Supporting Information for

A novel chiral porous metal-organic framework: asymmetric ring opening reaction of epoxide with amine in the chiral open space

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Optical resolution of rac-1: rac-1(0.81 g, 2.16 mmol) and cinchonidine (2) (1.27 g, 4.32 mmol) were dissolved in MeOH (120 ml) and the solution was allowed to stand at room temperature for 24 h. The precipitate was filtered to give a 1:2 complex of (R)-(+)1 of 91% ee and 2 as colorless prisms (0.59 g). Recrystallization of the complex from MeOH gave almost pure 1:2 complex crystals (0.35 g, mp 195-196 °C), which were acidified by using dil. HCl and the mixture was extracted with AcOEt. The organic layer was washed with brine and dried over MgSO4. Evaporation of the solvent gave almost optically pure (R)-(+)1(0.14 g, mp 316-318 °C) of >99% ee in 35% yield. From the MeOH solution left after separation of the complex of (R)-(+)1 of 91% ee and 2, (S)-(−)-1 (0.57 g) of 74% ee was obtained. Treatment of (S)-(−)-1 (0.57 g, 1.52 mmol) of 74% ee with 1,4-diazabicyclo[3.3.3]octane (DABCO)(0.34 g, 3.04 mmol) in MeOH gave 1:1 complex (0.058 g, mp 290-291°C) of rac-1 and DABCO. From the filtrate, (S)-(−)-1 (0.13 g, mp 316-318 °C) of >99% ee was obtained in 32% yield. The optical purity was determined by HPLC analysis using a Chiralpak AD-H (Daicel) column, (hexane/EtOH/TFA: 75/25/0.01, flow rate 1.0 ml/min, tR 14 min (S), 17 min (R)).
Synthesis of (R)-3, [Cu₂(5,5’BDA)₂(H₂O)₂]•MeOH•2H₂O: N,N-dimethylaniline was slowly diffused into a mixture solution of MeOH (50 ml) and water (10 ml) containing Cu(NO₃)₂ • 6H₂O, (2.67 mmol) and (R)-(+) -1 (2.67 mmol) at room temperature. After several days, (R)-3 , [Cu₂(5,5’BDA)₂(H₂O)₂]•MeOH•2H₂O (0.94 g, 33% yield) were obtained as green needles.

**General procedure for the asymmetric ring-opening reaction:** A mixture of cyclohexene oxide (4a, 1 mmol), aniline (5a, 1 mmol) and the evacuated (R)-3 (0.1 mmol) was stirred at 25 °C for 24 h under solvent-free conditions. Then, the solid catalyst was collected by filtration, washed with EtOH, and the solvent of the filtrate were removed in vacuo to give (1S, 2S)-(+) -2-phenylaminocyclohexanol (6a) of 51% ee in 51% yield. ¹H NMR (270 MHz, CDCl₃, δppm): 7.2-7.12 (m, 2H), 6.76-6.68 (m, 3H), 3.37-3.27 (m, 1H), 3.18-3.06 (m, 1H), 2.80 (bs, 1H), 2.15-2.04 (m, 2H), 1.76-1.60 (m, 2H), 1.41-1.29 (m, 3H), 1.1-0.9 (m, 1H). The optical purity was determined by HPLC using Chiralpak AD-H (Daicel) column. (hexane/EtOH/DEA: 80/20/0.01, flow rate 0.5 ml/min, t_R 15 min (-), 20 min (+)).
Figure S1. CD spectra for (R)-(+) and (S)-(−)-1 in CHCl₃.

Figure S2. ORTEP structure of 1:2 complex of (R)-(+) and 2.
Figure S3. TGA curves for (R)-(+-)\textsubscript{-}3.

Figure S4. ORTEP structure of (R)-3.