Electronic Supplementary Information (ESI)

High-speed network of nanoswitches for on/off control of catalysis

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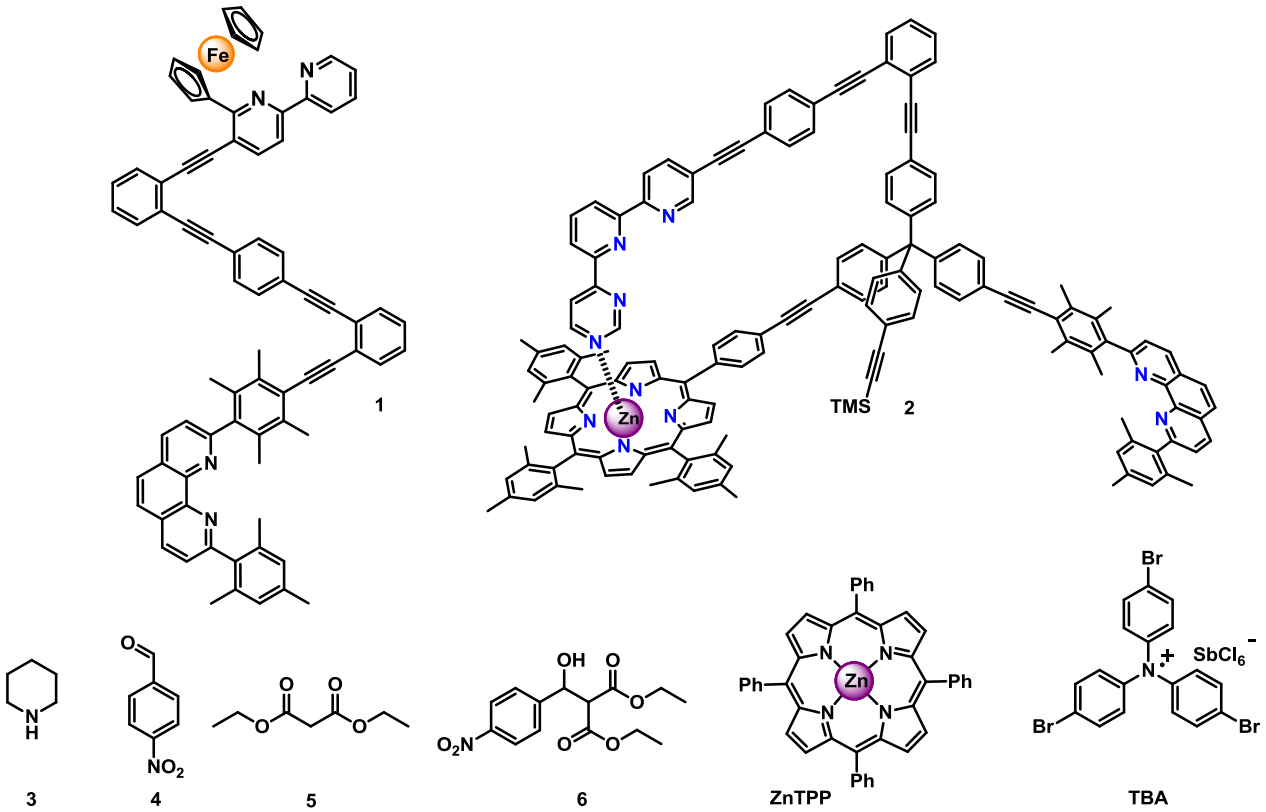
1. Synthesis

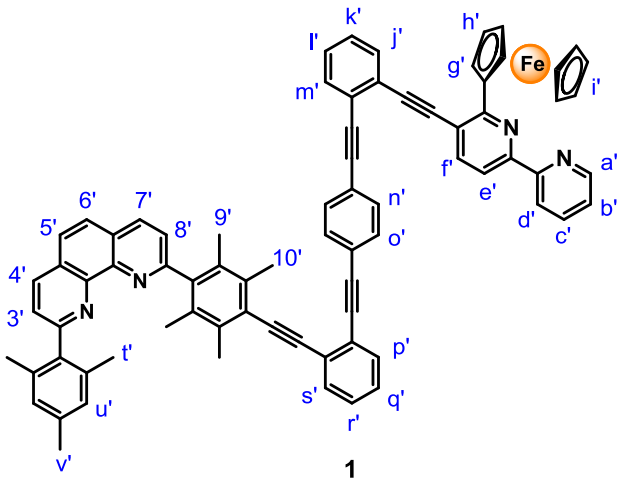
1a) General information

All reagents were obtained from commercial suppliers and were used without further purification. All technical grade solvents were distilled prior to use. UV-vis spectra were measured on a Cary 50. NMR spectra were recorded on either Bruker Avance 400 MHz or Varian NMR-S 600 MHz spectrometers using deuterated solvents as the lock. The chemical shifts refer to the residual protiated fraction of the solvent ($CHCl_3$: δ_H = 7.26 ppm, $CHDCl_2$: δ_H = 5.32 ppm). The following abbreviations were used in ^1H NMR assignments to describe splitting patterns: (s: singlet, d: doublet, t: triplet, dd: doublet of doublets, ddd: doublet of doublets of doublets, bs: broad singlet, td: triplet of doublets, m: multiplet), the value of coupling constant(s) in Hertz (Hz), the number of protons implied, and the assignments of protons wherever possible. The numbering of carbon atoms shown in the experimental section are only used for the assignments and are not in accordance with IUPAC nomenclature rules. Electrospray ionization mass spectra (ESI-MS) were measured on a Thermo-Quest LCQ DECA.



1b). Characterization of ligands and metal complexes

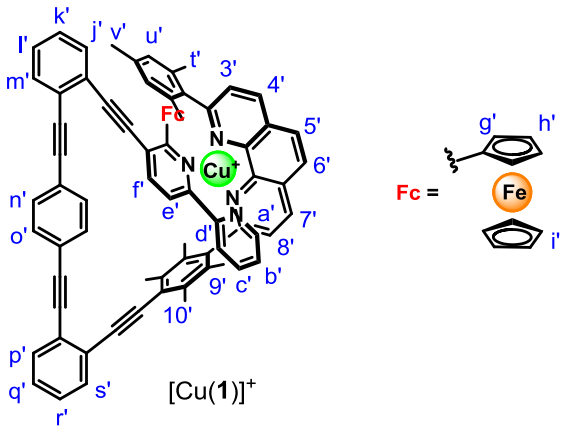
Characterization data of nanoswitch **1**[1]



1

^{1}H NMR (CD_2Cl_2, 400 MHz, 298 K): δ = 8.68 (ddd, ^3J = 4.8 Hz, ^4J = 1.2 Hz, ^5J = 1.2 Hz, 1H, a′-H), 8.54 (dt, ^3J = 8.0 Hz, ^4J = 1.2 Hz, ^5J = 1.2 Hz, 1H, d′-H), 8.33 (d, ^3J = 8.0 Hz, 1H, 7′-H), 8.32 (d, ^3J = 8.0 Hz, 1H, 4′-H), 8.23 (d, ^3J = 8.4 Hz, 1H, e′-H), 7.95 (d, ^3J = 8.4 Hz, 1H, f′-H), 7.90 (s, 2H, 5′-, 6′-H), 7.78 (td, ^3J = 8.0 Hz, ^4J = 1.2 Hz, 1H, c′-H), 7.70–7.72 (m, 1H, s′-H), 7.61–7.67 (m, 3H, j′-, m′-, p′-H), 7.56 (d, ^3J = 8.0 Hz, 1H, 8′-H), 7.54 (s, 4H, n′-, o′-H), 7.52 (d, ^3J = 8.0 Hz, 1H, 3′-H), 7.40–7.46 (m, 2H, q′-, r′-H), 7.33–7.39 (m, 2H, k′-, l′-H), 7.21 (ddd, ^3J = 8.0 Hz, ^3J = 4.8 Hz, ^4J = 1.2 Hz, 1H, b′-H), 6.95 (s, 2H, u′-H), 5.57 (t, ^3J = 2.0 Hz, 2H, g′-H), 4.32 (t, ^3J = 2.0 Hz, 2H, h′-H), 4.06 (s, 5H, i′-H), 2.56 (s, 6H, 9′-H), 2.32 (s, 3H, v′-H), 2.03 (s, 6H, t′-H), 1.91 (s, 6H, 10′-H) ppm. **ESI-MS:** Calcd. for $[C_{77}H_{56}FeN_4•H]^+$ = [**1**•H]$^+$, *m/z* = 1093.4; Found: [**1**•H]$^+$, *m/z* (%) = 1093.3 (100).

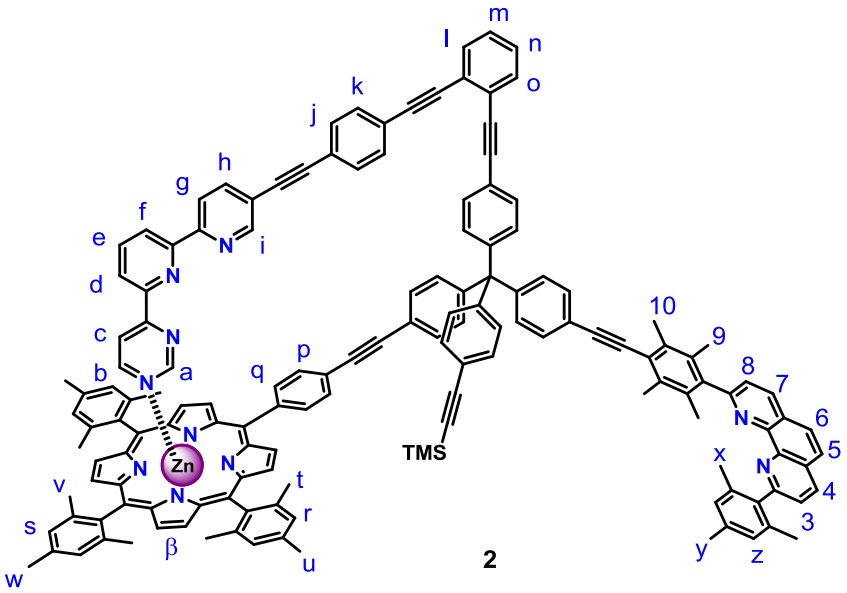
Synthesis of $[Cu(\mathbf{1})]^+$ complex[1]



To a mixture of $[Cu(CH_3CN)_4]B(C_6F_5)_4$ (362.0 µg, 0.399 µmol) and nanoswitch **1** (436 µg, 0.399 µmol) in an NMR tube was added CD_2Cl_2. The sample was analyzed without any purification. **Yield:** Quantitative (by NMR).

^{1}H NMR (CD_2Cl_2, 400 MHz, 298 K): δ = 8.65 (d, ^3J = 8.0 Hz, 1H, 7′/4′-H), 8.63 (d, ^3J = 8.0 Hz, 1H, 4′/7′-H), 8.19 (s, 2H, 5′-, 6′-H), 8.02 (dd, ^3J = 4.6 Hz, ^4J = 1.2 Hz, 1H, a′-H), 7.80 (td, ^3J = 8.0 Hz, ^4J = 1.2 Hz, 1H, c′-H), 7.77 (2 d, ^3J = 8.4 Hz, 2H, 8′-, 3′-H), 7.66–7.71 (m, 3H, d′-, p′-, s′-H), 7.60–7.64 (m, 3H, j′-, m′-, f′-H), 7.52 (s, 4H, n′-, o′-H), 7.46–7.49 (m, 2H, q′-, r′-H), 7.40–7.42 (m, 2H, k′-, l′-H), 7.31 (ddd, ^3J = 8.0 Hz, ^3J = 4.6 Hz, ^4J = 1.2 Hz, 1H, b′-H), 7.28 (d, ^3J = 8.4 Hz, 1H, e′-H), 6.42 (s, 1H, u′-H), 6.35 (s, 1H, u′-H), 4.92 (bs, 1H, h′-H), 4.54 (bs, 1H, h′-H), 3.88 (bs, 5H, i′-H), 3.66 (bs, 1H, g′-H), 3.31 (bs, 1H, g′-H), 2.17 (s, 3H, 10′-H), 1.98 (s, 3H, v′-H), 1.87 (s, 3H, 10′-H), 1.77 (s, 3H, t′-H), 1.72 (s, 3H, 9′-H), 1.64 (s, 3H, t′-H), 1.53 (s, 3H, 9′-H) ppm. **ESI-MS:** Calcd. for $[C_{77}H_{56}CuFeN_4]^+$ = $[Cu(\mathbf{1})]^+$, *m/z* = 1155.3; Found: $[Cu(\mathbf{1})]^+$, *m/z* (%) = 1155.6 (100).

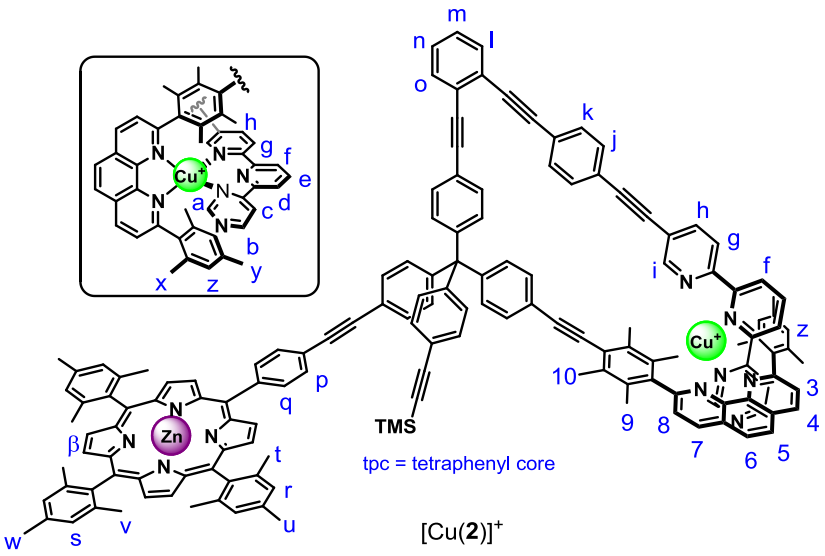
Characterization data of nanoswitch **2**[2]



^{1}H NMR[2] (CD_2Cl_2, 600 MHz, 298 K): δ = 8.85 (d, ^3J = 4.6 Hz, 2H, β-H), 8.71 (d, ^3J = 4.6 Hz, 2H, β-H), 8.68 (d, ^4J = 2.1 Hz, 1H, i-H), 8.66 (d, ^3J = 4.6 Hz, 2H, β-H), 8.64 (d, ^3J = 4.6 Hz, 2H, β-H), 8.35 (d, ^3J = 8.2 Hz, 1H, 7/4-H), 8.34 (d, ^3J = 8.2 Hz, 1H, 4/7-H), 8.26 (d, ^3J = 8.1 Hz, 2H, q-H), 8.20 (dd, ^3J = 7.8 Hz, ^3J = 7.8 Hz, 1H, e-H), 8.15 (d, ^3J = 8.0 Hz, 1H, g-H), 7.95 (d, ^3J = 8.1 Hz, 2H, p-H), 7.91 (s, 2H, 5-, 6-H), 7.87 (dd, ^3J = 8.0 Hz, ^4J = 2.1 Hz, 1H, h-H), 7.66 (d, ^3J = 8.4 Hz, 2H, j/k-H), 7.54–7.63 (m, 14H, l-, o-, 3-, 8-, d-, f-, tpc-H), 7.44 (d, ^3J = 8.4 Hz, 2H, k/j-H), 7.36–7.38 (m, 4H, m-, n-, tpc-H), 7.35 (d, ^3J = 8.6 Hz, 2H, tpc-H), 7.33 (s, 2H, s-H), 7.29 (d, ^3J = 8.6 Hz, 2H, tpc-H), 7.27 (d, ^3J = 8.6 Hz, 2H, tpc-H), 7.24 (s, 4H, r-H), 6.96 (s, 2H, z-H), 6.85 (dd, ^3J = 5.8 Hz, ^5J = 1.0 Hz, 1H, c-H), 3.76 (s, 1H, a-H), 2.73 (d, ^3J = 5.8 Hz, 1H, b-H), 2.64 (s, 3H, w-H), 2.58 (s, 6H, u-H), 2.54 (s, 6H, 9-H), 2.33 (s, 3H, y-H), 2.04 (s, 6H, x-H), 1.92 (s, 12H, v-, 10-H), 1.74 (s, 12H, t-H), 0.26 (s, 9H, TMS-H) ppm. **UV/vis:** λ_{max} = 429 nm. **ESI-MS:** Calcd. for $[C_{150}H_{116}N_{10}SiZn•2H]^{2+}$ = [**2**•2H]$^{2+}$, *m/z* = 1076.9; Found: [**2**•2H]$^{2+}$, *m/z* (%) = 1076.9 (100).

Synthesis of [Cu(**2**)]$^+$ complex[2]

CD_2Cl_2 was added to a mixture of $[Cu(CH_3CN)_4]PF_6$ (172 µg, 0.461 µmol) and nanoswitch **2** (1.01 mg, 0.461 µmol) in an NMR tube. Upon sonication for 5 min, the deep pink solution was analyzed by NMR without further purification. **Yield:** Quantitative (by NMR). Some of the signals attest the occurrence of two diastereomers (due to the stereogenic center and axis).



^{1}H NMR[2] (CD_2Cl_2, 600 MHz, 298 K): δ = 8.91 (d, ^3J = 4.6 Hz, 1H, β-H), 8.89 (d, ^3J = 4.6 Hz, 1H, β-H), 8.77 (d, ^3J = 4.6 Hz, 1H, β-H), 8.76 (d, ^3J = 4.6 Hz, 1H, β-H), 8.68–8.72 (m, 5H, 4/7-, β-H), 8.44 (d, ^3J = 8.4 Hz, 1H, 7/4-H), 8.27 (d, ^3J = 8.1 Hz, 1H, q-H), 8.24 (d, ^3J = 8.1 Hz, 1H, q-H), 8.15 (dd, ^3J = 8.8 Hz, ^4J = 1.2 Hz, 1H, h-H), 8.07–8.13 (m, 2H, d-, e-H), 8.04 (d, ^3J = 8.8 Hz, 1H, g-H), 7.92–7.98 (m, 6H, f-, p-, 5-, 6-, 3/8-H), 7.88 (s, ^4J = 1.2 Hz, 1H, i-H), 7.67–7.70 (m, 2H, 8/3-, tpc-H), 7.55–7.65 (m, 11H, tpc-, l-, o-, j/k-, c-H), 7.45–7.51 (m, 2H, tpc-H), 7.34–7.43 (m, 9H, a-, m-, n-, k/j-, tpc-H), 7.27–7.31 (m, 9H, r-, s-, tpc-H), 7.18 (d, ^3J = 4.8 Hz, ^4J = 0.8 Hz, 1H, b-H), 6.30 (2 s, 1H, z-H), 6.285 (s, 1H, z-H), 2.61–2.63 (2 s, 6H, u-H), 2.61–2.62 (2 s, 3H, w-H), 2.48 (s, 3H, 10/9-H), 2.01 (2 s, 3H, y-H), 1.92 (s, 3H, x-H), 1.90 (s, 3H, x-H), 1.84 (s, 6H, v-H), 1.83 (2 s, 12H, t-H), 1.79 (s, 3H, 10/9-H), 1.67 (s, 3H, 9/10-H), 1.52 (s, 3H, 9/10-H), 0.26 & 0.28 (2 s, 9H, TMS-H) ppm. **UV/vis absorption:** λ_{max} = 421 nm. **ESI-MS:** Calcd. for $[C_{150}H_{116}CuN_{10}SiZn•MeOH•H_2O]^+$ = [Cu(**2**)•MeOH•H_2O)]$^+$ *m/z* = 2262.8; Found: [Cu(**30**)•MeOH•H_2O)]$^+$, *m/z* (%) = 2262.1 (100).

1c). Self-sorting experiments

To a solution of nanoswitches **1** (450.0 µg, 0.412 µmol) and **2** (886.0 µg, 0.412 µmol) in CD_2Cl_2 (500 µL) was added $[Cu(CH_3CN)_4]B(C_6F_5)_4$ (373.0 µg, 0.412 µmol). The reaction mixture was sonicated for 10 min to yield a 90:10 mixture of $[Cu(\mathbf{1})]^+$:$[Cu(\mathbf{2})]^+$ (see Figure S7 and Figure S29). Addition of one equiv. of nanoswitch **1** to a solution of $[Cu(\mathbf{2})]^+$ complex in CD_2Cl_2 gave same selectivity ratio i.e. $[Cu(\mathbf{1})]^+$:$[Cu(\mathbf{2})]^+$, 90:10 (see Figure S8).

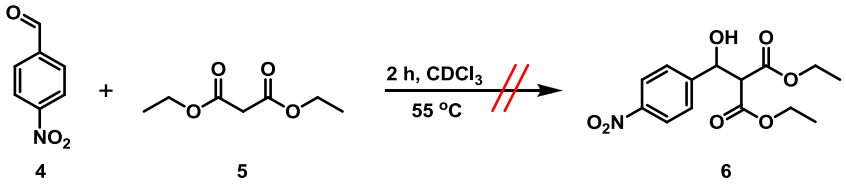
Copper selectivity in presence of piperidine

Addition of 1.0 equiv. of piperidine to 90:10 mixture of $[Cu(\mathbf{1})]^+$:$[Cu(\mathbf{2})]^+$ changed the selectivity of $[Cu(\mathbf{1})]^+$:$[Cu(\mathbf{2})]^+$ ratio to 80:20 (see Figure S9).

2. Control and catalytic experiments

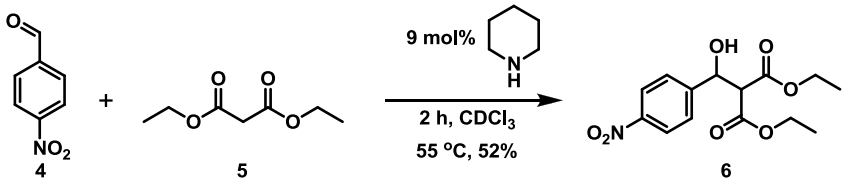
All experiments below were performed in $CDCl_3$ at 55 °C. Prior to use, $CDCl_3$ was stirred over basic alumina (Brockman activity 1) and filtered over a short pad of basic alumina. The yield of product **6**[3] (doublet at δ = 5.15 ppm) was determined using 1,1,2,2-tetrachloroethane (TCE) (singlet at δ = 5.93 ppm) or 1,3,5-trimethoxybenzene (singlet at δ = 6.07 ppm) as an internal standard.

Catalytic experiment A1



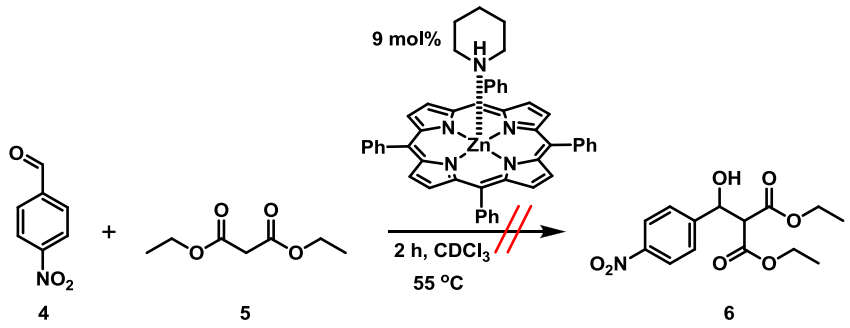
A solution of 4-nitrobenzaldehyde (**4**, 2.39 mg, 15.8 µmol) and diethyl malonate (**5**, 253 mg, 1.58 mmol) in $CDCl_3$ (500 µL) was heated at 55 °C for 2 h. No formation of product **6** was observed (see Figure S11).

Catalytic experiment A2



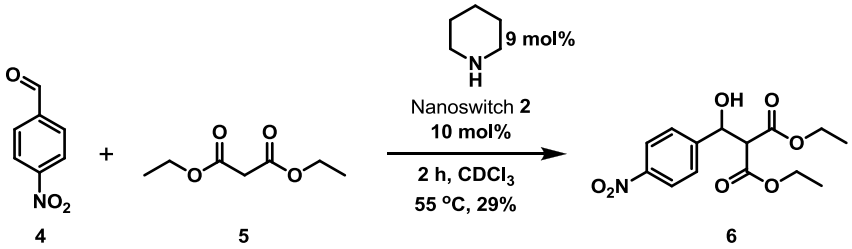
A solution of 4-nitrobenzaldehyde (**4**, 2.22 mg, 14.7 µmol), diethyl malonate (**5**, 235 mg, 1.47 mmol), 1,3,5-trimethoxybenzene (2.47 mg, 14.7 µmol) and piperidine (**3**, 113 µg, 1.32 µmol) in $CDCl_3$ (500 µL) was heated at 55 °C for 2 h. Product **6** was formed in 52% yield (see Figure S12).

Catalytic experiment A3



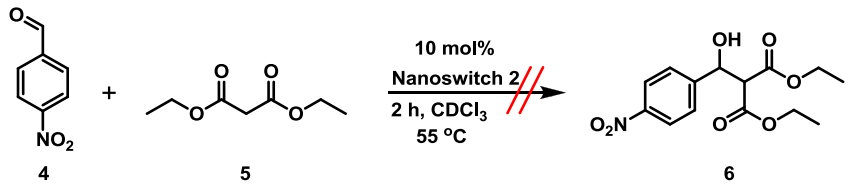
A solution of 4-nitrobenzaldehyde (**4**, 2.22 mg, 14.7 µmol), diethyl malonate (**5**, 235 mg, 1.47 mmol), 1,3,5-trimethoxybenzene (2.47 mg, 14.7 µmol), piperidine (**3**, 113 µg, 1.32 µmol) and ZnTPP (996 µg, 1.47 µmol) in $CDCl_3$ (500 µL) was heated at 55 °C for 2 h. No formation of product **6** was observed (see Figure S13).

Catalytic experiment A4



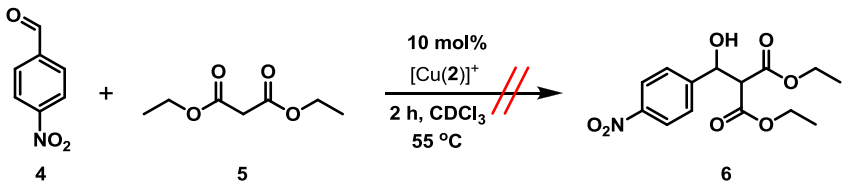
A solution of 4-nitrobenzaldehyde (**4**, 2.22 mg, 14.7 µmol), diethyl malonate (**5**, 235 mg, 1.47 mmol), 1,3,5-trimethoxybenzene (2.47 mg, 14.7 µmol), nanoswitch **2** (3.16 mg, 1.47 µmol) and piperidine (**3**, 113 µg, 1.32 µmol) in $CDCl_3$ (500 µL) was heated at 55 °C for 2 h. Product **6** was formed in 29% yield (see Figure S14).

Catalytic experiment A5



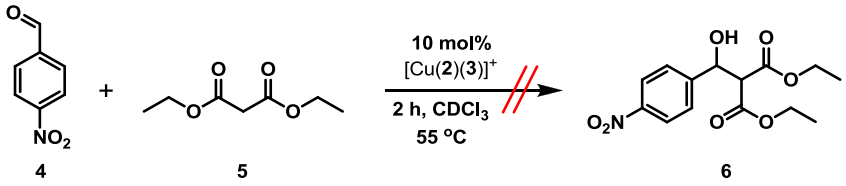
A solution of 4-nitrobenzaldehyde (**4**, 2.32 mg, 15.4 µmol), diethyl malonate (**5**, 246 mg, 1.54 mmol) and nanoswitch **2** (3.30 mg, 1.54 µmol) in $CDCl_3$ (500 µL) was heated at 55 °C for 2 h. No formation of product **6** was observed (see Figure S15).

Catalytic experiment A6



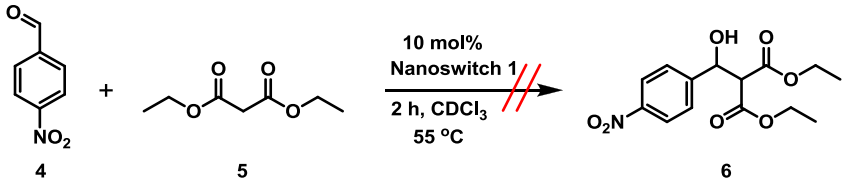
$[Cu(\mathbf{2})]^+$ complex was prepared by addition of $[Cu(CH_3CN)_4]PF_6$ (572 µg, 1.54 µmol) to nanoswitch **2** (3.30 mg, 1.54 µmol) in $CDCl_3$ (500 µL). Thereafter, 4-nitrobenzaldehyde (**4**, 2.32 mg, 15.4 µmol) and diethyl malonate (**5**, 246 mg, 1.54 mmol) were added. The reaction was allowed to stir at 55 °C for 2 h. NMR analysis revealed no product formation (see Figure S16).

Catalytic experiment A7



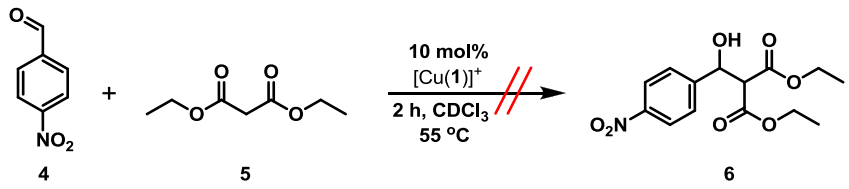
To a solution of $[Cu(\mathbf{2})]^+$ (2.00 mg, 0.79 µmol) in $CDCl_3$ (500 µL) piperidine (68 µg, 0.79 µmol), 4-nitrobenzaldehyde (**4**, 1.20 mg, 7.94 µmol) and diethyl malonate (**5**, 127 mg, 0.79 mmol) were added. The reaction was allowed to stir at 55 °C for 2 h. NMR analysis revealed no product formation (see Figure S17).

Catalytic experiment A8



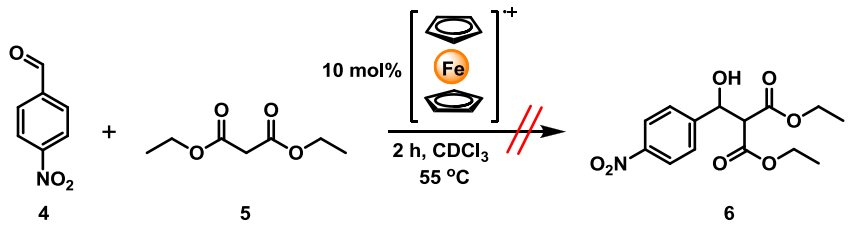
A solution of 4-nitrobenzaldehyde (**4**, 2.28 mg, 15.1 µmol), diethyl malonate (**5**, 241 mg, 1.51 mmol) and nanoswitch **1** (1.65 mg, 1.51 µmol) in $CDCl_3$ (500 µL) was heated at 55 °C for 2 h. No formation of product **6** was observed (see Figure S18).

Catalytic experiment A9



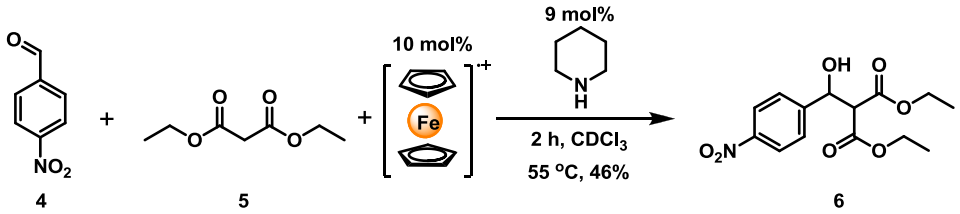
$[Cu(\mathbf{1})]^+$ complex was prepared by addition of $[Cu(CH_3CN)_4]PF_6$ (563 µg, 1.51 µmol) to nano-switch **1** (1.65 mg, 1.51 µmol) in $CDCl_3$ (500 µL). Thereafter, 4-nitrobenzaldehyde (**4**, 2.28 mg, 15.1 µmol) and diethyl malonate (**5**, 241 mg, 1.51 mmol) were added. The reaction was allowed to stir at 55 °C for 2 h. Subsequently NMR analysis revealed no product formation (see Figure S19).

Catalytic experiment A10



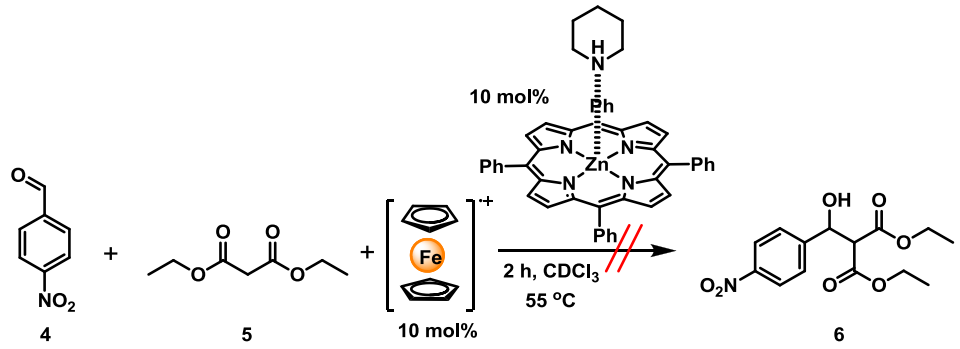
To a solution of ferrocene (568 µg, 3.05 µmol) in $CDCl_3$ (1000 µL) was added tris-(4-bromo-phenyl)aminium hexachloroantimonate (TBA, 2.50 mg, 3.05 µmol). Thereafter, 4-nitrobenzaldehyde (**4**, 4.62 mg, 30.5 µmol) and diethyl malonate (**5**, 490 mg, 3.05 mmol) were added. The reaction mixture was stirred at 55 °C for 2 h. After cooling to room temperature, de-ionized water was added and reaction mixture was vigorously stirred. The organic layer was removed, dried over anhydrous $MgSO_4$ and concentrated. The crude residue was analyzed by ^1H NMR spectroscopy. No product formation of product **6** was observed (see Figure S20).

Catalytic experiment A11



To a solution of ferrocene (547 µg, 2.94 µmol) in $CDCl_3$ (1000 µL) was added tris-(4-bromo-phenyl)aminium hexachloroantimonate (TBA, 2.40 mg, 2.94 µmol). Afterwards, 1,3,5-trimethoxybenzene (4.94 mg, 29.4 µmol), piperidine (**3**, 225 µg, 2.64 µmol), 4-nitrobenzaldehyde (**4**, 4.44 mg, 29.4 µmol) and diethyl malonate (**5**, 471 mg, 2.94 mmol) were added. The reaction mixture was stirred at 55 °C for 2 h. After cooling to room temperature, de-ionized water was added and the reaction mixture was stirred vigorously at ambient temperature. The organic layer was removed, dried over anhydrous $MgSO_4$ and concentrated. The crude residue was analyzed by ^{1}H NMR spectroscopy. Product **6** was formed in 46% yield (see Figure S21).

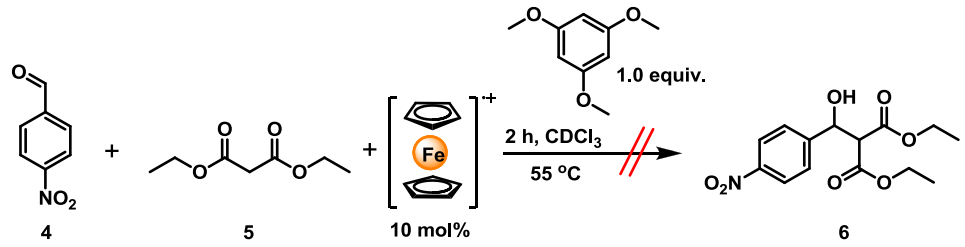
Catalytic experiment A12



To a solution of ferrocene (568 µg, 3.06 µmol) in $CDCl_3$ (1000 µL) was added tris-(4-bromo-phenyl)aminium hexachloroantimonate (TBA, 2.49 mg, 3.05 µmol). Subsequently, complex **3**→ZnTPP (2.34, 3.06 µmol), 4-nitrobenzaldehyde (**4**, 4.62 mg, 30.6 µmol) and diethyl malonate (**5**, 490 mg, 3.6 mmol) were added. The reaction mixture was stirred at 55 °C for 2 h. After cooling to room temperature, de-ionized water was added and the reaction mixture was stirred vigorously at room temperature. The organic layer was removed, dried over anhydrous $MgSO_4$

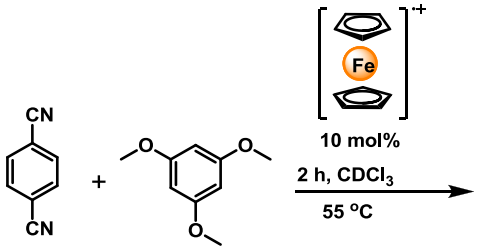
and concentrated. The crude residue was analyzed by ^{1}H NMR spectroscopy. Formation of product **6** was not observed (see Figure S22).

Catalytic experiment A13



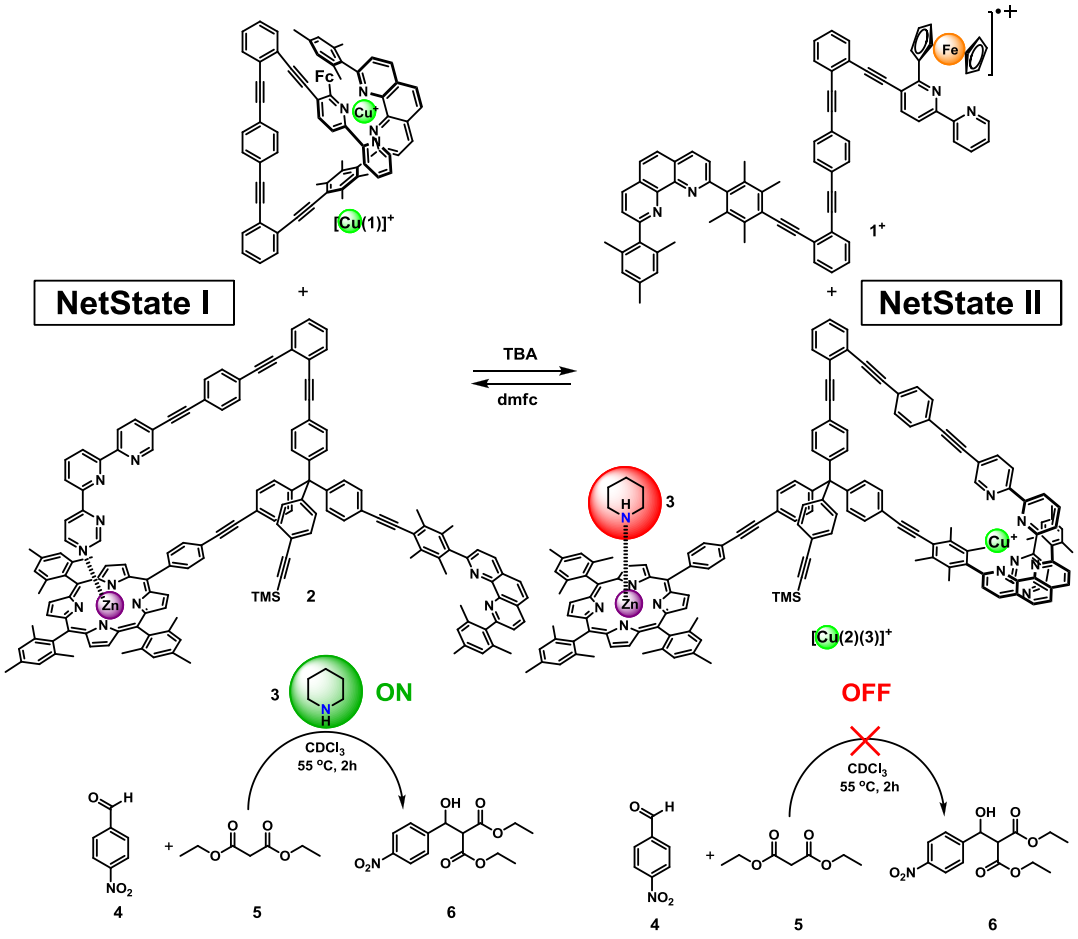
To a solution of ferrocene (551 µg, 2.96 µmol) and 1,3,5-trimethoxybenzene (4.98 mg, 29.6 µmol) in $CDCl_3$ (1000 µL) was added tris-(4-bromophenyl)aminium hexachloroantimonate (TBA, 2.42 mg, 2.96 µmol). Then, 4-nitrobenzaldehyde (**4**, 4.48 mg, 29.6 µmol), diethyl malonate (**5**, 475 mg, 2.96 mmol) was added. The reaction mixture was stirred at 55 °C for 2 h. After cooling to room temperature, de-ionized water was added and the reaction mixture was stirred vigorously at room temperature. The organic layer was removed, dried over anhydrous $MgSO_4$ and concentrated. The crude residue was analyzed by ^{1}H NMR spectroscopy. No product formation was observed (see Figure S23).

Catalytic experiment A14



To a solution of ferrocene (473 µg, 2.54 µmol) in $CDCl_3$ (500 µL) was added tris-(4-bromo-phenyl)aminium hexachloroantimonate (TBA, 2.08 mg, 2.54 µmol). Then, 1,2-dicyanobenzene (3.26 mg, 25.4 µmol) and 1,3,5-trimethoxybenzene (4.32 mg, 25.4 µmol) were added. The reaction mixture was stirred at 55 °C for 2 h. After cooling to room temperature, de-ionized water was added and reaction mixture was stirred vigorously at room temperature. The organic layer was removed, dried over anhydrous $MgSO_4$ and evaporated (see Figure S24). Decomposition of 1,3,5-trimethoxybenzene did not happen under these conditions.

Catalytic experiment A15



This catalytic experiment with nanoswitches **1** and **2** was performed at same concentration and conditions as mentioned in catalytic experiment **A4**. Initially, equivalent amounts of nanoswitch **1**, nanoswitch **2** and $[Cu(CH_3CN)]B(C_6F_5)_4$ were added (**NetState I**). Afterwards, the equivalent amount of tris-(4-bromophenyl)aminium hexachloroantimonate (**TBA**) was added (**NetState II**) and subsequently the equivalent amount of decamethylferrocene (**dmfc**) was used to reset **NetState I**.

Addition of 1.0 equivalent of $[Cu(CH_3CN)]B(C_6F_5)_4$ to a mixture of nanoswitches **1** and **2** furnished **NetState I** [= $(Cu•\mathbf{1})^+$ and **2**] leaving behind piperidine (**3**) free in solution that acts as catalyst for the addition reaction between 4-nitrobenzaldehyde (**4**) and diethyl malonate (**5**). However, after addition of oxidant (TBA), the catalysis was completely terminated due to formation of **NetState II** [= $\mathbf{1}^{+\cdot}$ and $(Cu•\mathbf{2}•\mathbf{3})^+$], in which piperidine is trapped by ZnPor unit so

that it is catalytically inactive. To ascertain comparable conditions, consumed 4-nitrobenzaldehyde was replaced in the reaction mixture. To reset **NetState I**, **dmfc** was used as reducing agent. Addition of 1.0 equivalent of **dmfc** resulted in reduction of switch $\mathbf{1}^{+\cdot}$ followed by Cu^{+} translocation from $(Cu\bullet\mathbf{2}\bullet\mathbf{3})^{+}$ to nanoswitch **1.** At the same time **3** was released in solution that consequently turned on the reaction between 4-nitrobenzaldehyde and diethyl malonate.

Procedure: To a solution of nanoswitch **1** (3.21 mg, 2.94 µmol), nanoswitch **2** (6.32 mg, 2.94 µmol) and $[Cu(CH_3CN)]B(C_6F_5)_4$ (2.67 mg, 2.94 µmol) in $CDCl_3$ (1000 µL) was added 4-nitro-benzaldehyde (**4**, 4.44 mg, 29.4 µmol), diethyl malonate (**5**, 471 mg, 2.94 mmol), piperidine (**3**, 225 µg, 2.64 µmol) and 1,3,5-trimethoxybenzene (4.94 mg, 29.4 µmol). The reaction mixture was allowed to stir at 55 °C for 2 h. The mixture was cooled to room temperature. 1/3 volume of reaction mixture (**part I**) was removed and analyzed by ^{1}H NMR. The yield of product **6** was 26% (see Figure S25A). To reinstate similar concentrations, equivalent amount of TBA (1.60 mg, 1.96 µmol) and consumed 4-nitrobenzaldehyde (**4**, 1.15 mg, 7.64 µmol) was added to the remaining 2/3 volume of reaction mixture and allowed to stir at 55 °C for 2 h. Therefrom half the volume (**part II**) was removed. The reaction mixture was cooled to room temperature, de-ionized water was added and the resulting mixture was vigorously stirred. The organic layer was removed and dried over anhydrous $MgSO_4$. Subsequently, ^{1}H NMR analysis corroborated that no further product **6** had formed (see Figure S25B, part II yield = 0%, total yield = 26%). To the remaining reaction mixture (**part III**), equivalent amount of **dmfc** (320 µg, 0.98 µmol was added and the mixture was heated to 55 °C for 2 h. The reaction was cooled to room temperature, de-ionized water was added and resulting mixture was vigorously stirred. The organic layer was removed and dried over anhydrous $MgSO_4$. Thereafter, ^{1}H NMR analysis confirmed formation of product **6** in additional 20% yield (see Figure S25C, part II yield = 20%, total yield = 46%).

3. NMR Spectra

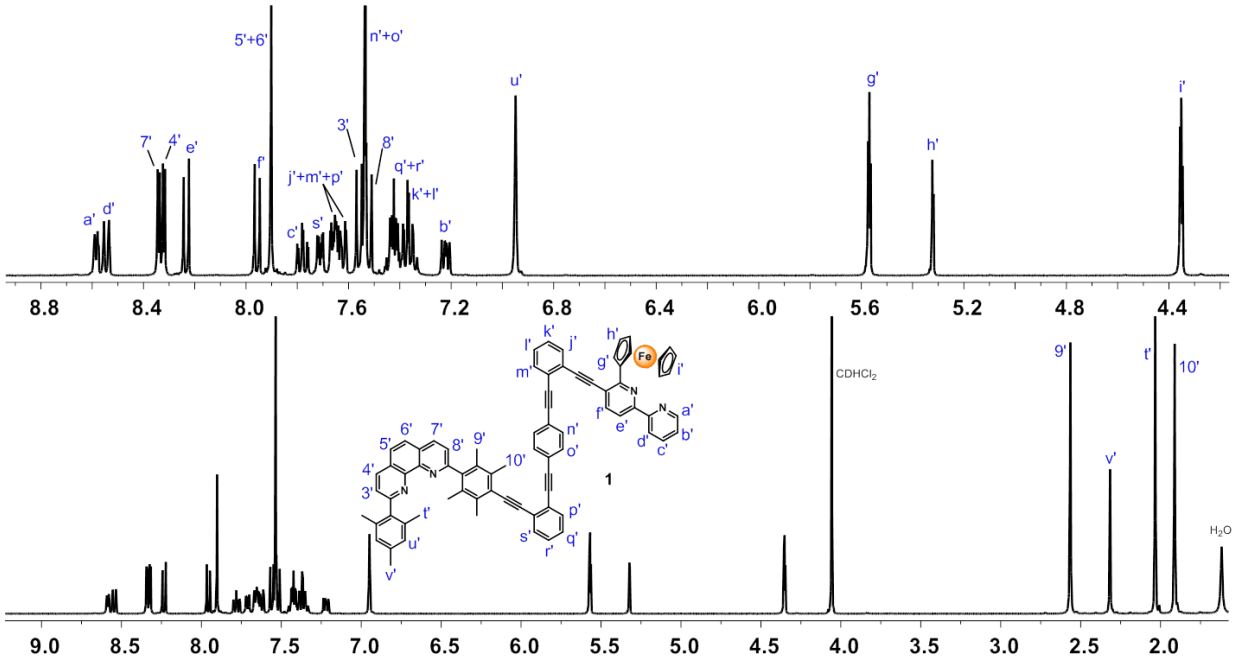


Figure S1. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of nanoswitch **1.**

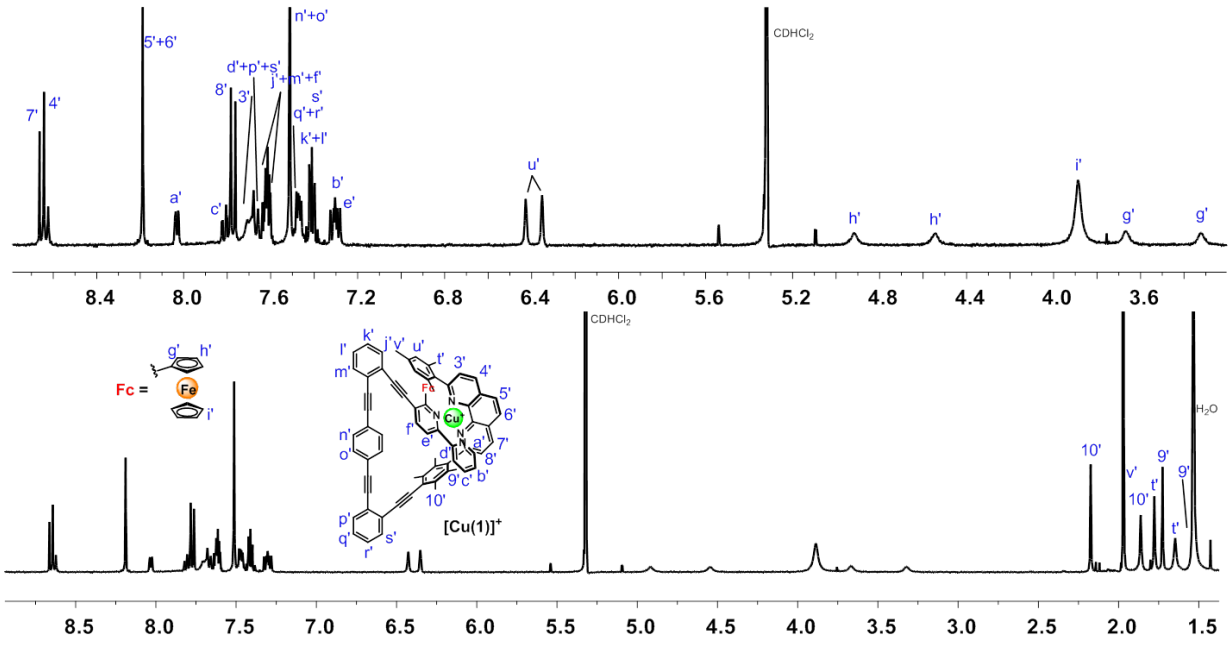


Figure S2. ^{1}H NMR spectrum (400 MHz, CD_2Cl_2, 298 K) of [Cu(**1**)]$^{+}$ complex.

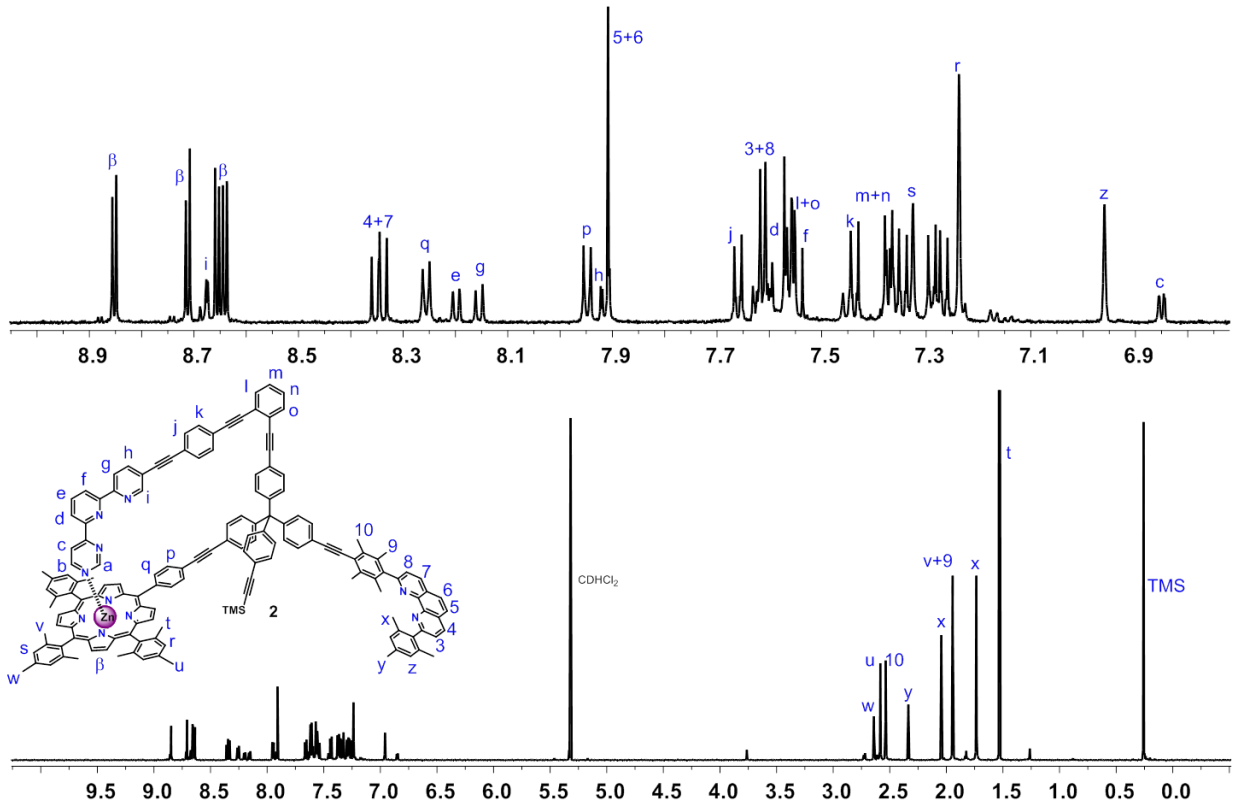


Figure S3. ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of nanoswitch **2.**

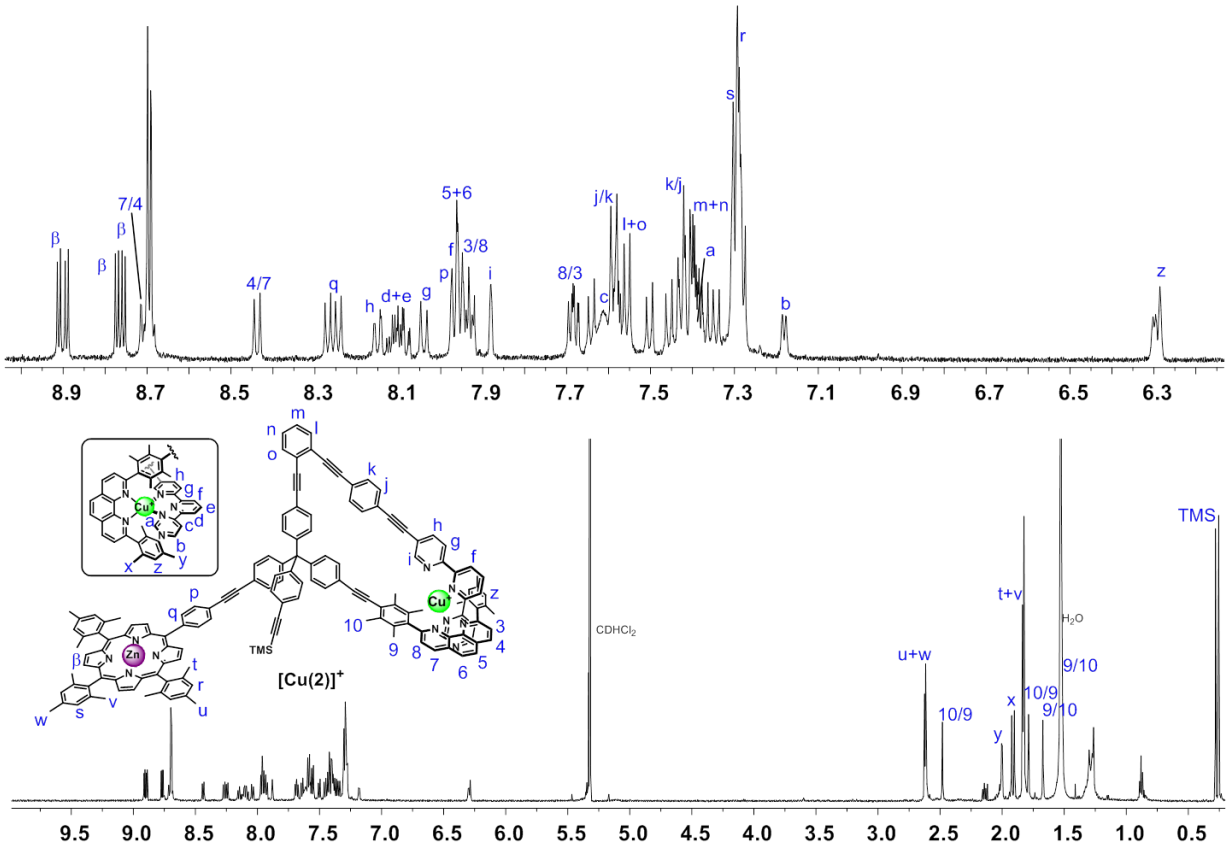


Figure S4. ^{1}H NMR spectrum (600 MHz, CD_2Cl_2, 298 K) of [Cu(**2**)]$^{+}$ complex.

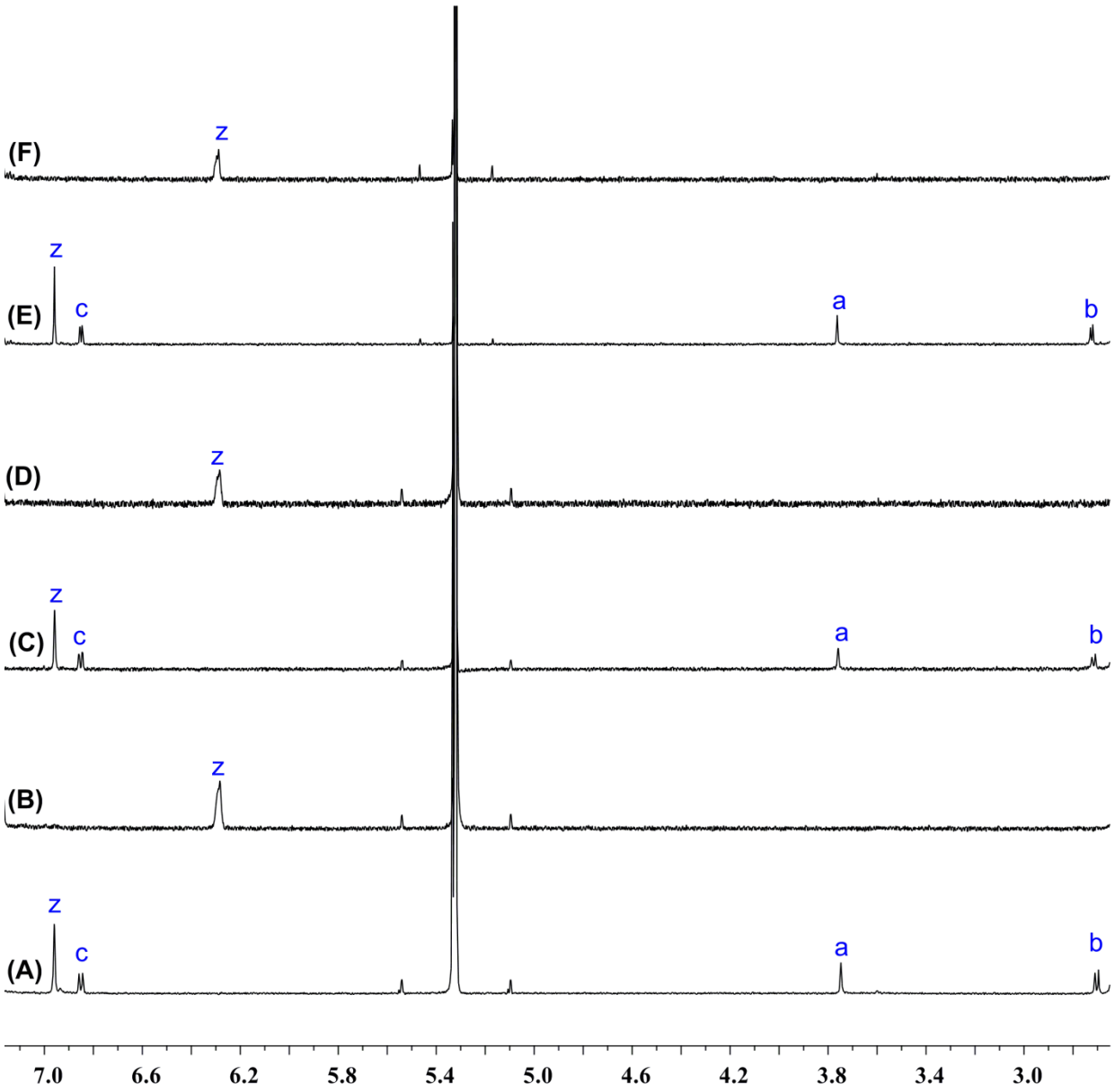


Figure S5. Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) demonstrating the reversibility of switching between both states of nanoswitch **2** realized by the successive addition of equimolar amounts of $[Cu(CH_3CN)]B(C_6F_5)_4$ (**B, D,** and **F**) and cyclam (**C, E**).

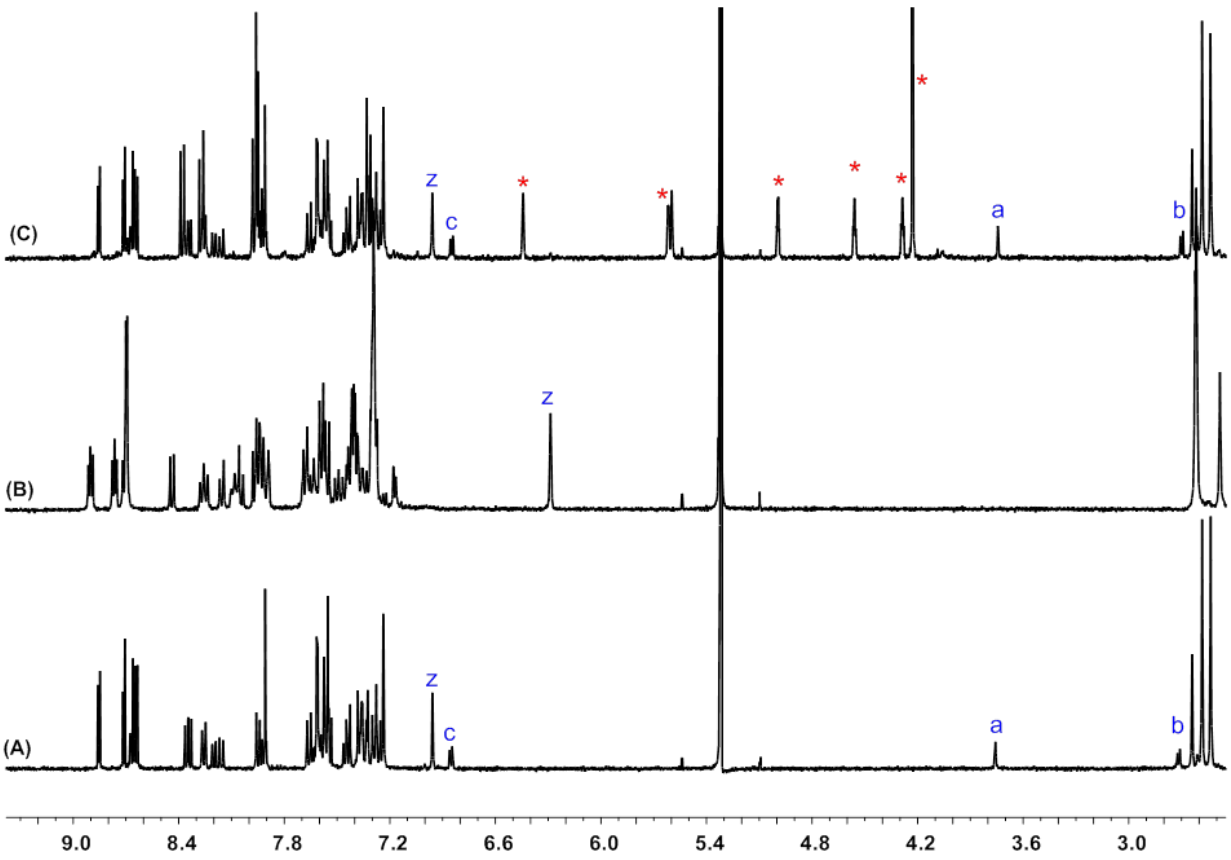


Figure S6. Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) demonstrating the reversibility of switching between both states of nanoswitch **2** realized by addition of equimolar amounts of $[Cu(CH_3CN)]B(C_6F_5)_4$ (**B**) and 2-ferrocenyl-9-mesityl-[1,10]-phenanthroline (**C**). Peaks of the homoleptic copper(I) complex of 2-ferrocenyl-9-mesityl-[1,10]-phenanthroline are indicated in asterisk.

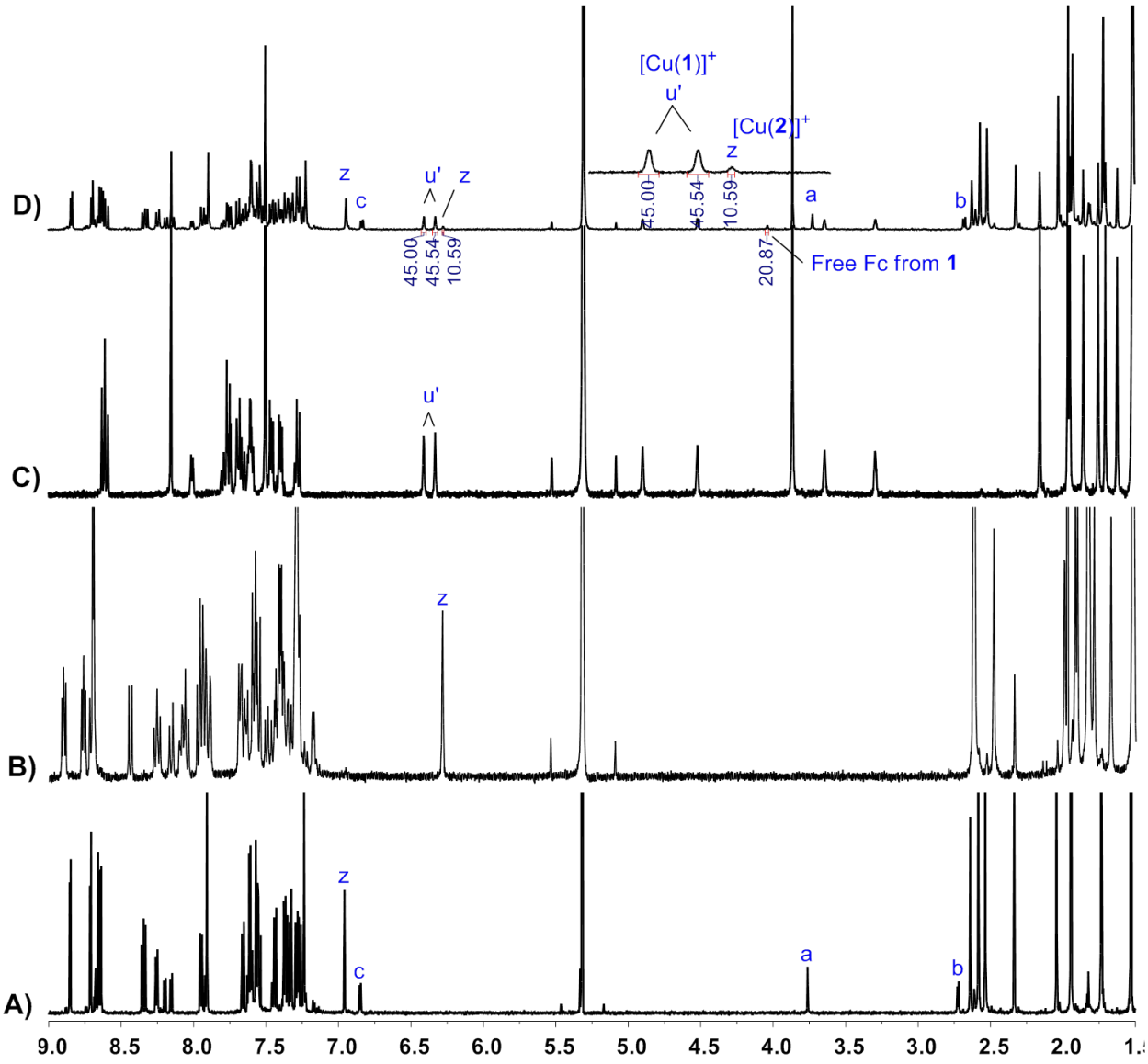


Figure S7. Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of A) nanoswitch **2**; B) [Cu(**2**)]$^{+}$ complex; C) [Cu(**1**)]$^{+}$ complex for comparision; and D) after addition of 1.0 equiv. of $[Cu(CH_3CN)_4](C_6F_5)_4B$ to solution of nanoswitches **1** and **2** giving 90:10 selectivity of [Cu(**1**)]$^{+}$:[Cu(**2**)]$^{+}$.

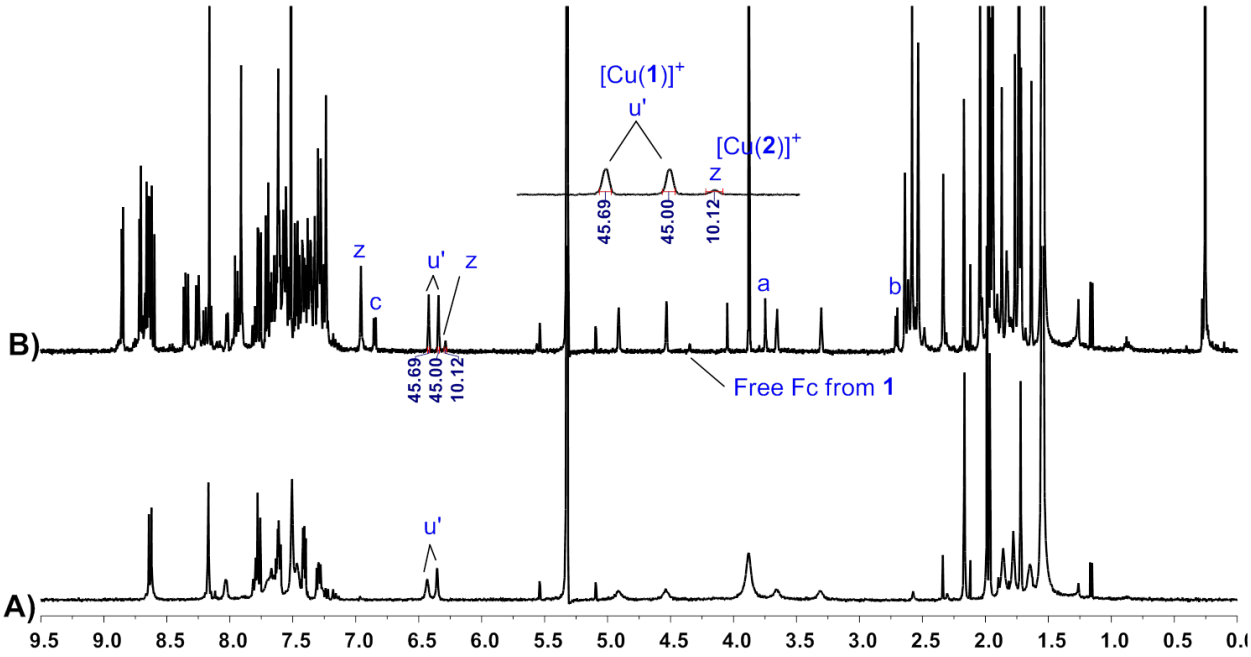


Figure S8. ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of A) [Cu(**1**)]$^{+}$ complex and B) after addition of 1.0 equiv. of nanoswitch **1** to a solution of [Cu(**2**)]$^{+}$ complex affording 90:10 mixture of [Cu(**1**)]$^{+}$:[Cu(**2**)]$^{+}$.

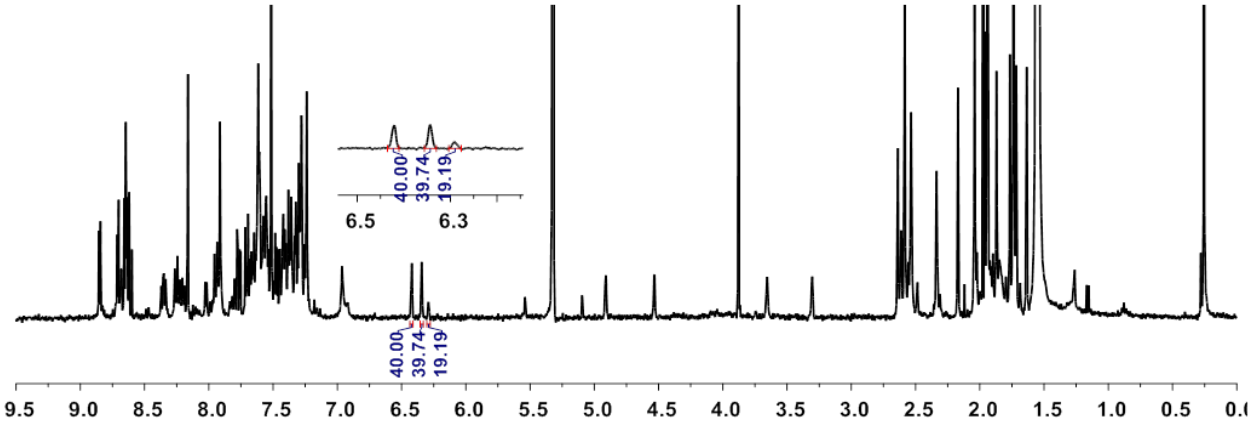


Figure S9. ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of 1:1:1 mixture of nanoswitch **1**, nanoswitch **2** and $[Cu(CH_3CN)_4](C_6F_5)_4B$ in presence of 1.0 equiv. of piperidine (**3**) affording 80:20 mixture of [Cu(**1**)]$^{+}$:[Cu(**2**)]$^{+}$.

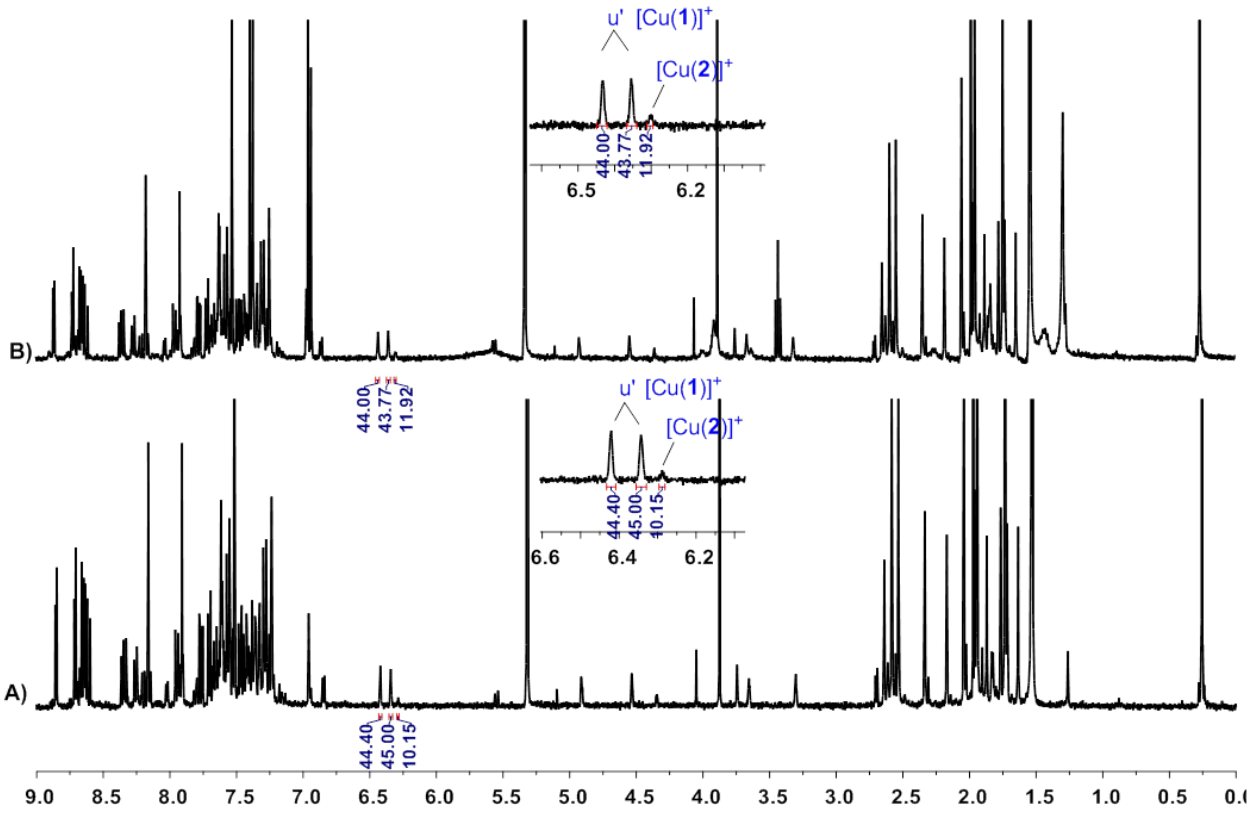


Figure S10. ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of A) mixture of **1** (452 µg, 0.413 µmol), **2** (890 µg, 0.413 µmol), and $[Cu(CH_3CN)_4]B(C_6F_5)_4$ (375 µg, 0.413 µmol) in CD_2Cl_2 revealed 90:10 ratio of $[Cu(\mathbf{1})]^+$:$[Cu(\mathbf{2})]^+$. B) The solution containing 90:10 ratio of $[Cu(\mathbf{1})]^+$:$[Cu(\mathbf{2})]^+$ in CD_2Cl_2 was then treated with tris-(4-bromophenyl)aminium tetrafluoroborate (234 µg, 0.413 µmol) and the resultant solution was heated at 35 °C for 10 min to ensure Cu^+ translocation. Then the solution was reduced with 3-(11-bromodecyl)1,1'-biferrocenylene[4] (BFD, 249 µg, 0.413 µmol). A subsequently recorded ^{1}H NMR spectrum confirmed reverse translocation of copper(I) ions in 88:12 $[Cu(\mathbf{1})]^+$:$[Cu(\mathbf{2})]^+$ selectivity.

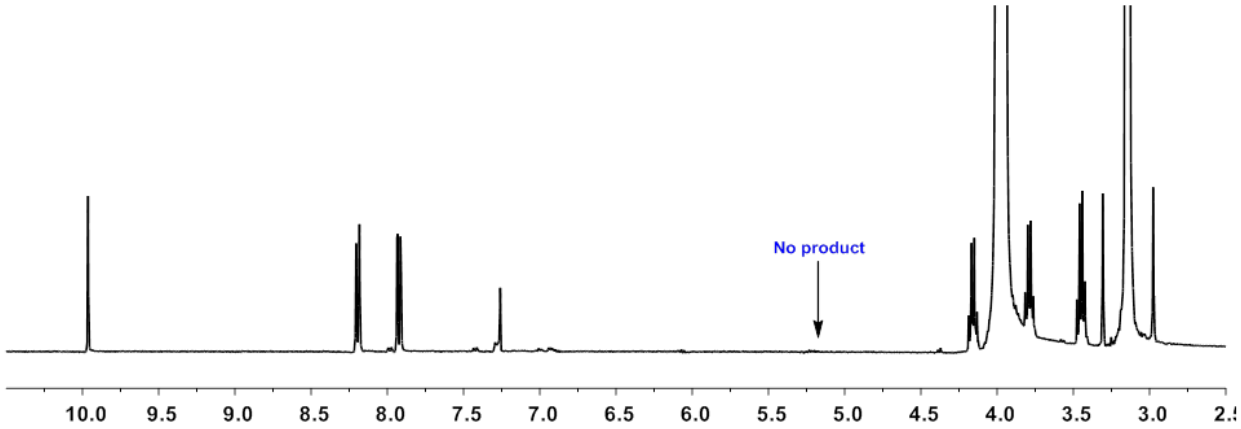


Figure S11. Catalytic experiment **A1:** Partial ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) obtained after heating **4** and **5** (1:100) at 55 °C for 2 h does not show formation of product **6**.

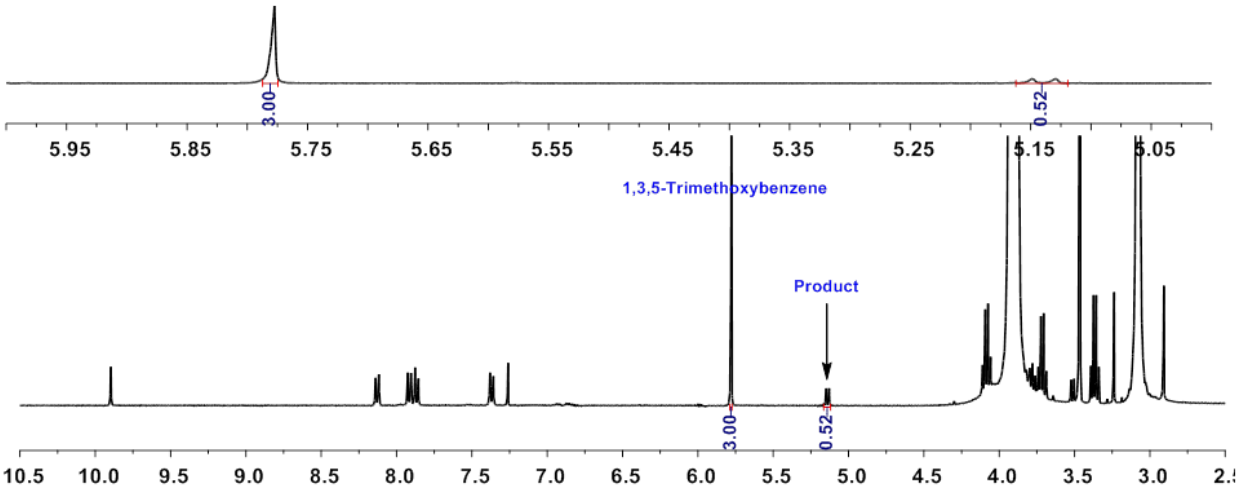


Figure S12. Catalytic experiment **A2:** Partial ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) obtained after heating the reaction mixture of piperidine (**3**), 1,3,5-trimethoxybenzene, **4** and **5** in 0.90:10:10:1000 ratio at 55 °C for 2 h shows formation of product **6** in 52% yield.

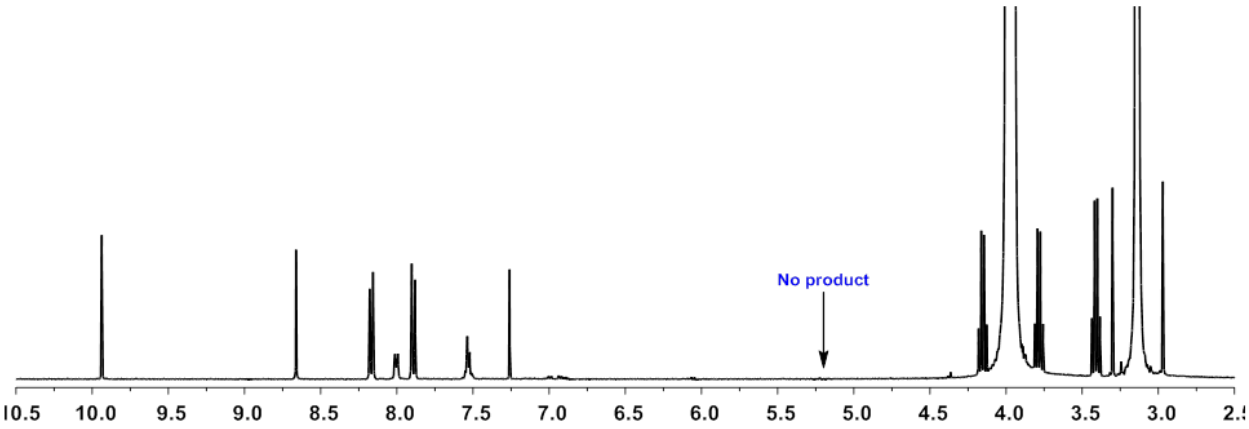


Figure S13. Catalytic experiment **A3:** Partial ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) obtained after heating the reaction mixture of piperidine, ZnTPP, **4** and **5** in 0.90:1:10:1000 ratio at 55 °C for 2 h does not show formation of product **6**.

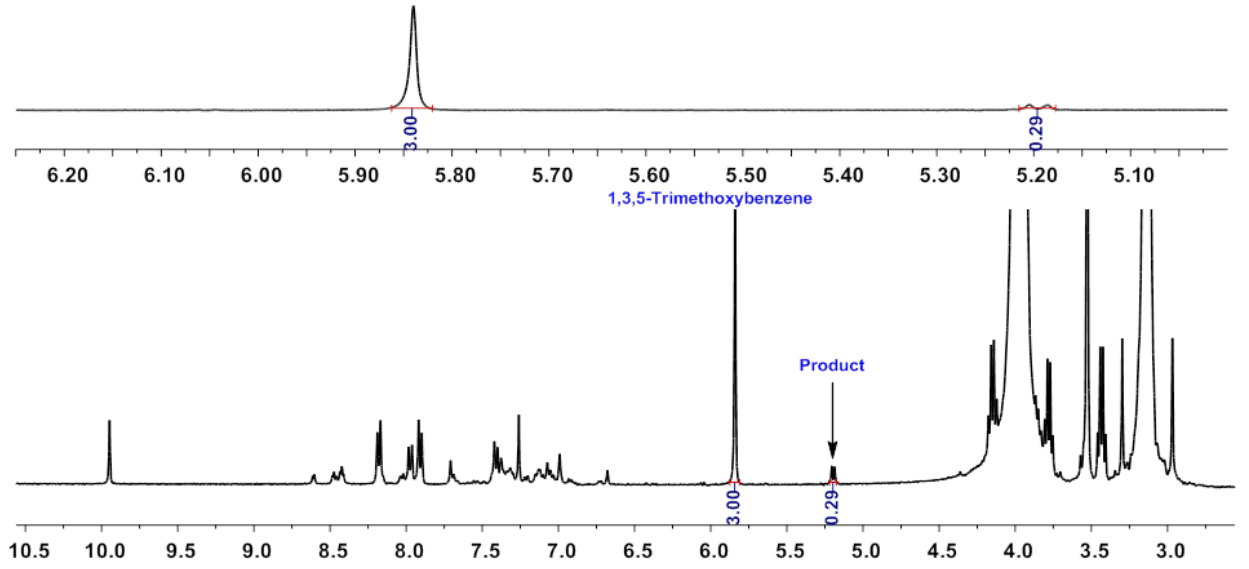


Figure S14. Catalytic experiment **A4:** Partial ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum obtained after heating the reaction mixture of piperidine (**3**), nanoswitch **2**, 1,3,5-trimethoxybenzene, **4** and **5** in 0.90:1:10:10:1000 ratio at 55 °C for 2 h shows formation of product **6** in 29% yield**.**

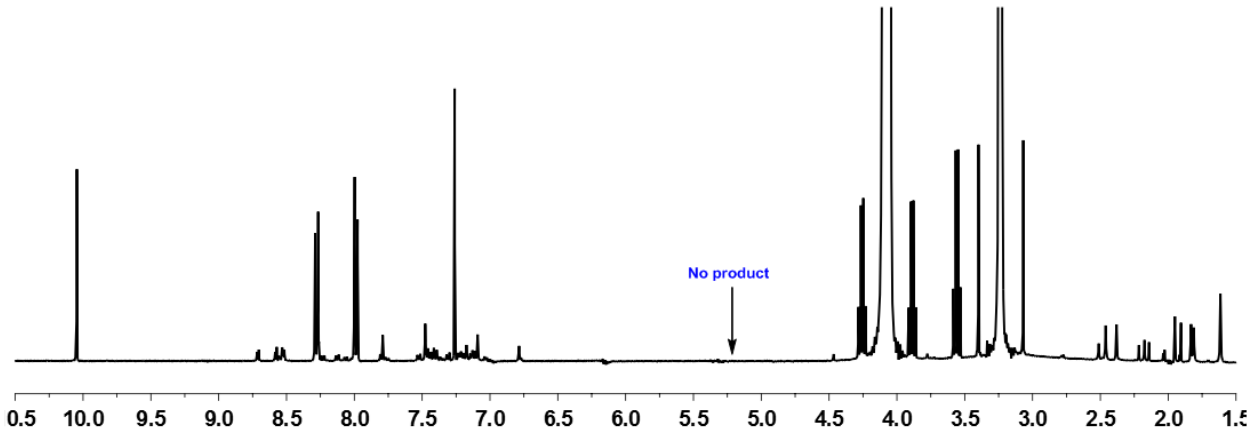


Figure S15. Catalytic experiment **A5:** Partial ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) obtained after heating the reaction mixture of nanoswitch **2**, **4** and **5** in 1:10:1000 ratio at 55 °C for 2 h does not show formation of product **6**.

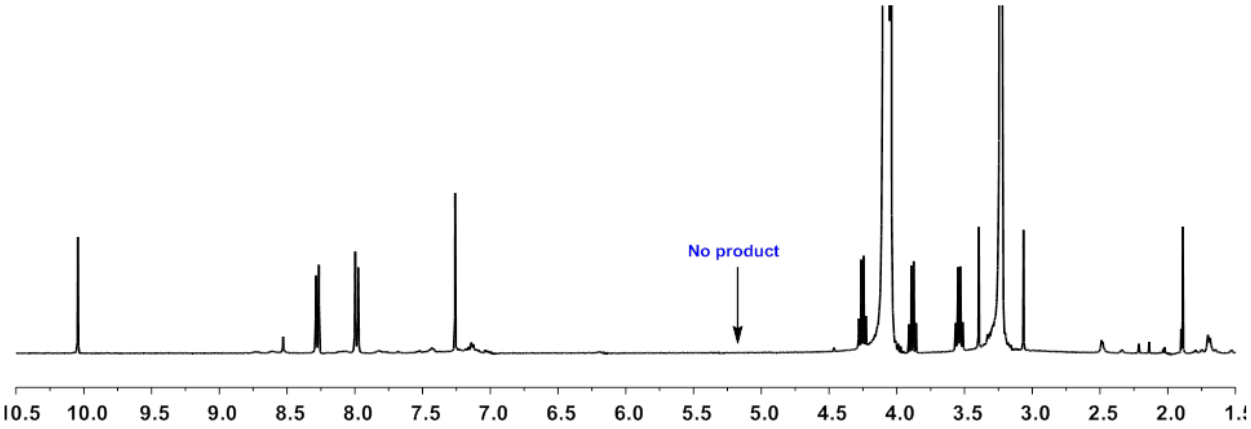


Figure S16. Catalytic experiment **A6:** Partial ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) obtained after heating the reaction mixture of [Cu(**2**)]$^{+}$, **4** and **5** in 1:10:1000 ratio at 55 °C for 2 h does not show formation of product **6**.

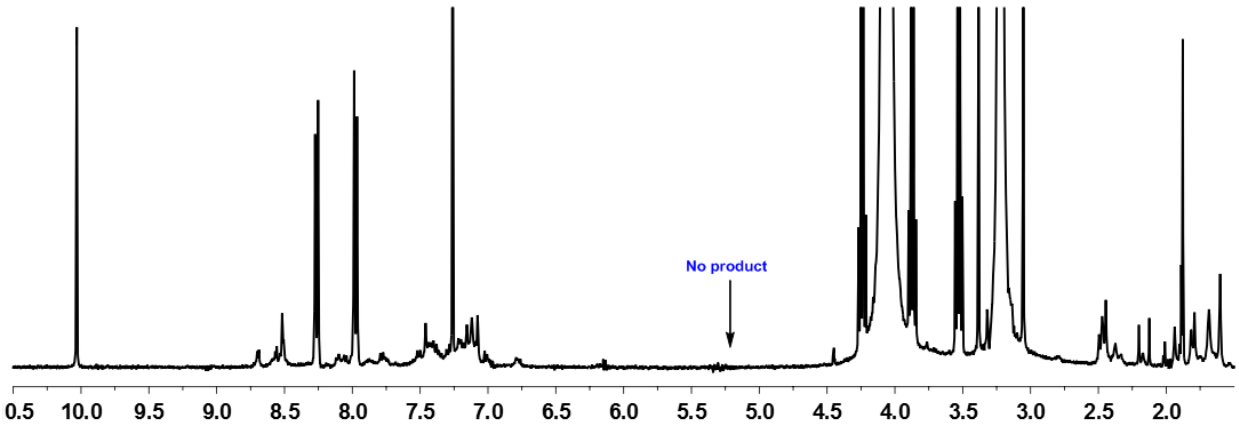


Figure S17. Catalytic experiment **A7:** Partial ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum obtained after heating the reaction mixture of complex [Cu(**2**)(**3**)]$^{+}$, **4** and **5** in 1:10:1000 ratio at 55 °C for 2 h does not show formation of product **6**.

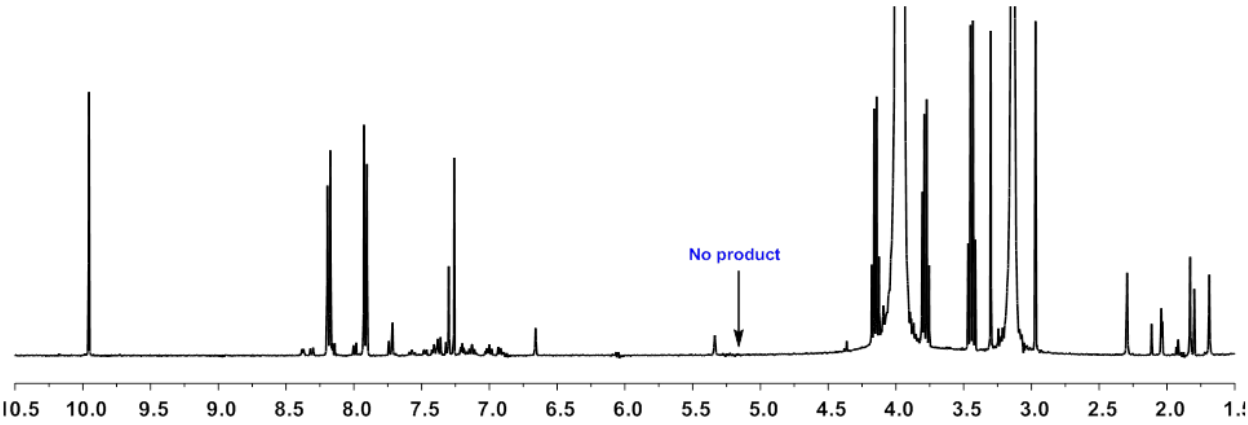


Figure S18. Catalytic experiment **A8:** Partial ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) obtained after heating the reaction mixture of nanoswitch **1**, **4** and **5** in 1:10:1000 ratio at 55 °C for 2 h does not show formation of product **6**.

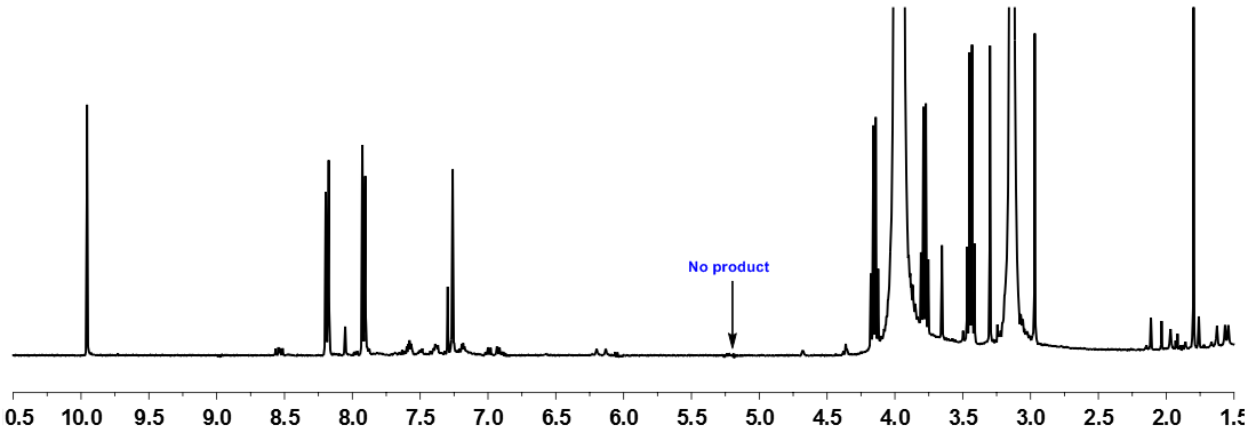


Figure S19. Catalytic experiment **A9:** Partial ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) obtained after heating the reaction mixture of nanoswitch [Cu(**1**)]$^{+}$, **4** and **5** in 1:10:1000 ratio at 55 °C for 2 h does not show formation of product **6**.

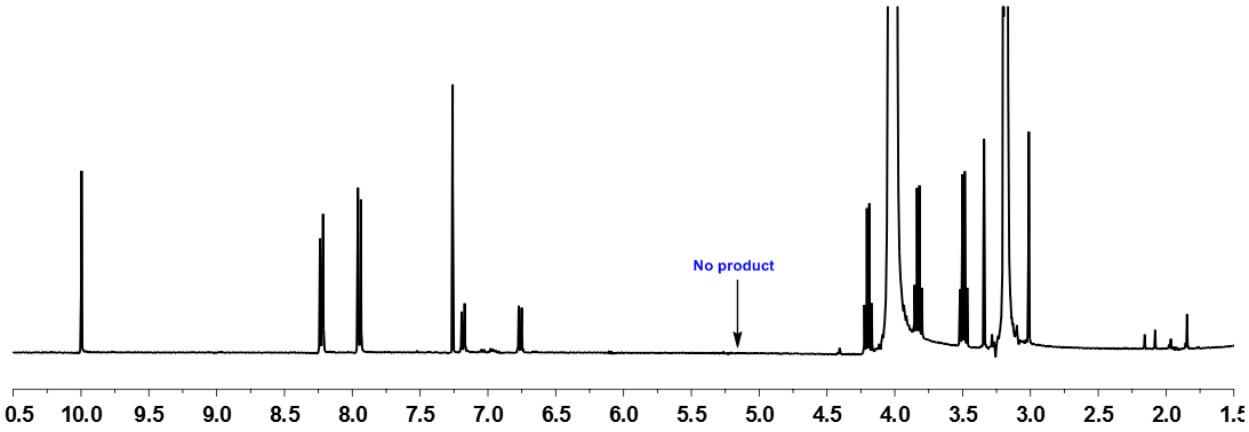


Figure S20. Catalytic experiment **A10:** Partial ^{1}H NMR spectrum (400 MHz, $CDCl_3$, 298 K) spectrum obtained after heating the reaction mixture of $[Cp_2Fe]^{+}$, **4** and **5** in 1:10:1000 ratio at 55 °C for 2 h does not show formation of product **6**.

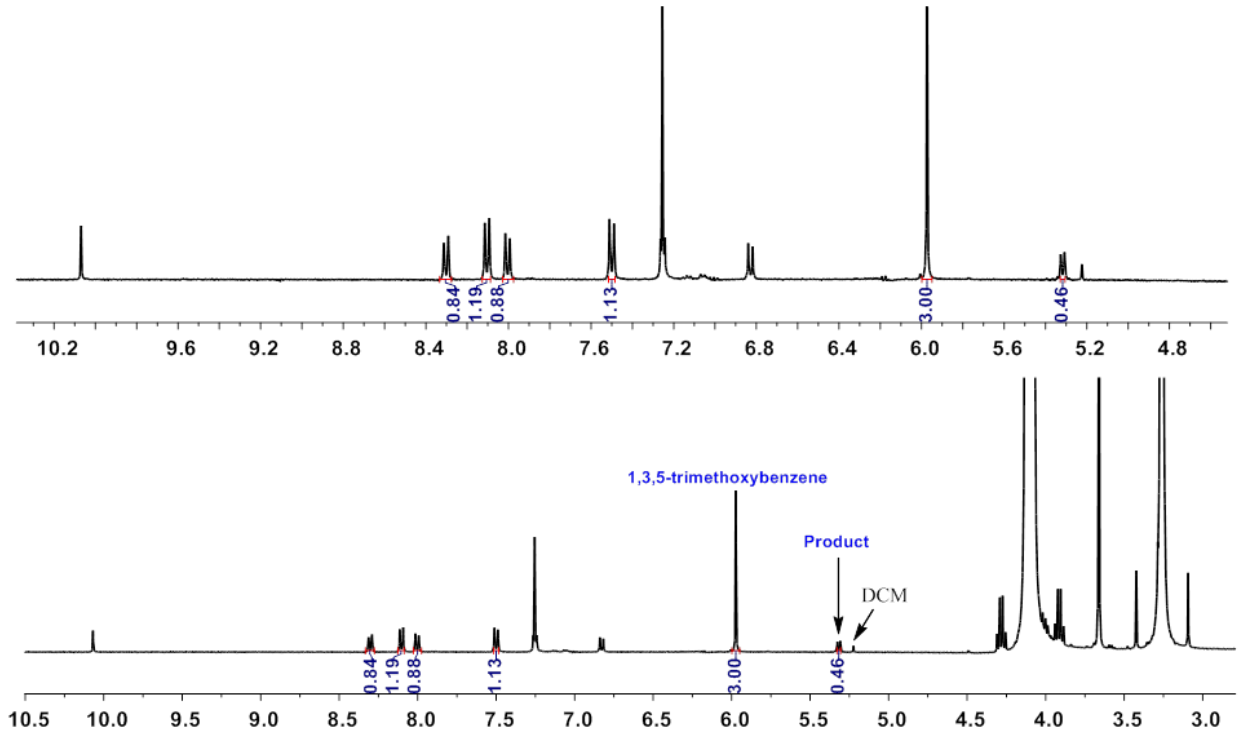


Figure S21. Catalytic experiment **A11:** Partial ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum obtained after heating the reaction mixture of $[Cp_2Fe]^+$, piperidine (**3**), 1,3,5-trimethoxybenzene, **4** and **5** in 1:0:0.9:10:10:1000 ratio at 55 °C for 2 h shows formation of product **6** in 46% yield.

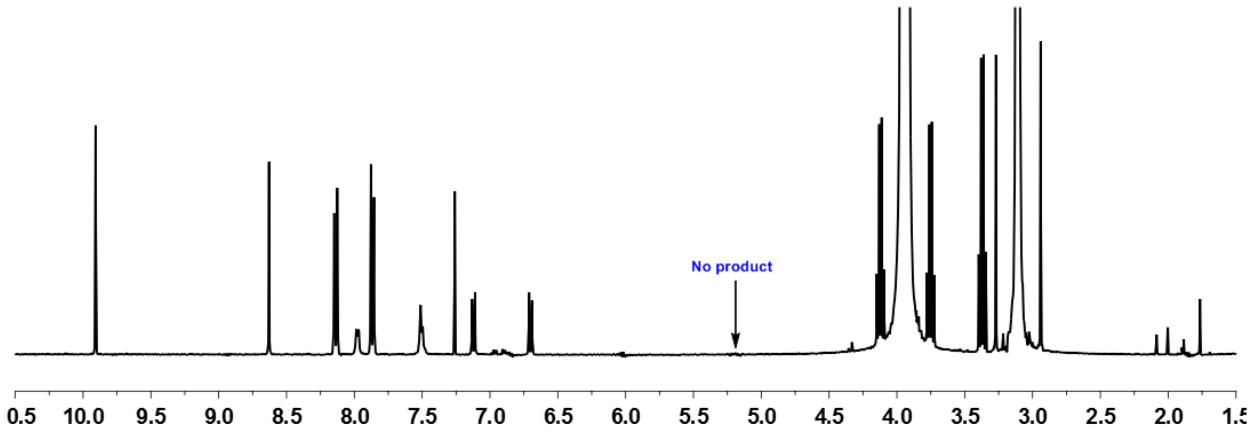


Figure S22. Catalytic experiment **A12:** Partial ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum obtained after heating the reaction mixture of $[Cp_2Fe]^+$, **3**→ZnTPP complex, **4** and **5** in 1:1:10:1000 ratio at 55 °C for 2 h. No formation of product **6** was observed.

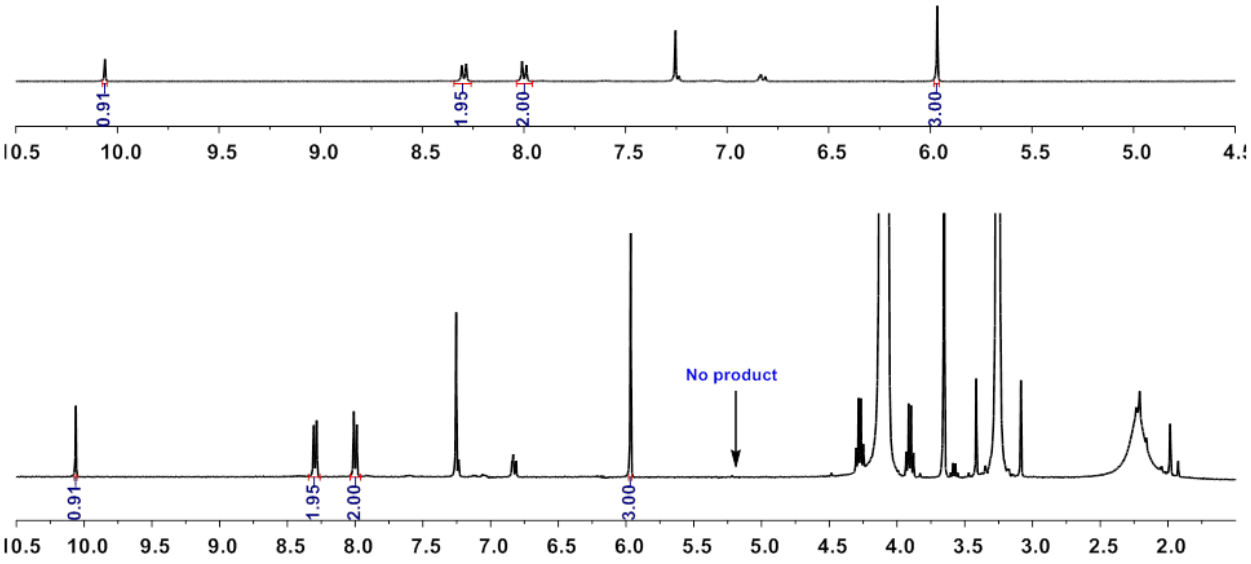


Figure S23. Catalytic experiment **A13:** Partial ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum obtained after heating the reaction mixture of $[Cp_2Fe]^+$, 1,3,5-trimethoxybenzene, **4** and **5** in 1:10:10:1000 ratio at 55 °C for 2 h shows no formation of product **6**.

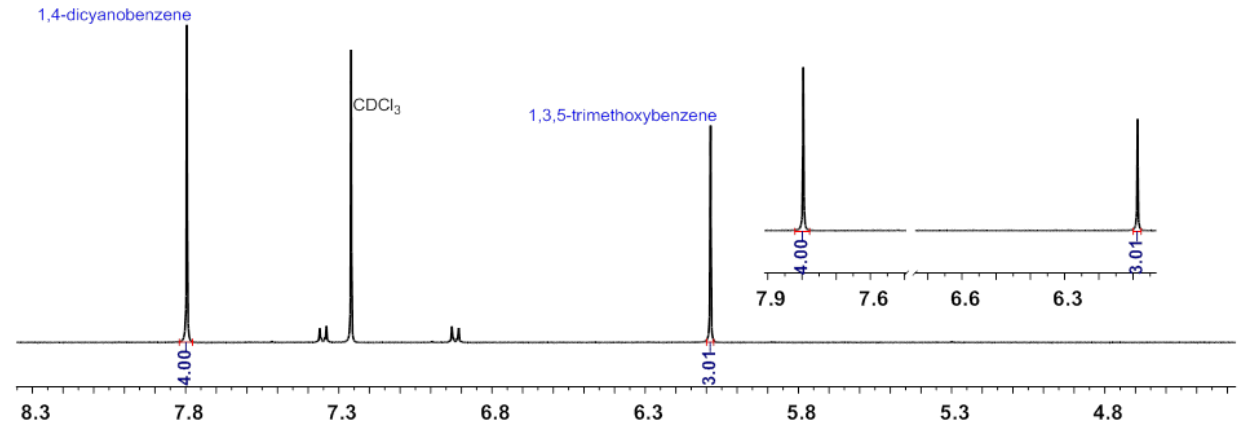


Figure S24. Catalytic experiment **A14:** Partial ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum obtained after heating 1:1 mixture of 1,3,5-trimethoxybenzene, 1,4-dicyanobenzene in presence of $[Cp_2Fe]^+$ at 55 °C for 2 h shows no oxidation or degradation of 1,3,5-trimethoxybenzene.

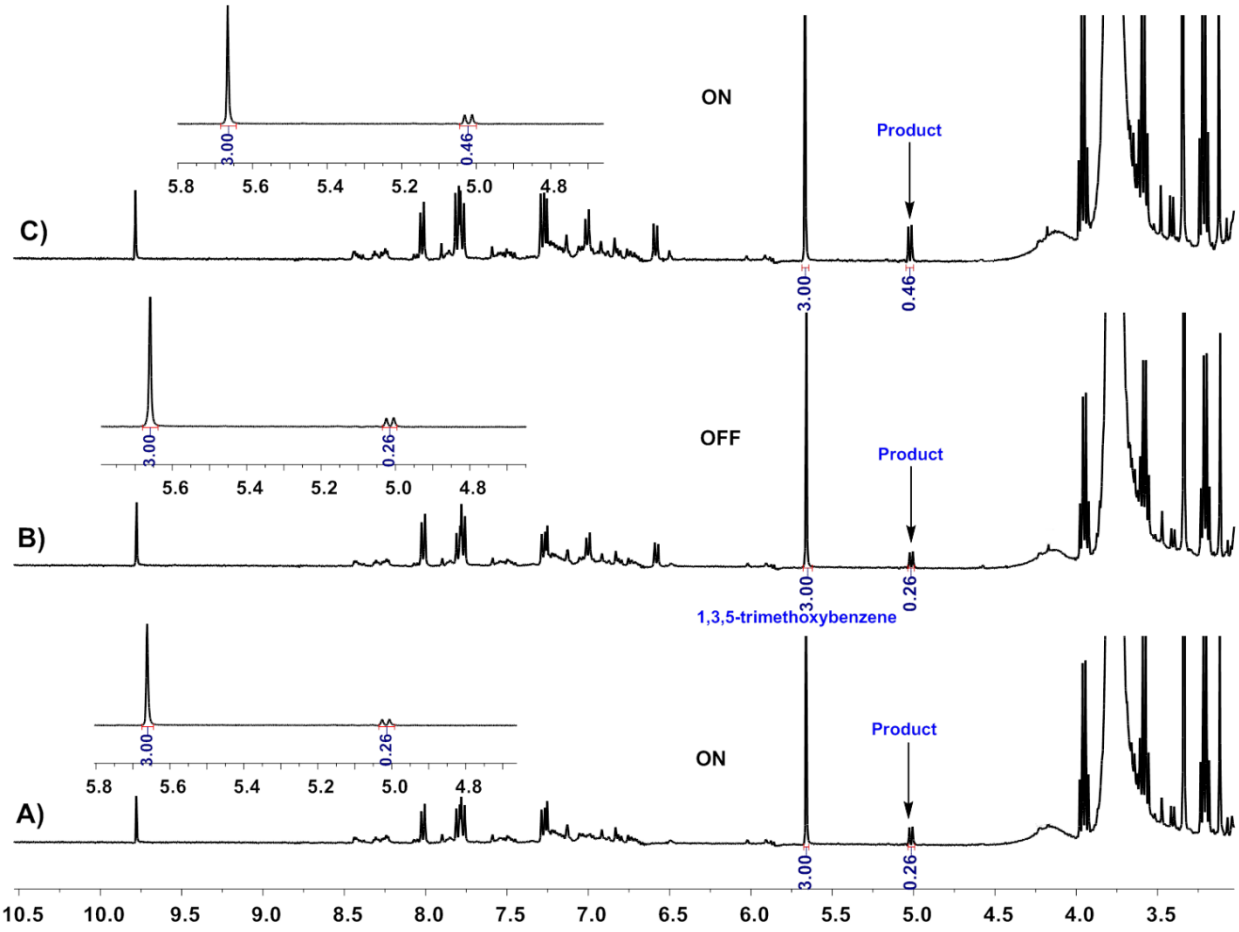


Figure S25. Catalytic experiment **A15:** Partial ^{1}H NMR (400 MHz, $CDCl_3$, 298 K) spectrum obtained after A) heating the reaction mixture of piperidine (**3**), nanoswitch **1**, nanoswitch **2**, $[Cu(CH_3CN)]B(C_6F_5)_4$, 1,3,5-trimethoxybenzene, **4** and **5** in 0.90:1:1:1:10:10:1000 ratio at 55 °C for 2 h shows formation of product **6** in 26% yield. The spectrum after B) heating and oxidation did not show any increase in product **6** (total yield = 26% yield). The spectrum after C) heating and reduction showed that product **6** was formed in 20% extra yield (total yield = 46% yield).

4. ESI-MS Spectra

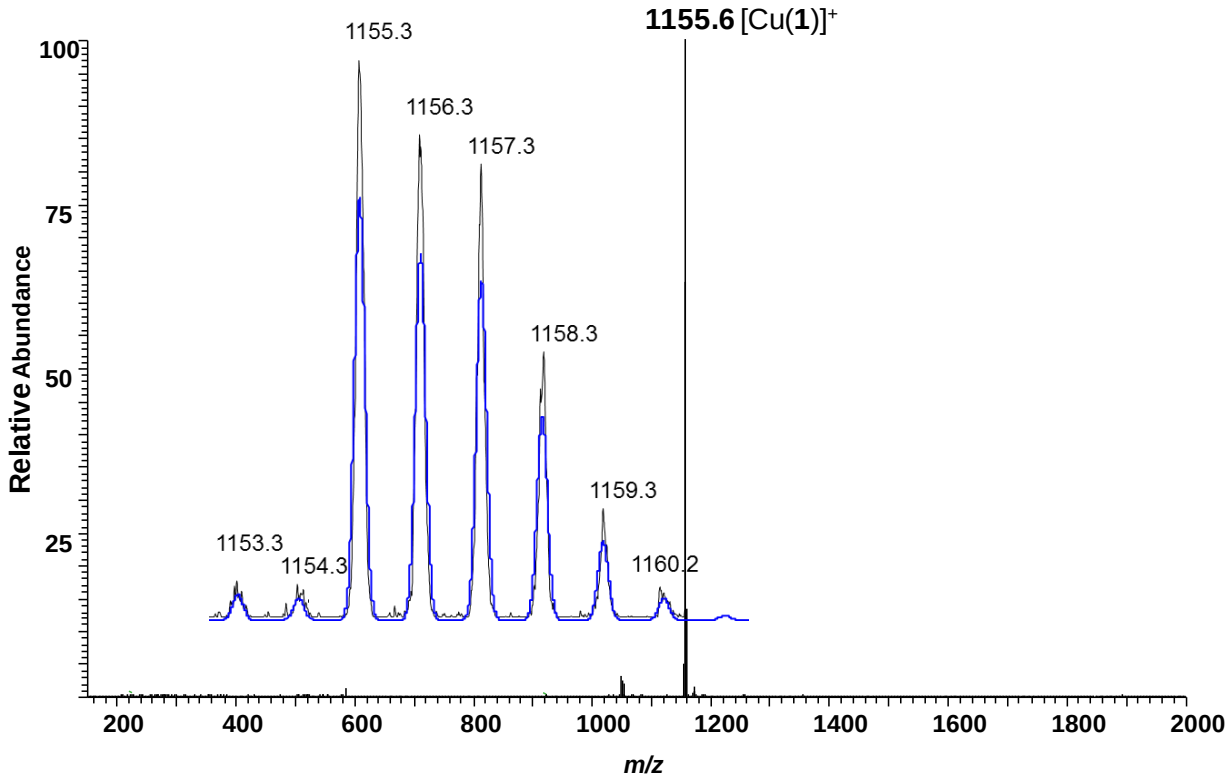


Figure S26. ESI-MS spectrum of [Cu(**1**)]$^{+}$ complex in dichloromethane.

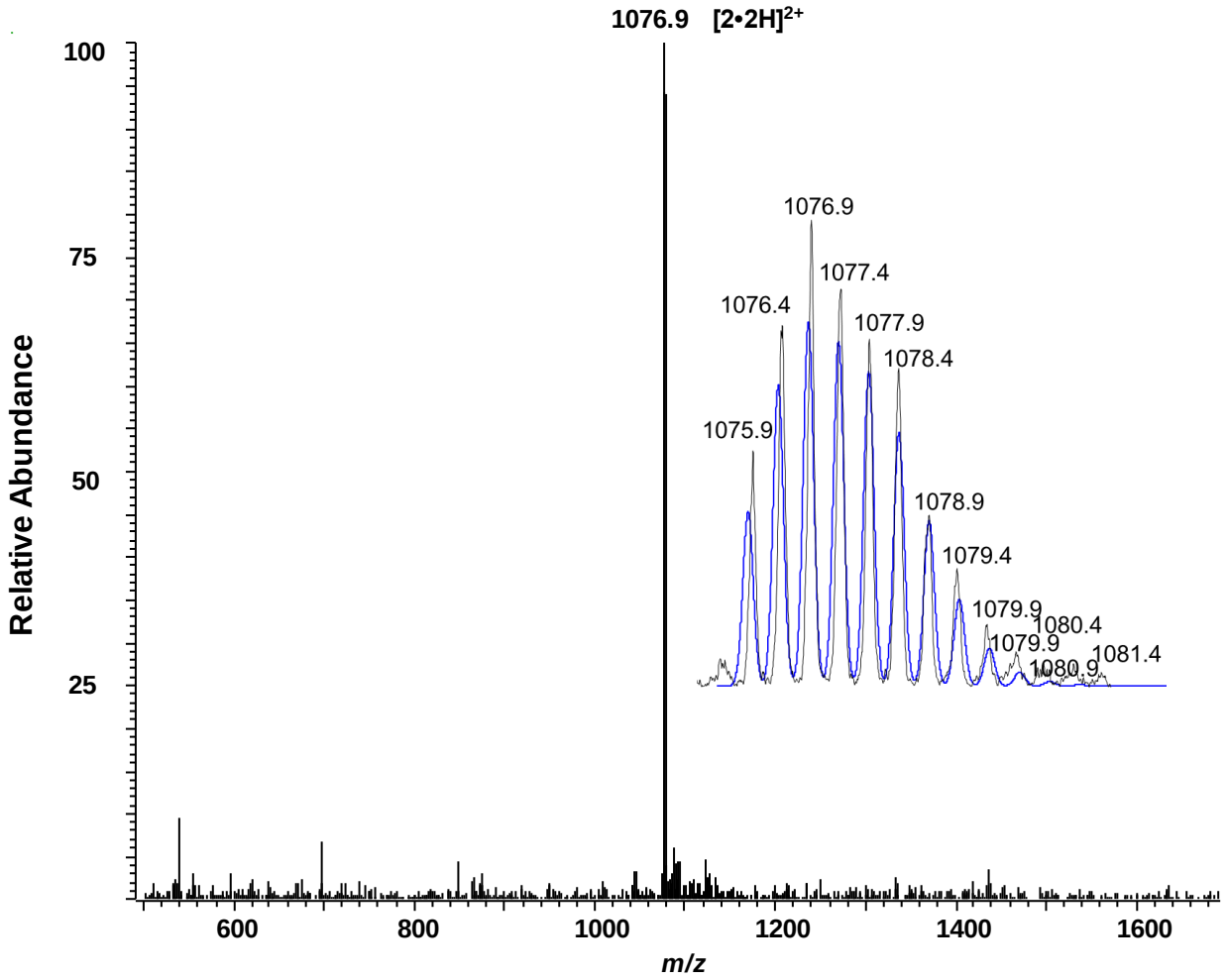


Figure S27. ESI-MS spectrum of nanoswitch **2** after protonation (in dichloromethane).

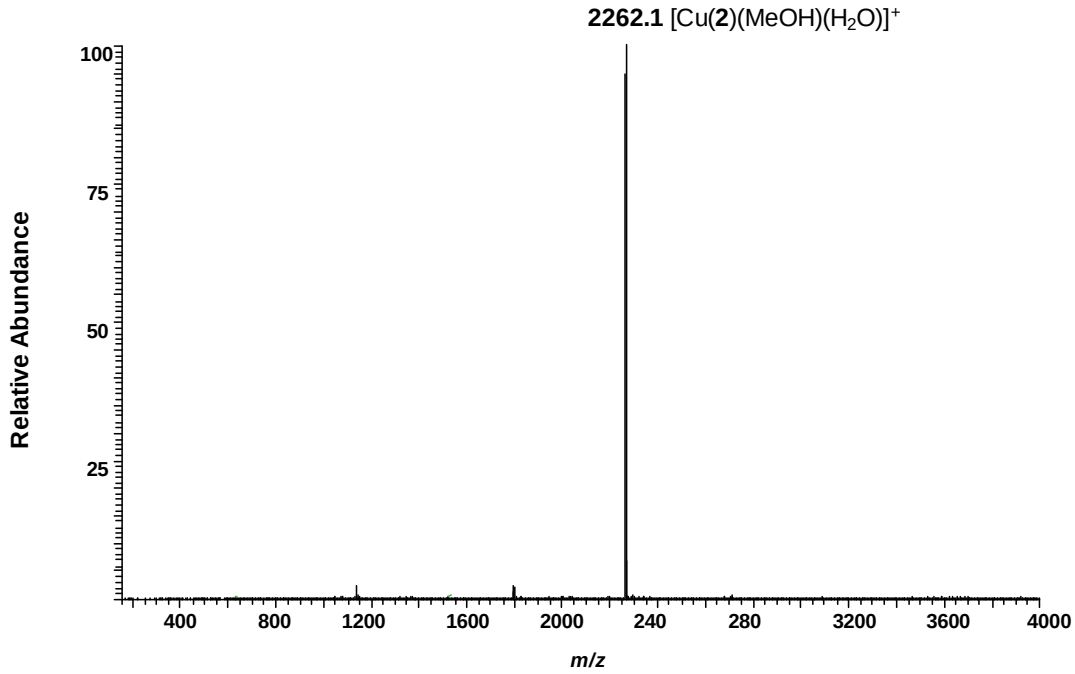


Figure S28. ESI-MS spectrum of $[Cu(\mathbf{2})]^+$ complex in dichloromethane.

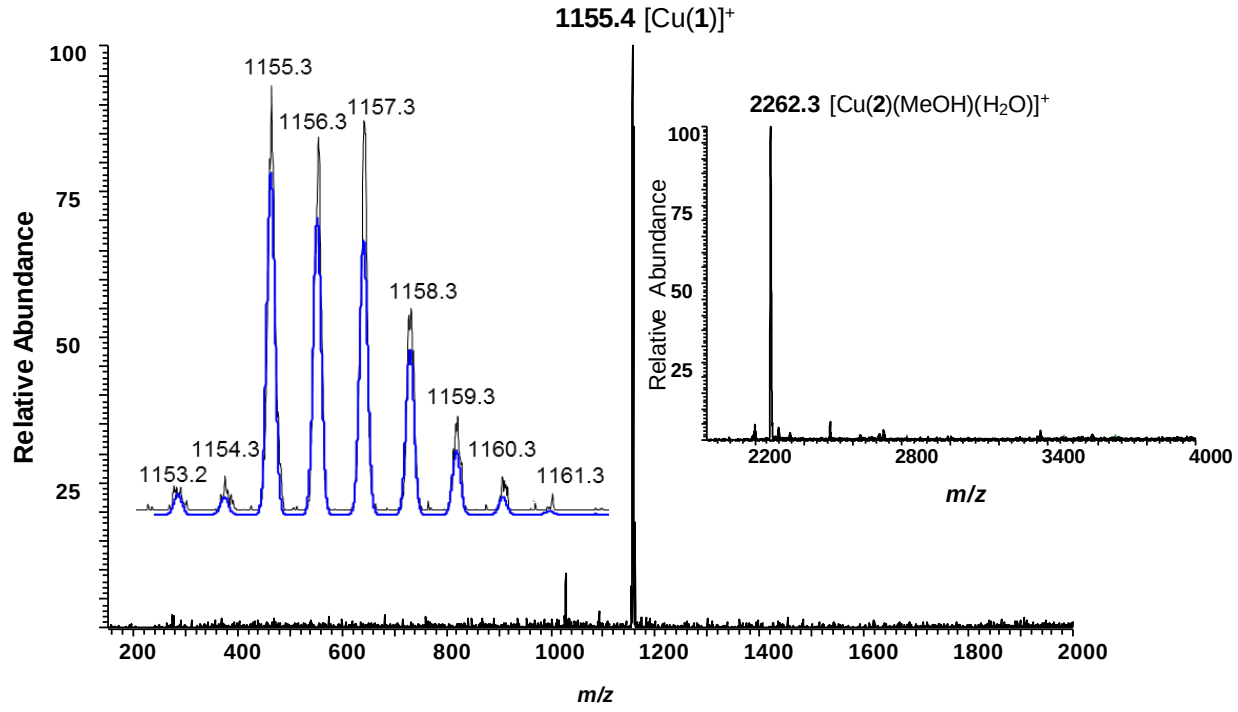


Figure S29. ESI-MS spectrum of 1:1:1 mixture of nanoswitch **1**, nanoswitch **2** and $[Cu(CH_3CN)_4]B(C_6F_5)_4$ in dichloromethane.

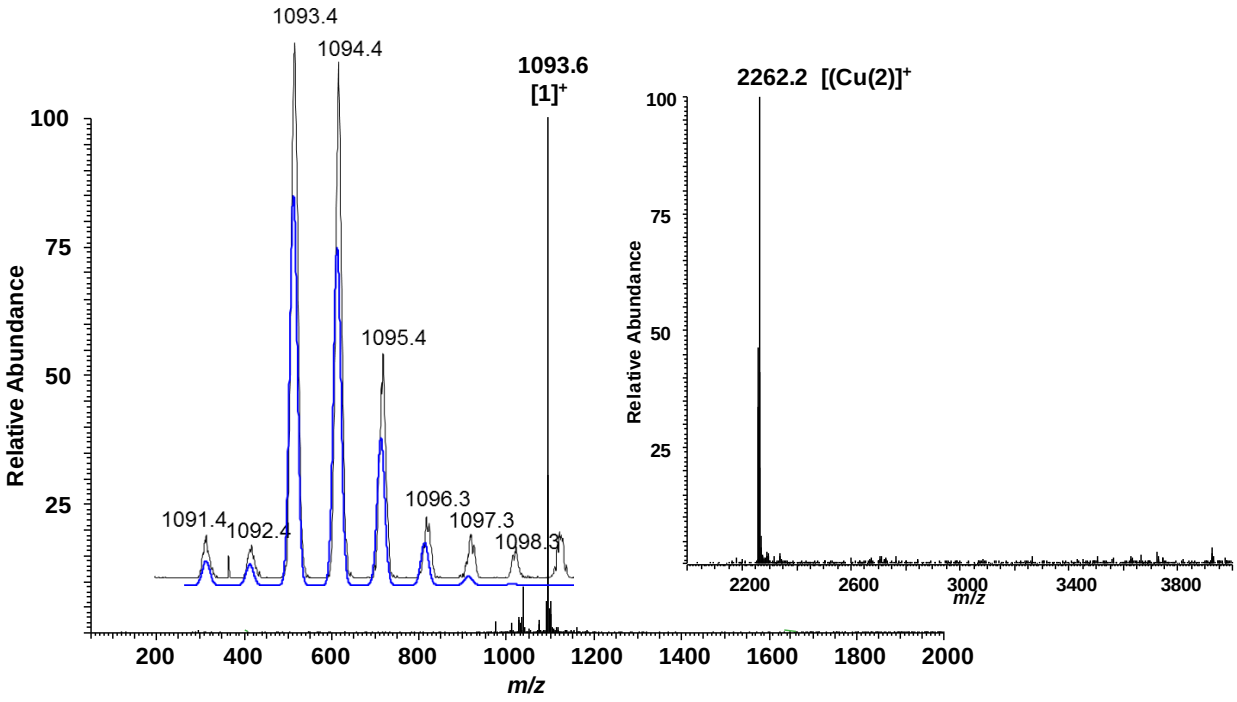


Figure S30. ESI-MS spectrum obtained after oxidation of **NetState I** that leads to formation of $[(\mathbf{1})]^{+}$ and $[\mathrm{Cu}(\mathbf{2})]^{+}$.

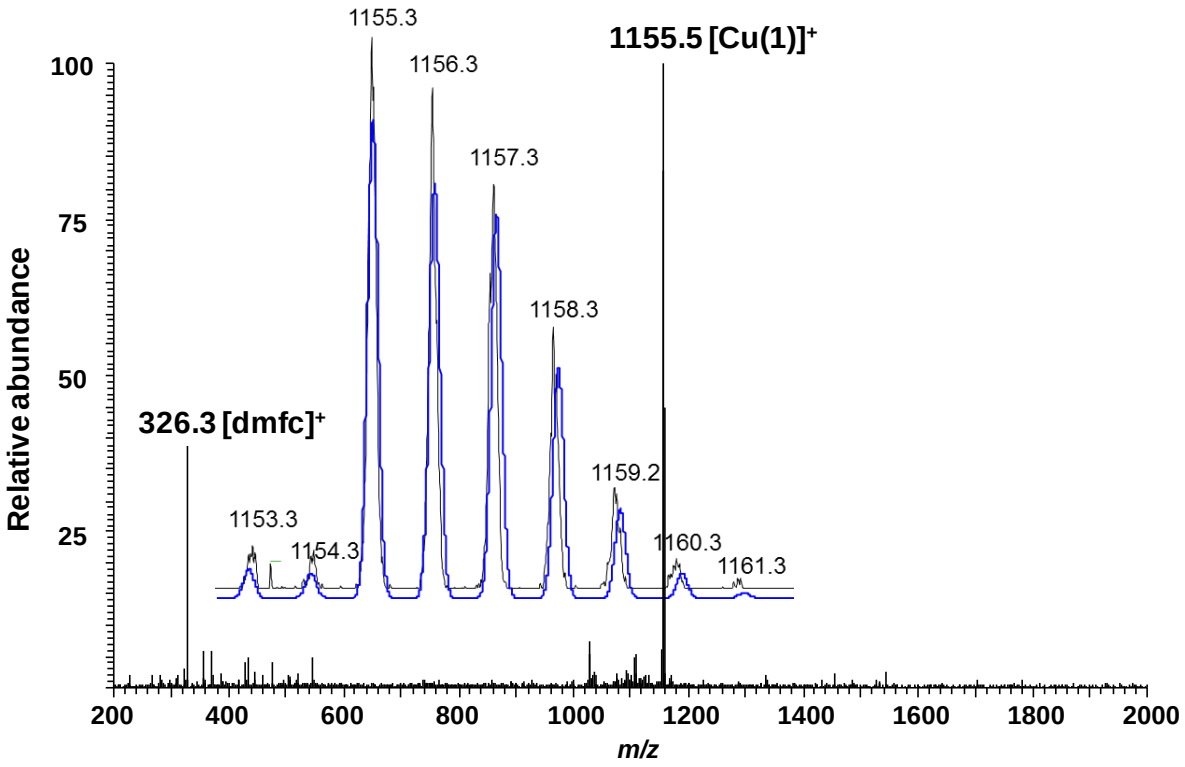


Figure S31. ESI-MS spectrum obtained after reduction of state II that leads formation of $[Cu(\mathbf{1})]^{+}$.

5. UV-vis Spectra

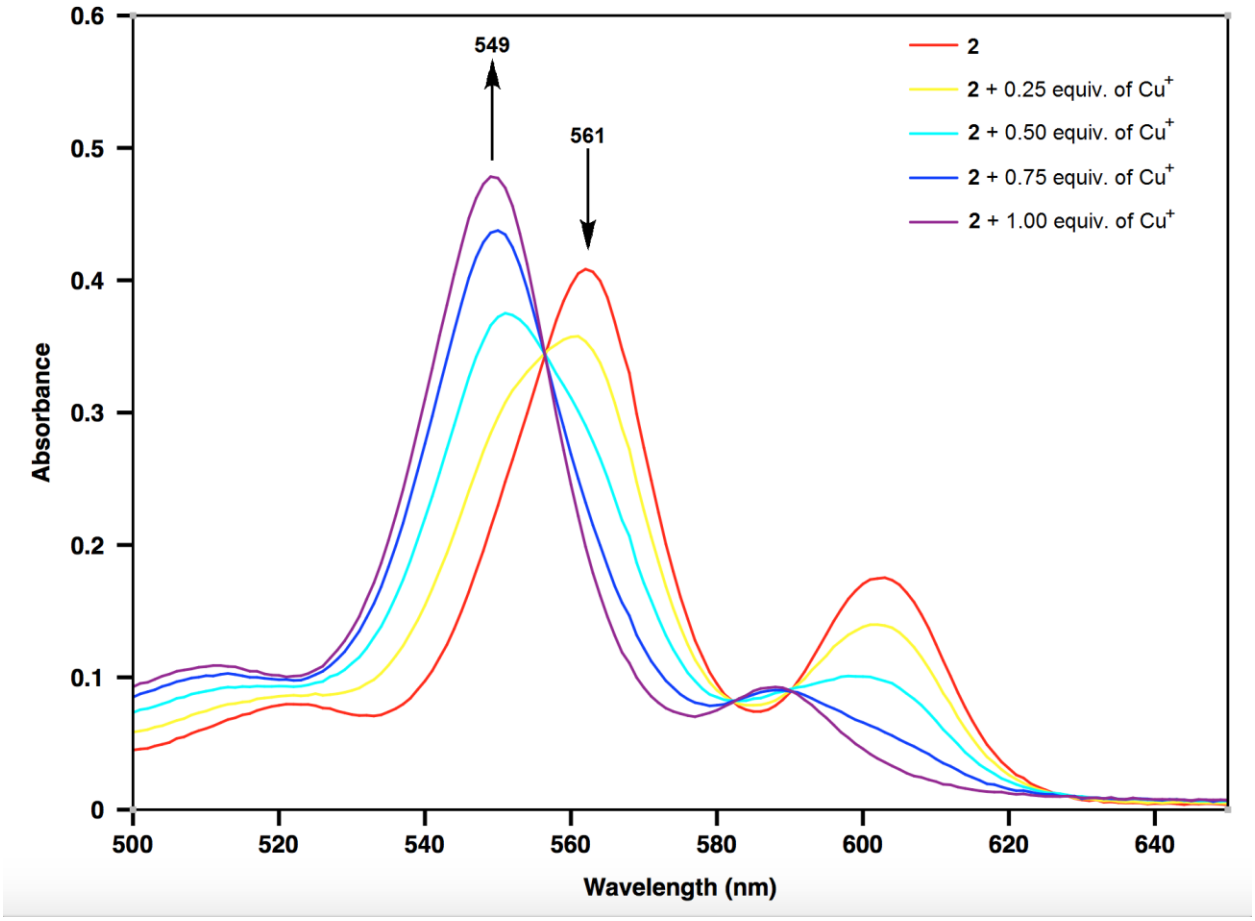


Figure S32. UV-vis titration of nanoswitch **2** (1×10^{-4} M) vs. copper(I) salt (2.5×10^{-3} M) in dichloromethane at 298 K. (Cu^{+} = $[Cu(CH_3CN)_4PF_6]$)

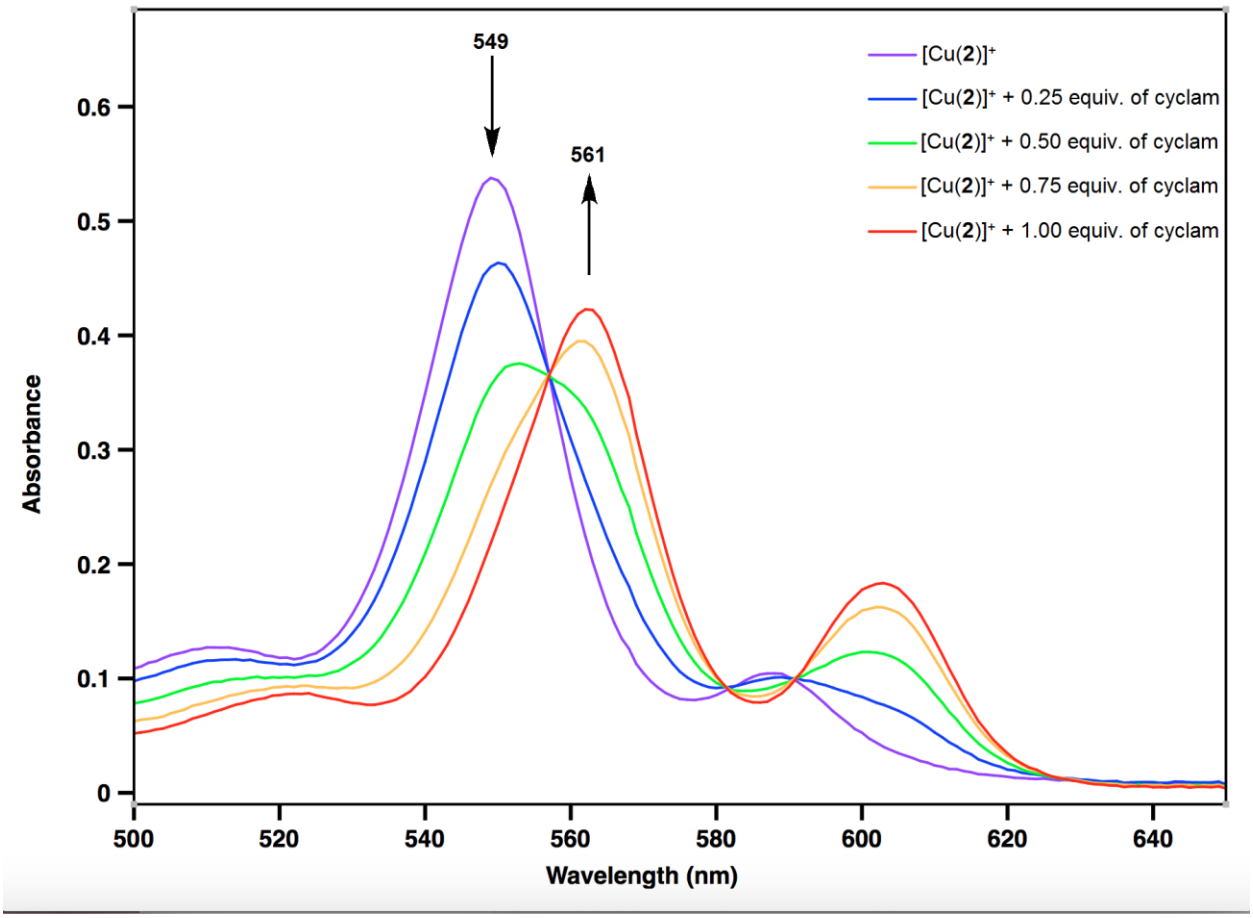


Figure S33. UV-vis titration of $[Cu(\mathbf{2})]^{+}$ complex (1×10^{-4} M) vs. cyclam (2.5×10^{-3} M) in dichloromethane at 298 K.

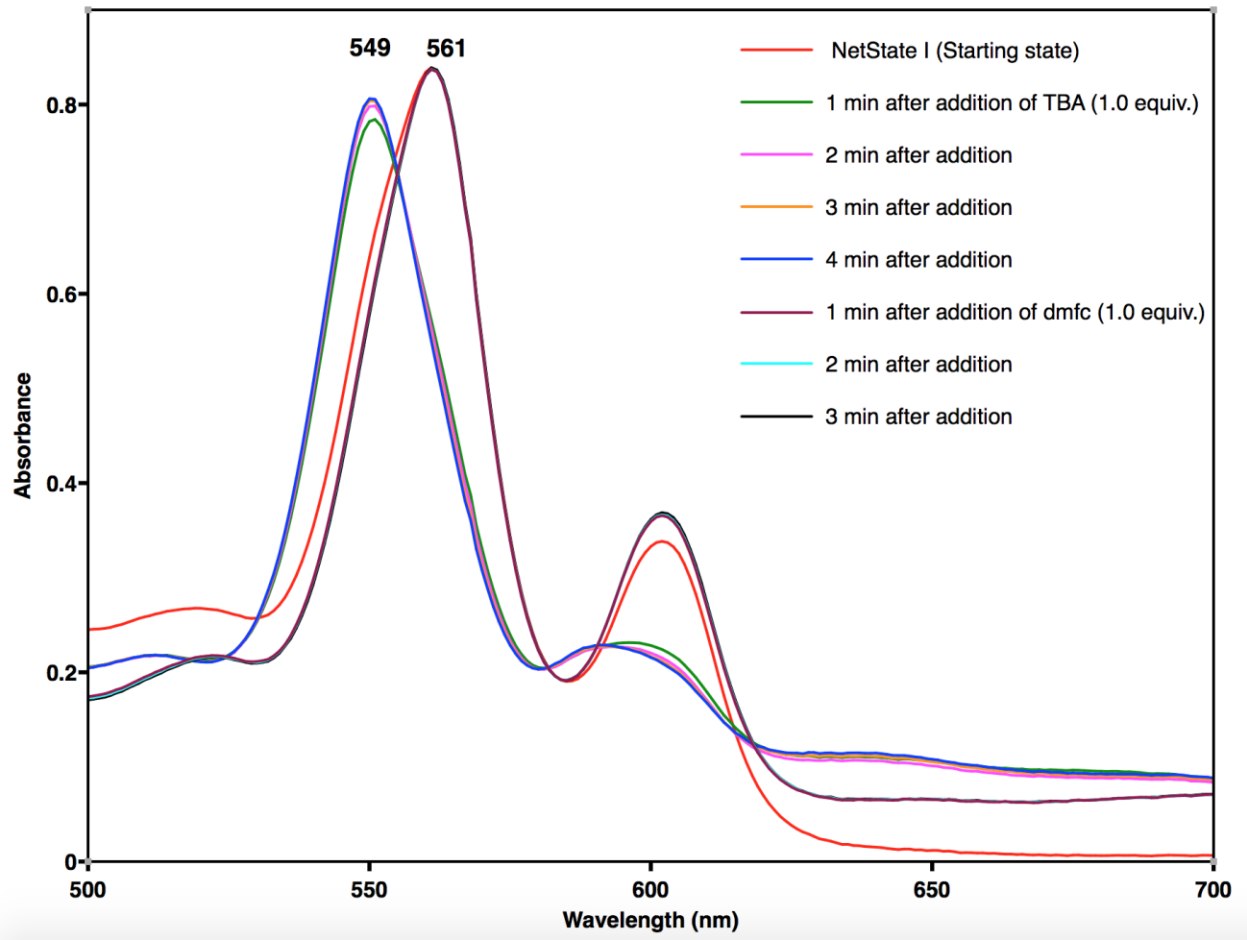


Figure S34. UV-vis spectra showing reversible copper(I) ion translocation between **1** and **2**.

To a solution of nanoswitches **1** (215 µg, 0.100 µmol) and **2** (111 µg, 0.100 µmol) in dichloromethane (500 µl, $c = 2\times 10^{-4}$ M) was added 1.0 equiv. of $[Cu(CH_3CN)_4]B(C_6F_5)_4$ (91 µg, 0.100 µmol) affording **NetState I** = $[Cu(\mathbf{1})]^+$ and **2** (red trace). The UV-vis spectra display the Q-band region. Then, the solution was treated with 1.0 equiv. of $TBA^{+\bullet}SbCl_6^-$ (82 µg, 0.100 µmol). The Q-band at 561 nm completely shifted to 549 nm after 4 min (magenta trace) what confirms the formation of **NetState II** = $[(\mathbf{1})]^+$ and $[Cu(\mathbf{2})]^+$. This shift is well agreement with copper(I) ion induced toggling of the rotary arm from the ZnPor station to the phenanthroline station.[1] After reduction of **NetState II** with 1.0 equiv. of **dmfc** (33 µg, 0.100 µmol), the Q-band at 549 nm was fully shifted back to 561 nm within 1 min (brown trace) indicating reorganization of rotary arm due to translocation of copper(I) ions from $[Cu(\mathbf{2})]^+$ to nanoswitch **1**.

6. Measurements of binding constants

Determination of Log *K* of $[Cu(2)]^+$ complex and cyclam

A UV-vis titration was used to measure the binding constant between cyclam and $[Cu(\mathbf{2})]^+$. A solution of $[Cu(\mathbf{2})]^+$ complex (2×10^{-4} M) in CH_2Cl_2 was titrated with a solution of cyclam (5×10^{-3} M) in CH_2Cl_2. The data (475–700) was analyzed using the SPECFIT/32 global analysis system (Spectrum Software Associates, Marlborough, MA).

Δ log *K* = 7.45 ± 0.71

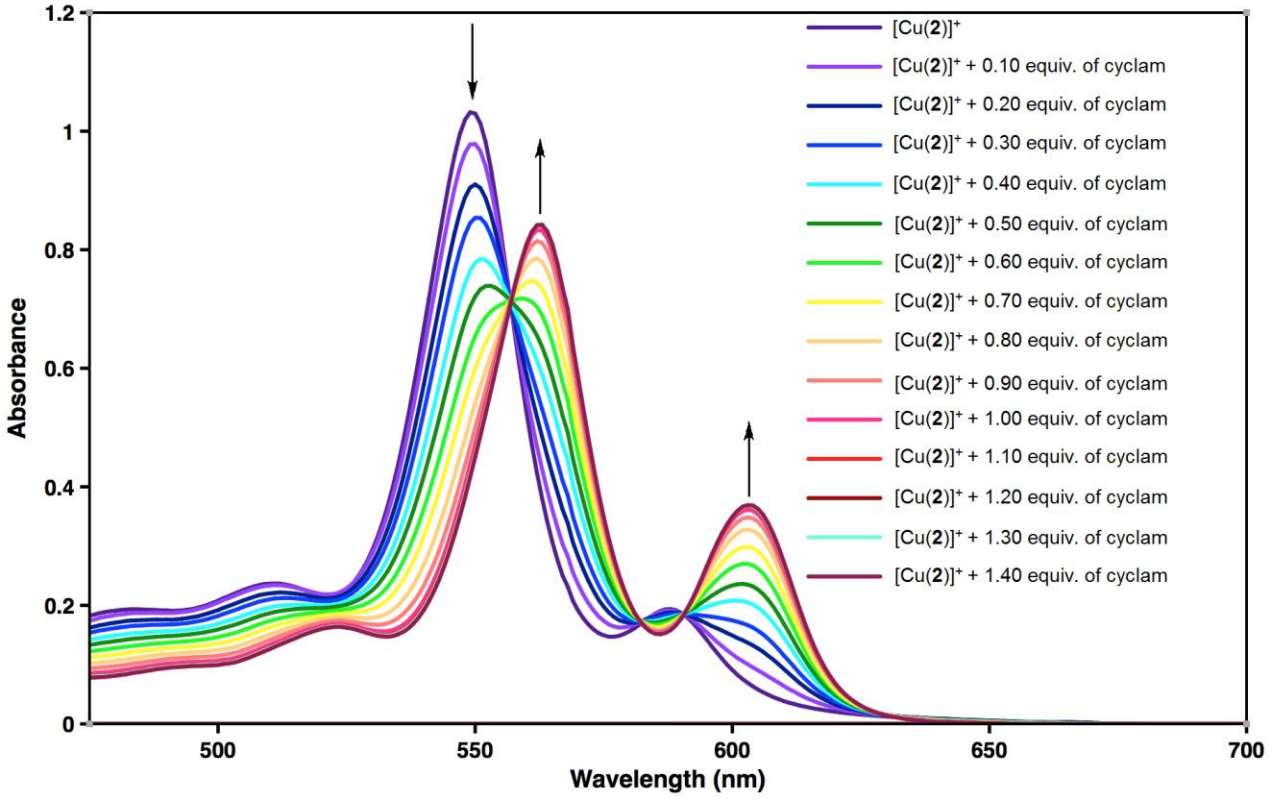
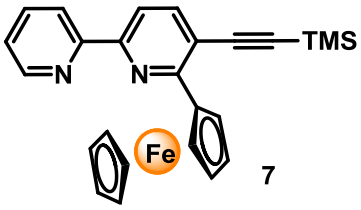


Figure S35. UV-vis titration between 2×10^{-4} M solution of $[Cu(\mathbf{2})]^+$ complex in CH_2Cl_2 and cyclam (5×10^{-3} M, CH_2Cl_2) at 298 K.

7. Cyclic Voltammetry

Cyclic voltammetry measurements were performed with a PARSTAT 2273 Advanced Electro-chemical System using a three-electrode set-up (1 mm Pt disk working electrode, a Pt auxiliary electrode, a silver wire as a pseudo-reference electrode). The compounds were dissolved in freshly distilled and degassed dichloromethane. All experiments were carried out in a solution containing 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. The values are provided against SCE using 2,4,6-triphenylpyrylium ($E_{+/0}$ = – 0.39 V vs SCE) as an internal standard.



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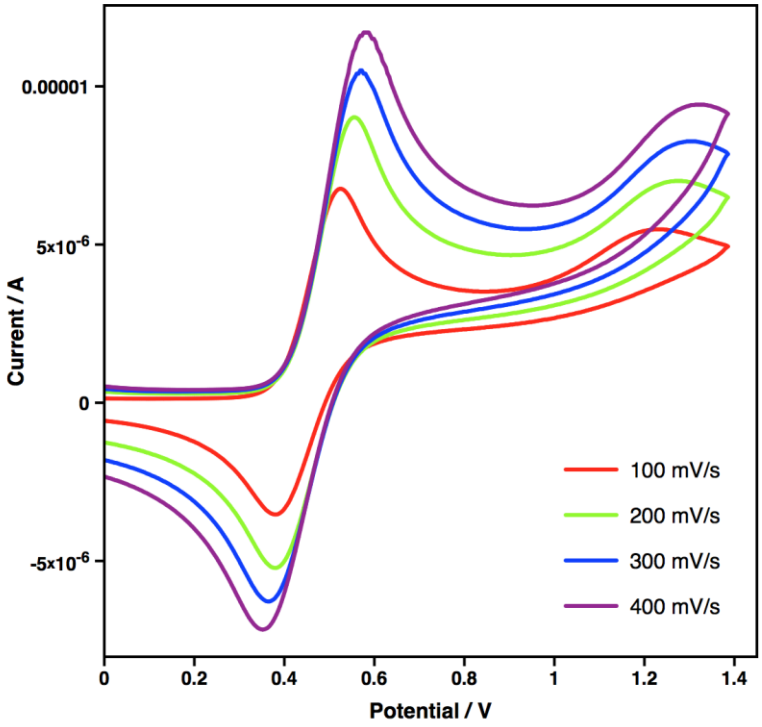

Figure S36. Cyclic voltammograms of 1:0.9 mixture of ligand **7**[1] and piperidine (**3**) at various scan rates in dry dichloromethane. $E_{1/2}^{Fc0/+}$ = 0.45 V_{SCE}. E_{pa} = 1.24 V_{SCE} at 100 mV/s.

8. Species distribution curves

The species distribution were calculated by the Hyperquad software HySS2009® version using binding constant log $K_{2\bullet3}$ = 2.66 ± 0.08 (at 298 K in dichloromethane). Always equivalent amounts of nanoswitch **2** and piperidine (**3**) were used in the simulations.

To investigate the communication-catalysis protocol at suitable concentrations, we calculated species distribution curves for **2** and **3** at concentrations from 1 to 10 mM (Figures S37–S39). The communication catalysis protocol was carried out at ~3 mM because (i) at lower concentration of **3** and [Cu(**2**)]$^+$ the OFF state of catalysis will not be achieved due to substantial dissociation of **3** from the intermolecular [Cu(**2**)(**3**)]$^+$ complex while (ii) at higher concentration of **2** and **3** the amount of released piperidine will drop (to 48% at 5 mM and 38% at 10 mM) and thus will drop its catalytic activity in NetState I.

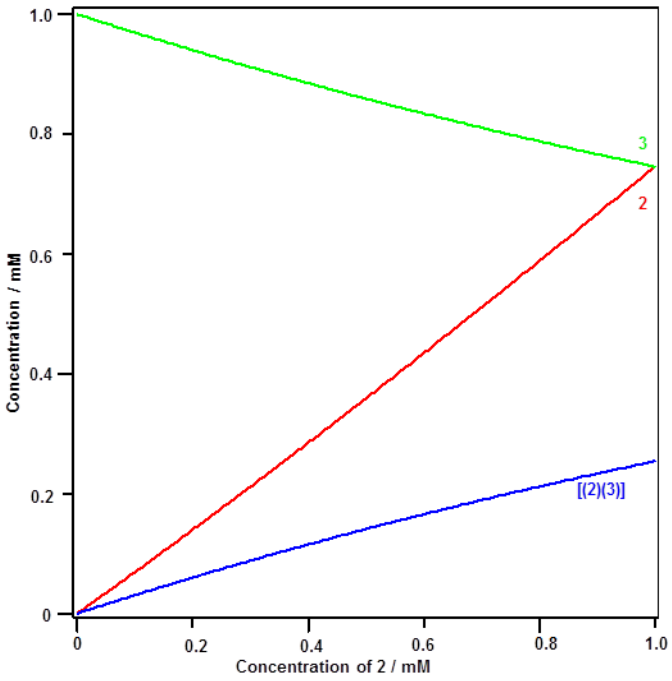

Figure S37. Calculated species distribution between nanoswitch **2** and piperidine (**3**) (0–1 mM).

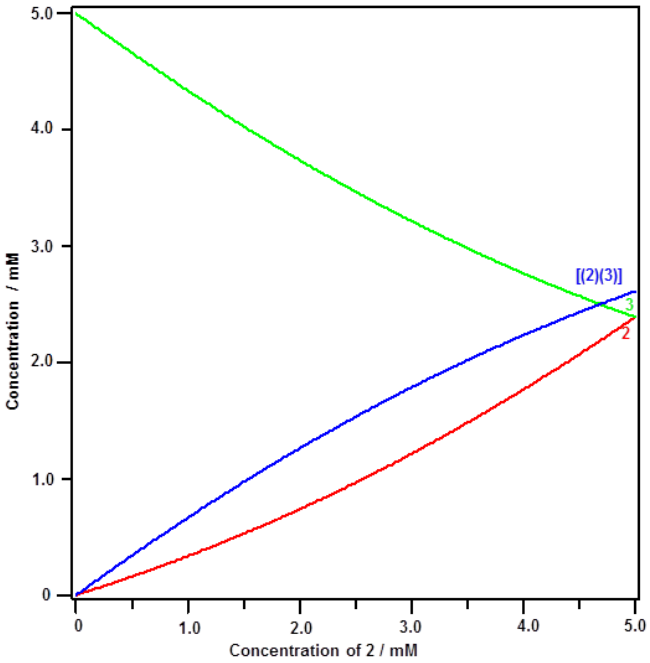

Figure S38. Calculated species distribution between nanoswitch **2** and piperidine (**3**) (0–5 mM).

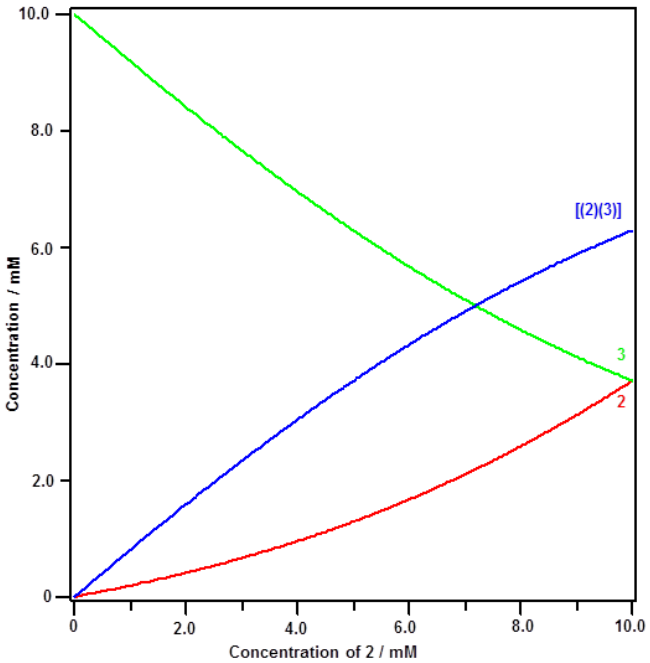

Figure S39. Calculated species distribution between nanoswitch **2** and piperidine (**3**) (0–10 mM).

8. References

1 S. Pramanik, S. De and M. Schmittel, *Chem. Commun.,* 2014, **50**, 13254–13257.

2 A) S. Gaikwad, A. Goswami, S. De, M. Schmittel, *Angew. Chem. Int. Ed.* 2016, **55**, 10512–10517; b) S. Gaikwad and M. Schmittel, *J. Org. Chem.,* 2017, **82**, 343–352.

3 S. Kinastowski, S. Wnuk, E. Kaczmarek, *Pol. J. Chem.* 1989, **63**, 495–503.

4 (a) R. Breuer and M. Schmittel, *Organometallics*, 2012, **31**, 6642–6651; (b) R. Breuer and M. Schmittel, *Organometallics*, 2013, **32**, 5980–5987.