

## **A Biomimetic Metal-Organic Framework with Cuboid Inner Cavities for Enantioselective Separation**

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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** were collected several times at 100 K at NFPS (Shanghai) synchrotron radiation on BL17B beamline using  $\lambda = 0.67006 \text{ \AA}$ , and the obtained dataset was indexed, integrated and scaled using the APEX4 program. The structure of (*S*)-**1** was solved by the direct methods with SHELXS-2018 and refined with SHELXL-2018 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** 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** can be best formulated as  $[\text{Cd}(\text{HL})\cdot(\text{bpy})]\cdot\text{DMF}\cdot\text{EtOH}$ , 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, while the selected bond distances and angles are presented in Tables S2. CCDC number of (*S*)-**1** is 2132120, 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). Thermogravimetric analysis of (*S*)-**1** was carried out in a nitrogen atmosphere with a heating rate of  $10 \text{ }^{\circ}\text{C}/\text{min}$  on a TGA-50 thermogravimetric analyzer. Powder X-ray diffraction (PXRD) data were collected on a DMAX2500 diffractometer using Cu  $K\alpha$  radiation. The simulated powder pattern was calculated using Mercury based on single crystal diffraction data of (*S*)-**1**. The date of dye absorption experiment was recorded on an Agilent Technologies carry UV/Vis Spectrometer. The IR (KBr pellet) spectrum was recorded ( $400\text{-}4000 \text{ cm}^{-1}$  region) on a Nicolet Magna 750 FTIR spectrometer. Fluorescence spectra were recorded on a Hitachi F-4500 spectrometer. Analytical high-performance liquid chromatography (HPLC) was performed on an Agilent Technologies 1260 Infinity II with UV detection. Analytical ChiralCel OD-H/OJ-H/AS-H/IC-H/AD-H/IA-H column ( $4.6 \text{ mm}\times 25 \text{ cm}$ ) from Daicel were used.

## 2. Synthesis of chiral MOF 1

First, the chiral ligand (1*S*,3*S*,5*S*)-benzene tricarbonyl tri-(phenylalanine acid), ((*S*)-H<sub>3</sub>L), was readily prepared through the condensation of trimesoyl chloride and enantiopure (*S*)-phenylalanine methyl ester, followed by hydrolysis. Then, a mixture of (*S*)-H<sub>3</sub>L (32.5 mg, 0.05 mmol), 4, 4'-bipyridine (7.8 mg, 0.05 mmol) and Cd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O (30.8 mg, 0.10 mmol), was placed in a glass vial containing DMF (5 mL) and EtOH (5 mL). The vial was sealed tightly and heated at 60°C for two days, colorless block single-crystals of (*S*)-**1** can be obtained. The crystals of (*R*)-**1** could be obtained under identical conditions except for the (*S*)-H<sub>3</sub>L ligand was replaced by (*R*)-H<sub>3</sub>L.

## 3. Table S1. Crystal data and structure refinement for (*S*)-**1**.

Empirical formula	C <sub>51</sub> H <sub>43</sub> CdN <sub>6</sub> O <sub>11</sub>
Formula weight	1028.31
Temperature (K)	100
Identification code	( <i>S</i> )- <b>1</b>
Wavelength (Å)	0.67006
Crystal system, space group	Trigonal, P321
Unit cell dimensions	a = 16.5211(1) Å    alpha = 90°. b = 25.850(2) Å    beta = 90°. c = 11.7081(8) Å    gamma = 90°.
Volume	5000.1(6) Å <sup>3</sup>
Z, Calculated density	4, 1.366 mg/m <sup>3</sup>
Absorption coefficient	0.432 mm <sup>-1</sup>
F(000)	2108
θ range for data collection (°)	1.485 to 27.313
Limiting indices	-22 ≤ h ≤ 22, -35 ≤ k ≤ 35, -16 ≤ l ≤ 16
Reflections collected independent reflections	79698 / 13274 [R(int) = 0.0842]
Completeness to theta Refinement method	99.7 %
Refinement method	Full-matrix least-squares on F <sup>2</sup>
Data / restraints / parameters	13274 / 169 / 612
Goodness-of-fit on F <sup>2</sup>	1.069
Final R indices [I > 2σ(I)]	R1 = 0.0550, wR2 = 0.1580
R indices (all data)	R1 = 0.0668, wR2 = 0.1639
Absolute structure parameter	0.077(9)

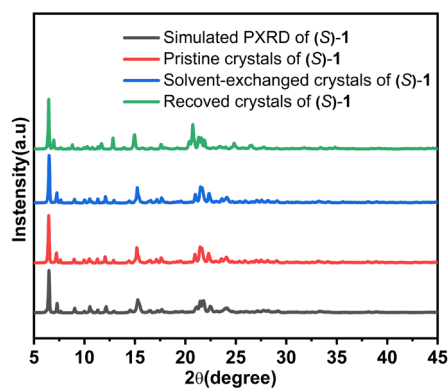
#### 4. Table S2. Selected Bond lengths [Å] and angles [°] for (*S*)-1.

Cd(1)-N(4)	2.312(4)
Cd(1)-N(5)#1	2.321(4)
Cd(1)-O(4)#2	2.379(4)
Cd(1)-O(5)#2	2.418(4)
Cd(1)-O(7)#3	2.356(4)
Cd(1)-O(7)	2.421(4)
Cd(1)-O(8)	2.438(4)
N(4)-Cd(1)-N(5)#1	179.34(16)
N(4)-Cd(1)-O(4)#2	91.32(18)
N(4)-Cd(1)-O(5)#2	94.40(16)
N(4)-Cd(1)-O(7)#3	88.34(16)
N(4)-Cd(1)-O(7)	88.48(16)
N(4)-Cd(1)-O(8)	92.13(16)
N(5)#1-Cd(1)-O(4)#2	89.21(17)
N(5)#1-Cd(1)-O(5)#2	85.58(15)
N(5)#1-Cd(1)-O(7)	91.16(16)
N(5)#1-Cd(1)-O(7)#3	92.09(16)
N(5)#1-Cd(1)-O(8)	87.21(16)
O(4)#2-Cd(1)-O(5)#2	54.71(13)
O(4)#2-Cd(1)-C(18)#2	27.18(15)
O(4)#2-Cd(1)-O(7)	159.58(13)
O(4)#2-Cd(1)-O(8)	147.07(12)
O(5)#2-Cd(1)-O(7)	145.65(13)
O(5)#2-Cd(1)-O(8)	92.37(13)
O(7)#3-Cd(1)-O(4)#2	86.38(13)
O(7)#3-Cd(1)-O(5)#2	141.01(14)
O(7)#3-Cd(1)-O(7)	73.20(15)
O(7)-Cd(1)-O(8)	53.29(12)
O(7)#3-Cd(1)-O(8)	126.44(13)

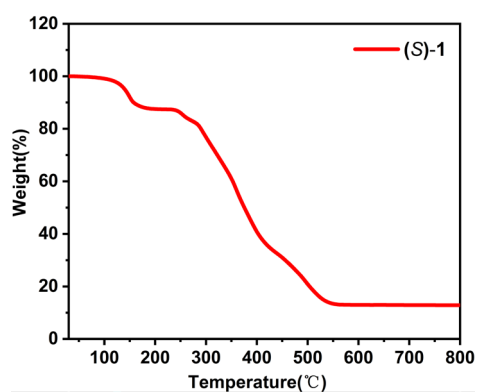
#### 5. Experimental procedure for enantioselective adsorption and separation.

Typical procedure for enantioselective adsorption and separation: The 50 mg solvent-exchanged crystals of chiral MOF (*S*)-1 were firstly immersed in 3  $\mu\text{mol/L}$  indicated racemic analyte in different solvent for 12 h at room temperature. After which, the solid crystals were filtered, washed with  $\text{CH}_2\text{Cl}_2$ , and soaked in  $\text{CH}_2\text{Cl}_2$  to extract the encapsulated guest substrates. The optical purity of encapsulated chiral guest molecules was determined by HPLC equipped with chiral column.

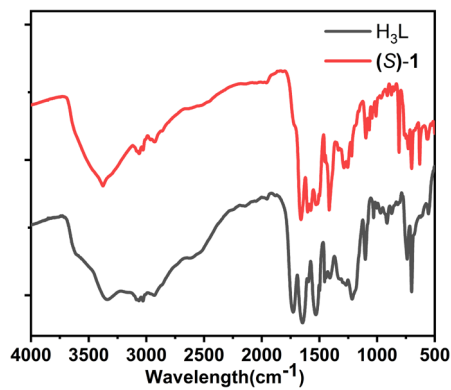
6. Figure S1. PXRD patterns of (S)-1.



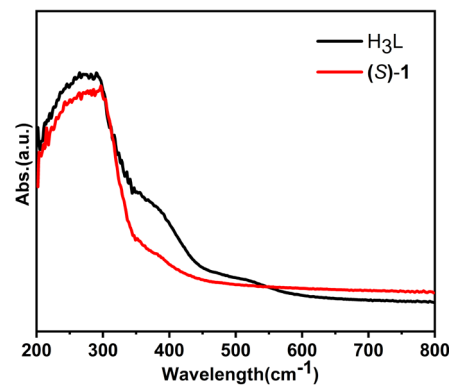
7. Figure S2. TGA curves of (S)-1.



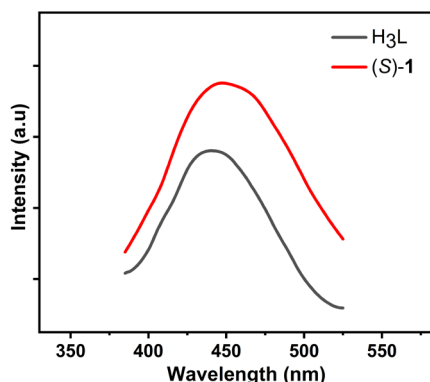
8. Figure S3. IR spectra of H<sub>3</sub>L and (S)-1.



9. Figure S4. UV-vis spectra of H<sub>3</sub>L and (S)-1.

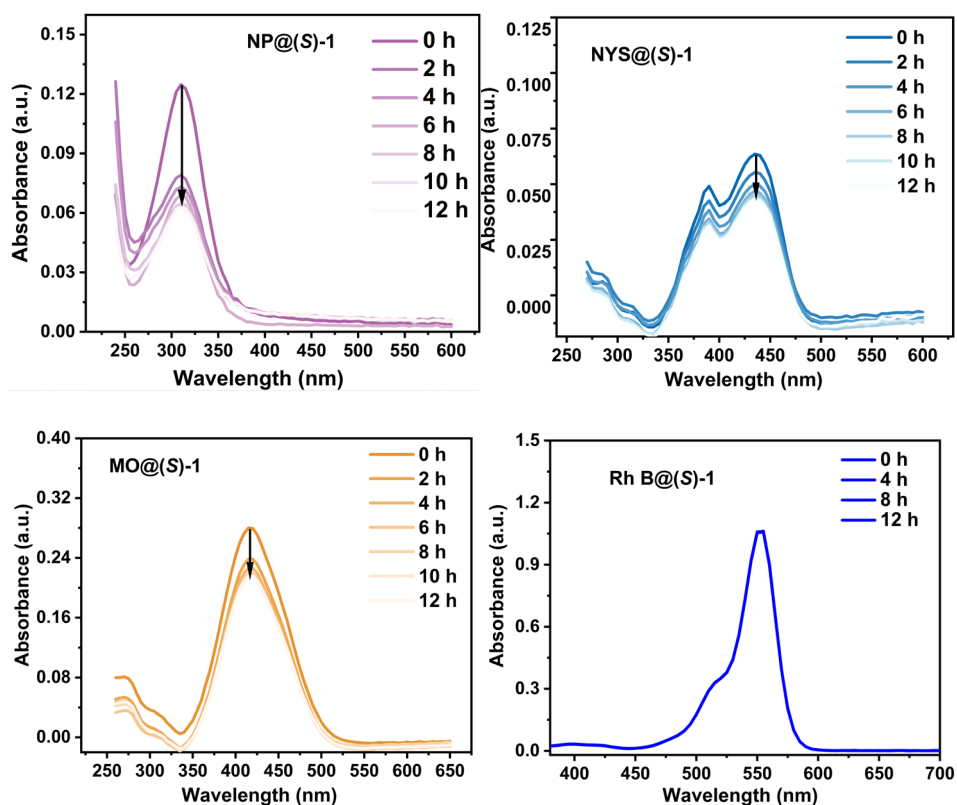


**10. Figure S5. FL spectra of H<sub>3</sub>L and (S)-1.**



**11. Figure S6. The adsorption of (S)-1 to dye molecules.**

The 50 mg pristine crystals of (S)-1 were immersed in methanol solution of 10  $\mu\text{mol/L}$  NP, NSY, MO and RhB, respectively. Then the dye content in solution was monitored by UV-Vis at different time periods.

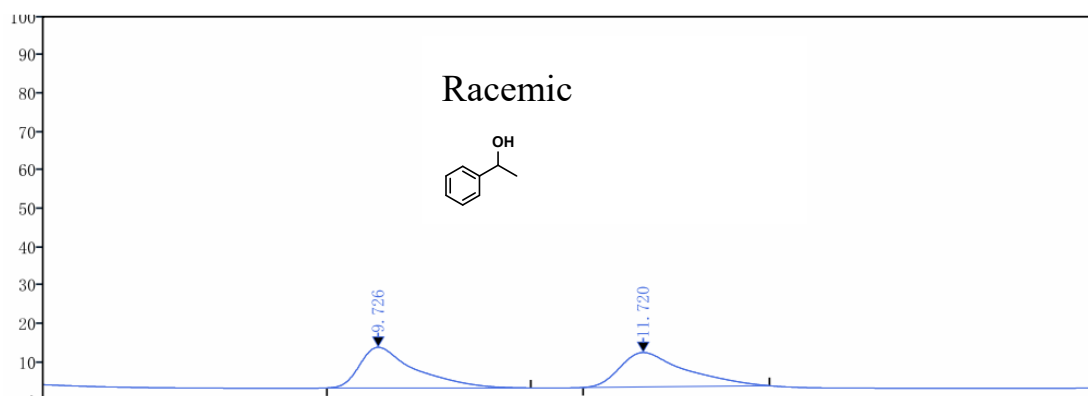


**12. Figure S7. HPLC results of enantioselective adsorption and separation of (S)-1 to 1-phenylethanol in different solvents (in Table 1).**

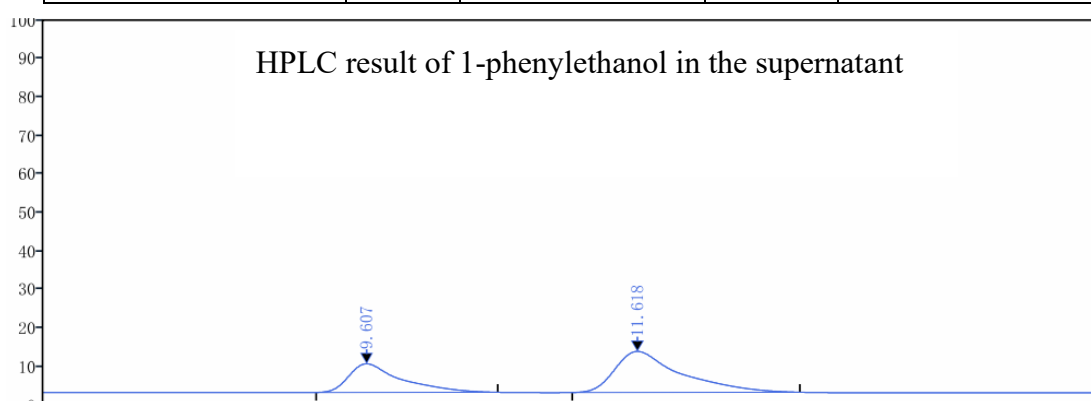
Entry 1 in table 1, DCM was acted as the solvent.

Chiral HPLC analysis: Daicel Chiralce OD: hexane/*i*-PrOH =96/4; flow rate =1.0 mL/min; 220 nm;

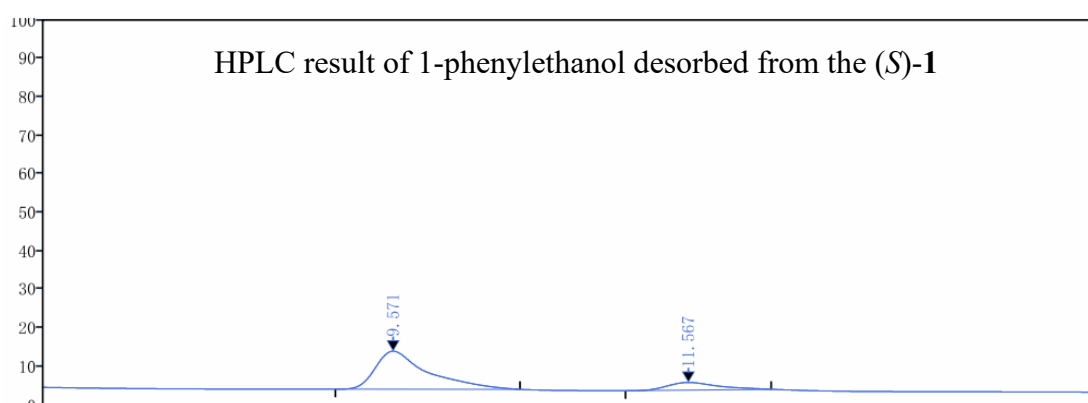
$t_R = 9.726\text{min}$ ,  $t_R = 11.720\text{ min}$ .



Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	9.726	3510.09	49.97
2	MM	11.720	3514.15	50.03
The Total			7024.25	



Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	9.607	1819.76	35.78
2	MM	11.618	3266.52	64.22
The Total			5086.28	

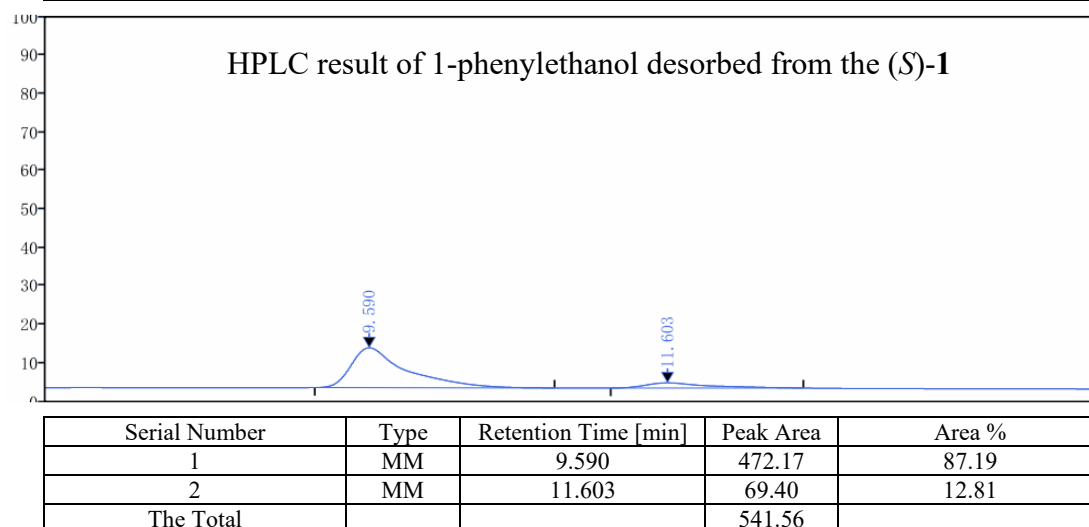
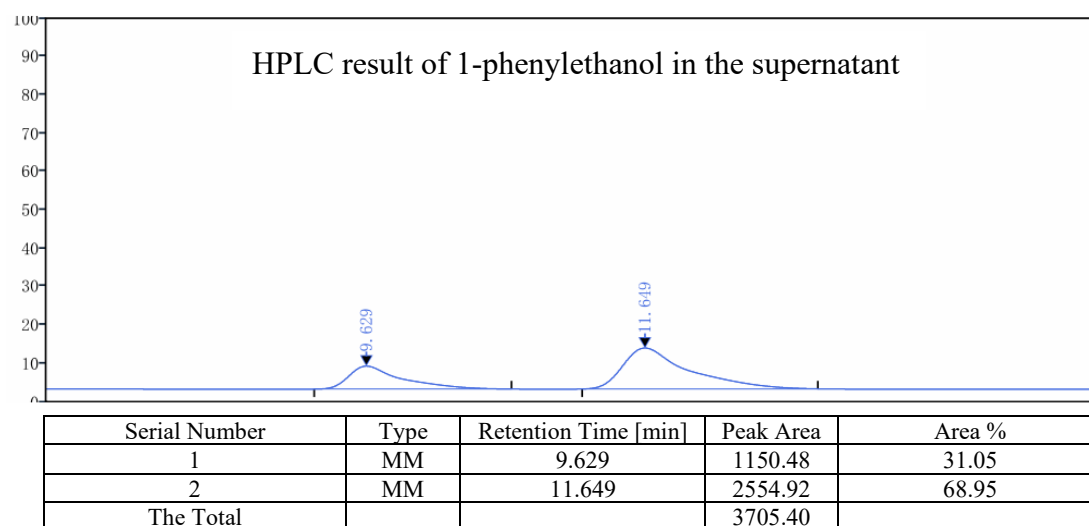
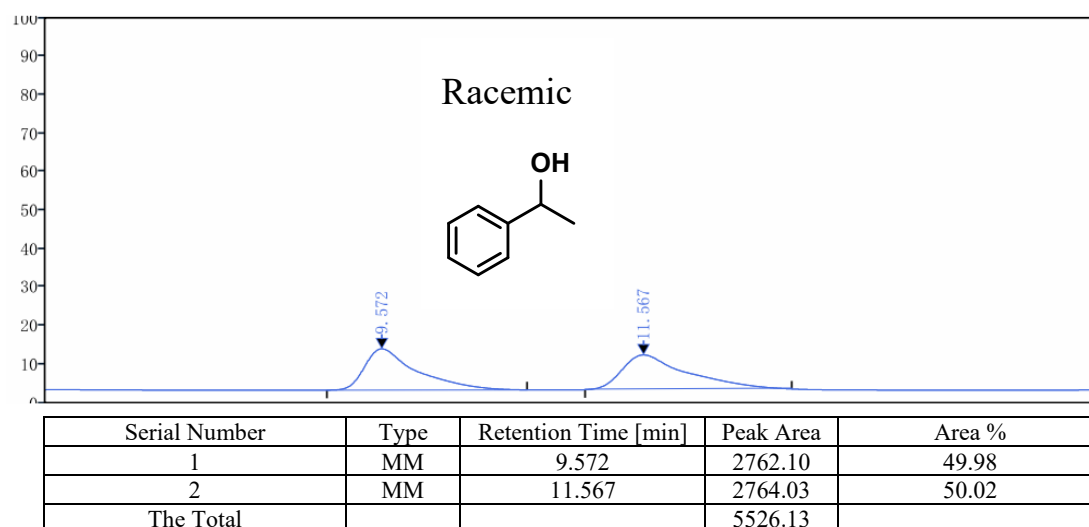


Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	BM	9.571	249.57	83.85
2	BM	11.567	48.07	16.15
The Total			297.64	

Entry 2 in table 1, MeCN was acted as the solvent.

Chiral HPLC analysis: Daicel Chiralce OD: hexane/*i*-PrOH =96/4; flow rate =1.0 mL/min; 220 nm;

$t_R = 9.572\text{min}$ ,  $t_R = 11.567\text{min}$ .

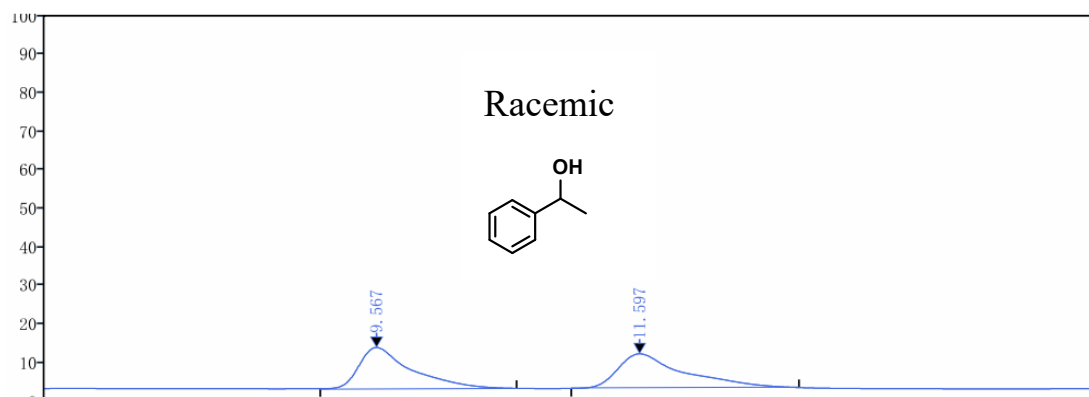




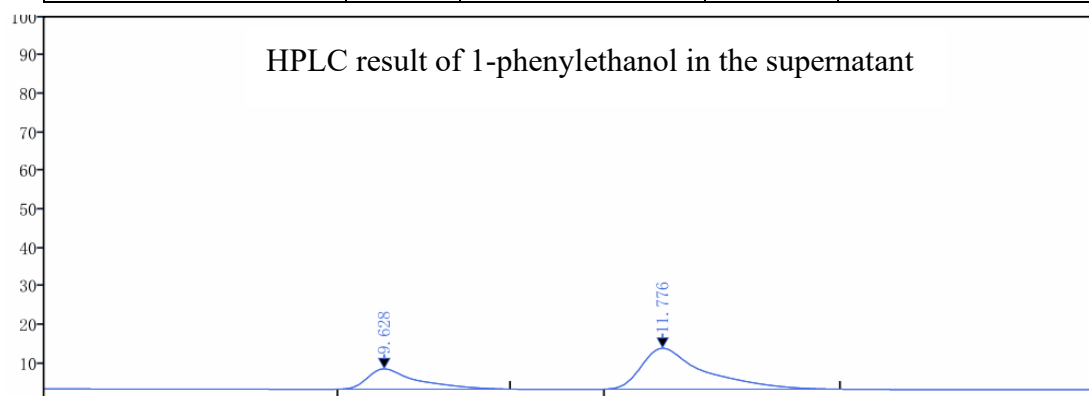
Entry 3 in table 1, EtOH was acted as the solvent.

Chiral HPLC analysis: Daicel Chiralce OD: hexane/*i*-PrOH =96/4; flow rate =1.0 mL/min; 220 nm;

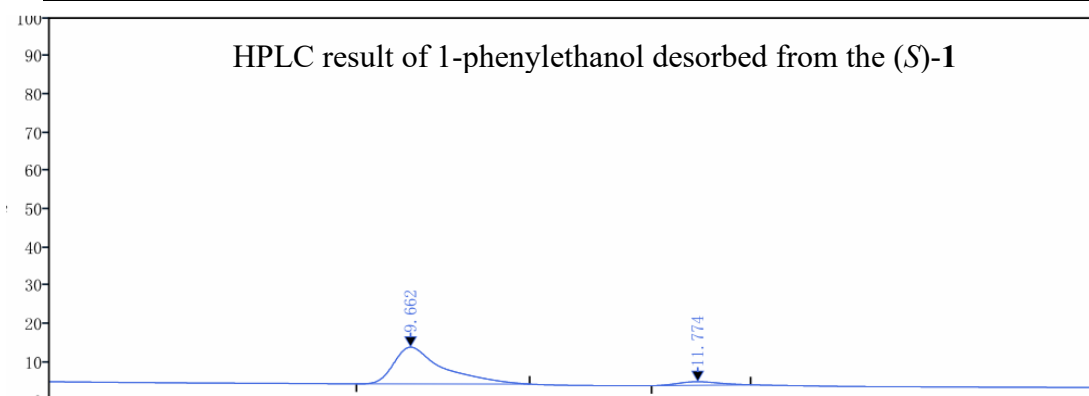
$t_R = 9.567\text{min}$ ,  $t_R = 11.597\text{min}$ .



Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	9.567	3151.60	50.04
2	MM	11.597	3145.96	49.96
The Total			6297.56	



Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	9.628	995.06	28.04
2	MM	11.776	2553.98	71.96
The Total			3549.04	

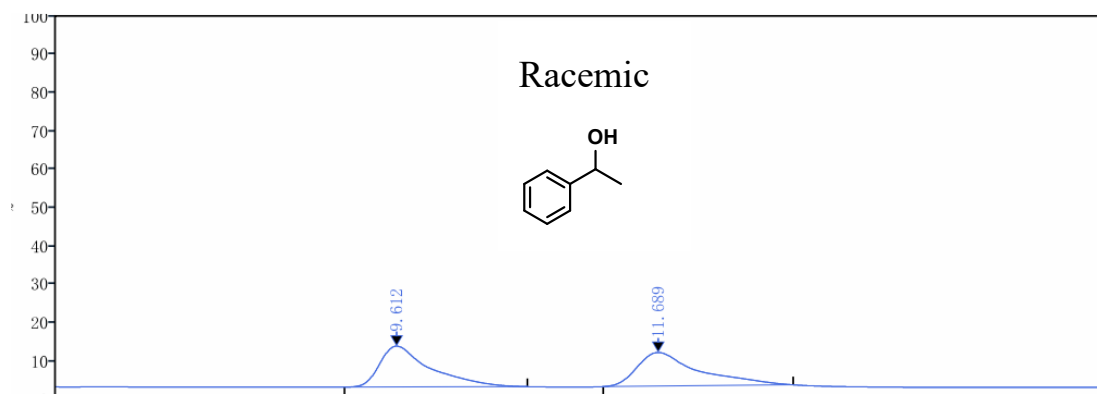


Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	BM	9.662	260.45	92.62
2	MM	11.774	20.76	7.38
The Total			281.22	

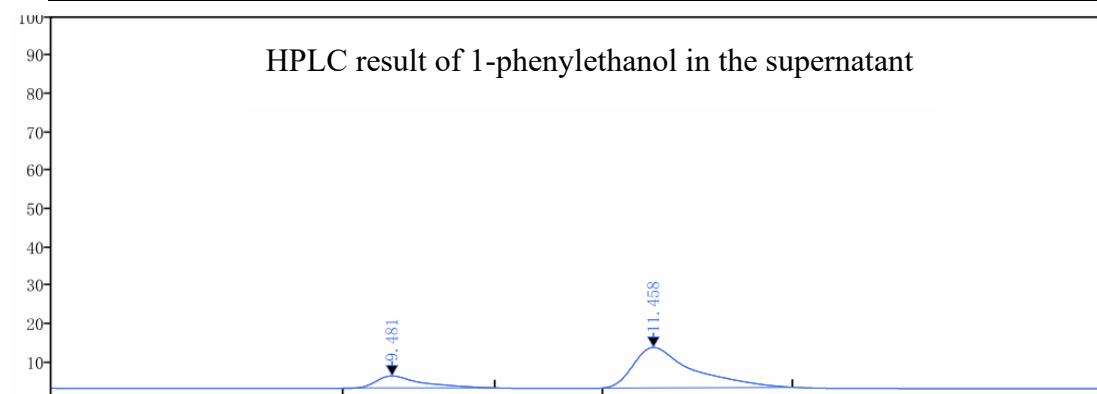
Entry 4 in table 1, acetone was acted as the solvent.

Chiral HPLC analysis: Daicel Chiralce OD: hexane/*i*-PrOH =96/4; flow rate =1.0 mL/min; 220 nm;

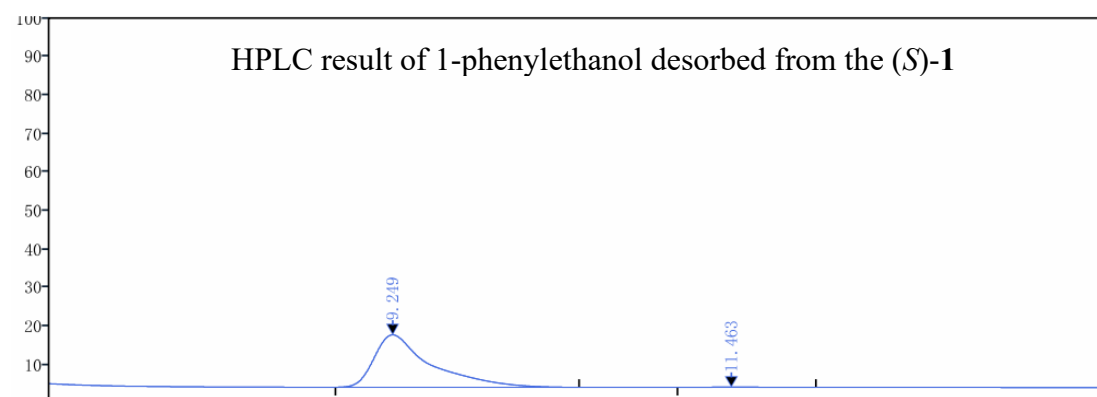
$t_R = 9.612\text{min}$ ,  $t_R = 11.689\text{min}$ .



Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	9.612	3345.70	50.01
2	MM	11.689	3344.55	49.99
The Total			6690.26	



Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	9.481	616.05	18.35
2	MM	11.458	2741.82	81.65
The Total			3357.88	



Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	9.249	1542.46	99.69
2	MM	11.463	4.73	0.31
The Total			1547.19	

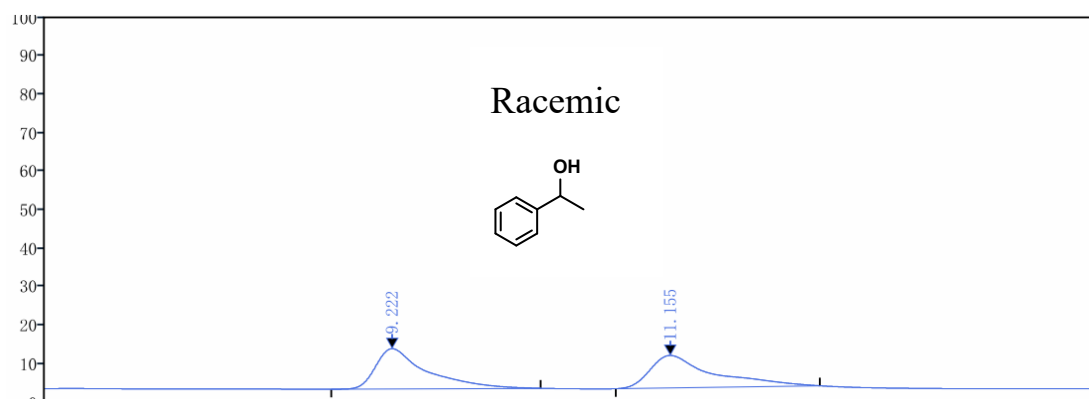
**13. Figure S8. HPLC results of enantioselective adsorption and separation (in Table 2).**

*The HPLC spectra of the consecutive five separation experiments of 1-phenylethanol by (S)-1.*

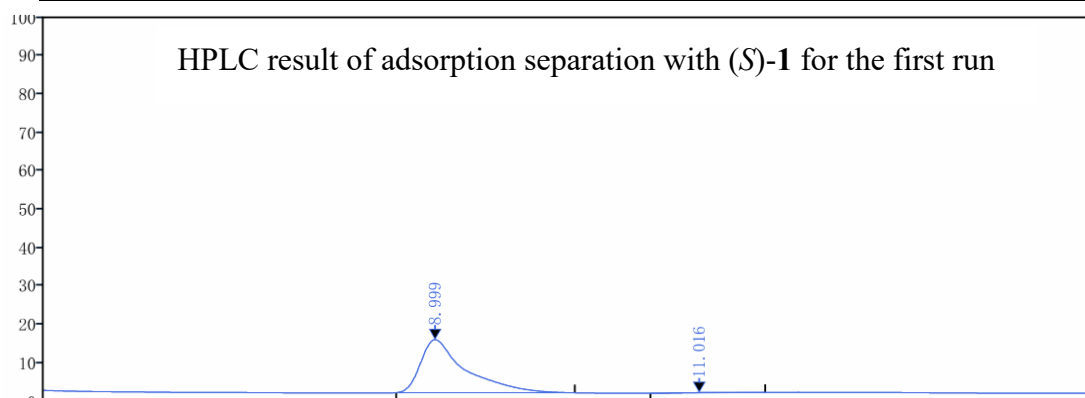


Chiral HPLC analysis: Daicel Chiralce OD: hexane/*i*-PrOH =96/4; flow rate =1.0 mL/min;

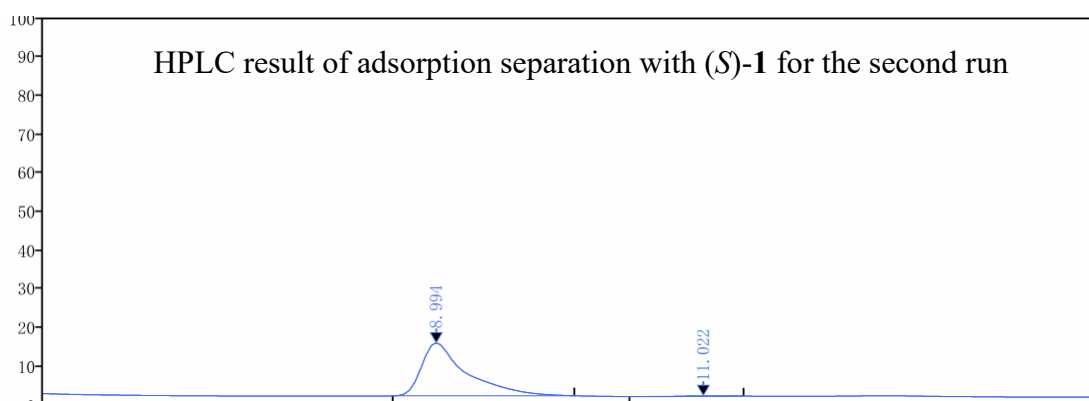
220 nm;  $t_R = 9.222\text{min}$ ,  $t_R = 11.155\text{ min}$ .



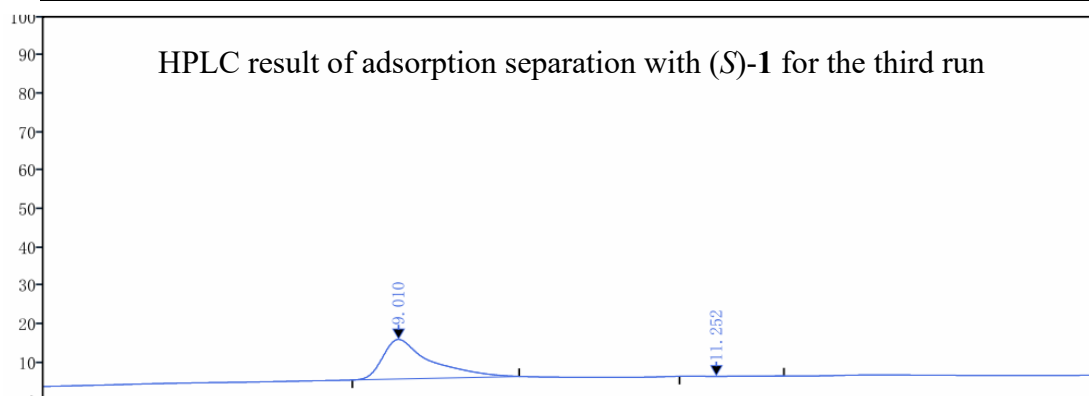
Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	BM	9.222	736.61	50.03
2	MM	11.155	735.59	49.97
The Total			1472.20	



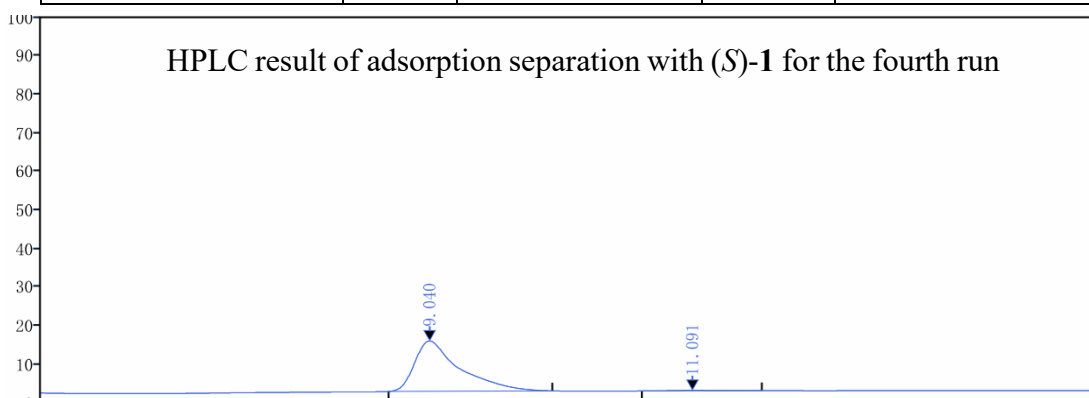
Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	8.999	647.45	99.76
2	MM	11.016	1.53	0.24
The Total			648.98	



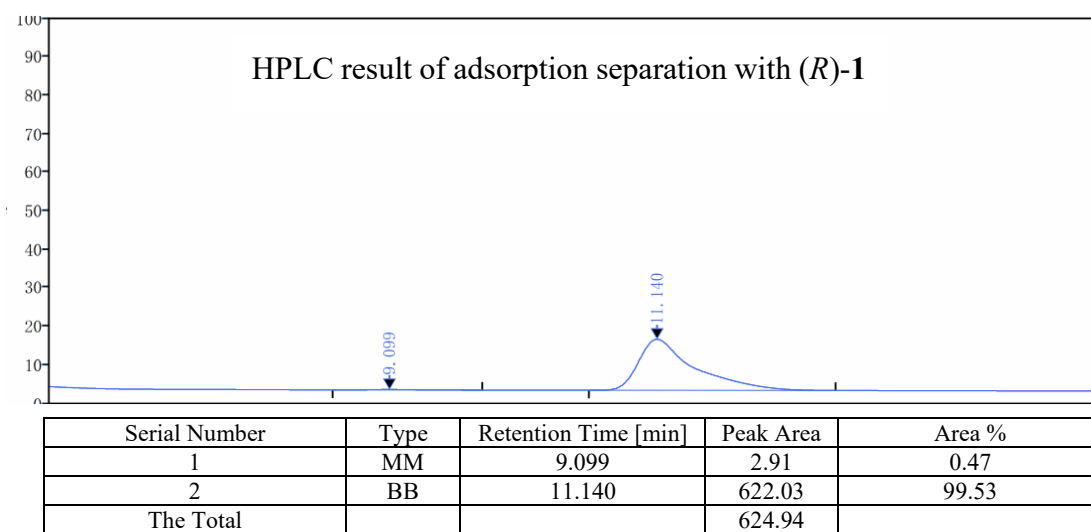
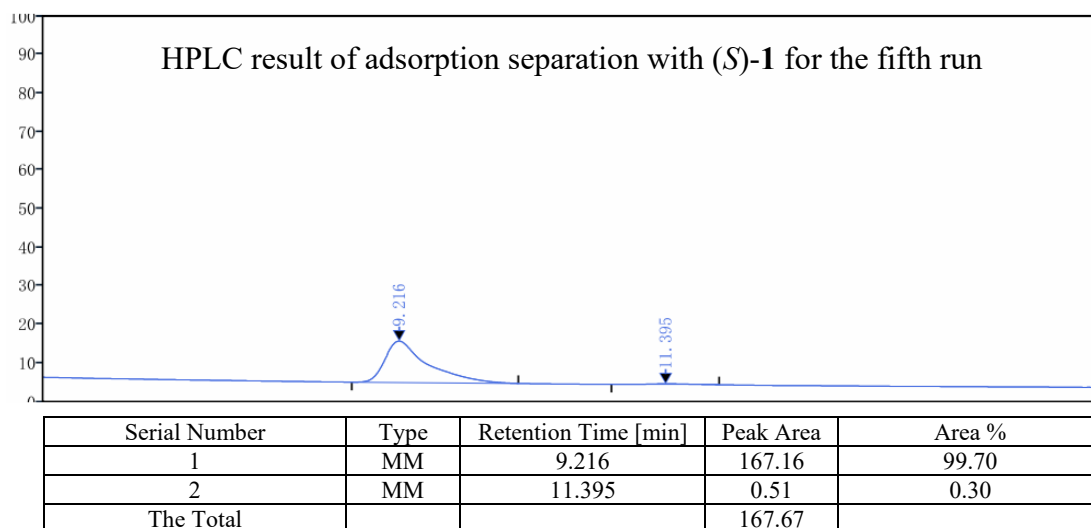
Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	8.994	712.68	99.68
2	MM	11.022	2.30	0.32
The Total			714.98	



Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	9.010	372.29	99.74
2	MM	11.252	0.98	0.26
The Total			373.26	



Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	9.040	1281.72	99.54
2	MM	11.091	5.95	0.46
The Total			1287.66	

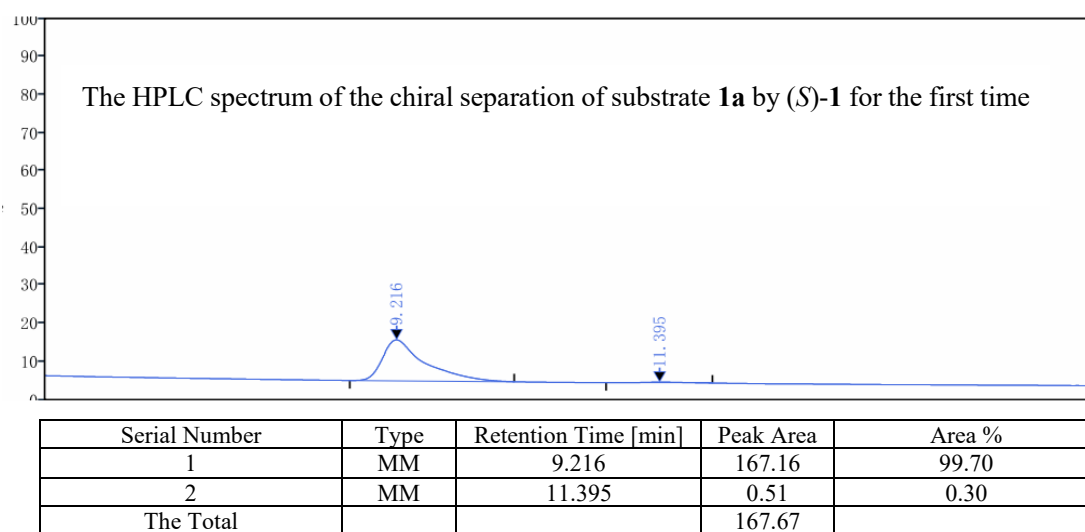
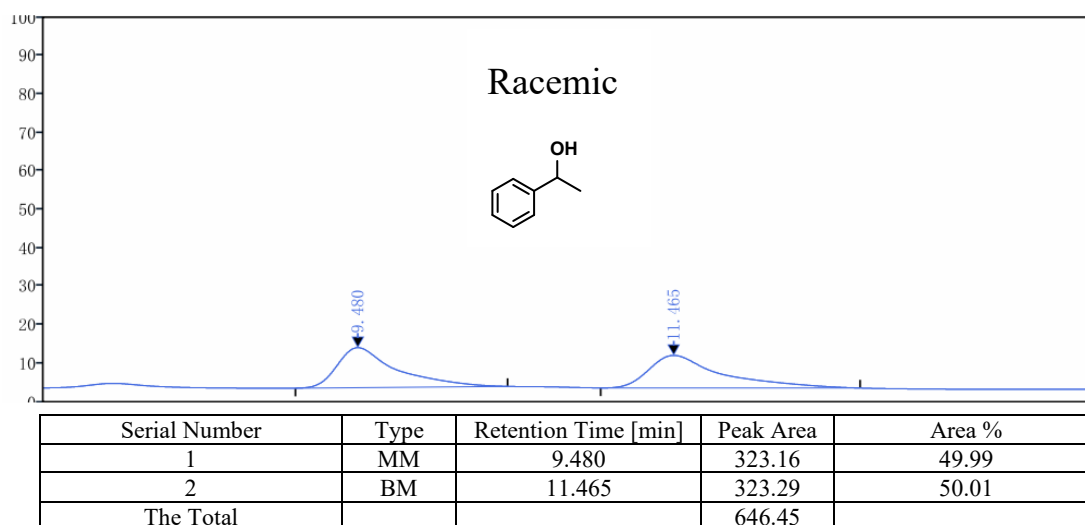


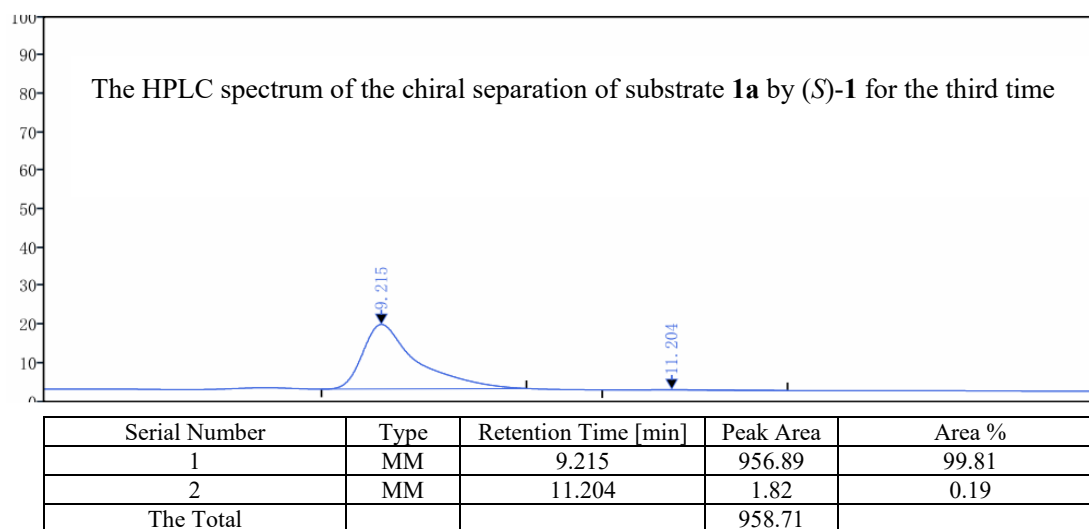
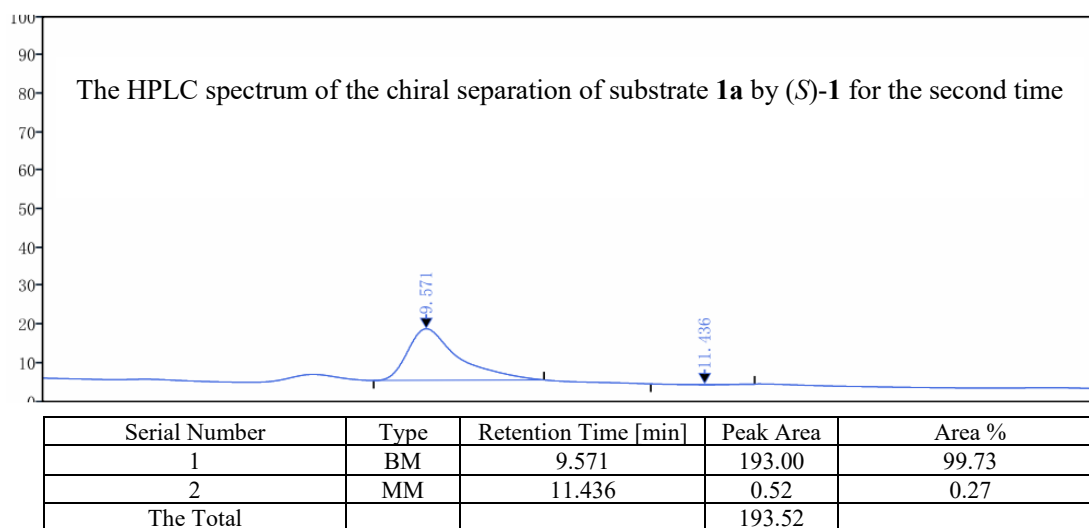
To ensure the accuracy of the separation result, we conducted multiple separation experiments under the identical conditions for each substrate in table 2, the average of the multiple experiments' results was used as final ee value. The HPLC spectra are listed as follows.

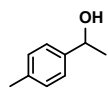


Chiral HPLC analysis: Daicel Chiralce OD: hexane/*i*-PrOH =96/4; flow rate =1.0 mL/min;

220 nm;  $t_R = 9.480\text{min}$ ,  $t_R = 11.465\text{ min}$ .

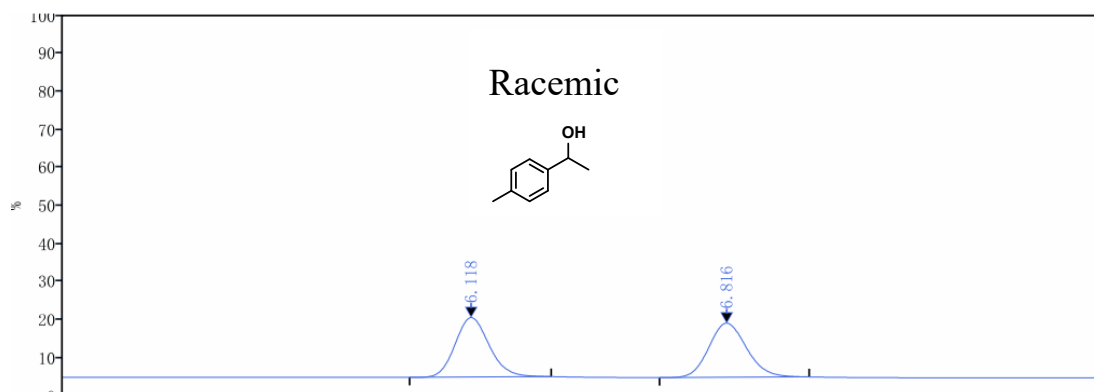




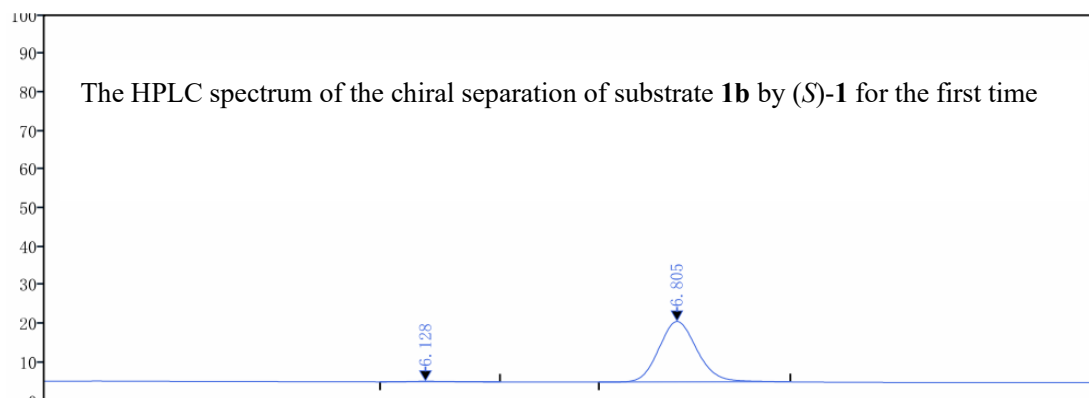


Chiral HPLC analysis: Daicel Chiralcel OJ: hexane/*i*-PrOH =99/1; flow rate =1.0 mL/min;

220 nm;  $t_R = 6.118$  min,  $t_R = 6.816$  min.

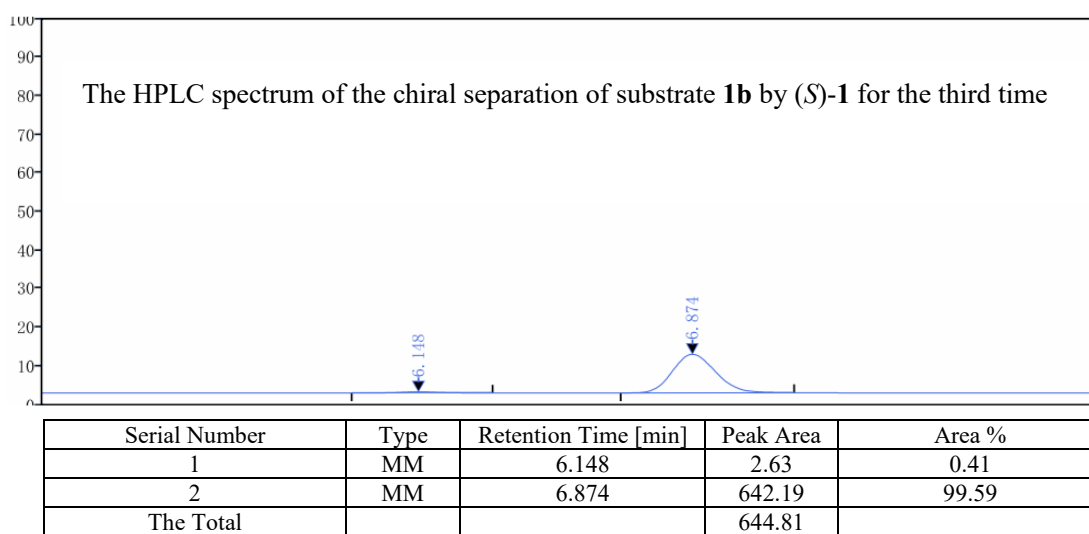
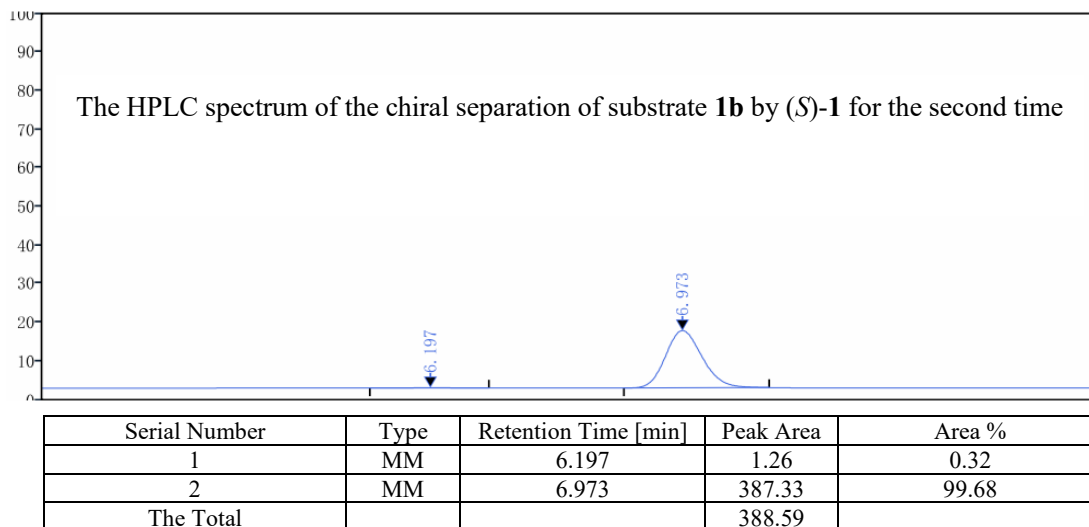


Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	BM	6.118	829.33	50.01
2	BM	6.816	828.88	49.99
The Total			1658.21	



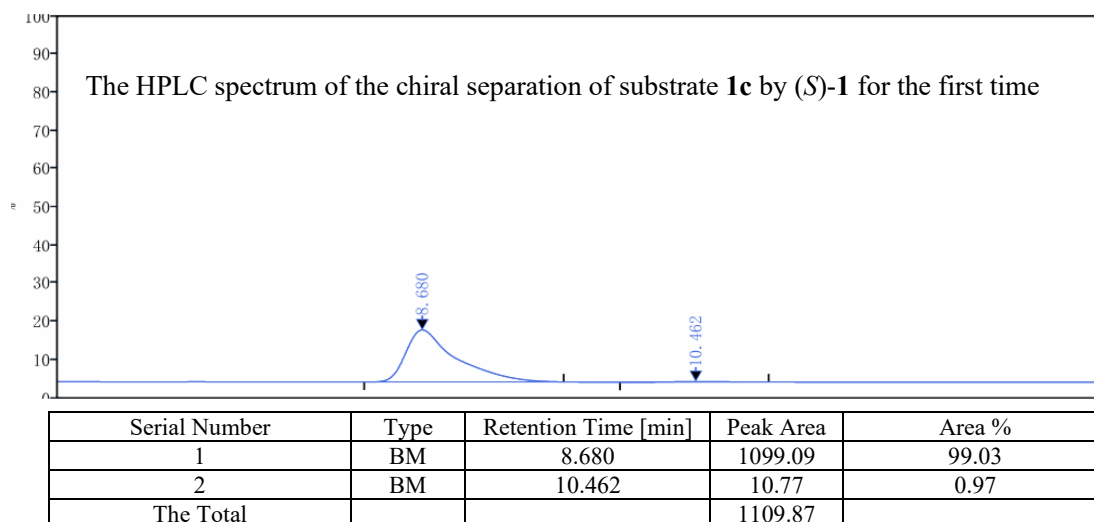
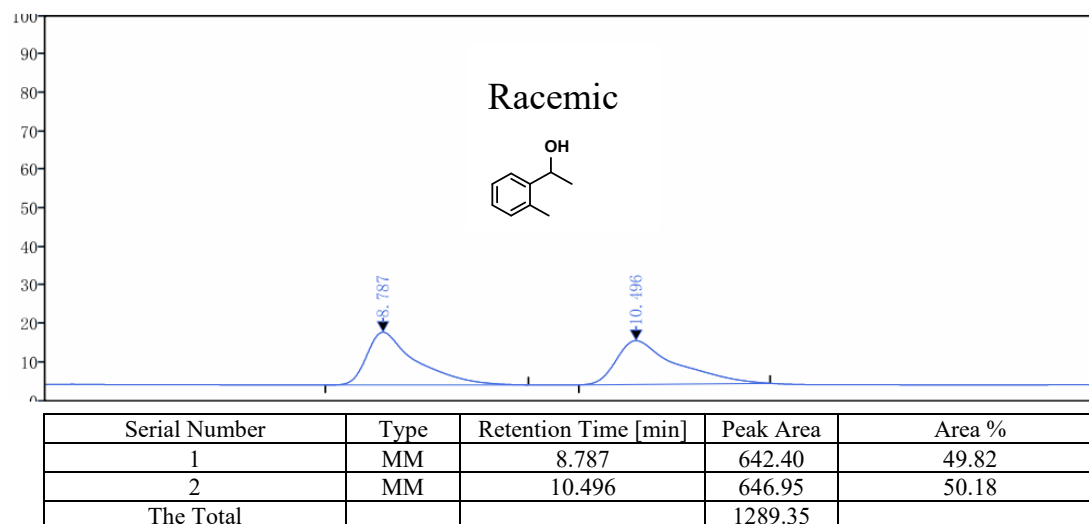
Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	6.128	1.94	0.43
2	MM	6.805	447.49	99.57
The Total			449.43	

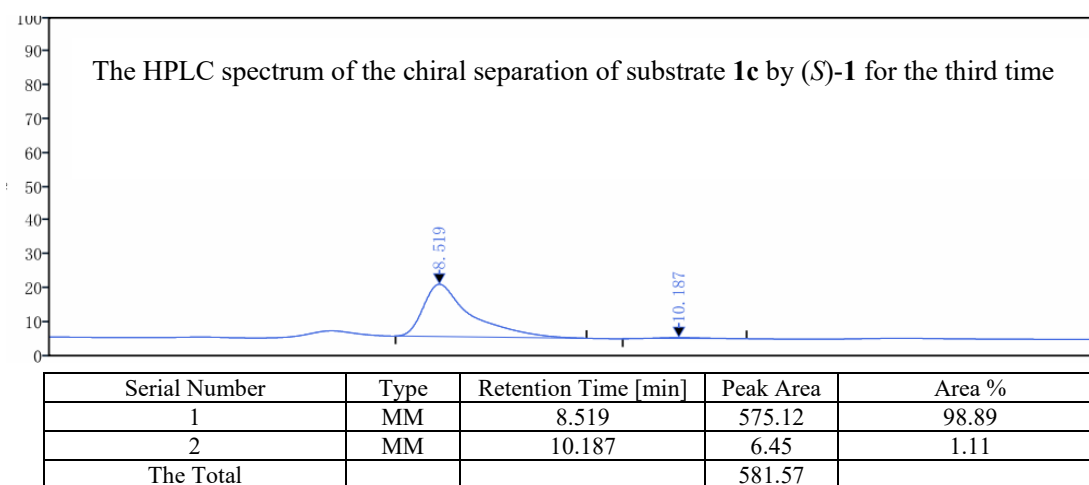
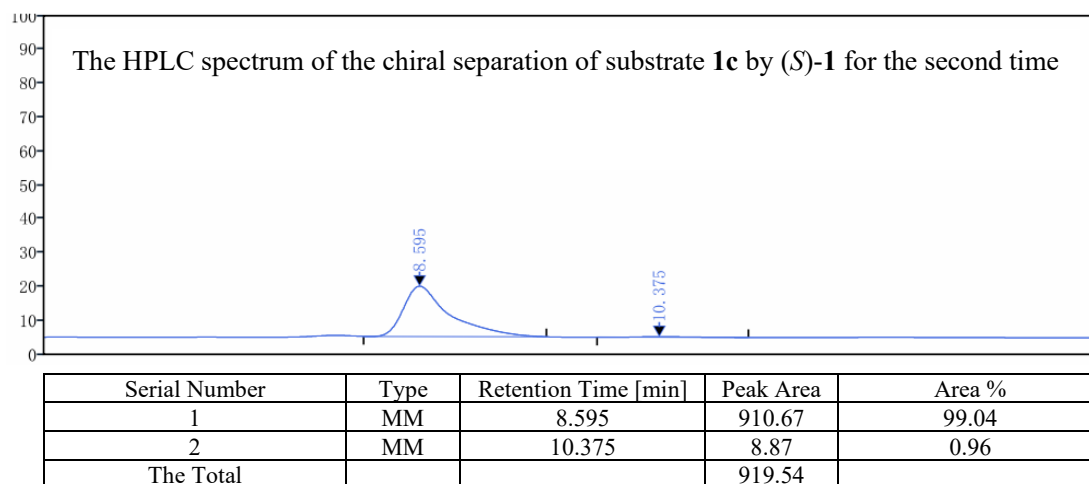


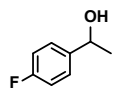




Chiral HPLC analysis: Daicel Chiralce AD: hexane/*i*-PrOH =98/2; flow rate =1.0 mL/min;  
220 nm;  $t_R$  = 8.787 min,  $t_R$  = 10.496 min.

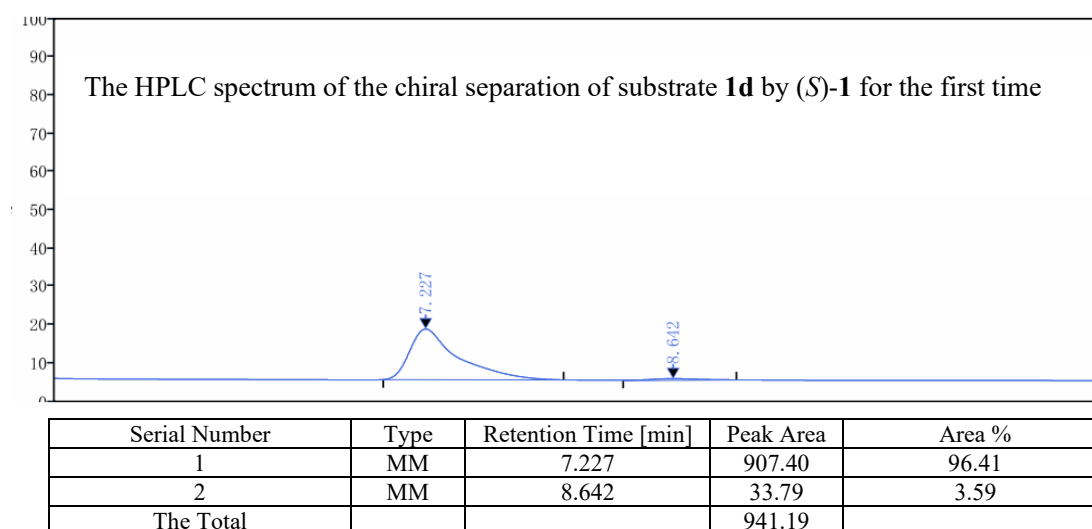
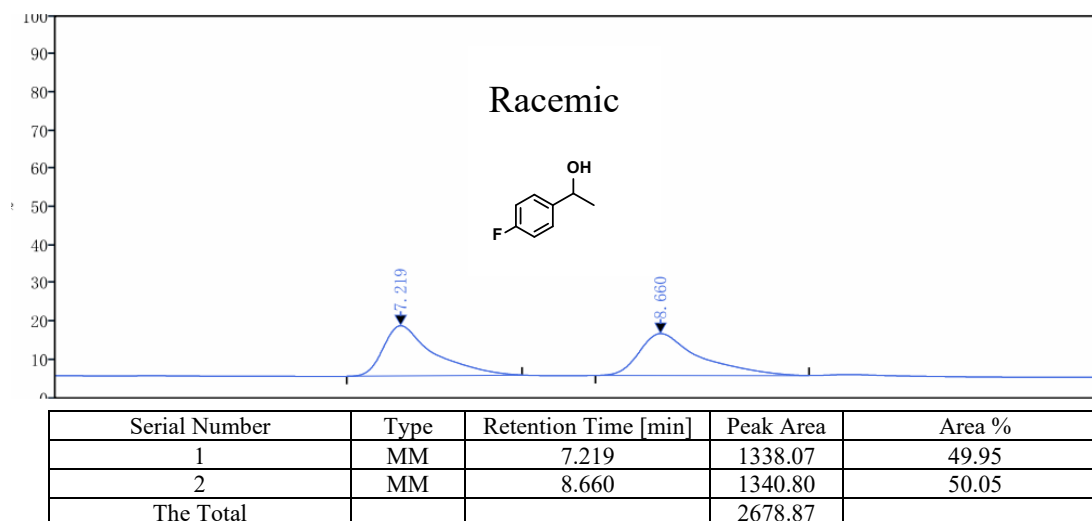


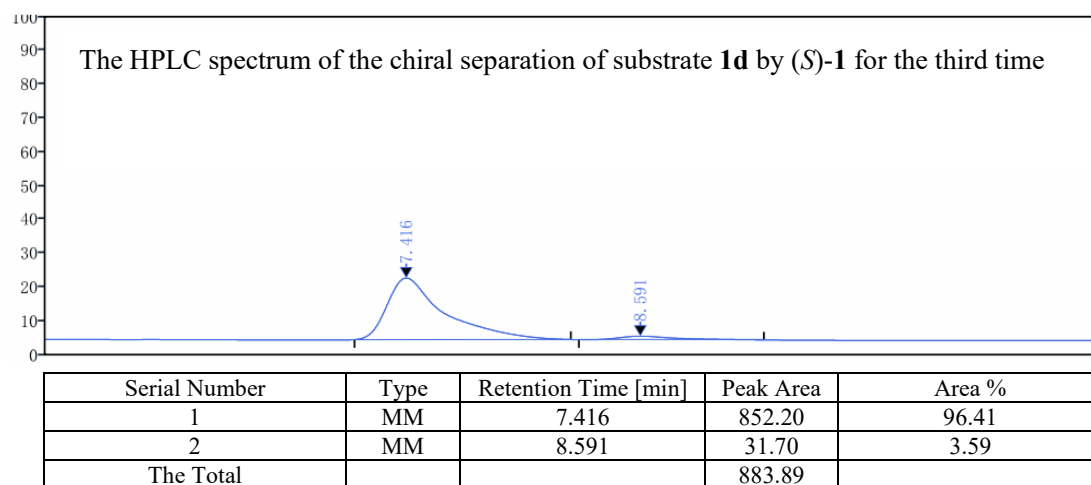
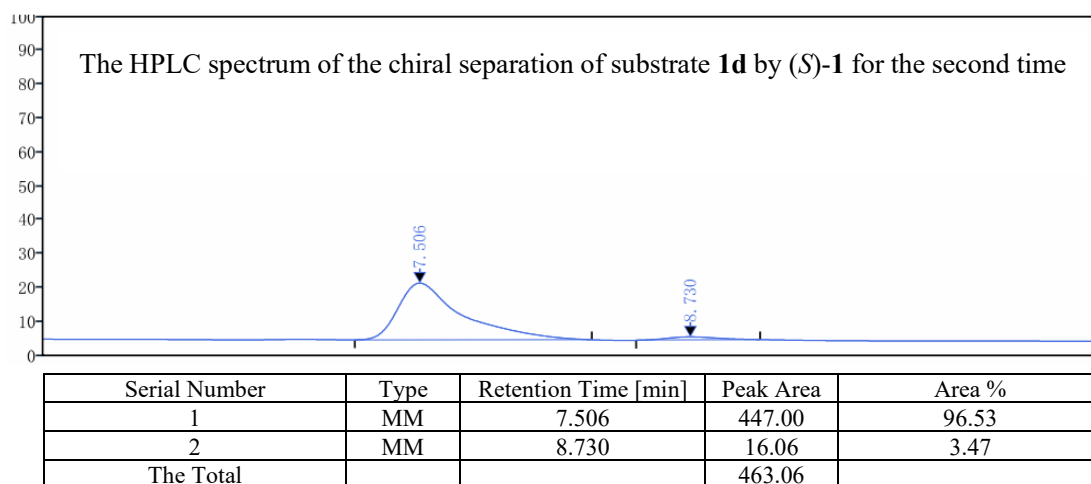


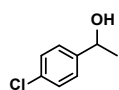


Chiral HPLC analysis: Daicel Chiralce AS: hexane/*i*-PrOH =96/4; flow rate =1.0 mL/min;

220 nm;  $t_R = 7.219$  min,  $t_R = 8.660$  min.

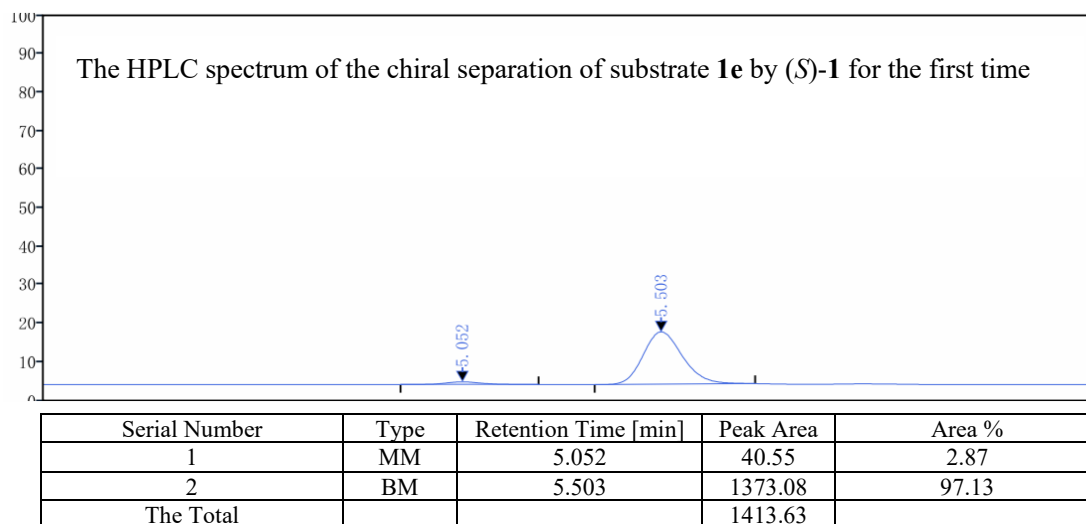
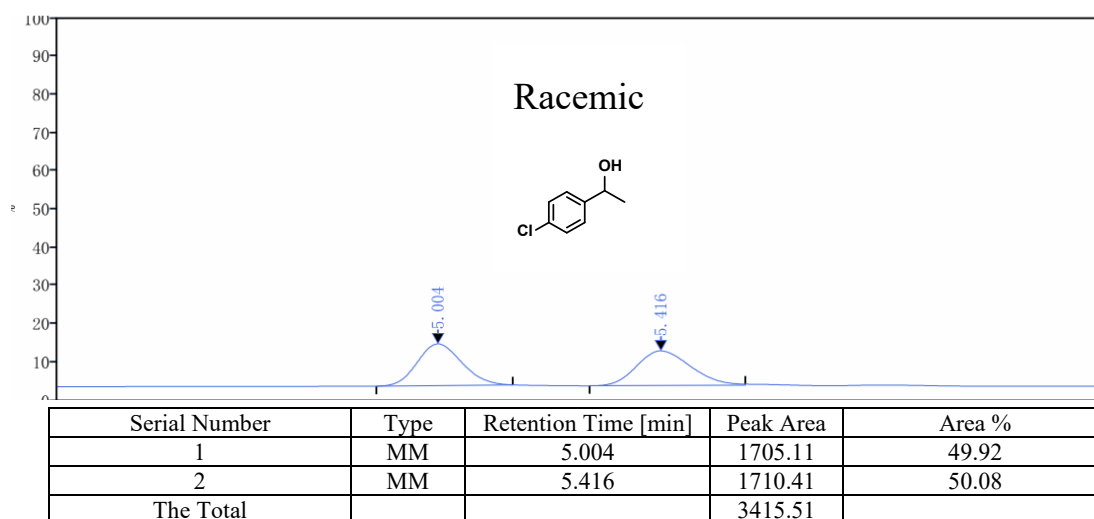


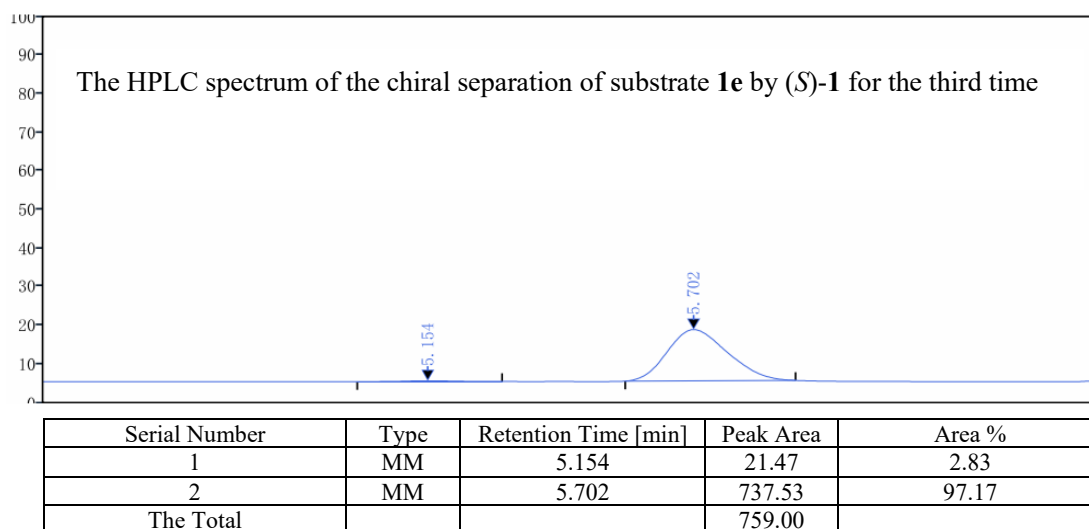
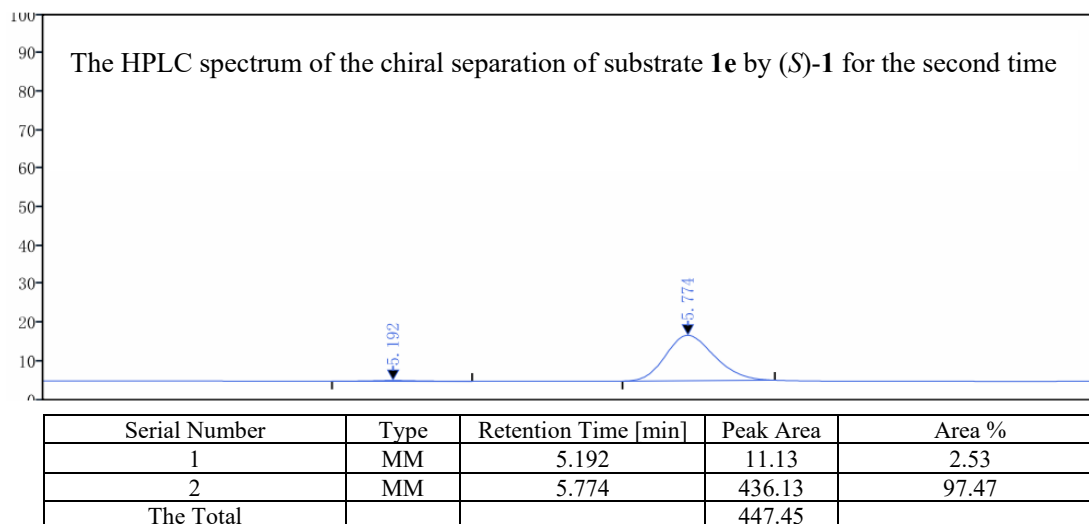


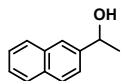


Chiral HPLC analysis: Daicel Chiralce OD: hexane/*i*-PrOH =99/1; flow rate =1.0 mL/min;

220 nm;  $t_R = 5.004$  min,  $t_R = 5.416$  min.

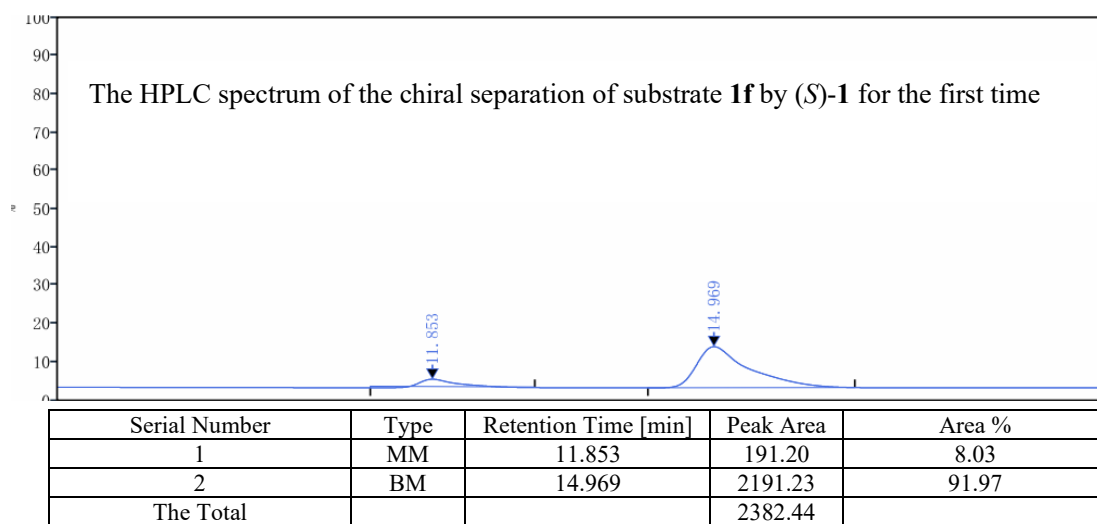
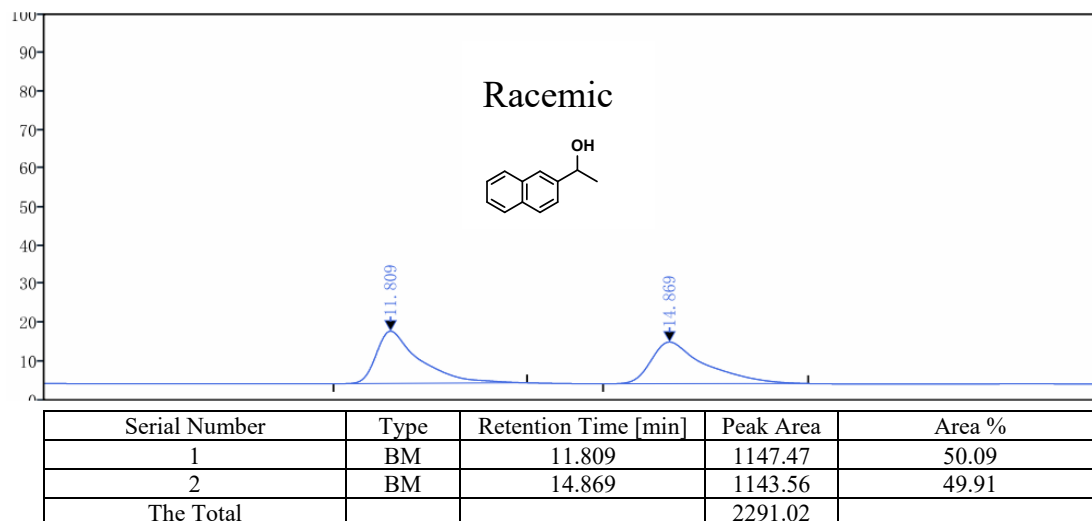




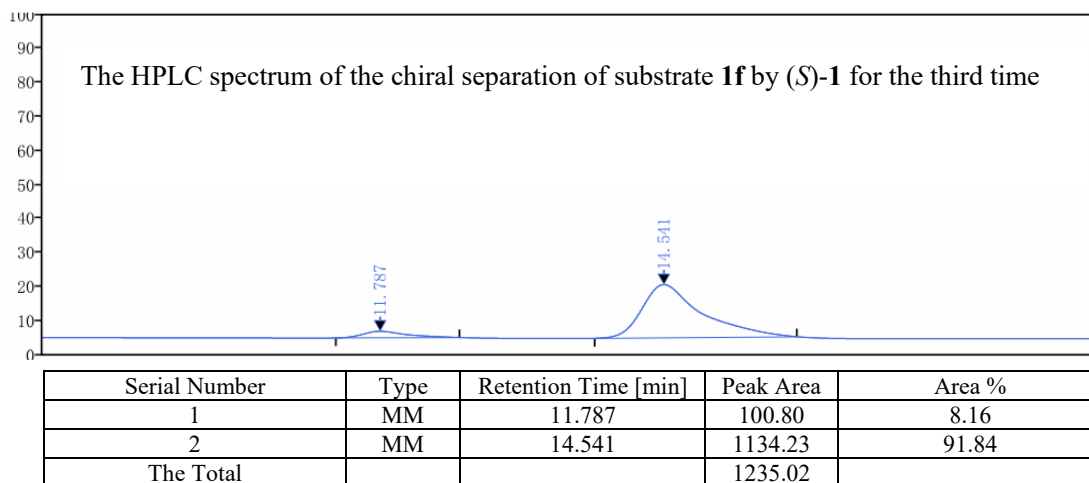
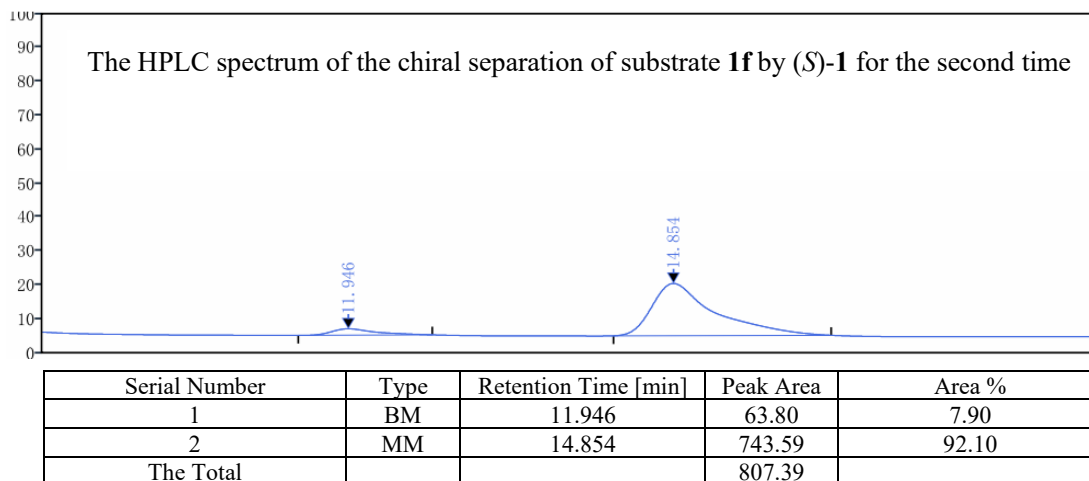


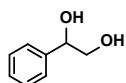
Chiral HPLC analysis: Daicel Chiralce OD hexane/*i*-PrOH =97/3; flow rate =1.0 mL/min;

220 nm;  $t_R = 11.809$  min,  $t_R = 14.869$  min.



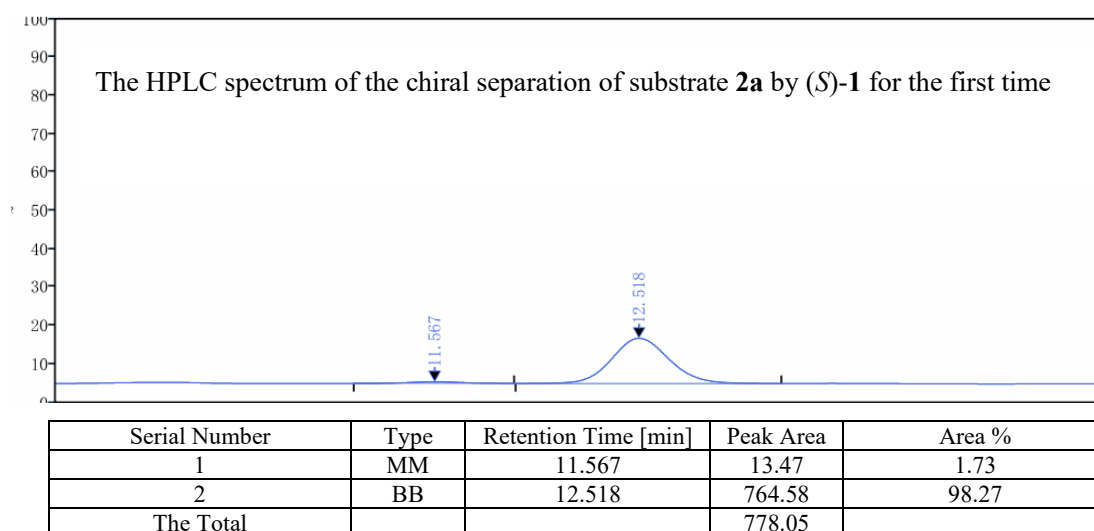
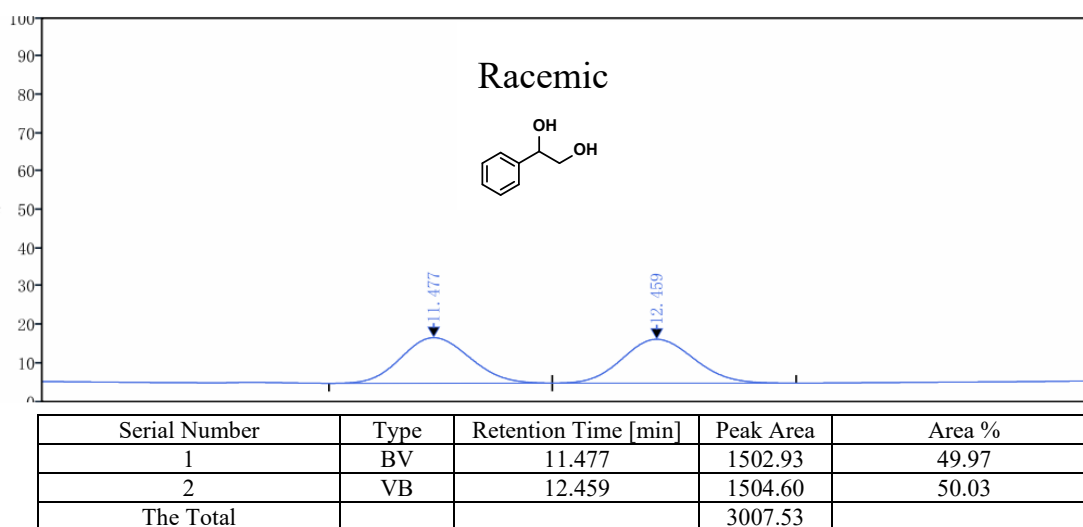


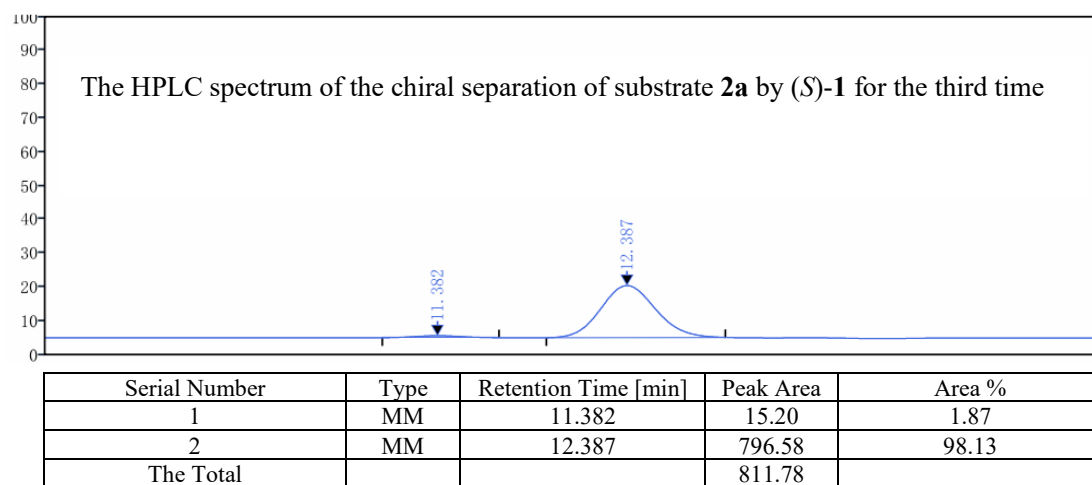
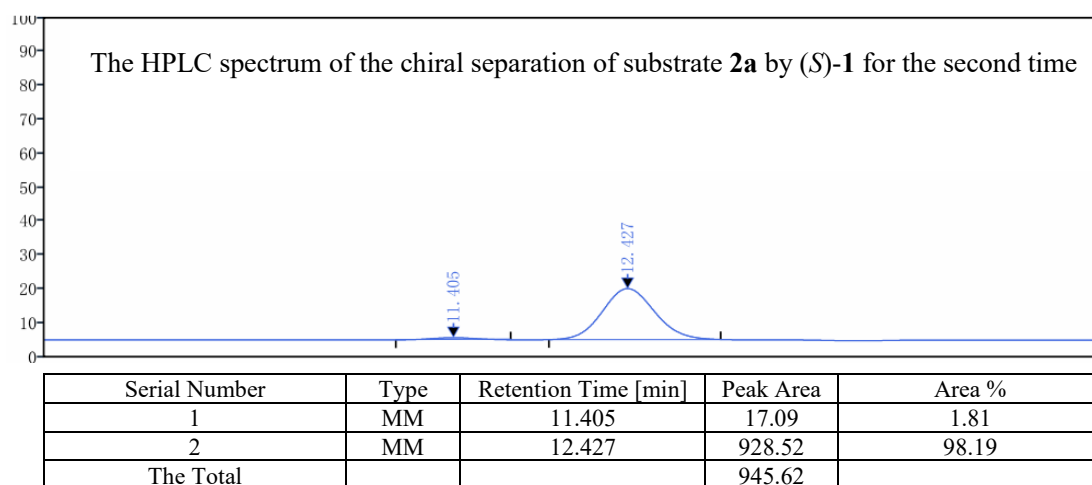


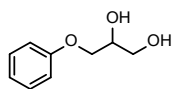


Chiral HPLC analysis: Daicel Chiralce IC: hexane/*i*-PrOH =90/10; flow rate =1.0

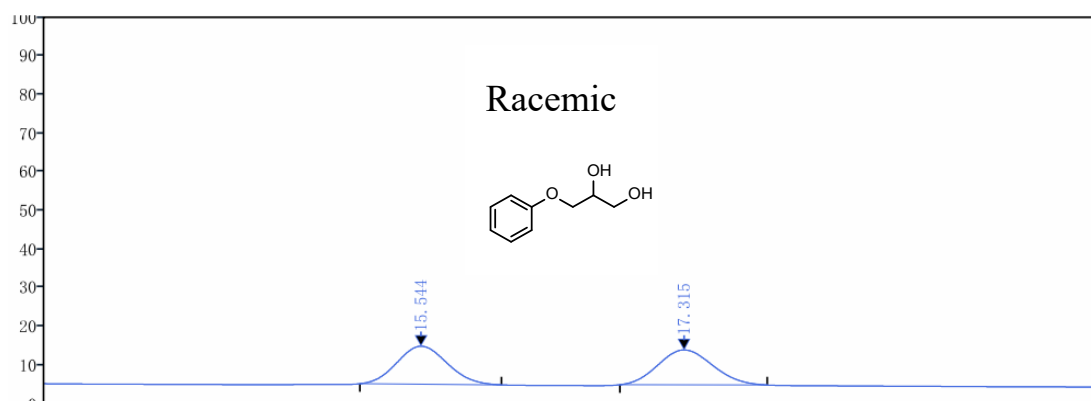
mL/min; 220 nm;  $t_R$  = 11.477 min,  $t_R$  = 12.459 min.



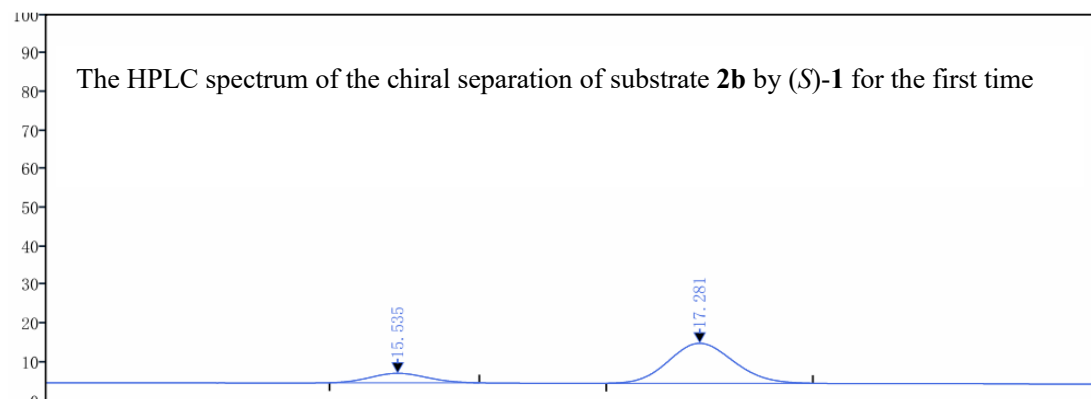




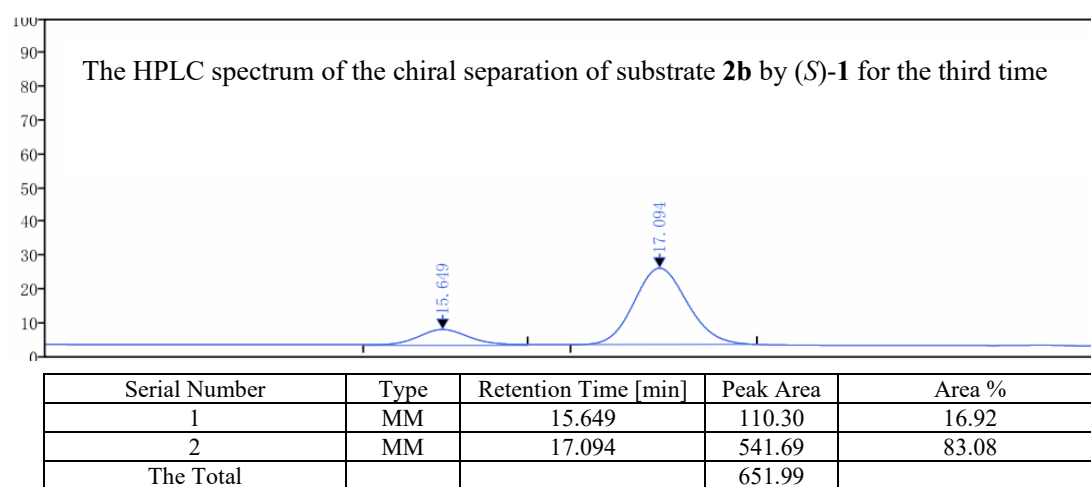
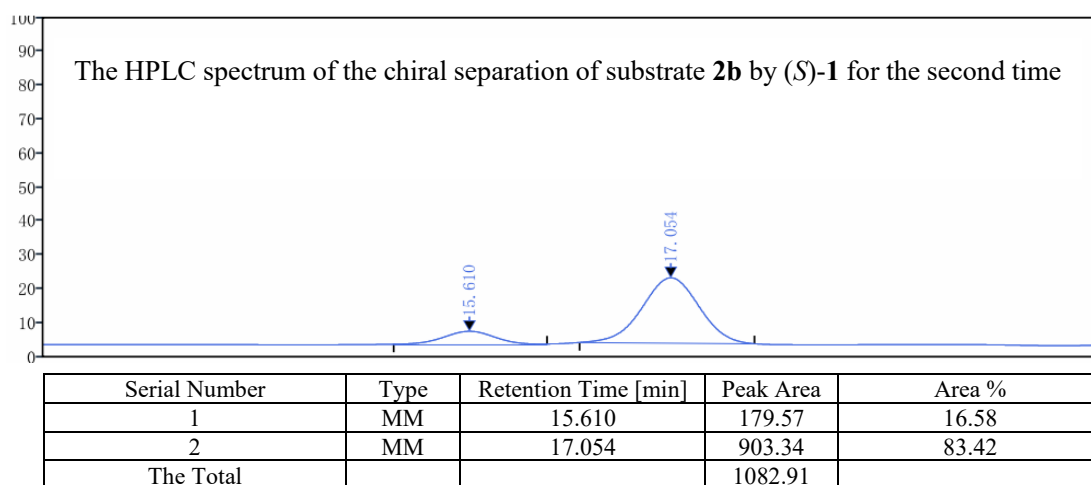
Chiral HPLC analysis: Daicel Chiralce IA: hexane/*i*-PrOH =90/10; flow rate =1.0 mL/min; 254nm;  $t_R$  = 15.544 min,  $t_R$  = 17.315 min.

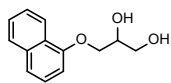


Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	15.544	402.16	49.98
2	MM	17.315	402.48	50.02
The Total			804.63	



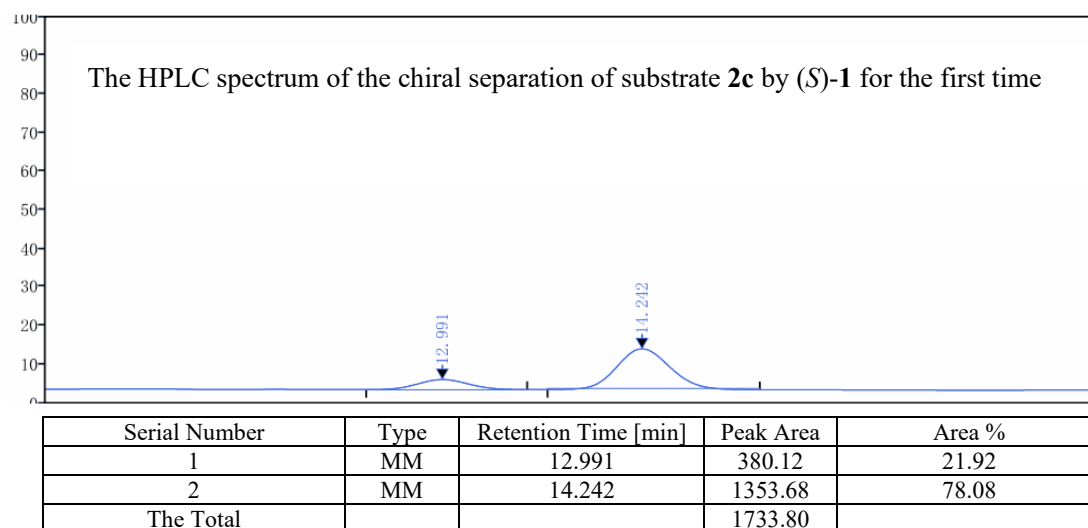
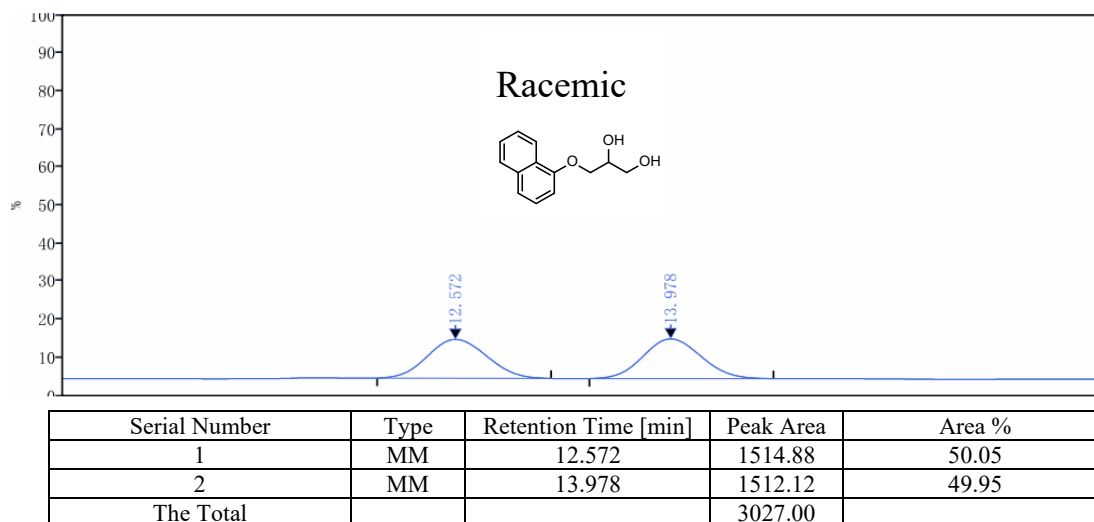
Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	15.535	106.94	17.03
2	MM	17.281	520.91	82.97
The Total			627.86	

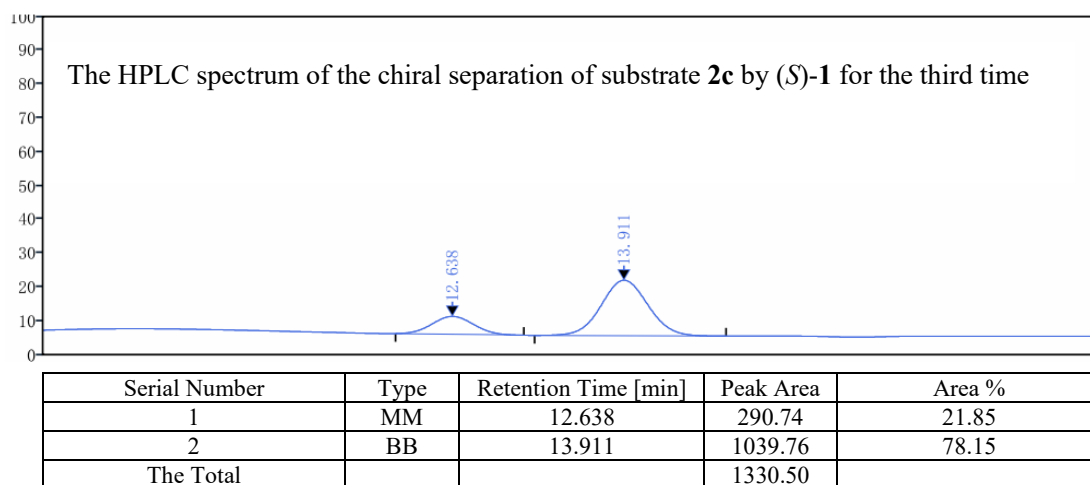
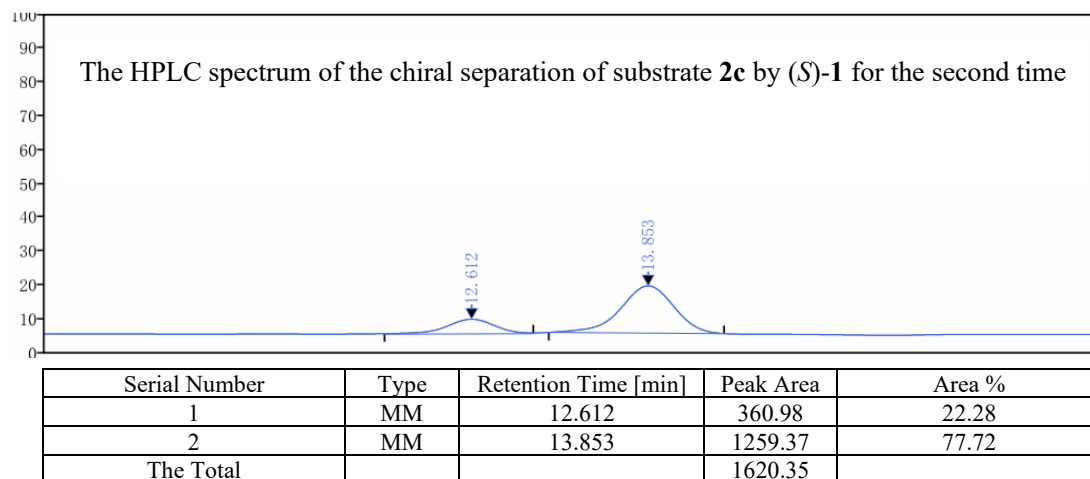


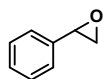


Chiral HPLC analysis: Daicel Chiralce IA: hexane/*i*-PrOH =90/10; flow rate =1.0

mL/min; 254nm;  $t_R = 12.572$  min,  $t_R = 13.978$ min.

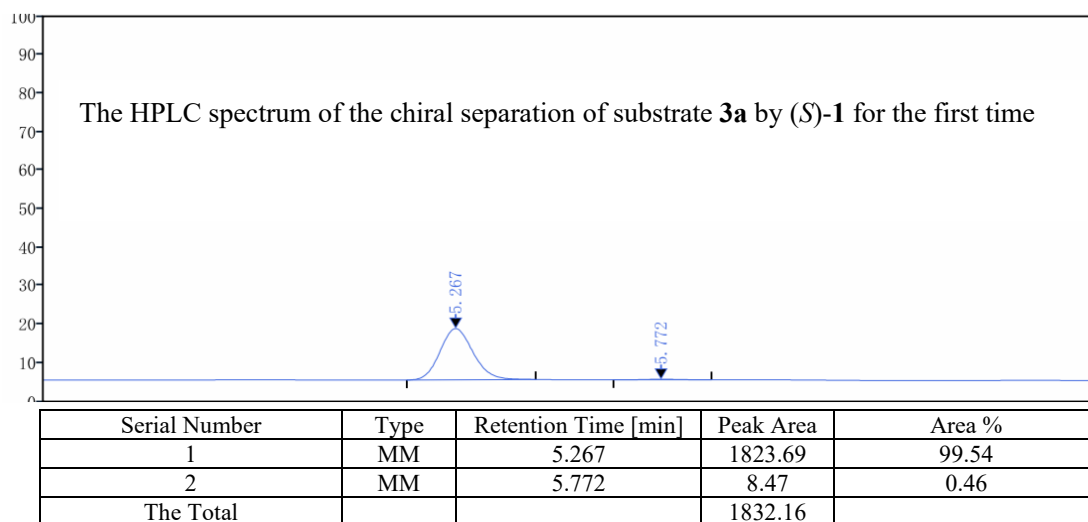
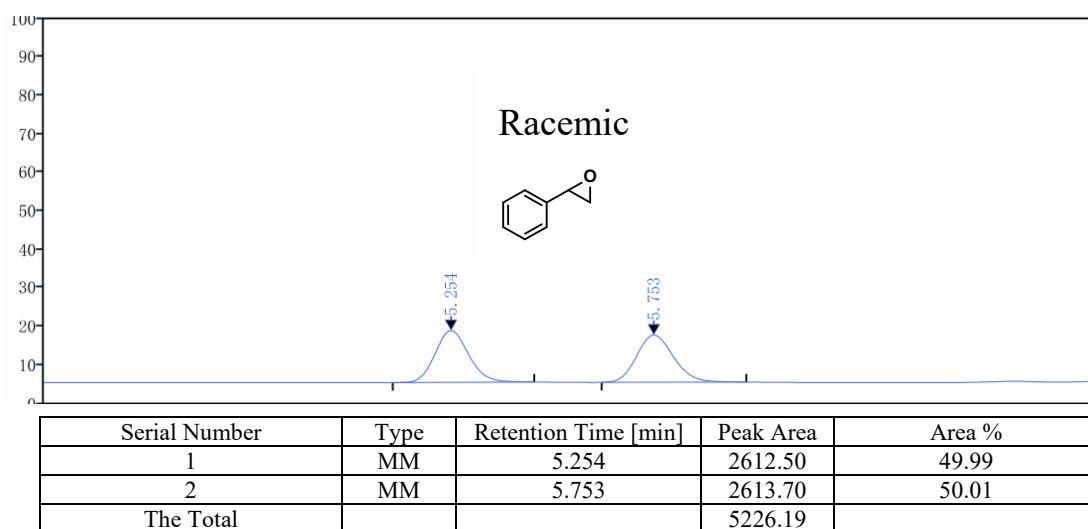




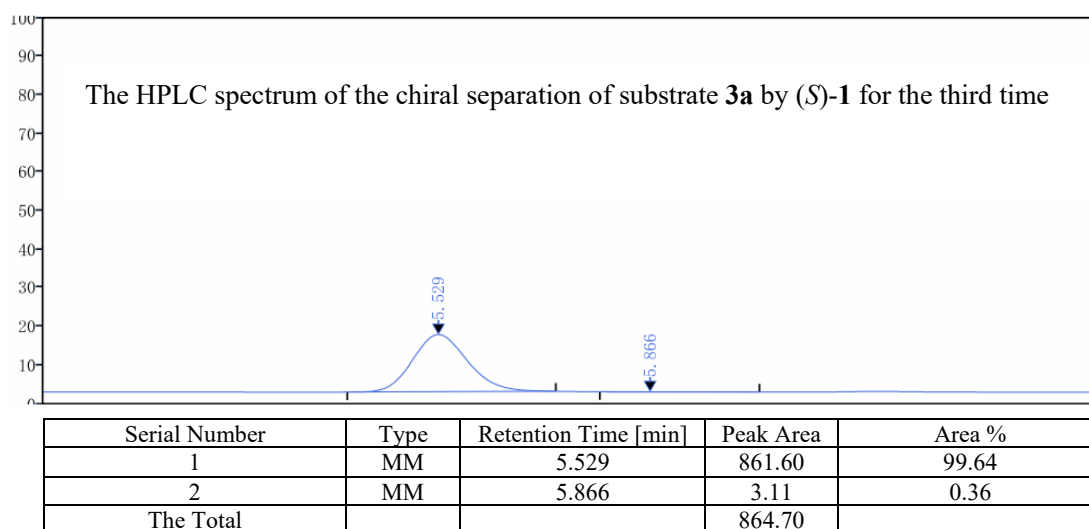
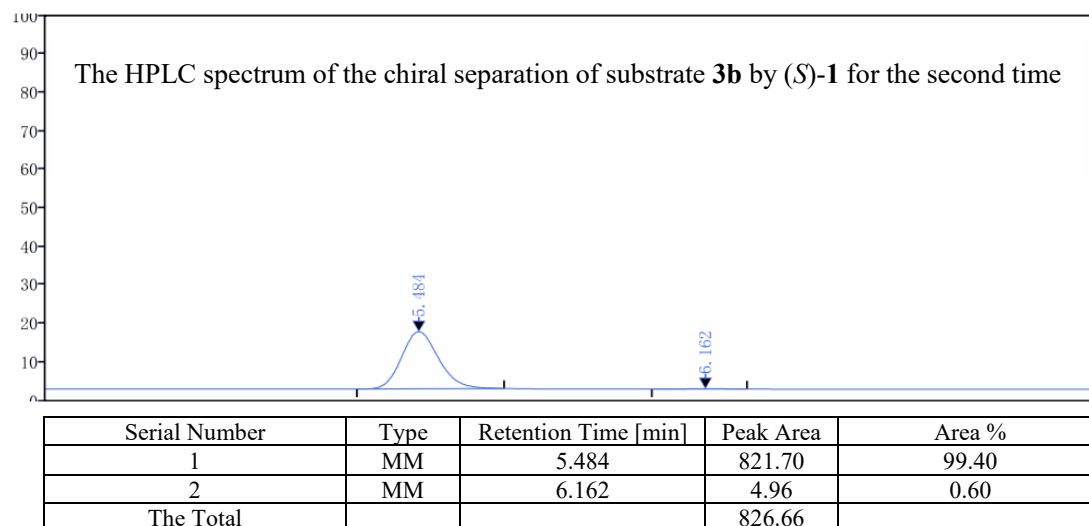


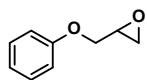
Chiral HPLC analysis: Daicel Chiralce IC: hexane/*i*-PrOH =95/5; flow rate =1.0 mL/min;

220 nm;  $t_R = 5.254$  min,  $t_R = 5.753$  min.



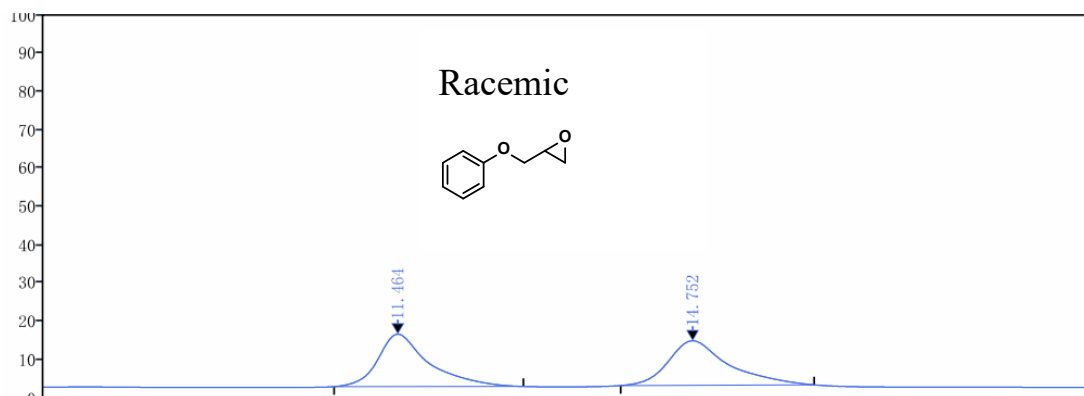




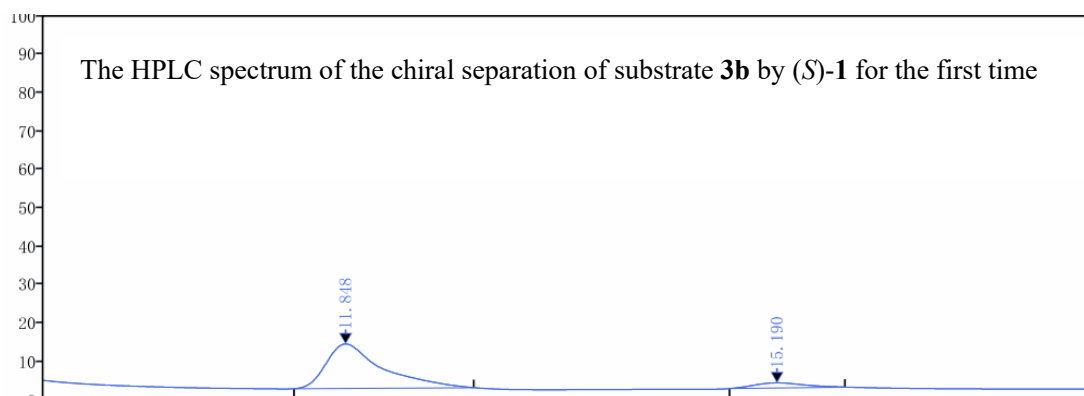


Chiral HPLC analysis: Daicel Chiralcel AS: hexane/*i*-PrOH =98/2; flow rate =0.8

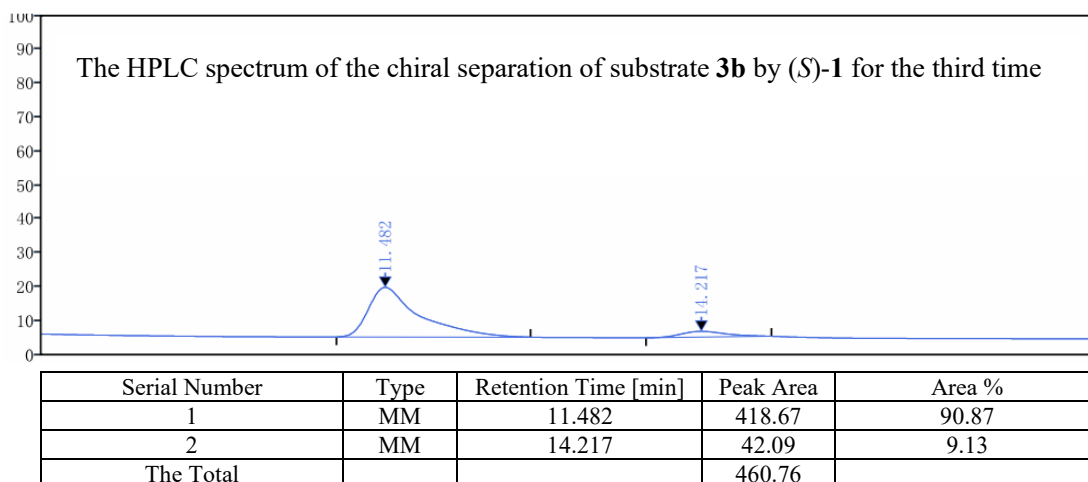
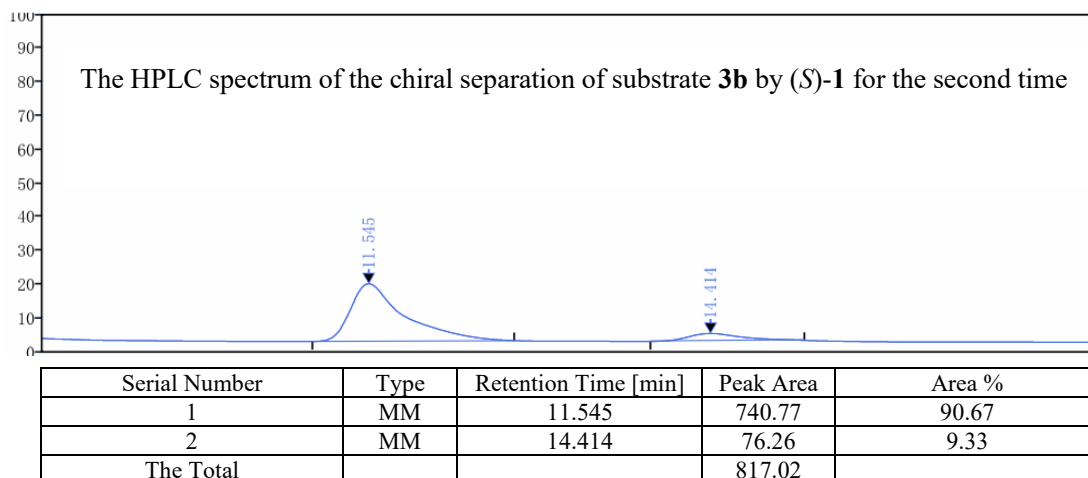
mL/min; 254nm;  $t_R$  = 11.464 min,  $t_R$  = 14.752min.

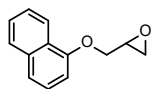


Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	11.464	2512.96	49.98
2	MM	14.752	2515.05	50.02
The Total			5028.01	

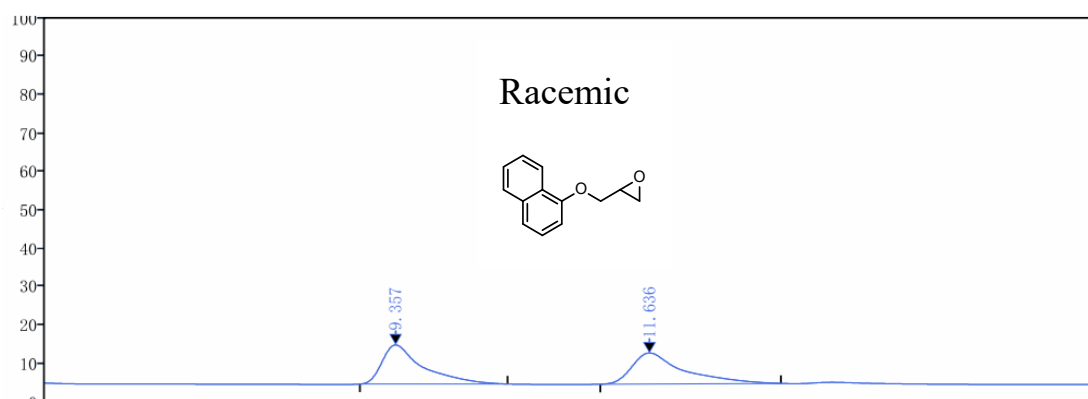


Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	11.848	225.03	90.78
2	MM	15.190	22.86	9.22
The Total			247.90	

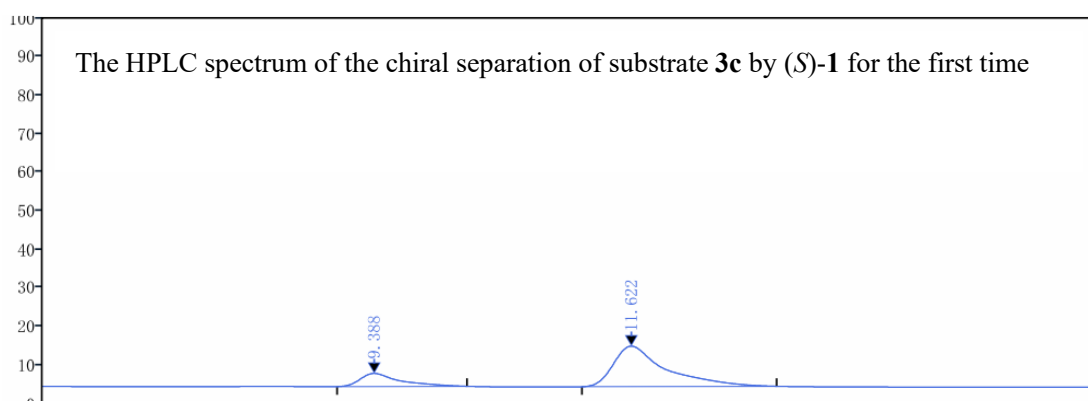




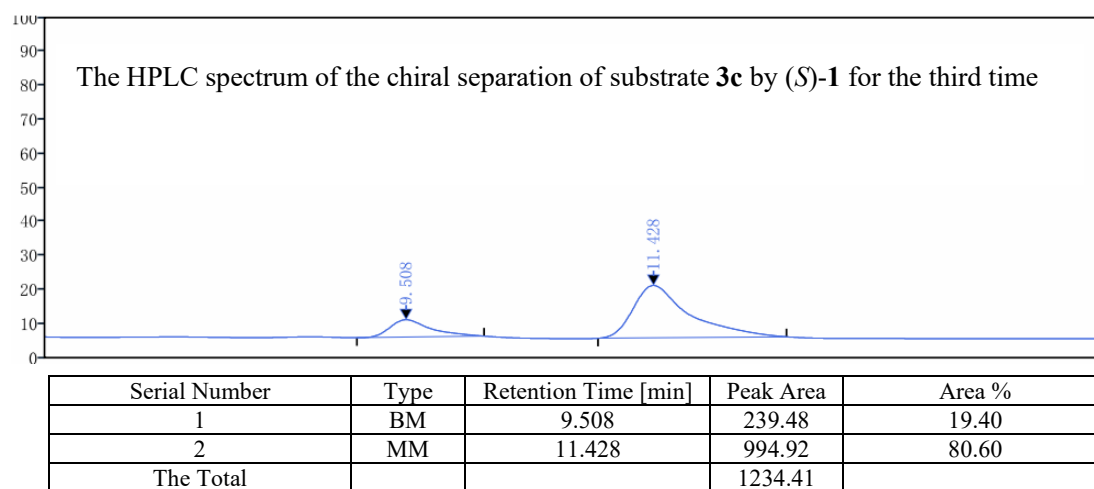
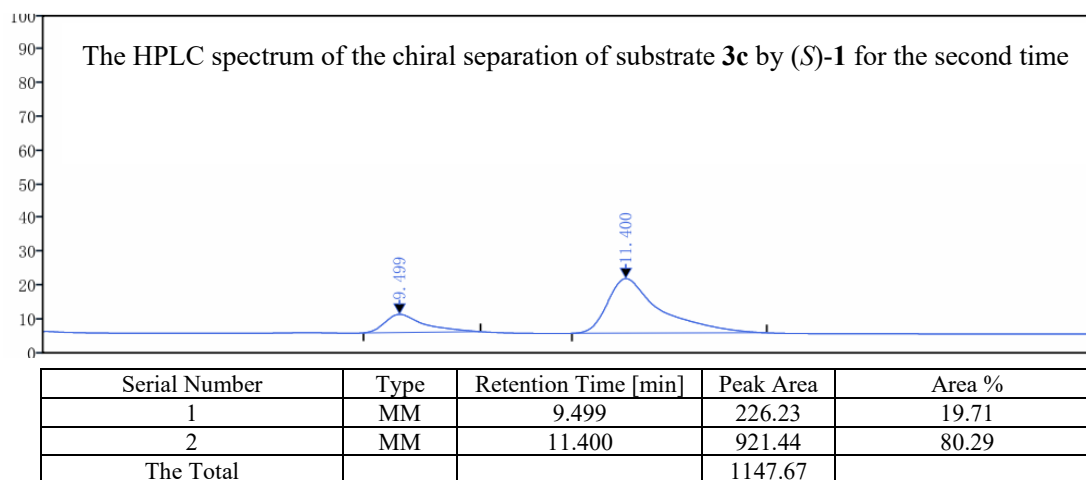
Chiral HPLC analysis: Daicel Chiralce AS: hexane/*i*-PrOH =97/3; flow rate =1.0 mL/min; 220nm;  $t_R$  = 9.357 min,  $t_R$  = 11.636min.

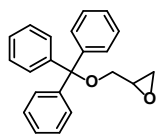


Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	9.357	1476.85	50.09
2	MM	11.636	1471.80	49.91
The Total			2948.65	



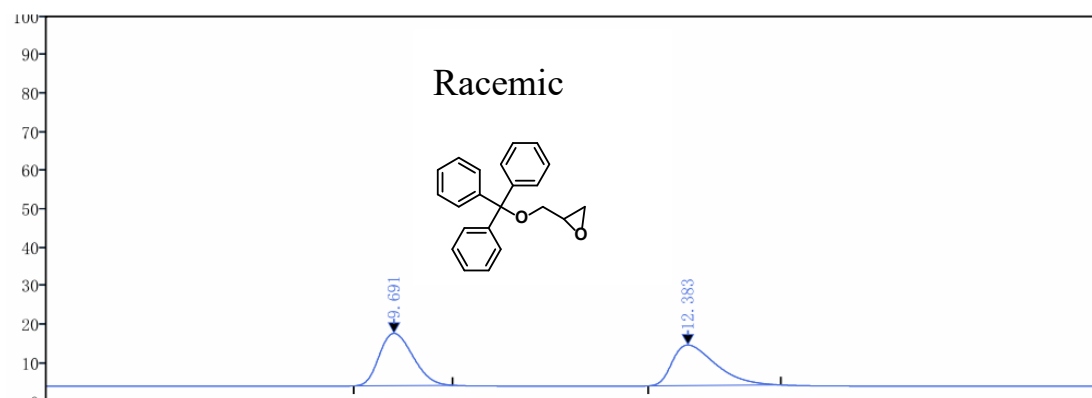
Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	9.388	257.41	19.60
2	MM	11.622	1056.03	80.40
The Total			1313.44	



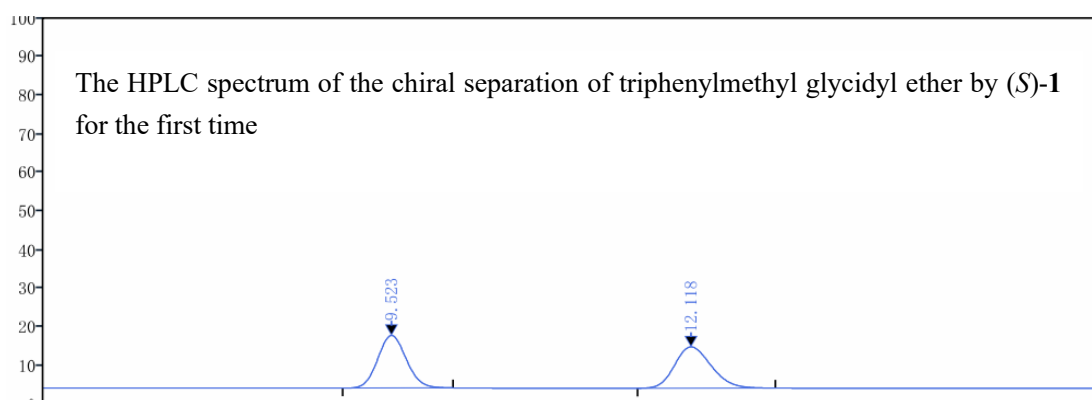


Chiral HPLC analysis: Daicel Chiralce OD: hexane/*i*-PrOH =95/5; flow rate =1.0

mL/min; 254nm;  $t_R = 9.691$  min,  $t_R = 12.383$  min.



Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	9.691	34869.04	50.00
2	MM	12.383	34871.64	50.00
The Total			69740.68	



Serial Number	Type	Retention Time [min]	Peak Area	Area %
1	MM	9.523	6874.22	49.92
2	MM	12.118	6896.86	50.08
The Total			13771.07	