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Electronic Supplementary Information

γ-Cyclodextrin metal-organic framework for efficient separation of chiral aromatic alcohols

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Materials and reagents. All chemicals and reagents used are at least of analytical grade. Ultrapure water was purchased from Wahaha Foods Co., Ltd (Tianjin, China). γ-CD was obtained from Dalian Meilun Biological Technology Co., Ltd (Dalian, China). KOH and cetyltrimethyl ammonium bromide (CTAB) were obtained from Aladdin Chemistry Co., Ltd (Shanghai, China). Methanol (MeOH), ethanol (EtOH), *iso*-propanol (*i*-PrOH), acetonitrile (ACN), hexane and dichloromethane (DCM) were purchased from Concord Fine Chemical Research Institute (Tianjin, China).

Instrumentation. X-ray diffraction spectrometry (XRD) patterns were recorded on a D/max-2500 diffractometer (Rigaku, Japan) with Cu Kα radiation (λ = 1.5418 Å). The scanning electron microscopy (SEM) image was characterized on a Shimadzu SS-550 scanning electron microscope at 15.0 kV. The Brunauer-Emmett-Teller (BET) surface area and pore size distribution were measured on A NOVA 2000e surface area and pore size analyzer (Quantachrome, Florida, FL, USA) using nitrogen adsorption at 77 K in the range $0.02 \leq P/P_0 \leq 0.20$.

The HPLC experiments were performed on a Waters 510 HPLC pump and a 486 tunable absorbance detector. HPLC data was collected on an N2000 chromatography data system. The column temperature was maintained on an Ameritech CO-5060 column heater during HPLC separation.

Synthesis of γ-CD MOF. The γ-CD MOF was synthesized according to Holcroft *et al*.[1] Typically, the γ-CD (8.15 g, 6.2 mmol) and KOH (2.80 g, 49.7 mmol) were dissolved in deionized water (250 mL). The mixture was filtrated through a 0.45 μm syringe filter and decanted into five separate beakers (50 mL). Each beaker was settled into a large beaker (250 mL). A 100 mL of MeOH was then added into each large beaker. MeOH was allowed to diffuse slowly into the reaction solutions for 24 h. Each solution was decanted into a fresh vial before CTAB (40 mg) was added, and

after the complete dissolution of CTAB, MeOH was diffused into the reaction solution for an additional 24 h. The white product is collected by centrifugation (5000 rpm, 5 min) and thoroughly washed with MeOH, and then dried under vacuum overnight.

Preparation of the γ-CD MOF packed column. A 4.50 g mass of γ-CD MOF was dispersed with 50 mL of hexane under ultrasonication. The suspension was then packed into a stainless steel column (25 cm long × 4.6mm i.d.) under 5000 psi for 20 min. The γ-CD MOF packed column was conditioned with hexane at a flow rate of 1 mL min^{-1} for 2 h before chromatographic experiments.

Reference:

1. J. M. Holcroft, K. J. Hartlieb, P. Z. Moghadam, J. G. Bell, G. Barin, D. P. Ferris, E. D. Bloch, M. M. Algaradah, M. S. Nassar, Y. Y. Botros, K. M. Thomas, J. R. Long, R. Q. Snurr and J. F. Stoddart. *J. Am. Chem. Soc.* 2015, **137**, 5706.

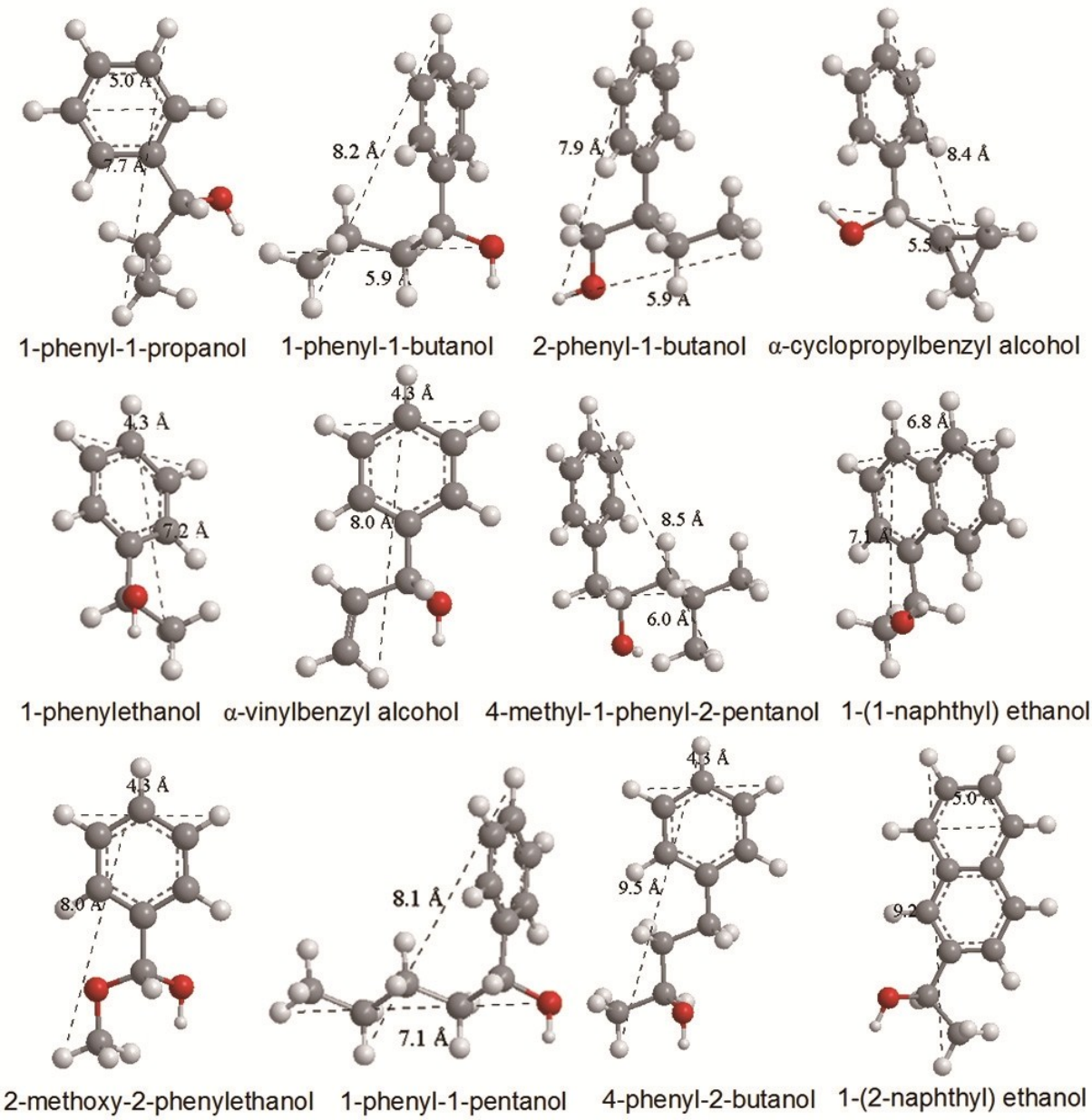

Fig. S1 The structure and molecular dimension (calculated from the software of Chem3D 2004) of the studied chiral aromatic alcohols.

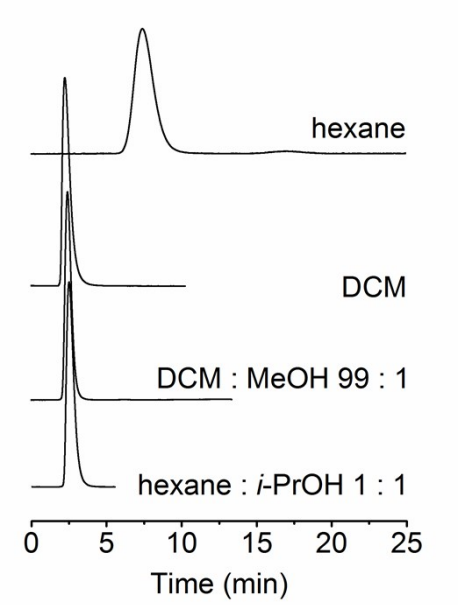

Fig. S2 Effect of mobile phase composition on HPLC separation of (R,S) 2-phenyl-1-butane on γ-CD MOF packed column. All the separations were performed at a flow rate of 1 mL min^{-1} under a UV detector at 254 nm.

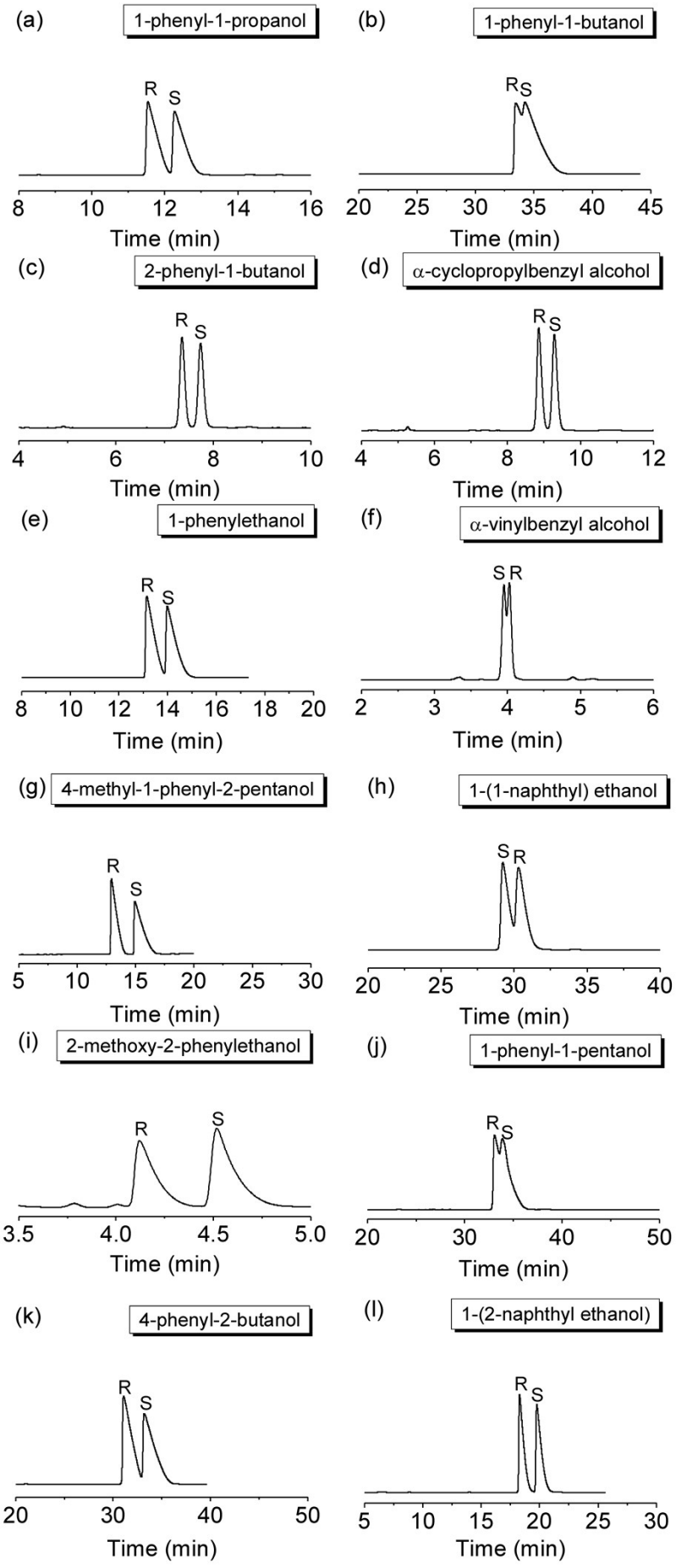
(a)
1-phenyl-1-propanol
R
S
8 10 12 14 16
Time (min)
(b)
1-phenyl-1-butanol
R S
20 25 30 35 40 45
Time (min)
(c)
2-phenyl-1-butanol
R
S
4 6 8 10
Time (min)
(d)
α-cyclopropylbenzyl alcohol
R S
4 6 8 10 12
Time (min)
(e)
1-phenylethanol
R
S
8 10 12 14 16 18 20
Time (min)
(f)
α-vinylbenzyl alcohol
S R
2 3 4 5 6
Time (min)
(g)
4-methyl-1-phenyl-2-pentanol
R
S
5 10 15 20 25 30
Time (min)
(h)
1-(1-naphthyl) ethanol
S R
20 25 30 35 40
Time (min)
(i)
2-methoxy-2-phenylethanol
R
S
3.5 4.0 4.5 5.0
Time (min)
(j)
1-phenyl-1-pentanol
R S
20 30 40 50
Time (min)
(k)
4-phenyl-2-butanol
R
S
20 30 40 50
Time (min)
(l)
1-(2-naphthyl ethanol)
R S
5 10 15 20 25 30
Time (min)

Fig. S3 HPLC chromatograms of commercial chiral CHIRALPAK IA column (25 cm long × 4.6 mm i.d.) for chiral separation: (a) (R,S) 1-phenyl-1-propanol using hexane : DCM 70 : 30 (v/v) as the mobile phase; (b) (R,S) 1-phenyl-1-butanol using hexane : *i*-PrOH 99.75 : 0.25 as the mobile phase; (c) (R,S) 2-phenyl-1-butanol using hexane : *i*-PrOH 95 : 5 as the mobile phase; (d) (R,S) α-cyclopropylbenzyl alcohol using hexane : *i*-PrOH 95 : 5 as the mobile phase; (e) (R,S) 1-phenylethanol using hexane : DCM 70 : 30 as the mobile phase; (f) (R,S) α-vinylbenzyl alcohol using hexane : *i*-PrOH 95 : 5 as the mobile phase; (g) (R,S) 4-methyl-1-phenyl-2-pentanol using hexane : DCM 90 : 10 as the mobile phase; (h) (R,S) 1-(1-naphthyl) ethanol using hexane : *i*-PrOH 99 : 1 as the mobile phase; (i) (R,S) 2-methoxy-2-phenylethanol using hexane : DCM 50 : 50 as the mobile phase; (j) (R,S) 1-phenyl-1-pentanol using hexane : *i*-PrOH 99.75 : 0.25 as the mobile phase; (k) (R,S) 4-phenyl-2-butanol using hexane : *i*-PrOH 99.5 : 0.5 as the mobile phase; (l) (R,S) 1-(2-naphthyl) ethanol using hexane : DCM 70 : 30 as the mobile phase. All the separations were performed at a flow rate of 1 mL min^{-1} under a UV detector at 254 nm.

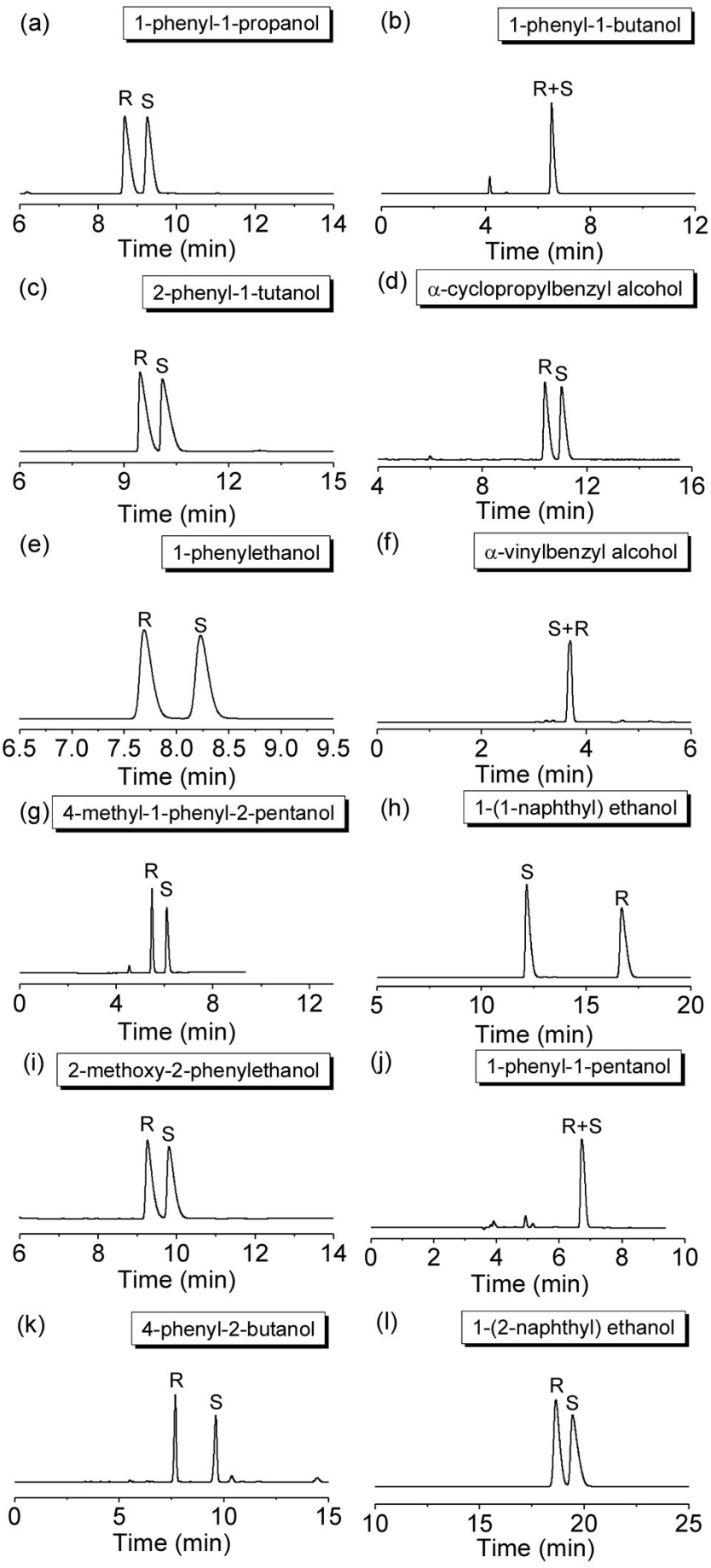
(a)
1-phenyl-1-propanol
R S
6 8 10 12 14
Time (min)
(b)
1-phenyl-1-butanol
R+S
0 4 8 12
Time (min)
(c)
2-phenyl-1-tutanol
R S
6 9 12 15
Time (min)
(d)
α-cyclopropylbenzyl alcohol
R S
4 8 12 16
Time (min)
(e)
1-phenylethanol
R S
6.5 7.0 7.5 8.0 8.5 9.0 9.5
Time (min)
(f)
α-vinylbenzyl alcohol
S+R
0 2 4 6
Time (min)
(g)
4-methyl-1-phenyl-2-pentanol
R S
0 4 8 12
Time (min)
(h)
1-(1-naphthyl) ethanol
S R
5 10 15 20
Time (min)
(i)
2-methoxy-2-phenylethanol
R S
6 8 10 12 14
Time (min)
(j)
1-phenyl-1-pentanol
R+S
0 2 4 6 8 10
Time (min)
(k)
4-phenyl-2-butanol
R S
0 5 10 15
Time (min)
(l)
1-(2-naphthyl) ethanol
R S
10 15 20 25
Time (min)

Fig. S4 HPLC chromatograms of commercial chiral CHIRALPAK IB column (25 cm long × 4.6 mm i.d.) for chiral separation: (a) (R,S) 1-phenyl-1-propanol using hexane : *i*-PrOH 97.5 : 2.5 (v/v) as the mobile phase; (b) (R,S) 1-phenyl-1-butanol using hexane : *i*-PrOH 97.5 : 2.5 as the mobile phase; (c) (R,S) 2-phenyl-1-butanol using hexane : DCM 70 : 30 as the mobile phase; (d) (R,S) α-cyclopropylbenzyl alcohol using hexane : *i*-PrOH 97.5 : 2.5 as the mobile phase; (e) (R,S) 1-phenylethanol using hexane : *i*-PrOH 95 : 5 as the mobile phase; (f) (R,S) α-vinylbenzyl alcohol using hexane : DCM 70 : 30 as the mobile phase; (g) (R,S) 4-methyl-1-phenyl-2-pentanol using hexane : *i*-PrOH 95 : 5 as the mobile phase; (h) (R,S) 1-(1-naphthyl) ethanol using hexane : *i*-PrOH 95 : 5 as the mobile phase; (i) (R,S) 2-methoxy-2-phenylethanol using hexane : *i*-PrOH 97.5 : 2.5 as the mobile phase; (j) (R,S) 1-phenyl-1-pentanol using hexane : *i*-PrOH 97.5 : 2.5 as the mobile phase; (k) (R,S) 4-phenyl-2-butanol using hexane : *i*-PrOH 95 : 5 as the mobile phase; (l) (R,S) 1-(2-naphthyl) ethanol using hexane : *i*-PrOH 97.5 : 2.5 as the mobile phase. All the separations were performed at a flow rate of 1 mL min^{-1} under a UV detector at 254 nm.

Table S1. Precision (RSD%, n = 5) of five replicate separation of (R,S) 1-phenyl-1-propanol on γ-CD MOF packed column.

Enantiomers	Retention time	Peak area	Peak height
(R)-1-phenyl-1-propanol	0.4	2.1	1.9
(S)-1-phenyl-1-propanol	0.3	1.5	1.1

Table S2. Effect of mobile phase composition on selectivity (α) and resolution (R_s) of γ-CD MOF packed column for the separation of (R,S) 1-phenyl-1-propanol.

DCM : MeOH	α	R_s
98.0 : 2.0	2.06	1.39
99.0 : 1.0	2.19	1.46
99.5 : 0.5	2.43	1.55
99.7 : 0.3	3.24	2.11