Copolymer-supported heterogeneous organocatalyst for asymmetric aldol addition in aqueous medium

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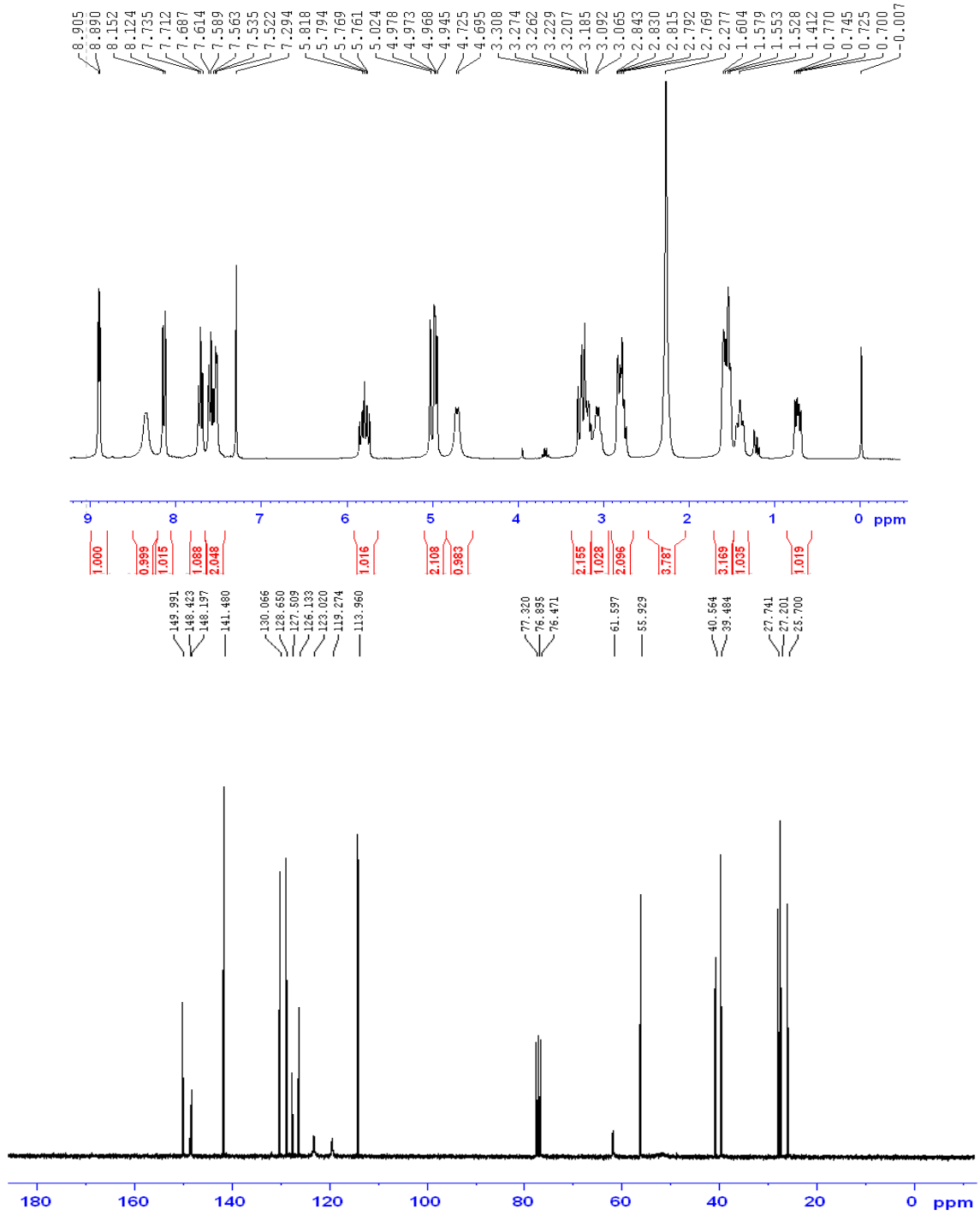
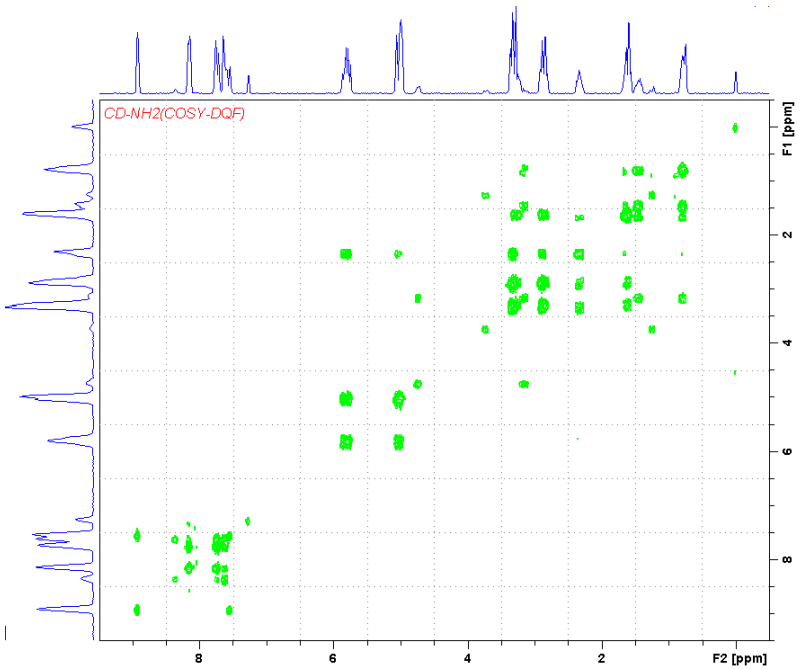
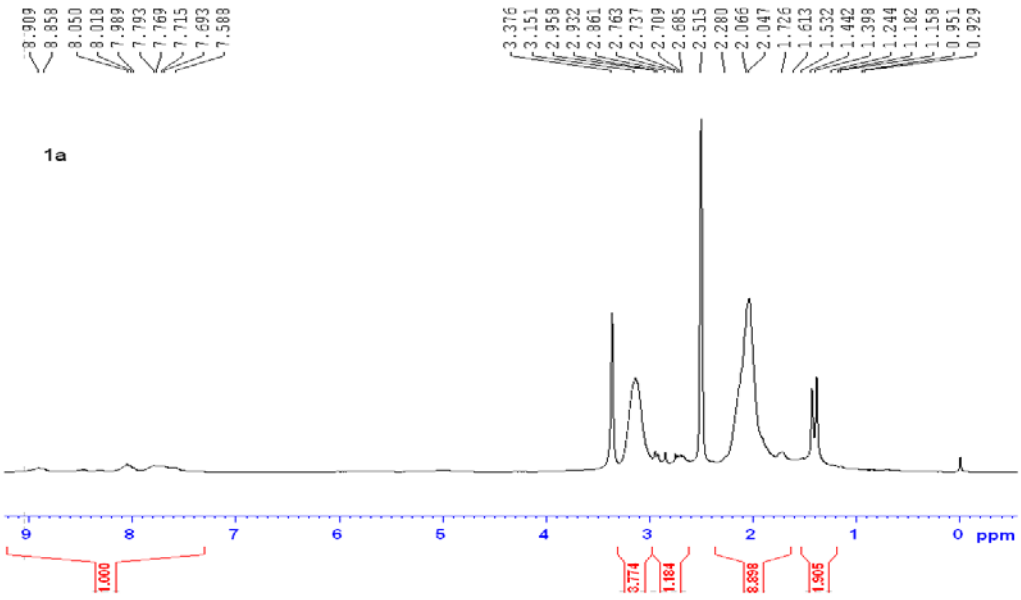
1. ^{1}H and ^{13}C NMR of 9-amino-9-deoxy-epi-cinc-honine

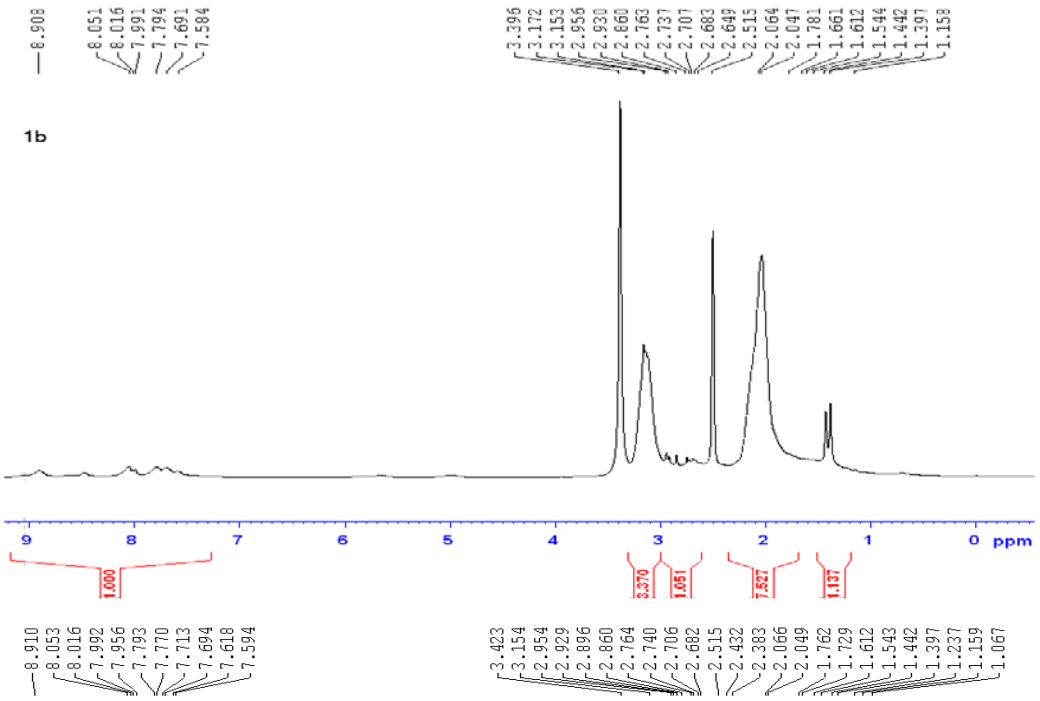


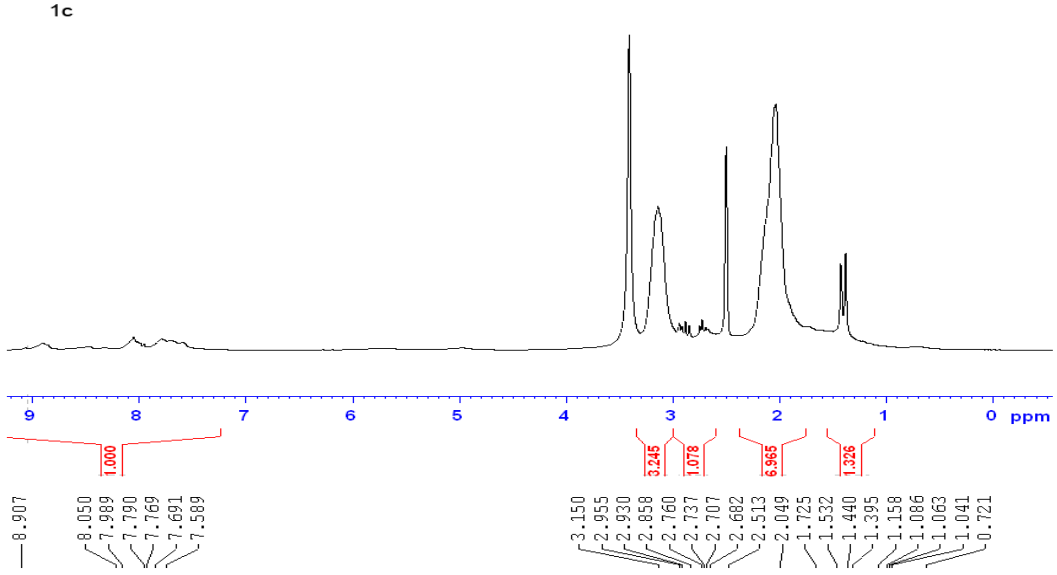


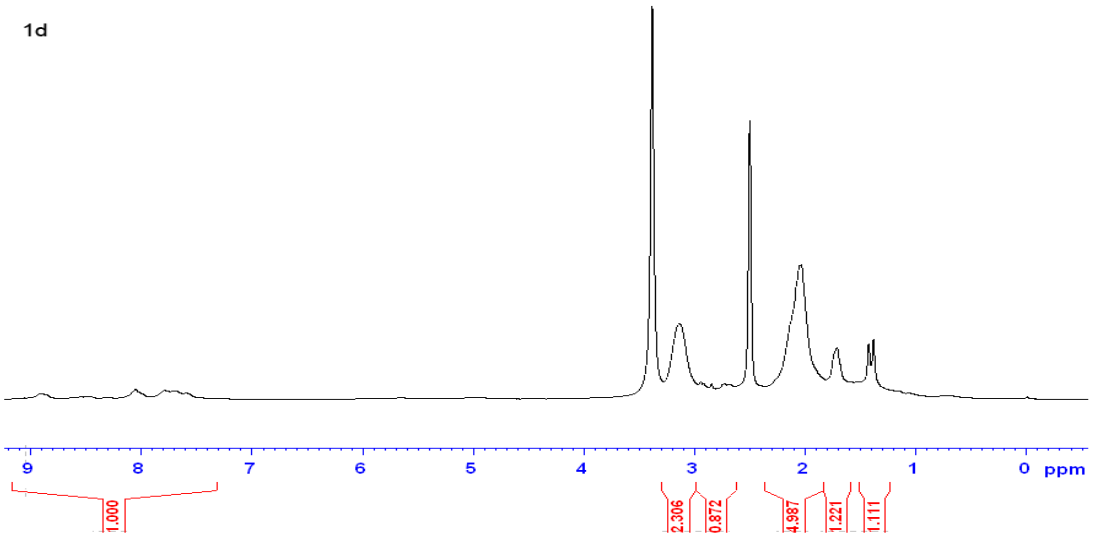
^{1}H NMR (300M Hz,$CDCl_3$, TMS): δ 8.90 (H-2′, 1 H, d, ^{3}J=6.0 Hz), 8.35 (H-5′, 1 H, br s, ^{3}J=9.0 Hz), 8.15 (H-8′, 1 H, d,^{3}J=3.0 Hz), 7.70 (H-7′, 1 H, t, ^{3}J=6.0 Hz),7.58 (H-6′,1 H, t, ^{3}J=6.0 Hz), 7.52 (H-3′,1 H, d, ^{3}J=2.0 Hz) , 5.78 (H-10,1 H, ddd) , 4.94-5.02 (H-11, 2 H, m), 4.70(H-9, 1 H, d, ^{3}J=9.0 Hz), 3.26 (H-6α, dd, 1 H) ,3.17(H-2-exo, q, 1 H), 3.06 (H-8, 1 H, d, ^{3}J=9.0 Hz), 2.73-2.83(H-6β, H-2-endo, 2 H), 2.26 (H-5α, s,1 H), 2.15 (-NH_2, s, 2 H), 1.57-1.59 (H-3, H-4, H-5β, 3 H), 1.40 (H-7β, 1 H), 0.73 (H-7α, dd,1H). ^{13}C NMR (75M Hz, $CDCl_3$, TMS): δ 150.1, 148.5, 148.3, 141.6, 130.2, 128.8, 127.6, 126.2, 123.1, 119.4, 114.1, 77.2, 61.7, 56.1, 40.7, 39.5, 27.9, 27.3, 25.8. Anal. calcd. for $C_{19}H_{23}N_3$: C, 77.78; H, 7.90; N, 14.32; Found: C, 77.82; H, 7.94; N,14.24.

2. ^{1}H NMR of 1a-c

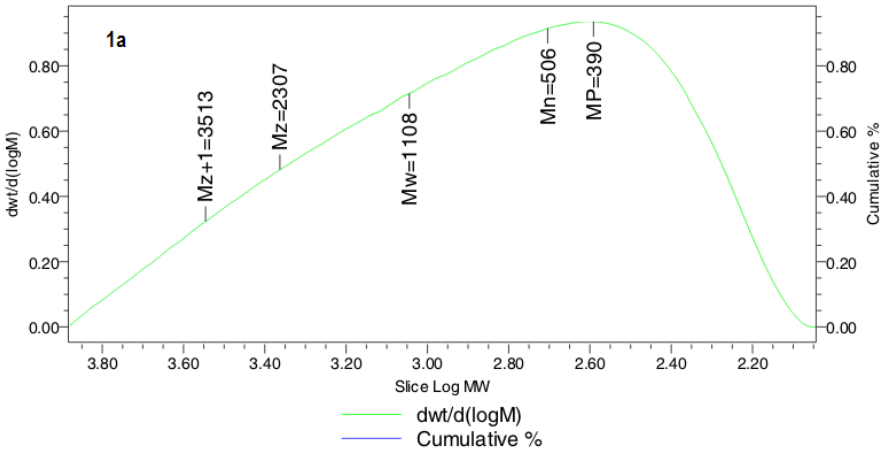






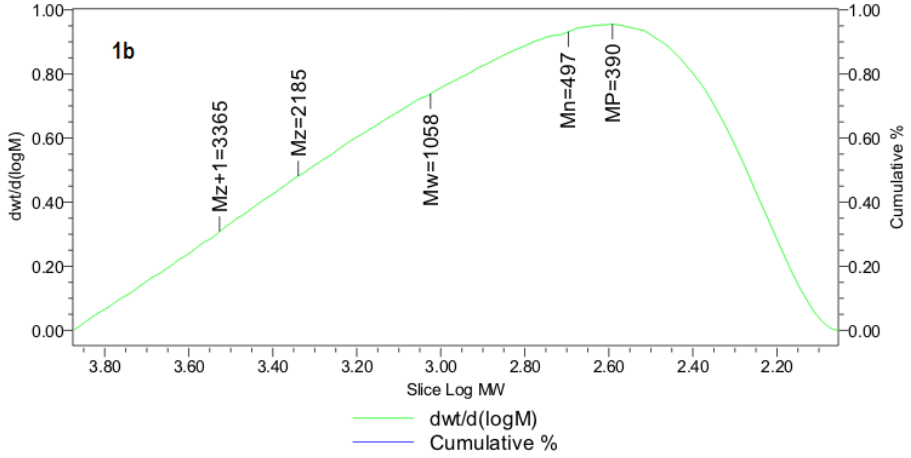


3. GPC analysis



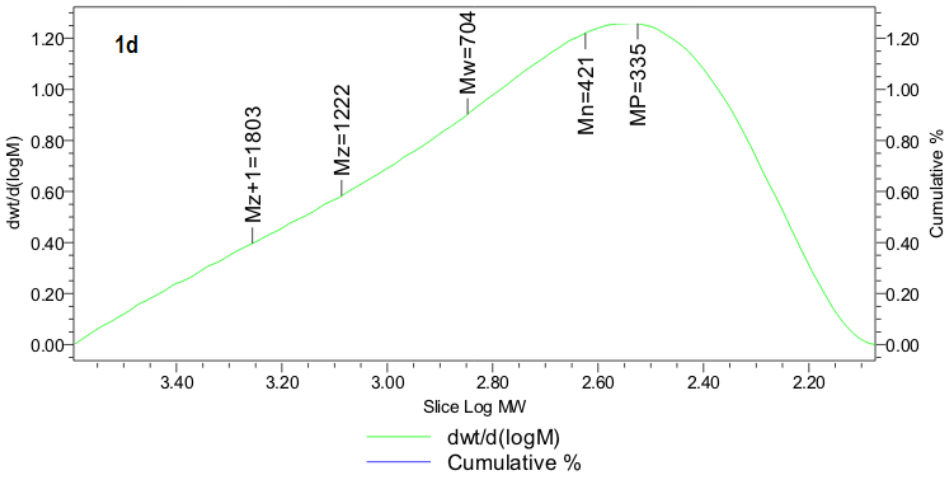
GPC 结果

	分布名称	Mn	Mw	MP	Mz	Mz+1	Mv	多分散性	MW 标记 1	MW 标记 2
1		506	1108	390	2307	3513		2.188282		



GPC 结果

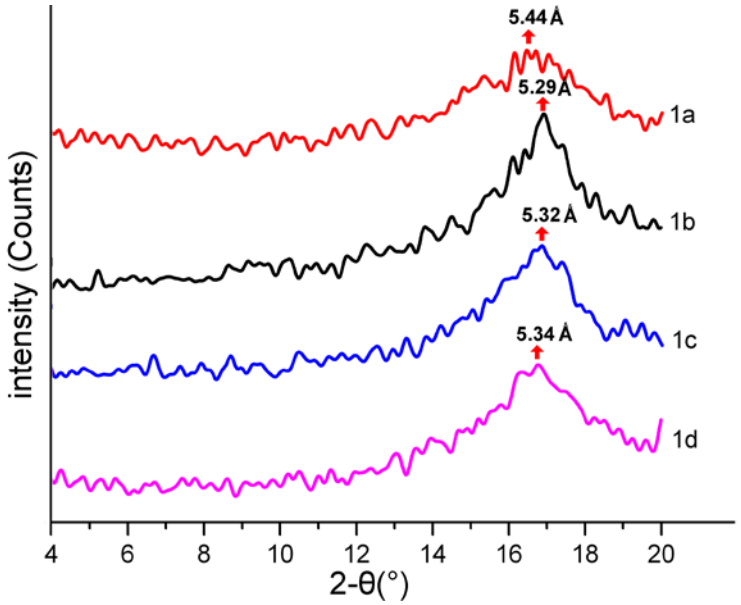
	分布名称	Mn	Mw	MP	Mz	Mz+1	Mv	多分散性	MW 标记 1	MW 标记 2
1		497	1058	390	2185	3365		2.128931		



GPC 结果

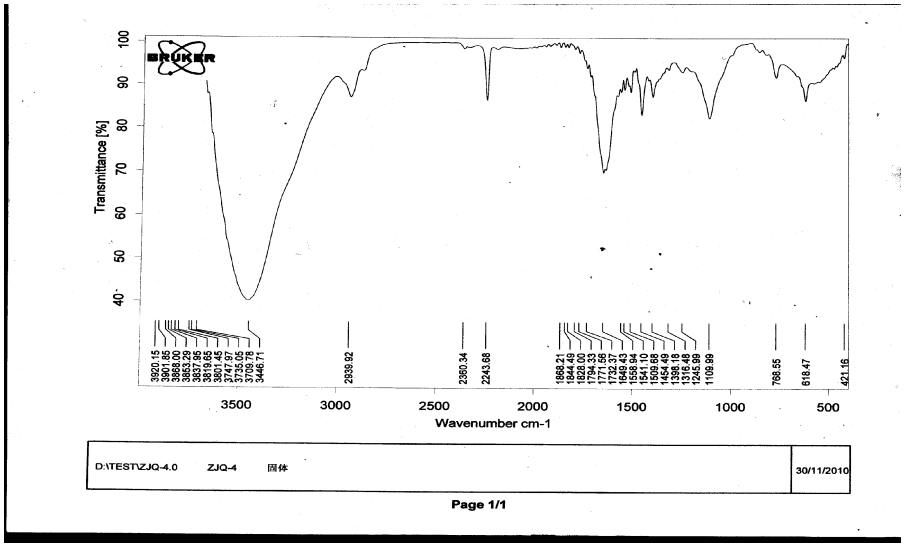
	分布名称	Mn	Mw	MP	Mz	Mz+1	Mv	多分散性	MW 标记 1	MW 标记 2
1		421	704	335	1222	1803		1.672845		

4.XRD

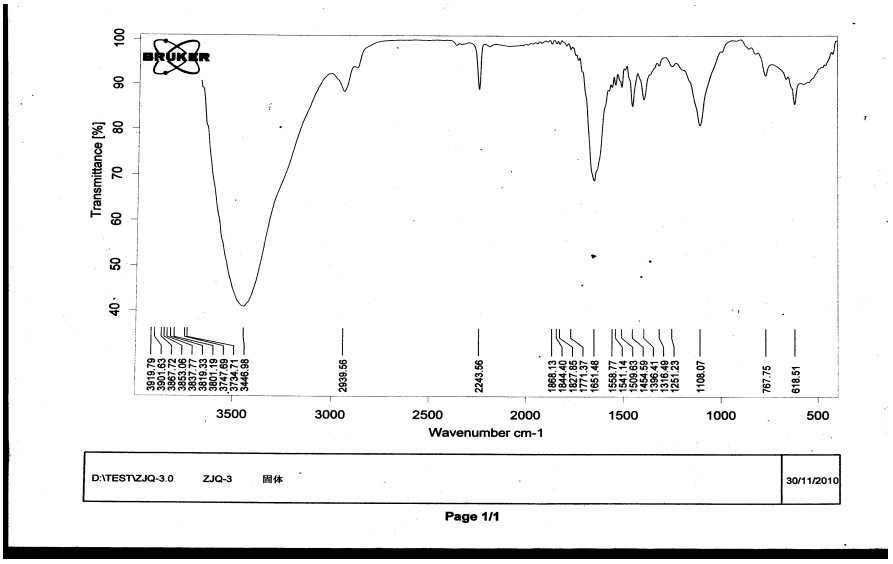


5. IR spectra

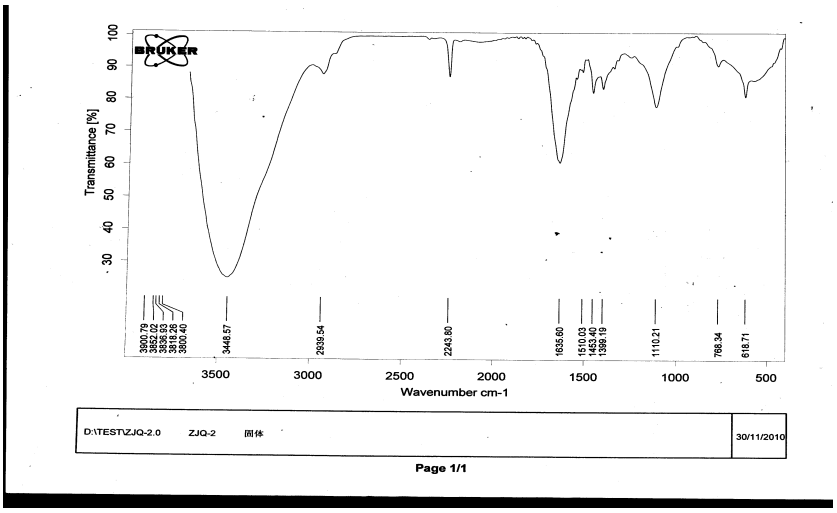
1a



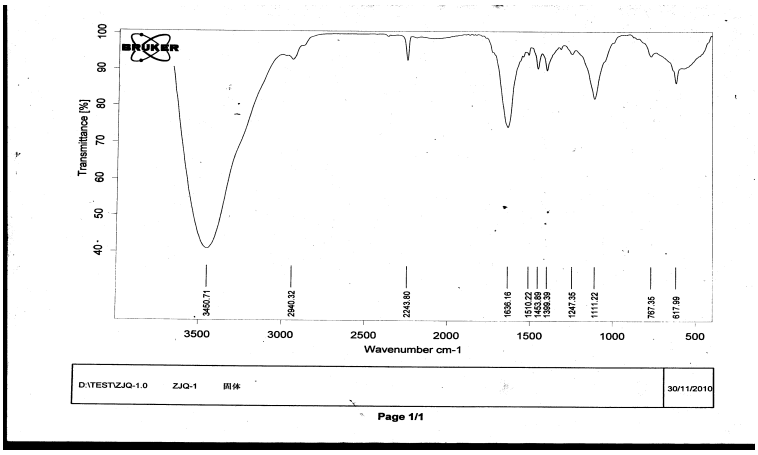
1b



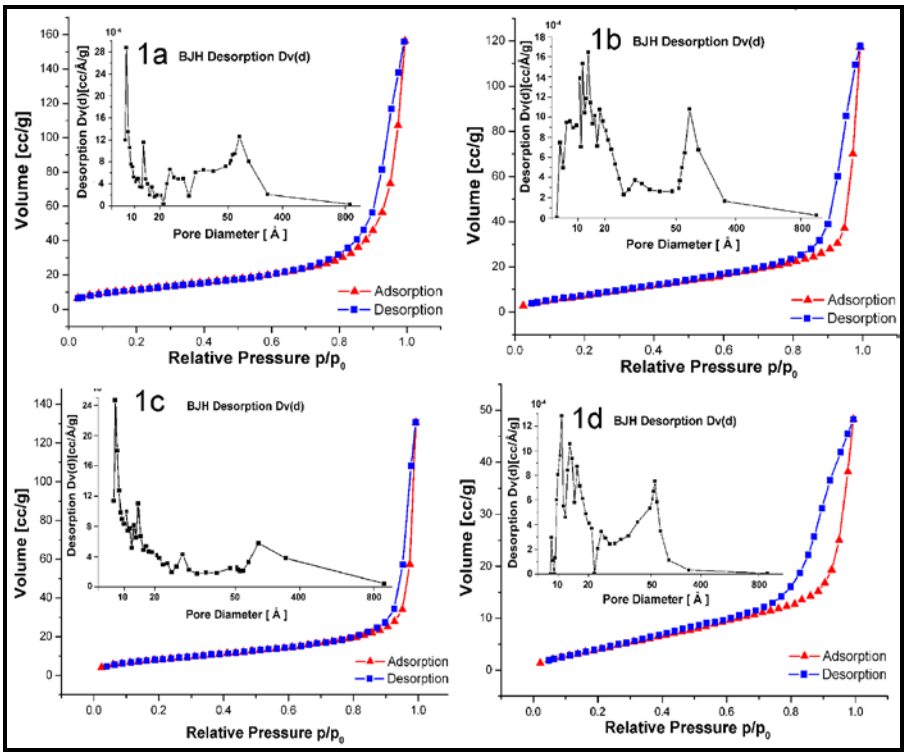
1c

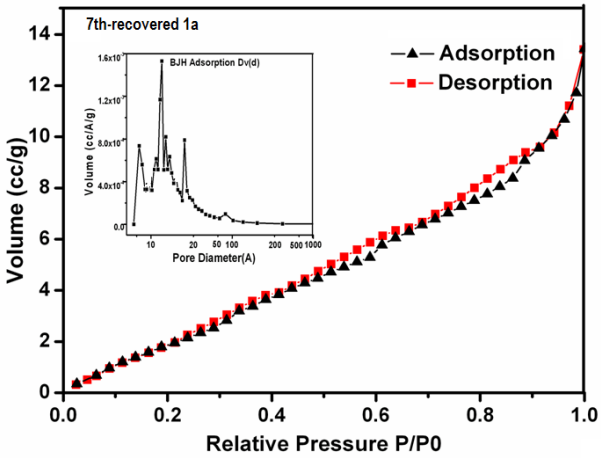


1d

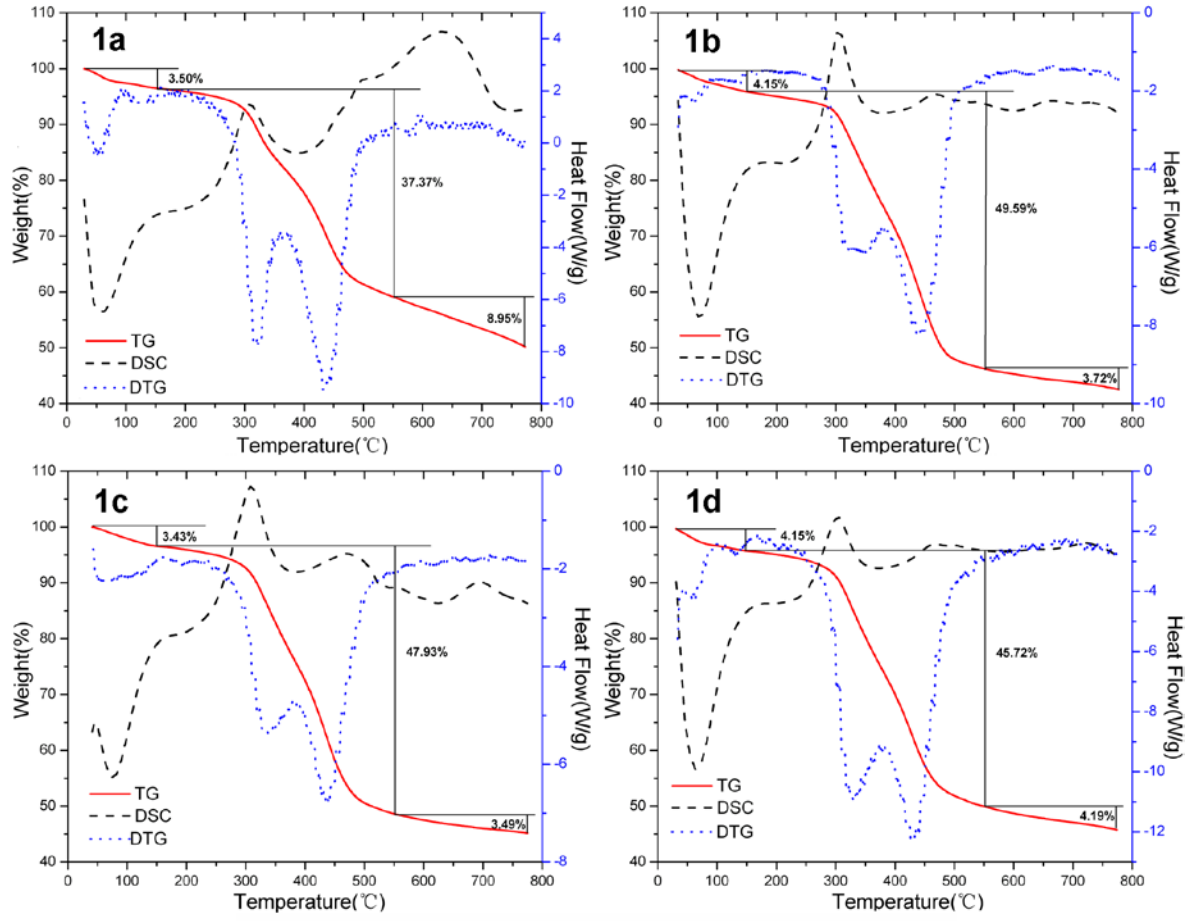


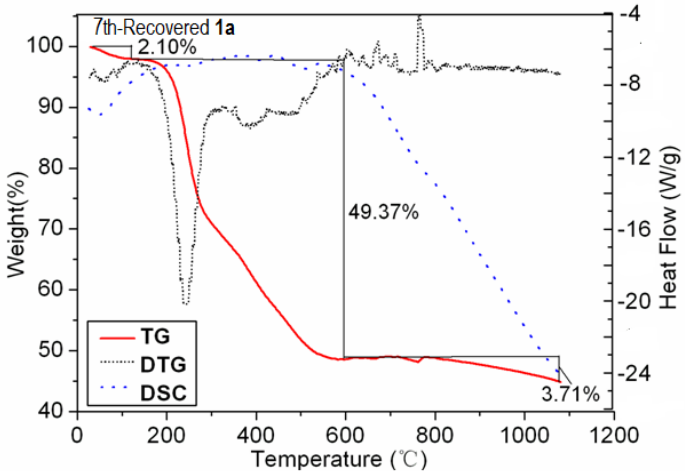
6. N_2 adsorption–desorption analysis




7th-recovered 1a
Adsorption
Desorption
BJH Adsorption Dv(d)
Volume (cc/A/g)
Pore Diameter(A)
Volume (cc/g)
Relative Pressure P/P0

7. TGA

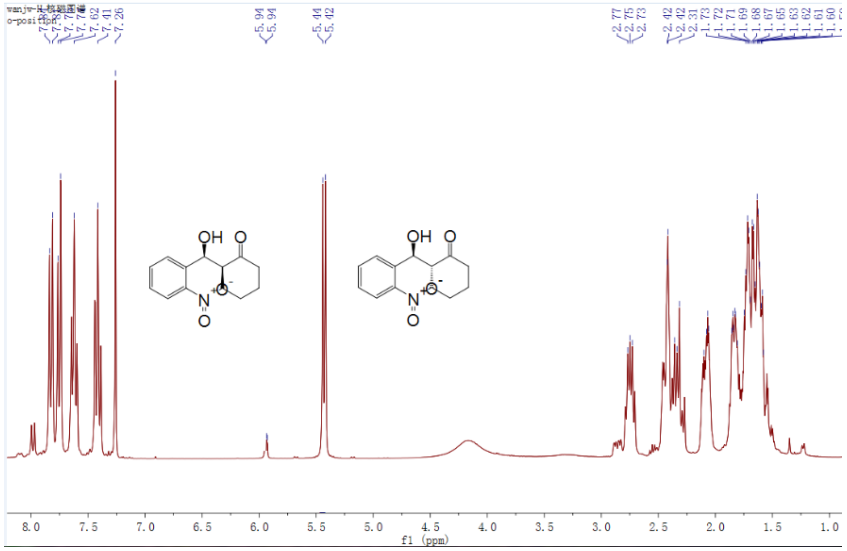

1a
3.50%
37.37%
8.95%
TG
DSC
DTG
Weight(%)
Heat Flow(W/g)
Temperature(℃)
1b
4.15%
49.59%
3.72%
1c
3.43%
47.93%
3.49%
1d
4.15%
45.72%
4.19%


7th-Recovered 1a
2.10%
49.37%
3.71%
TG
DTG
DSC
Weight(%)
Heat Flow (W/g)
Temperature (℃)

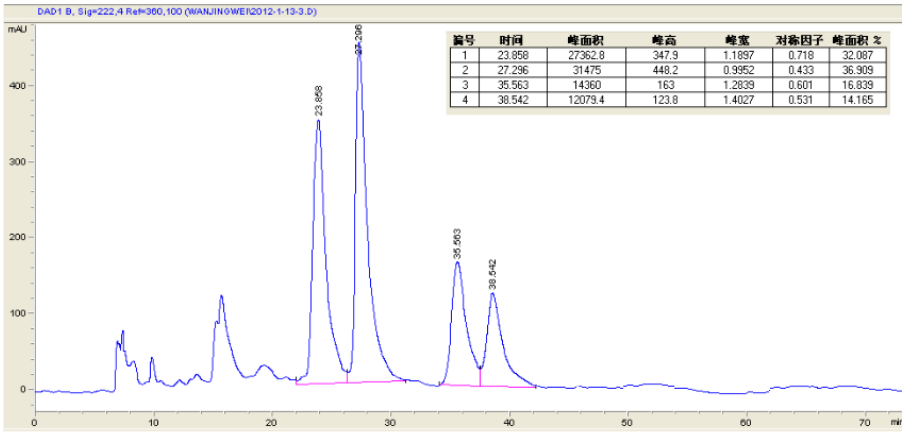
8. ^{1}H NMR and HPLC spectra

(1) (*S*)-2-[(*R*)-Hydroxy(2-nitrophenyl)methyl]cyclohexanone

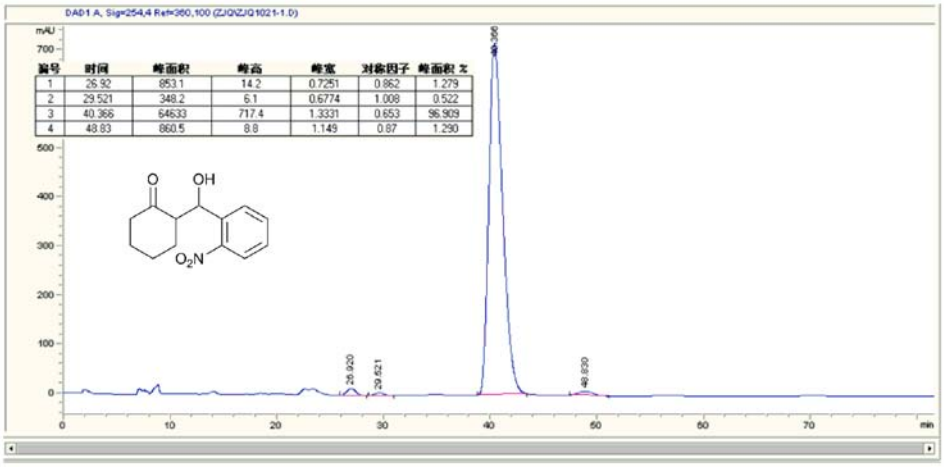
^{1}H-NMR (300 MHz, $CDCl_3$, TMS, ppm) : δ 7.83 (1 H, d, *J*=8.1 Hz), 7.76 (1 H, d, *J*=7.8 Hz), 7.62 (1 H, t, *J*=7.0 Hz), 7.41 (1 H, t, *J*=7.0 Hz), 5.43 (1H, d, *J*=6.0 Hz), 4.20 (1H, s), 2.70-2.78 (1 H, m), 2.42-2.51 (1 H, m), 2.24-2.31 (1 H, m), 2.10-2.24 (1 H, m), 1.83- 1.86 (1 H, m), 1.60-1.83 (4 H, m).



Racemes



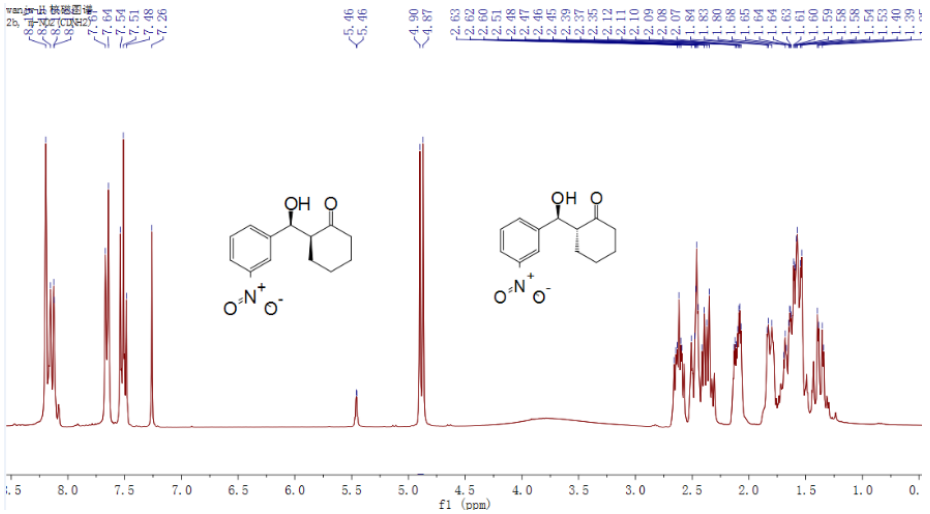
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	23.858	27362.8	347.9	1.1897	0.718	32.087
2	27.296	31475	448.2	0.9952	0.433	36.909
3	35.563	14360	163	1.2839	0.601	16.839
4	38.542	12079.4	123.8	1.4027	0.531	14.165



编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	26.92	853.1	14.2	0.7251	0.862	1.279
2	29.521	348.2	6.1	0.6774	1.008	0.522
3	40.366	64633	717.4	1.3331	0.653	96.909
4	48.83	860.5	8.8	1.149	0.87	1.290

(2) (*S*)-2-[(*R*)-Hydroxy(3-nitrophenyl)methyl]cyclohexanone

^{1}H-NMR (300 MHz, $CDCl_3$, TMS, ppm) : δ 8.17 (1 H, s), 8.14 (1 H, d, *J*=9.0 Hz), 7.62 (1 H, d, *J*=9.0 Hz), 7.51 (1 H, t, *J*=9.0 Hz), 4.88 (1 H, d, *J*=9.0 Hz), 2.65-2.62 (1 H, m), 2.51-2.63 (1 H, m), 2.45-2.51 (1 H, m), 2.35 -2.39 (1 H, m), 2.07-2.11(1 H, m), 1.76-1.84 (1 H, m), 1.53-1.65 (2 H, m), 1.34-1.40 (1 H, m).



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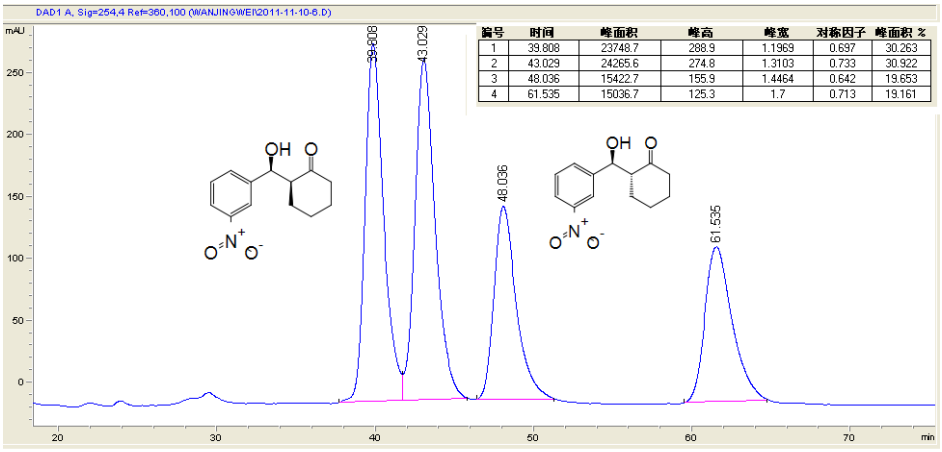
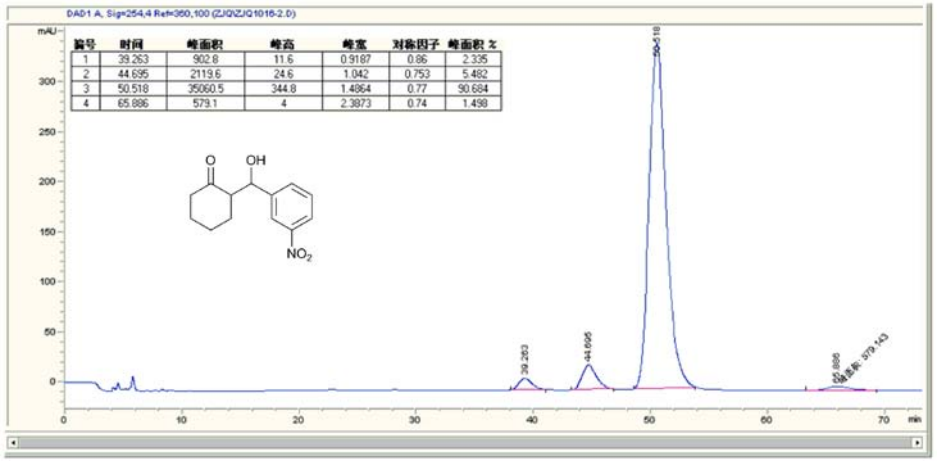


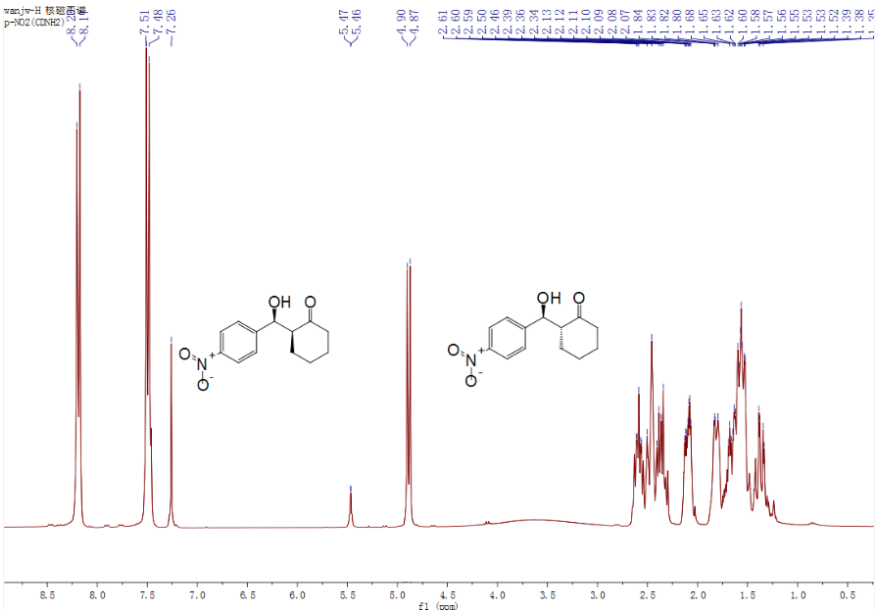
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	39.808	23748.7	288.9	1.1969	0.697	30.263
2	43.029	24265.6	274.8	1.3103	0.733	30.922
3	48.036	15422.7	155.9	1.4464	0.642	19.653
4	61.535	15036.7	125.3	1.7	0.713	19.161



编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	39.263	902.8	11.6	0.9187	0.86	2.335
2	44.695	2119.6	24.6	1.042	0.753	5.482
3	50.518	35060.5	344.8	1.4864	0.77	90.684
4	65.886	579.1	4	2.3873	0.74	1.498

(3) (*S*)-2-[(*R*)-Hydroxy(4-nitrophenyl)methyl]cyclohexanone

^{1}H-NMR (300 MHz, $CDCl_3$, TMS, ppm) : δ 8.18 (2 H, d, *J*=9.0 Hz), 7.49 (2H, d, *J*=9.0 Hz), 4.90 (1 H, d, *J*=9.0 Hz), 2.59-2.63 (1 H, m), 2,46-2.50 (1 H, m), 2.34-2.39 (1 H, m), 2.07-2.13 (1 H, m), 1.80-1.84 (1 H, m), 1.52-1.68 (3 H, m), 1.32-1.39 (1 H, m).



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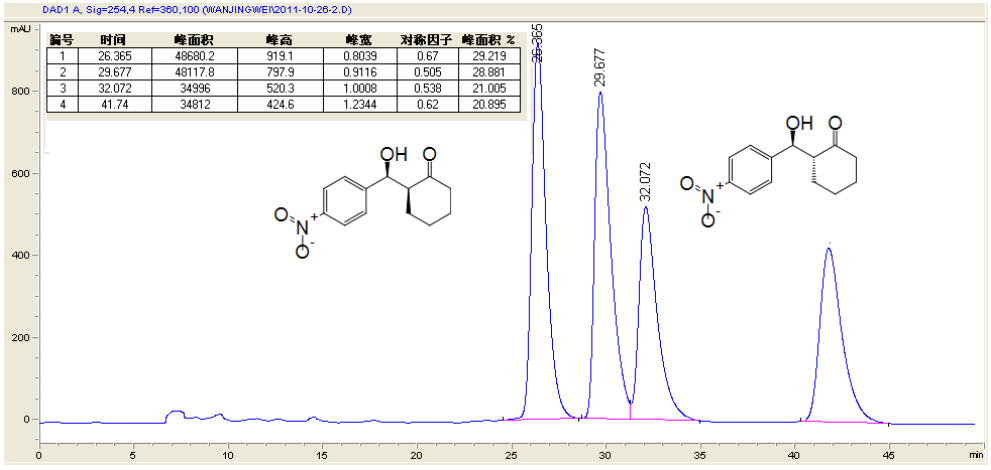
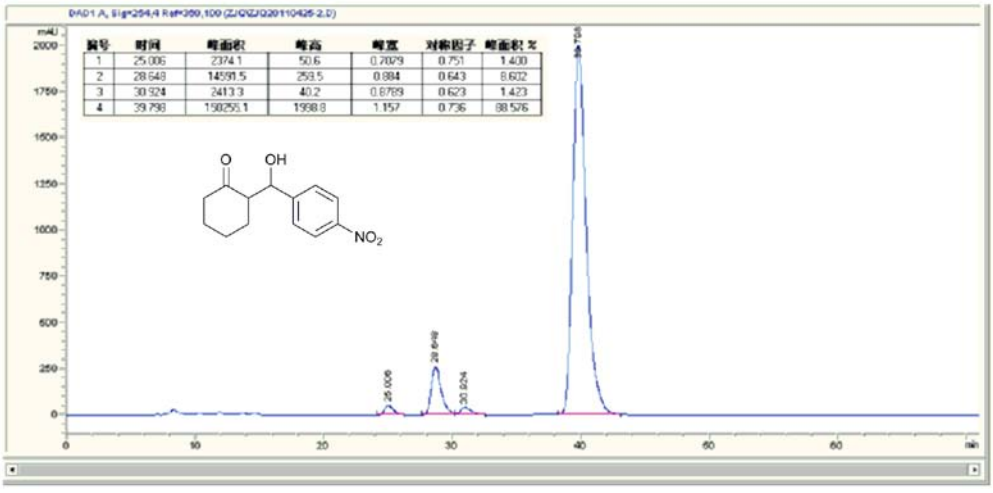


编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	26.365	48680.2	919.1	0.8039	0.67	29.219
2	29.677	48117.8	797.9	0.9116	0.505	28.881
3	32.072	34996	520.3	1.0008	0.538	21.005
4	41.74	34812	424.6	1.2344	0.62	20.895



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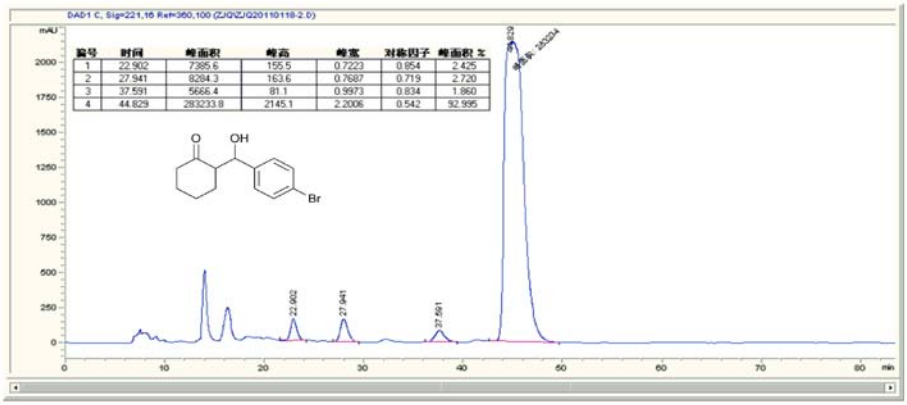
1	25.006	2374.1	50.6	0.7079	0.751	1.400
2	28.648	14591.5	259.5	0.884	0.643	8.602
3	30.924	2413.3	40.2	0.8769	0.623	1.423
4	39.798	150255.1	1998.8	1.157	0.736	88.576

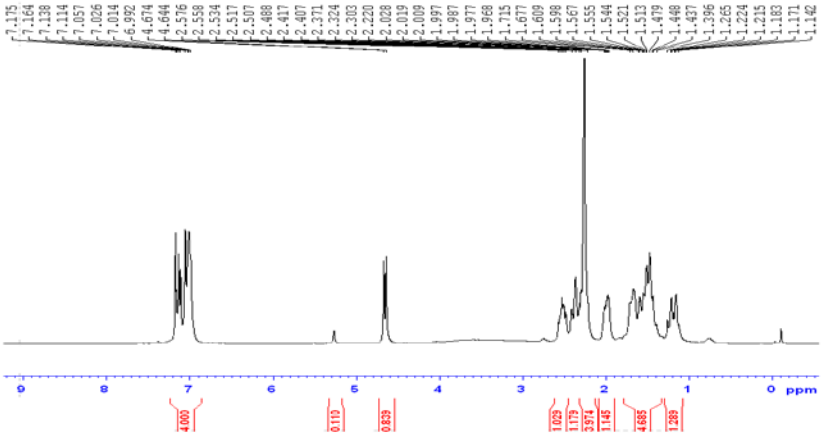
(4) (*S*)-2-[(*R*)-(4-Bromophenyl)(hydroxy)methyl]cyclohexanone

^{1}H-NMR (300 MHz, $CDCl_3$, TMS, ppm): δ 7.48-7.45 (2 H, m), 7.21-7.18 (2 H, m), 4.75 (1H, d, *J*=8.6 Hz), 3.99 (1 H, d, *J*=2.7 Hz), 2.60-2.52 (1 H, m), 2.51-2.43 (1 H, m), 2.40-2.30 (1 H, m), 2.13-2.06 (1 H, m), 1.85-1.74 (1 H, m), 1.73-1.49 (3 H, m), 1.34-1.25 (1 H, m).



(5) (*S*)-2-[(*R*)-(4-Methylphenyl)(hydroxy)methyl]cyclohexanone

^{1}H-NMR (300 MHz, $CDCl_3$, TMS, ppm): δ 6.99-7.18 (4 H, m), 4.65 (1 H, d, *J*=9.0 Hz), 2.22-2.58 (6 H, m), 1.97-2.03 (1 H, m), 1.40-1.72 (5 H, m), 1.14-1.27 (1 H, m).



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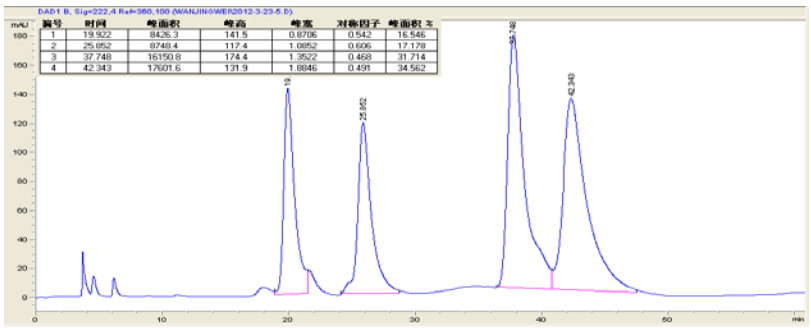
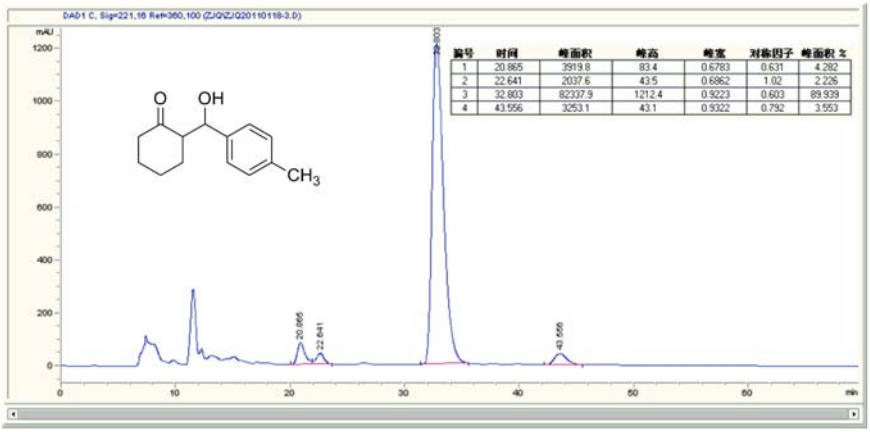
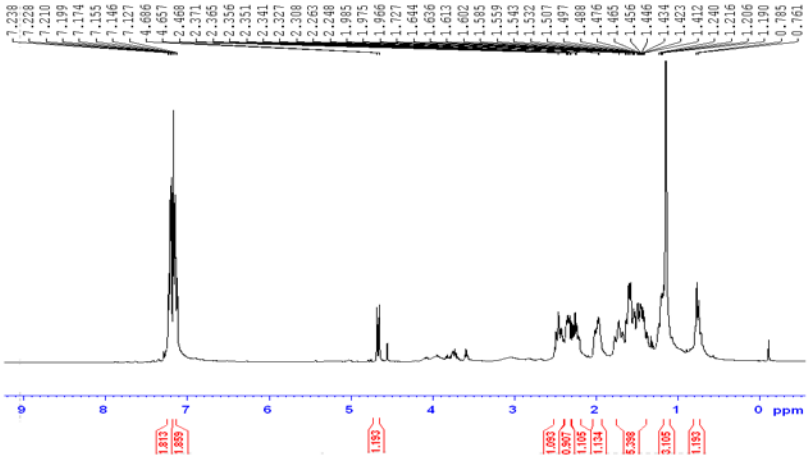




峰号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	20.865	3919.8	83.4	0.6783	0.631	4.282
2	22.641	2037.6	43.5	0.6862	1.02	2.226
3	32.803	82337.9	1212.4	0.9223	0.603	89.939
4	43.556	3253.1	43.1	0.9322	0.792	3.553

(6) (*S*)-2-[(*R*)-(4-Chlorophenyl)(hydroxy)methyl]cyclohexanone

^{1}H-NMR (300 MHz, $CDCl_3$, TMS, ppm): δ 7.22 (2 H, d), 7.17 (2 H, d), 4.67 (1 H, d, *J*=8.7 Hz), 2.25-2.37 (3 H, m), 1.96-1.99 (1 H, m), 1.41-1.72 (5 H, m), 1.20 (3 H, s).



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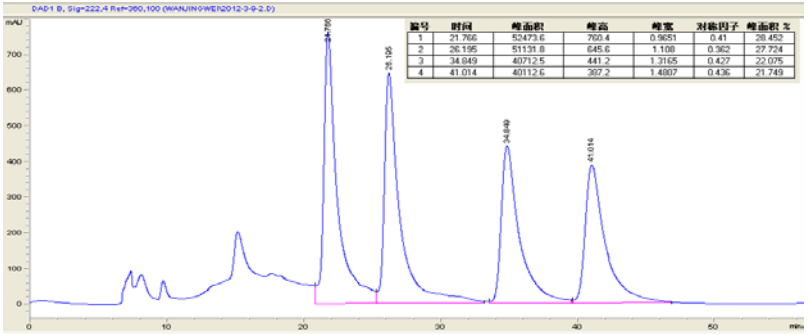
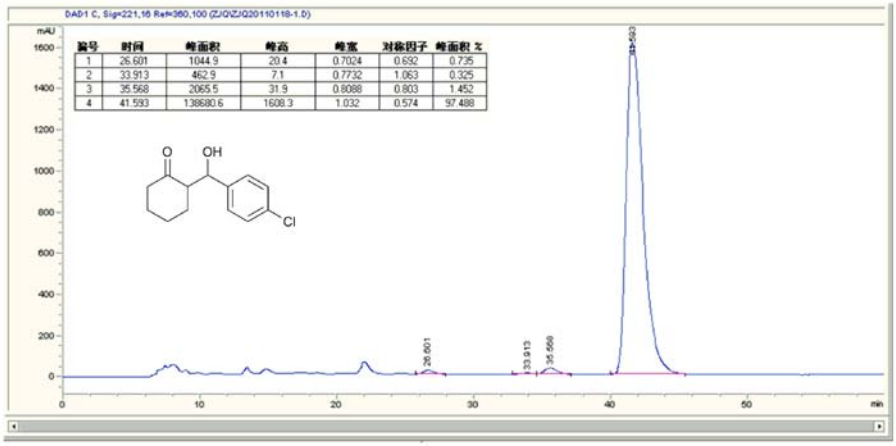
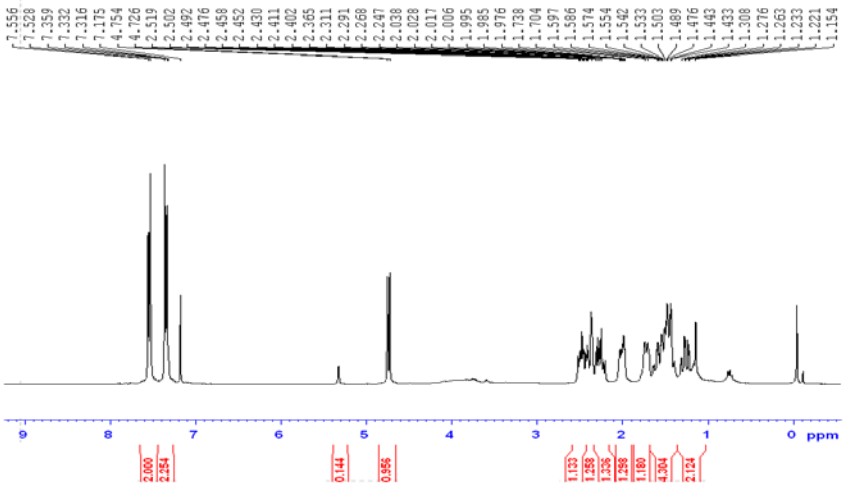


峰号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	21.766	52473.6	760.4	0.9651	0.41	26.452
2	26.195	51131.8	645.6	1.108	0.362	27.724
3	34.849	40712.5	441.2	1.3165	0.427	22.075
4	41.014	40112.6	397.2	1.4807	0.436	21.749

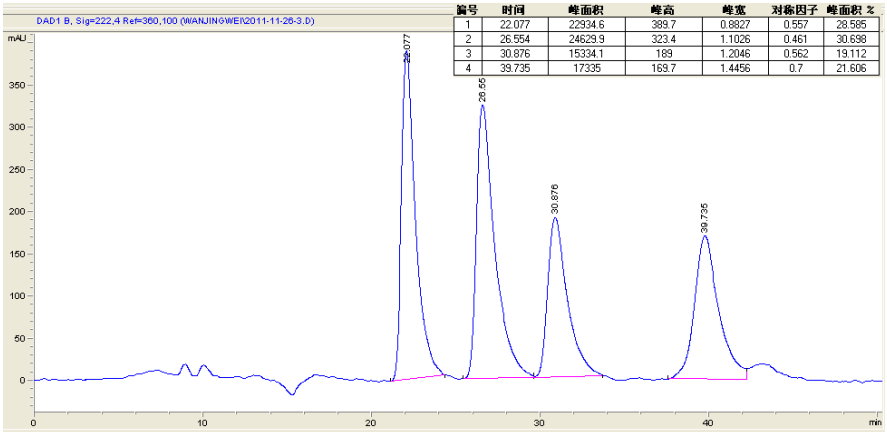


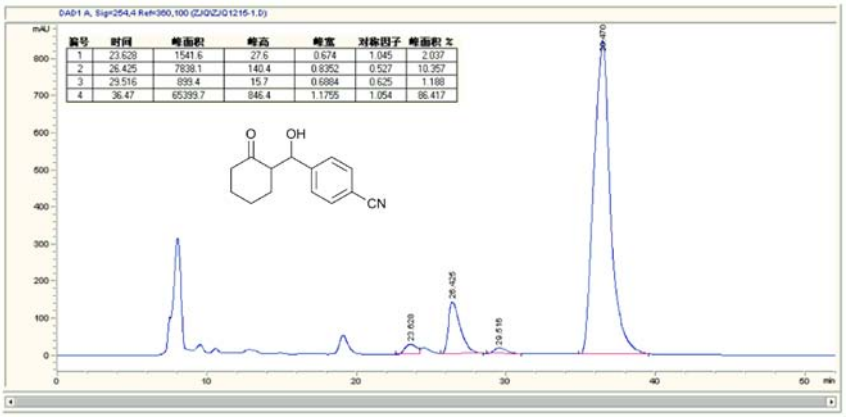
(7) (*S*)-2-[(*R*)-(4-Cyanophenyl)(hydroxy)methyl]cyclohexanone

^{1}H-NMR (300 MHz, $CDCl_3$, TMS, ppm): δ 7.54 (2 H, d, *J*=8.4 Hz), 7.35 (2 H, d, *J*=8.1 Hz), 4.74 (1 H, d, *J*=8.4 Hz), 2.25-2.52 (3 H, m), 1.98-2.04 (1 H, m), 1.43-1.74 (4 H, m), 1.22-1.27 (1 H, m).



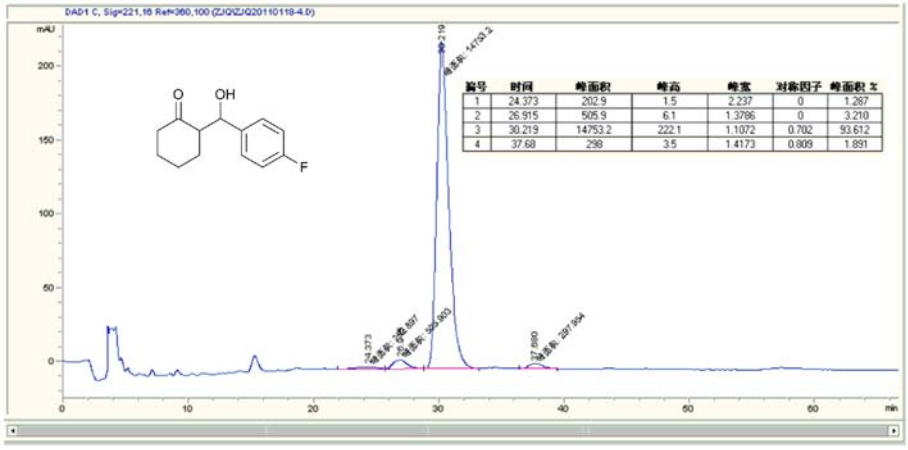
Racemes





峰号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	23.628	1541.6	27.6	0.674	1.045	2.037
2	26.425	7838.1	140.4	0.8352	0.527	10.357
3	29.516	899.4	15.7	0.6884	0.625	1.188
4	36.47	65399.7	846.4	1.1755	1.054	86.417

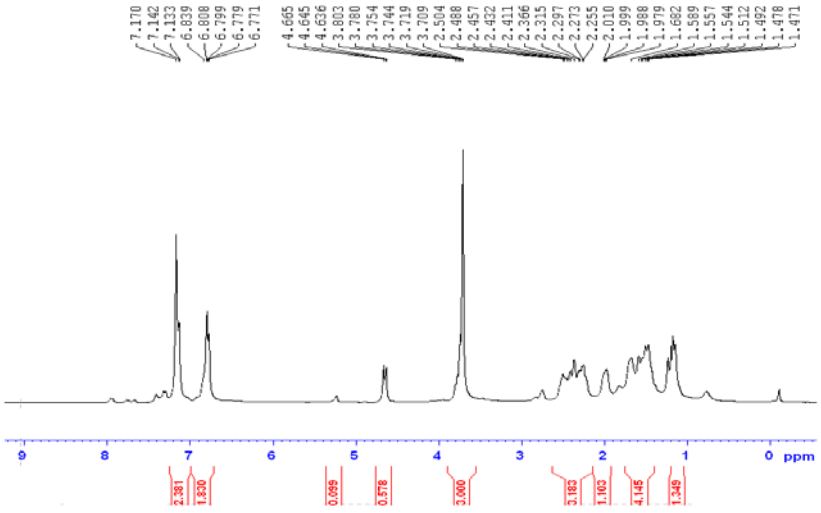
(8) (*S*)-2-[(*R*)-(4-fluorophenyl)(hydroxy)methyl]cyclohexanone



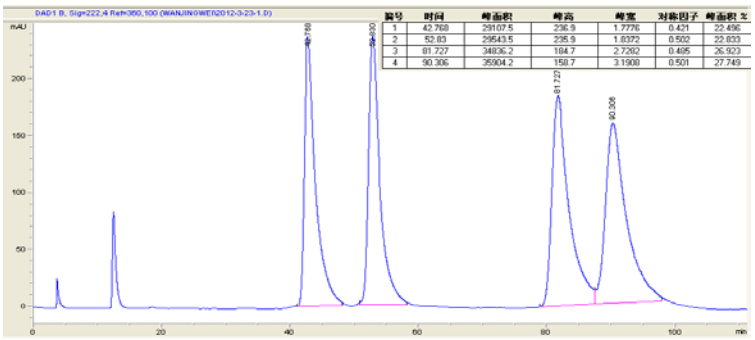
峰号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	24.373	202.9	1.5	2.237	0	1.267
2	26.915	505.9	6.1	1.3786	0	3.210
3	30.219	14753.2	222.1	1.1072	0.702	93.612
4	37.68	298	3.5	1.4173	0.809	1.891

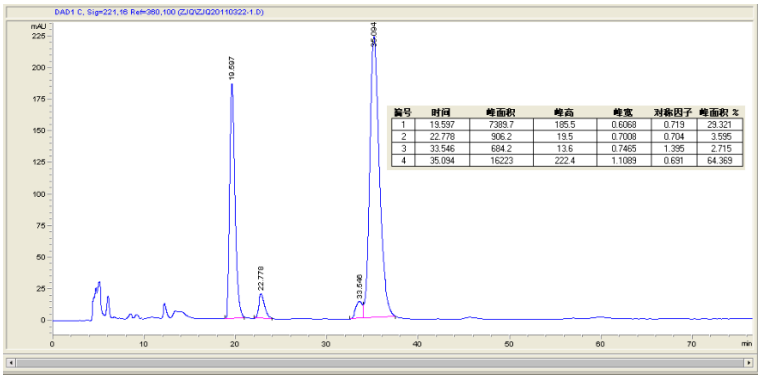
(9) **(*S*)-2-[(*R*)-Hydroxy(4-methoxyphenyl)methyl]cyclohexanone**

^{1}H-NMR (300 MHz, $CDCl_3$, TMS, ppm): δ 7.14 (2 H, d), 6.80 (2H, d), 4.65 (1 H, d, *J*=6.0 Hz), 3.75 (3 H, s), 2.26-2.50 (3 H, m), 1.98-2.01 (1 H, m), 1,47-1.68 (4 H, m), 1.26-1.34 (1 H, m).



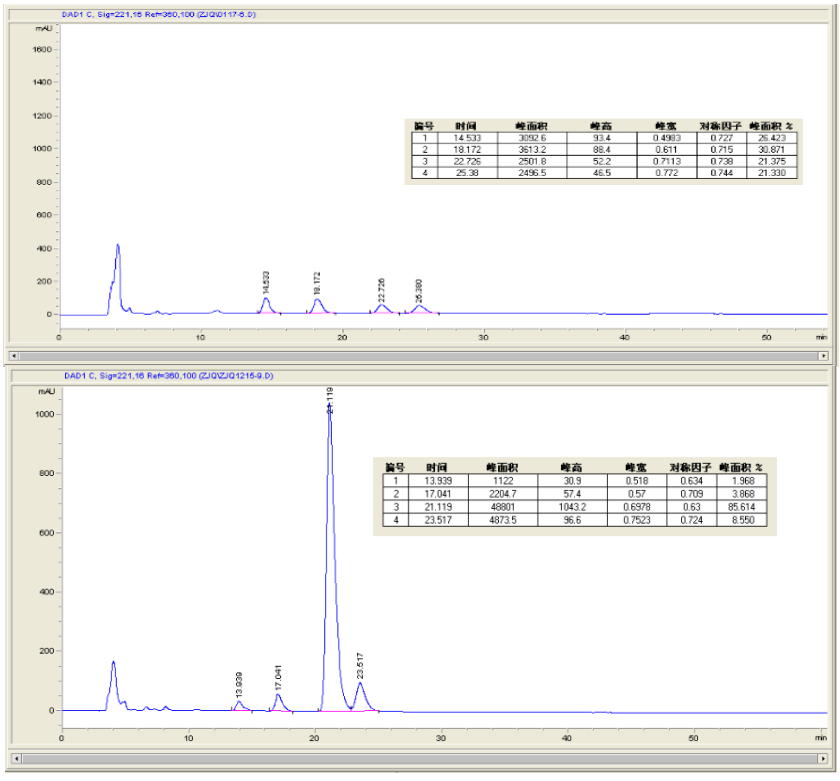
Racemes



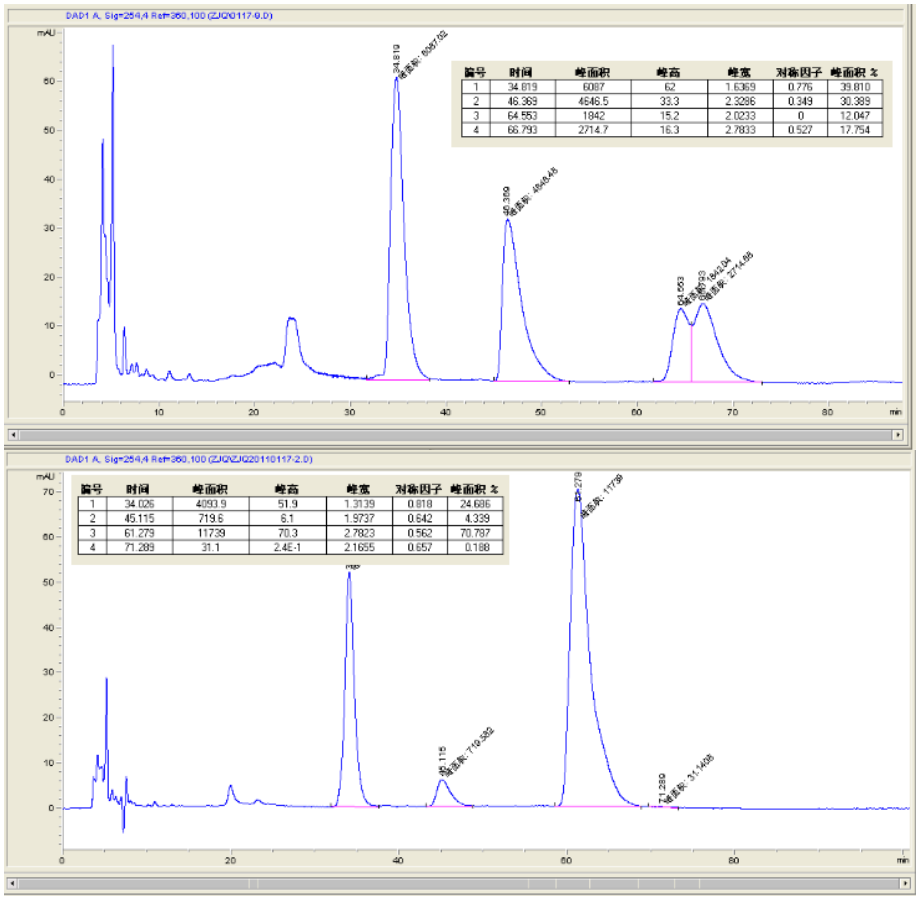


(10) (*S*)-2-((*R*)-hydroxy(4-methoxyphenyl)methyl)cyclopentanone

Racemes



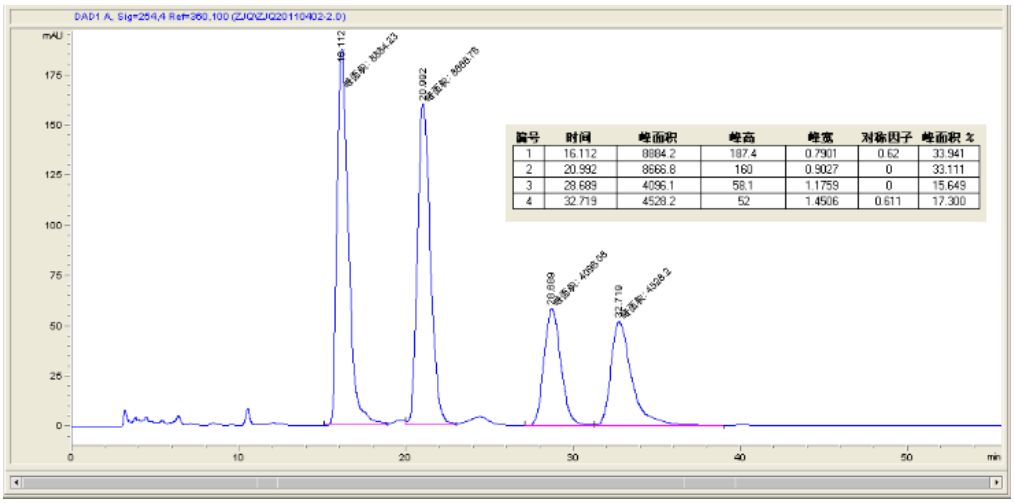
(11) (*S*)-2-((*R*)-hydroxy(4-cyanophenyl)methyl)cyclopentanone



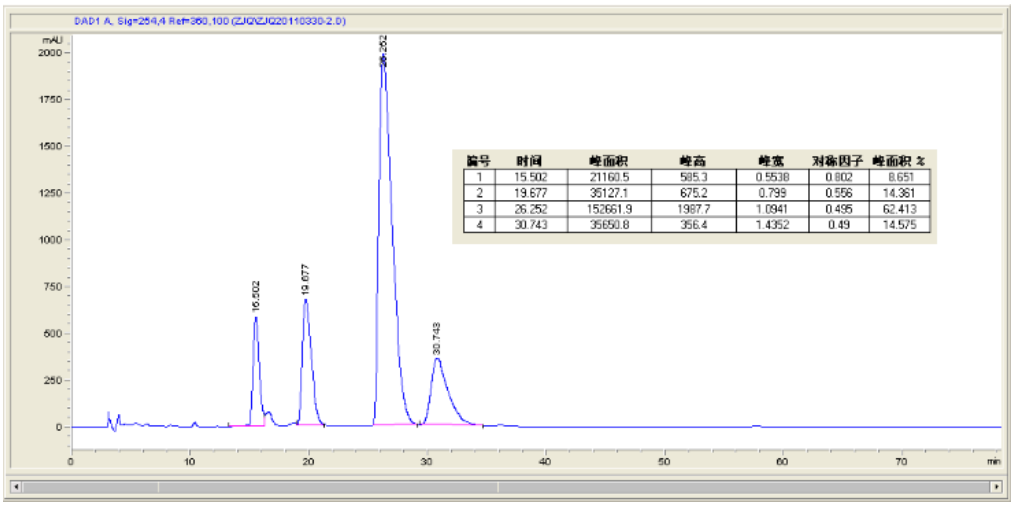
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	34.819	6087	62	1.6369	0.776	39.810
2	46.369	4646.5	33.3	2.3286	0.349	30.389
3	64.553	1842	15.2	2.0233	0	12.047
4	66.793	2714.7	16.3	2.7833	0.527	17.754

编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	34.026	4093.9	51.9	1.3139	0.818	24.686
2	45.115	719.6	6.1	1.9737	0.642	4.339
3	61.279	11739	70.3	2.7823	0.562	70.787
4	71.289	31.1	2.4E-1	2.1655	0.657	0.188

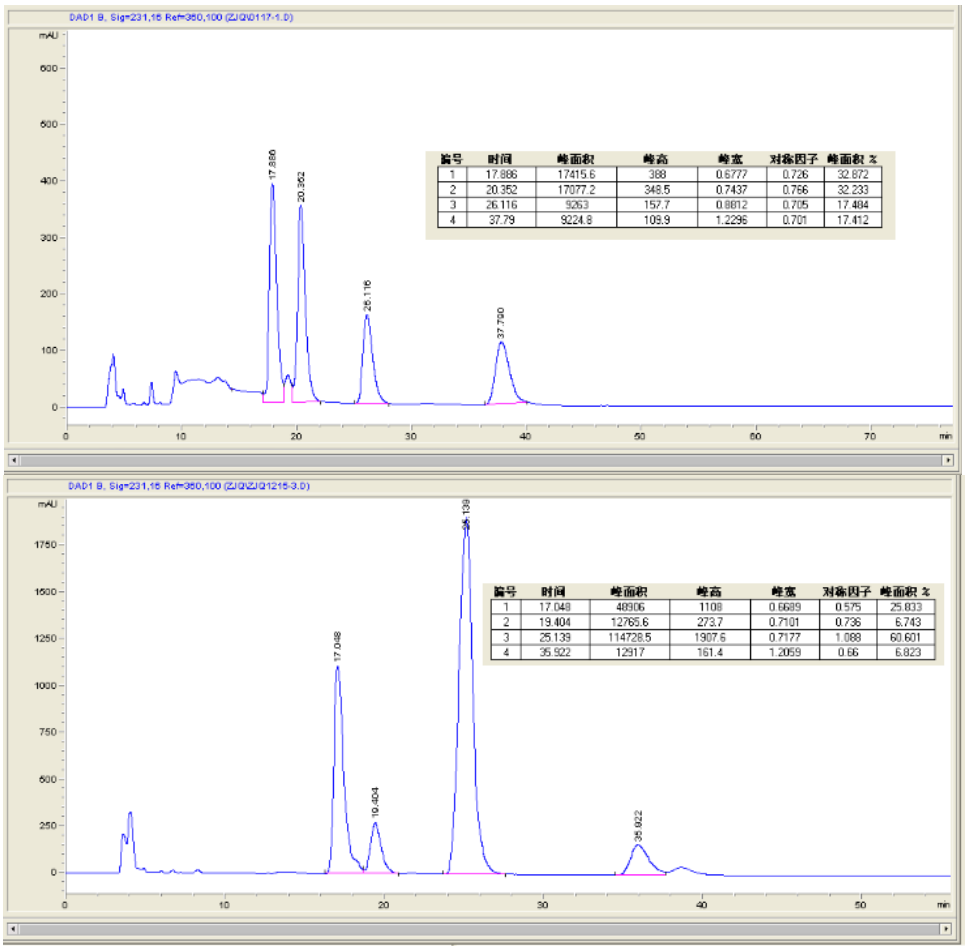
(12) (*S*)-2-((*R*)-hydroxy(2-nitrophenyl)methyl)cyclopentanone



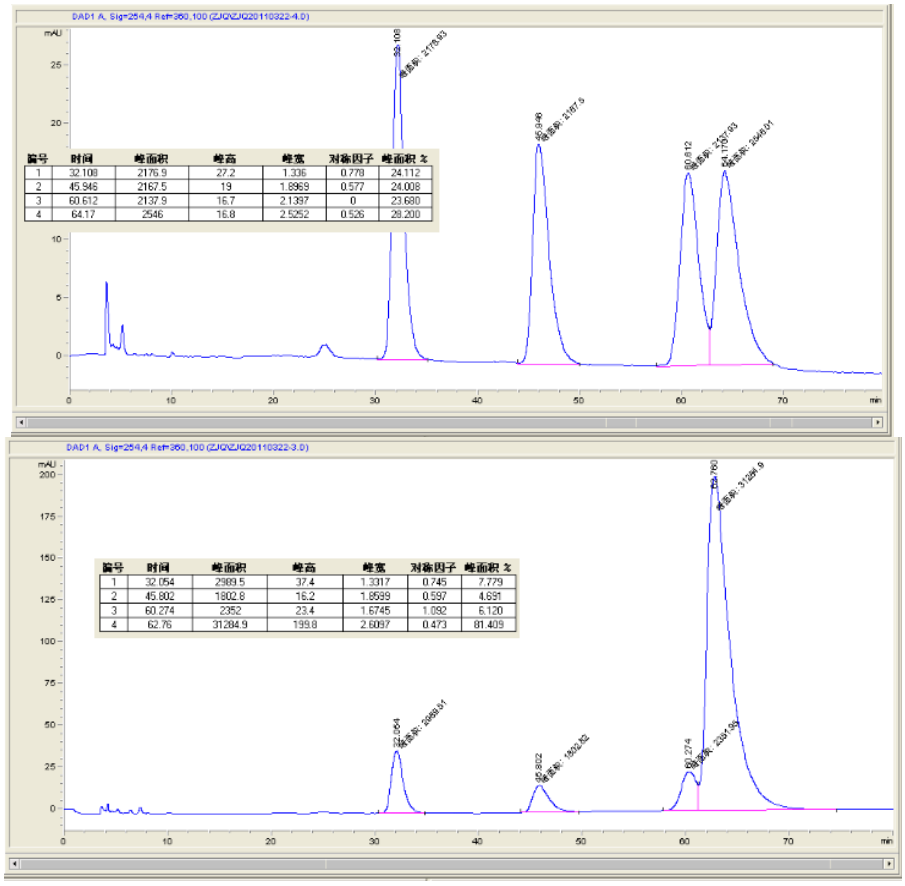
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	16.112	8884.2	187.4	0.7901	0.62	33.941
2	20.992	8668.8	160	0.9027	0	33.111
3	28.689	4096.1	58.1	1.1759	0	15.649
4	32.719	4528.2	52	1.4506	0.611	17.300



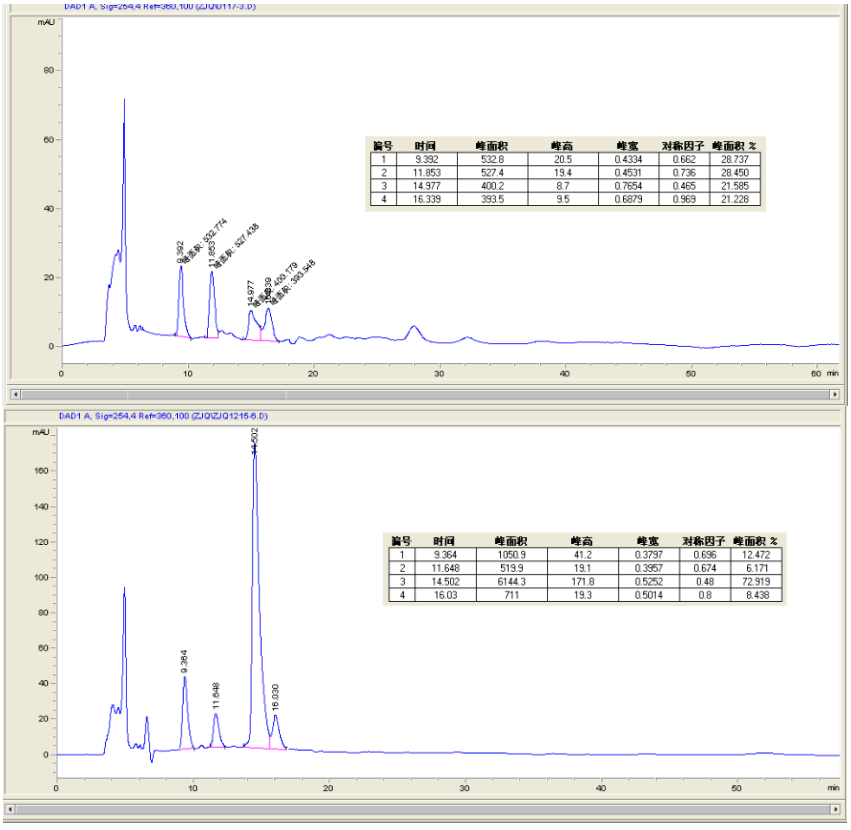
(13) (*S*)-2-((*R*)-hydroxy(3-nitrophenyl)methyl)cyclopentanone



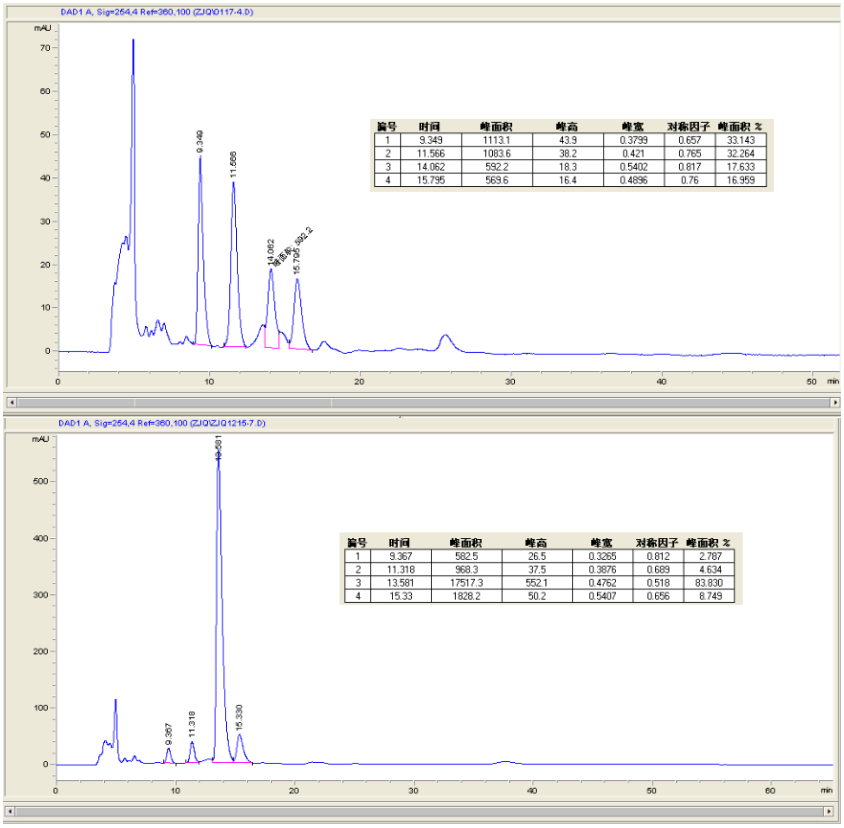
(14) (*S*)-2-((*R*)-hydroxy(4-nitrophenyl)methyl)cyclopentanone



(15) (*S*)-2-((*R*)-hydroxy(4-nitrophenyl)methyl)cyclopentanone



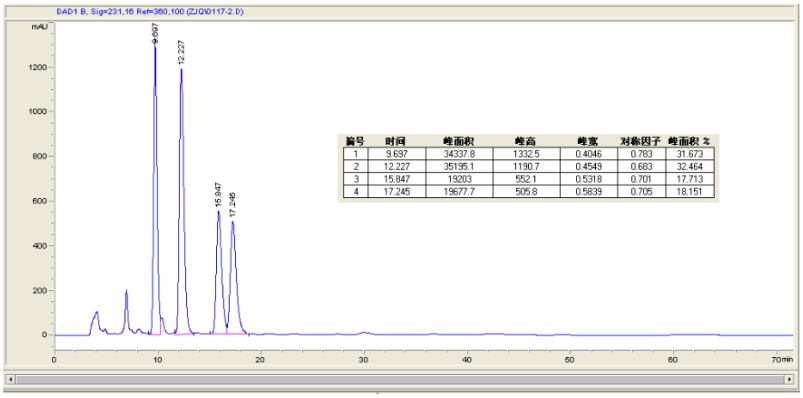
(16) (*S*)-2-((*R*)-hydroxy(4-fulorophenyl)methyl)cyclopentanone



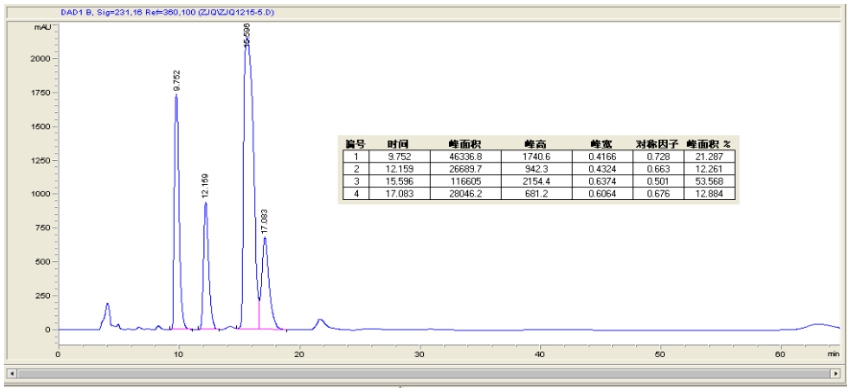
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	9.349	1113.1	43.9	0.3799	0.657	33.143
2	11.566	1083.6	38.2	0.421	0.765	32.264
3	14.062	592.2	18.3	0.5402	0.817	17.633
4	15.795	569.6	16.4	0.4896	0.76	16.959

编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	9.367	582.5	26.5	0.3265	0.812	2.787
2	11.318	968.3	37.5	0.3876	0.689	4.634
3	13.581	17517.3	552.1	0.4762	0.518	83.830
4	15.33	1828.2	50.2	0.5407	0.656	8.749

(17) (*S*)-2-((*R*)-hydroxy(4-fulorophenyl)methyl)cyclopentanone

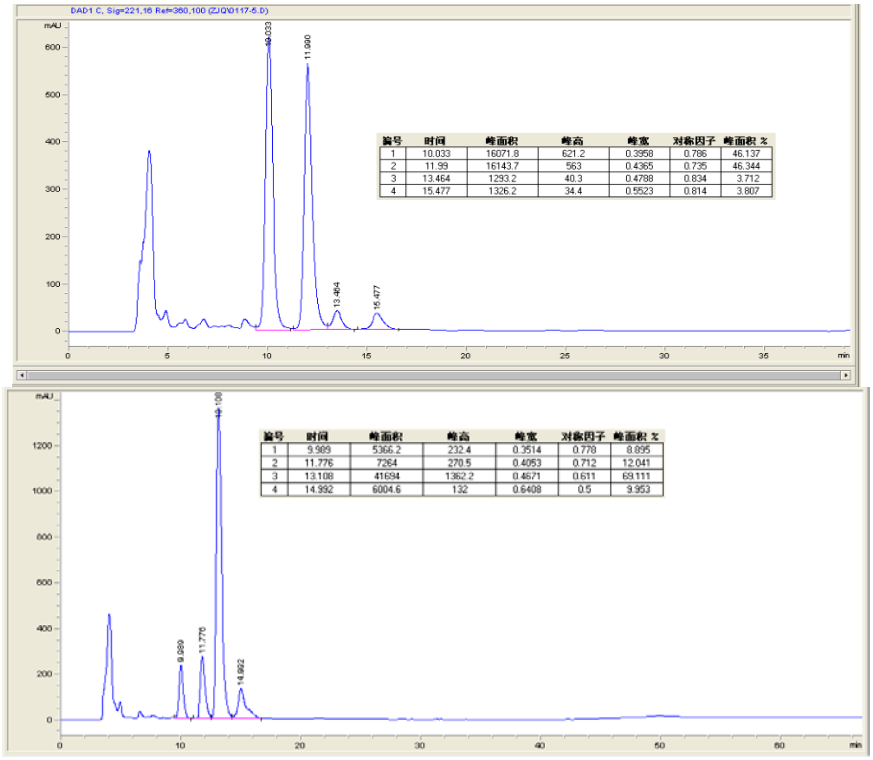


编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	9.697	34337.8	1332.5	0.4046	0.783	31.673
2	12.227	35195.1	1190.7	0.4549	0.683	32.464
3	15.847	19203	552.1	0.5318	0.701	17.713
4	17.245	19677.7	505.8	0.5839	0.705	18.151



编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	9.752	46336.8	1740.6	0.4166	0.728	21.287
2	12.159	26689.7	942.3	0.4324	0.663	12.261
3	15.596	116605	2154.4	0.6374	0.501	53.568
4	17.083	28046.2	681.2	0.6064	0.676	12.884

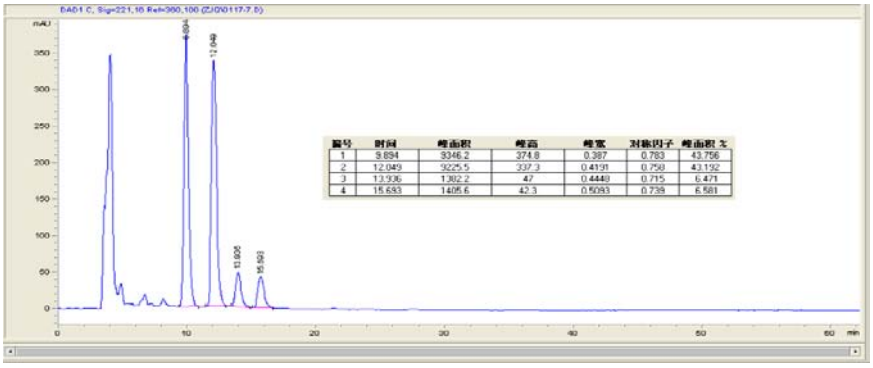
(18) (*S*)-2-((*R*)-hydroxy(4-methylphenyl)methyl)cyclopentanone



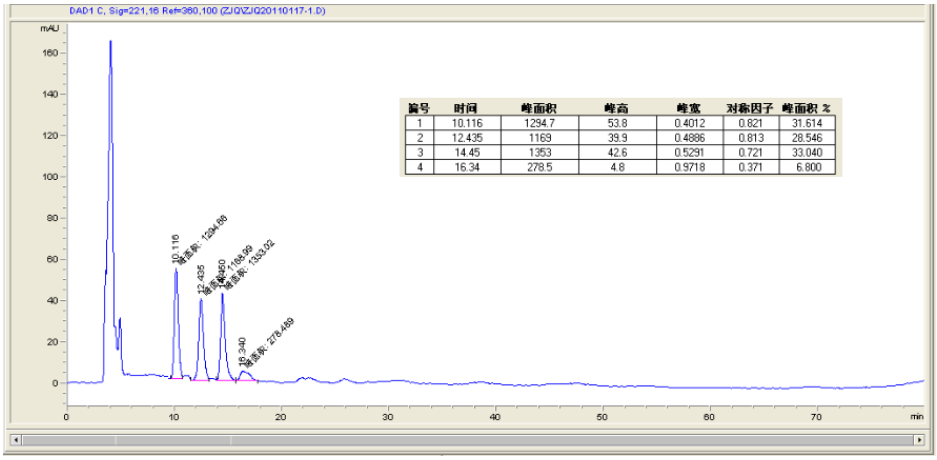
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	10.033	16071.8	621.2	0.3958	0.786	46.137
2	11.99	16143.7	563	0.4365	0.735	46.344
3	13.464	1293.2	40.3	0.4788	0.834	3.712
4	15.477	1326.2	34.4	0.5523	0.814	3.807

编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	9.989	5366.2	232.4	0.3514	0.778	8.895
2	11.776	7264	270.5	0.4053	0.712	12.041
3	13.108	41694	1362.2	0.4671	0.611	69.111
4	14.992	6004.6	132	0.6408	0.5	9.953

(19) (*S*)-2-((*R*)-hydroxy(phenyl)methyl)cyclopentanone

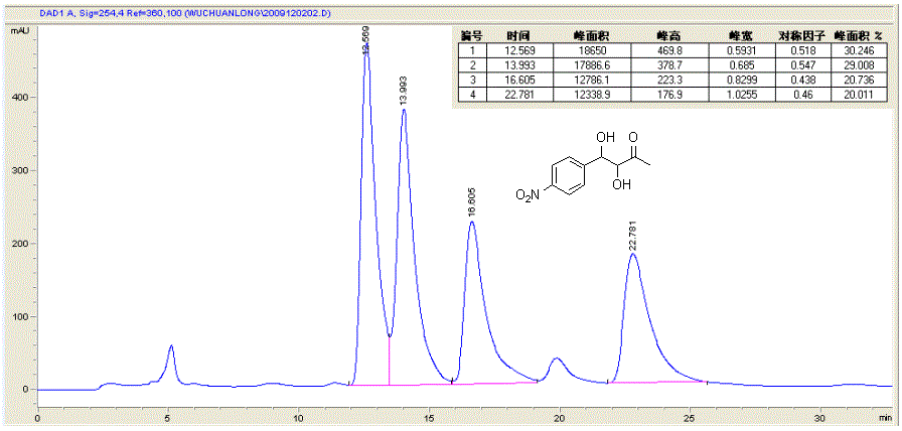


编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	9.894	3346.2	374.8	0.387	0.783	43.756
2	12.049	3225.5	337.3	0.4191	0.758	43.192
3	13.936	1302.2	47	0.4449	0.715	6.471
4	15.693	1405.6	42.3	0.5093	0.739	6.581

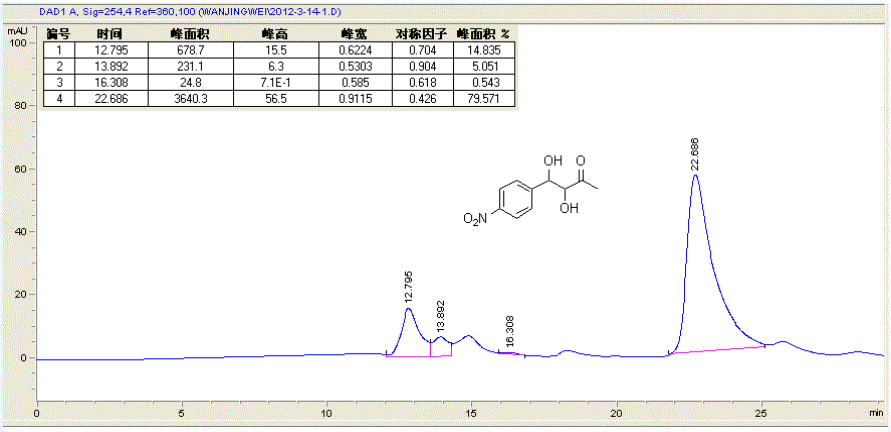


峰号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	10.116	1294.7	53.8	0.4012	0.821	31.614
2	12.435	1169	39.9	0.4886	0.813	28.546
3	14.45	1353	42.6	0.5291	0.721	33.040
4	16.34	278.5	4.8	0.9718	0.371	6.800

Racemes

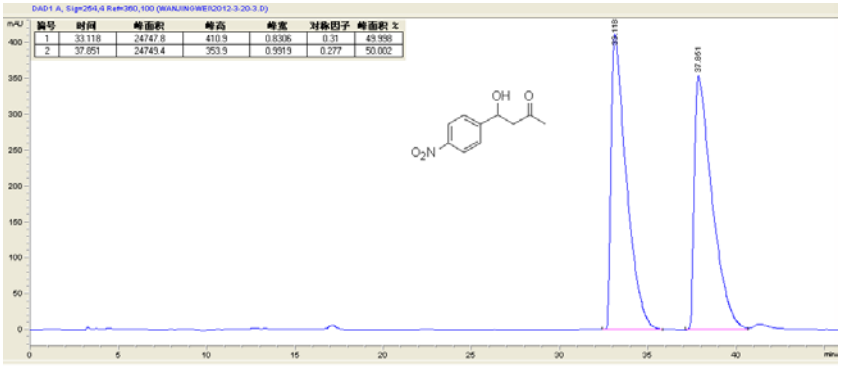


峰号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	12.569	18650	469.8	0.5931	0.518	30.246
2	13.993	17886.6	378.7	0.685	0.547	29.008
3	16.605	12786.1	223.3	0.8299	0.438	20.736
4	22.781	12338.9	176.9	1.0255	0.46	20.011

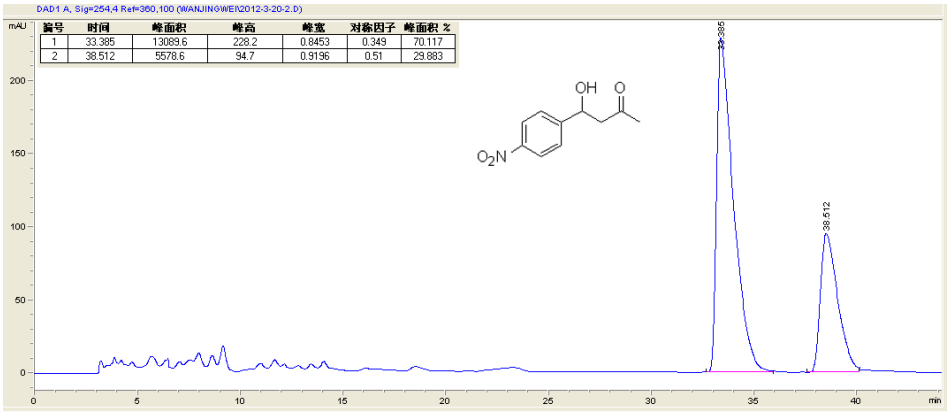


峰号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	12.795	678.7	15.5	0.6224	0.704	14.835
2	13.892	231.1	6.3	0.5303	0.904	5.051
3	16.308	24.8	7.1E-1	0.585	0.618	0.543
4	22.686	3640.3	56.5	0.9115	0.426	79.571

Racemes



峰号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	33.118	24747.8	410.9	0.8306	0.31	49.998
2	37.851	24749.4	353.9	0.9919	0.277	50.002



编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	33.385	13089.6	228.2	0.8453	0.349	70.117
2	38.512	5578.6	94.7	0.9196	0.51	29.883