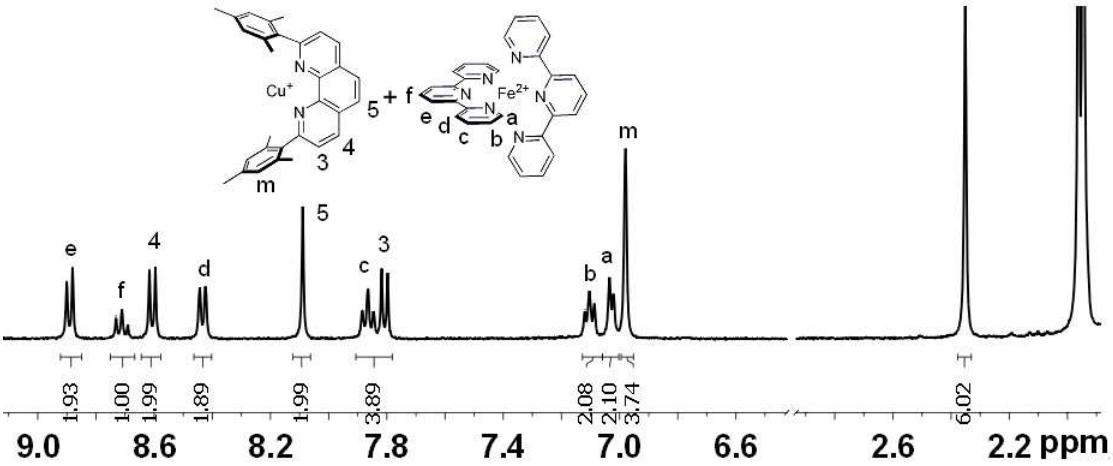


Figure S24: ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) obtained after adding 0.5 equiv. of Fe^{2+} to [Cu(**2**)(**3**)]$^{+}$. The spectrum indicates presence of [Cu(**2**)]$^{+}$ and [Fe(**3**)$_2$]$^{2+}$.

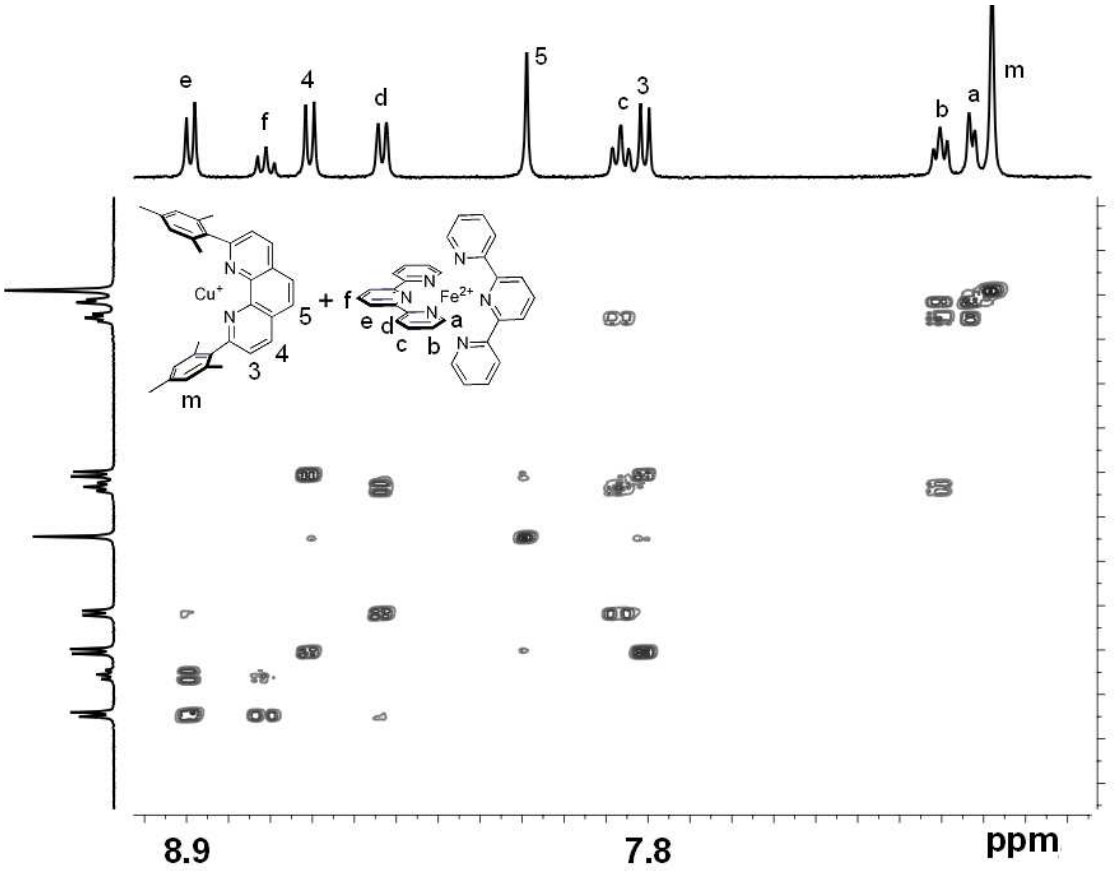


Figure S 25: ^{1}H-^{1}H COSY spectrum (400 MHz, CD_2Cl_2, 298 K) of compounds $[Cu(\mathbf{2})]^{+}$ and $[Fe(\mathbf{3})_2]^{2+}$.

ESI-MS data

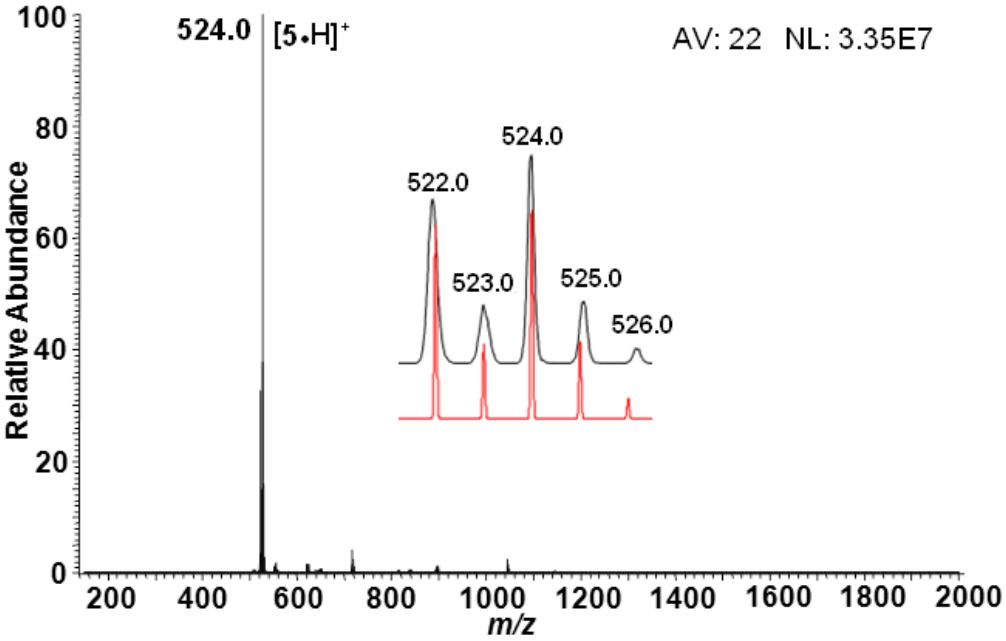


Figure S26: ESI-MS of compound **5** in CH_2Cl_2 at 298K**.**

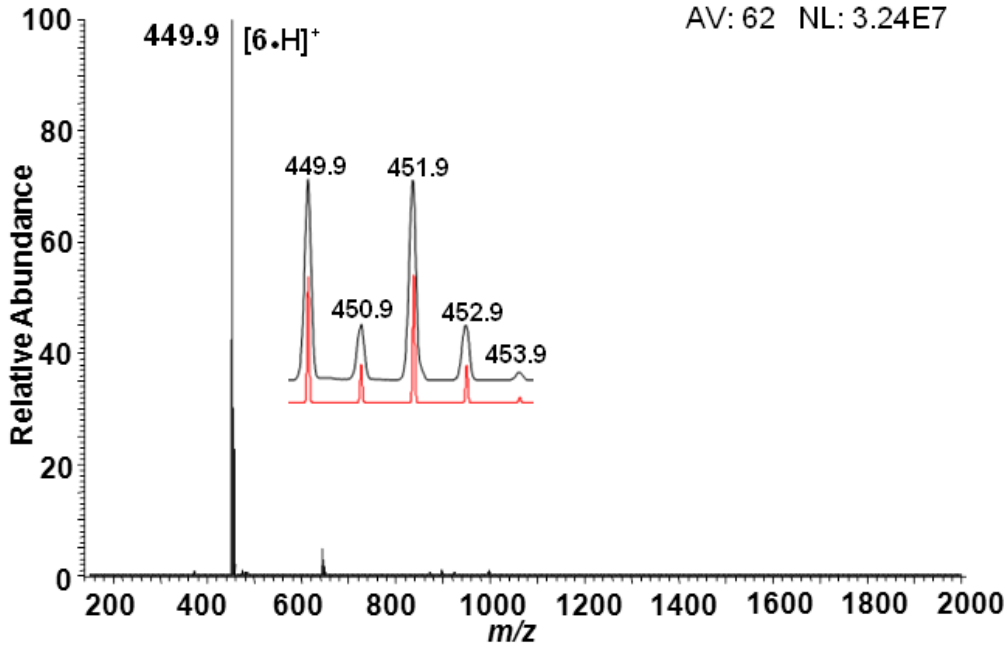


Figure S27: ESI-MS of compound **6** in CH_2Cl_2 at 298K**.**

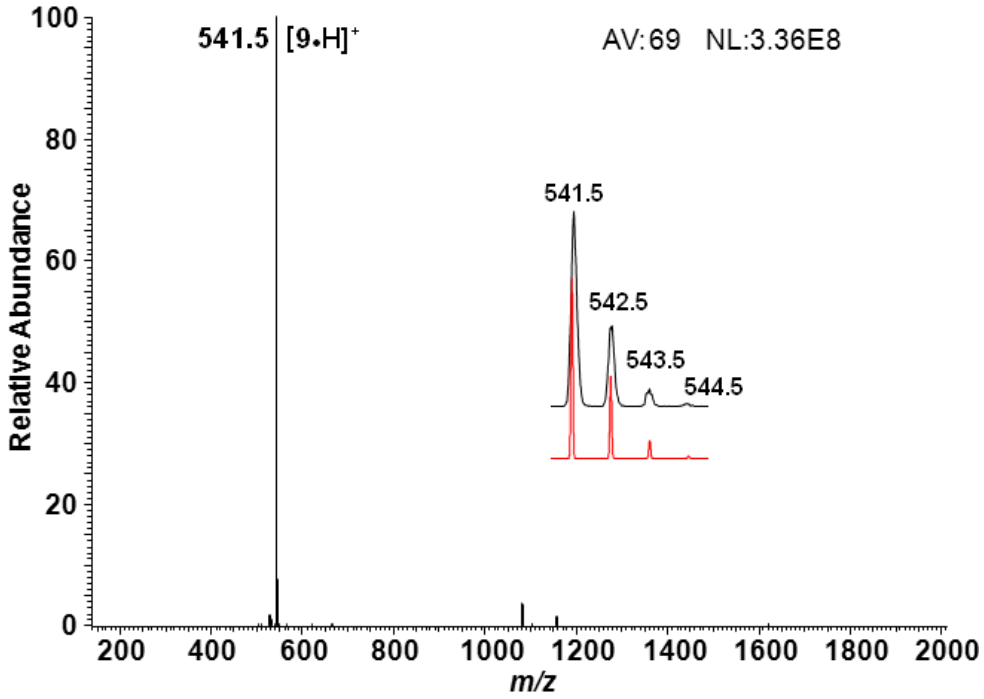


Figure S28: ESI-MS of compound **9** in CH_2Cl_2 at 298K**.**

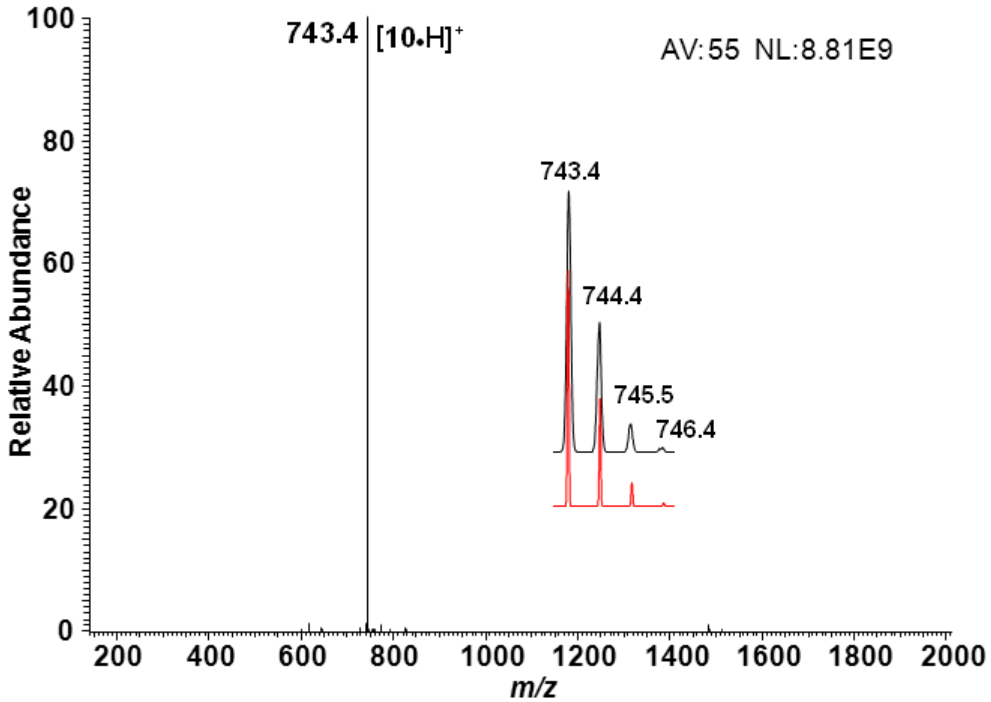


Figure S 29: ESI-MS of compound **10** in CH_2Cl_2 at 298K**.**

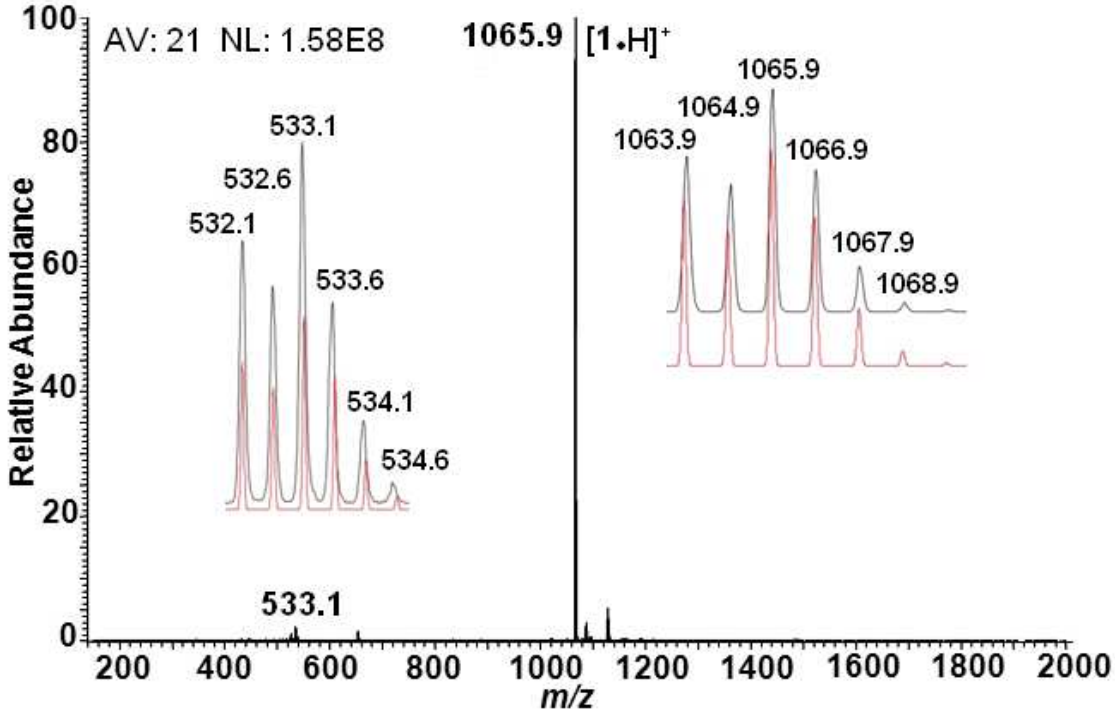


Figure S30: ESI-MS spectrum of nanoswitch [**1**•H]$^+$ in DCM.

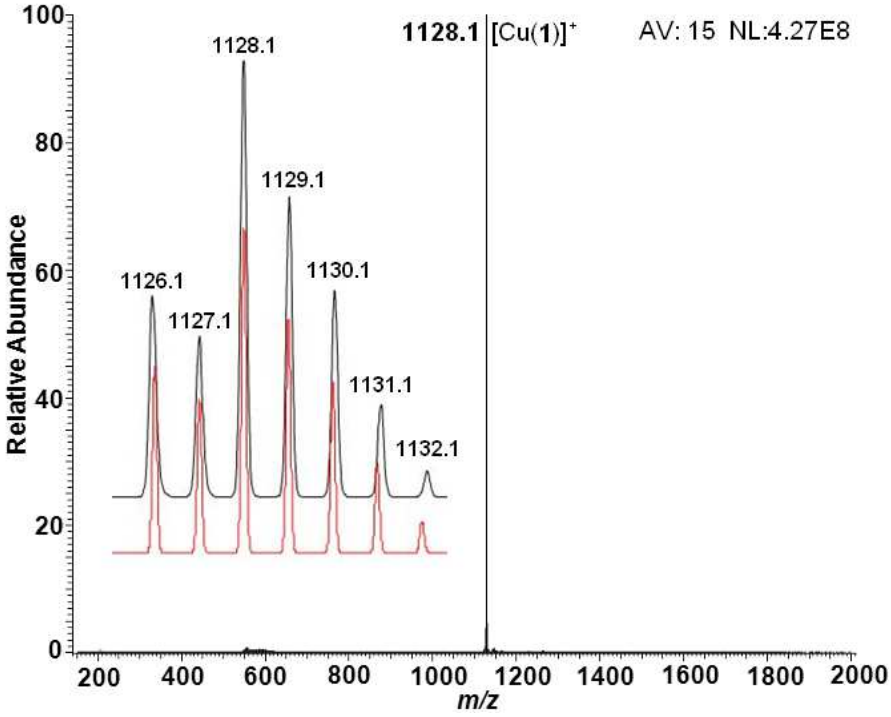


Figure S31: ESI-MS spectrum of complex [Cu(**1**)]$^+$ in DCM.

Reversible switching

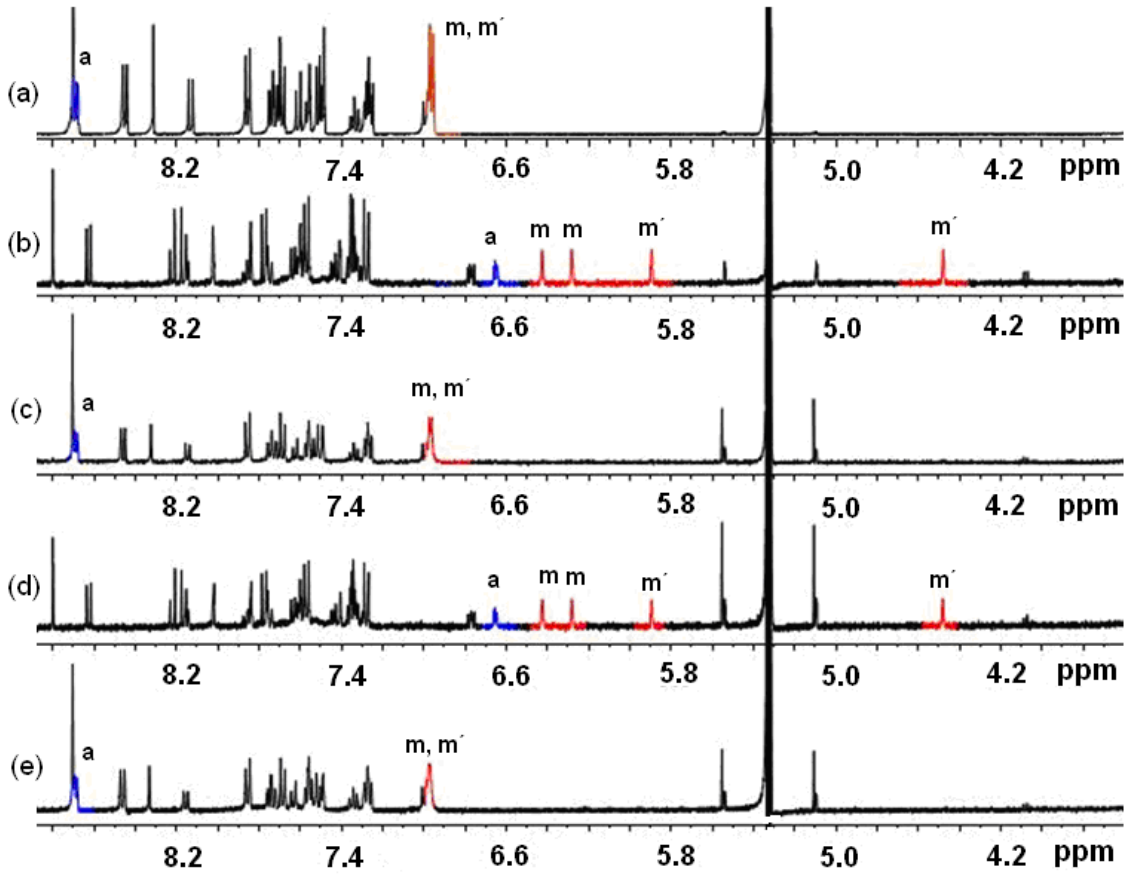


Figure S32: Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) demonstrating reversible toggling between open and closed form of nanoswitch **1** over 2 cycles. The different NMR traces represent: (a) free ligand **1**; (b) **1** after adding 1 equiv. of $[Cu(CH_3CN)_4]PF_6$ furnishing $[Cu(\mathbf{1})]^{+}$; (c) NMR after addition of 1 equiv. of cyclam to (b); (d) NMR after adding 1 equiv. of $[Cu(CH_3CN)_4]PF_6$ to (c); (e) NMR after addition of 1 equiv. of cyclam to (d).

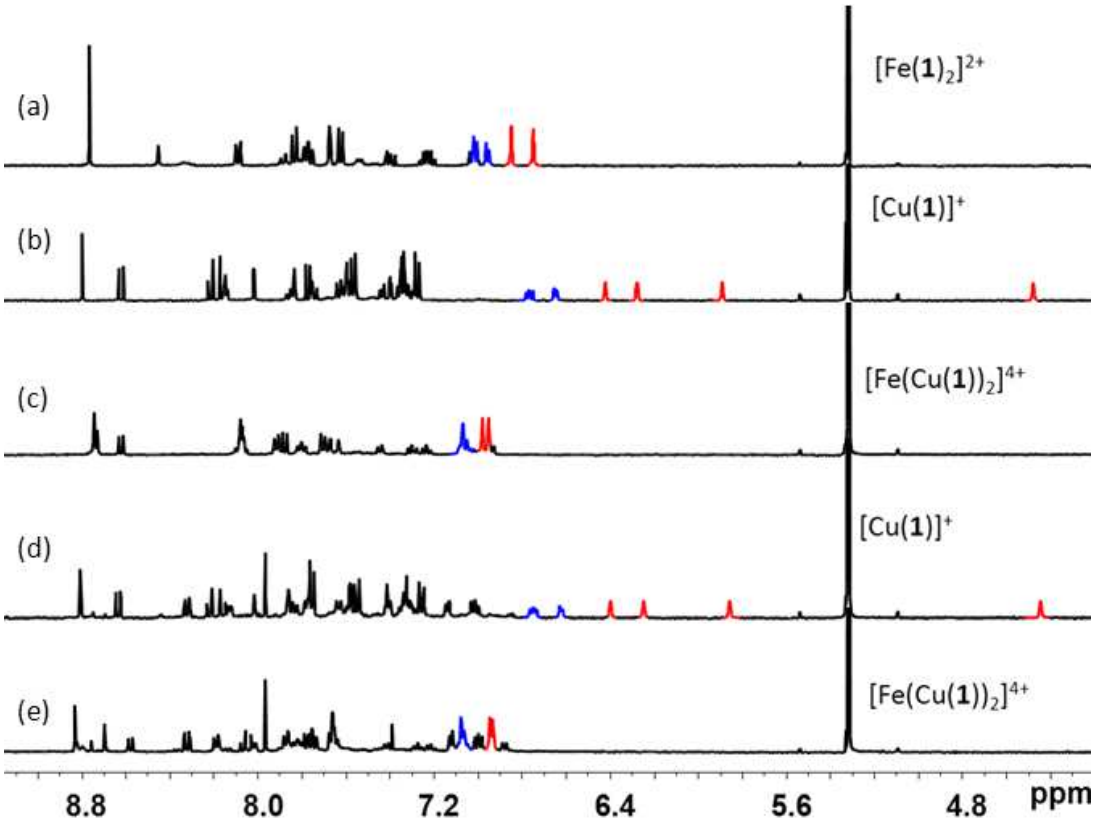
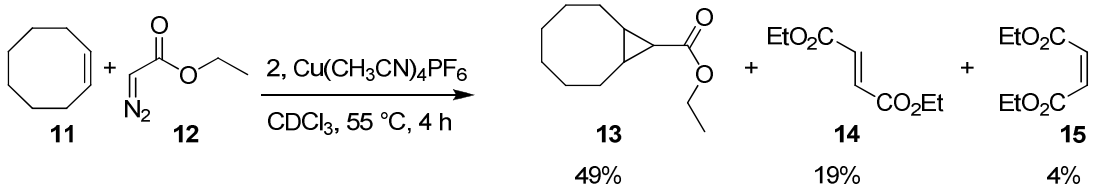


Figure S33: Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) showing the reversible switching between monomer and dimer over 2 cycles. The different NMR traces represent: (a) $[Fe(\mathbf{1})_2]^{2+}$; (b) $[Cu(\mathbf{1})]^{+}$ (c) after adding 0.5 equiv. of $Fe(ClO_4)_2$ to (b) affording $[Fe(Cu(\mathbf{1}))_2]^{4+}$; (d) NMR after addition of 2 equiv. of 4-*N*,*N*-dimethylaminoterpyridine to (c) furnishing $[Cu(\mathbf{1})]^{+}$ and $[Fe(4\text{-}N,N\text{-dimethylaminoterpyridine})_2]^{2+}$; (e) NMR after adding 0.5 equiv. of $Fe(ClO_4)_2$ to (d).

Model catalysis



Catalytic cyclopropanation reactions were performed at a 10 mM scale. A mixture of *Z*-cyclooctene, ethyl diazoacetate and $[Cu(CH_3CN)_4]PF_6$ were heated at 55 °C (± 0.1) for 4 h in an NMR tube in a HAAKE-N2 thermostat. The literature known addition adducts **13**, **14** and **15** were characterised by ^{1}H NMR. The above reaction was also carried out by heating an equimolar mixture of of *Z*-cyclooctene and ethyl diazoacetate in presence of 10 mol% of $[Cu(\mathbf{2})]PF_6$ to mimic the situation in $[Fe(Cu(\mathbf{1}))_2)]^{4+}$.

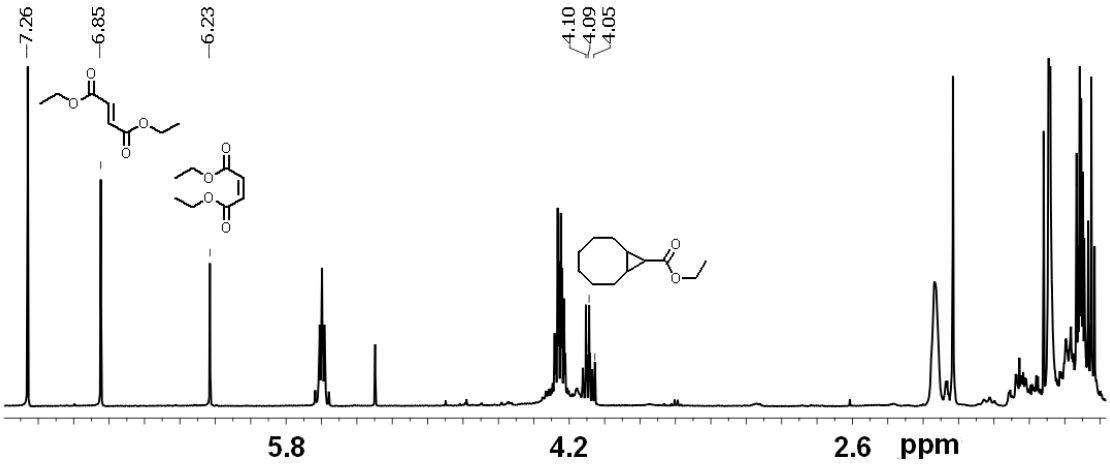


Figure S34: Model catalytic reaction between **11** and **12** in presence of 10 mol% of $[Cu(CH_3CN)_4]PF_6$ at 55 °C for 4 h in $CDCl_3$.

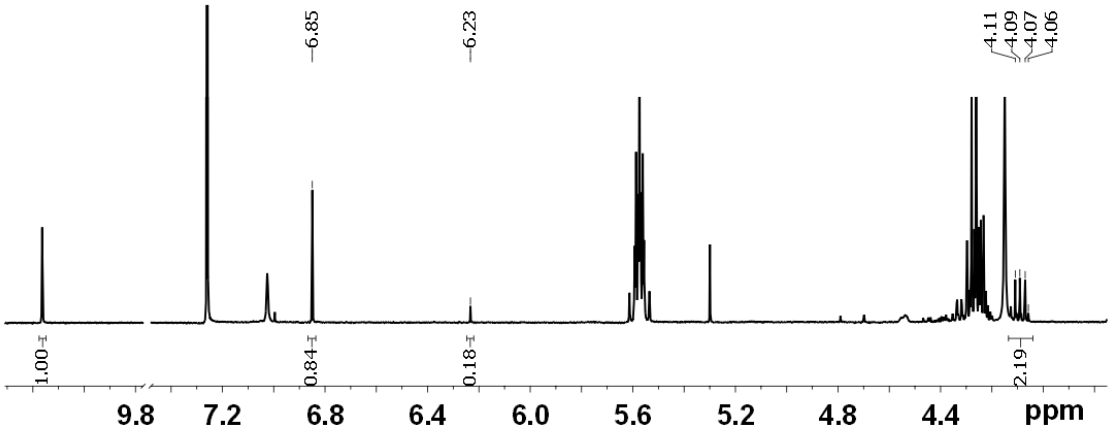


Figure S35: ^{1}H NMR obtained after heating a mixture of **11** and **12** at 55 °C for 4 h in presence of 10 mol% of [Cu(**2**)]$^{+}$ (≈ 1 mM). The peaks at 4.06-4.11 ppm show the formation of cyclopropanated product **13** and the peaks at 6.23 and 6.85 ppm represent **14** and **15** respectively. The cyclopropanated product **13** was obtained in 49% yield along with 19% of **14** and 4% of **15**.

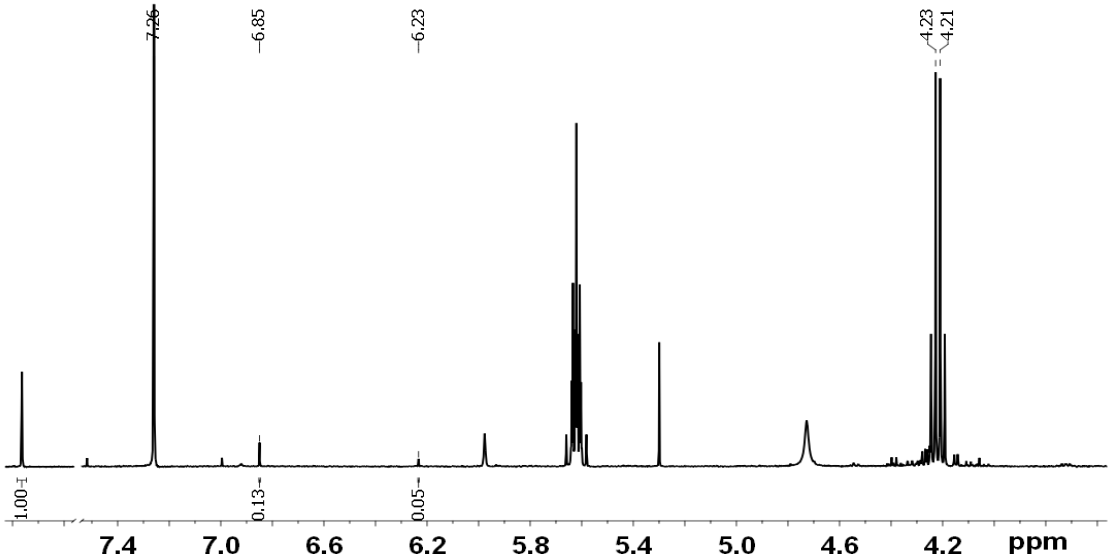
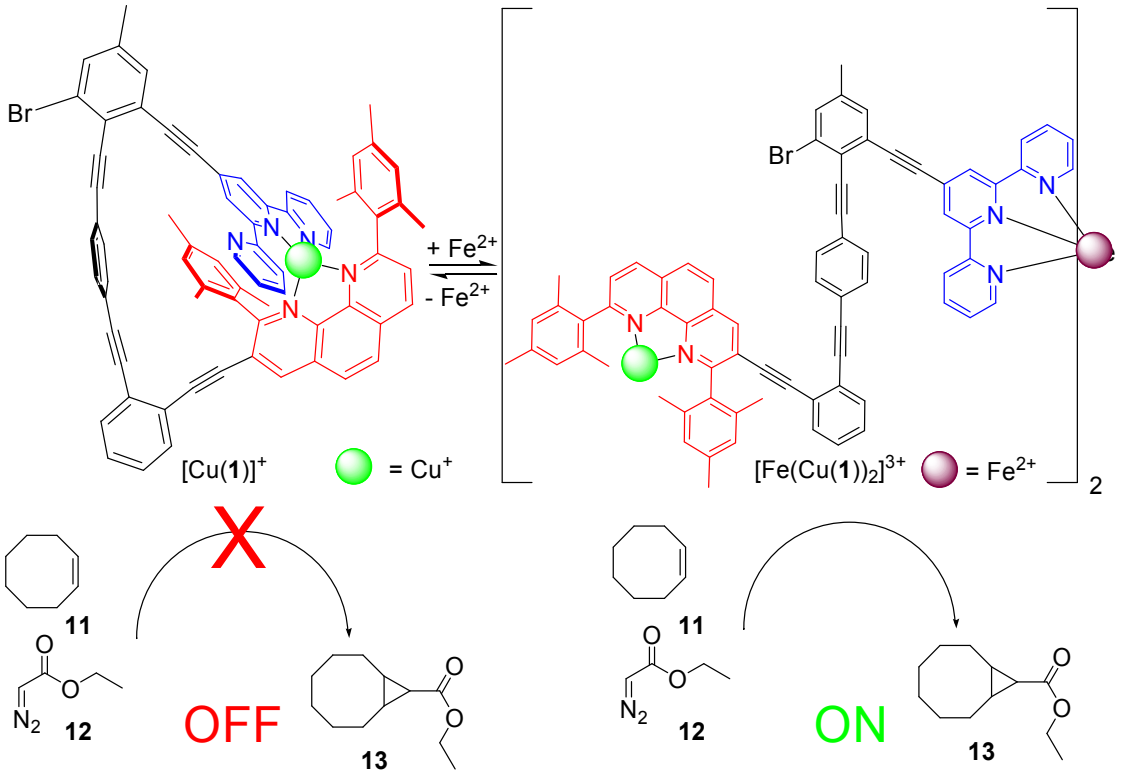


Figure S36: ^{1}H NMR obtained after heating a mixture of **11** and **12** at 55 °C for 4 h in presence of 10 mol% of [Cu(**2**)(phen)]$^{+}$ (≈ 1 mM). The peaks at 6.23 and 6.85 ppm indicate formation of **14** and **15**, respectively, whereas the absence of peaks at 4.06-4.11 ppm demonstrate that the HETPHEN complex [Cu(**2**)([1,10]phenanthroline)]$^{+}$ is unable to carry out the cyclopropanation. No cyclopropane **13** was formed, but **14** and **15** were formed in 3% and 1% yield, respectively.

Catalyis experiments with the nanoswitch

The catalytic reaction with the nanoswitch was probed at a similar scale using the same conditions as described above for the model compounds. Equivalent amounts of *Z*-cyclo-octene (677 µmg, 6,14 µmol) and ethyl diazoacetate (701 µmg, 6.14 µmol) were mixed with 10 mol% of nanoswitch **1** (654 µmg, 0.614 µmol) and $[Cu(CH_3CN)_4]PF_6$ (229 µmg, 0.614 µmol). With the closed form of the nanoswitch, *i.e.* $[Cu(\mathbf{1})]PF_6$, no cyclopropane **13** was formed in detectable amount. However, upon addition of 0.5 equivalent of $Fe(ClO_4)_2$ (111 µmg, 0.306 µmol) with respect to nanoswitch **1**, the dimeric form $[Fe(Cu(\mathbf{1}))_2]^{4+}$ is generated. In this case, Cu^+ is accessible to the reagent, and after heating the mixture for 4 h at 55 °C the cyclopropanated product **13** was observed.



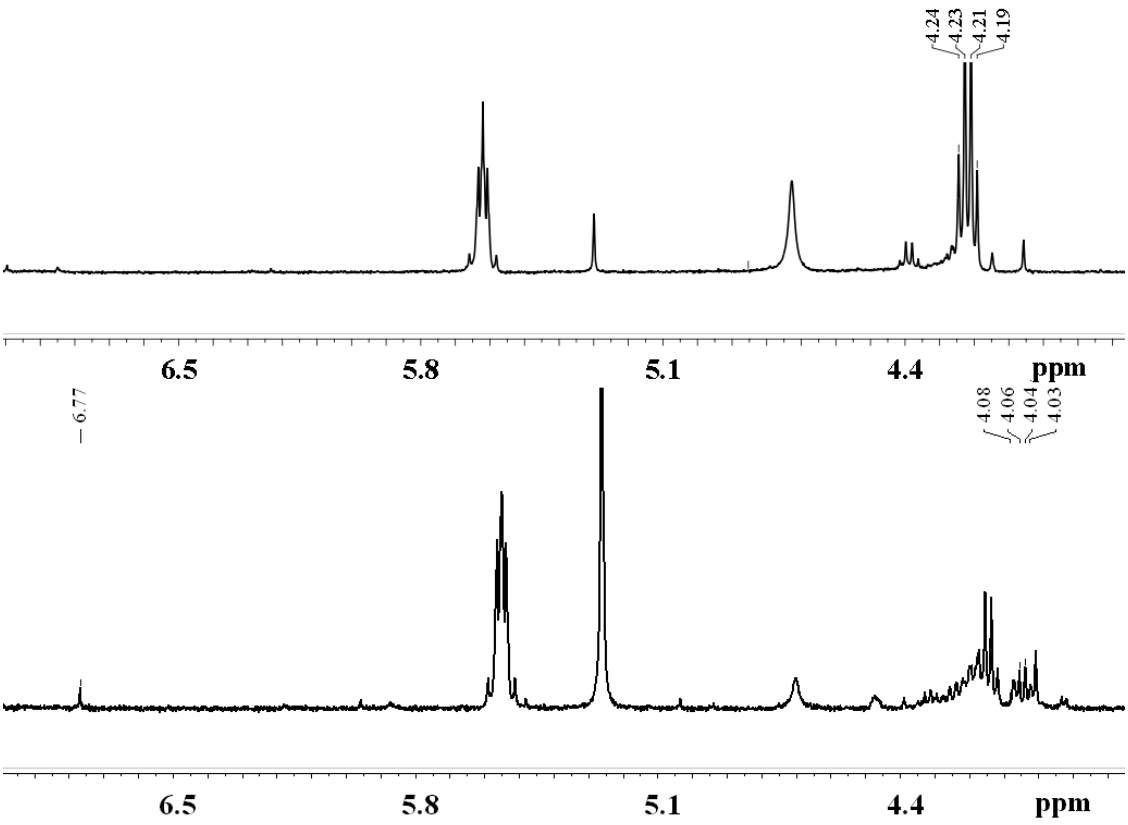


Figure S37: ^{1}H NMR obtained after heating a mixture of **11** and **12** at 55 °C for 4 h (top) in presence of 10 mol% of $[Cu(\mathbf{1})]^{+}$ (≈ 1 mM) and (bottom) after addition of 0.5 equivalent of Fe^{2+} to the above solution to generate dimer $[Fe(Cu(\mathbf{1}))_2]^{4+}$. The absence of peaks at 4.03-4.08 ppm in the top spectrum indicates that cyclopropanated product **13** is not formed, whereas the appearance of peaks at 4.03-4.08 ppm in the bottom spectrum signifies that $[Fe(Cu(\mathbf{1}))_2]^{4+}$ with its opened copper sites is able to carry out the cyclopropanation reaction in 35% yield.

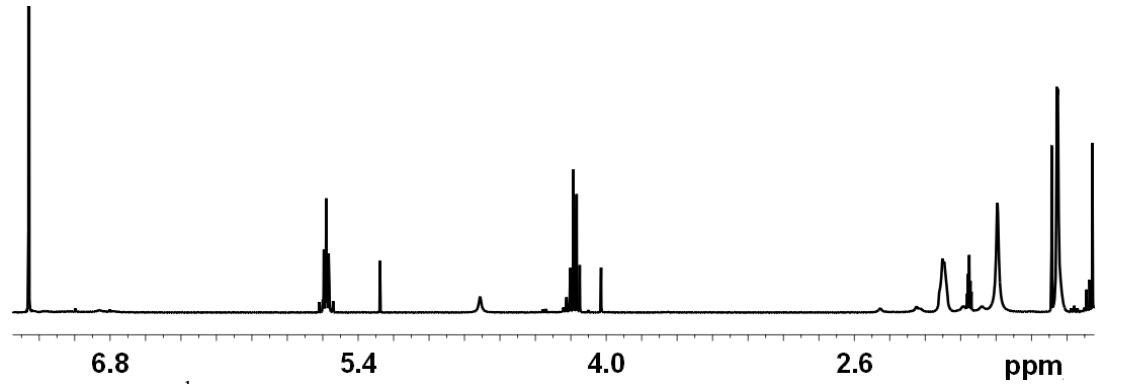


Figure S 38: ^{1}H NMR received after the thermolysis (55 °C for 4 h) of **11** and **12** had been performed in presence of $[Fe(\mathbf{1})_2]^{2+}$. No product was formed as indicated from the spectrum.