Electronic Supplementary Information

Chiral aggregates of rod-coil molecules inside nanopores as efficient nanoreactor for asymmetric synthesis

Hui-Yu Zhao[a], Qing Xu[a], Gui-Lang Liu[a], Yi-Rong Pei[a]*, Long Yi Jin[a]*

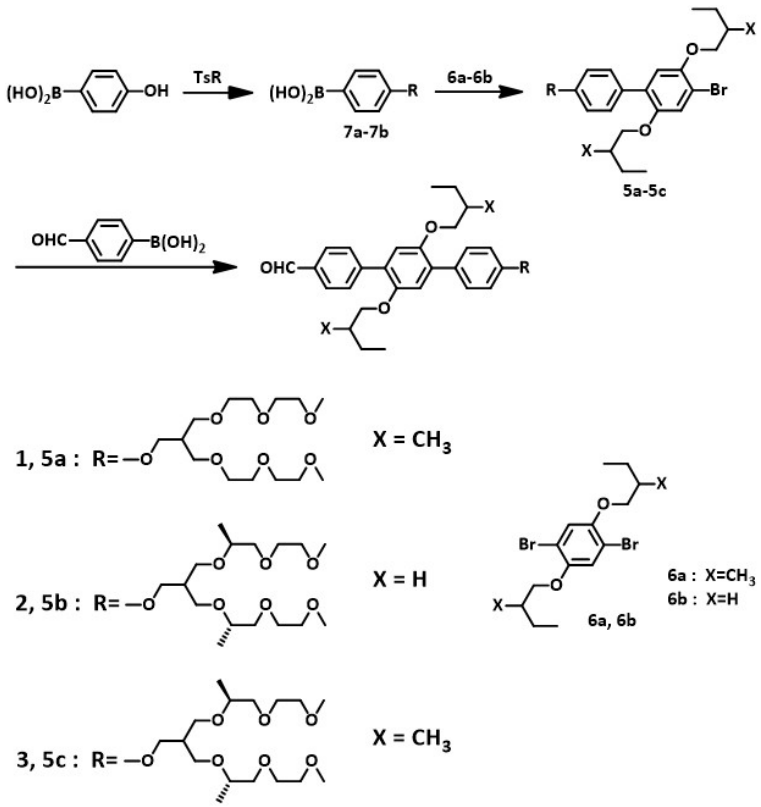
[a]Department of Chemistry, National Demonstration Centre for Experimental Chemistry Education, Yanbian University, Yanji 133002, People's Republic of China,

*Corresponding authors.

E-mail address: pyr@ybu.edu.cn (Y.-R. Pei), lyjin@ybu.edu.cn (L. Y. Jin)

1.Materials and Methods

1.1 Synthetic route



Scheme S1. Synthetic route of molecule **1-3**.

1.2 Materials

Diethylene glycol monomethyl ether, 3-Chloro-2-chloromethyl-1-propene, lithium aluminum hydride, 2-Methoxyethanol, Borane-tetrahydrofuran complex, Calcium chloride, Sodium hydroxide, Hydrogen peroxide, (S)-(+)-1-Bromo-2-methylbutane, 3,4-Dihydro-2H-pyran, sodium hydride, 2,5-Dibromobenzene-1,4-diol, Sodium carbonate anhydrous, L-Lactic acid ethyl ester, 1-Bromobutane, 4-Formylphenylboronic acid, toluene-p-sulfonyl chloride (TsCl, 99%), pyridine, Sodium bicarbonate, Hydrochloric acid, 4-Hydroxybenzeneboronic acid, potassium carbonate, p-Toluenesulfonic acid monohydrate, tetrakis(triphenylphosphine) palladium(0), Magnesium sulfate anhydrous and conventional reagents were used as received. All manipulations involving air-sensitive reagents were performed under an atmosphere of dry nitrogen.

1.3 Synthetic process

The preparation methods of all intermediate compounds and SBA-15 are similar to those in other literature [S1, S2, S3].

1.4 Techniques

Column chromatography filled silica gel (100-200 mesh) was proceeded for further purification. ^{1}H-NMR (300 MHz) spectra were recorded in $CDCl_3$ on the Bruker AM-300 instrument. Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF-MS) was performed on the PerSeptive Biosystems Voyager-DE STR time-of-flight mass spectrometer using 2-cyano-3-(4-hydroxyphenyl) acrylic acid (CHCA) as the matrix. N_2 adsorption-desorption experiment was carried out by Micromeritics ASAP 2460 instrument. The TGA experiment was proceeded with the Perkin Elmer STA 6000 instrument. FT-IR spectra were obtained using Bruker VERTEX 70 spectrometer. UV-vis experiments were performed through the Shimadzu UV-1650PC spectrometer. CD spectra was obtained by a Biologic PMS450. The morphology was observed by scanning electron microscopy (SEM, SU-8010, Hitachi, Japan) and transmission electron microscopy (TEM, JEOL 2100 plus, Japan). HPLC-MS (TSQ Fortis, ThermoFisher SCIENTIFIC) was performed to confirm the obtained standard sample. The ee (%) was estimated on a Shimadzu LC-16 high performance liquid chromatography (HPLC) equipped with a Daicel CHIRALPAK® AYH0CE-VB023 column. The mobile phase is n-Hexane/EtOH/Diethylamine = 90/10/0.1 (v/v/v), and flow rate is 1.0 mL/min.

1.5 Supramolecular Co-Assemblies with DCCS

1) Prepare a DCCS solution at a given concentration: dissolve 1.0 mg of DCCS in 1 mL THF as stuck solution.

2) Prepare three initial assembly systems of **SA-M1**, **SA-M2**, and **SA-M3**: weigh 1 mg solid samples, and dispense them in 10 mL H_2O/THF (v/v = 9/1) separately.

3) 100 μL of stuck solution from 1) was added to the three initial solutions and the vials were seal-capped. The mixture was sonicated for 30 minutes and stand for two hours to form supramolecular co-assembly.

2.Supporting data

2.1 ^{1}H-NMR spectra of molecules 1-3 in $CDCl_3$.

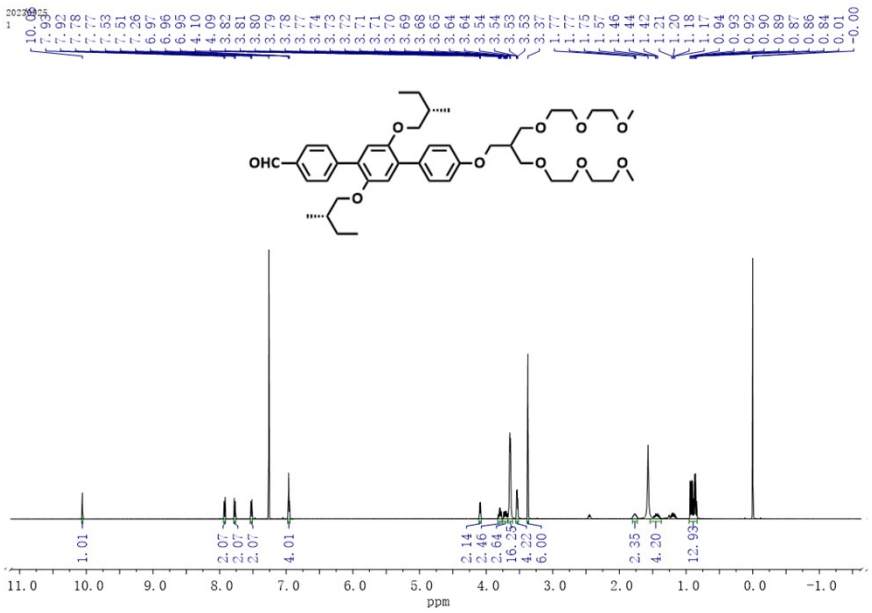


Figure S1. ^{1}H-NMR spectrum of molecule **1** in $CDCl_3$.

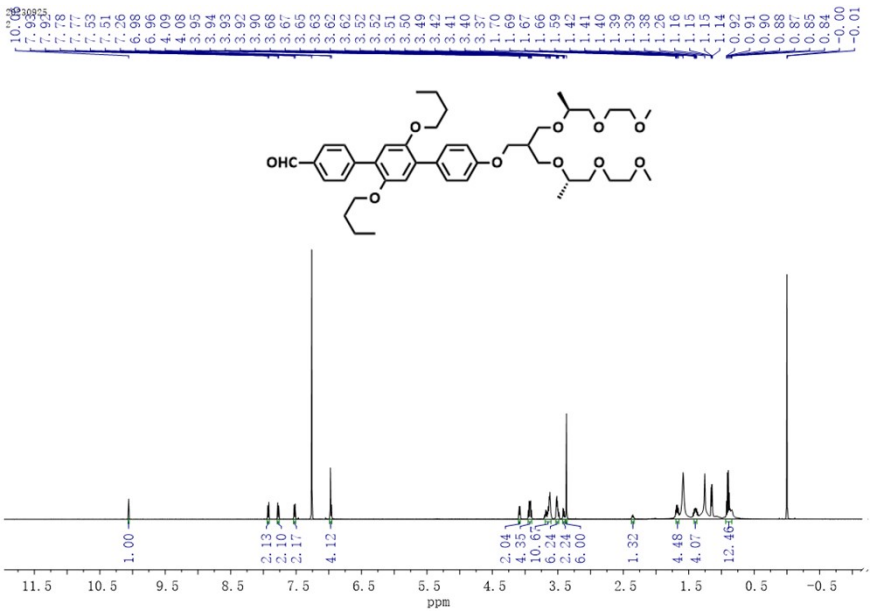


Figure S2. ^{1}H-NMR spectrum of molecule **2** in $CDCl_3$.

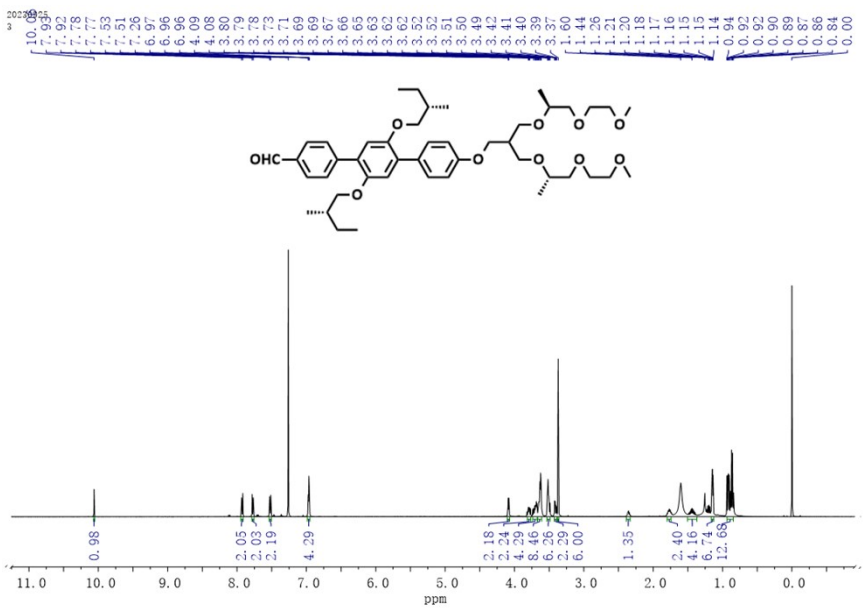


Figure S3. ^{1}H-NMR spectrum of molecule **3** in $CDCl_3$.

2.2 MALDI-TOF-Mass spectra of molecules 1-3.

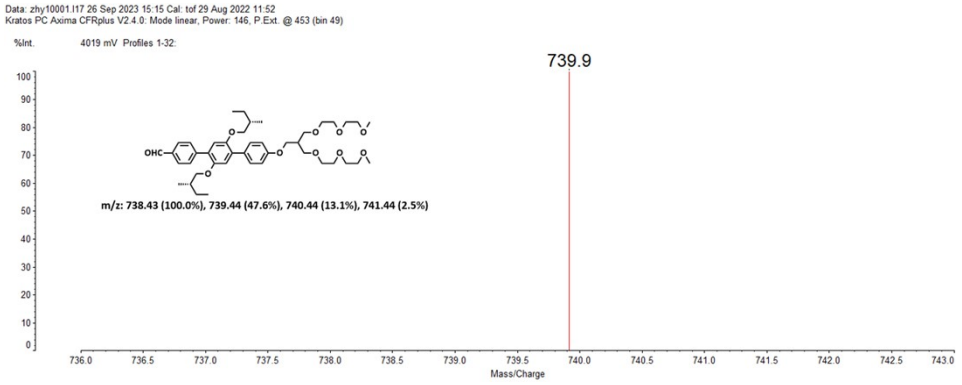


Figure S4. MALDI-TOF-Mass spectrum of molecule **1**.

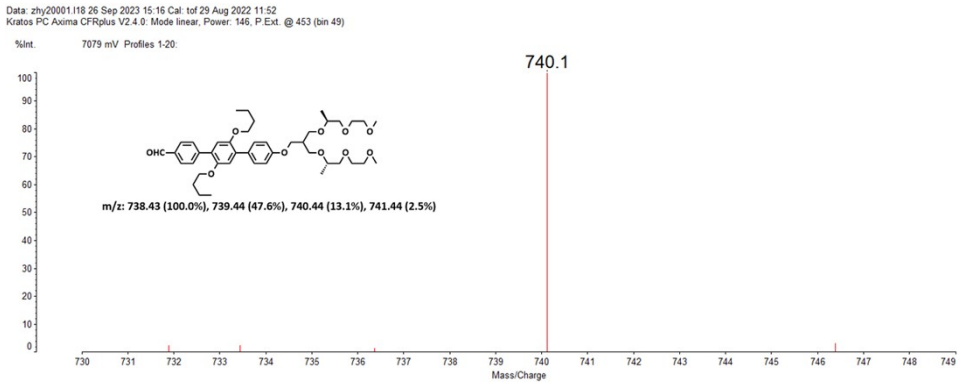


Figure S5. MALDI-TOF-Mass spectrum of molecule **2**.

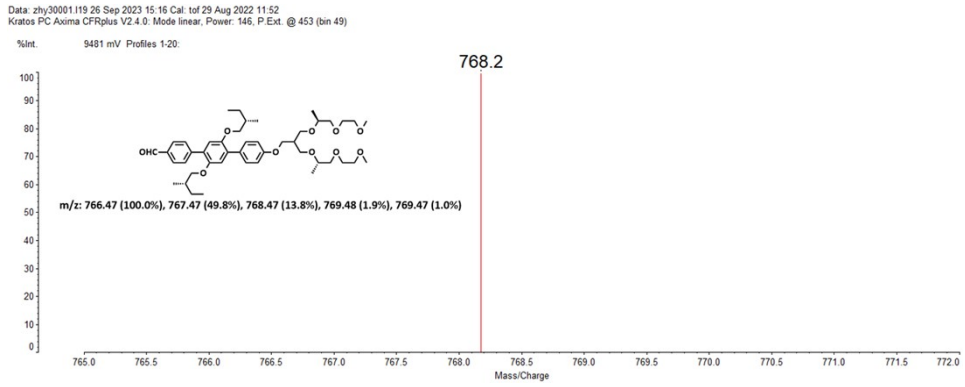


Figure S6. MALDI-TOF-Mass spectrum of molecule **3**.

2.3 Porosity Analysis

Table S1. Porosity analysis of materials.

	S_{BET}[1] (m^2/g)	V_{Total}[2] (cm^3/g)	V_{BJH}[3] (cm^3/g)	D_{Pore}[4] (nm)
SBA-15	490.45	1.08	0.98	10.55
SBA-APT	377.71	0.78	0.57	8.99
SA-M1	96.98	0.15	0.11	4.62
SA-M2	44.74	0.07	0.06	4.62
SA-M3	107.62	0.16	0.12	4.40

[1]Specific surface area calculated from the Brunauer-Emmett-Teller equation.

[2]Total pore volume at the adsorption value of P/P0 = 0.99.

[3]Cumulative volume in the mesopore range of 2-50 nm.

[4]Pore diameter derived from the Barrett, Joyner, and Halenda (BJH) plot.

2.4 TEM and SEM images

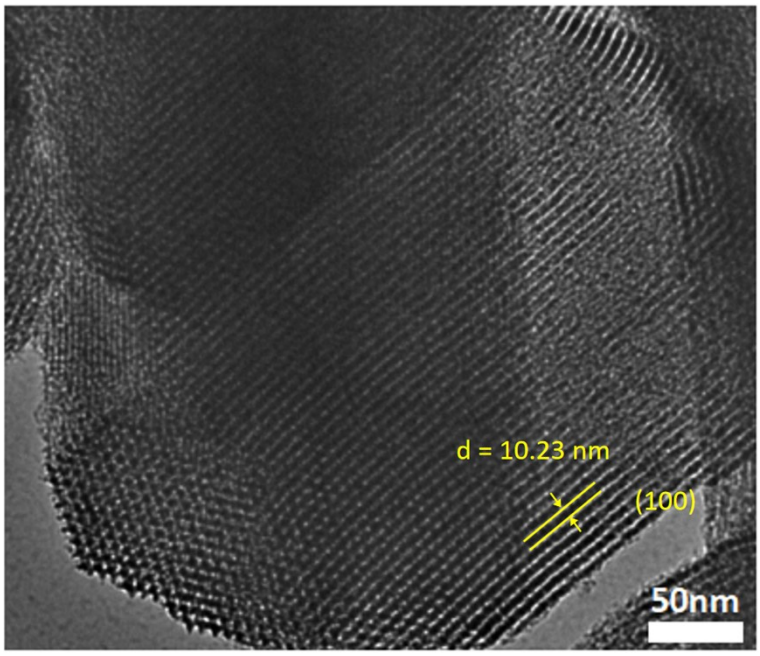


Figure S7. Negative-stained TEM image of SBA-15 with lattice fringe.

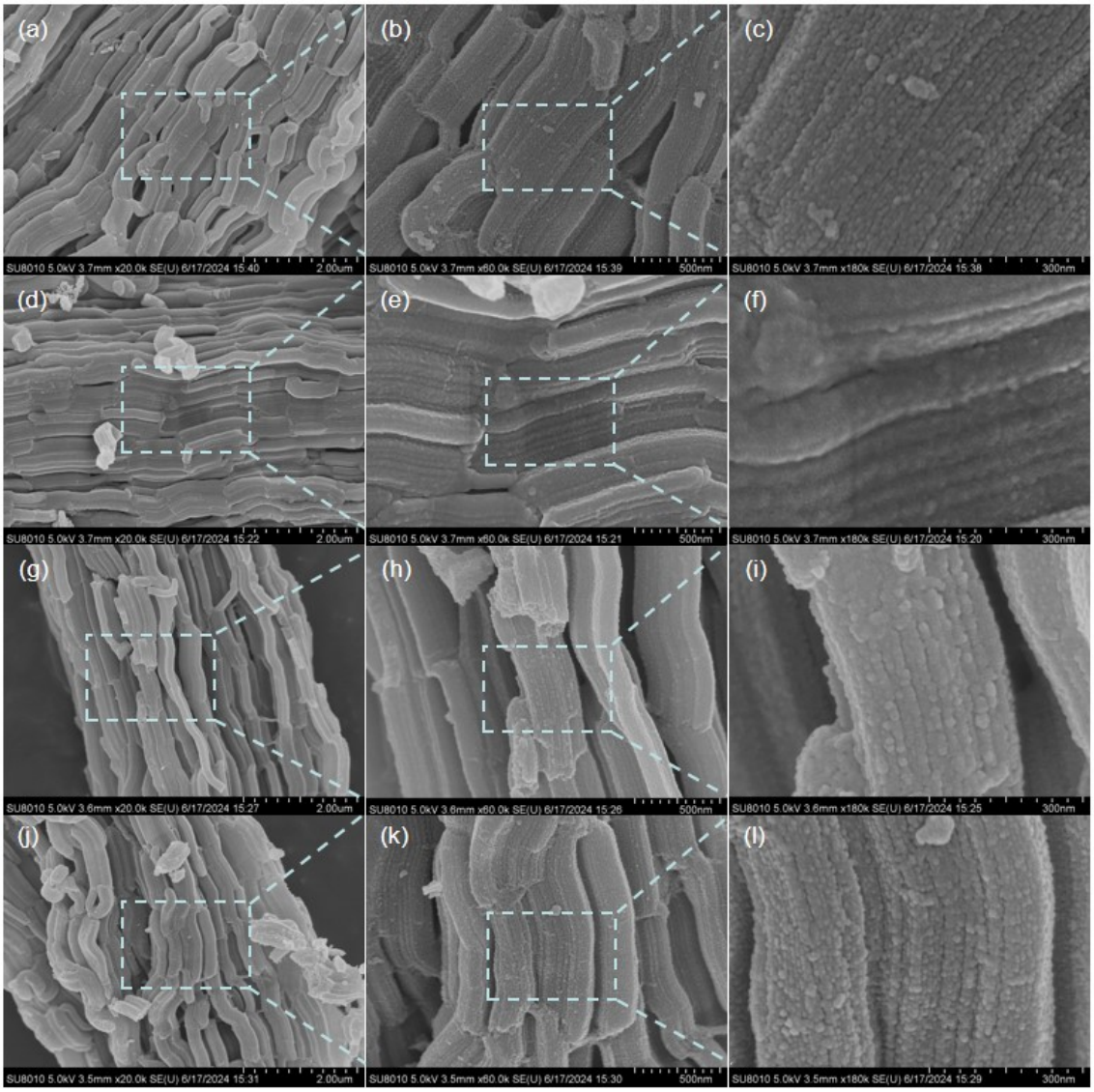


Figure S8. SEM images of SBA-15 (a-c), **SA-M1** (d-f), **SA-M2** (g-i), and **SA-M3** (j-l).

2.5 UV-Vis absorption spectra

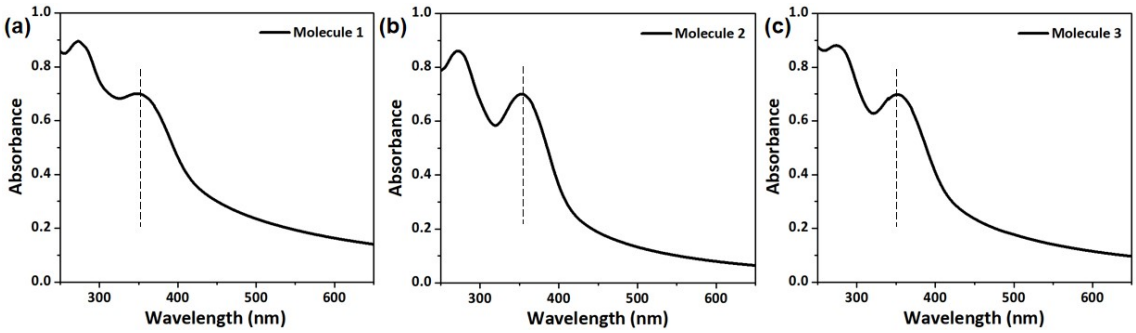


Figure S9. Absorption spectrum of molecule **1** (a), molecule **2** (b), and molecule **3** (c) in H_2O/THF (v/v = 9/1) mixed solvent under the concentration of 25 μM.

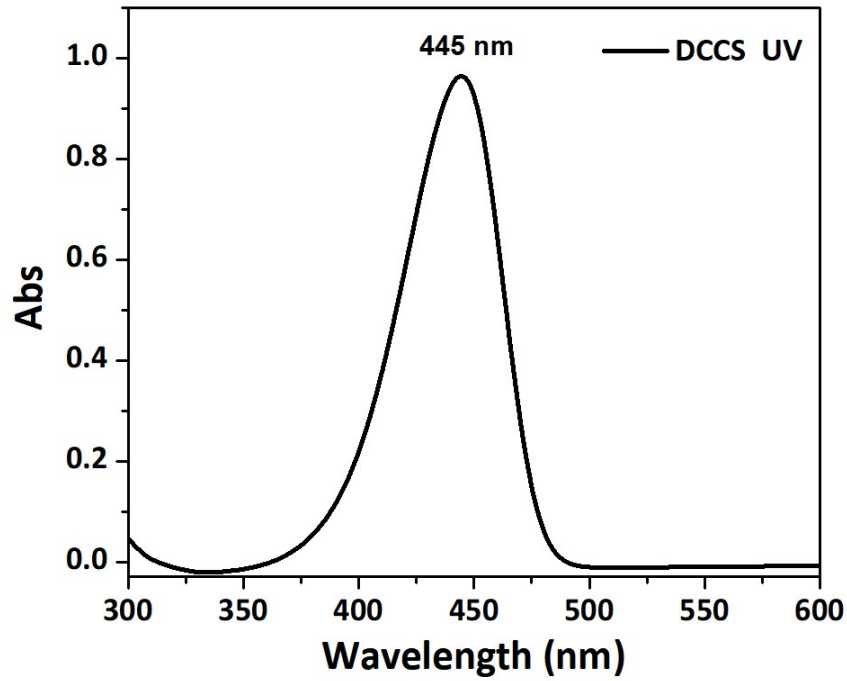


Figure S10. Absorption spectrum of DCCS in H_2O/THF (v/v = 9/1) mixed solvent under the concentration of 25 μM.

2.6 CD spectra in THF

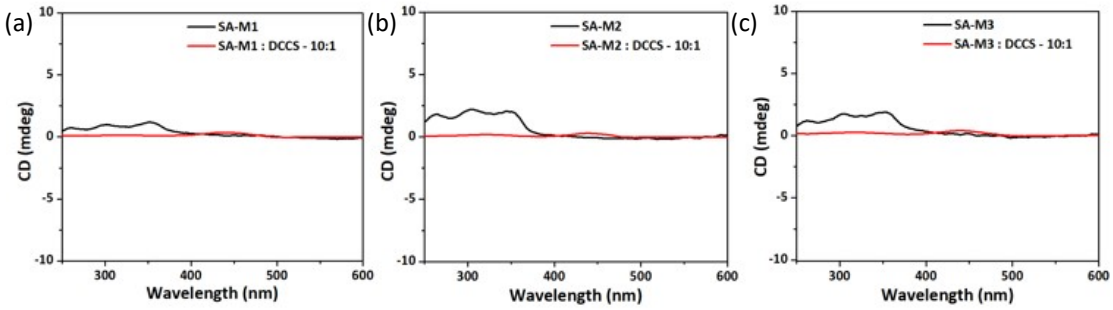


Figure S11. CD spectra of **SA-M1** (a), **SA-M2** (b), **SA-M3** (c) in THF before and after adding DCCS.

2.7 HPLC-MS graph

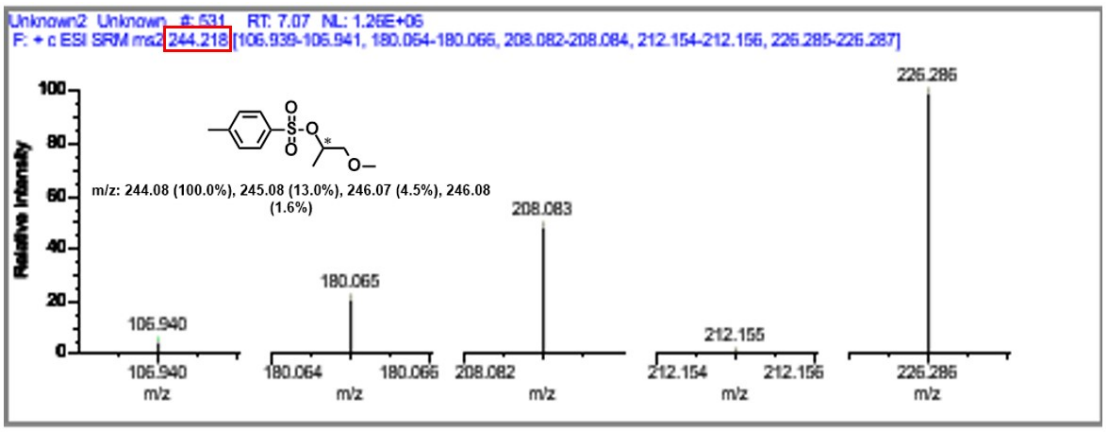


Figure S12. HPLC-MS graph of PM-Ts standard sample.

2.8 HPLC chromatograms

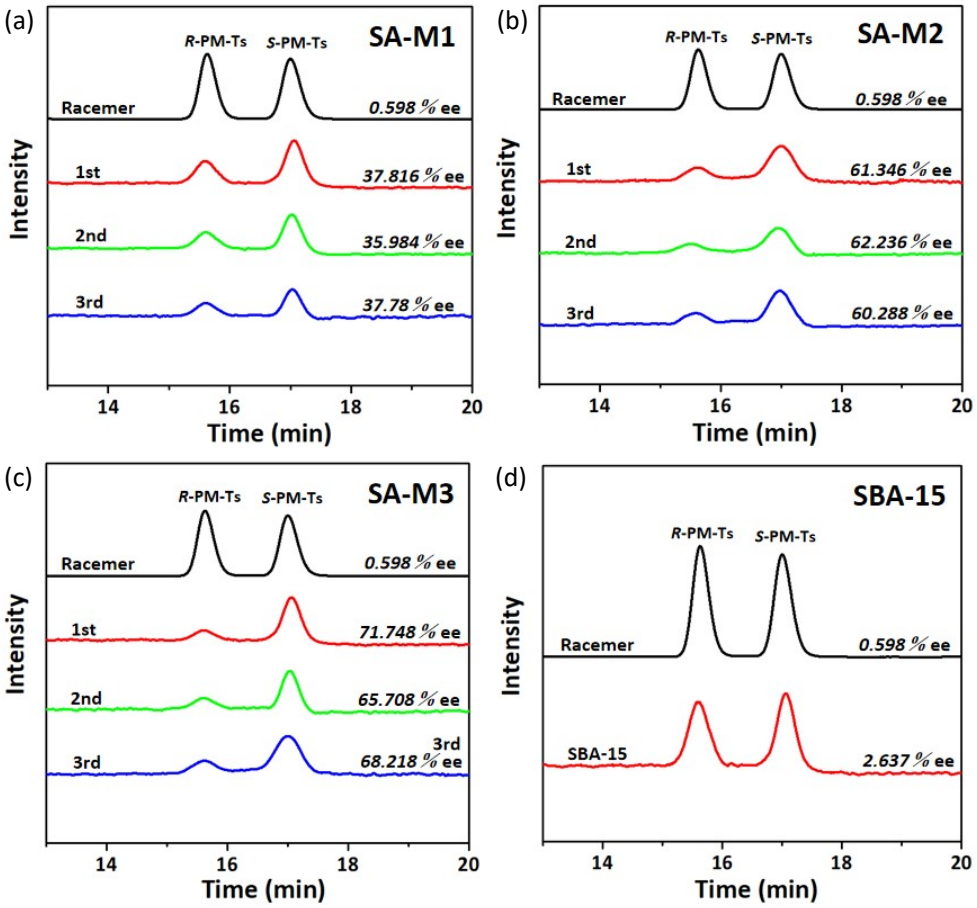


Figure S13. Chiral HPLC chromatograms of the nucleophilic substitution reaction between PM and TsCl in the present of **SA-M1** (a), **SA-M2** (b), **SA-M3** (c) and SBA-15 (d), compared with racemer.

2.9 Catalytic activity for asymmetric synthesis

Table S2. Catalytic activity for asymmetric nucleophilic substitution reaction.

	ee value	loss of efficiency after cyclic utilization	references
Aggregate 1	25.43 %	-	S4
Aggregate 2	24.89 %	-	S5
SA-M1	37.82 %	< 2 %	This work
SA-M2	62.24 %	< 2 %	This work
SA-M3	71.75 %	< 2 %	This work

[S1] Yu, S.; Yang, Y.; Chen, T.; Xu, J.; Jin, L. Y. *Nanoscale*, **2017**, *9*, 17975-17982.
[S2] Wu, Z.; Li, T.; Ding, Y.;Hu, A. *ACS Applied Polymer Materials*, **2020**, *2*, 5414-5422.
[S3] Li, X.; Meng, C.; Meng, Y.; Gu, L.; Chen, Q.; Liu, H. *Colloids Surf. A*, **2019**, *581*, 123789.
[S4] Zhao, H. -Y.; Gou, X.; Pei, Y. -R., Jin, L. Y. *Langmuir*, **2023**, *39*, 8824-8832.
[S5] Zhao, H. -Y.; Liu, G. -L.; Xu, Q.; Pei, Y. -R., Jin, L. Y. *Soft Matter*, **2024**, *20*, 1884-1891.