

Supporting Information for

**A Bifunctionalized Organic-Inorganic Hybrid Silica: Synergistic Effect
Enhances Enantioselectivity**

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Experimental

1. General

All experiments, which are sensitive to moisture or air, were carried out under an Ar atmosphere using the standard Schlenk techniques. (*S,S*)-1,2-diphenylenediamine [(*S,S*)-DPEN] and [Cp*IrCl₂]₂ were purchased from Sigma-Aldrich Company Ltd. Compound [(*S,S*)-DPEN-SO₂Ph(CH₂)₂Si(OMe)₃] and the pure materials IBOIHS were synthesized according to the reported literature [a) *Chem Commun.* **2011**, 47, 2583. b) *Chem. Commun.* **2010**, 46, 6947.].

2. Characterization

Ir and Rh loading amounts in the catalysts were 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 CuK α radiation. Scanning electron microscopy (SEM) images were obtained using a JEOL JSM-6380LV microscope operating at 20 kV. 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. 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 ($p/p_0 = 0.05-1.00$). Thermal gravimetric analysis (TGA) was performed with a Perkin-Elmer Pyris Diamond TG analyzer under air atmosphere with a heating ramp of 5 K/min. Solid-state ¹³C (100.5 MHz) and ²⁹Si (79.4 MHz) CP MAS NMR were obtained on a Bruker DRX-400 spectrometer. Elemental analysis was performed with a Carlo Erba 1106 Elemental Analyzer.

3. Preparation of Cp*IrTsDPEN- IBOIHS (3).

Under argon atmosphere, to a stirred suspension of IBOIHS (**1**) (2.0 g) in 20 mL dry toluene was added a solution of TsDPEN-derived silane (**2**) (0.40 g, 0.80 mmol) in 5 mL dry toluene at room temperature. The resulting mixture was refluxed for 24 h. 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 CH₂Cl₂ to afford (*R,R*)-TsDPEN-modified IBOIHS as a white powder. The collected white powder was suspended in 20 mL of CH₂Cl₂ again. To this stirred suspension was added [Cp*IrCl₂]₂ (0.39 g, 0.49 mmol) and excess NEt₃ 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 CH₂Cl₂. After Soxlet extraction in dry CH₂Cl₂ to remove homogeneous and unreacted start materials, the solid was dried under reduced pressure overnight to afford Cp*IrTsDPEN-IBOIHS (**3**) (2.50, 0.58 mmol, 72% relative to **1**) as a light yellow powder. ICP analysis showed that the Ir loading-amount was 44.12 mg (0.23 mmol) per gram catalyst. IR (KBr) cm⁻¹: 3433.3 (s), 3138.5 (s), 2928.7 (w), 2364.4 (w), 2344.4 (w), 1637.5 (w), 1560.8 (s), 1458.6 (s), 1328.1 (w), 1129.8 (s), 1051.0 (s), 921.3 (w), 764.1 (w), 700.4(w), 586.5(w), 485.4 (w); ²⁹Si MAS/NMR (300 MHz): T³ (δ = -68.9 ppm), T² (δ = -59.6 ppm), T¹ (δ = -50.2 ppm); ¹³C CP/MAS (161.9 MHz): 9.8 (CH₂-Si), 14.1 (CH₃-Cp*), 24.3 (PhCH₂, and SiCH₂CH₂CH₂N), 52.4 (CH₃-O, and imidazolium N-CH₂), 73.0, 77.7 (PhN-CH₂), 96.8 (C-Cp), 123.4 (CH of imidazolium) 128.8 (CH-Ph), 136.6 CH of imidazolium) ppm; Elemental analysis (%): C 32.78, H 5.11, N 5.42, S 0.48.

4. Catalytic experiments. A typical procedure was as follows: The catalyst **3** (26.7 mg, 4.0 μmol of Ir based on the ICP analysis), HCO₂Na (0.27 g, 10.0 mmol), ketone (0.40 mmol) and 2.0 mL of water were added in a 10 mL roundbottom flask in turn. The mixture was allowed to react at 40 °C for 30 min to 5 h. During that time, the reaction was monitored constantly by TLC. After completion of the reaction, the catalyst was separated *via* centrifuge (10000 r/min) for the recycle experiment. The aqueous solution was extracted by Et₂O (3 × 3.0 mL). The combined Et₂O was washed with brine twice and dehydrated with Na₂SO₄. After the evaporation of Et₂O, 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 Chiralcel columns (Φ 0.46 × 25 cm).

Figure S1. FT-IR spectra of the IBOIHS (**1**) and the catalyst **3**.

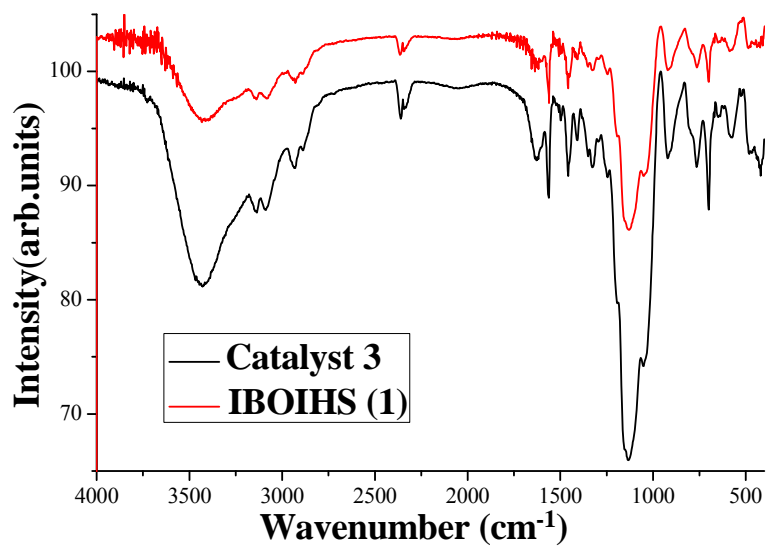


Figure S2. ¹³C CP MAS NMR spectra of the IBOIHS (**1**) and the catalyst **3**.

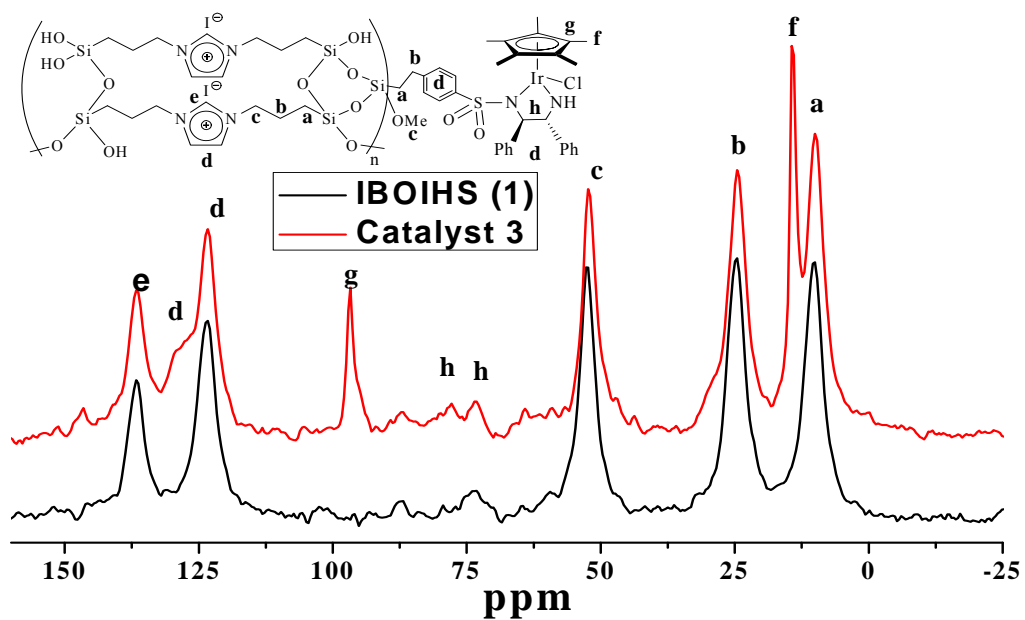


Figure S3. ^{31}Si CP MAS NMR spectra of the pure IBOIHS material and the catalyst **3**.

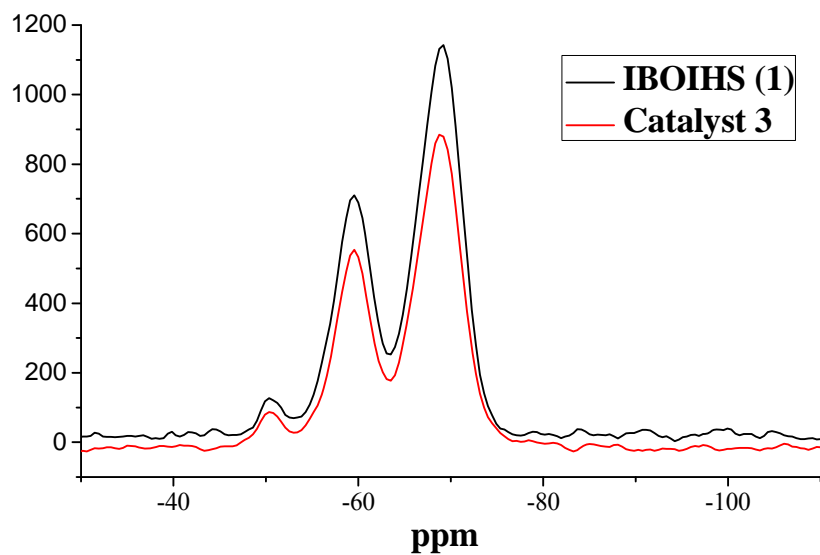
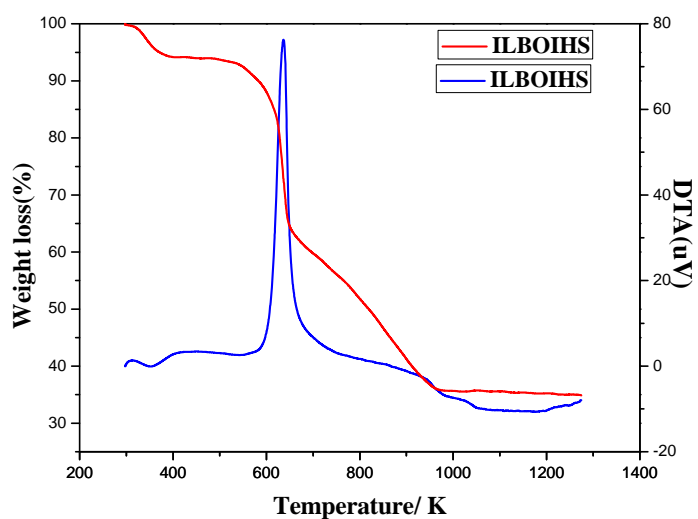
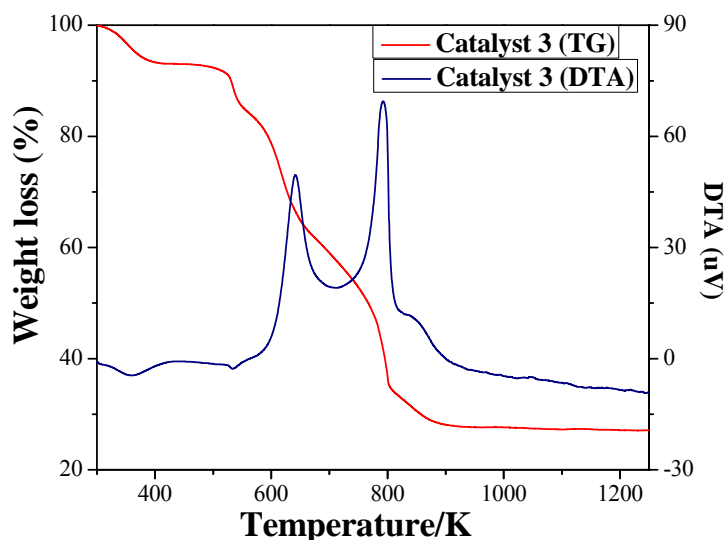


Figure S4. TG/DTA curves of the IBOIHS (**1**) and the catalyst **3**.





Explanation: The TG/DTA curve of the IBOIHS (**1**) was treated in the air as shown in Figure S5. An endothermic peak around 351K with weight loss of 5.8% could be attributed to the release of physical adsorption water. In addition, the weight loss of 58.4% between 453 and 1100K could be assigned to the oxidation of alkyl fragments and parts of imidazolium fragments. When eliminated the contribution of water, the total weight loss the oxidation of alkyl fragments and parts of imidazolium fragments is 62.0% (58.4/94.2).

In sharp contrast to TG/DTA curve of the IBOIHS (**1**), an endothermic peak around 351K with weight loss of 6.9% could be attributed to the release of physical adsorption water. In addition, the weight loss of 65.4% between 453 and 1100K could be assigned to the oxidation of organic moiety (including alkyl fragments, parts of imidazolium fragments and Cp*IrTsDPEN fragments). When eliminated the contribution of water, the total weight loss the oxidation of organic moiety is 70.2% (65.4/93.1).

Thus, in sharp contrast to TG/DTA curve of **1**, the true weight loss of Cp*IrTsDPEN organic molecules is 8.2% (70.2-62.0), meaning the mole amounts of Cp*IrTsDPEN is 28.61 mg/g (0.149 mmol), which was nearly consistent with 28.86 mg (0.150 mmol) of Ir loading per gram catalyst detected by inductively coupled plasma (ICP) optical emission spectrometer analysis.

Figure 5. Nitrogen adsorption-desorption isotherms of the IBOIHS (1) and the catalyst 3.

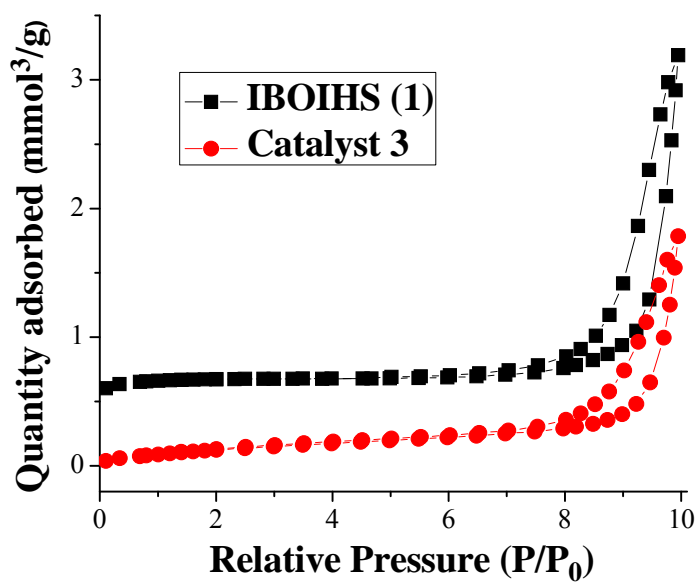


Figure 6. The SEM image of the catalyst 3.

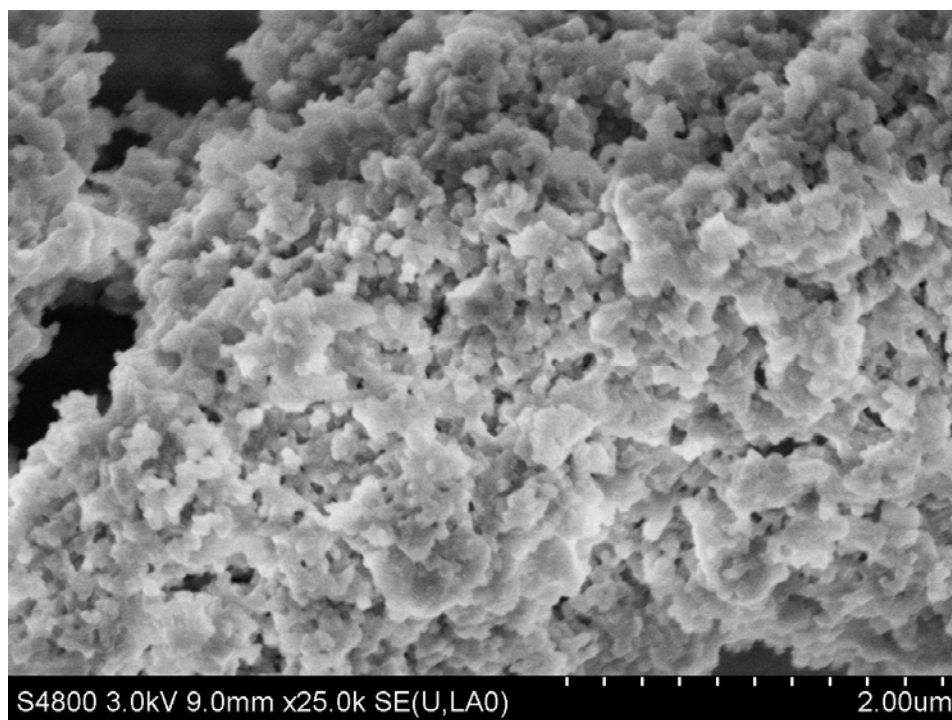


Figure 7. A comparison of the asymmetric transfer hydrogenation of 4-methylacetophenone catalyzed by the catalyst 3 and the homogeneous Cp*IrTsDPEN without Bu₄NBr as a phase transfer catalyst in aqueous medium (Reactions were carried out at an S/C ratio of 100).

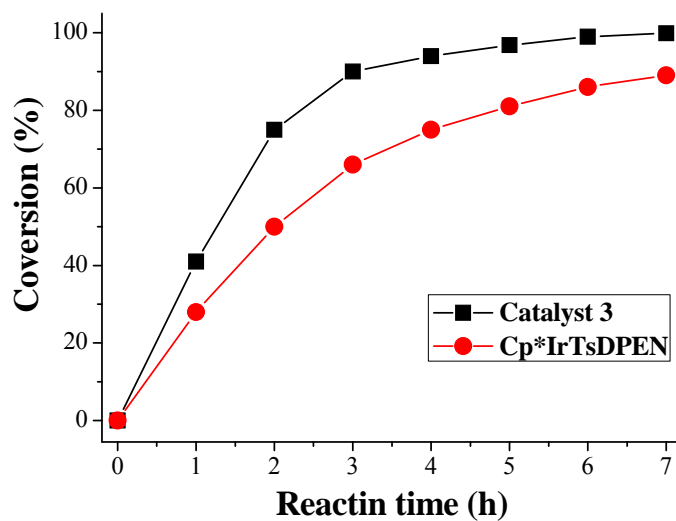
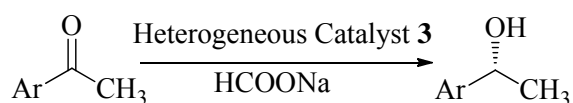


Table 1. Asymmetric transfer hydrogenation of the catalyst **3**.^[a]



Entry	Ar	Time	Conv. (%) ^b	Ee. (%) ^b
1	Ph	3(3.5)	>99 (95)	95(92) ^[c]
2	Ph	3	78	92 ^[d]
3	Ph	3	>99(>99)	92(92) ^[e]
4	4-FPh	3(4)	>99(97)	94(89) ^[c]
5	4-ClPh	3(4)	>99 (99)	90(84) ^[c]
6	4-MePh	7(15)	>99 (96)	92(88) ^[c]
7	4-OMePh	20(24)	>99 (97)	92(91)
8	3-OMePh	5(8)	>99(97)	95(90) ^[c]
9	4-NO ₂ Ph	1.0(2)	>99 (98)	82(73) ^[c]
10	4-CNPh	2(2)	>99	84(84)
11	4-CF ₃ Ph	12	>99	88
12	2-naphthyl	9(10)	>99(99)	83(80)

^[a] Reaction conditions: catalyst **3** (26.7 mg, 4.0 μmol of Ir based on the ICP analysis), HCO₂Na (0.27 g, 10.0 mmol), ketone (0.40 mmol) and 2.0 mL water, reaction temperature (40 °C).

^[b] Determined by chiral GC and HPLC analysis (see SI in Figure S8).

^[c] Data in bracket were obtained in the literature (*Chem. Eur. J.* **2008**, *14*, 2209) using homogeneous Cp*IrDPEN as a catalyst with Bu₄NBr as a phase transfer catalyst.

^[d] Data in bracket were obtained using homogeneous Cp*IrDPEN as a catalyst without Bu₄NBr as a phase transfer catalyst.

^[e] Data were obtained using IBOIHS (or 1,3-dibutyl-1H-imidazolium iodide) plus Cp*IrTsDPEN as a heterogeneous catalyst.

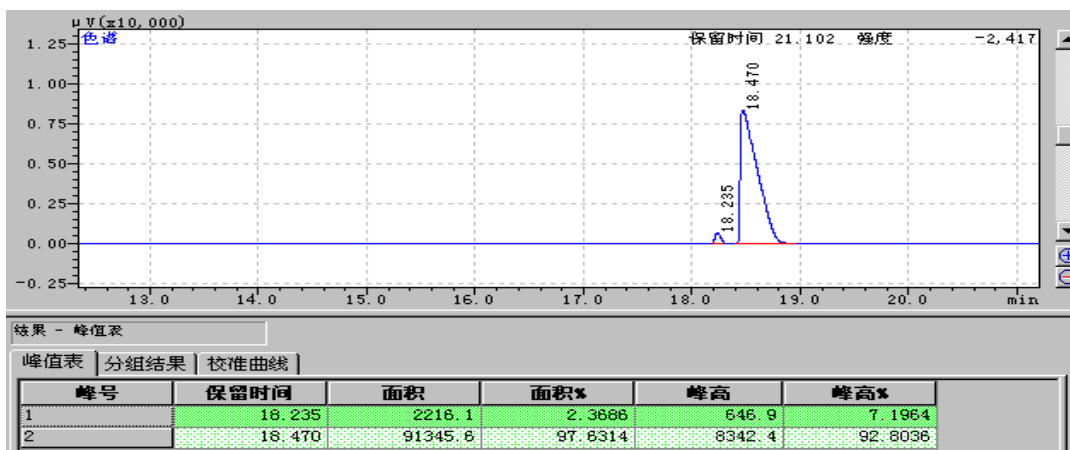
Translation of Chinese to English is as follows:

Peak	RetTime [min]	Heigh	Area	Concentration	half-width
1	20.773	1109	5632.2	49.9035	5.08
2	21.187	1099	5654.0	50.0965	5.14
总计:		Σ=2208	Σ=11286.2	Σ=100.0000	

Peak	RetTime [min]	Area	Area%	Heigh	Heigh%
1	18.474	235819.9	92.0500	13927.2	79.0895
2	19.395	9109.7	3.5589	1042.4	5.9806

Figure S8. Asymmetric transfer hydrogenation of the catalyst **3**.

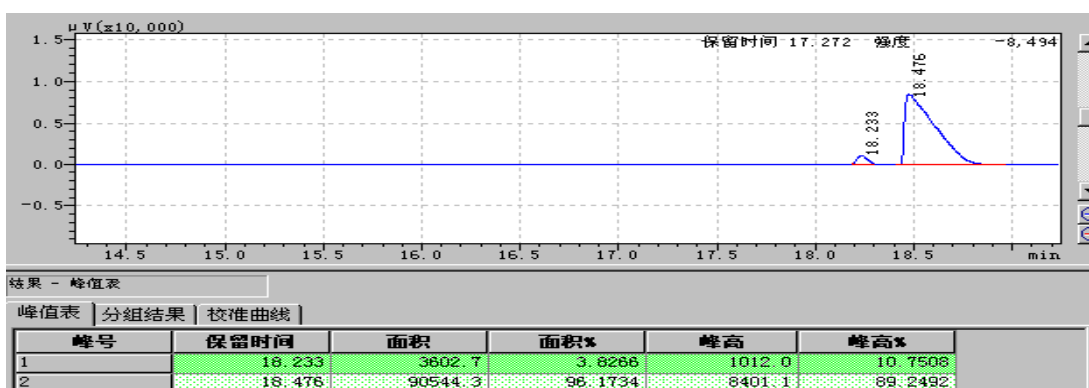
Asymmetric transfer hydrogenation of acetophenone using **3** as a catalyst.



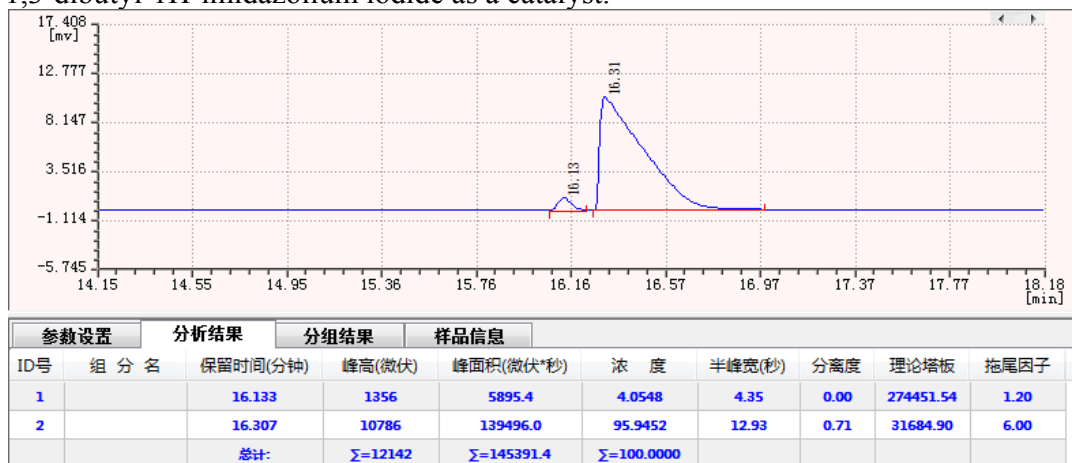
Asymmetric transfer hydrogenation of acetophenone using **3** as a catalyst without Bu₄NBr.



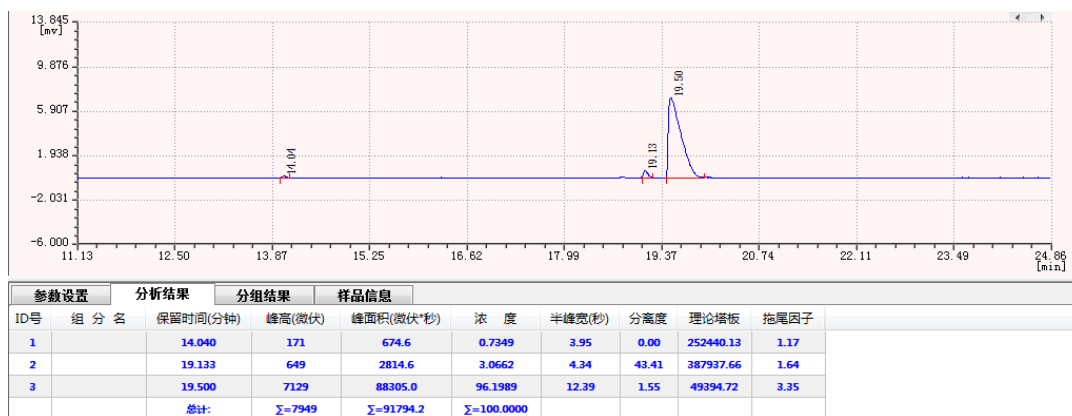
Asymmetric transfer hydrogenation of acetophenone using IBOIHS (**1**) plus Cp*IrTsDPEN as a catalyst.



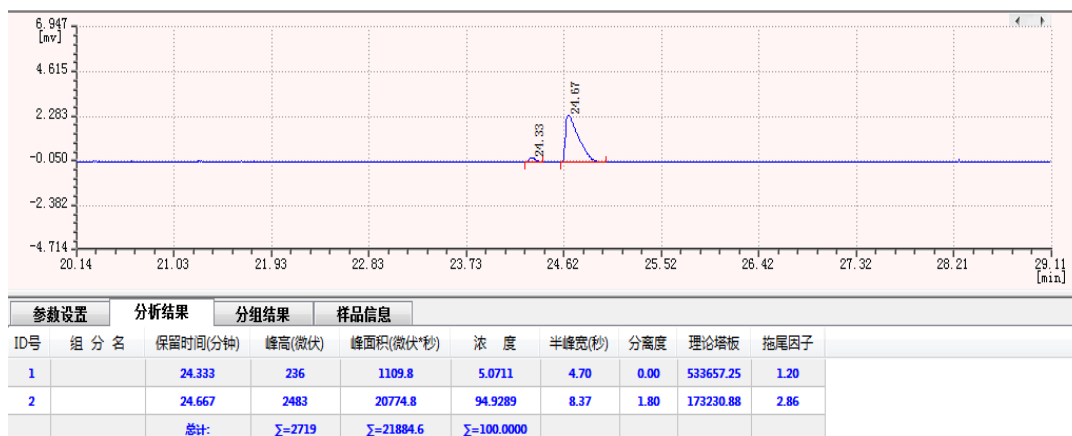
Asymmetric transfer hydrogenation of acetophenone using Cp*IrTsDPEN plus 1,3-dibutyl-1H-imidazolium iodide as a catalyst.



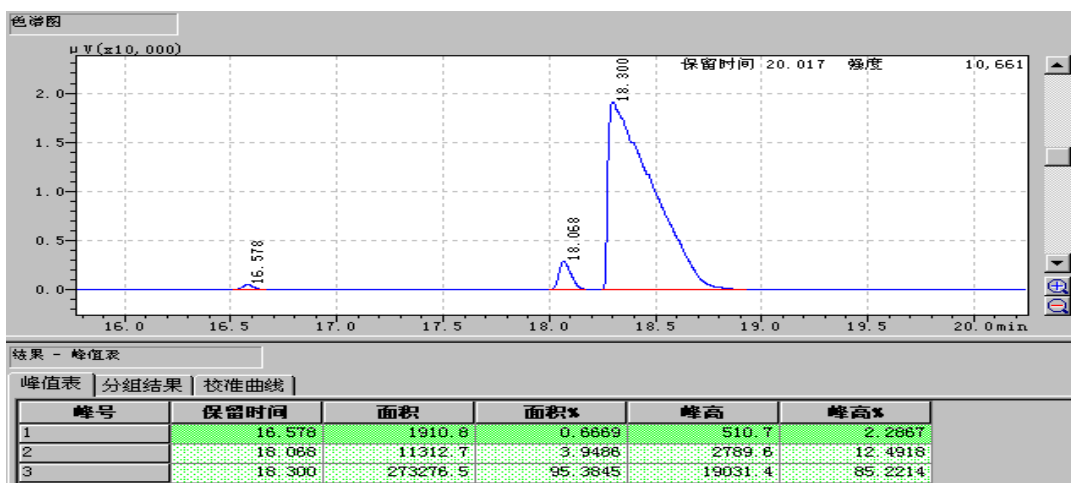
Asymmetric transfer hydrogenation of 4-fluoroacetophenone using **3** as a catalyst.



Asymmetric transfer hydrogenation of 4-chloroacetophenone using **3** as a catalyst.



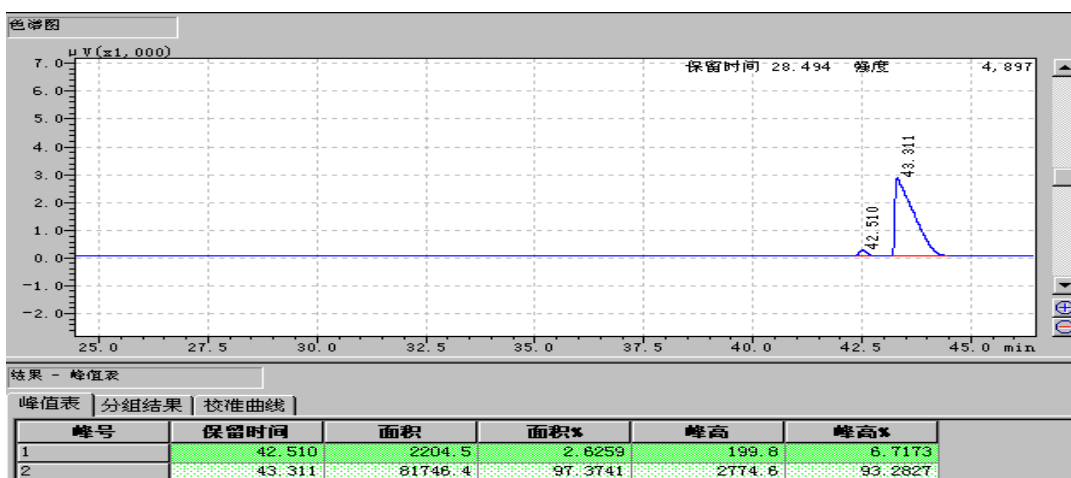
Asymmetric transfer hydrogenation of 4-methylacetophenone using **3** as a catalyst.



Asymmetric transfer hydrogenation of 4-methoxyacetophenone using **3** as a catalyst.



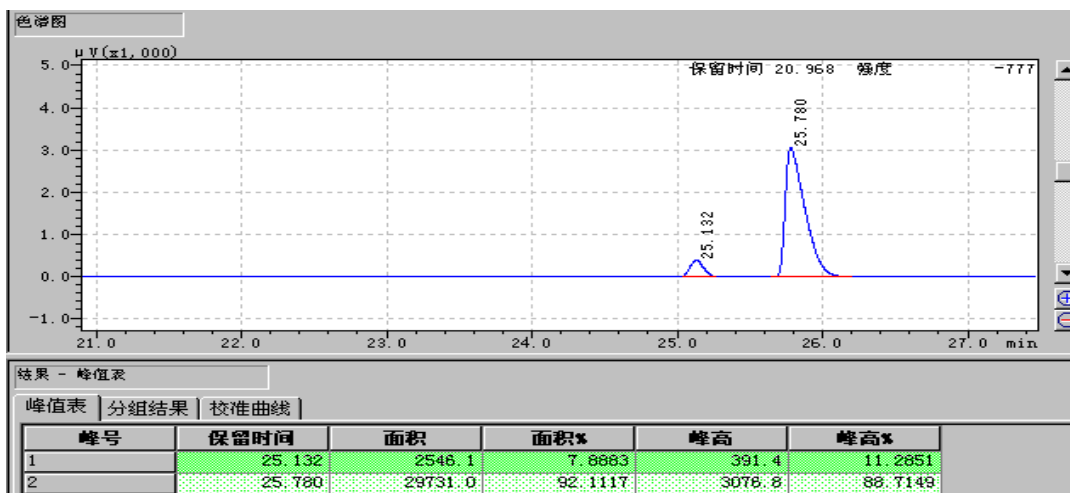
Asymmetric transfer hydrogenation of 3-methoxyacetophenone using **3** as a catalyst.



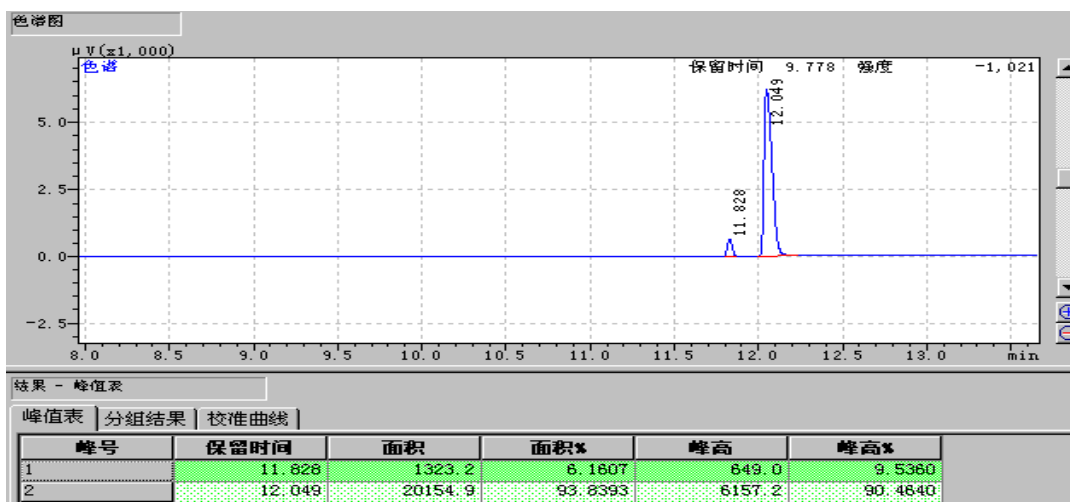
Asymmetric transfer hydrogenation of 4-nitroacetophenone using **3** as a catalyst.



Asymmetric transfer hydrogenation of 4-cyanoacetophenone using **3** as a catalyst.



Asymmetric transfer hydrogenation of 4-(trifluoromethyl)acetophenone.



Asymmetric transfer hydrogenation of 2-acetonaphthone. (Daicel OJ-H chiralcel columns: 1.0 mL/min, 2-propanol: n-hexane=7:93, T=40 °C.) ref: [Liu, P. N.; Gu, P. M.; Wang F.; Tu, Y. Q. Org. Lett., 2004, 6, 169.].

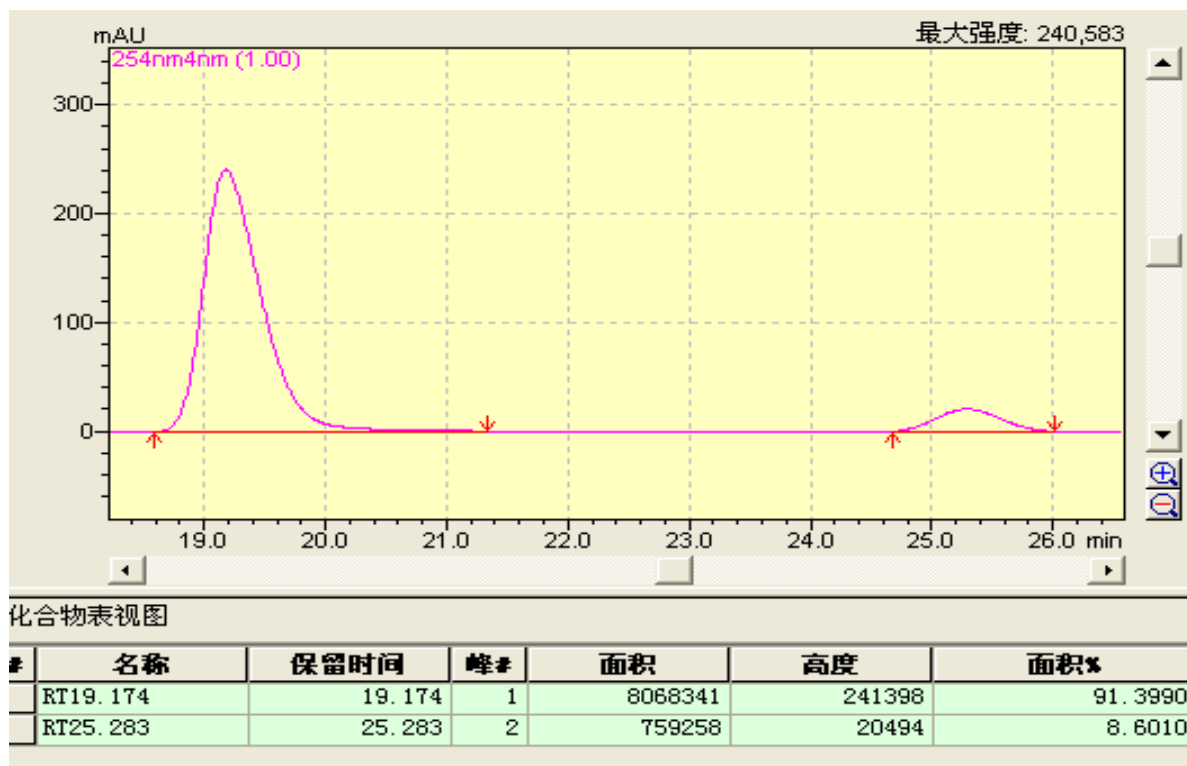


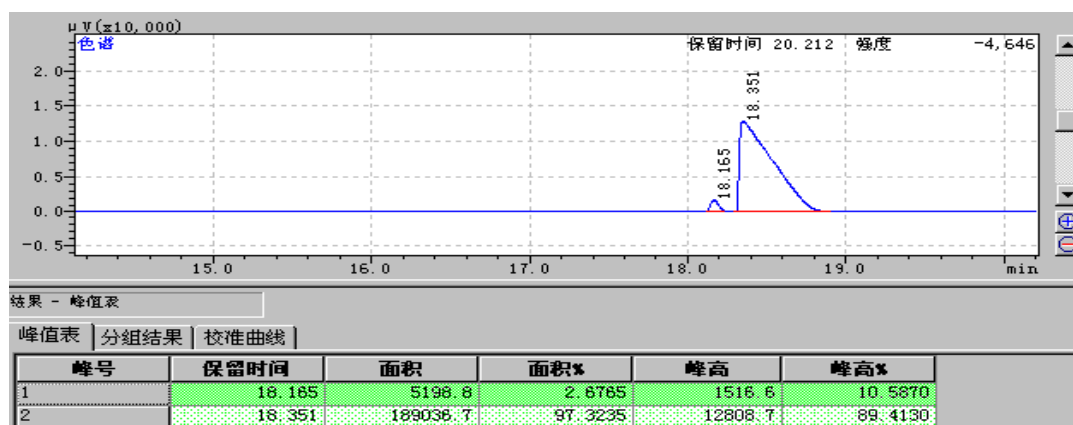
Table S1. Reusability of the catalyst **3** for asymmetric transfer hydrogenation of acetophenone.^a

Run time	1	2	3	4	5	6	7	8	9	10	11
Conv. [%]	99.9	99.9	99.1	99.9	99.9	99.9	97.6	99.9	99.9	99.5	99.2
ee [%]	95.3	94.6	94.7	94.5	94.4	94.4	94.5	94.2	94.2	94.2	93.5

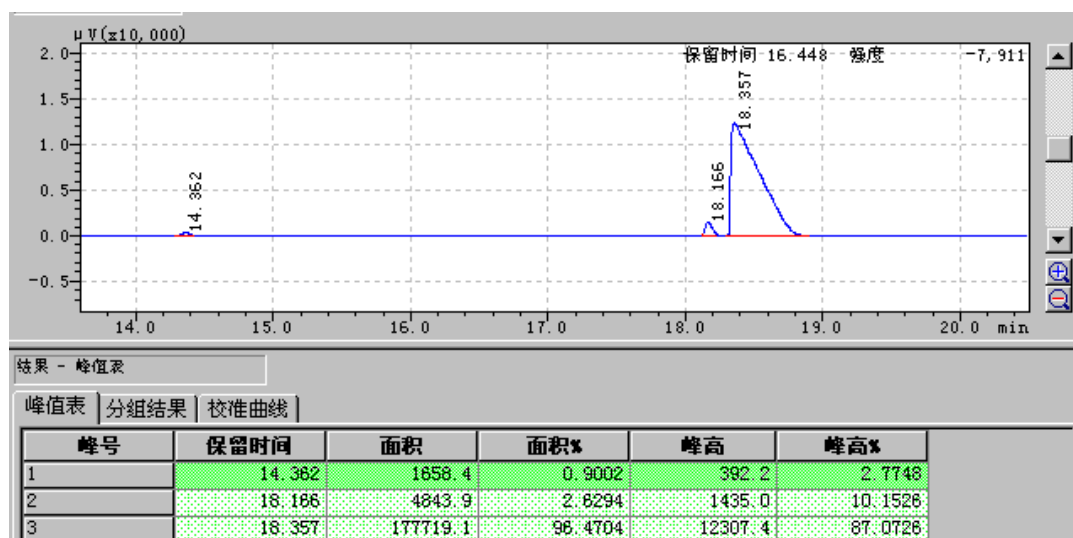
^[a] Reaction conditions: catalyst **3** (26.7 mg, 4.0 μmol of Ir based on the ICP analysis), HCO₂Na (0.27 g, 10.0 mmol), ketone (0.40 mmol) and 2.0 mL water, reaction temperature (40 °C). ^[b] Determined by chiral GC analysis (Fig. S9).

Figure S9. Reusability of the catalyst **3** using acetophenone as a substrate.

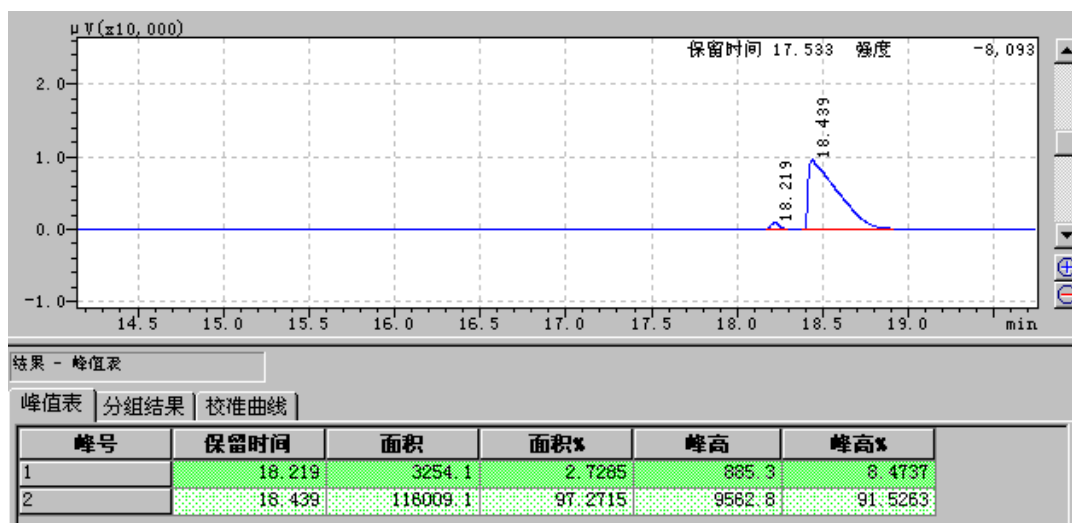
Recycle 2 of the catalyst **3** using acetophenone as a substrate.



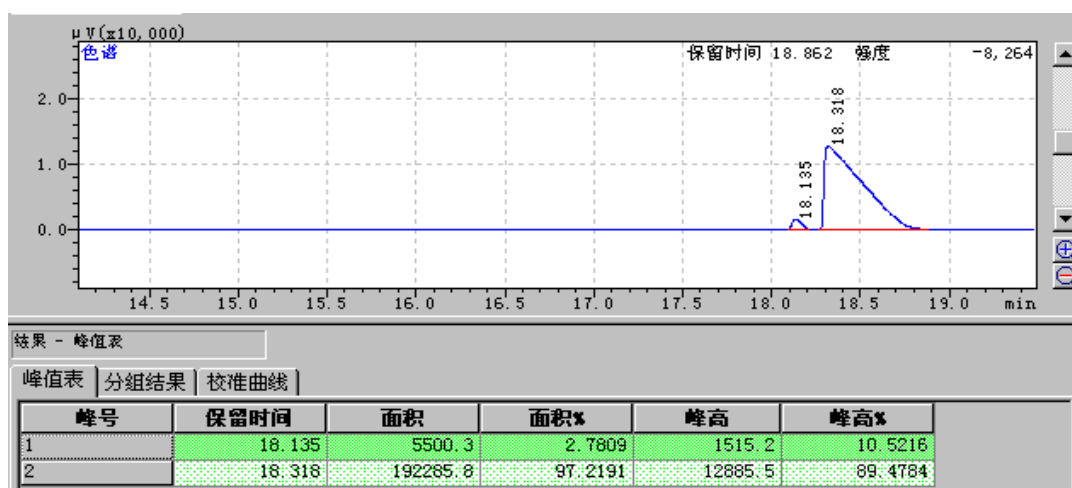
Recycle 3 of the catalyst **3** using acetophenone as a substrate.



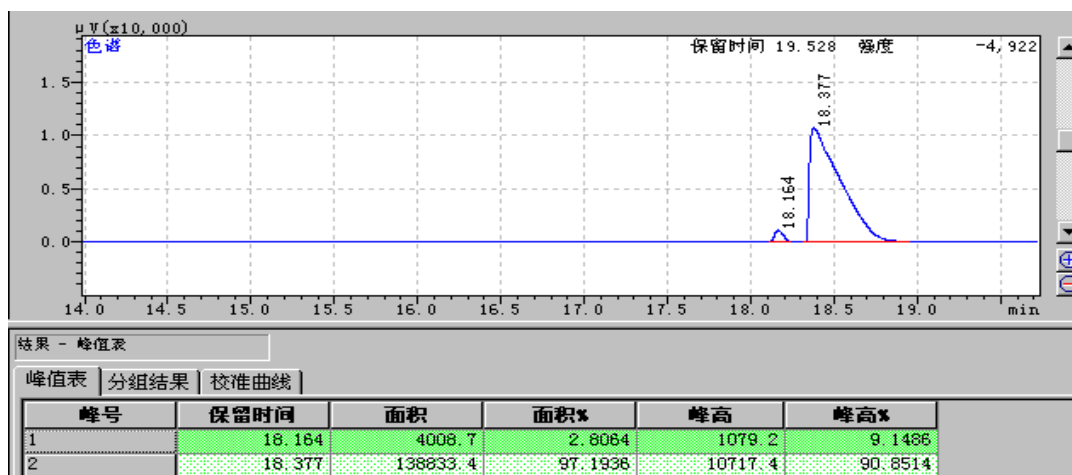
Recycle 4 of the catalyst **3** using acetophenone as a substrate.



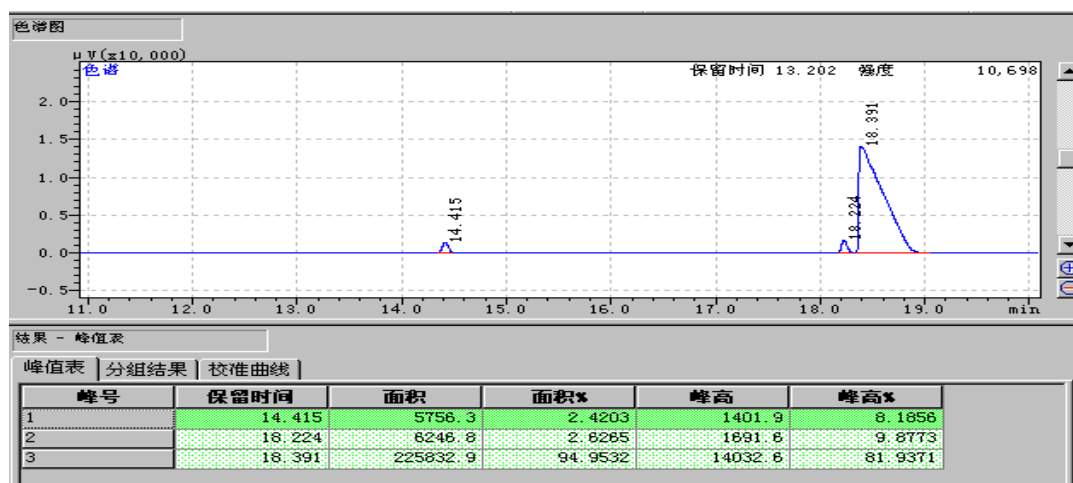
Recycle 5 of the catalyst **3** using acetophenone as a substrate.



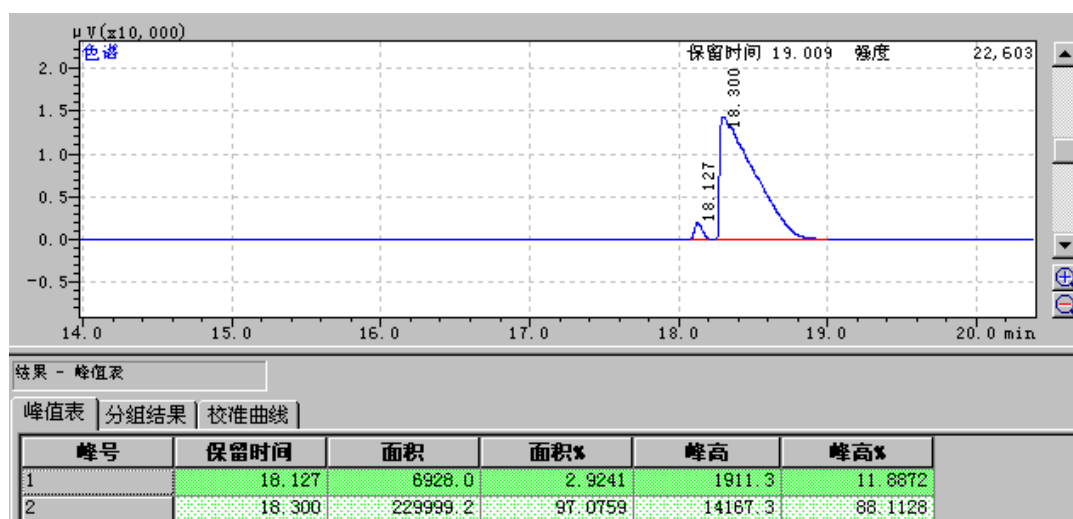
Recycle 6 of the catalyst **3** using acetophenone as a substrate.



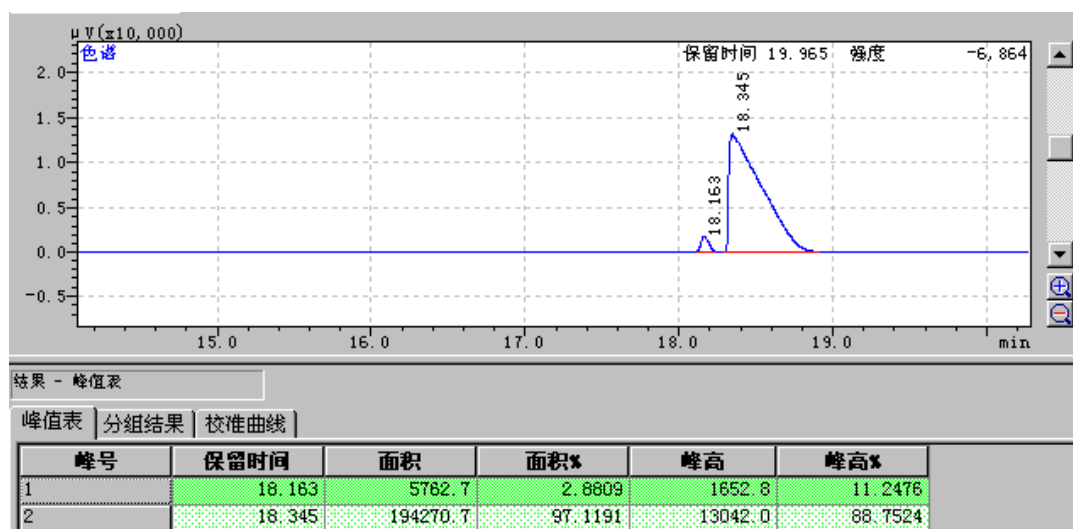
Recycle 7 of the catalyst **3** using acetophenone as a substrate.



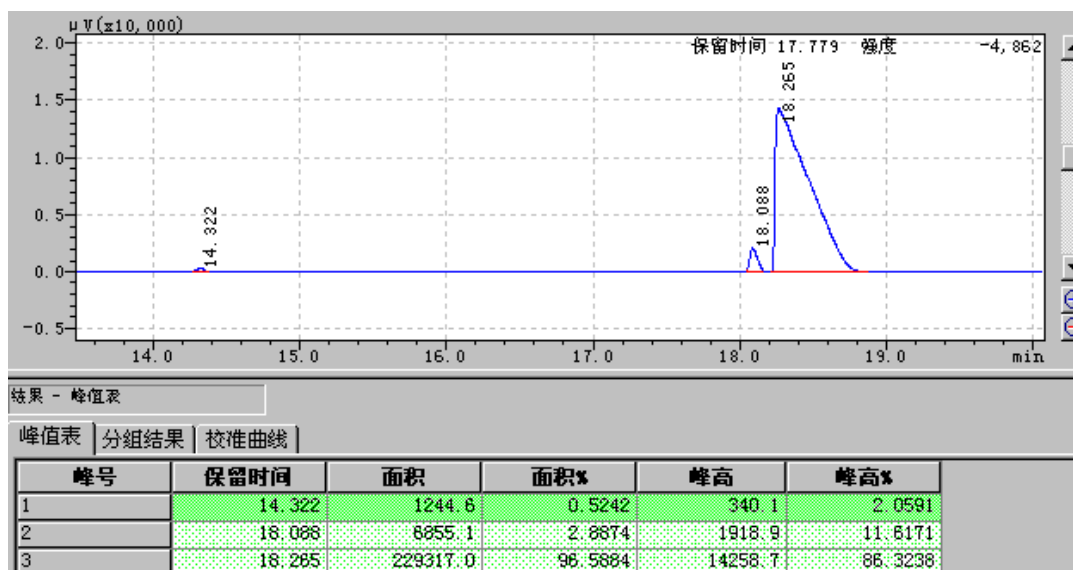
Recycle 8 of the catalyst **3** using acetophenone as a substrate.



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



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



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

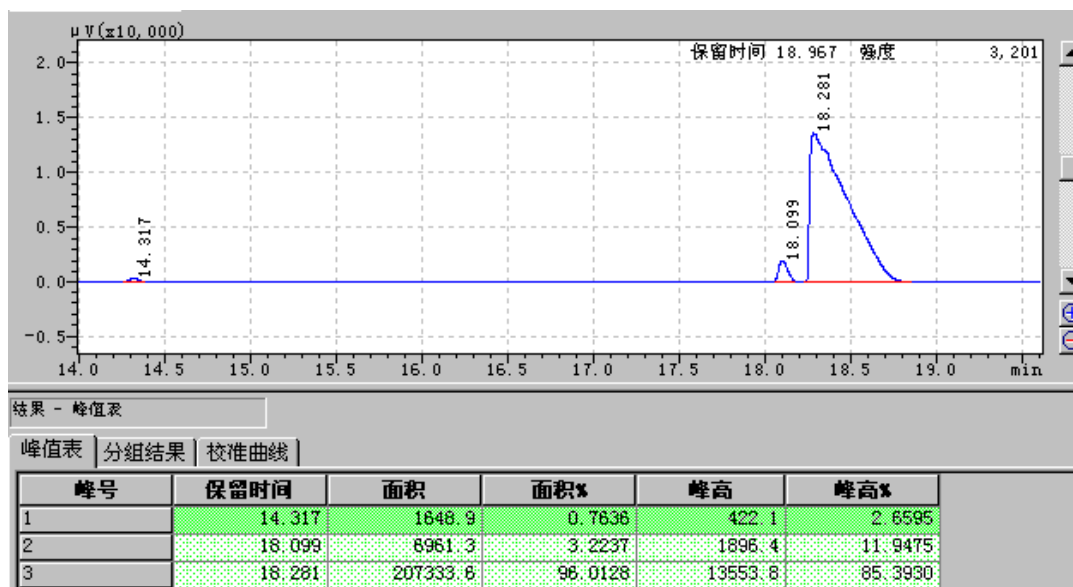
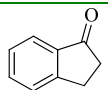
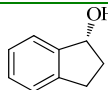
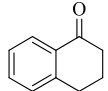
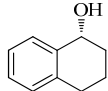
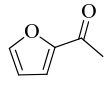
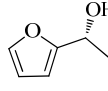
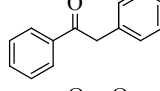
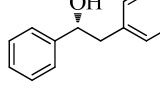
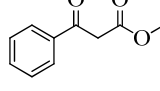
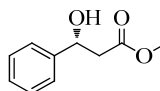
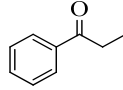
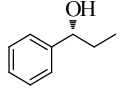
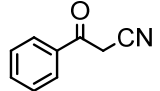
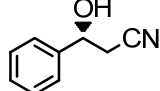


Table 2. Scope of **3**-catalyzed asymmetric transfer hydrogenation.^[a]

Entry	Substrate	Product	Time	Conv (%)	Ee (%) ^[b]
1			7 (8)	>99	96(95) ^[c]
2			7 (8)	>99	98(97) ^[c]
3			1 (1.5)	>99	97(96) ^[c]
4			6	>99	93
5			6 (7)	>99	92(67) ^[c]
6			3	>99	92
7			18	>99	92

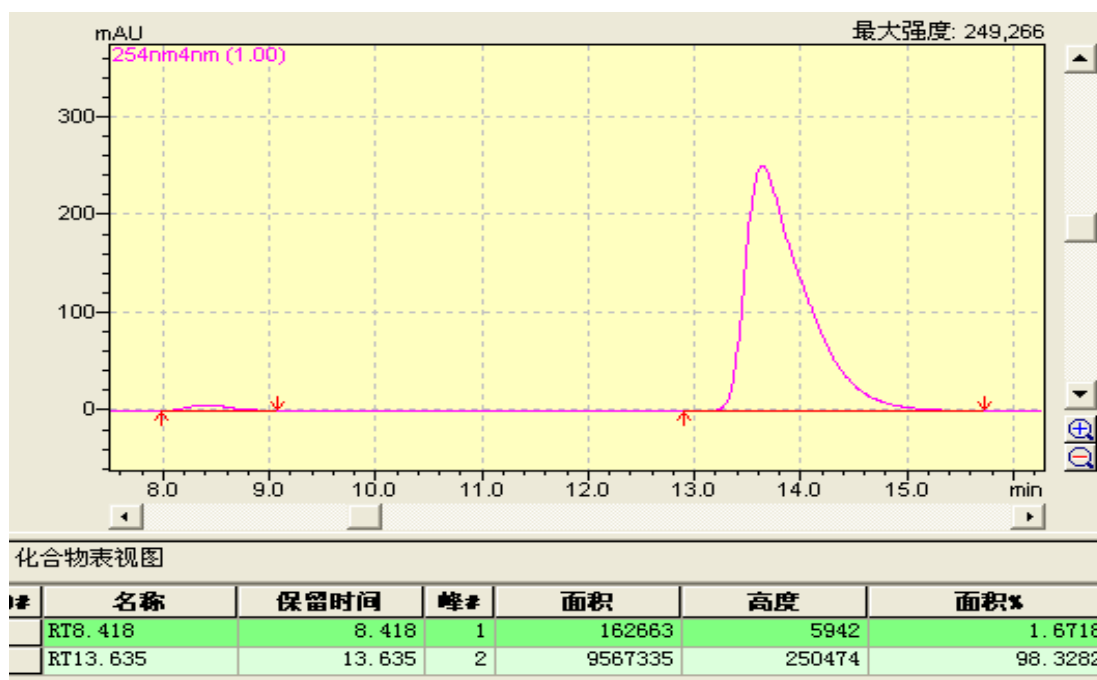
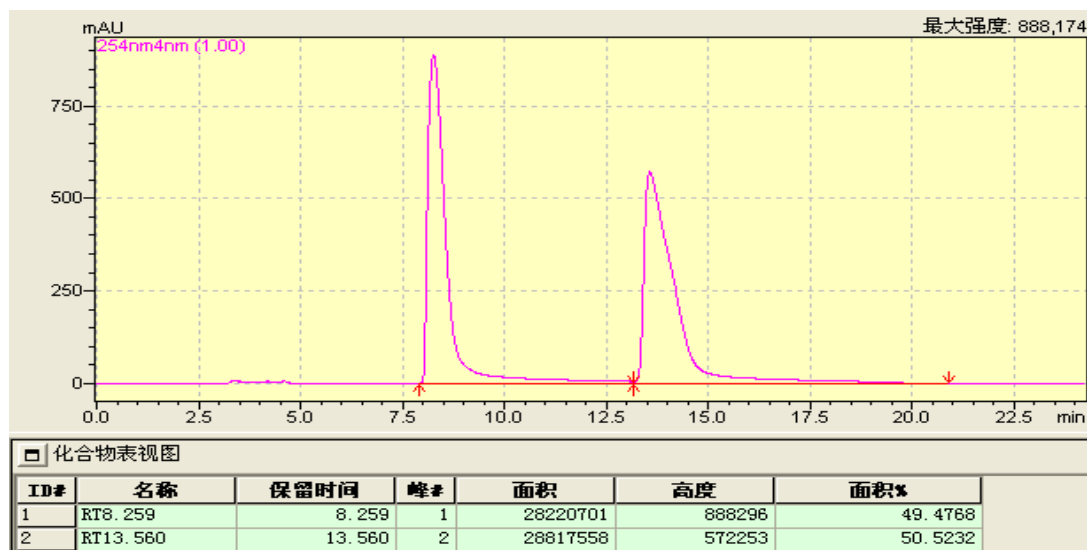
^[a] Reaction conditions: catalyst **3** (26.7 mg, 4.0 μmol of Ir based on the ICP analysis), HCO_2Na (0.27 g, 10.0 mmol), ketone (0.40 mmol) and 2.0 mL water, at 40 °C for 1.0-18.0 h.

^[b] Determined by chiral GC and HPLC analysis (Fig. S10).

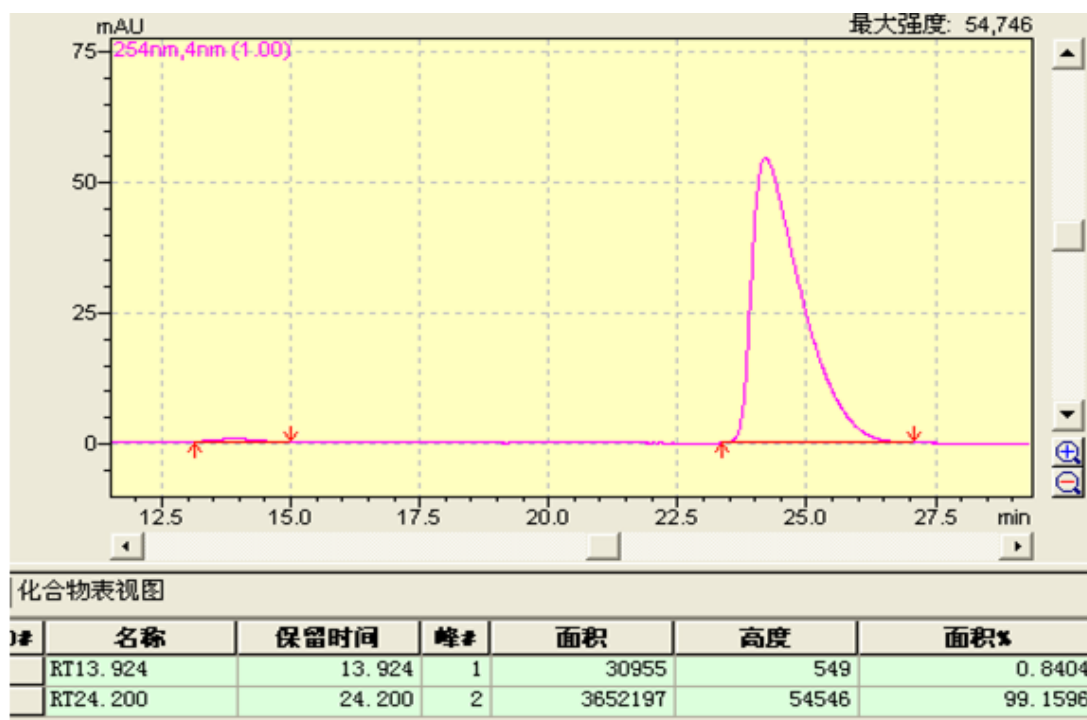
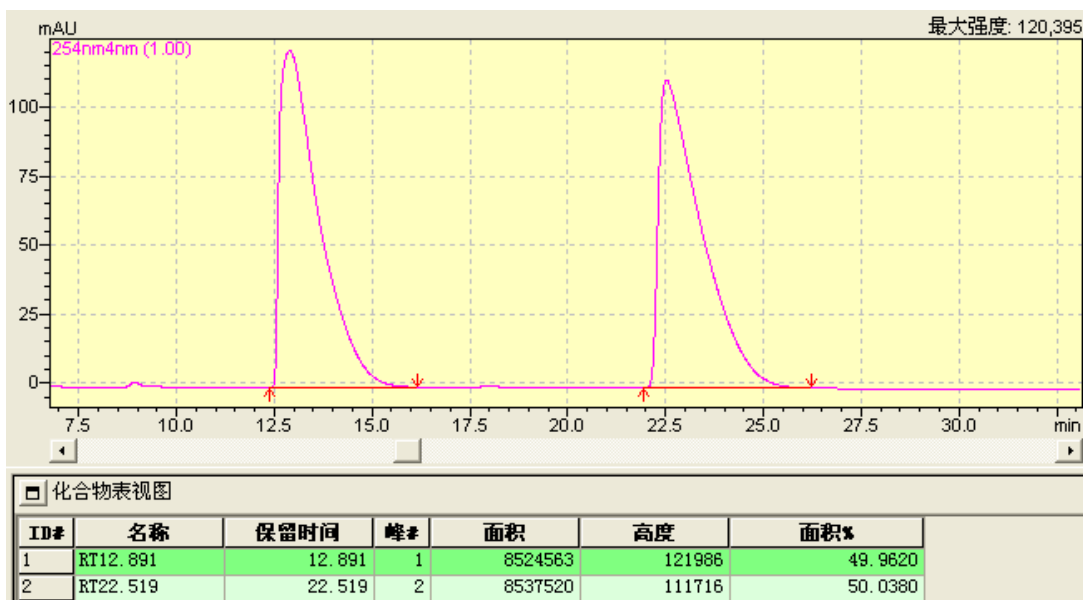
^[c] Data in bracket were obtained in the literature using homogeneous $\text{Cp}^*\text{IrTsDPEN}$ as a catalyst with Bu_4NBr as a phase transfer catalyst.^[7a]

Figure S10. Scope of **3**-catalyzed asymmetric transfer hydrogenation.

Asymmetric transfer hydrogenation of 1-indanone (S: HPLC analysis with a UV-Vis detector using a Daicel OB-H chiralcel columns(Φ 0.46 x 25 cm), Hexane/2-propanol 95:5, 1.0 mL/min, 254 nm, 25 °C) (ref: *Org. Lett.* **2004**, 6, 169).



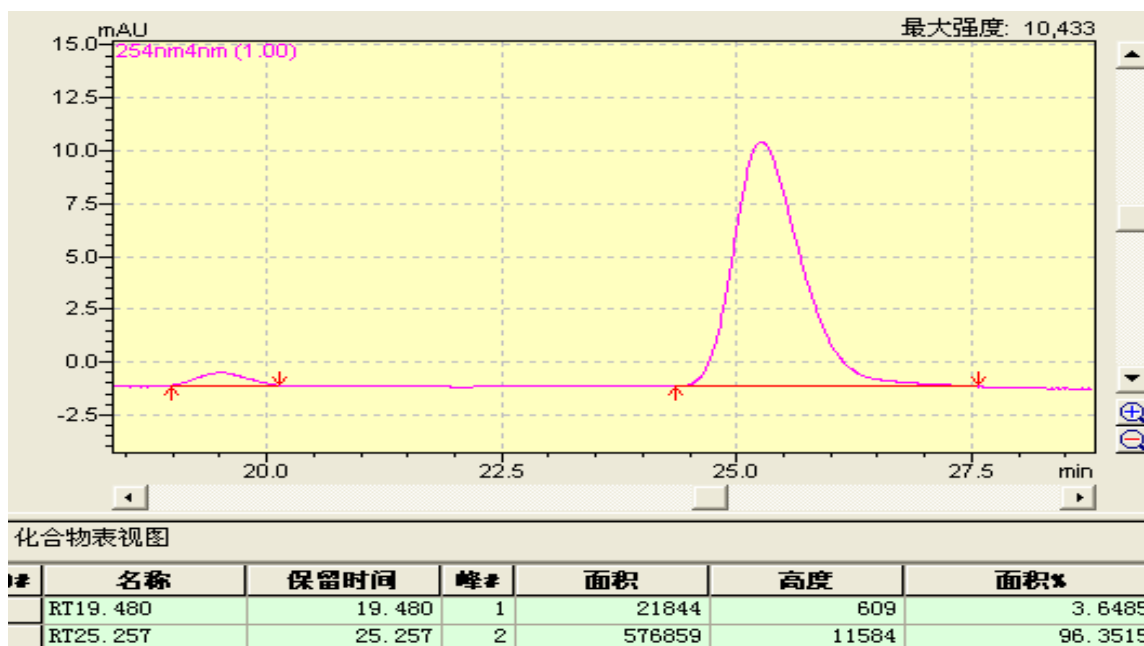
Asymmetric transfer hydrogenation of 1-teralone (S: HPLC analysis with a UV-Vis detector using a Daicel OB-H chiralcel columns(Φ 0.46 x 25 cm), Hexane/2-propanol 98.5:1.5, 1.0 mL/min, 254 nm, 25 °C) (ref: *Org. Lett.* **2004**, 6, 169).



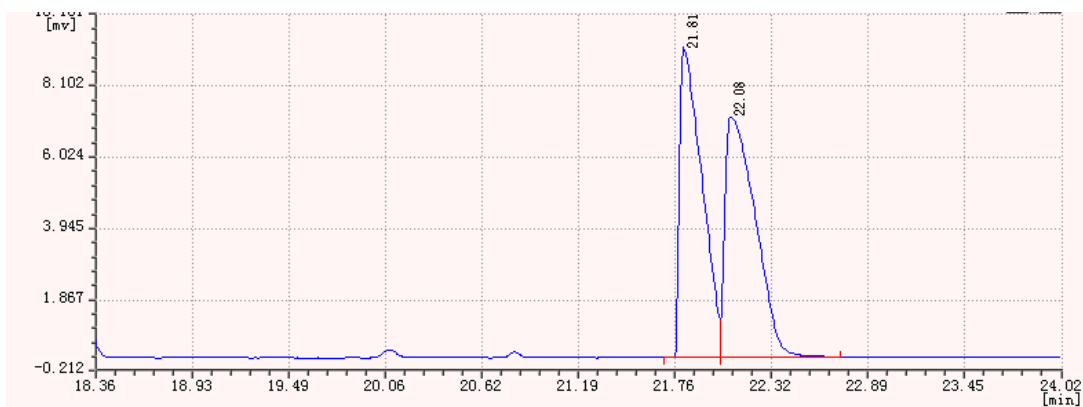
Asymmetric transfer hydrogenation of 2-furyl methyl ketone. (ref: *Org. Lett.* **2004**, 6, 169).



Asymmetric transfer hydrogenation of 1,2-diphenylethanone. (S: HPLC analysis with a UV-Vis detector using a Daicel OD-H chiralcel columns.(Φ 0.46 x 25 cm) Hexane/2-propanol 98:2, 1 mL/min, 254 nm, 25 °C) (ref: *Chem. Eur. J.*, 2008, **14**, 2209).



Asymmetric transfer hydrogenation of propiophenone.

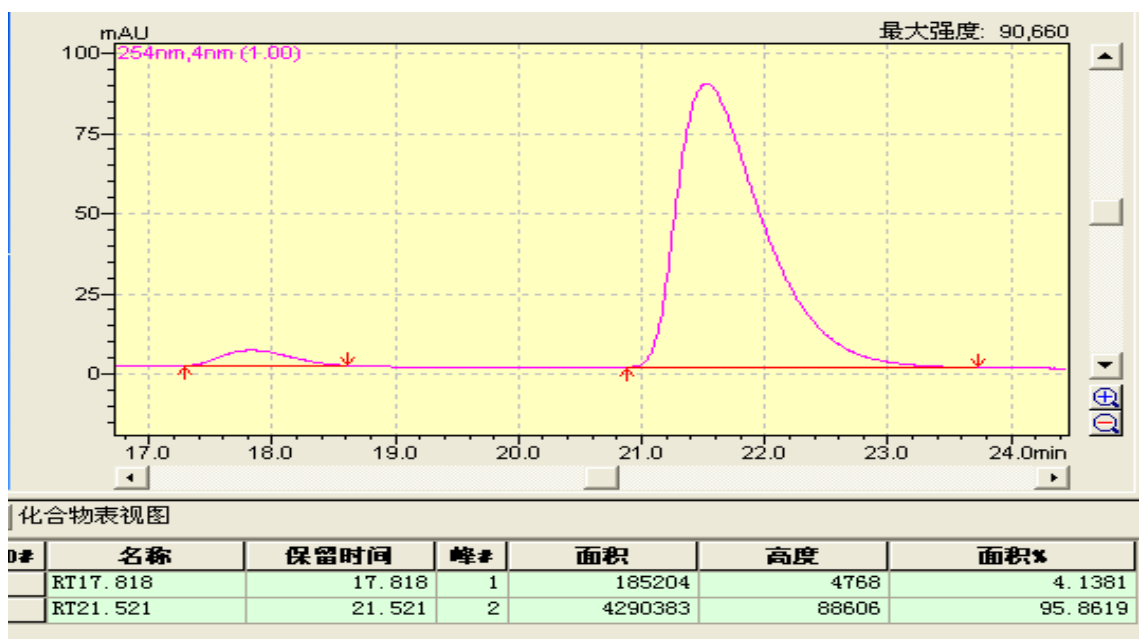
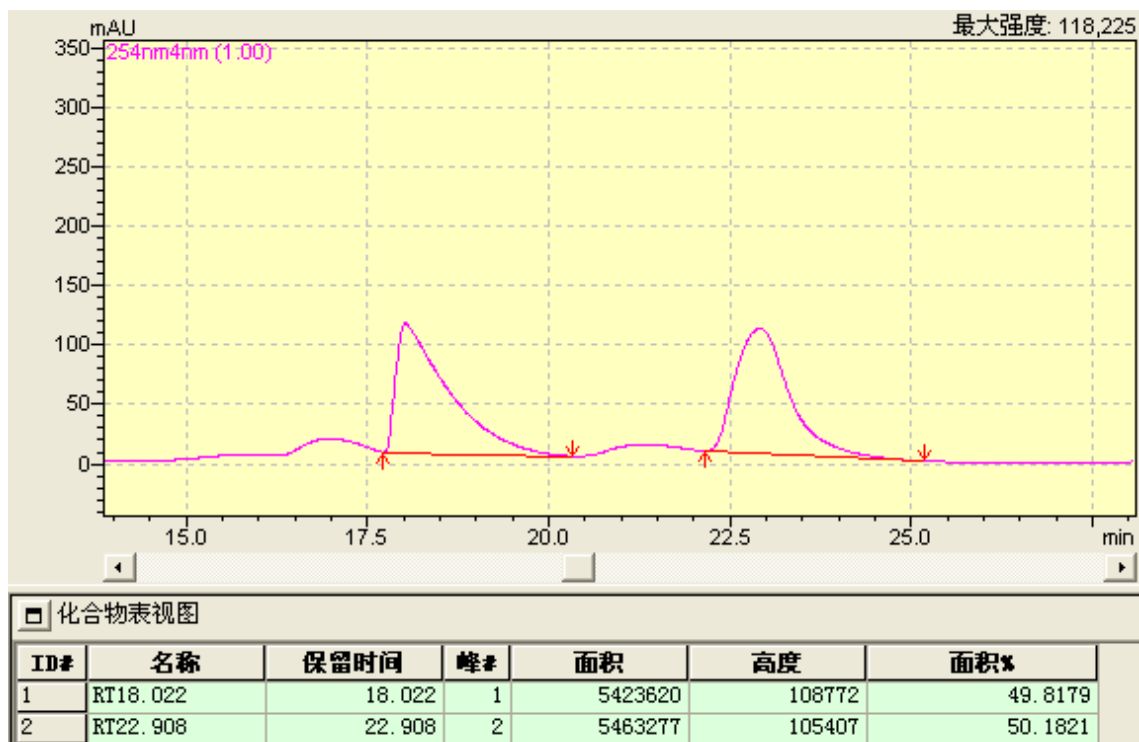


参数设置		分析结果	分组结果	样品信息					
ID号	组分名	保留时间(分钟)	峰高(微伏)	峰面积(微伏*秒)	浓度	半峰宽(秒)	分离度	理论塔板	拖尾因子
1		21.807	9049	81225.4	48.6052	8.98	0.00	117630.61	2.92
2		22.080	7000	85887.2	51.3948	12.27	0.91	64544.85	3.00
		总计:	Σ=16049	Σ=167112.7	Σ=100.0000				

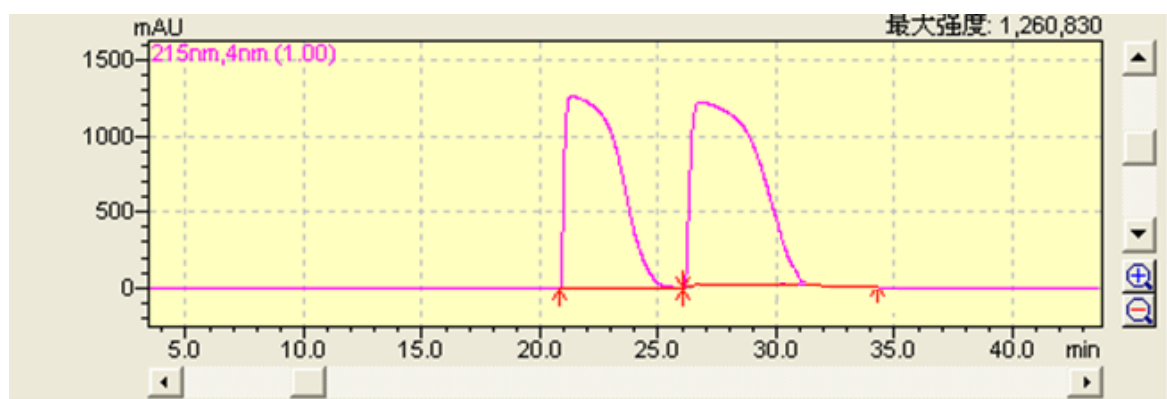


参数设置		分析结果	分组结果	样品信息					
ID号	组分名	保留时间(分钟)	峰高(微伏)	峰面积(微伏*秒)	浓度	半峰宽(秒)	分离度	理论塔板	拖尾因子
1		21.680	198	721.0	4.7698	3.64	0.00	706485.17	1.18
2		21.813	1588	14395.0	95.2302	9.06	0.74	115410.78	3.80
		总计:	Σ=1786	Σ=15116.0	Σ=100.0000				

Asymmetric transfer hydrogenation of ethyl 3-oxo-3-phenylpropanoate. (S: HPLC analysis with a UV-Vis detector using a Daicel OB-H chiralcel columns ($\Phi 0.46 \times 25$ cm), Hexane/2-propanol 90:10, 0.5 mL/min, 254 nm, 25 °C) (ref: *J. Org. Chem.* **2001**, 66, 8682).

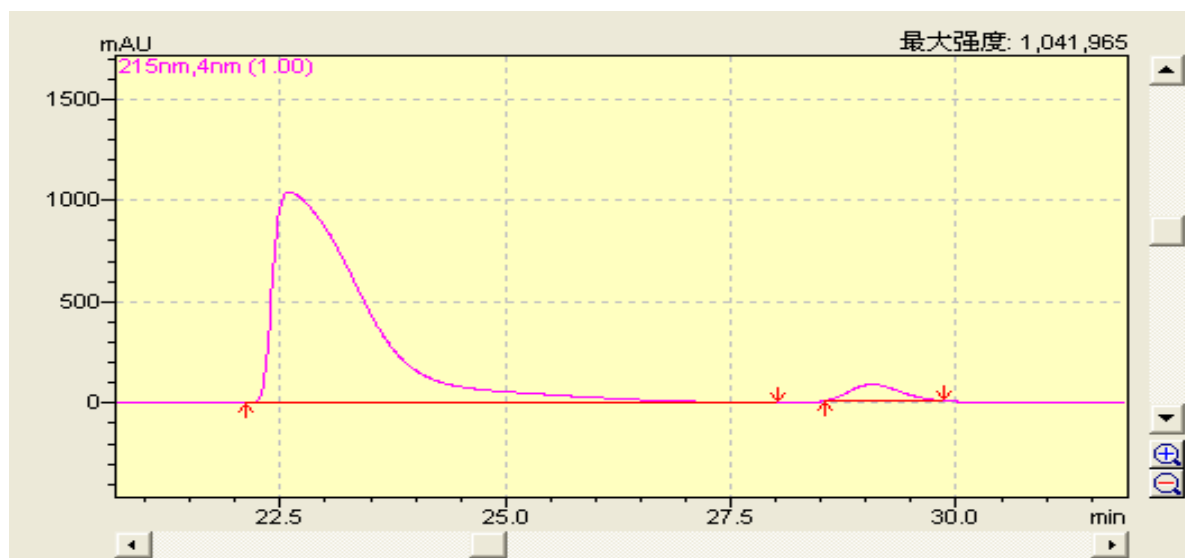


Asymmetric transfer hydrogenation of benzoylacetonitrile (S: HPLC analysis with a UV-Vis detector using a Daicel OJ-H chiralcel columns (Φ 0.46 x 25 cm), Hexane/2-propanol 90:10, 1 mL/min, 215 nm, 25 °C) (ref: O. Soltani, M. A. Ariger, H. Vázquez-Villa, and E. M. Carreira, *Org. Lett.* **2010**, *12*, 2893.).



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.317	21.317	1	195328773	1258468	48.0427
2	RT26.731	26.731	2	211244175	1190812	51.9573



化合物表视图

#	名称	保留时间	峰#	面积	高度	面积%
1	RT22.592	22.592	1	72635013	1041426	95.8045
2	RT29.063	29.063	2	3180866	82021	4.1955