

## Supporting Information

for

# **Four-Component Catalytic Machinery: Reversible Three-State Control of Organocatalysis by Walking Back and Forth on Track**

Nikita Mittal, Merve S. Özer, Michael Schmittle\*

*Center of Micro and Nanochemistry and Engineering, Organische Chemie I, Universität  
Siegen, Adolf-Reichwein-Str. 2, D-57068 Siegen, Germany*

### *Table of Contents*

1	Synthesis	S2
	General information	S2
	Synthetic procedures	S4
	Synthesis and characterization of walking states	S9
	<i>In-situ</i> stepwise walking from state I to state III and back to state I	S13
2	Establishing the Catalytic Conjugate Addition	S14
	General procedure for the catalytic conjugate addition	S14
	Catalytic cycle	S18
3	<sup>1</sup> H and <sup>13</sup> C NMR Spectra	S20
4	DOSY NMR	S37
5	ESI-MS spectra	S40
6	UV-vis Spectra	S42
	Binding constant measurements	S42
7	References	S44

### Abbreviations:

DCM : dichloromethane

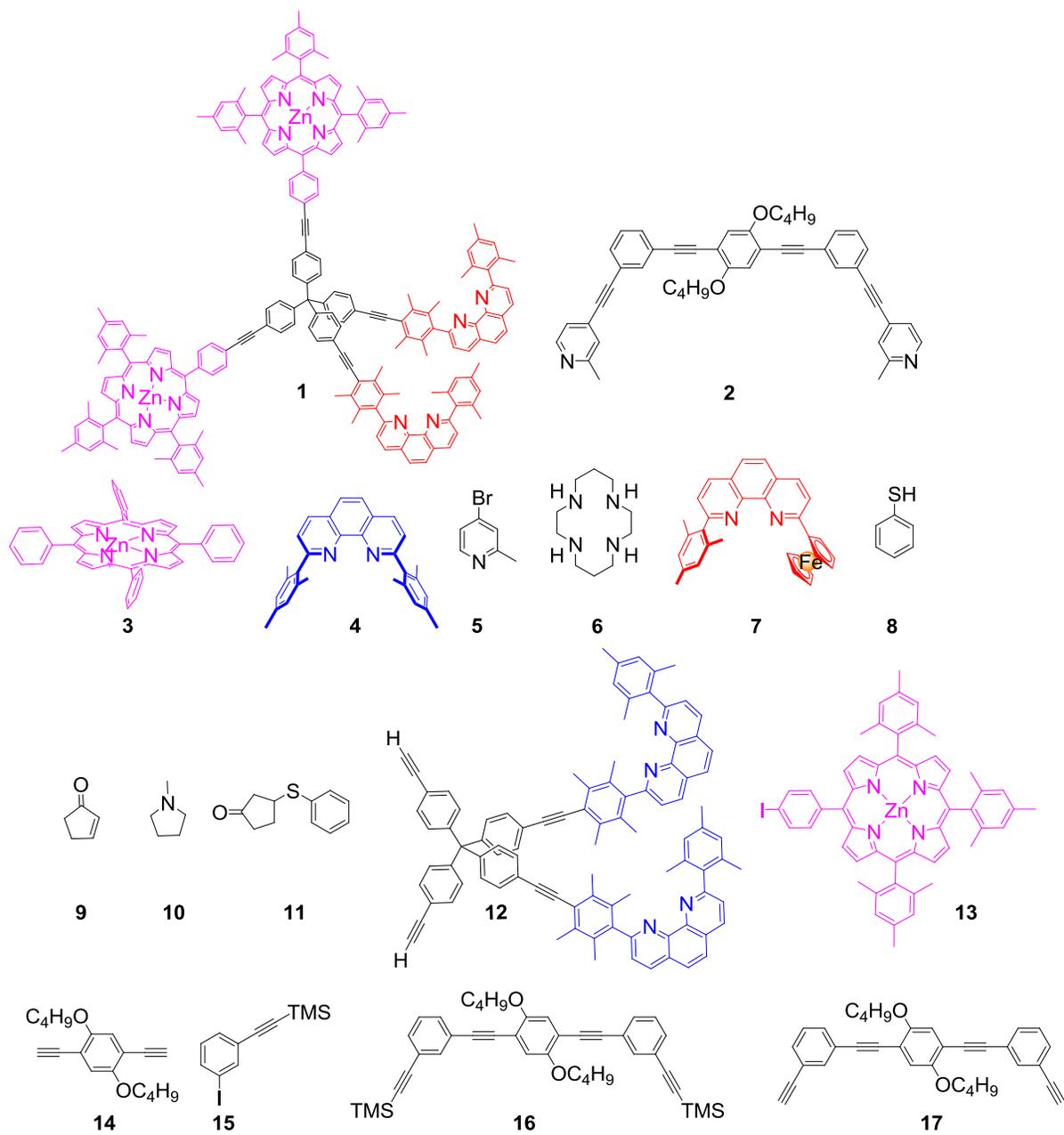
ZnTPP : zinc(II)-5,10,15,20-tetraphenylporphyrin (**3**)

TCE : 1,1,2,2-tetrachloroethane

## Synthesis

### General information

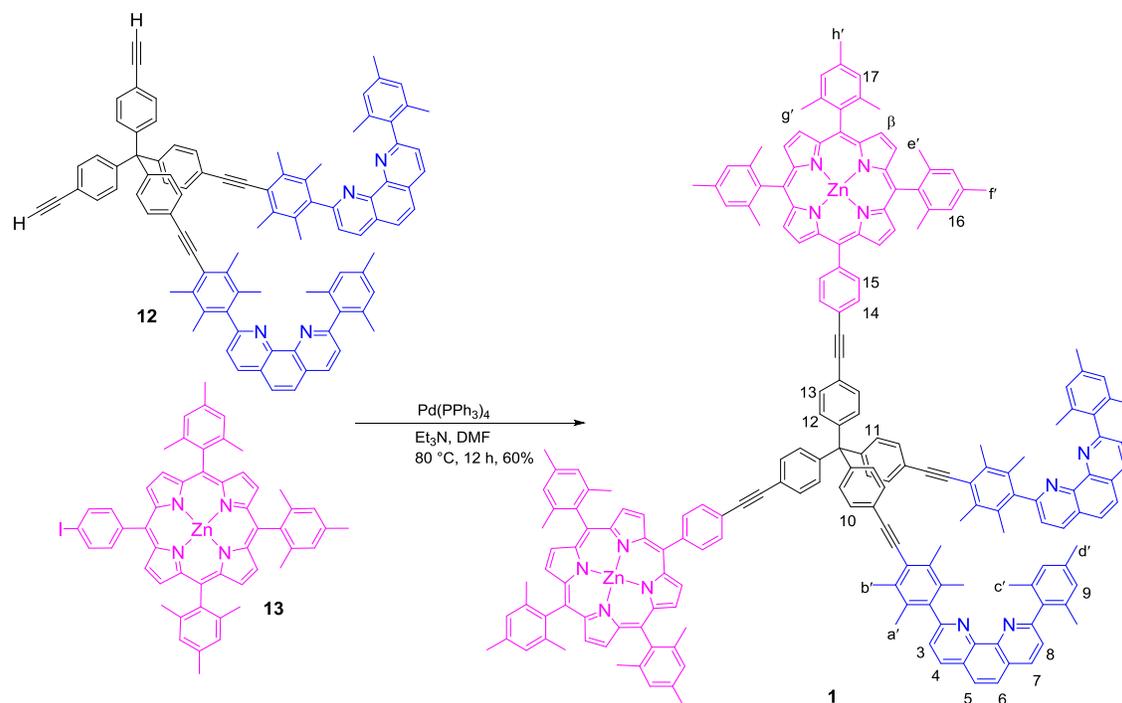
All commercial reagents were used without further purification. Solvents were dried with the appropriate desiccants and distilled prior to use.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR were recorded on a Bruker Avance 400 (400 MHz) or on Varian-S 600 (600 MHz) using the deuterated solvent as the lock and the residual protonated solvent as the internal reference ( $\text{CD}_2\text{Cl}_2$ :  $\delta_{\text{H}} = 5.32$  ppm and  $\delta_{\text{C}} = 53.8$  ppm;  $\text{CDCl}_3$ :  $\delta_{\text{H}} = 7.26$  ppm and  $\delta_{\text{C}} = 77.2$  ppm). The following abbreviations were utilized to describe peak patterns: s = singlet, d = doublet, t = triplet, dd = doublet of doublet, td = triplet of doublet, dt = doublet of triplet, br = broad, bs = broad singlet, bd = broad doublet and m = multiplet. The numbering of the carbon atoms in the molecular formulae (*vide infra*) is used only for the assignments of the NMR signals and thus is not necessarily in accordance with IUPAC nomenclature. Electrospray ionization mass spectra (ESI-MS) were recorded on a Thermo-Quest LCQ Deca. Melting points were measured on a Büchi SMP-20 instrument. Infrared spectra were recorded using a Varian 1000 FT-IR instrument. UV-vis spectra were recorded on a Varian Cary 100 BioUV/Vis spectrometer. Elemental analysis was done on the EA 3000 CHNS. Compounds **4**,<sup>1</sup> **7**,<sup>2</sup> **11**,<sup>3</sup> **13**,<sup>4</sup> **14**<sup>5</sup> and **15**<sup>6</sup> were synthesized according to known procedures.



**Chart S1:** Chemical structures of compounds 1-17.

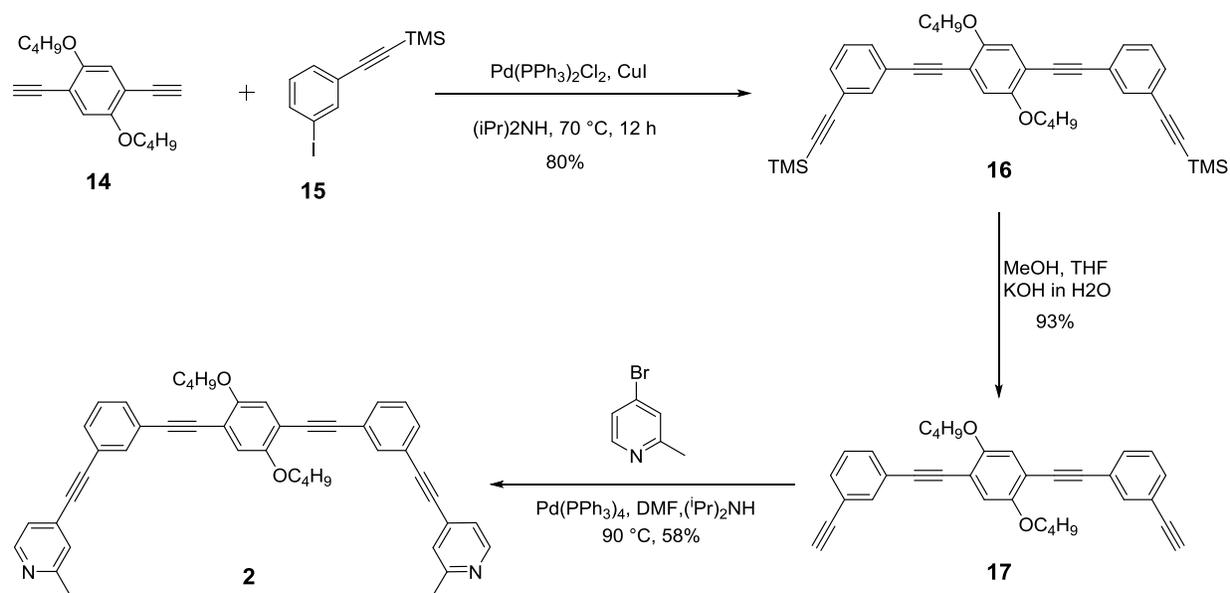
## Synthetic procedures

### Synthesis of track 1



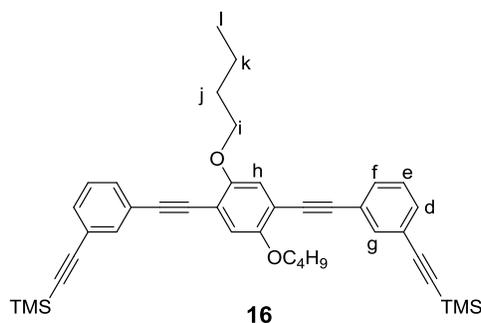
Compound **12** (50.0 mg, 39.0  $\mu\text{mol}$ ) and compound **13** (109 mg, 117  $\mu\text{mol}$ ) were dissolved in a mixture of dry DMF (10 mL) and dry  $\text{Et}_3\text{N}$  (10 mL). The solution was trice subjected to freeze-pump-thaw cycles to remove atmospheric oxygen. Then,  $\text{Pd}(\text{PPh}_3)_4$  (4.50 mg, 4.00  $\mu\text{mol}$ ) was added into the mixture under  $\text{N}_2$  atmosphere and subjected to heating at  $80\text{ }^\circ\text{C}$  for overnight. The reaction mixture then was cooled and solvents were evaporated under reduced pressure. The crude mixture was purified by column chromatography eluting with 2% EtOAc in DCM on silica gel ( $R_f = 0.37$ , 5% ethyl acetate in DCM) to furnish a violet solid in 60% yield.  $\text{Mp} > 250\text{ }^\circ\text{C}$ .  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  8.91 (d,  $^3J = 4.7\text{ Hz}$ , 4H,  $\beta$ -H), 8.76 (d,  $^3J = 4.7\text{ Hz}$ , 4H,  $\beta$ -H), 8.70 (s, 8H,  $\beta$ -H), 8.36 (d,  $^3J = 8.4\text{ Hz}$ , 2H, [4/7]-H), 8.34 (d,  $^3J = 8.3\text{ Hz}$ , 2H, [7/4]-H), 8.25 (d,  $^3J = 8.3\text{ Hz}$ , 4H, [15/14]-H), 7.95 (d,  $^3J = 8.3\text{ Hz}$ , 4H, [14/15]-H), 7.91 (s, 4H, 5- & 6-H), 7.69 (d,  $^3J = 8.6\text{ Hz}$ , 4H, [13/10]-H), 7.62 (d,  $^3J = 8.7\text{ Hz}$ , 4H, [10/13]-H), 7.57 (d,  $^3J = 8.4\text{ Hz}$ , 2H, [3/8]-H), 7.56 (d,  $^3J = 8.3\text{ Hz}$ , 2H, [8/3]-H), 7.44 (d,  $^3J = 8.6\text{ Hz}$ , 4H, [11/12]-H), 7.40 (d,  $^3J = 8.7\text{ Hz}$ , 4H, [12/11]-H), 7.30 (s, 8H, 16-H), 7.29 (s, 4H, 17-H), 6.96 (s, 4H, 9-H), 2.62 (s, 18H, f'- & h'-H), 2.57 (s, 12H, [b'/a']-H), 2.34 (s, 6H, d'-H), 2.05 (s, 12H, c'-H), 1.96 (s, 12H, [a'/b']-H), 1.84 (s, 12H, g'-H), 1.83 (s, 24H, e'-H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  161.5, 160.5, 150.3, 150.2,

150.1, 150.1, 146.8, 146.7, 146.2, 143.5, 142.0, 139.6, 139.5, 139.3, 139.3, 138.5, 137.9 (2C), 137.8, 136.6, 136.4, 136.3, 136.1, 134.9, 132.3, 132.2, 131.6, 131.5, 131.4 (2C), 131.3, 131.2, 131.0, 130.2, 128.6, 128.0, 128.0, 127.6, 127.6, 126.6, 126.5, 124.9, 124.8, 123.2, 122.7, 122.5, 121.8, 119.6, 119.3, 119.2, 96.9, 90.3, 90.2, 89.7, 65.5, 21.8, 21.7, 21.7, 21.5, 21.2, 20.4, 18.6, 17.7; IR (KBr):  $\nu$  2923, 1609, 1490, 1378, 1334, 1203, 1061, 998, 882, 850, 824, 798, 722  $\text{cm}^{-1}$ ; ESI-MS:  $m/z$  (%) 1440.3 (100)  $[\text{M}+2\text{H}]^{2+}$ ; UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}} = 550 \text{ nm}$  (Q band,  $\epsilon = 1.45 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ); Anal. Calcd. for  $\text{C}_{201}\text{H}_{164}\text{N}_{12}\text{Zn}_2 \cdot \text{CH}_2\text{Cl}_2$ : C, 81.88; H, 5.65; N, 5.67; found: C, 81.55; H, 5.36; N, 5.51.



**Scheme S1:** Synthetic scheme for the preparation of biped ligand **2**.

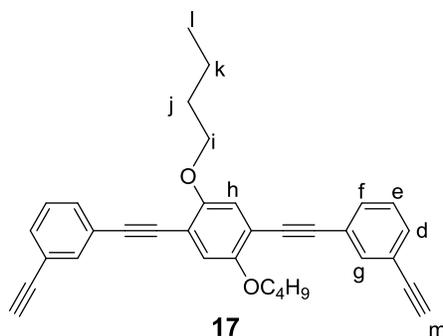
**Synthesis of (((2,5-dibutoxy-1,4-phenylene)bis(ethyne-2,1-diyl))bis(3,1-phenylene))-bis(ethyne-2,1-diyl)bis(trimethylsilane) (**16**)**



Under  $\text{N}_2$  atmosphere an oven-dry Schlenk tube was charged with 1,4-dibutoxy-2,5-diethynylbenzene (**14**, 200 mg, 740  $\mu\text{mol}$ ), ((3-iodophenyl)ethynyl)trimethylsilane (**15**, 666 mg, 2.22

mmol), Pd(PPh<sub>3</sub>)<sub>2</sub>Cl<sub>2</sub> (25.9 mg, 37.0 μmol) and CuI (7.04 mg, 37.0 μmol). After addition of dry (<sup>i</sup>Pr)<sub>2</sub>NH (20 mL), the mixture was heated at 70 °C for 12 h under N<sub>2</sub> atmosphere. Following removal of solvent, the resulting solid was dissolved in DCM and washed with water. The residue was purified by column chromatography using 3% ethyl acetate in *n*-hexane as eluent affording **16** as yellow solid (*R*<sub>f</sub> = 0.4 [SiO<sub>2</sub>, ethylacetate/*n*-hexane = 5:95]). Yield = 370 mg (80%). Mp = 125-127 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.65 (t, <sup>4</sup>*J* = 1.2 Hz, 2 H, g-H), 7.46 (dt, <sup>3</sup>*J* = 7.6 Hz, <sup>4</sup>*J* = 1.2 Hz, 2 H, [d/f]-H), 7.42 (dt, <sup>3</sup>*J* = 7.6 Hz, <sup>4</sup>*J* = 1.2 Hz, 2 H, [f/d]-H), 7.28 (t, <sup>3</sup>*J* = 7.6 Hz, 2 H, e-H), 7.00 (s, 2 H, h-H), 4.03 (t, <sup>3</sup>*J* = 6.4 Hz, 4 H, i-H), 1.88-1.81 (m, 4 H, j-H), 1.64-1.62 (m, 4 H, k-H), 1.02 (t, <sup>3</sup>*J* = 7.6 Hz, 6 H, l-H), 0.26 (s, 18 H, TMS-H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): δ = δ 153.7, 135.0, 131.5, 131.4, 128.3, 123.7, 123.4, 116.9, 113.9, 104.2, 94.9, 94.0, 86.5, 69.3, 31.4, 19.2, 13.9, -0.1; IR (KBr): ν 3254, 2958, 2923, 2869, 2159, 1590, 1569, 1503, 1423, 1384, 1248, 1222, 1199, 1148, 1122, 1063, 1024, 949, 844, 799, 759 cm<sup>-1</sup>; Anal. calcd. for C<sub>40</sub>H<sub>46</sub>O<sub>2</sub>Si<sub>2</sub>• 0.5H<sub>2</sub>O: C, 77.00; H, 7.59; found: C, 76.88; H, 7.49.

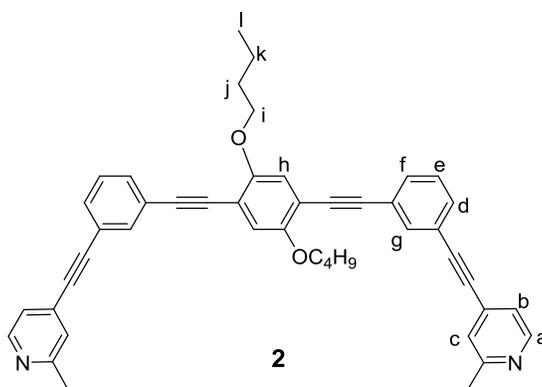
### Synthesis of 3,3'-((2,5-dibutoxy-1,4-phenylene)bis(ethyne-2,1-diyl))bis(ethynylbenzene) (**17**)



Compound **15** (350 mg, 0.57 mmol) and KOH (38.4 mg, 0.68 mmol) were stirred in THF (15 mL), MeOH (15 mL) and H<sub>2</sub>O (5 mL) at room temperature. After completion of the reaction as confirmed by TLC, the organic solvents were evaporated and the resultant suspension was extracted with DCM (150 mL). Finally DCM was evaporated under reduced pressure to furnish **17** as yellow solid. Yield = 250 mg (93%). Mp = 133-135 °C; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ = 7.66 (t, <sup>4</sup>*J* = 1.2 Hz, 2 H, g-H), 7.50 (dt, <sup>3</sup>*J* = 7.6 Hz, <sup>4</sup>*J* = 1.2 Hz, 2 H, [d/f]-H), 7.45 (dt, <sup>3</sup>*J* = 7.6 Hz, <sup>4</sup>*J* = 1.2 Hz, 2 H, [f/d]-H), 7.31 (t, <sup>3</sup>*J* = 7.6 Hz, 2 H, e-H), 7.01 (s, 2 H, h-H), 4.04 (t, <sup>3</sup>*J* = 6.4 Hz, 4 H, i-H), 3.10 (s, 2 H, m-H), 1.88-1.81 (m, 4 H, j-H), 1.63-1.54 (m, 4 H, k-H), 1.02 (t, <sup>3</sup>*J* = 7.6 Hz, 6 H, l-H); <sup>13</sup>C NMR (100 MHz, CD<sub>2</sub>Cl<sub>2</sub>): δ = δ 153.7, 135.1, 131.8 (2C), 128.4, 123.8,

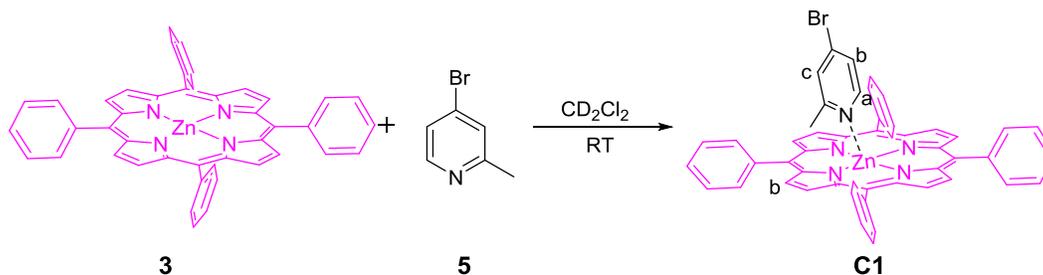
122.4, 116.9, 113.9, 93.8, 86.7, 82.8, 77.7, 69.3, 31.4, 19.3, 13.9; IR (KBr):  $\nu$  3302, 3253, 2956, 2920, 2871, 2212, 1592, 1568, 1504, 1475, 1418, 1385, 1276, 1218, 1024, 896, 862, 791, 743  $\text{cm}^{-1}$ ; Anal. calcd. for  $\text{C}_{34}\text{H}_{30}\text{O}_2$ : C, 86.78; H, 6.43; found: C, 86.83; H, 6.40.

**Synthesis of 4,4'-(((2,5-dibutoxy-1,4-phenylene)bis(ethyne-2,1-diyl))bis(3,1-phenylene))-bis(ethyne-2,1-diyl)bis(2-methylpyridine) (2)**



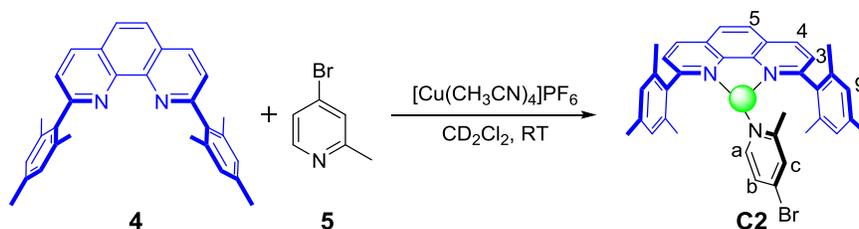
Compound **17** (50.0 mg, 106  $\mu\text{mol}$ ) and 4-bromo-2-methylpyridine (73.1 mg, 425  $\mu\text{mol}$ ) were taken in a dry Schlenk flask and dissolved in dry DMF (15 mL) and dry  $(^i\text{Pr})_2\text{NH}$  (15 mL). The mixture was subjected trice to freeze-pump-thaw cycles to remove atmospheric gases. At room temperature and under  $\text{N}_2$   $\text{Pd}(\text{PPh}_3)_4$  (12.3 mg, 10.6  $\mu\text{mol}$ ) was added into the mixture that was heated at 80  $^\circ\text{C}$  for overnight. After removal of all solvents, the resulting solid was dissolved in DCM and washed with water. The residue was purified by column chromatography using 20% ethyl acetate in DCM as eluent affording **20** as yellow solid ( $R_f=0.2$  [ $\text{SiO}_2$ , DCM: EtOAc = 8:2]). Yield = 40 mg (58%). Mp = 83-85  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ )  $\delta$  = 8.47 (d,  $^3J = 5.2$  Hz, 2 H, a-H), 7.72 (t,  $^4J = 1.2$  Hz, 2 H, g-H), 7.56-7.52 (m, 4 H, d- & f-H), 7.40 (t,  $^3J = 7.6$  Hz, 2 H, e-H), 7.28 (bs, 2 H, c-H), 7.21 (d,  $^3J = 5.2$  Hz, 2 H, b-H), 7.05 (s, 2 H, h-H), 4.06 (t,  $^3J = 6.4$  Hz, 4 H, i-H), 2.54 (s, 6 H, Me-H), 1.88-1.82 (m, 4 H, j-H), 1.65-1.56 (m, 4 H, k-H), 1.03 (t,  $^3J = 7.2$  Hz, 6 H, l-H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 159.2, 154.1, 149.6, 134.9, 132.3, 131.9, 131.3, 129.1, 125.2, 124.3, 123.1, 122.8, 117.28, 114.1, 94.0, 92.3, 87.8, 87.2, 69.7, 31.8, 24.5, 19.7, 14.1; IR (KBr):  $\nu$  2953, 2921, 2869, 2212, 1599, 1569, 1536, 1504, 1465, 1420, 1387, 1277, 1218, 1120, 1090, 1065, 1025, 976, 955, 895, 863, 832, 793  $\text{cm}^{-1}$ ; ESI-MS:  $m/z$  (%) 653.4 (100)  $[\text{M}+\text{H}]^+$ ; Anal. calcd. for  $\text{C}_{46}\text{H}_{40}\text{N}_2\text{O}_2 \cdot \text{H}_2\text{O}$ : C, 82.36; H, 6.31; N, 4.18; found: C, 82.65; H, 6.00, N, 4.29.

## Synthesis of Model Complex C1



Tetraphenyl zinc(II) porphyrin (**3**, 1.81 mg, 2.67  $\mu\text{mol}$ ) and 4-bromo-2-methylpyridine (**5**, 459  $\mu\text{g}$ , 2.67  $\mu\text{mol}$ ) were loaded in an NMR tube and dissolved in  $\text{CD}_2\text{Cl}_2$ . The resultant mixture was subjected to analytical characterization without any further purification. Yield quantitative.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 8.92 (s, 8 H,  $\beta$ -H), 8.22-8.20 (m, 8 H, Ph-H), 7.81-7.73 (m, 12 H, Ph-H), 6.88 (d,  $^4J$  = 2.0 Hz, 1 H, c-H), 6.81 (dd,  $^3J$  = 5.6 Hz,  $^4J$  = 2.0 Hz, 1 H, b-H), 6.44 (d,  $^3J$  = 5.6 Hz, 1 H, a-H), 1.35 (s, 3 H, Me);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 159.6, 150.6, 149.1, 143.5, 134.9, 132.9, 132.2, 127.7, 126.8, 126.6, 124.0, 121.3, 22.9; IR (KBr):  $\nu$  3434, 2924, 1595, 1582, 1523, 1484, 1439, 1338, 1292, 1203, 1173, 1066, 1001, 992, 851, 816, 798, 750  $\text{cm}^{-1}$ ; Anal. calcd. for  $\text{C}_{50}\text{H}_{34}\text{BrN}_5\text{Zn}\cdot 0.5 \text{CH}_2\text{Cl}_2$ : C, 67.95; H, 3.95; N, 7.85; found: C, 67.96; H, 3.71; N, 7.98.

## Synthesis of Model Complex C2

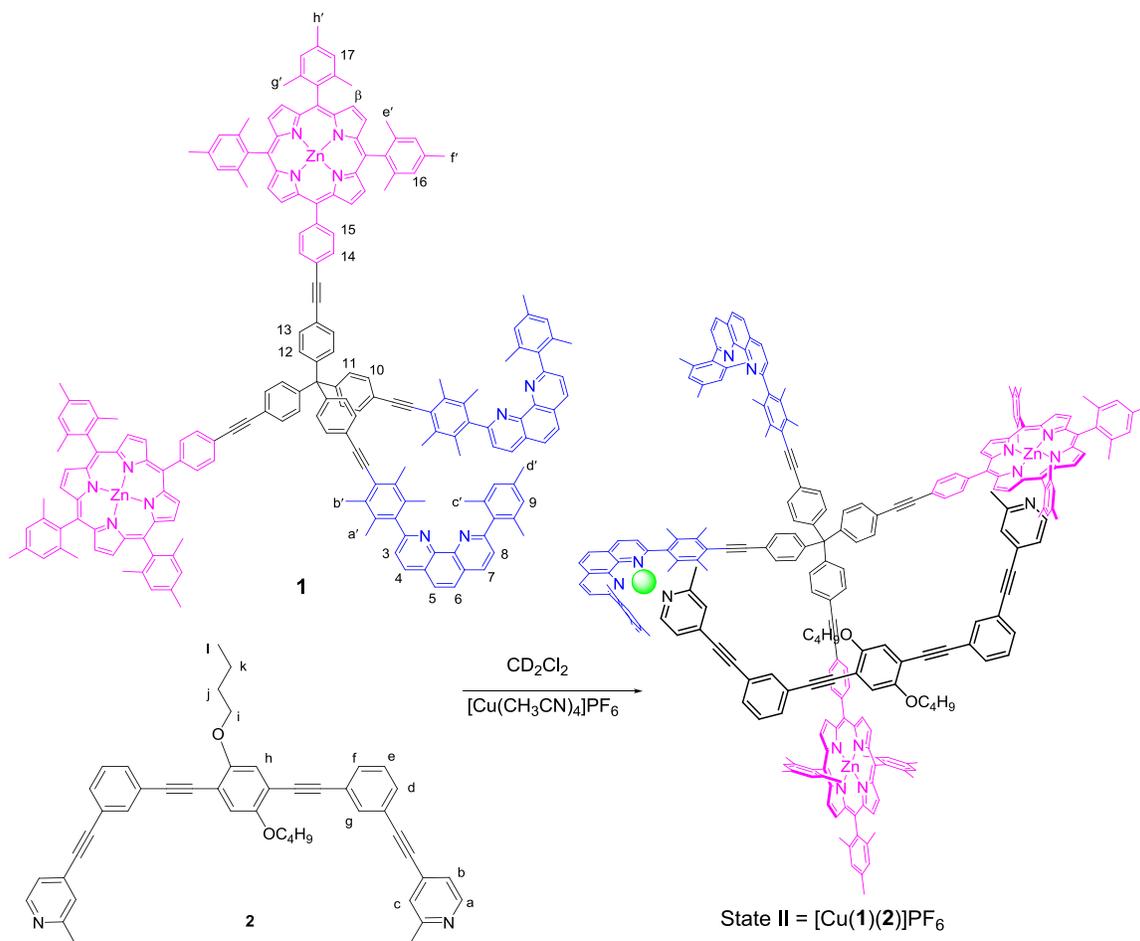


2,9-Dimesityl-[1,10]-phenanthroline (**4**, 1.24 mg, 2.98  $\mu\text{mol}$ ), 4-bromo-2-methylpyridine (**5**, 152  $\mu\text{g}$ , 2.98  $\mu\text{mol}$ ) and  $[\text{Cu}(\text{MeCN})_4]\text{PF}_6$  (1.11 mg, 2.98  $\mu\text{mol}$ ) were loaded in an NMR tube and dissolved in  $\text{CD}_2\text{Cl}_2$ . The resultant mixture was subjected to analytical characterisation without any further purification. Yield quantitative. mp > 180  $^\circ\text{C}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 8.72 (d,  $^3J$  = 8.3 Hz, 2 H, 4-H), 8.18 (s, 2 H, 5-H), 7.93 (d,  $^3J$  = 8.3 Hz, 2 H, 3-H), 7.61 (d,  $^3J$  = 5.9 Hz, 1 H, a-H), 7.29 (bs, 1 H, c-H), 7.21 (dd,  $^3J$  = 5.9 Hz,  $^4J$  = 1.4 Hz, 1 H, b-H), 6.74 (s, 4 H, 9-H), 2.17 (s, 6 H, Me), 2.06 (s, 3 H, Me), 1.99 (s, 12 H, Me);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  =



= 1.6 Hz, 2H, g-H), 7.47 (dt,  $^3J = 7.6$  Hz,  $^4J = 1.6$  Hz, 2H, [d/f]-H), 7.43 (d,  $^3J = 8.7$  Hz, 4H, [11/12]-H), 7.40 (d,  $^3J = 8.6$  Hz, 4H, [12/11]-H), 7.37 (dt,  $^3J = 7.6$  Hz,  $^4J = 1.6$  Hz, 2H, [f/d]-H), 7.31 (t,  $^3J = 7.6$  Hz, 2H, e-H), 7.28 (s, 12H, 16-&17-H), 6.98 (s, 2H, h-H), 6.97 (s, 4H, 9-H), 6.61 (s, 2H, c-H), 6.52 (d,  $^3J = 5.6$  Hz, 2H, b-H), 5.98 (br, 2H, a-H), 3.99 (t,  $^3J = 6.4$  Hz, 4 H, i-H), 2.61 (s, 18H, f'- & h'-H), 2.57 (s, 12H, [b'/a']-H), 2.34 (s, 6H, d'-H), 2.05 (s, 12H, c'-H), 1.96 (s, 12H, [a'/b']-H), 1.82 (s, 12H, g'-H), 1.81 (s, 24H, e'-H), 1.82-1.75 (m, 4 H, j-H), 1.58-1.48 (m, 4 H, k-H), 0.96 (m, 12 H, Me-&l-H); IR (KBr):  $\nu$  3435, 2950, 2920, 2850, 2211, 1599, 1503, 1478, 1379, 1337, 1279, 1203, 1062, 995, 852, 826, 797, 725  $\text{cm}^{-1}$ ; UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}} = 560$  nm (Q band,  $\epsilon = 1.43 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ); Anal. calcd. for  $\text{C}_{247}\text{H}_{204}\text{N}_{14}\text{O}_2\text{Zn}_2 \cdot 2 \text{CH}_2\text{Cl}_2$ : C, 80.81; H, 5.66; N, 5.30; found: C, 81.15; H, 5.53; N, 5.19.

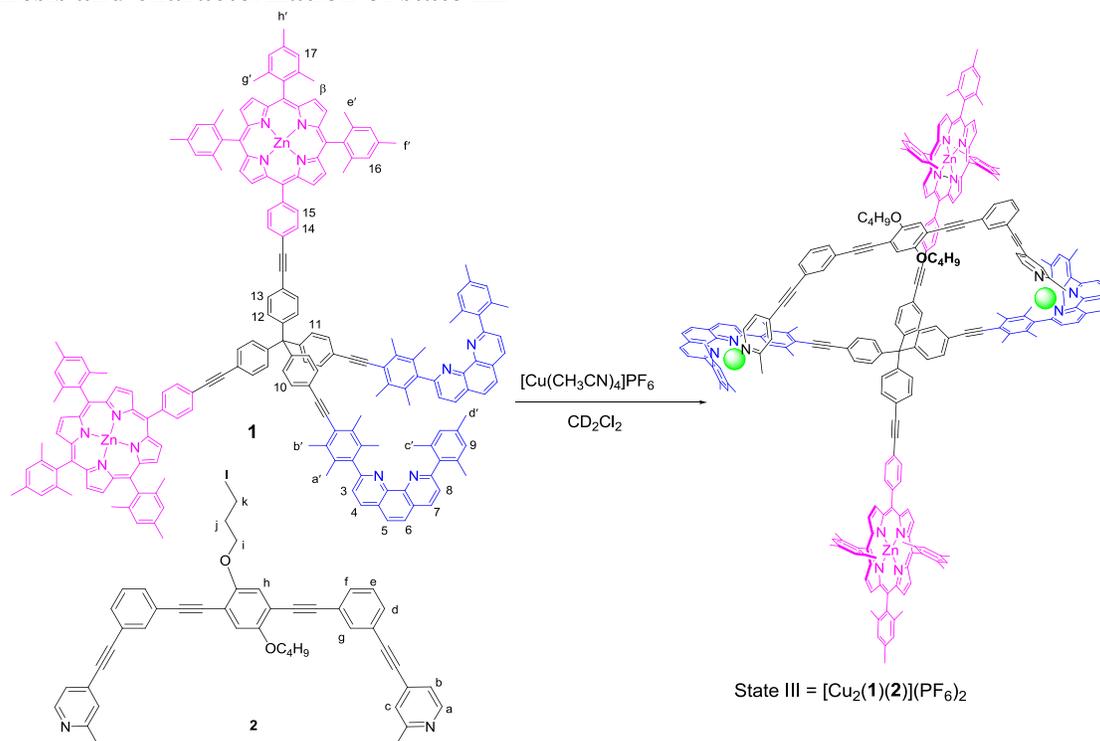
### Synthesis and characterization of state II



Track **1** (1.71 mg, 0.594  $\mu\text{mol}$ ), biped ligand **2** (388  $\mu\text{g}$ , 0.594  $\mu\text{mol}$ ) and  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (221  $\mu\text{g}$ , 0.594  $\mu\text{mol}$ ) were loaded in an NMR tube and dissolved in  $\text{CD}_2\text{Cl}_2$ . The resultant mixture

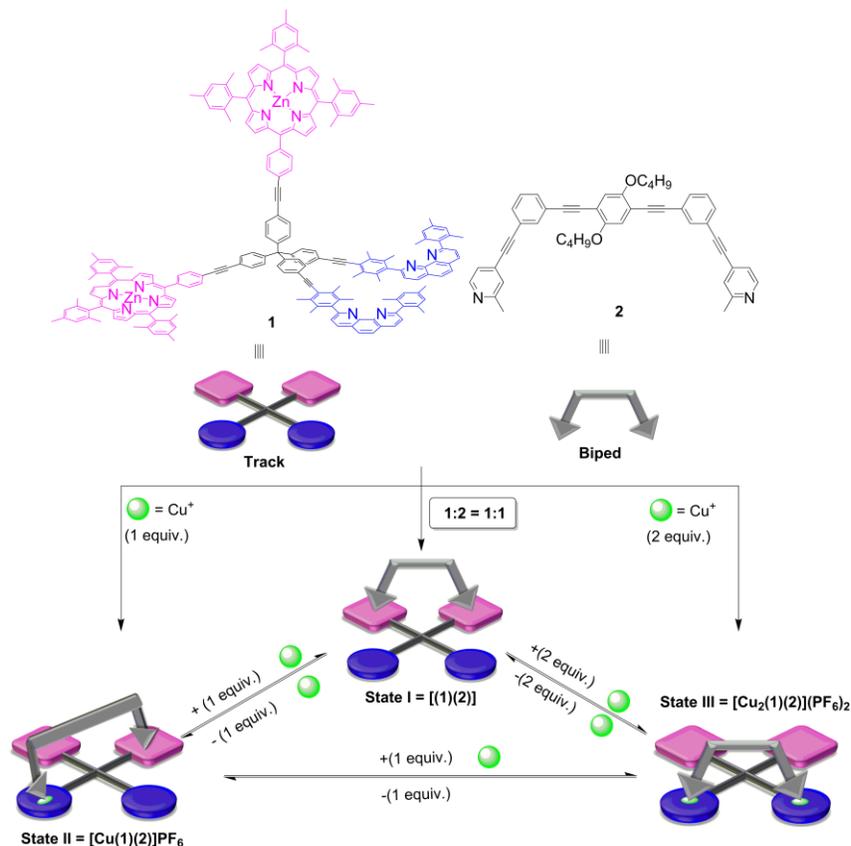
was subjected to analytical characterization without any further purification. Yield quantitative.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ) of two diastereomers in ratio of 1:1 (diastereotopic characteristic protons marked as \* and subscript C and UC in proton assignments are used for complexed and uncomplexed phenanthroline respectively):  $\delta$  = 8.86 (d,  $^3J$  = 4.8 Hz, 1H,  $\beta$ -H), 8.83-8.81 (m, 3H,  $\beta$ -H), 8.74-8.62 (m, 14H,  $4_{\text{C-}}$ ,  $7_{\text{C-}}$  &  $\beta$ -H), 8.38-8.32 (m, 2H,  $4_{\text{UC-}}$  &  $7_{\text{UC-H}}$ ), 8.23-8.15 (m, 6H,  $5_{\text{C-}}$ ,  $6_{\text{C-}}$  & [14/15]-H), 7.96-7.88 (m, 8H,  $8_{\text{C-}}$ ,  $3_{\text{C-}}$ ,  $5_{\text{UC-}}$ ,  $6_{\text{UC-}}$  & [15/14]-H), 7.69-7.50 (m, 12H, g-, 13-, 14-,  $3_{\text{UC-}}$ ,  $8_{\text{UC-}}$ , d-, f-H), 7.44-7.39 (m, 4H, 11- & 12-H), 7.34-7.18 (m, 8H, e-, c- & mes-H), 7.05 (s, 2H, h-H), 6.96 (s, 1H,  $9_{\text{UC*}}\text{-H}$ ), 6.95 (s, 1H,  $9_{\text{UC}}\text{-H}$ ), 6.82 (bs, 2H, b-H), 6.75 (s, 1H,  $9_{\text{C*}}\text{-H}$ ), 6.72 (bs, 3H, a- &  $9_{\text{C}}\text{-H}$ ), 4.01 (t,  $^3J$  = 6.0 Hz, 4H, i-H), 2.60 (s, 18H, f'- & h'-H), 2.56 (s, 3H, [b'/a'] $_{\text{UC*}}\text{-H}$ ), 2.54 (s, 3H, [b'/a'] $_{\text{UC}}\text{-H}$ ), 2.38 (s, 3H, [b'/a'] $_{\text{C*}}\text{-H}$ ), 2.36 (s, 3H, [b'/a'] $_{\text{C}}\text{-H}$ ), 2.34 (s, 1.5H, d' $_{\text{UC*}}\text{-H}$ ), 2.32 (s, 1.5H, d' $_{\text{UC}}\text{-H}$ ), 2.15 (s, 3H, d' $_{\text{C}}\text{-H}$ ), 2.05 (s, 3H, c' $_{\text{UC*}}\text{-H}$ ), 2.04 (s, 3H, c' $_{\text{UC}}\text{-H}$ ), 2.02 (s, 6H, c' $_{\text{C}}\text{-H}$ ), 1.96 (s, 3H, [a'/b'] $_{\text{UC*}}\text{-H}$ ), 1.94 (s, 3H, [a'/b'] $_{\text{UC}}\text{-H}$ ), 1.92 (bs, 6H, [a'/b'] $_{\text{C}}\text{-H}$ ), 1.82-1.77 (m, 40H, j-, g'- & e'-H), 1.57-1.47 (m, 10H, k- & Me-H), 0.94 (t,  $^3J$  = 7.2 Hz, 6H, l-H); IR (KBr):  $\nu$  3436, 2922, 2858, 2219, 1641, 1610, 1511, 1463, 1376, 1333, 1272, 1220, 1202, 1083, 1060, 997, 979, 852, 829, 798  $\text{cm}^{-1}$ ; UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}}$  = 554 nm (Q band,  $\epsilon$  =  $1.46 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ); Anal. calcd. for  $\text{C}_{247}\text{H}_{204}\text{CuF}_6\text{N}_{14}\text{O}_2\text{PZn}_2 \cdot 2.5 \text{ CH}_2\text{Cl}_2$ : C, 75.83; H, 5.33; N, 4.96; found: C, 75.59; H, 4.94; N, 4.69.

## Synthesis and characterization of state III



Track **1** (811  $\mu\text{g}$ , 0.282  $\mu\text{mol}$ ), biped ligand **2** (184  $\mu\text{g}$ , 0.282  $\mu\text{mol}$ ) and  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (210  $\mu\text{g}$ , 0.564  $\mu\text{mol}$ ) were loaded in an NMR tube and dissolved in  $\text{CD}_2\text{Cl}_2$ . The resultant mixture was subjected to characterization without any further purification. Yield quantitative.  $^1\text{H}$  NMR (400 MHz,  $\text{CD}_2\text{Cl}_2$ ):  $\delta$  = 8.89 (d,  $^3J = 4.6$  Hz, 4H,  $\beta$ -H), 8.76 (d,  $^3J = 4.6$  Hz, 4H,  $\beta$ -H), 8.75-8.69 (m, 12H,  $\beta$ -, 4- & 7-H), 8.23 (d,  $^3J = 7.6$  Hz, 2H, [15/14]-H), 8.21 (s, 4H, 5- & 6-H), 7.95 (d,  $^3J = 8.4$  Hz, 2H, [3/8]-H), 7.94 (d,  $^3J = 8.4$  Hz, 2H, [8/3]-H), 7.90 (d,  $^3J = 7.6$  Hz, 4H, [14/15]-H), 7.81 (bs, 2H, g-H), 7.62-7.48 (m, 14H, a-, d-, f-, 10- & 13-H), 7.43-7.30 (m, 10H, 11-, 12- & e-H), 7.29 (s, 6H, 16- & 17-H), 7.17 (bs, 2H, c-H), 7.12 (s, 2H, h-H), 7.06 (bd, 2H, b-H), 6.71 (s, 4H, 9-H), 4.00 (t,  $^3J = 6.0$  Hz, 4H, i-H), 2.61 (s, 18H, f'- & h'-H), 2.41 (s, 12H, [b'/a']-H), 2.15 (s, 6H, d'-H), 2.02 (s, 12H, c'-H), 1.93 (s, 12H, [a'/b']-H), 1.92 (s, 6H, Me-H), 1.84 (s, 12H, g'-H), 1.83 (s, 24H, e'-H), 1.76-1.72 (m, 4 H, j-H), 1.49-1.46 (m, 4 H, k-H), 0.88 (t, 6 H, l-H); IR (KBr):  $\nu$  3435, 2920, 2213, 1642, 1612, 1512, 1463, 1376, 1336, 1275, 1204, 1085, 998, 979, 892, 853, 826, 799, 774, 756, 725  $\text{cm}^{-1}$ ; ESI-MS:  $m/z$  (%) 1829.1 (100)  $[\text{M}-2\text{PF}_6]^{2+}$ ; UV-vis ( $\text{CH}_2\text{Cl}_2$ ):  $\lambda_{\text{max}} = 550$  nm (Q band,  $\epsilon = 1.36 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$ ); Anal. calcd. for  $\text{C}_{247}\text{H}_{204}\text{Cu}_2\text{F}_{12}\text{N}_{14}\text{O}_2\text{P}_2\text{Zn}_2 \cdot 3 \text{CH}_2\text{Cl}_2$ : C, 71.44; H, 5.04; N, 4.67; found: C, 71.24; H, 4.71; N, 4.58.

## In-situ stepwise walking from state I to state III and back to state I



**Scheme S2:** Reversible stepwise walking of biped **2** on the tetrahedral track **1** upon addition and removal of copper(I) metal ions.

**State I:** In an NMR tube, track **1** (728  $\mu\text{g}$ , 0.253  $\mu\text{mol}$ ) and biped **2** (165  $\mu\text{g}$ , 0.253  $\mu\text{mol}$ ) were dissolved in  $\text{CD}_2\text{Cl}_2$  (500  $\mu\text{L}$ ). After formation of a clear solution, the sample was subjected to NMR measurement (See Figure S19a). **State II:** One equiv of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (229  $\mu\text{g}$ , 0.253  $\mu\text{mol}$ ) was added to the NMR tube containing state I. This sample was subjected to NMR analysis without any further purification (see Figure S19b). **State III:** One more equiv of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (229  $\mu\text{g}$ , 0.253  $\mu\text{mol}$ ) was added to the NMR tube containing state II. The resulting sample was subjected to NMR measurement without any further purification (see Figure S19c).

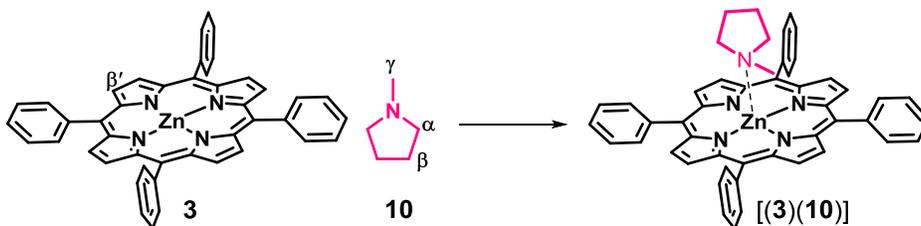
### Reversibility of the cycle in Scheme S2:

To study the reversibility of the system presented in Scheme S2 we started from state III prepared in the above described walking process. **State II:** 2-Ferrocenyl-9-mesityl-1,10-phenanthroline (**7**,

244  $\mu\text{g}$ , 0.506  $\mu\text{mol}$ ) was added into the NMR tube containing state III. The mixture was directly subjected to NMR measurement (See Figure S19d). **State I:** After addition of two more equiv. of 2-ferrocenyl-9-mesityl-1,10-phenanthroline (**7**, 244  $\mu\text{g}$ , 0.506  $\mu\text{mol}$ ) to state II, the resultant mixture was analyzed by  $^1\text{H}$  NMR without any further purification (See Figure S19e).

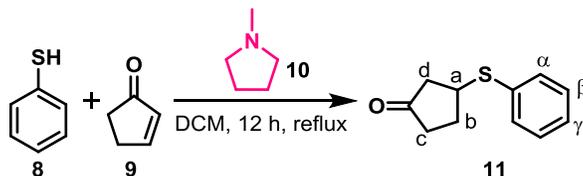
## Establishing the Catalytic Conjugate Addition

### Synthesis of complex [(3)(10)]<sup>3</sup>



$^1\text{H}$  NMR (400 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ):  $\delta = 8.88$  (s, 8 H,  $\beta'$ -H), 8.23-8.19 (m, 8 H, Ph-H), 7.80-7.72 (s, 12 H, Ph-H), -1.21 (bs, 2 H,  $\beta$ -H), -1.83 (bs, 2 H,  $\alpha$ -H), -2.42 (s, 3 H,  $\gamma$ -H) ppm.

### Synthesis of compound 11<sup>3</sup>



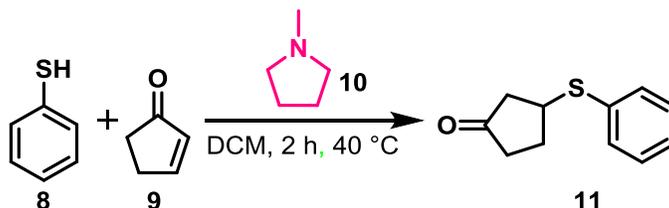
$^1\text{H}$  NMR (400 MHz, 298 K,  $\text{CDCl}_3$ ):  $\delta = 7.44$ -7.41 (m, 2 H,  $\alpha$ -H), 7.36-7.26 (m, 3 H,  $\beta$ -,  $\gamma$ -H), 3.94-3.88 (m, 1 H, a-H), 2.65-2.59 (m, 1 H, d-H), 2.53-2.45 (m, 1 H, c-H), 2.40-2.19 (m, 3 H, d- & b-H), 2.08-1.99 (m, 1 H, c-H) ppm.

## General procedure for the catalytic conjugate addition

All catalytic reactions were performed in  $\text{CD}_2\text{Cl}_2$  directly in an NMR tube held at 40 ( $\pm 1$ )  $^\circ\text{C}$  in a thermostat. Prior to use, spurious acid traces were removed from  $\text{CD}_2\text{Cl}_2$  by a short filtration over basic alumina (Brockman activity 1). Solids were transferred first, followed by addition of

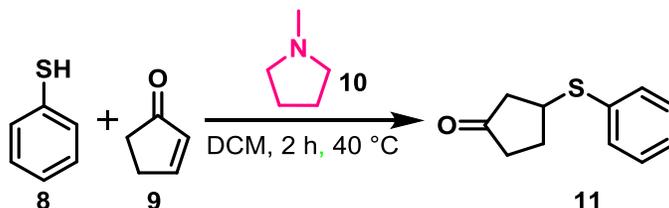
the solvent and finally liquids were added (as standard solutions in CD<sub>2</sub>Cl<sub>2</sub>). Product yields were determined by using tetrachloroethane (TCE) as an internal standard.

### Catalysis control experiment Cat1



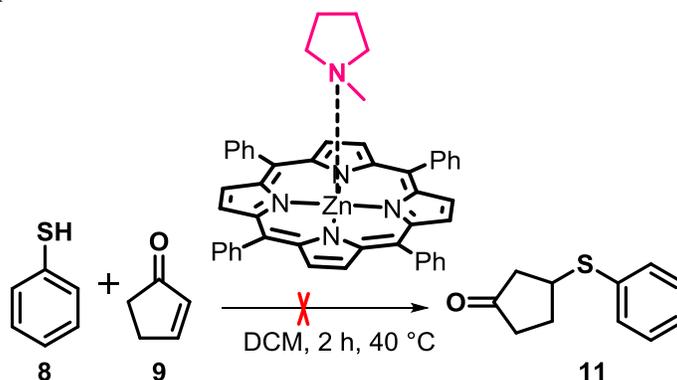
CD<sub>2</sub>Cl<sub>2</sub> (500 μL) was added to a mixture of thiophenol (**8**) (635 μg, 5.76 μmol), cyclopentenone **9** (470 μg, 5.76 μmol) and *N*-methylpyrrolidine (**10**) (44.1 μg, 0.518 μmol). The reaction was heated at 40 °C for 2 h, then the mixture was cooled to room temperature and subjected to <sup>1</sup>H NMR measurements without workup. The yield of product **11** was 32% (See Figure S22).

### Catalysis control experiment Cat2



CD<sub>2</sub>Cl<sub>2</sub> (500 μL) was added to a mixture of thiophenol (**8**) (635 μg, 5.76 μmol), cyclopentenone **9** (470 μg, 5.76 μmol) and *N*-methylpyrrolidine (**10**) (19.6 μg, 0.230 μmol). The reaction was heated at 40 °C for 2 h, then the mixture was cooled to room temperature and subjected to <sup>1</sup>H NMR measurements without workup. The yield of product **11** was 16% (See Figure S23).

### Catalysis control experiment Cat3



Thiophenol (**8**) (592  $\mu\text{g}$ , 5.37  $\mu\text{mol}$ ), cyclopentenone **9** (441  $\mu\text{g}$ , 5.37  $\mu\text{mol}$ ), *N*-methylpyrrolidine (**10**) (41.0  $\mu\text{g}$ , 0.483  $\mu\text{mol}$ ) and ZnTPP (327  $\mu\text{g}$ , 0.483  $\mu\text{mol}$ ) were dissolved in 500  $\mu\text{L}$  of  $\text{CD}_2\text{Cl}_2$ . The mixture was then heated at 40  $^\circ\text{C}$  for 2 h and characterized by  $^1\text{H}$  NMR. No product formation was observed (See Figure S24).

### Catalysis control experiment Cat4

Thiophenol (**8**) (290  $\mu\text{g}$ , 2.63  $\mu\text{mol}$ ), cyclopentenone **9** (216  $\mu\text{g}$ , 2.63  $\mu\text{mol}$ ) and track **1** (755  $\mu\text{g}$ , 0.263  $\mu\text{mol}$ ) were dissolved in 500  $\mu\text{L}$  of  $\text{CD}_2\text{Cl}_2$  and heated at 40  $^\circ\text{C}$  for 2 h. The reaction mixture was then cooled down to 0  $^\circ\text{C}$  (to stop the reaction) and analyzed by  $^1\text{H}$  NMR. No product was observed (See Figure S25).

### Catalysis control experiment Cat5

Thiophenol (**8**) (355  $\mu\text{g}$ , 3.22  $\mu\text{mol}$ ), cyclopentenone **9** (265  $\mu\text{g}$ , 3.22  $\mu\text{mol}$ ) and bided ligand **2** (210  $\mu\text{g}$ , 0.322  $\mu\text{mol}$ ) were dissolved in 500  $\mu\text{L}$  of  $\text{CD}_2\text{Cl}_2$  and heated at 40  $^\circ\text{C}$  for 2 h. The reaction mixture was then cooled down to 0  $^\circ\text{C}$  (to stop the reaction) and analyzed by  $^1\text{H}$  NMR. No product was observed (See Figure S26).

### Catalysis control experiment Cat6 (state I)

Track **1** (830  $\mu\text{g}$ , 0.288  $\mu\text{mol}$ ), bided ligand **2** (188  $\mu\text{g}$ , 0.288  $\mu\text{mol}$ ), thiophenol (**8**) (635  $\mu\text{g}$ , 5.76  $\mu\text{mol}$ ), cyclopentenone **9** (470  $\mu\text{g}$ , 5.76  $\mu\text{mol}$ ) and *N*-methylpyrrolidine (**10**) (44.1  $\mu\text{g}$ , 0.518  $\mu\text{mol}$ ) were dissolved in 500  $\mu\text{L}$  of  $\text{CD}_2\text{Cl}_2$  and allowed to heat at 40  $^\circ\text{C}$  for 2 h. The reaction

mixture was then cooled down to 0 °C to stop the reaction and analyzed by <sup>1</sup>H NMR. The product **11** was formed in 28% yield (See Figure S27).

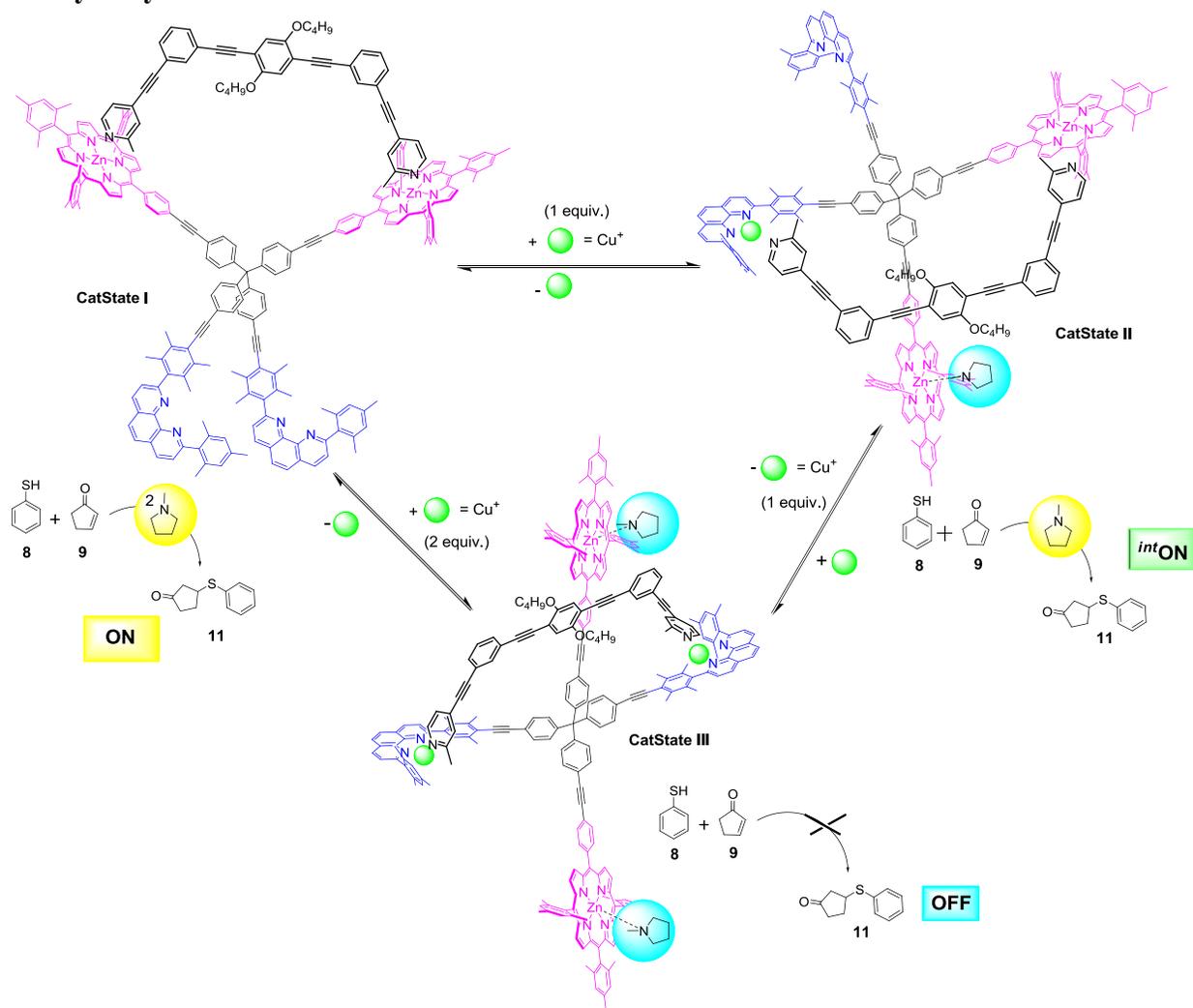
#### **Catalysis control experiment Cat7 (state II)**

Track **1** (807 μg, 0.280 μmol) and bided ligand **2** (183 μg, 0.280 μmol) were mixed in 500 μL of CD<sub>2</sub>Cl<sub>2</sub> to prepare state II. Thiophenol (**8**) (618 μg, 5.60 μmol), cyclopentenone **9** (460 μg, 5.60 μmol) and *N*-methylpyrrolidine (**10**) (43.0 μg, 0.504 μmol) were added and allowed to heat at 40 °C for 2 h. The reaction mixture was then cooled down to 0 °C to stop the reaction and analyzed by <sup>1</sup>H NMR. The product **11** was formed in 12% yield (See Figure S28).

#### **Catalysis control experiment Cat8 (State III)**

Track **1** (801 μg, 0.278 μmol), bided ligand **2** (182 μg, 0.278 μmol) and [Cu(CH<sub>3</sub>CN)<sub>4</sub>]PF<sub>6</sub> (207 μg, 0.556 μmol) were dissolved in 500 μL of CD<sub>2</sub>Cl<sub>2</sub> to afford State III. To the same NMR tube, thiophenol (**8**) (613 μg, 5.56 μmol), cyclopentenone **9** (461 μg, 5.56 μmol) and *N*-methylpyrrolidine (**10**) (42.5 μg, 0.500 μmol) were added and the mixture was heated at 40 °C for 2 h. The reaction mixture was then cooled down to 0 °C (to stop the reaction) and analyzed by <sup>1</sup>H NMR. Formation of product **11** was not observed (See Figure S29).

## Catalytic cycle



**Scheme S3:** Representation of stepwise (100% ON/ *int*ON/ OFF) regulation of a conjugate addition reaction at different states by addition and removal of Cu<sup>+</sup> ions in walker system.

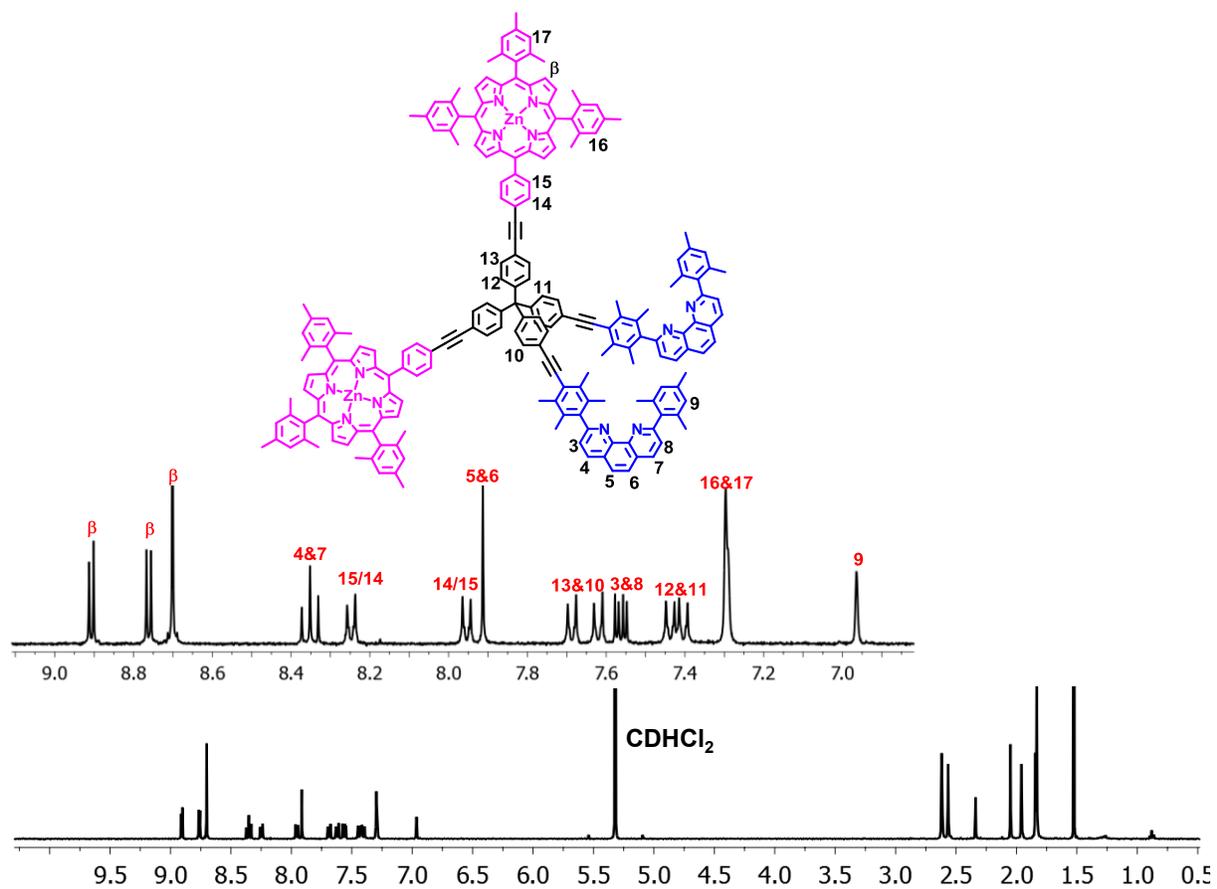
## Reversible regulation of the conjugated addition reaction in the stepwise walking process

**Cycle I starting with CatState I:** The forward catalytic reaction was started with CatState I prepared directly in the NMR tube. Track 1 (830 μg, 0.288 μmol) and biped ligand 2 (188 μg, 0.288 μmol) were dissolved in 500 μL of CD<sub>2</sub>Cl<sub>2</sub>. To generate CatState I, compounds 8 (635 μg, 5.76 μmol), 9 (470 μg, 5.76 μmol) and 10 (44.1 μg, 0.518 μmol) were added and the resultant mixture was heated at 40 °C for 2 h. The reaction mixture was then cooled down to 0 °C (to stop the reaction) and immediately subjected to <sup>1</sup>H NMR analysis. Formation of product 11 (27%)

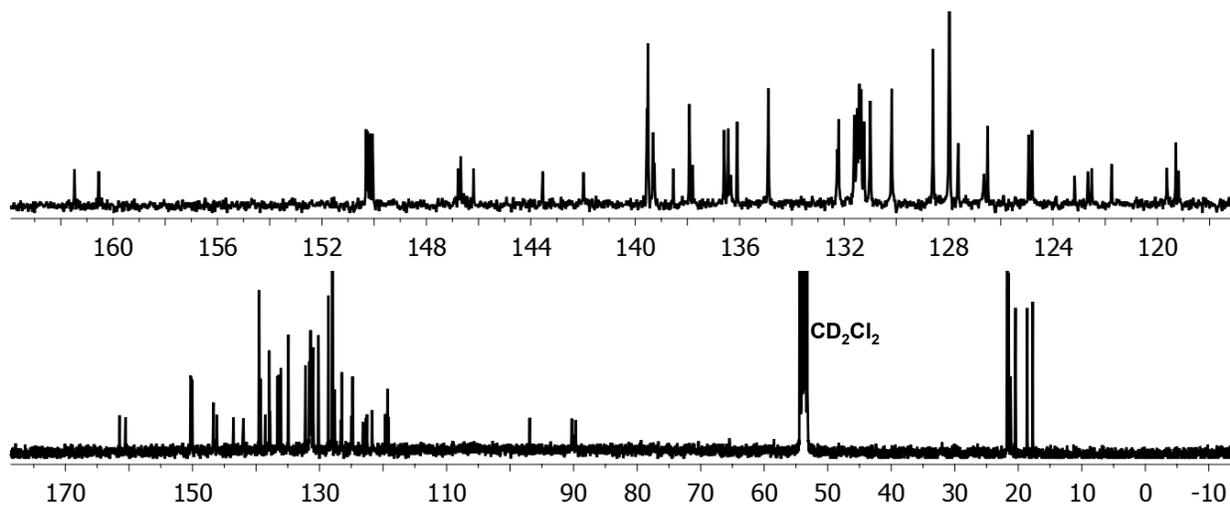
was observed (100% ON) (see Figure S30(a)). Thereafter, one equiv of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (107  $\mu\text{g}$ , 0.288  $\mu\text{mol}$ ) was added along with the consumed amounts of substrates **8** and **9** (CatState II). The mixture was heated for 2 h at 40  $^\circ\text{C}$ . The total yield of product **11** improved to 39%, indicating an increase by 12% (*int*ON) (see Figure S30(b)). Again one more equiv of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (107  $\mu\text{g}$ , 0.288  $\mu\text{mol}$ ) and consumed amounts of substrates **8** and **9** were added (CatState III). After heating for 2 h at 40  $^\circ\text{C}$ , no further increase in the yield of product **11** (total of 39%) was observed in the NMR (see Figure S30(c)). Now backward walking was initiated by addition of 2-ferrocenyl-9-mesityl-1,10-phenanthroline (**7**, 278  $\mu\text{g}$ , 0.576  $\mu\text{mol}$ ) and the used-up thiophenol (**8**) and 2-cyclopentenone (**9**). The thus generated CatState II, led to a total yield of 51% of **11**, thus a 12% increase (see Figure S30(d)). To regenerate CatState I, two more equiv. of 2-ferrocenyl-9-mesityl-1,10-phenanthroline (**7**, 278  $\mu\text{g}$ , 0.576  $\mu\text{mol}$ ) and consumed amount of substrates **8** and **9** were added. The mixture was subjected to heating at 40  $^\circ\text{C}$  for 2 h. Total yield of 75% of product **11** was observed in  $^1\text{H}$  NMR (see Figure S30(e)).

**Cycle 2 starting with CatState III:** To prepare **CatState III** directly in the NMR tube, track **1** (800  $\mu\text{g}$ , 0.278  $\mu\text{mol}$ ), biperid ligand **2** (181  $\mu\text{g}$ , 0.278  $\mu\text{mol}$ ) and  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (207  $\mu\text{g}$ , 0.556  $\mu\text{mol}$ ) were dissolved in 500  $\mu\text{L}$  of  $\text{CD}_2\text{Cl}_2$ . Compounds **8** (613  $\mu\text{g}$ , 5.56  $\mu\text{mol}$ ), **9** (461  $\mu\text{g}$ , 5.56  $\mu\text{mol}$ ) and **10** (42.6  $\mu\text{g}$ , 0.500  $\mu\text{mol}$ ) were then added and the mixture was heated at 40  $^\circ\text{C}$  for 2 h. The reaction mixture was immediately subjected to  $^1\text{H}$  NMR measurement after cooling down to 0  $^\circ\text{C}$  to stop the reaction. No formation of product **11** was observed (see Figure S31(a)). Thereafter, 2 equiv of **7** (268  $\mu\text{g}$ , 0.556  $\mu\text{mol}$ ) was added and the sample heated again for 2 h at 40  $^\circ\text{C}$ . Now 12% yield of product **11** was observed (*int*ON) (see Figure S31(b)). Again two more equiv. of **7** (268  $\mu\text{g}$ , 0.556  $\mu\text{mol}$ ) and consumed amounts of substrates **8** and **9** were added. After heating for 2 h at 40  $^\circ\text{C}$ , a further increase in the yield of product **11** (total of 35%) was observed in the NMR (see Figure S31(c)). To start the reverse cycle, one equiv of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (103  $\mu\text{g}$ , 0.278  $\mu\text{mol}$ ) and the used up thiophenol (**8**) and 2-cyclopentenone (**9**) were added to regenerate CatState II. After the heating a further increase in the yield of product **11** (total of 46%) was observed in the NMR (see Figure S31(d)). Now to regenerate CatState III (OFF state) one more equiv of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  (103  $\mu\text{g}$ , 0.278  $\mu\text{mol}$ ) and consumed amount of substrates **8** and **9** were added. After heating for 2 h at 40  $^\circ\text{C}$ , a minute (2%) increment in the product yield of **11** was observed (see Figure S31(e)).

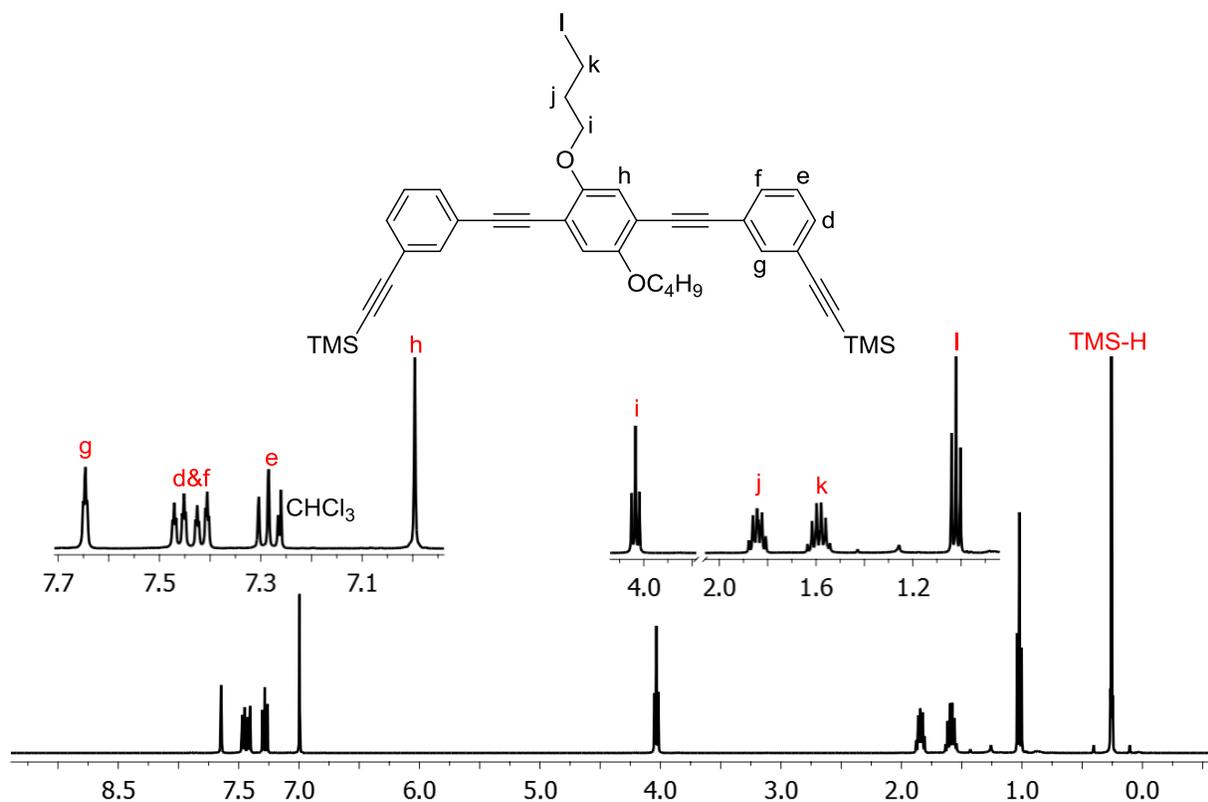
# $^1\text{H}$ and $^{13}\text{C}$ NMR Spectra



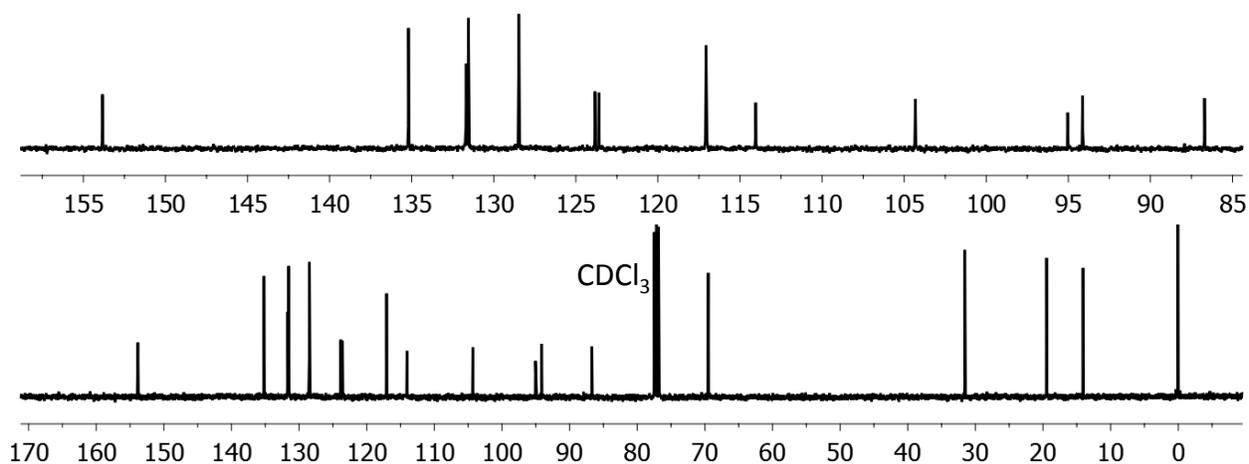
**Figure S1:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of track 1. An expanded part of the aromatic region is shown at the top with characteristic protons assigned.



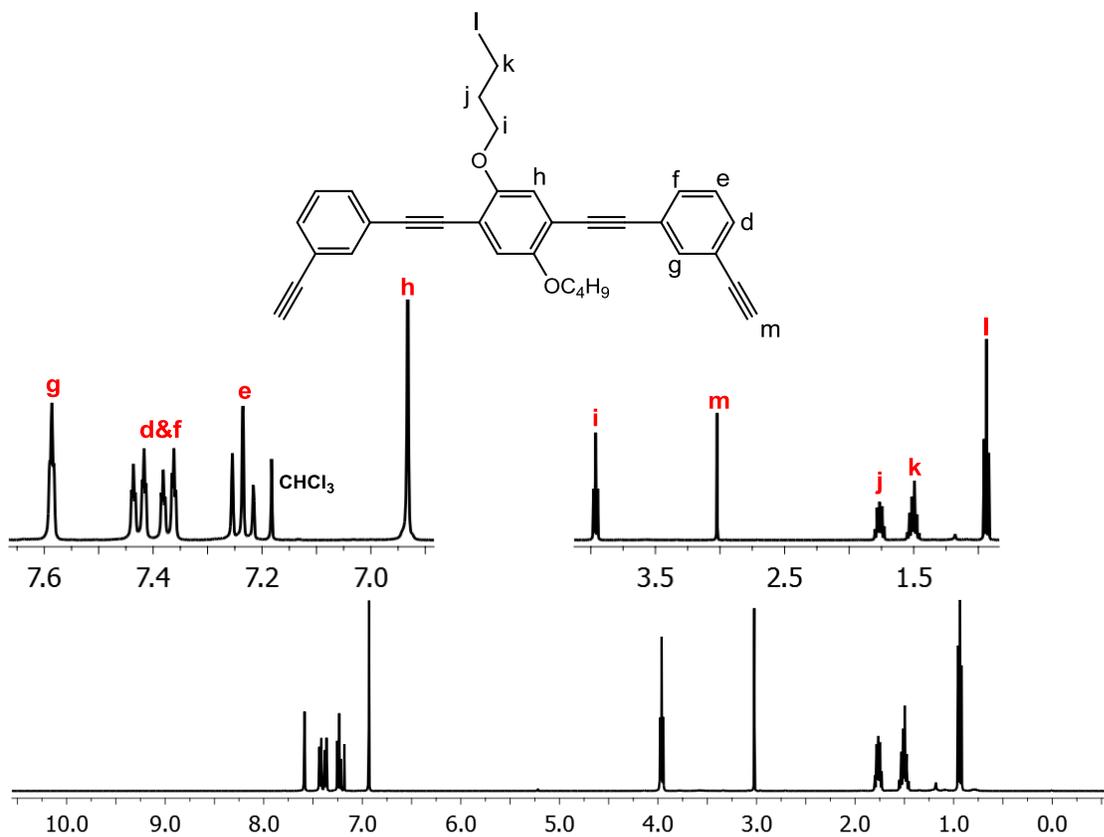
**Figure S2:**  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of track 1. An expanded part of the aromatic region is shown at the top.



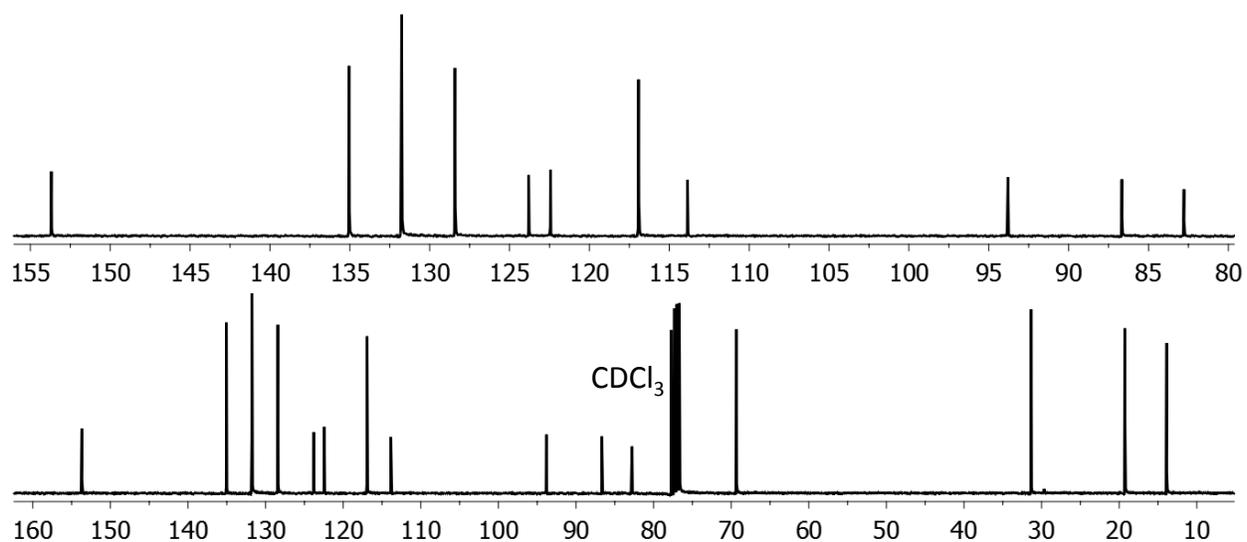
**Figure S3:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of compound 16. The expanded parts of the aromatic and aliphatic region are shown at the top with characteristic protons assigned.



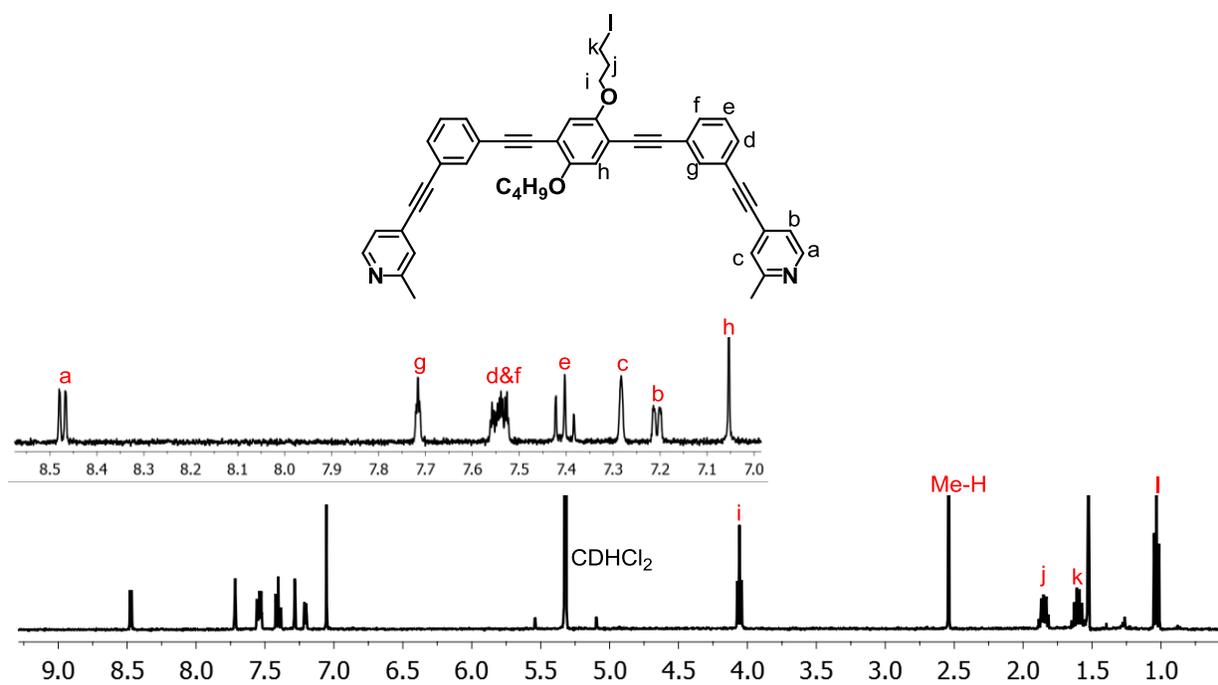
**Figure S4:**  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of compound **16**. An expanded part of the aromatic region is shown at the top.



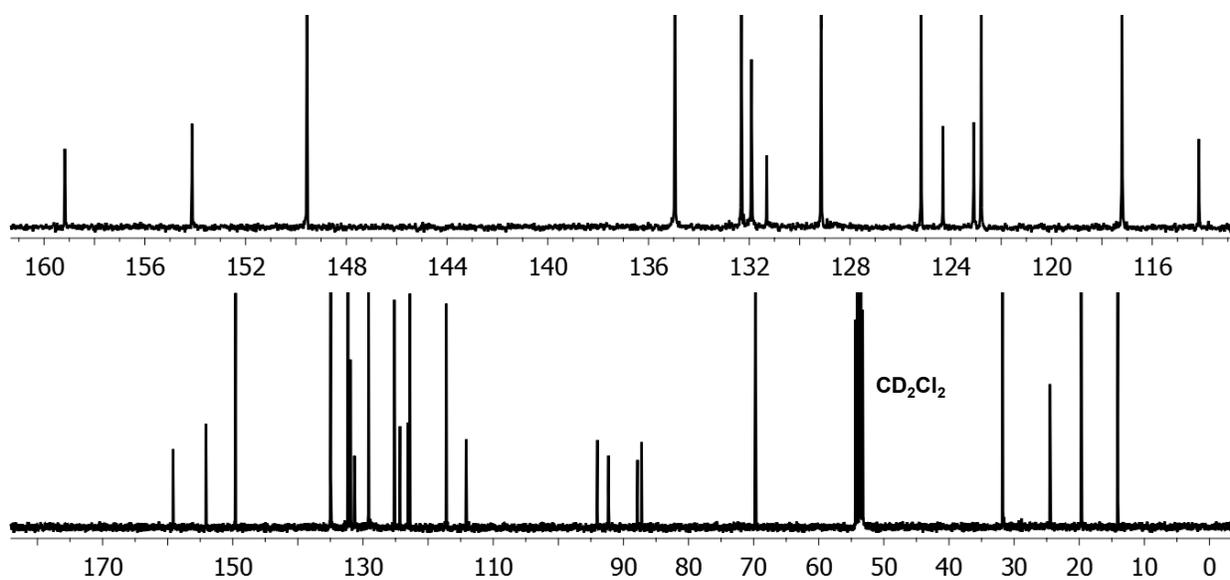
**Figure S5:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of compound **17**. The expanded parts of the aromatic and aliphatic region are shown at the top with characteristic protons assigned.



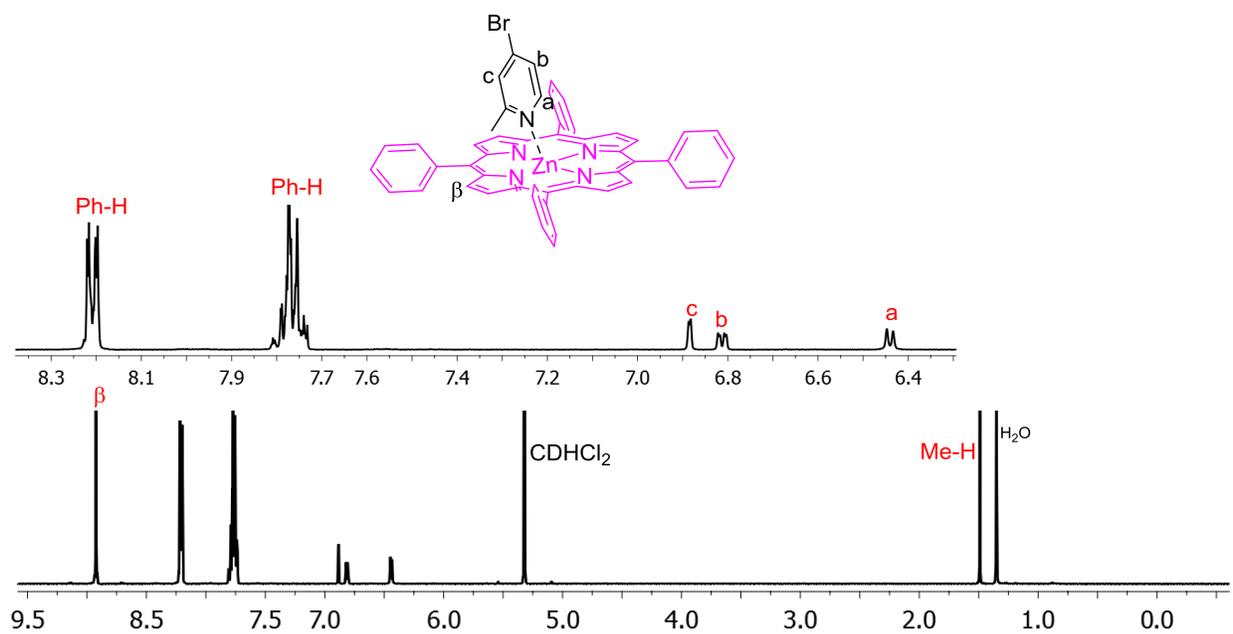
**Figure S6:**  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of compound **17**. An expanded part of the aromatic region is shown at the top.



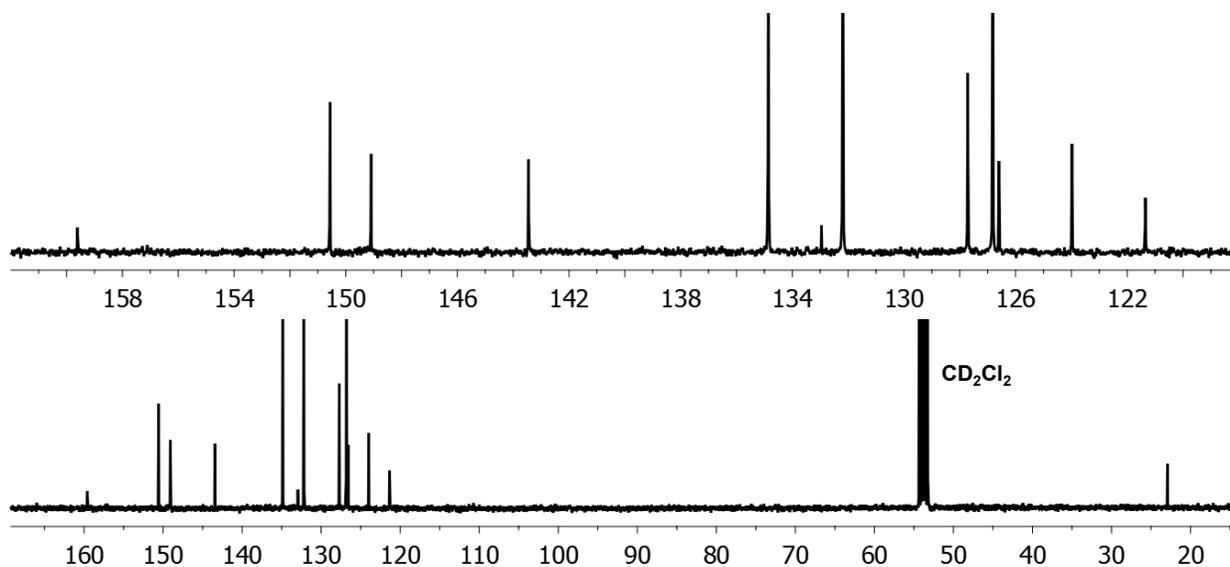
**Figure S7:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of biped ligand **2**. An expanded part of the aromatic region is shown at the top with characteristic protons assigned.



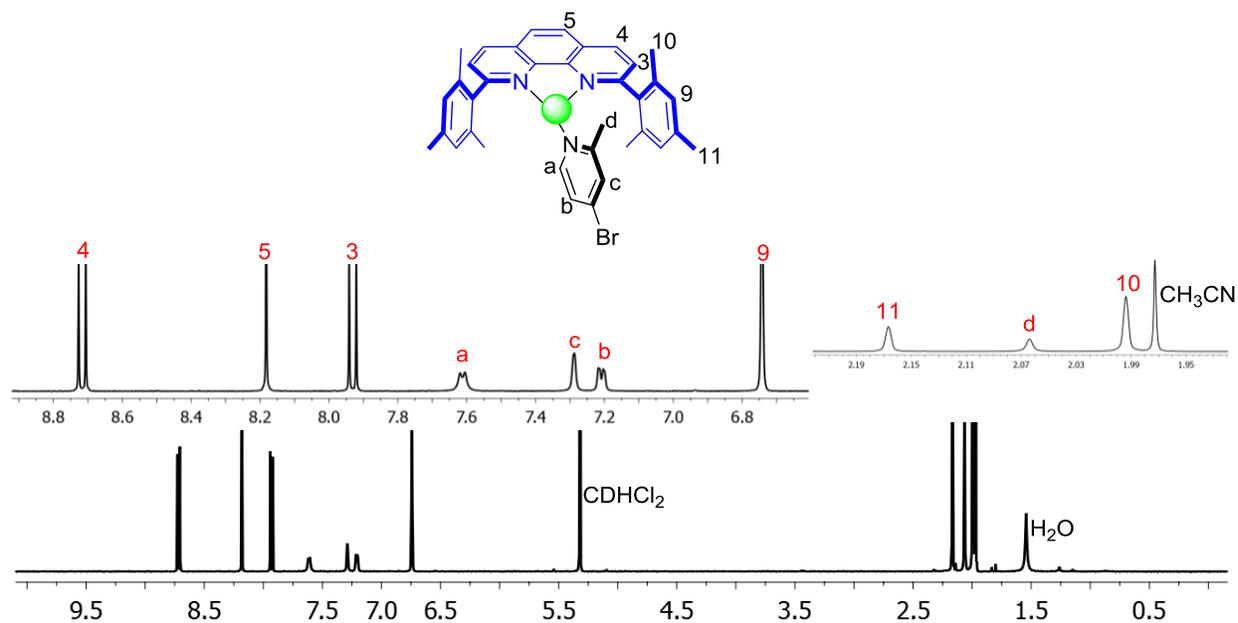
**Figure S8:**  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of biped ligand **2**. An expanded part of the aromatic region is shown at the top.



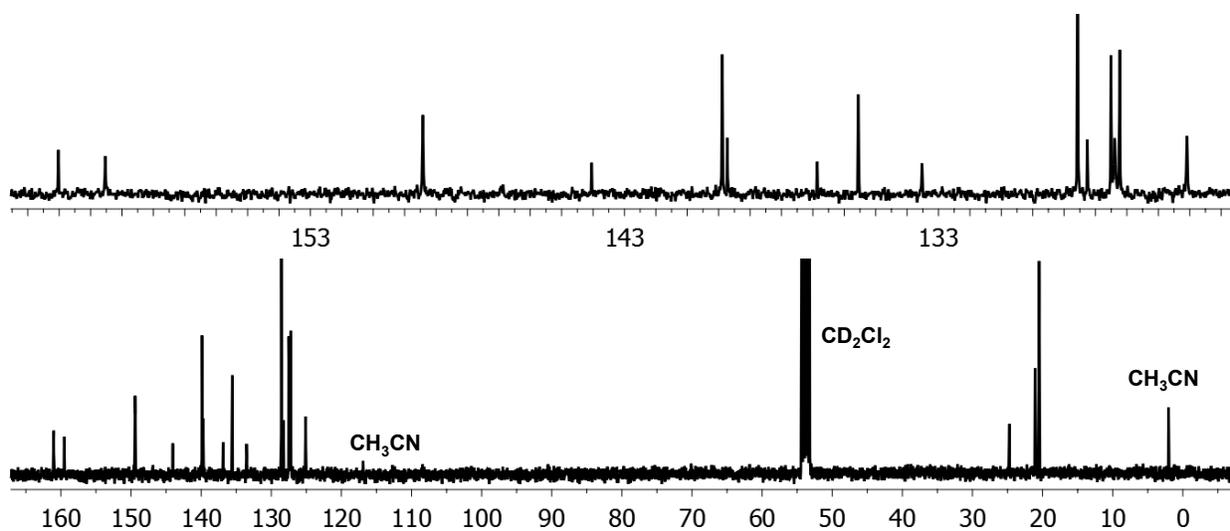
**Figure S9:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of Complex **C1**. An expanded part of the aromatic region is shown at the top with characteristic protons assigned.



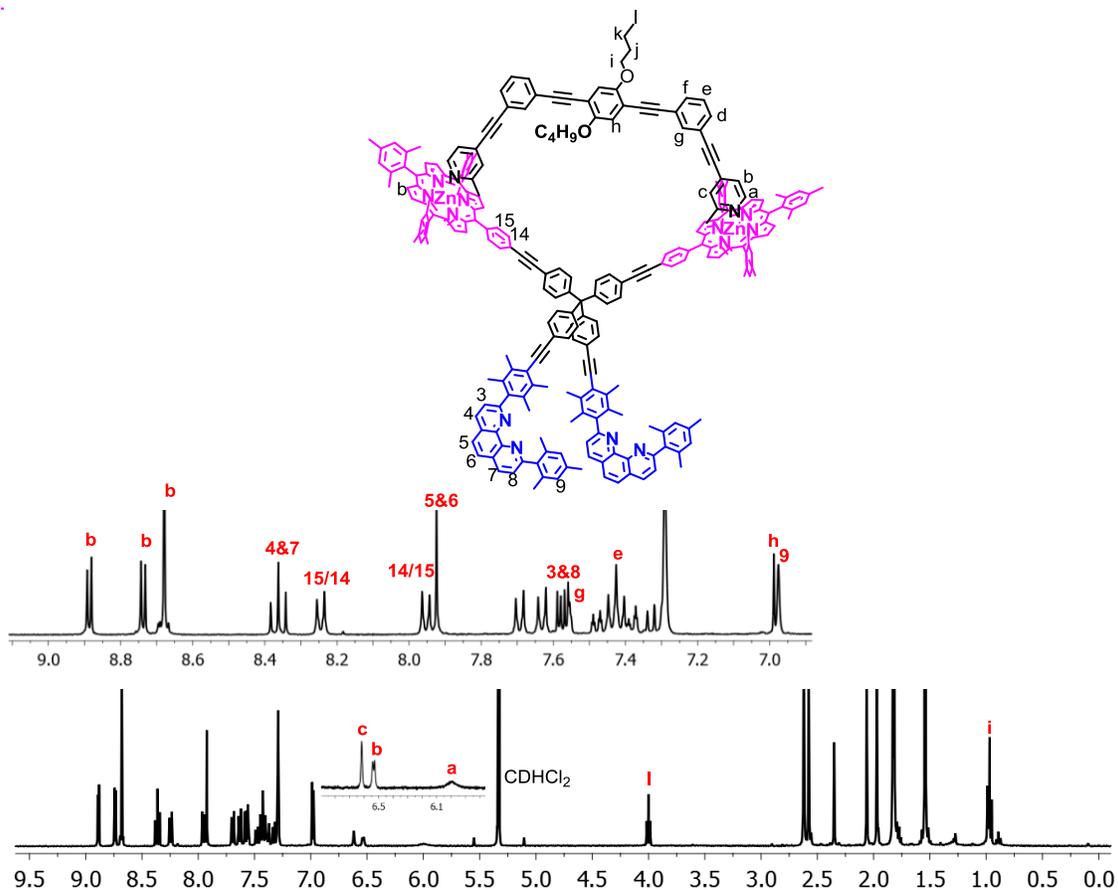
**Figure S10:**  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of Complex C1. An expanded part of the aromatic region is shown at the top.



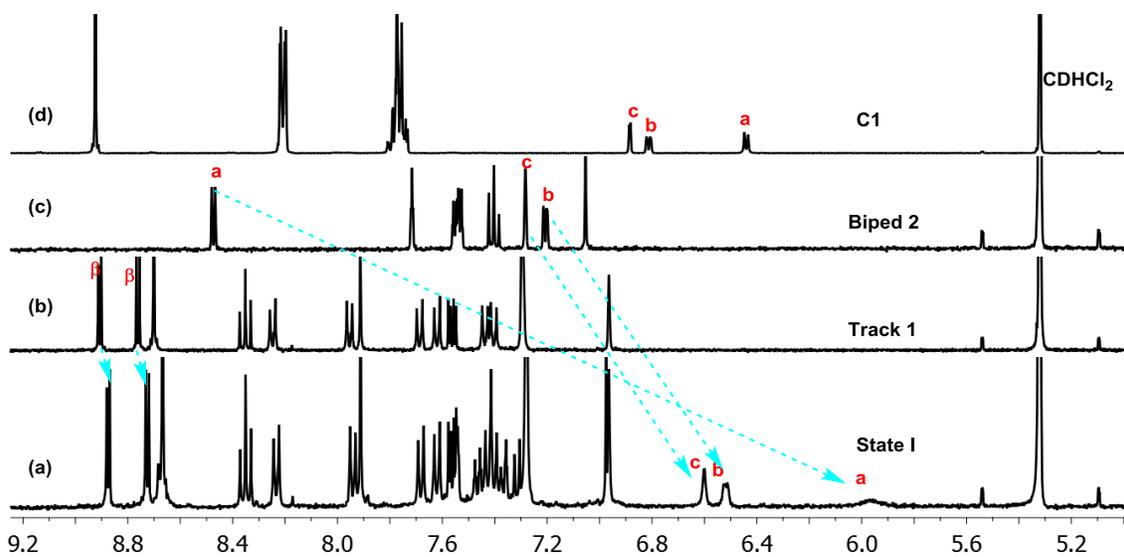
**Figure S11:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of complex C2. Expanded parts of the aromatic and aliphatic region are shown at the top with characteristic protons assigned.



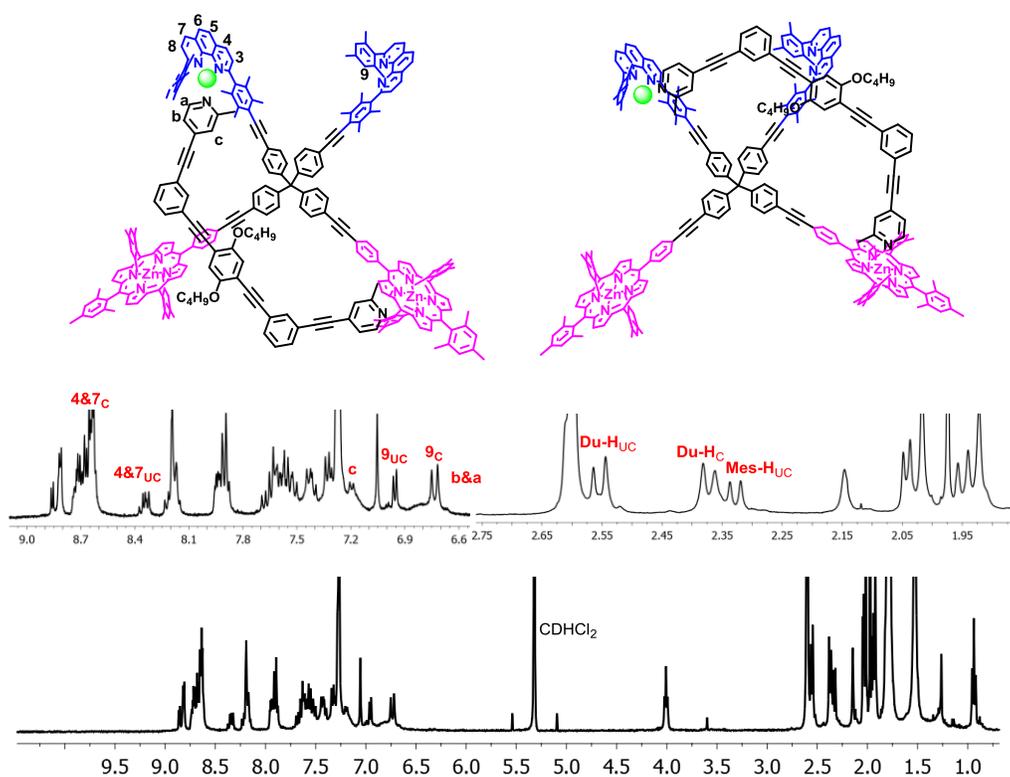
**Figure S12:**  $^{13}\text{C}$  NMR spectrum (100 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of complex **C2**. Expanded part of the aromatic region is shown at the top.



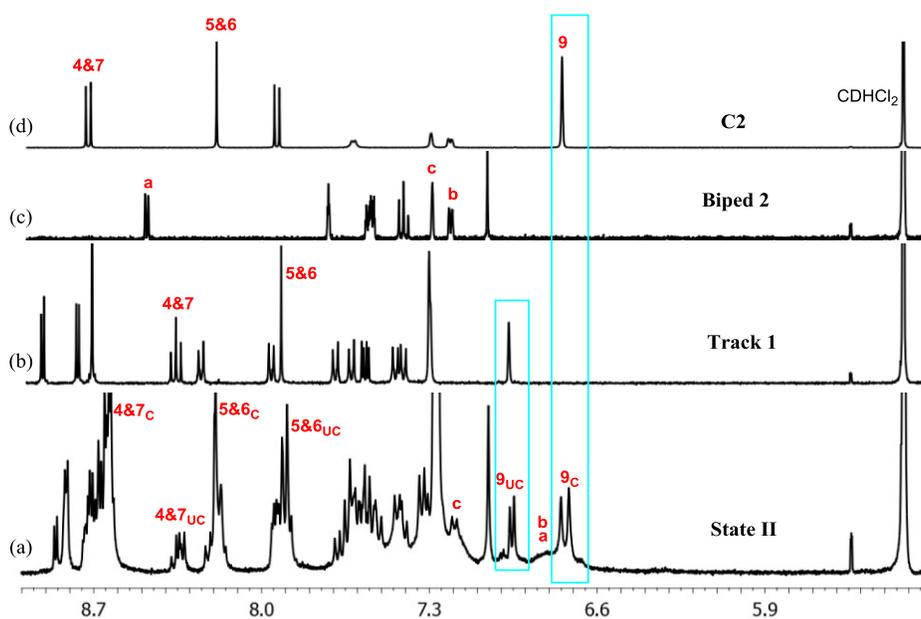
**Figure S13:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of State I = [(1)(2)]. An expanded part of the aromatic region is shown at the top with characteristic protons assigned.



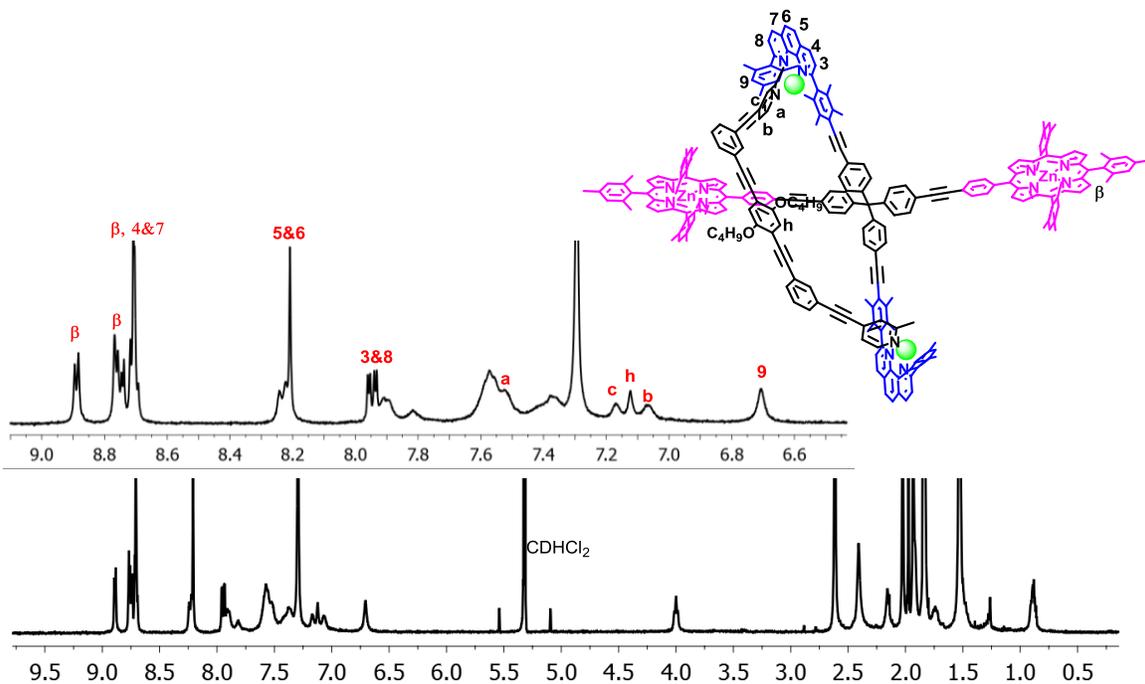
**Figure S14:** Partial  $^1\text{H}$  NMR spectra for comparison (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of (a) State I = [(1)(2)], (b) track 1, (c) biped ligand 2 and (d) prototypical complex C1 = [(3)(5)].



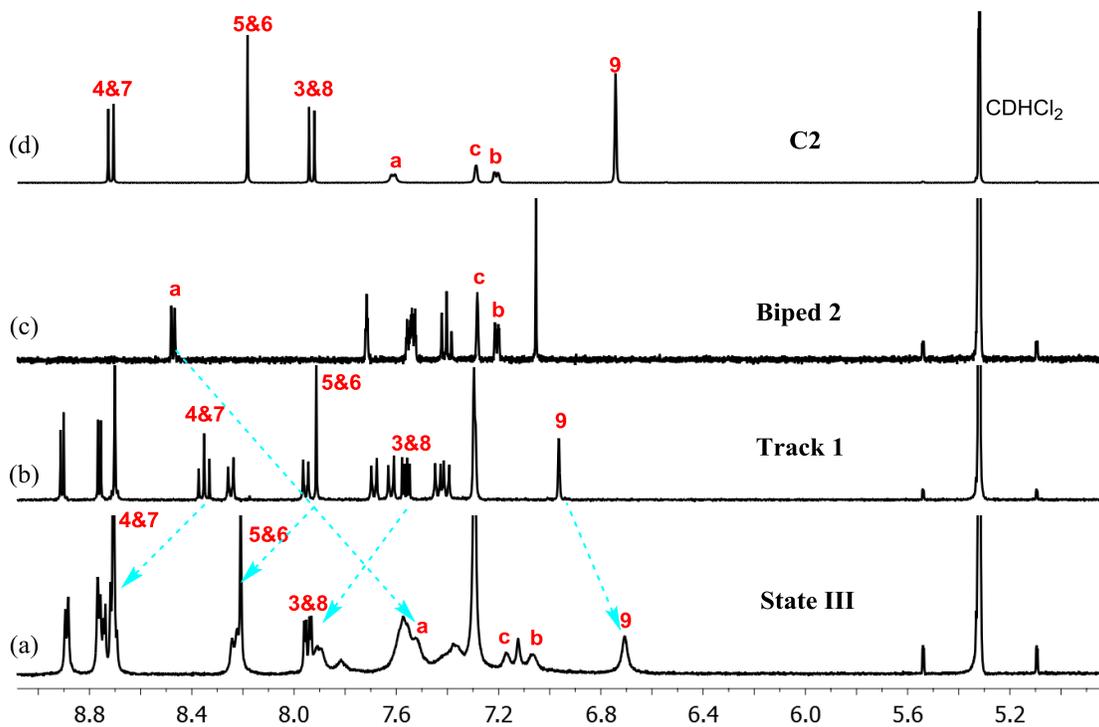
**Figure S15:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of **State II** =  $[\text{Cu}(\mathbf{1})(\mathbf{2})]\text{PF}_6$ . The expanded parts of the aromatic and aliphatic region are shown at the top with protons assigned.



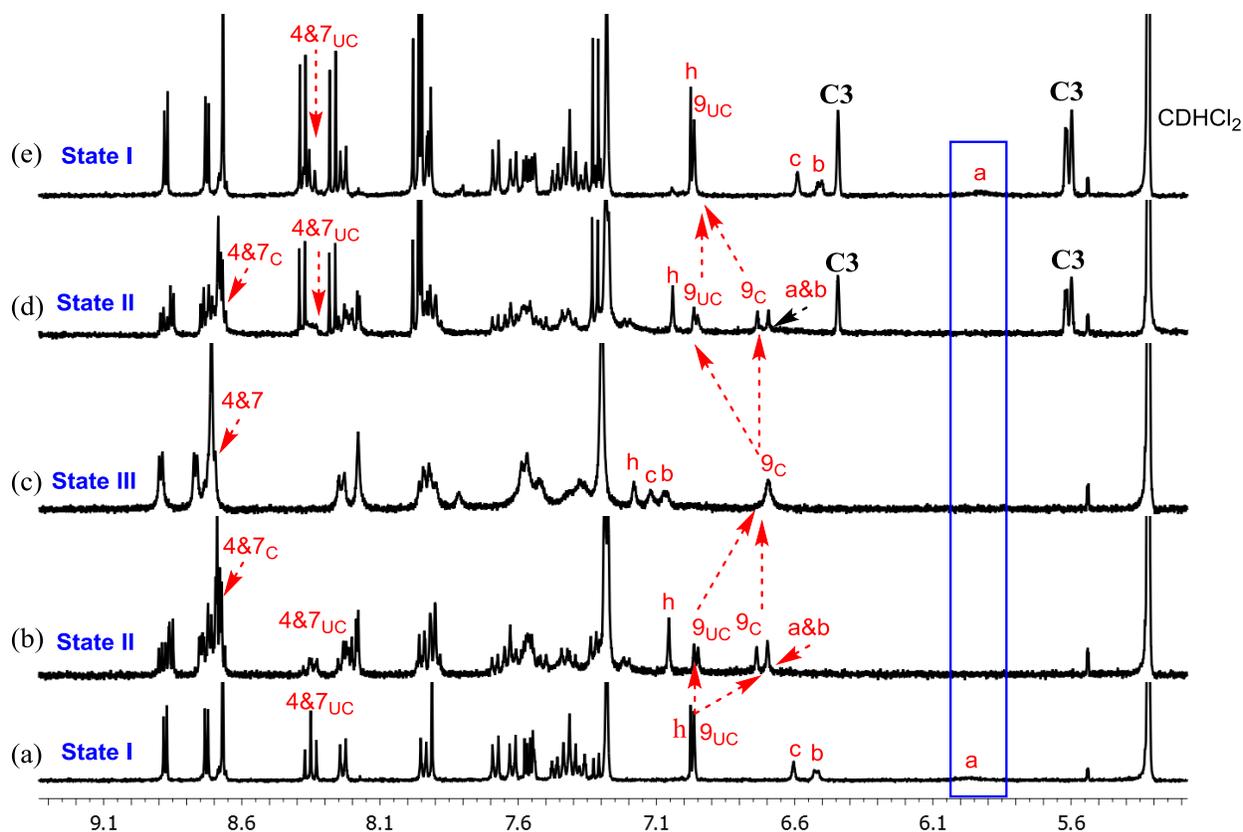
**Figure S16:** Partial  $^1\text{H}$  NMR spectra for comparison (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of (a) **State II** =  $[\text{Cu}(\mathbf{1})(\mathbf{2})]\text{PF}_6$ , (b) **track 1**, (c) **biped ligand 2** and (d) **prototypical complex C2** =  $[\text{Cu}(\mathbf{4})(\mathbf{5})]\text{PF}_6$ .



**Figure S17:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of State III =  $[\text{Cu}_2(\mathbf{1})(\mathbf{2})](\text{PF}_6)_2$ . An expanded part of the aromatic region is shown at the top with characteristic protons assigned.

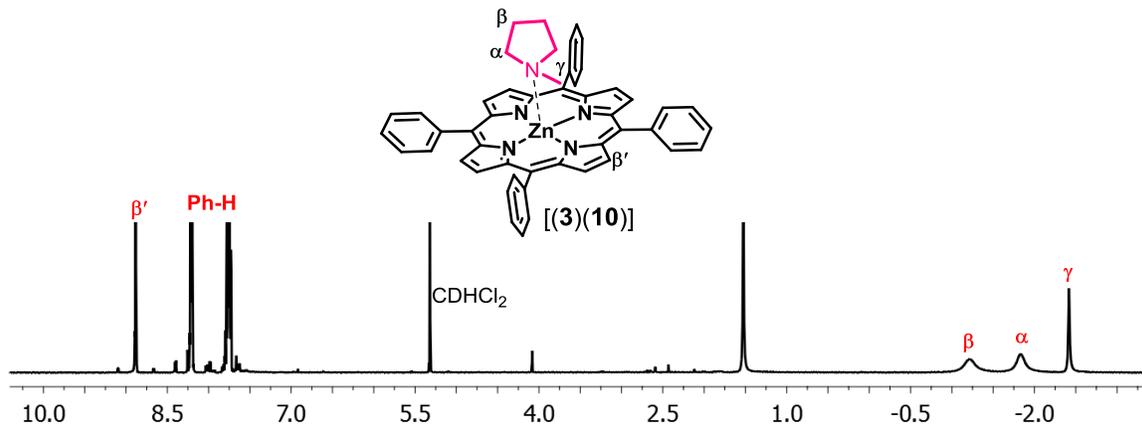


**Figure S18:** Partial  $^1\text{H}$  NMR spectra for comparison (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of (a) State III =  $[\text{Cu}_2(\mathbf{1})(\mathbf{2})](\text{PF}_6)_2$ , (b) track 1, (c) biped ligand 2 and (d) complex  $\mathbf{C2} = [\text{Cu}(\mathbf{4})(\mathbf{5})]\text{PF}_6$ .

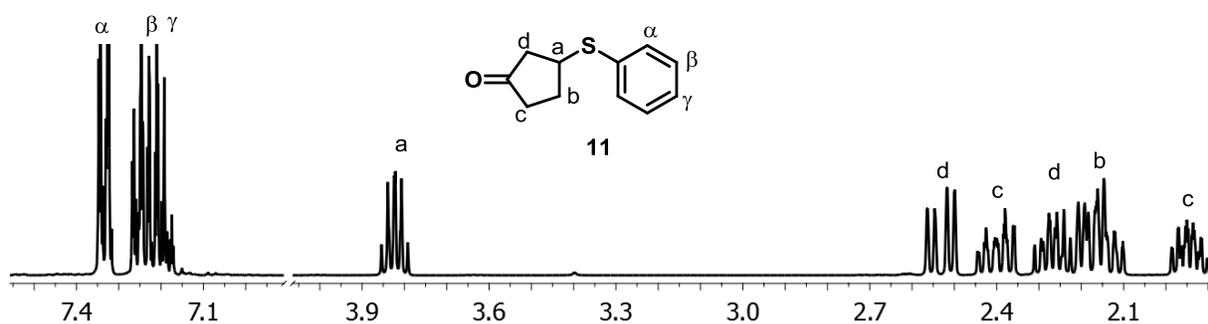


**Figure S19:**  $^1\text{H}$  NMR (400 MHz, 298 K,  $\text{CD}_2\text{Cl}_2$ ) showing *in situ* reversible stepwise walking of biped **2** on track **1** upon sequential addition and removal of  $\text{Cu}^+$  ions to switch between different states of the system. (a) Track **1** and biped **2** are mixed in 1:1 ratio affording state I ( $[(\mathbf{1})(\mathbf{2})]$ ); (b) addition of 1 equiv.  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  to state I depicted in spectrum (a) generates state II, i.e.  $[\text{Cu}(\mathbf{1})(\mathbf{2})]\text{PF}_6$ ; (c) addition of 1 more equiv. of  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$  to state II depicted in spectrum (b) generates state III, i.e.  $[\text{Cu}_2(\mathbf{1})(\mathbf{2})](\text{PF}_6)_2$ ; (d) addition of two equiv. of ligand **7** to state III displayed in spectrum (c) to remove 1 equiv. of  $\text{Cu}^+$  regenerates state II and complex **C3** and (e) addition of 2 more equiv. of ligand **7** to remove the remaining  $\text{Cu}^+$ , regenerates state I along with complex **C3**. The subscript terms free and com indicate uncomplexed and complexed proton.

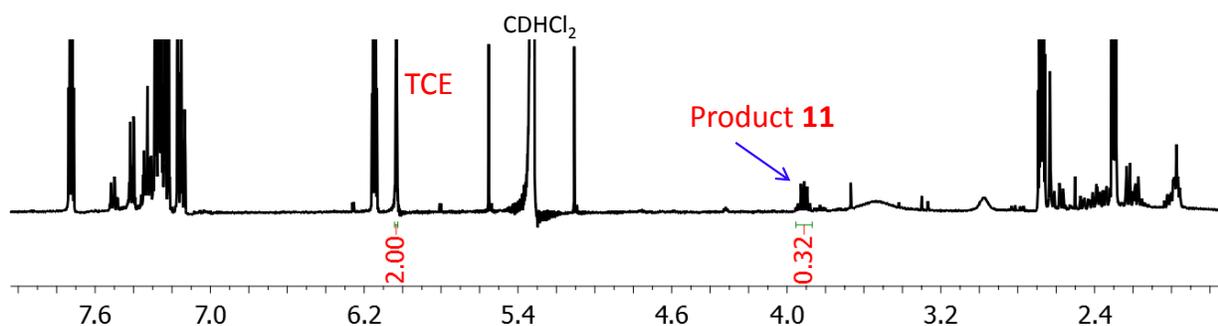
## $^1\text{H}$ NMR for catalytic experiments



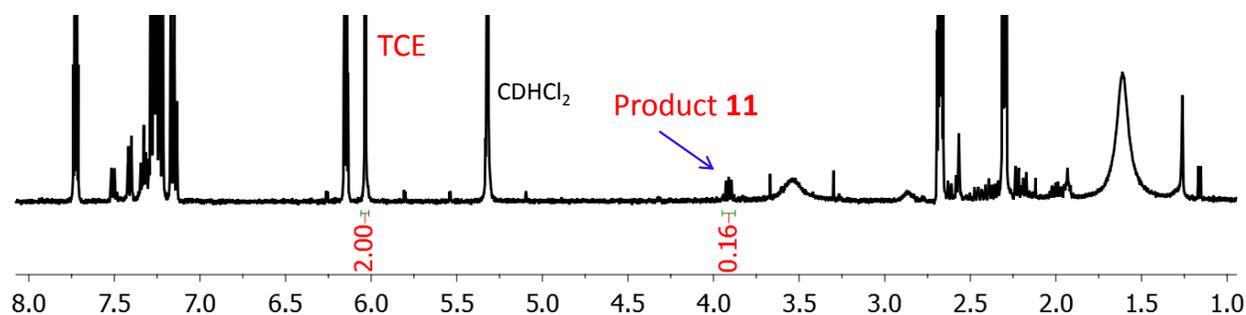
**Figure S20:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of complex  $[(3)(10)]$  upon mixing ligand 3 and 10 in 1:1 ratio.



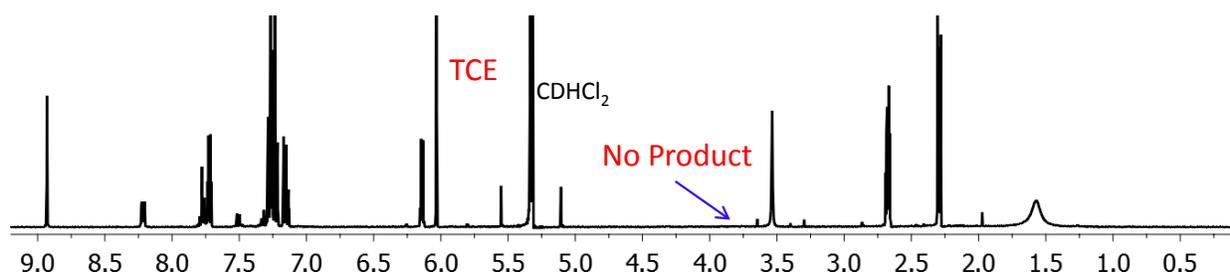
**Figure S21:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CDCl}_3$ , 298 K) of product 11.



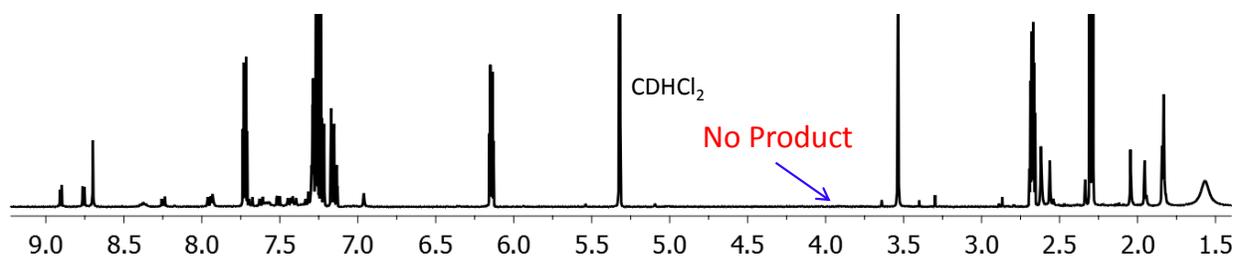
**Figure S22:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of the reaction of substrates 8 and 9 in presence of 9 mol% of *N*-methylpyrrolidine (10) at 40 °C in  $\text{CD}_2\text{Cl}_2$  for 2 h. Product 11 was formed in 32% yield (analyzed with respect to the internal standard TCE).



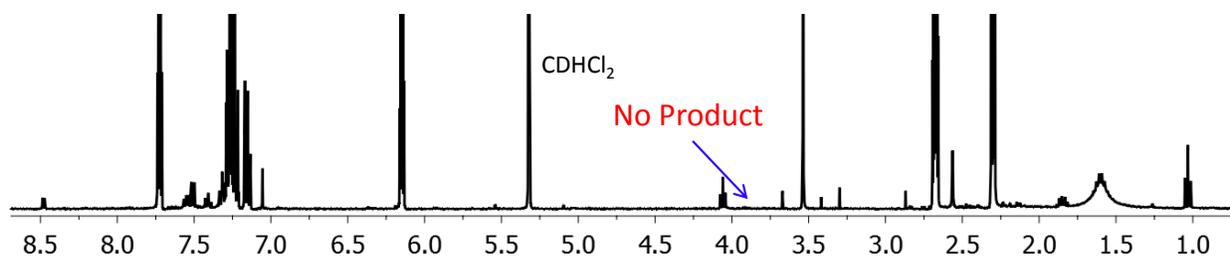
**Figure S23:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of the reaction of substrates **8** and **9** in presence of 4 mol% of *N*-methylpyrrolidine (**10**) at 40 °C in  $\text{CD}_2\text{Cl}_2$  for 2 h. Product **11** was formed in 16% yield (analyzed with respect to the internal standard TCE).



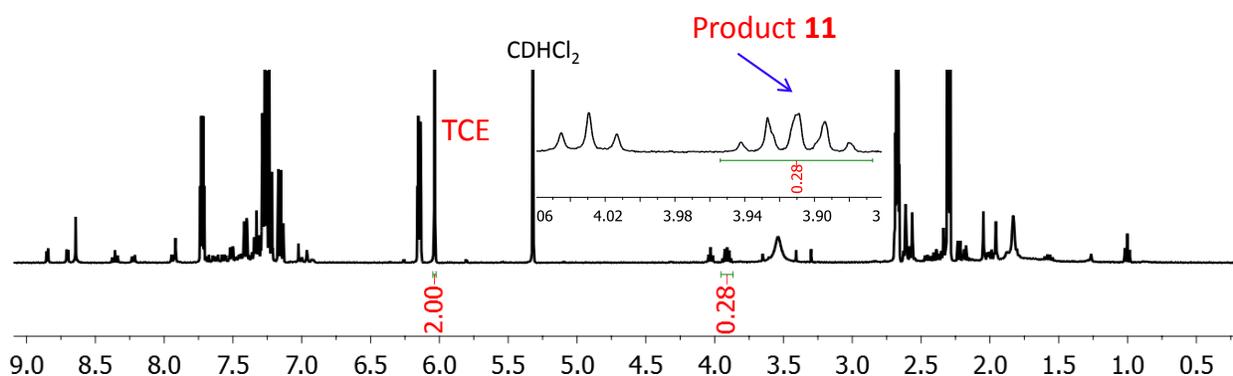
**Figure S24:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of the reaction of substrates **8** and **9** in presence of catalytic amounts (9 mol%) of *N*-methylpyrrolidine (**10**) and ZnTPP (in a 1:1 ratio) at 40 °C in  $\text{CD}_2\text{Cl}_2$  for 2 h. No product **11** was observed (analyzed with respect to the internal standard TCE).



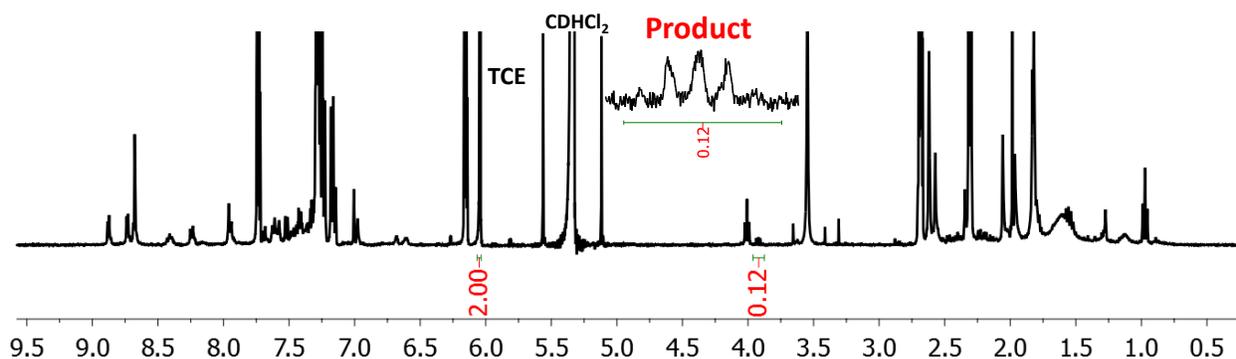
**Figure S25:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of the reaction of substrates **8** and **9** in presence of catalytic amount (10 mol%) of track **1** at 40 °C for 2 hr. No reaction was observed (analyzed with respect to the internal standard TCE).



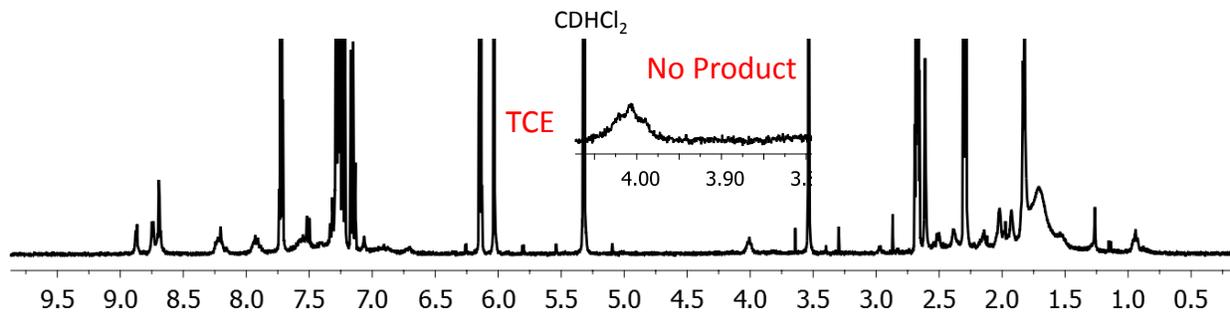
**Figure S26:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) after the reaction of substrates **8** and **9** in presence of catalytic amounts (10 mol%) of bided ligand **2** at 40 °C for 2 h. No reaction was observed.



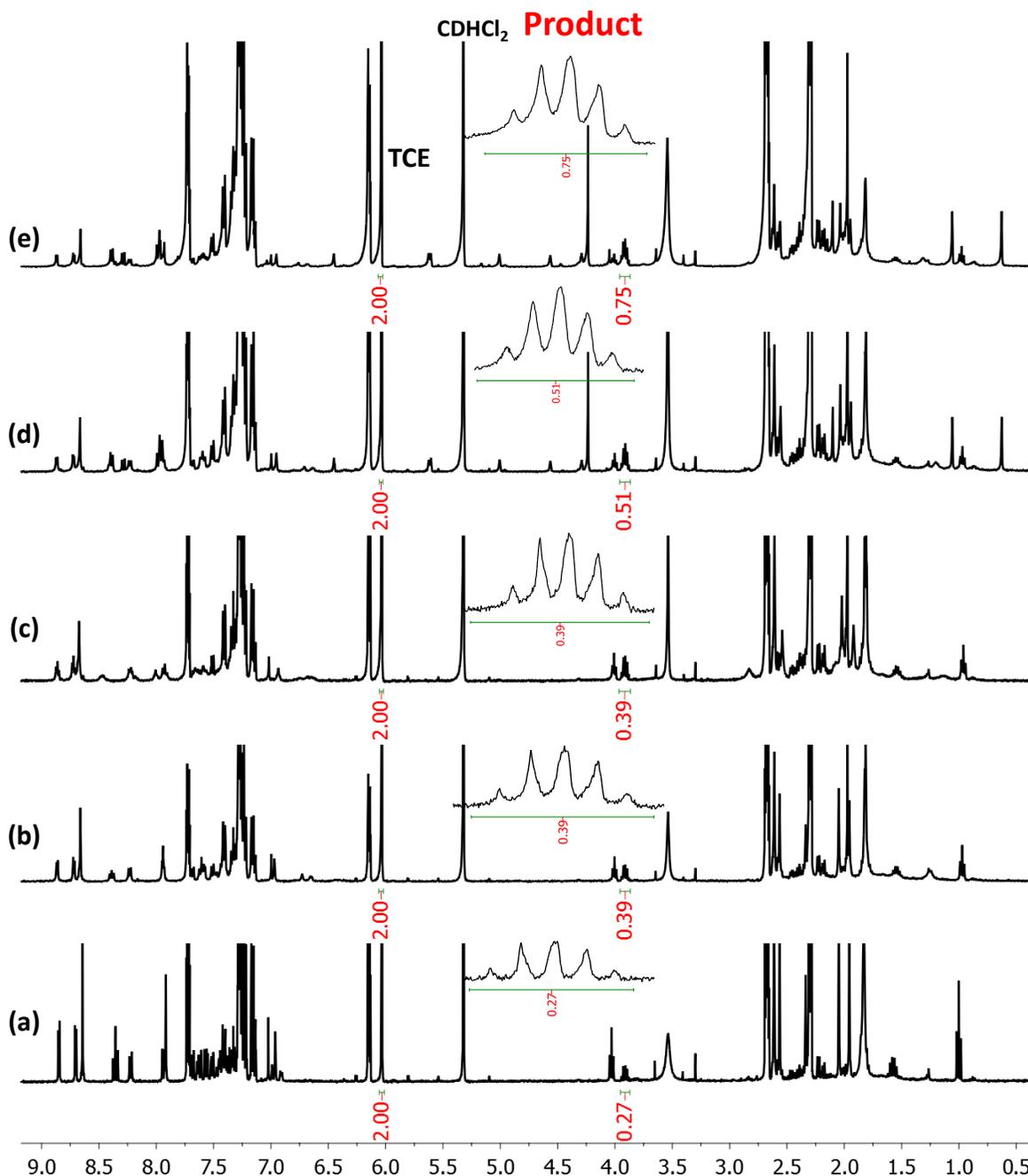
**Figure S27:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of the reaction of substrates **8** and **9** in presence of catalytic amounts (9 mol%) of *N*-methylpyrrolidine (**10**) and State I, *i.e.* [(**1**)(**2**)] (5 mol%) at 40 °C in  $\text{CD}_2\text{Cl}_2$  for 2 h. Product **11** was formed in 28% yield.



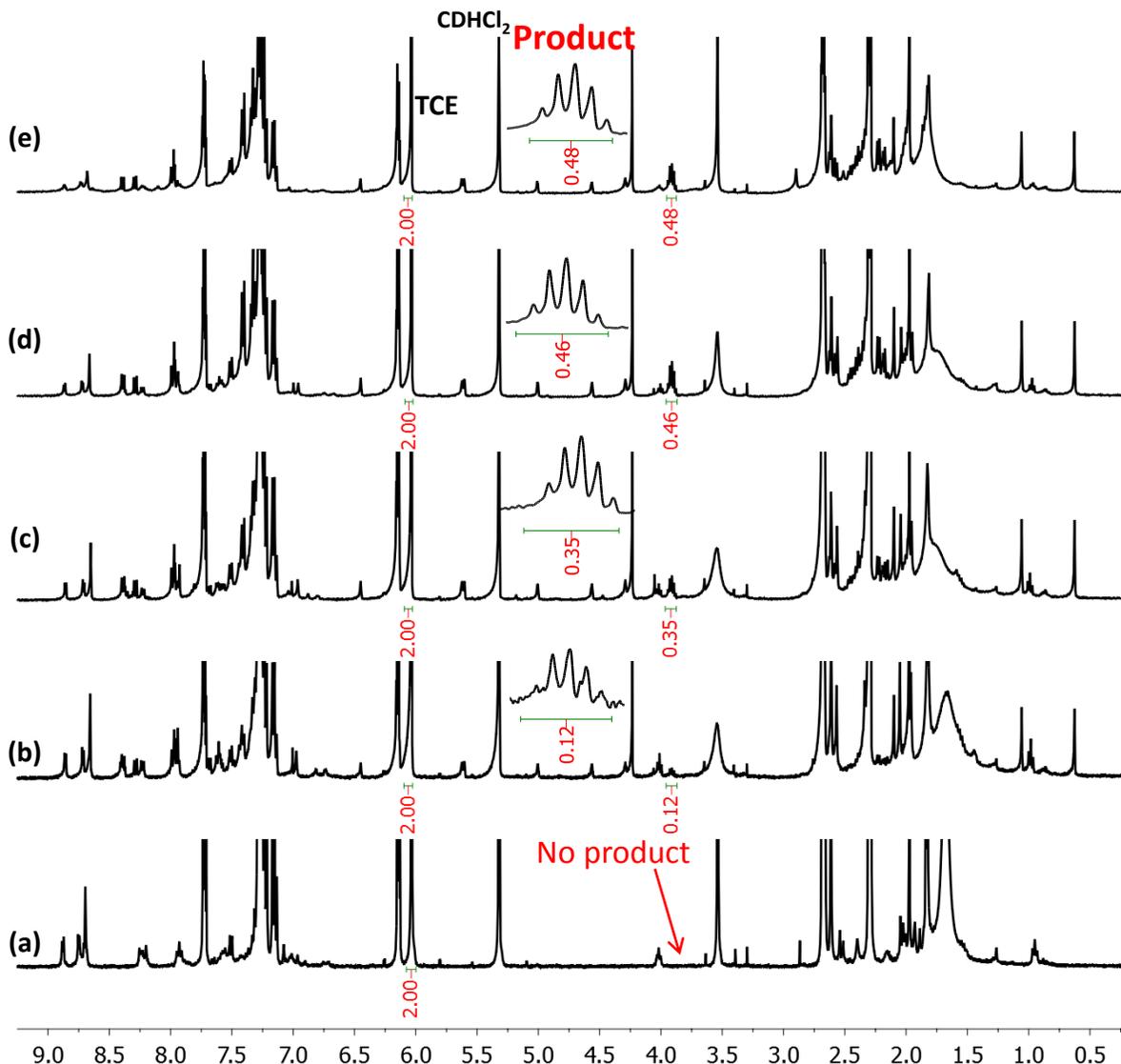
**Figure S28:**  $^1\text{H}$  NMR spectrum (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) after the reaction of substrates **8** and **9** in presence of catalytic amounts (9 mol%) of *N*-methylpyrrolidine (**10**) and State II, *i.e.* [ $\text{Cu}(\mathbf{1})(\mathbf{2})\text{PF}_6$ ] (5 mol%) at 40 °C in  $\text{CD}_2\text{Cl}_2$  for 2 h. Product **11** was formed in 12% yield.



**Figure S29:** <sup>1</sup>H NMR spectrum (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) of the reaction of substrates **8** and **9** in presence of catalytic amount (9 mol%) of *N*-methylpyrrolidine (**10**) and State III, *i.e.* [Cu<sub>2</sub>(**1**)(**2**)](PF<sub>6</sub>)<sub>2</sub> (5 mol%) at 40 °C in CD<sub>2</sub>Cl<sub>2</sub> for 2 h. No Product **11** was observed at 3.91 ppm.

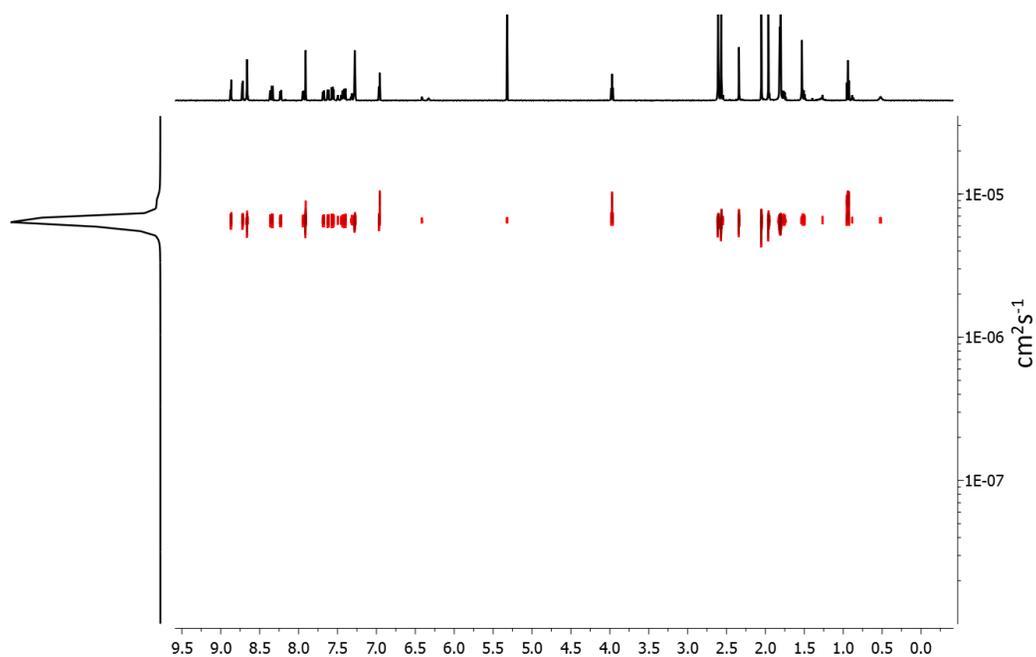


**Figure S30:** Track 1, biperid ligand **2**, **8**, **9** and catalyst **10** (5:5:100:100:9 in mol%) were combined in an NMR tube. Prior to each NMR the mixture was heated at 40 °C for 2 h and then cooled (for details, see page S15). Partial  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) after (a) the first heating of CatState I (= 100% ON state), (b) addition of 5 mol% of  $\text{Cu}^+$  to form CatState II ( $^{int}$ ON state), (c) addition of 5 more mol% of  $\text{Cu}^+$  to form CatState III (OFF state), (d) addition of 10 mol% of **7** to regenerate CatState II ( $^{int}$ ON state) and (e) again regeneration of CatState I (100% ON state) by addition of **7** (10 mol%). Consumed amounts of **8** and **9** were also added in each step. Insets show the product signal used for integration.

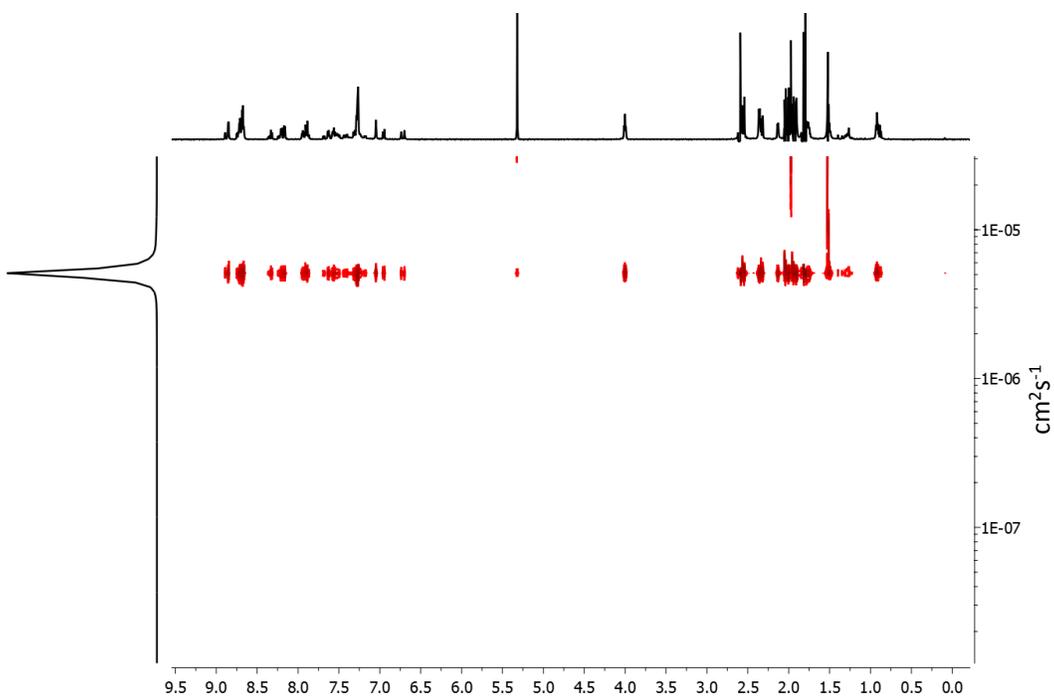


**Figure S31:** Track **1**, biped **2**,  $[\text{Cu}(\text{CH}_3\text{CN})_4]\text{PF}_6$ , **8**, **9** and catalyst **10** (10:10:20:200:200:18 mol%) were combined in an NMR tube. Prior to each NMR the mixture was heated at 40 °C for 2 h and then cooled (for details, see page S16). Partial  $^1\text{H}$  NMR spectra (400 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) after (a) the first heating of CatState III (= OFF state), (b) addition of 20 mol% of **7** to form CatState II (*int*ON state), (c) addition of 20 more mol% of **7** to form CatState I (100% ON state), (d) addition of 10 mol% of  $\text{Cu}^+$  to regenerate CatState II (*int*ON state) and (e) again regeneration of CatState III (OFF state) by addition of  $\text{Cu}^+$  (10 mol%). Consumed amounts of **8** and **9** were also added in each step. Insets show the product signal used for integration.

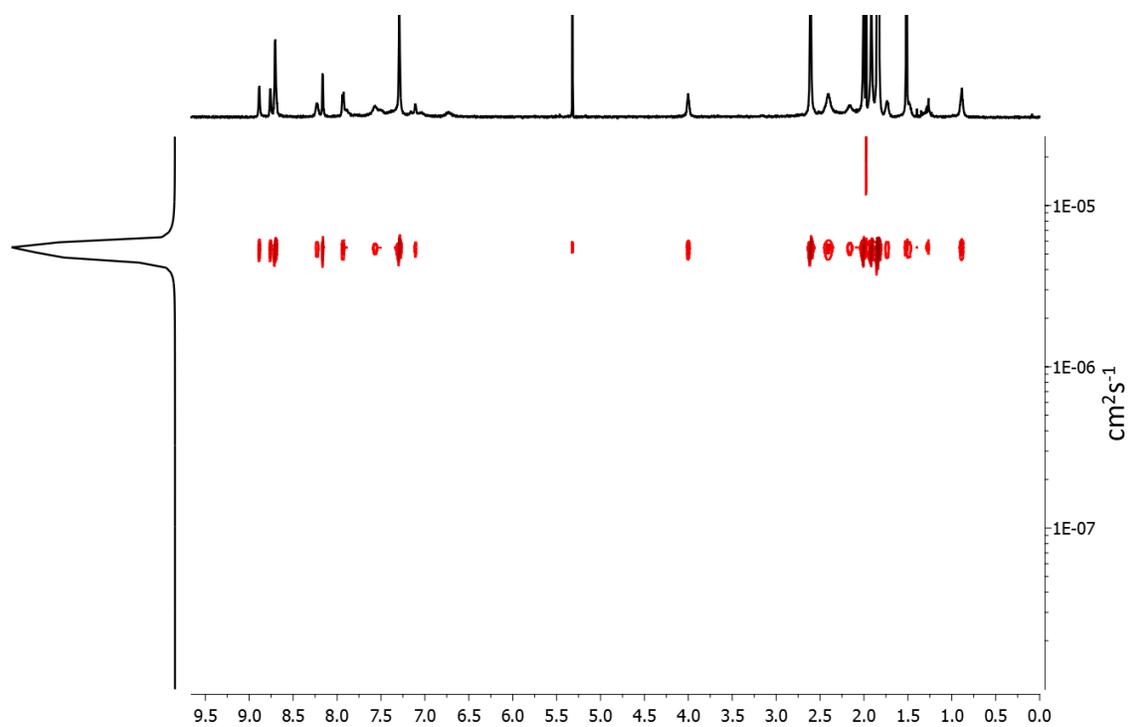
## DOSY NMR:



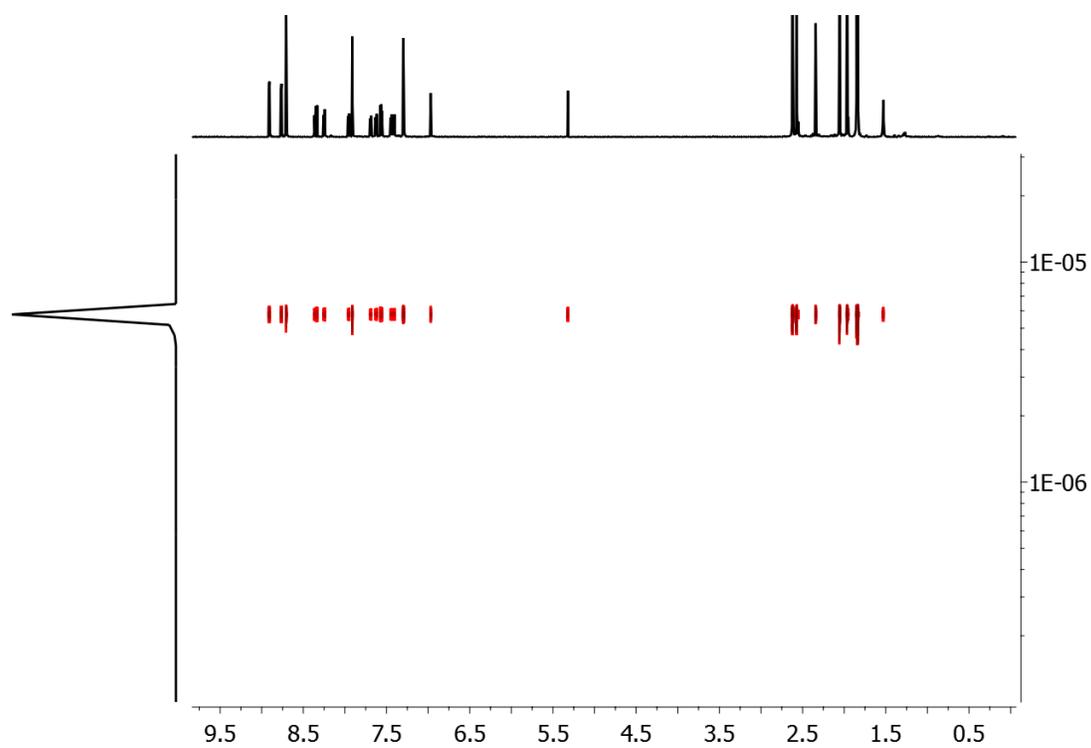
**Figure S32:** DOSY NMR spectrum (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) of State I = [(1)(2)] with a single diffusion coefficient  $D = 3.5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  ( $r \sim 15.1 \text{ \AA}$ ).



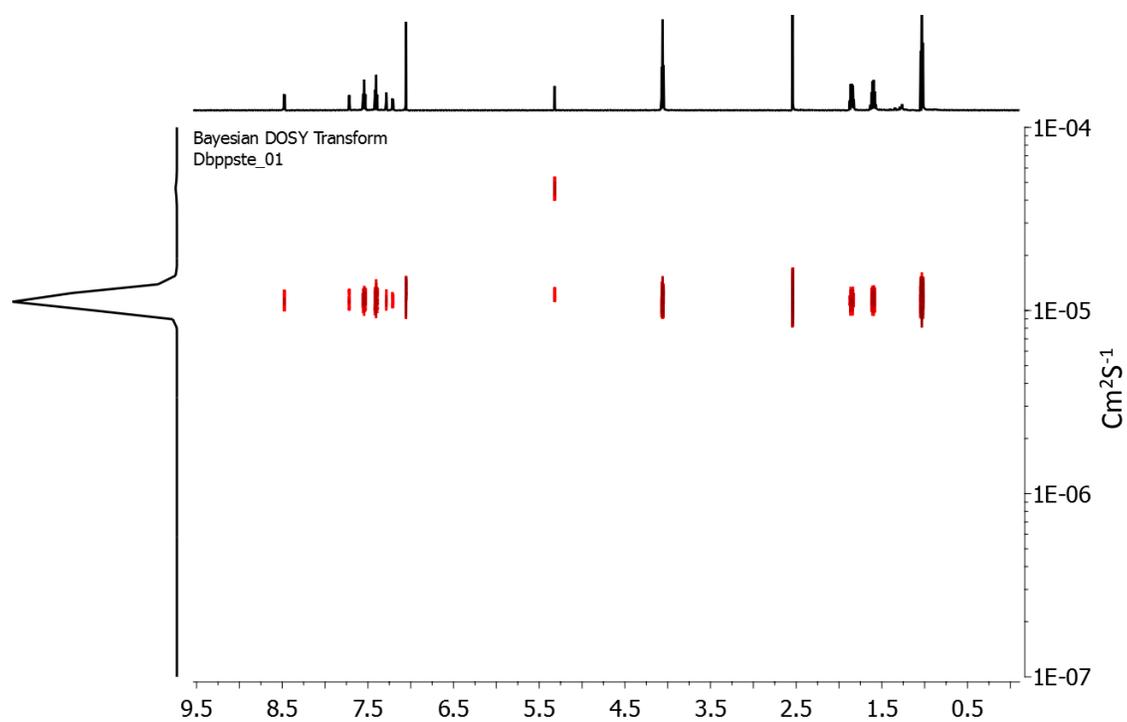
**Figure S33:** DOSY NMR spectrum (600 MHz, CD<sub>2</sub>Cl<sub>2</sub>, 298 K) of State II = [Cu(1)(2)]PF<sub>6</sub> with a single diffusion coefficient  $D = 3.44 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$  ( $r \sim 15.3 \text{ \AA}$ ).



**Figure S34:** DOSY NMR spectrum (600 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of State III =  $[\text{Cu}_2(\mathbf{1})(\mathbf{2})](\text{PF}_6)_2$  with a single diffusion coefficient  $D = 3.36 \times 10^{-10} \text{ m}^2\text{s}^{-1}$  ( $r \sim 15.7 \text{ \AA}$ ).

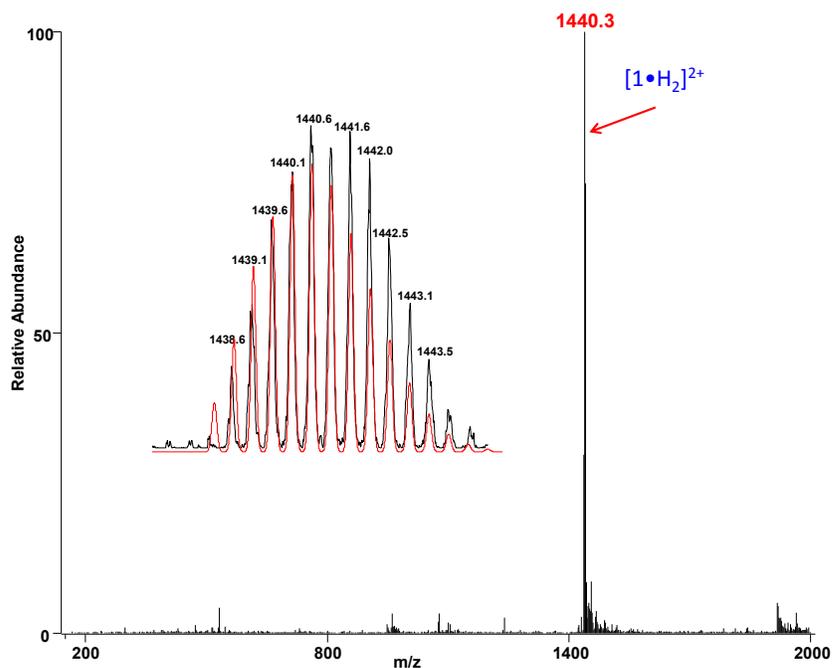


**Figure S35:** DOSY NMR spectrum (600 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of track 1 showing a single diffusion coefficient at  $D = 4.25 \times 10^{-10} \text{ m}^2\text{s}^{-1}$  ( $r \sim 12.4 \text{ \AA}$ ).

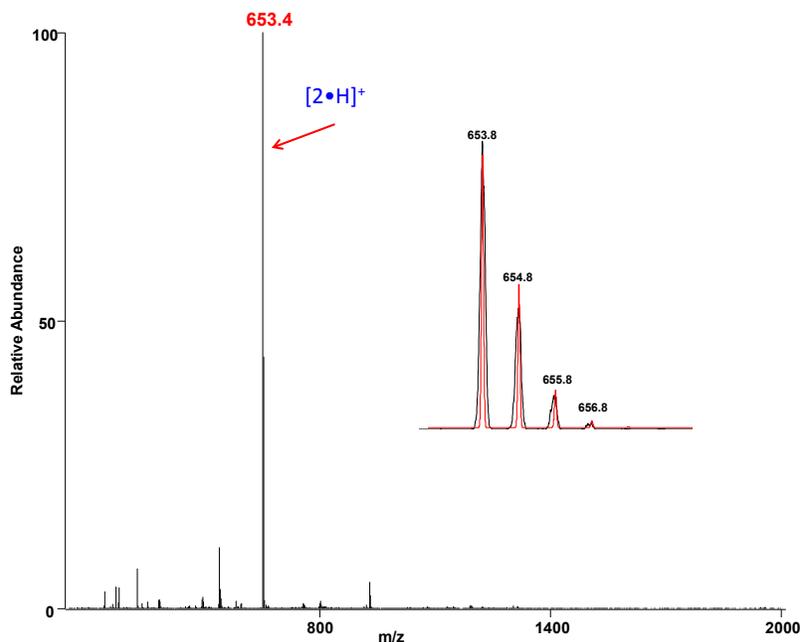


**Figure S36:** DOSY NMR spectrum (600 MHz,  $\text{CD}_2\text{Cl}_2$ , 298 K) of biped ligand **2** showing a single diffusion coefficient at  $D = 8.34 \times 10^{-10} \text{ m}^2\text{s}^{-1}$  ( $r \sim 6.3 \text{ \AA}$ ).

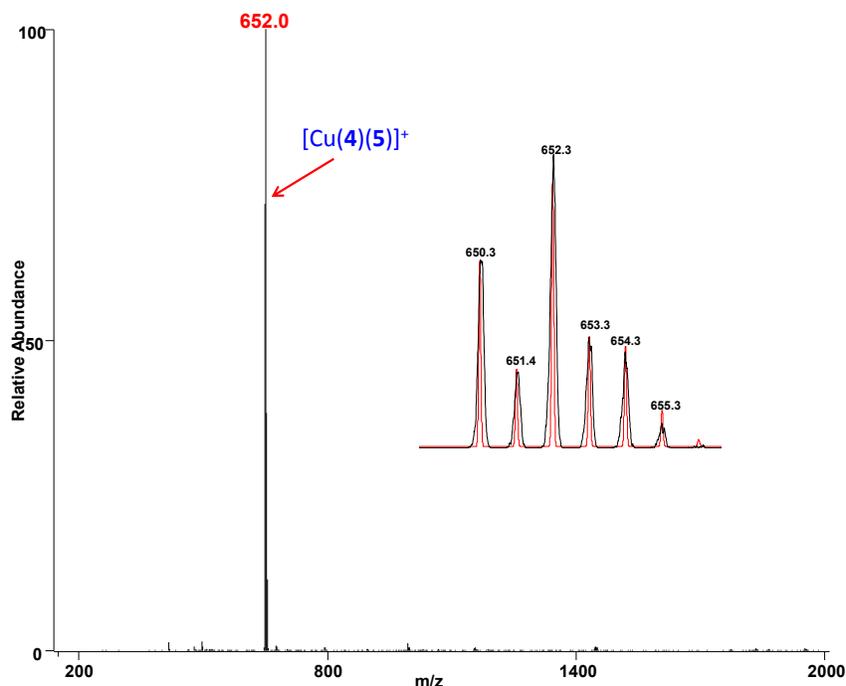
## ESI-MS Spectra:



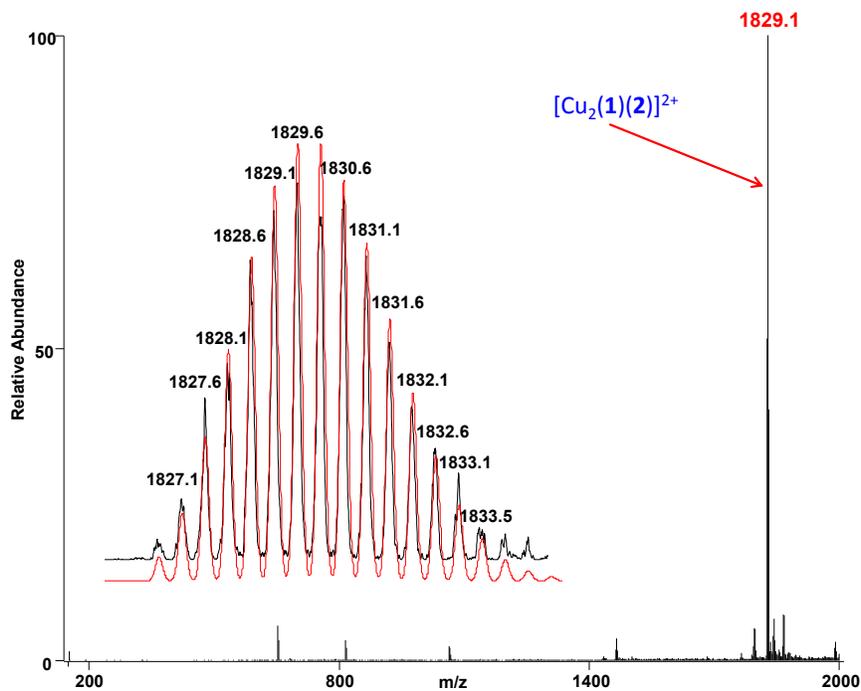
**Figure S37:** ESI-MS spectrum of track 1 as  $[1\bullet H_2]^{2+}$  in  $CH_2Cl_2$  as well as experimental (black lines) and calculated isotopic distribution (red lines) for the peak associated with  $[1\bullet H_2]^{2+}$ .



**Figure S38:** ESI-MS spectrum of biped 2 as  $[2\bullet H]^+$  in  $CH_2Cl_2$  as well as experimental (black lines) and calculated isotopic distribution (red lines) for the peak associated with  $[2\bullet H]^+$ .

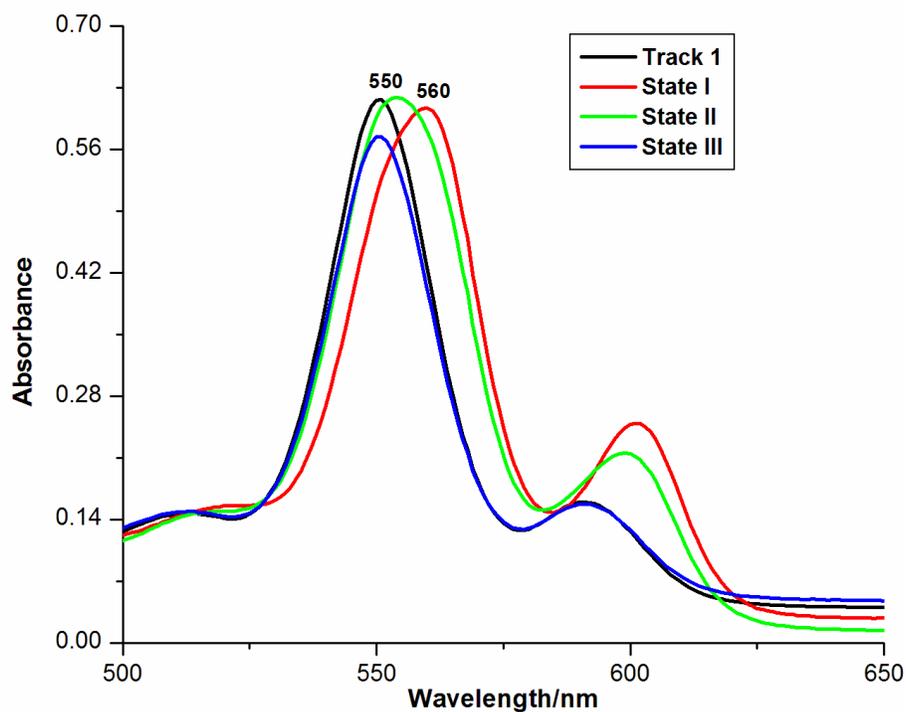


**Figure S39:** ESI-MS spectrum of Complex **C2** =  $[\text{Cu}(4)(5)]\text{PF}_6$  in  $\text{CH}_2\text{Cl}_2$  as well as experimental (black lines) and calculated isotopic distribution (red lines) for the peak associated with  $[\text{Cu}(4)(5)]^+$ .



**Figure S40:** ESI-MS spectrum of State III =  $[\text{Cu}_2(1)(2)](\text{PF}_6)_2$  in  $\text{CH}_2\text{Cl}_2$  as well as experimental (black lines) and calculated isotopic distribution (red lines) for the peak associated with  $[\text{Cu}_2(1)(2)]^{2+}$ .

## UV-vis Spectra



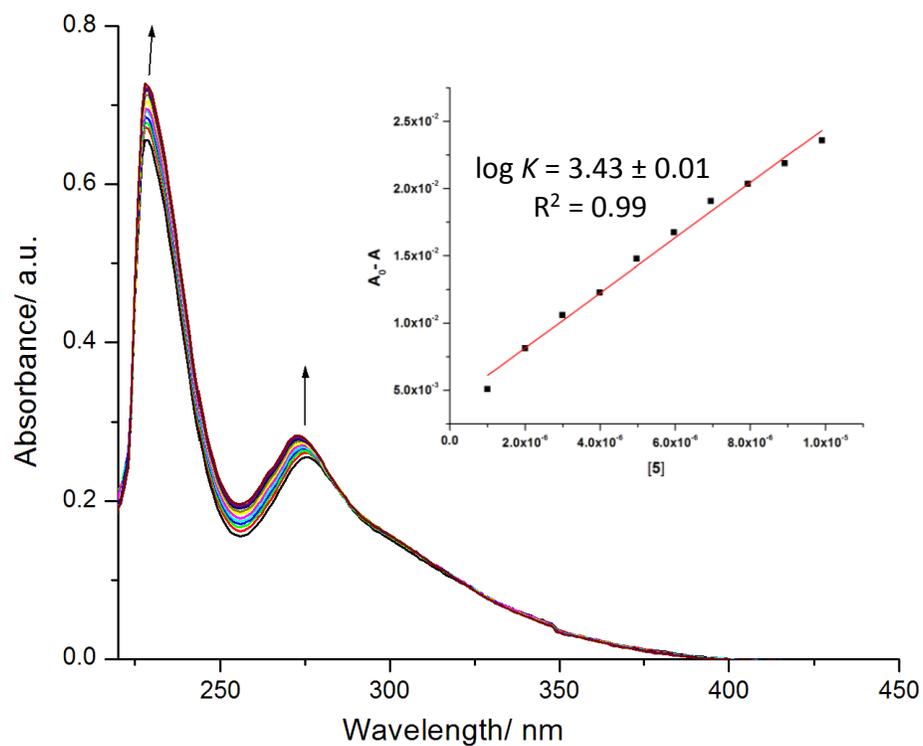
**Figure S41:** Comparison of UV-vis spectra of track **1**, state I, state II and state III at 298 K at  $c = 4.24$  mM.

## Binding constant measurement

### Log $K$ of $[\text{Cu}(\mathbf{4})]^+$ and 4-bromo-2-methylpyridine (**5**)

The binding constant was determined from a UV-vis titration. A solution of  $[\text{Cu}(\mathbf{4})]^+$  ( $7.79 \times 10^{-6}$  M) was titrated against a  $1.0 \times 10^{-3}$  M solution of **5**. To calculate the binding constant the non-linear curve-fitting method was used.  $\Delta A$  value was monitored at 275 nm. The equation<sup>7</sup> used for fitting is

$$\Delta A = (L \cdot (1 + K \cdot X + K \cdot A) - \text{SQRT}(L^2(K \cdot X + K \cdot A + 1)^2 - 4 \cdot K^2 \cdot A \cdot X \cdot L^2)) / 2 \cdot K \cdot A$$



**Figure S42:** UV-vis absorption of [Cu(4)]PF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> (2 mL) upon addition of 4-bromo-2-methylpyridine (**5**) at 298 K to afford complex [Cu(4)(5)]PF<sub>6</sub> (inset: fitting curve for binding constant measurement).

## References

---

- (1) Schmittl, M.; Michel, C.; Wiegrefe, A.; Kalsani, V. Synthesis of Soluble, Linear Bisphenanthrolines for the Construction of Heteroleptic NanoGrids and Nanoboxes. *Synthesis* **2001**, *10*, 1561–1567.
- (2) Saha, M. L.; Mittal, N.; Bats, J. W.; Schmittl, M. A six-component metallocupramolecular pentagon via self-sorting. *Chem. Commun.* **2014**, *50*, 12189–12192.
- (3) Mittal, N.; Pramanik, S.; Paul, I.; De, S.; Schmittl, M. Networking Nanoswitches for ON/OFF Control of Catalysis. *J. Am. Chem. Soc.* **2017**, *139*, 4270–4273.
- (4) Wagner, R. W.; Johnson, T. E.; Lindsey, J. S. Soluble Synthetic Multiporphyrin Arrays. 1. Modular Design and Synthesis. *J. Am. Chem. Soc.* **1996**, *118*, 11166–11180.
- (5) Shinomiya, M.; Higashiguchi, K.; Matsuda, K. Evaluation of the  $\beta$  value of the phenylene ethynylene unit by probing the exchange interaction between two nitronyl nitroxides. *J. Org. Chem.* **2013**, *78*, 9282–9290.
- (6) Block, M. A. B.; Hecht, S. Poly(propylene oxide)–Poly(phenylene ethynylene) Block and Graft Copolymers. *Macromolecules* **2008**, *41*, 3219–3227.
- (7) Hajjaj, F.; Tashiro, K.; Nikawa, H.; Mizorogi, N.; Akasaka, T.; Nagase, S.; Furukawa, K.; Kato, T.; Aida, T. Ferromagnetic spin coupling between endohedral metallofullerene La@C<sub>82</sub> and a cyclodimeric copper porphyrin upon inclusion. *J. Am. Chem. Soc.* **2011**, *133*, 9290–9292.