

Supporting Information *for*

An Imidazolium-Modified Chiral Rhodium/diamine-Functionalized Periodic Mesoporous Organosilica for Asymmetric Transfer Hydrogenation of α -Haloketones and Benzils in Aqueous Medium

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	Content	Page
Experimental	General, characterization, and recycle experiments	S2
Figure S1	FT-IR spectra of 3 and catalyst 5	S3
Figure S2	Asymmetric transfer hydrogenation of aryl-substituted 2-haloketones.	S4
Figure S3	Reusability of the catalyst 5 using 2-bromo-1-phenylethanone as a substrate	S18
Figure S4	Asymmetric transfer hydrogenation of benzil catalyzed by catalyst 5 , PMO-supported analog and SBA-supported analog. Reactions were carried out at 40 °C, using 10.0 μ mol of the catalyst, 5 equiv HCOONa, and at an S/C ratio of 100 in 5.0 mL of water.	S21
Figure S5	Asymmetric transfer hydrogenation of benzils	S22
Table S1	Reusability of catalyst 5 for asymmetric transfer hydrogenation of benzil	S29
Figure S6	Reusability of catalyst 5 for asymmetric transfer hydrogenation of benzil	S29

Experimental

1. General

All experiments, which are sensitive to moisture or air, were carried out under an Ar atmosphere using the standard Schlenk techniques. (*R,R*)-1,2-diphenylenediamine, [Cp*RhCl₂]₂, 1,2-bis(triethoxysilyl)ethane and surfactant P123 (CH₂-CH₂O)₂₀(CH₂(CH₃)CH₂O)₇₀(CH₂CH₂O)₂₀) were purchased from Sigma-Aldrich Company Ltd. Compounds (*R,R*)-4-(trimethoxysilyl)ethylphenylsulfonyl-1,2-diphenylethylenediamine and 1,3-bis(3-(triethoxysilyl)propyl)-1*H*-imidazol-3-ium iodide (**2**) were synthesized according to the reported literatures [*J. Mater. Chem.* **2010**, *20*, 1970 and *Tetrahedron* **2008**, *64*, 4637.]

2. Characterization

Rh loading amounts in catalysts were analyzed using an inductively coupled plasma optical emission spectrometer (ICP, Varian VISTA-MPX). Fourier transform infrared (FT-IR) spectra were collected on a Nicolet Magna 550 spectrometer using KBr method. Transmission electron microscopy (TEM) images were performed on a JEOL JEM2010 electron microscope at an acceleration voltage of 220 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Perkin-Elmer PHI 5000C ESCA system. A 200 μm diameter spot size was scanned using a monochromatized Aluminum *Kα* X-ray source (1486.6 eV) at 40 W and 15 kV with 58.7 eV pass energies. All the binding energies were calibrated by using the contaminant carbon (C_{1s} = 284.6 eV) as a reference. Nitrogen adsorption isotherms were measured at 77 K with a Quantachrome Nova 4000 analyzer. The samples were measured after being outgassed at 423 K overnight. Pore size distributions were calculated by using the BJH model. The specific surface areas (SBET) of samples were determined from the linear parts of BET plots (*p/p*₀ = 0.05-1.00). Solid state NMR experiments were explored on a Bruker AVANCE spectrometer at a magnetic field strength of 9.4 T with ¹H frequency of 400.1 MHz, ¹³C frequency of 100.5 MHz and ²⁹Si frequency of 79.4 MHz with 4 mm rotor at two spinning frequency of 5.5 kHz and 8.0 kHz, TPPM decoupling is applied in the during acquisition period. ¹H cross polarization in all solid state NMR experiments was employed using a contact time of 2 ms and the pulse lengths of 4 μs.

3. General procedure for the recycle experiments. The catalyst **5** (215.0 mg, 20.0 μmol of Rh based on the ICP analysis), 2-bromo-phenylethanone or benzil (2.0 mmol), HCO₂Na (0.68 g, 10.0 mmol), 10.0 mL of water were added sequentially to a 50.0 mL round-bottom flask. The mixture was then stirred at room temperature (40 °C). After completion of the reaction, the catalyst was separated by centrifugation (10,000 rpm). The collected solids was transferred to a fresh 50.0 mL round-bottom flask and 2-bromo-phenylethanone or benzil (2.0 mmol), HCO₂Na (0.68 g, 10.0 mmol), and

10.0 mL of water were added again for next recycle. The aqueous solution was extracted with ethyl ether (3×3.0 mL). The combined ethyl ether extracts were washed with NaHCO_3 and brine, and then dehydrated with Na_2SO_4 . After evaporation of ethyl ether, the residue was purified by silica gel flash column chromatography to afford the desired products.

Figure S1. FT-IR spectra of **3** and catalyst **5**.

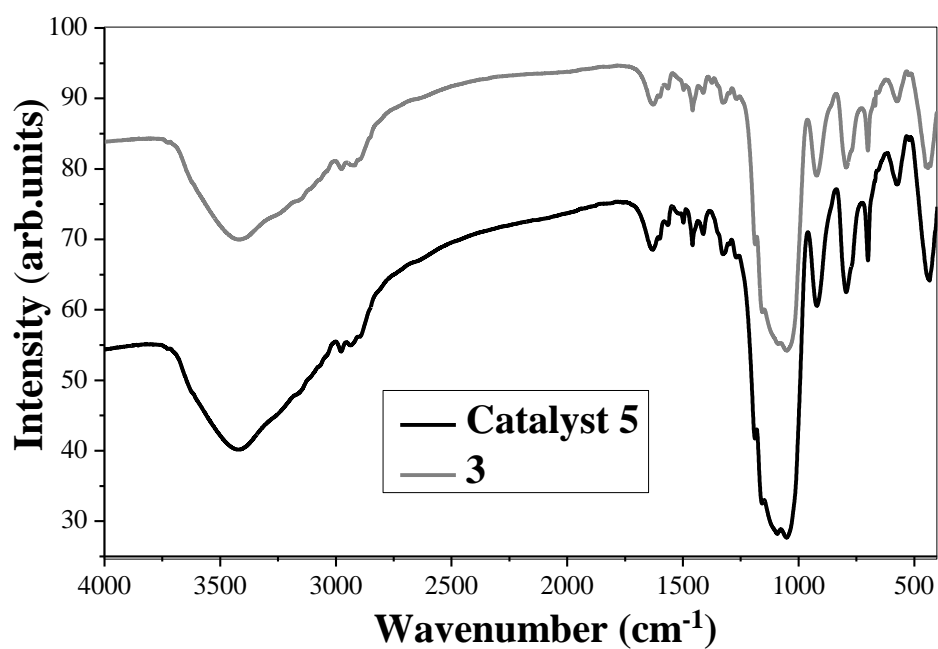


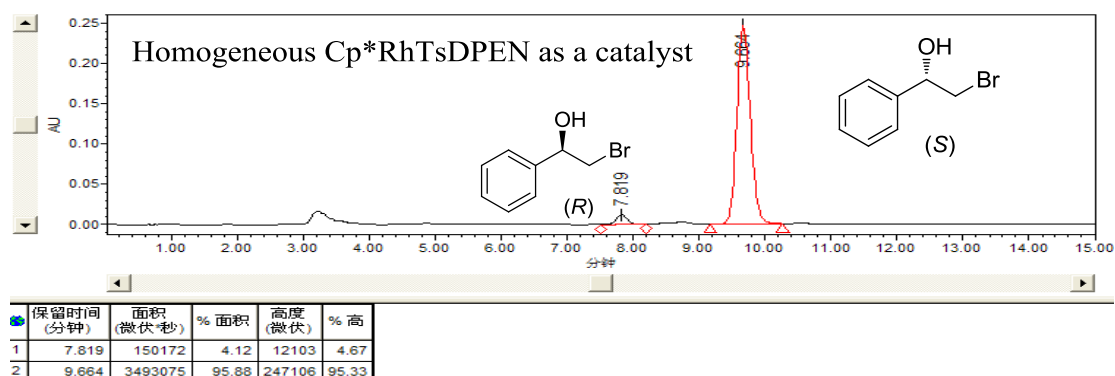
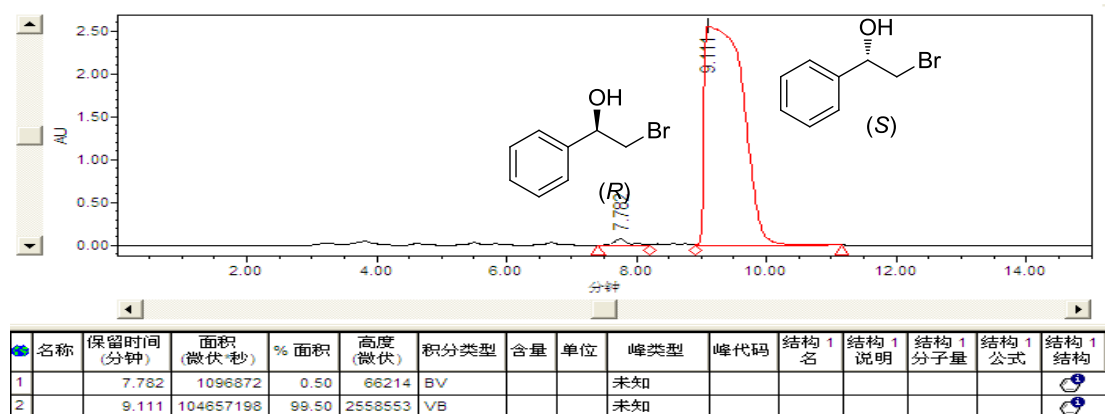
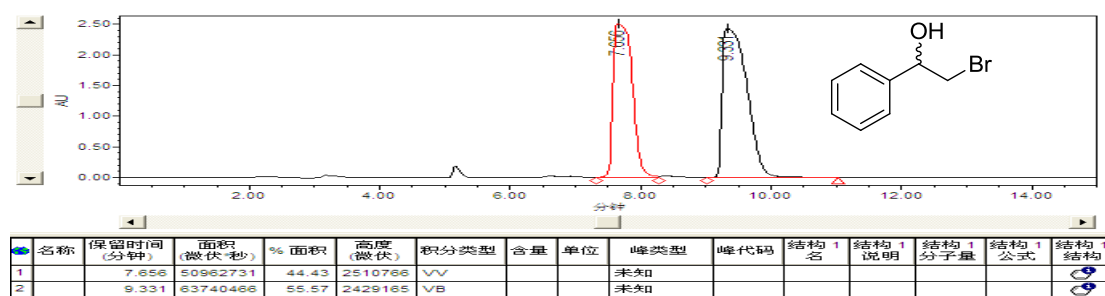
Figure S2. Asymmetric transfer hydrogenation of of aryl-substituted 2-haloketones. [The products were analyzed by a HPLC with a UV-Vis detector using a Daicel OB-H or OJ-H chiralcel column (Φ 0.46×25 cm)].

Translation of Chinese to English is as follows:

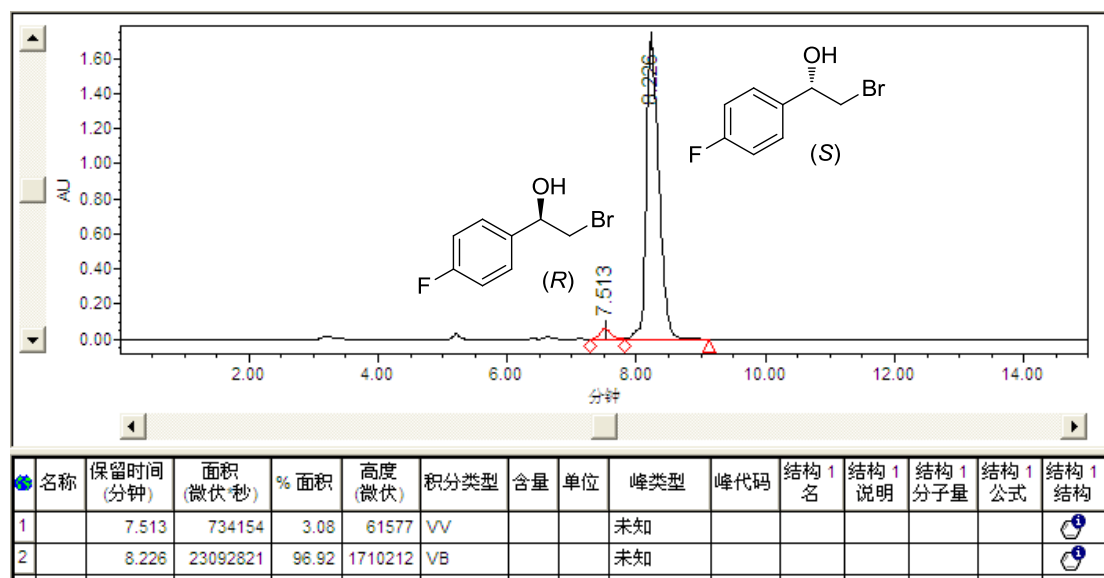
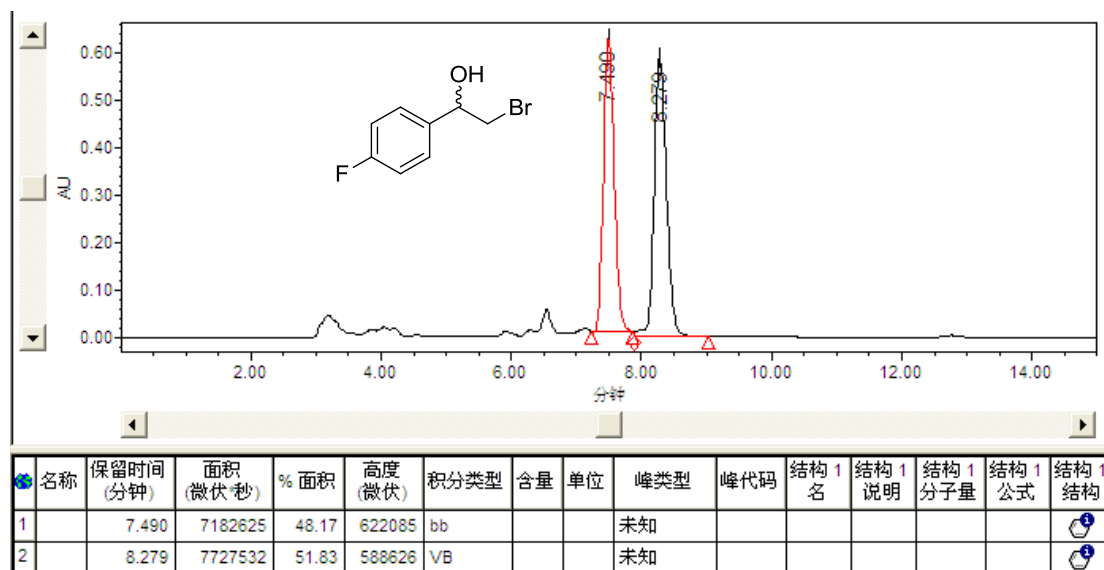
Peak	RetTime [min]	Area	Area ratio %	Height
1	8.498	18644684	49.95	1331866
2	9.358	18683896	50.05	1150448

名称	保留时间 (分钟)	面积 (微伏·秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	结构 1 名	结构 1 说明	结构 1 分子量	结构 1 公式	结构 1 结构
1	8.498	18644684	49.95	1331866	VV			未知						
2	9.358	18683896	50.05	1150448	VV			未知						

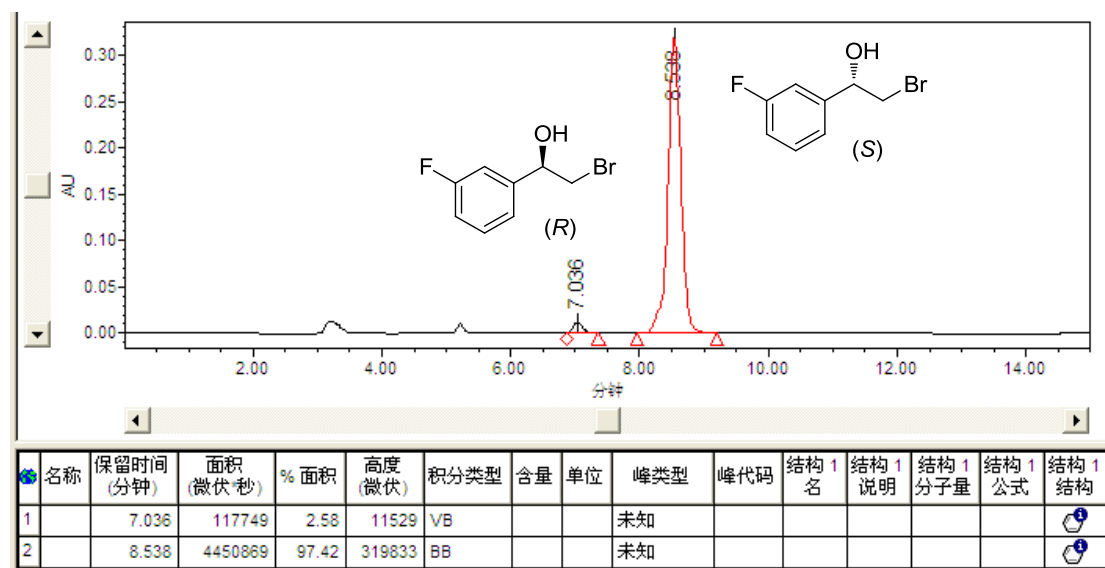
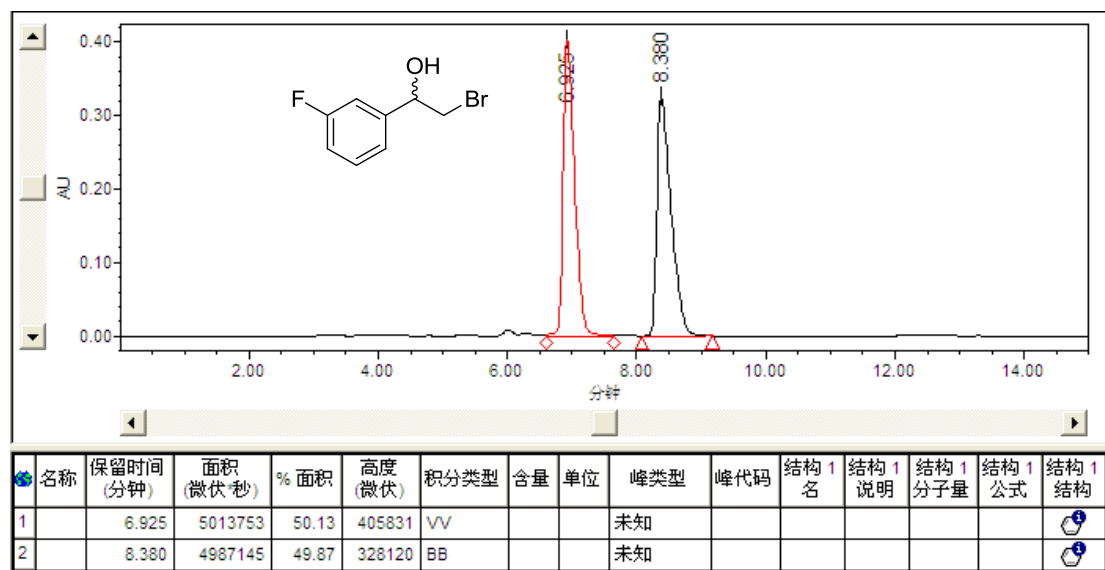
(S)-2-bromo-1-phenylethanol (6a): (HPLC: Chiralcel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1 mL/min, 25 °C).



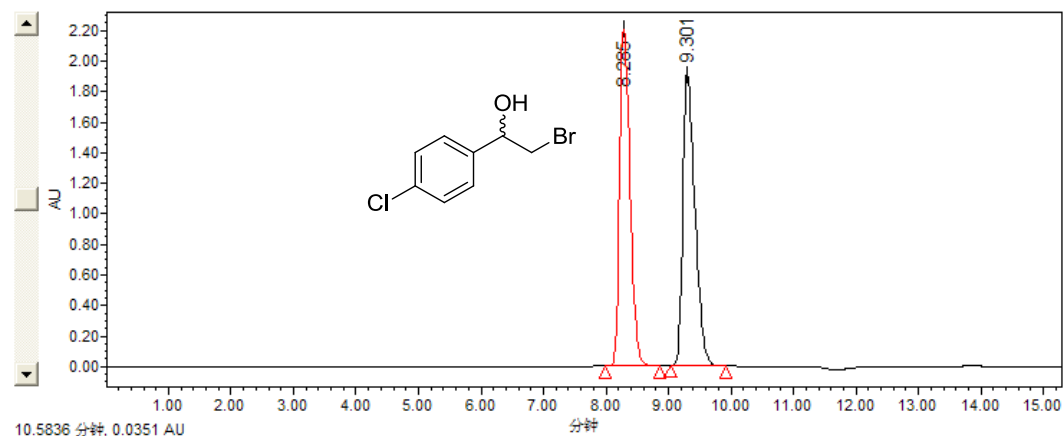
(S)-2-bromo-1-(4-fluorophenyl)ethanol (6b): (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1 mL/min, 25 °C).



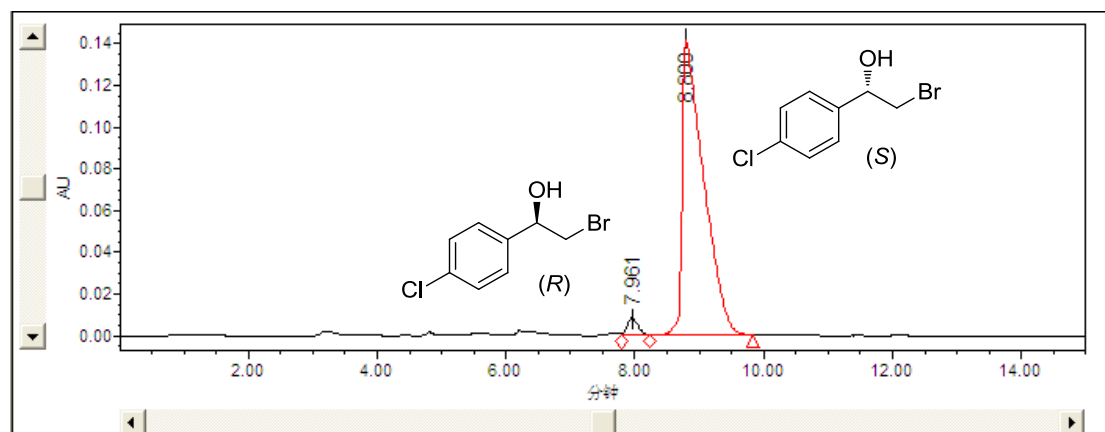
(S)-2-bromo-1-(3-fluorophenyl)ethanol (6c): (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1 mL/min, 25 °C).



(S)-2-bromo-1-(4-chlorophenyl)ethanol (6d): (HPLC: Chiralcel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1 mL/min, 25 °C).

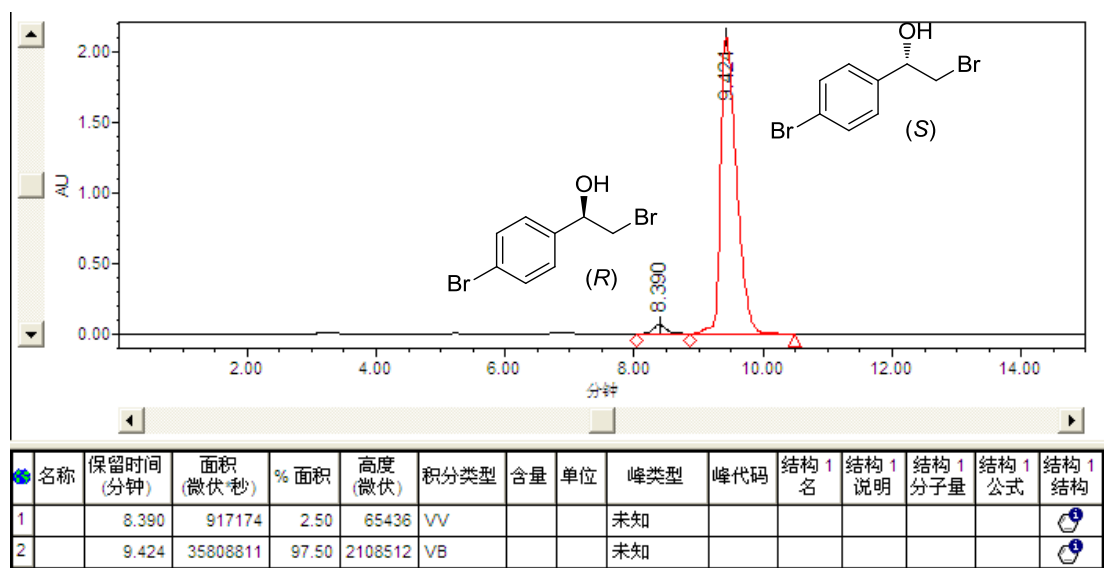
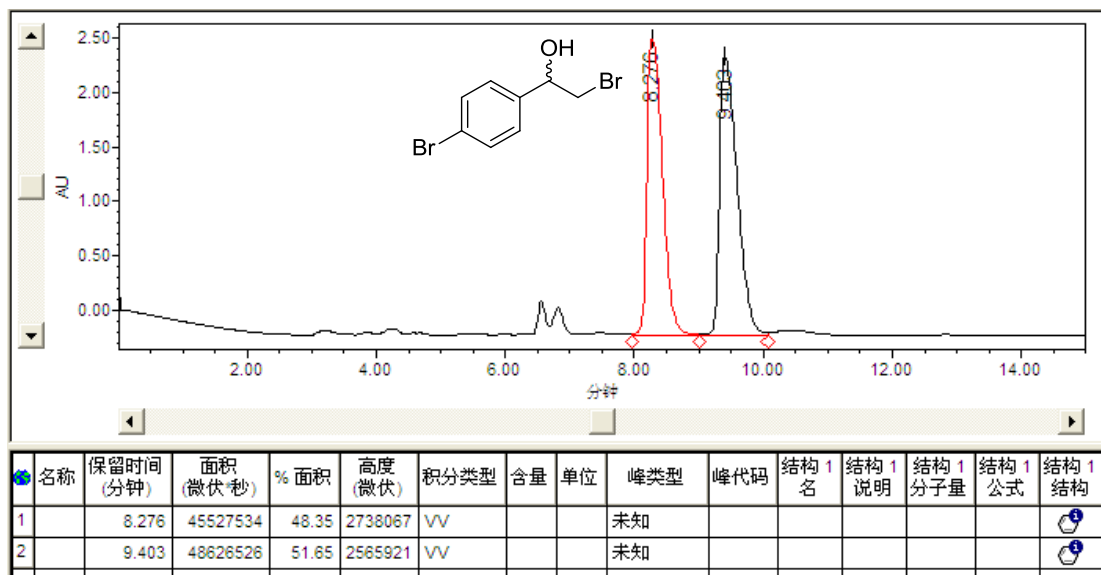


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2	26060496	50.28	1915310	46.49

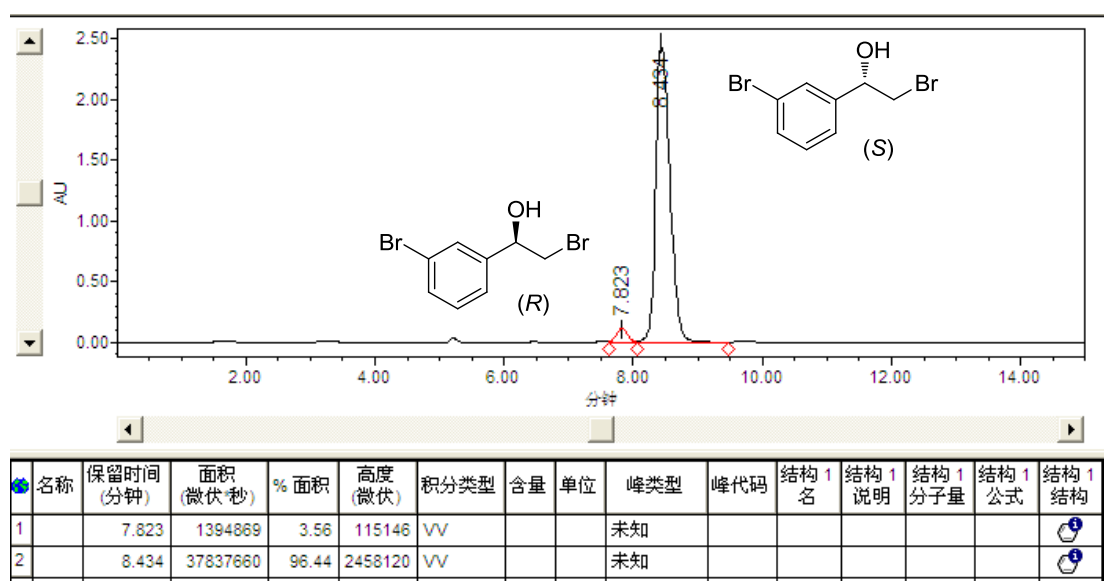
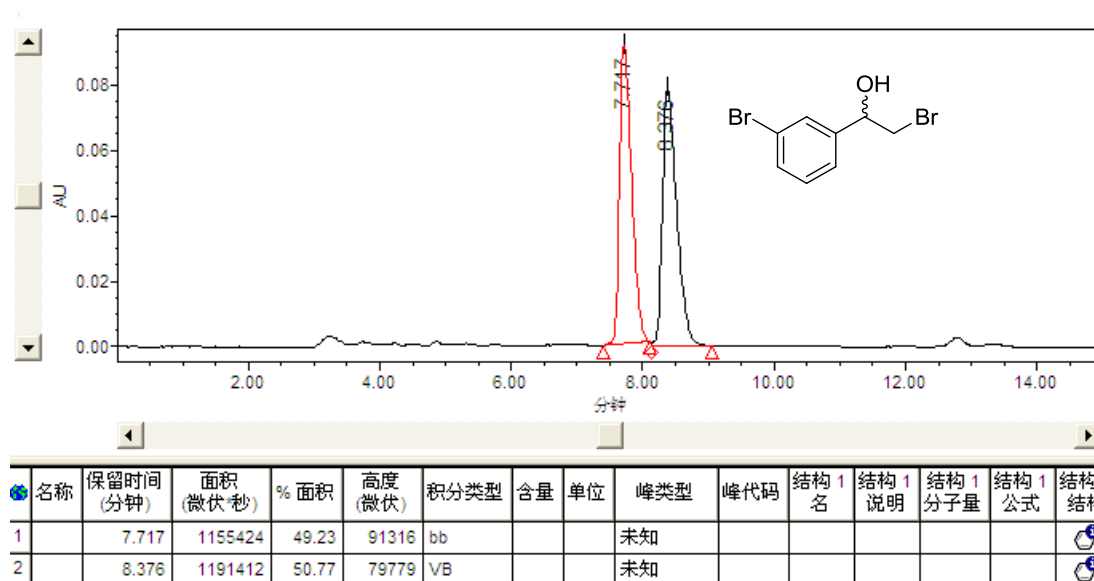


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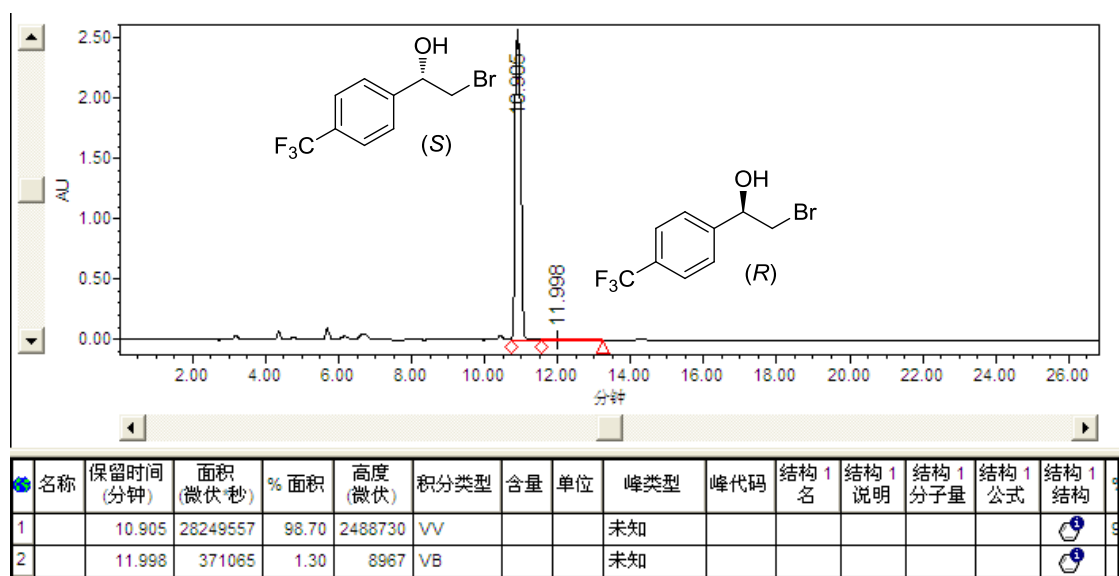
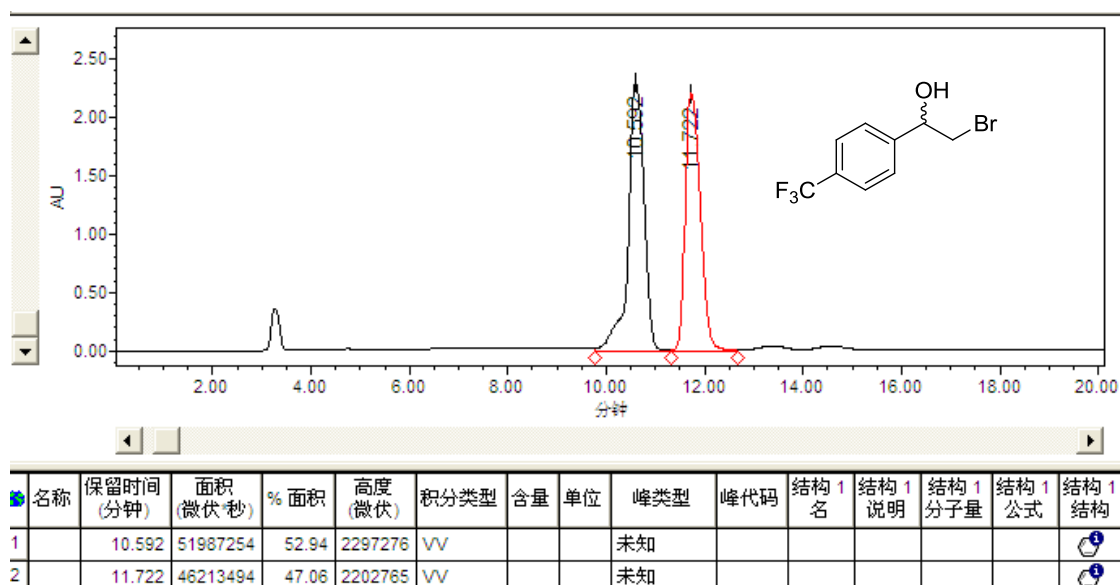
(S)-2-bromo-1-(4-bromophenyl)ethanol (6e): (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1 mL/min, 25 °C).



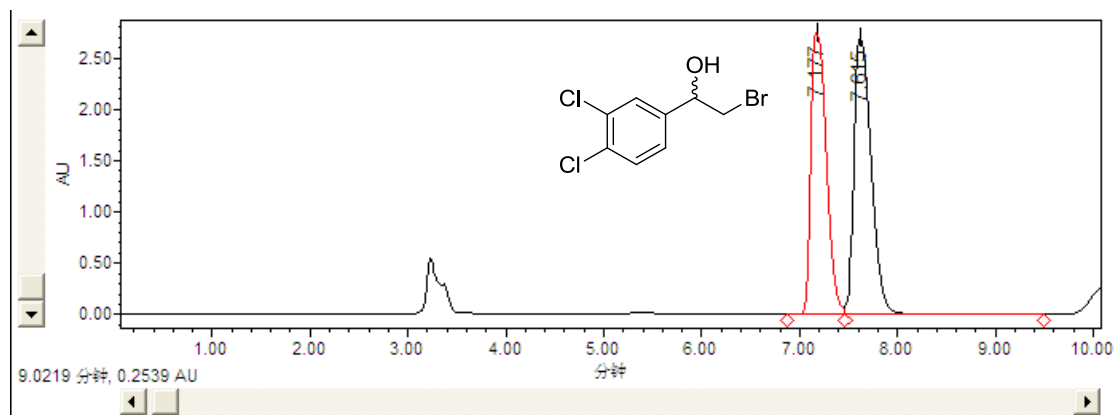
(S)-2-bromo-1-(3-bromophenyl)ethanol (6f): (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1 mL/min, 25 °C).



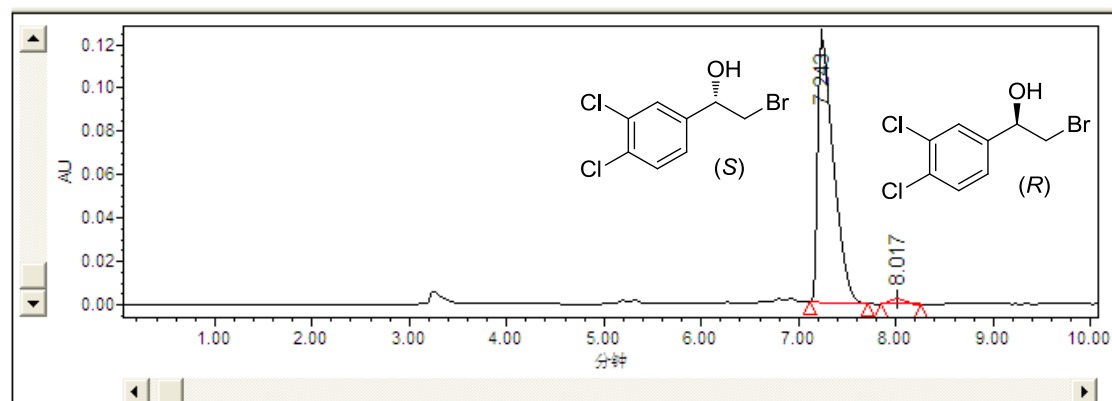
(S)-2-bromo-1-(4-(trifluoromethyl)phenyl)ethanol (6g): (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1 mL/min, 25 °C).



(S)-2-bromo-1-(3,4-dichlorophenyl)ethanol (6h): (HPLC: Chiracel OB-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1 mL/min, 25 °C).

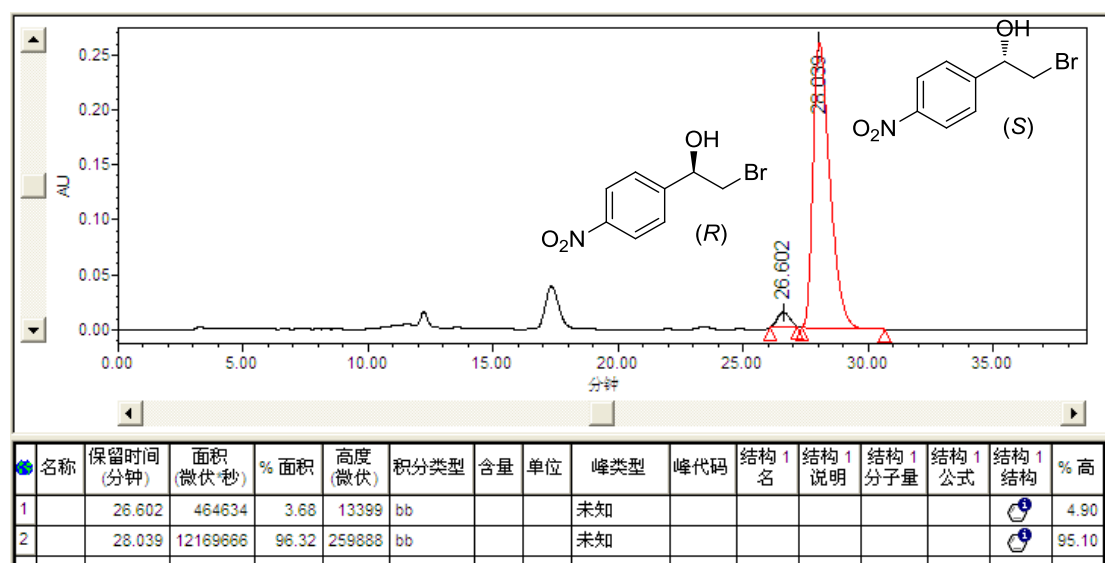
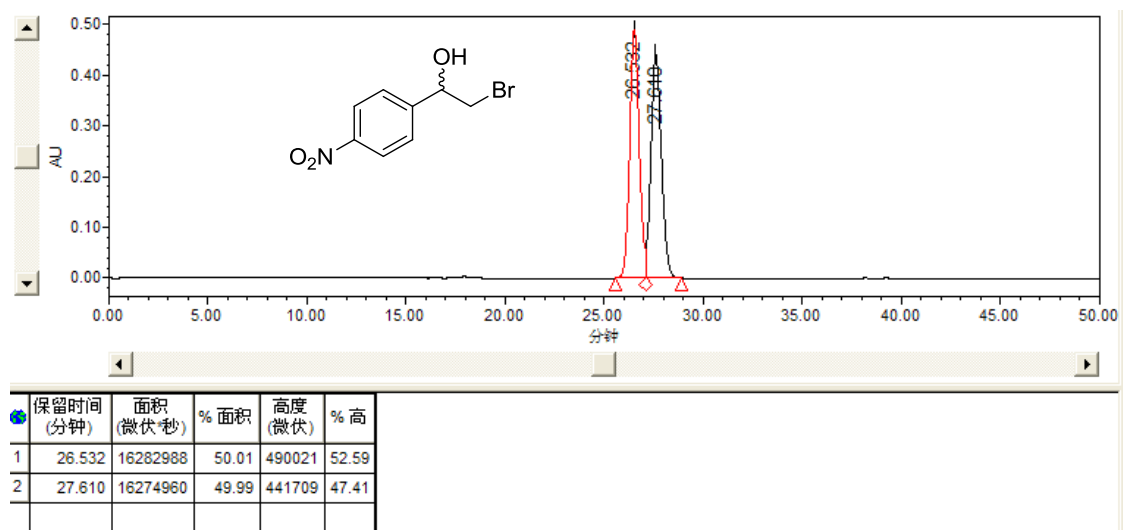


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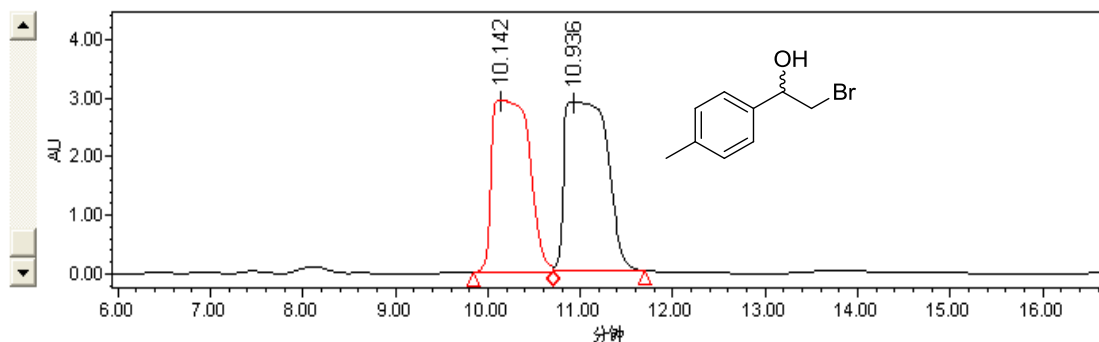


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2	8.017	26488	1.86	2429	bb			未知						

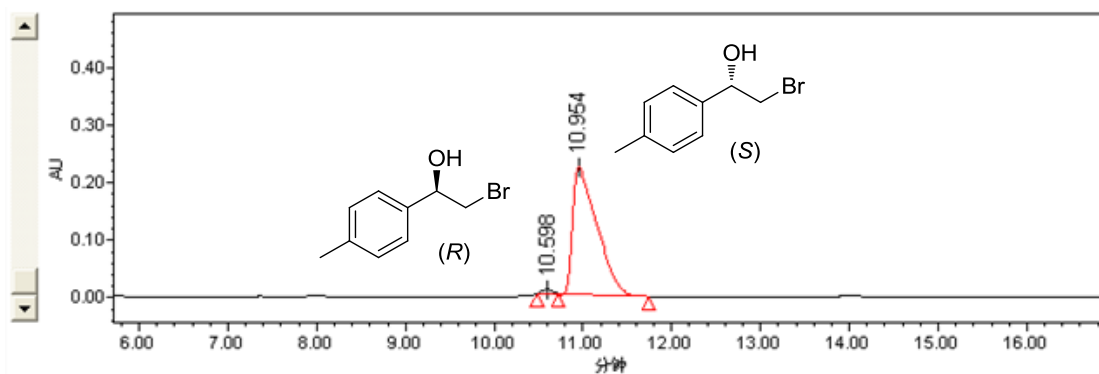
(S)-2-bromo-1-(4-nitrophenyl)ethanol (6i): (HPLC: Chiralcel OJ-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1 mL/min, 25 °C).



(S)-2-bromo-1-(p-tolyl)ethanol (6j): (HPLC: Chiralcel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1 mL/min, 25 °C).

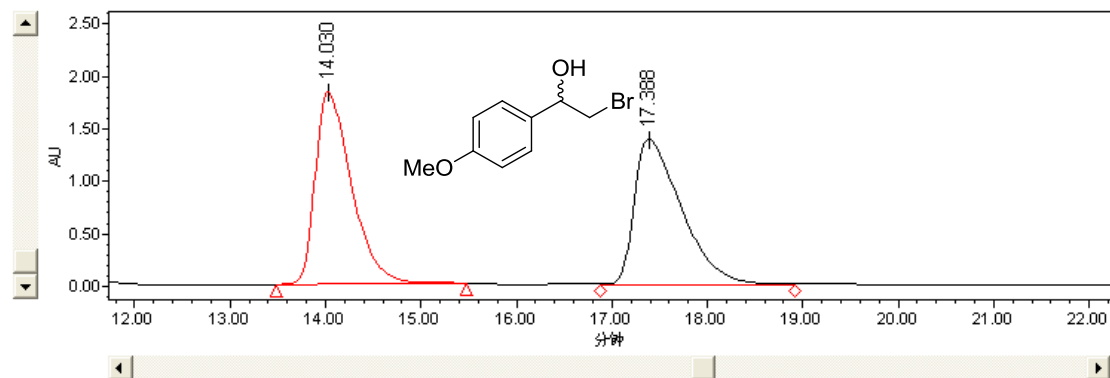


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2	10.936	92717409	52.62	2889987	Vb			未知						

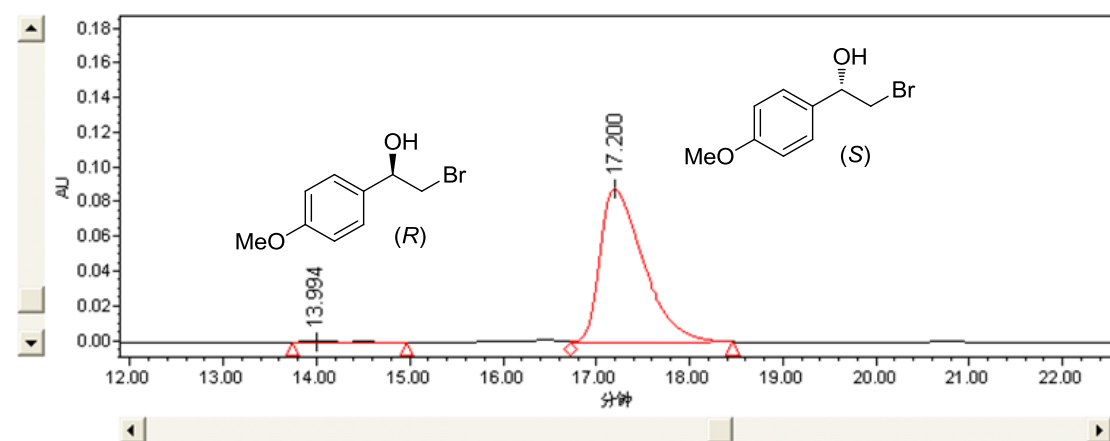


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1	10.598	57053	1.34	6806	bb			未知						
2	10.954	4208183	98.66	223301	bb			未知						

(S)-2-bromo-1-(4-methoxyphenyl)ethanol (6k): (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1 mL/min, 25 °C).

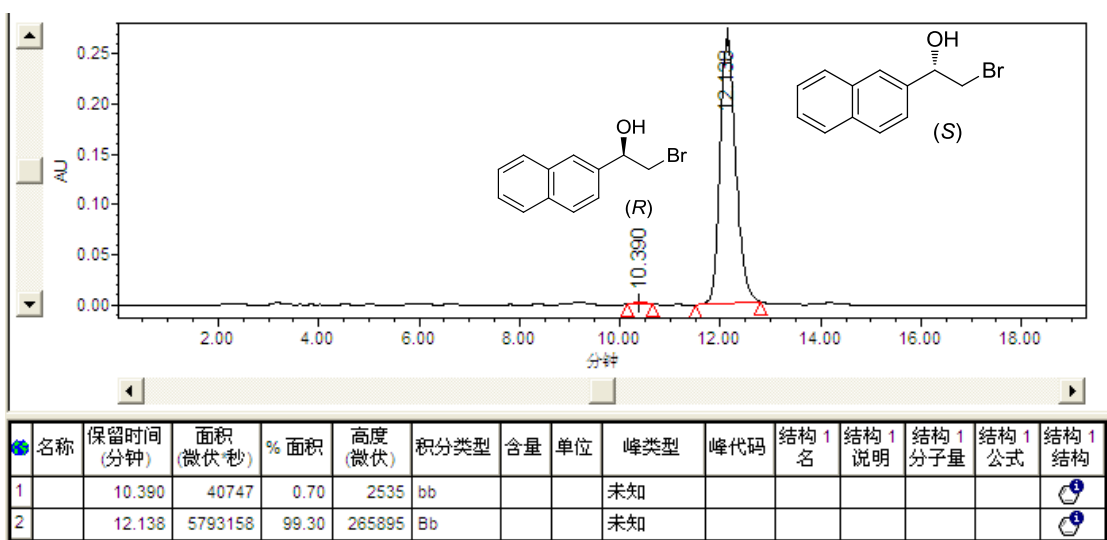
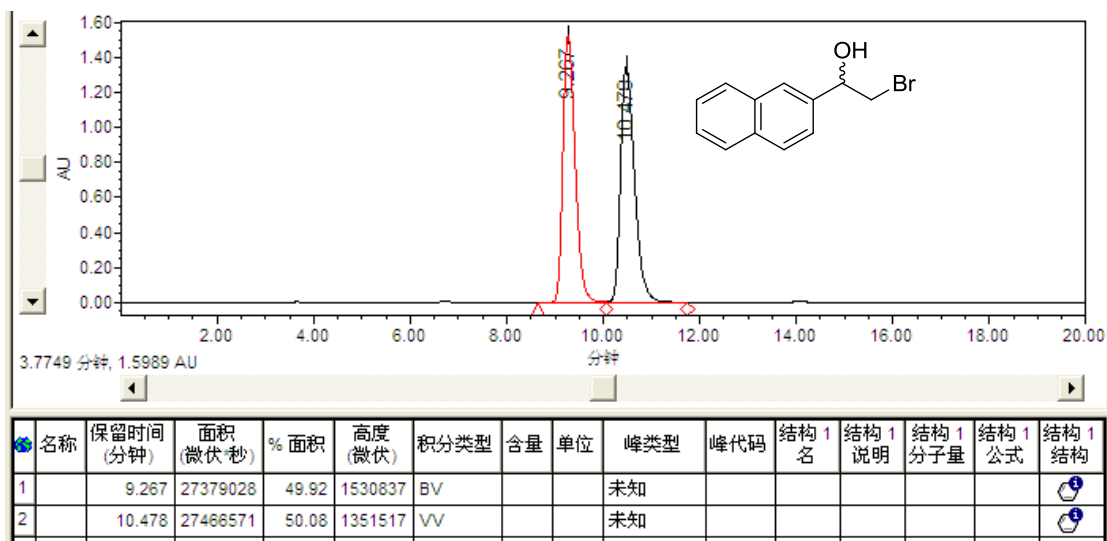


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2	17.388	48226683	49.92	1386227	VV			未知						

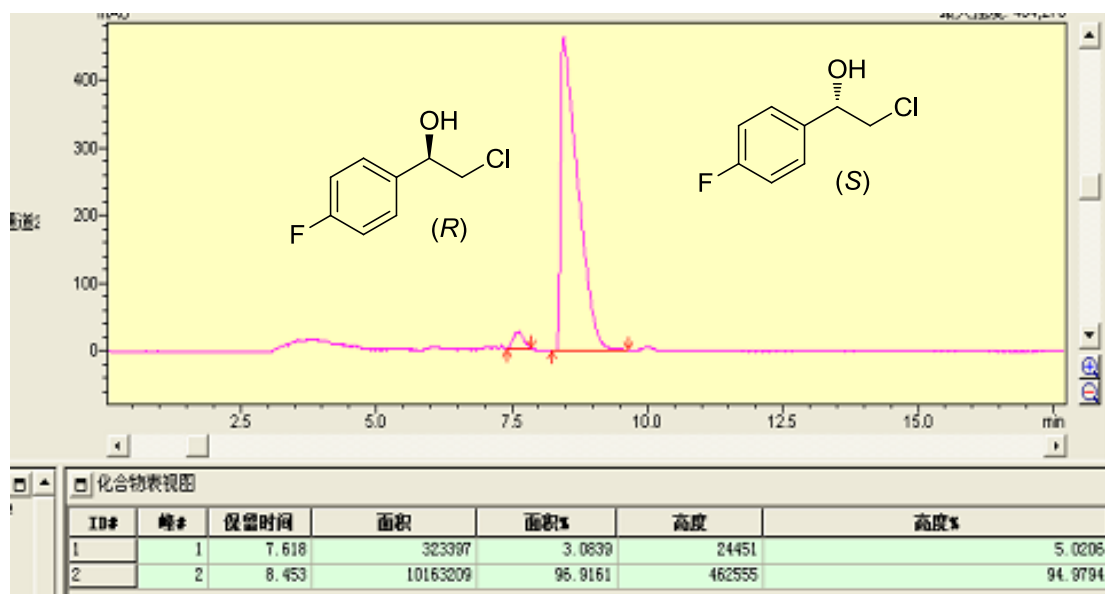
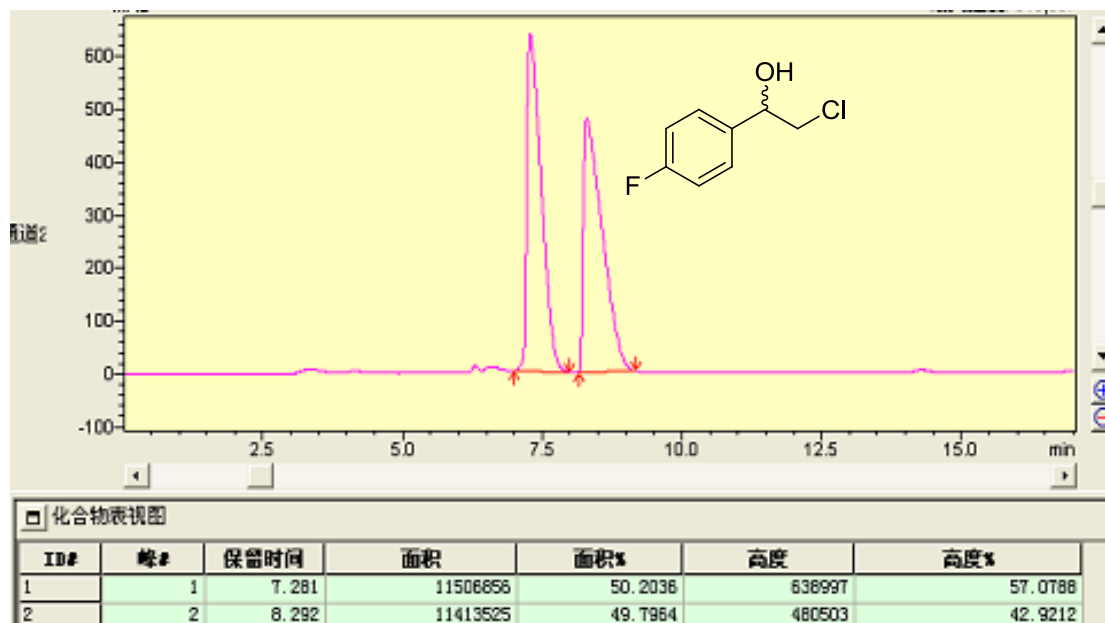


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1	13.994	21226	0.74	601	BB			未知						
2	17.200	2830286	99.26	88502	VB			未知						

(S)-2-bromo-1-(naphthalen-2-yl)ethanol (6l): (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1 mL/min, 25 °C).



(S)-2-chloro-1-(4-fluorophenyl)ethanol (6m): (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1 mL/min, 25 °C).



(S)-2-chloro-1-(4-chlorophenyl)ethanol (6n): (HPLC: Chiracel OB-H, detected at 215 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1 mL/min, 25 °C).

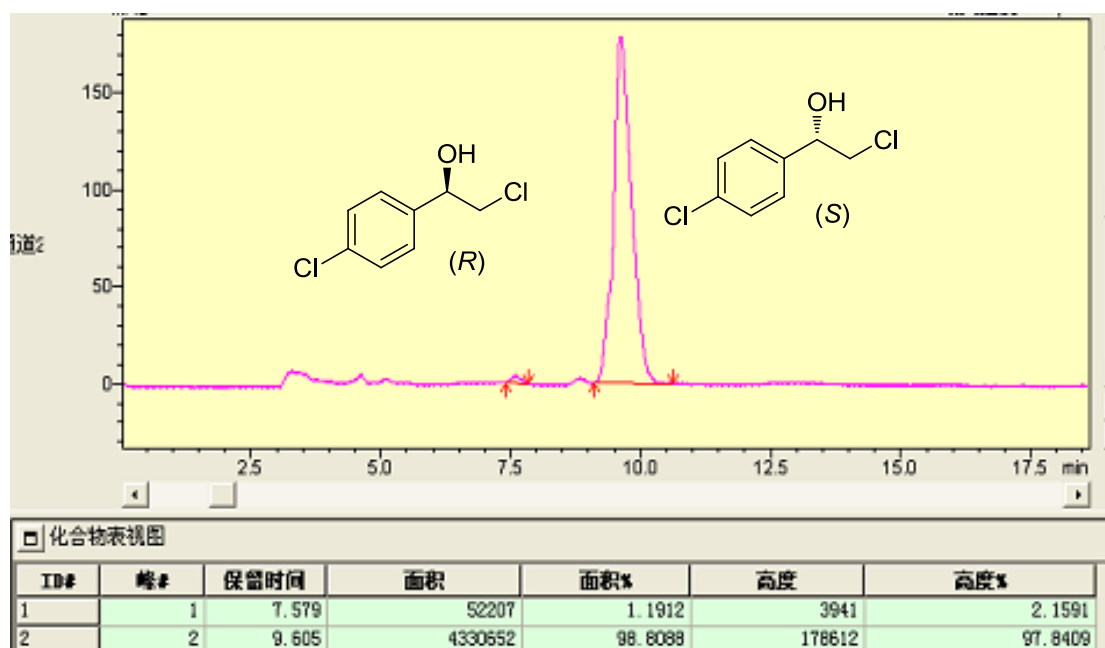
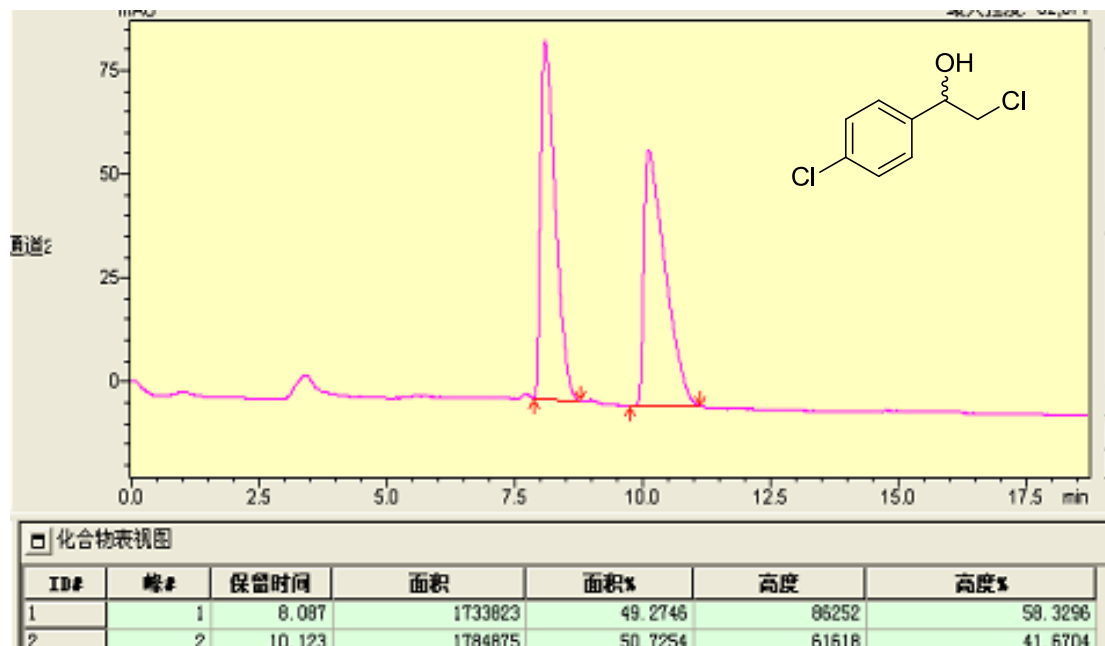
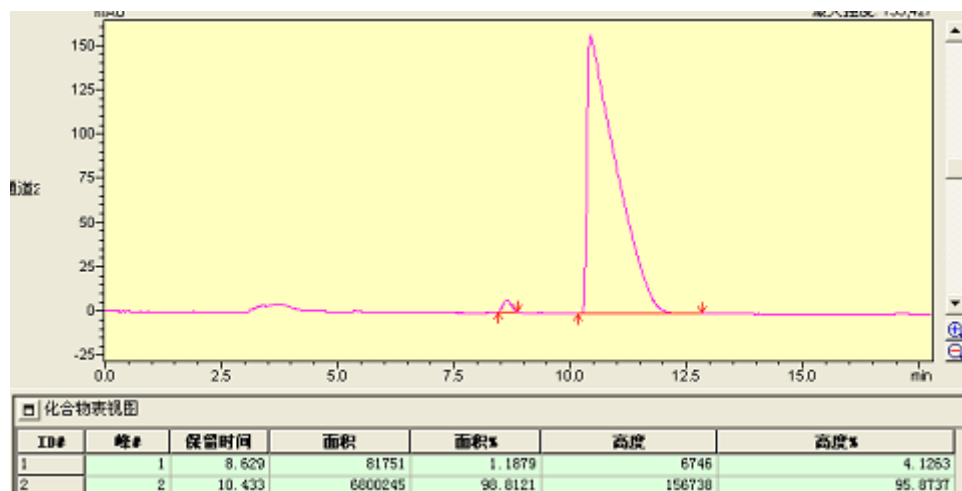
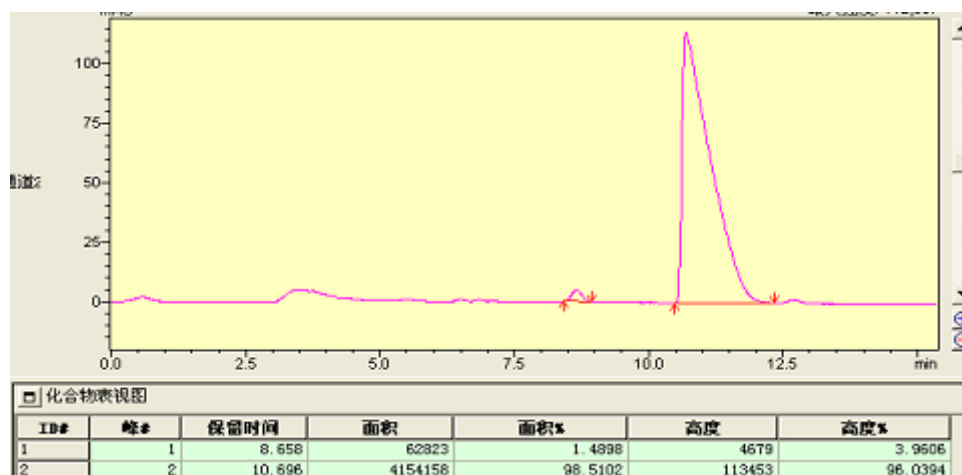


Figure S3. Reusability of the catalyst **5** using 2-bromo-1-phenylethanone as a substrate.

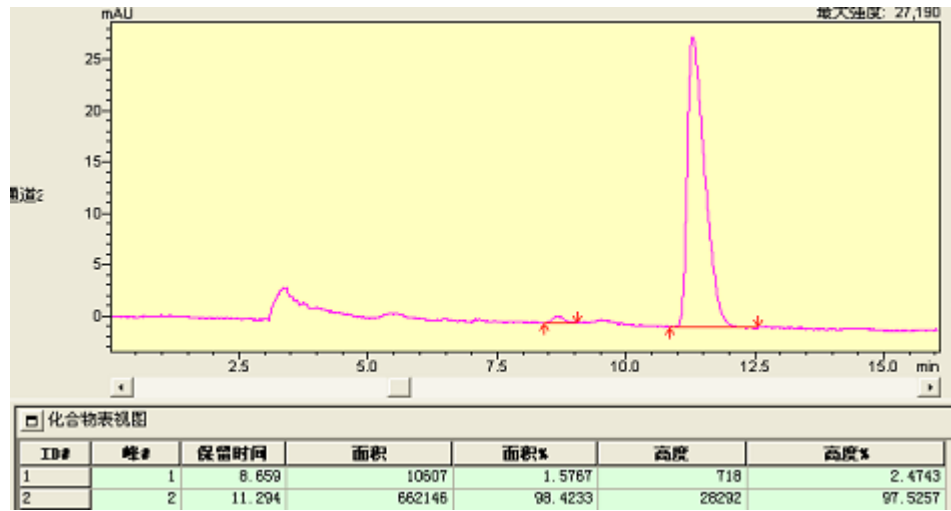
Recycle 2.



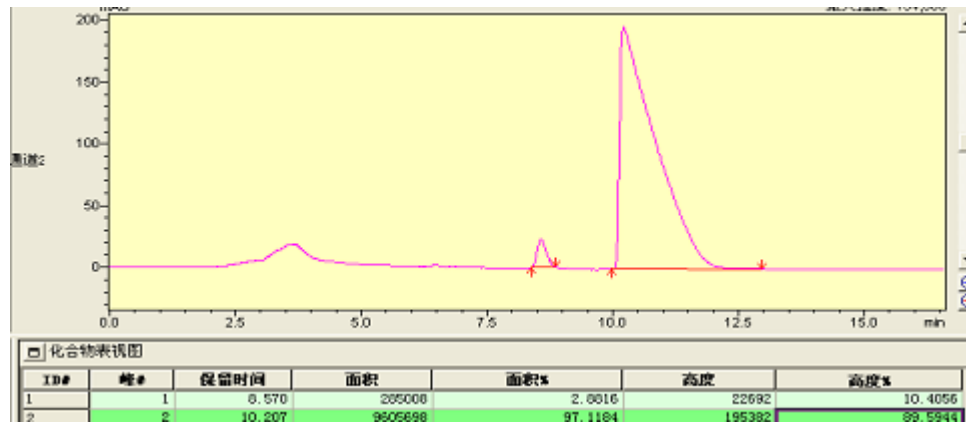
Recycle 3.



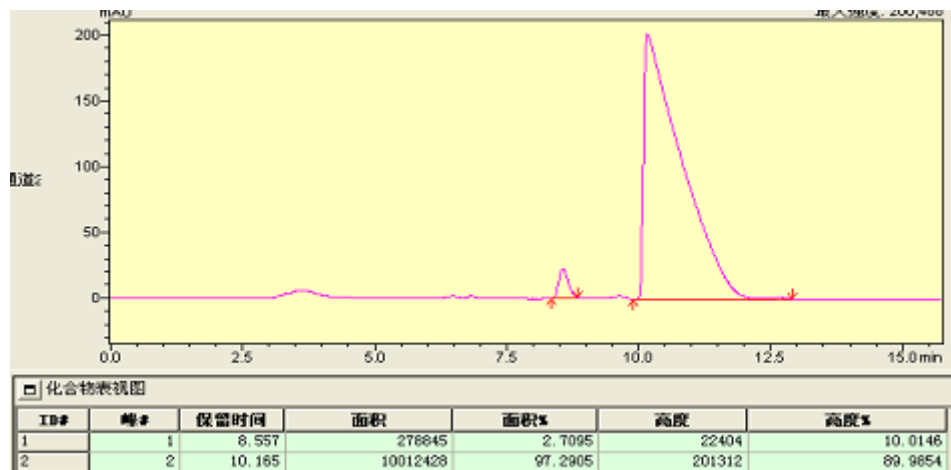
Recycle 4.



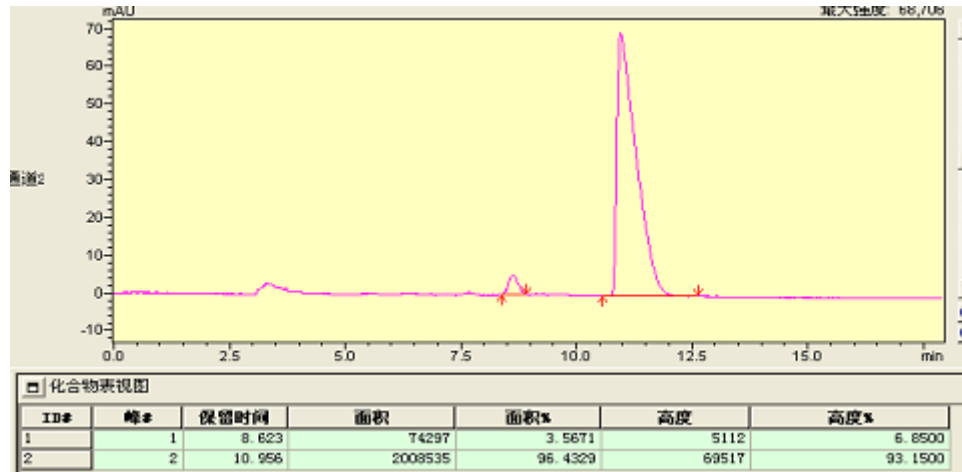
Recycle 5.



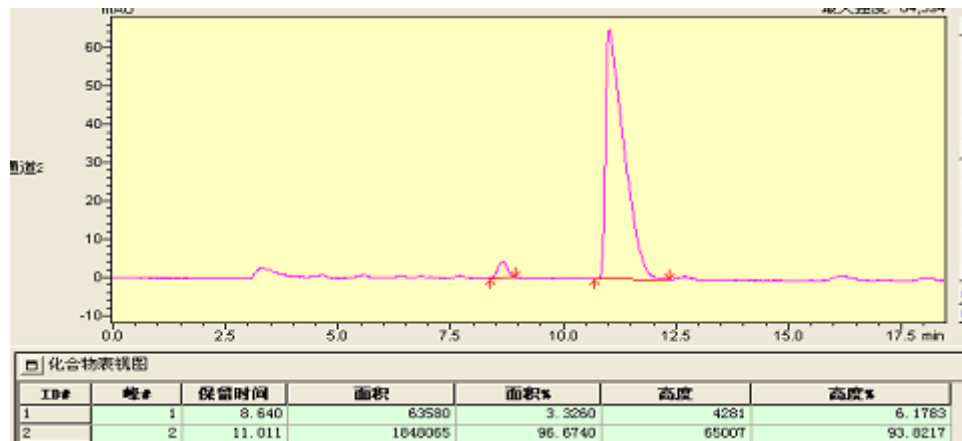
Recycle 6.



Recycle 7.



Recycle 8.



Recycle 9.

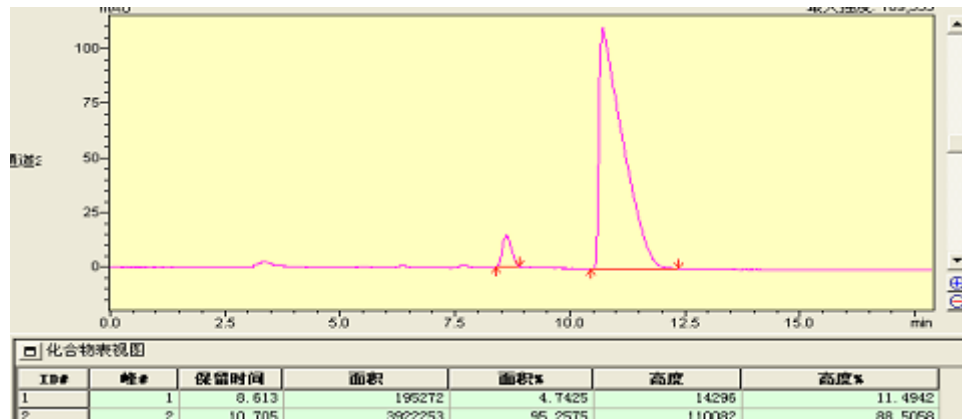


Figure S4. Asymmetric transfer hydrogenation of benzil catalyzed by catalyst **5**, PMO-supported analogue and SBA-supported analogue. Reactions were carried out at 40 °C, using 10.0 μmol of the catalyst, 5 equiv HCOONa, and at an S/C ratio of 100 in 5.0 mL of water.

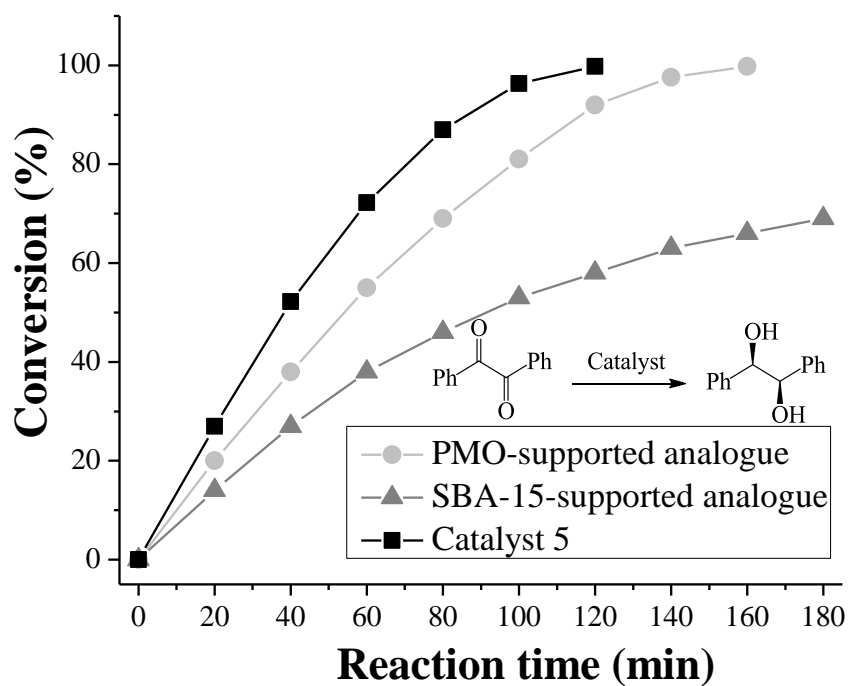
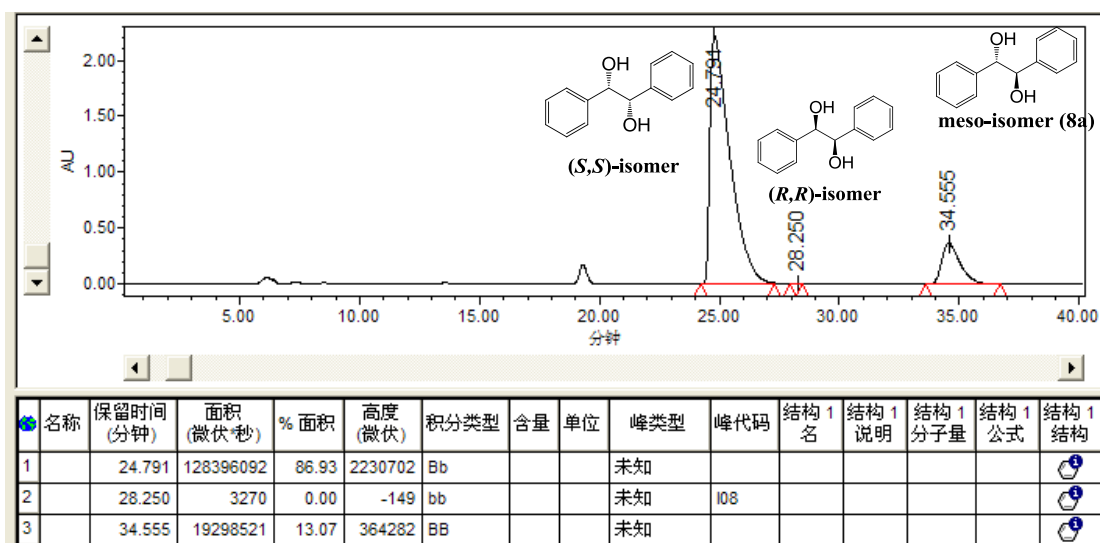
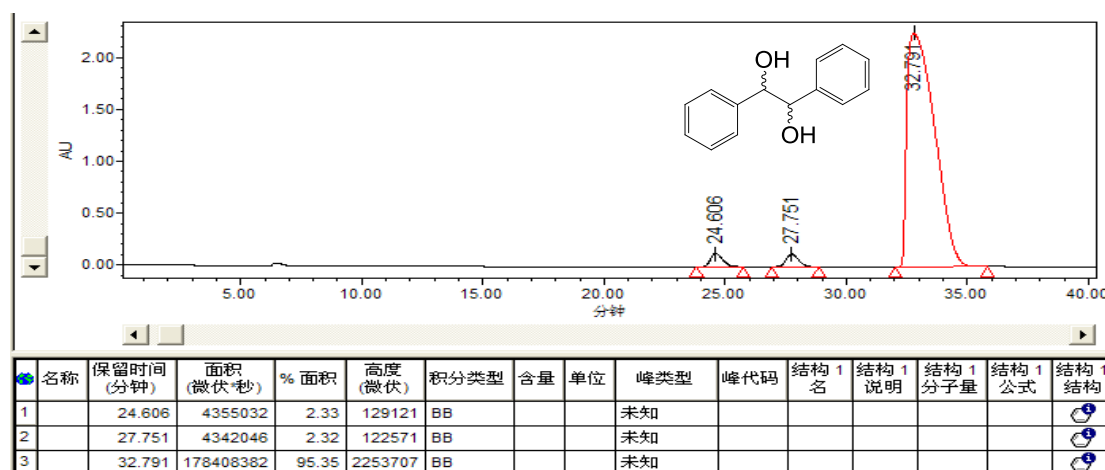


Figure S5. Asymmetric transfer hydrogenation of symmetrical benzils [The products were analyzed by a HPLC with a UV-Vis detector using a Daicel OD-H or OJ-H chiralcel column (Φ 0.46×25 cm)] (Literature: *Chin. J. Chem.* 2012, 30, 2657).

Translation of Chinese to English is as follows:

Peak	RetTime [min]	Area	Area ratio %	Height										
名称	保留时间 (分钟)	面积 (微伏·秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	结构 1 名	结构 1 说明	结构 1 分子量	结构 1 公式	结构 1 结构
1	8.499	18644684	49.95	1331866	VV			未知						
2	9.358	18683896	50.05	1150448	VV			未知						

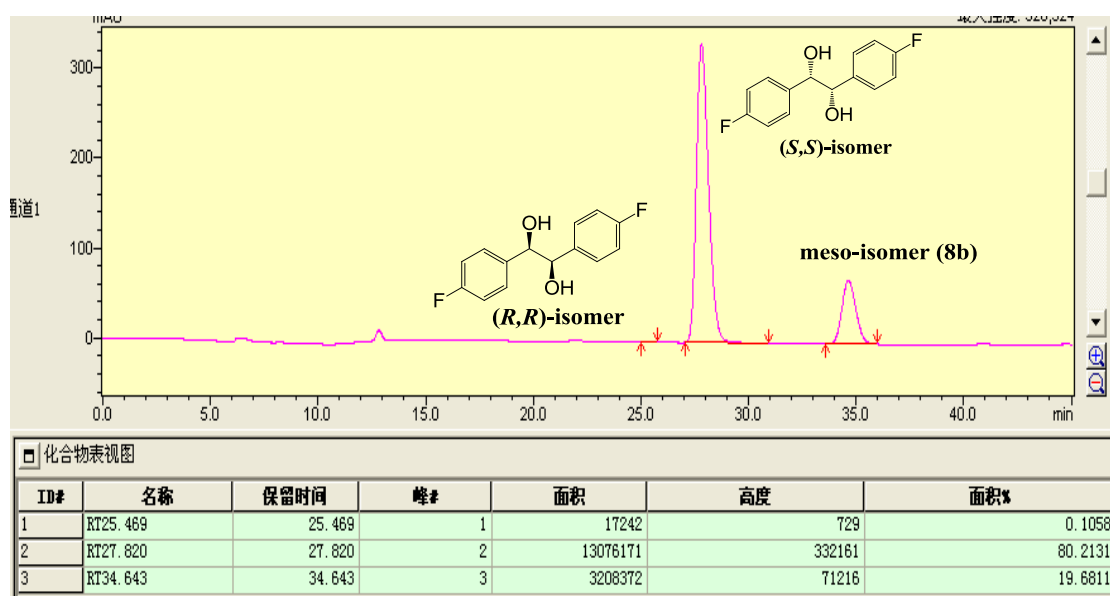
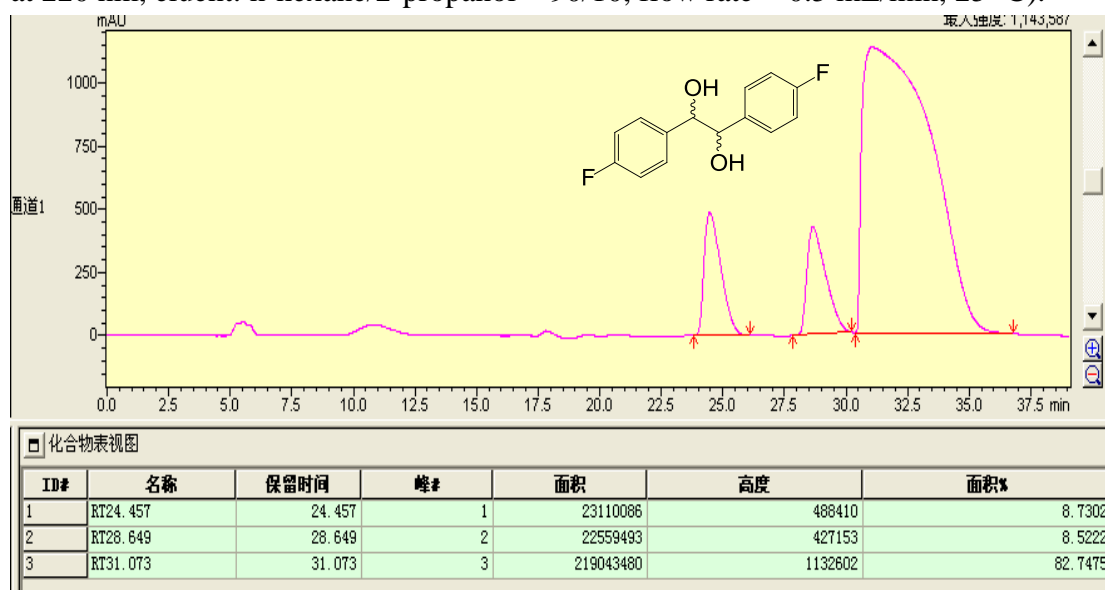
***(S,S)*-1,2-diphenylethane-1,2-diol (6a):** (HPLC: Chiralcel OJ-H, detected at 220 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 0.5 mL/min, 25 °C).



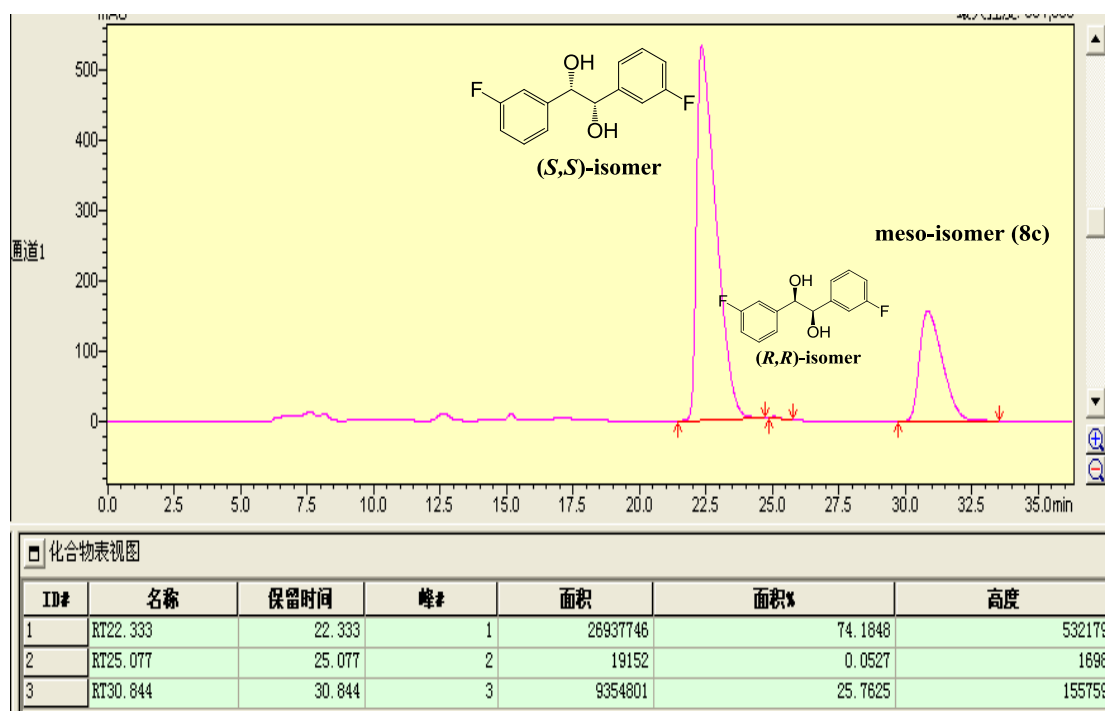
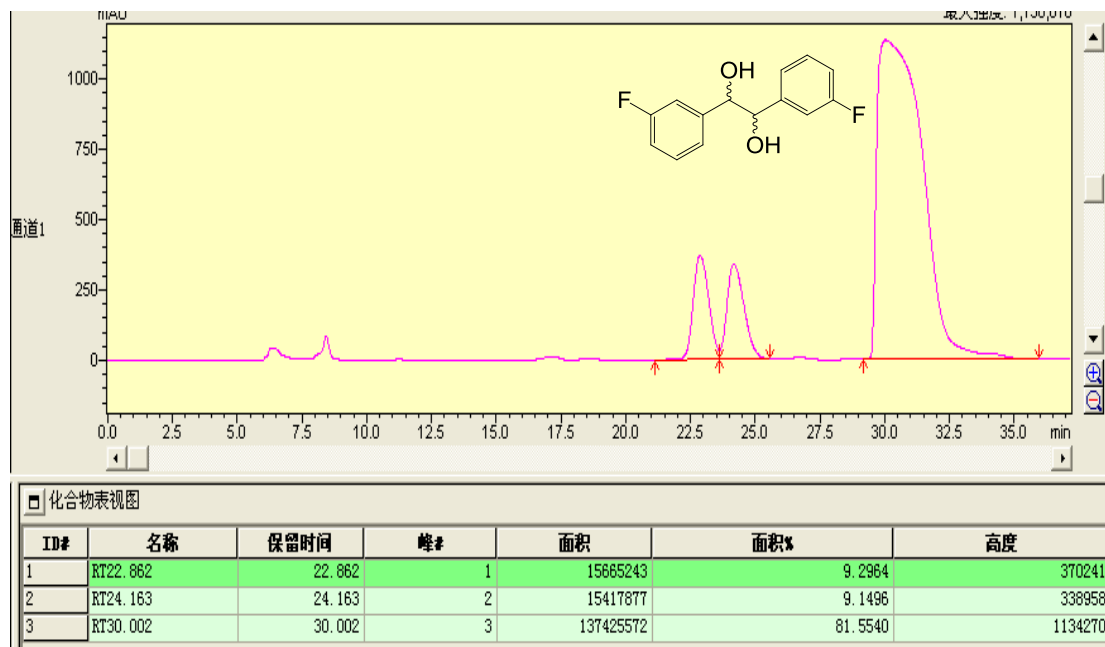
Translation of Chinese to English is as follows:

Peak	RetTime [min]	Area	Area%	Height	Height%
峰号	保留时间	面积	面积%	峰高	峰高%
1	18.474	235619.9	92.0500	13827.2	79.0665
2	19.395	9109.7	3.5589	1042.4	5.9606

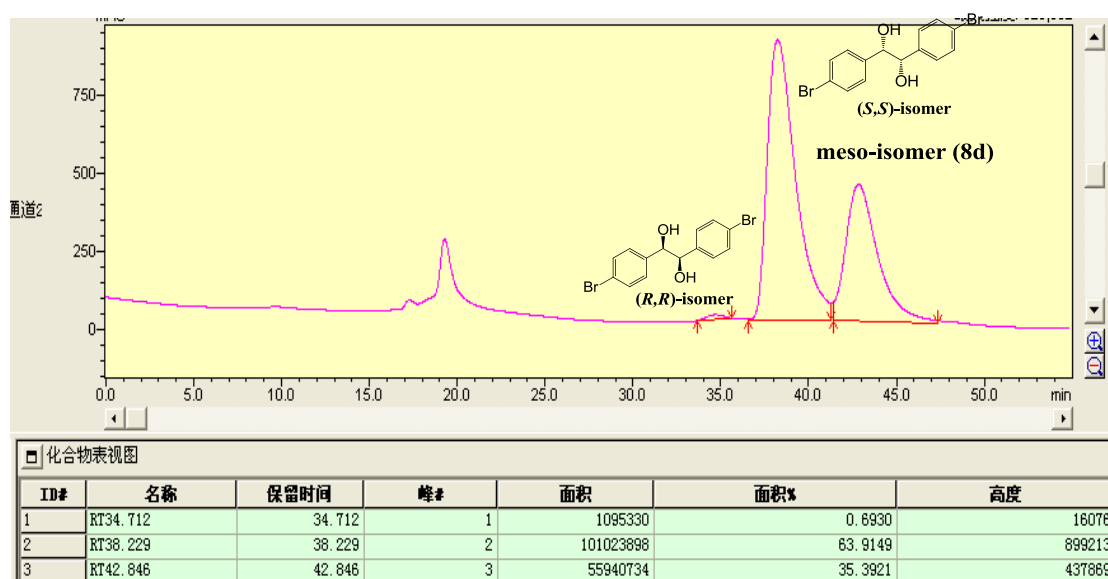
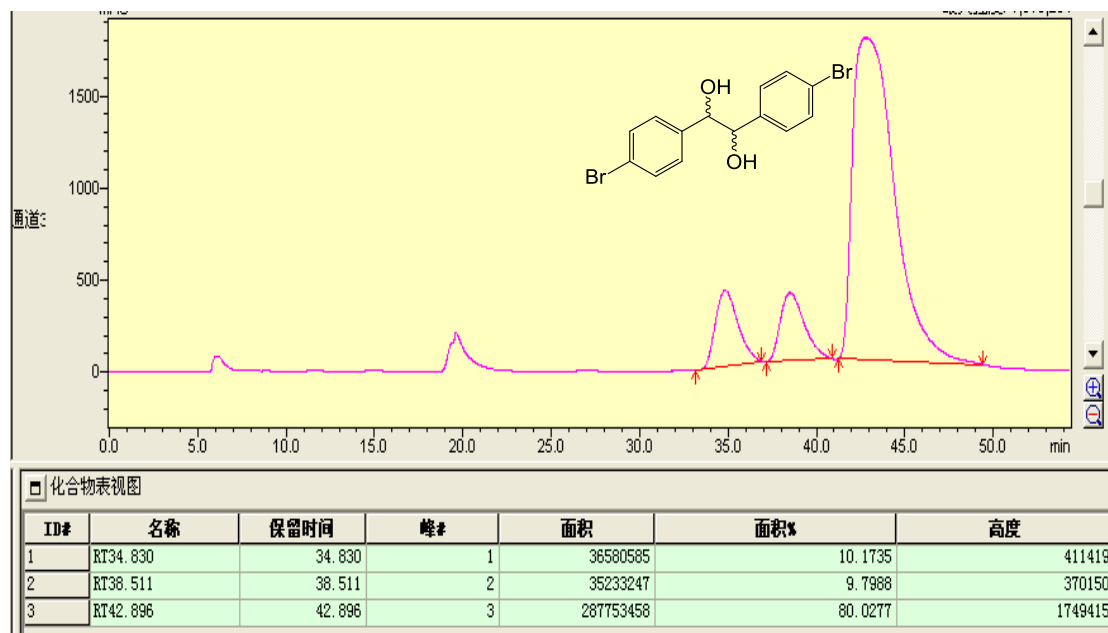
(S,S)-1,2-bis(4-fluorophenyl)ethane-1,2-diol (7b): (HPLC: Chiracel OJ-H, detected at 220 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 0.5 mL/min, 25 °C).



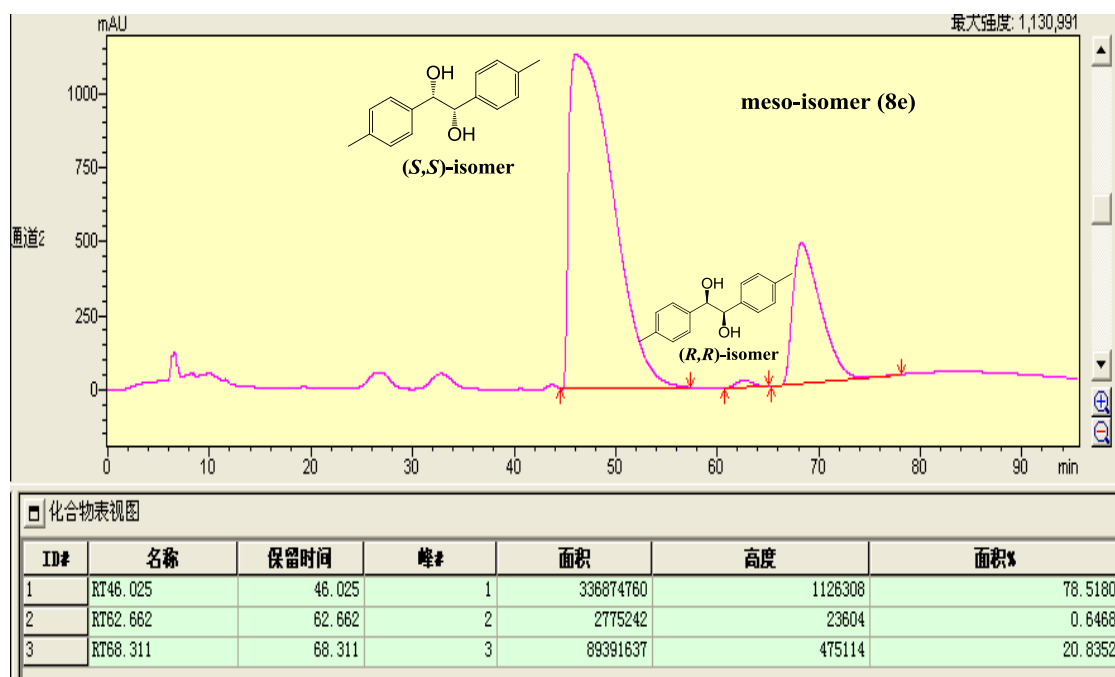
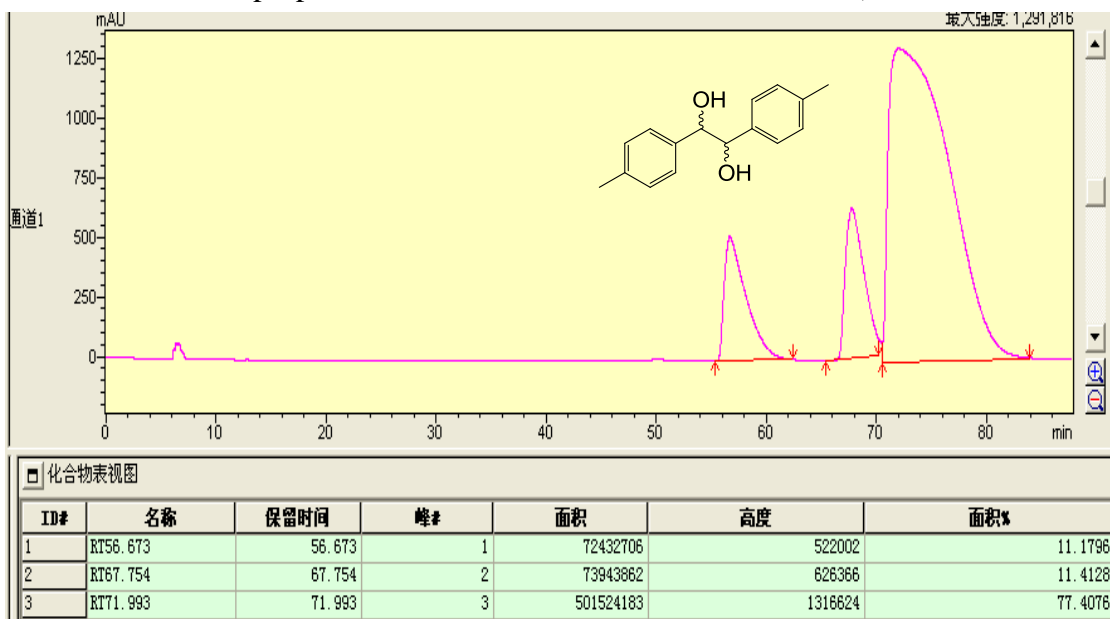
(S,S)-1,2-bis(3-fluorophenyl)ethane-1,2-diol (7c): (HPLC: Chiracel OJ-H, detected at 220 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 0.5 mL/min, 25 °C).



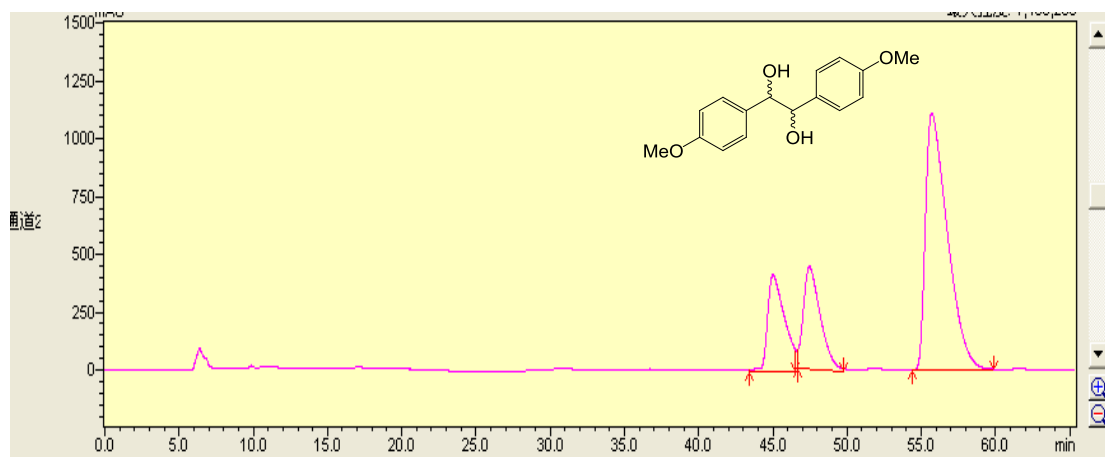
(S,S)-1,2-bis(4-bromophenyl)ethane-1,2-diol (7d): (HPLC: Chiracel AD-H, detected at 220 nm, eluent: n-hexane/2-propanol = 92/8, flow rate = 0.5 mL/min, 25 °C).



(S,S)-1,2-di-p-tolyethane-1,2-diol (7e): (HPLC: Chiralcel OJ-H, detected at 220 nm, eluent: n-hexane/2-propanol = 96/4, flow rate = 0.5 mL/min, 25 °C).

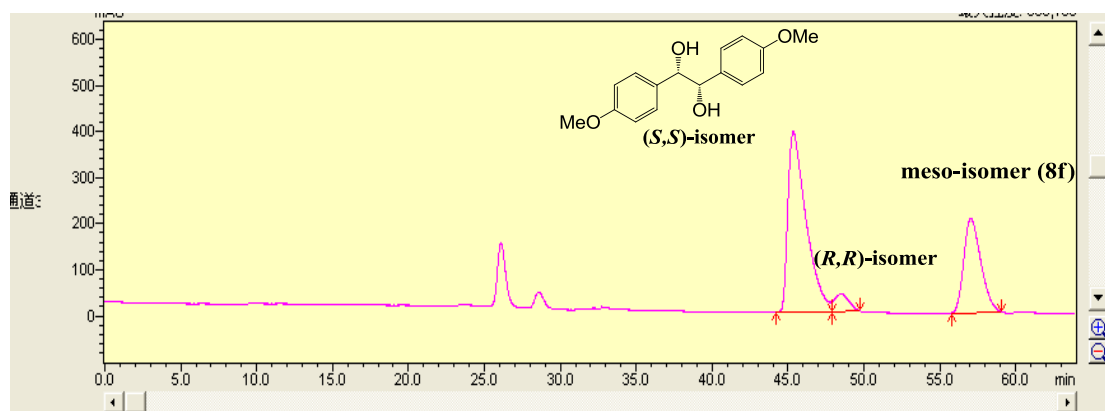


(S,S)-1,2-bis(4-methoxyphenyl)ethane-1,2-diol (7f): (HPLC: Chiracel OJ-H, detected at 220 nm, eluent: n-hexane/2-propanol = 80/20, flow rate = 0.5 mL/min, 25 °C).



化合物表视图

ID#	名称	保留时间	峰#	面积	面积%	高度
1	RT45.004	45.004	1	33382014	18.2583	419170
2	RT47.465	47.465	2	35335351	19.3267	442701
3	RT55.717	55.717	3	114114211	62.4149	1112095



化合物表视图

ID#	名称	保留时间	峰#	面积	面积%	高度
1	RT45.346	45.346	1	32967794	64.1862	392279
2	RT48.517	48.517	2	2537718	4.9408	39795
3	RT57.046	57.046	3	15857258	30.8731	203465

(S,S)-1,2-bis(3-methoxyphenyl)ethane-1,2-diol (7g): (HPLC: Chiracel AS-H, detected at 220 nm, eluent: n-hexane/2-propanol = 93/7, flow rate = 1 mL/min, 25 °C).

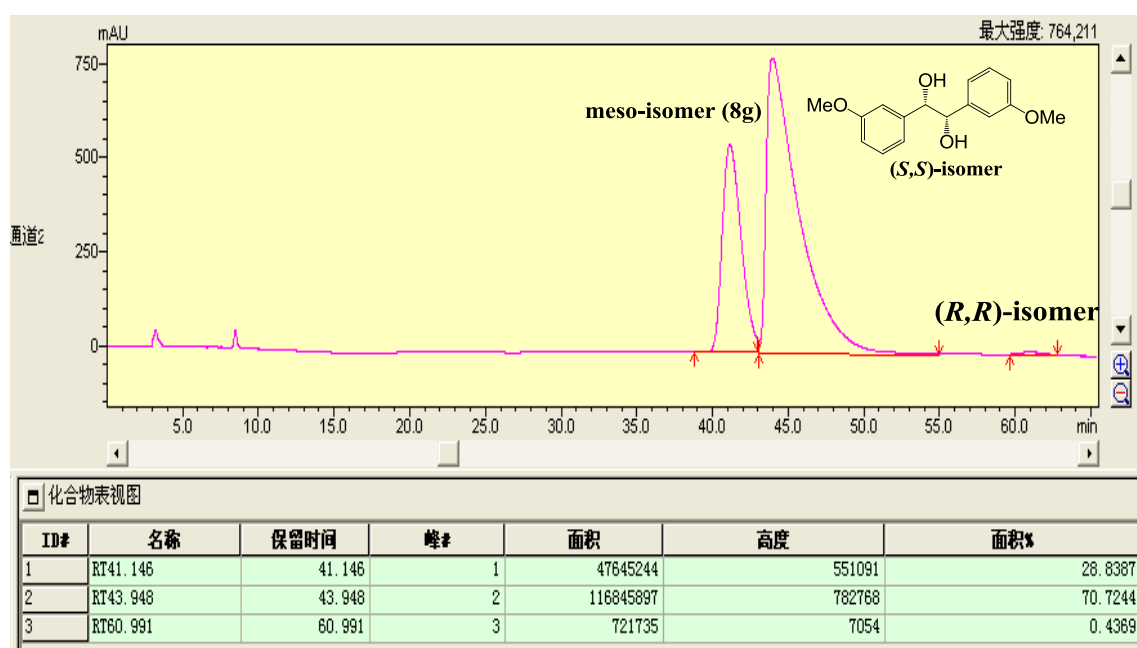
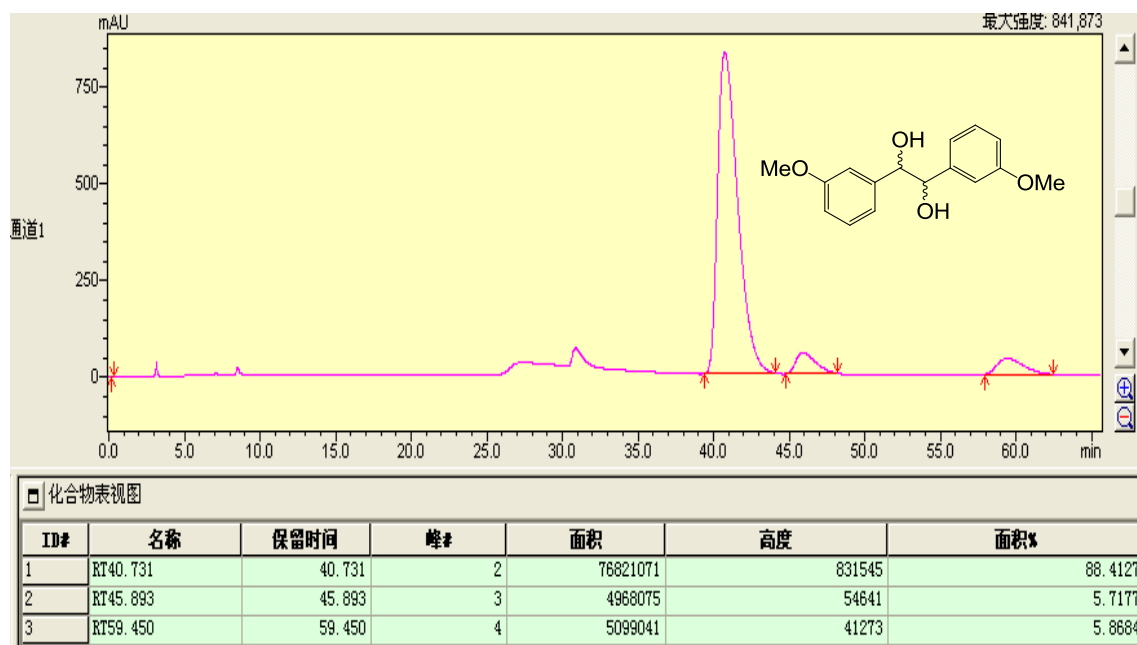


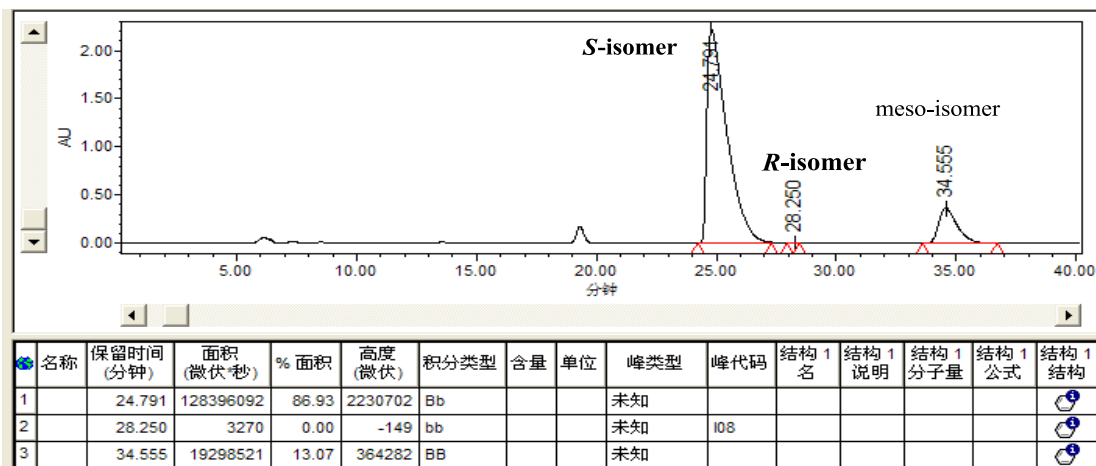
Table S1. Reusability of catalyst **5** for transfer hydrogenation of benzil.^[a]

Run time	1	2	3	4	5	6	7	8
% Yield ^[b]	99	99	99	97	99	97	99	89
<i>dl/meso</i>	87/13	87/13	66/34	64/36	57/43	56/44	56/44	56/44
% <i>ee</i> ^[b]	99	99	99	99	99	99	99	99

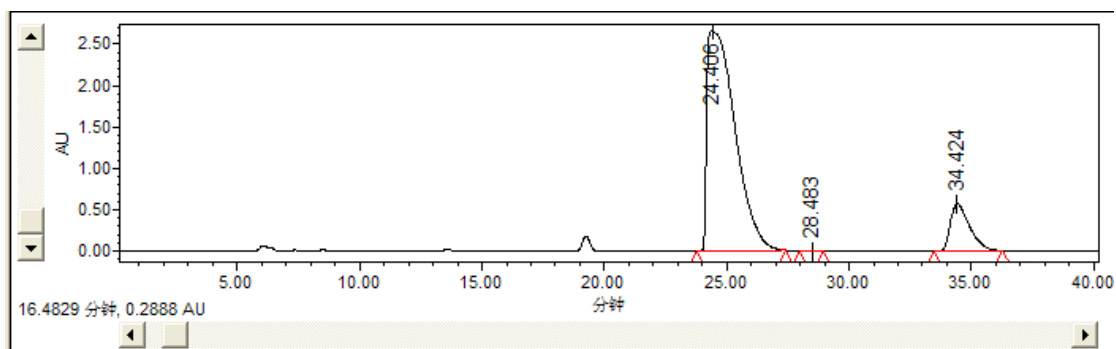
[a] Reaction conditions: catalyst **5** (215.0 mg, 20.0 μmol of Rh based on the ICP analysis), HCO_2Na (10.0 mmol), 2-bromo-phenylethanone (2.0 mmol) and 10.0 mL water, reaction temperature (40 $^\circ\text{C}$), reaction time (2.0 h). [b] Yields were determined by $^1\text{H-NMR}$ and *ee* values were determined by chiral HPLC analysis.

Figure S6. Reusability of catalyst **5** for asymmetric transfer hydrogenation of benzil. [(HPLC: Chiracel OJ-H, detected at 220 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 0.5 mL/min, 25 $^\circ\text{C}$).

Recycle 1.

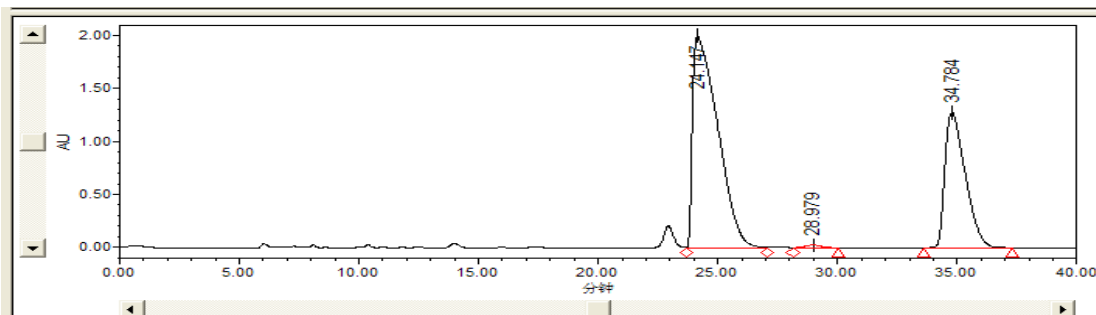


Recycle 2



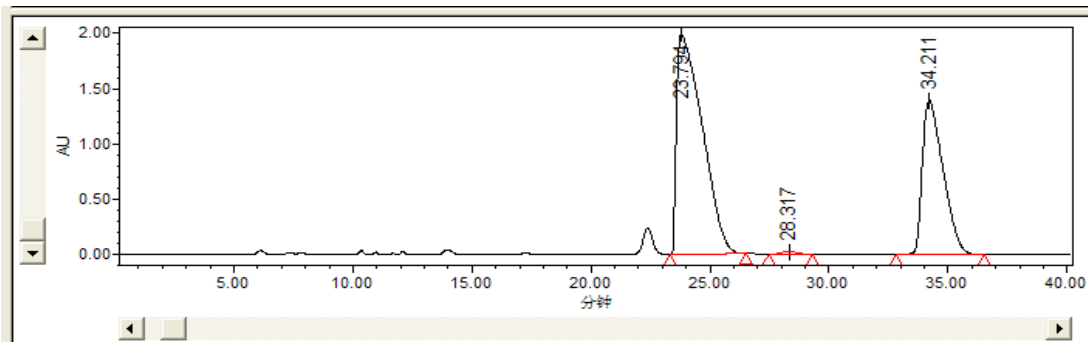
名称	保留时间 (分钟)	面积 (微伏秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	结构 1 名	结构 1 说明	结构 1 分子量	结构 1 公式	结构 1 结构
1	24.406	212319779	87.13	2655656	bb			未知						
2	28.483	27536	0.01	-893	bb			未知	108					
3	34.424	31344392	12.86	574260	bb			未知						

Recycle 3



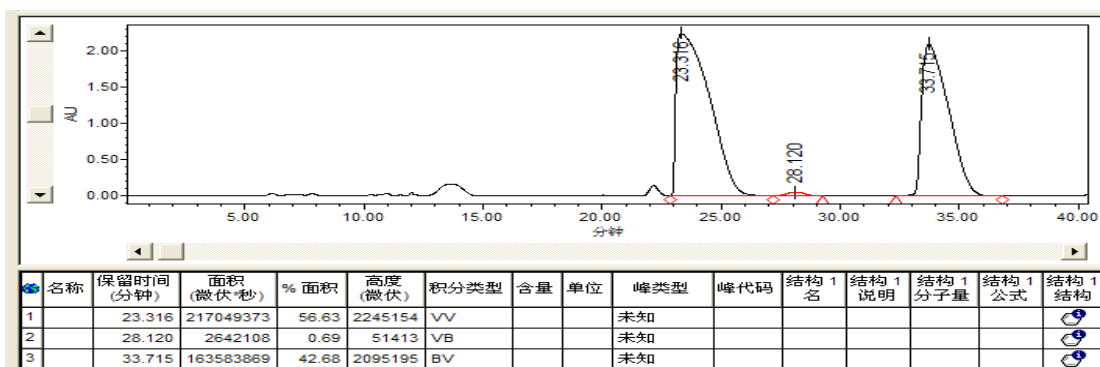
名称	保留时间 (分钟)	面积 (微伏秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	结构 1 名	结构 1 说明	结构 1 分子量	结构 1 公式	结构 1 结构
1	24.147	146567121	65.68	1996941	VV			未知						
2	28.979	1132633	0.51	25450	VB			未知						
3	34.784	75449406	33.81	1279952	BB			未知						

Recycle 4

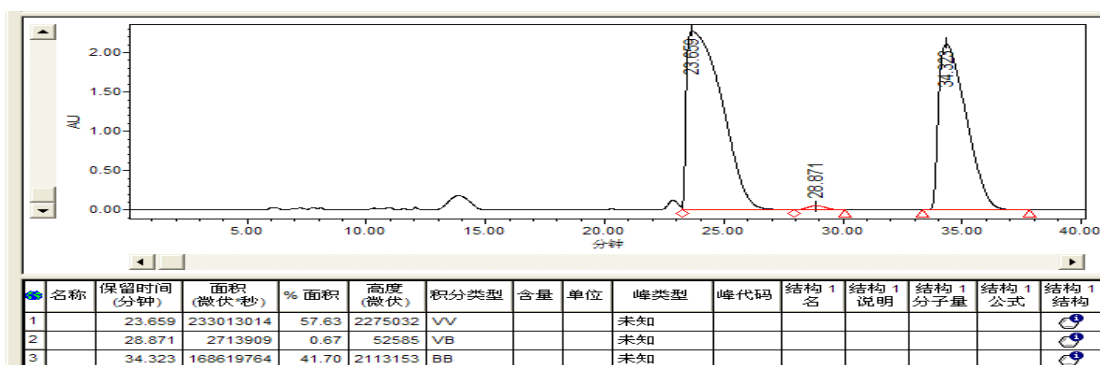


名称	保留时间 (分钟)	面积 (微伏秒)	% 面积	高度 (微伏)	积分类型	含量	单位	峰类型	峰代码	结构 1 名	结构 1 说明	结构 1 分子量	结构 1 公式	结构 1 结构
1	23.794	148819972	63.54	1988376	BB			未知						
2	28.317	1165689	0.50	25548	BB			未知						
3	34.211	84221410	35.96	1394400	BB			未知						

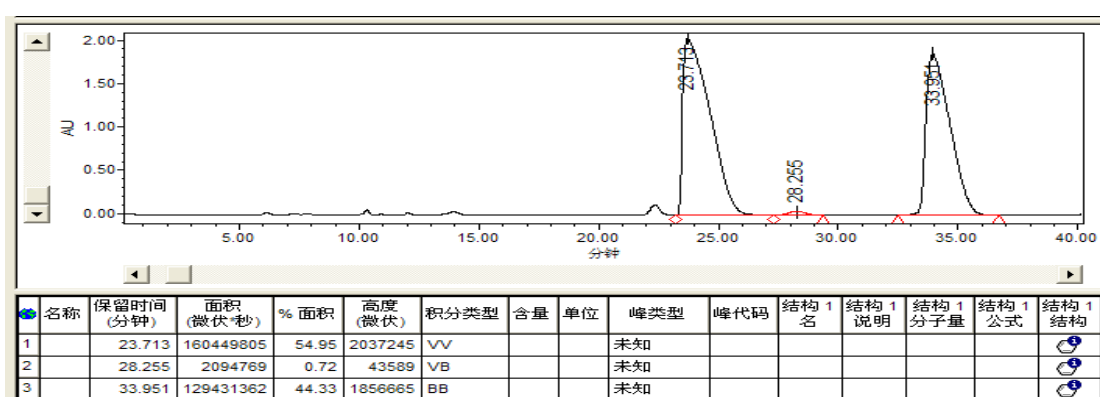
Recycle 5



Recycle 6



Recycle 7



Recycle 8

