Reversible Multicomponent AND Gate Triggered by Stoichiometric Chemical Pulses Commands the Self-Assembly and Actuation of Catalytic Machinery

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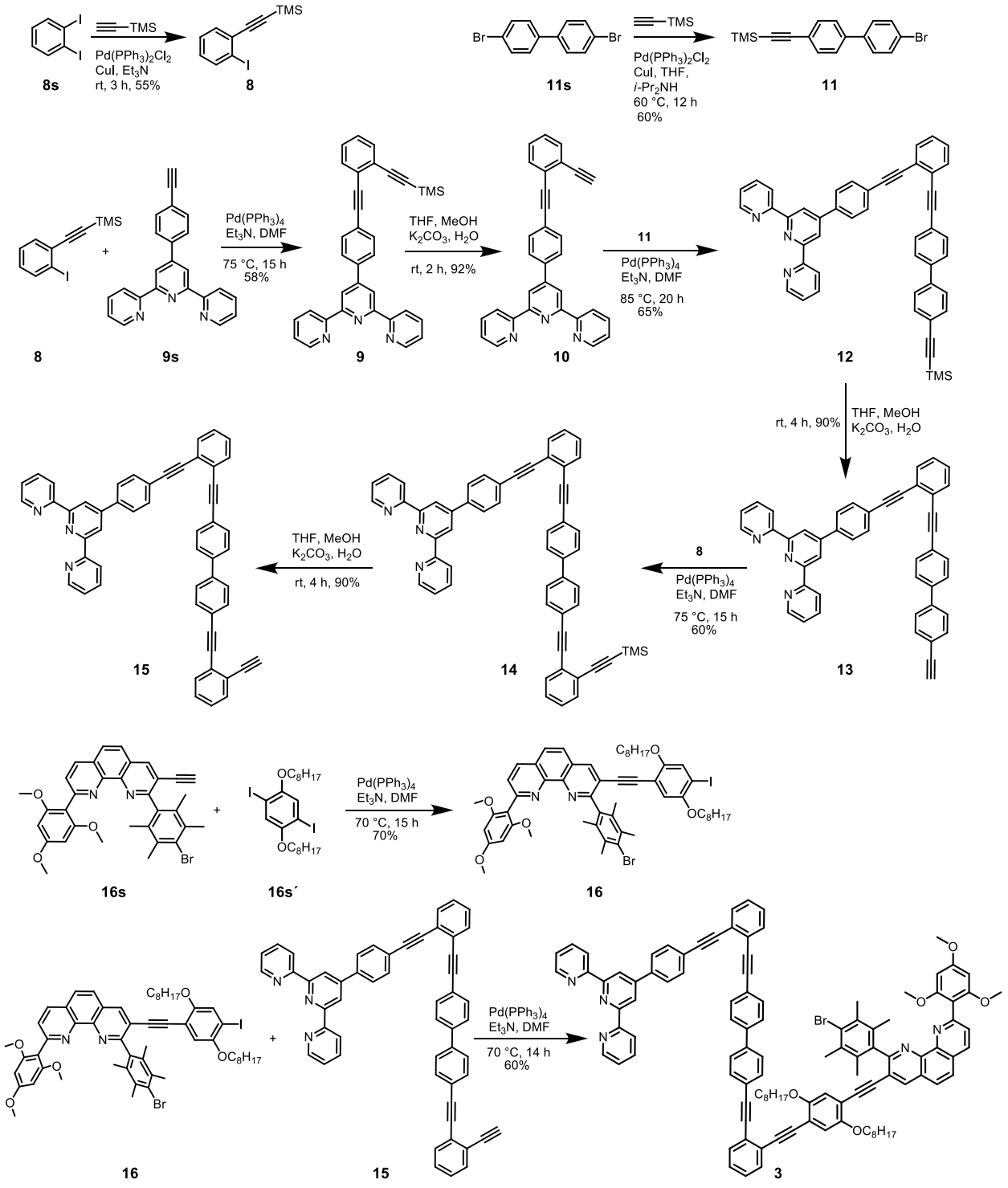
1. Synthesis

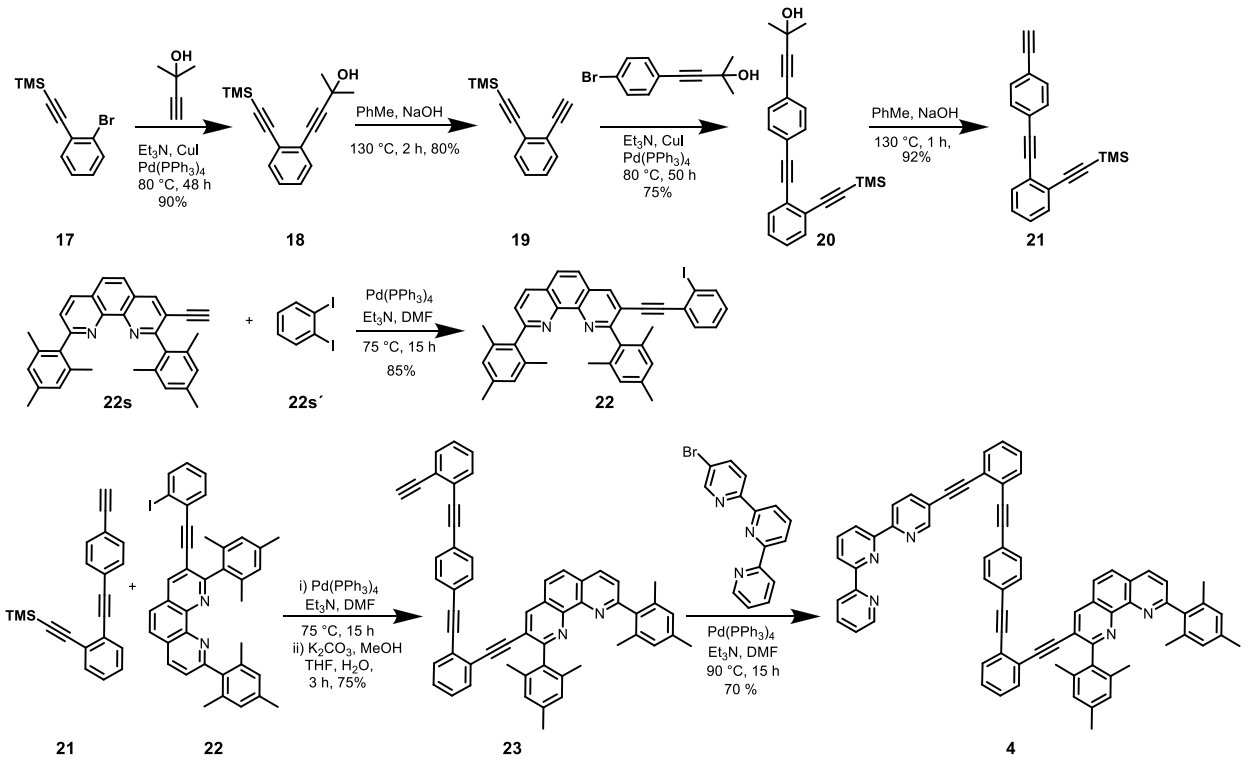
1.1 General information

All reagents were obtained from commercial suppliers and used without further purification. Technical grade solvents were distilled prior to use. Tetrahydrofuran (THF) was predried over basic alumina and then distilled over potassium. Dimethylformamide (DMF) and triethylamine (Et_3N) were distilled over calcium hydride. Diethyl ether (Et_2O) was predried over calcium hydride and then distilled from sodium. Melting points of compounds were measured using a Büchi SMP-11 instrument. ^1H, ^{13}C, and $^1H–^1H$ COSY NMR spectra were recorded on a Bruker Avance 400 and Jeol ECZ 500 at 298 K. DOSY NMR was recorded on a Varian VNMR-S600 MHz. Chemical shifts refer to the residual protiated fraction of the NMR solvent ($CDCl_3$: δ_H = 7.26 ppm, δ_C = 77.0 ppm; CD_2Cl_2: δ_H = 5.32 ppm, δ_C = 53.8 ppm). Abbreviations in ^1H NMR assignments are used 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) is reported in Hertz (Hz) and the number of protons are implied. Numbering of the carbon atoms is not in accordance with IUPAC nomenclature. UV-vis spectra were measured on Cary Win 50. Electrospray ionization-mass spectra (ESI-MS) were recorded on a Thermo-Quest LCQ Deca instrument. Infrared spectra were recorded using a Perkin Elmer Spectrum-Two FT-IR spectrometer. Column chromatography was performed on silica gel 60 (60−230 mesh) or on neutral alumina (0.05−0.15 mm, Brockmann Activity 1). Thin layer chromatography (TLC) was performed using Merck silica gel (60 F254) or on neutral Al_2O_3 (150 F254) sheets. Size exclusion chromatography was performed on BioRad Biobeads-SX3 using toluene or THF as an eluent.

1.2 Synthesis and characterization of ligands and complexes



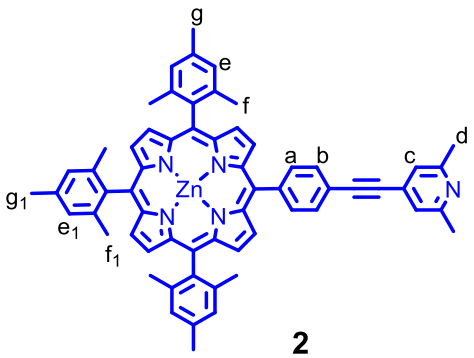
Scheme S1: Synthesis of nanoswitch **3**.



Scheme S2: Synthesis of nanoswitch **4**.

Synthesis of rotator 2

Zinc(II) 5-(4-((2,6-dimethylpyridin-4-yl)ethynyl)phenyl)-10,15,20-trimesitylporphyrin (**2**)



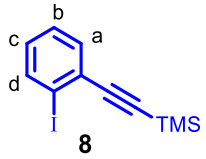
2

Zinc (II) 5-(4-iodophenyl)-10,15,20-trimesitylporphyrin (100 mg, 107 µmol) and 4-ethynyl-2,6-dimethylpyridine (70.5 g, 537 µmol) were dissolved in 15 mL of DMF and 15 mL of Et_3N in a sealed tube. The reaction mixture was degassed by the freeze-pump-thaw method three times. Then, $Pd(PPh_3)_4$ (24.7 mg, 21.4 µmol) was added, a further freeze-pump-thaw cycle applied and

the mixture allowed to stir at 75 °C for 12 h. All the solvents were then evaporated under vacuum. After adding dichloromethane and ice cold water, the organic part was dried over anhydrous Na_2SO_4. Firstly, the crude product was separated by column chromatography using 40% dichloromethane/hexane (R_f = 0.40, SiO_2, 40% dichloromethane /hexane) and secondly purified by size exclusion chromatography using SX-3 biobead to afford the pure compound **2** in 65% (65 mg, 70.0 µmol) yield. **IR (KBr)**: $\tilde{\nu}$ = 559, 722, 762, 799, 831, 852, 998, 1062, 1204, 1335, 1382, 1438, 1478, 1523, 1551, 1600, 2211, 2732, 2855, 2917, 2948 cm^{-1}. **Mp.** > 250 ºC. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 1.85 (s, 12H, f-H), 1.86 (s, 6H, f_1-H), 2.58 (s, 6H, d-H), 2.64 (s, 9H, [g+g_1]-H), 7.24 (s, 2H, c-H), 7.28 (s, 6H, [e+e_1]-H), 7.92 (d, ^3J = 8.0 Hz, 2H, b-H), 8.24 (d, ^3J = 8.0 Hz, 2H, a-H), 8.72 (s, 4H, β-H), 8.78 (d, ^3J = 5.6 Hz, 2H, β-H), 8.86 (d, ^3J = 5.6 Hz, 2H, β-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 21.5, 21.7 (2C), 21.8, 24.3, 88.1, 93.1, 118.8, 118.9, 121.3, 122.2, 127.6 (2C), 130.0, 130.8, 131.1, 131.2, 131.7, 131.9, 134.5 (2C), 137.4 (2C), 138.9, 139.0, 139.3 (2C), 144.0, 149.5, 149.7, 149.9, 150.0, 157.9 ppm. **Elemental analysis:** Anal. Calcd for $C_{62}H_{53}N_5Zn$: C, 79.77; H, 5.72; N, 7.50. Found: C, 79.71; H, 5.63; N, 7.23. **ESI-MS:** *m/z* (%) 933.0 (100) $[M+H]^+$.

Synthesis of nanoswitch 3

((2-Iodophenyl)ethynyl)trimethylsilane (**8**)[1]

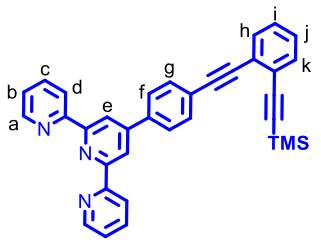


8

In a sealed tube, 1,2-diiodobenzene (10.0 g, 30.3 mmol) was dissolved in 200 mL of Et_3N. The solution was deaerated for 30 min with a continuous flow of nitrogen gas. To this solution, $Pd(PPh_3)_2Cl_2$ (213 mg, 303 µmol) and CuI (57.7 mg, 303 µmol) were added. Finally trimethylsilylacetylene (6.50 mL, 45.4 mmol) was added and the mixture stirred for 3 h at room temperature. After evaporation of the solvent in vacuum, the product was separated (5.00 g, 16.7 mmol, 55%) by column chromatography on silica gel using hexane as eluent (R_f = 0.40, SiO_2, *n*-hexane). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 0.28 (s, 9H, TMS-H), 6.99 (td, ^3J = 8.0 Hz, ^4J = 1.6

Hz, 1H, b-H), 7.28 (td, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 1H, c-H), 7.47 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 1H, d-H), 7.83 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 1H, a-H) ppm.

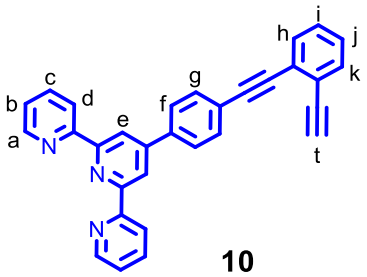
4'-(4-((2-((Trimethylsilyl)ethynyl)phenyl)ethynyl)phenyl)-2,2':6',2''-terpyridine (**9**)



9

Compounds 4'-(4-ethynylphenyl)-2,2':6',2''-terpyridine (800 mg, 2.40 mmol) and **8** (1.64 g, 7.20 mmol) were placed in a sealed tube that was evacuated and filled with N_2. Then freshly distilled Et_3N (20 mL) and DMF (15 mL) were added. The solution was degassed twice by using the freeze-pump-thaw method. Finally, $Pd(PPh_3)_4$ (277 mg, 240 µmol) was added to this mixture that was allowed to stir at 75 °C for 15 h. After cooling to room temperature the solvents were removed under reduced pressure. The residue was extracted in DCM (75 mL) and washed with ice-cold water (75 mL) and brine (30 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated. The column chromatographic purification of the crude product on silica gel using 40% ethyl acetate in hexane (R_f = 0.30, SiO_2, 40% ethyl acetate/hexane) afforded compound **9** as a colorless solid in 58% yield (705 mg, 1.39 mmol). **IR (KBr)**: $\tilde{\nu}$ = 621, 670, 758, 791, 843, 1038, 1093, 1208, 1248, 1386, 1411, 1442, 1467, 1514, 1566, 1584, 1603, 2158, 2214, 2852, 2920, 2954, 3057 cm^{-1}. **Mp**. > 250 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 0.30 (s, 9H, TMS-H), 7.27–7.34 (m, 2H, [i+j]-H), 7.37 (ddd, ^3J = 7.6 Hz, ^3J = 4.8 Hz, ^4J = 1.0 Hz, 2H, b-H), 7.52–7.58 (m, 2H, [h+k]-H), 7.71 (d, ^3J = 8.4 Hz, 2H, g-H), 7.89 (td, ^3J = 7.6 Hz, ^4J = 1.8 Hz, 2H, c-H), 7.93 (d, ^3J = 8.4 Hz, 2H, f-H), 8.69 (ddd, ^3J = 7.6 Hz, ^4J = 1.0 Hz, ^5J = 1.0 Hz, 2H, d-H), 8.75 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 1.0 Hz, 2H, a-H), 8.76 (s, 2H, e-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 0.07, 89.6, 93.1, 98.8, 103.4, 118.6, 121.3, 123.9, 124.1, 125.7, 125.9, 127.2, 128.0, 128.2, 131.7, 132.2, 132.3, 136.9, 138.2, 149.1, 149.4, 156.0, 156.1 ppm. **Elemental analysis:** Anal. Calcd. for $C_{34}H_{27}N_3Si$: C, 80.75; H, 5.38; N, 8.31. Found: C, 81.01; H, 5.55; N, 8.10. **ESI-MS:** *m/z* (%) 506.7 (100) $[M+H]^+$.

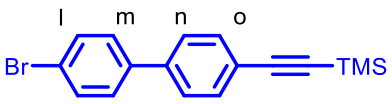
4'-(4-((2-Ethynylphenyl)ethynyl)phenyl)-2,2':6',2''-terpyridine (**10**)



10

Compound **9** (600 mg, 1.19 mmol) was dissolved in 30 mL of THF. To this solution, K_2CO_3 (820 mg, 5.93 mmol) dissolved in 20 mL of water and 30 mL of methanol was added. The reaction mixture was stirred at rt for 2 h. The organic solvents were evaporated under vacuum. The crude was then extracted with dichloromethane. It was passed through a small pad of SiO_2 using 40% ethyl acetate/hexane furnishing the colorless solid compound **10** in 92% yield (475 mg, 1.09 mmol). **IR (KBr)**: $\tilde{\nu}$ = 615, 788, 843, 1038, 1085, 1209, 1250, 1385, 1410, 1445, 1467, 1515, 1567, 1585, 1605, 2160, 2215, 2850, 2920, 2952, 3055 cm^{-1}. **Mp.** > 250 ºC. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 3.43 (s, 1H, t-H), 7.30 (td, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1H, [i/j]-H), 7.32–7.37 (m, 3H, [b+j/i]-H), 7.54–7.58 (m, 2H, [h+k]-H), 7.70 (d, ^3J = 8.4 Hz, 2H, g-H), 7.86 (td, ^3J = 8.0 Hz, ^4J = 1.8 Hz, 2H, c-H), 7.90 (d, ^3J = 8.4 Hz, 2H, f-H), 8.66 (ddd, ^3J = 8.0 Hz, ^4J = 1.0 Hz, ^5J = 1.0 Hz, 2H, d-H), 8.73 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 1.0 Hz, 2H, a-H), 8.74 (s, 2H, e-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 81.3, 82.1, 89.3, 93.2, 118.6, 121.3, 123.8, 124.6, 126.1, 127.2, 128.0, 128.5, 131.8, 132.3, 132.6, 136.8, 138.3, 149.2 (2C), 149.3, 155.9, 156.0 ppm. **Elemental analysis:** Anal. Calcd. for $C_{31}H_{19}N_3 \bullet 0.5H_2O$: C, 84.14; H, 4.56; N, 9.49. Found: C, 84.41; H, 4.95; N, 9.10. **ESI-MS:** *m/z* (%) 434.5 (100) $[M+H]^+$.

((4'-Bromo-[1,1'-biphenyl]-4-yl)ethynyl)trimethylsilane (**11**)[2]

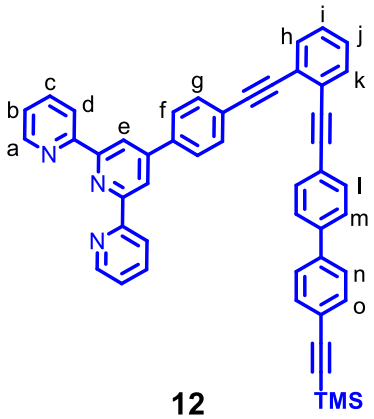


11

In a sealed tube, 4,4′-dibromobiphenyl (3.56 g, 11.4 mmol) was dissolved in 30 mL of THF and 50 mL of diisopropylamine. It was deaerated for 20 min using N_2 gas flow. To this solution,

$Pd(Ph_3)_2Cl_2$ (800 mg, 1.14 mmol) and CuI (217 mg, 1.14 mmol) were added and finally trimethylsilylacetylene (1.80 mL, 12.6 mmol). Then it was stirred at 60 °C for 12 h. All the solvents were evaporated under vacuum. The crude mixture was worked up using dichloromethane and water. The organic solution was evaporated and the product was separated by column chromatography (R_f = 0.60, SiO_2, hexane) using hexane as eluent with 60% yield (2.25 g, 6.84 mmol). **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 0.28 (s, 9H, TMS-H), 7.44 (d, ^3J = 8.8 Hz, 2H, l-H), 7.49 (d, ^3J = 8.8 Hz, 2H, m-H), 7.53 (d, ^3J = 8.8 Hz, 2H, n-H), 7.56 (d, ^3J = 8.8 Hz, 2H, o-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 0.04, 95.2, 104.7, 121.9, 122.4, 126.6, 128.6, 131.9, 132.5, 139.2, 139.9 ppm.

4'-(4-((2-((4'-((Trimethylsilyl)ethynyl)-[1,1'-biphenyl]-4-yl)ethynyl)phenyl)ethynyl)phenyl)-2,2':6',2''-terpyridine (**12**)

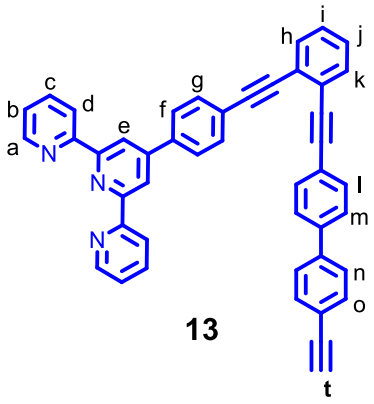


12

Compounds **10** (800 mg, 1.84 mmol) and **11** (3.03 g, 9.22 mmol) were dissolved in 15 mL of DMF and 15 mL of Et_3N in a sealed tube. The reaction mixture was degassed by freeze-pump-thaw method three times. Then, $Pd(PPh_3)_4$ (212 mg, 184 nmol) was added. After a further freeze-pump-thaw treatment, the mixture was allowed to stir at 85 °C for 20 h. All the solvents were then evaporated under vacuum. The crude product was worked up with dichloromethane and ice cold water. The organic part was dried over anhydrous Na_2SO_4. Finally, the product was separated by column chromatography using 30% ethyl acetate/hexane (R_f = 0.30, SiO_2, 30% ethyl acetate /hexane) furnishing the colorless solid in 65% (815 mg, 1.20 mmol) yield. **IR (KBr)**: $\tilde{\nu}$ = 660, 822, 840, 758, 792, 863, 1035, 1249, 1384, 1468, 1493, 1514, 1567, 1585, 2027, 2157, 2214, 2310,

2853, 2924, 2958 cm^{-1}. **Mp.** > 250 ºC. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 0.26 (s, 9H, TMS-H), 7.34–7.39 (m, 4H, [i+j+b]-H), 7.53 (d, ^3J = 8.4 Hz, 2H, o-H), 7.55–7.62 (m, 6H, [h+k+n+o]-H), 7.63 (d, ^3J = 8.4 Hz, 2H, m-H), 7.67 (d, ^3J = 8.4 Hz, 2H, l-H), 7.73 (d, ^3J = 8.4 Hz, 2H, g-H), 7.90 (td, ^3J = 8.0 Hz, ^4J = 2.0 Hz, 2H, c-H), 7.93 (d, ^3J = 8.4 Hz, 2H, f-H), 8.69 (ddd, ^3J = 8.0 Hz, ^4J = 1.0 Hz, ^5J = 0.8 Hz, 2H, d-H), 8.74 (ddd, ^3J = 4.8 Hz, ^4J = 2.0 Hz, ^5J = 0.8 Hz, 2H, a-H), 8.76 (s, 2H, e-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 0.03, 89.3, 89.8, 93.3, 93.6, 95.1, 104.9, 118.6, 121.4, 122.4, 122.6, 123.9, 124.1, 125.7, 125.9, 126.8, 127.0, 127.3, 128.1, 128.2, 131.8 (2C), 132.1, 132.2, 132.5 (2C), 136.9, 138.3, 140.2, 149.1, 149.3, 156.0, 156.1 ppm. **Elemental analysis:** Anal. Calcd for $C_{48}H_{35}N_3Si\bullet0.3CH_2Cl_2$: C, 82.01; H, 5.07; N, 5.94. Found: C, 82.18; H, 4.70; N, 5.69. **ESI-MS:** *m/z* (%) 682.7 (100) $[M+H]^+$.

4'-(4-((2-((4'-Ethynyl-[1,1'-biphenyl]-4-yl)ethynyl)phenyl)ethynyl)phenyl)-2,2':6',2''-terpyridine(**13**)

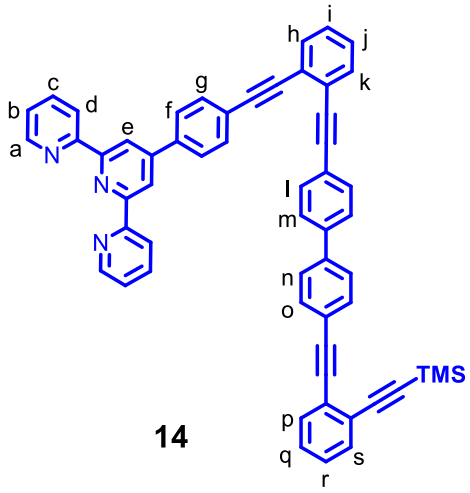


13

Compound **12** (400 mg, 587 µmol) was dissolved in 30 mL of THF. To this solution K_2CO_3 (405 mg, 2.93 mmol) dissolved in 20 mL of water and 30 mL of methanol was added. The reaction mixture was stirred at rt for 4 h. The organic solvents were evaporated under vacuum. The crude was then extracted with dichloromethane. It was passed through a small pad of SiO_2 using 40% ethyl acetate/hexane giving a colorless solid compound **13** in 90% yield (322 mg, 528 µmol). **IR (KBr)**: $\tilde{\nu}$ = 543, 625, 758, 792, 823, 1004, 1038, 1116, 1164, 1267, 1384, 1410, 1567, 1584, 1635, 1710, 2027, 2341, 2364, 2852, 2926, 2965 cm^{-1}. **Mp.** > 250 ºC. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 3.14 (s, 1H, t-H), 7.33–7.38 (m, 4H, [i+j+b]-H), 7.58–7.61 (m, 6H, [h+k+n+o]-H), 7.62 (d, ^3J = 8.4 Hz, 2H, m-H), 7.67 (d, ^3J = 8.4 Hz, 2H, l-H), 7.73 (d, ^3J = 8.4 Hz, 2H, g-H), 7.87 (td, ^3J = 8.0 Hz, ^4J = 2.0 Hz, 2H, c-H), 7.92 (d, ^3J = 8.4 Hz, 2H, f-H), 8.68 (ddd, ^3J = 8.0 Hz, ^4J = 1.0 Hz, ^5J =

0.8 Hz, 2H, d-H), 8.73 (ddd, ^{3}J = 4.8 Hz, ^{4}J = 2.0 Hz, ^{5}J = 0.8 Hz, 2H, a-H), 8.76 (s, 2H, e-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 78.0, 83.5, 89.3, 89.8, 93.3, 93.5, 118.6, 121.2, 121.3, 122.6, 123.9, 124.0, 125.7, 125.8, 126.8, 126.9, 127.0, 127.3, 128.1, 128.2, 131.8, 132.1, 132.2, 132.6, 136.9, 138.2, 140.0, 140.5, 149.1, 149.2, 156.0, 156.1 ppm. **Elemental analysis:** Anal. Calcd for $C_{45}H_{27}N_3 \bullet 0.3CH_2Cl_2$: C, 85.66; H, 4.38; N, 6.62. Found: C, 85.99; H, 3.97; N, 6.41. **ESI-MS:** *m/z* (%) 610.8 (100) $[M+H]^+$.

4'-(4-((2-((4'-((2-((Trimethylsilyl)ethynyl)phenyl)ethynyl)-[1,1'-biphenyl]-4-yl)ethynyl)phenyl)ethynyl)phenyl)-2,2':6',2''-terpyridine(**14**)

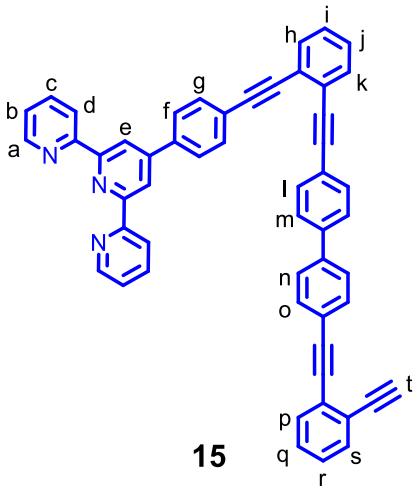


14

Compounds **13** (250 mg, 410 µmol) and **8** (246 mg, 820 µmol) were placed in a sealed tube. It was evacuated and filled with N_2, then freshly distilled Et_3N (20 mL) and DMF (15 mL) were added. The solution was degassed twice by using the freeze-pump-thaw method. To this mixture $Pd(PPh_3)_4$ (47.4 mg, 41.0 nmol) was added and it was allowed to stir at 75 °C for 15 h. The mixture was cooled to rt and solvents were removed under reduced pressure. The residue was extracted into DCM (75 mL) and washed with ice-cold water (75 mL) and brine (30 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated. The column chromatographic purification on silica gel using 40% ethyl acetate in hexane (R_f = 0.40, SiO_2, 40% ethyl acetate/hexane) afforded compound **14** as colorless solid in 60% yield (192 mg, 246 µmol). **IR (KBr)**: $\tilde{\nu}$ = 543, 692, 721, 757, 842, 1096, 1120, 1158, 1249, 1384, 1412, 1437, 1499, 1500, 1567, 1586, 1607, 1636, 1713, 2026, 2147, 2213, 2852, 2926, 2955 cm^{-1}. **Mp.** > 250 ºC. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 0.28, (s, 9H, TMS-H), 7.27–7.31 (m, 2H, [q+r]-H), 7.34–7.38 (m, 4H, [i+j+b]-H), 7.50–7.54 (m, 2H,

[s+p]-H), 7.60–7.62 (m, 2H, [h+k]-H), 7.63 (d, ^3J = 8.0 Hz, 2H, o-H), 7.64 (d, ^3J = 8.0 Hz, 2H, n-H), 7.69 (d, ^3J = 8.0 Hz, 2H, m-H), 7.70 (d, ^3J = 8.0 Hz, 2H, l-H), 7.74 (d, ^3J = 8.4 Hz, 2H, g-H), 7.89 (td, ^3J = 8.0 Hz, ^3J = 1.8 Hz, 2H, c-H), 7.94 (d, ^3J = 8.4 Hz, 2H, f-H), 8.68 (ddd, ^3J = 8.0 Hz, ^4J = 1.0 Hz, ^5J = 0.8 Hz, 2H, d-H), 8.74 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 0.8 Hz, 2H, a-H), 8.76 (s, 2H, e-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 0.04, 89.1, 89.3, 89.8, 93.3, 93.4, 93.6, 98.6, 103.4, 118.6, 121.4, 122.5, 122.6, 123.9, 124.1, 125.6, 125.7, 125.9, 126.0, 126.9, 127.0, 127.3, 127.9, 128.1, 128.2 (2C), 131.7, 131.8, 131.9, 132.1, 132.2 (2C), 132.3, 136.9, 138.3, 140.1, 140.2, 149.1, 149.3, 156.0, 156.1 ppm. **Elemental analysis:** Anal. Calcd for $C_{56}H_{39}N_3Si$: C, 86.01; H, 5.03; N, 5.37. Found: C, 85.99; H, 5.37; N, 5.50. **ESI-MS:** *m/z* (%) 783.0 (100) $[M+H]^+$.

4'-(4-((2-((4'-((2-Ethynylphenyl)ethynyl)-[1,1'-biphenyl]-4-yl)ethynyl)phenyl)ethynyl)phenyl)-2,2':6',2''-terpyridine(**15**)

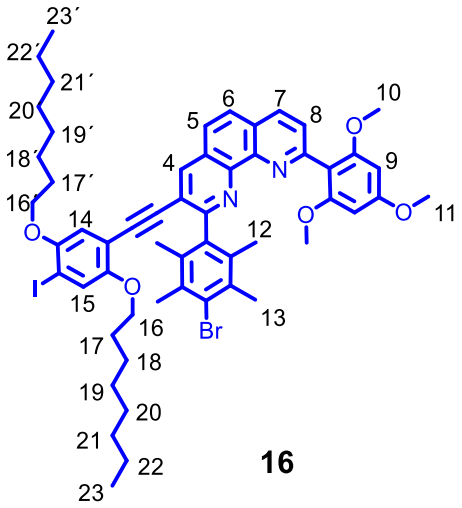


15

Compound **14** (170 mg, 217 µmol) was dissolved in 30 mL of THF. To this solution K_2CO_3 (405 mg, 2.93 mmol) dissolved in 20 mL of water and 30 mL of methanol was added. The reaction mixture was stirred at rt for 2 h. The organic solvents were evaporated under vacuum. The crude product was then extracted with dichloromethane. The solution was passed through a small pad of SiO_2 using 40% ethyl acetate/hexane (R_f = 0.40, SiO_2, 40% ethyl acetate/hexane) giving the colorless solid compound **15** in 90% yield (139 mg, 195 µmol). **IR (KBr)**: $\tilde{\nu}$ = 519, 620, 660, 718, 757, 821, 868, 998, 1039, 1158, 1248, 1309, 1386, 1411, 1435, 1467, 1481, 1514, 1556, 1584, 1603, 1638, 2152, 2216, 2350, 2956, 3052 cm^{-1}. **Mp.** > 250 ºC. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 3.38 (s, 1H, t-H), 7.32–7.39 (m, 6H, [q+i+r+j+b]-H), 7.53–7.57 (m, 2H, [p+s]-H), 7.60–7.63 (m,

2H, [h+k]-H), 7.64–7.70 (m, 8H, [l+m+n+o]-H), 7.74 (d, ^3J = 8.0 Hz, 2H, g-H), 7.89 (td, ^3J = 8.0 Hz, ^4J = 1.8 Hz, 2H, c-H), 7.94 (d, ^3J = 8.0 Hz, 2H, f-H), 8.69 (ddd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, ^5J = 1.2 Hz, 2H, d-H), 8.74 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 1.2 Hz, 2H, a-H), 8.76 (s, 2H, e-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 81.2, 82.2, 88.8, 89.3, 89.8, 93.3, 93.4, 93.6, 118.6, 121.3, 122.3, 122.5, 123.9, 124.6, 125.6, 125.9, 126.2, 126.9, 127.0, 127.3, 127.9, 128.1, 128.2, 128.4, 128.5, 131.7, 131.8, 131.9, 132.0, 132.1 (2C), 132.2, 132.6, 136.9, 138.2, 140.2, 149.1, 149.2, 156.0, 156.1 ppm. **Elemental analysis:** Anal. Calcd for $C_{53}H_{31}N_3 \bullet 0.9CH_2Cl_2$: C, 82.34; H, 4.20; N, 5.34. Found: C, 82.18; H, 4.40; N, 5.39. **ESI-MS:** *m/z* (%) 710.9 (100) $[M+H]^+$.

2-(4-Bromo-2,3,5,6-tetramethylphenyl)-3-((4-ethynyl-2,5-bis(octyloxy)phenyl)ethynyl)-9-(2,4,6-trimethoxyphenyl)-1,10-phenanthroline(**16**)

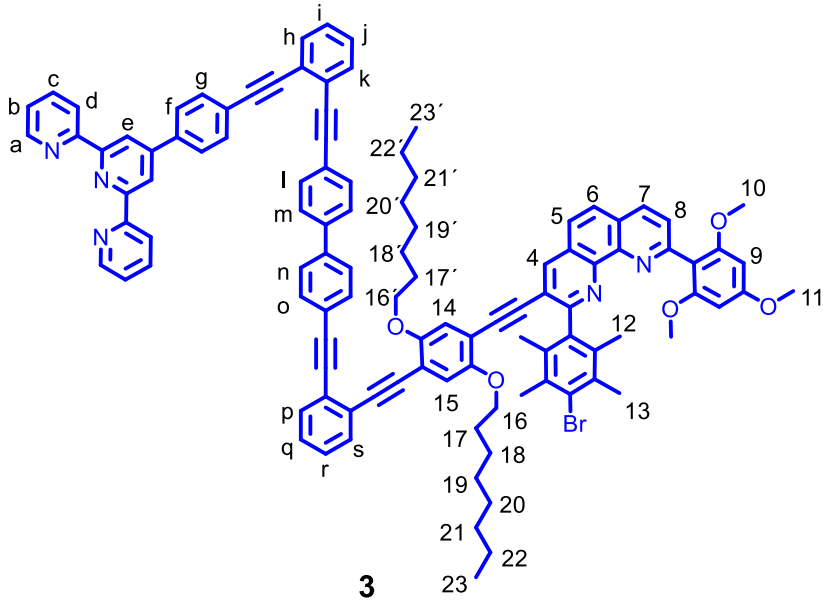


16

Compounds 2-(4-bromo-2,3,5,6-tetramethylphenyl)-3-ethynyl-9-(2,4,6-trimethoxyphenyl)-1,10-phenanthroline (250 mg, 430 µmol) and 1,4-diiodo-2,5-bis(octyloxy)benzene (1.26 g, 2.15 mmol) were placed in a sealed tube. It was evacuated and filled with N_2, then freshly distilled Et_3N (20 mL) and DMF (25 mL) were added. The solution was degassed twice by using the freeze-pump-thaw method. To this mixture, $Pd(PPh_3)_4$ (49.6 mg, 43.0 µmol) was added and it was allowed to stir at 70 °C for 15 h. The mixture was cooled to room temperature and solvents were removed under reduced pressure. The residue was extracted in DCM (75 mL) and washed with ice-cold water (75 mL) and brine (30 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated. The column chromatographic purification of the crude product on silica gel using 25% ethyl acetate in hexane (R_f = 0.30, SiO_2, 25% ethyl acetate/hexane) afforded compound **16** as

colorless solid in 70% yield (313 mg, 300 µmol). **IR (KBr)**: $\tilde{\nu}$ = 540, 563, 809, 847, 990, 1032, 1129, 1156, 1205, 1222, 1335, 1384, 1413, 1457, 1500, 1587, 1609, 2023, 2208, 2368, 2860, 2828, 2951 cm^{-1}. **Mp.** > 250 °C. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 0.87 (t, ^3J = 7.2 Hz, 3H, [23/23´]-H), 0.90, (t, ^3J = 7.2 Hz, 3H, [23´/23]-H), 1.27–1.34 (m, 8H, [21+22+21´+22´]-H), 1.35–1.42 (m, 8H, [19+20+19´+20´]-H), 1.48–1.58 (m, 4H, [18+18´]-H), 1.76–1.86 (m, 4H, [17+17´]-H), 2.01 (s, 6H, 13-H), 2.43 (s, 6H, 12-H), 3.73 (s, 6H, 10-H), 3.80 (t, ^3J = 6.4 Hz, 2H, 16´-H), 3.84 (s, 3H, 11-H), 3.93 (t, ^3J = 6.4 Hz, 2H, 16-H), 6.08 (s, 1H, 15-H), 6.23 (s, 2H, 9-H), 7.25 (s, 1H, 14-H), 7.66 (d, ^3J = 8.4 Hz, 1H, 8-H), 7.78 (d, ^3J = 8.4 Hz, 1H, [5/6]-H), 7.85 (d, ^3J = 8.4 Hz, 1H, [6/5]-H), 8.23 (d, ^3J = 8.4 Hz, 1H, 7-H), 8.41 (s, 1H, 4-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 14.1 (2C), 18.6 (2C), 21.0 (2C), 22.7, 26.0, 26.1, 29.2, 29.3, 29.3, 29.4, 29.5, 31.8, 31.9, 55.4, 56.4, 69.1, 69.6, 90.1, 91.3, 91.4, 91.6, 113.6, 114.0, 116.5, 117.3, 119.9, 125.3, 126.8, 127.0, 127.3, 127.9, 128.8, 133.3, 133.8, 135.2, 138.1, 139.4, 144.9, 145.9, 152.8, 154.2, 155.4, 159.3, 161.5, 162.1 ppm. **Elemental analysis:** Anal. Calcd for $C_{55}H_{64}BrIN_2O_5$: C, 63.52; H, 6.20; N, 2.69. Found: C, 63.46; H, 6.09; N, 2.36. **ESI-MS:** *m/z* (%) 1040.9 (100) $[M+H]^+$.

Synthesis of switch **3**



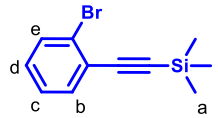
3

In a dry sealed tube compounds **15** (75.0 mg, 106 µmol) and **16** (121 mg, 116 µmol) were taken, dissolved in 15 mL DMF and 10 mL of Et_3N. The solution was degassed twice by the freeze-pump-thaw method. To this mixture, $Pd(PPh_3)_4$ (12.3 mg, 10.6 µmol) was added and again the

freeze-pump-thaw method was followed once. Then the solution was allowed to stir for 14 h at 70 °C. All the solvents were evaporated under vacuum. The residue was dissolved in CH_2Cl_2 and worked up with ice cold water to remove DMF. The organic part was dried over anhydrous Na_2SO_4. Purification was performed by column chromatography on SiO_2 (R_f = 0.3, SiO_2, 40% ethyl acetate in hexane) using CH_2Cl_2 as eluent. It was eventually purified by size exclusion chromatography with SX-3 biobead using distilled THF as the eluent to furnishing a yellow solid in 60% yield (103 mg, 63.6 µmol). **IR (KBr)** $\tilde{\nu}$ = 533, 622, 660, 757, 792, 822, 830, 898, 919, 946, 994, 1004, 1035, 1127, 1156, 1205, 1225, 1273, 1384, 1334, 1410, 1466, 1500, 1566, 1573, 1585, 1605, 1635, 2026, 2204, 2250, 2334, 2854, 2926, 2954 cm^{-1}. **Mp.** > 250 ºC. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 0.80 (t, ^3J = 6.8 Hz, 3H, [23/23´]-H), 0.85 (t, ^3J = 6.8 Hz, 3H, [23´/23]-H), 1.18–1.34 (m, 16H, [22+22´]-H + [21+21´]-H + [20+20´]-H + [19+19´]-H), 1.41 (t, ^3J = 6.8 Hz, 2H, 18´-H), 1.49 (t, ^3J = 6.8 Hz, 2H, 18-H), 1.70 (t, ^3J = 6.8 Hz, 2H, 17´-H), 1.78 (t, ^3J = 6.8 Hz, 2H, 17-H), 1.98 (s, 6H, 13-H), 2.46 (s, 6H, 12-H), 3.67 (s, 6H, 10-H), 3.80 (t, ^3J = 6.8 Hz, 2H, 16´-H), 3.85 (t, ^3J = 6.8 Hz, 2H, 16-H), 3.86 (s, 3H, 11-H), 6.24 (s, 2H, 9-H), 6.25 (s, 1H, 14-H), 6.98 (s, 1H, 15-H), 7.32–7.36 (m, 4H, [i+j+b]-H), 7.36–7.41 (m, 3H, [8+q+r]-H), 7.55–7.60 (m, 2H, [h+k]-H), 7.62–7.65 (m, 2H, [s+p]-H), 7.66 (d, ^3J = 8.0 Hz, 2H, [m/n]-H), 7.67 (d, ^3J = 8.0 Hz, 2H, [n/m]-H), 7.70 (d, ^3J = 8.0 Hz, 1H, [5/6]-H), 7.71 (d, ^3J = 8.0 Hz, 1H, [6/5]-H), 7.76–7.79 (m, 4H, [l+o]-H), 7.84 (d, ^3J = 8.0 Hz, 2H, g-H), 7.85 (td, ^3J = 8.0 Hz, ^4J = 1.8 Hz, 2H, c-H), 7.96 (d, ^3J = 8.0 Hz, 2H, f-H), 8.25 (d, ^3J = 8.0 Hz, 1H, 7-H), 8.39 (s, 1H, 4-H), 8.66 (ddd, ^3J = 8.0 Hz, ^4J = 1.0 Hz, ^5J = 0.8 Hz, 2H, d-H), 8.70 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 0.8 Hz, 2H, a-H), 8.80 (s, 2H, e-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 14.1 (2C), 18.6 (2C), 21.0 (2C), 22.7, 26.0, 26.1, 29.2, 29.3, 29.3, 29.4, 29.5, 31.8, 31.8, 55.4, 56.3, 69.4, 69.4, 89.3, 89.4, 89.8, 90.3, 91.7, 92.0, 92.2, 93.3, 93.4, 93.6, 93.9, 113.6, 114.4, 116.9, 117.0, 118.6, 119.9, 121.3, 122.7, 123.9, 124.1, 125.4, 125.7, 125.9, 126.1, 126.7, 126.8, 126.8, 126.9, 126.9, 127.0, 127.1, 127.2, 127.3, 127.3, 127.9, 128.0, 128.1, 128.2, 128.8, 131.6, 131.8, 131.9, 132.1, 132.2, 132.2, 132.2, 133.3, 133.8, 135.3, 136.9, 138.2, 138.3, 139.4, 140.1, 144.8, 145.9, 149.1, 149.1, 149.3, 153.0, 153.6, 155.4, 156.0, 156.1, 159.2, 161.6, 162.1 ppm. **Elemental analysis:** Anal. Calcd. for $C_{108}H_{94}BrN_5O_5 \bullet CH_2Cl_2$: C, 76.70; H, 5.67; N, 4.10. Found: C, 76.50; H, 5.48; N, 4.11. **ESI-MS:** *m/z* (%) 1622.9 (100) $[M+H]^+$.

Synthesis of nanoswitch 4

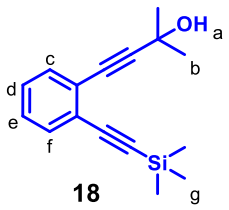
((2-Bromophenyl)ethynyl)trimethylsilane (**17**)[3]



17

A mixture of 1-bromo-2-iodobenzene (5.00 g, 17.7 mmol), $PdCl_2(PPh_3)_2$ (124 mg, 180 µmol) and CuI (67.0 mg, 350 µmol) were placed in a sealed tube. The tube was evacuated and filled with N_2 (3×). Pre-degassed anhydrous Et_3N (55 mL) and trimethylsilylacetylene (TMSA, 1.93 g, 2.80 mL, 19.5 mmol) were added under N_2 atmosphere, and the reaction mixture was stirred at room temperature for 3 h (TLC). The mixture was filtered, washed with *n*-hexane (30 mL × 2) and the solvent was evaporated. The residue was purified by column chromatography on silica gel using *n*-hexane (R_f = 0.65, SiO_2, *n*-hexane) to furnish **17** as a tan oil in 90% yield (4.03 g, 15.9 mmol). **IR (neat):** $\tilde{\nu}$ = 3064, 2960, 2900, 2163, 1951, 1584, 1465, 1427, 1251, 1119, 1028, 863, 756, 704, 671, 549 cm^{-1}. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 0.28 (s, 9H, a-H), 7.15 (td, ^3J = 7.6 Hz, ^4J = 1.2 Hz, 1H, c-H), 7.24 (ddd, ^3J = 8.0 Hz, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1H, d-H), 7.49 (dd, ^3J = 7.6 Hz, ^4J = 1.6 Hz, 1H, b-H), 7.57 (dd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, 1H, e-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = −0.2, 99.6, 103.0, 125.2, 125.7, 126.9, 129.5, 132.3, 133.6 ppm.

2-Methyl-4-(2-((trimethylsilyl)ethynyl)phenyl)but-3-yn-2-ol (**18**)[4]

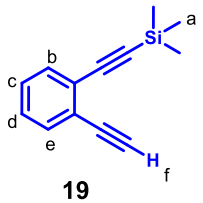


18

2-Methylbut-3-yn-2-ol (16.7 g, 19.2 mL, 19.8 mmol) was added to a mixture of **17** (5.00 g, 19.8 mmol) and CuI (188 mg, 987 µmol) in anhydrous Et_3N (150 mL). The resultant mixture was purged with N_2 for 45 min. $Pd(PPh_3)_4$ (1.14 g, 987 µmol) was added and the reaction mixture was heated to 80 °C for 48 h (TLC). The solvent was removed by rotary evaporation. The residue was dissolved in DCM (150 mL), successively washed with deionized water (150 mL × 3) and saturated brine solution (150 mL). The organic layer was removed, dried over anhydrous Na_2SO_4

and evaporated in *vacuo*. The dark brown residue was purified by column chromatography on silica gel using 10% EtOAc in *n*-hexane (R_f = 0.44, SiO_2, 30% EtOAc in *n*-hexane) to furnish **18** as a viscous brown oil in 90% yield (4.57 g, 17.8 mmol). **IR (neat):** $\tilde{\nu}$ = 502, 561, 642, 697, 757, 869, 958, 1032, 1152, 1248, 1368, 1505, 1597, 1644, 1682, 1835, 1935, 2149, 2220, 2977, 3056, 3446, 3579 cm^{-1}. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 0.27 (s, 9H, g-H), 1.64 (s, 6H, b-H), 2.16 (bs, 1H, a-H), 7.22–7.24 (m, 2H, [d+e]-H), 7.40 (ddd, ^3J = 7.2 Hz, ^4J = 2.0 Hz, ^5J = 0.4 Hz, 1H, f-H), 7.46 (ddd, ^3J = 7.2 Hz, ^4J = 2.0 Hz, ^5J = 0.4 Hz, 1H, c-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 0.01, 31.5, 65.7, 80.8, 97.7, 98.1, 103.3, 125.3, 125.6, 127.9, 128.1, 131.8, 132.3 ppm.

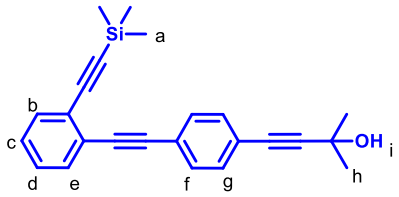
((2-Ethynylphenyl)ethynyl)trimethylsilane (**19**)[4]



19

A solution of **18** (1.82 g, 7.10 mmol) in anhydrous PhMe (125 mL) was heated in an oil bath (130 °C). The reaction mixture was allowed to reflux for ~10 min, then granular NaOH (315 mg, 7.81 mmol) was added in one portion under inert atmosphere. The resulting mixture was further heated to reflux for 2 h (TLC). The reaction mixture was allowed to cool to room temperature, diluted with deionized water and extracted with PhMe (50 mL). The organic layer was washed with brine (50 mL) and dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography (ϕ = 3.5 cm, l = 45 cm) on silica gel using *n*-hexane (R_f = 0.60, SiO_2, *n*-hexane) to afford compound **19** as viscous yellow oil with 80% yield (1.13 g, 5.68 mmol). **IR (neat):** $\tilde{\nu}$ = 509, 642, 759, 863, 1036, 1096, 1474, 1591, 1713, 1957, 2160, 2484, 2899, 2960, 3063, 3296 cm^{-1}. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 0.27 (s, 9H, a-H) 3.30 (s, 1H, f-H), 7.24–7.30 (m, 2H, [c+d]-H), 7.46–7.51 (m, 2H, [b+e]-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 80.0, 81.1, 99.0, 103.1, 125.0, 126.1, 128.1, 128.4, 132.0, 132.4 ppm.

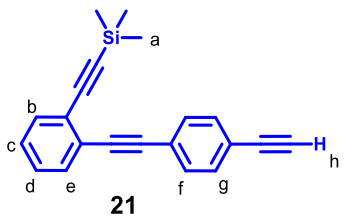
2-Methyl-4-(4-((2-((trimethylsilyl)ethynyl)phenyl)ethynyl)phenyl)but-3-yn-2-ol (**20**)



20

A 250 mL flask was charged with **19** (1.50 g, 7.56 mmol), 4-(4-bromophenyl)-2-methylbut-3-yn-2-ol (1.44 g, 6.05 mmol), and CuI (72.0 mg, 378 µmol). Freshly distilled anhydrous Et_3N (65 mL) was added and the solution was purged with N_2 for 40 min. After addition of $Pd(PPh_3)_4$ (436 mg, 377 µmol), the reaction mixture was heated to 80 °C for 50 h (TLC). The reaction was allowed to cool to room temperature and the solvent was removed by rotary evaporation. The residue was dissolved in DCM (50 mL) and successively washed with deionized water (50 mL × 3) and saturated brine (50 mL). The organic layer was removed, dried over anhydrous Na_2SO_4 and evaporated. The chromatographic purification of the crude product on silica gel (ϕ = 3.5 cm, l = 15 cm) using 10% EtOAc in *n*-hexane (R_f = 0.50, SiO_2, EtOAc in *n*-hexane) furnished **20** as a yellow solid (2.10 g, 75%). **Mp:** 60–62 °C. **IR (KBr):** $\tilde{\nu}$ = 504, 561, 642, 759, 842, 958, 1009, 1155, 1247, 1368, 1439, 1505, 1935, 2148, 2971, 3056, 3451 cm^{-1}. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 0.24 (s, 9H, a-H), 1.61 (s, 6H, h-H), 2.01 (bs, 1H, i-H), 7.24–7.28 (m, 2H, [c+d]-H), 7.38 (d, ^3J = 8.8 Hz, 2H, g-H), 7.47–7.50 (m, 4H, [b+e+f]-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 0.0, 31.4, 65.6, 81.8, 89.9, 92.9, 95.6, 98.7, 103.3, 122.7, 123.2, 125.7 (2C), 128.1, 128.2, 131.5 (2C), 131.7, 132.3 ppm. **Elemental analysis:** Calcd. for $C_{24}H_{24}OSi$: C, 80.85; H, 6.78; Found: C, 80.84; H, 6.88.

((2-((4-Ethynylphenyl)ethynyl)phenyl)ethynyl)trimethylsilane (**21**)[4]

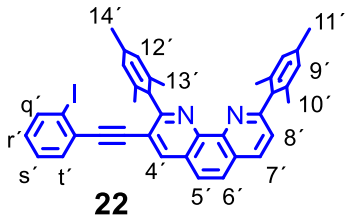


21

A solution of compound **20** (1.10 g, 3.09 mmol) in anhydrous PhMe (40 mL) was heated in an oil bath (130 °C). The reaction mixture was refluxed, then granular NaOH (135 mg, 3.39 mmol) was

added in one portion. The resultant mixture was stirred at 130 °C for 1 h. After completion (TLC), the reaction mixture was allowed to cool to room temperature. Then it was diluted with deionized water and extracted in PhMe (25 mL). The organic phase was washed with a saturated brine solution (75 mL) and dried over anhydrous Na_2SO_4. The solvent was removed in *vacuo* furnishing a brown oil that was purified by column chromatography on silica gel using *n*-hexane (R_f = 0.15, SiO_2, *n*-hexane). Purification yielded **21** as a bright yellow solid in 92% yield (850 mg, 2.84 mmol). **Mp:** 55–56 °C. **IR (KBr):** $\tilde{\nu}$ = 463, 503, 603, 660, 752, 846, 948, 1033, 1092, 1244, 1318, 1404, 1499, 1597, 1797, 1913, 2152, 2958, 3056, 3291 cm^{-1}. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 0.27 (s, 9H, a-H), 3.18 (s, 1H, h-H), 7.27–7.30 (m, 2H, [c+d]-H), 7.47–7.52 (m, 6H, [b+e+f+g]-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 0.0, 78.9, 83.3, 90.2, 92.8, 98.8, 103.3, 122.0, 123.8, 125.7 (2C), 128.1, 128.2, 131.5, 131.7, 132.0, 132.3 ppm. **Elemental analysis:** Calcd. for $C_{21}H_{18}Si$: C, 84.51; H, 6.08; Found: C, 84.89; H, 6.08.

3-((2-Iodophenyl)ethynyl)-2,9-dimesityl-1,10-phenanthroline (**22**)

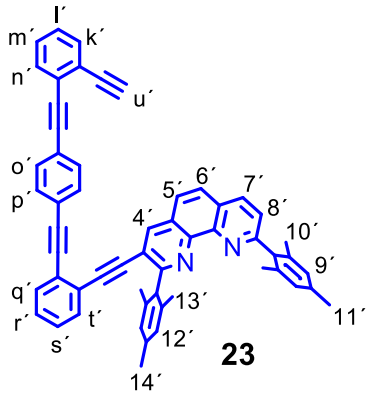


22

3-Ethynyl-2,9-dimesityl-1,10-phenanthroline (100 mg, 0.227 mmol) and 1,2-diiodobenzene (373 mg, 1.13 mmol) were placed in a sealed tube. It was evacuated and filled with N_2, then freshly distilled Et_3N (20 mL) and DMF (15 mL) were added. The solution was degassed twice by using the freeze-pump-thaw method. $Pd(PPh_3)_4$ (26.3 mg, 22.7 nmol) was added to this mixture that was stirred at 75 °C for 15 h. After cooling to room temperature the solvents were removed under reduced pressure. The residue was extracted in DCM (75 mL) and washed with ice-cold water (75 mL) and brine (30 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated. The column chromatographic purification of the crude product on silica gel using 10% ethyl acetate in hexane (R_f = 0.30, SiO_2, 10% ethyl acetate/hexane) afforded compound **22** as colorless solid in 85% yield (124 mg, 0.193 mmol). **IR (KBr):** $\tilde{\nu}$ = 510, 519, 613, 641, 691, 750, 848, 888, 942, 993, 1016, 1094, 1236, 1384, 1433, 1465, 1480, 1507, 1584, 1614, 2023, 2160, 2214, 2345, 2854,

2915, 2951, 3002, 3050 cm^{-1}. **Mp.** > 250 ºC. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 2.09 (s, 6H, 10´-H), 2.11 (s, 6H, 13´-H), 2.30 (s, 3H, 11´-H), 2.31 (s, 3H, 14´-H), 6.90 (s, 2H, 9´-H), 6.93 (s, 2H, 12´-H), 6.97 (td, ^3J = 8.0 Hz, ^4J = 1.8 Hz, s´-H), 7.13 (dd, ^3J = 8.0 Hz, ^4J = 1.8 Hz, q´-H), 7.24 (td, ^3J = 8.0 Hz, ^4J = 1.8 Hz, r´-H), 7.58 (d, ^3J = 8.2 Hz, 1H, 8´-H), 7.79 (dd, ^3J = 8.0 Hz, ^4J = 1.8 Hz, t´-H), 7.85 (d, ^3J = 8.2 Hz, 1H, 6´-H), 7.88 (d, ^3J = 8.2 Hz, 1H, 5´-H), 8.29 (d, ^3J = 8.2 Hz, 1H, 7´-H), 8.55 (s, 1H, 4´-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 20.1, 20.5, 21.1, 21.2, 90.8, 93.4, 98.6, 120.1, 125.0, 125.1, 125.6, 125.7, 127.9, 128.0, 128.2, 128.5, 128.6, 128.7, 132.1, 132.3, 135.8, 136.1, 136.3, 136.8, 137.3, 137.5, 137.8, 138.9, 144.9, 145.9, 160.5, 161.9 ppm. **Elemental analysis:** Anal. Calcd for $C_{38}H_{31}IN_2$: C, 71.03; H, 4.86; N, 4.36. Found: C, 71.28; H, 4.57; N, 4.13. **ESI-MS:** *m/z* (%) 643.5 (100) $[M+H]^+$.

2,9-Dimethylsilyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)phenyl)ethynyl)-1,10-phenanthroline (**23**)

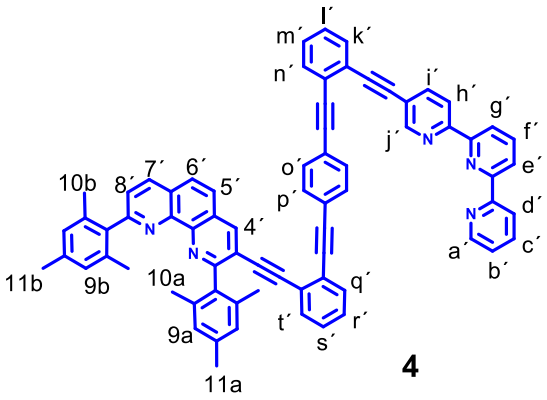


23

Compounds **21** (76.5 mg, 257 µmol) and **22** (100 mg, 171 µmol) were placed in a sealed tube. It was evacuated and filled with N_2, then freshly distilled Et_3N (20 mL) and DMF (15 mL) were added. The solution was degassed twice by using the freeze-pump-thaw method. To this mixture $Pd(PPh_3)_4$ (19.7 mg, 25.7 µmol) was added and it was allowed to stir at 75 °C for 15 h. The mixture was cooled to room temperature and solvents were removed under reduced pressure. The residue was extracted in DCM (75 mL) and washed with ice-cold water (75 mL) and brine (30 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated. The column chromatographic purification of the crude product on silica gel using 15% ethyl acetate in hexane (R_f = 0.30, SiO_2, 15% ethyl acetate/hexane) afforded a colorless solid compound. This compound was dissolved in

30 mL of THF and 30 mL of methanol. Aqueous solution (30 mL) of KOH (355 mg, 2.58 mmol) was added to this mixture and stirred for 3 h at room temperature. The organic residue was extracted using dichloromethane and this solution was dried over anhydrous Na_2SO_4 and evaporated under vacuum. Finally the product was separated after passing through a small pad of neutral alumina using dichloromethane (R_f = 0.40, SiO_2, 100% dichloromethane) as eluent furnishing the pale yellow product in 75% yield (95.0 mg, 128 µmol). **IR (KBr):** $\tilde{\nu}$ = 508, 543, 559, 644, 757, 949, 1017, 1094, 1161, 1249, 1261, 1310, 1384, 1404, 1441, 1472, 1556, 1591, 1694, 1916, 2157, 2215, 2256, 2312, 2898, 2957, 3058 cm^{-1}. **Mp.** > 250 ºC. **^{1}H NMR ($CDCl_3$, 400 MHz):** δ = 2.14 (s, 6H, 10´-H), 2.15 (s, 6H, 13´-H), 2.32 (s, 3H, 11´-H), 2.33 (s, 3H, 14´-H), 3.41 (s, 1H, u´-H), 6.91 (s, 2H, 9´-H), 6.93 (s, 2H, 12´-H), 7.02 (dd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, 1H, k´-H), 7.23 (td, ^3J = 8.0 Hz, ^4J = 1.2 Hz, m´-H), 7.28 (td, ^3J = 8.0 Hz, ^4J = 1.6 Hz, l´-H), 7.33 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, n´-H), 7.36 (td, ^3J = 8.0 Hz, ^4J = 1.4 Hz, s´-H), 7.52 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, q´-H), 7.56–7.59 (m, 3H, [8´+r´+t´]-H), 7.62 (bs, 4H, [o´+p´]-H), 7.75 (d, ^3J = 8.4 Hz, 1H, 6´-H), 7.87 (d, ^3J = 8.4 Hz, 1H, 5´-H), 8.27 (d, ^3J = 8.4 Hz, 1H, 7´-H), 8.47 (s, 1H, 4´-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 20.2, 20.6, 21.1, 21.2, 71.3, 82.1, 89.9, 90.2, 91.3, 93.1, 93.2, 93.4, 119.9, 123.3, 123.4, 124.7, 125.0, 125.2, 125.5, 125.6, 126.0, 126.8, 127.0, 127.5, 127.9, 128.2, 128.3, 128.5, 128.6, 131.6 (2C), 131.7 (2C), 131.8, 132.4, 132.7, 135.7, 136.2, 136.3, 136.9, 137.2, 137.5, 138.0, 139.0, 145.1, 146.0, 160.4, 161.7 ppm. **Elemental analysis:** Anal. Calcd for $C_{56}H_{40}N_2 \bullet H_2O$: C, 88.62; H, 5.58; N, 3.69. Found: C, 88.54; H, 5.62; N, 3.49. **ESI-MS:** *m/z* (%) 741.3 (100) $[M+H]^+$.

Synthesis of nanoswitch **4**



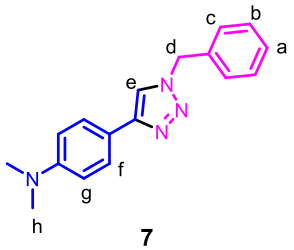
4

Compounds **23** (70.0 mg, 94.5 µmol) and 5-bromo-2,2':6',2"-terpyridine (88.5 mg, 312 µmol) were placed in a sealed tube. It was evacuated and filled with N_2, then freshly distilled Et_3N (20 mL) and DMF (15 mL) were added. The solution was degassed twice by using the freeze-pump-thaw method. To this mixture $Pd(PPh_3)_4$ (10.9 mg, 9.45 nmol) was added and it was allowed to stir at 90 °C for 15 h. The mixture was cooled to room temperature, then the solvents were removed under reduced pressure. The residue was extracted in DCM (75 mL) and washed with ice-cold water (75 mL) and brine (30 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated. The column chromatographic purification of the crude product on silica gel using 30% ethyl acetate in hexane (R_f = 0.30, SiO_2, 30% ethyl acetate/hexane) afforded nanoswitch **4** as pale yellow solid in 70% yield (64.5 mg, 66.2 µmol). **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 2.01 (s, 6H, 10b-H), 2.05 (s, 6H, 10a-H), 2.32 (s, 3H, 11b-H), 2.35 (s, 3H, 11a-H), 6.93 (s, 2H, 9b-H), 6.95 (s, 2H, 9a-H), 7.00 (dd, ^3J = 7.8 Hz, ^4J = 1.0 Hz, 1H, t´-H), 7.23–7.34 (m, 3H, [b´+r´+s´]-H), 7.39–7.46 (m, 2H, [m´+k´]-H), 7.49 (d, ^3J = 8.0 Hz, 1H, 8´-H), 7.54 (dd, ^3J = 7.8 Hz, ^4J = 1.0 Hz, 1H, q´-H), 7.63–7.70 (m, 6H, [o´+p´+n´+l´]-H), 7.74–7.79 (m, 3H, [c´+5´+6´]-H), 7.89 (t, ^3J = 7.8 Hz, 1H, f´-H), 8.06 (dd, ^3J = 8.2 Hz, ^4J = 2.0 Hz, 1H, i´-H), 8.19 (d, ^3J = 8.0 Hz, 1H, 7´-H), 8.41–8.45 (m, 2H, [g´+e´]-H), 8.51 (s, 1H, 4´-H), 8.53 (ddd, ^3J = 8.0 Hz, ^4J = 0.8 Hz, ^5J = 0.8 Hz 1H, d´-H), 8.64 (ddd, ^3J = 4.8 Hz, ^4J = 1.8 Hz, ^5J = 0.8 Hz, 1H, a´-H), 8.68 (dd, ^3J = 8.2 Hz, ^4J = 0.8 Hz, 1H, h´-H), 8.91 (dd, ^4J = 2.0 Hz, ^5J = 0.8 Hz, 1H, j´-H) ppm. **^{13}C NMR ($CDCl_3$, 100 MHz):** δ = 20.1, 20.5, 21.1, 21.2, 90.1, 90.3, 90.7, 91.2, 92.3, 93.1, 93.4, 93.5, 119.9, 120.3, 120.5, 121.1, 121.2, 121.3, 123.2, 123.5, 123.8, 125.0, 125.1, 125.2, 125.5, 125.6, 125.7, 126.8, 127.0, 127.5, 128.0, 128.2, 128.3, 128.4, 128.5, 128.6, 131.6, 131.7, 131.8, 132.0, 132.1, 132.5, 135.8, 136.1, 136.2,

136.8, 137.3, 137.5, 137.8, 137.9, 138.9, 139.2, 144.9, 145.8, 149.1, 151.6, 154.5, 155.2, 155.5, 155.9, 160.4, 161.7 (2C) ppm. **ESI-MS:** *m/z* (%) 972.8 (100) $[M + H]^+$.

Synthesis of other compounds

4-(1-Benzyl-1H-1,2,3-triazol-4-yl)-*N*,*N*-dimethylaniline (**7**)[5]

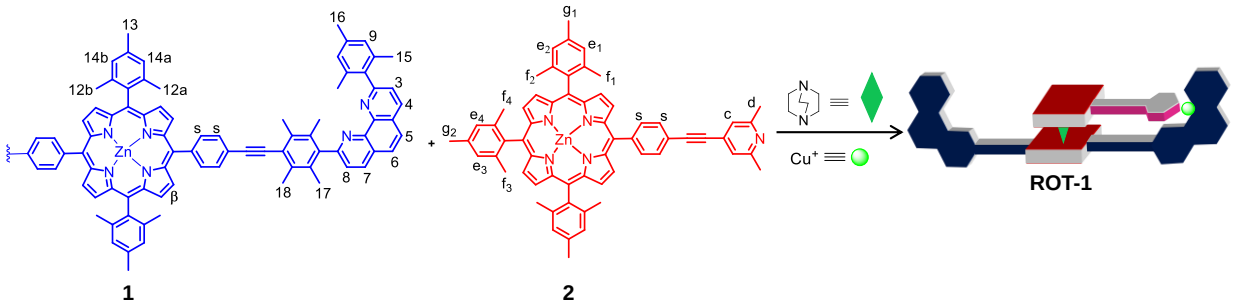


7

In a 100 mL flask 4-ethynyl-*N*,*N*-dimethylaniline (60.0 mg, 413 µmol) and benzyl azide (55.0 mg, 413 µmol) were dissolved in 100 mL of CH_2Cl_2:$CHCl_3$ (v/v 1:4). Tetrakis(acetonitrile)copper(I) tetrafluoroborate was added to this solution that was refluxed for 3 h. After work-up, the organic phase was collected, dried over anhydrous Na_2SO_4 and filtered. The product was separated (91.8 mg, 330 µmol, 80%) by column chromatography over SiO_2 using 1% ethyl acetate/dichloromethane as eluent (R_f = 0.30, SiO_2, in 1% ethyl acetate/dichloromethane). **^{1}H NMR ($CDCl_3$, 500 MHz):** δ = 2.97 (s, 6H, h-H), 5.55 (s, 2H, d-H), 6.74 (d, ^3J = 8.0 Hz, 2H, g-H), 7.27–7.30 (m, 2H, b-H), 7.35–7.38 (m, 3H, [a+c]-H), 7.52 (s, 1H, e-H), 7.66 (d, ^3J = 8.0 Hz, 2H, f-H) ppm. **^{13}C NMR ($CDCl_3$, 125 MHz):** δ = 40.4, 54.1, 112.4, 118.0, 118.8, 126.6, 128.0, 128.6, 129.1, 135.0, 148.7, 150.4 ppm. **ESI-MS:** *m/z* (%) 279.4 (100) $[M+H]^+$.

1.3 Synthesis and characterization of metal complexes

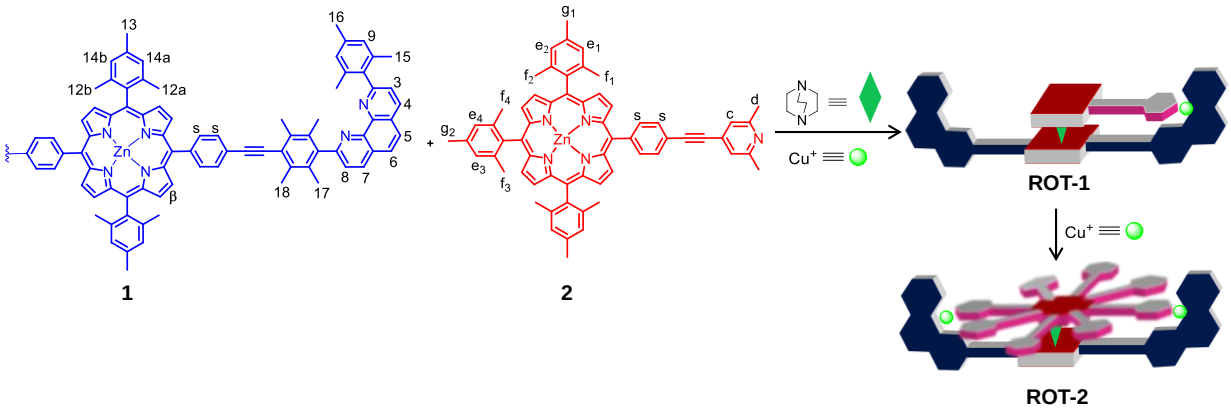
Pre-rotor complex **ROT-1**



Protons at the complexed (c) vs. uncomplexed (u) phenanthroline site appear as a rule at different shifts.

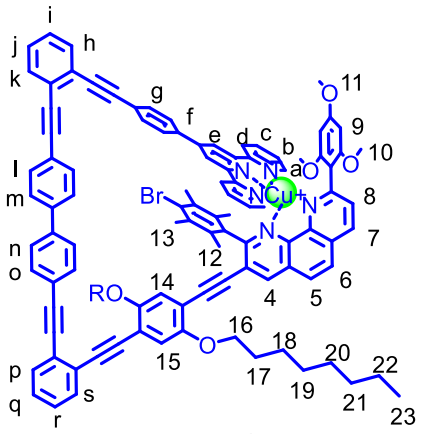
In an NMR tube, stator **1**[6] (2.09 mg, 1.25 µmol) was mixed with 1 equiv of $[Cu(CH_3CN)_4]PF_6$ (466 µg, 1.25 µmol) and dissolved in 100 µL of CD_2Cl_2, followed by addition of rotator **2** (1.17 mg, 1.25 µmol), DABCO (145 µg, 1.25 µmol) and additional 400 µL of CD_2Cl_2. After subsequent sonication for 2 min the complex was obtained in quantitative yield. **Mp:**. > 250 ºC. **IR (KBr):** $\tilde{\nu}$ = 558, 721, 797, 845, 995, 1063, 1203, 1338, 1380, 1458, 1492, 1585, 1609, 1680, 2222, 2852, 2920, 2951 cm^{-1}. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = –[4.54-4.49] (m, 6H, CH_2, DABCO), –[4.46-4.41] (m, 6H, CH_2, DABCO), 1.10 (s, 6H, [f_1/f_2]-H), 1.15 (s, 6H, [f_2/f_1]-H), 1.72 (s, 6H, [12a/12b]-H), 1.77 (s, 6H, [12b/12a]-H), 1.91 (s, 6H, [f_3+f_4]-H), 2.06 (s, 6H, 17u-H), 2.08 (s, 6H, d-H), 2.10 (s, 6H, 17c-H), 2.13 (s, 6H, 15u-H), 2.23 (s, 6H, 15c-H), 2.23 (s, 3H, 16u-H), 2.39 (s, 3H, 16c-H), 2.50 (s, 6H, 18u-H), 2.58–2.59 (s, 12H, [13+g_1]-H), 2.73 (s, 3H, g_2-H), 2.75 (s, 6H, 18c-H), 6.92 (s, 2H, 9u-H), 6.96 (bs, 2H, s-H), 7.00 (s, 2H, c-H), 7.02 (s, 2H, 9c-H), 7.08 (bs, 4H, [14a+14b]-H), 7.19 (s, 2H, [e_1/e_2]-H), 7.26–7.29 (m, 4H, [s+e_2/e_1]-H), 7.33 (bs, 2H, [e_3+e_4]-H), 7.47 (bs, 2H, s-H), 7.60 (d, ^3J = 8.0 Hz, 1H, [8/3]u-H), 7.63 (d, ^3J = 8.0 Hz, 1H, [3/8]u-H), 7.90 (d, ^3J = 8.0 Hz, 4H, s-H), 7.94–7.97 (m, 5H, (5u+6u+[3/8]c+s)-H), 8.05 (d, ^3J = 8.0 Hz, 1H, [8/3]c-H), 8.25 (s, 4H, β(**1**)-H), 8.27 (d, ^3J = 4.4 Hz, 2H, β(**1**)-H), 8.33 (d, ^3J = 4.4 Hz, 2H, β(**1**)-H), 8.34 (s, 2H, [5c+6c]-H), 8.38 (d, ^3J = 4.4 Hz, 2H, β(**2**)-H), 8.39 (d, ^3J = 8.0 Hz, 1H, [7/4]u -H), 8.42 (d, ^3J = 8.0 Hz, 1H, [4/7]u-H), 8.52 (d, ^3J = 4.4Hz, 2H, β(**2**)-H), 8.53 (d, ^3J = 4.4 Hz, 2H, β(**2**)-H), 8.57 (d, ^3J = 4.6 Hz, 2H, β(**2**)-H), 8.78 (d, ^3J = 8.0 Hz, 1H, [7/4]c-H), 8.79 (d, ^3J = 8.0 Hz, 1H, [4/7]c-H) ppm. **Elemental analysis:** Anal. Calcd for $C_{182}H_{159}CuN_{15}Zn_2$•$2CH_2Cl_2$: C, 75.29; H, 5.54; N, 7.15. Found: C, 75.04; H, 5.60; N, 6.80. **ESI-MS:** *m/z* (%) = 2662.6 (100) $[Cu(\mathbf{1})(\mathbf{2})]^+$.

Nanorotor **ROT-2**



One equiv of $[Cu(CH_3CN)_4]PF_6$ (466 µg, 1.25 µmol) was added to complex **ROT-1** (3.87 mg, 1.25 µmol). Sonication for 2 min afforded **ROT-2** quantitatively. **Mp**:. > 250 ºC. **IR (KBr):** $\tilde{\nu}$ = 558, 726, 798, 847, 996, 1063, 1203, 1336, 1379, 1438, 1457, 1493, 1589, 1611, 2222, 2852, 2922, 2954 cm^{-1}. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = –[4.51-4.47] (m, 6H, CH_2, DABCO), –[4.44-4.40] (m, 6H, CH_2, DABCO), 1.09 (s, 6H, [f_1/f_2]-H), 1.13 (s, 6H, [f_2/f_1]-H), 1.45 (s, 3H, [f_3/f_4]-H), 1.55 (s, 3H, [f_4/f_3]-H), 1.72 (s, 6H, [12a/12b]-H), 1.91 (s, 6H, [12b/12a]-H), 2.05 (s, 6H, d-H), 2.11 (bs, 12H, 15-H), 2.22 (s, 12H, 17-H), 2.37 (s, 6H, 16-H), 2.49 (s, 6H, 13-H), 2.58 (s, 12H, 18-H), 2.71 (s, 3H, g_2-H), 2.75 (s, 6H, g_1-H), 6.93 (s, 2H, s-H), 7.04–7.10 (m, 6H, [14a+14b+e_1/e_2]-H), 7.23 (s, 2H, [e_2/e_1]-H), 7.24 (s, 2H, s-H), 7.27 (s, 4H, 9-H), 7.31–7.35 (m, 4H, [c+e_3+e_4]-H), 7.44 (bs, 2H, s-H), 7.87–7.96 (m, 6H, [s+3/8]-H), 8.01 (d, ^3J = 8.0 Hz, 2H, [8/3]-H), 8.18–8.23 (s, 6H, [5+6+s]-H), 8.28 (d, 4H, ^3J = 4.6 Hz, β(**1**)-H), 8.31 (d, ^3J = 4.6 Hz, 2H, β(**1**)-H), 8.34–8.38 (m, 6H, β(**1**)+β(**2**)-H), 8.50 (bs, 2H, β(**2**)-H), 8.54 (d, ^3J = 4.6 Hz, 2H, β(**2**)-H), 8.77 (d, ^3J = 8.0 Hz, 2H, [4/7]-H), 8.78 (d, ^3J = 8.0 Hz, 4H, [7/4]-H) ppm. **ESI-MS:** *m/z* (%) = 1363.2 (100) $[Cu_2(\mathbf{1})(\mathbf{2})]^{2+}$, 1829.5 (15) $[Cu_2(\mathbf{1})(\mathbf{2})_2]^{2+}$.

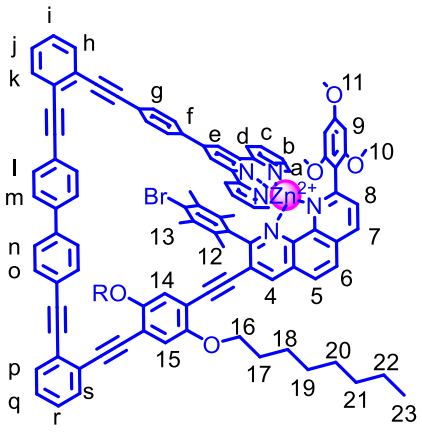
Synthesis of [Cu(**3**)]$^+$



[Cu(**3**)]$^+$

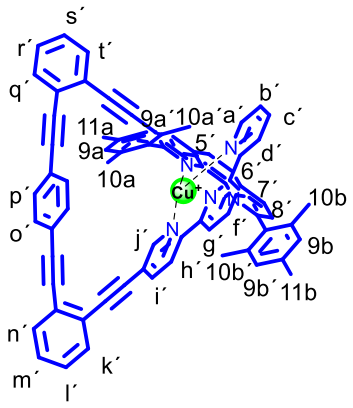
In an NMR tube, compound **3** (725 µg, 447 nmol) was dissolved in 500 mL of CD_2Cl_2, then $[Cu(CH_3CN)_4]PF_6$ (167 µg, 447 nmol) was added. Immediately the solution assumed a reddish-brown color indicating the formation of the metal complex. The complex was unambiguously characterized by ^{1}H NMR, ^{1}H-^{1}H COSY, ESI-MS and elemental analysis. **IR (KBr):** $\tilde{\nu}$ = 557, 690, 757, 792, 844, 1004, 1021, 1127, 1157, 1206, 1222, 1280, 1338, 1384, 1427, 1467, 1499, 1587, 1610, 2027, 2142, 2204, 2347, 2856, 2927, 2954 cm^{-1}. **Mp.** > 250 ºC. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 0.76 (t, ^3J = 7.2 Hz, 3H, [23/23′]-H), 0.82 (t, ^3J = 7.2 Hz, 3H, [23′/23]-H), 1.05–1.08 (m, 4H, [22+22′]-H), 1.20–1.29 (m, 16H, [18+19+20+21+18′+19′+20′+21′]-H), 1.40 (s, 6H, 13-H), 1.47 (t, ^3J = 7.2 Hz, 2H, [17/17′]-H), 1.60 (t, ^3J = 7.2 Hz, 2H, [17′/17]-H), 1.89 (s, 6H, 12-H), 3.27 (s, 12H, 10-H), 3.58 (s, 6H, 11-H), 3.66 (t, ^3J = 7.2 Hz, 2H, [16/16′]-H), 3.82 (t, ^3J = 7.2 Hz, 2H, [16′/16]-H), 5.72 (s, 2H, 9-H), 6.11 (s, 1H, 14-H), 6.97 (s, 1H, 15-H), 7.15 (ddd, ^3J = 7.8 Hz, ^3J = 4.8 Hz, ^4J = 1.2 Hz, 1H, b-H), 7.32–7.38 (m, 2H, [i+j]-H), 7.39 (td, ^3J = 7.8 Hz, ^4J = 1.2 Hz, 2H, c-H), 7.41–7.44 (m, 2H, [q+r]-H), 7.54 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 1H, k-H), 7.58 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 1H, h-H), 7.59–7.61 (m, 4H, [n+o]-H), 7.62–7.64 (m, 3H, [m+p]-H), 7.66–7.69 (m, 3H, [l+s]-H), 7.92 (d, ^3J = 8.0 Hz, 2H, g-H), 7.95 (d, ^3J = 8.0 Hz, 1H, 8-H), 8.04 (d, ^3J = 8.0 Hz, 2H, f-H), 8.06 (d, ^3J = 8.0 Hz, 1H, [5/6]-H), 8.12 (ddd, ^3J = 4.8 Hz, ^4J = 1.2 Hz, ^5J = 0.8 Hz, 2H, a-H), 8.20 (d, ^3J = 8.0 Hz, 1H, [6/5]-H), 8.25 (ddd, ^3J = 7.8 Hz, ^4J = 1.2 Hz, ^5J = 0.8 Hz, 2H, d-H), 8.39 (s, 2H, e-H), 8.58 (s, 1H, 4-H), 8.66 (d, ^3J = 8.0 Hz, 1H, 7-H) ppm. **Elemental analysis:** Anal. Calcd for $C_{108}H_{94}BrCuF_6N_5O_{5P}$•$4CH_2Cl_2$•$H_2O$: C, 66.05; H, 4.94; N, 3.50. Found: C, 65.88; H, 4.97; N, 3.25. **ESI-MS:** *m/z* (%) 1684.5 (100) [Cu(**3**)]$^+$.

Synthesis of **[Zn(3)]$^{2+}$**



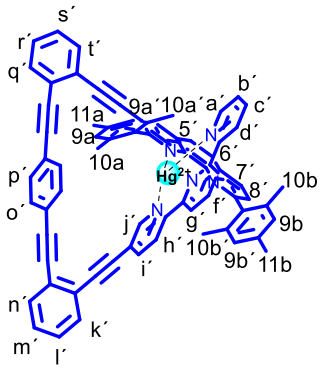
In an NMR tube, compound **3** (754 µg, 464 nmol) was dissolved in 500 mL of CD_2Cl_2. A solution of $Zn(OTf)_2$ (169 µg, 447 nmol) in CD_3CN (7 µL) was added to it. The complex was then unambiguously characterized by ^{1}H NMR, ^{1}H-^{1}H COSY, ESI-MS and elemental analysis. **IR (KBr):** $\tilde{\nu}$ = 639, 761, 1031, 1163, 1227, 1256, 1384, 1476, 1604, 1715, 2060, 2150, 2224, 2320, 2864, 2929, 2940 cm^{-1}. **Mp.** > 250 ºC. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 0.75 (t, ^3J = 7.2 Hz, 3H, [23/23′]-H), 0.82 (t, ^3J = 7.2 Hz, 3H, [23′/23]-H), 0.96 (s, 6H, 13-H), 1.05–1.11 (m, 8H, [21+21′+22+22′]-H), 1.17–1.25 (m, 12H, [18+19+20+18′+19′+20′]-H), 1.45 (t, ^3J = 7.2 Hz, 2H, [17/17′]-H), 1.54 (merged with H_2O signal, 2H, [17′/17]-H), 1.89 (s, 6H, 12-H), 3.27 (s, 6H, 10-H), 3.58 (s, 3H, 11-H), 3.66 (t, ^3J = 7.2 Hz, 2H, [16/16′]-H), 3.82 (t, ^3J = 7.2 Hz, 2H, [16′/16]-H), 5.72 (s, 2H, 9-H), 6.11 (s, 1H, 14-H), 6.97 (s, 1H, 15-H), 7.32–7.35 (m, 2H, [i+j]-H), 7.42–7.45 (m, 2H, [q+r]-H), 7.53 (dd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, 1H, k-H), 7.59–7.61 (m, 7H, [b+n+o+h]-H), 7.62–7.64 (m, 3H, [m+p]-H), 7.66–7.69 (m, 3H, [l+s]-H), 7.76 (ddd, ^3J = 4.8 Hz, ^4J = 1.2 Hz, ^5J = 0.8 Hz, 2H, a-H), 7.99 (d, ^3J = 8.4 Hz, 2H, g-H), 8.13 (^3J = 8.4 Hz, 1H, 8-H), 8.25 (d, ^3J = 8.4 Hz, 2H, f-H), 8.35 (td, ^3J = 8.0 Hz, ^4J = 1.2 Hz, c-H), 8.39 (d, ^3J = 8.0 Hz, [5/6]-H), 8.52 (d, ^3J = 8.0 Hz, [6/5]-H), 8.72 (s, 2H, e-H), 8.78 (ddd, ^3J = 8.0 Hz, ^4J = 0.8 Hz, ^5J = 0.8 Hz, 2H, d-H), 8.93 (s, 1H, 4-H), 9.02 (d, ^3J = 8.4 Hz, 2H, 7-H) ppm. **Elemental analysis:** Anal. Calcd for $C_{110}H_{94}BrF_6N_5O_{11}S_2Zn_2$•1.5$CH_2Cl_2$: C, 63.39; H, 4.63; N, 3.31. Found: C, 63.36; H, 4.74; N, 2.91. **ESI-MS:** *m/z* (%) 843.1 (100) [Zn(**3**)]$^{2+}$.

Synthesis of [Cu(**4**)]$^{+}$



In an NMR tube, compound **4** (423 µg, 435 nmol) was dissolved in 500 mL of CD_2Cl_2, then $[Cu(CH_3CN)_4]PF_6$ (162 µg, 435 nmol) was added. Immediately, the solution assumed a reddish-brown color, indicating the formation of the metal complex. The complex was then unambiguously characterized by ^{1}H NMR, ^{1}H-^{1}H COSY, ESI-Ms and elemental analysis. **Mp.** > 250 ºC. **IR (KBr):** $\tilde{\nu}$ = 557, 587, 610, 633, 666.1, 695, 722, 755, 781, 843, 868, 897, 923, 953, 986, 1015, 1039, 1042, 1073, 1200, 1240, 1263, 1299, 1329, 1384, 1451, 1510.7, 1603, 1636, 1725, 2223, 2224, 2230, 2235, 2856, 2922, 2952 cm^{-1}. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 1.32 (s, 3H, [10b/10b´]-H), 1.49 (s, 3H, [10b´/10b]-H), 1.78 (s, 3H, [10a/10a´]-H), 1.79 (s, 3H, [10a´/10a]-H), 1.92 (s, 3H, 11b-H), 1.99 (s, 3H, 11a-H), 6.12 (s, 1H, [9b/9b´]-H), 6.23 (s, 1H, [9b´/9b]-H), 6.34 (s, 1H, [9a/9a´]-H), 6.38 (s, 1H, [9a´/9a]-H), 7.21–7.26 (m, 2H, [q´+n´]-H), 7.27–7.31 (m, 3H, [r´+m+c´]-H), 7.32–7.38 (m, 3H, [g´+h´+b´]-H), 7.39–7.43 (m, 4H, [o´+p´]-H), 7.44–7.49 (m, 2H, [l´+s´]-H), 7.56–7.61 (m, 2H, [t´+k´]-H), 7.69 (ddd, ^{3}J = 8.0 Hz, ^{3}J = 1.8 Hz, ^{5}J = 0.8 Hz, 1H, d´-H), 7.76 (d, ^{3}J = 8.2 Hz, 1H, 8´-H), 7.78 (d, ^{3}J = 8.2 Hz, 1H, 6´-H), 7.88–7.94 (m, 3H, [e´+j´+f´]-H), 8.02–8.08 (m, 2H, [a´+i´]-H), 8.12 (d, ^{3}J = 8.2 Hz, 1H, 5´-H), 8.51 (s, 1H, 4´-H), 8.56 (d, ^{3}J = 8.2 Hz, 1H, 7´-H) ppm. **ESI-MS:** *m/z* (%) 1034.9 (100) [Cu(**4**)]$^{+}$.

Synthesis of $[Hg(\mathbf{4})]^{2+}$



In an NMR tube, compound **4** (423 µg, 435 nmol) was dissolved in 500 mL of CD_2Cl_2, then a solution of $HgClO_4$ (197 µg, 435 nmol) in CD_3CN was added. The complex was then unambiguously characterized by ^{1}H NMR, ^{1}H-^{1}H COSY, ESI-MS and elemental analysis. **Mp.** > 250 ºC. **IR (KBr):** $\tilde{\nu}$ = 501, 523, 560, 573, 610.0, 639, 668, 702, 761, 804, 824, 847, 867, 1033.0, 1065, 1108, 1161, 1230, 1259, 1385, 1451, 1484, 1510, 1563, 1632, 2220, 2215, 2230, 2235, 2853, 2922, 2959 cm^{-1}. **^{1}H NMR (CD_2Cl_2, 400 MHz):** δ = 1.17 (s, 3H, [10b/10b´]-H), 1.47 (s, 3H, [10b´/10b]-H), 1.52 (s, 3H, [10a/10a´]-H), 1.69 (s, 3H, [10a/10a´+11b)-H), 1.78 (s, 3H, 11a-H), 6.06 (s, 1H, [9b/9b´]-H), 6.12 (s, 1H, [9b´/9b]-H), 6.20 (s, 1H, [9a/9a´]-H), 6.28 (s, 1H, [9a´/9a]-H), 7.20 (d, ^3J = 8.4 Hz, 2H, [o´/p´]-H), 7.26 (d, ^3J = 8.4 Hz, 2H, [p´/o´]-H), 7.31 (td, ^3J = 8.0 Hz, ^4J = 1.6 Hz, l´-H), 7.37 (td, ^3J = 8.0 Hz, ^4J = 1.6 Hz, s´-H), 7.38–7.46 (m, 5H, [a´+q´+m´+n´+r´]-H), 7.53 (ddd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, ^5J = 0.8 Hz, 1H, k´-H), 7.62 (ddd, ^3J = 8.0 Hz, ^4J = 1.6 Hz, ^5J = 0.8 Hz, 1H, t´-H), 7.74 (ddd, ^3J = 8.0 Hz, ^3J = 4.8 Hz, ^4J = 1.8 Hz, 1H, b´-H), 7.94 (d, ^3J = 2.0 Hz, 1H, j´-H), 8.14 (d, ^3J = 8.2 Hz, 1H, 8´-H), 8.25 (t, ^3J = 8.0 Hz, 1H, f´-H), 8.27 (td, ^3J = 8.0 Hz, ^4J = 1.8 Hz, 1H, c´-H), 8.38 (d, ^3J = 8.2 Hz, 1H, 6´-H), 8.40 (dd, ^3J = 8.0 Hz, ^4J = 2.0 Hz, 1H, i´-H), 8.46 (dd, ^3J = 8.2 Hz, ^4J = 1.2 Hz, 1H, 5´-H), 8.48 (dd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, 1H, g´-H), 8.58 (dd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, 1H, e´-H), 8.63 (d, ^3J = 8.0 Hz, 1H, h´-H), 8.70 (ddd, ^3J = 8.0 Hz, ^4J = 1.8 Hz, ^5J = 0.8 Hz, 1H, d´-H), 9.00 (d, ^3J = 8.2 Hz, 1H, 7´-H), 9.14 (s, 1H, 4´-H) ppm. **Elemental analysis:** Anal. Calcd for $C_{71}H_{49}HgN_5$•$2ClO_4$: C, 62.17; H, 3.60; N, 5.11, Found: C, 62.34; H, 3.68; N, 5.43. **ESI-MS:** *m/z* (%) 586.9 (100) $[Hg(\mathbf{4})]^{2+}$.

2. NMR Spectra: ^{1}H, ^{13}C, ^{1}H-^{1}H COSY

For the numbering of protons, check the individual experimental procedure.

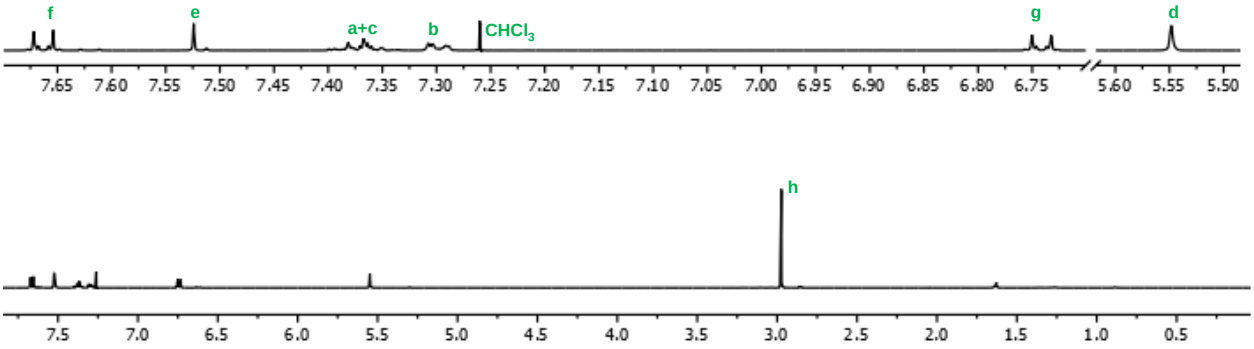


Figure S1: ^{1}H NMR spectrum ($CDCl_3$, 500 MHz, 298 K) of product **7**.

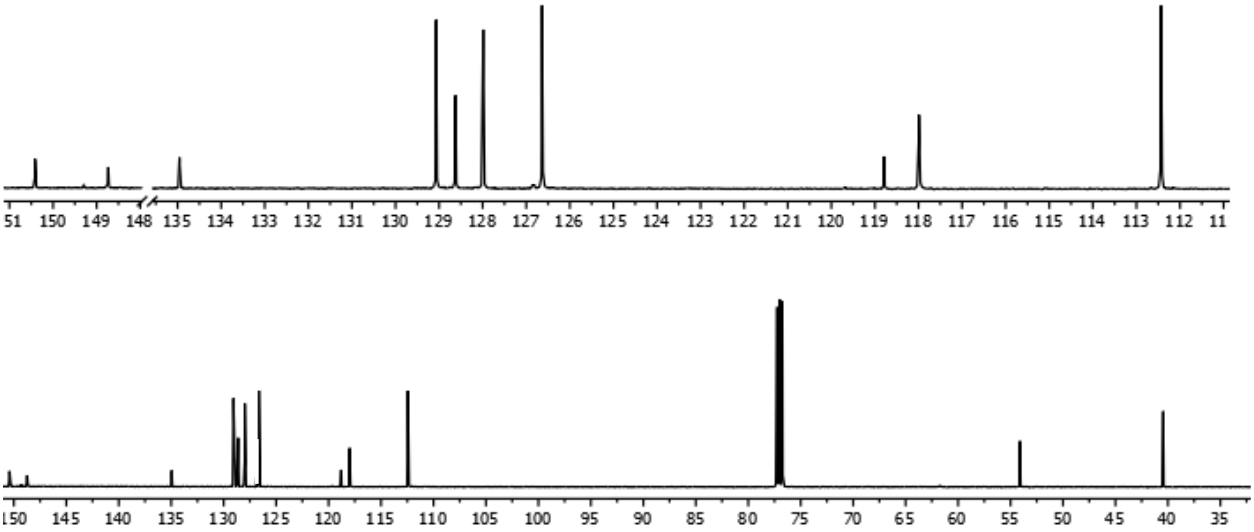


Figure S2: ^{13}C NMR spectrum ($CDCl_3$, 125 MHz, 298 K) of product **7**.

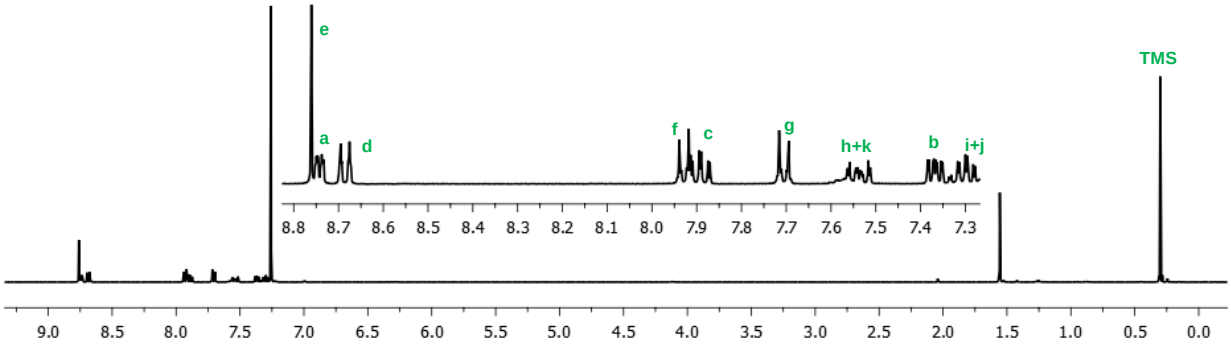


Figure S3: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of ligand **9**.

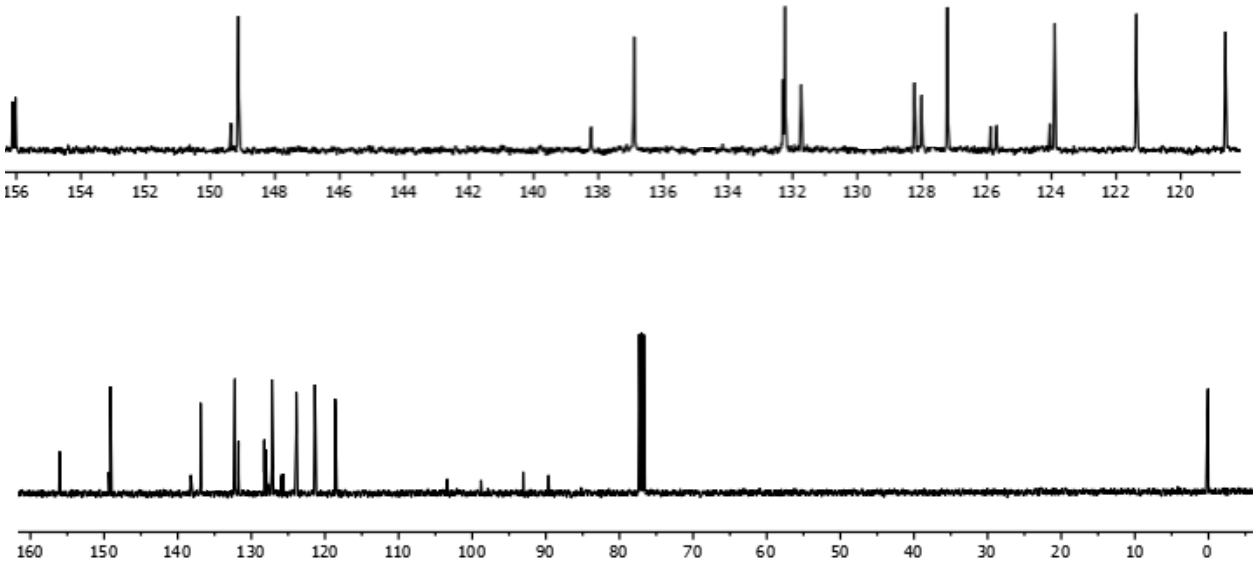


Figure S4: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of ligand **9**.

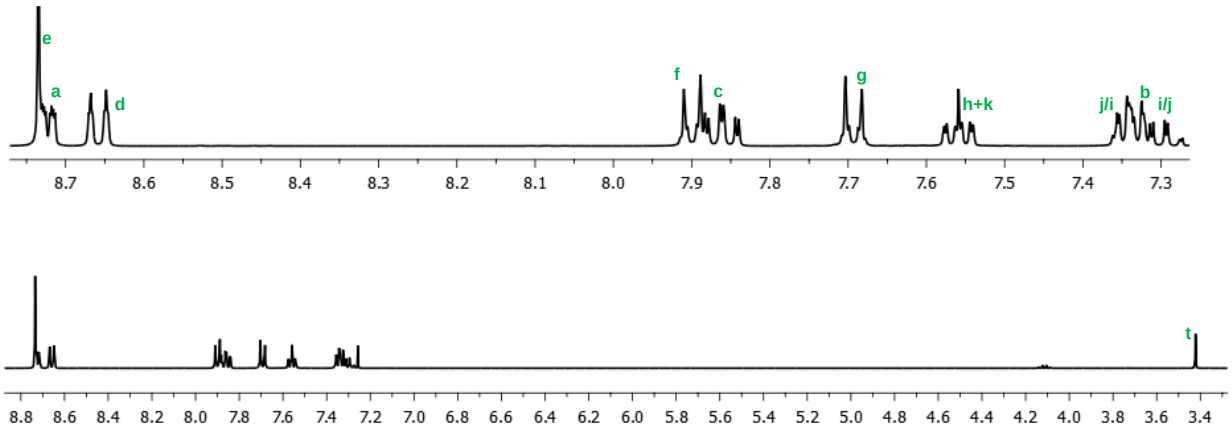


Figure S5: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of ligand **10**.

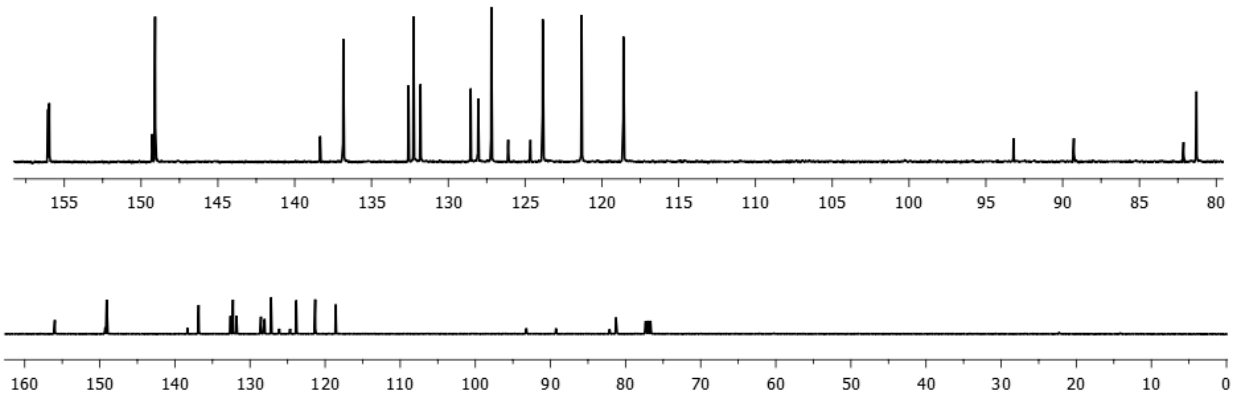


Figure S6: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of ligand **10**.

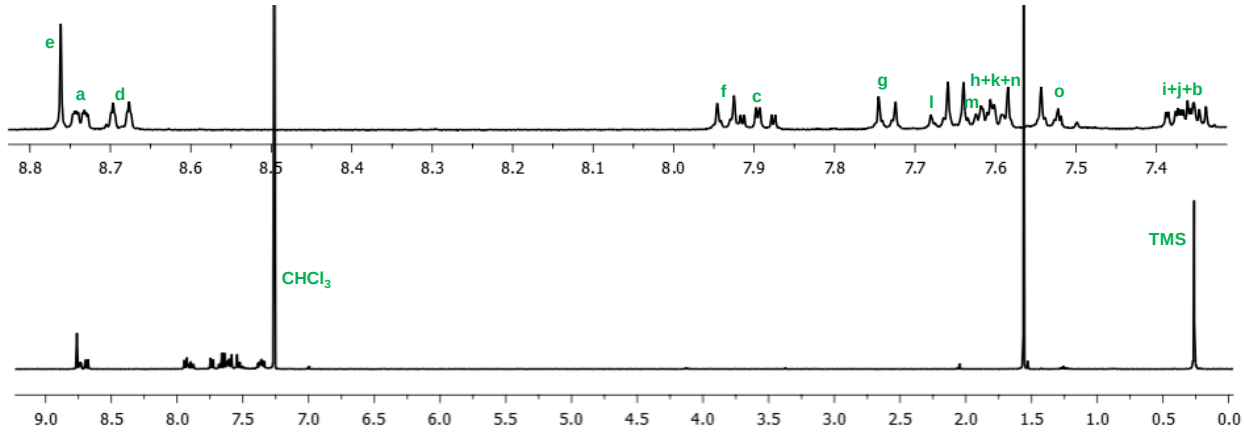


Figure S7: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of ligand **12**.

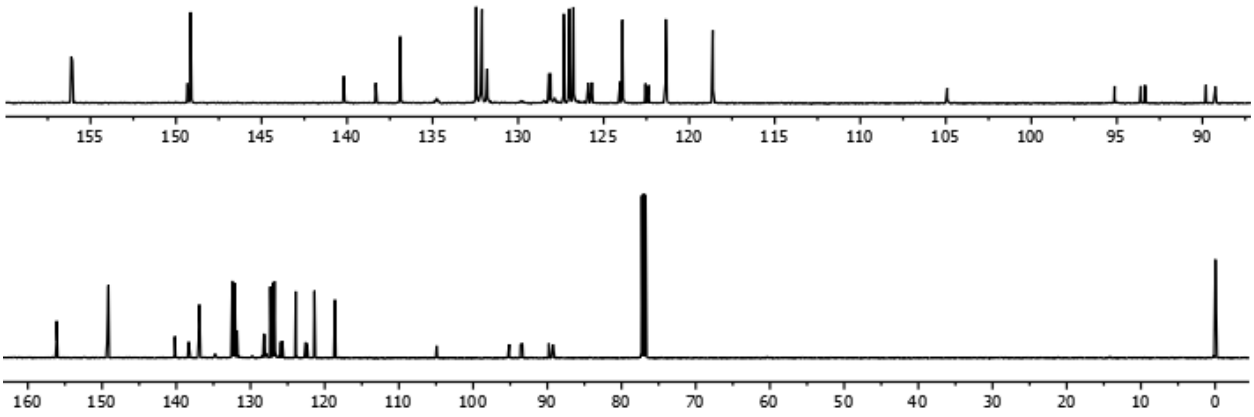


Figure S8: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of ligand **12**.

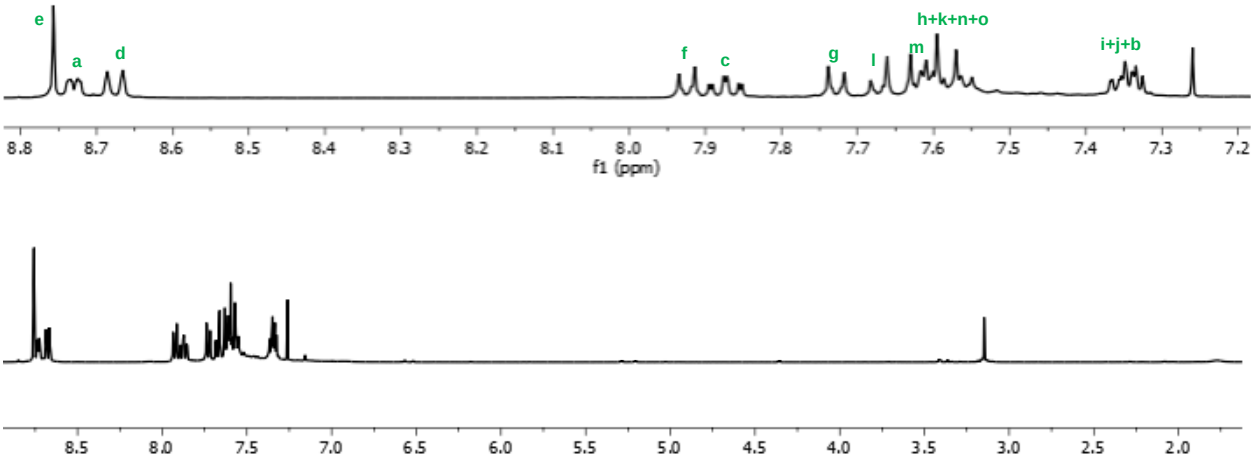


Figure S9: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of ligand **13**.

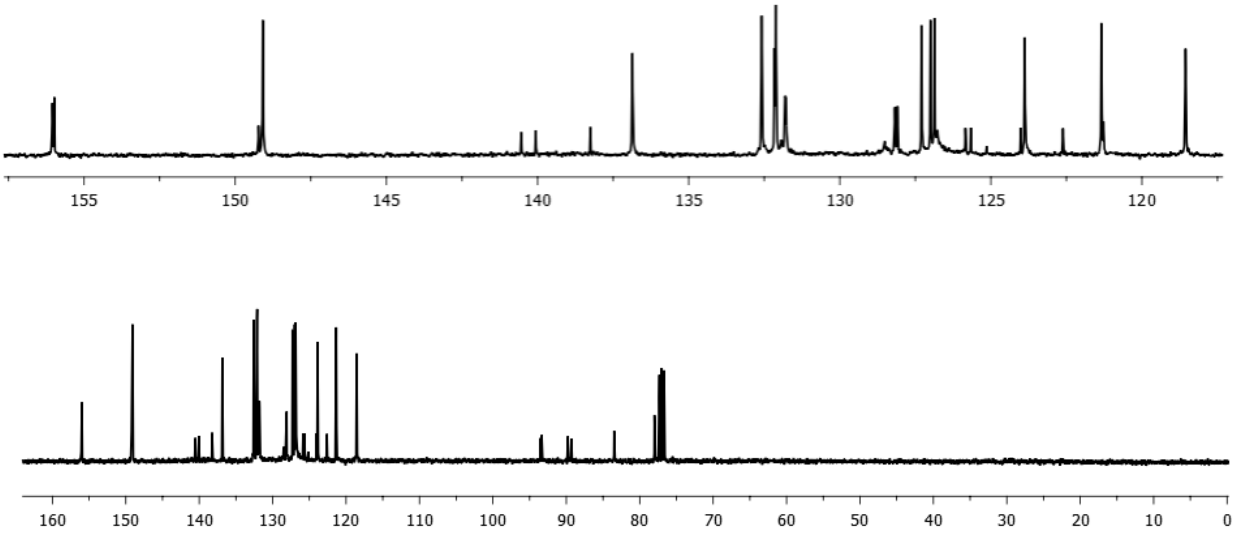


Figure S10: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of ligand **13**.

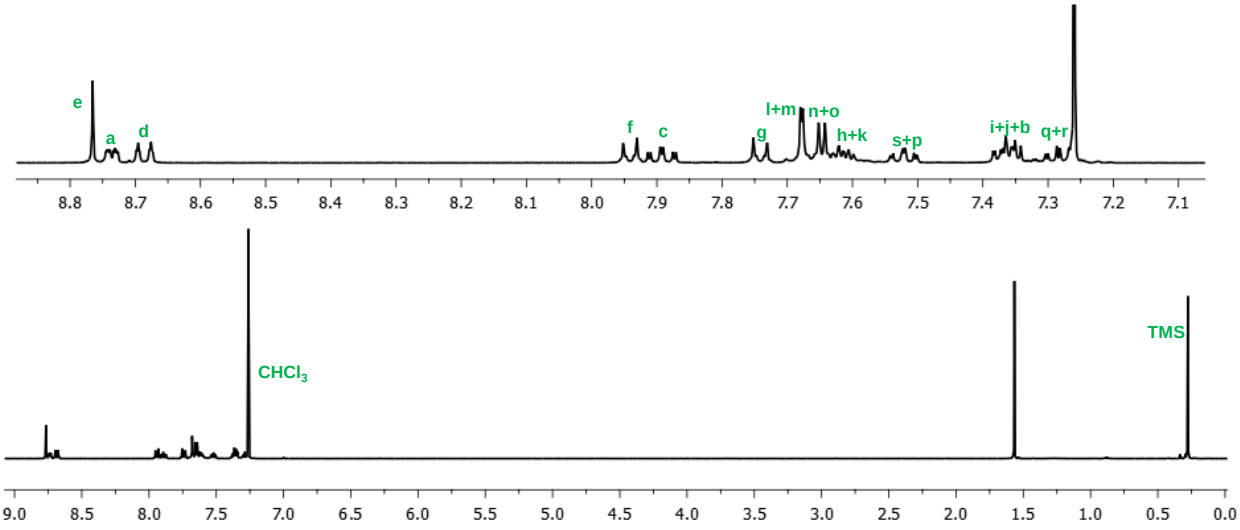


Figure S11: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of ligand **14**.

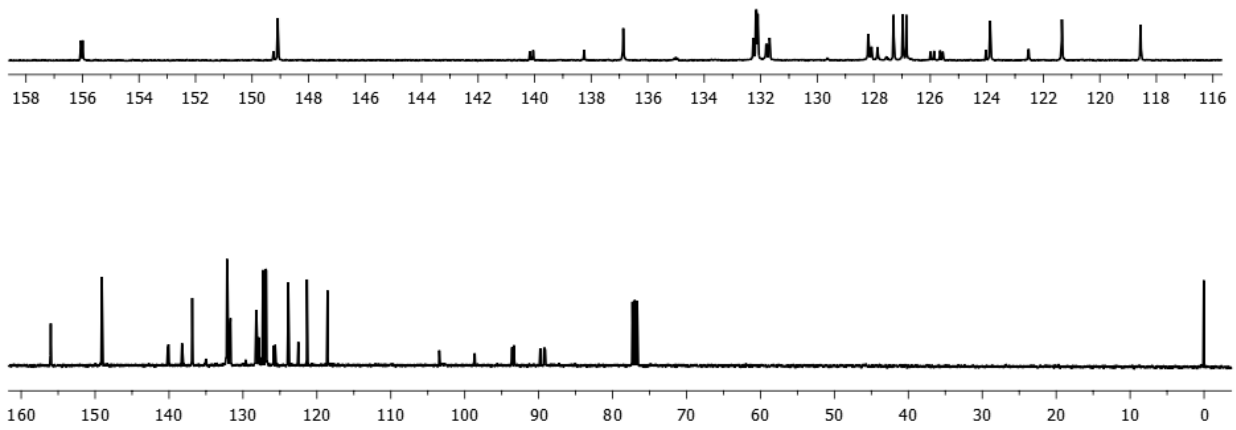


Figure S12: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of ligand **14**.

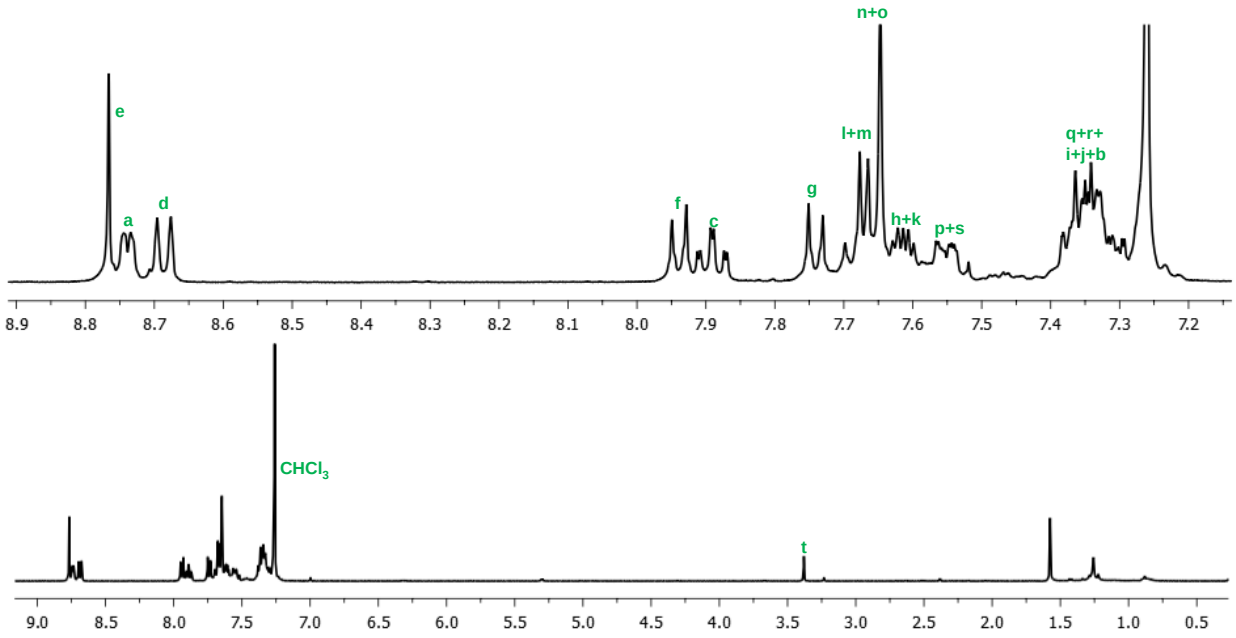


Figure S13: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of ligand **15**.

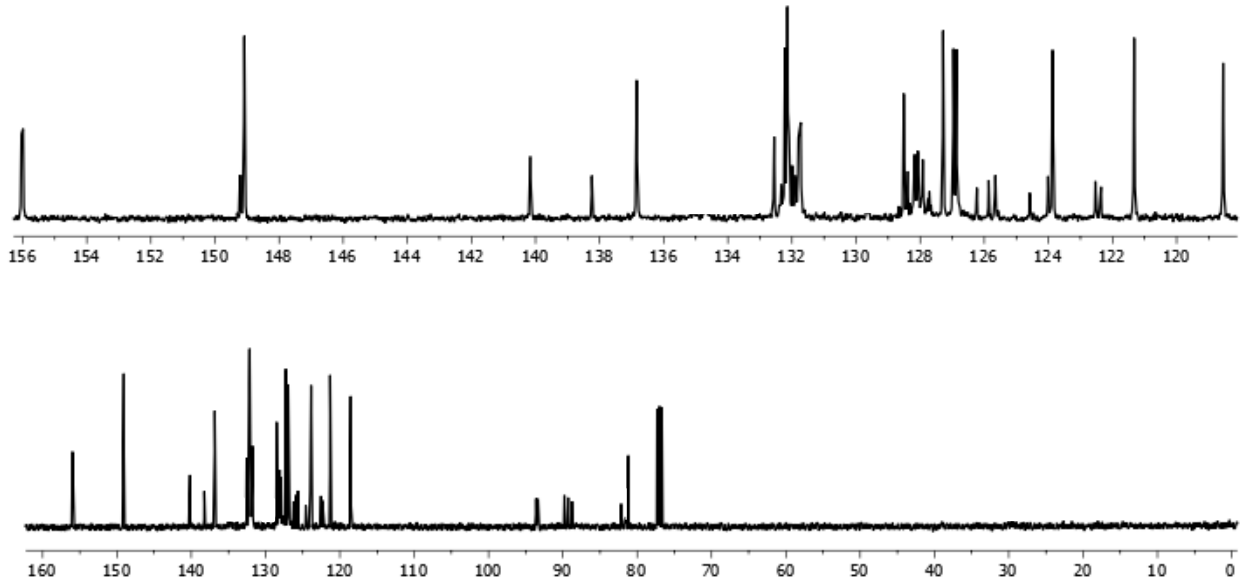


Figure S14: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of ligand **15**.

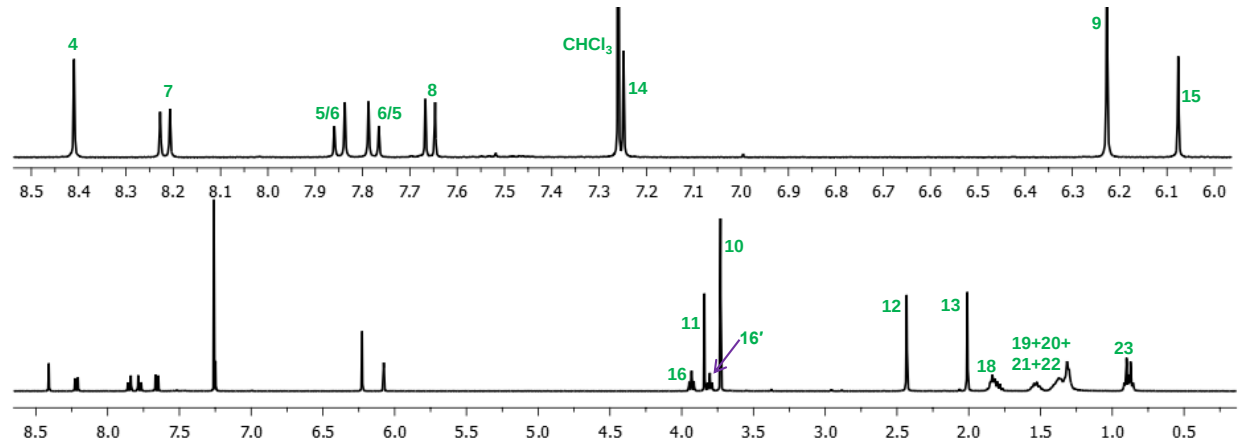


Figure S15: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of ligand **16**.

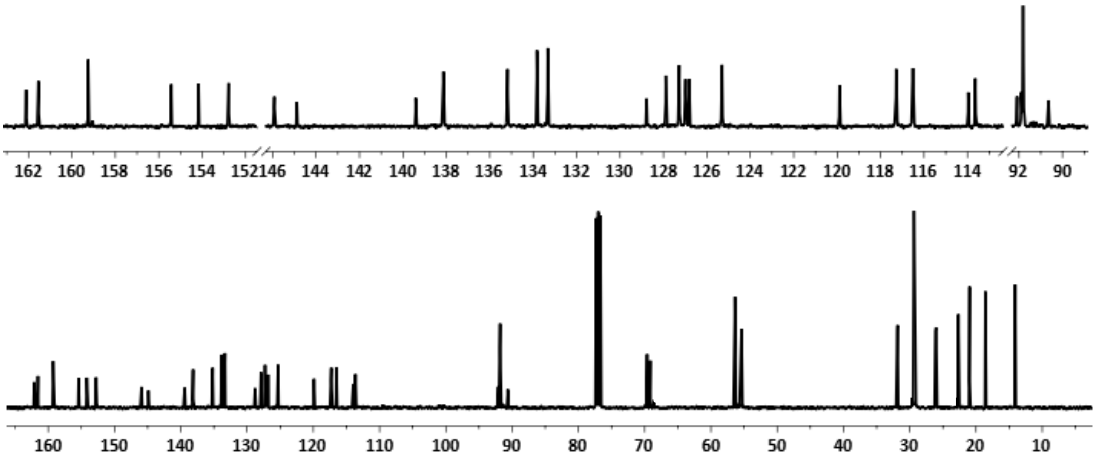


Figure S16: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of ligand **16**.

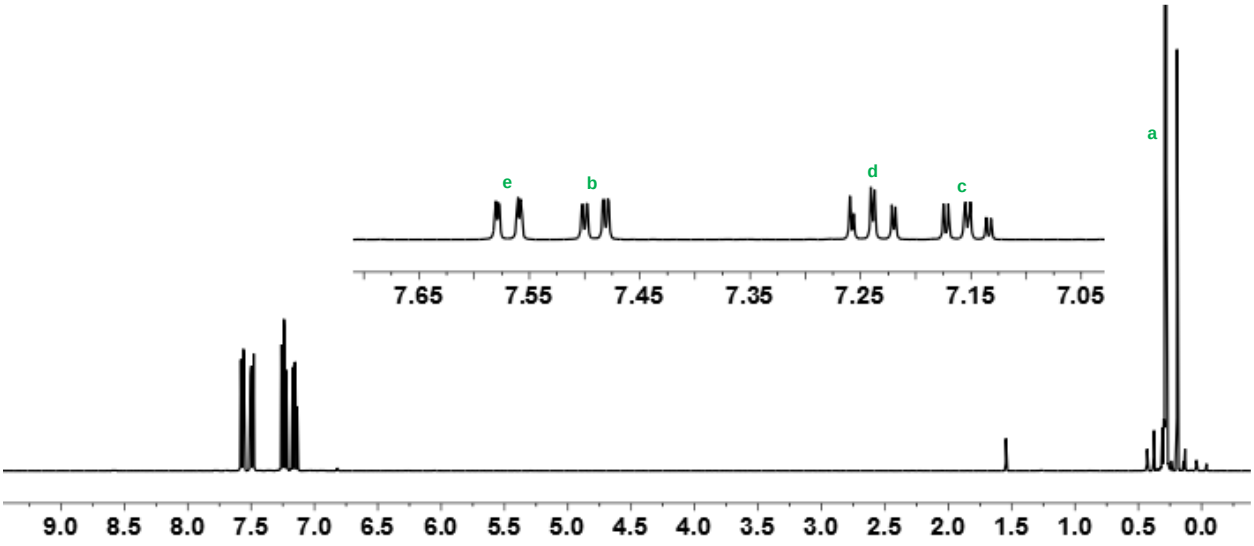


Figure S17: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of ligand **17**.

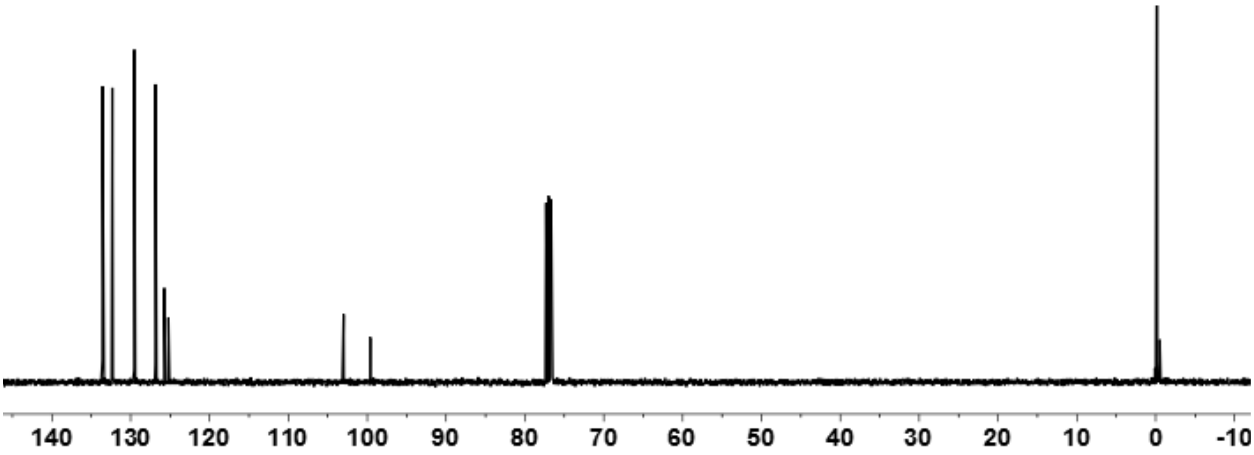


Figure S18: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of ligand **17**.

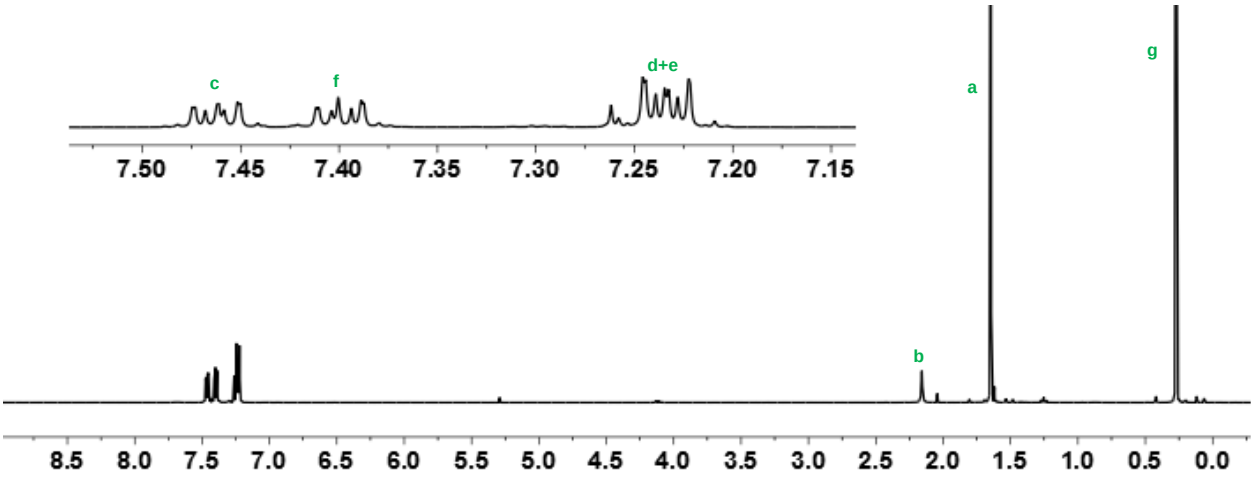


Figure S19: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of ligand **18.**

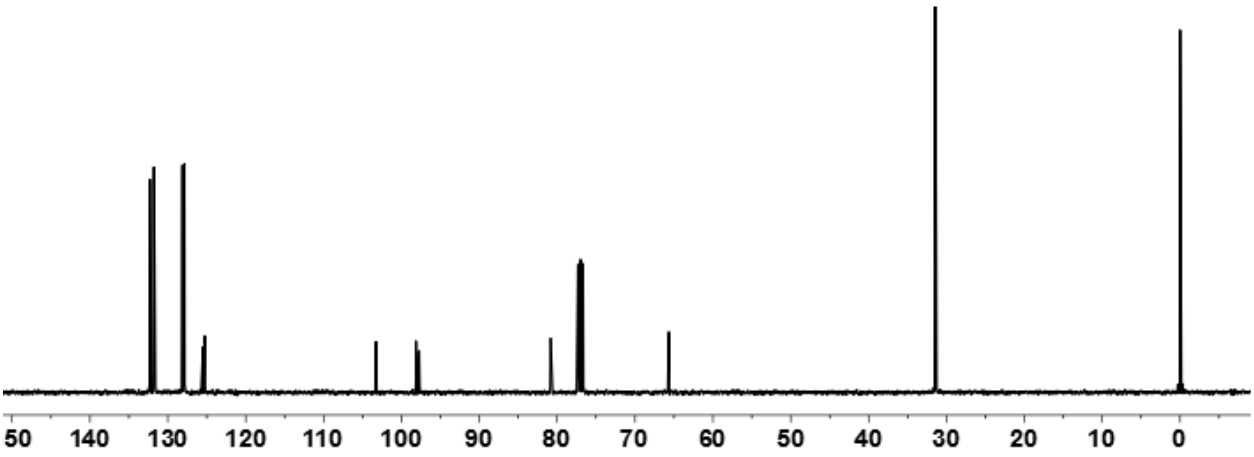


Figure S20: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of ligand **18**.

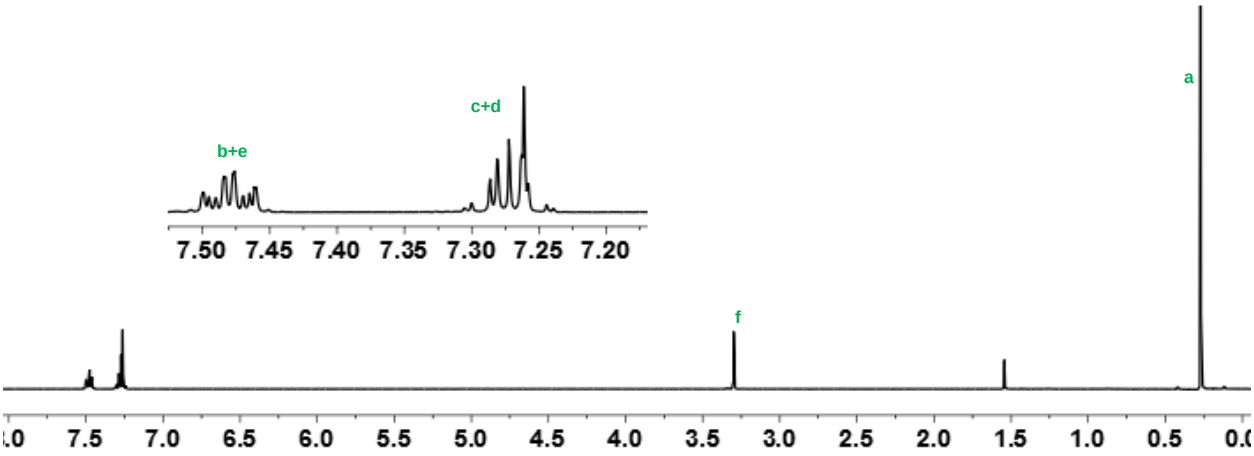


Figure S21: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of ligand **19**.

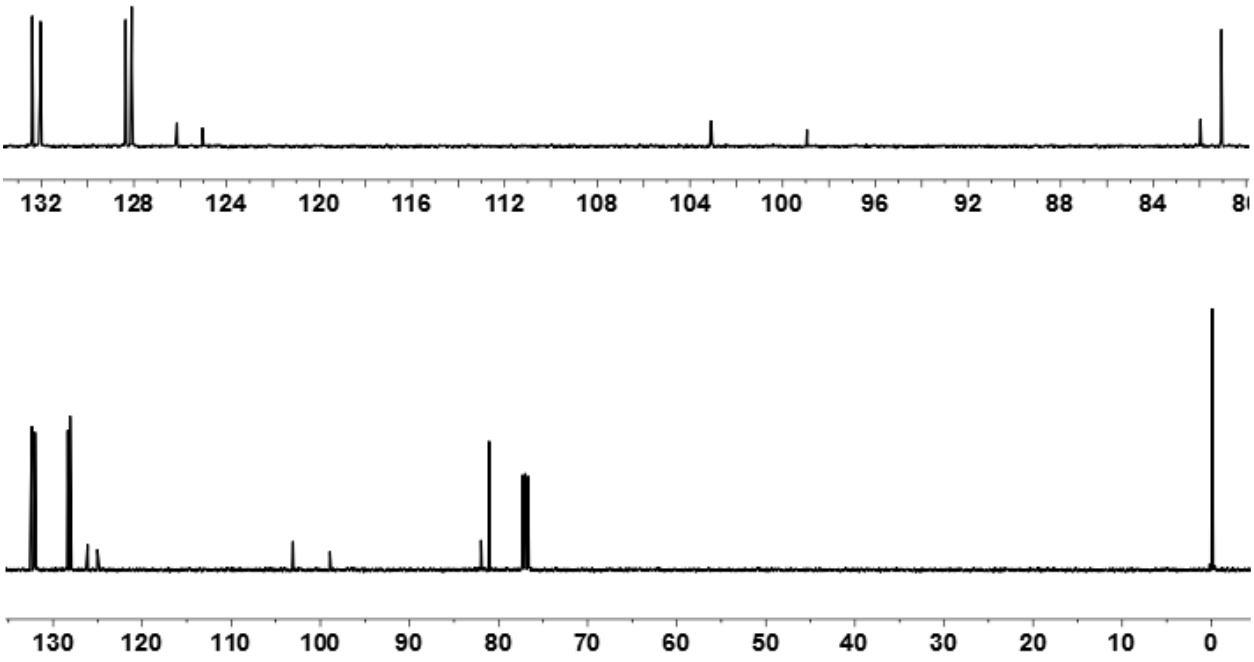


Figure S22: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of ligand **19**.

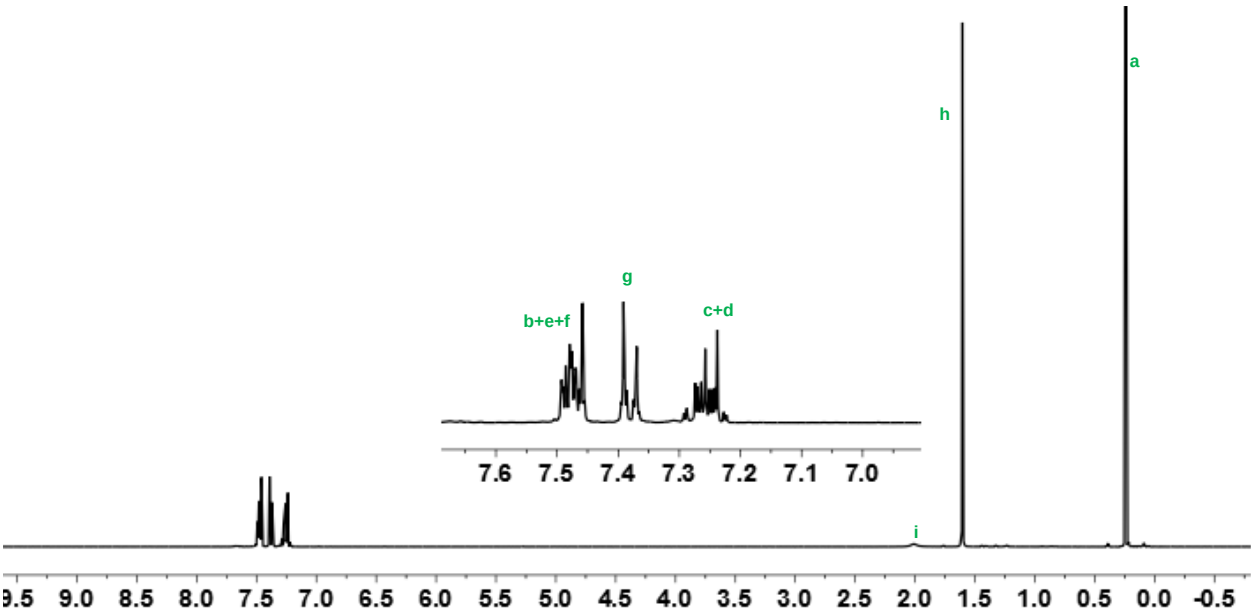


Figure S23: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of ligand **20**.

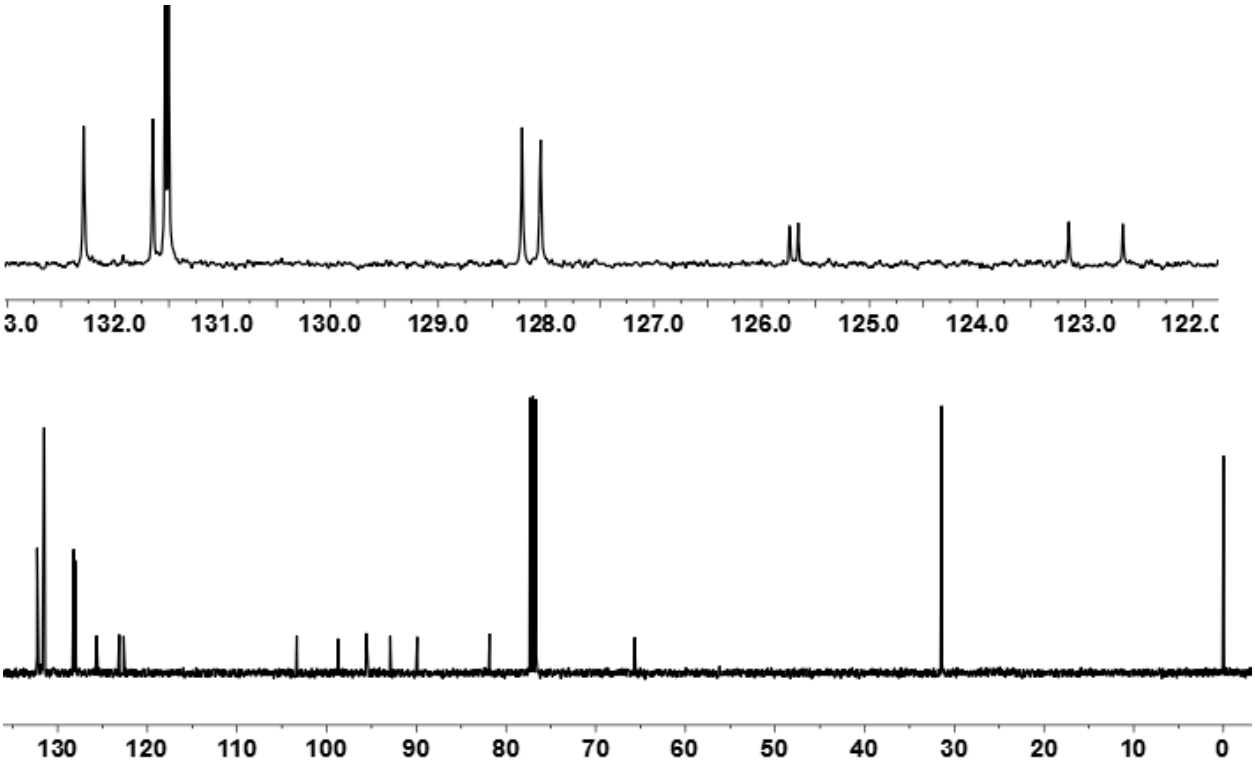


Figure S24: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of ligand **20**.

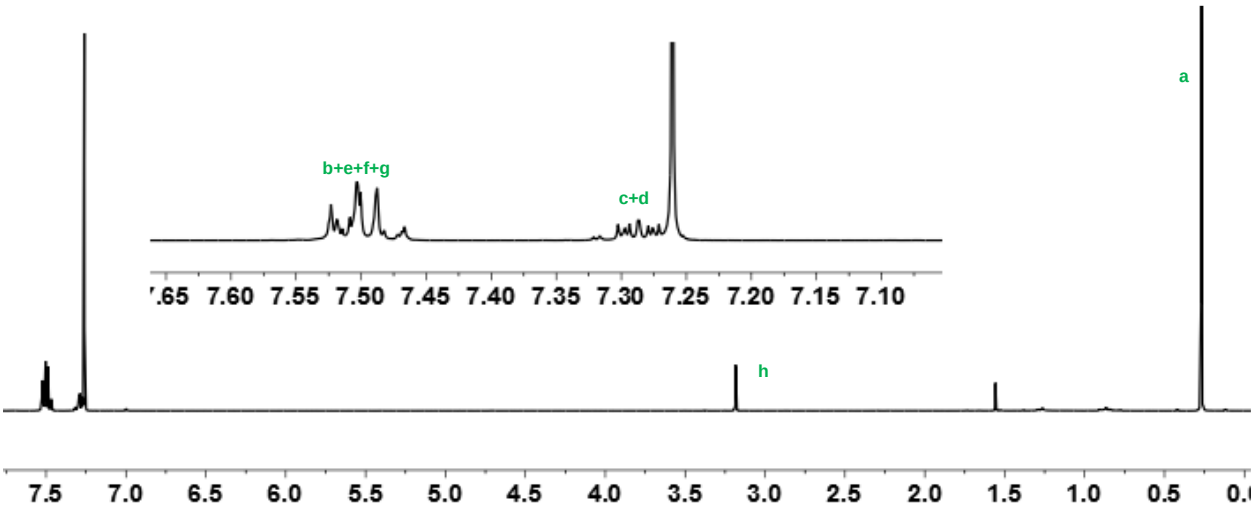


Figure S25: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of ligand **21**.

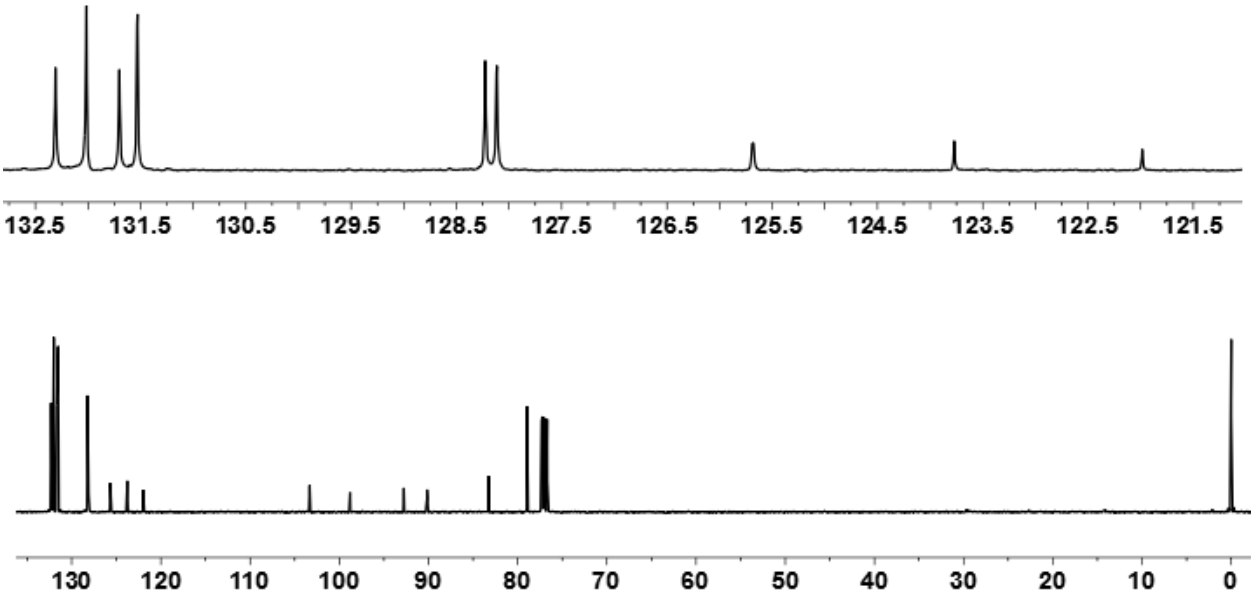


Figure S26: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of ligand **21**.

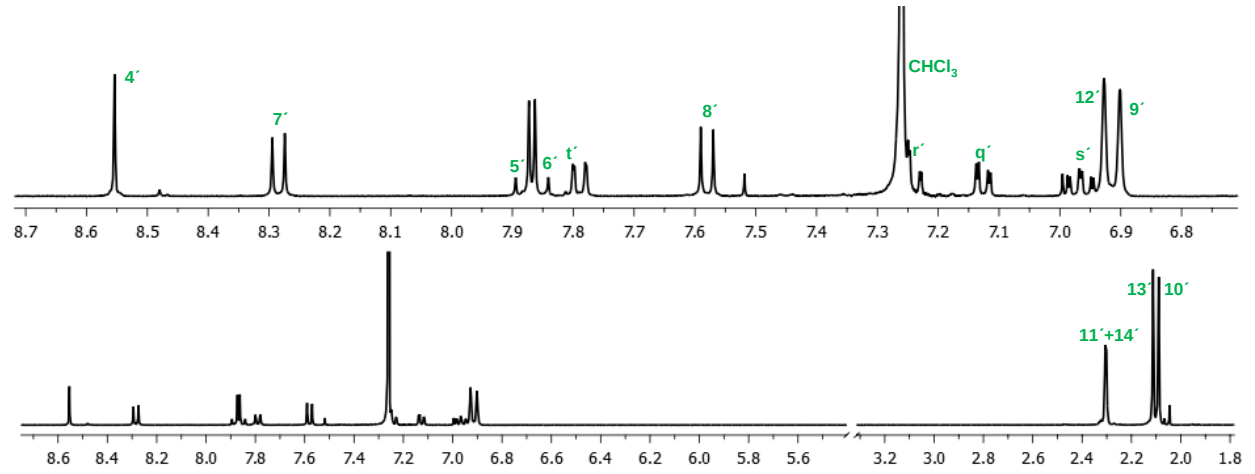


Figure S27: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of ligand **22**.

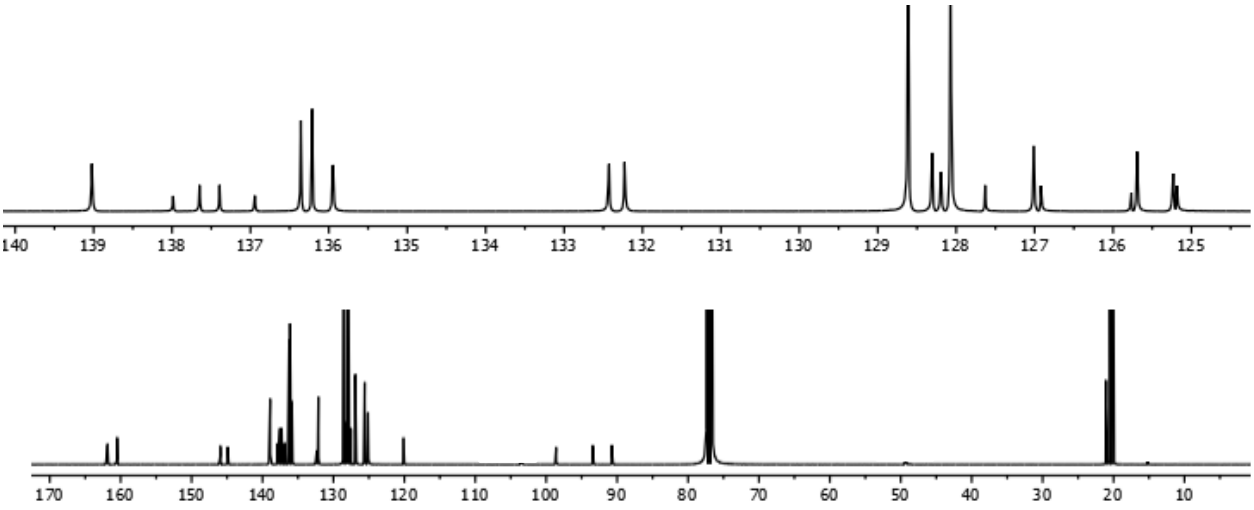


Figure S28: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of ligand **22**.

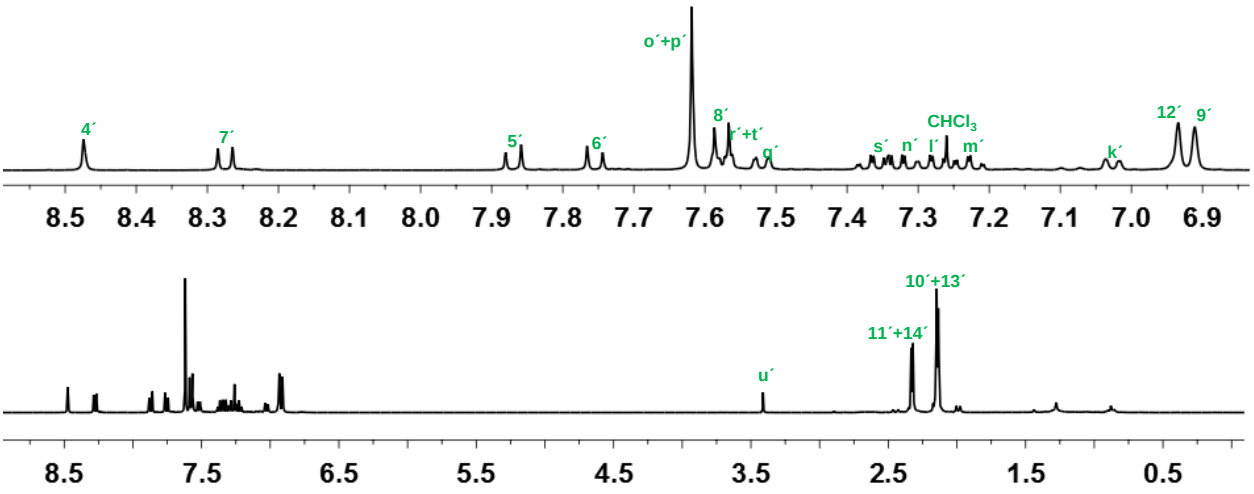


Figure S29: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of ligand **23**.

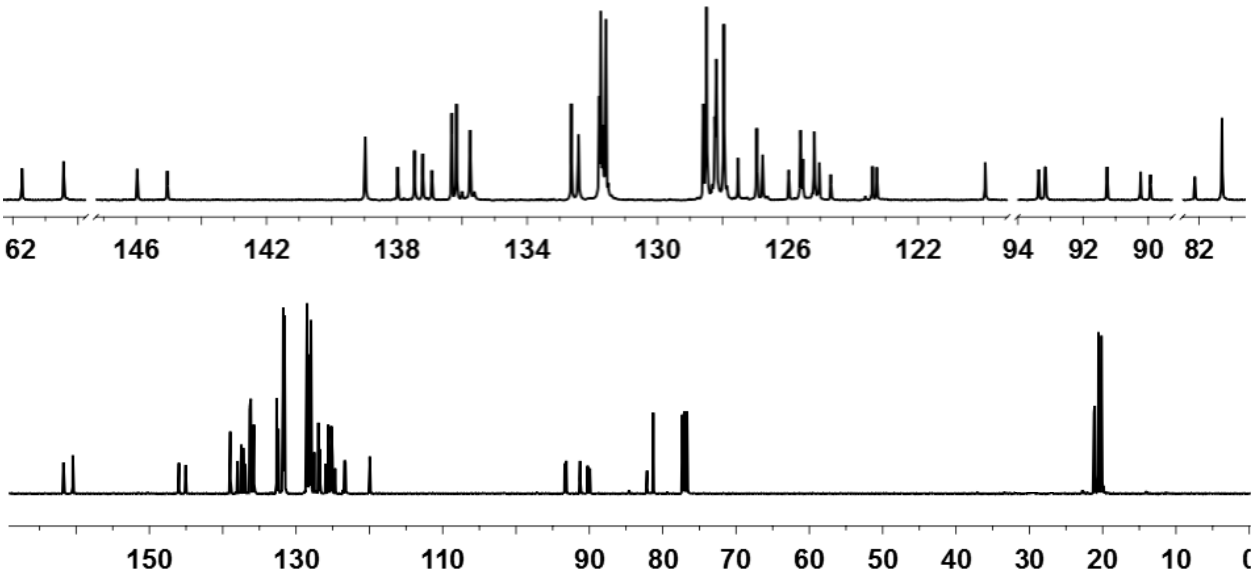


Figure S30: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of ligand **23**.

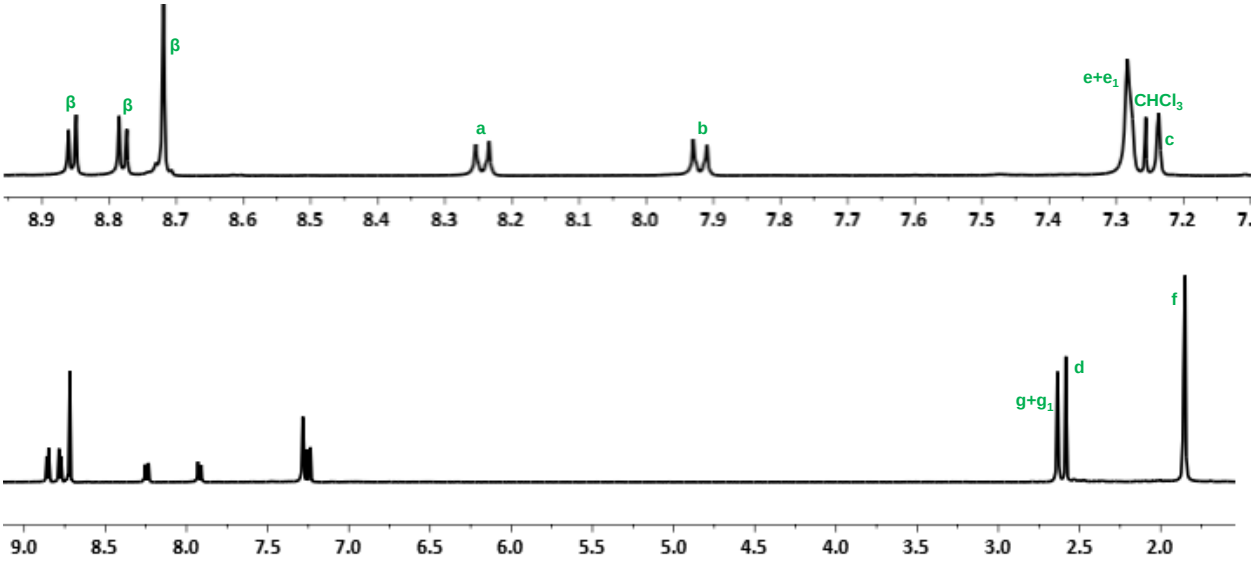


Figure S31: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of rotator **2**.

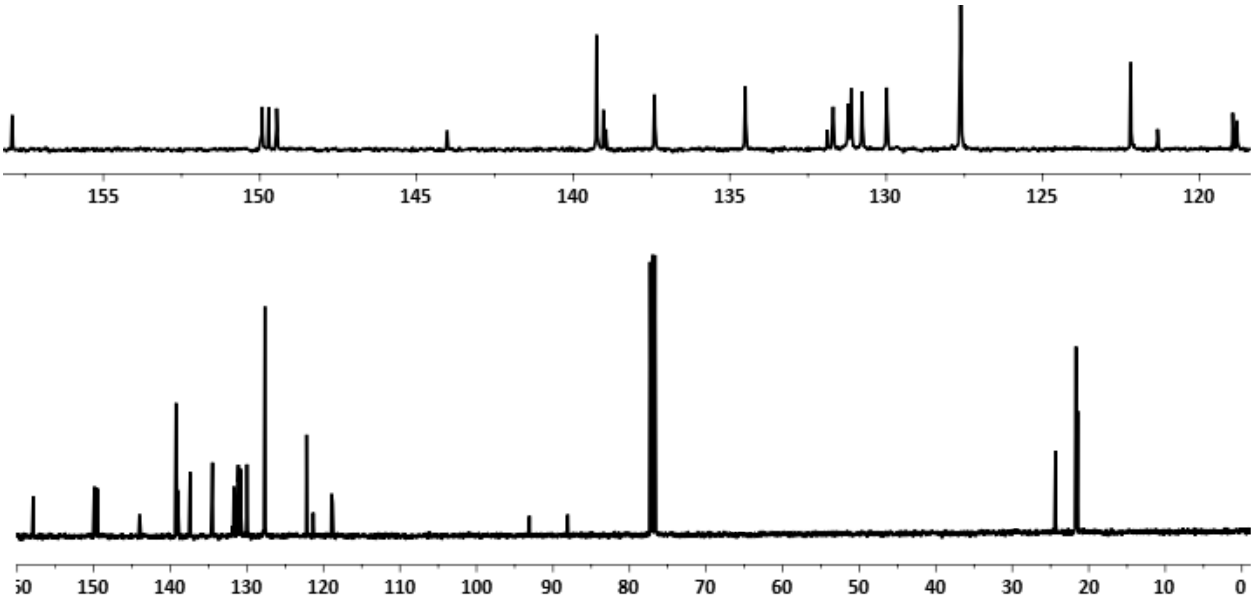


Figure S32: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of rotator **2**.

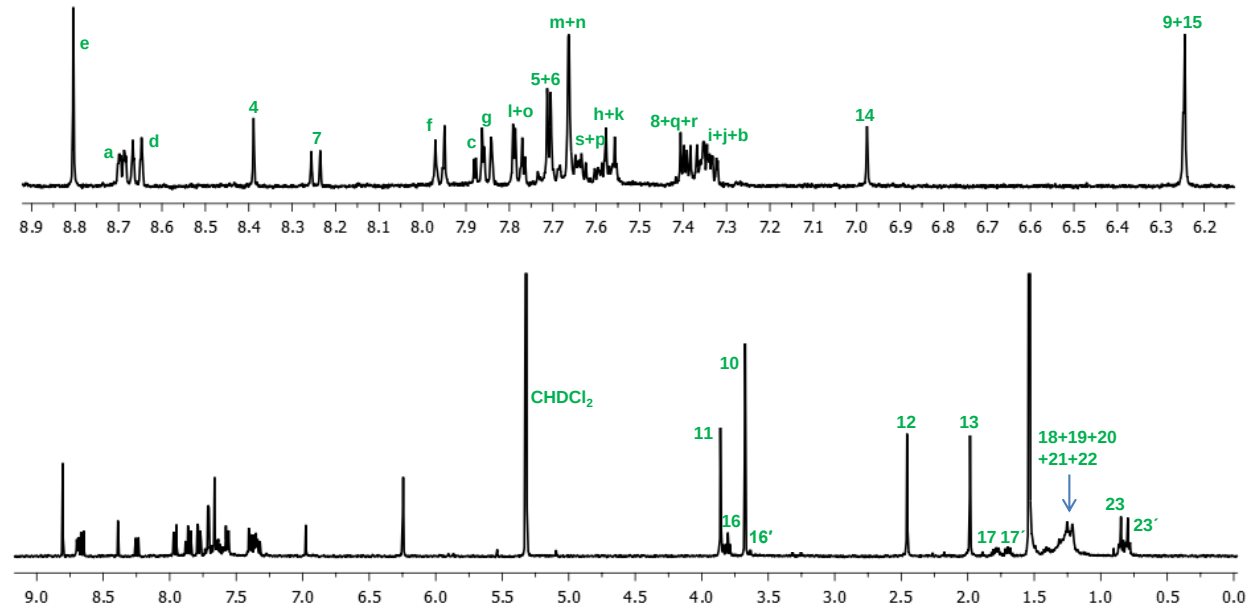


Figure S33: ^{1}H NMR spectrum ($CDCl_3$, 400 MHz, 298 K) of nanoswitch **3**.

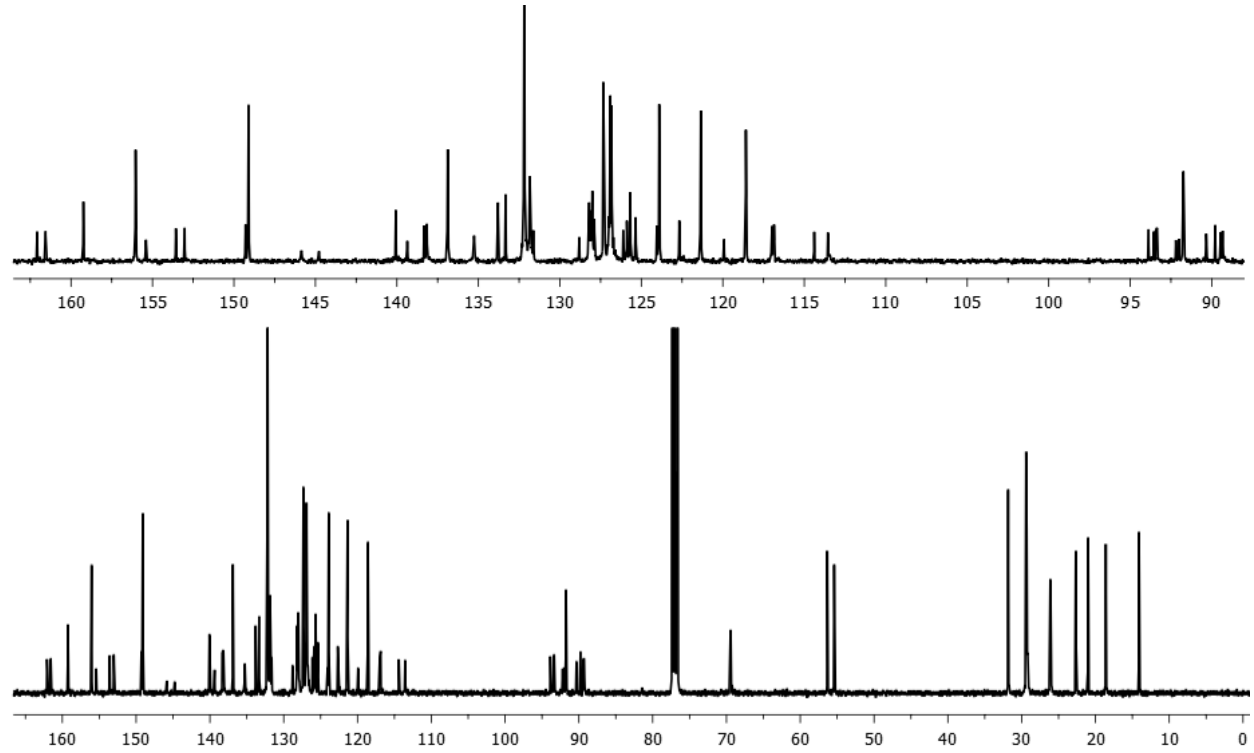


Figure S34: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of nanoswitch **3**.

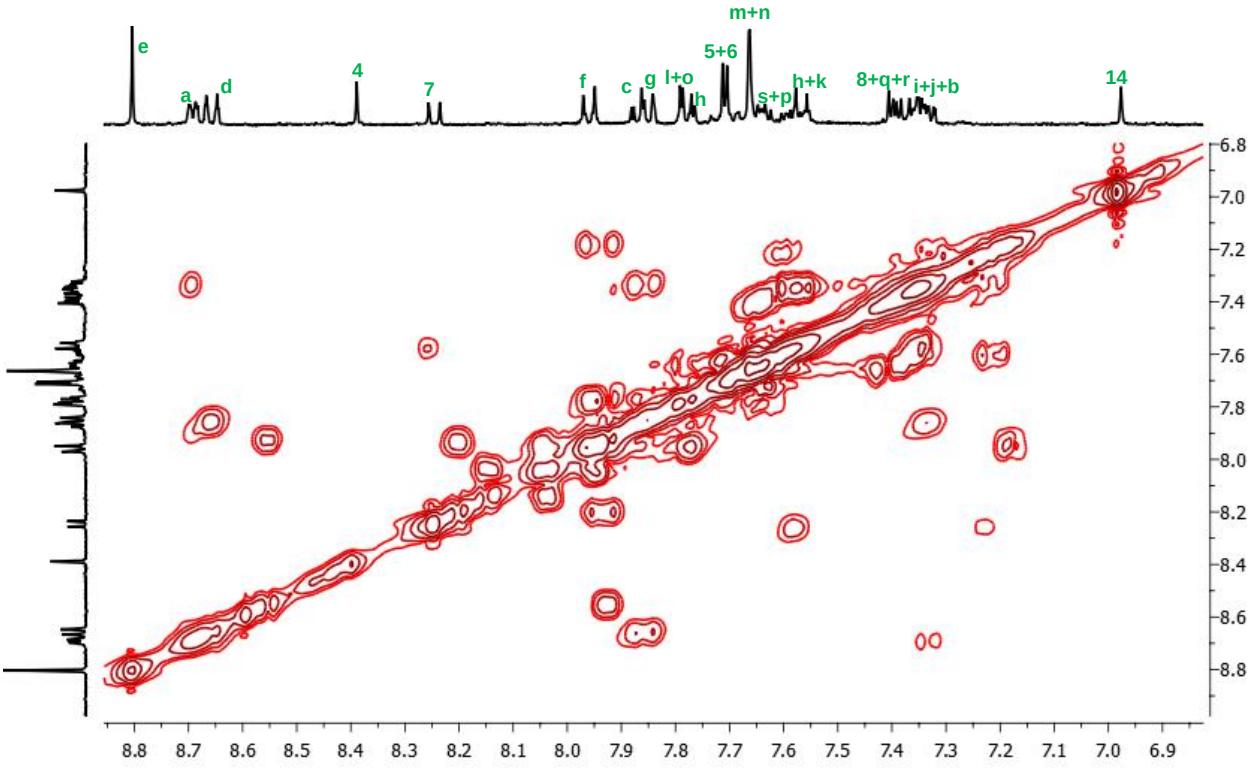


Figure S35: ^{1}H-^{1}H COSY NMR spectrum (CD_2Cl_2, 400 MHz, 298 K) of nanoswitch **3**.

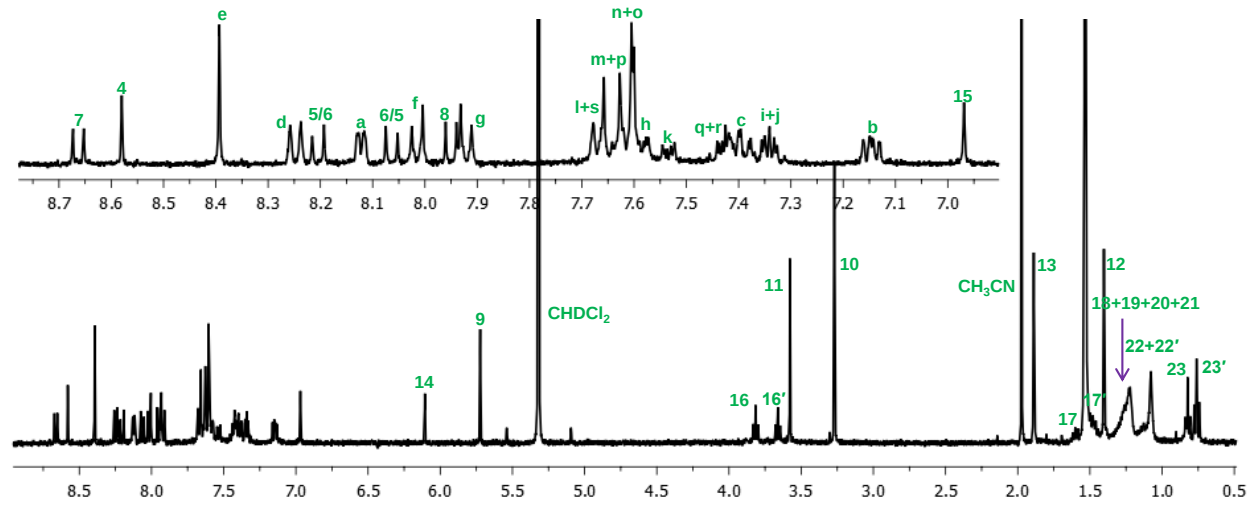


Figure S36: ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 298 K) of [Cu(**3**)]$^{+}$.

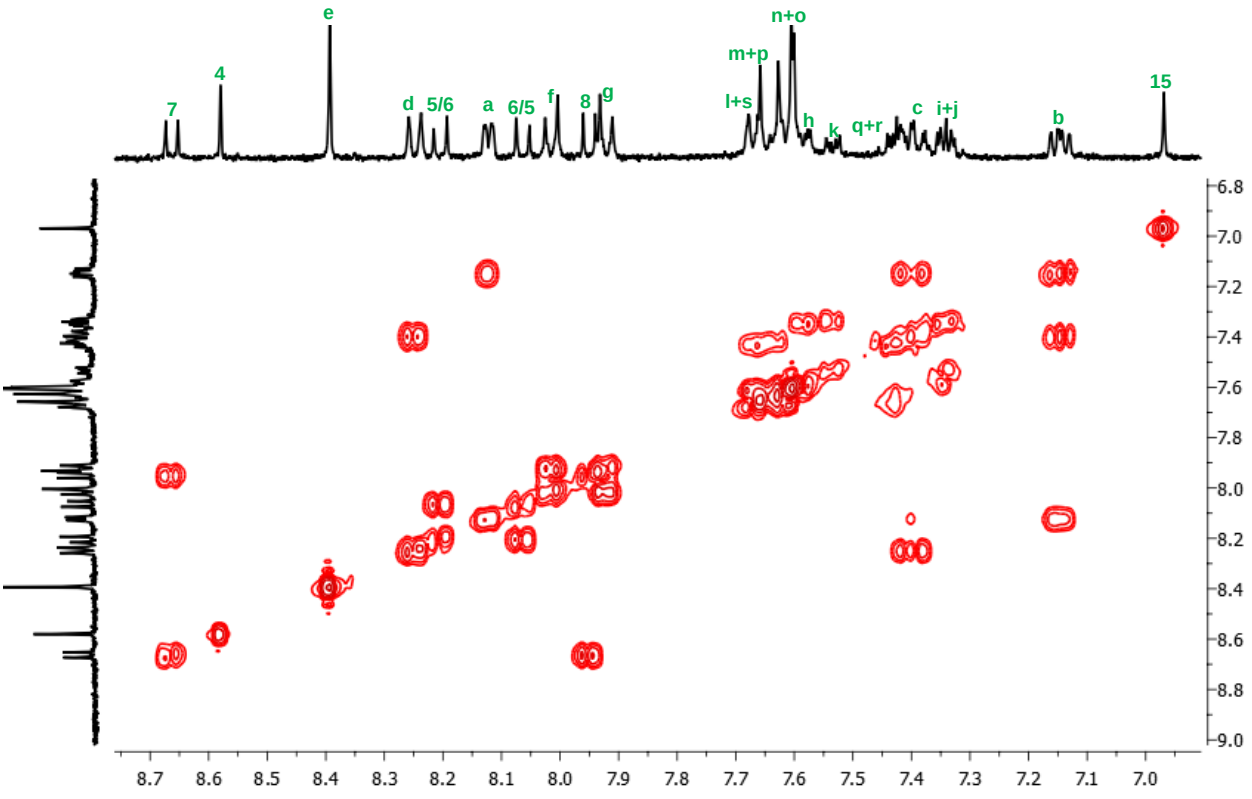


Figure S37: ^{1}H-^{1}H COSY NMR spectrum (CD_2Cl_2, 400 MHz, 298 K) of [Cu(**3**)]$^{+}$.

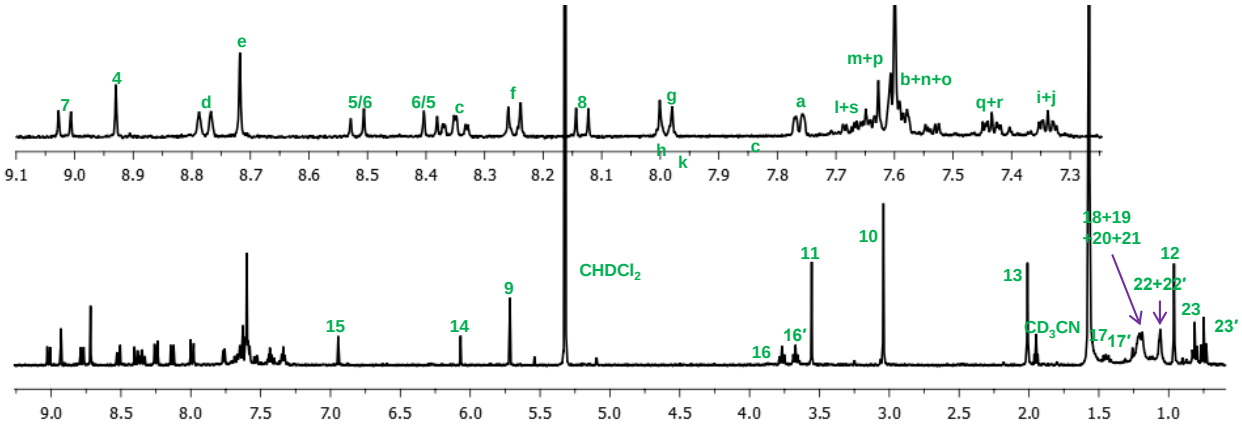


Figure S38: ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 298 K) of $[Zn(\mathbf{3})]^{2+}$.

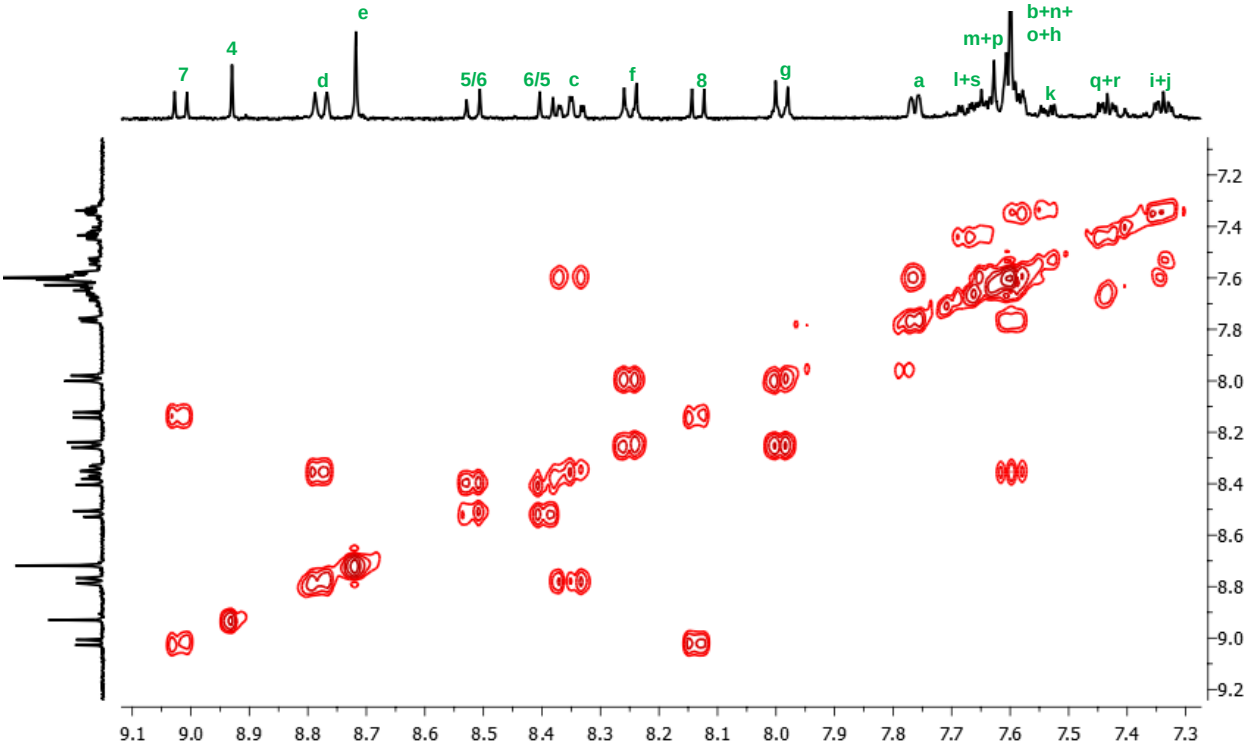


Figure S39: ^{1}H-^{1}H COSY NMR spectrum (CD_2Cl_2, 400 MHz, 298 K) of $[Zn(\mathbf{3})]^{2+}$.

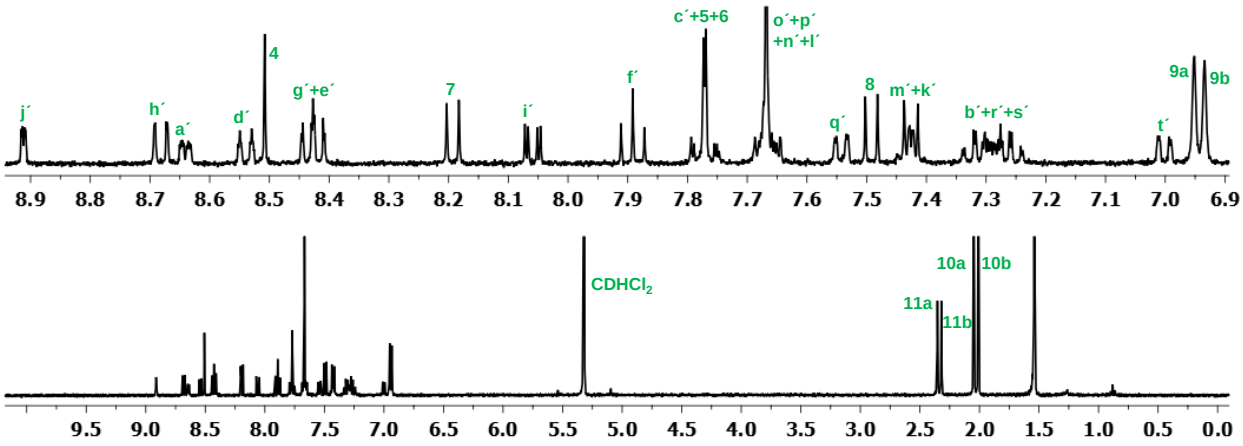


Figure S40: ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 298 K) of nanoswitch **4**.

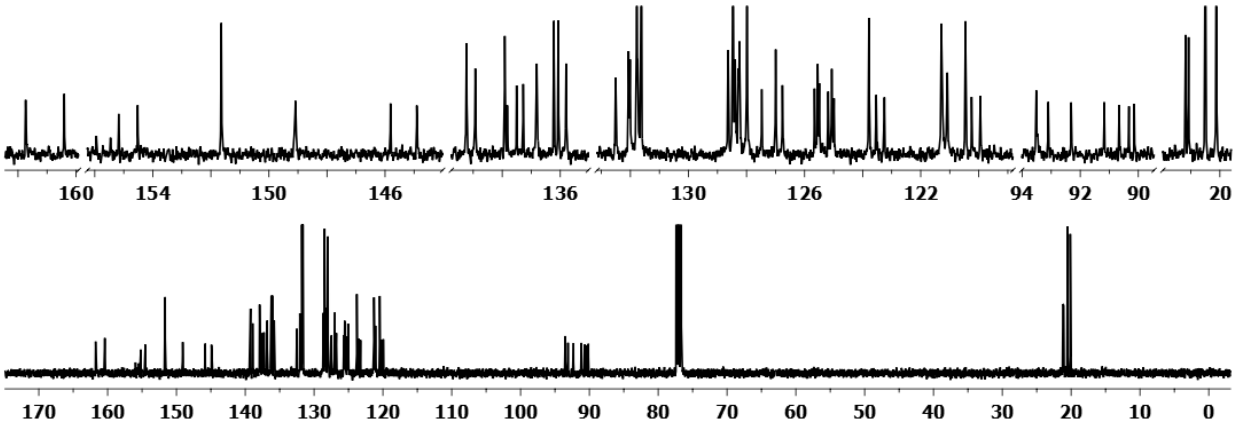


Figure S41: ^{13}C NMR spectrum ($CDCl_3$, 100 MHz, 298 K) of nanoswitch **4**.

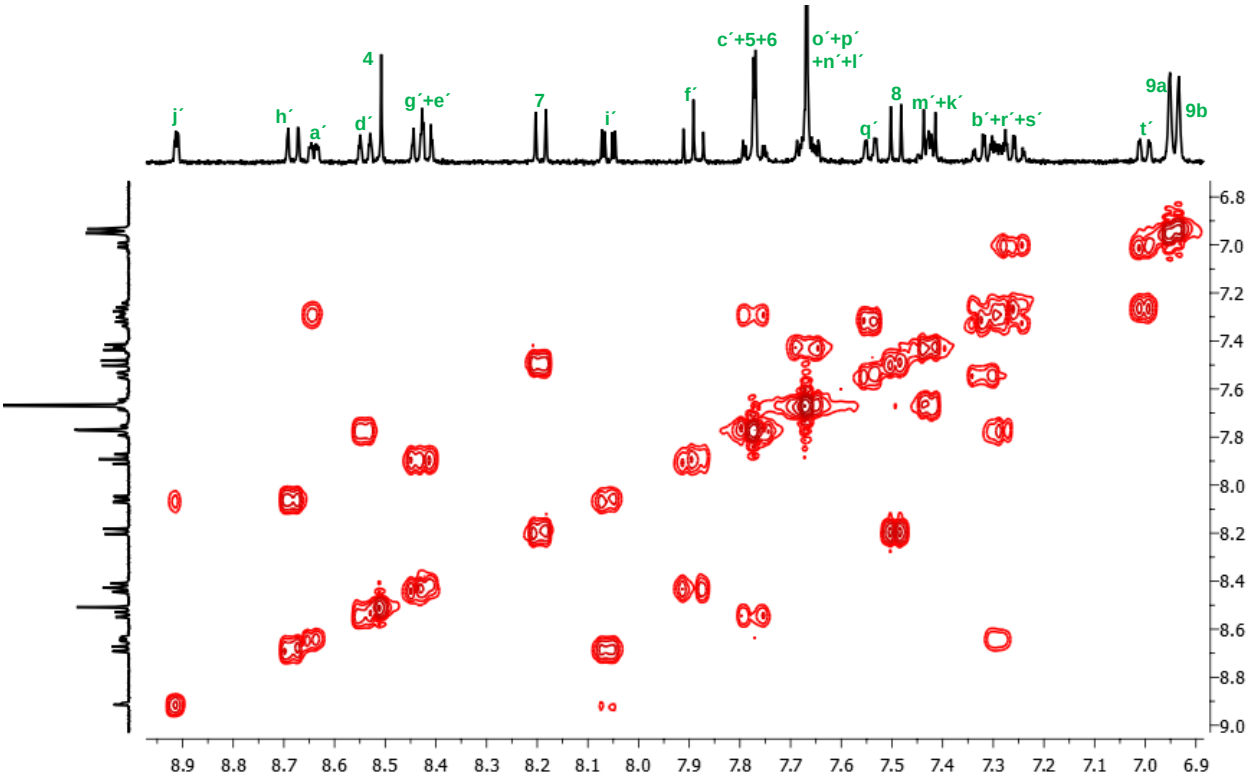


Figure S42: ^{1}H-^{1}H COSY NMR spectrum (CD_2Cl_2, 400 MHz, 298 K) of nanoswitch **4**.

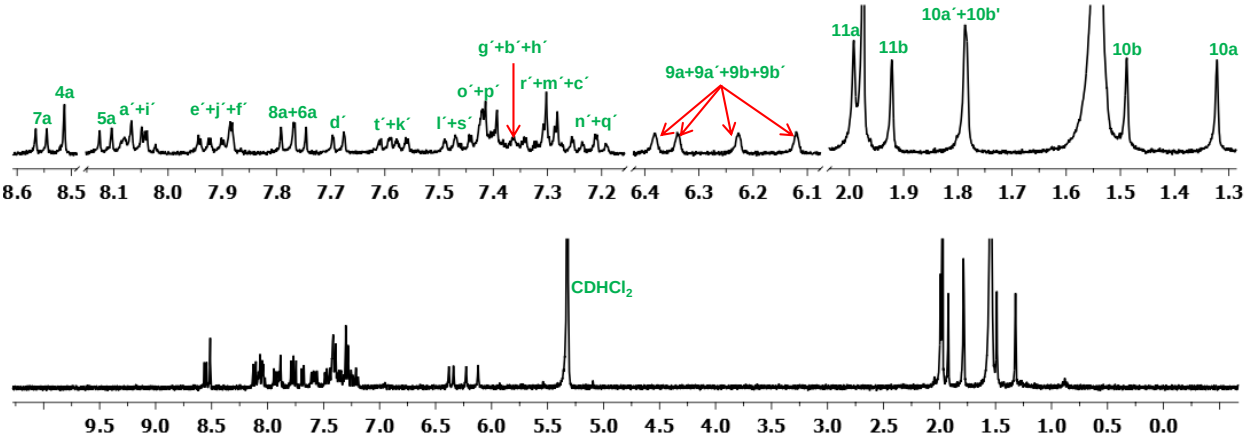


Figure S43: ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 298 K) of $[Cu(\mathbf{4})]^{+}$.

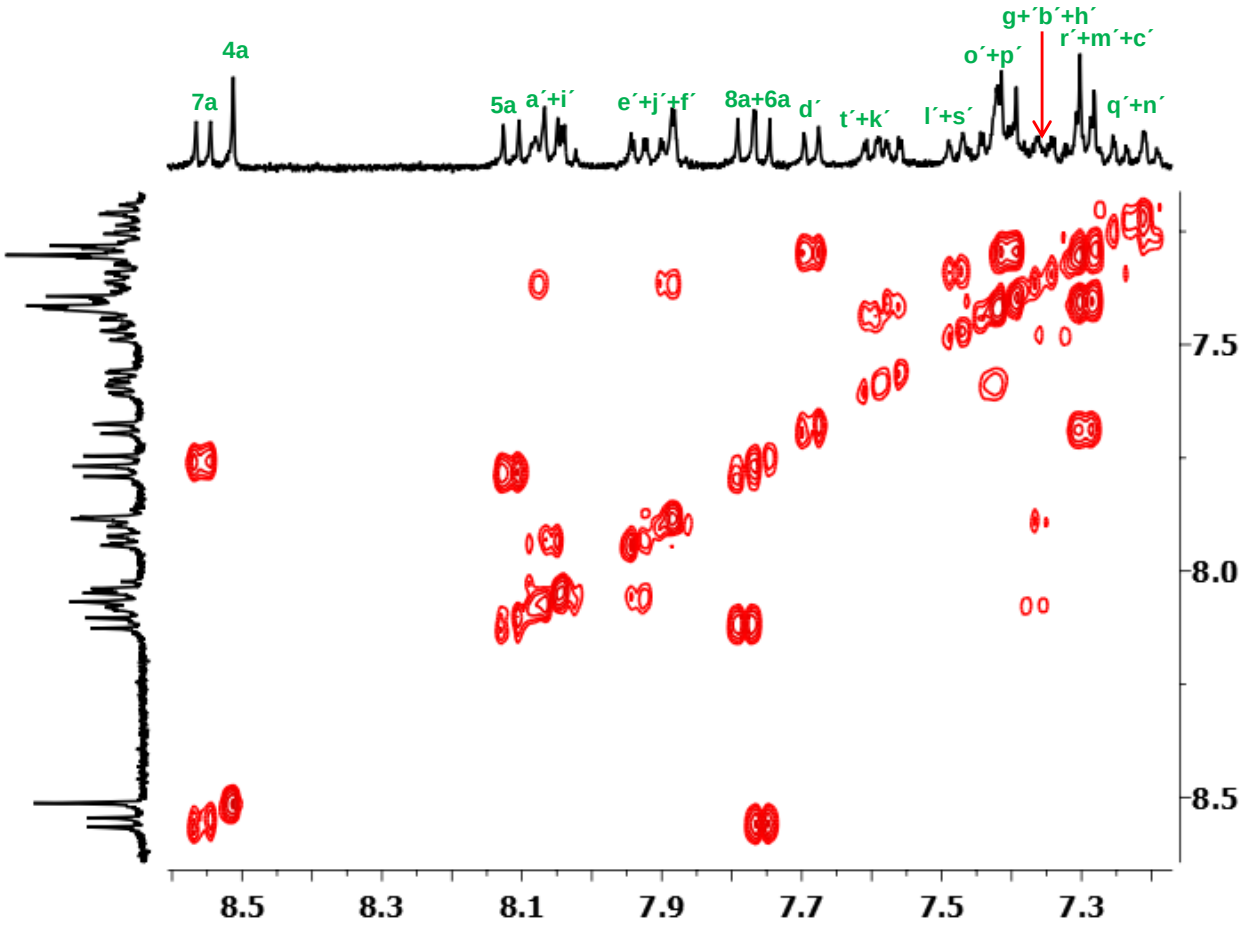


Figure S44: ^{1}H-^{1}H COSY NMR spectrum (CD_2Cl_2, 400 MHz, 298 K) of [Cu(**4**)]$^{+}$.

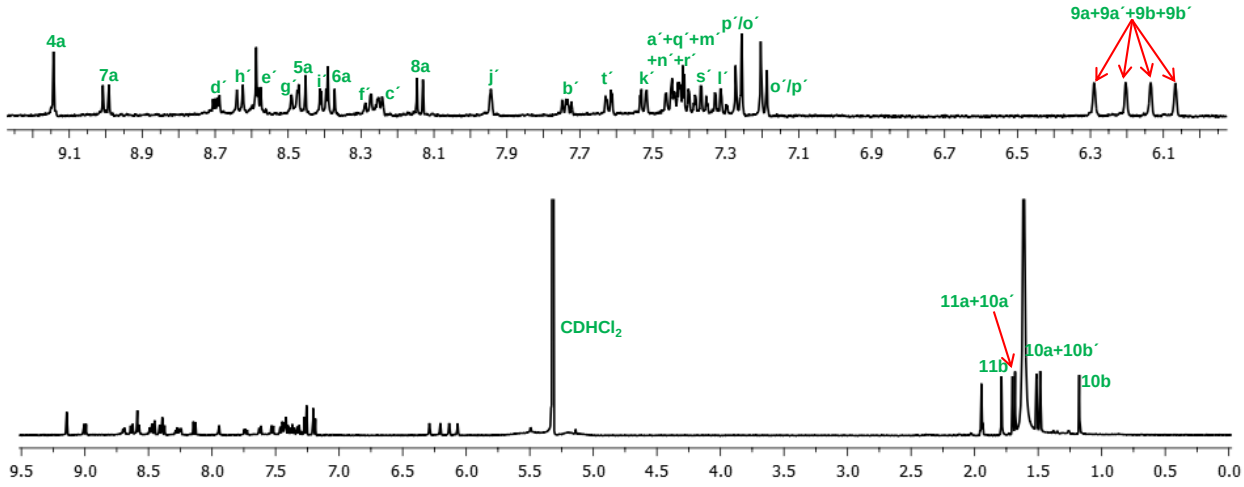


Figure S45: ^{1}H NMR spectrum (CD_2Cl_2, 500 MHz, 298 K) of [Hg(**4**)]$^{2+}$.

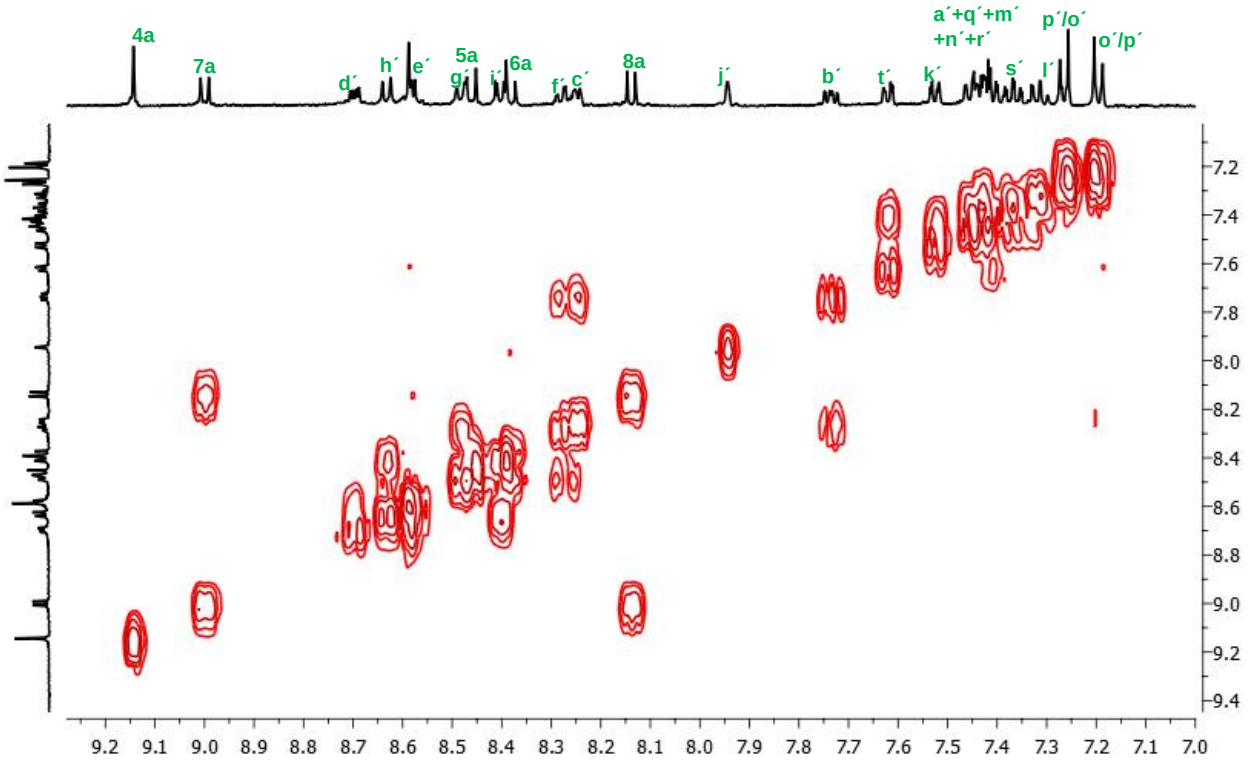


Figure S46: ^{1}H-^{1}H COSY NMR spectrum (CD_2Cl_2, 500 MHz, 298 K) of $[Hg(\mathbf{4})]^{2+}$.

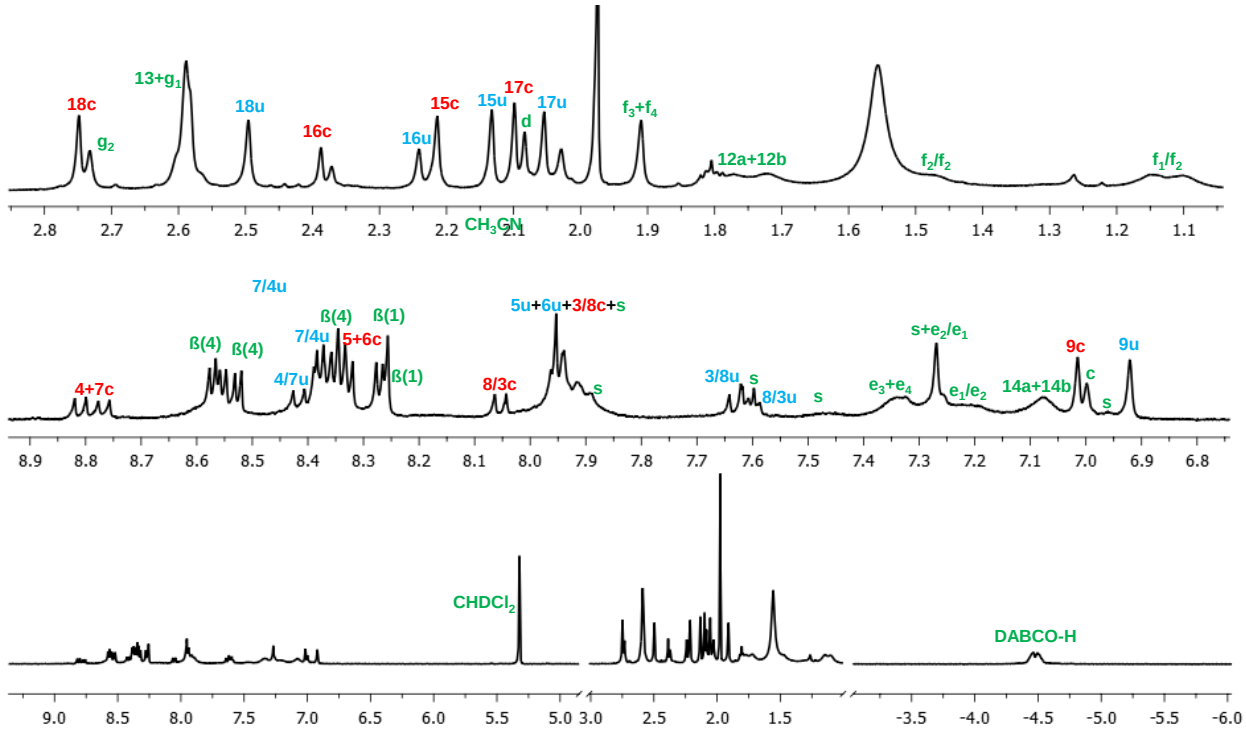


Figure S47: ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 298 K) of **ROT-1**.

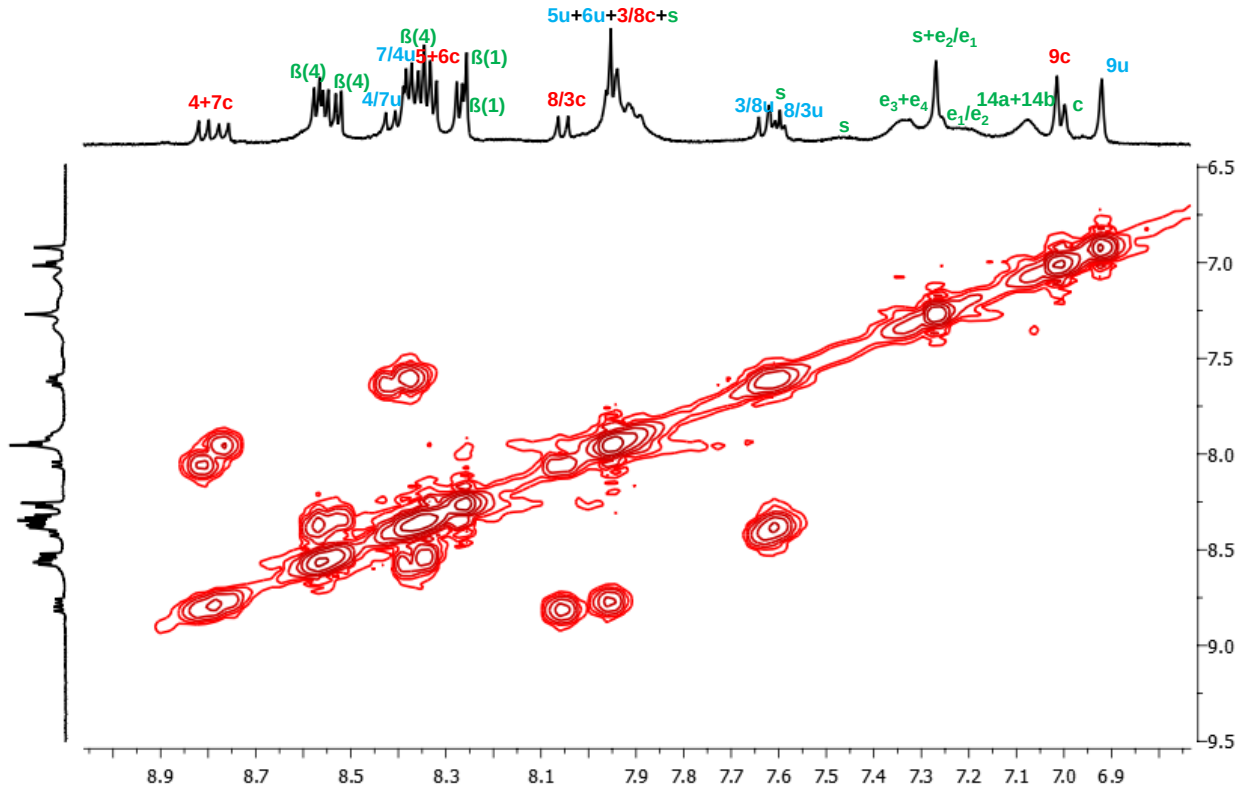


Figure S48: ^{1}H-^{1}H COSY NMR spectrum (CD_2Cl_2, 400 MHz, 298 K) of **ROT-1**.

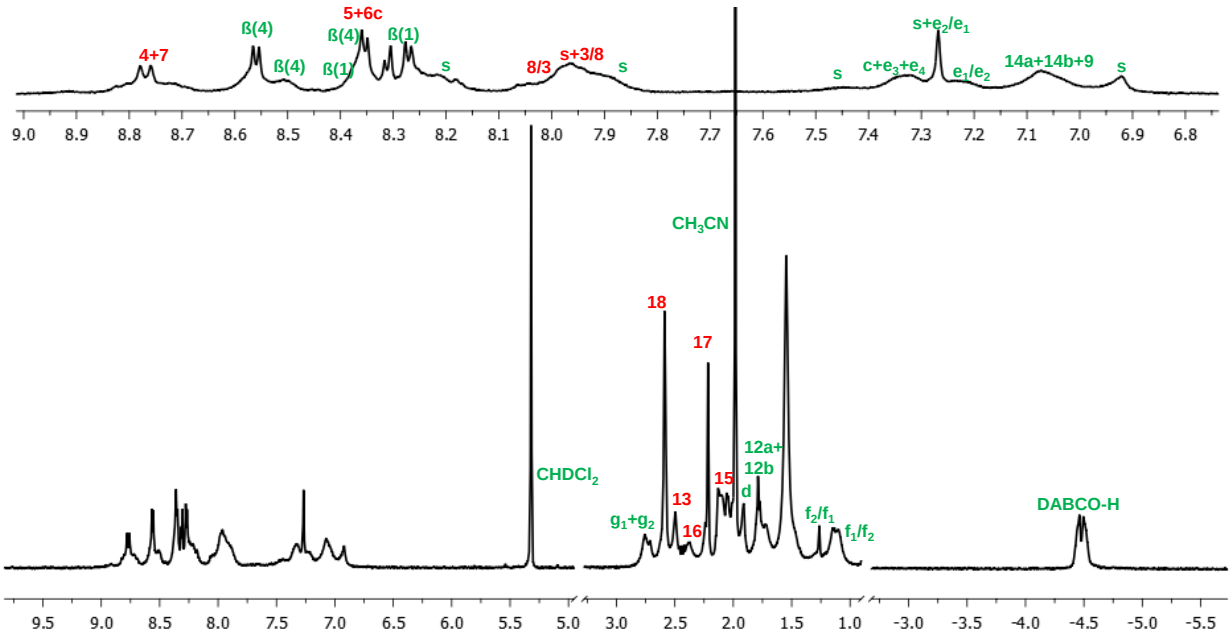


Figure S49: ^{1}H NMR spectrum (CD_2Cl_2, 400 MHz, 298 K) of **ROT-2**.

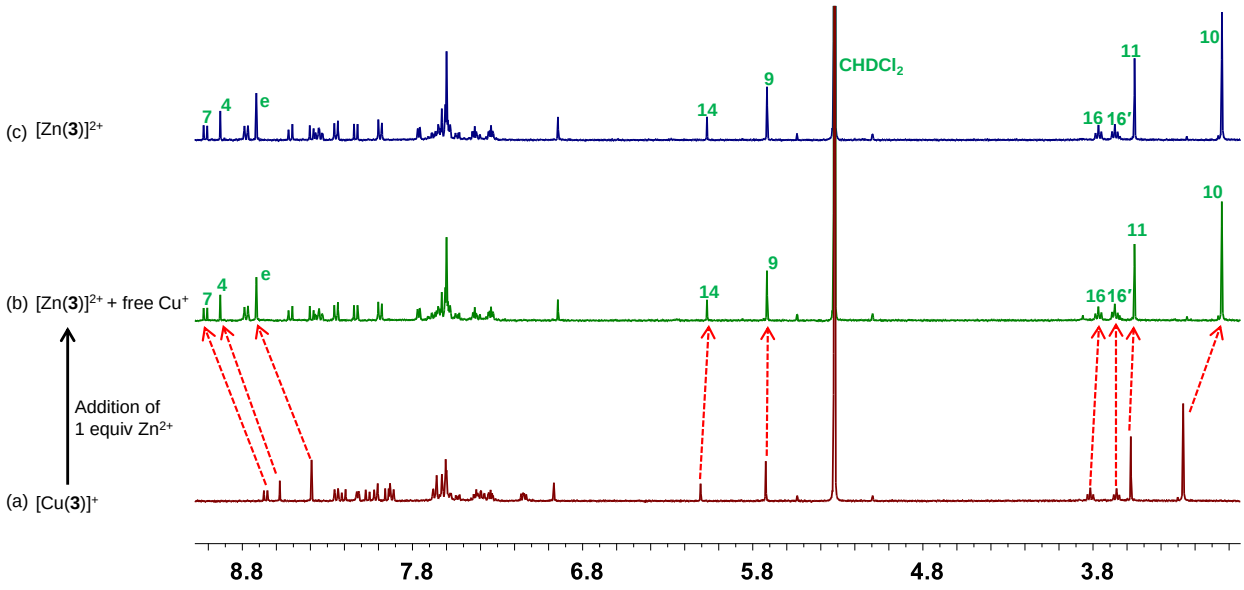


Figure S50. Partial ^{1}H NMR (CD_2Cl_2, 400 MHz, 298 K) of (a) [Cu(**3**)]$^{+}$**,** (b) [Cu(**3**)]$^{+}$ upon addition of 1 equiv of Zn^{2+} after 3 h, (c) [Zn(**3**)]$^{2+}$.

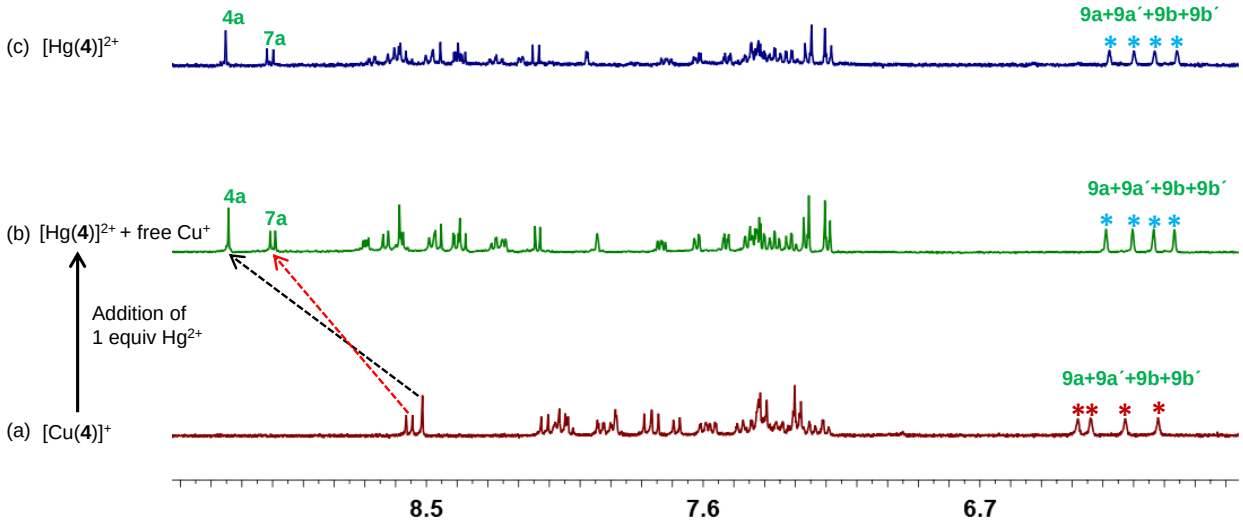


Figure S51: Partial ^{1}H NMR (CD_2Cl_2, 400 MHz, 298 K) of (a) [Cu(**4**)]$^{+}$**,** (b) [Cu(**4**)]$^{+}$ upon addition of 1 equiv of Hg^{2+} (c) [Hg(**4**)]$^{2+}$.

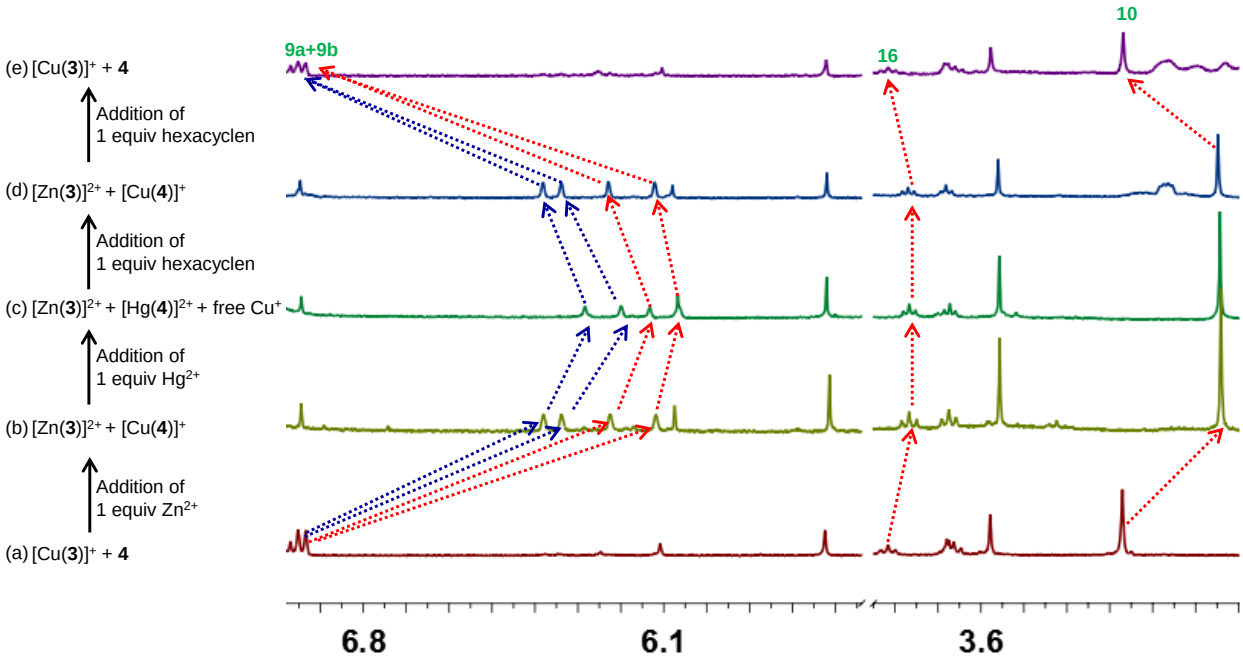


Figure S52: Partial ^{1}H NMR (CD_2Cl_2, 500 MHz, 298 K) of (a) [Cu(**3**)]$^{+}$ + **4**, (b) upon addition of 1 equiv of Zn^{2+} to (a) after 3 h, (c) upon addition of 1 equiv of Hg^{2+} to (b), (d) after addition of 1 equiv of hexacyclen to (c), (e) after addition of 1 equiv of hexacyclen to (d).

3. DOSY NMR Spectra

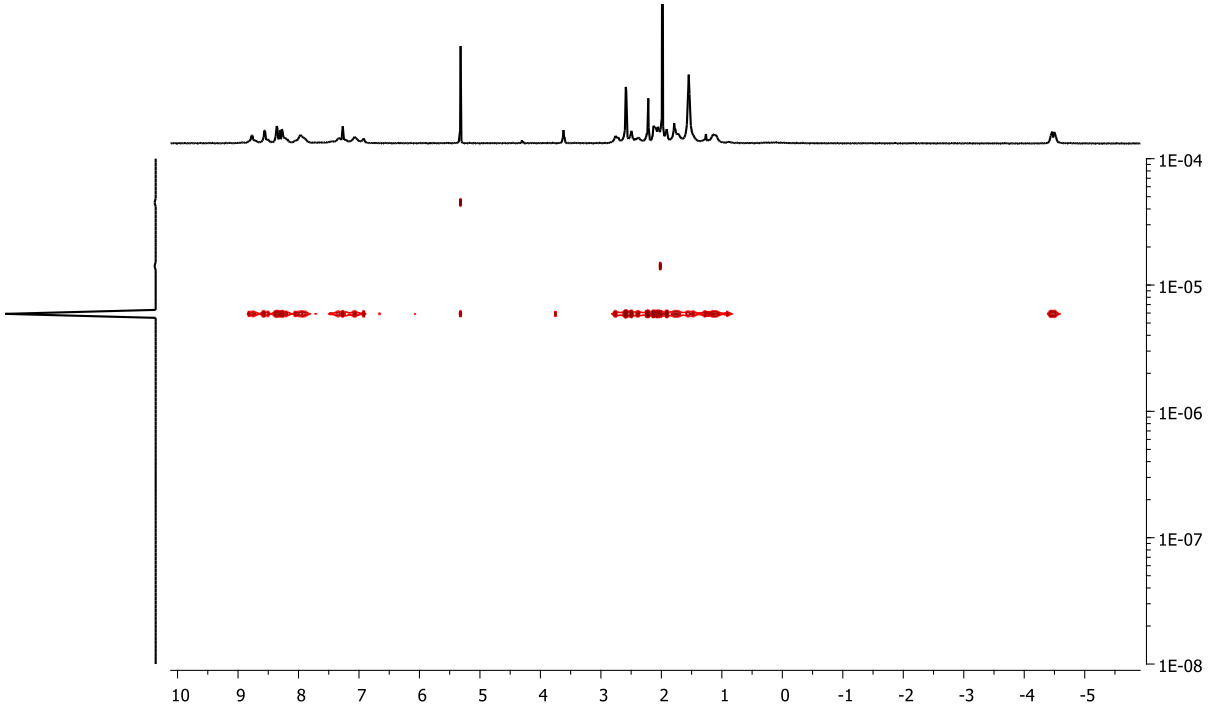


Figure S53: ^{1}H-DOSY NMR spectrum (CD_2Cl_2, 400 MHz, 298 K) of **ROT-2**. Diffusion coefficient D = 4.3 × 10^{-10} m^2s^{-1}, hydrodynamic radius r = 10.3 Å.

4. VT ^{1}H-NMR Spectra

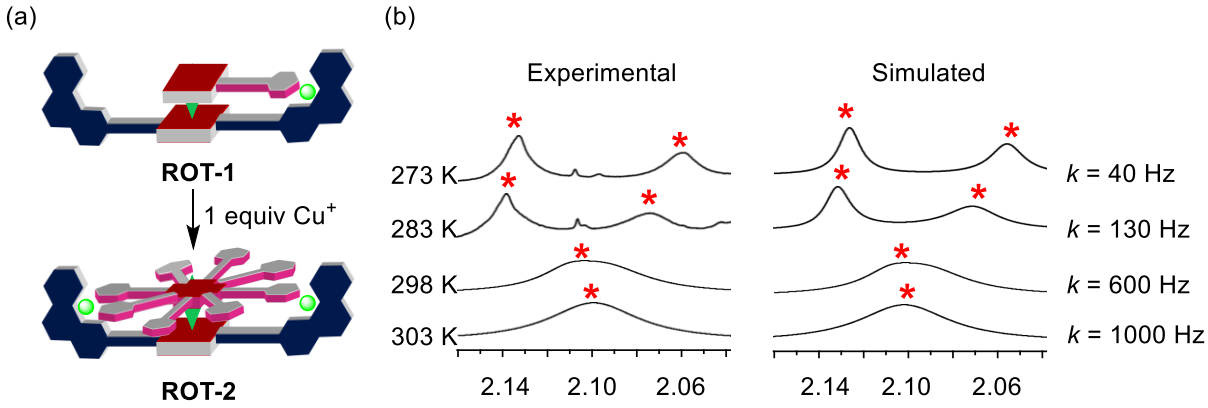


Figure S54: (a) Cartoon structure of **ROT-1** and **ROT-2**. (b) Partial VT-^{1}H NMR (CD_2Cl_2, 600 MHz) of **ROT-2** showing the splitting of 15-H (red asterisk marked).

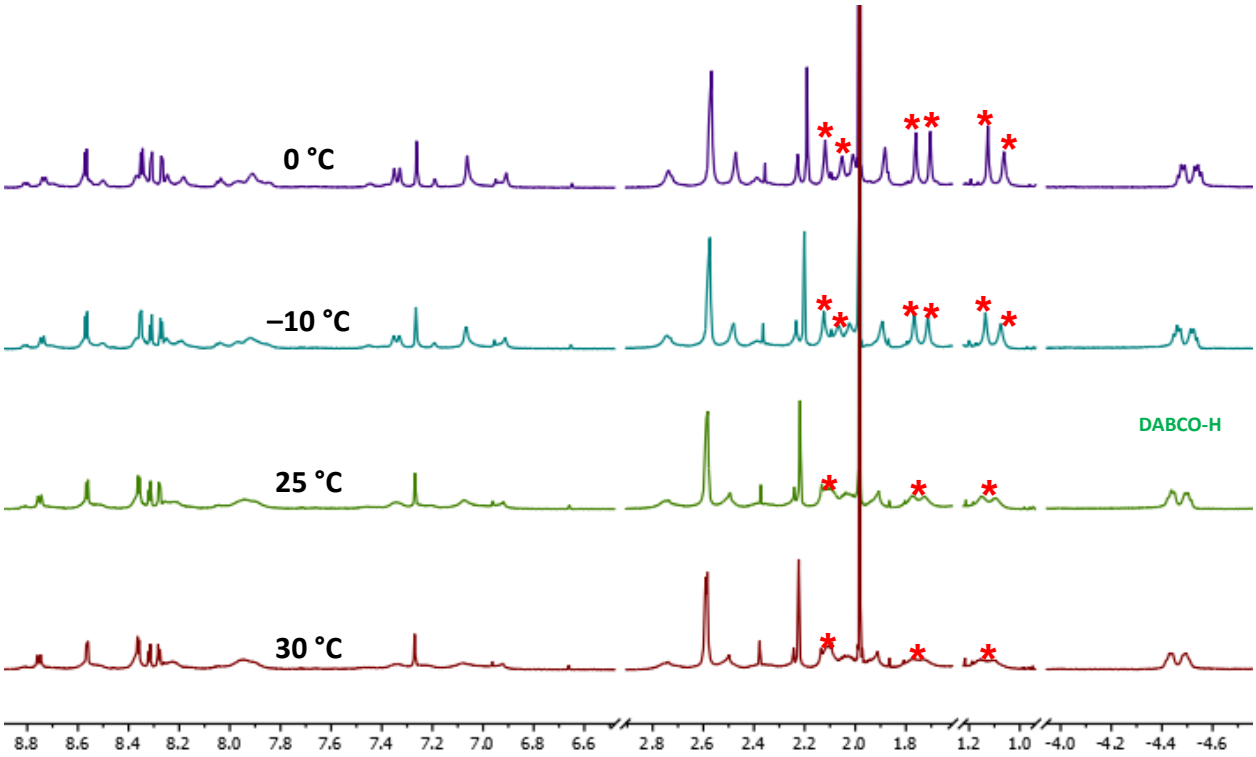


Figure S55: VT ^{1}H-NMR spectrum of **ROT-2** (600 MHz, CD_2Cl_2) showing the splitting of protons 15-H, [f_1/f_2]-H and [12a/12b]-H (red asterisk marked). Characteristic signals for DABCO-H corroborate the intactness of the assembly throughout the temperature range.

5. NMR Simulation Analysis to Determine the Rotational Frequency

NMR simulation. Using a conventional dynamic NMR spectroscopic method,[7] a model involving a two-spin system undergoing mutual exchange was applied to simulate the spectra and determine the exchange frequency. The NMR signal used for the simulation is indicated in the corresponding spectra by *. The exchange frequency in the rotor is identical with the rotational frequency and was obtained from an analysis of the exchange-broadened NMR of proton 16-H of the stator. Activation enthalpy ($\Delta H^{\ddagger}$) and activation entropy ($\Delta S^{\ddagger}$) were determined from transition state theory.

$k = (k_B T/h)e^{-\Delta G^{\ddagger}/RT}$

$\ln(k/T) = -\Delta H^{\ddagger}/RT + \ln(k_B/h) + \Delta S^{\ddagger}/R$, where R = universal gas constant.

The free energy barrier at 298 K was determined using the equation $\Delta G^{\ddagger}_{298} = \Delta H^{\ddagger} - 298T\Delta S^{\ddagger}$.

The temperature dependency of the rotational motion was fitted to the Eyring[8] equation:

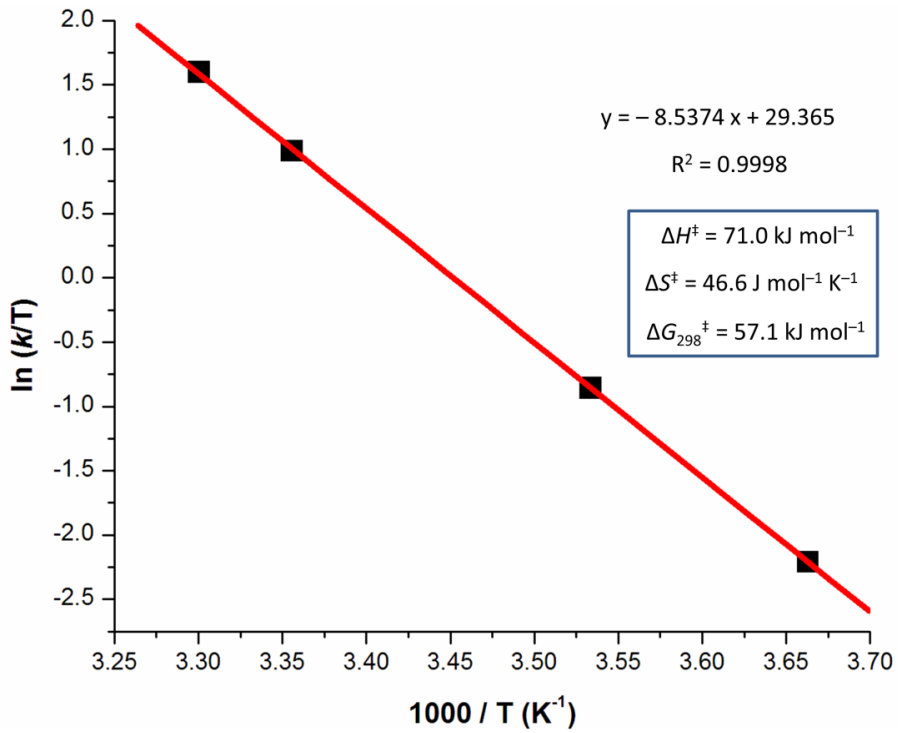
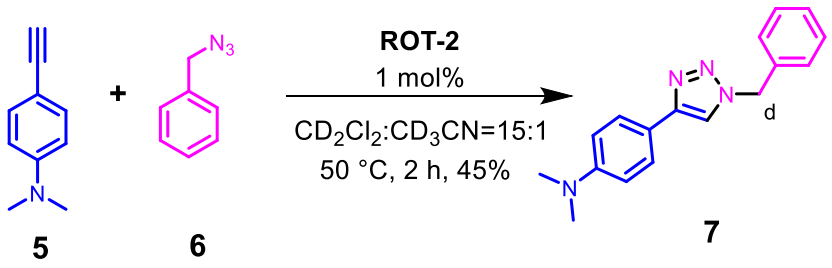


Figure S56: Eyring plot for the rotational dynamics in **ROT-2**.

6. Catalytic Experiments

a) Rotors as catalyst



In an NMR tube, substrates **5** (3.72 mg, 25.6 µmol) and **6** (3.41 mg, 25.6 µmol) were taken. Then 0.01 equiv of **ROT-2** was used as a catalyst for the click reaction. After 2 h at 50 °C in CD_2Cl_2:CD_3CN = 15:1 (total 500 µL) the yield of click product **7** (d-H at δ = 5.52 ppm) was

determined using 1,3,5-trimethoxybenzene as internal standard. Integration of proton d-H was monitored with respect to the aryl protons of trimethoxybenzene (δ = 6.06 ppm) for yield calculation showing formation of 45% of **7**.

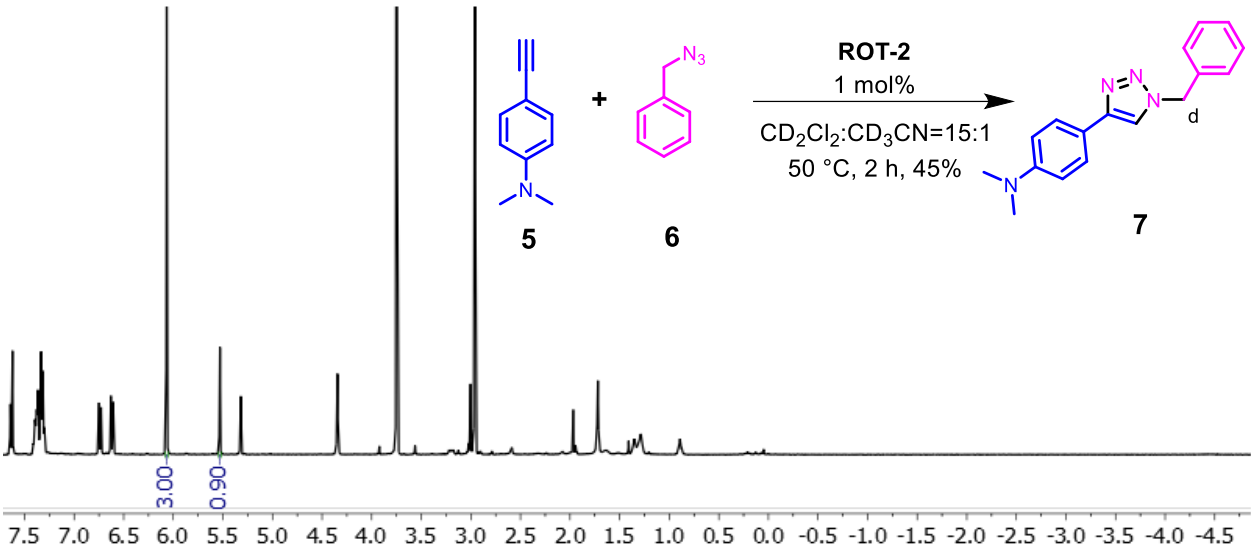


Figure S57: ^{1}H NMR (CD_2Cl_2:CD_3CN=15:1, 298 K, 500 MHz) after reacting **5** and **6** in presence of 1 mol% of **ROT-2**, showing the formation of 45% of product **7**. Formation of **7** was quantified via proton d-H (δ = 5.52 ppm) in regard to 1,3,5-trimethoxybenzene (δ = 6.06 ppm).

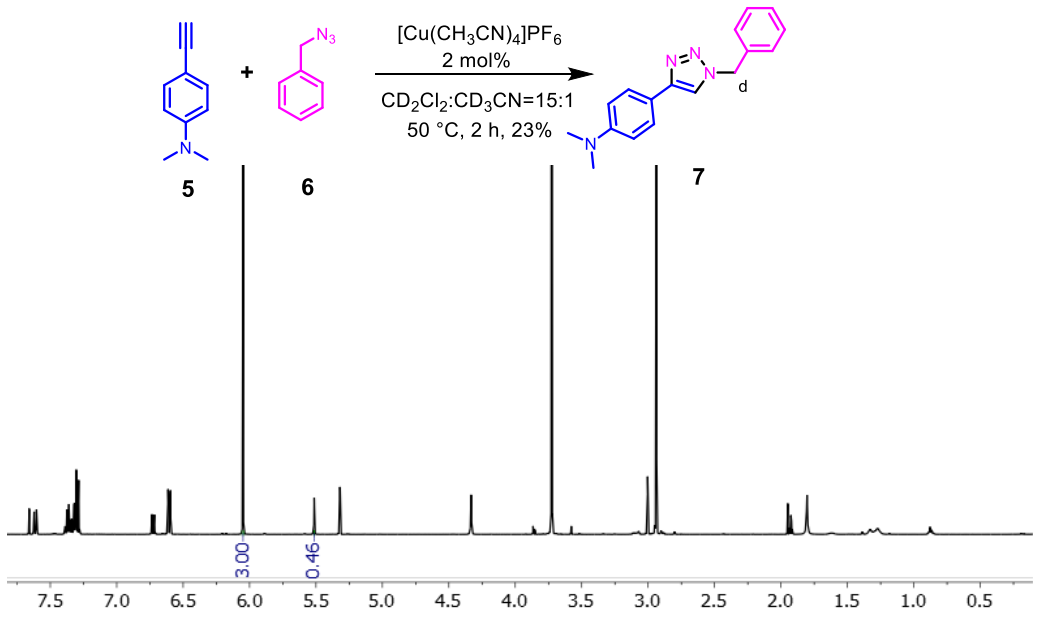


Figure S58: ^{1}H NMR (CD_2Cl_2:CD_3CN=15:1, 298 K, 500 MHz) after reacting **5** and **6** in presence of 2 mol% of $[Cu(CH_3CN)_4]PF_6$, showing the formation of 23% of product **7** that was quantified via proton d-H (δ = 5.52 ppm) in regard to 1,3,5-trimethoxybenzene (δ = 6.06 ppm).

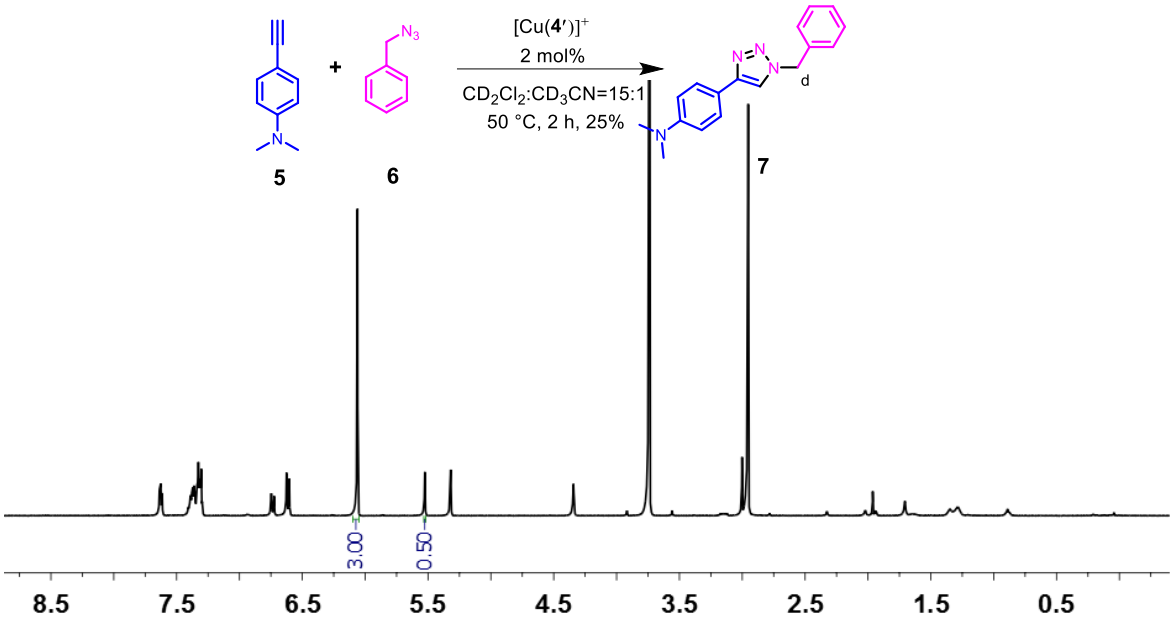


Figure S59: ^{1}H NMR (CD_2Cl_2:CD_3CN=15:1, 298 K, 400 MHz) after reacting **5** and **6** in presence of 2 mol% of [Cu(**4′**)]$^{+}$, showing the formation of 25% of product **7**. Quantification was made via integration of proton d-H (δ = 5.52 ppm) in regard to 1,3,5-trimethoxybenzene (δ = 6.06 ppm).

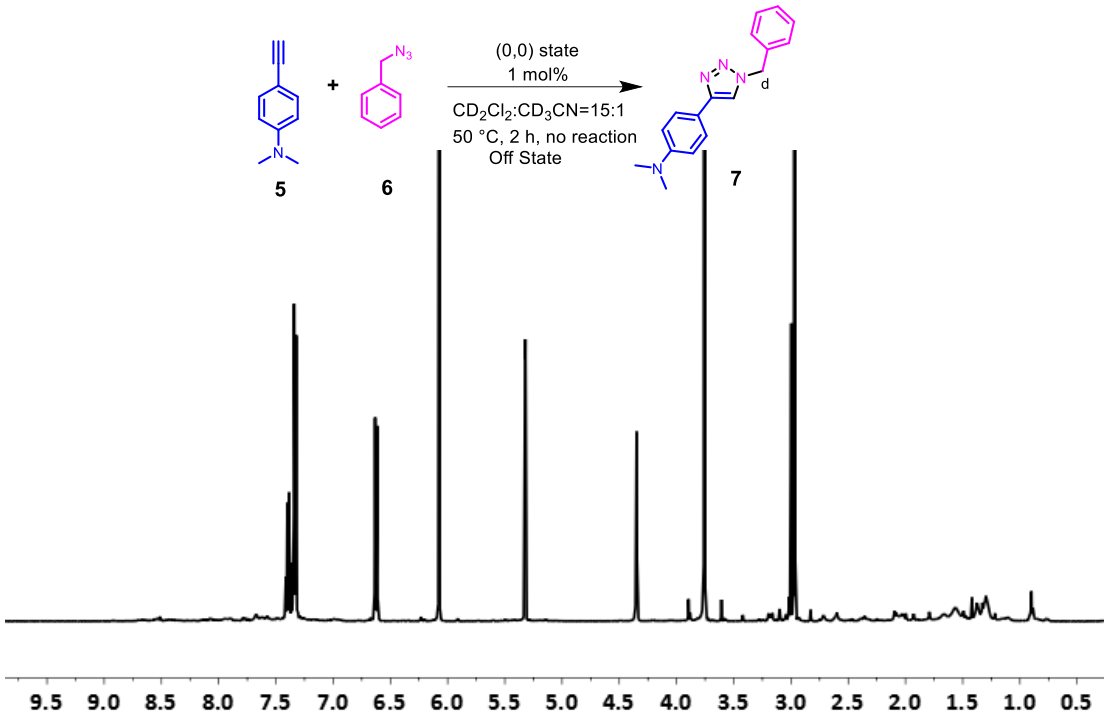


Figure S60: ^{1}H NMR (CD_2Cl_2:CD_3CN=15:1, 298 K, 500 MHz) after reacting **5** and **6** in presence of 1 mol% of the 12-component logic gate in state (0,0), showing no formation of product **7** (no singlet at δ = 5.52).

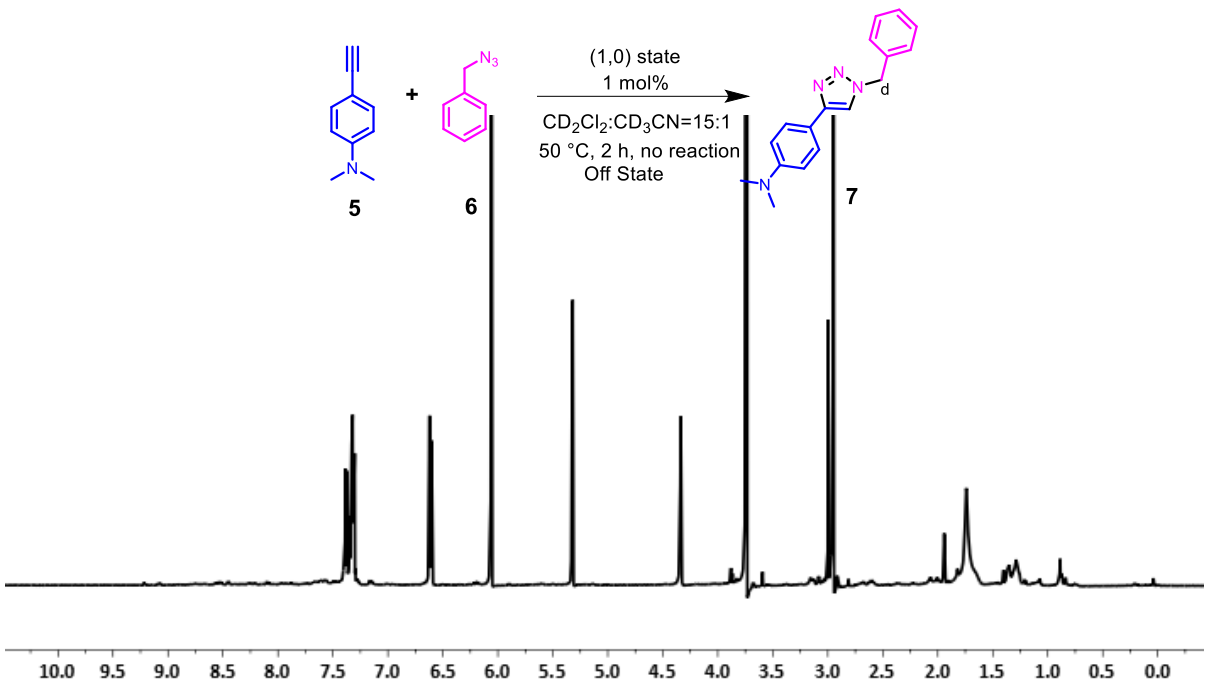


Figure S61: ^{1}H NMR (CD_2Cl_2:CD_3CN=15:1, 298 K, 500 MHz) after reacting **5** and **6** in presence of 1 mol% of the 12-component logic gate in state (1,0), showing no formation of product **7** (no singlet at δ = 5.52).

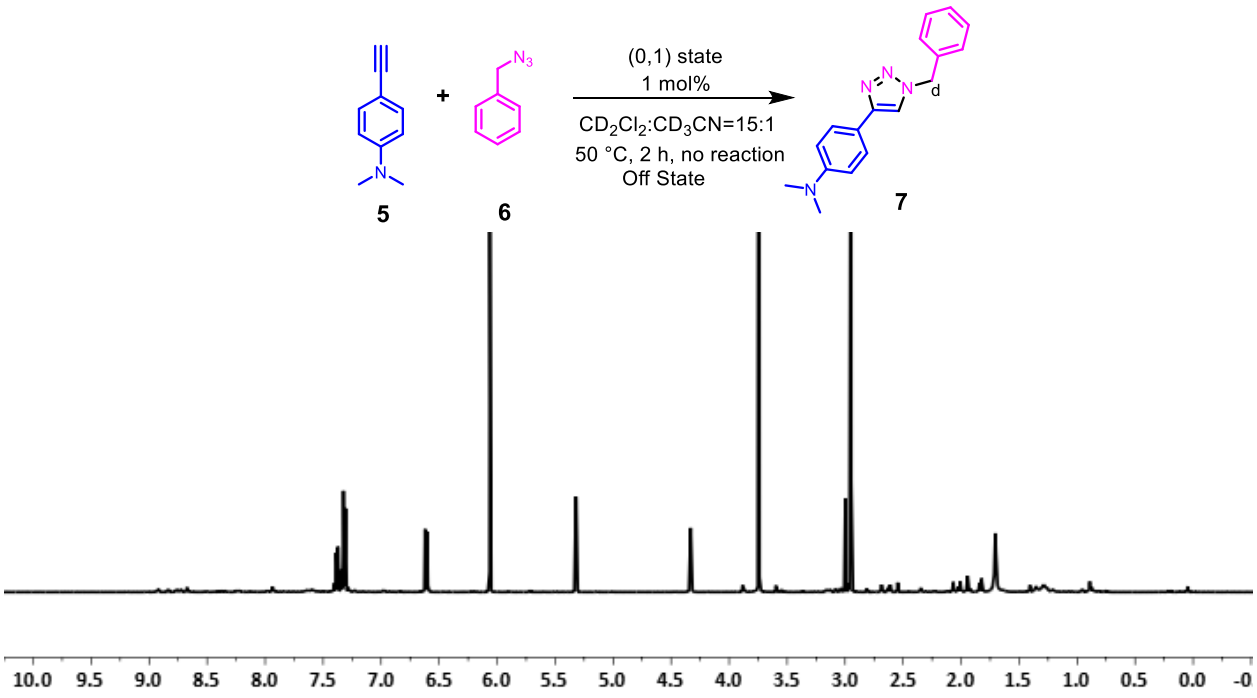


Figure S62: ^{1}H NMR (CD_2Cl_2:CD_3CN=15:1, 298 K, 500 MHz) after reacting **5** and **6** in presence of 1 mol% of the 12-component logic gate in state (0,1), showing no formation of product **7** (no singlet at δ = 5.52).

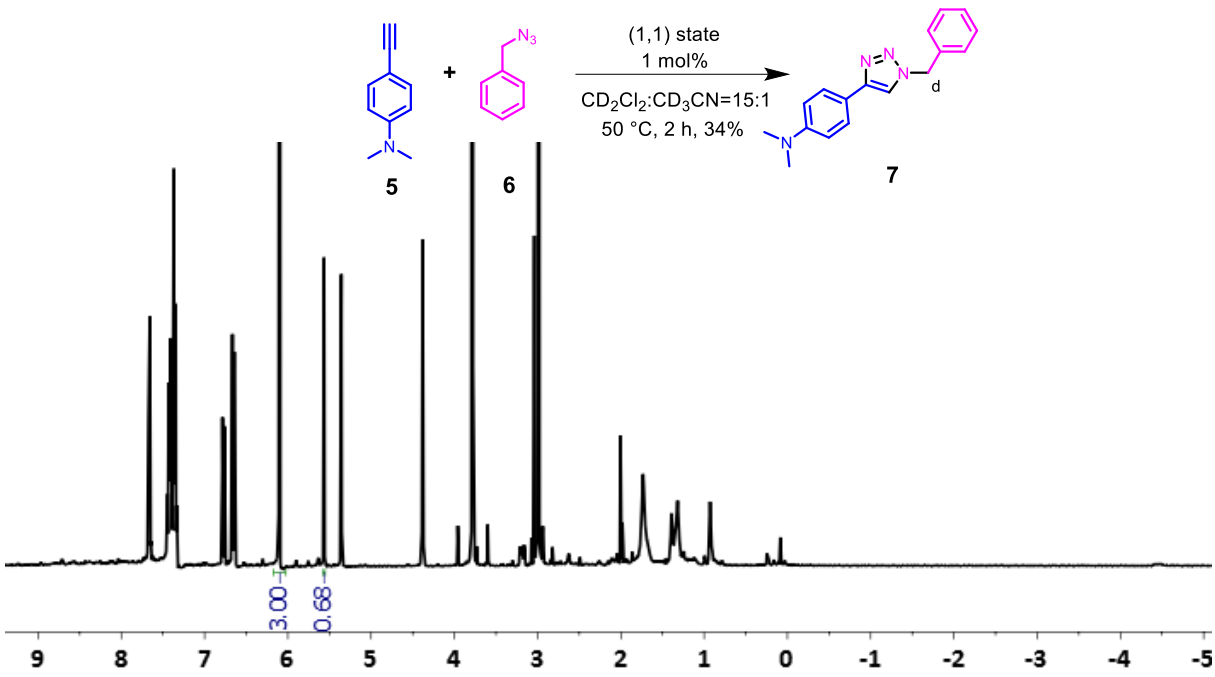


Figure S63: ^{1}H NMR (CD_2Cl_2:CD_3CN=15:1, 298 K, 400 MHz) after reacting **5** and **6** in presence of 1 mol% of the 12-component logic gate in state (1,1) state, showing formation of product **7** in 34% yield that was quantified via proton d-H (δ = 5.52 ppm) in regard to 1,3,5-trimethoxybenzene (δ = 6.06 ppm).

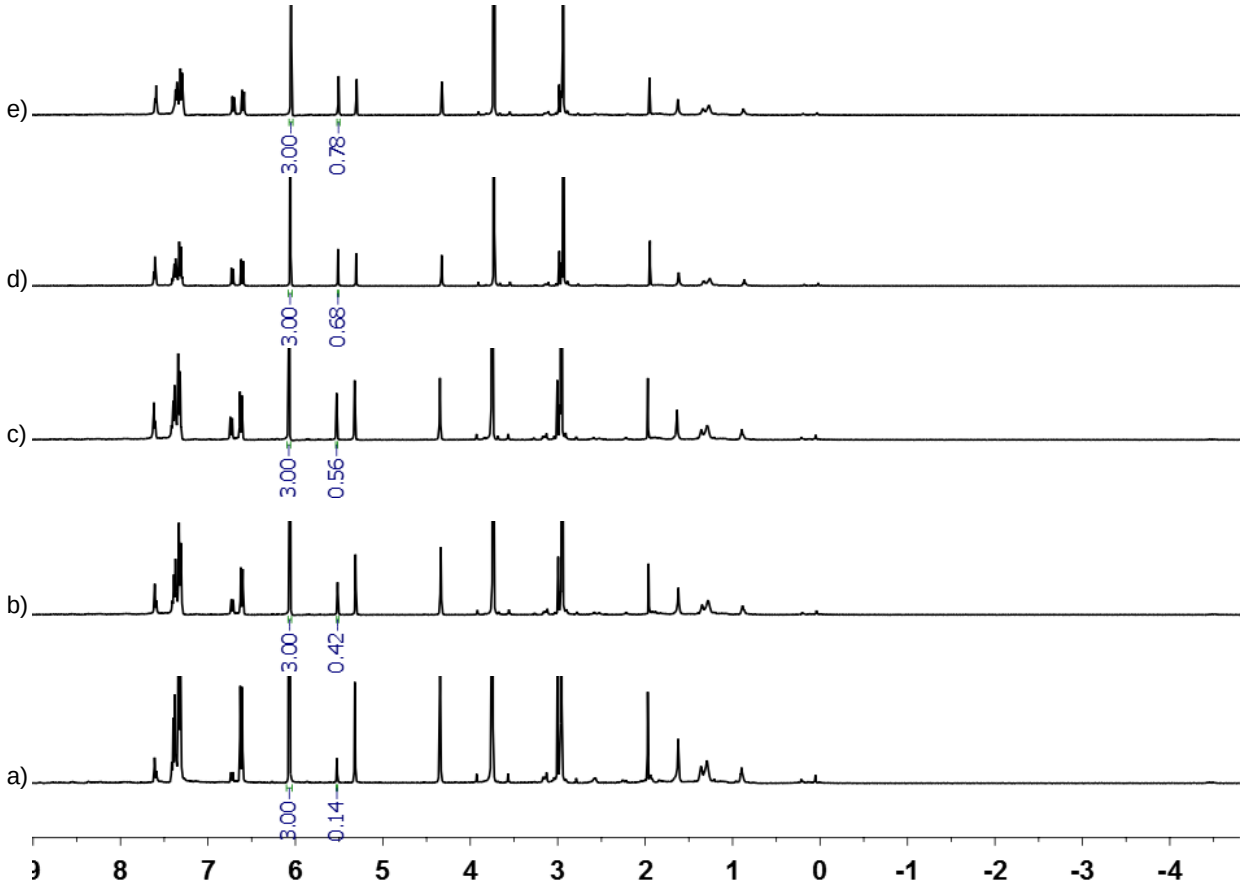


Figure S64: ^{1}H NMR (CD_2Cl_2:CD_3CN=15:1, 400 MHz) spectra obtained during heating **5** and **6** at 50 °C in presence of 1 mol% of AND gate after activating state (1,1). Samples were taken after a) 30 min (yield 7%), b) 60 min (yield 21%), c) 90 min (yield 28%), d) 120 min (yield 34%), and e) 150 min (yield 39%). Due to the delayed release of Cu^{+} from the ensemble gate, initial conversion is slower than expected.

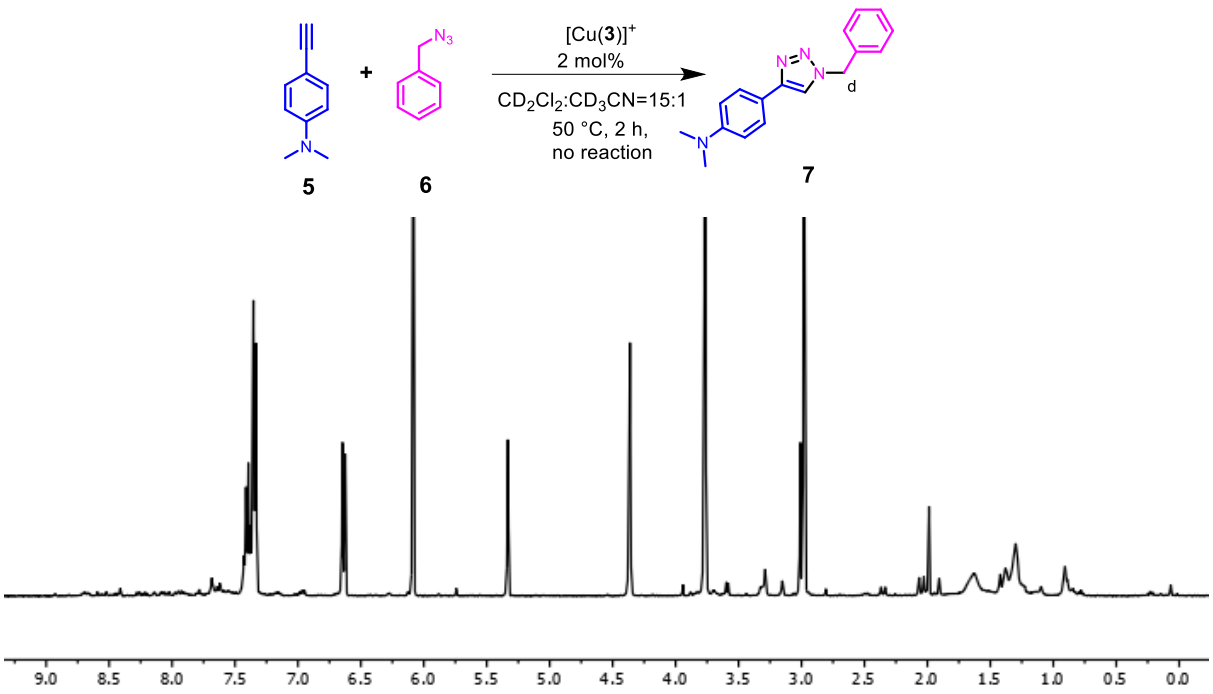


Figure S65: ^{1}H NMR (CD_2Cl_2:CD_3CN=15:1, 298 K, 500 MHz) after reacting **5** and **6** in presence of 2 mol% of [Cu(**3**)]$^{+}$, showing no product (**7**) formation (no singlet at δ = 5.52).

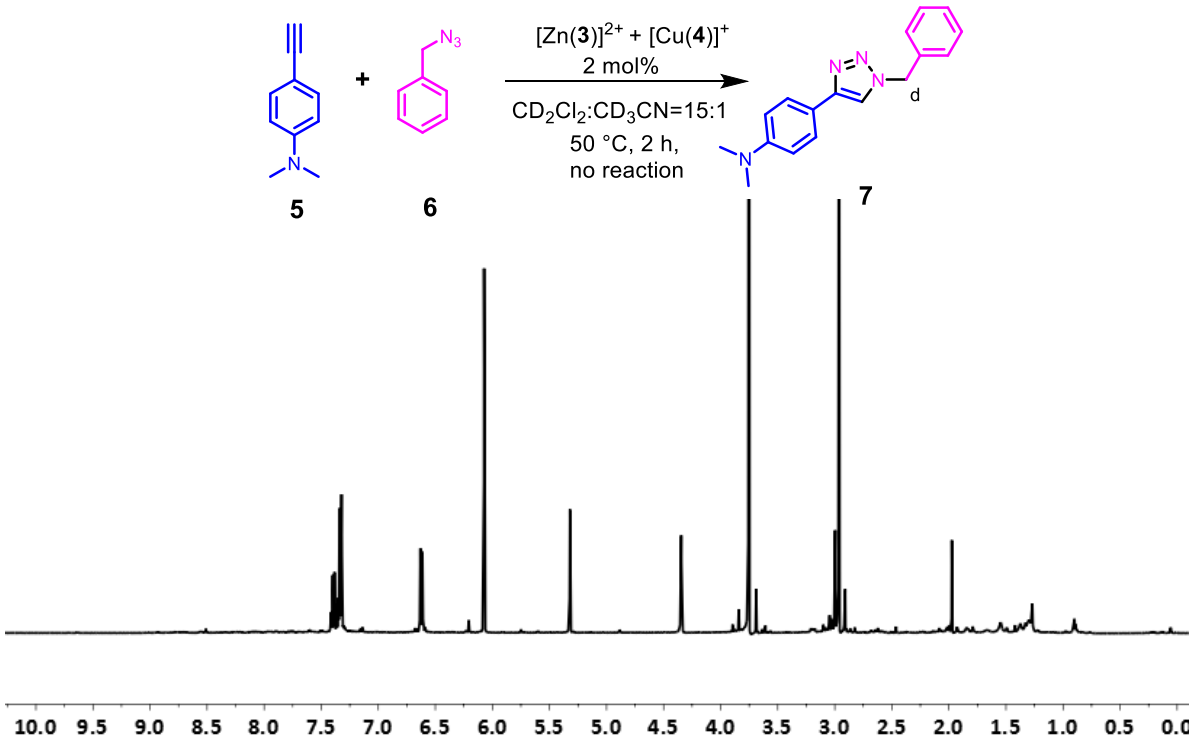


Figure S66: ^{1}H NMR (CD_2Cl_2:CD_3CN=15:1, K, 500 MHz) after reacting **5** and **6** in presence of 2 mol% of [Zn(**3**)]$^{2+}$ + [Cu(**4**)]$^{+}$, showing no product (**7**) formation (no singlet at δ = 5.52).

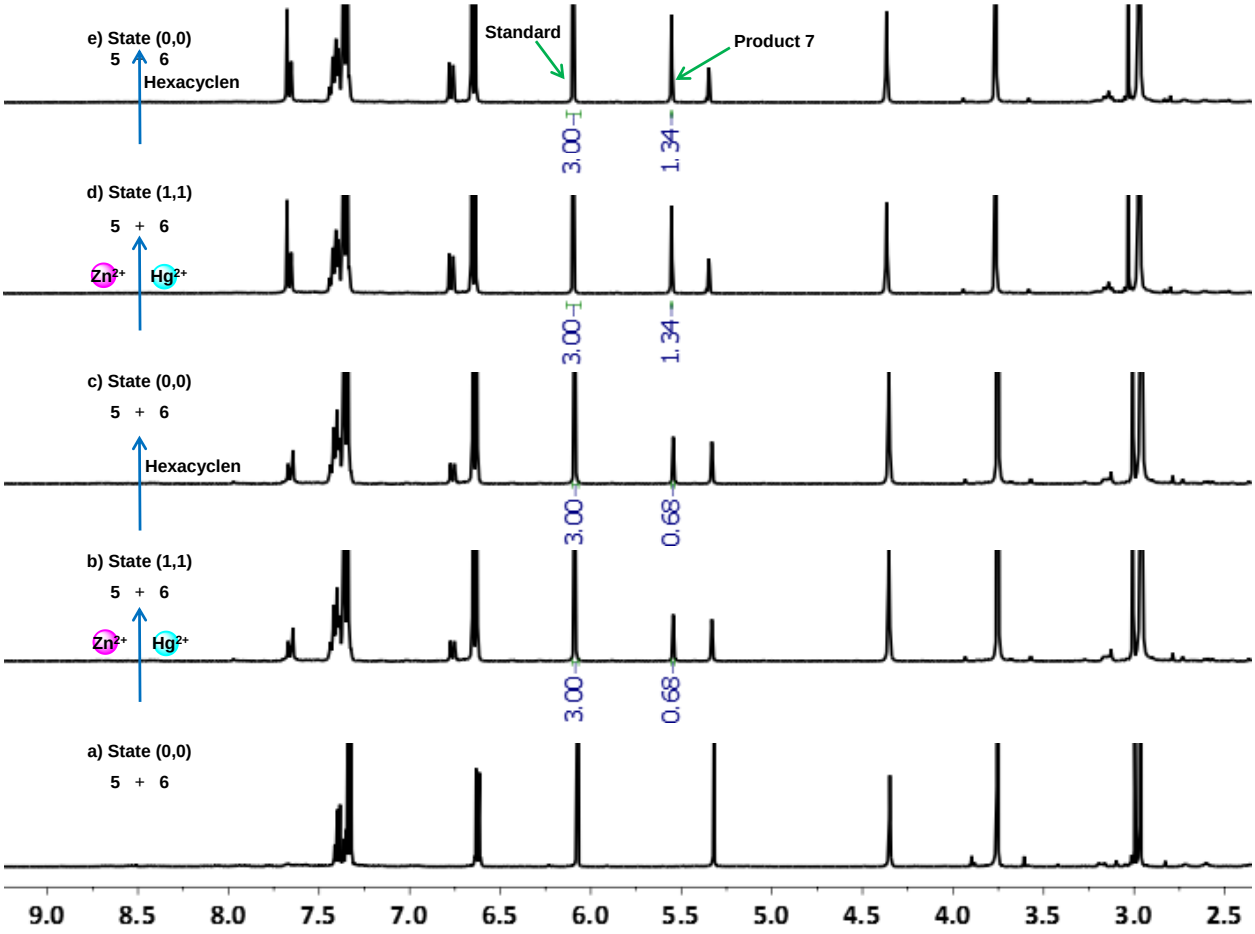


Figure S67: Partial ^{1}H NMR (400 MHz, CD_2Cl_2:CD_3CN = 15:1) spectrum obtained after (a) heating the reaction mixture of **5** and **6** in presence of 1 mol% (0,0) state of AND gate at 50 °C for 2 h in an NMR tube revealed that click catalysis was OFF (no singlet at δ = 5.52). (b) After addition of 2.0 equiv. of $Zn(OTf)_2$ and 2.0 equiv. of $Hg(ClO_4)_2$ with respect to stator **1** and subsequent heating at 50 °C for 2 h click product **7** was formed (yield = 34% calculated with respect to the internal standard). (c) After adding the consumed substrates and 4.0 equiv. of hexacyclen with respect to **1** and heating at 50 °C for 2 h. (d) Addition of 2.0 equiv. of $Zn(OTf)_2$ and 2.0 equiv. of $Hg(ClO_4)_2$ with respect to **1** and heating at 50 °C for 2 h resulted in an increase of the click product **7** by 33% (total yield = 67%). (e) After adding the consumed substrates and 4.0 equiv. of hexacyclen with respect to **1** and heating at 50 °C for 2 h.

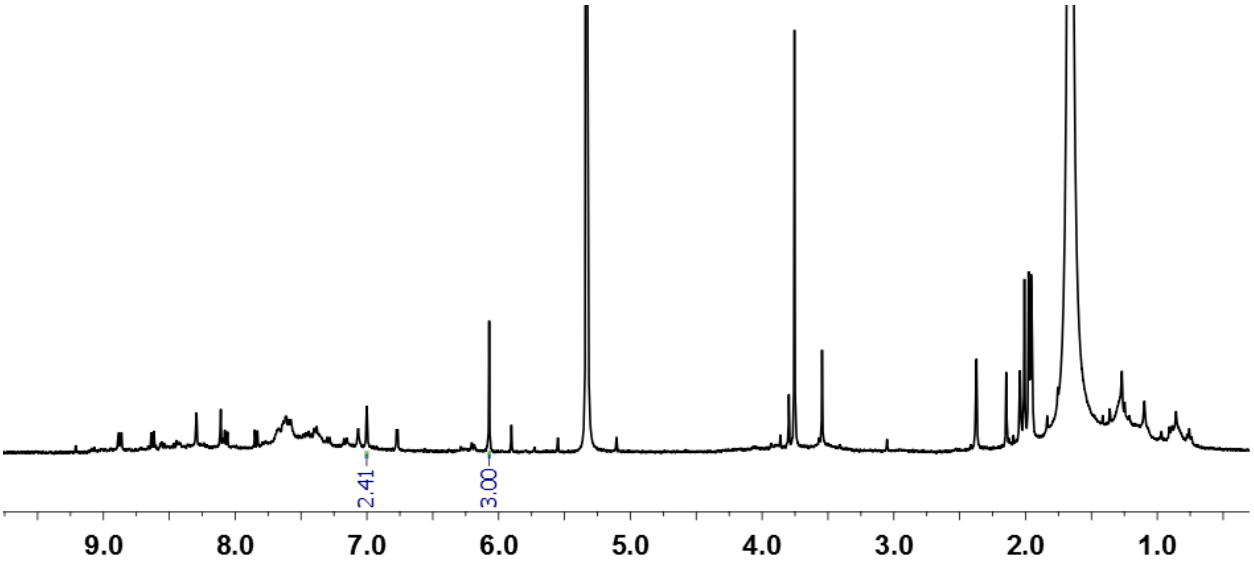


Figure S68: ^{1}H NMR spectra of quantification of copper(I) release, ascertained by using 2,9-dimesitylphenanthroline (**4'**) as the copper(I) binding receptor. 1,3,5-Trimethoxybenzene (δ = 6.06 ppm) was used in a 1:1 ratio with respect to **4'** as internal standard. Signal corresponding to 9-H of [Cu(**4'**)]$^{+}$ (at 6.99 ppm) is used to measure the release of copper(I) into solution. It shows that 60% (2.41/4 x 100 = 60%) of copper(I) is released which is captured by **4'**.

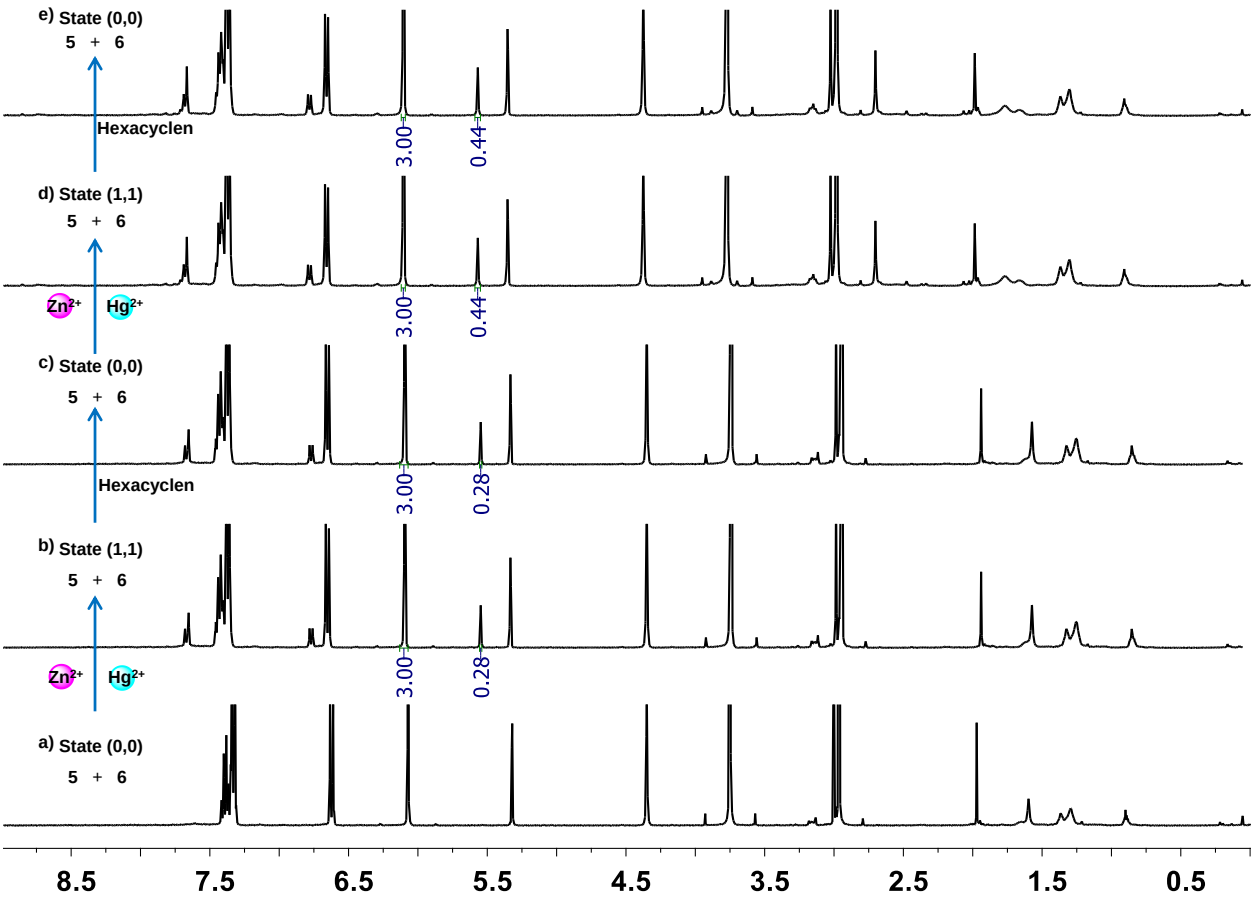


Figure S69: ^{1}H NMR (400 MHz, CD_2Cl_2:CD_3CN = 15:1) spectrum obtained after (a) heating the reaction mixture of **5** and **6** in presence of 2 mol% of both ([Cu(**3**)]$^+$ + **4**) at 50 °C for 2 h in an NMR tube revealing that click catalysis was OFF (no singlet at δ = 5.52). (b) After addition of 2 mol% of $Zn(OTf)_2$ and 2 mol% of $Hg(ClO_4)_2$ with respect to compound **5** and subsequent heating at 50 °C for 2 h, click product **7** was formed in 14% yield (calculated with respect to the internal standard). (c) After adding the consumed substrates and 4 mol% of hexacyclen (with respect to **5**) further heating at 50 °C for 2 h did not provide new click product. (d) Addition of 2 mol% of $Zn(OTf)_2$ and 2 mol% of $Hg(ClO_4)_2$ with respect to **5** and heating at 50 °C for 2 h resulted in an increase of click product **7** by 8% (total yield = 22%). (e) After adding the consumed substrates and 4 mol% of hexacyclen (with respect to **5**) further heating at 50 °C for 2 h did not provide new click product.

7. ESI-MS Spectra

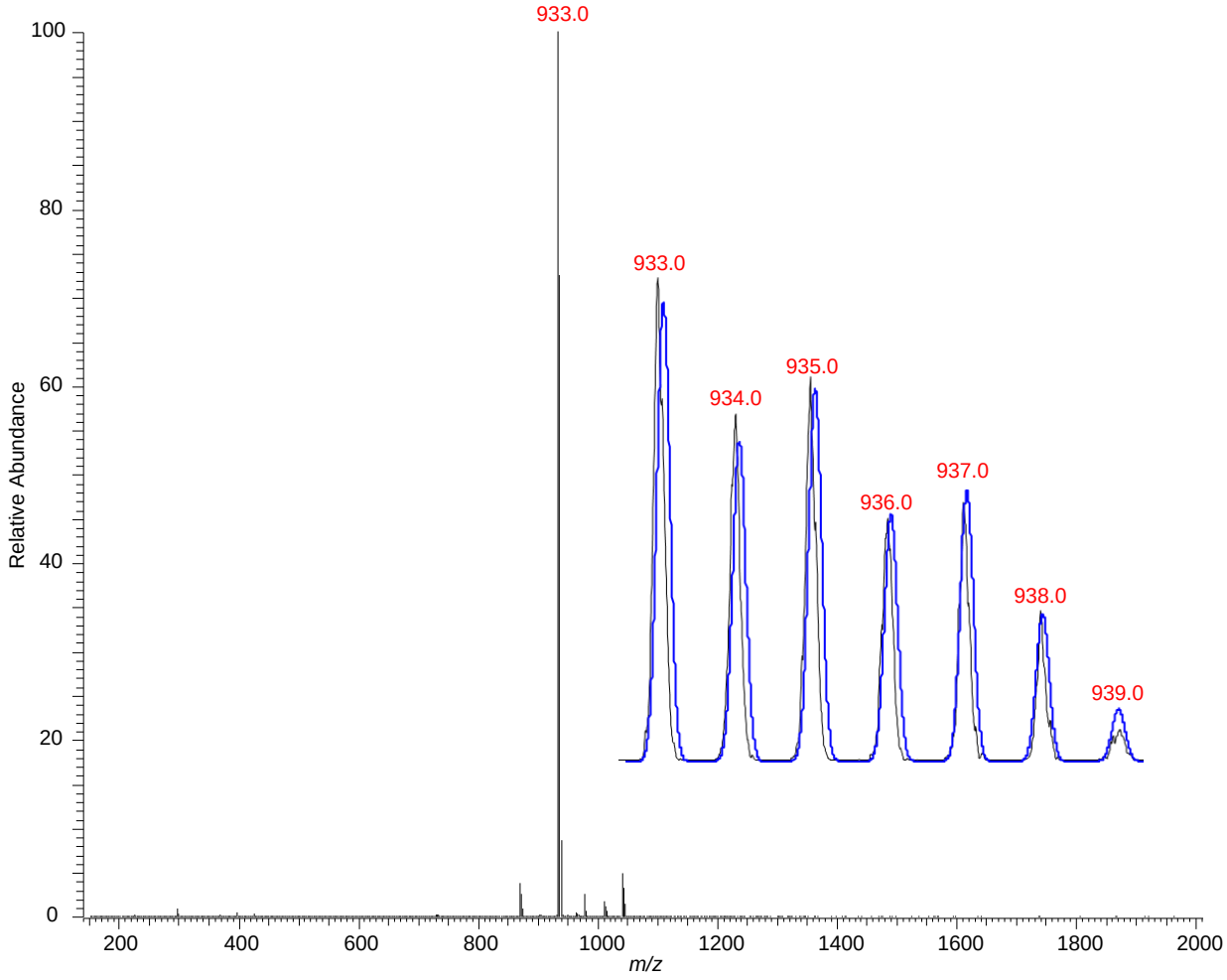


Figure S70: ESI-MS spectrum of rotator [**2**+H^+].

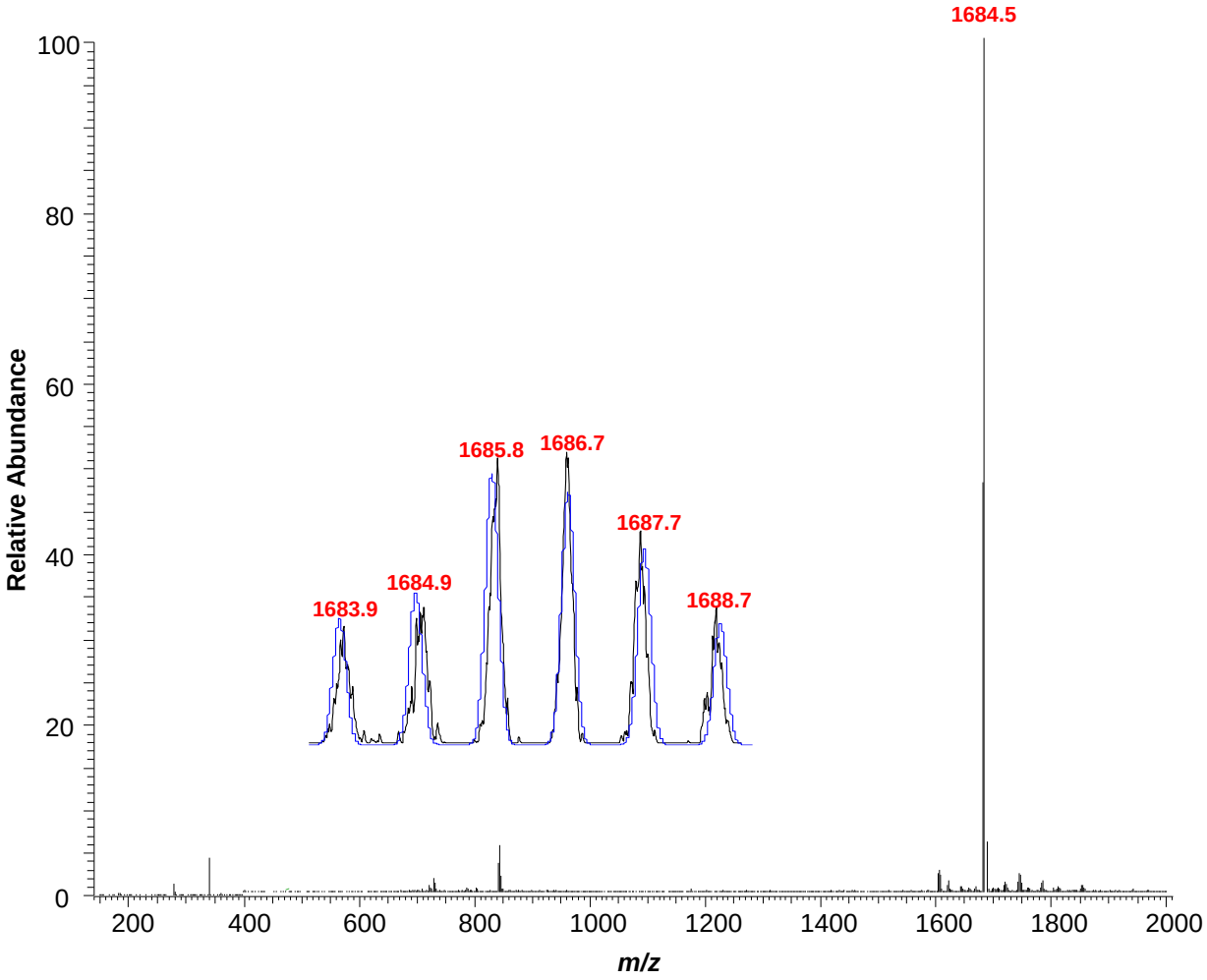


Figure S71: ESI-MS spectrum of complex $[Cu(\mathbf{3})]^{+}$.

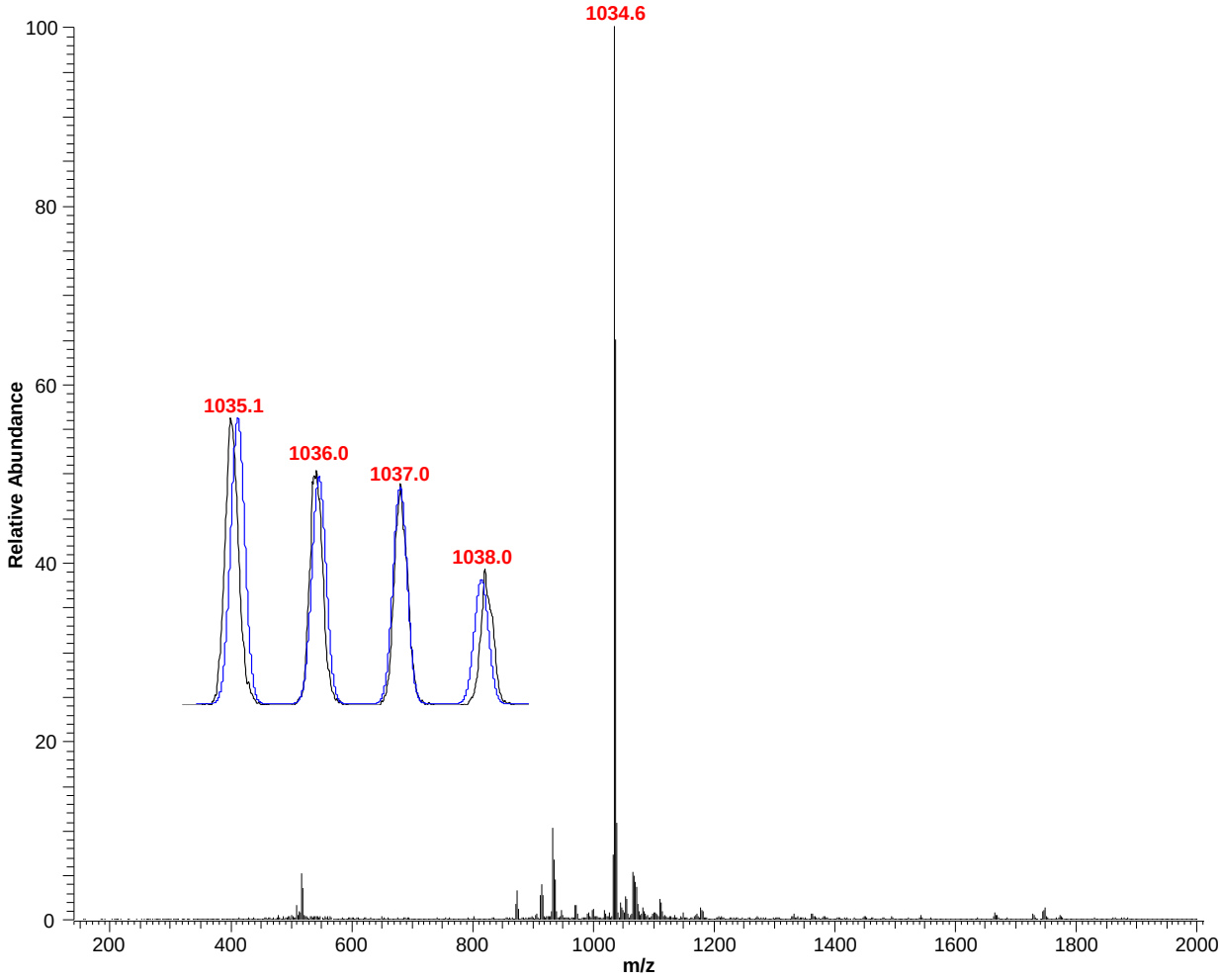


Figure S72: ESI-MS spectrum of complex $[Cu(\mathbf{4})]^{+}$.

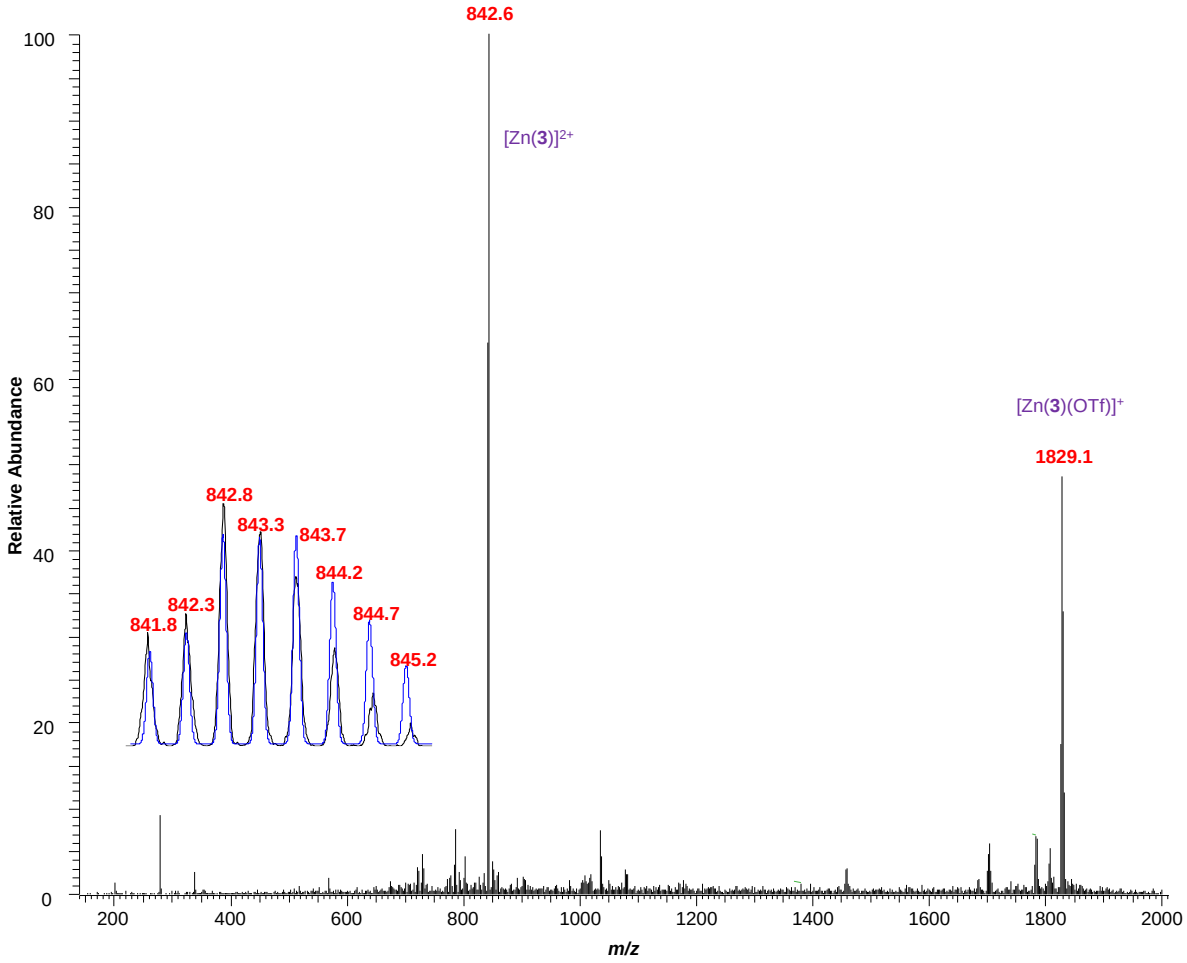


Figure S73: ESI-MS spectrum of complex $[Zn(\mathbf{3})]^{2+}$.

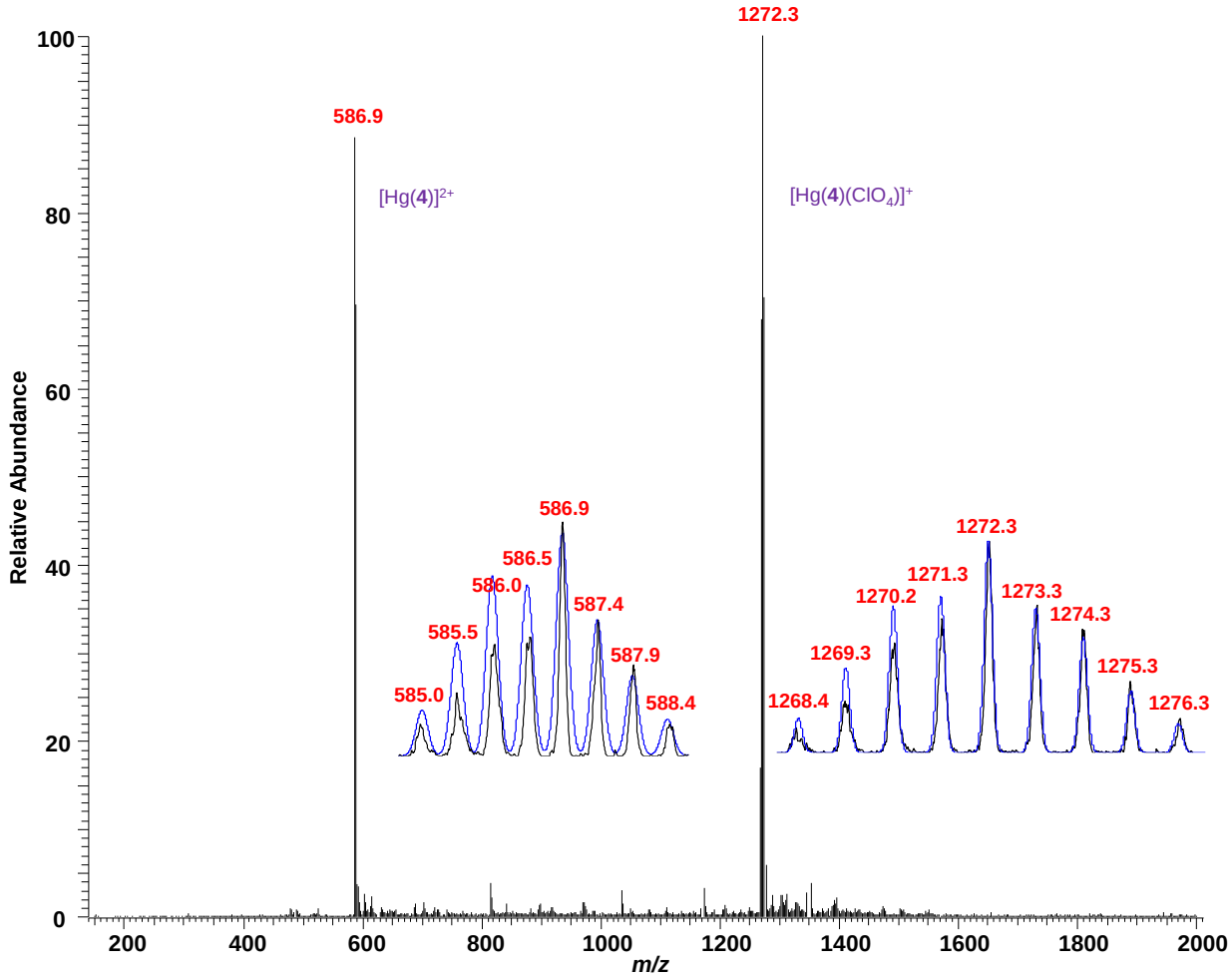


Figure S74: ESI-MS spectrum of complex $[Hg(\mathbf{4})]^{2+}$.

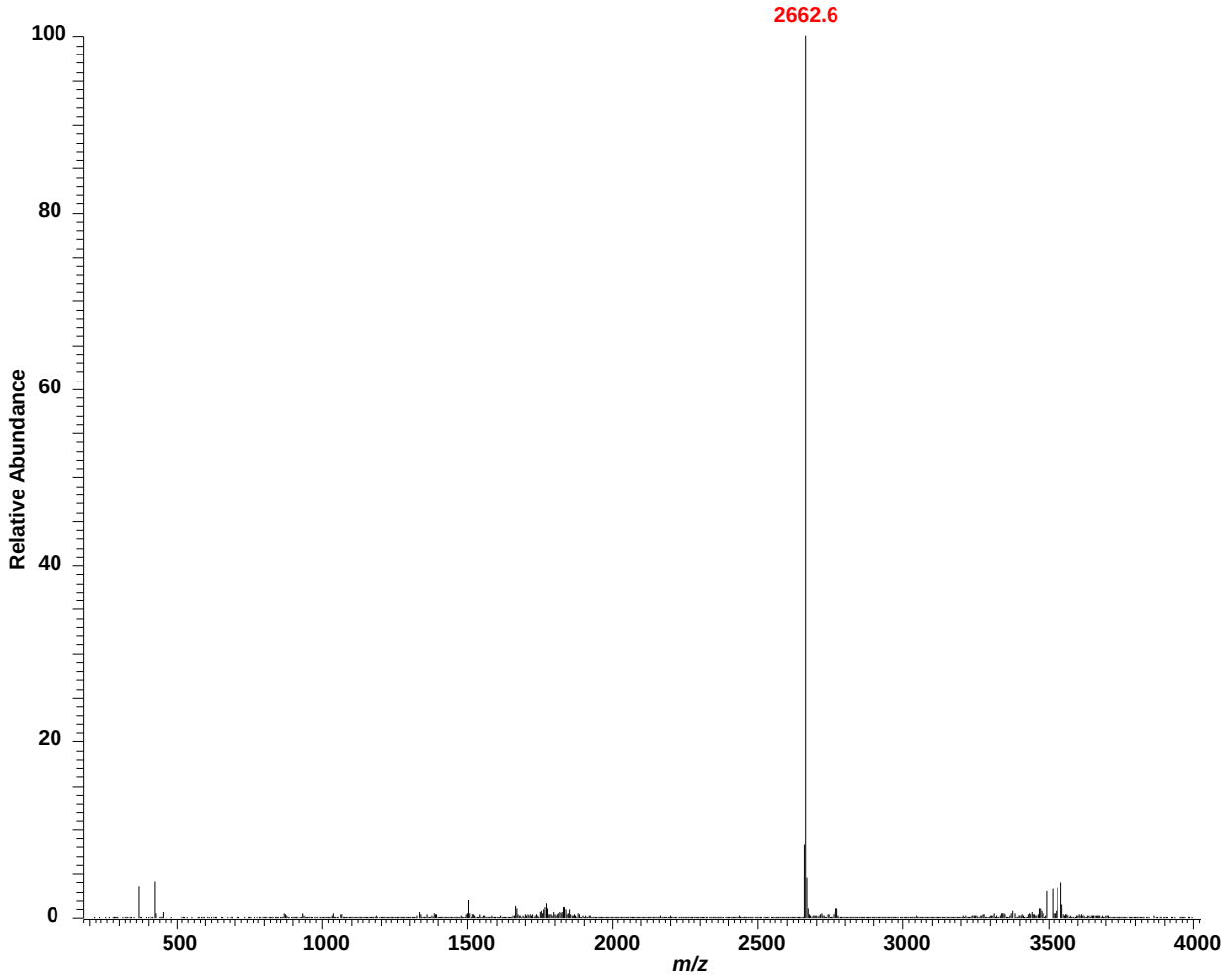


Figure S75: ESI-MS spectrum of **ROT-1**.

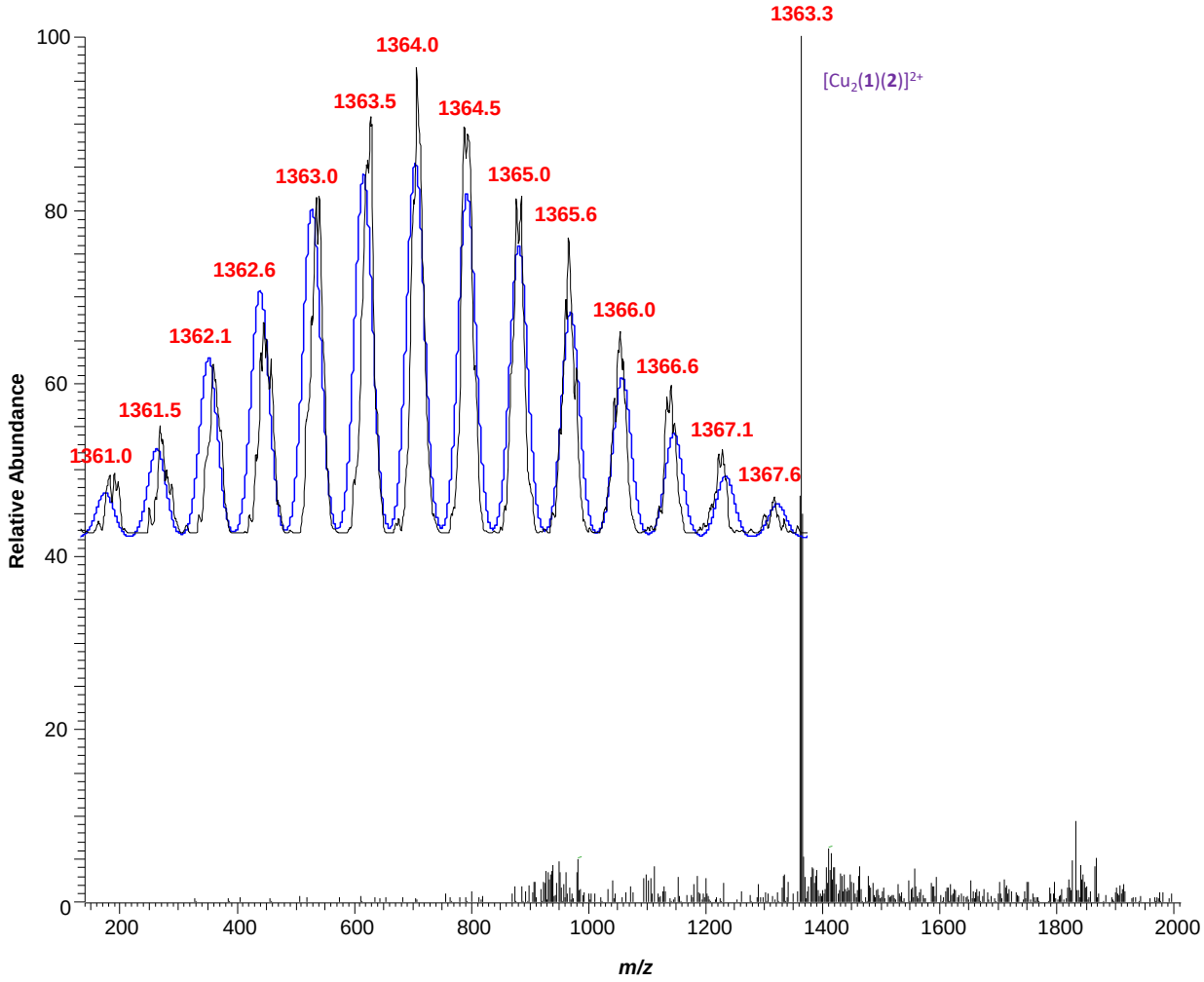


Figure S76: ESI-MS spectrum of **ROT-2**.

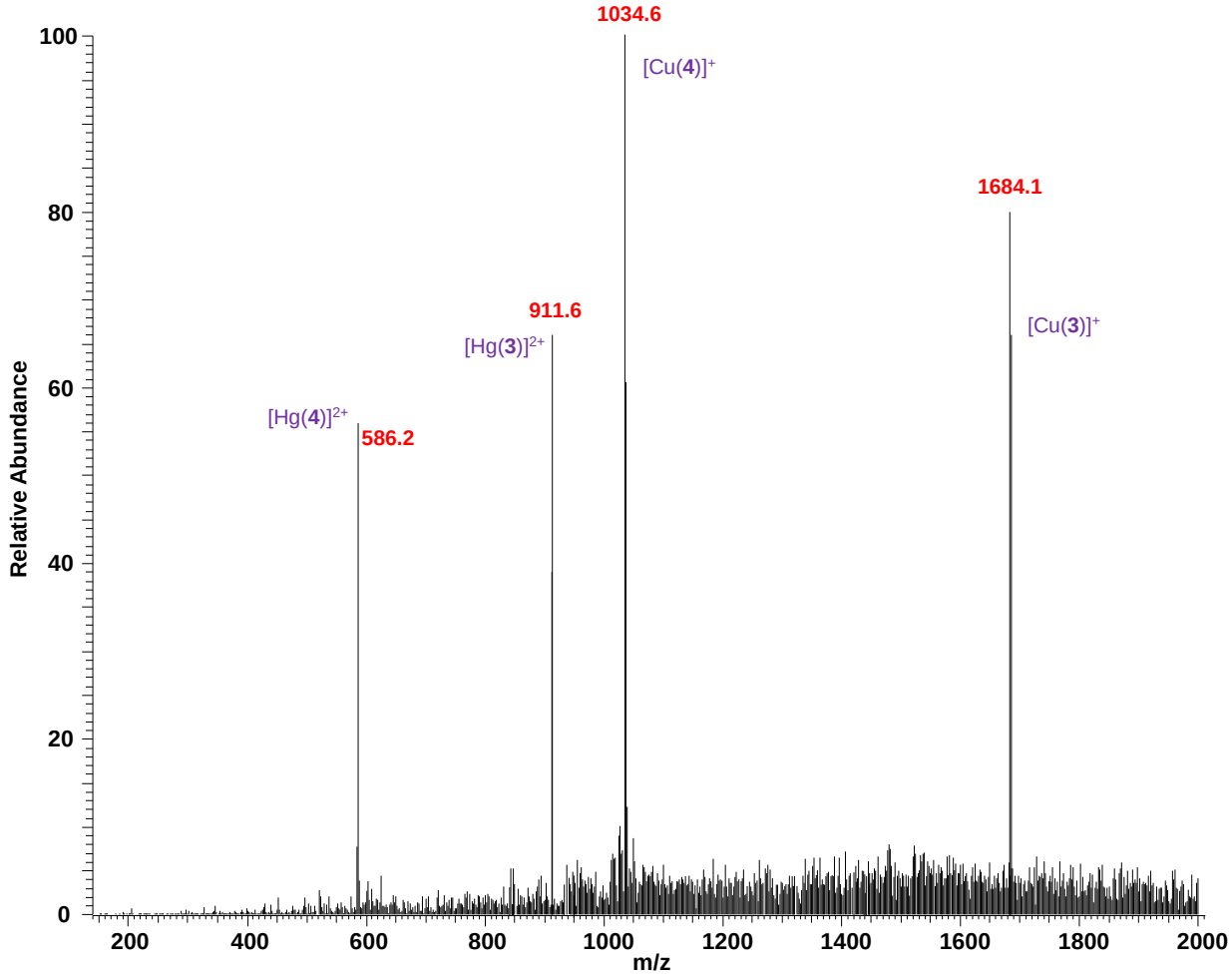


Figure S77: ESI-MS of state (0,1) (without rotor assembly) showing the metal ion distribution on nanoswitches **3** and **4** when Hg^{2+} was added. The spectrum was measured immediately after addition of Hg^{2+}.

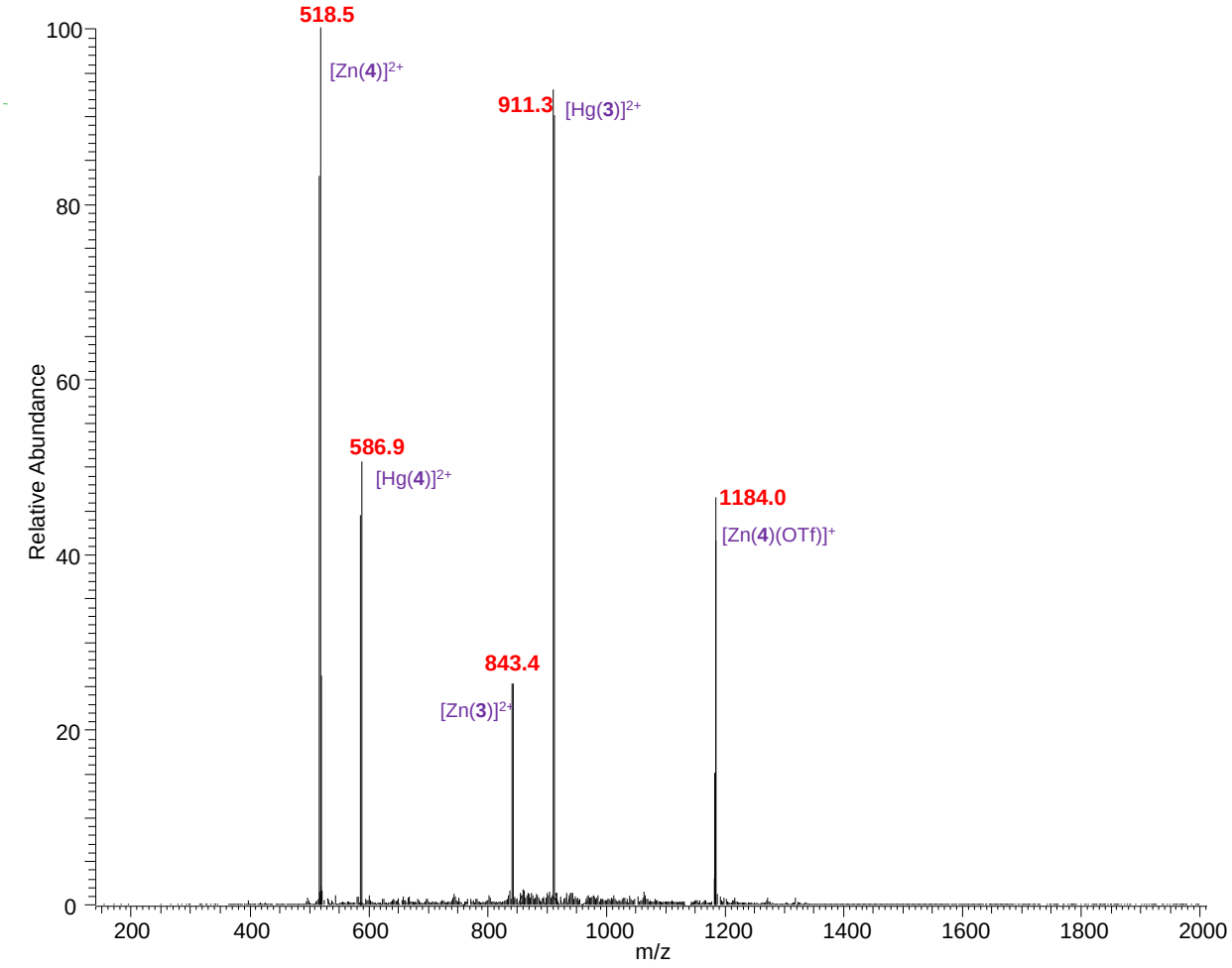


Figure S78: ESI-MS of state (1,1) (without rotor assembly) showing the metal ion distribution on nanoswitches **3** and **4** after addition of Hg^{2+} and Zn^{2+}. The spectrum was taken 30 min after addition of Zn^{2+} to state (0,1).

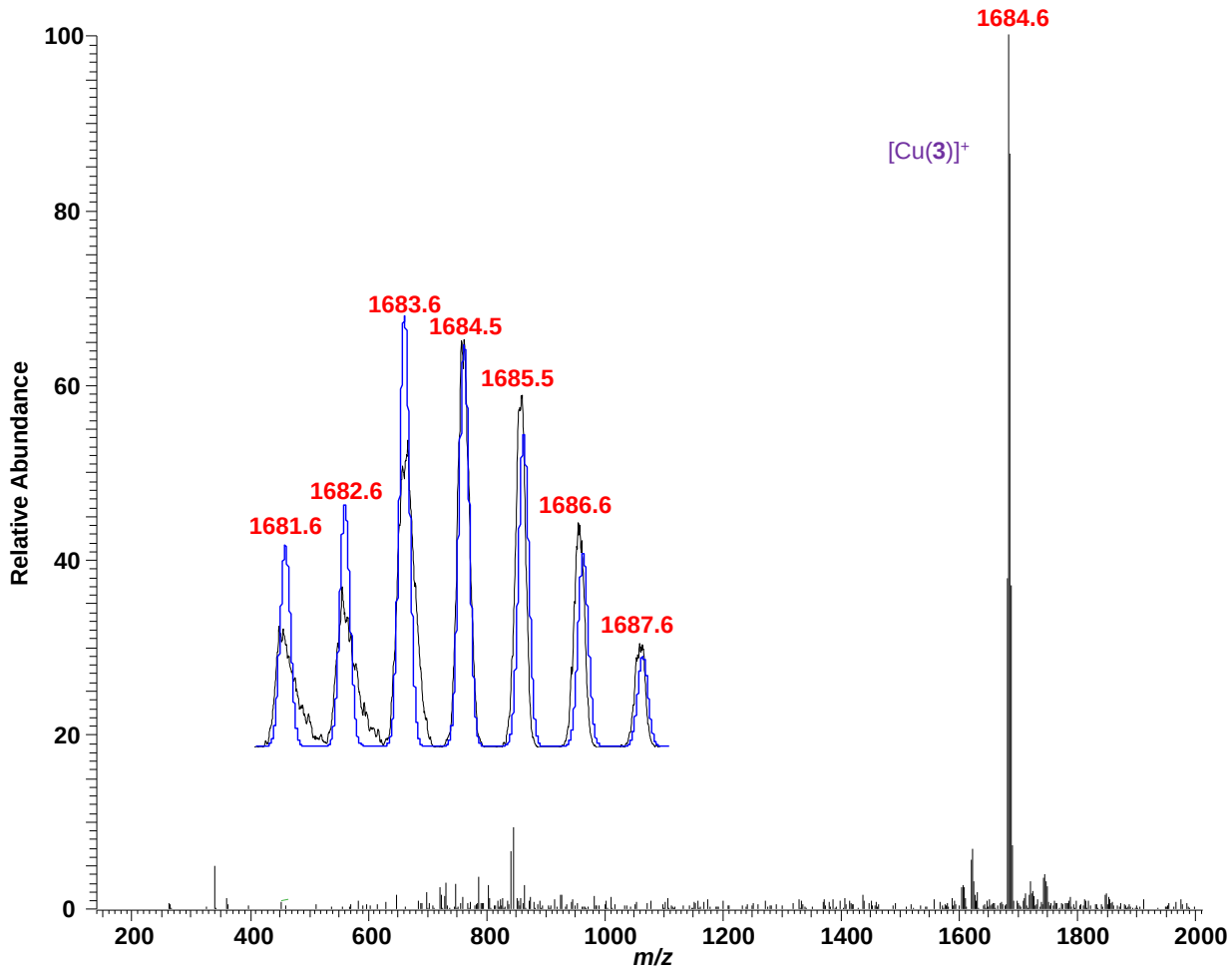


Figure S79: ESI-MS spectrum of state (0,0).

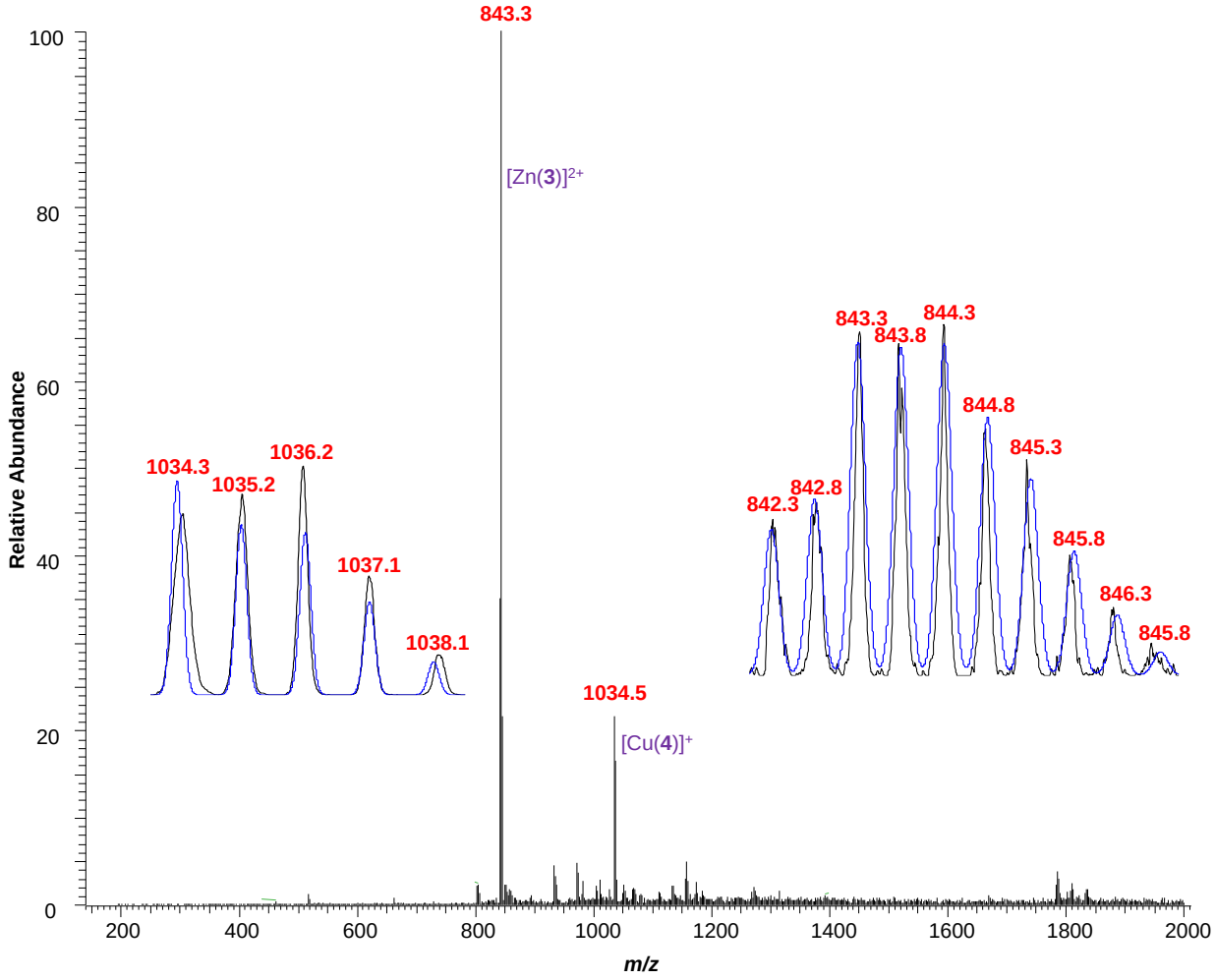


Figure S80: ESI-MS spectrum of state (1,0).

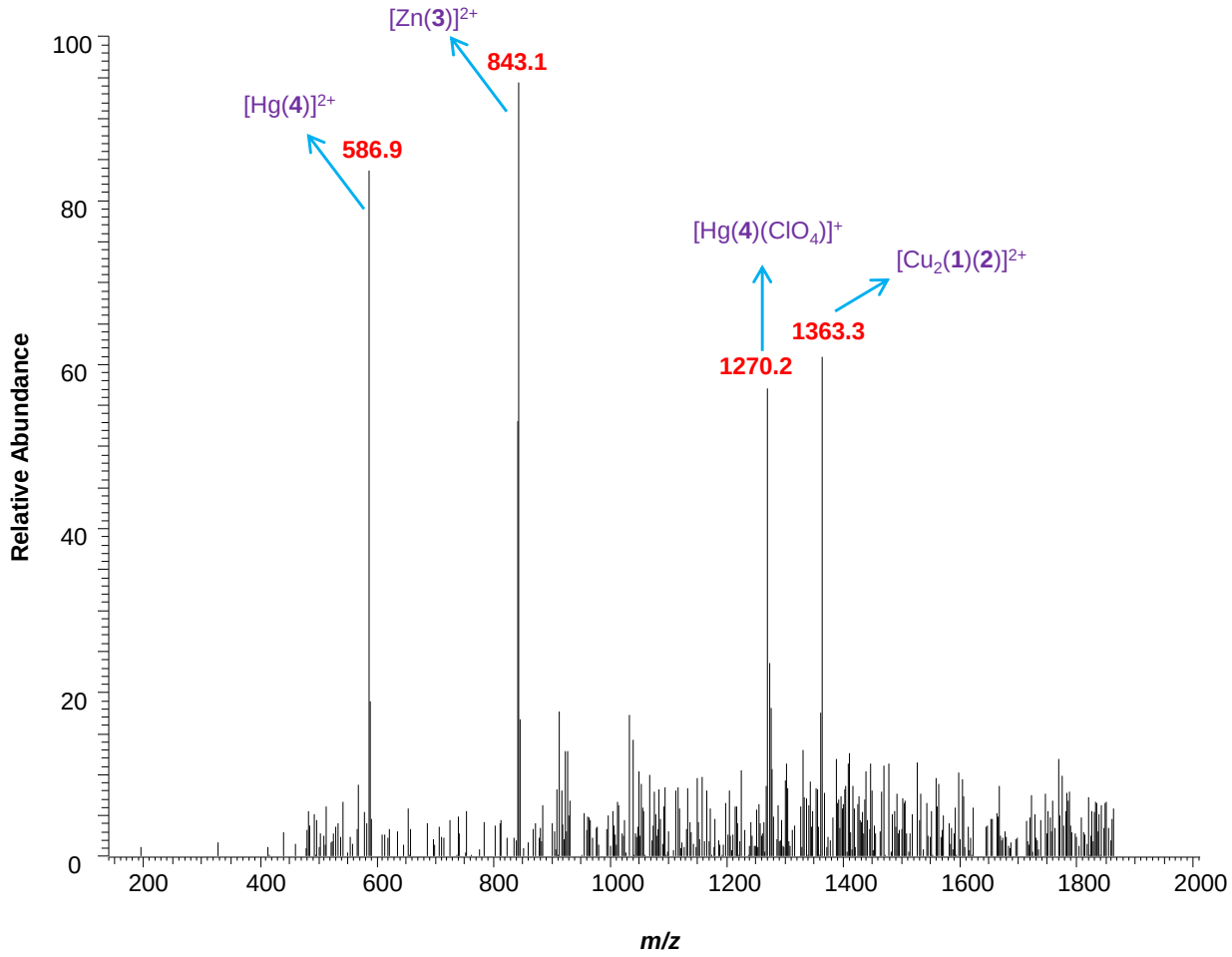


Figure S81: ESI-MS spectrum of state (1,1).

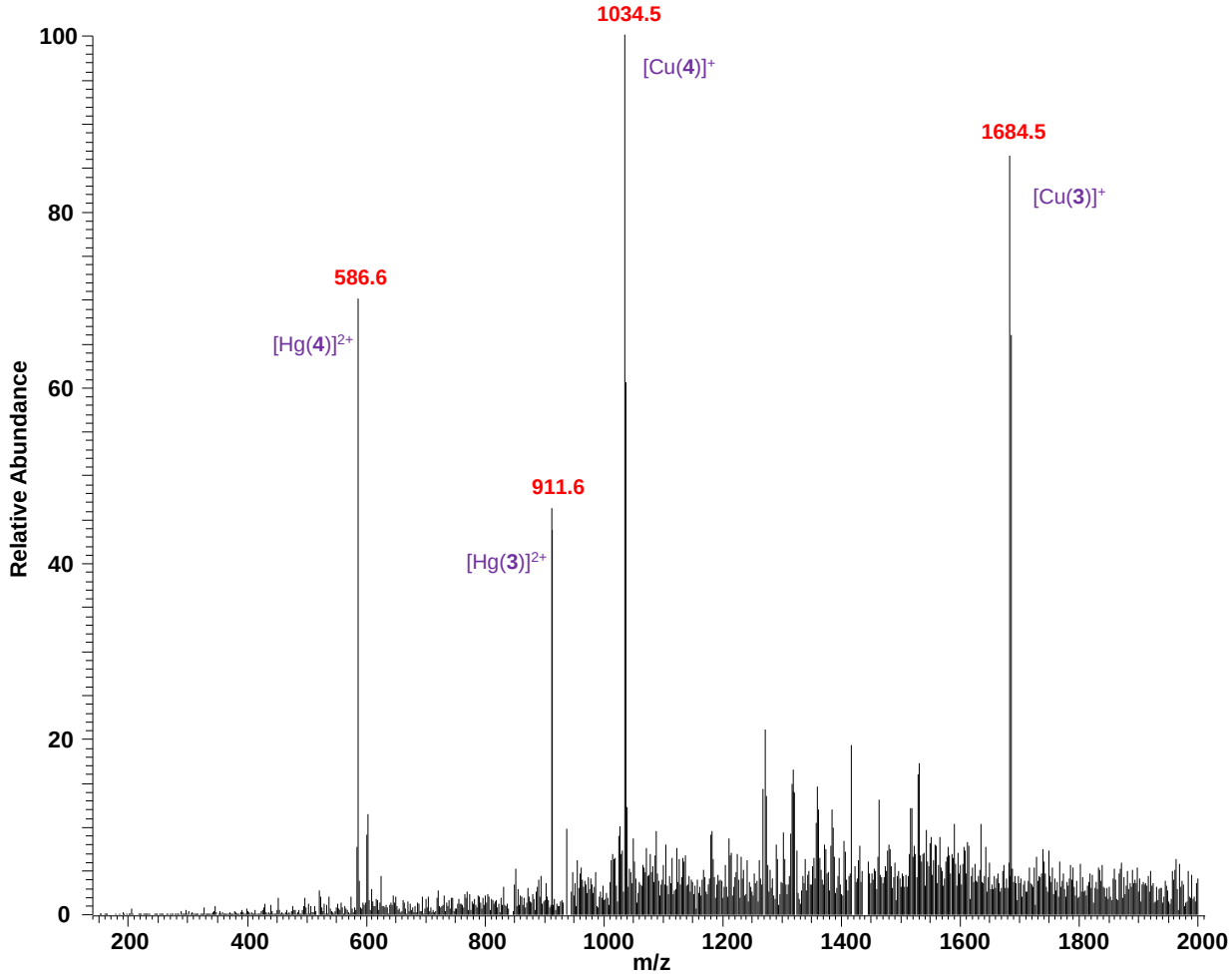


Figure S82: ESI-MS of (0,1) state when Hg^{2+} is added first.

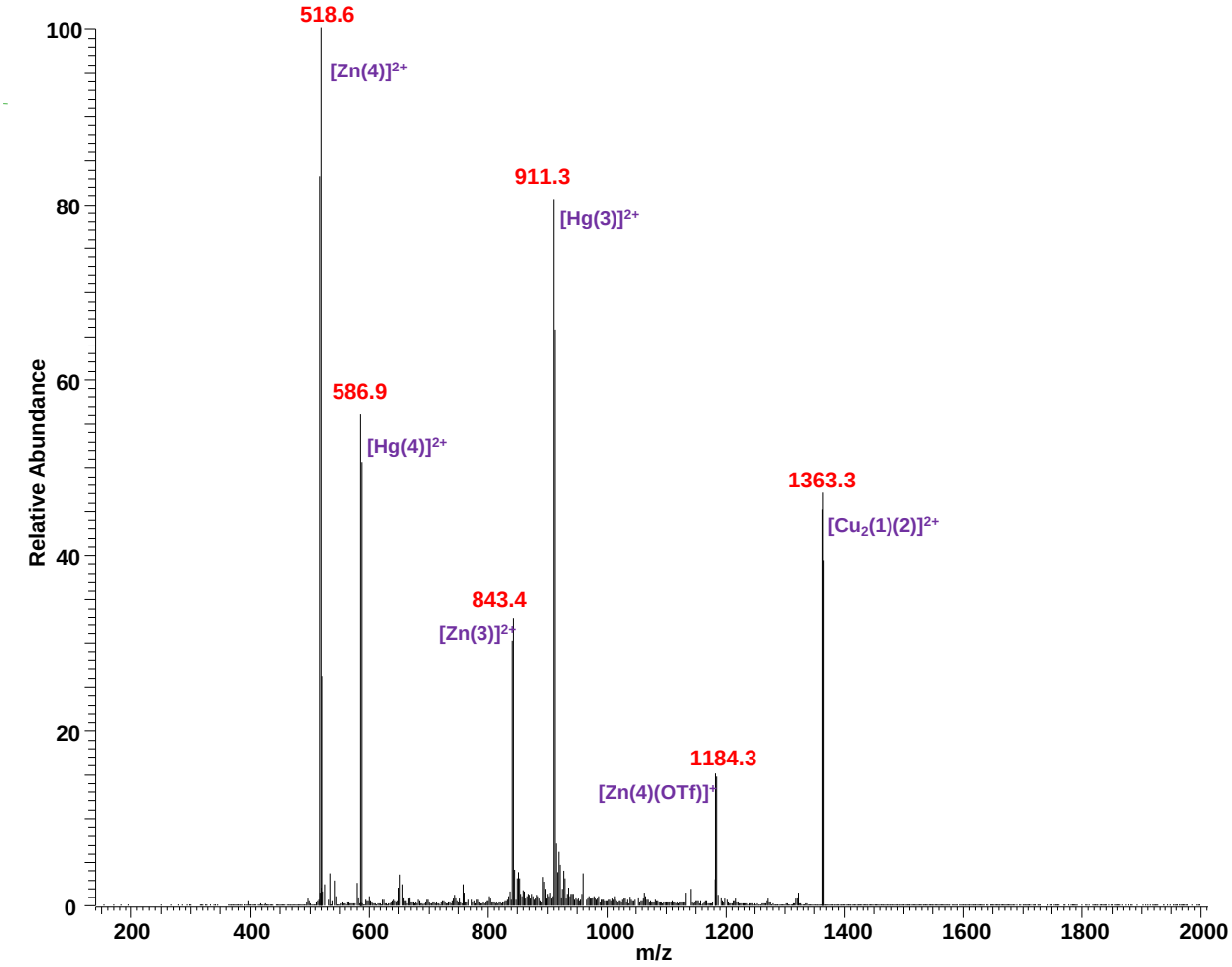


Figure S83: ESI-MS of state (1,1) when Hg^{2+} is used as **IN-1** and Zn^{2+} as **IN-2**.

8. Speciation Distribution Analysis

With the binding constant between Cu^+ and 2,9-dimesityl-1,10-phenanthroline at hand (log K = 5.1) we analyzed the formation of the corresponding complex using the Hyperquad software (http://www.hyperquad.co.uk/hyss.htm). **A** refers to Cu^+ from $[Cu(CH_3CN)_4]PF_6$ and **B** corresponds to 2,9-dimesityl-1,10-phenanthroline. **AB** represents the complex [Cu(2,9-dimesityl-1,10-phenanthroline)]$^+$.

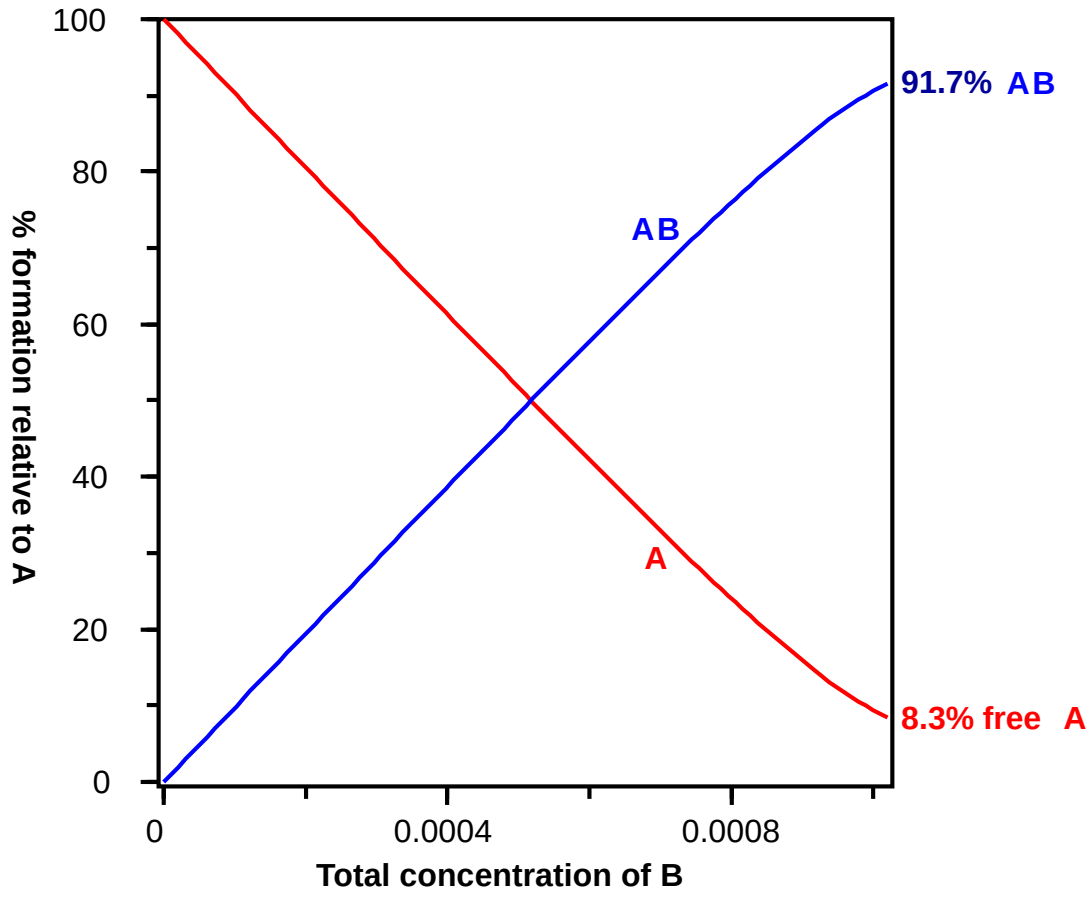


Figure S84: Speciation distribution of free and complexed Cu^+ (distribution was calculated for 1.02×10^{-3} M **A** = Cu^+).

9. References

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