

## **Polypeptide-Inspired Supramolecular Assemblies for Enantioselective Sorption of Chiral Molecules**

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## 1. Materials and general procedures.

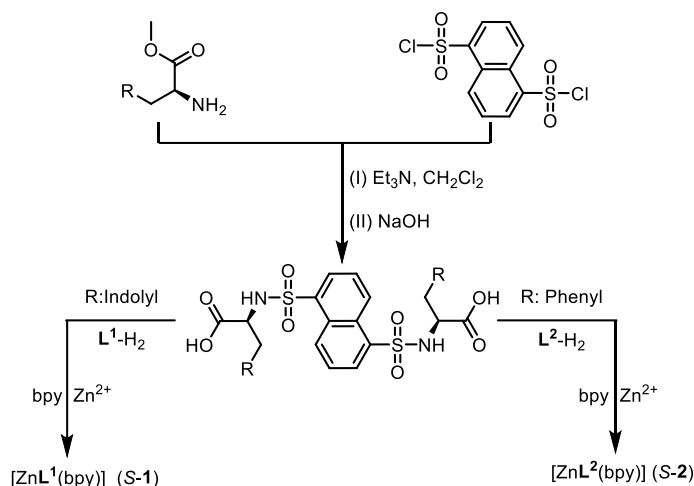
All of the chemicals are commercially available and used without any further purification. Single-crystal XRD data for *S-1* and *S-2* were collected several times at 100 K at NFPS (Shanghai) synchrotron radiation on BL17B beamline, and the obtained dataset was indexed, integrated and scaled using the APEX4 program. The structure of *S-1* and *S-2* was solved by the direct methods with SHELXS-2014 and refined with SHELXL-2014 using *OLEX 2-1.2*. All the hydrogen atoms attached to the ligand were placed in calculated positions and refined using a riding model. Contributions to scattering due to these highly disordered guest molecules in *S-1* and *S-2* were removed using the SQUEEZE subroutine of the PLATON software package. The structure was then refined again using the resulting new HKL file. *S-1* and *S-2* can be best formulated as  $[\text{ZnL}^1(\text{bpy})]$  and  $[\text{ZnL}^2(\text{bpy})]$ , respectively, on the basis of single-crystal diffraction, IR spectra, UV-vis spectra, FL spectra and thermogravimetric analyses (TGA). Crystal data and details of the data collection are given in Table S1 and S2, while the selected bond distances and angles are presented in Tables S3 and S4. CCDC number of *S-1* and *S-2* are 2291733 and 2291734, which contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

Adsorption experiment of 4-nitrophenol (NP): The solvent-exchanged crystals of *S-1* (27 mg) and *S-2* (39 mg), respectively, were immersed in a methanol solution of NP at a concentration of 70  $\mu\text{mol/L}$ . Then, the content of NP molecules in the solution was monitored by UV-Vis at different times. The adsorption results of NP by *S-1* and *S-2* are shown in Fig. S7.

Enantioselective separation experiment: Solvent-exchanged crystals of *S-1* (100 mg) are immersed in 1-phenylethanol (1-PE) solution at a concentration of 100  $\text{mM}^{-1}$  for 12 hours. Then, the crystals of *S-1* were filtered, washed several times with hexane, and soaked in fresh dichloromethane to extract the encapsulated chiral 1-PE molecules in *S-1*. The optical purity of chiral 1-PE molecules was determined by HPLC equipped with chiral column. The enantioseparation of 1-phenylethane-1,2-diol (PED), styrene oxide (SO) and its derivatives by using crystals of *S-1* and *S-2* as

chiral adsorbent, respectively, were conducted under the identical separation procedures as above. The separation results are shown in Table 1 and Fig.S8-11.

## 2. Synthesis of L<sup>1</sup>-H<sub>2</sub>, L<sup>2</sup>-H<sub>2</sub>, S-1 and S-2.

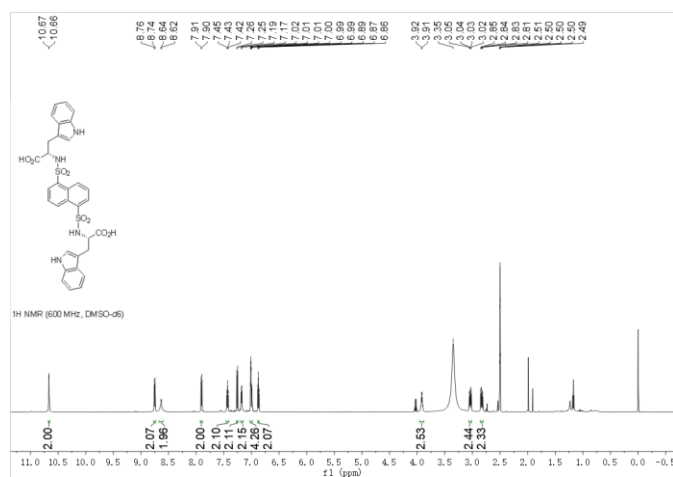


### 2.1 Synthesis of L<sup>1</sup>-Me<sub>2</sub>.

Methyl *L*-tryptophanate (567 mg, 2.6 mmol), naphthalene-1,5-disulfonyl dichloride (423 mg, 1.3 mmol) and Et<sub>3</sub>N (2 mL) were respectively added to a flask containing 50 mL dichloromethane, then the reaction mixture was stirred at room temperature for 12 hours. After which, the resulting crude product was poured into 100 mL of water, and washed by 2M HCl and 2M NaHCO<sub>3</sub>, respectively. The organic phase was extracted with ethyl acetate, dried over Na<sub>2</sub>SO<sub>4</sub>, and concentrated under reduced pressure. About 804 mg of the crude product of L<sup>1</sup>-Me<sub>2</sub> was obtained, which can be used for the next reaction without further purification.

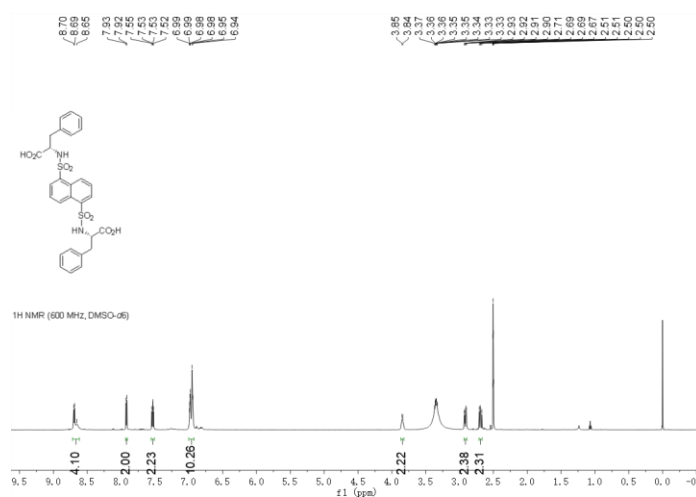
### 2.2 Synthesis of L<sup>1</sup>-H<sub>2</sub>.

L<sup>1</sup>-Me<sub>2</sub> (804 mg, 1.17 mmol) and NaOH (234 mg, 5.85 mmol) were dissolved in a mixture solvent of THF, MeOH and H<sub>2</sub>O (50 mL, volume ratio is 2:4:1) and stirred at 80°C. After 12 hours, the mixed solvent was removed under vacuum, and the residue was diluted with H<sub>2</sub>O and acidified with 2M HCl. The resulting precipitate was filtered and dried, then purified with a silica gel column. Finally, about 650 mg of light-yellow powder of chiral ligand L<sup>1</sup>-H<sub>2</sub> was obtained (the total yield of the two-step reaction is about 75%).



### 2.3 Synthesis of **L**<sup>2</sup>-H<sub>2</sub>.

The synthesis of **L**<sup>2</sup>-H<sub>2</sub> is under a similar reaction routine as that of **L**<sup>1</sup>-H<sub>2</sub>, except that the chiral source is replaced by methyl *L*-phenylalaninate (the total yield of the two-step reaction is about 80%).



### 2.4 Synthesis of **S**-1.

A mixture of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (11.9 mg, 0.04 mmol), *S*-enantiomers of **L**<sup>1</sup>-H<sub>2</sub> (27.7 mg, 0.04 mmol) and 4,4'-bipyridine (bpy, 6.0 mg, 0.04 mmol) was placed in a glass vial containing DMF (1.25 mL), MeCN (3.75 mL). The vial was sealed tightly and heated at 65°C for 72 hours, light-yellow block crystals of [Zn**L**<sup>1</sup>(bpy)] (**S**-1) were generated. When using *R*-enantiomers of **L**<sup>1</sup>-H<sub>2</sub> as the bridging ligand, **R**-1 can be obtained under the identical solvothermal reaction condition.

### 2.5 Synthesis of **S**-2.

A mixture of Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (11.9 mg, 0.04 mmol), *S*-enantiomers of **L**<sup>2</sup>-H<sub>2</sub> (26.4 mg, 0.04 mmol) and 4,4'-bipyridine (bpy, 6.0 mg, 0.04 mmol) was placed in a glass

vial containing DMF (0.8 mL), MeCN (4.2 mL). The vial was sealed tightly and heated at 65°C for 72 hours, colorless block crystals of [ZnL<sup>2</sup>(bpy)] (*S*-**2**) were generated. When using *R*-enantiomers of L<sup>2</sup>-H<sub>2</sub> as the bridging ligand, *R*-**2** can be obtained under the identical solvothermal reaction condition.

### 3. Table S1. Crystal data and structure refinements for S-1.

Identification code	S-1
Empirical formula	C <sub>42</sub> H <sub>34</sub> N <sub>6</sub> O <sub>8</sub> S <sub>2</sub> Zn
Formula weight	880.24
Temperature (K)	100
Wavelength (Å)	0.68871
Crystal system, space group	Monoclinic, <i>P</i> 2 <sub>1</sub>
Unit cell dimensions	a = 13.3072(5) Å alpha = 90 deg. b = 18.7479(8) Å beta = 108.06 (1) deg. c = 19.9060(9) Å gamma = 90 deg.
Volume	4721.5(3) Å <sup>3</sup>
Z, Calculated density	4, 1.238 mg/m <sup>3</sup>
Absorption coefficient	0.610 mm <sup>-1</sup>
F(000)	1816
θ range for data collection (°)	1.585 to 29.827
Limiting indices	-19<=h<=19, -26<=k<=26, -27<=l<=27
Reflections collected independent reflections	77240 / 24603 [R(int) = 0.0491]
Completeness to theta Refinement method	98.0 %
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	24603/79/1051
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.008
Final R indices [ <i>I</i> >2σ( <i>I</i> )]	R1 = 0.0446, wR2 = 0.1159
R indices (all data)	R1 = 0.0542, wR2 = 0.1223

**4. Table S2. Crystal data and structure refinements for S-2.**

Identification code	S-2
Empirical formula	C <sub>36</sub> H <sub>30</sub> N <sub>4</sub> O <sub>8</sub> S <sub>2</sub> Zn
Formula weight	790.89
Temperature (K)	100
Wavelength (Å)	0.67022
Crystal system, space group	Orthorhombic, <i>P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub></i>
Unit cell dimensions	a = 15.6146(7) Å    alpha = 90 deg. b = 16.0947(9) Å    beta = 90 deg. c = 18.7996(1) Å    gamma = 90 deg.
Volume	4724.6(4) Å <sup>3</sup>
Z, Calculated density	4, 1.112 mg/m <sup>3</sup>
Absorption coefficient	0.559 mm <sup>-1</sup>
F(000)	1629
θ range for data collection (°)	1.571 to 27.347
Limiting indices	-18<=h<=18, -21<=k<=21, -24<=l<=24
Reflections collected independent reflections	79150 / 11782 [R(int) = 0.1503]
Completeness to theta Refinement method	97.6 %
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	11782 / 121 / 506
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.082
Final R indices [ <i>I</i> >2σ( <i>I</i> )]	R1 = 0.0726, wR2 = 0.2024
R indices (all data)	R1 = 0.0854, wR2 = 0.2168



**5. Table S3. Selected Bond lengths [Å] and angles [°] for S-1.**

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Zn(2)-O(15)	1.922(3)
Zn(2)-O(9)	1.931(3)
Zn(2)-N(12)#1	2.071(3)
Zn(2)-N(11)	2.027(3)
Zn(1)-O(1)	1.937(3)
Zn(1)-O(8)	1.918(3)
Zn(1)-N(6)#2	2.053(3)
Zn(1)-N(5)	2.050(3)
O(15)-Zn(2)-O(9)	124.65(13)
O(15)-Zn(2)-N(12)#1	96.73(12)
O(15)-Zn(2)-N(11)	115.90(13)
O(9)-Zn(2)-N(12)#1	112.49(12)
O(9)-Zn(2)-N(11)	98.97(13)
N(11)-Zn(2)-N(12)#1	107.80(13)
O(1)-Zn(1)-N(6)#2	112.98(12)
O(1)-Zn(1)-N(5)	98.44(13)
O(8)-Zn(1)-O(1)	124.56(13)
O(8)-Zn(1)-N(6)#2	97.63(13)
O(8)-Zn(1)-N(5)	115.98(13)
N(5)-Zn(1)-N(6)#2	106.82(13)

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Symmetry transformations used to generate equivalent atoms:

#1  $-x+1, y-1/2, -z+1$       #2  $-x, y+1/2, -z$

#3  $-x+1, y+1/2, -z+1$       #4  $-x, y-1/2, -z$

**6. Table S4. Selected Bond lengths [Å] and angles [°] for S-2.**

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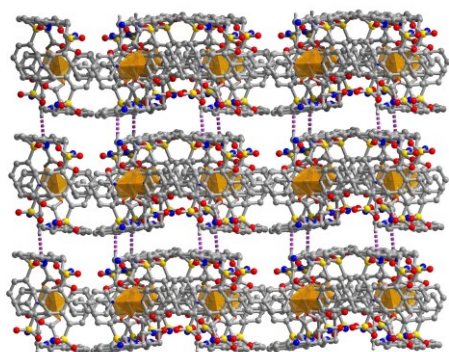
Zn(1)-O(2)	1.929(4)
Zn(1)-O(8)	1.972(4)
Zn(1)-N(3)	2.040(5)
Zn(1)-N(4)#1	2.067(5)
O(2)-Zn(1)-O(8)	112.0(2)
O(2)-Zn(1)-N(3)	122.2(2)
O(2)-Zn(1)-N(4)#1	115.5(2)
O(8)-Zn(1)-N(3)	107.5(2)
O(8)-Zn(1)-N(4)#1	95.1(2)
N(3)-Zn(1)-N(4)#1	100.7(2)

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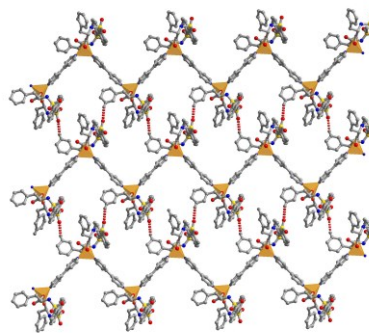
Symmetry transformations used to generate equivalent atoms:

#1  $-x+1, y-1/2, -z+1/2$       #2  $-x+1, y+1/2, -z+1/2$

## 7. Figure S1. Additional X-ray structures of S-1 and S-2.

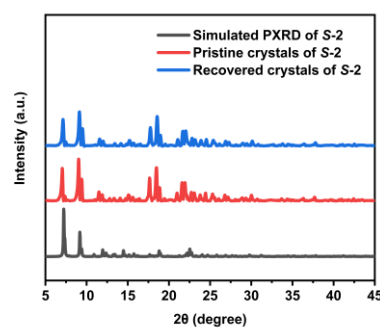
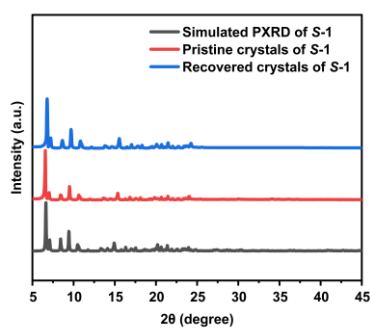


View of the 3D supramolecular structure and C-H... $\pi$  interactions of S-1.

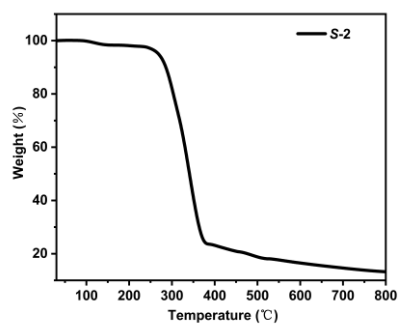
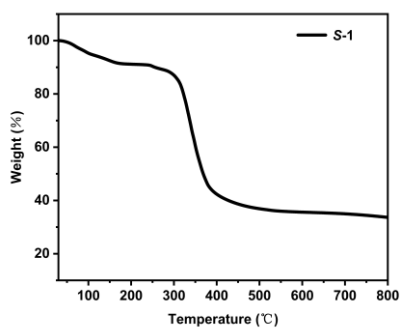


View of the 2D network and H-bonding of S-2.

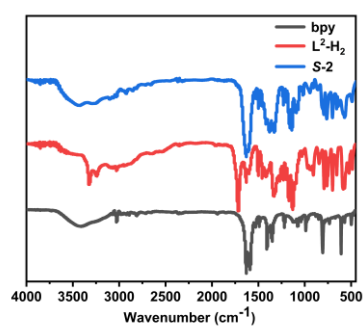
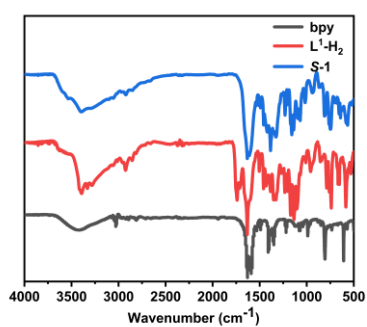
## 8. Figure S2. PXRD patterns of S-1 and S-2.



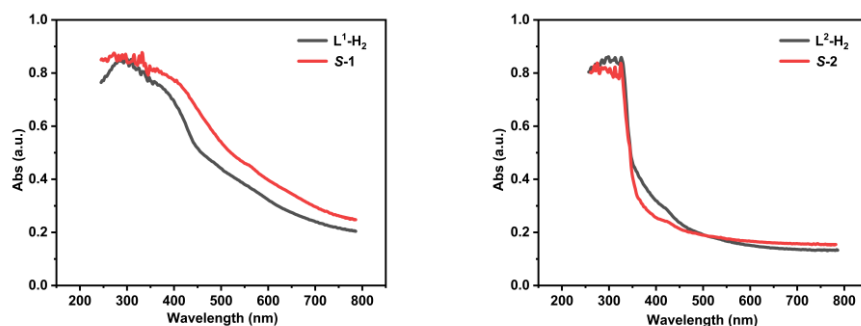
## 9. Figure S3. TGA curves of S-1 and S-2.



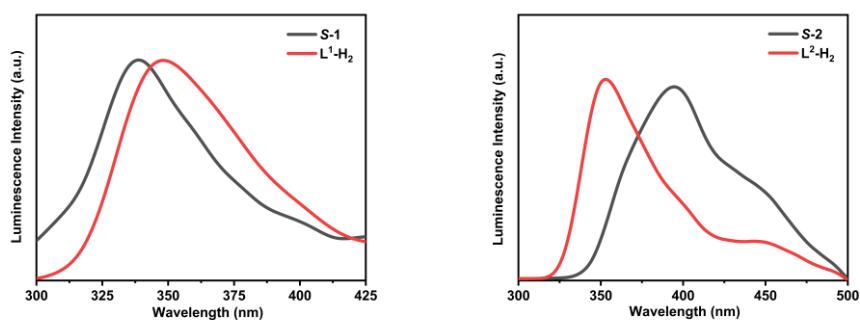
## 10. Figure S4. IR spectra of L<sup>1</sup>-H<sub>2</sub>, L<sup>2</sup>-H<sub>2</sub>, S-1 and S-2.



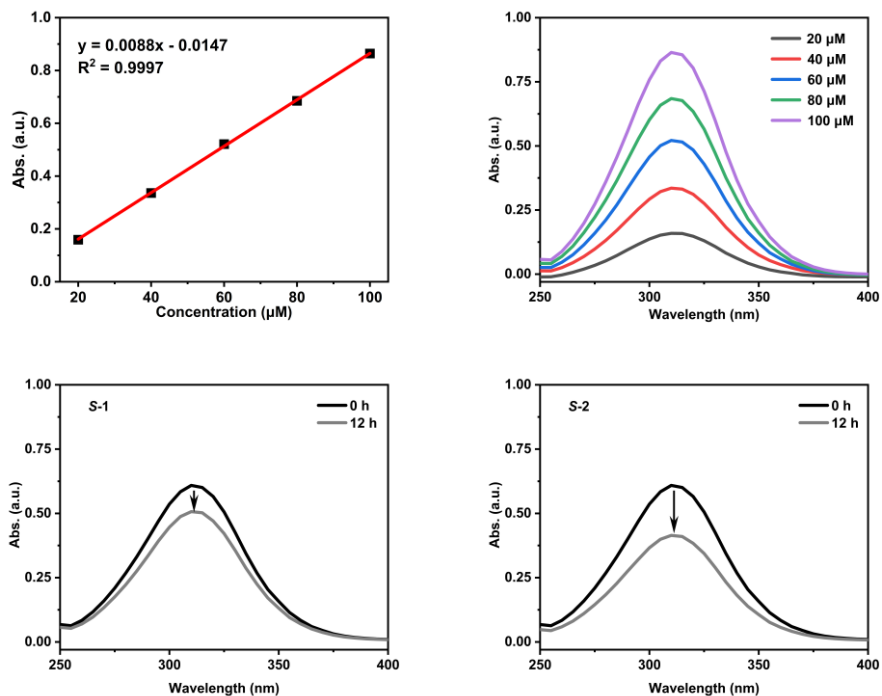
11. Figure S5. UV-vis spectra of L<sup>1</sup>-H<sub>2</sub>, L<sup>2</sup>-H<sub>2</sub>, S-1 and S-2.



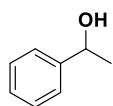
12. Figure S6. FL spectra of L<sup>1</sup>-H<sub>2</sub>, L<sup>2</sup>-H<sub>2</sub>, S-1 and S-2.



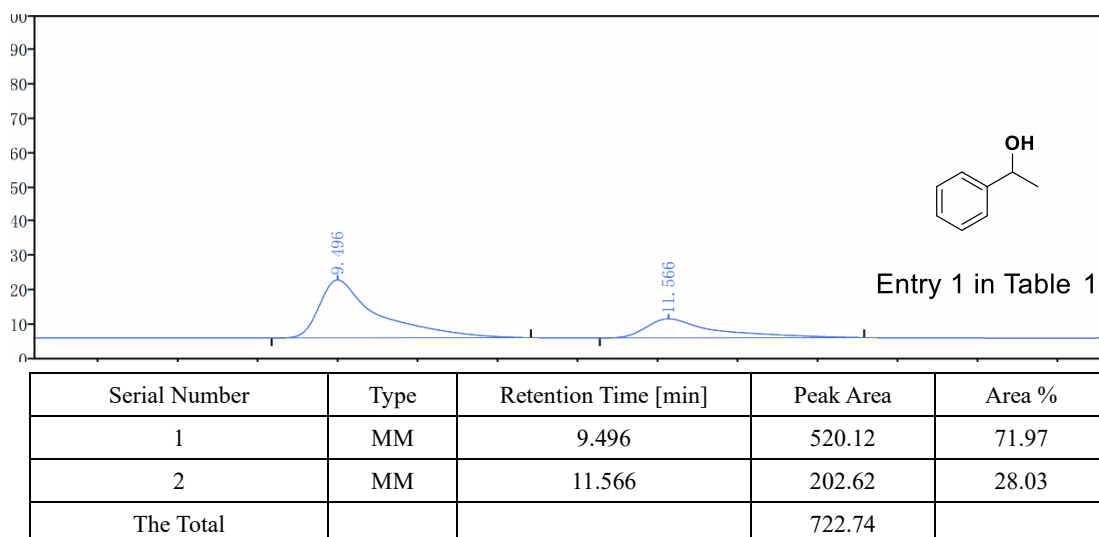
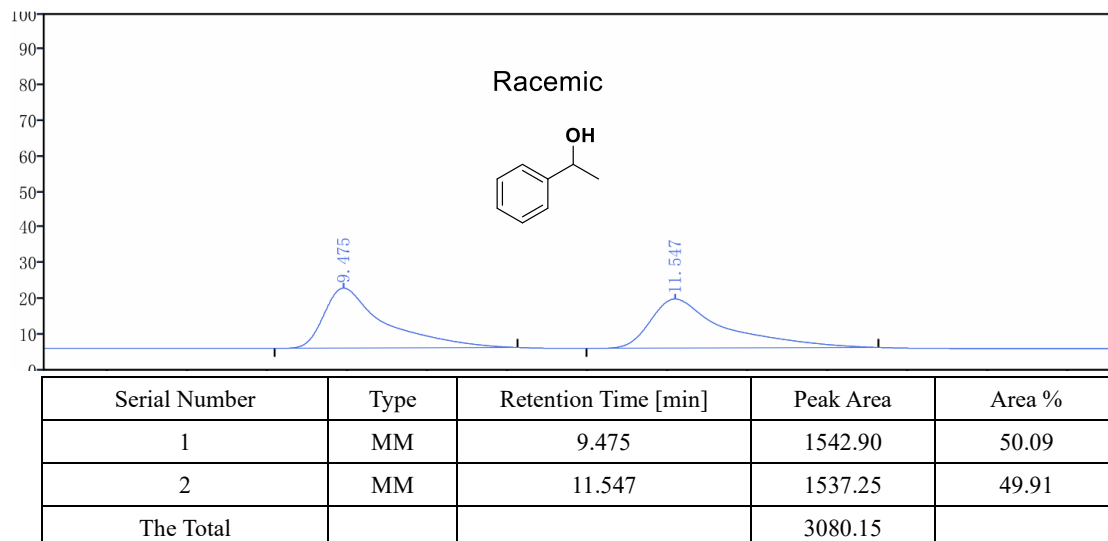
13. Figure S7. The adsorption of S-1 and S-2 to NP molecules.

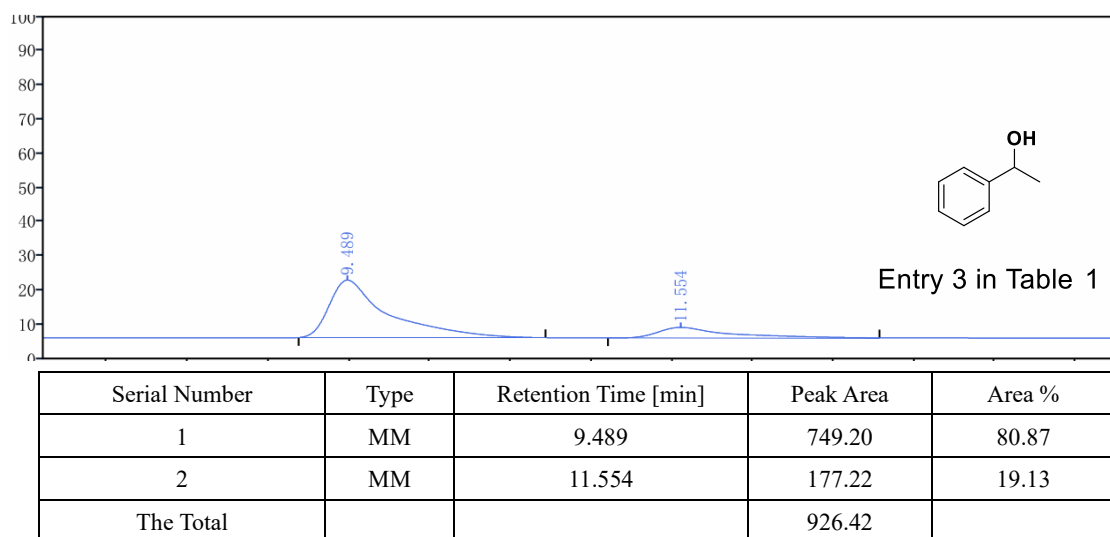
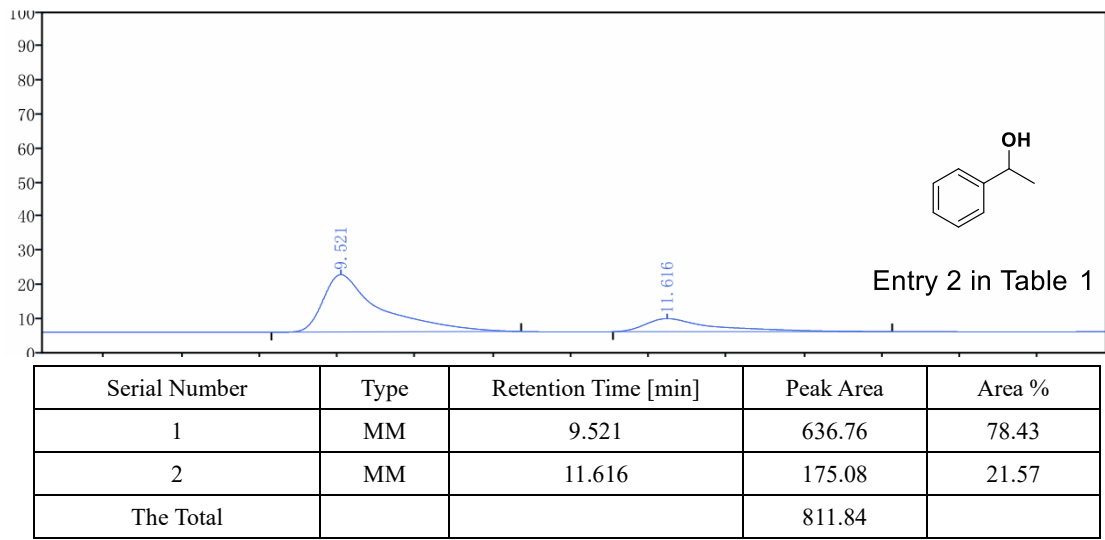


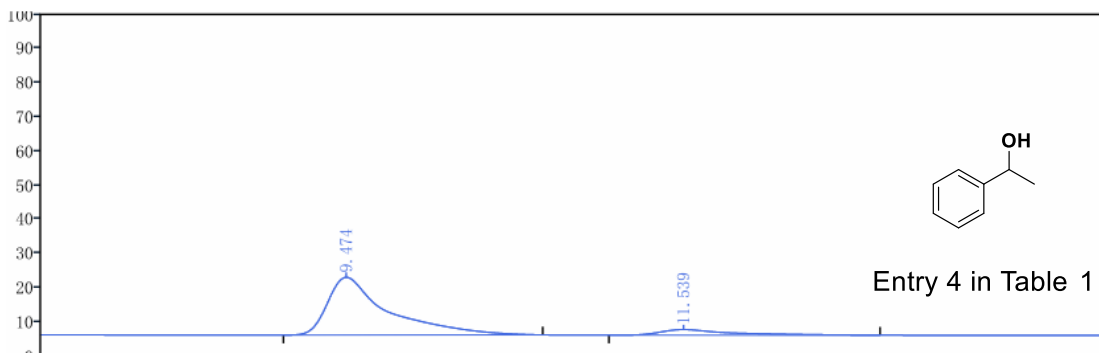
#### 14. Figure S8. HPLC results (in Table 1).



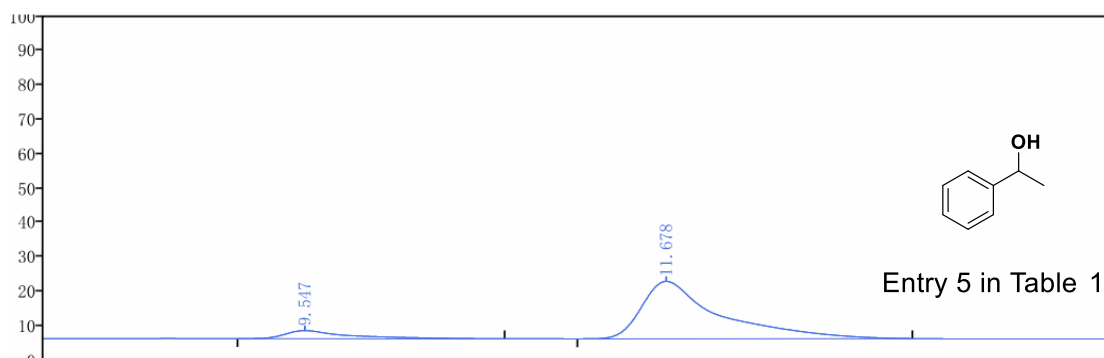
Chiral HPLC analysis: Daicel Chiralce OD: hexane/*i*-PrOH = 97/3; flow rate = 1.0 mL/min; 220 nm.





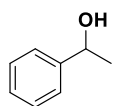


Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	9.474	1051.16	89.42
2	MM	11.539	124.41	10.58
The Total			1175.57	



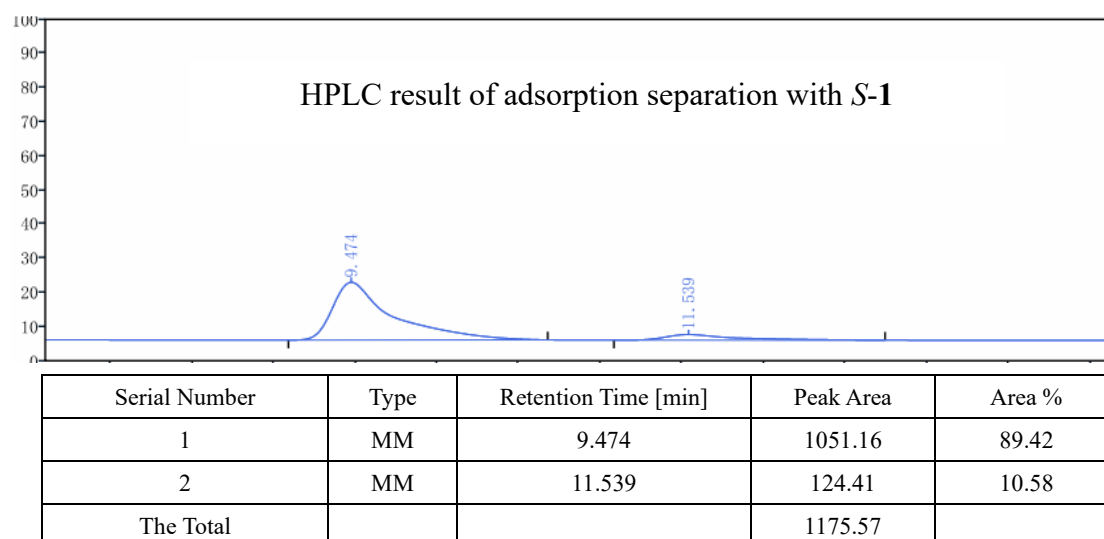
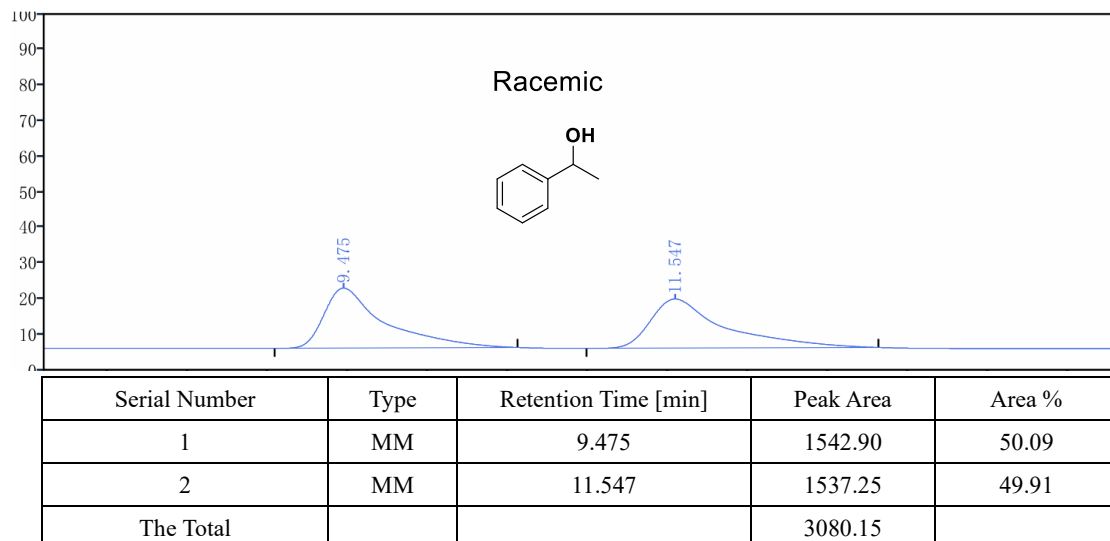
Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	9.547	88.25	10.47
2	MM	11.678	754.93	89.53
The Total			843.18	

**15. Figure S9. HPLC results (in Figure 2).**

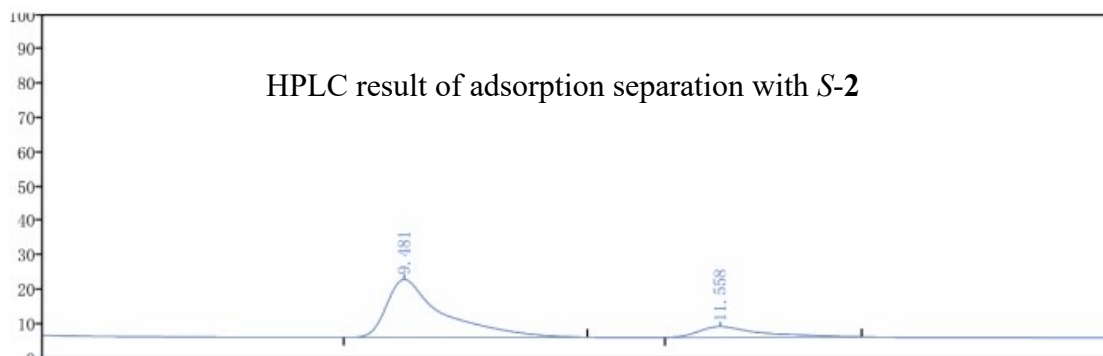


Chiral HPLC analysis: Daicel Chiralce OD: hexane/*i*-PrOH = 97/3; flow rate = 1.0

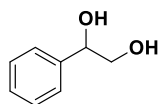
mL/min; 220 nm.



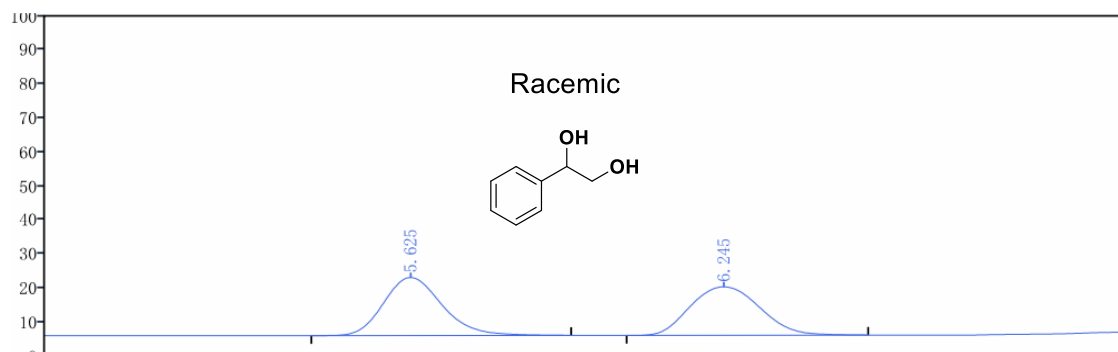




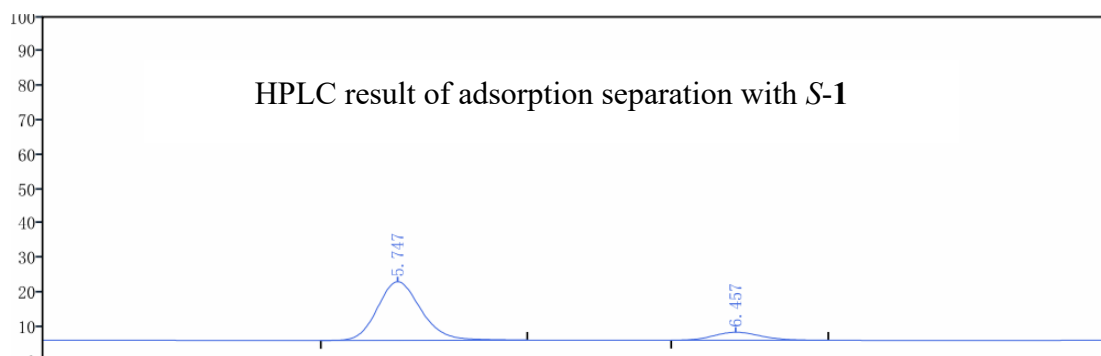
Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	9.481	1061.13	83.38
2	MM	11.558	211.48	16.62
The Total			1272.61	



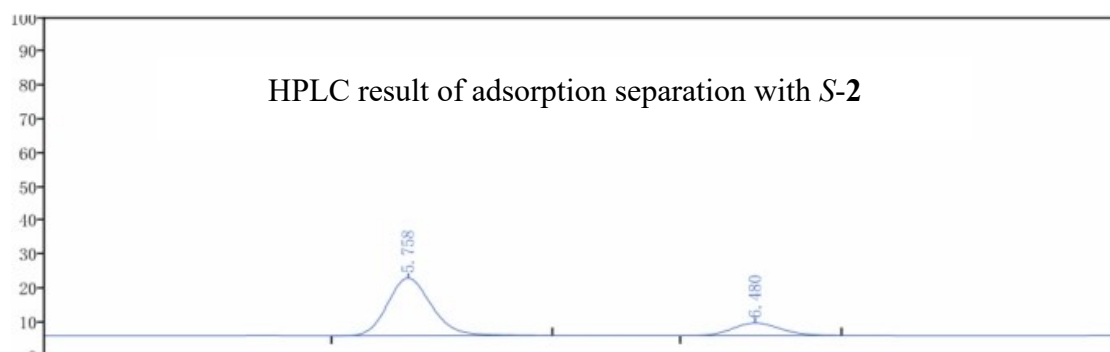
Chiral HPLC analysis: Daicel Chiralce OD: hexane/*i*-PrOH = 97/3; flow rate = 1.0 mL/min; 220 nm;  $t_R = 5.625$  min,  $t_R = 6.245$  min.



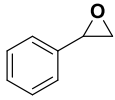
Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	5.625	6806.18	50.07
2	MM	6.245	6786.34	49.93
The Total			13592.52	



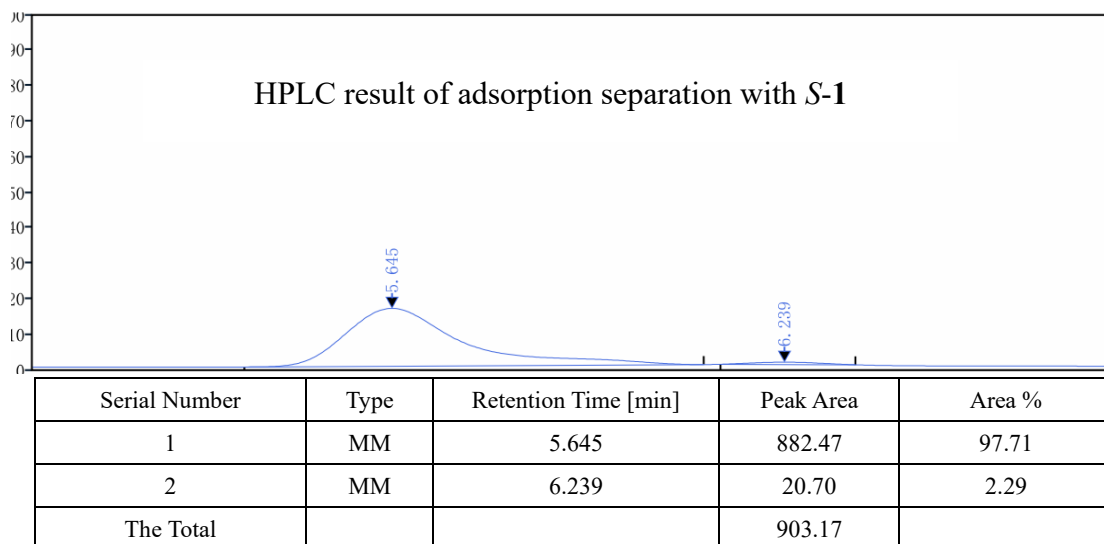
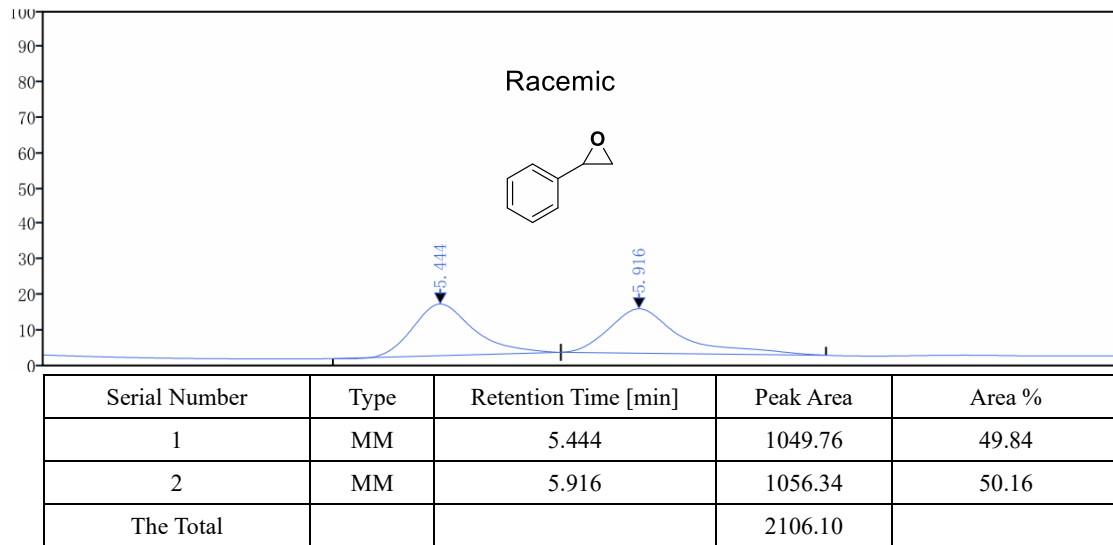
Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	5.747	736.95	86.98
2	MM	6.457	110.33	13.02
The Total			847.28	

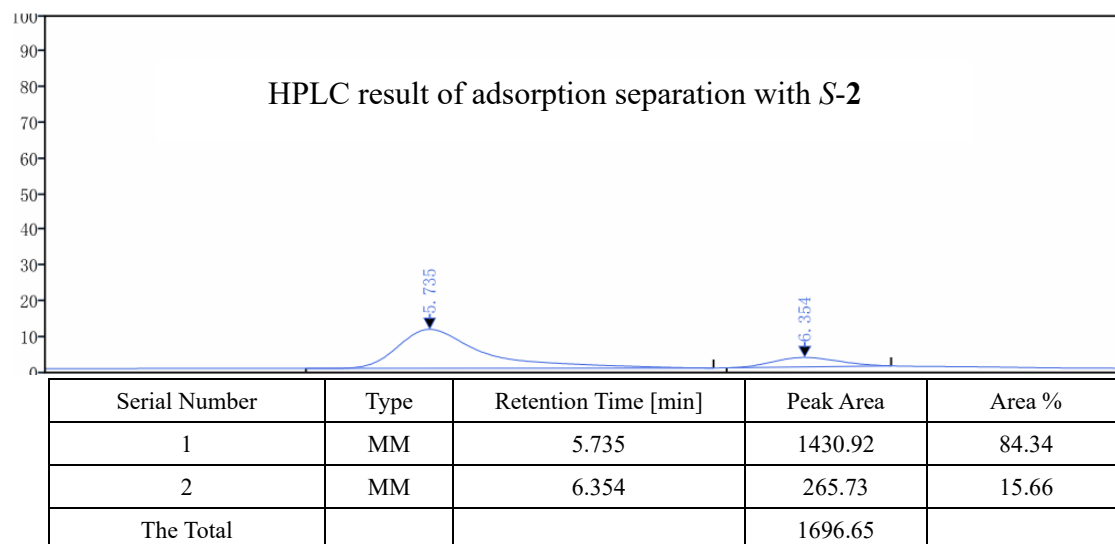


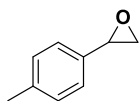
Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	5.758	675.10	80.74
2	MM	6.480	161.01	19.26
The Total			836.11	



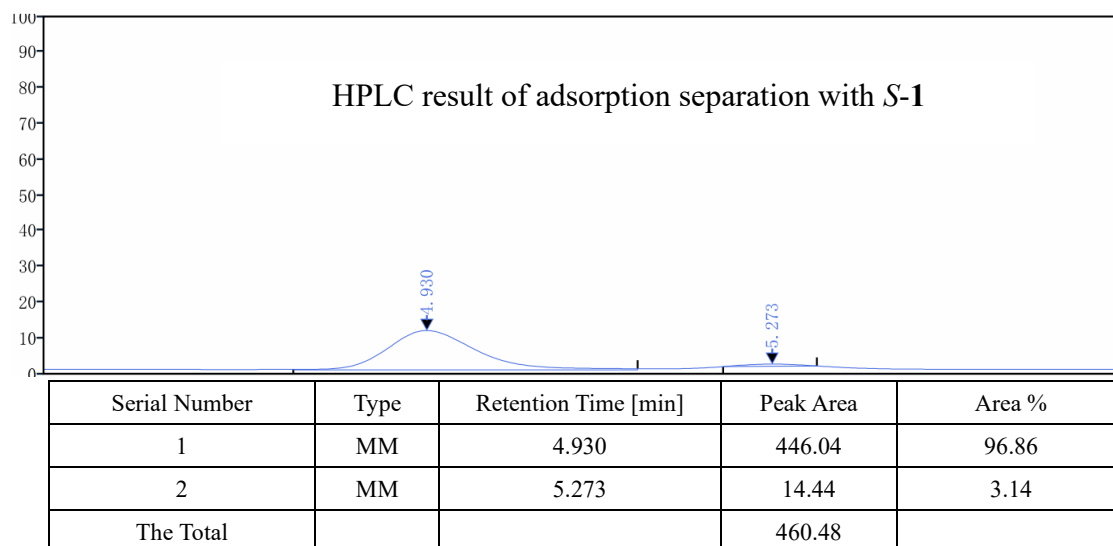
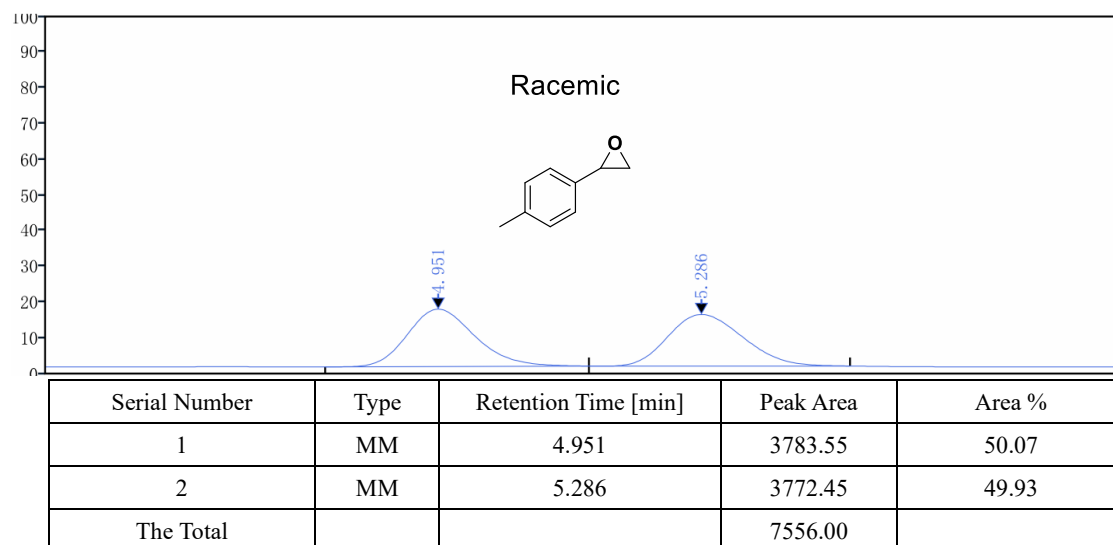
Chiral HPLC analysis: Daicel Chiralce IC-H: hexane/*i*-PrOH = 95/5; flow rate = 1.0 mL/min; 220 nm;  $t_R = 5.444$  min,  $t_R = 5.916$  min.

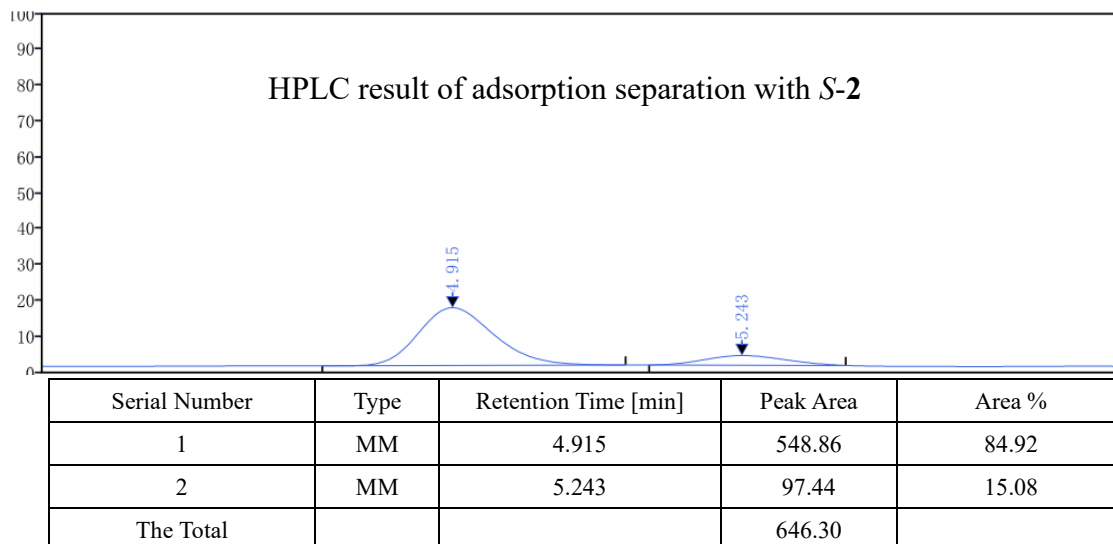


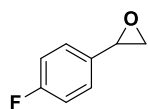




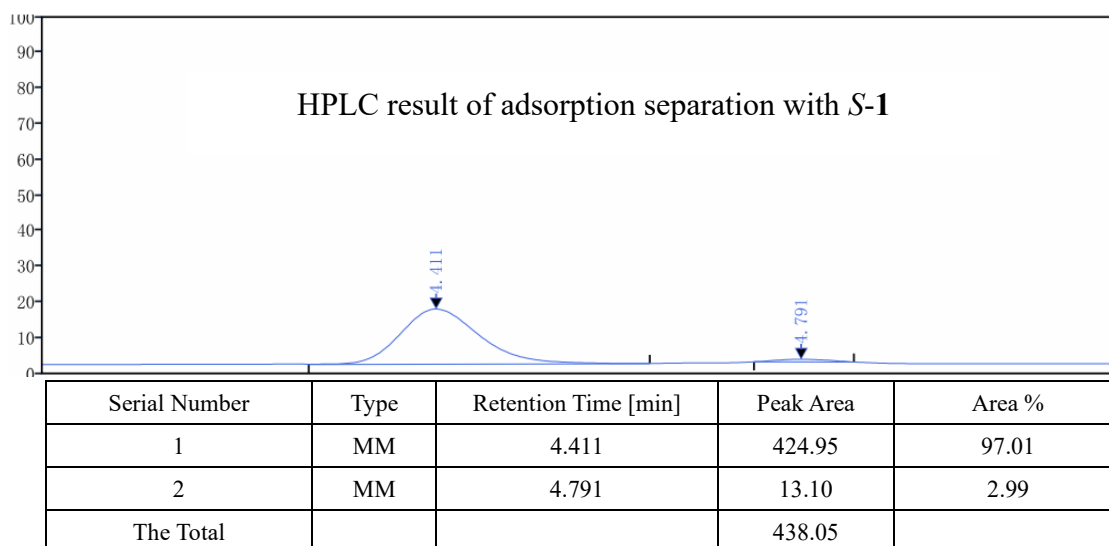
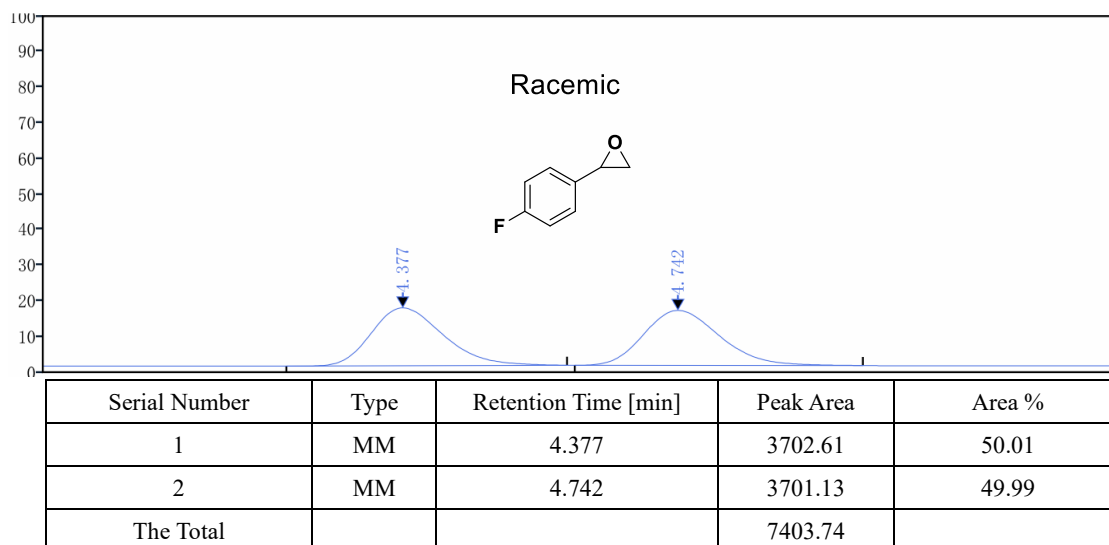
Chiral HPLC analysis: Daicel Chiralce IC-H: hexane/*i*-PrOH = 95/5; flow rate = 1.0 mL/min; 220 nm;  $t_R = 4.951$  min,  $t_R = 5.286$  min.



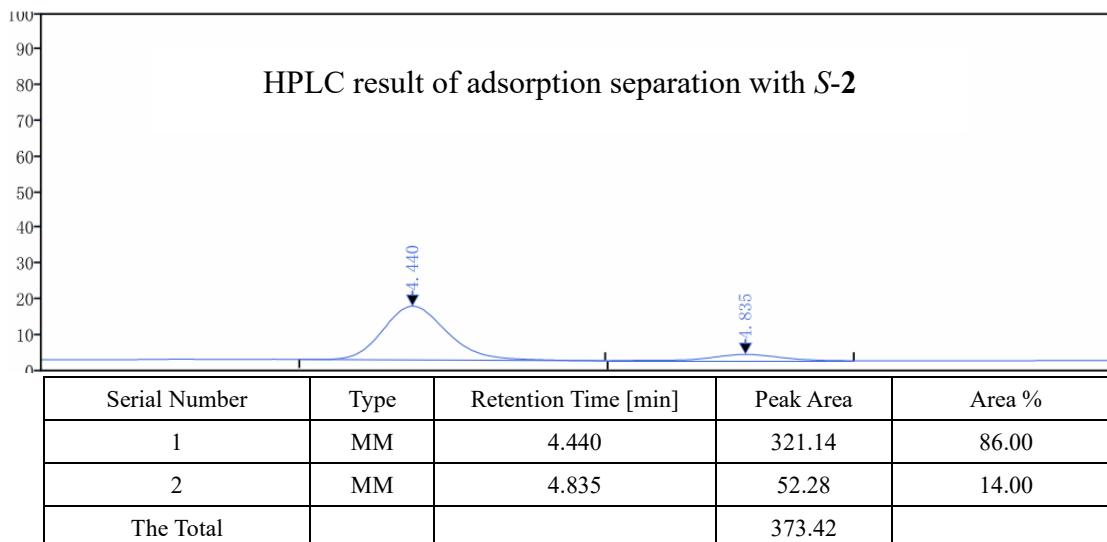


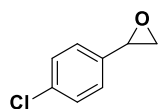


Chiral HPLC analysis: Daicel Chiralce IC-H: hexane/*i*-PrOH = 95/5; flow rate = 1.0 mL/min; 220 nm;  $t_R = 4.377$  min,  $t_R = 4.742$  min.

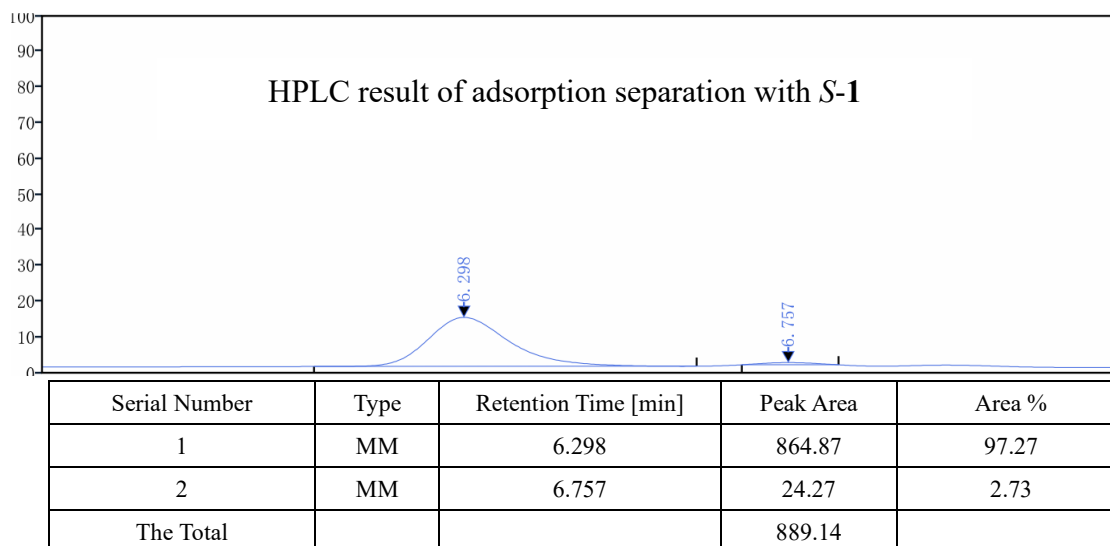
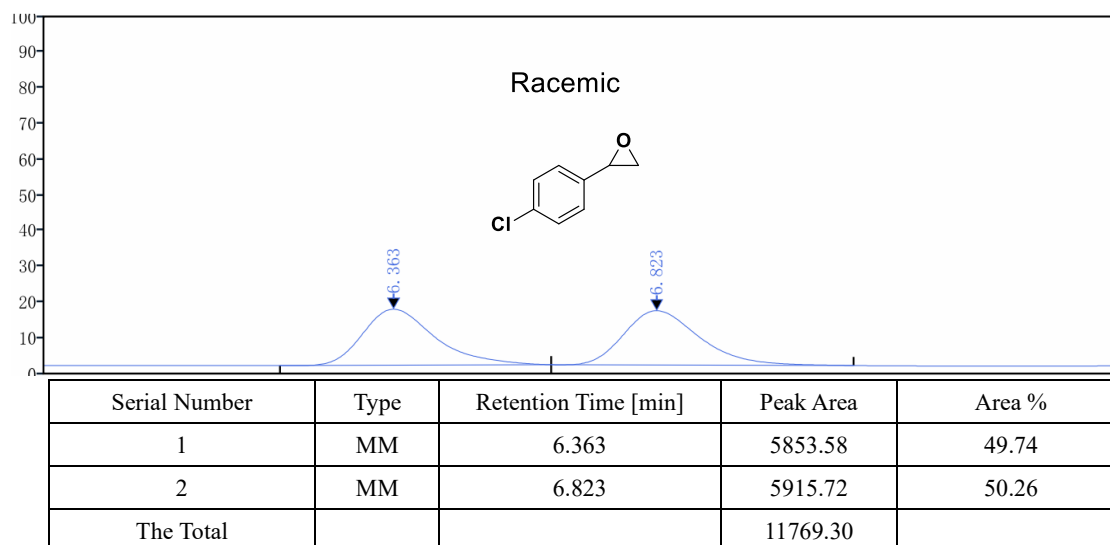


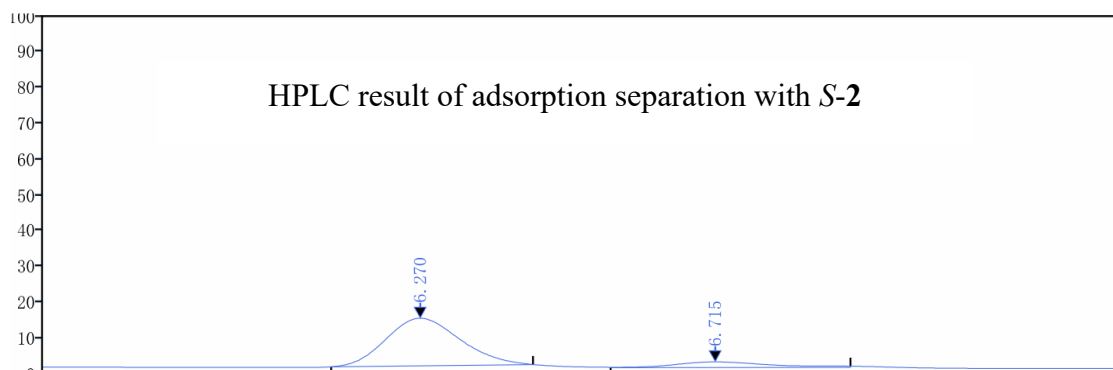






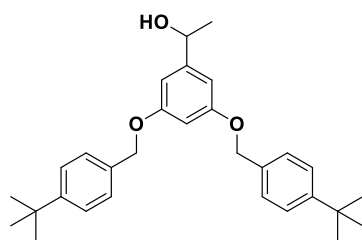
Chiral HPLC analysis: Daicel Chiralce IC-H: hexane/*i*-PrOH = 95/5; flow rate = 1.0 mL/min; 220 nm;  $t_R = 6.363$  min,  $t_R = 6.823$  min.



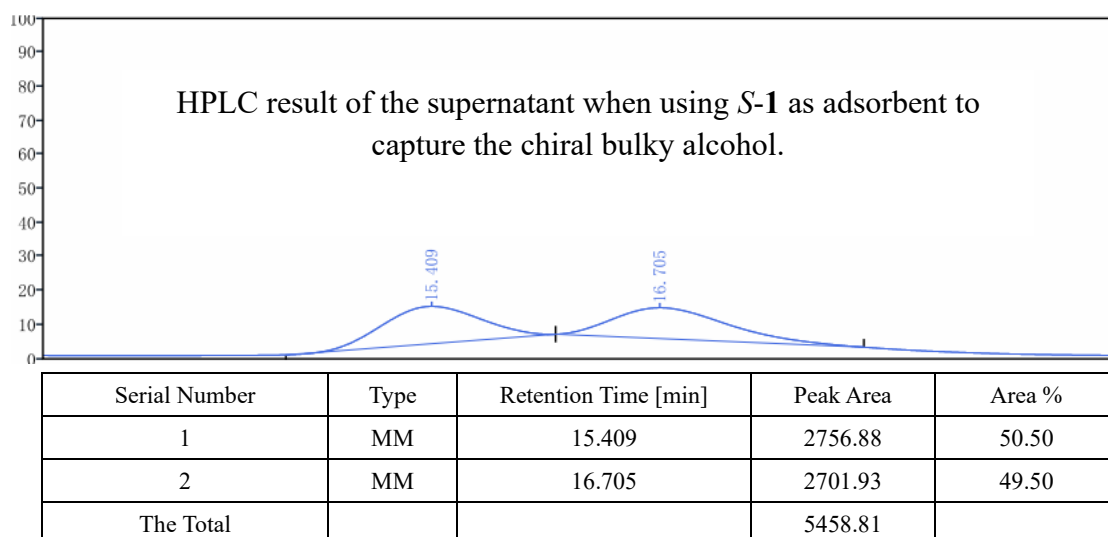
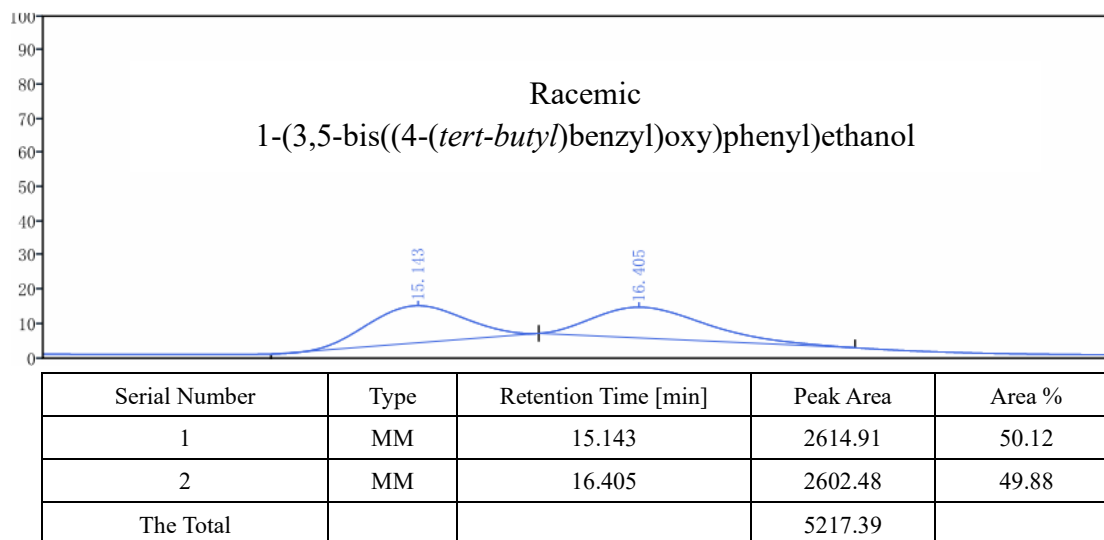


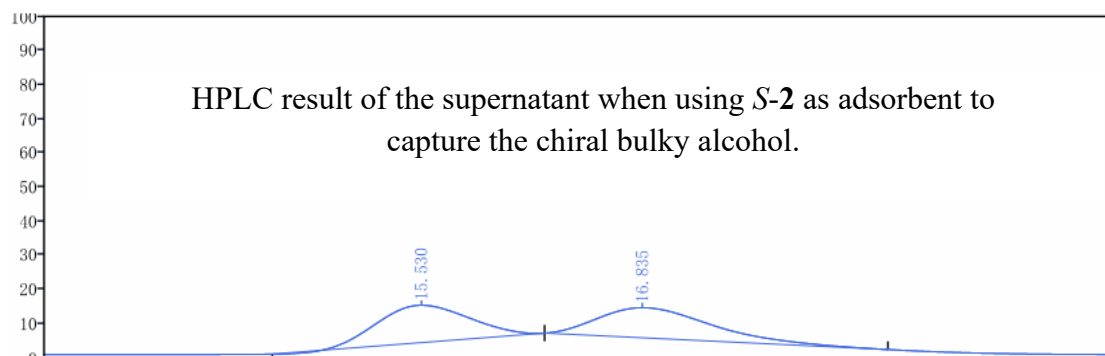
Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	6.270	974.29	86.01
2	MM	6.715	158.44	13.99
The Total			1132.73	

**16. Figure S10. HPLC results of the chiral sorption towards bulky substrates.**

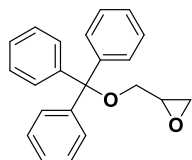


Chiral HPLC analysis: Daicel Chiralce OD: hexane/*i*-PrOH = 95/5; flow rate = 1.0 mL/min; 220 nm;  $t_R = 15.143$  min,  $t_R = 16.405$  min.

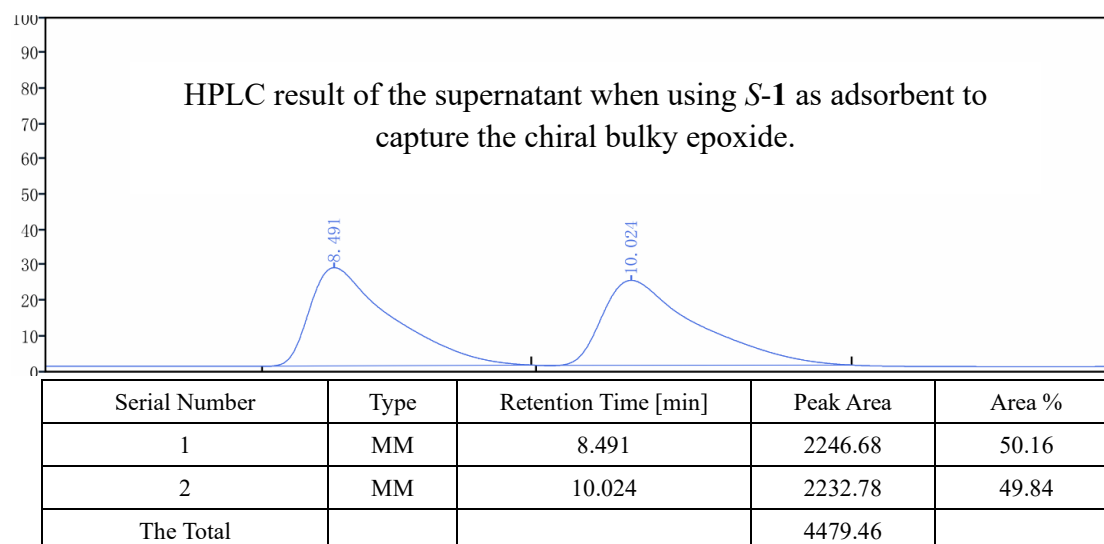
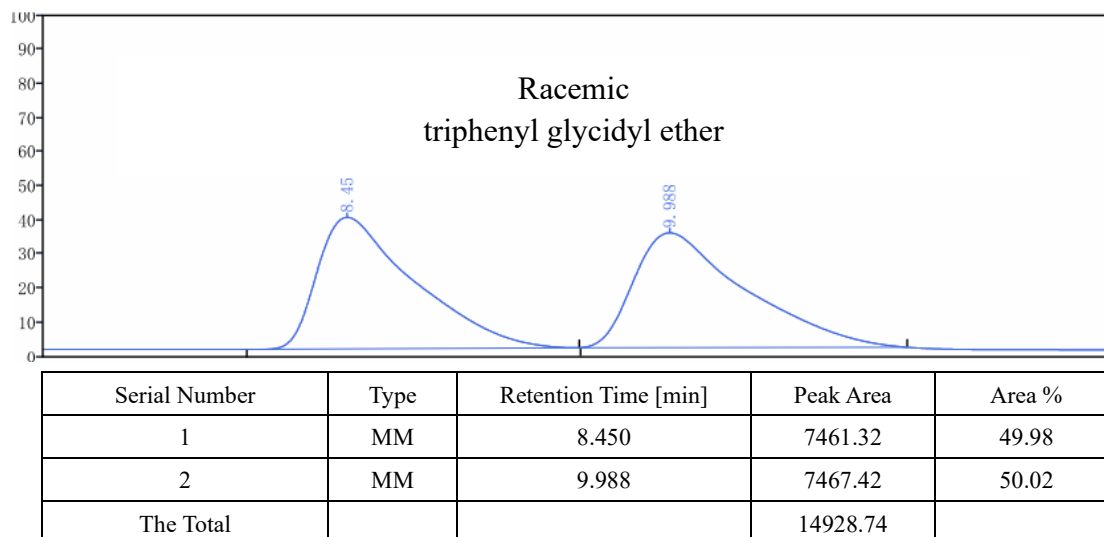


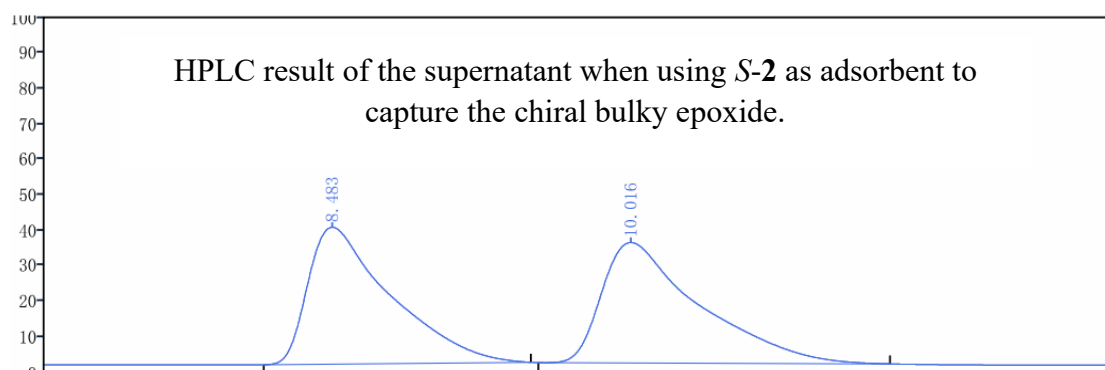


Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	15.530	2924.42	49.72
2	MM	16.835	2957.51	50.28
The Total			5881.93	



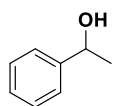
Chiral HPLC analysis: Daicel Chiralcel OD: hexane/*i*-PrOH = 95/5; flow rate = 1.0 mL/min; 220 nm;  $t_R = 8.450$  min,  $t_R = 9.988$  min.



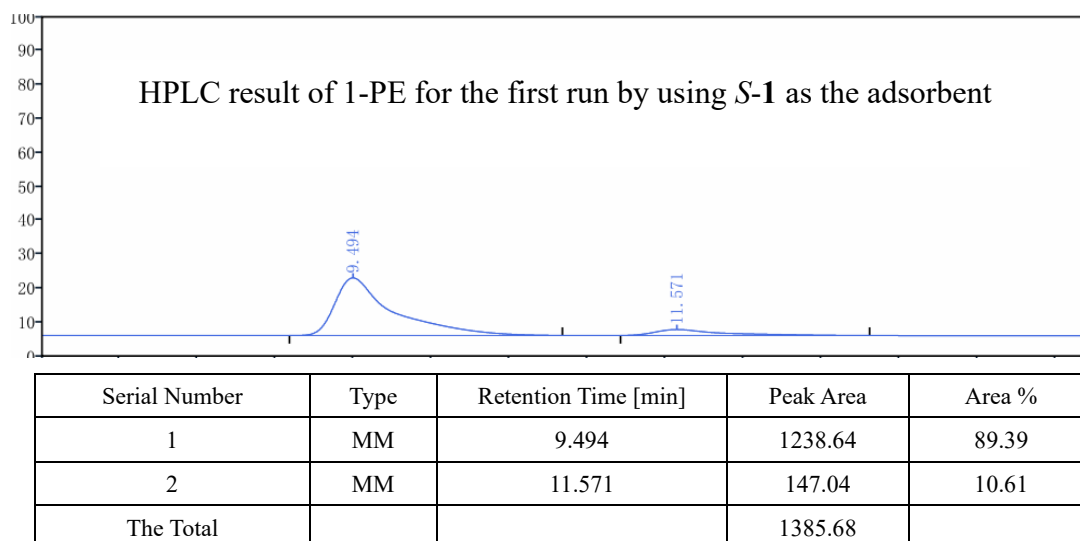
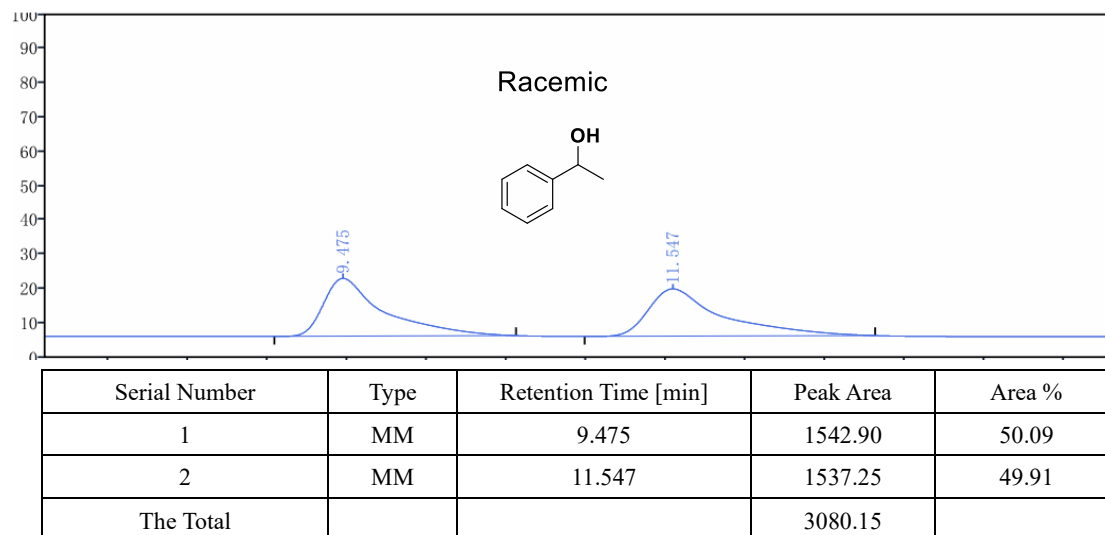


Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	8.483	3254.25	49.08
2	MM	10.016	3376.60	50.92
The Total			6630.84	

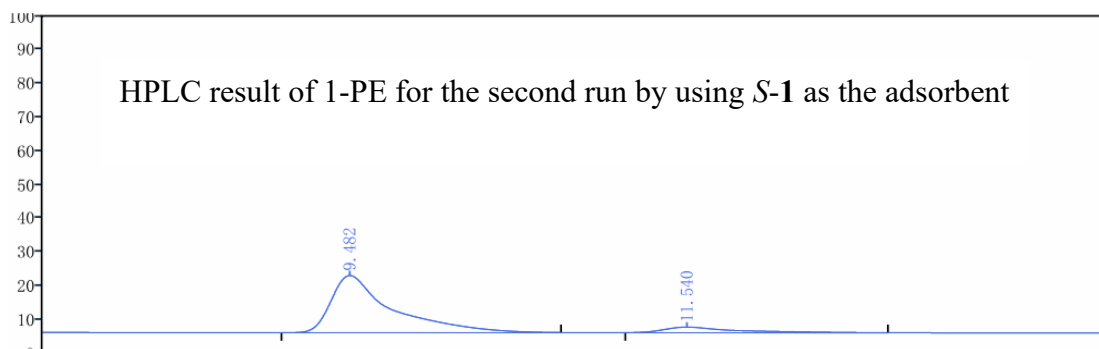
### 17. Figure S11. HPLC results of cyclic chiral sorption experiments.



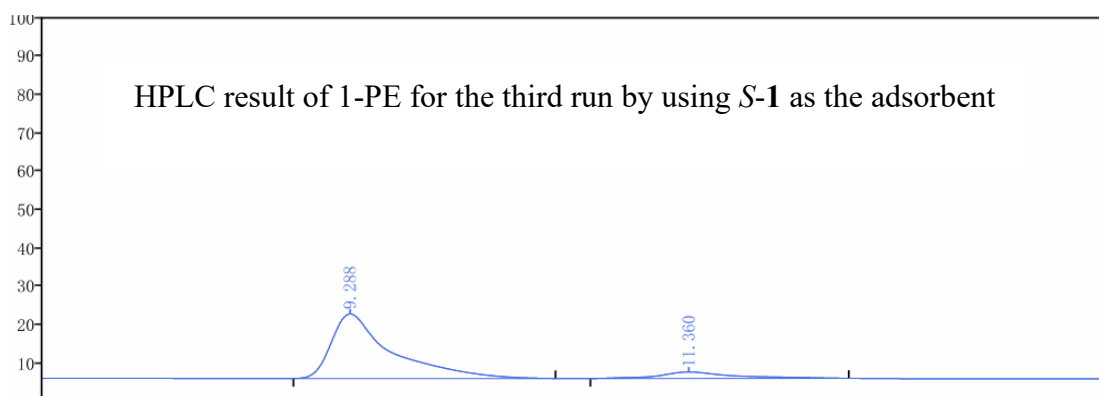
Chiral HPLC analysis: Daicel Chiralce OD: hexane/*i*-PrOH = 97/3; flow rate = 1.0 mL/min; 220 nm;  $t_R = 9.475$  min,  $t_R = 11.547$  min.



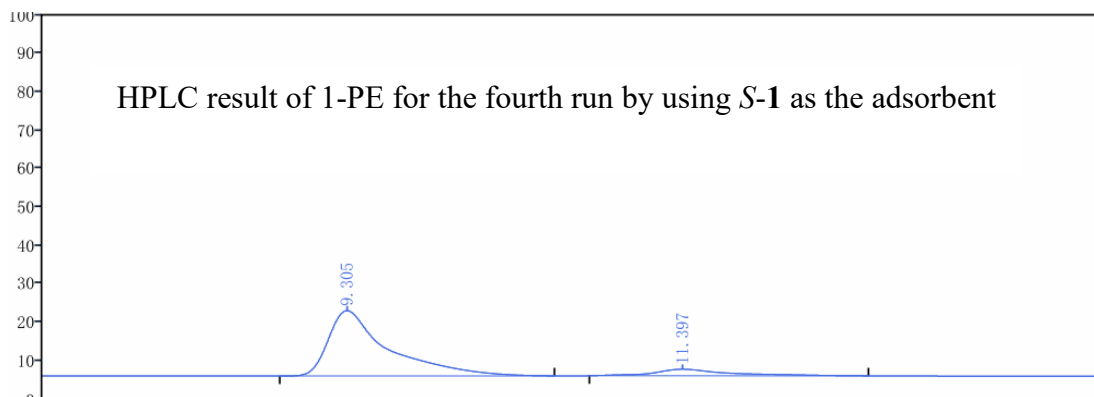




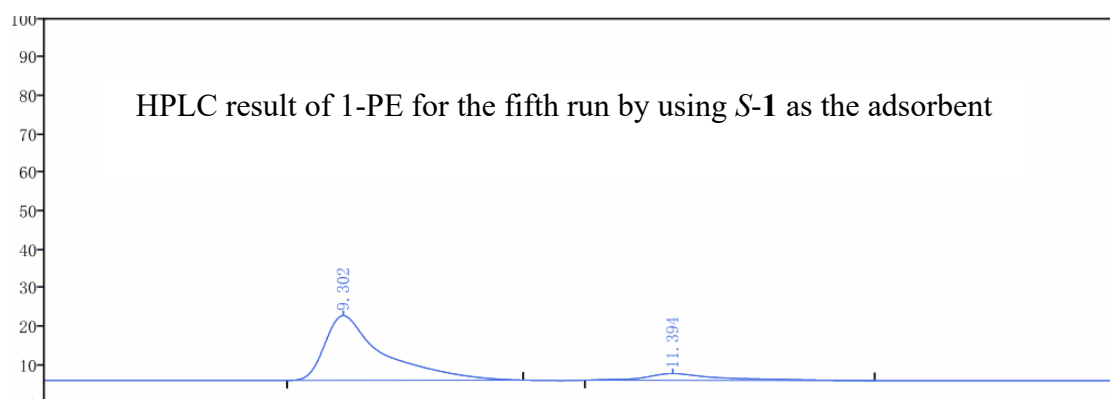
Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	9.482	954.80	89.17
2	MM	11.540	115.92	10.83
The Total			1070.72	



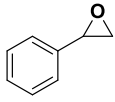
Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	9.288	1022.98	89.00
2	MM	11.360	126.46	11.00
The Total			1149.44	



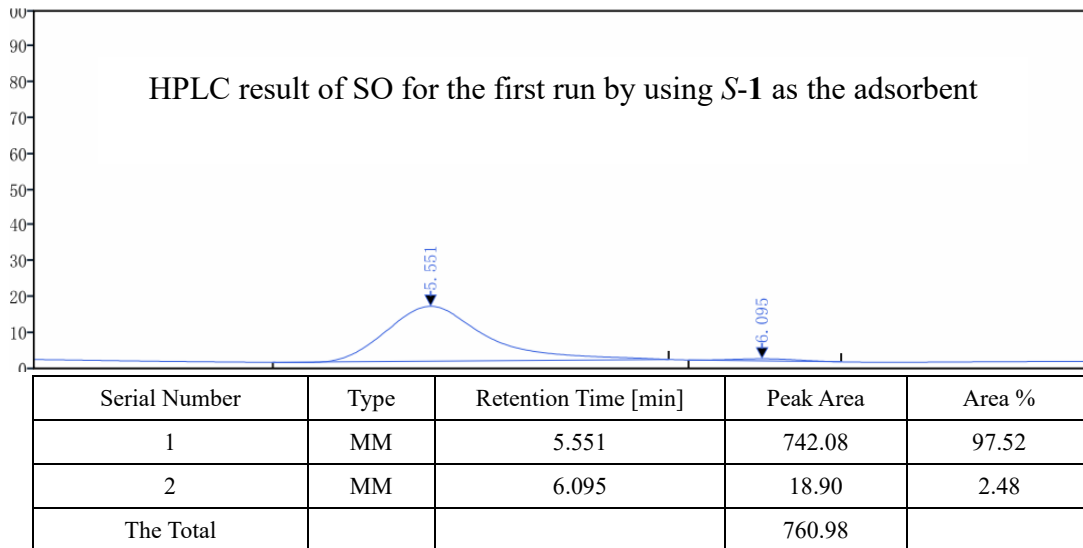
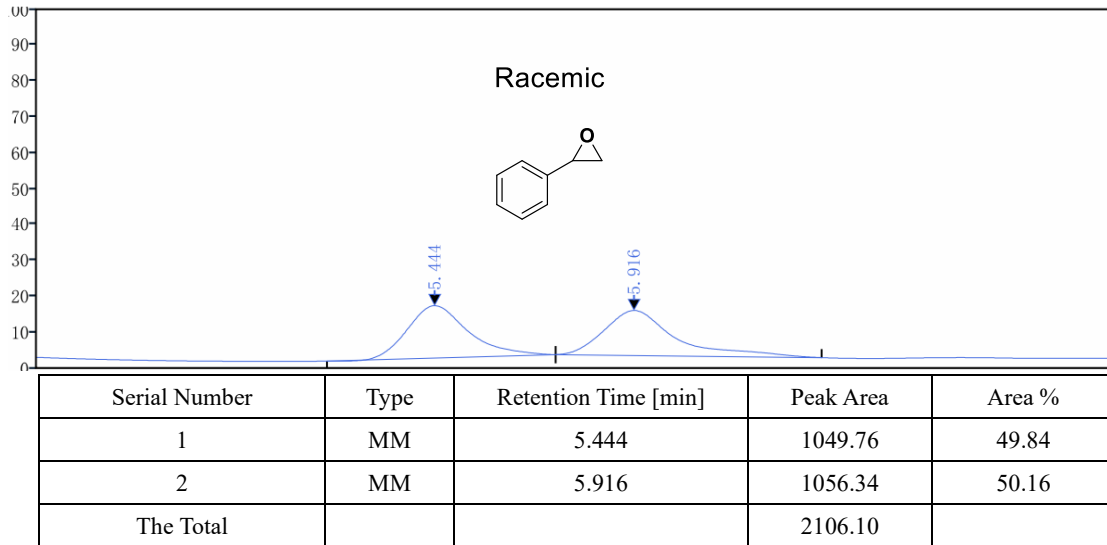
Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	9.305	1123.76	88.82
2	MM	11.397	141.48	11.18
The Total			1265.24	

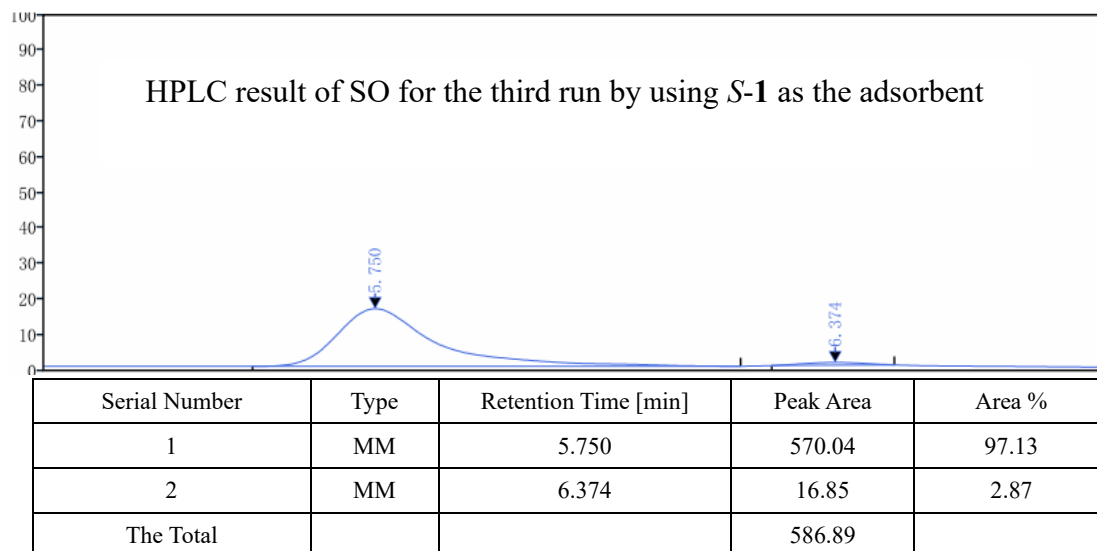
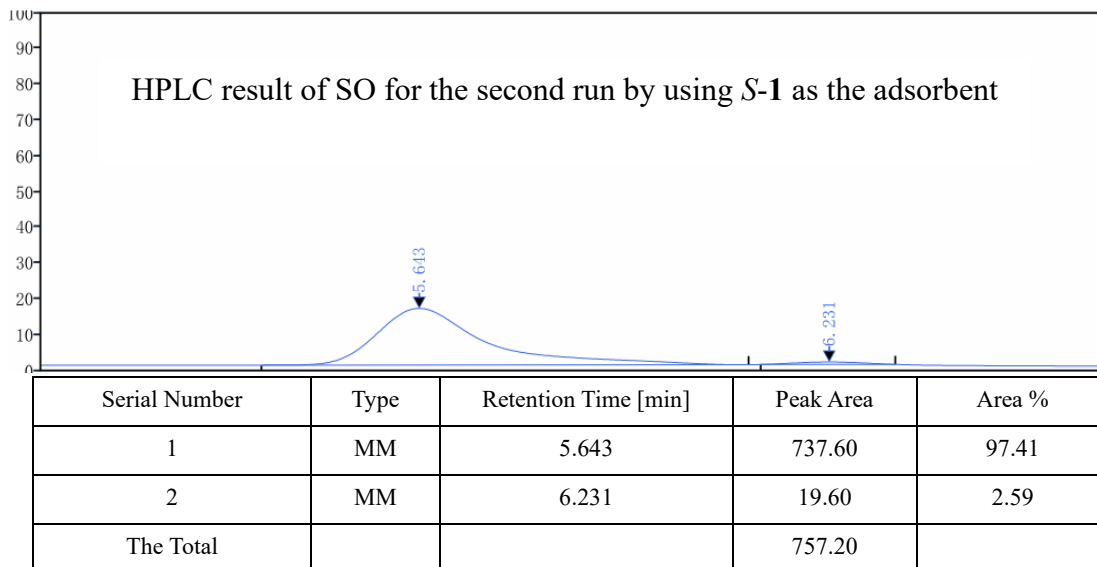


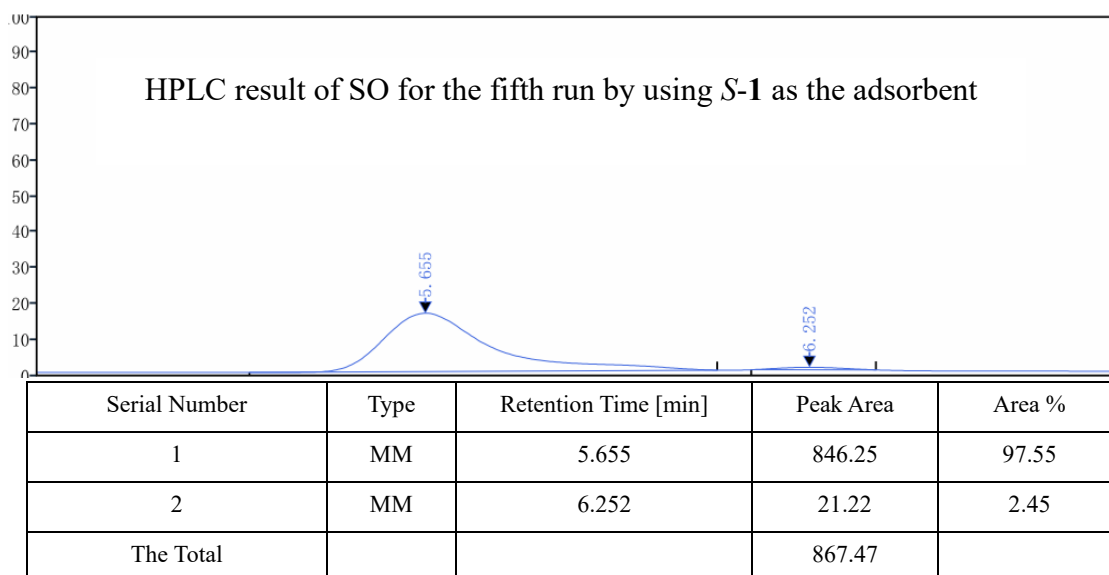
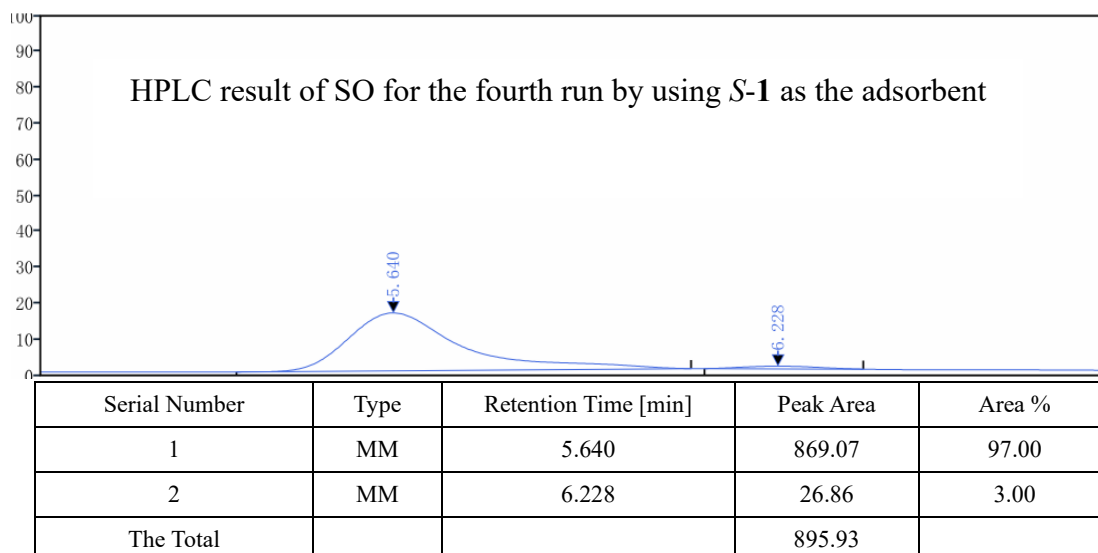
Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	9.302	1299.80	88.36
2	MM	11.394	171.15	11.64
The Total			1470.95	

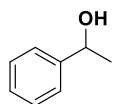


Chiral HPLC analysis: Daicel Chiralce IC-H: hexane/*i*-PrOH = 95/5; flow rate = 1.0 mL/min; 220 nm;  $t_R = 5.444$  min,  $t_R = 5.916$  min.

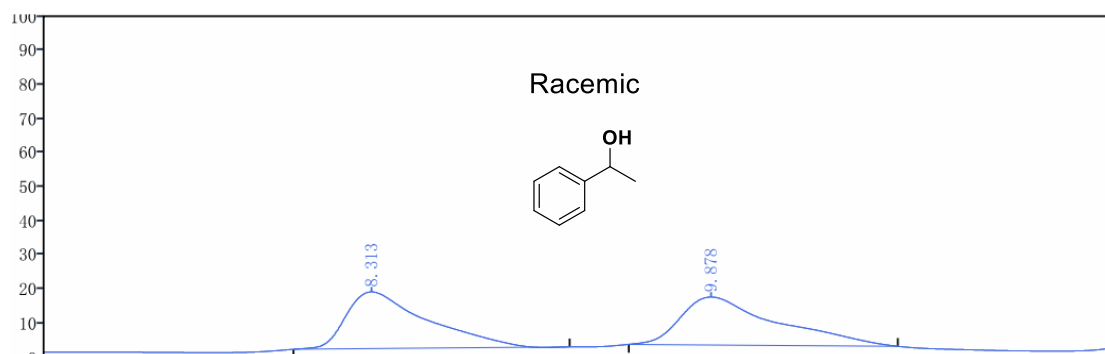




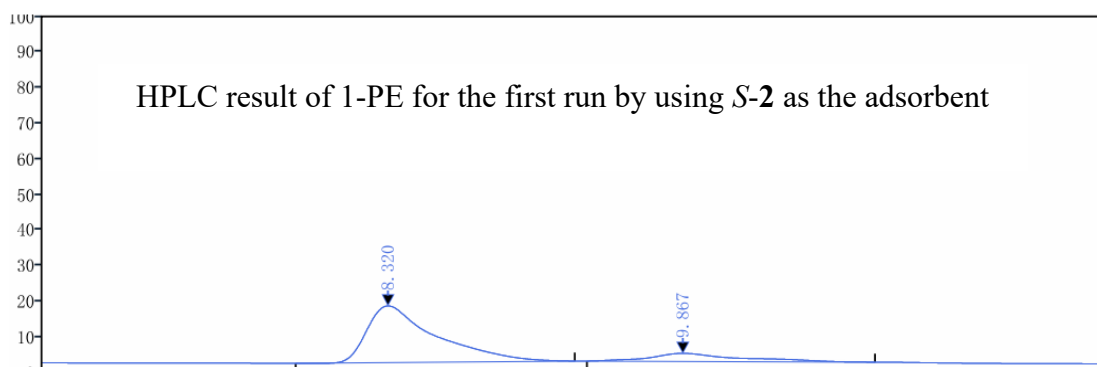




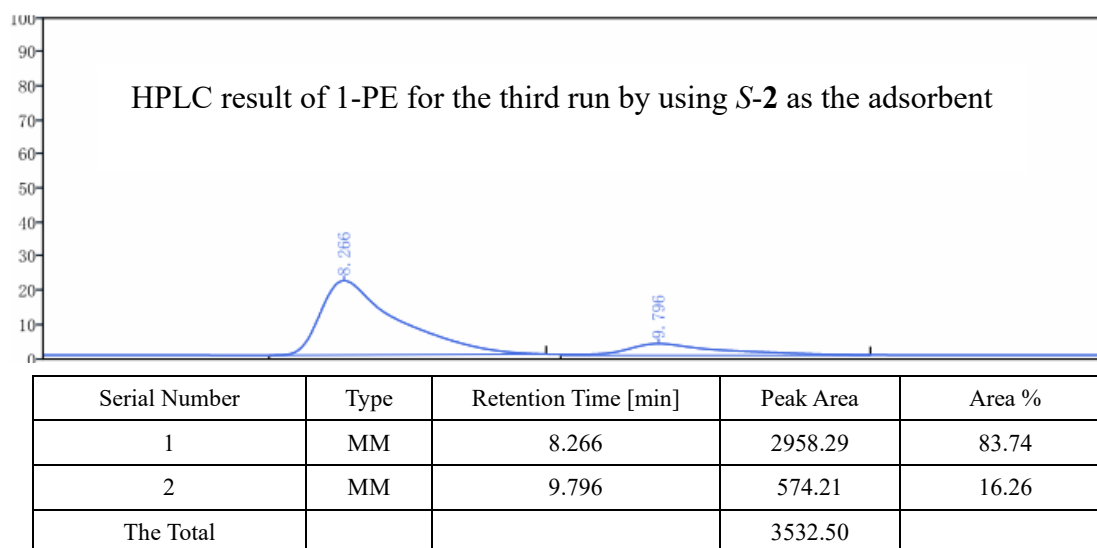
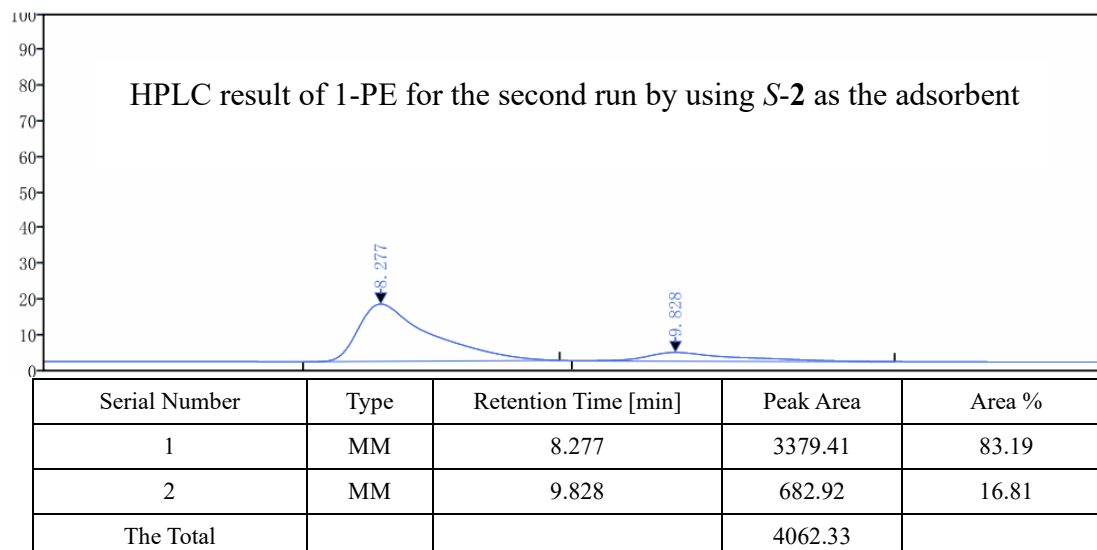
Chiral HPLC analysis: Daicel Chiralce OD: hexane/*i*-PrOH = 97/3; flow rate = 1.0 mL/min; 220 nm;  $t_R = 8.313$  min,  $t_R = 9.878$  min.

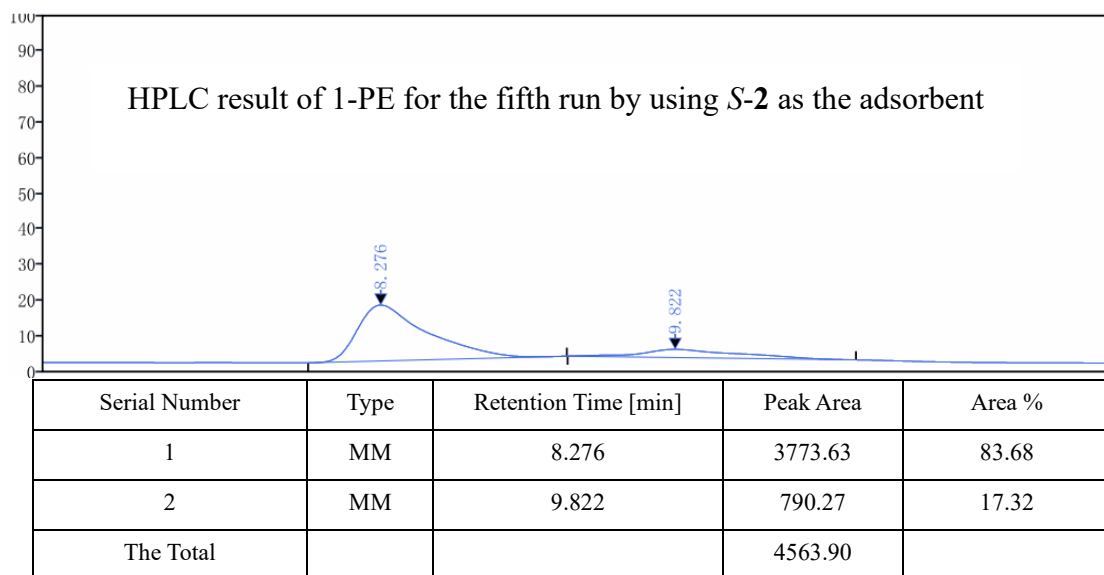
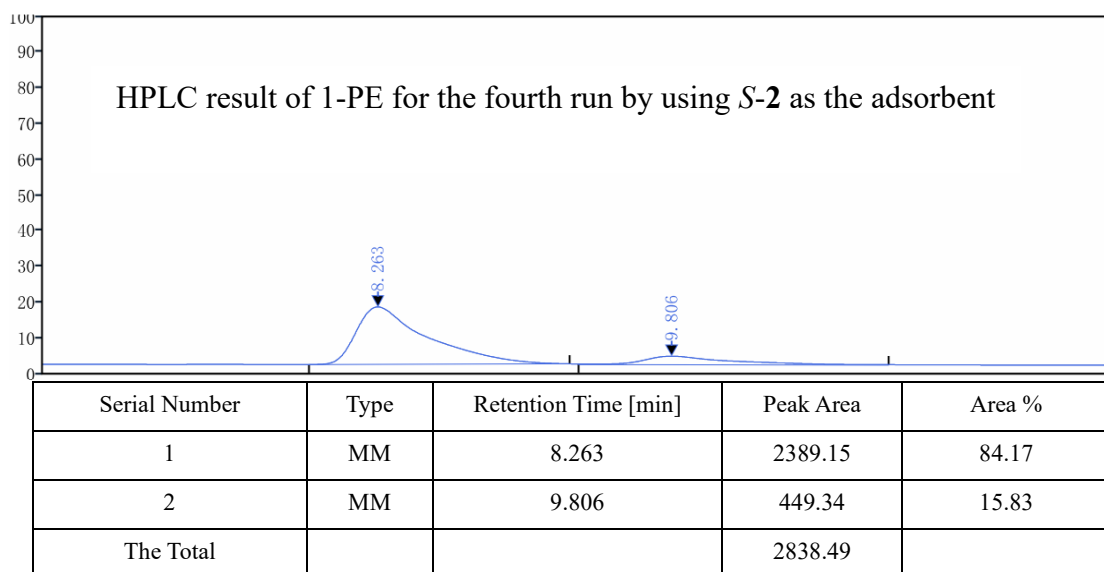


Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	8.313	5680.94	49.92
2	MM	9.878	5698.20	50.08
The Total			11379.14	

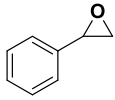


Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	8.320	1604.91	83.93
2	MM	9.867	307.32	16.07
The Total			1912.23	

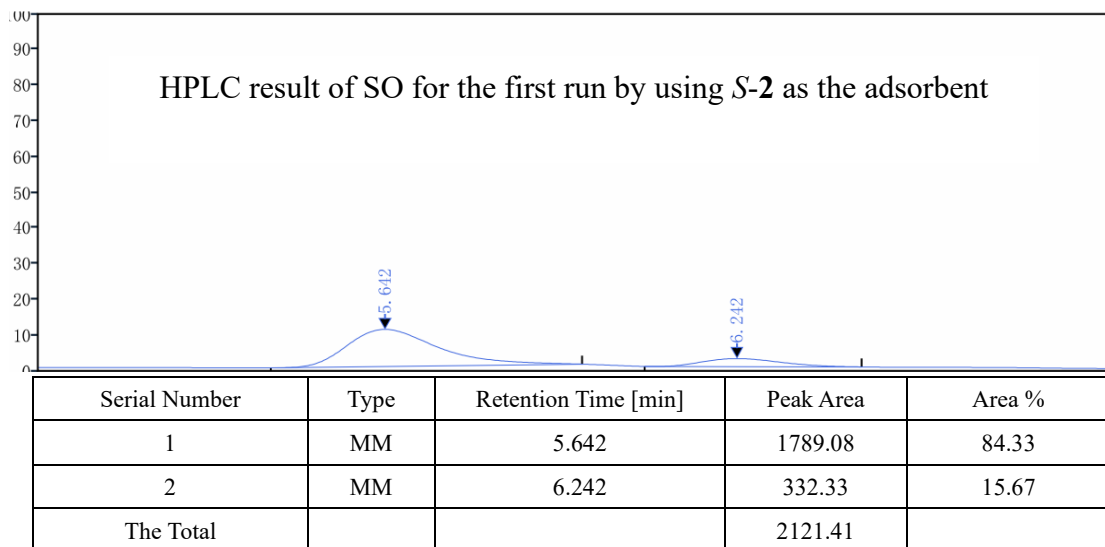
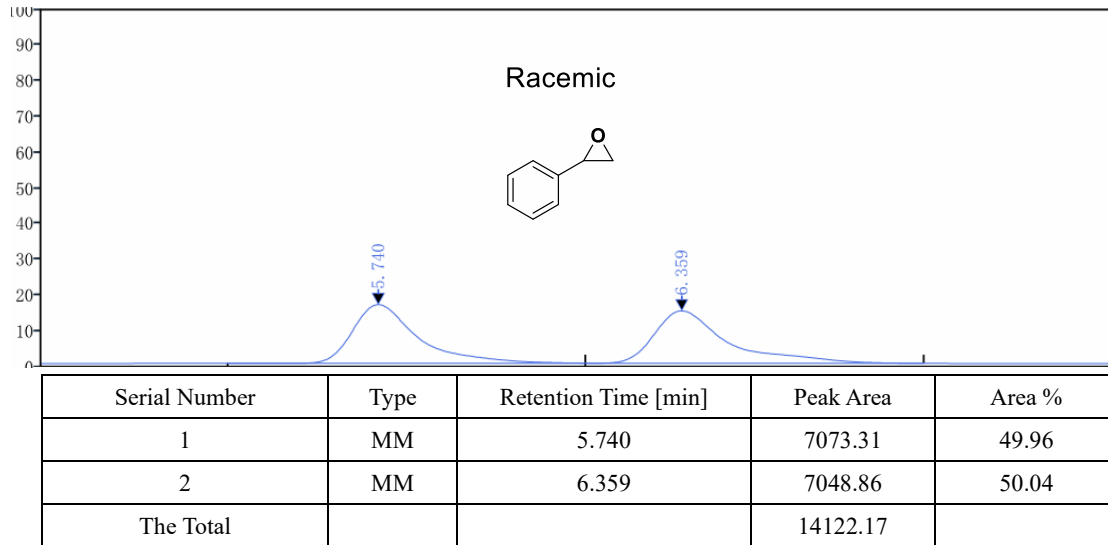


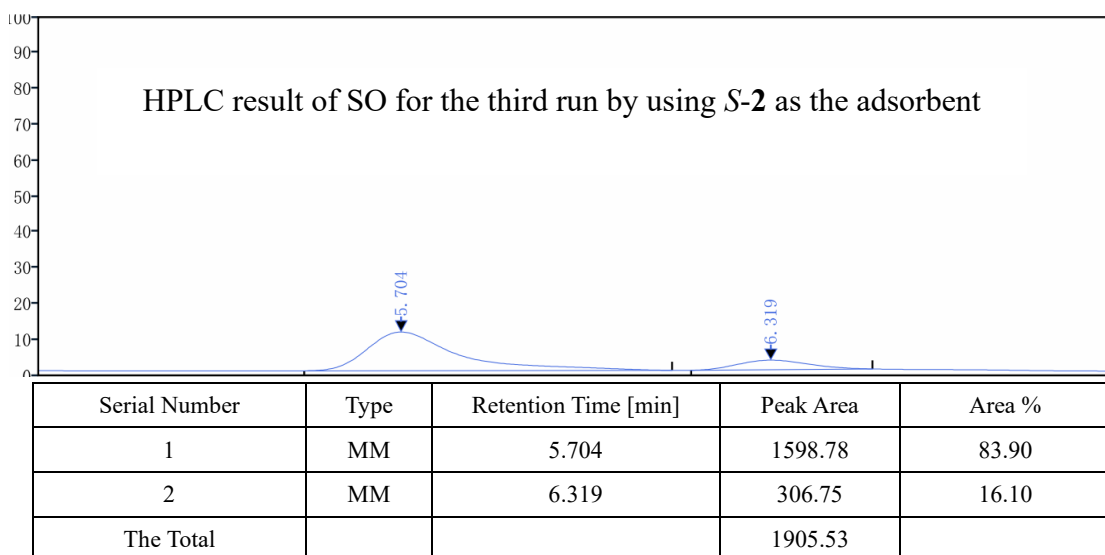
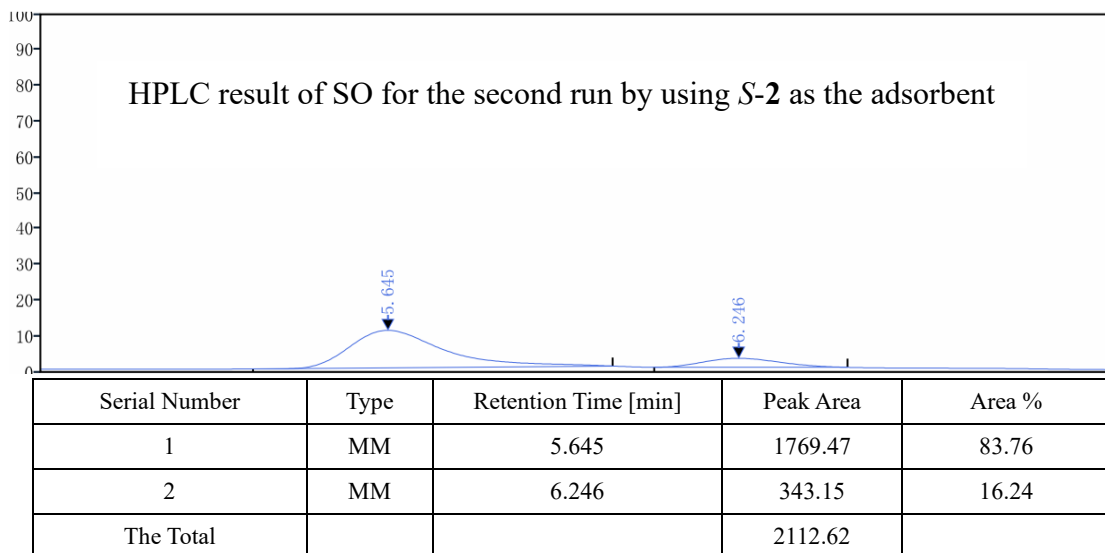


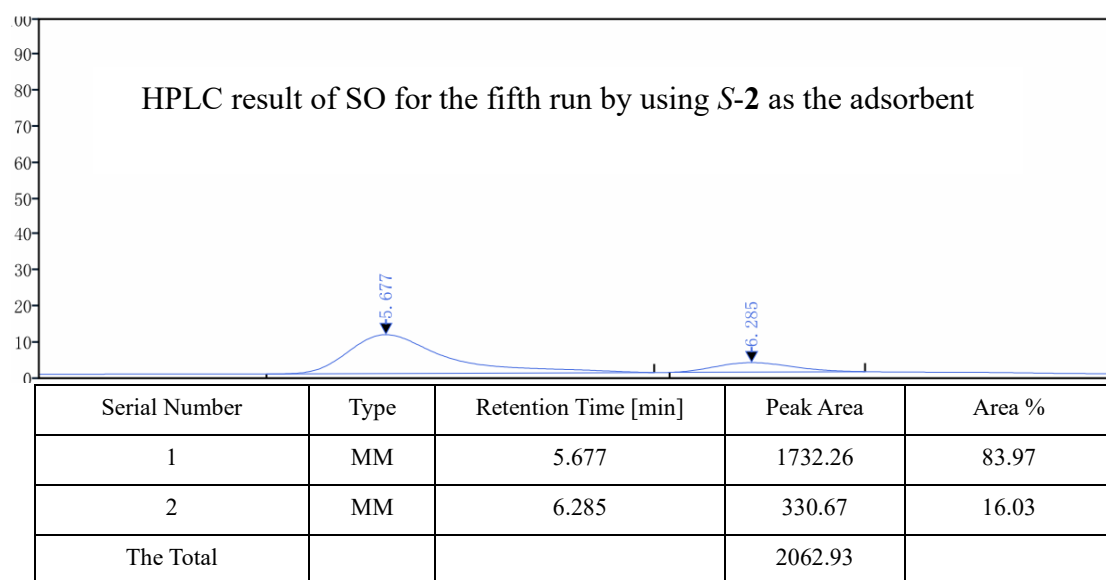
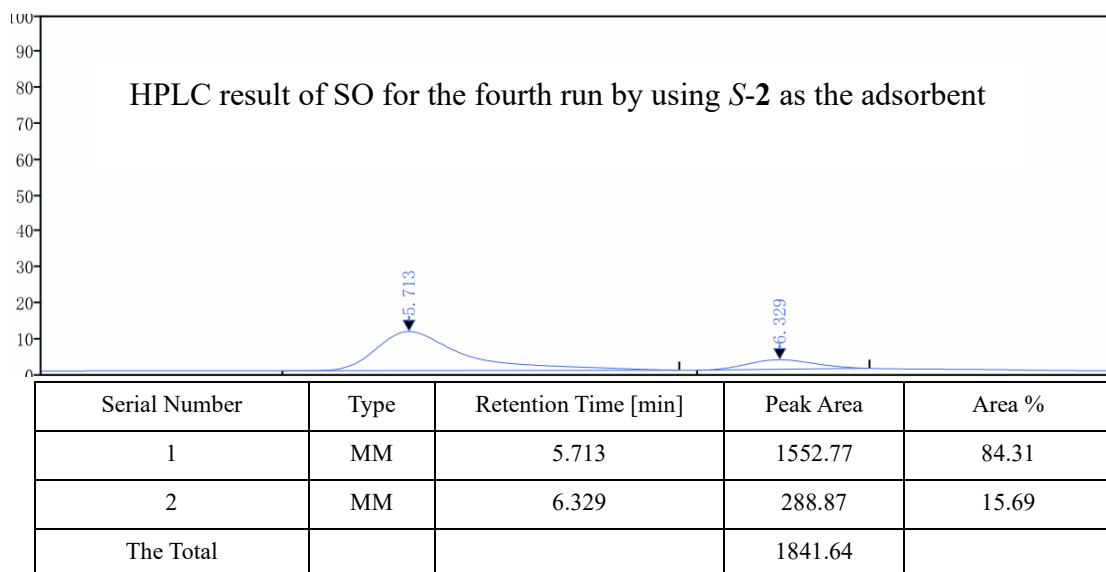




Chiral HPLC analysis: Daicel Chiralce IC-H: hexane/*i*-PrOH = 95/5; flow rate = 1.0 mL/min; 220 nm;  $t_R = 5.740$  min,  $t_R = 6.359$  min.







18. Figure S12. The separation of racemic SO with *S*-1 column and *S*-2 column, respectively.

