Electronic Supplementary Information (ESI)

for

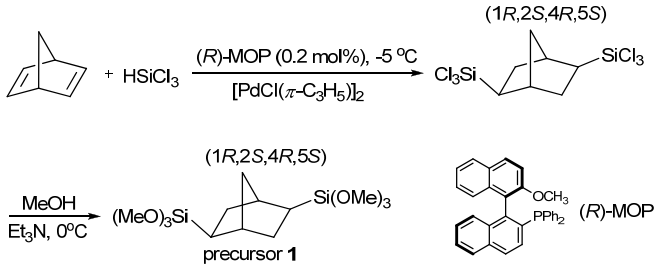
Chiral norbornane-bridged periodic mesoporous organosilicas

Ting-Yan Zhuang, Jiao-Yi Shi, Bao-Chun Ma and Wei Wang*

State Key Laboratory of Applied Organic Chemistry, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, Gansu 730000, P. R. China
E-mail: wang_wei@lzu.edu.cn; Fax: +86 931 891 5557

A: Experimental procedures

Preparation of (1*R*,2*S*,4*R*,5*S*)-*exo,exo*-2,5-bis(trimethoxysilyl)bicyclo[2,2,1]heptane (chiral precursor 1) [1, 2]



The chiral precursor **1**, *i.e.*, (1*R*,2*S*,4*R*,5*S*)-*exo,exo*-2,5-bis(trimethoxysilyl)bicycle-[2,2,1]heptane was prepared and purified according to the literature.[1,2] $HSiCl_3$ (24 mL, 237 mmol) was slowly added to a mixture of allyl palladium chloride (17.5 mg, 0.048 mmol), (*R*)-MOP (94.4mg, 0.201 mmol) and norbornadiene (10 mL, 97.6 mmol) under N_2 gas at –15 °C. The reaction mixture was stirred at –5 °C for 72 h. After removal of the excess trichlorosilane in *vacuo*, the obtained solid was dissolved in THF (30 mL). The resulting solution was then slowly added to a mixture of Et_3N (150 mL) in MeOH (100 mL) at 0 °C. After being stirred for 30min, the mixture was concentrated in *vacuo*. To the residue was added H_2O (50 mL) and extracted with Et_2O (4 × 20 mL). ***Note:*** *the extraction should be performed as quickly as possible because the Si(OMe)₃ groups could not survive in aqueous solution for a long time.* The organic phase was washed with 2% HCl (2 × 10 mL), and then with sat. $NaHCO_3$ (2 × 10 mL). After drying over $MgSO_4$, the organic solvent was removed in *vacuo* to give the crude product in the yield of 91%.[1] Distillation the crude product under reduced pressure gave the chiral precursor **1** as a colorless transparent liquid (26.4 g, 81%). ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm): 3.57 (s, 18H, CH_3), 2.37 (d, J = 1.2 Hz, 2H, bridgehead), 1.63-1.68 (m, 2H, C3 and C6 *endo*), 1.44 (t, J = 10.4 Hz, 2H, C3 and C6 *exo*), 1.37 (s, 2H, bridge), 0.80 (t, J = 8.4 Hz, 2H, C2 and C5 *endo*). ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm): 50.63 (CH_3), 37.54 (bridge), 37.46 (bridgehead), 34.72 (CH_2), 23.29 (Si–CH). In accordance with the literature[1-3], the enantiomeric excess (*ee* value) of the chiral precursor **1** is 99%. This value was derived from that of (1*R*,2*R*,4*R*,5*R*)-*exo,exo*-2,5-diphenylbicyclo[2,2,1]heptane-*endo,endo*-2,5-diol, which could be prepared from precursor **1**, and its *ee* value of 99% was determined by HPLC analyses[1] (Daicel chiral OD-H column, 0.5 mL/min, hexane-*i*-PrOH, 60:40).

Synthesis of chiral PMO materials

Chiral PMO: In a typical synthesis, 0.3 g of P123 was dissolved in deionized water (10.0 g) and 0.25 mL of concentrated HCl (36 wt.%). Afterwards, 0.588 g of precursor **1** was added to the solution and stirred at 40 °C for 20 h followed by a hydrothermal treatment in a closed PTFE autoclave at 100 °C under static conditions for 24 h. The as-synthesized chiral PMO material (denotes as PMO) was obtained as a white powder after filtration and washing thoroughly with water. After twice

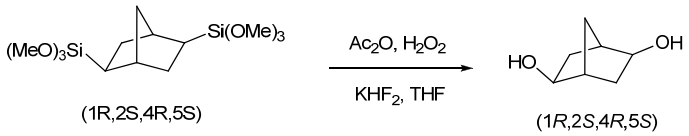
extraction with 100 mL mixture of ethanol/HCl (conc.) (100:0.5 v/v) for 1 g of sample at room temperature for 6 h, the surfactant-free PMO material was obtained.

Chiral Al–PMOs: 0.6 g of P123 was dissolved in deionized water (20.0 g) and 0. 25 mL of concentrated HCl. 1.176 g of precursor **1** was added to the solution and stirred at 40 °C for 4 h, and then the desired amount of $NaAlO_2$ was added. The mixture was then transferred into a closed PTFE autoclave and aged at 100 °C for 24 h. Afterwards, ammonia was added to adjust the pH value of the synthesis system up to pH = 8.0 at room temperature followed by another hydrothermal treatment at 100 °C for 24 h. The as-synthesized Al–PMO material was obtained after filtration and washing thoroughly with water. The samples were denoted as Al–PMO-X, where X stands for the Si/Al ratios in the initial gels.

Chiral B–PMOs: 0.3 g of P123 was dissolved in deionized water (10.0 g) and 0.25 mL of concentrated HCl. 0.588 g of precursor **1** was added to the solution and stirred at 40 °C for 4 h, and then the desired amount of H_3BO_3 was added. The mixture was then transferred into a closed PTFE autoclave and aged at 120 °C for 6 d. The as-synthesized B–PMO material was obtained after filtration and washing thoroughly with water. The samples were denoted as B–PMO-X, where X stands for the Si/B ratios in the initial gels.

Measurement of enantiomeric purity of organic units in the PMO framework[3]

*(1R,2S,4R,5S)-exo,exo-bicyclo[2,2,1]heptane-2,5-diol synthesized from precursor **1**:*



(1R,5S)

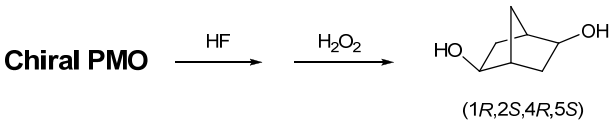
Precursor **1**

(1*R*,2*S*,4*R*,5*S*)

(1*R*,2*S*,4*R*,5*S*)-*exo*,*exo*-Bicyclo[2,2,1]heptane-2,5-diol derived from chiral precursor **1** was prepared and purified according to the literature.[1-3] H_2O_2 (30%, 2.1 g, 19.3 mmol) was added to Ac_2O (2 mL, 19.3 mmol) at 0 °C and stirred until the mixture became clear. The resulting mixture was added to a suspension of precursor **1** (1.0 g, 2.97 mmol) and KHF_2 (1.4 g, 17.8 mmol) in MeOH (10 mL) and THF (10 mL) at 0 °C and the reaction was stirred at room temperature for 6 h. To the reaction mixture was added a solution of $NaHSO_3$ (10 wt.%, 10 mL). Then concentrated NaOH solution was added to the reaction system until pH > 10. The entire mixture was stirred for 1 h, and then filtered. The filtrate was concentrated in *vacuo*, and the resulting residue was extracted with Et_2O (4 × 10 mL). After the residue was dried over $MgSO_4$, the solvent was removed in *vacuo*, and then the crude product obtained was purified by column chromatography (ethyl acetate–MeOH, 13:1). ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm): 4.44 (s, 2H, OH), 3.41 (d, J = 6.3 Hz, 2H, C2 and C5 *endo*) , 1.93 (d, J = 5.7 Hz, 2H, bridgehead), 1.40 (s, 2H, bridge), 1.26-1.33 (m, 2H, C3 and C6 *exo*), 1.01-1.08 (m, 2H, C3 and C6 *endo*). ^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm): 72.09

(HO–CH), 42.72 (bridgehead), 36.47 (bridge), 30.01 (CH_2). MS：m/z = 128 $[M]^+$. $[a]_D^{20}$ –8 (*c* 1.0, MeOH).

(1R,2S,4R,5S)-exo,exo-bicyclo[2,2,1]heptane-2,5-diol derived from chiral PMO:



(1*R*,2*S*,4*R*,5*S*)

(1*R*,2*S*,4*R*,5*S*)-*exo*,*exo*-Bicyclo[2,2,1]heptane-2,5-diol derived from the chiral PMO was prepared and purified according to the method developed by Inagaki *et al*.[4] The chiral PMO material (200 mg), CH_3CN (3 mL) and HF (30%, 3 mL) were added to polypropylene tube in-order. The mixture became clear after stirred at room temperature for 15 h, then $KHCO_3$ (4 g) and KF (2 g) were added to the mixture and stirred for 10 min. The resulting mixture was denoted as *Mixture 1*.

H_2O_2 (30%, 2.1 g, 19.3 mmol) was added to Ac_2O (2 mL, 19.3 mmol) at 0 °C with stirring. After stirred at 0 °C for 30 min, the solution became clear and was added to the *Mixture 1* as oxidant with stirring at 0 °C, and the reaction was stirred at room temperature for 6 h. Afterwards, an aqueous solution of $NaHSO_3$ (10 wt.%, 10 mL) was added to the mixture to remove the residual oxidant, then concentrated NaOH solution was added until pH > 10. The reaction was stirred at room temperature for 1 h, and then filtered. The filtrate was concentrated in *vacuo* and the residue was extracted with Et_2O (4 × 10 mL). The organic phase was dried by $MgSO_4$ and the solvent was removed under reduced pressure to give (1*R*,2*S*,4*R*,5*S*)-*exo*,*exo*-bicyclo[2,2,1]heptane-2,5-diol as a white crystalloid. ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm): 4.39 (d, J = 3.9 Hz, 2H, OH), 3.39-3.42 (m, 2H, C2 and C5 *endo*) ,1.94 (d, J = 5.7 Hz, 2H, bridgehead), 1.40 (s, 2H, bridge), 1.26-1.33 (m, 2H, C3 and C6 *exo*), 1.05-1.08 (m, 2H, C3 and C6 *endo*).^{13}C NMR (75 MHz, DMSO-d_6): δ (ppm): 71.99 (HO–CH), 42.63 (bridgehead), 36.41 (bridge), 29.90 (CH_2). MS：m/z = 128 $[M]^+$. $[a]_D^{20}$ –9 (*c* 1.0, MeOH). The value of optical rotation is well agreed with that of (1*R*,2*S*,4*R*,5*S*)-*exo*,*exo*-bicyclo[2,2,1]heptane-2,5-diol derived from chiral precursor **1**.

The analytic data for diol products derived from chiral precusor **1** and from chiral PMO are identical within the error limits, indicating that no racemization occurred during the PMO formation.

References:

[1] C. Cai and C. Xia, *Synthesis,* 2006, **14,** 2297.

[2] Y. Uozumi, S.-Y. Lee and T. Hayashi, *Tetrahedron Lett.,* 1992, **33,** 7185.

[3] T. Hayashi, K. Ueyama, N. Tokunaga and K. Yoshida, *J. Am. Chem. Soc.,* 2003,

125, 11508.

[4] S. Inagaki, S. Guan, Q. Yang, M. P. Kapoor and T. Shimada, *Chem. Commun.,* 2008, 202.

B: Analysis equipments

Liquid ^{1}H and ^{13}C NMR spectra were recorded in $CDCl_3$ or DMSO-d_6 solution on a Varian Mercury-300 MHz or Bruker Avance III 400 MHz instruments using tetramethylsilane (TMS) as internal standard. Solid-state NMR measurements were performed on a Bruker WB Avance II 400 MHz spectrometer. The ^{13}C CP/MAS NMR spectra were recorded with a 4-mm double-resonance MAS probe, a sample spinning rate of 10.0 KHz, with a contact time of 2 ms (ramp 100) and pulse delay of 3 s. The ^{29}Si high-power proton-decoupling (HPDEC) MAS NMR spectra were recorded with a 4-mm double-resonance MAS probe, a sample spinning rate of 10.0 KHz, and with $\pi/4$ single-pulse excitation of 2.0 μs and pulse delay of 30.0 s. The ^{27}Al MAS NMR spectra were recorded with a 4-mm double-resonance MAS probe, a sample spinning rate of 10.0 KHz, and with $\pi/6$ single-pulse excitation of 1.6 μs and pulse delay of 0.5 s. The ^{11}B MAS NMR spectra were recorded with a 7-mm double-resonance MAS probe, a sample spinning rate of 5.0 KHz, and with $\pi/6$ single-pulse excitation of 1.8 μs and pulse delay of 2 s.

Powder X-ray diffraction (XRD) measurements were taken with a Rigaku D/MAX-2400 with Cu Kα radiation at a scan rate of 1°/min.

The nitrogen adsorption and desorption isotherms were measured at -196 ^{o}C using a Micromeritics ASAP 2010M or 2020M system. The samples were outgassed at 100 ^{o}C for 8 h before the measurements. Surface areas were calculated from adsorption data using Brunauer-Emmett-Teller (BET) method. The pore size distribution curves were obtained from the adsorption branches using Barrett-Joyner-Halenda (BJH) method.

Si/Al ratios of the chiral Al–PMOs and Si/B ratios of the chiral B–PMOs were determined by ICP spectroscope (IRIS Advantage ER/S).

Mass spectra (MS) were measured on a Thermo Finnigan TRACE DSQ GC/MS by direct inlet at 70 eV and signals were given in m/z.

Optical rotations were measured on a Perkin-Elmer 341 polarimeter (Perkin-Elmer, Überlingen, Germany).

Surface morphologies and microstructures of the materials were examined by a scanning electron microscope (SEM, JEOL, JSM-6701F, Japan), and by transmission electron microscopy (TEM, JEOL, JEM-2010, Japan) operated at 200 KV. For TEM analysis, the samples were dispersed in ethanol, and then dipped and dried on Cu grid coated with transparent graphite or on micro-grid.

The thermal properties of PMOs were evaluated using a thermogravimetric analysis (TGA)-differential scanning calorimetry (DSC) instrument (STA 449C Jupiter) from ambient temperature to 900 °C under N_2 atmosphere with a heating rate of 10 °C/min.

C: Analytical data for chiral precursor 1

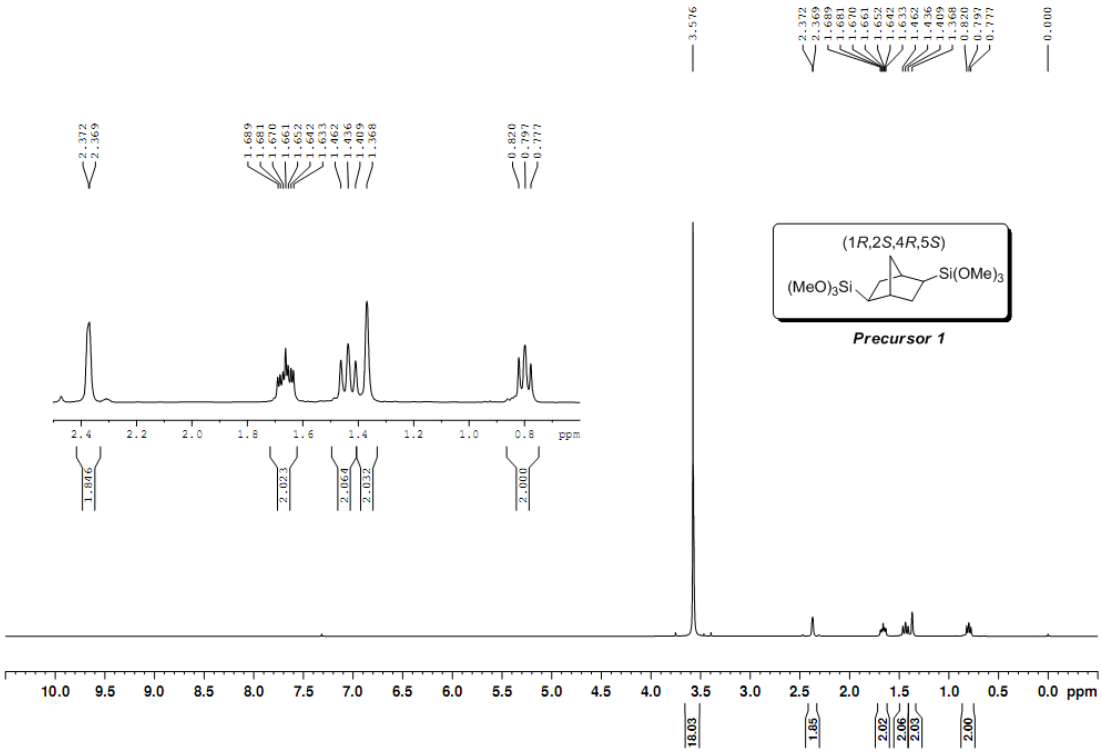


Fig. S1 ^{1}H NMR spectrum of chiral precursor **1.**

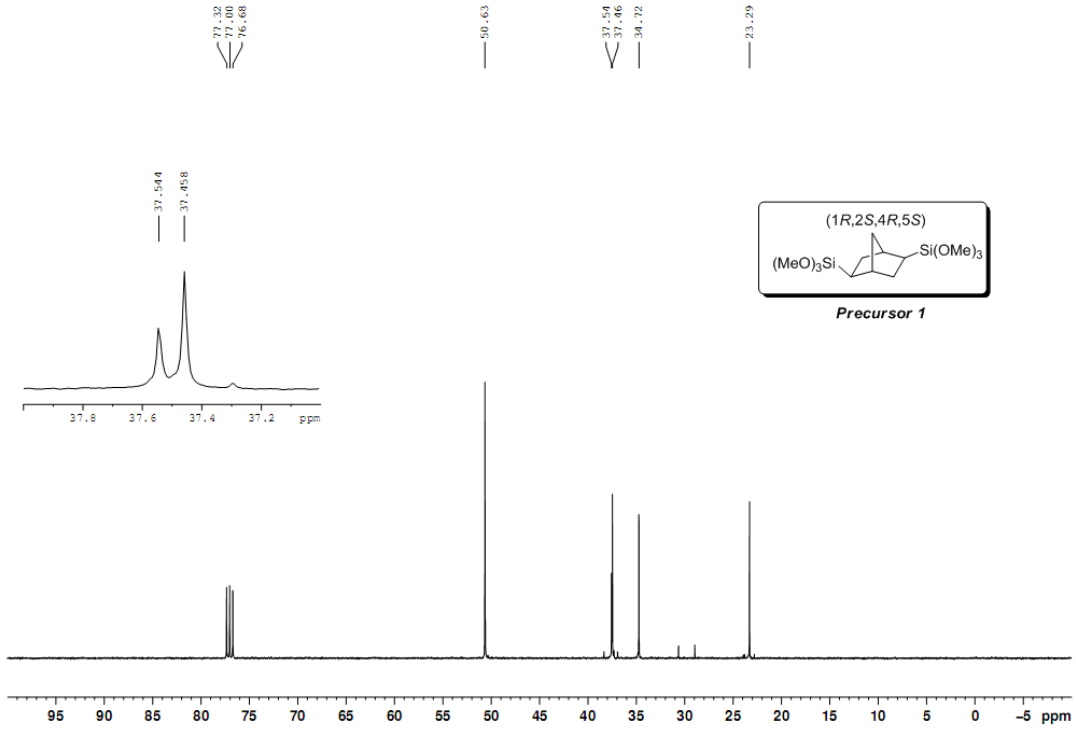


Fig. S2 ^{13}C NMR spectrum of chiral precursor **1.**

D: Analytical data for the synthesized chiral PMO, Al–PMOs and B–PMOs

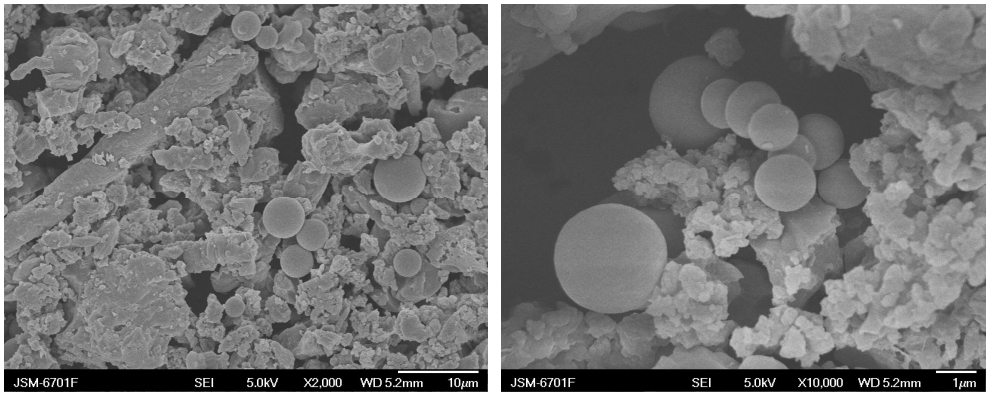


Fig. S3 SEM images of the synthesized chiral PMO material.

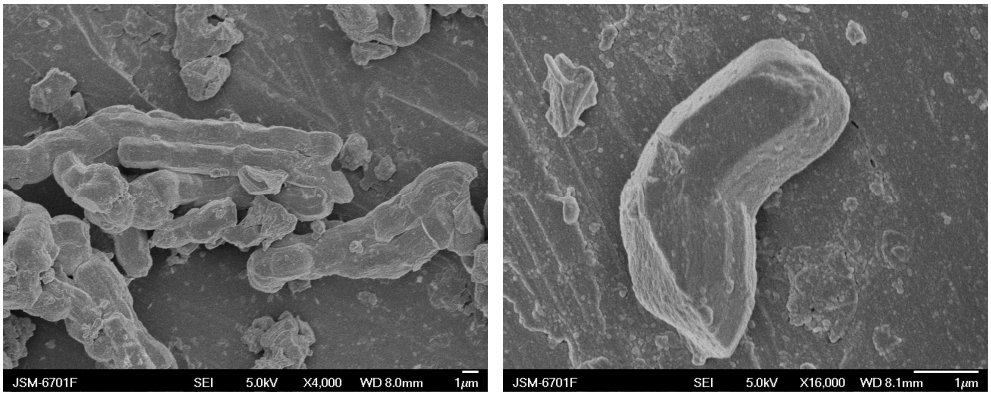


Fig. S4 SEM images of the synthesized chiral Al–PMO-40 material.

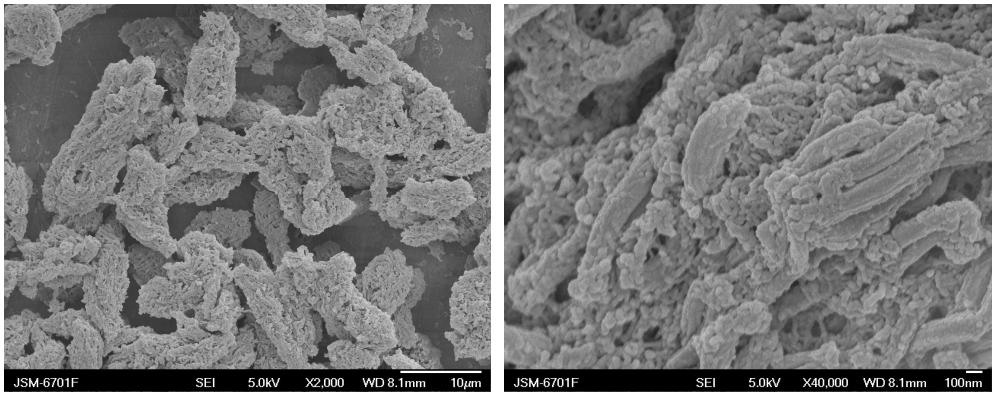


Fig. S5 SEM images of the synthesized chiral B–PMO-1 material.

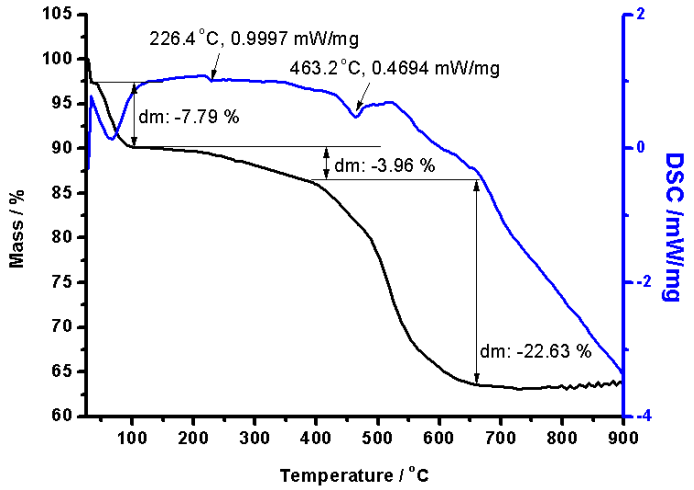


Fig. S6 TGA-DSC curves of the chiral norbornane-bridged PMO material

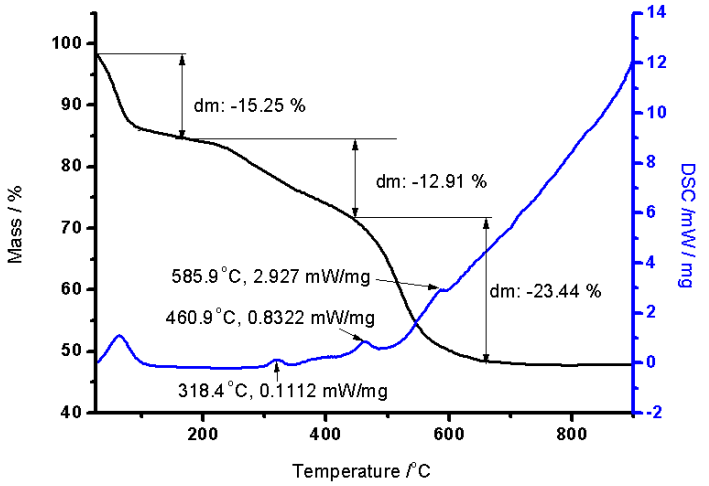


Fig. S7 TGA-DSC curves of the chiral Al–PMO-20 material

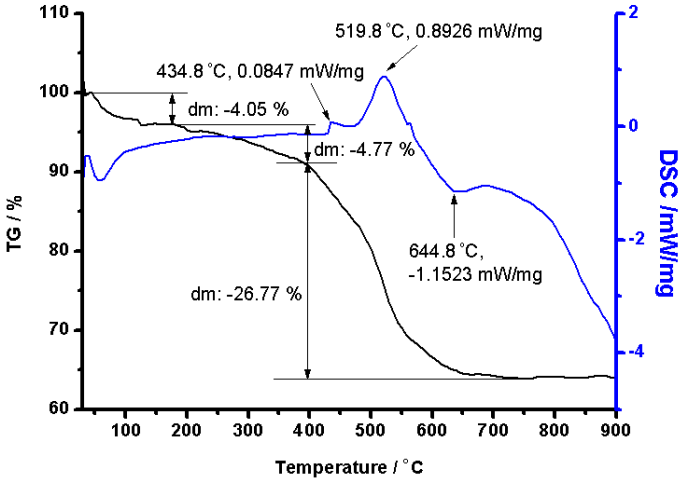


Fig. S8 TGA-DSC curves of the chiral B–PMO-1 material.

E: Identification of the chirality of PMO materials

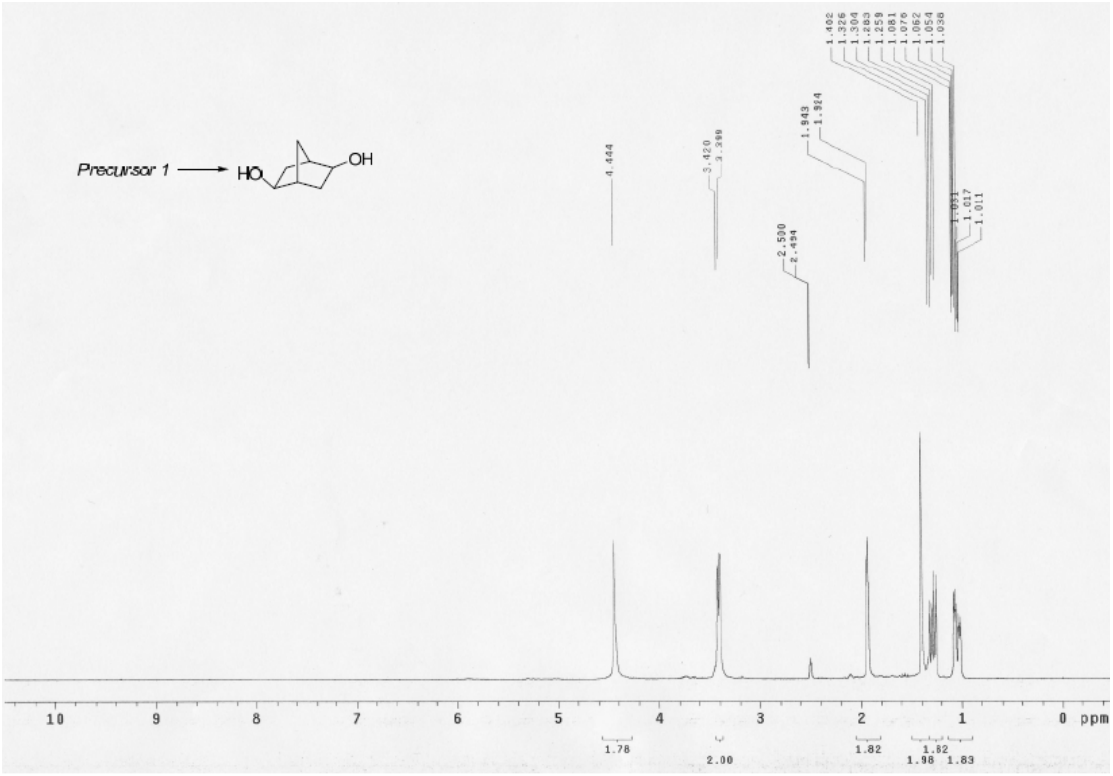


Fig. S9 ^{1}H NMR spectrum of (1*R*,2*S*,4*R*,5*S*)-*exo*,*exo*-bicyclo[2,2,1]heptane-2,5-diol derived from precursor **1.**

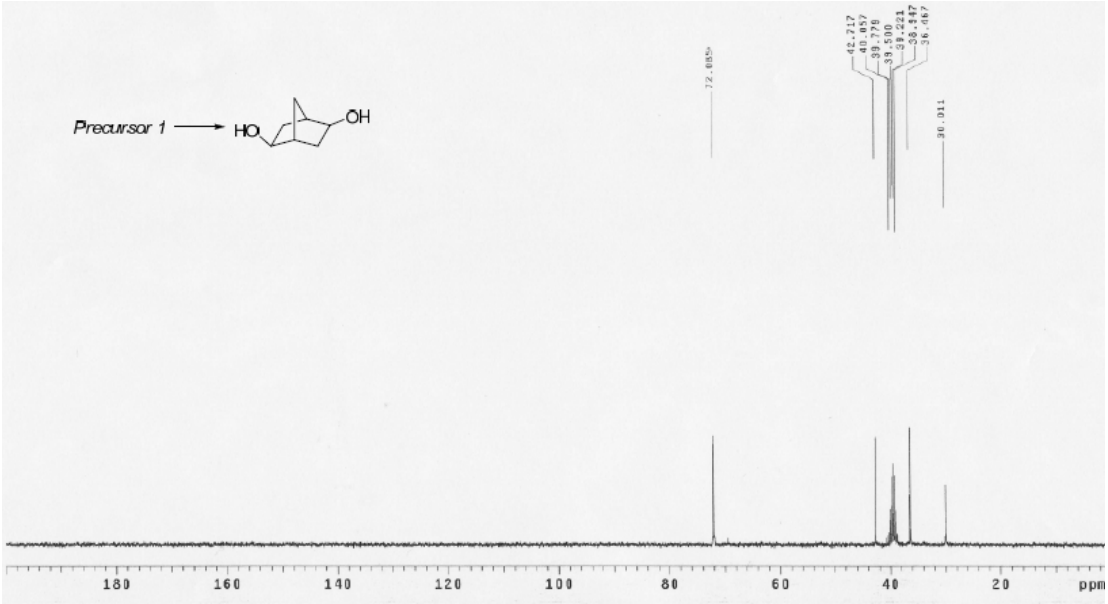


Fig. S10 ^{13}C NMR spectrum of (1*R*,2*S*,4*R*,5*S*)-*exo*,*exo*-bicyclo[2,2,1]heptane-2,5-diol derived from precursor **1.**

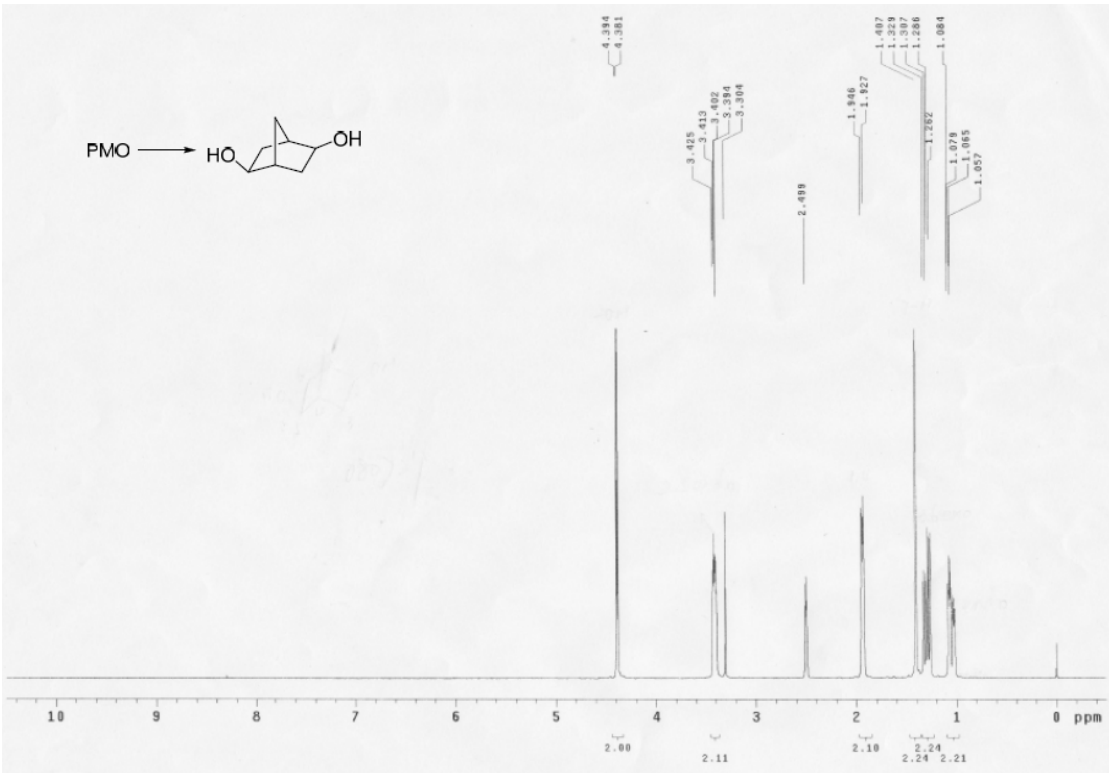


Fig. S11 ^{1}H NMR spectrum of (1*R*,2*S*,4*R*,5*S*)-*exo*,*exo*-bicyclo[2,2,1]heptane-2,5-diol derived from chiral PMO.

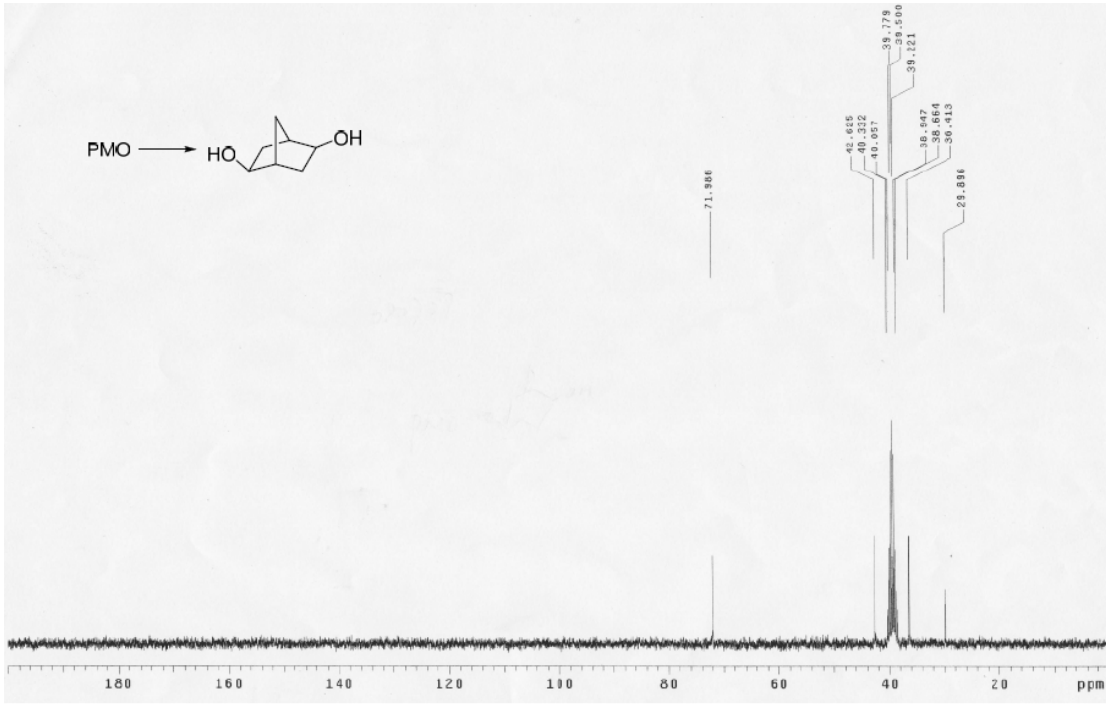


Fig. S12 ^{13}C NMR spectrum of (1*R*,2*S*,4*R*,5*S*)-*exo*,*exo*-bicyclo[2,2,1]heptane-2,5-diol derived from chiral PMO.

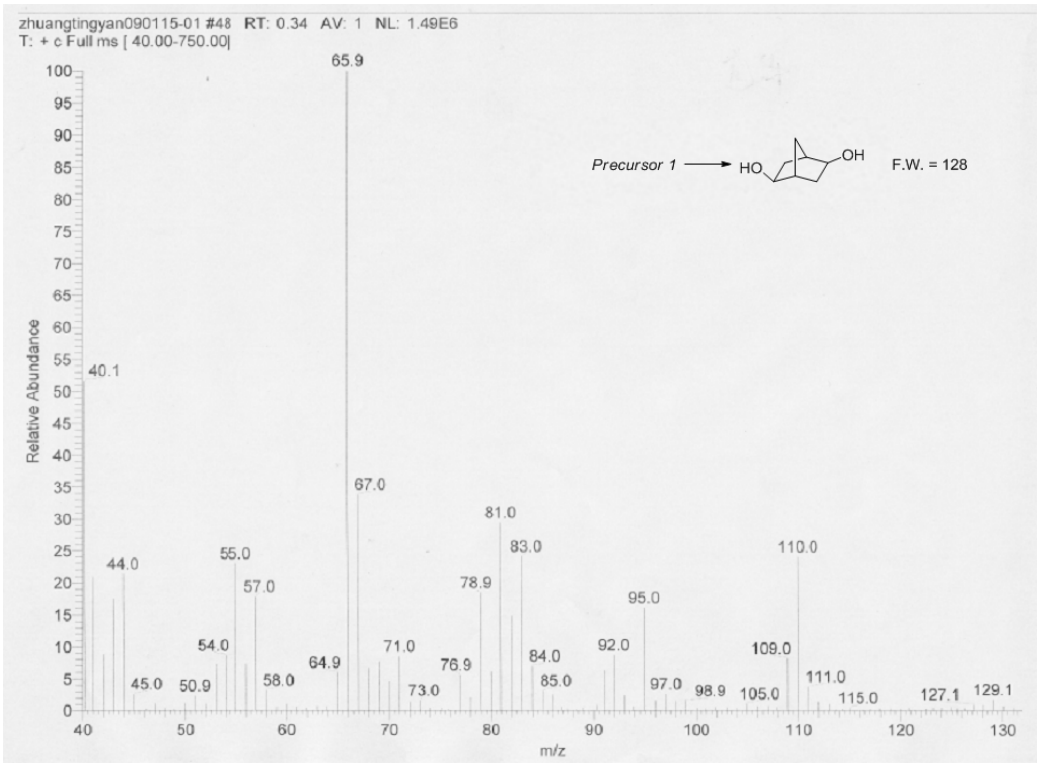


Fig. S13 EI-MS spectrum of (1*R*,2*S*,4*R*,5*S*)-*exo*,*exo*-bicyclo[2,2,1]heptane-2,5-diol derived from Precursor **1.**

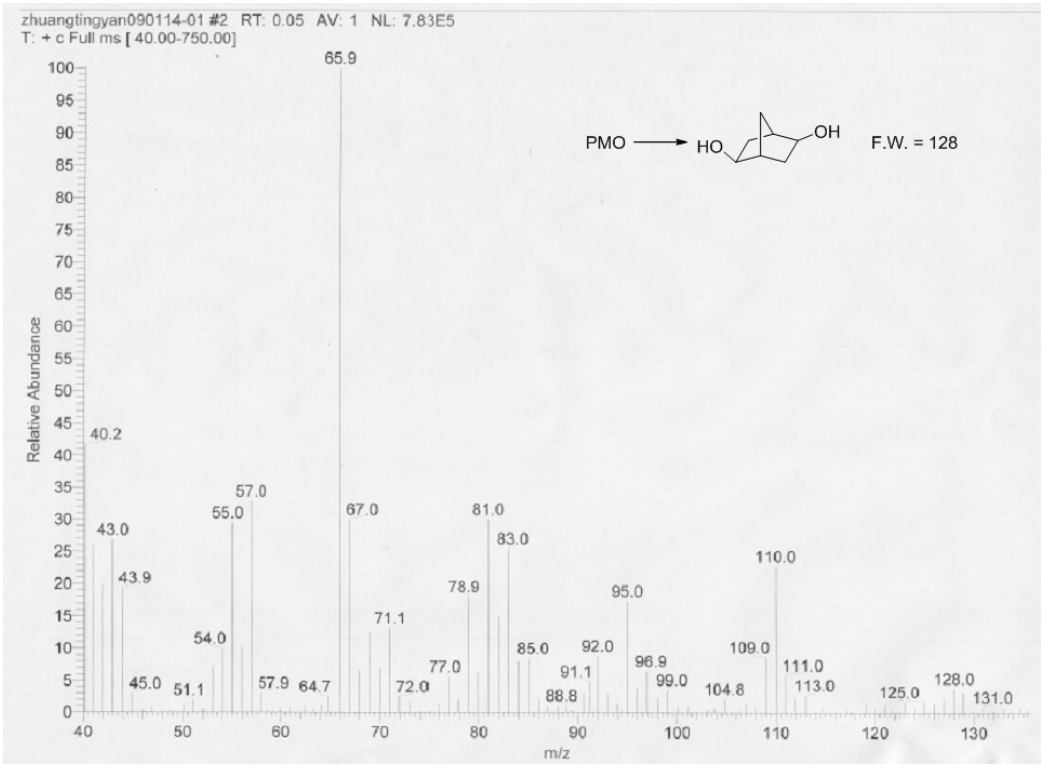


Fig. S14 EI-MS spectrum of (1*R*,2*S*,4*R*,5*S*)-*exo*,*exo*-bicyclo[2,2,1]heptane-2,5-diol derived from chiral PMO.