Supplementary Information

$NaNO_2$-Activated, Iron-TEMPO Catalyst System for Aerobic Alcohol Oxidation under Mild Conditions

Naiwei Wang, Renhua Liu*, Jiping Chen, Xinmiao Liang*

Dalian Institute of Chemical Physics, the Chinese Academy of Sciences, Dalian, 116023, People's Republic of China

*To whom correspondence should be address.

E-mail: liangxm@dicp.ac.cn; renhua@dicp.ac.cn

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Experimental Section

General. Equipment and Material

Experimental Section

General Equipment and Material GC analysis of determination of conversions and selectivities was performed on a GC-9790. Benzyl alcohol, 1-octanol, 2-octanol, 4-chloro-benzyl, 4-methyl-benzyl alcohol, 2-pyridinyl methanol, cyclohexanol, 3-Methyl-but-2-en-1-ol, dichloromethane, trifluorotoluene were domestic reagent without further purification. TEMPO, methyl phenyl sulfide, α-methyl-benzyl alcohol, and 2-thionyl methanol are purchased from Acros directly used for oxidation without further purification.

General procedure of TEMPO-catalyzed aerobic oxidation under air: The oxidation of alcohols was carried out under air in a 50ml three-necked round-bottom flask equipped a magnetic stirrer. Typically, the alcohol (10.0mmol) and TEMPO (0.5mmol) were dissolved in 10ml trifluorotoluene. $FeCl_3 \cdot 6H_2O$(0.5mmol) was added followed by $NaNO_2$(0.5mmol). The resulting mixture was stirred at room temperature and ambient pressure. The conversion and selectivity of the reaction was detected by GC without any purification.

General procedure of TEMPO-catalyzed aerobic oxidation under oxygen: All experiments were carried out in a closed Teflon-lined 316L stainless steel autoclave (300 mL), the initial atmospheric air in the autoclave did not exchange for all oxidations. To a Teflon-lines 316L stainless steel autoclave (300 mL), added 10.00 mL of CH_2Cl_2, 135.2mg of $FeCl_3 \cdot 6H_2O$ (0.5mmol), 15.6 mg of TEMPO (0.1 mmol), 34.5mg of $NaNO_2$ (0.5 mmol) and 10.0 mmol of alcohol substrate. Then closed the autoclave and charged oxygen to 0.1MPa. Put the autoclave into the oil bath, which was preheated to 80℃. A heating period of autoclave to desired temperature was excluded. After the reaction complete, cooled to room temperature and carefully depressurized the autoclave. Diluted the sample with CH_2Cl_2 and detected the conversion and selectivity by GC without any purification. the liquid in the autoclave was transferred into a separation funnel, carefully washed the autoclave with CH_2Cl_2, combined all organic solutions. The organic mixture was washed with aqueous $Na_2S_2O_3$ to remove the residual oxidants and TEMPO. The organic layer was dried over anhydrous Na_2SO_4, concentrated to dryness. The yield was calculated based on 10.0 mmol of substrate.

General GC conditions: HP-5 column, 30m x 0.32mm (id); FID detector, 250 ^{o}C; injection: 250 ^{o}C; carrier gas: nitrogen; carrier gas rate: 0.8 mL / min; area normalization. The products were detected under a condition as: column temperature: 40℃ for 10 minutes, raising to 250℃in a rate of 10℃/ min. TEMPO and solvent were also detected under this condition, and their corresponding peak areas were deleted in the GC diagrams.

Table 1 $FeCl_3$-catalysed oxidation of Octan-2-ol to 2-Octanone

Entry	$FeCl_3$	TEMPO	$NaNO_2$	Conversion(%)
1	No	Yes	Yes	trace
2	Yes	No	Yes	trace.
3	Yes	Yes	No	1.7
4	Yes	Yes	Yes	45.3

Reaction conditions: alcohol (10 mmol), CH_3CN (10 mL), 80℃(oil bath temperature), $FeCl_3·6H_2O$(0.5mmol), TEMPO (0.5 mmol), $NaNO_2$ (0.5 mmol), 0.1 MPa oxygen pressure, 1h.

$FeCl_2$-catalysed oxidation of Octan-2-ol to 2-Octanone

Reaction conditions: alcohol (10 mmol), CH_3CN (10 mL), 80℃(oil bath temperature), $FeCl_2$ (0.5mmol), TEMPO (0.5 mmol), $NaNO_2$ (0.8 mmol), 0.1 MPa oxygen pressure.

$CuCl_2$-catalysed oxidation of Octan-2-ol to 2-Octanone

Reaction conditions: alcohol (10 mmol), CH_3CN (10 mL), 80℃(oil bath temperature), $CuCl_2$ (0.5mmol), TEMPO (0.5 mmol), $NaNO_2$ (0.8 mmol), 0.1 MPa oxygen pressure

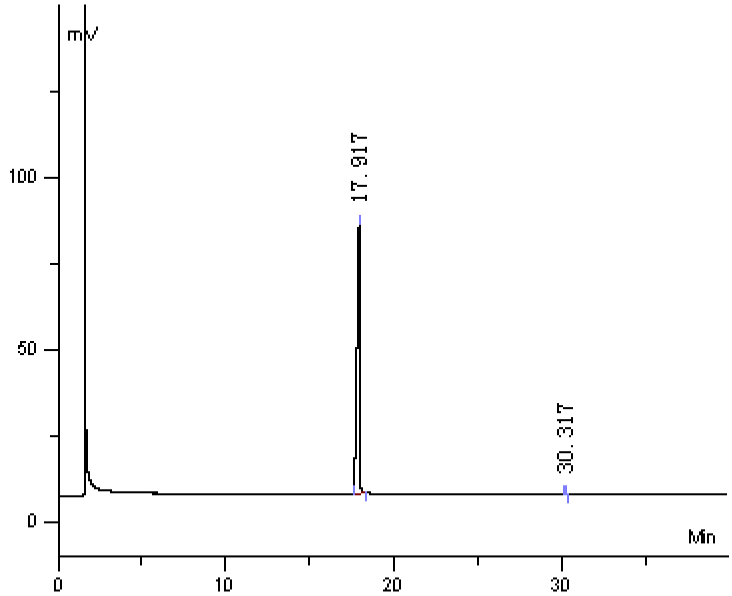
Table 2. Catalytic Aerobic Alcohols Oxidation under oxygen[a]

Entry	Substrate	Method	Time (h)	Conv[b] (%)	Yield (%)[c]
1	Benzyl alcohol	A	1	100	95
		B	6	100	-
		B[d]	8	100	-
2	1-Phenyl ethanol	A	1	100	96
3	4-Chloro-Benzyl alcohol	A	1	100	96
4	4-Methyl-Benzyl alcohol	A	1	100	95
5	Cinnamyl alcohol	B	6	100	97
6	3-Methyl-but-2-en-1-ol	B	6	100	83
7	2-pyridinal alcohol	B[e]	6	100	89
8	Cyclohexanol	B	6	100	91
9	2-Thiophenemethol	B	6	100	92
10	PhCHO + $PhSCH_3$	B	8	100	—
11	2- Octanol	C	6	100	89
12	1- Octan-ol	C	6	100[f]	—

[a]Reaction conditions: alcohol (10 mmol), $FeCl_3·6H_2O$ (0.5 mmol), CH_2Cl_2 (10 mL), 80℃ (oil bath temperature). Method A: TEMPO (0.1 mmol), $NaNO_2$ (0.5 mmol), 0.1 MPa oxygen pressure; Method B: TEMPO (0.2 mmol), $NaNO_2$ (0.5 mmol), 0.2 MPa oxygen pressure, room temperature; Method C: TEMPO (0.5 mmol), $NaNO_2$ (0.8 mmol), 0.1 MPa oxygen pressur, CH_3CN(10ml). [b]Conversions and selectivities are based on the gas chromatography (GC) with area normalization [c].Selectivities >99%(GC). All yields are for pure, isolated products. [d] a balloon filled with oxygen instead of 0.1Mpa oxygen pressure. [e] 1mL CH_3COOH was added. [f]Selectivity 71.0 , acid (22.7) and ester (6.3) was formed.

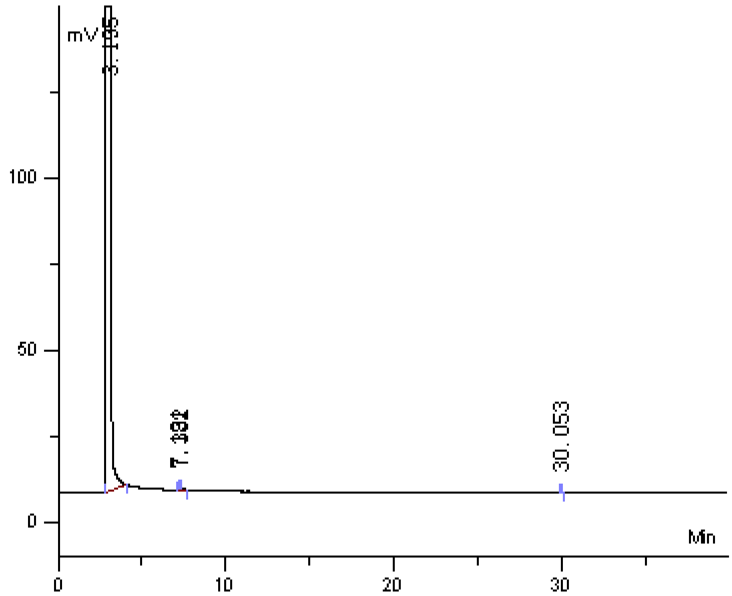
Figure List

Figure 1: GC diagram of TEMPO



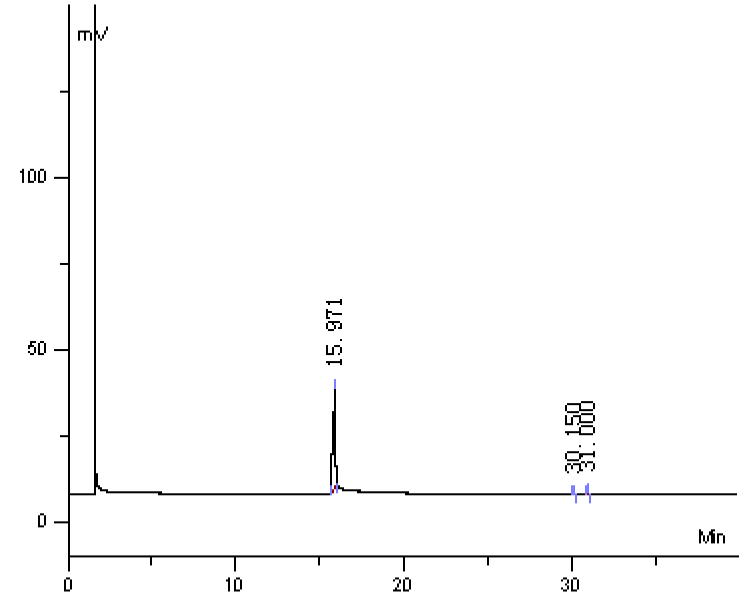
Peak	RetTime (min)	Height	Area	Area %
1	17.917	78399.2	1462145.4	99.6774
2	30.317	411.0	4732.7	0.3226
Totals:		78810.2	1466878.0	100.0000

Figure 2: GC diagram of trifluorotoluene



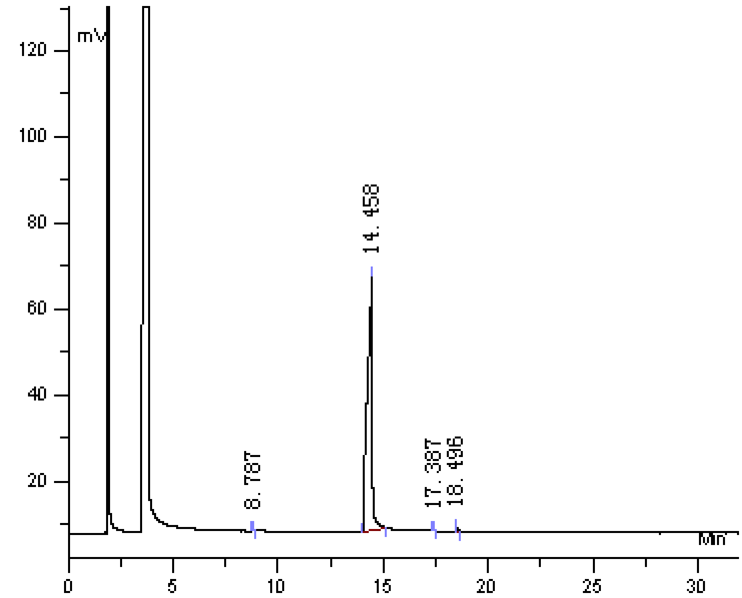
Peak	RetTime (min)	Height	Area	Area %
1	3.195	686976.1	19042465.4	99.8701
2	7.191	698.3	8948.4	0.0469
3	7.382	549.3	11641.9	0.0611
4	30.053	328.9	4172.9	0.0219
Totals:		688552.6	19067228.5	100.0000

Figure 3: GC diagram of benzyl alcohol



Peak	RetTime (min)	Height	Area	Area %
1	15.971	29109.1	638903.2	99.5150
2	30.150	88.5	1035.5	0.1613
3	31.000	90.8	2078.2	0.3237
Totals:		29288.4	642016.9	100.0000

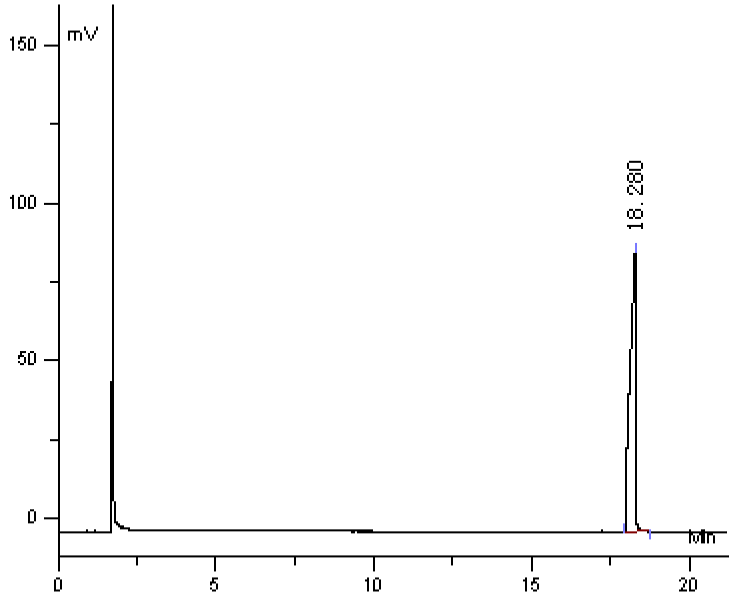
Figure 4: GC diagram of oxidation of benzyl alcohol under air



Peak	RetTime (min)	Height	Area	Area %
1	8.787	209.3	2153.1	0.1092
2	14.458	59182.3	1962195.0	99.5072
3	17.387	86.1	481.2	0.0244
4	18.496	957.8	7082.8	0.3592

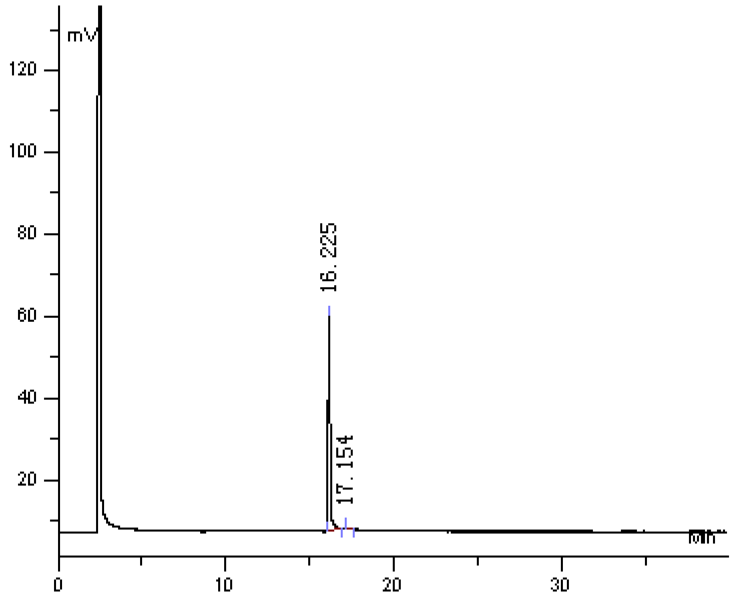
Totals: 60435.4 1971912.1 100.0000

Figure 5: GC diagram of 4-methyl-benzyl alcohol



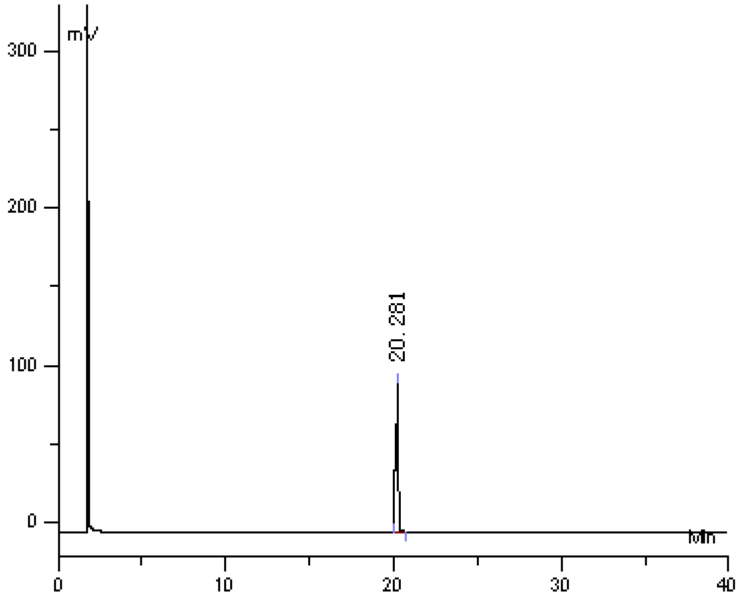
Peak	RetTime (min)	Height	Area	Area %
1	18.280	88933.3	2114593.0	100.0000
Totals:		88933.3	2114593.0	100.0000

Figure 6: GC diagram of oxidation of 4-methyl-benzyl alcohol under air



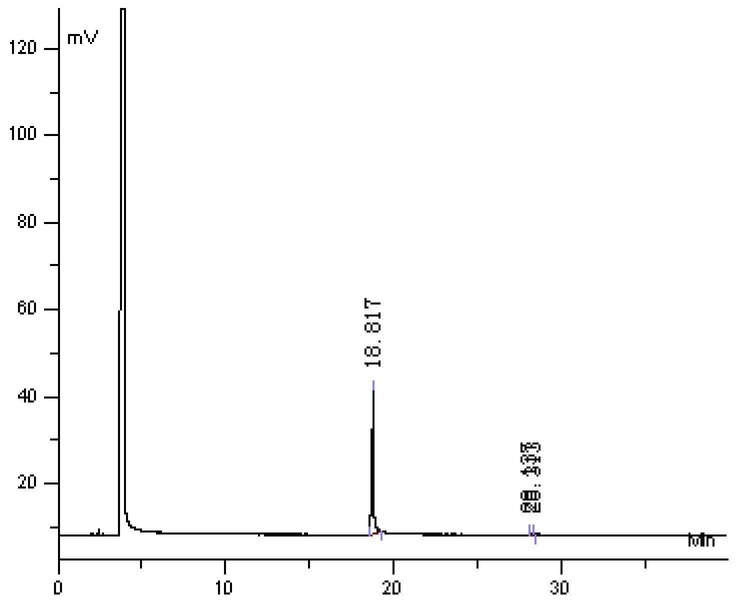
Peak	RetTime (min)	Height	Area	Area %
1	16.225	52860.0	957276.5	99.6861
2	17.154	490.9	3014.7	0.3139
Totals:		53350.9	960291.2	100.0000

Figure 7: GC diagram of 4-chloro-benzyl alcohol



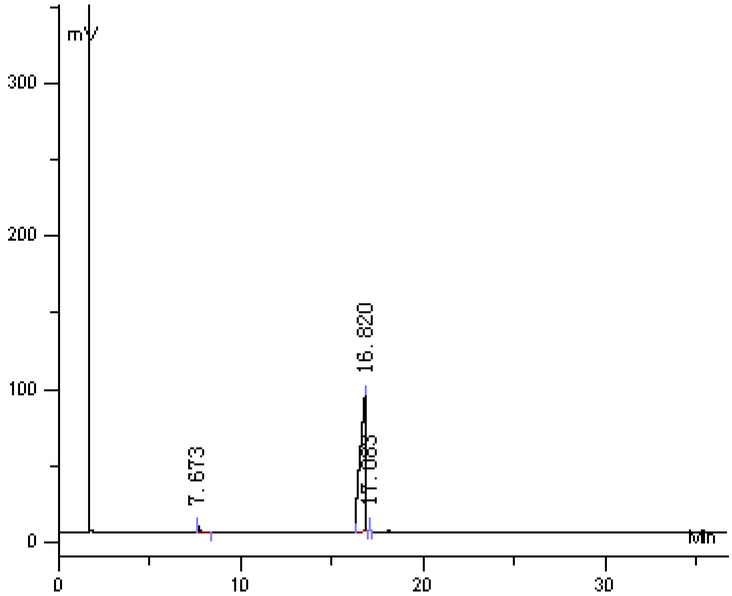
Peak	RetTime (min)	Height	Area	Area %
1	20.281	94926.8	2296819.5	100.0000
Totals:		94926.8	2296819.5	100.0000

Figure 8: GC diagram of oxidation of 4-chloro-benzyl alcohol under air



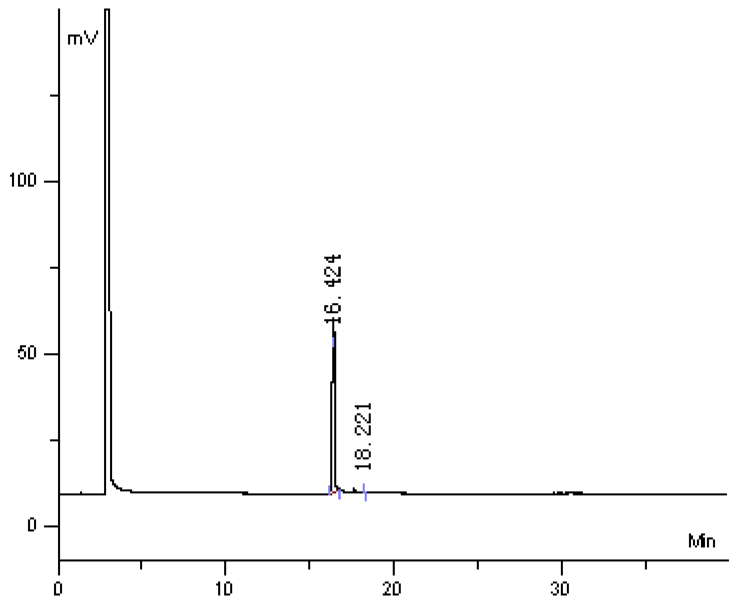
Peak	RetTime (min)	Height	Area	Area %
1	18.817	33424.9	587547.9	99.4285
2	28.137	141.8	1993.8	0.3374
3	28.313	117.3	1383.1	0.2341
Totals:		33684.1	590924.8	100.0000

Figure 9: GC diagram of α-methyl-benzyl alcohol



Peak	RetTime (min)	Height	Area	Area %
1	7.673	3955.7	47969.8	1.3389
2	16.820	89435.7	3522544.0	98.3169
3	17.083	2532.3	12332.3	0.3442
Totals:		95923.7	3582846.1	100.0000

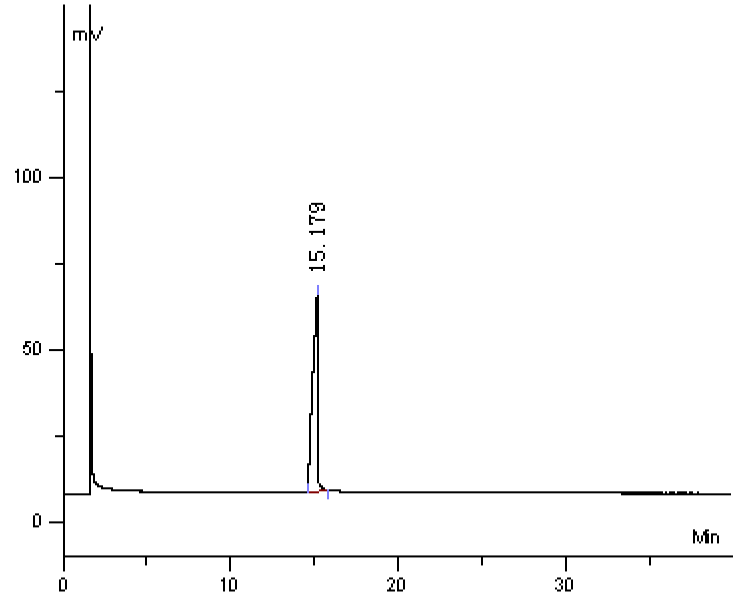
Figure 10: GC diagram of oxidation of α-methyl-benzyl alcohol under air



Peak	RetTime (min)	Height	rea	Area %
1	16.424	42149.5	978842.8	99.9459
2	18.221	53.2	529.7	0.0541

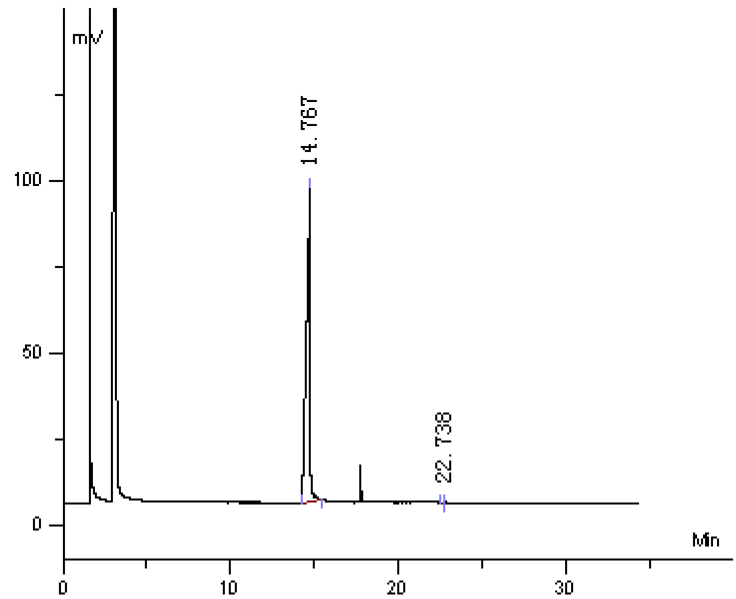
Totals:		42202.6	979372.5	100.0000

Figure 11: GC diagram of 2-octanol



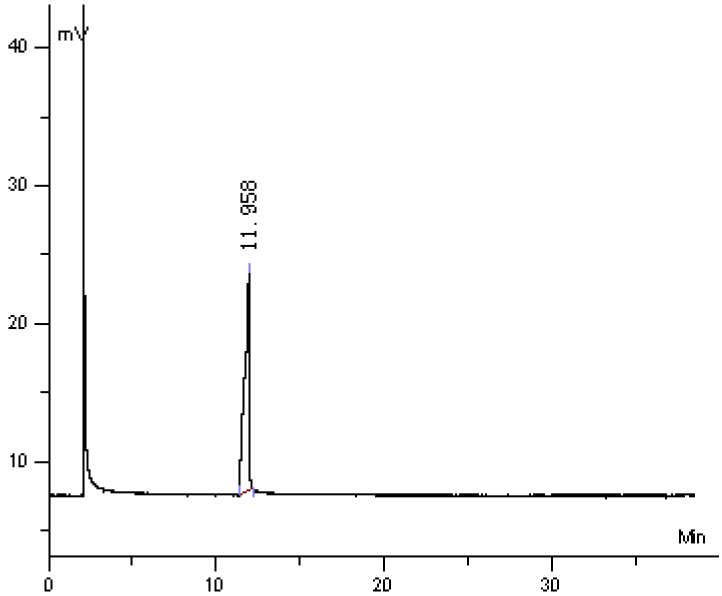
Peak	RetTime (min)	Height	Area	Area %
1	15.179	57507.8	2244776.8	100.0000
Totals:		57507.8	2244776.8	100.0000

Figure 12: GC diagram of oxidation of 2-octanol under air



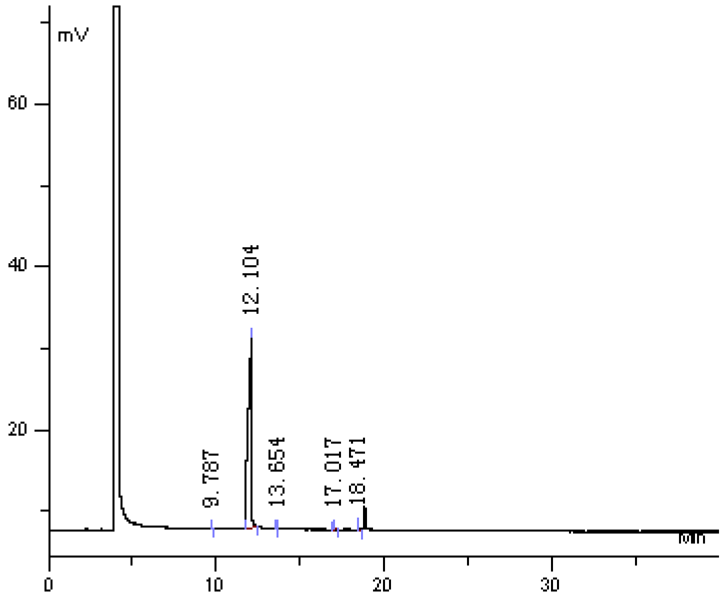
Peak	RetTime (min)	Height	Area	Area %
1	14.767	91639.6	2859365.0	99.8462
2	22.738	120.6	4405.6	0.1538
Totals:		91760.1	2863770.6	100.0000

Figure 13: GC diagram of cyclohexanol



Peak	RetTime (min)	Height	Area	Area %
1	11.958	15812.7	559039.7	100.0000
Totals:		15812.7	559039.7	100.0000

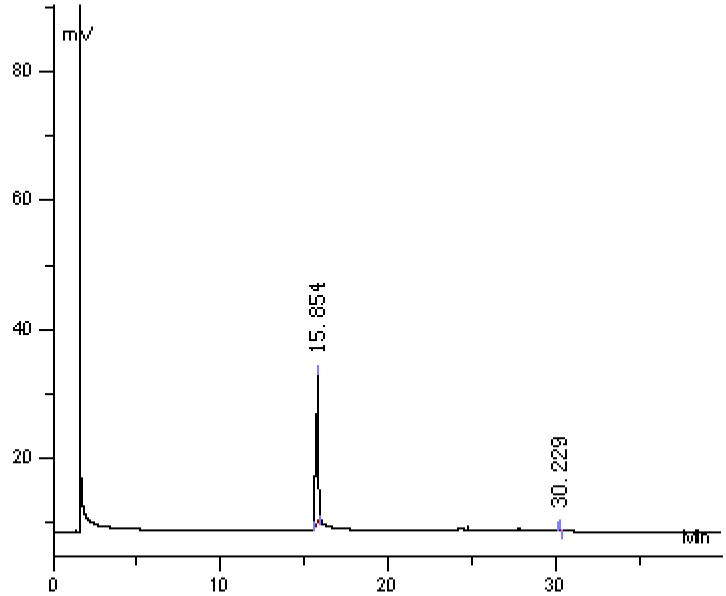
Figure 14: GC diagram of oxidation of cyclohexanol under air



Peak	RetTime (min)	Height	Area	Area %
1	9.787	31.4	441.9	0.0658
2	12.104	23464.2	666131.4	99.1930
3	13.654	25.0	584.0	0.0870
4	17.017	80.1	1452.2	0.2162
5	18.471	311.8	2941.3	0.4380

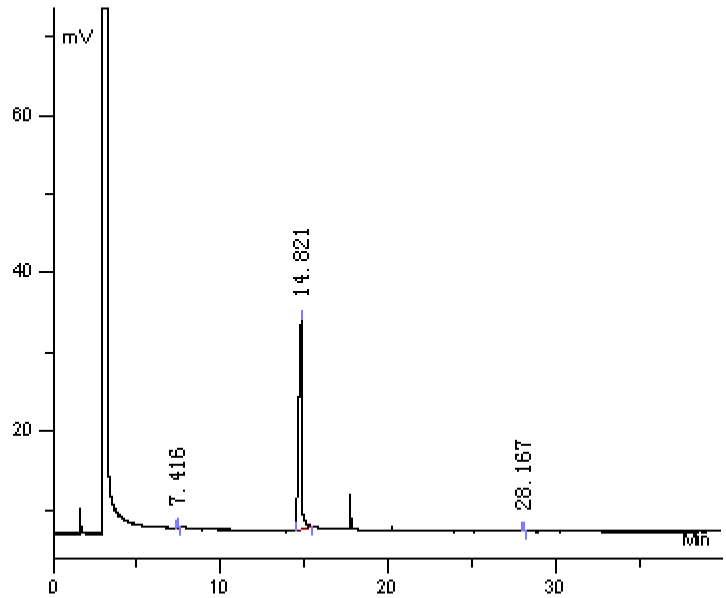
Totals:		23912.6	671550.8	100.0000

Figure 15: GC diagram of 2-thiophene methanol.



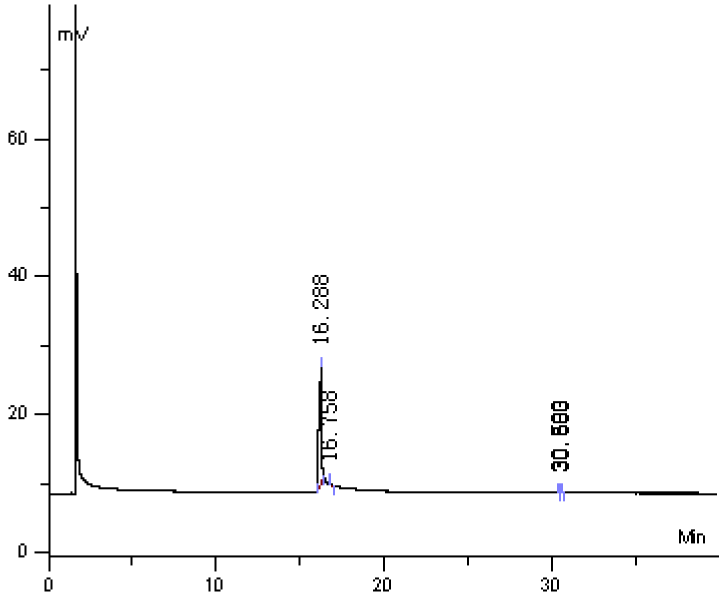
Peak	RetTime (min)	Height	Area	Area %
1	15.854	22643.1	490041.6	98.7863
2	30.229	489.6	6020.5	1.2137
Totals:		23132.7	496062.1	100.0000

Figure 16: GC diagram of oxidation of 2-thiophene methanol under air



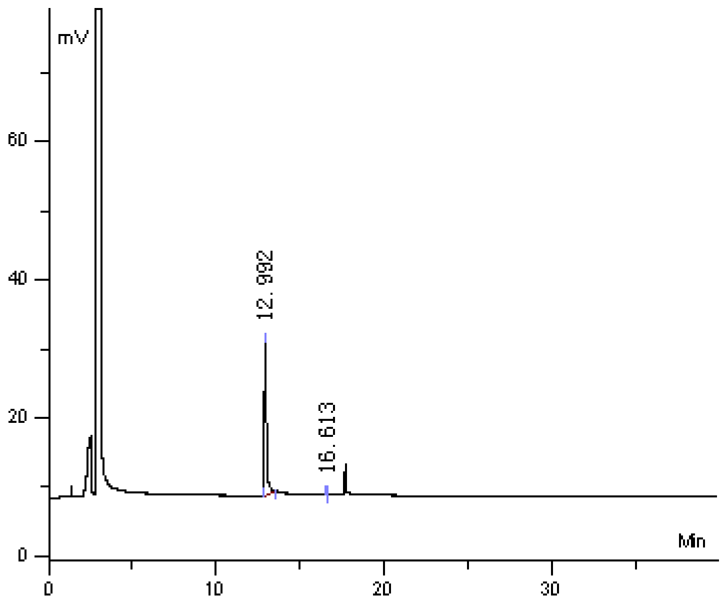
Peak	RetTime (min)	Height	Area	Area %
1	7.416	153.3	3110.8	0.4822
2	14.821	26785.8	639924.6	99.1982
3	28.167	46.2	2061.3	0.3195
Totals:		26985.3	645096.7	100.0000

Figure 17: GC diagram of 2-pyridinal alcohol



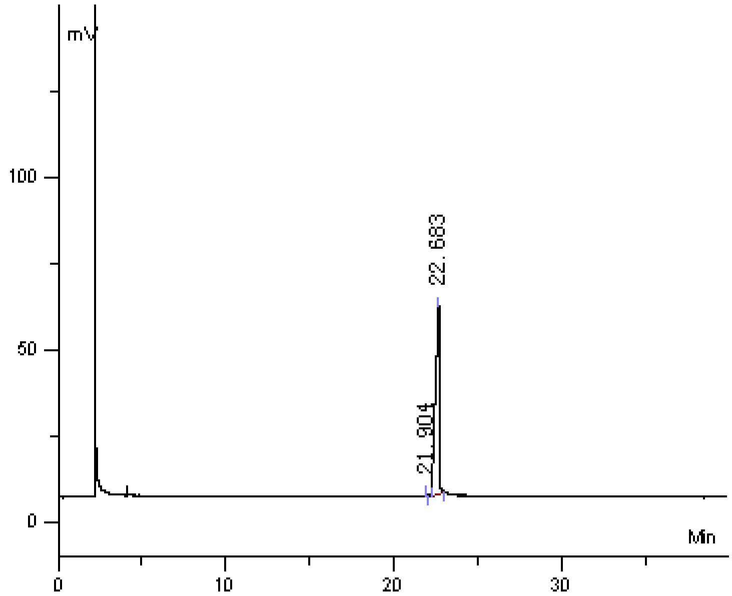
Peak	RetTime (min)	Height	Area	Area %
1	16.288	16751.0	361018.7	99.0891
2	16.758	417.6	2594.6	0.7121
3	30.500	66.9	724.2	0.1988
Totals:		17235.6	364337.5	100.0000

Figure 18: GC diagram of oxidation of 2-pyridinal alcohol under air



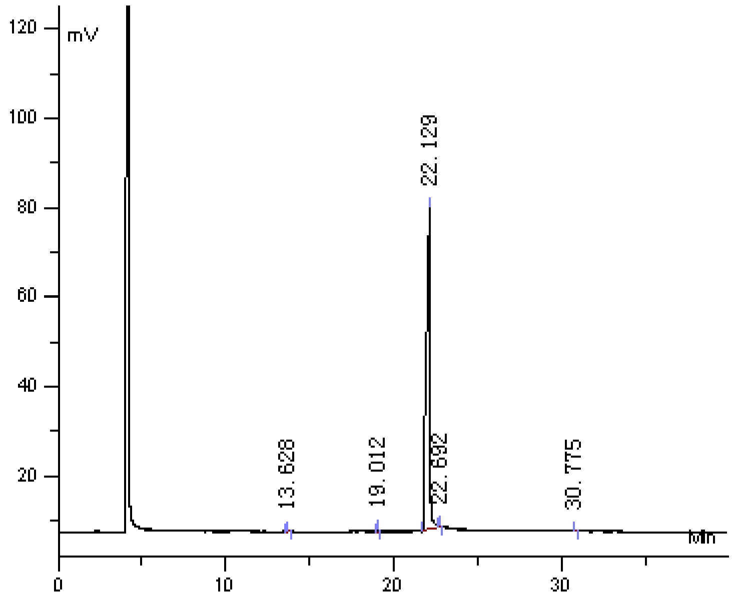
Peak	RetTime (min)	Height	Area	Area %
1	12.992	22105.1	445286.6	99.8499
2	16.613	97.5	669.4	0.1501
Totals:		22202.6	445956.0	100.0000

Figure 19: GC diagram of Cinnamyl alcohol



Peak	RetTime (min)	Height	Area	Area %
1	21.904	419.2	4467.2	0.2814
2	22.683	54469.7	1583284.9	99.7186
Totals:		54888.9	1587752.1	100.0000

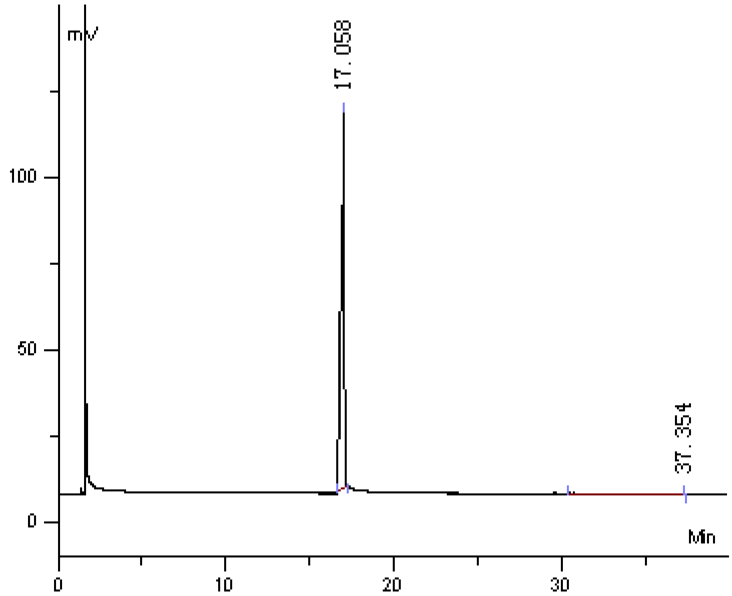
Figure 20: GC diagram of oxidation of Cinnamyl alcohol under air



Peak	RetTime (min)	Height	Area	Area %
1	13.628	448.2	6921.4	0.3292
2	19.012	857.8	5780.7	0.2749
3	22.129	72209.9	2084876.4	99.1490
4	22.692	275.7	3160.1	0.1503
5	30.775	229.9	2032.9	0.0967

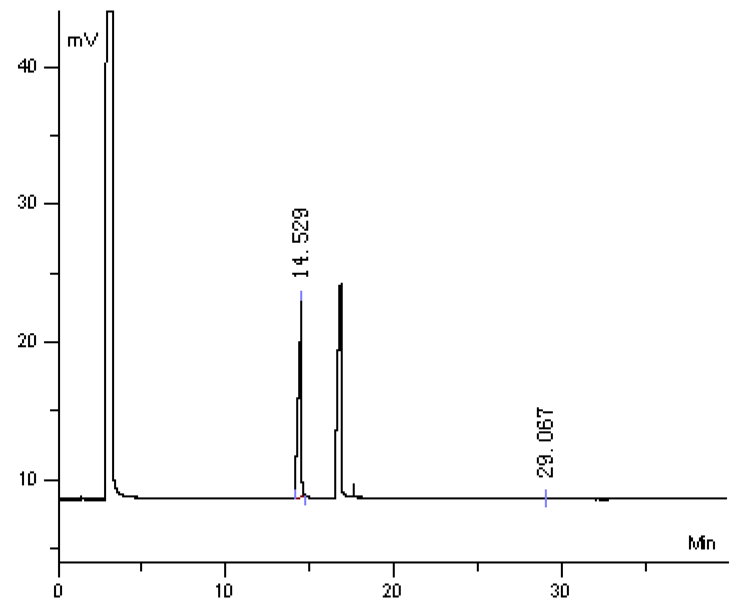
Totals:		74021.5	2102771.5	100.0000

Figure 21: GC diagram of methyl phenyl sulfide



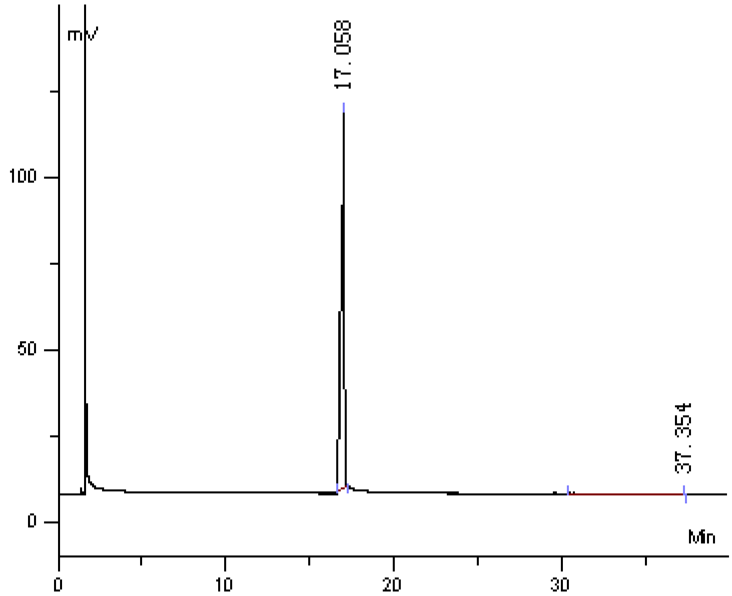
Peak	RetTime (min)	Height	Area	Area %
1	17.058	109178.2	2888454.0	100.0000
Totals:		109178.2	2888454.0	100.0000

Figure 22: GC diagram of oxidation of 2-octanol and methyl phenyl sulfide under air (Methyl phenyl sulfide corresponding peak areas was deleted in the GC diagrams)



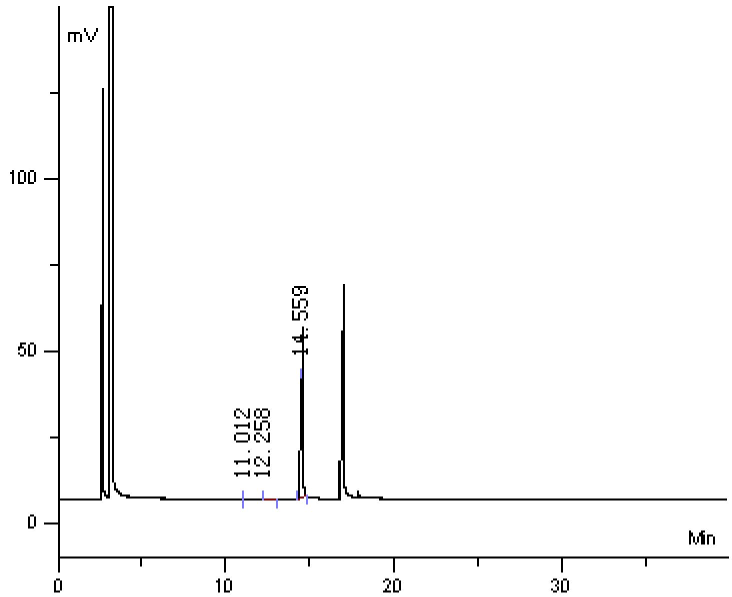
Peak	RetTime (min)	Height	Area	Area %
1	14.529	14257.1	380889.9	99.9408
2	29.067	33.7	225.6	0.0592
Totals:		14290.8	381115.5	100.0000

Figure 23: GC diagram of methyl phenyl sulfide



Peak	RetTime (min)	Height	Area	Area %
1	17.058	109178.2	2888454.0	100.0000
Totals:		109178.2	2888454.0	100.0000

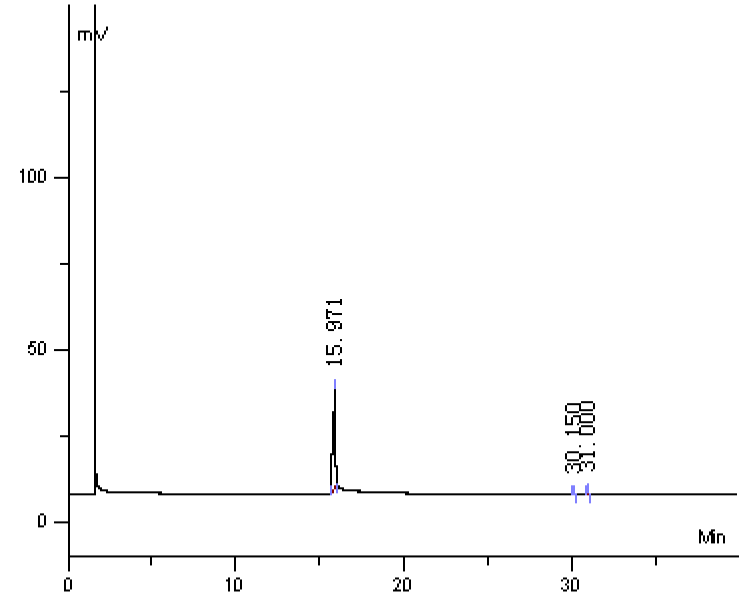
Figure 24: GC diagram of oxidation of benzyl alcohol and methyl phenyl sulfide under air (Methyl phenyl sulfide corresponding peak areas was deleted in the GC diagrams)



Peak	RetTime (min)	Height	Area	Area %
1	11.012	103.4	462.9	0.0496
2	12.258	159.3	5378.5	0.5765
3	14.559	34888.0	927159.2	99.3739

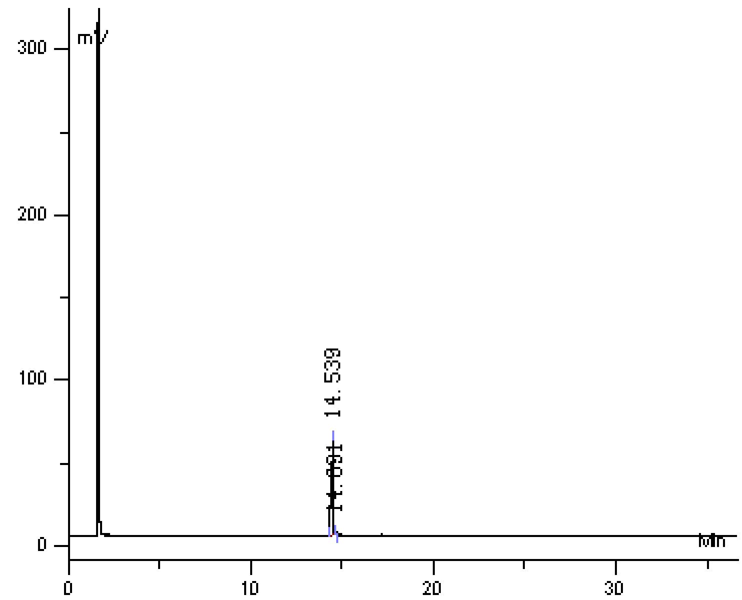
Totals:		35150.7	933000.6	100.0000

Figure 25: GC diagram of benzyl alcohol



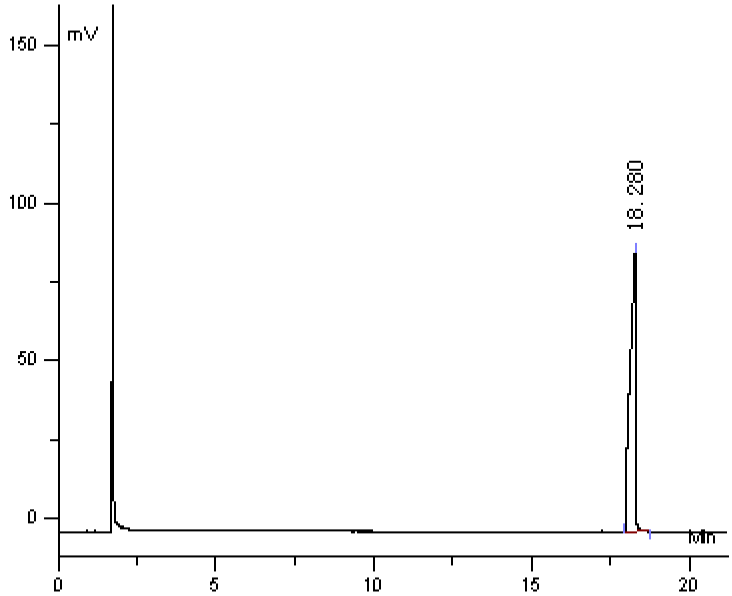
Peak	RetTime (min)	Height	Area	Area %
1	15.971	29109.1	638903.2	99.5150
2	30.150	88.5	1035.5	0.1613
3	31.000	90.8	2078.2	0.3237
Totals:		29288.4	642016.9	100.0000

Figure 26: GC diagram of oxidation of benzyl alcohol under oxygen



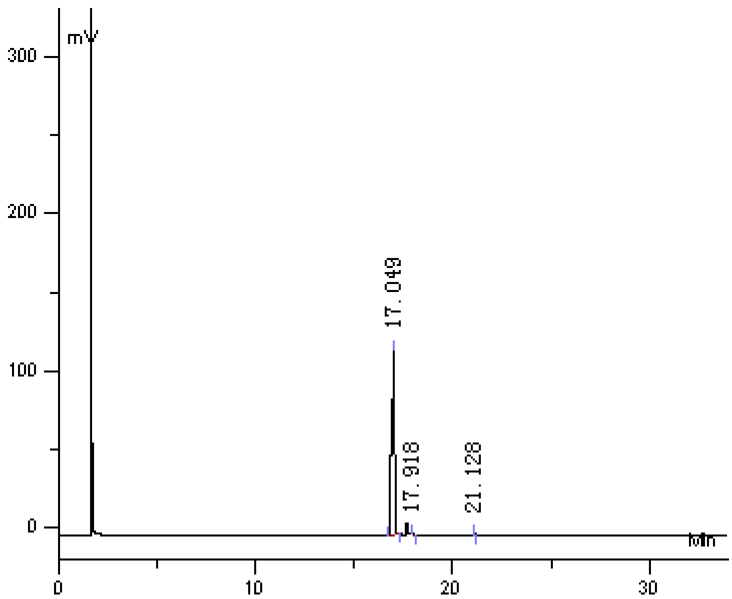
Peak	RetTime (min)	Height	Area	Area %
1	14.539	58124.4	969553.5	99.2197
2	14.691	161.0	7624.8	0.7803
Totals:		58285.4	977178.3	100.0000

Figure 27: GC diagram of 4-methyl-benzyl alcohol



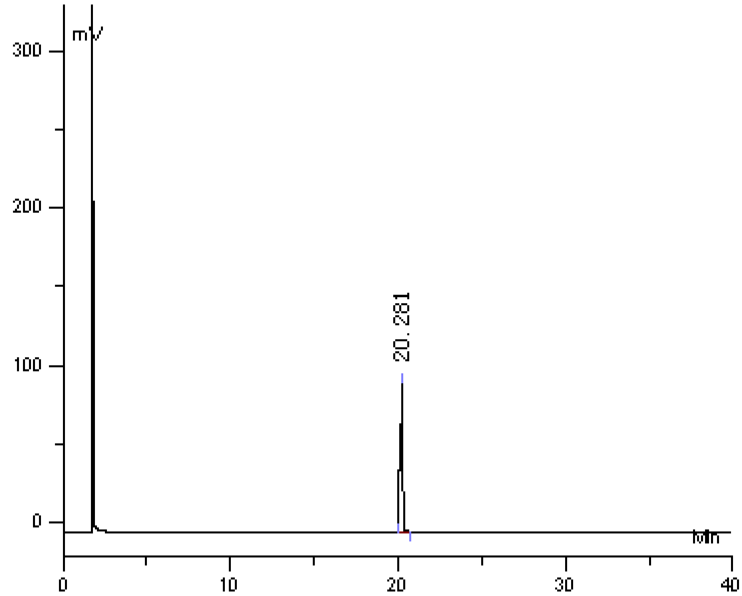
Peak	RetTime (min)	Height	Area	Area %
1	18.280	88933.3	2114593.0	100.0000
Totals:		88933.3	2114593.0	100.0000

Figure 28: GC diagram of oxidation of 4-methyl-benzyl alcohol under oxygen



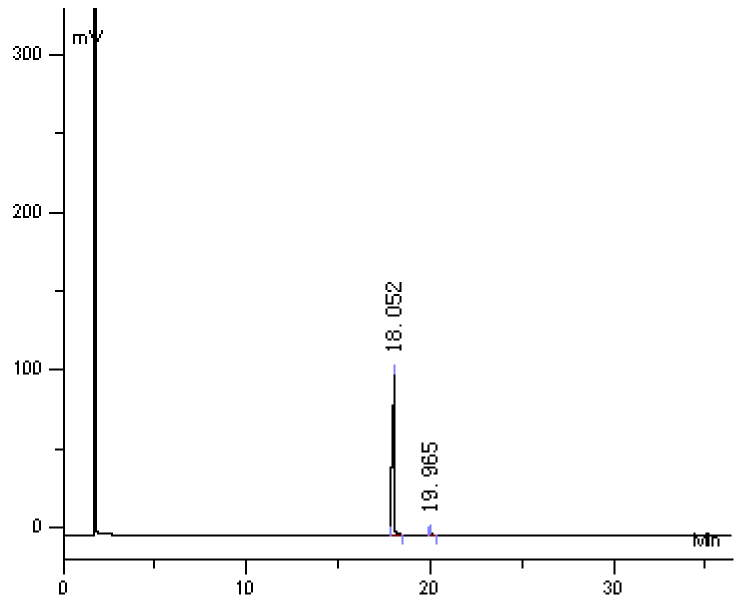
Peak	RetTime (min)	Height	Area	Area %
1	17.049	117659.4	2501797.2	99.7794
2	17.918	699.9	3624.2	0.1445
3	21.128	297.5	1906.7	0.0760
Totals:		118656.8	2507328.1	100.0000

Figure 29: GC diagram of 4-chloro-benzyl alcohol



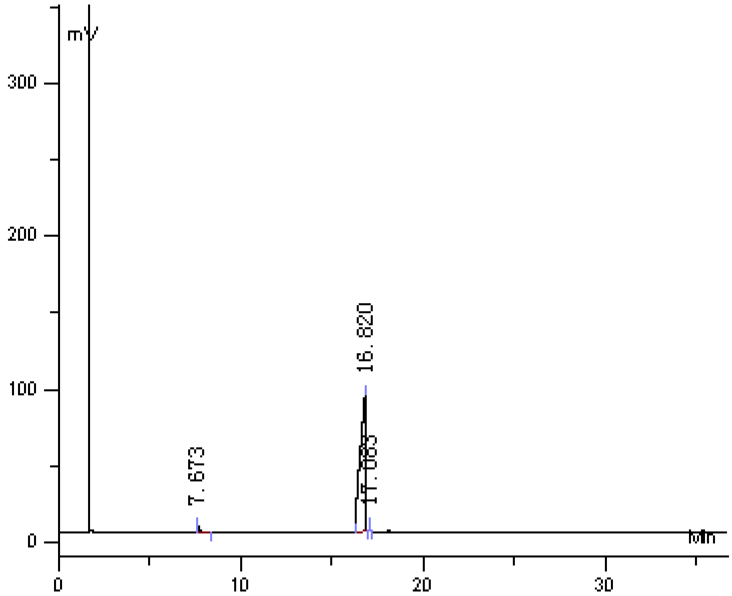
Peak	RetTime (min)	Height	Area	Area %
1	20.281	94926.8	2296819.5	100.0000
Totals:		94926.8	2296819.5	100.0000

Figure 30: GC diagram of oxidation of 4-chloro-benzyl alcohol under oxygen



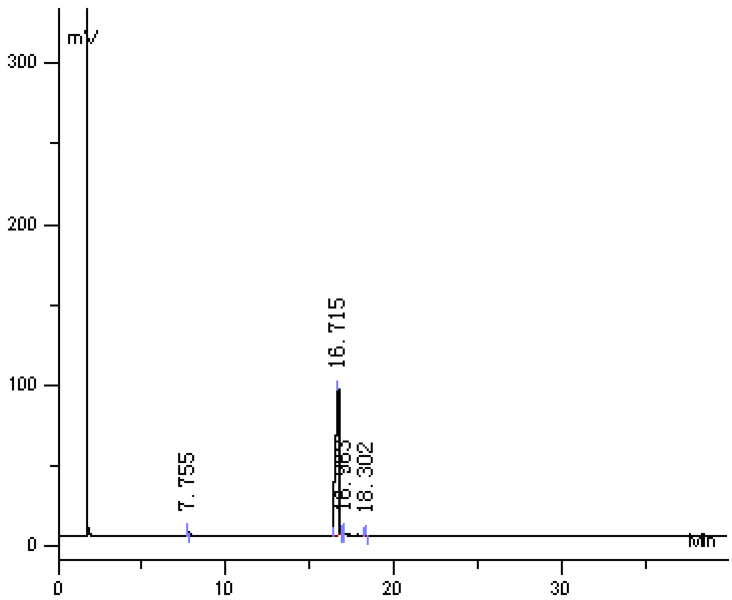
Peak		RetTime (min)	Height	Area	Area %
1		18.052	102131.0	1836093.0	99.1387
2	2	19.965	1418.1	15951.1	0.8613
Totals:			103549.0	1852044.1	100.0000

Figure 31: GC diagram of α-methyl-benzyl alcohol



Peak	RetTime (min)	Height	Area	Area %
1	7.673	3955.7	47969.8	1.3389
2	16.820	89435.7	3522544.0	98.3169
3	17.083	2532.3	12332.3	0.3442
Totals:		95923.7	3582846.1	100.0000

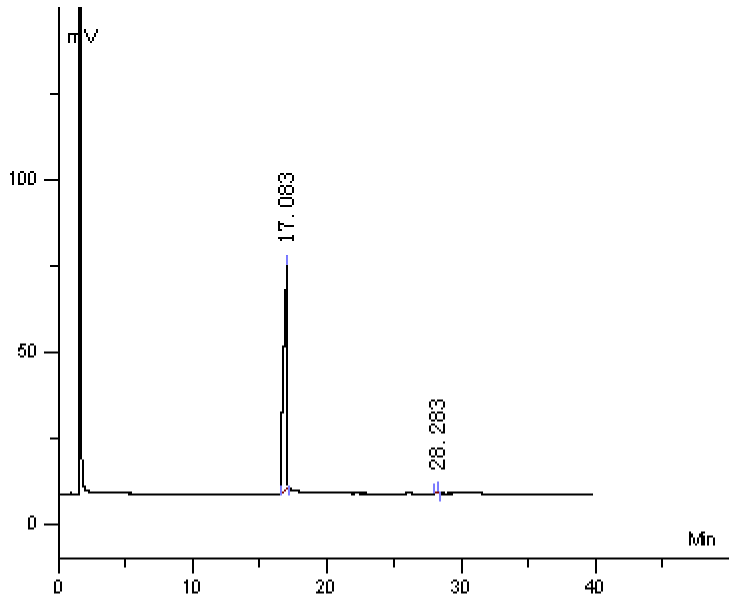
Figure 32: GC diagram of oxidation of α-methyl-benzyl alcohol under oxygen



Peak	RetTime (min)	Height	Area	Area %
1	7.755	2243.6	15661.5	0.7074
2	16.715	90070.5	2189509.4	98.8893
3	16.963	929.5	5321.3	0.2403
4	18.302	451.6	3609.2	0.1630

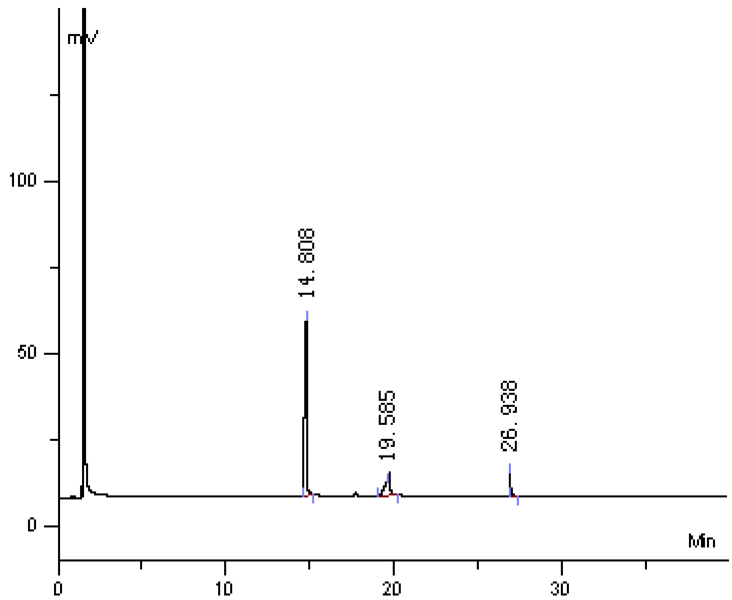
Totals:		93695.1	2214101.4	100.0000

Figure 33: GC diagram of 1-octanol



Peak	RetTime (min)	Height	Area	Area %
1	17.083	65361.0	2259306.6	99.3671
2	28.283	658.4	14389.7	0.6329
Totals:		66019.3	2273696.2	100.0000

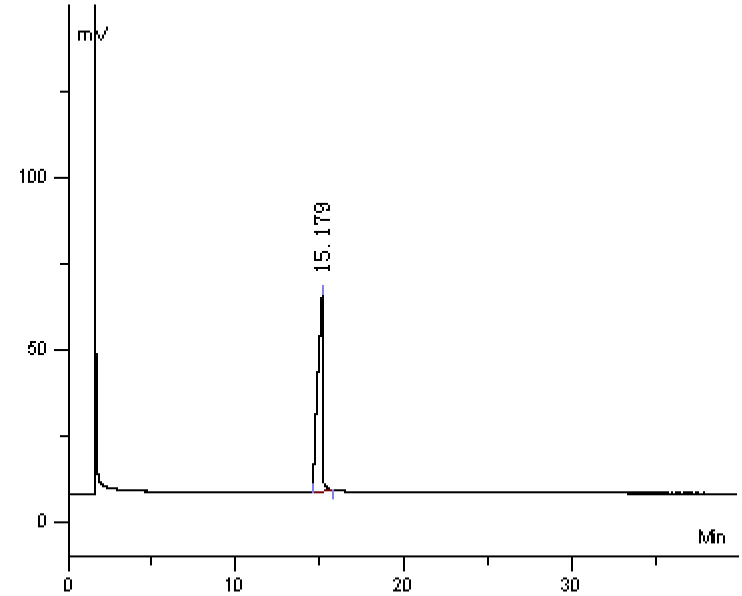
Figure 34: GC diagram of oxidation of 1-octanol under oxygen



Peak	RetTime (min)	Height	Area	Area %
1	14.808	50925.6	813888.1	70.9515
2	19.585	4154.0	261313.9	22.7803
3	26.938	7341.9	71902.5	6.2682

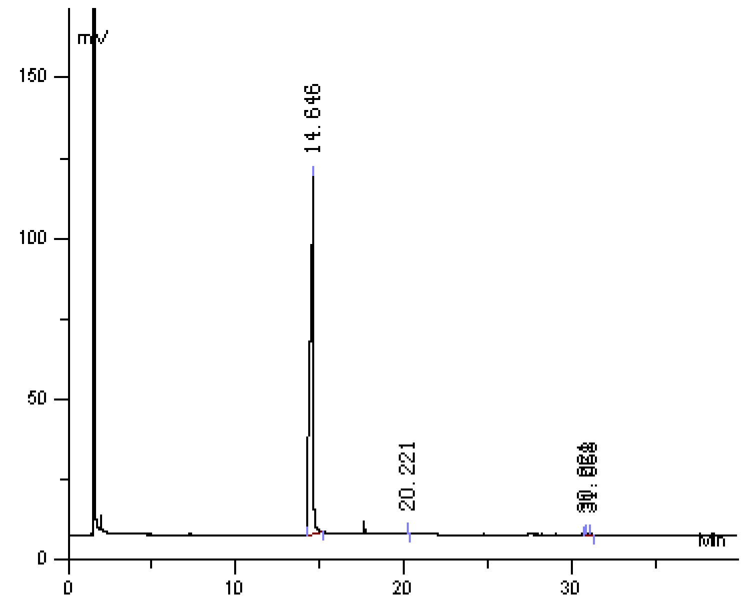
Totals:		62421.5	1147104.5	100.0000

Figure 35: GC diagram of 2-octanol



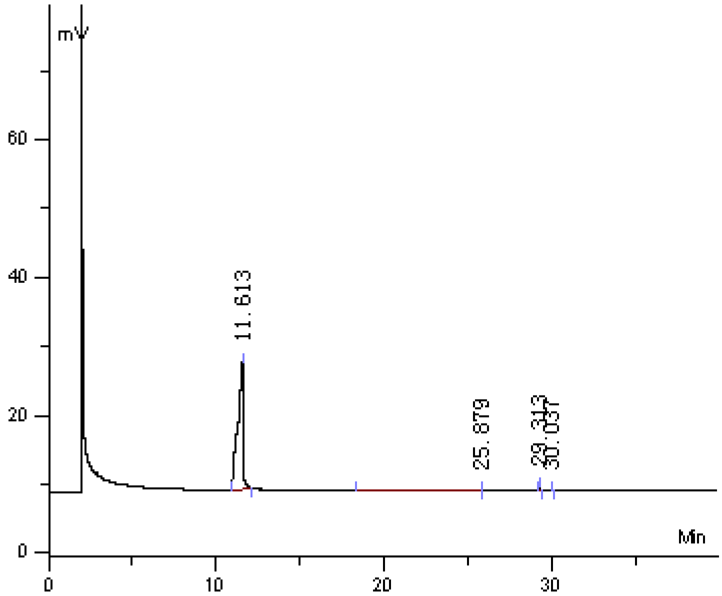
Peak	RetTime (min)	Height	Area	Area %
1	15.179	57507.8	2244776.8	100.0000
Totals:		57507.8	2244776.8	100.0000

Figure 34: GC diagram of oxidation of 2-octanol under oxygen



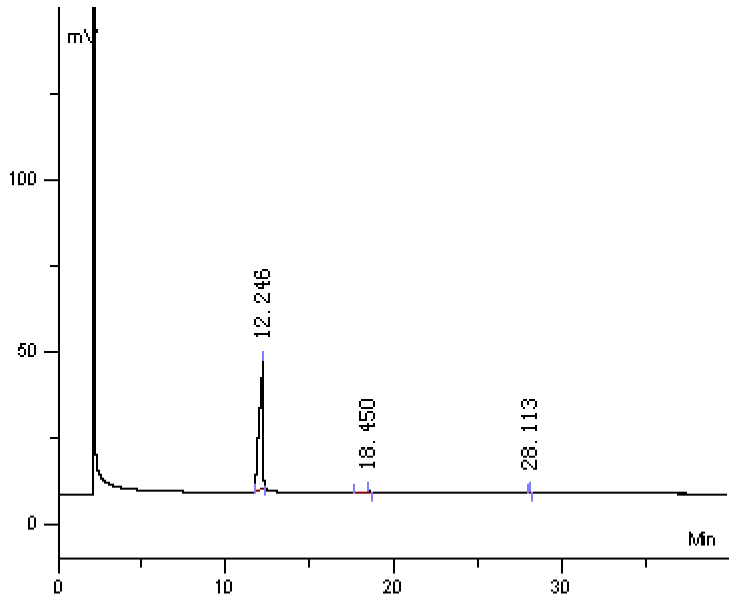
Peak	RetTime (min)	Height	Area	Area %
1	14.646	111835.7	3173912.5	99.1180
2	20.221	1152.6	9784.0	0.3055
3	30.921	382.7	4701.9	0.1468
4	31.058	671.8	13757.7	0.4296
Totals:		114042.8	3202156.1	100.0000

Figure 37: GC diagram of cyclohexanol



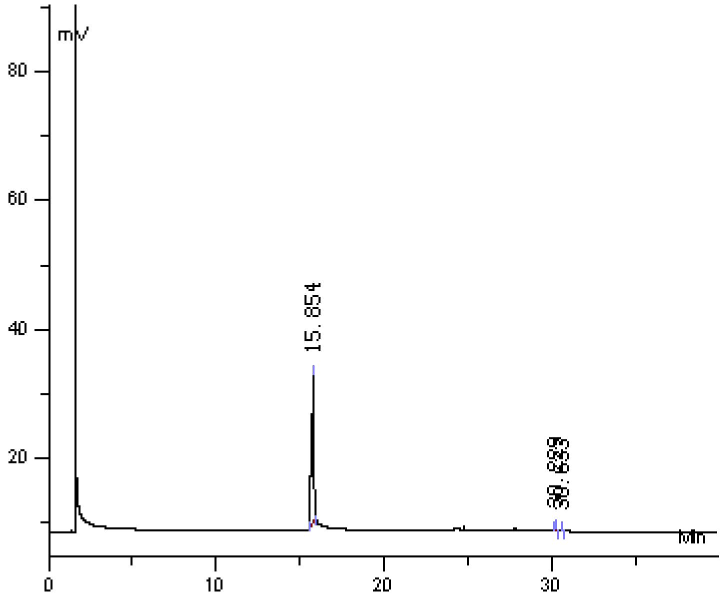
Peak	RetTime (min)	Height	Area	Area %
1	11.613	18483.9	830036.6	99.1934
2	25.879	12.8	1446.8	0.1729
3	29.313	453.0	4811.4	0.5750
4	30.037	91.0	491.1	0.0587
Totals:		19040.7	836785.9	100.0000

Figure 38: GC diagram of oxidation of cyclohexanol under oxygen



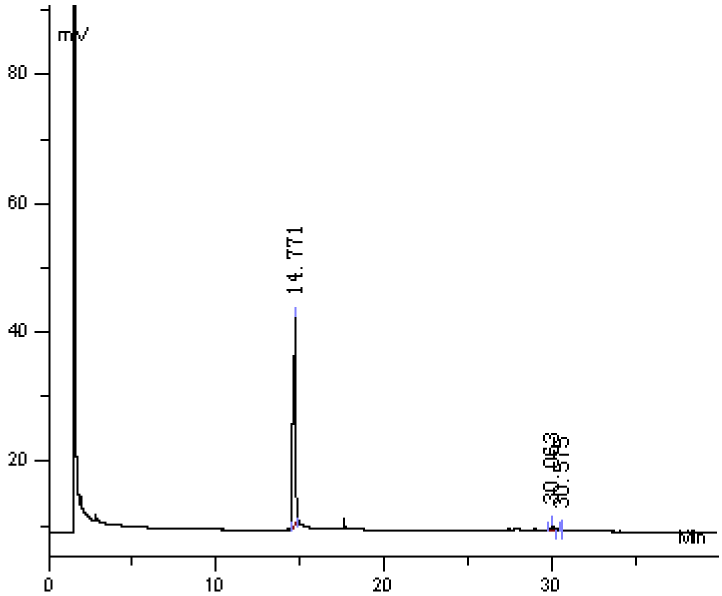
Peak	RetTime (min)	Height	Area	Area %
1	12.246	36841.6	1197839.3	99.2568
2	18.450	627.8	4783.5	0.3964
3	28.113	329.3	4185.6	0.3468
Totals:		37798.7	1206808.4	100.0000

Figure 39: GC diagram of 2-thiophene methanol.



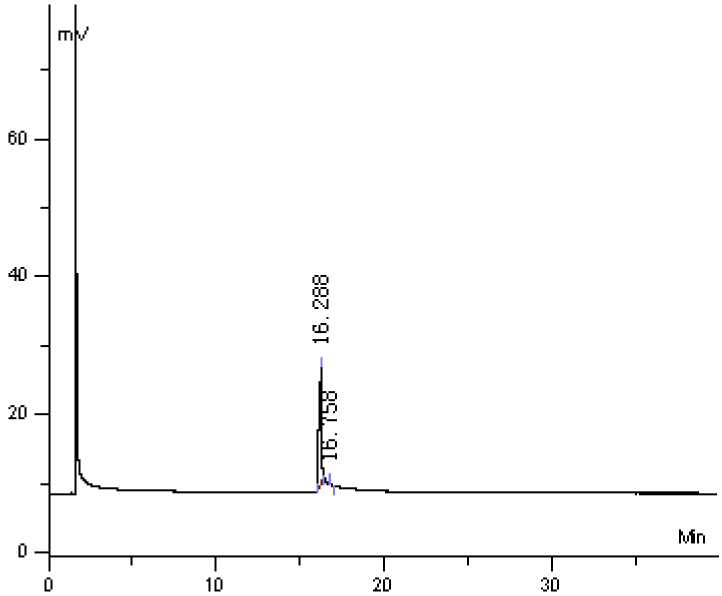
Peak	RetTime (min)	Height	Area	Area %
1	15.854	22643.1	490041.6	98.6334
2	30.229	489.6	6020.5	1.2118
3	30.633	131.1	769.2	0.1548
Totals:		23263.8	496831.3	100.0000

Figure 40: GC diagram of oxidation of 2-thiophene methanol under oxygen



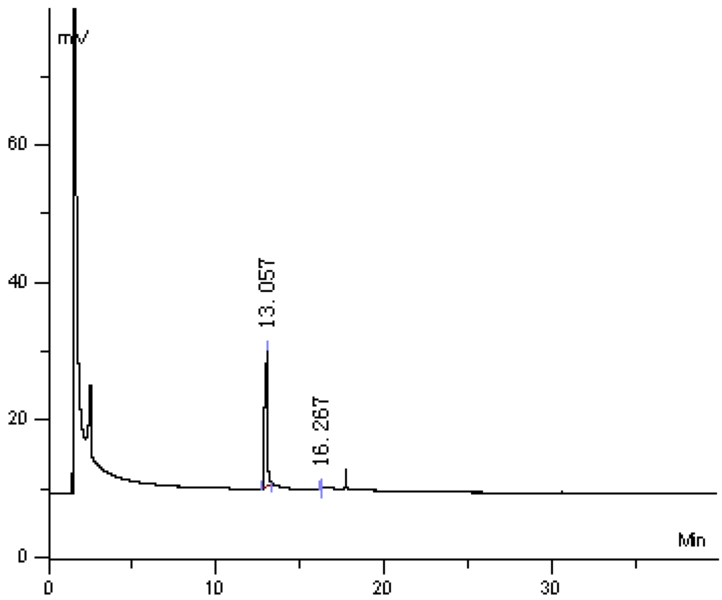
Peak	RetTime (min)	Height	Area	Area %
1	14.771	31882.3	794538.5	97.8339
2	30.063	759.4	16358.9	2.0143
3	30.575	180.3	1232.3	0.1517
Totals:		32822.0	812129.7	100.0000

Figure 41: GC diagram of 2-pyridinal alcohol



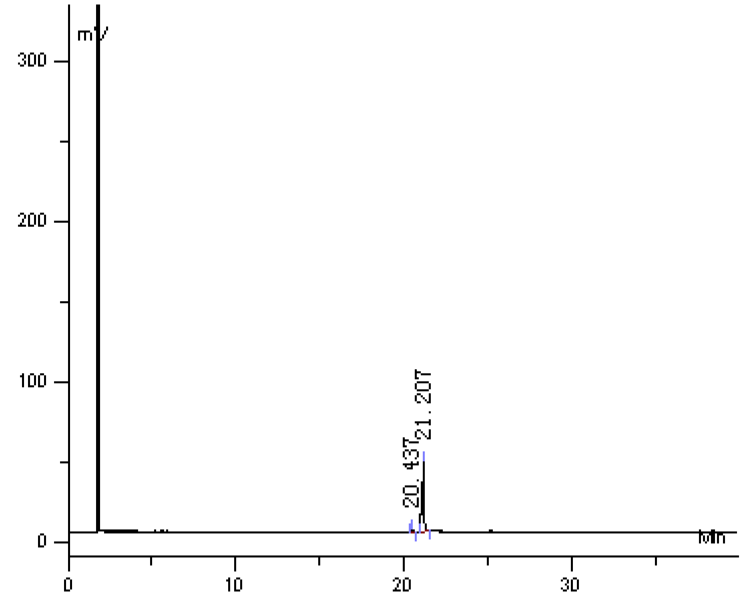
Peak	RetTime (min)	Height	Area	Area %
1	16.288	16751.0	361018.7	99.2864
2	16.758	417.6	2594.6	0.7136
Totals:		17168.6	363613.3	100.0000

Figure 42: GC diagram of oxidation of 2-pyridinal alcohol under oxygen



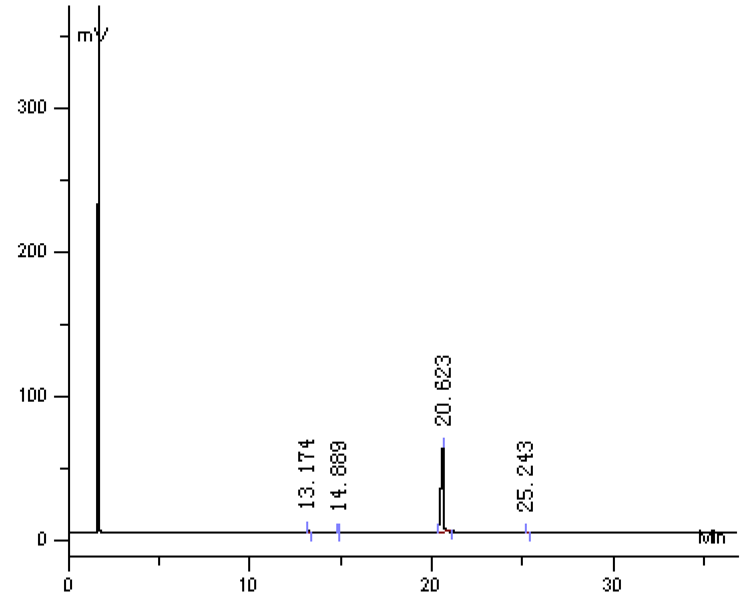
Peak	RetTime (min)	Height	Area	Area %
1	13.057	19794.0	531054.1	99.9496
2	16.267	58.7	267.6	0.0504
Totals:		19852.7	31321.7	100.0000

Figure 43: GC diagram of Cinnamyl alcohol



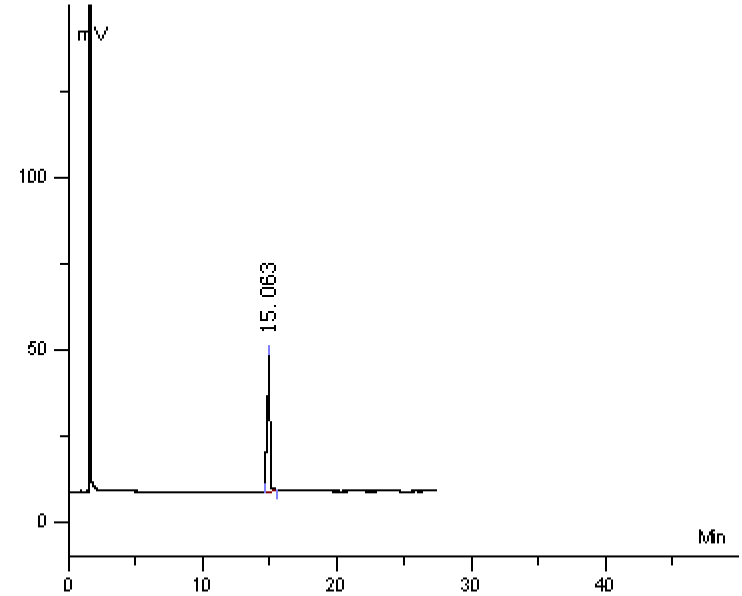
Peak	RetTime (min)	Height	Area	Area %
1	20.437	1806.0	16762.2	2.0388
2	21.207	44354.1	805408.5	97.9612
Totals:		46160.1	822170.7	100.0000

Figure 44: GC diagram of oxidation of Cinnamyl alcohol under oxygen



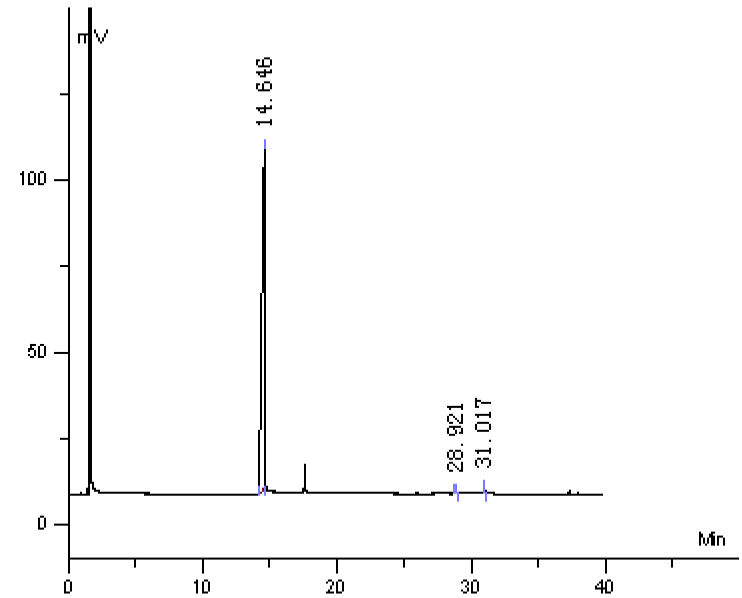
Peak	RetTime (min)	Height	Area	Area %
1	13.174	519.7	7624.1	0.7056
2	14.889	148.9	842.1	0.0779
3	20.623	58788.9	1070173.3	99.0439
4	25.243	374.6	1864.3	0.1725
Totals:		59832.1	1080503.7	100.0000

Figure 45: GC diagram of 2-octanol



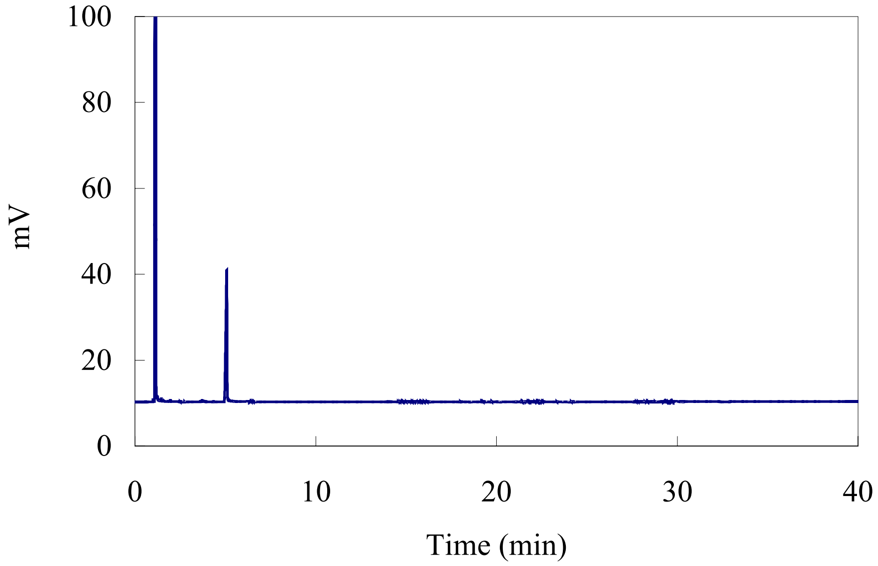
Peak	RetTime (min)	Height	Area	Area %
1	15.063	39683.2	1053751.9	100.0000
Totals:		39683.2	1053751.9	100.0000

Figure 46: GC diagram of oxidation of 2-octanol under oxygen (using $CuCl_2$ instead of $FeCl_3$)



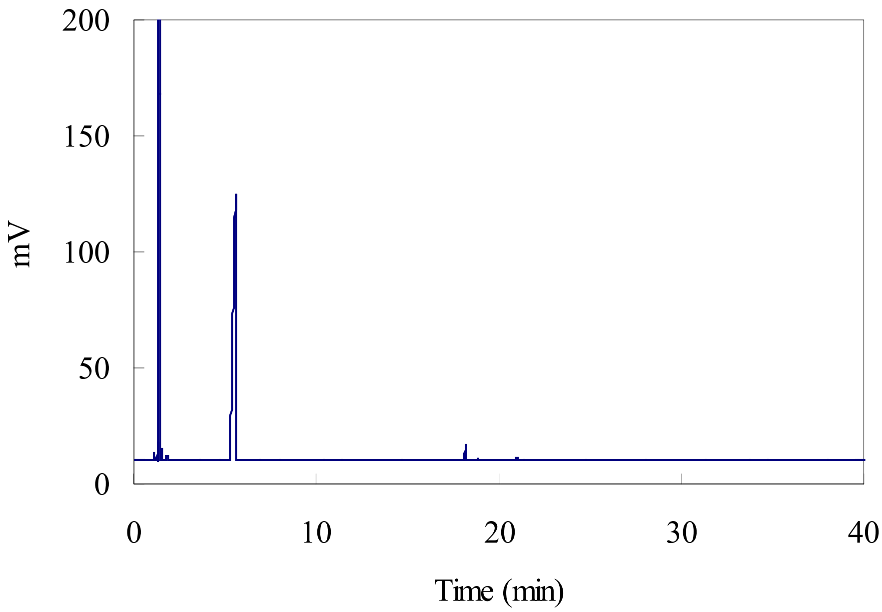
Peak	RetTime (min)	Height	Area	Area %
1	14.646	99209.0	2443658.6	99.2460
2	28.921	492.0	6342.9	0.2576
3	31.017	1275.4	12221.7	0.4964
Totals:		100976.4	2462223.1	100.0000

Figure 47: GC diagram of 2-octanol of 3-Methyl-but-2-en-1-ol



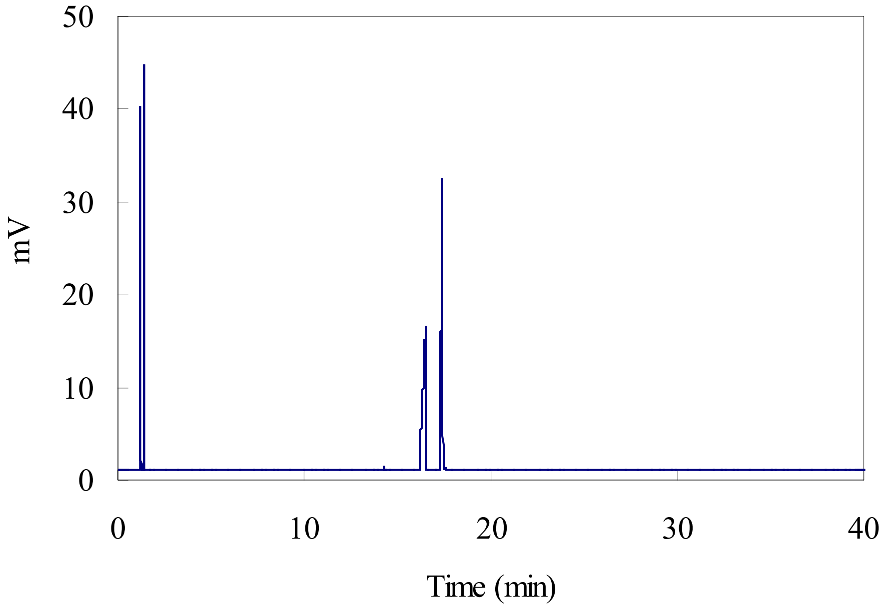
Peak	RetTime (min)	Height	Area	Area %
1	5.08	$6.125*10^4$	$3.096*10^5$	100.00
Totals:		$6.125*10^4$	$3.096*10^5$	100.00

Figure 48: GC diagram of 2-octanol of 3-Methyl-but-2-en-1-ol under oxygen



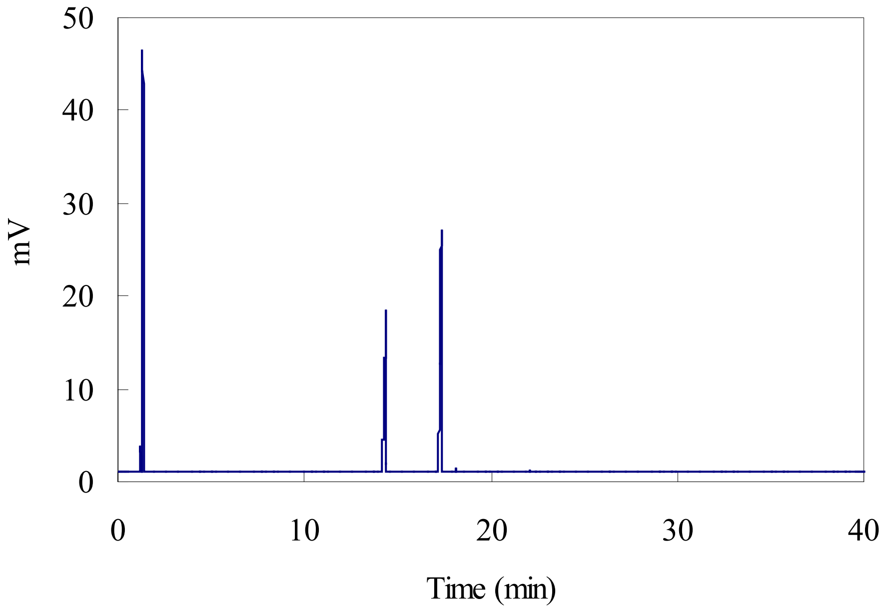
Peak	RetTime (min)	Height	Area	Area %
1	5.57	$2.293*10^5$	$2.419*10^6$	100.00
Totals:		$2.293*10^5$	$2.419*10^6$	100.00

Figure 49: GC diagram of benzyl alcohol and methyl phenyl sulfide



Peak	RetTime (min)	Height	Area	Area %
1	14.26	$7.810*10^3$	$3.682*10^4$	0.50
2	16.50	$3.101*10^5$	$3.624*10^6$	49.63
3	17.41	$6.288*10^5$	$3.641*10^6$	49.87
Totals:		$9.467*10^5$	$7.302*10^6$	100.00

Figure 50: GC diagram of oxidation of benzyl alcohol and methyl phenyl sulfide under oxygen



Peak	RetTime (min)	Height	Area	Area %
1	14.38	$3.512*10^5$	$2.461*10^6$	99.53

2	22.10	$2.661*10^3$	$1.156*10^4$	0.47
Totals:		$3.539*10^5$	$2.473*10^6$	100.00