

Supplementary information

Half-Sandwich Ru(η^6 -C₆H₆) Complexes with Chiral Aroylthioureas for Enhanced Asymmetric Transfer Hydrogenation of Ketones – Experimental and Theoretical Studies

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A. Experimental Part

The molecular structure of the ligands (L2 and L4)

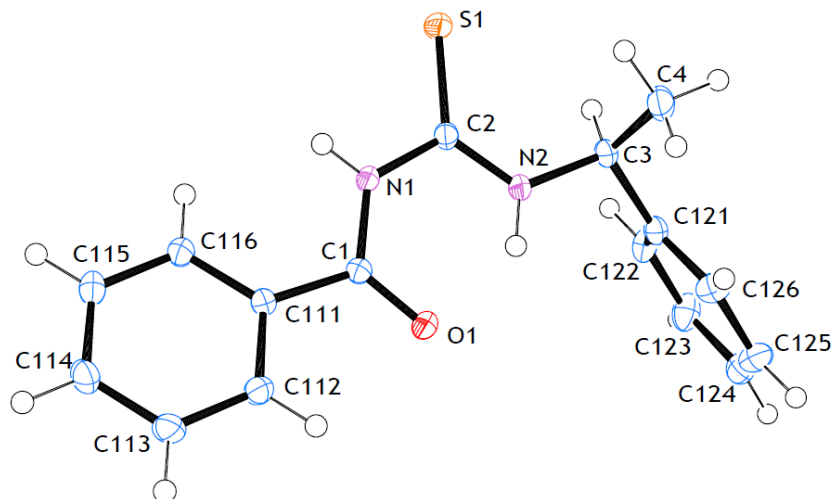


Figure S1. ORTEP view of L2 showing the atomic labeling scheme and thermal ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (°): S1–C2 1.6733(12), O1–C1 1.2262(14), N1–C2–S1 117.95(9), N2–C2–S1 125.63(9), N1–C2–N2 116.42(10).

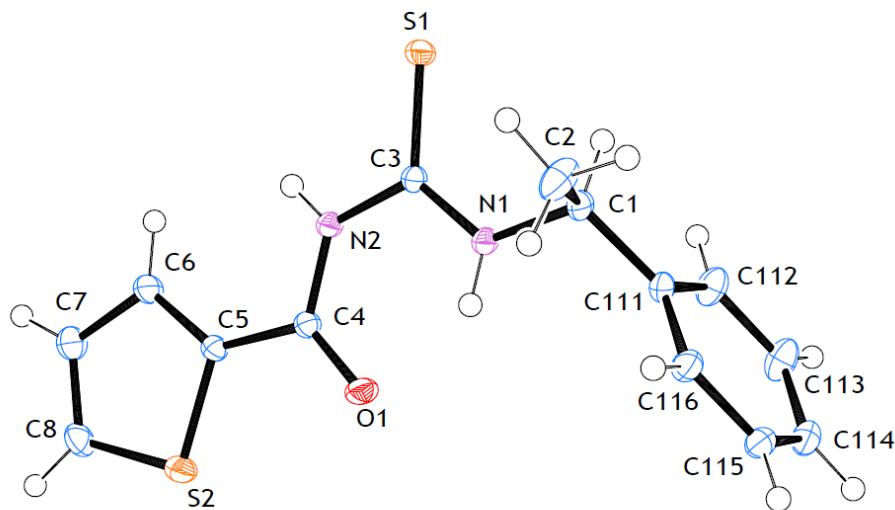


Figure S2. ORTEP view of L4 showing the atomic labeling scheme and thermal ellipsoids at the 50% probability level. Selected bond distances (Å) and angles (°): S1–C3 1.6720(8), O1–C4 1.2310(10), N1–C3–N2 116.17(7), N1–C3–S1 125.51(6), N2–C3–S1 118.32(6).

Supplementary Table S1. Experimental details for the x-ray diffraction studies.

Compound formula	C ₁₆ H ₁₆ N ₂ OS	C ₁₄ H ₁₄ N ₂ OS ₂	C ₂₄ H ₂₅ Cl ₁₂ N ₄ ORuS	C ₂₀ H ₂₀ Cl ₂ N ₂ ORuS ₂	C ₂₀ H ₂₀ Cl ₂ N ₂ O ₂ RuS
Compound name	L2	L4	2	4	5
Crystal color	colourless	colourless	orange	orange	orange
<i>M_r</i>	284.37	290.29	575.5	540.47	524.41
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>P</i> 2 ₁ 2 ₁ 2 ₁
Crystal system	orthorhombic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
<i>a</i> /Å	7.2412(3)	7.1805(1)	10.0568(7)	6.6174(10)	6.5030(1)
<i>b</i> /Å	10.1066(4)	9.8395(1)	14.9314(11)	17.1016(3)	10.2867(1)
<i>c</i> /Å	19.6810(8)	19.6096(3)	16.7695(12)	19.4048(4)	31.8305(4)
<i>V</i> /Å ³	1440.33(10)	1385.47(3)	2518.1(3)	2196.0(7)	2129.28(5)
<i>Z</i>	4	4	4	4	4
<i>D_{calc}</i> /g cm ⁻³	1.311	1.392	1.518	1.635	1.636
<i>λ</i> /Å	0.71073	0.71073	0.71073	0.71073	0.71073
<i>μ</i> /mm ⁻¹	0.222	0.377	0.939	1.161	1.104
Temperature/K	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal size/mm	0.61×0.51×0.42	0.53×0.45×0.29	0.5×0.5×0.4	0.80×0.29×0.15	0.52×0.51×0.18
θ range/deg	2.07 – 30.0	2.08 – 35.0	2.36 – 32.97	2.10 – 35.03	2.08 – 34.99
No. of merged data	34963	96584	65424	83354	72807
No. of unique data	4204	6086	9486	9662	9381
<i>hkl</i> range	-10 ≤ <i>h</i> ≤ 10 -14 ≤ <i>k</i> ≤ 14 -27 ≤ <i>l</i> ≤ 27	-11 ≤ <i>h</i> ≤ 11 -15 ≤ <i>k</i> ≤ 15 -31 ≤ <i>l</i> ≤ 31	-15 ≤ <i>h</i> ≤ 15 -22 ≤ <i>k</i> ≤ 22 -25 ≤ <i>l</i> ≤ 25	-10 ≤ <i>h</i> ≤ 10 -27 ≤ <i>k</i> ≤ 27 -31 ≤ <i>l</i> ≤ 31	-10 ≤ <i>h</i> ≤ 10 -16 ≤ <i>k</i> ≤ 16 -51 ≤ <i>l</i> ≤ 51
<i>R_{int}</i>	0.022	0.027	0.059	0.035	0.024
<i>R_σ</i>	0.026	0.025	0.046	0.032	0.028
No. of data in refinement	4204	6086	9486	9962	9381
No. of refined parameters	204	193	330	281	281
Final <i>R</i> [<i>I</i> > 2σ(<i>I</i>)] (all data)	0.023(0.024)	0.021 (0.022)	0.050 (0.054)	0.018(0.020)	0.015(0.016)
<i>R_w</i> ² [<i>I</i> > 2σ(<i>I</i>)] (all data)	0.063(0.064)	0.061 (0.061)	0.128 (0.126)	0.044(0.044)	0.038(0.038)
Goodness of fit <i>S</i>	1.04	1.046	1.065	1.05	1.06
Flack parameter	0.011(12)	-0.002(10)	0.092(11)	-0.009(7)	0.014(6)
Extrema in residual map/ e Å ⁻³	0.30 → -0.19	0.35 → -0.26	1.21 → -2.04	0.64 → -0.64	0.56 → -0.64
Max shift/esd in last cycle	1.0×10 ⁻³	1.0×10 ⁻³	1.0×10 ⁻³	5.0×10 ⁻³	1.0×10 ⁻²

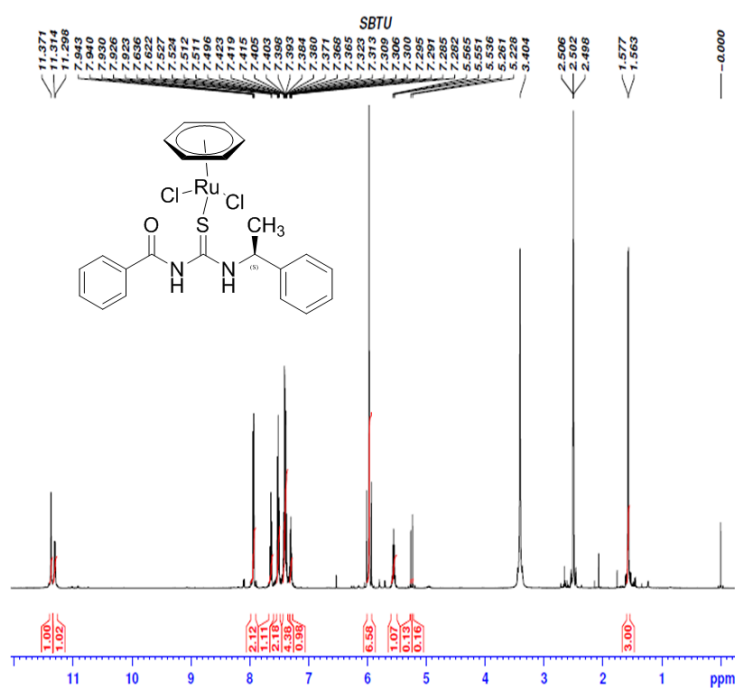
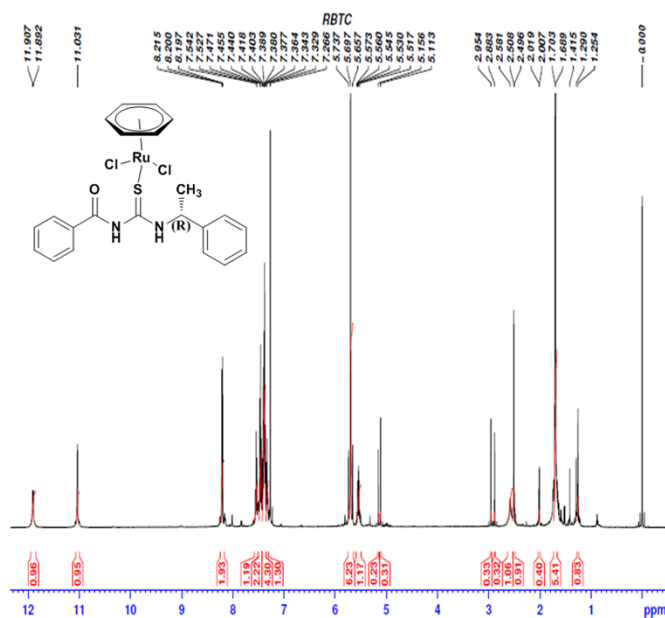
$$R = \sum (|F_o| - |F_c|) / \sum (F_o)$$

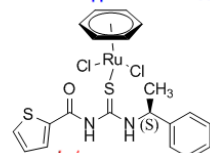
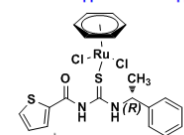
$$R_w = \{\sum (w(F_o - F_c)^2) / \sum (w(F_o)^2)\}^{1/2}$$

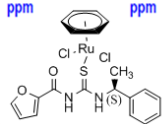
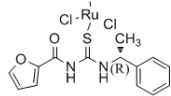
$$R_w^2 = \{\sum (w(F_o^2 - F_c^2)^2) / \sum (w(F_o^2)^2)\}^{1/2} \quad R_\sigma = \sum [\sigma(F_o^2)] / \sum [F_o^2]$$

$$R_{int} = \sum \{n/(n-1)^{1/2} | F_o^2 - F_o^2(\text{mean}) | / \sum F_o^2 \text{ (summation carried out when more than one symmetry equivalent is averaged)}\}$$

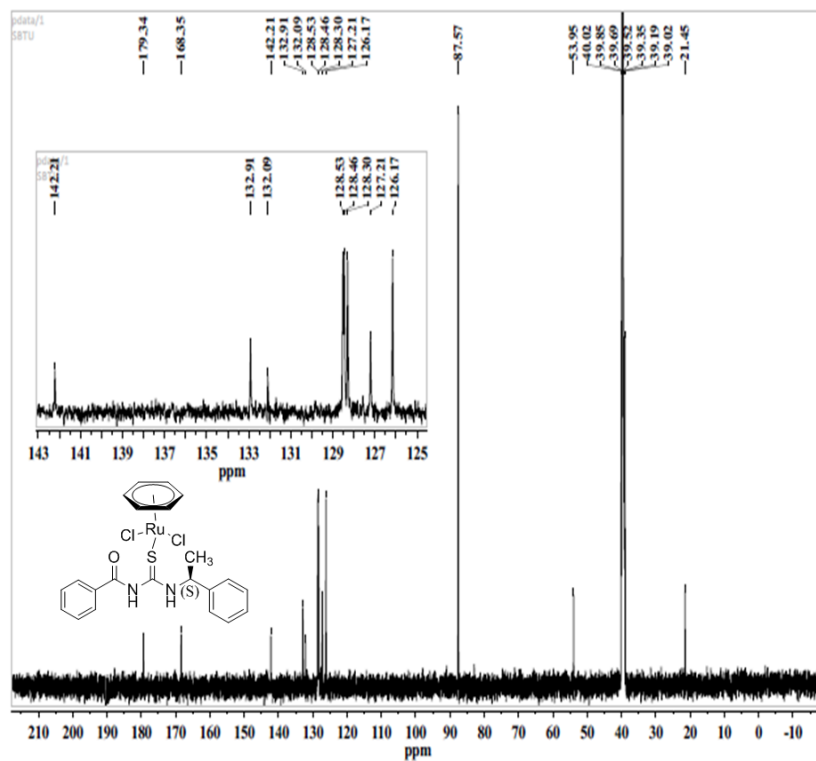
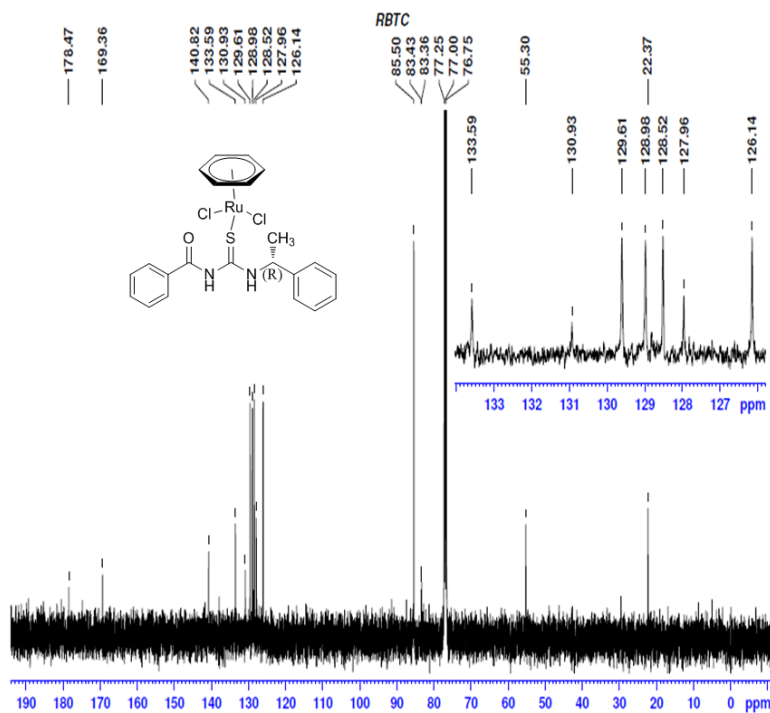
¹H NMR Spectra of the Complexes

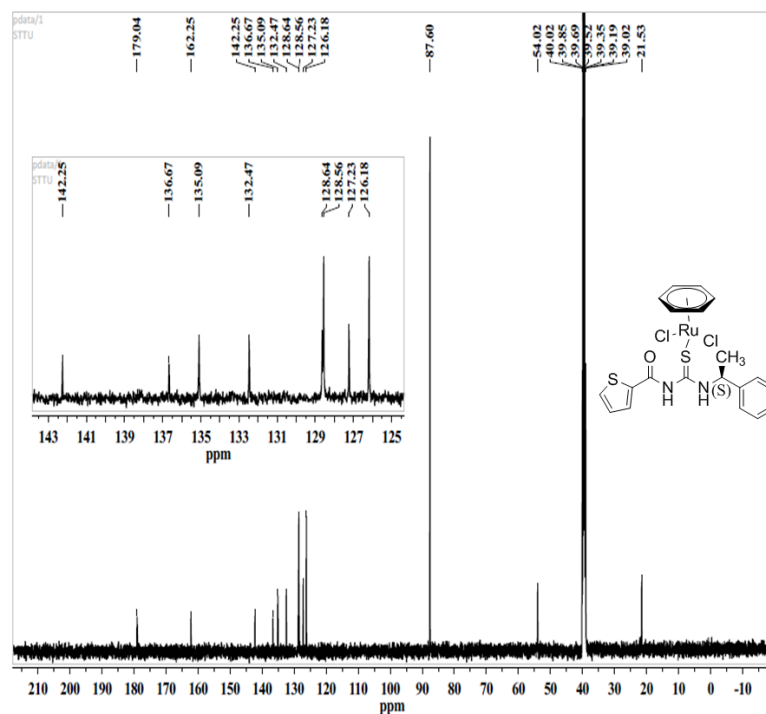
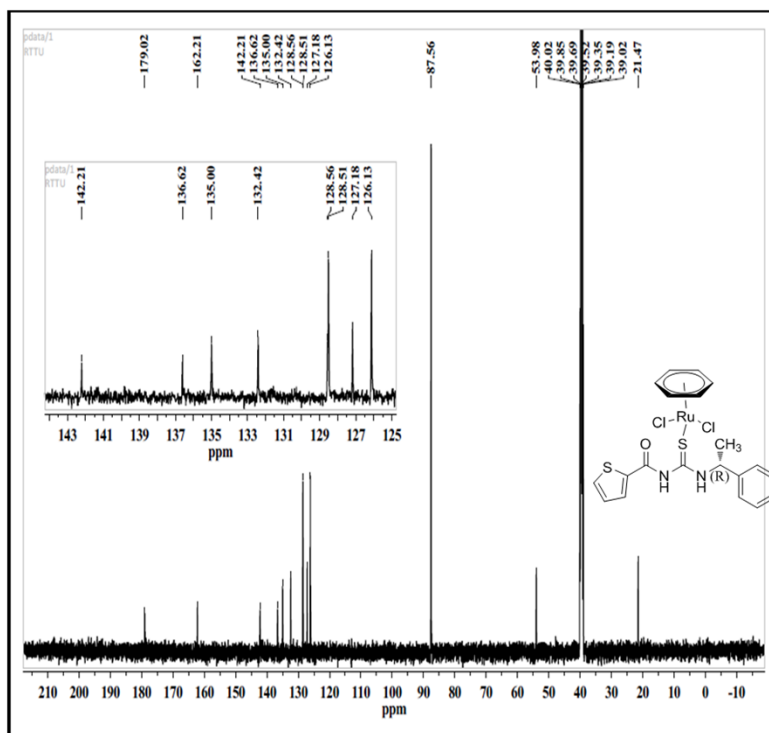


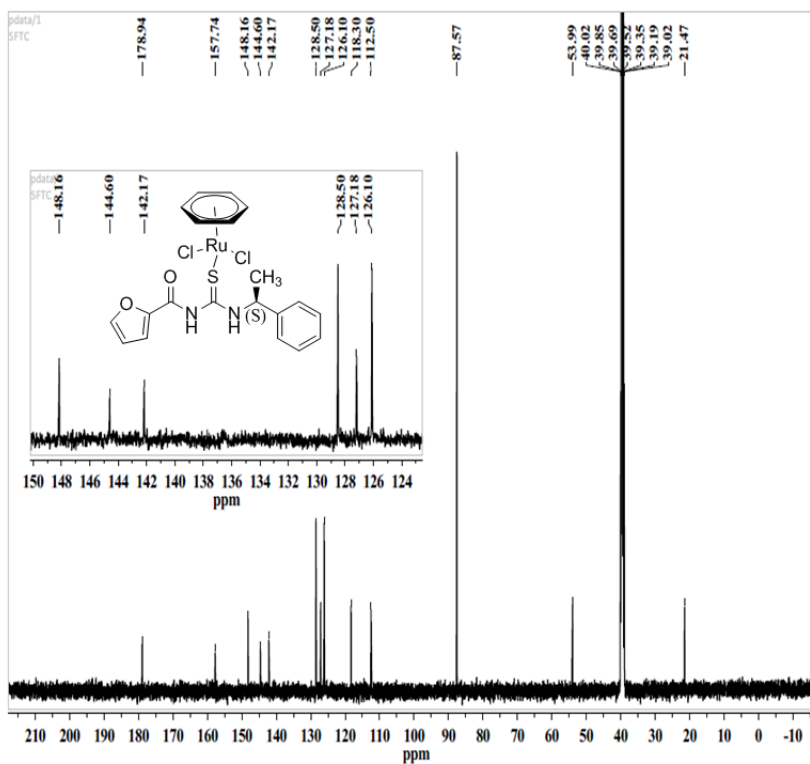
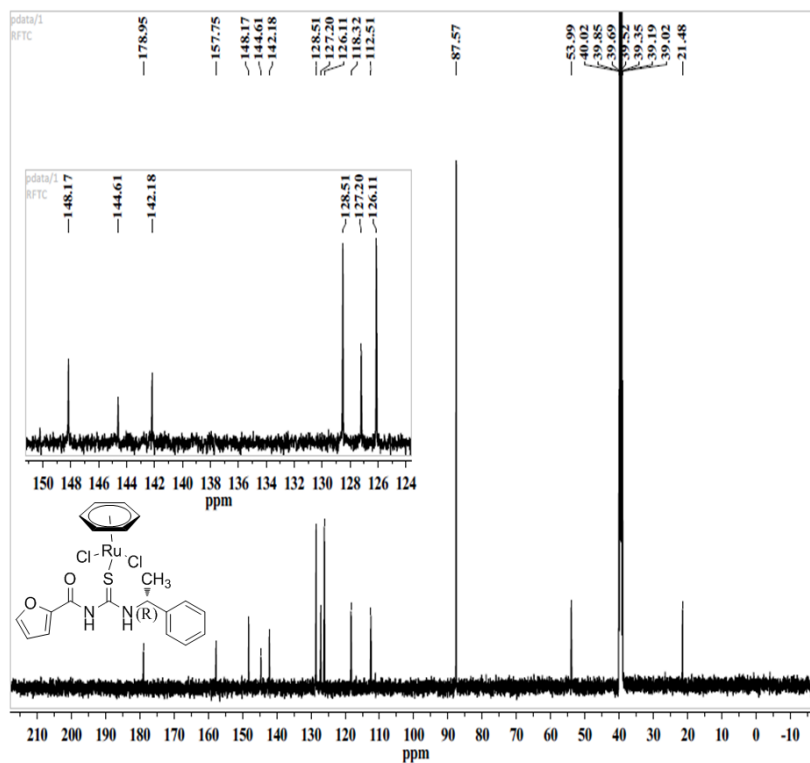




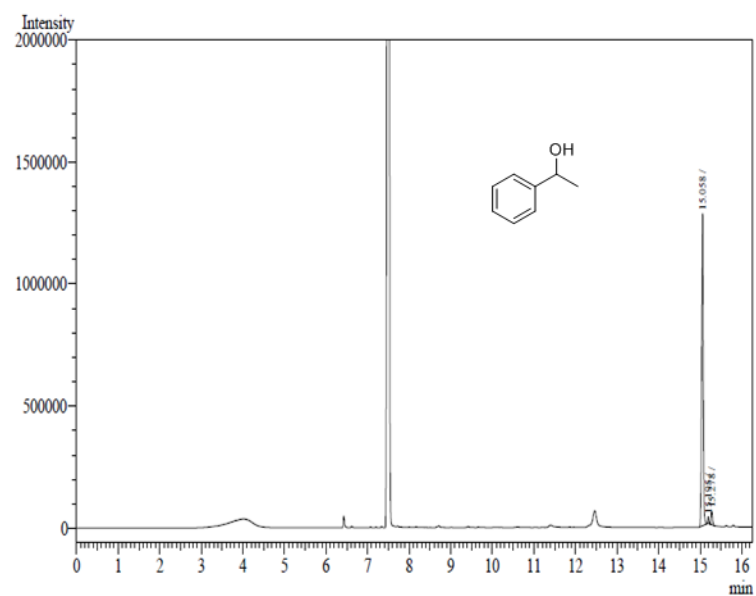
¹³C NMR Spectra of the Complexes



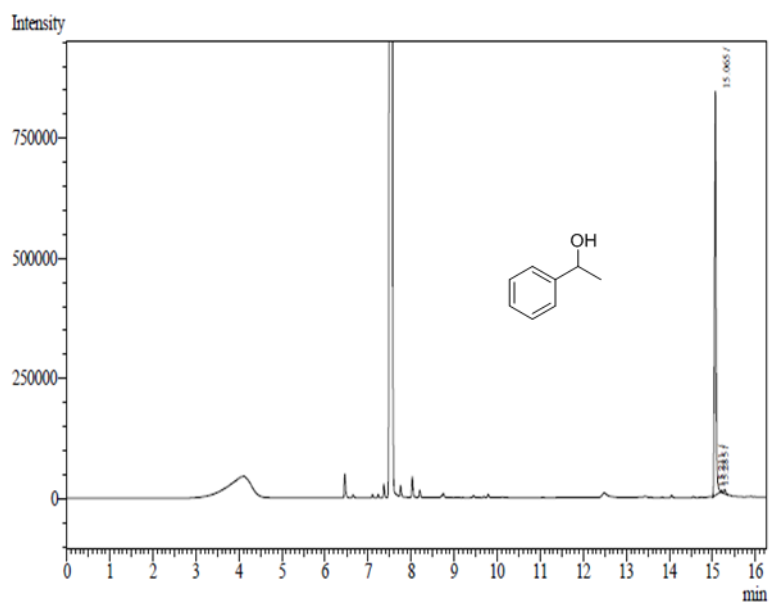




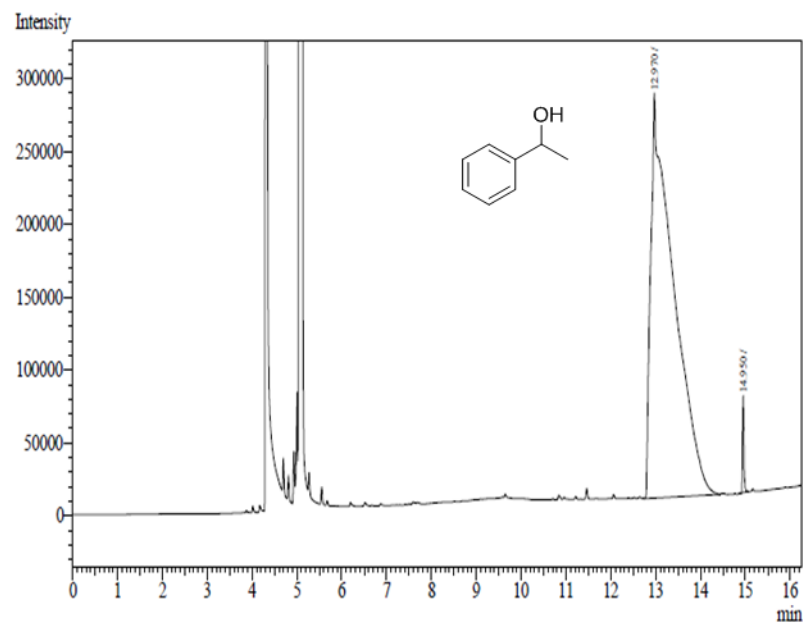
GC Data



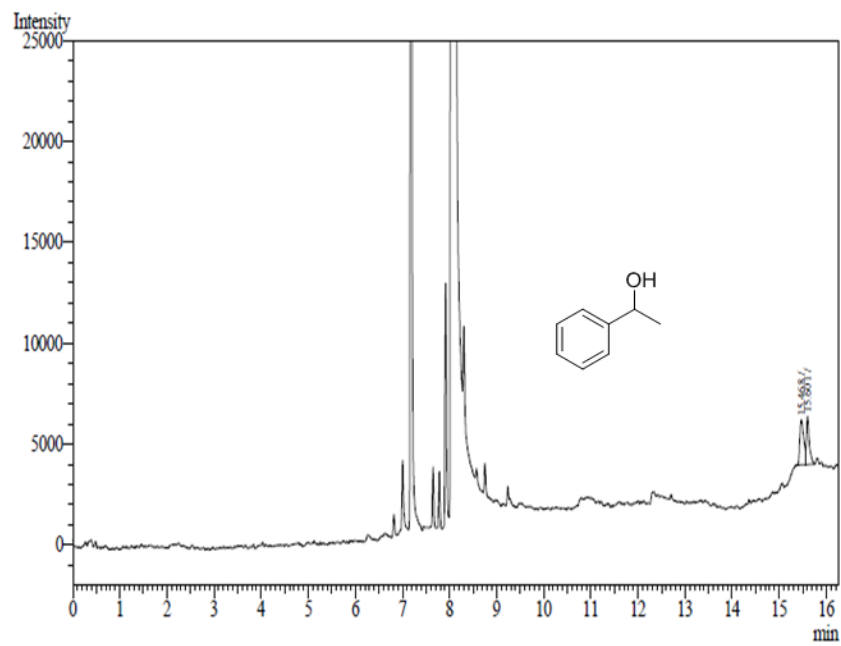
Peak#	Ret.Time	Area	Height	Area%	Conc.
1	15.058	3385909	1273204	94.8604	94.860
2	15.195	47405	27043	1.3281	1.328
3	15.278	136044	56250	3.8114	3.811
Total		3569358	1356497	100.0000	



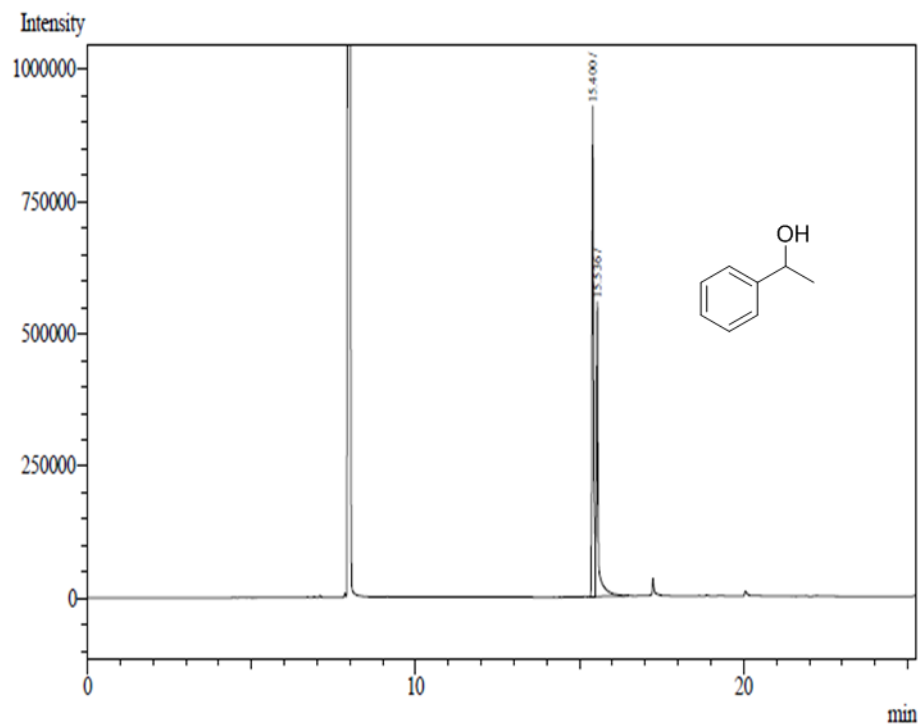
Peak#	Ret.Time	Area	Height	Area%	Conc.
1	15.065	2025903	834032	98.4573	98.457
2	15.211	7976	4885	0.3876	0.388
3	15.285	23767	8846	1.1550	1.155
Total		2057646	847763	100.0000	



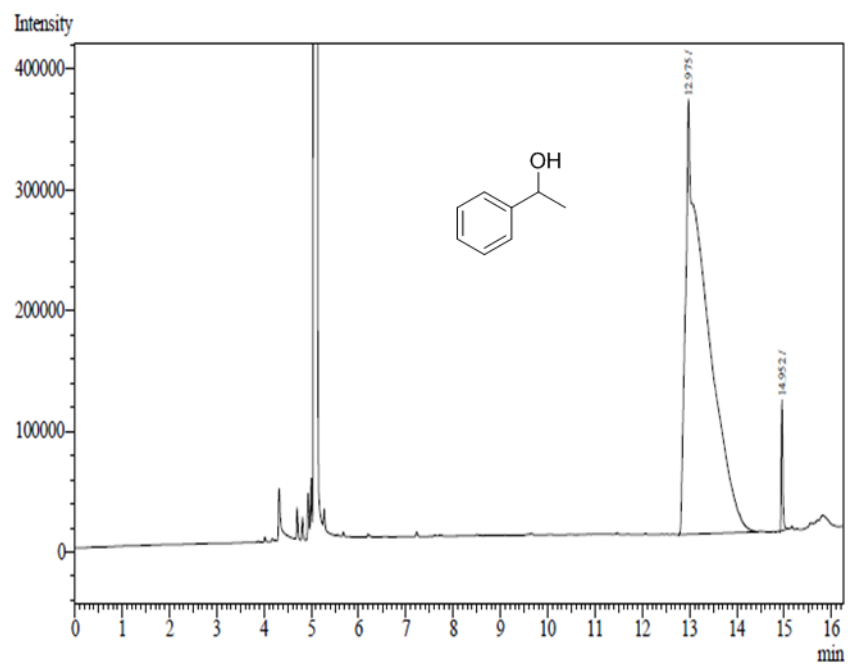
Peak#	Ret. Time	Area	Area%	Height	Conc.
1	12.970	9804353	98.5709	277470	98.571
2	14.950	142142	1.4291	66031	1.429
Total		9946495	100.0000	343501	100.000



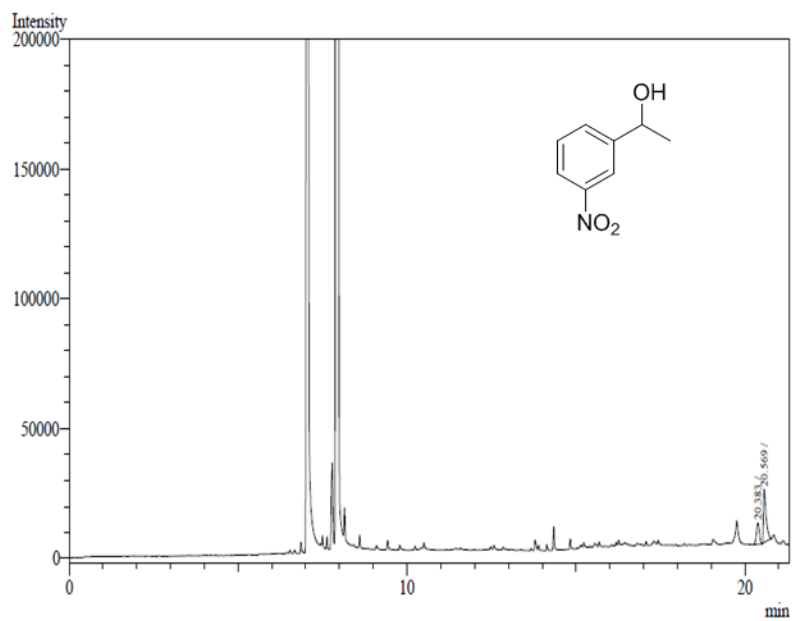
Peak#	Ret. Time	Area	Area%	Height
1	15.468	13000	56.5393	2234
2	15.601	9993	43.4607	2385
Total		22993	100.0000	4619



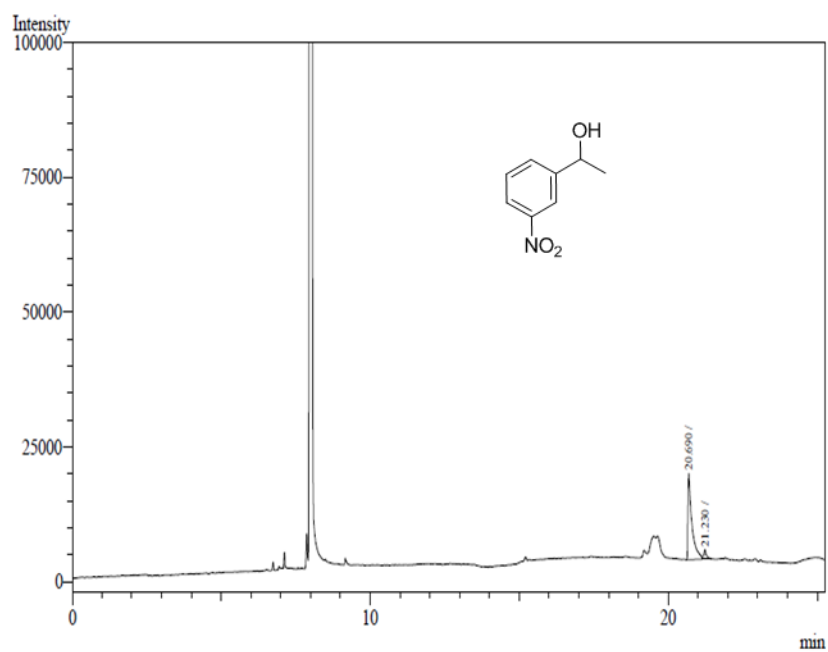
Peak#	Ret. Time	Area	Height	Area%	Conc.
1	15.400	3098933	919703	59.5906	59.591
2	15.536	2101435	552029	40.4094	40.409
Total		5200368	1471732	100.0000	



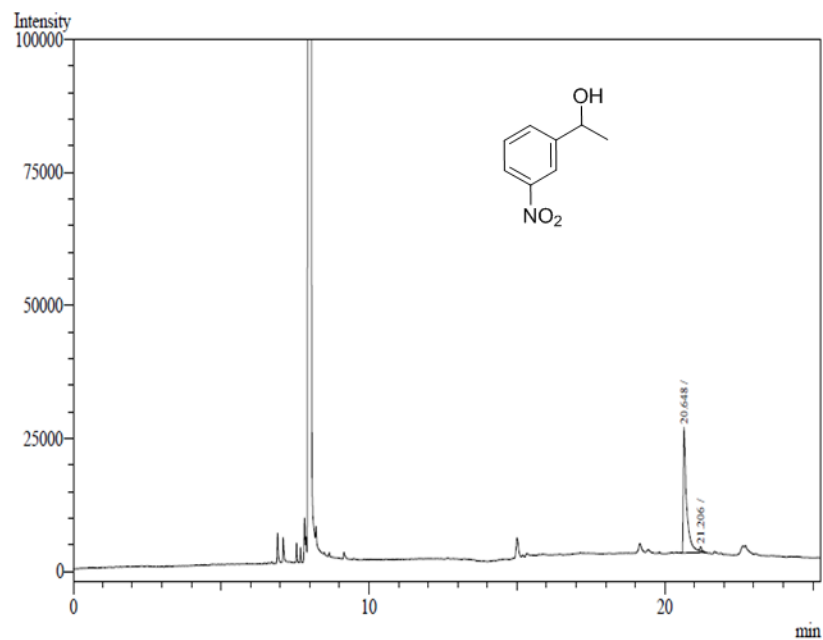
Peak#	Ret. Time	Area	Area%	Height	Conc.
1	12.975	10943117	97.8717	359473	97.872
2	14.952	237964	2.1283	106956	2.128
Total		11181081	100.0000	466429	100.000



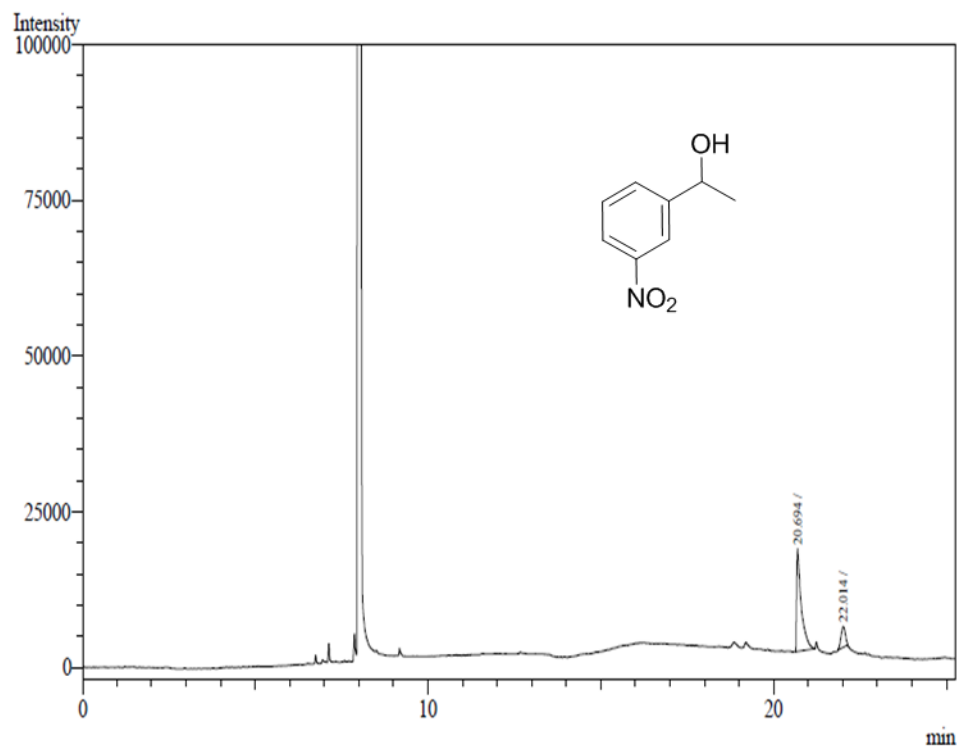
Peak#	Ret.Time	Area	Area%	Height	Conc.
1	20.383	49196	31.0899	8201	31.090
2	20.569	109041	68.9101	20501	68.910
Total		158237	100.0000	28702	100.000



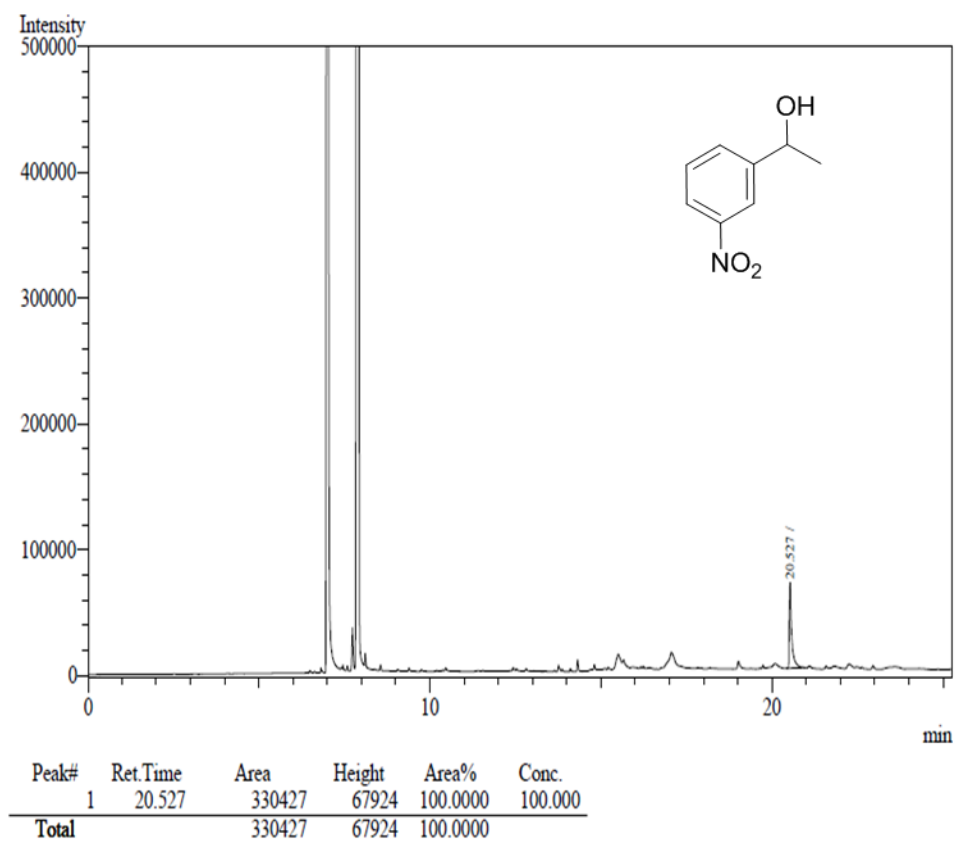
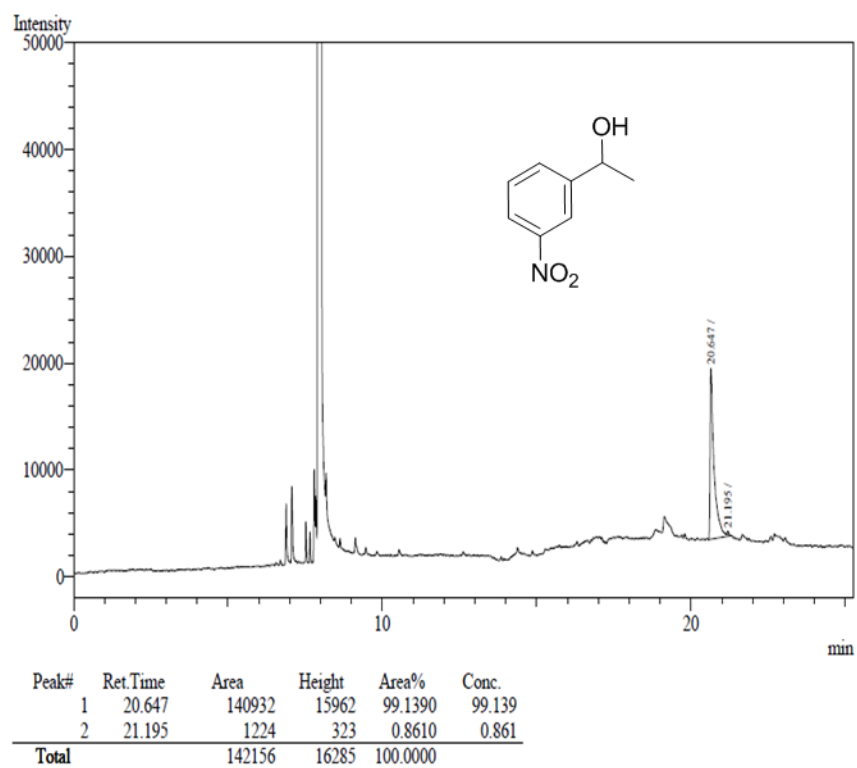
Peak#	Ret.Time	Area	Area%	Height	Conc.
1	20.690	145625	92.8958	15962	92.896
2	21.230	11137	7.1042	1784	7.104
Total		156762	100.0000	17746	100.000

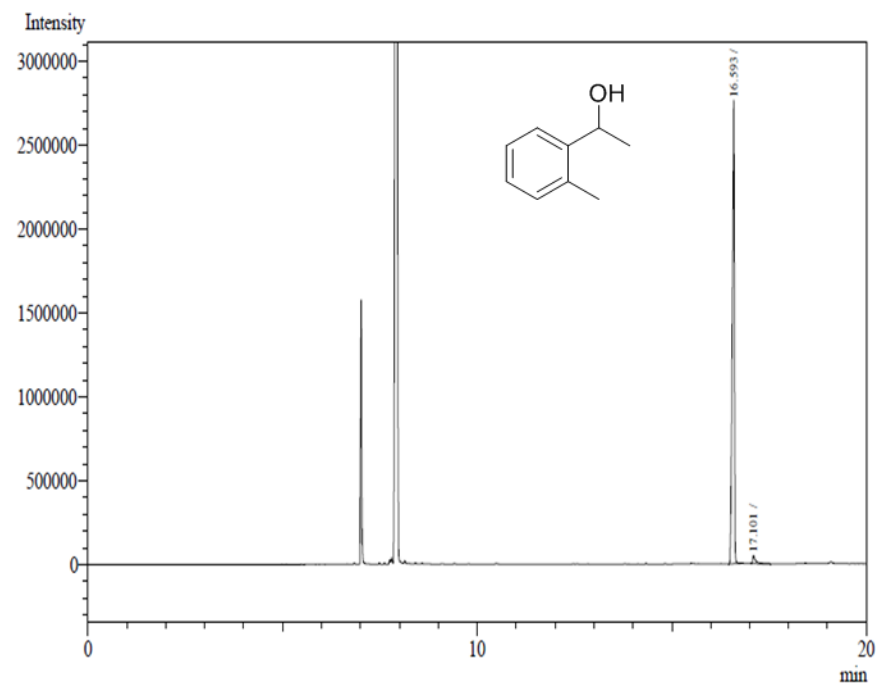


Peak#	Ret.Time	Area	Height	Area%	Conc.
1	20.648	181698	23561	97.9406	97.941
2	21.206	3821	830	2.0594	2.059
Total		185519	24391	100.0000	

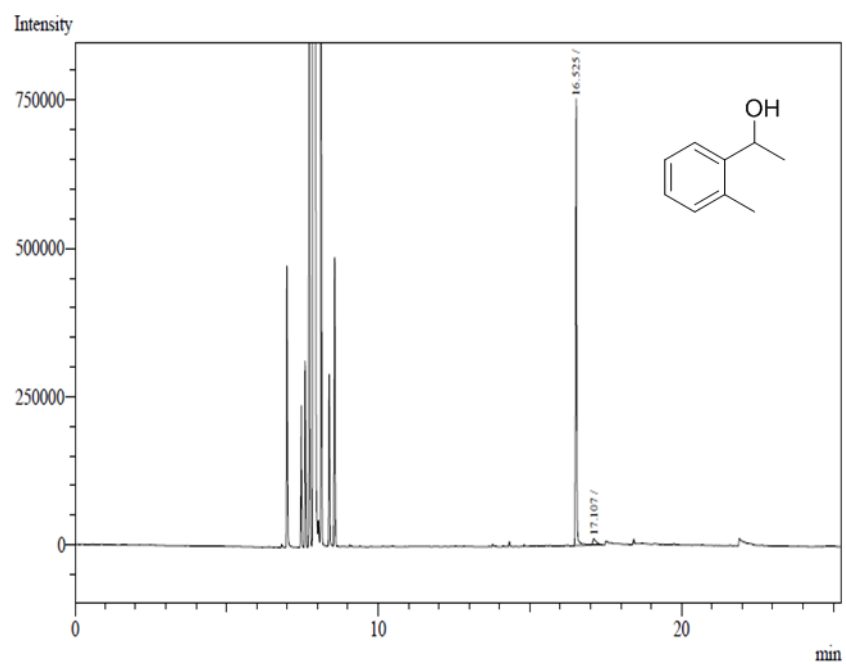


Peak#	Ret.Time	Area	Area%	Height	Conc.
1	20.694	153934	84.4444	16469	84.444
2	22.014	28356	15.5556	3331	15.556
Total		182290	100.0000	19800	100.000

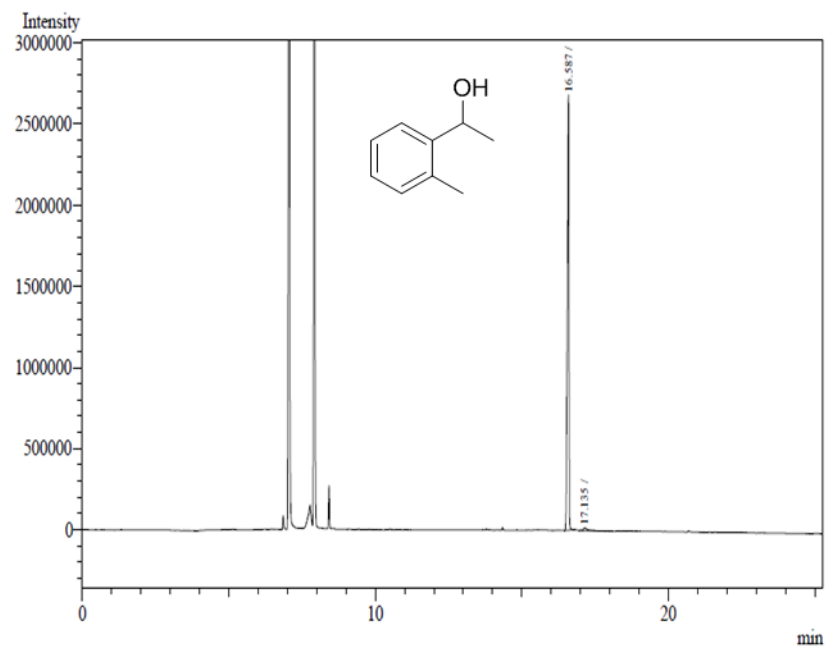




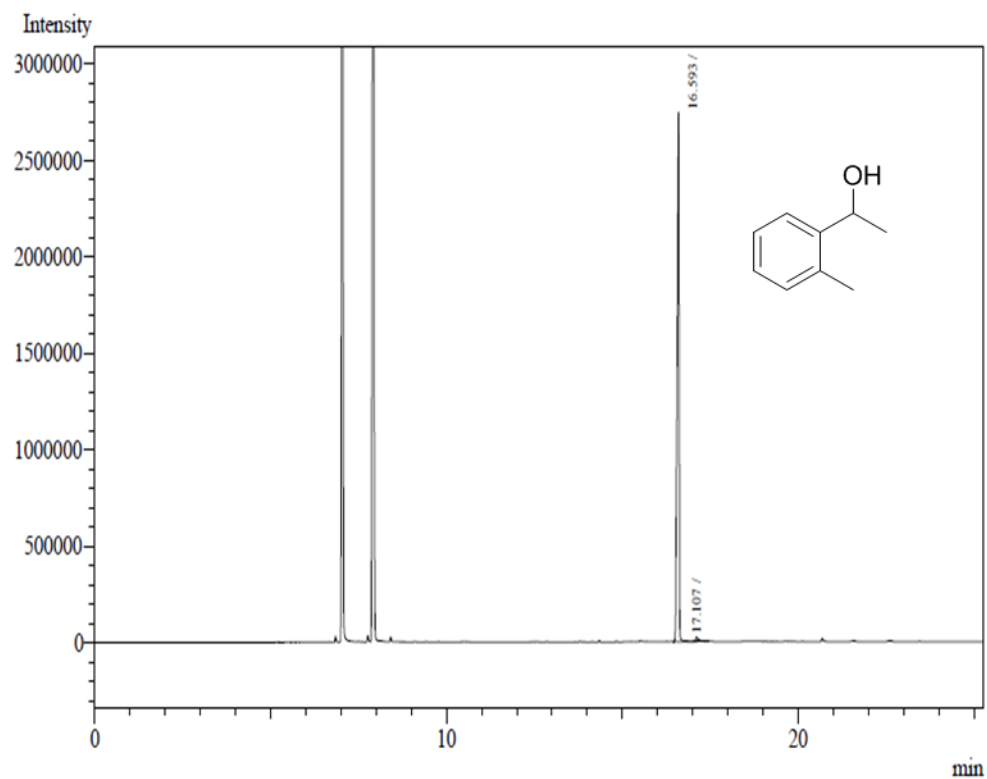
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1	16.593	10461960	2756838	97.5828	97.583
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Total		10721112	2807054	100.0000	



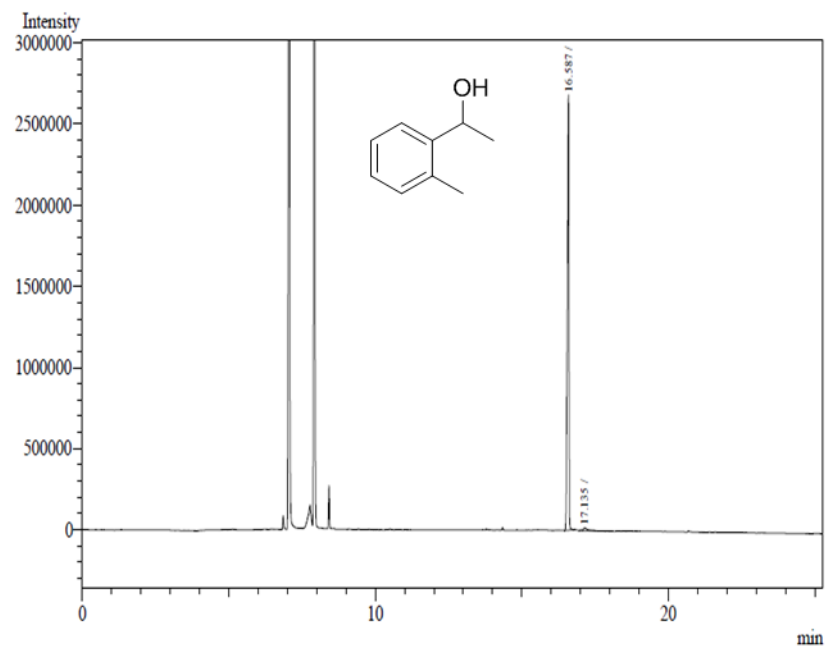
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2	17.107	82544	10056	4.1299	4.130
Total		1998704	755333	100.0000	



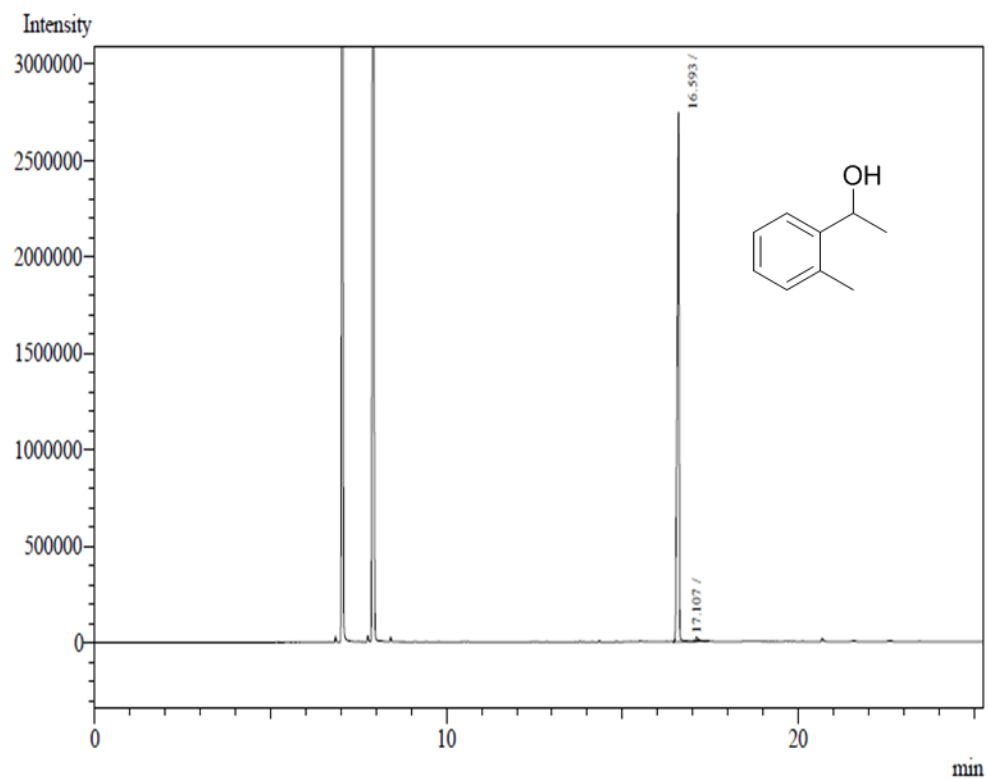
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1	16.587	10049818	2670929	98.8142	98.814
2	17.135	120596	15848	1.1858	1.186
Total		10170414	2686777	100.0000	



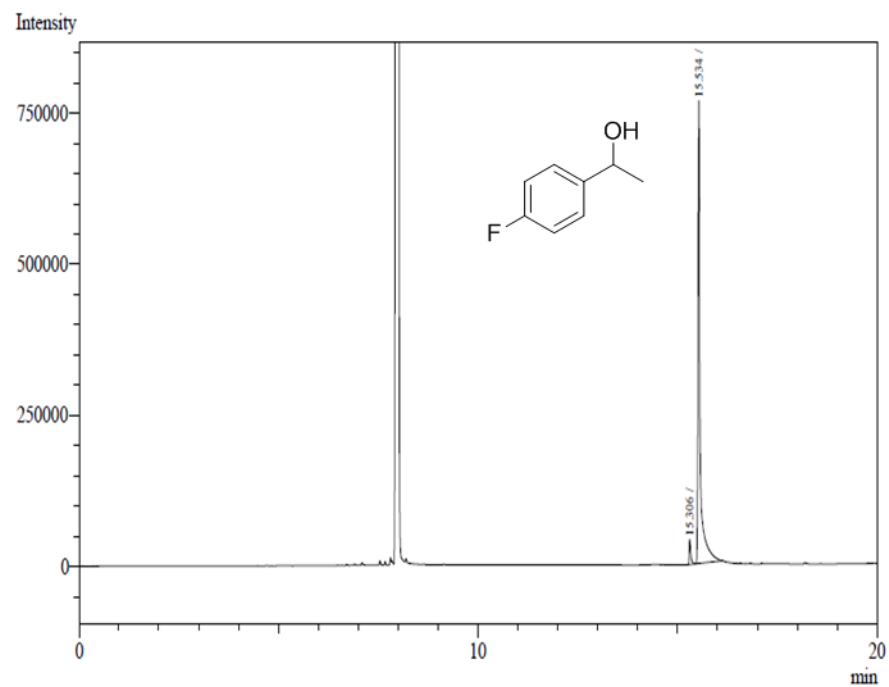
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1	16.593	10291514	2734735	98.6781	98.678
2	17.107	137869	22160	1.3219	1.322
Total		10429383	2756895	100.0000	



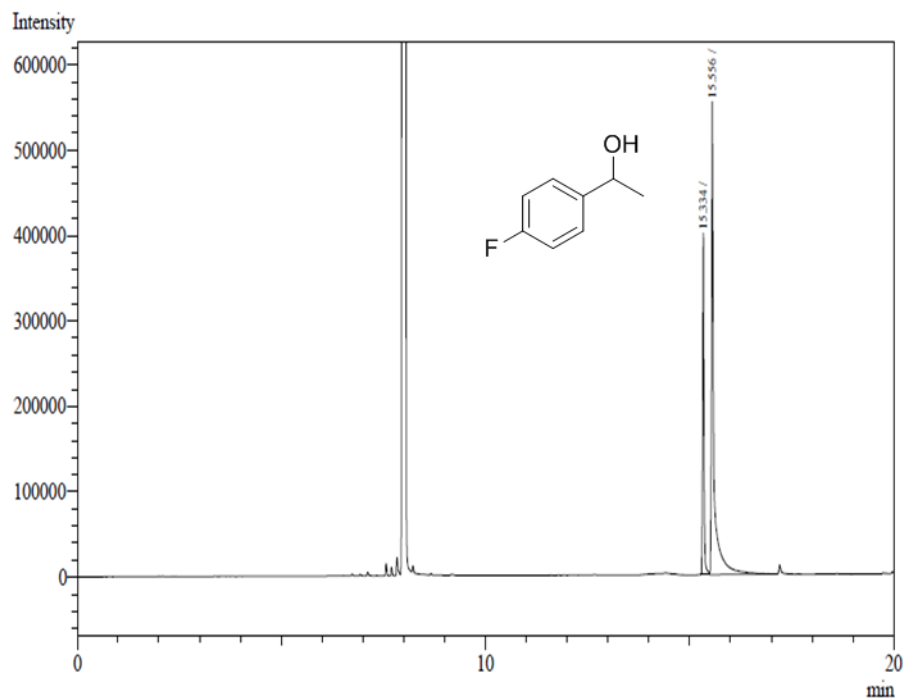
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2	17.135	120596	15848	1.1858	1.186
Total		10170414	2686777	100.0000	



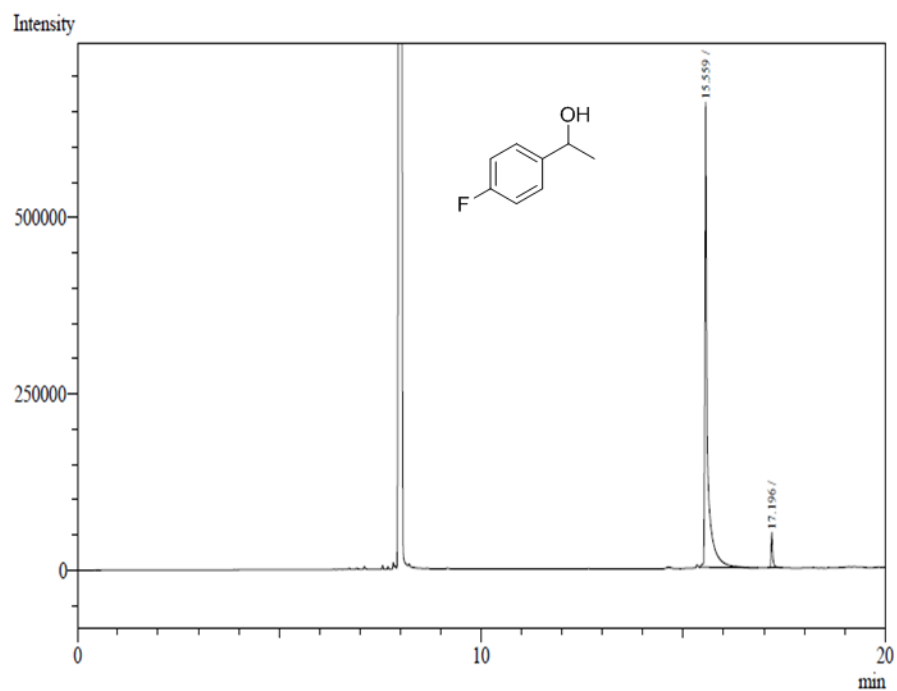
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2	17.107	137869	22160	1.3219	1.322
Total		10429383	2756895	100.0000	



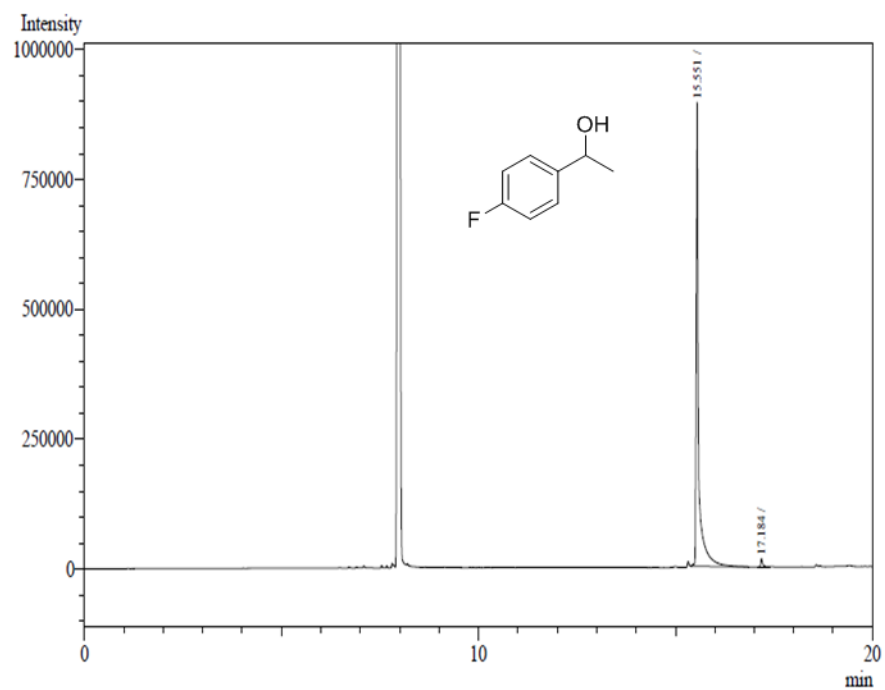
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1	15.306	118403	41360	3.9292	3.929
2	15.534	2895028	763750	96.0708	96.071
Total		3013431	805110	100.0000	



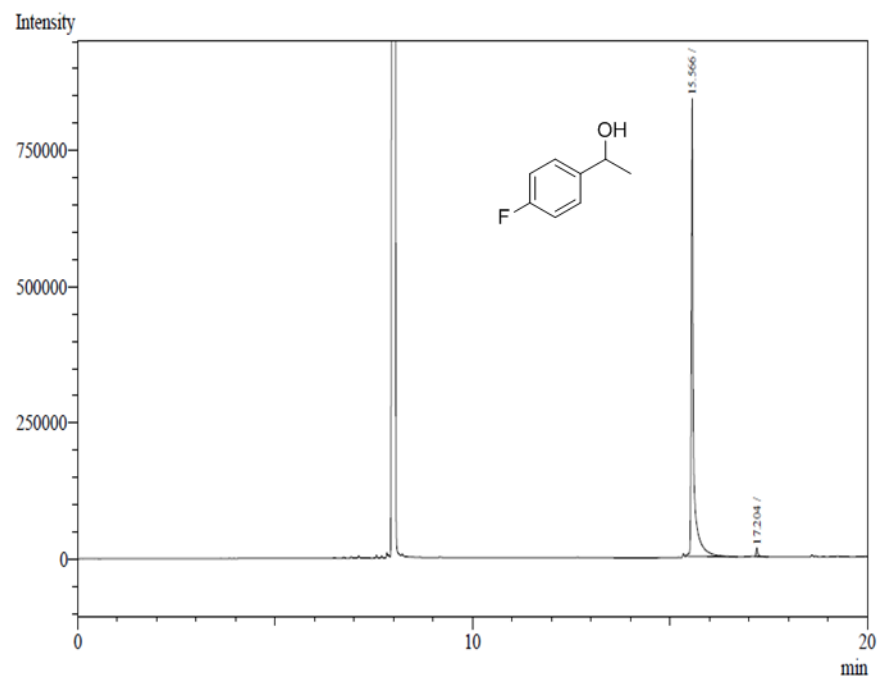
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1	15.334	923409	396874	28.9779	28.978
2	15.556	2263183	550043	71.0221	71.022
Total		3186592	946917	100.0000	



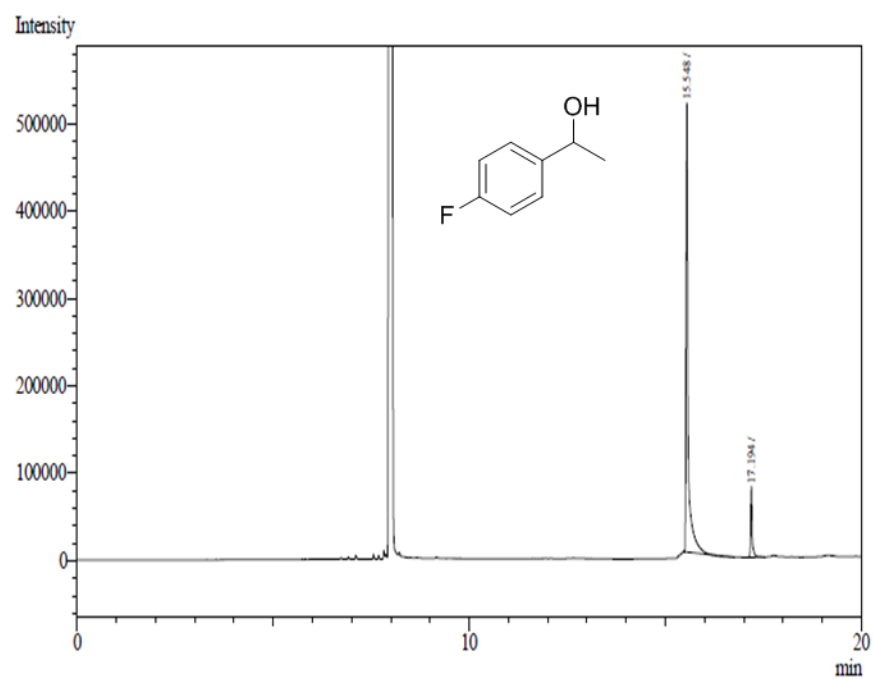
Peak#	Ret.Time	Area	Height	Area%	Conc.
1	15.559	2846490	649608	95.2814	95.281
2	17.196	140965	49617	4.7186	4.719
Total		2987455	699225	100.0000	



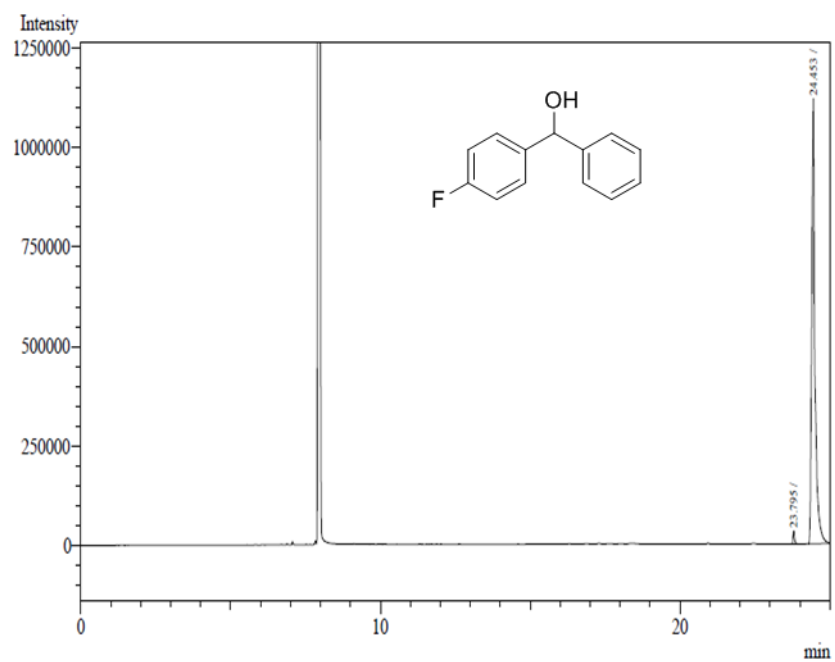
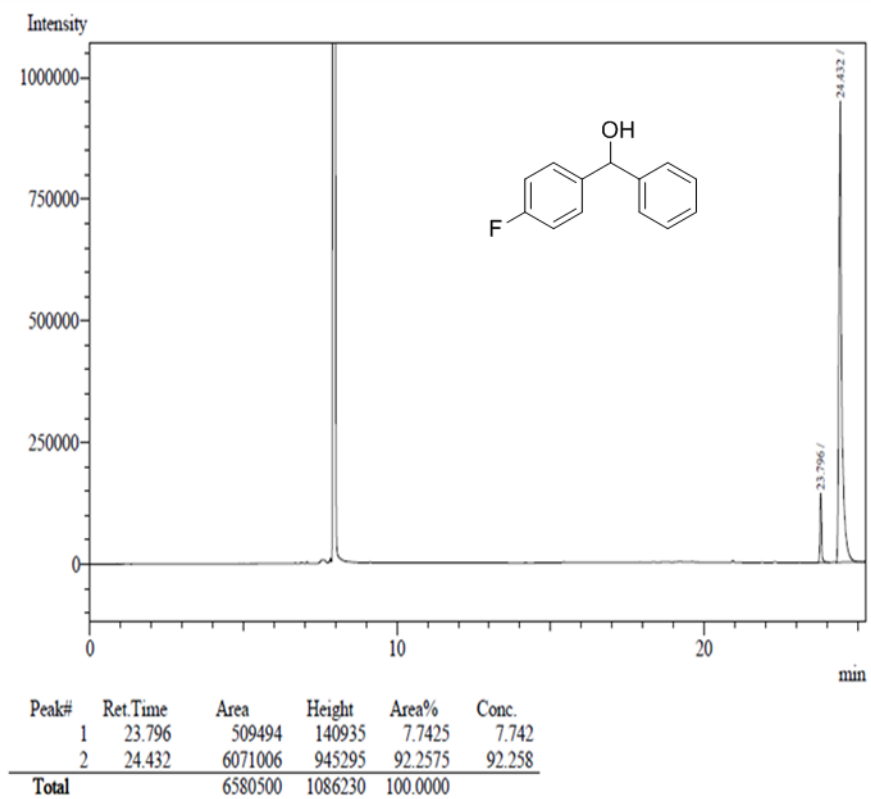
Peak#	Ret.Time	Area	Height	Area%	Conc.
1	15.551	3760568	887362	98.6130	98.613
2	17.184	52892	16105	1.3870	1.387
Total		3813460	903467	100.0000	

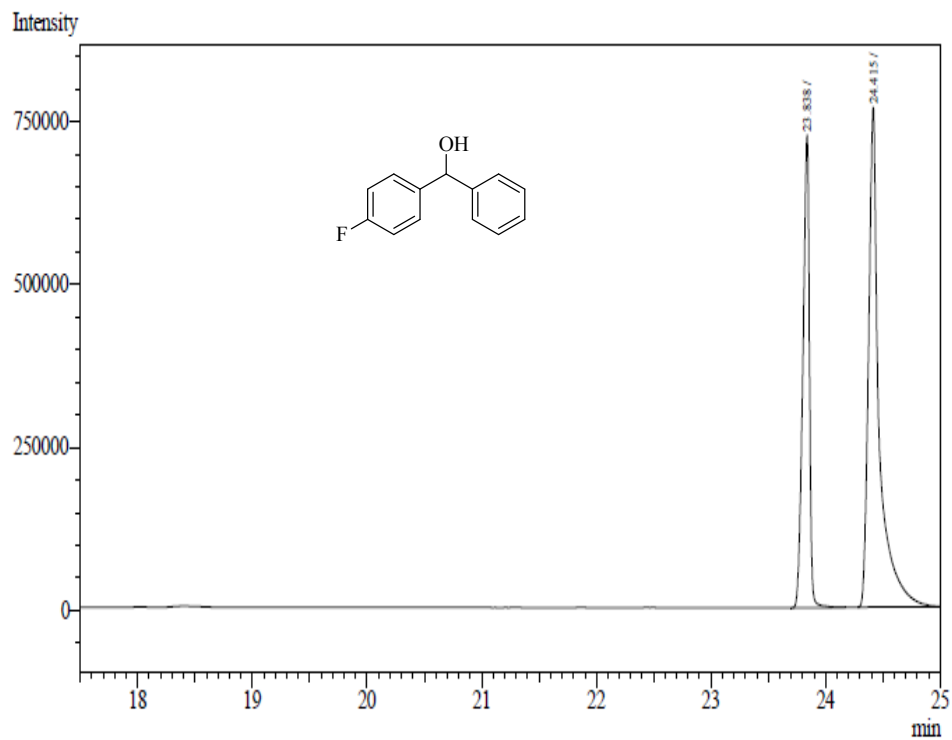


Peak#	Ret.Time	Area	Area%	Height	Conc.
1	15.566	3283664	98.5471	836908	98.547
2	17.204	48413	1.4529	15878	1.453
Total		3332077	100.0000	852786	100.000

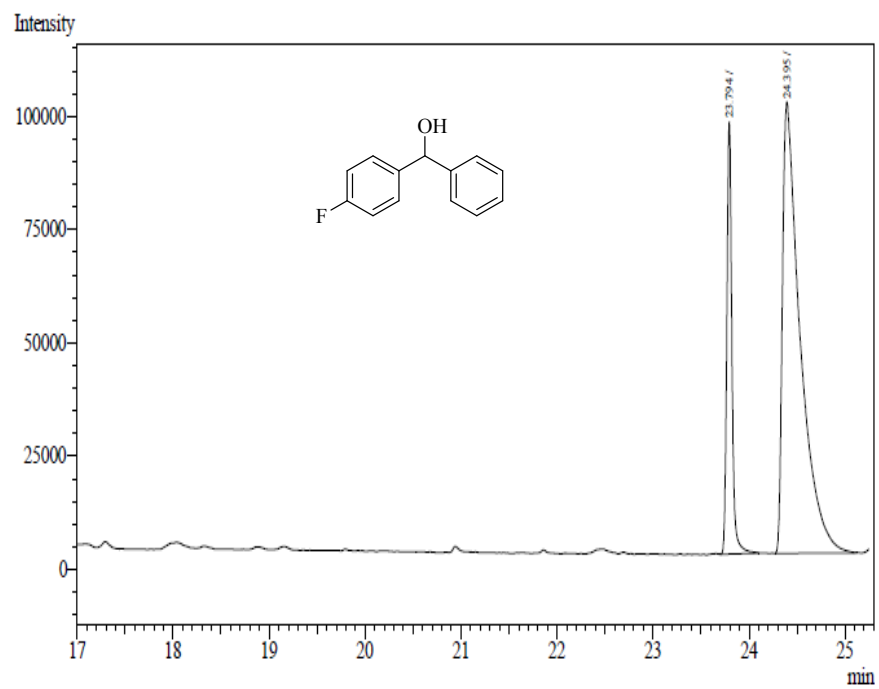


Peak#	Ret.Time	Area	Height	Area%	Conc.
1	15.548	1820702	511895	89.0021	89.002
2	17.194	224981	80286	10.9979	10.998
Total		2045683	592181	100.0000	

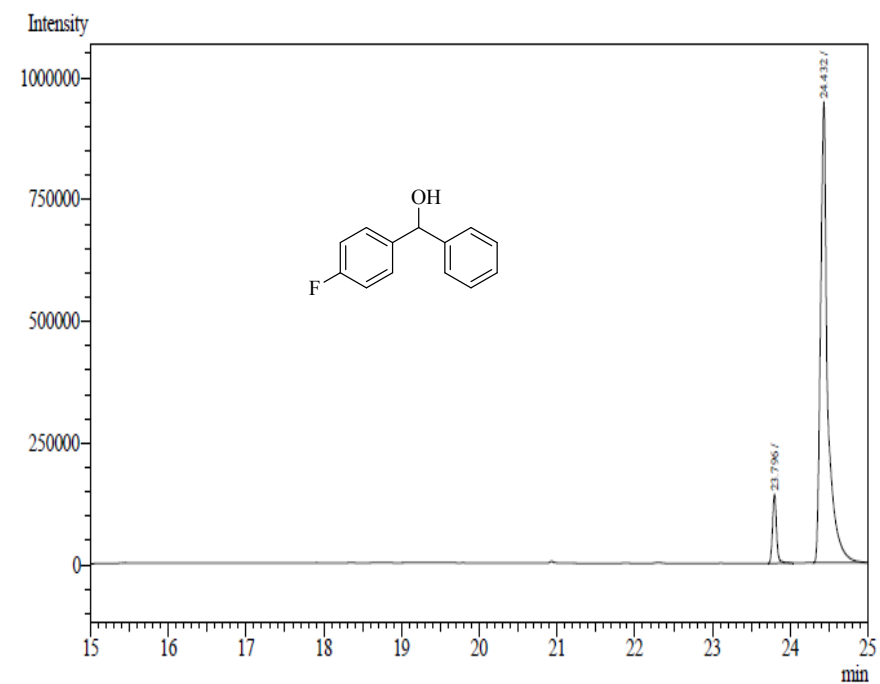




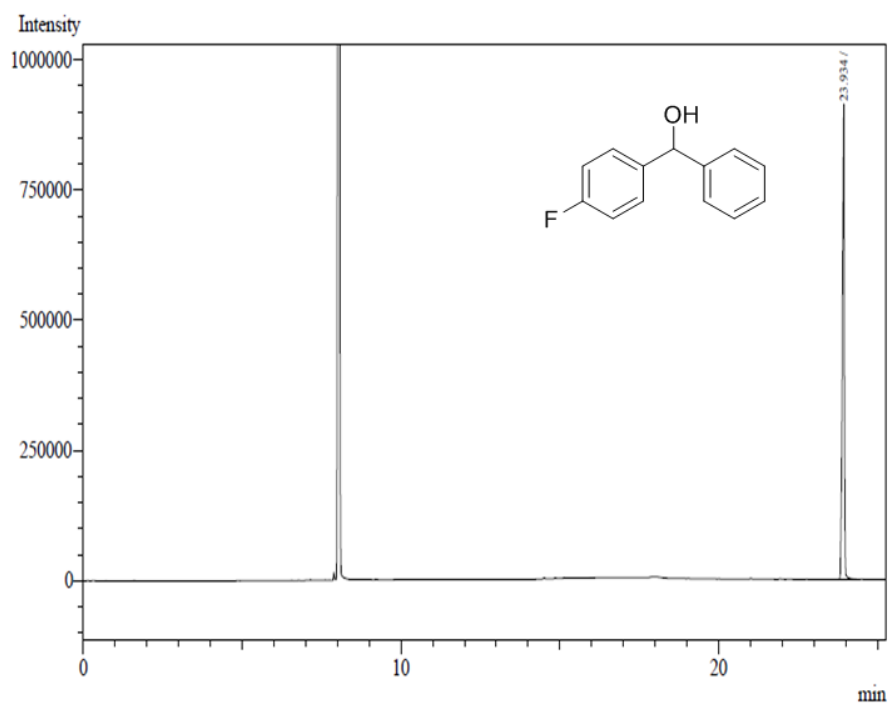
Peak#	Ret.Time	Area	Height	Conc.	Area%
1	23.838	2872318	720157	36.669	36.6690
2	24.415	4960777	766303	63.331	63.3310
Total		7833095	1486460		100.0000



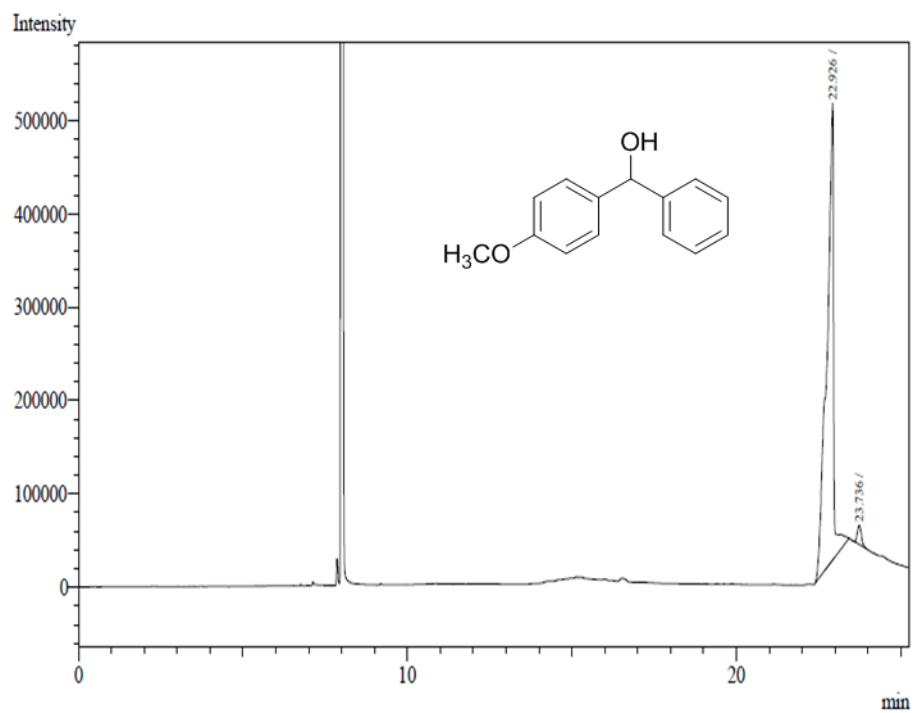
Peak#	Ret.Time	Area	Area%	Height	Conc.
1	23.794	350723	21.4955	95102	21.495
2	24.395	1280893	78.5045	99539	78.505
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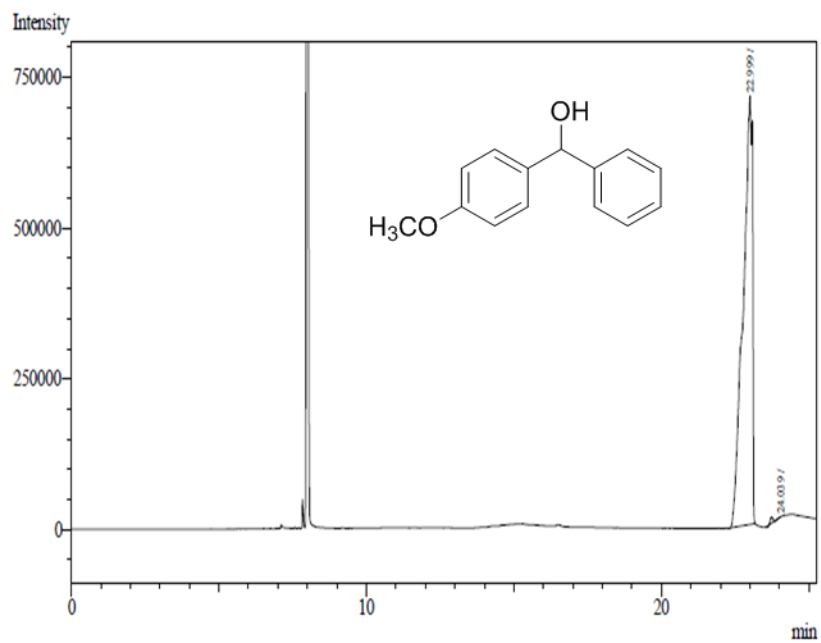
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1	23.796	7.7046	7.705	12.9630
2	24.432	92.2954	92.295	87.0370
Total		100.0000	100.000	100.0000



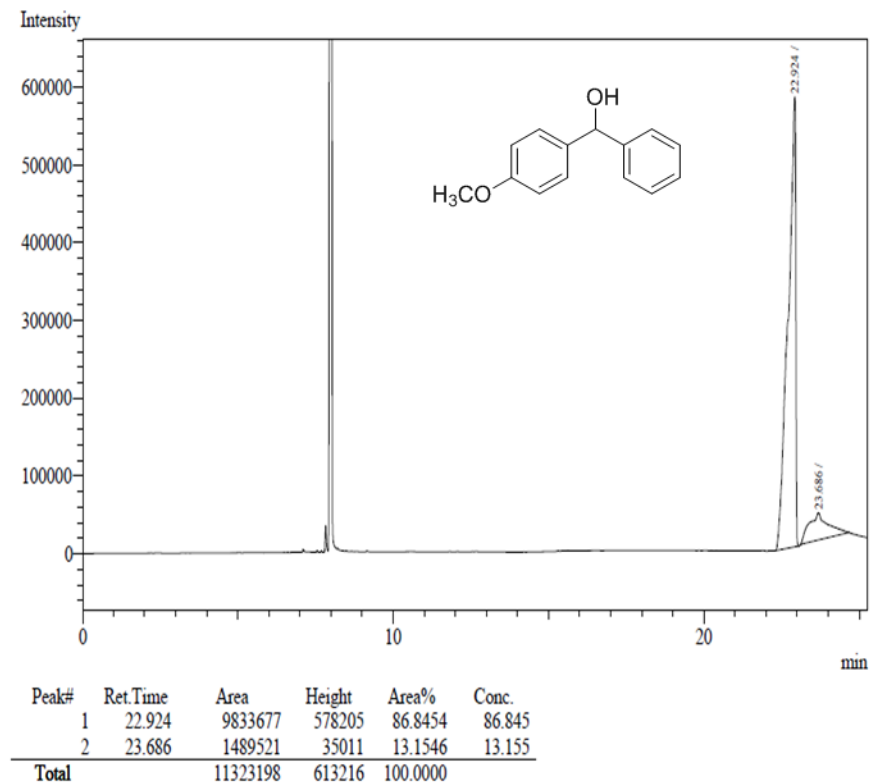
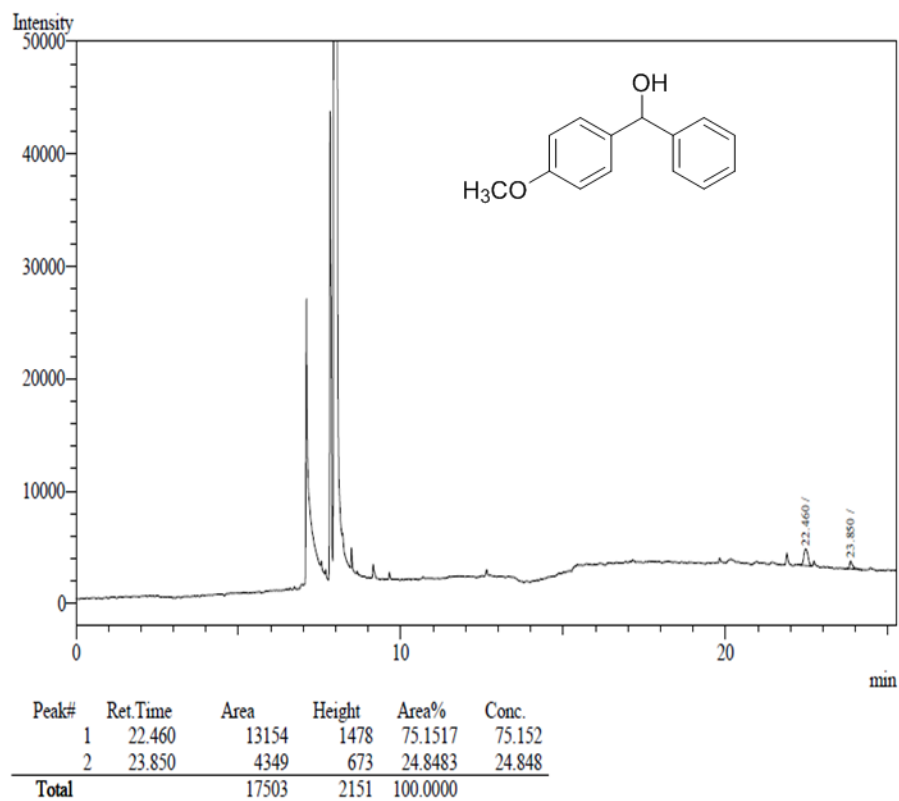
Peak#	Ret.Time	Area	Height	Area%	Conc.
1	23.934	3992150	911505	100.0000	100.000
Total		3992150	911505	100.0000	

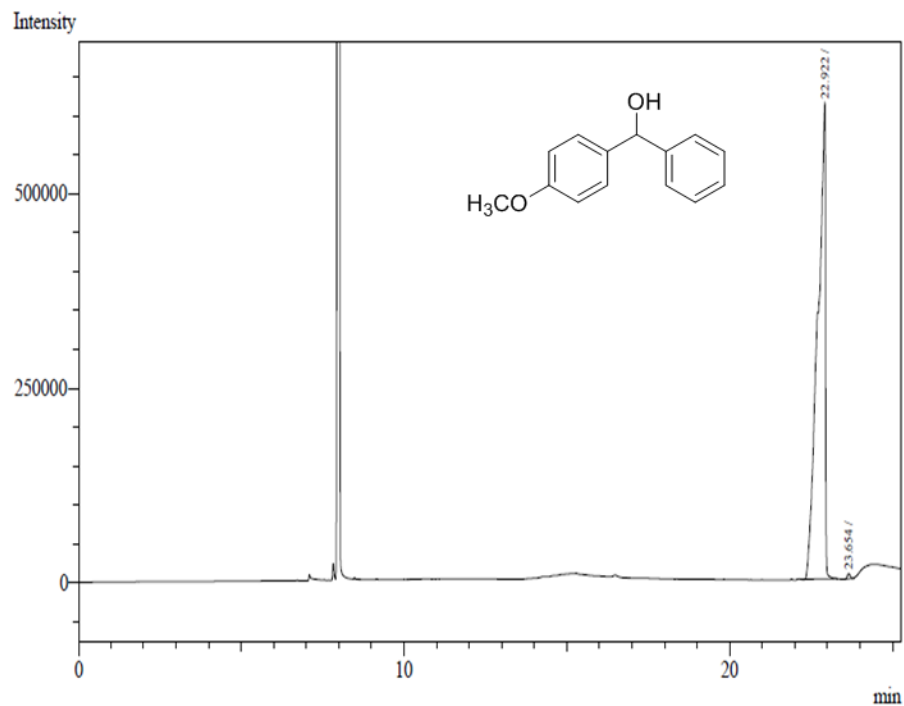


Peak#	Ret.Time	Area	Height	Area%	Conc.
1	22.926	6970665	488641	97.5797	97.580
2	23.736	172893	20437	2.4203	2.420
Total		7143558	509078	100.0000	

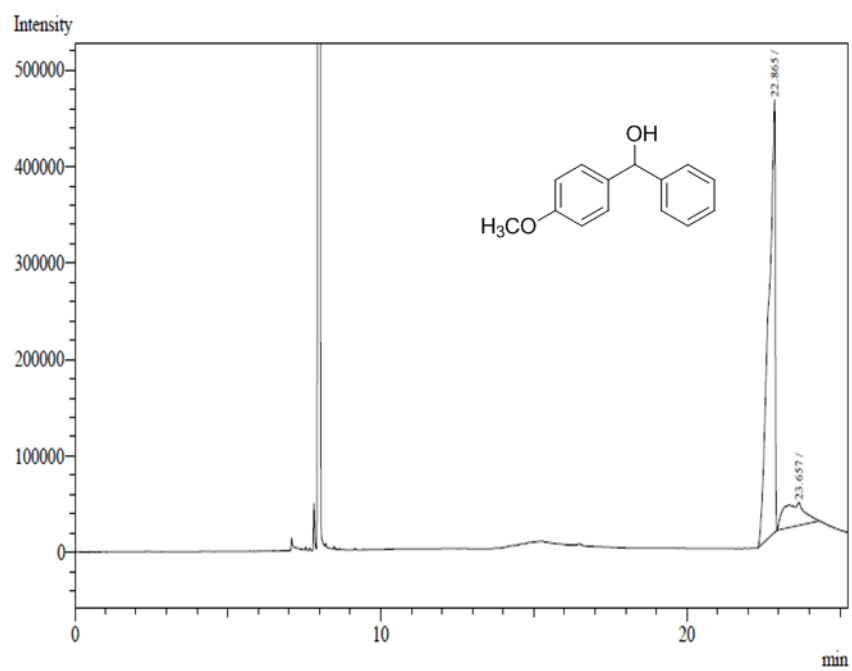


Peak#	Ret.Time	Area	Height	Area%
1	22.999	15592204	711038	99.6915
2	24.039	48248	4	0.3085
Total		15640452	711042	100.0000

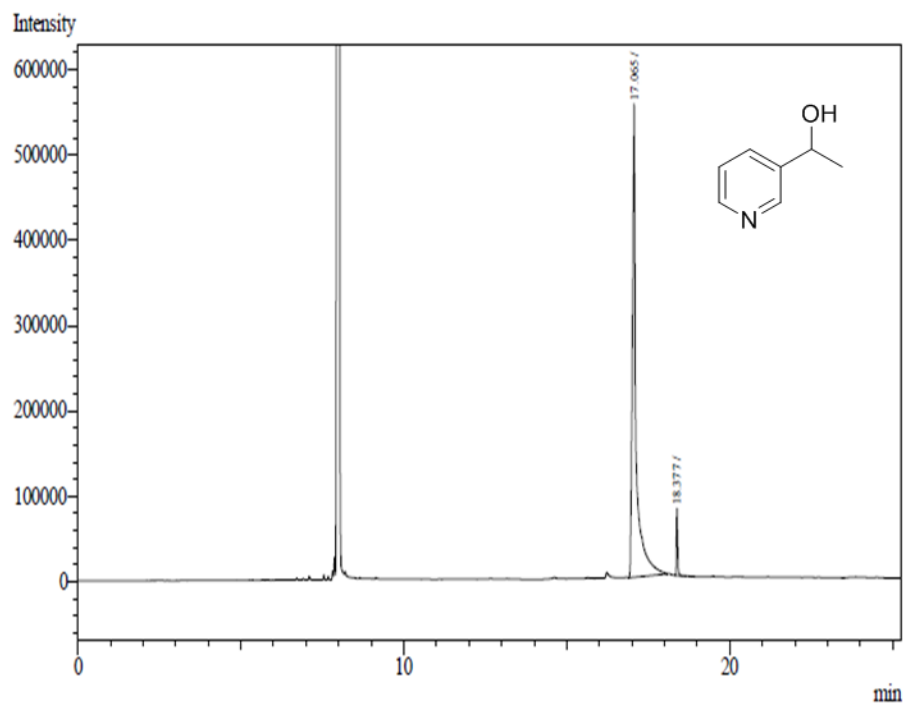




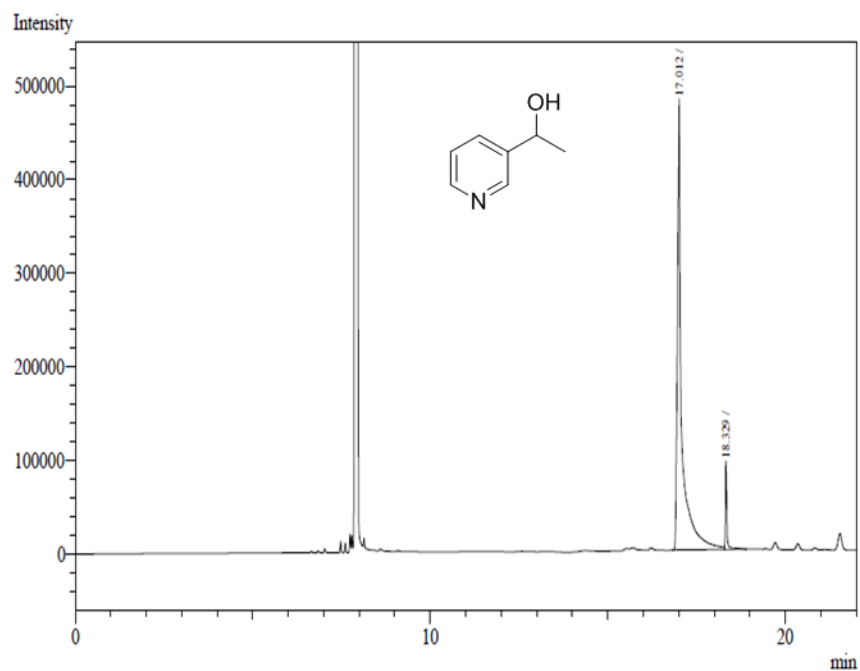
Peak#	Ret.Time	Area	Height	Area%	Conc.
1	22.922	10004628	612457	99.6185	99.618
2	23.654	38319	6749	0.3815	0.382
Total		10042947	619206	100.0000	



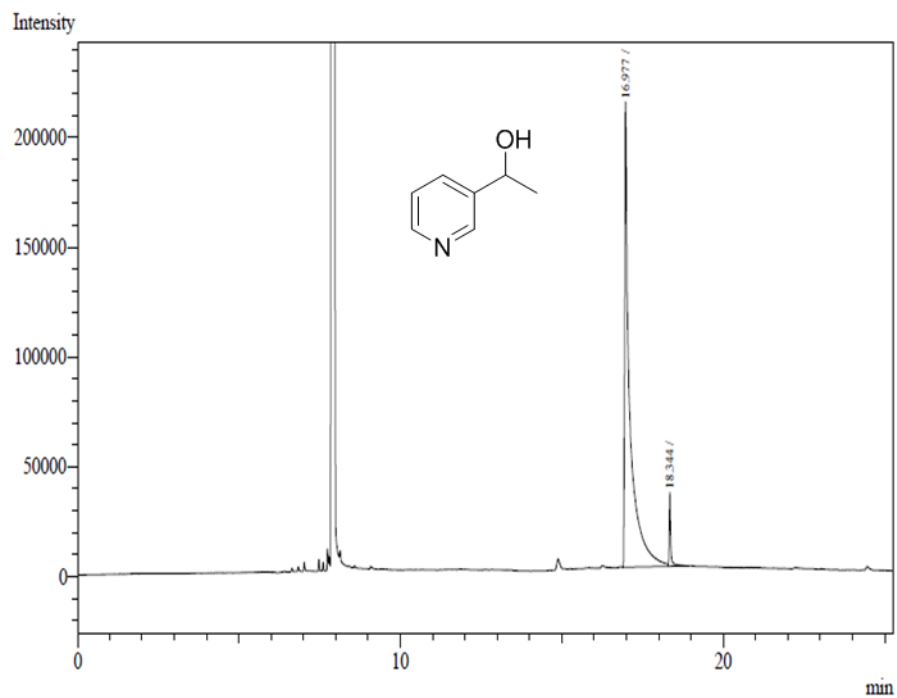
Peak#	Ret.Time	Area	Height	Area%	Conc.
1	22.865	6662390	448404	85.0023	85.002
2	23.657	1175508	23661	14.9977	14.998
Total		7837898	472065	100.0000	



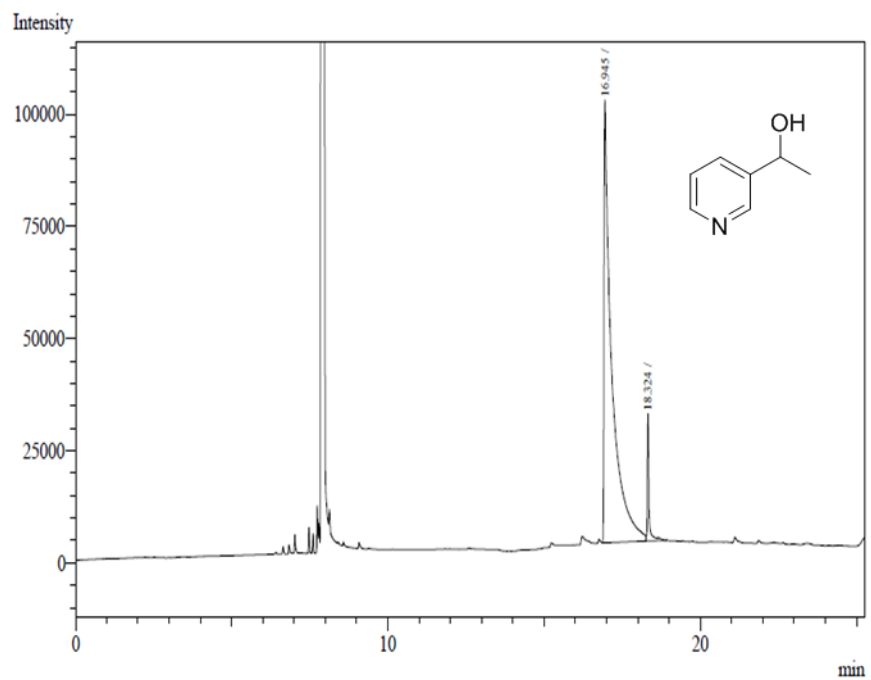
Peak#	Ret.Time	Area	Height	Area%	Conc.
1	17.065	4401844	553703	95.5909	95.591
2	18.377	203035	77906	4.4091	4.409
Total		4604879	631609	100.0000	



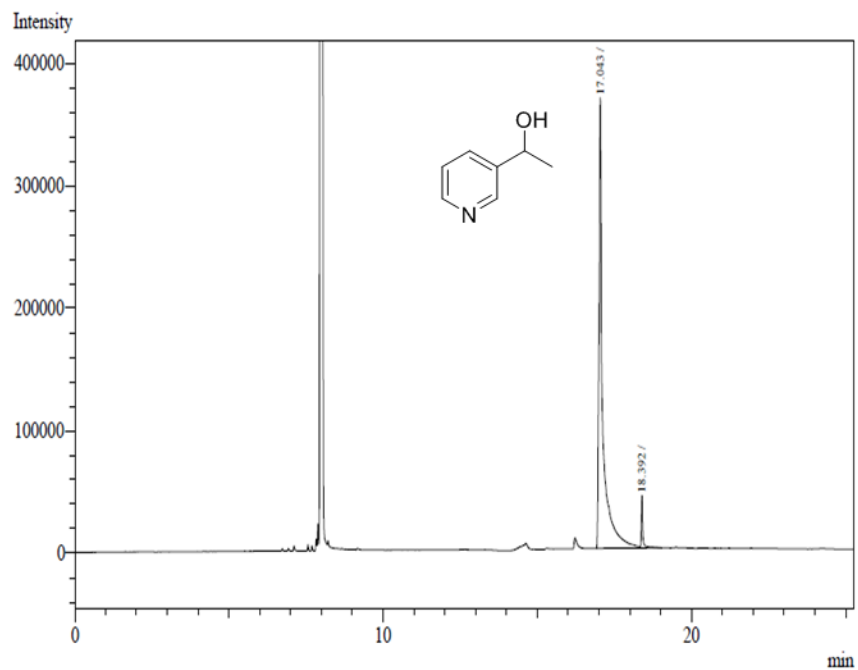
Peak#	Ret.Time	Area	Height	Area%	Conc.
1	17.012	4083885	479402	93.7050	93.705
2	18.329	274351	93790	6.2950	6.295
Total		4358236	573192	100.0000	



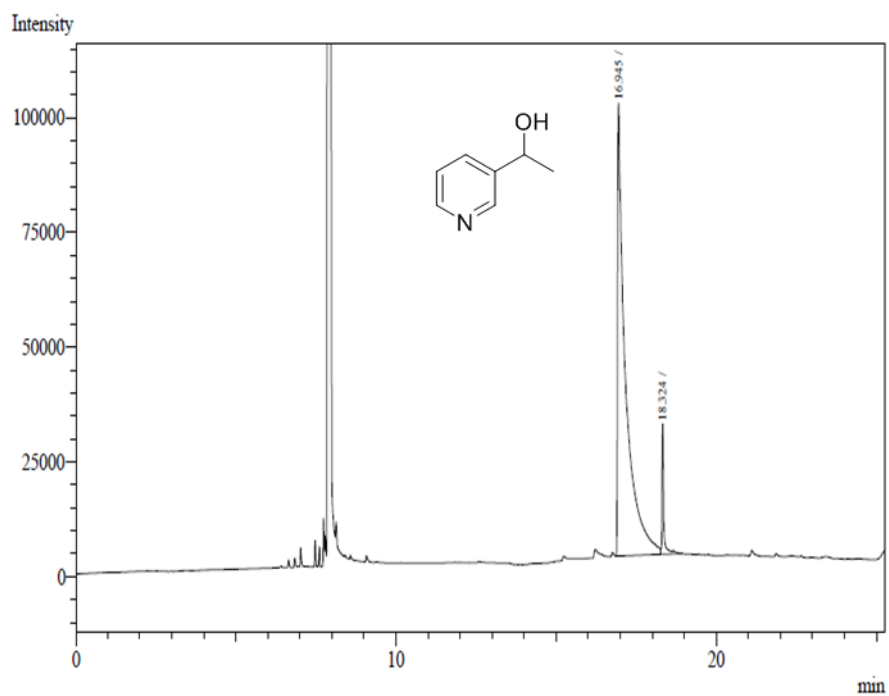
Peak#	Ret.Time	Area	Height	Area%	Conc.
1	16.977	2298800	211507	95.3596	95.360
2	18.344	111864	33449	4.6404	4.640
Total		2410664	244956	100.0000	



Peak#	Ret.Time	Area	Height	Area%	Conc.
1	16.945	1678593	98510	94.3260	94.326
2	18.324	100973	28311	5.6740	5.674
Total		1779566	126821	100.0000	

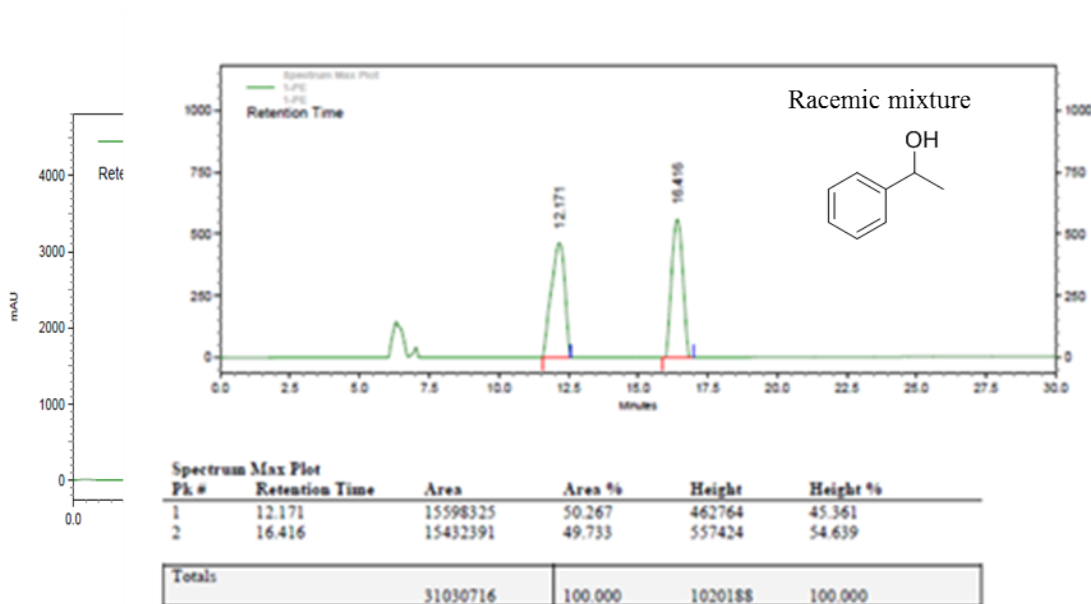


Peak#	Ret.Time	Area	Height	Area%	Conc.
1	17.043	3150636	366240	95.7665	95.767
2	18.392	139278	42294	4.2335	4.233
Total		3289914	408534	100.0000	



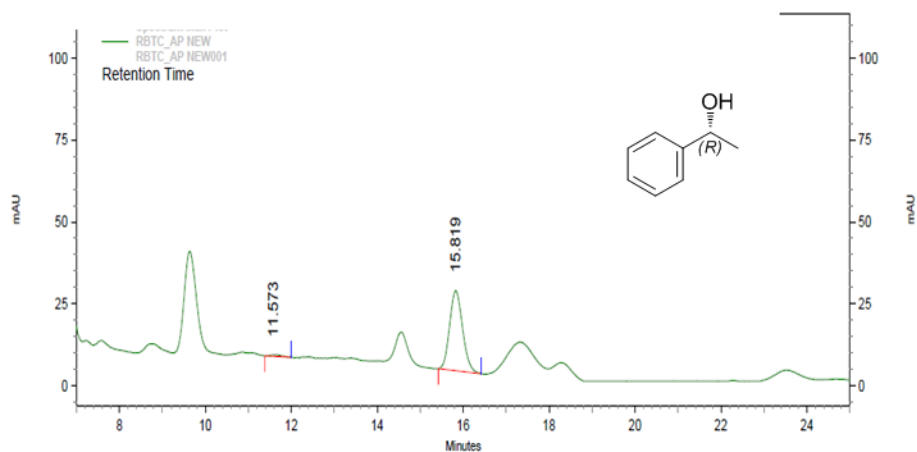
Peak#	Ret.Time	Area	Height	Area%	Conc.
1	16.945	1678593	98510	94.3260	94.326
2	18.324	100973	28311	5.6740	5.674
Total		1779566	126821	100.0000	

HPLC Data

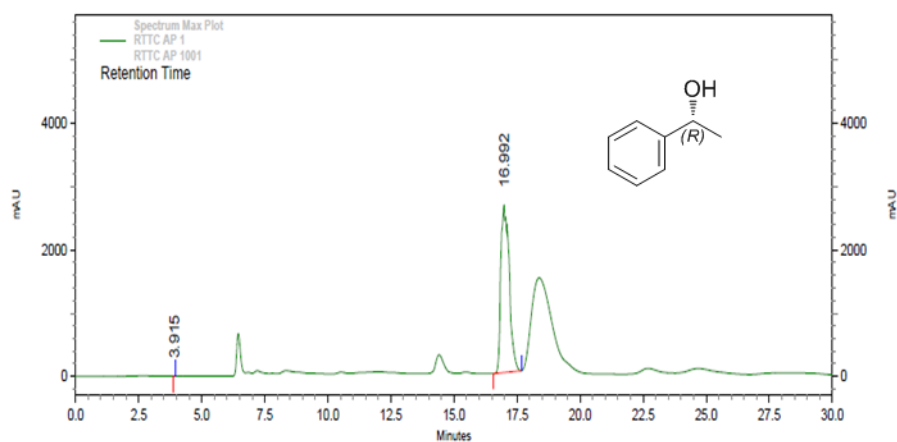


Spectrum Max	
PK #	Ret
1	11.6
2	15.829

Totals		41108535	96.876	2261597	97.110
		42434326	100.000	2328897	100.000



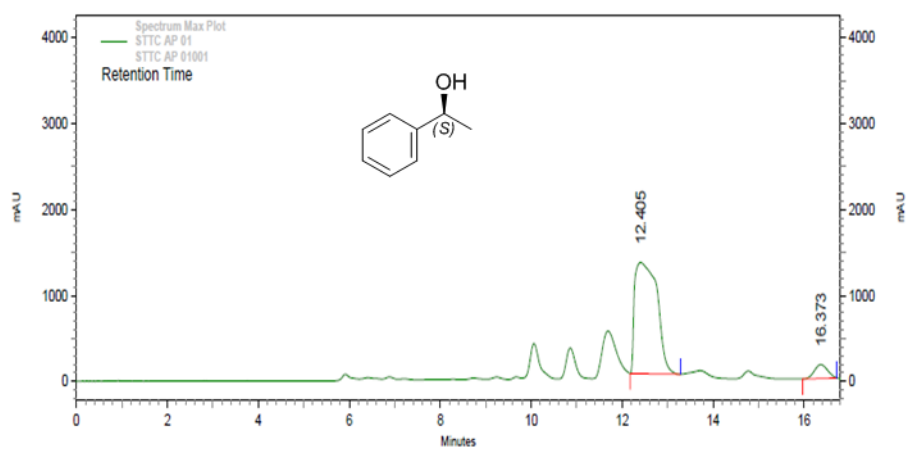
Spectrum Max Plot					
PK #	Retention Time	Area	Area %	Height	Height %
1	11.573	8428	1.625	501	2.010
2	15.819	510183	98.375	24423	97.990
Totals		518611	100.000	24924	100.000



Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	3.915	366	0.001	474	0.018
2	16.992	61468955	99.999	2649756	99.982

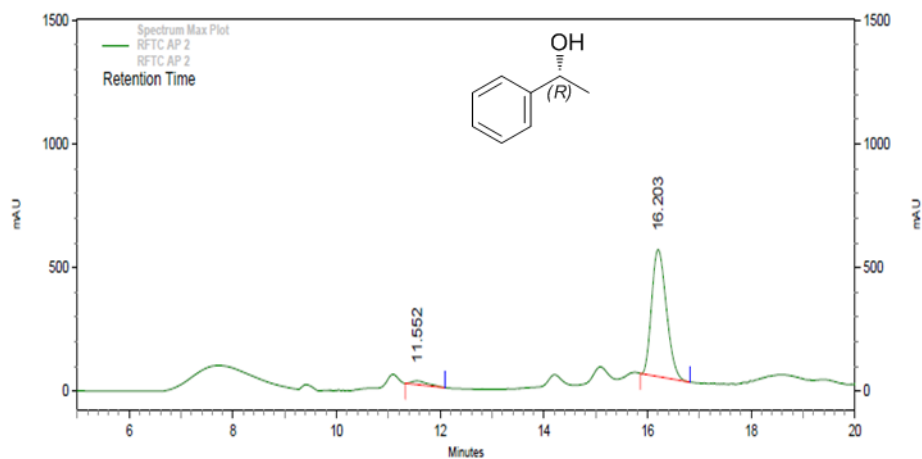
Totals		61469321	100.000	2650230	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	12.405	44380321	93.186	1295563	88.939
2	16.373	3245170	6.814	161132	11.061

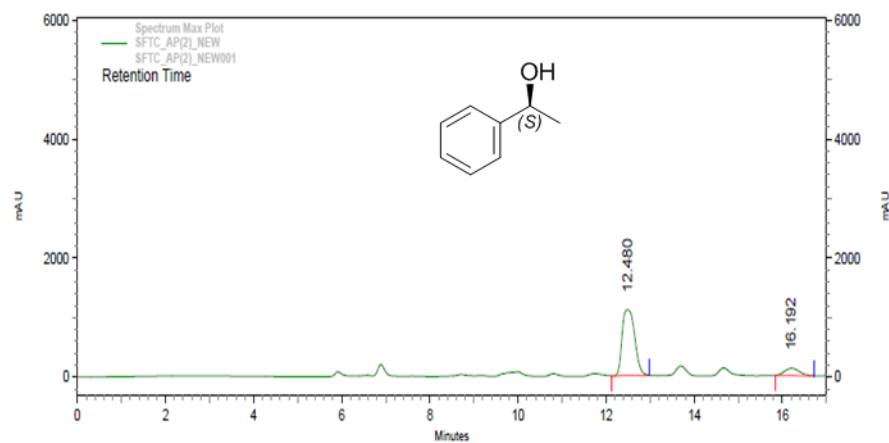
Totals		47625491	100.000	1456695	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	11.552	339142	3.223	15300	2.892
2	16.203	10184872	96.777	513704	97.108

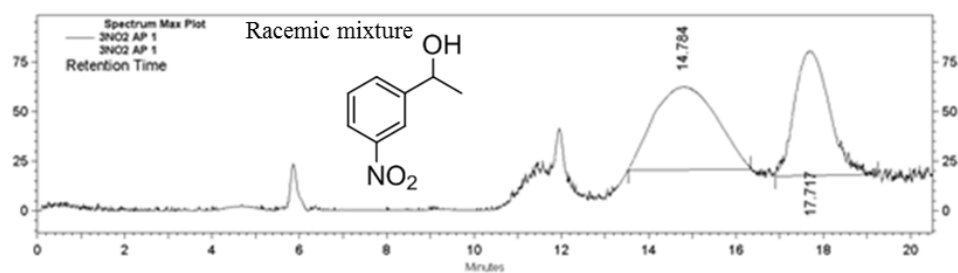
Totals		10524014	100.000	529004	100.000
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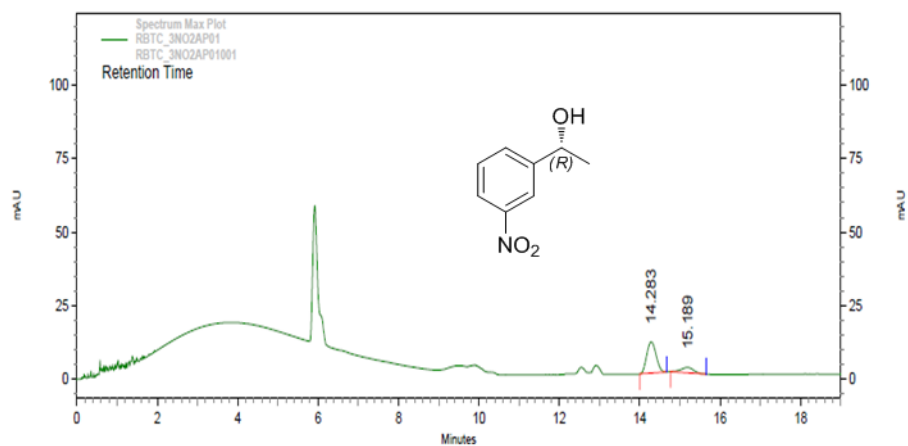
Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	12.480	21976623	88.214	1110337	89.781
2	16.192	2936185	11.786	126381	10.219

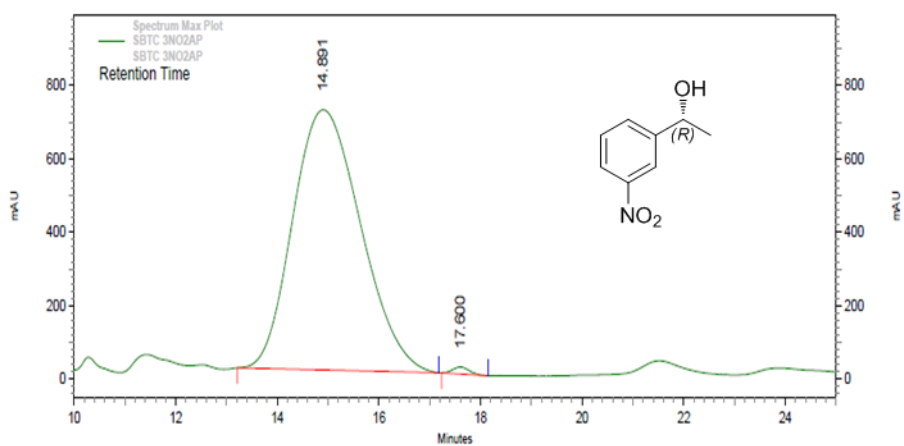
Totals		24912808	100.000	1236718	100.000
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Peak #	Retention Time	Area	Area %	Height	Height %
1	14.784	4204514	54.674	41692	39.954
2	17.717	3485573	45.326	62657	60.046
Totals		7690087	100.000	104349	100.000



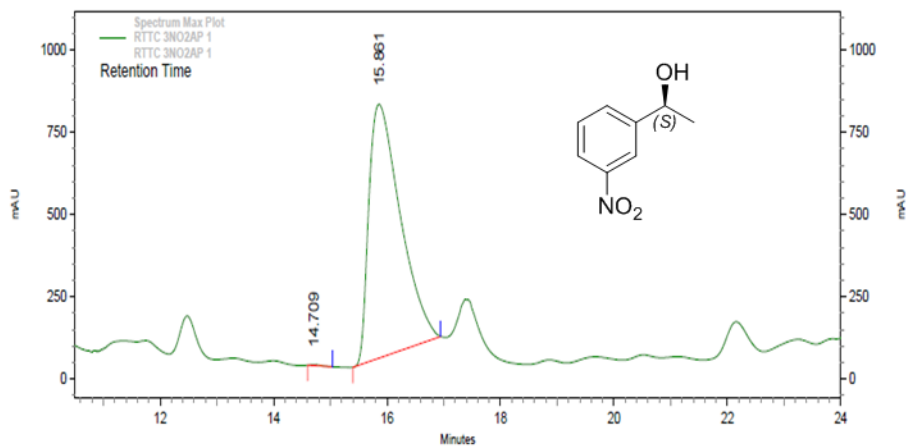
Peak #	Retention Time	Area	Area %	Height	Height %
1	14.283	171260	81.469	10634	85.366
2	15.189	38954	18.531	1823	14.634
Totals		210214	100.000	12457	100.000



Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	14.891	65951622	99.353	708786	97.364
2	17.600	429199	0.647	19193	2.636

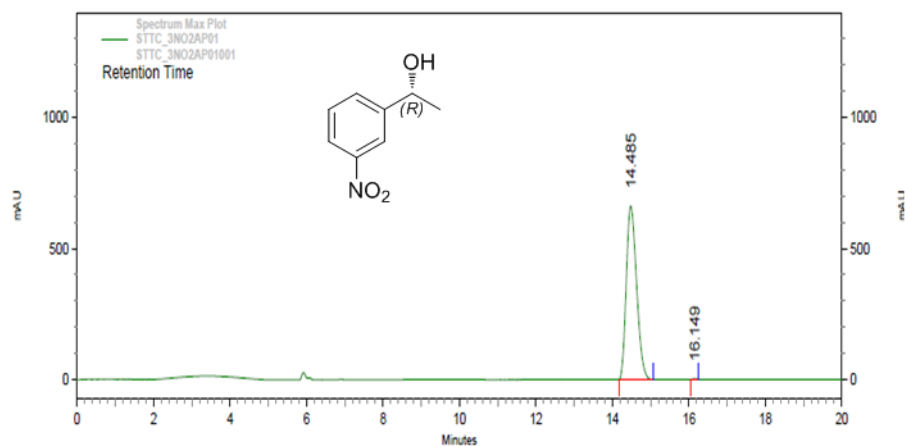
Totals		66380821	100.000	727979	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	14.709	34318	0.115	2576	0.333
2	15.861	29813921	99.885	771672	99.667

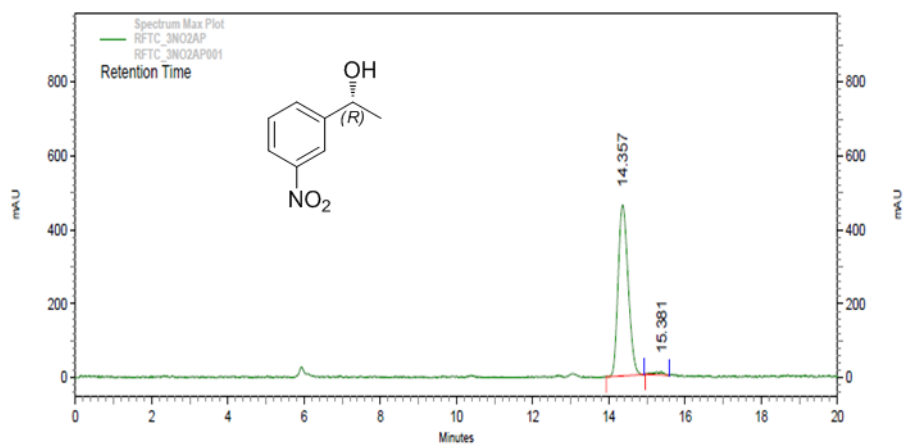
Totals		29848239	100.000	774248	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	14.485	12376682	99.809	661136	99.532
2	16.149	23693	0.191	3109	0.468

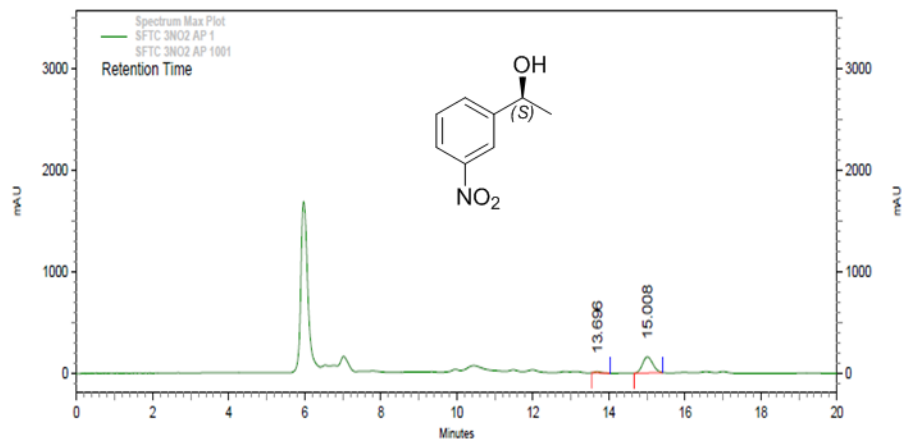
Totals		12400375	100.000	664245	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	14.357	8465748	98.416	463070	98.040
2	15.381	136269	1.584	9258	1.960

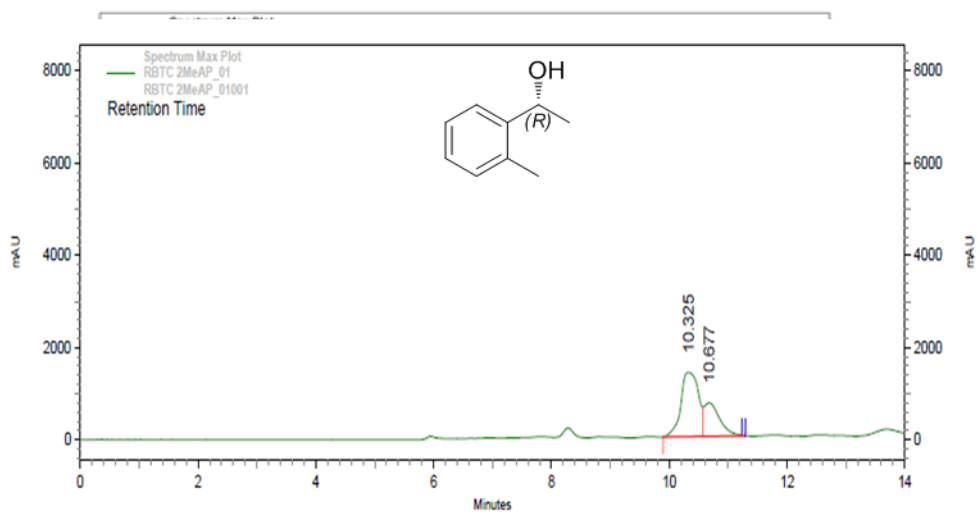
Totals		8602017	100.000	472328	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	13.696	124538	4.043	10451	6.192
2	15.008	2955820	95.957	158320	93.808

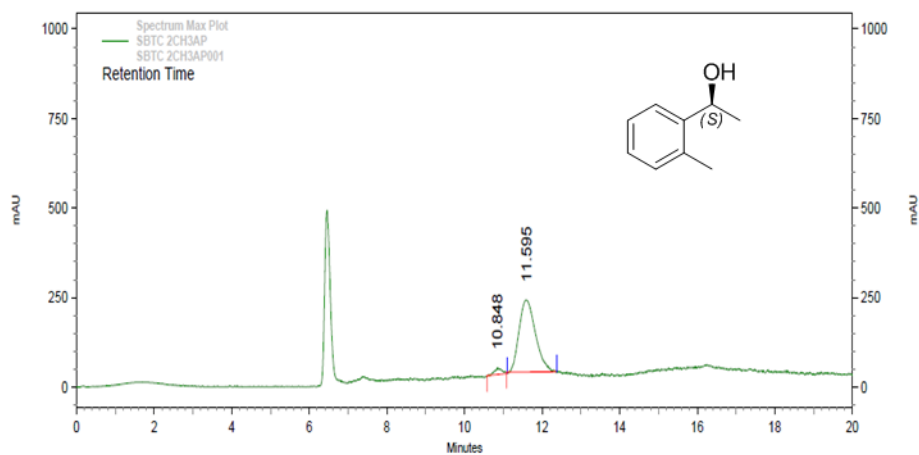
Totals		3080358	100.000	168771	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	10.325	42334339	75.802	1392238	65.655
2	10.677	13514384	24.198	728306	34.345

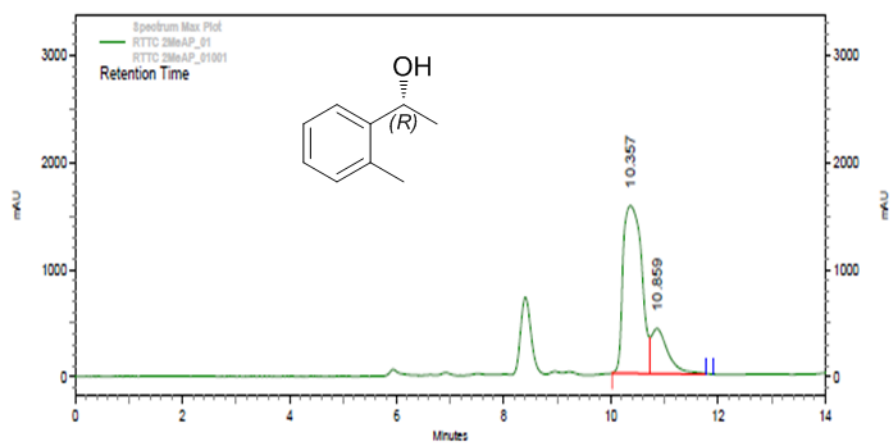
Totals		55848723	100.000	2120544	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	10.848	227895	3.723	18775	8.539
2	11.595	5893789	96.277	201091	91.461

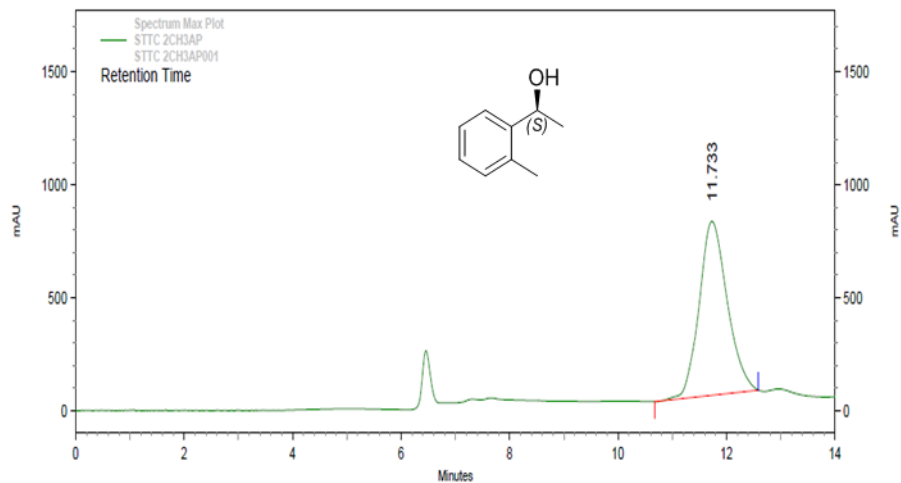
Totals		6121684	100.000	219866	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	10.357	46870929	83.452	1565666	78.814
2	10.859	9294299	16.548	420879	21.186

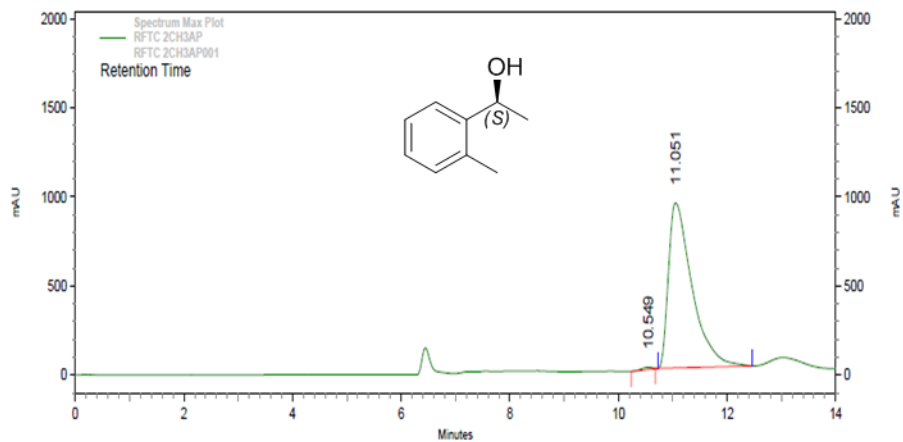
Totals		56165228	100.000	1986545	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	11.733	27670190	100.000	769013	100.000

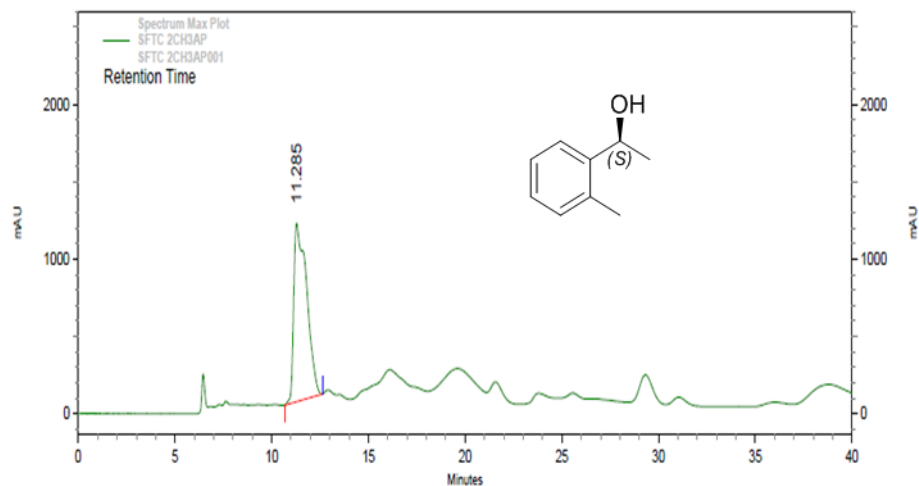
Totals		27670190	100.000	769013	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	10.549	169491	0.596	12154	1.277
2	11.051	27900830	98.064	926347	97.355
3	30.283	381328	1.340	13013	1.368

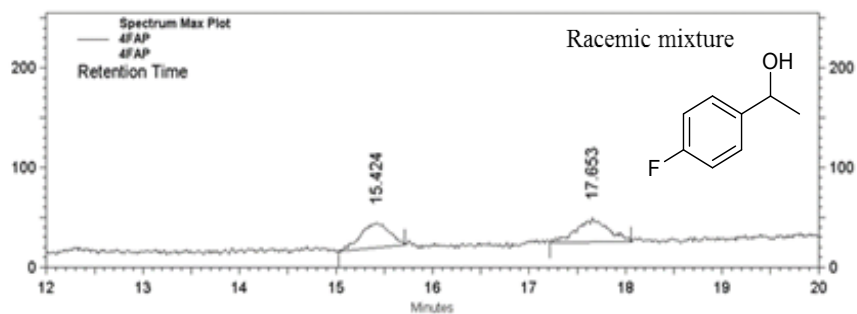
Totals		28451649	100.000	951514	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	11.285	53559760	100.000	1154070	100.000

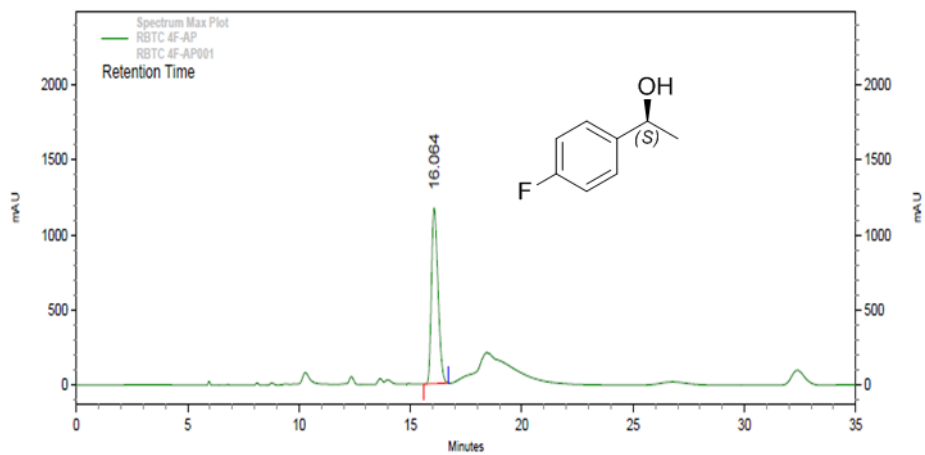
Totals		53559760	100.000	1154070	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	15.424	508489	48.176	24551	50.479
2	17.653	546993	51.824	24085	49.521

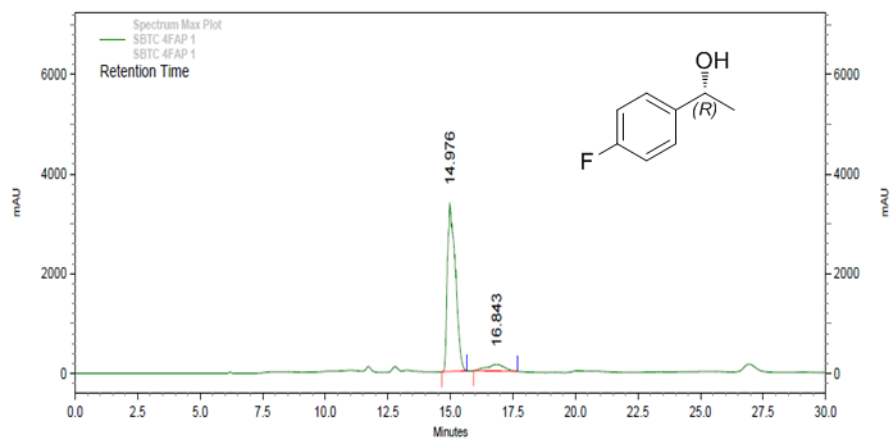
Totals		1055482	100.000	48636	100.000
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Spectrum Max Plot

PK #	Retention Time	Area	Area %	Height	Height %
1	16.064	23901229	100.000	1170343	100.000

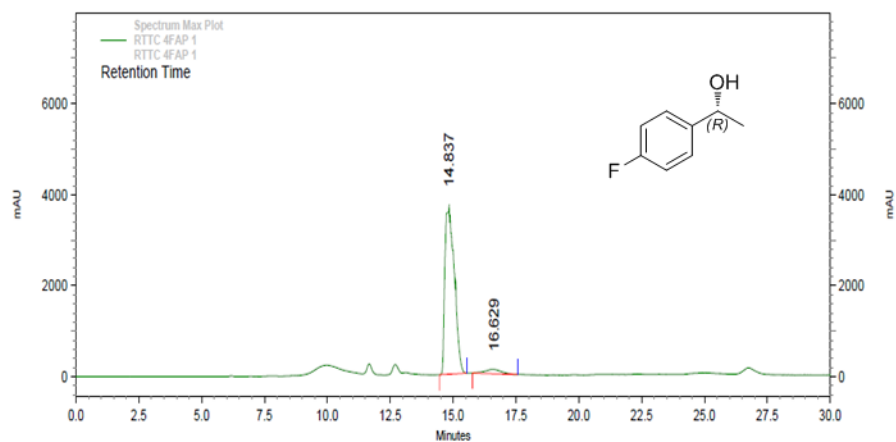
Totals		23901229	100.000	1170343	100.000
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Spectrum Max Plot

PK #	Retention Time	Area	Area %	Height	Height %
1	14.976	75185846	92.087	3385060	96.224
2	16.843	6460514	7.913	132853	3.776

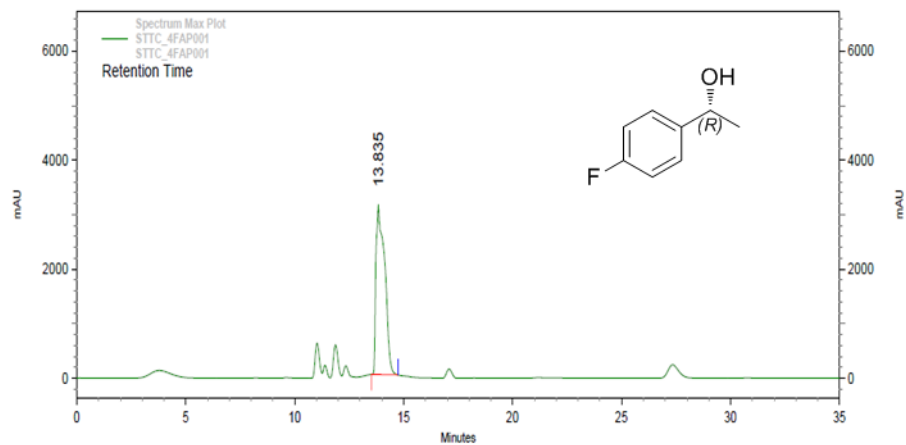
Totals		81646360	100.000	3517913	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	14.837	96125369	95.752	3724964	97.478
2	16.629	4264575	4.248	96390	2.522

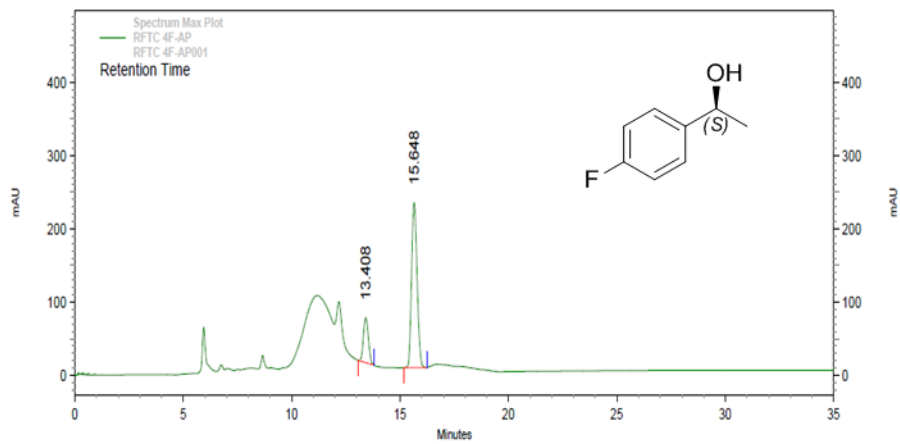
Totals		100389944	100.000	3821354	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	13.835	86756047	100.000	3114391	100.000

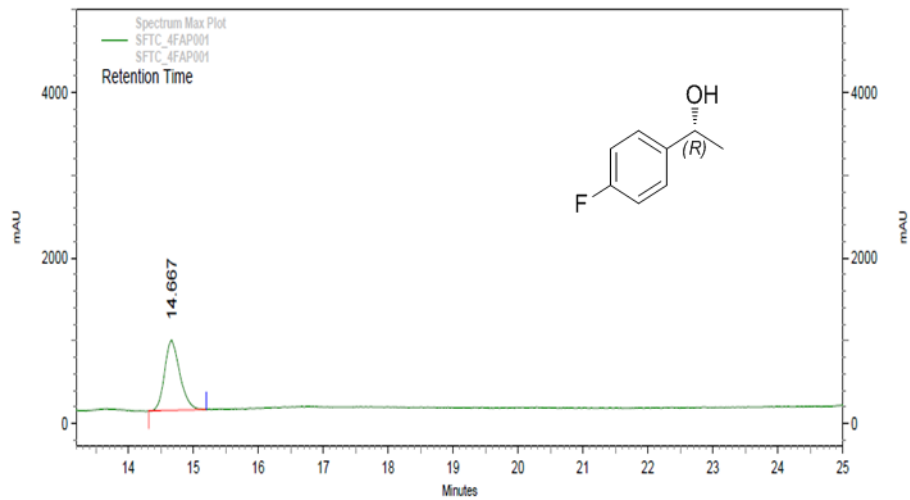
Totals		86756047	100.000	3114391	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	13.408	986364	19.881	61249	21.398
2	15.648	3974857	80.119	224984	78.602

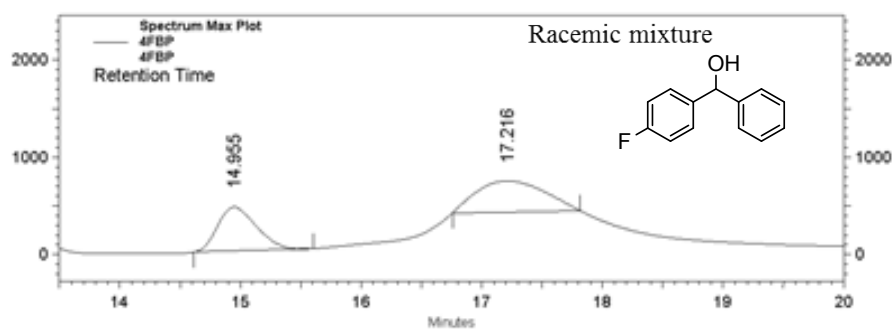
Totals		4961221	100.000	286233	100.000
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Spectrum Max Plot

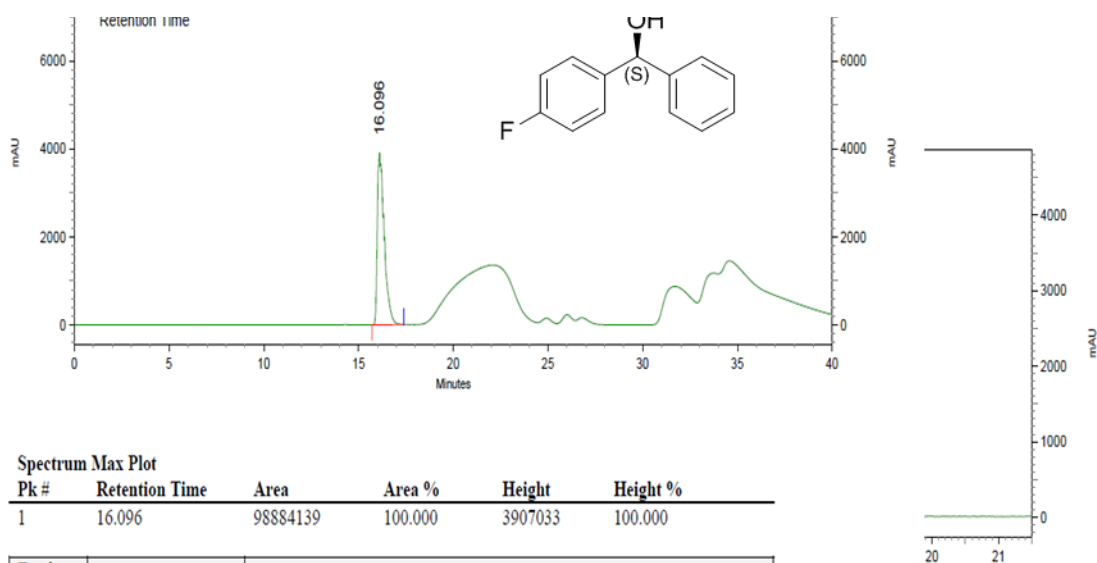
Pk #	Retention Time	Area	Area %	Height	Height %
1	14.667	13763888	100.000	849463	100.000

Totals		13763888	100.000	849463	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	14.955	10011274	44.452	454572	58.840
2	17.216	12510071	55.548	317983	41.160
Totals		22521345	100.000	772555	100.000

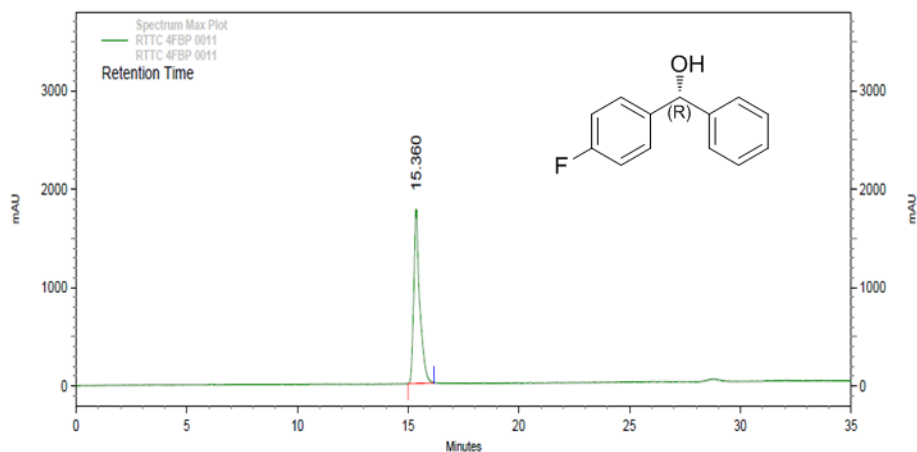


Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	16.096	98884139	100.000	3907033	100.000
Totals		98884139	100.000	3907033	100.000

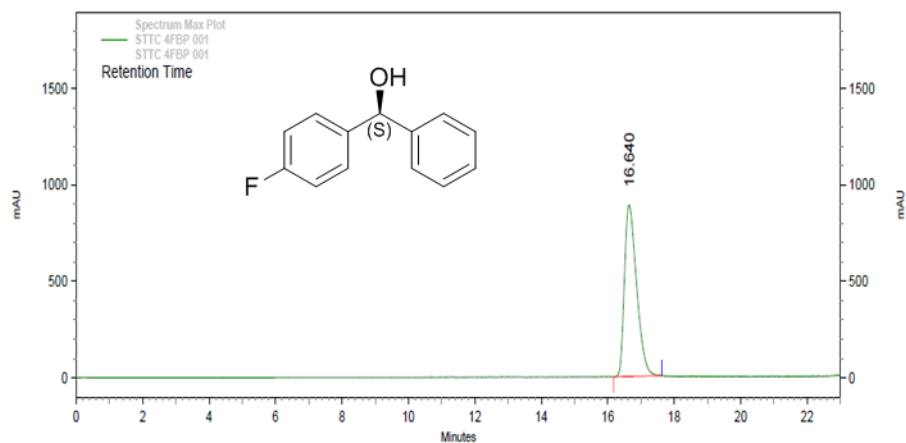
Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	16.651	53085532	100.000	2291490	100.000
Totals		53085532	100.000	2291490	100.000



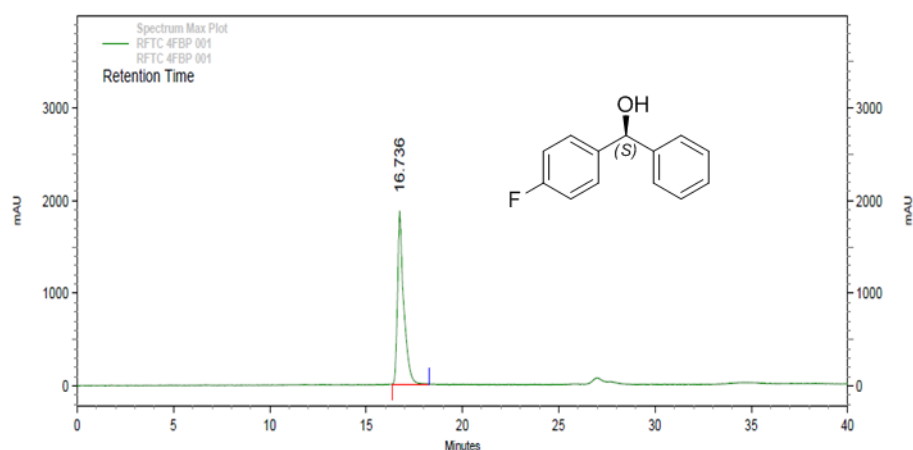
Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	15.360	32940552	100.000	1770435	100.000
Totals		32940552	100.000	1770435	100.000



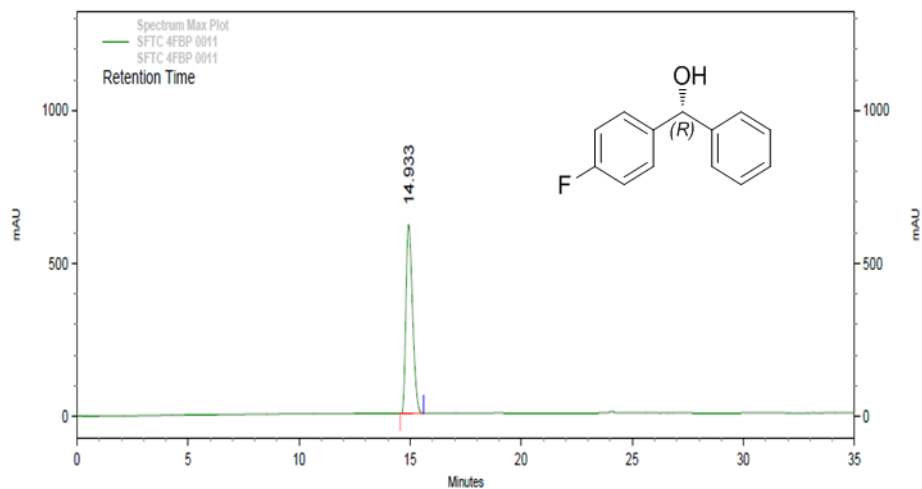
Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	16.640	22572687	100.000	889376	100.000
Totals		22572687	100.000	889376	100.000



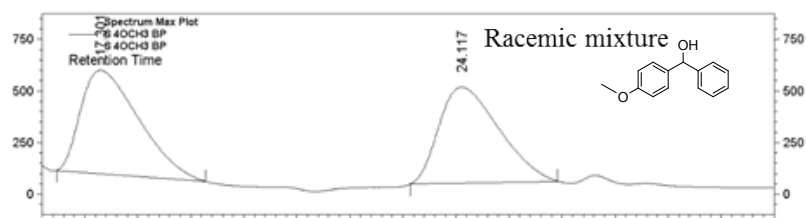
Spectrum Max Plot

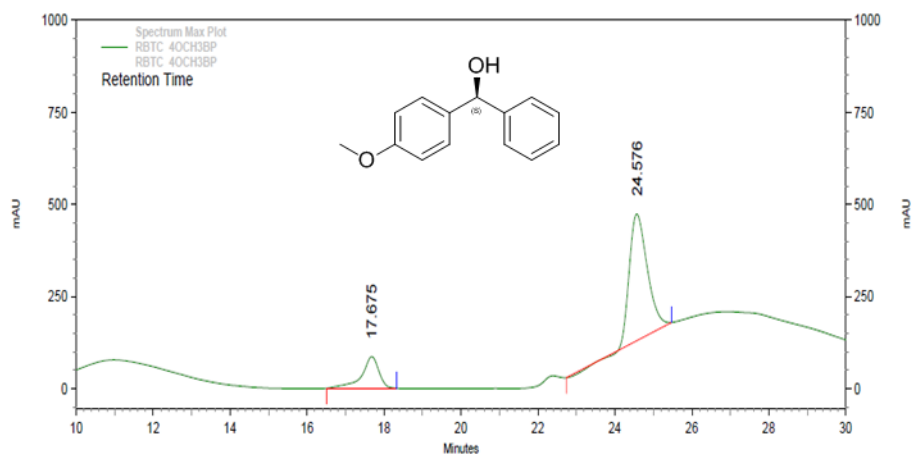
Pk #	Retention Time	Area	Area %	Height	Height %
1	16.736	41403364	100.000	1871480	100.000
Totals		41403364	100.000	1871480	100.000



Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	14.933	12743609	100.000	615975	100.000
Totals		12743609	100.000	615975	100.000

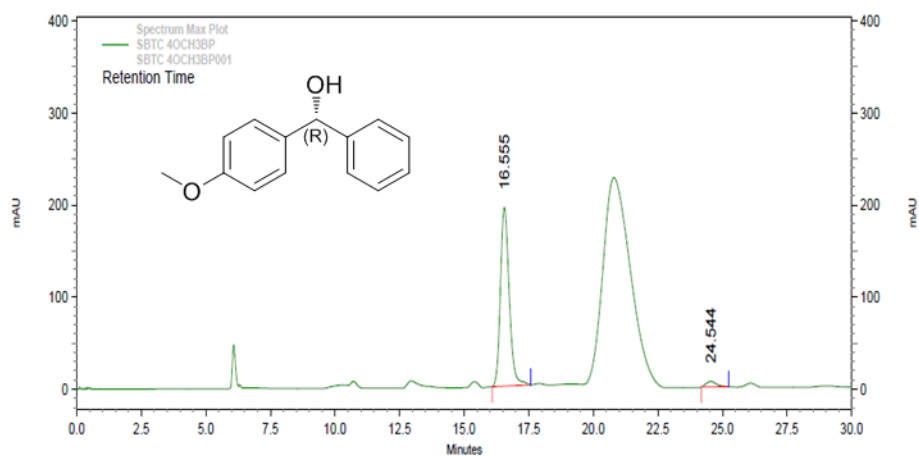




Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	17.675	2677698	19.467	86077	20.042
2	24.576	11077671	80.533	343416	79.958

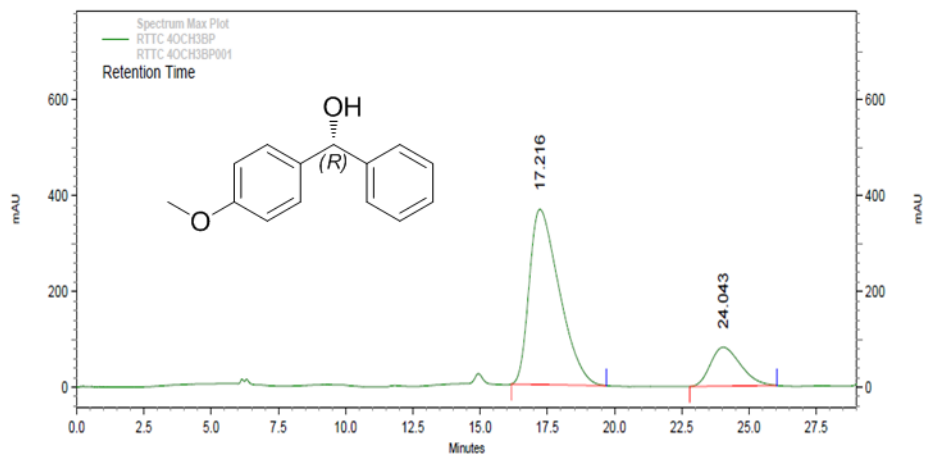
Totals		13755369	100.000	429493	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	16.555	4583990	96.514	193960	97.010
2	24.544	165551	3.486	5979	2.990

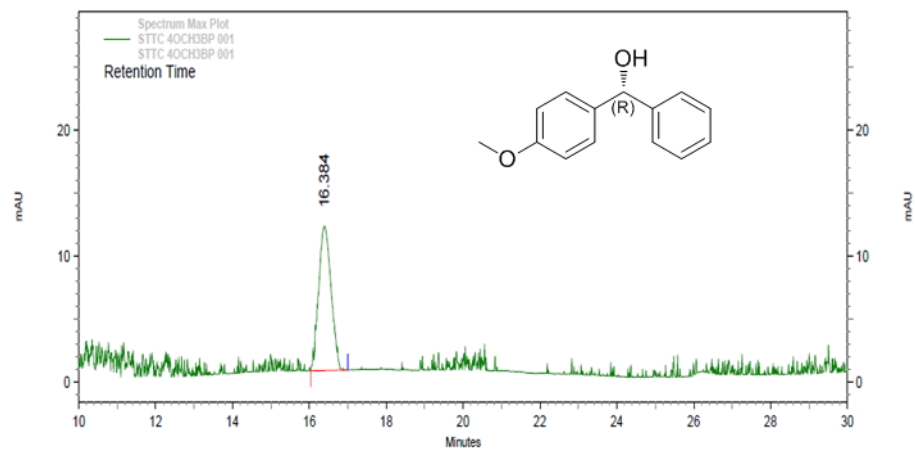
Totals		4749541	100.000	199939	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	17.216	28507653	81.805	366082	81.805
2	24.043	6340639	18.195	81424	18.195

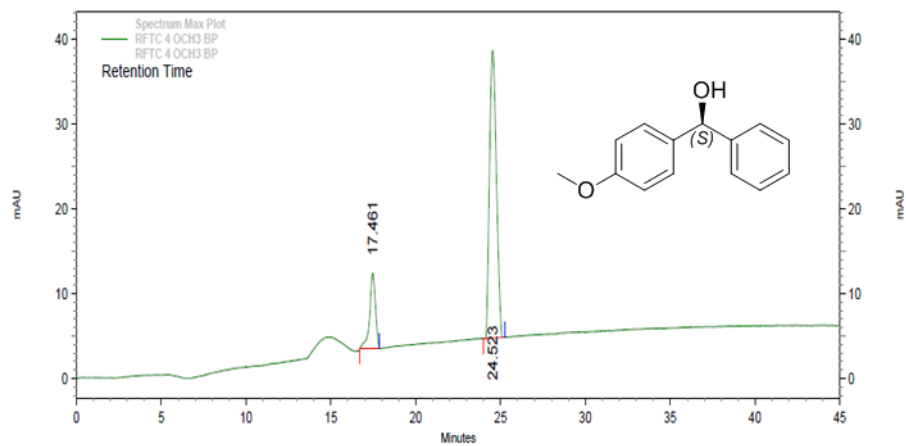
Totals		34848292	100.000	447506	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	16.384	257887	100.000	11480	100.000

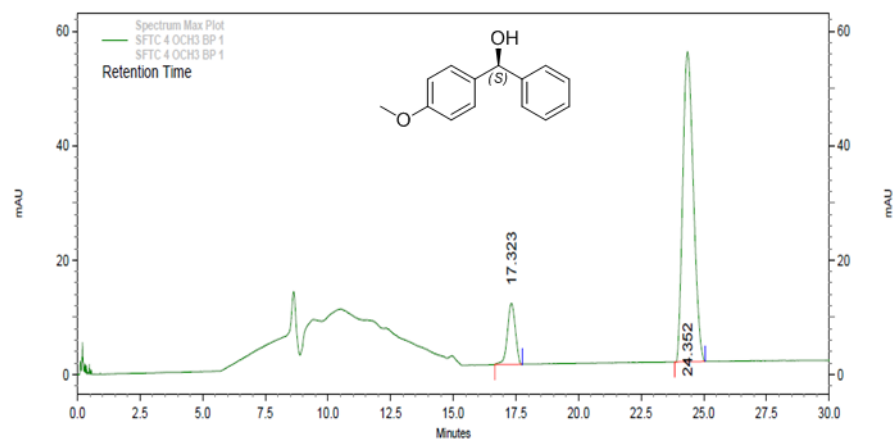
Totals		257887	100.000	11480	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	17.461	210092	18.009	8876	20.774
2	24.523	956507	81.991	33851	79.226

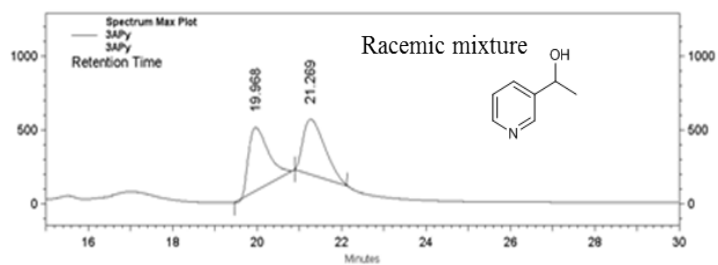
Totals		1166599	100.000	42727	100.000
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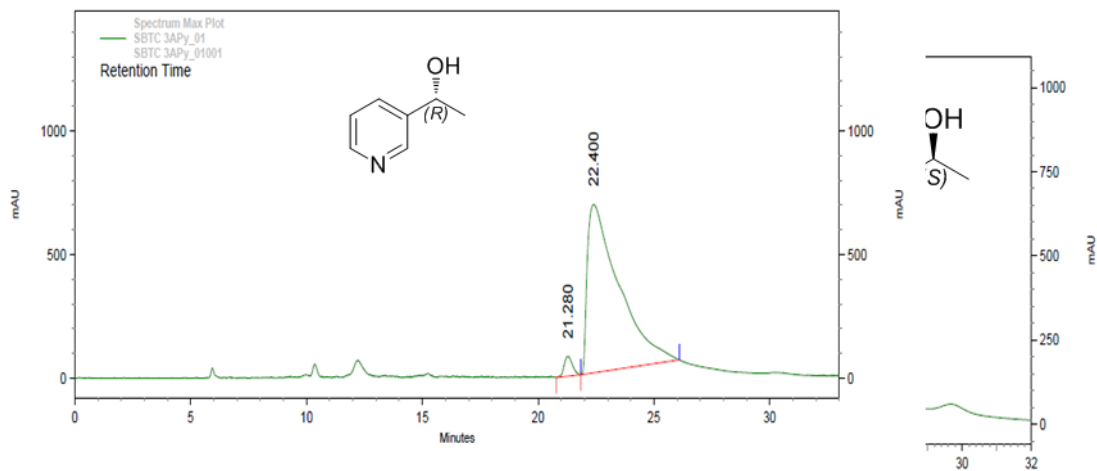
Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	17.323	231858	12.718	10673	16.467
2	24.352	1591270	87.282	54143	83.533

Totals		1823128	100.000	64816	100.000
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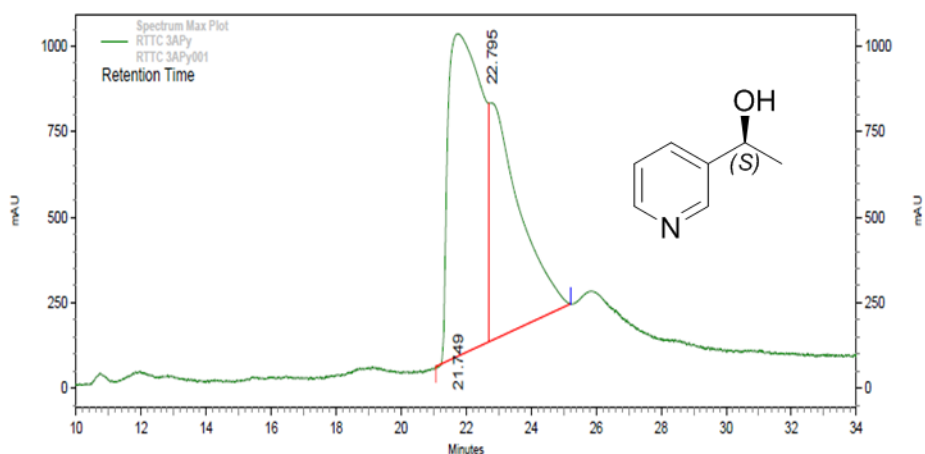


Spectrum Max Plot					
Pk #	Retention Time	Area	Area %	Height	Height %
1	19.968	13798958	50.654	429821	53.595
2	21.269	13442750	49.346	372160	46.405
Totals		27241708	100.000	801981	100.000



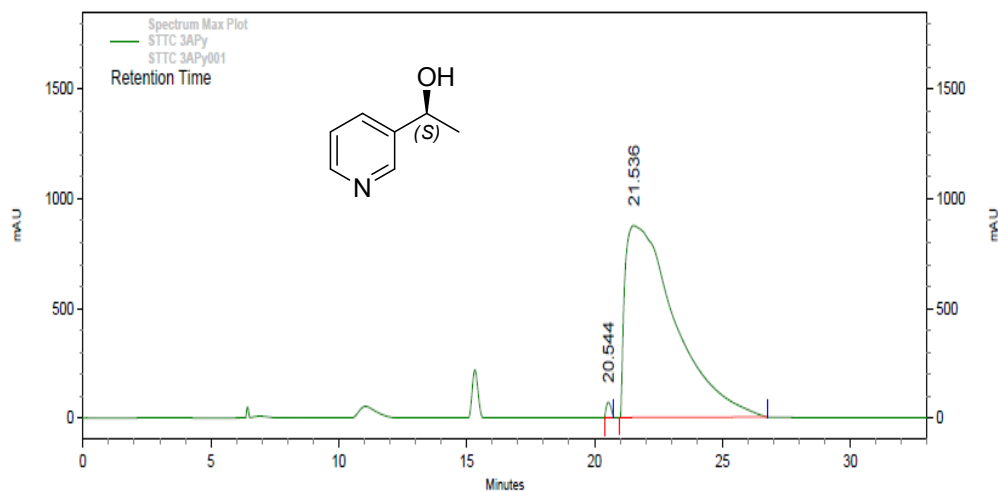
Spectrum Max Plot					
Pk #	Retention Time	Area	Area %	Height	Height %
1	21.280	1986406	2.978	80409	10.573
2	22.400	64710564	97.022	680108	89.427
Totals		66696970	100.000	760517	100.000

		165665734	100.000	1533378	100.000
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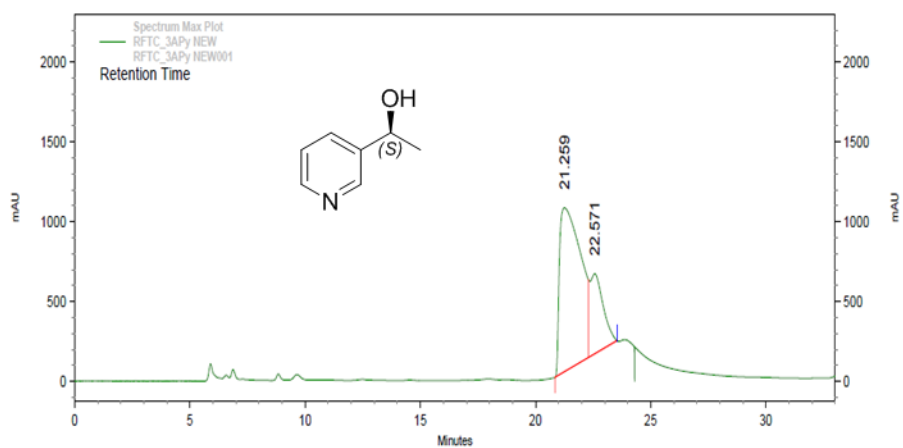
Spectrum Max Plot

PK #	Retention Time	Area	Area %	Height	Height %
1	21.749	111558882	71.488	941796	57.607
2	22.795	44494101	28.512	693075	42.393
Totals		156052983	100.000	1634871	100.000



Spectrum Max Plot

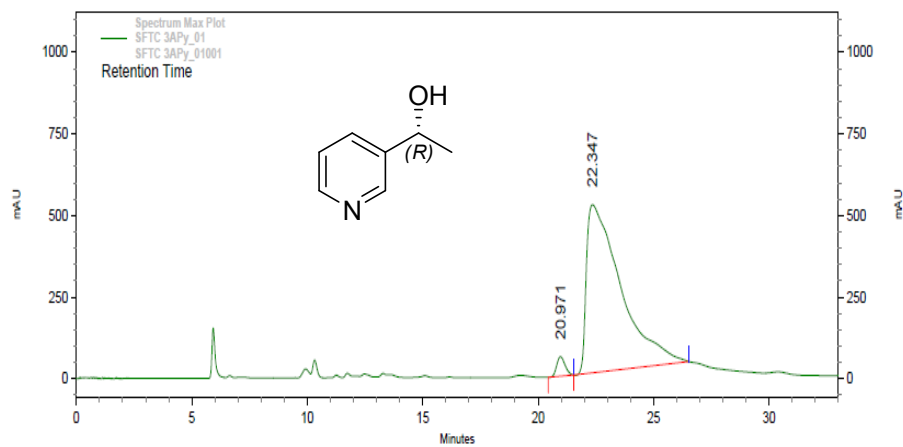
PK #	Retention Time	Area	Area %	Height	Height %
1	20.544	917256	0.759	69579	7.367
2	21.536	119885751	99.241	874869	92.633
Totals		120803007	100.000	944448	100.000



Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	21.259	84818378	80.330	1027463	67.218
2	22.571	20768577	19.670	501098	32.782

Totals		105586955	100.000	1528561	100.000
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Spectrum Max Plot

Pk #	Retention Time	Area	Area %	Height	Height %
1	20.971	1494475	2.734	59547	10.371
2	22.347	53159553	97.266	514632	89.629

Totals		54654028	100.000	574179	100.000
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B. Computational Part

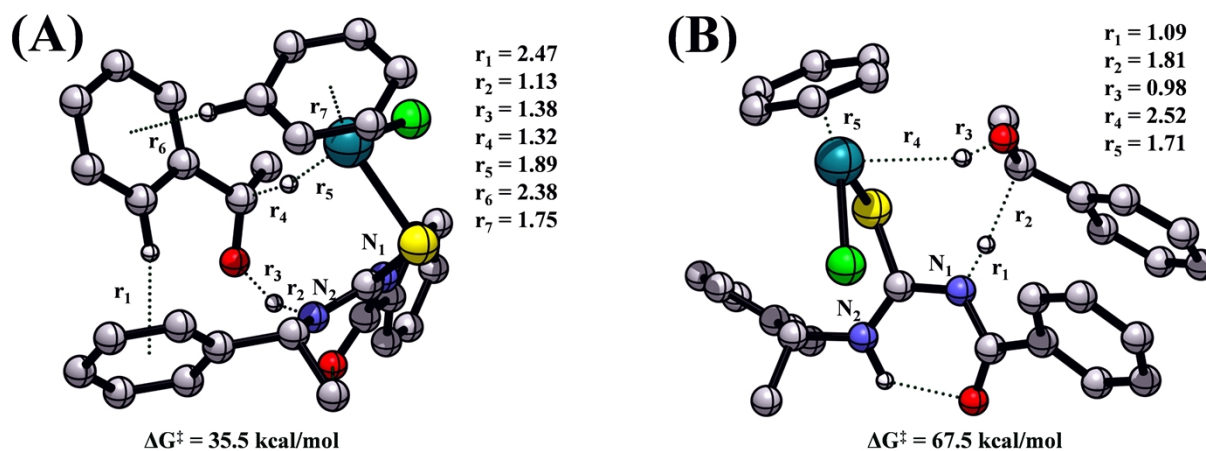


Figure S3. Optimized geometries and activation free energies (in kcal/mol) for the low energy TSs corresponding to unfavorable ATH mechanisms in which (A) the H – atom from N₂ instead of that from N₁ would be transferred and (B) transfer of H from N to carbonyl C and H from Ru to O.

Ru-benzene complex catalyzed reactions (shown in Figure 6)

1. Reactant complex for ATH in *R*-fashion (Ru-benzene catalyst).

$E_{\text{elec}} = -2373.3868858$ Hartree $E_{\text{ZPE}} = -2372.838637$ Hartree $H = -2372.800718$ Hartree
 $G = -2372.914977$ Hartree
 Low frequencies (cm^{-1}) = 9.0335 16.2795 17.4952 20.0325
 23.9330 30.5004 34.0334 41.3187 46.4774 48.6022
 56.3949 65.2426.

16	1.668148	0.306825	1.053441
8	0.271318	-3.341741	-1.36707
7	2.289552	-1.821734	-0.446202
7	0.043437	-1.51013	-0.010381
6	3.65997	-1.348795	-0.641576
1	3.597422	-0.26754	-0.808039
6	4.205116	-2.0218	-1.902134
1	5.222214	-1.671437	-2.095344
1	3.573633	-1.776162	-2.761577
1	4.243124	-3.109822	-1.774446
6	1.343053	-1.11164	0.134013
6	-0.432915	-2.452439	-0.912968
6	4.543192	-1.617302	0.562321
6	5.620901	-0.767615	0.819999
1	5.771237	0.108695	0.192306
6	6.490479	-1.025089	1.877089
1	7.321704	-0.352938	2.0697
6	6.286899	-2.13783	2.693075
1	6.959873	-2.337677	3.521541
6	5.210214	-2.986861	2.443989
1	5.040465	-3.851302	3.079277
6	4.343406	-2.727896	1.38304
1	3.497335	-3.385894	1.200997
1	1.973482	-2.636447	-0.976309
6	-1.868025	-2.300555	-1.28589
6	-2.416908	-1.032747	-1.502464
6	-2.630568	-3.450634	-1.498577
6	-3.73891	-0.923945	-1.926381
1	-1.793824	-0.147512	-1.390753
6	-3.959152	-3.333403	-1.8999
1	-2.172792	-4.424298	-1.350771
6	-4.510993	-2.070074	-2.116915
1	-4.166661	0.05711	-2.110376
1	-4.558865	-4.225198	-2.055698
1	-5.544728	-1.978237	-2.438518
44	0.704851	2.057521	-0.474809
6	0.05546	3.91023	0.524868
6	-0.304302	3.974488	-0.85759
6	0.704295	3.821148	-1.83041
6	2.098412	3.83771	-1.462718

6	2.447497	3.779541	-0.130036
6	1.407179	3.695813	0.866974
1	-0.703973	3.952098	1.296706
1	-1.34346	4.052305	-1.154214
1	0.431424	3.738442	-2.875938
1	2.854591	3.79347	-2.238632
1	3.486338	3.697313	0.170686
1	1.677236	3.555222	1.908116
1	-0.676736	1.396691	-0.182527
8	-2.176086	-0.688876	1.562103
6	-2.932346	0.228071	1.834531
17	0.824078	0.515997	-2.414241
1	-0.63948	-0.937774	0.489014
6	-2.388608	1.56701	2.271998
1	-2.72197	2.352091	1.583626
1	-2.751525	1.819781	3.274371
1	-1.298062	1.516995	2.265864
6	-4.409201	0.027122	1.726196
6	-4.875045	-1.198048	1.2344
6	-5.323968	1.023391	2.084627
6	-6.240635	-1.423515	1.105662
1	-4.150398	-1.954886	0.945782
6	-6.692151	0.794851	1.95839
1	-4.974558	1.978925	2.464813
6	-7.150004	-0.42851	1.469299
1	-6.596567	-2.373174	0.717133
1	-7.399466	1.568671	2.240341
1	-8.217	-0.605675	1.369828

2. TS for ATH in *R*-fashion (Ru-benzene catalyst).

$E_{\text{elec}} = -2373.354654$ Hartree $E_{\text{ZPE}} = -2372.809642$ Hartree $H = -2372.773542$ Hartree
 $G = -2372.880101$ Hartree
 Low frequencies (cm^{-1}) = -482.6960 12.6051 18.5515 23.9126
 30.0575 34.7967 37.8259 43.4706 49.5026.

16	-0.910646	-1.201805	0.821806
8	-1.823825	2.918312	-0.958173
7	-2.049213	0.2923	-1.066359
7	-0.787732	1.459061	0.493247
6	-2.439546	-0.894258	-1.822655
1	-1.567828	-1.557749	-1.850747
6	-2.78298	-0.443925	-3.244501
1	-3.05599	-1.310294	-3.852128
1	-1.926531	0.057801	-3.705098

1	-3.638366	0.240747	-3.233515
6	-1.273795	0.30163	0.007001
6	-0.952579	2.696442	-0.122637
6	-3.600499	-1.642584	-1.190621
6	-3.770726	-2.99725	-1.485871
1	-3.042698	-3.502386	-2.118738
6	-4.853924	-3.705642	-0.972586
1	-4.971801	-4.759676	-1.207045
6	-5.781643	-3.062698	-0.152589
1	-6.624982	-3.613028	0.253509
6	-5.615694	-1.712392	0.14731
1	-6.329195	-1.206188	0.790777
6	-4.530388	-1.005075	-0.36974
1	-4.398705	0.044493	-0.119774
1	-2.290476	1.215771	-1.435479
6	0.005248	3.747978	0.30834
6	1.321157	3.418507	0.636669
6	-0.414311	5.081554	0.313913
6	2.215369	4.422995	0.997127
1	1.650566	2.386713	0.576972
6	0.477166	6.080596	0.688942
1	-1.435708	5.316479	0.029726
6	1.790763	5.750056	1.033164
1	3.238638	4.160329	1.252183
1	0.152627	7.116562	0.711678
1	2.485366	6.533213	1.324028
44	1.486228	-1.563982	0.583522
6	2.015656	-3.254595	1.982813
6	3.214081	-2.599815	1.564192
6	3.52259	-2.473924	0.194621
6	2.592825	-2.947749	-0.774725
6	1.398718	-3.586383	-0.381858
6	1.110167	-3.723102	1.010798
1	1.760851	-3.306611	3.034431
1	3.865473	-2.144678	2.303866
1	4.397152	-1.918113	-0.121987
1	2.761941	-2.725014	-1.82228
1	0.665103	-3.882678	-1.121823
1	0.151447	-4.126512	1.320236
1	1.590972	-0.179672	1.747861
8	0.422016	1.275159	2.700986
6	1.49519	0.536274	2.770624
17	1.644416	0.1312	-1.160481
1	-0.206367	1.401179	1.45365
6	1.450341	-0.484379	3.91474
1	2.347588	-1.112647	3.952832

1	1.379225	0.071577	4.855755
1	0.550441	-1.097773	3.808156
6	2.826095	1.294049	2.734829
6	3.031062	2.245659	3.741333
6	3.820716	1.101236	1.776514
6	4.225051	2.957264	3.812442
1	2.234076	2.433951	4.456115
6	5.015511	1.823885	1.837997
1	3.641115	0.422299	0.945891
6	5.226727	2.743395	2.862813
1	4.370976	3.689403	4.601732
1	5.77327	1.676583	1.073268
1	6.156213	3.303255	2.912452

3. Product complex for ATH in *R*-fashion (Ru-benzene catalyst).

$E_{\text{elec}} = -2373.3777887$ Hartree $E_{\text{ZPE}} = -2372.826292$ Hartree $H = -2372.789113$ Hartree
 $G = -2372.901022$ Hartree
 Low frequencies (cm^{-1}) = 6.6782 10.4072 20.6120 24.4249
 35.4370 38.2291 40.9542 41.9617 47.8715.

16	-1.386346	-0.038124	1.001521
8	0.276553	3.934543	-0.503615
7	-1.719937	2.195425	-0.443984
7	0.444409	1.795671	0.399785
6	-3.001338	1.726589	-0.95894
1	-2.845258	0.734717	-1.402164
6	-3.43179	2.689044	-2.068526
1	-4.385694	2.366423	-2.493441
1	-2.679445	2.713415	-2.86299
1	-3.565178	3.699636	-1.666707
6	-0.814293	1.470247	0.224161
6	0.947912	2.958872	-0.165002
6	-4.076897	1.618882	0.10827
6	-5.124452	0.713282	-0.074147
1	-5.127772	0.073897	-0.956317
6	-6.157319	0.621743	0.856171
1	-6.966503	-0.086662	0.701695
6	-6.150142	1.439858	1.986125
1	-6.950607	1.369219	2.716449
6	-5.108135	2.34671	2.172667
1	-5.093578	2.983975	3.05201
6	-4.077307	2.436817	1.238087
1	-3.256837	3.132618	1.39396
1	-1.360544	3.093316	-0.77296
6	2.431479	2.967359	-0.335574

6	3.131537	1.772502	-0.50888
6	3.110403	4.188556	-0.373178
6	4.511173	1.791018	-0.696869
1	2.584699	0.835403	-0.521311
6	4.490705	4.206566	-0.546909
1	2.544491	5.108364	-0.260057
6	5.191169	3.008084	-0.706152
1	5.048708	0.855175	-0.827166
1	5.023144	5.153101	-0.560139
1	6.269102	3.025525	-0.841149
44	-1.10425	-1.764827	-0.491502
6	-0.992251	-3.546607	0.831163
6	-0.128713	-3.737264	-0.291686
6	-0.645206	-3.691428	-1.608706
6	-1.992125	-3.330186	-1.813864
6	-2.835631	-3.060986	-0.696932
6	-2.35107	-3.233069	0.630664
1	-0.577433	-3.550262	1.832183
1	0.934442	-3.882068	-0.131181
1	0.027908	-3.762162	-2.45499
1	-2.352117	-3.136956	-2.817567
1	-3.842459	-2.692828	-0.858136
1	-2.984633	-2.985499	1.474911
1	1.466919	-0.93649	0.651775
8	2.04643	0.252352	2.232628
6	2.154218	-0.952126	1.5133
17	-0.214877	-0.339354	-2.183207
1	1.553905	0.894801	1.675592
6	1.751255	-2.083574	2.458892
1	1.840696	-3.066582	1.979635
1	2.409652	-2.073948	3.33396
1	0.724058	-1.916242	2.80078
6	3.557721	-1.183305	0.981143
6	4.670423	-0.819554	1.743081
6	3.753894	-1.789246	-0.261414
6	5.95778	-1.079837	1.278103
1	4.512198	-0.307154	2.688202
6	5.041733	-2.051093	-0.731617
1	2.889299	-2.024546	-0.882927
6	6.147733	-1.701582	0.042251
1	6.817091	-0.7877	1.875212
1	5.18121	-2.510988	-1.706037
1	7.15201	-1.898555	-0.32166

4. Reactant complex for ATH in *S*-fashion (Ru-benzene catalyst).

$E_{\text{elec}} = -2373.4042448$ Hartree $E_{\text{ZPE}} = -2372.855488$ Hartree $H = -2372.818142$ Hartree
 $G = -2372.927091$ Hartree
 Low frequencies (cm^{-1}) = 11.3081 19.4962 24.2239 35.3829
 46.7558 52.3807 53.9892 55.8021 63.0145.

16	0.658187	0.444573	-1.853596
8	-0.982428	-3.683587	-0.906966
7	0.894583	-2.191022	-2.023613
7	-1.150686	-1.429451	-1.250802
6	2.30766	-2.087689	-2.371454
1	2.420508	-1.232889	-3.046083
6	2.708354	-3.366419	-3.107838
1	3.761461	-3.312598	-3.394935
1	2.100059	-3.50201	-4.007155
1	2.582197	-4.239992	-2.458205
6	0.115195	-1.161872	-1.704518
6	-1.581879	-2.632695	-0.718079
6	3.179772	-1.864671	-1.147115
6	4.21801	-0.93249	-1.186366
1	4.356079	-0.324099	-2.077888
6	5.064377	-0.769259	-0.089725
1	5.868786	-0.039903	-0.130945
6	4.870479	-1.533939	1.059714
1	5.519551	-1.399453	1.920067
6	3.827088	-2.458476	1.107645
1	3.65748	-3.042615	2.007362
6	2.986417	-2.623737	0.009441
1	2.152289	-3.319233	0.068075
1	0.490771	-3.113961	-1.858625
6	-2.80654	-2.582622	0.139009
6	-3.549514	-1.420438	0.371922
6	-3.16536	-3.777809	0.773358
6	-4.641864	-1.463355	1.236854
1	-3.312824	-0.476317	-0.111508
6	-4.248576	-3.810782	1.644317
1	-2.573159	-4.666025	0.579875
6	-4.988932	-2.650502	1.878642
1	-5.220314	-0.560231	1.405674
1	-4.516978	-4.739254	2.13913
1	-5.837326	-2.674517	2.556593
44	-0.852542	2.059379	-0.777574
6	0.070908	3.287885	0.813258
6	-1.323538	3.598454	0.759017
6	-1.880204	4.033989	-0.456729
6	-1.041752	4.361554	-1.580228
6	0.310359	4.077539	-1.525369

6	0.851608	3.444943	-0.349636
1	0.510609	2.878256	1.714889
1	-1.959483	3.412476	1.616381
1	-2.954255	4.149217	-0.545542
1	-1.493301	4.737694	-2.49127
1	0.944937	4.241438	-2.389764
1	1.890276	3.131652	-0.334335
1	-1.12923	0.922774	0.264308
8	0.288725	-1.631421	1.21313
6	0.057572	-0.884463	2.145736
17	-2.83933	1.180115	-1.982326
6	1.010763	0.224947	2.48204
6	0.876087	0.987537	3.647948
6	2.066545	0.490219	1.601886
6	1.793116	1.99693	3.939637
1	0.058612	0.798265	4.337145
6	2.97839	1.500807	1.892153
1	2.152707	-0.095396	0.690709
6	2.845719	2.254081	3.060893
1	1.686012	2.580222	4.849226
1	3.79784	1.694538	1.205184
1	3.560321	3.040642	3.286257
6	-1.18792	-1.05356	2.986474
1	-0.933924	-1.188792	4.04306
1	-1.819479	-0.161223	2.901267
1	-1.744993	-1.921944	2.631575
1	-1.757455	-0.605805	-1.205928

5. TS for ATH in S-fashion (Ru-benzene catalyst).

$E_{\text{elec}} = -2373.3569799$ Hartree $E_{\text{ZPE}} = -2372.812903$ Hartree $H = -2372.776544$ Hartree
 $G = -2372.884218$ Hartree
 Low frequencies (cm^{-1}) = -904.5956 11.2454 20.1696 25.6678
 27.6270 33.9229 37.2625 45.0281 50.0988.

16	-0.619474	-1.376615	0.121533
8	-1.820492	2.905306	-0.885898
7	-1.998878	0.33655	-1.351288
7	-0.467302	1.311711	0.105011
6	-2.641413	-0.758089	-2.069719
1	-1.858446	-1.4726	-2.345428
6	-3.276026	-0.177353	-3.335632
1	-3.748375	-0.975724	-3.913452
1	-2.520261	0.312021	-3.957376
1	-4.051404	0.551656	-3.075052
6	-1.045572	0.219611	-0.432061

6	-0.82012	2.60921	-0.233474
6	-3.679617	-1.482202	-1.227651
6	-3.988867	-2.811031	-1.525874
1	-3.443492	-3.322413	-2.317299
6	-4.976323	-3.487245	-0.81374
1	-5.203808	-4.522076	-1.053026
6	-5.665664	-2.837546	0.210331
1	-6.432967	-3.363184	0.770745
6	-5.35941	-1.512581	0.514108
1	-5.886787	-1.001716	1.314304
6	-4.371217	-0.8375	-0.201953
1	-4.127264	0.19175	0.049899
1	-2.304955	1.295883	-1.533778
6	0.104838	3.665352	0.262586
6	1.478052	3.429722	0.336924
6	-0.417553	4.920746	0.583898
6	2.329036	4.449788	0.754863
1	1.867204	2.462541	0.031199
6	0.433834	5.930522	1.019706
1	-1.486576	5.087183	0.492075
6	1.807513	5.694173	1.105924
1	3.3997	4.273292	0.803482
1	0.030684	6.90245	1.287648
1	2.472113	6.485535	1.440801
44	1.784517	-1.792136	0.092178
6	2.190851	-3.544919	1.438009
6	3.437374	-2.950653	1.062656
6	3.773734	-2.782891	-0.293129
6	2.844156	-3.180787	-1.302343
6	1.617753	-3.772877	-0.949589
6	1.289505	-3.942865	0.434694
1	1.90786	-3.593335	2.485603
1	4.089571	-2.561752	1.837748
1	4.674327	-2.249386	-0.572426
1	3.047821	-2.935422	-2.338478
1	0.882861	-4.003375	-1.711604
1	0.30399	-4.303295	0.710768
1	1.839478	-0.556543	1.353024
8	0.756749	0.962484	2.234959
6	1.80332	0.177057	2.347461
17	2.239769	0.116656	-1.334549
6	1.676726	-0.866646	3.454184
6	2.771814	-1.387598	4.148261
6	0.397598	-1.357621	3.739402
6	2.597225	-2.403302	5.092595
1	3.770599	-0.998401	3.972077

6	0.222942	-2.3758	4.672413
1	-0.445187	-0.926725	3.207841
6	1.324187	-2.908355	5.348814
1	3.456511	-2.791635	5.632391
1	-0.774959	-2.752423	4.879373
1	1.187521	-3.698722	6.081284
6	3.165267	0.858541	2.22858
1	3.303408	1.521019	3.09078
1	3.992321	0.143204	2.179736
1	3.184774	1.454039	1.315367
1	0.210888	1.148501	1.067273

6. Product complex for ATH in S-fashion (Ru-benzene catalyst).

$E_{\text{elec}} = -2373.38205$ Hartree $E_{\text{ZPE}} = -2372.830302$ Hartree $H = -2372.793228$ Hartree
 $G = -2372.904361$ Hartree
 Low frequencies (cm^{-1}) = 10.4716 13.1863 15.3437 27.6476
 31.4493 32.9759 38.8587 47.4094 51.3033.

16	0.831674	-0.188868	0.642719
8	-2.005664	-3.715834	0.157778
7	0.438135	-2.757493	-0.030437
7	-1.481879	-1.463024	0.416724
6	1.824461	-2.902792	-0.459691
1	2.043503	-2.09122	-1.16419
6	1.939886	-4.234558	-1.204491
1	2.964767	-4.377143	-1.556438
1	1.26405	-4.246575	-2.065266
1	1.692182	-5.068571	-0.538297
6	-0.179742	-1.617664	0.285129
6	-2.334169	-2.52768	0.194387
6	2.816347	-2.835474	0.688597
6	4.11937	-2.401727	0.434475
1	4.385864	-2.07683	-0.570537
6	5.072702	-2.377843	1.449799
1	6.082499	-2.037226	1.238501
6	4.727949	-2.787764	2.73787
1	5.466358	-2.766276	3.533751
6	3.429046	-3.221484	2.997633
1	3.151708	-3.53744	3.999064
6	2.47817	-3.246294	1.978053
1	1.46161	-3.569886	2.18689
1	-0.196246	-3.551944	-0.13616
6	-3.768706	-2.151085	-0.005755
6	-4.130297	-0.87824	-0.451335
6	-4.752229	-3.122552	0.200536

6	-5.470711	-0.577405	-0.683799
1	-3.352869	-0.143688	-0.638971
6	-6.092079	-2.81407	-0.011631
1	-4.447384	-4.112085	0.526633
6	-6.452482	-1.540764	-0.45629
1	-5.749829	0.408575	-1.044698
1	-6.85617	-3.56576	0.162729
1	-7.497857	-1.301893	-0.629808
44	1.157967	0.966209	-1.318713
6	1.604194	2.991444	-0.507038
6	0.795678	3.10624	-1.677503
6	1.232941	2.570157	-2.91561
6	2.421124	1.814922	-2.964385
6	3.181735	1.615775	-1.777567
6	2.803379	2.255286	-0.560889
1	1.238123	3.372597	0.440129
1	-0.176639	3.579946	-1.600005
1	0.579978	2.602907	-3.779751
1	2.680547	1.273391	-3.86648
1	4.037025	0.949745	-1.792361
1	3.362714	2.063402	0.347991
1	-1.995655	1.593713	0.047454
8	-2.21077	0.826703	1.945977
6	-2.27978	1.919	1.065356
17	0.004235	-0.658509	-2.63224
6	-1.296844	3.004553	1.491566
6	-1.302095	4.266752	0.882585
6	-0.379101	2.763961	2.518255
6	-0.416262	5.265204	1.288146
1	-2.014324	4.481633	0.088354
6	0.50653	3.762209	2.929504
1	-0.380978	1.785958	2.98715
6	0.492325	5.016797	2.318691
1	-0.442279	6.239475	0.807496
1	1.205894	3.559688	3.736163
1	1.176101	5.795223	2.644587
6	-3.716484	2.448367	1.046655
1	-3.98004	2.809831	2.04569
1	-3.854244	3.264847	0.330692
1	-4.39742	1.633548	0.787926
1	-1.991789	0.012464	1.438145

Ru-p-cymene complex catalyzed reactions (shown in Figure 7)

7. Reactant complex for ATH in *S*-fashion (Ru-p-cymene catalyst).

$E_{\text{elec}} = -2530.5943924$ Hartree $E_{\text{ZPE}} = -2529.932079$ Hartree $H = -2529.888997$ Hartree
 $G = -2530.008763$ Hartree
 Low frequencies (cm^{-1}) = 11.5005 23.1935 27.3059 31.7789
 41.8702 47.5840 52.0835 56.8921 62.2073.

16	-0.556943	0.232074	-1.718869
8	3.072167	2.849327	-0.931398
7	0.619881	2.594215	-1.864612
7	1.986132	0.851631	-1.17017
6	-0.640838	3.224924	-2.24179
1	-1.143479	2.555565	-2.94797
6	-0.31931	4.54322	-2.94566
1	-1.246309	5.031133	-3.256881
1	0.303864	4.36708	-3.827549
1	0.208734	5.225688	-2.270388
6	0.755536	1.303533	-1.575383
6	3.046412	1.637764	-0.75392
6	-1.557245	3.444498	-1.049482
6	-2.881323	3.005232	-1.091866
1	-3.227725	2.441344	-1.955638
6	-3.750562	3.272394	-0.033857
1	-4.779801	2.925356	-0.079255
6	-3.296393	3.978896	1.07913
1	-3.968631	4.184247	1.907371
6	-1.968255	4.402952	1.135356
1	-1.602224	4.931478	2.010453
6	-1.102574	4.13317	0.077788
1	-0.059695	4.435819	0.142334
1	1.447741	3.172109	-1.714249
6	4.159778	0.940134	-0.039341
6	4.27192	-0.450107	0.064986
6	5.102763	1.765396	0.584619
6	5.321964	-1.002306	0.796532
1	3.571369	-1.124132	-0.422044
6	6.140733	1.207859	1.322684
1	4.996222	2.840808	0.488634
6	6.250789	-0.179573	1.431006
1	5.409177	-2.082243	0.865916
1	6.863758	1.853248	1.812185
1	7.06251	-0.617222	2.005025
44	-0.150802	-1.949744	-0.683482
6	-1.721551	-2.378706	0.824774
6	-0.671121	-3.333402	0.971407
6	-0.27972	-4.144252	-0.112895
6	-1.054308	-4.079402	-1.323861

6	-2.094251	-3.174104	-1.471054
6	-2.382012	-2.233699	-0.41765
1	-1.970128	-1.717959	1.648176
1	-0.121428	-3.384894	1.906002
1	-0.755437	-4.700858	-2.163358
1	-2.617653	-3.108437	-2.417719
1	0.715204	-1.12755	0.33714
8	0.908257	1.810706	1.318782
6	0.800364	0.939918	2.162134
17	1.971835	-2.291144	-1.938944
6	-0.557802	0.514921	2.642022
6	-0.721969	-0.347609	3.731567
6	-1.686198	1.026142	1.990947
6	-1.999626	-0.675929	4.184676
1	0.143594	-0.763731	4.238052
6	-2.960428	0.702249	2.447905
1	-1.545213	1.669066	1.125855
6	-3.120199	-0.143457	3.547726
1	-2.11889	-1.340343	5.035261
1	-3.831552	1.106199	1.938703
1	-4.116514	-0.392797	3.902501
6	2.019685	0.277809	2.762212
1	2.020179	0.368996	3.853333
1	2.025579	-0.78907	2.508006
1	2.918331	0.746833	2.359839
1	2.048355	-0.16777	-1.102752
6	0.889103	-5.083744	-0.024044
1	0.547099	-6.12474	0.000532
1	1.546221	-4.946502	-0.888167
1	1.475136	-4.889482	0.878058
6	-3.460443	-1.17153	-0.556812
1	-3.034086	-0.240086	-0.159533
6	-4.677407	-1.553119	0.297294
1	-4.404033	-1.690986	1.348102
1	-5.441662	-0.769258	0.24226
1	-5.122683	-2.487649	-0.064488
6	-3.891017	-0.912179	-2.001058
1	-4.568351	-0.052149	-2.030185
1	-3.039304	-0.691834	-2.652214
1	-4.435523	-1.768862	-2.41634

8. TS for ATH in *S*-fashion (Ru-p-cymene catalyst).

$E_{\text{elec}} = -2530.550544$ Hartree $E_{\text{ZPE}} = -2529.892950$ Hartree $H = -2529.850707$
Hartree $G = -2529.970483$ Hartree
Low frequencies (cm^{-1}) = -759.8233 10.0691 13.7373 19.3046

30.0421	32.6633	37.4044	42.9177	48.6318.
16	-0.63996	-1.332501	0.13946	
8	-1.801387	2.941397	-0.948111	
7	-2.010143	0.361148	-1.35842	
7	-0.4803	1.353154	0.087611	
6	-2.626992	-0.744195	-2.084321	
1	-1.823619	-1.426832	-2.384034	
6	-3.300882	-0.165432	-3.330468	
1	-3.752876	-0.970477	-3.915176	
1	-2.572683	0.360741	-3.955137	
1	-4.097574	0.530857	-3.045975	
6	-1.059847	0.252534	-0.434707	
6	-0.811809	2.649255	-0.278995	
6	-3.624849	-1.521266	-1.240802	
6	-3.888889	-2.854974	-1.559611	
1	-3.342053	-3.329426	-2.373128	
6	-4.831678	-3.584424	-0.839067	
1	-5.02279	-4.622943	-1.094464	
6	-5.52244	-2.982925	0.212876	
1	-6.255055	-3.549545	0.779794	
6	-5.264042	-1.651601	0.53449	
1	-5.793651	-1.177461	1.355547	
6	-4.320389	-0.923855	-0.189467	
1	-4.110906	0.109186	0.077241	
1	-2.309329	1.318175	-1.561745	
6	0.122882	3.701112	0.205698	
6	1.491359	3.446192	0.302157	
6	-0.384914	4.970396	0.494543	
6	2.352031	4.46233	0.709667	
1	1.870456	2.467402	0.021508	
6	0.476095	5.976324	0.919909	
1	-1.450205	5.150398	0.38635	
6	1.844893	5.721252	1.028311	
1	3.419149	4.270946	0.77597	
1	0.084392	6.959439	1.16281	
1	2.517175	6.509406	1.355339	
44	1.766172	-1.784779	0.136648	
6	2.240966	-3.458345	1.538599	
6	3.464093	-2.880173	1.077401	
6	3.753454	-2.76843	-0.29697	
6	2.762618	-3.244717	-1.217485	
6	1.563319	-3.829739	-0.771686	
6	1.275877	-3.942704	0.631409	
1	2.018896	-3.445355	2.602884	
1	4.143247	-2.445306	1.805157	

1	2.905482	-3.064224	-2.278418
1	0.810624	-4.106201	-1.500212
1	1.826916	-0.518256	1.374068
8	0.741678	1.012824	2.240504
6	1.780107	0.223585	2.365551
17	2.244855	0.101029	-1.330351
6	1.642369	-0.820889	3.472398
6	2.724922	-1.31481	4.204095
6	0.367568	-1.34875	3.709927
6	2.545299	-2.343799	5.133871
1	3.718641	-0.899357	4.063404
6	0.188983	-2.382998	4.624215
1	-0.467618	-0.936904	3.151111
6	1.280183	-2.891003	5.33612
1	3.395431	-2.712471	5.701289
1	-0.80445	-2.791862	4.79005
1	1.140256	-3.693936	6.054338
6	3.149402	0.894406	2.256531
1	3.287109	1.560028	3.116544
1	3.971119	0.171848	2.216624
1	3.180493	1.486125	1.340997
1	0.179866	1.200208	1.027282
6	4.986318	-2.078037	-0.801442
1	5.679358	-2.80546	-1.237757
1	4.715202	-1.341262	-1.563717
1	5.497535	-1.55393	0.009949
6	-0.027829	-4.508669	1.169616
1	-0.455978	-3.734521	1.822701
6	0.26613	-5.749107	2.026528
1	0.929571	-5.517349	2.865379
1	-0.667056	-6.149052	2.435286
1	0.736316	-6.533577	1.422039
6	-1.04967	-4.841797	0.082694
1	-1.980365	-5.178748	0.548999
1	-1.292127	-3.970408	-0.532968
1	-0.68806	-5.652207	-0.563246

9. Product complex for ATH in S-fashion (Ru-*p*-cymene catalyst).

E _{elec} = -2530.5799763 Hartree		E _{ZPE} = -2529.914626 Hartree		H = -2529.871806 Hartree	
G = -2529.992741 Hartree					
Low frequencies (cm ⁻¹) =		11.0196	16.6693	23.4588	30.7337
35.6688	42.6524	44.0445	49.9448	55.9403.	
16	-0.275033	-0.508023	-0.838126		
8	3.428174	-3.110476	-0.481748		

7	0.825694	-2.834037	-0.077933
7	2.301735	-1.084997	-0.65531
6	-0.399752	-3.31354	0.554043
1	-0.698646	-2.578018	1.311527
6	-0.055799	-4.624002	1.268648
1	-0.938752	-5.019159	1.776993
1	0.731187	-4.455178	2.010197
1	0.283797	-5.374579	0.546285
6	1.097468	-1.576233	-0.457264
6	3.419748	-1.87791	-0.472914
6	-1.563821	-3.518819	-0.400302
6	-2.855652	-3.575543	0.132366
1	-2.995793	-3.429727	1.20362
6	-3.956607	-3.823283	-0.685142
1	-4.953648	-3.868699	-0.255057
6	-3.775714	-4.010881	-2.055719
1	-4.63003	-4.199257	-2.699134
6	-2.490847	-3.950646	-2.59373
1	-2.342213	-4.088958	-3.660732
6	-1.390449	-3.708669	-1.770912
1	-0.391477	-3.648523	-2.194639
1	1.657367	-3.422583	-0.009514
6	4.698495	-1.131275	-0.261874
6	4.705477	0.153686	0.283819
6	5.905748	-1.773635	-0.550713
6	5.916816	0.794714	0.535282
1	3.761219	0.627262	0.535941
6	7.113473	-1.122303	-0.322062
1	5.877573	-2.78164	-0.952854
6	7.119818	0.162425	0.22426
1	5.92294	1.787379	0.976614
1	8.050448	-1.616298	-0.561575
1	8.062837	0.667783	0.412177
44	-1.135446	0.373698	1.109347
6	-2.202597	2.196822	0.537511
6	-1.816814	2.326774	1.905964
6	-2.19785	1.365503	2.870405
6	-2.905816	0.228446	2.403108
6	-3.29035	0.096874	1.034021
6	-2.985717	1.106442	0.081317
1	-1.825817	2.913303	-0.185012
1	-1.150926	3.137488	2.185093
1	-3.083137	-0.600182	3.081475
1	-3.744918	-0.832422	0.705941
1	1.874995	1.958487	0.193926
8	2.276509	1.548038	-1.787702

6	2.038751	2.482728	-0.764465
17	0.665116	-0.457371	2.454502
6	0.790316	3.304588	-1.064604
6	0.416673	4.367205	-0.230277
6	0.022099	3.047899	-2.203337
6	-0.681131	5.170712	-0.537226
1	0.998122	4.578975	0.664828
6	-1.079874	3.849516	-2.512352
1	0.313701	2.218347	-2.839812
6	-1.432498	4.918113	-1.687394
1	-0.946002	5.998316	0.115493
1	-1.661307	3.64222	-3.407665
1	-2.281866	5.548215	-1.936193
6	3.261384	3.398483	-0.644788
1	3.394194	3.943353	-1.585003
1	3.162741	4.123265	0.1694
1	4.154288	2.791985	-0.47462
1	2.282678	0.643788	-1.400425
6	-1.71053	1.439802	4.287278
1	-2.488658	1.861368	4.932803
1	-1.446034	0.444881	4.654077
1	-0.818804	2.066797	4.35655
6	-3.324292	1.000721	-1.391245
1	-2.402565	1.249715	-1.936361
6	-4.381931	2.057674	-1.738821
1	-4.038578	3.066797	-1.486718
1	-4.600447	2.030192	-2.811085
1	-5.31504	1.864817	-1.196616
6	-3.771477	-0.396633	-1.81643
1	-3.913166	-0.420593	-2.901211
1	-3.028055	-1.159524	-1.561735
1	-4.729005	-0.670229	-1.355162