Electronic Supplementary Information (ESI) for

Post-synthetic modification of metal-organic frameworks for chiral gas chromatography

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Materials and reagents. All the reagents used were at least of analytical grade. BOC-L-proline (BOC-L-Pro) and (1S)-(+)-10-camphorsulfonyl chloride (1S-(+)-Cam) were supplied by Macklin Biochemical Co., Ltd. (Shanghai, China). (+)-diacetyl-L-tartaric anhydride ((+)-Ac-L-Ta) and 4-dimethylaminopyridine (DMAP) was obtained from Tokyo chemical industry Co. Ltd. (Shanghai, China). (S)-2-Phenylpropionic acid (S-2-Ppa) was purchased from J&K scientific Co., Ltd. (Beijing, China). (R)-1,2-epoxyethylbenzene (R-Epo) and 2-aminoterephthalic acid (NH_2-BDC) were obtained from Energy Chemical Co. (Shanghai, China). Aluminum chloride hexahydrate, triethylamine and sodium methylate were obtained from Aladdin Chemistry Co. Ltd. (Shanghai, China). Bromo-tris-pyrrolidino-phosphonium hexafluorophosphate (PyBrOP) was supplied by Adamas Reagent Co., Ltd. (Shanghai, China). *N,N*-Dimethylformamide, dichloromethane and anhydrous ethanol were obtained from Concord Fine Chemical Research Institute (Tianjin, China). Ultrapure water was obtained from Wahaha Foods Co., Ltd. (Tianjin, China). HCl and NaOH were purchased from Guangfu Fine Chemical Research Institute (Tianjin, China).

Instrumentation. The powder X-ray diffraction spectrometry (PXRD) data were performed on a D/max-2500 diffractometer (Rigaku, Japan) using CuK radiation. The Fourier transform infrared spectroscopy (FT-IR) spectra were performed on the Magna-560 spectrometer (Nicolet, Madison, WI). Scanning electron microscopy (SEM) images were performed on a Zeiss Gemini 500 scanning electron microscope. The thermogravimetric analysis (TGA) was performed on a PTC-10A thermal gravimetric analyzer (Rigaku, Japan) from room temperature to 700 °C at a ramp rate of 10 °C min^{-1}. ^1H NMR spectra were performed on a Bruker AV400. Brunner-Emmet-Teller (BET) data were collected on the NOVA2000e surface area and pore size analyzer (Quantachrome, USA) using N_2 adsorption at 77 K. ^1H NMR analysis Microwave irradiation reaction was performed on a XH-300A combined microwave-ultrasound with Computer Controlled System for Synthesis and Solvent Extraction (XiangHu, Beijing). Gas chromatographic measurements were performed on an Agilent 7890 GC system with flame ionization detector (FID). Nitrogen (99.999%) was used as the carrier gas. The circular dichroism spectra were recorded on J-715 (Jasco, Japan).

Synthesis of MIL-101 (Al)-NH_2. The MIL-101 (Al)-NH_2 was synthesized according to Freek, K. *et al*.[1] Typically, $AlCl_3 \cdot 6H_2O$ (0.255 g, 1 mmol), NH_2-BDC (0.28 g, 1.5 mmol) were mixed with

DMF (15 mL). The obtained mixture was transferred into a Teflon-lined bomb. Then, the Teflon-lined bomb was sealed, placed in an oven, and left at 403 K for 72 h. The resulting yellow powder was washed with acetone and collected by centrifugation at 10000 rpm for 5 min. The samples need to be activated in boiling methanol overnight before further use. Prior to the modification reactions, MIL-101 (Al)-NH_2 was dried for 2 h at 120 °C in an oven.

Synthesis of M**IL-101-S-2-Ppa**. The MIL-101-S-2-Ppa was synthesized refer to Bonnefoy, J. et al.[2] PyBrOP (200 mg, 0.43 mmol) was dissolved in 5 mL dehydrated dichloromethane. (S)-2-Phenylpropionic acid (55 μL, 0.4 mmol) was then dropwise added. After stirring for 1 h, MIL-101 (Al)-NH_2 (50 mg) and DMAP (104 mg, 0.85 mmol) were added, stirring under room temperature for 4 days. After washing with dehydrated dichloromethane, the yellow solid was collected by centrifugation at 8000 rpm for 5 min. The process was repeated at least 3 times to eliminate the residual (S)-2-Phenylpropionic acid. Finally, the solid was dried in vacuum at room temperature overnight.

Synthesis of MIL-101-R-Epo. For post-synthesis of MIL-101-R-Epo, MIL-101 (Al)-NH_2 (50 mg) was dispersed in 5 mL anhydrous ethanol. Then, (R)-1,2-Epoxyethylbenzene (45 μL, 0.4 mmol) was dropwise added. After that, the sodium methanolate was slowly added till the pH reach 8. The mixture was stirred at room temperature overnight. After washing with ethanol, the yellow solid was collected by centrifugation at 8000 rpm for 5 min. The process was repeated at least 3 times to eliminate the residual (R)-1,2-Epoxyethylbenzene. Finally, the yellow solid was dried in vacuum at room temperature overnight.

Synthesis of MIL-101-(+)-Ac-L-Ta. For post-synthesis of MIL-101-(+)-Ac-L-Ta, MIL-101 (Al)-NH_2 (50 mg) and (+)-diacetyl-L-tartaric anhydride (648 mg, 3 mmol) were dispersed in 5 mL dehydrated dichloromethane. The reaction mixture was stirred under reflux for 3 days. After washing with dehydrated dichloromethane, the yellow solid was collected by centrifugation at 8000 rpm for 5 min. The process was repeated at least 3 times to remove the residual (+)-diacetyl-L-tartaric anhydride. Finally, the yellow solid was dried in vacuum at room temperature overnight.

Synthesis of MIL-101-L-Pro. The MIL-101-L-Pro was synthesized according to Bonnefoy et al.[2] PyBrOP (300 mg, 0.64 mmol) and BOC-L-proline (130 mg, 0.6 mmol) were dissolved in 5 mL

dehydrated dichloromethane. After stirring for 1 h, MIL-101 (Al)-NH_2 (50 mg) and DMAP (156 mg, 1.28 mmol) were added. The mixture was then stirred under room-temperature for 4 days. After washing with dehydrated dichloromethane, the yellow solid was collected by centrifugation at 8000 rpm for 5 min. The process was repeated 3 at least times to eliminate the residual BOC-L-proline. Finally, the yellow solid was dried in vacuum at room temperature overnight.

To remove the Boc protecting group, the resulting MIL-101-BOC-L-Pro was dispersed in 15 mL DMF. The obtained mixture was transferred to a 50 mL microwave glass vial and reacted under microwave irradiation for 20 minutes at 150 °C (600 watts).

Synthesis of MIL-101-1S-(+)-Cam. For post-synthesis of MIL-101-1S-(+)-Cam, MIL-101 (Al)-NH_2 (50 mg) and (1S)-(+)-10-camphorsulfonyl chloride (112.5 mg, 0.45 mmol) were dispersed in 5 mL dehydrated dichloromethane. The reaction mixture was stirred under reflux for 24 h. After washing with dehydrated dichloromethane, the yellow solid was collected by centrifugation at 8000 rpm for 5 min. The process was repeated at least 3 times to remove the residual (1S)-(+)-10-Camphorsulfonyl chloride. Finally, the yellow solid was dried in vacuum at room temperature overnight.

Preparation of MIL-101 (Al)-X coated capillary columns. The fused silica capillary (30 m long × 0.25 mm inner diameter, Yongnian Optic Fiber Plant, Hebei, China) was treated according to the following recipe before dynamic coating: the capillary was washed with 1 M NaOH for 2 h, ultrapure water for 30 min, 0.1 M HCl for 2 h, and ultrapure water until the outflow reached pH 7.0 and methanol for 30 min. Then, the column filled with methanol was dried with a nitrogen stream of 100 °C overnight for further use.

MIL-101-S-2-Ppa was coated onto the pre-treated capillary column by a dynamic coating method as follows. 1 mL ethanol suspension of 1 mg MIL-101-S-2-Ppa was first filled into the capillary column under gas pressure, and then pushed through the column at a velocity of 20 cm min^{-1} to leave a wet coating layer on the inner wall of the capillary column. To avoid acceleration of the solution plug near the end of the column, a 1 m long buffer tube was attached to the capillary column end as a restrictor. After coating, the capillary columns settled overnight for conditioning under nitrogen. Further conditioning of the capillary column was carried out using a

temperature program: 30 °C for 10 min, ramp from 30 °C to 250 °C at a rate of 3 °C min^{-1}, and 250 °C for 120 min. All these processes were repeated twice.

MIL-101-(+)-Ac-L-Ta, MIL-101-L-Pro, and MIL-101-R-Epo coated columns were fabricated using the same recipes as MIL-101-S-2-Ppa at a concentration of 1 mg mL^{-1}, 1 mg mL^{-1}, and 0.5 mg mL^{-1}, respectively. The MIL-101-1S-(+)-Cam coated column was prepared using the similar recipes at a concentration of 0.5 mg mL^{-1} unless only once coated process were employed.

Calculation of thermodynamic parameters. The enthalpy change (ΔH) and entropy change (ΔS) for the transfer of the analyte between the mobile phase and the stationary phase were calculated according to the van't Hoff equation 1:

$$\ln k' = -(\Delta H / R)\, 1/T + (\Delta S / R + \ln \Phi) \qquad (1)$$

where k' stands for retention factor, R stands for gas constant, T stands for absolute temperature, and Φ stands for the phase ratio, which is defined as the volume ratio of the stationary phase (Vs) to the mobile phase (Vm). The chiral part of enthalpy change (ΔΔH) and entropy change (ΔΔS) of the enantiomer-selector phase transfer were calculated as $\Delta H_2 - \Delta H_1$ and $\Delta S_2 - \Delta S_1$ for the enantiomers, respectively, where the footnotes 1 and 2 refer to the first and second peaks of the enantiomers, respectively.[3]

References:

1. P. Serra-Crespo, E. V. Ramos-Fernandez, J. Gascon and F. Kapteijn. *Chem. Mater*. 2011, **23**, 2565.
2. J. Bonnefoy, A. Legrand, E. A. Quadrelli, J. Canivet and D. Farrusseng. *J. Am. Chem. Soc.* 2015, **137**, 9409.
3. H.-L. Qian, C.-X. Yang and X.-P. Yan. *Nat. Commun*. 2016, **7**, 12104.

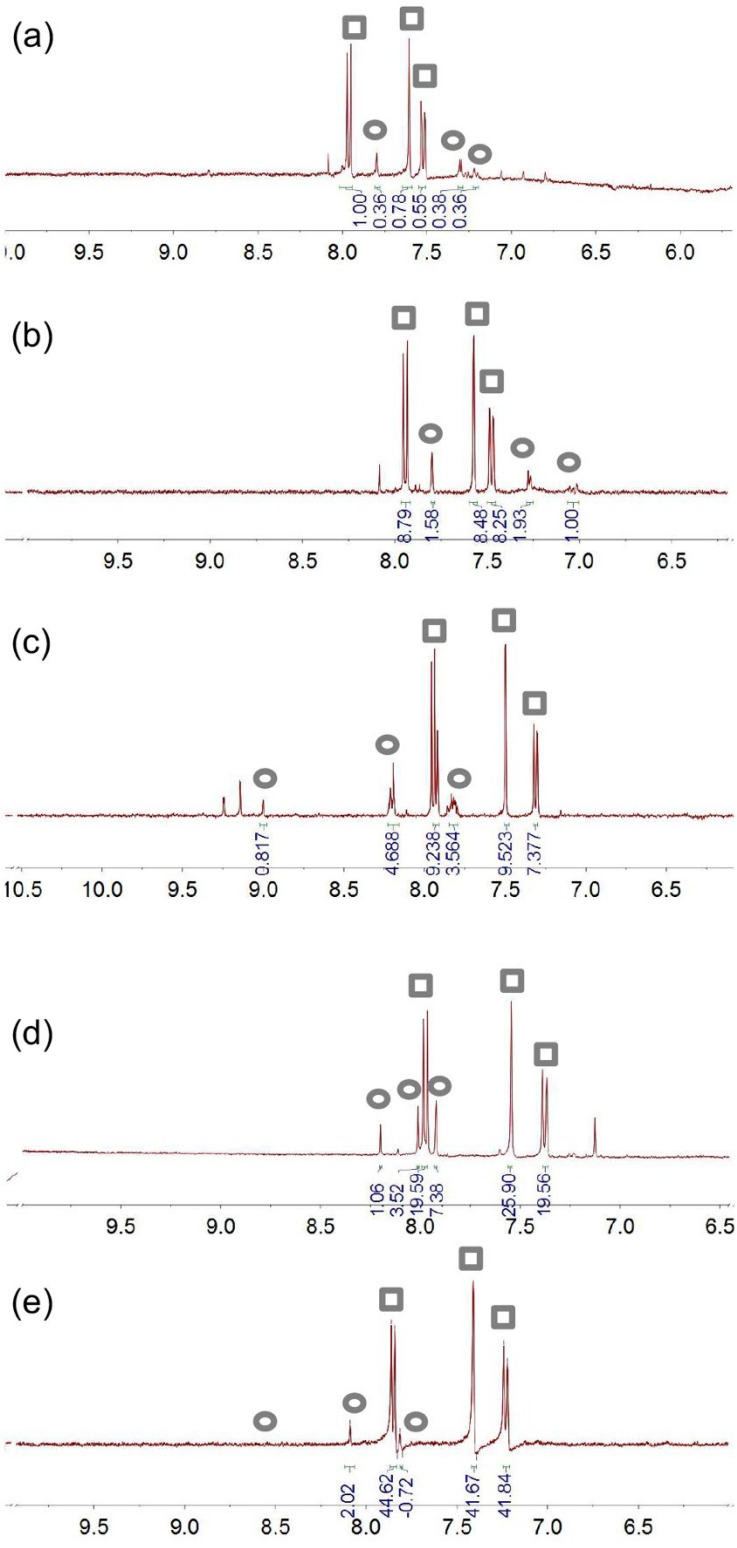

Figure S1. ^{1}H NMR spectra of (a) MIL-101-S-2-Ppa; (b) MIL-101-R-Epo; (c) MIL-101-(+)-Ac-L-Ta; (d) MIL-101-L-Pro; (e) MIL-101-1S-(+)-Cam in HF-H_2O/DMSO-d_6. Unmodified BDC-NH_2 and functionalized linker are indicated by squares and circles, respectively.

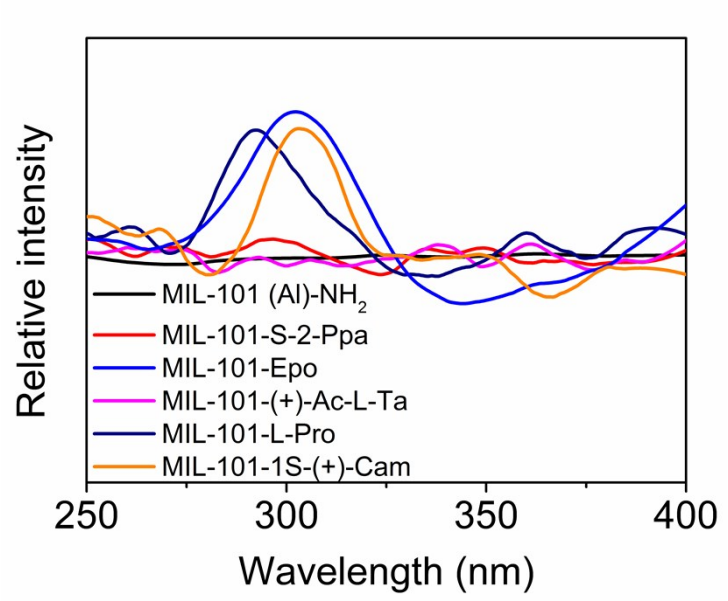

Figure S2. The circular dichroism spectra of MIL-101 (Al)-NH_2 and MIL-101 (Al)-Xs.

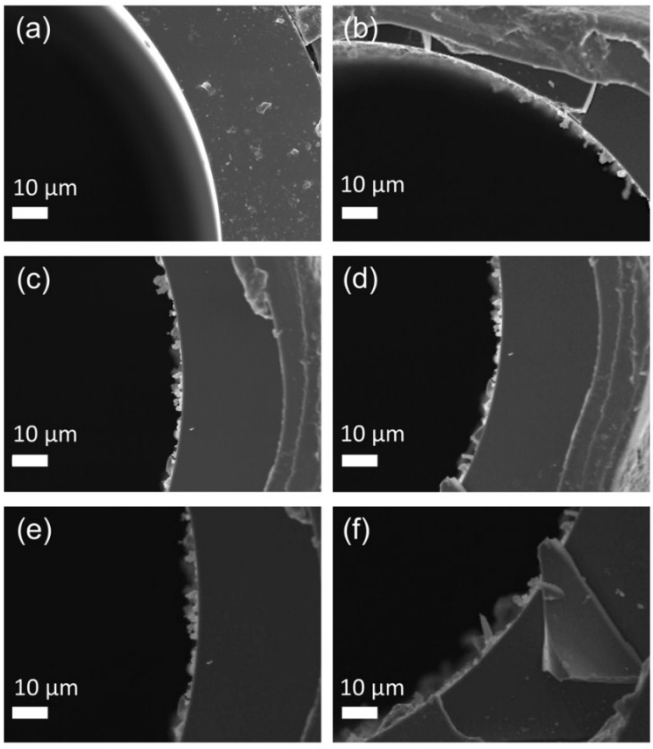

Figure S3. SEM images of the cross section: (a) bare capillary column; (b) MIL-101-S-2-Ppa coated column; (c) MIL-101-R-Epo coated column; (d) MIL-101-(+)-Ac-L-Ta coated column; (e) MIL-101-L-Pro coated column; (f) MIL-101-1S-(+)-Cam coated column.

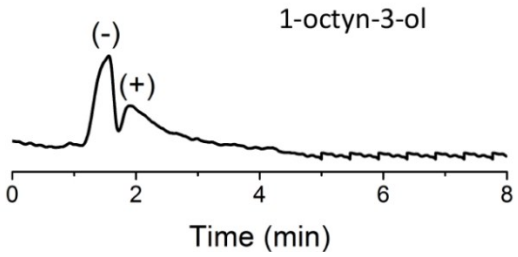

Figure S4. GC separation of (-/+) 1-octyn-3-ol (200 °C, 2 mL min^{-1}) on MIL-101-R-Epo coated column.

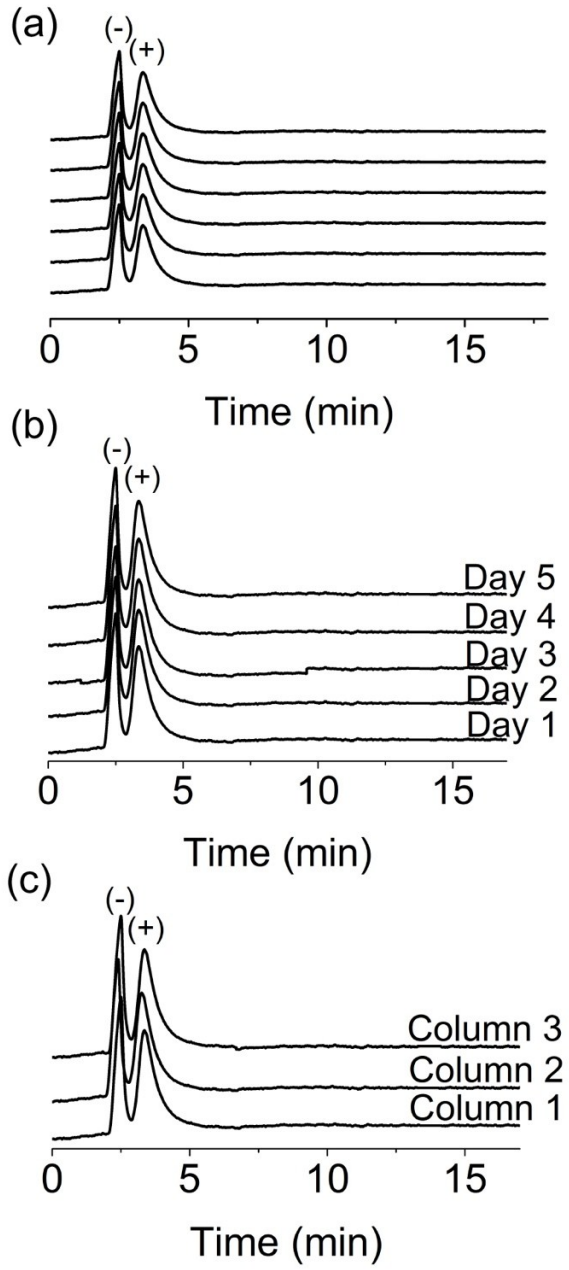

Figure S5. Reproducibility of citronellal on MIL-101-S-2-Ppa coated column: GC chromatograms of (a) six replicate; (b) five days; (c) three columns.

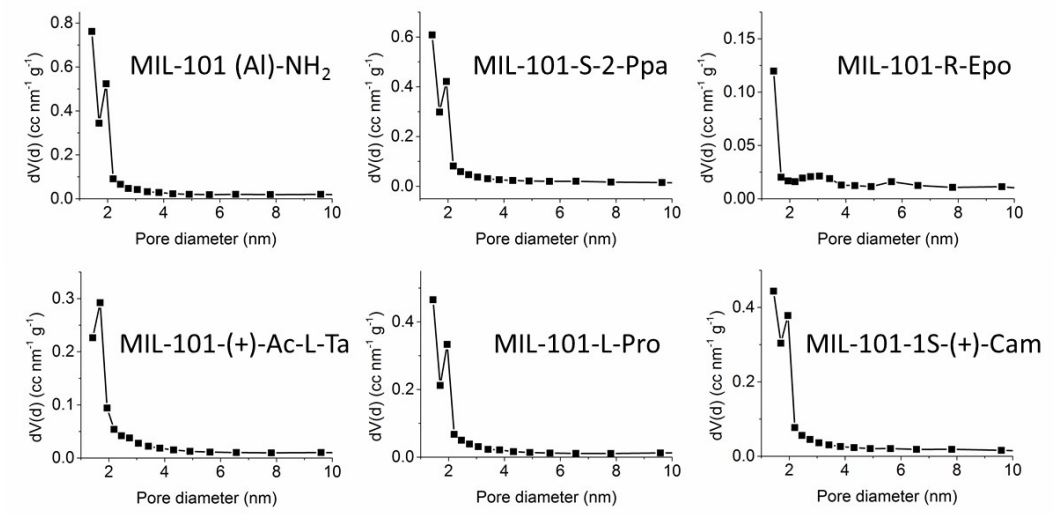

Figure S6. Pore size distribution of MIL-101 (Al)-NH_2 and MIL-101 (Al)-Xs.

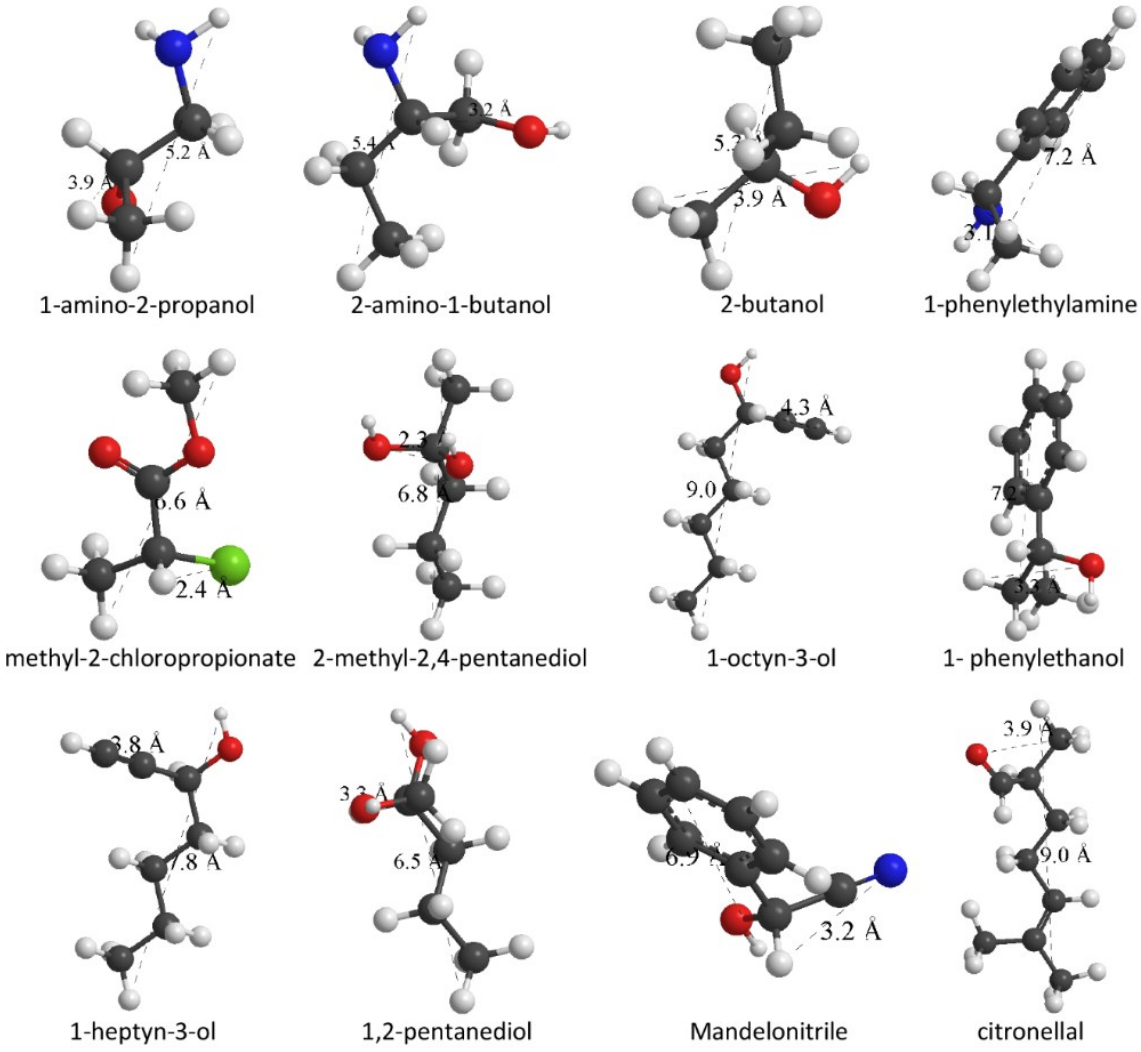

Figure S7. The structure and molecular dimension (calculated from the software of Chem3D 2004) of the studied racemates.

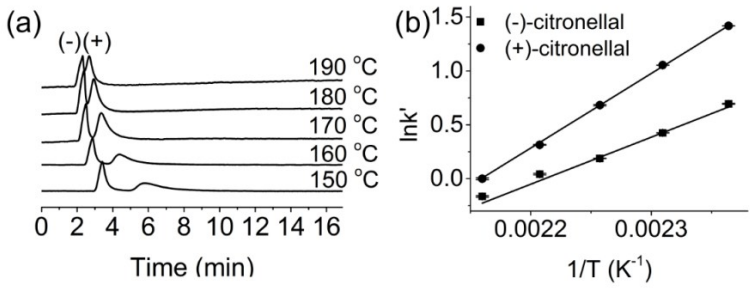

Figure S8. (a) GC chromatograms for (-/+) citronellal on the MIL-101-S-2-Ppa coated column (30 m long × 0.25 mm i.d.) at 150-190 °C, 2 ml min^{-1} N_2. (b) van't Hoff plots for (-/+) citronellal on the MIL-101-S-2-Ppa coated column.

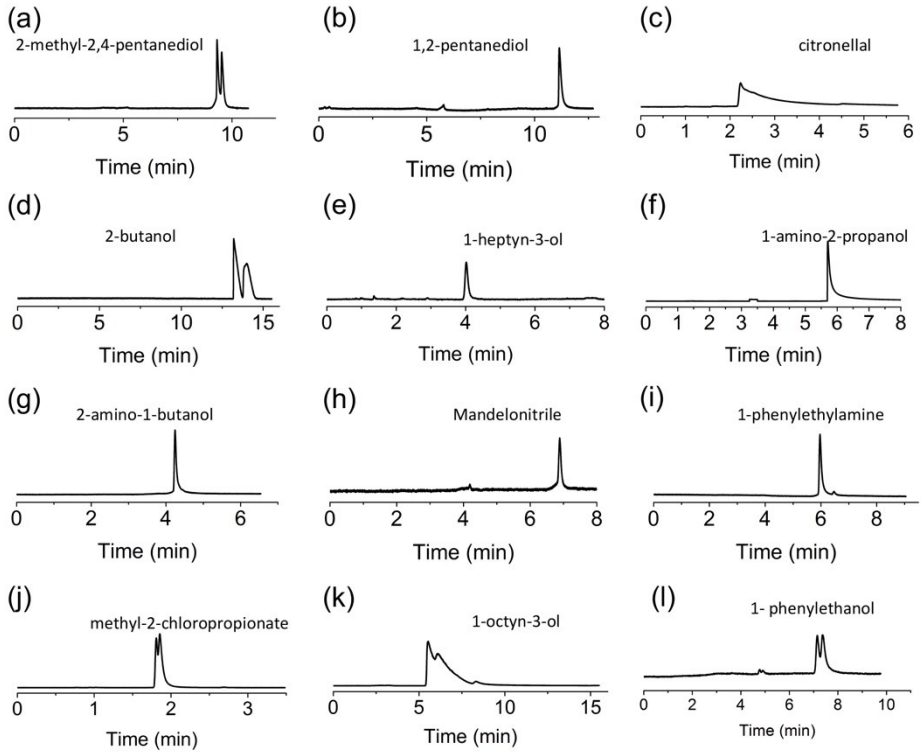

Figure S9. Gas chromatograms for separation of racemates: (a) 2-mathyl-2,4-pentanediol (190 °C, 1.5 mL min^{-1}); (b) 1,2-pentanediol (200 °C, 1.5 mL min^{-1}); (c) citronellal (130 °C, 1.5 mL min^{-1}); (d) 2-butanol (60 °C, 1.5 mL min^{-1}); (e) 1-heptyn-3-ol (70 °C, 1.5 mL min^{-1}); (f) 1-amino-2-propanol (180 °C, 1.5 mL min^{-1}); (g) 2-amino-1-butanol (180 °C, 1.5 mL min^{-1}); (h) Mandelonitrille (140 °C, 1.5 mL min^{-1}); (i) 1-phenylethylamine (130 °C, 1.5 mL min^{-1}); (j) Methyl-2-chloropropionate (70 °C, 1.5 mL min^{-1}); (k) 1-octyn-3-ol (70 °C, 1.5 mL min^{-1}); (l) 1-phenylethanol (100 °C, 1.5 mL min^{-1}) on β-DEX 225 capillary column (30 m long × 0.25 mm i.d.).

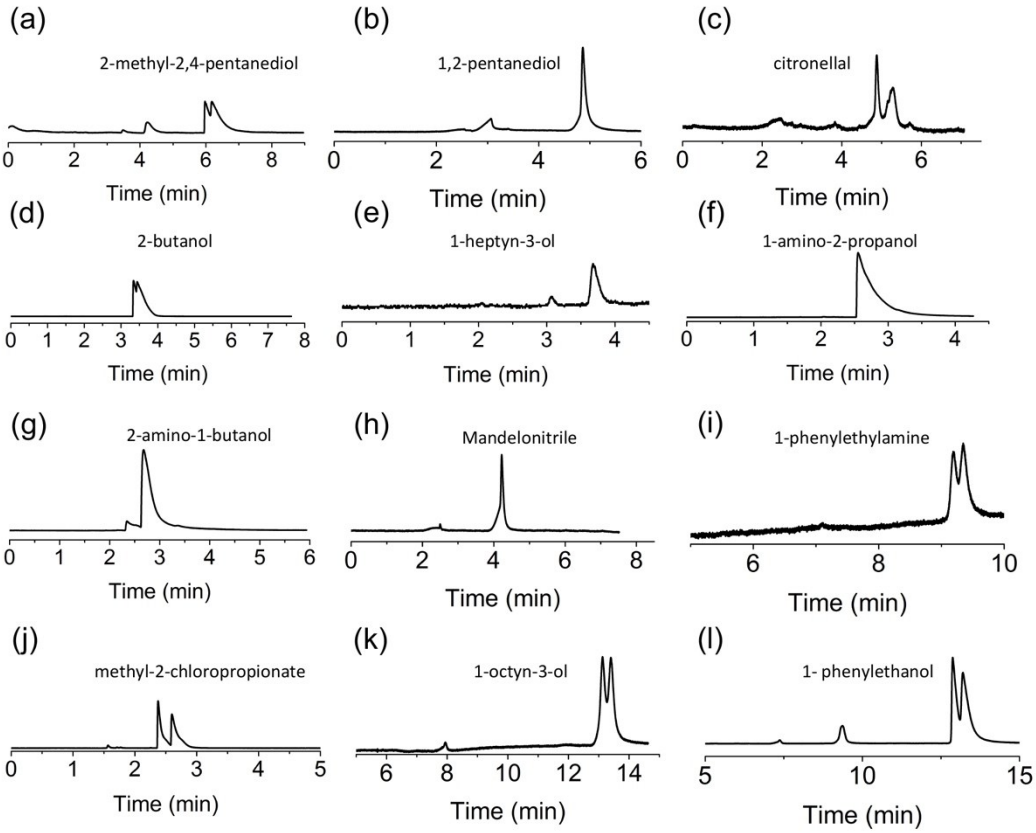

Figure S10. Gas chromatograms for the separation of racemates: (a) 2-mathyl-2,4-pentanediol (120 °C, 1.5 mL min^{-1}); (b) 1,2-pentanediol (140 °C, 1.5 mL min^{-1}); (c) citronellal (140 °C, 1.5 mL min^{-1}); (d) 2-butanol (80 °C, 1.5 mL min^{-1}); (e) 1-heptyn-3-ol (140 °C, 1.5 mL min^{-1}); (f) 1-amino-2-propanol (130 °C, 1.5 mL min^{-1}); (g) 2-amino-1-butanol (140 °C, 1.5 mL min^{-1}); (h) mandelonitrille (140 °C, 1.5 mL min^{-1}); (i) 1-phenylethylamine (65 °C, 1.5 mL min^{-1}); (j) methyl-2-chloropropionate (120 °C, 1.5 mL min^{-1}); (k) 1-octyn-3-ol (120 °C, 1.5 mL min^{-1}); (l) 1-phenylethanol (65 °C, 1.5 mL min^{-1}) on Cyclosil B capillary column (30 m long × 0.32 mm i.d.).

Table S1. Resolution for the racemates tested on MIL-101 (Al)-Xs columns and commercial columns.

Racemates	Columns						
	MIL-101-S-2-Ppa	MIL-101-R-Epo	MIL-101-(+)-Ac-L-Ta	MIL-101-L-Pro	MIL-101-1S-(+)-Cam	Cyclosil B	β-DEX 225
1-phenethylalcohol	-	-	-	-	-		
2-amino-1-butanol	-	-	1.18	-	-	-	-
Amino-2-propanol	-	-	0.34	-	-	-	-
Methyl-2-chloropropionate	-	-	-	0.73	-	0.71	0.40
Phenylethylamine	-	-	-	0.38	-	0.62	-
2-butanol	-	1.38	-	-	-	0.36	1.11
Citronellal	1.20	1.67	-	-	-	0.70	-
2-pentanol	-	-	-	-	-		
3-methyl-2-butanol	-	-	-	-	-		
2-methyl-1-butanol	-	-	-	-	-		
2-hexanol	-	-	-	-	-		
2-heptanol	-	-	-	-	-		
4-methyl-2-pentanol	-	-	-	-	-		
2-methyl-2,4-pentanediol	1.78	-	-	-	-	0.55	0.50
1-octyn-3-ol	-	0.50	-	-	-	0.54	0.31
2-ethylhexanol	-	-	-	-	-		
1-heptyn-3-ol	-	0.36	-	-	-	-	-
1,2-pentanediol	1.43	-	0.72	-	-	-	-
1,2-hexanediol	-	-	-	-	-		
1,2,6-hexanetriol	-	-	-	-	-		
3-(methylthio)-1-hexanol	-	-	-	-	-		
Mandelonitrile	-	-	-	0.67	-	-	-
1,2-butanediol	-	-	-	-			

The “-”represent as “cannot be separated”.

Table S2. Precision (RSD%, n = 6) of six replicate separation of (+,-)-citronellal on MIL-101-S-2-Ppa coated capillary column.

Enantiomers	Retention time	Peak area	Peak height
(-)-citronellal	0.23	4.5	5.1
(+)- citronellal	0.25	4.4	5.1

Table S3. Precision (RSD%) for the retention time of (+,-)-citronellal on the MIL-101-S-2-Ppa coated capillary column.

Enantiomers	Run-to-run	Day-to-day	Column-to-column
	n=6	n=5	n=3
(-)-citronellal	0.23	2.01	5.04
(+)-citronellal	0.25	2.64	7.13

Table S4. Thermodynamic parameters for the chiral separation of citronellal racemates on the MIL-101-S-2-Ppa coated capillary column.

Analyte	$-\Delta H$ (KJ mol^{-1})	$-\Delta S$ (J mol^{-1} K^{-1})	$-\Delta\Delta H$ (KJ mol^{-1})	$-\Delta\Delta S$ (J mol^{-1} K^{-1})
(-)-citronellal	36.34±2.03	36.01±2.08	21.23±2.54	43.91±3.24
(+)-citronellal	57.57±0.85	79.92±1.29		