Supporting Information for

Recoverable Organorhodium-functionalized Polyhedral Oligomeric Silsesquioxane: A Bifunctional Heterogeneous Catalyst for Asymmetric Transfer Hydrogenation of Aromatic Ketones in Aqueous Medium

Shuang Tang, Ronghua Jin, Huaisheng Zhang, Hui Yao, Jinglan Zhuang,
Guohua Liu* and Hexing Li*

Key Laboratory of Resource Chemistry of Ministry of Education, Shanghai Key Laboratory of Rare Earth Functional Materials, Shanghai Normal University, Shanghai 200234, P. R. China

Experimental

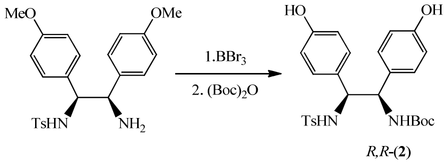
1. General

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 [(*R,R*)-DPEN] and [Cp*$RhCl_2$]$_2$ were purchased from Sigma-Aldrich Company Ltd. Compound (*R,R*)-4-(methylphenylsulfonyl)-1,2-bis(4-methoxyphenyl)enediamine and octa((benzylchloride)ethenyl)silsesquioxane POSS-(**1**) was synthesized according to the reported literature. The products of the ATH were analyzed by a GC using a Supelco β-Dex 120 chiral column (30 m×0.25 mm(i.d.), 0.25 μm film) or a HPLC with a UV-Vis detector using a Daicel OJ-H chiralcel columns (Φ 0.46 x 25 cm).

2. Characterization

Rh loading amount in the catalyst was analyzed using an inductively coupled plasma optical emission spectrometer (ICP, Varian VISTA-MPX). Fourier transform infrared (FTIR) spectra were collected on a Nicolet Magna 550 spectrometer using KBr method. X-ray powder diffraction (XRD) was carried out on a Rigaku D/Max-RB diffractometer with Cu*K*α radiation. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-6380LV microscope operating at 20 kV. X-ray photoelectron spectroscopy (XPS) measurements were performed on a Perkin-Elmer PHI 5000C ESCA system. All the binding energies were calibrated by using the contaminant carbon (C_{1s} = 284.6 eV) as a reference. Liquid-state ^{1}H NMR, ^{13}C NMR, and Solid-state ^{29}Si MAS NMR and ^{13}C CP MAS NMR spectra were recorded on a Bruker AV-400 spectrometer. Elemental analysis was performed with a Carlo Erba 1106 Elemental Analyzer.

3. Synthesis of (R,R)-2:



Under argon atmosphere, to a stirred solution of (*1R,2R*)-N-p-toluenesulfonyl-1,2-di(4-methoxyphenyl)ethylenediamine (0.43g, 1.00 mmol) in 10 mL dry CH_2Cl_2 was added dropwise BBr_3 (0.21 mL, 2.20 mmol) in 2 mL dry CH_2Cl_2 at -78 °C. The resulting mixture was then allowed to warm to room temperature slowly and stirred for another 12 h. After the solvent was removed in *vacuo*, the residue was suspended in 10 mL CH_3CN again. To this stirred solution was added di-*tert*-butyl dicarbonate (0.13 g, 0.60 mmol) and Et_3N (1.0 mL) at room temperature. The resulting mixture was stirred for another 2 h. After the solvent was removed in *vacuo*, the residue was fast passed through a short column (silica gel, eluent: Hexane/EtOAc = 1/1) and concentrated *in vacuo* to afford (*R,R*)-**2** (0.38 g, 0.76 mmol) as a white solid. Yield: 76.3%; mp: 206-207°C; $[\alpha]_D^{20}$ = + 100.6 (c 0.20, methanol); IR (KBr) cm^{-1}: 3380.0 (w), 3288.4 (m), 3069.6 (s), 3039.3 (s), 2999.9 (s), 2974.0 (s), 2928.5 (s), 1689.5 (w), 1610.2 (s), 1514.5 (w), 1454.1 (s), 1406.9 (s), 1365.8 (s), 1308.0 (s), 1280.6 (s), 1248.4 (m), 1227.8 (s), 1169.0 (m), 1148.1 (w), 1094.7 (s), 1061.7 (s), 1017.2 (s), 942.2 (s), 816.1 (s), 780.1 (s), 731.5 (s), 704.1 (s), 672.8 (s), 606.4 (s), 566.7 (s), 536.8 (s),; Elemental analysis (%): C 4.29, H 1.36, N 0.30; ^1H NMR (400 MHz, DMSO): δ 9.07, 9.14 (s, 2H, OH), 7.95-7.92 (d, *J* = 9.6 Hz, 1H, NH), 7.21-7.19 (d, *J* = 8.0 Hz, 2H), 7.13-7.10 (d, *J* = 9.6 Hz, 1H, NH), 7.03-7.01 (d, *J* = 8.0 Hz, 2H), 6.89-6.87 (d, *J* = 8.0 Hz, 2H), 6.79-6.77 (d, *J* = 8.0 Hz, 2H), 6.49-6.47 (d, *J* = 8.0 Hz, 2H), 6.39-6.37 (d, *J* = 8.0 Hz, 2H), 4.63-4.59 (m, *J* = 8.0 Hz, 1H), 4.43-4.39 (m, *J* = 8.0 Hz, 1H), 2.27 (s, 3H), 1.29 (s, 9H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 21.7, 28.9, 59.4, 62.7, 78.4, 114.7, 115.0, 126.9, 128.8, 129.5, 130.4, 131.8, 139.3, 142.2, 155.6, 156.6; Anal. calcd for $C_{26}H_{30}N_2O_6S$ (%): C 62.63, H 6.06, N 5.62, S 6.43. Found: C 62.72, H 6.05, N 5.82, S 6.39; HPLC-MS m/z: [M^+] 498.20 (25.6%), [$M-1^+$] 497.20 (86.2%), 423.1 (100%), 326.1 (11.2%), 209.1 (26.0%), 155.0 (12.1%). The FT-IR, ^1H-NMR, ^{13}C-NMR and HPLC-MS spectra of *R,R*-(**2**) were presented in figure S1.

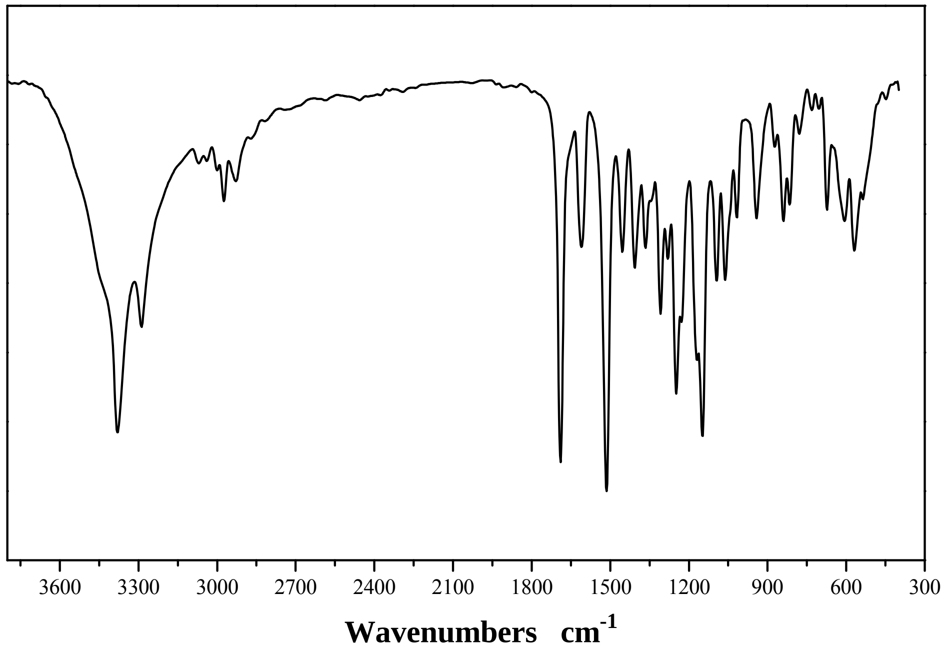
*4. Preparation of Cp*RhTsDPEN-POSS (3).*

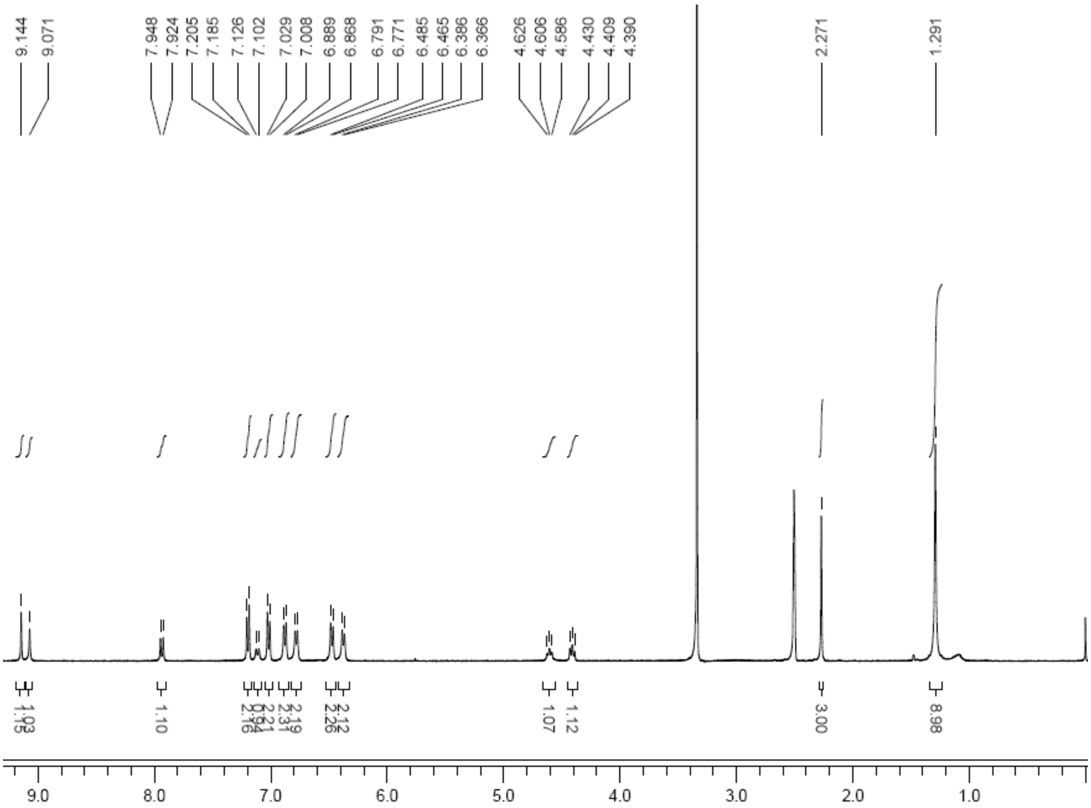
A typical procedure is as follows: Under argon atmosphere, to a stirred suspension of (*R,R*)-**2** (0.50 g, 1.00 mmol) and excess anhydrous K_2CO_3 (1.50 g) in 20 mL dry DMF was added POSS (**1**) (0.82 mg, 0.50 mmol) at room temperature. The resulting mixture was stirred at 40 °C for 24h. After cooling to room temperature, the volatiles were removed in *vacuo* and 50 mL of water was added. The residues were filtrated and washed twice with 50 mL of water and 50 mL of CH_2Cl_2 to afford (*R,R*)-TsDPEN-modified POSS as a white powder (1.06 g, 0.40 mmol, 80%) (The part of them was used for characterization). The powder (0.5 g) was suspended in 10 mL of CH_2Cl_2 again and excess trifluroacetic acid (0.58 mL, 7.5 mmol) was added at room temperature. The resulting mixture was stirred for 48 h at room temperature. After being filtrated, the residues were washed twice with 20 mL of water and 20 mL of CH_2Cl_2. The collected white powder was suspended in 10 mL of CH_2Cl_2 again. To this stirred suspension was added $[Cp^*RhCl_2]_2$ (0.15 g, 0.24 mmol) and excess NEt_3 (2.00 mL, 33.08 mmol) at room temperature. The resulting mixture was stirred and refluxed for 12 h. Then the residues were filtrated and washed twice with 20 mL of dry CH_2Cl_2. After Soxlet extraction in dry CH_2Cl_2 to remove homogeneous and unreacted start materials, the solid was dried under reduced pressure overnight to afford Cp*RhTsDPEN-POSS (**3**) (0.71, 0.18 mmol, 89% relative to TsDPEN-modified POSS) as a light yellow powder. ICP analysis showed that the Rh loading-amount was 77.88 mg (0.76 mmol) per gram catalyst. IR (KBr) cm^{-1}: 3398.4(w), 2996.2 (s), 1687.6 (m), 1607.5 (s), 1568.5 (s), 1512.0 (s), 1568.5 (s), 1459.8 (s), 1417.1 (s), 1299.5 (s), 1202.6 (m), 1129.5 (w), 1038.2 (m), 830.7 (m), 720.3 (s), 662.1 (s), 545.8 (s), 464.9 (s); Elemental analysis (%): C 58.59, H 6.19, N 3.89, S 2.42; ^{29}Si MAS/NMR (300 MHz): T^3 (δ = -71.0 ppm), T^2 (δ = -62.2 ppm); ^{13}C CP/MAS (161.9 MHz): 7.1-8.3($\underline{C}H_3$-NEt_3Cl, and $\underline{C}H_3$-Cp*), 20.8 (Ph$\underline{C}H_3$), 64.2-72.8 (Ph$\underline{C}H_2$-O, N-$\underline{C}$H), 94.2 ($\underline{C}$-Cp), 126.7 ($\underline{C}$-Ph), 136.2 ($\underline{C}$-Ph) ppm. The FT-IR, ^{13}C CP MAS NMR, ^{29}Si CP MAS NMR and TG/DTA curves were presented in figure S2-S5.

2.3. Catalytic Reaction

A typical procedure was as follows: The catalyst **3** (10.58 mg, 8.00 μmol based on Rh from ICP), ketone (2.0 mmol) and 2.0 mL water were added in a 10 mL roundbottom flask in turn. The mixture was allowed to react at 40 °C for 1h. During that time, the reaction was monitored constantly by TLC. After completion of the reaction, the catalyst was separated *via* centrifuge (10000r/min) for the recycle experiment. The aqueous solution was extracted by Et_2O (3 × 3.0 mL). The combined Et_2O was washed with brine twice and dehydrated with Na_2SO_4. After the evaporation of Et_2O, the residue was purified by silica gel flash column chromatography to afford the desired product. The conversion and the ee value could be determined by chiral GC using a Supelco β-Dex 120 chiral column (30 m × 0.25 mm(i.d.), 0.25 μm film) or a HPLC analysis with a UV-Vis detector using a Daicel OJ-H chiralcel columns (Φ 0.46 x 25 cm)

Figure S1. FT-IR, ^{1}H-NMR, ^{13}C-NMR and HPLC-MS spectra of *(R,R)*-**2**.

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6.771
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6.465
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4.626
4.606
4.586
4.430
4.409
4.390
2.271
1.291
1.15
1.03
1.10
2.16
0.94
2.21
2.31
2.19
2.26
2.12
1.07
1.12
3.00
8.98
9.0
8.0
7.0
6.0
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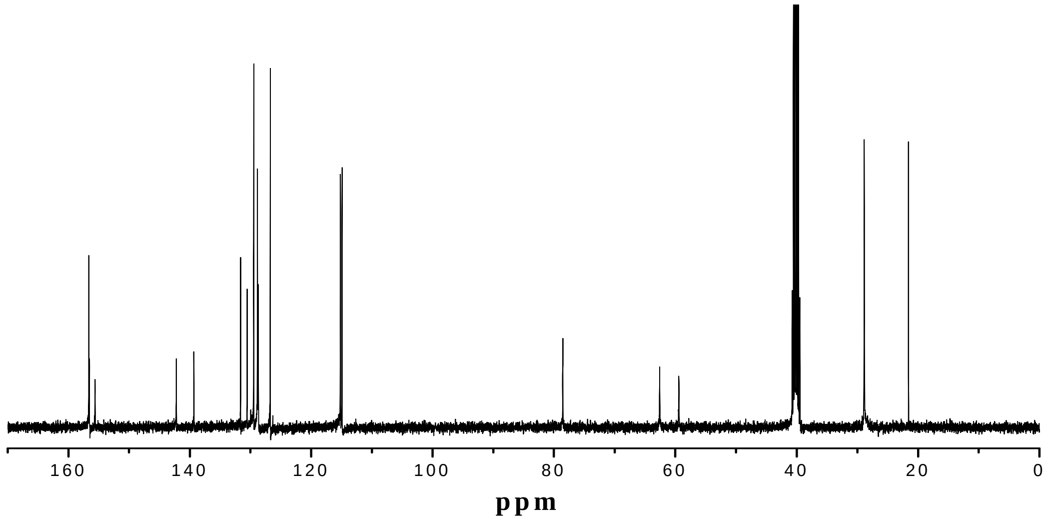
4.0
3.0
2.0
1.0


160
140
120
100
80
60
40
20
0
ppm

Qualitative Analysis Report

Data Filename	scan(neg.)-1.d	**Sample Name**	1
Sample Type	Sample	**Position**	Vial 81
Instrument Name	Instrument 1	**User Name**	
Acq Method		**Acquired Time**	2012-01-11 10:57:50
IRM Calibration Status	Not Applicable	**DA Method**	1.m
Comment			
Data Filename	pro-(neg-497.2.)-1.d	**Sample Name**	1
Sample Type	Sample	**Position**	Vial 81
Instrument Name	Instrument 1	**User Name**	
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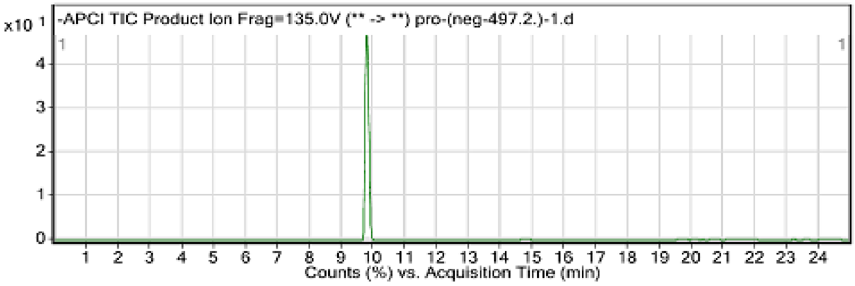
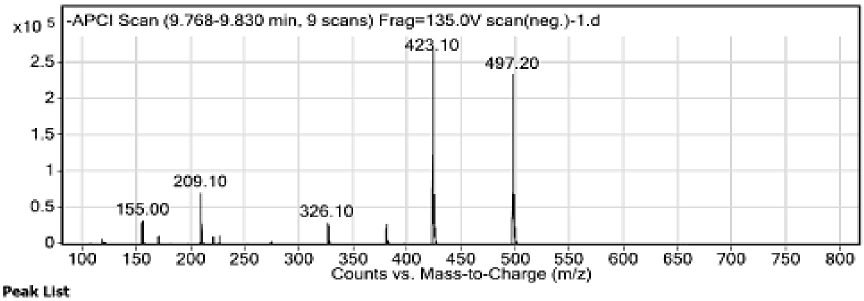
IRM Calibration Status	Not Applicable	**DA Method**	1.m
Comment			

User Chromatograms



User Spectra

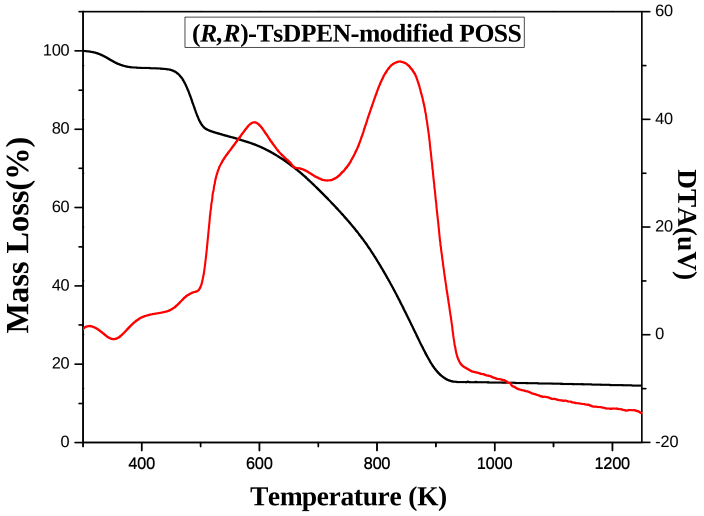
Fragmentor Voltage	Collision Energy	Ionization Mode
135	0	Apci

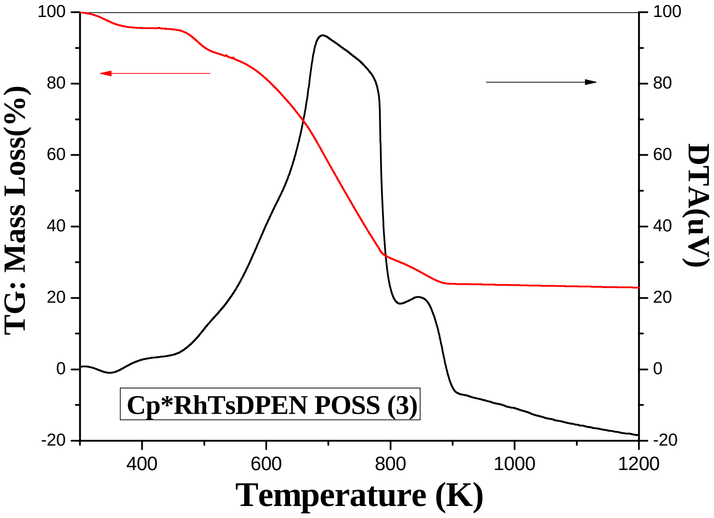


Peak List

m/z	z	Abund
155		33042
209.1	1	70826
326.1		29983
423.1	1	272081
424.1	1	69852
497.2	1	234529
498.2	1	69627

Figure S2. TG/DTA curves of TsDPEN-modified POSS and the catalyst **3**.





<u>Explanation:</u> The TG/DTA curve of TsDPEN-modified POSS was treated in the air as shown in Figure S5. An endothermic peak around 361K with weight loss of 5% could be attributed to the release of physical adsorption water while the another endothermic peak around 452K with weight loss of 14% could be assigned to the release of physical adsorption small moiety silsesquioxane (**1**) due to sublimation <u>(H. Araki and K. Naka, *Macromolecules,* 2011, **44**, 6039)</u>. In addition, an exothermic peak around 590 K with weight loss of 10% could be assigned to the oxidation of vinyl and alkyl fragments while another exothermic peak at 840 K with the weight loss of 54% was resulted from the oxidation of the chiral diamine ligands and phenyl fragments within POSS.

In sharp contrast to TG/DTA curve of TsDPEN-modified POSS, it was found easily that both endothermic peaks in the heterogeneous catalyst **3** were strongly similar to that of parent TsDPEN-modified POSS. It was worth mentioning that two exothermic peaks were combined into one complicated exothermic peak around 688 K with weight loss of 56% could be assigned to the oxidation of Cp*RhTsDPEN complexes and organic fragments (including small vinyl, alkyl and phenyl fragments). Apparently, a new exothermic peak around 850 K with weight loss of 8% could be assigned to the oxidation of rhodium chloride, which was nearly consistent with 7.79% (0.76 mmol) of Rh loading per gram catalyst detected by inductively coupled plasma (ICP) optical emission spectrometer analysis.

Figure S3. FT-IR spectra of TsDPEN-modified POSS and the catalyst **3.**

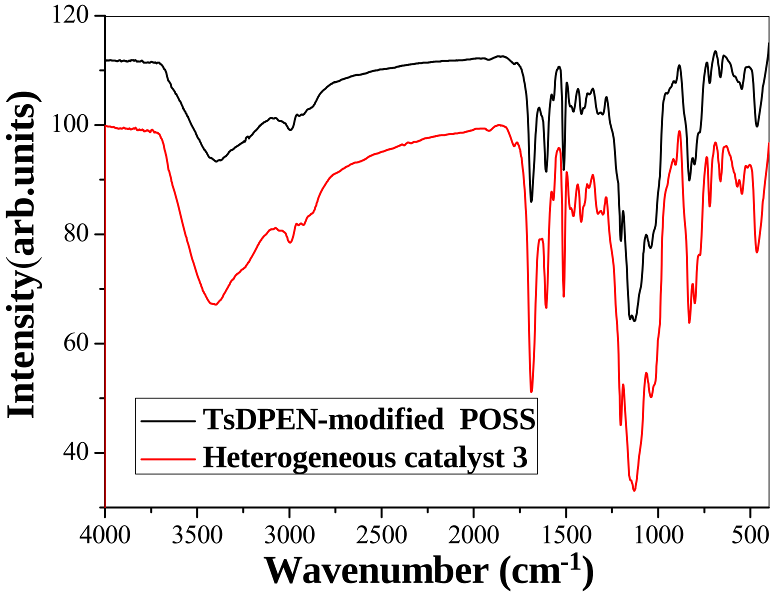
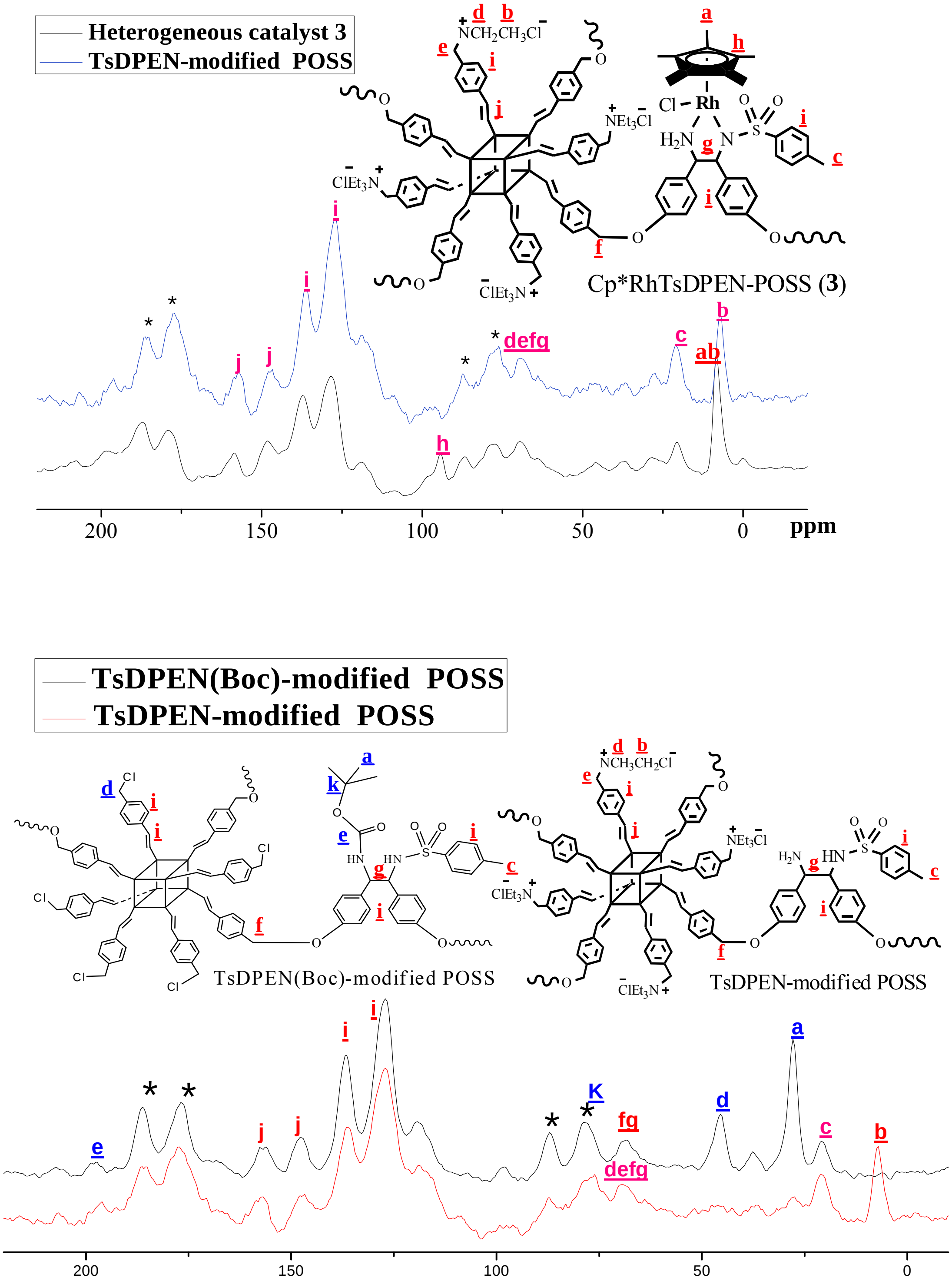


Figure S4. ^{13}C CP MAS NMR spectra of the catalyst **3,** TsDPEN-modified POSS, and TsDPEN-modified POSS without the deprotection of Boc groups.



Explanation: From the ^{13}C CP MAS NMR in Fig.S3, the typical peaks of TsDPEN moieties [21 ppm for Ar-CH_2 and 126-136 ppm for C_6H_5] and the typical peaks of $CpMe_5$ moieties (94 ppm for C_5 and 8 ppm $CpCH_3$) could be observed clearly. These structural arrangements were strongly similar to those of Cp*RhTsDPEN, proving the complexation between ligand and $[Cp^*RhCl_2]_2$.

In particular, when compared (*R,R*)-TsDPEN-modified POSS to the that (*R,R*)-TsDPEN-modified POSS without the deprotection of Boc groups, it was found the peak around 27.6 indicative of the C atoms of Boc groups ($\underline{C}H_3$-Boc) disappeared, confirming the deprotection of Boc groups. In addition, the peak of the quaternary carbon (k) on -Boc group should appear in ca. 80 ppm, however, it was difficult to distinguish because of the overlap of the rotational sideband denoted by asterisk. More importantly, the peak around 46 ppm indicative of the C atoms in benzyl chloride ($Ph\underline{C}H_2Cl$) groups disappeared that appeared in more low field (64-72 ppm) due to the deshielding effect of quaternary ammonium salt, suggesting the formation of quaternary ammonium salt. All these observations demonstrated that the heterogeneous catalyst **3** was prepared steadily, possessing the same single-site well-defined active centers as the homogeneous Cp*RhTsDPEN.

Figure S5. ^{31}Si CP MAS NMR spectrum of the catalyst **3**.

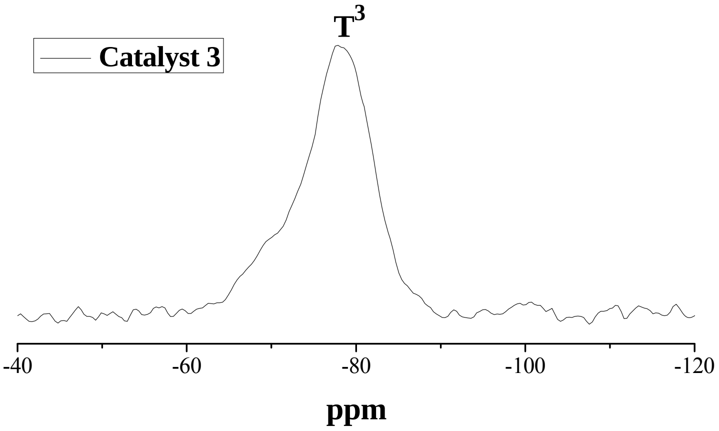
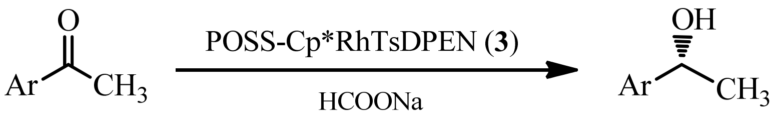


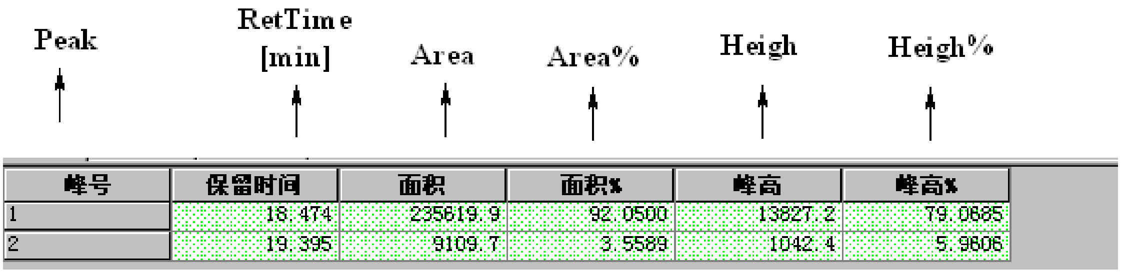
Table S1. Asymmetric transfer hydrogenation of aromatic ketones.[a]



Entry	Ar	Conv. (%)[b]	Ee. (%)[b]
1	Ph	>99(88)[c]	96(96)[c]
2	Ph	93	92[d]
3	Ph	84	96[e]
4	4-FPh	99	93
5	4-ClPh	>99	92
6	4-BrPh	>99	92
7	3-BrPh	>99	95
8	4-MePh	97	91
9	4-OMePh	>99	94
10	3-OMePh	>99	93
11	2-naphthy	>99	92

[a] Reaction conditions: catalysts (10.58 mg, 8.00 μmol of Rh based on ICP analysis), HCO_2Na (0.68 g, 10.0 mmol),ketone (2.0 mmol) and 2.0 mL water, reaction temperature (40 °C), reaction time (1.0 h). [b] Determined by chiral GC or HPLC analysis (see ESI in Fig. S6). [c] Data were obtained using the homogeneous Cp*RhTsDPEN catalyst. [d] Data were obtained using (*R*,*R*)-TsDPEN-modified POSS plus $[Cp^*RhCl_2]_2$ as a catalyst. [e] Data were obtained using (*R*,*R*)-TsDPEN-modified POSS plus RhTsDPEN as a catalyst.

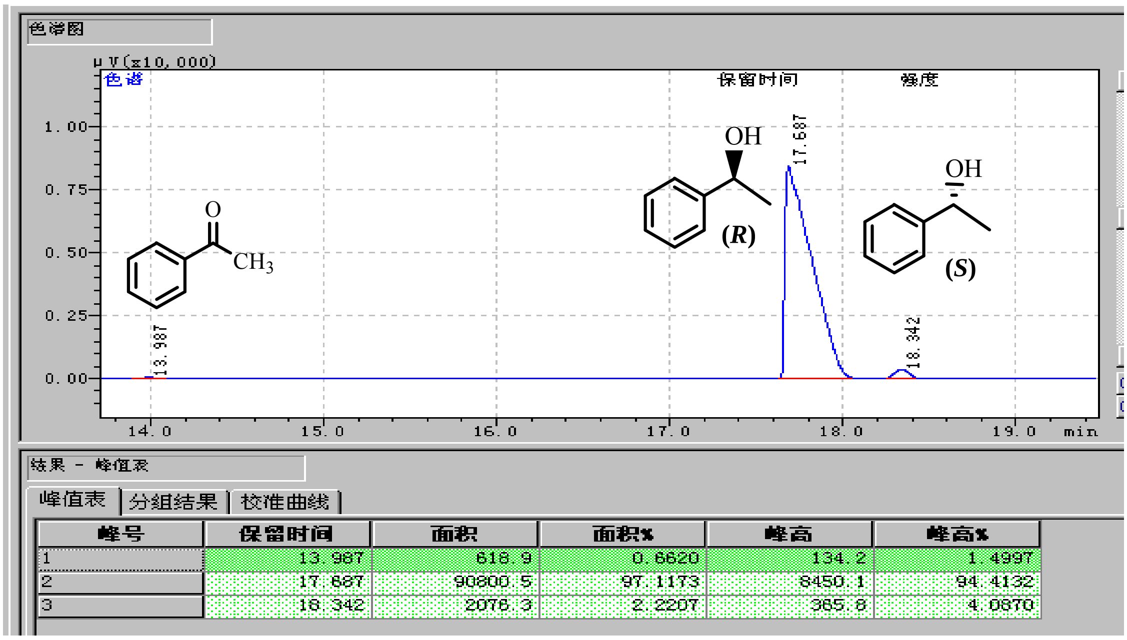
Translation of Chinese to English is as follows:



峰号	保留时间	面积	面积%	峰高	峰高%
1	18.474	235619.9	92.0500	13827.2	79.0685
2	19.395	9109.7	3.5589	1042.4	5.9606

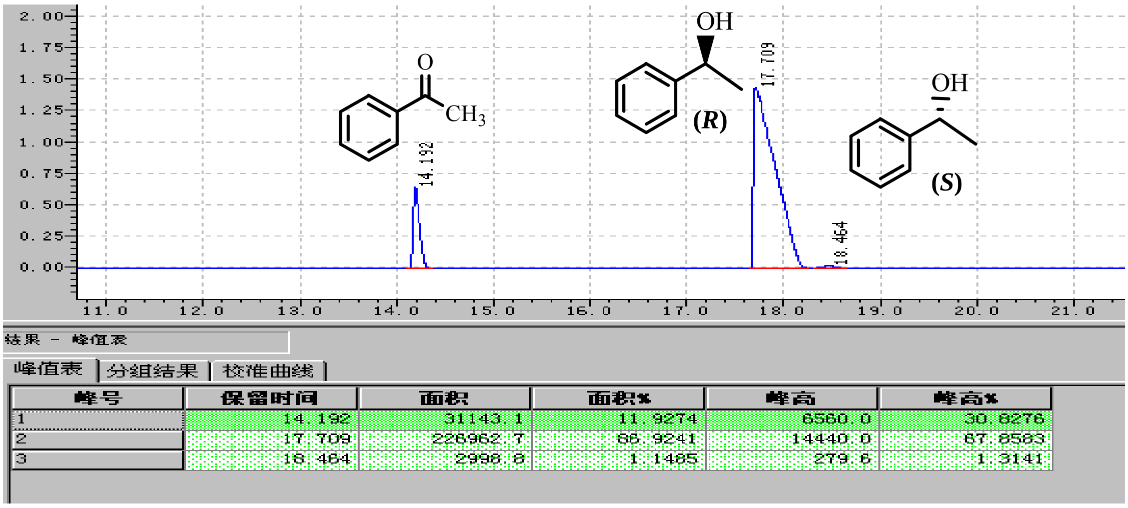
Figure S6. Asymmetric transfer hydrogenation of aromatic ketones.

Asymmetric transfer hydrogenation of acetophenone using **3** as a catalyst.



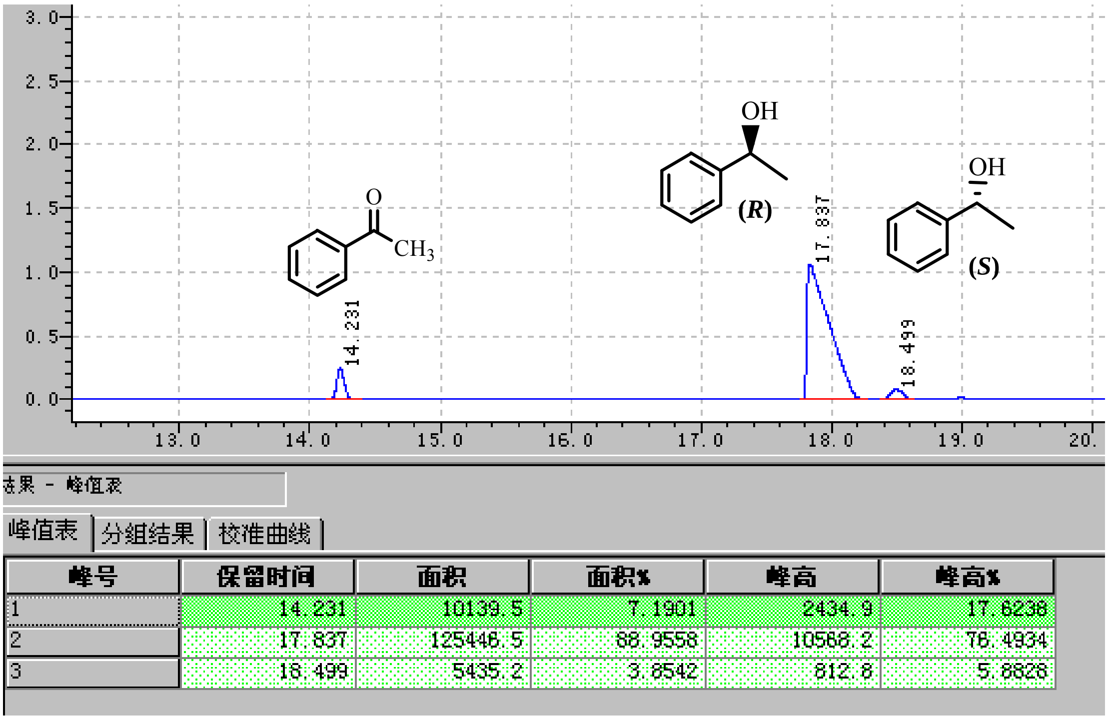
峰号	保留时间	面积	面积%	峰高	峰高%
1	13.987	618.9	0.6620	134.2	1.4997
2	17.687	90800.5	97.1173	8450.1	94.4132
3	18.342	2076.3	2.2207	365.8	4.0870

Asymmetric transfer hydrogenation of acetophenone using the homogeneous RhTsDPEN as a catalyst without additive of Bu_4NBr as a phase transfer catalyst.



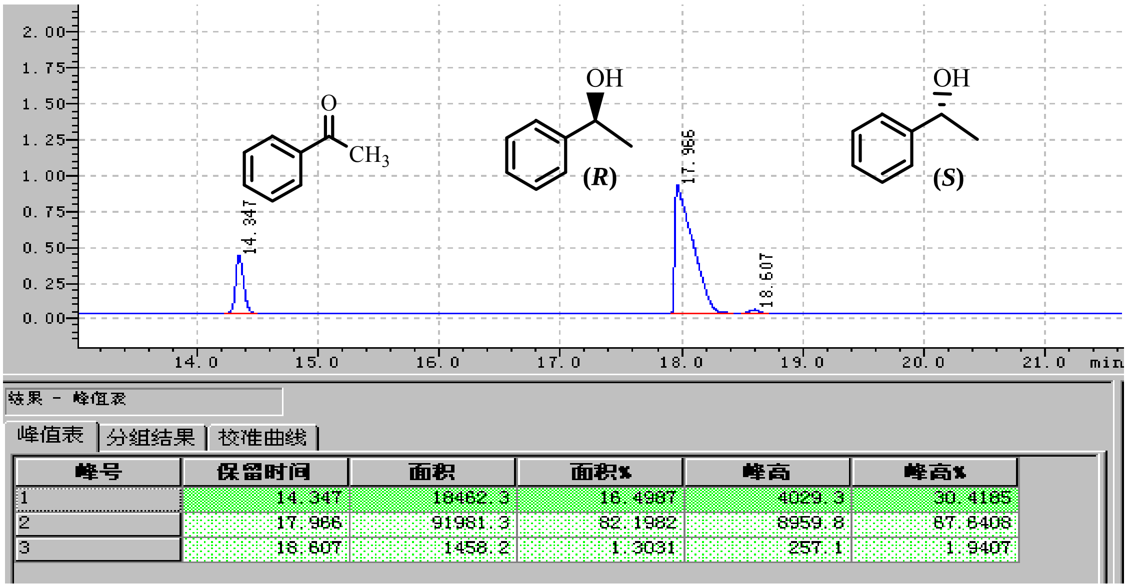
峰号	保留时间	面积	面积%	峰高	峰高%
1	14.192	31143.1	11.9274	6560.0	30.8276
2	17.709	226962.7	86.9241	14440.0	67.8583
3	18.464	2998.8	1.1485	279.6	1.3141

Asymmetric transfer hydrogenation of acetophenone using (*R*,*R*)-TsDPEN-modified POSS plus $[Cp^*RhCl_2]_2$ as a catalyst.



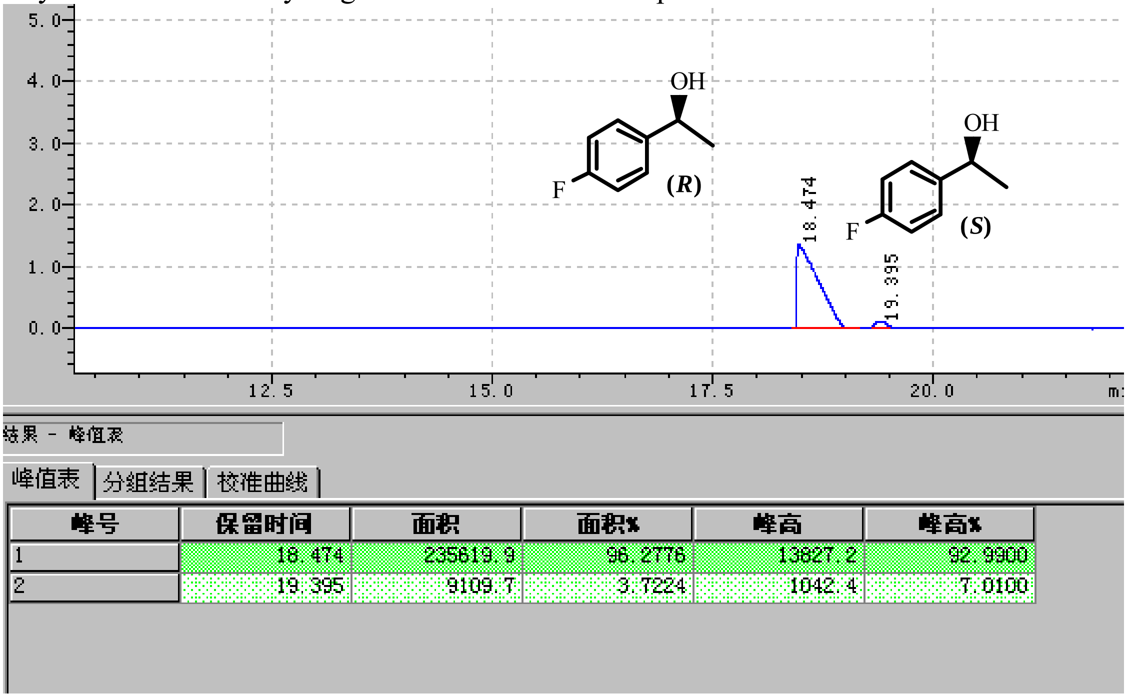
峰号	保留时间	面积	面积%	峰高	峰高%
1	14.231	10139.5	7.1901	2434.9	17.6238
2	17.837	125446.5	88.9558	10568.2	76.4934
3	18.499	5435.2	3.8542	812.8	5.8828

Asymmetric transfer hydrogenation of acetophenone using (*R*,*R*)-TsDPEN-modified POSS plus RhTsDPEN as a catalyst.



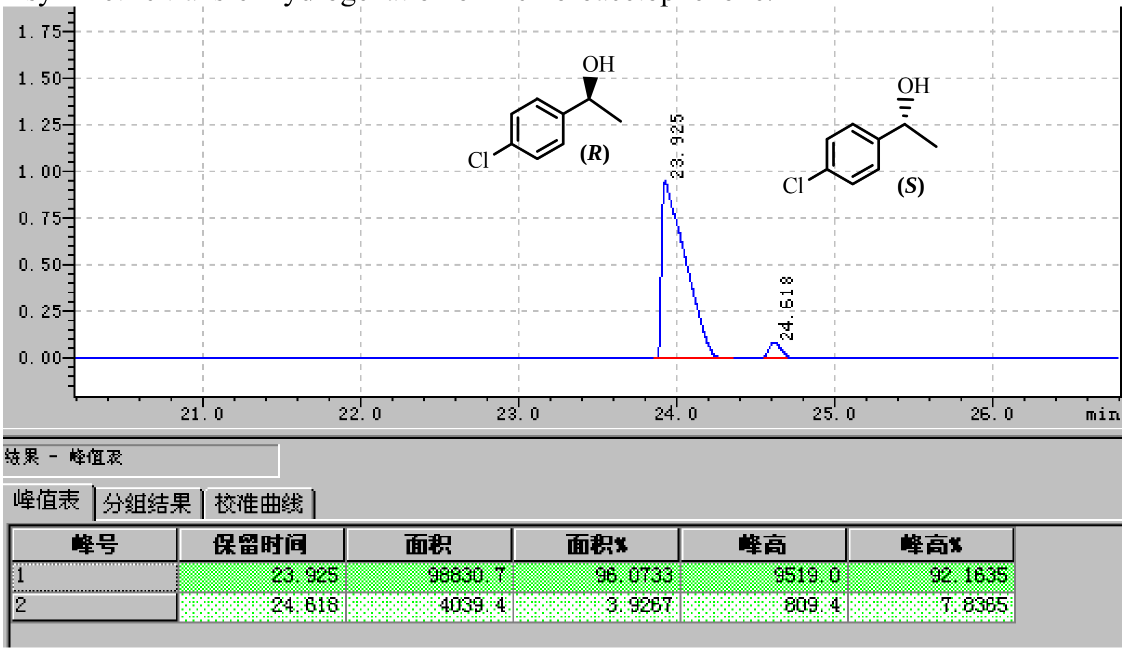
峰号	保留时间	面积	面积%	峰高	峰高%
1	14.347	18462.3	16.4987	4029.3	30.4185
2	17.966	91981.3	82.1982	8959.8	67.6408
3	18.607	1458.2	1.3031	257.1	1.9407

Asymmetric transfer hydrogenation of 4-fluoroacetophenone.



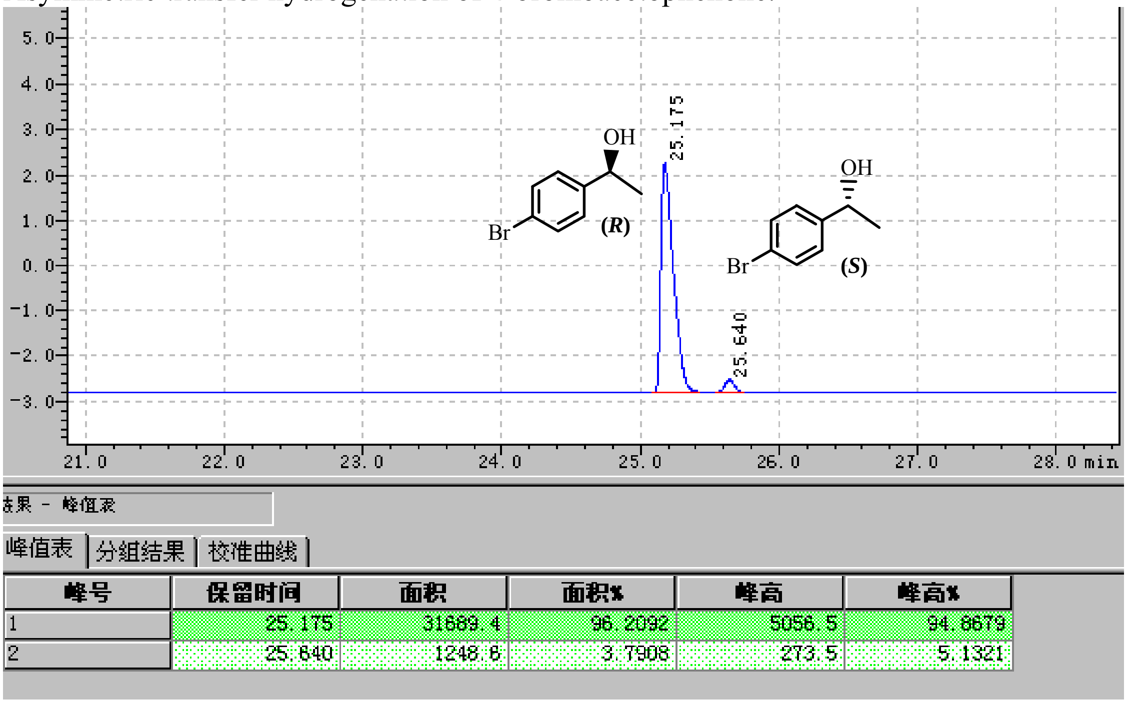
峰号	保留时间	面积	面积%	峰高	峰高%
1	18. 474	235619. 9	96. 2776	13827. 2	92. 9900
2	19. 395	9109. 7	3. 7224	1042. 4	7. 0100

Asymmetric transfer hydrogenation of 4-chloroacetophenone.



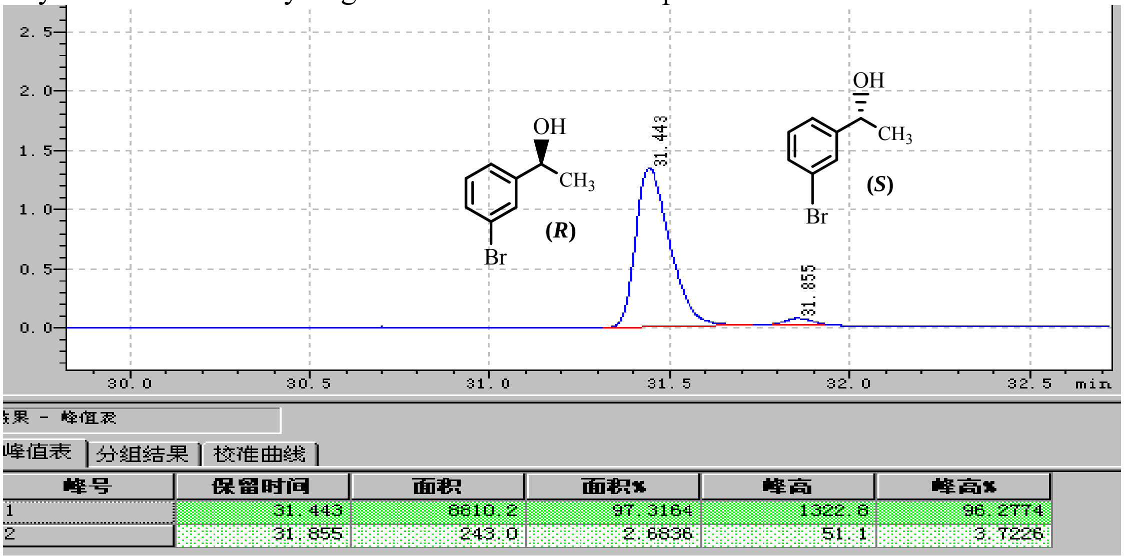
峰号	保留时间	面积	面积%	峰高	峰高%
1	23. 925	98830. 7	96. 0733	9519. 0	92. 1635
2	24. 618	4039. 4	3. 9267	809. 4	7. 8365

Asymmetric transfer hydrogenation of 4-bromoacetophenone.



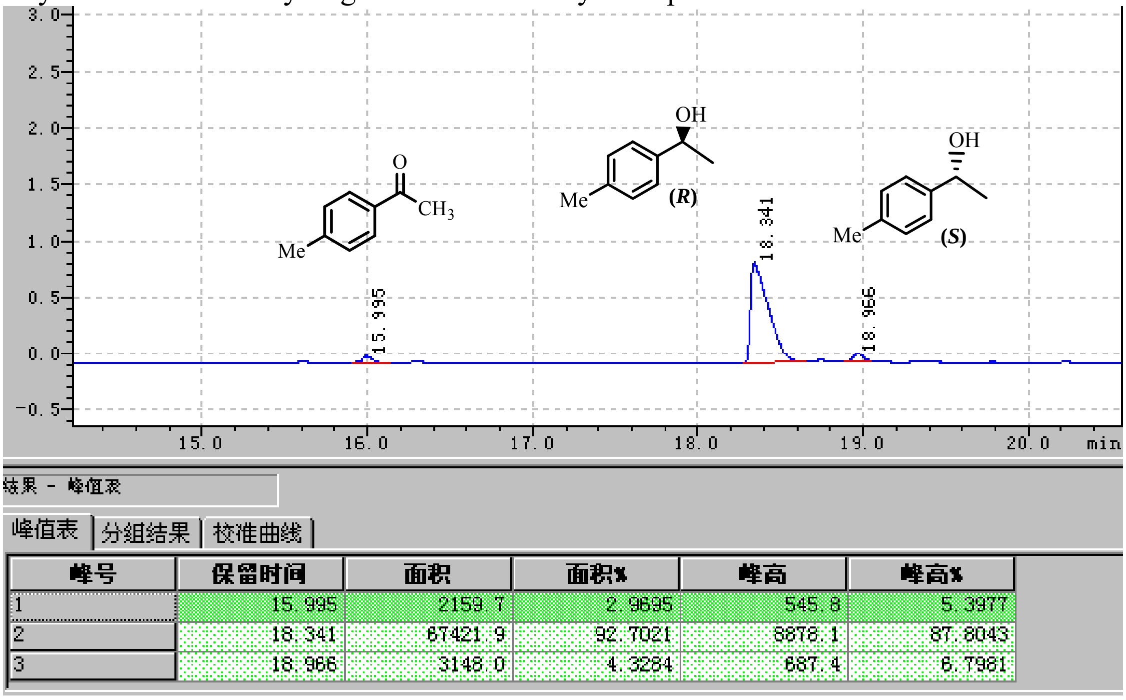
峰号	保留时间	面积	面积%	峰高	峰高%
1	25.175	31689.4	96.2092	5056.5	94.8679
2	25.640	1248.6	3.7908	273.5	5.1321

Asymmetric transfer hydrogenation of 3-bromoacetophenone.



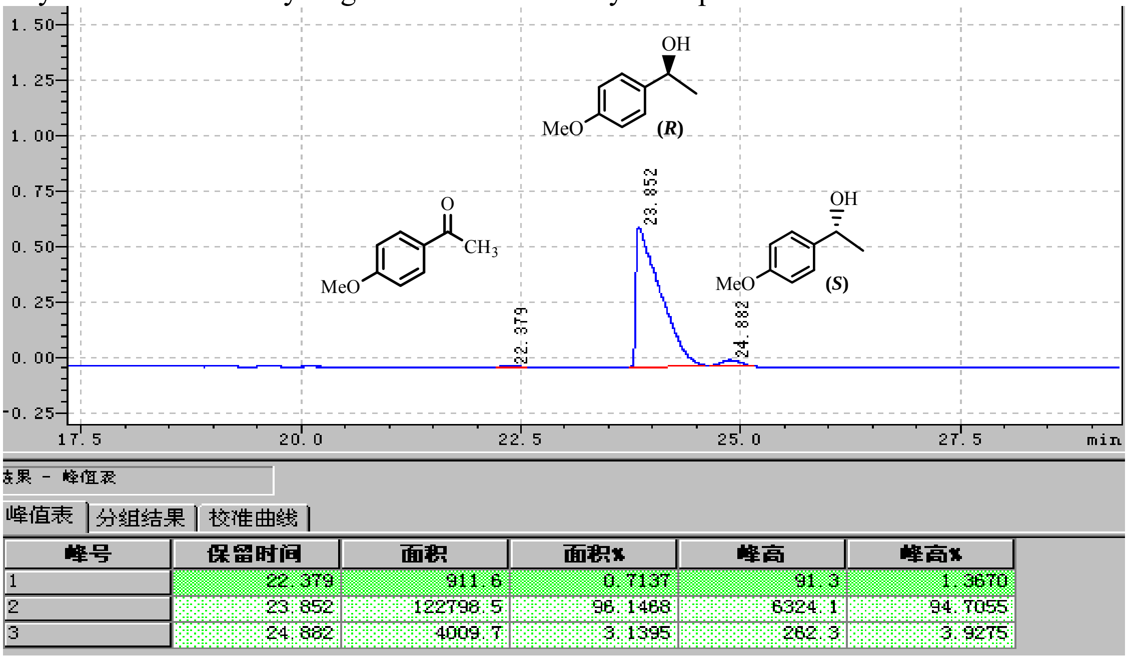
峰号	保留时间	面积	面积%	峰高	峰高%
1	31.443	8810.2	97.3164	1322.8	96.2774
2	31.855	243.0	2.6836	51.1	3.7226

Asymmetric transfer hydrogenation of 4-methylacetophenone.



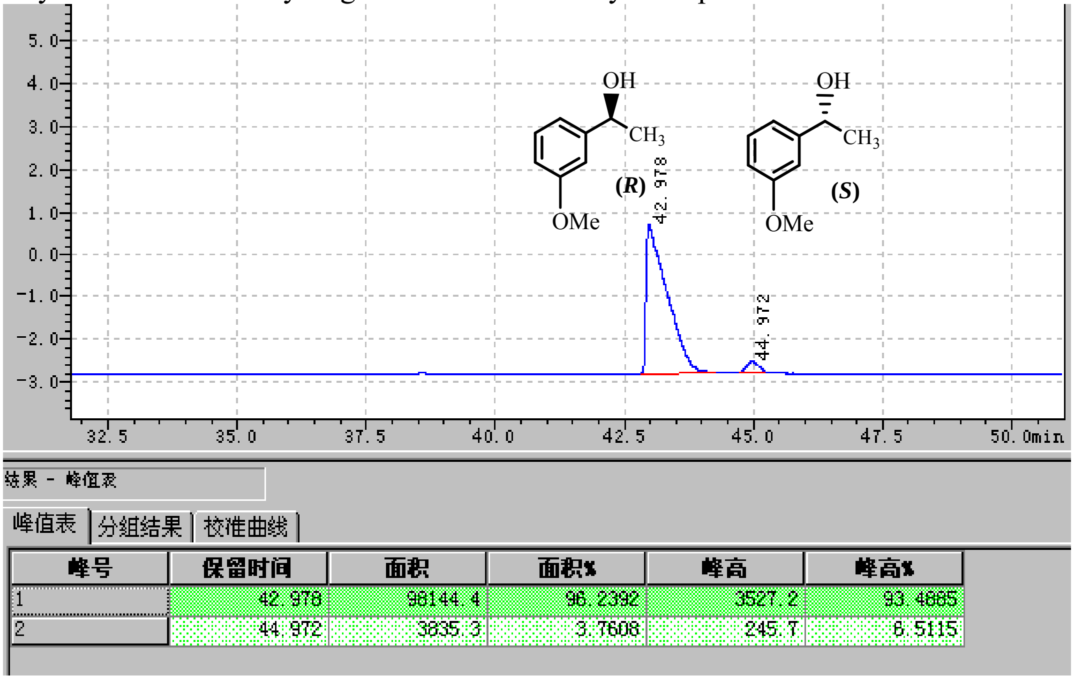
峰号	保留时间	面积	面积%	峰高	峰高%
1	15. 995	2159. 7	2. 9695	545. 8	5. 3977
2	18. 341	67421. 9	92. 7021	8878. 1	87. 8043
3	18. 966	3148. 0	4. 3284	687. 4	6. 7981

Asymmetric transfer hydrogenation of 4-methoxylacetophenone.



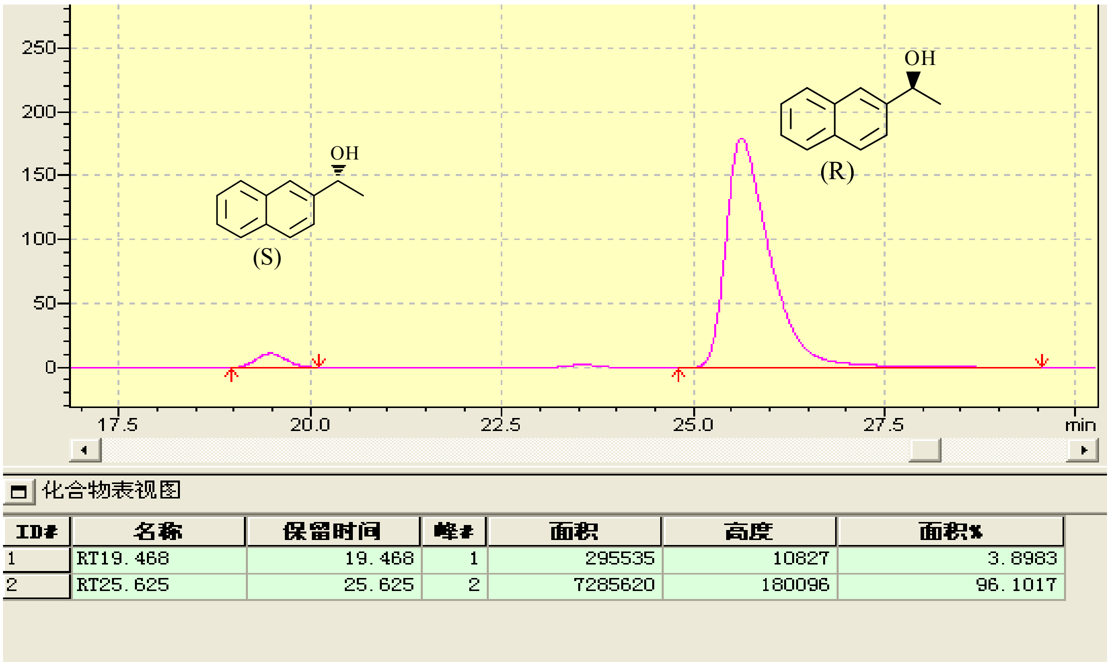
峰号	保留时间	面积	面积%	峰高	峰高%
1	22. 379	911. 6	0. 7137	91. 3	1. 3670
2	23. 852	122798. 5	96. 1468	6324. 1	94. 7055
3	24. 882	4009. 7	3. 1395	262. 3	3. 9275

Asymmetric transfer hydrogenation of 3-methoxylacetophenone.



峰号	保留时间	面积	面积%	峰高	峰高%
1	42.978	98144.4	96.2392	3527.2	93.4885
2	44.972	3835.3	3.7608	245.7	6.5115

Asymmetric transfer hydrogenation of 2-acetonaphthone. (Daicel OJ-H chiralcel columns: 1.0 mL/min, hex/IPA=93:7.) ref: [Liu, P. N.; Gu, P. M.; Wang F.; Tu, Y. Q. Org. Lett., 2004, 6, 169.]



ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT19.468	19.468	1	295535	10827	3.8983
2	RT25.625	25.625	2	7285620	180096	96.1017

Table S2. Reusability of the catalyst **3** using acetophenone as a substrate.

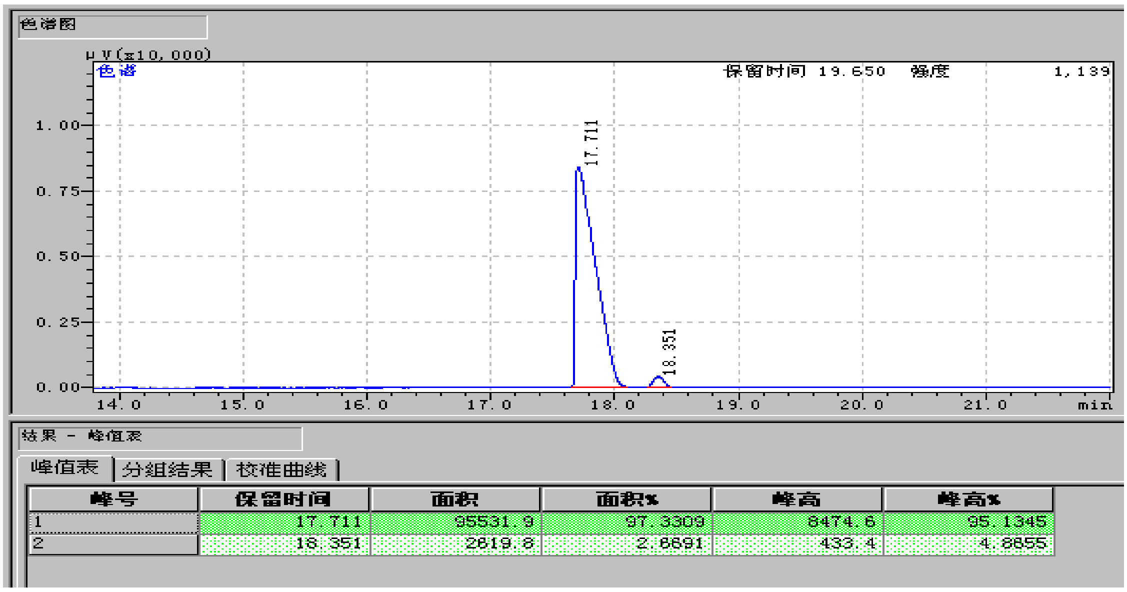
Recycle	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Conv. [%]	99.3	99.9	99.5	97.5	99.9	99.9	99.3	99.9	99.9	98.7	97.7	96.2
ee [%]	95.5	94.7	94.5	94.3	93.5	93.4	93.1	92.7	92.4	92.4	92.2	92.8

[a] Reaction conditions: catalysts (10.58 mg, 8.00 μmol of Rh based on ICP analysis), HCO_2Na (0.68 g, 10.0 mmol), ketone (2.0 mmol) and 2.0 mL water, reaction temperature (40 ^{o}C), reaction time (1.0 h).

[b] Determined by chiral GC or HPLC analysis (see ESI in Fig. S7).

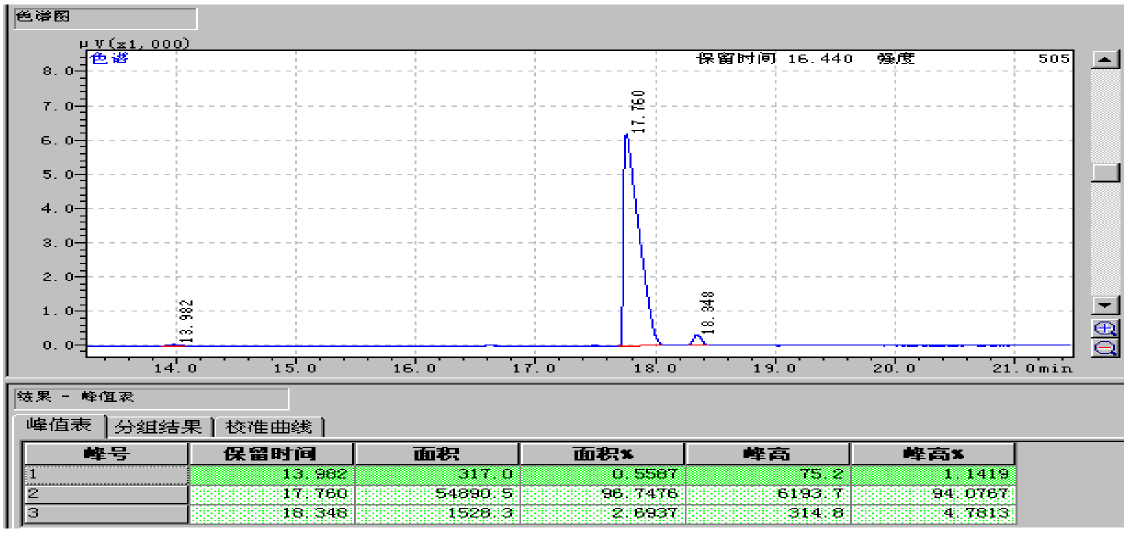
Figure S7. Reusability in Asymmetric Transfer Hydrogenation of Acetophenone**.**

Recycle 2 of the catalyst **3** using acetophenone as a substrate.



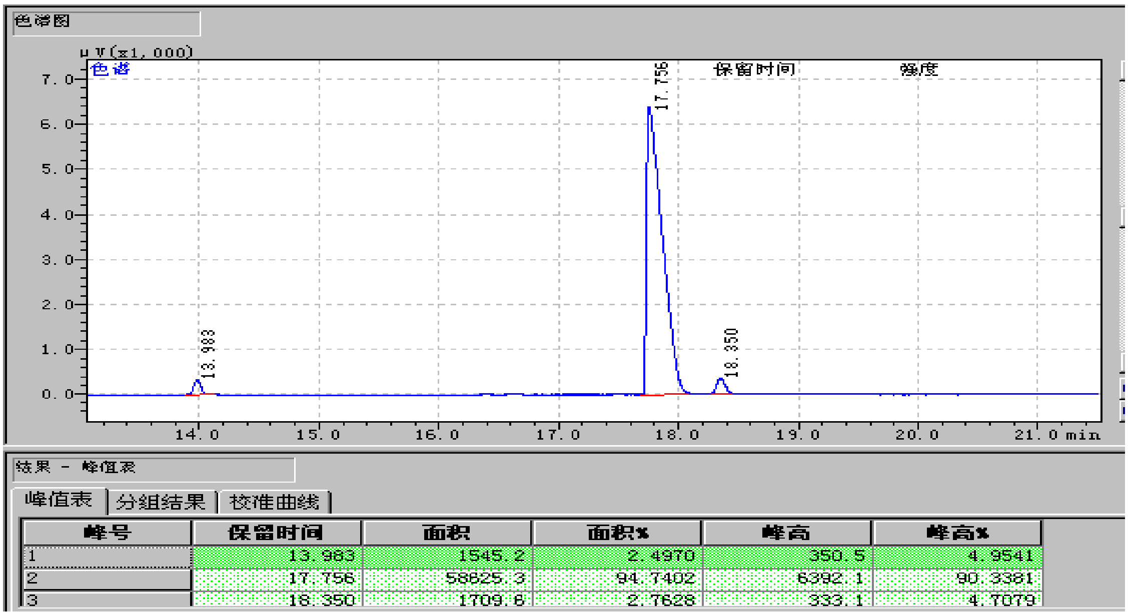
峰号	保留时间	面积	面积%	峰高	峰高%
1	17.711	95531.9	97.3309	8474.6	95.1345
2	18.351	2619.8	2.6691	433.4	4.8655

Recycle 3 of the catalyst of the catalyst **3** using acetophenone as a substrate.



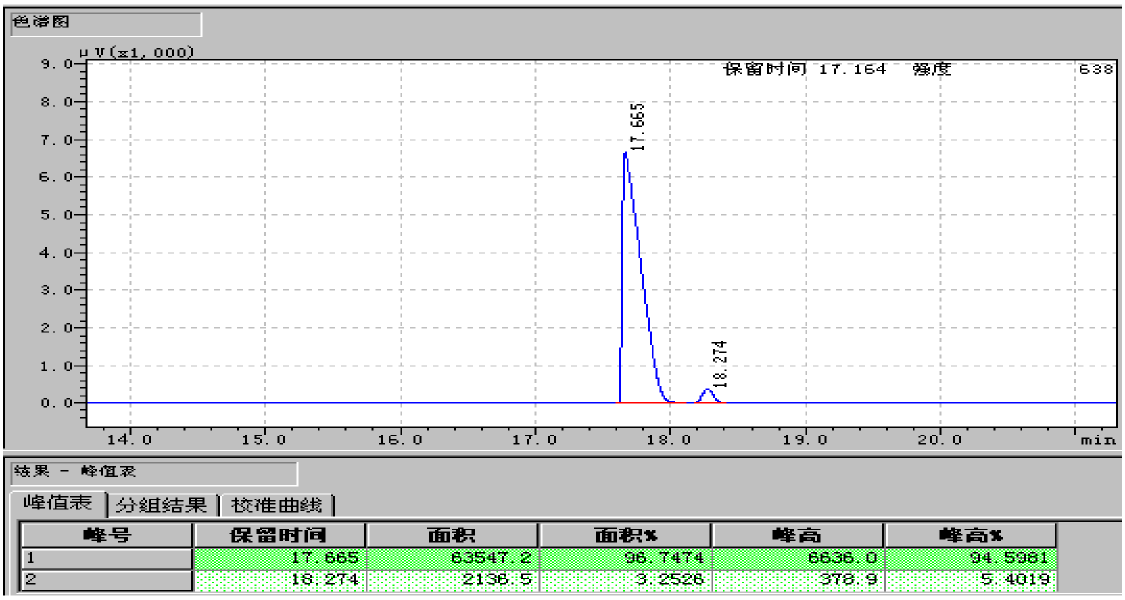
峰号	保留时间	面积	面积%	峰高	峰高%
1	13.982	317.0	0.5587	75.2	1.1419
2	17.760	54890.5	96.7476	6193.7	94.0767
3	18.348	1528.3	2.6937	314.8	4.7813

Recycle 4 of the catalyst **3** using acetophenone as a substrate.



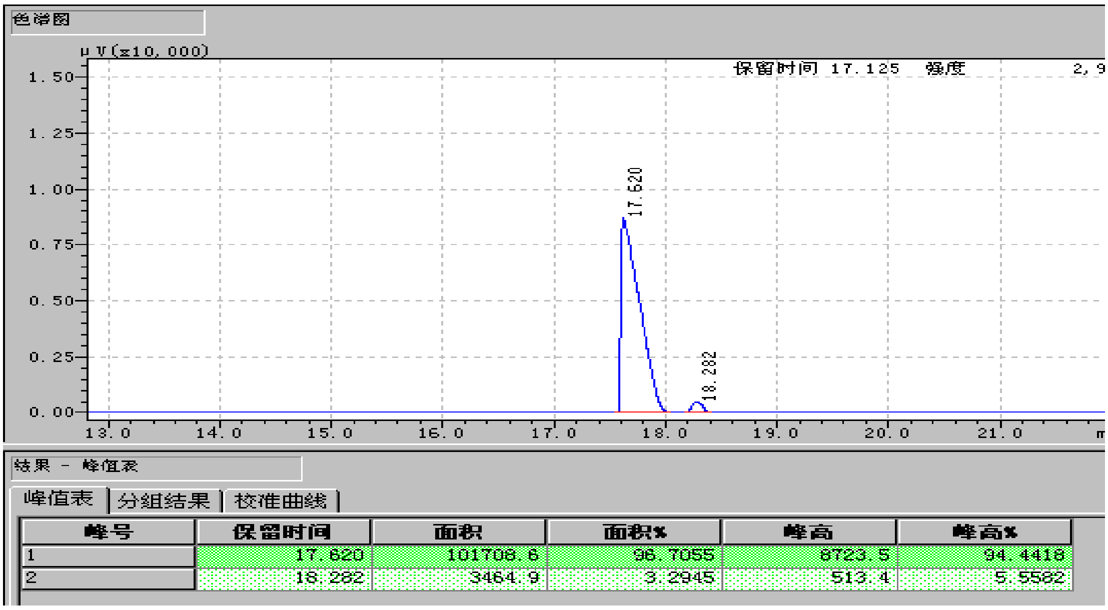
峰号	保留时间	面积	面积%	峰高	峰高%
1	13.983	1545.2	2.4970	350.5	4.9541
2	17.756	58625.3	94.7402	6392.1	90.3381
3	18.350	1709.6	2.7628	333.1	4.7079

Recycle 5 of the catalyst **3** using acetophenone as a substrate.



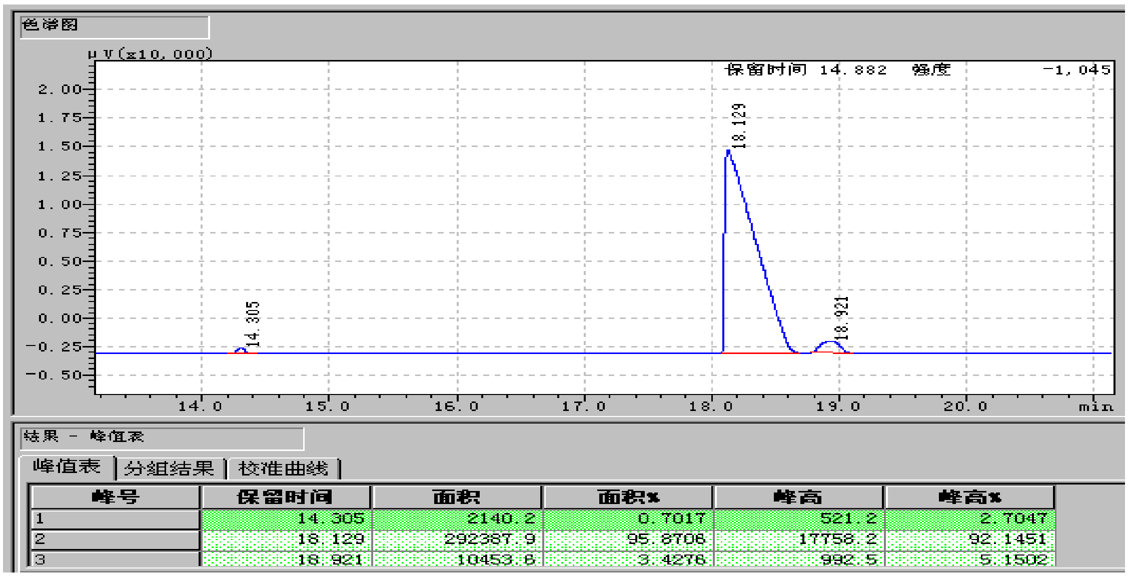
峰号	保留时间	面积	面积%	峰高	峰高%
1	17.665	63547.2	96.7474	6636.0	94.5981
2	18.274	2136.5	3.2526	378.9	5.4019

Recycle 6 of the catalyst **3** using acetophenone as a substrate.



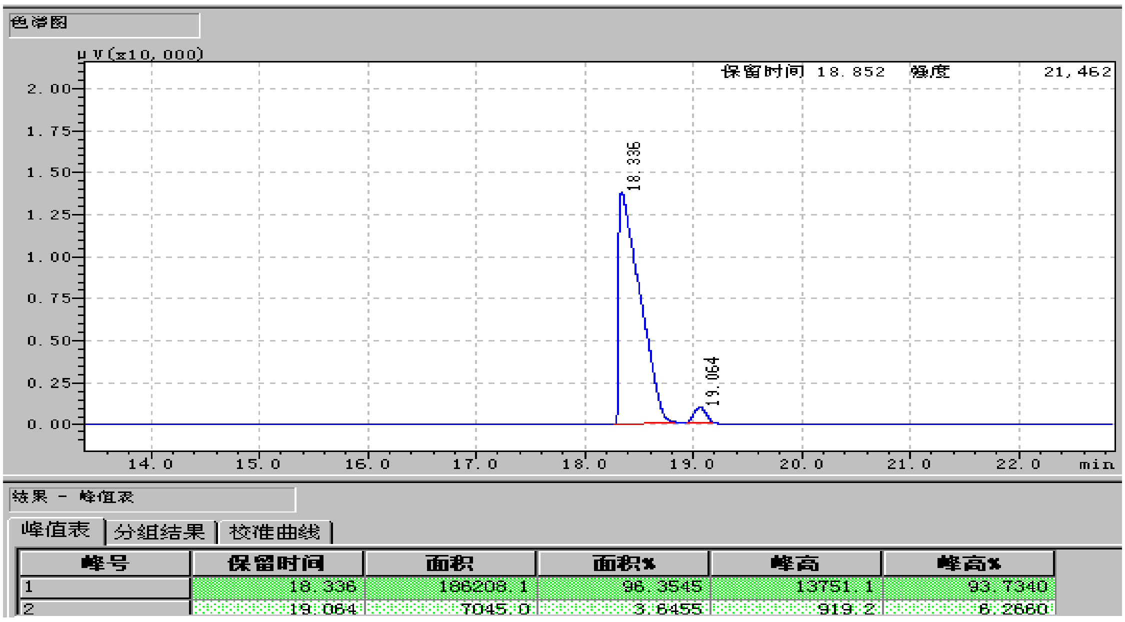
峰号	保留时间	面积	面积%	峰高	峰高%
1	17.620	101708.6	96.7055	8723.5	94.4418
2	18.282	3464.9	3.2945	513.4	5.5582

Recycle 7 of the catalyst **3** using acetophenone as a substrate.



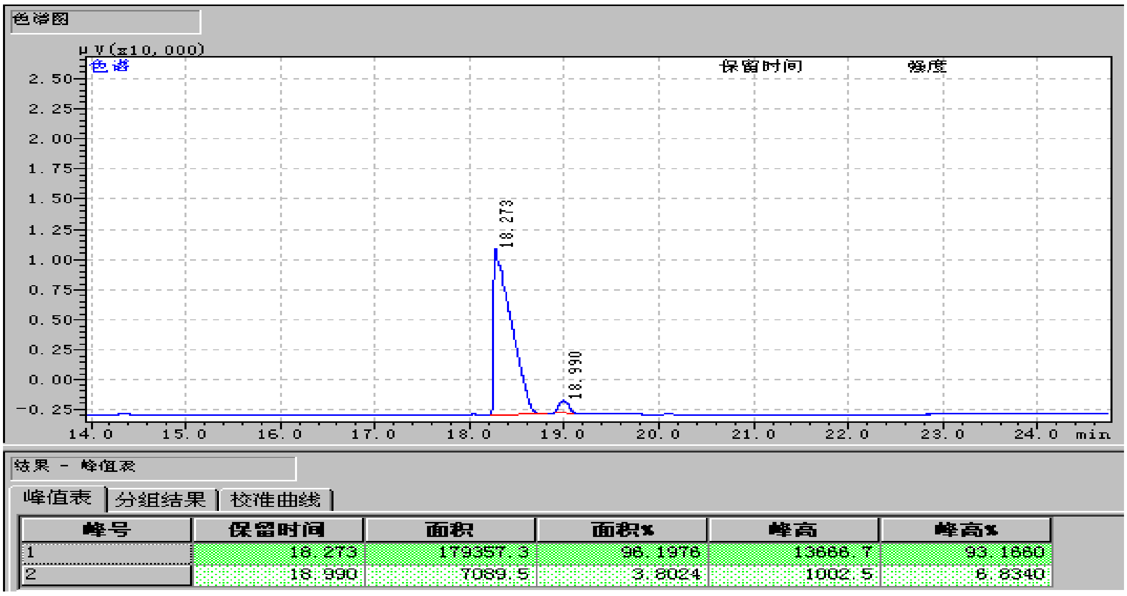
峰号	保留时间	面积	面积%	峰高	峰高%
1	14.305	2140.2	0.7017	521.2	2.7047
2	18.129	292387.9	95.8706	17758.2	92.1451
3	18.921	10453.6	3.4276	992.5	5.1502

Recycle 8 of the catalyst **3** using acetophenone as a substrate.



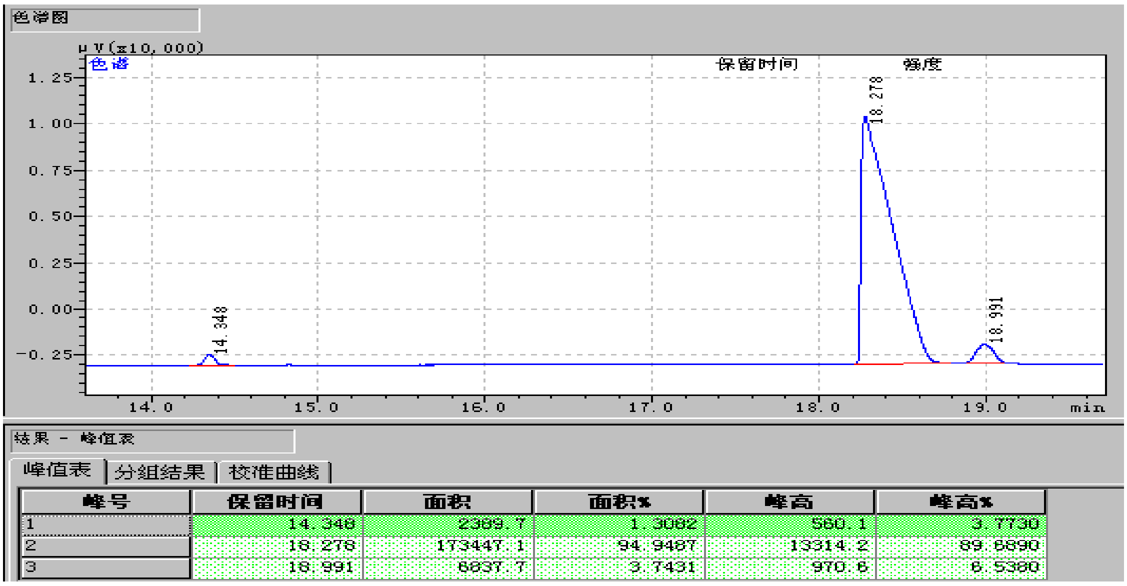
峰号	保留时间	面积	面积%	峰高	峰高%
1	18.336	186208.1	96.3545	13751.1	93.7340
2	19.064	7045.0	3.6455	919.2	6.2660

Recycle 9 of the catalyst **3** using acetophenone as a substrate.



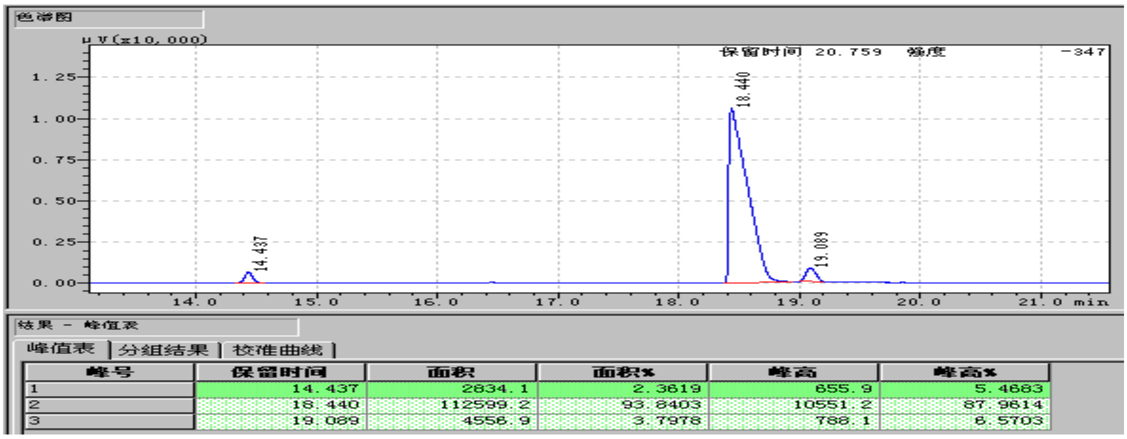
峰号	保留时间	面积	面积%	峰高	峰高%
1	18.273	179357.3	96.1976	13666.7	93.1660
2	18.990	7089.5	3.8024	1002.5	6.8340

Recycle 10 of the catalyst **3** using acetophenone as a substrate.



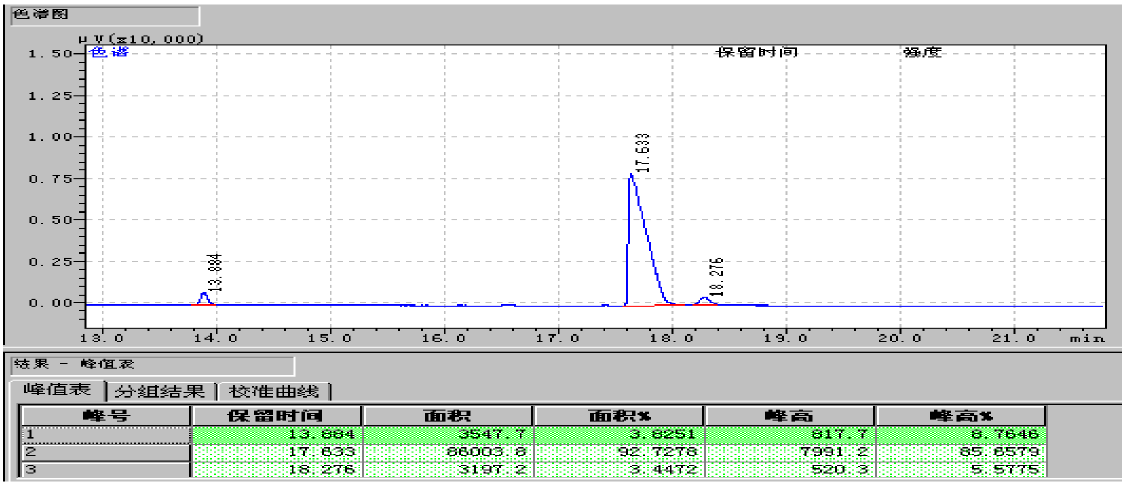
峰号	保留时间	面积	面积%	峰高	峰高%
1	14.348	2389.7	1.3082	560.1	3.7730
2	18.278	173447.1	94.9487	13314.2	89.6890
3	18.991	6837.7	3.7431	970.6	6.5380

Recycle 11 of the catalyst **3** using acetophenone as a substrate.



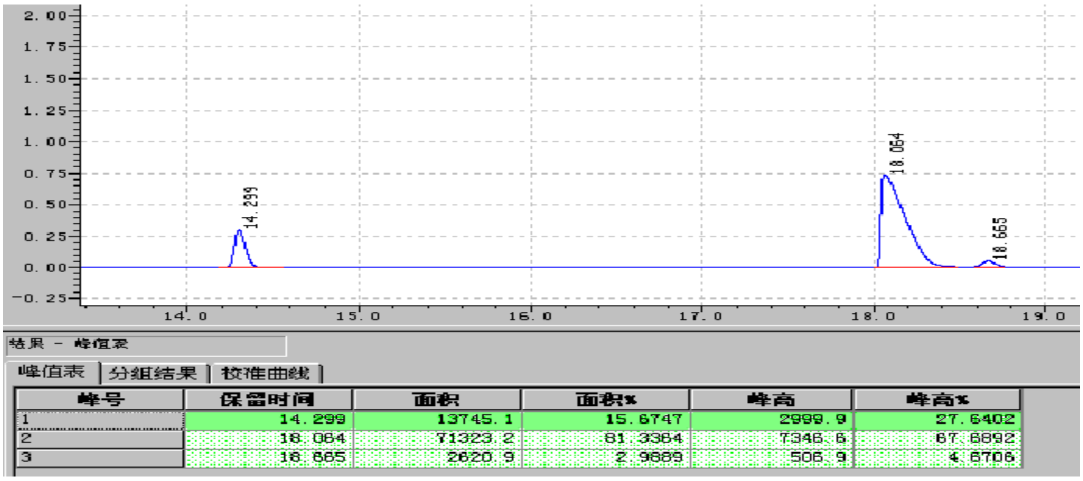
峰号	保留时间	面积	面积%	峰高	峰高%
1	14.437	2834.1	2.3619	655.9	5.4683
2	18.440	112599.2	93.8403	10551.2	87.9614
3	19.089	4556.9	3.7978	788.1	6.5703

Recycle **12** of the catalyst **3** using acetophenone as a substrate.



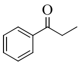
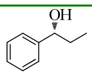
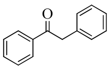
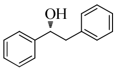
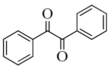
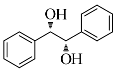
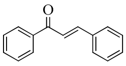
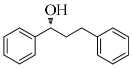
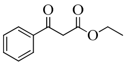
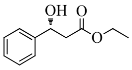
峰号	保留时间	面积	面积%	峰高	峰高%
1	13.884	3547.7	3.8251	817.7	8.7646
2	17.633	86003.8	92.7278	7991.2	85.6579
3	18.276	3197.2	3.4472	520.3	5.5775

Recycle 13 of the catalyst **3** using acetophenone as a substrate. Conversion: 84.3% and ee: 92.9%.



峰号	保留时间	面积	面积%	峰高	峰高%
1	14.299	13745.1	15.6747	2999.9	27.6402
2	18.064	71323.2	81.3364	7346.6	67.6892
3	18.665	2620.9	2.9889	506.9	4.6706

Table S3. Asymmetric transfer hydrogenation of ketones and analogues.[a]

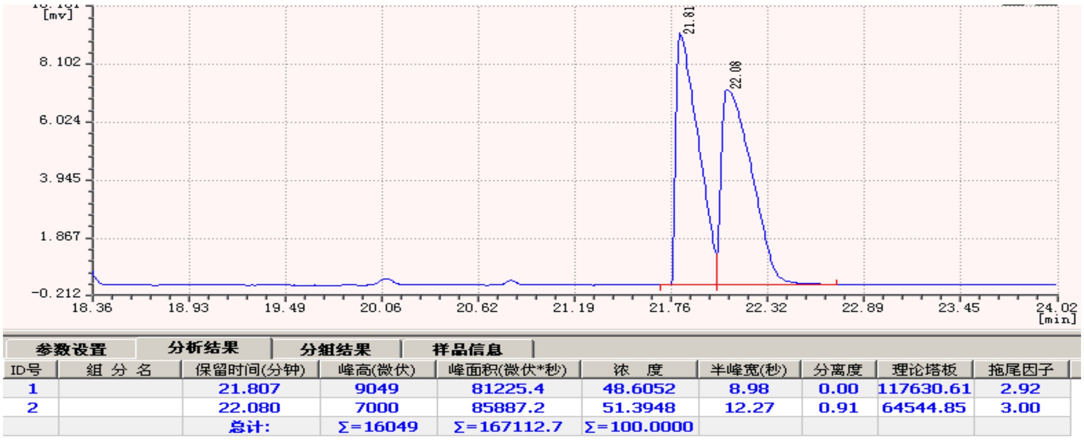
Entry	**Substrate**	**Product**	**Conv. (%)** [b]	**Ee.(%)**[b]
1			>99	92
2			99	94
3			>99	99
4			99	92
5			>99	97

[a] Reaction conditions: catalysts (10.58 mg, 8.00 μmol of Rh based on ICP analysis), HCO_2Na (0.68 g, 10.0 mmol), ketone (2.0 mmol) and 2.0 mL water, reaction temperature (40 ^{o}C), reaction time (1.0 h).

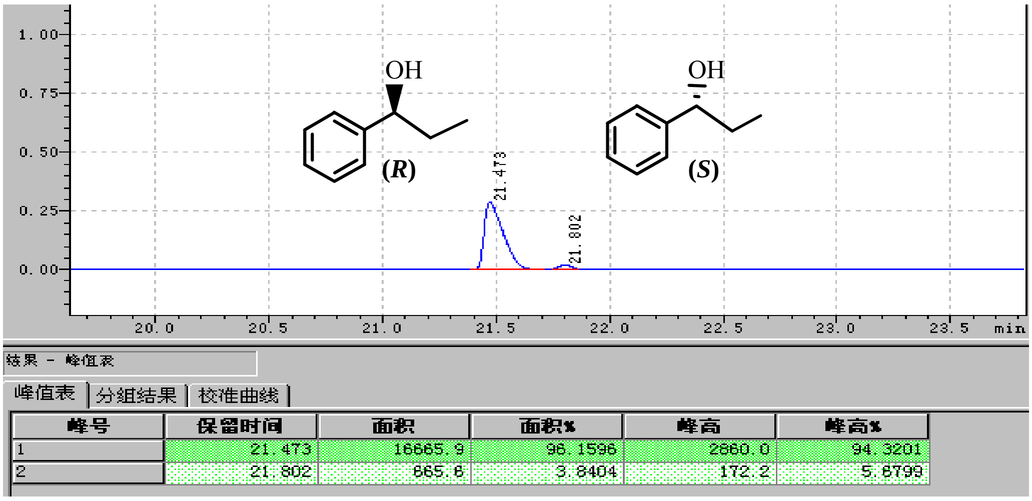
[b] Determined by chiral HPLC analysis (see ESI in Fig. S8).

Figure S8. Asymmetric transfer hydrogenation of ketones and analogues.

Asymmetric transfer hydrogenation of propiophenone.

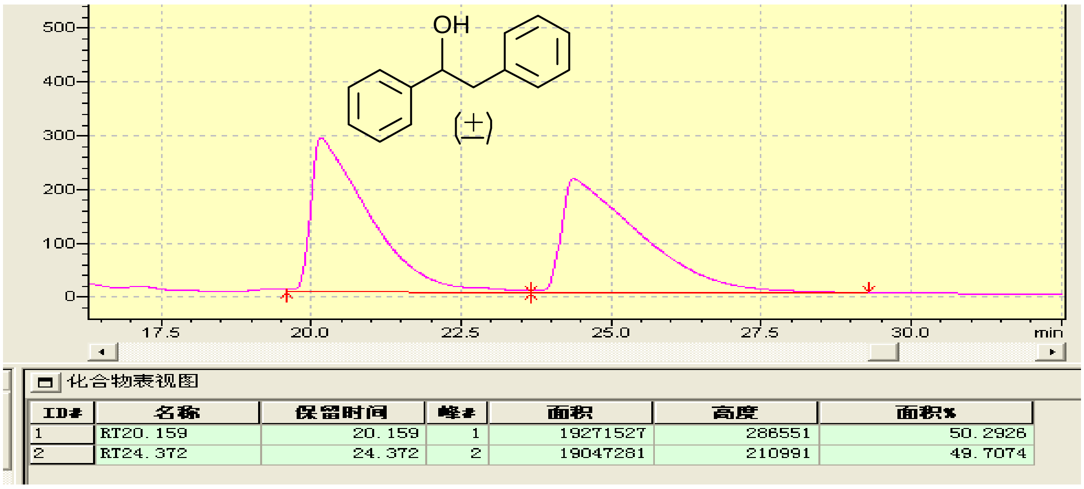


ID号	组 分 名	保留时间(分钟)	峰高(微伏)	峰面积(微伏*秒)	浓　度	半峰宽(秒)	分离度	理论塔板	拖尾因子
1		21.807	9049	81225.4	48.6052	8.98	0.00	117630.61	2.92
2		22.080	7000	85887.2	51.3948	12.27	0.91	64544.85	3.00
		总计:	Σ=16049	Σ=167112.7	Σ=100.0000				



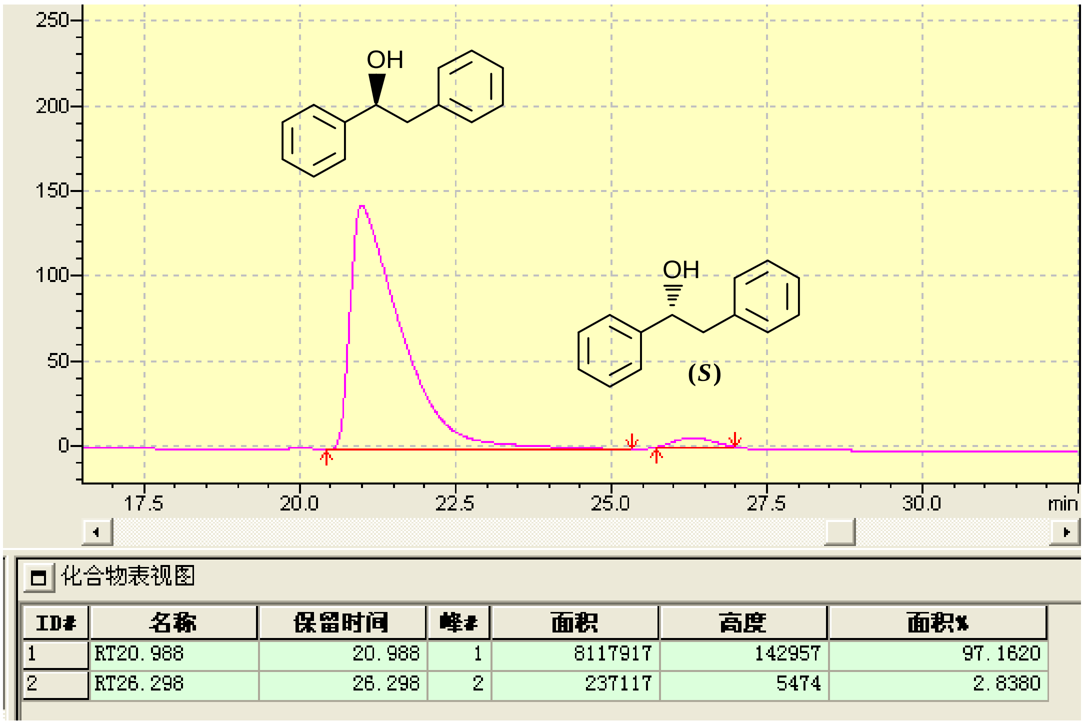
峰号	保留时间	面积	面积%	峰高	峰高%
1	21.473	16665.9	96.1596	2860.0	94.3201
2	21.802	665.6	3.8404	172.2	5.6799

Asymmetric transfer hydrogenation of 2-Phenylacetophenone (Daicel OD-H chiralcel columns: 1.0 mL/min, hex/IPA = 98:2) (ref: *Chem. Eur. J.*, 2008, **14**, 2209)



化合物表视图

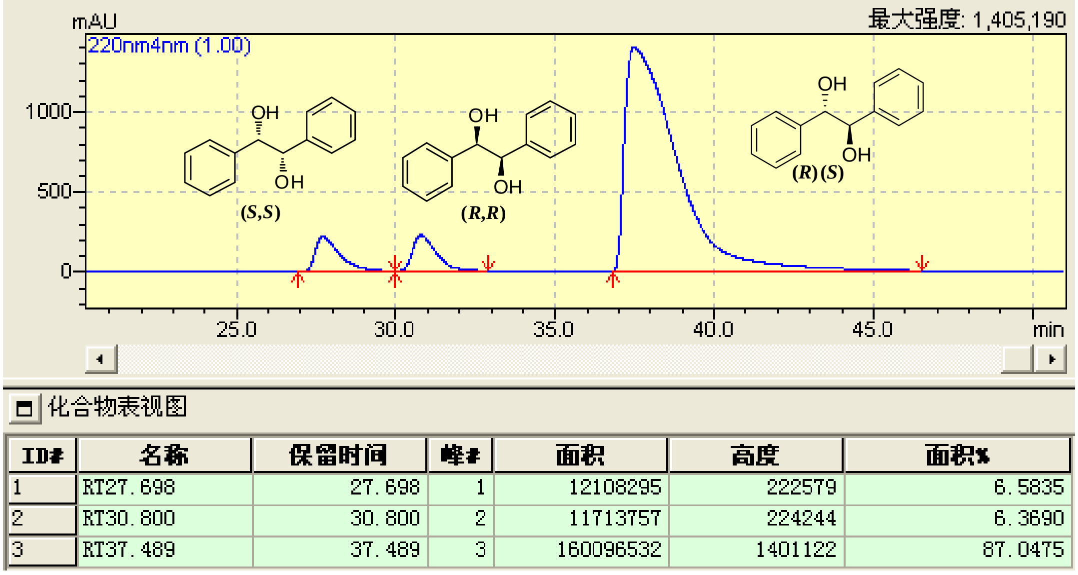
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT20.159	20.159	1	19271527	286551	50.2926
2	RT24.372	24.372	2	19047281	210991	49.7074



化合物表视图

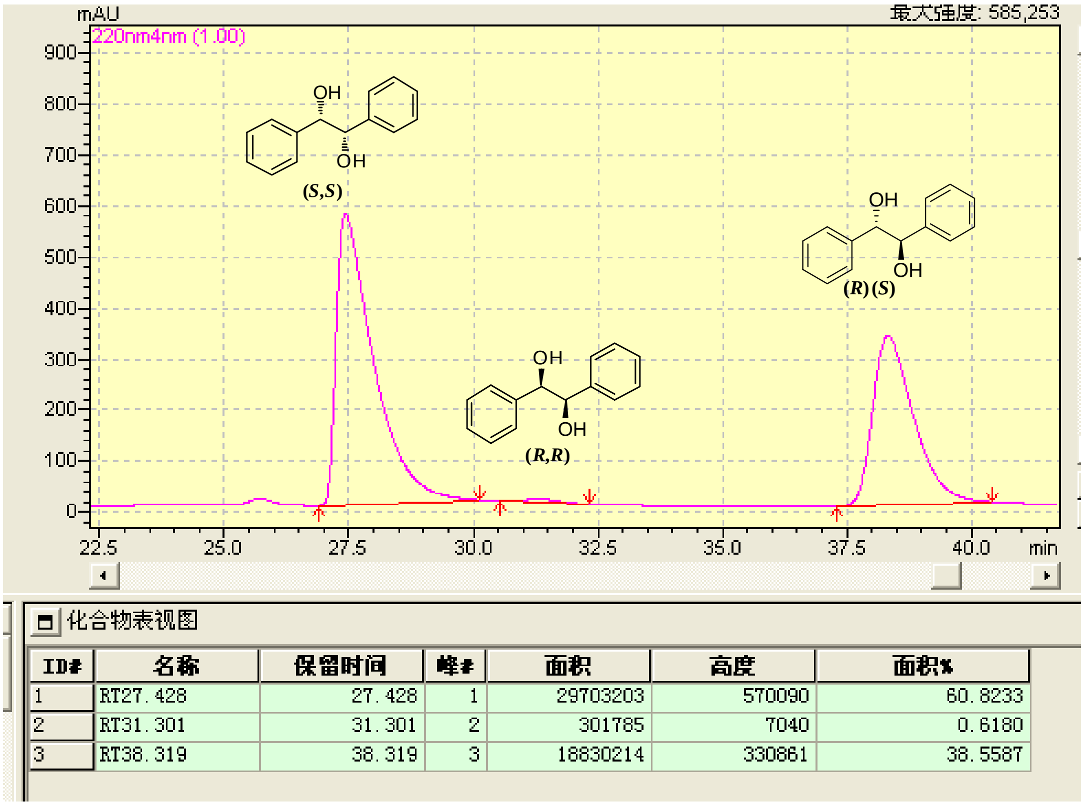
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT20.988	20.988	1	8117917	142957	97.1620
2	RT26.298	26.298	2	237117	5474	2.8380

Asymmetric transfer hydrogenation of Benzil (Daicel OJ-H chiralcel columns: 0.5 mL/min, hex/IPA = 90:10. d:r = 1.6 : 1) (ref: *J. Am. Chem. Soc.*, 2011, **133**, 14960)



化合物表视图

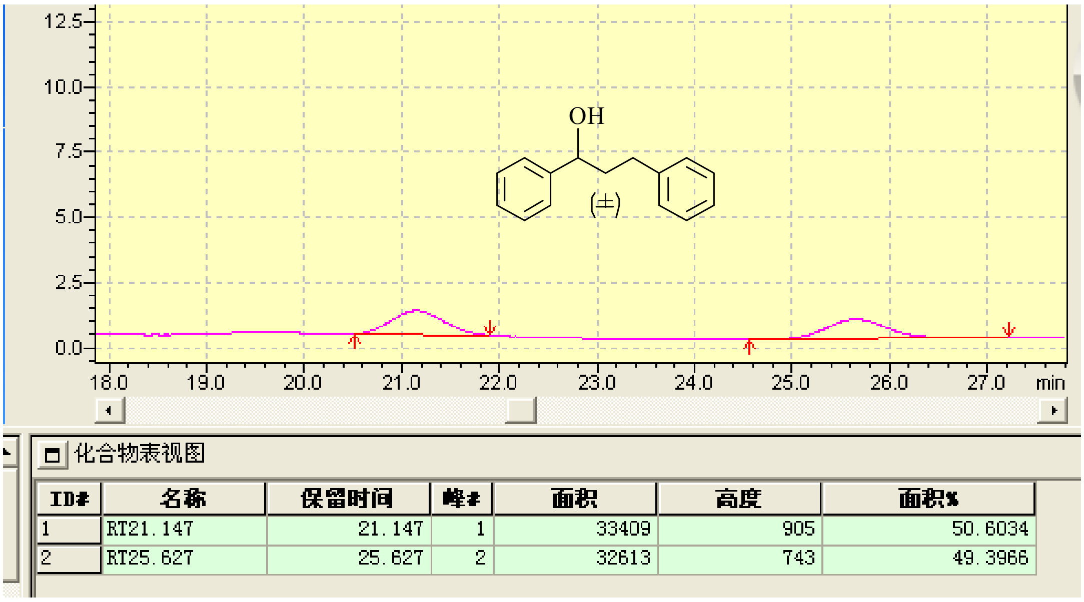
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT27.698	27.698	1	12108295	222579	6.5835
2	RT30.800	30.800	2	11713757	224244	6.3690
3	RT37.489	37.489	3	160096532	1401122	87.0475



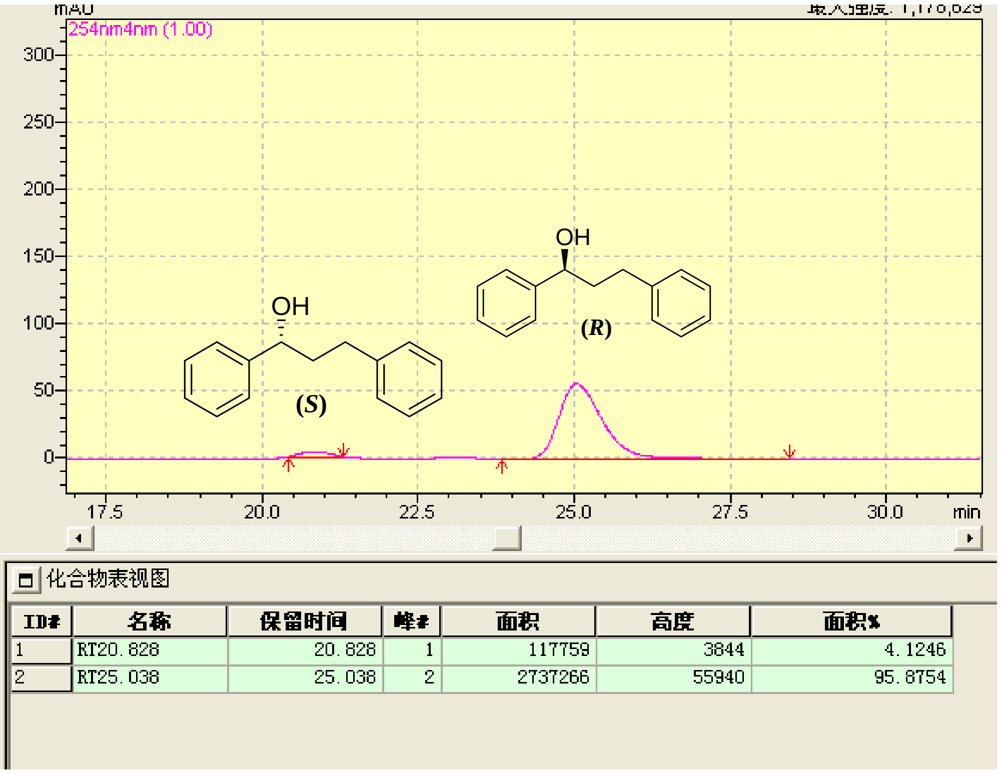
化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT27.428	27.428	1	29703203	570090	60.8233
2	RT31.301	31.301	2	301785	7040	0.6180
3	RT38.319	38.319	3	18830214	330861	38.5587

Asymmetric transfer hydrogenation of E-Chalcone.(Daicel OD-H chiralcel columns: 1 mL/min, hex/IPA=96:4) (ref: *Chem. Eur. J.*, 2008, **14**, 2209)

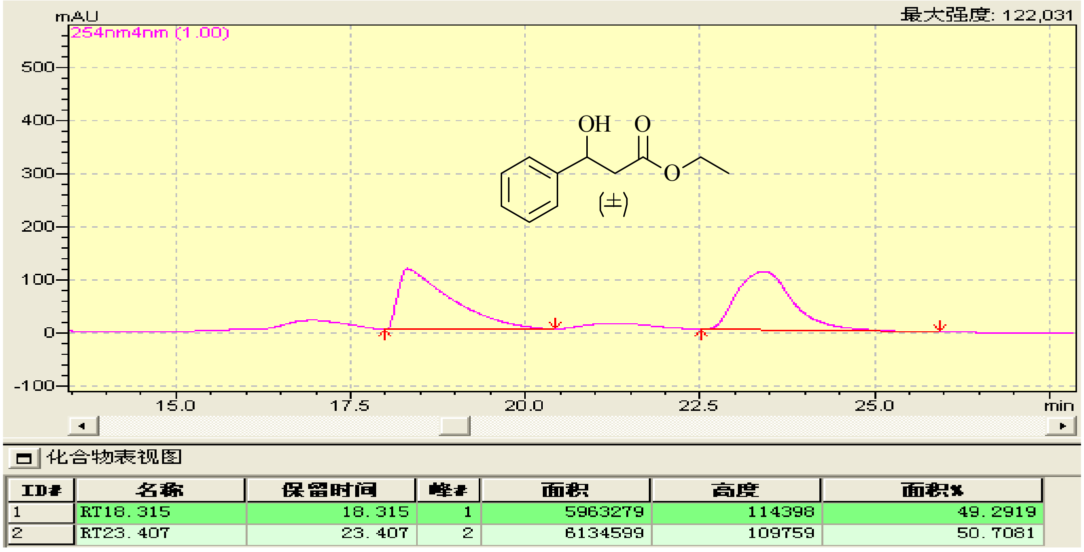


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21. 147	21. 147	1	33409	905	50. 6034
2	RT25. 627	25. 627	2	32613	743	49. 3966

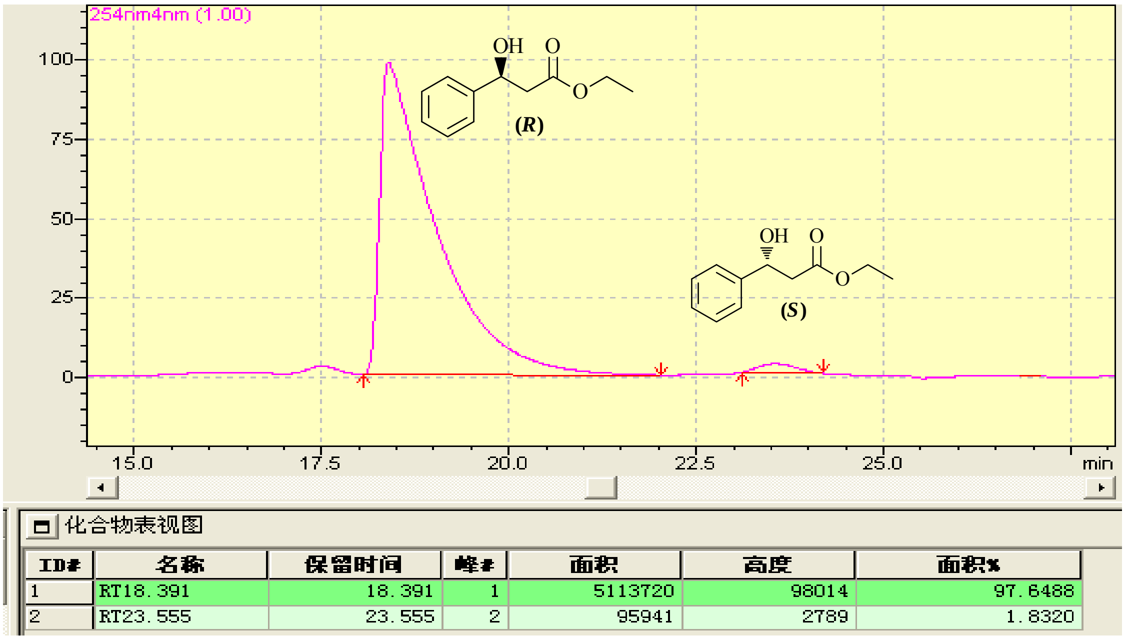


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT20. 828	20. 828	1	117759	3844	4. 1246
2	RT25. 038	25. 038	2	2737266	55940	95. 8754

Asymmetric transfer hydrogenation of Ethyl Benzoylacetate. (Daicel OB-H chiralcel columns: 0.5 mL/min, hex/IPA=90:10) (ref: *J. Org. Chem.* **2001,** *66,* 8682)



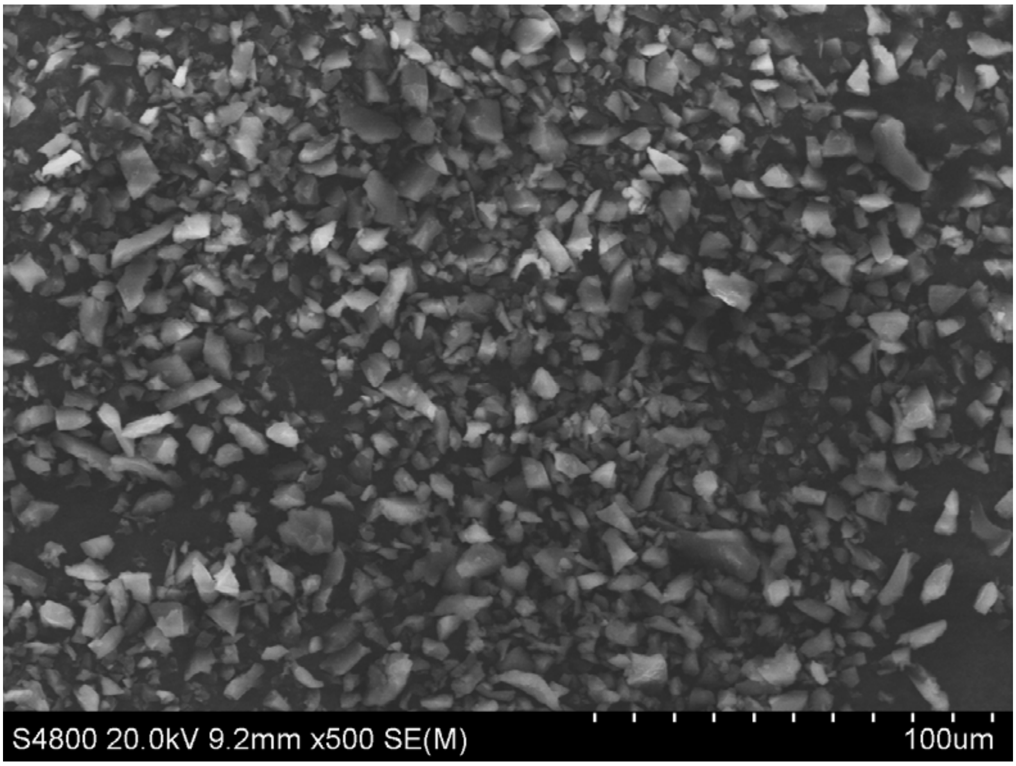
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT18.315	18.315	1	5963279	114398	49.2919
2	RT23.407	23.407	2	6134599	109759	50.7081



ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT18.391	18.391	1	5113720	98014	97.6488
2	RT23.555	23.555	2	95941	2789	1.8320

Figure S9. The SEM (a) and TEM (b) images of the catalyst **3.**

(a)



(b)

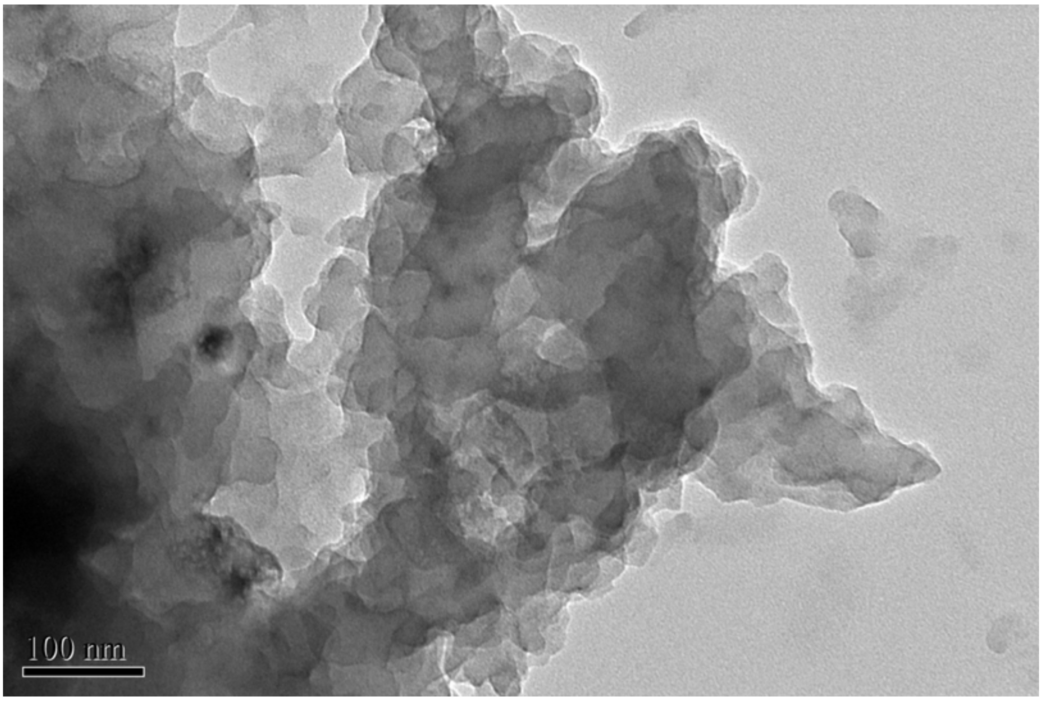
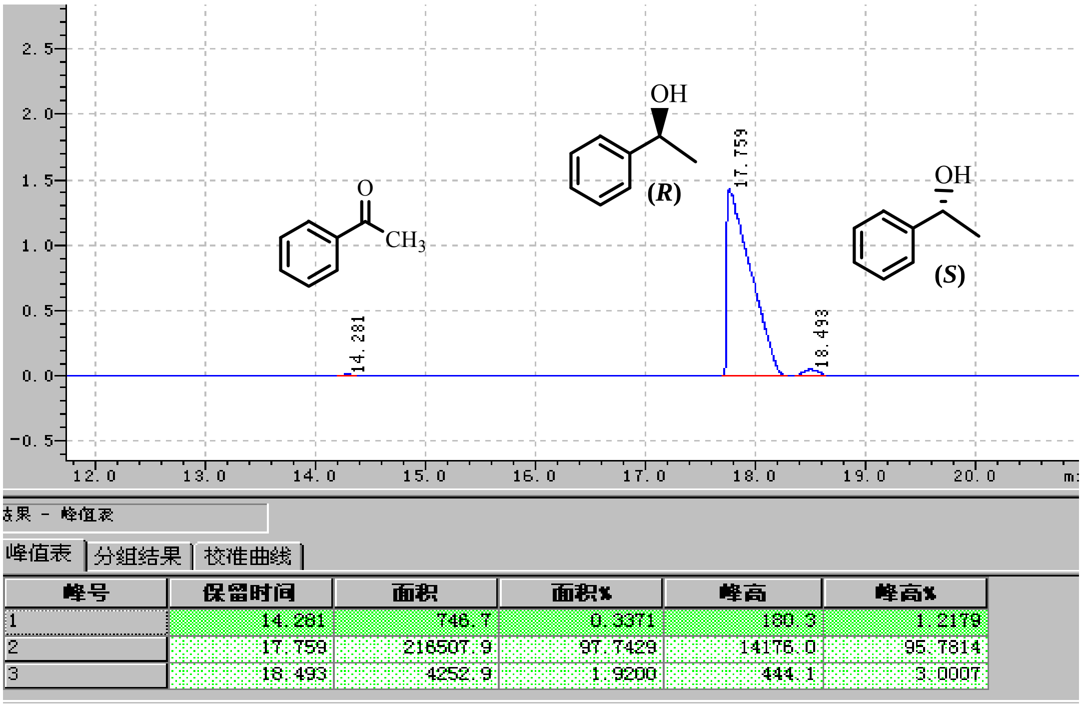


Figure S10. Asymmetric transfer hydrogenation using 10.0 mmol of acetophenone as a substrate.



峰号	保留时间	面积	面积%	峰高	峰高%
1	14.281	746.7	0.3371	180.3	1.2179
2	17.759	216507.9	97.7429	14176.0	95.7814
3	18.493	4252.9	1.9200	444.1	3.0007