Supplementary Material (ESI) for Chemical Communications

Supporting Information for

Facile synthesis of mesoporous silica-supported catalyst for Ru-catalyzed transfer hydrogenation of ketones

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Experimental

1. General Methods.

1.1. Materials and general methods.

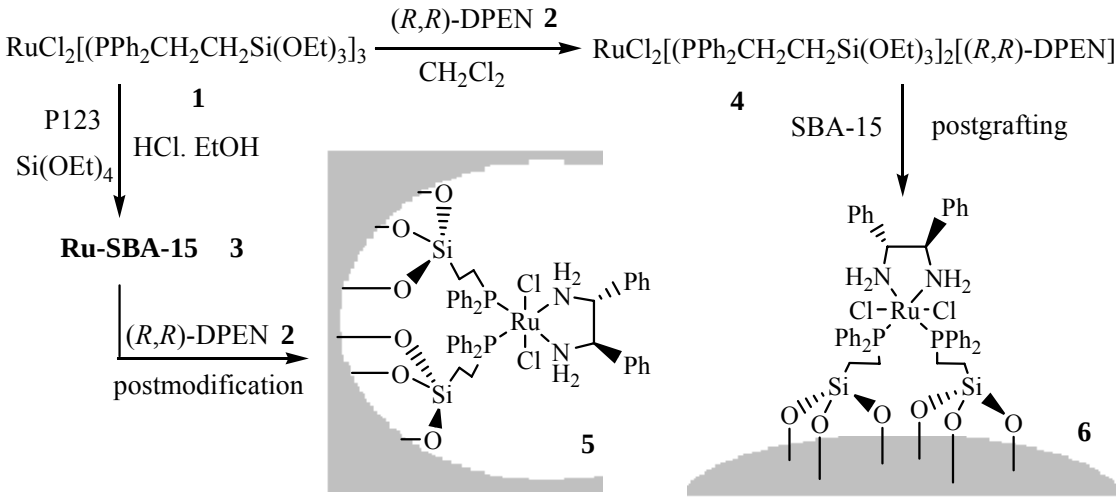
All experiments, which are sensitive to moisture or air, were carried out under an Ar atmosphere using standard Schlenk techniques. Commercial reagents were used without further purification unless otherwise noted. Triblock PEO-PPO-PEO copolymer **P123** [$HO(CH_2CH_2O)_{20}(CH_2CH(CH_3)O)_{70}(CH_2\text{-}CH_2O)_{20}H$], (Trisethoxysilyl)ethyldiphenylphosphine, diphenylshosphine, (1*R*,2*R*)-1,2-diphenylethylenediamine [*(R,R)*-DPEN], (Trisethoxysilyl)ethyldiphenylphosphine and Ruthenium(III) chloride were purchased from Sigma-Aldrich Company Ltd. and used as received. SBA-15 (pore size 7.6 nm) and Ru-SBA-15 (pore sizes 5.7 nm) were synthesized and characterized as described in our previous reports (a) Li, H. X.; Zhang, F.; Wan, Y.; Lu, Y. F. *J. Phys. Chem. B:* **2006**, *110*, 22942. b) Wan, Y.; Zhang, F.; Lu, Y. F.; Li, H. X. *J. Mol. Catal. A: Chem.* **2007**, *267*, 165. c) Wan, Y.; Chen, J.; Zhang, D. Q.; Li, H. X. *J. Mol. Catal. A: Chem.* **2006**, *258*, 89). $RuCl_2\{PPh_2(CH_2)_2Si(OEt)_3\}_3$ **1** was synthesized by the literatrue (Kröcher, O.; Köppel, R. A.; Fröba, M.; Baiker, A. *J. Catal.* **1998***, 178,* 284-298.)The representative ketones were chosen as model substrates to test the heterogeneous Ruthenium catalysts. The corresponding racemic alcohol were prepared by hydrogenation these ketones by $LiAlH_4$ in THF at 0

°C. The *ee* values were determined by GC using a Supelco β-Dex 120 chiral column (30 m×0.25 mm (i.d.), 0.25 μm film).

1.2. Characterization

Ru loadings in the catalysts **5-6** were analyzed by inductively coupled plasma optical emission spectrometer (ICP, Varian VISTA-MPX). The X-ray powder diffraction (XRD) experiments were carried out on a Rigaku D/Max-RB diffractometer with Cu Kα radiation. Transmission electron microscopy (TEM) studies were performed on a JEOL JEM2010 electron microscope, operated at an acceleration voltage of 200 kV. Fourier transform infrared (FTIR) spectra were collected with a Nicolet Magna 550 spectrometer by using the KBr method. N2 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 (S_{BET}) of samples were determined from the linear parts of BET plots (p/p_0 = 0.05-0.95). Solid-state ^{29}Si MAS NMR, ^{13}C CP MAS NMR, and ^{31}P CP MAS NMR spectra were recorded at 79.5, 100.6, and 169.3 MHz, respectively, using a Bruker AV-400 spectrometer.

2. Synthetic procedures.



2.1. Preparations of the mesoporous silica-supported Ruthenium chiral catalysts

*2.1.1. Synthesis of catalyst **6** by postgrafting method.* The typical procedures as follows: Under argon

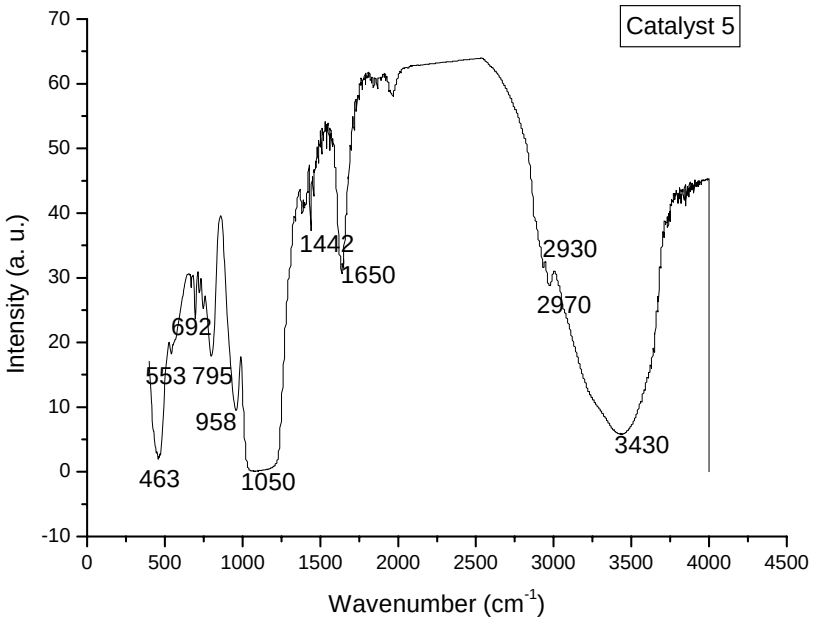
atmosphere, to a stirred solution of $RuCl_2\{PPh_2(CH_2)_2Si(OEt)_3\}_3$ **1** (0.20 g, 0.15 mmol) in 2 mL dry CH_2Cl_2 was added dropwise (1*R*,2*R*)-1,2-diphenylethylenediamine (0.033 g, 0.15 mmol) in 2 mL dry CH_2Cl_2 at room temperature. The resulting mixture was stirred and refluxed for 24 h.. After evaporation of most of the solvent, the residues were washed thoroughly with hexane to afford $RuCl_2\{PPh_2(CH_2)_2Si(OEt)_3\}_2$-DPEN **4** (0.13 g, 0.11 mmol, 73.3%) as a red solid, which is not purified and used directly in following reaction. Then pure siliceous support [SBA-15 (poresize of 7.6), 1.0 g] was dehydrated at 125 ºC under 0.01 Torr for 4 h before the addition of the fresh **4** in dry toluene (25 mL). The resulting mixture was stirred and refluxed for 24 h under Argon atmosphere, during which time the various Ru were grafted onto the supports. After being cooled, filtrated, and washed thoroughly with toluene and C_2H_5OH : CH_2Cl_2 (v:v = 1:1), the solid was dried at 60 ºC under reduced pressure overnight to afford the mesoporous catalyst **6** (1.08 g, 72.7% relative to **4**) in the form of a red powder (Scheme 1). **ICP** analyses show that the Ru loadings amount in the catalyst **6** is about 6.80 mg per gram catalyst **6** (theoretic amounts 7.18 mg relative to **6**). IR 3450, 2960, 2920, 2870, 1650, 1440, 1050, 959, 806, 692, 545, 468 cm^{-1} (IR spectrum was shown in Fig.S1); Elemental analysis (%): C 3.39, H 2.55, N 0.19; d_{pore}: 6.3 nm; S_{BET}: 431 m^2/g. ^{29}Si MAS/NMR (79.5 MHz): Q^4 (δ = -116 ppm), Q^3 (δ = -106 ppm), and Q^2 (δ = -97 ppm); ^{13}C CP/MAS (100.6 MHz): 129, 72, 63, 22 ppm; ^{31}P CP/MAS (169.3 MHz): 71 ppm (NMR spectrum was shown in Fig.S2); The TEM images was shown in Fig.S3.

2.1.2. Synthesis of the catalyst **5** *by the postmodification method through reaction of Ru-SBA-15 with (1R,2R)-1,2-DPEN.* The typical procedures as follows: Under argon atmosphere, 1.0 g of Ru-SBA-15 (Ru, 62 μmol) prepared by reported method was added into a stirred solution of (1*R*, 2*R*)-DPEN **2** (0.0132 g, 62 μmol) in 25 mL of toluene and the mixture was reflux for 10 h. After being cooled, filtrated, and washed thoroughly with toluene and C_2H_5OH : CH_2Cl_2 (v:v = 1:1), the solid was dried at 60 ºC under reduced pressure overnight to afford the mesoporous catalyst **5** (1.01 g, 75.7% relative to **2**) in the form of a light red powder (Scheme 1). **ICP** analyses show that the Ru loadings amount in the catalyst **5** is 6.26 mg per gram catalyst **5** (theoretic amounts 6.26 mg relative to **5**). IR 3430, 2970,

2930, 1650, 1442, 1050, 958, 795, 692, 553, 463 cm^{-1} (IR spectrum was shown in Fig.S1); Elemental analysis (%): C 3.08, H 2.14, N 0.17; d_{pore}: 4.8 nm; S_{BET}: 371 m^2/g. ^{29}Si MAS/NMR (79.5 MHz): Q^4 (δ = -112 ppm), Q^3 (δ = -104 ppm), and Q^2 (δ = -96 ppm); ^{13}C CP/MAS (100.6 MHz): 128, 69, 73, 65, 23 ppm; ^{31}P CP/MAS (169.3 MHz): 69, 19 ppm (NMR spectrum was shown in Fig.S2); The TEM images was shown in Fig.S3.

3. *General Procedures for Asymmetric Transfer Hydrogenation of ketones***.** Under argon atmosphere, the catalyst **6** (0.074 g, 5.03 μmol based on Ru from ICP) and potassium *tert*-butoxide (11.20 mg, 0.10 mol) in a test tube were stirred in dry CH_2Cl_2 (5 mL) for 1 h at room temperatute. Then anhydrous 2-propanol (1 mL, 0.013 mol) and the ketone (0.5 mmol) were added with a syringe and mixture was stirred at 50 °C for 24-48 h. After the completion of the reaction, dry CH_2Cl_2 (1 mL) was added and the mixture was stirred for 1 min, then the reactor was centrifuged (2000 r/min) for 1-2 min. The solution was fast passed through a short column (silica gel, eluent: Et_2O). 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) as shown in Fig. 4S.

Figure S1. FTIR spectra of Catalysts **5-6**,.



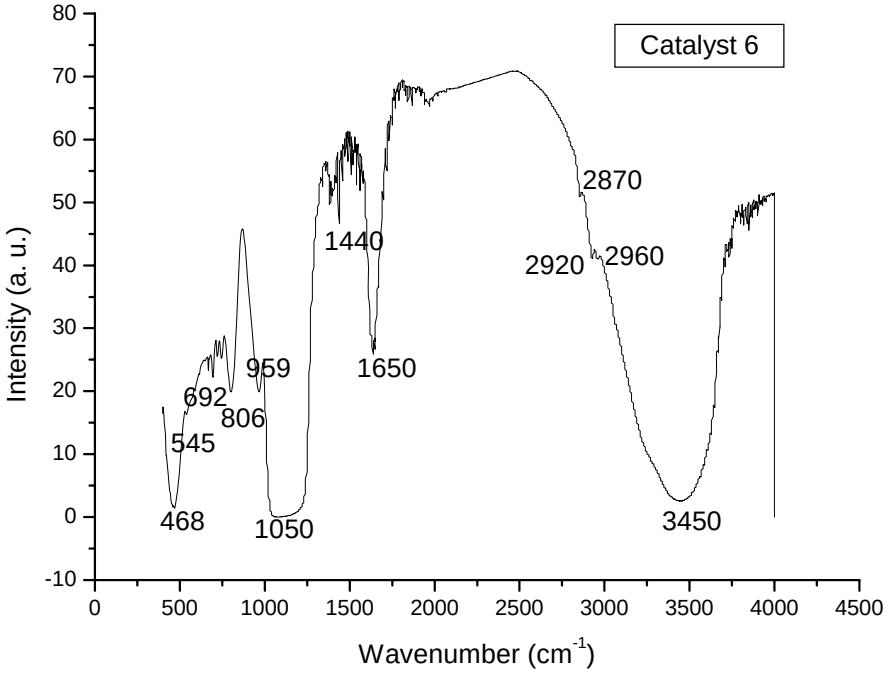
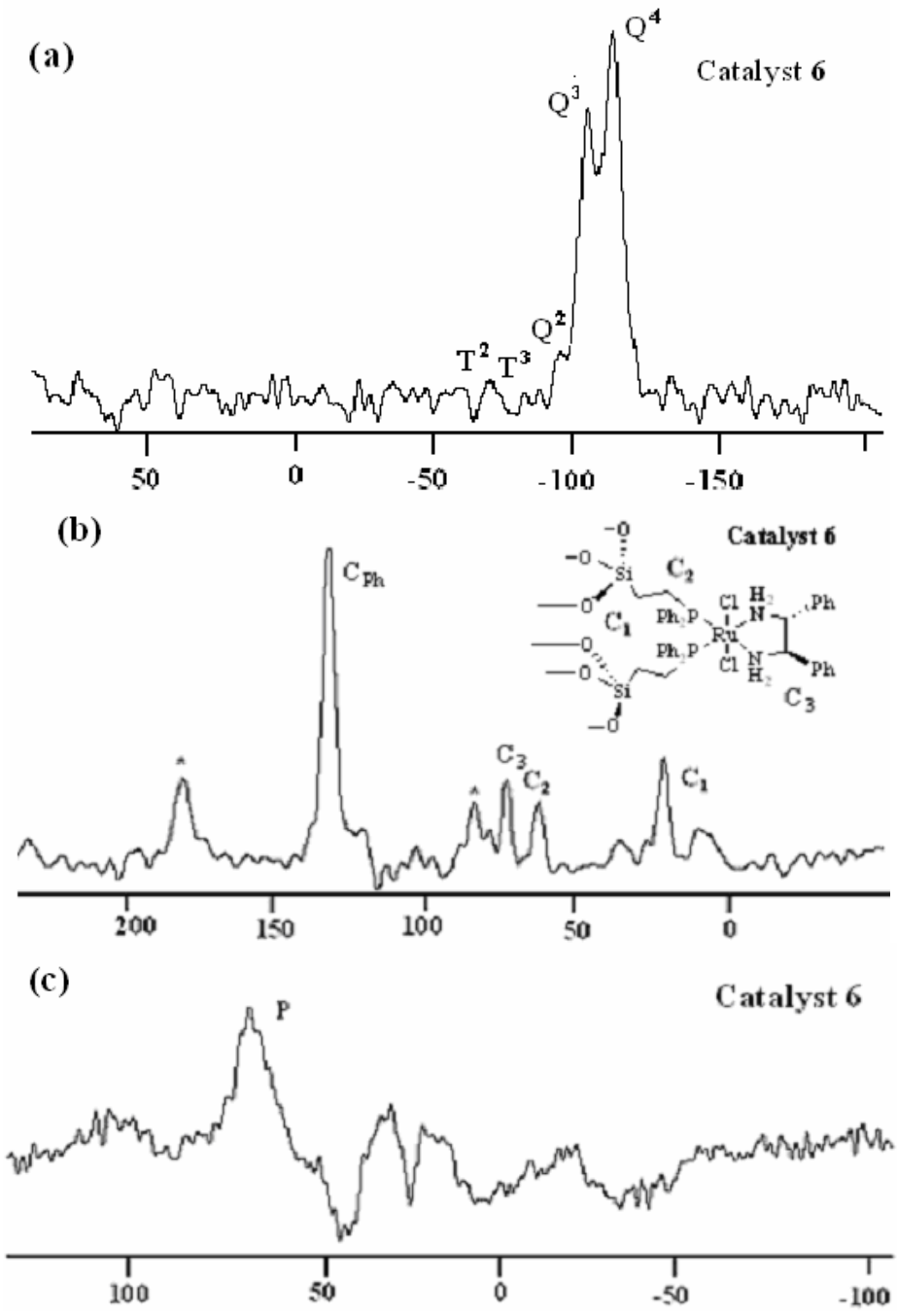


Figure S2. NMR spectra of the catalyst **5** and **6**: (a) ^{29}Si MAS NMR, (b) ^{13}C CP MAS NMR, and (c) ^{31}P CP MAS NMR



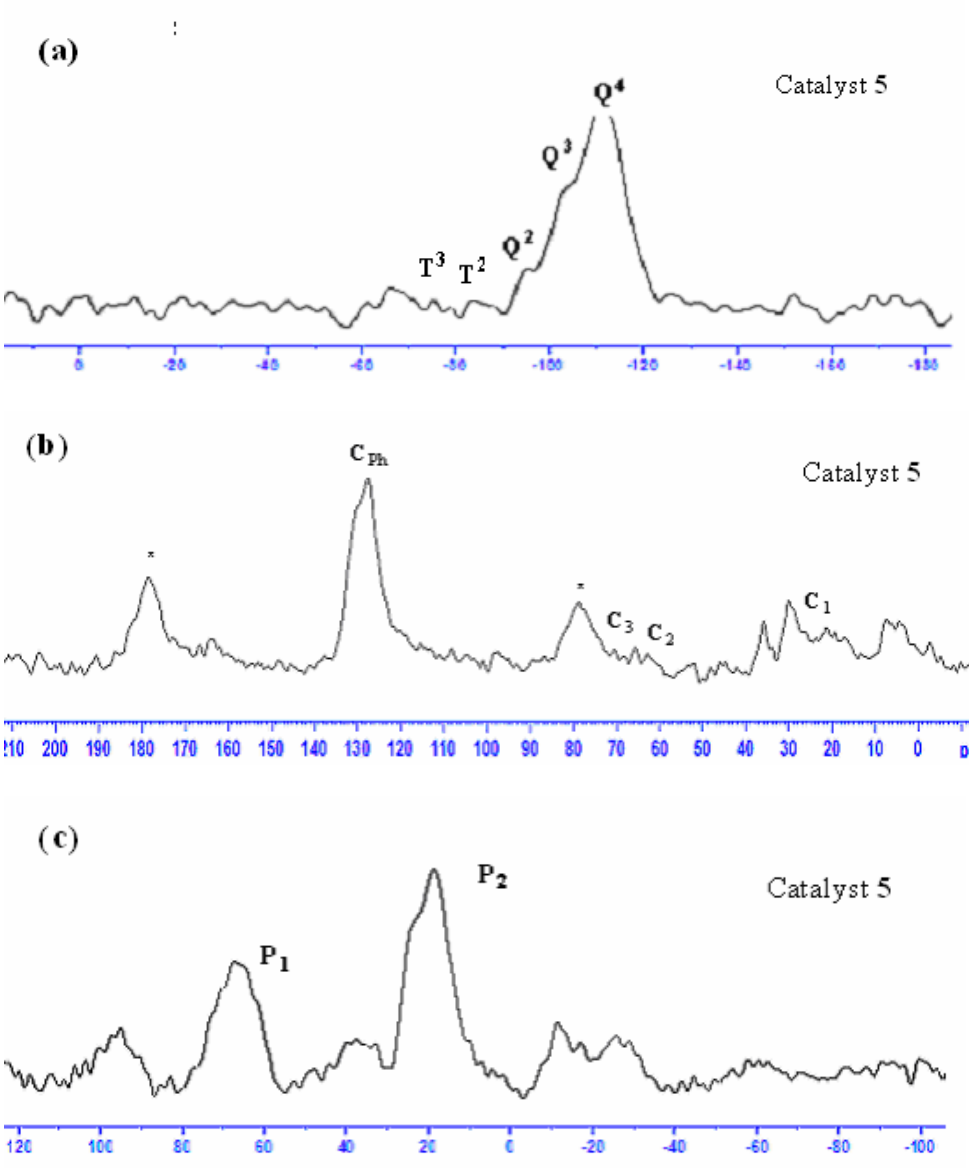

(a)
Catalyst 5
Q4
Q3
Q2
T3
T2
(b)
Catalyst 5
CPh
C3
C2
C1
ppm
(c)
Catalyst 5
P2
P1

Figure S3. The TEM images of the catalysts **5-6** viewed along [001] directions.

Catalyst 5: **Catalyst 6:**

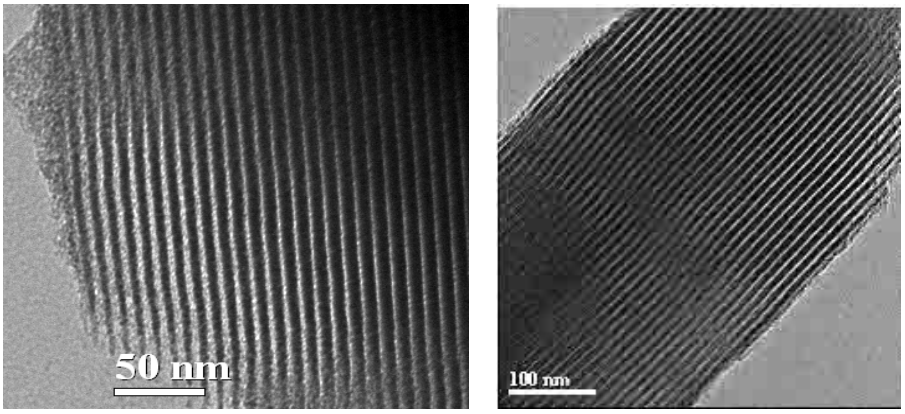
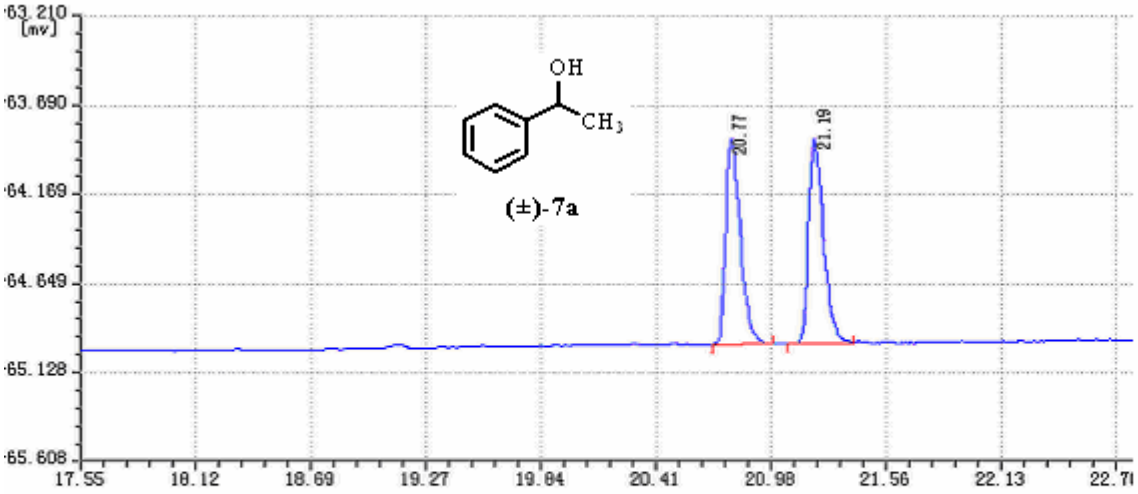


Figure S4. The catalytic activity and enantiomeric excess were determined by chiral GC using a Supelco β-Dex 120 chiral column (30 m×0.25 mm (i.d.), 0.25 μm film)



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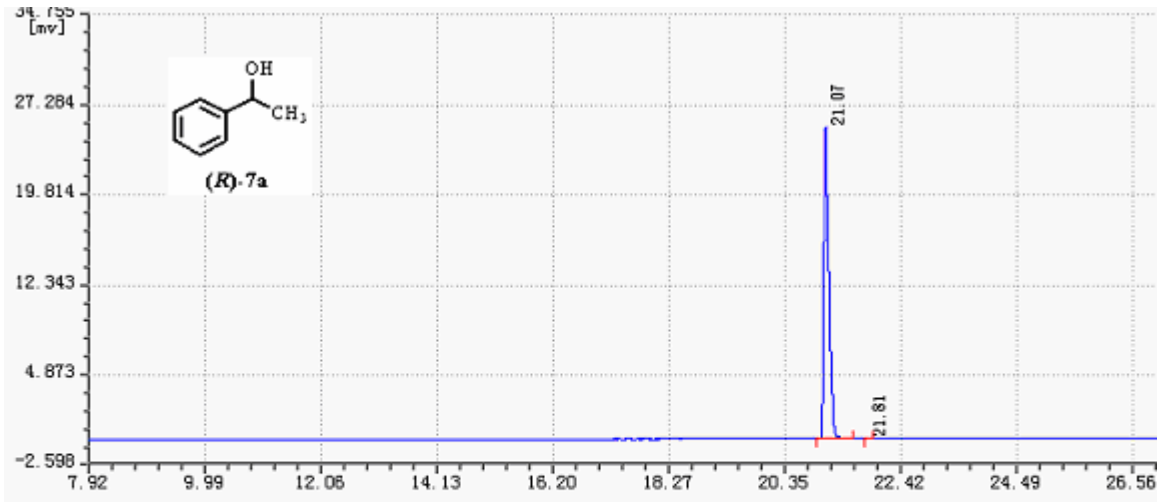
1		20.773	1109	5632.2	49.9035	5.08	0.00	333457.60
2		21.187	1099	5654.0	50.0965	5.14	2.85	338012.73
		总计:	Σ=2208	Σ=11286.2	Σ=100.0000			



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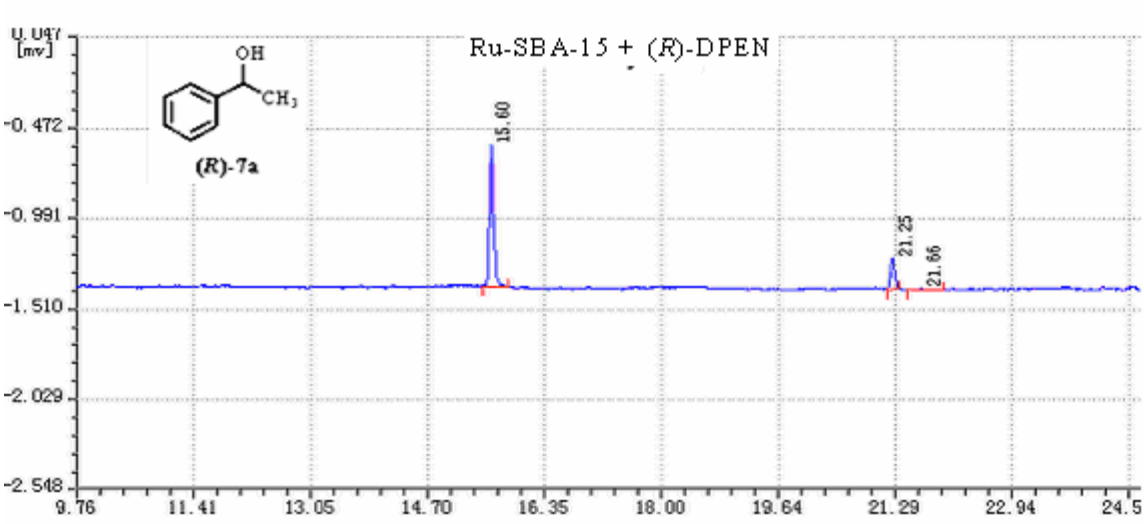
1		21.067	25800	161786.9	99.7531	6.27	0.00	224941.08
2		21.807	47	400.4	0.2469	8.52	3.53	130590.26
		总计:	Σ=25847	Σ=162187.3	Σ=100.0000			



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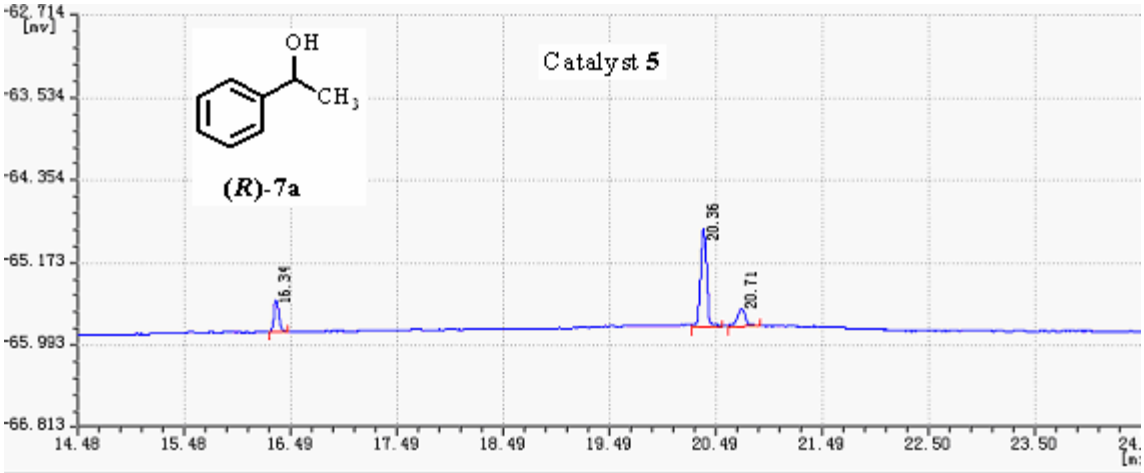
1		15.600	812	3767.6	82.0923	4.64	0.00	225295.67
2		21.253	171	736.8	16.0539	4.31	44.59	484933.07
3		21.660	7	85.1	1.8538	12.15	1.74	63299.40
		总计:	Σ=990	Σ=4589.5	Σ=100.0000			



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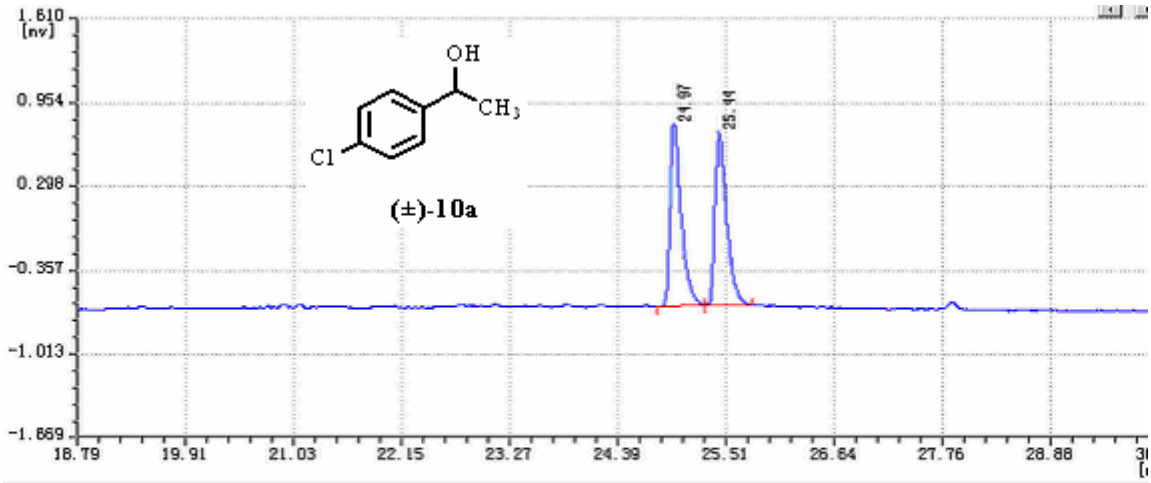
1		16.340	318	1060.4	18.0527	3.33	0.00	478541.14	1.59
2		20.360	983	3827.8	65.1647	3.89	39.26	544858.02	1.31
3		20.713	175	985.8	16.7825	5.63	2.62	269468.15	1.14
		总计:	Σ=1476	Σ=5874.1	Σ=100.0000				



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1		24.973	1436	11427.4	50.0136	7.96	0.00	196286.60	1.77
2		25.440	1361	11421.2	49.9864	8.39	2.01	183168.42	1.72
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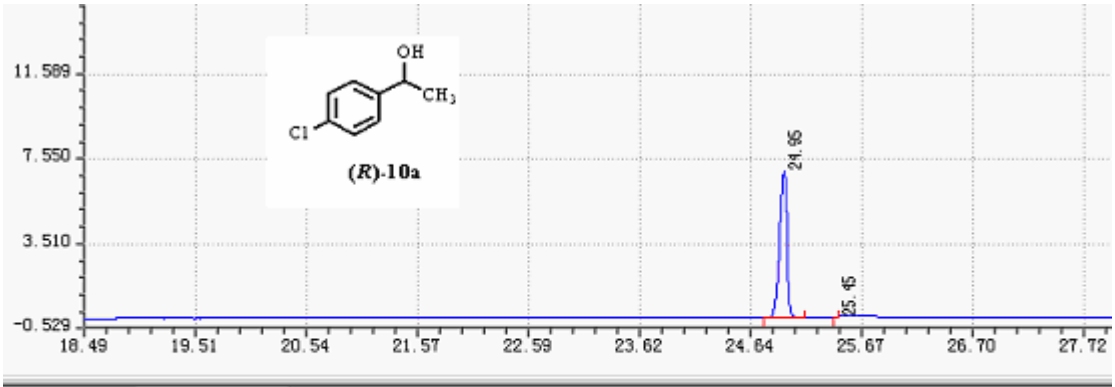

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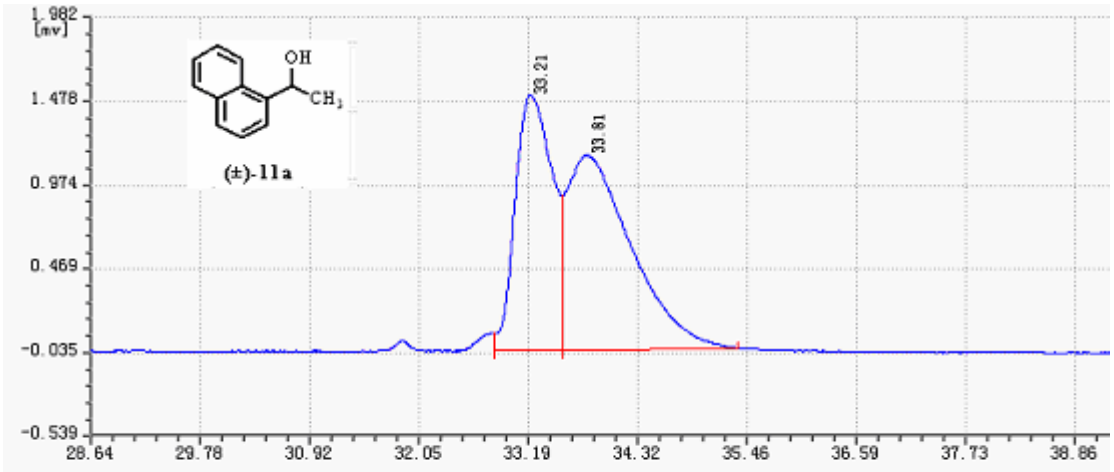
1		24.947	6934	32436.3	99.5275	4.68	0.00	566832.50
2		25.447	56	154.0	0.4725	2.75	4.75	170655...
		总计:	Σ=6990	Σ=32590.3	Σ=100.0000			



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1		33.207	1536	41653.8	43.8945	27.12	0.00	29884.65
2		33.807	1170	53241.4	56.1055	45.51	0.58	11000.24
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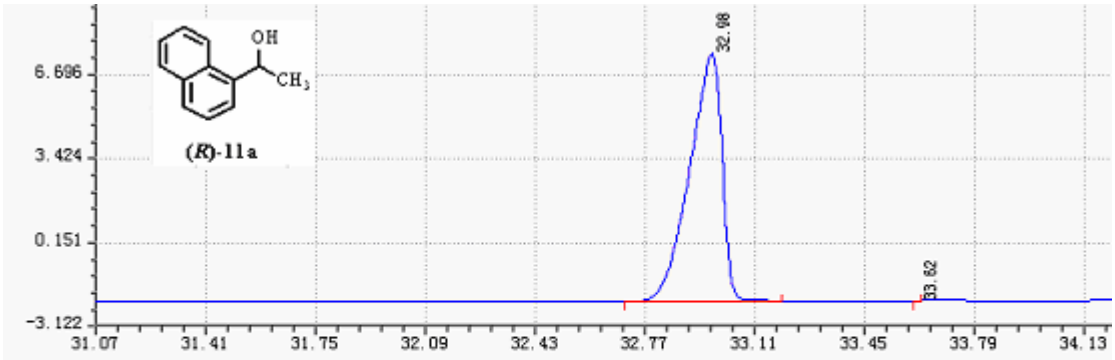

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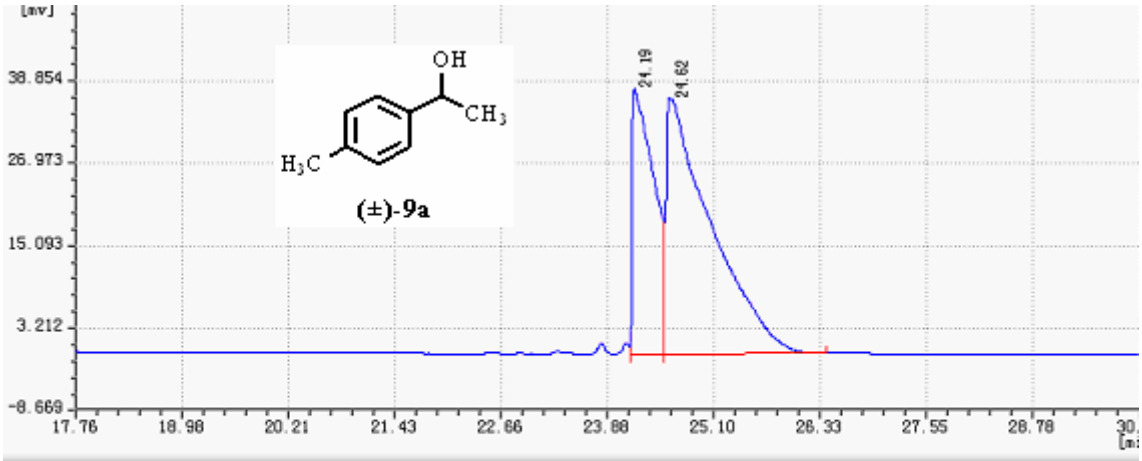
1		32.980	9611	66252.2	99.9177	6.89	0.00	456207.27
2		33.620	36	54.6	0.0823	1.52	5.37	979354...
		总计:	Σ=9647	Σ=66306.8	Σ=100.0000			



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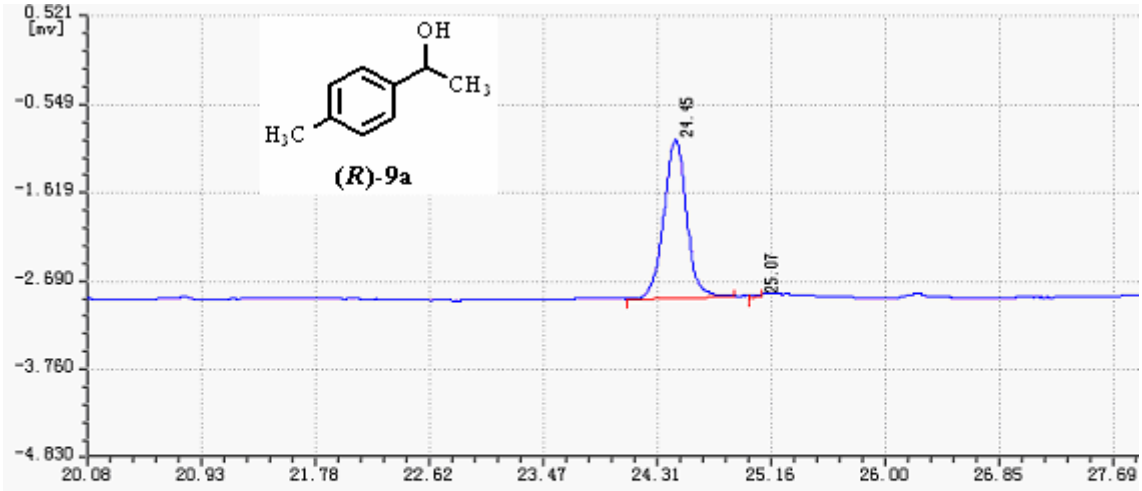
1		24.187	38119	655852.2	33.3863	17.21	0.00	39386.52	4.92
2		24.620	36803	1308584.0	66.6137	35.56	0.58	9555.73	7.55
		总计:	Σ=74922	Σ=1964436.3	Σ=100.0000				



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1		24.447	1920	22434.9	99.1750	11.68	0.00	87240.88
2		25.073	26	186.6	0.8250	7.18	2.35	243177.90
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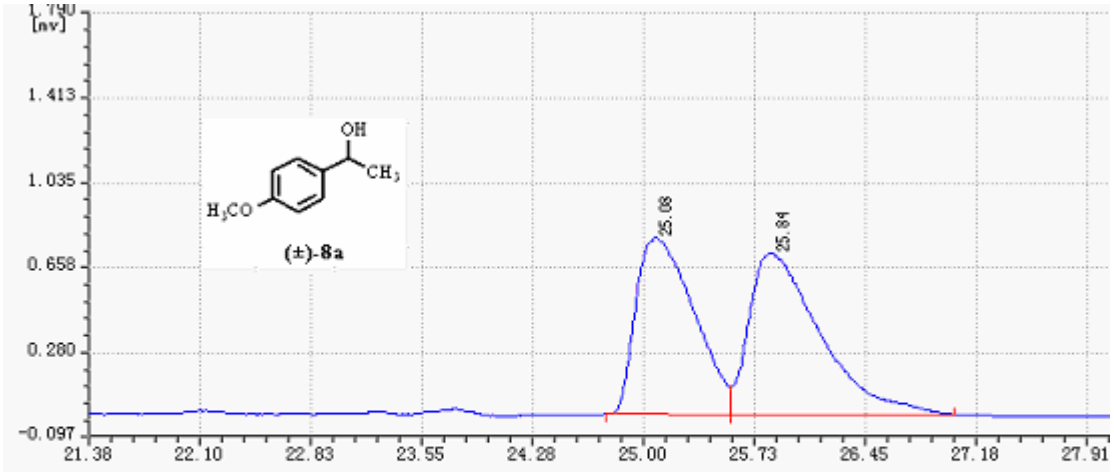

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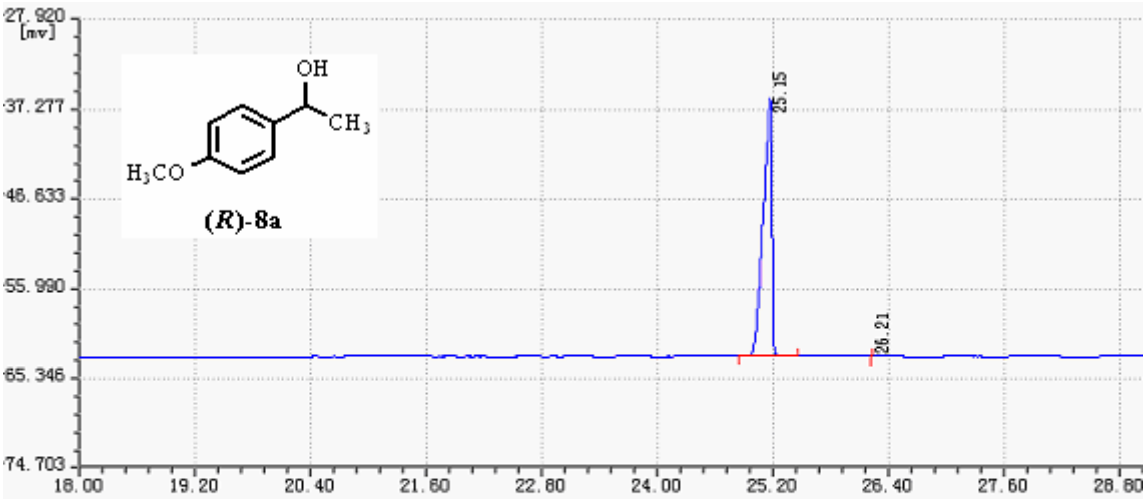
1		25.080	787	20610.2	47.2880	26.19	0.00	18279.52
2		25.840	718	22974.2	52.7120	32.00	0.92	12998.04
		总计:	Σ=1505	Σ=43584.4	Σ=100.0000			



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1		25.153	26840	170175.8	99.9524	6.34	0.00	313678.70
2		26.213	77	81.0	0.0476	1.05	10.12	123676...
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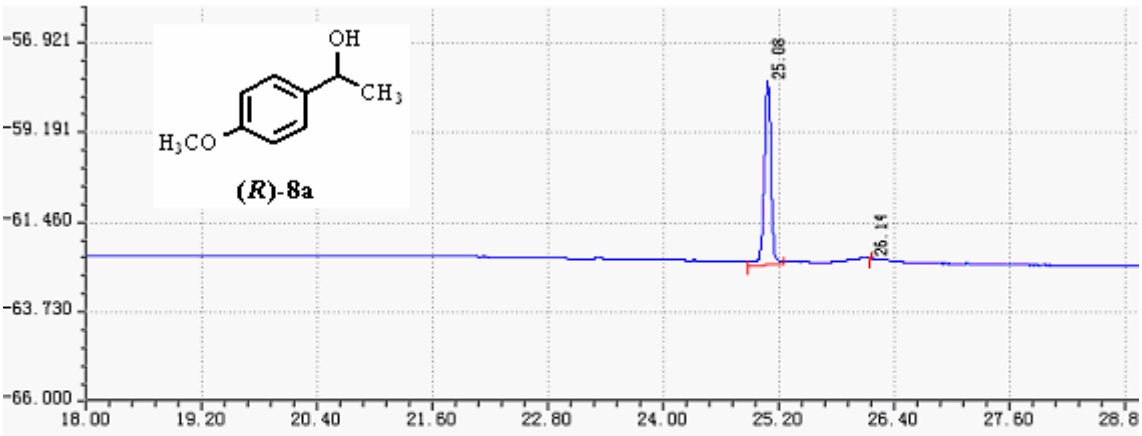

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1		25.080	4638	22929.3	99.8754	4.94	0.00	512929.94
2		26.140	21	28.6	0.1246	1.36	11.87	733889...
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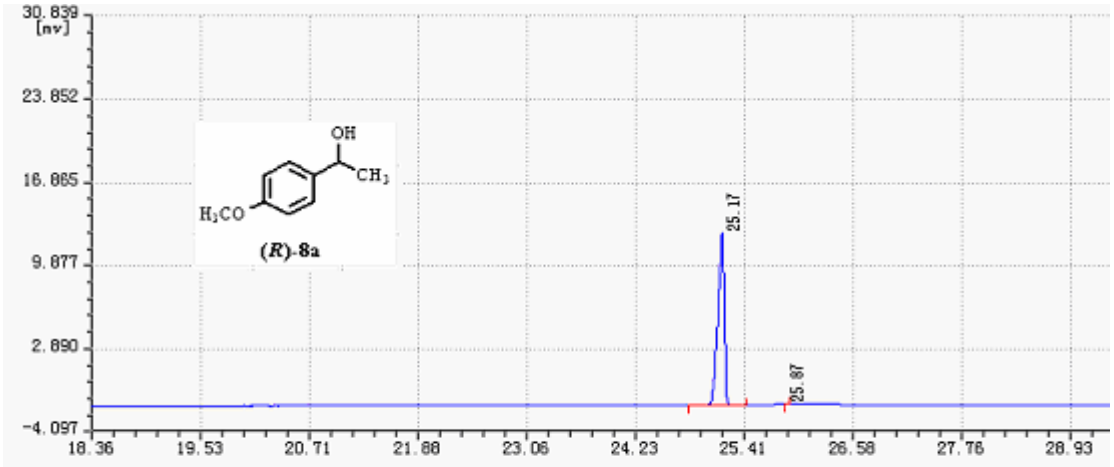

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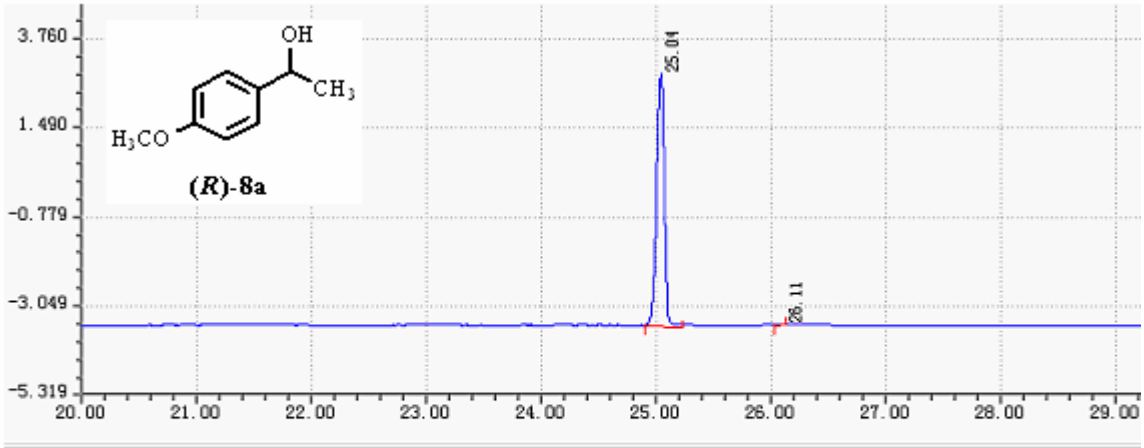
D号	组 分 名	保留时间(分钟)	峰高(微伏)	峰面积(微伏*秒)	浓 度	半峰宽(秒)	分离度	理论塔板
1		25.167	14522	71900.0	99.7929	4.95	0.00	514956.84
2		25.867	57	149.2	0.2071	2.62	6.53	194633...
		总计:	Σ=14579	Σ=72049.2	Σ=100.0000			

Recycling-experiment 4：



参数设置 | 分析结果 | 分组结果 | 样品信息

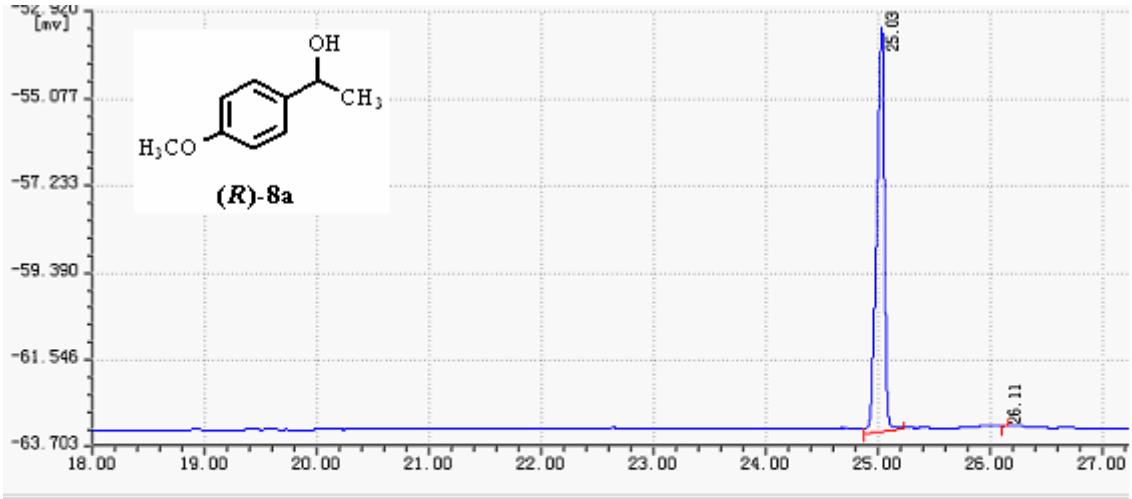
号	组 分 名	保留时间(分钟)	峰高(微伏)	峰面积(微伏*秒)	浓 度	半峰宽(秒)	分离度	理论塔板
1		25.040	6448	30275.5	99.6039	4.70	0.00	566839.98
2		26.107	16	120.4	0.3961	7.52	6.16	239923.22
		总计:	Σ=6464	Σ=30395.9	Σ=100.0000			

Recycling-experiment 5：

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
1		25.007	1948	8626.2	99.7710	4.43	0.00	635581.99
2		26.053	11	19.8	0.2290	1.80	11.86	417547...
		总计:	Σ=1959	Σ=8646.0	Σ=100.0000			

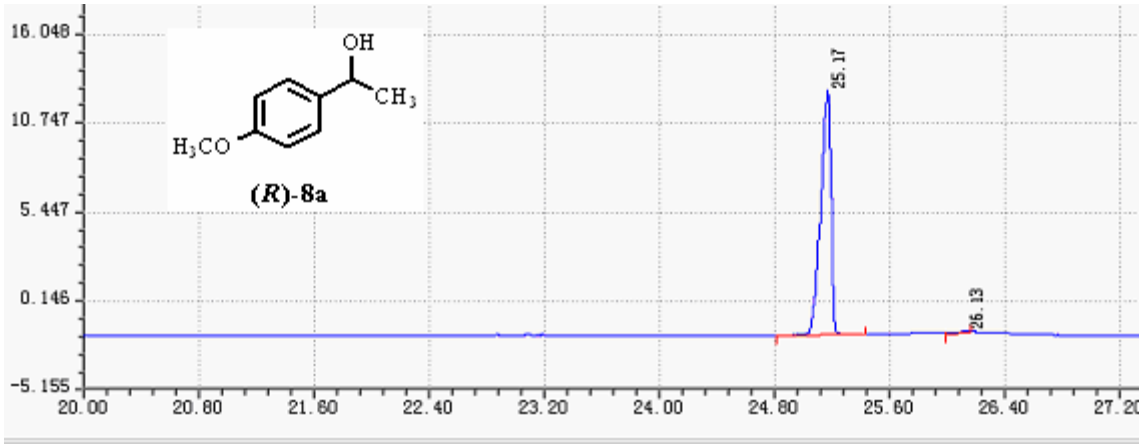
Recycling-experiment 6：



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
1		25.027	10016	48871.2	99.7328	4.88	0.00	524339.92
2		26.107	55	130.9	0.2672	2.38	10.50	239727...
		总计:	Σ=10071	Σ=49002.1	Σ=100.0000			

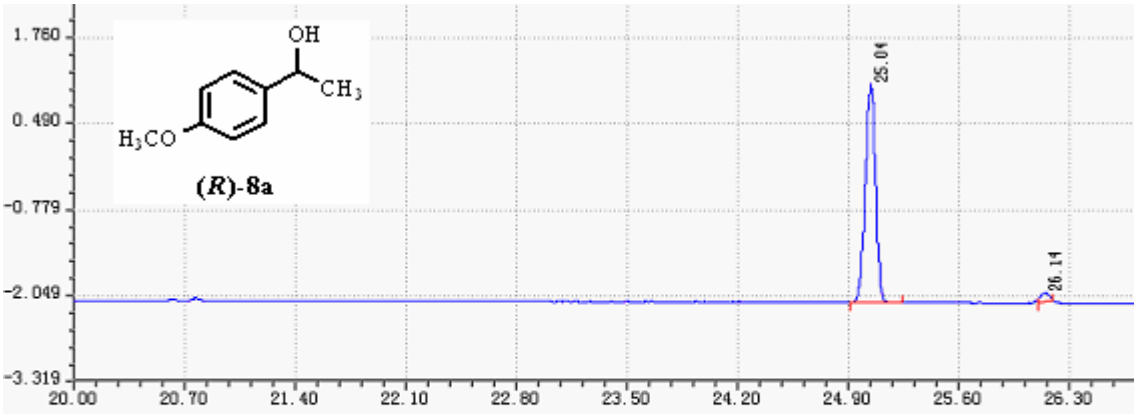
Recycling-experiment 7：



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
1		25.167	14522	71900.0	99.1963	4.95	0.00	514956.84
2		26.127	42	582.5	0.8037	13.87	3.60	70718.73
		总计:	Σ=14564	Σ=72482.6	Σ=100.0000			

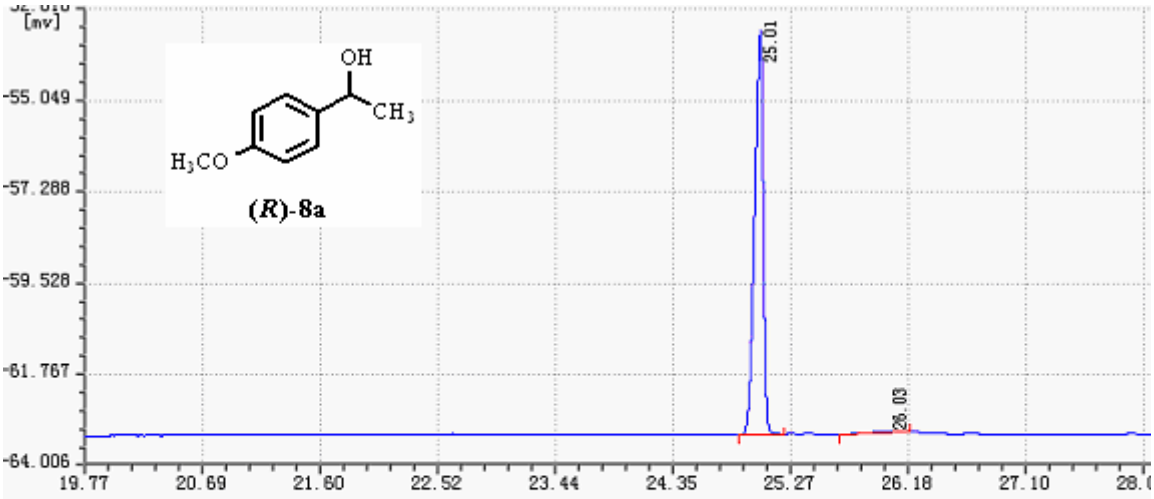
Recycling-experiment 8:



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
1		25.040	3229	14633.8	96.3167	4.53	0.00	608437.02	0.
2		26.140	142	559.6	3.6833	3.94	9.16	876840.71	1.
		总计:	Σ=3371	Σ=15193.4	Σ=100.0000				

Data were obtained at S/C = 500 using 8 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
1		25.013	9918	46901.5	98.6084	4.73	0.00	557625.79
2		26.027	41	661.9	1.3916	16.14	3.43	51801.40
		总计:	Σ=9959	Σ=47563.4	Σ=100.0000			