Electronic Supplementary Material (ESI) for Inorganic Chemistry Frontiers.

Supporting Information

Highly stable chiral Cr(III)-based metal–organic frameworks for enantioadsorption separation of aromatic alcohols

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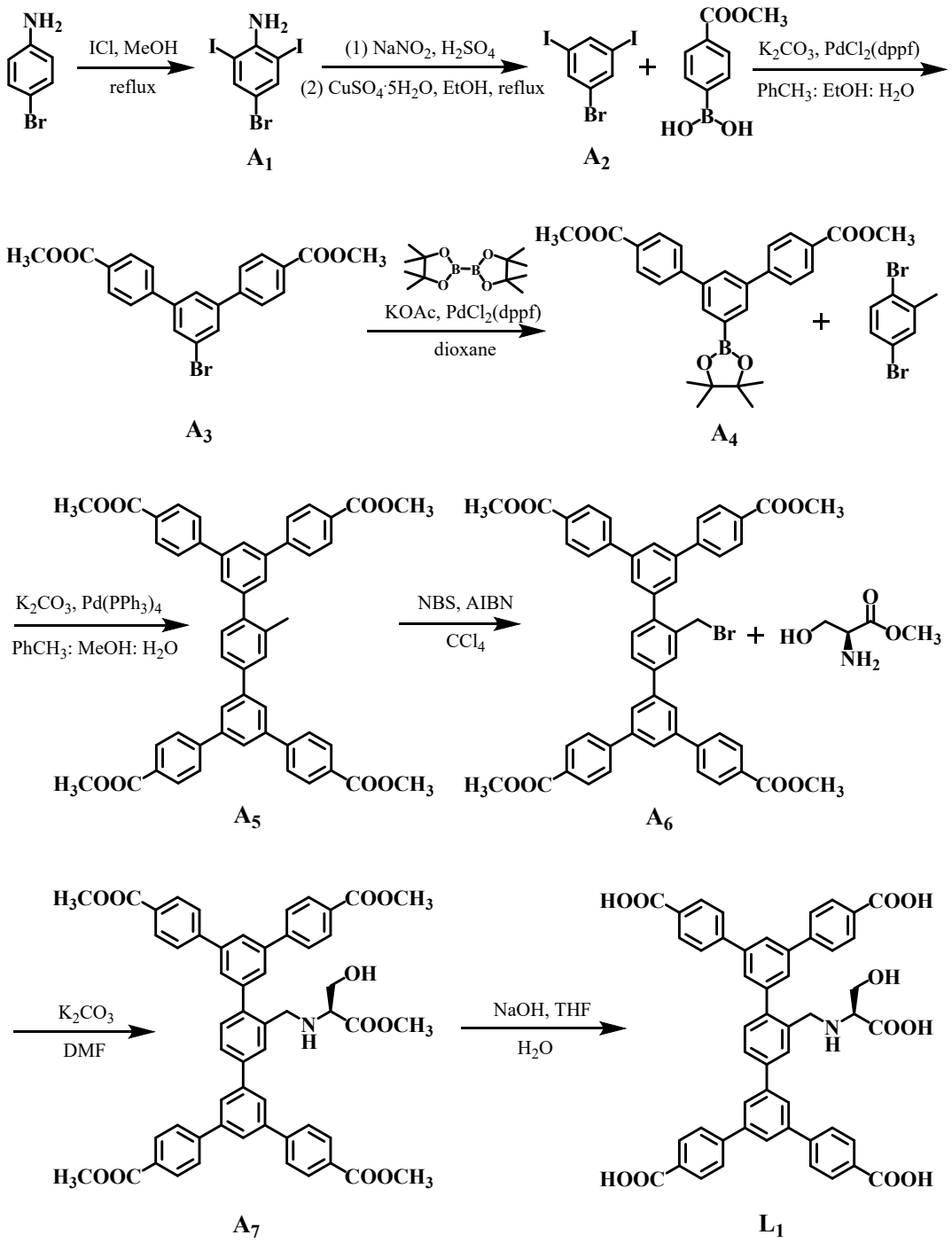
Table of Contents

1. Experimental section

1.1 Materials and general procedures

All reagents and solvents used in synthetic studies were commercially available and used without further purification. The ligands L_1, L_2 and L_3 were synthesized by routes in Schemes S1–S3. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DPX-300 spectrometer. Thermogravimetric analyses (TGA) were measured using a STA 409 PC thermal analyzer with a heating rate of 10 °C min^{-1} under air atmosphere. The powder X-ray diffraction (PXRD) patterns of the samples were measured on a RIGAKU-DMAX2500 X-ray diffractometer with Cu-K*a* radiation. Elemental analyses of C, H and N were measured on a Perkin-Elmer 240 elemental analyzer. Nitrogen adsorption experiments were performed on a Shimadzu ASAP2010. Solid-state and solution-state circular dichroism (CD) spectra were recorded on a MOS-450 spectrometer at room temperature. Optical absorption spectra were recorded on a T2602 Dual-Beam UV-Vis Spectrophotometer. X-ray photoelectron spectroscopy was carried out by THERMO SCIENTIFIC ESCALAB 250Xi. Scanning electron microscope (SEM) images and Energy Dispersive X-ray Spectroscopy (EDS) were carried out using JSM-7610FPlus and ULTIM MAX 40, respectively. High performance liquid chromatography (HPLC) was performed on a Shimadzu LC 20A with a specific chiral column and UV detector.

1.2. Ligand synthesis



Scheme S1. Synthetic route of L_1.

Synthesis of compound A_1. 4-bromoaniline (246.44 mmol, 42.40 g) and ICl (616.10 mmol, 100 g) were refluxed in methanol solution (700 mL) at 78 ℃ for 36 h. After cooling to room temperature, a brown powder was filtered off, washed with methanol (3 × 30 mL), saturated Na_2SO_3 solution (3 × 30 mL) and water, and dried to give a brown solid. Yield: 79.38 g (76%).

Synthesis of compound A_2. Compound A_1 (18.05 g, 42.60 mmol), H_2SO_4 (6 mL),

EtOH (300 mL), and $NaNO_2$ (7.32 g, 106.2 mmol), $CuSO_4.5H_2O$ (1.05g, 4.26 mmol) were added to a 500 mL round-bottom flask. The reaction mixture was heated to reflux for 1.5 hours and then cooled to room temperature. The orange powders were filtered and washed with ethanol and water. Yield: 16.06 g (92 %).

Synthesis of compound A_3. A 250 mL three round-bottom flask was charged with compound A_2 (2.1 mmol, 0.86 g) and 4-methoxycarbonylphenylboronic acid (4.62 mmol, 0.83 g) in a mixture solvent of $PhCH_3$/EtOH/H_2O (180 mL, V/V/V, 4/1/4). After stirring for 30 min under N_2, K_2CO_3 (10 mmol, 1.38 g) and $PdCl_2$(dppf) (0.11 mmol, 80.19 mg) were added. The reaction mixture was heated at 60 °C for 5~6 h under N_2. The mixture was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by flash chromatography using dichloromethane/petroleum ether (V/V, 2:1) as eluent to obtain a white solid. Yield: 0.64 g (72 %).

Synthesis of compound A_4. Compound A_3 (12 mmol, 5.10 g), Bis(pinacolato)diboron (19.89 mmol, 5.04 g) and KOAc (56.12 mmol, 5.5 g) were added to 1,4-dioxane (20 ml) at room temperature under N_2 for 30 min, $PdCl_2$(dppf) (0.69 mmol, 503.1 mg) was added. The reaction mixture was heated at 80 °C for 12 h under N_2. The mixture was extracted with $CHCl_3$ (3 × 100 mL). The combined organic extracts were dried over anhydrous Na_2SO_4 and the solvent removed under reduced pressure. The crude product was purified by flash chromatography using dichloromethane/petroleum ether (V/V, 3/1) as eluent to obtain a white solid. Yield: 5.10 g (90 %).

Synthesis of compound A_5. 2,5-dibromotoluene (8 mmol, 2 g), compound A_4 (18.4 mmol, 8.68 g) and K_2CO_3 (80 mmol, 11.06 g) were added to a mixture solvent of $PhCH_3$/MeOH/H_2O (180 mL, V/V/V, 4/1/4) at room temperature under N_2 for 30 min, $Pd(PPh_3)_4$ (0.56 mmol, 650 mg) was added. The mixture was extracted with $CHCl_3$ (3×100 mL). The organic layer was dried over anhydrous Na_2SO_4 and evaporated, then the grey crude product was purified by flash chromatography using dichloromethane/petroleum ether (V/V, 2/1) as eluent to obtain a white solid. Yield: 4.31 g (69 %). ^{1}H NMR (600 MHz, $CDCl_3$), δ (ppm): 8.17 (8 H, t, J = 8.7 Hz), 7.90 (2

H, s), 7.86 (2 H, d, J = 11.6 Hz), 7.78 (8 H, dd, J = 13.6 Hz), 7.67 (3 H, s), 7.63 (1 H, s), 7.48 (1 H, d, J = 7.7 Hz), 3.96 (12 H, d, J = 4.4 Hz), 2.48 (3 H, s).

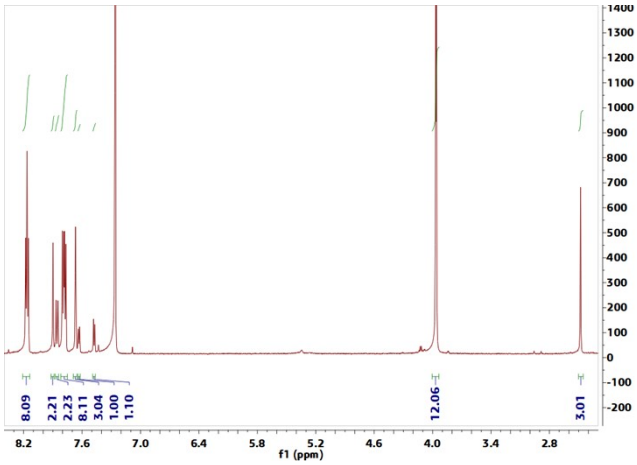


Figure S1. (a) ^{1}H NMR analysis of compound A_5.

Synthesis of compound A_6. Compound A_5 (6.92 mmol, 5.4 g), N-bromosuccinimide (12.92 mmol, 2.3 g) and 2,2′-azobis(2-methylpropionitrile) (AIBN) (1.17 mmol, 0.2 g) were added to a round bottom flask containing CCl_4 (120 mL) and $CHCl_3$ (40 mL). The flask was equipped with a water condenser and reflux at 80 °C under nitrogen atmosphere for 24 h. Yield: 5.66 g (95%).

Synthesis of methyl *L*-serinate. Under the condition of ice water bath, thionyl chloride (0.14 mol, 10 mL) was slowly added to 120 mL methanol solution for 6 h, and then *L*-serine (0.08 mol, 8.41 g) was added to the above solution, reacted at 60 °C for 8 h, cooled to room temperature and evaporated. The corresponding *L*-serine methyl ester hydrochloride was obtained. Then *L*-serine methyl ester hydrochloride was added to the mixed solution of dichloromethane (150 mL) and saturated K_2CO_3 aqueous solution (150 mL). The organic phase was dried with anhydrous Na_2SO_4 and evaporated to obtain a viscous yellowish liquid methyl *L*-serinate. Yield: 5.24 g (55%).

Synthesis of compound A_7. A mixture of methyl *L*-serinate (20 mmol, 2.38 g) and anhydrous K_2CO_3 (20 mmol, 2.76 g) in DMF solution (35 mL) were stirring at room temperature for 24 h, and then compound A_6 (5 mmol, 4.30 g) and $CHCl_3$ (18 mL) were added to the mixed solution. The reaction mixture was heated at 50 °C for 72 h, and then slowly cooled to room temperature. The mixture was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts evaporated under reduced pressure. The

crude product was purified by flash chromatography using dichloromethane/methyl alcohol (V/V, 100:1) as eluent to obtain white powder product. Yield: 2.29 g (51%).

Synthesis of compound L_1. Compound A_7 (5 mmol, 4.49 g) was added to a mixed solution of NaOH aqueous solution (1.8 M, 70 mL) and THF (15 mL). The reaction mixture was heated at 67 °C for 18 h, and then the THF was removed under a vacuum. Adding dilute HCl to the remaining aqueous solution until the pH value of the solution attained 1~2. The resulted solid was collected by filtration, washed with water, and dried to give the final product as white powder. Yield: 3.97 g (96%). ^{1}H NMR (600 MHz, DMSO), δ (ppm): 8.30 (1 H, s), 8.12 – 8.06 (16 H, m), 8.04 (5 H, d, J = 8.6 Hz), 8.01 (2 H, d, J = 8.3 Hz), 7.89 (2 H, d, J = 1.2 Hz), 7.62 (1 H, d, J = 7.9 Hz), 4.18 (2 H, dd, J = 45.8 Hz), 3.73 – 3.64 (2 H, m), 3.34 (1 H, s). ^{13}C NMR (151 MHz, DMSO) δ (ppm): 167.65, 144.45, 144.28, 141.80, 141.25, 140.53, 139.68, 130.62, 130.55, 130.41, 128.11, 128.11, 127.86, 125.83, 63.20, 61.64 – 61.58, 48.36 – 48.30, 40.63 – 39.48.

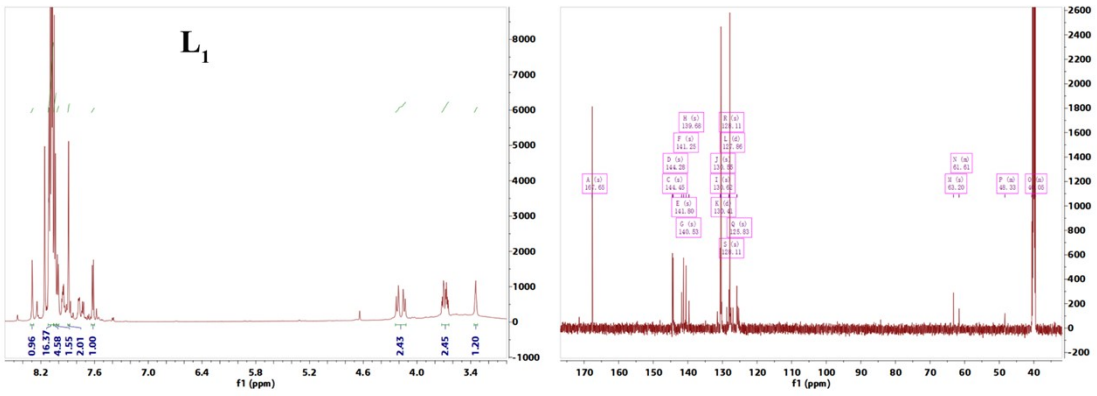
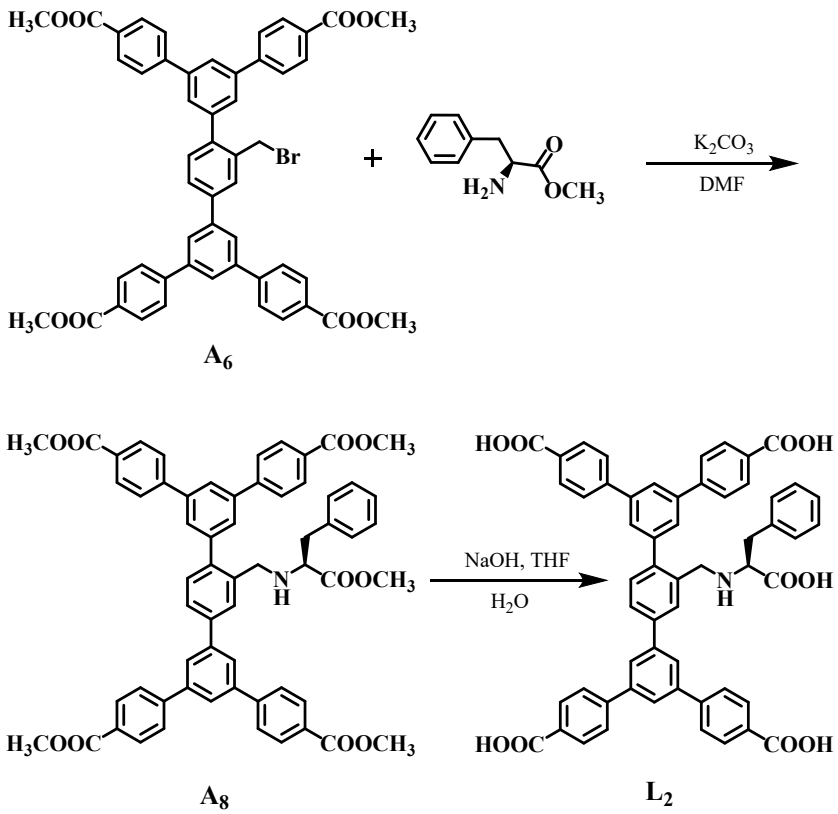


Figure S2. (a) ^{1}H NMR and (b) ^{13}C NMR analysis of ligand L_1.



Scheme S2. Synthetic route of L_2.

Synthesis of methyl *L*-phenylalaninate. Under the condition of ice water bath, thionyl chloride (0.14 mol, 10 mL) was slowly added to 150 mL methanol solution for 6 h, and then *L*-phenylalanine (0.08 mol, 13.2 g) was added to the above solution, reacted at 60 °C for 8 h, cooled to room temperature and evaporated. The corresponding methyl *L*-phenylalaninate hydrochloride was obtained. Then methyl *L*-phenylalaninate hydrochloride was added to the mixed solution of dichloromethane (150 mL) and saturated K_2CO_3 aqueous solution (150 mL). The organic phase was dried with anhydrous Na_2SO_4 and evaporated to obtain a viscous yellowish liquid methyl *L*-phenylalaninate. Yield: 8.75 g (61%).

Synthesis of compound A_8. A mixture of methyl *L*-phenylalaninate (20 mmol, 3.58 g) and anhydrous K_2CO_3 (20 mmol, 2.76 g) in DMF solution (35 mL) were stirring at room temperature for 24 h, and then compound A_6 (5 mmol, 4.30 g) and $CHCl_3$ (18 mL) were added to the mixed solution. The reaction mixture was heated at 50 °C for 72 h, and then slowly cooled to room temperature. The mixture was extracted with CH_2Cl_2 (3 × 100 mL). The combined organic extracts evaporated under reduced pressure. The

crude product was purified by flash chromatography using dichloromethane/methyl alcohol (V/V, 100:1) as eluent to obtain white powder product. Yield: 2.78 g (58%).

Synthesis of compound L_2. Compound A_8 (5 mmol, 4.79 g) was added to a mixed solution of NaOH aqueous solution (1.8 M, 70 mL) and THF (15 mL). The reaction mixture was heated at 67 °C for 18 h, and then the THF was removed under a vacuum. Adding dilute HCl to the remaining aqueous solution until the pH value of the solution attained 1~2. The resulted solid was collected by filtration, washed with water, and dried to give the final product as white powder. Yield: 4.26 g (96%). ^{1}H NMR (600 MHz, DMSO), δ (ppm): 8.12 – 8.07 (18 H, m), 8.03 (4 H, d, J = 8.5 Hz), 7.97 (1 H, d, J = 7.0 Hz), 7.87 (2 H, d, J = 1.4 Hz), 7.60 (1 H, d, J = 7.9 Hz), 7.09 (2 H, d, J = 7.4 Hz), 7.04 (2 H, t, J = 7.3 Hz), 6.99 (1 H, d, J = 6.8 Hz), 3.96 (2 H, d, J = 73.7 Hz), 2.95 (2 H, s), 2.54 – 2.52 (1 H, m). ^{13}C NMR (151 MHz, DMSO) δ (ppm): 167.59, 144.55, 144.39, 142.02 – 141.88, 141.21, 140.47, 139.56 – 139.53, 131.33 – 131.23, 130.46, 129.55, 128.34, 128.10 – 128.08, 127.88, 126.69 – 126.61, 125.87 – 125.80, 125.55 – 125.47, 40.72 – 39.28.

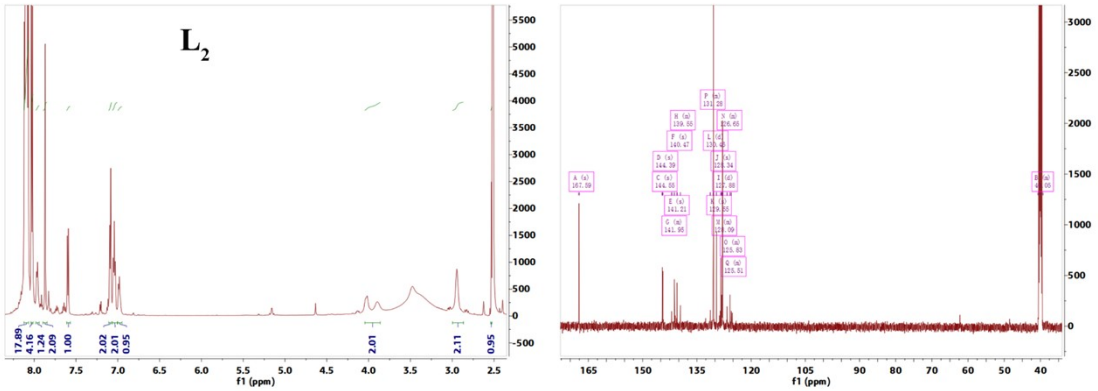
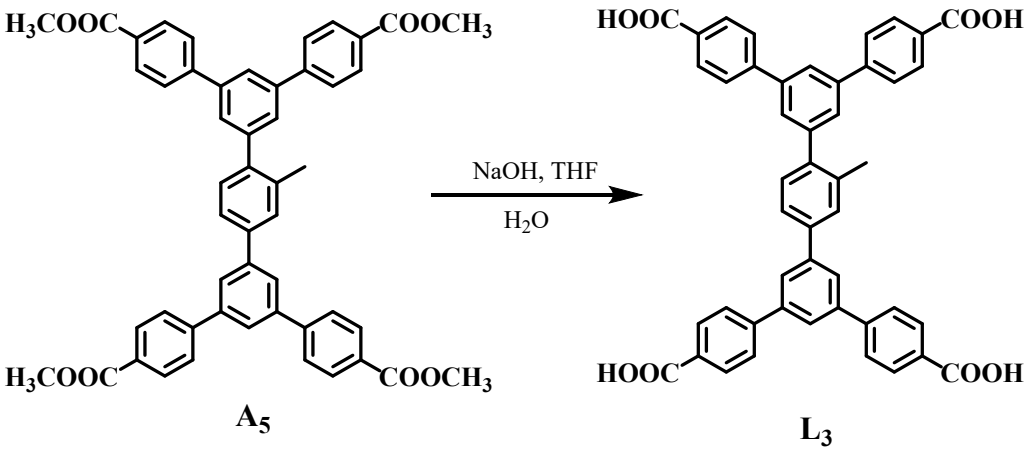


Figure S3. (a) ^{1}H NMR and (b) ^{13}C NMR analysis of ligand L_2.



Scheme S3. Synthetic route of L_3.

Synthesis of compound L_3. Compound A_5 (2 mmol, 1.56 g) was added to a mixed solution of NaOH aqueous solution (1.8 M, 40 mL), CH_3OH (20 mL) and THF (20 mL). The reaction mixture was heated at 78 °C for 18 h, and then the THF was removed under a vacuum. Adding dilute HCl to the remaining aqueous solution until the pH value of the solution attained 1~2. The resulted solid was collected by filtration, washed with water, and dried to give the final product as white powder. Yield: 1.42 g (98%). ^{1}H NMR (600 MHz, DMSO), δ (ppm): 13.05 (s, 4H), 8.08 (dd, J = 12.4, 6.4 Hz, 16H), 8.02 (d, J = 8.3 Hz, 4H), 7.95 (s, 1H), 7.86 (s, 1H), 7.81 (s, 2H), 7.56 (d, J = 7.9 Hz, 1H), 2.49 (s, 3H). ^{13}C NMR (151 MHz, DMSO) δ (ppm): 167.61, 167.58, 144.57, 144.41, 142.94, 142.02, 141.15, 140.76, 140.50, 139.51, 136.23, 130.44, 130.41, 130.34, 128.00, 127.89, 127.82, 125.78, 125.36, 20.92.

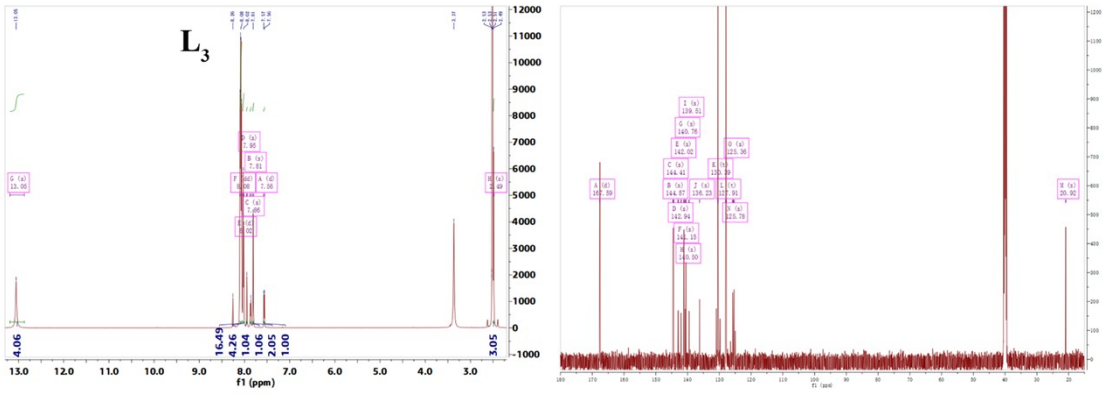


Figure S4. (a) ^{1}H NMR and (b) ^{13}C NMR analysis of ligand L_3.

1.3. Fe-HMOFs synthesis

Synthesis of Fe-HMOF-1: L_1 (0.1 mmol, 83 mg), $FeCl_3 \cdot 6H_2O$ (0.3 mmol, 80

mg), acetic acid (1.1 mL) and ethanol (1 mL) were dissolved in 10 mL DMF. The mixture was heated in oven at 140 °C for 10 hours. The resulting brown-red microcrystalline powders were centrifuged and washed with fresh DMF and acetone several times and finally stored in fresh acetone.

Synthesis of Fe-HMOF-2: L_2 (0.1 mmol, 89 mg), $FeCl_3 \cdot 6H_2O$ (0.3 mmol, 80 mg), acetic acid (1.3 mL) and ethanol (1 mL) were dissolved in 10 mL DMF. The mixture was heated in oven at 140 °C for 10 hours. The resulting brown-red microcrystalline powders were centrifuged and washed with fresh DMF and acetone several times and finally stored in fresh acetone.

Synthesis of Fe-MOF-CH_3: L_3 (0.05 mmol, 36.25 mg), $FeCl_3 \cdot 6H_2O$ (0.15 mmol, 40 mg), acetic acid (0.55 mL) and ethanol (0.5 mL) were dissolved in 6 mL DMF. The mixture was heated in oven at 140 °C for 10 hours. The resulting brown-red microcrystalline powders were centrifuged and washed with fresh DMF and acetone several times and finally stored in fresh acetone.

1.4. Cr-HMOFs synthesis

Synthesis of Cr-HMOF-1, Cr-HMOF-2 and Cr-MOF-CH_3: 50 mg, 100 mg, 200 mg and 400 mg $CrCl_3 \cdot 6H_2O$ were separately dissolved in 100 mL acetone to form a series of Cr^{3+} stock solutions with different concentrations (0.5 mg/mL, 1 mg/mL, 2 mg/mL, 4 mg/mL), respectively. Freshly prepared **Fe-HMOF-1**, **Fe-HMOF-2** and **Fe-MOF-CH_3** (about 800 mg) stored in acetone were separately soaked in each of the above stock solutions (20 mL) for about 2~3 hours at 80 °C. Notably, the replacement of the stock solution is carried out in ascending order of concentration, and the process is repeated several times until Fe-HMOFs turn dark green. After exchange, the resulting dark green powders were separately dispersed in 9 ml DMF and heated at 80 °C for about 48 hours, during which the DMF solution was changed 6 times. After that, these samples were further dispersed in 0.25 M hydrochloric acid aqueous solution for about 10 hours at 50 °C, and washed with water 3 times. And then, the solvent was exchanged sequentially with fresh THF (6 × 9 mL) and acetone (6 × 9 mL) at room temperature for four days. These solvent-exchanged samples **Cr-HMOF-1, Cr-HMOF-2 and Cr-MOF-CH_3** were then activated at 100 °C for 12 h under dynamic vacuum.

1.5. Experimental procedure for enantioadsorption separation in solution.

The activated samples **Cr-HMOF-1** or **Cr-HMOF-2** (200 mg) were separately soaked in 100 mL ethanol solutions of racemic 1-phenylethanol, 1-phenyl-1-propanol, 1-phenylbutan-1-ol and 1-phenyl-2-propanol (250 ppm) for adsorption with a stirring speed of 350 rpm at room temperature. After 30 minutes of adsorption, the soaked samples were filtered and washed 6 times with fresh anhydrous ethanol solution to remove the residual guest molecules on the outer surface of the sample particles. Then the samples were immersed in 9 mL fresh anhydrous ethanol solution at room temperature, and soaked 6 times within 2 days to extract the encapsulated guest molecules inside the pores. Finally, the ethanol solutions containing the extracted chiral compounds were collected together and concentrated to 0.3 mL for further detection of *ee* values by HPLC analysis. The solid adsorbents **Cr-HMOF-1** and **Cr-HMOF-2** could be reactivated by immersing them in hydrochloric acid methanol solution (0.30 M), tetrahydrofuran and acetone solutions for 2 days, respectively. Afterwards, they were dried under vacuum at 100 °C and reused for continuous separation.

2. General characterization

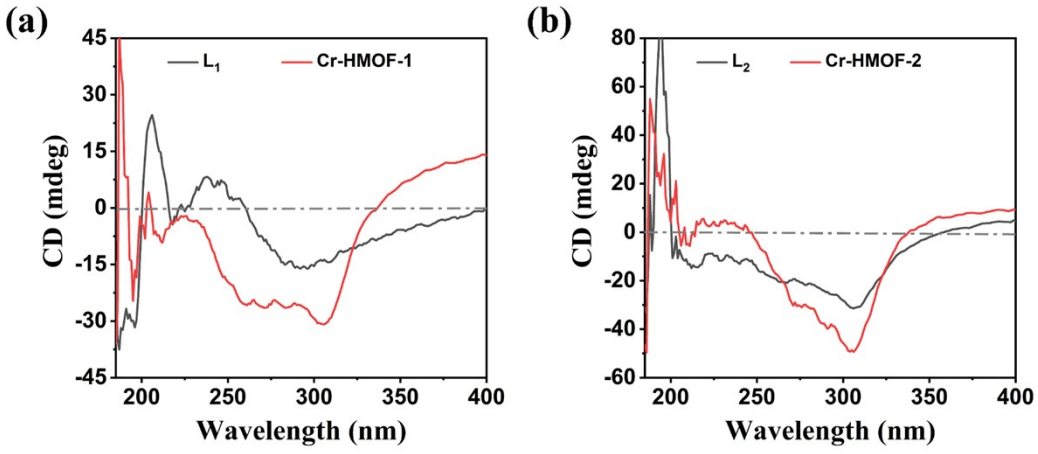


Figure S5. Solid-state CD spectra of free ligands L_1 and L_2, and **Cr-HMOF-1** and **Cr-HMOF-2**.

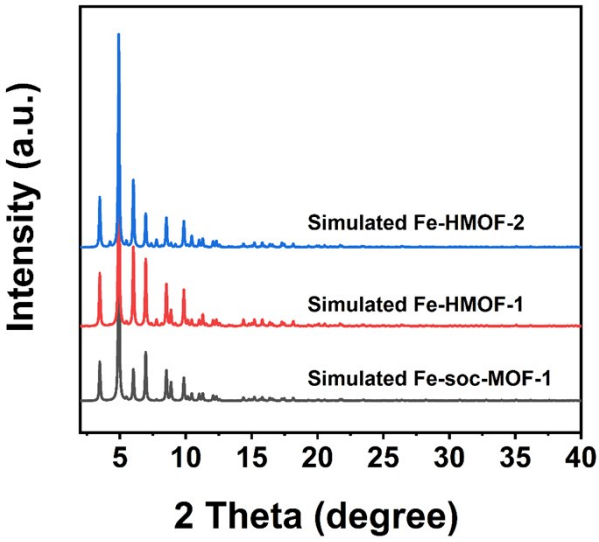


Figure S6. PXRD patterns of simulated **Fe-HMOF-1** and **Fe-HMOF-2** and **Fe-soc-MOF-1**.

2.1 Crystal structure analysis

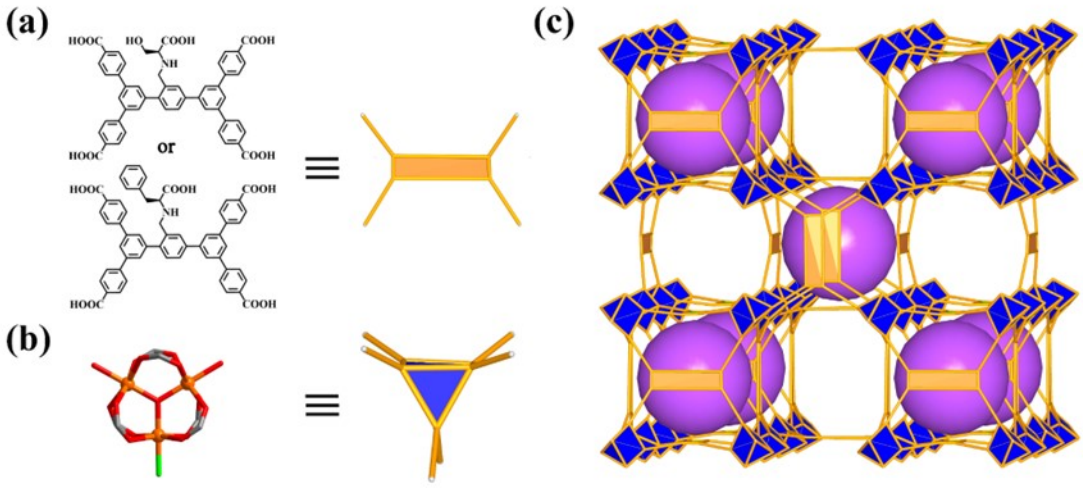


Figure S7. (a) L_1 or L_2 and simplified 4-connected node; (b) $Fe_3(\mu_3\text{-}O)(H_2O)_2Cl(COO^-)_6$ SBU and simplified 6-connected node; (c) the augmented *soc* net.

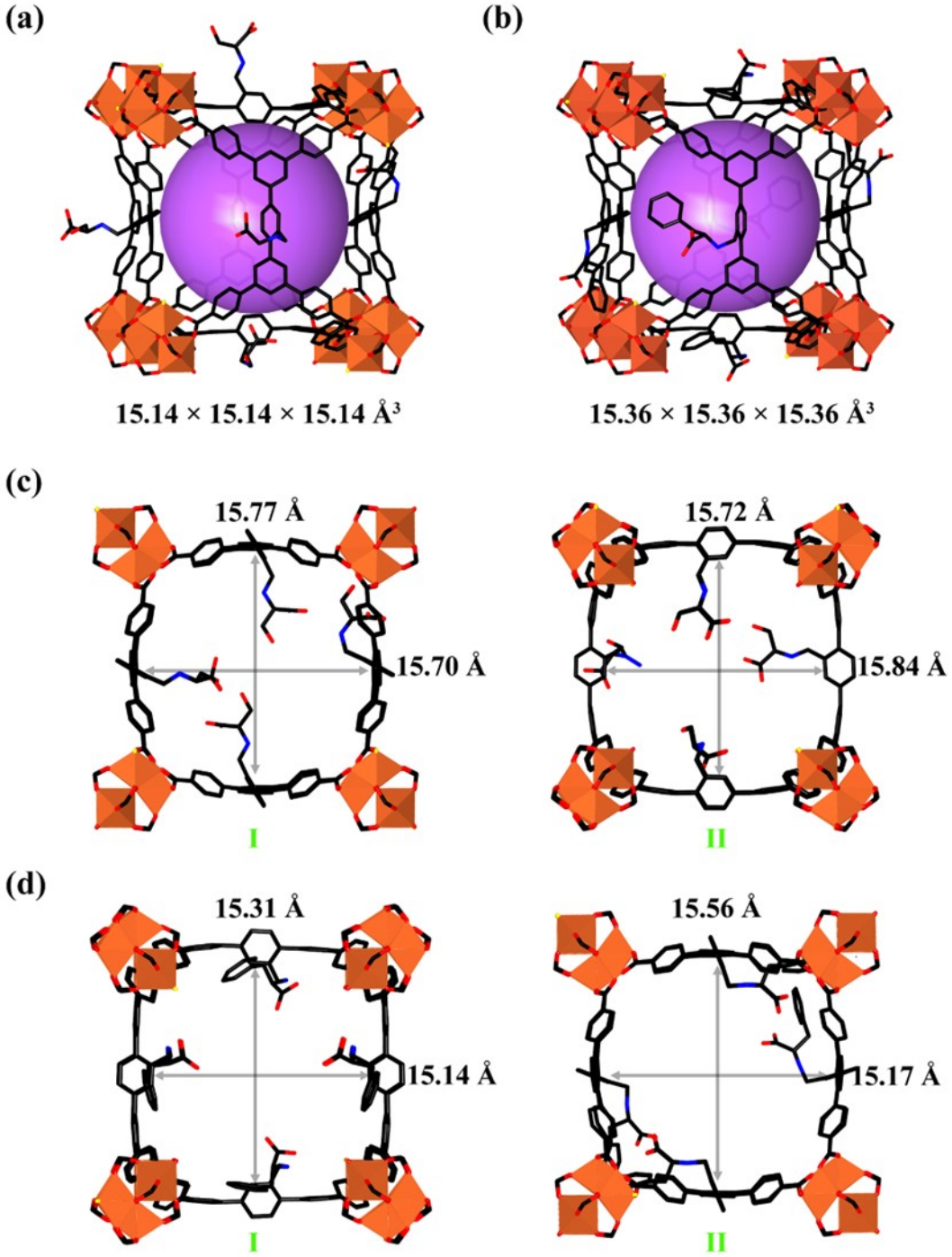


Figure S8. The sizes of (a and b) cubic cages and (c and d) two types of 1D channels in **Fe-HMOF-1** and **Fe-HMOF-2**.

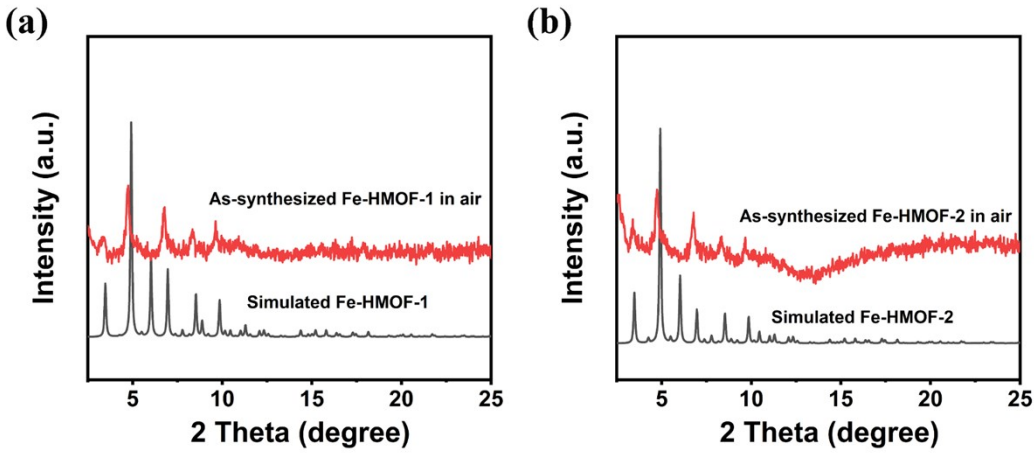


Figure S9. Comparison of PXRD patterns of simulated **Fe-HMOF-1** and **Fe-HMOF-2** and as-synthesized **Fe-HMOF-1** and **Fe-HMOF-2**.

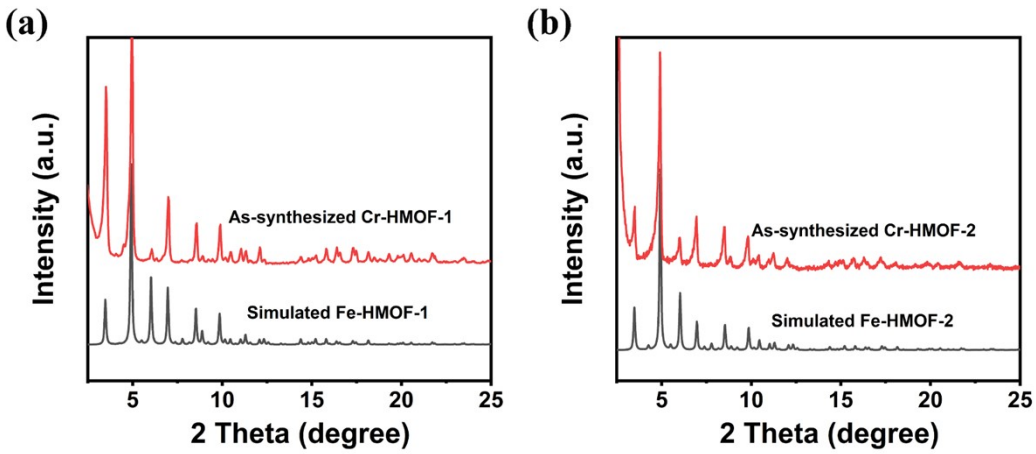


Figure S10. Comparison of PXRD patterns of simulated **Fe-HMOF-1** and **Fe-HMOF-2**, and as-synthesized **Cr-HMOF-1** and **Cr-HMOF-2**.

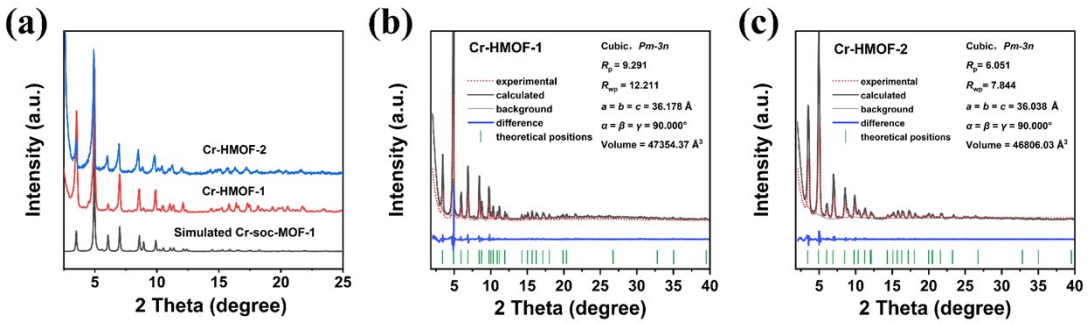


Figure S11. (a) Comparison of PXRD patterns of as-synthesized **Cr-HMOF-1**, **Cr-HMOF-2** and simulated Cr-soc-MOF-1; (b and c) Rietveld refinement results based on the experimental PXRD

data

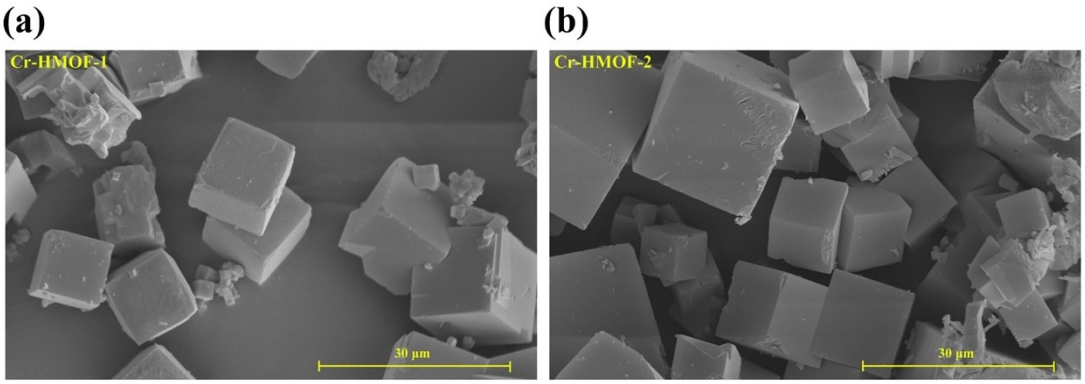


Figure S12. (a) SEM images of **Cr-HMOF-1** and **Cr-HMOF-2**.

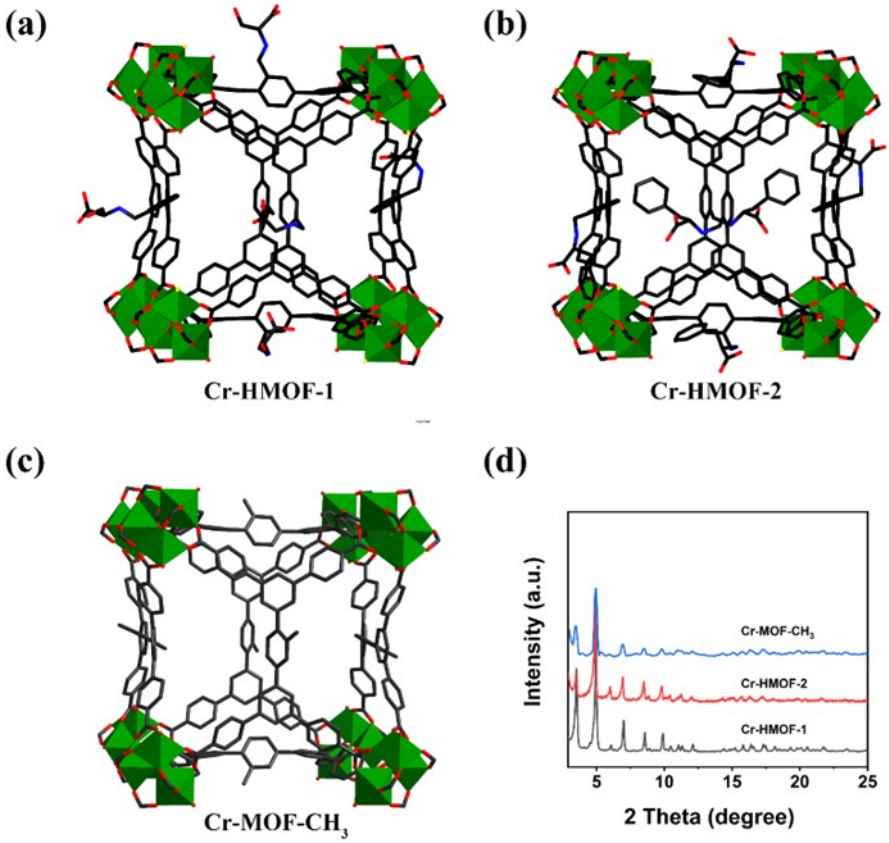


Figure S13. (a–c) Cubic cage structures and (d) PXRD patterns of **Cr-HMOF-1** and **Cr-HMOF-2** and **Cr-MOF-CH_3**.

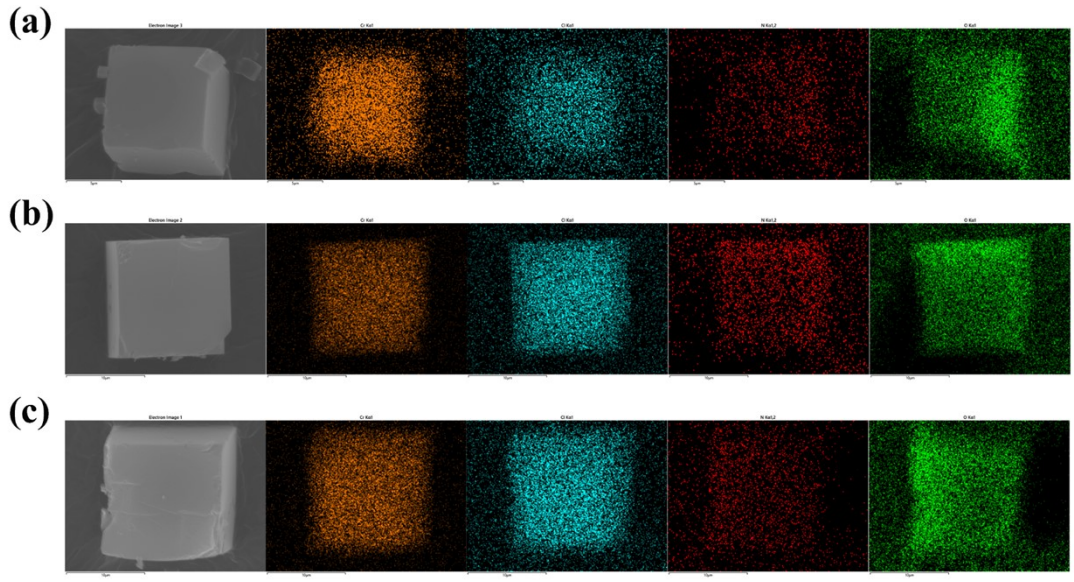


Figure S14. Energy-dispersive X-ray spectroscopy elemental mapping analysis of (a) **Cr-MOF-CH_3**, (b) **Cr-HMOF-1** and (c) **Cr-HMOF-2** (Cr, orange; Cl, blue; N, red; O, green).

Table S1 Elemental analysis

	Experimental Value			Theoretical Value		
	C (%)	N (%)	H (%)	C (%)	N (%)	H (%)
Decomposed L_1	71.93	1.27	4.52	72.54	1.69	4.51
Decomposed L_2	72.40	1.05	4.51	75.75	1.58	4.65
Fe-HMOF-1	61.34	1.54	3.87	60.13	1.40	3.57
Fe-HMOF-2	62.00	1.15	3.71	63.52	1.32	3.84
Cr-HMOF-1	60.06	1.00	4.06	60.60	1.41	3.60
Cr-HMOF-2	59.35	1.19	4.32	63.99	1.33	3.87

Table S2 ICP-MS results of metal metathesis synthesized **Cr-HMOF-1** and **Cr-HMOF-2**

Sample	Metal 1	C_o (mg L^{-1})	Metal 2	C_o (mg L^{-1})	Molar percentage (Cr^{3+})
Cr-HMOF-1	Cr^{3+}	6.860	Fe^{3+}	0.236	96.90 %
Cr-HMOF-2	Cr^{3+}	8.435	Fe^{3+}	0.055	99.35 %

Table S3 ICP-MS results of supernatant of **Cr-HMOF-1** and **Cr-HMOF-2** treated under different

conditions

Sample	Sample Mass (mg)	Volume of supernatant (mL)	Concentration of Cr^{3+} (mg L^{-1})	Leaching ratio (%)
1 M HCl treated **Cr-HMOF-1**	60	10	0.406	0.193
3 M HCl treated **Cr-HMOF-1**	60	10	0.444	0.211
pH = 12 treated **Cr-HMOF-1**	60	10	0.118	0.056
1 M HCl treated **Cr-HMOF-2**	60	10	0.086	0.041
3 M HCl treated **Cr-HMOF-2**	60	10	0.291	0.139
pH = 12 treated **Cr-HMOF-2**	60	10	0.027	0.013

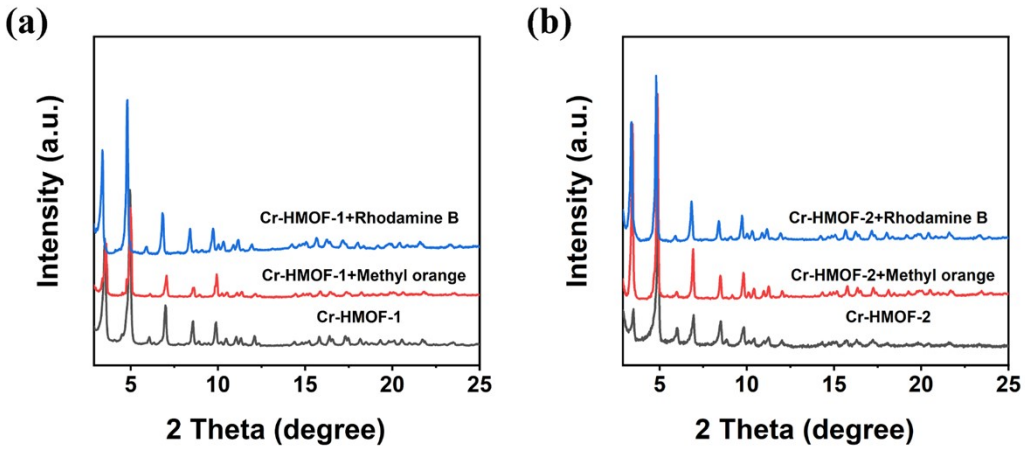


Figure S15. Comparison of PXRD patterns of **Cr-HMOF-1** and **Cr-HMOF-2** before and after dye adsorption.

Dye uptake experiments

The activated **Cr-HMOF-1** (5 mg) or **Cr-HMOF-2** (5 mg) were soaked in a

saturated solution of methyl orange or rhodamine B in ethanol for 24 h, respectively. To remove the dye adsorbed on the surface of crystals, the resulting crystals were washed with ethanol until the solution became colorless. Then the samples were sonicated and soaked with ethanol and the resulting solution was diluted to 250 mL. The amounts of dyes were determined by comparing the UV absorptions with the standard curves.

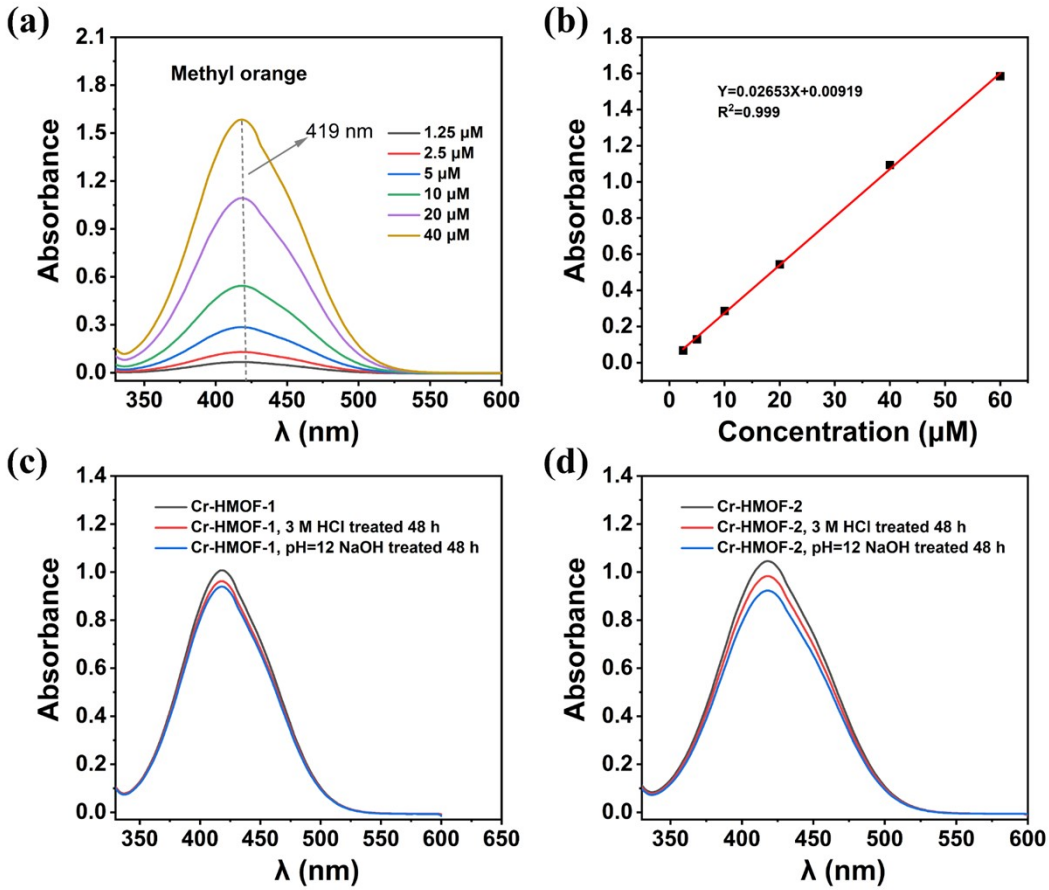


Figure S16. (a) UV-Vis absorption spectra of methyl orange with different concentrations; (b) the standard curves; (c and d) adsorption capacity of methyl orange by **Cr-HMOF-1** and **Cr-HMOF-2** treated under different conditions (selected wavelength = 419 nm, concentration range from 1.25 to 40 μM).

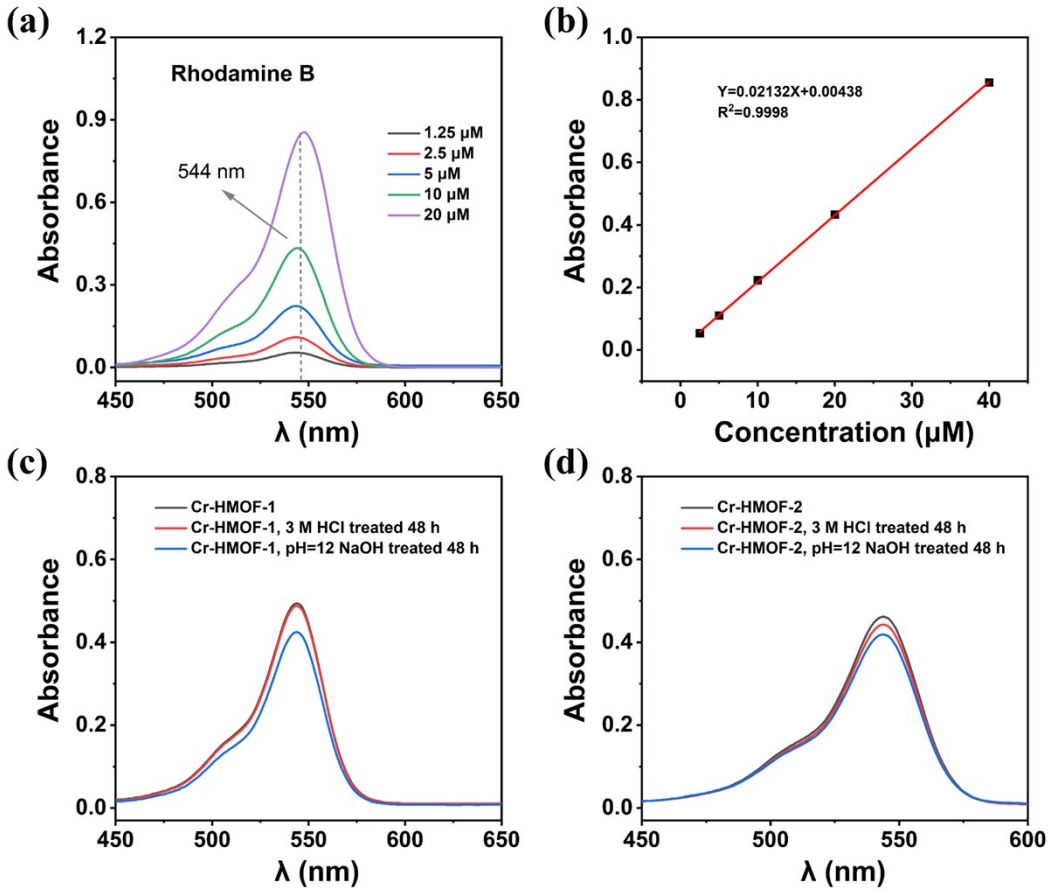


Figure S17. (a) UV-Vis absorption spectra of rhodamine B with different concentrations; (b) the standard curves; (c and d) adsorption capacity of rhodamine B by **Cr-HMOF-1** and **Cr-HMOF-2** treated under different conditions (selected wavelength = 544 nm, concentration range from 1.25 to 20 μM).

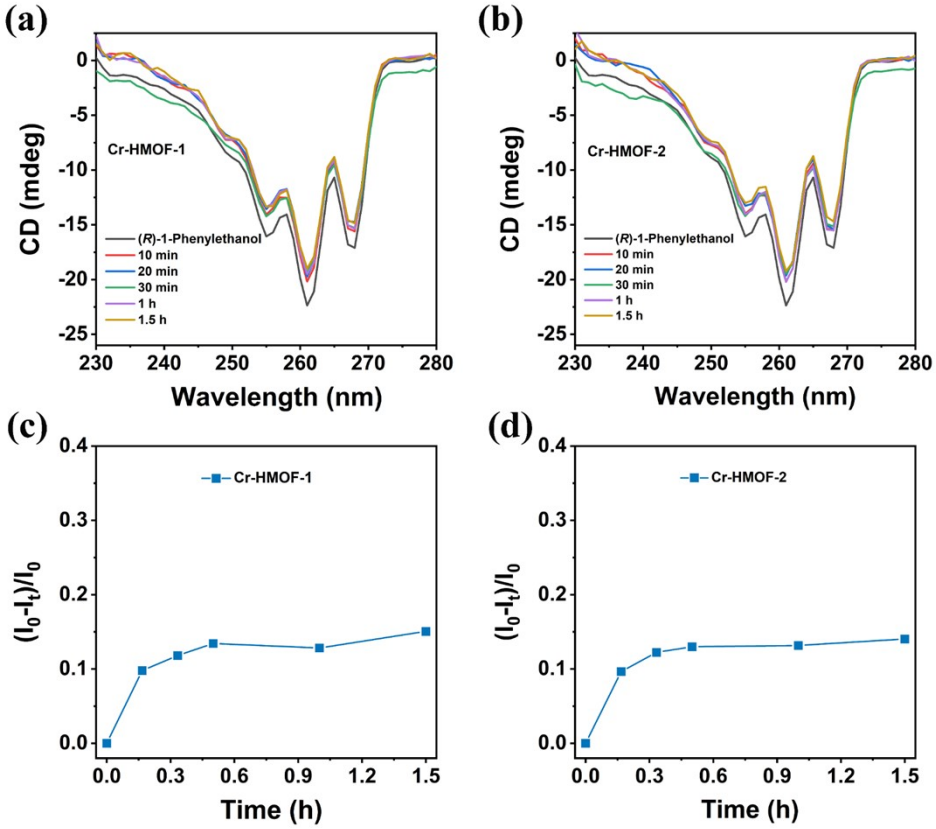


Figure S18. (a and b) CD spectra of *R*-1-phenylethanol ethanol solution after adsorbed by materials **Cr-HMOF-1** or **Cr-HMOF-2** at different contact time; (c and d) the adsorption efficiency $[(I_0 - I_t)/I_0]$ was calculated from the changes of CD signals at the maximum wavelength. [V = 25 mL, m (adsorbent) = 50 mg, temperature = 25 °C, initial concentration (adsorbate) = 4×10^{-3} M]

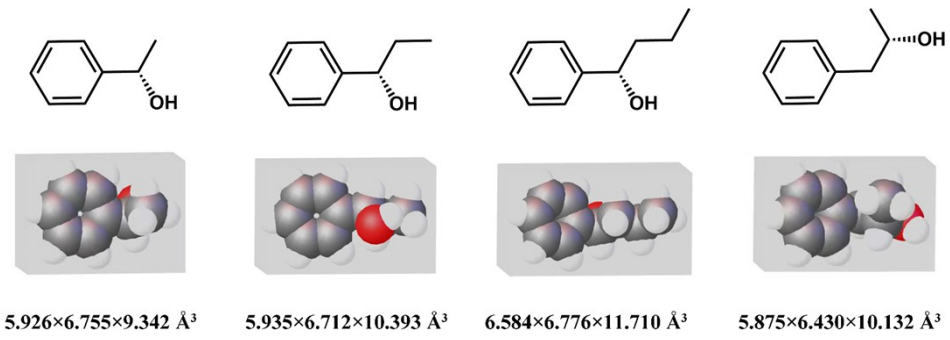


Figure S19. Molecular dimensions of 1-phenylethanol, 1-phenyl-1-propanol, 1-phenylbutan-1-ol and 1-phenyl-2-propanol

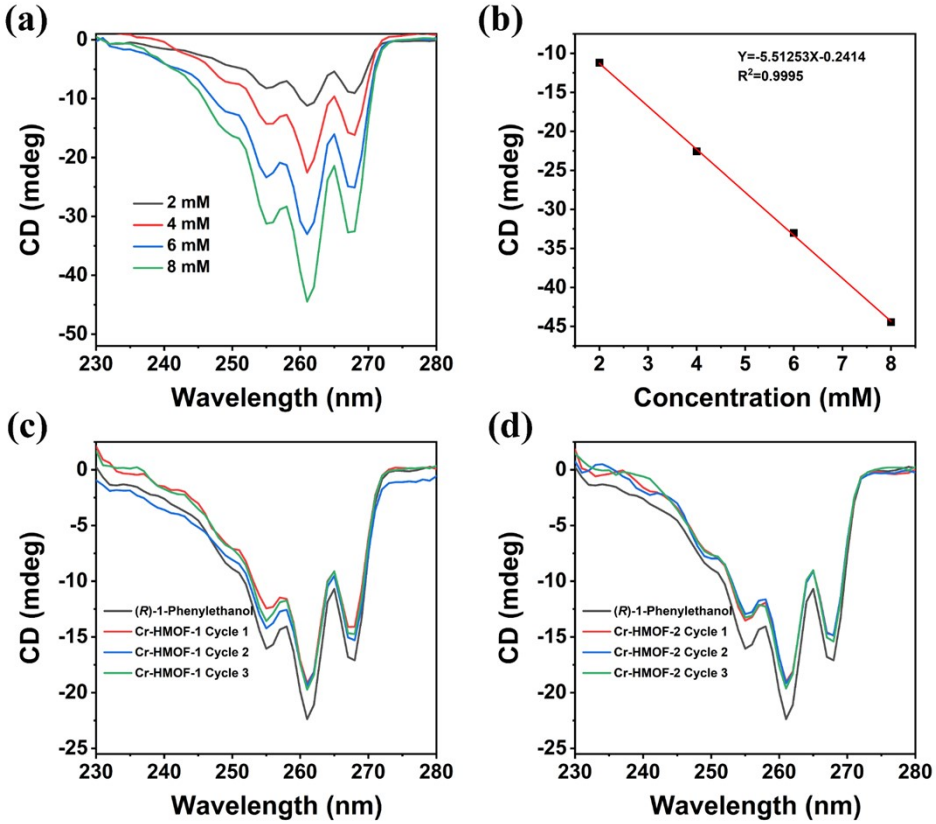


Figure S20. (a) CD spectra of (*R*)-1-phenylethanol ethanol solution with different concentrations; (b) the standard curves; (c and d) CD spectra of (*R*)-1-phenylethanol adsorbed by materials **Cr-HMOF-1** and **Cr-HMOF-2** in three cycles [V = 25 mL, m (adsorbent) = 50 mg, temperature = 25 °C, initial concentration (adsorbate) = 4×10^{-3} M, t = 2 h].

Table S4 Recyclable Q_e and *ee* values on **Cr-HMOF-1** and **Cr-HMOF-2** for 1-phenylethanol

	Cr-HMOF-1			**Cr-HMOF-2**		
	Cycle 1	Cycle 2	Cycle 3	Cycle 1	Cycle 2	Cycle 3
Q_e (mg g^{-1})	28.65	26.65	23.44	29.7	28.43	24.29
ee (%)	86.8	85.8	80.8	98.6	95.2	94.6

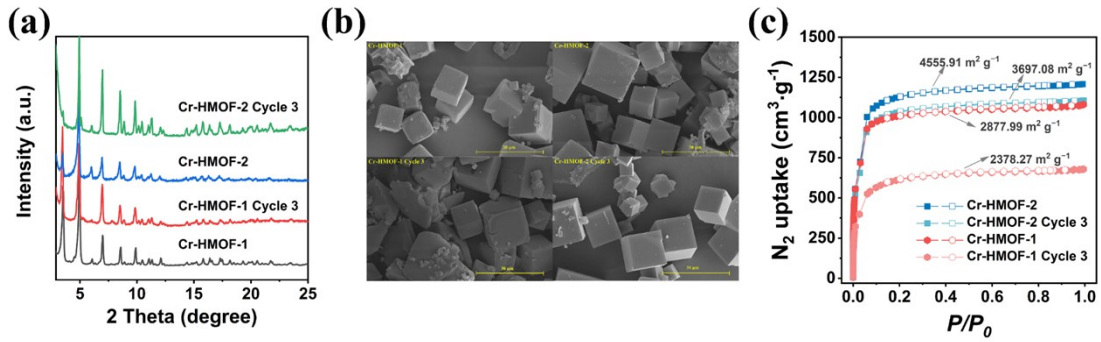
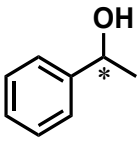
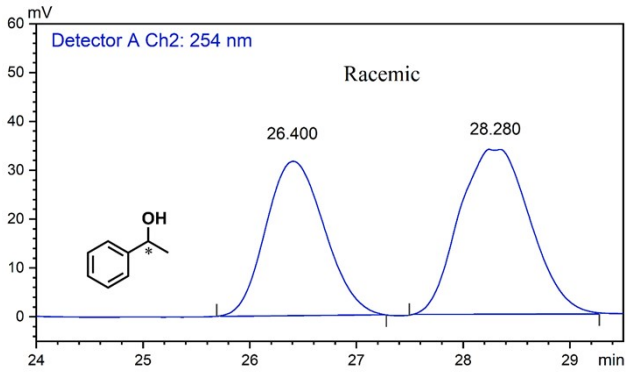


Figure S21. (a) PXRD patterns, (b) SEM images and (c) N_2 adsorption and desorption isotherms of **Cr-HMOF-1** and **Cr-HMOF-2** after three cycles.

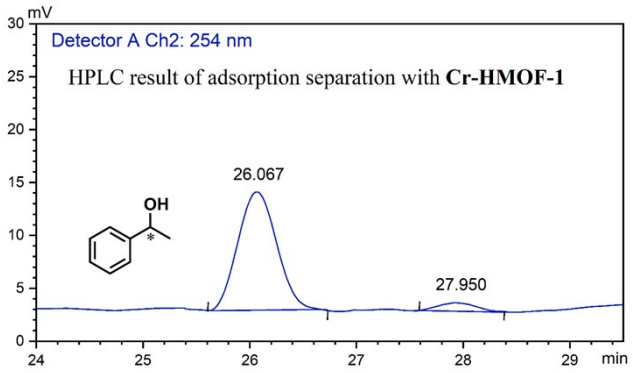
3. HPLC results of enantioseparation



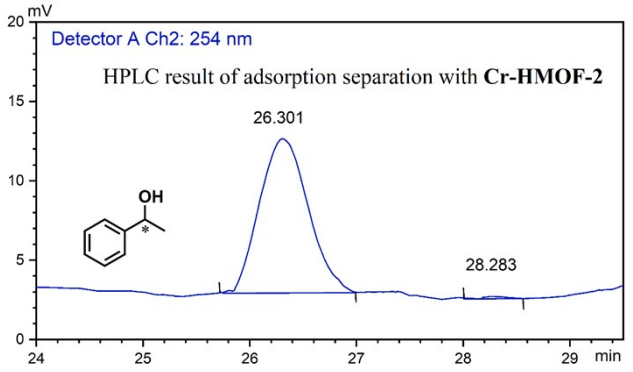
Chiral HPLC analysis: IG column; n-hexane/ethanol = 95/5 (v/v); flow rate = 0.3 mL min^{-1}; 254 nm; 35 °C; t_R = 26.400 min, t_S = 28.280 min.



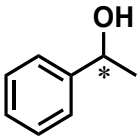
Serial Number	Type	Retention Time	Peak Area	Area %
1	(*R*)-1-phenylethanol	26.400	68003.91	43.7
2	(*S*)-1-phenylethanol	28.280	87487.53	56.3
The Toal			155491.44	



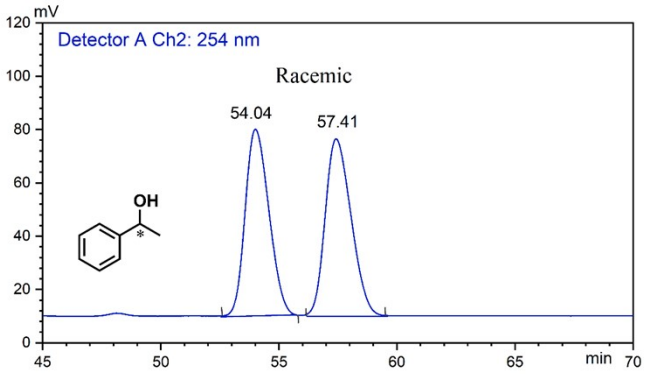
Serial Number	Type	Retention Time	Peak Area	Area %
1	(*R*)-1-phenylethanol	26.067	18599.904	93.4
2	(*S*)-1-phenylethanol	27.950	1312.913	6.6
The Toal			19912.817	



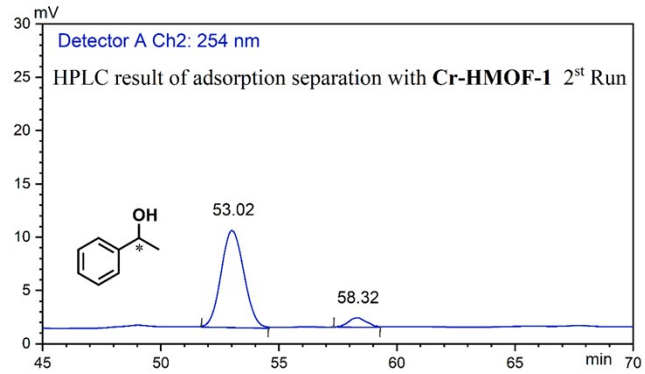
Serial Number	Type	Retention Time	Peak Area	Area %
1	(*R*)-1-phenylethanol	26.301	1525.24	99.3
2	(*S*)-1-phenylethanol	28.283	10.854	0.7
The Toal			1536.094	



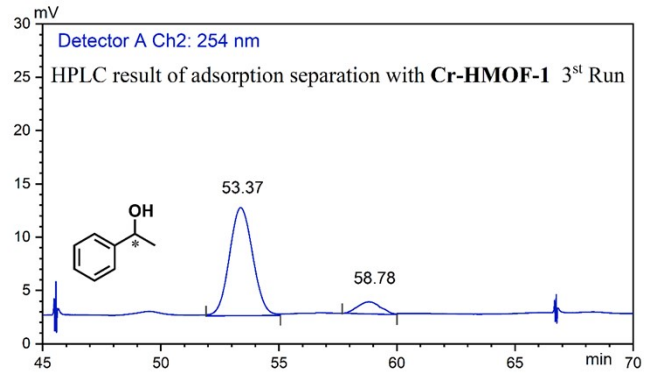
Chiral HPLC analysis: IG column; A: n-hexane/ isopropanol = 98/2 (v/v), B: ethanol = 100 (v); flow rate = 0.3 mL min^{-1}; 254 nm; 25 ℃; t_R = 54.04 min, t_S = 57.41 min.



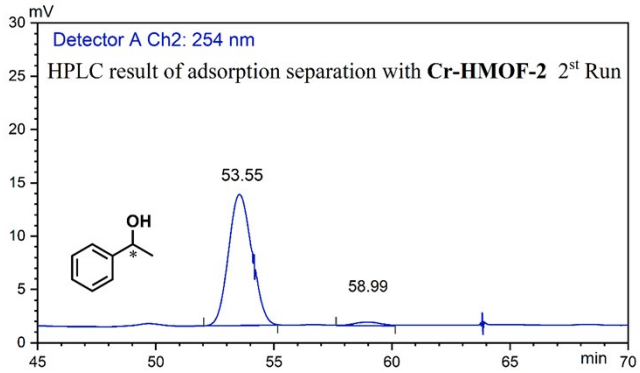
Serial Number	Type	Retention Time	Peak Area	Area %
1	(*R*)-1-phenylethanol	54.04	588093.34	48.6
2	(*S*)-1-phenylethanol	57.41	621639.31	51.4
The Toal			1209732.65	



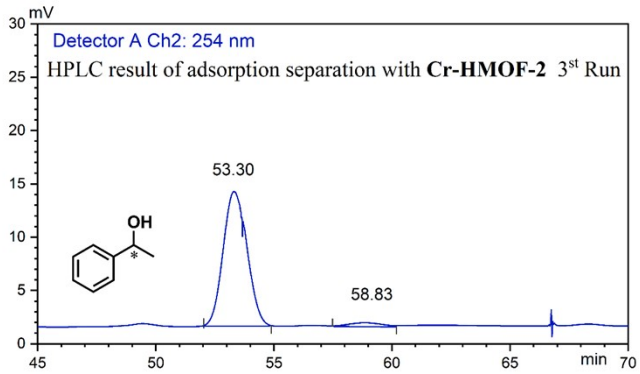
Serial Number	Type	Retention Time	Peak Area	Area %
1	(*R*)-1-phenylethanol	53.02	4012.85	92.9
2	(*S*)-1-phenylethanol	58.32	305.30	7.1
The Toal			4318.35	



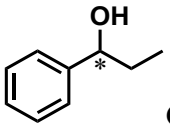
Serial Number	Type	Retention Time	Peak Area	Area %
1	(*R*)-1-phenylethanol	53.37	3376.14	90.4
2	(*S*)-1-phenylethanol	58.78	357.70	9.6
The Toal			3733.84	



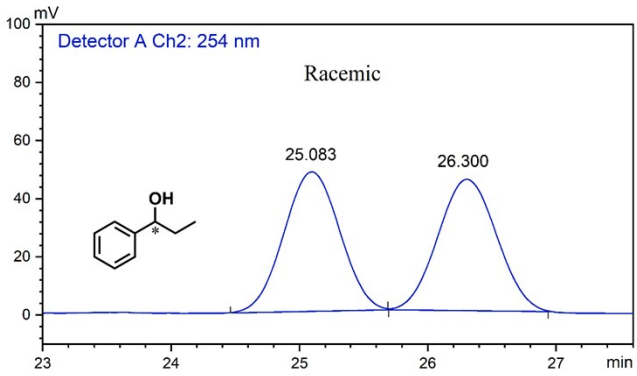
Serial Number	Type	Retention Time	Peak Area	Area %
1	(*R*)-1-phenylethanol	53.55	3520.02	97.6
2	(*S*)-1-phenylethanol	58.99	87.57	2.4
The Toal			3607.59	



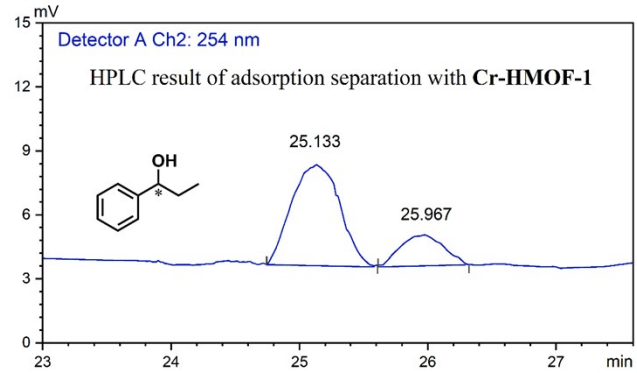
Serial Number	Type	Retention Time	Peak Area	Area %
1	(*R*)-1-phenylethanol	35.30	4421.76	97.3
2	(*S*)-1-phenylethanol	58.83	120.39	2.7
The Toal			4542.15	



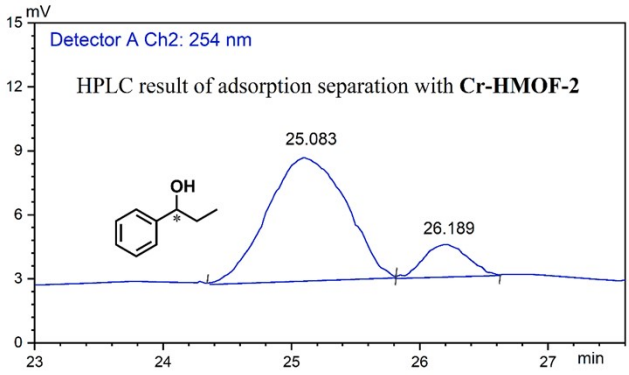
Chiral HPLC analysis: IG column; n-hexane/ethanol = 95/5 (v/v); flow rate = 0.3 mL min^{-1}; 254 nm; 35 °C; t_R = 25.083 min, t_R = 26.300 min.



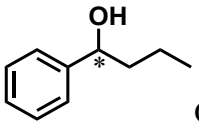
Serial Number	Type	Retention Time	Peak Area	Area %
1	1-phenyl-1-propanol	25.083	62891.76	49.8
2	1-phenyl-1-propanol	26.300	63337.97	50.2
The Toal			126229.73	



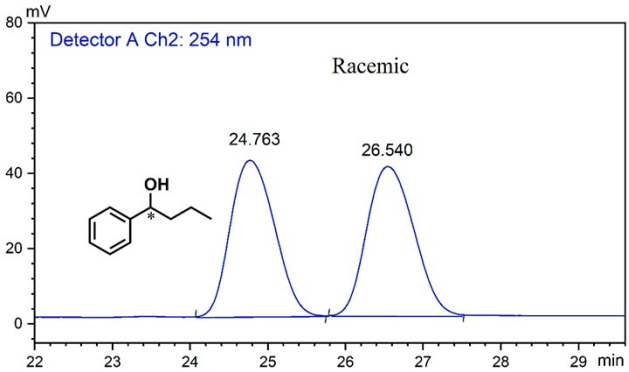
Serial Number	Type	Retention Time	Peak Area	Area %
1	1-phenyl-1-propanol	25.133	297.98	79.0
2	1-phenyl-1-propanol	25.967	78.99	21.0
The Toal			376.97	



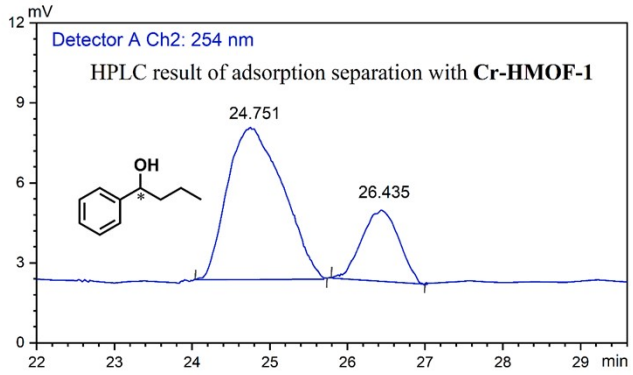
Serial Number	Type	Retention Time	Peak Area	Area %
1	1-phenyl-1-propanol	25.083	728.141	89.0
2	1-phenyl-1-propanol	26.189	90.025	11.0
The Toal			818.166	



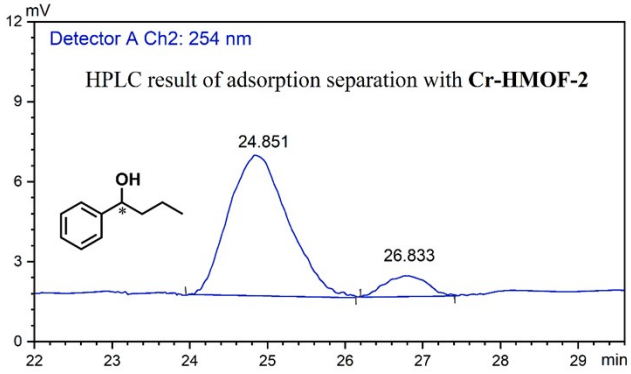
Chiral HPLC analysis: OJ-H column; n-hexane/isopropanol/trifluoroacetic acid = 95/5/0.1 (v/v/v); flow rate = 0.3 mL min^{-1}; 254 nm; 25 ℃; t_R = 24.763 min, t_R = 26.540 min.



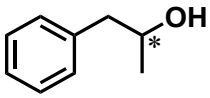
Serial Number	Type	Retention Time	Peak Area	Area %
1	1-phenylbutan-1-ol	24.763	1540255	49.9
2	1-phenylbutan-1-ol	26.540	1543884	50.1
The Toal			3084139	



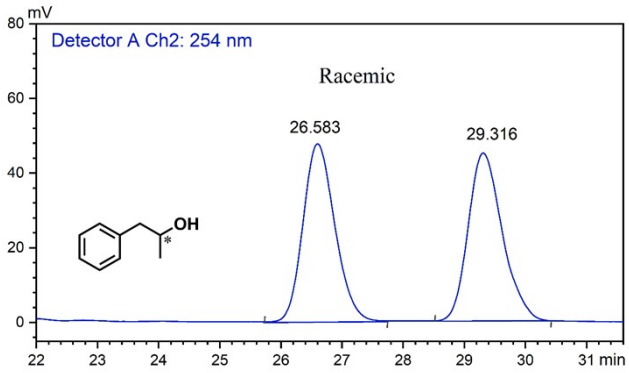
Serial Number	Type	Retention Time	Peak Area	Area %
1	1-phenylbutan-1-ol	24.751	4664.579	78.4
2	1-phenylbutan-1-ol	26.435	1281.566	21.6
The Toal			5946.145	



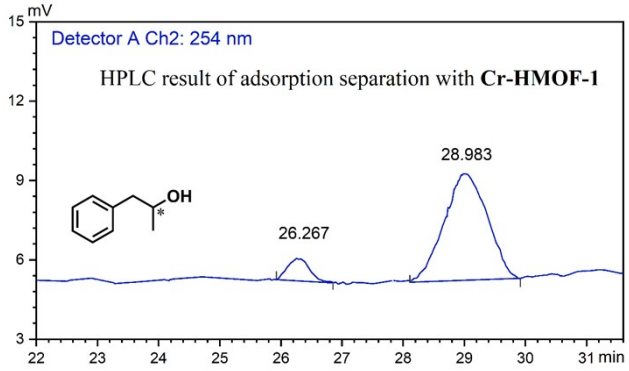
Serial Number	Type	Retention Time	Peak Area	Area %
1	1-phenylbutan-1-ol	24.851	5611.259	92.5
2	1-phenylbutan-1-ol	26.833	455.492	7.5
The Toal			6066.751	



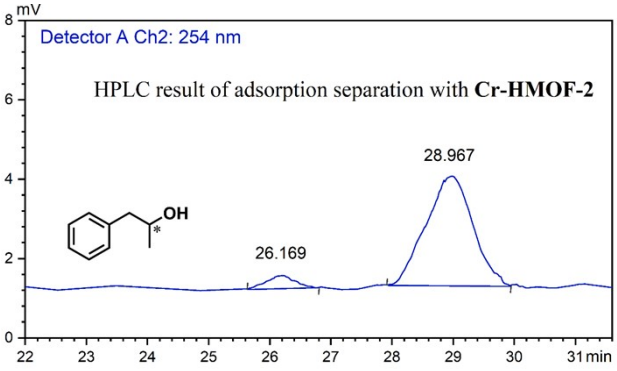
Chiral HPLC analysis: IG column; n-hexane/ethanol = 95/5 (v/v); flow rate = 0.3 mL min^{-1}; 254 nm; 35 °C; t_R = 26.583 min, t_R = 29.316 min.



Serial Number	Type	Retention Time	Peak Area	Area %
1	1-phenyl-2-propanol	26.583	150802.333	49.2
2	1-phenyl-2-propanol	29.316	156006.534	50.8
The Toal			306808.867	



Serial Number	Type	Retention Time	Peak Area	Area %
1	1-phenyl-2-propanol	26.267	120.920	8.6
2	1-phenyl-2-propanol	28.983	1284.886	91.4
The Toal			1405.806	



Serial Number	Type	Retention Time	Peak Area	Area %

1	1-phenyl-2-propanol	26.169	114.283	5.4
2	1-phenyl-2-propanol	28.967	2006.233	94.6
The Toal			2120.516	