Supporting Information for

Coordination-driven self-assembly of anthraquinone-based metal-organic cages for photocatalytic selective [2 + 2] cycloaddition

Yao Jin, Hong Jiang, Xianhui Tang, Wenqiang Zhang, Yan Liu* and Yong Cui*

School of Chemistry and Chemical Engineering, Frontiers Science Center for Transformative Molecules and State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, P. R. China;

Email: liuy@sjtu.edu.cn;yongcui@sjtu.edu.cn

Table of Content

1. Materials and general procedures

All of the chemicals are commercially available, and used without further purification. Elemental analyses were performed with an EA1110 CHNS-0 CE elemental analyzer. The IR (KBr pellet) spectra were recorded (400-4000 cm^{-1} region) on a Nicolet Magna 750 FT-IR spectrometer. All UV-Vis absorption spectra were recorded on a Lambda 20 UV/Vis Spectrometer (Perkin Elmer, Inc., USA). Thermogravimetric analyses (TGA) were carried out in an air atmosphere with a heating rate of 10 ^{o}C/min on a STA449C integration thermal analyzer. Powder X-ray diffraction (PXRD) data were collected on a Bruke D8 advance diffractometer using Cu-*Kα* radiation. The calculated PXRD patterns were generated using the SHELXTL-XPOW program and single crystal reflection data. ^{1}H and ^{13}C NMR experiments were carried out on a MERCURY plus 400 spectrometer operating at resonance frequencies of 400 MHz or a Bruker 500 spectrometer operating at resonance frequencies of 500 MHz. $CDCl_3$ (δ 7.26 ppm) or DMSO-d_6 (δ 2.50 ppm) was used as the internal standard for ^{1} H NMR analysis and $CDCl_3$ (δ 77.04 ppm) or DMSO-d_6 (δ 39.93 ppm) were used as the internal standards for ^{13}C NMR analyses of compounds. The mass spectra were recorded on Matrix-Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometry (MALDI-TOF-MS).

X-ray Crystallography. Single-crystal XRD data for **1-Co** was collected on the BL17B beamline in Shanghai Synchrotron Facility. The crystal for **1-Co** was diffracted using '\w scans' method with exposure time of 8 s and redundancy of 3.9. The detector distance was set as 99.99 mm. The resolution for crystal data was 0.85 Å with mean I/sigma of 29.7. The collected diffraction data was processed with HKL3000 software program. According to the resolution vs I/sigma and R(int) table below, the R(int) values for 0.81-0.95 Å shell was 0.0977-0.3081, which were larger than values for inner shells. Moreover, there are some degree of rotational/vibrational disorder of the anthraquinone dicarboxylate ligands and t-Bu groups. Thus, we truncated the data up to 0.95 Å to improve the overall quality of the data and provide the most accurate chemical composition. The structure was solved by direct method and then refined by full-matrix least-squares on F^2 with the SHELXTL 2018/3[1] using Olex2-1.3[2]. DFIX, DANG, FLAT, SADI, and SIMU restraints were used to obtain reasonable parameters. All the non-hydrogen atoms except guest molecules were refined by full-matrix least-squares techniques with anisotropic displacement parameters, and the hydrogen atoms were geometrically fixed at the calculated positions attached to their parent atoms, treated as riding atoms. The benzene ring atoms were geometrically restrained to fit idealized six membered atoms, respectively. Anisotropic least-squares refinement for the framework on 76840 independent

merged reflections (R_{int} = 0.105) converged at residual R_1 = 0.1068, wR_2 = 0.3788 for all data; residual R_1 = 0.1126 and wR_2 = 0.3993 for observed data [I > 2sigma(I)], and goodness of fit (GOF) = 1.024. The ratio for data / restraints / parameters was 76840 / 19610 / 5107. Contributions to scattering due to these highly disordered solvent molecules were removed using PLATON/SQUEEZE[3]; and the structures were then refined again using the data generated.

Single-crystal XRD data for **2-Co** was collected on a Bruker SMART ApexII CCD-based X-ray diffractometer with Cu-Kα radiation (λ = 1.54178 Å) at 173 K. The crystal was diffracted using 'phi and omega scans' method with exposure time of 5 s and redundancy of 10. The detector distance was set as 45 mm. The resolution for crystal data was 0.9 Å with mean I/sigma of 4.00. The data was reduced with the Bruker SAINT program and solved with SHELXT 2018/2 (Sheldrick, 2018). The structure was solved by direct mehod and then refined by full-matrix least-squares on F^2 with the SHELXTL 2018/3[1] using Olex2-1.3[2]. All the non-hydrogen atoms except guest molecules were refined by full-matrix least-squares techniques with anisotropic displacement parameters, and the hydrogen atoms were geometrically fixed at the calculated positions attached to their parent atoms, treated as riding atoms. The benzene ring atoms were geometrically restrained to fit idealized six membered atoms, respectively. DFIX, SADI, FLAT, SIMU, and RIGU restrains were used to obtain reasonable parameters. Anisotropic least-squares refinement for the framework on 8771 independent merged reflections (R_{int} = 0.1236) converged at residual R1 = 0.0924, wR2 = 0.2524 for all data; residual R_1 = 0.1283 and wR_2 = 0.2853 for observed data [I > 2sigma(I)], and goodness of fit (GOF) = 1.073. The ratio for data / restraints / parameters was 8771 / 1127 / 513. Contributions to scattering due to these highly disordered solvent molecules were removed using PLATON/SQUEEZE [3]; and the structures were then refined again using the data generated.

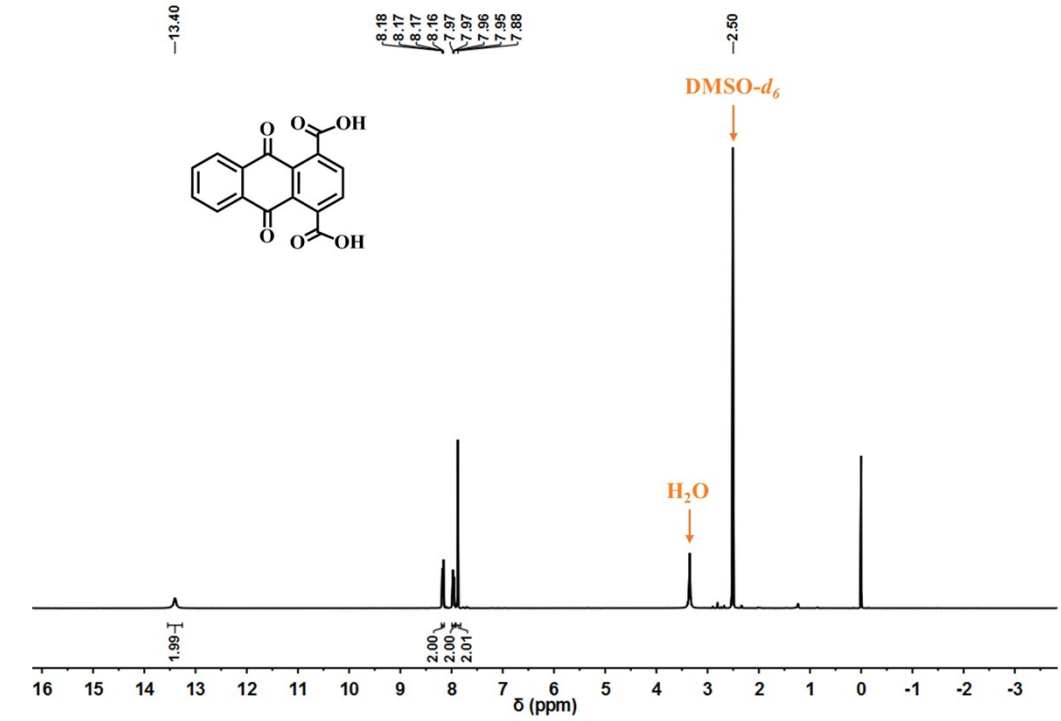
Crystal data and details of the data collection are given in **Table S1**, while the selected bond lengths and angles are presented in **Tables S2-S3**. CCDC 2049320 (**1-Co**), and 2078332 (**2-Co**) contain the supplementary crystallographic data for this paper. The data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

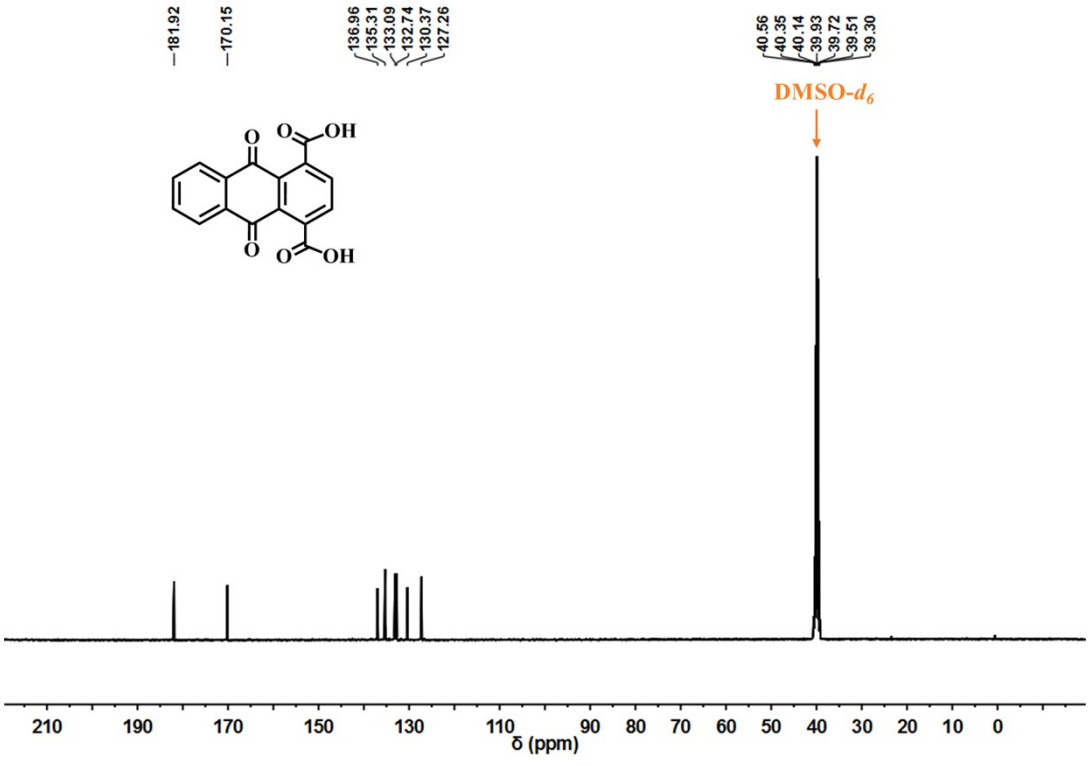
2. Synthesis

2.1 Synthesis of the ligands

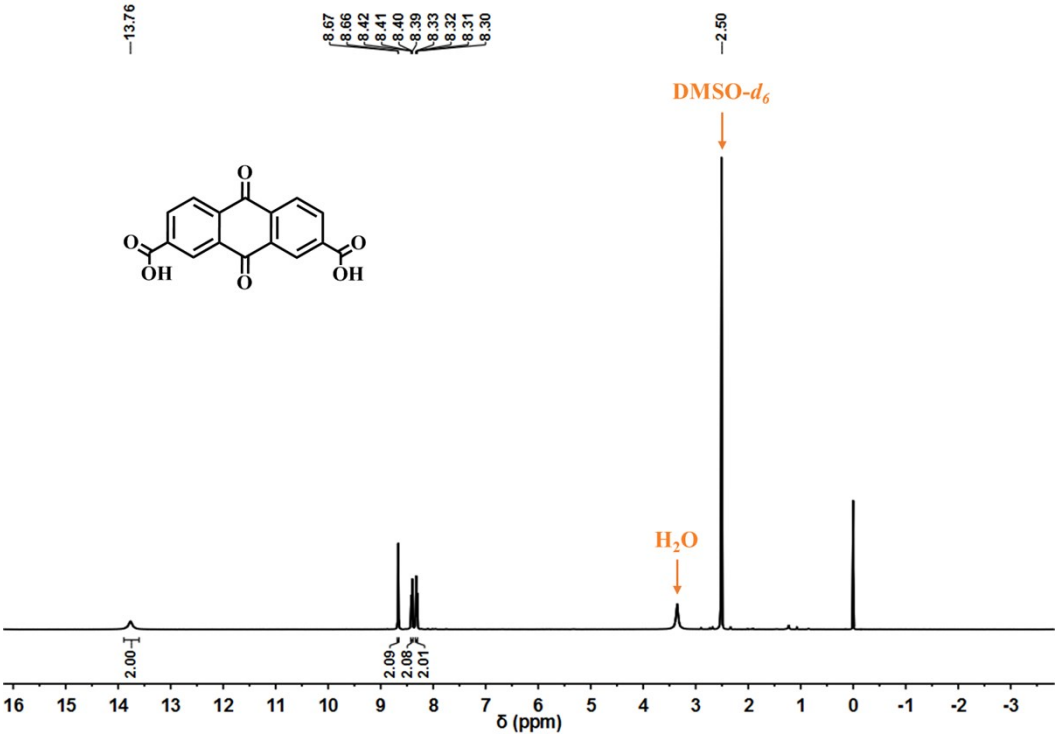
1, 4-H_2AQDC (**H_2L^1**) and 2, 7-H_2AQDC (**H_2L^2**) were synthesized as described in the literature.[4,5]

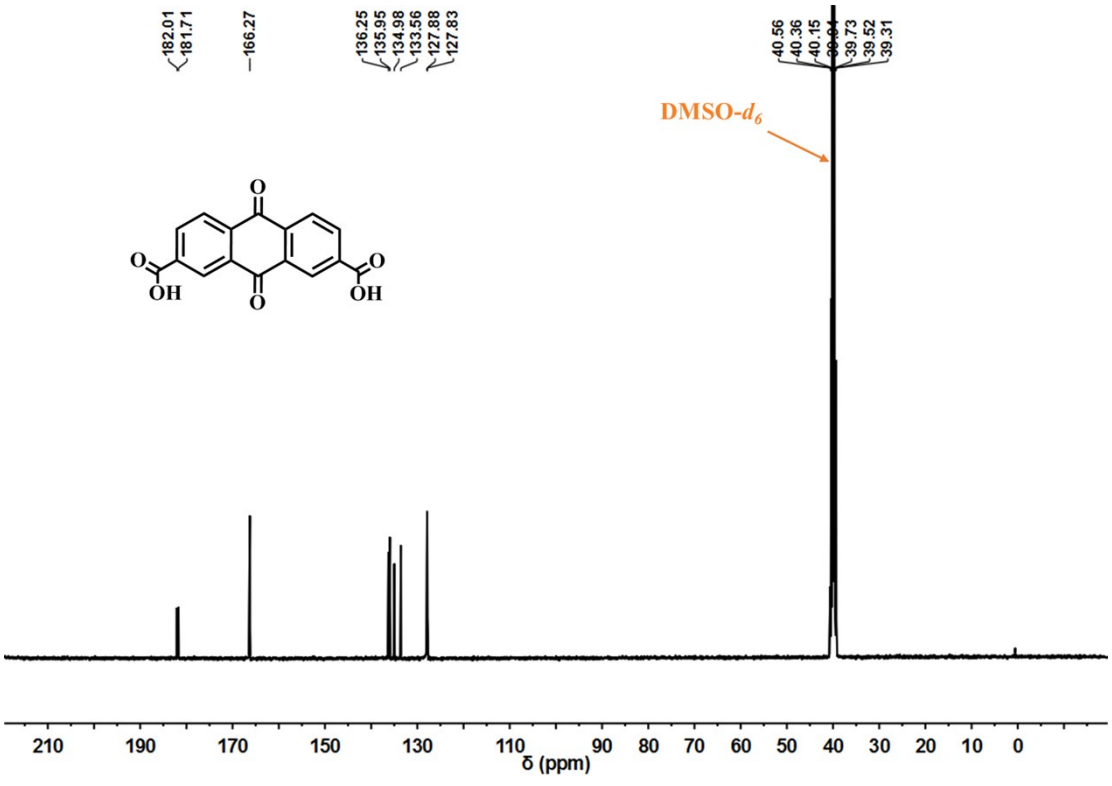
H_2L^1: ^{1}H NMR (400 MHz, DMSO-d_6) δ: 13.40 (s, 2H), 8.17 (dd, J = 5.8, 3.3 Hz, 2H), 7.96 (dd, J = 5.7, 3.3 Hz, 2H), 7.88 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 181.9, 170.2, 136.9, 135.3, 133.1, 132.7, 130.4, 127.3.





H_2L^2: ^{1}H NMR (400 MHz, DMSO-d_6) δ: 13.76 (s, 2H), 8.67 (d, J = 1.8 Hz, 2H), 8.41 (dd, J = 7.9, 1.1 Hz, 2H), 8.32 (dd, J = 8.0, 3.4 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ: 182.0, 181.7, 166.3, 136.2, 136.0, 135.0, 133.6, 127.9, 127.8.





2.2 Synthesis of the MOCs

Synthesis of 1-Co. A mixture of $\mathbf{H_2L^1}$ (6.0 mg, 0.02 mmol), H_4TBSC (8.5 mg, 0.01 mmol), and $Co(NO_3)_2{\cdot}6H_2O$ (23.2 mg, 0.08 mmol) were dissolved in 1.2 mL DMF and 2.4 mL MeOH, and the mixture was heated at 80 °C for 48 hours. After cooling to room temperature, 1-Co was collected as pink crystals, washed with DMF and MeOH, and dried at 50 °C. Yield: 8.0 mg, 40%. Elemental Analysis for $[Co_4(\mu_4\text{-}O)(TBSC)]_6(\mathbf{L^1})_{12}{\cdot}12DMF{\cdot}MeOH{\cdot}36H_2O$. Anal (%). Calcd for $C_{469}H_{496}O_{199}N_{12}S_{24}Co_{24}$: C, 48.27; H, 4.25; N, 1.44; S, 6.59. Found: C, 48.35; H, 4.26; N, 1.45; S, 6.53. FTIR (KBr pellet, cm^{-1}): 3453(m), 967(m), 872(w), 1683(w), 1596(s), 1492(s), 1405(m), 1331(w), 1262(s), 1137(w), 1073(m), 796(m), 738(w), 626(w), 570(s), 525(w).

Synthesis of 2-Co. A mixture of $\mathbf{H_2L^2}$ (6.0 mg, 0.02 mmol), H_4TBSC (8.5 mg, 0.01 mmol), and $Co(NO_3)_2{\cdot}6H_2O$ (11.6 mg, 0.04 mmol) were dissolved in 1.2 mL DMF and 4.8 mL MeOH, and the mixture was heated at 100 °C for 24 hours. After cooling to room temperature, 2-Co was collected as pink crystal, washed with DMF and MeOH, and dried at 50 °C. Yield: 15.0 mg, 80%. Elemental Analysis for $[Co_4(\mu_4\text{-}O)(TBSC)]_4(\mathbf{L^2})_8{\cdot}4DMF{\cdot}2MeOH{\cdot}12H_2O$. Anal (%). Calcd for $C_{302}H_{284}O_{118}N_4S_{16}Co_{16}$: C, 49.57; H, 3.88; N, 0.76; S, 7.00. Found: C, 49.55; H, 3.87; N, 0.76; S, 7.02. FTIR (KBr pellet, cm^{-1}): 2962(m), 2870(w), 1678(m), 1614(s), 1562(w), 1494(s), 1411(m), 286(s), 1135(w), 1079(m), 936(w), 799(m), 729(w), 632(w), 559(s).

Synthesis of 2-Ni. A mixture of $\mathbf{H_2L^2}$ (6.0 mg, 0.02 mmol), H_4TBSC (8.5 mg, 0.01 mmol), and $NiCl_2{\cdot}6H_2O$ (9.5 mg, 0.04 mmol) were dissolved in 2.5 mL DMF and 2.5 mL MeOH, and the mixture was heated at 100 °C for 24 hours. After cooling to room temperature, 2-Ni was collected as green crystals, washed with DMF and MeOH, and dried at 50 °C. Yield: 15.0 mg, 76%. Elemental Analysis for $[Ni_4(\mu_4\text{-}O)(TBSC)_4](\mathbf{L^2})_8{\cdot}10DMF{\cdot}8MeOH{\cdot}12H_2O$. Anal (%). Calcd for $C_{326}H_{350}O_{130}N_{10}S_{16}Ni_{16}$: C, 49.31; H, 4.41; N, 1.77; S, 6.44. Found: C, 48.95; H, 4.52; N, 1.76; S, 6.45. FTIR (KBr pellet, cm^{-1}): 3422(m), 2966(m), 2879(w), 1676(w), 1612(s), 1557(w), 1496(s), 1405(s), 1297(s), 1133(w), 1076(m), 928(w), 803(m), 728(w), 634(w), 572(s), 532(w).

Synthesis of 2-Zn. A mixture of $\mathbf{H_2L^2}$ (6.0 mg, 0.02 mmol), H_4TBSC (8.5 mg, 0.01 mmol), and $Zn(NO_3)_2{\cdot}6H_2O$ (11.9 mg, 0.04 mmol) were dissolved in 1.2 mL DMF and 4.8 mL MeOH, and the mixture was heated at 100 °C for 24 hours. After cooling to room temperature, 2-Zn was collected as colorless crystals, washed with DMF and MeOH, and dried at 50 °C. Yield: 13.0 mg, 60%. Elemental Analysis for $[Zn_4(\mu_4\text{-}O)(TBSC)]_4(\mathbf{L^2})_8{\cdot}9DMF{\cdot}20MeOH{\cdot}19H_2O$. Anal (%). Calcd for $C_{335}H_{405}O_{148}N_9S_{16}Zn_{16}$: C, 47.72; H, 4.78; N, 1.49; S, 6.04. Found: C, 47.87; H, 4.69;

N, 1.48; S, 6.06. FTIR (KBr pellet, cm^{-1}): 3589(w), 2965(m), 2869(w), 1676(m), 1602(s), 1565(w), 1496(s), 1410(m), 1297(s), 1291(s), 1219(w), 1128(w), 1076(m), 937(w), 795(s), 727(m), 629 (w), 555(s).

3. General procedure for photocatalysis

3.1 Synthesis of the substrates

Substrates were synthesized as described in the literature.[6]

In a 100 mL flask, a solution of aldehyde (21.0 mmol) in 50 mL ethanol at 0 ºC was added 10 ml of 10% aqueous NaOH solution slowly and stirred for 10 min, then 2-acetylpyridine (21.0 mmol) was added in portions at 0 ºC. After being stirred for another 2 h, the reaction mixture was filtered and washed with ethanol to get the pure products in satisfactory yield.

3.2 Photocatalytic [2 + 2] cycloaddition

A 25 mL Schlenk flask equipped with a magnetic stir bar was charged with substrate (0.124 mmol), MOC (0.6 mol%) or 2, 7-DMAQ (4.8 mol%), DMSO (0.5 mL) and H_2O (1.5 mL). The solution was degassed and refilled with N_2 for three times. The mixture was irradiated with 440 nm LEDs. Upon completion of the reaction (3 to 48 h), the residue was extracted with DCM (3 × 15 mL). The combined organic phase was washed with brine, dried over Na_2SO_4, and concentrated in vacuum. Then the desired product was obtained by flash chromatography on silica gel using PE/EA as the eluents. The reaction mixture was dissolved in $CDCl_3$ for ^1H NMR analysis to test the d.r. value.

4. Table S1. Crystal data and structure refinement

Identification code	**1-Co**	**2-Co**
Empirical formula	$C_{864}H_{670}Co_{48}O_{300}S_{48}$	$C_{288}H_{224}Co_{16}O_{100}S_{16}$
Formula weight	20221.50	6740.50
Temperature (K)	173 K	173 K
Wavelength (Å)	0.71073	1.54178
Crystal system	Triclinic	Tetragonal
Space group	P-1	I4/m

Unit cell dimensions	a = 28.353(6) Å;
	b = 31.497(6) Å;
	c = 37.991(8) Å;
	α = 97.01(3)°, β = 96.18(3)°,
	γ = 95.09(3)°
		a = 31.0736(6) Å;
		b = 31.0736(6) Å;
		c = 25.0692(10) Å;
		$\alpha = \beta = \gamma = 90°$

Volume (Å^3)	33299(12)	24206.0(13)
Z	1	2
Density (calculated) (mg/m^3)	1.008	0.925
Absorption coefficient (mm^{-1})	0.715	5.274
F(000)	10320	6880
θ range for data collection (º)	2.550 to 21.967	2.264 to 59.074
Limiting indices	$-29 \le h \le 29$, $-33 \le k \le 33$, $-39 \le l \le 39$	$-34 \le h \le 34$, $-34 \le k \le 34$, $-27 \le l \le 27$
Reflections collected	76840	133041
Independent reflections	76840 [R(int) = 0.105]	8771 [R(int) = 0.1236]
Completeness to theta	94.5%	97.5%
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	76840 / 19610 / 5107	8771 / 1127 / 513
Goodness-of-fit on F^2	1.024	1.073
Final R indices [I>2sigma(I)]	R_1 = 0.1068, wR_2 = 0.3788	R_1 = 0.0924, wR_2 = 0.2524
R indices (all data)	R_1 = 0.1126, wR_2 = 0.3993	R_1 = 0.1283, wR_2 = 0.2853
Largest diff. peak and hole	1.596 and –1.677 e.A^{-3}	0.808 and –0.456 e·A^{-3}

[a] $R_1 = \Sigma \mid\mid F_o \mid - \mid F_c \mid\mid / \Sigma \mid F_o \mid$. [b] $wR_2 = [\Sigma[w(F_o^2 - F_c^2)^2] / \Sigma w(F_o^2)^2]^{1/2}$, $w = 1/[\sigma^2(F_o)^2 + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$.

5. Table S2. Selected bond lengths [Å] and angles [º]

Selected Bond Lengths [Å] and Angles [º] for **1-Co**			
Co(20)-O(121)	2.073(4)	Co(22)-O(149)	2.046(4)
Co(20)-O(122)	2.093(4)	Co(22)-O(129)	2.104(4)
Co(20)-O(130)	2.165(4)	Co(14)-O(82)	2.104(4)
Co(20)-O(118)	2.104(4)	Co(14)-O(85)	2.088(4)
Co(20)-O(116)	2.035(4)	Co(14)-O(81)	2.168(4)
Co(20)-O(132)	2.064(4)	Co(14)-O(93)	2.045(4)
Co(10)-O(62)	2.212(4)	Co(14)-O(80)	2.035(5)
Co(10)-O(60)	2.040(4)	Co(14)-O(138)	2.024(5)
Co(19)-O(101)	2.146(4)	Co(15)-O(82)	2.048(4)
Co(19)-O(102)	2.033(4)	Co(15)-O(81)	2.267(5)
Co(19)-O(109)	2.125(4)	Co(15)-O(87)	2.100(5)
Co(19)-O(113)	2.007(5)	Co(15)-O(83)	2.050(4)
Co(5)-O(40)	2.071(4)	Co(15)-O(94)	2.015(5)
Co(5)-O(39)	2.087(4)	Co(15)-O(79)	2.024(5)
Co(5)-O(51)	2.068(5)	Co(18)-O(101)	2.099(4)
Co(5)-O(47)	2.093(5)	Co(18)-O(100)	2.043(5)
Co(23)-O(143)	2.259(4)	Co(18)-O(112)	2.025(5)
Co(23)-O(142)	2.020(5)	Co(18)-O(107)	2.125(5)
Co(23)-O(144)	2.030(4)	Co(18)-O(99)	2.005(5)
Co(22)-O(121)	2.039(4)	Co(7)-Co(6)	2.9819(15)
Co(22)-O(130)	2.237(4)	Co(7)-Co(8)	2.9844(15)
Co(22)-O(131)	2.050(4)	Co(7)-O(21)	2.066(4)
Co(22)-O(120)	2.100(4)	Co(7)-O(22)	2.080(5)
Co(3)-O(41)	2.073(4)	Co(7)-O(28)	2.078(4)
Co(3)-O(38)	2.090(5)	Co(7)-O(19)	2.207(4)
Co(3)-O(73)	2.041(5)	Co(7)-O(32)	2.009(5)
Co(3)-O(36)	2.049(5)	Co(7)-O(63)	2.031(5)
Co(3)-O(43)	2.098(5)	Co(6)-O(21)	2.071(4)
Co(9)-O(20)	2.077(4)	Co(6)-O(27)	2.101(5)
Co(21)-O(119)	2.052(5)	Co(6)-O(20)	2.077(4)
Co(21)-O(130)	2.275(4)	Co(6)-O(19)	2.224(5)
Co(21)-O(118)	2.085(4)	Co(6)-O(33)	2.041(5)
Co(21)-O(125)	2.107(5)	Co(6)-O(17)	2.032(5)

Co(21)-O(117)	2.024(5)	Co(2)-O(13)	2.053(5)
Co(13)-O(75)	2.044(5)	Co(2)-O(4)	2.093(4)
Co(1)-O(1)	2.089(4)	Co(24)-O(143)	2.213(4)
Co(1)-O(150)	2.196(5)	Co(24)-O(145)	2.010(5)
Co(1)-O(6)	2.120(5)	Co(17)-O(84)	2.050(5)
Co(1)-O(14)	2.025(5)	Co(17)-O(85)	2.078(4)
Co(1)-O(4)	2.095(4)	Co(17)-O(81)	2.377(5)
Co(11)-O(69)	1.985(5)	Co(17)-O(135)	2.016(5)
Co(11)-O(67)	2.021(5)	Co(17)-O(91)	2.111(5)
Co(2)-O(3)	2.109(4)	Co(17)-O(137)	2.014(5)
Co(2)-O(150)	2.247(5)	Co(4)-O(38)	2.067(4)
Co(2)-O(12)	2.072(5)	Co(4)-O(39)	2.091(5)
Co(2)-O(54)	2.027(5)	Co(4)-O(37)	2.030(5)
Co(8)-O(31)	2.108(6)	Co(4)-O(50)	2.031(5)
Co(8)-O(64)	2.024(5)	Co(4)-O(45)	2.101(5)
Co(8)-O(56)	2.023(5)	Co(16)-O(84)	2.142(5)
Co(9)-O(23)	2.107(5)	Co(16)-O(81)	2.118(4)
Co(9)-O(19)	2.194(5)	Co(16)-O(83)	2.081(4)
Co(9)-O(18)	2.045(6)	Co(16)-O(136)	2.046(5)
Co(9)-O(25)	2.108(5)	Co(16)-O(89)	2.103(5)
Co(9)-O(57)	2.046(5)	Co(16)-O(95)	2.069(5)
Co(9)-O(57)	2.046(5)	Co(12)-O(68)	2.011(5)
Co(8)-O(19)	2.286(6)	Co(8)-O(22)	2.069(4)
Co(8)-O(23)	2.057(5)		

O(121)-Co(20)-O(122)	87.16(16)	O(102)-Co(19)-O(101)	88.34(16)
O(121)-Co(20)-O(130)	83.98(15)	O(102)-Co(19)-O(109)	84.00(17)
O(121)-Co(20)-O(118)	89.73(15)	O(109)-Co(19)-O(101)	90.42(16)
O(122)-Co(20)-O(130)	168.44(15)	O(113)-Co(19)-O(101)	95.17(18)
O(122)-Co(20)-O(118)	88.07(16)	O(113)-Co(19)-O(102)	172.53(19)
O(118)-Co(20)-O(130)	84.48(16)	O(113)-Co(19)-O(109)	89.4(2)
O(116)-Co(20)-O(121)	172.34(19)	O(40)-Co(5)-O(39)	90.98(16)
O(116)-Co(20)-O(122)	86.02(18)	O(40)-Co(5)-O(47)	86.03(17)
O(116)-Co(20)-O(130)	103.22(18)	O(39)-Co(5)-O(47)	86.0(2)
O(116)-Co(20)-O(118)	93.53(17)	O(51)-Co(5)-O(40)	173.58(18)

O(116)-Co(20)-O(132)	83.09(18)	O(51)-Co(5)-O(39)	93.60(18)
O(132)-Co(20)-O(121)	93.20(17)	O(93)-Co(14)-O(82)	87.77(17)
O(132)-Co(20)-O(122)	88.12(18)	O(93)-Co(14)-O(85)	88.18(17)
O(132)-Co(20)-O(130)	99.76(17)	O(93)-Co(14)-O(81)	170.17(17)
O(132)-Co(20)-O(118)	175.07(18)	O(80)-Co(14)-O(82)	92.96(19)
O(60)-Co(10)-O(62)	99.89(17)	O(80)-Co(14)-O(81)	98.26(19)
O(51)-Co(5)-O(47)	89.80(19)	O(80)-Co(14)-O(93)	87.53(19)
O(142)-Co(23)-O(143)	97.41(19)	O(138)-Co(14)-O(82)	174.03(19)
O(142)-Co(23)-O(144)	86.3(2)	O(138)-Co(14)-O(85)	93.9(2)
O(144)-Co(23)-O(143)	105.57(18)	O(138)-Co(14)-O(81)	101.2(2)
O(121)-Co(22)-O(130)	82.99(15)	O(138)-Co(14)-O(93)	87.3(2)
O(121)-Co(22)-O(131)	94.53(17)	O(138)-Co(14)-O(80)	83.5(2)
O(121)-Co(22)-O(120)	89.79(16)	O(82)-Co(15)-O(81)	82.85(16)
O(121)-Co(22)-O(149)	173.70(18)	O(82)-Co(15)-O(87)	89.00(17)
O(121)-Co(22)-O(129)	86.47(15)	O(82)-Co(15)-O(83)	89.85(16)
O(131)-Co(22)-O(130)	100.51(17)	O(87)-Co(15)-O(81)	167.45(17)
O(131)-Co(22)-O(120)	175.09(17)	O(83)-Co(15)-O(81)	80.50(17)
O(131)-Co(22)-O(129)	90.05(18)	O(83)-Co(15)-O(87)	89.99(19)
O(120)-Co(22)-O(130)	82.33(16)	O(94)-Co(15)-O(82)	175.1(2)
O(120)-Co(22)-O(129)	87.87(17)	O(94)-Co(15)-O(81)	101.64(19)
O(149)-Co(22)-O(130)	102.05(17)	O(94)-Co(15)-O(87)	86.9(2)
O(149)-Co(22)-O(131)	80.91(18)	O(94)-Co(15)-O(83)	92.9(2)
O(149)-Co(22)-O(120)	94.60(18)	O(94)-Co(15)-O(79)	82.4(2)
O(149)-Co(22)-O(129)	89.17(18)	O(79)-Co(15)-O(82)	94.64(18)
O(129)-Co(22)-O(130)	165.61(15)	O(79)-Co(15)-O(81)	102.20(18)
O(82)-Co(14)-O(81)	84.02(16)	O(79)-Co(15)-O(87)	87.9(2)
O(85)-Co(14)-O(82)	89.23(16)	O(79)-Co(15)-O(83)	175.0(2)
O(85)-Co(14)-O(81)	86.32(16)	O(101)-Co(18)-O(107)	92.62(17)
O(112)-Co(18)-O(107)	86.6(2)	O(100)-Co(18)-O(101)	89.66(17)
O(99)-Co(18)-O(101)	178.0(2)	O(100)-Co(18)-O(107)	84.03(19)
O(99)-Co(18)-O(100)	92.2(2)	O(112)-Co(18)-O(101)	92.12(18)
O(99)-Co(18)-O(112)	86.0(2)	O(112)-Co(18)-O(100)	170.6(2)
O(21)-Co(7)-O(22)	88.77(16)	O(41)-Co(3)-O(38)	86.70(16)
O(21)-Co(7)-O(28)	89.17(17)	O(41)-Co(3)-O(43)	89.06(17)
O(21)-Co(7)-O(19)	83.97(16)	O(38)-Co(3)-O(43)	87.57(19)

O(22)-Co(7)-O(19)	85.08(18)	O(73)-Co(3)-O(41)	93.64(18)
O(28)-Co(7)-O(22)	88.16(18)	O(73)-Co(3)-O(38)	174.3(2)
O(28)-Co(7)-O(19)	170.46(17)	O(73)-Co(3)-O(36)	85.6(2)
O(32)-Co(7)-O(21)	93.78(19)	O(73)-Co(3)-O(43)	86.8(2)
O(32)-Co(7)-O(22)	174.97(19)	O(36)-Co(3)-O(41)	175.92(19)
O(32)-Co(7)-O(28)	87.55(19)	O(36)-Co(3)-O(38)	93.69(19)
O(32)-Co(7)-O(19)	99.5(2)	O(36)-Co(3)-O(43)	86.9(2)
O(32)-Co(7)-O(63)	82.5(2)	O(119)-Co(21)-O(130)	82.57(16)
O(63)-Co(7)-O(21)	173.4(2)	O(119)-Co(21)-O(118)	89.09(17)
O(63)-Co(7)-O(22)	94.5(2)	O(119)-Co(21)-O(125)	87.93(19)
O(63)-Co(7)-O(28)	85.2(2)	O(118)-Co(21)-O(130)	82.20(15)
O(63)-Co(7)-O(19)	102.0(2)	O(118)-Co(21)-O(125)	89.93(17)
O(21)-Co(6)-O(20)	90.01(17)	O(125)-Co(21)-O(130)	167.72(17)
O(21)-Co(6)-O(19)	83.42(17)	O(117)-Co(21)-O(119)	175.65(19)
O(27)-Co(6)-O(19)	167.51(17)	O(117)-Co(21)-O(130)	100.77(19)
O(20)-Co(6)-O(27)	88.96(18)	O(117)-Co(21)-O(118)	94.10(18)
O(20)-Co(6)-O(19)	81.62(18)	O(117)-Co(21)-O(125)	89.1(2)
O(33)-Co(6)-O(21)	94.40(18)	O(3)-Co(2)-O(150)	81.27(17)
O(33)-Co(6)-O(27)	88.71(19)	O(12)-Co(2)-O(3)	89.56(18)
O(33)-Co(6)-O(20)	175.0(2)	O(12)-Co(2)-O(150)	165.34(16)
O(33)-Co(6)-O(19)	101.30(19)	O(12)-Co(2)-O(4)	85.73(18)
O(17)-Co(6)-O(21)	176.5(2)	O(54)-Co(2)-O(3)	93.5(2)
O(17)-Co(6)-O(27)	89.4(2)	O(54)-Co(2)-O(150)	102.1(2)
O(17)-Co(6)-O(20)	92.7(2)	O(54)-Co(2)-O(12)	89.8(2)
O(17)-Co(6)-O(19)	99.2(2)	O(54)-Co(2)-O(13)	86.2(2)
O(17)-Co(6)-O(33)	82.8(2)	O(54)-Co(2)-O(4)	175.4(2)
O(1)-Co(1)-O(150)	83.27(16)	O(13)-Co(2)-O(3)	178.4(2)
O(1)-Co(1)-O(6)	90.12(16)	O(13)-Co(2)-O(150)	100.3(2)
O(1)-Co(1)-O(4)	88.10(17)	O(13)-Co(2)-O(12)	88.9(2)
O(6)-Co(1)-O(150)	166.43(17)	O(13)-Co(2)-O(4)	92.4(2)
O(14)-Co(1)-O(1)	178.35(19)	O(4)-Co(2)-O(3)	87.77(17)
O(14)-Co(1)-O(150)	97.9(2)	O(4)-Co(2)-O(150)	82.53(16)
O(14)-Co(1)-O(6)	89.0(2)	O(145)-Co(24)-O(143)	101.7(2)
O(14)-Co(1)-O(4)	93.18(19)	O(84)-Co(17)-O(85)	88.48(16)
O(4)-Co(1)-O(150)	83.73(17)	O(136)-Co(16)-O(83)	176.0(2)

O(4)-Co(1)-O(6)	84.22(17)	O(136)-Co(16)-O(89)	90.7(2)
O(69)-Co(11)-O(67)	83.4(2)	O(136)-Co(16)-O(95)	83.3(2)
O(84)-Co(17)-O(81)	80.99(17)	O(89)-Co(16)-O(84)	88.5(2)
O(84)-Co(17)-O(91)	90.0(2)	O(89)-Co(16)-O(81)	168.40(19)
O(85)-Co(17)-O(81)	81.32(16)	O(95)-Co(16)-O(84)	177.9(2)
O(85)-Co(17)-O(91)	86.80(19)	O(95)-Co(16)-O(81)	96.5(2)
O(135)-Co(17)-O(84)	92.6(2)	O(95)-Co(16)-O(83)	93.8(2)
O(135)-Co(17)-O(85)	174.9(2)	O(95)-Co(16)-O(89)	89.9(2)
O(135)-Co(17)-O(81)	103.8(2)	O(22)-Co(8)-O(19)	83.33(17)
O(135)-Co(17)-O(91)	88.2(2)	O(22)-Co(8)-O(31)	88.95(19)
O(91)-Co(17)-O(81)	165.25(17)	O(23)-Co(8)-O(22)	88.45(17)
O(137)-Co(17)-O(84)	178.2(2)	O(23)-Co(8)-O(19)	82.64(18)
O(137)-Co(17)-O(85)	93.24(19)	O(23)-Co(8)-O(31)	89.3(2)
O(137)-Co(17)-O(81)	99.6(2)	O(31)-Co(8)-O(19)	168.99(17)
O(137)-Co(17)-O(135)	85.7(2)	O(64)-Co(8)-O(22)	93.4(2)
O(137)-Co(17)-O(91)	89.7(2)	O(64)-Co(8)-O(23)	176.2(2)
O(38)-Co(4)-O(39)	89.51(17)	O(64)-Co(8)-O(19)	100.9(2)
O(38)-Co(4)-O(45)	88.4(2)	O(64)-Co(8)-O(31)	87.4(2)
O(39)-Co(4)-O(45)	87.8(2)	O(56)-Co(8)-O(22)	174.8(2)
O(37)-Co(4)-O(38)	92.77(19)	O(18)-Co(9)-O(20)	95.3(2)
O(37)-Co(4)-O(39)	174.6(2)	O(18)-Co(9)-O(19)	96.1(2)
O(37)-Co(4)-O(50)	84.2(2)	O(18)-Co(9)-O(25)	92.5(2)

Symmetry transformations used to generate equivalent atoms:
#1 -x,-y+2,-z+1 #2 -x+1,-y+1,-z

Selected Bond Lengths [Å] and Angles [º] for **2-Co**

Co(1)-O(1)	2.024(5)	Co(2)-O(15)	2.225(2)
Co(2)-O(14)	2.089(5)	Co(2)-O(5)	2.022(5)
Co(2)-O(11)	2.091(5)	Co(3)-O(13)	2.078(5)
Co(2)-O(13)	2.083(5)	Co(3)-O(15)	2.234(7)
Co(3)-O(9)	2.096(7)	Co(3)-O(6)	2.022(5)
O(14)-Co(2)-O(11)	87.47(19)	O(13)-Co(2)-O(14)	90.09(19)
O(14)-Co(2)-O(15)	84.2(2)	O(13)-Co(2)-O(11)	88.5(2)
O(11)-Co(2)-O(15)	168.3(2)	O(13)-Co(2)-O(15)	83.4(2)

O(5)-Co(2)-O(14)	175.0(2)	O(13)-Co(3)-O(15)	83.32(18)
O(5)-Co(2)-O(11)	89.0(2)	O(13)-Co(3)-O(9)	87.61(19)
O(5)-Co(2)-O(13)	93.3(2)	O(9)-Co(3)-O(15)	167.2(3)
O(5)-Co(2)-O(15)	99.8(2)	O(6)-Co(3)-O(13)	94.1(2)
O(6)-Co(3)-O(15)	100.1(2)	O(6)-Co(3)-O(9)	89.5(2)

Symmetry transformations used to generate equivalent atoms:

#1 x,y,-z+1 #2 y,-x+1,-z+1 #3 y,-x+1,z #4 -y+1,x,z #5 -y+1,x,-z+1

6. Additional X-ray crystallographic structures

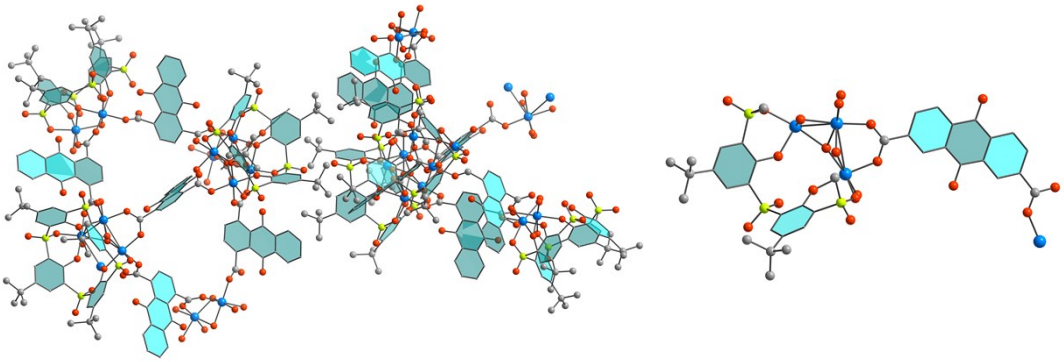


Figure S1. The asymmetric unit of 1-Co (left) and 2-Co (right)

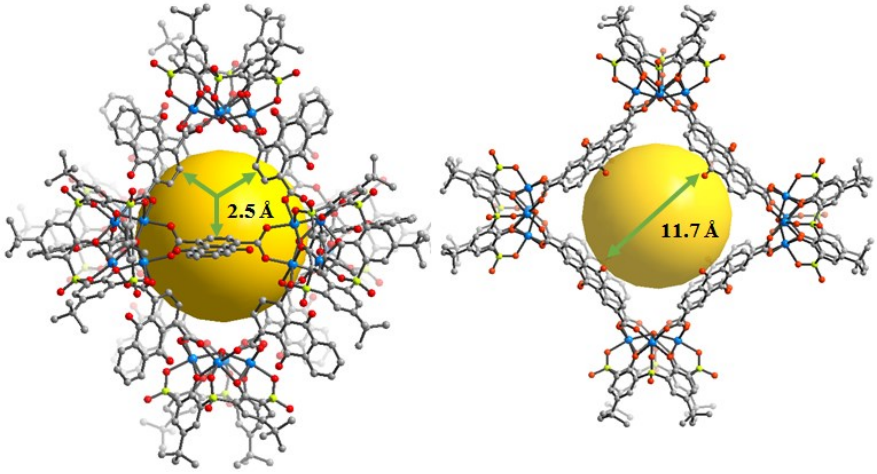
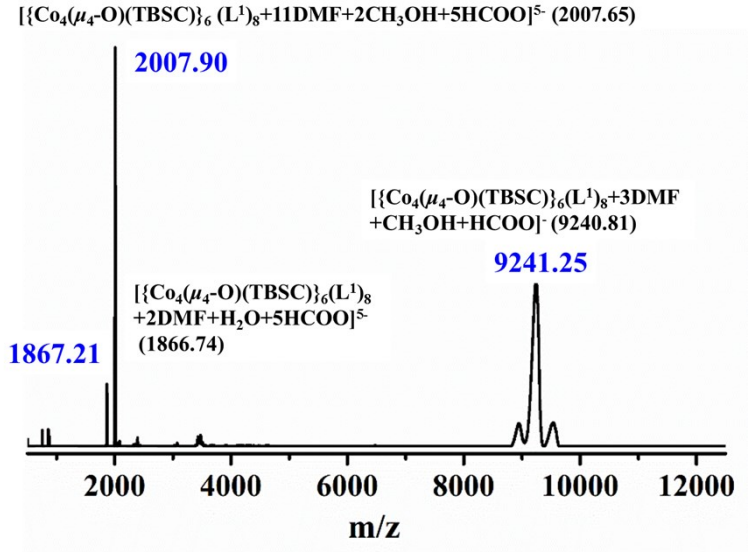


Figure S2. The window for 1-Co (left) and 2-Co (right)

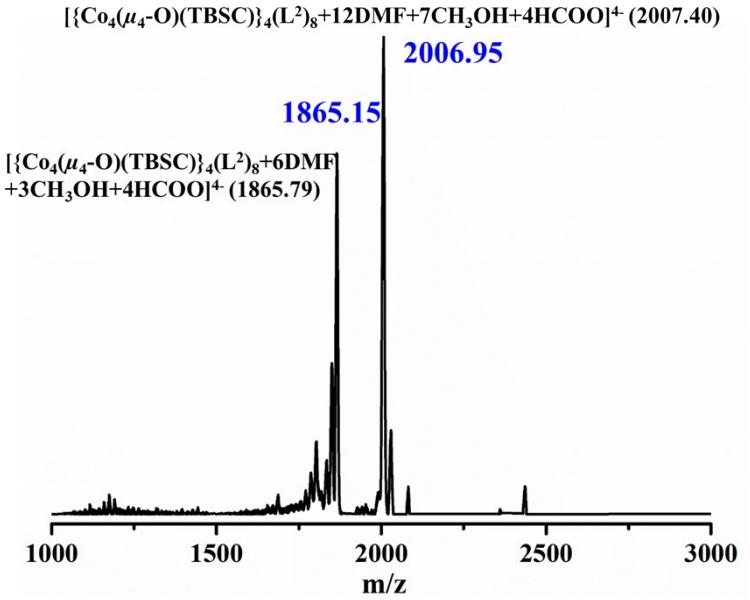
7. Figure S3. MALDI-TOF-MS spectra

(a) 1-Co



Fragment	m/z
$[\{Co_4(\mu_4\text{-}O)(TBSC)\}_6(L^1)_8+2DMF+H_2O+5HCOO]^{5-}$	1867.21
$[\{Co_4(\mu_4\text{-}O)(TBSC)\}_6(L^1)_8+11DMF+2CH_3OH+5HCOO]^{5-}$	2007.90
$[\{Co_4(\mu_4\text{-}O)(TBSC)\}_6(L^1)_8+3DMF+CH_3OH+HCOO]^{-}$	9241.25

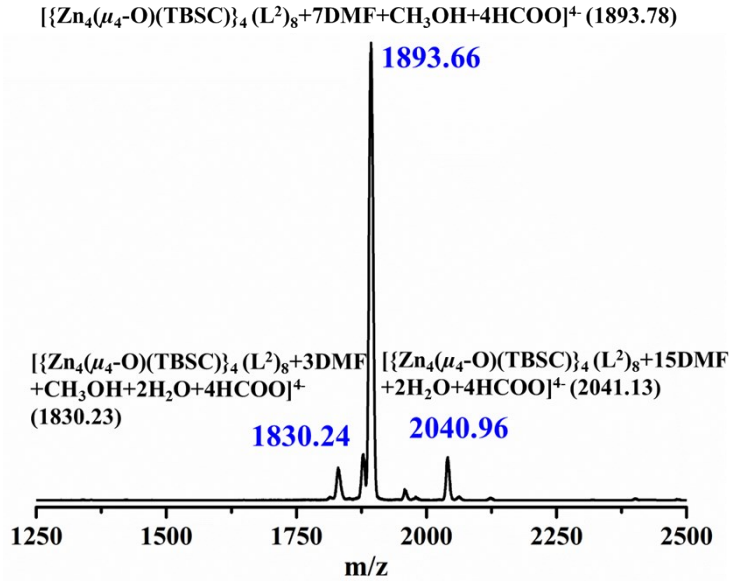
(b) 2-Co



Fragment	m/z
$[\{Co_4(\mu_4\text{-}O)(TBSC)\}_4(L^2)_8+6DMF+3CH_3OH+4HCOO]^{4-}$	1865.15

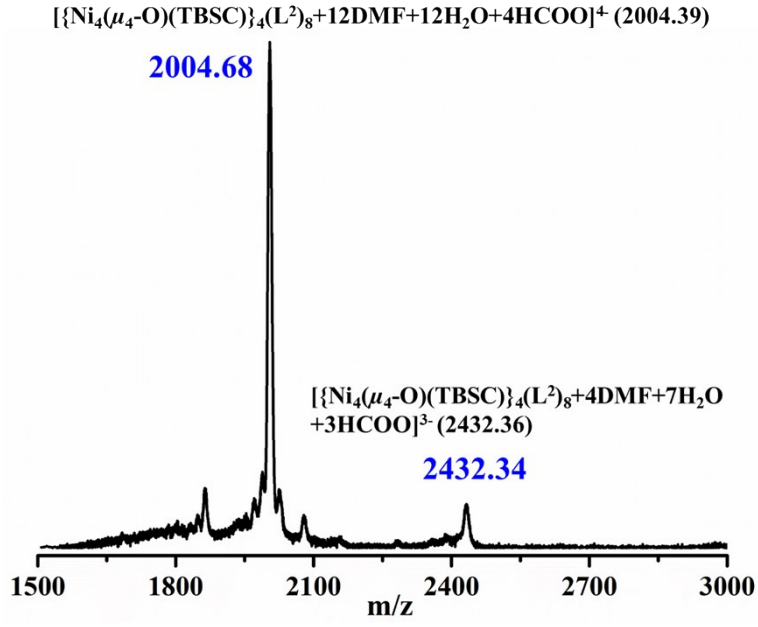
$[\{Co_4(\mu_4\text{-}O)(TBSC)\}_4(L^2)_8+12DMF+7CH_3OH+4HCOO]^{4-}$	2006.95

(c) 2-Zn



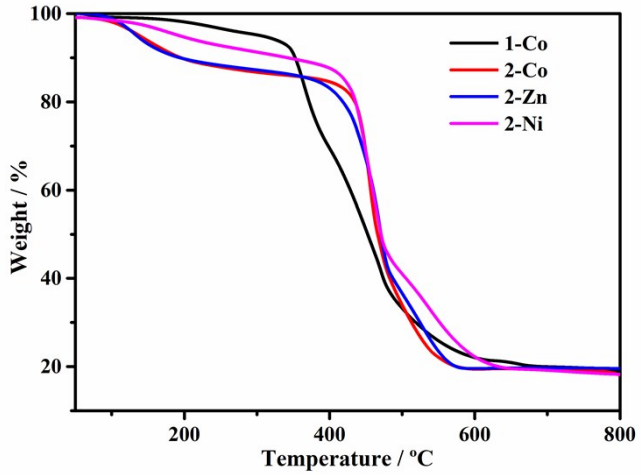
Fragment	m/z
$[\{Zn_4(\mu_4\text{-}O)(TBSC)\}_4(L^2)_8+3DMF+CH_3OH+2H_2O+4HCOO]^{4-}$	1830.24
$[\{Zn_4(\mu_4\text{-}O)(TBSC)\}_4(L^2)_8+7DMF+CH_3OH+4HCOO]^{4-}$	1893.66
$[\{Zn_4(\mu_4\text{-}O)(TBSC)\}_4(L^2)_8+15DMF+2H_2O+4HCOO]^{4-}$	2040.96

(d) 2-Ni

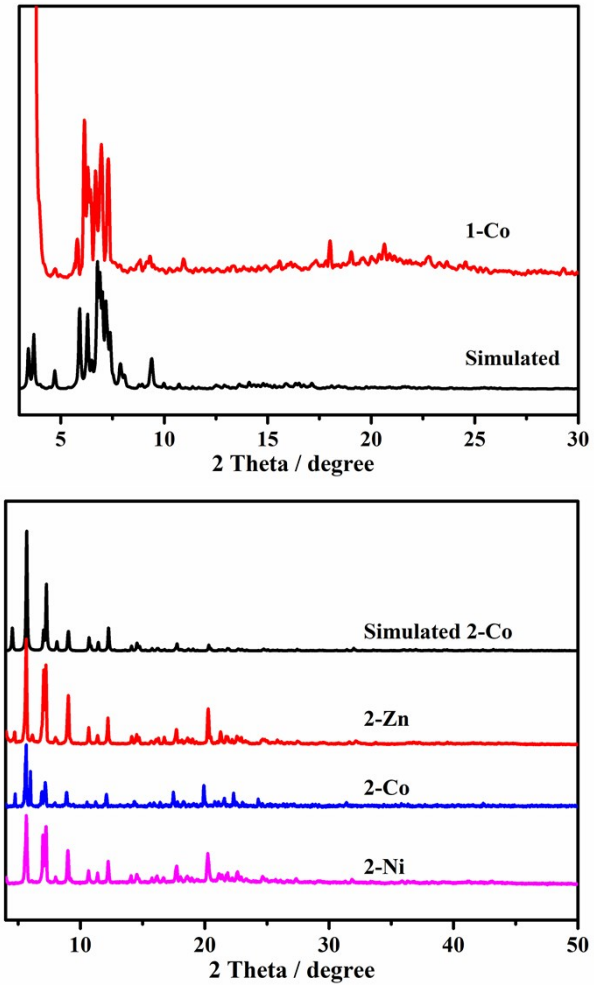


Fragment	m/z
$[\{Ni_4(\mu_4\text{-}O)(TBSC)\}_4(L^2)_8+12DMF+12H_2O+4HCOO]^{4-}$	2004.68
$[\{Ni_4(\mu_4\text{-}O)(TBSC)\}_4(L^2)_8+4DMF+7H_2O+3HCOO]^{3-}$	2432.34

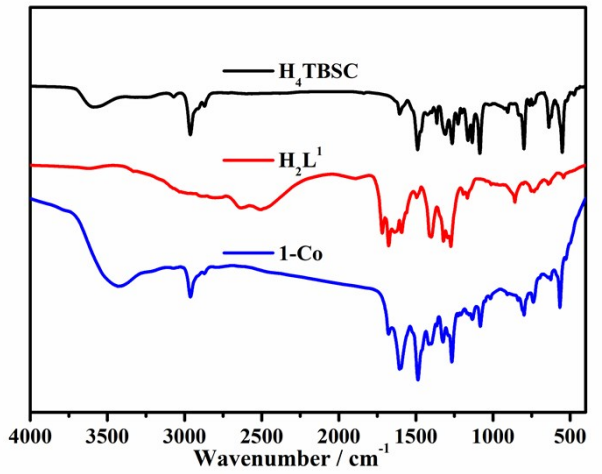
8. Figure S4. TGA curves

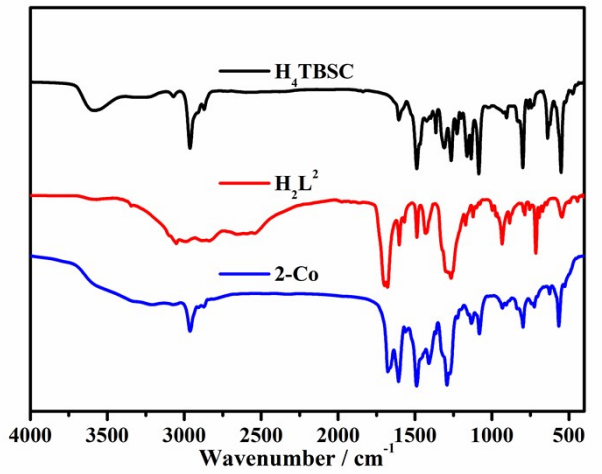


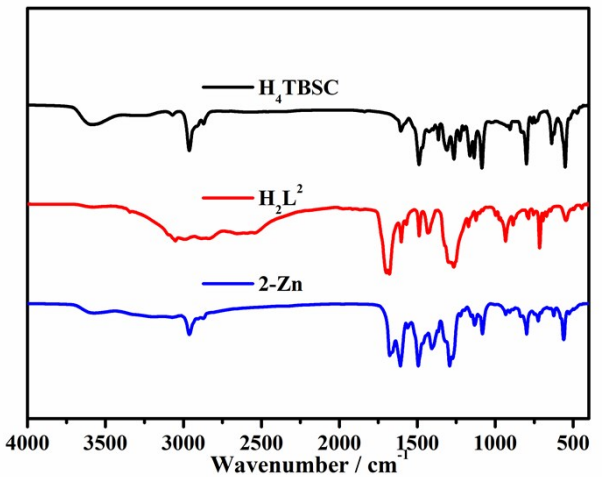
9. Figure S5 PXRD patterns

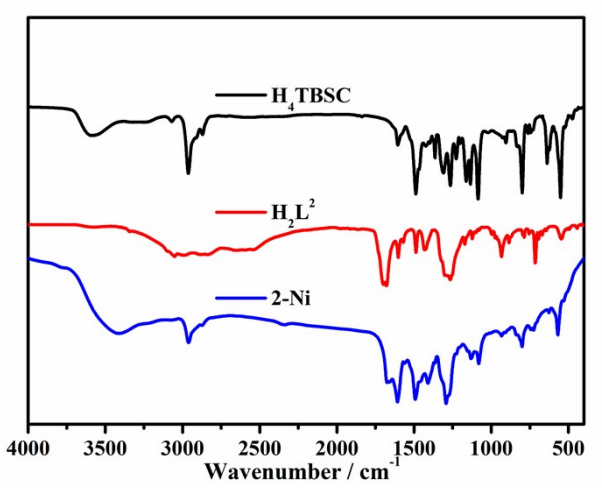


10. Figure S6. FT-IR spectra



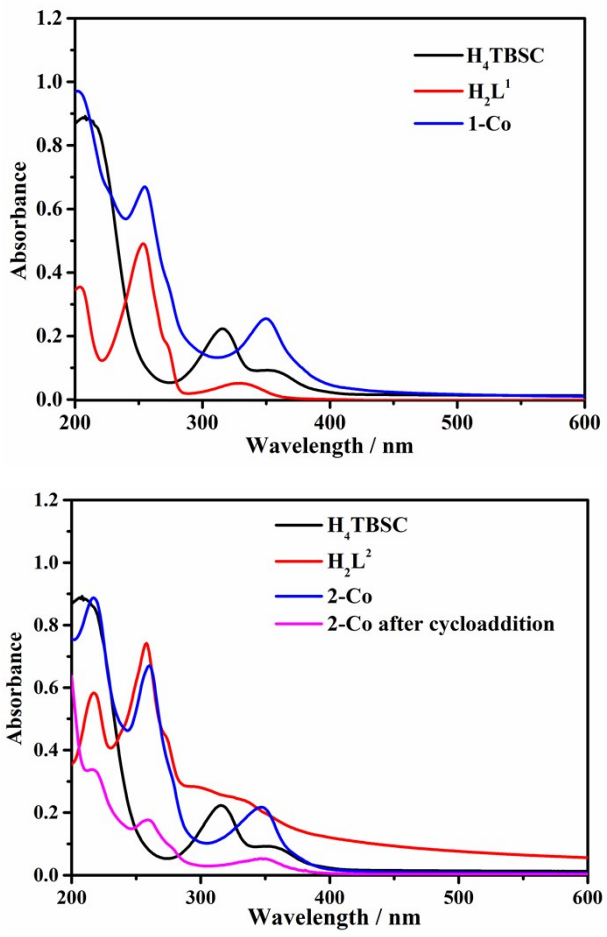


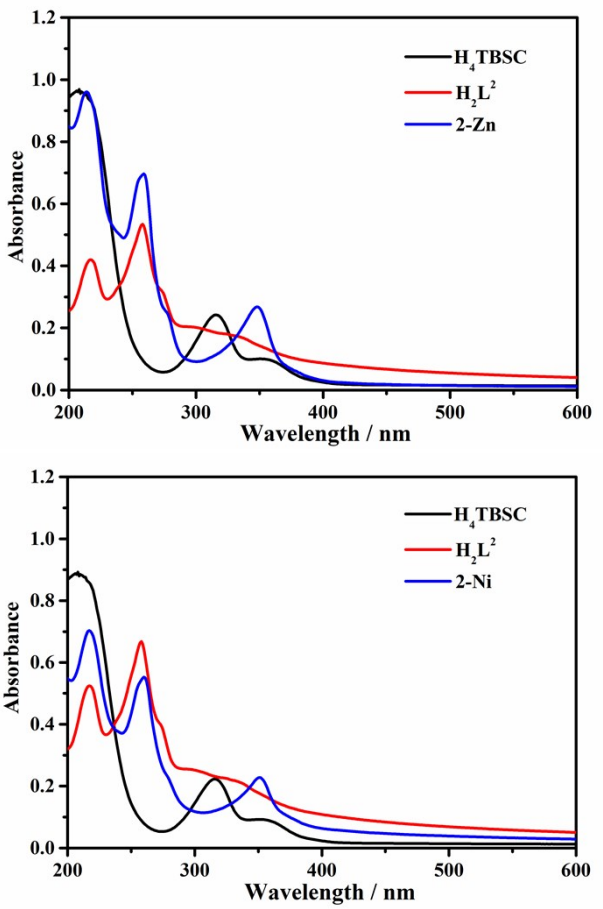




11. Figure S7. UV-Vis absorption spectra.

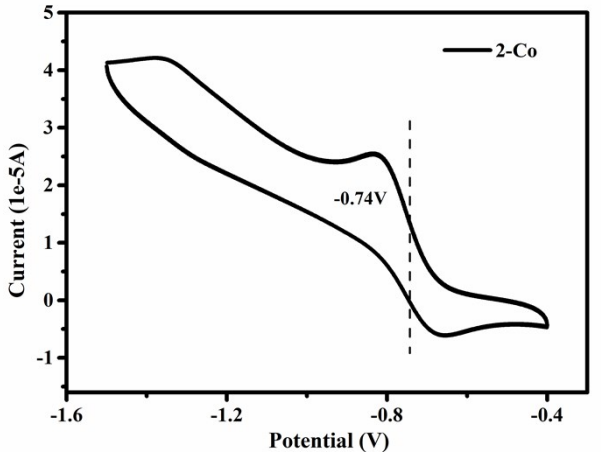
UV-Vis absorption spectra was measured in acetonitrile solution with concentration of 1.0 mg/mL.

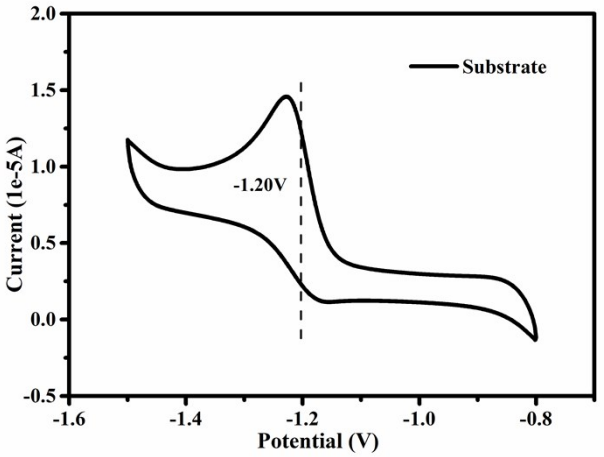




12. Figure S8. Cyclic voltammetry curves.

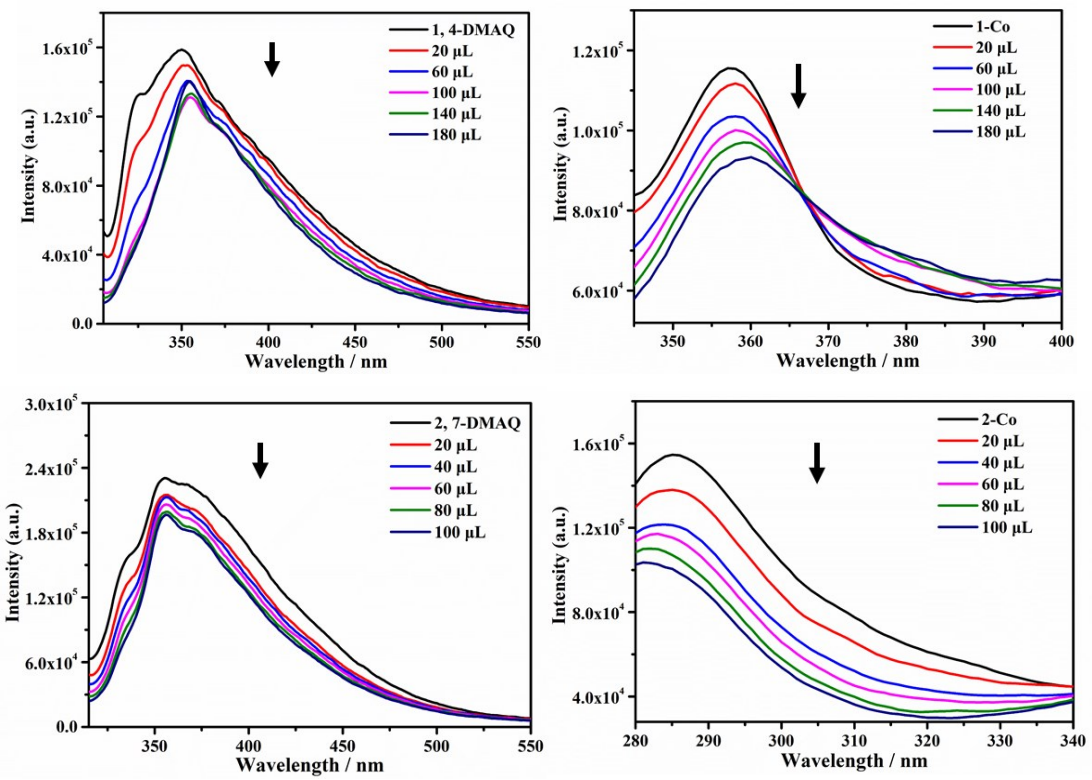
Cyclic voltammetry curves measured in acetonitrile solution, containing 0.1 M $TBAPF_6$ as the supporting electrolyte at room temperature, glassy carbon electrodes as the working electrodes, and the scanning rate at 50 mV s^{-1}.

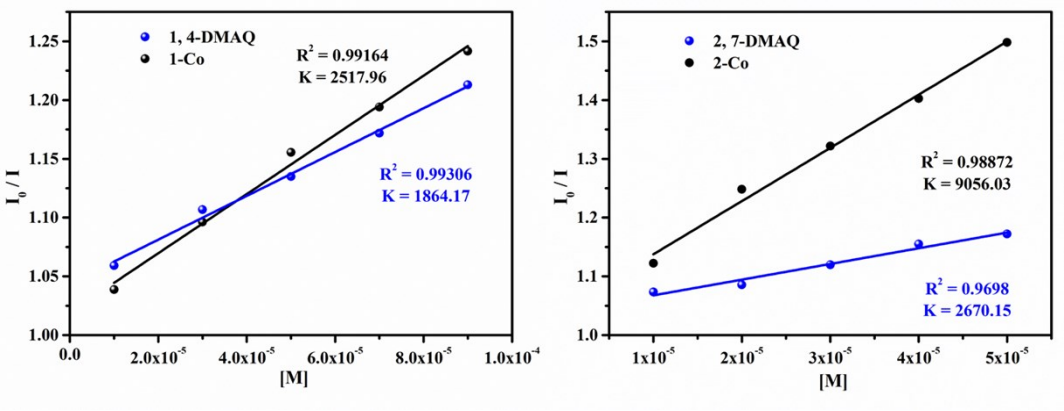




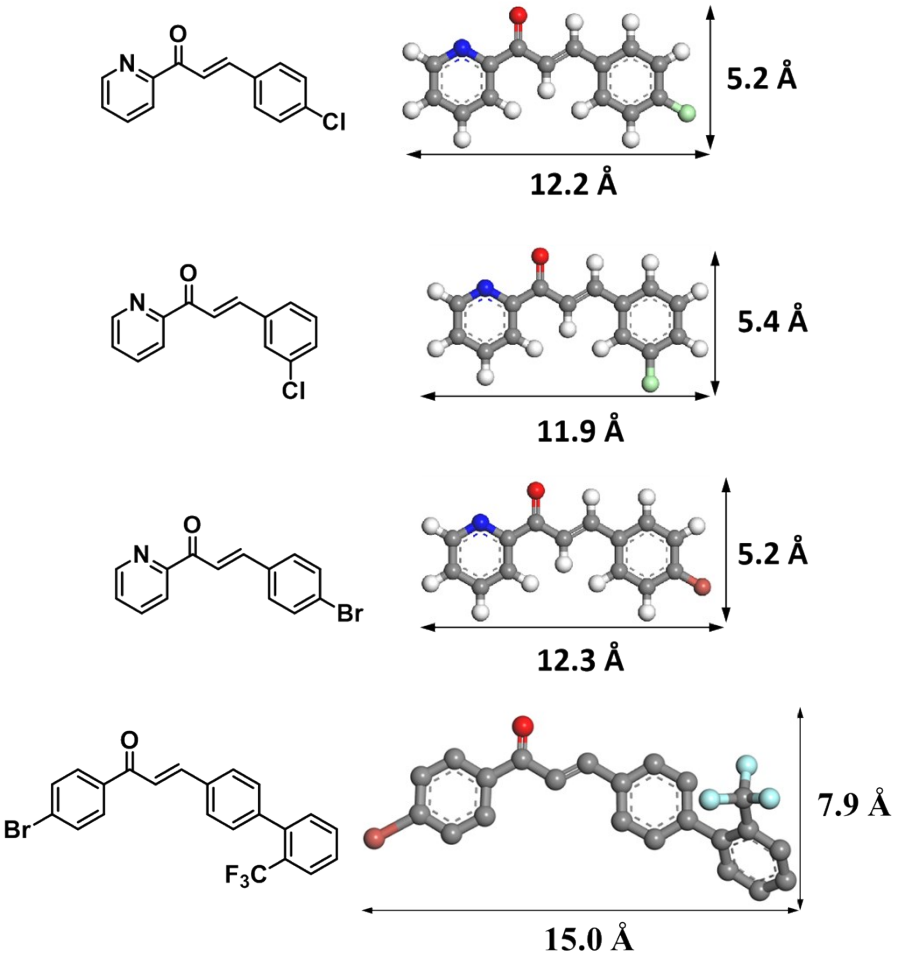
13. Figure S9. The titration experiments

The titration experiments were carried out by adding solution of substrate **4a** (1.0×10^{-3} mol/L) in DMSO to a solution of 1, 4-DMAQ, 2, 7-DMAQ, **1-Co** or **2-Co** (1.0×10^{-5} mol/L) in 2.0 mL DMSO, respectively. The slit width is set as 15 nm/15 nm.



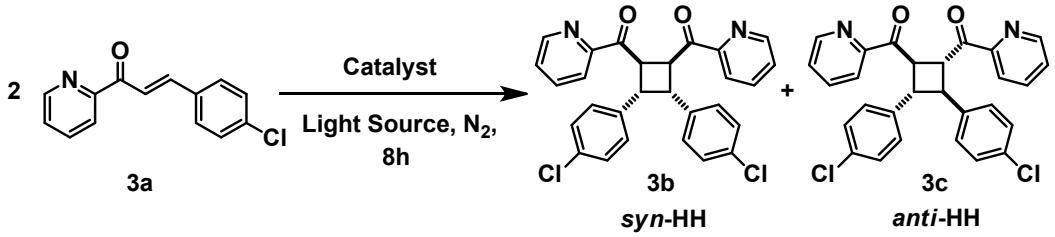


14. Figure S10. Molecular simulations of the substrates



15. Table S3-S8. Additional catalytic results

Table S3. Optimization of the reaction conditions[a]

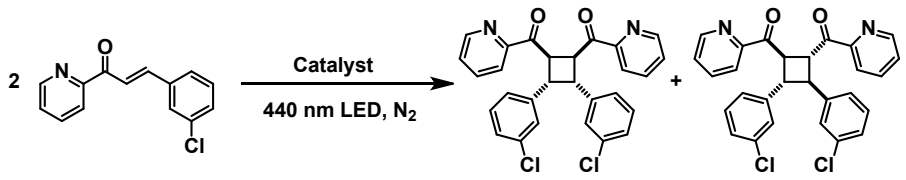


Entry	Catalyst (mol%)	Solvent	Light Source	T/ºC	Yield(%)[b] / (d.r.[c])
1	2-Co (0.6)	DMSO	440 nm	20	52 (1:2.5)
2	2-Co (0.6)	DMSO:H_2O (1:3)	440 nm	20	60 (6:1)
3	2-Co (0.6)	DMF:H_2O (1:3)	440 nm	20	41 (5.3:1)
4	2-Co (0.6)	CH_3CN:H_2O (1:3)	440 nm	20	60 (1.1:1)
5	2-Co (0.6)	Acetone:H_2O (1:3)	440 nm	20	48 (1.1:1)
6	2-Co (0.6)	DMSO:H_2O (1:3)	440 nm	10	54 (4.2:1)
7	2-Co (0.6)	DMF:H_2O (1:3)	440 nm	10	51 (5.1:1)
8	2-Co (0.12)	DMSO:H_2O (1:3)	440 nm	20	50 (4.5:1)
9	2-Co (0.3)	DMSO:H_2O (1:3)	440 nm	20	49 (4.4:1)
10	2-Co (0.9)	DMSO:H_2O (1:3)	440 nm	20	62 (6:1)
11[d]	2-Co (0.6)	DMSO:H_2O (1:3)	In the dark	20	0
12[e]	2-Co (0)	DMSO:H_2O (1:3)	440 nm	20	□5
13	2-Zn (0.6)	DMSO:H_2O (1:3)	440 nm	20	55 (4.5:1)
14	2-Ni (0.6)	DMSO:H_2O (1:3)	440 nm	20	58 (5.2:1)
15	2-Co (0.6)	DMSO:H_2O (1:3)	365 nm	20	40 (4.8:1)
16	2-Zn (0.6)	DMSO:H_2O (1:3)	365 nm	20	36 (4.7:1)
17	2-Ni (0.6)	DMSO:H_2O (1:3)	365 nm	20	30 (4.2:1)
18	2-Co (0.6)	DMSO:H_2O (1:3)	525 nm	20	38 (2.4:1)

19	2-Zn (0.6)	DMSO:H_2O (1:3)	525 nm	20	32 (2.0:1)
20	2-Ni (0.6)	DMSO:H_2O (1:3)	525 nm	20	35 (1.4:1)

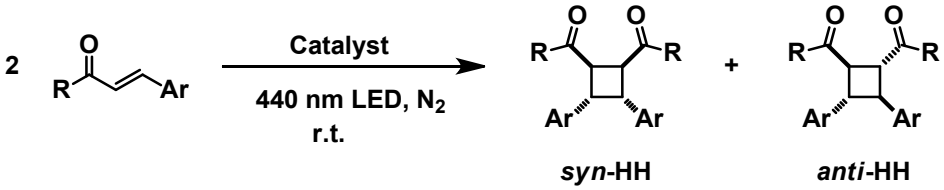
[a]Reaction conditions: **3a** (0.124 mmol), solvent (2 mL) under N_2 atmosphere by LED for 8 h. [b]Isolated yields after column chromatography. [c]d.r. values were obtained by ^{1}H NMR. [d]In the dark. [e]Without catalyst.

Table S4. Recycle results for **2-Co** catalyzed cycloadditions of **4a**



Run	1	2	3	4	5
Yield	72	70	71	72	69
d.r.	13	13	12	12.5	12

Table S5. Results for H_2L^1 and H_2L^2 catalyzed cycloaddition reactions[a]

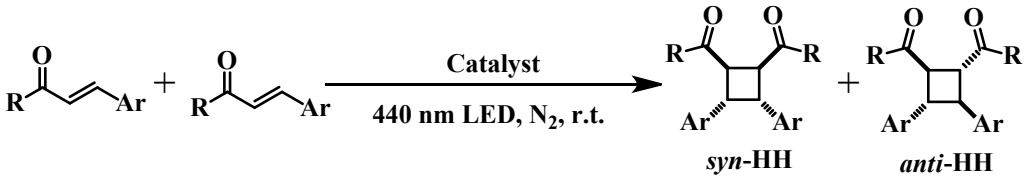


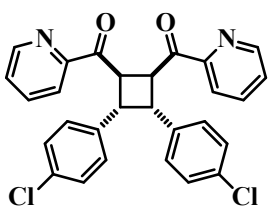
Entry	Catalyst (mol%)	R/Ar	t/h	Yield[b]/% (d.r.[c])
1	**H_2L^1** (7.2)	Py/4-ClPh	8	53(2.9:1)
2	**H_2L^2** (4.8)		8	51 (3:1)
3	**H_2L^1** (7.2)	Py/3-ClPh	3	52 (5.1:1)
4	**H_2L^2** (4.8)		3	56 (5:1)
5	**H_2L^1** (7.2)	Py/4-BrPh	8	41 (2.5:1)
6	**H_2L^2** (4.8)		8	40 (3.2:1)
7	**H_2L^1** (7.2)	Py/3-NO_2Ph	12	22 (4.3:1)
8	**H_2L^2** (4.8)		12	26 (4.7:1)
9	**H_2L^1** (7.2)	Py/4-OMePh	8	20 (1.5:1)

10	H_2L^2 (4.8)		8	22 (1.2:1)
11	H_2L^1 (7.2)	5-BrPy/4-BrPh	8	26 (2.6:1)
12	H_2L^2 (4.8)		8	30 (2.1:1)

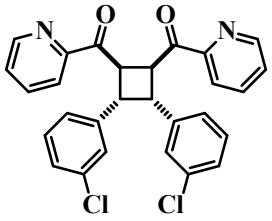
[a]Reaction conditions: subatrates (0.124 mmol), solvent (DMSO:H_2O/1:3, 2 mL) under N_2 atmosphere by 440 nm LED.

Table S6. Results for $Ru(bpy)_3(Cl)_2$ and $Ir(ppy)_3$ catalyzed cycloadditions[a]

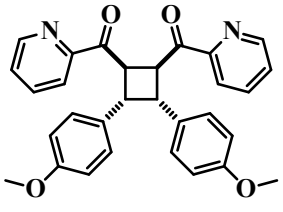




Cat.	yield(d.r.)
$Ru(bpy)_3(Cl)_2$	19%(1.7:1)
$Ir(ppy)_3$	21%(2.1:1)



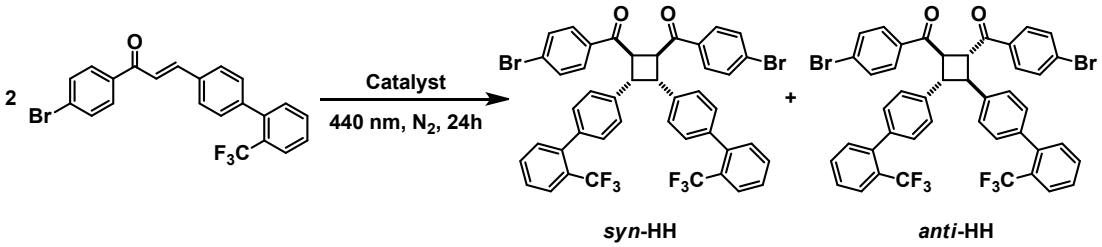
Cat.	yield(d.r.)
$Ru(bpy)_3(Cl)_2$	28%(2.8:1)
$Ir(ppy)_3$	30%(3.1:1)



Cat.	yield(d.r.)
$Ru(bpy)_3(Cl)_2$	12%(1:1)
$Ir(ppy)_3$	16%(1.2:1)

[a]Reaction conditions: subatrates (0.124 mmol), solvent (DMSO:H_2O/1:3, 2 mL) under N_2 atmosphere by 440 nm LED.

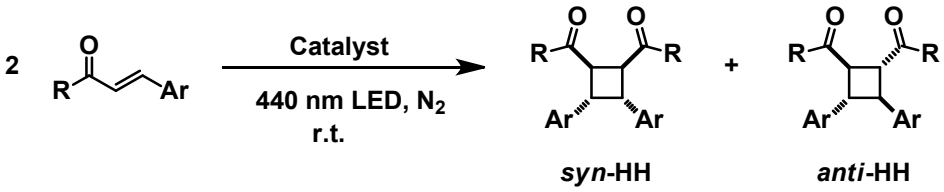
Table S7. [2 + 2] cycloaddition of bulky substrate[a]



Cata.	Loading/mol%	Solvent	T/ºC	Yield/% (d.r.)
2-Co	0.6	DMSO:H_2O 1:3	20	□5
2, 7-DMAQ	4.8	DMSO:H_2O 1:3	20	32% (3:1)

[a]Reaction conditions: subatrates (0.124 mmol), solvent (DMSO:H_2O/1:3, 2 mL) under N_2 atmosphere by 440 nm LED.

Table S8. Results for **1-Co** and 1, 4-DMAQ catalyzed cycloaddition reactions[a]



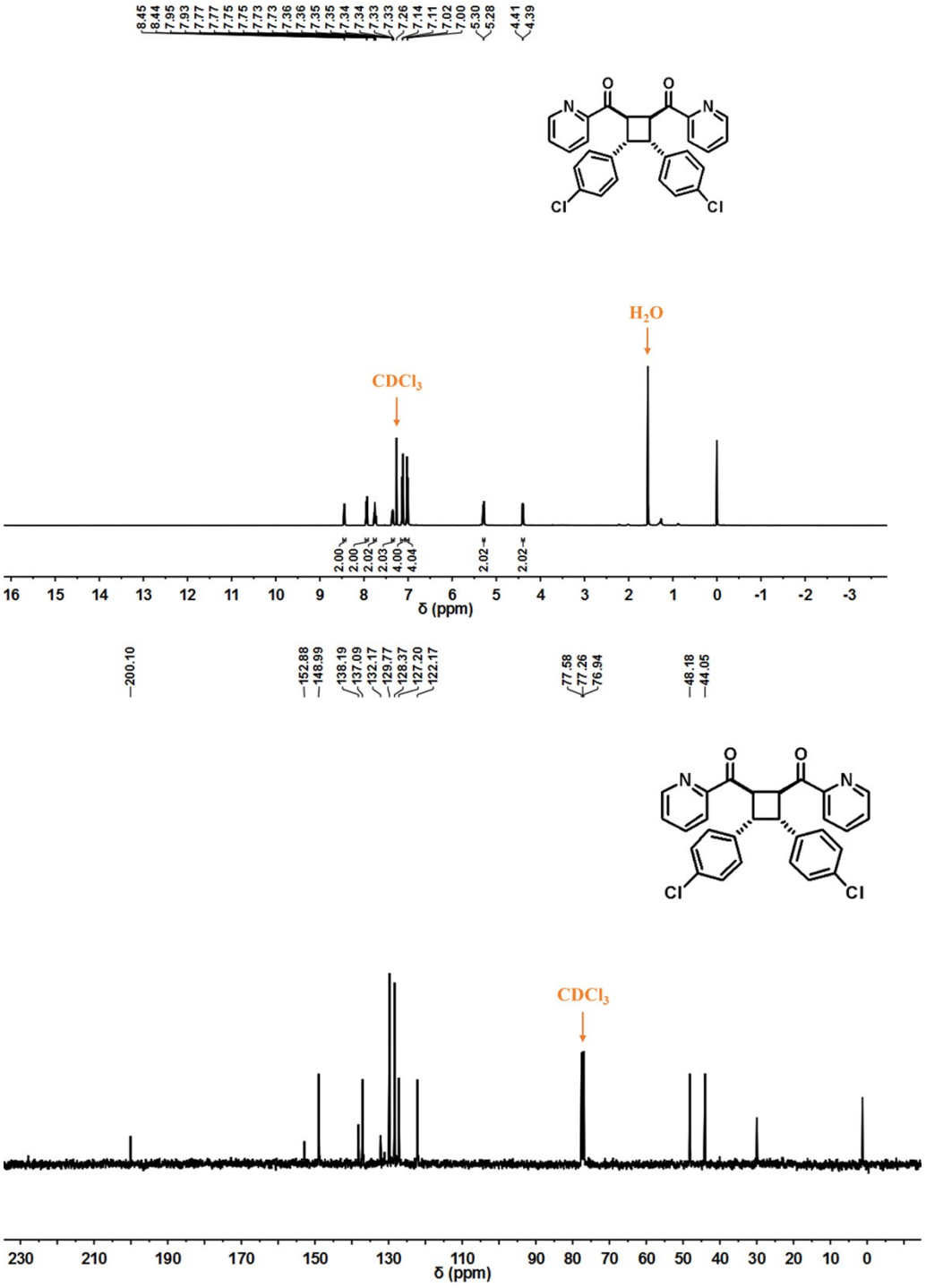
***syn*-HH** ***anti*-HH**

Entry	Catalyst (mol%)	R/Ar	t/h	Yield[b]/% (d.r.[c])
1	**1-Co** (0.6)	Py/4-ClPh	8	55 (3:1)
2	1, 4-DMAQ (7.2)		8	60 (4:1)
3	**1-Co** (0.6)	Py/3-ClPh	3	58 (6:1)
4	1, 4-DMAQ (7.2)		3	60 (6:1)
5	**1-Co** (0.6)	Py/4-BrPh	8	60 (2.5:1)
6	1, 4-DMAQ (7.2)		8	63 (3:1)

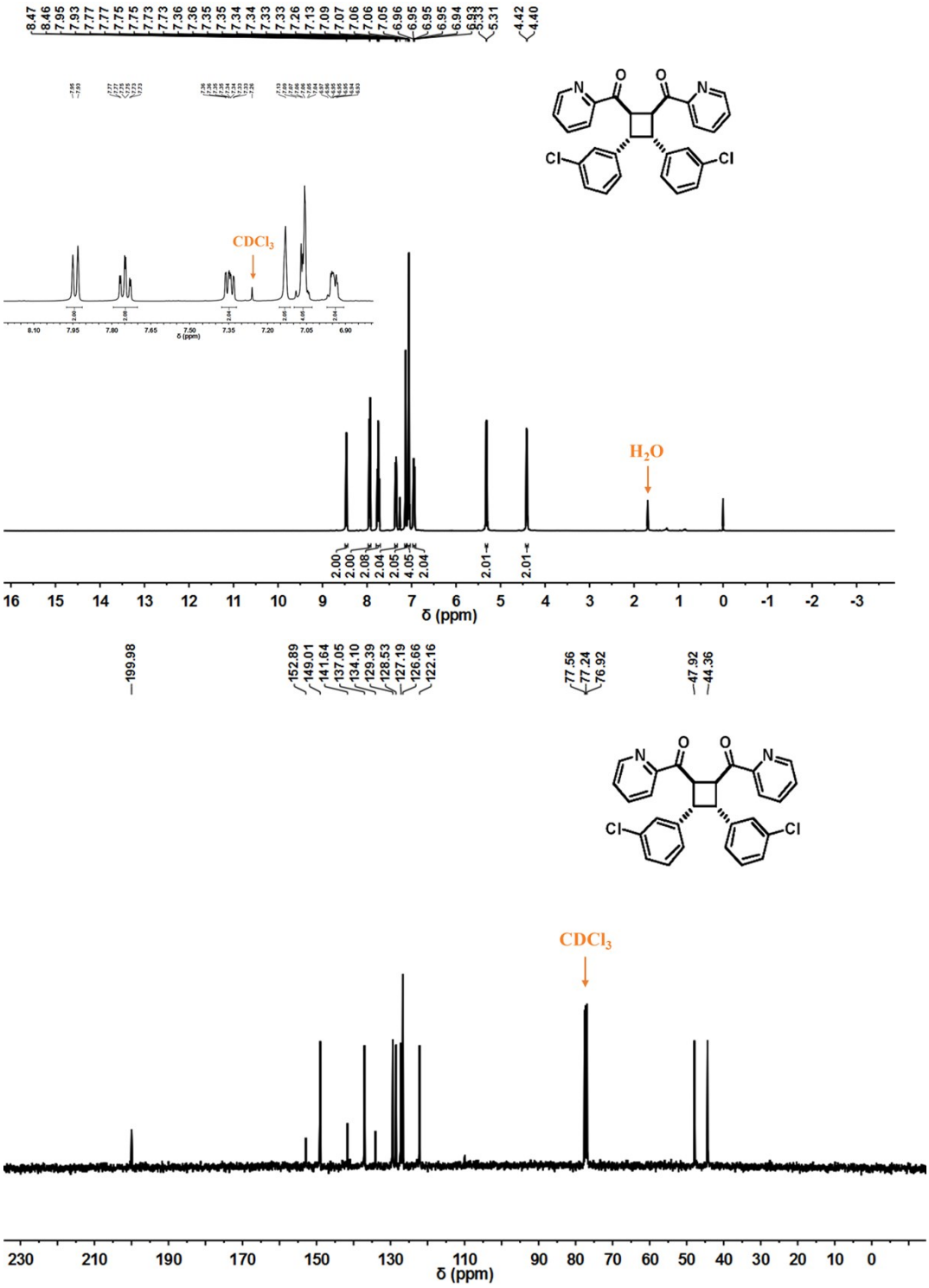
[a]Reaction conditions: subatrates (0.124 mmol), solvent (DMSO:H_2O/1:3, 2 mL) under N_2 atmosphere by 440 nm LED.

16. Figure S11. Additional NMR Spectra

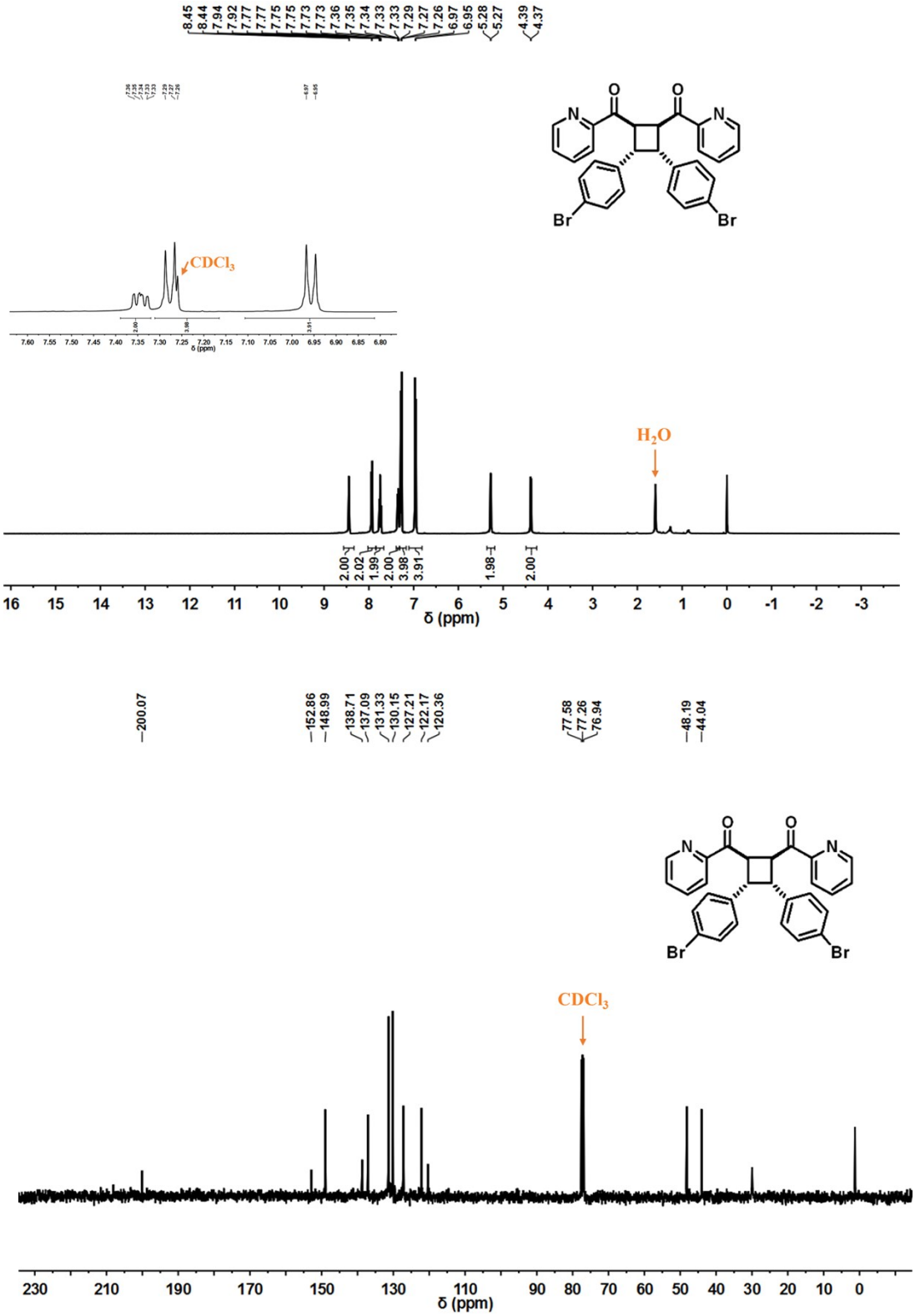
3b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (d, *J* = 4.6 Hz, 2H), 7.94 (d, *J* = 7.8 Hz, 2H), 7.75 (td, *J* = 7.7, 1.6 Hz, 2H), 7.35 (ddd, *J* = 7.5, 4.8, 1.0 Hz, 2H), 7.13 (d, *J* = 8.4 Hz, 4H), 7.01 (d, *J* = 8.5 Hz, 4H), 5.29 (d, *J* = 6.3 Hz, 2H), 4.40 (d, *J* = 6.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 152.9, 149.0, 138.2, 137.1, 132.17, 129.8, 128.4, 127.2, 122.2, 48.2, 44.0. ESI-TOF-MS Calcd. for $C_{28}H_{21}Cl_2N_2O_2$ $[M+H]^+$: 487.0902. Found: 487.0983.



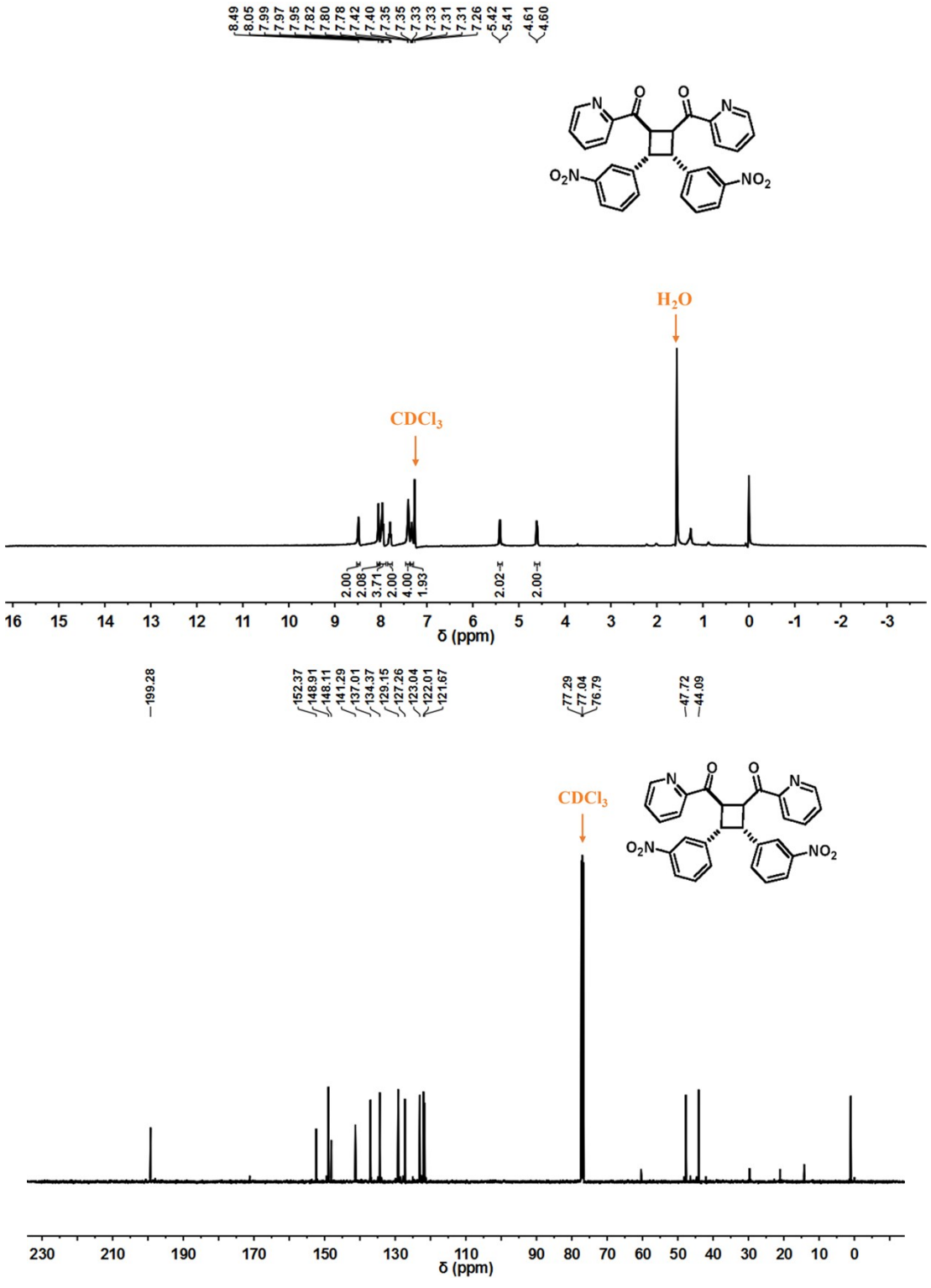
4b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.4 Hz, 2H), 7.94 (d, *J* = 7.8 Hz, 2H), 7.75 (td, *J* = 7.7, 1.7 Hz, 2H), 7.35 (ddd, *J* = 7.5, 4.8, 1.0 Hz, 2H), 7.13 (s, 2H), 7.08 – 7.04 (m, 4H), 6.98 – 6.91 (m, 2H), 5.34 (d, *J* = 6.3 Hz, 2H), 4.43 (d, *J* = 6.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.0, 152.9, 149.0, 141.6, 137.0, 134.1, 129.4, 128.5, 127.2, 126.7, 122.2, 47.9, 44.4. ESI-TOF-MS Calcd. for $C_{28}H_{21}Cl_2N_2O_2$ $[M+H]^+$: 487.0902. Found: 487.0983.



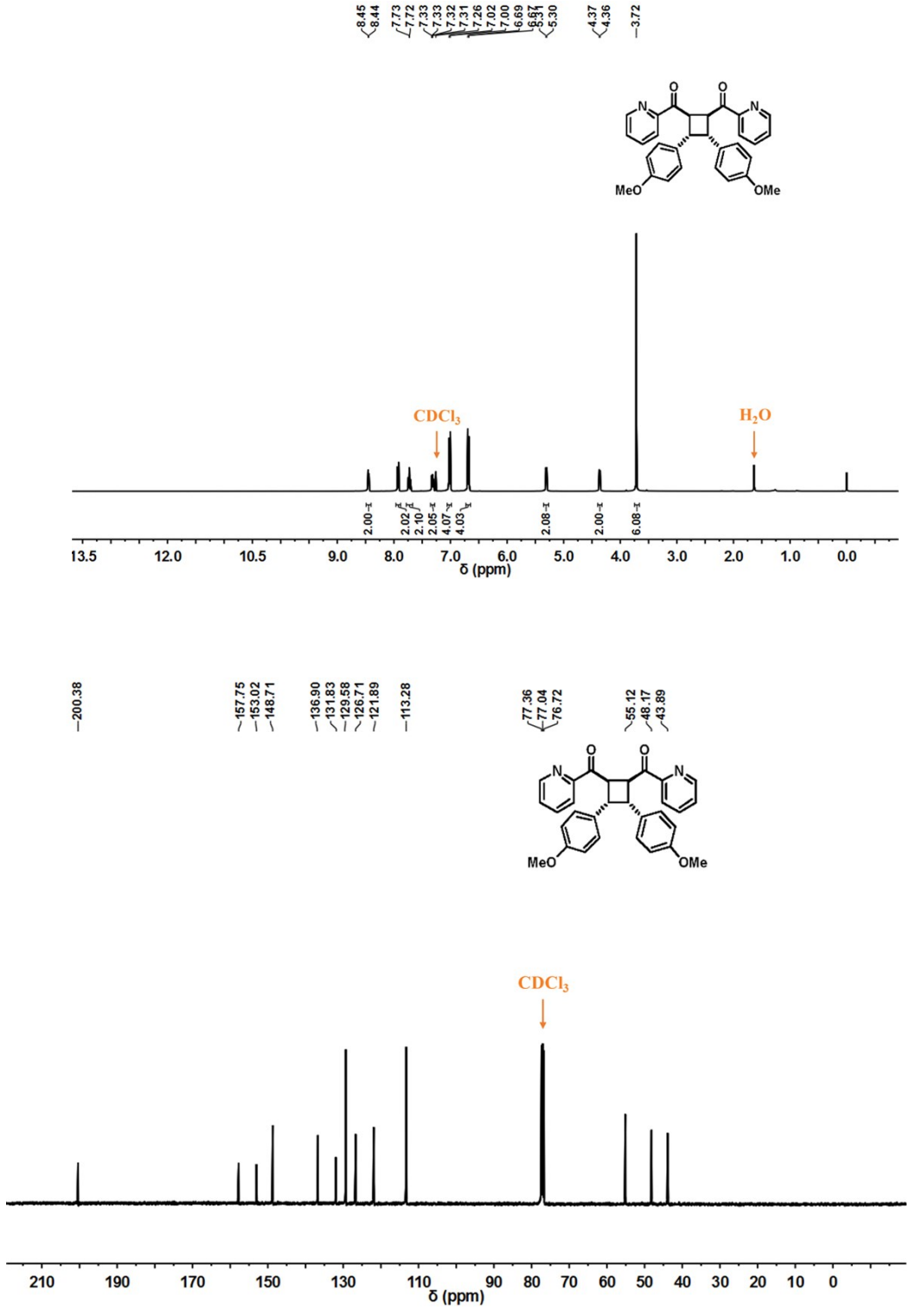
5b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, *J* = 4.6 Hz, 2H), 7.93 (d, *J* = 7.8 Hz, 2H), 7.75 (td, *J* = 7.7, 1.6 Hz, 2H), 7.38 – 7.31 (m, 2H), 7.28 (d, *J* = 8.4 Hz, 4H), 6.96 (d, *J* = 8.4 Hz, 4H), 5.28 (d, *J* = 6.4 Hz, 2H), 4.38 (d, *J* = 6.5 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.1, 152.9, 149.0, 138.7, 137.1, 131.3, 130.2, 127.2, 122.2, 120.4, 48.2, 44.0. ESI-TOF-MS Calcd. for $C_{28}H_{21}Br_2N_2O_2$ $[M+H]^+$: 576.9871. Found: 576.9976.



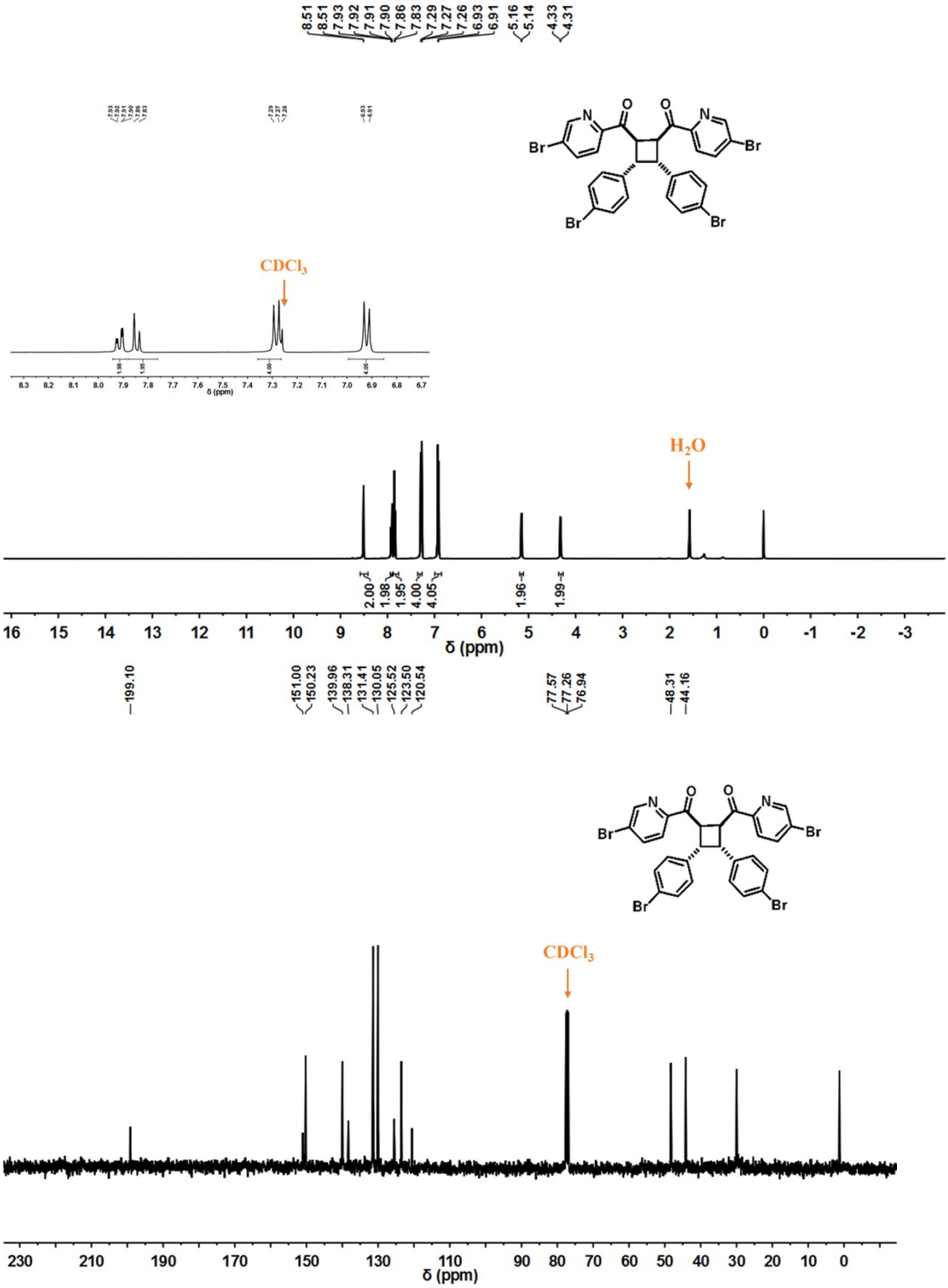
6b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.49 (s, 2H), 8.05 (s, 2H), 7.97 (t, J = 8.7 Hz, 4H), 7.80 (t, J = 7.4 Hz, 2H), 7.41 (d, J = 6.9 Hz, 4H), 7.33 (td, J = 7.9, 2.0 Hz, 2H), 7.26 (d, J = 2.4 Hz, 2H), 5.41 (d, J = 3.9 Hz, 2H), 4.61 (d, J = 4.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.3, 152.4, 148.9, 148.1, 141.3, 137.0, 134.4, 129.2, 127.3, 123.0, 122.0, 121.7, 47.7, 44.1. ESI-TOF-MS Calcd. for $C_{28}H_{21}N_4O_6$ $[M+H]^+$: 509.1416. Found: 509.1472.



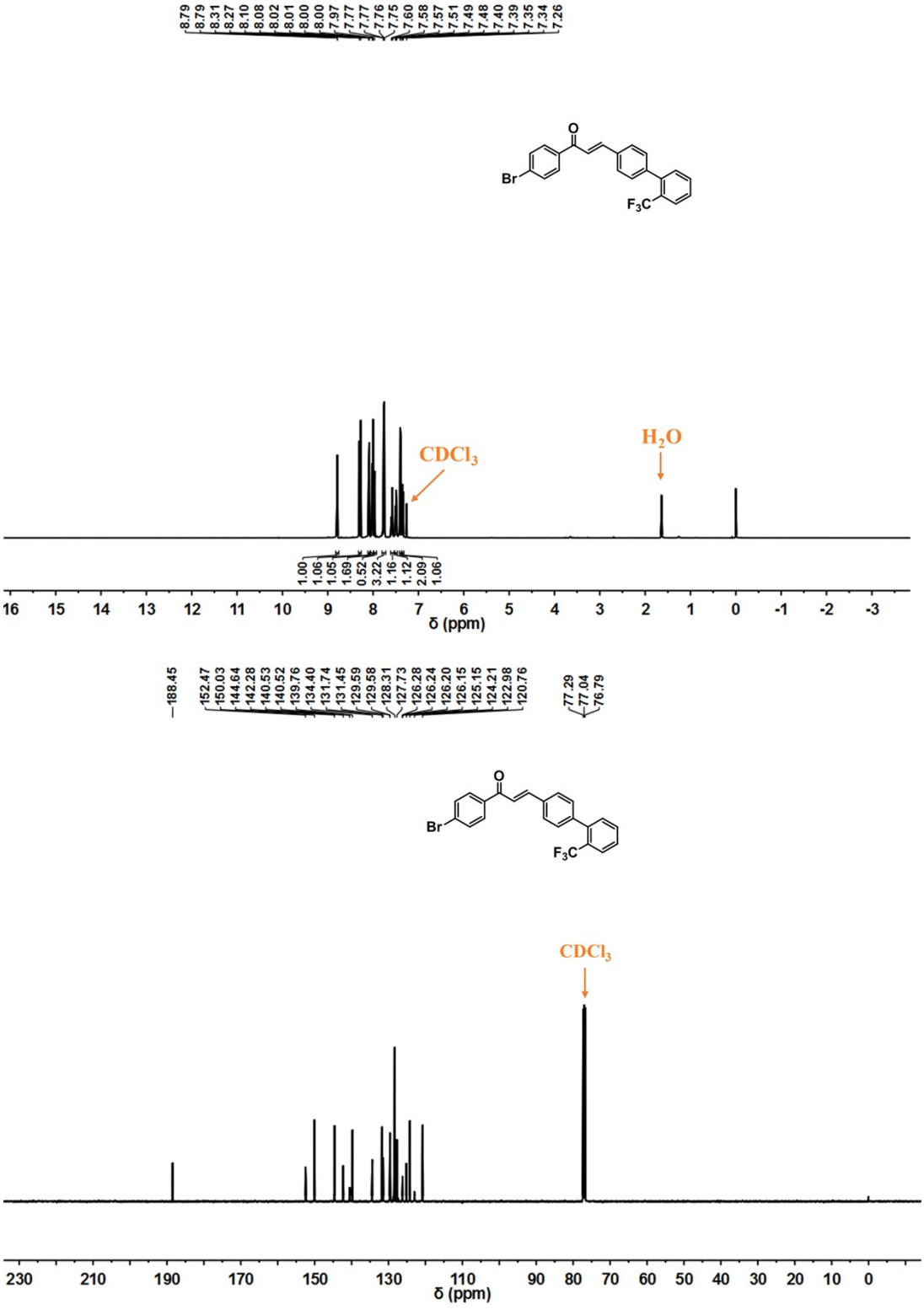
7b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.45 (dd, *J* = 4.7, 0.6 Hz, 2H), 7.92 (d, *J* = 7.8 Hz, 2H), 7.73 (td, *J* = 7.7, 1.7 Hz, 2H), 7.32 (ddd, *J* = 7.5, 4.8, 1.1 Hz, 2H), 7.01 (d, *J* = 8.7 Hz, 4H), 6.68 (d, *J* = 8.7 Hz, 4H), 5.31 (d, *J* = 6.3 Hz, 2H), 4.36 (d, *J* = 6.4 Hz, 2H), 3.72 (s, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 200.4, 157.8, 153.0, 148.71, 136.9, 131.8, 129.6, 126.7, 121.9, 113.3, 55.1, 48.1, 43.9. ESI-TOF-MS Calcd. for $C_{30}H_{27}N_2O_4$ $[M+H]^+$: 479.1926. Found: 479.1982.

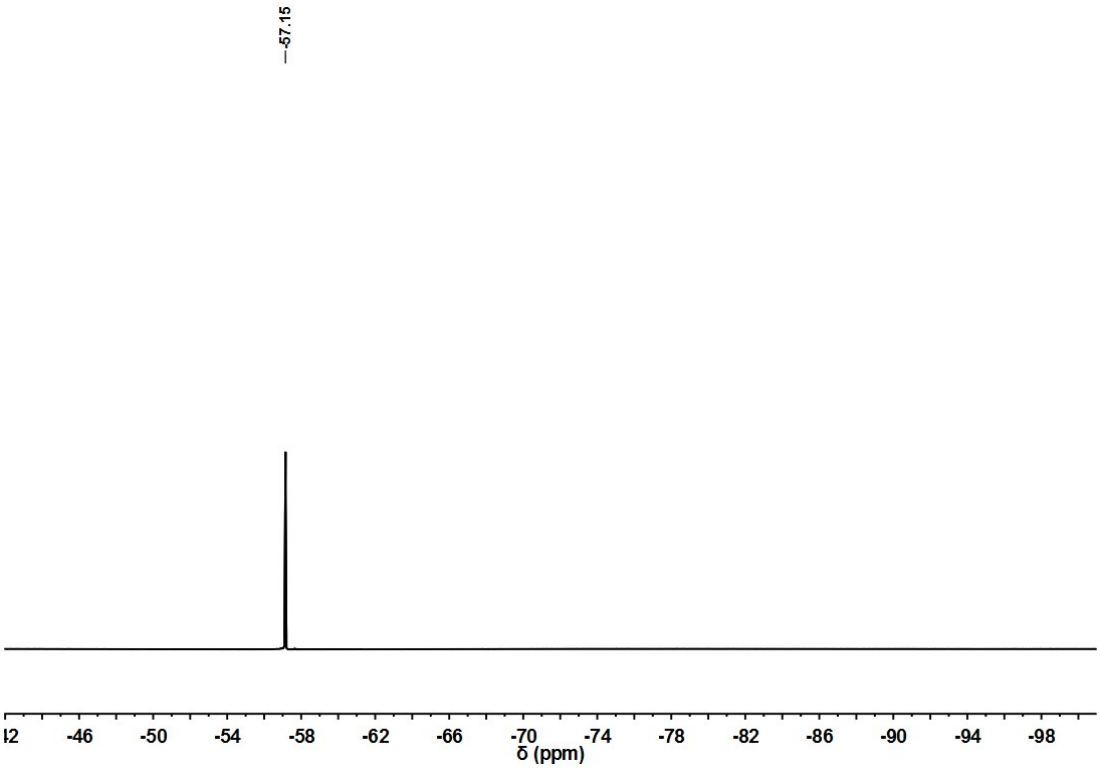


8b: ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.51 (d, *J* = 2.1 Hz, 2H), 7.91 (dd, *J* = 8.4, 2.1 Hz, 2H), 7.84 (d, *J* = 8.4 Hz, 2H), 7.28 (d, *J* = 8.3 Hz, 4H), 6.92 (d, *J* = 8.4 Hz, 4H), 5.15 (d, *J* = 6.3 Hz, 2H), 4.32 (d, *J* = 6.4 Hz, 2H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.1, 151.0, 150.2, 140.0, 138.3, 131.4, 130.1, 125.5, 123.5, 120.5, 48.3, 44.2. ESI-TOF-MS Calcd. for $C_{28}H_{19}Br_4N_2O_2$ $[M+H]^+$: 734.8061. Found: 734.8152.

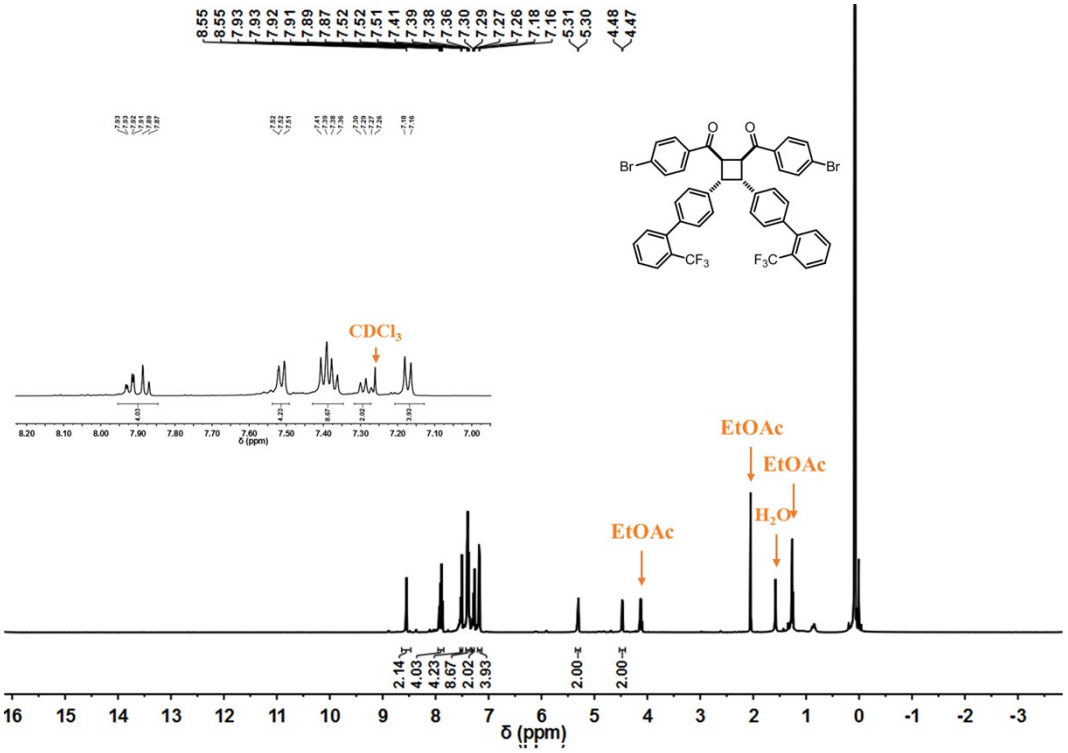


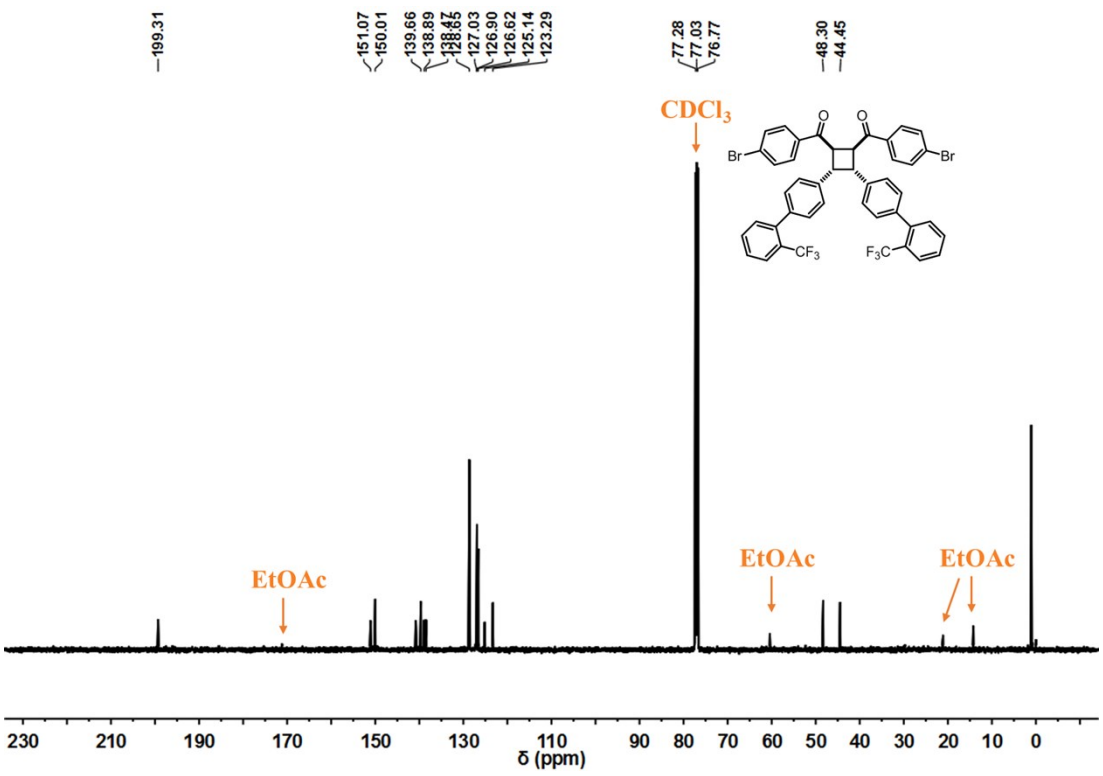
9a: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.79 (d, *J* = 1.9 Hz, 1H), 8.29 (d, *J* = 16.0 Hz, 1H), 8.09 (d, *J* = 8.4 Hz, 1H), 8.01 (dd, *J* = 8.3, 2.1 Hz, 2H), 7.97 (d, *J* = 6.1 Hz, 1H), 7.76 (dd, *J* = 8.2, 1.9 Hz, 3H), 7.63 – 7.55 (m, 1H), 7.48 (dd, *J* = 15.2, 7.5 Hz, 1H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 188.4, 152.5, 150.0, 144.6, 142.3, 140.5, 139.8, 134.4, 131.7, 131.4, 129.6, 128.3, 127.7, 126.2, 125.2, 124.2, 123.0, 120.8. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.15. ESI-TOF-MS Calcd. for $C_{22}H_{15}BrF_3O$ $[M+H]^+$: 431.0180. Found: 431.0192.

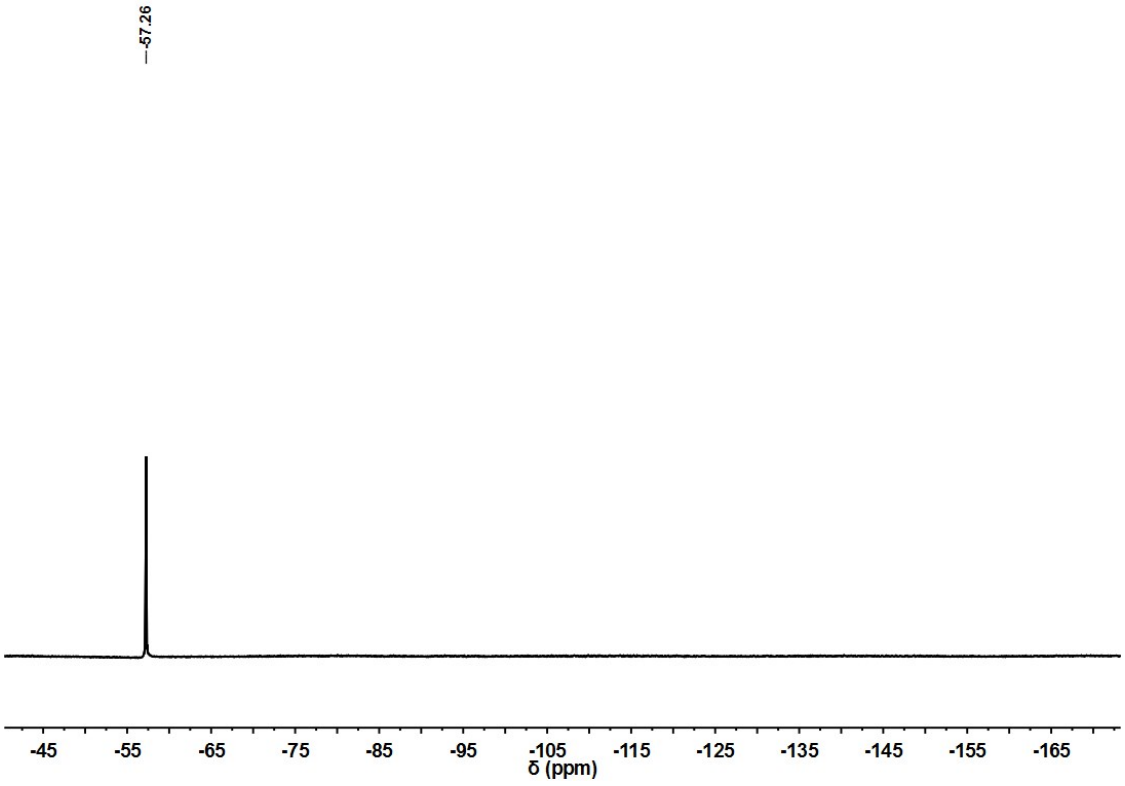




9b: ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.55 (d, J = 1.7 Hz, 2H), 7.91 (dt, J = 20.4, 5.3 Hz, 4H), 7.51 (d, J = 7.2 Hz, 4H), 7.38 (dd, J = 14.5, 7.9 Hz, 8H), 7.29 (t, J = 7.4 Hz, 2H), 7.17 (d, J = 8.2 Hz, 4H), 5.31 (d, J = 6.3 Hz, 2H), 4.47 (d, J = 6.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 199.3, 151.1, 150.0, 140.8, 139.7, 138.9, 138.5, 128.6, 127.0, 126.9, 126.6, 125.1, 123.3, 48.3, 44.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ -57.26. ESI-TOF-MS Calcd. for $C_{44}H_{29}Br_2F_6O_2$ $[M+H]^+$: 861.0360. Found: 861.0394.




199.31
151.07
150.01
139.66
138.89
127.03
126.90
126.62
125.14
123.29
77.28
77.03
76.77
48.30
44.45
CDCl3
Br
Br
CF3
F3C
EtOAc
EtOAc
EtOAc
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
δ (ppm)


-57.26
-45
-55
-65
-75
-85
-95
-105
-115
-125
-135
-145
-155
-165
δ (ppm)

17. References

[1] Sheldrick, G. M. SHELXT-2014, 2013.

[2] Dolomanov, O. V.; Bourhis, L. J.; Gildea, R. J.; Howard, J. A. K.; Puschmann, H. *J. Appl. Crystallogr.* **2009**, *42*, 339.

[3] Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7-13.

[4] Celis-Salazar, P. J.; Epley, C. C.; Ahrenholtz, S. R.; Maza, W. A.; Usov, P. M.; Morris, A. J. *Inorg. Chem*. **2017**, *56*, 13741-13747.

[5] Akpinar, H.; Schlueter, J. A.; Cassaro, R. A. A.; Friedman, J. R.; Lahti, P. M. *Cryst. Growth Des*. **2016**, *16*, 4051-4059.

[6] Otto, S.; Bertoncin, F.; Engberts, J. B. F. N. *J. Am. Chem. Soc.* **1996**, *118*, 7702–7707.