Electronic Supplementary Material (ESI) for RSC Advances.

Phosphotungstic acid-supported multifunctional organocatalyst containing 9-amino(9-deoxy)*epi*-cinchonidine and Brønsted acid and its application in asymmetric aldol reaction

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1. Acid capacity

Table S1 The acid capacities of various $CDNH_2(n2)$–HPW catalysts

Entry	Cat.	Mass (mg)	V_{NaOH} (mL)	Acid capacity（mmol g^{-1}）
1	$CDNH_2(n2)$–HPW/2	100	79	39.5
2	$CDNH_2(n6)$–HPW/2	100	78	39.0
3	$CDNH_2(n4)$–HPW/4	100	90	45.0
4	$CDNH_2(n4)$–HPW/2	100	81	40.5
5	$CDNH_2(n4)$–HPW/1	100	24	12.0
6	$CDNH_2(n4)$–HPW/0.5	100	123	61.5

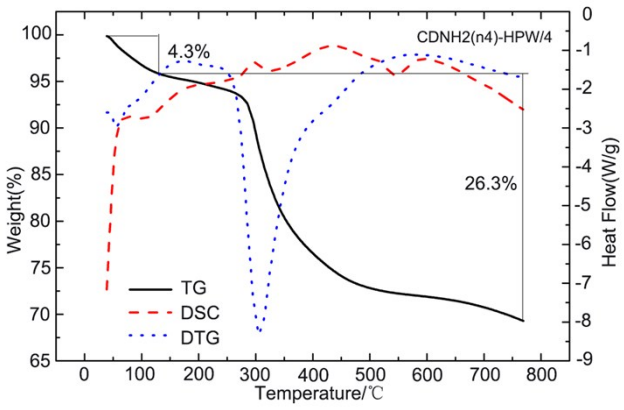
After the sample was well-ground, 30 mg of the sample was charged into a transparent tube, added 10 mL of cyclohexane and two drops of Hammett indicator, and stirred for 12 h at 30 °C. The results were listed in Table S2, in which the mark (+) indicated that the color of the base form is changed to that of the conjugated acid form, while the mark (–) meant that the color is not changed.

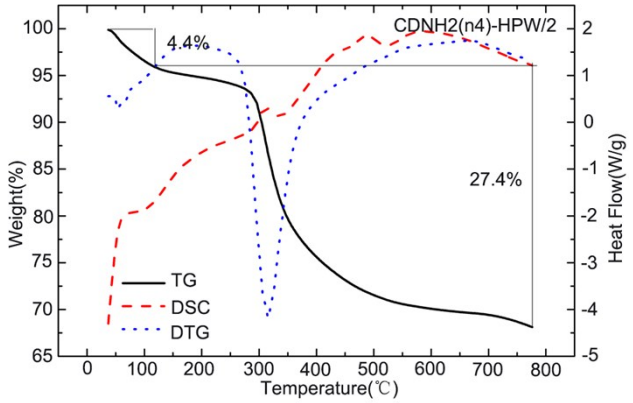
Table S2 The acid strengths of $CDNH_2(n)$–HPW determined by Hammett indicators

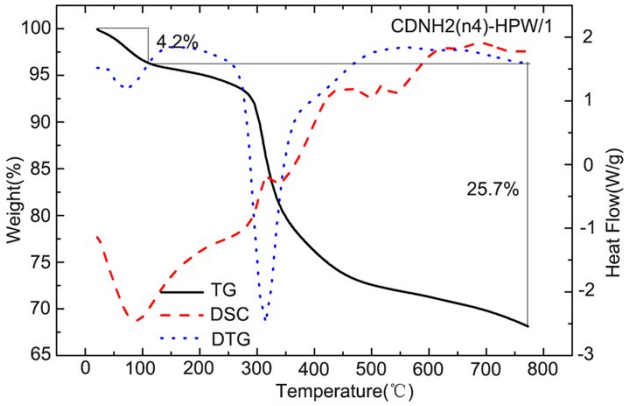
	$CDNH_2(n2)$ –HPW/2	$CDNH_2(n6)$ –HPW/2	$CDNH_2(n4)$ –HPW/0.5	$CDNH_2(n4)$ –HPW/1	$CDNH_2(n4)$ –HPW/2	$CDNH_2(n4)$ –HPW/4
Neutral red (pKa = 6.8)	+	+	+	+	+	+
Methyl red (pKa = 4.8)	+	+	+	+	+	+
Bromophenol blue (pKa = 3.86)	+	+	+	+	+	+
Dimethyl yellow (pKa = 3.3)	+	+	+	–	+	+
Crystal violet (pKa = 0.8)	–	–	+		–	–
Anthraquinone (pKa = -8.0)			-			

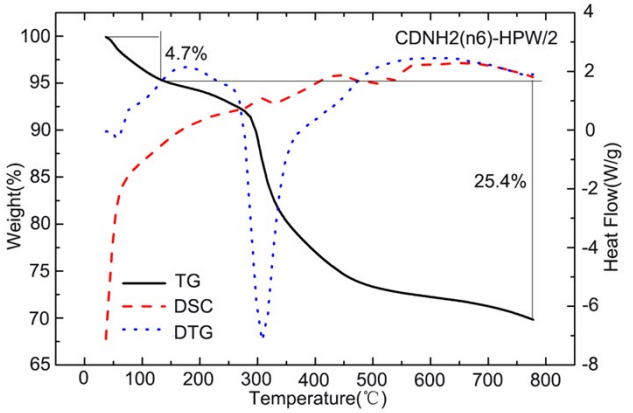
"+" represented the color of acid type; "–" represented the color of alkali type.

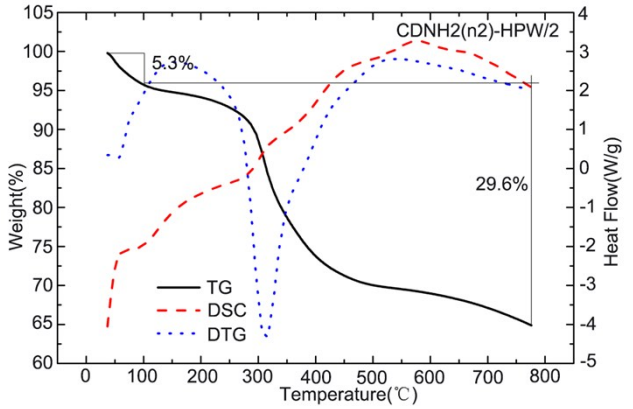
2. TGA



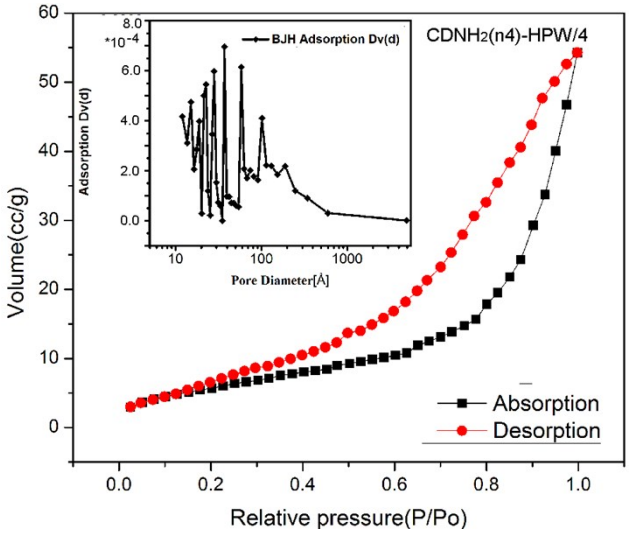


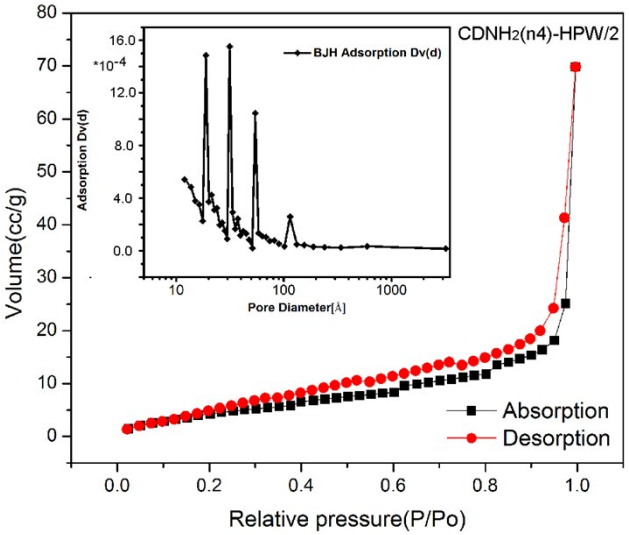


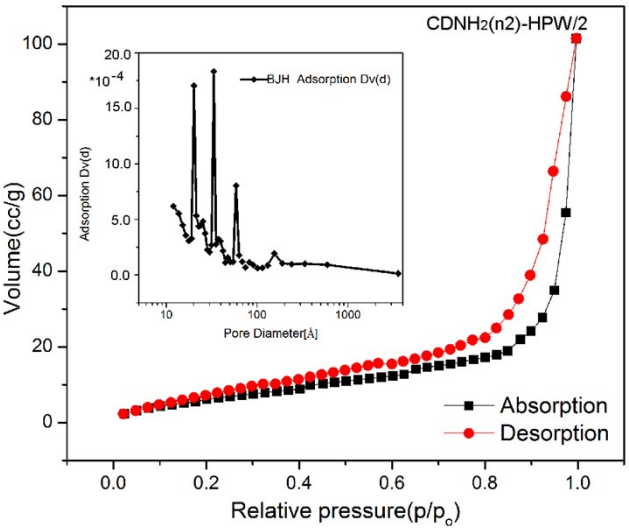


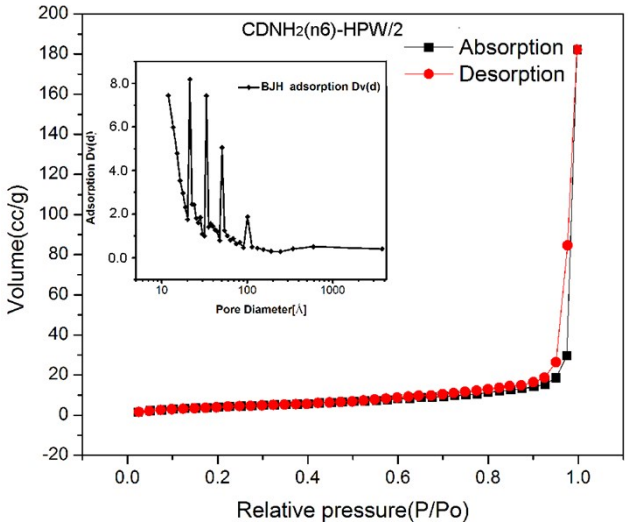


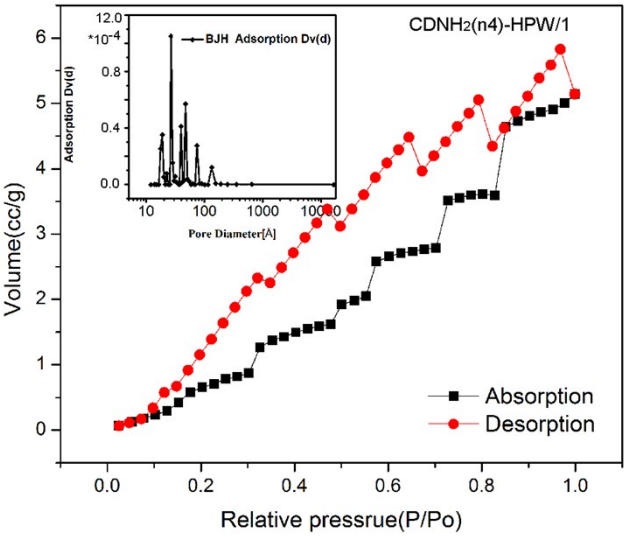
3. N_2 adsorption-desorption isotherm

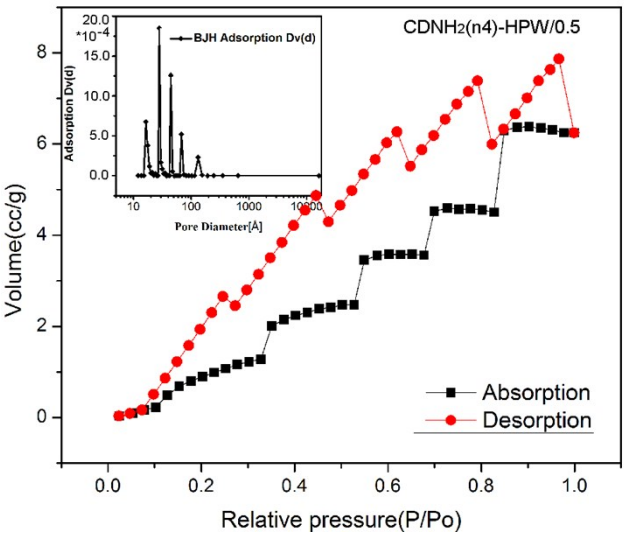

CDNH2(n4)-HPW/4
BJH Adsorption Dv(d)
Adsorption Dv(d)
*10-4
Pore Diameter[Å]
Volume(cc/g)
Relative pressure(P/Po)
Absorption
Desorption


CDNH2(n4)-HPW/2
BJH Adsorption Dv(d)
Adsorption Dv(d)
*10-4
Pore Diameter[Å]
Volume(cc/g)
Relative pressure(P/Po)
Absorption
Desorption

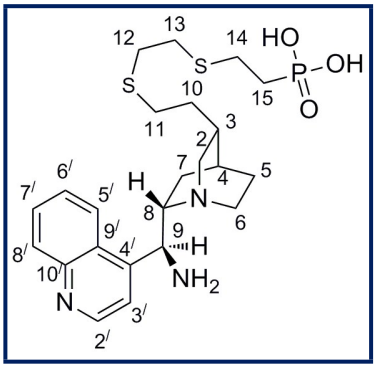

CDNH2(n2)-HPW/2
BJH Adsorption Dv(d)
Adsorption Dv(d)
*10-4
Pore Diameter[Å]
Volume(cc/g)
Relative pressure(p/po)
Absorption
Desorption


CDNH2(n6)-HPW/2
Absorption
Desorption
BJH adsorption Dv(d)
Adsorption Dv(d)
Pore Diameter[Å]
Volume(cc/g)
Relative pressure(P/Po)

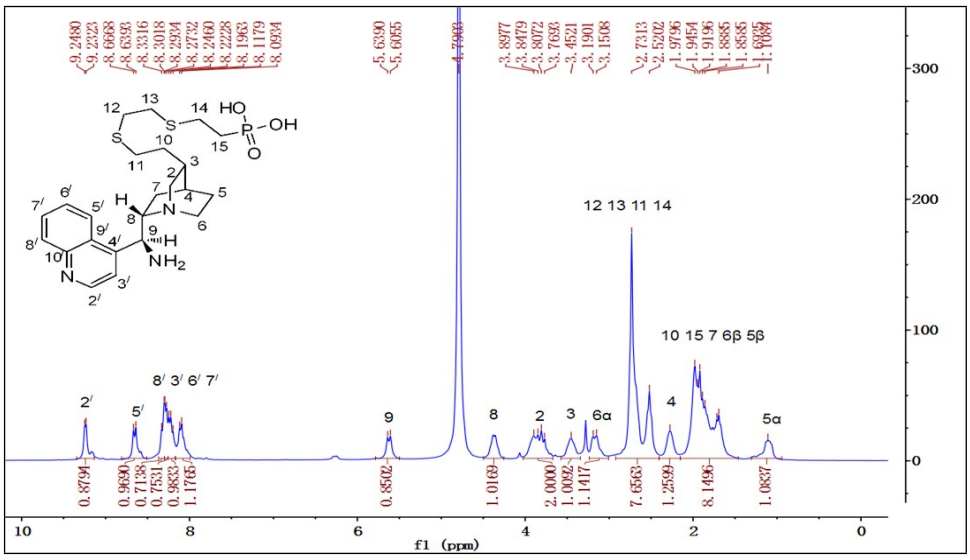

CDNH2(n4)-HPW/1
BJH Adsorption Dv(d)
Adsorption Dv(d)
Pore Diameter[Å]
Absorption
Desorption
Volume(cc/g)
Relative pressrue(P/Po)

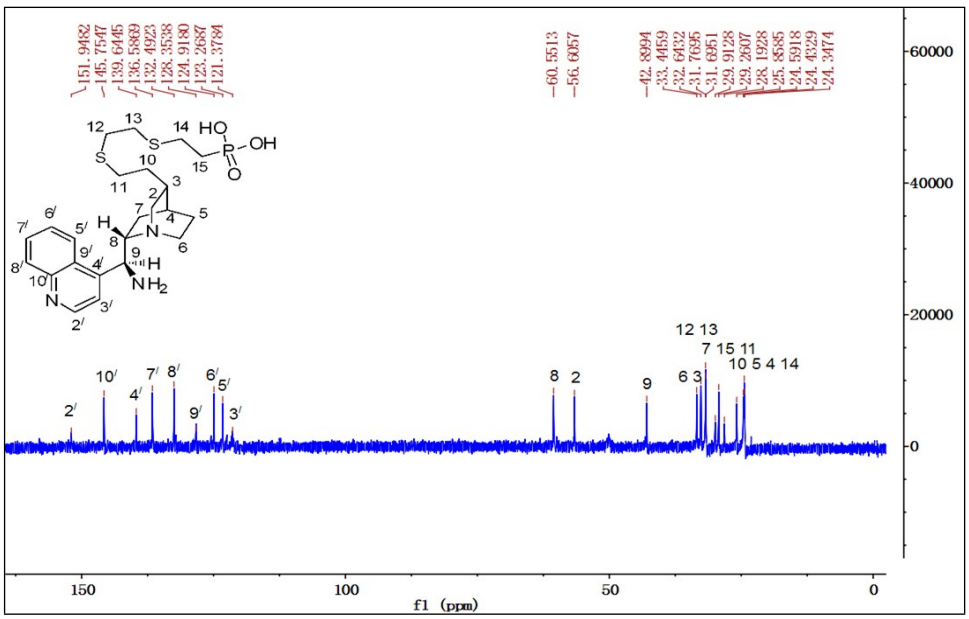

CDNH2(n4)-HPW/0.5
BJH Adsorption Dv(d)
Adsorption Dv(d)
Pore Diameter[Å]
Absorption
Desorption
Volume(cc/g)
Relative pressure(P/Po)

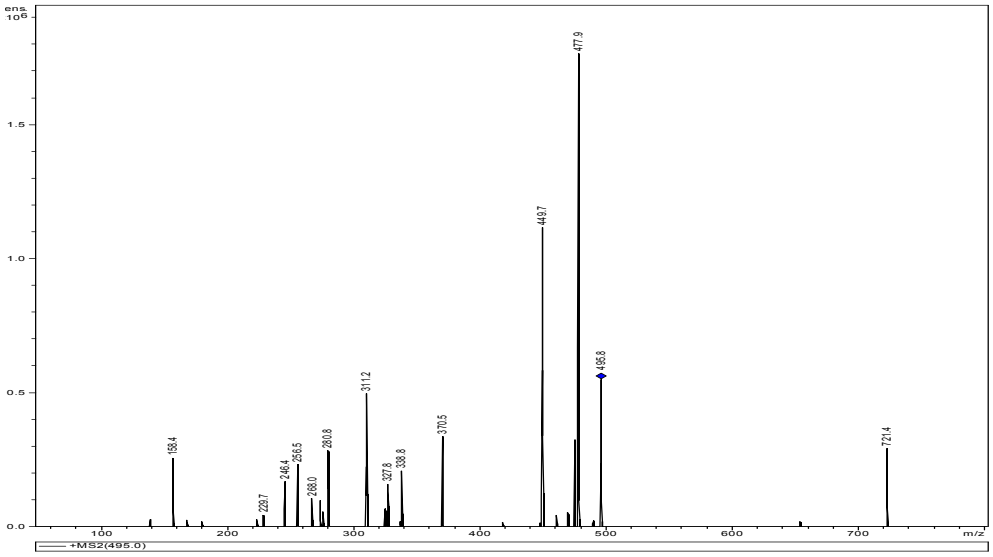
4. ^{1}H and ^{13}C NMR spectra of $CDNH_2(n)–PO_3H_2$

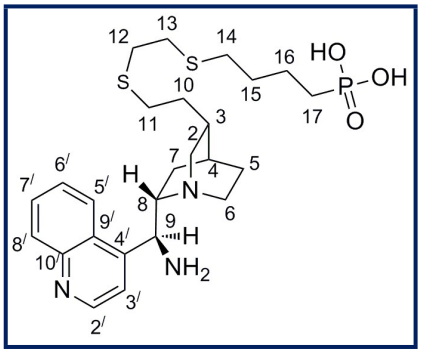


$CDNH_2$(n2)–PO_3H_2: pale yellow solid, mp: 155-156 °C, δ_H (300.1 MHz, D_2O, Me_4Si): 9.24 (1 H, d, ^3J =6.0 Hz), 8.65 (1 H, d, ^3J = 9.0 Hz), 8.32 (1 H, d, ^3J = 9.0 Hz), 8.28 (1 H, d, ^3J = 6.0 Hz), 8.22 (1 H, t, ^3J = 6.0 Hz), 8.09 (1 H, t, ^3J = 6.0 Hz), 5.63 (1 H, d, ^3J = 9.0 Hz), 4.37 (1 H, d, ^3J = 6.0 Hz), 3.77-3.90 (2 H, m), 3.45 (1 H, s), 3.17 (1 H, d, ^3J = 12.0 Hz), 2.52-2.73 (8 H, m), 2.28 (1 H, s), 1.69-1.98 (8 H, m), 1.11 (1 H, s). δ_C (75.0 MHz, $CDCl_3$): 151.9, 145.8, 139.6, 136.6, 132.5, 128.4, 124.9, 123.3, 121.4, 60.6, 56.6, 42.9, 33.4, 32.6, 31.8, 31.7, 29.9, 29.3, 28.2, 25.9, 24.6, 24.4, 24.3. Anal. Calcd for $C_{23}H_{34}N_3O_3PS_2$: C, 55.74; H, 6.91; N, 8.48. Found: C, 55.78; H, 6.90; N, 8.49. MS (ESI+) *m/z* 495.8 $[M+H]^+$.

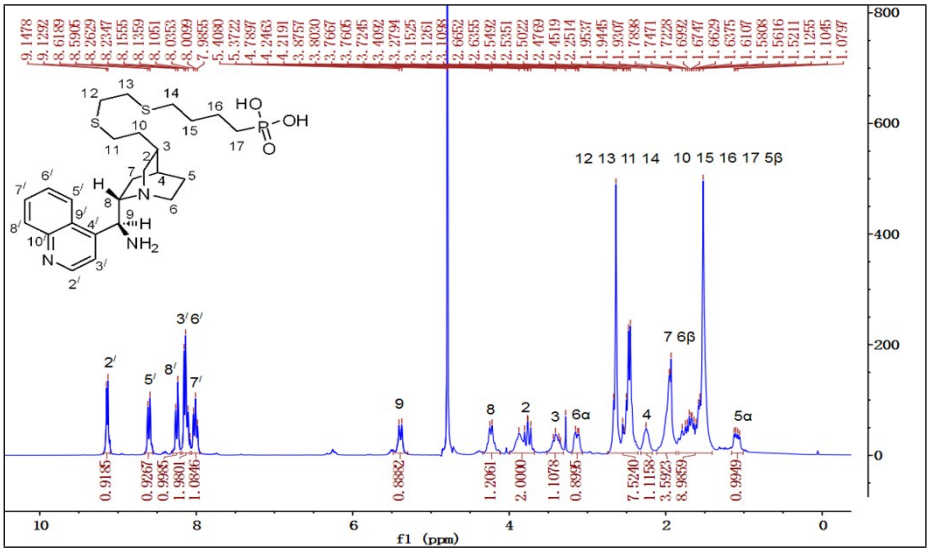


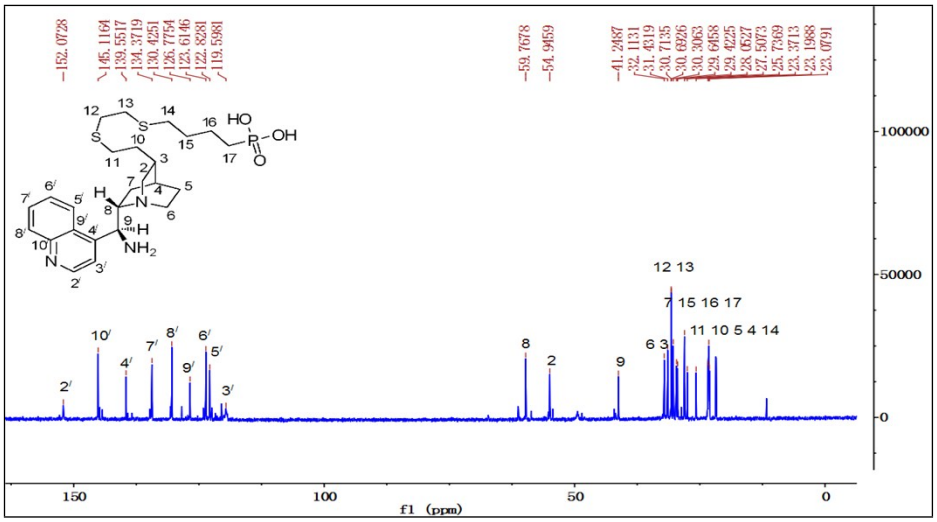


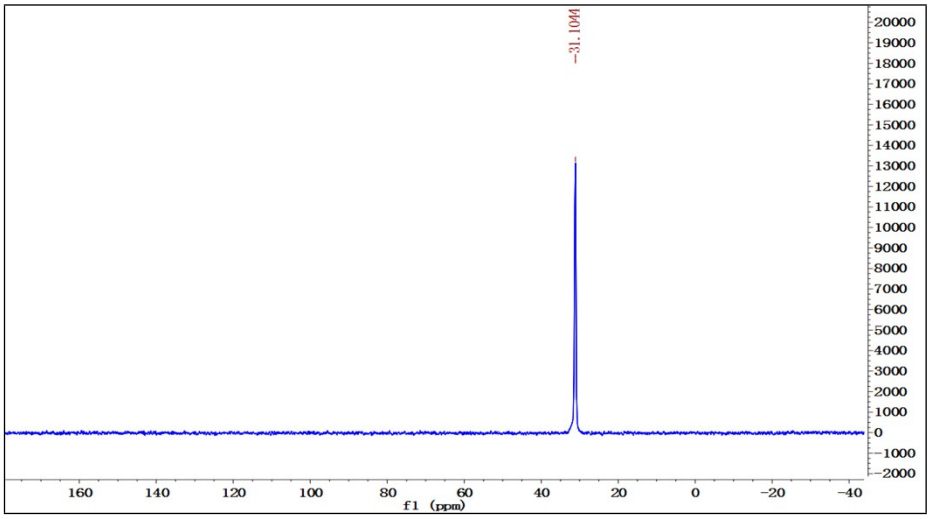


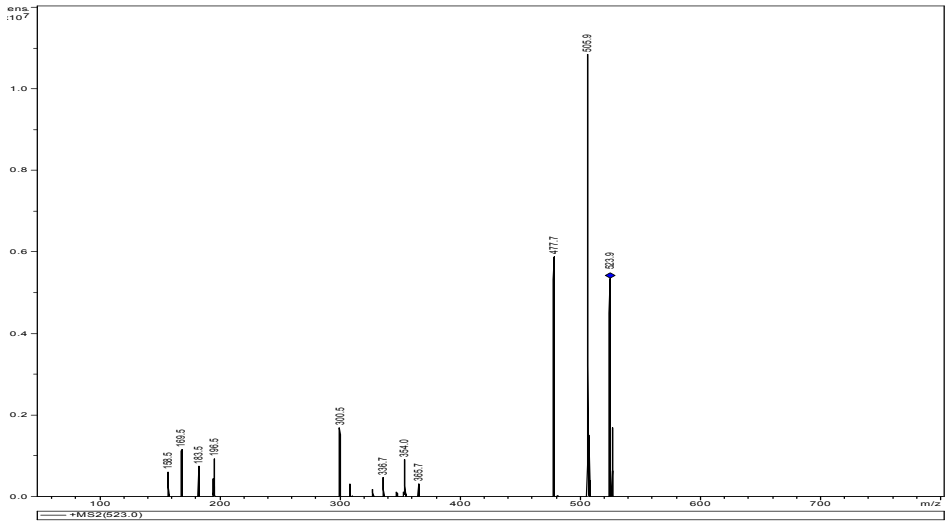


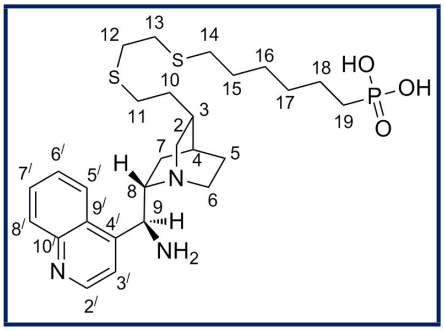
CDNH$_2$(n4)–PO$_3$H$_2$: pale yellow solid, mp: 155-157 °C, δ_H (300.1 MHz, D_2O, Me_4Si): 9.14 (1 H, d, ^3J = 6.0 Hz), 8.61 (1 H, d, ^3J = 9.0 Hz), 8.25 (1 H, d, ^3J = 9.0 Hz), 8.08-8.16 (2 H, m), 8.01 (1 H, t, ^3J = 6.0 Hz), 5.39 (1 H, d, ^3J = 9.0 Hz), 4.23 (1 H, d, ^3J = 6.0 Hz), 3.72-3.88 (2 H, m), 3.34-3.44 (1 H, m), 3.11-3.15 (1 H, m), 2.45-2.67 (8 H, m), 2.25 (1 H, s), 1.93-1.95 (3 H, m), 1.52-1.79 (9 H, m), 1.09 (1 H, q, ^3J = 6.0 Hz). δ_C (75.0 MHz, $CDCl_3$): 153.4, 146.4, 140.9, 135.7, 131.7, 128.1, 124.9, 124.1, 120.9, 61.1, 56.3, 42.6, 33.4, 32.7, 32.0, 32.0, 31.6, 31.0, 30.7, 29.4, 28.8, 27.1, 24.7, 24.5, 24.4. δ_p (121.5 MHz, $\delta_{85\%H3PO4}$ = 0 ppm): 31.1 (s). Anal. Calcd for $C_{25}H_{38}N_3O_3PS_2$: C, 57.34; H, 7.31; N, 8.02. Found: C, 57.30; H, 7.30; N, 8.05. MS (ESI+) *m/z* 523.9 $[M+H]^+$.



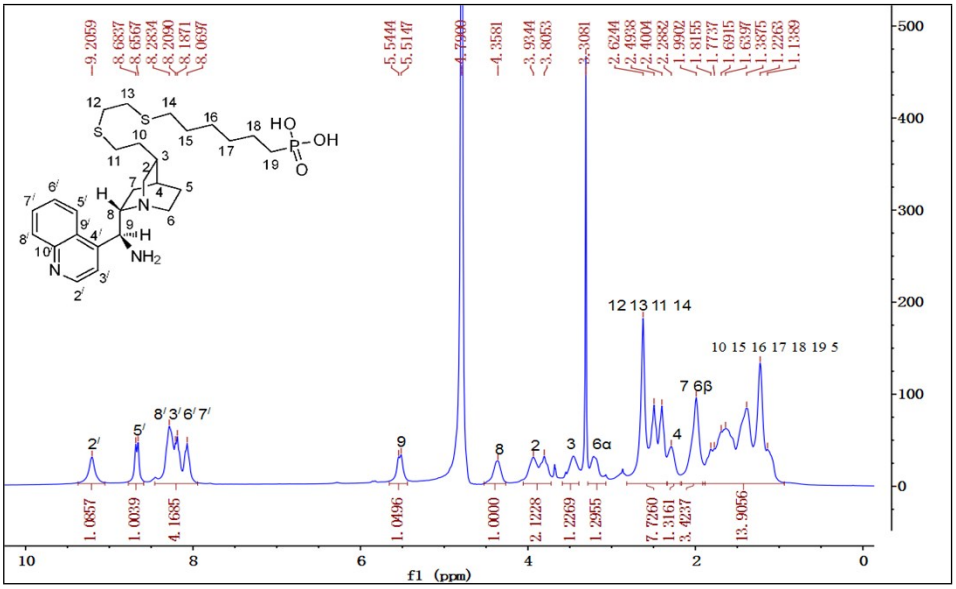

f1 (ppm)

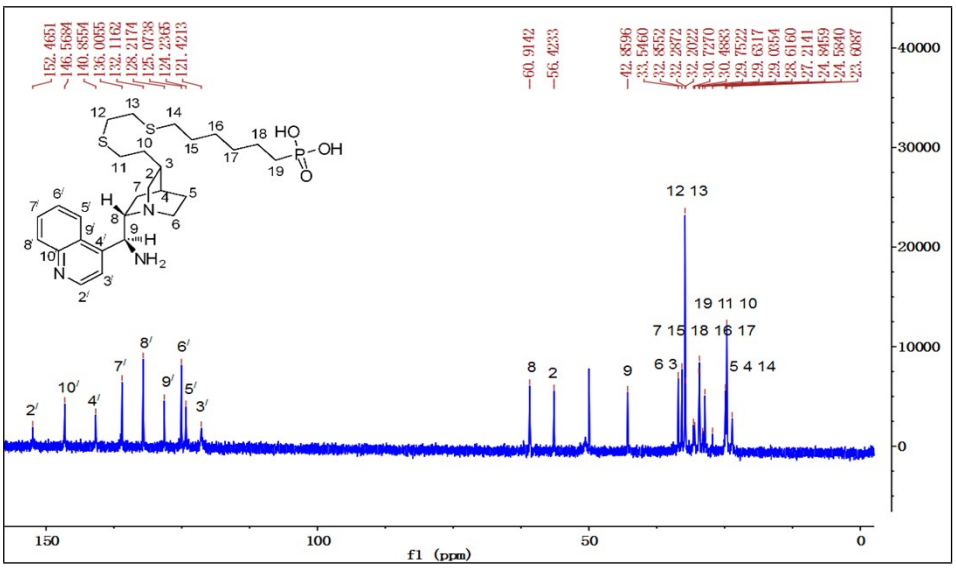

f1 (ppm)

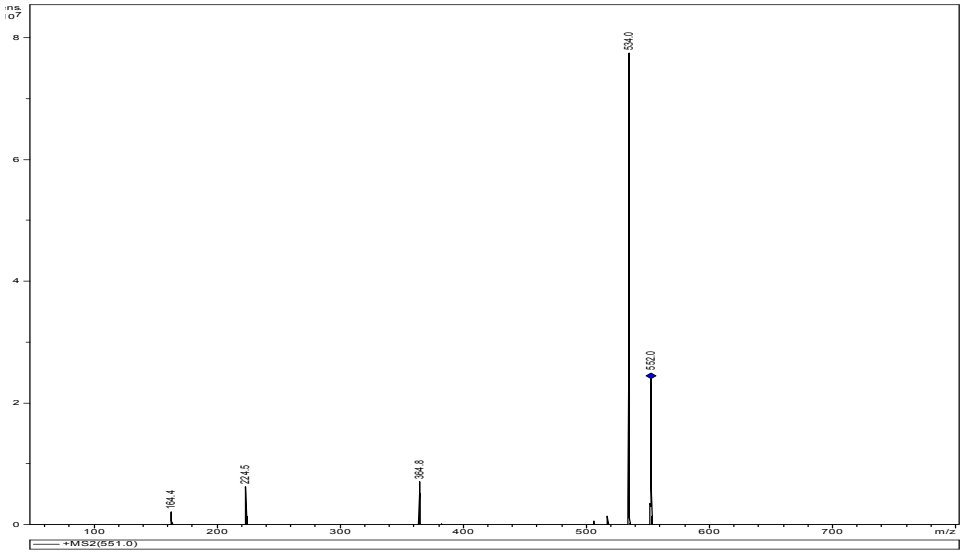

+MS2(523.0)



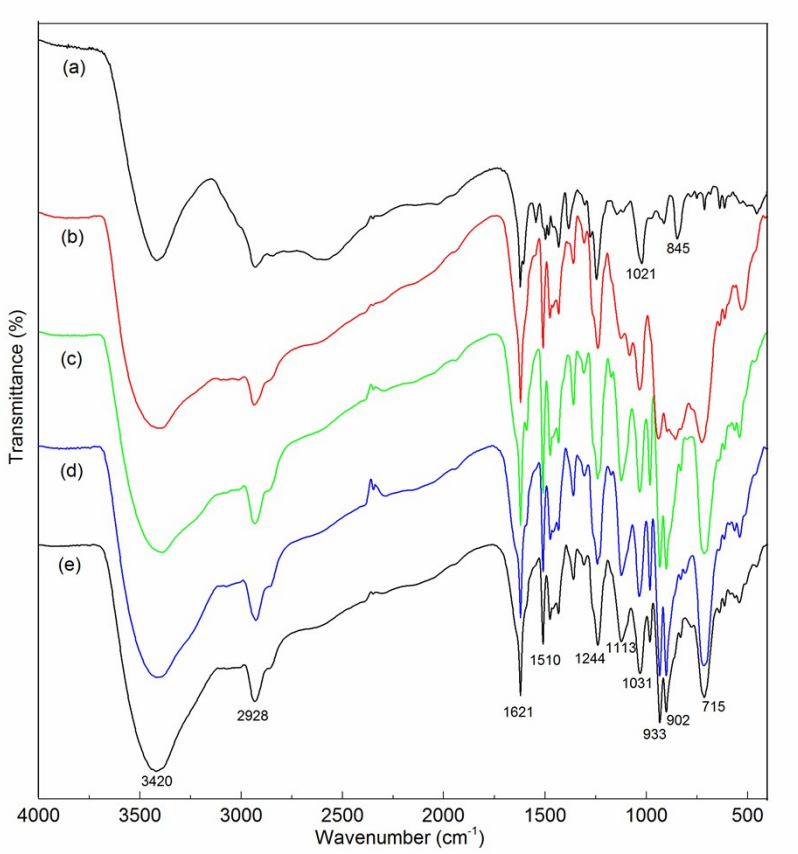
CDNH$_2$(n4)–PO$_3$H$_2$: pale yellow solid, mp: 160-162 °C, δ_H (300.1 MHz, D_2O, Me_4Si): 9.21 (1 H, s), 8.67 (1 H, d, ^3J = 9.0 Hz), 8.07-8.28 (4 H, m), 5.53 (1 H, d, ^3J = 9.0 Hz), 4.36 (1 H, s), 3.80-3.93 (2 H, m), 3.46 (1 H, s), 3.22 (1 H, s), 2.40-2.62 (8 H, m), 2.29 (1 H, s), 1.99 (3 H, m), 1.14-1.82 (14 H, m). δ_C (75.0 MHz, $CDCl_3$): 152.5, 146.6, 140.9, 136.0, 132.1, 128.2, 125.1, 124.2, 121.4, 60.9, 56.4, 42.9, 33.5, 32.9, 32.3, 32.3, 32.2, 30.7, 30.5, 29.7, 29.6, 29.0, 28.6, 27.2, 24.8, 24.6, 23.6. Anal. Calcd for $C_{27}H_{42}N_3O_3PS_2$: C, 58.78; H, 7.67; N, 7.62. Found: C, 58.85; H, 7.70; N, 7.60. MS (ESI+) *m/z* 552.0 $[M+H]^+$.







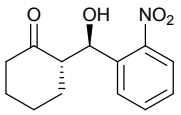
5. IR spectra

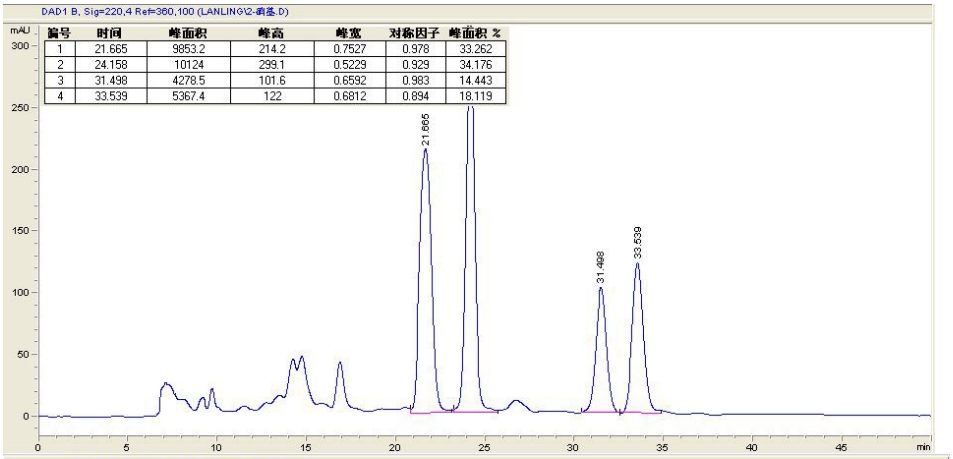


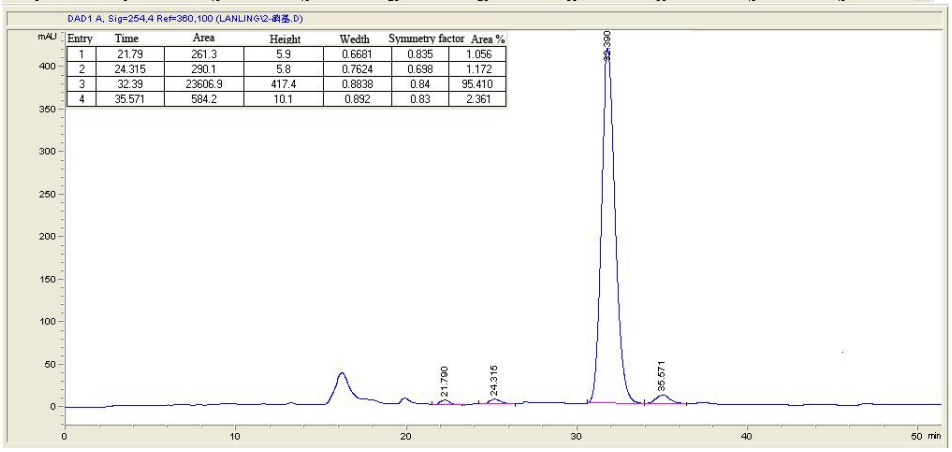
IR spectra of $CDNH_2$(*n*4)–PO_3H_2 (a), $CDNH_2$(*n*4)–HPW/0.5 (b), $CDNH_2$ (*n*4)–HPW/1 (c), $CDNH_2$ (*n*4)–HPW/2 and $CDNH_2$ (*n*4)–HPW/4.

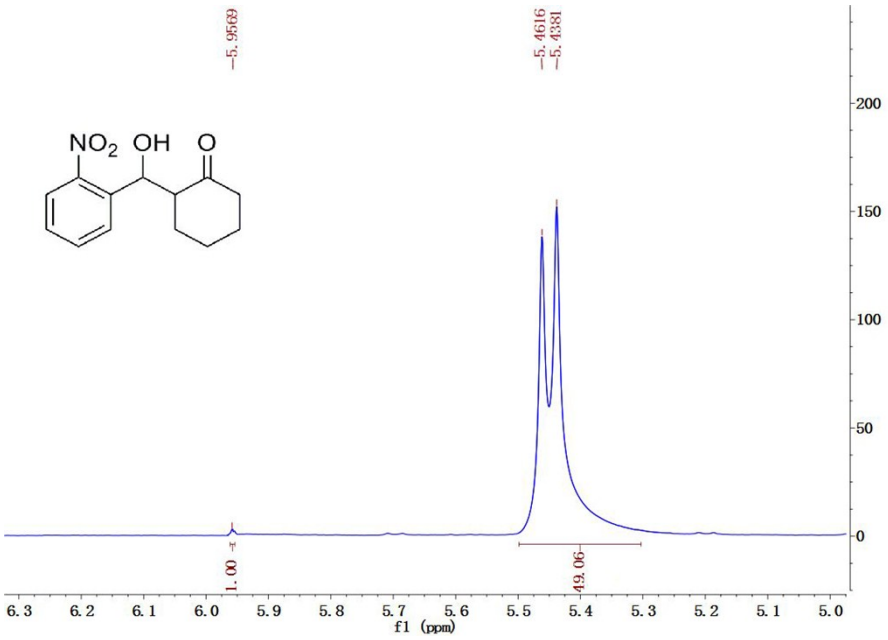
6. HPLC and ^{1}H NMR spectra for enantioselectivity and diastereoselectivity of aldol adducts

(1)









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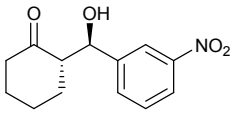
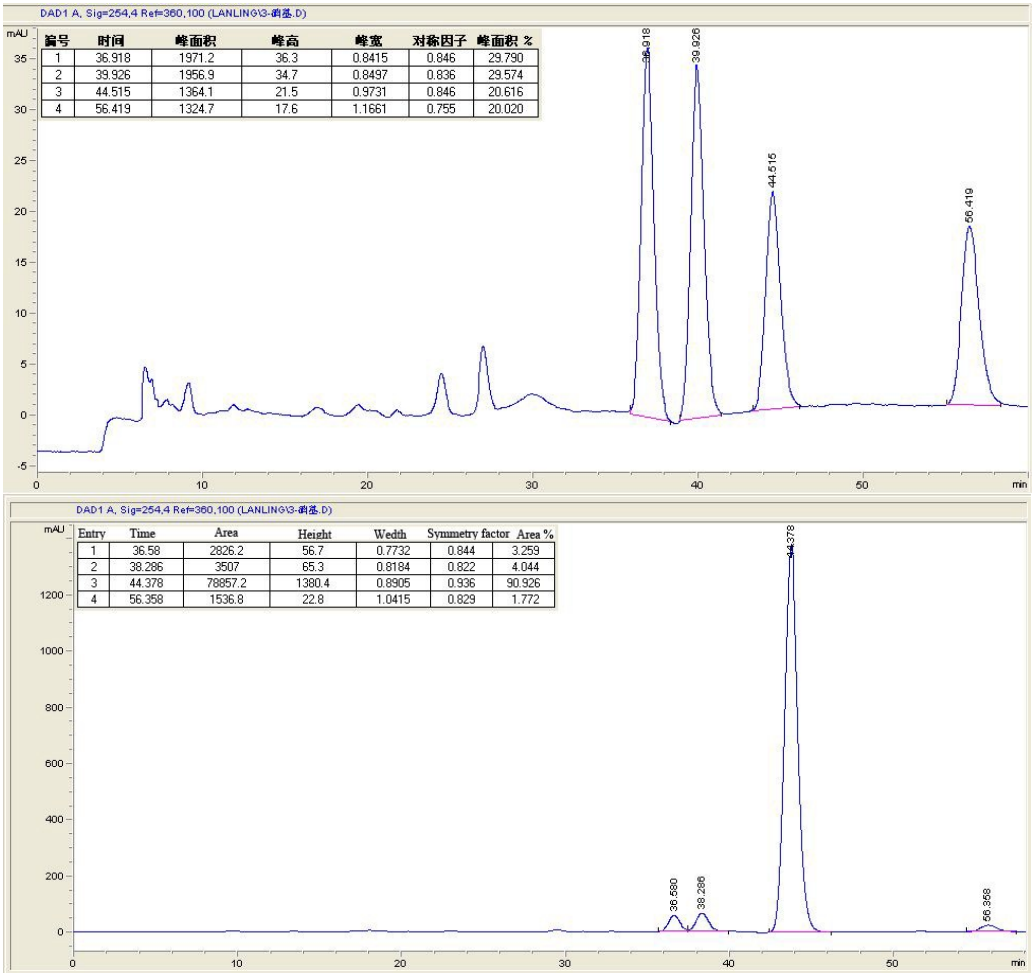
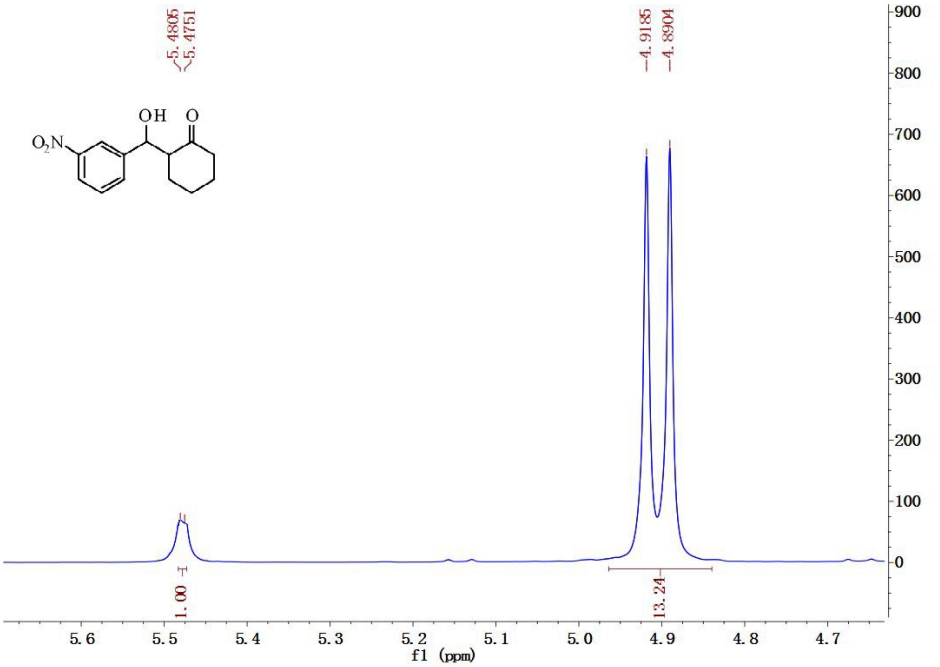




编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	36.918	1971.2	36.3	0.8415	0.846	29.790
2	39.926	1956.9	34.7	0.8497	0.836	29.574
3	44.515	1364.1	21.5	0.9731	0.846	20.616
4	56.419	1324.7	17.6	1.1661	0.755	20.020

Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	36.58	2826.2	56.7	0.7732	0.844	3.259
2	38.286	3507	65.3	0.8184	0.822	4.044
3	44.378	78857.2	1380.4	0.8905	0.936	90.926
4	56.358	1536.8	22.8	1.0415	0.829	1.772



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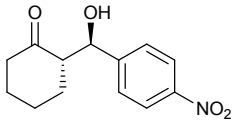
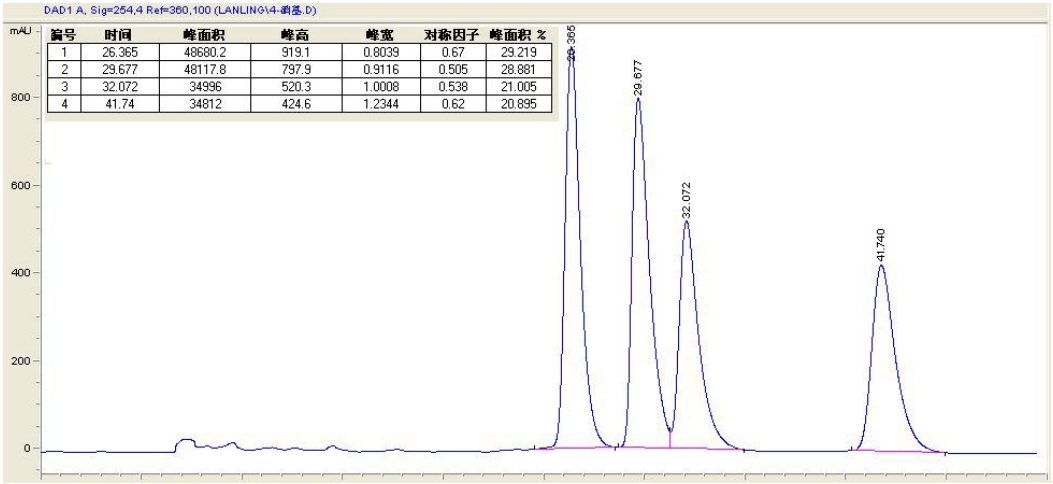
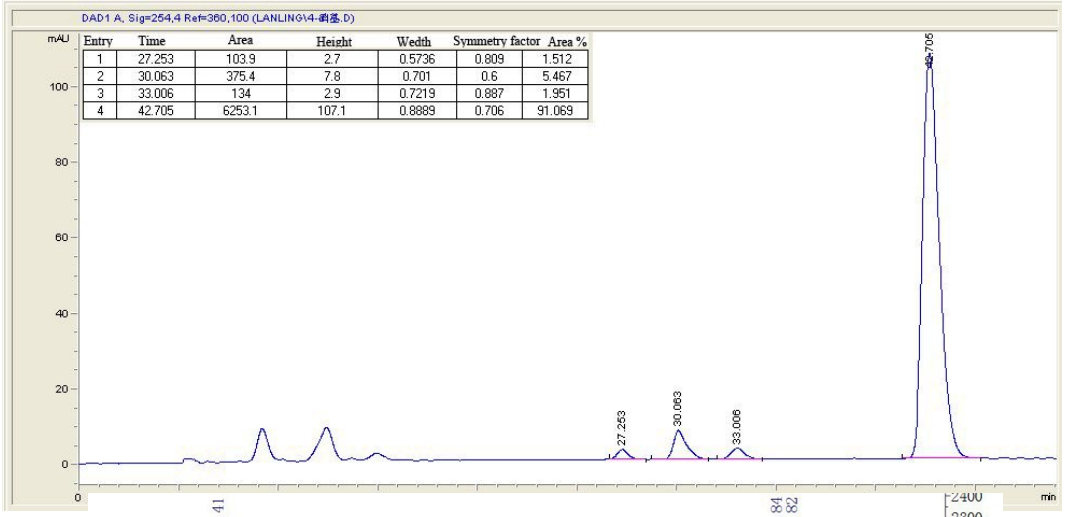
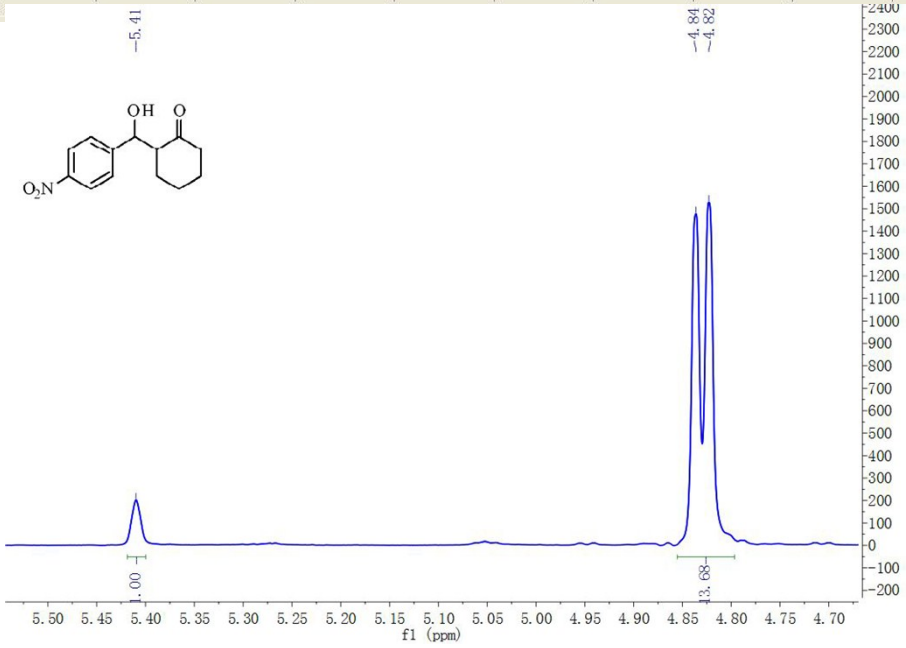




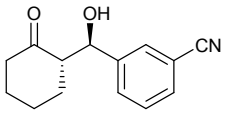
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	26.365	48680.2	919.1	0.8039	0.67	29.219
2	29.677	48117.8	797.9	0.9116	0.505	28.881
3	32.072	34996	520.3	1.0008	0.538	21.005
4	41.74	34812	424.6	1.2344	0.62	20.895

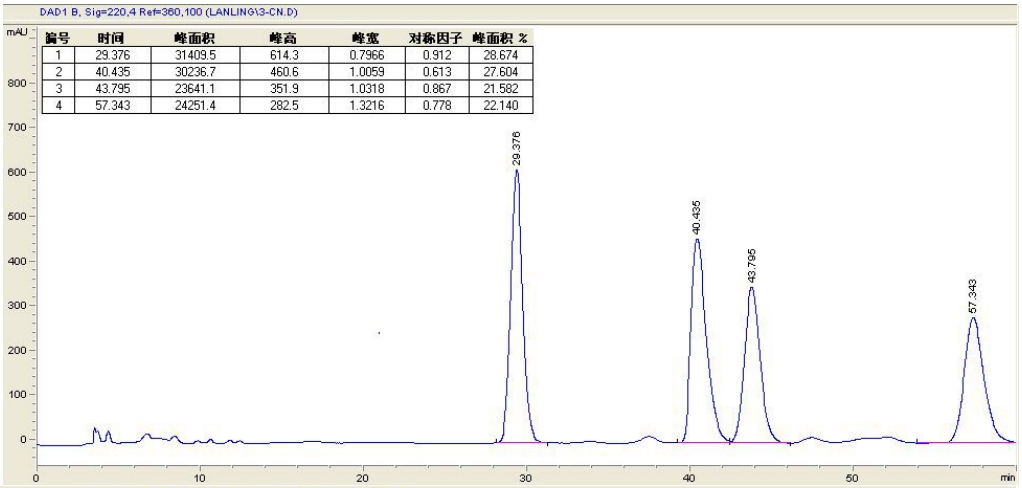


Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	27.253	103.9	2.7	0.5736	0.809	1.512
2	30.063	375.4	7.8	0.701	0.6	5.467
3	33.006	134	2.9	0.7219	0.887	1.951
4	42.705	6253.1	107.1	0.8889	0.706	91.069

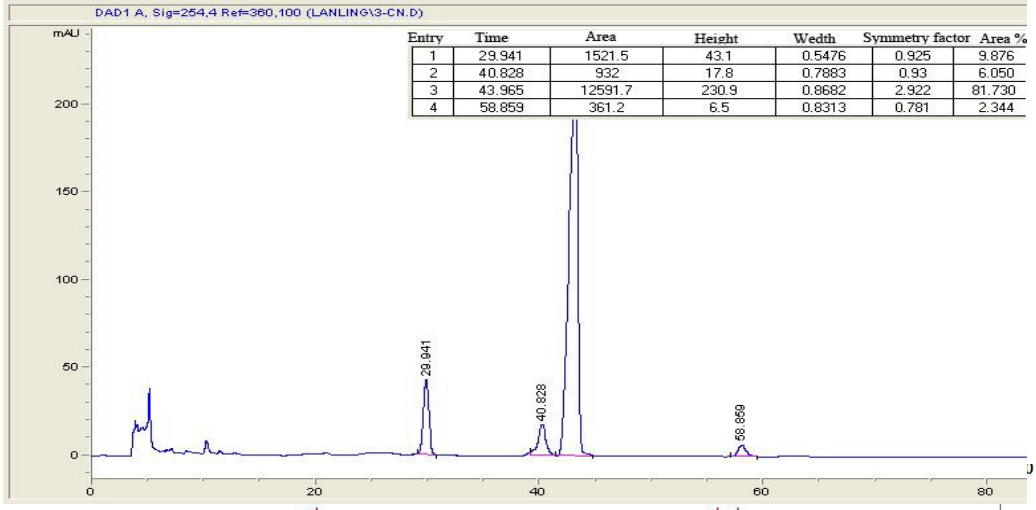


(4)

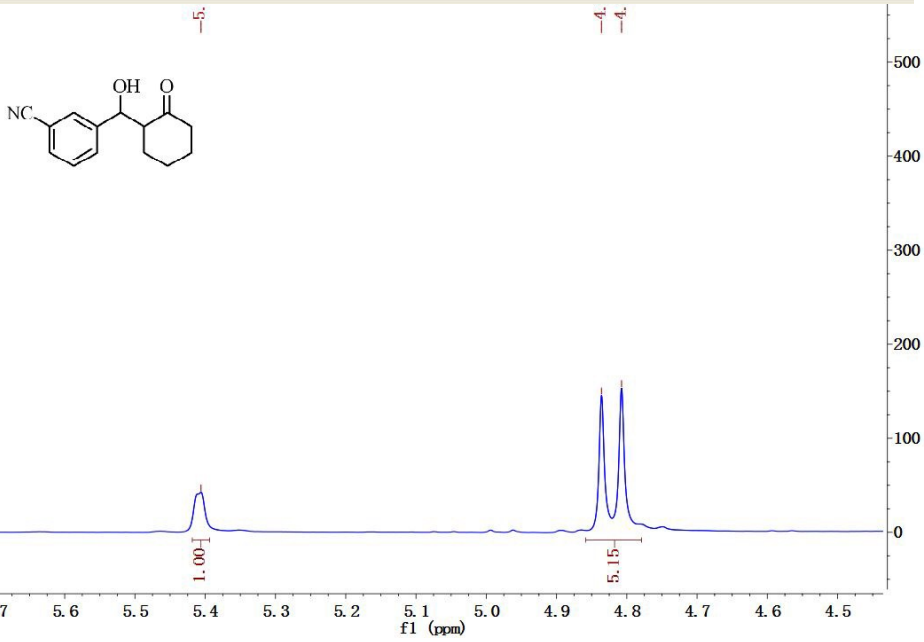




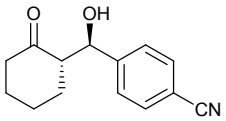
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	29.376	31409.5	614.3	0.7966	0.912	28.674
2	40.435	30236.7	460.6	1.0059	0.613	27.604
3	43.795	23641.1	351.9	1.0318	0.867	21.582
4	57.343	24251.4	282.5	1.3216	0.778	22.140

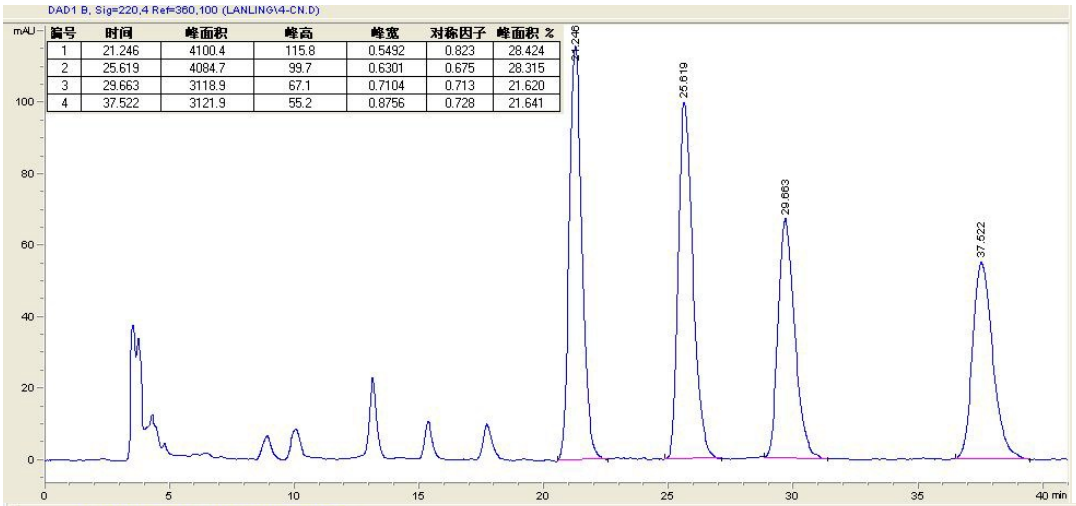


Entry	Time	Area	Height	Wedth	Symmetry factor	Area %
1	29.941	1521.5	43.1	0.5476	0.925	9.876
2	40.828	932	17.8	0.7883	0.93	6.050
3	43.965	12591.7	230.9	0.8682	2.922	81.730
4	58.859	361.2	6.5	0.8313	0.781	2.344

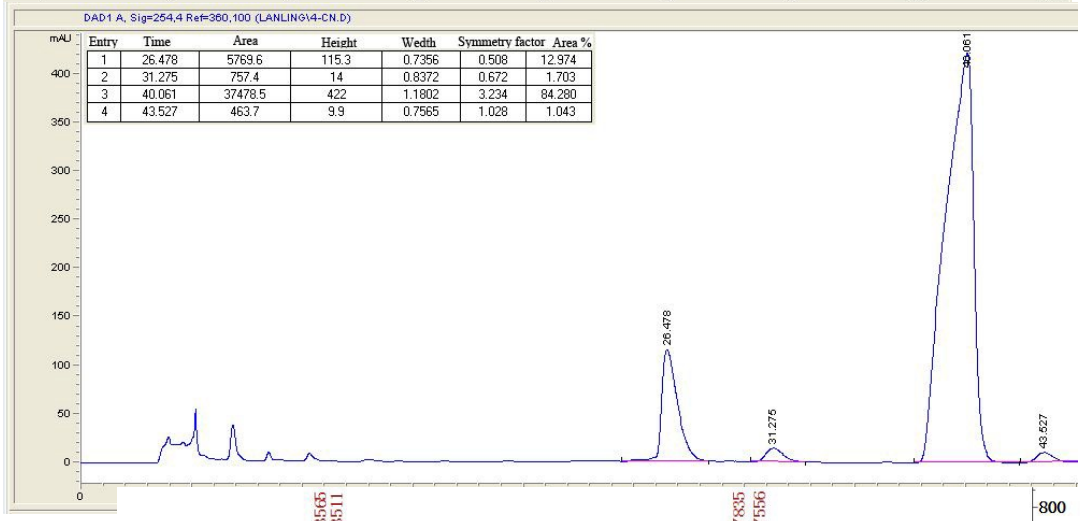


(5)

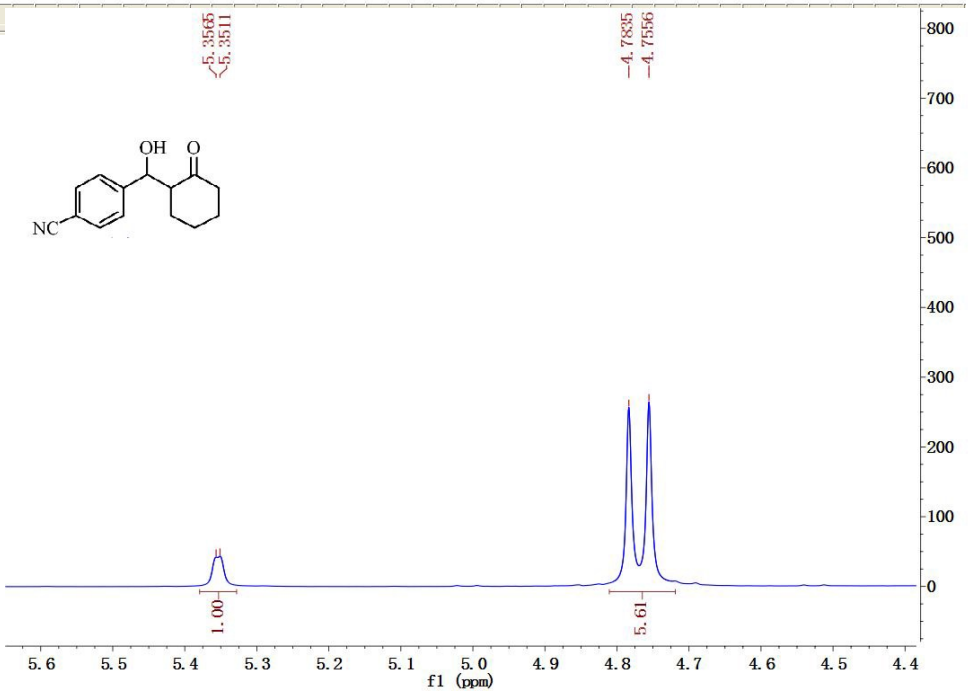




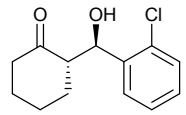
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	21.246	4100.4	115.8	0.5492	0.823	28.424
2	25.619	4084.7	99.7	0.6301	0.675	28.315
3	29.663	3118.9	67.1	0.7104	0.713	21.620
4	37.522	3121.9	55.2	0.8756	0.728	21.641

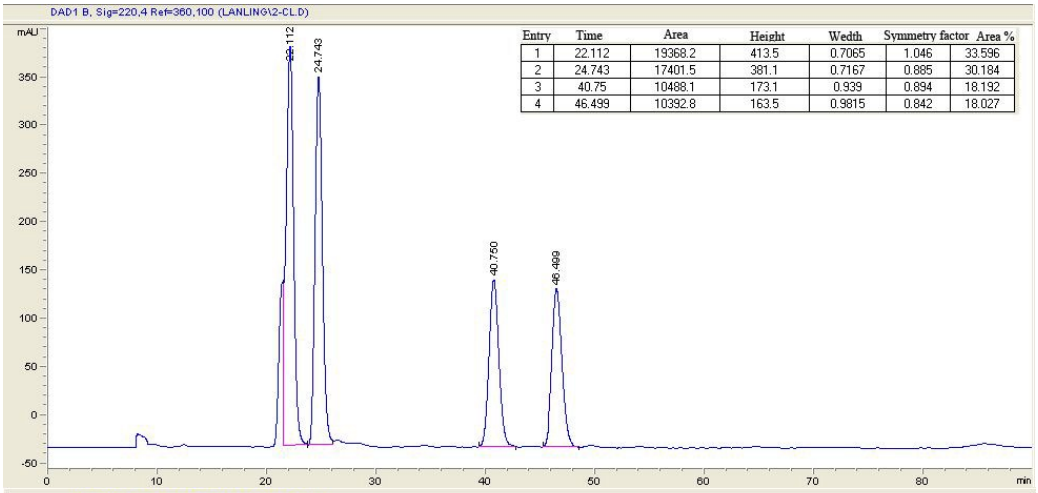


Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	26.478	5769.6	115.3	0.7356	0.508	12.974
2	31.275	757.4	14	0.8372	0.672	1.703
3	40.061	37478.5	422	1.1802	3.234	84.280
4	43.527	463.7	9.9	0.7565	1.028	1.043

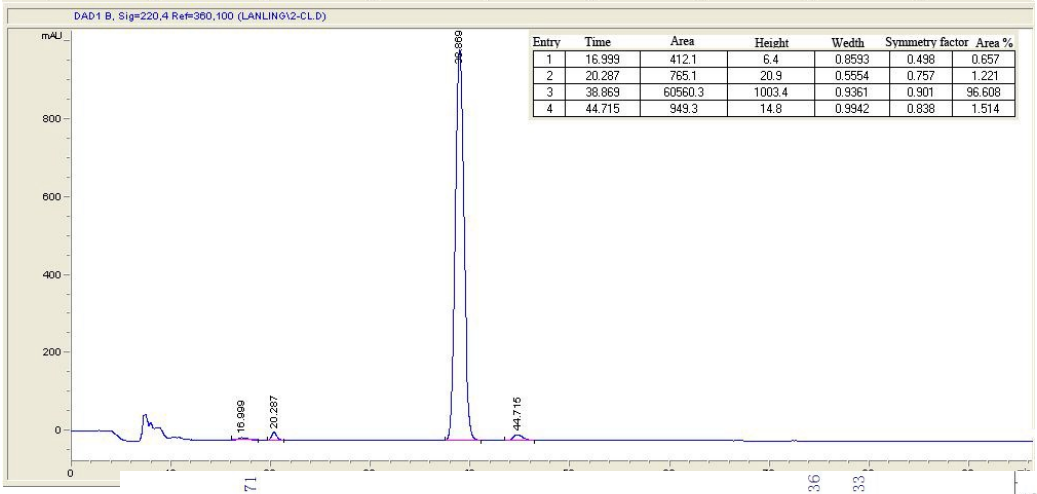


(6)

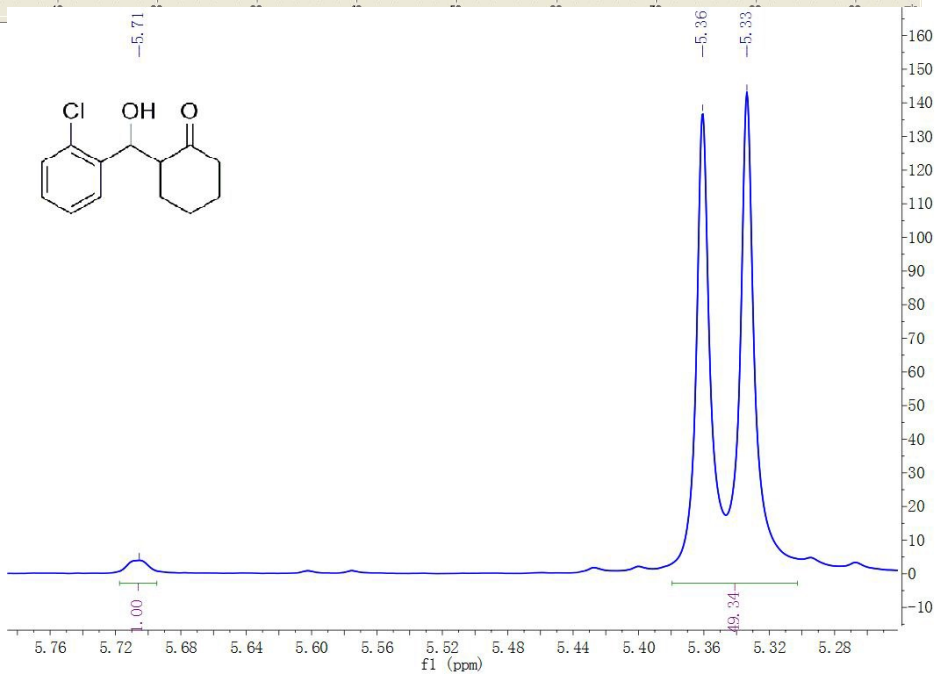




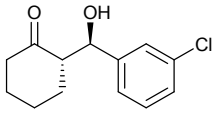
Entry	Time	Area	Height	Wedth	Symmetry factor	Area %
1	22.112	19368.2	413.5	0.7065	1.046	33.596
2	24.743	17401.5	381.1	0.7167	0.885	30.184
3	40.75	10488.1	173.1	0.939	0.894	18.192
4	46.499	10392.8	163.5	0.9815	0.842	18.027

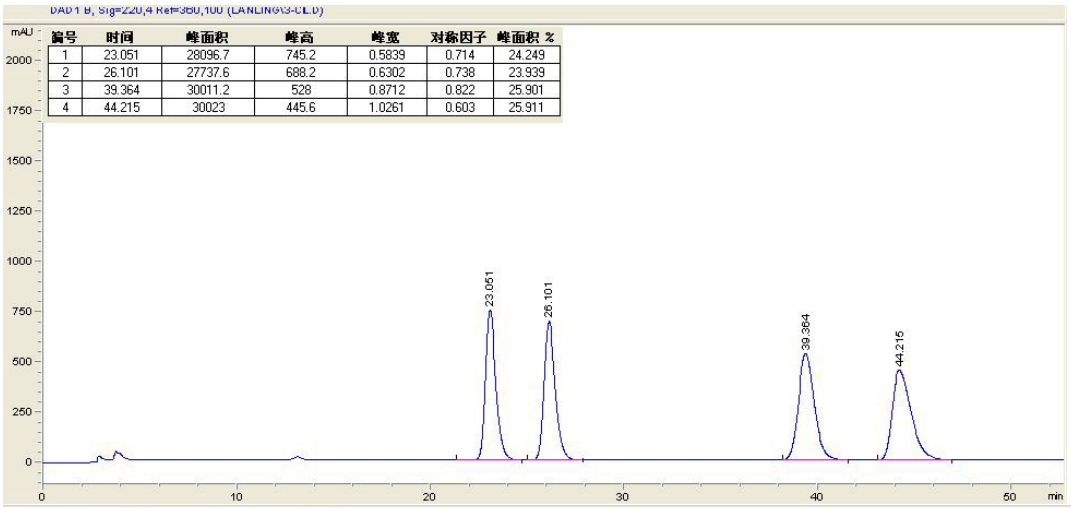


Entry	Time	Area	Height	Wedth	Symmetry factor	Area %
1	16.999	412.1	6.4	0.8593	0.498	0.657
2	20.287	765.1	20.9	0.5554	0.757	1.221
3	38.869	60560.3	1003.4	0.9361	0.901	96.608
4	44.715	949.3	14.8	0.9942	0.838	1.514

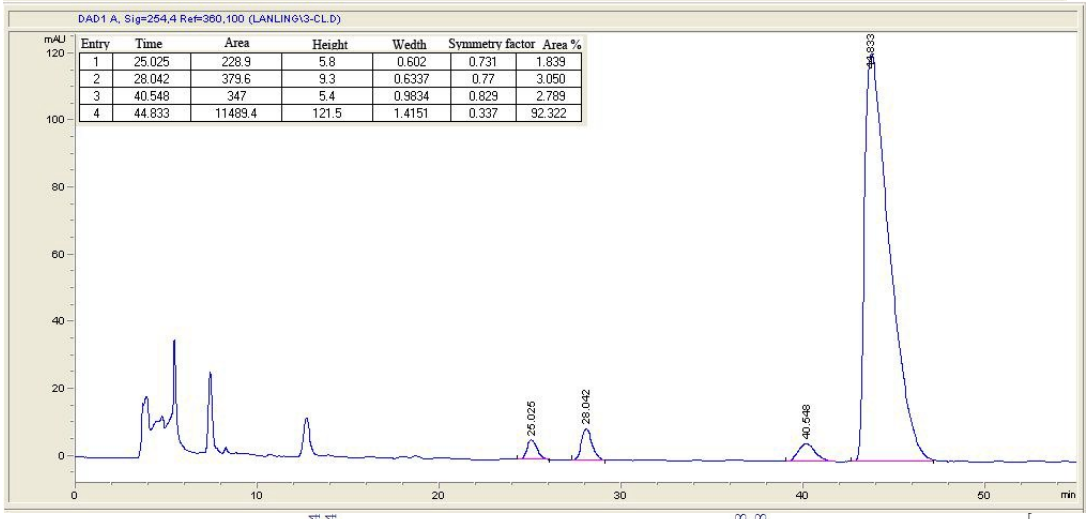


(7)

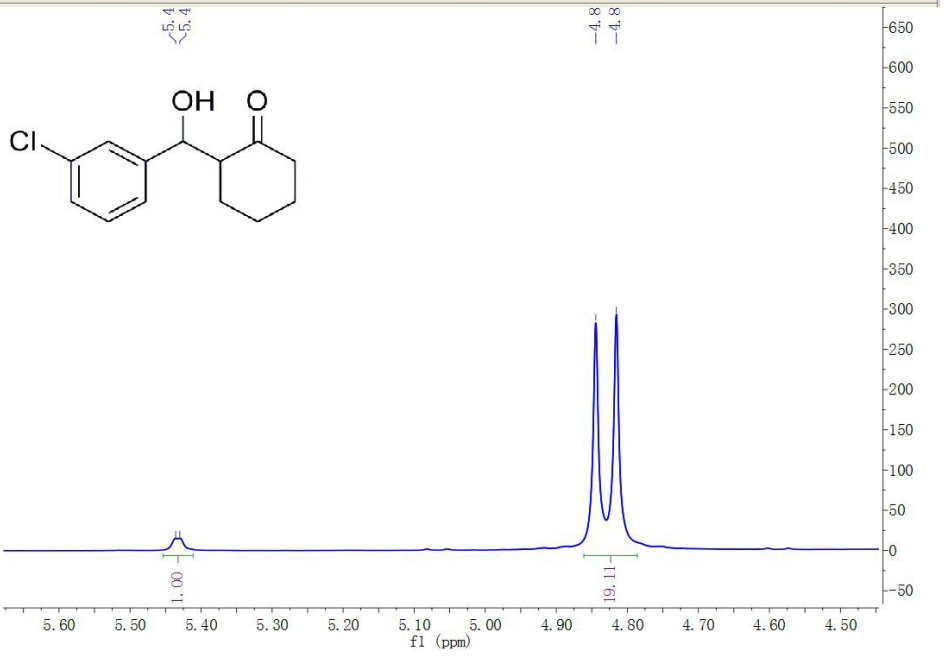




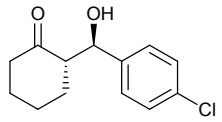
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	23.051	28096.7	745.2	0.5839	0.714	24.249
2	26.101	27737.6	688.2	0.6302	0.738	23.939
3	39.364	30011.2	528	0.8712	0.822	25.901
4	44.215	30023	445.6	1.0261	0.603	25.911

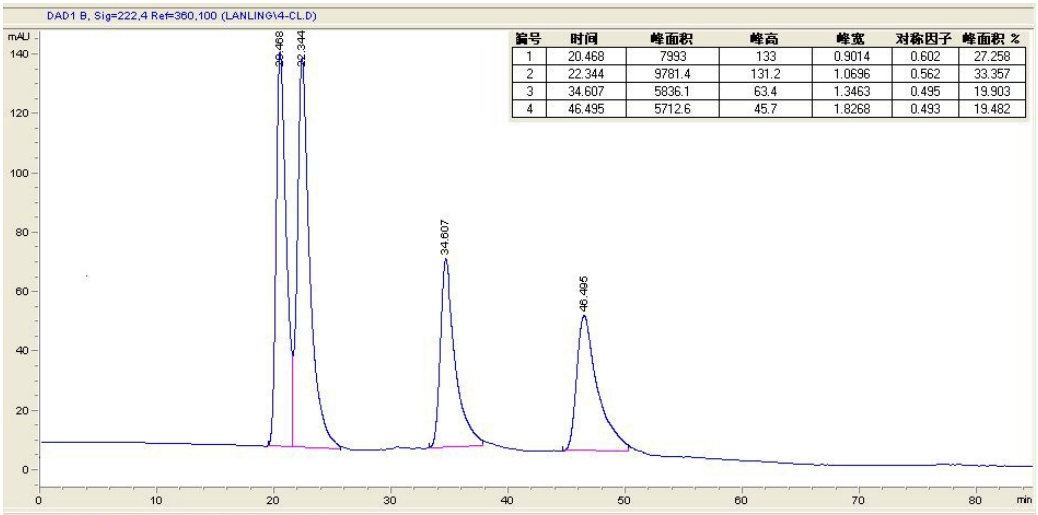


Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	25.025	228.9	5.8	0.602	0.731	1.839
2	28.042	379.6	9.3	0.6337	0.77	3.050
3	40.548	347	5.4	0.9834	0.829	2.789
4	44.833	11489.4	121.5	1.4151	0.337	92.322

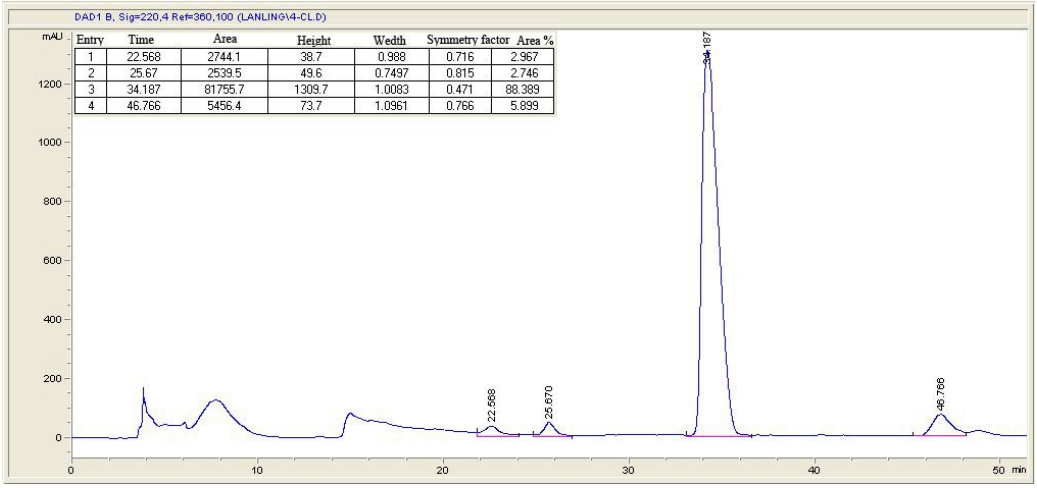


(8)

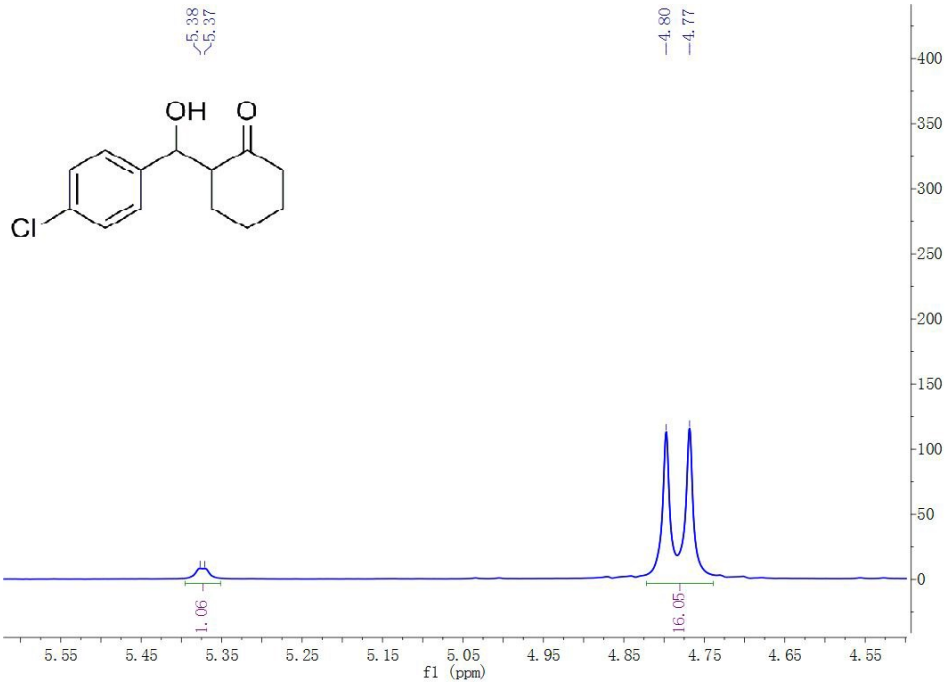




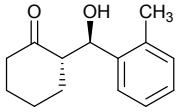
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	20.468	7993	133	0.9014	0.602	27.258
2	22.344	9781.4	131.2	1.0696	0.562	33.357
3	34.607	5836.1	63.4	1.3463	0.495	19.903
4	46.495	5712.6	45.7	1.8268	0.493	19.482

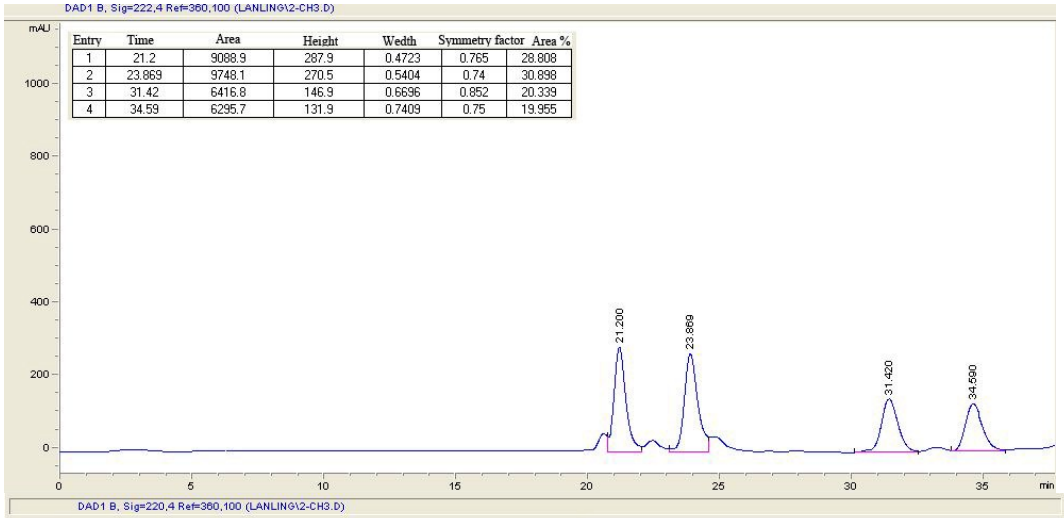


Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	22.568	2744.1	38.7	0.988	0.716	2.967
2	25.67	2539.5	49.6	0.7497	0.815	2.746
3	34.187	81755.7	1309.7	1.0083	0.471	88.389
4	46.766	5456.4	73.7	1.0961	0.766	5.899

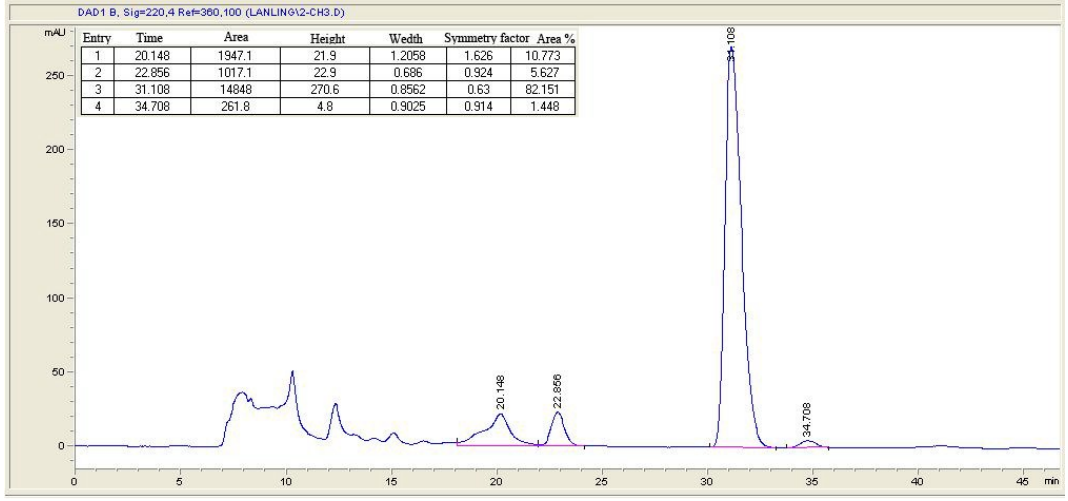


(9)

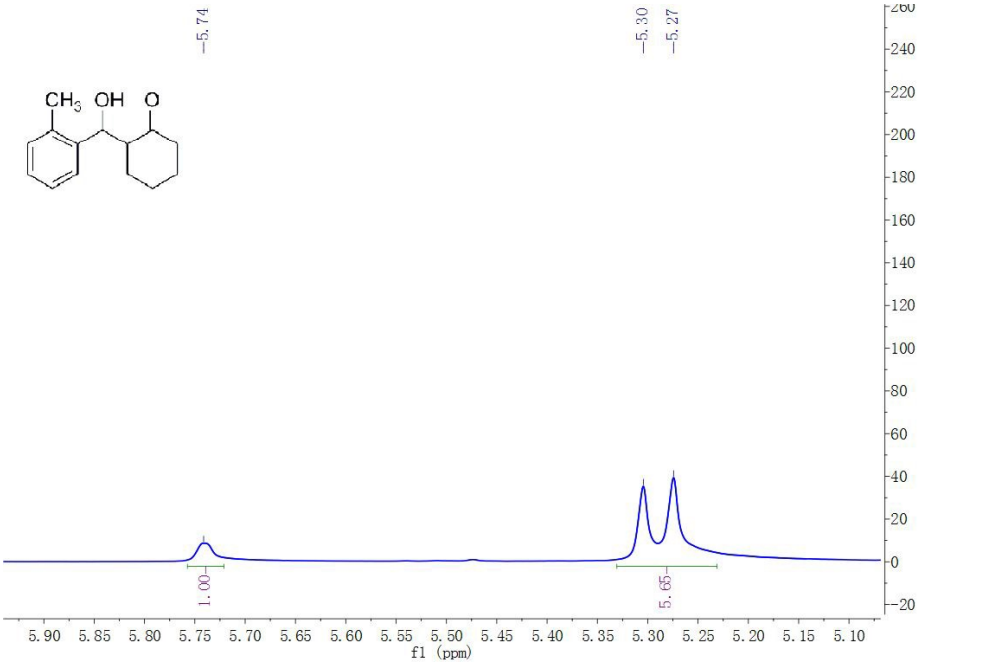




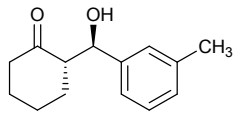
Entry	Time	Area	Height	Wedth	Symmetry factor	Area %
1	21.2	9088.9	287.9	0.4723	0.765	28.808
2	23.869	9748.1	270.5	0.5404	0.74	30.898
3	31.42	6416.8	146.9	0.6696	0.852	20.339
4	34.59	6295.7	131.9	0.7409	0.75	19.955

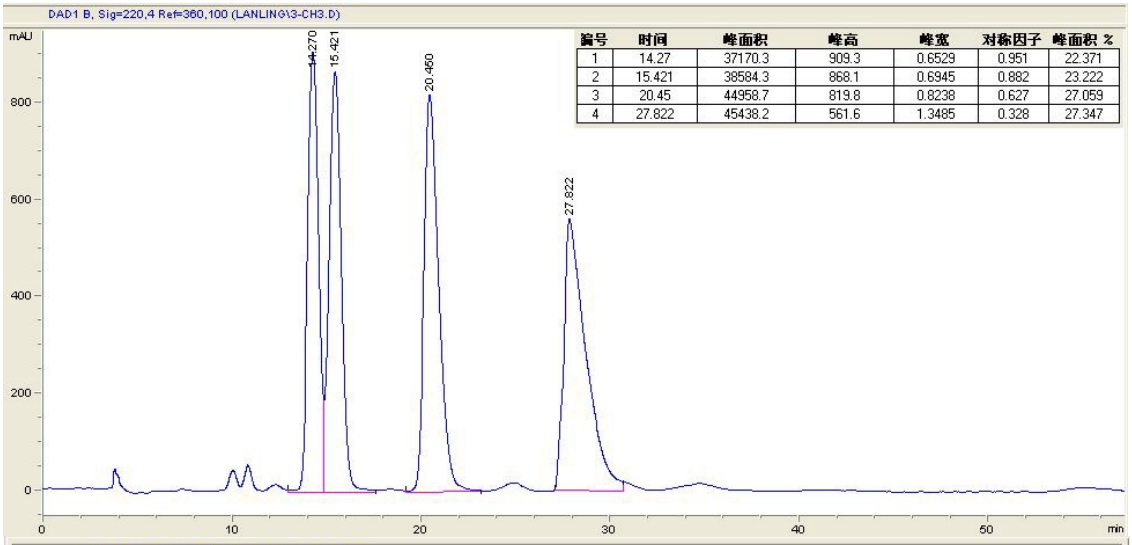


Entry	Time	Area	Height	Wedth	Symmetry factor	Area %
1	20.148	1947.1	21.9	1.2058	1.626	10.773
2	22.856	1017.1	22.9	0.686	0.924	5.627
3	31.108	14848	270.6	0.8562	0.63	82.151
4	34.708	261.8	4.8	0.9025	0.914	1.448

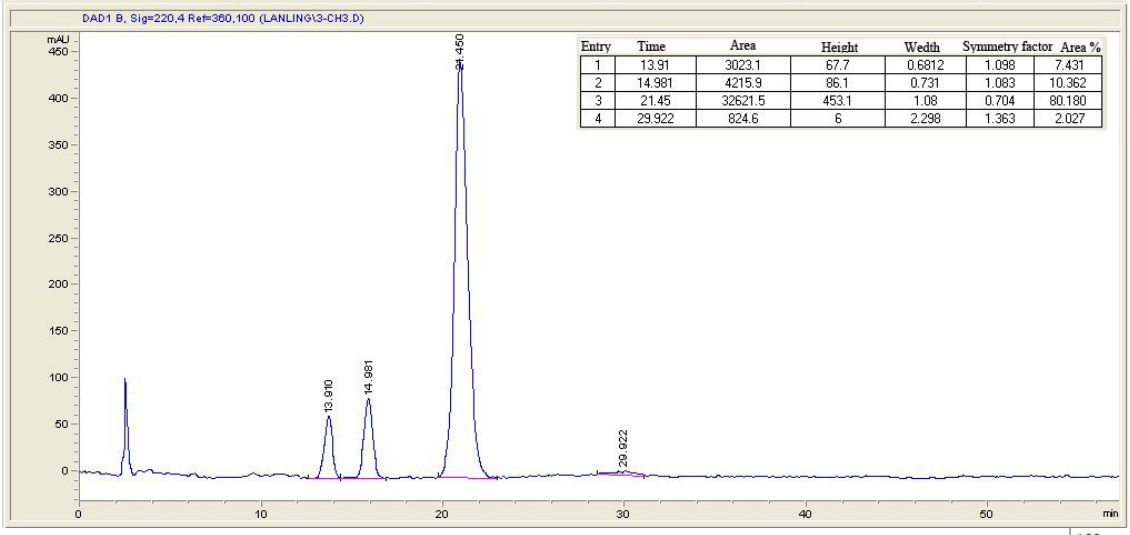


(10)

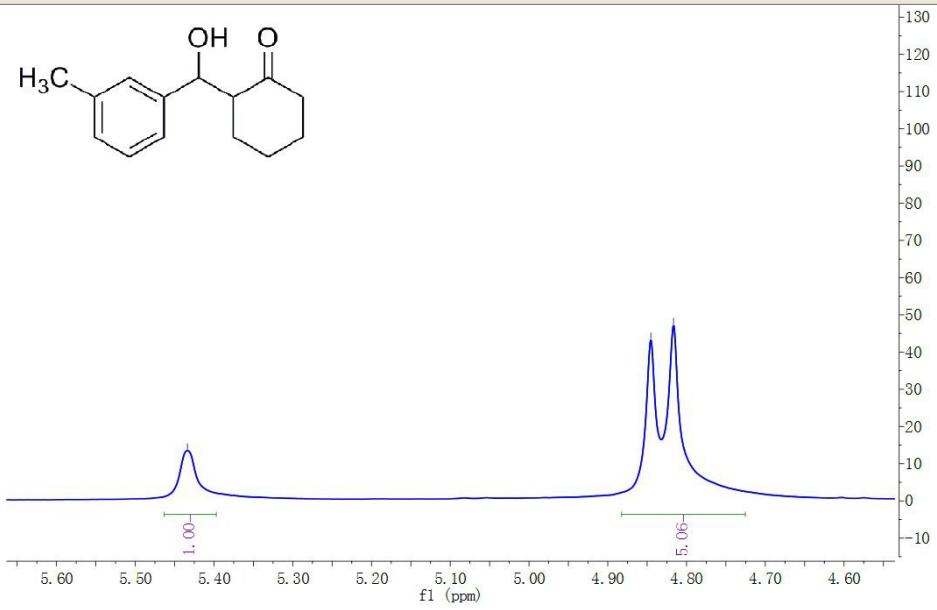




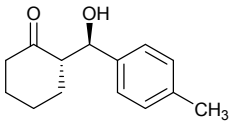
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	14.27	37170.3	909.3	0.6529	0.951	22.371
2	15.421	38584.3	868.1	0.6945	0.882	23.222
3	20.45	44958.7	819.8	0.8238	0.627	27.059
4	27.822	45438.2	561.6	1.3485	0.328	27.347

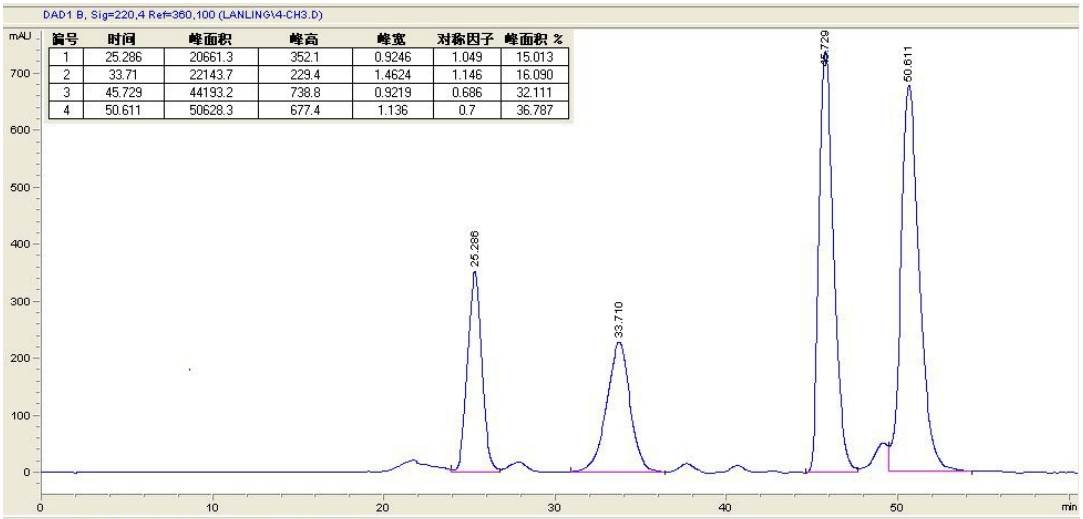


Entry	Time	Area	Height	Wedth	Symmetry factor	Area %
1	13.91	3023.1	67.7	0.6812	1.098	7.431
2	14.981	4215.9	86.1	0.731	1.083	10.362
3	21.45	32621.5	453.1	1.08	0.704	80.180
4	29.922	824.6	6	2.298	1.363	2.027

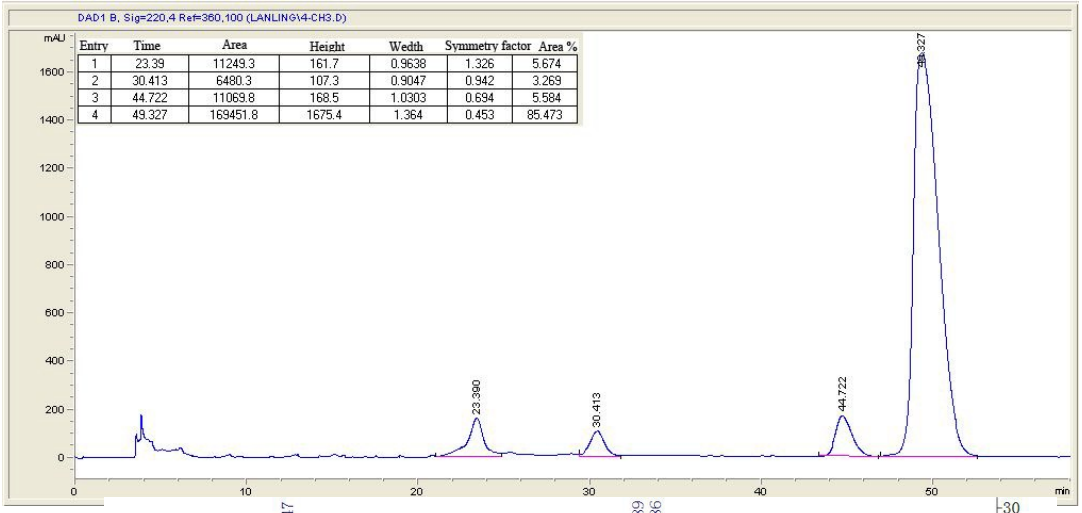


(11)

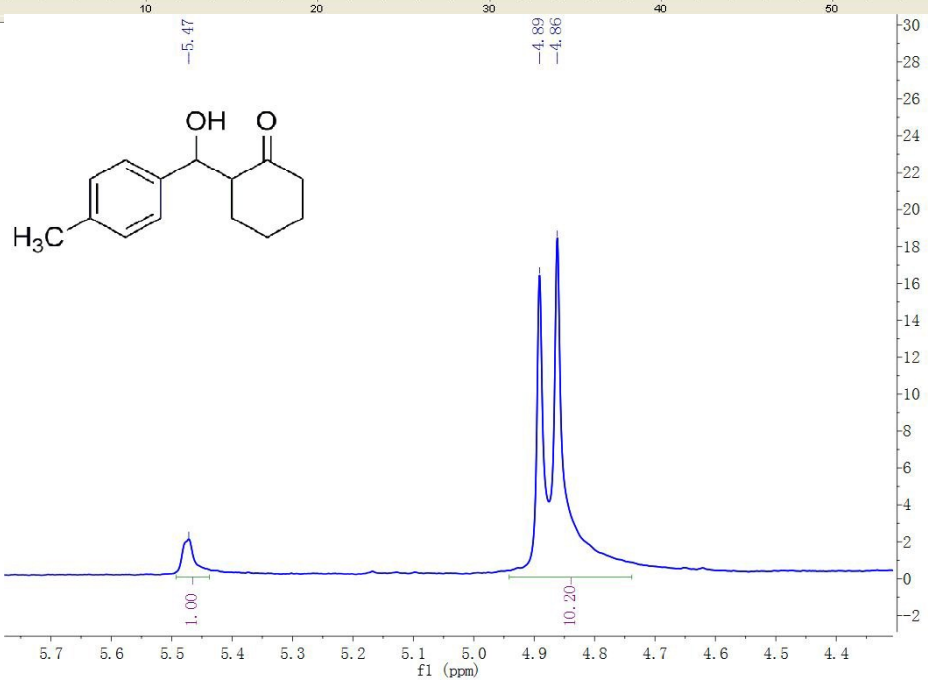




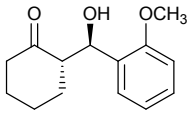
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	25.286	20661.3	352.1	0.9246	1.049	15.013
2	33.71	22143.7	229.4	1.4624	1.146	16.090
3	45.729	44193.2	738.8	0.9219	0.686	32.111
4	50.611	50628.3	677.4	1.136	0.7	36.787

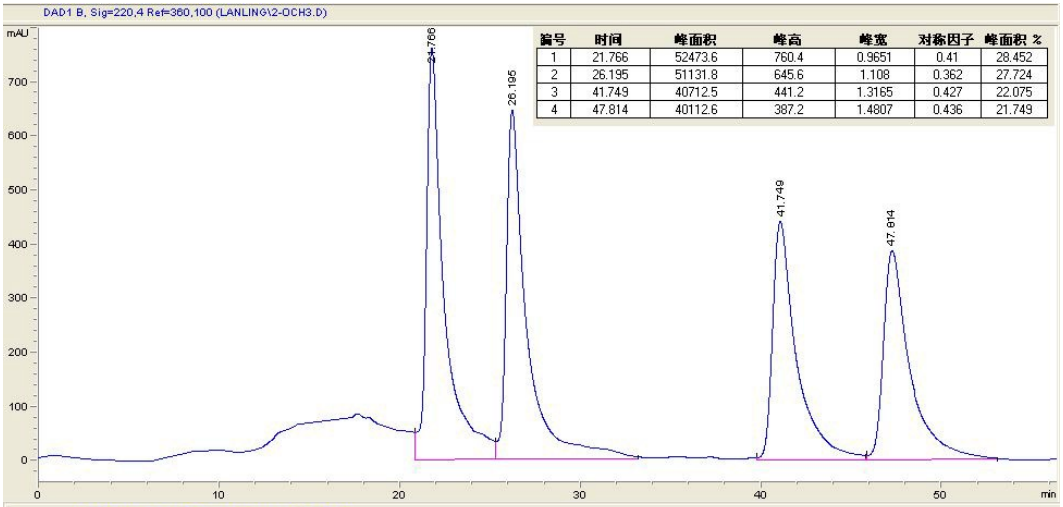


Entry	Time	Area	Height	Width	Symmetry factor	Area %
1	23.39	11249.3	161.7	0.9638	1.326	5.674
2	30.413	6480.3	107.3	0.9047	0.942	3.269
3	44.722	11069.8	168.5	1.0303	0.694	5.584
4	49.327	169451.8	1675.4	1.364	0.453	85.473

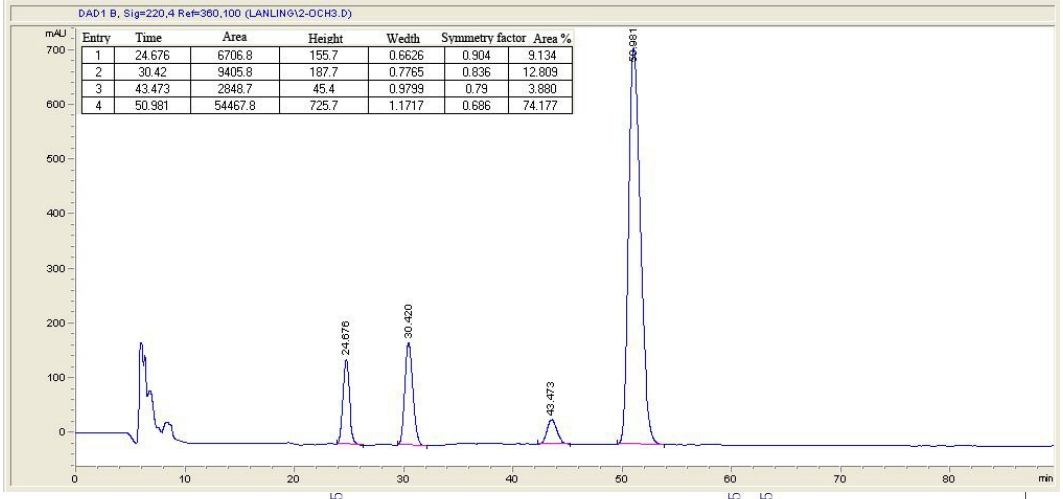


(12)

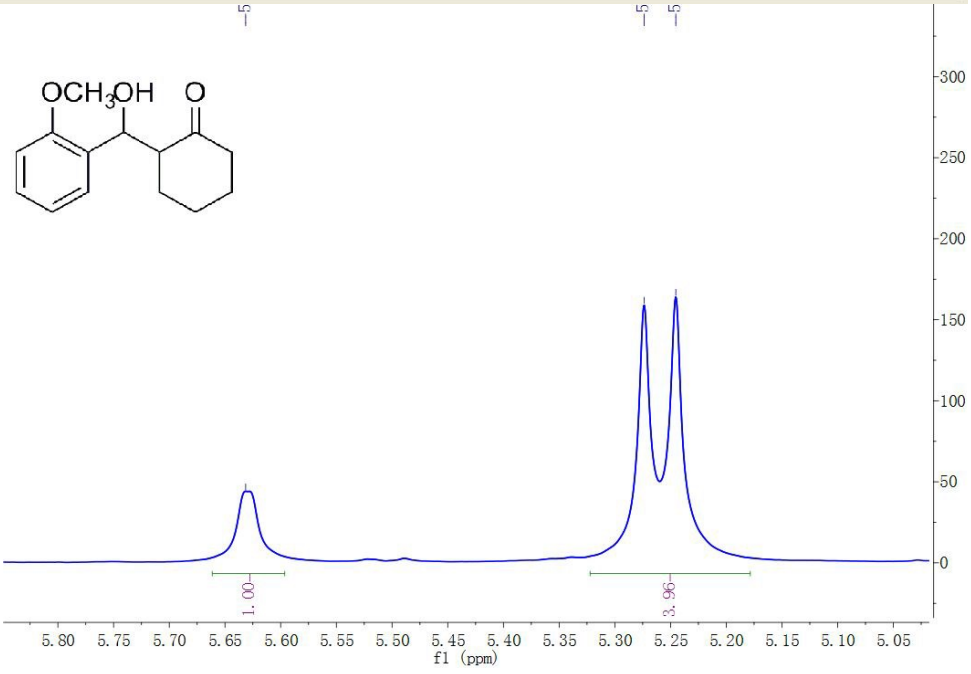




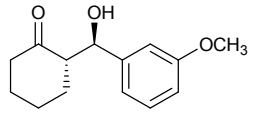
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	21.766	52473.6	760.4	0.9651	0.41	28.452
2	26.195	51131.8	645.6	1.108	0.362	27.724
3	41.749	40712.5	441.2	1.3165	0.427	22.075
4	47.814	40112.6	387.2	1.4807	0.436	21.749

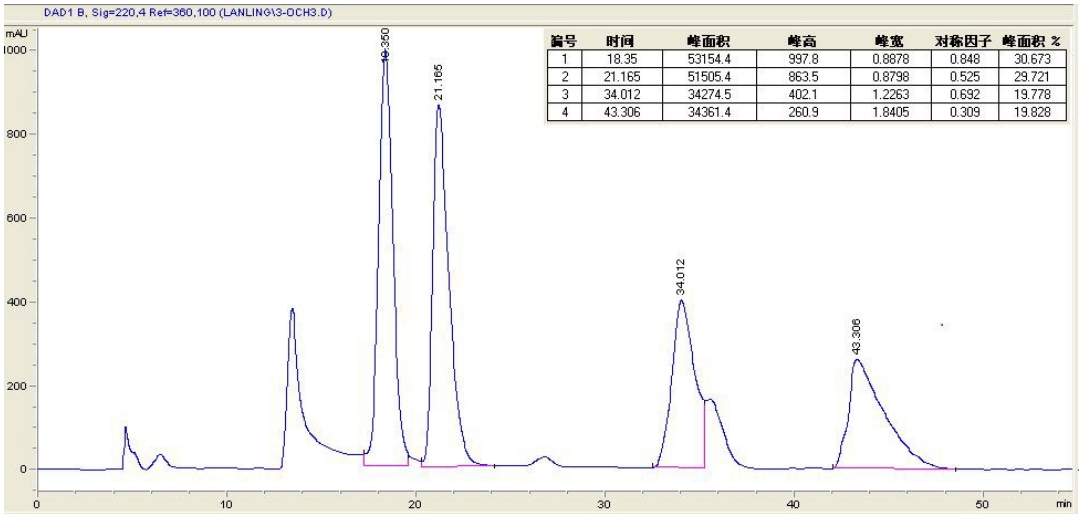


Entry	Time	Area	Height	Wedth	Symmetry factor	Area %
1	24.676	6706.8	155.7	0.6626	0.904	9.134
2	30.42	9405.8	187.7	0.7765	0.836	12.809
3	43.473	2848.7	45.4	0.9799	0.79	3.880
4	50.981	54467.8	725.7	1.1717	0.686	74.177

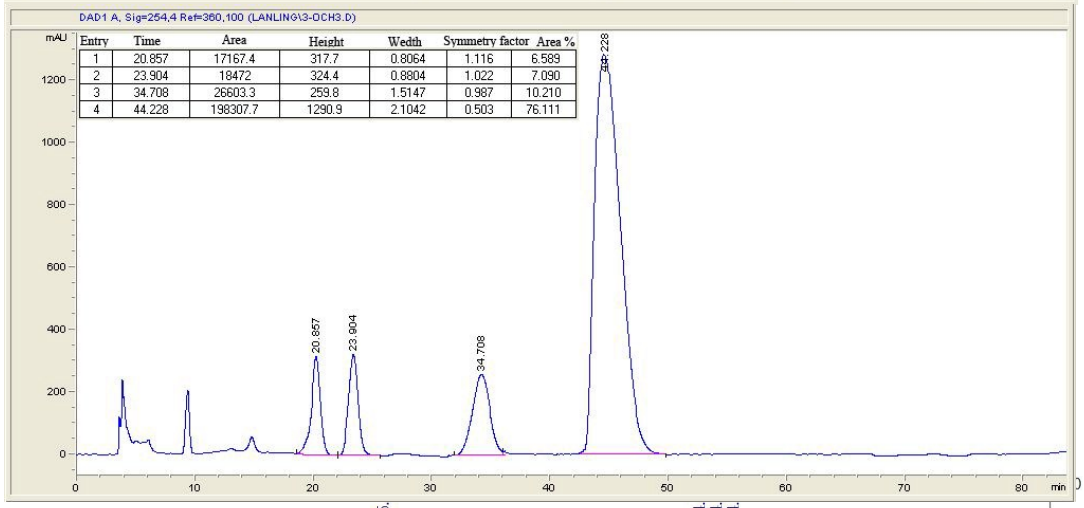


(13)

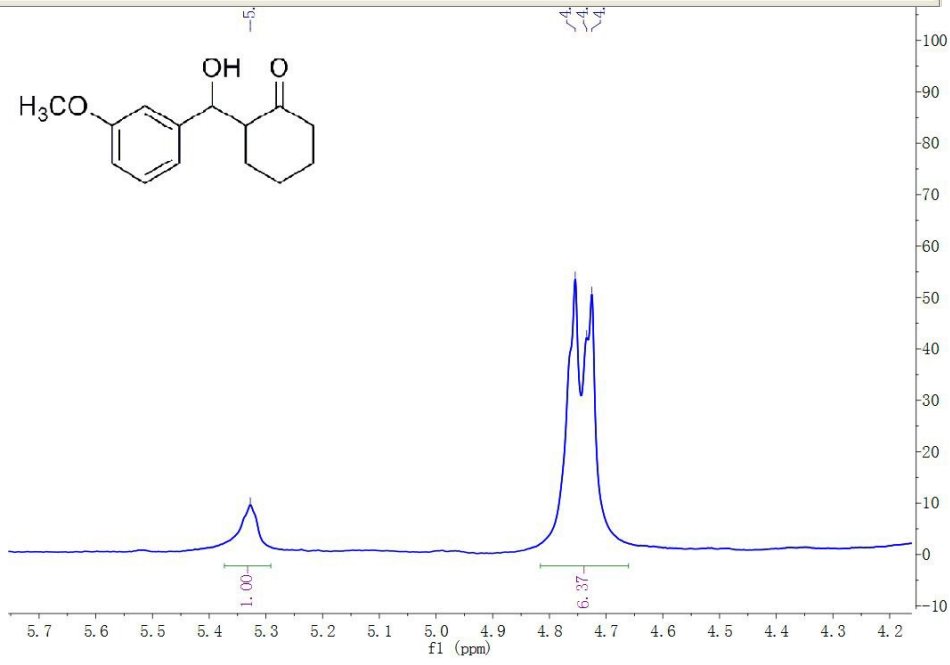




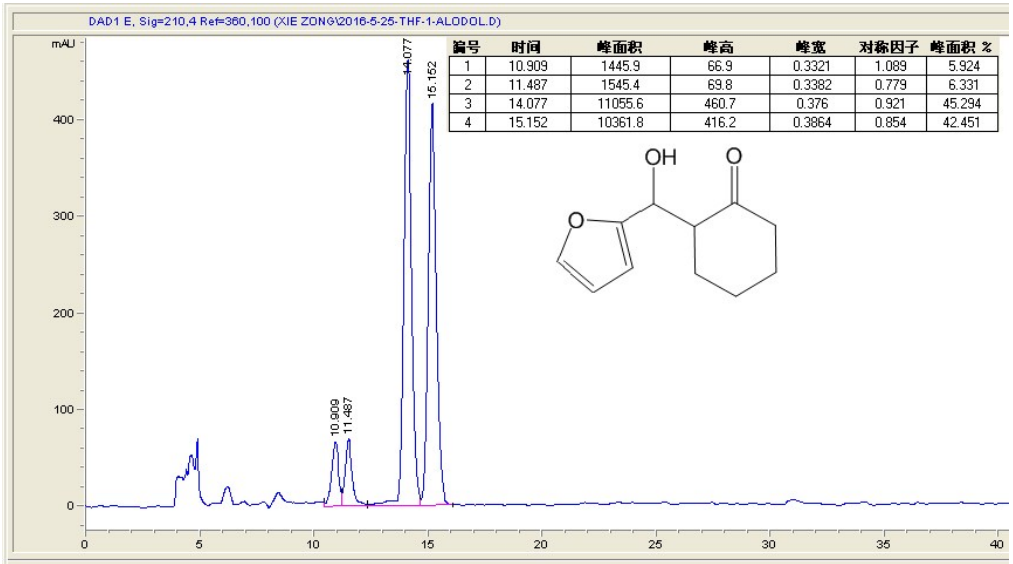
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	18.35	53154.4	997.8	0.8878	0.848	30.673
2	21.165	51505.4	863.5	0.8798	0.525	29.721
3	34.012	34274.5	402.1	1.2263	0.692	19.778
4	43.306	34361.4	260.9	1.8405	0.309	19.828



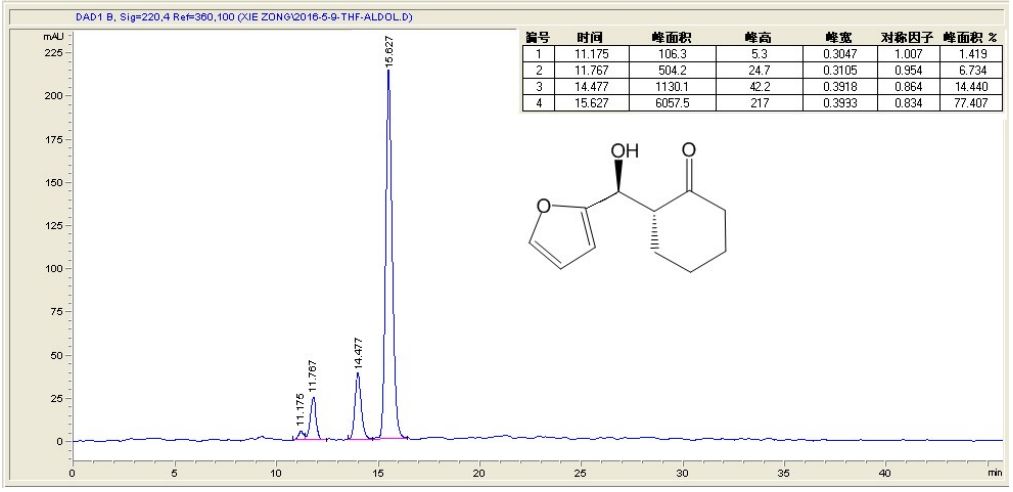
Entry	Time	Area	Height	Wedth	Symmetry factor	Area %
1	20.857	17167.4	317.7	0.8064	1.116	6.589
2	23.904	18472	324.4	0.8804	1.022	7.090
3	34.708	26603.3	259.8	1.5147	0.987	10.210
4	44.228	198307.7	1290.9	2.1042	0.503	76.111



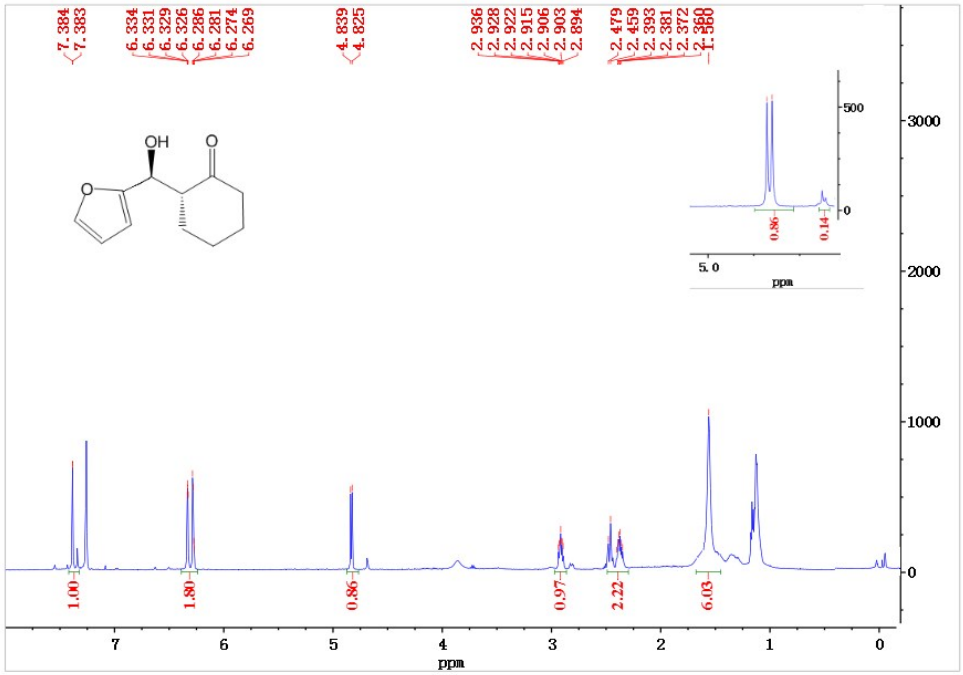
(14)



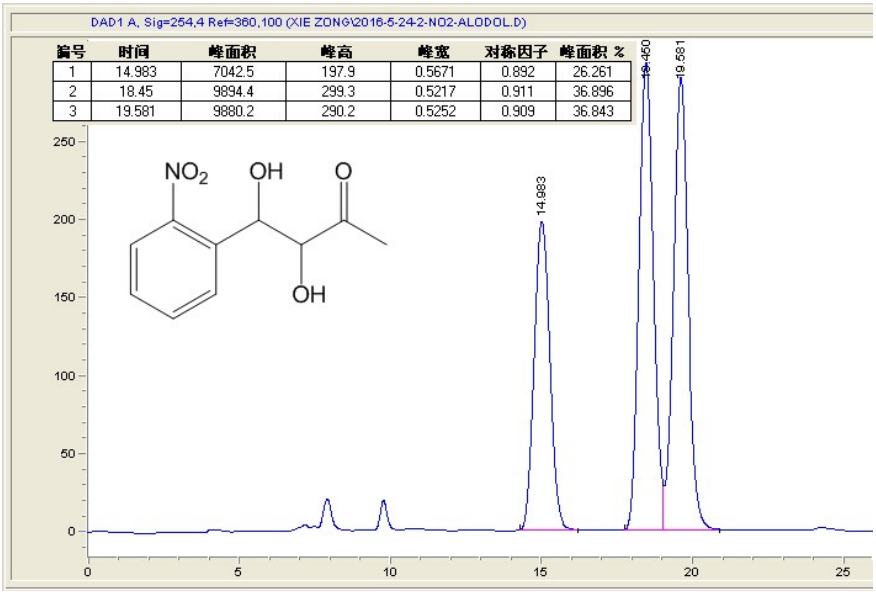
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	10.909	1445.9	66.9	0.3321	1.089	5.924
2	11.487	1545.4	69.8	0.3382	0.779	6.331
3	14.077	11055.6	460.7	0.376	0.921	45.294
4	15.152	10361.8	416.2	0.3864	0.854	42.451



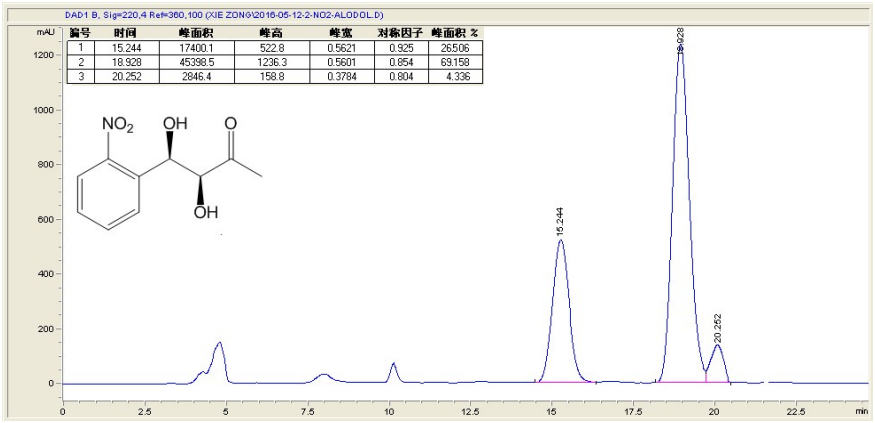
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	11.175	106.3	5.3	0.3047	1.007	1.419
2	11.767	504.2	24.7	0.3105	0.954	6.734
3	14.477	1130.1	42.2	0.3918	0.864	14.440
4	15.627	6057.5	217	0.3933	0.834	77.407



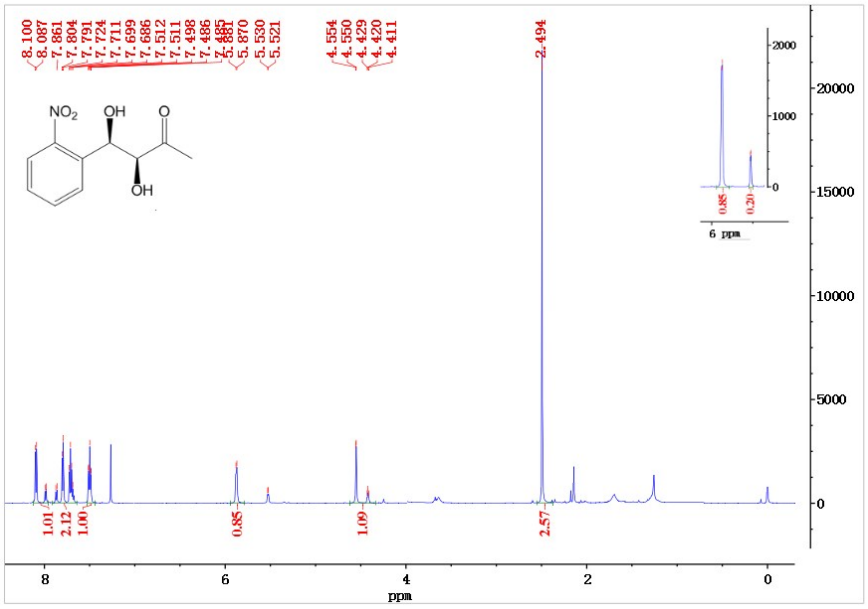
(15)



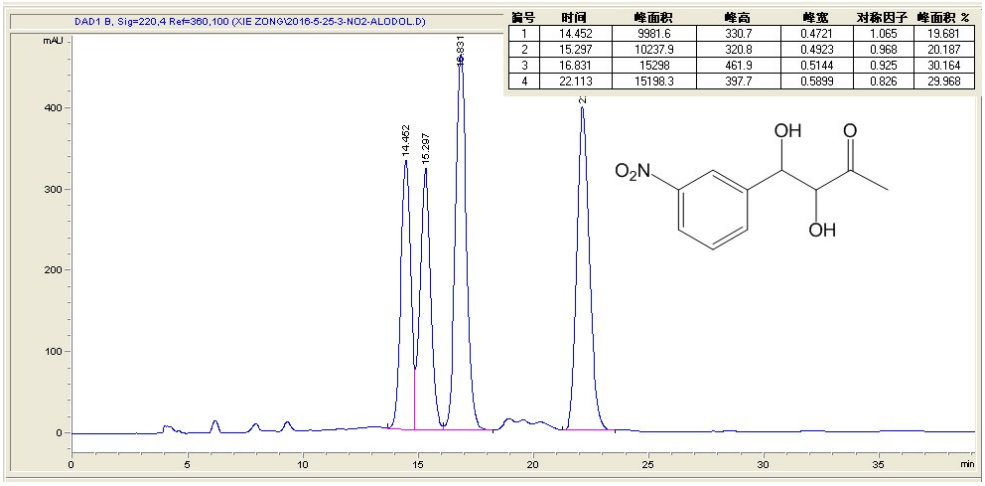
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	14.983	7042.5	197.9	0.5671	0.892	26.261
2	18.45	9894.4	299.3	0.5217	0.911	36.896
3	19.581	9880.2	290.2	0.5252	0.909	36.843



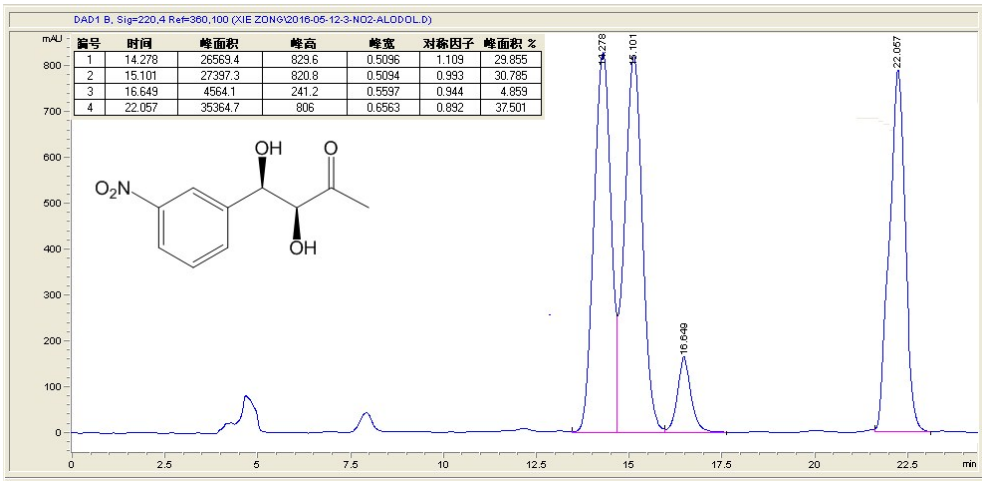
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	15.244	17400.1	522.8	0.5621	0.925	26.506
2	18.928	45398.5	1236.3	0.5601	0.854	69.158
3	20.252	2846.4	158.8	0.3784	0.804	4.336



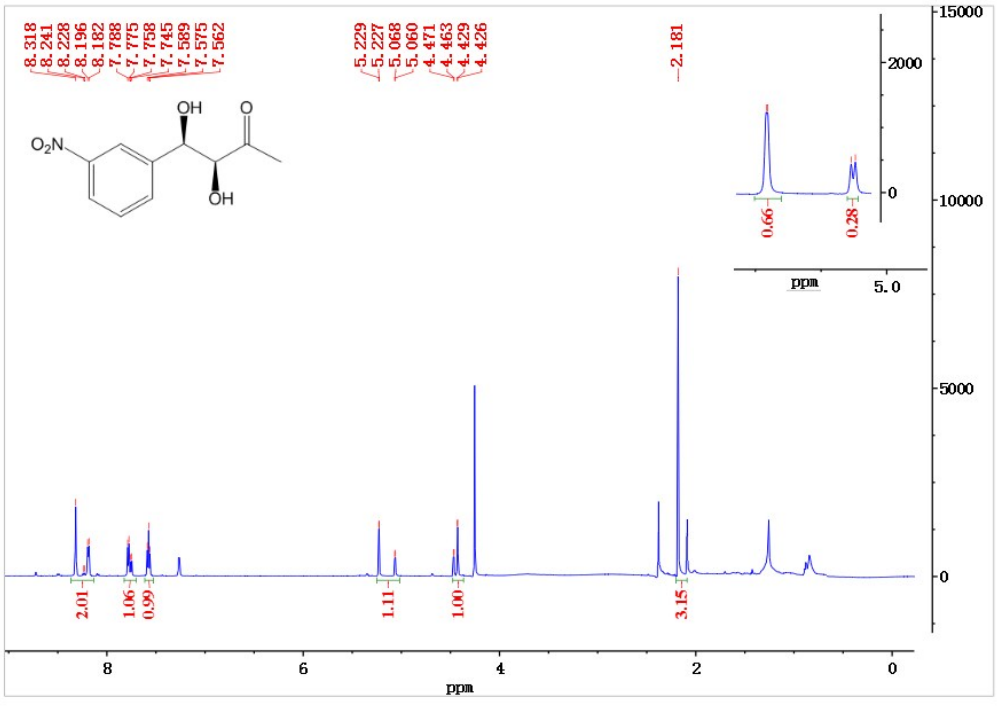
(16)



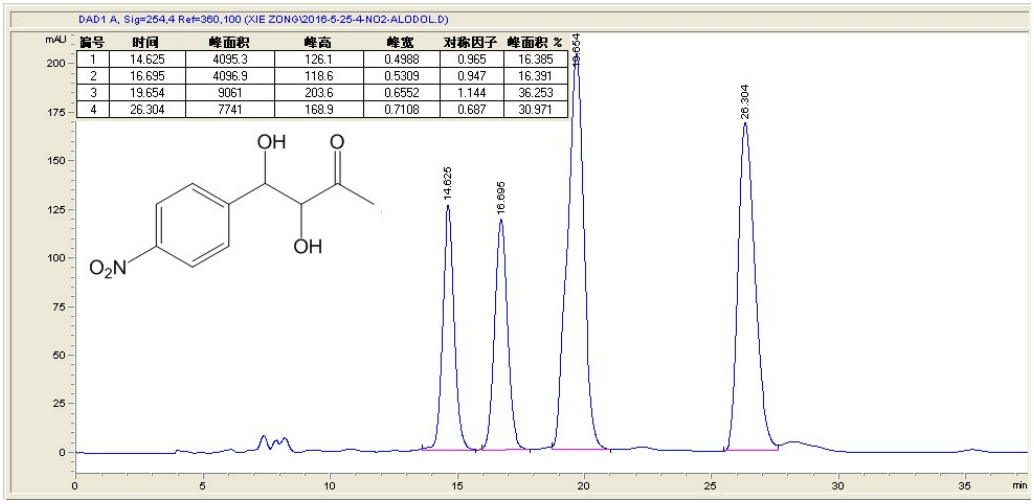
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	14.452	9981.6	330.7	0.4721	1.065	19.681
2	15.297	10237.9	320.8	0.4923	0.968	20.187
3	16.831	15298	461.9	0.5144	0.925	30.164
4	22.113	15198.3	397.7	0.5899	0.826	29.968



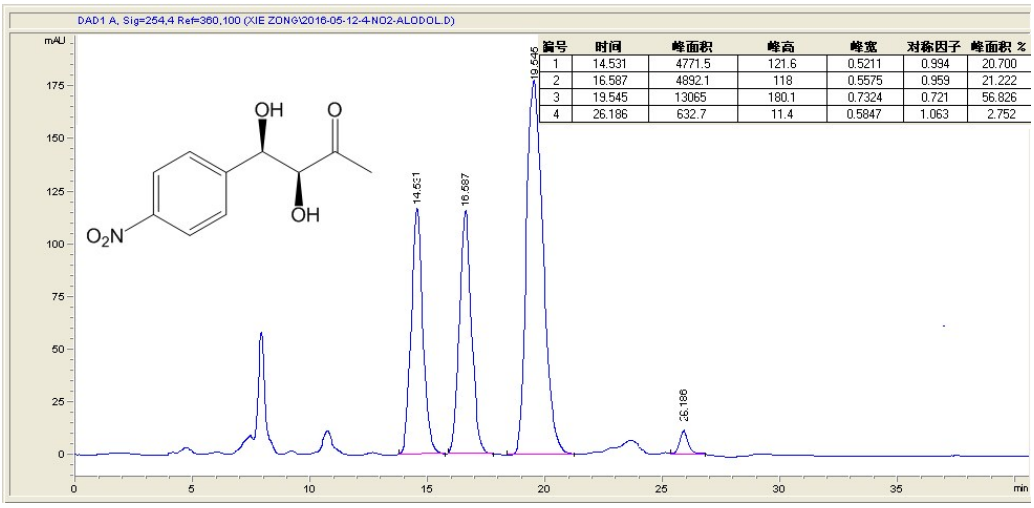
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	14.278	26569.4	829.6	0.5096	1.109	29.855
2	15.101	27397.3	820.8	0.5094	0.993	30.785
3	16.649	4564.1	241.2	0.5597	0.944	4.859
4	22.057	35364.7	806	0.6563	0.892	37.501



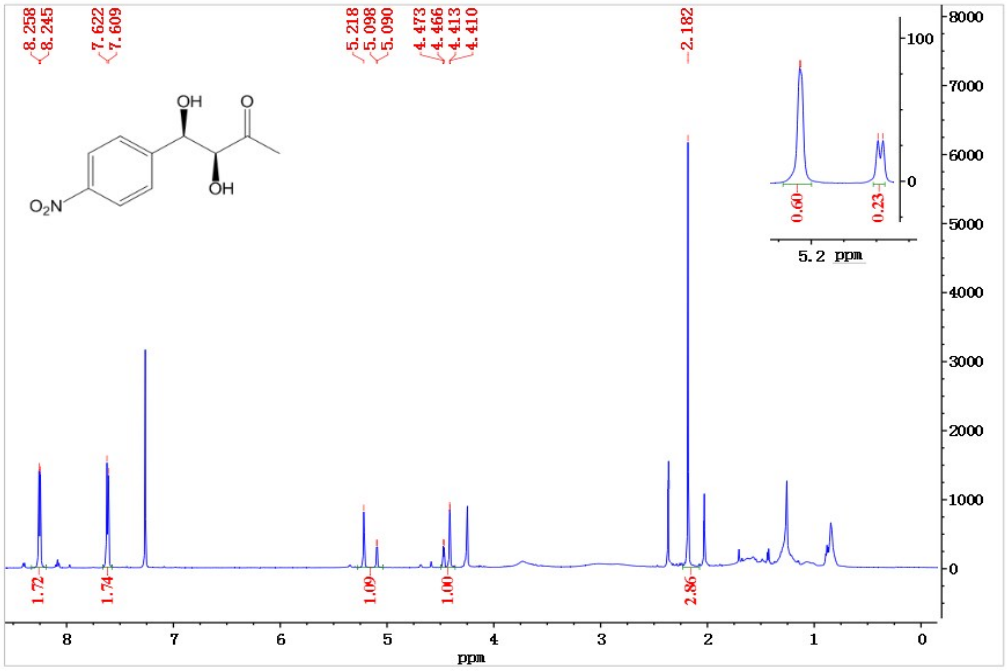
(17)



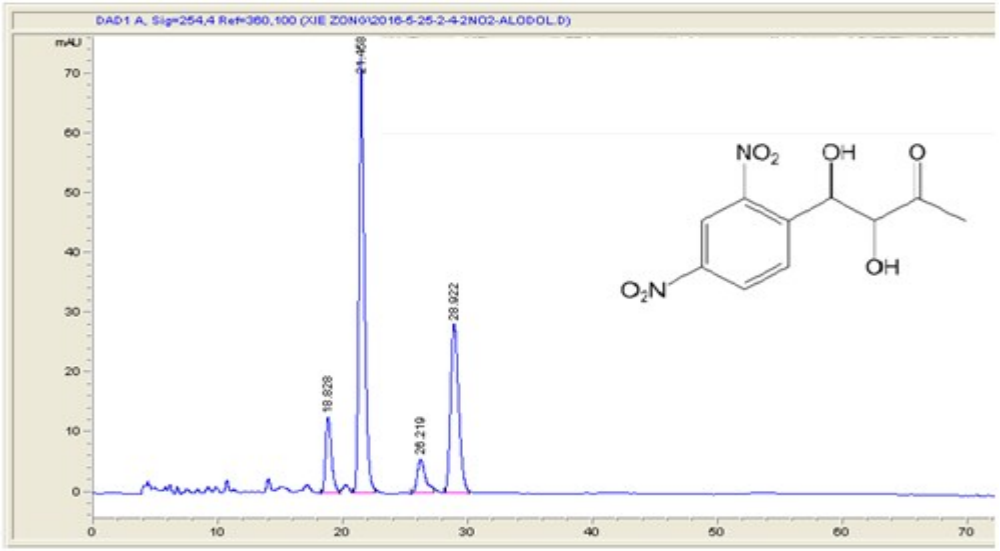
编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	14.625	4095.3	126.1	0.4988	0.965	16.385
2	16.695	4096.9	118.6	0.5309	0.947	16.391
3	19.654	9061	203.6	0.6552	1.144	36.253
4	26.304	7741	168.9	0.7108	0.687	30.971

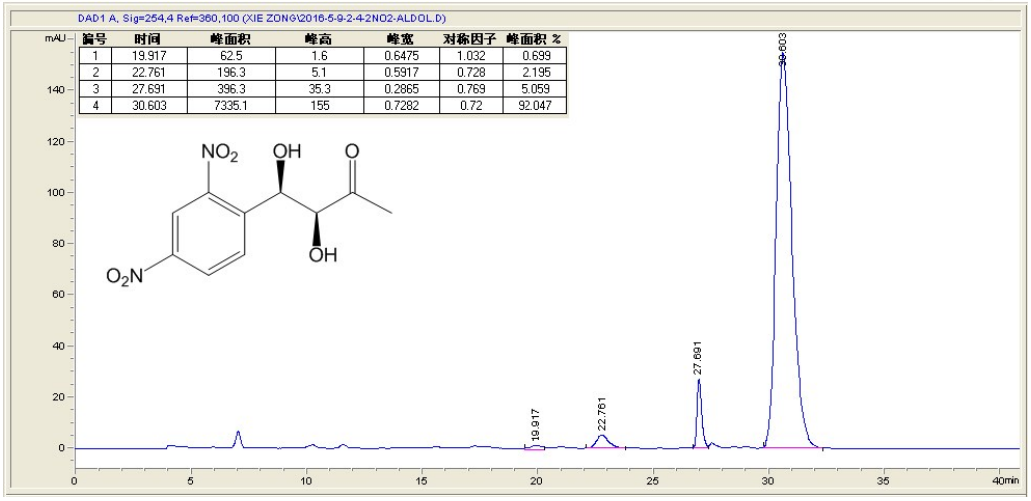


编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	14.531	4771.5	121.6	0.5211	0.994	20.700
2	16.587	4892.1	118	0.5575	0.959	21.222
3	19.545	13065	180.1	0.7324	0.721	56.826
4	26.186	632.7	11.4	0.5847	1.063	2.752

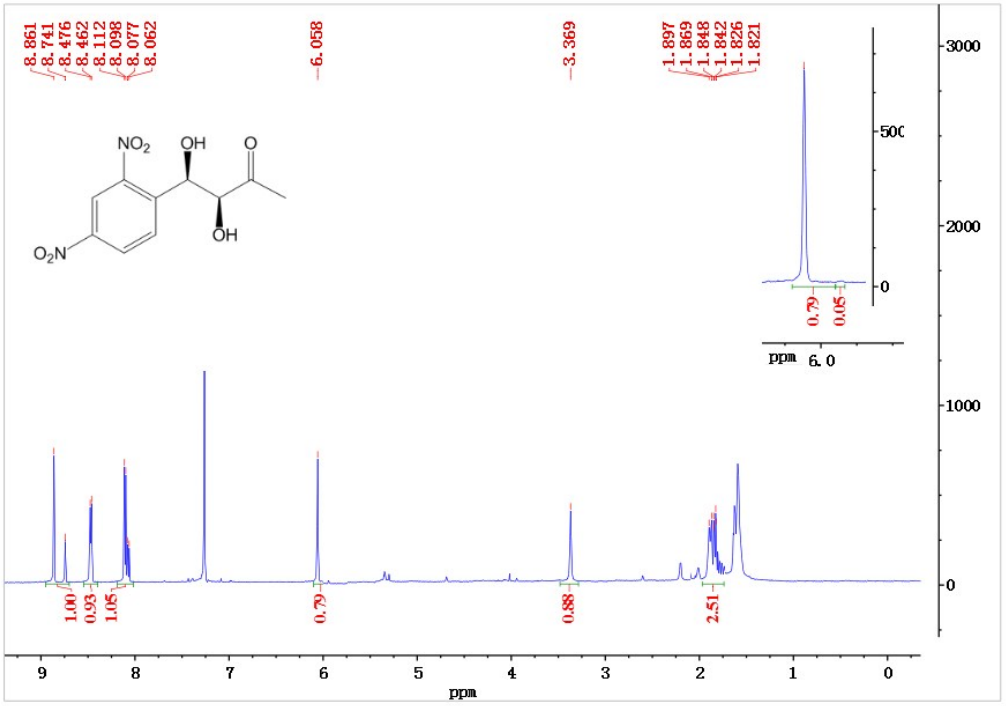


(18)





编号	时间	峰面积	峰高	峰宽	对称因子	峰面积 %
1	19.917	62.5	1.6	0.6475	1.032	0.699
2	22.761	196.3	5.1	0.5917	0.728	2.195
3	27.691	396.3	35.3	0.2865	0.769	5.059
4	30.603	7335.1	155	0.7282	0.72	92.047



7. Reusability of $CDNH_2(n4)$–HPW/0.5

Table s3. Recycling experiments of $CDNH_2(n4)$–HPW/0.5 in aldol addition reaction [a]

Run	Yield (%) [b]	*syn/anti* [c]	% ee (*Syn*) [d]
1	96	93/7	96
2	96	93/7	95
3	97	92/8	96
4	96	93/7	96
5	96	93/7	96
6	95	92/8	95
7	94	90/10	95
8	94	89/11	94

[a] Reaction conditions: 40 mg $CDNH_2(n4)$–HPW/0.5 (0.012 mmol, 6 mol%), cyclohexanone (0.5 mL), *p*-nitrobenzaldehyde (30.2 mg, 0.2 mmol), water (0.5 mL), 15 °C, 72 h. [b] Isolated yield. [c] Determined by ^{1}H NMR. [d] Determined by chiral HPLC.