Supporting Information *for*

Asymmetric transfer hydrogenation–Sonogashira coupling one–pot enantioselective tandem reaction catalysed by a Pd(0)–Ru(III)/diamine–bifunctionalized Periodic Mesoporous Organosilica

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Experimental

1). General. All experiments, which are sensitive to moisture or air, were carried out under an Ar atmosphere using the standard Schlenk techniques. 3-mercaptopropyltriethoxysilane, 1,4-bis(triethyoxysilyl)ethane, 4-(2-(trimethoxysilyl)ethyl)benzene-1-sulfonyl chloride, 4-(methylphenylsulfonyl)-1,2-diphenylethylenediamine [(*S*,*S*)-TsDPEN], surfactant P123 (CH_2-$CH_2O)_{20}(CH_2(CH_3)CH_2O)_{70}(CH_2CH_2O)_{20}$), [mesityleneRu$Cl_2$]$_2$ were purchased from Sigma-Aldrich Company Ltd and used as received. 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). Preparation of PdCl2@mestyleneRuArDPEN-PMO (3'). In a typical synthesis, 2.0 g of structure-directing agent, pluronic P123 (CH_2-$CH_2O)_{20}(CH_2(CH_3)CH_2O)_{70}(CH_2CH_2O)_{20}$), was completely dissolved in a mixture of 80 mL of hydrochloric acid (0.2 N) and 6.0 g of KCl. The mixture was stirred at room temperature for 1.0 h. Subsequently, 6.39 g (18.00 mmol) of the silica precursor 1,2-bis(triethoxysilyl)ethane was added at 40 °C. After a pre-hydrolysis period of 60 minute, 0.50 g (1.00 mmol) of (*S*,*S*)-DPEN-$SO_2Ph(CH_2)_2Si(OMe)_3$ (**1**) and 0.24 g (1.00 mmol) of 3-mercaptopropyltriethoxysilane was added. The reaction mixture was stirred at 40 °C for 24 h and then aged at 100 °C for 24 h. The resulting solid was filtered, rinsed with excess ethanol, and then dried overnight on a filter. The surfactant template was removed by refluxing in acidic ethanol (400 mL per gram) for 24 h. The solid was filtered, rinsed with ethanol again, and then dried at 60 °C under reduced pressure overnight to afford SH@ArDPEN@PMO (**2**) (3.62 g) in the form of a white powder. The part of collected solids (1.0 g) was suspended in 40 mL of dry ethanol, and 116.2 mg (0.66 mmol) of $PdCl_2$ was added to the solution at ambient temperature. The resulting mixture was stirred for 12 h. The mixture was filtered through filter paper and then rinsed with excess water and CH_2Cl_2, and then dried at 60 °C under reduced pressure overnight to afford $PdCl_2$@ArDPEN@PMO as in the form of a yellow powder. The part of collected $PdCl_2$@ArDPEN@PMO (0.50 g) was suspended in 20 mL of dry CH_2Cl_2 again, and 87.0 mg (0.15 mmol) of [$RuCl_2$(mestylene)]$_2$ was added to the solution at ambient temperature. The resulting mixture was stirred for 12 h. The mixture was filtered through filter paper and then rinsed with excess water and CH_2Cl_2. After Soxhlet extraction for 12 h in CH_2Cl_2 to remove homogeneous and unreacted starting materials, the solid was dried at ambient temperature under vacuum overnight to afford catalyst **3'** (0.45 g) as a brown powder.

Figure S1. FT-IR spectra of **2** and catalyst **3.**

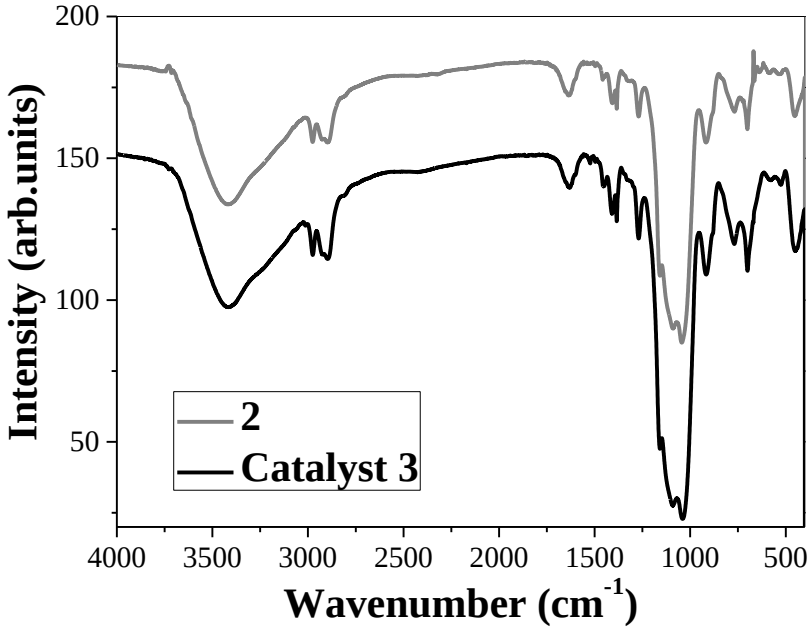


Figure 2. Solid-state ^{29}Si CP MAS NMR spectra of **2** and catalyst **3**.

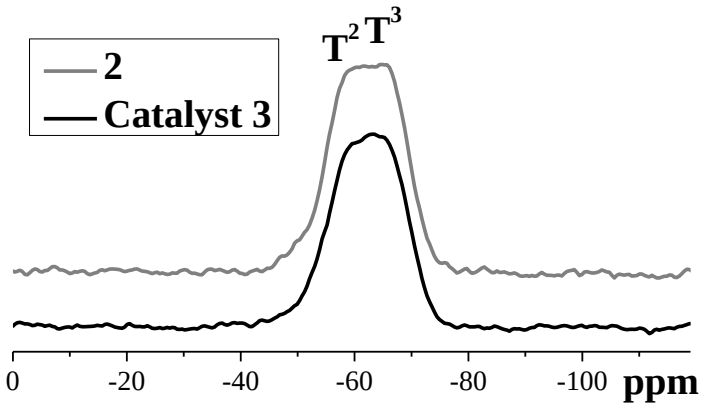


Figure S3. Small-angle powder XRD patterns of **2** and catalyst **3**.

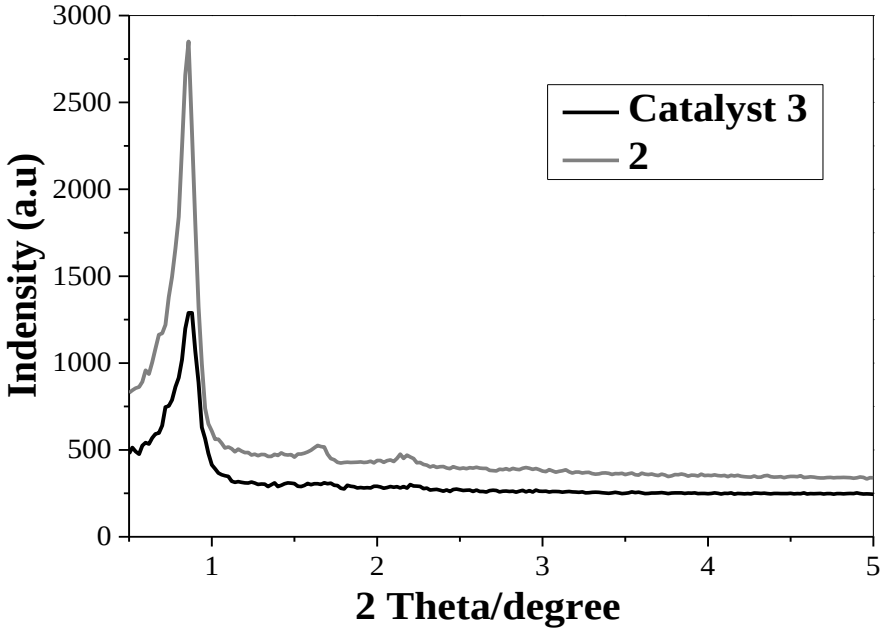


Figure S4. TEM images of catalyst 3 viewed along the [001] directions.

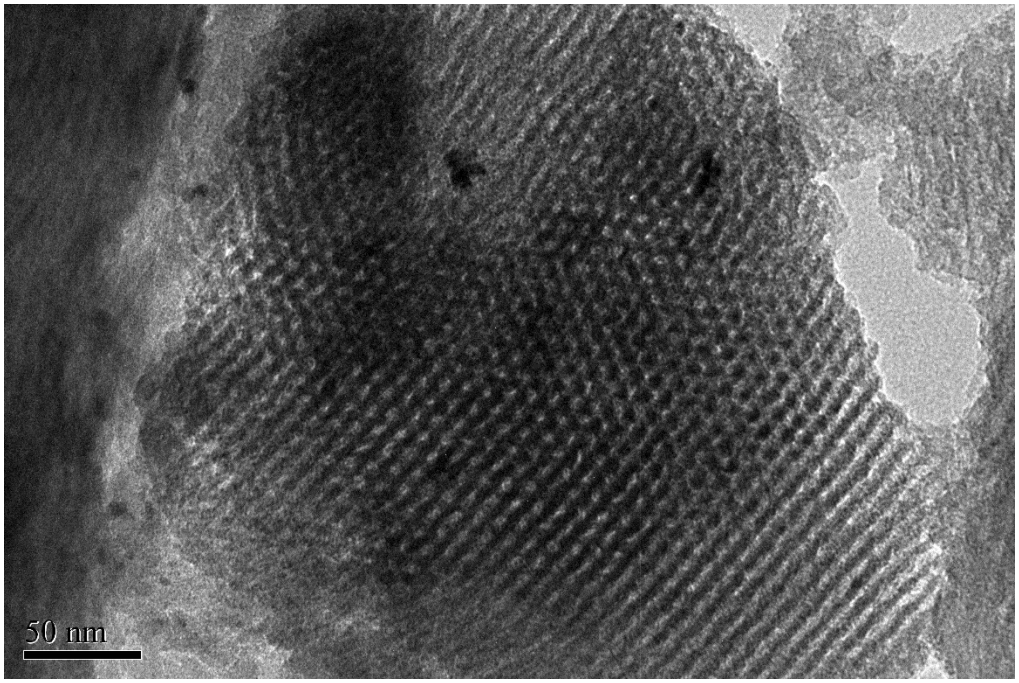
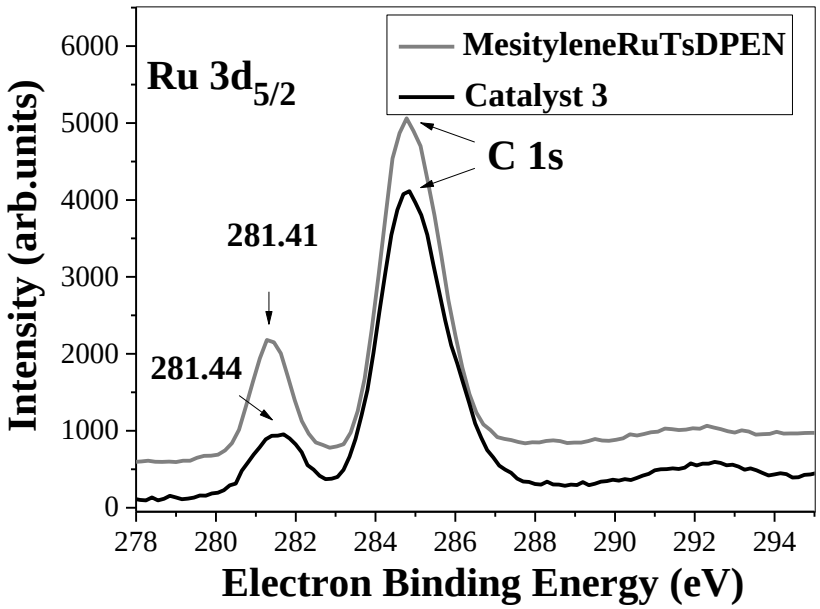


Figure S5. XPS spectra of the homogeneous MesityleneRuArDPEN and catalyst **3** for Ru species, and catalyst **3** for Pd species.



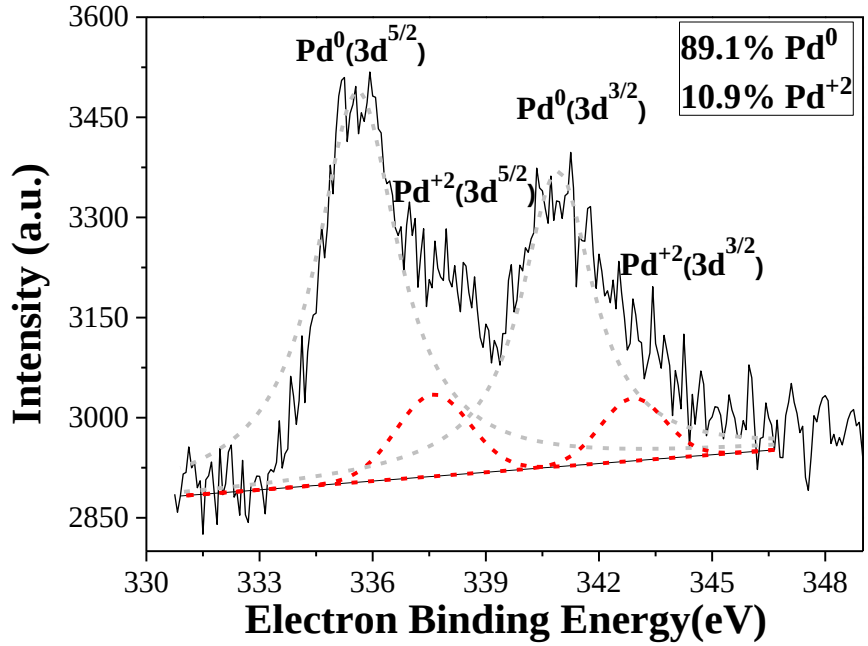


Figure S6. Time course for one-pot transformation of 4-iodoacetophenone and ethynylbenzene with catalyst **3' (**65°C, cat. = 2.6 mmol % of Ru and 2.0 mmol % or Pd, based on ICP analysis)

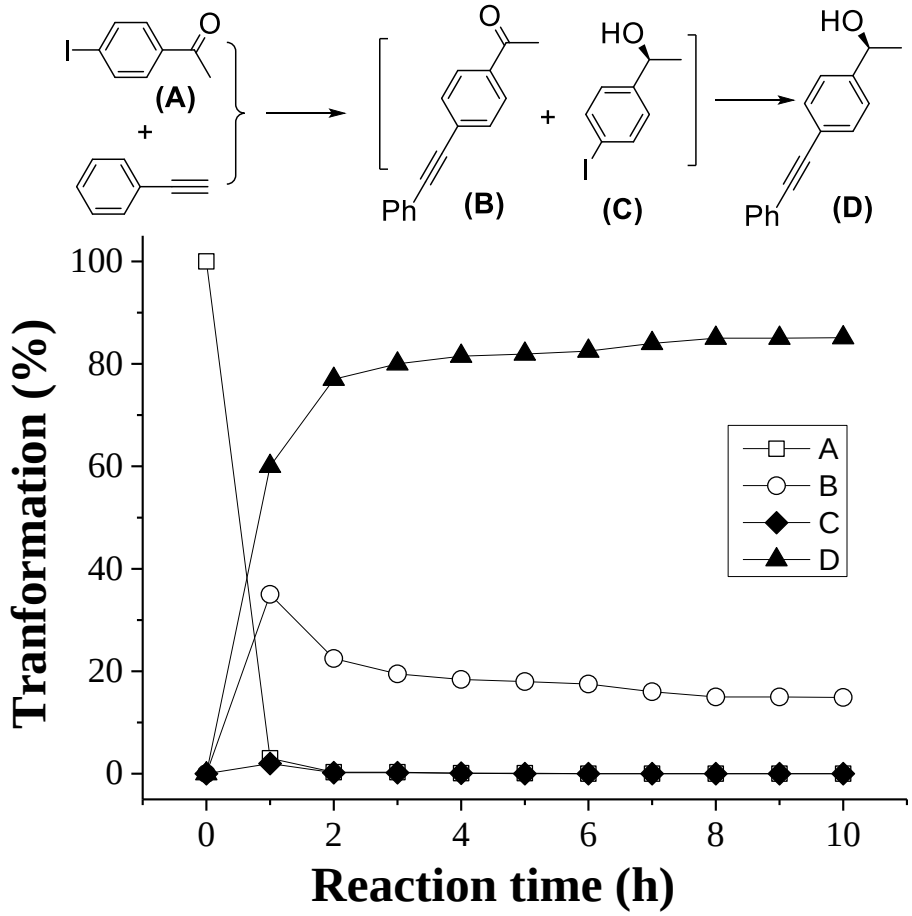
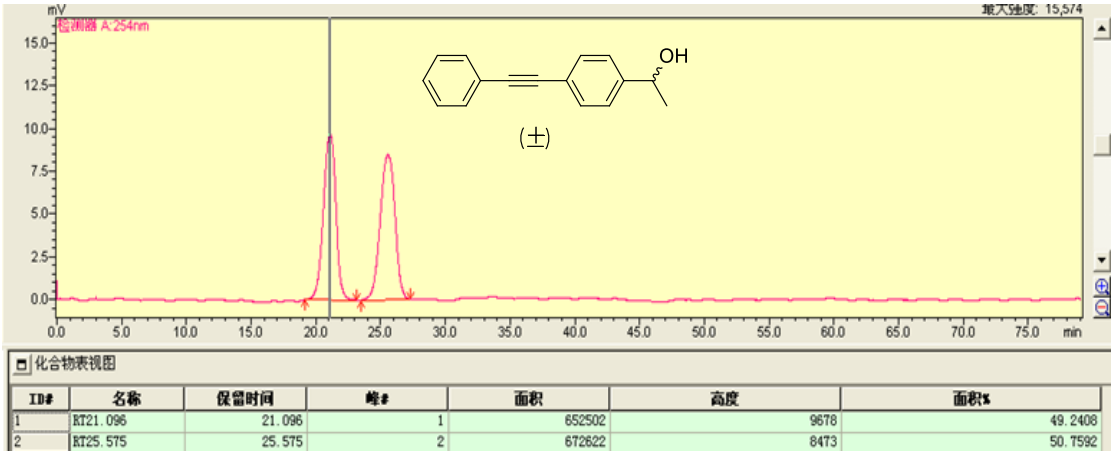
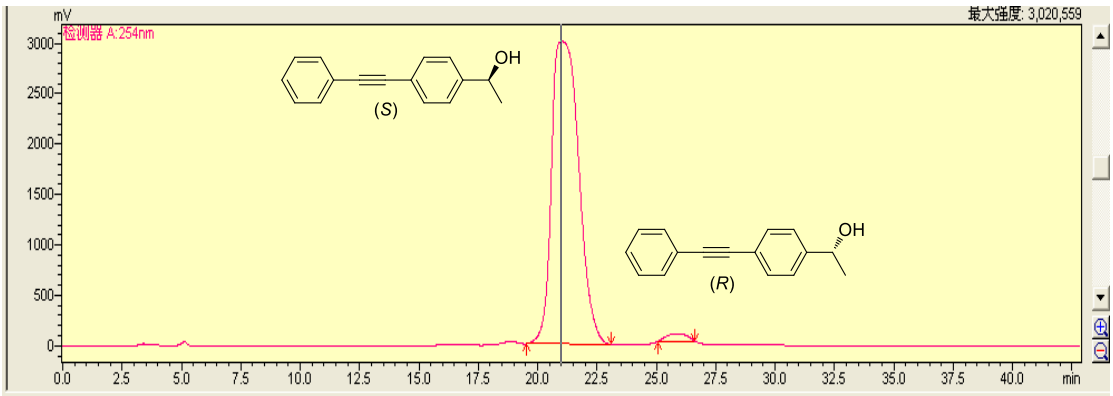


Figure S7. The ATH–Sonogashira coupling one-pot enantioselective cascade reactions.

(*S*)-1-(4-(phenylethynyl)phenyl)ethanol. (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1 mL/min, 20 ºC).

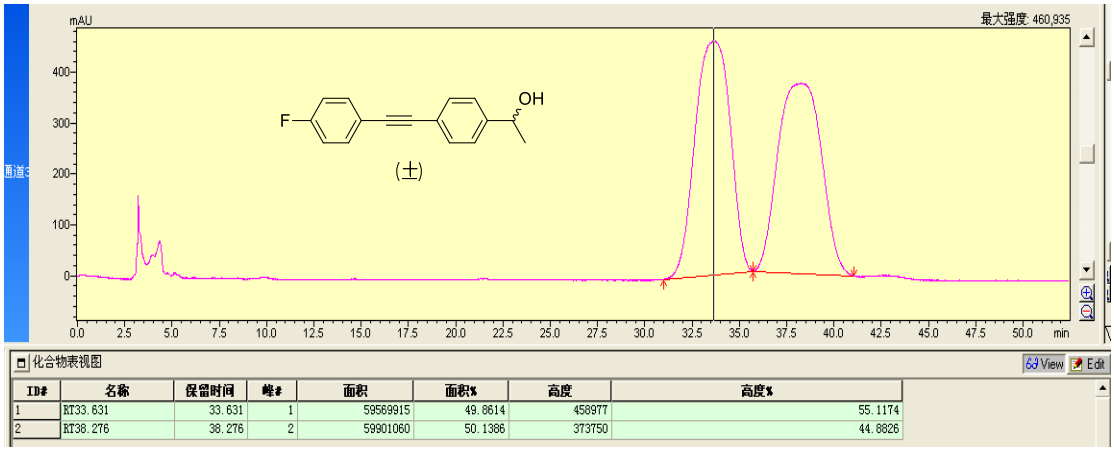


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.096	21.096	1	652502	9678	49.2408
2	RT25.575	25.575	2	672622	8473	50.7592



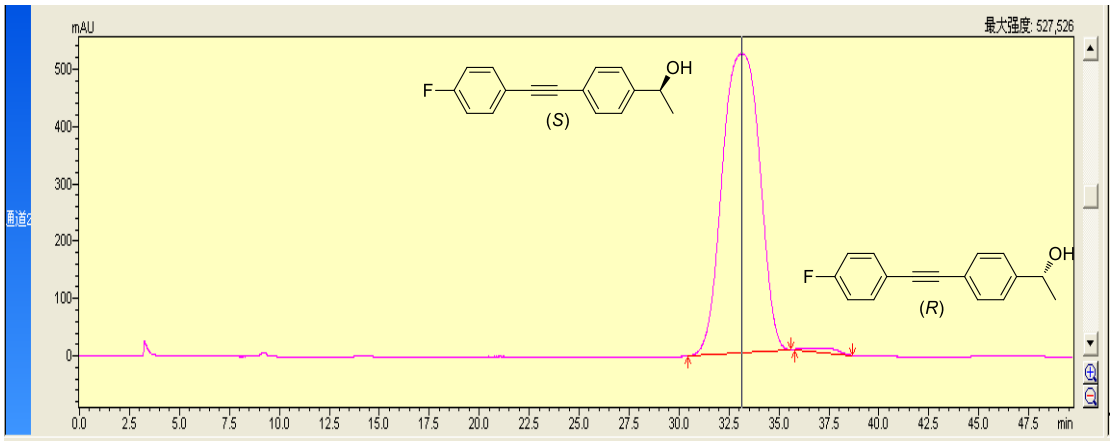
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT20.988	20.988	1	239633377	3003523	98.1510
2	RT25.883	25.883	2	4514253	75093	1.8490

(*S*)-1-(4-((4-fluorophenyl)ethynyl)phenyl)ethanol. (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 99/1, flow rate = 1 mL/min, 20 ºC).



化合物表视图

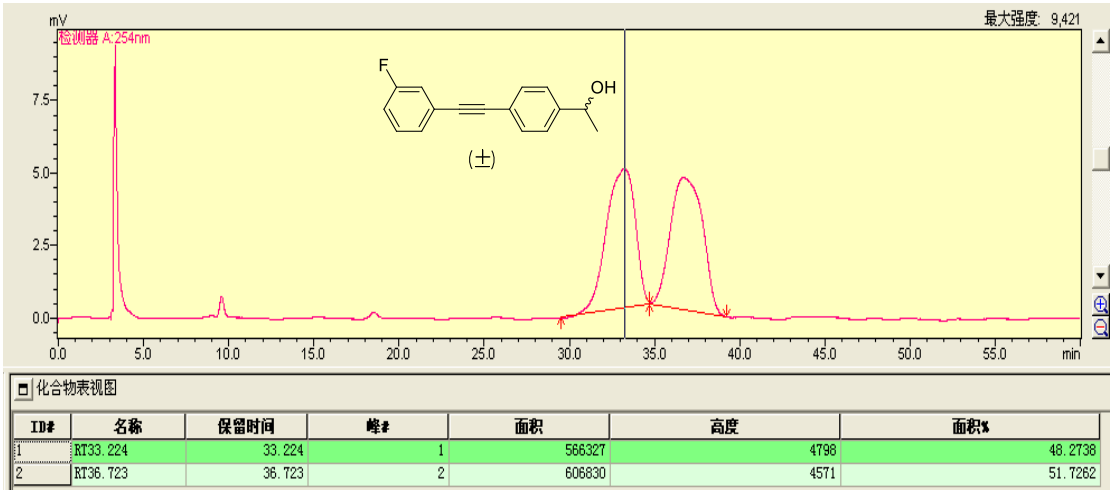
ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT33.631	33.631	1	59569915	49.8614	458977	55.1174
2	RT38.276	38.276	2	59901060	50.1386	373750	44.8826



化合物表视图

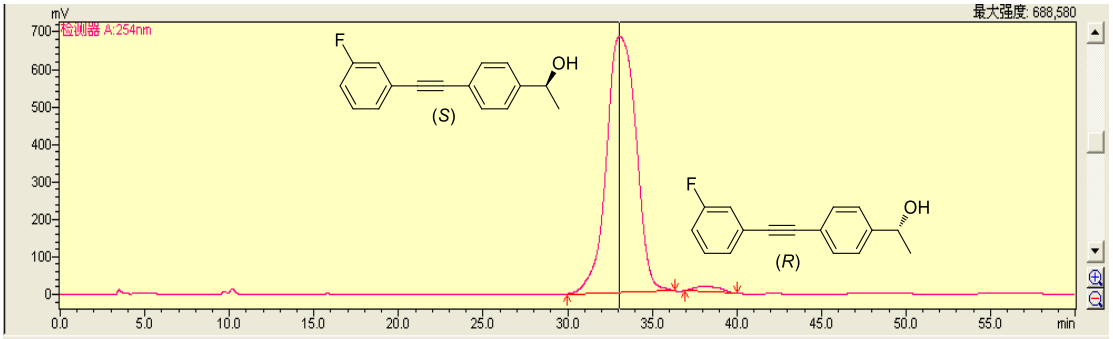
ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT33.128	33.128	1	68204585	98.8418	522027	98.9322
2	RT36.627	36.627	2	799226	1.1582	5635	1.0678

(*S*)-1-(4-((3-fluorophenyl)ethynyl)phenyl)ethanol. (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 99/1, flow rate = 1 mL/min, 20 ºC).



化合物表视图

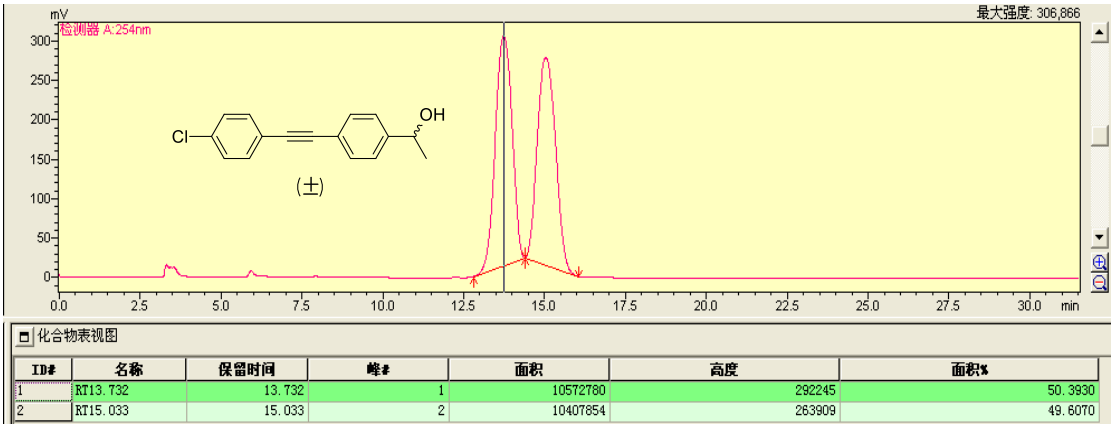
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT33.224	33.224	1	566327	4798	48.2738
2	RT36.723	36.723	2	606830	4571	51.7262



化合物表视图

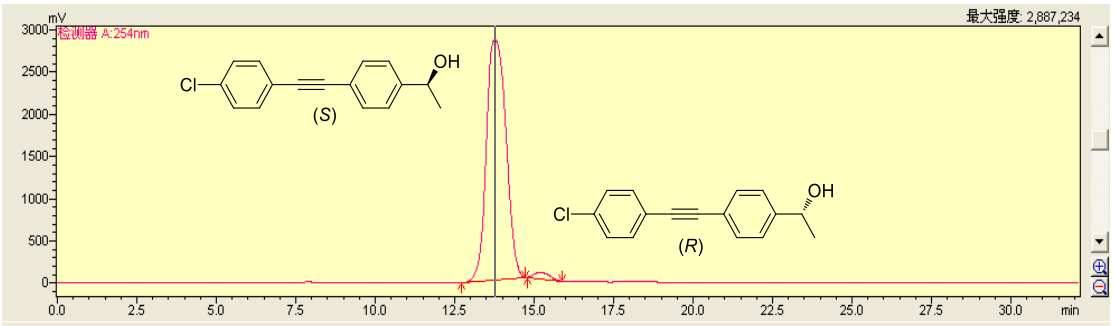
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT33.066	33.066	1	83665390	683424	98.1284
2	RT38.035	38.035	2	1595764	13562	1.8716

(*S*)-1-(4-((4-chlorophenyl)ethynyl)phenyl)ethanol. (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1 mL/min, 20 ºC).



化合物表视图

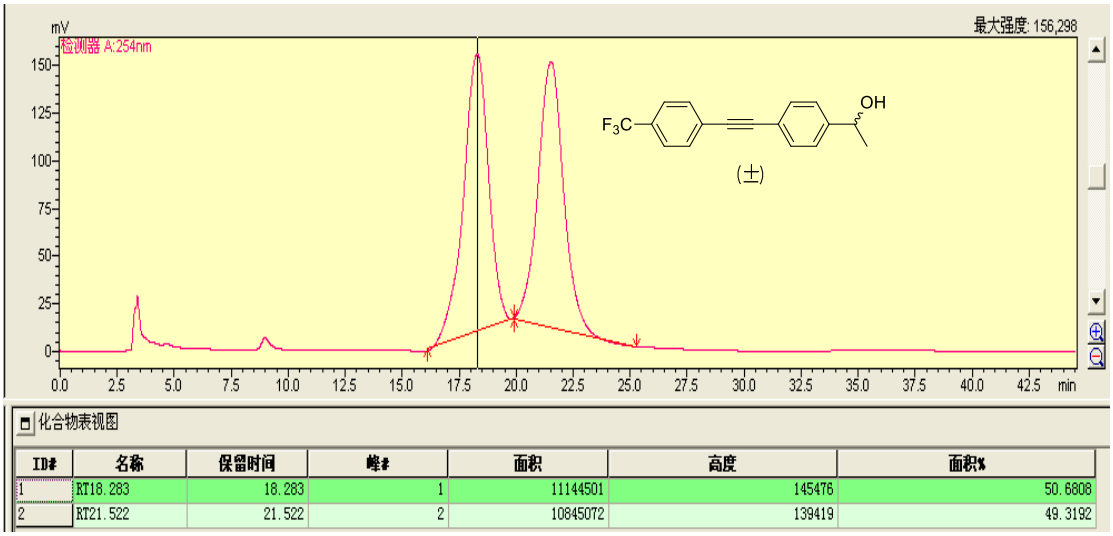
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT13.732	13.732	1	10572780	292245	50.3930
2	RT15.033	15.033	2	10407854	263909	49.6070



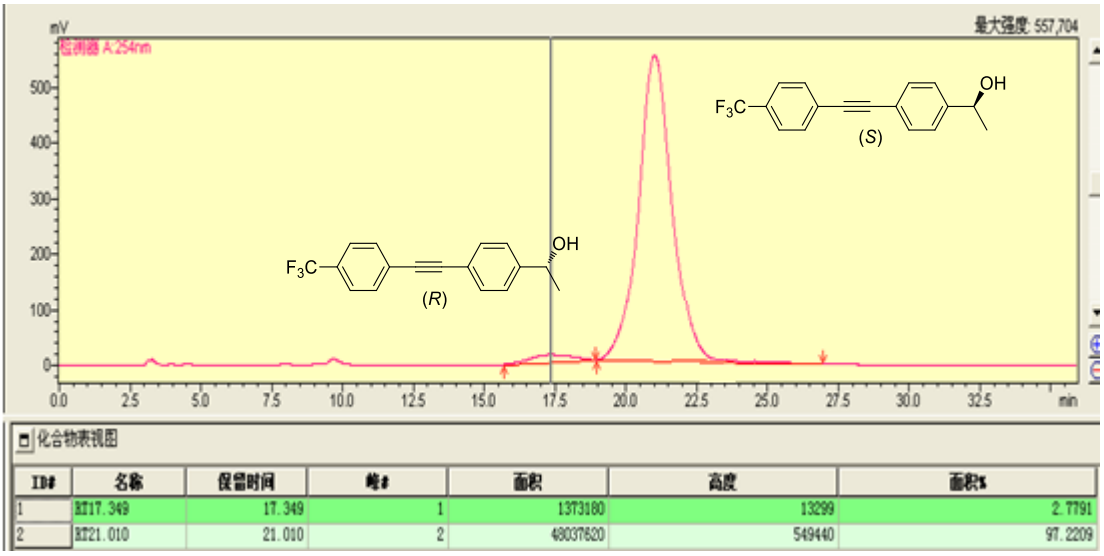
化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT13.768	13.768	1	122885894	2851291	97.9957
2	RT15.190	15.190	2	2513351	71942	2.0043

(*S*)-1-(4-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)ethanol. (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1 mL/min, 20 ^{o}C).

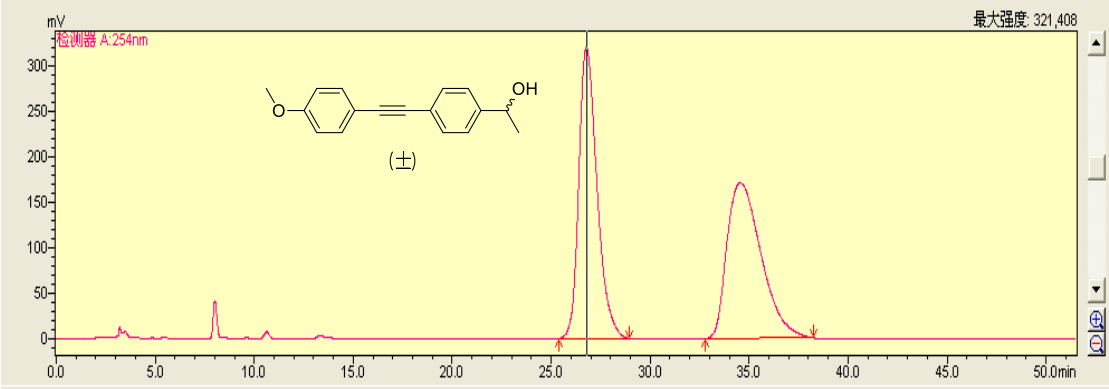


ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT18.283	18.283	1	11144501	145476	50.6808
2	RT21.522	21.522	2	10845072	139419	49.3192



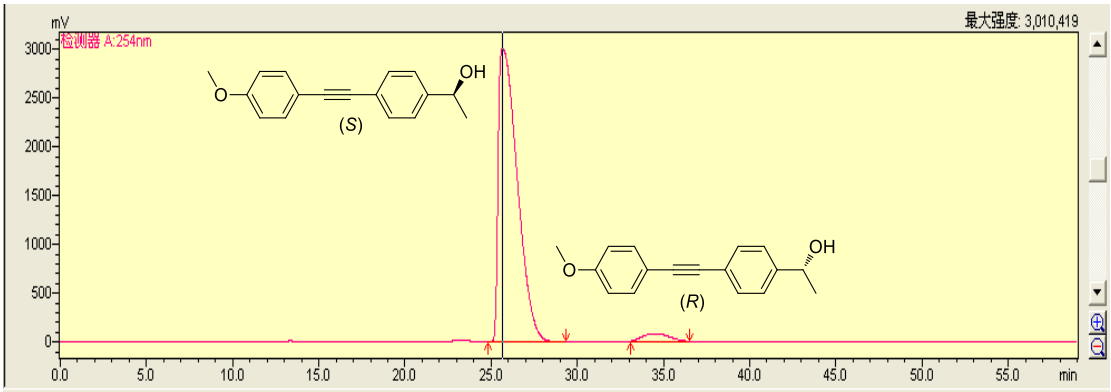
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT17.349	17.349	1	1373180	13299	2.7791
2	RT21.010	21.010	2	48037820	549440	97.2209

(*S*)-1-(4-((4-methoxyphenyl)ethynyl)phenyl)ethanol. (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1 mL/min, 20 ºC).



化合物表视图

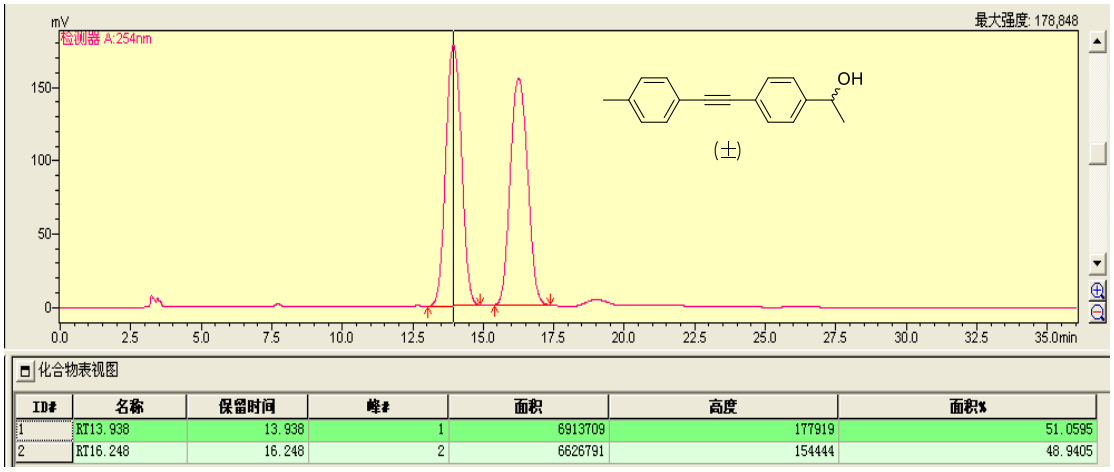
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT26.778	26.778	1	20548104	321282	49.8551
2	RT34.553	34.553	2	20667561	171265	50.1449



化合物表视图

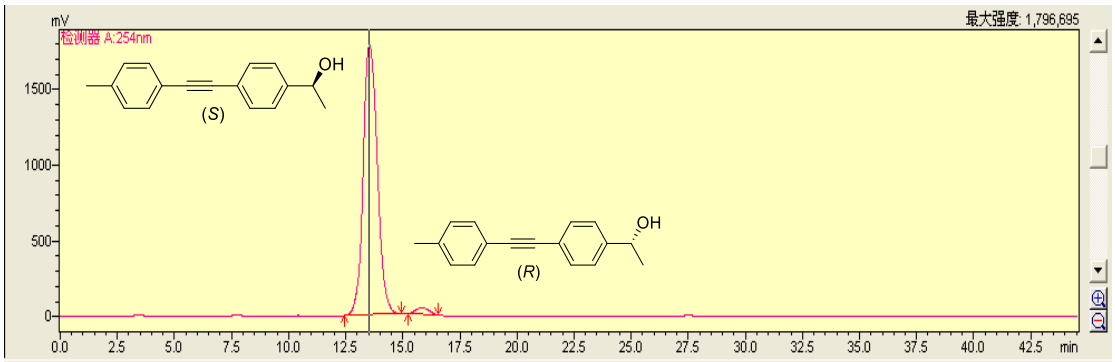
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT25.674	25.674	1	231531693	3008453	96.4558
2	RT34.515	34.515	2	8507512	78423	3.5442

(*S*)-1-(4-(p-tolylethynyl)phenyl)ethan-1-ol. (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1 mL/min, 20 ºC).



化合物表视图

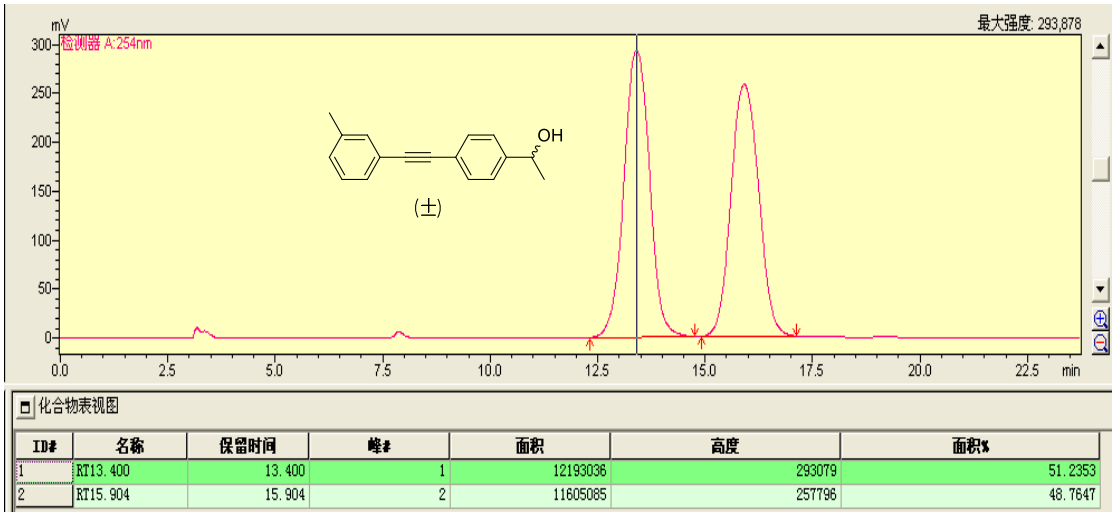
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT13.938	13.938	1	6913709	177919	51.0595
2	RT16.248	16.248	2	6626791	154444	48.9405



化合物表视图

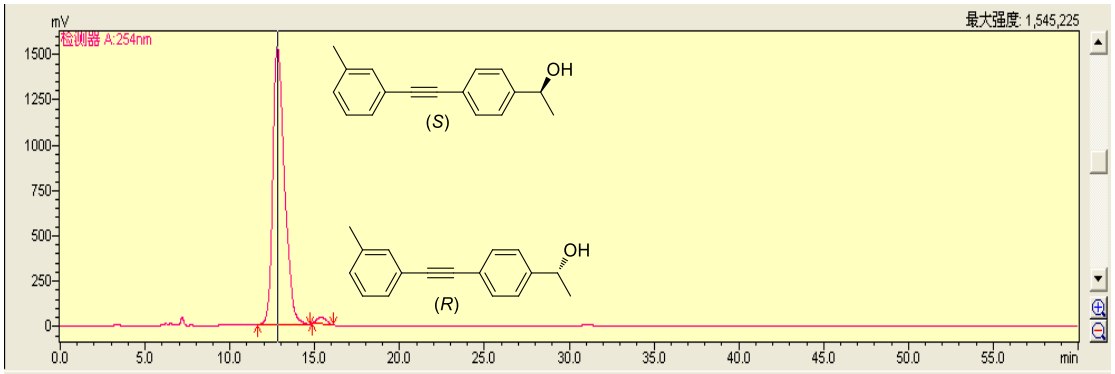
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT13.534	13.534	1	76883092	1783263	97.8135
2	RT15.831	15.831	2	1718174	41044	2.1865

(*S*)-1-(4-(m-tolylethynyl)phenyl)ethanol. (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1 mL/min, 20 ºC).



化合物表视图

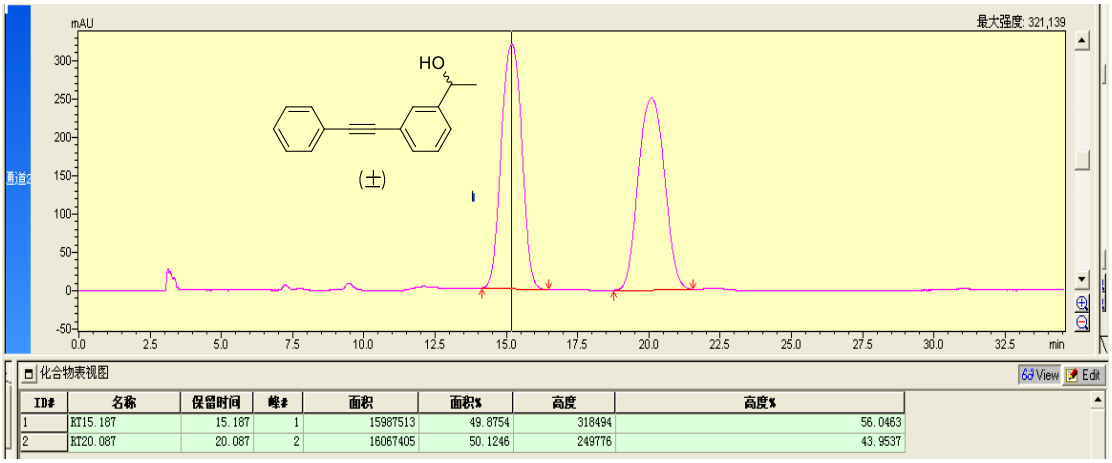
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT13.400	13.400	1	12193036	293079	51.2353
2	RT15.904	15.904	2	11605085	257796	48.7647



化合物表视图

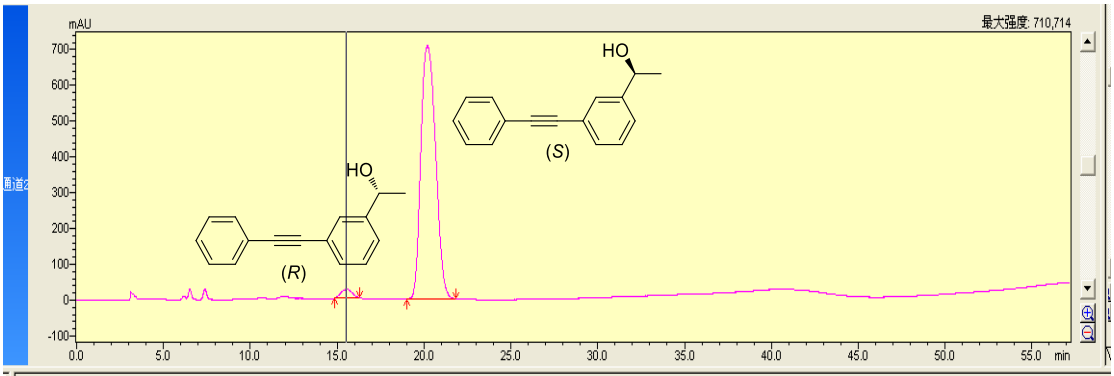
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT12.795	12.795	1	73499753	1532388	98.0509
2	RT15.374	15.374	2	1461044	34762	1.9491

(*S*)-1-(3-(phenylethynyl)phenyl)ethanol. (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1 mL/min, 20 ºC).



化合物表视图

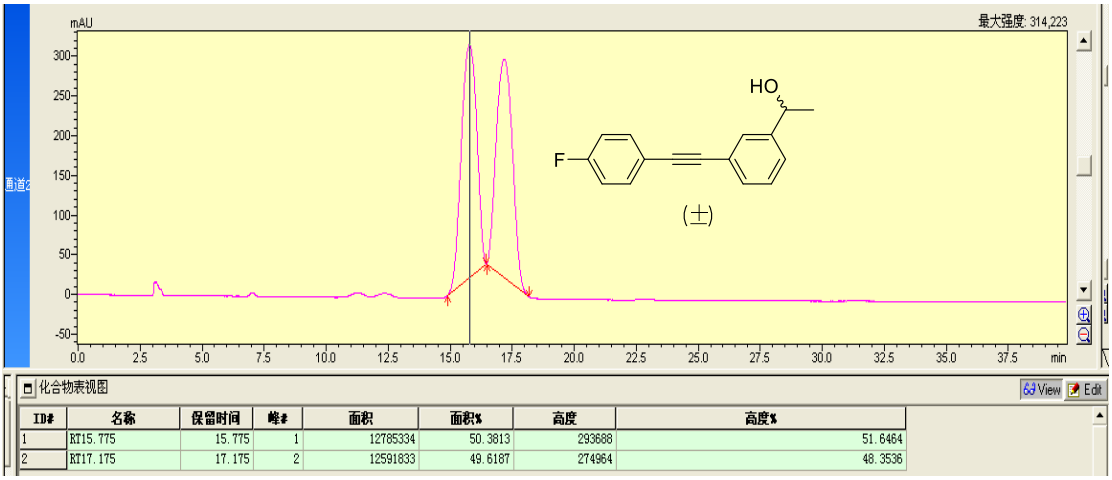
ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT15.187	15.187	1	15987513	49.8754	318494	56.0463
2	RT20.087	20.087	2	16067405	50.1246	249776	43.9537



化合物表视图

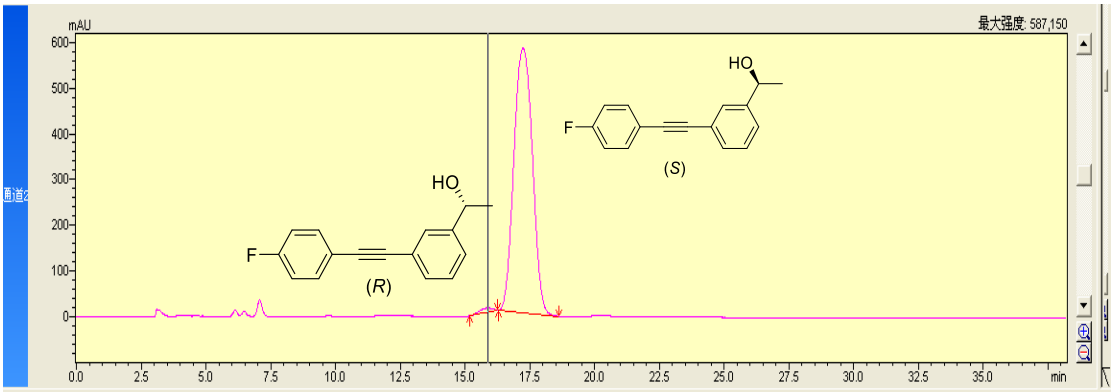
ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT15.536	15.536	1	1094281	2.5536	24483	3.3455
2	RT20.195	20.195	2	41757383	97.4464	707333	96.6545

(*S*)-1-(3-((4-fluorophenyl)ethynyl)phenyl)ethanol. (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1 mL/min, 20 ºC).



化合物表视图

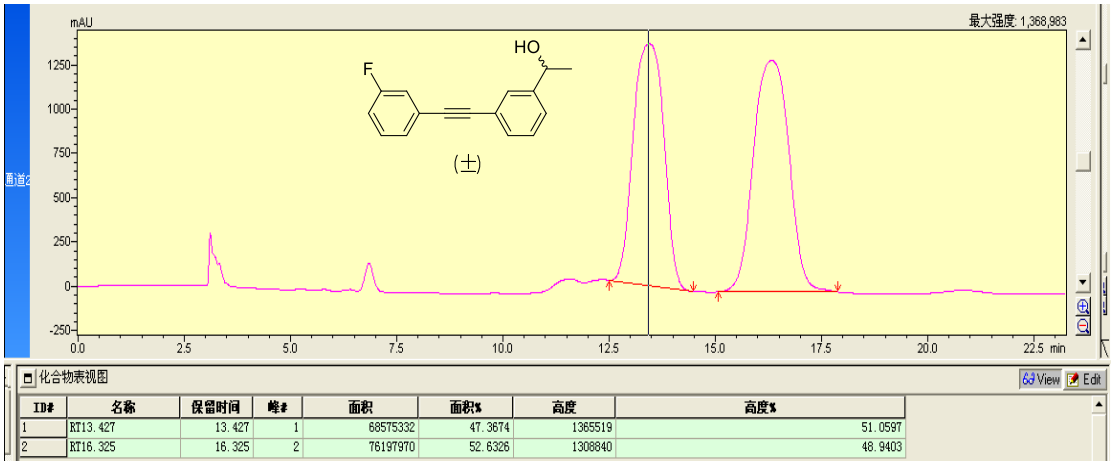
ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT15.775	15.775	1	12785334	50.3813	293688	51.6464
2	RT17.175	17.175	2	12591833	49.6187	274964	48.3536



化合物表视图

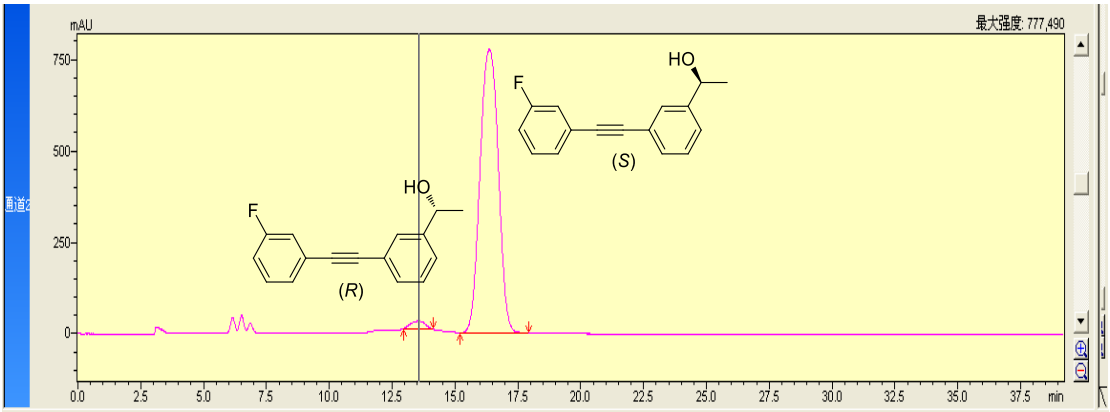
ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT15.877	15.877	1	347949	1.1900	9555	1.6244
2	RT17.237	17.237	2	28892619	98.8100	578629	98.3756

(*S*)-1-(3-((3-fluorophenyl)ethynyl)phenyl)ethanol. (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1 mL/min, 20 ºC).



化合物表视图

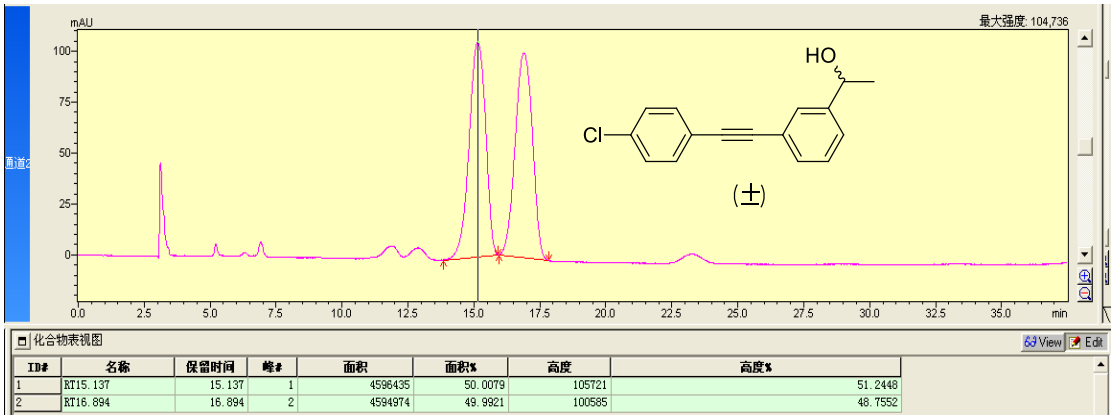
ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT13.427	13.427	1	68575332	47.3674	1365519	51.0597
2	RT16.325	16.325	2	76197970	52.6326	1308840	48.9403



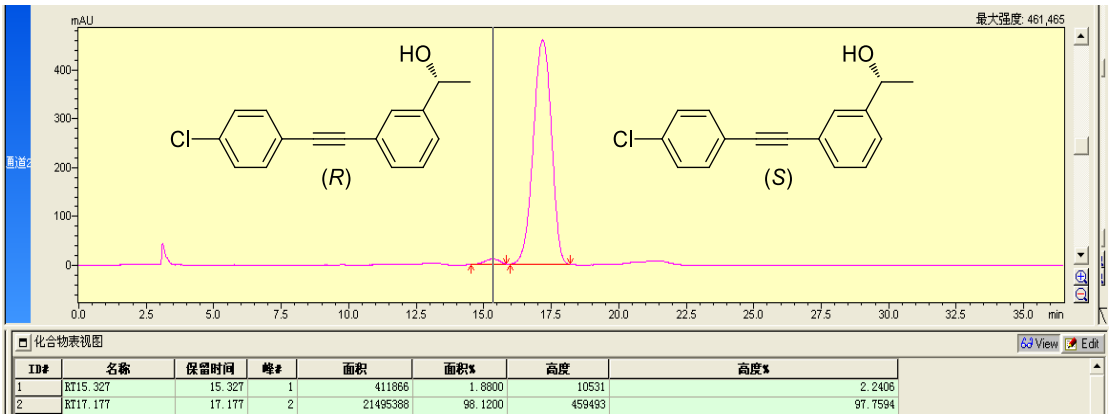
化合物表视图

ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT13.546	13.546	1	861269	2.1480	21565	2.7079
2	RT16.359	16.359	2	39234389	97.8520	774828	97.2921

(*S*)-1-(3-((4-chlorophenyl)ethynyl)phenyl)ethanol. (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1 mL/min, 20 ºC).

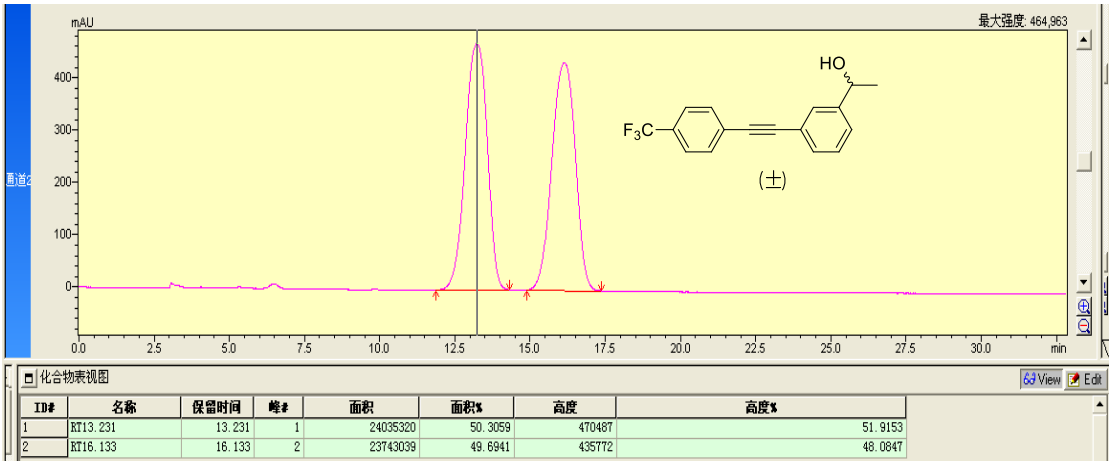


ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT15.137	15.137	1	4596435	50.0079	105721	51.2448
2	RT16.894	16.894	2	4594974	49.9921	100585	48.7552

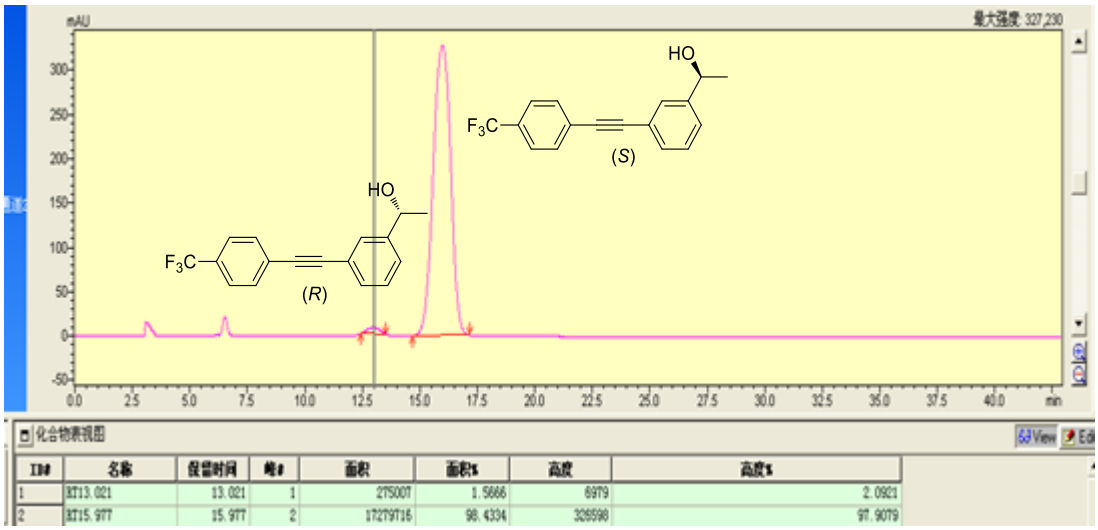


ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT15.327	15.327	1	411866	1.8800	10531	2.2406
2	RT17.177	17.177	2	21495388	98.1200	459493	97.7594

(*S*)-1-(3-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)ethanol. (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1 mL/min, 20 ^{o}C).

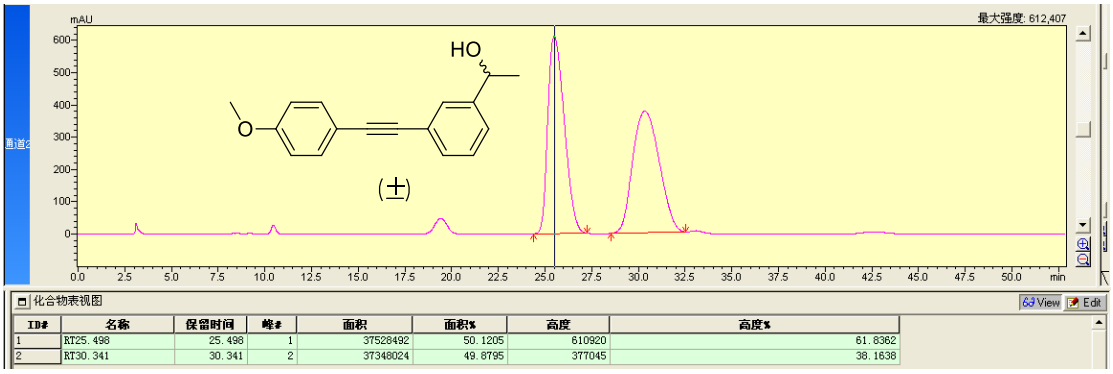


ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT13.231	13.231	1	24035320	50.3059	470487	51.9153
2	RT16.133	16.133	2	23743039	49.6941	435772	48.0847

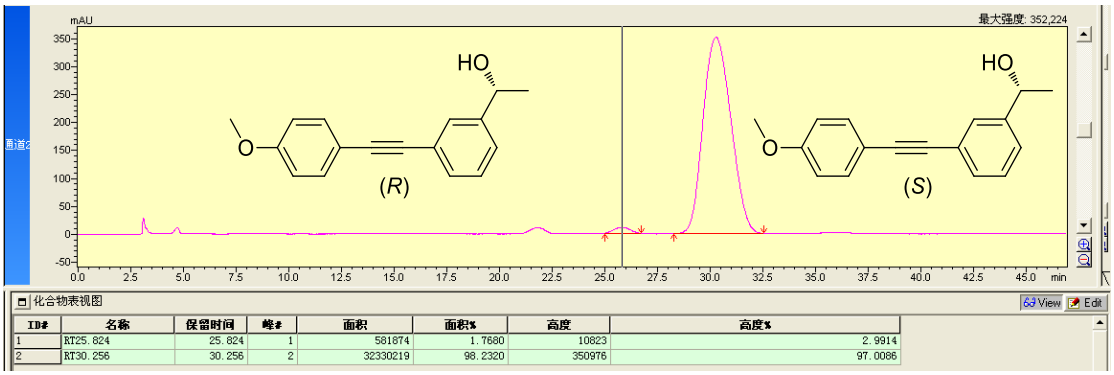


ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT13.021	13.021	1	275007	1.5666	6979	2.0921
2	RT15.977	15.977	2	17279716	98.4334	326598	97.9079

(*S*)-1-(3-((4-methoxyphenyl)ethynyl)phenyl)ethanol. (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1 mL/min, 20 ºC).

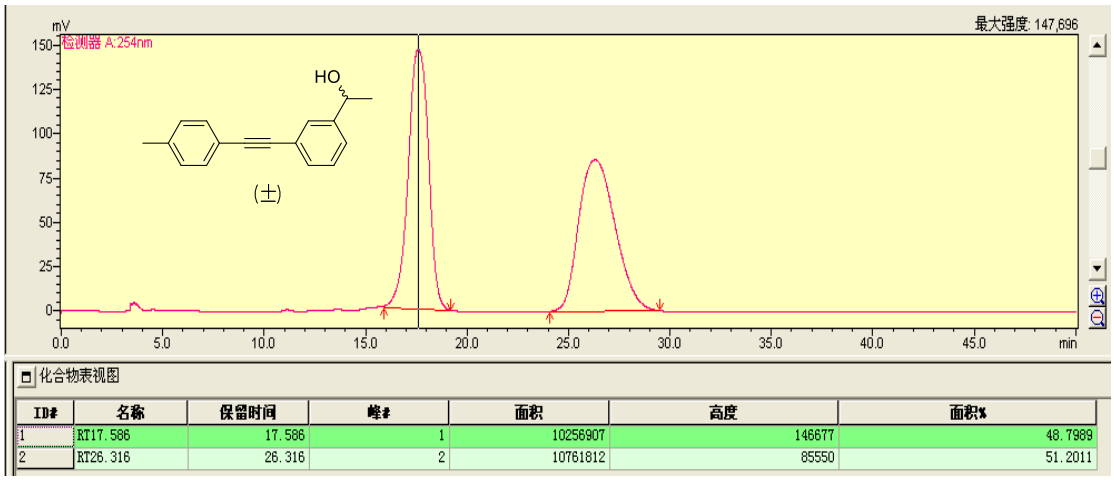


ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT25.498	25.498	1	37528492	50.1205	610920	61.8362
2	RT30.341	30.341	2	37348024	49.8795	377045	38.1638



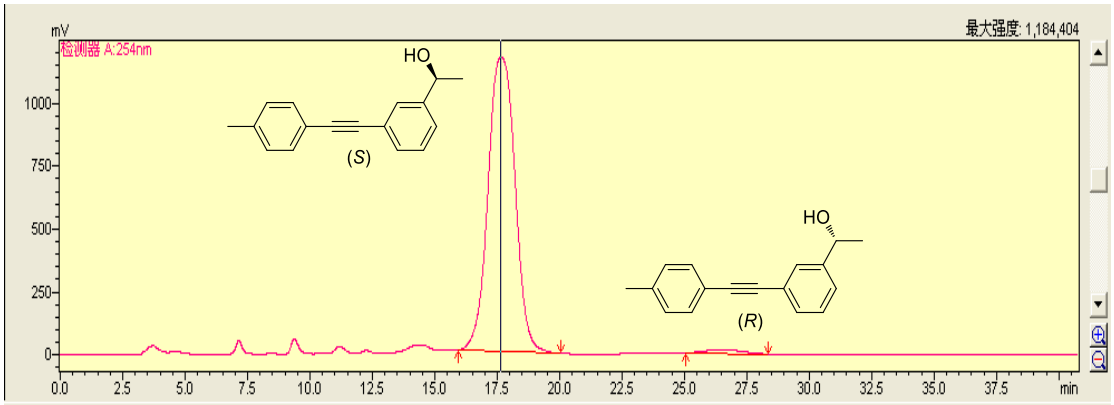
ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT25.824	25.824	1	581874	1.7680	10823	2.9914
2	RT30.256	30.256	2	32330219	98.2320	350976	97.0086

(*S*)-1-(3-(p-tolylethynyl)phenyl)ethanol. (HPLC: Chiracel AS-H, detected at 254 nm, eluent: n-hexane/2-propanol = 98/2, flow rate = 1 mL/min, 20 ºC).



化合物表视图

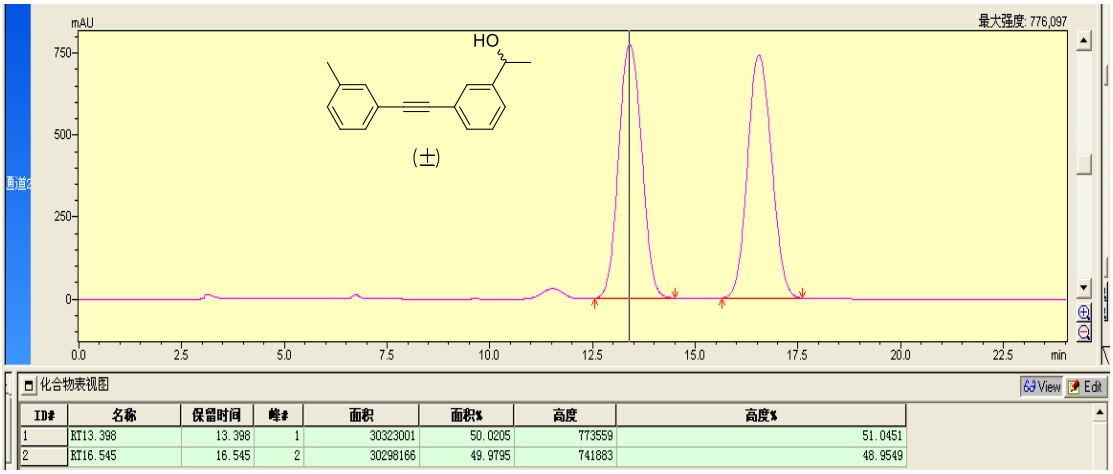
ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT17.586	17.586	1	10256907	146677	48.7989
2	RT26.316	26.316	2	10761812	85550	51.2011



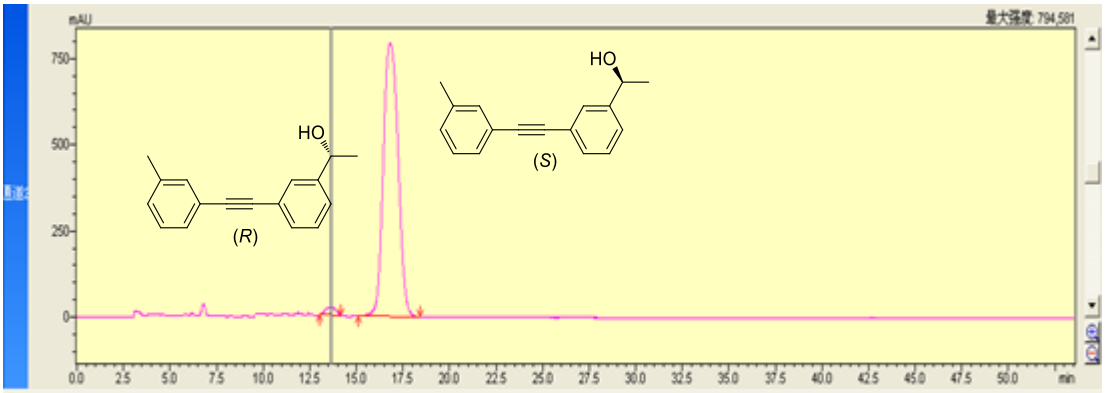
化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT17.653	17.653	1	88269510	1170383	98.2590
2	RT26.541	26.541	2	1563965	14686	1.7410

(*S*)-1-(3-(m-tolylethynyl)phenyl)ethanol. (HPLC: Chiracel OD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 97/3, flow rate = 1 mL/min, 20 ºC).

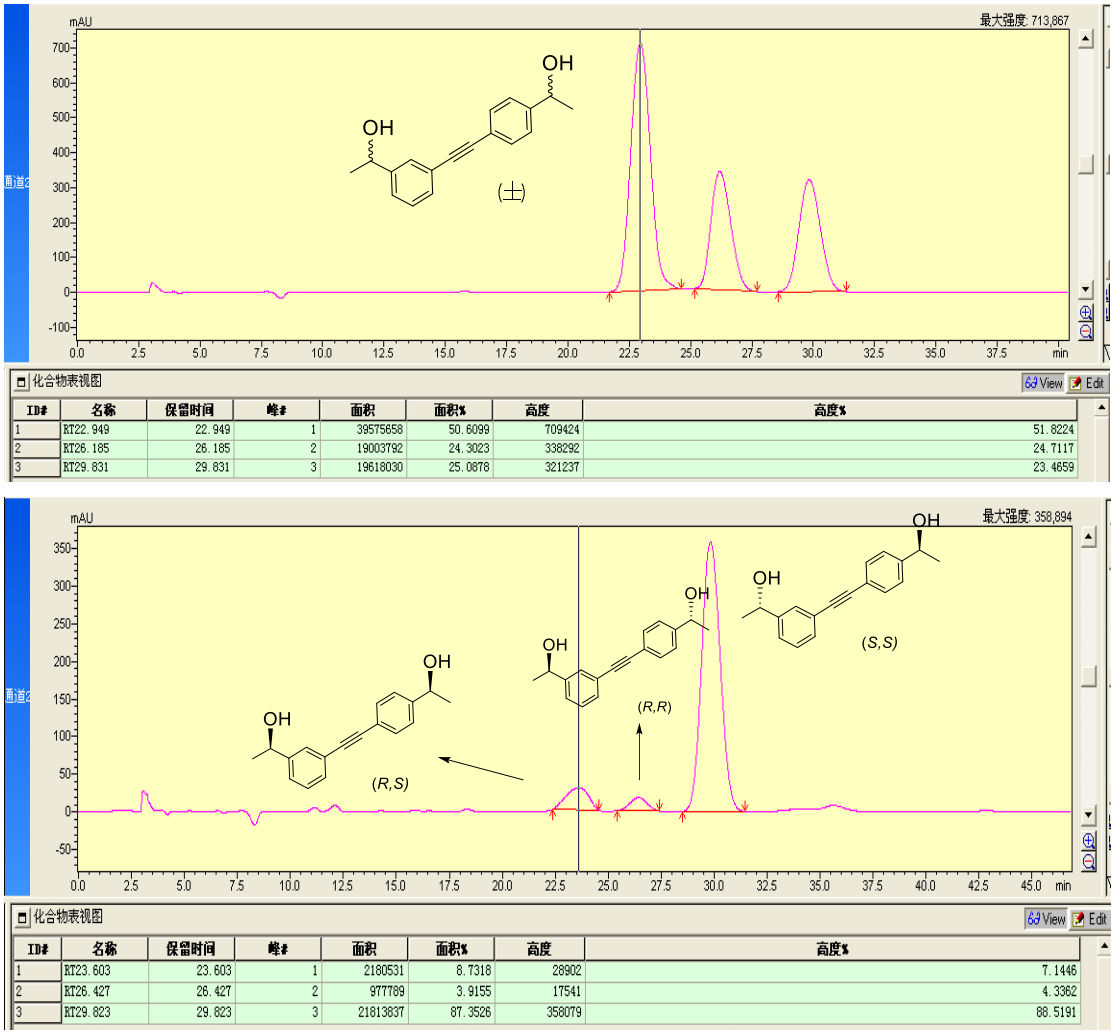


ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT13.398	13.398	1	30323001	50.0205	773559	51.0451
2	RT16.545	16.545	2	30298166	49.9795	741883	48.9549



ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT13.632	13.632	1	858067	1.9142	22174	2.7207
2	RT16.818	16.818	2	43969448	98.0858	792949	97.2793

(*S*)-1-(3-((4-((*S*)-1-hydroxyethyl)phenyl)ethynyl)phenyl)ethan-1-ol. (HPLC: Chiracel AD-H, detected at 254 nm, eluent: n-hexane/2-propanol = 90/10, flow rate = 1 mL/min, 20 ºC).

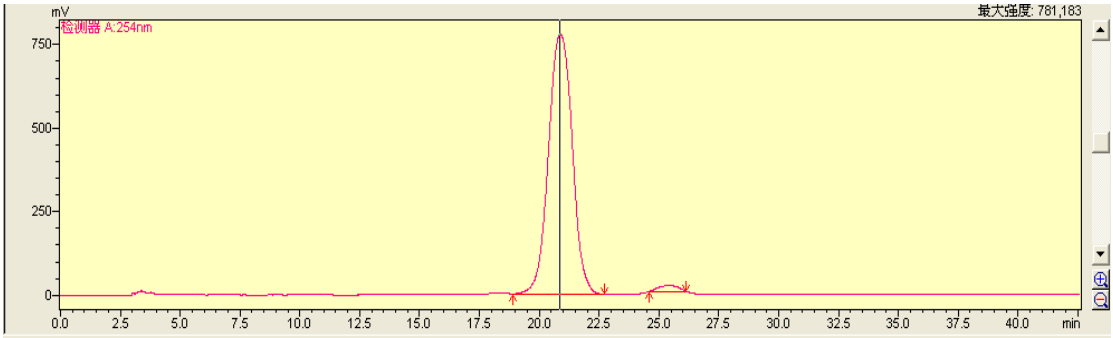


ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT22.949	22.949	1	39575658	50.6099	709424	51.8224
2	RT26.185	26.185	2	19003792	24.3023	338292	24.7117
3	RT29.831	29.831	3	19618030	25.0878	321237	23.4659

ID#	名称	保留时间	峰#	面积	面积%	高度	高度%
1	RT23.603	23.603	1	2180531	8.7318	28902	7.1446
2	RT26.427	26.427	2	977789	3.9155	17541	4.3362
3	RT29.823	29.823	3	21813837	87.3526	358079	88.5191

Figure 8. Reusability of catalyst **3** for the ATH–Sonogashira coupling reaction of 4-iodoacetophenone and phenylacetylene.

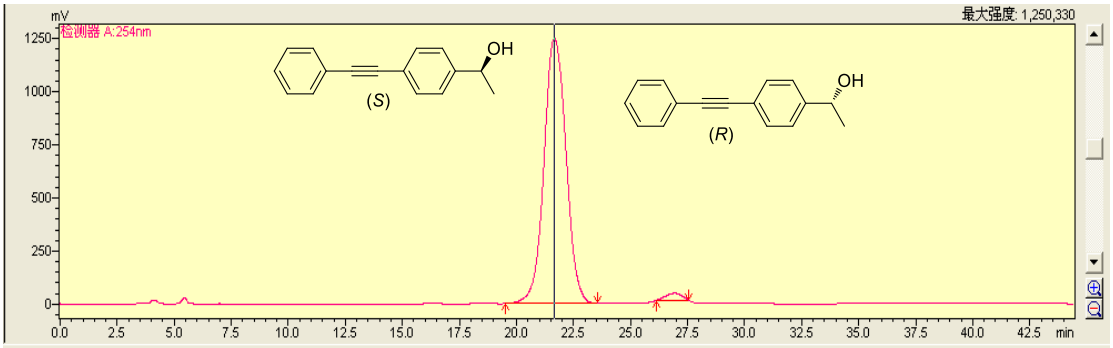
Recycle 2



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT20.871	20.871	1	53767173	777628	98.0651
2	RT25.417	25.417	2	1060869	17817	1.9349

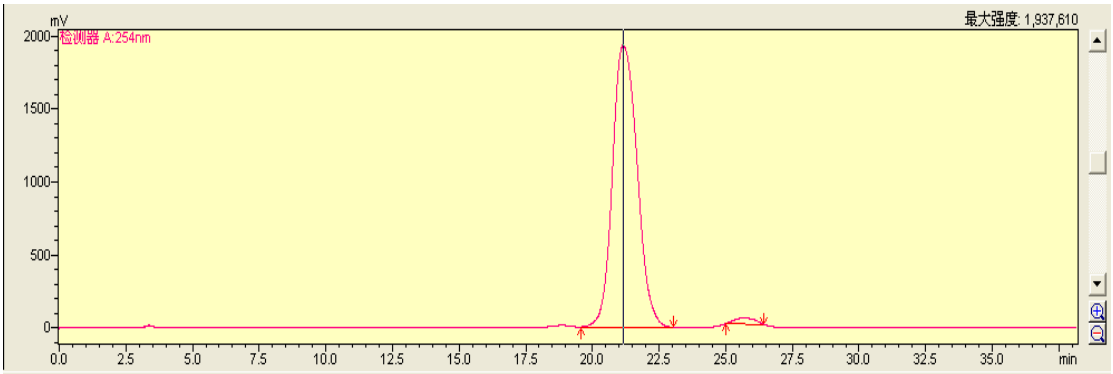
Recycle 3



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.656	21.656	1	84161239	1247652	98.1408
2	RT26.918	26.918	2	1594362	32657	1.8592

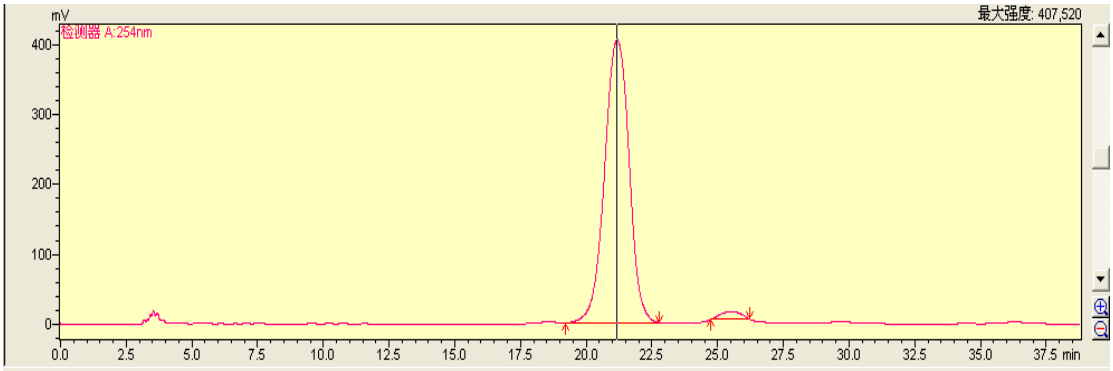
Recycle 4



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.152	21.152	1	124159551	1931325	98.2403
2	RT25.696	25.696	2	2223977	40574	1.7597

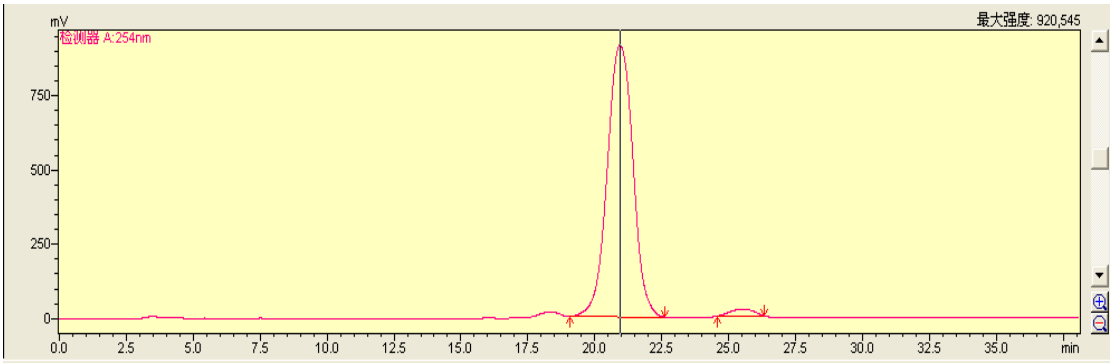
Recycle 5



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.170	21.170	1	26364642	405755	97.7612
2	RT25.507	25.507	2	603768	10960	2.2388

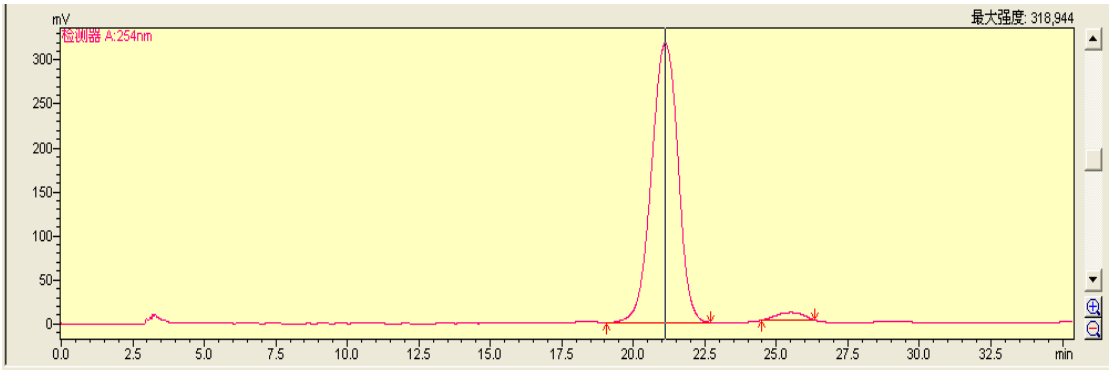
Recycle 6



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT20.943	20.943	1	61239660	914739	97.7696
2	RT25.523	25.523	2	1397065	22393	2.2304

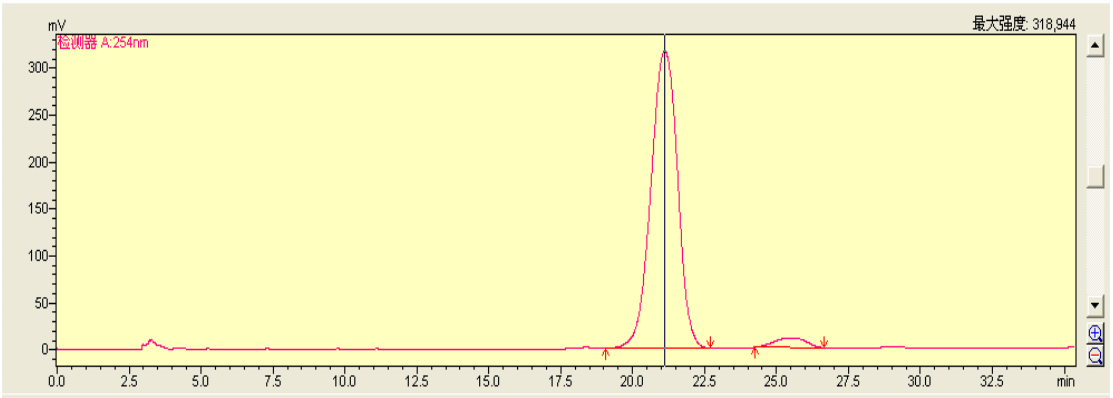
Recycle 7



化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.110	21.110	1	20451675	317346	97.1702
2	RT25.496	25.496	2	595591	8842	2.8298

Recycle 8

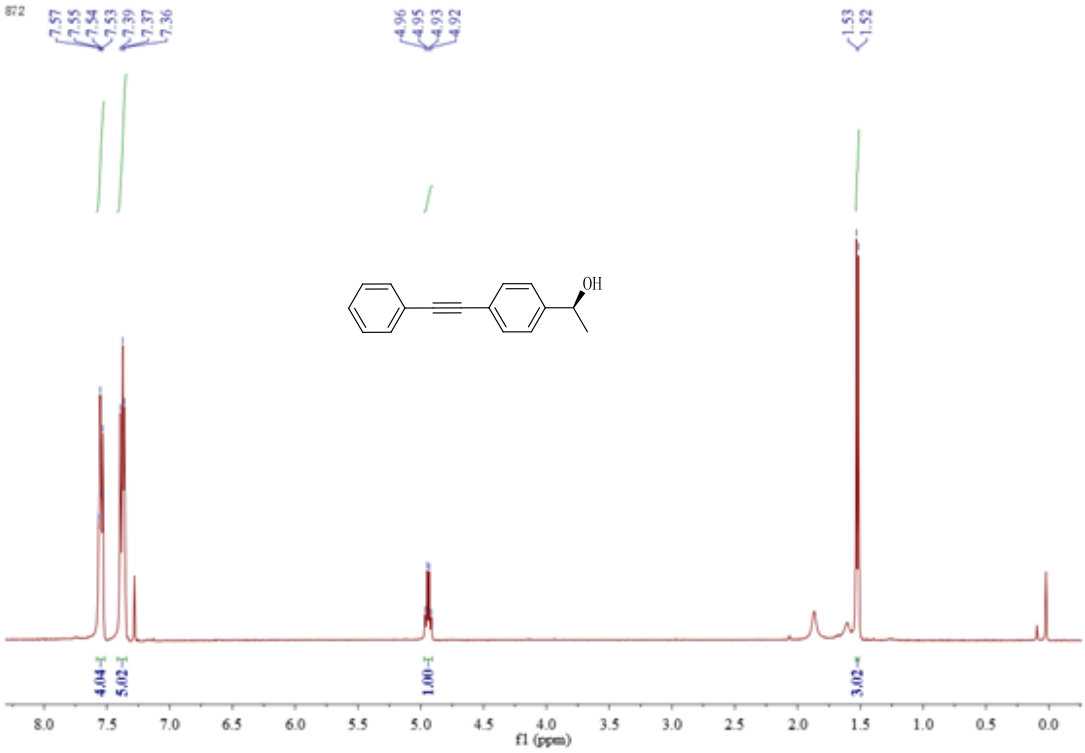


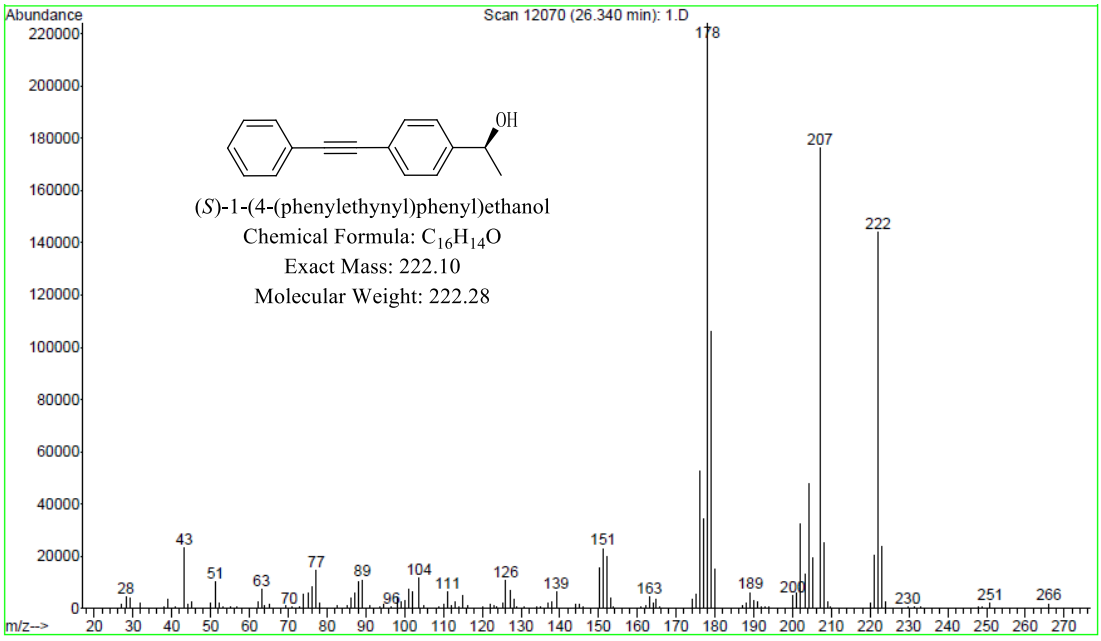
化合物表视图

ID#	名称	保留时间	峰#	面积	高度	面积%
1	RT21.110	21.110	1	20451675	317346	96.2110
2	RT25.496	25.496	2	805440	10511	3.7890

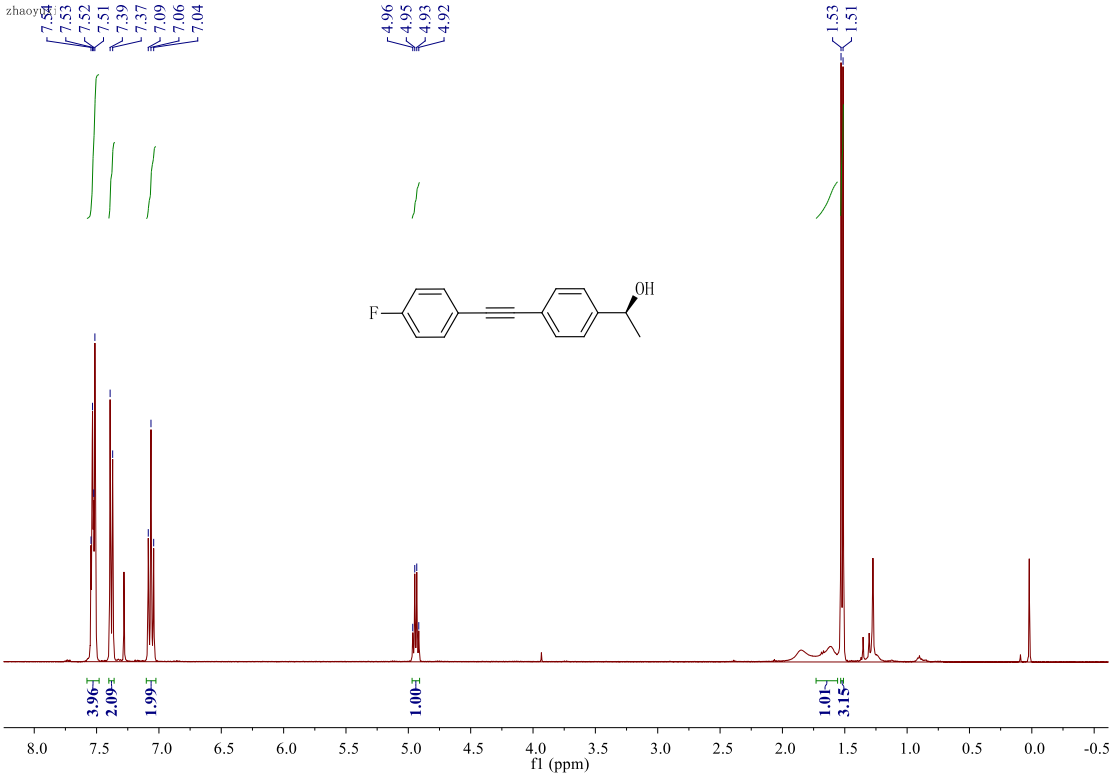
Figure S9. The ^{1}H NMR and GC/MS of chiral products.

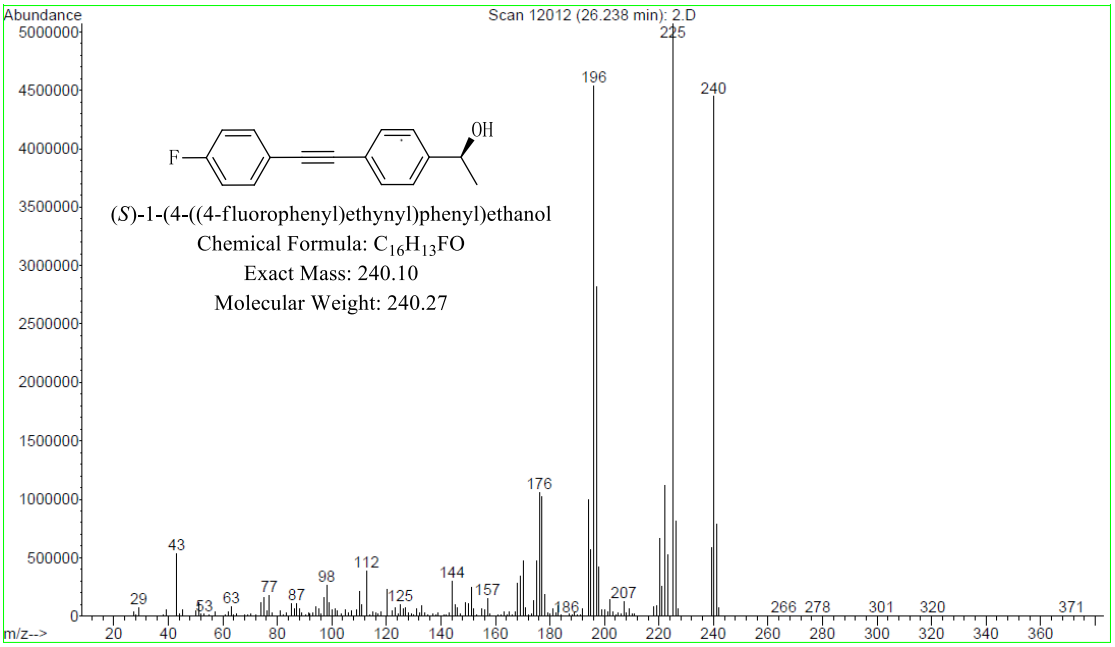
(*S*)-1-(4-(phenylethynyl)phenyl)ethanol



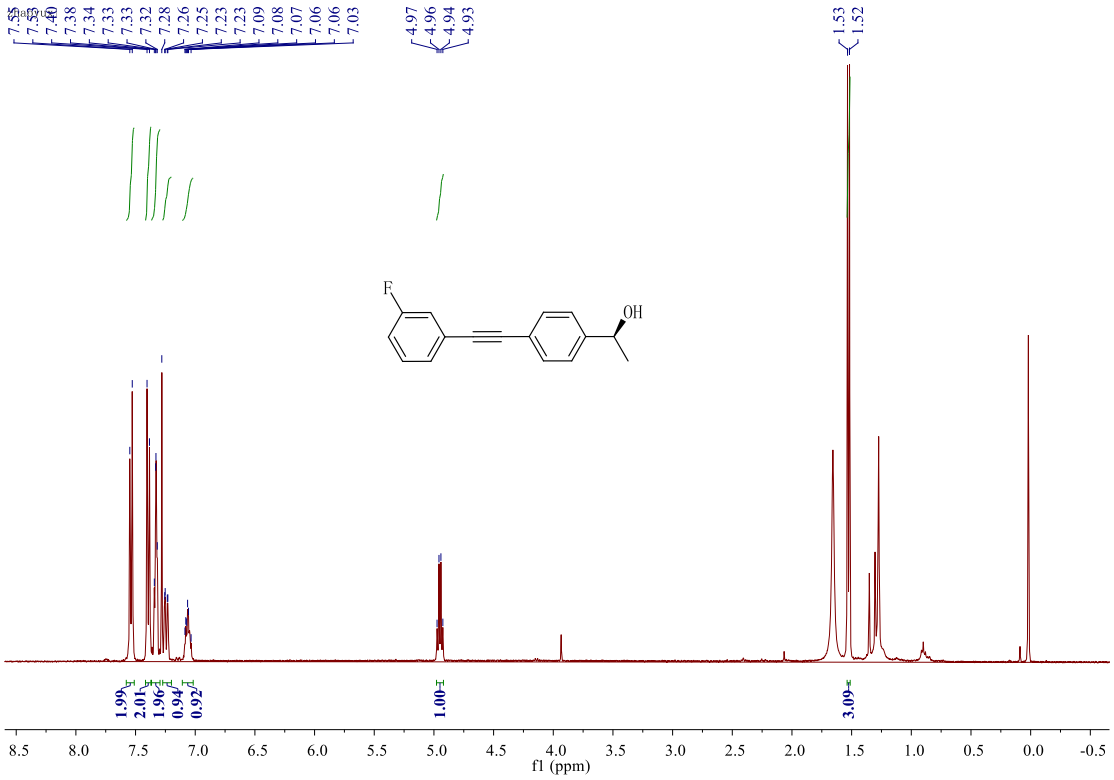


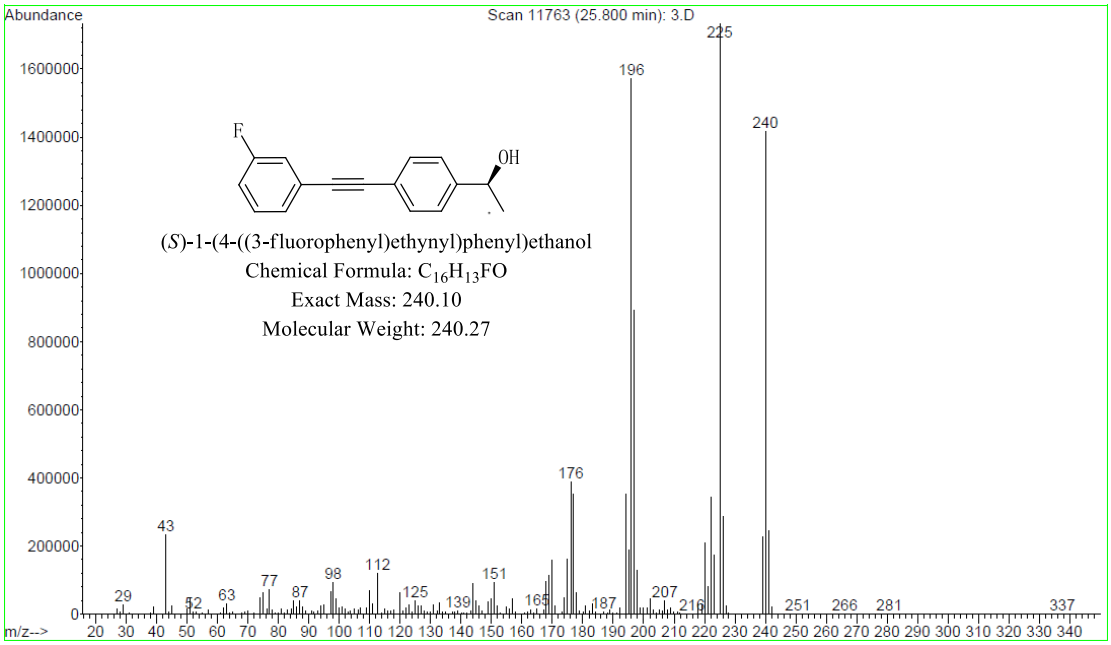
(*S*)-1-(4-((4-fluorophenyl)ethynyl)phenyl)ethanol



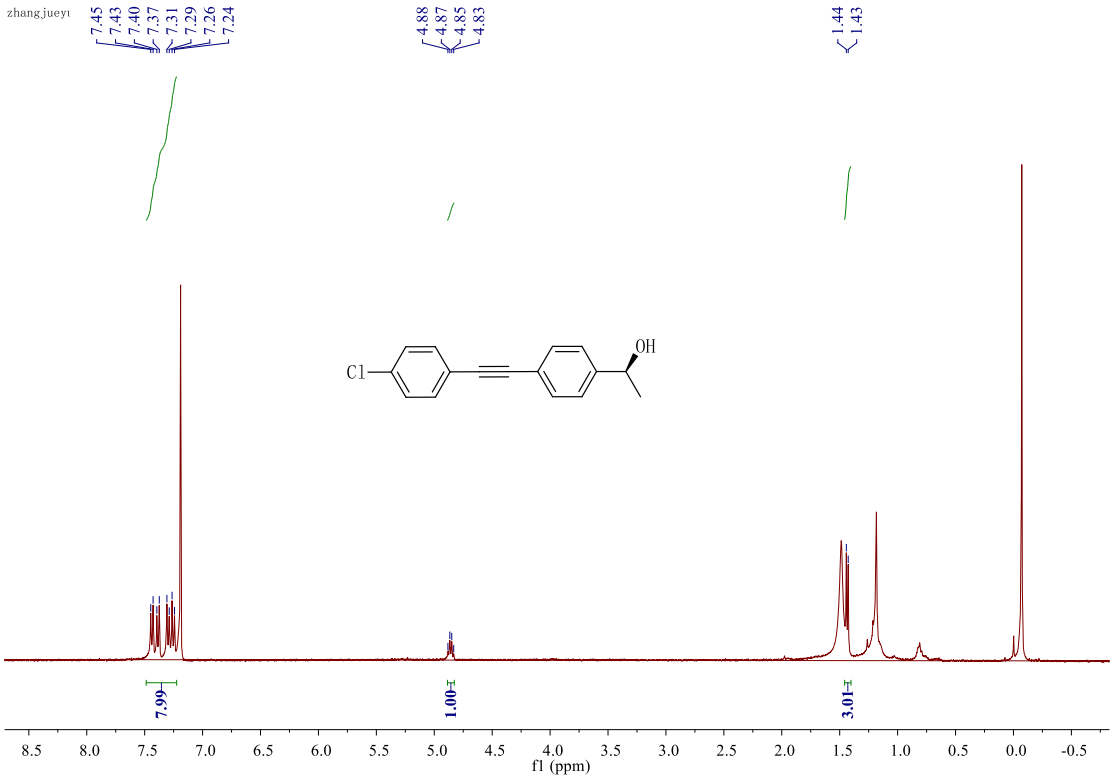


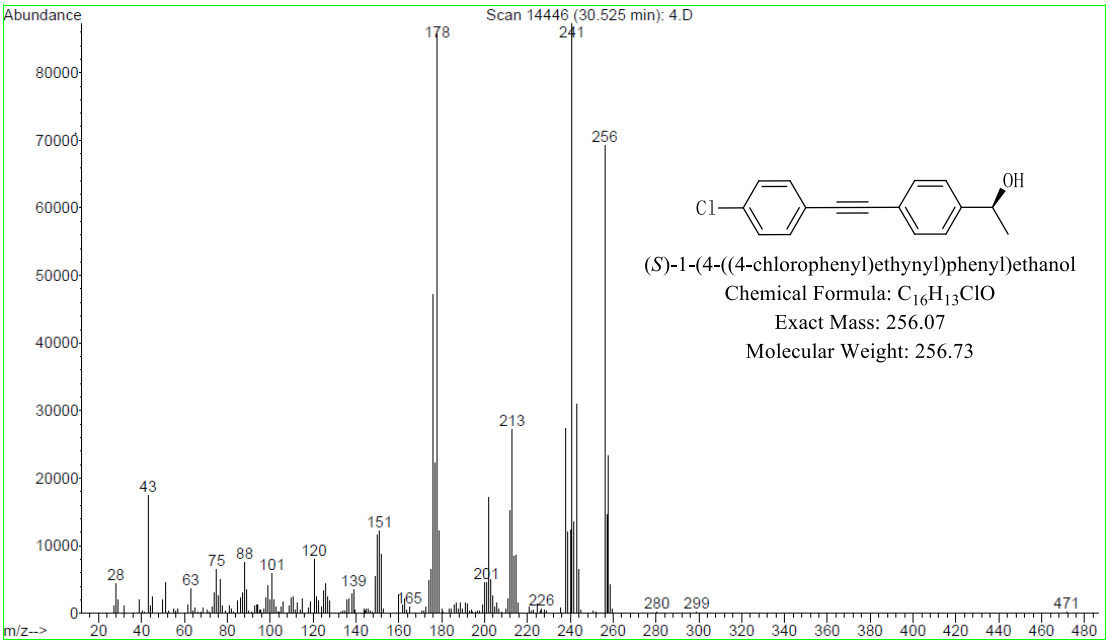
(*S*)-1-(4-((3-fluorophenyl)ethynyl)phenyl)ethanol



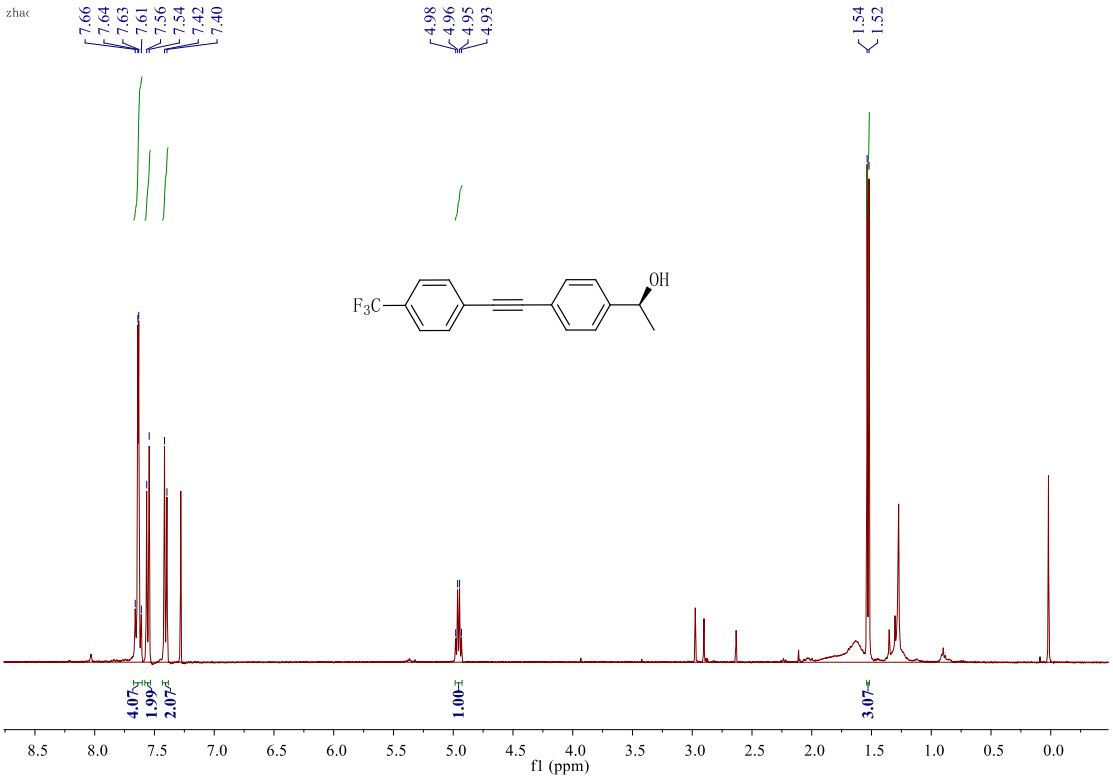


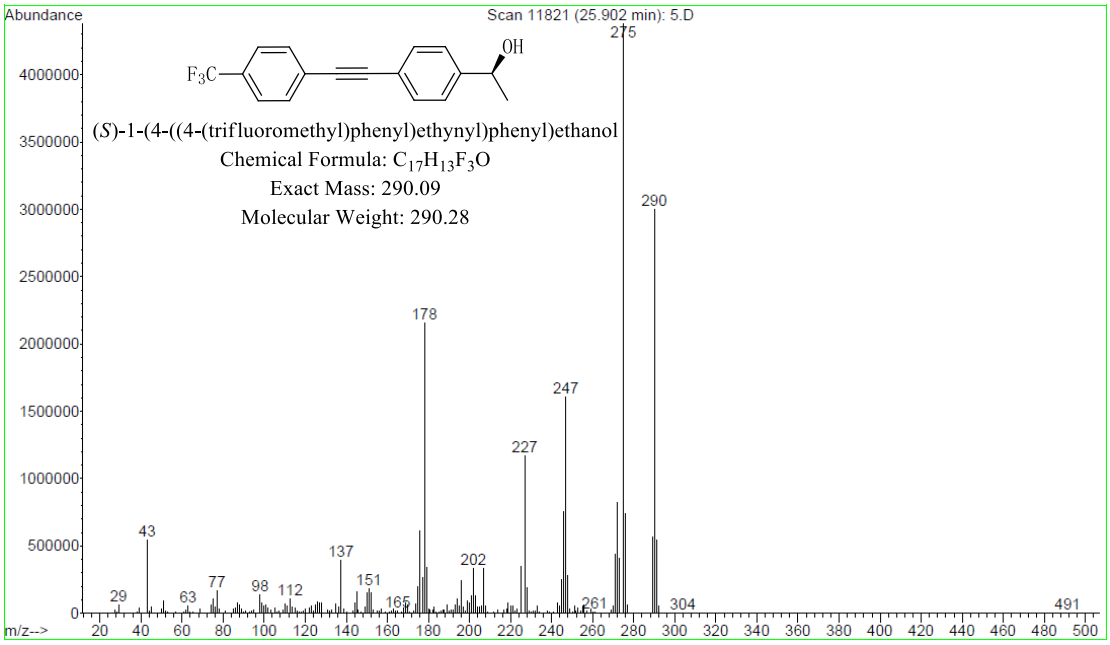
(S)-1-(4-((4-chlorophenyl)ethynyl)phenyl)ethanol



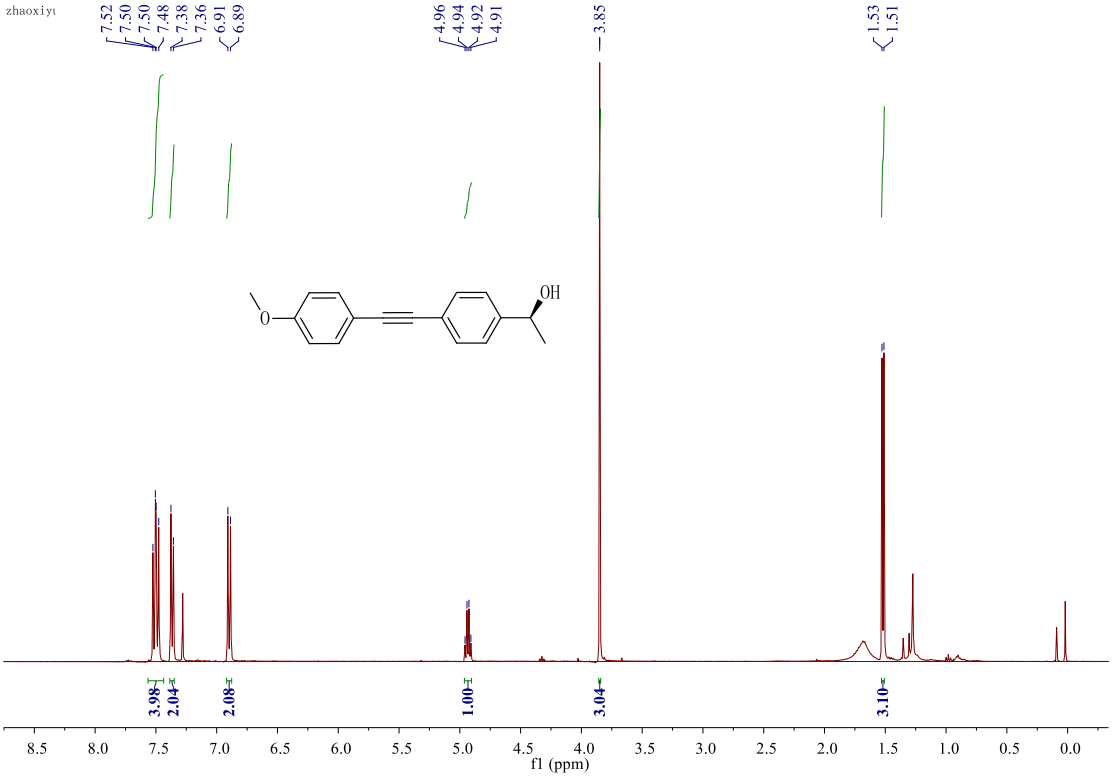


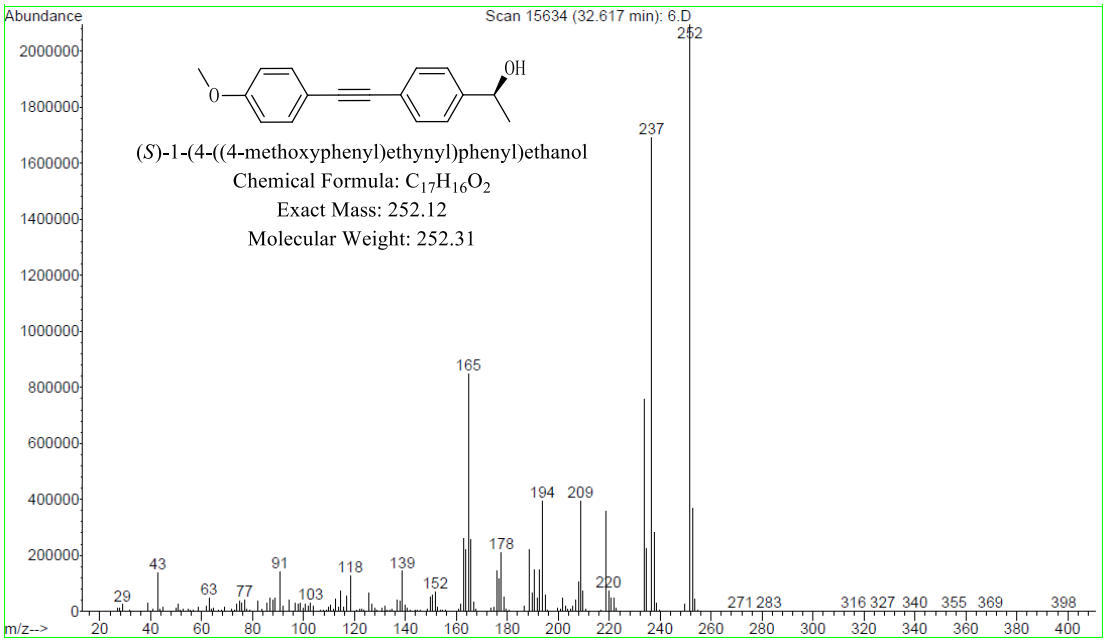
(*S*)-1-(4-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)ethanol



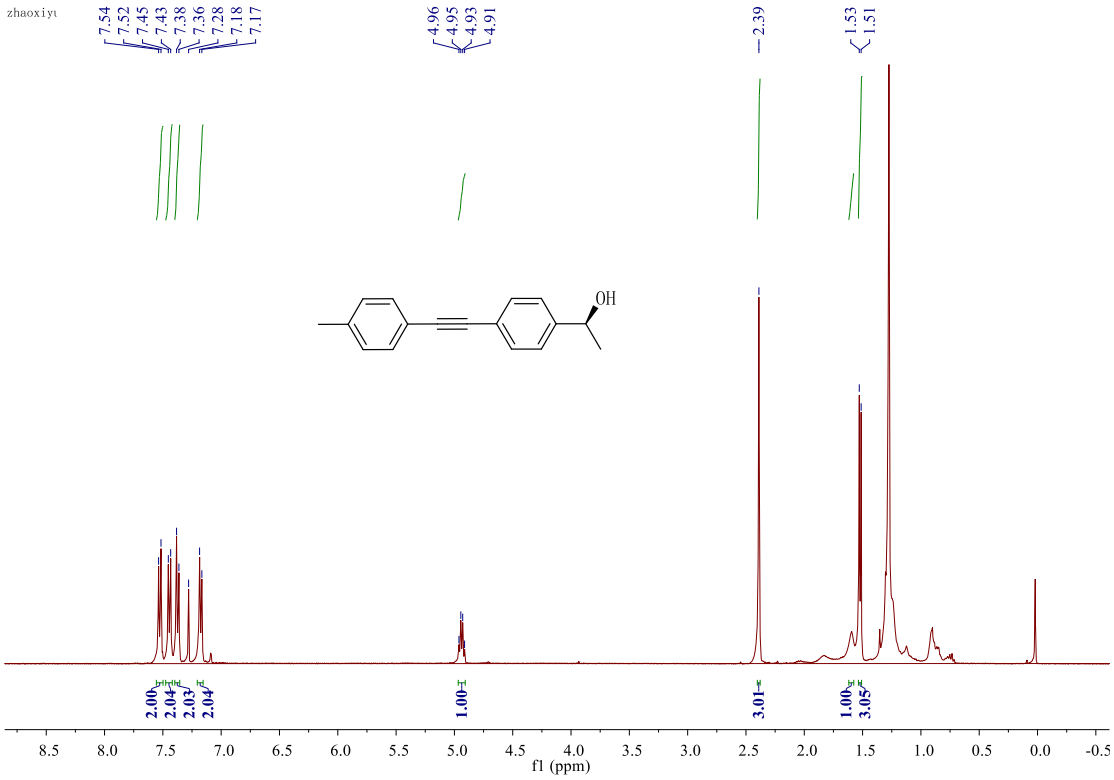


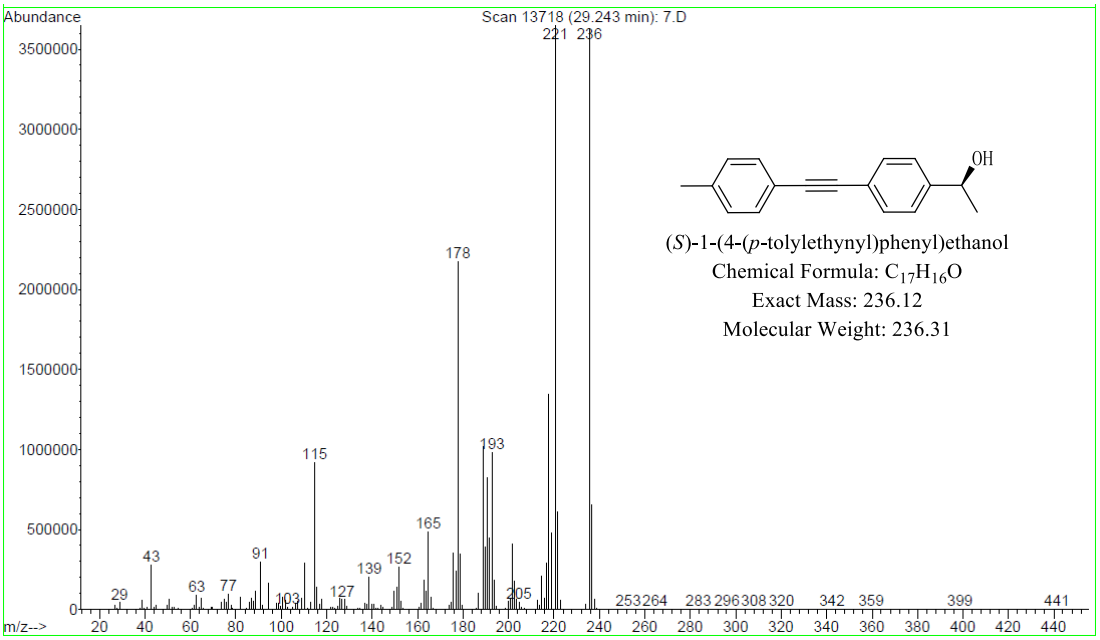
(*S*)-1-(4-((4-methoxyphenyl)ethynyl)phenyl)ethanol



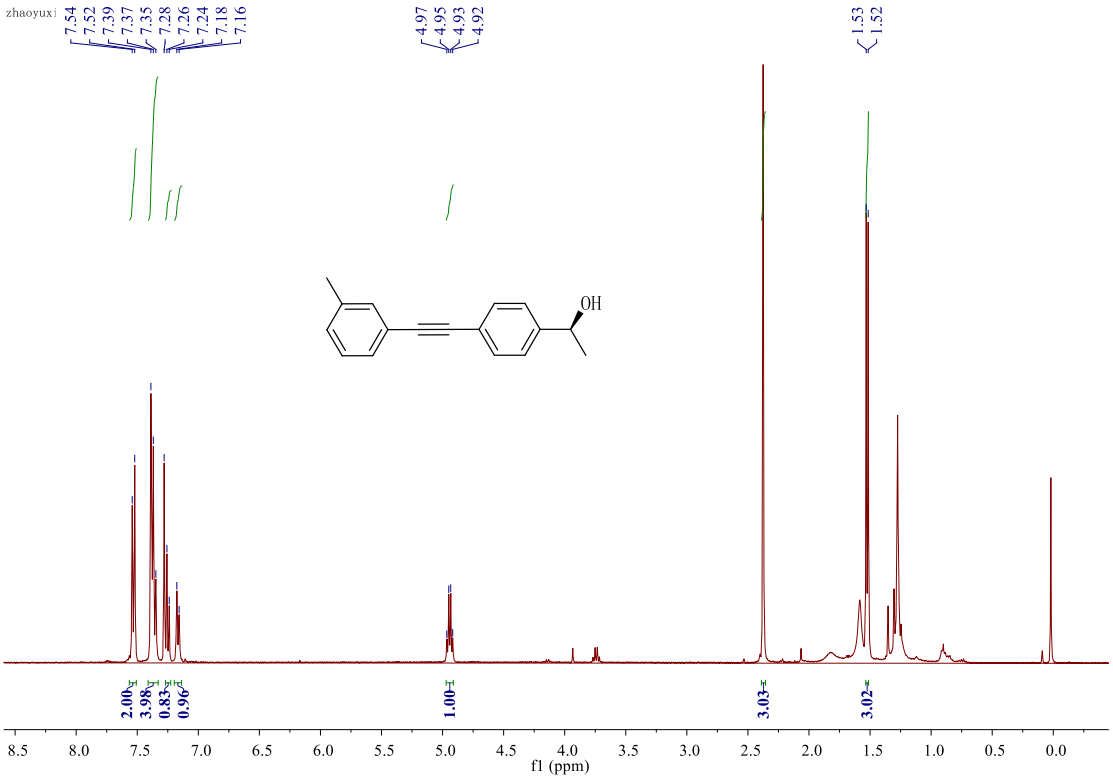


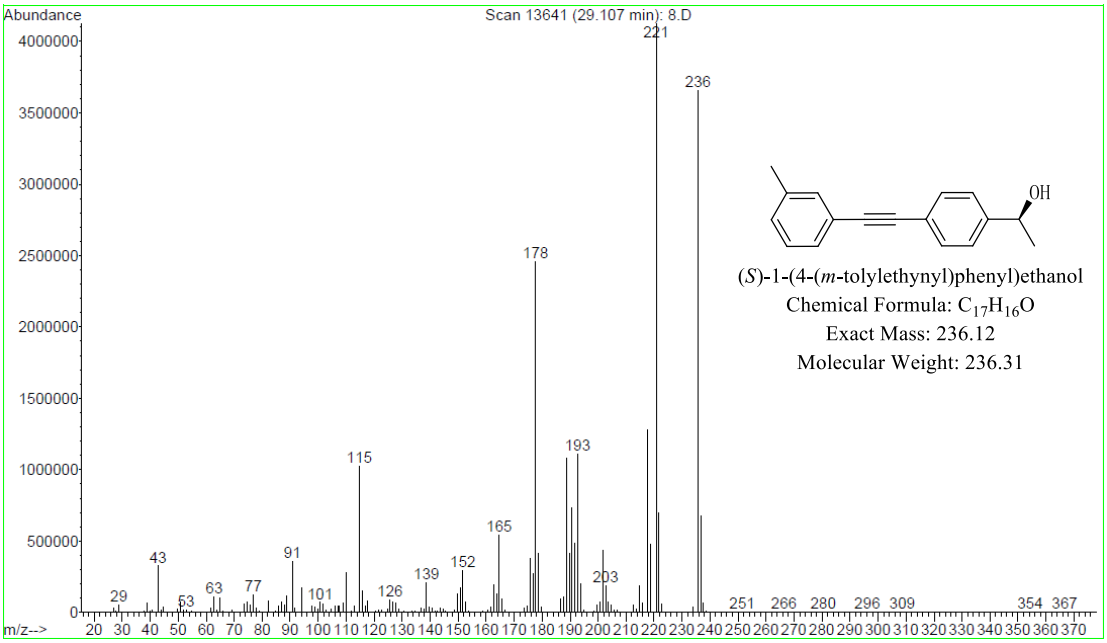
(S)-1-(4-(p-tolylethynyl)phenyl)ethanol



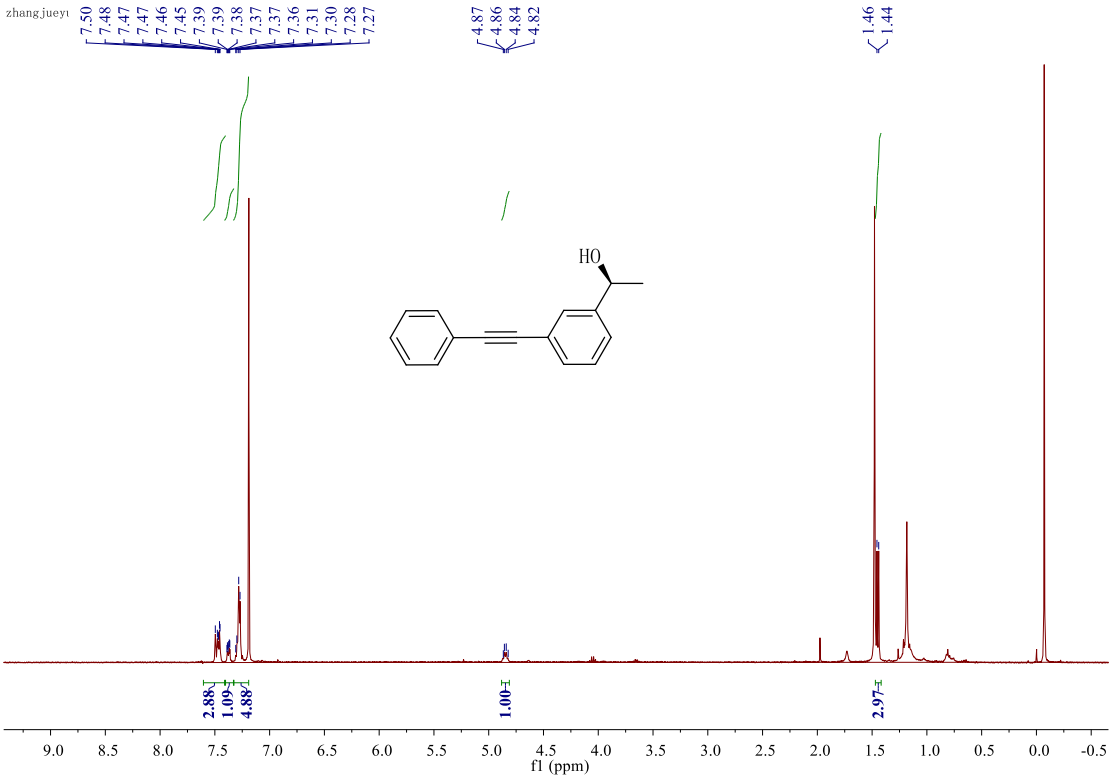


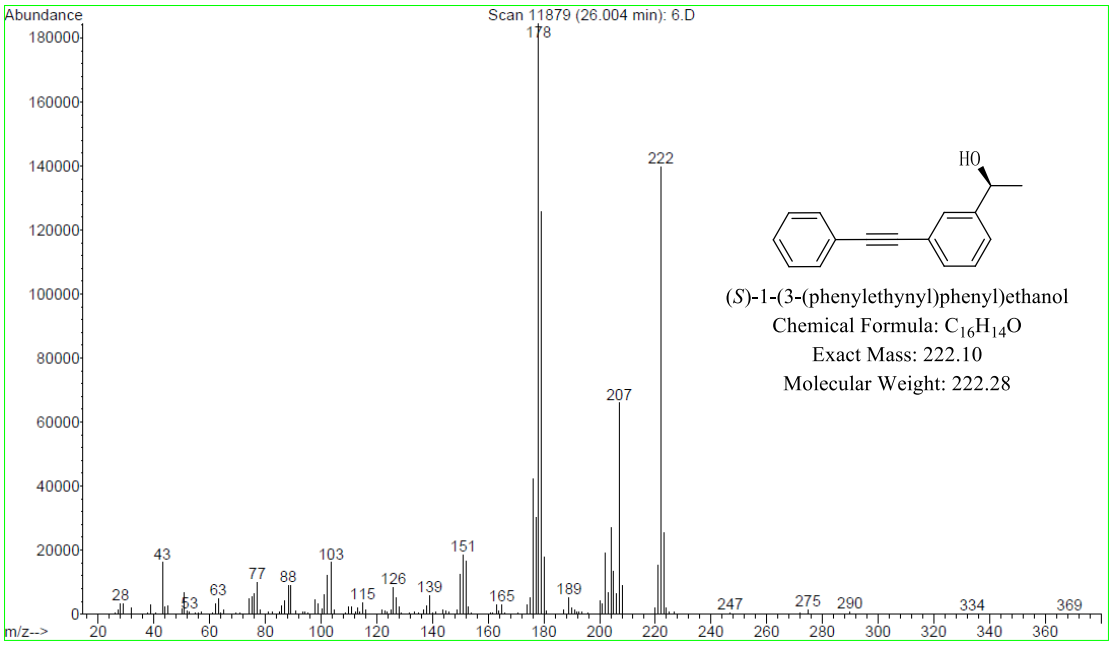
(*S*)-1-(4-(m-tolylethynyl)phenyl)ethanol



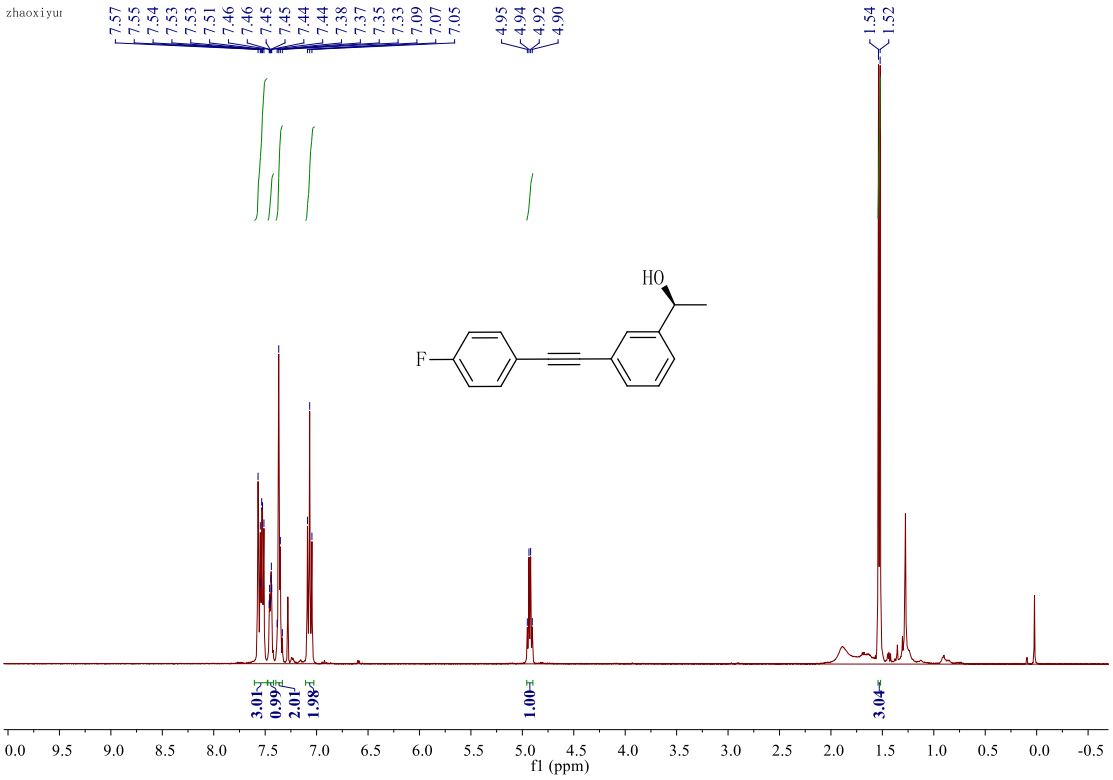


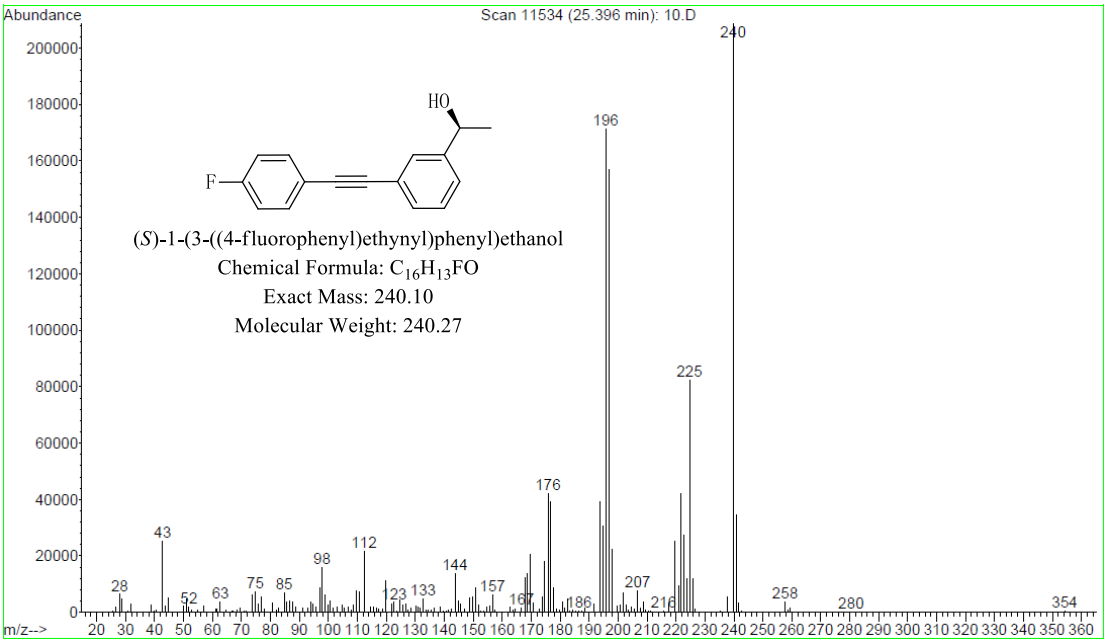
(*S*)-1-(3-(phenylethynyl)phenyl)ethanol



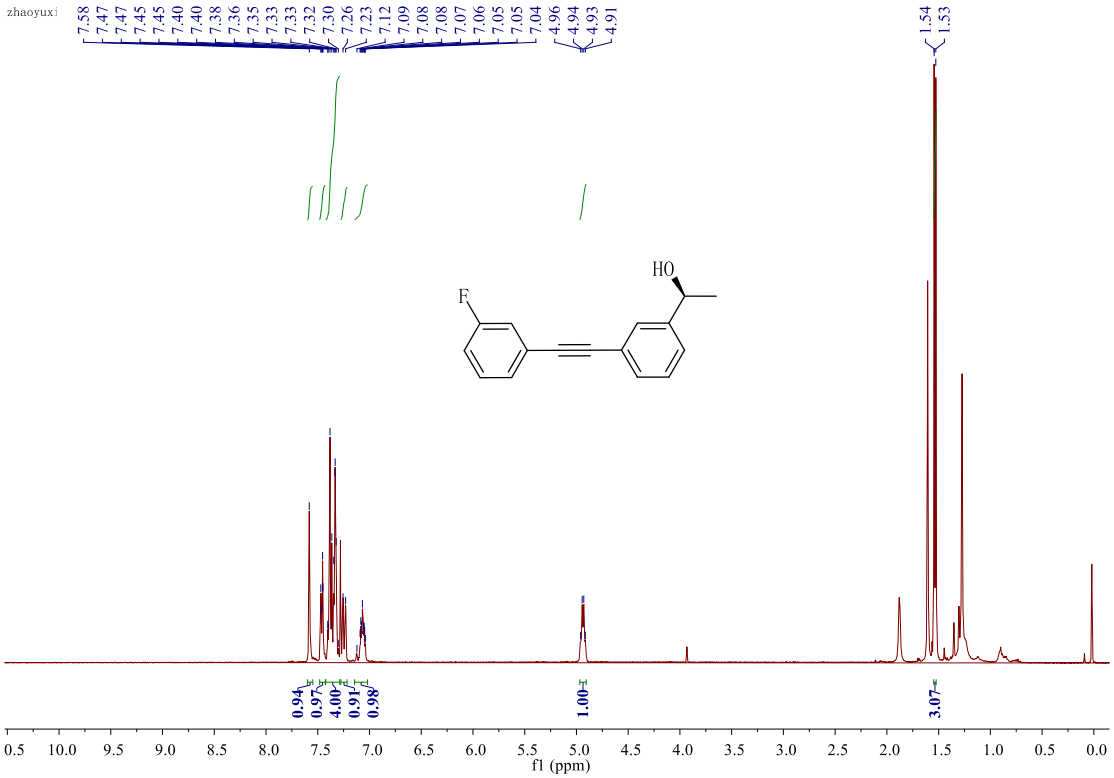


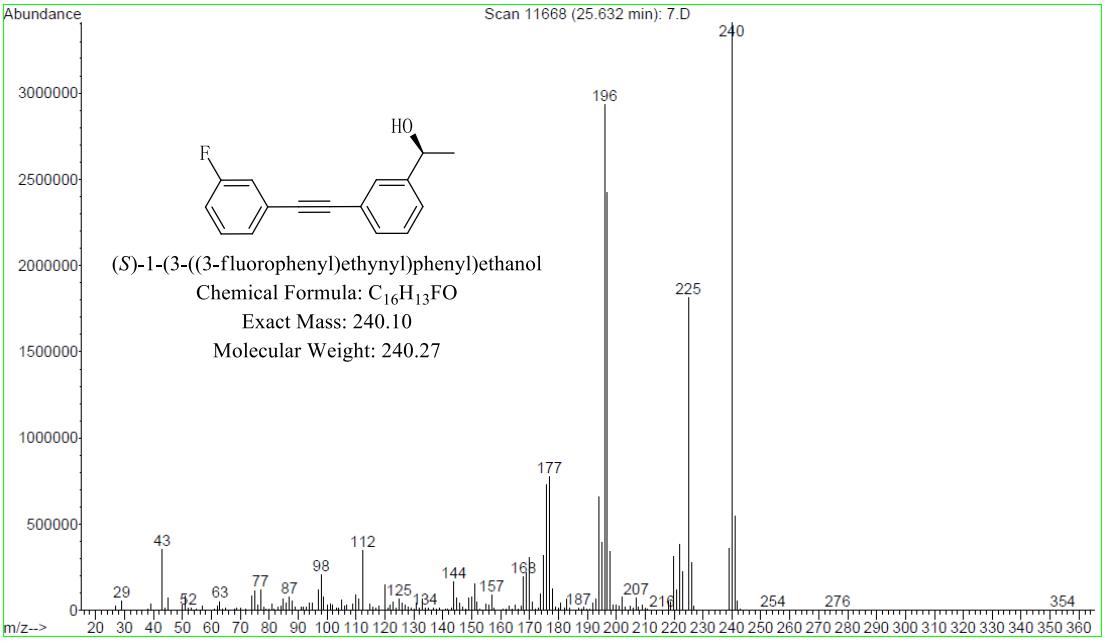
(*S*)-1-(3-((4-fluorophenyl)ethynyl)phenyl)ethanol.



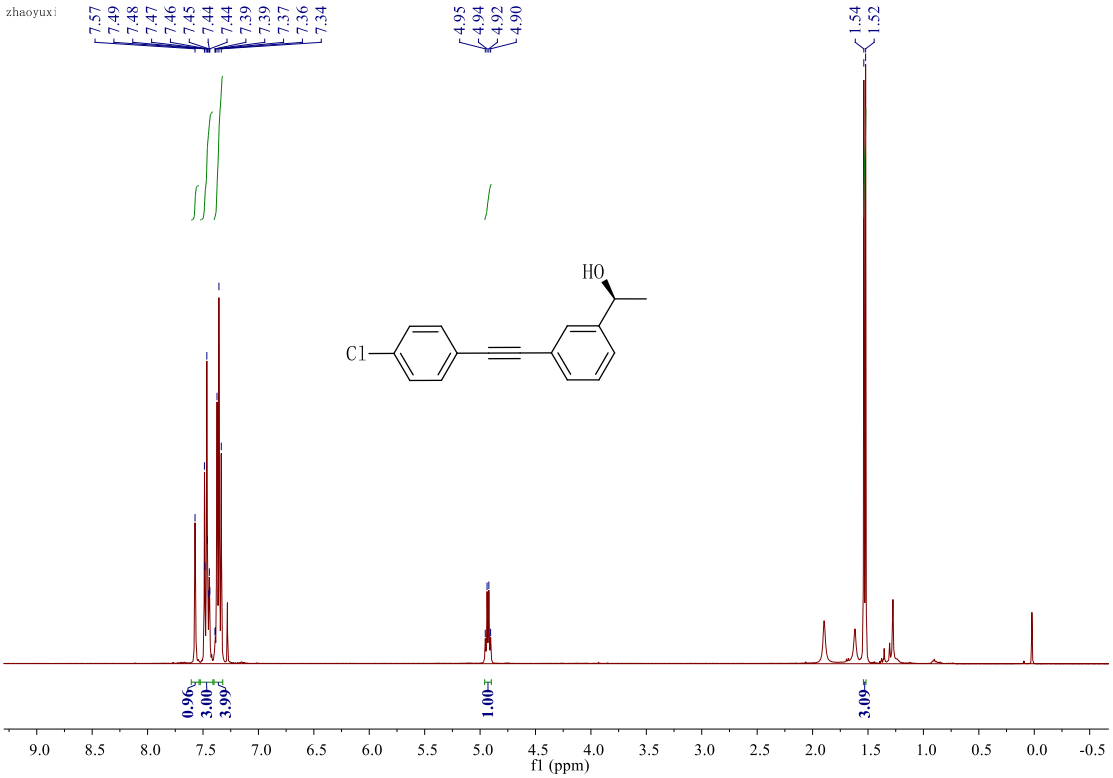


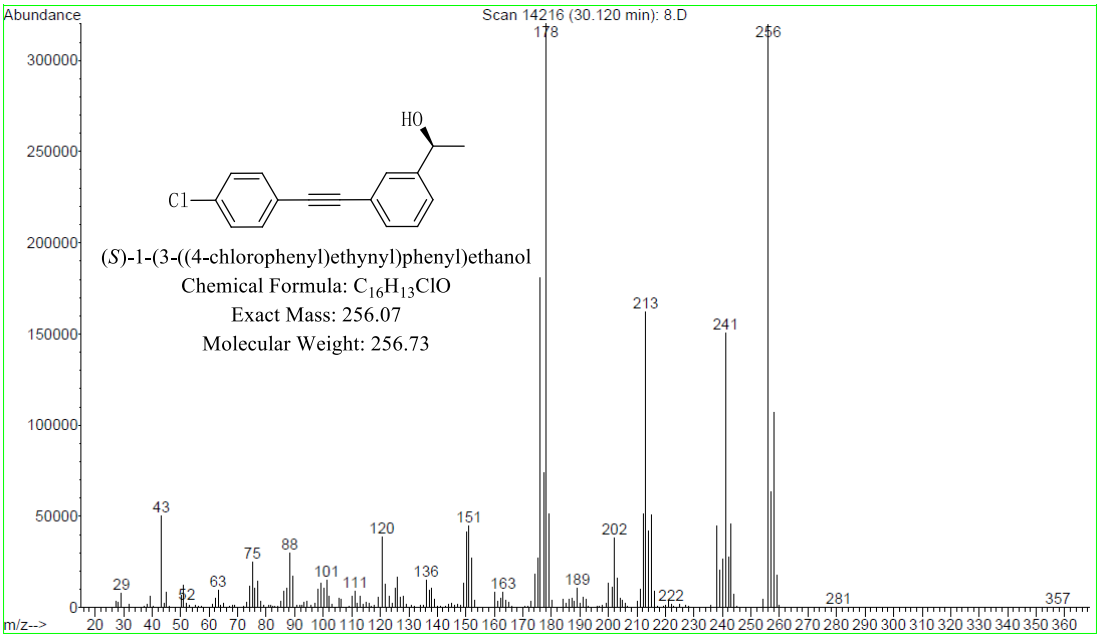
(*S*)-1-(3-((3-fluorophenyl)ethynyl)phenyl)ethanol.



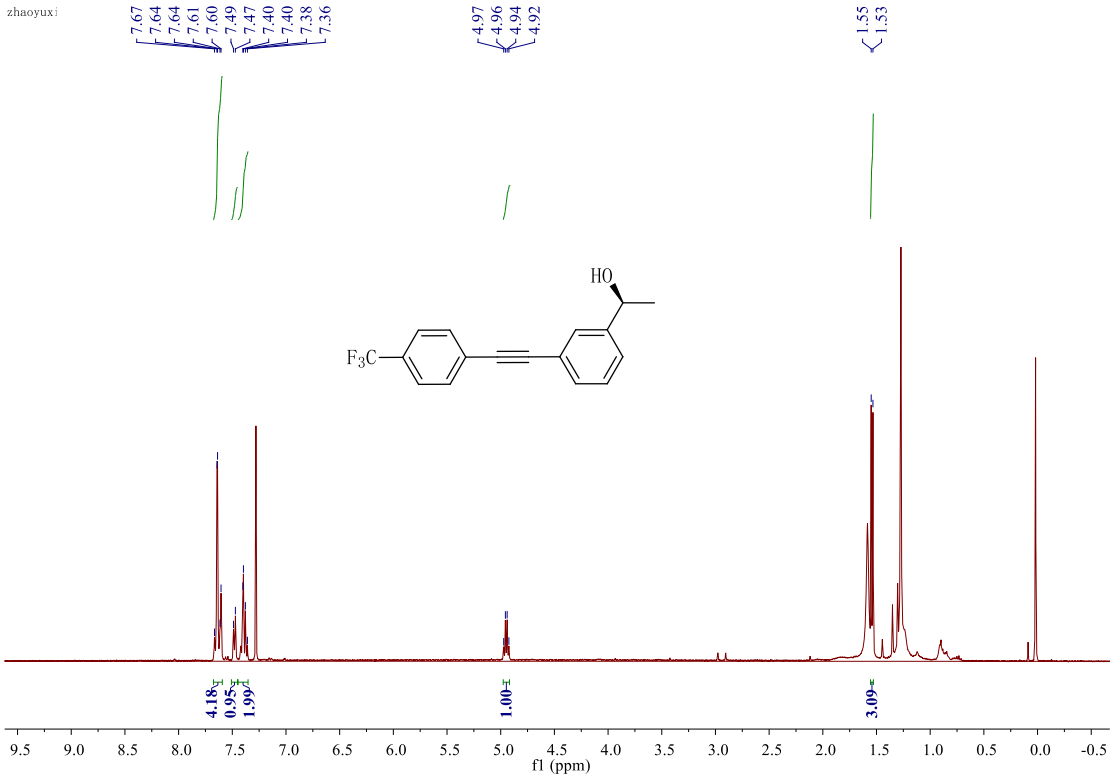


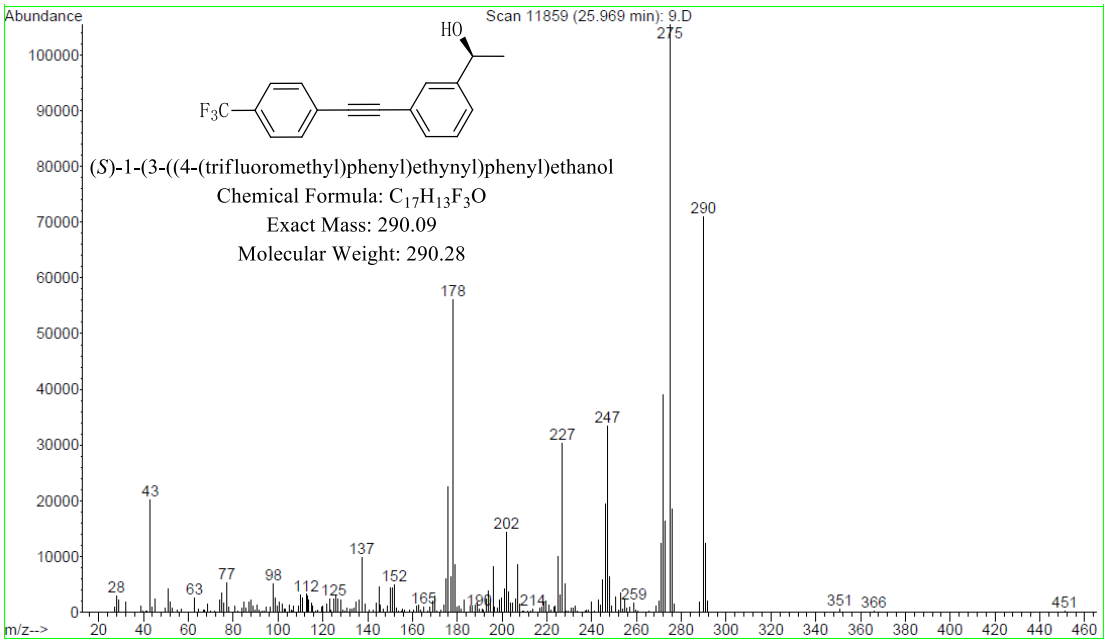
(S)-1-(3-((4-chlorophenyl)ethynyl)phenyl)ethanol.



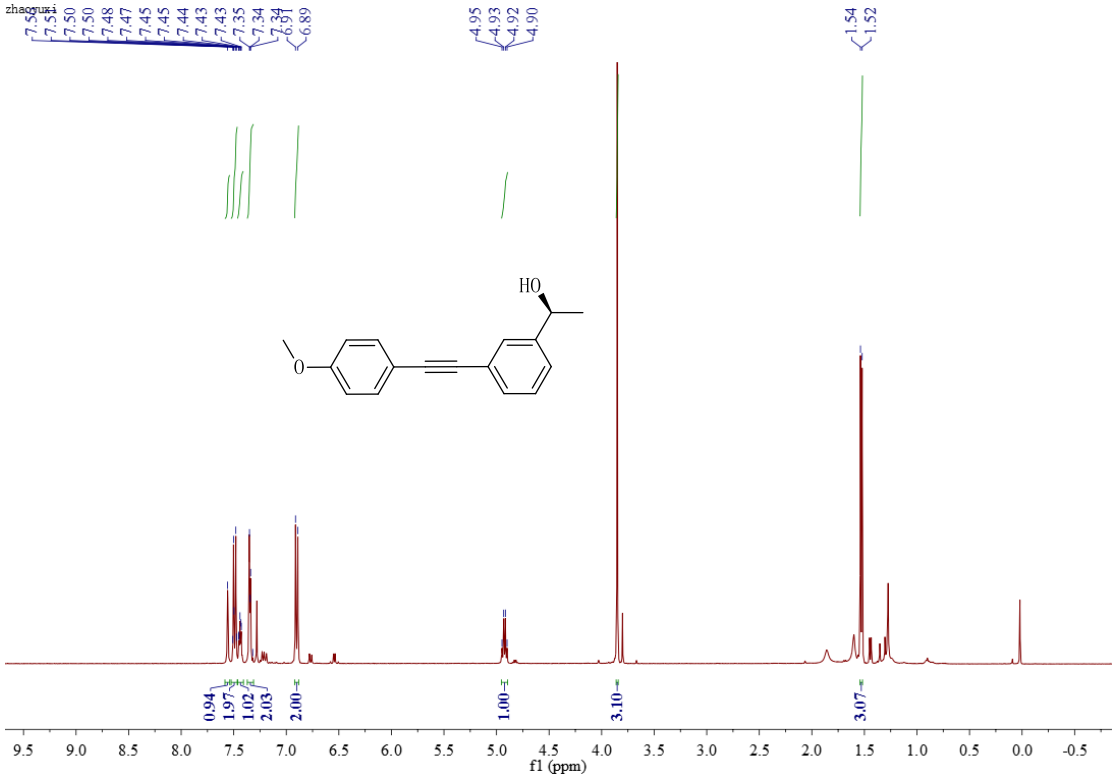


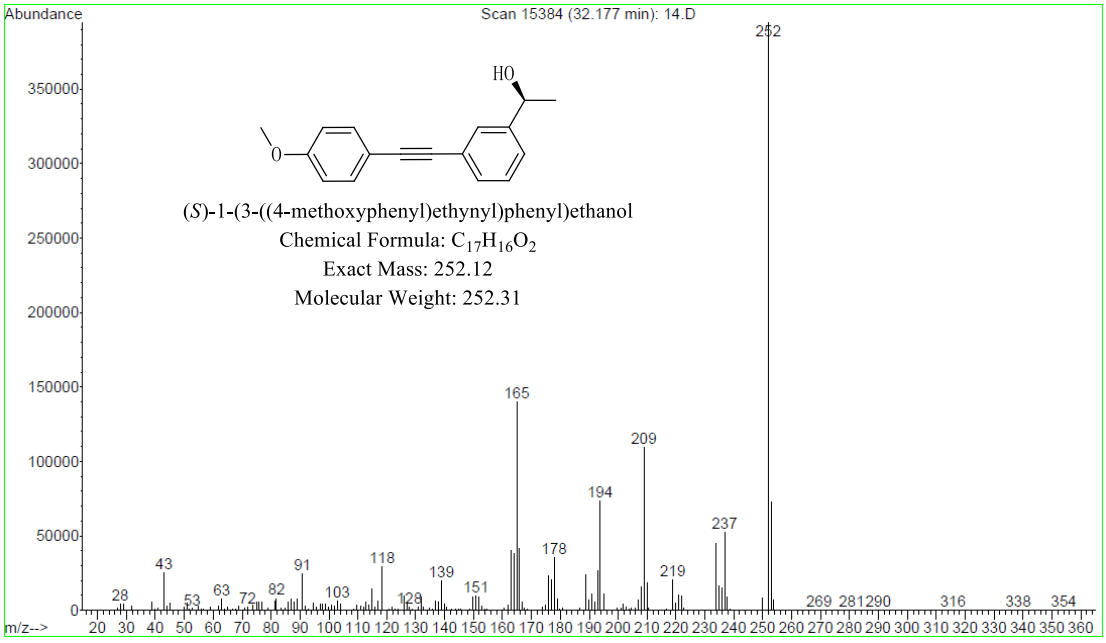
(*S*)-1-(3-((4-(trifluoromethyl)phenyl)ethynyl)phenyl)ethanol.



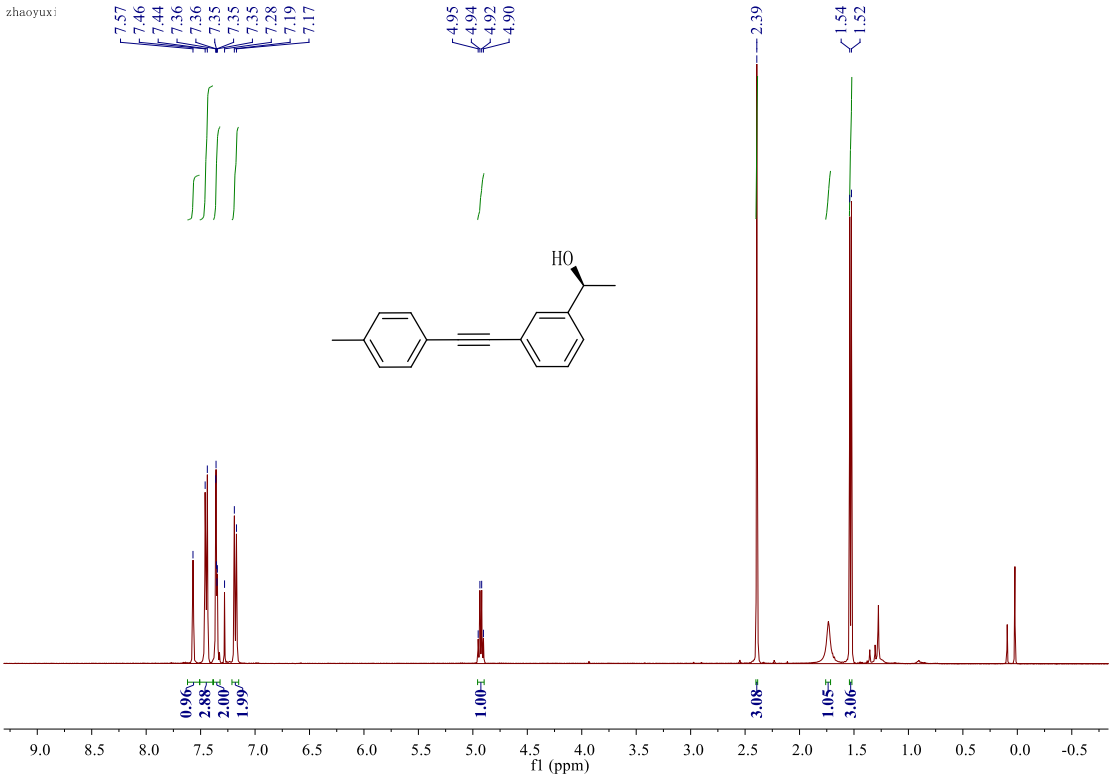


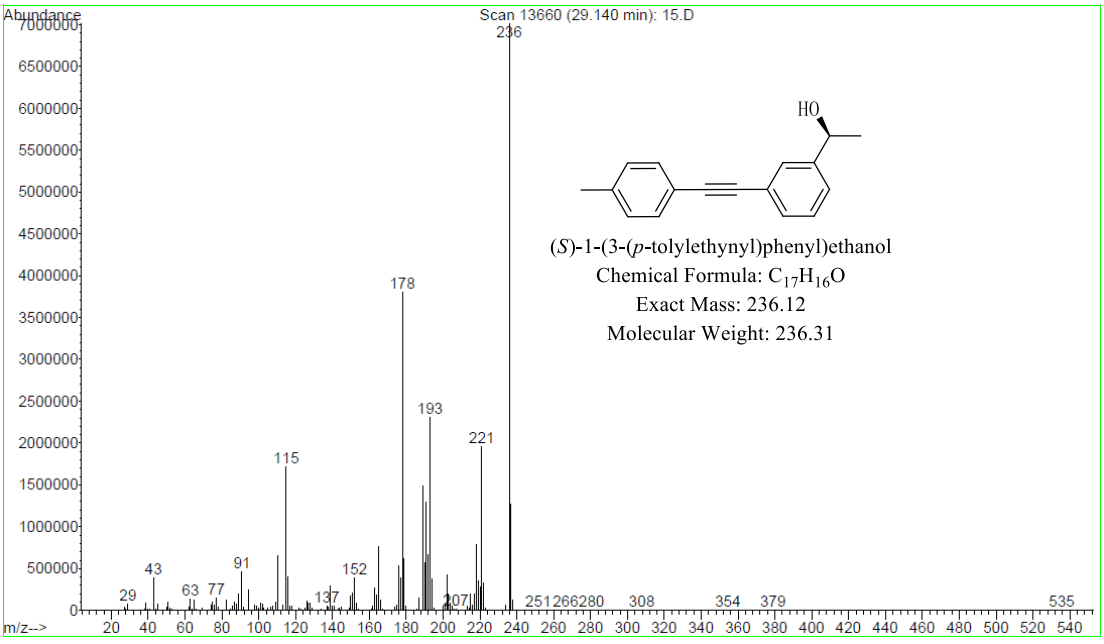
(*S*)-1-(4-((4-methoxyphenyl)ethynyl)phenyl)ethanol.



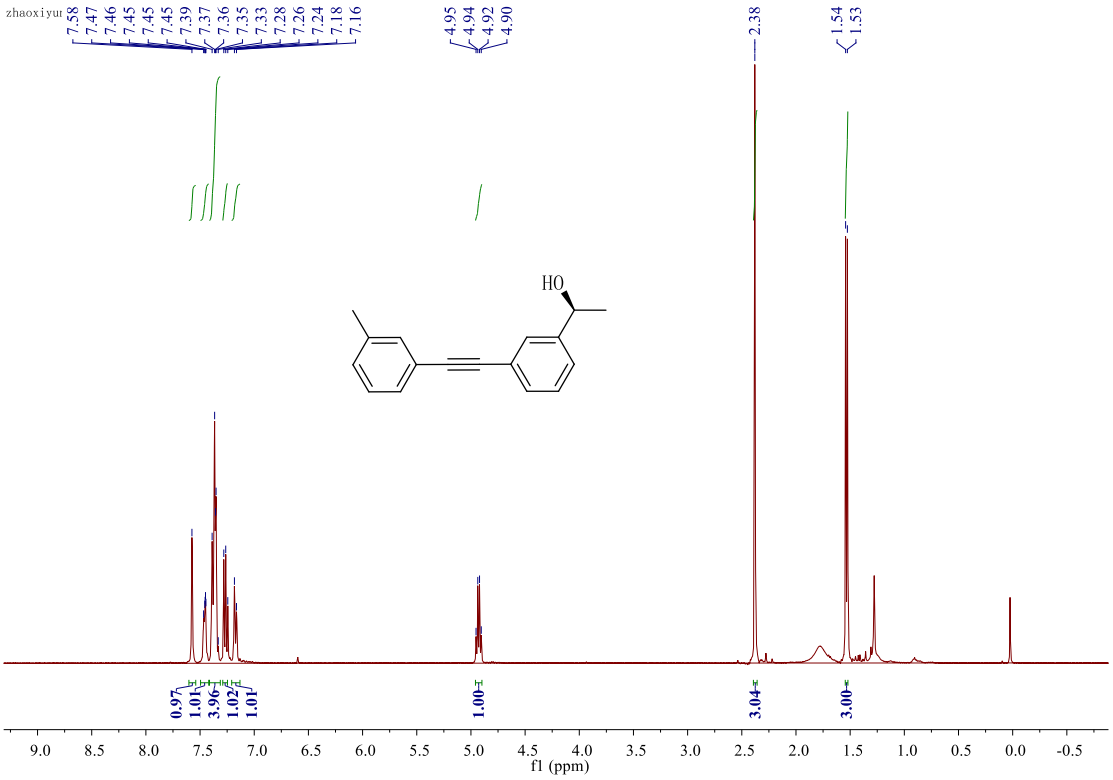


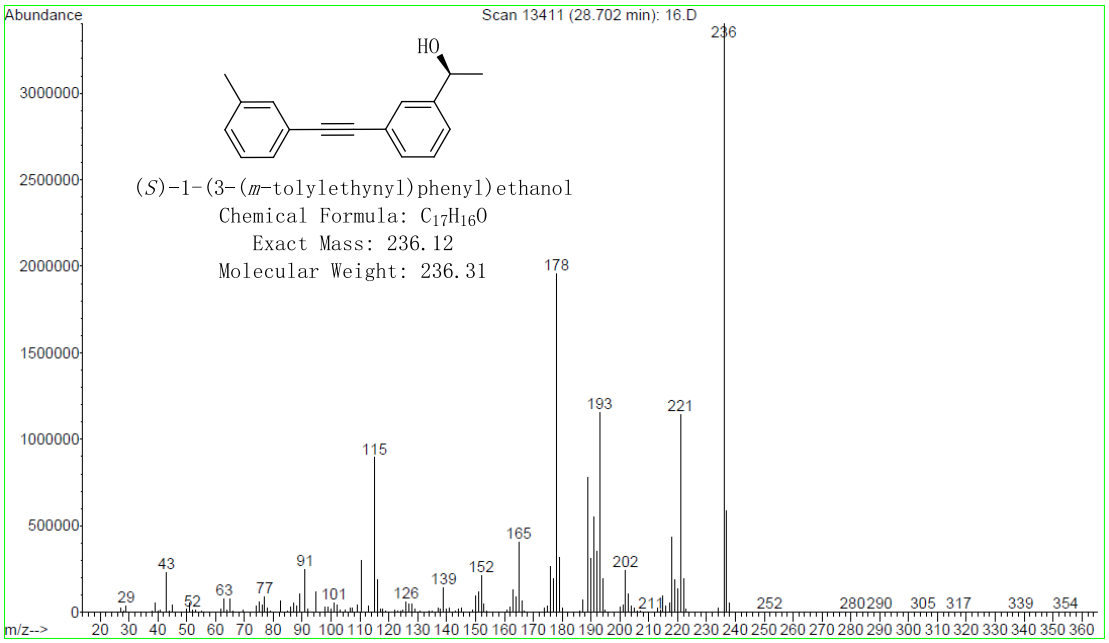
(S)-1-(4-(p-tolylethynyl)phenyl)ethanol.





(*S*)-1-(4-(m-tolylethynyl)phenyl)ethanol





(*S*)–1–(3–((4–((*S*)–1–hydroxyethyl)phenyl)ethynyl)phenyl)ethanol.