Supporting information

Co(II)-Cluster-Based Metal-Organic Frameworks as Efficient Heterogeneous Catalysts for Selective Oxidation of Arylalkanes

Yanru Fan, Xiao Li, Kuan Gao, Yu Liu, Xiangru Meng, Jie Wu* and Hongwei Hou*

The College of Chemistry and Molecular Engineering, Zhengzhou University,

Zhengzhou, Henan, 450052, P. R. China.

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1. General method.

All reagents and solvents were commercially available and used as received without further purification. Ligand was synthesized according to the modified procedures reported previously.¹ ¹H NMR and ¹³C NMR spectra were obtained with Bruker Avance-400 and 600 spectrometers. Powder X-ray diffraction (PXRD) analyses were performed on a Bruker D8 Advance X-ray diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å). The thermal decomposition characteristic of the samples was analyzed by thermogravimetric analysis (TGA) using a NETZSCH STA 409 PC/PG thermal analyzer at a heating rate of 10 °C min⁻¹ in air. Elemental analyzer STA 409 RC/PG thermal analyzer at a Bruker Vector 22 FT-IR spectrophotometer using KBr pellets.

2. Synthesis.

(1) The synthesis of carboxyl acid ligand.



9,9'-(1,4-phenylenebis(methylene))bis(9H-carbazole-3,6-dicarboxylic acid) (H₄pmbcd) was prepared according to a modified procedure from the literature.¹

N³,N³,N⁶,N⁶-tetramethyl-9*H*-carbazole-3,6-dicarboxamide (1): Carbazole (11 g, 65.8 mmol), dimethylcarbamoyl chloride (17.7 g, 164.5 mmol) were combined in a round-bottom flask with 1,2-dichloroethane (300 mL). The flask was stirred under ice bath condition .Then AlCl₃ (22.8 g, 171.0 mmol) was slowly added to the flask. After 2 hours, the flask was heated to 90 °C and stirred for another 24 hours. The reaction mixture was cooled to room temperature and poured into H₂O (500 mL). The mixture was extracted with dichloromethane for several times. The combined organics were dried over anhydrous Na₂SO₄ and evaporated on a rotary evaporator. The residue was purified by column chromatography (silica, dichloromethane-methanol, v/v = 80:1) to give compound 1 (55%, 11.2 g) as a white solid. ¹H NMR (400MHz, DMSO): δ = 11.70 (s, 1H), 8.34 (s, 2H), 7.53 (dd, *J*=21.6 Hz, 8.4 Hz, 4H), 3.04 (s, 12H) ppm. ¹³C

NMR (101 MHz, DMSO): δ = 171.51, 141.05, 127.43, 126.03, 122.21, 120.59, 111.18, 39.97 ppm.

9,9'-(1,4-phenylenebis(methylene))bis(N³,N³,N⁶,N⁶-tetramethyl-9*H*-carbazole-3,6dicarboxamide) (2): NaH (0.312 g, 13 mmol) was slowly added to a solution of compound 1 (4 g, 12.93 mmol) in dimethylformamide (40 mL). The resulting suspension was stirred at room temperature for 15 minutes. Then, 1,4bis(bromomethyl)benzene (1.7 g, 6.46 mmol) was added, and stirred for another 24 hours at room temperature. The mixture was added into H₂O (500 mL). The precipitate was collected by filtration, washed with water, and dried in a vacuum oven. The compound 2 (4.2 g, 91%) was obtained as a white solid. ¹H NMR (400 MHz, CDCl₃): δ = 8.19 (d, *J* = 1.2 Hz, 4H), 7.52 (dd, *J* = 8.4, 1.5 Hz, 4H), 7.32 (d, *J* = 8.4 Hz, 4H), 6.97 (s, 4H), 5.46 (s, 4H), 3.12 (s, 6H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 172.25, 141.50, 135.97, 127.69, 126.89, 126.02, 122.42, 120.21, 108.90, 77.31, 46.32 ppm.

9,9'-(1,4-phenylenebis(methylene))bis(9*H*-carbazole-3,6-dicarboxylic acid) (3): A mixture of the compound 2 (4 g, 5.6 mmol), NaOH (4.4 g, 110.9 mmol), ethanol (50 mL) and DMSO (100 mL) was heated at 80 °C for 24 hours. After cooling to room temperature, the mixture was added into H₂O (500 mL) and stirred for several minutes. After acidification by diluted hydrochloric acid, the white solid was filtrated. The solid was washed three times with H₂O and ethanol, and dried in vacuum drying chamber at 50 °C The white compound 3 (3.2 g) was obtained in the yield of 95%. ¹H NMR (400 MHz, DMSO): δ = 8.90 (d, *J* = 1.3 Hz, 4H), 8.07 (dd, *J* = 8.6, 1.5Hz, 4H), 7.73 (d, *J* = 8.7 Hz, 4H), 7.11 (s, 4H), 5.71 (s, 4H) ppm. ¹³C NMR (101 MHz, DMSO): δ = 172.95, 148.55, 141.53, 133.07, 132.28, 128.09, 127.73, 127.29, 115.03, 45.55 ppm.

(2) The synthesis of ketones.



1-Indanone (**5a**): The concentrate was purified by column chromatography (silica, petroleum ether-ethyl acetate, v/v = 10:1) to give compound **5a** (92%) as a white solid. This compound had been reported.² ¹H NMR (400 MHz, CDCl₃): δ = 8.10 (dd, *J* = 7.8, 0.8 Hz, 1H), 7.55 (td, *J* = 7.5, 1.3Hz, 1H), 7.40 (t, *J* = 7.6Hz, 1H), 7.30 - 7.25 (m, 1H), 4.57 - 4.51 (m, 2H), 3.07 (t, *J* = 6.0 Hz, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 207.14, 155.19, 137.11, 134.62, 127.30, 126.72, 123.75, 36.24, 25.83 ppm.



1-Tetralone (**5b**): The concentrate was purified by column chromatography (silica, petroleum ether- ethyl acetate, v/v = 10:1) to give compound **5b** (85%) as a brown liquid. This compound had been reported.² ¹H NMR (400 MHz, CDCl₃): δ = 8.06 (dd, J = 7.8, 1.1 Hz, 1H), 7.52 - 7.47 (m, 1H), 7.34 (dd, J = 11.2, 3.9 Hz, 1H), 7.28 (d, J = 7.8 Hz, 1H), 3.00 (t, J = 6.1 Hz, 2H), 2.71 - 2.66 (m, 2H), 2.21 - 2.13 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 198.49, 144.52, 133.43, 132.62, 128.80, 127.19, 126.66, 39.20, 29.73, 23.31 ppm.



1-Phthalanone (5c): The concentrate was purified by column chromatography (silica, petroleum ether-ethyl acetate, v/v = 10:1) to give compound 5c (86%) as a

white solid. This compound had been reported.² ¹H NMR (400 MHz, CDCl₃): $\delta =$ 7.92 (d, J = 7.7 Hz, 1H), 7.70 (t, J = 7.5 Hz, 1H), 7.53 (dd, J = 15.2, 7.6 Hz, 2H), 5.33 (s, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta = 171.15$, 146.56, 134.05, 129.05, 125.75, 125.73, 122.14, 69.69 ppm.



1-Isochromanone (**5d**): The concentrate was purified by column chromatography (silica, petroleum ether- ethyl acetate, v/v = 10:1) to give compound **5d** (83%) as a colorless liquid. This compound had been reported.³ ¹H NMR (600 MHz, CDCl₃): δ = 8.09 (d, *J* = 7.7 Hz, 1H), 7.54 (t, *J* = 7.5Hz, 1H), 7.39 (t, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 7.5 Hz, 1H), 4.54 (t, *J* = 5.9 Hz, 2H), 3.07 (t, *J* = 5.9 Hz, 2H) ppm. ¹³C NMR (151 MHz, CDCl₃): δ = 165.13, 139.61, 133.69, 130.29, 127.65, 127.30, 125.28, 67.34, 27.79 ppm.



9*H*-Fluoren-9-one (**5e**): The concentrate was purified by column chromatography (silica, petroleum ether-ethyl acetate, v/v = 10:1) to give compound **5e** (95%) as a yellow solid. This compound had been reported.² ¹H NMR (400 MHz, CDCl₃): δ = 7.63 (d, *J* = 7.3 Hz, 2H), 7.51-7.42 (m, 4H), 7.30 - 7.24 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 193.91, 144.42, 134.69, 134.14, 129.07, 124.29, 120.32 ppm.



10*H*-Acridin-9-one (**5f**): The concentrate was purified by column chromatography (silica, petroleum ether-ethyl acetate, v/v = 10:1) to give compound **5f** (93%) as a yellow solid. This compound had been reported.⁴ ¹H NMR (600 MHz, CDCl₃): δ = 8.75 (s, 1H), 8.24 (d, *J* = 8.7 Hz, 2H), 7.98 (d, *J* = 8.3 Hz, 2H), 7.78 (t, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.3 Hz, 2H) ppm. ¹³C NMR (151 MHz, CDCl₃): δ = 149.11, 136.06, 130.31, 129.45, 128.22, 126.61, 125.70 ppm.



Benzophenone (**5g**): The concentrate was purified by column chromatography (silica, petroleum ether- ethyl acetate, v/v = 10:1) to give compound **5g** (98%) as a white solid. This compound had been reported.² ¹H NMR (400 MHz, CDCl₃): δ = 7.85 - 7.75 (m, 4H), 7.59 (ddd, *J* = 8.6, 2.4, 1.2 Hz, 2H), 7.48 (dd, *J* = 10.5, 4.6 Hz, 4H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 196.79, 137.62, 132.43, 130.08, 128.30 ppm.



1-Phenylethanone (**5h**): The concentrate was purified by column chromatography (silica, petroleum ether- ethyl acetate, v/v = 10:1) to give compound **5h** (81%) as a colorless liquid. This compound had been reported.³ ¹H NMR (400 MHz, CDCl₃): δ = 7.96 (dd, *J* = 5.2, 3.4 Hz, 2H), 7.60 – 7.53 (m, 1H), 7.46 (dd, *J* = 10.5, 4.7 Hz, 2H), 2.61 (s, 3H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 198.20, 137.12, 133.14, 128.59, 128.33, 26.65 ppm.



Benzenecarbonyl chloride (**5i**): The concentrate was purified by column chromatography (silica, petroleum ether- ethyl acetate, v/v = 10:1) to give compound **5i** (74%) as a colorless liquid. This compound had been reported.³ ¹H NMR (400 MHz, CDCl₃): $\delta = 8.12$ (dd, J = 8.3, 1.0 Hz, 2H), 7.69 (t, J = 7.5 Hz, 1H), 7.57 – 7.47 (m, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): $\delta = 168.48$, 135.38, 133.27, 131.46, 129.00 ppm.



Benzaldehyde (**5j**): The concentrate was purified by column chromatography (silica, petroleum ether- ethyl acetate, v/v = 10:1) to give compound **5j** (89%) as a colorless liquid. This compound had been reported.³ ¹H NMR (400 MHz, CDCl₃): δ = 10.02 (s, 1H), 7.89 (dt, *J* = 8.4, 1.6 Hz, 2H), 7.64 (ddt, *J* = 6.8, 5.1, 1.4 Hz, 1H), 7.53 (dd, *J* = 10.4, 4.6 Hz, 2H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 192.46, 136.39, 134.50, 129.77, 129.02 ppm.

3. Crystal data collection and refinement

The structures of MOFs **1-3** were tested on a Bruker D8 VENTURE diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å). The SAINT program was used to control the integration of the diffraction data, polarization effects, and the intensity corrections for the Lorentz.⁵ We used the SADABS program to perform semiempirical absorption correction and solved structures by immediate ways and refined by a full matrix leastsquares technique relied on F^2 with the SHELXL-2014 software package.⁶ The hydrogen atoms were generated geometrically and refined isotropically using the riding model. The summary of crystallographic data for MOFs **1-3** is listed in Table S1. Corresponding bond lengths (Å) and bond angles (deg) are provided in Table S2. Crystallographic data for MOFs **1-3** have been deposited at the Cambridge Crystallographic data Centre with CCDC reference numbers 1882631, 1882634, and 1882637.

MOF	1	2	3
formula	$C_{90}H_{92}Co_5N_{10}O_{28}$	$C_{66}H_{62}Co_2N_8O_{12}\\$	$C_{68}H_{68}Co_2N_8O_{13}$
Formula weight	2056.38	1277.13	1323.16
Temperature/K	293(2)	293(2)	298(2)
Radiation	Mo <i>K</i> α (λ =0.71073)	Μο Κα (λ =0.71073)	Mo <i>K</i> α (λ =0.71073)
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	<i>P</i> -1	<i>P</i> 2 ₁
a/Å	14.7342(5)	10.8175(5)	10.6338(4)
b/Å	12.3434(4)	13.0914(6)	22.9546(9)
c/Å	25.1181(9)	22.9369(10)	12.9795(4)
α/°	90	96.939(2)	90
β/°	103.2750(10)	99.947(2)	96.7800(10)
γ/°	90	100.570(2)	90
Volume/Å ³	4446.2(3)	3105.9(2)	3146.1(2)
Ζ	2	2	2
$\rho_{calc} \left(g/cm^3\right)$	1.536	1.171	1.397
Reflections collected	90092	121101	126860
Independent reflections	10270	14447	14532
F(000)	2122.0	1128.0	1380.0
GOF	1.026	1.032	0.986
R ₁ (I>2sigma(I)) ^a	0.0357	0.0556	0.0389
$wR_2(I > 2sigma(I))^b$	0.0941	0.1647	0.1049

 Table S1. Crystallographic data and structure refinement details for MOFs 1-3

 ${}^{a}R_{1} = \sum ||F_{o}| - |F_{c}|| \sum /|F_{o}|. {}^{b}wR_{2} = [\sum w(F_{o}{}^{2}-F_{c}{}^{2})^{2}/\sum w(F_{o}{}^{2})^{2}]^{1/2}.$

MOF 1					
Co(1) - O(1)#1	1.9787(15)	Co(3) - O(6)	2.0251(15)		
Co(1) - O(3)	1.9385(15)	Co(3) - O(11)	2.0929(19)		
Co(1) - O(8)#2	2.0117(16)	Co(3) - O(12)	2.1028(17)		
Co(1) - O(10)	1.9660(14)	Co(3) - O(10)#4	2.1107(15)		
Co(2) - O(5)#4	2.0621(14)	Co(3) - O(9)#4	2.2093(17)		
Co(2) - O(5)#5	2.0621(14)	O(1) - Co(1)#1	1.9787(15)		
Co(2) - O(9)	2.1891(16)	O(2) - Co(3)#7	2.0163(17)		
Co(2) - O(9)#3	2.1891(16)	O(5) - Co(2)#8	2.0621(14)		
Co(2) - O(10)	2.0362(15)	O(8) - Co(1)#9	2.0118(16)		
Co(2) - O(10)#3	2.0362(15)	O(9) - Co(3)#4	2.2094(17)		
Co(3) - O(2)#6	2.0163(17)	O(10) - Co(3)#4	2.1108(15)		
O(3) - Co(1) - O(10)	132.59(7)	O(6) - Co(3) - O(10)#4	91.52(6)		
O(3) - Co(1) - O(1)#1	102.01(7)	O(11) - Co(3) - O(10)#4	89.40(8)		
O(10) - Co(1) - O(1)#1	108.31(6)	O(12) - Co(3) - O(10)#4	177.16(7)		
O(3) - Co(1) - O(8)#2	100.01(7)	O(2)#6 - Co(3) - O(9)#4	92.47(8)		
O(10) - Co(1) - O(8)#2	103.40(7)	O(6) - Co(3) - O(9)#4	87.50(7)		
O(1)#1 - Co(1) - O(8)#2	108.96(7)	O(11) - Co(3) - O(9)#4	171.82(8)		
O(10) - Co(2) - O(10)#3	180	O(12) - Co(3) - O(9)#4	94.13(7)		
O(10) - Co(2) - O(5)#4	93.63(6)	O(10)#4 - Co(3) - O(9)#4	83.23(6)		
O(10)#3 - Co(2) - O(5)#4	86.37(6)	C(45) - O(1) - Co(1)#1	124.35(14)		
O(10) - Co(2) - O(5)#5	86.37(6)	C(45) - O(2) - Co(3)#7	144.30(16)		
O(10)#3 - Co(2) - O(5)#5	93.63(6)	C(1) - O(3) - Co(1)	125.78(15)		
O(5)#4 - Co(2) - O(5)#5	180	C(34) - O(5) - Co(2)#8	126.47(14)		
O(10) - Co(2) - O(9)#3	94.51(6)	C(34) - O(6) - Co(3)	132.56(13)		
O(10)#3 - Co(2) - O(9)#3	85.49(6)	C(35) - O(8) - Co(1)#9	125.53(16)		
O(5)#4 - Co(2) - O(9)#3	89.60(6)	Co(2) - O(9) - Co(3)#4	88.87(6)		
O(5)#5 - Co(2) - O(9)#3	90.40(6)	Co(2) - O(9) - H(9A)	106(2)		
O(10) - Co(2) - O(9)	85.49(6)	Co(3)#4 - O(9) - H(9A)	119(2)		
O(10)#3 - Co(2) - O(9)	94.51(6)	Co(2) - O(9) - H(9B)	120(2)		
O(5)#4 - Co(2) - O(9)	90.40(6)	Co(3)#4 - O(9) - H(9B)	114(2)		
O(5)#5 - Co(2) - O(9)	89.60(6)	Co(1) - O(10) - Co(2)	117.71(7)		
O(9)#3 - Co(2) - O(9)	180	Co(1) - O(10) - Co(3)#4	116.70(7)		
O(2)#6 - Co(3) - O(6)	173.92(7)	Co(2) - O(10) - Co(3)#4	95.89(6)		
O(2)#6 - Co(3) - O(11)	91.65(9)	Co(1) - O(10) - H(10)	103(2)		

 Table S2. Selected Bond Lengths (Å) and Bond Angles (deg) for MOFs 1 - 3.

MOF 1					
O(6) - Co(3) - O(11)	89.15(8)	Co(2) - O(10) - H(10)	118(2)		
O(2)#6 - Co(3) - O(12)	84.55(7)	Co(3)#4 - O(10) - H(10)	105(2)		
O(6) - Co(3) - O(12)	89.39(7)	Co(3) - O(11) - H(11A)	104(2)		
O(11) - Co(3) - O(12)	93.30(8)	Co(3) - O(11) - H(11B)	113(3)		
O(2)#6 - Co(3) - O(10)#4	94.51(7)	C(36) - O(12) - Co(3)	125.5(2)		

Symmetry transformations used to generate equivalent atoms:

#1 -x+1, y, -z+1; #2 x+1/2, -y+3/2, z+1/2; #3 -x+2, -y, -z+1; #4 -x+2, -y+1, -z+1;

#5 x, y-1, -z;	#6 x+1, y+1, z;	#7 x-1, y-1, z;	#8 x, y+1, z;	#9 x-1/2,	-y+3/2, z-1/2
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MOF 2					
Co(1) - O(4)	1.987(2)	Co(2) - N(3)	2.137(2)		
Co(1) - O(6)	2.010(2)	Co(2) - O(7)#4	2.171(2)		
Co(1) - O(1)#1	2.144(2)	Co(2) - O(8)#4	2.230(2)		
Co(1) - N(4)#2	2.151(3)	O(8) - Co(2)#1	2.230(2)		
Co(1) - N(6)#3	2.152(2)	O(7) - Co(2)#1	2.171(2)		
Co(1) - O(2)#1	2.236(2)	O(2) - Co(1)#4	2.235(2)		
Co(2) - O(5)	2.005(2)	O(1) - Co(1)#4	2.144(2)		
Co(2) - O(3)	2.014(2)	N(4) - Co(1)#2	2.151(3)		
Co(2) - N(5)	2.137(2)	N(6) - Co(1)#3	2.152(2)		
O(4) - Co(1) - O(6)	114.34(9)	N(5) - Co(2) - O(7)#4	91.21(9)		
O(4) - Co(1) - O(1)#1	153.03(9)	N(3) - Co(2) - O(7)#4	87.01(8)		
O(6) - Co(1) - O(1)#1	92.26(8)	O(5) - Co(2) - O(8)#4	89.66(8)		
O(4) - Co(1) - N(4)#2	92.20(10)	O(3) - Co(2) - O(8)#4	151.82(8)		
O(6) - Co(1) - N(4)#2	89.88(10)	N(5) - Co(2) - O(8)#4	92.05(9)		
O(1)#1 - Co(1) - N(4)#2	92.18(10)	N(3) - Co(2) - O(8)#4	87.33(8)		
O(4) - Co(1) - N(6)#3	88.45(10)	O(7)#4 - Co(2) - O(8)#4	59.60(8)		
O(6) - Co(1) - N(6)#3	89.89(10)	C(1) - O(3) - Co(2)	135.96(19)		
O(1)#1 - Co(1) - N(6)#3	87.21(9)	C(19) - O(6) - Co(1)	144.89(19)		
N(4)#2 - Co(1) - N(6)#3	179.34(10)	C(19) - O(5) - Co(2)	147.1(2)		
O(4) - Co(1) - O(2)#1	93.63(9)	C(32) - O(8) - Co(2)#1	88.80(18)		
O(6) - Co(1) - O(2)#1	151.92(8)	C(32) - O(7) - Co(2)#1	91.64(17)		
O(1)#1 - Co(1) - O(2)#1	59.66(8)	C(14) - O(2) - Co(1)#4	88.26(19)		
N(4)#2 - Co(1) - O(2)#1	91.55(10)	C(1) - O(4) - Co(1)	147.4(2)		
N(6)#3 - Co(1) - O(2)#1	88.36(10)	C(14) - O(1) - Co(1)#4	92.04(17)		
O(5) - Co(2) - O(3)	118.49(9)	C(41) - N(3) - Co(2)	120.6(2)		
O(5) - Co(2) - N(5)	92.72(9)	C(37) - N(3) - Co(2)	121.9(2)		
O(3) - Co(2) - N(5)	88.01(9)	C(49) - N(5) - Co(2)	123.5(2)		
O(5) - Co(2) - N(3)	88.99(9)	C(53) - N(5) - Co(2)	121.5(2)		
O(3) - Co(2) - N(3)	91.73(9)	C(46) - N(4) - Co(1)#2	120.8(3)		
N(5) - Co(2) - N(3)	178.19(9)	C(47) - N(4) - Co(1)#2	124.6(2)		
O(5) - Co(2) - O(7)#4	149.14(9)	C(58) - N(6) - Co(1)#3	122.3(2)		
O(3) - Co(2) - O(7)#4	92.22(8)	C(59) - N(6) - Co(1)#3	120.9(2)		

#1 x, y+1 ,z; #2 -x+1, -y+1, -z; #3 -x, -y+1, -z+1;

#4 x, y-1, z; #5 -x+2, -y+2, -z+1; #6 -x-1, -y, -z.

MOF 3					
Co(1) - O(7)#1	2.014(3)	Co(2) - O(4)#2	2.180(2)		
Co(1) - O(5)#2	2.028(3)	Co(2) - O(3)#2	2.220(3)		
Co(1) - N(5)	2.126(4)	O(3) - Co(2)#4	2.220(3)		
Co(1) - N(4)	2.146(3)	O(4) - Co(2)#4	2.180(2)		
Co(1) - O(1)	2.207(3)	O(5) - Co(1)#4	2.028(3)		
Co(1) - O(2)	2.212(3)	O(6) - Co(2)#5	1.994(3)		
Co(2) - O(6)#3	1.994(3)	O(7) - Co(1)#6	2.014(3)		
Co(2) - O(8)	2.035(3)	N(3) - Co(2)#4	2.127(4)		
Co(2) - N(3)#2	2.127(4)	N(6) - Co(2)#2	2.139(4)		
Co(2) - N(6)#4	2.139(4)				
O(7)#1 - Co(1) - O(5)#2	113.51(12)	N(3)#2 - Co(2) - O(4)#2	87.30(12)		
O(7)#1 - Co(1) - N(5)	89.60(13)	N(6)#4 - Co(2) - O(4)#2	87.66(12)		
O(5)#2 - Co(1) - N(5)	92.77(13)	O(6)#3 - Co(2) - O(3)#2	95.78(12)		
O(7)#1 - Co(1) - N(4)	92.80(13)	O(8) - Co(2) - O(3)#2	151.84(10)		
O(5)#2 - Co(1) - N(4)	85.62(13)	N(3)#2 - Co(2) - O(3)#2	87.06(14)		
N(5) - Co(1) - N(4)	177.49(13)	N(6)#4 - Co(2) - O(3)#2	90.91(13)		
O(7)#1 - Co(1) - O(1)	152.27(11)	O(4)#2 - Co(2) - O(3)#2	59.36(9)		
O(5)#2 - Co(1) - O(1)	94.20(11)	C(14) - O(1) - Co(1)	90.0(2)		
N(5) - Co(1) - O(1)	87.84(12)	C(14) - O(2) - Co(1)	90.0(2)		
N(4) - Co(1) - O(1)	90.36(12)	C(29) - O(3) - Co(2)#4	89.6(2)		
O(7)#1 - Co(1) - O(2)	93.07(11)	C(29) - O(4) - Co(2)#4	91.0(2)		
O(5)#2 - Co(1) - O(2)	153.24(11)	C(36) - O(5) - Co(1)#4	131.5(3)		
N(5) - Co(1) - O(2)	90.36(12)	C(36) - O(6) - Co(2)#5	158.0(3)		
N(4) - Co(1) - O(2)	90.22(13)	C(1) - O(7) - Co(1)#6	158.3(3)		
O(1) - Co(1) - O(2)	59.36(10)	C(1) - O(8) - Co(2)	134.8(3)		
O(6)#3 - Co(2) - O(8)	112.30(12)	C(41) - N(3) - Co(2)#4	125.4(3)		
O(6)#3 - Co(2) - N(3)#2	94.48(14)	C(37) - N(3) - Co(2)#4	118.3(3)		
O(8) - Co(2) - N(3)#2	88.60(14)	C(47) - N(4) - Co(1)	121.2(3)		
O(6)#3 - Co(2) - N(6)#4	90.36(15)	C(48) - N(4) - Co(1)	121.9(3)		
O(8) - Co(2) - N(6)#4	91.01(13)	C(50) - N(5) - Co(1)	124.2(3)		
N(3)#2 - Co(2) - N(6)#4	174.92(13)	C(54) - N(5) - Co(1)	119.9(3)		
O(6)#3 - Co(2) - O(4)#2	155.01(12)	C(61) - N(6) - Co(2)#2	119.9(3)		
O(8) - Co(2) - O(4)#2	92.65(10)	C(60) - N(6) - Co(2)#2	124.0(4)		

Symmetry transformations used to generate equivalent atoms:

#1 x ,y, z+1; #2 -x, y-1/2, -z; #3 -x, y-1/2, -z-1;

#4 -x, y+1/2, -z; #5 -x, y+1/2, -z-1; #6 x, y, z-1.



4. Additional structure figures and characterizations of Co MOFs.



Figure S1. (a) The asymmetric unit of MOF 1 (hydrogen atoms and guest molecules are omitted for clarity). (b) The coordination mode of $pmbcd^{4-}$ in MOF 1. (c) TGA curves for MOF 1.





Figure S2. (a) The asymmetric unit of MOF **2** (hydrogen atoms are omitted for clarity). (b) The coordination mode of pmbcd⁴⁻ in MOF **2**. (c) TGA curves for MOF **2**. (d) Recycling tests for the conversion of aromatics into ketones with MOF **2**. (e) Comparison of the PXRD patterns of MOF **2** before and after recycling catalysis.





Figure S3. (a) The asymmetric unit of MOF **3**. (hydrogen atoms and free water and DMF molecules are omitted for clarity) (b) The coordination mode of pmbcd⁴⁻ in MOF **3**. (c) TGA curves for MOF **3**. (d) Recycling tests for the conversion of aromatics into ketones with MOF **3**. (e) Comparison of the PXRD patterns of MOF **3** before and after recycling catalysis.

5. Spectra of ¹H NMR and ¹³C NMR of compounds obtained in this study.























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