Supplementary Information for

Selective Synthesis of a Heterotetranuclear Complex from a Macrocyclic Ligand with Identical Chelating Units

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1. Materials and Methods

Unless otherwise noted, solvents and reagents were purchased from Tokyo Chemical Industry Co., Ltd., Fujifilm Wako Pure Chemical Co., Kanto Chemical Co., Inc., Nacalai Tesque, Inc. or Sigma-Aldrich Japan G.K., and used without further purification. Dry THF was purified by Glass Contour Ultimate Solvent System.

Measurements were performed at 298 K unless otherwise noted. ^{1}H, ^{13}C, ^{19}F, and other 2D NMR spectra were recorded on Bruker AVANCE III 400 and 600 spectrometers. Negative values were depicted in red in the spectra. Tetramethylsilane was used as an internal standard (δ 0.00 ppm) for ^{1}H and ^{13}C NMR measurements when $CDCl_3$ was used as a solvent. Hexafluorobenzene in $CDCl_3$ (1 wt%) was used as an external standard (δ –163.0 ppm) for ^{19}F NMR measurements. The assignments of the ^{1}H and ^{13}C signals were based on ^{1}H-^{1}H COSY, ^{1}H-^{1}H NOESY, ^{1}H-^{13}C HSQC, and ^{1}H-^{13}C HMBC experiments. Negative values were shown in red in the spectra.

ESI-TOF mass data were recorded on an AB SCIEX TripleTOF 4600 system. When the intensity of the monoisotopic peak with the lowest molecular weight was too low, the isotopic peak with the highest intensity was used for the calculated value, which was obtained using ChemDraw 23.1.1.

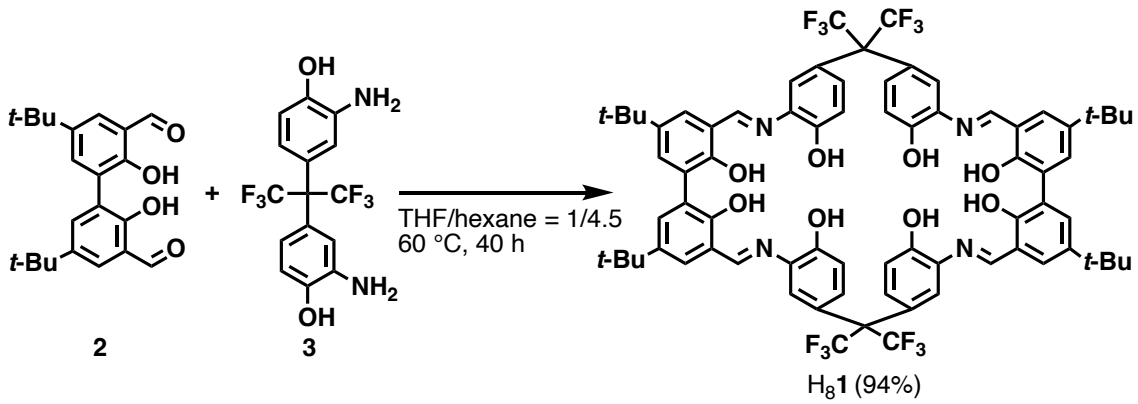
Single-crystal X-ray crystallographic measurements were performed using Bruker APEX II ULTRA with Mo Kα radiation at 100 K. Obtained data were collected using Bruker APEX2[S1a] and processed using Bruker APEX3[S1b] and Yadokari-XG[S2] crystallographic software package. The initial structures were solved using SHELXT-2018/3[S3], and refined using SHELXL-2018/3[S4]. We appreciate Prof. Takahiro Sasamori (Univ. of Tsukuba) for the support in the X-ray diffraction measurements.

Elemental analysis was performed on a Yanaco MT-6 analyzer with tin boats purchased from Elementar. We appreciate Mr. Masao Sasaki (Univ. of Tsukuba) for the measurements.

We appreciate the Open Facility Network Office, Research Facility Center for Science and Technology, University of Tsukuba, for MALDI-TOF MS measurements. We appreciate the Organization for Open Facility Initiatives (Univ. of Tsukuba) for the NMR, MALDI-TOF MS, and ESI-TOF MS measurements.

2. Synthesis and Characterization of Macrocyclic Ligands and Complexes

Scheme S1. Synthesis of H_8**1**



To a 100 mL Schlenk tube, **2**[S5] (339.4 mg, 957.5 μmol, 1.0 eq.), **3** (350.2 mg, 956.1 μmol, 1.0 eq.), dry THF (8.5 mL) and hexane (37.5 mL) were added under Ar atmosphere, and the mixture was stirred at 60 °C for 40 h. Resulting precipitate was filtered, and the obtained solid was dried in vacuo to give H_8**1** as orange solid (617.5 mg, 451.2 μmol, 94%).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 11.63 (br, 4H), 8.41 (s, 4H), 7.60 (d, J = 8.1 Hz, 4H), 7.46 (d, J = 2.1 Hz, 4H), 7.37 (d, J = 2.1 Hz, 4H), 7.05 (d, J = 8.1 Hz, 4H), 6.74 (s, 4H), 5.90 (br, 4H), 1.33 (s, 36H);

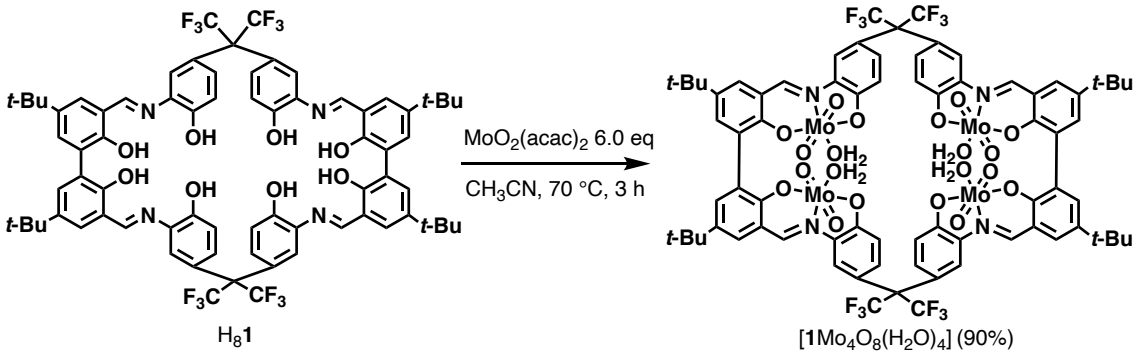
^{13}C NMR ($CDCl_3$, 151 MHz): δ 166.2, 155.9, 150.2, 141.9, 136.8, 134.0, 129.3, 128.8, 125.77, 125.75, 121.5, 118.5, 115.0, 34.1, 31.4;

^{19}F NMR ($CDCl_3$, 565 MHz): δ –63.8;

HRMS (ESI): *m*/*z* calcd for $C_{74}H_{69}N_4F_{12}O_8$ ($[H_8$**1**$+H]^+$): 1369.4918; found: 1368.4884;

Elemental analysis: calcd for $C_{74}H_{68}N_4F_{12}O_8$ (H_8**1**); C, 64.91; H, 5.01; N, 4.09. found: C, 64.61; H, 5.29; N, 3.89.

Scheme S2. Synthesis of [**1**$Mo_4O_8(H_2O)_4$]



To a 50 mL eggplant flask, H_8**1** (70.57 mg, 51.58 μmol, 1.0 eq.), $MoO_2(acac)_2$ (100.28 mg, 307.4 μmol, 6.0 eq.), and CH_3CN (16 mL) were added, then the mixture was stirred at 70 °C for 3 h. The mixture was cooled to room temperature, and was filtered to remove solids. The filtrate was concentrated under reduced pressure. To the residue was added CH_3CN (4.0 mL), and the CH_3CN solution together with the remaining solid was added dropwise to H_2O (60 mL) with stirring at room temperature. The resulting solid was filtered and dried in vacuo to give [**1**$Mo_4O_8(H_2O)_4$] as a yellow solid (91.6 mg, 46.9 μmol, 90%).

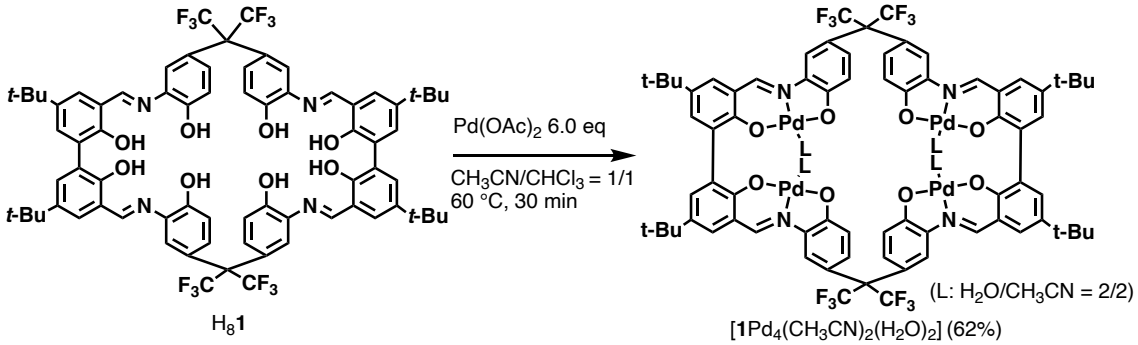
^{1}H NMR ($CDCl_3/CD_3CN$ = 10/1, 600 MHz): δ 8.50 (s, 4H), 7.71 (d, J = 2.4 Hz, 4H), 7.67 (d, J = 8.7 Hz, 4H), 7.52 (d, J = 2.4 Hz, 4H), 6.96 (d, J = 8.7 Hz, 4H), 6.75 (s, 4H), 1.37 (s, 36H);

^{13}C NMR ($CDCl_3/CD_3CN$ = 10/1, 151 MHz): δ 159.9, 158.9, 158.0, 144.6, 137.8, 137.0, 131.4, 130.6, 127.0, 125.8, 121.7, 119.5, 116.6, 34.5, 31.3;

^{19}F NMR (565 MHz, $CDCl_3/CD_3CN$ = 10/1): δ –64.0;

Elemental analysis: calcd for $C_{74}H_{68}N_4F_{12}O_{20}$ ([**1**$Mo_4O_8(H_2O)_4$]); C, 45.69; H, 3.52; N, 2.88. found: C, 46.04; H, 3.91; N, 2.85.

Scheme S3. Synthesis of [**1**$Pd_4(CH_3CN)_2(H_2O)_2$]



H_8**1** [**1**$Pd_4(CH_3CN)_2(H_2O)_2$] (62%)

To a 50 mL eggplant flask, H_8**1** (57.91 mg, 42.32 μmol, 1.0 eq.), $Pd(OAc)_2$ (54.30 mg, 241.8 μmol, 6.0 eq.), CH_3CN (6.0 mL) and $CHCl_3$ (6.0 mL) were added, then the mixture was stirred at 60 °C for 30 min. The mixture was concentrated under reduced pressure. To the residue was added CH_3CN (4.0 mL), and the CH_3CN solution together with the remaining solid was added dropwise to H_2O (60 mL) with stirring at room temperature. The resulting solid was filtered and dried in vacuo to give [**1**$Pd_4(CH_3CN)_2(H_2O)_2$]·$6H_2O$ as orange solid (52.8 mg, 26.2 μmol, 62%). ^{1}H NMR measurement in $CDCl_3/CD_3CN$ = 10/1 confirmed that the sample contained CH_3CN in a ratio of $\mathbf{1}^{8-}$:CH_3CN = 1:2.

^{1}H NMR ($CDCl_3/CD_3CN$ = 10/1, 600 MHz): δ 7.67 (d, *J* = 2.7 Hz, 4H), 7.45 (s, 4H), 7.41 (d, *J* = 8.7 Hz, 4H), 7.23 (d, *J* = 2.7 Hz, 4H), 6.81 (d, *J* = 8.7 Hz, 4H), 6.62 (s, 4H), 1.34 (s, 36H);

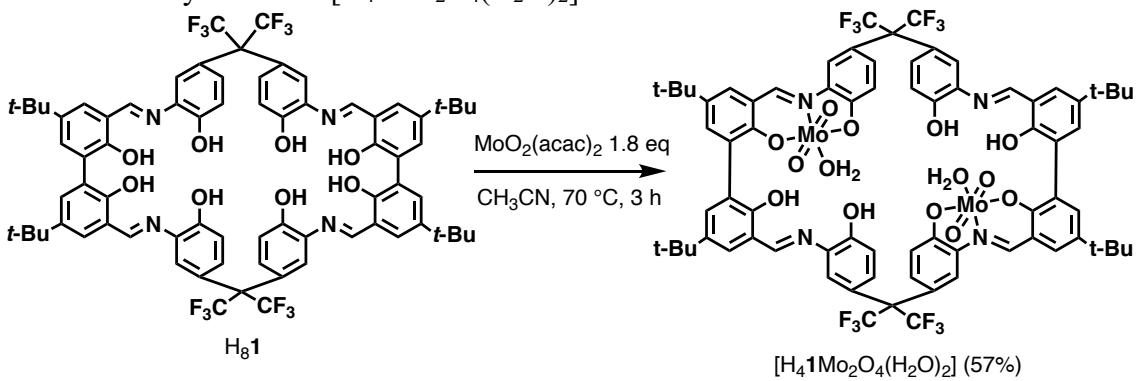
^{13}C NMR ($CDCl_3/CD_3CN$ = 10/1, 151 MHz): δ 165.8, 159.6, 149.6, 141.5, 137.4, 136.6, 129.4, 128.4, 127.3, 122.0, 120.5, 119.4, 116.0, 33.8, 31.5;

^{19}F NMR ($CDCl_3/CD_3CN$ = 10/1, 565 MHz): δ −64.0;

ESI-MS: *m*/*z* calcd for $C_{74}H_{62}N_4F_{12}O_8Pd_4$ ([**1**Pd_4+2H]$^{2+}$): 883.5262; found: 883.5326;

Elemental analysis: calcd for $C_{78}H_{82}N_6F_{12}O_{16}Pd_4$ ([**1**$Pd_4(CH_3CN)_2(H_2O)_2$]·$6H_2O$); C, 46.54; H, 4.11; N, 4.17. found: C, 46.76; H, 4.09; N, 3.79.

Scheme S4. Synthesis of $[H_4\mathbf{1}Mo_2O_4(H_2O)_2]$



In a 30 mL eggplant flask, $H_8\mathbf{1}$ (90.38 mg, 66.04 μmol, 1.0 eq.), $MoO_2(acac)_2$ (38.87 mg, 119.1 μmol, 1.8 eq.), and CH_3CN (5.0 mL) were added, then the mixture was stirred at 70 °C for 3 h. The precipitation was filtered and dried in vacuo to give $[H_4\mathbf{1}Mo_2O_4(H_2O)_2]$ as an orange solid (56.2 mg, 33.9 μmol, 57%).

^{1}H NMR ($CDCl_3/CD_3CN$ = 10/1, 600 MHz): δ 12.27 (s, 2H), 8.55 (s, 2H), 8.36 (s, 2H), 7.82 (d, J = 2.4 Hz, 2H), 7.71 (d, J = 8.1 Hz, 2H), 7.67 (d, J = 9.0 Hz, 2H), 7.49 (d, J = 2.7 Hz, 2H), 7.48 (d, J = 2.4 Hz, 2H), 7.34 (d, J = 2.7 Hz, 2H), 7.14 (d, J = 8.1 Hz, 2H), 7.08 (s, 2H), 6.98 (d, J = 9.0 Hz, 2H), 6.56 (s, 2H), 6.41 (s, 2H), 1.37 (s, 18H), 1.33 (s, 18H);

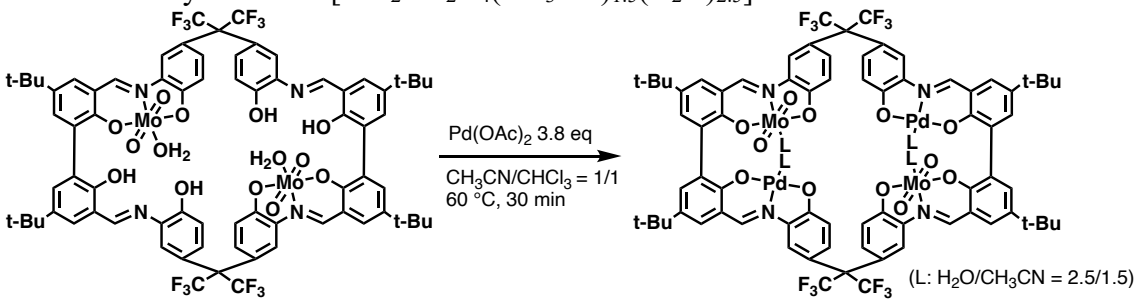
^{13}C NMR ($CDCl_3/CD_3CN$ = 10/1, 151 MHz): δ 165.6, 160.5, 158.4, 157.5, 155.7, 150.5, 143.9, 142.4, 137.0, 136.9, 135.4, 135.4, 131.2, 131.1, 129.4, 129.2, 125.99, 125.96, 125.2, 124.4, 123.4, 121.9, 118.9, 118.0, 117.5, 115.4, 34.4, 34.3, 31.4, 31.3;

^{19}F NMR ($CDCl_3/CD_3CN$ = 10/1, 565 MHz): δ –64.0, –64.2;

ESI-MS: *m*/*z* calcd for $C_{74}H_{65}N_4F_{12}O_{12}Mo_2$ ($[H_4\mathbf{1}Mo_2O_4+H]^+$): 1613.25; found: 1613.18;

Elemental analysis: calcd for $C_{74}H_{68}N_4F_{12}O_{14}Mo_2$ ($[H_4\mathbf{1}Mo_2(H_2O)_2]$); C, 53.63; H, 4.14; N, 3.38. found: C, 53.38; H, 4.42; N, 3.41.

Scheme S5. Synthesis of [**1**$Pd_2Mo_2O_4(CH_3CN)_{1.5}(H_2O)_{2.5}$]



[H_4**1**$Mo_2O_4(H_2O)_2$] [**1**$Pd_2Mo_2O_4(CH_3CN)_{1.5}(H_2O)_{2.5}$] (77%)

In a 50 mL eggplant flask, [H_4**1**$Mo_2O_4(H_2O)_2$] (58.31 mg, 35.94 μmol, 1.0 eq.), $Pd(OAc)_2$ (30.71 mg, 136.7 μmol, 3.8 eq.), CH_3CN (6.0 mL), and $CHCl_3$ (6.0 mL) were added, then the mixture was stirred at 60 °C for 30 min. After heating and stirring, the reaction mixture was concentrated under reduced pressure. To the residue was added CH_3CN (4.0 mL), and the CH_3CN solution together with the remaining solid was added dropwise to H_2O (60 mL) with stirring at room temperature. The resulting solid was filtered and dried in vacuo to give [**1**$Pd_2Mo_2O_4(CH_3CN)_{1.5}(H_2O)_{2.5}]\cdot 2H_2O$ as an orange solid (54.6 mg, 27.7 μmol, 77%). ^{1}H NMR measurement in $CDCl_3/CD_3CN$ = 10/1 confirmed that the sample contained CH_3CN in a ratio of $\mathbf{1}^{8-}$:CH_3CN = 1:1.5.

^{1}H NMR (600 MHz, $CDCl_3/CD_3CN$ = 10/1): δ 8.39 (s, 2H), 7.83 (d, J = 2.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 7.59 (s, 2H), 7.48 (d, J = 8.7 Hz, 2H), 7.45 (m, 4H), 7.32 (d, J = 2.4 Hz, 2H), 6.91 (d, J = 8.4 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 6.78 (s, 2H), 6.56 (s, 2H), 1.37 (s, 18H), 1.36 (s, 18H);

^{13}C NMR (151 MHz, $CDCl_3/CD_3CN$ = 10/1): δ 165.9, 159.4, 159.3, 158.6, 157.9, 148.9, 142.6, 141.3, 138.7, 137.5, 137.3, 135.9, 130.3, 130.1, 130.0, 129.0, 127.6, 127.4, 125.5, 121.66, 121.63, 120.8, 119.8, 118.8, 116.3, 116.2, 34.2, 33.9, 31.2;

^{19}F NMR (565 MHz, $CDCl_3/CD_3CN$ = 10/1): δ –64.2, –63.8;

HRMS (ESI): m/z calcd for $C_{74}H_{61}N_4F_{12}O_{12}Pd_2Mo_2$ ([**1**$Pd_2Mo_2O_4$+H]$^+$): 1819.0321; found: 1819.0345;

Elemental analysis: calcd for $C_{77}H_{73.5}N_{5.5}F_{12}O_{16.5}Mo_2Pd_2$ ([**1**$Pd_2Mo_2O_4(CH_3CN)_{1.5}(H_2O)_{2.5}]\cdot 2H_2O$); C, 46.88; H, 3.76; N, 3.91. found: C, 46.90; H, 3.98; N, 3.68.

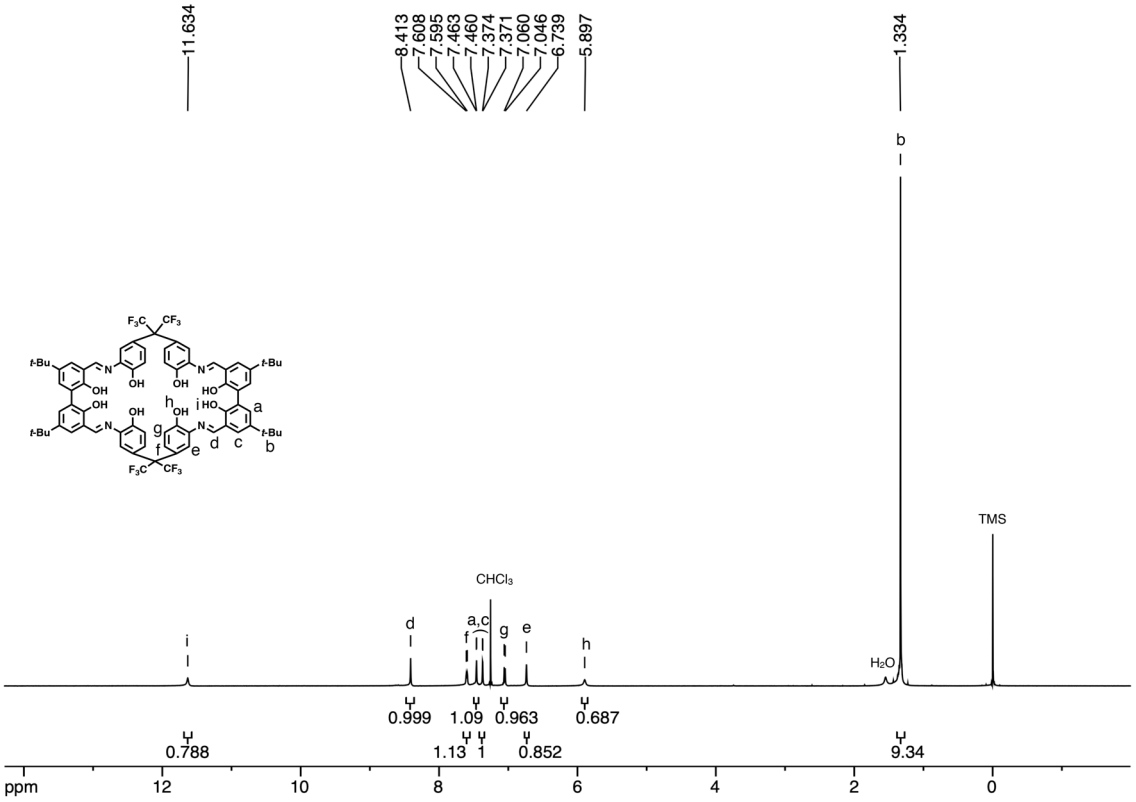


Figure S1. ^{1}H NMR spectrum of H_8**1** ($CDCl_3$, 600 MHz).

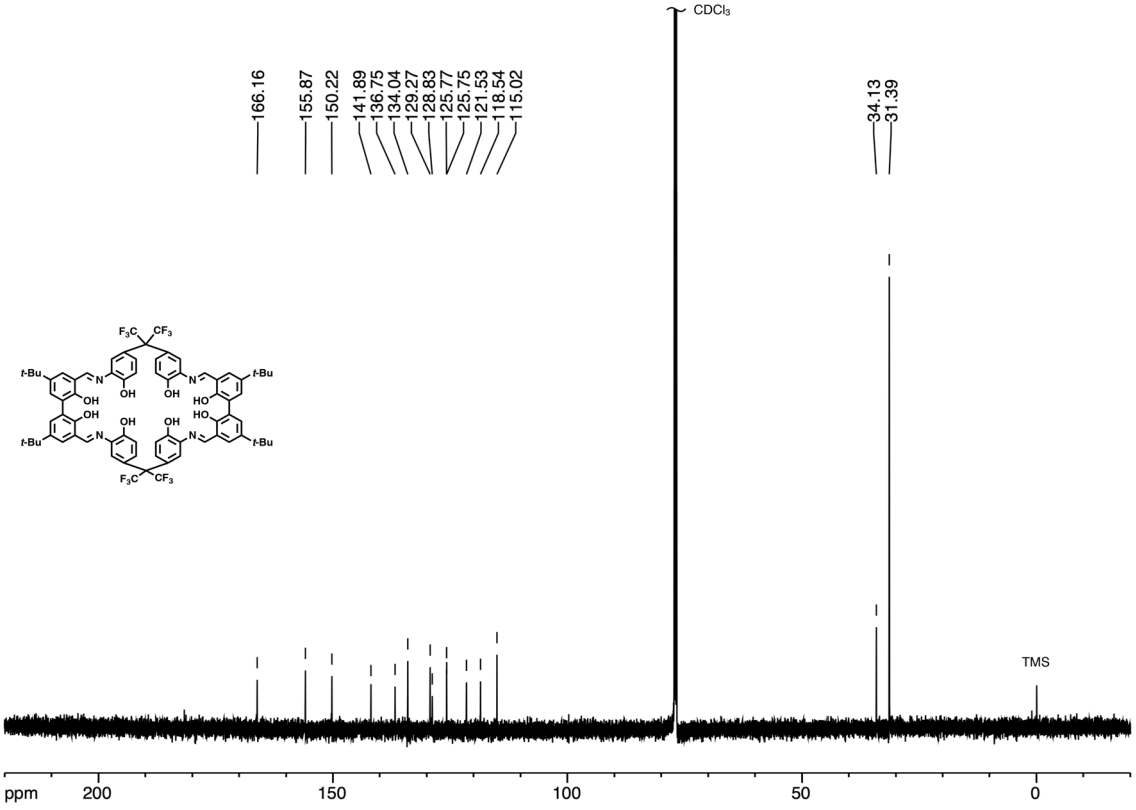


Figure S2. ^{13}C NMR spectrum of H_8**1** ($CDCl_3$, 151 MHz).

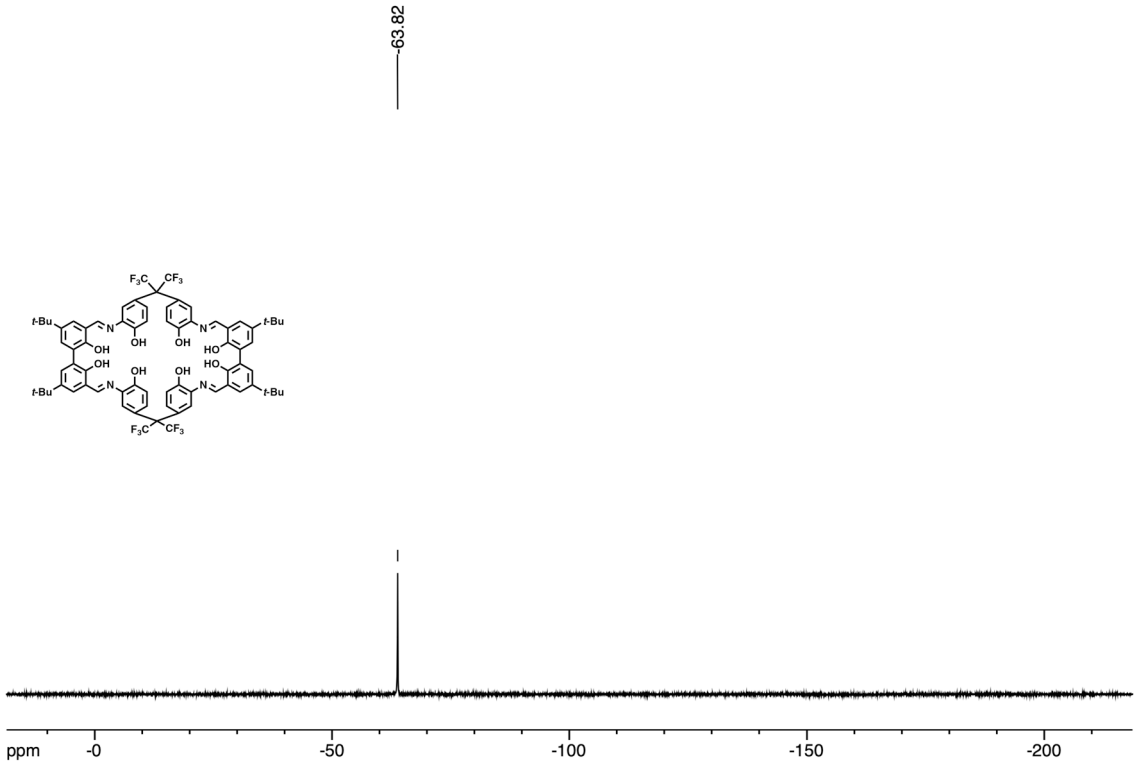


Figure S3. ^{19}F NMR spectrum of H_8**1** ($CDCl_3$, 565 MHz).

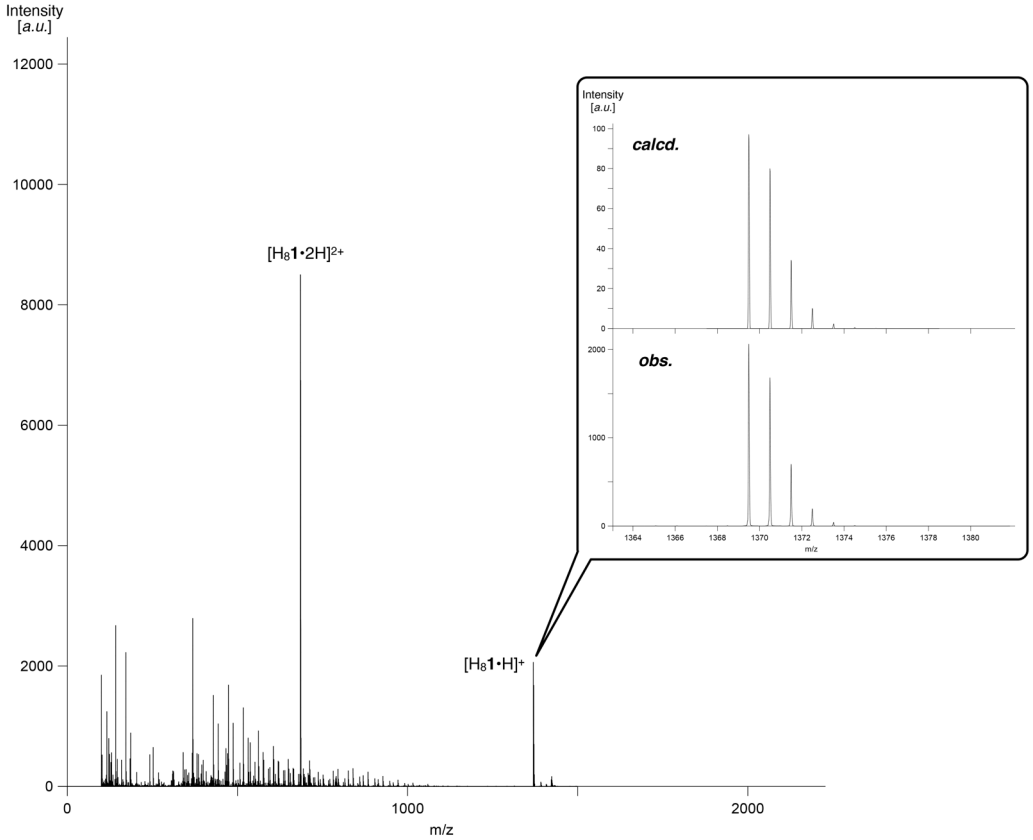


Figure S4. ESI-TOF mass spectrum of H_8**1** (positive, CH_3CN).

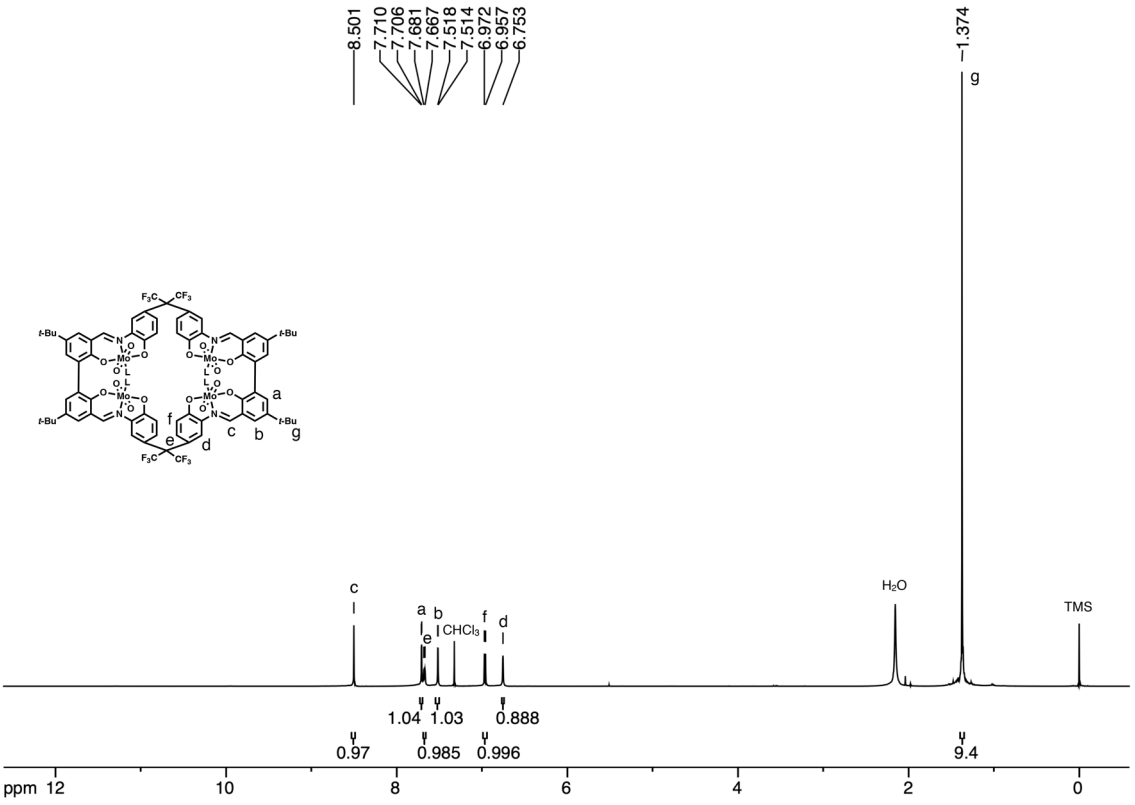


Figure S5. ^{1}H NMR spectrum of [**1**$Mo_4O_8L_4$] ($CDCl_3$/CD_3CN = 10/1, 600 MHz).

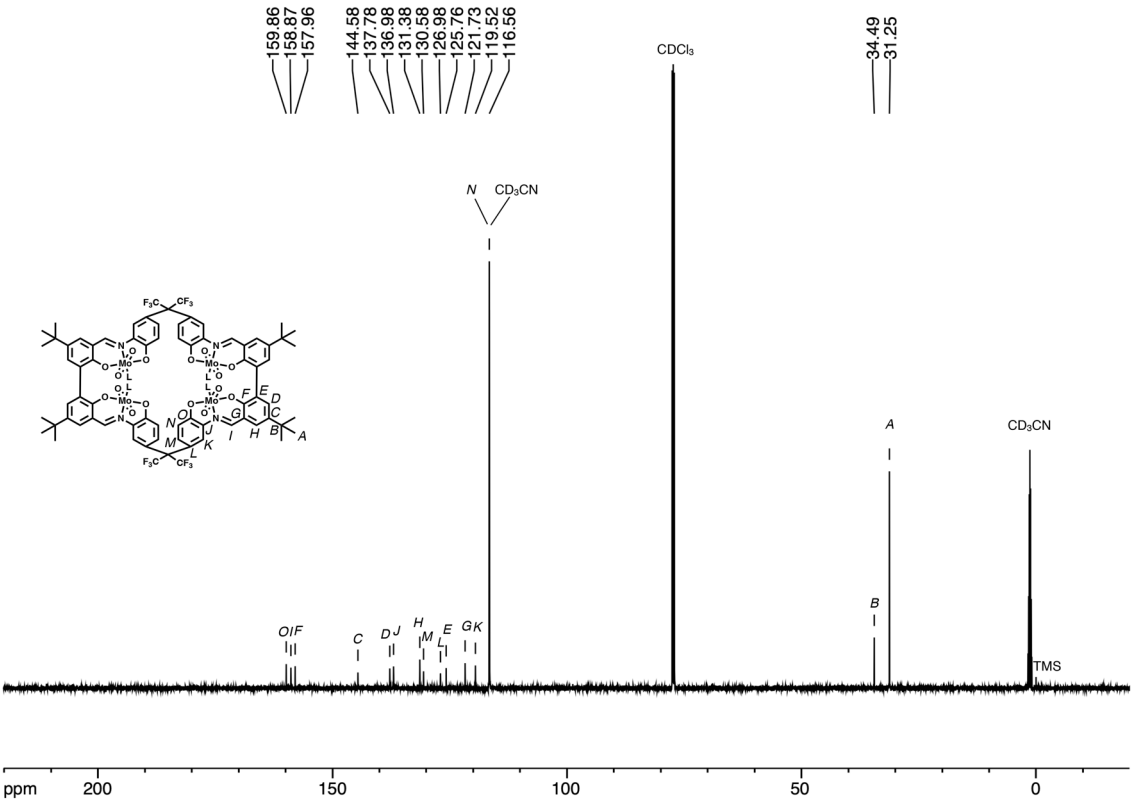


Figure S6. ^{13}C NMR spectrum of [**1**$Mo_4O_8L_4$] ($CDCl_3$/CD_3CN = 10/1, 151 MHz).

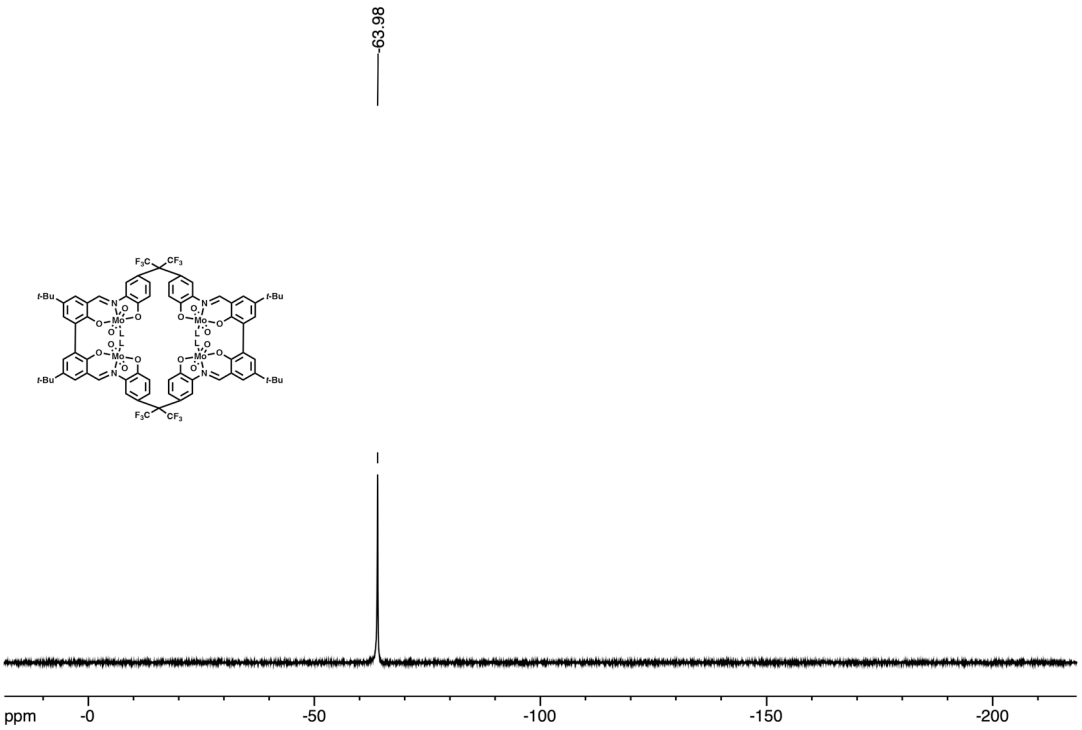


Figure S7. ^{19}F NMR spectrum of [**1**$Mo_4O_8L_4$] ($CDCl_3/CD_3CN$ = 10/1, 565 MHz).

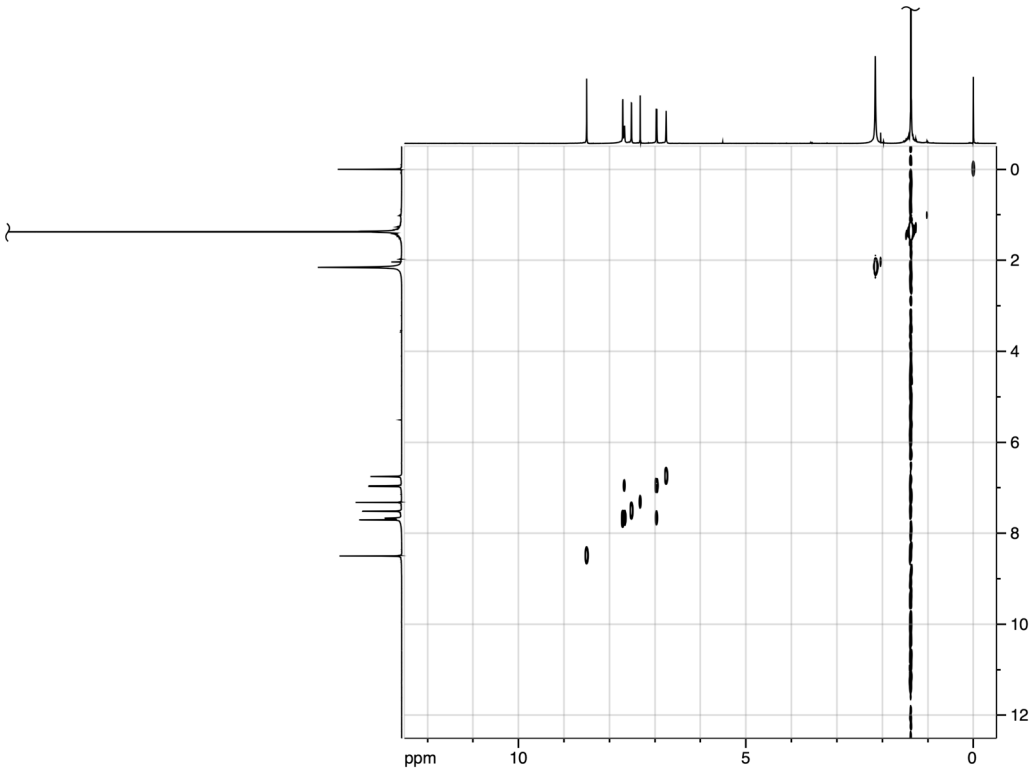


Figure S8. $^1H–^1H$ COSY spectrum of [**1**$Mo_4O_8L_4$] ($CDCl_3/CD_3CN$ = 10/1, 600 MHz).

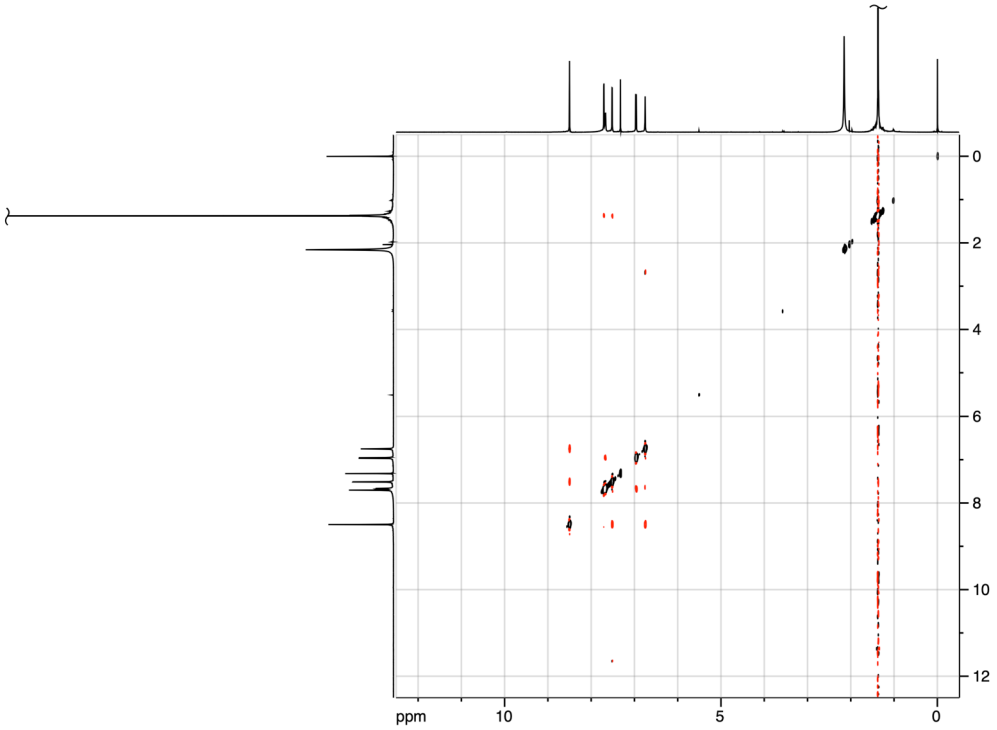


Figure S9. $^{1}H–^{1}H$ ROESY spectrum of [**1**$Mo_4O_8L_4$] ($CDCl_3/CD_3CN$ = 10/1, 600 MHz).

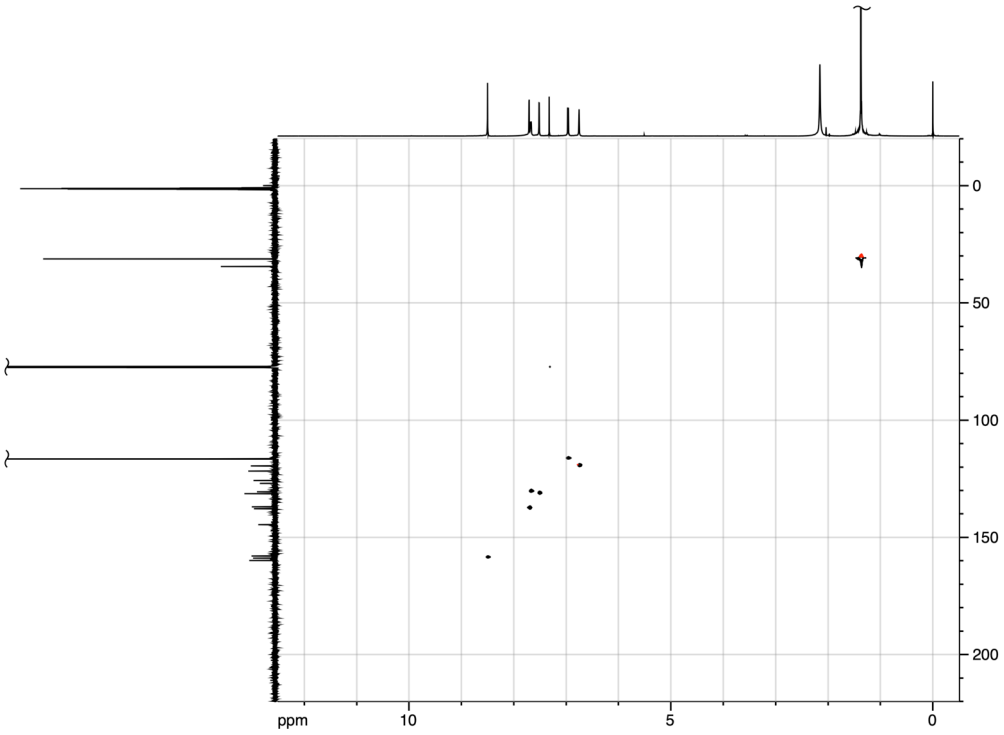


Figure S10. $^{1}H–^{13}C$ HSQC spectrum of [**1**$Mo_4O_8L_4$] ($CDCl_3/CD_3CN$ = 10/1, 600 MHz)

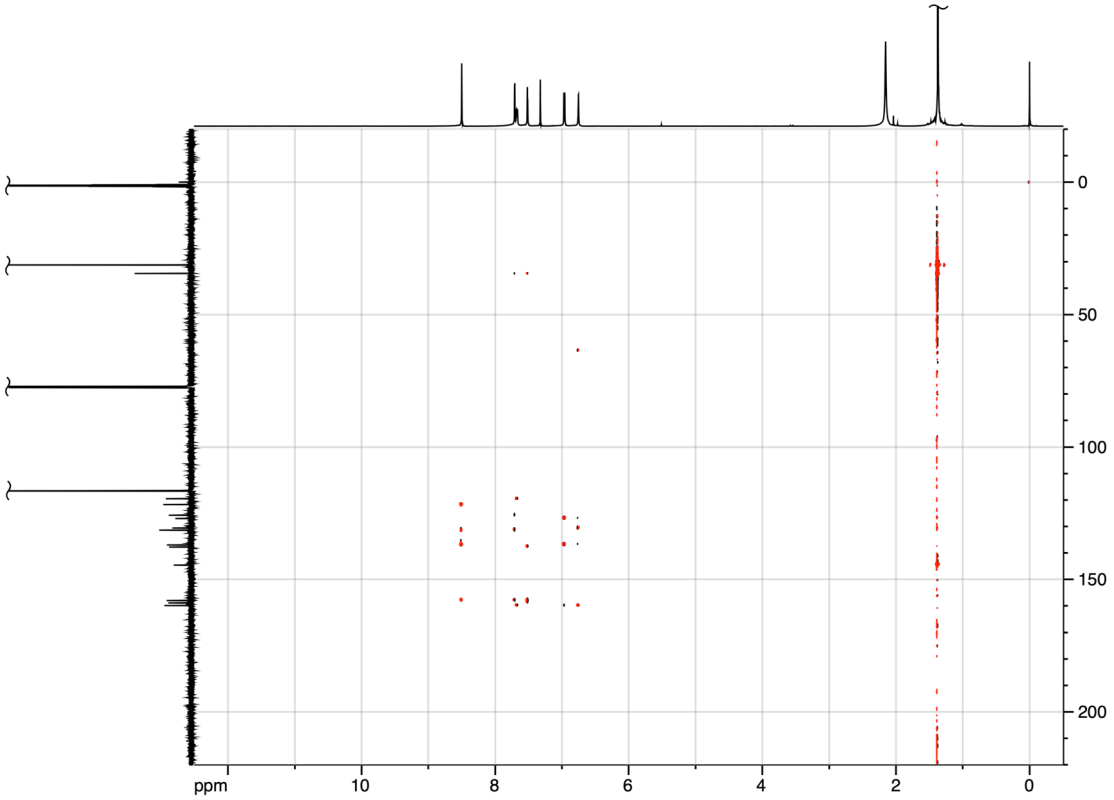


Figure S11. $^{1}H–^{13}C$ HMBC spectrum of [**1**$Mo_4O_8L_4$] ($CDCl_3/CD_3CN$ = 10/1, 600 MHz)

A single crystal of [**1**$Mo_4O_8(CH_3CN)_3$]·12CH_3CN suitable for an X-ray diffraction analysis was obtained by slow evaporation from CH_3CN solution.
Crystallographic data for $C_{104}H_{105}N_{19}O_{16}F_{12}Mo_4$ ([**1**$Mo_4O_8(CH_3CN)_3$]·12CH_3CN), Fw = 2488.82, orange column, 0.57 × 0.10 × 0.08 mm^3, monoclinic, space group $P\ 2_1/c$ (No. 14), a = 24.989(6) Å, b = 18.289(4) Å, c = 26.175(6) Å, β = 107.081(2)°, V = 11435(4) $Å^3$, Z = 4, T = 100 K, λ (Mo Kα) = 0.71073 Å, θ_{max} = 26.571°, R_1 = 0.0793 ($I > 2\sigma$), wR_2 = 0.2380 (all), GOF = 1.112. CCDC 2424093.

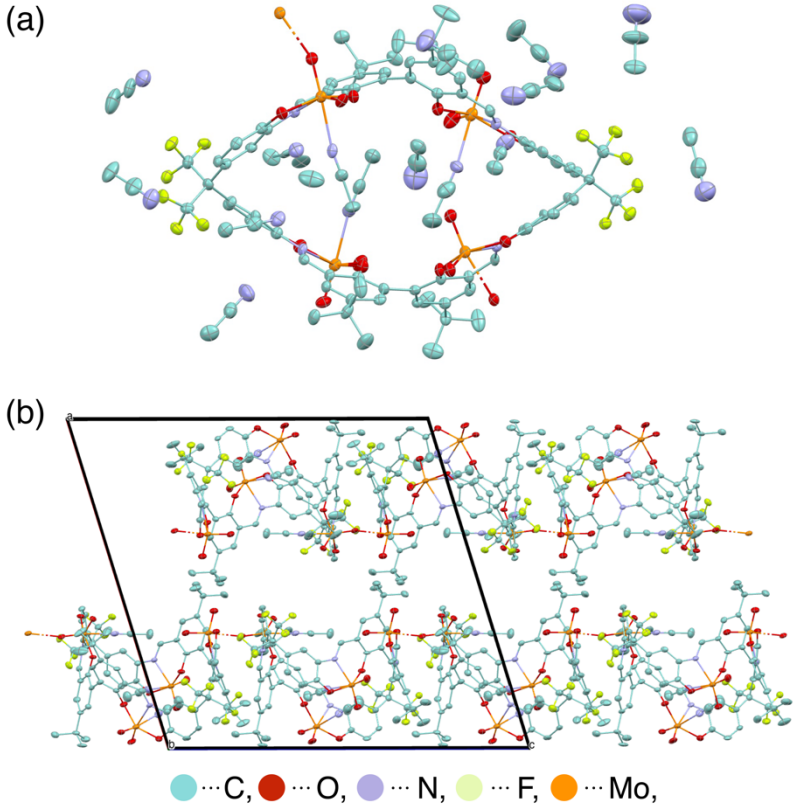


Figure S12. Structure of [**1**$Mo_4O_8(CH_3CN)_3$]·12CH_3CN determined by X-ray diffraction analysis. An ellipsoidal model (50% probability). Hydrogen atoms were omitted for clarity. (a) Top view. (b) Side view of packing. Solvents were omitted for clarity.

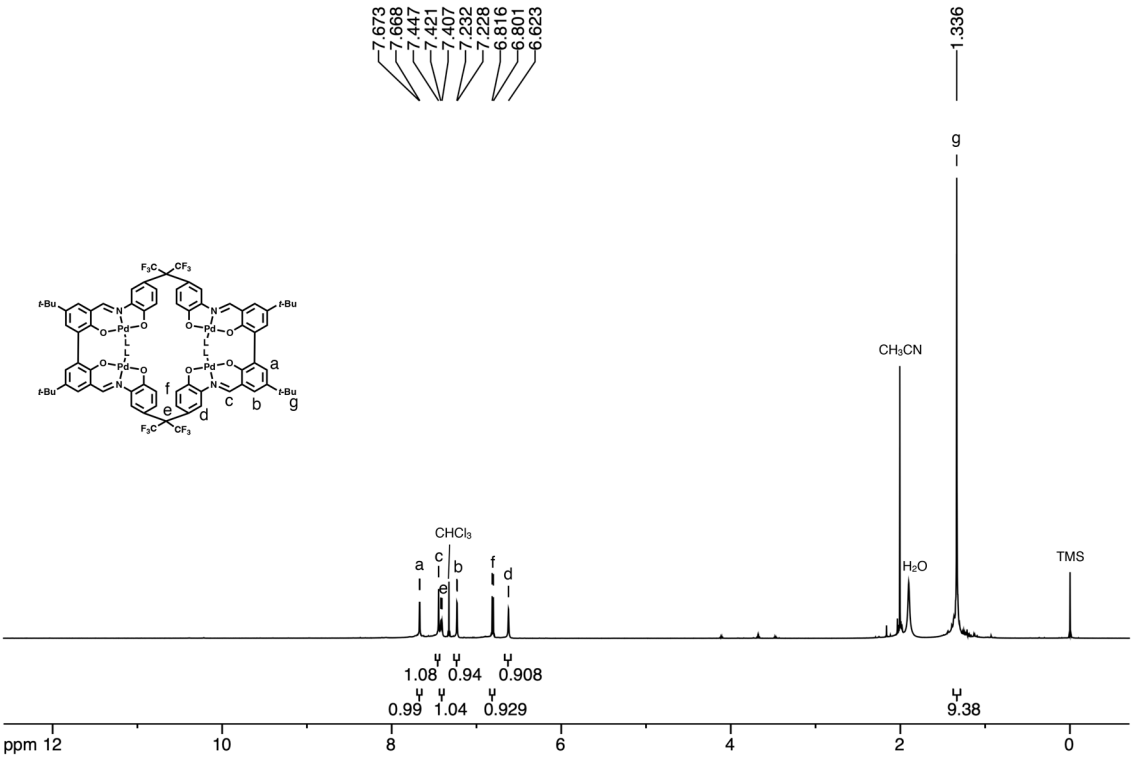


Figure S13. ^{1}H NMR spectrum of [**1**Pd$_4$L$_4$] (CDCl$_3$/CD$_3$CN = 10/1, 600 MHz).

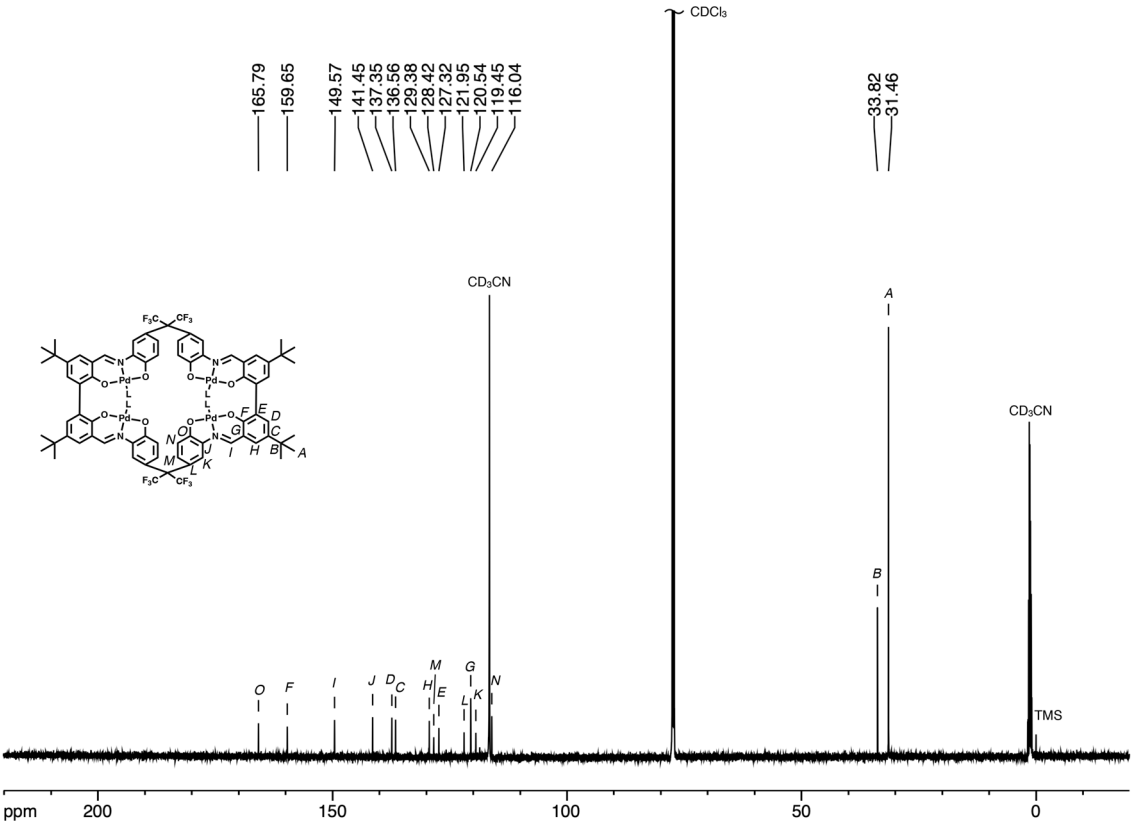


Figure S14. ^{13}C NMR spectrum of [**1**Pd$_4$L$_4$] (CDCl$_3$/CD$_3$CN = 10/1, 151 MHz).

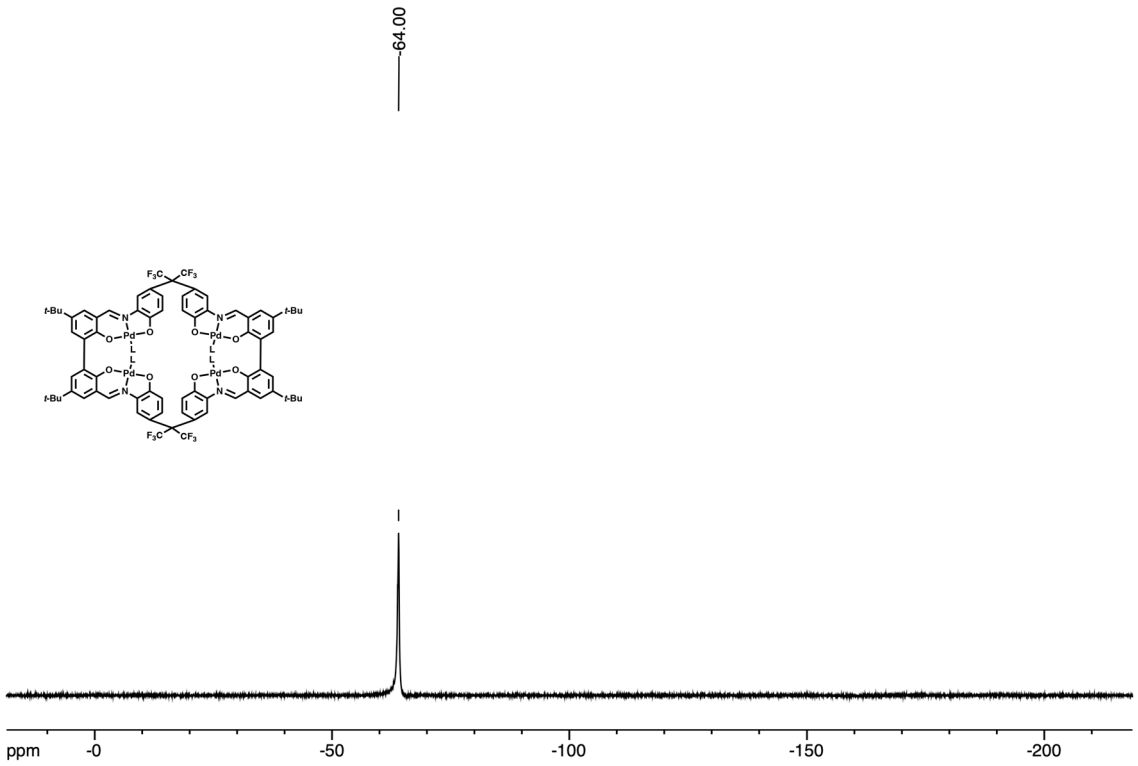


Figure S15. ^{19}F NMR spectrum of [**1**Pd_4L_4] ($CDCl_3/CD_3CN$ = 10/1, 565 MHz).

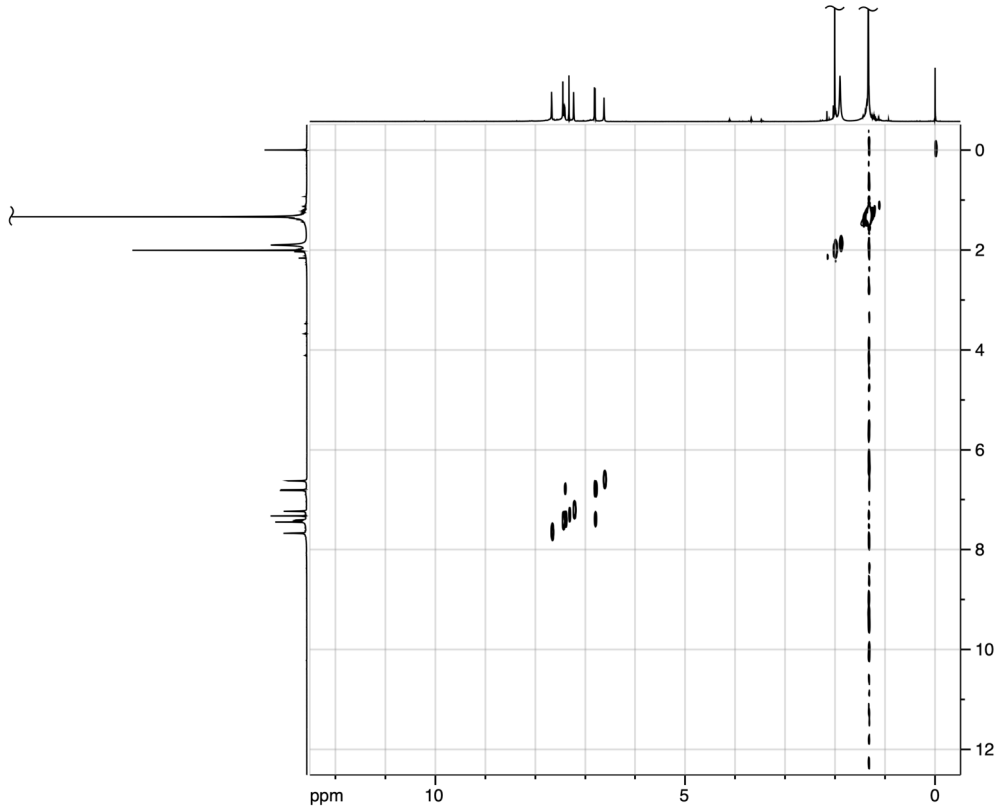


Figure S16. $^{1}H–^{1}H$ COSY spectrum of [**1**Pd_4L_4] ($CDCl_3/CD_3CN$ = 10/1, 600 MHz).

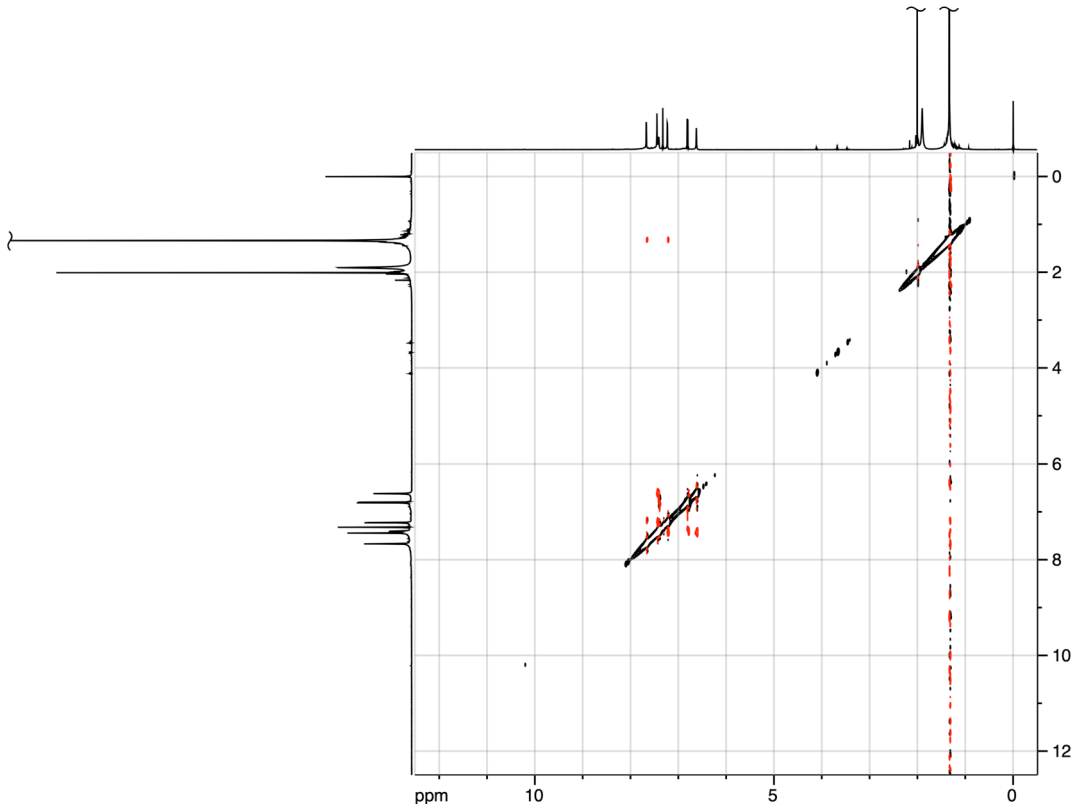


Figure S17. ^{1}H–^{1}H ROESY spectrum of [**1**Pd$_4$L$_4$] (CDCl$_3$/CD$_3$CN = 10/1, 600 MHz).

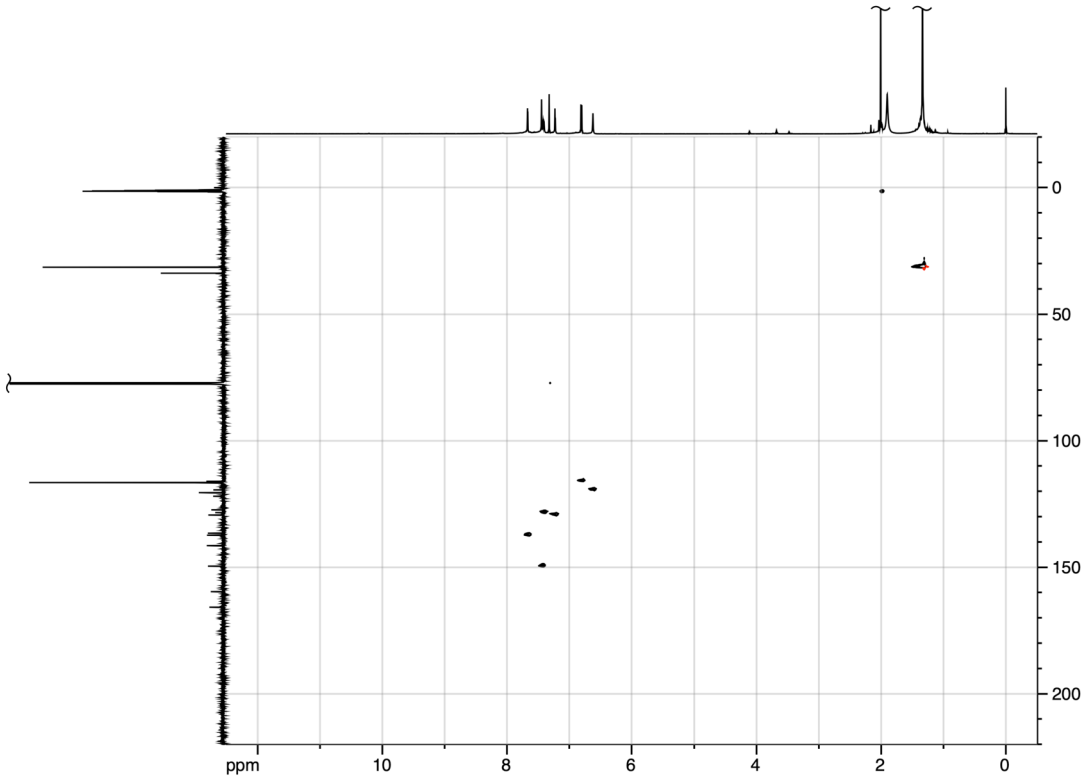


Figure S18. ^{1}H–^{13}C HSQC spectrum of [**1**Pd$_4$L$_4$] (CDCl$_3$/CD$_3$CN = 10/1, 600 MHz).

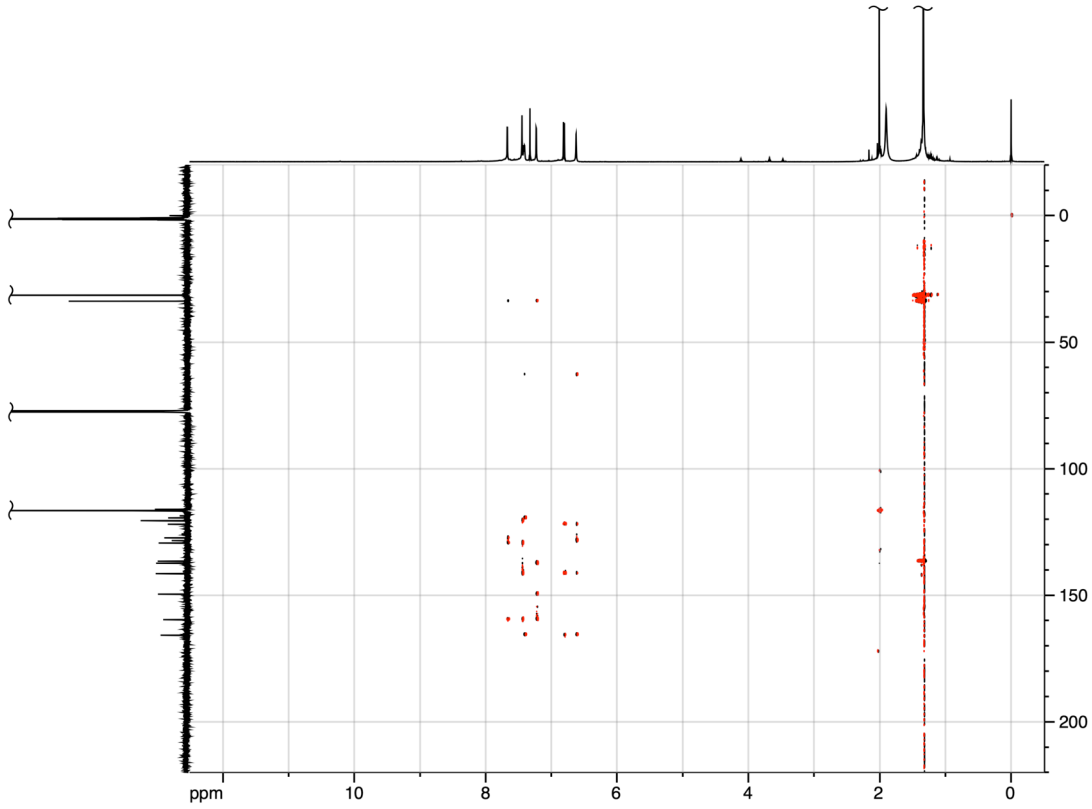


Figure S19. ^{1}H–^{13}C HMBC spectrum of [**1**Pd_4L_4] ($CDCl_3/CD_3CN$ = 10/1, 600 MHz).

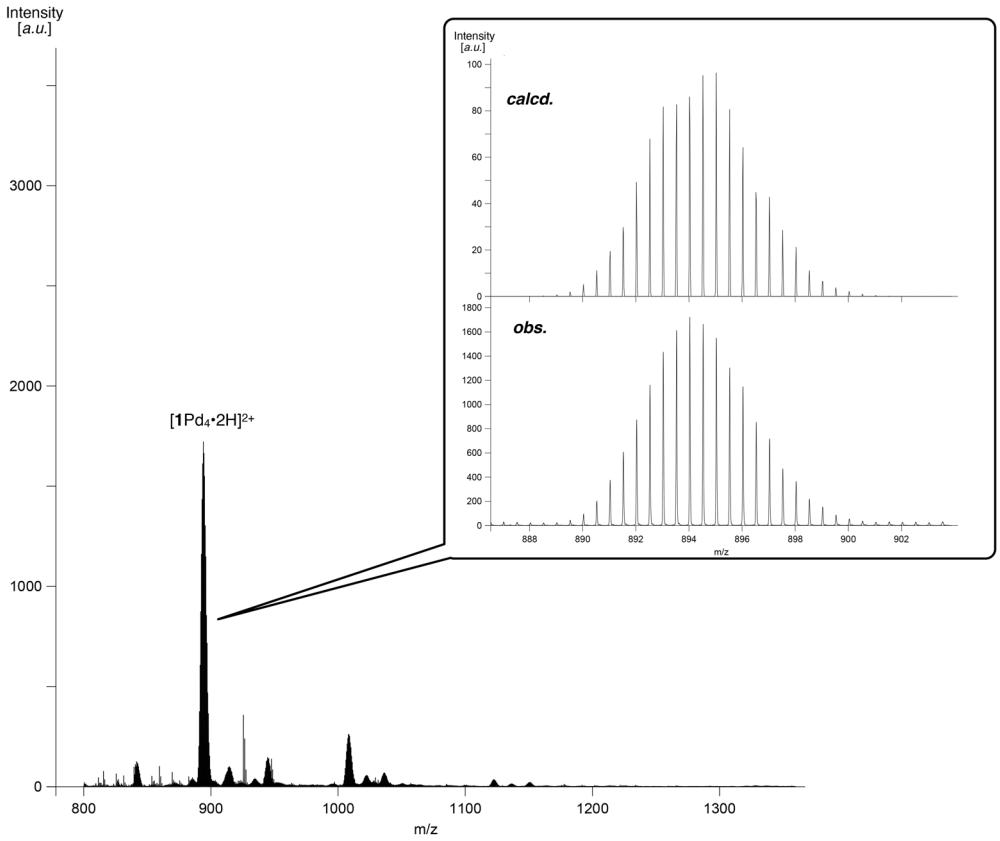


Figure S20. ESI-TOF mass spectrum of [**1**Pd_4L_4] (positive, CH_3CN).

A single crystal of [**1**$Pd_4(CH_3CN)_4$]·3.5AcOEt·0.5CH_3CN·$CHCl_3$ suitable for an X-ray diffraction analysis was obtained by AcOEt vapor diffusion into a $CHCl_3$/CH_3CN solution of [**1**$Pd_4(CH_3CN)_2(H_2O)_2$].
Crystallographic data for $C_{98}H_{102.5}N_{8.5}O_{15}Cl_3F_{12}Pd_4$, Fw = 2399.33, red column, 0.39 × 0.10 × 0.06 mm^3, monoclinic, space group C 2/c (No.15), a = 31.334(4) Å, b = 21.718(3) Å, c = 30.168(4) Å, β = 95.600(1)°, V = 20432(5) Å^3, Z = 8, T = 100 K, λ (Mo Kα) = 0.71073 Å, θ_{max} = 26.424°, R_1 = 0.0790 ($I > 2\sigma$), wR_2 = 0.2560 (all), GOF = 1.042. CCDC 2424094.

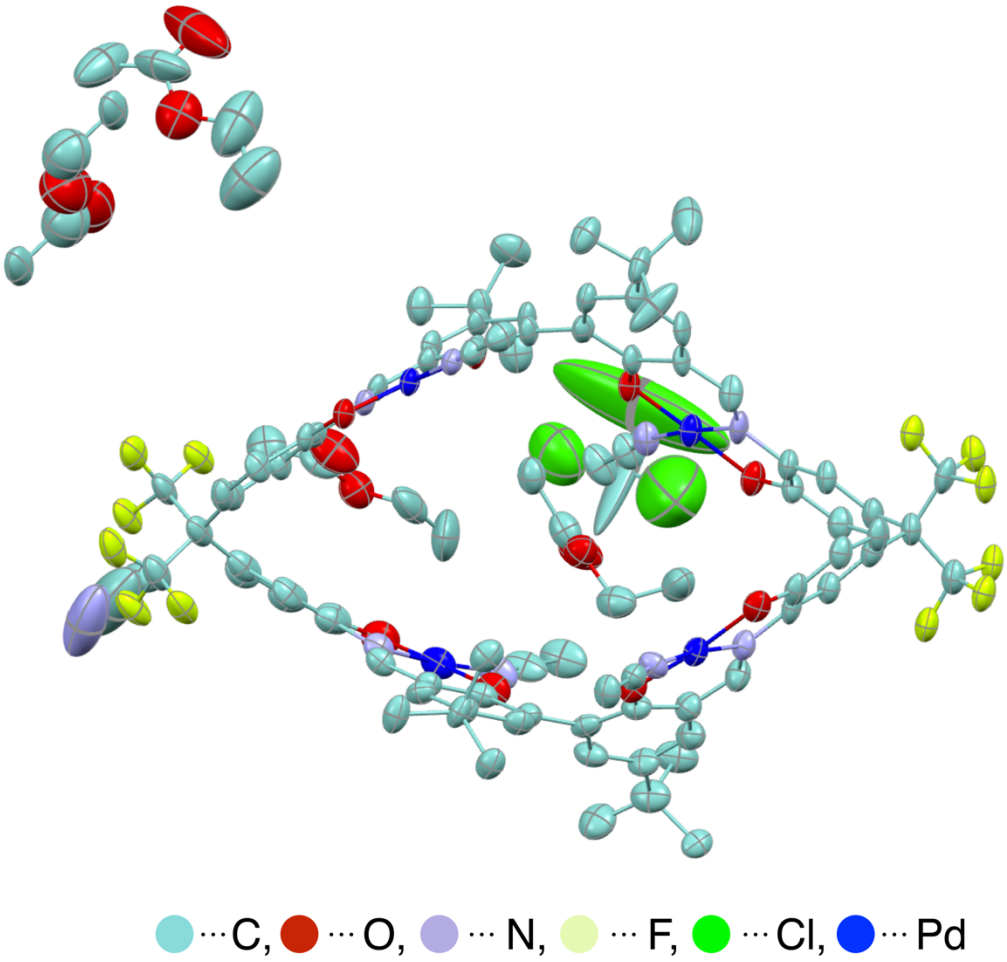


Figure S21. The molecular structure of [**1**$Pd_4(CH_3CN)_4$]·3.5AcOEt·0.5CH_3CN·$CHCl_3$ determined by X-ray diffraction analysis. An ellipsoidal model (50% probability). One of the disordered models is shown. Hydrogen atoms were omitted for clarity.

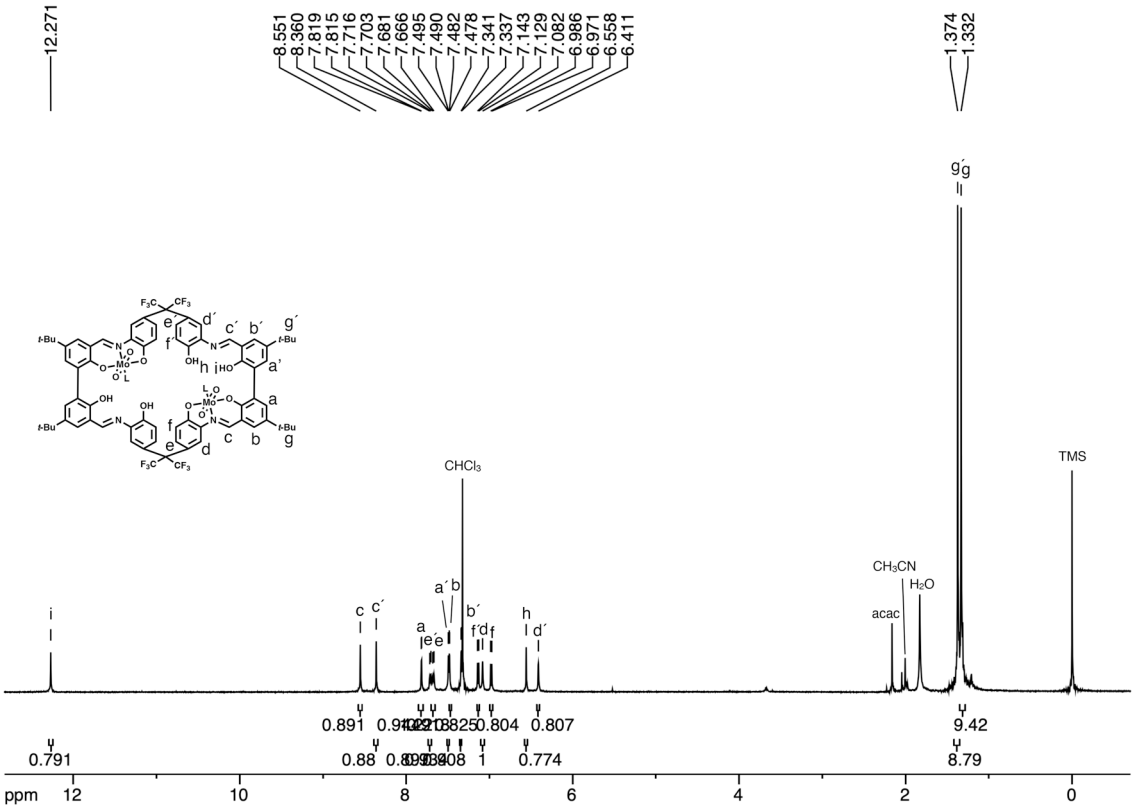


Figure S22. ^{1}H NMR spectrum of [H_4**1**$Mo_2O_4L_2$] ($CDCl_3/CD_3CN$ = 10/1, 600 MHz).

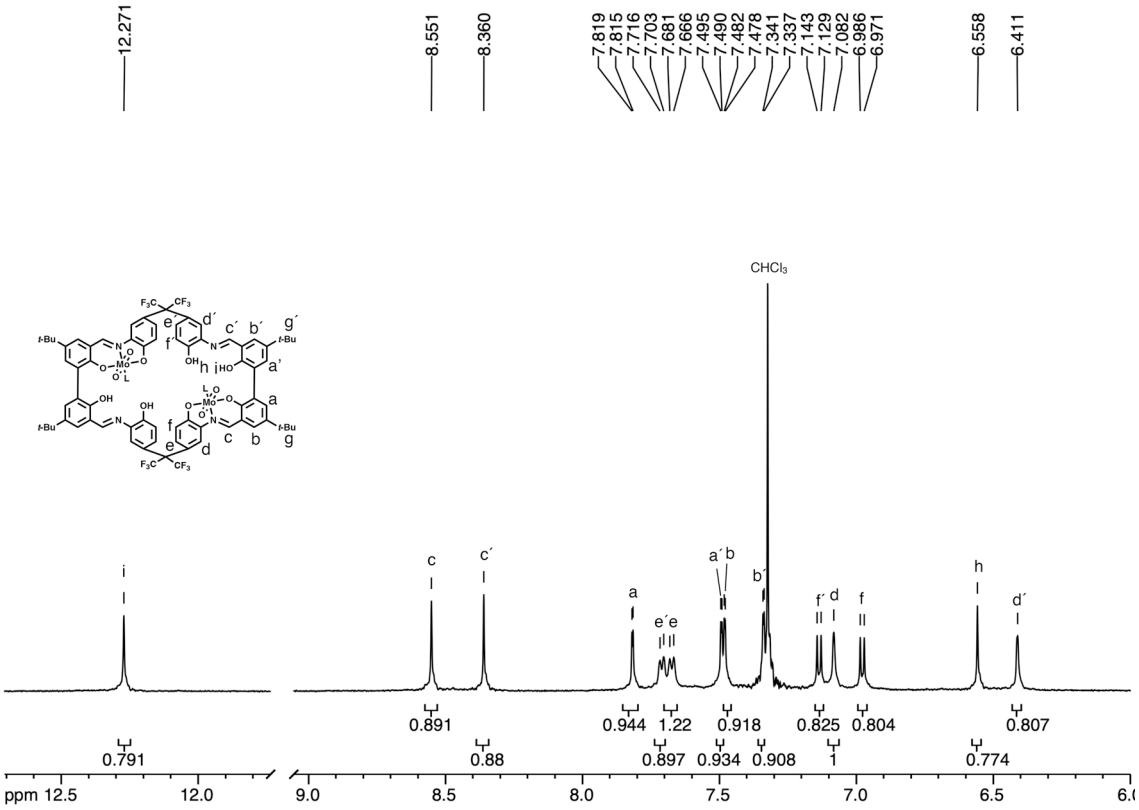


Figure S23. ^{1}H NMR spectrum (aromatic region (5.75–12.70 ppm)) of [H_4**1**$Mo_2O_4L_2$] ($CDCl_3/CD_3CN$ = 10/1, 600 MHz).

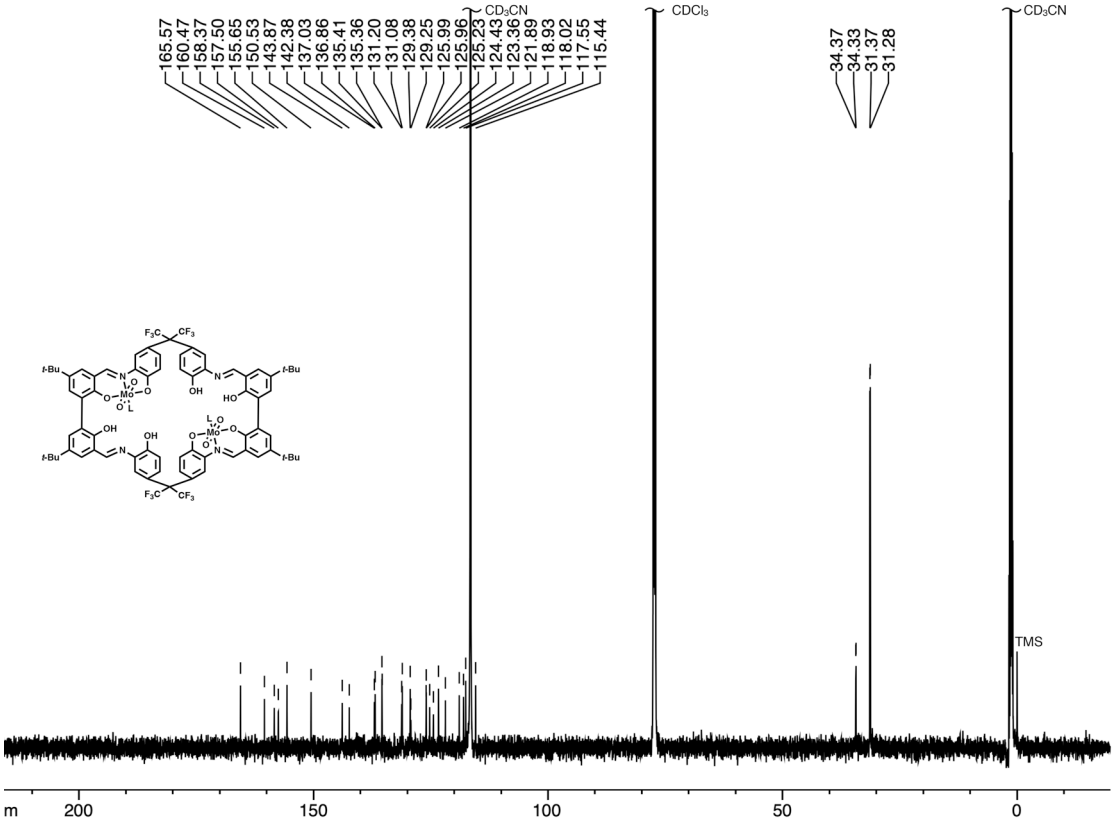


Figure S24. ^{13}C NMR spectrum of [H_4**1**$Mo_2O_4L_2$] ($CDCl_3$/CD_3CN = 10/1, 151 MHz).

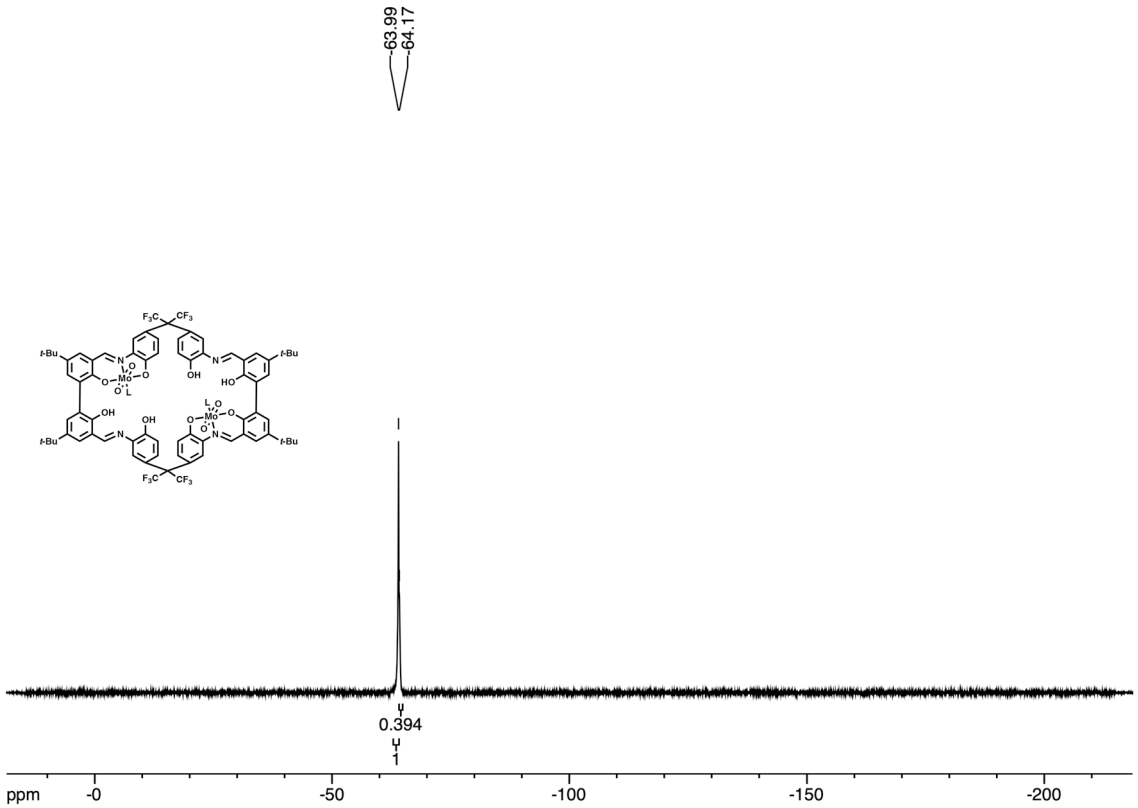


Figure S25. ^{19}F NMR spectrum of [H_4**1**$Mo_2O_4L_2$] ($CDCl_3$/CD_3CN = 10/1, 565 MHz).

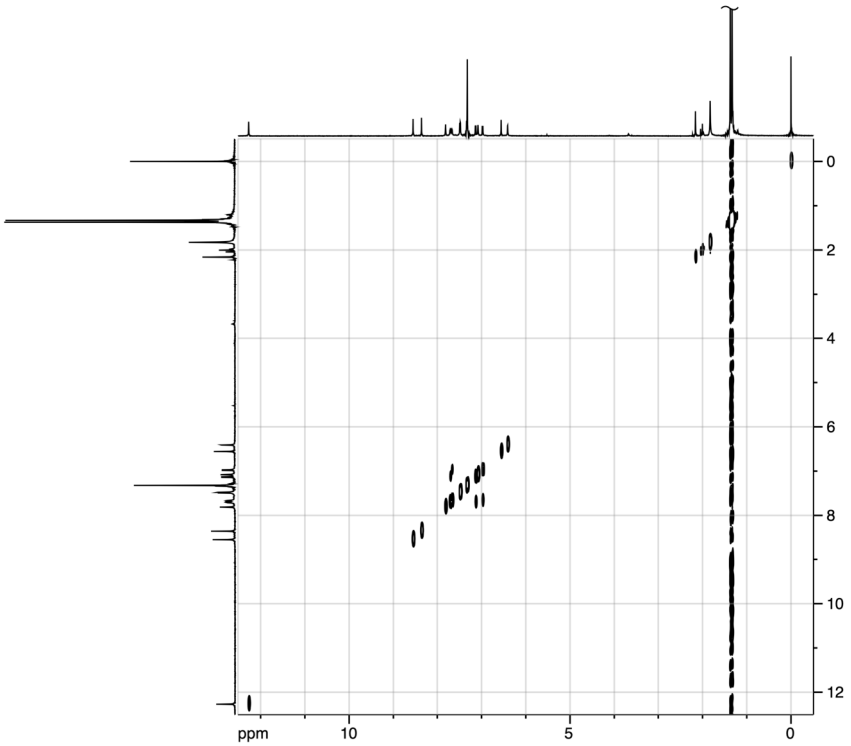


Figure S26. ^{1}H–^{1}H COSY spectrum of [H_4**1**$Mo_2O_4L_2$] ($CDCl_3/CD_3CN$ = 10/1, 600 MHz).

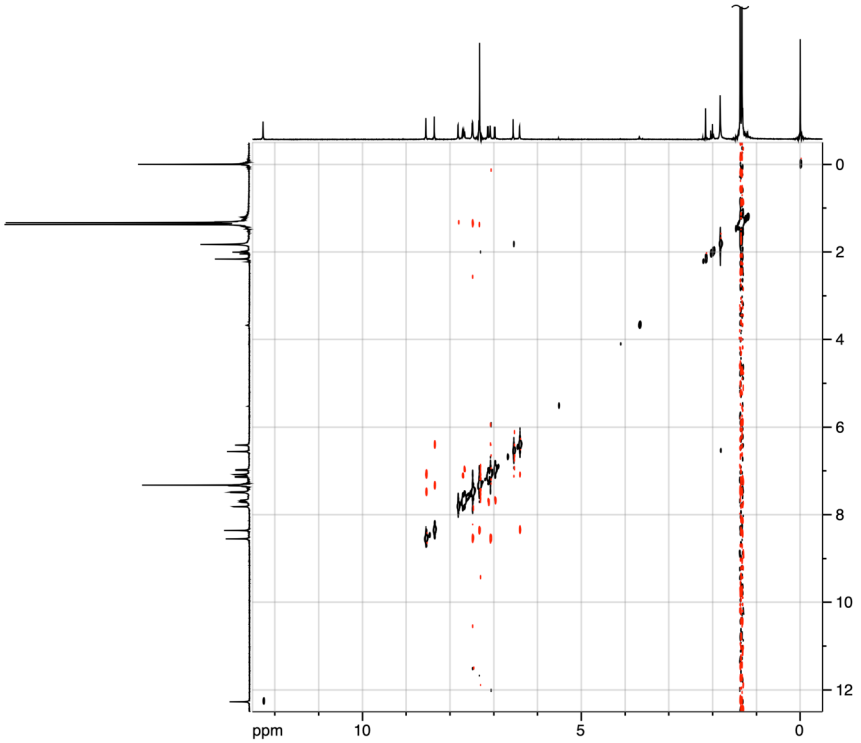


Figure S27. ^{1}H–^{1}H ROESY spectrum of [H_4**1**$Mo_2O_4L_2$] ($CDCl_3/CD_3CN$ = 10/1, 600 MHz).

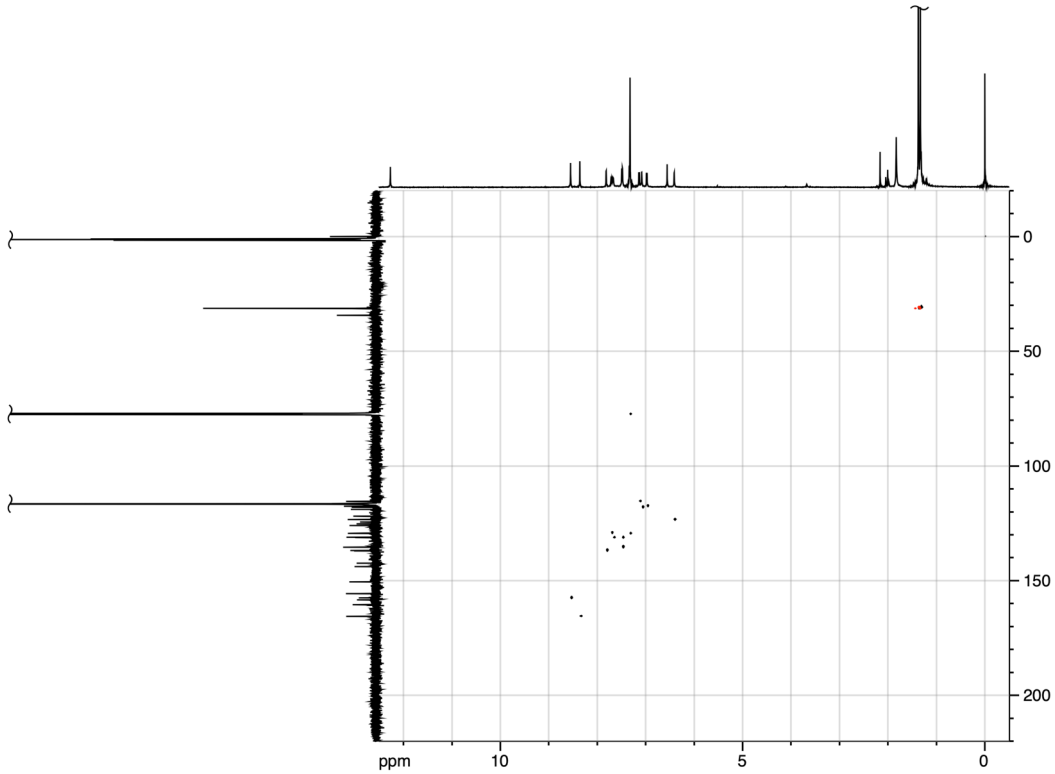


Figure S28. $^{1}H–^{13}C$ HSQC spectrum of $[H_4\mathbf{1}Mo_2O_4L_2]$ ($CDCl_3/CD_3CN$ = 10/1, 600 MHz).

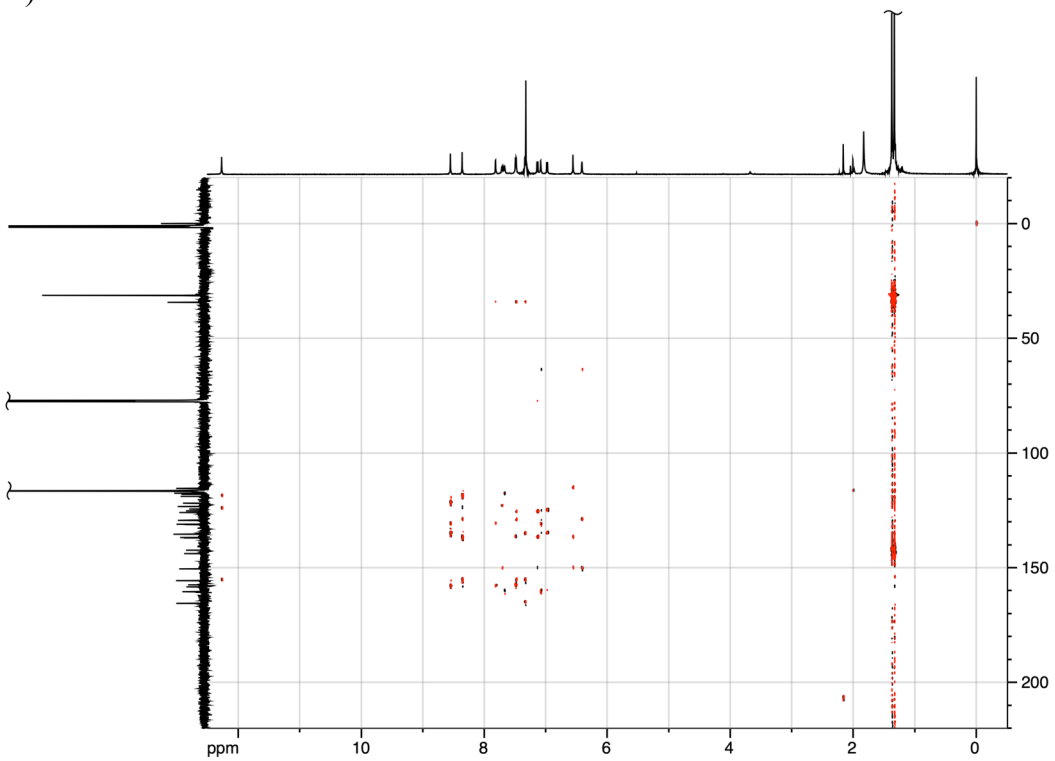


Figure S29. $^{1}H–^{13}C$ HMBC spectrum of $[H_4\mathbf{1}Mo_2O_4L_2]$ ($CDCl_3/CD_3CN$ = 10/1, 600 MHz).

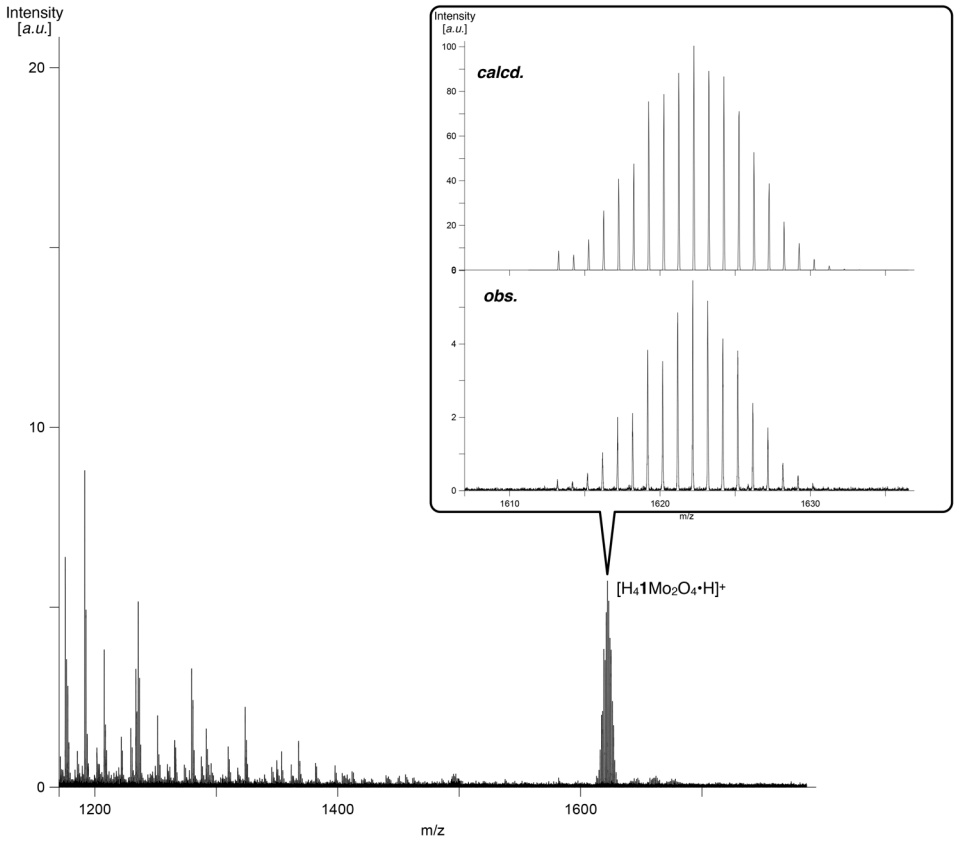


Figure S30. ESI-TOF mass spectrum of $[H_4\mathbf{1}Mo_2O_4L_2]$ (positive, CH_3CN).

A single crystal of $[H_4\mathbf{1}Mo_2O_4(H_2O)(C_4H_8O)]\cdot 5.5CHCl_3\cdot 2C_4H_8O$ suitable for an X-ray diffraction analysis was obtained by heptane vapor diffusion into $CHCl_3$ and THF mixed solution of $[H_4\mathbf{1}Mo_2O_4(H_2O)_2]$.
Crystallographic data for $C_{91.5}H_{95.5}N_4O_{16}F_{12}Cl_{16.5}Mo_2$ ($[H_4\mathbf{1}Mo_2O_4(H_2O)(C_4H_8O)]\cdot 5.5CHCl_3\cdot 2C_4H_8O$), Fw = 2512.02, yellow column, 0.50 × 0.06 × 0.03 mm^3, triclinic, space group P-1 (No.2), a = 14.7987(4) Å, b = 17.5747(5) Å, c = 22.7001(6) Å, α = 100.427(1)°, β = 90.674(1)°, γ = 107.221(1)°, V = 5532.7(3) Å^3, Z = 2, T =100 K, λ (Mo Kα) = 0.71073 Å, θ_{max} = 27.500°, R_1 = 0.0900 ($I > 2\sigma$), wR_2 = 0.2775 (all), GOF = 1.066. CCDC 2424096.

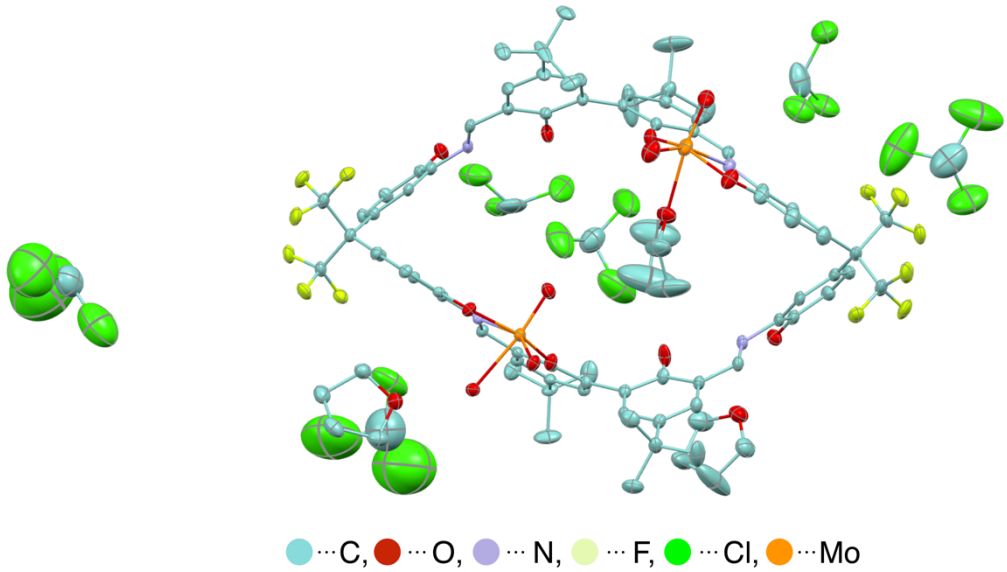


Figure S31. The molecular structure of $[H_4\mathbf{1}Mo_2O_4(H_2O)(C_4H_8O)]\cdot 5.5CHCl_3\cdot 2C_4H_8O$ determined by X-ray diffraction analysis. An ellipsoidal model (50% probability). One of the disordered models is shown. Hydrogen atoms were omitted for clarity.

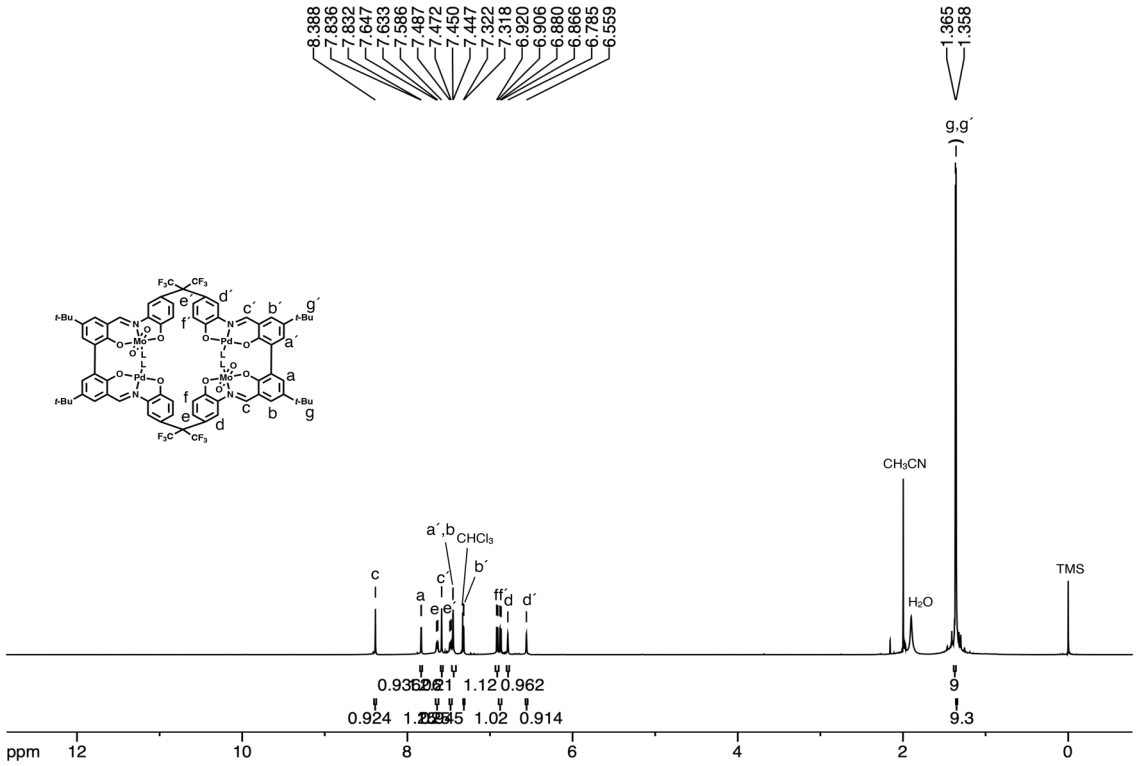


Figure S32. ^{1}H NMR spectrum of [**1**$Pd_2Mo_2O_4L_4$] ($CDCl_3/CD_3CN$ = 10/1, 600 MHz).

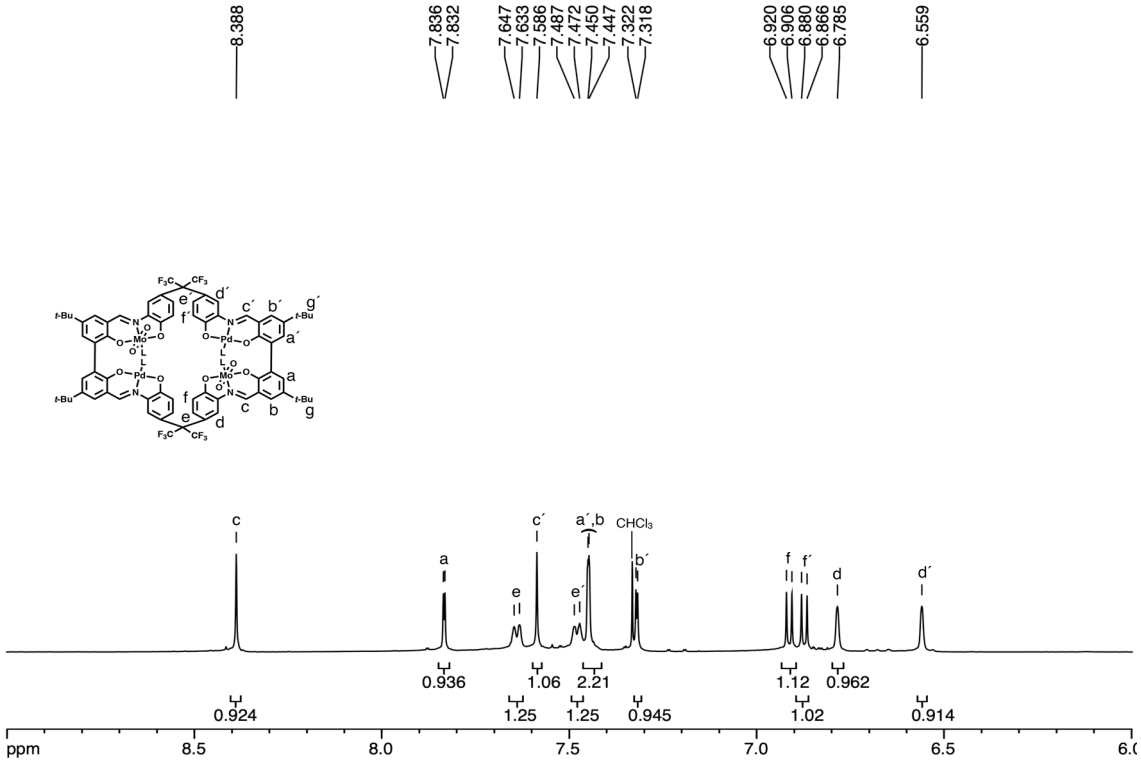


Figure S33. ^{1}H NMR spectrum (aromatic region (6.0–9.0 ppm)) of [**1**$Pd_2Mo_2O_4L_4$] ($CDCl_3/CD_3CN$ = 10/1, 600 MHz).

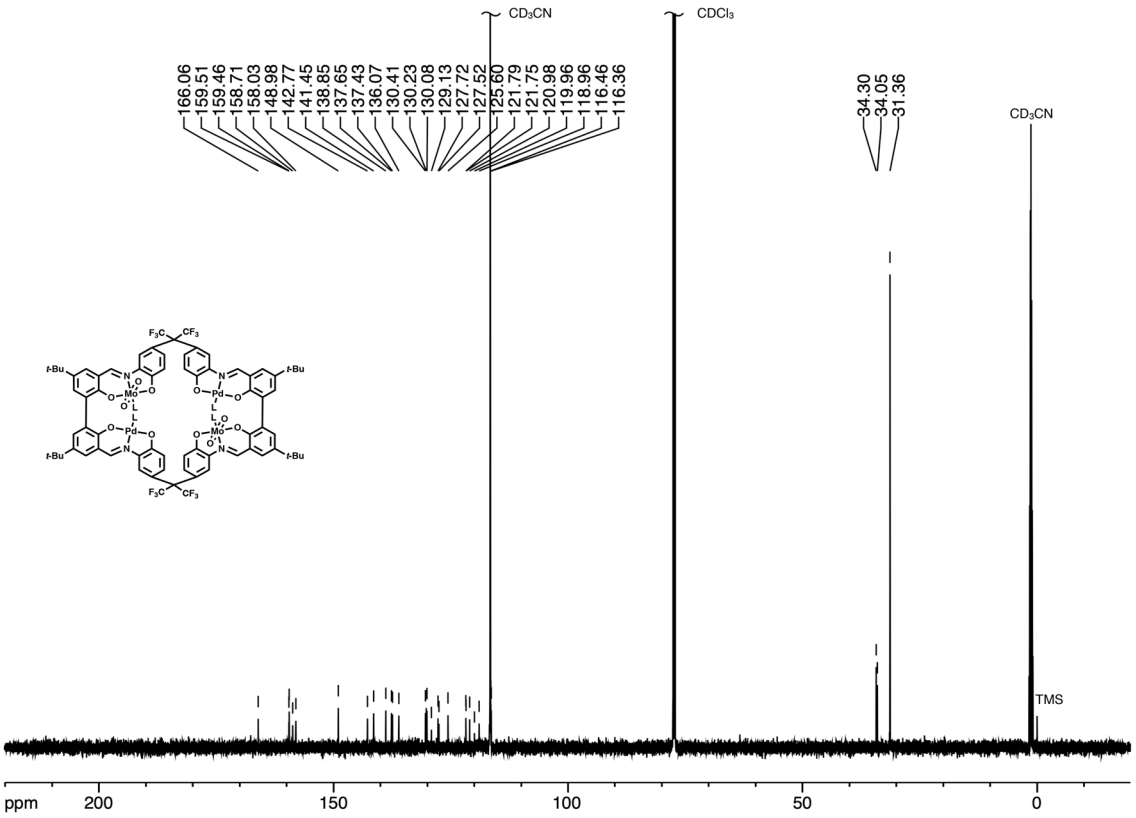


Figure S34. ^{13}C NMR spectrum of [**1**$Pd_2Mo_2O_4L_4$] ($CDCl_3/CD_3CN$ = 10/1, 151 MHz).

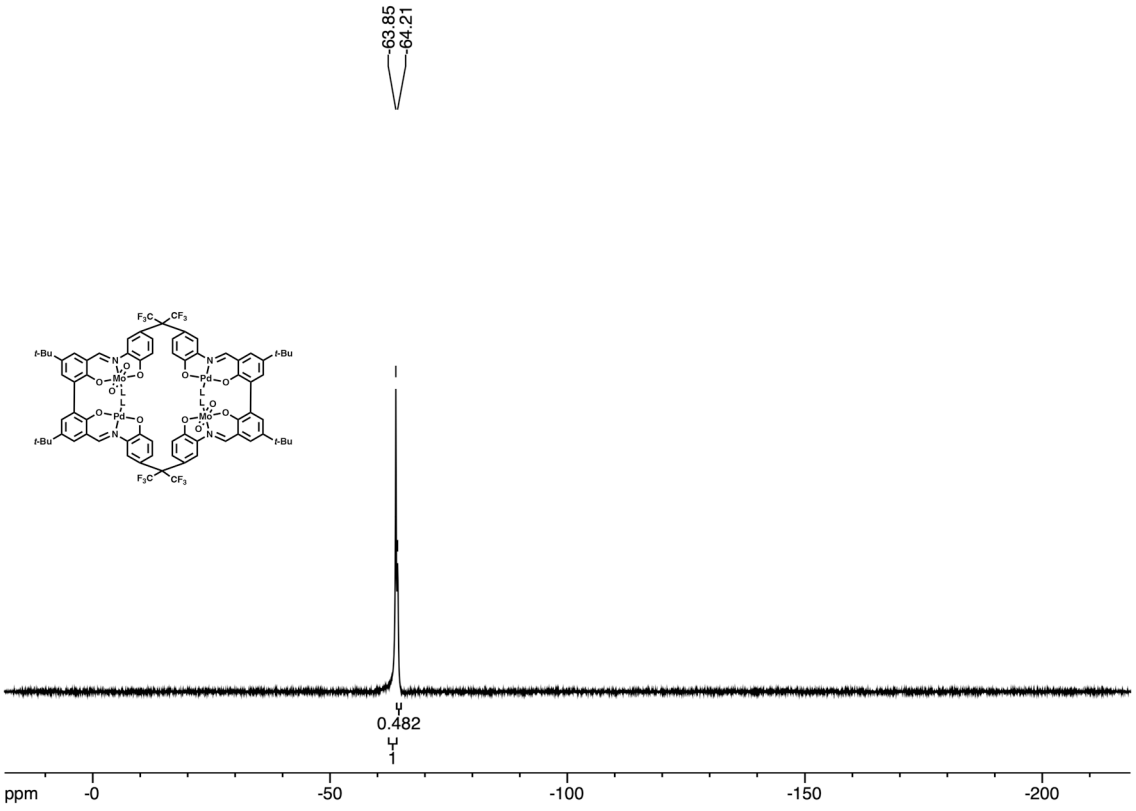


Figure S35. ^{19}F NMR spectrum of [**1**$Pd_2Mo_2O_4L_4$] ($CDCl_3/CD_3CN$ = 10/1, 565 MHz).

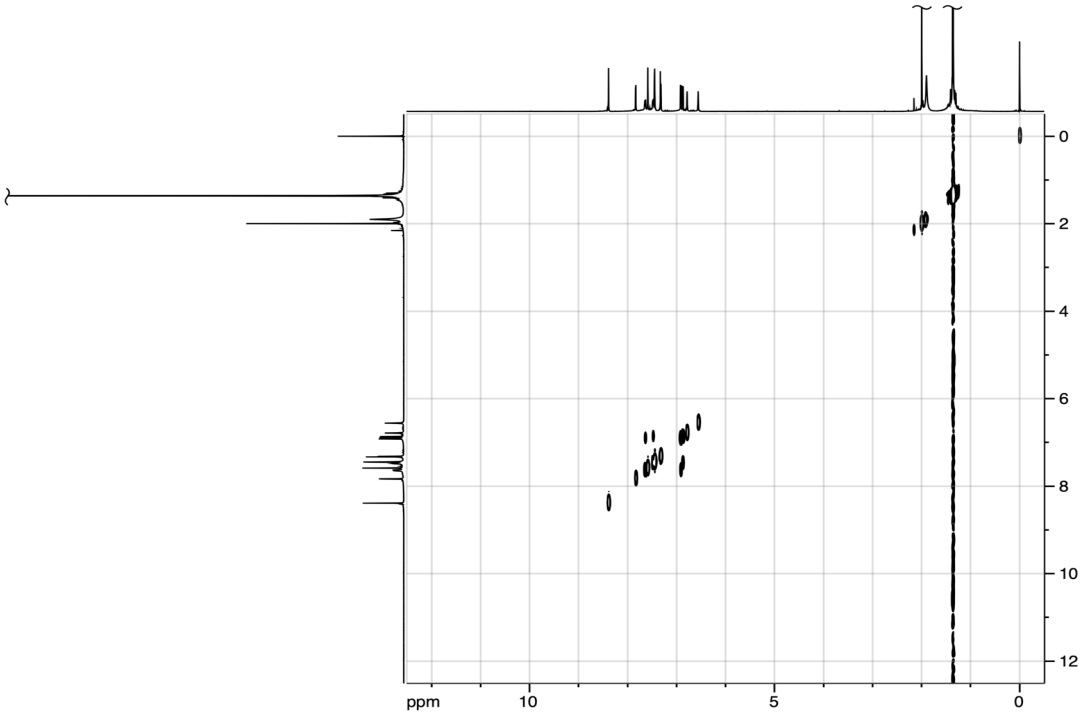


Figure S36. ^{1}H–^{1}H COSY spectrum of [**1**$Pd_2Mo_2O_4L_4$] ($CDCl_3/CD_3CN$ = 10/1, 600 MHz).

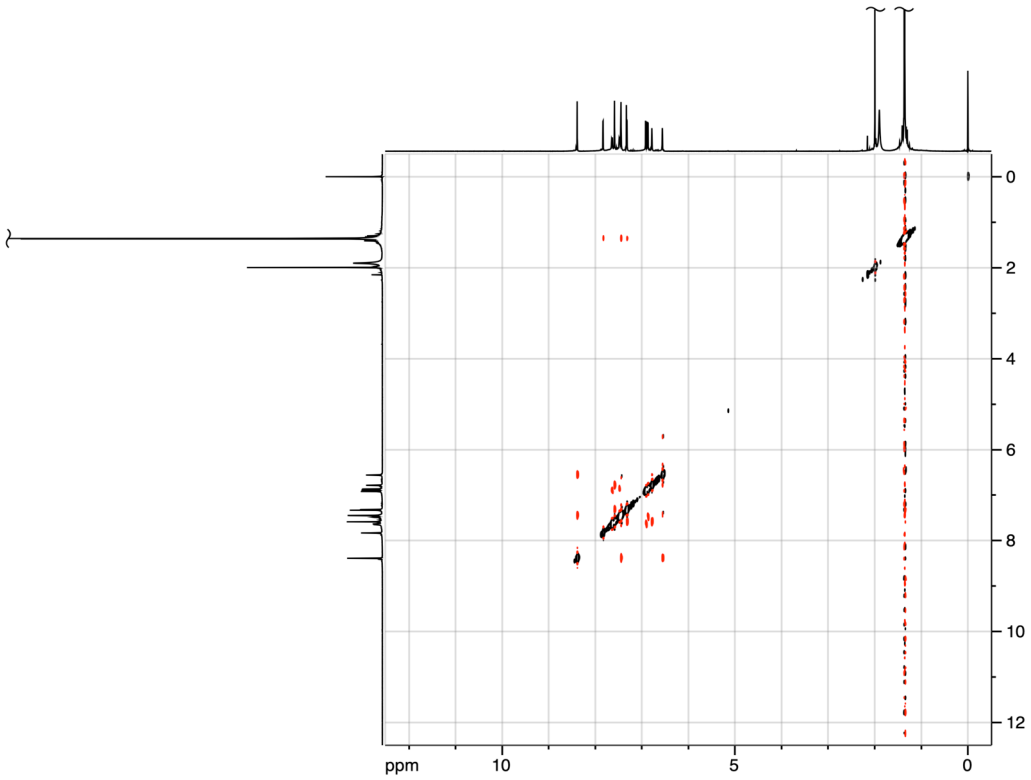


Figure S37. ^{1}H–^{1}H ROESY spectrum of [**1**$Pd_2Mo_2O_4L_4$] ($CDCl_3/CD_3CN$ = 10/1, 600 MHz).

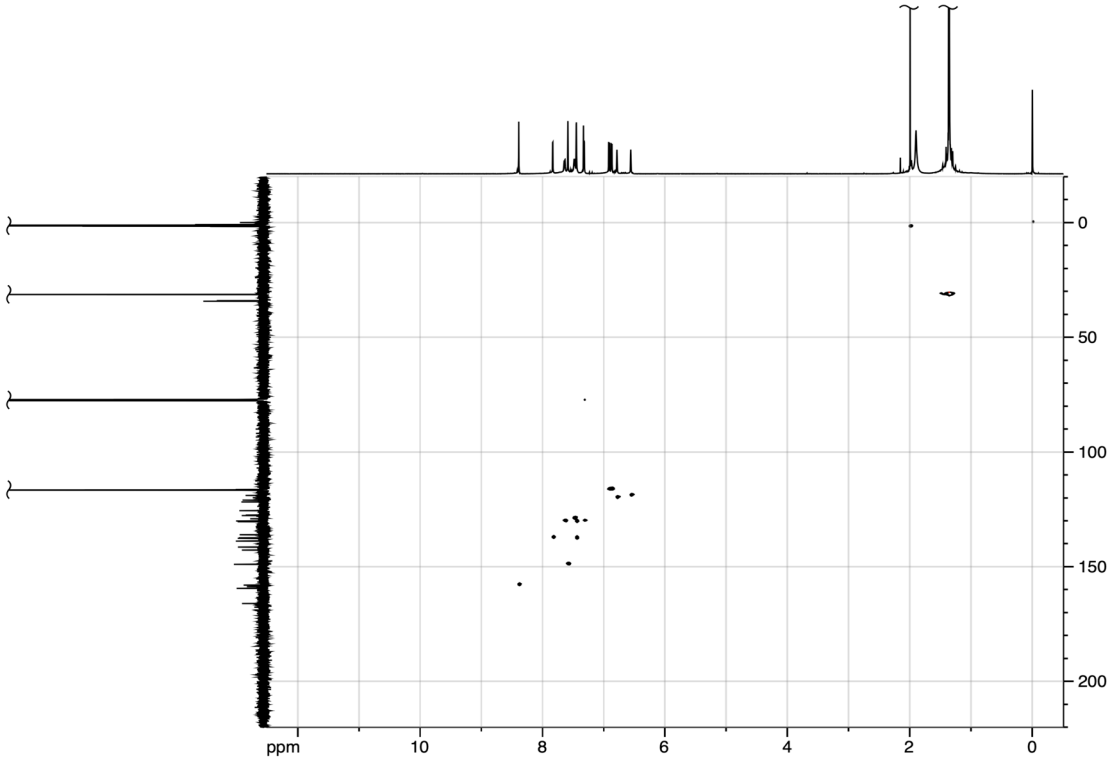


Figure S38. $^{1}H–^{13}C$ HSQC spectrum of [**1**$Pd_2Mo_2O_4L_4$] ($CDCl_3/CD_3CN$ = 10/1, 600 MHz).

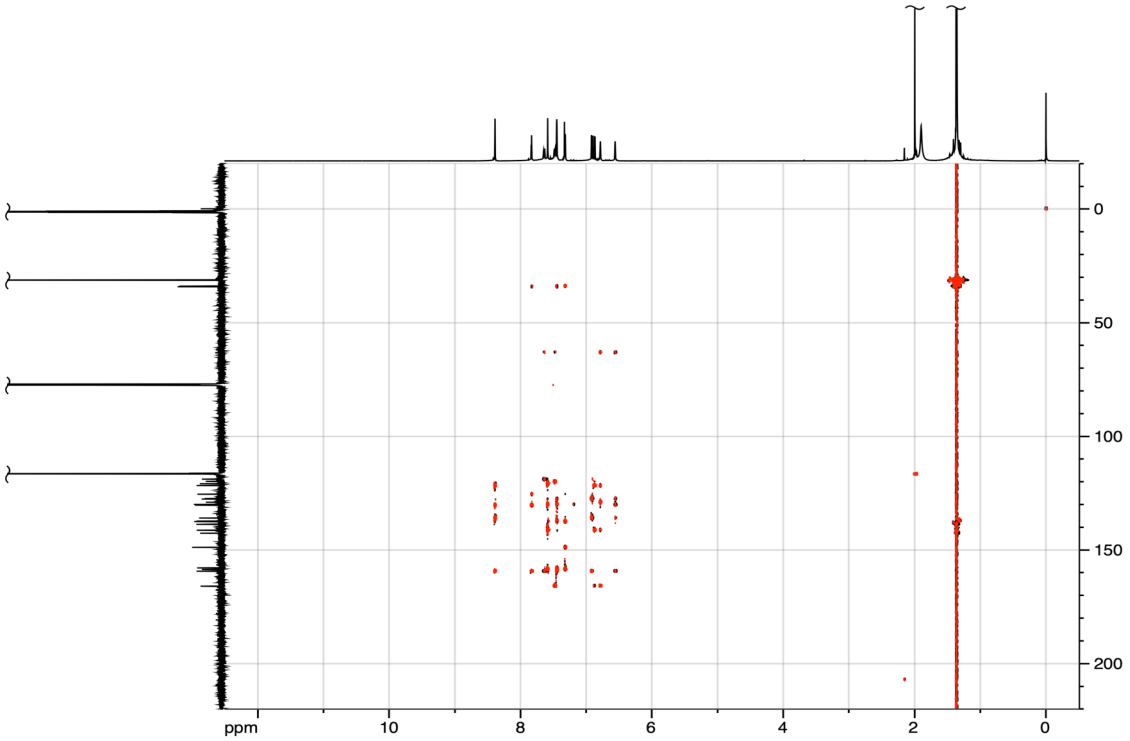


Figure S39. $^{1}H–^{13}C$ HMBC spectrum of [**1**$Pd_2Mo_2O_4L_4$] ($CDCl_3/CD_3CN$ = 10/1, 600 MHz).

A single crystal of 2[**1**$Pd_2Mo_2O_4(H_2O)_2(C_4H_8O)_2$]·4$C_7H_{16}$·2$CHCl_3$·9$C_4H_8O$ suitable for an X-ray diffraction analysis was obtained by heptane vapor diffusion into $CHCl_3$ and THF mixed solution of [**1**$Pd_2Mo_2O_4(CH_3CN)_{1.5}(H_2O)_{2.5}$].
Crystallographic data for $C_{230}H_{290}Cl_6F_{24}Mo_4N_8O_{41}Pd_4$ (2[**1**$Pd_2Mo_2O_4(H_2O)_2(C_4H_8O)_2$]·4$C_7H_{16}$·2$CHCl_3$·9$C_4H_8O$), Fw = 5300.74, red column, 0.52 × 0.11 × 0.10 mm^3, triclinic, space group P-1 (No. 2), a = 15.983(3) Å, b = 21.323(4) Å, c = 42.169(8) Å, α = 102.033(2)°, β = 91.537(2)°, γ = 111.172(2)°, V = 13204(5) Å^3, Z = 2, T = 100 K, λ (Mo Kα) = 0.71073 Å, θ_{max} = 26.614°, R_1 = 0.1239 ($I > 2\sigma$, after SQUEEZE), wR_2 = 0.3083 (all, after SQUEEZE), GOF = 1.143. CCDC 2424095.

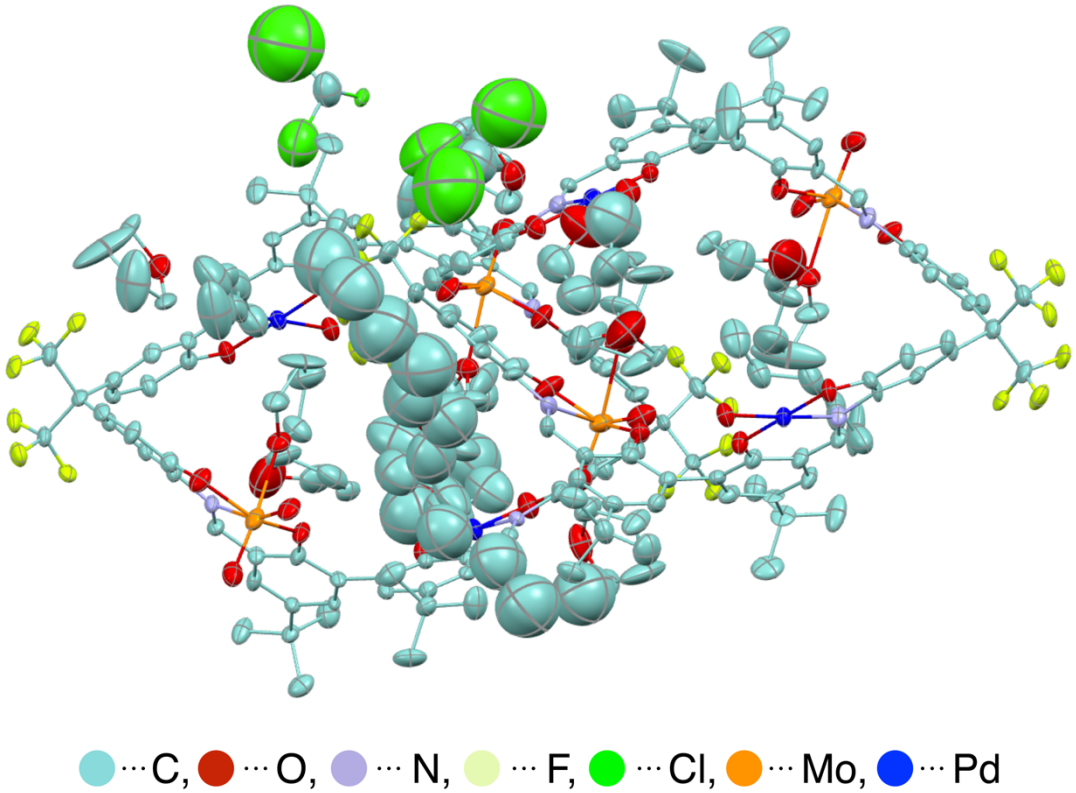
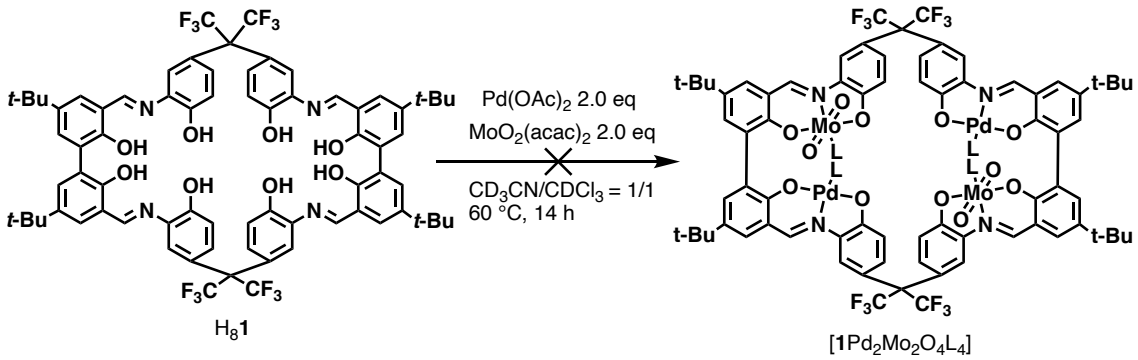


Figure S40. The molecular structure of 2[**1**$Pd_2Mo_2O_4(H_2O)_2(C_4H_8O)_2$]·4$C_7H_{16}$·2$CHCl_3$·9$C_4H_8O$ determined by X-ray diffraction analysis. An ellipsoidal model (50% probability). One of the disordered models is shown. Hydrogen atoms were omitted for clarity.

An attempt to synthesize the heteronuclear complex by simultaneous addition of Pd and Mo salts

Scheme S6. A complexation experiment to add $Pd(OAc)_2$ and $MoO_2(acac)_2$ simultaneously against H_8**1.**



H_8**1** (1.93 mg, 1.41 μmol, 1.0 eq.) was weighed in an NMR tube and dissolved in $CDCl_3/CD_3CN$ = 1/1 (500 μL). $Pd(OAc)_2$ (6.48 mg, 28.86 μmol) was weighed in a microtube and dissolved in $CDCl_3/CD_3CN$ = 1/1 (300 μL). $MoO_2(acac)_2$ (9.58 mg, 29.37 μmol) was also weighed in another microtube and dissolved in $CDCl_3/CD_3CN$ = 1/1 (300 μL). 30 μL each of $Pd(OAc)_2$ (2.88 μmol, 2.0 eq.) and $MoO_2(acac)_2$ solution (2.93 μmol, 2.0 eq.) was added to the solution of the ligand, then the solution was heated at 60 °C for 14 h.^{1}H NMR measurements were carried out before and after heating.

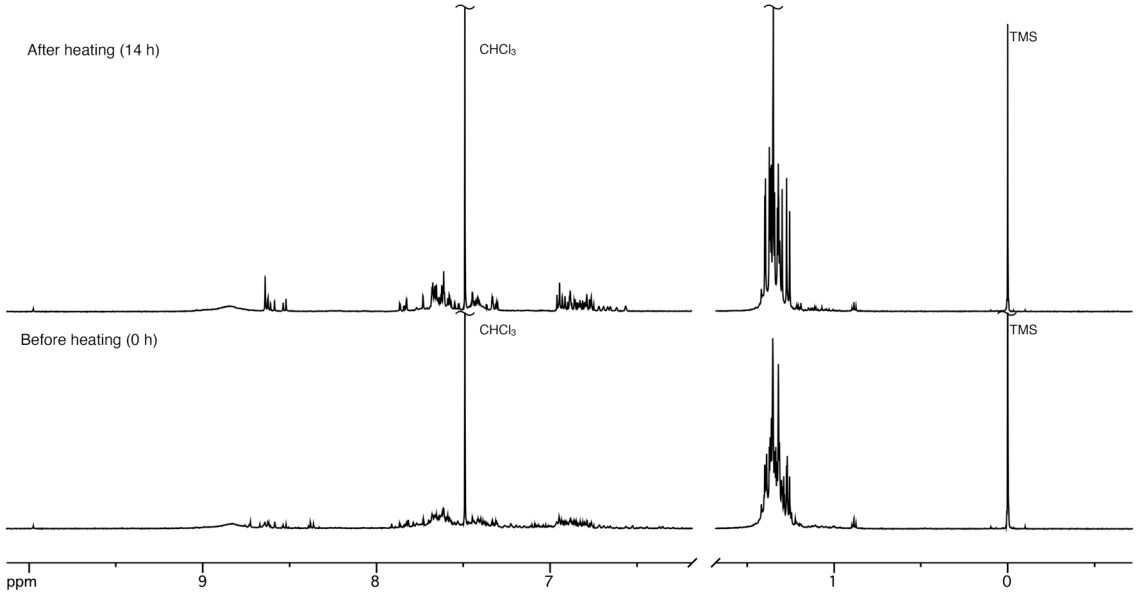


Figure S41. A complexation experiment to add $Pd(OAc)_2$ and $MoO_2(acac)_2$ simultaneously against H_8**1** (^{1}H NMR, 600 MHz, $CDCl_3/CD_3CN$ = 1/1).

Mixing pre-formed tetranuclear Mo complex and tetranuclear Pd complex

[**1**$Mo_4O_8(H_2O)_4$] (1.30 mg, 0.67 μmol) and [**1**$Pd_4(CH_3CN)_2(H_2O)_2$] (1.17 mg, 0.63 μmol) were weighed in an NMR tube and dissolved in $CDCl_3/CD_3CN$ = 10/1 (550 μL), then the solution was heated at 60 °C for 22 h.^{1}H NMR measurements were carried out before and after heating.

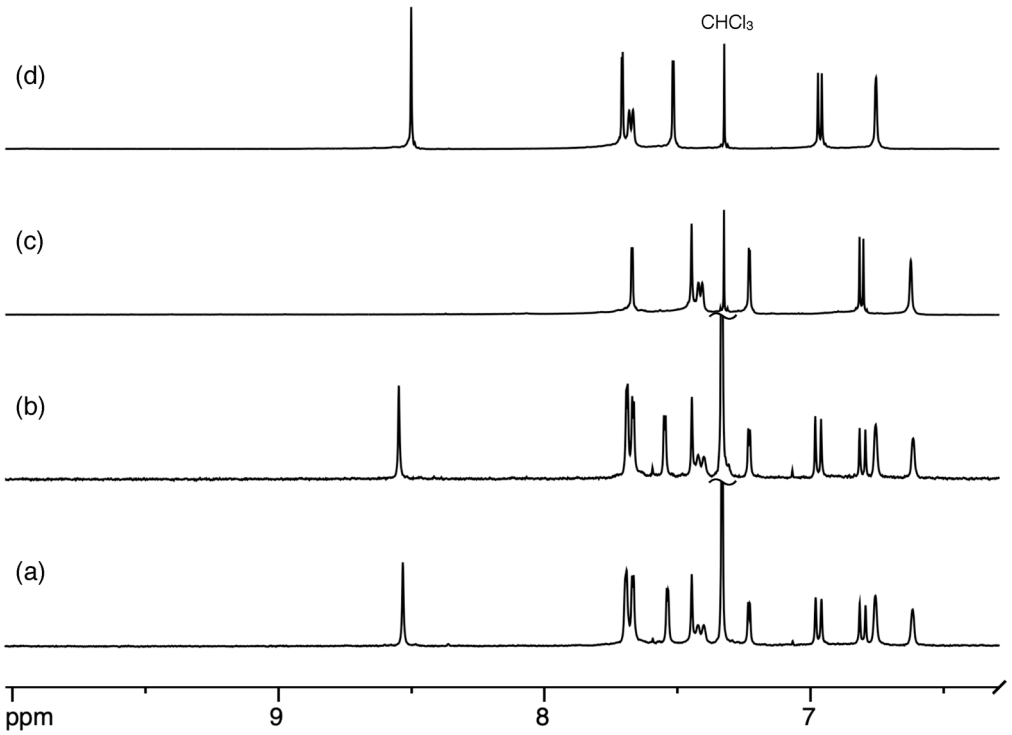


Figure S42. Mixing and heating preformed [**1**$Mo_4O_8L_4$] and [**1**Pd_4L_4] complexes (^{1}H NMR, $CDCl_3/CD_3CN$ = 10/1, (a,b) 400 MHz, (c,d) 600 MHz). (a) A mixture of [**1**$Mo_4O_8L_4$] and [**1**Pd_4L_4]. (b) The sample (a) heated at 60 °C for 22 h. (c) [**1**Pd_4L_4]. (d) [**1**$Mo_4O_8L_4$].

DFT calculation of H_8**1**

An energy-minimized structure of $(CF_3)_2C$-tetrasap H_8**1** was obtained by a DFT calculation using a result of a preliminary XRD measurement as an initial structure. The DFT calculation was performed by Spartan'20[S6] at the B3LYP/6-31G* level in gas phase.

E = –4879.771975 Hartree

F	0.3308	-2.1626	7.6975
F	4.3124	0.3714	6.9409
O	-4.1113	1.3015	0.2651
F	-3.5283	-0.1302	-8.9553
F	-4.4019	1.5605	-7.9223
O	-2.9156	-0.004	2.7953
O	-3.6917	3.9529	-2.5672
O	1.1572	-3.6022	-5.9017
F	-2.1433	2.5913	-8.8147
F	1.0379	-0.7697	9.2039
C	5.877	1.7437	-1.1543
F	2.1433	-2.5913	8.8147
C	-1.4192	-0.4133	-6.7746
F	-1.0379	0.7697	-9.2039
F	-4.3124	-0.3714	-6.9409
N	1.7632	-0.998	-4.9531
N	-3.7869	1.2325	-2.379
C	-0.3079	2.5748	6.2054
C	-3.6339	0.4729	-7.7486
C	5.967	2.4462	0.0667
F	3.5283	0.1303	8.9553
C	4.6979	-0.0996	-0.1423
O	-1.1572	3.6022	5.9017
F	4.4019	-1.5605	7.9223
C	-4.333	0.0573	-2.3325
C	-5.2653	0.214	2.5939
C	-4.1247	1.1655	4.5274
C	-3.3504	1.7971	-3.5911
F	-0.3308	2.1626	-7.6975
C	-4.0668	0.458	3.2995
C	1.4366	-1.5997	8.2248
C	-0.6258	1.2818	5.7323
C	-5.3713	1.5941	5.0298
C	2.9295	-1.4363	-5.2998
C	0.2634	0.2384	6.0018
O	2.9156	0.004	-2.7953
C	-1.7026	-1.699	-7.2497
C	-2.533	3.1166	-5.9202
C	-5.2614	-0.5017	1.2874
O	4.1113	-1.3015	-0.2651
C	-6.5658	1.3394	4.3687
C	-5.4257	-1.8225	-1.182
C	6.5658	-1.3394	-4.3687
C	-3.3085	3.2094	-3.6324
C	6.4696	-0.6438	-3.1457
C	7.8359	-2.5342	-6.2341
C	-2.2499	0.839	-7.1334
C	-2.8925	3.854	-4.7966
C	-2.9483	1.0743	-4.7191
C	-7.9427	1.7724	4.8996
C	4.7998	0.5583	1.1099

C	-8.8236	0.5215	5.1264
C	-4.7998	-0.5583	-1.1099
C	-6.6378	-3.8295	-0.1065
C	-2.9295	1.4363	5.2998
C	6.6448	4.4301	1.5249
C	2.5452	-1.7132	5.8963
C	5.2653	-0.214	-2.5939
C	-2.5452	1.7132	-5.8963
O	3.6916	-3.9529	2.5672
C	5.2614	0.5017	-1.2874
C	7.9427	-1.7724	-4.8996
C	-5.8733	-4.7979	0.8267
C	-0.8575	-2.7646	-6.9461
C	0.8575	2.7646	6.9461
C	-8.1042	-3.7115	0.3716
N	-1.7632	0.998	4.9531
C	-0.2634	-0.2384	-6.0018
C	6.6378	3.8295	0.1065
C	2.9483	-1.0743	4.7191
C	8.6312	-2.7003	-3.8706
C	5.4257	1.8225	1.182
C	5.3713	-1.5941	-5.0298
C	-8.6312	2.7003	3.8706
C	0.6258	-1.2818	-5.7323
C	2.2499	-0.839	7.1334
C	-5.967	-2.4462	-0.0667
C	2.533	-3.1166	5.9202
C	-6.4696	0.6438	3.1457
C	8.8236	-0.5215	-5.1264
C	4.1247	-1.1655	-4.5274
C	4.0668	-0.458	-3.2995
C	-4.6979	0.0996	0.1423
C	2.8925	-3.854	4.7966
N	3.7869	-1.2325	2.379
C	-7.8359	2.5342	6.2341
C	3.3504	-1.797	3.5911
C	1.7026	1.699	7.2497
C	-5.877	-1.7437	1.1543
C	-6.6448	-4.4301	-1.5249
C	8.1042	3.7115	-0.3716
C	3.3085	-3.2094	3.6324
C	5.8733	4.7979	-0.8267
C	4.333	-0.0573	2.3325
C	1.4192	0.4133	6.7746
C	-1.4366	1.5997	-8.2248
C	3.6339	-0.4729	7.7486
C	0.3079	-2.5748	-6.2054
H	-3.7472	1.5359	-0.6268
H	-2.1898	0.2436	3.4334
H	-4.0001	3.3317	-1.8825
H	0.7649	-4.4337	-6.2104
H	6.2959	2.1869	-2.0537
H	-0.7649	4.4338	6.2104
H	-4.494	-0.5196	-3.2509
H	-5.3677	2.1318	5.9733
H	3.0665	-2.0182	-6.2168
H	0.0115	-0.7388	5.6061
H	2.1898	-0.2436	-3.4334
H	-2.5739	-1.896	-7.8588
H	-2.2426	3.6521	-6.8141

H	3.7472	-1.5359	0.6268
H	-5.4761	-2.2962	-2.1575
H	7.374	-0.4355	-2.5804
H	8.8359	-2.8213	-6.5783
H	7.3811	-1.9199	-7.0199
H	7.2461	-3.4527	-6.1335
H	-2.8743	4.9388	-4.8135
H	-2.9332	-0.0084	-4.6717
H	-9.813	0.8123	5.4996
H	-8.3666	-0.1524	5.8601
H	-8.9717	-0.0448	4.2006
H	-3.0665	2.0182	6.2168
H	7.1275	5.4136	1.5085
H	7.2014	3.8021	2.2303
H	5.6297	4.5676	1.9152
H	4.0001	-3.3317	1.8825
H	-6.3419	-5.7896	0.8159
H	-5.8676	-4.4434	1.8628
H	-4.8308	-4.9091	0.5077
H	-1.1019	-3.7616	-7.3091
H	1.1019	3.7616	7.3091
H	-8.5902	-4.6948	0.3586
H	-8.6769	-3.0409	-0.2795
H	-8.1723	-3.325	1.3942
H	-0.0115	0.7388	-5.6061
H	2.9332	0.0084	4.6717
H	9.6142	-3.0179	-4.2402
H	8.0301	-3.5979	-3.6862
H	8.7859	-2.1989	-2.9092
H	5.4761	2.2962	2.1575
H	5.3677	-2.1318	-5.9733
H	-9.6142	3.0179	4.2402
H	-8.7859	2.1989	2.9092
H	-8.0301	3.5979	3.6862
H	2.2426	-3.6521	6.8141
H	-7.374	0.4355	2.5804
H	9.813	-0.8123	-5.4996
H	8.9717	0.0448	-4.2006
H	8.3666	0.1524	-5.8601
H	2.8743	-4.9388	4.8135
H	-8.8359	2.8213	6.5783
H	-7.2461	3.4527	6.1335
H	-7.3811	1.9199	7.0199
H	2.5739	1.896	7.8588
H	-6.2959	-2.1869	2.0537
H	-7.1275	-5.4136	-1.5085
H	-5.6297	-4.5676	-1.9152
H	-7.2014	-3.8021	-2.2303
H	8.5902	4.6948	-0.3586
H	8.1723	3.325	-1.3942
H	8.6769	3.0409	0.2795
H	6.3419	5.7896	-0.8159
H	4.8308	4.9091	-0.5077
H	5.8676	4.4434	-1.8628
H	4.494	0.5196	3.2509

3. References for the Supplementary Information

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