

Supporting Information for

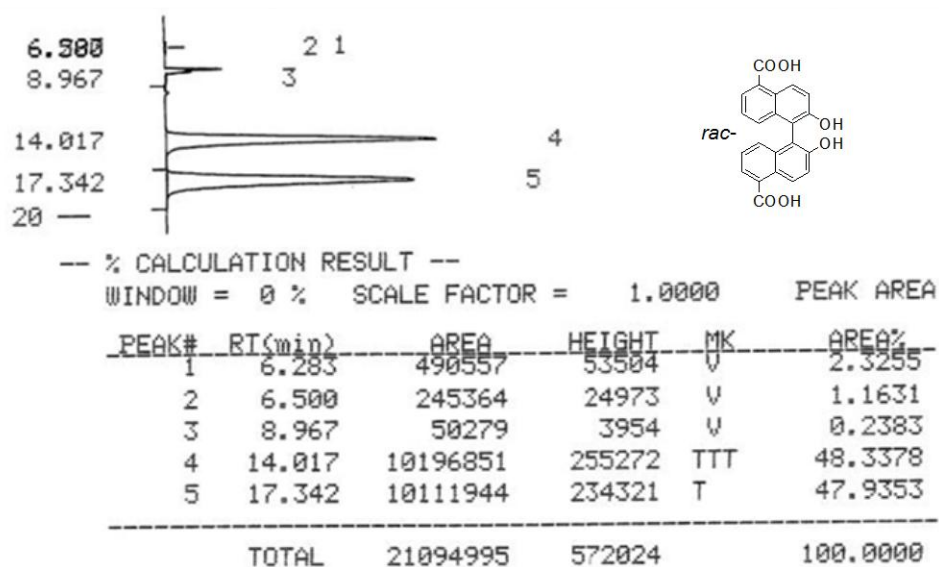
A novel chiral porous metal-organic framework: asymmetric ring opening reaction of epoxide with amine in the chiral open space

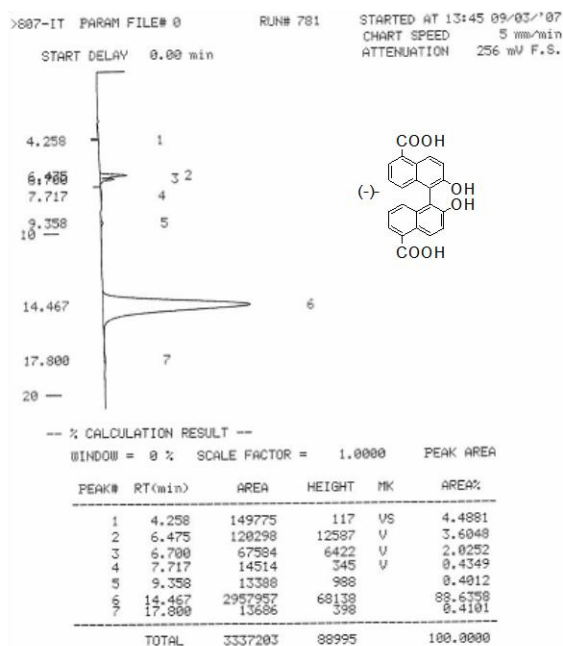
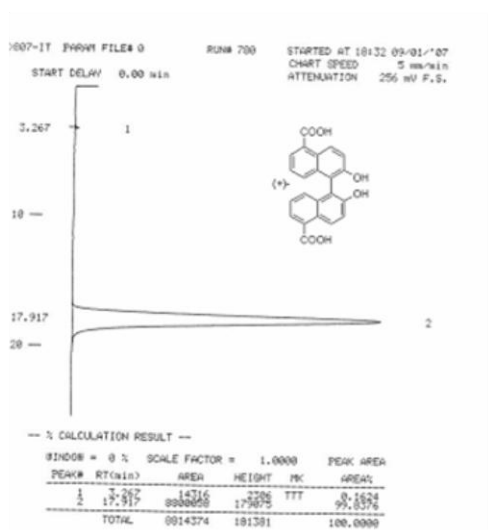
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Optical resolution of *rac*-1: *rac*-1 (0.81 g, 2.16 mmol) and cinchonidine (**2**) (1.27 g, 4.32 mmol) were dissolved in MeOH (120 ml) and the solution was allowed to stand at room temperature for 24 h. The precipitate was filtered to give a 1:2 complex 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, *t*_R 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 (1*S*, 2*S*)-(+)-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 (+)).

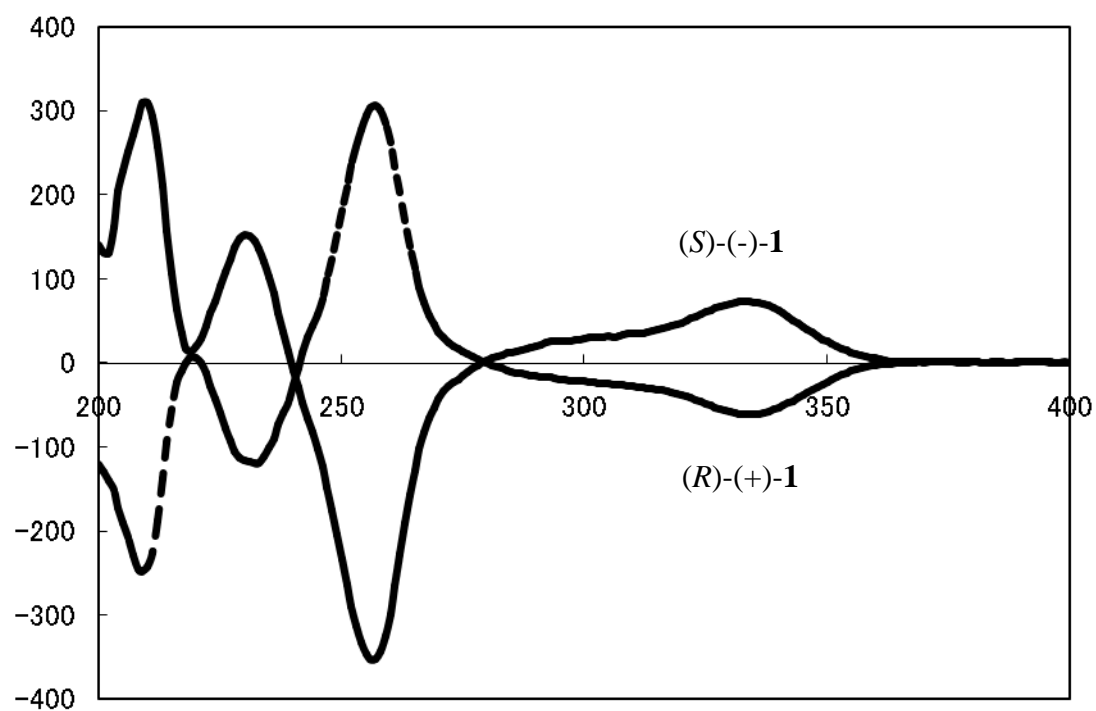


Figure S1. CD spectra for (*R*)-(+)- and (*S*)-(-)-**1** in CHCl_3 .

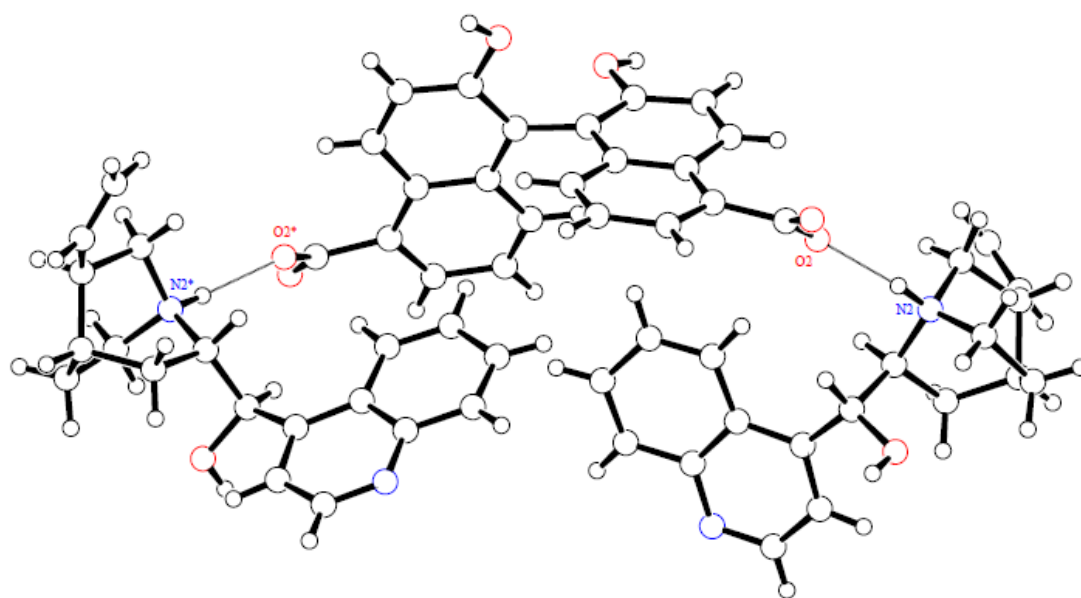


Figure S2. ORTEP structure of 1:2 complex of (*R*)-(+)-**1** and **2**.

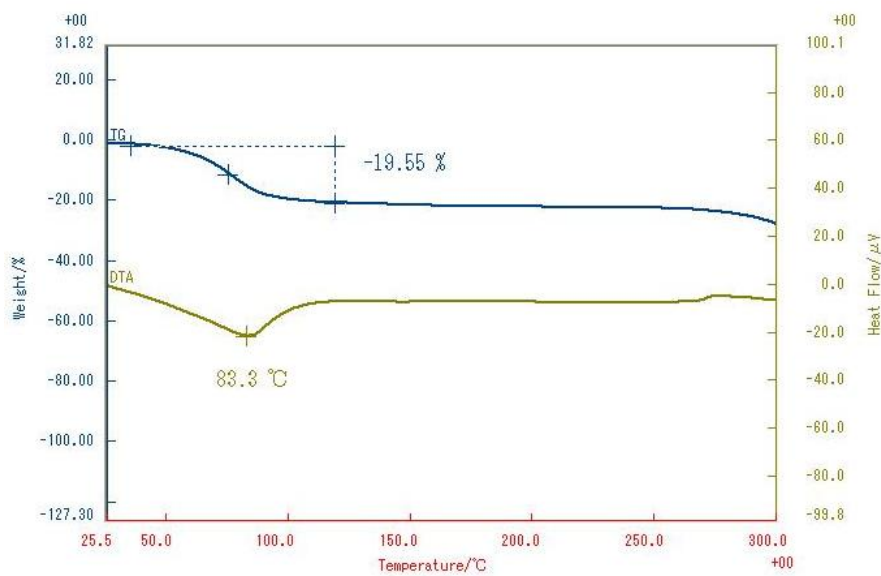


Figure S3. TGA curves for (R)-(+)-3.

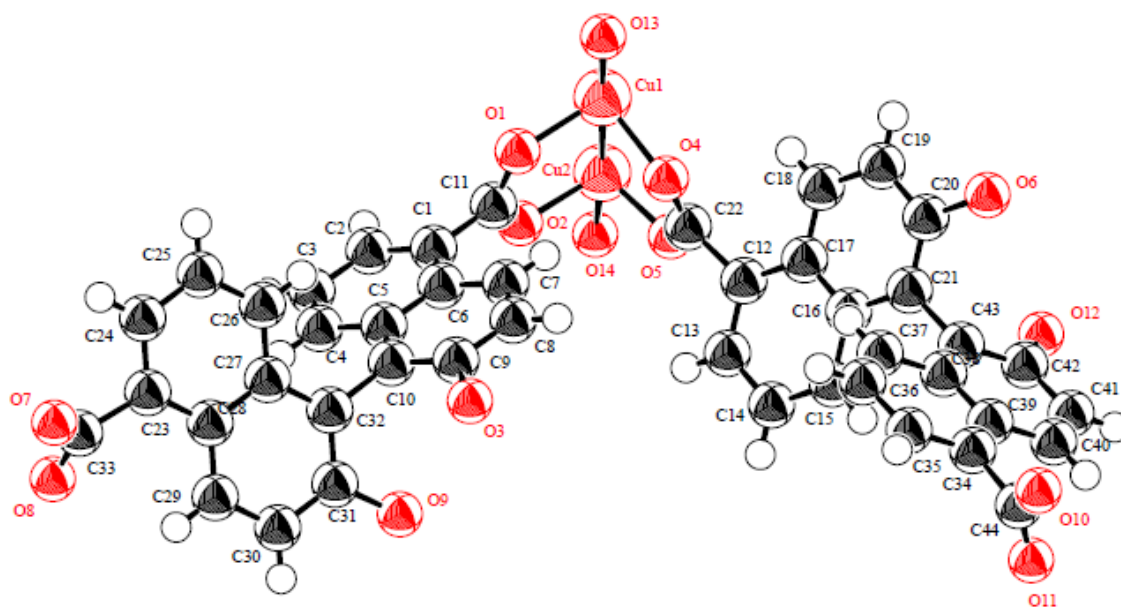


Figure S4. ORTEP structure of (R)-3.