Supporting Information for

Magnetically recoverable SiO_2-coated Fe_3O_4 Nanoparticles: A New Platform for Asymmetric Transfer Hydrogenation of Aromatic Ketones in Aqueous Medium

Yunqiang Sun, Guohua Liu, Hongyuan Gu, Tianzeng Huang, Yuli Zhang, Hexing Li

The Key Laboratory of Resource Chemistry of Ministry of Education, 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 standard Schlenk techniques. 2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane, (*1S,2S*)-1,2-diphenylethylenediamine [*(S,S)*-TsDPEN] and $[Cp^*RhCl_2]_2$ were purchased from Sigma-Aldrich Company Ltd. and used as received. Compound **2** [*(S,S)*-DPEN-$SO_2Ph(CH_2)_2Si(OMe)_3$] 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. 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. The magnetic measurements were performed with a Lake Shore VSM 736 at room temperature.

3. Catalyst preparation

*3.1. Preparation of TsDPEN-MNPs (**4**)*. To a stirred suspension of the SiO_2-coated Fe_3O_4 magnetic nanoparticles (**3**) (1.0 g) in 15 mL dry toluene was added *(S,S)*-DPEN-$SO_2Ph(CH_2)_2Si(OMe)_3$ (0.10 g, 0.20 mmol) in 5 mL dry toluene. The resulting mixture was refluxed for 24 h under argon atmosphere. After magnetic separation, the red crude solid was extracted thoroughly in toluene solvent using a Soxlet apparatus to remove homogeneous and unreacted start materials. The solid was dried at 60 ^oC *in vacuum* for 12 h to afford TsDPEN-MNPs (**4**) (1.028 g, 28.0% relative to **3**) as a white powder. IR (KBr) cm^{-1}: 3419 (s), 3063 (w), 3027 (w), 2928 (w), 2865 (w), 1624 (m), 1593 (w), 1452 (w), 1331 (w), 1155 (m), 1096 (s), 813 (w), 700 (w), 668 (w), 569 (w), 465 (m); Elemental analysis (%): C 11.19, H 1.81, N 0.54, S 0.62.

3.2. Preparation of Cp-Rh-TsDPEN-MNPs (**5**)*. A typical procedure is as follows: Under argon atmosphere, to a stirred suspension of TsDPEN-MNPs (**4**) (1.0 g) and NEt_3 (1.30 mL, 21.5 mmol) in 20 mL dry CH_2Cl_2 was added $[Cp^*RhCl_2]_2$ (0.050 g, 0.092 mmol) at room temperature. The resulting mixture was stirred at room temperature for 12h. After magnetic separation, the red crude solid was extracted thoroughly in toluene solvent using a Soxlet apparatus to remove homogeneous and unreacted start materials. The solid was dried at 60 ^oC *in vacuum* for 12 h to afford Cp*-Rh-TsDPEN-MNPs (**5**) (1.14 g, 95.2% relative to **4**) as a light yellow powder. IR (KBr) cm^{-1}: 3424 (s), 3029 (w), 2932 (w), 2848 (w), 1629 (m), 1593 (w), 1440 (w), 1349 (w), 1209 (m), 1155 (m), 1092 (s), 794 (w), 700 (w), 623 (w), 550 (w), 465 (m); Elemental analysis (%):C 13.92, H 1.71, N 0.46, S 0.53.

4. General procedures for asymmetric transfer hydrogenation of ketones in water. A typical procedure is as follows: The magnetic catalyst Cp*-Rh-TsDPEN-MNPs (**5**) (24.4

mg, 4.00 μmol based on Rh from ICP), HCO_2Na (0.68 g, 10.0 mmol), Bu_4NBr (0.29 g, 0.80 mmol), ketone (2.0 mmol) and 4.0 mL water were added in a 10 mL roundbottom flask in turn. The mixture was allowed to react at 40°C for a certain period of time. Duing that time, the reaction was monitored constantly by TLC. After completion of the reaction, the magnetic catalyst was seperated by a small magnet near the bottle and was washed with H_2O (2.0 mL twice) for the recycle experiment. The aqueous solutions were 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 (eluent, hexane/ethyl acetate = 1 : 1) 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. The wide-angle powder XRD patterns of **3** and the catalyst **5**.

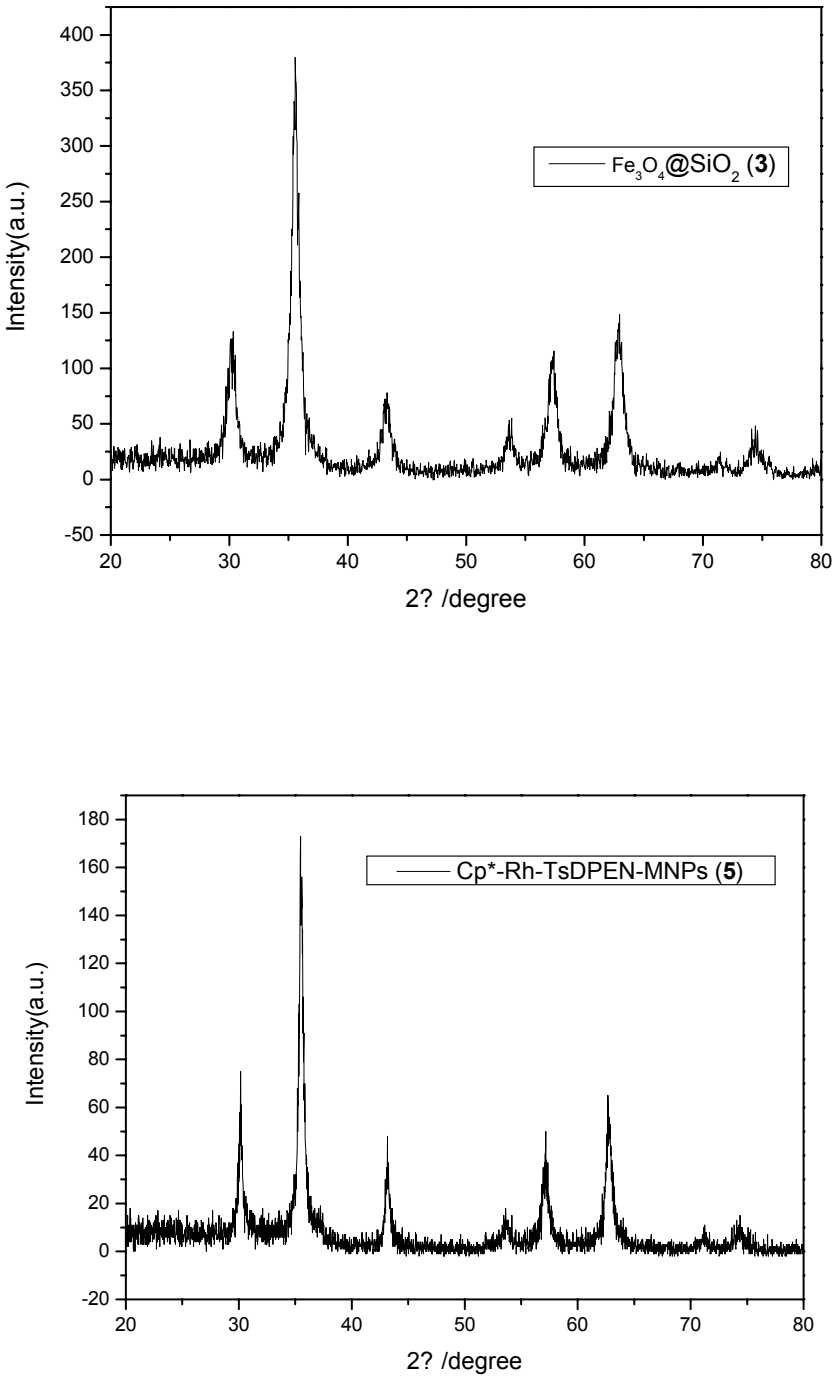
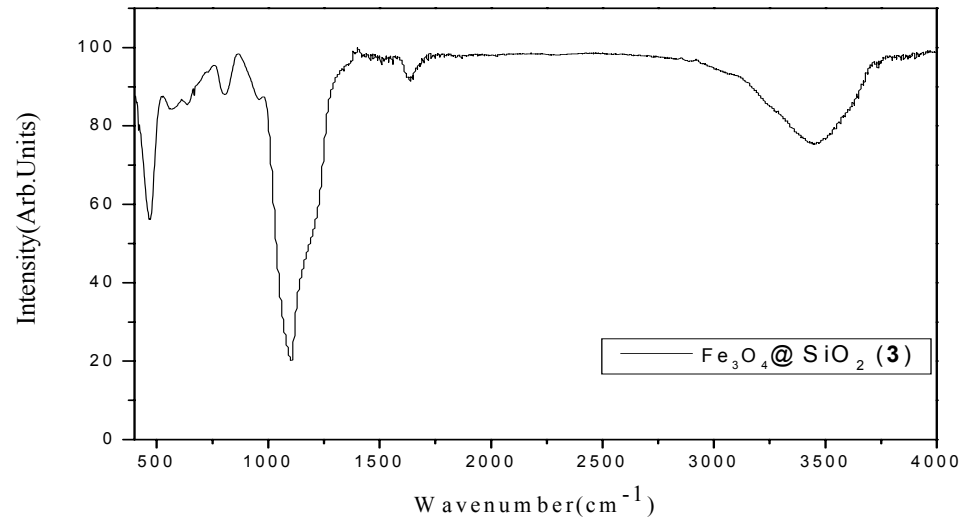


Figure S2. The FT-IR spectra of **3** and the catalyst **5**.



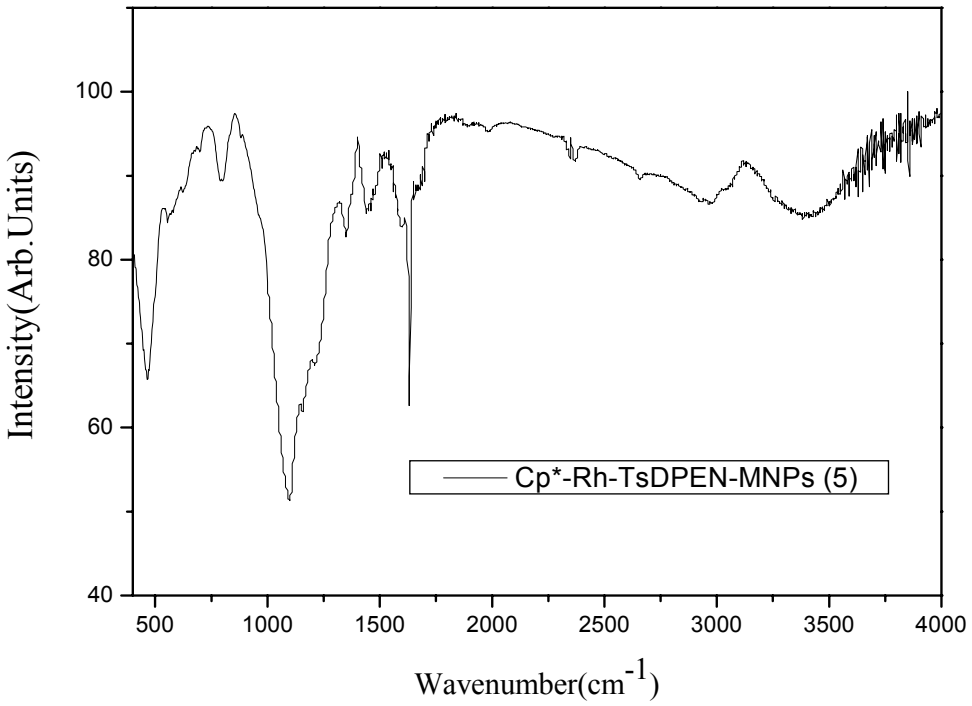
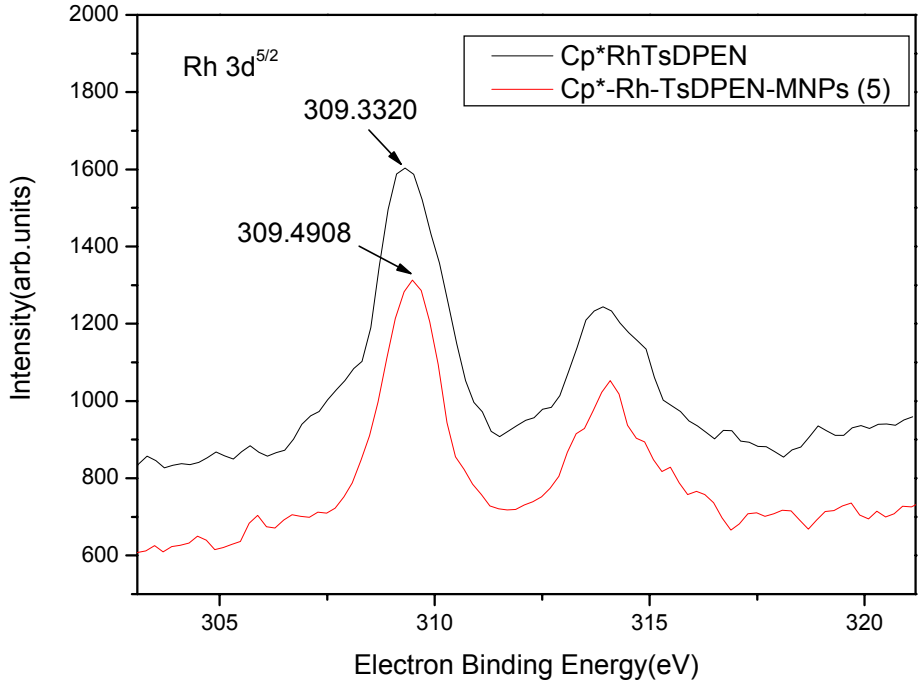


Figure S3. XPS spectra of Cp*-Rh-TsDPEN-MNPs (**5**), Cp*RhTsDPEN and $[Cp^*RhCl_2]_2$.



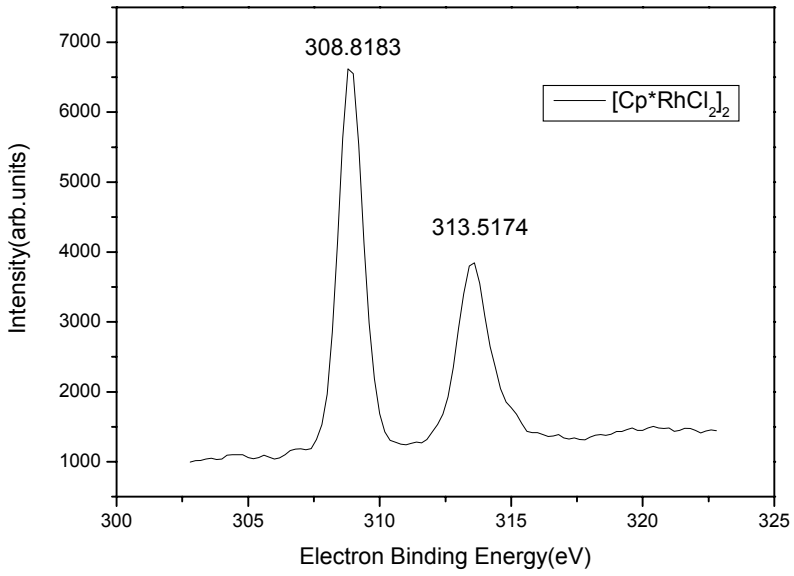
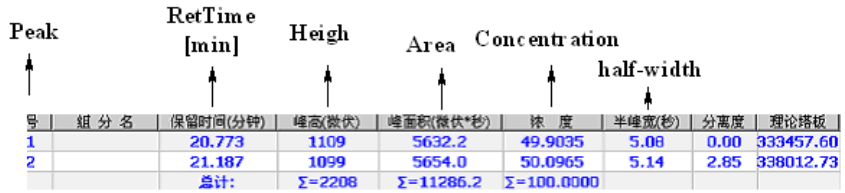


Figure S4. The catalytic activity and enantiomeric excess were determined by chiral GC using a Supelco β-Dex 120 chiral column (30 m×0.25 mm (i.d.), 0.25 μm film)

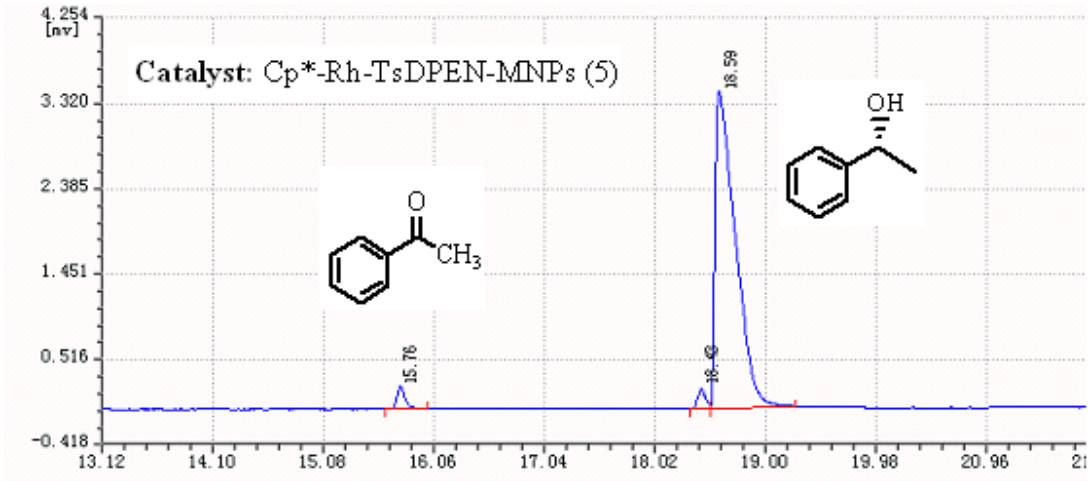
Translation of Chinese to English is as follows:



号	組 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
1		20.773	1109	5632.2	49.9035	5.08	0.00	333457.60
2		21.187	1099	5654.0	50.0965	5.14	2.85	338012.73
		总计:	Σ=2208	Σ=11286.2	Σ=100.0000			

Asymmetric transfer hydrogenation of acetophenone.

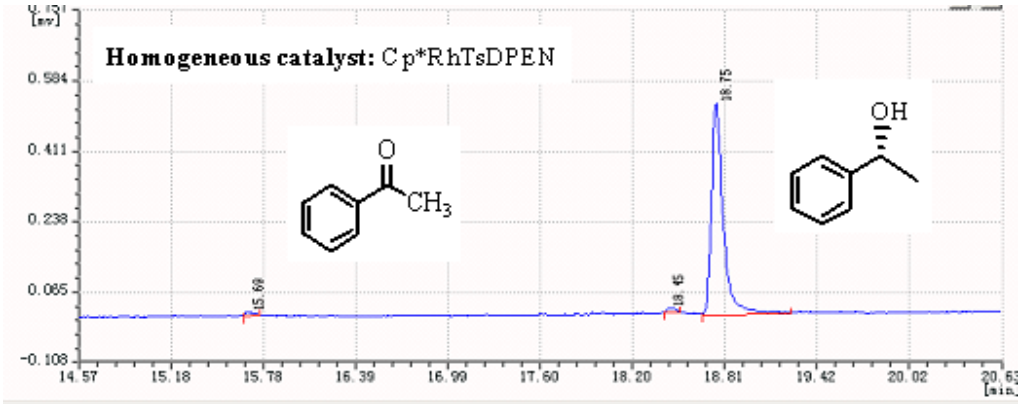
Asymmetric transfer hydrogenation of acetophenone as substrate with 1h reaction time.



参数设置 | 分析结果 | 分组结果 | 样品信息

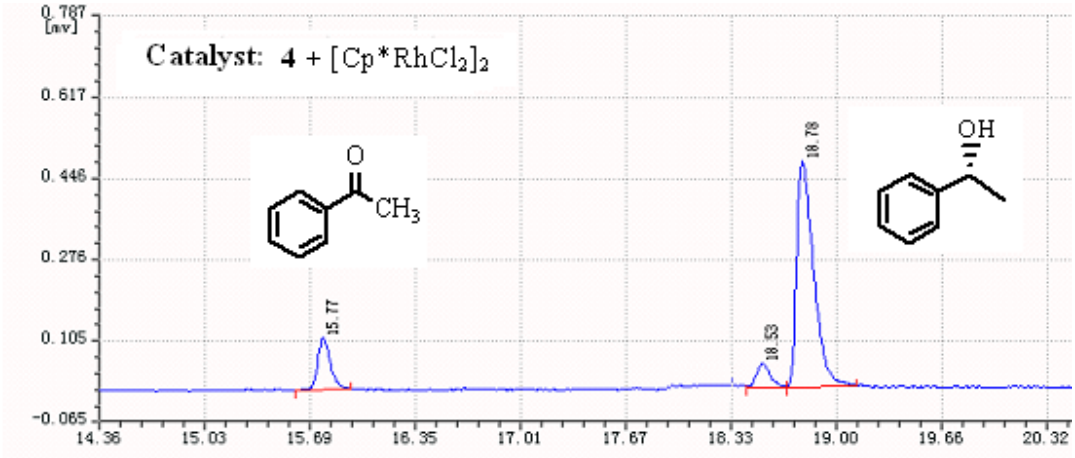
ID号	組 分 名	保留时间(分钟)	峰高(微伏)	峰面积(微伏*秒)	浓 度	半峰宽(秒)	分离度	理论塔板
1		15.760	252	1259.0	2.8196	5.00	0.00	198324.
2		18.427	233	812.4	1.0673	4.35	20.15	358422.
3		18.587	3465	42381.4	96.1131	12.23	0.68	46023.8
		总计:	Σ=3950	Σ=44652.9	Σ=100.0000			

Asymmetric transfer hydrogenation of acetophenone as substrate with 0.5h reaction time using Homogeneous Cp*RhTsDPEN as a catalyst.



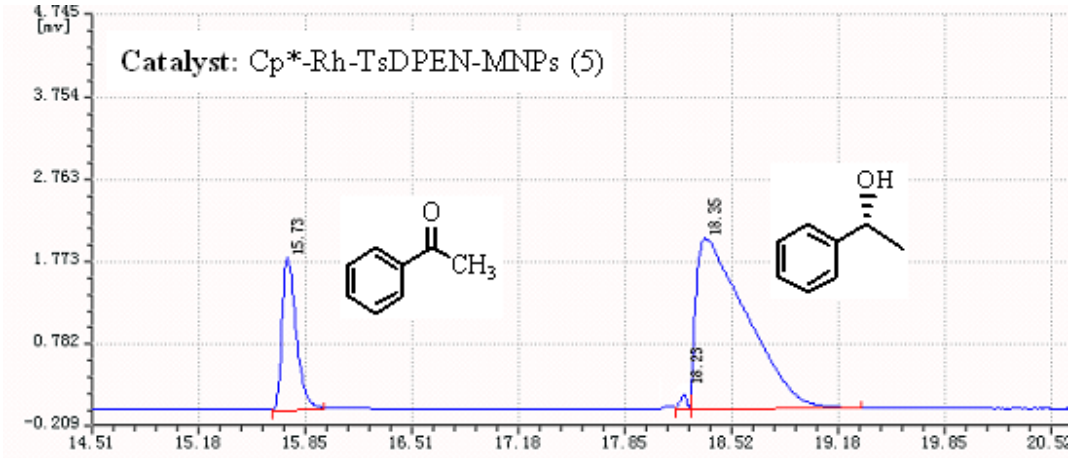
参数设置	分析结果	分组结果	样品信息					
ID号	组 分 名	保留时间(分钟)	峰高(微伏)	峰面积(微伏*秒)	浓 度	半峰宽(秒)	分离度	理论塔板	拖尾因子
1		15.687	10	42.6	1.4549	4.26	0.00	270482.47	1.60
2		18.447	11	42.8	1.4624	3.89	23.91	447979.64	1.42
3		18.753	522	2841.4	97.0827	5.44	2.32	236569.10	1.61
		总计:	Σ=543	Σ=2926.8	Σ=100.0000				

Asymmetric transfer hydrogenation of acetophenone as substrate using **4** + $[Cp^*RhCl_2]_2$ as a catalyst.



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
1		15.767	109	612.4	13.8582	5.62	0.00	156961.23
2		18.527	51	304.8	6.8976	5.98	16.80	191520.40
3		18.780	474	3501.8	79.2442	7.39	1.34	128791.37
		总计:	Σ=634	Σ=4419.0	Σ=100.0000			

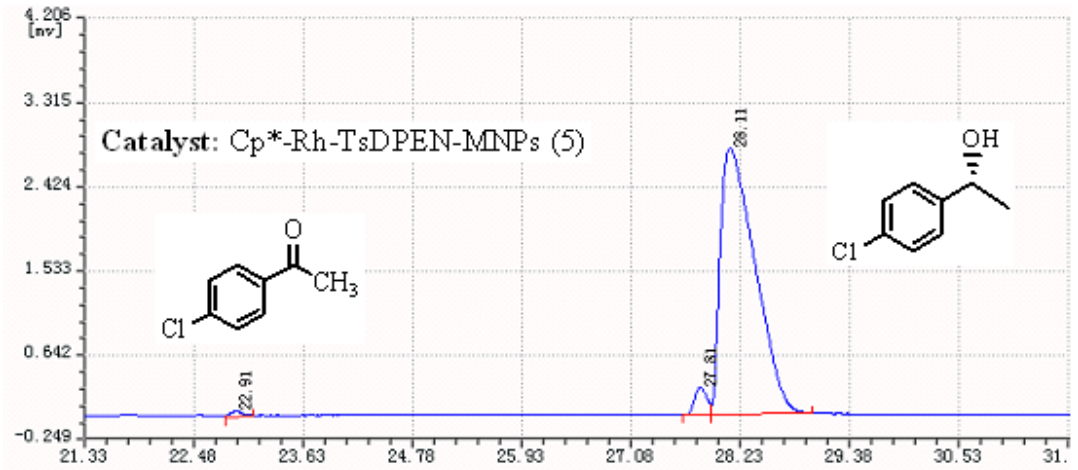
Asymmetric transfer hydrogenation of acetophenone as substrate using **3** + Cp*RhTsDPEN as a catalyst.



参数设置 | 分析结果 | 分组结果 | 样品信息

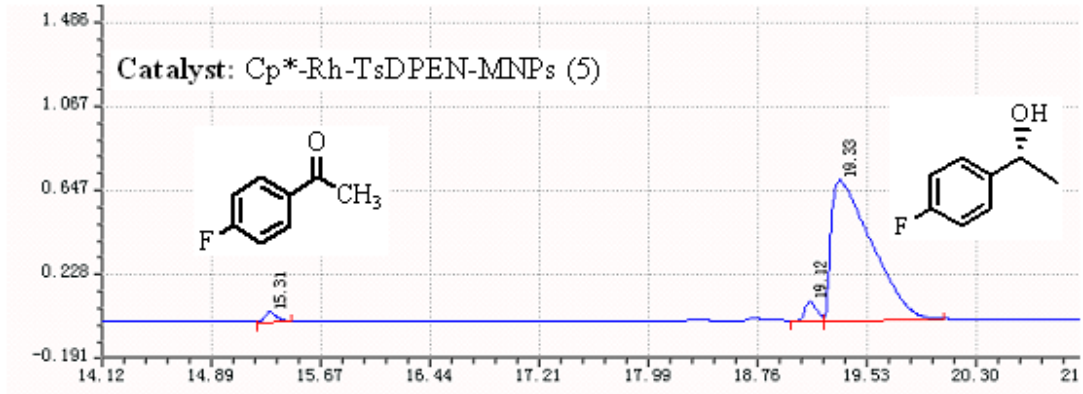
ID号	组 分 名	保留时间(分钟)	峰高(微伏)	峰面积(微伏*秒)	浓 度	半峰宽(秒)	分离度	理论塔板
1		15.733	1834	11253.5	19.6967	6.14	0.00	131036.70
2		18.227	263	885.6	1.5501	3.37	18.52	583930.84
3		18.347	2048	44994.6	78.7532	21.97	0.33	13898.82
		总计:	Σ=4145	Σ=57133.7	Σ=100.0000			

Asymmetric transfer hydrogenation of 4-chloroacetophenone.



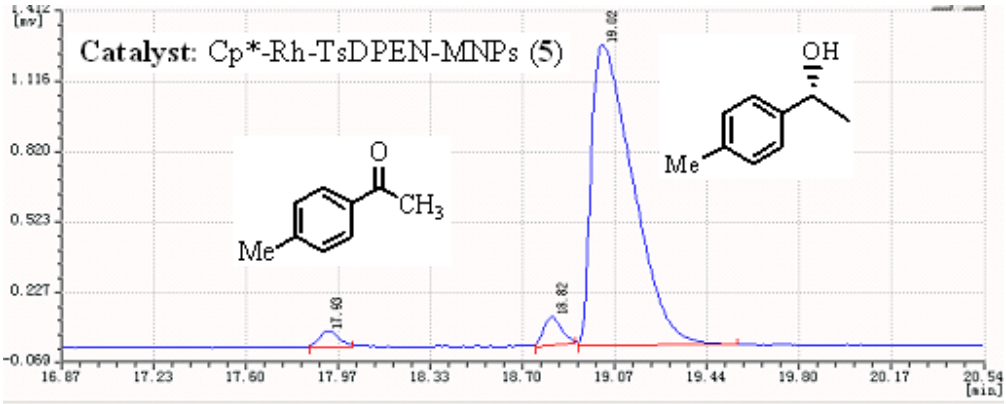
参数设置	分析结果	分组结果	样品信息					
ID号	组 分 名	保留时间(分钟)	峰高(微伏)	峰面积(微伏*秒)	浓 度	半峰宽(秒)	分离度	理论塔板
1		22.913	63	620.0	0.8356	9.84	0.00	108032.5
2		27.807	281	2492.8	3.3595	8.87	18.46	195819.4
3		28.113	2813	71089.2	95.8049	25.27	0.63	24665.01
		总计:	Σ=3157	Σ=74202.1	Σ=100.0000			

Asymmetric transfer hydrogenation of 4-fluoroacetophenone.



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
1		15.307	52	326.2	2.2167	6.27	0.00	118654.8
2		19.120	95	543.8	3.6954	5.72	22.44	222352.0
3		19.333	695	13846.0	94.0879	19.92	0.59	18769.7
		总计:	Σ=842	Σ=14716.0	Σ=100.0000			

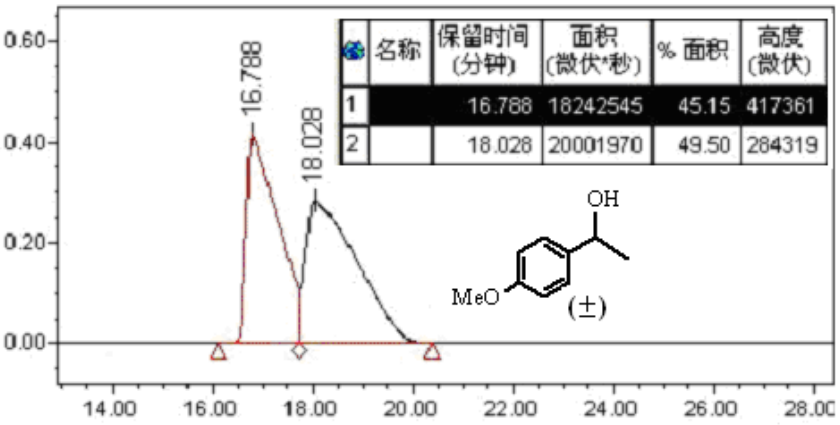
Asymmetric transfer hydrogenation of 4-methylacetophenone.

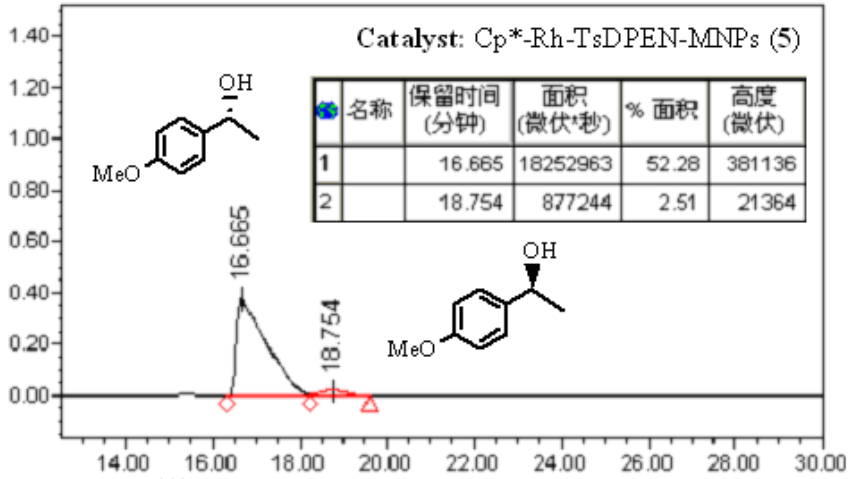


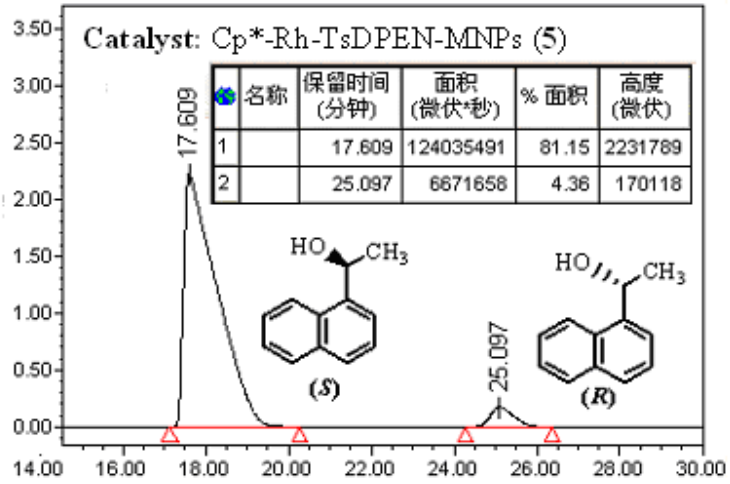
参数设置	分析结果	分组结果	样品信息						
号	组 分 名	保留时间(分钟)	峰高(微伏)	峰面积(微伏*秒)	浓 度	半峰宽(秒)	分离度	理论塔板	拖尾因子
1		17.927	69	371.8	2.3929	5.39	0.00	220601.91	1.16
2		18.820	116	572.3	3.6836	4.93	6.11	289985.96	1.25
3		19.020	1267	14593.2	93.9235	11.52	0.86	54349.71	2.35
		总计:	Σ=1452	Σ=15537.3	Σ=100.0000				

Asymmetric transfer hydrogenation of 4-methoxylacetophenone. (Daicel OJ-H chiralcel columns: 1.0 mL/min, hex/IPA=93:7.)

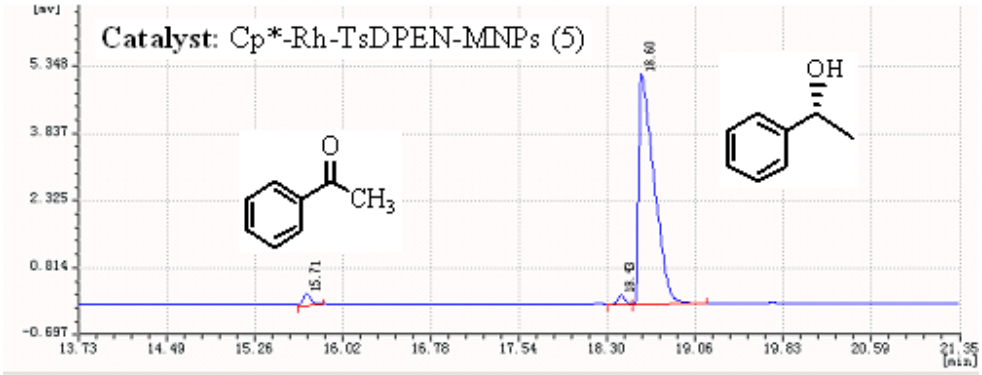
Asymmetric transfer hydrogenation of α-acetonaphthone. (Daicel OJ-H chiralcel columns: 1.0 mL/min, hex/IPA=93:7.) **ref:** [Liu, P. N.; Gu, P. M.; Wang F.; Tu, Y. Q. Org. Lett., 2004, 6, 169.].







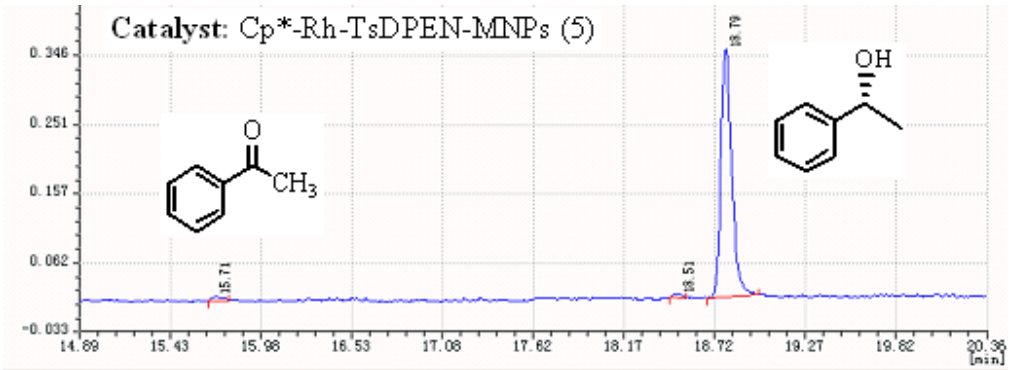
Recycle **2** using Cp*-Rh-TsDPEN-MNPs (**5**) as a catalyst and acetophenone as substrate.



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		15.707	276	1513.1	3.0504	5.48	0.00	163590.52	1.38
2		18.427	201	809.6	1.6322	4.03	20.19	417108.65	1.18
3		18.600	5185	47281.2	95.3174	9.12	0.93	82922.16	3.24
		总计:	Σ=5662	Σ=49604.0	Σ=100.0000				

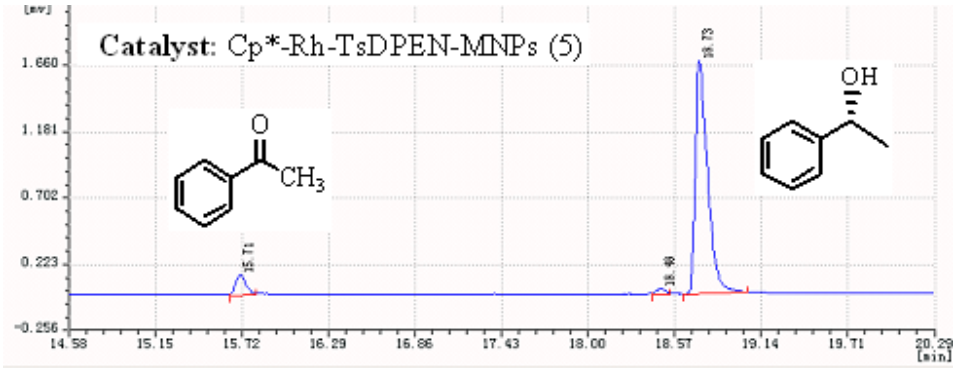
Recycle **3** using Cp*-Rh-TsDPEN-MNPs (**5**) as a catalyst and acetophenone as substrate.



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		15.713	7	29.4	1.8345	4.20	0.00	278973.34	1.19
2		18.507	7	28.2	1.7603	4.03	23.96	420326.03	0.80
3		18.787	340	1545.0	96.4052	4.54	2.31	340676.14	1.31
		总计:	Σ=354	Σ=1602.6	Σ=100.0000				

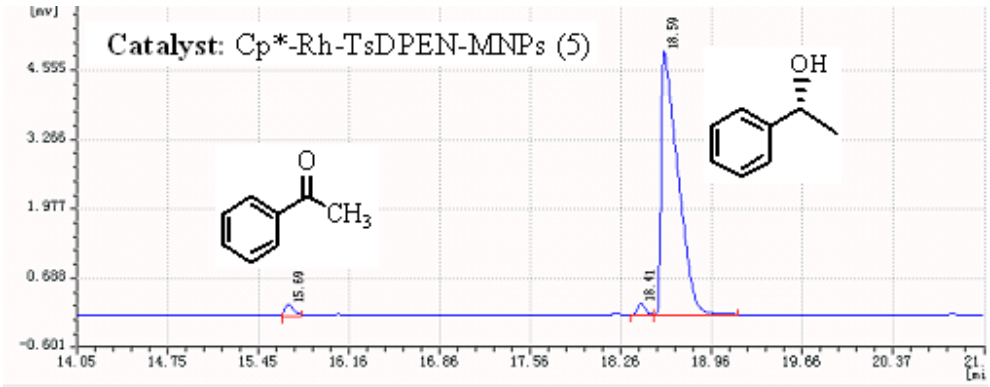
Recycle **4** using Cp*-Rh-TsDPEN-MNPs (**5**) as a catalyst and acetophenone as substrate.



参数设置 | 分析结果 | 分组结果 | 样品信息

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		15.707	147	654.6	6.3602	4.45	0.00	247921.35	1.29
2		18.480	42	186.8	1.8149	4.45	21.99	344091.08	1.00
3		18.733	1681	9451.4	91.8249	5.62	1.78	221257.60	1.85
		总计:	Σ=1870	Σ=10292.8	Σ=100.0000				

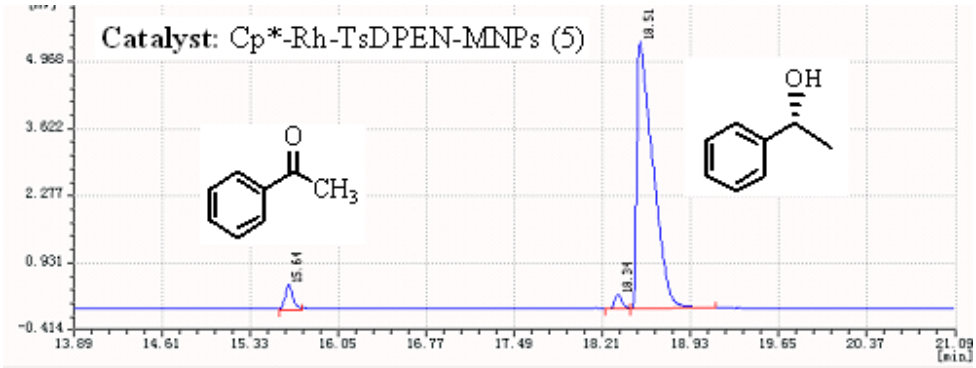
Recycle **5** using Cp*-Rh-TsDPEN-MNPs (**5**) as a catalyst and acetophenone as substrate.



参数设置 | 分析结果 | 分组结果 | 样品信息

D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		15.693	215	1001.6	2.1814	4.66	0.00	226174.34	1.28
2		18.413	221	898.2	1.9562	4.06	22.01	409085.03	1.33
3		18.593	4898	44016.6	95.8625	8.99	0.97	85318.51	3.26
		总计:	Σ=5334	Σ=45916.4	Σ=100.0000				

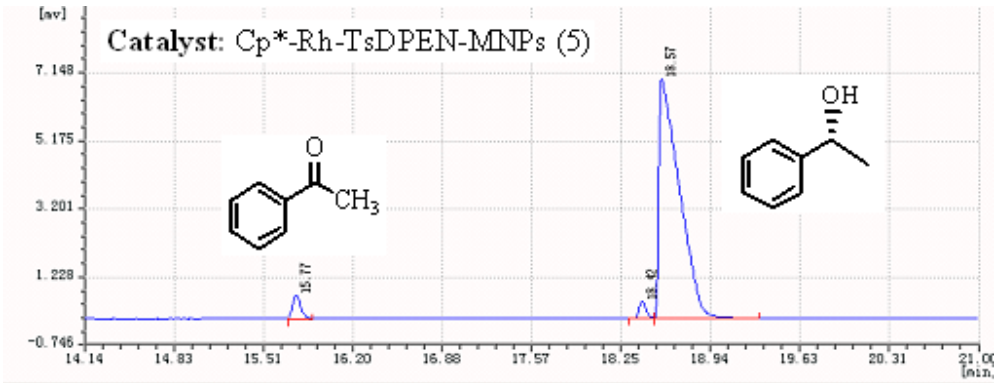
Recycle **6** using Cp*-Rh-TsDPEN-MNPs (**5**) as a catalyst and acetophenone as substrate.



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		15.640	499	2238.8	4.2826	4.49	0.00	242196.93	1.35
2		18.340	283	1140.0	2.1807	4.03	22.38	413115.72	1.18
3		18.513	5329	48897.8	93.5367	9.18	0.93	81134.63	3.35
		总计:	Σ=6111	Σ=52276.6	Σ=100.0000				

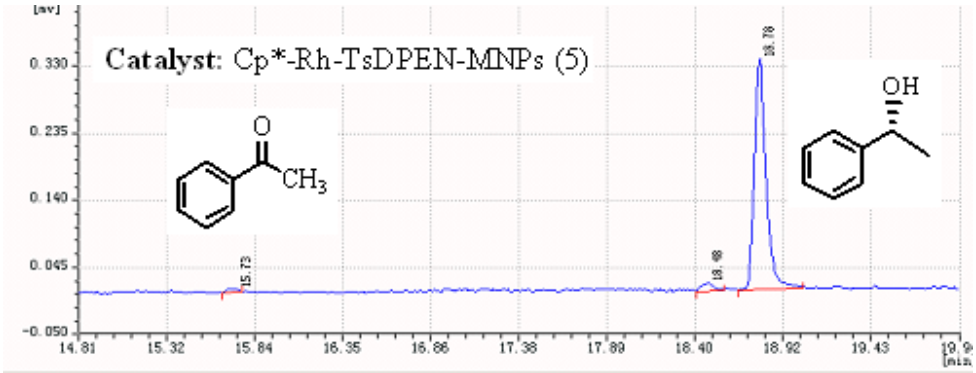
Recycle **7** using Cp*-Rh-TsDPEN-MNPs (**5**) as a catalyst and acetophenone as substrate.



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		15.767	701	3116.8	3.8557	4.45	0.00	250623.95	1.33
2		18.420	498	1920.3	2.3756	3.86	22.56	454795.98	1.17
3		18.567	6928	75799.4	93.7688	10.94	0.70	57395.34	4.06
		总计:	Σ=8127	Σ=80836.5	Σ=100.0000				

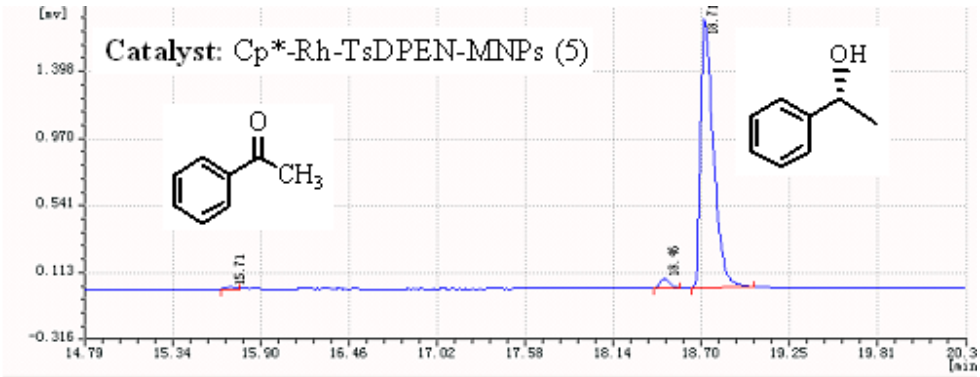
Recycle **8** using Cp*-Rh-TsDPEN-MNPs (**5**) as a catalyst and acetophenone as substrate with 1.5h reaction time.



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		15.733	5	27.2	1.6649	5.44	0.00	166785.15	0.70
2		18.480	12	62.4	3.8200	5.20	18.22	251755.36	1.12
3		18.780	325	1543.8	94.5151	4.75	2.13	311524.76	1.32
		总计:	Σ=342	Σ=1633.4	Σ=100.0000				

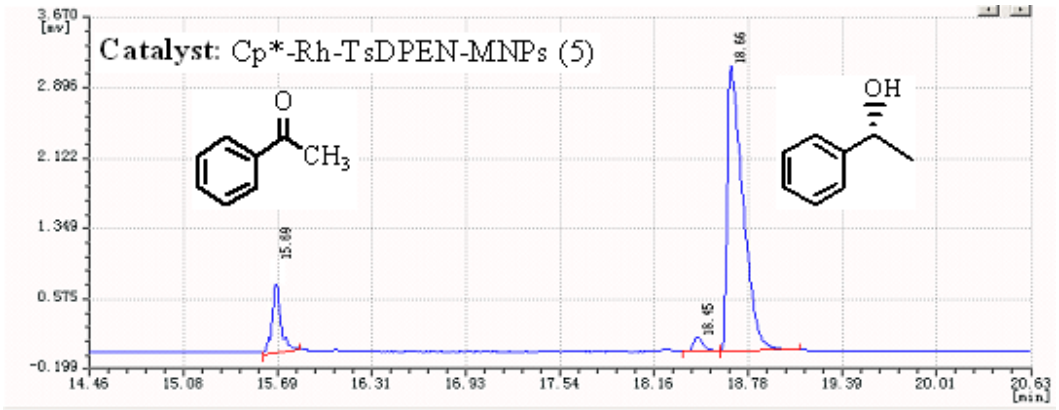
Recycle **9** using Cp*-Rh-TsDPEN-MNPs (**5**) as a catalyst and acetophenone as substrate with 1.5h reaction time..



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		15.713	11	46.4	0.4596	4.22	0.00	276575.34	0.95
2		18.460	63	284.0	2.8132	4.51	22.22	334226.97	1.26
3		18.713	1718	9764.6	96.7271	5.68	1.75	216054.28	1.91
		总计:	Σ=1792	Σ=10095.0	Σ=100.0000				

Recycle **10** using Cp*-Rh-TsDPEN-MNPs (**5**) as a catalyst and acetophenone as substrate with 1.5h reaction time.



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		15.687	1010	2347.1	8.0828	4.40	0.00	252978.79	1.62
2		18.447	151	776.7	3.4472	4.48	21.93	337717.22	1.33
3		18.660	3133	24527.2	88.4700	7.19	1.29	134231.17	2.63
		总计:	Σ=4294	Σ=27651.0	Σ=100.0000				