Enantioselective Ring-Opening Reaction of Epoxides with MeOH Catalyzed by Homochiral Metal–Organic Framework

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Two new copper metal–organic frameworks containing 2,2′-dihydroxy-1,1′-binaphthalene-5,5′-dicarboxylic acid (5,5′-H_2BDA) and 2,2′-dihydroxy-1,1′-binaphthalene-4,4′-dicarboxylic acid (4,4′-H_2BDA) have been prepared. X-ray structure determination of $[Cu_2(5,5'\text{-BDA})_2(H_2O)_2]\cdot MeOH\cdot 2H_2O$ (MOF-**1**) and $[Cu_2(4,4'\text{-BDA})_2(H_2O)_2]\cdot 4H_2O$ (MOF-**2**) revealed similar 2D sheet structures, containing square-grid coordination networks, but differences in the stacking motif. The desolvated MOF-**1** and -**2** were used as Lewis acid catalysts in the asymmetric ring-opening reaction of epoxides with MeOH.

In recent years, design and synthesis of metal–organic frameworks (MOFs)[1] aiming at developing functional zeolite analogs have been a subject of research interest owing to their potential applications in gas storage,[2] separation,[3] luminescence,[4] and heterogeneous catalysis.[5] In particular, the design of MOFs with homochirality has attracted considerable attention because of their applications in enantioselective separation and catalysis.[6] Recently, we have synthesized a novel chiral MOF (*R*)-MOF-**1** (Scheme 1) and examined its use as an effective catalyst for the asymmetric ring-opening of epoxides with amines[7a] and alcohols[7b] under heterogeneous conditions. Herein, we report the synthesis and X-ray structure determination of the isomeric chiral MOF (*R*)-MOF-**2** from 2,2′-dihydroxy-1,1′-binaphthalene-4,4′-dicarboxylic acid (4,4′-H_2BDA, (*R*)-**2**) and the catalytic behavior of both (*R*)-MOF-**1** and (*R*)-MOF-**2** in the asymmetric ring-opening reactions of several epoxides with MeOH (Scheme 2).

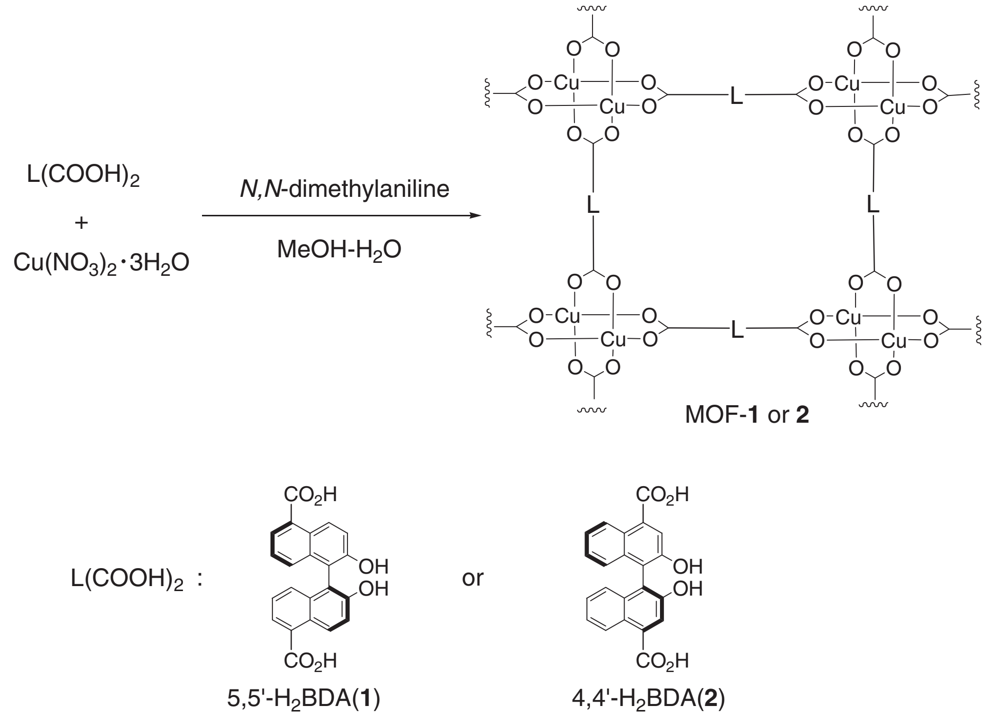
Results and Discussion

(*R*)-MOF-**1** was prepared according to our previously reported method[7a] and dried under vacuum at 80 °C for 3 h prior to use. (*R*)-MOF-**2** was prepared by a similar reaction using (*R*)-**2**[8] instead of 2,2′-dihydroxy-1,1′-binaphthalene-5,5′-dicarboxylic acid ((*R*)-**1**). Treatment of enantiopure 4,4′-H_2BDA ((*R*)-**2**) with $Cu(NO_3)_2$ in an aqueous MeOH solution with slow diffusion of *N*,*N*-dimethylaniline at room temperature for several days afforded $[Cu_2(4,4'\text{-BDA})_2(H_2O)_2]\cdot 4H_2O$ ((*R*)-MOF-**2**) as dark green prisms in 83% yield. The product was characterized by infrared (IR) spectroscopy, thermogravimetric analysis (TGA), and X-ray analysis. The IR spectrum of (*R*)-MOF-**2** exhibited peaks for νOH and νCO_2^- at 3289 and 1609 cm^{-1}, respectively. TGA showed that (*R*)-MOF-**2** loses 17% of its total weight within the temperature range 25–120 °C, corresponding to the loss of six water molecules per formula unit.

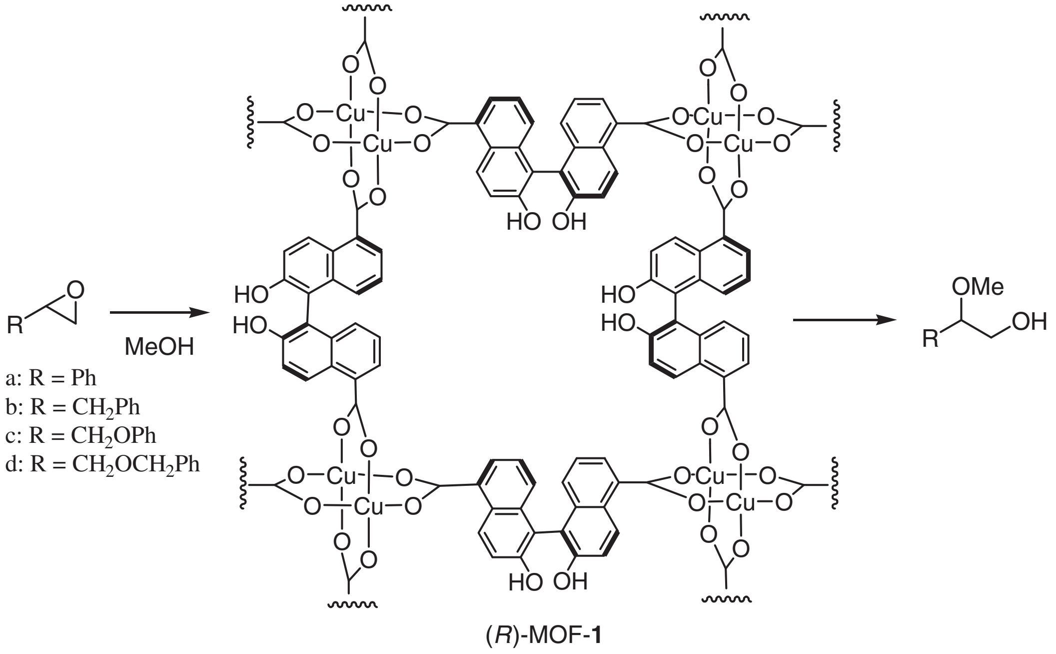
The crystal structure of the chiral polymeric metal–organic complex (*R*)-MOF-**2** viewed down the (100) axis is shown in Figure 1. The complex is a neutral molecule with a dinuclear structure in which two identical Cu(II) centers related by two-fold symmetry are bridged by four carboxylate groups from two 4,4′-BDA ligands. Each Cu(II) atom is five-coordinated by the combination of four O atoms from the carboxylate groups and one O atom from a water molecule. The Cu atoms are separated by a distance of 2.692(1) Å. The Cu···O distances in (*R*)-MOF-**2** range from 1.917(5) to 2.104(5) Å and are very close to the corresponding distances in (*R*)-MOF-**1** (1.926(7)–2.138(8) Å).[7a]

In both MOF's the longest Cu···O distances are those involving O atoms from water molecules in apical positions that are likely to be replaced by coordinated epoxide during catalytic course. The neighboring layers are "glued" by a system of hydrogen bonds involving four water molecules and the hydroxy groups of BDA molecules. The long channels are filled with four water molecules per asymmetric unit. The crystals of (*R*)-MOF-**1** have larger pores containing six waters and one methanol molecule that is hydrogen bonded with O2 of the carboxy group from Cu···Cu motif (Figure 2). In (*R*)-MOF-**2** available space is more restricted than in (*R*)-MOF-**1** due to smaller pore volume (Figure 3). The crystallographic data for MOF-**1** and MOF-**2** are shown in Table 1.

Ring-Opening Reactions of Epoxides. The catalytic activity of (*R*)-MOF-**1** and (*R*)-MOF-**2** toward asymmetric ring-opening reactions of epoxides with MeOH was examined (Table 2). In a typical experiment, a solution of styrene oxide (*rac*-**3a**, 0.5 mmol) in MeOH (0.5 mL) in the presence of (*R*)-MOF-**1** (20 mg, 0.046 mmol based on the formula unit) was stirred at 25 °C for 24 h, and 2-methoxy-2-phenylethanol ((*S*)-**4a**, 80% ee) and unreacted (*S*)-**3a** (7% ee) were obtained in 5% and 89% yields, respectively (Entry 1). In the absence of



Scheme 1. Synthesis of homochiral MOF.



Scheme 2. Enantioselective ring-opening reaction of epoxide.

catalyst, unreacted *rac*-**3a** was recovered. When the reactions were performed at higher temperatures (40 and 60 °C), the enantiomeric excess (ee) of unreacted **3a** increased, while that of product **4a** decreased (Entries 2 and 3). The highest ee of recovered **3a** (98%) was obtained in the reaction performed at 60 °C (Entry 3). It has been reported that desolvation can generate coordinatively unsaturated sites, that is, Lewis acid sites, in MOFs with similar paddle-wheel Cu_2 clusters.[9] Thus, we compared the catalytic results using the samples desolvated and un-desolvated and make clear the effect of desolvation. However, almost the same reactivity and enantioselectivity were obtained using the un-solvated (*R*)-MOF-**1** (Entry 4), assuming that one water molecule located on Cu atom of (*R*)-MOF-**1** is easily exchanged for epoxide substrate during catalytic cycles. The effect of the particle sizes of MOF on the catalytic activities was not recognized by using the grinding powder of (*R*)-MOF-**1** (Entry 5). Next, we performed reactions using (*R*)- and (*S*)-**3a** as substrates to evaluate the relative rate at each temperature. When the reaction was carried out at 25 °C, (*S*)-**4a** (>99% ee) and (*R*)-**4a** (>99% ee) were obtained

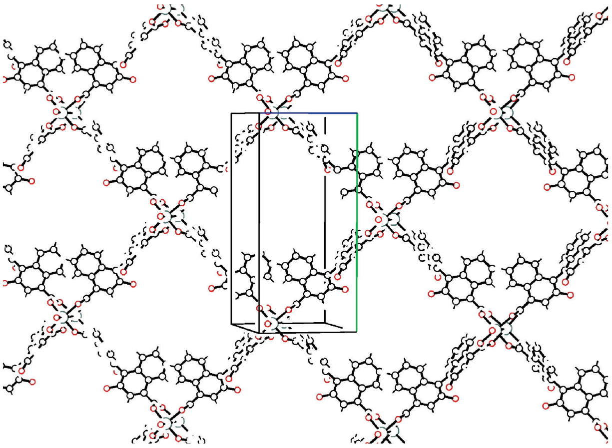


Figure 1. Crystal structure of (*R*)-MOF-**2** viewed down the (100) axis; four water molecules of crystallization omitted for clarity.

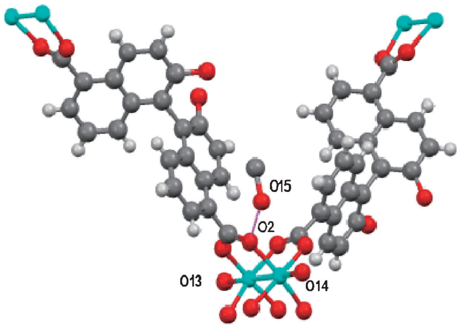


Figure 2. Stereochemistry of the coordination sphere in (*R*)-MOF-**1**[7a] with close proximity of methanol molecule: O15…O2 distance 2.873(6) Å and apical water molecules O13 and O14.

in 13% and 1% yields, respectively (Entries 6 and 7). Similar reactions at 40 and 60 °C afforded (*S*)-**4a** and (*R*)-**4a** in 48% and 5% yields (at 40 °C) (Entries 8 and 9), and in 95% and 25% yields (at 60 °C) (Entries 10 and 11), respectively. This implies that the (*R*)-**3a** enantiomer of styrene oxide reacts with MeOH approximately 13 times (at 25 °C), 10 times (at 40 °C) and 4 times (at 60 °C) faster than its (*S*)-**3a** counterpart in the presence of (*R*)-MOF-**1**. However, the same reaction using (*R*)-MOF-**2** as the catalyst showed poor results in terms of reactivity and enantioselectivity. For example, when a solution of *rac*-**3a** (0.5 mmol) in MeOH (0.5 mL) in the presence of (*R*)-MOF-**2** (20 mg) was stirred at 40 °C for 24 h, (*R*)-**4a** (7% ee) and unreacted *rac*-**3a** were obtained in 4% and 90% yields, respectively (Entry 12). The poor results may be due to the low accessibility of the substrate to Lewis acidic Cu sites of (*R*)-MOF-**2**. In (*R*)-MOF-**2** available space is more restricted than in (*R*)-MOF-**1** due to smaller pore volume (Figures 3 and 4). Another factor that might influence reaction yield and stereospecifity in the case of (*R*)-MOF-**2**, is lack of precisely localized MeOH molecules that can be directly utilized during the methanolysis reaction. Moreover, when the reaction was performed using (*R*)-1,1′-bi-2-naphthol (BINOL) as the catalyst, almost no reactivity or enantioselectivity was observed (Entry 13). On the other hand, when the reaction was performed using $Cu(OAc)_2$ or $Cu(NO_3)_2$ as catalyst, *rac*-**4a** was obtained in 16% and 23% yield, respectively (Entries 14 and 16). This suggests that the reaction is catalyzed by Lewis acidic Cu sites in the chiral MOF. With a combination of (*R*)-BINOL and $Cu(OAc)_4$ as catalyst, the reaction proceeded more efficiently than in the presence of only (*R*)-BINOL (Entry 15).

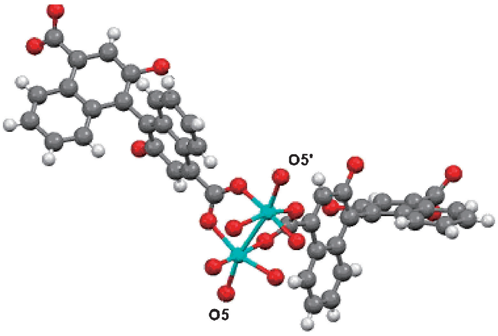


Figure 3. Stereochemistry of the coordination sphere in (*R*)-MOF-**2**.

Table 1. Crystallographic Data for MOF-**1** and MOF-**2**

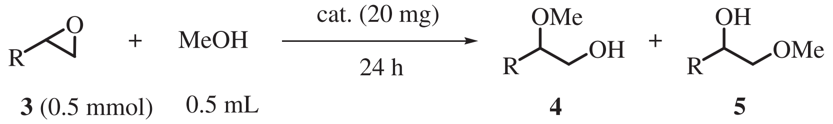
	MOF-**1**[7a]	MOF-**2**
Crystal system	monoclinic	monoclinic
Space group	$P2_1$	$C2$
a/Å	15.620(5)	13.445(1)
b/Å	11.377(4)	20.102(1)
c/Å	15.620(5)	9.1833(7)
α/°		
β/°	94.88(5)	90.374(6)
γ/°		
V/Å^3	2766(2)	2481.4(3)
Z	2	4
$F(000)$	1032	904
d_{calcd}/Mg m^{-3}	1.210	1.191
μ (Mo/Cu Kα)/mm^{-1}	0.833	1.565
$N_{refl/total\ indep.}/2\sigma(I)$	19335/8263	12458/3548
R_1	0.0745	0.0856

The reaction could be extended to several epoxides, such as 1,2-epoxy-3-phenylpropane (**3b**), 1,2-epoxy-3-phenoxypropane (**3c**), and 1-benzyloxy-2,3-epoxypropane (**3d**). In these reactions, however, the regioselectivity changed, and 1-methoxy-3-phenylpropan-2-ol (**5b**), 1-methoxy-3-phenoxypropan-2-ol (**5c**), and 1-benzyloxy-3-methoxypropan-2-ol (**5d**) were formed in relatively low yields and lower enantioselectivities (Entries 17–22).

Reaction Heterogeneity. To confirm the heterogeneity of the reaction, methanolysis of styrene oxide was performed at 40 °C under the conditions described in Table 2, and the solid (*R*)-MOF-**1** catalyst was filtered from the reaction mixture when the formation of 2-methoxy-2-phenylethanol (**4a**) reached 20% conversion. After removal of the solid catalyst, the solution was further stirred at 40 °C in the absence of the catalyst. After 72 h, no additional product formation was observed in the absence of the solid catalyst (Figure 4).

Recycling Test. The reusability of the (*R*)-MOF-**1** catalyst was also investigated for the methanolysis of styrene oxide

Table 2. Ring-Opening Reactions of Various Epoxides with MeOH



a: R = Ph c: R = CH_2OPh
b: R = CH_2Ph d: R = CH_2OCH_2Ph

Entry	Catalyst	Epoxide	Temp/°C	Unreacted **3** Yield/%, Ee/%	Product **4** or **5** Yield/%, Ee/%
1	(*R*)-MOF-**1**	*rac*-**3a**	25	89, 7(*S*)	**4a**, 5, 80(*S*)
2	(*R*)-MOF-**1**	*rac*-**3a**	40	76, 23(*S*)	**4a**, 21, 70(*S*)
3	(*R*)-MOF-**1**	*rac*-**3a**	60	29, 98(*S*)	**4a**, 66, 37(*S*)
4	(*R*)-MOF-**1**[a]	*rac*-**3a**	40	76, 23(*S*)	**4a**, 21, 72(*S*)
5	(*R*)-MOF-**1**[b]	*rac*-**3a**	40	72, 22(*S*)	**4a**, 21, 72(*S*)
6	(*R*)-MOF-**1**	(*R*)-**3a**	25	80, >99(*R*)	**4a**, 13, >99(*S*)
7	(*R*)-MOF-**1**	(*S*)-**3a**	25	96, >99(*S*)	**4a**, 1, >99(*R*)
8	(*R*)-MOF-**1**	(*R*)-**3a**	40	50, >99(*R*)	**4a**, 48, >99(*S*)
9	(*R*)-MOF-**1**	(*S*)-**3a**	40	92, >99(*S*)	**4a**, 5, >99(*R*)
10	(*R*)-MOF-**1**	(*R*)-**3a**	60	0	**4a**, 95, >99(*S*)
11	(*R*)-MOF-**1**	(*S*)-**3a**	60	72, >99(*S*)	**4a**, 25, >99(*R*)
12	(*R*)-MOF-**2**	*rac*-**3a**	40	90, 0	**4a**, 4, 7(*R*)
13	(*R*)-BINOL[c]	*rac*-**3a**	40	96, 2(*R*)	**4a**, 3, 6(*S*)
14	$Cu(OAc)_2$	*rac*-**3a**	40	81, 0	**4a**, 16, 0
15	(*R*)-BINOL[c] + $Cu(OAc)_2$	*rac*-**3a**	40	56, 3(*R*)	**4a**, 39, 11(*S*)
16	$Cu(NO_3)_2$	*rac*-**3a**	40	65, 0	**4a**, 23, 0
17	(*R*)-MOF-**1**	*rac*-**3b**	60	83, 23(*S*)	**5b**, 11, 24(*R*)
18	$Cu(NO_3)_2$	*rac*-**3b**	60	0, 0	**5b**, 80, 0
19	(*R*)-MOF-**1**	*rac*-**3c**	60	66, 8(*S*)	**5c**, 25, 27(*R*)
20	$Cu(NO_3)_2$	*rac*-**3c**	60	0, 0	**5c**, 92, 0
21	(*R*)-MOF-**1**	*rac*-**3d**	60	77, 2(*S*)	**5d**, 15, 9(*R*)
22	$Cu(NO_3)_2$	*rac*-**3d**	60	0, 0	**5d**, 82, 0

a) Un-desolvated. b) Powdered. c) 1,1′-Bi-2-naphthol.

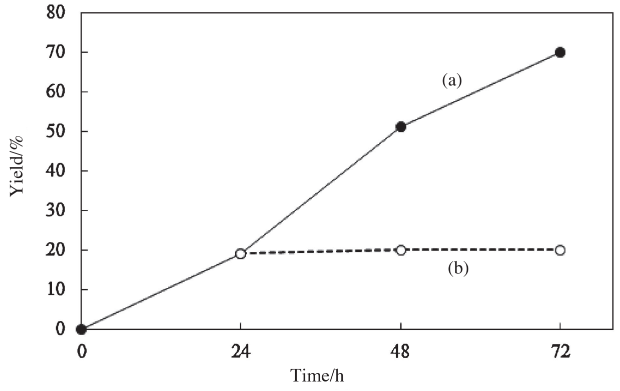


Figure 4. Heterogeneity test of styrene oxide methanolysis at 40 °C a) in the presence of (*R*)-MOF-**1** or b) after filtration of the catalyst at 20% conversion.

Table 3. Recycling Tests on (*R*)-MOF-**1** in the Methanolysis of Styrene Oxide at 40 °C

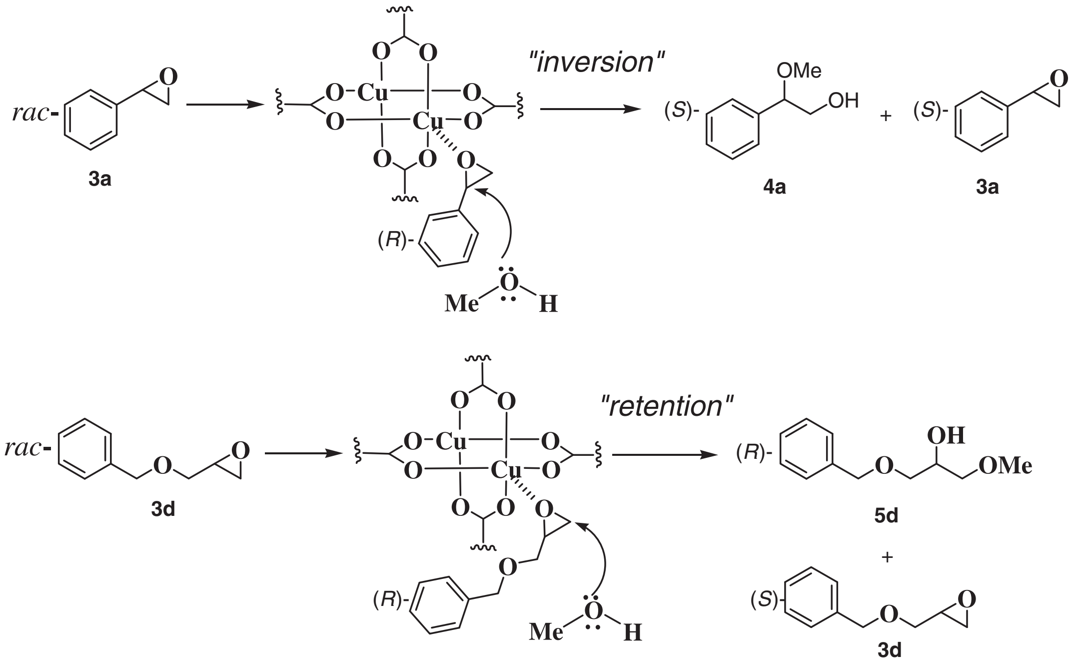
Recycle run	**3a**	
	Yield/%	Ee/%
1st	20	62
2nd	18	72
3rd	22	69

at 40 °C under the conditions described in Table 2. As shown in Table 3, (*R*)-MOF-**1** maintained a high level of performance for up to at least two recycles.

Reaction Mechanism. The mechanism of kinetic resolution of styrene oxide (*rac*-**3a**) catalyzed by (*R*)-MOF-**1** could be inferred from the methanolysis of styrene oxide, because the methoxy group was incorporated at the α-carbon of **3a** to afford product **4a** exclusively. The suggested mechanism proceeds as follows: Initially, only (*R*)-**3a** from the racemic mixture coordinates to a Lewis acidic Cu site on (*R*)-MOF-**1** to form an adduct predominantly owing to steric reasons. Next, methanol attacks the α-carbon atom (benzyl position) of the coordinated (*R*)-**3a** from the backside to give (*S*)-**4a** with inversion of stereochemistry, while the other enantiomer from the starting racemate, (*S*)-**3a**, remains unchanged. On the other hand, methanol would likely attack the less hindered side of (*R*)-**3d** to afford (*S*)-**5d** with no inversion of the stereogenic center (Scheme 3).

Conclusion

In summary, we have synthesized two isomeric homochiral MOFs (MOF-**1** and MOF-**2**) having chiral BINOL units. Homochiral MOF-**1** was found to be highly active in catalyzing



Scheme 3. Possible reaction mechanism.

the asymmetric ring-opening reaction of epoxides with methanol and was shown to function as a heterogeneous, recyclable, and reusable catalyst. Further investigation of the scope and limitations of this catalytic system are currently underway.

Experimental

^{1}H NMR spectra were recorded on a JEOL JNM-GSX 400 spectrometer with tetramethylsilane as the internal standard. IR spectra were recorded on a JASCO FT-IR 4100 spectrometer. TGA was performed on a Rigaku TG-8120 instrument. Enantiomeric excesses were determined either by high-performance liquid chromatography (HPLC) on a Chiralpak OD, OD-H, or AS (Daisel), or by a Shimadzu GC-2014 system equipped with a flame ionization detector and a Chiraldex γ-TA column.

Synthesis of [Cu_2(4,4′-BDA)$_2$(H_2O)$_2$]·4H_2O ((*R*)-MOF-2). *N*,*N*-Dimethylaniline was slowly diffused into a mixture solution of MeOH (5 mL) and water (1.5 mL) containing $Cu(NO_3)_2 \cdot 3H_2O$, (48 mg, 0.2 mmol) and (*R*)-(+)-**2**[8] (75 mg, 0.2 mmol) at room temperature. After several days, (*R*)-MOF-**2**, [Cu_2(4,4′-BDA)$_2$(H_2O)$_2$]·4H_2O (86 mg, 83% yield) were obtained as dark green prisms. IR(cm^{-1}): 3289, 1609, 1513, 1340, 1267, 1234, 992, 903, 803, 767, 737.

X-ray Crystallography. X-ray data of the (*R*)-MOF-**2** were collected on a Bruker ApexII system using Cu Kα radiation at 293 K. Unit cell parameters: $a = 13.445(1)$, $b = 20.102(1)$, $c = 9.1833(7)$ Å, $\beta = 90.374(6)°$, $V = 2481.4(3)$ Å^3, $d_{\text{calcd}} = 1.191$ Mg m^{-3}, μ(Cu Kα) $= 1.565$ mm^{-1}, $F(000) = 1044$; monoclinic, space group $C2$, $Z = 4$. 12458 reflections were collected. The structure was solved by direct methods and refined by full-matrix least squares using SHELXS97 and SHELXL97 programs.[10] Final $R_1 = 0.0856$ and $wR_2 = 0.2155$ for 3548 unique reflections with $I > 2\sigma(I)$. Several hydrogen atoms from water molecules could not be found from difference Fourier maps. CCDC-730355, contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at "http://www.ccdc.cam.ac.uk/conts/retrieving.html" (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, U.K.; E-mail: deposit@ccdc.cam.sc.uk).

Typical Procedure for the Methanolysis of Styrene Oxide (3a). (*R*)-MOF-**1** (20 mg) is desolvated at 80 °C for 3 h prior to reaction. The resultant solid catalyst is suspended in a MeOH (0.5 mL) solution of styrene oxide **3a** (0.06 g, 0.5 mmol) and stirred for 24 h. Then, the solid catalyst was collected by filtration, washed with MeOH. All MeOH portions are combined and evaporated under reduced pressure, and the yield is determined by NMR. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39–7.25 (m, Ph, 5H), 4.31 (dd, $J = 3.8$, 8.5 Hz, 1H), 3.72–3.56 (m, CH_2OH, 2H), 3.30 (s, OMe, 3H), 2.74 (bs, OH, 1H). The optical purity of 2-methoxy-2-phenylethanol (**4a**) was determined by HPLC using Chiralpak IA (Daicel) column (hexane/2-PrOH: 97/3, flow rate 0.3 mL min^{-1}, $t = 37$ min (*S*), $t = 45$ min (*R*)). The optical purity of styrene oxide **3a** was determined by HPLC using Chiralpak AS (Daicel) column. (hexane/2-PrOH: 99/1, flow rate 0.3 mL min^{-1}, $t = 26$ min (*R*), $t = 29$ min (*S*)).

Typical Procedure for the Methanolysis of 1,2-Epoxy-3-phenylpropane (3b). (*R*)-MOF-**1** (20 mg) desolvated as above is suspended in a MeOH (0.5 mL) solution of 1,2-epoxy-3-phenylpropane (**3b**) (0.067 g, 0.5 mmol) and stirred at 60 °C for 24 h. Then, the solid catalyst was collected by filtration, washed with MeOH. All MeOH portions are combined and evaporated under reduced pressure, and the yield is determined by NMR. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33–7.21 (m, 5H), 4.04 (m, 1H), 3.42–3.39 (m, 2H), 3.37 (s, 3H), 2.80–2.78 (m, 2H). The optical purity of 1-methoxy-3-phenylpropan-2-ol (**5b**) was determined by HPLC using Chiralcel OD-H (Daicel) column (hexane/2-PrOH: 18/1, flow rate 0.5 mL min^{-1}, $t =$

21.9 min (*S*), $t = 26.8$ min (*R*)). The optical purity of 1,2-epoxy-3-phenylpropane (**3b**) was determined by HPLC using Chiralcel OD-H (Daicel) column. (hexane/2-PrOH: 18/1, flow rate 0.5 mL min^{-1}, $t = 14.4$ min (*R*), $t = 17.4$ min (*S*)).

Typical Procedure for the Methanolysis of 1,2-Epoxy-3-phenoxypropane (3c). (*R*)-MOF-**1** (20 mg) desolvated as above is suspended in a MeOH (0.5 mL) solution of 1,2-epoxy-3-phenoxypropane (**3c**) (0.075 g, 0.5 mmol) and stirred at 60 °C for 24 h. Then, the solid catalyst was collected by filtration, washed with MeOH. All MeOH portions are combined and evaporated under reduced pressure, and the yield of 1,2-epoxy-3-phenoxypropane (**3c**) and 1-methoxy-3-phenoxypropan-2-ol (**5c**) was determined by GC (Chiraldex γ-TA, 140 °C, N_2 gas, linear velocity of 29.8 cm min^{-1}, $t = 6.84$ min (**3c**), $t = 14.8$ min (**5c**)). The optical purity of 1-methoxy-3-phenoxypropan-2-ol (**5c**) was determined by HPLC using Chiralpak OD (Daicel) column (hexane/2-PrOH: 90/10, flow rate 1.0 mL min^{-1}, $t = 10.4$ min (*S*), $t = 19.8$ min (*R*)). The optical purity of 1,2-epoxy-3-phenoxypropane (**3c**) was determined by HPLC using Chiralpak OD (Daicel) column (hexane/2-PrOH: 90/10, flow rate 1.0 mL min^{-1}, $t = 7.94$ min (*S*), $t = 13.0$ min (*R*)).

Typical Procedure for the Methanolysis of 1-Benzyloxy-2,3-epoxypropane (3d). (*R*)-MOF-**1** (20 mg) desolvated as above is suspended in a MeOH (0.5 mL) solution of 1-benzyloxy-2,3-epoxypropane (**3d**) (0.082 g, 0.5 mmol) and stirred at 60 °C for 24 h. Then, the solid catalyst was collected by filtration, washed with MeOH. All MeOH portions are combined and evaporated under reduced pressure, and the yield of 1-benzyloxy-2,3-epoxypropane (**3d**) and 1-benzyloxy-3-methoxypropan-2-ol (**5d**) was determined by GC (Chiraldex γ-TA, 140 °C, N_2 gas, linear velocity of 29.8 cm min^{-1}, $t = 8.85$ min (**3d**), $t = 29.8$ min (**5d**)). The optical purity of 1-benzyloxy-3-methoxypropan-2-ol (**5d**) was determined by HPLC using Chiralcel AS (Daicel) column (hexane/2-PrOH: 90/10, flow rate 0.5 mL min^{-1}, $t = 19.2$ min (*R*), $t = 26.3$ min (*S*)). The optical purity of 1-benzyloxy-2,3-epoxypropane (**3d**) was determined by HPLC using Chiralcel AS (Daicel) column (hexane/2-PrOH: 90/10, flow rate 0.5 mL min^{-1}, $t = 12.8$ min (*R*), $t = 16.0$ min (*S*)).

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