Supporting Information *for*

A super–hydrophobic mesostructured silica as a chiral organometallics immobilization platform for heterogeneous asymmetric catalysis

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CONTENTS

Experimental

1). General. All of the reagents were of analytical grade and used as received without further purification. Cetyltrimethylammonium bromide (CTAB) were purchased from SigmaAldrich Company Ltd (USA). Tetraethoxysilane (TEOS) and ethyl acetate were obtained from Sinopharm Chemical Reagent Co., Ltd. 4-(2-(trimethoxysilyl)ethyl)benzene-1-sulfonyl chloride, 4-(methylphenylsulfonyl)-1,2-diphenylethylenediamine [(*S*,*S*)-TsDPEN], 1,3,5-trimethyl-benzene (TMB), diphenyldichlorosilane (Ph_2SiCl_2), $[Cp^*RhCl_2]_2$ and $[mesityleneRuCl_2]_2$ were purchased from Aladdin Industrial Corporation in Shang Hai (China). Other reagents were purchased from Shanghai Chemical Reagent, Inc. of the Chinese Medicine Group. Compound of (*S*,*S*)-4-(trimethoxysilyl)ethyl)phenylsulfonyl-1,2-diphenylethylenediamine [*J. Mater. Chem.*, **2010**, *20*, 1970.] was synthesized according to the reported literature.

2). Characterization. Ru, Rh loading amounts 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. 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. Nitrogen 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 = 0.05-1.00). Solid state NMR experiments were explored on a Bruker AVANCE spectrometer at a magnetic field strength of 9.4 T with ^{1}H frequency of 400.1 MHz, ^{13}C frequency of 100.5 MHz, and ^{29}Si frequency of 79.4 MHz with 4 mm rotor at two spinning frequency of 5.5 kHz and 8.0 kHz, TPPM decoupling is applied in the during acquisition period. ^{1}H cross polarization in all solid state NMR experiments was employed using a contact

time of 2 ms and the pulse lengths of 4 μs. Water contact angle measurements were performed on KRÜSS DSA100, and the sample films were prepared *via* pressing the material powder at a pressure of 8 MPa on tablet press.

3). Preparation of the analogue 5'. In a typical synthesis, 0.40 g (0.27 mmol) of cetyltrimethylammonium bromide (CTAB) was added to an aqueous solution (180 mL) of NaOH (1.40 mL, 2 M) at 70 ℃. After dissolution of CTAB, 1.136 mL (0.50 mmol) of TMB was added to the system. The mixture was sonicated for one hour for the formation of stable white emulsion. TEOS (2. 00 mL, 9.0 mmol) was added followed by the addition of ethyl acetate (1.60 mL), and the mixture was stirred for 5~10 min. After that, 0.50 g (1.0 mmol) of (*S*,*S*)-4-(trimethoxysilyl)ethyl)phenylsulfonyl-1,2-diphenylethylenediamine (**1**) was added to the system by dropwise, the mixture was stirred for another two hours at 70 ℃. Then, the mixture was transferred to the autoclaves and kept aging at 100 ℃ for 24 h. After cooling to room temperature, the solids were collected by centrifugation and washed repeatedly with excess distilled water. The surfactant template was removed by refluxing in a solution (160.0 mg of ammounium nitrate in 250 mL of ethanol) at 60 ℃ for 12 h. The solids was filtered and washed with excess water and ethanol, and dried at ambient temperature under vacuum overnight to afford Ph@ArDPEN@MSNs (**3′**) as a white powder. The collected solids (0.50 g) was suspended in 20.0 mL of dry CH_2Cl_2, 61.80 mg (0.10 mmol) of $[Cp^*RhCl_2]_2$ (**3**) was added at room temperature and the resulting mixture was stirred at 25 ℃ for 12 h. The mixture was filtered through filter paper and then rinsed with excess CH_2Cl_2. After Soxhlet extraction for 24 h in CH_2Cl_2 to remove homogeneous and unreacted starting materials, the solid was dried at ambient temperature under vacuum overnight to afford analogue **5'** as a light−yellow powder. ICP analysis showed that the Rh loadings were 10.336 mg (0.10035 mmol of Rh) per gram of catalyst.

Figure S1. The FT-IR spectra of **3** and catalyst **5**, and catalyst **8**.

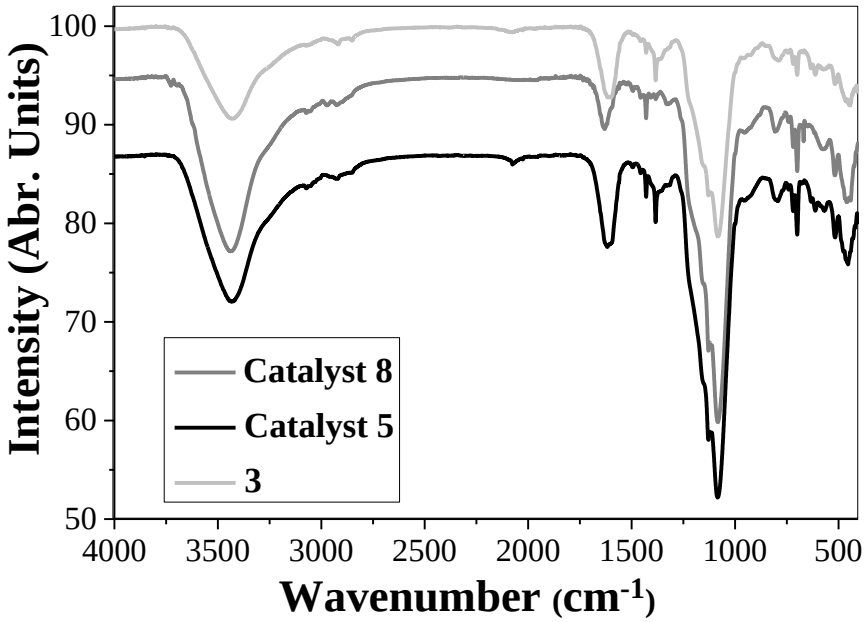


Figure S2. The XPS spectra of the Cp*RhTsDPEN and catalyst **5**.

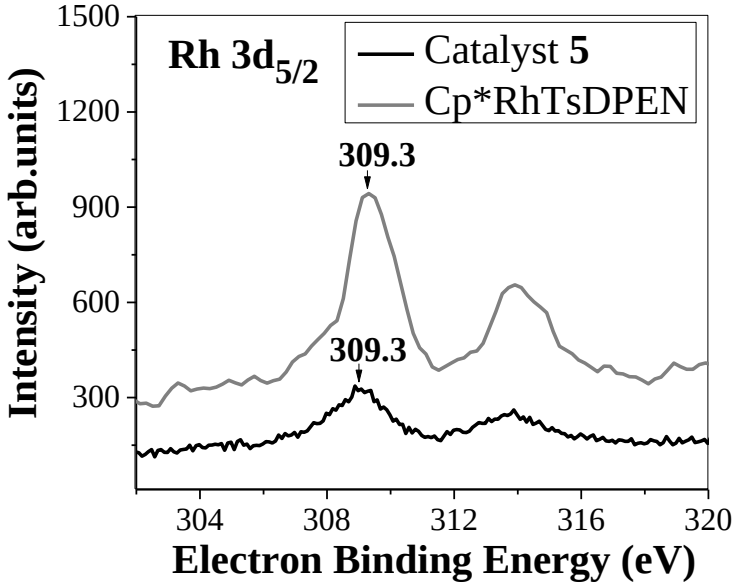


Figure S3. The solid-state ^{13}C CP MAS NMR spectra of **3** and catalyst **8**.

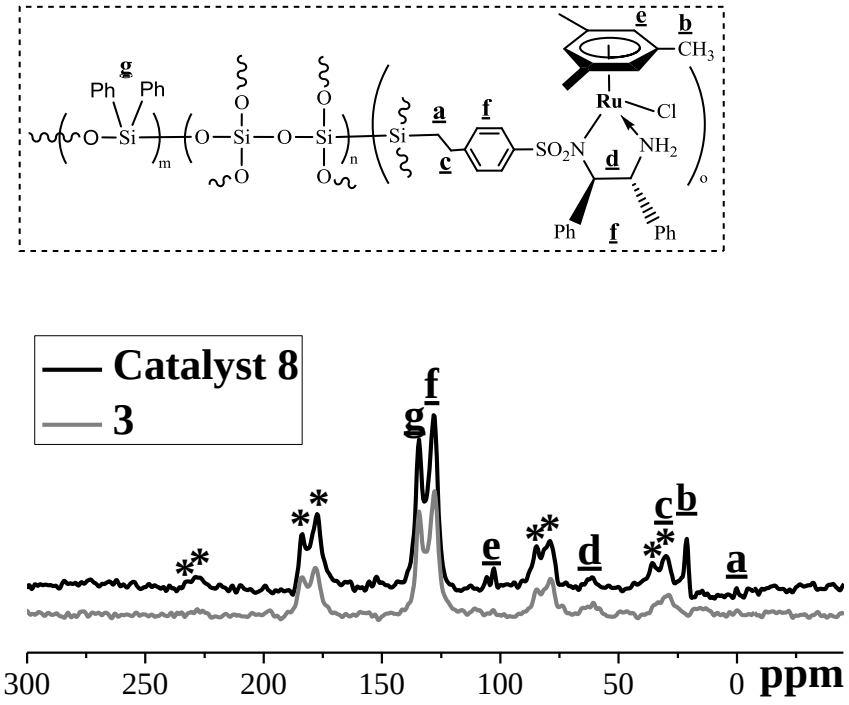


Figure S4. The solid-state ^{29}Si CP MAS NMR spectra of **2** and catalyst **6**.

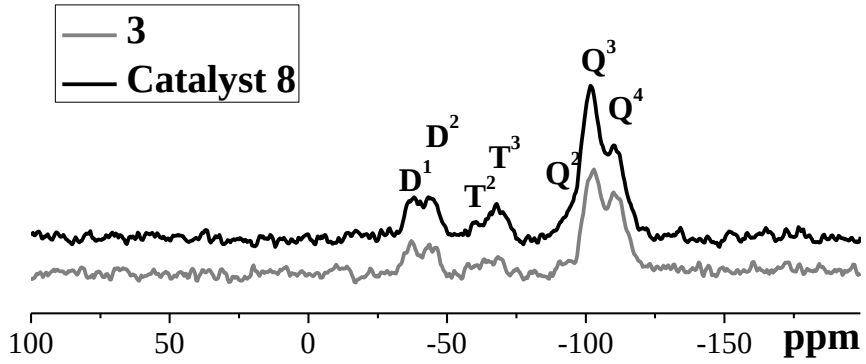


Figure S5. The nitrogen adsorption-desorption isotherms of catalyst **5**.

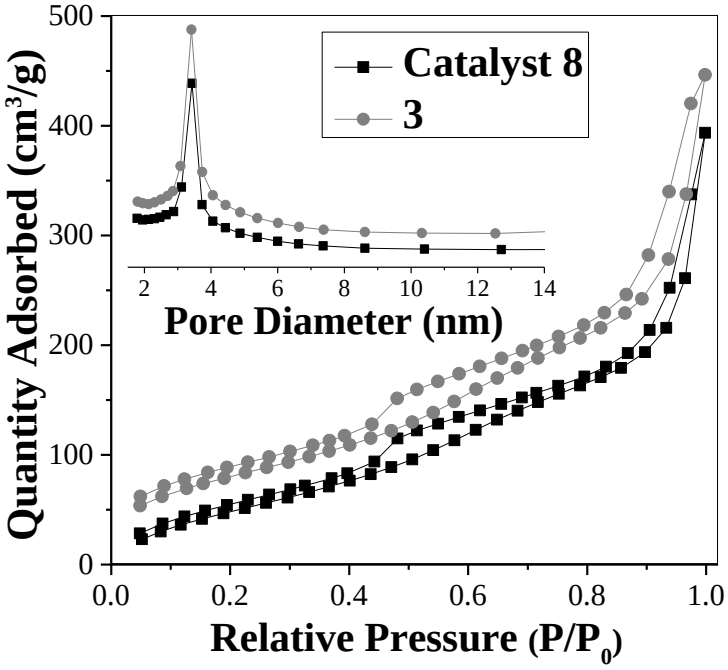
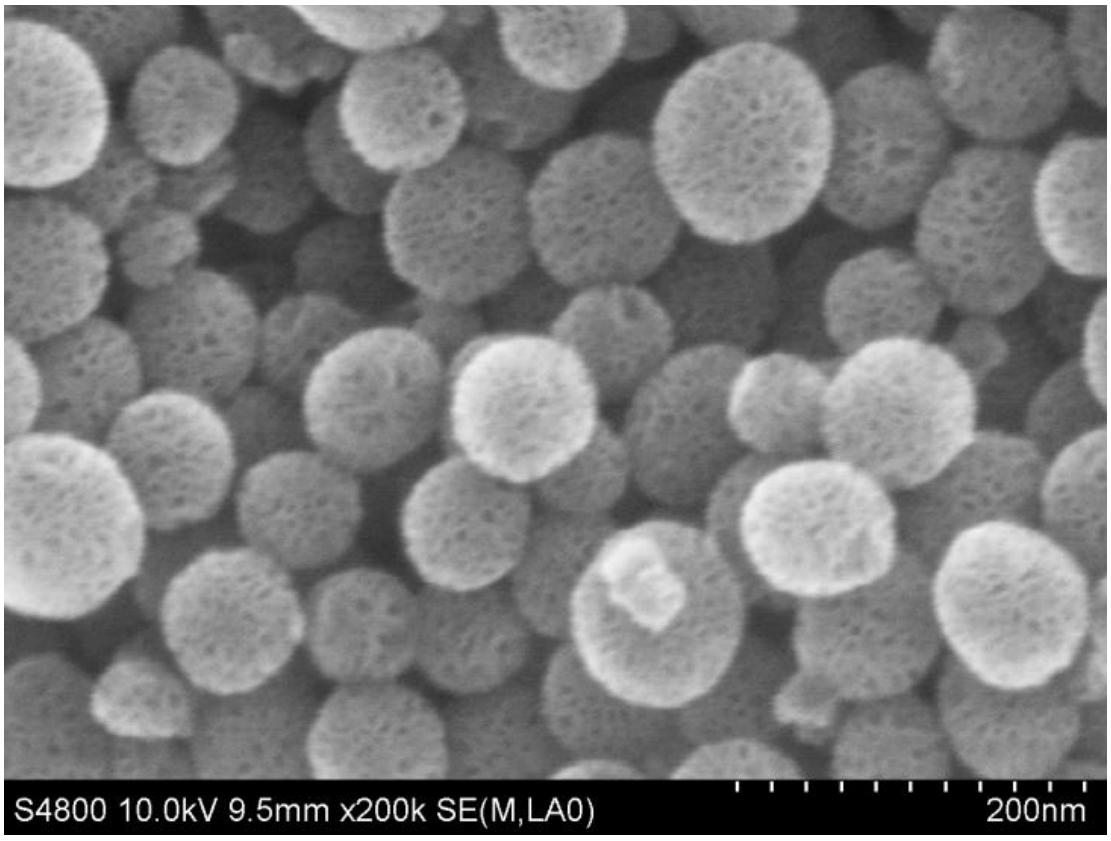
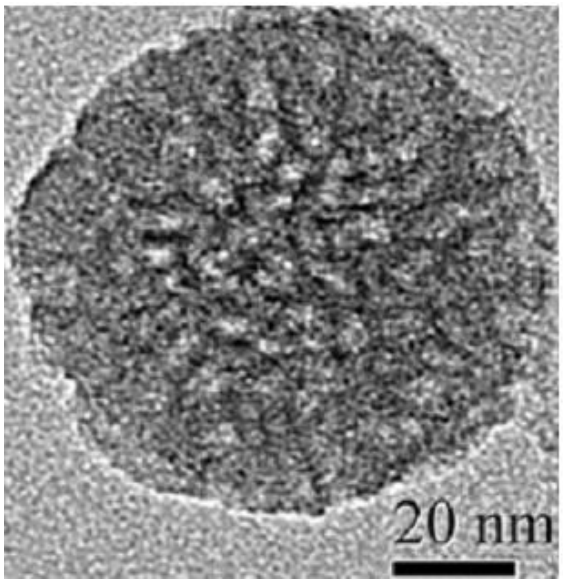


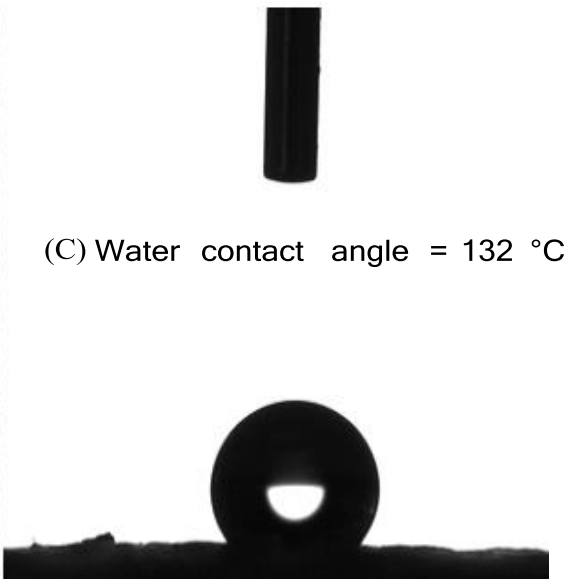
Figure S6. The (a) SEM image of catalyst **8**, (b) TEM image of catalyst **8**, (c) water contact angleof catalyst **8,** and (d) water contact angle of inorganosilicate analogue **5'**.

(a) SEM image of Catalyst **8**.

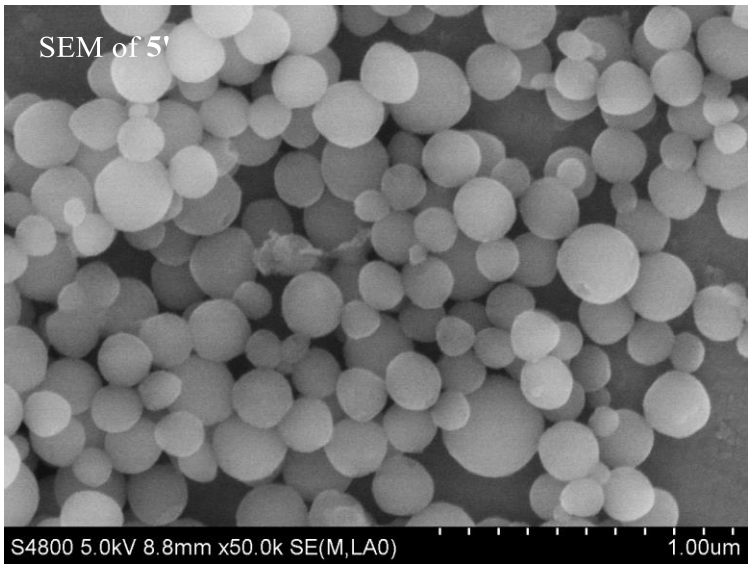


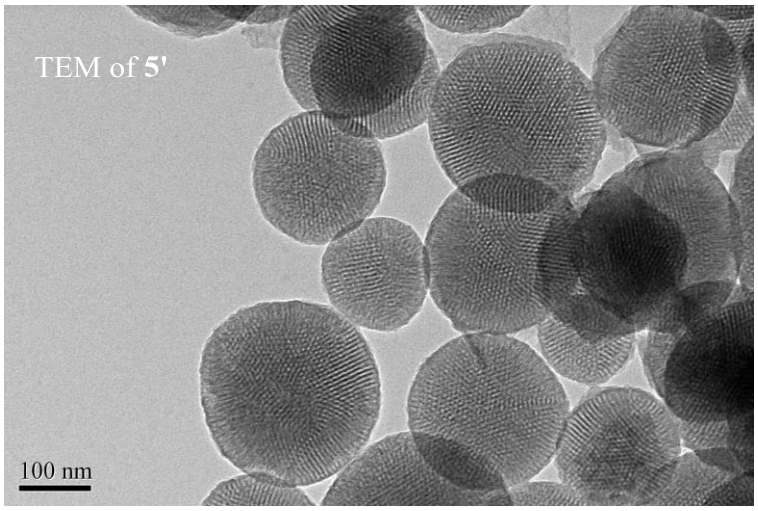
(b) TEM image and (c) water contact angle of Catalyst **8**.





(d) The SEM, TEM, and the water contact angle of inorganosilicate analogue **5'**.





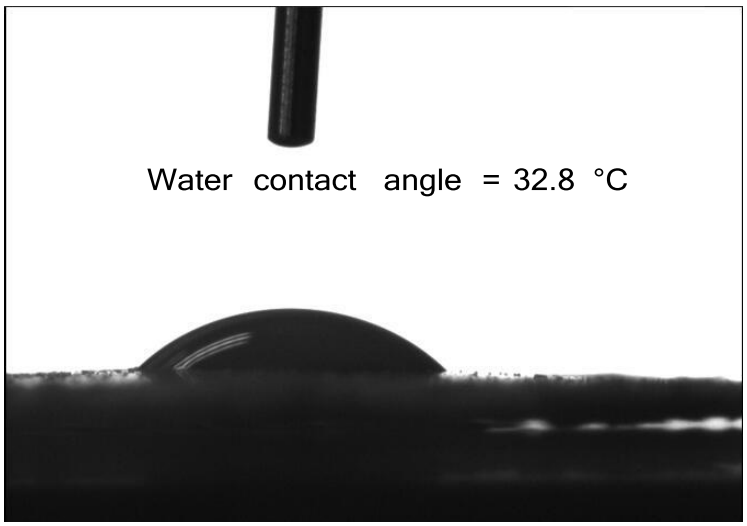
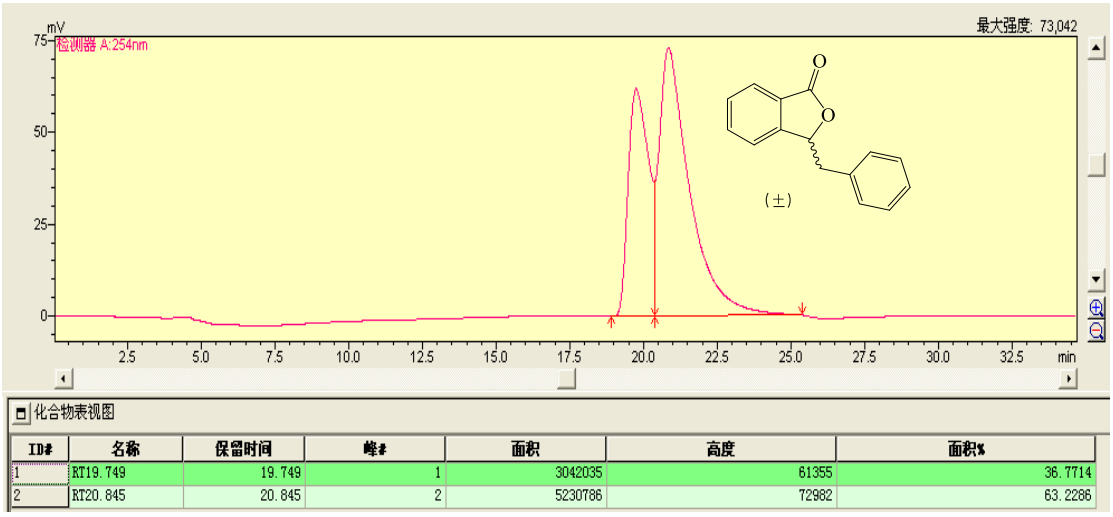


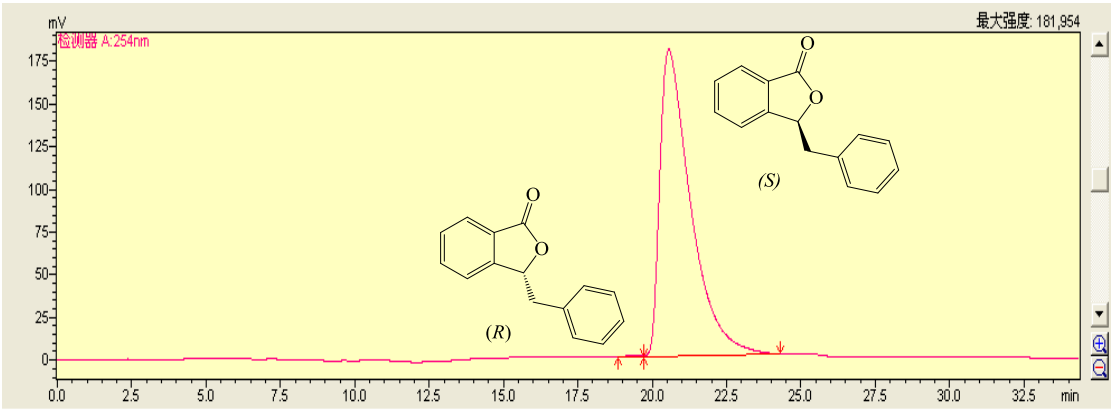
Figure S7. HPLC analyses of chiral Phthalides (the tandem reduction/lactonization of ethyl 2-acylarylcarboxylate)**.**

6a: (*S*)-3-benzylisobenzofuran-1(3*H*)-one. **(**HPLC: AD-H, elute: Hexanes/i-PrOH = 95/5, detector: 254 nm, flow rate: 0.7 mL/min, 25 ºC), t_1 = 19.4 min, t_2 = 20.5 min (major).**)**



化合物表视图

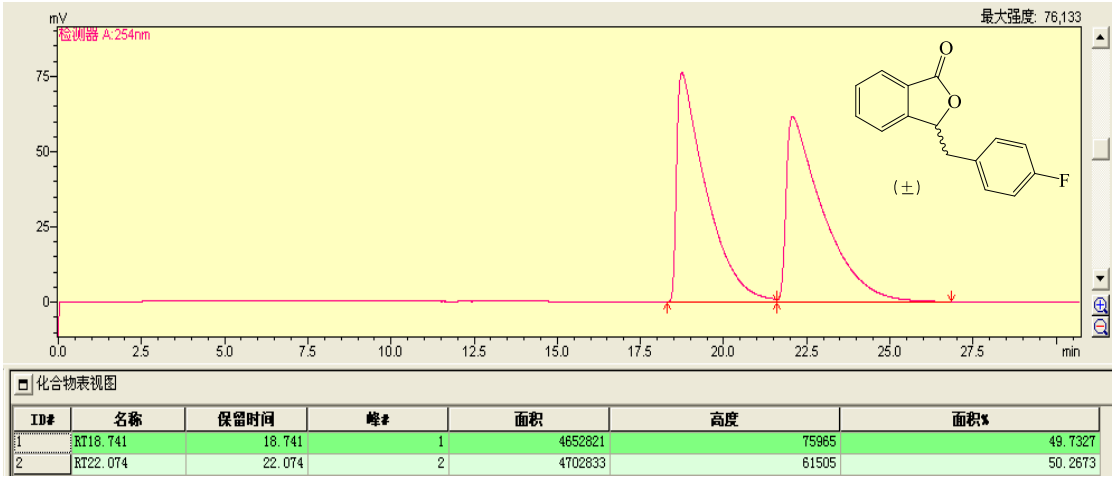
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT19.749	19.749	1	3042035	61355	36.7714
2	RT20.845	20.845	2	5230786	72982	63.2286



化合物表视图

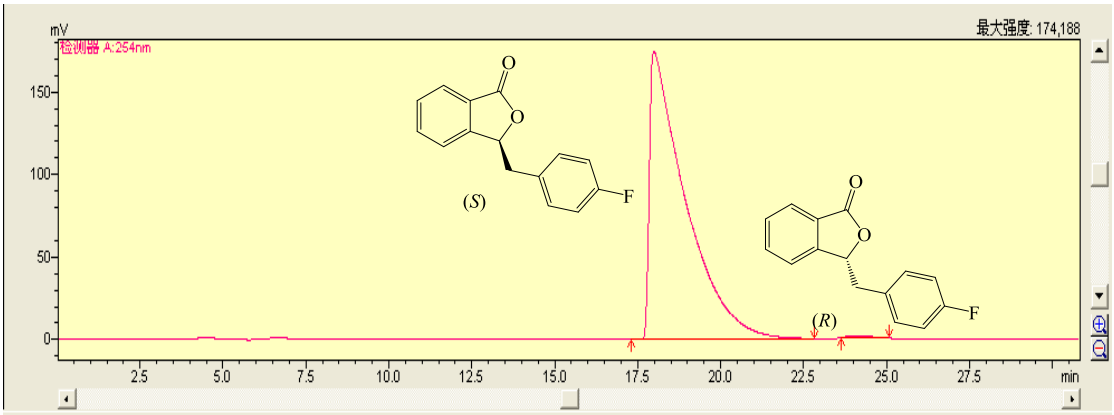
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT19.443	19.443	1	42802	1221	0.3286
2	RT20.552	20.552	2	12983936	179698	99.6714

6b: (*S*)-3-(4-fluorobenzyl)isobenzofuran-1(3*H*)-one. **(**HPLC: OB-H, elute: Hexanes/i-PrOH = 80/20, detector: 254 nm, flow rate: 1 mL/min, 25 ^{o}C), t_1 = 17.9 min (major), t_2 = 24.1 min.**)**



化合物表视图

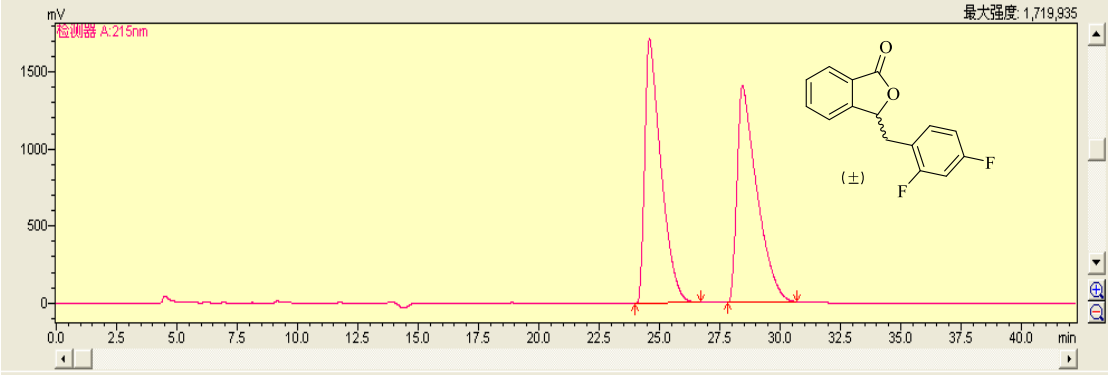
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT18.741	18.741	1	4652821	75965	49.7327
2	RT22.074	22.074	2	4702833	61505	50.2673



化合物表视图

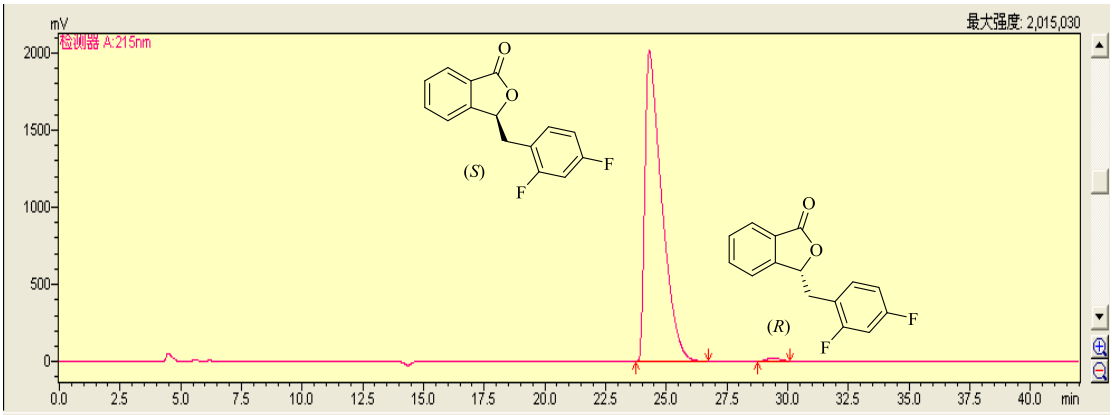
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT17.990	17.990	1	13120493	173962	99.4698
2	RT24.102	24.102	2	69930	1454	0.5302

6c: (*S*)-3-(2,4-difluorobenzyl)isobenzofuran-1(3*H*)-one. **(**HPLC: OJ-H, elute: Hexanes/i-PrOH = 90/10, detector: 215 nm, flow rate: 0.7 mL/min, 25 ºC), t_1 = 24.3 min (major), t_2 = 29.4 min.**)**



化合物表视图

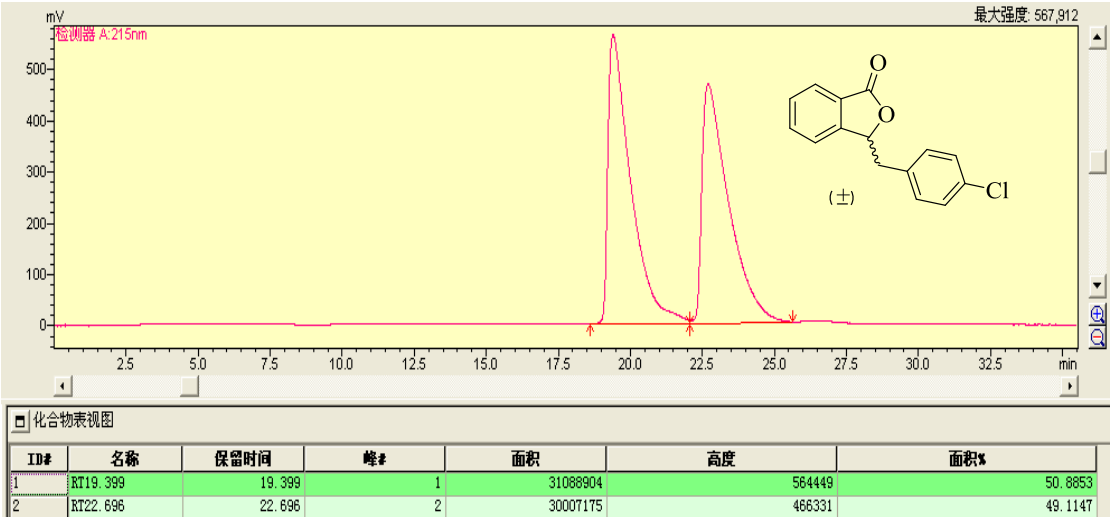
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT24.579	24.579	1	80309847	1718624	49.9668
2	RT28.433	28.433	2	80352217	1409308	50.0132



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT24.303	24.303	1	97424081	2013949	99.1495
2	RT29.393	29.393	2	835686	23130	0.8505

6d: (*S*)-3-(4-chlorobenzyl)isobenzofuran-1(3*H*)-one. **(**HPLC: OB-H, elute: Hexanes/i-PrOH = 80/20, detector: 215 nm, flow rate: 1 mL/min, 25 ^{o}C), t_1 = 19.4 min (major), t_2 = 23.7 min.**)**



化合物表视图

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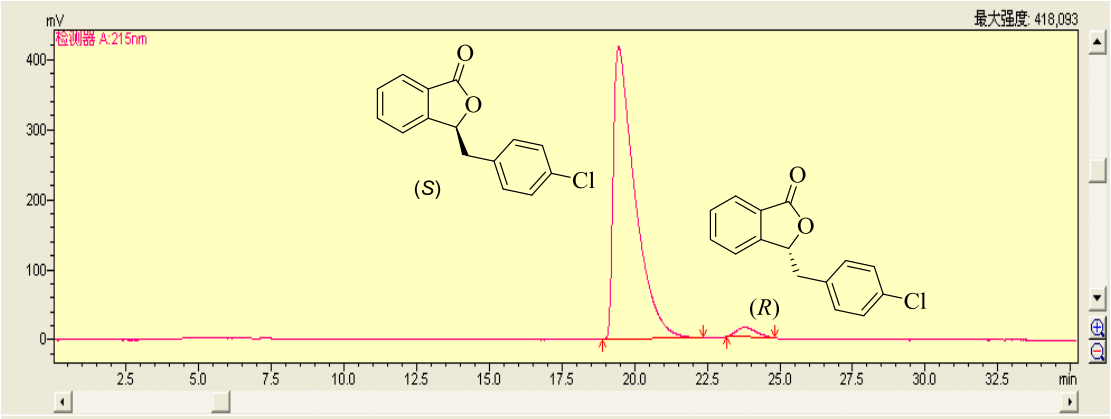
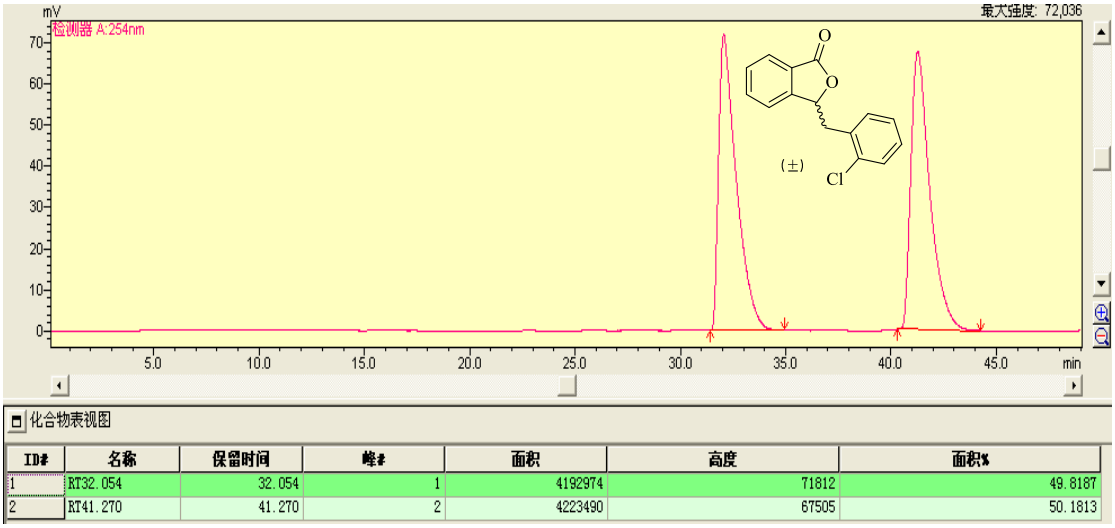
1	RT19.399	19.399	1	31088904	564449	50.8853
2	RT22.696	22.696	2	30007175	466331	49.1147



化合物表视图

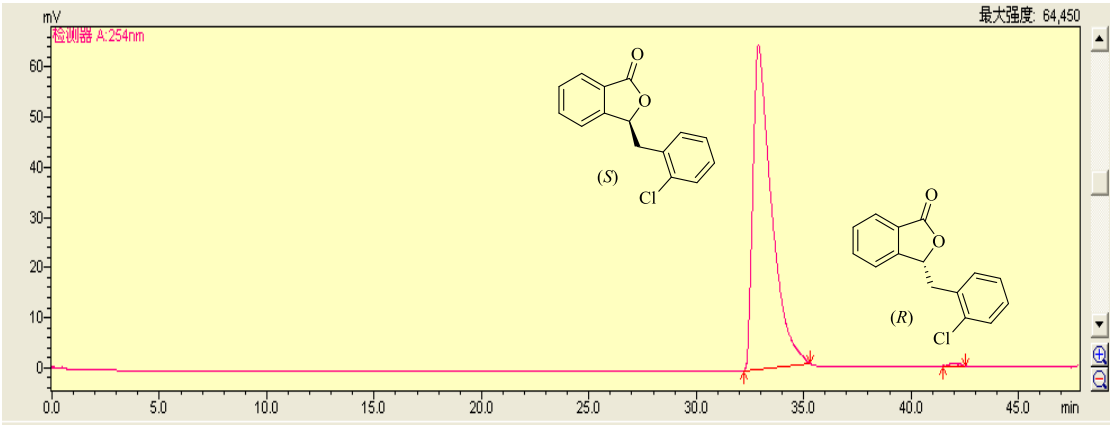
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT19.445	19.445	1	21597801	417272	96.9639
2	RT23.758	23.758	2	675580	13828	3.0330

6e: (*S*)-3-(2-chlorobenzyl)isobenzofuran-1(3*H*)-one. **(**HPLC: OJ-H, elute: Hexanes/i-PrOH = 95/5, detector: 254 nm, flow rate: 0.7 mL/min, 25 °C), t_1 = 32.9 min (major), t_2 = 41.9 min.**)**



化合物表视图

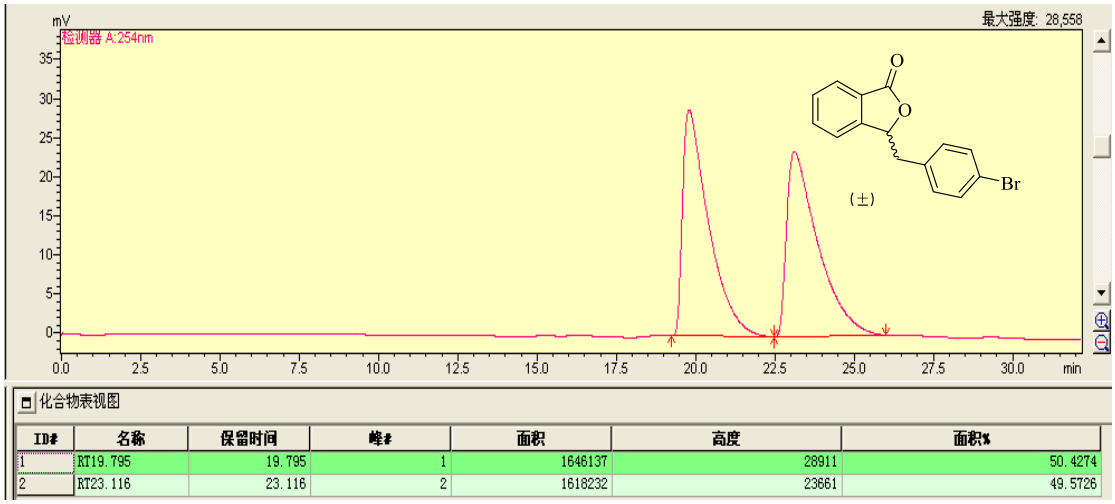
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT32.054	32.054	1	4192974	71812	49.8187
2	RT41.270	41.270	2	4223490	67505	50.1813



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT32.889	32.889	1	3936115	64828	99.4818
2	RT41.889	41.889	2	20504	719	0.5182

6f: (S)-3-(4 bromobenzyl) isobenzofur an-1(3H)-one. **(**HPLC: OB-H, elute: Hexanes/i-PrOH = 80/20, detector: 254 nm, flow rate: 1 mL/min, 25 ^{o}C), t_1 = 18.1 min (major), t_2 = 24.1 min.**)**



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
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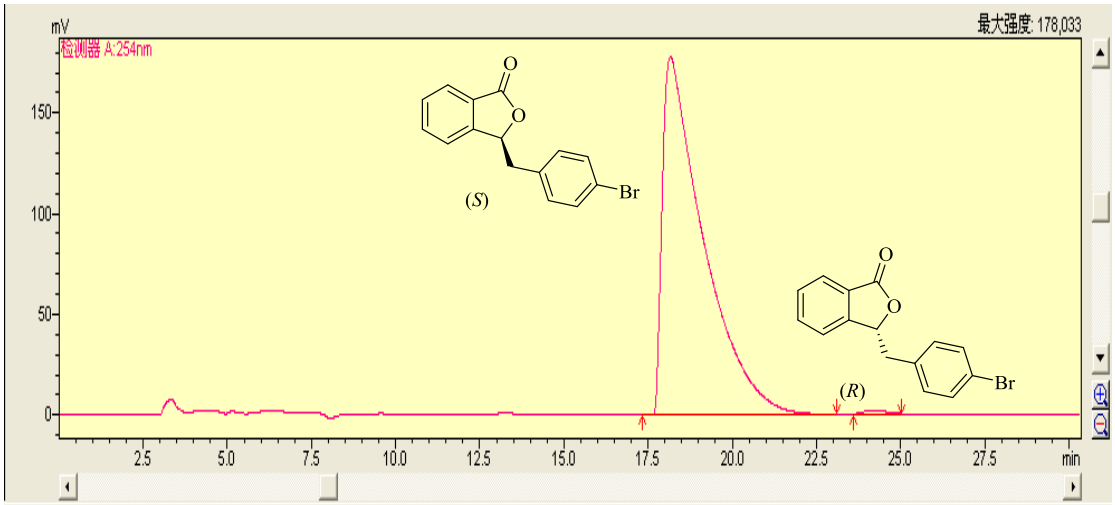
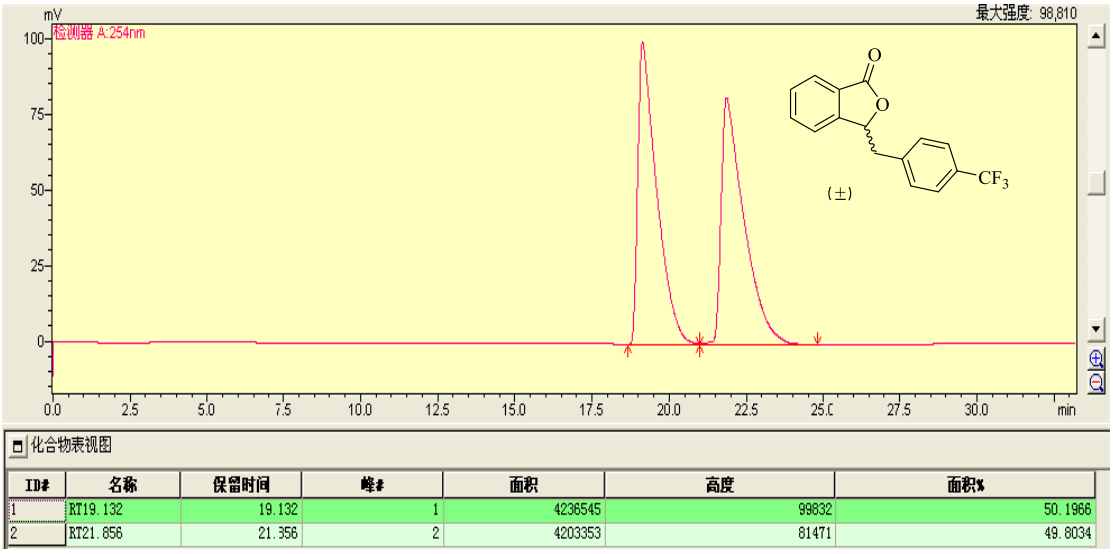
2	RT23.116	23.116	2	1618232	23661	49.5726



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT18.163	18.163	1	15030138	177966	99.4828
2	RT24.189	24.189	2	78143	1689	0.5172

6g: (*S*)-3-(4-(trifluoromethyl)benzyl)isobenzofuran-1(3*H*)-one**.** **(**HPLC: OJ-H, elute: Hexanes/i-PrOH = 90/10, detector: 254 nm, flow rate: 1 mL/min, 25 ^{o}C), t_1 = 18.8 min (major), t_2 = 22.9 min.**)**



化合物表视图

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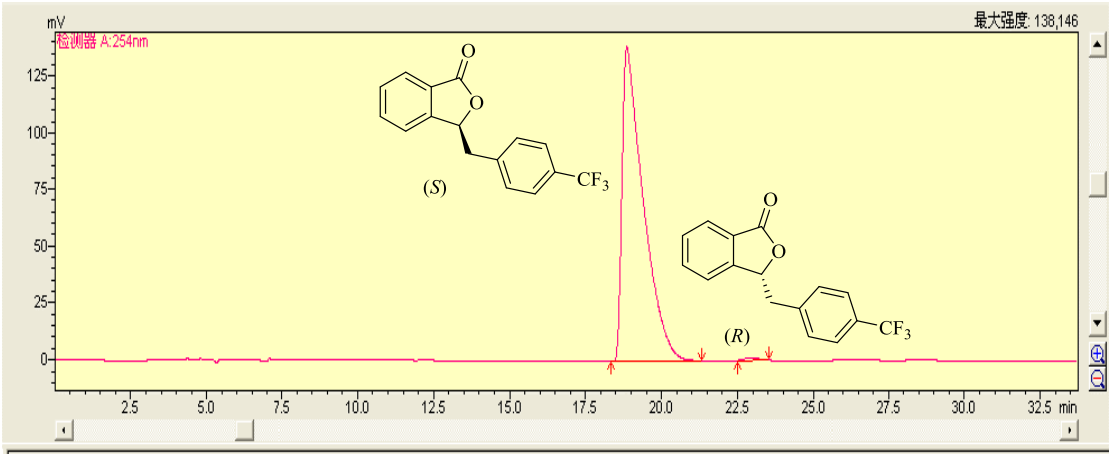
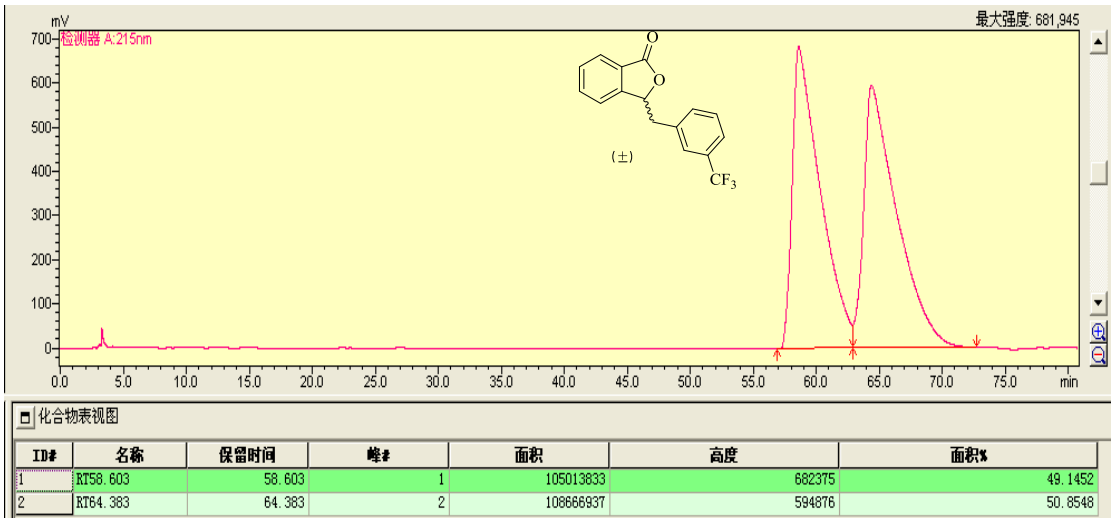
1	RT19.132	19.132	1	4236545	99832	50.1966
2	RT21.856	21.356	2	4203353	81471	49.8034



化合物表视图

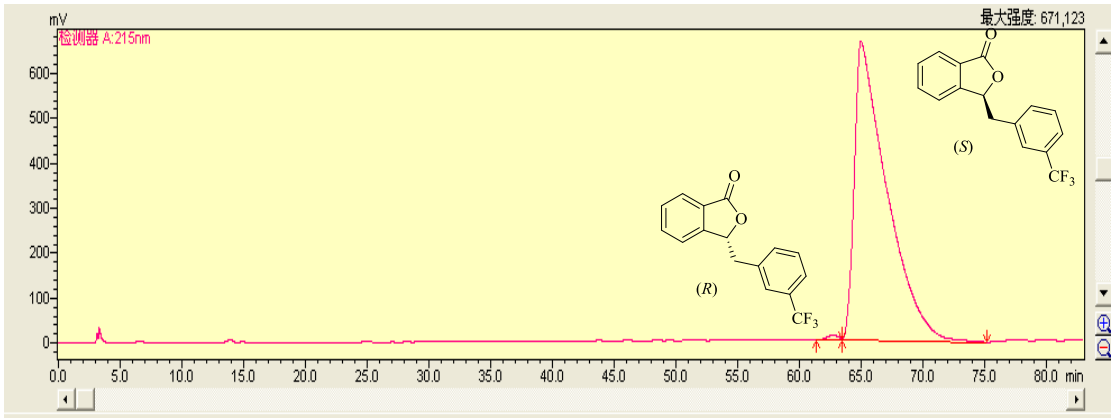
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT18.853	18.853	1	6672604	138602	99.4103
2	RT22.950	22.950	2	39578	1268	0.5897

6h: (*S*)-3-(3-(trifluoromethyl)benzyl)isobenzofuran-1(3*H*)-one. **(**HPLC: OJ-H, elute: Hexanes/i-PrOH = 98/2, detector: 215 nm, flow rate: 1 mL/min, 25 ºC), t_1 = 62.6 min, t_2 = 64.9 min(major).**)**



化合物表视图

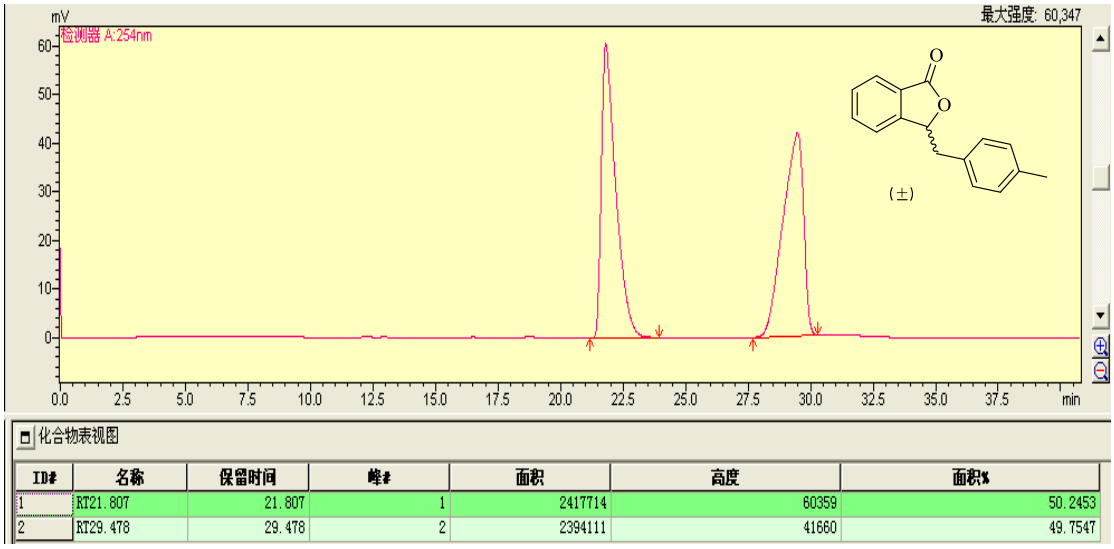
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT58.603	58.603	1	105013833	682375	49.1452
2	RT64.383	64.383	2	108866937	594876	50.8548



化合物表视图

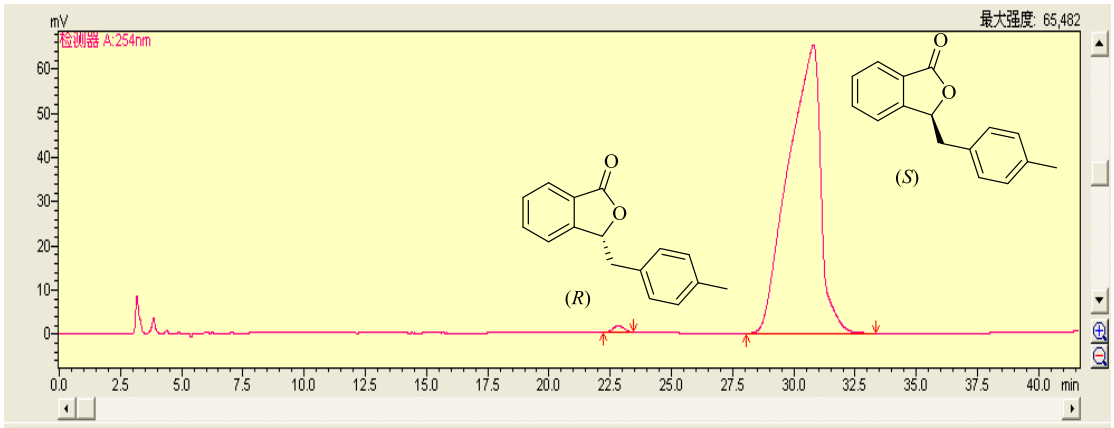
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT62.663	62.663	1	799642	11234	0.6531
2	RT64.963	64.963	2	121646407	665887	99.3469

6i: (*S*)-3-(4-methylbenzyl)isobenzofuran-1(3*H*)-one. (HPLC: OJ-H, elute: Hexanes/i-PrOH = 90/10, detector: 254 nm, flow rate: 1 mL/min, 25 °C), t_1 = 22.8 min, t_2 = 30.7 min (major).)



化合物表视图

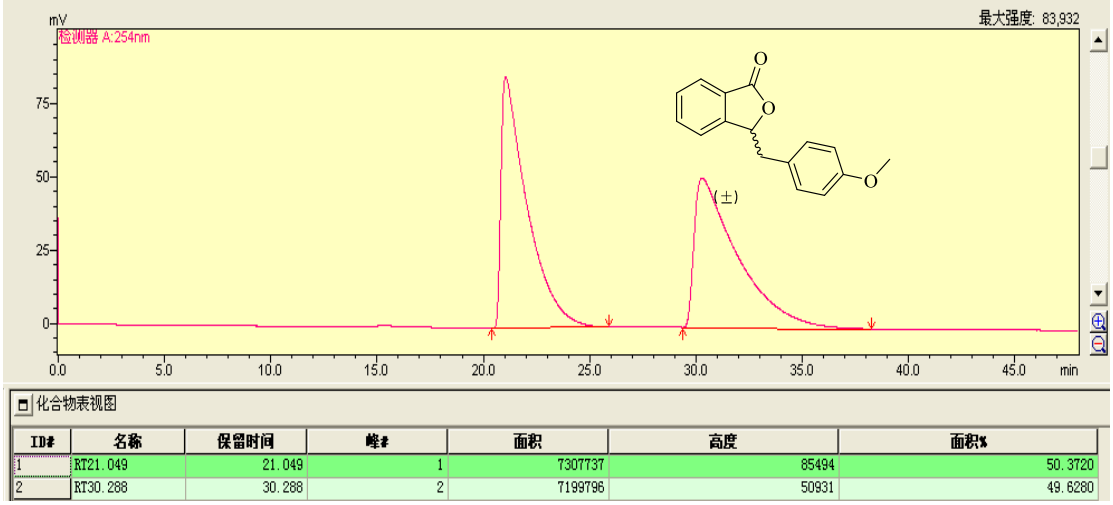
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.807	21.807	1	2417714	60359	50.2453
2	RT29.478	29.478	2	2394111	41660	49.7547



化合物表视图

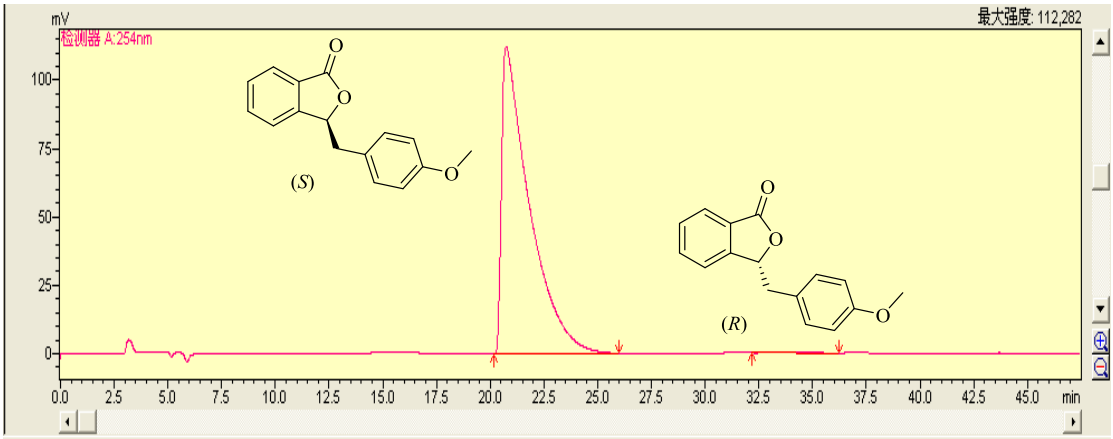
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT22.825	22.825	1	49965	1571	0.8240
2	RT30.789	30.789	2	6013982	65306	99.1760

6j: (*S*)-3-(4-methoxybenzyl)isobenzofuran-1(3*H*)-one. **(**HPLC: OB-H, elute: Hexanes/i-PrOH = 70/30, detector: 254 nm, flow rate: 1 mL/min, 25 ^{o}C), t_1 = 20.7 min (major), t_2 = 34.4 min.**)**



化合物表视图

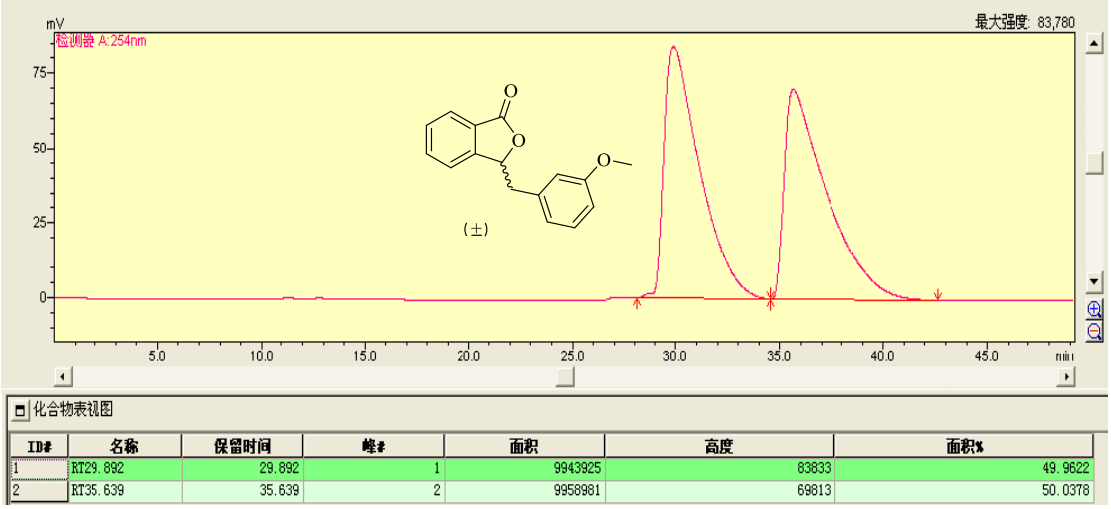
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.049	21.049	1	7307737	85494	50.3720
2	RT30.288	30.288	2	7199796	50931	49.6280



化合物表视图

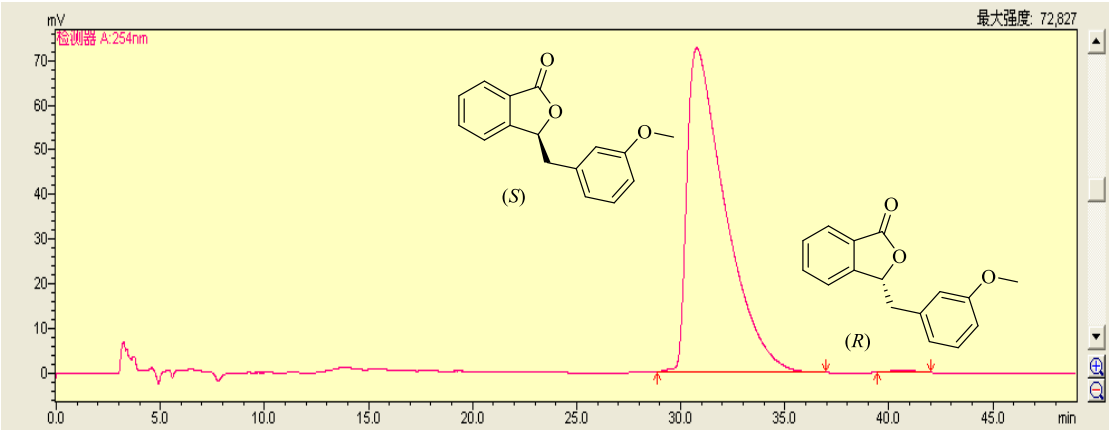
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT20.739	20.739	1	10073231	112377	99.5137
2	RT34.477	34.477	2	49228	502	0.4863

6k: (*S*)-3-(3-methoxybenzyl)isobenzofuran-1(3*H*)-one. **(**HPLC: OB-H, elute: Hexanes/i-PrOH = 80/20, detector: 254 nm, flow rate: 1 mL/min, 25 ^{o}C), t_1 = 30.7 min (major), t_2 = 40.6 min.**)**



化合物表视图

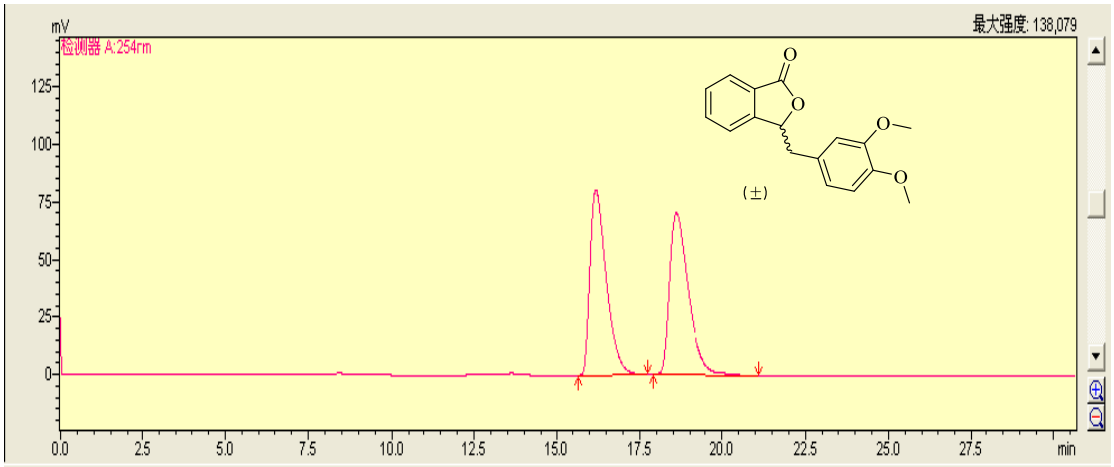
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT29.892	29.892	1	9943925	83833	49.9622
2	RT35.639	35.639	2	9958981	69813	50.0378



化合物表视图

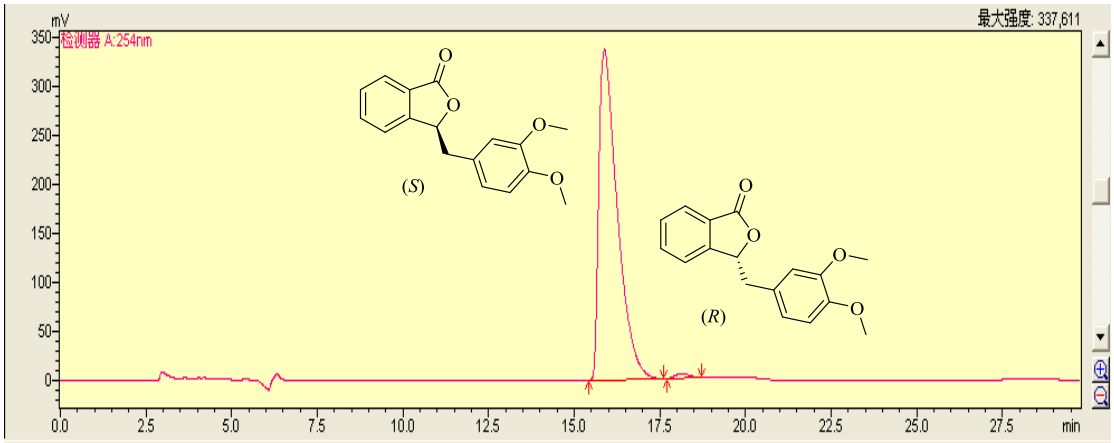
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT30.769	30.769	1	9241606	72516	99.5653
2	RT40.605	40.605	2	40348	465	0.4347

6l: (*S*)-3-(3,4-dimethoxybenzyl)isobenzofuran-1(3*H*)-one. **(**HPLC: OD-H, elute: Hexanes/i-PrOH = 80/20, detector: 254 nm, flow rate: 1 mL/min, 25 ^{o}C), t_1 = 15.8 min (major), t_2 = 18.1 min.**)**



化合物表视图

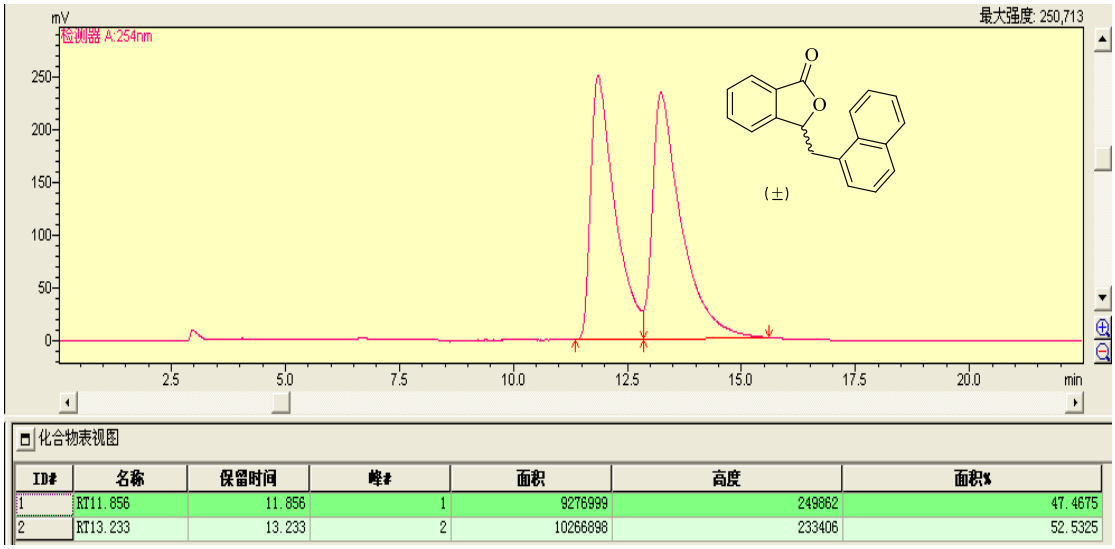
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT16.185	16.185	1	2735740	80579	49.3454
2	RT18.600	18.600	2	2808318	70240	50.6546



化合物表视图

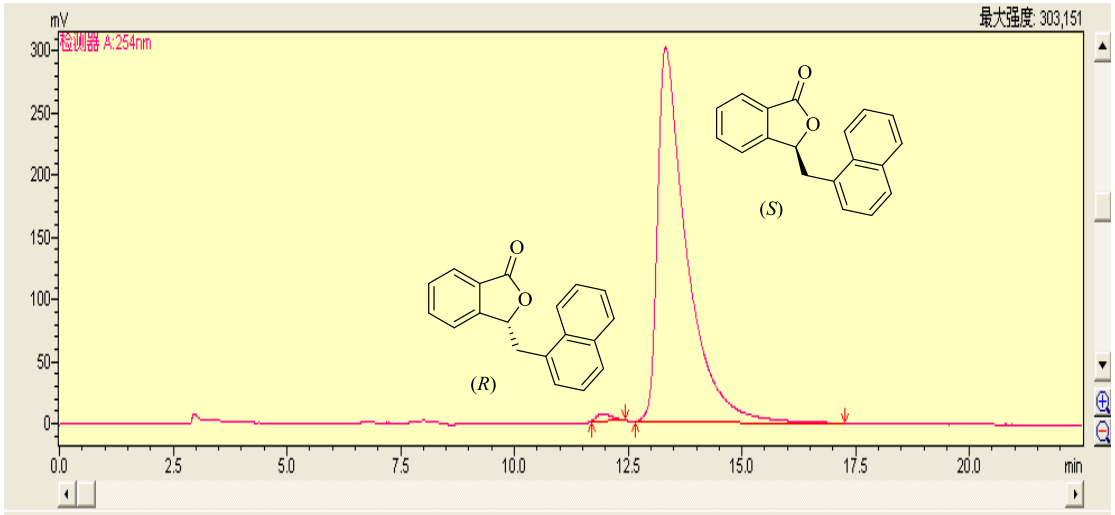
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT15.877	15.877	1	12628385	337016	98.9565
2	RT18.143	18.143	2	133168	4552	1.0435

6m: (*S*)-3-(naphthalen-1-ylmethyl)isobenzofuran-1(3*H*)-one. **(**HPLC: AD-H, elute: Hexanes/i-PrOH = 90/10, detector: 254 nm, flow rate: 1 mL/min, 25 ^{o}C), t_1 = 11.9 min, t_2 = 13.3 min(major).**)**



化合物表视图

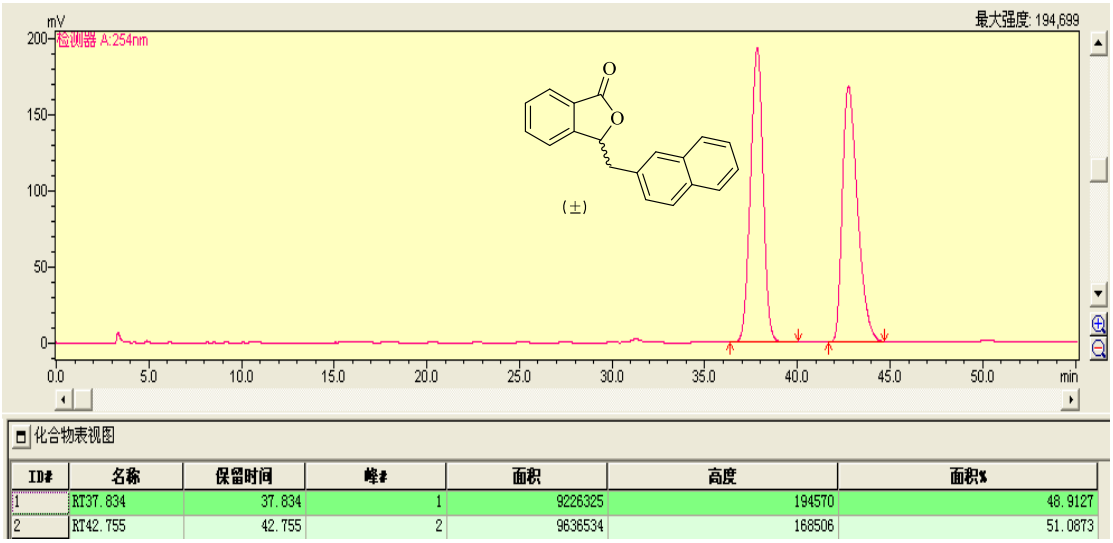
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT11.856	11.856	1	9276999	249862	47.4675
2	RT13.233	13.233	2	10266898	233406	52.5325



化合物表视图

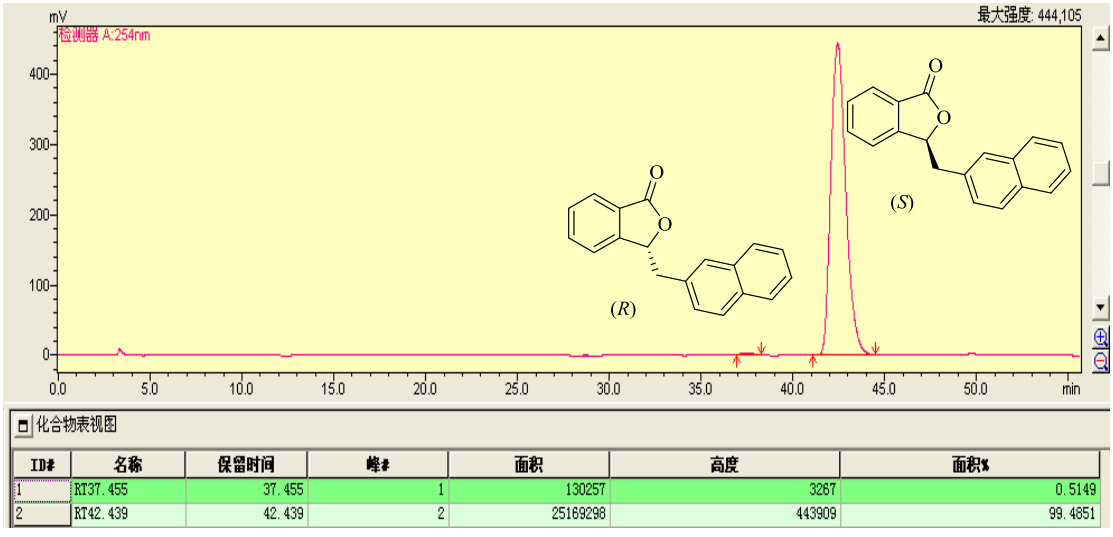
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT11.908	11.908	1	139331	5858	1.0270
2	RT13.326	13.326	2	13427164	301767	98.9730

6n: (*S*)-3-(naphthalen-2-ylmethyl)isobenzofuran-1(3*H*)-one. **(**HPLC: AD-H, elute: Hexanes/i-PrOH = 98/2, detector: 254 nm, flow rate: 1 mL/min, 25 °C), t_1 = 37.4 min, t_2 = 42.4 min (major).**)**



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT37.834	37.834	1	9226325	194570	48.9127
2	RT42.755	42.755	2	9636534	168506	51.0873

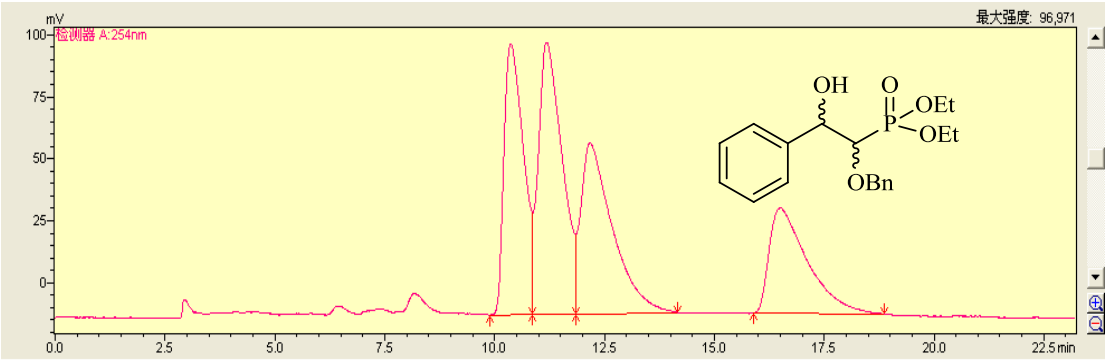


化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT37.455	37.455	1	130257	3267	0.5149
2	RT42.439	42.439	2	25169298	443909	99.4851

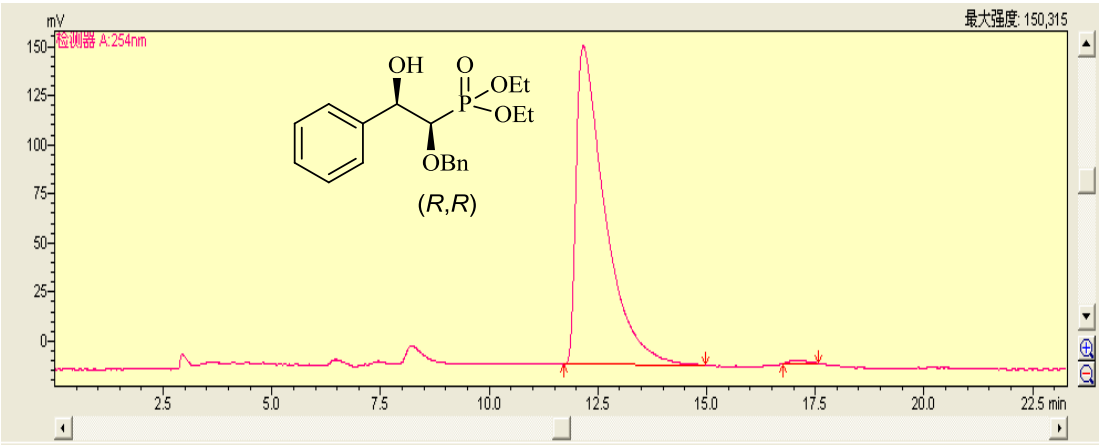
Figure S8. HPLC analyses diethyl α-benzoyl-β-hydroxyphosphonates (the DKR-ATH of α-benzoyl-β-ketophosphonates).

9a: Diethyl ((1*R*,2*R*)-1-(benzyloxy)-2-hydroxy-2-phenylethyl)phosphonate. (HPLC (AD-H, elute: Hexanes/i-PrOH = 90/10, detector: 254 nm, flow rate: 1.0 mL/min, 25 ^{o}C), t_1 = 10.7 min, t_2 = 12.2 min, t_3 = 15.4, t_4 = 19.6)).



化合物表视图

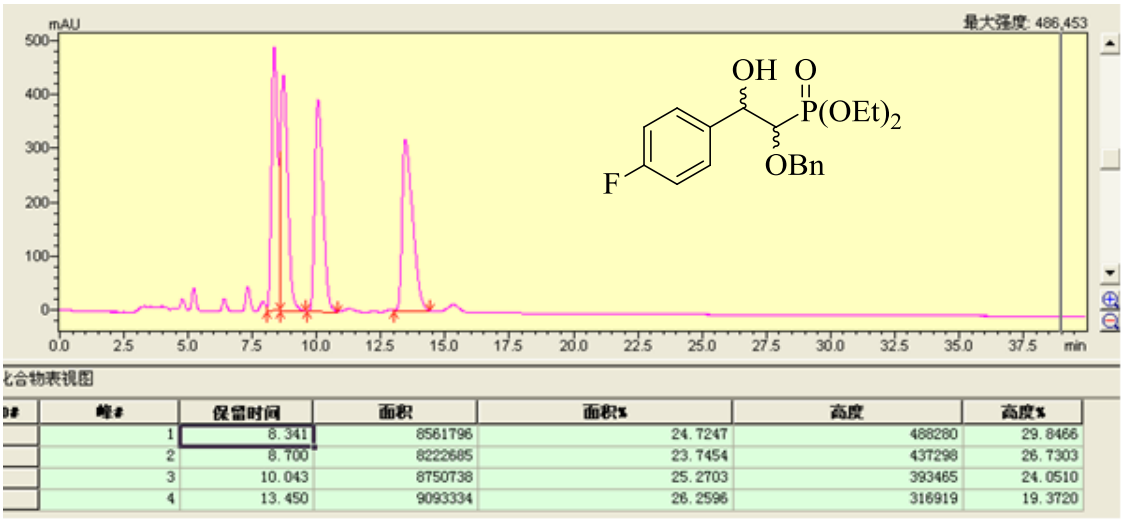
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT10.365	10.365	1	3392132	109429	24.9201
2	RT11.185	11.185	2	4172028	109737	30.6496
3	RT12.177	12.177	3	3460014	68839	25.4188
4	RT16.507	16.507	4	2587853	42620	19.0115



化合物表视图

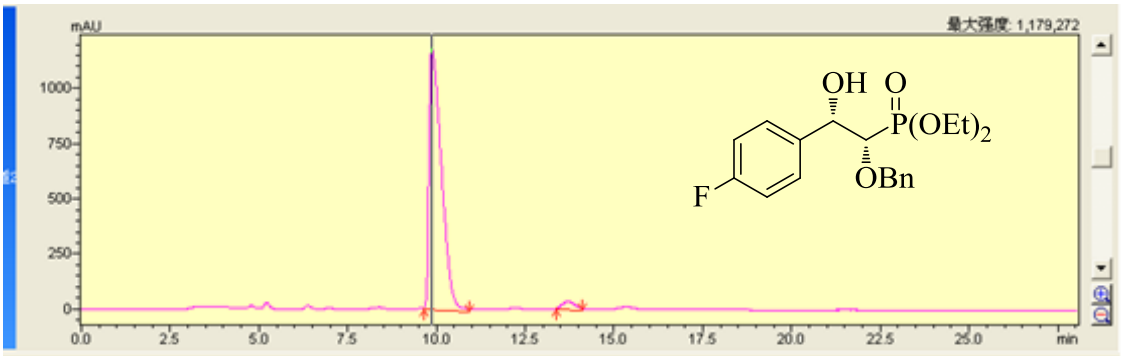
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT12.164	12.164	1	7509621	162357	99.3577
2	RT17.075	17.075	2	48548	1871	0.6423

9b: Diethyl(1*R*,2*R*)-[1-benzyloxy-2-(4-fluoro-phenyl)-2-hydroxyethyl]phosphonate. (HPLC (AD-H, elute: Hexanes/i-PrOH=90/10,detector:254nm,flowrate: 1.0 mL/min, 25 °C), t_1 =8.3min, t_2 = 8.7min, t_3=10.0,t_4=13.5))



化合物表视图

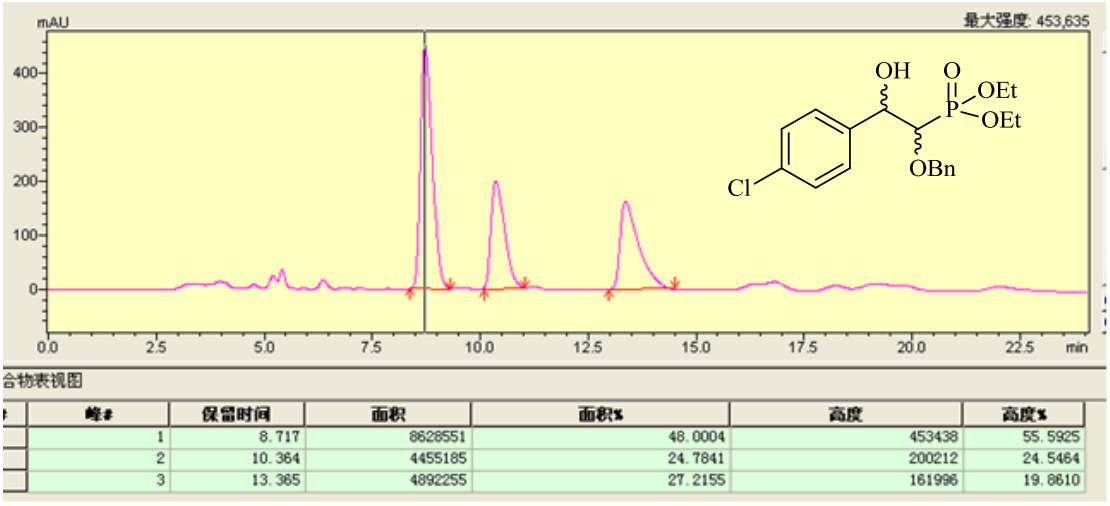
ID#	峰#	保留时间	面积	面积%	高度	高度%
	1	8.341	8561796	24.7247	488280	29.8466
	2	8.700	8222685	23.7454	437298	26.7303
	3	10.043	8750738	25.2703	393465	24.0510
	4	13.450	9093334	26.2596	316919	19.3720



化合物表视图

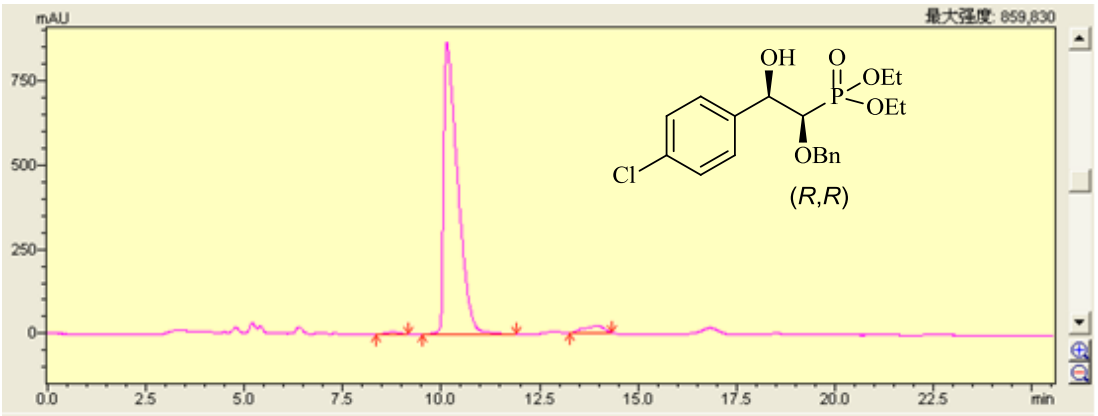
ID#	峰#	保留时间	面积	面积%	高度	高度%
	1	9.871	28924001	96.7228	1182318	96.9636
	2	13.699	980011	3.2772	37025	3.0364

9c: Diethyl (1*R*,2*R*)-[1-benzyloxy-2-(4-chloro-phenyl)-2-hydroxyethyl]phosphonate. (HPLC (AD-H, elute: Hexanes/i-PrOH = 90/10, detector: 254 nm, flowrate: 1.0 mL/min, 25 °C), t_1 = 8.7min, t_2 = 10.4 min, t_3=13.4))



合物表视图

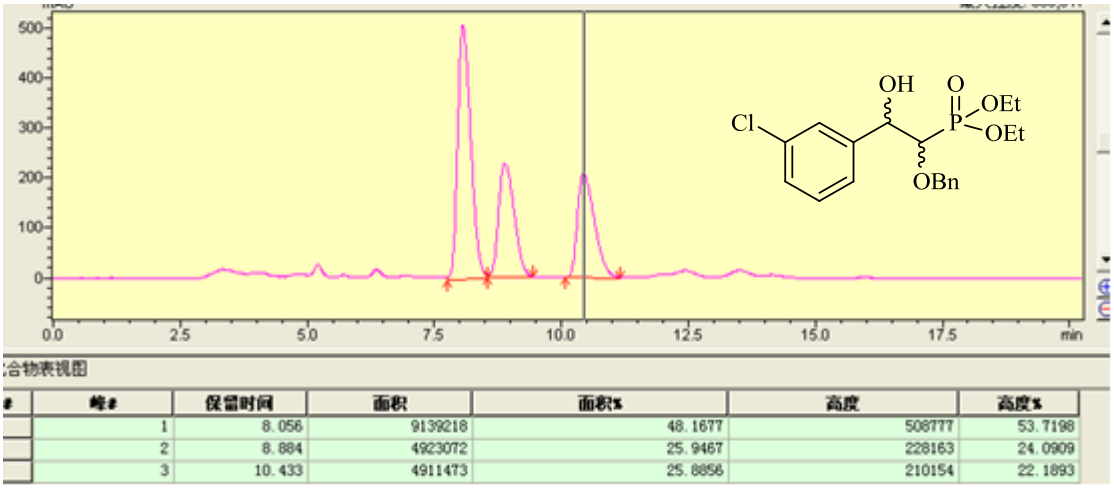
峰#	保留时间	面积	面积%	高度	高度%
1	8.717	8628551	48.0004	453438	55.5925
2	10.364	4455185	24.7841	200212	24.5464
3	13.365	4892255	27.2155	161996	19.8610



化合物表视图

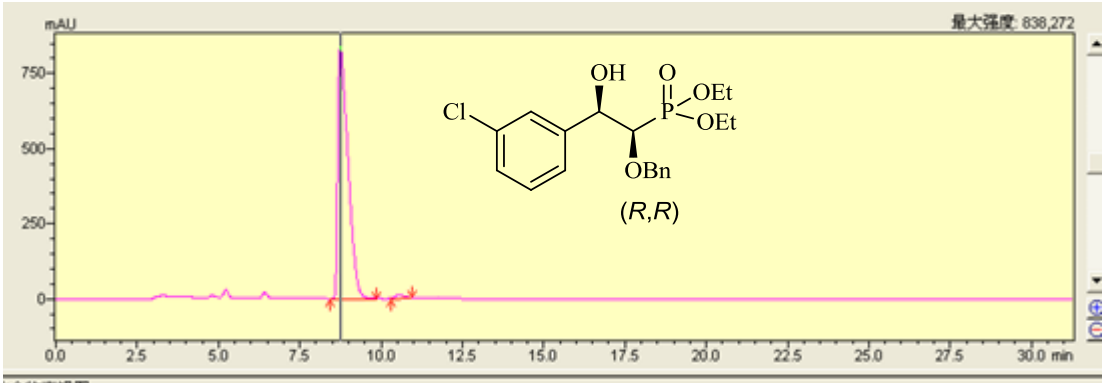
ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	8.763	125165	0.5680	6599	0.7425
2	2	10.143	21141064	95.9395	860822	96.8505
3	3	13.950	769609	3.4925	21394	2.4070

9d: Diethyl (1*R*,2*R*)-[1-benzyloxy-2-(3-chloro-phenyl)-2-hydroxyethyl]phosphonate. (HPLC (AD-H, elute: Hexanes/i-PrOH=90/10, detector:254 nm, flowrate: 1.0 mL/min, 25 °C), t_1 = 8.1min, t_2 = 8.9 min, t_3 = 10.4)).



合物表视图

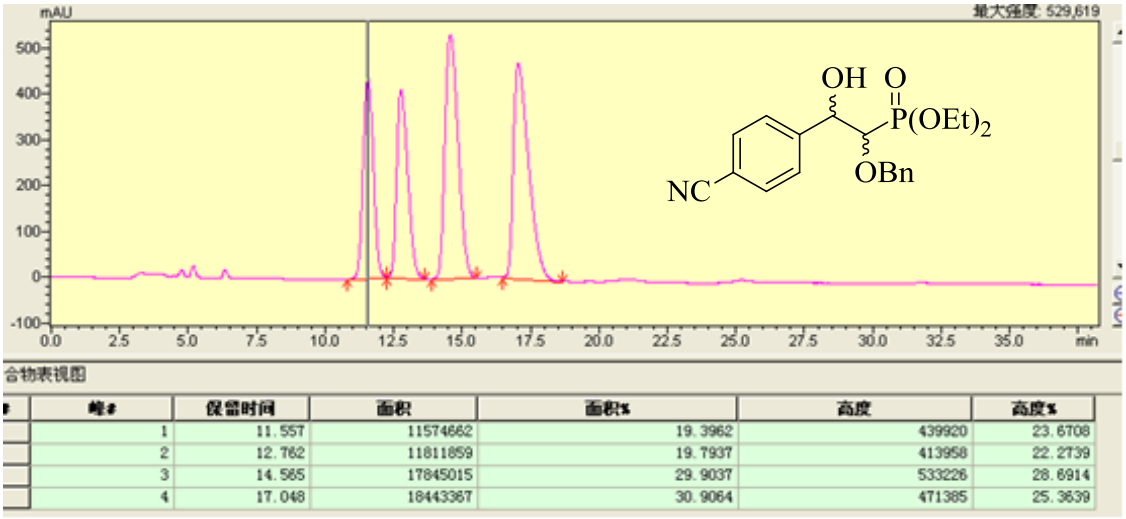
峰#	保留时间	面积	面积%	高度	高度%
1	8.056	9139218	48.1677	508777	53.7198
2	8.884	4923072	25.9467	228163	24.0909
3	10.433	4911473	25.8856	210154	22.1893



合物表视图

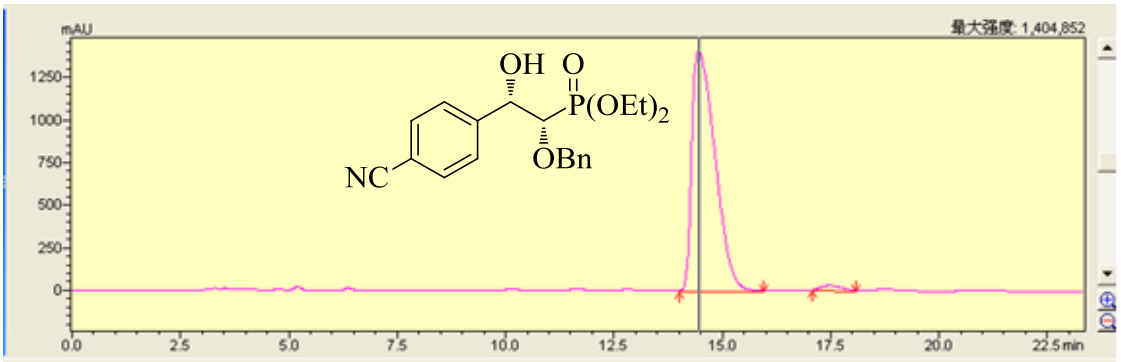
峰#	保留时间	面积	面积%	高度	高度%
1	8.741	18445636	98.3788	839064	98.5481
2	10.567	303961	1.6212	12362	1.4519

9e: Diethyl(1R,2R)-[1-benzyloxy-2-(4-cyano-phenyl)-2-hydroxyethyl]phosphonate. (HPLC (AD-H, elute: Hexanes/i-PrOH=90/10,detector:254nm,flowrate: 1.0 mL/min, 25 ^{o}C), t_1 =11.6min, t_2 = 12.8min, t_3=14.6,t_4=17.0))



合物表视图

	峰#	保留时间	面积	面积%	高度	高度%
	1	11.557	11574662	19.3962	439920	23.6708
	2	12.762	11811859	19.7937	413958	22.2739
	3	14.585	17845015	29.9037	533226	28.6914
	4	17.048	18443367	30.9064	471385	25.3639

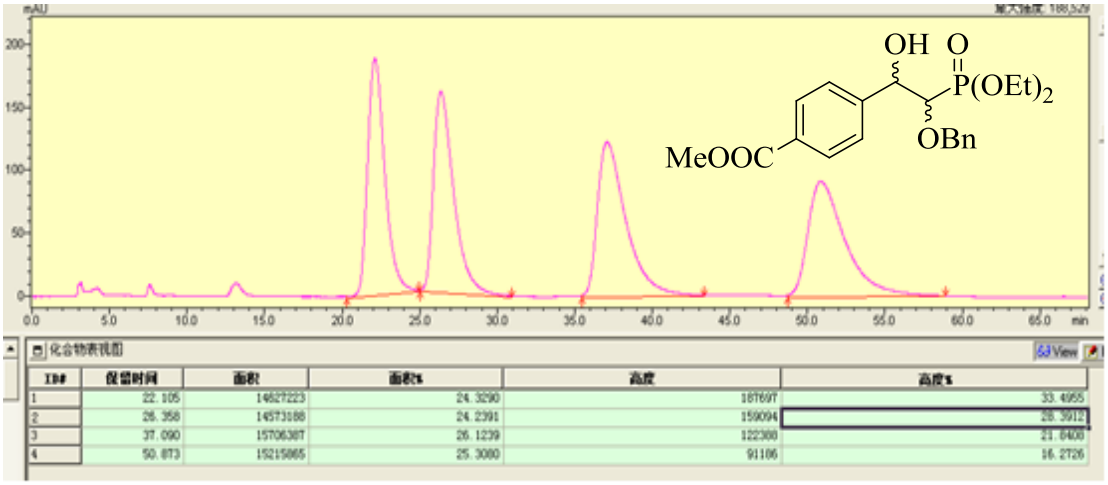


化合物表视图

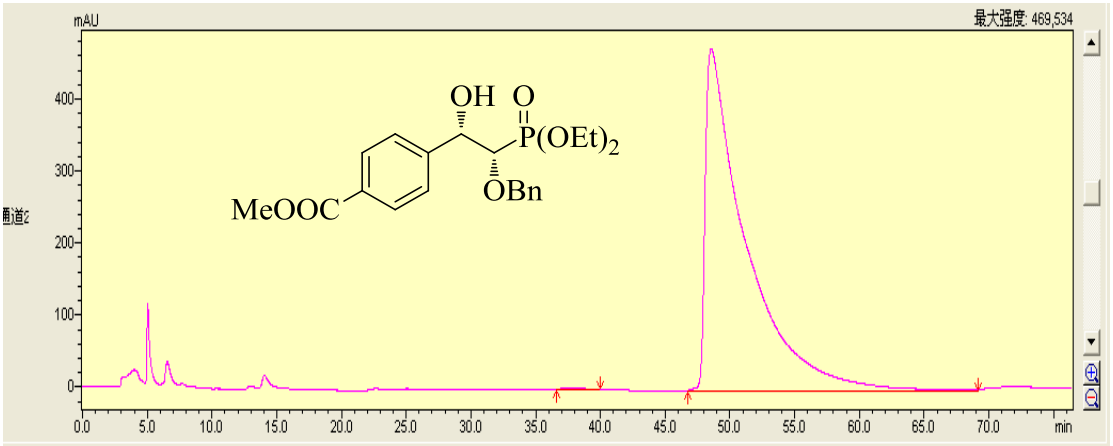
ID#	峰#	保留时间	面积	面积%	高度	高度%
	1	14.454	52989956	97.6871	1413287	97.7210
	2	17.476	1254647	2.3129	32960	2.2790

9f: Diethyl (1*R*,2*R*)-[1-benzyloxy-2-(4-carbomethoxy-phenyl)-2-hydroxy-ethyl]phosphonate.

(HPLC (AD-H, elute: Hexanes/i-PrOH=90/10,detector:254nm,flowrate: 1.0 mL/min, 25 ºC), t_1 =22.1min, t_2 = 26.3min, t_3=27.0min,t_4=50.8min))



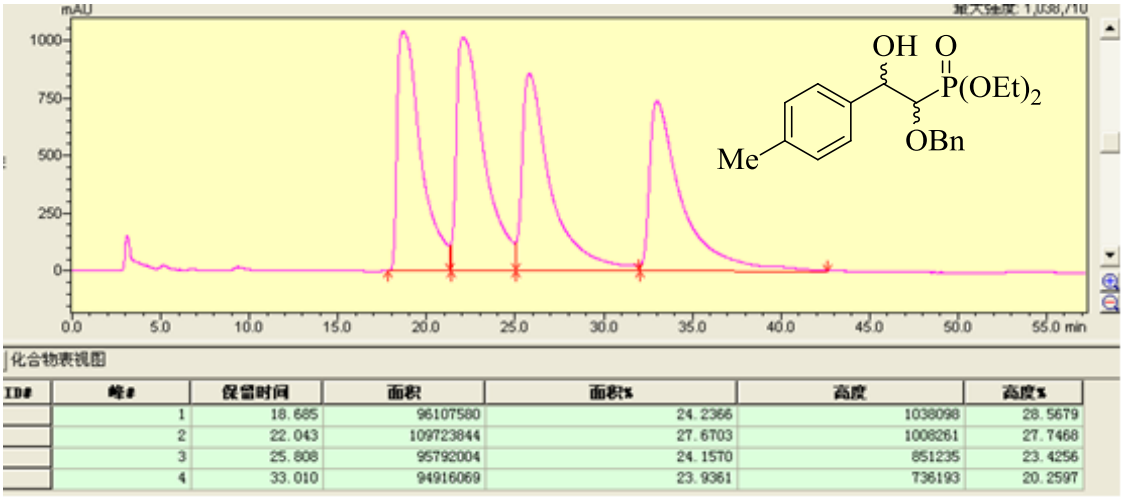
ID#	保留时间	面积	面积%	高度	高度%
1	22.105	14627223	24.3290	187697	33.4955
2	26.358	14573188	24.2391	159094	28.3912
3	37.090	15706387	26.1239	122308	21.8308
4	50.873	15215865	25.3080	91106	16.2726



化合物表视图

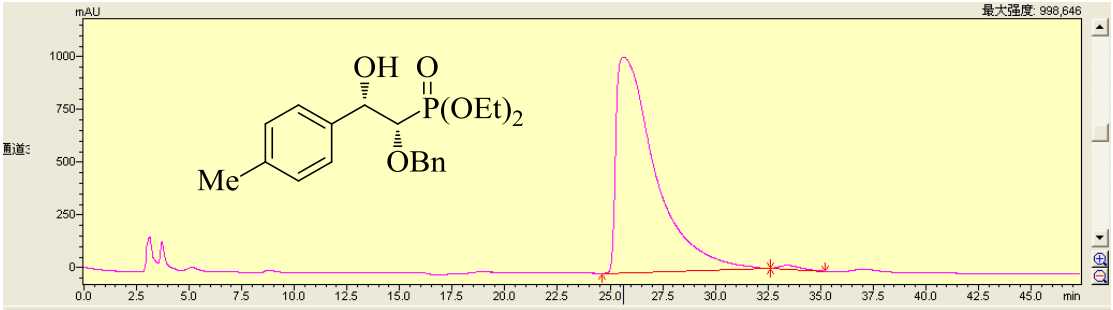
ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT37.777	37.777	1	250867	0.2419	2682	0.5612
2	RT48.547	48.547	2	103453994	99.7581	475152	99.4388

9g: Diethyl (1*R*,2*R*)-[1-benzyloxy-2-hydroxy-2-(p-tolyl)-ethyl] phosphonate. (HPLC (AD-H, elute: Hexanes/i-PrOH = 95/5, detector: 215 nm, flow rate: 1.0 mL/min, 25 ^{o}C), t_1 = 18.7 min, t_2 = 22.0 min, t_3 = 25.8, t_4 = 33.0))



化合物表视图

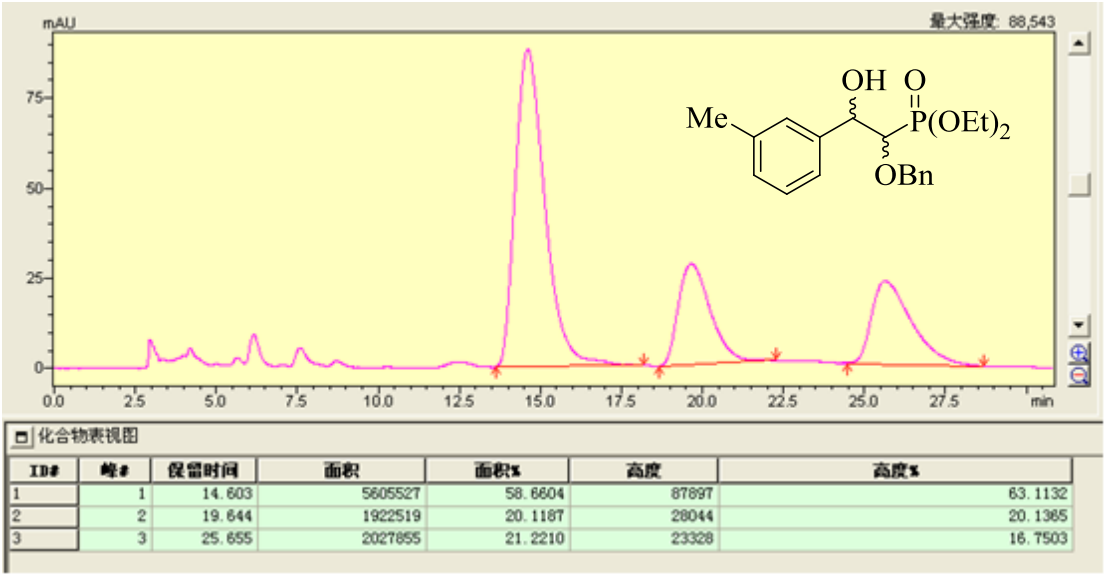
ID#	峰#	保留时间	面积	面积%	高度	高度%
	1	18.685	96107580	24.2366	1038098	28.5679
	2	22.043	109723844	27.6703	1008261	27.7468
	3	25.808	95792004	24.1570	851235	23.4256
	4	33.010	94916069	23.9361	736193	20.2597



化合物表视图

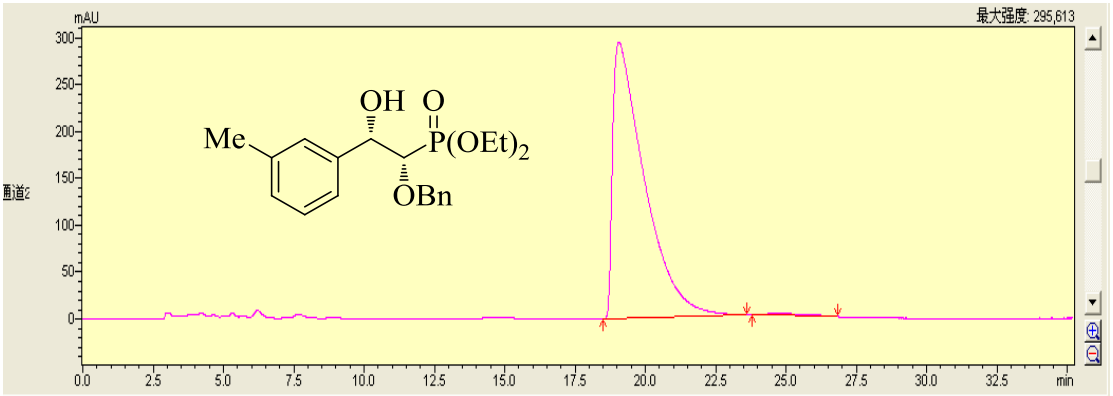
ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT25.660	25.660	1	132119718	99.0469	1022391	98.2770
2	RT33.368	33.368	2	1271379	0.9531	17924	1.7230

9h: Diethyl (1*R*,2*R*)-[1-benzyloxy-2-hydroxy-2-(m-tolyl)-ethyl] phosphonate. (HPLC (AD-H, elute: Hexanes/i-PrOH=95/5,detector:254nm,flowrate: 1.0 mL/min, 25 °C), t_1 = 14.6 min, t_2 = 19.6 min, t_3 = 25.7))



化合物表视图

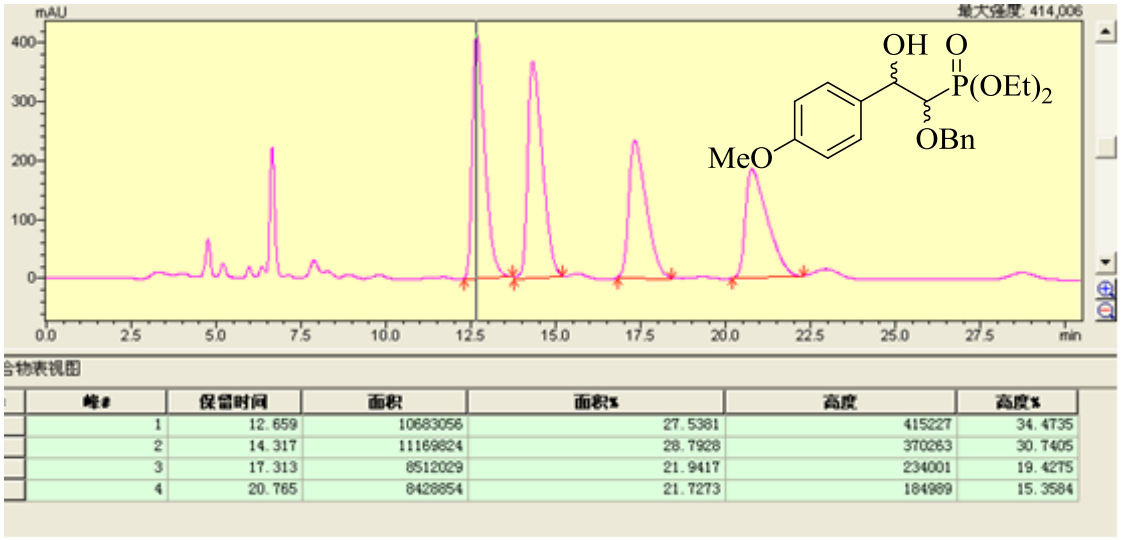
ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	14.603	5605527	58.6604	87897	63.1132
2	2	19.644	1922519	20.1187	28044	20.1365
3	3	25.655	2027855	21.2210	23328	16.7503



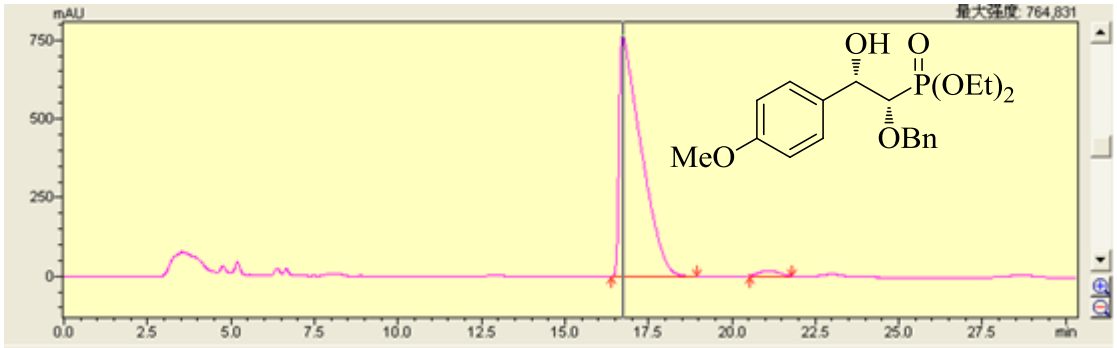
化合物表视图

ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT19.057	19.057	1	23201108	98.8891	295100	99.1472
2	RT24.743	24.743	2	260647	1.1109	2538	0.8528

9i: Diethyl(1*R*,2*R*)-[1-benzyloxy-2-hydroxy-2-(4-methoxy-phenyl)-ethyl]phosphonate. (HPLC (AD-H, elute: Hexanes/i-PrOH=95/5,detector:254nm,flowrate: 1.0 mL/min, 25 ^{o}C), t_1 =127min, t_2 = 14.3min, t_3=17.3,t_4=21.1))

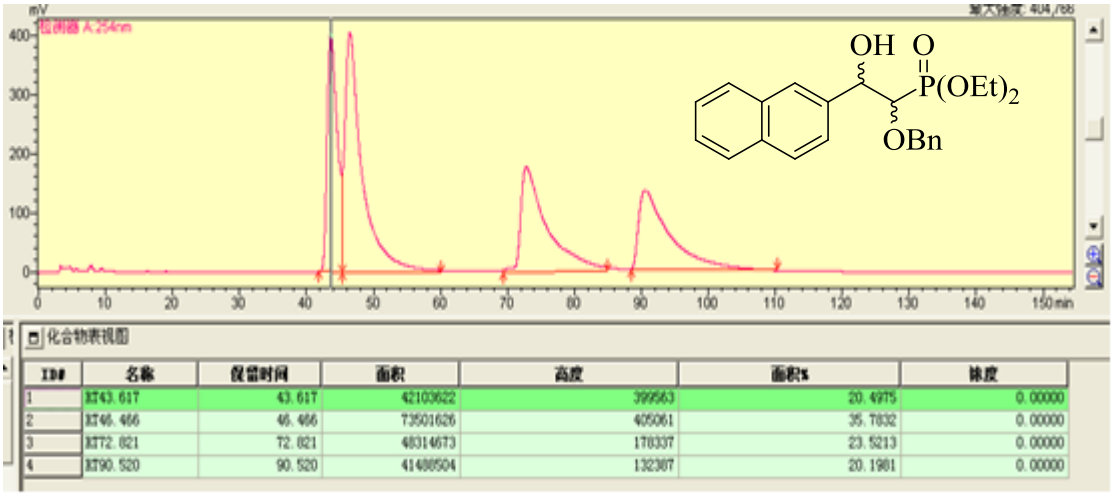


峰#	保留时间	面积	面积%	高度	高度%
1	12.659	10683056	27.5381	415227	34.4735
2	14.317	11169824	28.7928	370263	30.7405
3	17.313	8512029	21.9417	234001	19.4275
4	20.765	8428854	21.7273	184989	15.3584



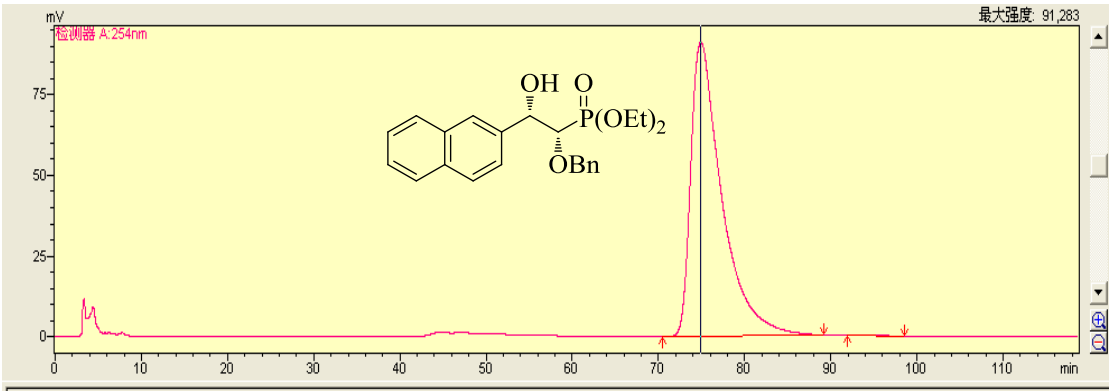
峰#	保留时间	面积	面积%	高度	高度%
1	16.731	35077698	97.8086	766666	97.7873
2	21.122	785922	2.1914	17348	2.2127

9j: Diethyl (1R,2R)-[1-benzyloxy-2-(naphthalen-2-yl)-2-hydroxyethyl]phosphonate. (HPLC (AD-H, elute: Hexanes/i-PrOH=90/10,detector:254nm,flowrate: 1.0 mL/min, 25 ^{o}C), t_1 =43.6. min, t_2 = 46.5min, t_3=72.0min,t_4=90.5min))



化合物表视图

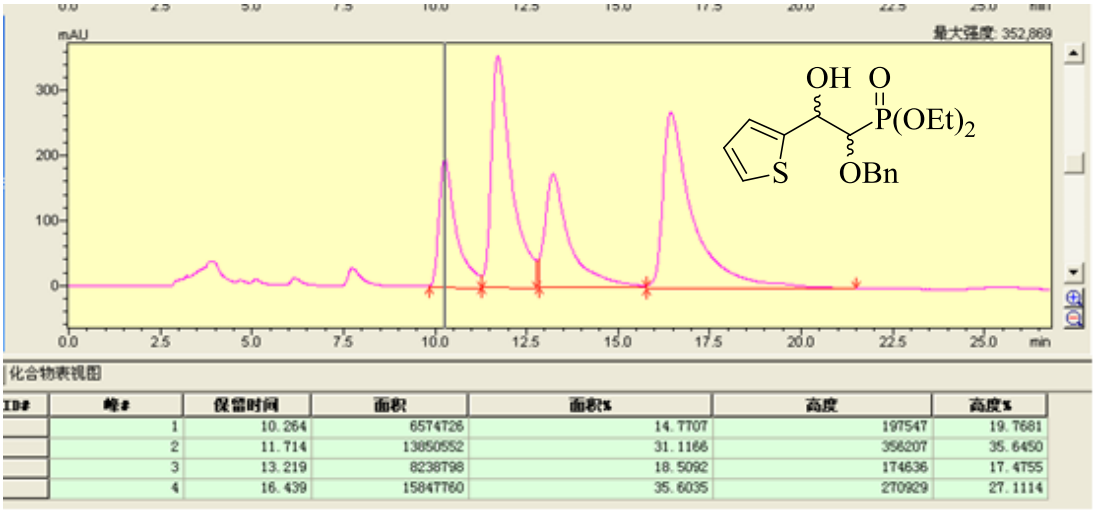
ID#	名称	保留时间	面积	高度	面积%	峰度
1	RT43.617	43.617	42103622	399563	20.4975	0.00000
2	RT46.466	46.466	73501626	405061	35.7832	0.00000
3	RT72.021	72.021	48314673	178337	23.5213	0.00000
4	RT90.520	90.520	41480504	132387	20.1981	0.00000



化合物表视图

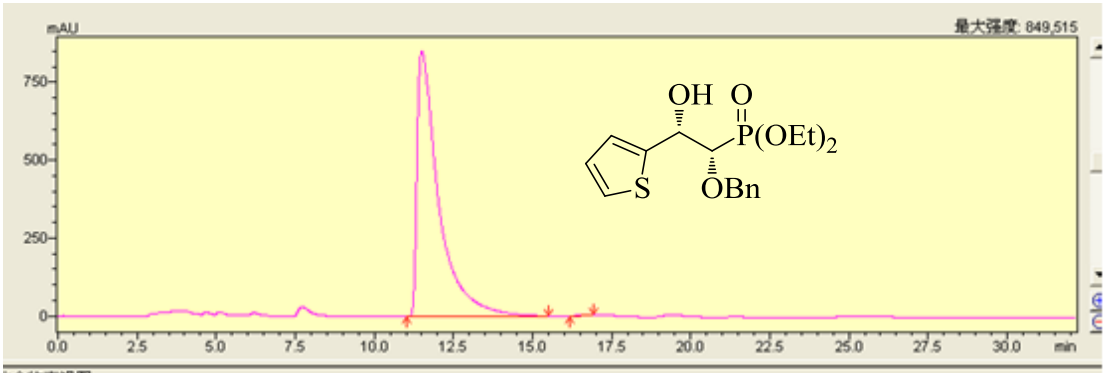
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT74.909	74.909	1	22740557	90973	99.7731
2	RT94.364	94.364	2	51720	236	0.2269

9k: Diethyl (1S,2S)-[1-benzyloxy-2-hydroxy-2-(thiophen-2-yl)-ethyl]phosphonate. (HPLC (AD-H, elute: Hexanes/i-PrOH=90/10,detector:254nm,flowrate: 1.0 mL/min, 25 ^{o}C), t_1 =10.3. min, t_2 = 11.8min, t_3=13.2min,t_4=16.4min))



化合物表视图

ID#	峰#	保留时间	面积	面积%	高度	高度%
	1	10.264	6574726	14.7707	197547	19.7681
	2	11.714	13850552	31.1166	356207	35.6450
	3	13.219	8238798	18.5092	174636	17.4755
	4	16.439	15847760	35.6035	270929	27.1114



化合物表视图

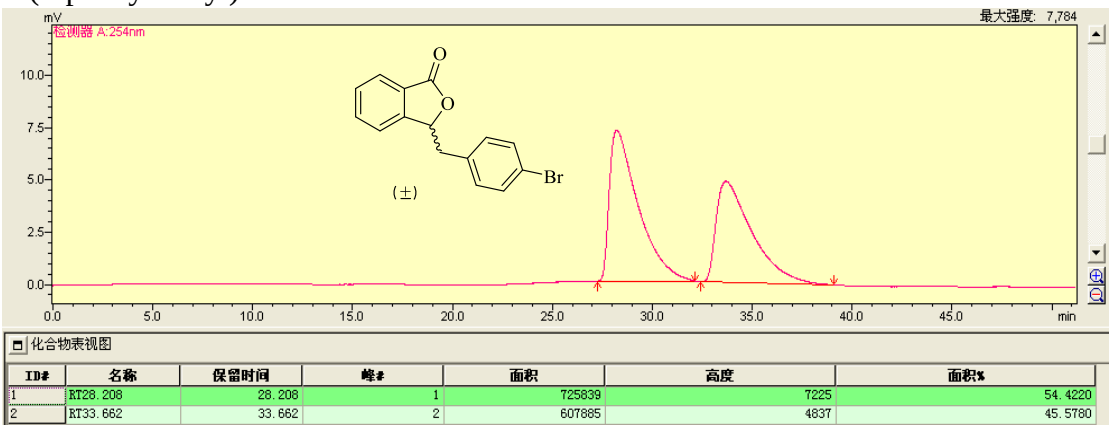
#	峰#	保留时间	面积	面积%	高度	高度%
	1	11.501	40886002	99.7397	852350	99.5608
	2	16.620	106702	0.2603	3760	0.4392

Table S1. Reusability of catalyst **5** for the reduction/lactonization of ethyl 2-(2-phenylacetyl)benzoate.[a]

Entry	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Yield [%]	99	99	95	93	92	92	92	90
ee [%]	99	99	99	99	99	98	98	98

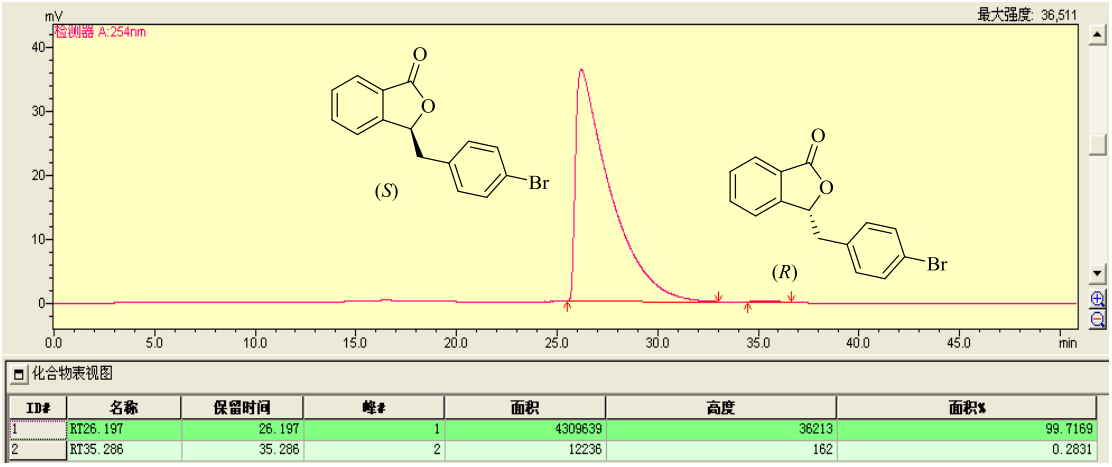
[a] Reaction conditions: catalyst **5** (196.80 mg), K_2CO_3 (138.0 mg, 1.0 mmol), HCO_2Na (680.0 mg, 10.0 mmol), iodoacetophenones (1.0 mmol), aryne (1.10 mmol), and 40.0 mL of the mixed solvents (H_2O/MeOH v/v = 1/3), reaction temperature (60 ℃), reaction time (16 h).

Figure 9. Reusability of catalyst **5** for the reduction/lactonization of ethyl 2-(2-phenylacetyl)benzoate.



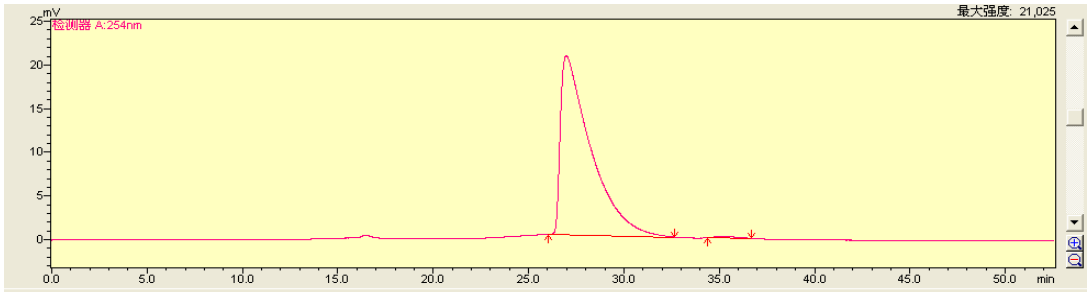
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT28.208	28.208	1	725839	7225	54.4220
2	RT33.662	33.662	2	607885	4837	45.5780

Recycle 1



ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT26.197	26.197	1	4309639	36213	99.7169
2	RT35.286	35.286	2	12236	162	0.2831

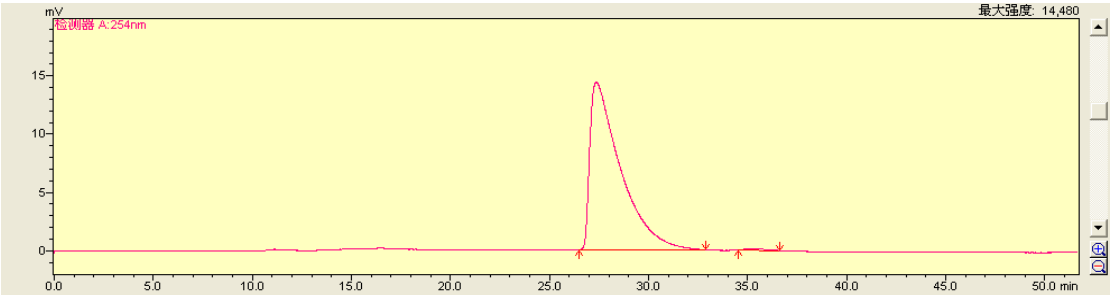
Recycle 2



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT26.978	26.978	1	2261554	20463	99.3946
2	RT35.190	35.190	2	13776	173	0.6054

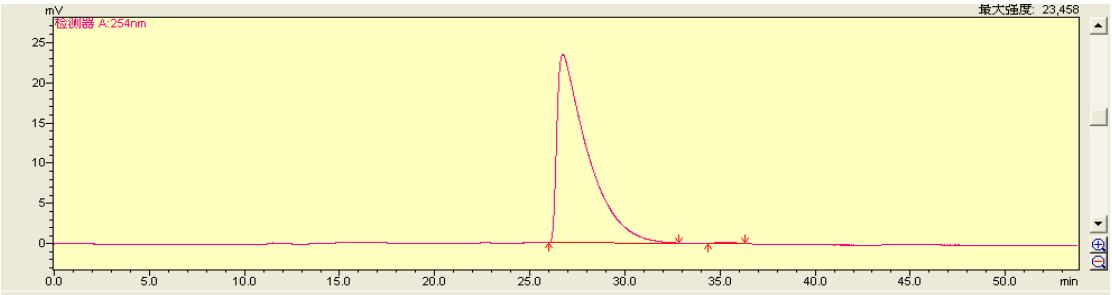
Recycle 3



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT27.360	27.360	1	1543630	14397	99.4825
2	RT35.314	35.314	2	8029	113	0.5175

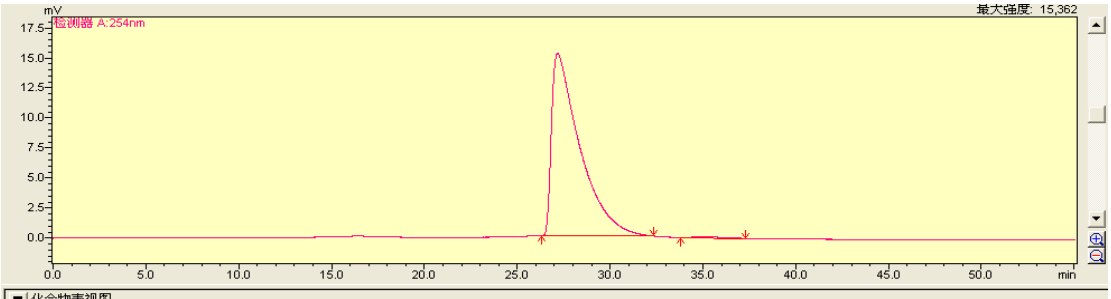
Recycle 4



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT26.725	26.725	1	2596886	23314	99.5684
2	RT35.190	35.190	2	11257	169	0.4316

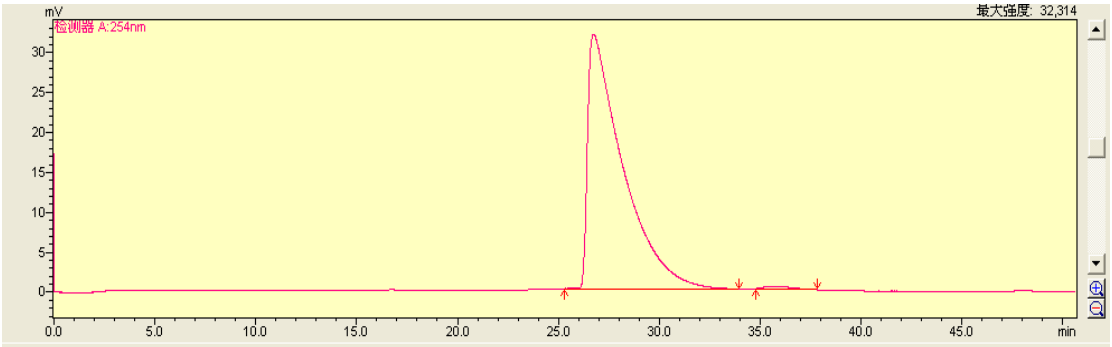
Recycle 5



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT27.176	27.176	1	1611671	15185	99.4469
2	RT35.261	35.261	2	8964	92	0.5531

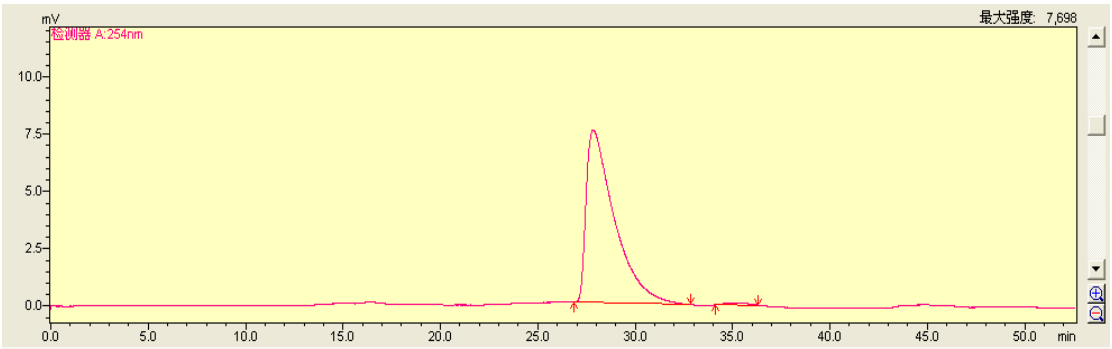
Recycle 6



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT26.744	26.744	1	3859606	31870	99.1826
2	RT35.682	35.682	2	31810	325	0.8174

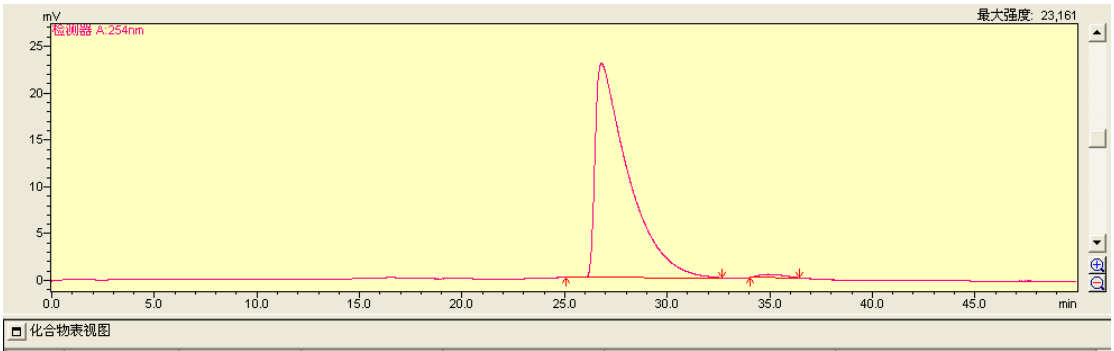
Recycle 7



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT27.837	27.837	1	761276	7540	98.9394
2	RT35.075	35.075	2	8160	102	1.0606

Recycle 8



化合物表视图

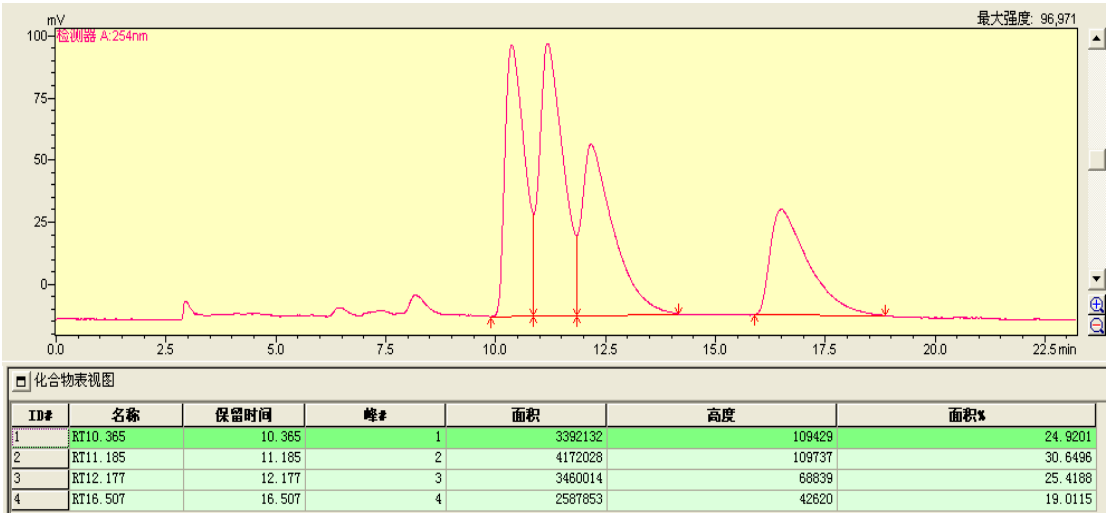
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT26.795	26.795	1	2548763	22827	98.8421
2	RT34.938	34.938	2	29858	358	1.1579

Table S2. Reusability of catalyst **8** for the DKR-ATH of 2-(benzyloxy)-3-oxo-3-phenylpropanoyl)phosphonite as a substrate.[a]

Entry	**1**	**2**	**3**	**4**	**5**	**6**	**7**
Yield [%]	99	97	95	95	93	92	90
ee [%]	99	99	99	99	98	98	98

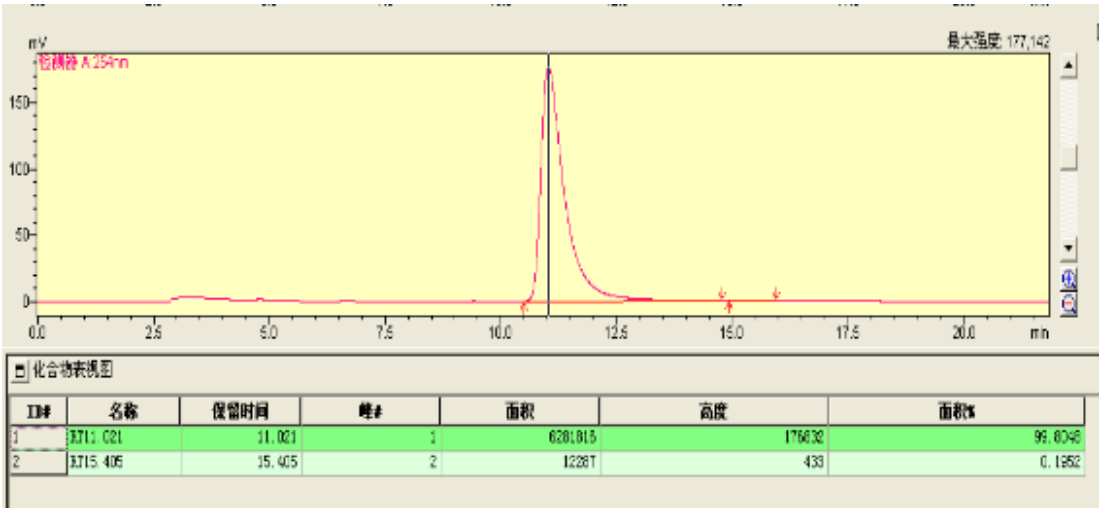
[a] Reaction conditions: catalyst **6** (196.80 mg), K_2CO_3 (138.0 mg, 1.0 mmol), HCO_2Na (680.0 mg, 10.0 mmol), iodoacetophenones (1.0 mmol), aryne (1.10 mmol), and 40.0 mL of the mixed solvents (H_2O/MeOH v/v = 1/3), reaction temperature (60 ℃), reaction time (16 h).

Figure S10. R Reusability of catalyst **8** for the DKR-ATH of 2-(benzyloxy)-3-oxo-3-phenylpropanoyl)phosphonite as a substrate.



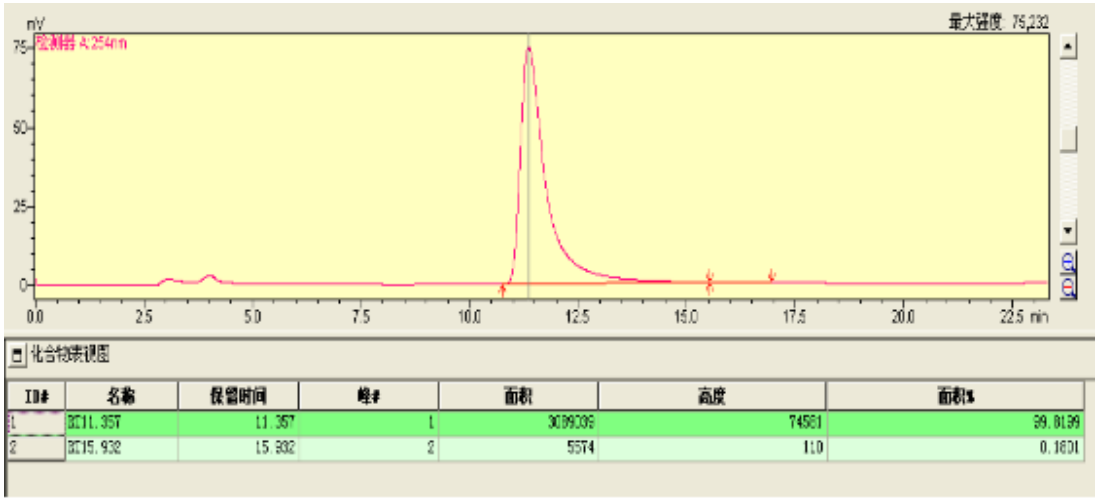
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT10.365	10.365	1	3392132	109429	24.9201
2	RT11.185	11.185	2	4172028	109737	30.6496
3	RT12.177	12.177	3	3460014	68839	25.4188
4	RT16.507	16.507	4	2587853	42620	19.0115

Recycle 2



ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT11.021	11.021	1	6281815	176632	99.8048
2	RT15.405	15.405	2	12287	433	0.1952

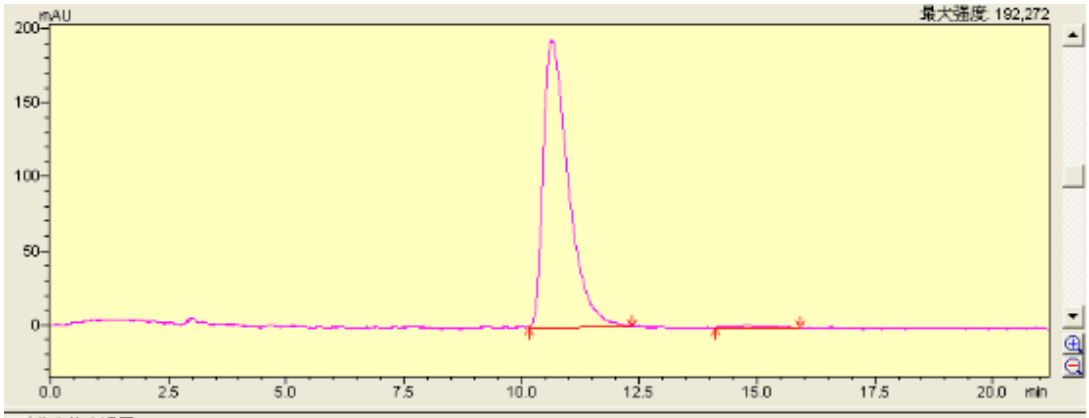
Recycle 3



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	BC11.357	11.357	1	3039039	74581	99.8199
2	BC15.932	15.932	2	5574	110	0.1831

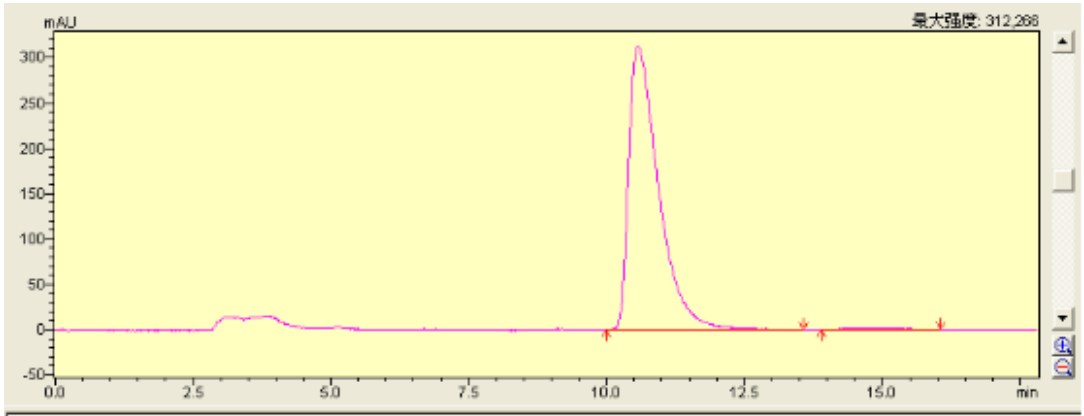
Recycle 4



化合物表视图

ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	10.639	7177520	98.7877	193682	99.1524
2	2	14.812	88083	1.2123	1656	0.8476

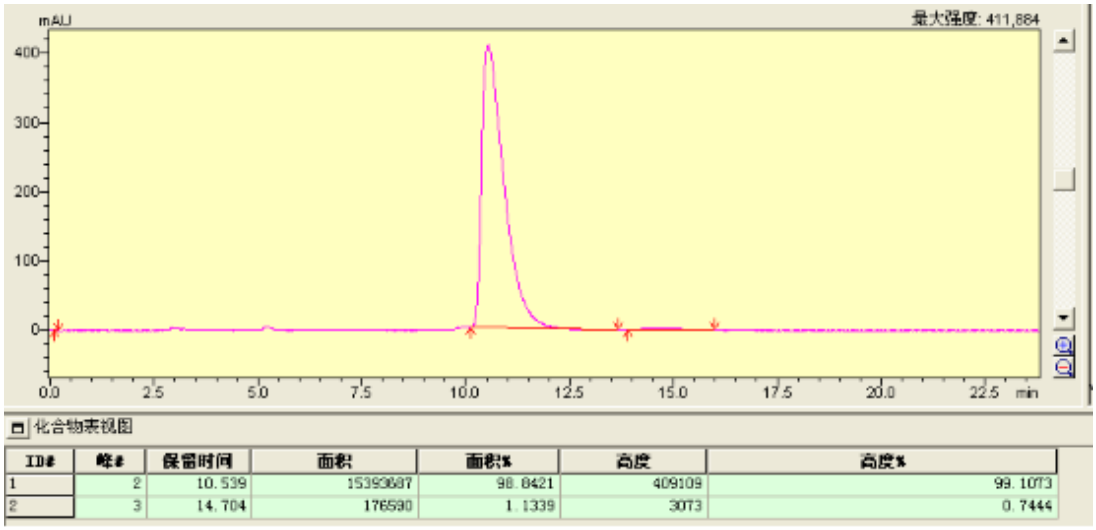
Recycle 5



化合物表视图

ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	10.580	11760874	98.9412	312304	99.2685
2	2	14.673	125855	1.0588	2301	0.7315

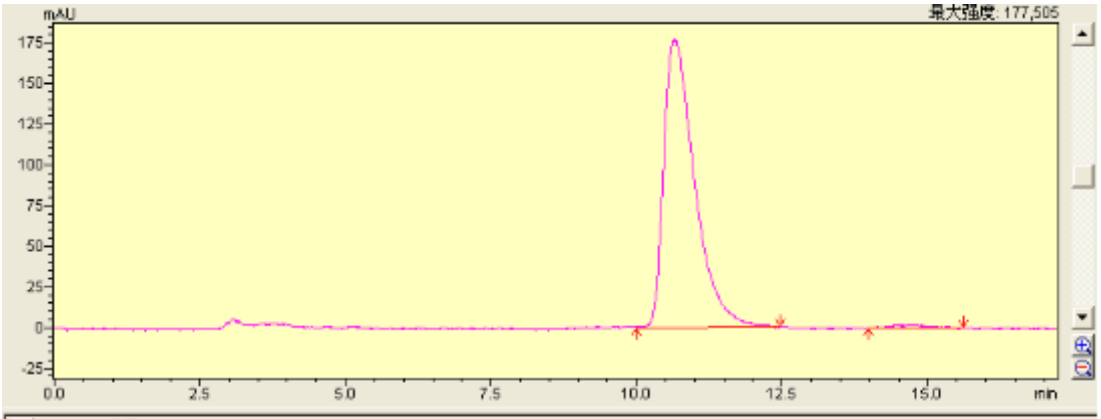
Recycle 6



化合物表视图

ID#	峰#	保留时间	面积	面积%	高度	高度%
1	2	10.539	15393687	98.8421	409109	99.1073
2	3	14.704	176590	1.1339	3073	0.7444

Recycle 7

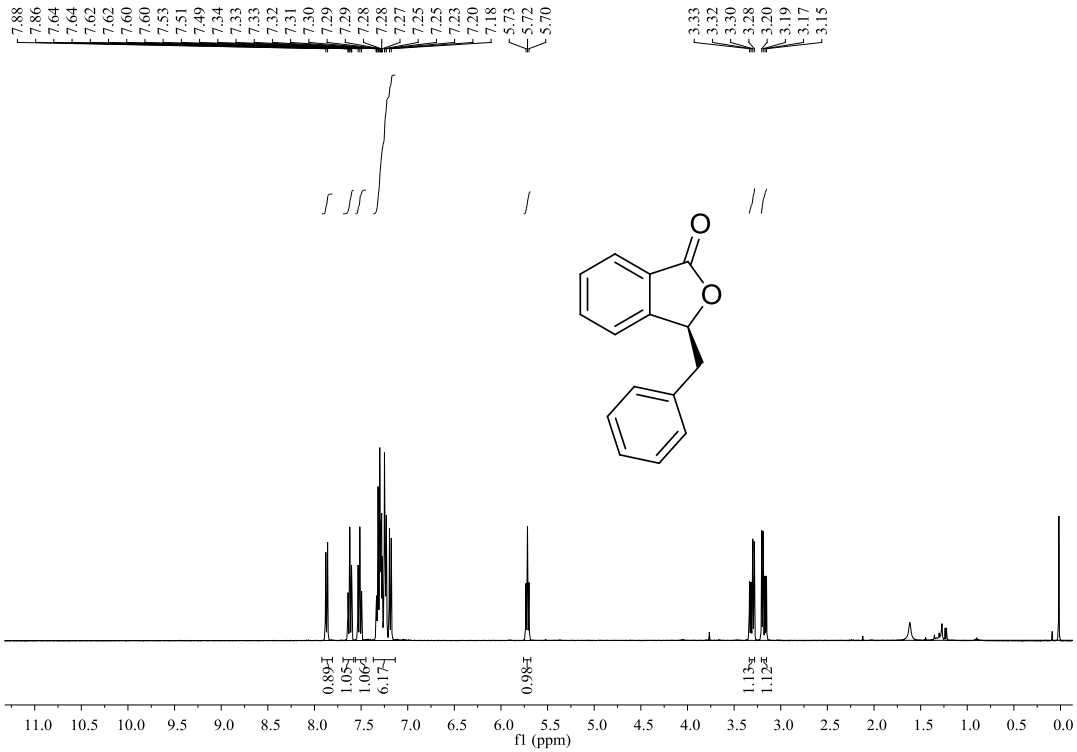


化合物表视图

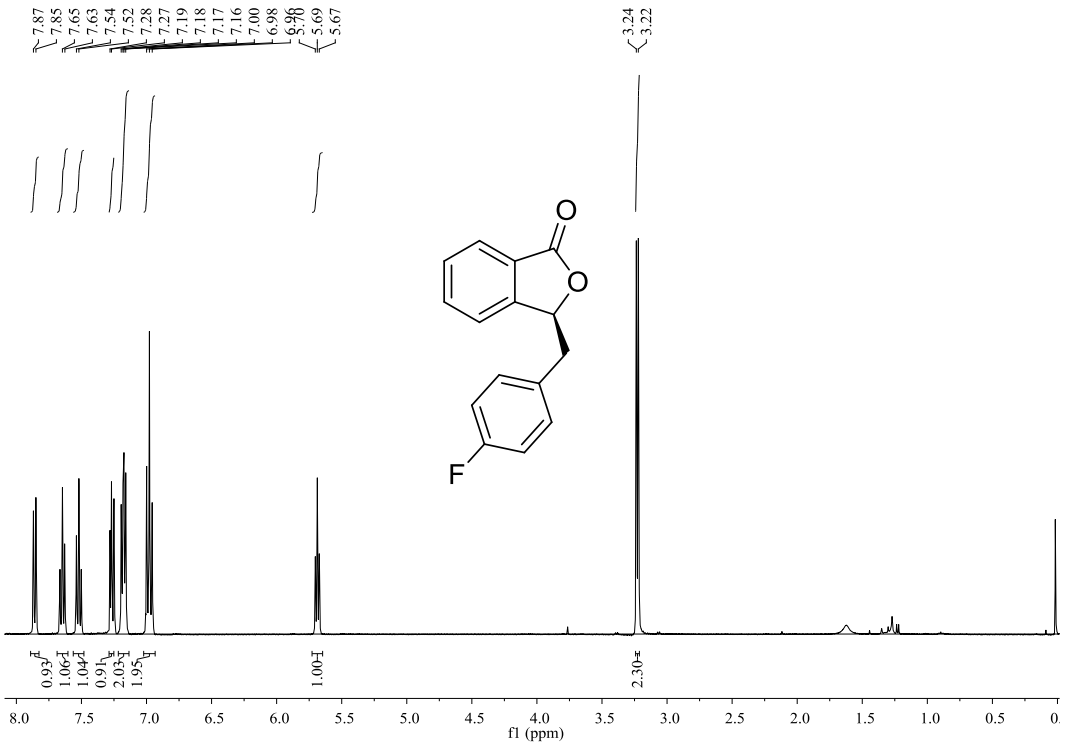
ID#	峰#	保留时间	面积	面积%	高度	高度%
1	1	10.651	6551862	98.7044	177369	98.8621
2	2	14.759	86003	1.2955	2042	1.1379

Figure S11. Characterizations of chiral products**.**

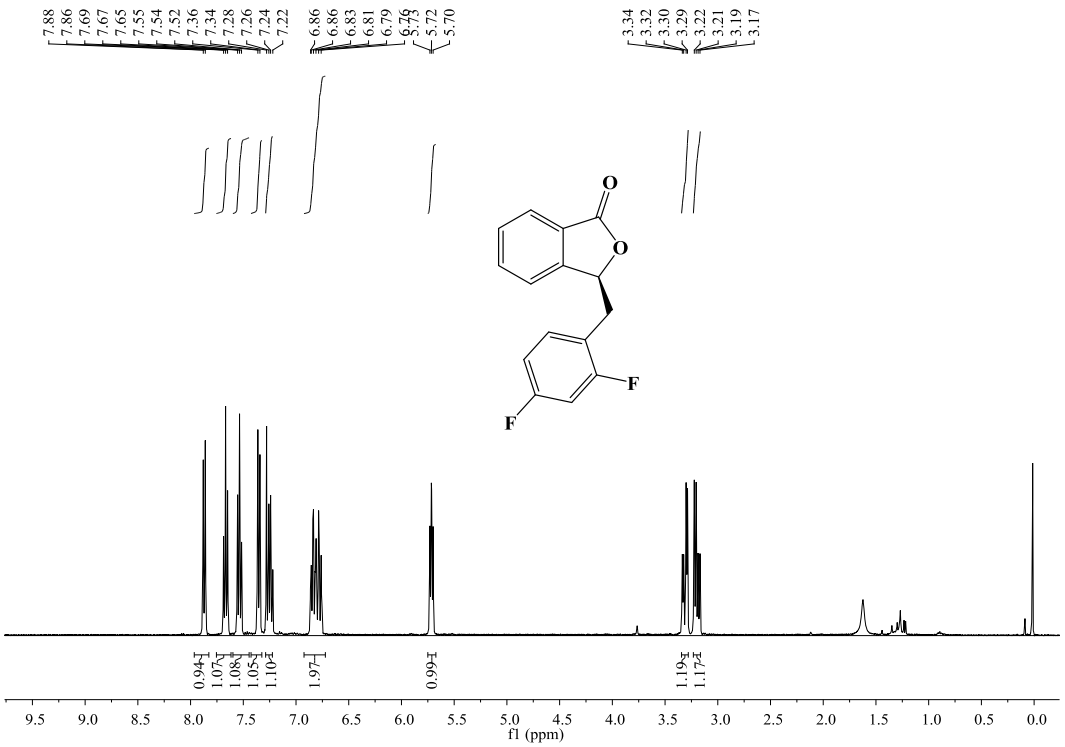
6a: (*S*)-3-benzylisobenzofuran-1(3*H*)-one.



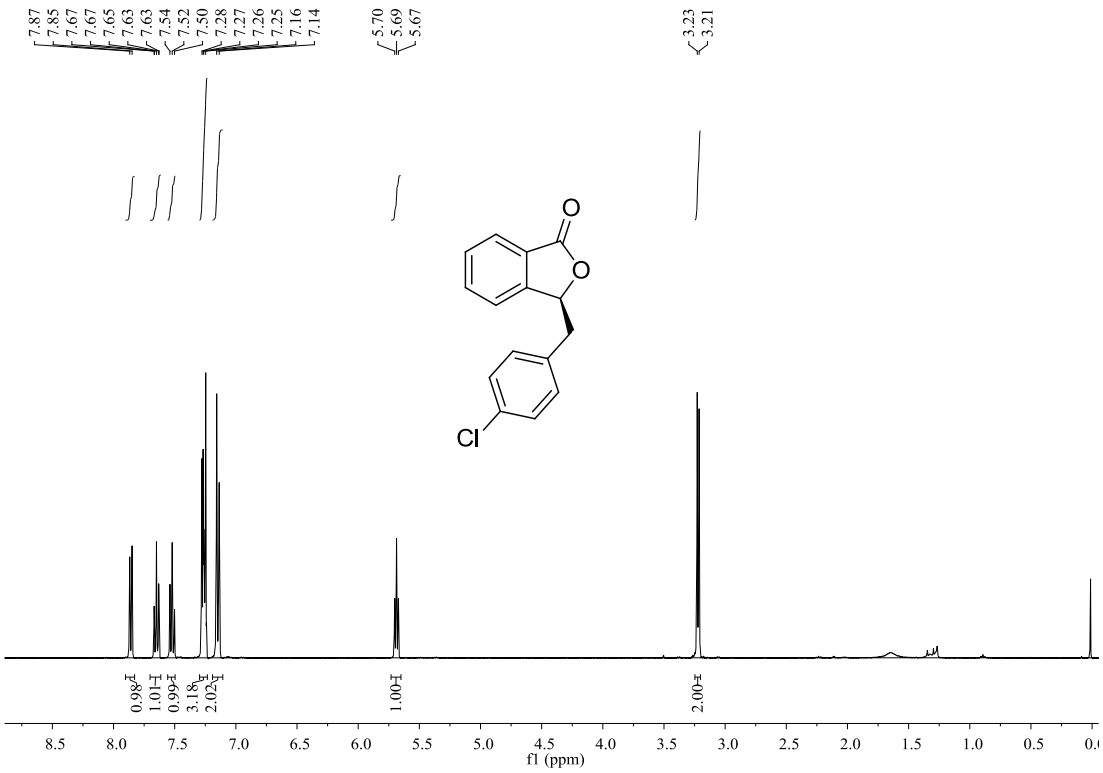
6b: (*S*)-3-(4-fluorobenzyl)isobenzofuran-1(3*H*)-one.



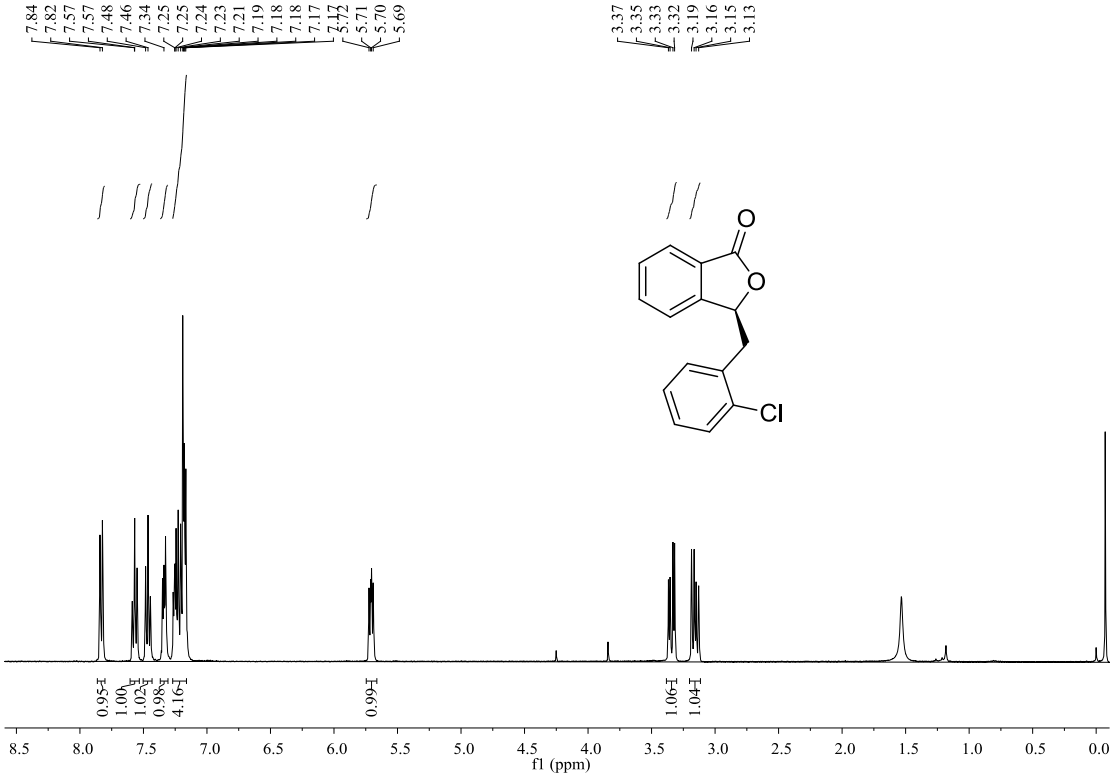
6c: (*S*)-3-(2,4-difluorobenzyl)isobenzofuran-1(3*H*)-one.



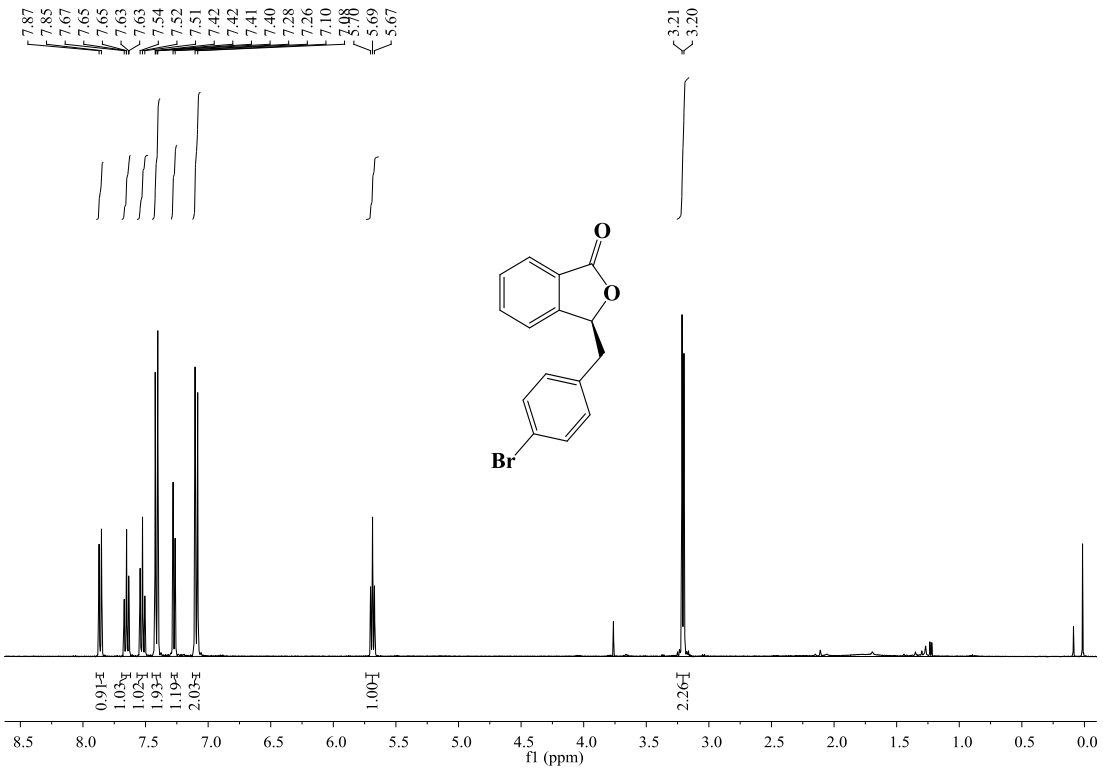
6d: (*S*)-3-(4-chlorobenzyl)isobenzofuran-1(3*H*)-one.



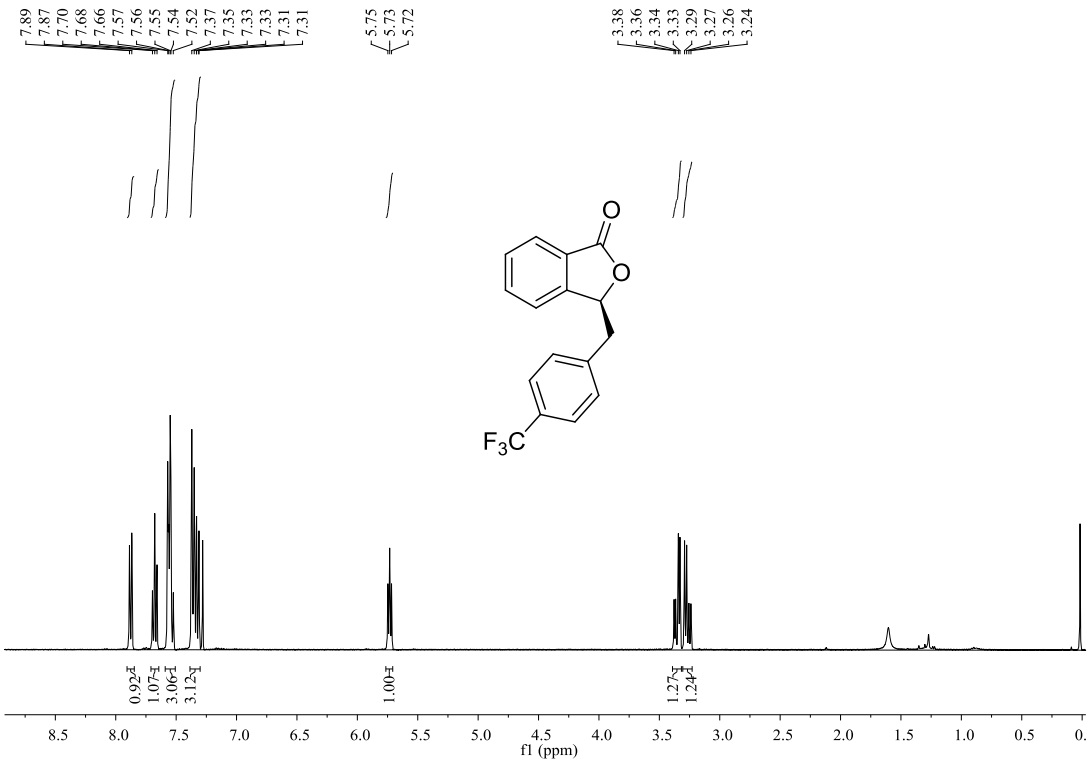
6e: (*S*)-3-(2-chlorobenzyl)isobenzofuran-1(3*H*)-one



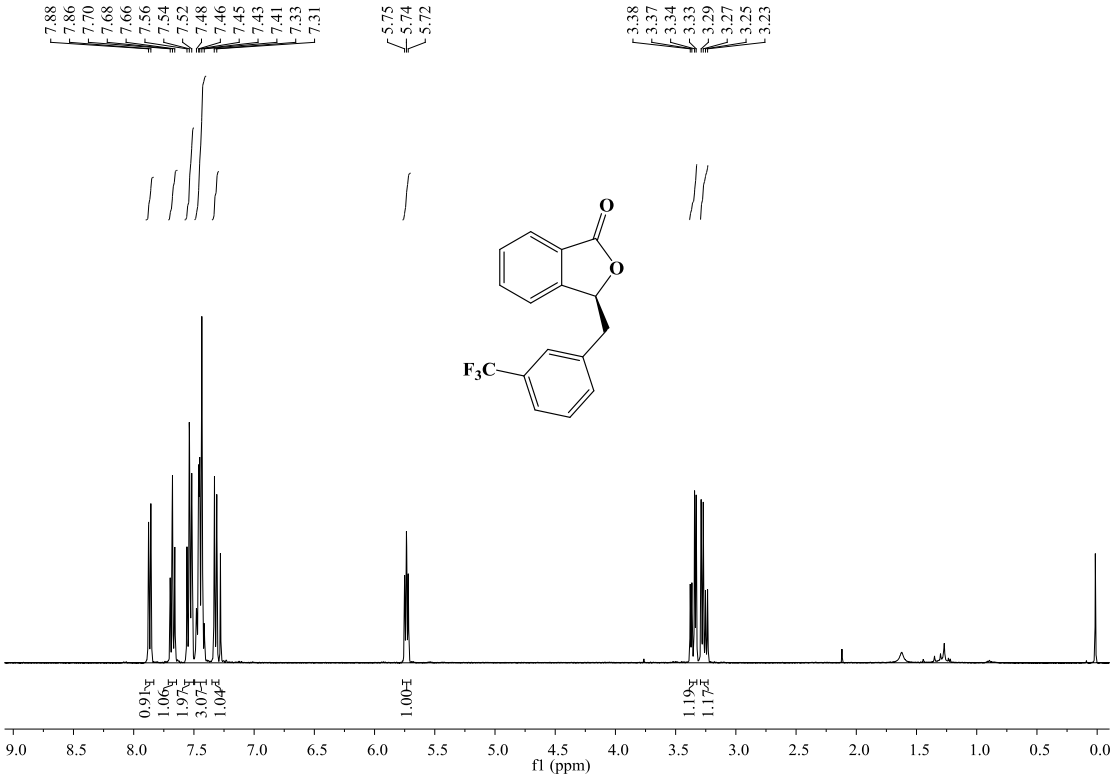
6f: (*S*)-3-(4-bromobenzyl)isobenzofuran-1(3*H*)-one.



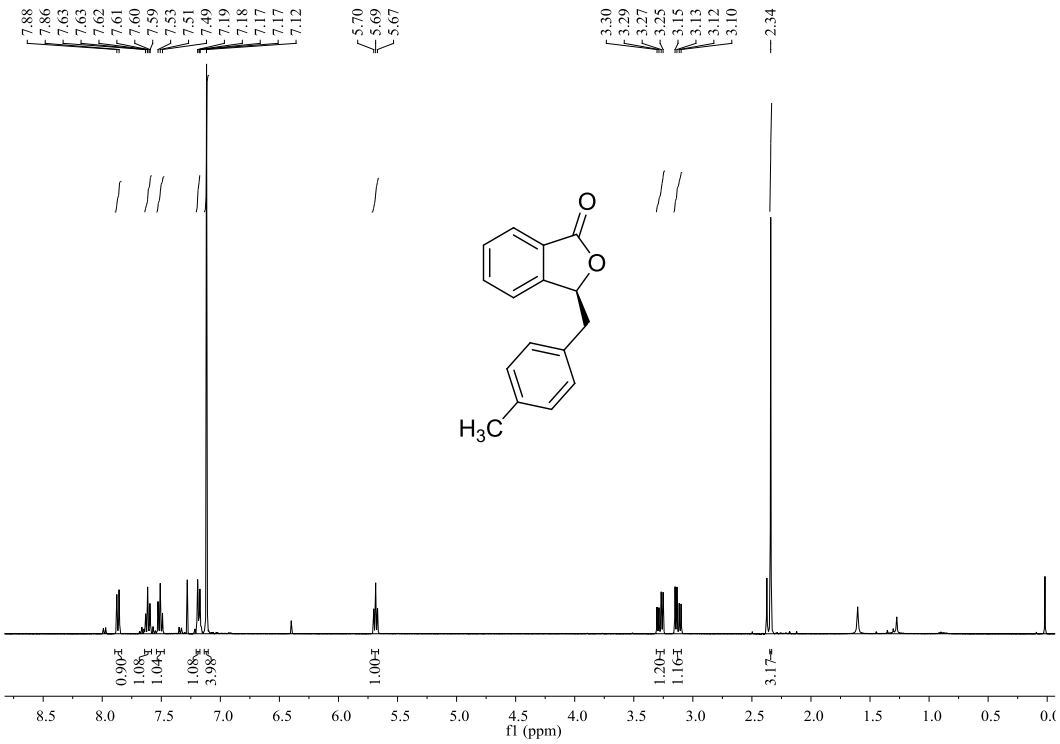
6g: (*S*)-3-(4-(trifluoromethyl)benzyl)isobenzofuran-1(3*H*)-one.



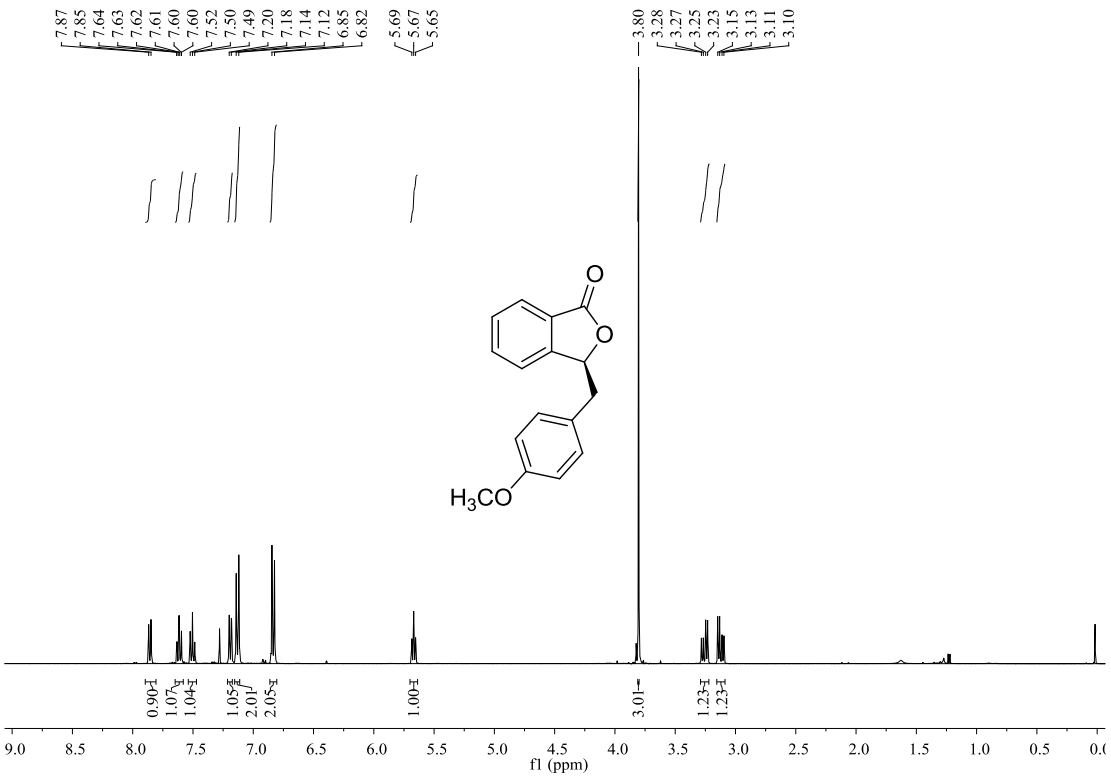
6h: (*S*)-3-(3-(trifluoromethyl)benzyl)isobenzofuran-1(3*H*)-one.



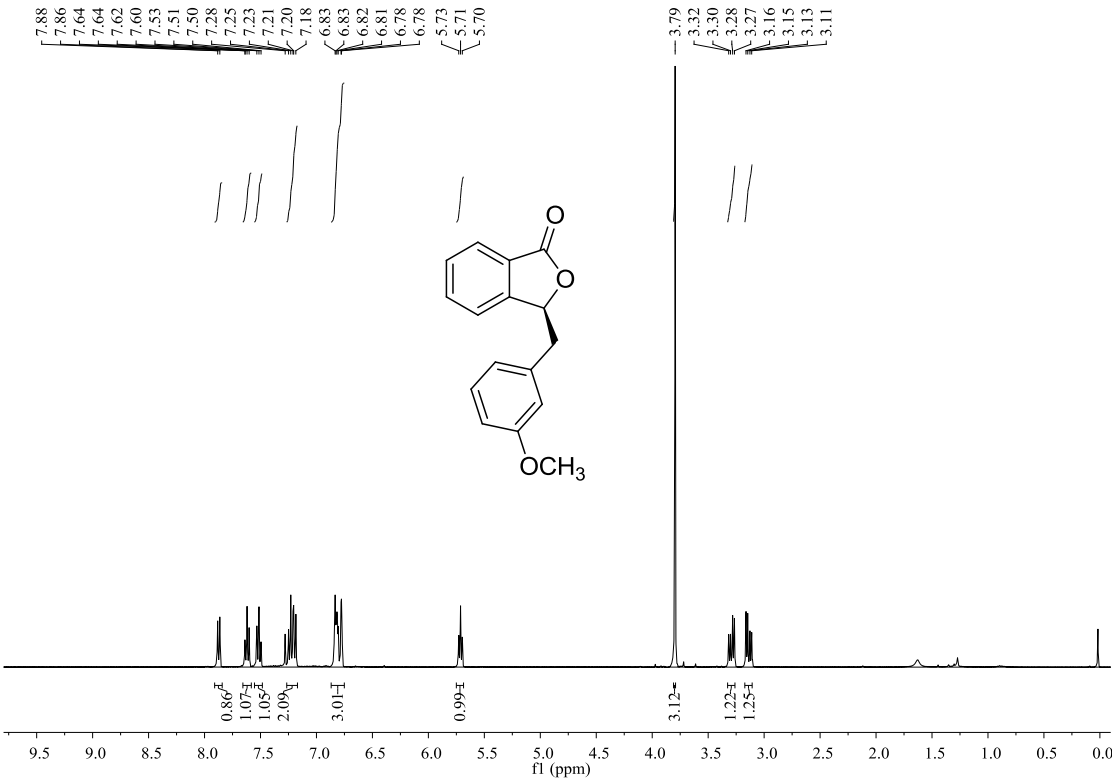
6i: (*S*)-3-(4-methylbenzyl)isobenzofuran-1(3*H*)-one.



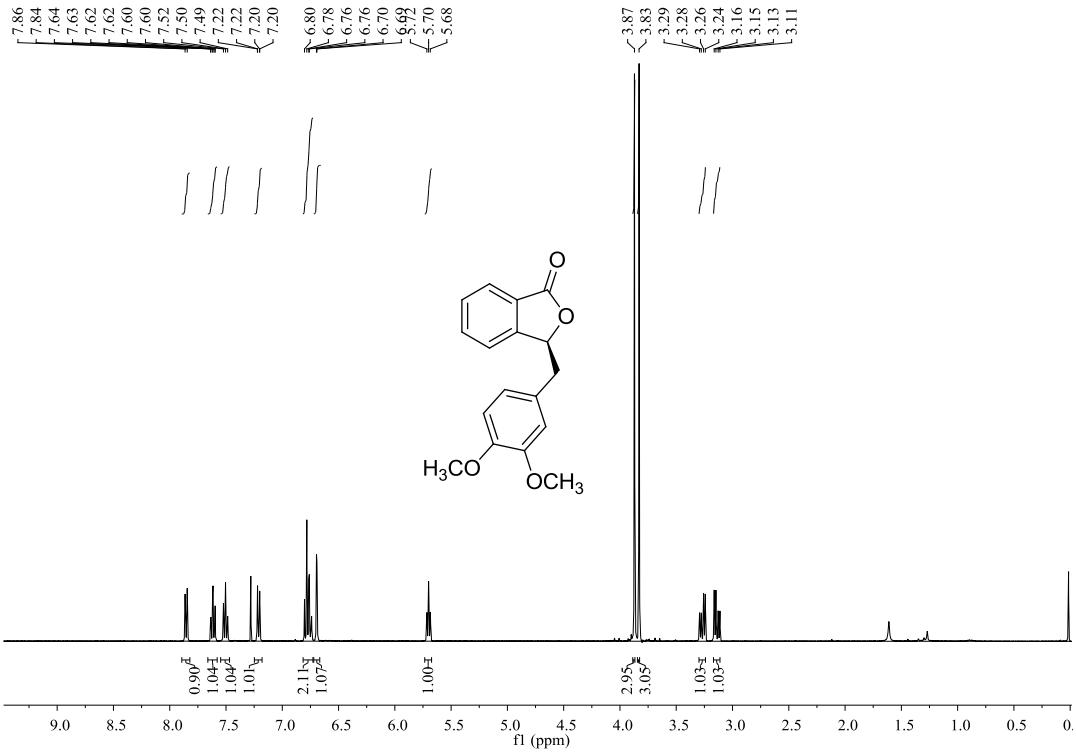
6j: (*S*)-3-(4-methoxybenzyl)isobenzofuran-1(3*H*)-one.



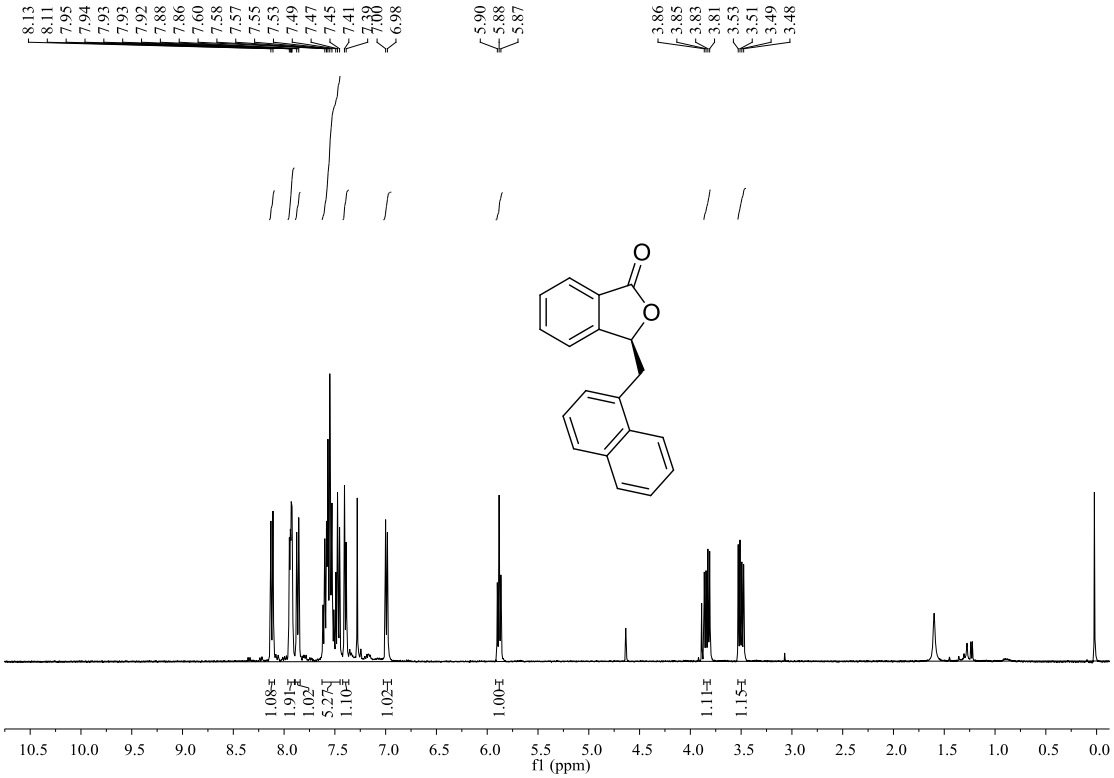
6k: (*S*)-3-(3-methoxybenzyl)isobenzofuran-1(3*H*)-one.



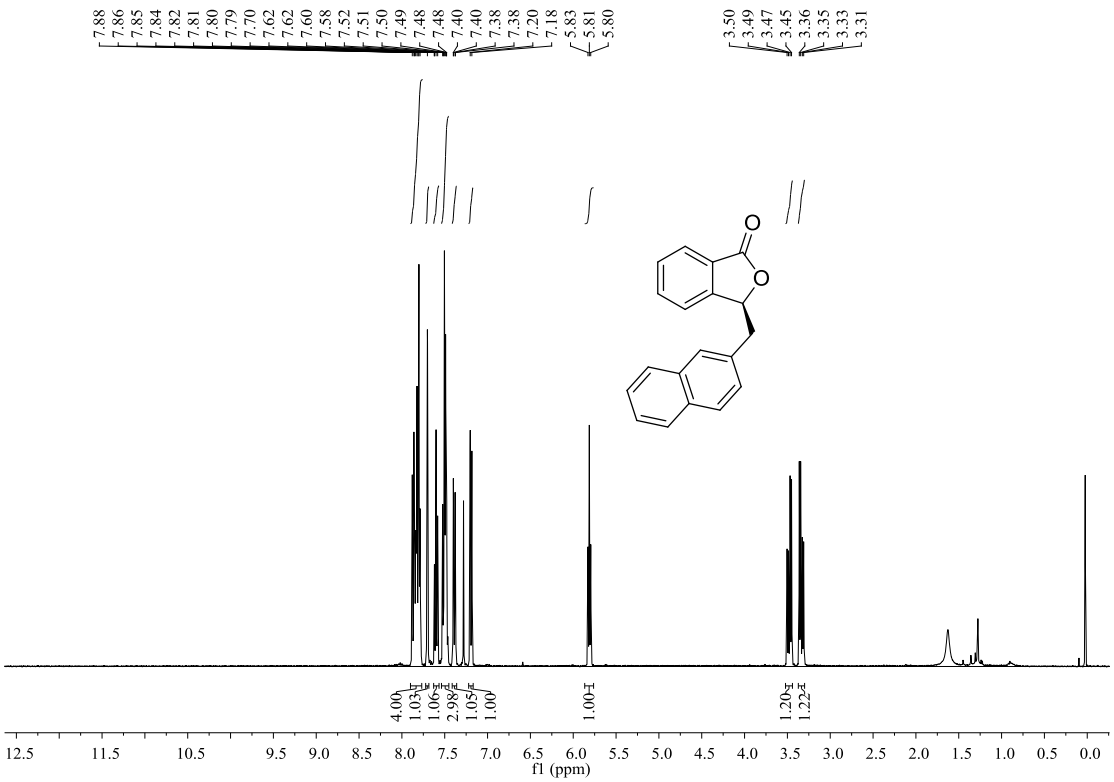
6l: (*S*)-3-(3,4-dimethoxybenzyl)isobenzofuran-1(3*H*)-one.



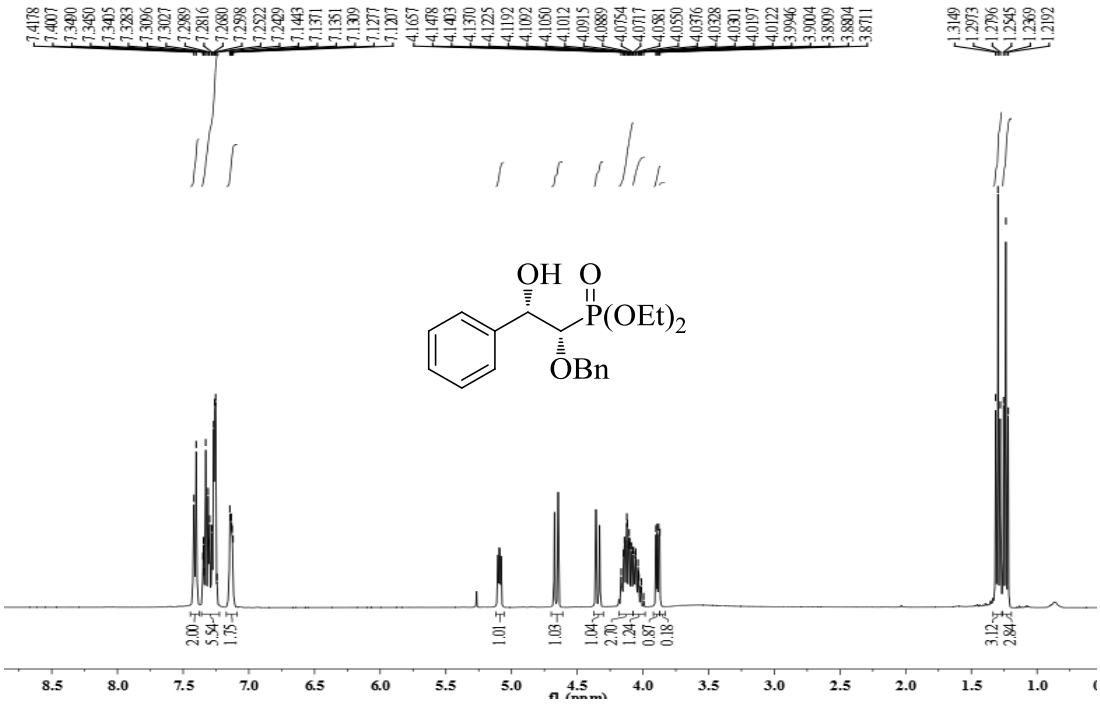
6m: (*S*)-3-(naphthalen-1-ylmethyl)isobenzofuran-1(3*H*)-one.



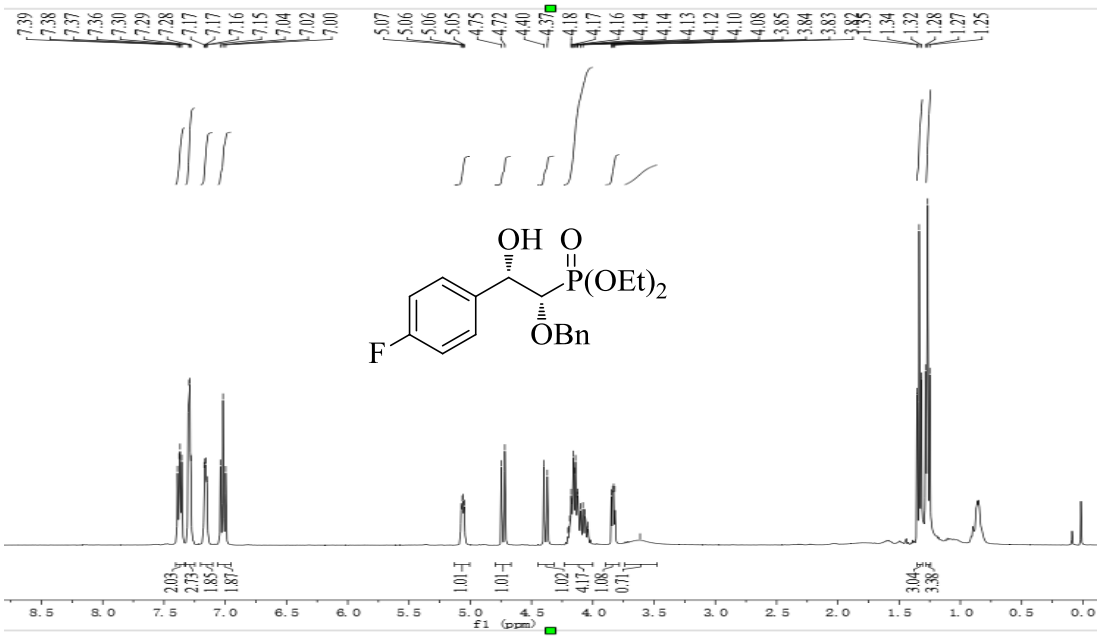
6n: (*S*)-3-(naphthalen-2-ylmethyl)isobenzofuran-1(3*H*)-one



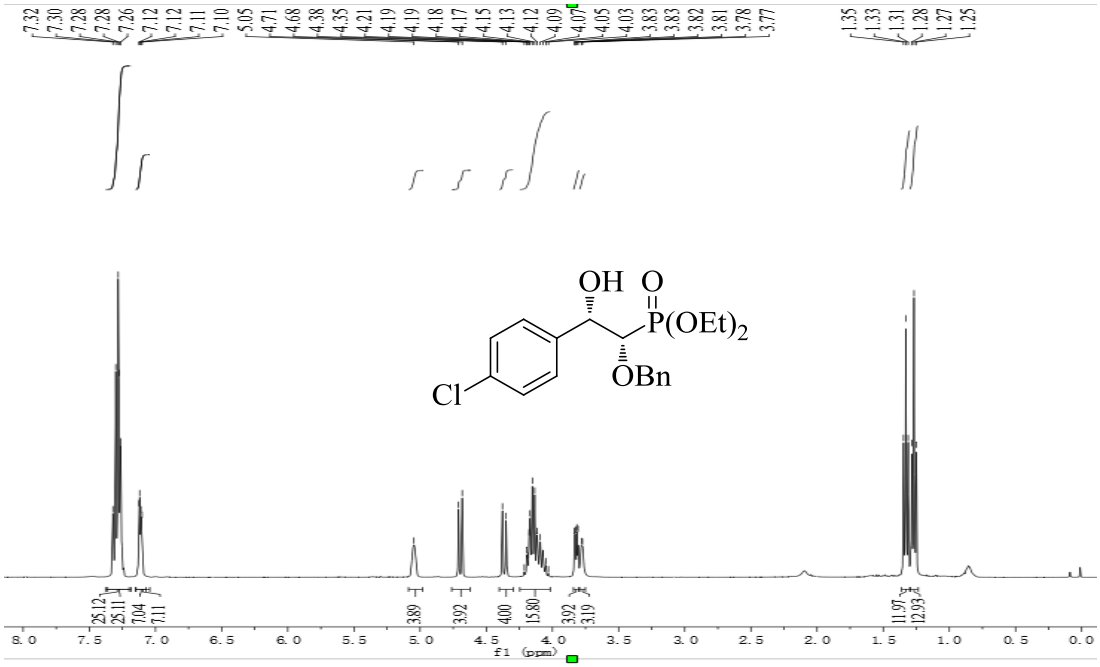
9a: Diethyl (1*R*,2*R*)-(1-benzyloxy-2-hydroxy-2-phenyl-ethyl)-phosphonate.



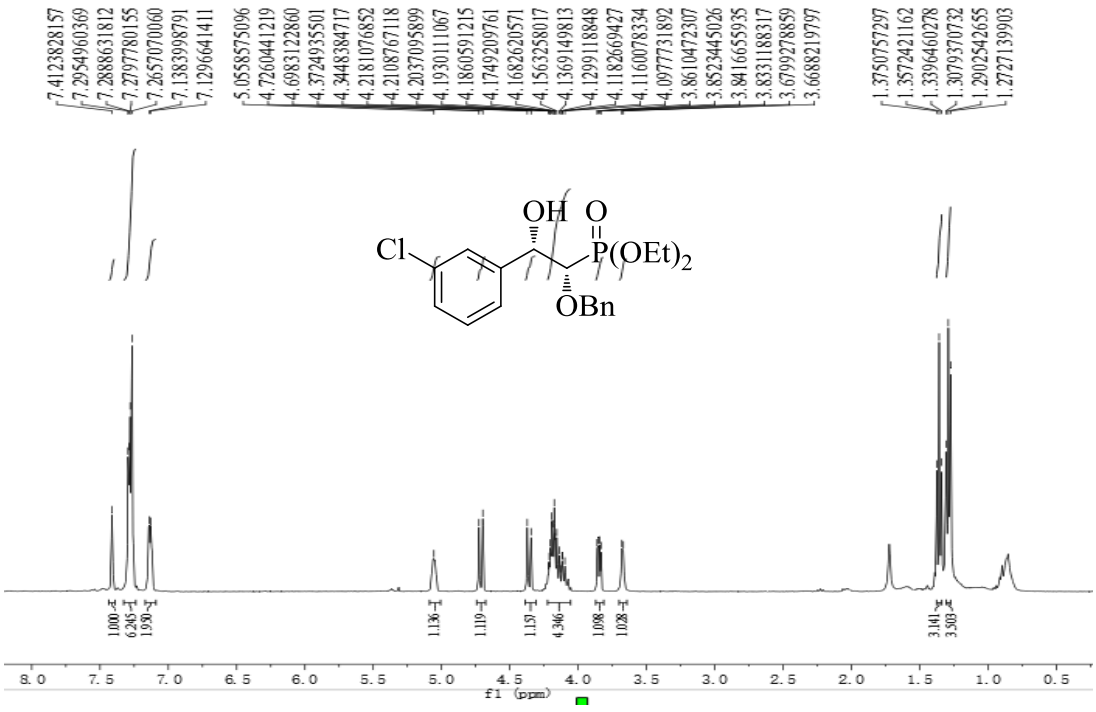
9b: Diethyl(1R,2R)-[1-benzyloxy-2-(4-fluoro-phenyl)-2-hydroxyethyl]phosphonate.



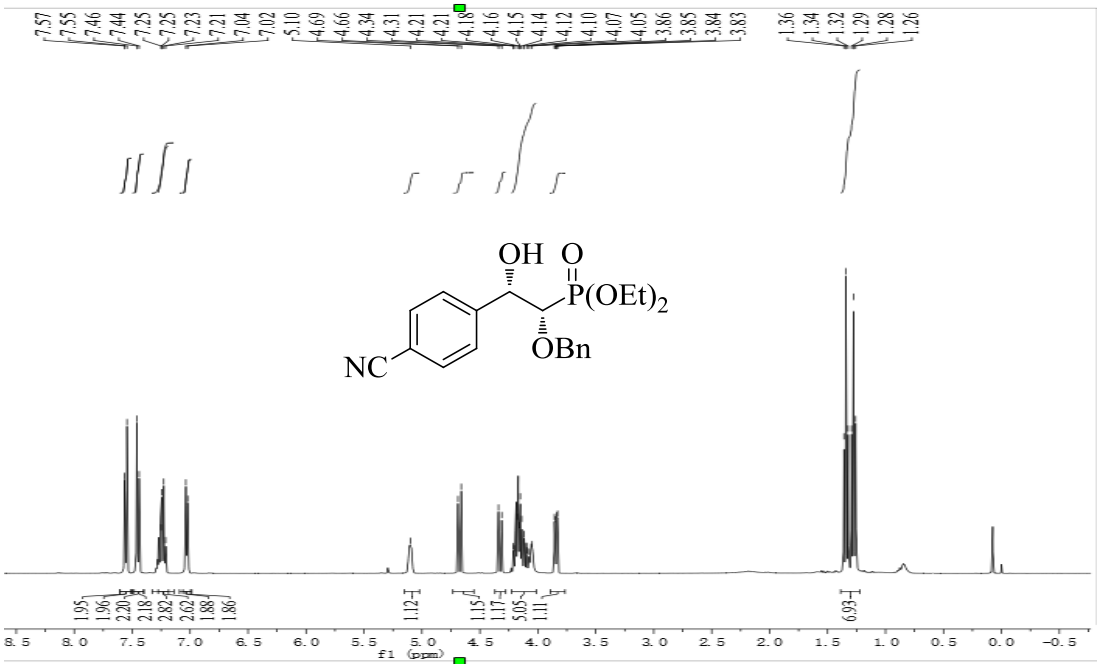
9c: Diethyl(1R,2R)-[1-benzyloxy-2-(4-chloro-phenyl)-2-hydroxyethyl]phosphonate.



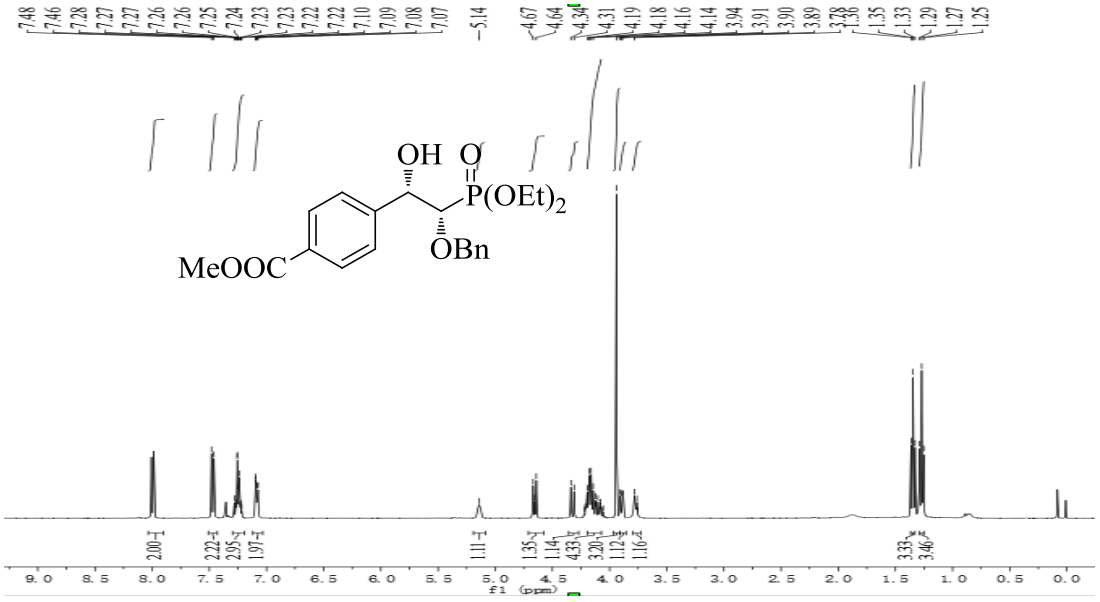
9d: Diethyl(1R,2R)-[1-benzyloxy-2-(3-chloro-phenyl)-2-hydroxyethyl]phosphonate.



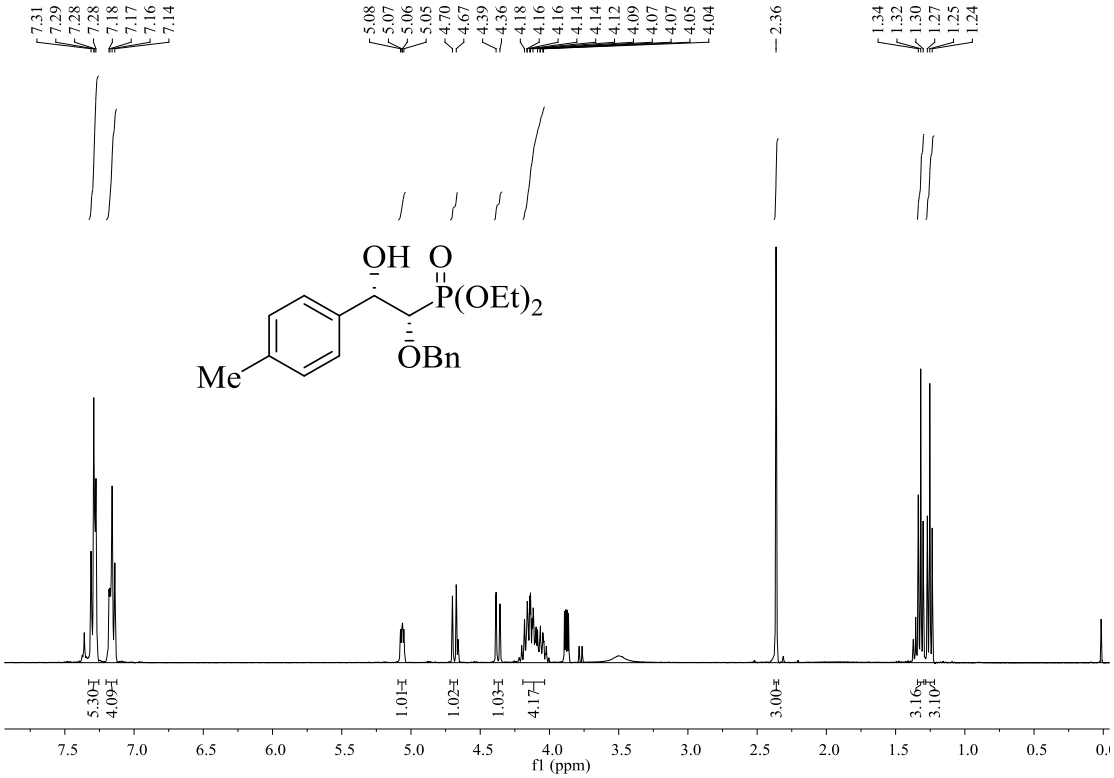
9e: Diethyl(1R,2R)-[1-benzyloxy-2-(4-cyano-phenyl)-2-hydroxyethyl]phosphonate.



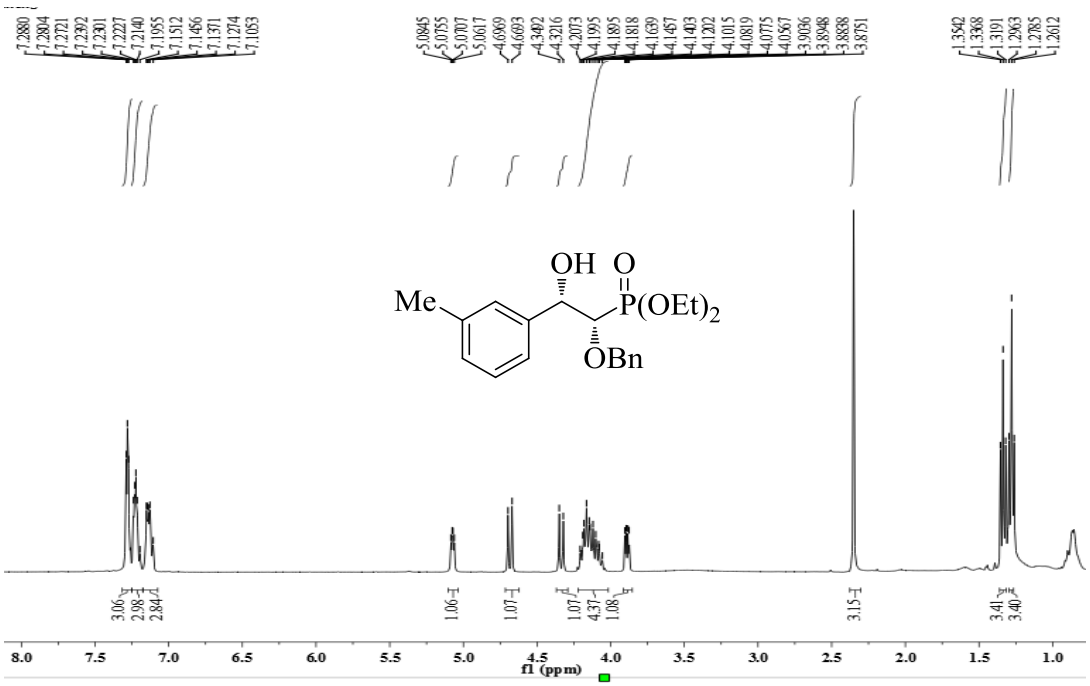
9f: Diethyl (1*R*,2*R*)-[1-benzyloxy-2-(4-carbomethoxy-phenyl)-2-hydroxy-ethyl]phosphonate.



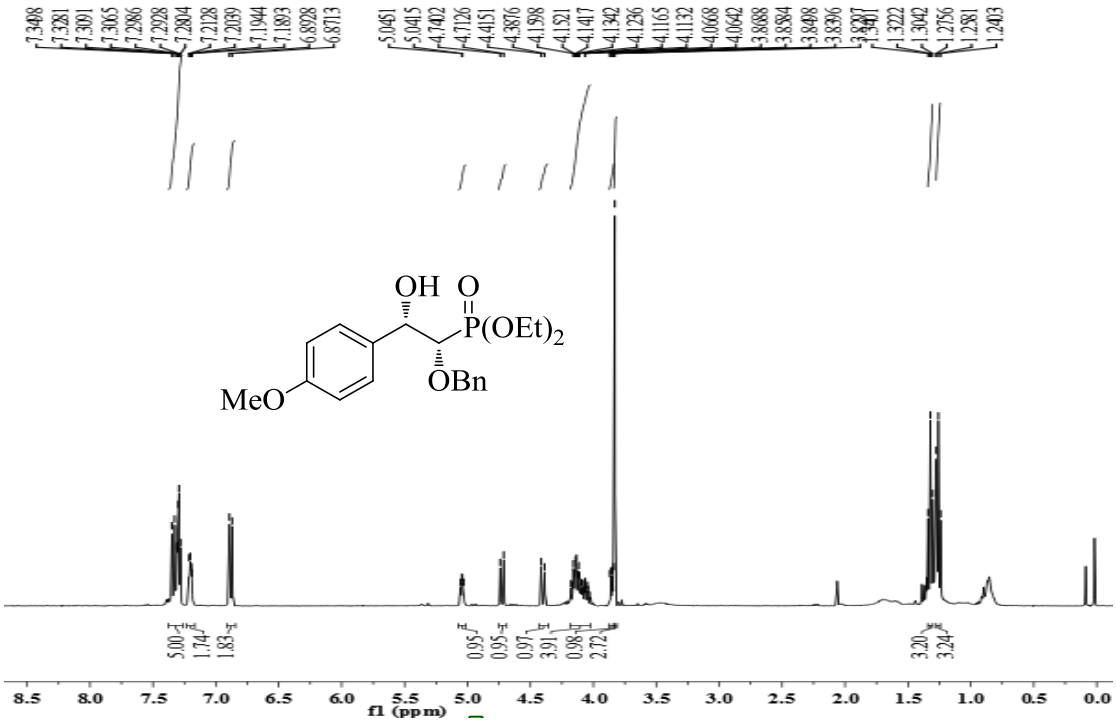
9g: Diethyl(1*R*,2*R*)-[1-benzyloxy-2-hydroxy-2-(p-tolyl)-ethyl] phosphonate.



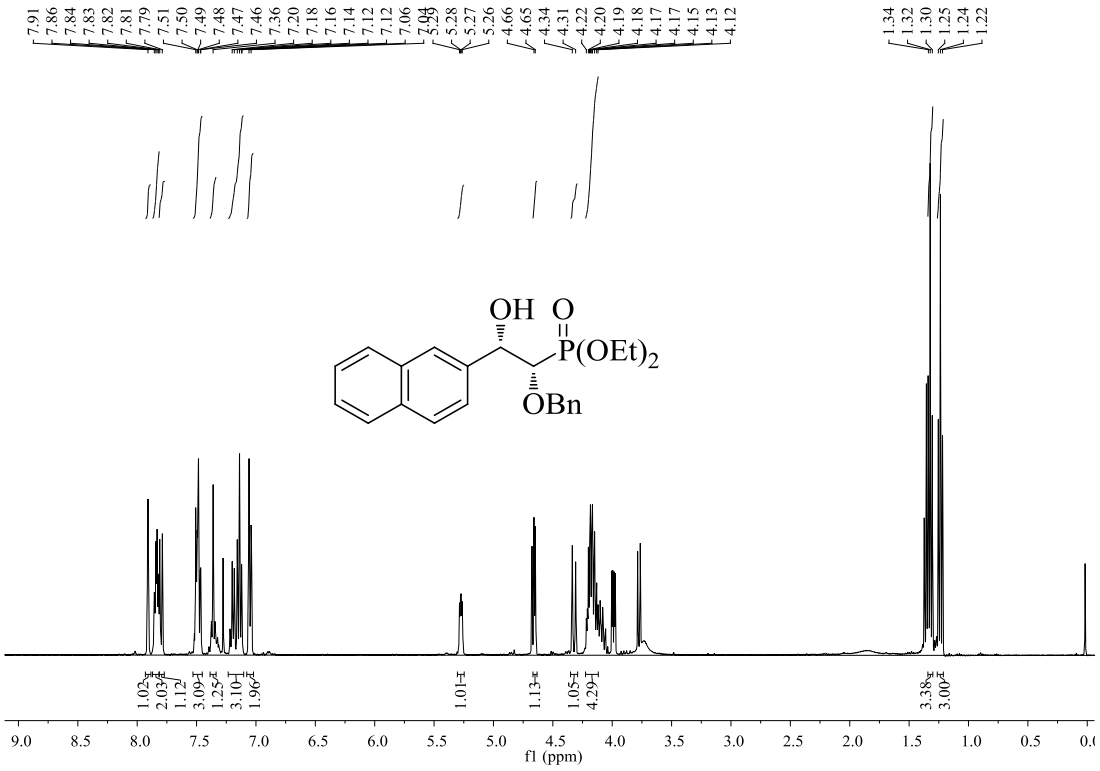
9h: Diethyl(1R,2R)-[1-benzyloxy-2-hydroxy-2-(m-tolyl)-ethyl] phosphonate.



9i: Diethyl(1*R*,2*R*)-[1-benzyloxy-2-hydroxy-2-(4-methoxy-phenyl)-ethyl]phosphonate.



9j: Diethyl (1*R*,2*R*)-[1-benzyloxy-2-(naphthalen-2-yl)-2-hydroxyethyl]phosphonate.



9k: Diethyl (1*R*,2*R*)-[1-benzyloxy-2-hydroxy-2-(thiophen-2-yl)-ethyl]phosphonate.