

Supporting Information for

**Flowerlike Mesoporous Silica: A Bifunctionalized Catalyst for
Rhodium-Catalyzed Asymmetric Transfer Hydrogenation of Aromatic Ketones
in Aqueous Medium**

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Experimental

1. General

All experiments, which were sensitive to moisture or air, were carried out under an Ar atmosphere using standard Schlenk techniques. 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane, 4-(methylphenylsulfonyl)-1,2-diphenylethylenediamine [(*S,S*)-TsDPEN], the surfactant cetyltrimethylammonium bromide (CTAB), tetraethoxysilane (TEOS) and [Cp**RhCl*₂]₂ were purchased from Sigma-Aldrich Company Ltd. and used as received. Compound [(*S,S*)-DPEN-SO₂Ph(CH₂)₂Si(OMe)₃] and the pure FMS material was synthesized according to the reported literature [*Chem. Commun.* **2011**, 47, 4087]. The products were analyzed by using a HPLC with a UV-Vis detector using a Daicel AD-H or OD-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 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. 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.

Figure S1. The FT-IR spectra of the pure FMS material and 2-3.

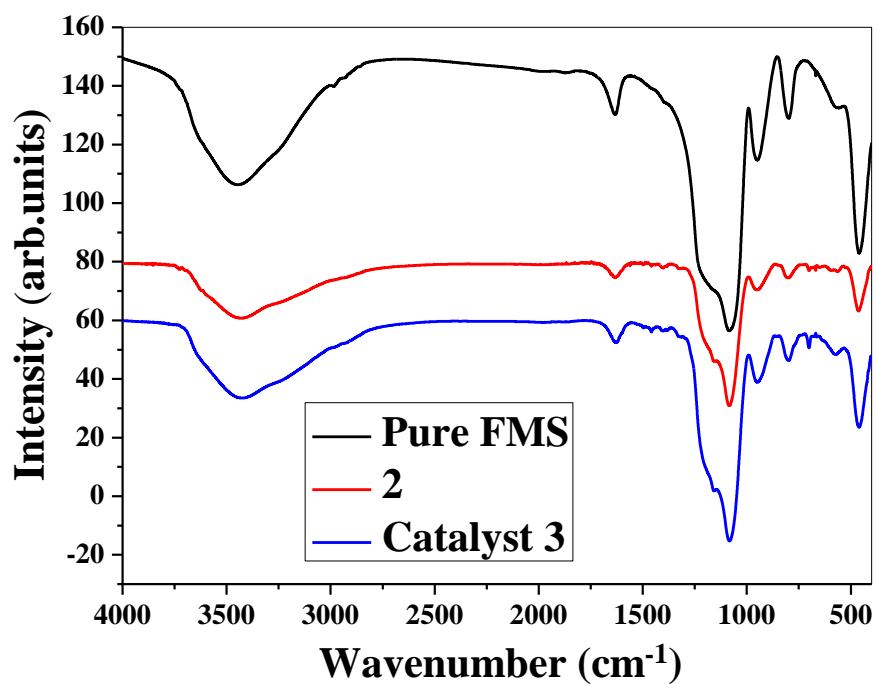
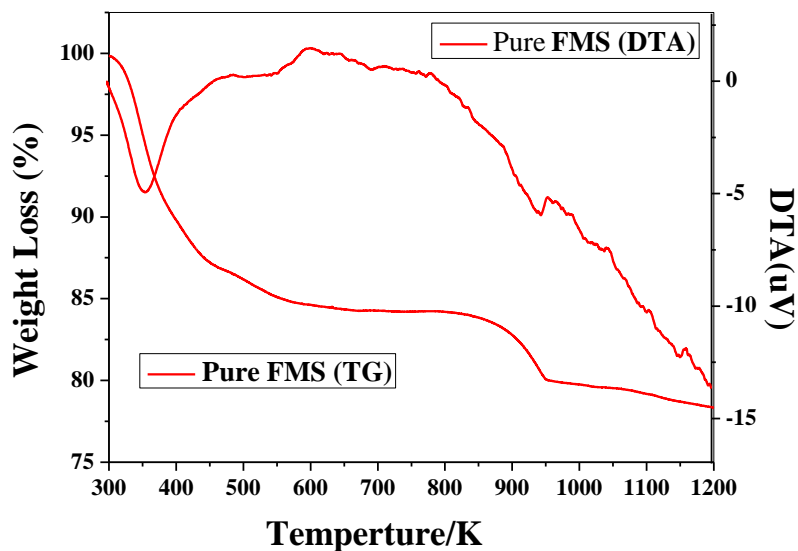
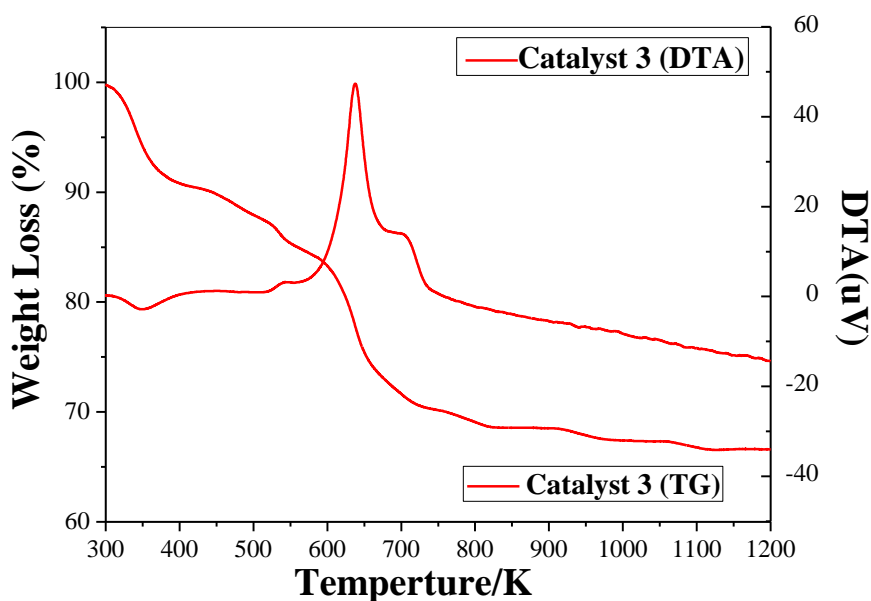
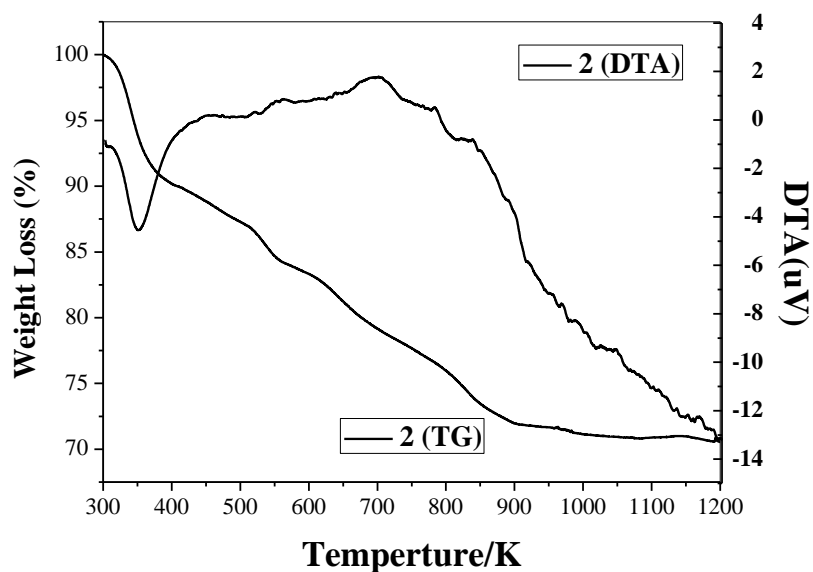


Figure S2. The TG/DTA curves of the pure FMS material and 2.





Explanation: The TG/DTA curve of the pure FMS and **2-3** were treated in the air. An endothermic peak around 355K with weight loss of 12.9% could be attributed to the release of physical adsorption water while the comprehensive endothermic peaks around 450-1120K with weight loss of 8.4% could be assigned to the release of the residual CTAB surfactant (cetyltrimethylammonium chloride) within FMS (V. Cauda, A. Schlossbauer, J. Kecht, A. Zürner, T. Bein, *Am. Chem. Soc.*, 2009, **131**, 11361). Thus, the totally weight loss of the residual CTAC surfactant was 8.4% in 87.1% FMS materials when eliminated the contribution of water, meaning the **9.6% weight**

loss of the residual CTAC surfactant per 100% materials.

Similarly, for TsDPEN-functionalized-FFMS (**2**), a similar endothermic peak around 355K with weight loss of 11.3% could be attributed to the release of physical adsorption water while the comprehensive endothermic peaks around 450-1120K with weight loss of 17.9% in 88.7% TsDPEN-functionalized-FFMS (**2**) could be assigned to the oxidation of organic molecules (including TsDPEN fragments and part of the residual CTAC surfactant), meaning that the totally weight loss of organic moieties was 20.2% per 100% materials.

Similarly, for catalyst **3**, a similar endothermic peak around 355K with weight loss of 10.2% in the heterogeneous catalyst **3** were due to the release of physical adsorption water. It was worth mentioning that two new typical exothermic peaks were combined into one complicated exothermic peak between 450-1120K with weight loss of 23.3% in 89.8% catalyst **3** could be assigned to the oxidation of organic molecules (including Cp*RhTsDPEN complexes and part of the residual CTAC surfactant), meaning that the totally weight loss of organic moieties was 25.9% per 100% materials.

When compared the pure FMS with **2**, the true weight loss of TsDPEN organic molecules was 10.6% (20.2-9.6) per 100% materials, meaning that mole amounts is 0.28 (10.4%/380) mmol per gram material **2**. Similarly, when compared the pure FMS material and **2** to the catalyst **3**, the true weight loss of [Cp*Cl₂] organic moiety was 5.7% (25.9-20.2) per 100% materials, meaning that mole amounts is 0.28 (5.7%/205) mmol per gram catalyst **3**. **This datum is nearly consistent with 27.18 mg (0.26 mmol) of Rh loadings per gram catalyst detected by ICP analysis.**

Figure 3. Low-angle and wide-angle powder XRD patterns of the catalysts **3**.

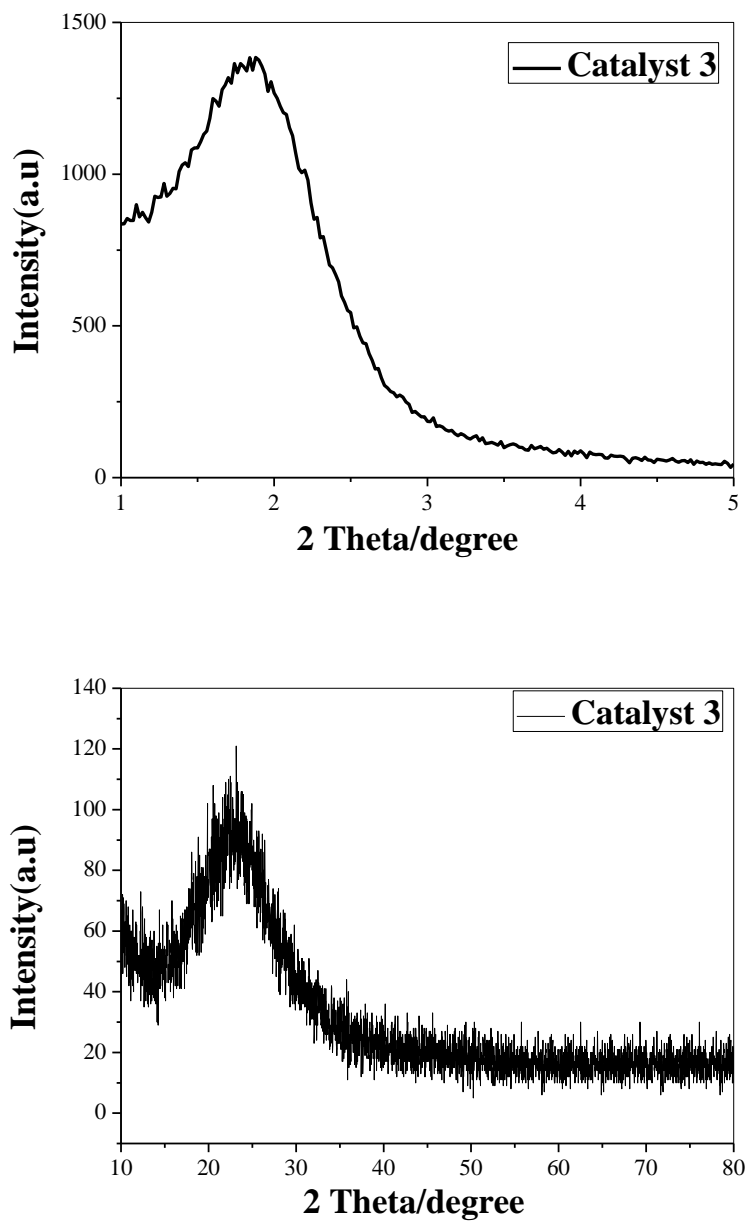
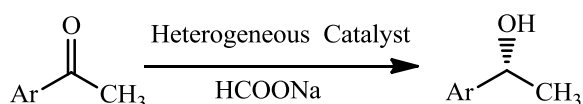


Table 1. Asymmetric transfer hydrogenation of aromatic ketones.^a



Entry	R	Time (h)	Conv.[%] ^b	ee [%] ^b
1	Ph	0.5	>99(88)	97 (96) ^c
2	Ph	4.0	86	97 ^d
3	Ph	0.5	97	95 ^e
4	Ph	0.5	>99	96 ^f
5	4-FPh	0.5	>99	92
6	4-ClPh	0.5	>99	94
7	4-BrPh	0.5	>99	94
8	3-BrPh	0.5	>99	97
9	4-MePh	2.0	>99	94
10	4-OMePh	4.0	97	94
11	3-OMePh	0.5	>99	95
12	4-CNPh	0.5	>99	89
13	4-CF ₃ Ph	0.5	>99	94
14	4-NO ₂ Ph	0.5	>99	86
15	1-pyrenyl	24.0	46 (79 ^g)	55(81 ^g)

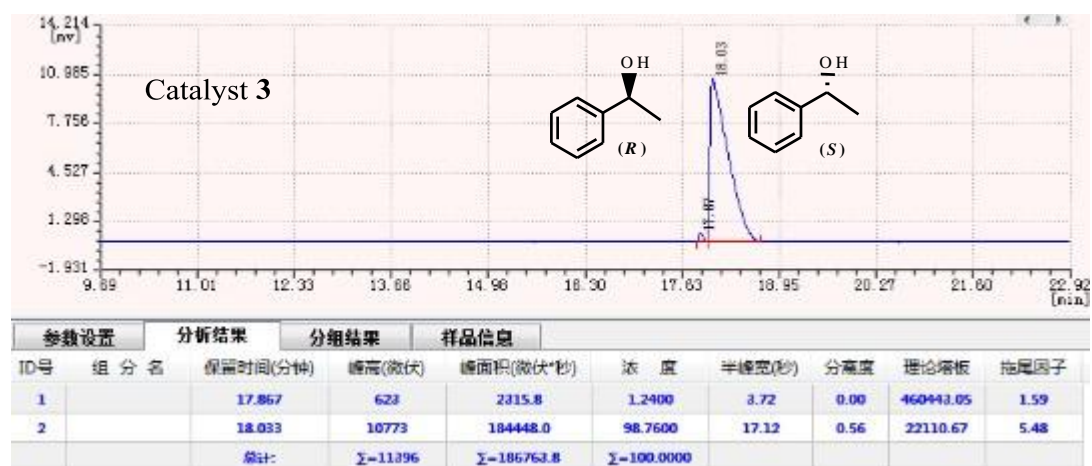
^a) Reaction conditions: catalysts (7.58 mg, 2.00 μmol of Rh based on ICP analysis), HCO₂Na (0.68 g, 10.0 mmol), ketone (2.0 mmol) and 2.0 mL water, reaction temperature (40 °C), reaction time (0.5-5.0 h). ^b) Determined by chiral GC or HPLC analysis (see SI in Figure S5). ^c) Data were obtained using the homogeneous Cp*RhTsDPEN catalyst without additive of Bu₄NBr in aqueous medium. ^d) Data was obtained with 0.2% mol of catalyst. ^e) Data were obtained using TsDPEN-functionalized-FFMS (**2**) plus (Cp*RhCl₂)₂ as a catalyst. ^f) Data were obtained using the pure FMS material plus Cp*RhTsDPEN as a catalyst. ^g) Data were obtained using the flowerlike silica prepared by *via* tetramethylammonium bromide (TAB) as a structure-directed template reagent.

Translation of Chinese to English is as follows:

Component Name		RetTime [min]	Height	Area	Concentration	Resolution half-width	Theoretical Plate	Tailing factor	
Peak	↑	↑	↑	↑	↑	↑	↑	↑	
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		18.360	29	100.0	3.0723	3.45	0.00	565022.82	1.05
2		18.720	535	3154.9	96.9277	5.90	2.72	200851.56	2.02
	总计:		Σ=564	Σ=3254.9	Σ=100.0000				

Figure S4. Asymmetric transfer hydrogenation of the catalyst 3 [The catalytic activity and enantiomeric excess were determined by chiral GC using a Supelco β -Dex 120 chiral column (30 m \times 0.25 mm (i.d.), 0.25 μ m film)].

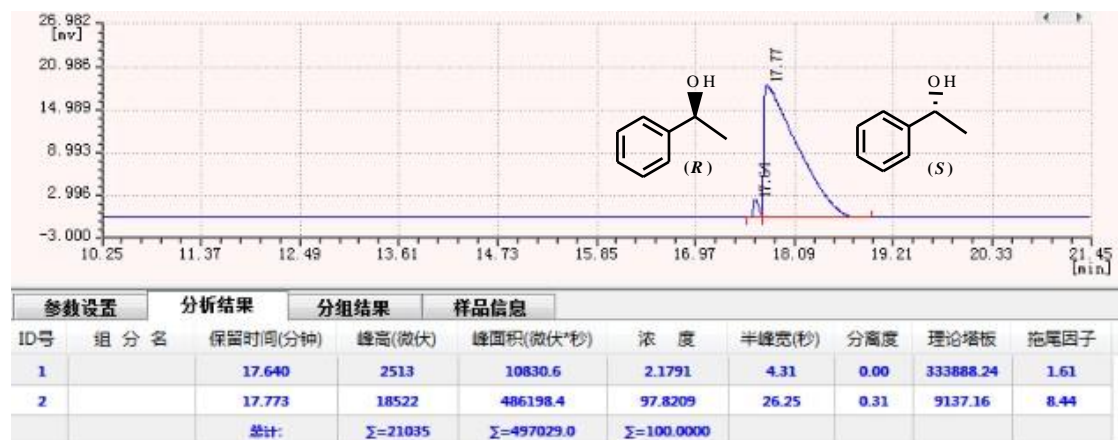
Asymmetric transfer hydrogenation of acetophenone.



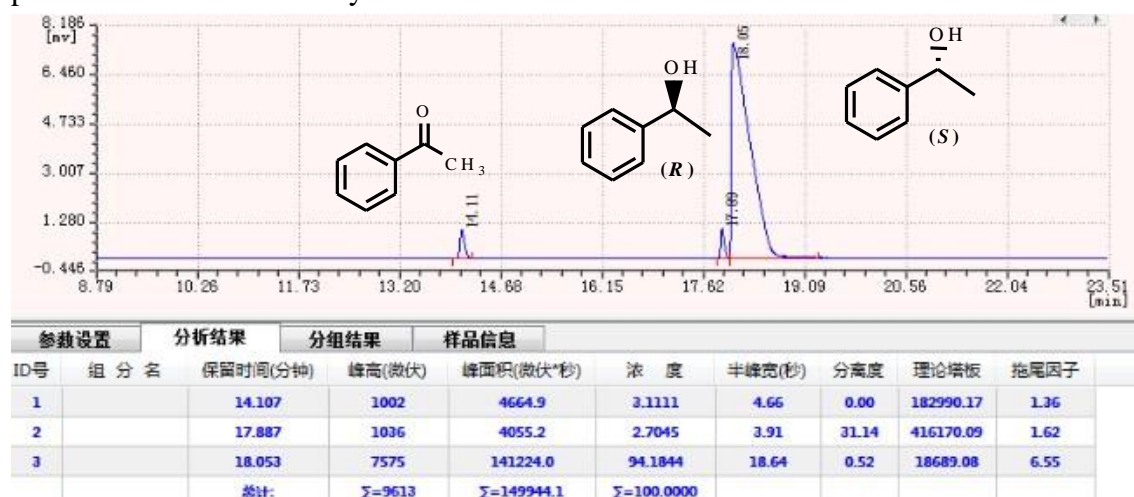
Asymmetric transfer hydrogenation of acetophenone with the substrate/catalyst =500.



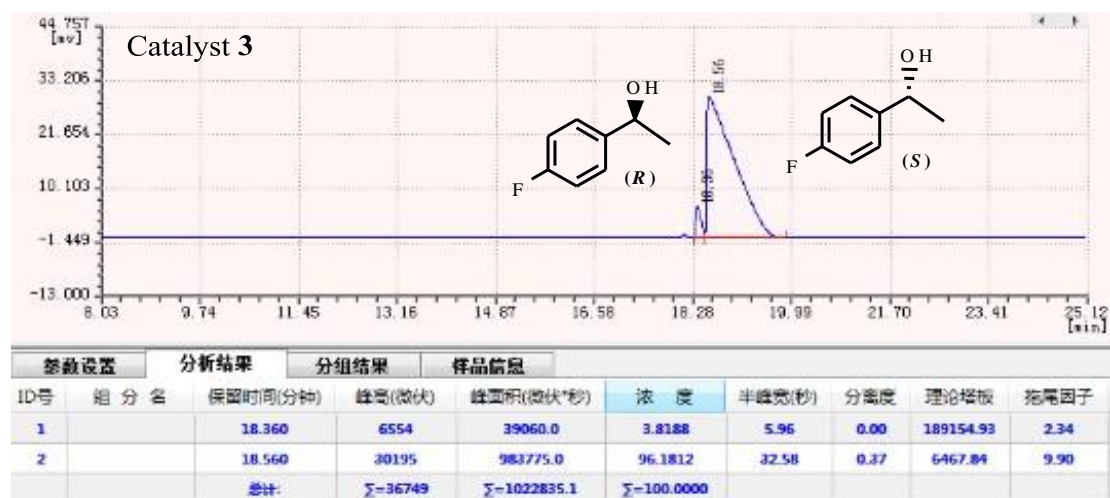
Asymmetric transfer hydrogenation of acetophenone using TsDPEN-functionalized-FFMS (2) plus $(\text{Cp}^*\text{RhCl}_2)_2$ as a catalyst



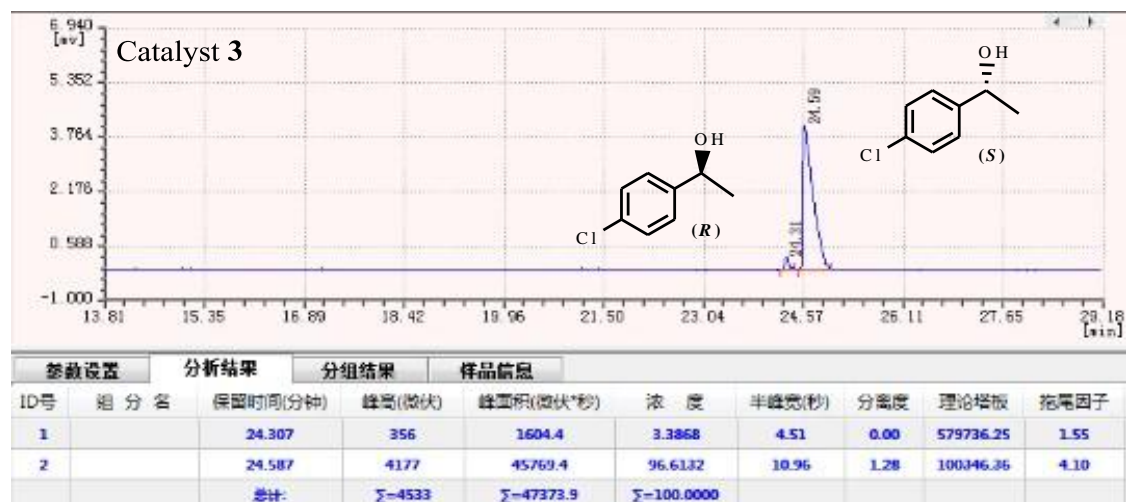
Asymmetric transfer hydrogenation of acetophenone using the pure FMS material plus RhTsDPEN as a catalyst.



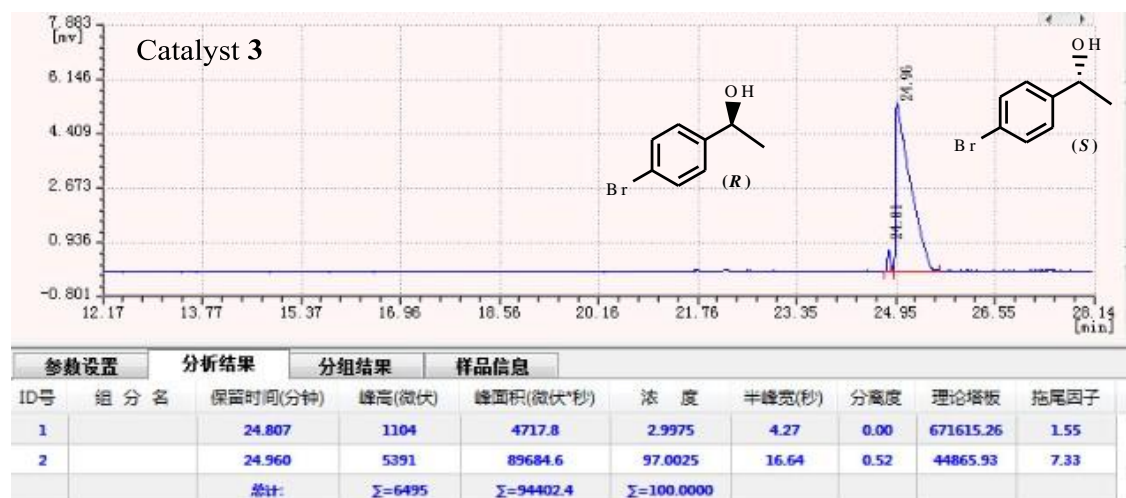
Asymmetric transfer hydrogenation of 4-fluoroacetophenone.



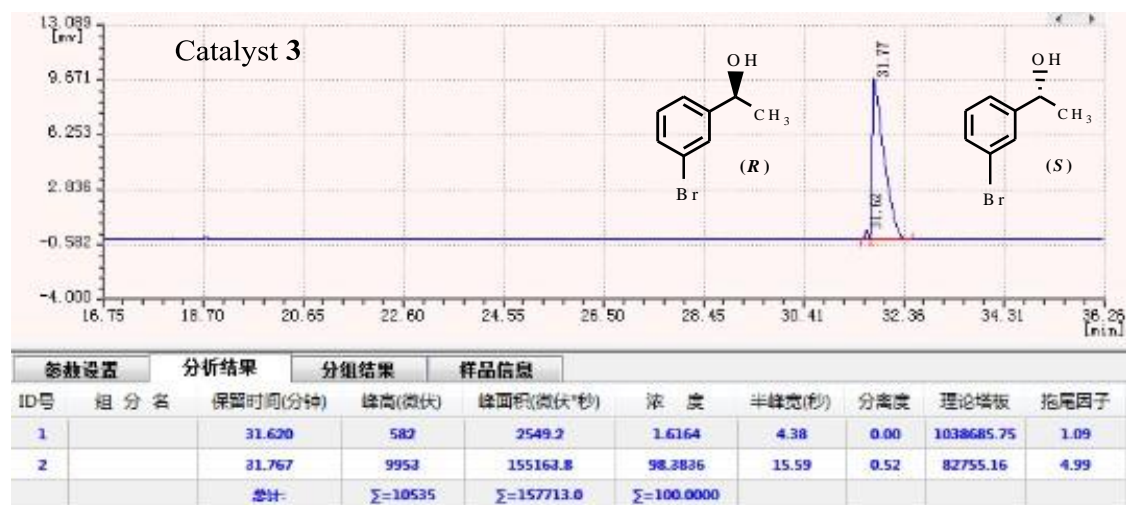
Asymmetric transfer hydrogenation of 4-chloroacetophenone.



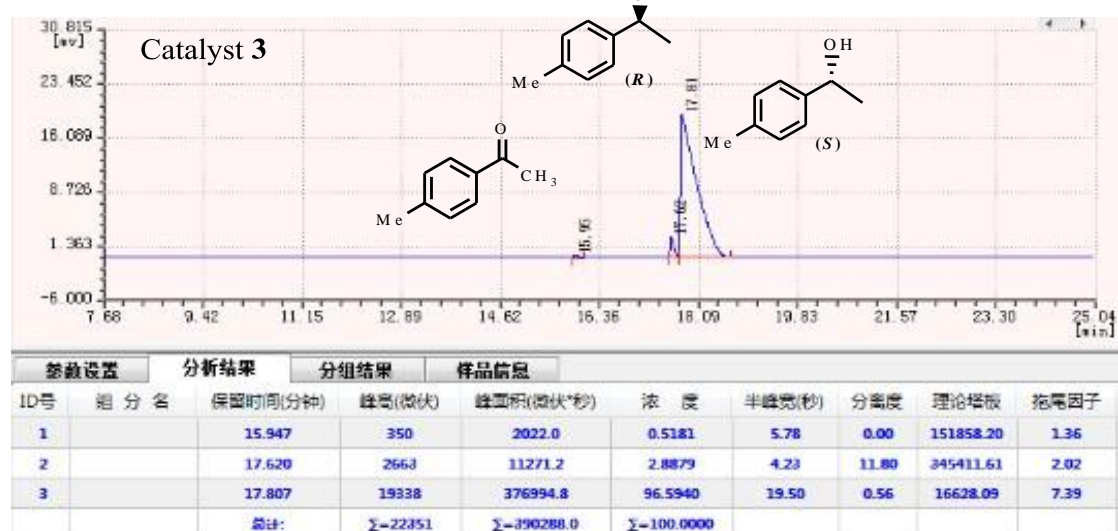
Asymmetric transfer hydrogenation of 4-bromoacetophenone.



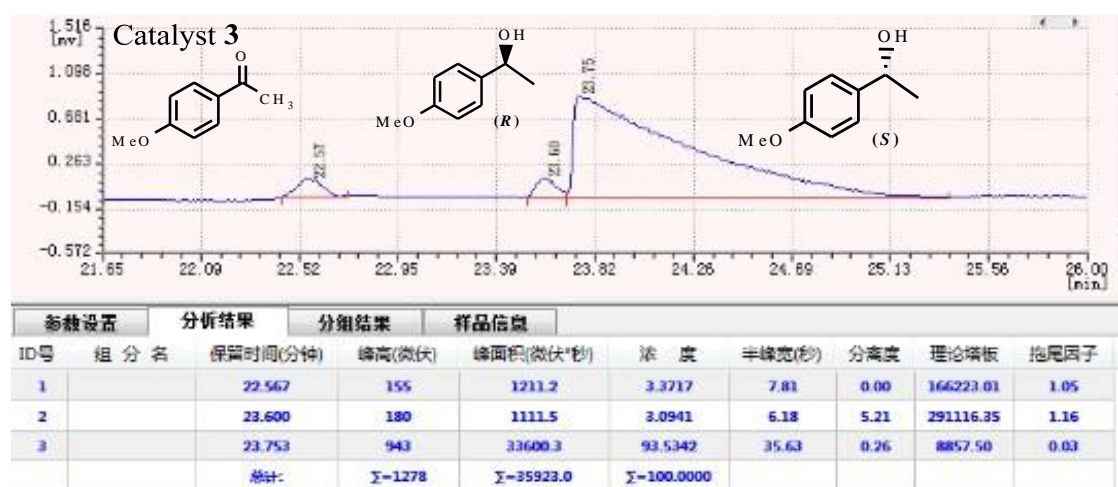
Asymmetric transfer hydrogenation of 3-bromoacetophenone.



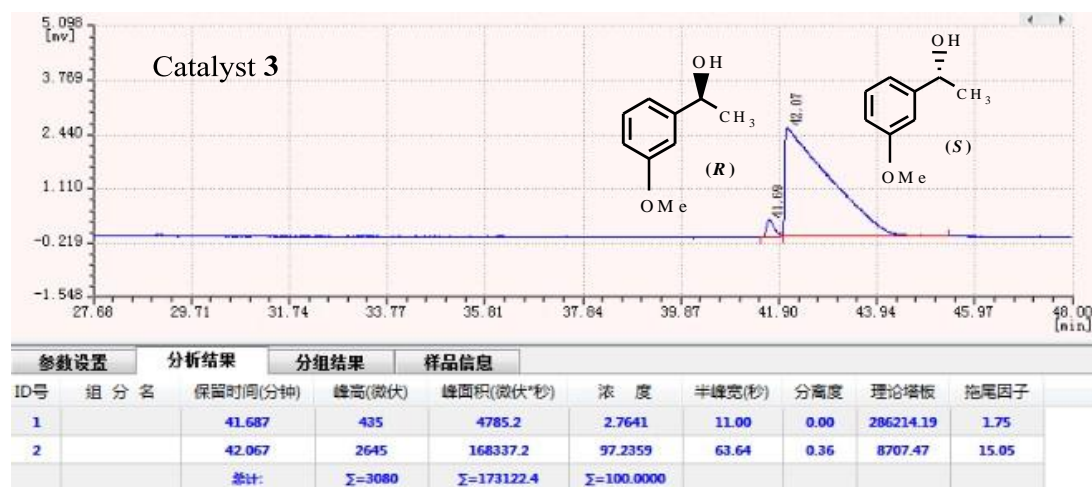
Asymmetric transfer hydrogenation of 4-methylacetophenone.



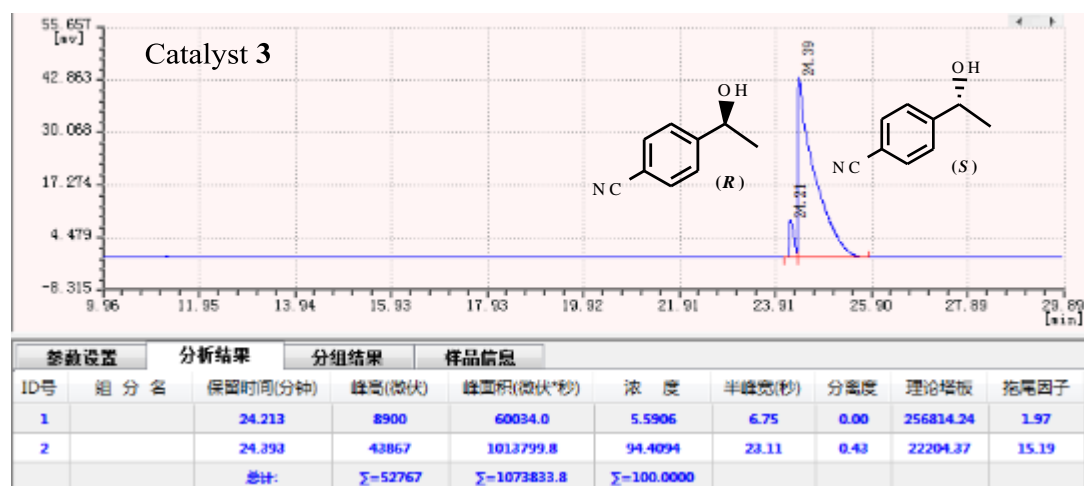
Asymmetric transfer hydrogenation of 4-methoxyacetophenone.



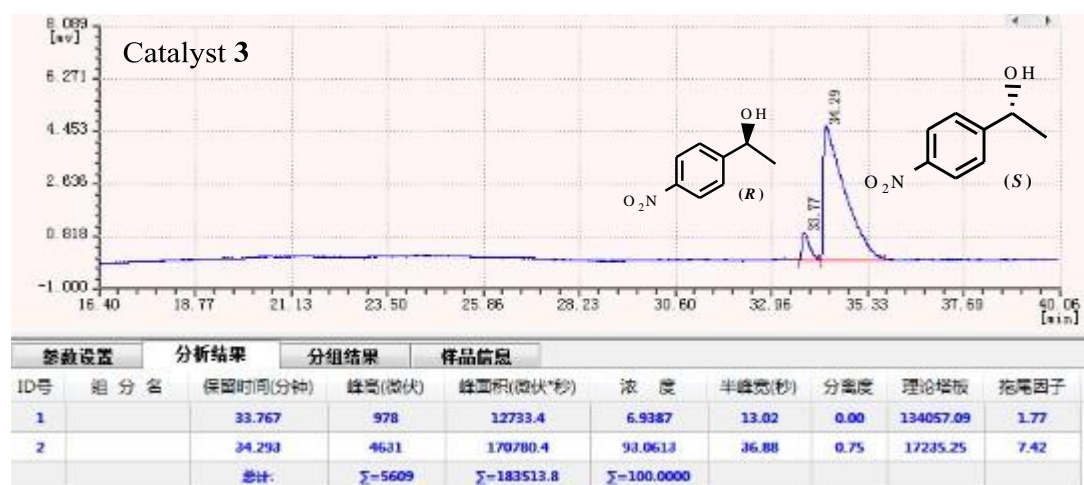
Asymmetric transfer hydrogenation of 3-methoxyacetophenone.



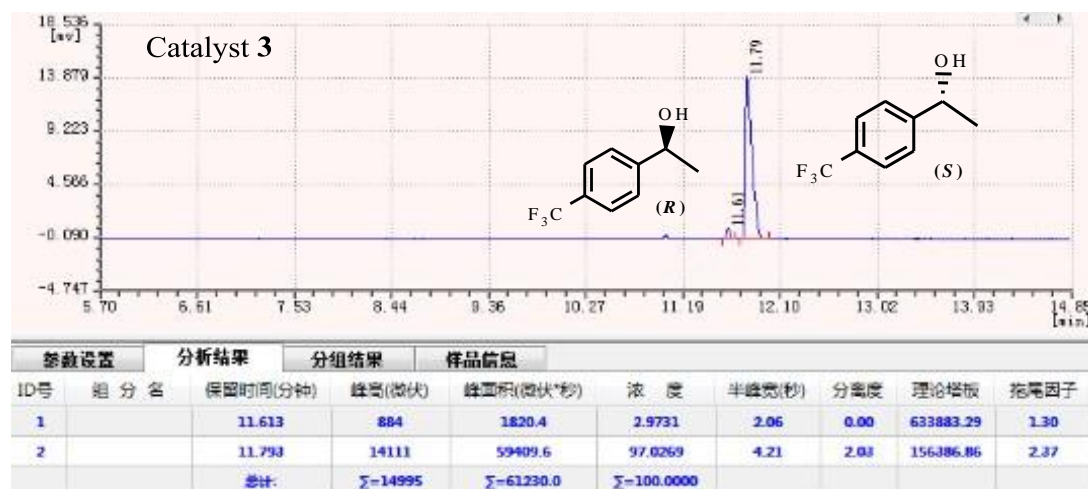
Asymmetric transfer hydrogenation of 4-cyanoacetophenone.



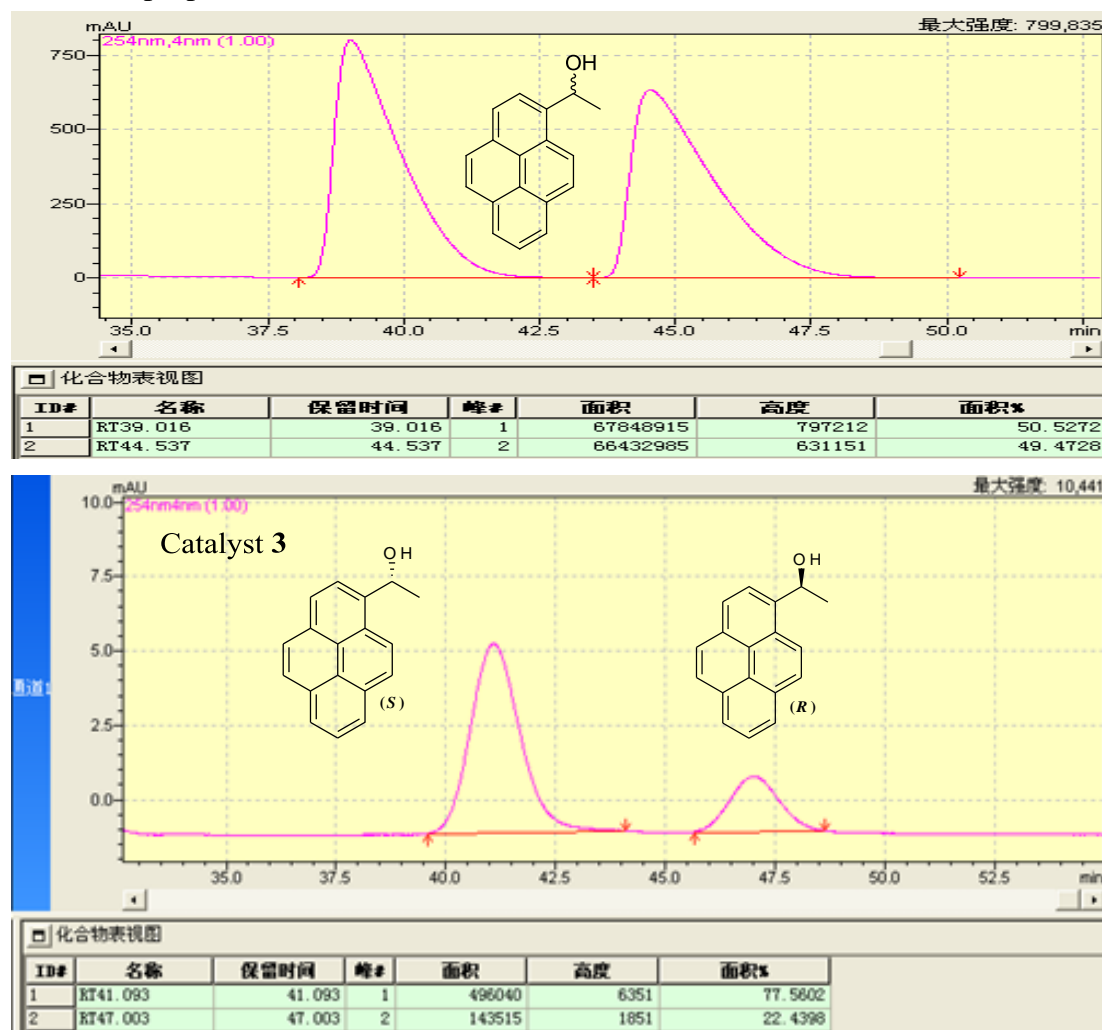
Asymmetric transfer hydrogenation of 4-nitroacetophenone.



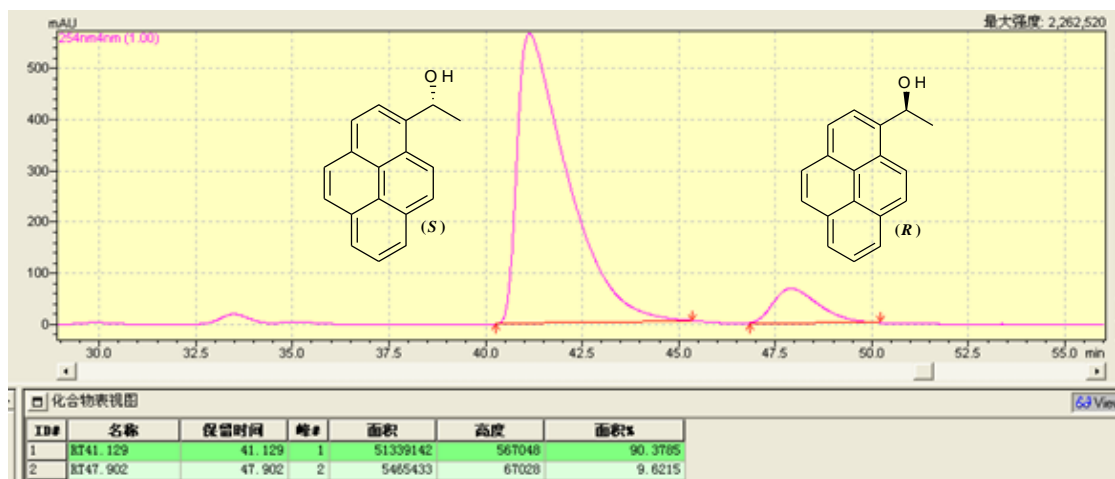
Asymmetric transfer hydrogenation of 4-trifluoromethylacetophenone.



Asymmetric transfer hydrogenation of 1-acetylpyrene. (HPLC analysis with a UV-Vis detector using a Daicel OD-H chiralcel columns ($\Phi 0.46 \times 25$ cm), Hexane/2-propanol 97:3, 1 mL/min, 254 nm, 40 °C)



Asymmetric transfer hydrogenation of 1-acetylpyrene, in which the catalyst prepared using the tetramethylammonium bromide (TAB) instead of cetyltrimethylammonium bromide (CTAB) as a structure-directed template reagent.



Asymmetric transfer hydrogenation of 1-acetylpyrene using the homogeneous Cp*RhTsDPEN as a catalyst. Conversion: 81%, ee: 83%

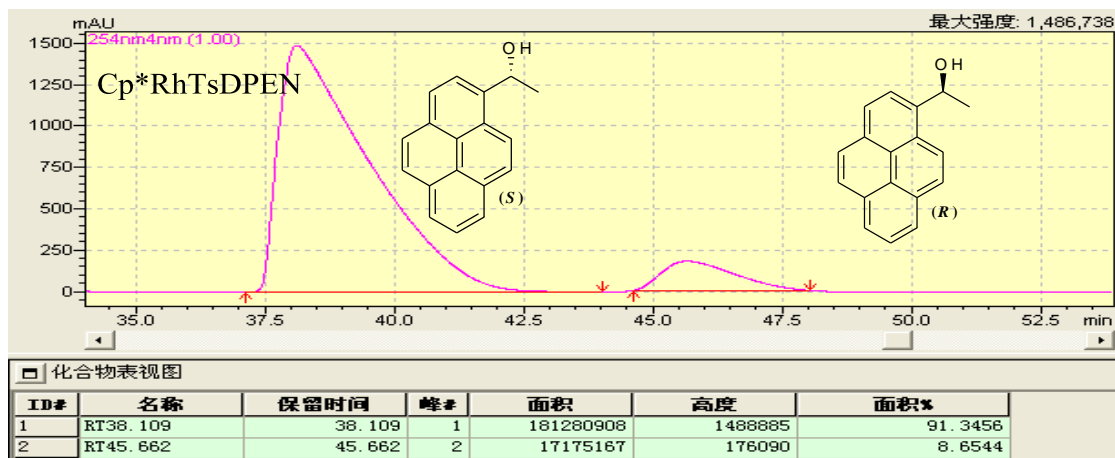


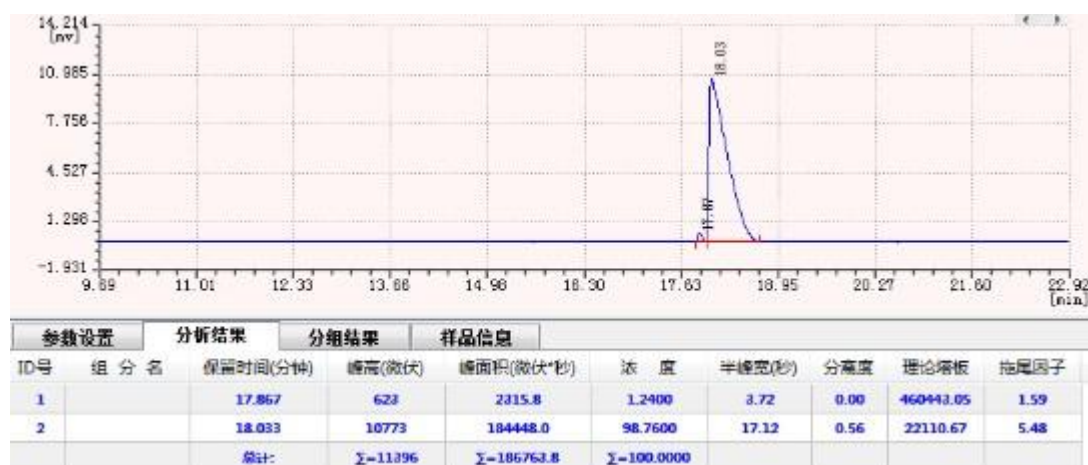
Table 2. Reusability of the catalyst **3** for asymmetric transfer hydrogenation of acetophenone.^a

Run time	1	2	3	4	5	6	7	8	9	10
Conv. [%]	99.9	99.9	99.9	99.9	99.9	99.9	99.7	99.6	99.1	98.3
ee [%]	97.5	97.5	97.5	97.4	97.4	97.0	97.4	97.2	97.0	96.0

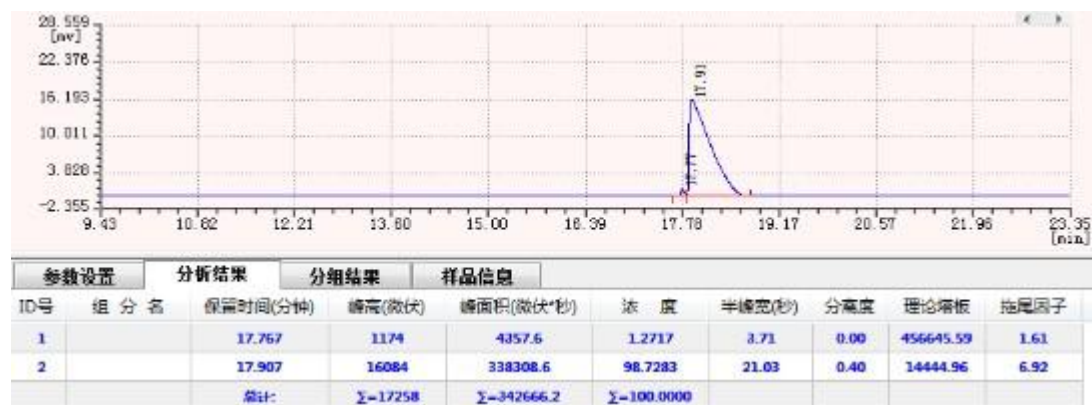
^a) Reaction conditions: catalyst (7.58 mg, 2.00 μmol of Rh based on ICP analysis), HCO₂Na (0.68 g, 10.0 mmol), ketone (2.0 mmol) and 2.0 mL water, reaction temperature (40 °C), reaction time (0.5-4.0 h).

Figure S5. Reusability of the catalyst **3** for asymmetric transfer hydrogenation of acetophenone.

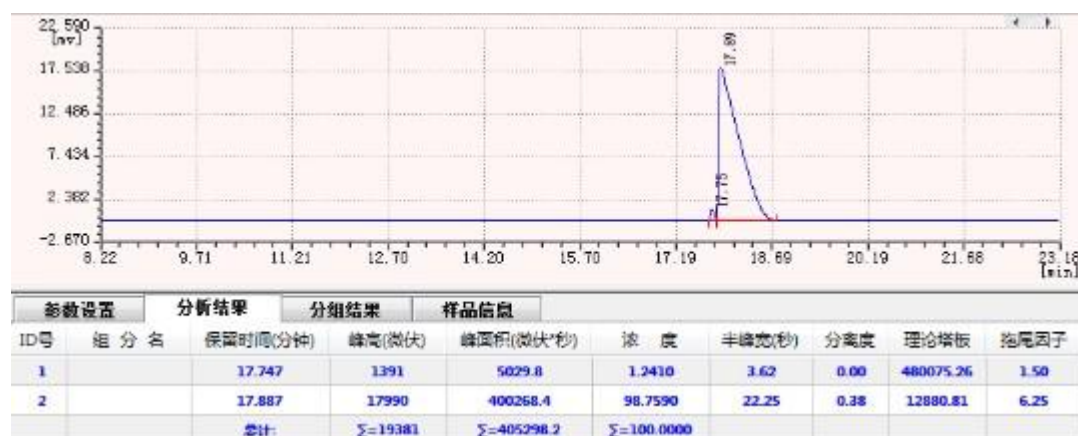
Recycle 1 of the catalyst **3** using acetophenone as a substrate.



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



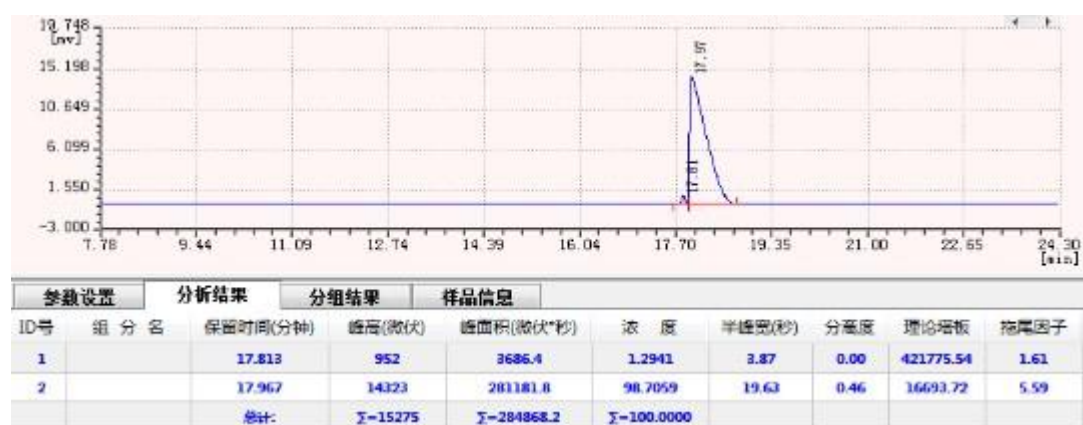
Recycle 3 of the catalyst **3** using acetophenone as a substrate.



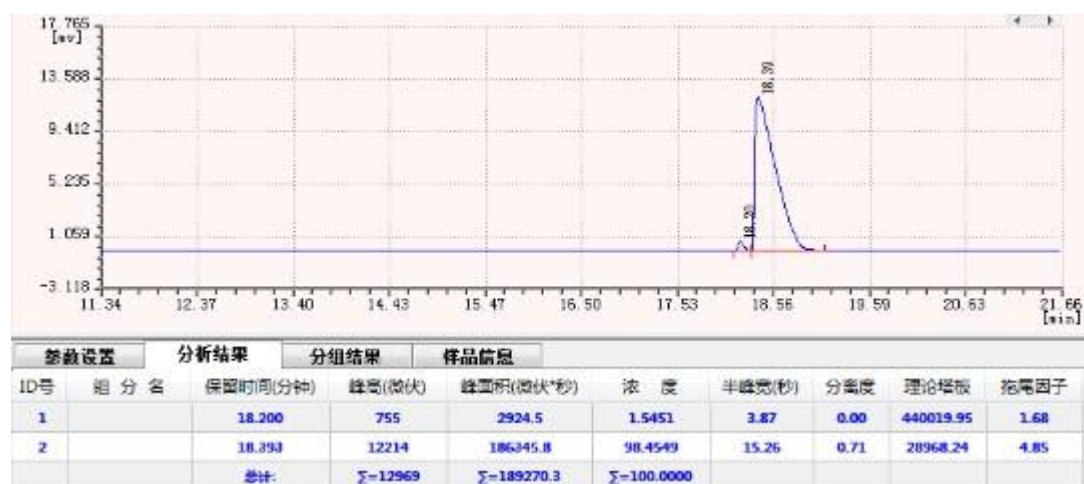
Recycle 4 of the catalyst **3** using acetophenone as a substrate.



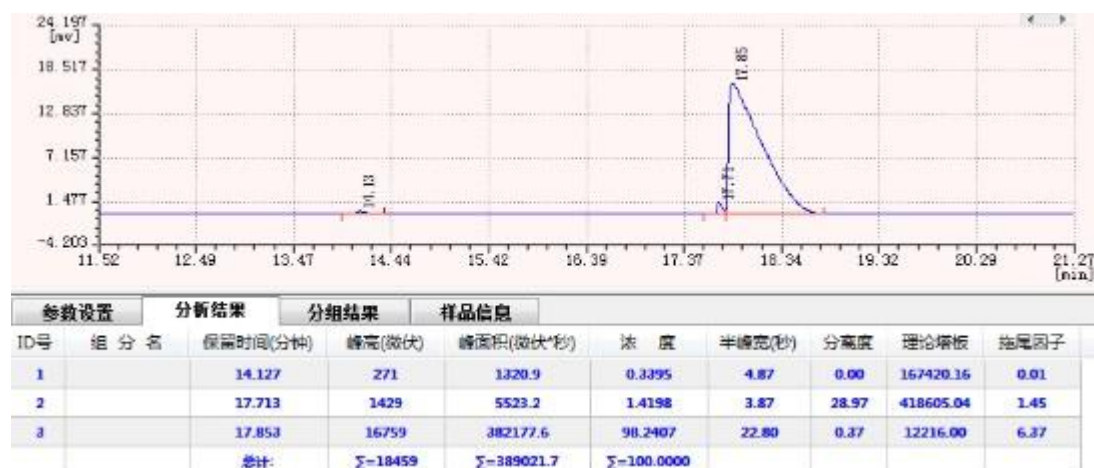
Recycle 5 of the catalyst **3** using acetophenone as a substrate.



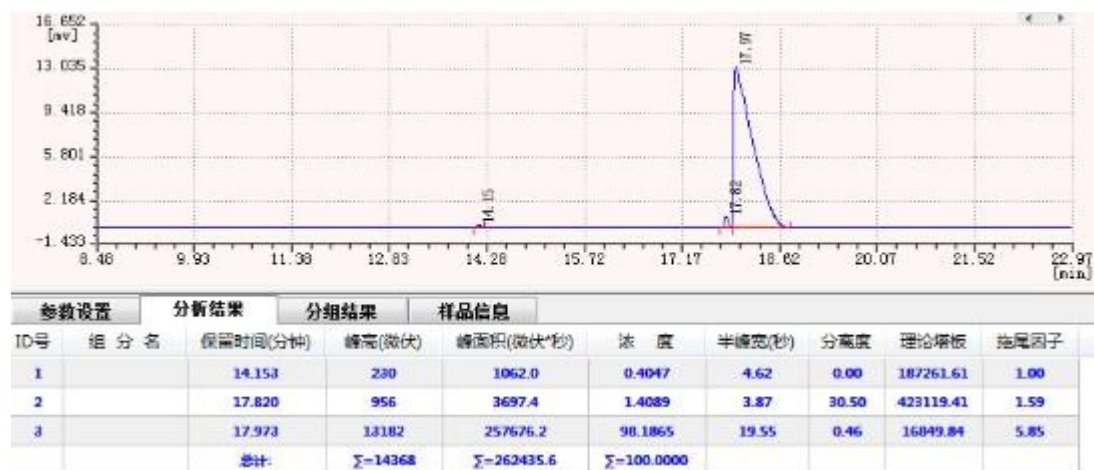
Recycle 6 of the catalyst **3** using acetophenone as a substrate.



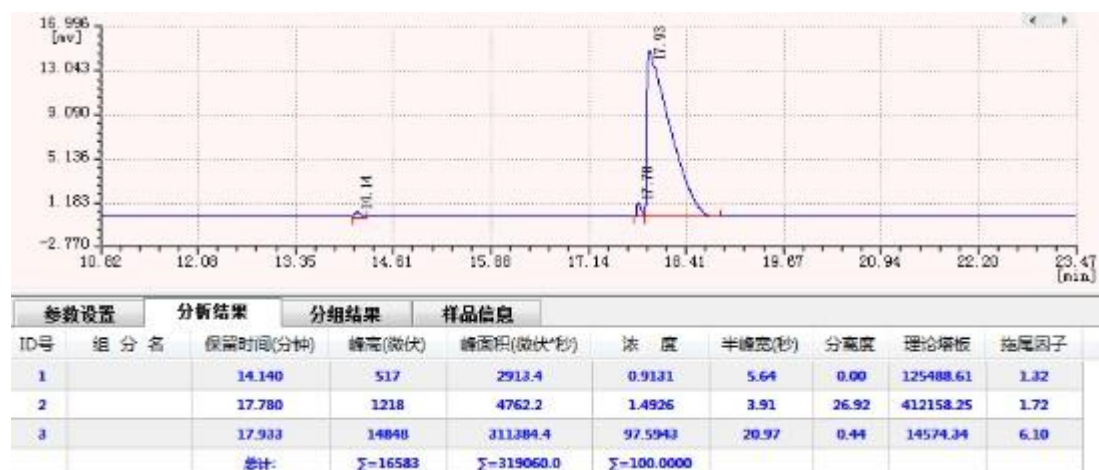
Recycle 7 of the catalyst **3** using acetophenone as a substrate.



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.

