Electronic Supplementary Material (ESI) for ChemComm.

Electronic Supporting Information

Dissipative sequential catalysis via six-component machinery

Debabrata Mondal,‡ Emad Elramadi,‡ Sohom Kundu, Michael Schmittel*

Center of Micro- and Nanochemistry and (Bio)Technology, Organische Chemie I&II, Universität Siegen, Adolf–Reichwein–Str. 2, D-57068 Siegen, Germany.

mail: schmittel@chemie.uni-siegen.de

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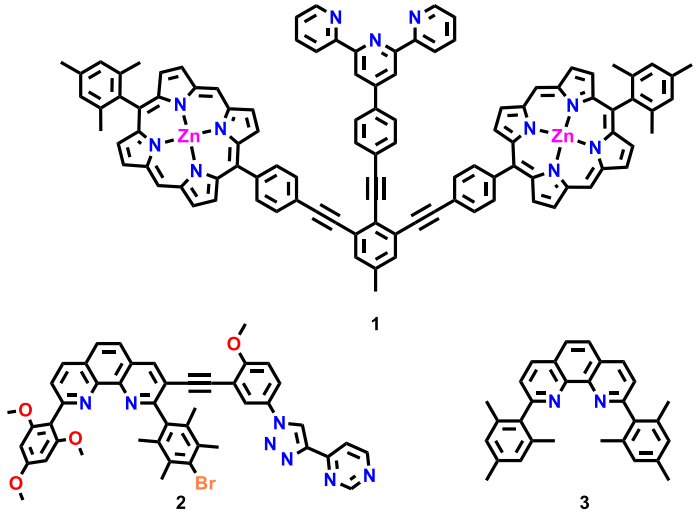
1. Synthesis

1.1 General information. All reagents were purchased from commercial suppliers and used without further purification. Technical grade solvents were distilled before use. Bruker Avance (400 MHz), Jeol ECZ (500 MHz), and Varian (600 MHz) NMR spectrometers were used to record ^{1}H, ^{13}C, ^{1}H-^{1}H COSY, and DOSY NMR spectra (at 298 K unless otherwise noted) using the deuterated solvent as the lock. Chemical shifts are referenced to the residual deuterated fraction of the solvent ($CHCl_3$: δ_H = 7.26 ppm, δ_C = 77.0 ppm; $CDHCl_2$: δ_H = 5.32 ppm, δ_C = 53.8 ppm). Abbreviations have been used in the ^{1}H NMR assignments to describe the splitting patterns (s: singlet, d: doublet, dd: doublet of doublets, td: triplet of doublets, ddd: doublet of doublets of doublets, q: quartet), the value of the coupling constant(s) is given in Hertz (Hz), and the number of protons is implied. The numbering of carbon atoms does not normally follow IUPAC nomenclature guidelines. Melting points were measured on a Büchi SMP-20 and are uncorrected. Electrospray ionization mass spectra (ESI-MS) were recorded on a Thermo-Quest LCQ Deca instrument. Elemental analysis was performed on an EA-3000 CHNS analyzer. Column chromatography was performed on silica gel 60 (60-230 mesh). Ligand **1** was synthesized according to known protocols, sometimes with slightly modified procedures. The spectral data of ligand **1**[1] were in full agreement with those reported in the literature.

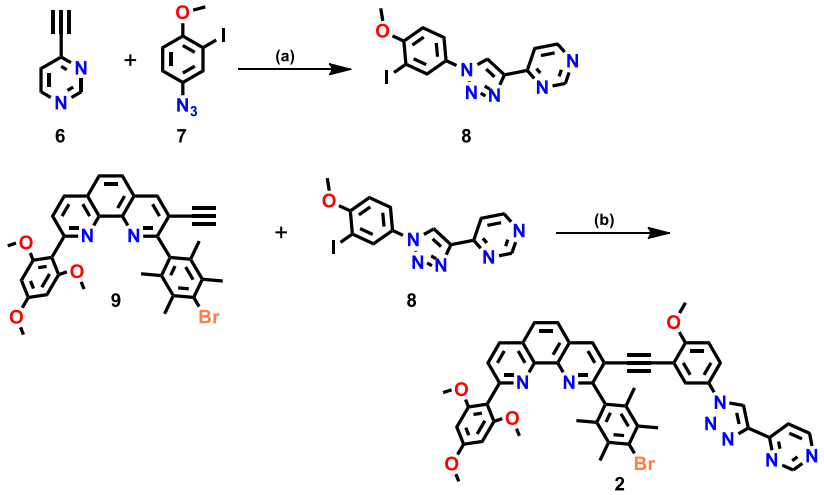
1.2 Ligands



Scheme 1. Ligands used in the study.

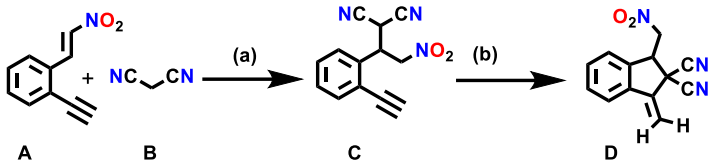
1.3 Synthesis and characterization of ligands

Synthetic route to ligand **2**



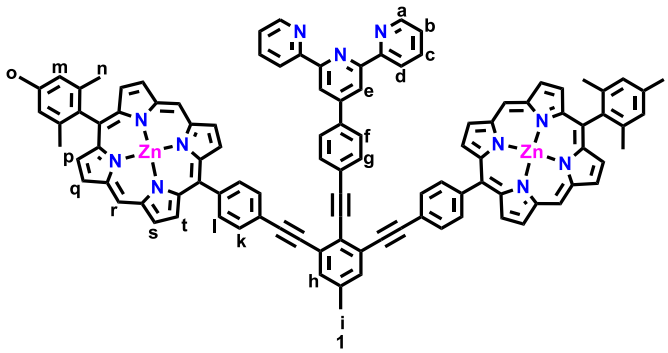
Scheme 2. Synthesis of ligand **2**. (a) $[Cu(CH_3CN)_4]PF_6$, DCM, 40 °C, 24 h; (b) $Pd(PPh_3)_4$, Et_3N/THF, 50 °C, 12 h.

Synthetic route to intermediate **C** and product **D**



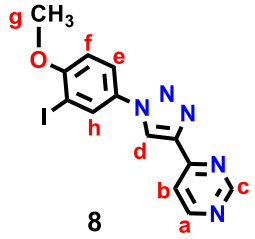
Scheme 3. Synthesis of intermediate **C** and product **D**. (a) Et_3N, DCM, rt, 4 h; (b) $[Cu(CH_3CN)_4]PF_6$, Et_3N/ DCM, 10 h.

^{1}H NMR data of the literature-known ligand **1**[1]



^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ = 1.82 (s, 12H, n-H), 2.62 (s, 3H, i-H), 2.70 (s, 6H, o-H), 7.11 (ddd, 3J = 8.0 Hz, ^3J = 5.0 Hz, ^4J = 1.2 Hz, 2H, b-H), 7.38 (s, 4H, m-H), 7.70 (td, ^3J = 8.0 Hz, ^4J = 1.2 Hz, 2H, c-H), 7.73 (s, 2H, h-H), 8.11 (d, ^3J = 8.4 Hz, 2H, g/f-H), 8.15 (d, ^3J = 8.4 Hz, 2H, f/g-H), 8.19 (d, ^3J = 8.0 Hz, 4H, k-H), 8.33 (ddd, ^3J = 5.0 Hz, ^4J = 1.2 Hz, ^5J = 0.8 Hz, 2H, a-H), 8.38 (d, ^3J = 8.0 Hz, 4H, l-H), 8.47 (ddd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, ^5J = 0.8 Hz, 2H, d-H), 8.75 (s, 2H, e-H), 8.95 (d, ^3J = 4.4 Hz, 4H, p-H), 9.23 (d, ^3J = 4.4 Hz, 4H, t-H), 9.43 (d, ^3J = 4.4 Hz, 4H, qH), 9.51 (d, ^3J = 4.4 Hz, 4H, s-H), 10.28 (s, 4H, r-H) ppm.

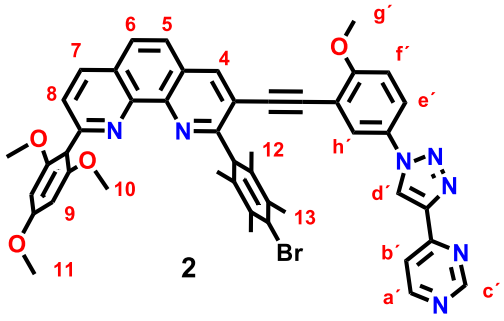
4-(1-(3-Iodo-4-methoxyphenyl)-1H-1,2,3-triazol-4-yl) pyrimidine (**8**)



8

Compound **6** (95.0 mg, 912 µmol) and **7** (291 mg, 1.05 mmol) were dissolved in 10 mL of DCM. Thereafter, $[Cu(CH_3CN)_4]PF_6$ (38.0 mg, 102 µmol) was added and the reaction mixture was stirred at 40 °C (oil bath) for 24 h. Next, cyclam (20.4 mg, 102 µmol) was added and the solvent removed under reduced pressure. The crude reaction mixture was purified by column chromatography (silica gel, DCM : MeOH = 98:2, R_f = 0.25) affording product **8** as yellowish solid (325 mg, 94%), **Mp**: 224-226 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 3.97 (s, 3H, g-H), 6.96 (d, ^3J = 8.9 Hz, 1H, f-H), 7.77 (dd, ^3J = 8.9 Hz, ^4J =2.7 Hz, 1H, e-H), 8.18 (dd, ^3J = 5.3 Hz, ^4J =1.4 Hz, 1H, a-H), 8.22 (d, ^4J = 2.7 Hz, 1H, h-H), 8.62 (s, 1H, d-H), 8.84 (d, ^3J = 5.3 Hz, 1H, b-H), 9.21 (d, ^4J = 1.4 Hz, 1H, c-H) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 56.8, 86.4, 110.9, 116.9, 121.7, 122.0, 130.8, 131.8, 146.2, 156.7, 157.9, 158.9, 159.0 ppm. **Anal. Calcd.** for $C_{13}H_{10}IN_5O$• ¼ CH_3OH: C, 41.10; H, 2.86; N, 18.09. **Found**: C, 41.31; H, 2.53; N, 17.78. **ESI-MS**: *m/z* (%) = 380.1 (100) $[\mathbf{8}+H]^+$.

Ligand **2**

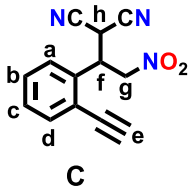


2

Compounds **8** (99.0 mg, 261 µmol) and **9** (122 mg, 209 µmol) were dissolved in deaerated THF (5 mL) and Et_3N (10 mL), then $[Pd(PPh_3)_4]$ (15.0 mg, 13.0 µmol) was added. The mixture was stirred overnight at 50 °C and the solvent evaporated to dryness. The crude rection mixture was purified by column chromatography (R_f = 0.25, EtOAc: hexane = 1:1) on silica gel using hexane:

EtOAc:DCM (7:2:1) to furnish compound **2** as a yellow solid (99.0 mg, 118 µmol, 56%). **Mp**: >250 °C. **^{1}H NMR** (500 MHz, CD_2Cl_2, 298 K): δ = 2.02 (s, 6H, 12-H), 2.48 (s, 6H, 13-H), 3.69 (s, 6H, 10-H), 3.83 (s, 3H, g'-H), 3.97 (s, 3H, 11-H), 6.25 (s, 2H, 9-H), 7.02 (d, ^3J = 8.9 Hz, 1H, f'-H), 7.50 (d, ^4J = 2.7 Hz, 1H, h'-H), 7.59 (d, ^3J = 8.2 Hz, 1H, 8-H),7.72 (dd, ^3J = 8.9 Hz, ^4J =2.7 Hz, 1H, e'-H), 7.87 (d, ^3J = 8.0 Hz, 1H, 6-H), 7.91 (d, ^3J = 8.0 Hz, 1H, 5-H), 8.16 (dd, ^3J = 5.3 Hz, ^4J =1.4 Hz, 1H, a'-H), 8.28 (d, ^3J = 8.2 Hz, 1H, 7-H), 8.55 (s, 1H, 4-H), 8.63 (s, 1H, d'-H), 8.83 (d, ^3J = 5.3 Hz, 1H, b'-H), 9.20 (d, ^4J = 1.4 Hz, 1H, c'-H) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ =18.6, 21.0, 55.4, 56.2, 56.3, 89.9, 91.7, 92.2, 111.5, 113.5, 116.9, 119.4, 122.0, 122.5, 125.3, 125.6, 125.9, 126.7, 127.2, 127.4, 128.0, 129.0, 129.8, 133.5, 133.6, 135.3, 139.0, 139.1, 145.0, 145.7, 146.7, 155.5, 156.8, 157.7, 159.0, 159.2, 160.3, 161.6, 162.0 ppm. **Anal. Calcd** for $C_{46}H_{38}BrN_7O_4$•1.5CH_2Cl_2•H_2O: C, 58.32; H, 4.43; N, 10.02. **Found**: C, 58.04; H, 4.09; N, 9.77. **ESI-MS**: *m/z* (%) = 833.7 (100) [**2**+H]$^+$.

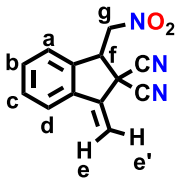
2-(1-(2-Ethynylphenyl)-2-nitroethyl)malononitrile (**C**)



C

1-Ethynyl-2-(2-nitrovinyl)benzene (**A**) (45.0 mg, 259 µmol) and malononitrile (**B**) (34.0 mg, 518 µmol) were dissolved in DCM (10 mL). Subsequently, triethylamine (718 µL) was added drop-wise, and the reaction was monitored till its completion (4 h) using TLC. Thereafter, the solvent was removed under reduced pressure. The residue was purified by flash column chromatography on silica gel using 30% DCM in hexane (R_f = 0.25, SiO_2, DCM: *n*-hexane =3: 7) to afford compound **C** as a colorless solid (35.0 mg, 146 µmol, 56%). **Mp**: 93.4-95.0 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 3.56 (s, 1H, e-H), 4.63 (d, ^3J = 7.0 Hz, 1H, h-H), 4.76 (q, ^3J = 7.0 Hz, 1H, f-H), 4.99 (dd, ^2J = 14.3 Hz, ^3J = 7.0 Hz, 1H, g-H), 5.07 (dd, ^2J = 14.3 Hz, ^3J = 7.0 Hz, 1H, g-H), 7.39 (dd, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1H, d-H), 7.43 (td, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1H, b-H), 7.48 (dd, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1H, c-H), 7.65 (dd, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1H, a-H) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 26.0, 41.4, 53.2, 74.1, 80.0, 85.2, 110.6, 126.7, 129.9, 130.3, 133.8, 134.6 ppm. **Anal. Calcd.** for $C_{13}H_9N_3O_2$•¼CH_2Cl_2•½H_2O: C, 59.28; H, 3.57; N, 15.65. **Found**: C, 59.66; H, 3.38; N, 15.77.

1-Methylene-3-(nitromethyl)-1*H*-indene-2,2(3H)-dicarbonitrile (**D**)

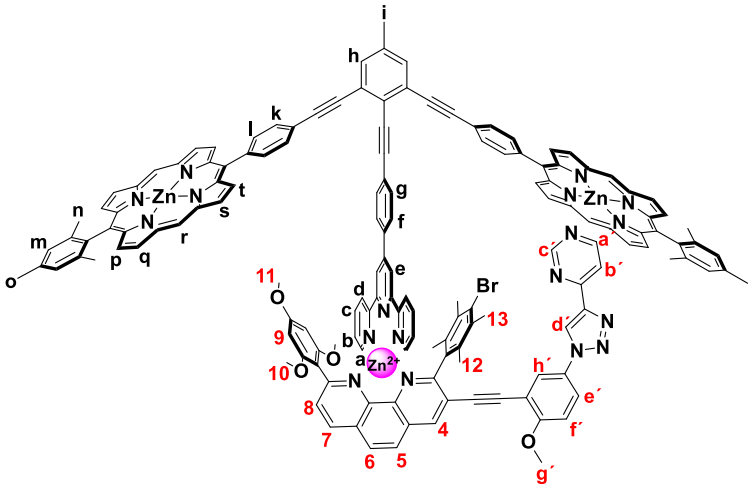


D

1-Ethynyl-2-(2-nitrovinyl)benzene (**A**) (35.0 mg, 202 µmol) and malonitrile (20.0 mg, 303 µmol) were dissolved in DCM (10 mL). Afterward, triethylamine (718 µL) and $[Cu(CH_3CN)_4]PF_6$ (10.0 mg, 26.8 µmol) were added, and the reaction was monitored till its completion by TLC (10 h). The crude reaction mixture was purified by column chromatography (R_f = 0.23, SiO_2, DCM:*n*-hexane =3:7), affording product **1** as colorless solid (35.0 mg, 72%), **Mp**: 109.0-110.6 °C. **^{1}H NMR** (500 MHz, $CDCl_3$, 298 K): δ = 4.69 (dd, ^3J = 5.5, 8.4 Hz, 1H, f-H), 4.86 (dd, ^2J = 15.0 Hz, ^3J = 5.5 Hz, 1H, g-H), 4.93 (dd, ^2J = 15.0 Hz, ^3J = 8.4 Hz, 1H, g-H), 5.92 (d, ^2J = 2.6 Hz, 1H, e/e'-H), 6.04 (d, ^2J = 2.6 Hz, 1H, e'/e-H), 7.28 (dd, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1H, d-H), 7.47 (td, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1H, b-H), 7.49 (dd, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1H, c-H), 7.63 (dd, ^3J = 7.6 Hz, ^4J = 1.4 Hz, 1H, a-H) ppm. **^{13}C NMR** ($CDCl_3$, 125 MHz): δ = 42.8, 49.9, 75.0, 112.6, 114.3, 122.8, 124.7, 130.7, 131.6, 135.5, 136.8, 142.2 ppm. **Anal. Calcd.** for $C_{13}H_9N_3O_2$•¼H_2O: C, 64.33; H, 3.53; N, 17.31. **Found**: C, 64.64; H, 3.64; N, 17.11.

1.4 Synthesis and characterization of complexes

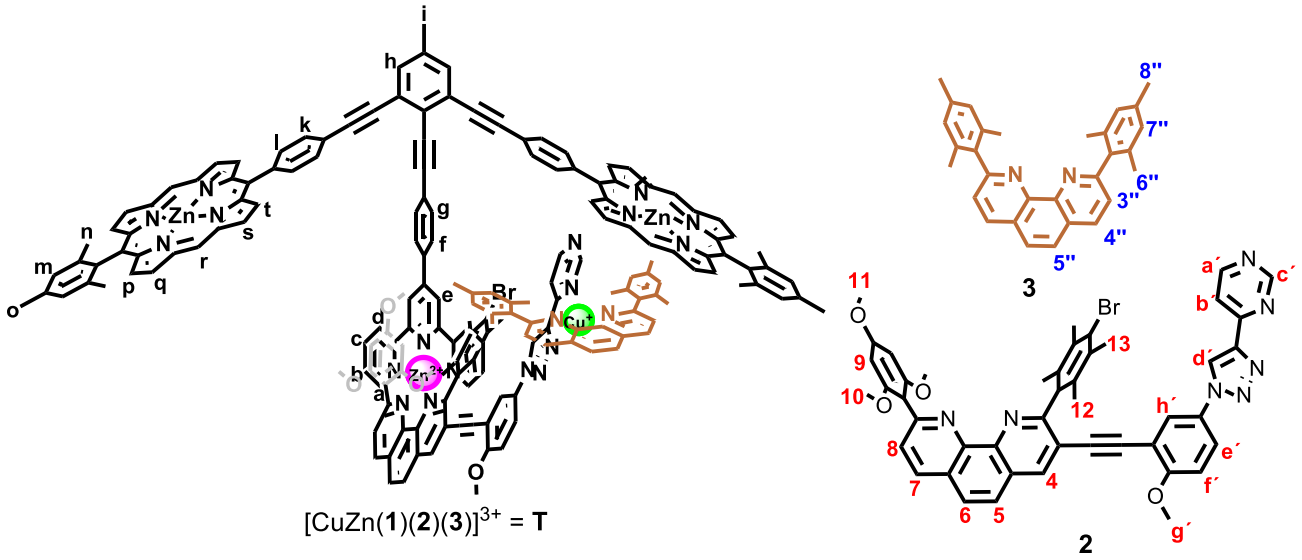
Rotor **R** = [Zn(**1**)(**2**)]$^{2+}$



[Zn(**1**)(**2**)]$^{2+}$

In an NMR tube, ligands **1** (0.534 mg, 0.333 µmol) and **2** (0.277 mg, 0.333 µmol) were dissolved in 500 µL of CD_2Cl_2. After the addition of $Zn(OTf)_2$ (0.121 mg, 0.333 µmol) as a standard solution in CD_3CN, NMR spectra were measured directly. Yield: quantitative. **Mp**: >250 °C. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 0.74 (s, 6H, 12-H), 1.65 (s, 6H, 13-H), 1.78 (s, 12H, n-H), 2.27 (dd, ^3J = 5.3 Hz, ^4J = 1.4 Hz, 1H, a'-H), 2.48 (s, 3H, i-H), 2.61 (s, 6H, o-H), 2.63 (s, 6H, 10-H), 2.65 (s, 3H, 11-H), 2.95 (d, ^4J = 1.4 Hz, 1H, c'-H), 3.75 (s, 3H, g'-H), 5.03 (s, 2H, 9-H), 6.14 (d, ^3J = 5.3 Hz, 1H, b'-H), 6.28 (d, ^4J = 2.7 Hz, 1H, h'-H), 6.71 (d, ^3J = 8.9 Hz, 1H, f'-H), 7.09 (dd, ^3J = 8.9 Hz, ^4J =2.7 Hz, 1H, e'-H), 7.33 (s, 4H, m-H), 7.39 (ddd, ^3J = 8.0 Hz, ^3J = 5.0 Hz, ^4J = 1.2 Hz, 2H, b-H), 7.45 (s, 1H, d'-H), 7.53 (ddd, ^3J = 5.0 Hz, ^4J = 1.2 Hz, ^5J = 0.8 Hz, 2H, a-H), 7.74 (s, 2H, h-H), 7.86 (d, ^3J = 8.2 Hz, 1H, 8-H), 8.13 (m, 6H, k+c-H), 8.16 (d, ^3J = 8.4 Hz, 2H, g/f-H), 8.20 (d, ^3J = 8.4 Hz, 2H, f/g-H), 8.29 (d, ^3J = 8.0 Hz, 1H, 6-H), 8.35 (d, ^3J = 8.0 Hz, 4H, l-H), 8.36 (d, ^3J = 8.0 Hz, 1H, 5-H), 8.49 (s, 2H, e-H), 8.51 (ddd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, ^5J = 0.8 Hz, 2H, d-H), 8.82 (d, ^3J = 8.2 Hz, 1H, 7-H), 8.88 (s, 1H, 4-H), 8.90 (d, ^3J = 4.4 Hz, 4H, p-H), 9.16 (d, ^3J = 4.4 Hz, 4H, t-H), 9.37 (d, ^3J = 4.4 Hz, 4H, q-H), 9.46 (d, ^3J = 4.4 Hz, 4H, s-H), 10.24 (s, 4H, r-H) ppm. **Anal. Calcd.** for $C_{152}H_{107}BrF_6N_{18}O_{10}S_2Zn_3 \cdot H_2O \cdot 2CH_2Cl_2$: C, 61.91; H, 3.81; N, 8.44; S, 2.15. **Found**: C, 62.02; H, 4.01; N, 8.51; S, 1.86. **ESI-MS**: *m*/*z* (%) = 1250.7 (100) [Zn(**1**)(**2**)]$^{2+}$.

Turnstile **T** = $[CuZn(\mathbf{1})(\mathbf{2})(\mathbf{3})]^{3+}$



In an NMR tube, ligands **1** (0.515 mg, 0.321 µmol) and **2** (0.267 mg, 0.321 µmol) were dissolved in 500 µL of CD_2Cl_2. After addition of $Zn(OTf)_2$ (0.117 mg, 0.321 µmol) as a standard solution in CD_3CN, 2,9-dimesityl-phenanthroline (**3**) (0.134 mg, 0.321 µmol) and $[Cu(CH_3CN)_4]PF_6$ (0.120 mg, 0.321 µmol) were added. NMR spectra were measured immediately. Yield: quantitative. **Mp**: >250 °C. ^{1}H NMR (600 MHz, CD_2Cl_2, 298 K): δ = 0.70 (s, 6H, 12-H), 1.04 (s, 6H, 8''-H), 1.26 (s, 6H, 13-H), 1.68 (s, 12H, 6''-H), 1.97 (s, 12H, n-H), 2.61 (s, 6H, o-H), 2.64 (s, 6H, 10-H), 2.67 (s, 3H, 11-H), 2.71 (s, 3H, i-H), 3.61 (s, 3H, g'-H), 4.93 (s, 2H, 9-H), 5.15 (s, 2H, 7''-H), 5.72 (s, 2H, 7''-H), 6.02 (d, ^3J = 5.3 Hz, 1H, b'-H), 6.70 (dd, ^3J = 5.3 Hz, ^4J =1.4 Hz, 1H, a'-H), 6.80 (d, ^4J = 1.4 Hz, 1H, c'-H), 7.00 (d, ^4J = 2.7 Hz, 1H, h'-H), 7.29 (s, 4H, m-H), 7.32 (d, ^3J = 8.9 Hz, 1H, f'-H), 7.34 (ddd, ^3J = 8.0 Hz, ^3J = 5.0 Hz, ^4J = 1.2 Hz, 2H, b-H), 7.45 (ddd, ^3J = 5.0 Hz, ^4J = 1.2 Hz, ^5J = 0.8 Hz, 2H, a-H), 7.49 (dd, ^3J = 8.9 Hz, ^4J =2.7 Hz, 1H, e'-H), 7.56 (d, ^3J = 8.0 Hz, 2H, 3''-H), 7.76 (s, 2H, h-H), 7.89 (d, ^3J = 8.2 Hz, 1H, 8-H), 8.03 (m, 6H, k+f/g-H), 8.10 (s, 2H, 5''-H), 8.14 (d, ^3J = 8.0 Hz, 1H, 6-H), 8.35 (d, ^3J = 8.0 Hz, 5H, l+5-H), 8.16 (m, 4H, c+f/g-H), 8.36 (ddd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, ^5J = 0.8 Hz, 2H, d-H), 8.49 (s, 3H, e+ d'-H), 8.60 (d, ^3J = 8.0 Hz, 2H, 4''-H), 8.83 (d, ^3J = 8.2 Hz, 1H, 7-H), 8.89 (d, ^3J = 4.4 Hz, 4H, p-H), 8.94 (s, 1H, 4-H), 9.14 (d, ^3J = 4.4 Hz, 4H, t-H), 9.38 (d, ^3J = 4.4 Hz, 4H, q-H), 9.44 (d, ^3J = 4.4 Hz, 4H, s-H), 10.28 (s, 4H, r-H) ppm. **Mp**: >250 °C. **Anal. Calcd.** for $C_{182}H_{135}BrCuF_{12}N_{20}O_{10}S_2Zn_3 \bullet CH_2Cl_2$: C, 62.62; H, 3.93; N, 7.98; S, 1.83. **Found**: C, 62.47; H, 4.00; N, 8.33; S, 1.92. **ESI-MS**: *m/z* (%) = 1564.6 (100) $[CuZn(\mathbf{1})(\mathbf{2})(\mathbf{3})(PF_6)]^{2+}$.

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

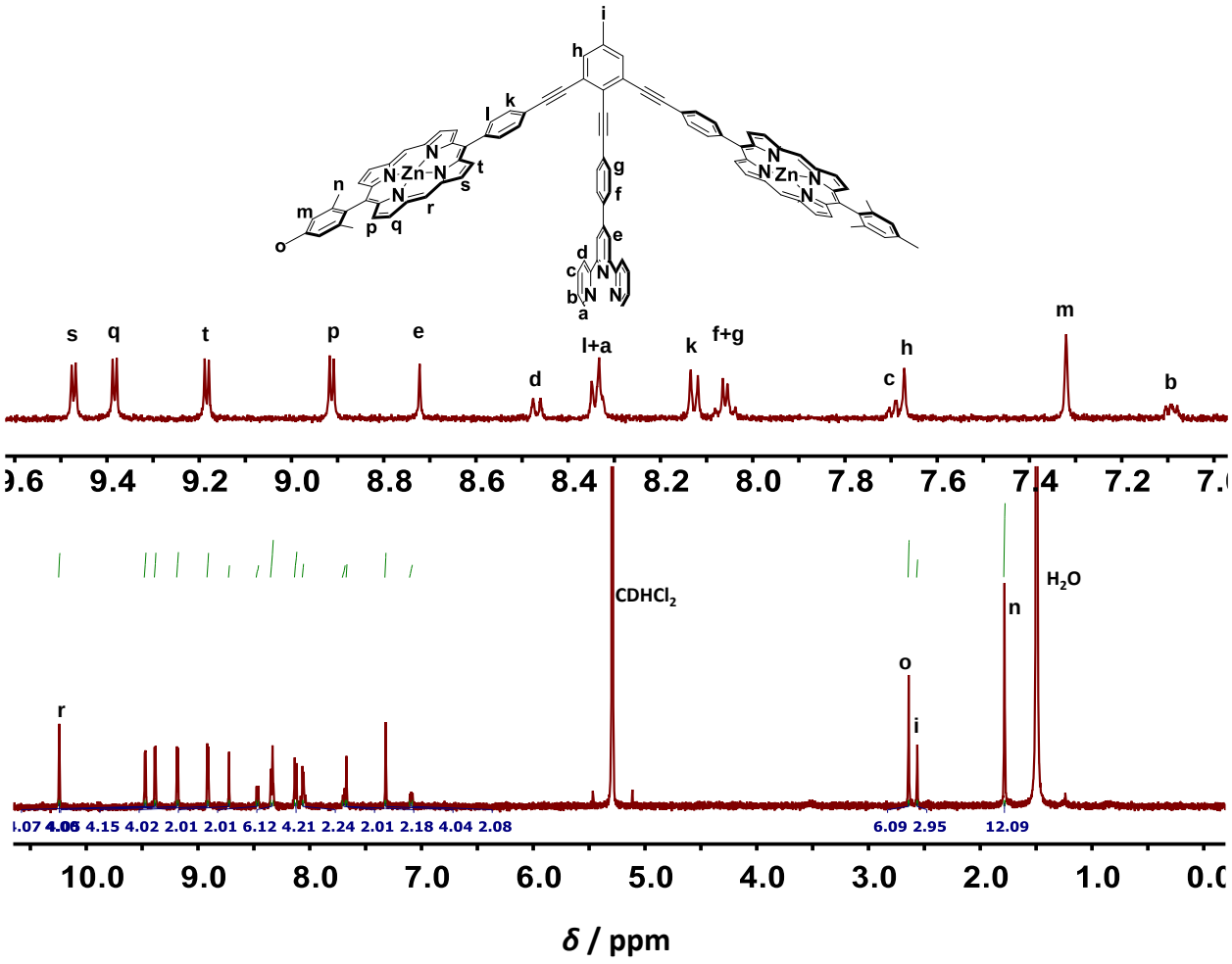


Figure S1. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 298 K) of ligand **1**.

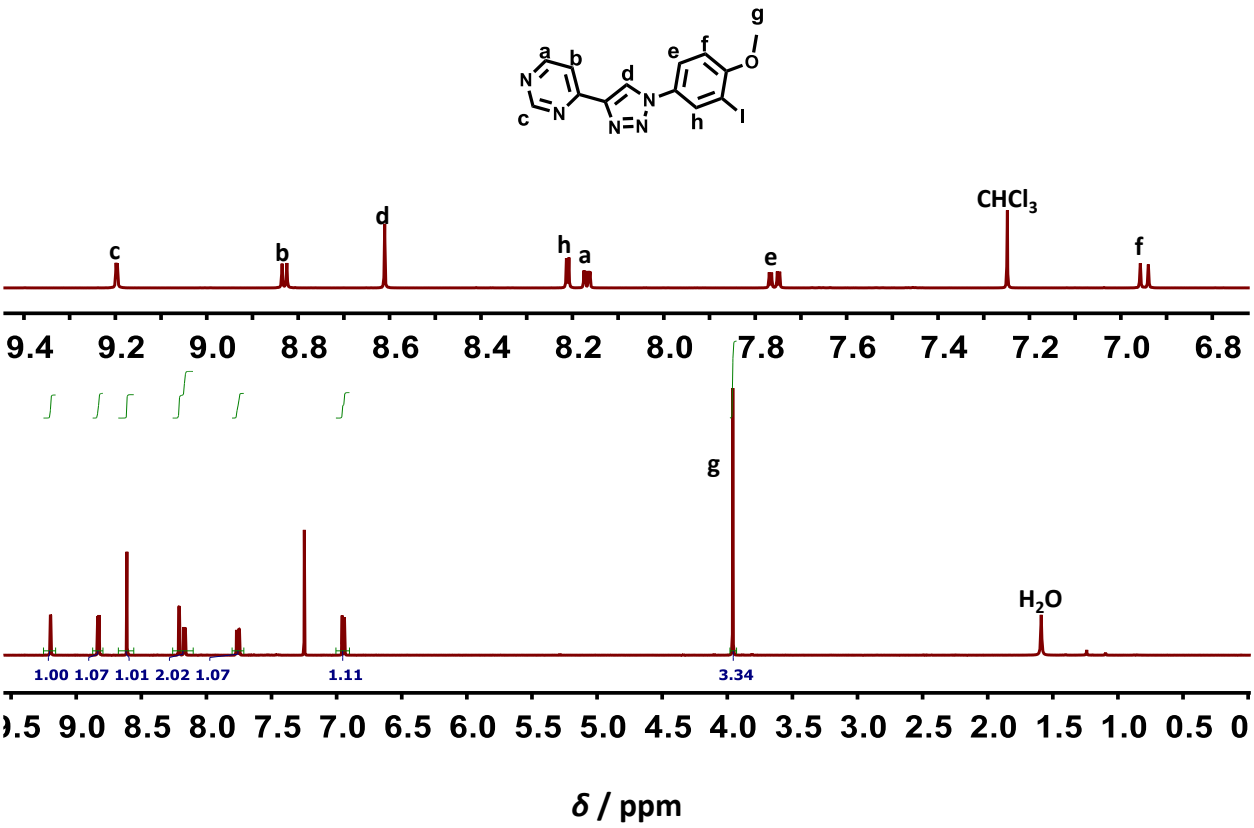


Figure S2. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **8**.

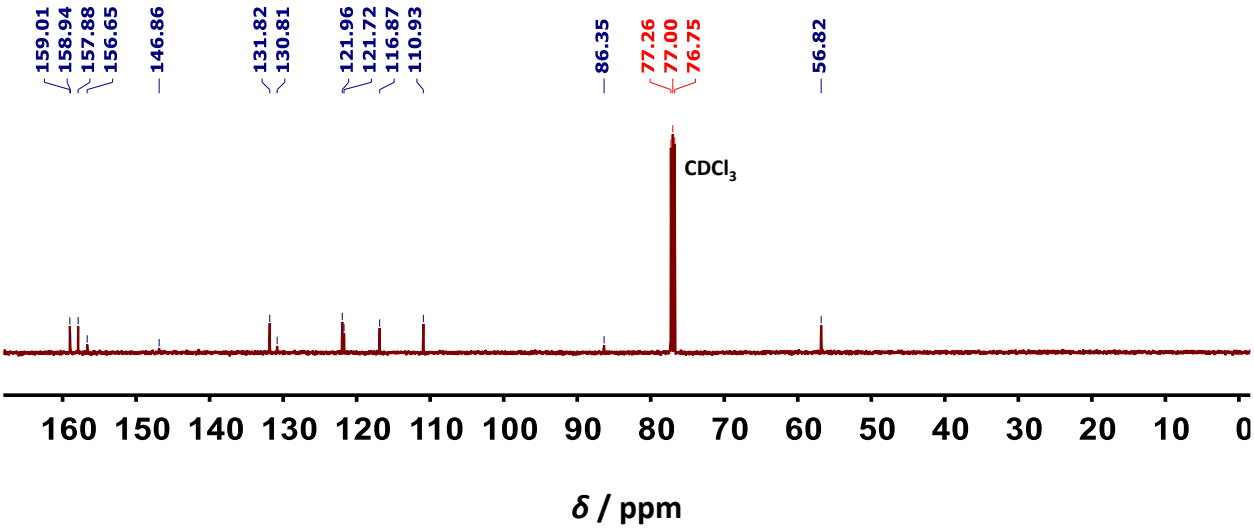


Figure S3. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **8**.

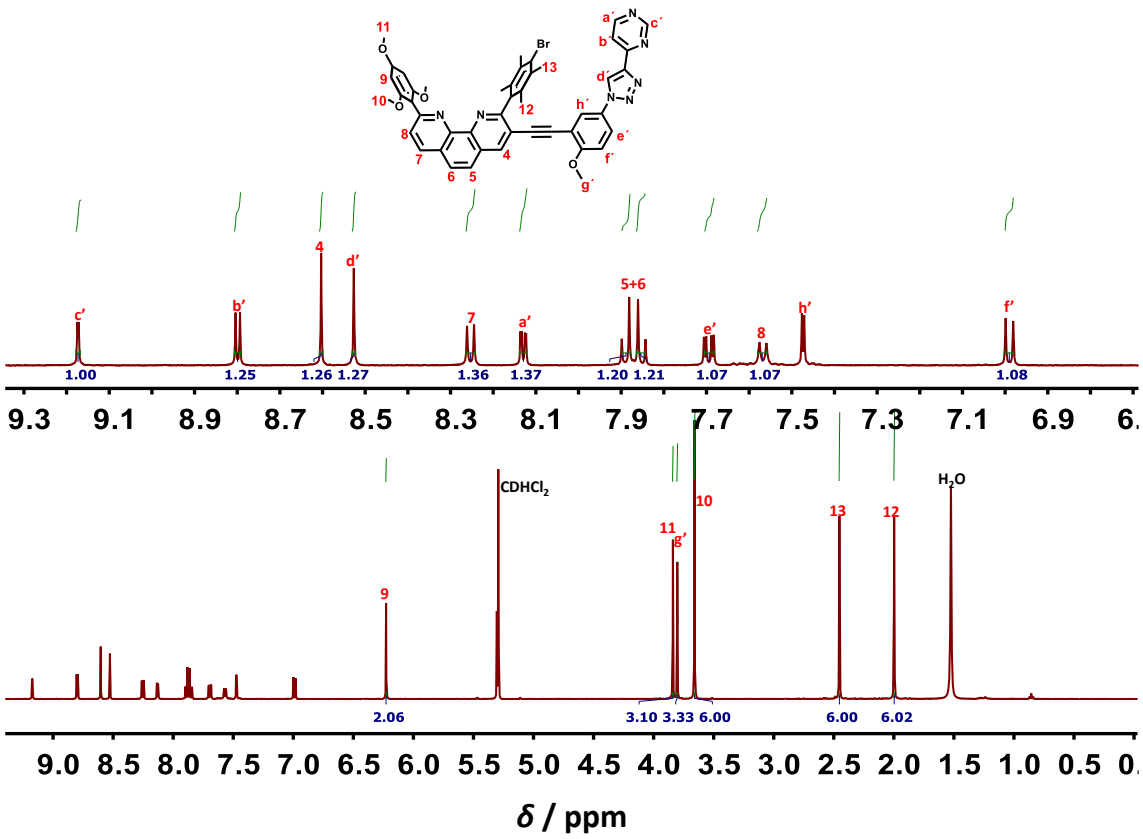


Figure S4. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2, 298 K) of ligand **2**.

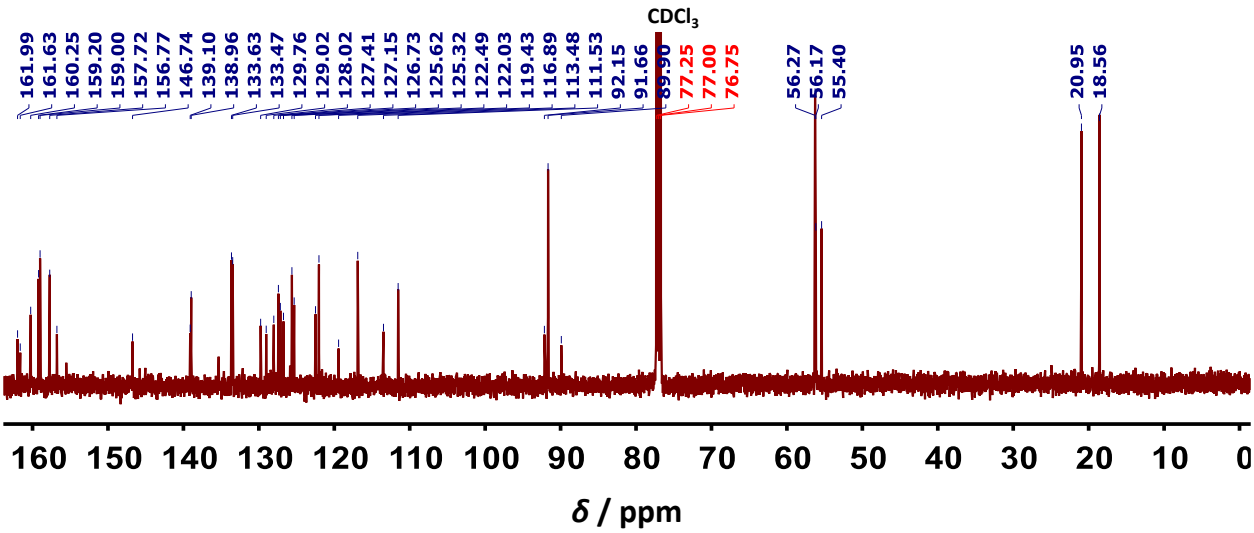


Figure S5. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of ligand **2**.

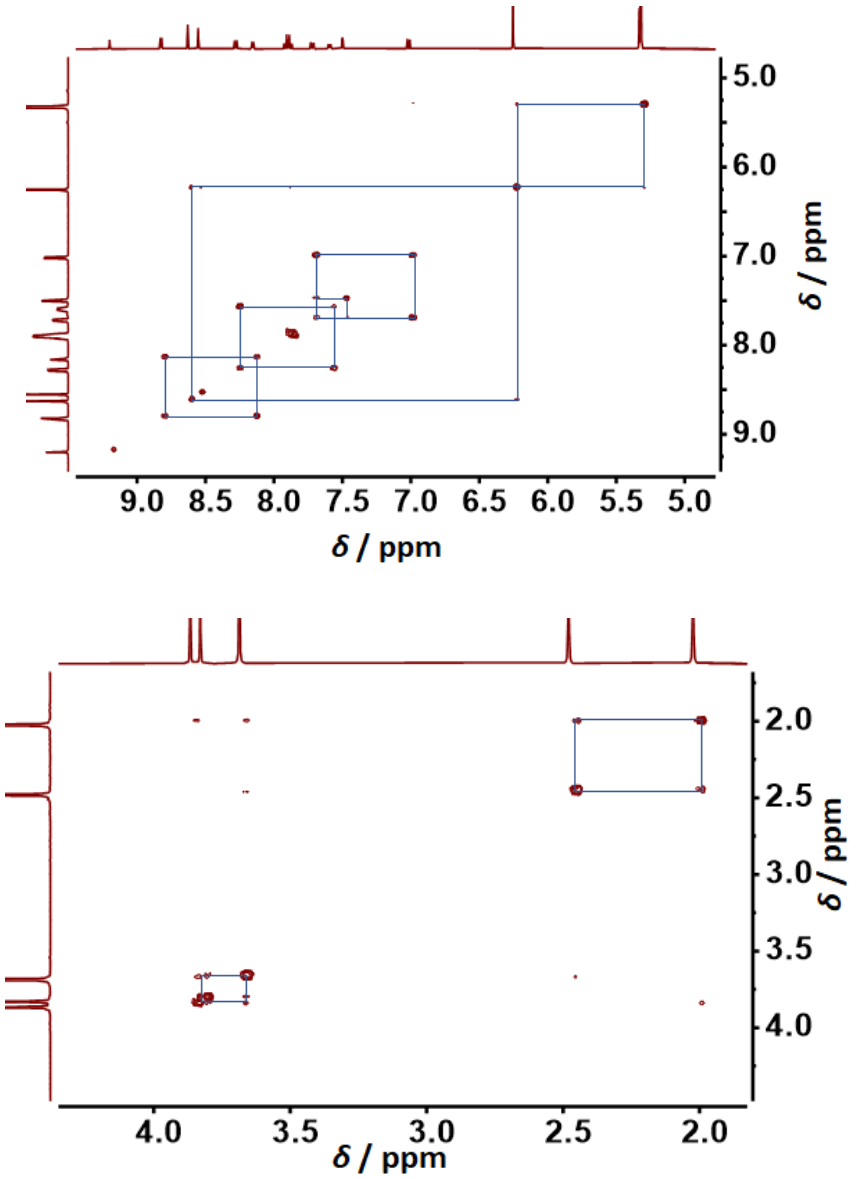


Figure S6. ^{1}H-^{1}H COSY NMR spectra (500 MHz, CD_2Cl_2, 298 K) of ligand **2**.

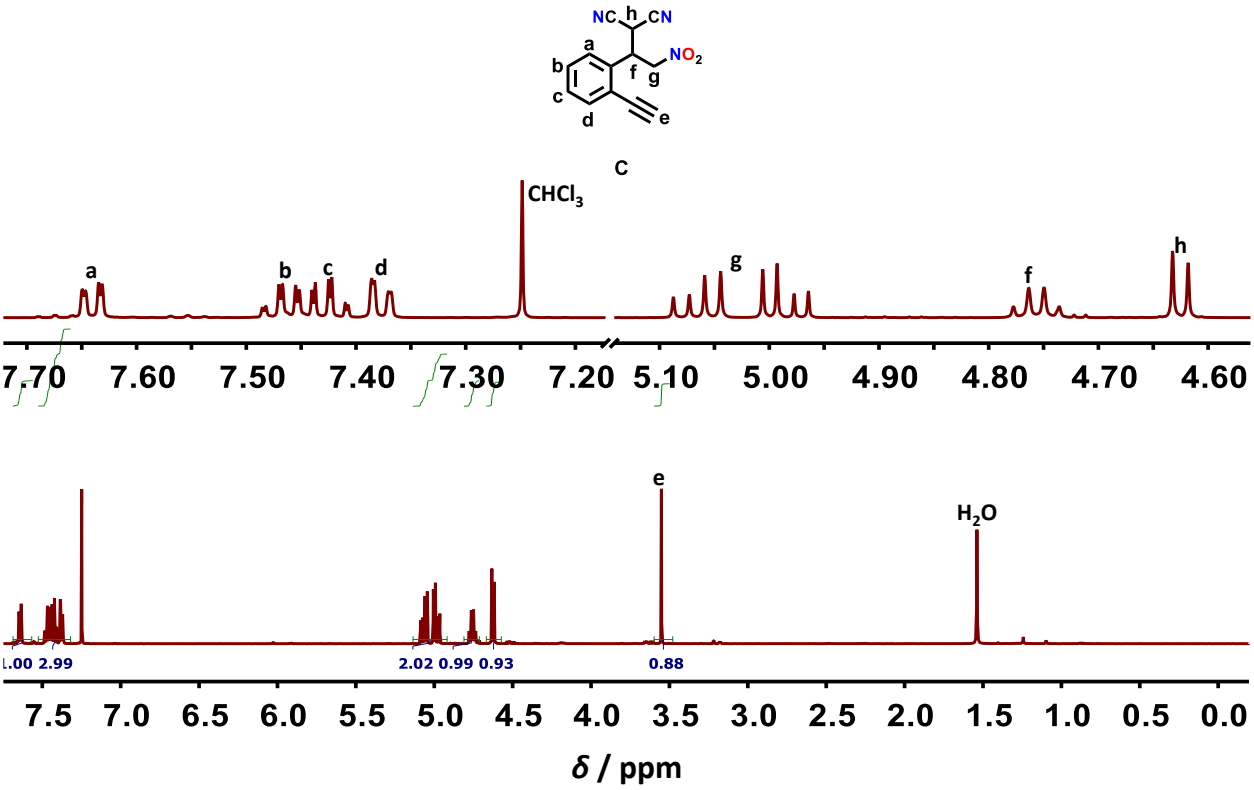


Figure S7. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **C**.

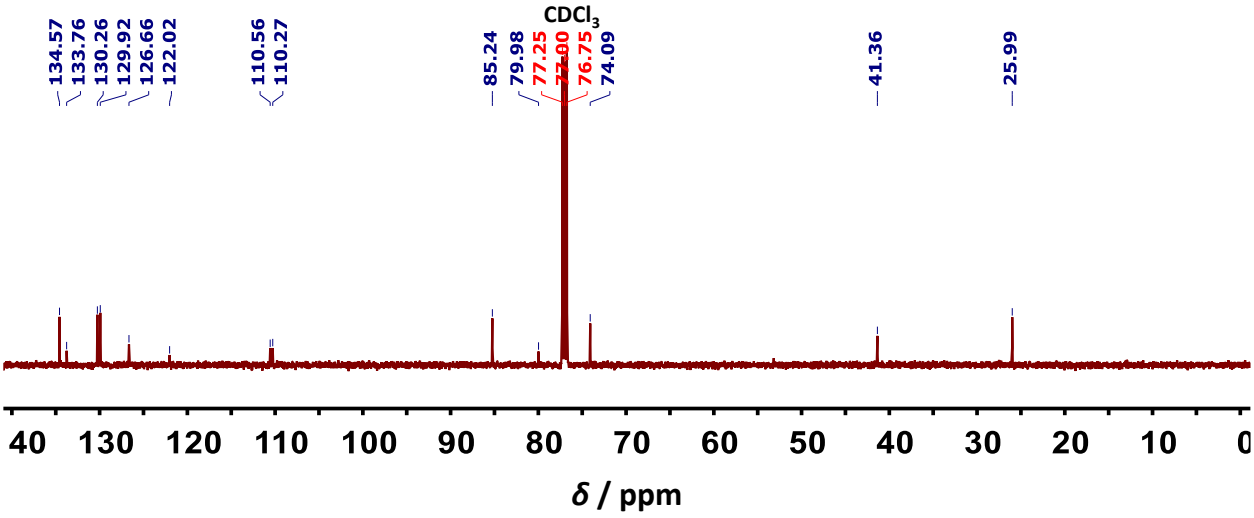


Figure S8. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **C**.

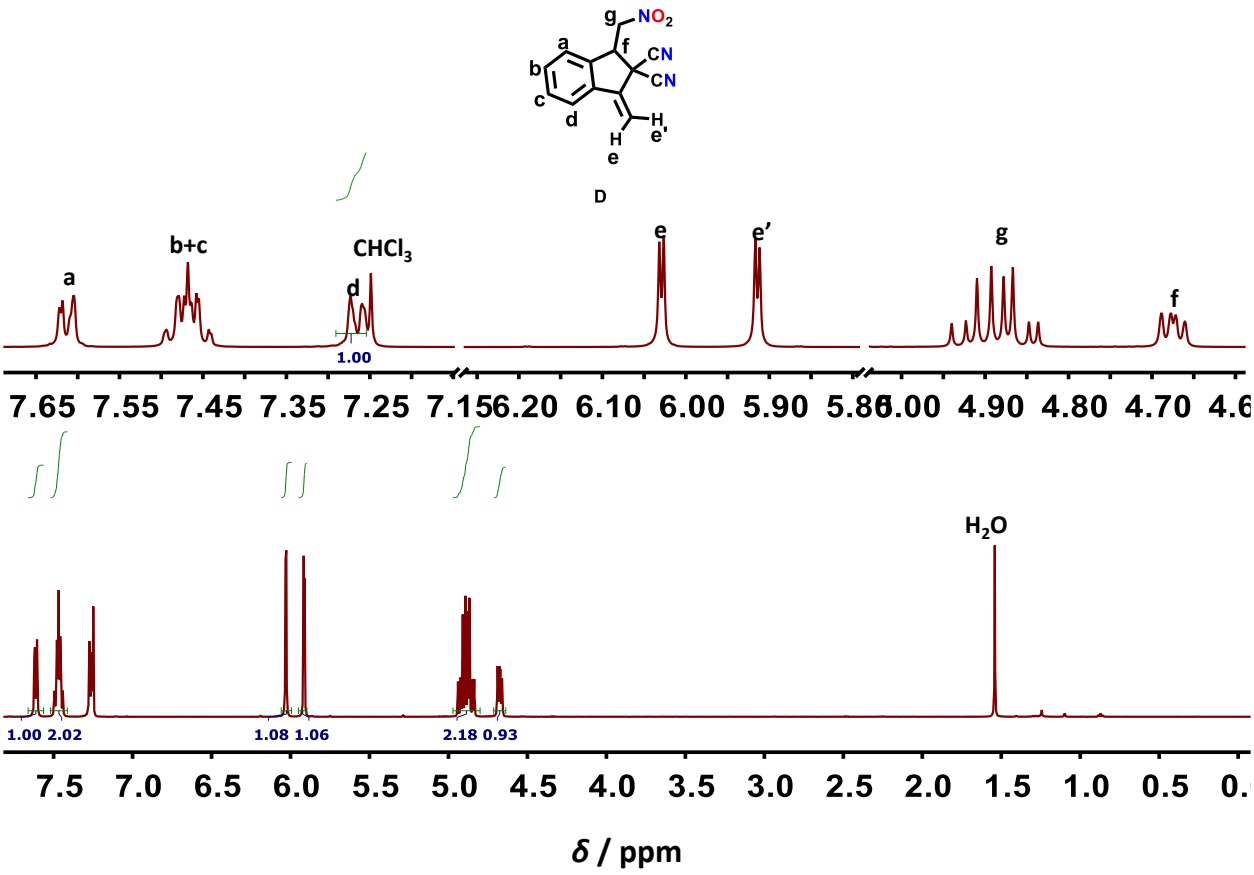


Figure S9. ^{1}H NMR spectrum (500 MHz, $CDCl_3$, 298 K) of **D**.

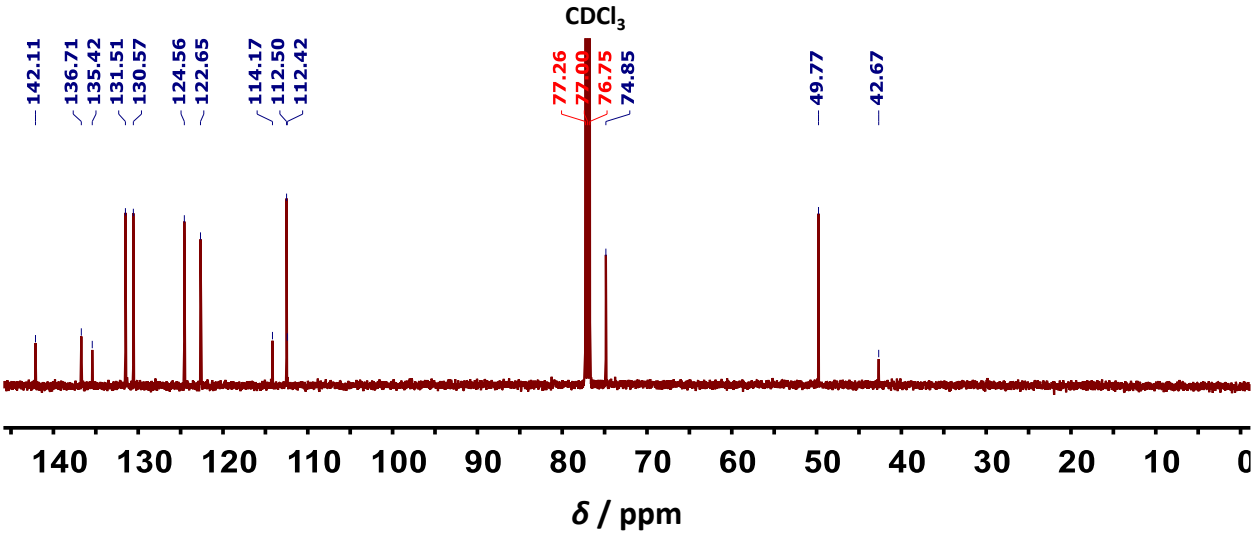


Figure S10. ^{13}C NMR spectrum (125 MHz, $CDCl_3$, 298 K) of **D**.

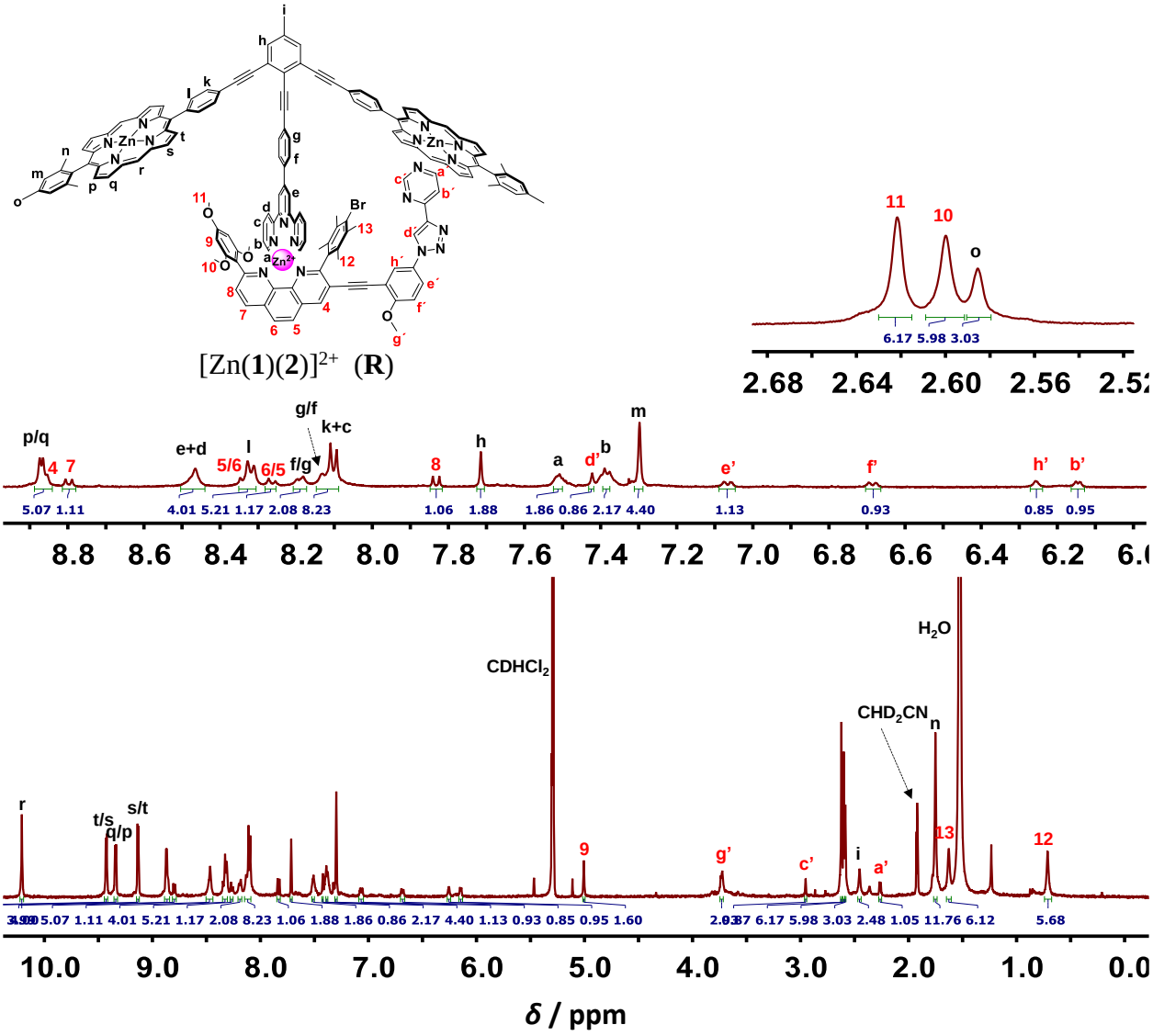


Figure S11. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2:CD_3CN = 20:1, 298 K) of **R** = $[Zn(\mathbf{1})(\mathbf{2})]^{2+}$.

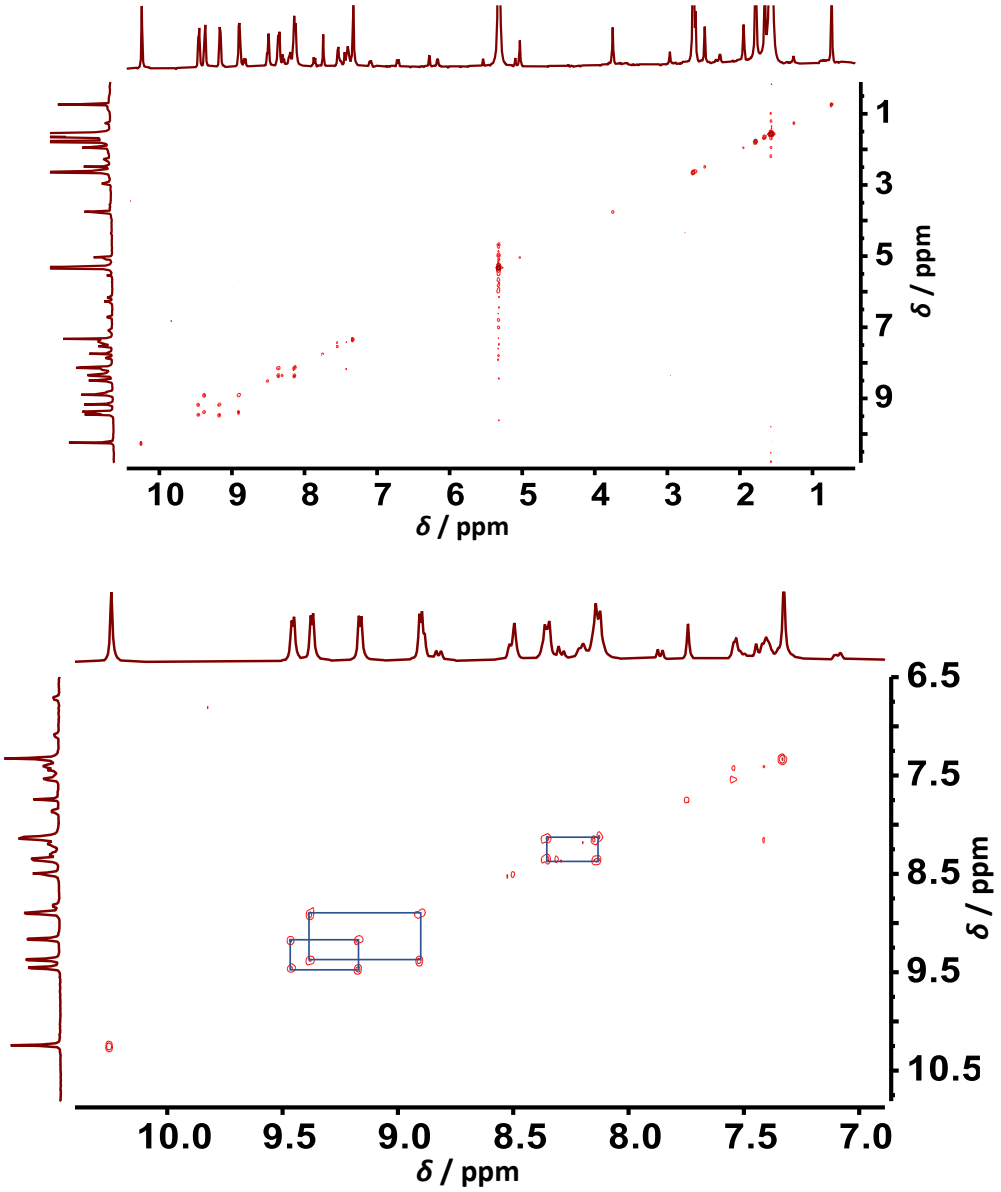


Figure S12. ^{1}H-^{1}H COSY spectra (500 MHz**,** CD_2Cl_2:CD_3CN = 20:1, 298 K) of **R** = $[Zn(\mathbf{1})(\mathbf{2})]^{2+}$**.**

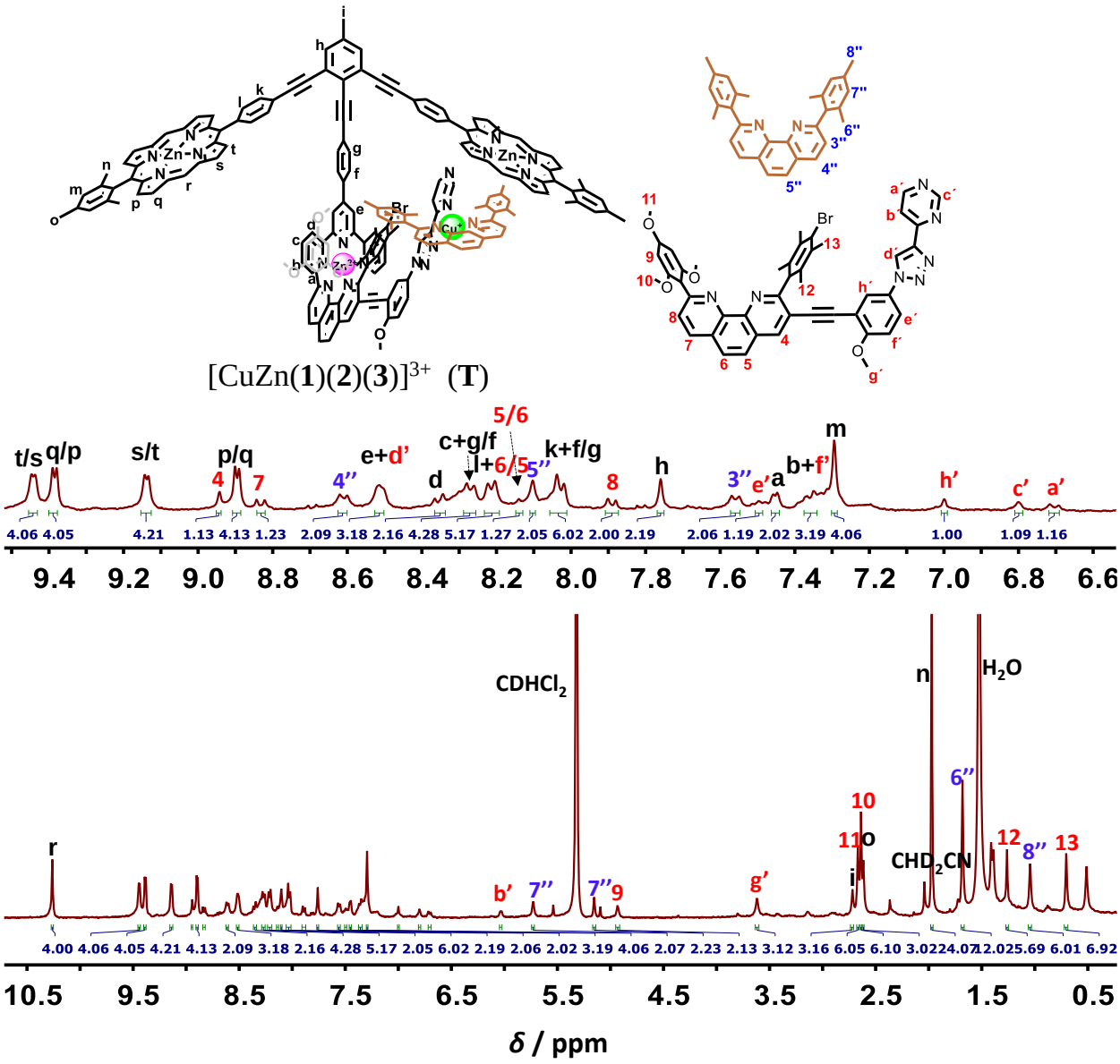


Figure S13. ^{1}H NMR spectrum (500 MHz, CD_2Cl_2:CD_3CN = 20:1, 298 K) of **T** = [CuZn(**1**)(**2**)(**3**)]$^{3+}$.

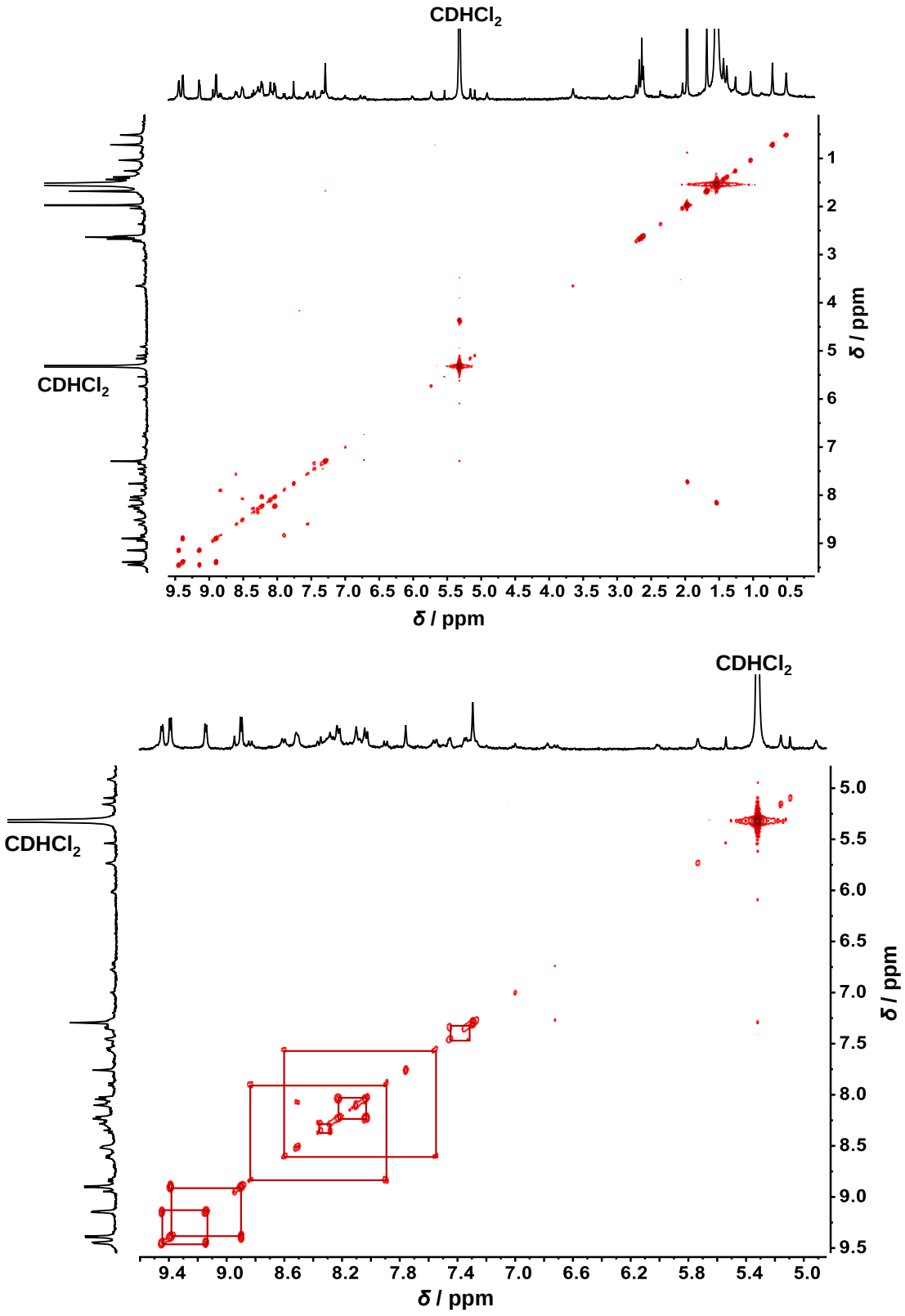


Figure S14. ^{1}H-^{1}H COSY spectrum (500 MHz**,** CD_2Cl_2:CD_3CN = 20:1, 298 K) of **T** = $[CuZn(\mathbf{1})(\mathbf{2})(\mathbf{3})]^{3+}$.

3. Comparison of NMR spectra of final complexes

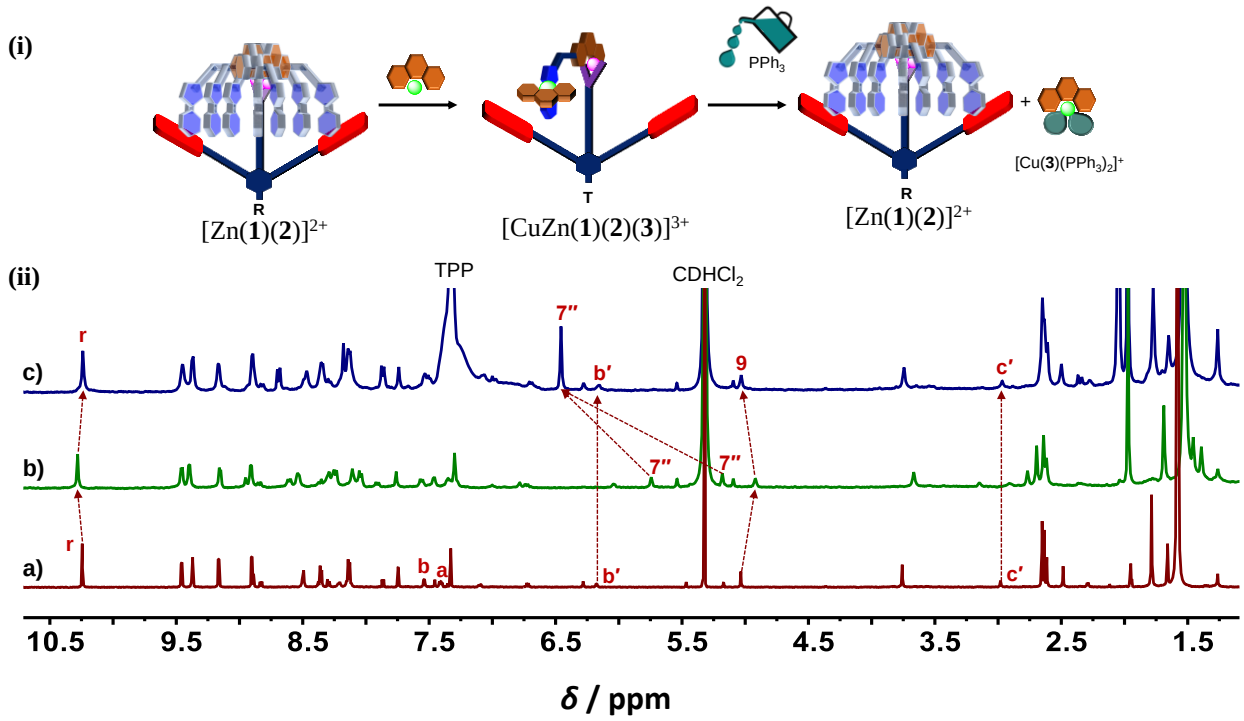


Figure S15. (i) Cartoon representation of the transformation **R** → **T** and regeneration of **R** from **T**; (ii) comparison of partial ^{1}H NMR spectra {600 MHz, CD_2Cl_2:CD_3CN (20:1), 298 K} of a) **R**, b) **T**, c) **R** and [Cu(**3**)$(PPh_3)_2]^+$.

4.Variable temperature (VT) study and determination of kinetic parameters

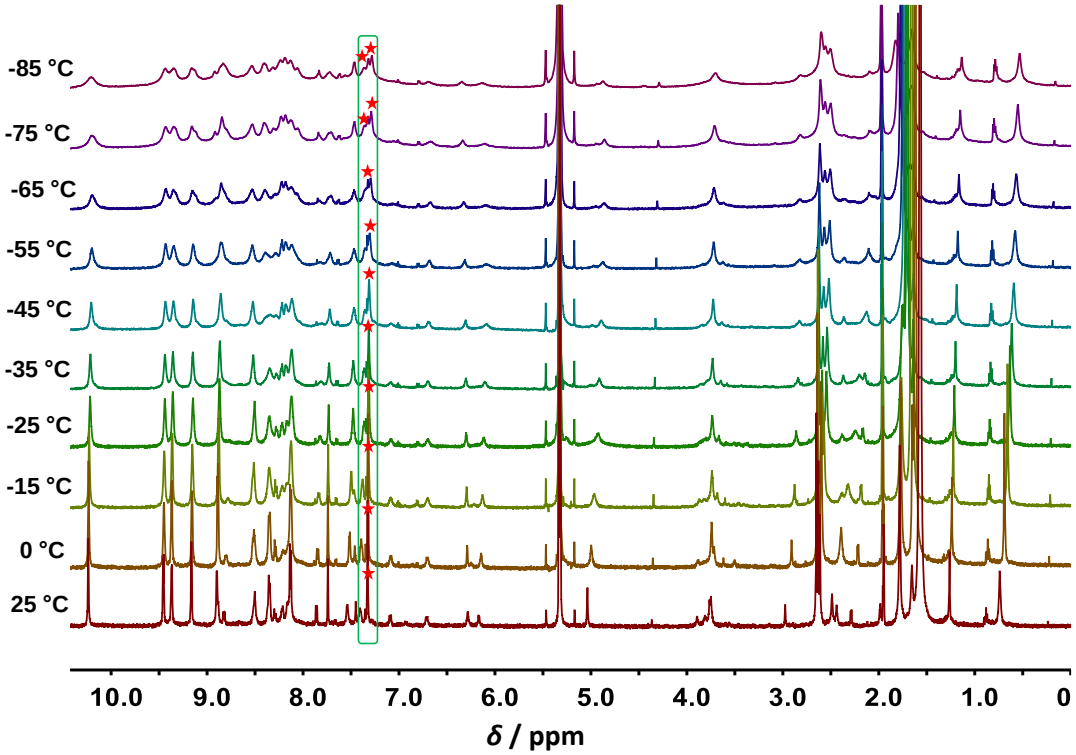


Figure S16. VT-^{1}H NMR spectra (600 MHz, CD_2Cl_2:CD_3CN =20:1) of rotor **R**.

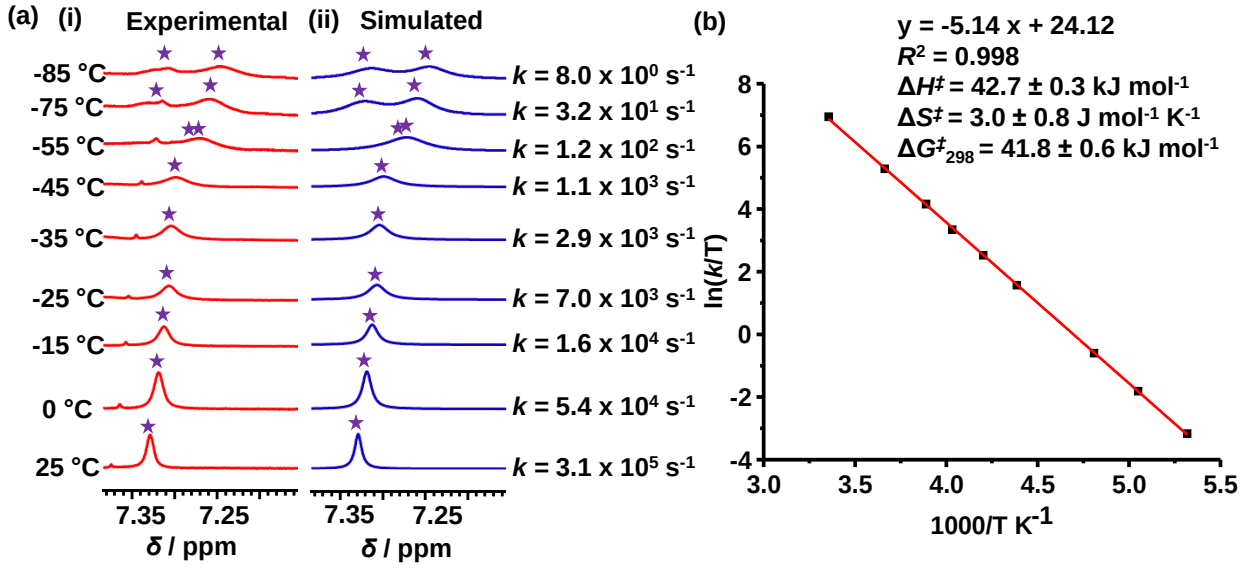


Figure S17. (a) Experimental (left) and simulated (right) VT-^{1}H NMR spectrum (600 MHz, CD_2Cl_2:CD_3CN =20:1) of proton signal m-H of $[Zn(\mathbf{1})(\mathbf{2})]^{2+}$, and (b) Eyring plot of rotational exchange in $[Zn(\mathbf{1})(\mathbf{2})]^{2+}$.

5. DOSY NMR spectra

Calculation of hydrodynamic radius: The diffusion coefficients *D* for the 3- and 5-component assemblies were obtained from their corresponding DOSY spectrum. The hydrodynamic radius *r* was calculated by using the Stokes Einstein equation $r = k_BT/6\pi\eta D$.

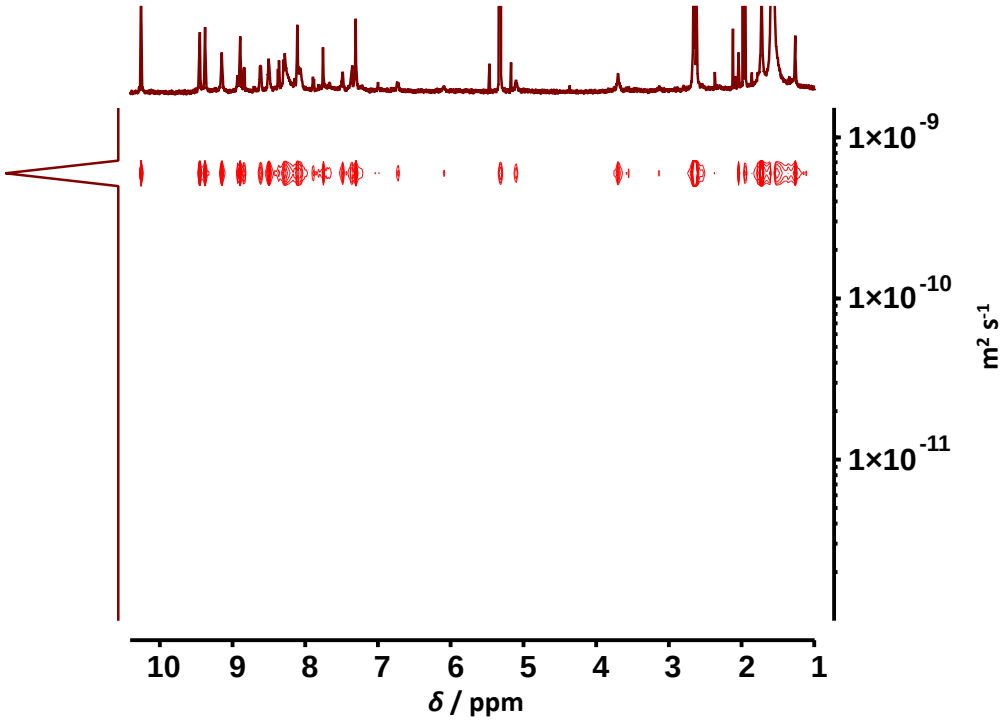


Figure S18. DOSY NMR of rotor **R** = $[Zn(\mathbf{1})(\mathbf{2})]^{2+}$ in (600 MHz, CD_2Cl_2:CD_3CN =20:1, 298 K). Diffusion coefficient $D = 5.90 \times 10^{-10}$ m^2 s^{-1}, hydrodynamic radius r = 9.0 Å.

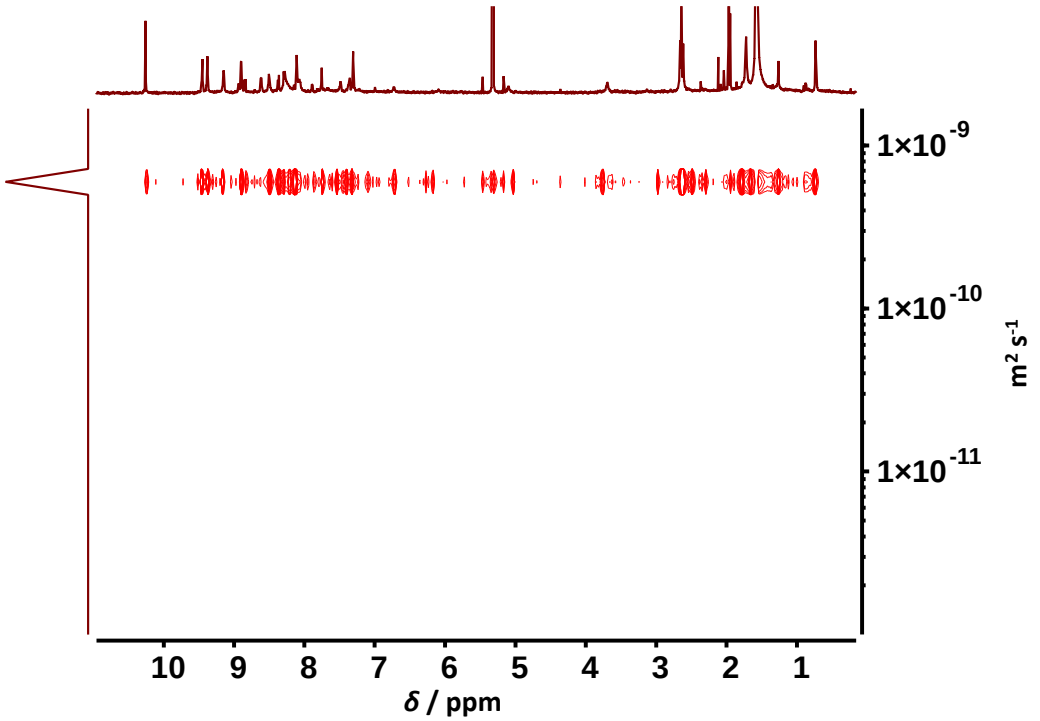


Figure S19. DOSY NMR of turnstile **T** = [CuZn(**1**)(**2**)(**3**)]$^{3+}$ in (600 MHz, CD_2Cl_2:CD_3CN =20:1, 298 K). Diffusion coefficient $D = 5.99 \times 10^{-10}$ m^2 s^{-1}, hydrodynamic radius $r = 8.9$ Å.

6. ESI-MS spectra

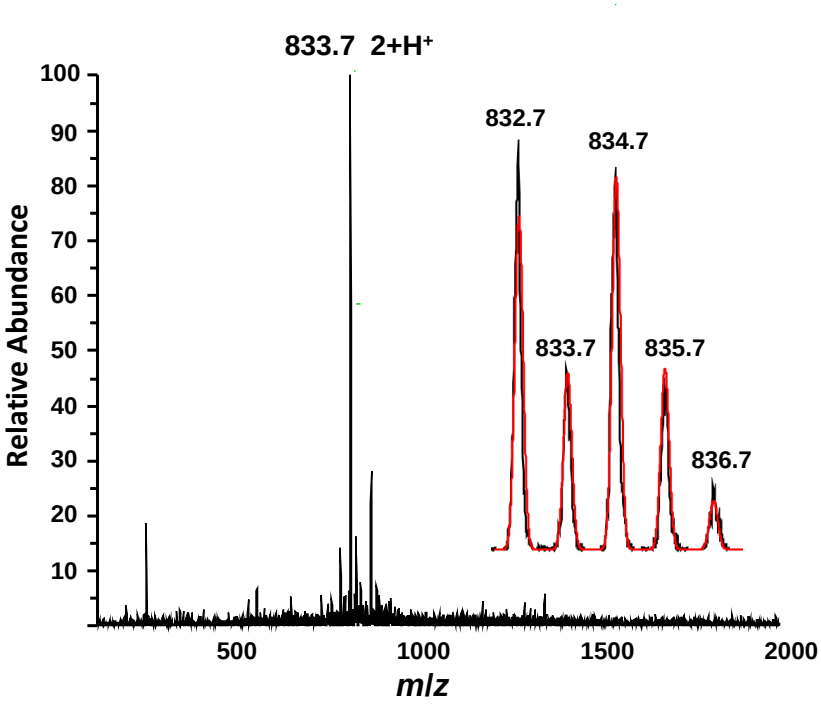


Figure S20. ESI-MS of Ligand **2** in CH_2Cl_2.

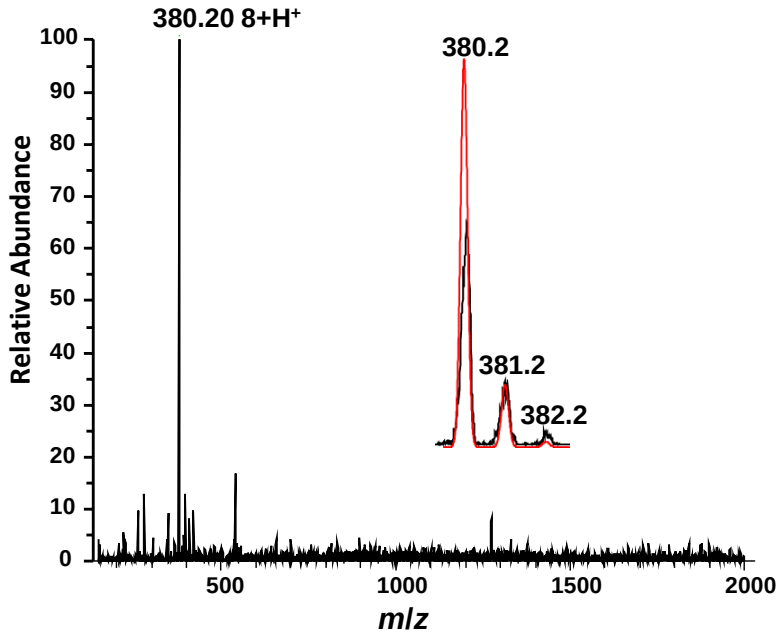


Figure S21. ESI-MS of **8** in CH_2Cl_2.

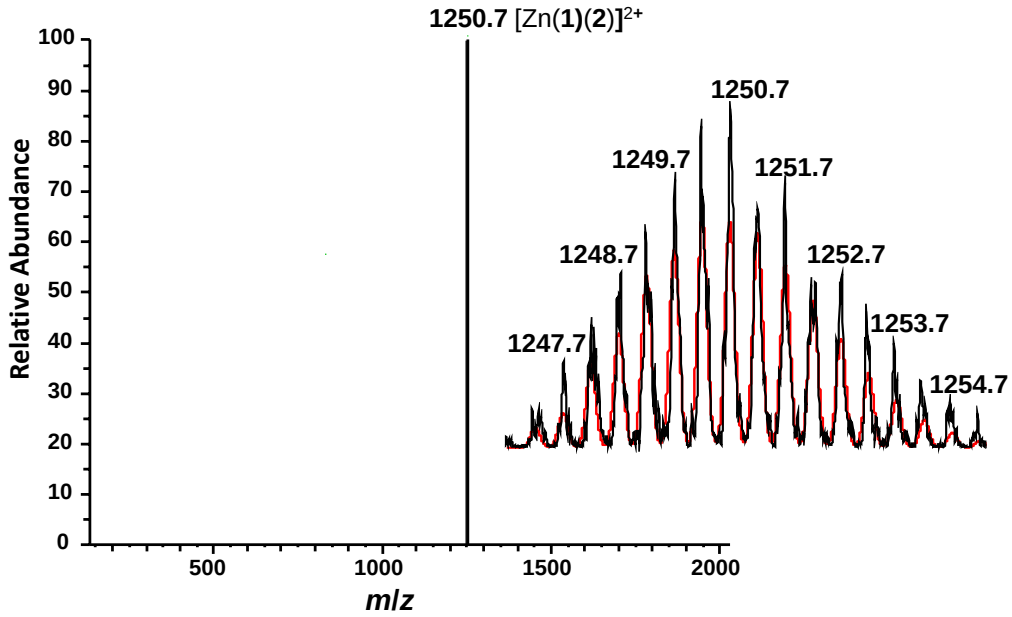


Figure S22. ESI-MS of **R** = $[Zn(\mathbf{1})(\mathbf{2})]^{2+}$ in CH_2Cl_2.

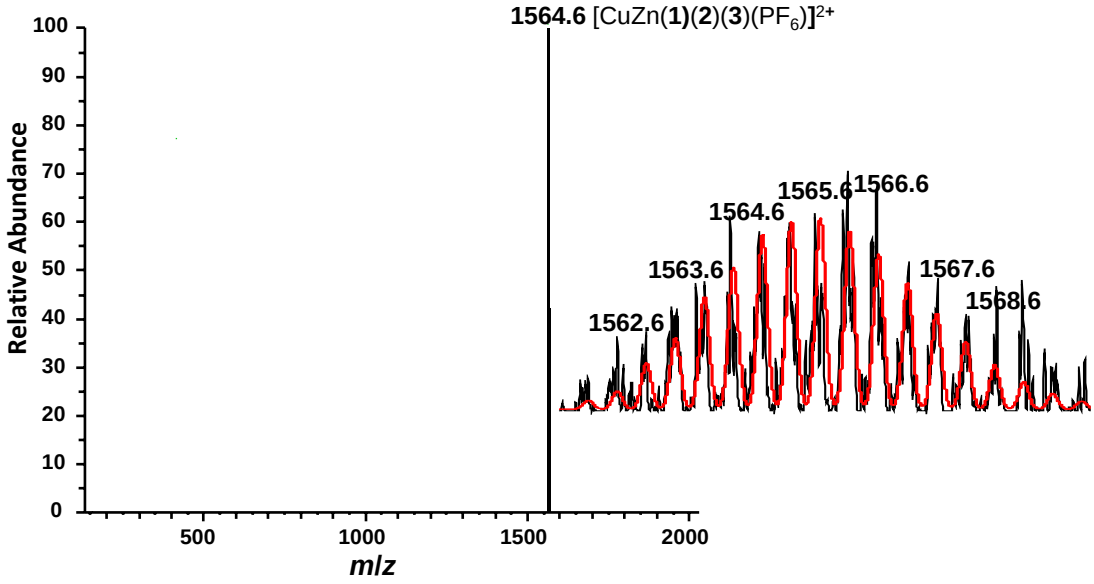
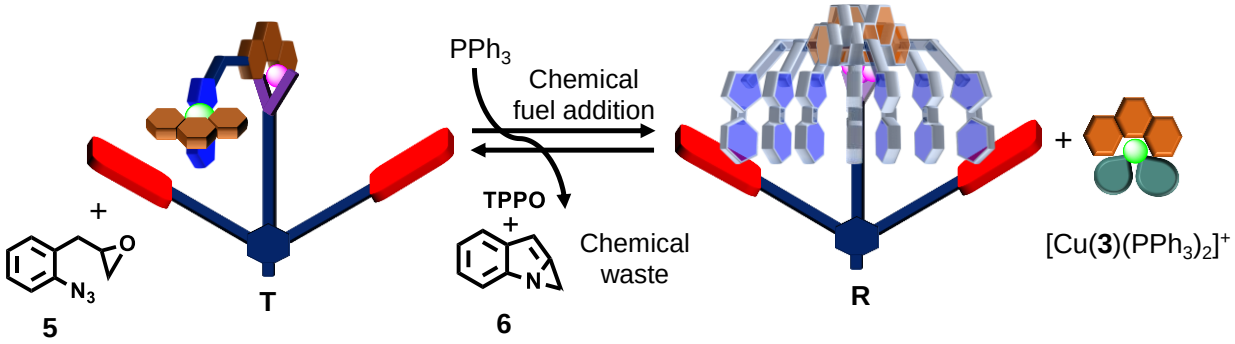


Figure S23. ESI-MS of T = $[CuZn(\mathbf{1})(\mathbf{2})(\mathbf{3})]^{3+}$ in CH_2Cl_2.

7. Chemical fuel driven transient formation of rotor R

To generate the transient rotor **R** upon addition of chemical fuel, firstly, turnstile **T** was synthesized by mixing of ligand **1** (0.515 mg, 0.321 μmol), **2** (0.267 mg, 0.321 μmol), 2,9-dimesitylphenanthroline (**3**) (0.134 mg, 0.321 μmol), ($Zn(OTf)_2$ (0.117 mg, 0.321 μmol), and $[Cu(CH_3CN)_4]PF_6$ (0.120 mg, 0.321 μmol) in 500 μL of CD_2Cl_2 in an NMR tube. After that, the co-fuel oxidant **5** (0.506 mg, 2.89 μmol) was added. For each dissipative cycle, the chemical fuel PPh_3 (0.168 mg, 0.642 μmol) was added to the mixture. The whole process was monitored by ^1H NMR spectroscopy.



7.1 Chemical fuel driven dissipative first cycle

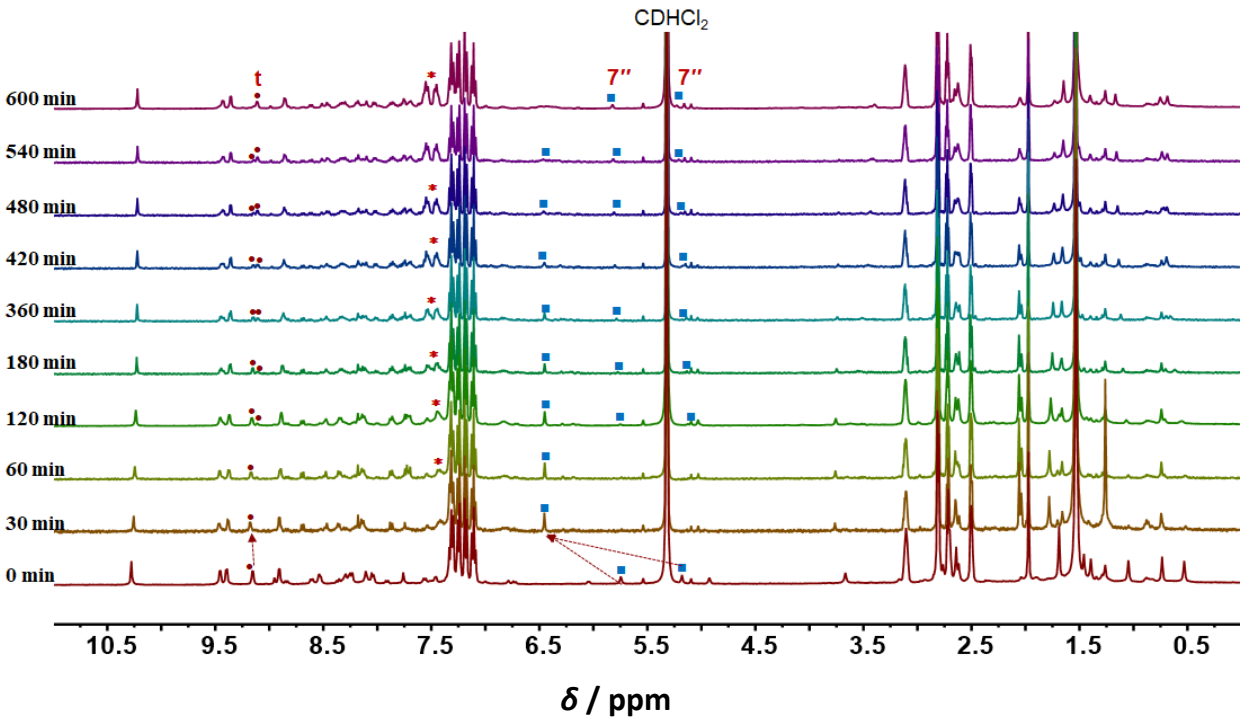


Figure S24. Partial ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) spectra recorded at various times after mixing the chemical fuel PPh_3 with a mixture of the turnstile **T** and oxidant **5** at 298 K. Addition of the chemical PPh_3 led to the instant formation of rotor **R**, which reverted back to the initial **T** over 10 h while producing the waste triphenylphosphine oxide ($OPPh_3$) and **6**. The symbols represent the following proton signals: ●, t-H proton signal of **R**; ■, 7''-H proton of signal of **3**; *, waste $OPPh_3$.

7.2 Chemical fuel driven second cycle

Before restarting the second dissipative cycle, reacted amount of oxidant **5** ((0.112 mg, 0.642 μmol) was added to the reaction mixture that obtained after the first dissipative cycle.

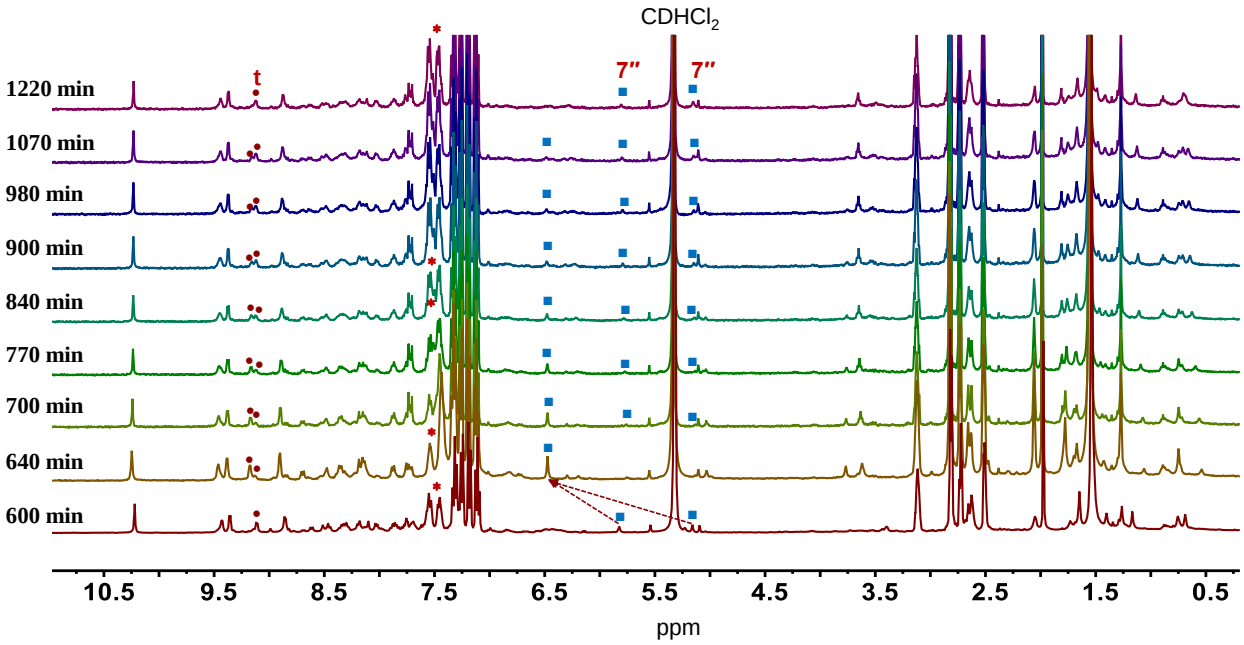


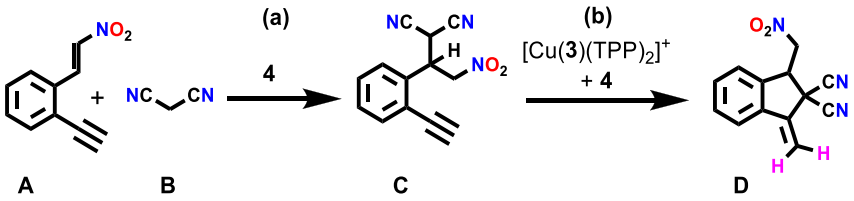
Figure S25. Partial ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K) spectra of recorded at various time after mixing of PPh_3 to the mixture of {**T** + **5** + **6** + $OPPh_3$} at 298 K. Addition of PPh_3 lead to instant formation of rotor **R** that reverted back to initial **T** after 10 h by producing more waste $OPPh_3$ and **6**. The symbols represent as follows: ●, t-H proton signal of **R**; ■, 7''-H proton of signal of **3**; ∗, waste $OPPh_3$.

8. Catalytic experiments

General procedure for all catalytic experiments.

All catalytic experiments were performed in CD_2Cl_2 in an NMR tube at 298 K. Ligands **1**-**3**, the chemical fuel PPh_3, salt $[Cu(CH_3CN)_4]PF_6$ and substrate **A** were transferred as solids to the NMR tube. The $Zn(OTf)_2$ was added as a standard solution in CD_3CN. The catalyst *N*-methylpyrrolidine (**4**), substrate **B** and TCE were added as a standard solution in deuterated DCM. Product yields were determined from ^{1}H NMR by using 1,1,2,2-tetrachloroethane (TCE) as an internal standard.

8.1 Model Catalysis



Scheme 4. Sequential Michael/5-*exo*-*dig* cyclization reaction by employing catalyst **4** and $[Cu(\mathbf{3})(TPP)]^+$.

8.1.1 Model catalysis of Michael-addition reaction in presence of only catalyst 4

Substrate 1-ethynyl-2-(2-nitrovinyl)benzene (**A**) (0.623 mg, 3.21 µmol), malononitrile (**B**) (0.635 mg, 9.63 µmol) and TCE (0.536 mg, 3.21 µmol) were dissolved in 500 µL of CD_2Cl_2 in an NMR tube. Then *N*-methyl pyrrolidine (**4**) (0.055 mg, 0.64 µmol) was added as catalyst. The reaction mixture was kept at 298 K for 10 h. The ^{1}H NMR revealed that 64% of product **C** had formed.

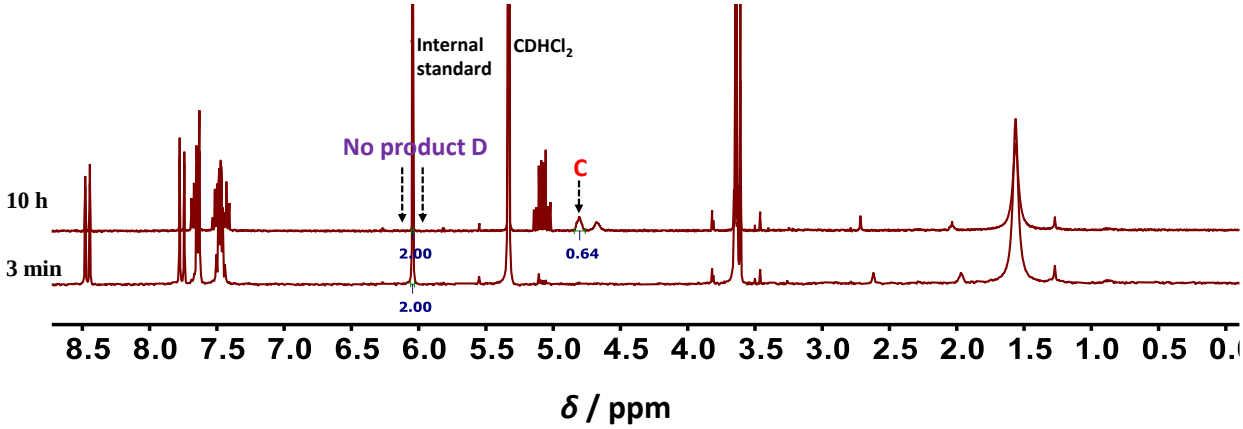


Figure S26. Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of the reaction between **A** and **B** in presence of **4**. Product **C** (64% yield) shows up at 4.76 ppm.

8.1.2 Model catalysis of Michael/5-*exo-dig* cyclization by using of both catalyst 4 and $[Cu(3)(TPP)_2]^+$.

Ligand **3** (0.134 mg, 0.321 µmol), $[Cu(CH_3CN)_4]PF_6$ (0.120 mg, 0.321 µmol), PPh_3 (0.188 mg, 0.642 µmol) were dissolved in 500 µL of CD_2Cl_2 in an NMR tube and then catalyst **4** (0.055 mg, 0.64 µmol) was added. Thereafter, substrates **A** (0.623 mg, 3.21 µmol), **B** (0.635 mg, 9.63 µmol) and TCE (0.536 mg, 3.21 µmol) were added, and the reaction mixture was maintained at 298 K for 10 h. The ^{1}H NMR revealed that the final product **D** was produced in 62% yield whereas 5% of the intermediate **C** was found.

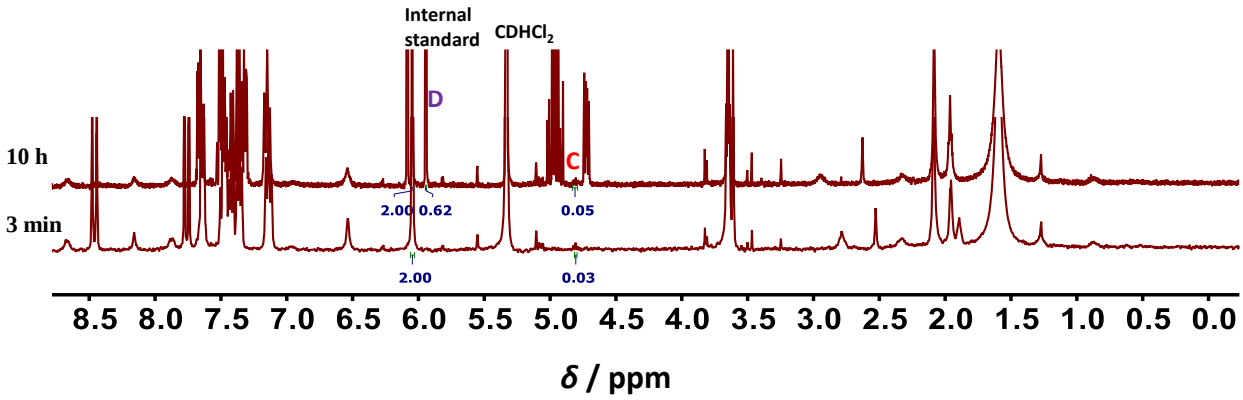


Figure S27. Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of the reaction between **A** and **B** in presence of **4** and $[Cu(\mathbf{3})(TPP)_2]^+$ at 298 K in CD_2Cl_2 for 10 h. Products **C** and **D** show up at 4.76 and 5.92 ppm, respectively.

In an NMR tube, various amounts of catalyst **4** (0.5, 1.0, 1.5, 2.0 equiv w.r.t. Cu^+) were used to catalyze the reaction of ligand **3** (0.134 mg, 0.321 µmol), $[Cu(CH_3CN)_4]PF_6$ (0.120 mg, 0.321 µmol), PPh_3 (0.188 mg, 0.642 µmol), substrate **A** (0.623 mg, 3.21 µmol), **B** (0.635 mg, 9.63 µmol) and TCE (0.536 mg, 3.21 µmol) in 500 µL of CD_2Cl_2 at 298 K for 10 h.

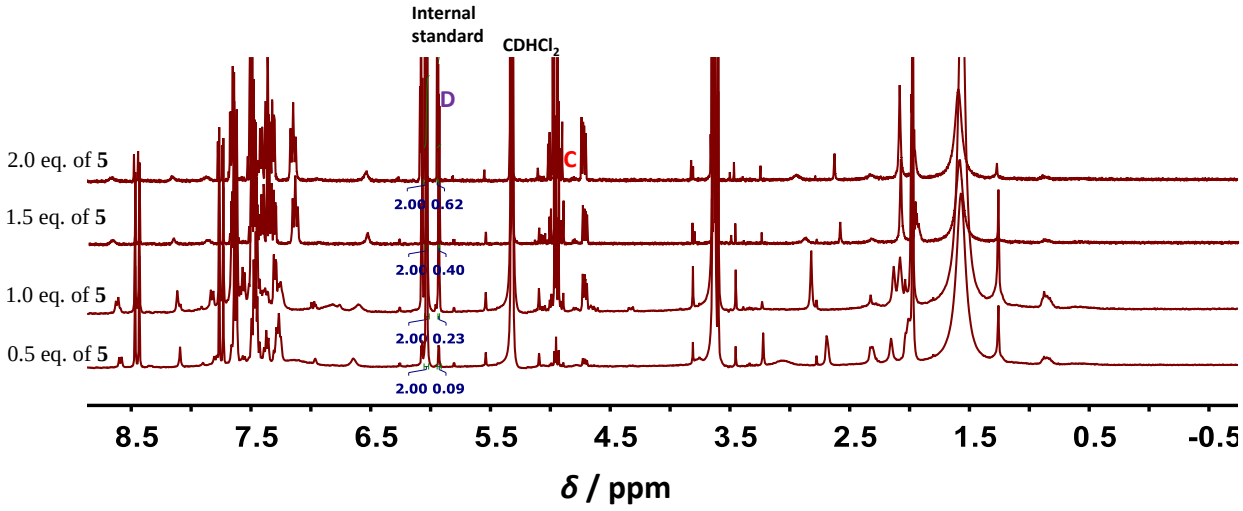


Figure S28. Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of the reaction of substrate **A** and **B** using the above reaction conditions {with fixed amount of catalyst $[Cu(\mathbf{3})(TPP)_2]^+$}and various amounts of **4** at 298 K in CD_2Cl_2 after 10 h. When 0.5, 1.0, 1.5, and 2.0 equiv (w.r.t. Cu^+) of **5** were used, the product **D** was detected at 5.92 ppm in 9%, 23%, 40%, and 62% yield respectively.

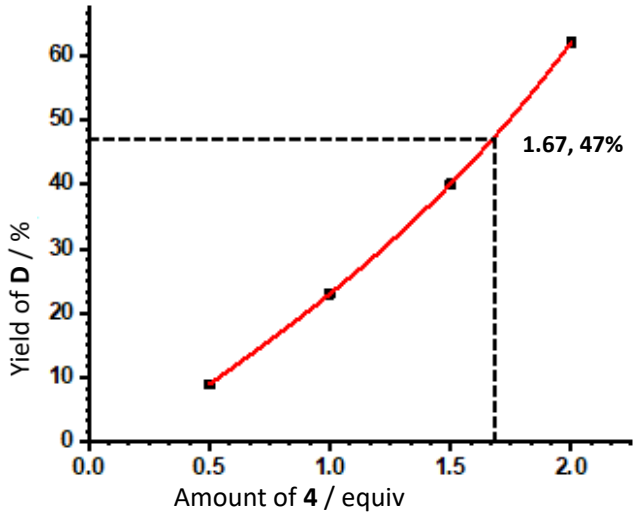


Figure S29. Plot of the yield (%) of **D** versus the amount of catalyst **4** (in equiv) using otherwise fixed reaction conditions. The curve fitting demonstrates that 1.67 equiv of **4** are required to furnish 47% of **D**.

8.1.3 Model catalysis of 5-*exo*-*dig* cyclization by employing $[Cu(3)(TPP)_2]^+$

In an NMR tube, ligand **3** (0.134 mg, 0.321 µmol), $[Cu(CH_3CN)_4]PF_6$ (0.120 mg, 0.321 µmol), PPh_3 (0.188 mg, 0.642 µmol) were placed and dissolved in 500 µL of CD_2Cl_2. Then, **C** (0.767 mg, 3.21 µmol) and TCE (0.536 mg, 3.21 µmol) were added, and the reaction mixture was allowed at 298 K for 10 h, resulting in the formation of only 4% of **D**.

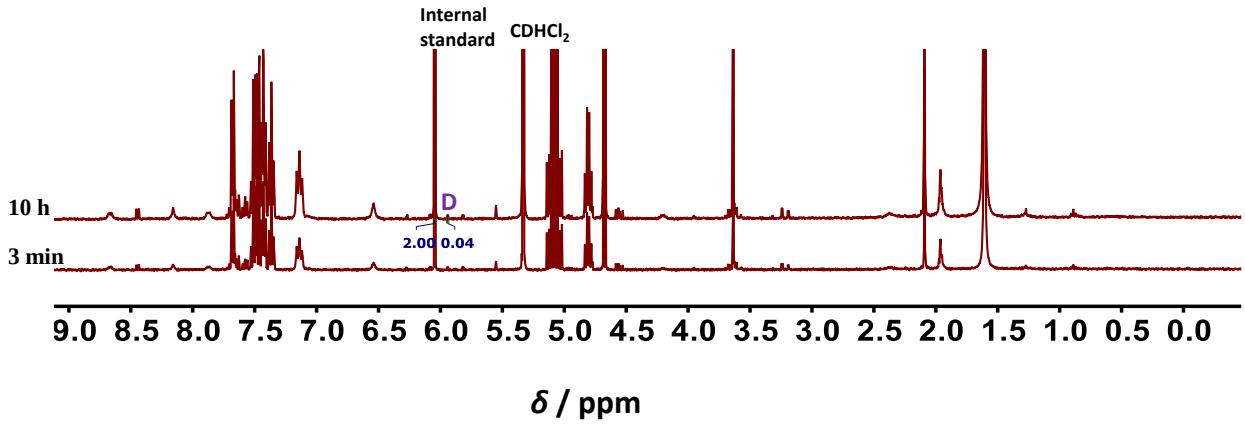


Figure S30. Partial ^1H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of the reaction of substrate **C** in presence of $[Cu(\mathbf{3})(TPP)_2]^+$ in CD_2Cl_2 after 10 h. Product **D** showed up at 5.92 ppm.

8.1.4 Model catalysis of sequential Michael/5-*exo-dig* cyclization in presence of 4 and [Cu(3)(TPP)]$^+$.

In an NMR tube, 2,9-dimesitylphenanthroline (**3**) (0.134 mg, 0.321 µmol), $[Cu(CH_3CN)_4]PF_6$ (0.120 mg, 0.321 µmol), and PPh_3 (0.188 mg, 0.642 µmol) were dissolved in 500 µL of CD_2Cl_2. Then, **4** (0.055 mg, 0.642 µmol), **C** (0.767 mg, 3.21 µmol) and TCE (0.536 mg, 3.21 µmol) were added. Thereafter, the mixture was allowed react at 298 K for 10 h, resulting in the formation of 90% of **D**.

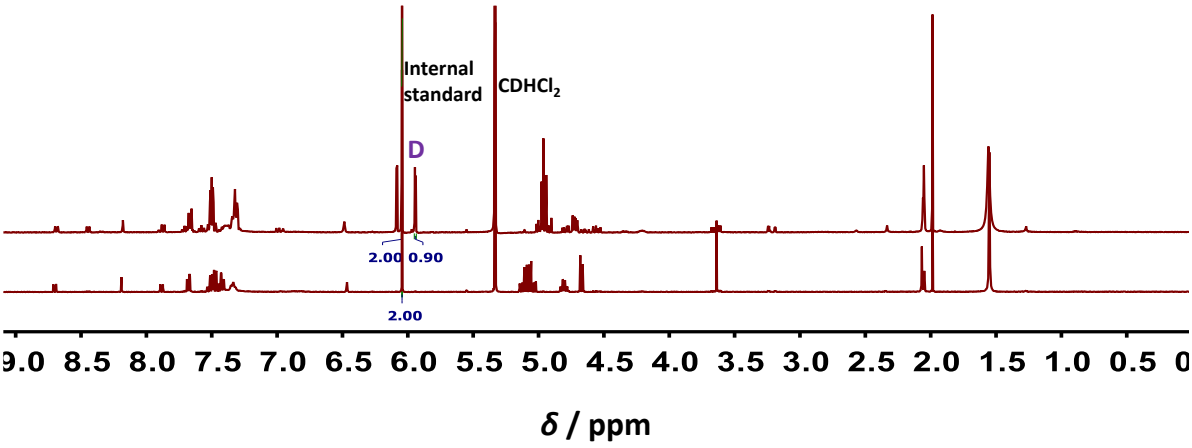


Figure S31. Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of the reaction of substrate **C** in presence of **4** and $[Cu(CH_3CN)_4]PF_6$. Product **D** shows up at 5.92 ppm.

8.2 Final catalysis

8.2.1 [(T)•(4)$_2$] catalyzed sequential reaction

Ligands **1** (0.515 mg, 0.321 µmol) and **2** (0.267 mg, 0.321 µmol) were dissolved in 500 µL of CD_2Cl_2, then $Zn(OTf)_2$ (0.117 mg, 0.321 µmol) was added. Afterward, the addition of 2,9-dimesitylphenanthroline (**3**) (0.134 mg, 0.321 µmol) and $[Cu(CH_3CN)_4]PF_6$ (0.120 mg, 0.321 µmol) led to the quantitative formation of **T**. Then, the catalyst **4** (0.055 mg, 0.64 µmol), substrate **A** (0.623 mg, 3.21 µmol), **B** (0.635 mg, 9.63 µmol) and internal standard TCE (0.536 mg, 3.21 µmol) were added to the turnstile **T** and the resultant reaction mixture was kept at 298 K for 10 h. The yield of **C** and **D** was calculated from the ^{1}H NMR spectra.

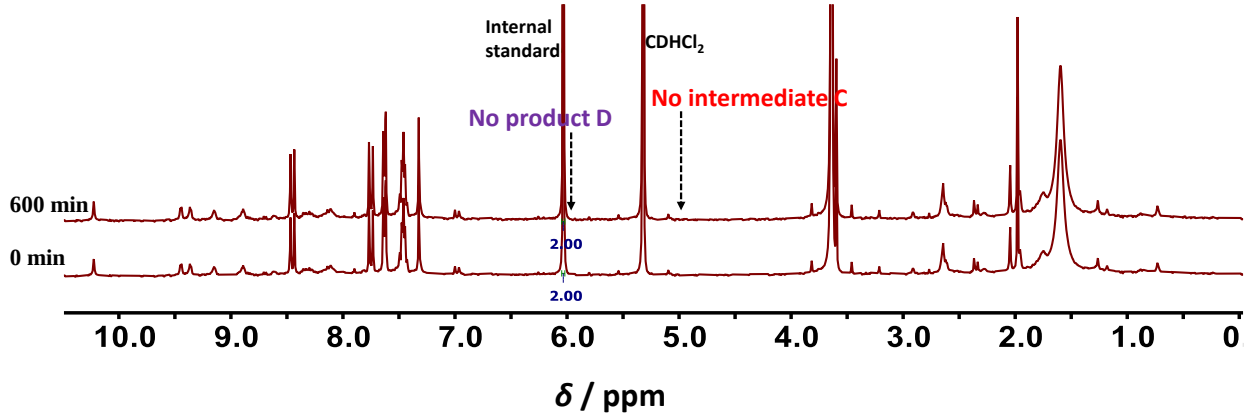


Figure S32. Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of the reaction of substrates **A** and **B** in presence [(**T**)•(**4**)$_2$]. No products **C** and **D** were observed at 4.76 and 5.92 ppm, respectively, after 10 h. We defined this state as the catalytically OFF state.

8.2.3 [(R)•(4)$_2$] and [Cu(3)(TPP)$_2$]$^+$ catalyzed sequential Michael/5-*exo*-*dig* cyclization

In an NMR tube, ligands **1** (0.515 mg, 0.321 µmol) and **2** (0.267 mg, 0.321 µmol) were dissolved in 500 µL of CD_2Cl_2, then subsequently $Zn(OTf)_2$ (0.117 mg, 0.321 µmol) was added. 2,9-Di-mesitylphenanthroline (0.134 mg, 0.321 µmol) and $[Cu(CH_3CN)_4]PF_6$ (0.120 mg, 0.321 µmol) were then added quantitively furnishing turnstile **T**. Next, **4** (0.055 mg, 0.64 µmol), **A** (0.623 mg, 3.21 µmol), **B** (0.635 mg, 9.63 µmol) and TCE (0.536 mg, 3.21 µmol) were added. The mixture was treated with PPh_3 (0.188 mg, 0.642 µmol) and allowed to react at 298 K for 10 h. Subsequently, the process was monitored using ^{1}H NMR and the yields of **C** and **D** were calculated at various time by reference to TCE as an internal standard.

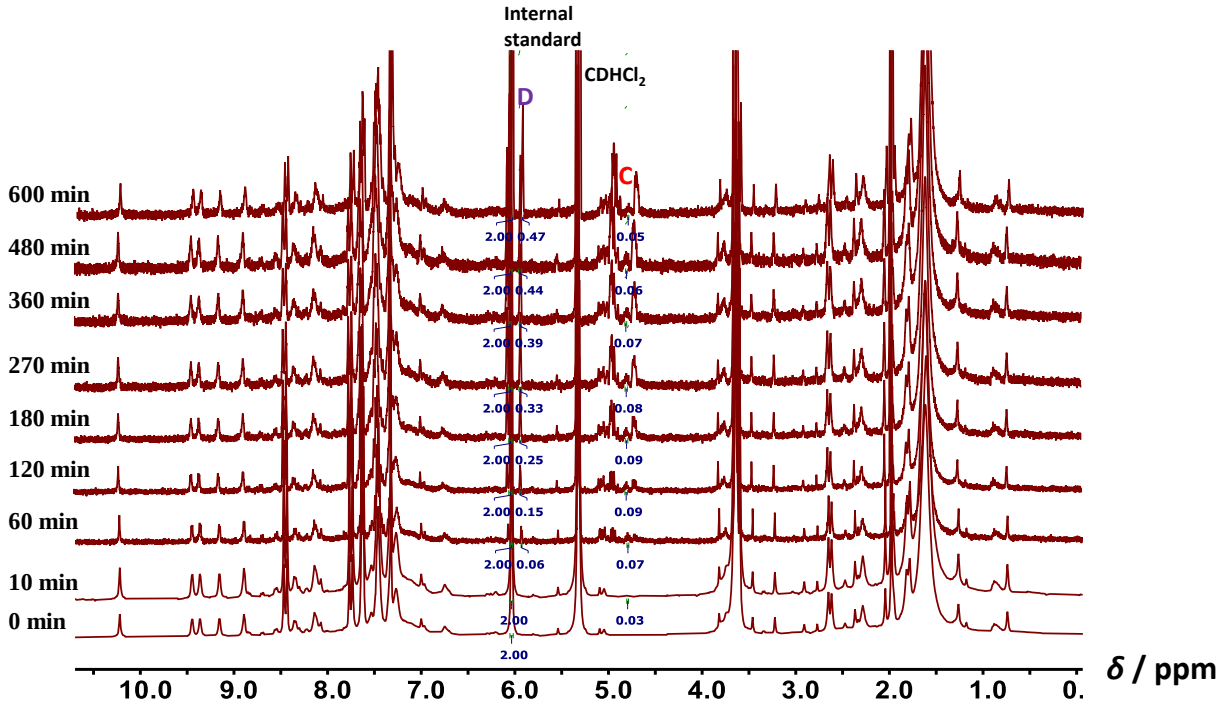


Figure S33. Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of the reaction between **A** and **B** by using rotor [(**R**)•(**4**)$_2$] and [Cu(**3**)(TPP)$_2$]$^+$ furnishing the intermediate **C** (5% yield) and product **D** (47% yield) after 10 h (**C** shows up at 4.76 and **D** at 5.92 ppm). This is denoted as the catalytically ON state.

8.2.3 [(**R**)•(**4**)$_2$] catalyzed Michael addition reaction

In an NMR tube, rotor **R** was prepared {from ligands **1** (0.515 mg, 0.321 μmol) and **2** (0.267 mg, 0.321 μmol) as well as $Zn(OTf)_2$ (0.117 mg, 0.321 μmol)} in 500 μL of CD_2Cl_2. Then, *N*-methylpyrrolidine (**4**) (0.055 mg, 0.64 μmol), **A** (0.623 mg, 3.21 μmol), **B** (0.635 mg, 9.63 μmol), and TCE (0.536 mg, 3.21 μmol) were added. The reaction mixture was maintained at 298 K for 10 h and the whole process was monitored with ^{1}H NMR. The yield of **C** was determined at various times from the ^{1}H NMR spectra by reference to the internal standard TCE.

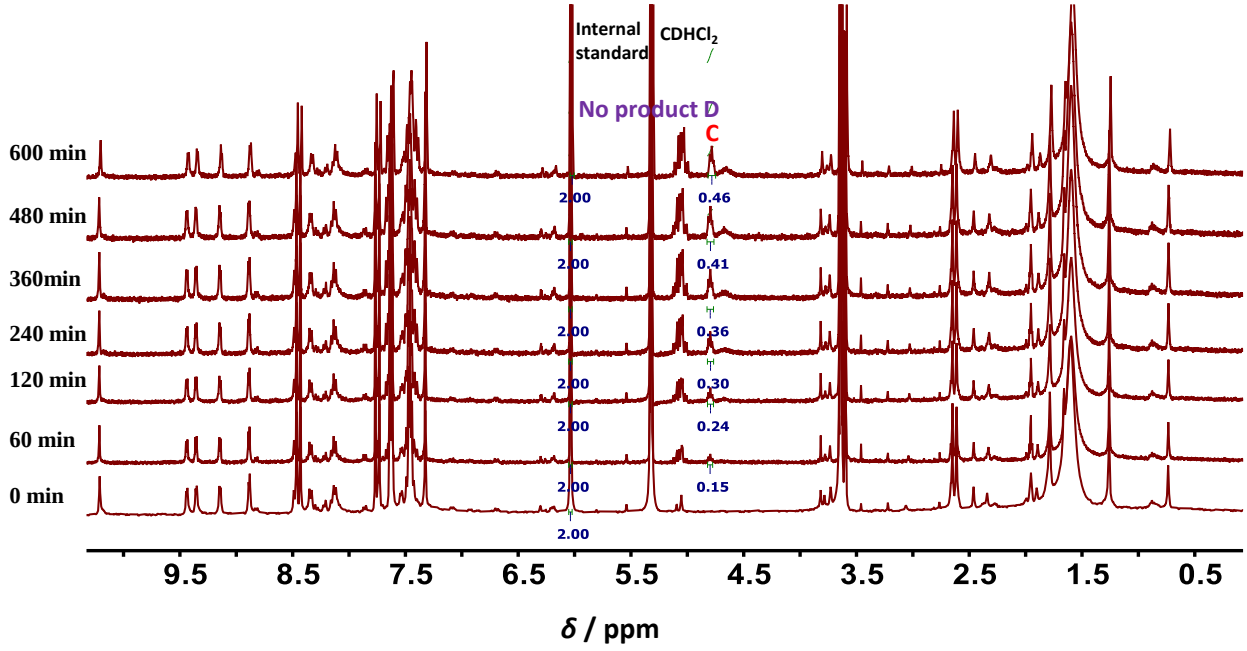


Figure S34. Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298 K) of the reaction between substrates **A** and **B** by using the catalytic rotor [(**R**)•(**4**)$_2$]. Intermediate **C** showed up at 4.76 in 46% yield.

8.3 Dissipative catalysis

General procedure: To perform dissipative catalysis, turnstile **T** was prepared in an NMR tube as reported above {from ligand **1** (0.515 mg, 0.321 µmol), **2** (0.267 mg, 0.321 µmol), 2,9-dimesitylphenanthroline (**3**) (0.134 mg, 0.321 µmol), ($Zn(OTf)_2$ (0.117 mg, 0.321 µmol), and $[Cu(CH_3CN)_4]PF_6$ (0.120 mg, 0.321 µmol)} in 500 µL of CD_2Cl_2. Thereafter, catalyst *N*-methyl-pyrrolidine (**4**) (0.055 mg, 0.64 µmol), substrate 1-ethynyl-2-(2-nitrovinyl)benzene (**A**) (0.623 mg, 3.21 µmol), malononitrile (**B**) (0.635 mg, 9.63 µmol), and oxidant **5** (0.506 mg, 2.89 µmol) were added. Thereafter, the reaction mixture was kept at rt for 10 h to test the activity in the catalytic OFF state. For each dissipative cycle, the chemical fuel PPh_3 (0.168 mg, 0.642 µmol) was added to the catalytic OFF state. The yield of **C** and **D** was calculated from the ^1H NMR spectra by using TCE (0.536 mg, 3.21 µmol) as an internal standard.

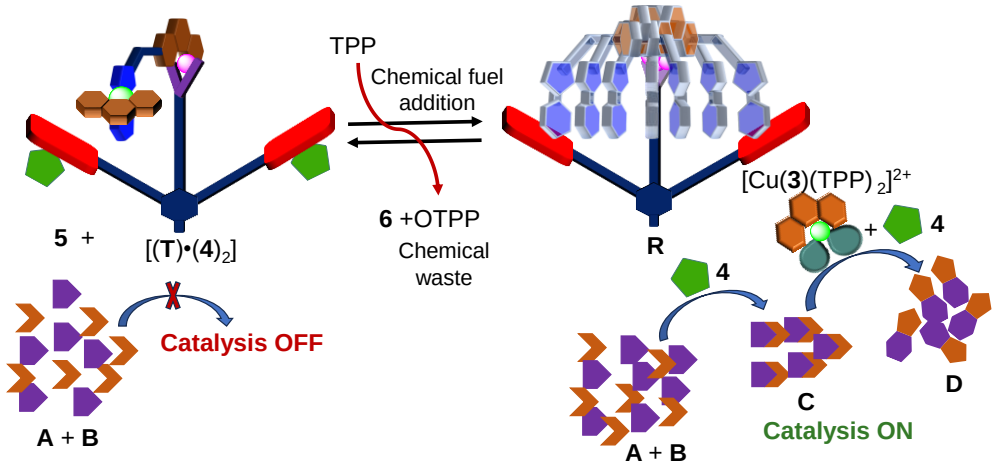


Figure S35. Cartoon representation of the dissipative catalytic process.

8.3.1 First dissipative catalytic cycle (OFF state)

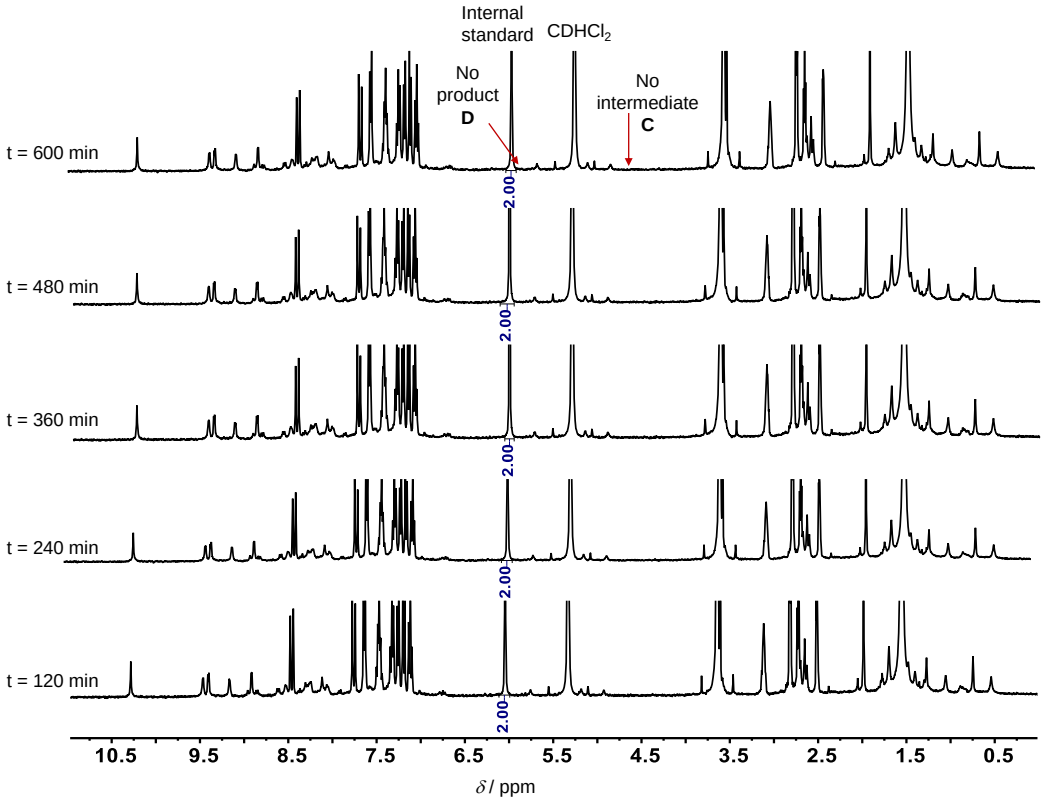


Figure S36. Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298K) of the catalytically OFF state (**T** + **4** + **5** + **A** + **B** + TCE) recorded at various time. The mixture was allowed to react at 298 K for 10 h, resulting in neither formation of intermediate **C** nor of final product **D**.

8.3.2 First dissipative catalytic cycle (ON state)

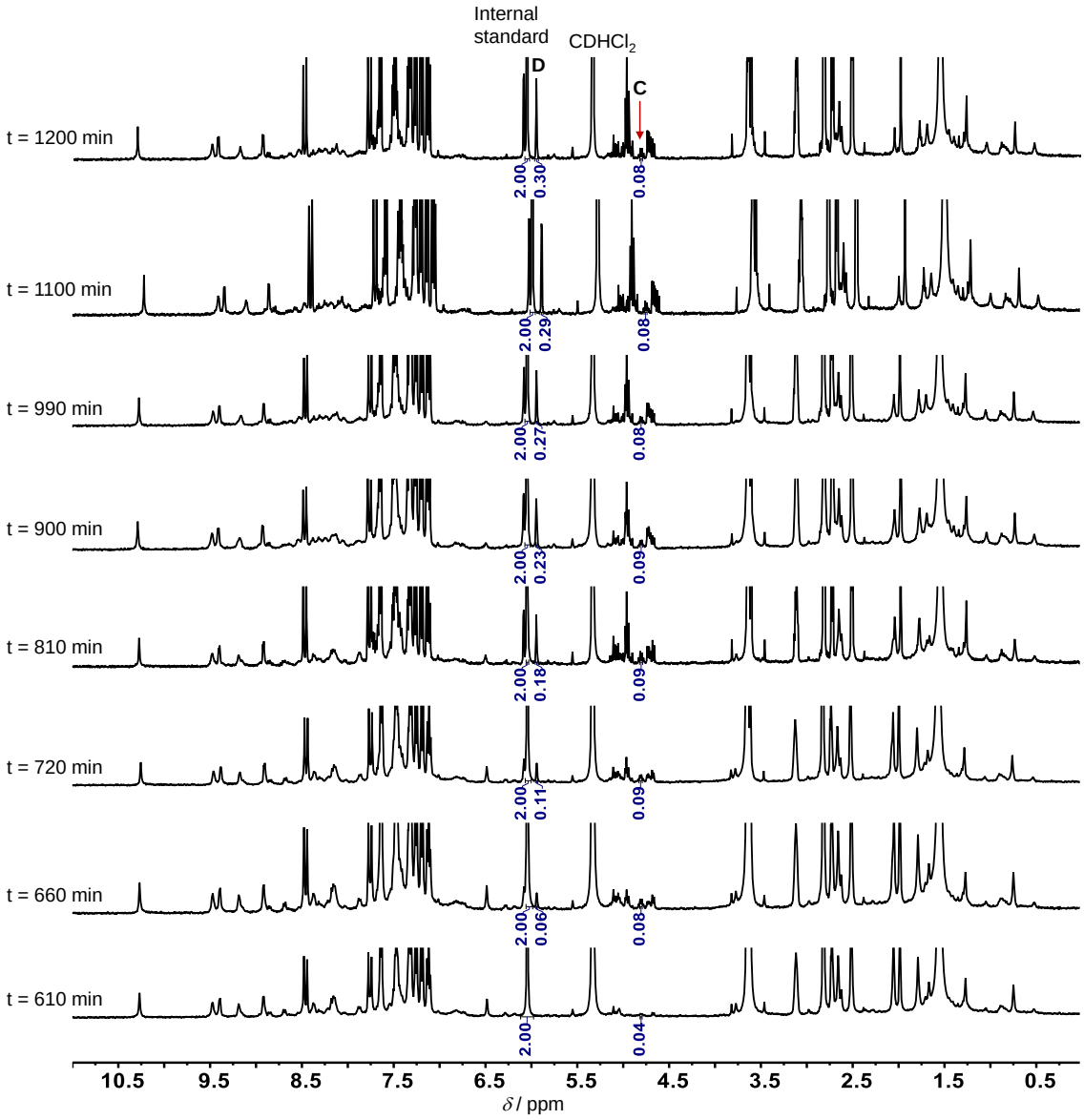


Figure S37. Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298K) of the first dissipative catalytic ON state recorded at various times. When two equiv of chemical fuel PPh_3 (w.r.t. **T**) were added to the catalytic OFF state, immediately the catalytic ON state was generated that reverted back to the catalytic OFF state over 10 h at 298 K, yielding 8% of intermediate **C** and 30% of final product **D**.

8.3.3 Second dissipative catalytic cycle (OFF state)

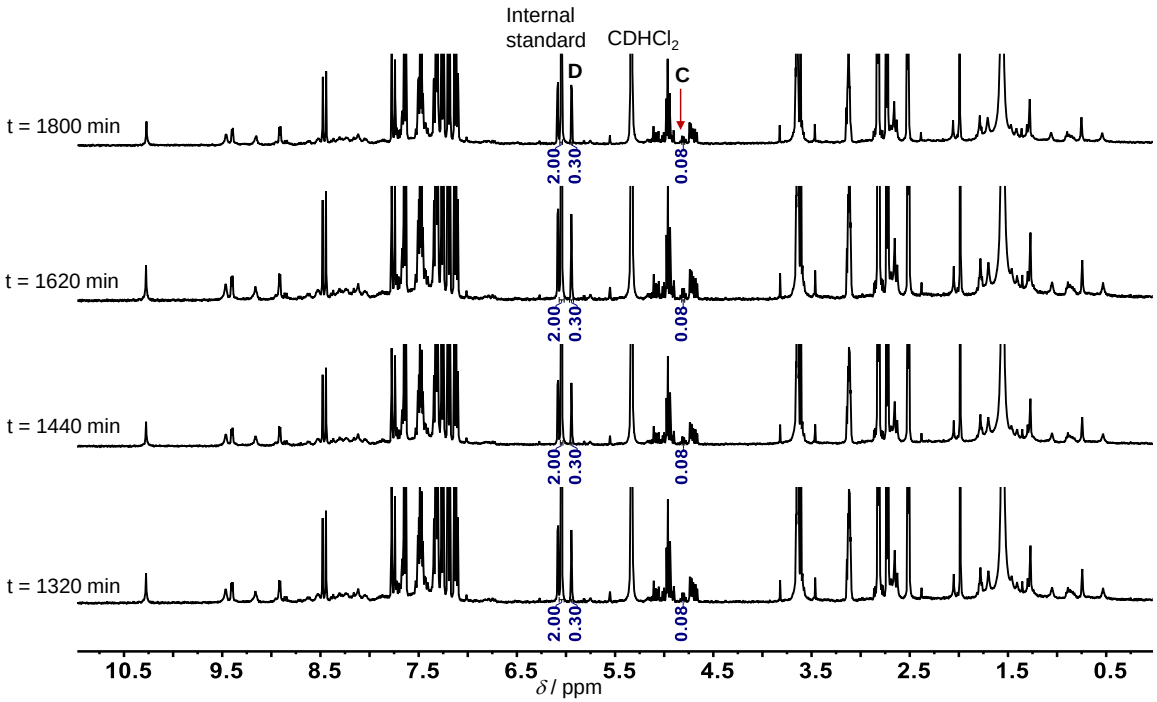


Figure S38. Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298K) of the second dissipative catalytic OFF state recorded at various times after replacing the consumed amounts of substrate **A** (0.241 mg, 1.22 μmol), **B** (0.081 mg, 1.22 μmol), and co-fuel **5** (0.112 mg, 0.642 μmol) from the first dissipative catalytic cycle. The reaction mixture was maintained at 298 K for 10 h, however, no change in the yields of intermediate **C** and of the final product **D** was registered.

8.3.4 Second dissipative catalytic cycle (ON state)

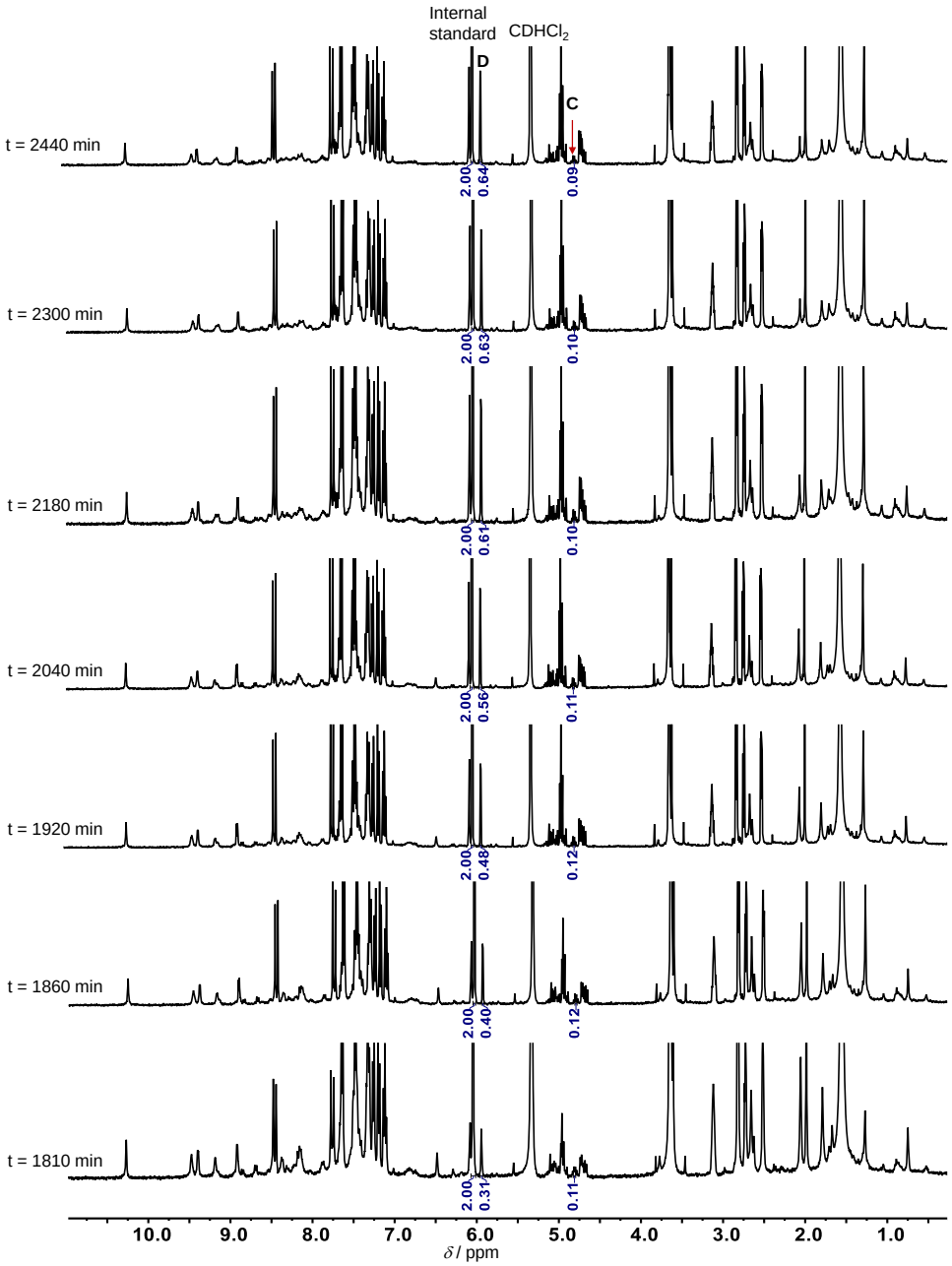


Figure S39. Partial ^{1}H NMR spectra (400 MHz, CD_2Cl_2, 298K) of the second dissipative catalytic ON state recorded at various times. When two equiv of chemical fuel PPh_3 (w.r.t. **T**) were added to the catalytic OFF state, immediately the catalytic ON state was generated that reverted back to the catalytic OFF state over 10 h at 298 K, yielding 9% of intermediate **C** and 64% of final product **D**.

9 References

1 A. Goswami, I. Paul, and M. Schmittel, *Chem. Commun.*, 2017, **53**, 5186−5189.