Supporting Information for

Chiral binary metal-organic frameworks for asymmetric sequential reactions

Zijian Li, Yan Liu,* Qingchun Xia, and Yong Cui*

School of Chemistry and Chemical Engineering and State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, China

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

Table of Content

1. Materials and general procedures.

All of the chemicals are commercial available, and used without further purification. Elemental analyses of C, N and H 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. CD spectra were recorded on a J-800 spectropolarimeter (Jasco, Japan). 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 DMAX2500 diffractometer using Cu Kα radiation. The calculated PXRD patterns were produced using the SHELXTL-XPOW program and single crystal reflection data. NMR experiments were carried out on a MERCURY plus 400 spectrometer operating at resonance frequencies of 400 M Hz. ICP-OES was performed on Optima 7300DV ICP-OES (Perkin Elmer Coporation, USA). Analytical high performance liquid chromatography (HPLC) was performed on a LC-2010HAT HPLC with UV detection at 220 nm or 250nm Analytical CHIRALCEL OD-H, AD-H column from Daicel was used. The N_2 adsorption isotherms were recorded at 273 K by using a micromeritics ASAP 2020 surface area and porosity analyzer. Before the adsorption measurement, the fresh crystals were subjected to Soxhlet extraction with chloroform for 12 h and were activated at room temperature under vacuum (< 10^{-3} torr) for 4 h.

X-ray Crystallography. Single-crystal XRD data for MOFs **1** and **2** was collected on a Bruker D8 VENTURE CMOS photon 100 diffractometer with helios mx multilayer monochromator Cu Kα radiation (λ = 1.54178 Å) at 100 K. The empirical absorption correction was applied by using the SADABS program (G. M. Sheldrick, SADABS, program for empirical absorption correction of area detector data; University of Göttingen, Göttingen, Germany, 1996). The structure was solved by direct methods with SHELXS-2014 and refined with SHELXL-2014[S1] using *OLEX2-1.2*[S2]. In the compounds, the all non-H atoms were subjected to anisotropic refinement by full-matri program. Contributions to scattering due to these highly disordered solvent molecules were removed using the *SQUEEZE* routine of *PLATON*[S3]; 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 distances and angles are presented in **Table S2** and **S3**.

2. Synthesis

2.1 Synthesis of $FeL^1(OAc)$, $VO(H_2L^2)$, MnL^1Cl

Fe**L**^{1}(OAc) was synthesized according to the published procedure (Yang, Z.; Zhu, C.; Li, Z.; Liu, Y.; Liu, G.; Cui, Y. *Chem. Commun.*, **2014,** *50*, 8775-8778).

VO(H_2**L**^{2}) was synthesized according to the published procedure (Xi, W.; Liu, Y.; Xia, Q.; Li, Z.; Cui, Y. *Chem. Eur. J.,* **2015**, *21*, 12581-12585).

Mn**L**^{1}Cl was synthesized according to the published procedure (S.-H. Cho, B. Ma, S. T. Nguyen, J. T. Hupp, T. E. Albrecht-Schmitt, *Chem. Comm.,* **2006**, 2563-2565).

2.2 Synthesis of 1, 1a and 2

Synthesis of 1. A mixture of $Cd(NO_3)_2 \cdot 6H_2O$ (21.2mg, 0.069 mmol), Fe$\mathbf{L^1}$(OAc) (28.1mg, 0.04 mmol), VO($H_2\mathbf{L^2}$) (23.5 mg, 0.04 mmol), DMF (4.3 mL), MeOH (2.85 mL) in a capped vial was heated at 80 °C for 24 h. Red block-like crystals were filtered, washed with MeOH and Et_2O, and dried at room temperature. Yield, 0.022 g, 41% based on $[Cd_2(Fe\mathbf{L^1})_2(VO\mathbf{L^2})_2]\bullet(DMF)_2(MeOH)_3(H_2O)_4$. Anal. Calcd for MOF-**1**: C, 57.87; H, 6.16; N, 6.52%. Found: C, 57.73; H, 6.56; N, 6.23%. ICP measurement indicated the ratio of Cd: Fe: V is 1:1:1. IR (KBr): 3435(br), 2932(s), 2869(w), 1599(vs), 1533(w), 1466(m), 1433(w), 1386 (s), 1332(m), 1310(w), 1200(w), 1029(w), 813(w), 727(w), 642(w) cm^{-1}.

Synthesis of 1a. To a suspension of activated **1** (0.05 mmol) in acetonitrile (4 mL) was added an acetonitrile solution (4 mL) of $(NH_4)_2Ce(NO_3)_6$ (0.066 g, 0.12 mmol) with stirring for 4 hours, and the resulting mixture was filtered, washed with acetonitrile (3×8 mL) and dried at 80 °C for 2 h to give compound **1a.**

Synthesis of 2. A mixture of $Cd(NO_3)_2 \cdot 6H_2O$ (17.3 mg, 0.056 mmol), Mn$\mathbf{L^1}$Cl (27 mg, 0.04 mmol), VO($H_2\mathbf{L^2}$) (11.7 mg, 0.02 mmol), DMF (1.1 mL), EtOH (6.5 mL) in a capped vial was heated at 80 °C for 24h. Green block-like crystals were filtered, washed with MeOH and Et_2O, and dried at room temperature. Yield, 0.020 g, 45% based on $[Cd_2(Mn\mathbf{L^1})_2(VO\mathbf{L^2})]\bullet(DMF)(EtOH)_2(H_2O)_3$. Anal. Calcd for MOF-**2**: C, 55.00; H, 5.84; N, 7.37%. Found: C, 55.31; H, 5.45; N, 7.28%. ICP measurement indicated the ratio of Cd: Mn: V is 2:2:1. IR (KBr): 3437(br), 3180(w), 3016(w), 2946(s), 2868(w), 1594(vs), 1560(w), 1437(w), 1381(vs), 1313(m), 1274(w), 1229(w), 1206(w), 1178(w), 1082(w), 1062(w), 976(m), 902(w), 818(m), 784(w), 728(m), 649(m), 571(m) cm^{-1}.

3. General procedure for asymmetric catalysis

3.1 Asymmetric one-pot sequential reaction: alkene epoxidation/epoxide aminolysis

To a suspension of **1a** (13.4 mg, 5 mol%) in dry chloroform (2 mL), alkene (0.1 mmol) and iodosylbenzene (24 mg, 0.11 mmol) were added, and the reaction was carried out at -20 °C for 48 h. After that, solvent was changed to CH_2Cl_2, aniline (0.11 mmol) was added, and then the reaction mixture reacted for 4 h at 0 °C. After that, the mixture was centrifuged at 9000 rpm for 5 min. The concentrate was analyzed by ^{1}H NMR to give the conversion and by HPLC to give the *ee* value.

3.2 Asymmetric one-pot sequential reaction: alkene epoxidation/epoxide hydrolysis

To a suspension of **2** (9.0 mg, 4 mol%) in dry CH_2Cl_2 (2 mL), alkene (0.1 mmol) and 2-(tert-butylsulfonyl)iodosylbenzene (2 mg, 0.006 mmol) were added. The same amount of oxidant was added 18 more times at 15 min intervals. Then the reaction was carried out for further 4 h at 0 °C. After that, the solvent was changed to *tert*-butyl methyl ether with addition of H_2O (18 μL, 1 mmol) and the solution was directly put in a Schlenk tube under CO_2 atomsphere. The reaction was carried out at 0 °C for 72 h. After that, the mixture was centrifuged at 9000 rpm for 5 min, and the supernatant was concentrated under vacuum. The concentrate was analyzed by ^{1}H NMR to calculate the conversion and by HPLC to give the *ee* value.

3.3 The recycled asymmetric one-pot sequential reaction: alkene epoxidation/ epoxide aminolysis

To a suspension of **1a** (13.4 mg, 5 mol%) in dry chloroform (2 mL), alkene (0.1 mmol) and iodosylbenzene (24 mg, 0.11 mmol) was added, then the reaction was carried out at -20 ^{o}C for 48 h. After that, solvent was changed to CH_2Cl_2, aniline (0.11 mmol) was added, and then the reaction mixture reacted for 4 h at 0 ^{o}C. After that, the mixture was centrifuged at 9000 rpm for 5 min. The concentrate was analyzed by ^{1}H NMR to give the conversion and by HPLC to give the *ee* value. The precipitate was washed with CH_2Cl_2 for three times, sonicated for 10 min, and dried for 1 hour under vacuum. Then the obtained solid can be used for the next run.

3.4 The recycled asymmetric one-pot sequential reaction: alkene epoxidation/ epoxide hydrolysis

To a suspension of **2** (9.0 mg, 4 mol%) in dry CH_2Cl_2 (2 mL), alkene (0.1 mmol) and 2-(tert-butylsulfonyl)iodosylbenzene (2 mg, 0.006 mmol) were added. The same amount of oxidant was added 18 more times at 15 min intervals. Then the reaction was carried out for further 4 h at 0 ^{o}C. After that, the solvent was changed to *tert*-butyl methyl ether with addition of H_2O (18 μL, 1 mmol) and the solution was directly put in a Schlenk tube under CO_2 atomsphere. The reaction was carried out at 0 ^{o}C for 72 h. After that, the mixture was centrifuged at 9000 rpm for 5 min, and the supernatant was concentrated under vacuum. The concentrate was analyzed by ^{1}H NMR to calculate the conversion and by HPLC to give the *ee* value. Then the obtained solid can be used for the next run.

4. Table S1. Crystal data and structure refinement for MOFs

Identification code	MOF-**1**	MOF-**2**
Empirical formula	$C_{136}H_{152}Cd_2Fe_2N_{12}O_{18.48}V_2$	$C_{106}H_{118}Cd_2Mn_2N_{12}O_{18.71}V$
Formula weight	2688.79	2245.06
Temperature	109.96 K	100.01 K
Wavelength	1.54178	1.54178
Crystal system, space group	Orthorhombic, $P222_1$	Orthorhombic, $P2_12_12$
Unit cell dimensions	a = 24.1093(6) Å α= 90^{o} b = 34.2098(8) Å β = 90^{o} c = 23.7848(7) Å γ = 90^{o}	a = 34.7570(10) Å α= 90^{o} b = 17.7053(5) Å β = 90^{o} c = 23.9558(6) Å γ = 90^{o}
Volume	19617.1(9) A^3	14742.0(7) $Å^3$
Z, Calculated density	4, 0.910 Mg/m^3	4, 1.012 Mg/m^3
Absorption coefficient	3.997 mm^{-1}	4.560 mm^{-1}
F(000)	5575	4627
Crystal size	0.08 × 0.06 × 0.05 mm	0.06 × 0.05 × 0.03 mm

Theta range for data collection	2.242 to 50.742 deg.	2.240 to 47.355 deg.
Limiting indices	-24<=h<=24 -34<=k<=34 -23<=l<=23	-20<=h<=33 -16<=k<=16 -22<=l<=22
Reflections collected / unique	72053 / 20479 [R(int) = 0.0684]	53769 / 13279 [R(int) = 0.0570]
Completeness	99.0 %	99.5 %
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	20479 / 2989 / 1456	13279 / 2496 / 1262
Goodness-of-fit on F^2	1.021	1.045
Final R indices [I>2sigma(I)]	R_1 = 0.0786, wR_2 = 0.2095	R_1 = 0.0639, wR_2 = 0.1649
R indices (all data)	R_1 = 0.1096, wR_2 = 0.2361	R_1 = 0.0715, wR_2 = 0.1712
Absolute structure parameter	0.157(5)	0.249(5)
Largest diff. peak and hole	1.261 and -0.856 e.A^{-3}	0.891 and -0.873 e.A^{-3}

5. Table S2. Selected bond lengths [Å] and angles [º] for MOF 1

Cd(1)-O(18)#1	2.248(8)
Cd(1)-O(17)	2.292(11)
Cd(1)-N(3)	2.340(5)
Cd(1)-O(12)#2	2.328(9)
Cd(1)-O(13)#2	2.379(10)
Cd(1)-N(4)#3	2.287(11)
Cd(2)-O(11)#4	2.210(11)
Cd(2)-O(20)	2.347(10)
Cd(2)-O(19)	2.371(12)
Cd(2)-O(10)	2.277(13)
Cd(2)-N(7)	2.308(7)
Cd(2)-N(8)#3	2.318(19)
Fe(1)-O(3)	1.752(4)
Fe(1)-O(1)	1.907(12)
Fe(1)-O(2)	1.937(11)
Fe(1)-N(2)	2.086(13)
Fe(1)-N(1)	2.103(14)
Fe(2)-O(4)	1.892(12)
Fe(2)-O(5)	1.956(13)
Fe(2)-N(5)	2.045(16)
Fe(2)-O(6)	1.756(4)
Fe(2)-N(6)	2.032(17)
V(2)-O(15)	1.897(10)
V(2)-N(12)	2.165(14)
V(2)-O(14)	1.984(11)

V(2)-N(11)	2.118(12)
V(2)-O(16)	1.668(7)
V(1)-O(9)	1.142(17)
V(1)-O(7)	2.22(2)
V(1)-O(8)	2.19(2)
V(1)-N(9)	2.15(2)
V(1)-N(10)	2.12(2)

O(18)#1-Cd(1)-O(17)	129.9(4)
O(18)#1-Cd(1)-N(3)	88.7(3)
O(18)#1-Cd(1)-O(12)#2	139.9(4)
O(18)#1-Cd(1)-O(13)#2	85.0(4)
O(18)#1-Cd(1)-N(4)#3	92(3)
O(17)-Cd(1)-N(3)	90.1(3)
O(17)-Cd(1)-O(12)#2	90.2(4)
O(17)-Cd(1)-O(13)#2	144.8(4)
N(3)-Cd(1)-O(13)#2	95.5(4)
O(12)#2-Cd(1)-N(3)	92.5(3)
O(12)#2-Cd(1)-O(13)#2	55.0(4)
N(4)#3-Cd(1)-O(17)	85(4)
N(4)#3-Cd(1)-N(3)	174(4)
N(4)#3-Cd(1)-O(12)#2	91(3)
N(4)#3-Cd(1)-O(13)#2	91(4)
O(11)#4-Cd(2)-O(20)	142.3(5)
O(11)#4-Cd(2)-O(19)	88.1(4)
O(11)#4-Cd(2)-O(10)	130.6(4)
O(11)#4-Cd(2)-N(7)	90.3(4)
O(11)#4-Cd(2)-N(8)#3	88(4)
O(20)-Cd(2)-O(19)	54.4(4)
O(10)-Cd(2)-O(20)	86.9(4)
O(10)-Cd(2)-O(19)	141.3(4)
O(10)-Cd(2)-N(7)	87.5(4)
O(10)-Cd(2)-N(8)#3	88(4)
N(7)-Cd(2)-O(20)	95.6(4)
N(7)-Cd(2)-O(19)	94.3(4)
N(7)-Cd(2)-N(8)#3	172(5)
N(8)#3-Cd(2)-O(20)	90(4)
N(8)#3-Cd(2)-O(19)	93(5)
O(3)-Fe(1)-O(1)	103.7(6)
O(3)-Fe(1)-O(2)	112.3(6)
O(3)-Fe(1)-N(2)	101.2(6)
O(3)-Fe(1)-N(1)	107.2(6)
O(1)-Fe(1)-O(2)	93.1(5)
O(1)-Fe(1)-N(2)	152.8(7)

O(1)-Fe(1)-N(1)	85.0(6)
O(2)-Fe(1)-N(2)	87.3(5)
O(2)-Fe(1)-N(1)	139.7(7)
N(2)-Fe(1)-N(1)	77.4(5)
O(4)-Fe(2)-O(5)	95.1(6)
O(4)-Fe(2)-N(5)	84.2(6)
O(4)-Fe(2)-N(6)	141.1(7)
O(5)-Fe(2)-N(5)	150.8(7)
O(5)-Fe(2)-N(6)	85.4(6)
O(6)-Fe(2)-O(4)	110.6(7)
O(6)-Fe(2)-O(5)	104.0(6)
O(6)-Fe(2)-N(5)	103.6(7)
O(6)-Fe(2)-N(6)	107.0(7)
N(6)-Fe(2)-N(5)	77.4(6)
O(15)-V(2)-N(12)	84.4(5)
O(15)-V(2)-O(14)	89.4(5)
O(15)-V(2)-N(11)	145.6(6)
O(14)-V(2)-N(12)	135.2(5)
O(14)-V(2)-N(11)	85.7(5)
N(11)-V(2)-N(12)	75.6(5)
O(16)-V(2)-O(15)	109.7(9)
O(16)-V(2)-N(12)	103.1(4)
O(16)-V(2)-O(14)	120.7(5)
O(16)-V(2)-N(11)	102.1(9)
O(9)-V(1)-O(7)	123.9(11)
O(9)-V(1)-O(8)	122(3)
O(9)-V(1)-N(9)	112(3)
O(9)-V(1)-N(10)	110.9(12)
O(8)-V(1)-O(7)	72.9(7)
N(9)-V(1)-O(7)	82.2(9)
N(9)-V(1)-O(8)	125.3(12)
N(10)-V(1)-O(7)	125.1(13)
N(10)-V(1)-O(8)	82.4(8)
N(10)-V(1)-N(9)	73.4(8)

Symmetry transformations used to generate equivalent atoms:

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

#5 -x+1, y, -z+5/2 #6 -x+1, y, -z+3/2 #7 x, y, z+1 #8 x+1, y, z

6. Table S3. Selected bond lengths [Å] and angles [°] for MOF 2

Cd(1)-N(3)	2.343(10)
Cd(1)-O(9)	2.355(10)
Cd(1)-N(4)#1	2.244(9)

Cd(1)-O(12)	2.482(10)
Cd(1)-O(11)	2.469(11)
Cd(1)-O(10)#2	2.396(10)
Cd(1)-O(10)	2.408(9)
Cd(2)-O(7)	2.419(8)
Cd(2)-O(7)#3	2.369(9)
Cd(2)-O(8)	2.367(9)
Cd(2)-N(8)	2.238(5)
Cd(2)-O(14)	2.479(10)
Cd(2)-N(7)#1	2.340(10)
Cd(2)-O(16)	2.490(11)
Mn(1)-O(2)	1.935(10)
Mn(1)-O(1)	1.905(10)
Mn(1)-N(2)	2.041(13)
Mn(1)-N(1)	2.026(12)
Mn(1)-O(17)	1.665(14)
Mn(2)-O(3)	1.919(11)
Mn(2)-O(4)	1.945(11)
Mn(2)-N(6)	2.086(13)
Mn(2)-N(5)	2.006(13)
Mn(2)-O(18)	1.625(16)

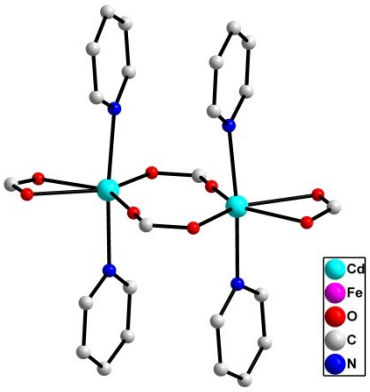
N(3)-Cd(1)-O(9)	88.6(3)
N(3)-Cd(1)-O(12)	91.3(4)
N(3)-Cd(1)-O(11)	97.7(4)
N(3)-Cd(1)-O(10)	93.0(3)
N(3)-Cd(1)-O(10)#2	89.5(4)
O(9)-Cd(1)-O(12)	133.3(4)
O(9)-Cd(1)-O(11)	82.5(3)
O(9)-Cd(1)-O(10)#2	129.4(3)
O(9)-Cd(1)-O(10)	54.8(3)
N(4)#1-Cd(1)-N(3)	173(3)
N(4)#1-Cd(1)-O(9)	98(3)
N(4)#1-Cd(1)-O(12)	83(3)
N(4)#1-Cd(1)-O(11)	82(3)
N(4)#1-Cd(1)-O(10)	92(3)
N(4)#1-Cd(1)-O(10)#2	87(3)
O(11)-Cd(1)-O(12)	51.3(4)
O(10)#2-Cd(1)-O(12)	97.2(4)
O(10)-Cd(1)-O(12)	170.9(4)
O(10)-Cd(1)-O(11)	135.6(3)
O(10)#2-Cd(1)-O(11)	147.6(3)
O(10)#2-Cd(1)-O(10)	74.9(3)
O(7)#3-Cd(2)-O(7)	75.0(3)

O(7)-Cd(2)-O(14)	170.6(3)
O(7)#3-Cd(2)-O(14)	96.8(3)
O(7)-Cd(2)-O(16)	135.4(3)
O(7)#3-Cd(2)-O(16)	146.8(3)
O(8)-Cd(2)-O(7)#3	129.8(3)
O(8)-Cd(2)-O(7)	55.0(3)
O(8)-Cd(2)-O(14)	133.4(3)
O(8)-Cd(2)-O(16)	82.3(3)
N(8)-Cd(2)-O(7)#3	88.5(3)
N(8)-Cd(2)-O(7)	93.5(3)
N(8)-Cd(2)-O(8)	91.4(3)
N(8)-Cd(2)-O(14)	90.9(3)
N(8)-Cd(2)-N(7)#1	173.1(3)
N(8)-Cd(2)-O(16)	100.2(4)
O(14)-Cd(2)-O(16)	51.6(4)
N(7)#1-Cd(2)-O(7)	90.3(3)
N(7)#1-Cd(2)-O(7)#3	86.9(3)
N(7)#1-Cd(2)-O(8)	95.5(3)
N(7)#1-Cd(2)-O(14)	84.6(4)
N(7)#1-Cd(2)-O(16)	81.0(4)
O(2)-Mn(1)-N(2)	87.0(5)
O(2)-Mn(1)-N(1)	150.6(5)
O(1)-Mn(1)-O(2)	87.3(4)
O(1)-Mn(1)-N(2)	140.7(5)
O(1)-Mn(1)-N(1)	87.0(5)
N(1)-Mn(1)-N(2)	79.5(5)
O(17)-Mn(1)-O(2)	103.7(5)
O(17)-Mn(1)-O(1)	109.4(6)
O(17)-Mn(1)-N(2)	109.7(6)
O(17)-Mn(1)-N(1)	105.4(6)
O(3)-Mn(2)-O(4)	88.8(5)
O(3)-Mn(2)-N(6)	141.6(5)
O(3)-Mn(2)-N(5)	87.2(5)
O(4)-Mn(2)-N(6)	85.9(5)
O(4)-Mn(2)-N(5)	150.1(6)
N(5)-Mn(2)-N(6)	79.1(5)
O(18)-Mn(2)-O(3)	105.9(6)
O(18)-Mn(2)-O(4)	104.3(6)
O(18)-Mn(2)-N(6)	112.3(7)
O(18)-Mn(2)-N(5)	105.3(7)

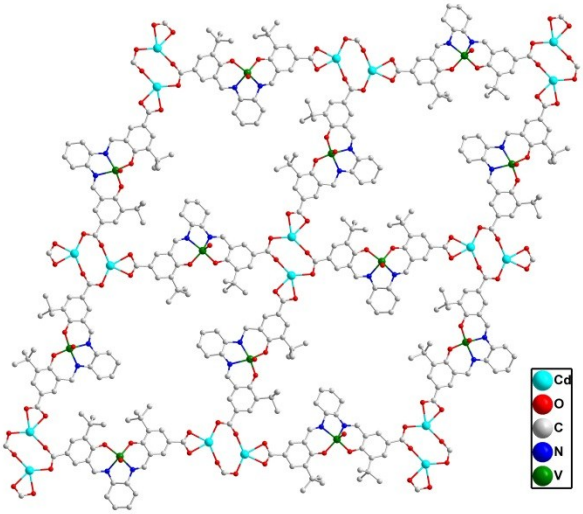
Symmetry transformations used to generate equivalent atoms:
#1 x,y,z+1 #2 -x+1,-y+1,z #3 -x,-y+1,z #4 x,y,z-1

7. Figures S1~S6. Additional X-ray crystallographic structures

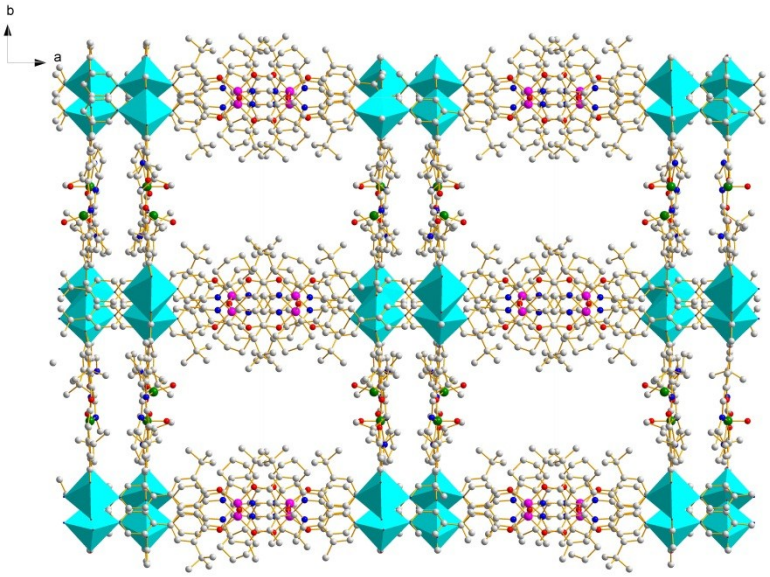
7.1 Figure S1. The Cd ions dimers in 1



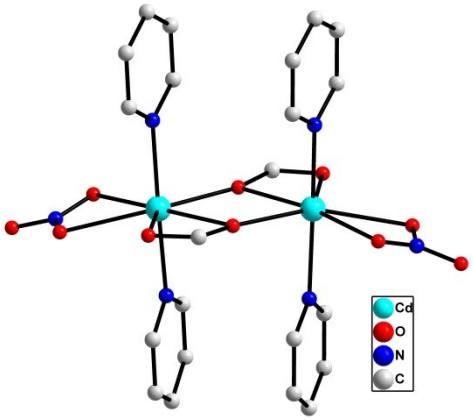
7.2 Figure S2. The 2D layered structure formed by Cd ions and VOL^2 in 1.



7.3 Figure S3. View of the 3D pillared-layer structure of 1 along the *c*-axis (Cd ions are shown in polyhedron)

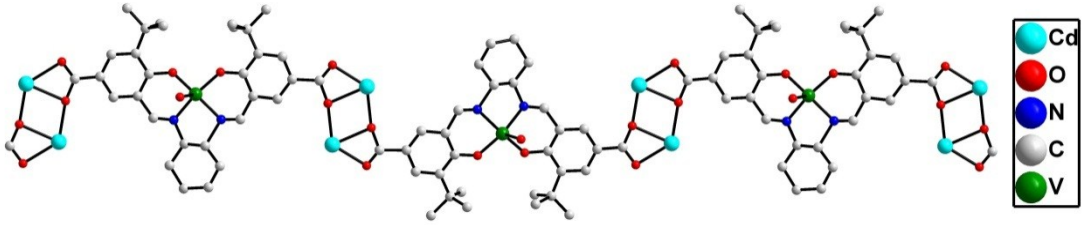


7.4 Figure S4. The Cd ions dimer in 2

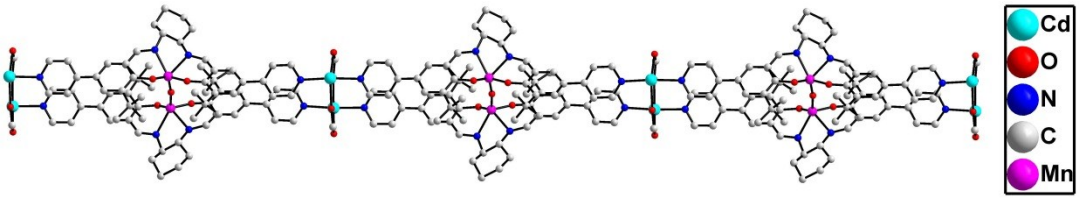


7.5 Figure S5. The 1D chain built by Cd ions and VOL^2 units (a), Cd ions and MnL^1 units (b) in 2

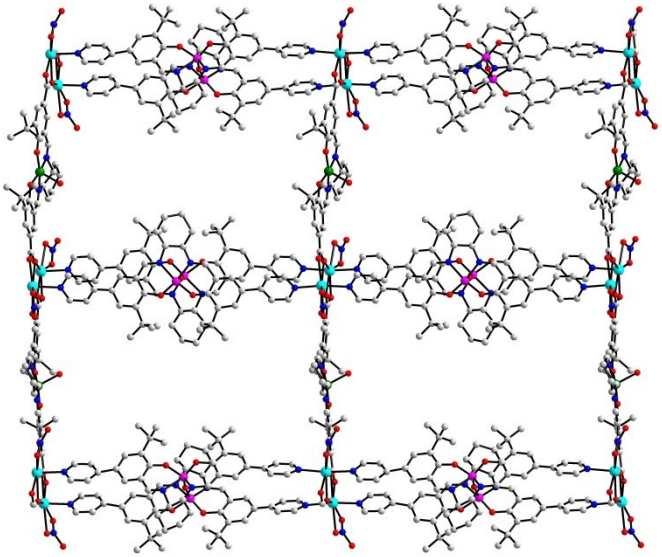
(a)



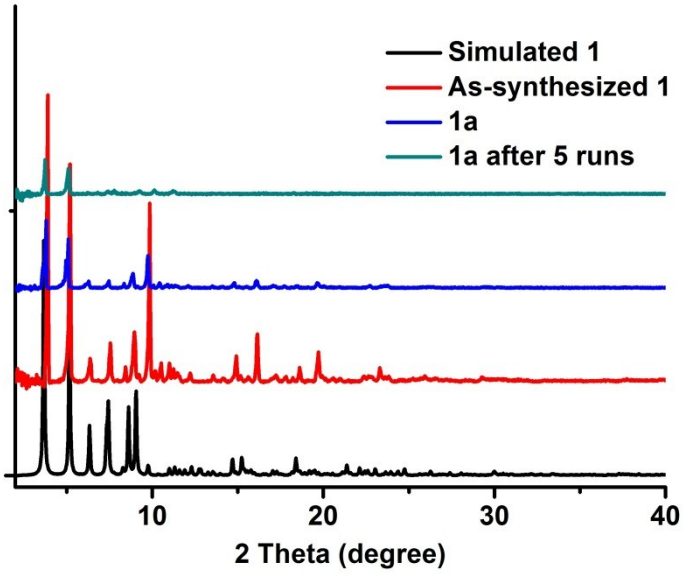
(b)

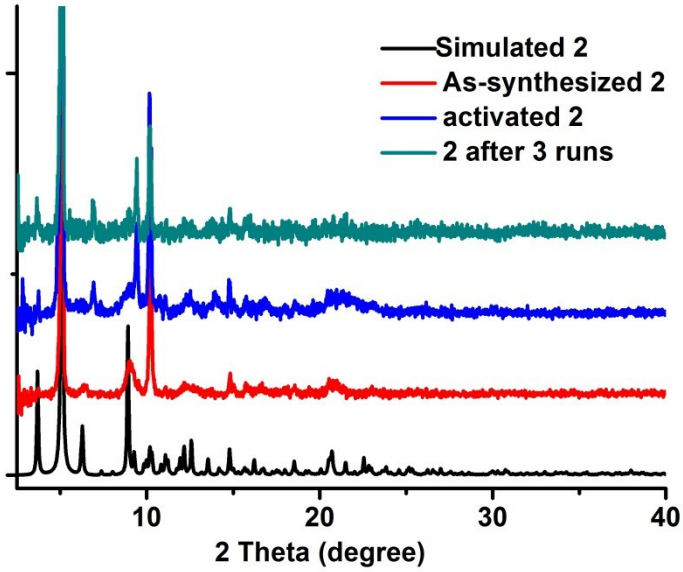


7.6 Figure S6. View of one independent chiral network of 2

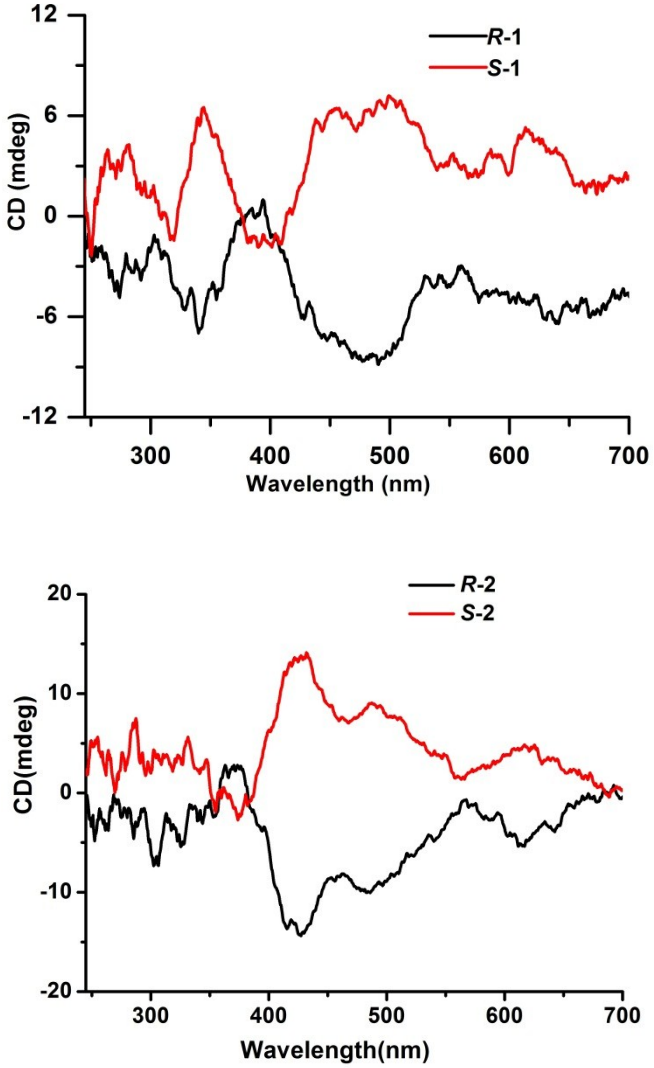


8. Figure S7. PXRD patterns

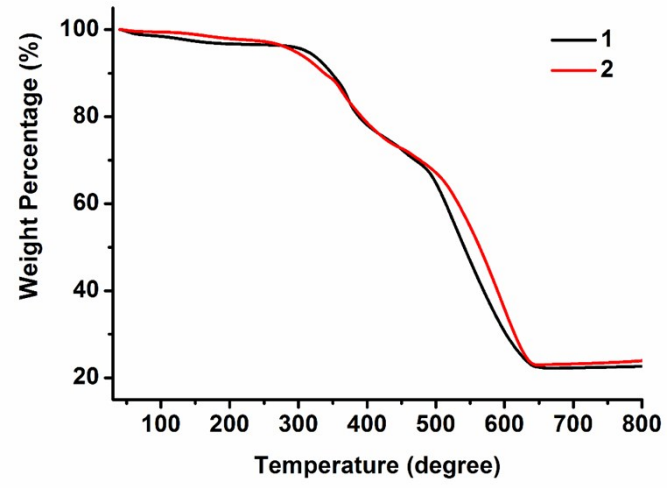




9. Figure S8. Solid-state CD spectra

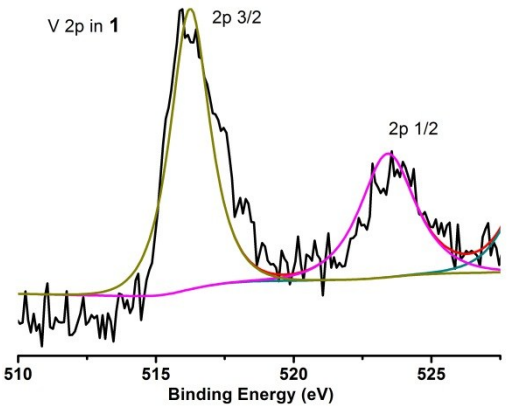


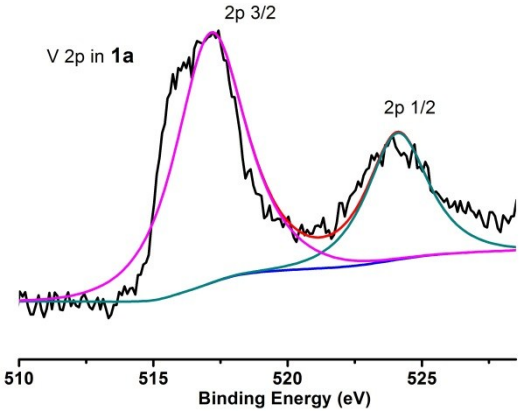
10. Figure S9. TGA curves

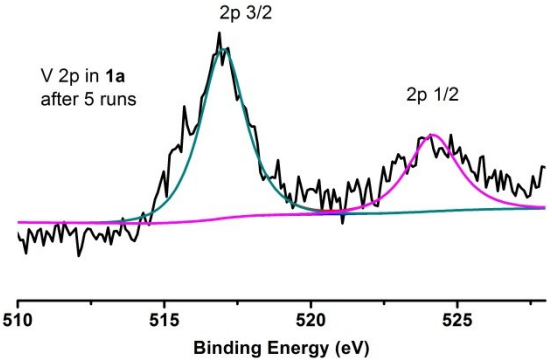


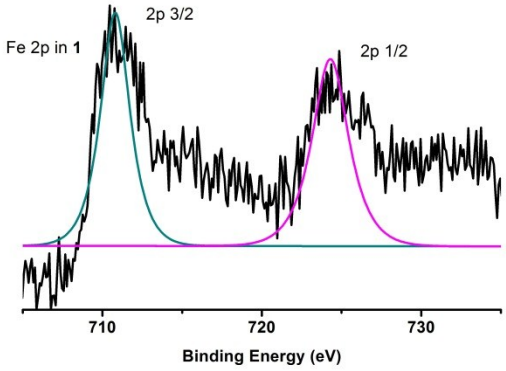
11. Figure S10. XPS spectra

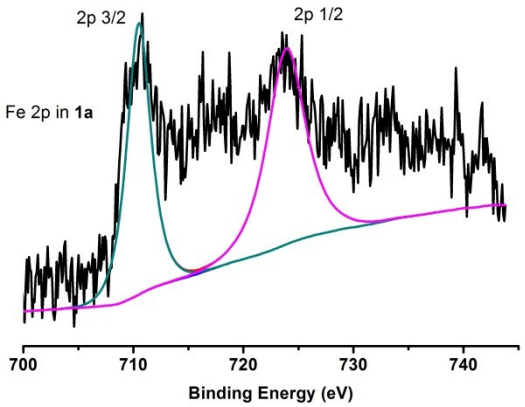
11.1. XPS spectra of MOF 1 and MOF 1a

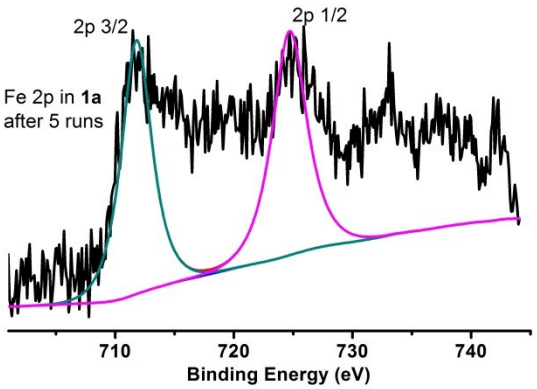




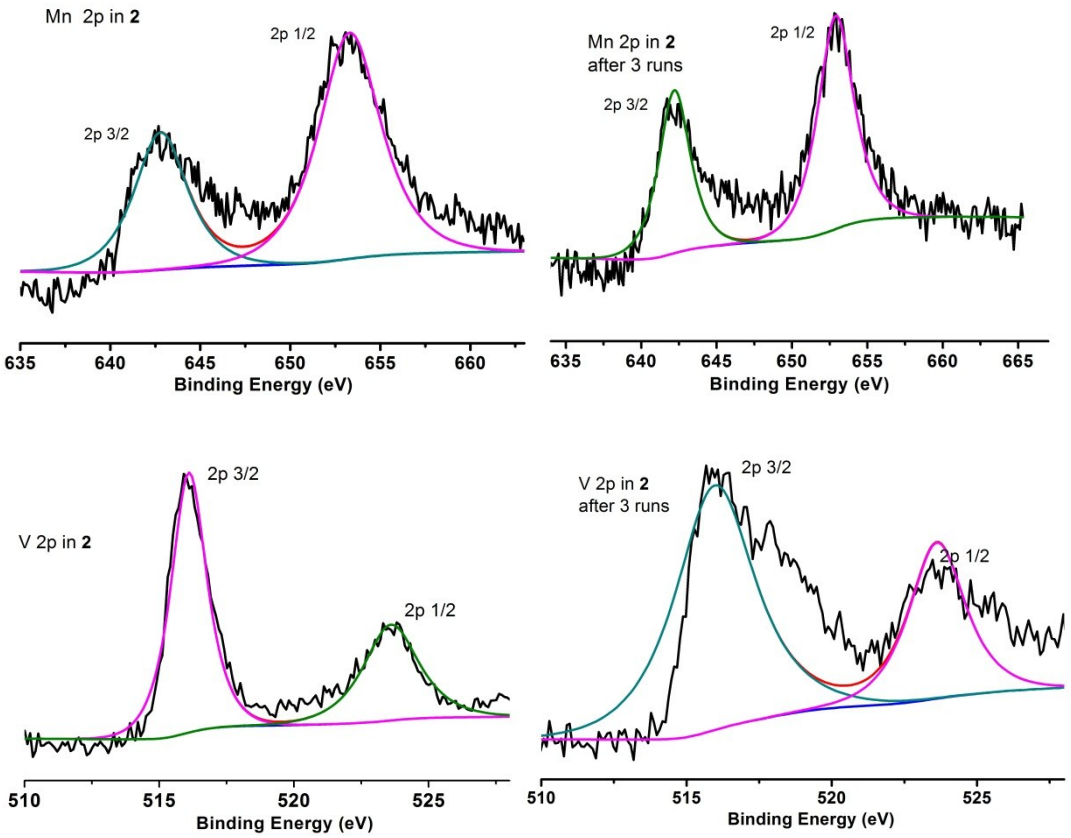




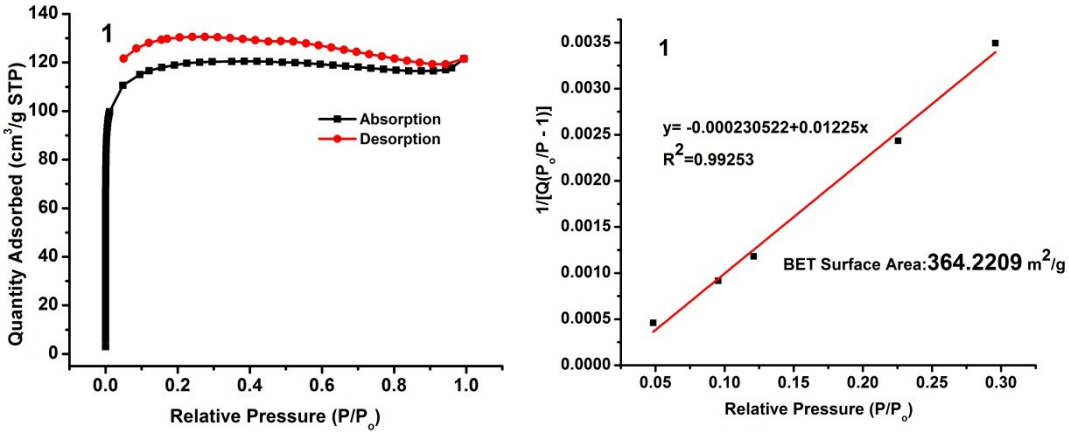


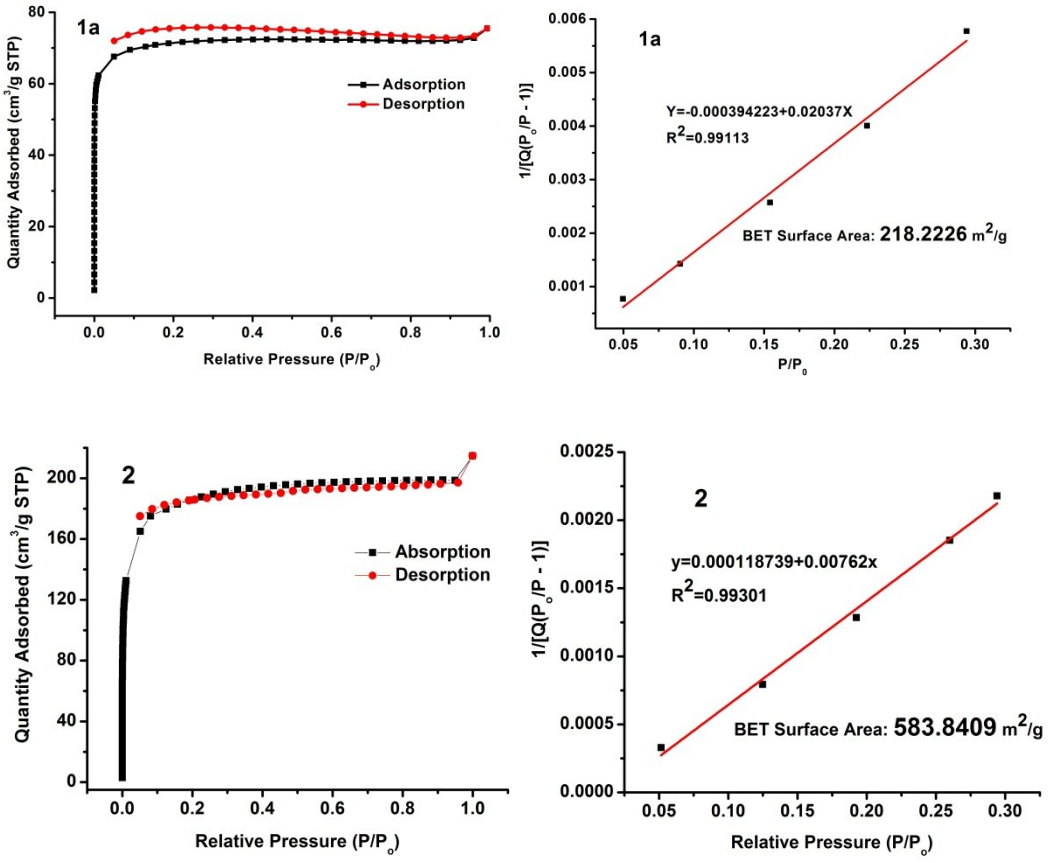


11.2 XPS spectra of MOF 2



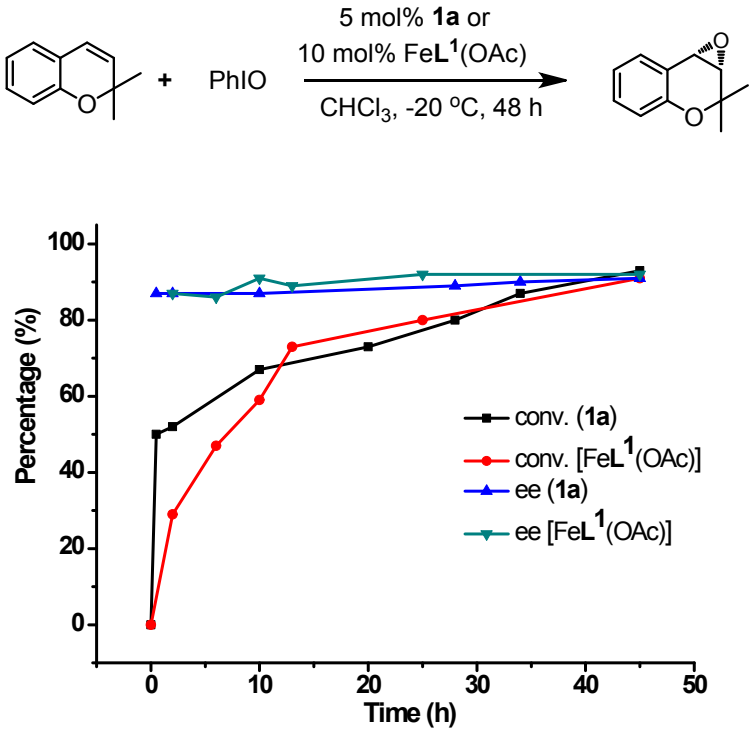
12. Figure S11. N_2 sorption isotherms and BET Surface Area plots





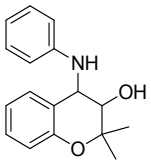
13.

13. Figure S12. Kinetic curves of MOF 1a and the homogenuous FeL[1](OAc) catalyzed epoxidation reaction

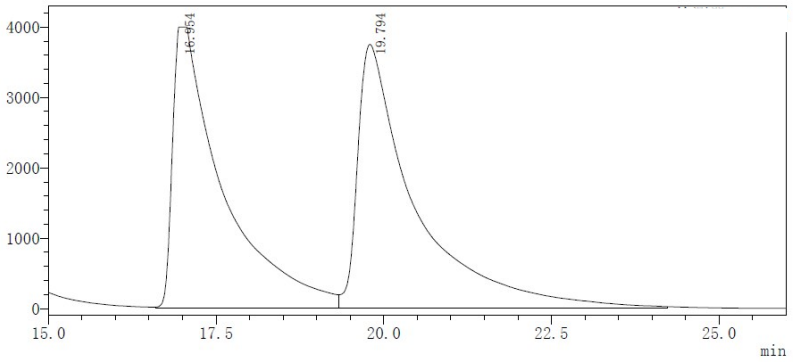


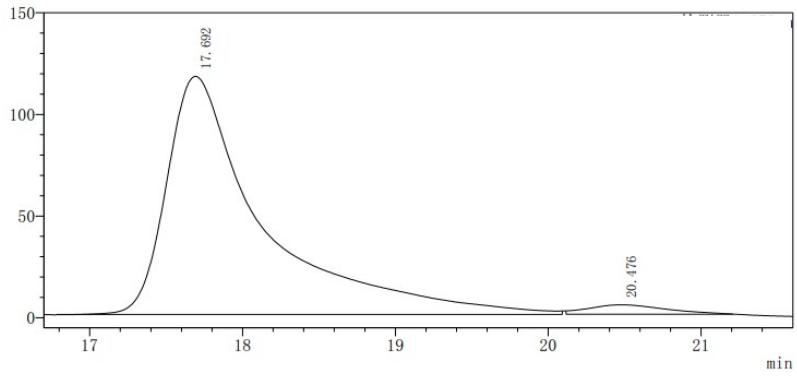
14. HPLC and NMR of the catalysis result[4]

14.1 Alkene epoxidation/epoxide aminolysis catalyzed by MOF 1a

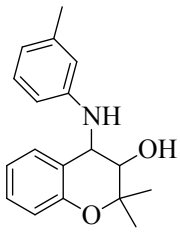


2,2-dimethyl-4-(phenylamino)chroman-3-ol: Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 95/5, 1.0 mL/min, 250 nm), t $_{major}$ = 17.69 min, t $_{minor}$ = 20.48 min; ee=94%.

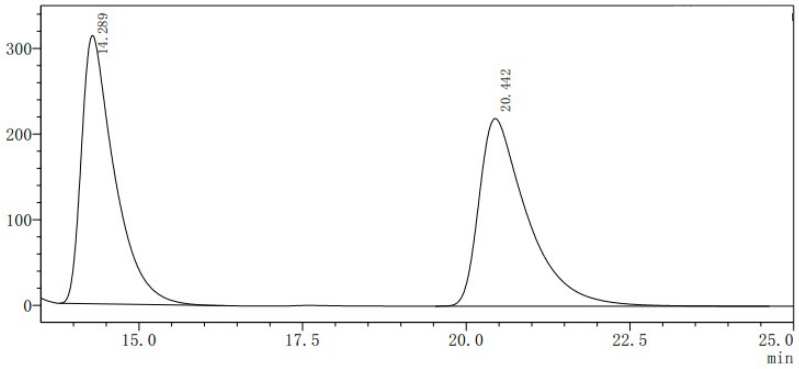


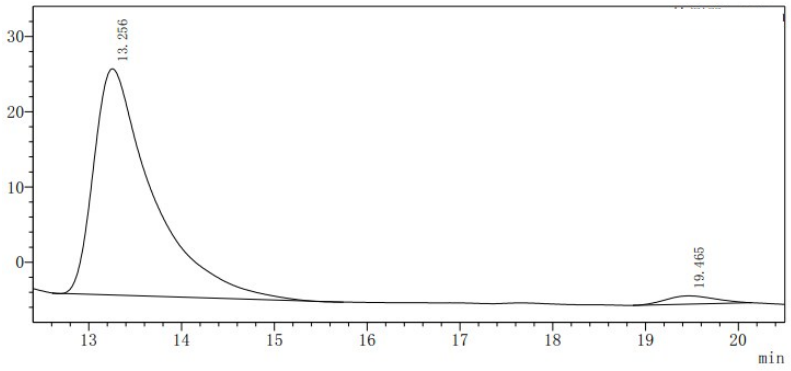


Serial Number	Retention Time [min]	Area	Area %
1	17.692	5126274	96.878
2	20.476	165179	3.122

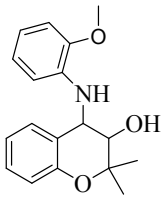


4-(m-toluidino)-2,2-dimethylchroman-3-ol: Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 95/5, 1.0 mL/min, 250 nm), t_{major} = 13.26 min, t_{minor} = 19.47 min; ee=94%.

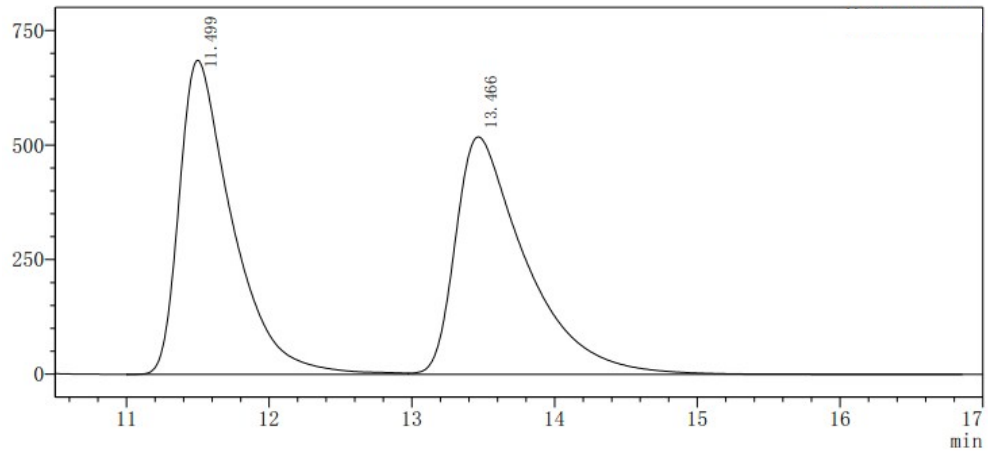


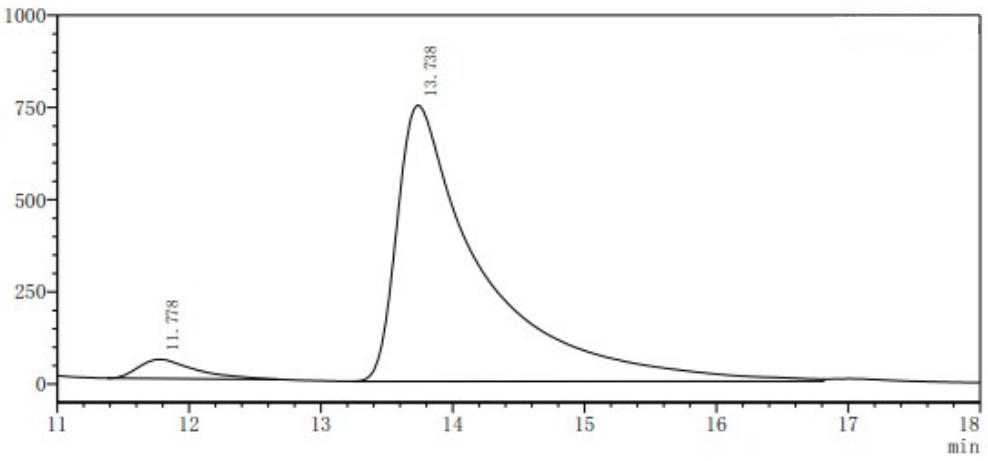


Serial Number	Retention Time [min]	Area	Area %
1	13.256	1325322	97.060
2	19.465	40149	2.940

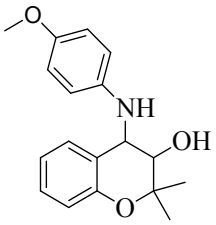


4-(2-methoxyphenylamino)-2,2-dimethylchroman-3-ol: Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 95/5, 1.0 mL/min, 250 nm), t_{minor} = 11.78 min, t_{major} =13.74 min,; ee=91%.

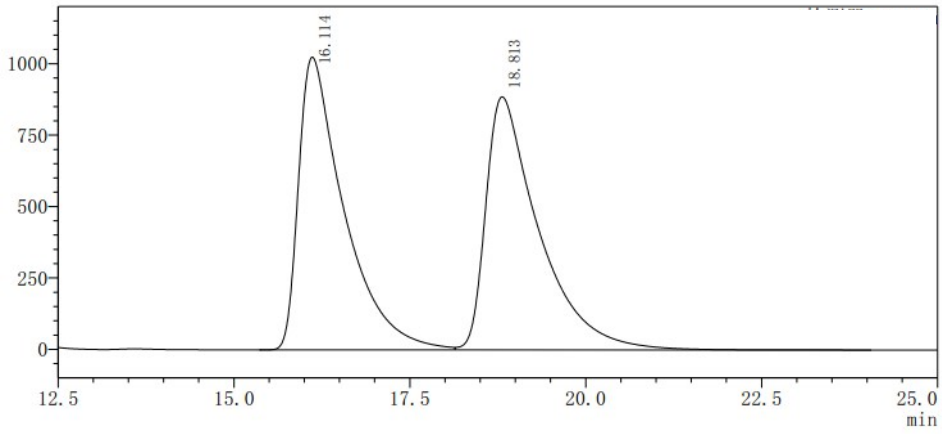


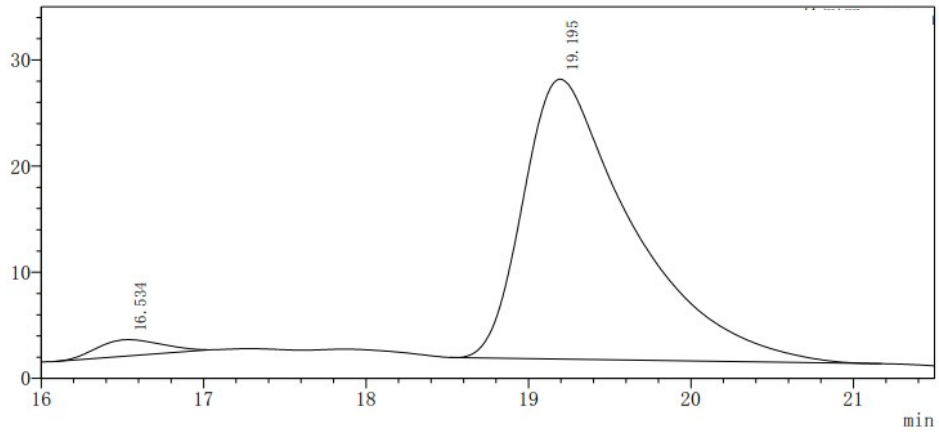


Serial Number	Retention Time [min]	Area	Area %
1	11.778	1547902	4.366
2	13.738	33906800	95.634

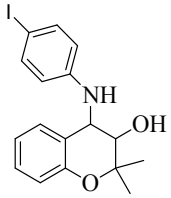


4-(4-methoxyphenylamino)-2,2-dimethylchroman-3-ol: Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 90/10, 1.0 mL/min, 250 nm), t $_{minor}$ = 16.53 min, t $_{major}$ =19.20 min; ee=93%.

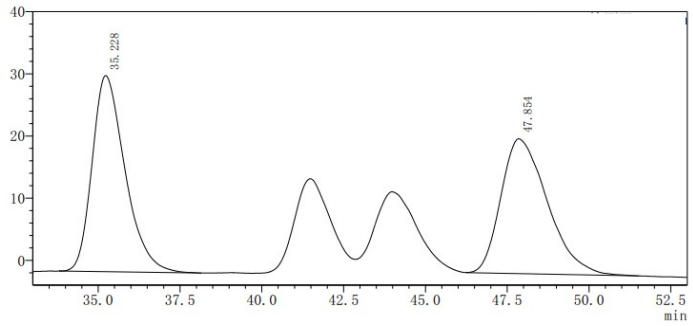


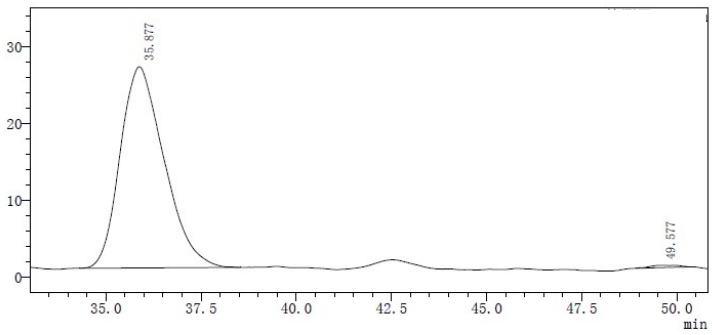


Serial Number	Retention Time [min]	Area	Area %
1	16.534	42425	3.324
2	19.195	1234025	96.676

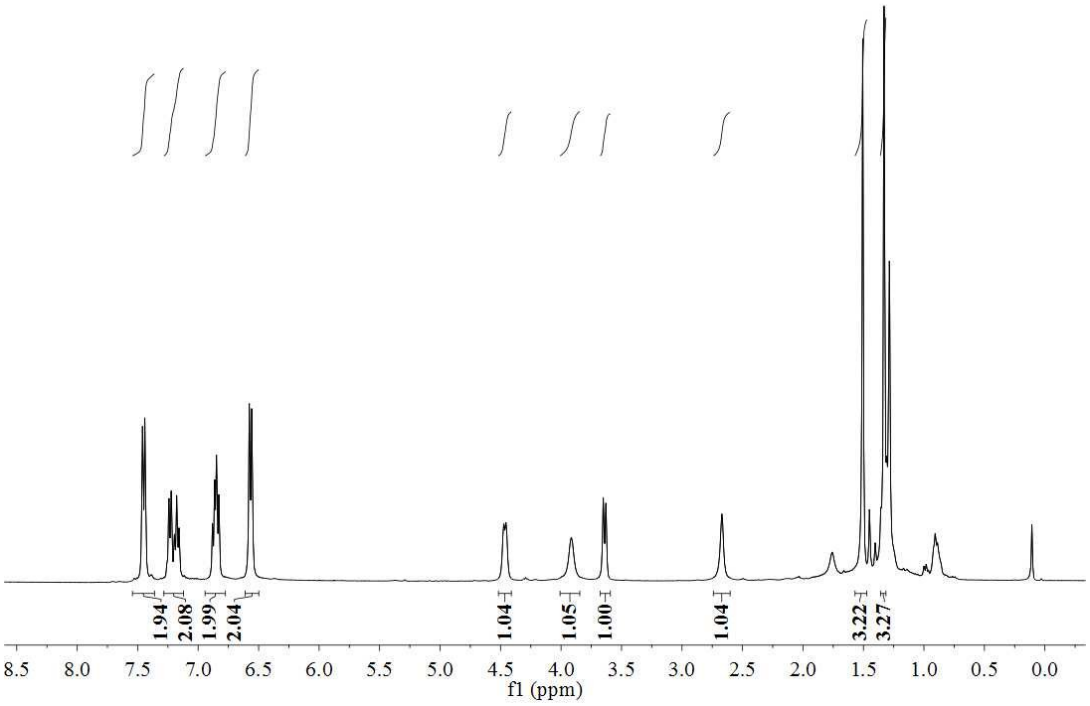


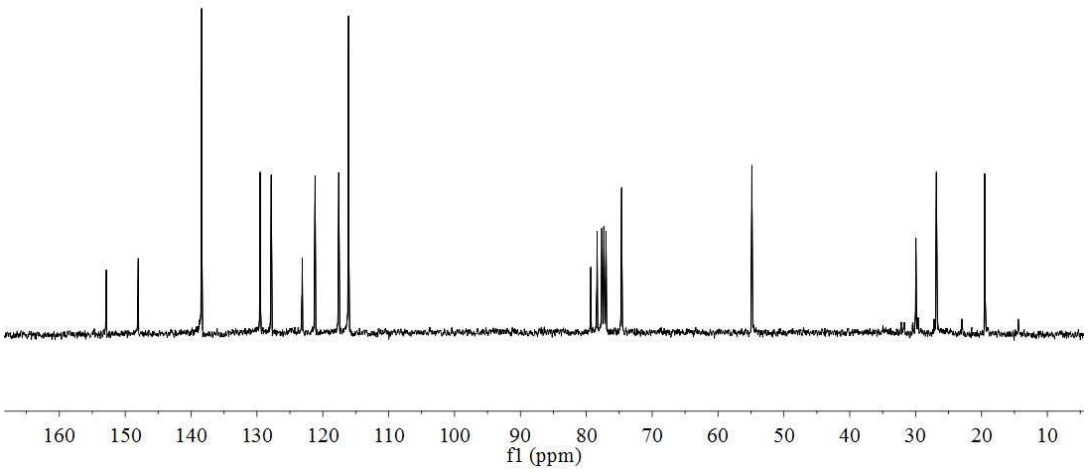
4-(4-iodophenylamino)-2,2-dimethylchroman-3-ol: Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 98/2, 1.0 mL/min, 250 nm), t $_{major}$ = 35.88 min, t $_{minor}$ = 49.58 min; ee=99%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.43 (d, *J* = 14.8 Hz, 2H), 7.28–7.12 (m, 2H), 6.86 (dd, *J* = 13.6, 7.6 Hz, 2H), 6.57 (d, *J* = 8.0 Hz, 2H), 4.46 (d, *J* = 7.4 Hz, 1H), 3.91 (s, 1H), 3.64 (d, *J* = 8.7 Hz, 1H), 2.67 (s, 1H), 1.51 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 152.86, 148.01, 138.39, 129.51, 127.82, 123.12, 121.18, 117.57, 115.79, 79.31, 78.36, 74.44, 54.87, 29.96, 26.85, 19.51. ESI-MS m/z: 418.0 (Calcd m/z 418.03 for $[M+Na]^+$).

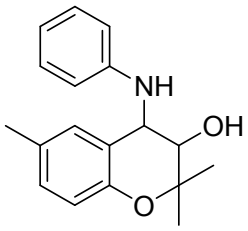




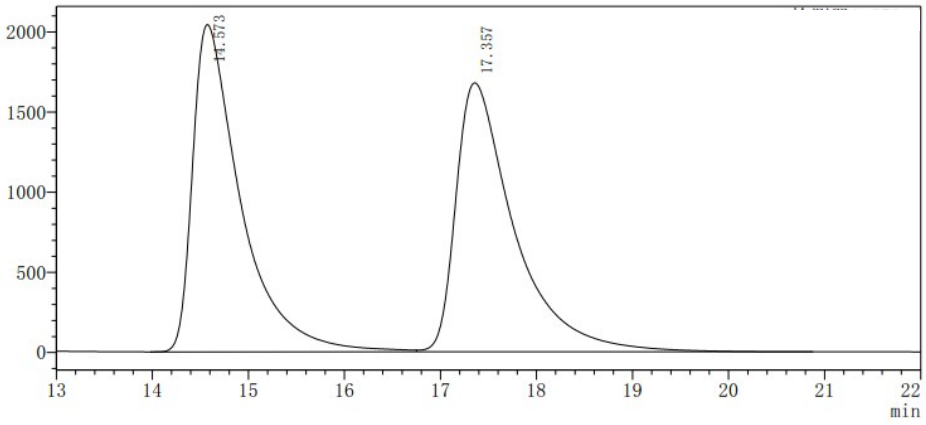
Serial Number	Retention Time [min]	Area	Area %
1	35.877	2100606	99.290
2	49.577	15020	0.710

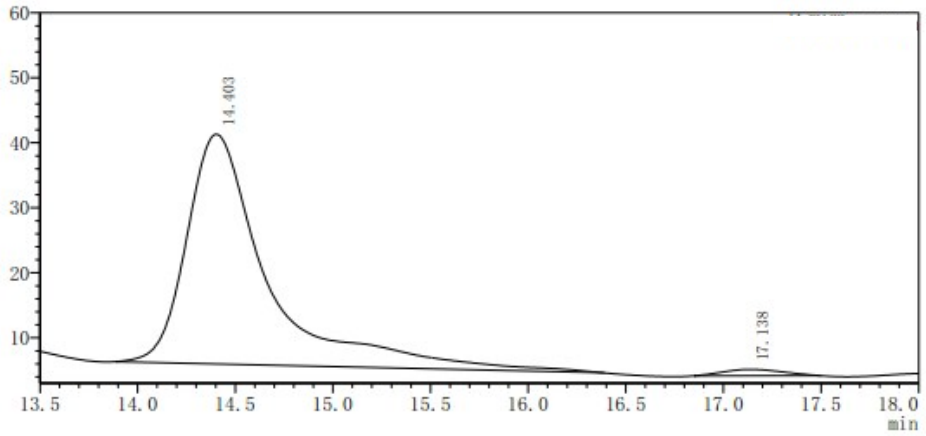

1.94
2.08
1.99
2.04
1.04
1.05
1.00
1.04
3.22
3.27
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

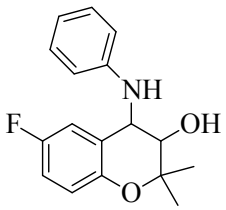


2,2,6-trimethyl-4-(phenylamino)chroman-3-ol: Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 95/5, 1.0 mL/min, 250 nm), t_{major} = 14.40 min, t_{minor} = 17.14 min; ee=96%.

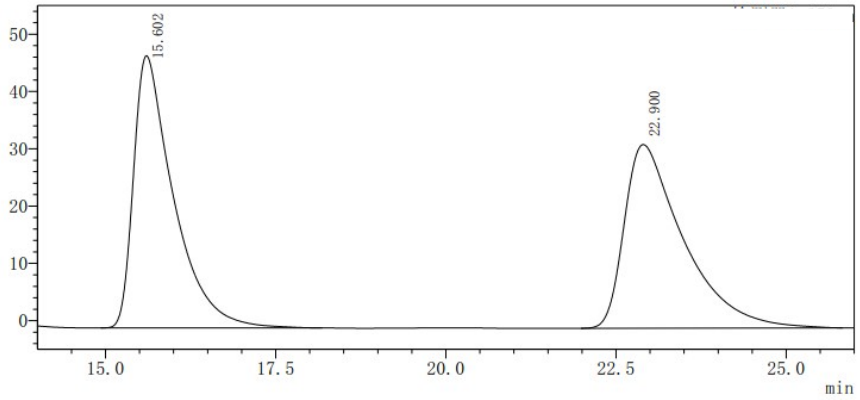


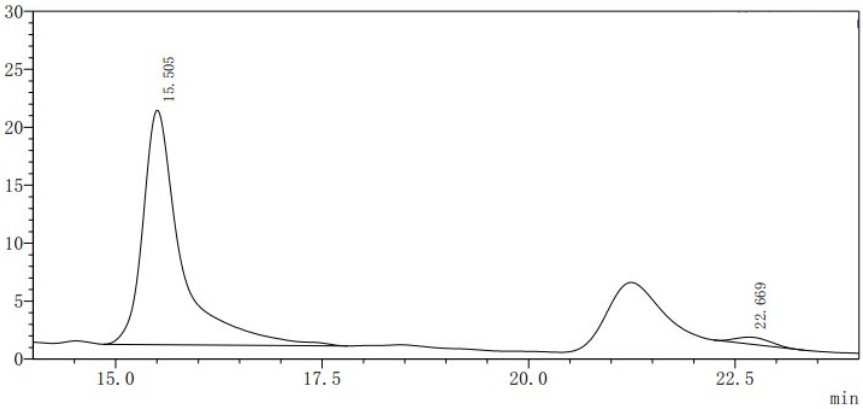


Serial Number	Retention Time [min]	Area	Area %
1	14.403	1019113	98.007
2	17.138	20727	1.993

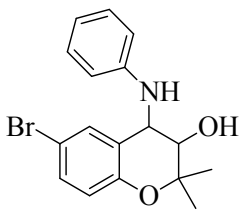


6-fluoro-2,2-dimethyl-4-(phenylamino)chroman-3-ol: Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 95/5, 1.0 mL/min, 250 nm), t_{major} = 15.51min, t_{minor} = 22.67 min; ee=95%.

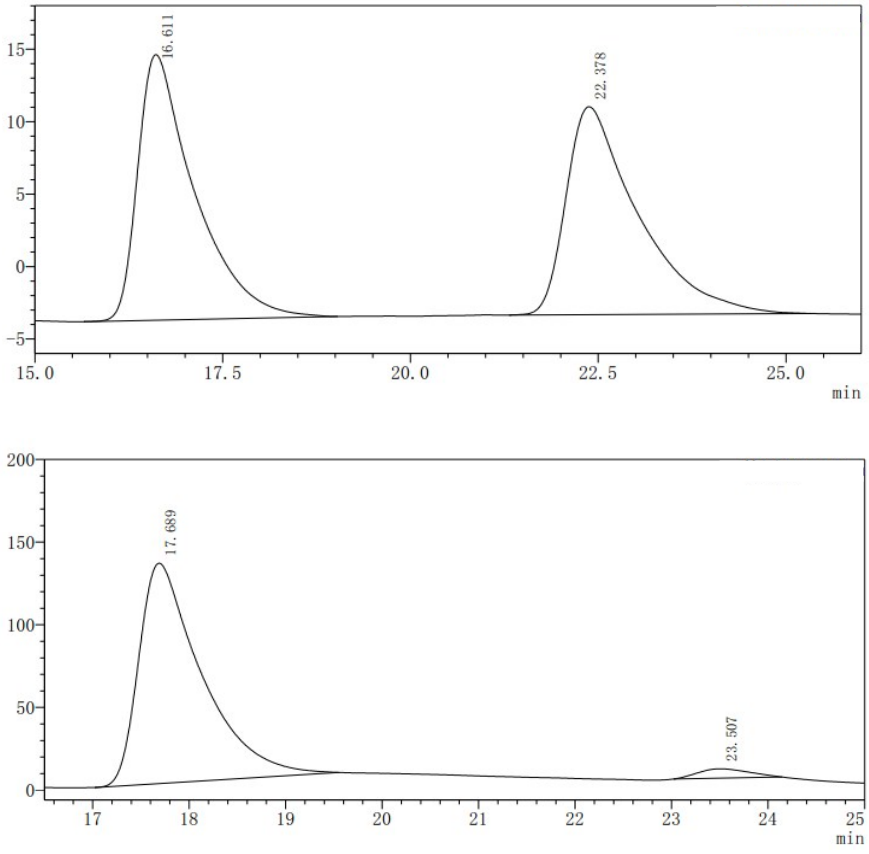




Serial Number	Retention Time [min]	Area	Area %
1	15.505	653486	97.376
2	22.669	17607	2.624

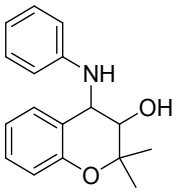


6-bromo-2,2-dimethyl-4-(phenylamino)chroman-3-ol: Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 95/5, 1.0 mL/min, 250 nm), t_{major} = 17.69 min, t_{minor} = 23.51 min; ee=93%.



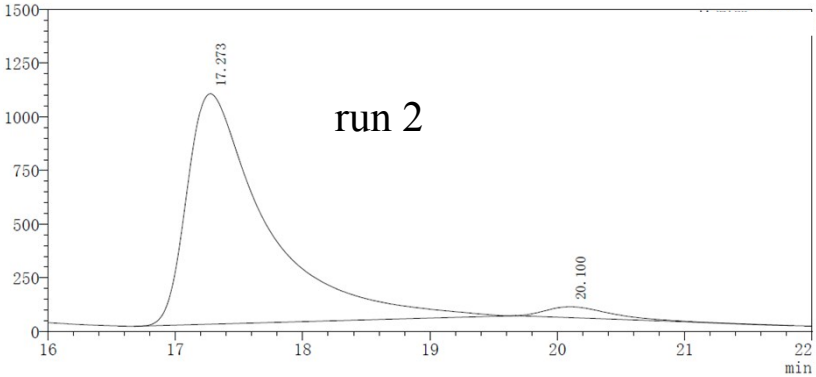
Serial Number	Retention Time [min]	Area	Area %
1	17.689	6020799	96.718
2	23.507	204335	3.282

14.2 HPLC for the recycled experiment of the alkene epoxidation/epoxide aminolysis catalyzed by MOF 1a

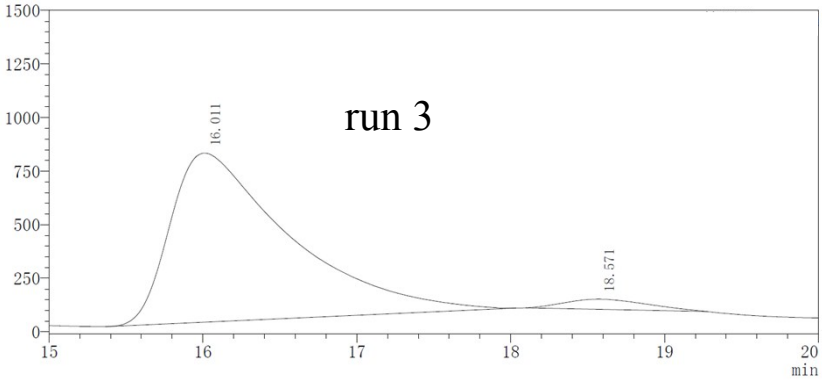


2,2-dimethyl-4-(phenylamino)chroman-3-ol

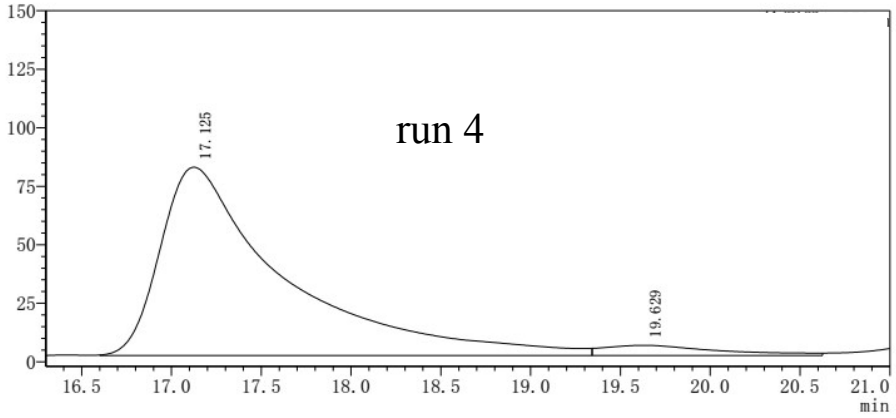
Serial Number	Retention Time [min]	Area	Area %
1	17.692	5126274	96.878
2	20.476	165179	3.122



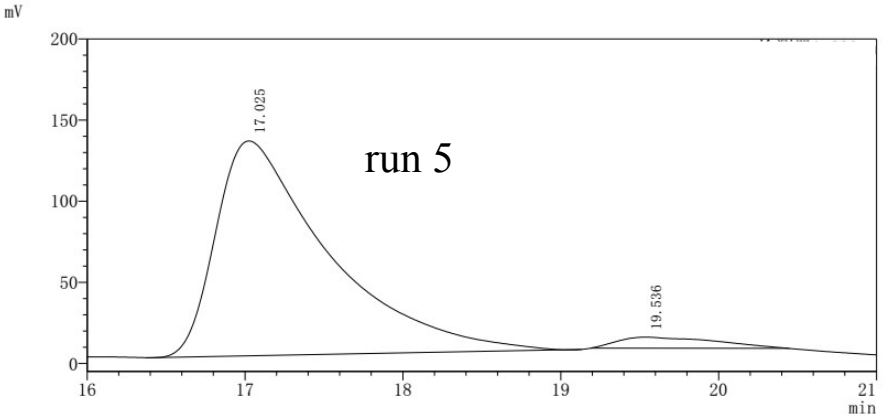
Serial Number	Retention Time [min]	Area	Area %
1	17.273	47164660	96.341
2	20.100	1791507	3.659



Serial Number	Retention Time [min]	Area	Area %
1	16.011	42673030	95.991
2	18.571	1782265	4.009

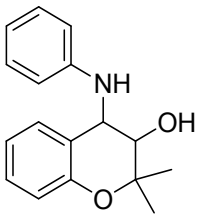


Serial Number	Retention Time [min]	Area	Area %
1	17.125	3866865	95.259
2	19.629	192456	4.741

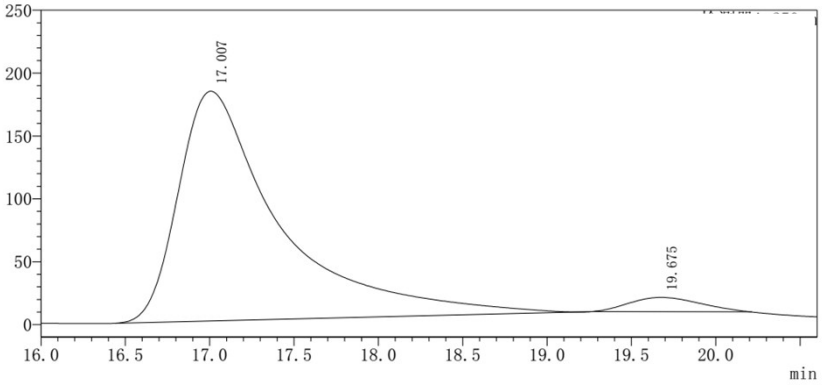


Serial Number	Retention Time [min]	Area	Area %
1	17.025	6549950	95.710
2	19.536	293620	4.290

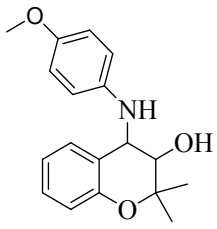
14.3 HPLC for the the alkene epoxidation/epoxide aminolysis catalyzed by MOF 1



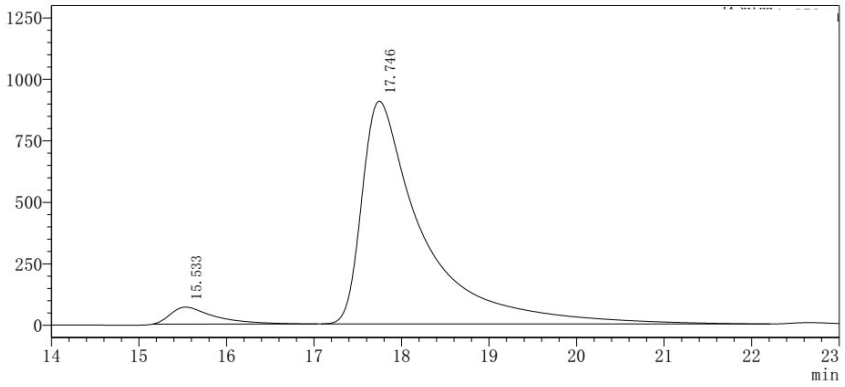
2,2-dimethyl-4-(phenylamino)chroman-3-ol: Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 95/5, 1.0 mL/min, 250 nm), t_{minor} = 17.00 min, t_{major} =19.68 min; ee=92%.



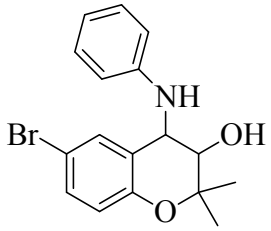
Serial Number	Retention Time [min]	Area	Area %
1	17.007	7641920	95.816
2	19.675	333719	4.184



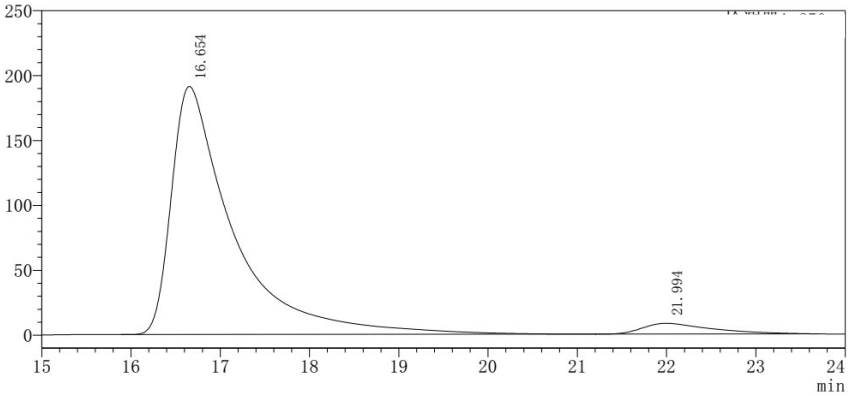
4-(4-methoxyphenylamino)-2,2-dimethylchroman-3-ol: Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 90/10, 1.0 mL/min, 250 nm), t_{minor} = 15.53 min, t_{major} =17.75 min; ee=90%.



Serial Number	Retention Time [min]	Area	Area %
1	15.533	2444930	5.221
2	17.746	44388087	94.779

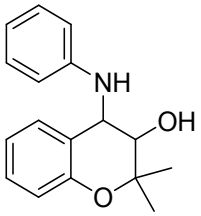


6-bromo-2,2-dimethyl-4-(phenylamino)chroman-3-ol: Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 95/5, 1.0 mL/min, 250 nm), t_{major} = 16.65 min, t_{minor} = 21.99 min; ee=91%.

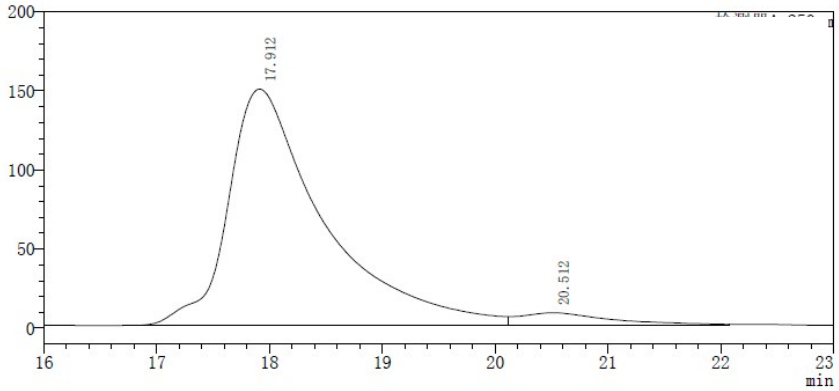


Serial Number	Retention Time [min]	Area	Area %
1	16.654	9221538	95.389
2	21.994	445729	4.611

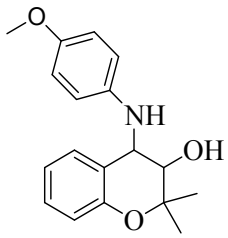
14.4 HPLC for the the alkene epoxidation/epoxide aminolysis catalyzed by the homogenuous 1 eq:1 eq mixture of Fe(salen) and V^{V}O(salen)



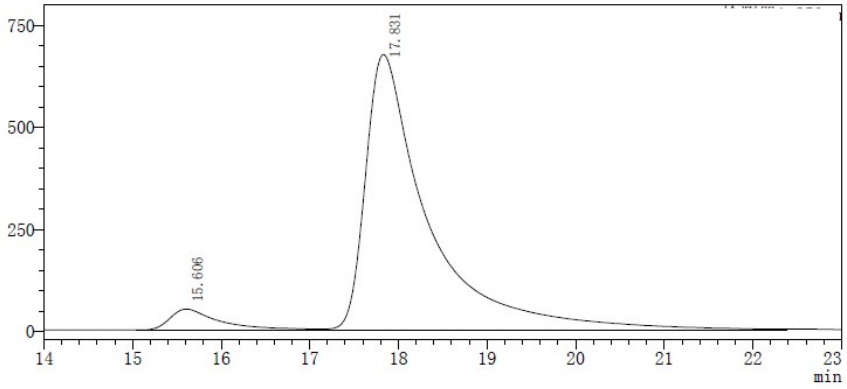
2,2-dimethyl-4-(phenylamino)chroman-3-ol: Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 95/5, 1.0 mL/min, 250 nm), t $_{major}$ = 17.91 min, t $_{minor}$ = 20.51 min; ee=90%.



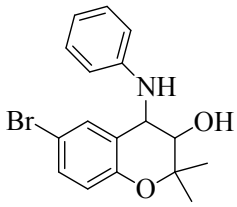
Serial Number	Retention Time [min]	Area	Area %
1	17.912	8842529	95.009
2	20.512	464557	4.991



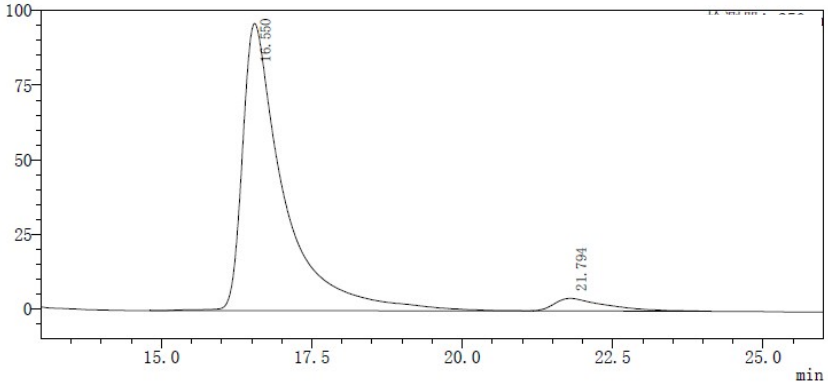
4-(4-methoxyphenylamino)-2,2-dimethylchroman-3-ol: Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 90/10, 1.0 mL/min, 250 nm), t $_{minor}$ = 15.61 min, t $_{major}$ =17.83 min; ee=89%.



Serial Number	Retention Time [min]	Area	Area %
1	15.606	2043212	5.735
2	17.831	33582458	94.265

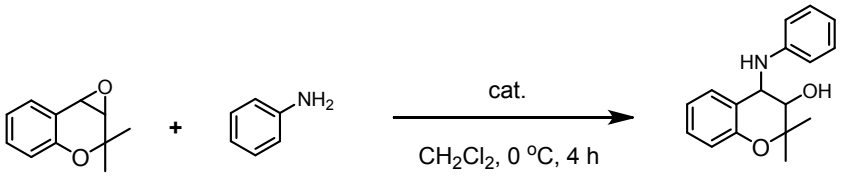


6-bromo-2,2-dimethyl-4-(phenylamino)chroman-3-ol: Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 95/5, 1.0 mL/min, 250 nm), t_{major} = 16.55 min, t_{minor} = 21.79 min; ee=90%.

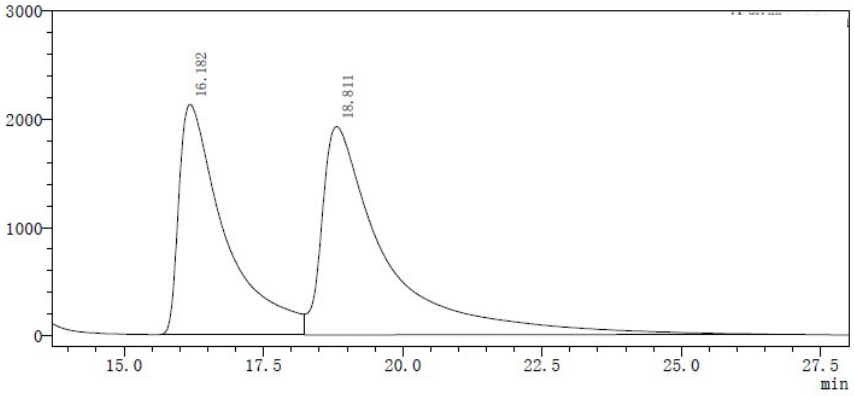


Serial Number	Retention Time [min]	Area	Area %
1	16.550	4611851	94.939
2	21.794	245865	5.061

14.5 HPLC for the epoxide aminolysis catalyzed by the homogenuous Fe(salen)



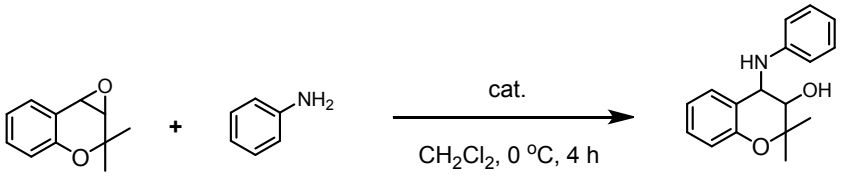
2,2-dimethyl-4-(phenylamino)chroman-3-ol: Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 95/5, 1.0 mL/min, 250 nm), t_{major} = 16.18 min, t_{minor} = 18.81 min; ee=11%.



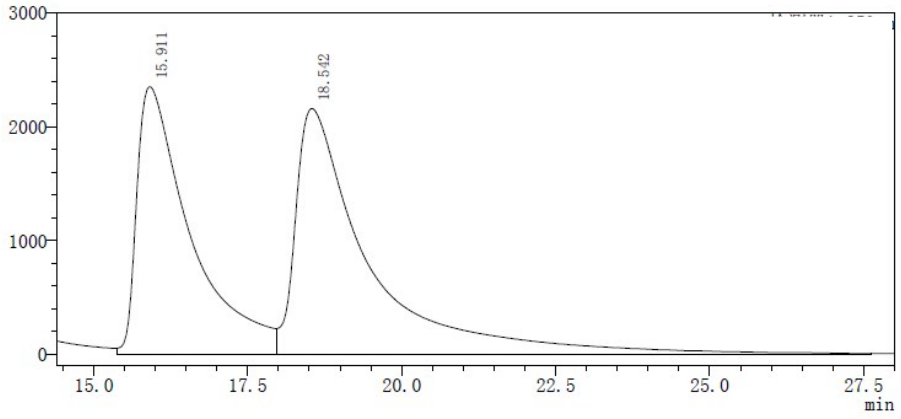
Serial Number	Retention Time [min]	Area	Area %
1	16.182	122229855	44.297
2	18.811	153700516	55.703

Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 95/5, 1.0 mL/min, 250 nm), t_{major} = 15.91 min, t_{minor} = 18.54 min; ee =12%.

14.6 HPLC for the epoxide aminolysis catalyzed by the homogenuous $V^{v}O$(salen)

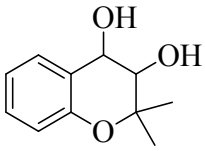


2,2-dimethyl-4-(phenylamino)chroman-3-ol: Enantiomeric excess was determined by HPLC with a chiralcel AD-H column (hexane/i-PrOH = 95/5, 1.0 mL/min, 250 nm), t_{major} = 16.18 min, t_{minor} = 18.81 min; ee=12%.

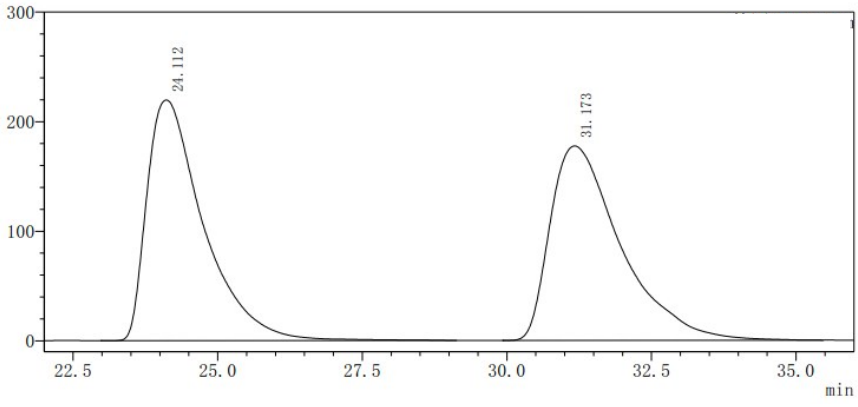


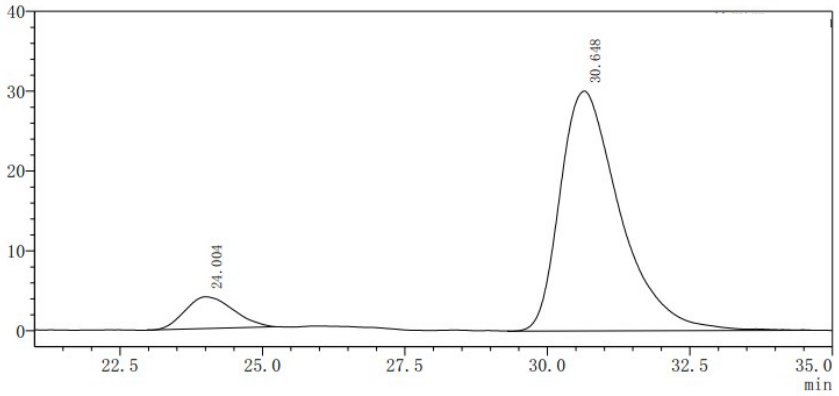
Serial Number	Retention Time [min]	Area	Area %
1	15.911	141705510	44.153
2	18.542	179238952	55.847

14.7 HPLC for the alkene epoxidation/epoxide hydrolysis catalyzed by the MOF 2

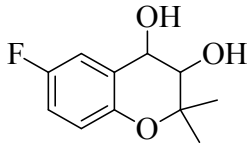


2,2-dimethyl-3,4-dihydro-2H-chromene-3,4-diol: Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/i-PrOH = 98/2, 1.5 mL/min, 230 nm), t_{minor} = 24.00 min, t_{major} = 30.65 min; ee=81%.

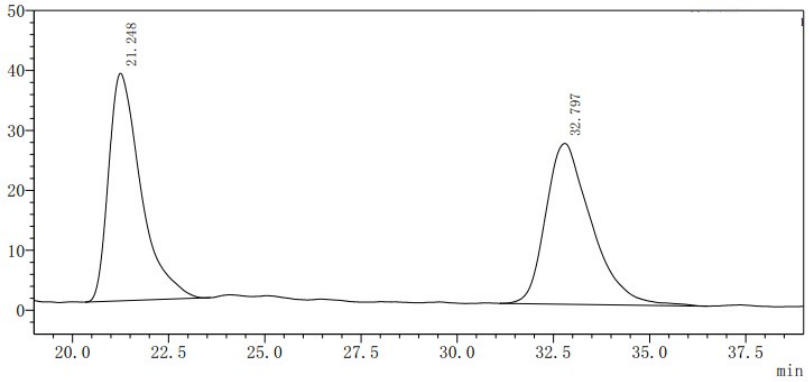


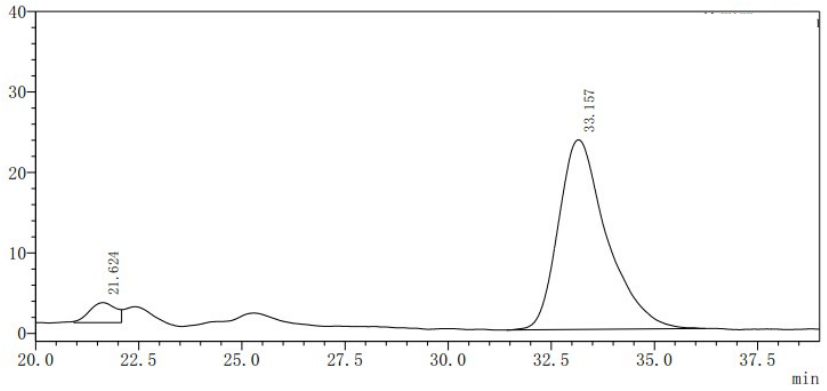


Serial Number	Retention Time [min]	Area	Area %
1	24.004	233560	9.610
2	30.648	2196705	90.390

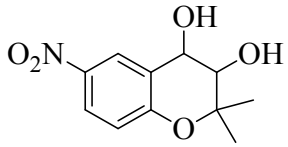


6-fluoro-2,2-dimethyl-3,4-dihydro-2H-chromene-3,4-diol: Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/i-PrOH = 98/2, 1.5 mL/min, 220 nm), t_{minor} = 21.62 min, t_{major} = 33.16 min; ee=89%.

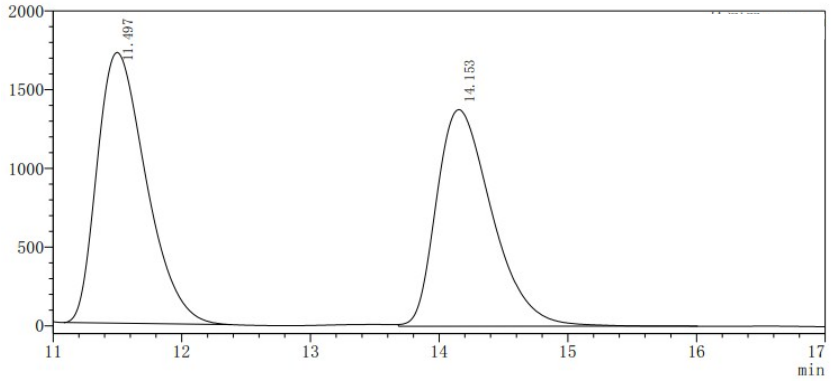


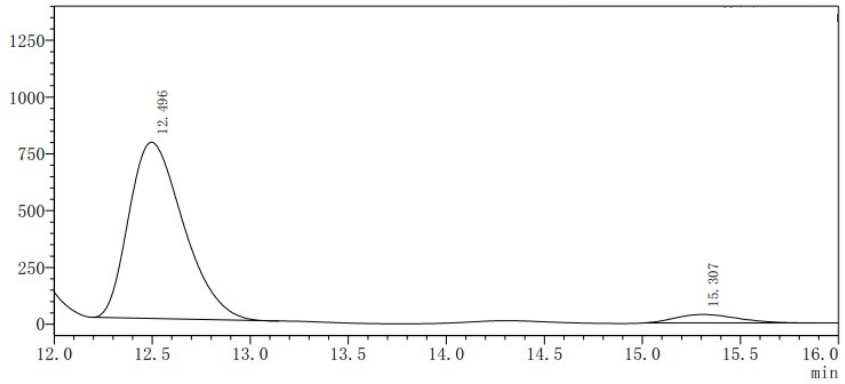


Serial Number	Retention Time [min]	Area	Area %
1	21.624	112078	5.501
2	33.157	1925344	94.499

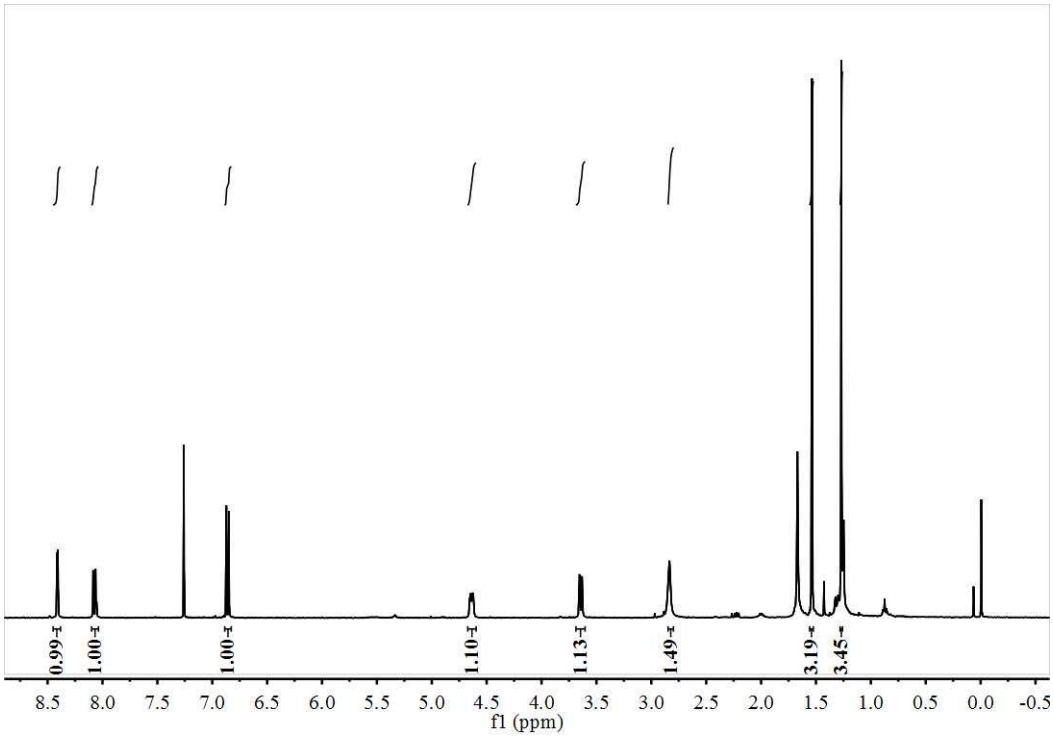


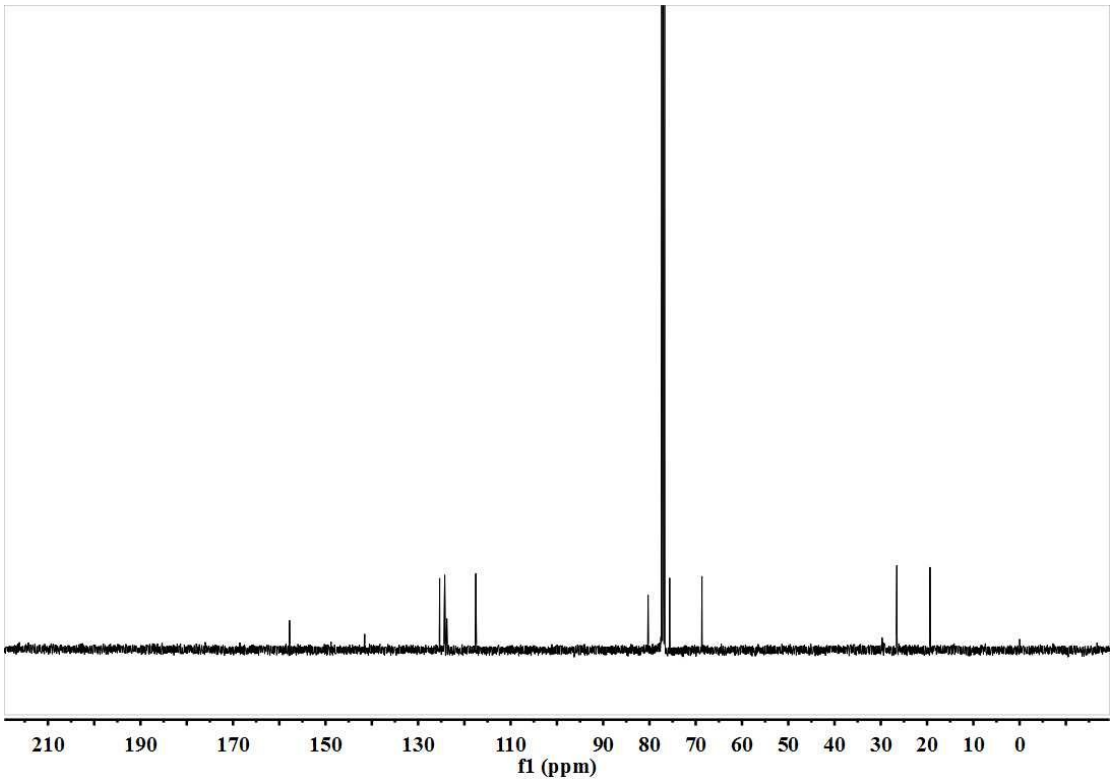
2,2-dimethyl-6-nitro-3,4-dihydro-2H-chromene-3,4-diol: Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/i-PrOH = 95/5, 1.0 mL/ min, 220 nm), t $_{major}$ = 12.50 min, t $_{minor}$ = 15.31 min;ee=90%.^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.41 (dd, J = 2.7, 0.9 Hz, 1H), 8.07 (dd, J = 9.1, 2.8 Hz, 1H), 6.86 (d, J = 9. 1 Hz, 1H), 4.64 (d, J = 8.3 Hz, 1H), 3.64 (d, J = 8.9 Hz, 1H), 2.84 (s, 1H), 1.54 (s, 3H), 1.27 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 157.77, 141.60, 125.44, 124.24, 123.77, 117.38, 80.35, 75.37, 68.54, 26.61, 19.10. ESI-MS m/z: 239.1 (Calcd m/z 239.08 for $[M+Na]^+$).

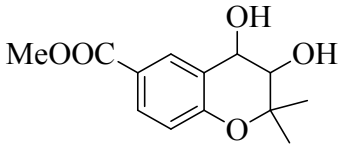




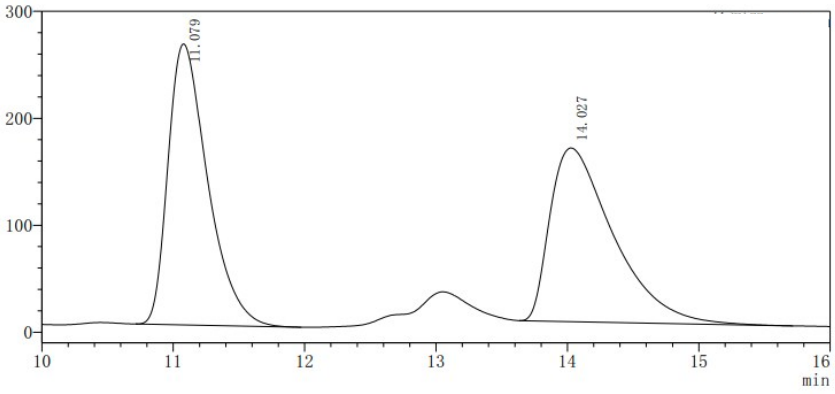
Serial Number	Retention Time [min]	Area	Area %
1	12.496	15031846	94.873
2	15.307	812312	5.127

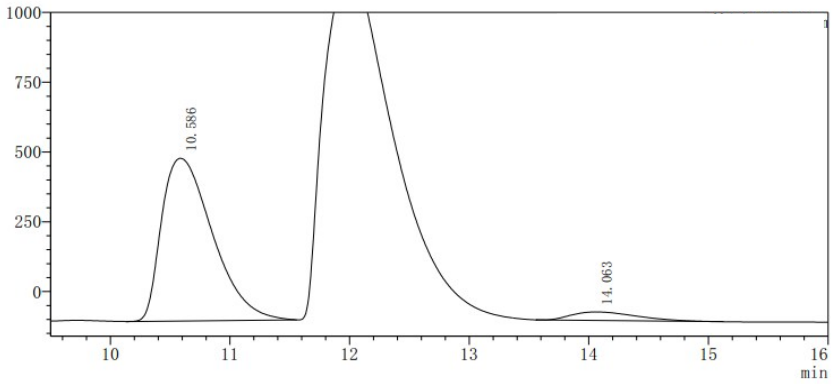




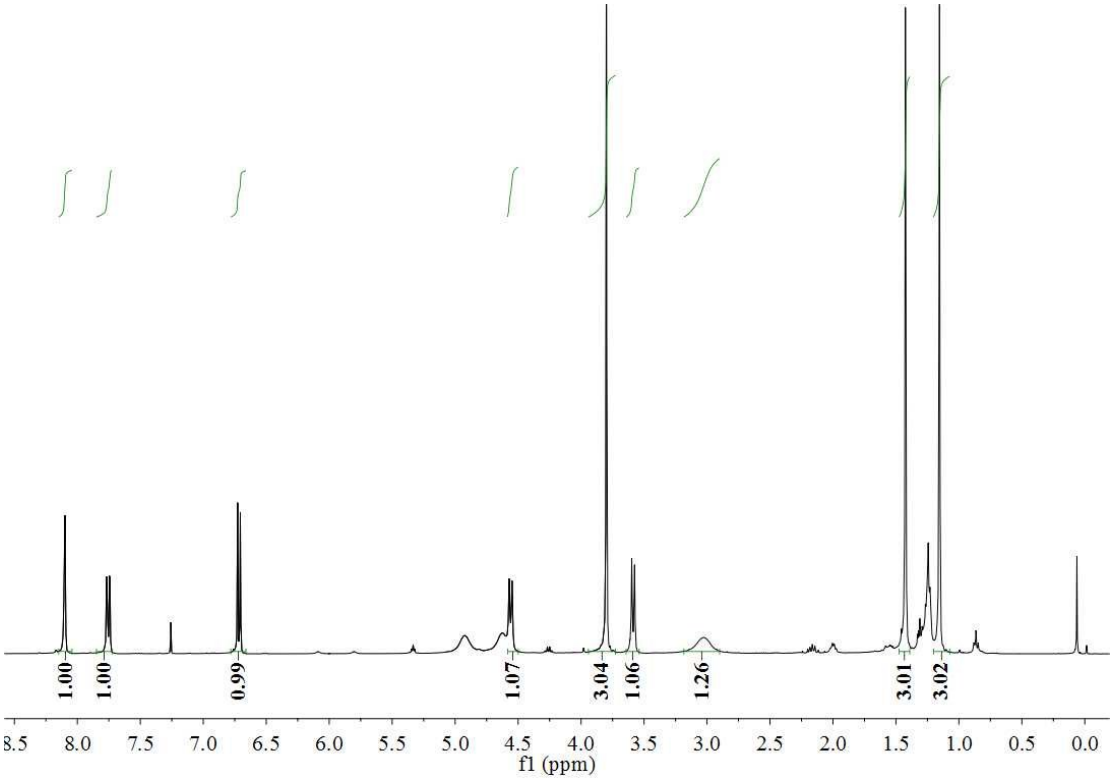


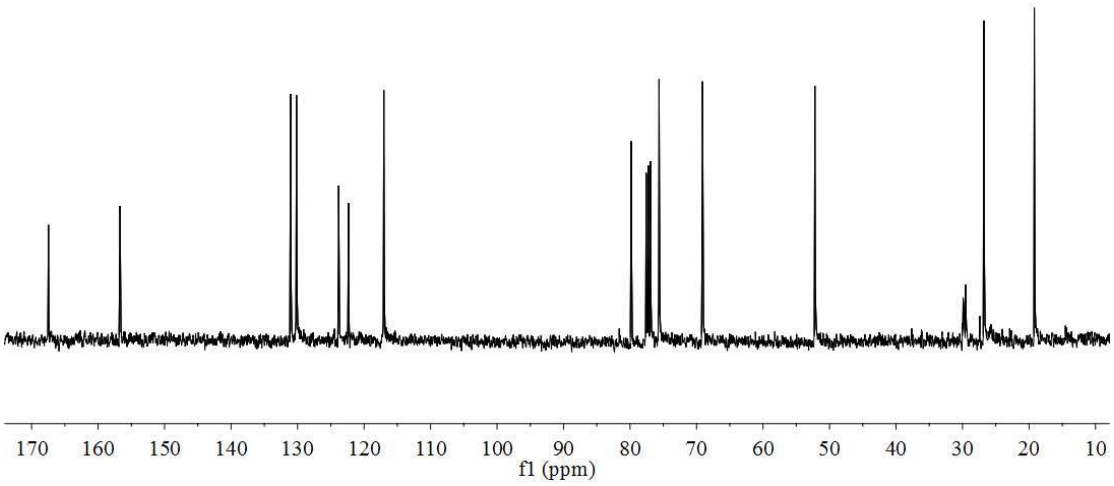
Methyl 3,4-dihydroxy-2,2-dimethyl-3,4-dihydro-2H-chromene-6-carboxylate: Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/i-PrOH = 98/2, 1.5 mL/min, 220 nm), t_{major} = 10.59 min, t_{minor} = 14.06 min; ee=87%. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.10 (s, *J* = 1.3 Hz, 1H), 7.75 (dd, *J* = 8.6, 1.9 Hz, 1H), 6.73 (d, *J* = 11.0 Hz, 1H), 4.56 (d, *J* = 8.9 Hz, 1H), 3.80 (s, 3H), 3.59 (d, *J* = 8.9 Hz, 1H), 3.02 (s, 1H), 1.44 (s, *J* = 12.5 Hz, 3H), 1.15 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ: 167.47, 156.70, 131.06, 130.17, 123.82, 122.34, 116.80, 79.82, 75.63, 69.09, 52.21, 26.79, 19.20. ESI-MS m/z: 252.0 (Calcd m/z 252.10 for $[M+Na]^+$).



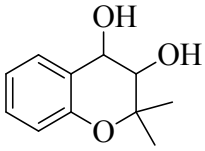


Serial Number	Retention Time [min]	Area	Area %
1	10.586	17280251	93.700
2	14.063	1161798	6.300



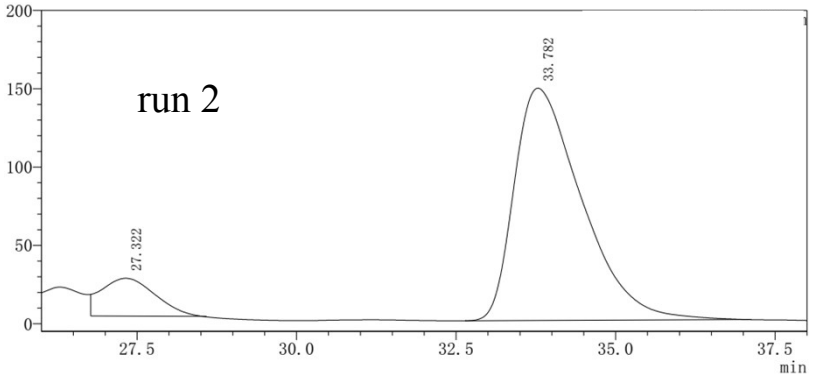


14.8 HPLC for the recycled experiment of the alkene epoxidation/epoxide hydrolysis catalyzed by MOF 2

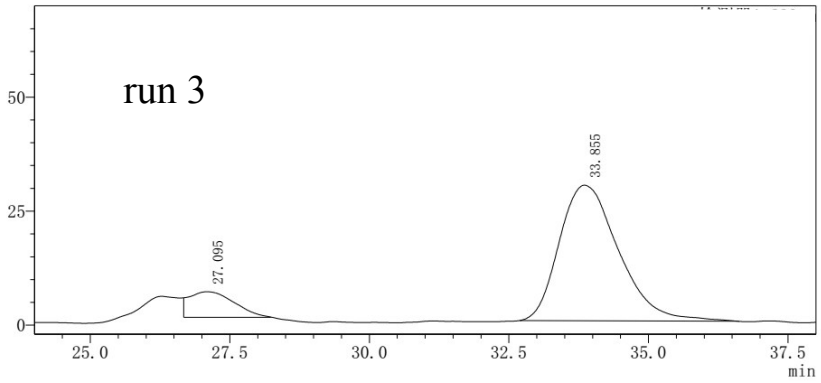


2,2-dimethyl-3,4-dihydro-2H-chromene-3,4-diol

Serial Number	Retention Time [min]	Area	Area %
1	24.004	233560	9.610
2	30.648	2196705	90.390



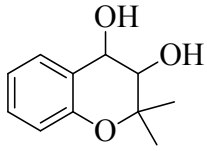
Serial Number	Retention Time [min]	Area	Area %
1	27.322	1410776	11.423
2	33.782	10939117	88.577



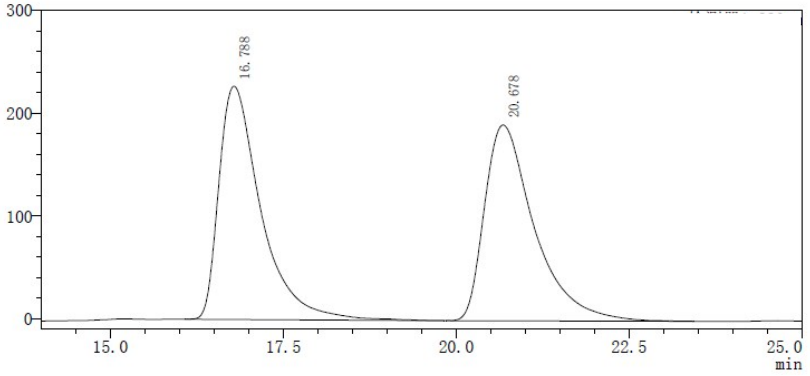
Serial Number	Retention Time [min]	Area	Area %

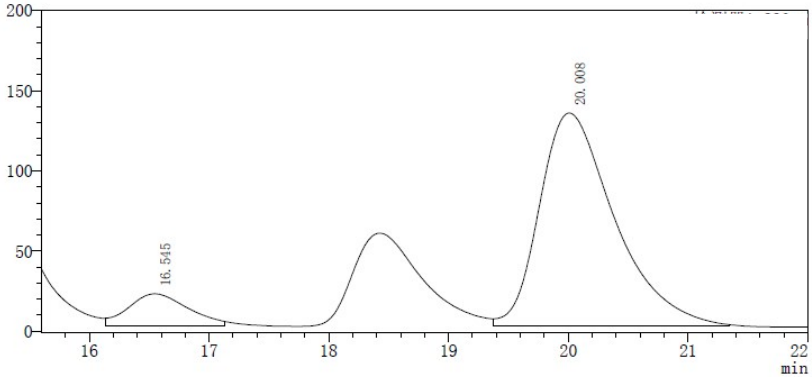
1	27.095	312840	12.463
2	33.855	2197254	87.537

14.9 HPLC for the the alkene epoxidation/ epoxide hydrolysis catalyzed by the homogenuous 1 eq:1 eq mixture of Mn(salen) and VO(salen)



2,2-dimethyl-3,4-dihydro-2H-chromene-3,4-diol: Enantiomeric excess was determined by HPLC with a chiralcel OD-H column (hexane/i-PrOH = 97/3, 1.5 mL/min, 220 nm), t_{major} = 20.00 min, t_{minor} = 16.55 min; ee=79%.

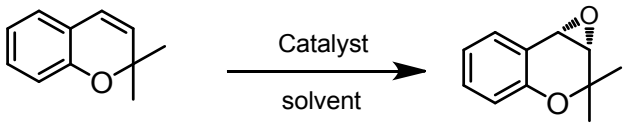




Serial Number	Retention Time [min]	Area	Area %
1	16.545	684881	10.624
2	20.008	5761944	89.376

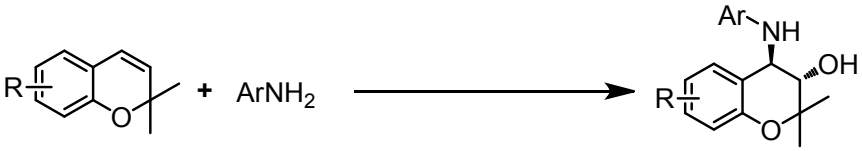
15. Additional results for catalysis

15.1 Table S4. Reported results of related asymmetric epoxidation of alkenes.



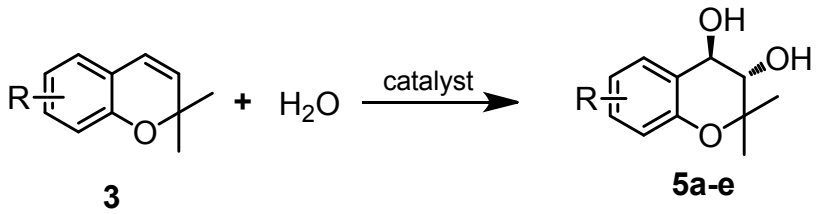
Entry	Catalyst	system	Oxidant	Conv.(%)	ee(%)
1	Mn(salen)Cl[S5]	Homogeneous	NaClO	87	98
2	Mn-salen complexes[S6]		H_2O_2	80	98
3	Mn(salen)-**L**$_3$-Me_2[S7]		sPhIO	90	92
4	$Zn_2(CO_2)_4N_2$Mn(salen)-MOF[S8]	Heterogeneous	sPhIO	71	82
5	Zn_4O-Mn(salen)-MOF[S7]		sPhIO	82	92
6	Mn(salen)-polymer[S9]		NaClO	90	95

15.2 Table S5. Reported results of related asymmetric epoxidation/aminolysis reactions



Entry	Catalyst	system	R	Ar	Conversion(%)	ee(%)
1	(R)-Me_2LMnCl and (R)-Me_2LCrCCl[S4]	Homogeneous	6-H	Ph	80	92
2	Salen^{CuMnCr}-MTV-MOF[S4]	Heterogeneous	6-H	Ph	84	94
3			6-H	2-OMePh	86	90
4			6-H	4-OMe	95	89
5			6-H	3-Me	85	92
6			6-Me	Ph	77	85
7			6-F	Ph	93	97
8			6-Br	Ph	89	96
9	Salen^{CrMn}-COF[S10]		6-H	Ph	84	91

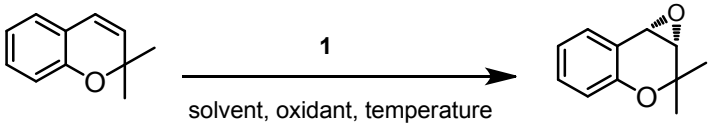
15.3 Table S6. Reported results of related asymmetric epoxidation/ hydrolysis of alkenes



3 5a-e

Entry	Catalyst	system	R	Conversion(%)	ee(%)
1	(R)-Me_2LMnCl and (R) Me_2LCoOAc[S4]	Homogeneous	6-H	83	94
2			6-OMe	80	94
3	Salen^{CuMnCo}-MTV-MOF[S4]	Heterogeneous	6-H	82	97
4			6-F	83	93
5			6-OMe	86	98

15.4 Table S7. Condition optimization of epoxidation catalyzed by **1**



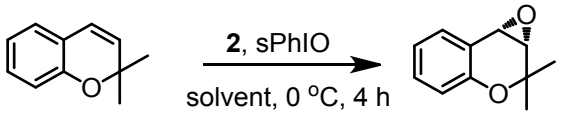
entry	solvent	Temperature(°C)	oxidant	Conv(%)	ee(%)
1	$CHCl_3$	0	MesIO	91	84
2	$CHCl_3$	0	PhIO	93	87
3	$CHCl_3$	0	sPhIO	81	62
4	toluene	0	PhIO	56	82
5	THF	0	PhIO	16	64
6	CH_3CN	0	PhIO	69	64
7	$CHCl_3$	-7	PhIO	94	87
8	$CHCl_3$	-15	PhIO	93	91
9	$CHCl_3$	-20	PhIO	93	91
10	$CHCl_3$	-30	PhIO	81	90

15.5 Table S8. Comparsion of asymmetric epoxidation/aminolysis reaction catalyzed by **1a** and **1**

entry	R	Ar	**4**/Conversion(%)		ee(%)	
			MOF **1a**	MOF **1**	MOF **1a**	MOF **1**
1	H	Ph	**a**/93	**a**/21	94	91
2	6-Br	Ph	**d**/87	**d**/17	93	91

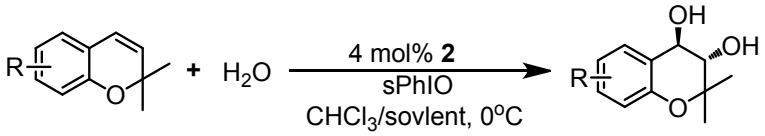
3	H	*p*-$MeOC_6H_4$	**g**/76	**g**/18	93	90

15.6 Table S9. Condition optimization of epoxidation catalyzed by **2**



Entry	solvent	Conversion(%)	ee(%)
1	$CHCl_3$	82	79
2	CH_2ClCH_2Cl	75	80
3	CH_2Cl_2	87	87
4	1,2-dimethyoxyethane	64	75
5	acetone	74	83
6	CH_3CN	52	7
7	THF	58	75

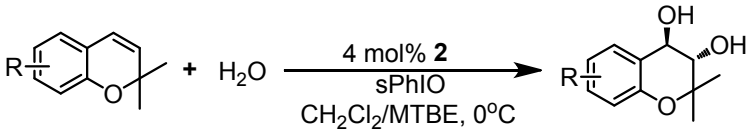
15.7 Table S10. Condition optimization of hydrolysis catalyzed by **2**



3 **5a-e**

Entry	solvent	Conversion(%)	ee
1	1,4-dioxane	67	78
2	Et_2O	64	77
3	CH_2Cl_2	75	78
4	CH_3Cl	63	79
5	CH_2ClCH_2Cl	64	75
6	CH_3CN	63	74
7	MTBE	87	80
8	anisole	trace	N.D.

15.8 Table S11. Sequential asymmetric epoxidation/ring-opening reactions of alkenes catalyzed by **2**.[a]



3 **5a-e**

Entry	R	**5**/Conv. (%)[b]	ee (%)[c]
1	H	**a**/79(81)	81(79)
2	6-OMe	**b**/74	86

3	6-F	**c**/61(64)	89(88)
4	6-NO_2	**d**/61	90
5	6-COOMe	**e**/63	87

[a]For reaction details see Experimental section; the data in parentheses are results catalyzed by 1:1 mixture of Mn**L**[1]Cl and $V^{IV}O(Me_2$**L**[2]). [b]conversions were calculated by ^{1}H NMR. [c]ee values were determined by HPLC.

16. References

[S1] G. M.Sheldrick, SHELXT-2014, 2013.

[S2] O. V. Dolomanov, L. J.Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, OLEX2: a complete structure solution, refinement and analysis program. *J. Appl. Crystallogr.* 2009, **42**, 339-341.

[S3] Spek, A. L. *J. Appl. Crystallogr.* 2003, **36**, 7.

[S4] Xia, Q., Li, Z., Tan, C., Liu, Y., Gong, W., Cui, Y. *J. Am. Chem. Soc*. 2017, **139**, 8259-8266.

[S5] Jacobsen, E. N., Zhang, W., Muci, A. R., Ecker, J. R., Deng, L. *J. Am. Chem. Soc.,* 1991, **113**, 7063.

[S6] H. Shitama and T. Katsuki, *Tetrahedron Lett.*, 2006, **47**, 3203-3207.

[S7] F. Song, C. Wang, J. M. Falkowski, L. Ma and W. Lin, *J. Am. Chem. Soc.*, 2010, **132**, 15390-15398.

[S8] S.-H. Cho, B. Ma, S. T. Nguyen, J. T. Hupp and T. E. Albrecht-Schmitt, *Chem. Commun*., 2006, 2563.

[S9]Song, C. E.; Roh, E. J.; Yu, B. M.; Chi, D. Y.; Kim, S. C.; Lee, K.-J. *Chem.Commun.,* 2000, 615.

[S10] X. Han, Q. Xia, J. Huang, Y. Liu, C. Tan and Y. Cui, *J. Am. Chem. Soc*., 2017, **139**, 8693−8697.