

Supporting Information

Lanthano-phosphotungstates: A water soluble and reusable catalyst for oxidation of alcohol using H₂O₂ as an oxidant

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I. Experimental section

Syntheses of lanthano-phosphotungstate POM catalysts

General: The monolacunary POM precursor $K_7[PW_{11}O_{39}] \cdot 14H_2O$ was prepared according to the literature procedure and its purity was subjected by FT-IR spectrum. All chemicals were commercially procured and were used without further purification. Fourier transform infrared (FT-IR) spectra were recorded with a Perkin-Elmer BX spectrum on KBr pellets. Thermogravimetric analysis (TGA) were performed using a TG/DTA instrument DTG-60 Shimadzu between temperature range of 25 and 700 °C in a nitrogen atmosphere with a heating rate of 5 °C/min. TGA was performed to evaluate the number of crystal water present in the synthesized compounds, and elemental analysis was performed using ICP-AES instrument.

Synthesis of $K_{11}[Pr(PW_{11}O_{39})_2] \cdot 22H_2O$ (Pr-POM). 0.6400 g (0.2 mmol) of $K_7[PW_{11}O_{39}] \cdot 14H_2O$ was dissolved in 25 ml of potassium acetate buffer (pH 4.8) with stirring. Later 0.0435 g (0.1 mmol) of $Pr(NO_3)_3 \cdot 6H_2O$ was slowly added to the reaction mixture. The solution was stirred continuously at 50 °C for 30 min, followed by cooling to room temperature then filtering to remove the precipitate if found. The addition of a 1 M KCl solution (1 ml) to the colorless filtrate and slow evaporation at room temperature led to rod like faint green crystals after about 4-5 weeks. Yield 51 % (based on $K_7[PW_{11}O_{39}] \cdot 14H_2O$. FT-IR (cm^{-1}): 1096(s), 1048(s), 951(s), 887(s), 836(m), 772(m), 727(m), 592(w), 512(m), 480(m). Elemental analysis (%); calcd.(found): W 63.9 (60.33), K 6.8 (6.02), P 0.98 (1.1).

Synthesis of $K_{11}[Nd(PW_{11}O_{39})_2] \cdot 25H_2O$ (Nd-POM). The above synthetic protocol was followed by using 0.0438 g (0.1 mmol) $Nd(NO_3)_3 \cdot 6H_2O$ instead of $Pr(NO_3)_3 \cdot 6H_2O$. Plate like crystals of faint violet color were obtained after about 4-5 weeks. Yield: 52 % (based on $K_7[PW_{11}O_{39}] \cdot 14H_2O$. FT-IR (cm^{-1}) 1100(s), 1048(s), 957(s), 891(s), 840(m), 772(m), 724(m), 592(w), 508(m), 482(m). Elemental analysis (%); calcd.(found): W 63.4 (61.39), K 6.7 (6.2), P 0.97 (1.1).

Synthesis of $K_{11}[Eu(PW_{11}O_{39})_2] \cdot 26H_2O$ (Eu-POM). The above synthetic protocol was followed by using 0.0428 g (0.1 mmol) $Eu(NO_3)_3 \cdot 5H_2O$ instead of $Pr(NO_3)_3 \cdot 6H_2O$. Colorless plate like crystals obtained after about 4-5 weeks. Yield: 48 % (based on $K_7[PW_{11}O_{39}] \cdot 14H_2O$. FT-IR (cm^{-1}) 1104(s), 1048(s), 953(s), 891(s), 838(m), 772(m), 727(m), 592(w), 512(m), 482(m). Elemental analysis (%); calcd.(found): W 63.1 (63.9), K 6.7 (6.3), P 0.97 (1.1).

Synthesis of $K_{11}[Gd(PW_{11}O_{39})_2] \cdot 32H_2O$ (Gd-POM). The above synthetic protocol was followed by using 0.0451 g (0.1 mmol) $Gd(NO_3)_3 \cdot 6H_2O$ instead of $Pr(NO_3)_3 \cdot 6H_2O$. Colorless needle like crystals obtained after about 4-5 weeks. Yield: 55 % (based on $K_7[PW_{11}O_{39}] \cdot 14H_2O$. FT-IR (cm^{-1}) 1104(s), 1050(s), 955(s), 891(s), 842(m), 770(m), 729(m), 592(w), 512(m), 480(m). Elemental analysis (%); calcd.(found): W 62.1 (62.2), K 6.6 (6.0), P 0.95 (1.0).

Synthesis of $K_{11}[Tb(PW_{11}O_{39})_2] \cdot 22H_2O$ (Tb-POM). The above synthetic protocol was followed by using 0.0435 g (0.1 mmol) $Tb(NO_3)_3 \cdot 5H_2O$ instead of $Pr(NO_3)_3 \cdot 6H_2O$. Colorless rod like crystals obtained after about 4-5 weeks. Yield: 53 % (based on $K_7[PW_{11}O_{39}] \cdot 14H_2O$. FT-IR (cm^{-1}) 1106(s), 1050(s), 951(s), 897(s), 838(m), 774(m), 729(m), 592(w), 516(m), 472(m). Elemental analysis (%); calcd.(found): W 63.8 (61.57), K 6.8 (7.2), P 0.98 (1.1).

Synthesis of $K_{11}[Dy(PW_{11}O_{39})_2] \cdot 25H_2O$ (Dy-POM). The above synthetic protocol was followed by using 0.0438 g (0.1 mmol) $Dy(NO_3)_3 \cdot 6H_2O$ instead of $Pr(NO_3)_3 \cdot 6H_2O$. Colorless needle like crystals obtained after about 4-5 weeks. Yield: 51 % (based on $K_7[PW_{11}O_{39}] \cdot 14H_2O$. FT-IR (cm^{-1}) 1106(s), 1052(s), 953(s), 891(s), 845(m), 770(m), 719(m), 594(w), 512(m), 482(m). Elemental analysis (%); calcd.(found): W 63.2 (61.32), K 6.7 (6.1), P 0.97 (1.1).

Synthesis of $K_{11}[Ho(PW_{11}O_{39})_2] \cdot 24H_2O$ (Ho-POM). The above synthetic protocol was followed by using 0.044 g (0.1 mmol) $Ho(NO_3)_3 \cdot 5H_2O$ instead of $Pr(NO_3)_3 \cdot 6H_2O$. Needle like faint yellow crystals obtained after about 4-5 weeks. Yield: 54 % (based on $K_7[PW_{11}O_{39}] \cdot 14H_2O$. FT-IR (cm^{-1}) 1110(s), 1050(s), 955(s), 893(s), 842(m), 770(m), 721(m), 594(w), 518(m), 486(m). Elemental analysis (%); calcd.(found): W 63.4 (63.25), K 6.7 (7.0), P 0.97 (1.1).

Synthesis of $K_{11}[Er(PW_{11}O_{39})_2] \cdot 31H_2O$ (Er-POM). The above synthetic protocol was followed by using 0.0443 g (0.1 mmol) $Er(NO_3)_3 \cdot 5H_2O$ instead of $Pr(NO_3)_3 \cdot 6H_2O$. Needle like faint pink crystals obtained after about 4-5 weeks. Yield: 56 % (based on $K_7[PW_{11}O_{39}] \cdot 14H_2O$. FT-IR (cm^{-1}) 1110(s), 1050(s), 955(s), 895(s), 842(m), 772(m), 724(m), 592(w), 510(m), 480(m). Elemental analysis (%); calcd.(found): W 62.1 (60.92), K 6.6 (6.24), P 0.95 (1.0).

Synthesis of $K_{11}[Tm(PW_{11}O_{39})_2] \cdot 23H_2O$ (Tm-POM). The above synthetic protocol was followed by using 0.0445 g (0.1 mmol) $Tm(NO_3)_3 \cdot 5H_2O$ instead of $Pr(NO_3)_3 \cdot 6H_2O$. Colorless needle like crystals obtained after about 4-5 weeks. Yield: 52 % (based on $K_7[PW_{11}O_{39}] \cdot 14H_2O$. FT-IR (cm^{-1}) 1110(s), 1050(s), 951(s), 893(s),

842(m), 774(m), 729(m), 594(w), 516(m), 480(m). Elemental analysis (%); calcd.(found): W 63.5 (61.62), K 6.75 (7.0), P 0.97 (1.1).

Synthesis of $K_{11}[Yb(PW_{11}O_{39})_2] \cdot 28H_2O$ (Yb-POM). The above synthetic protocol was followed by using 0.0449 g (0.1 mmol) $Yb(NO_3)_3 \cdot 5H_2O$ instead of $Pr(NO_3)_3 \cdot 6H_2O$. Colorless needle like crystals obtained after about 4-5 weeks. Yield: 52 % (based on $K_7[PW_{11}O_{39}] \cdot 14H_2O$). FT-IR (cm^{-1}) 1097(s), 1049(s), 951(s), 893(s), 835(m), 768(m), 718(m), 591(w), 506(m), 478(m). Elemental analysis (%); calcd.(found): W 62.6 (62.59), K 6.65 (6.13), P 0.96 (1.1).

Chemicals used in catalysis

Reagent grade solvents were used for extraction and gas chromatography. All the reagents and chemicals were purchased from Sigma – Aldrich Chemical Co, Alfa Aesar, Lancaster and were used directly without further purification. The progress of reactions was checked by thin-layer chromatography (TLC, Merck silica gel 60 F-254 plates). The plates were visualized first with UV illumination followed by iodine. Gas chromatography was performed using DCM as a solvent. 1H -NMR spectra were recorded at 400 MHz and are reported in parts per million (ppm) on the δ scale relative to TMS as an internal standard.

II. Supplementary catalysis section

Catalytic reaction designed for 1-phenylethanol oxidation

0.24 mol % of $K_{11}[Ln(PW_{11}O_{39})_2] \cdot xH_2O$ was dissolved in 0.4 ml of distilled water in 25 ml round bottom flask with stirring. Then 2 mmol of 1-phenylethanol was added in it. And then 4 mmol of 30 % aq. H_2O_2 was added dropwise to stirring solution and temperature of the reaction was set to be 90 °C for 3 hours. During the reaction a homogeneous reaction mixture was obtained. Reaction was monitored by TLC and per hour samples were collected to check the product conversion with the help of gas chromatography. After the catalytic reaction catalyst was recovered by the extraction with diethyl ether. When diethyl ether was added to the reaction mixture then organic product extract in organic solvent and catalyst remains in water. The catalyst containing water can be reused without further adding of POM catalyst.

Table S1. Gas chromatography data for 1-phenylethanol oxidations with all lanthano-phosphotungstate POM catalysts at 90 °C temperature and 3h^a

Entry	Catalyst	Acetophenone conversion (%) at 3h
01.	$K_{11}[Pr(PW_{11}O_{39})_2] \cdot 22H_2O$	100
02.	$K_{11}[Nd(PW_{11}O_{39})_2] \cdot 25H_2O$	98
03.	$K_{11}[Eu(PW_{11}O_{39})_2] \cdot 26H_2O$	87
04.	$K_{11}[Gd(PW_{11}O_{39})_2] \cdot 32H_2O$	95
05.	$K_{11}[Tb(PW_{11}O_{39})_2] \cdot 22H_2O$	86
06.	$K_{11}[Dy(PW_{11}O_{39})_2] \cdot 25H_2O$	76
07.	$K_{11}[Ho(PW_{11}O_{39})_2] \cdot 24H_2O$	89
08.	$K_{11}[Er(PW_{11}O_{39})_2] \cdot 31H_2O$	90
09.	$K_{11}[Tm(PW_{11}O_{39})_2] \cdot 23H_2O$	97
10.	$K_{11}[Yb(PW_{11}O_{39})_2] \cdot 28H_2O$	85

^aThe reaction conditions were, a suspension of 2 mmol of 1-phenylethanol, 0.24 mol % of Ln-POM catalysts, 0.4 ml of H₂O and 4 mmol of H₂O₂ stirred at 90 °C for 3 h.

Table S2. Comparison of $K_{11}[\text{Pr}(\text{PW}_{11}\text{O}_{39})_2] \cdot 22\text{H}_2\text{O}$ catalyst for the oxidation of 1-phenylethanol with reported literature

Catalysts	Solvent	Catalysts Loading (mol %)	H_2O_2 : substrate (mmol)	Temperature ($^{\circ}\text{C}$)	Time (h)	Conversion	TOF ^a (h^{-1})
$K_8[\beta\text{-SiW}_{11}\text{O}_{39}] \cdot 14\text{H}_2\text{O}^{4(i)}$	H_2O	0.93	5:1	90	7	99	15.2
$K_8[\text{BW}_{11}\text{O}_{39}\text{H}] \cdot 13\text{H}_2\text{O}^{4(f)}$	H_2O	1.5	2:1	90	3	99	2.2
$K_8[\gamma\text{-SiW}_{10}\text{O}_{36}] \cdot 13\text{H}_2\text{O}^{4(e)}$	H_2O	0.67	5:1	90	7	100	2.1
$K_{10}\text{Zn}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2 \cdot 20\text{H}_2\text{O}^{4(g)}$	H_2O	0.9	5:1	90	3	99	36.7
$[(\text{C}_{18}\text{H}_{37})_2(\text{CH}_3)_2\text{N}]_8\text{K}_2[\text{Zn}_4(\text{H}_2\text{O})^{4(g)}(\text{PW}_9\text{O}_{34})_2]$	H_2O	0.45	5:1	90	3	99	73.3
$\text{Na}_{12}[(\text{WZn}_3(\text{H}_2\text{O})_2)[\text{ZnW}_9\text{O}_{34}]_2]^{4(b)}$	H_2O	0.4	5:1	75	7	100	35.7
$\text{Na}_{12}[(\text{WZn}_3(\text{H}_2\text{O})_2)[\text{ZnW}_9\text{O}_{34}]_2]^{4(a)}$ With TEMPO	H_2O	0.4	5:1	85	7	100	35.7
$\text{Na}_6[\text{SiW}_{11}\text{ZnH}_2\text{O}_{40}] \cdot 12\text{H}_2\text{O}^{4(c)}$	$\text{H}_2\text{O}/\text{oil}$	0.21	2:1	90	7	100	68.0
$\text{Na}_8\text{HPW}_9\text{O}_{34}$ + Cetylpyridinium chloride ⁴⁽ⁱ⁾	H_2O	0.7	5:1	85	5	94	26.9
$[(\text{C}_{18}\text{H}_{37})_2(\text{CH}_3)_2\text{N}]_{10}[\text{SiW}_9\text{O}_{34}]^{4(h)}$	H_2O	0.6	5:1	65	6	99	27.5
$[(\text{C}_{18}\text{H}_{37})_2(\text{CH}_3)_2\text{N}]_7[\text{PW}_{11}\text{O}_{39}]^{2(k)}$	1,4-dioxane	0.8	5:1	85	7	98	17.5
$\text{TBA}_8[\{\text{Zn}(\text{OH}_2)(\mu_3\text{-OH})\}_2\{\text{Zn}(\text{OH}_2)_2\}_2\{\gamma\text{-HSiW}_{10}\text{O}_{36}\}_2] \cdot 9\text{H}_2\text{O}^{2(i)}$	acetone	0.4	1:2	56	1.5	83	138.3
$\text{TBA}_8[\{\text{Zn}_2\text{W}(\text{O})\text{O}_3\}_2\text{H}_4\{\alpha\text{-SiW}_9\text{O}_{33}\}_2] \cdot 5\text{H}_2\text{O}^{2(i)}$	acetone	0.4	1:2	56	1.5	92	153.3
$\text{TBA}_8[\{\text{Zn}_2\text{W}(\text{O})\text{O}_3\}_2\text{H}_4\{\beta\text{-SiW}_9\text{O}_{33}\}_2] \cdot 7\text{H}_2\text{O}^{2(i)}$	acetone	0.4	1:2	56	1.5	94	156.7
$[\text{n-C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3]\text{PW}_{12}\text{O}_{40}^{3(b)}$	solvent free	0.25	1:1	90	6	95	63.3
$[\text{Hmim}]_3\text{PW}_{12}\text{O}_{40}^{2(e)}$	CH_3CN	0.3 g	3:1	80	12	100	-
$\text{H}_3\text{PMo}_{12}\text{O}_{40}$, $\text{H}_3\text{SiMo}_{12}\text{O}_{40}$, $\text{H}_4\text{PW}_{12}\text{O}_{40}$, $\text{H}_4\text{SiW}_{12}\text{O}_{40}$, $\text{H}_6\text{PMo}_{11}\text{AlO}_{40}$, $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$, $\text{H}_4\text{PMo}_{11}\text{Al}_{0.5}\text{V}_{0.5}\text{O}_{40}^{2(i)}$	CH_3CN	3.0	10:0.7	70	9	95	3.5
$K_{11}[\text{Pr}(\text{PW}_{11}\text{O}_{39})_2] \cdot 22\text{H}_2\text{O}$ (this work)	H_2O	0.24	2:1	90	3	>99	137.5

^aTurn over frequencies (TOF) were calculated by using $\text{TOF} = \text{conversion of product (mmol)}/\text{Catalyst (mmol)} \times \text{Time (h)}$

Table S3. Kinetics data for 1-phenylethanol oxidation reaction using **Pr-POM** catalyst at 90 °C for 120 minutes^a

Substrate (mol %)	Time (min)	Product conversion with time in (mol %)	C/C ₀ after t time for substrate	ln(C/C ₀)
2	20	0.8434	0.5783	-0.54766
	40	1.104	0.448	-0.80296
	60	1.2754	0.3623	-1.05128
	80	1.4506	0.2747	-1.29208
	100	1.5526	0.2237	-1.49745
	120	1.6838	0.1581	-1.84453

^aThe reaction conditions were, a suspension of 2 mmol of 1-phenylethanol, 0.24 mol% of Pr-POM catalyst, 0.4 ml of H₂O and 4 mmol of H₂O₂ stirred at 90 °C for 120 minutes.

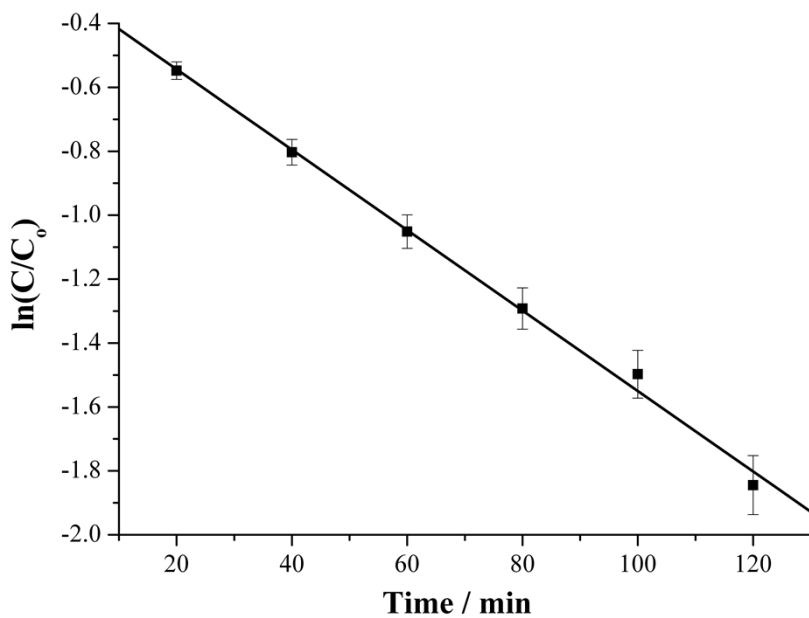
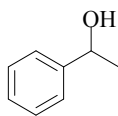


Figure S1 Kinetics of 1-phenylethanol oxidation reaction for Pr(III)-POM at 90 °C for 120 min.

III Gas chromatographic analysis

Gas chromatogram of standard 1-phenylethanol

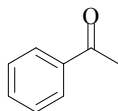


GC conditions for standard 1-phenylethanol. Column information Rtx-5, L = 30m, 0.25mmID, injector temperature 220 °C, column flow rate 1.00 ml/min, column temperature 100 – 120 °C, temperature program 5 °C/min, detector temperature 250 °C.

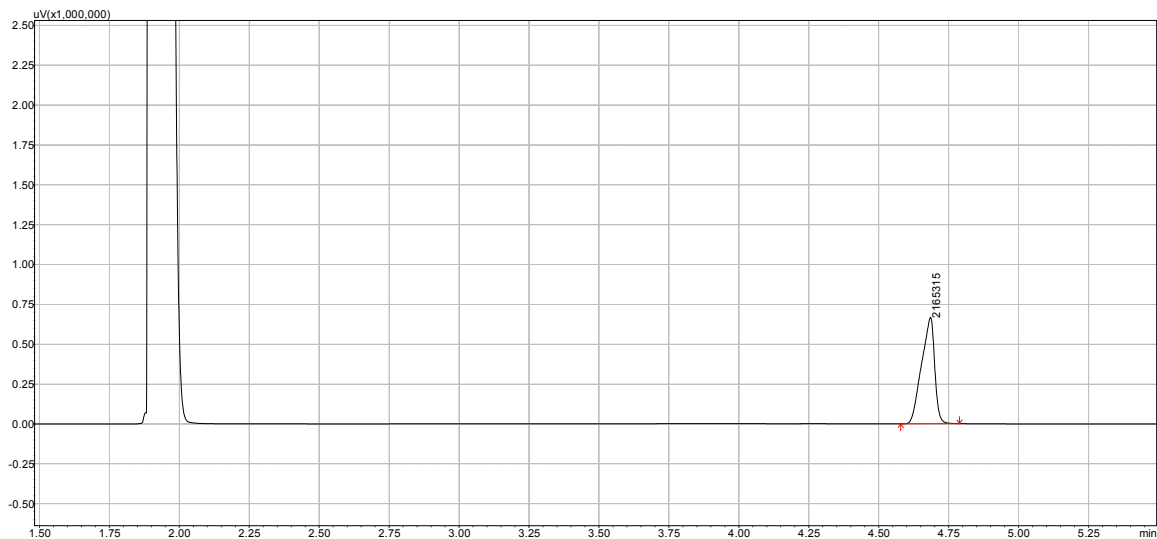


Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	4.607	6032640.1	1220520.9	100.00000	100.0000	1-phenylethanol

GC chromatogram for standard acetophenone

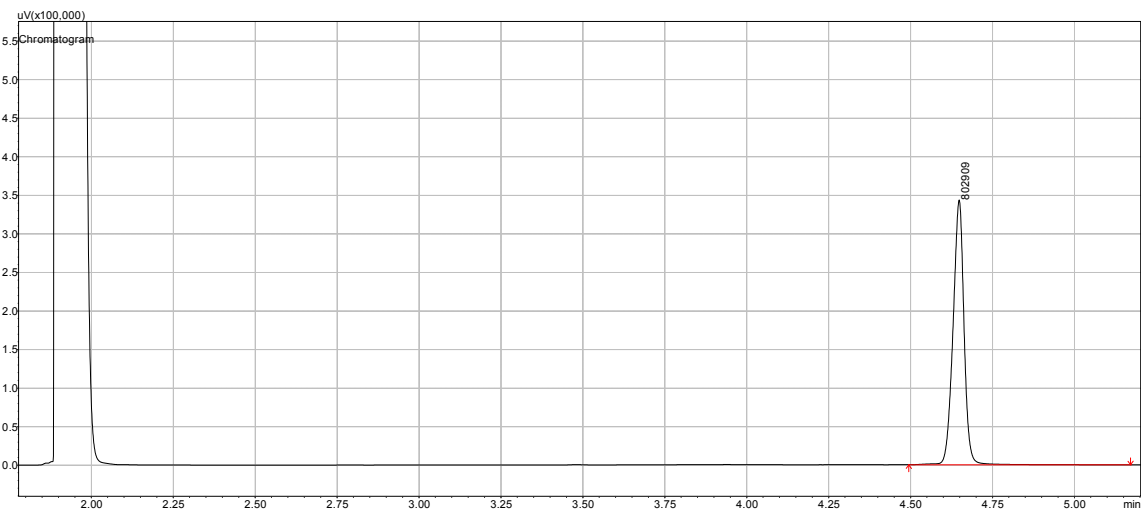


GC conditions for standard acetophenone are same as above mentioned for 1-phenylethanol.



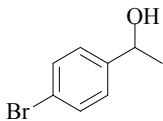
Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	4.685	2165315.0	648175.9	100.00000	100.0000	Acetophenone

Gas chromatogram for the oxidation of 1-phenylethanol to acetophenone product
 GC conditions are same as standard 1-phenylethanol.

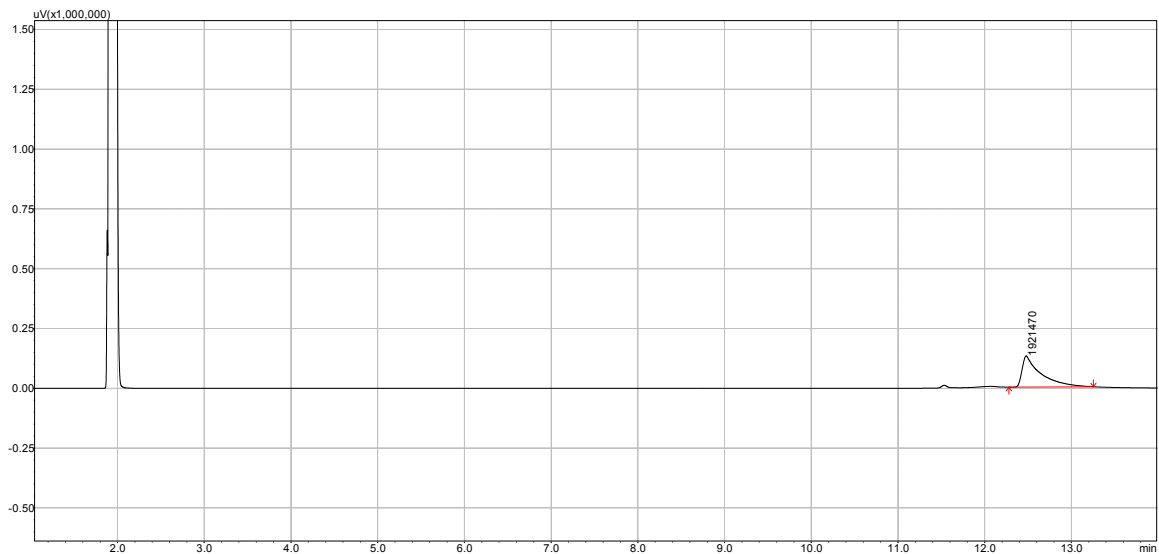


Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	4.648	802908.5	338694.7	100.00000	100.0000	Acetophenone

Gas chromatogram for standard 1-(4-bromophenyl)ethanol

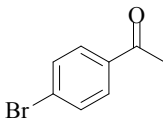


GC conditions for standard 1-(4-bromophenyl)ethanol. Column information Rtx-5, L = 30m, 0.25mmID, injector temperature 220 °C, column flow rate 1.00 ml/min, column temperature 100 – 180 °C, temperature program 3 °C/min, detector temperature 250 °C.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	12.480	1921469.9	129947.7	100.00000	100.0000	1-(4-bromophenyl)ethanol

Gas chromatogram for standard 1-(4-bromophenyl)ethanone



GC conditions are same as standard 1-(4-bromophenyl)ethanol.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	11.658	2931756.1	448673.3	100.00000	100.0000	1-(4-bromophenyl)ethanone

Gas chromatogram for the oxidation of 1-(4-bromophenyl)ethanol to 1-(4-bromophenyl)ethanone product

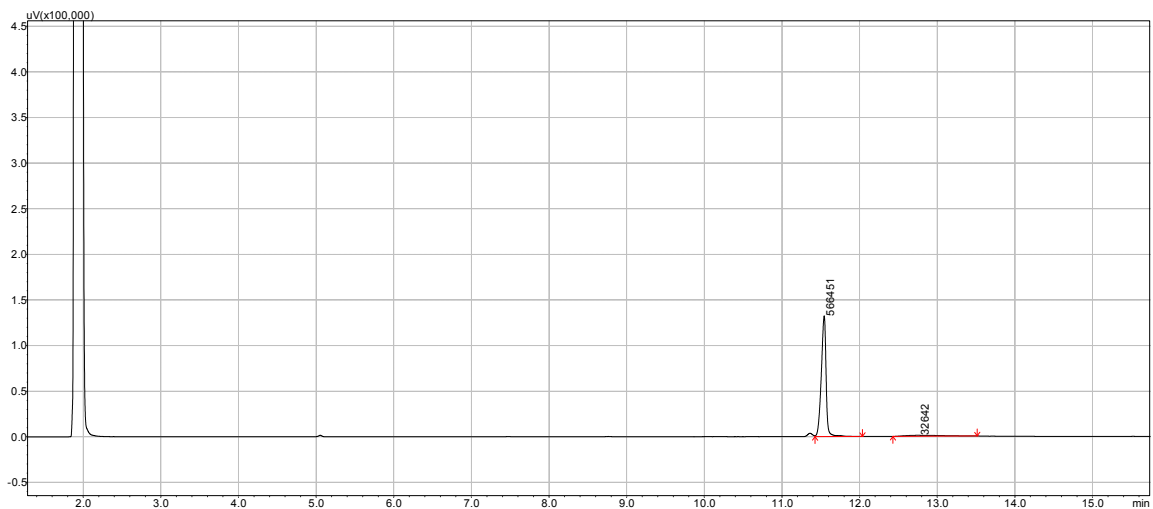
GC conditions are same as standard 1-(4-bromophenyl)ethanol.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	11.562	744146.0	169589.4	37.77522	37.7752	1-(4-bromophenyl)ethanone
2	12.503	1225785.6	33121.3	62.22478	62.2248	1-(4-bromophenyl)ethanol

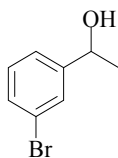


Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	11.550	888122.2	196085.3	65.60045	65.6005	1-(4-bromophenyl)ethanone
2	12.571	465713.2	12418.6	34.39955	34.3995	1-(4-bromophenyl)ethanol



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	11.544	566450.6	132140.9	94.55150	94.5515	1-(4-bromophenyl)ethanone
2	12.764	32641.6	1045.2	5.44850	5.4485	1-(4-bromophenyl)ethanol

Gas chromatogram for standard 1-(3-bromophenyl)ethanol

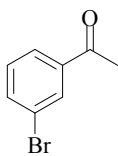


GC conditions for standard 1-(3-bromophenyl)ethanol. Column information Rtx-5, L = 30m, 0.25mmID, injector temperature 220 °C, column flow rate 1.00 ml/min, column temperature 100 – 180 °C, temperature program 3 °C/min, detector temperature 250 °C.

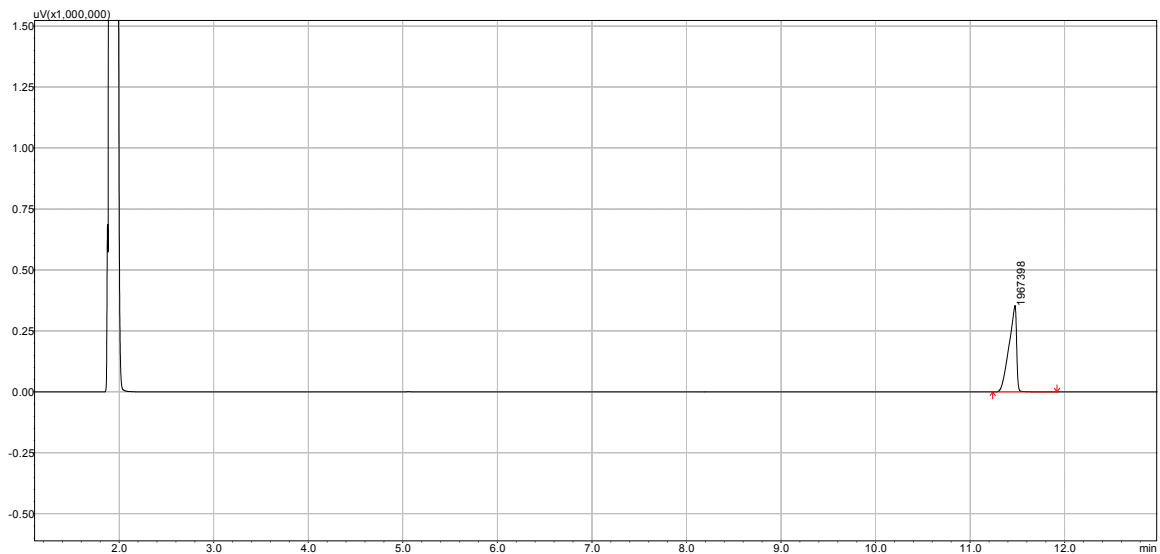


Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	12.732	11864761.1	847191.6	100.00000	100.0000	1-(3-bromophenyl)ethanol

Gas chromatogram for standard 1-(3-bromophenyl)ethanone



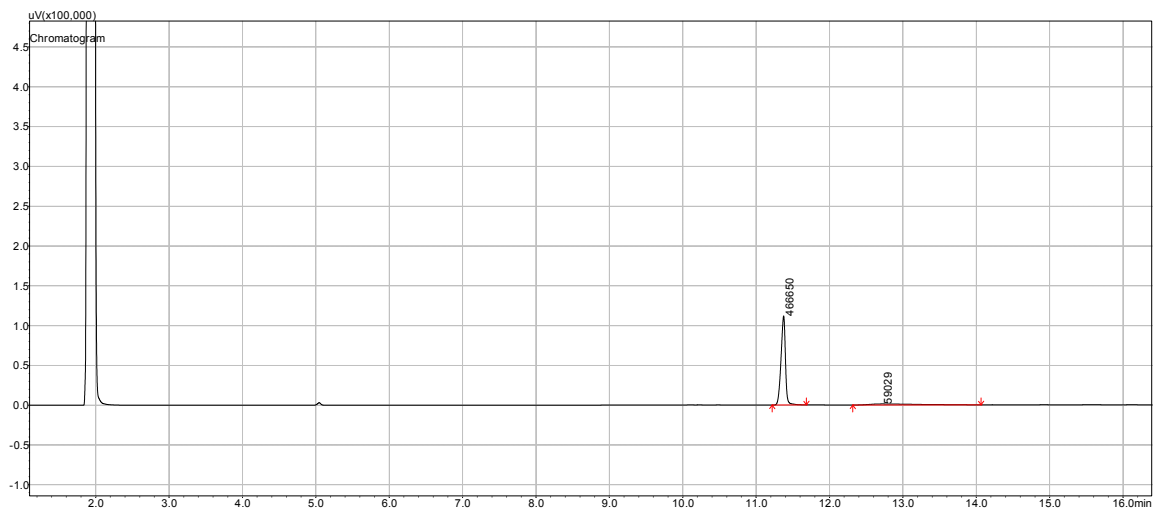
GC conditions are same as standard 1-(3-bromophenyl)ethanol.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	11.474	1967398.3	351967.6	100.00000	100.0000	1-(3-bromophenyl)ethanone

Gas chromatogram for the oxidation of 1-(3-bromophenyl)ethanol to 1-(3-bromophenyl)ethanone product

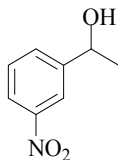
GC conditions are same as standard 1-(3-bromophenyl)ethanol.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	11.375	466649.7	111601.7	88.77084	88.7708	1-(3-bromophenyl)ethanone

2	12.716	59029.3	1301.4	11.22916	11.2292	1-(3-bromophenyl)ethanol
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Gas chromatogram for standard 1-(3-nitrophenyl)ethanol

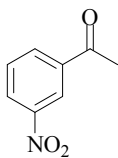


GC conditions for standard 1-(3-nitrophenyl)ethanol. Column information Rtx-5, L = 30m, 0.25mmID, injector temperature 220 °C, column flow rate 1.00 ml/min, column temperature 100 – 180 °C, temperature program 3 °C/min, detector temperature 250 °C.

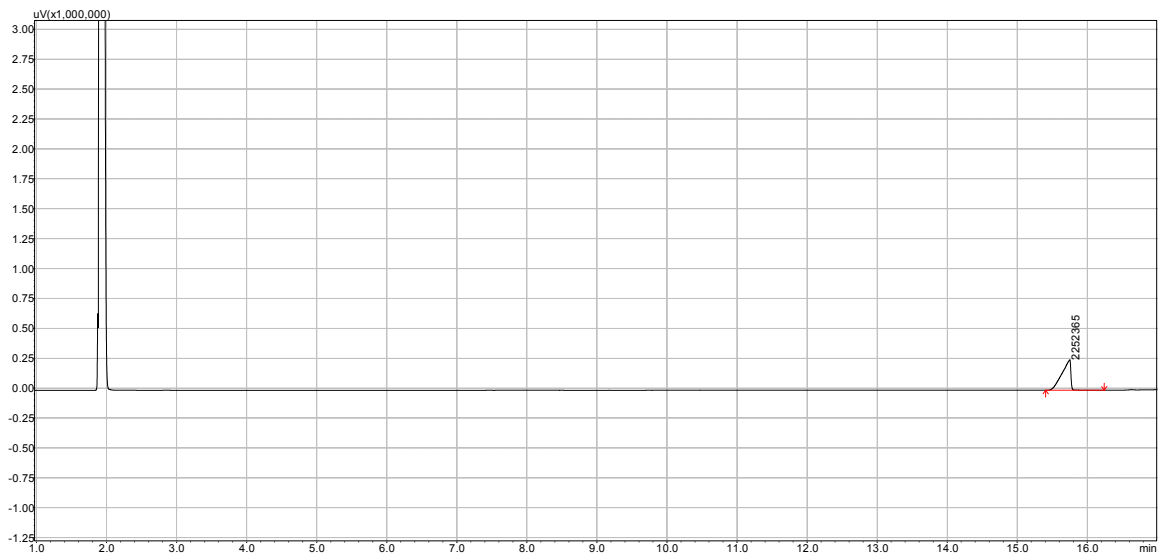


Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	19.034	12650388.3	576160.6	100.00000	100.0000	1-(3-nitrophenyl)ethanol

Gas chromatogram for standard 1-(3-nitrophenyl)ethanone



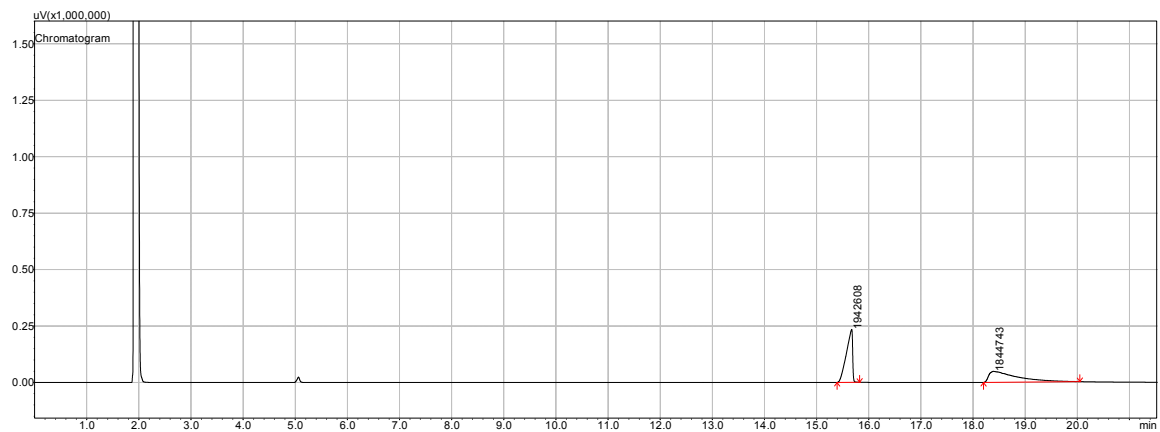
GC conditions are same as standard 1-(3-nitrophenyl)ethanol.



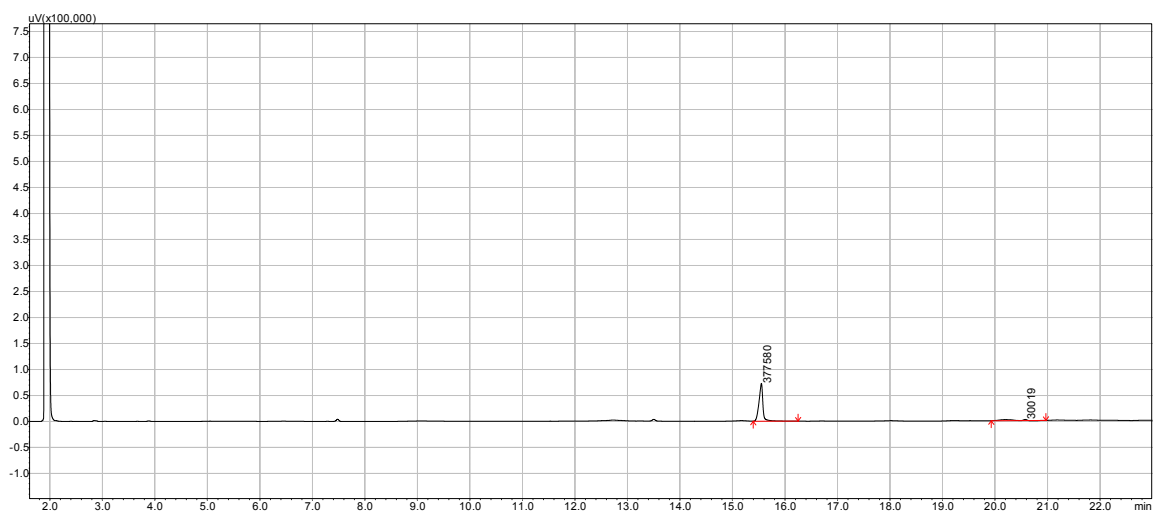
Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	15.749	2252365.3	255628.5	100.00000	100.0000	1-(3-nitrophenyl)ethanone

Gas chromatogram for the oxidation of 1-(3-nitrophenyl)ethanol to 1-(3-nitrophenyl)ethanone product

GC conditions are same as standard 1-(3-nitrophenyl)ethanol.

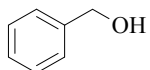


Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	15.673	1942608.5	234145.0	51.29201	51.2920	1-(3-nitrophenyl)ethanone
2	18.394	1844742.8	48879.4	48.70799	48.7080	1-(3-nitrophenyl)ethanol

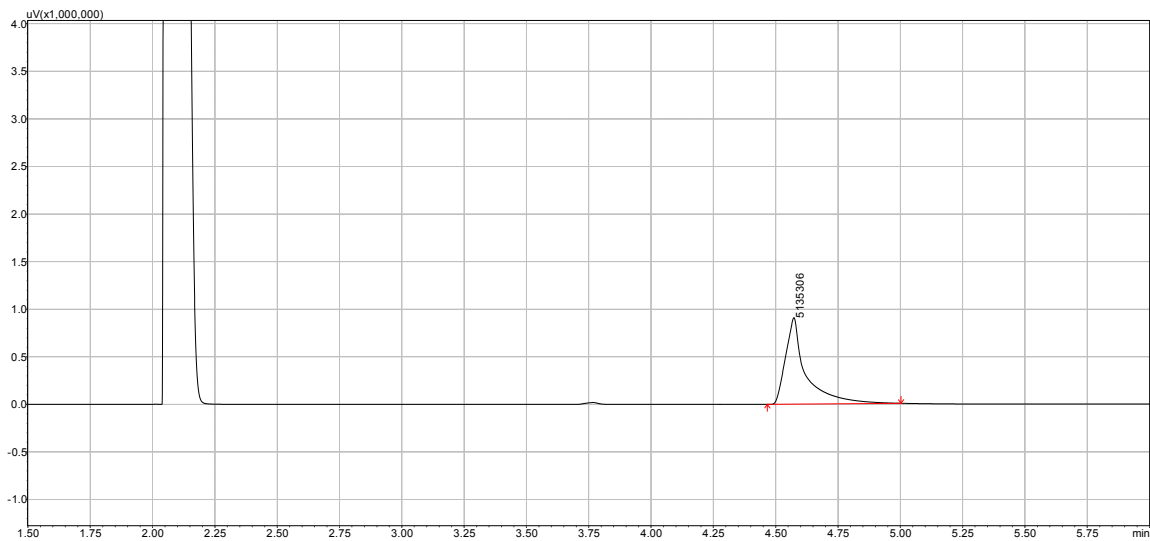


Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	15.551	377580.3	72505.2	92.6352	15.551	1-(3-nitrophenyl)ethanone
2	20.575	30018.9	1912.8	7.36480	7.3648	1-(3-nitrophenyl)ethanol

Gas chromatogram for standard benzyl alcohol

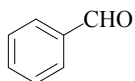


GC conditions for standard benzyl alcohol. Column information Rtx-5, L = 30m, 0.25mmID, injector temperature 220 °C, column flow rate 0.90 ml/min, column temperature 100 – 120 °C, temperature program 5 °C/min, detector temperature 250 °C.

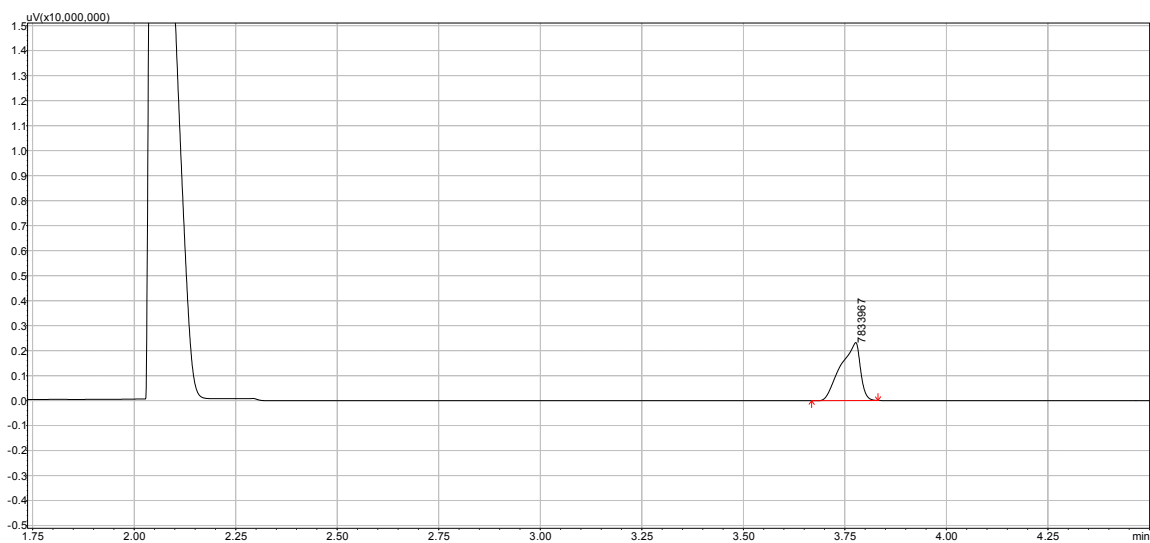


Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	4.573	5135306.2	892431.6	100.0000	100.0000	Benzyl alcohol

Gas chromatogram for standard benzaldehyde



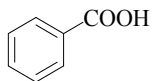
GC conditions are same as benzyl alcohol.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name

1	3.776	7833967.4	2288133.8	100.00000	100.0000	Benzaldehyde
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Gas chromatogram for standard benzoic acid



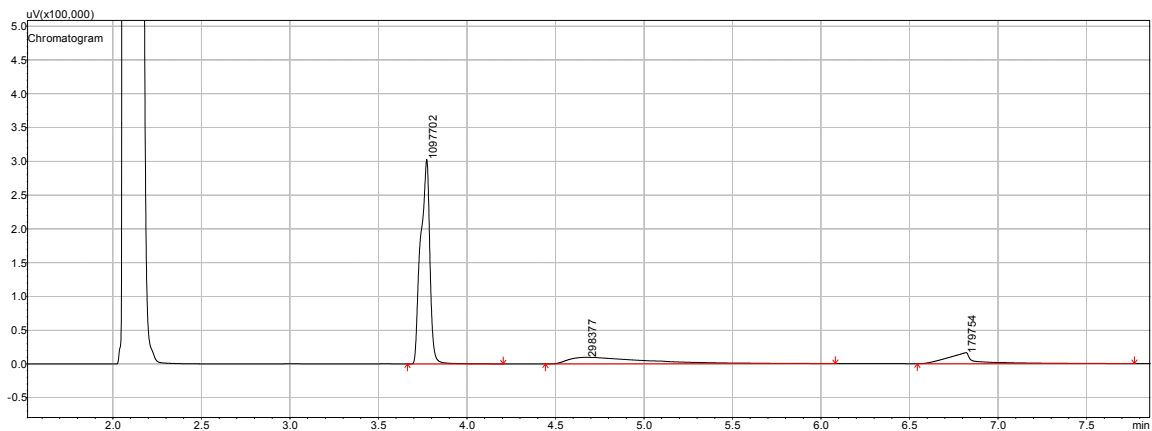
GC conditions are same as benzyl alcohol.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	7.879	3672339.7	113485.1	100.00000	100.0000	Benzoic acid

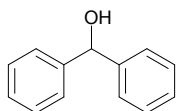
Gas chromatogram for the oxidation of benzyl alcohol to corresponding carbonyl compounds

GC conditions are same as standard benzyl alcohol.

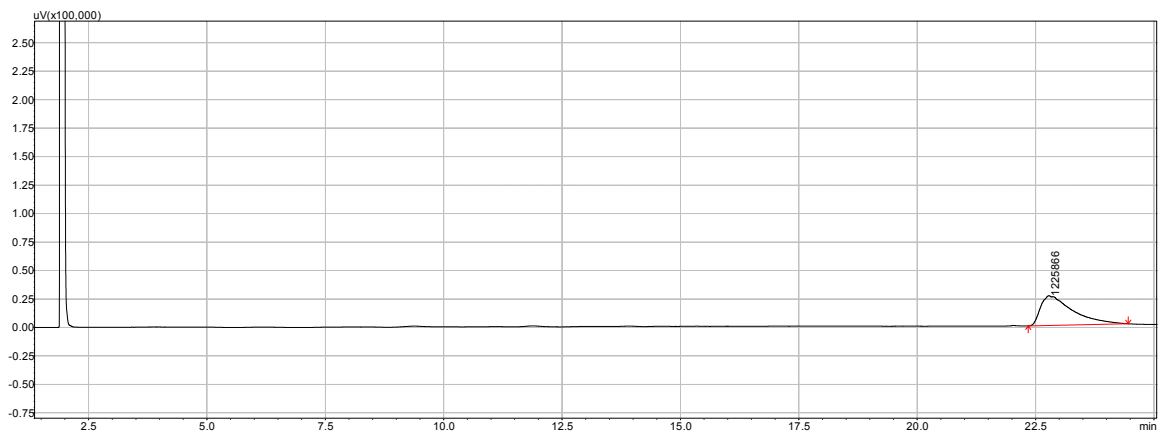


Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	3.773	1097701.6	300968.8	69.65849	69.6585	Benzaldehyde
2	4.673	298377.4	9731.8	18.93458	18.9346	Benzyl alcohol
3	6.819	179754.2	16263.9	11.40693	11.4069	Benzoic acid

Gas chromatogram for standard diphenylmethanol



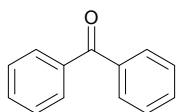
GC conditions for standard diphenylmethanol. Column information Rtx-5, L = 30m, 0.25mmID, injector temperature 220 °C, column flow rate 1.00 ml/min, column temperature 100 – 180 °C, temperature program 3 °C/min, detector temperature 250 °C.



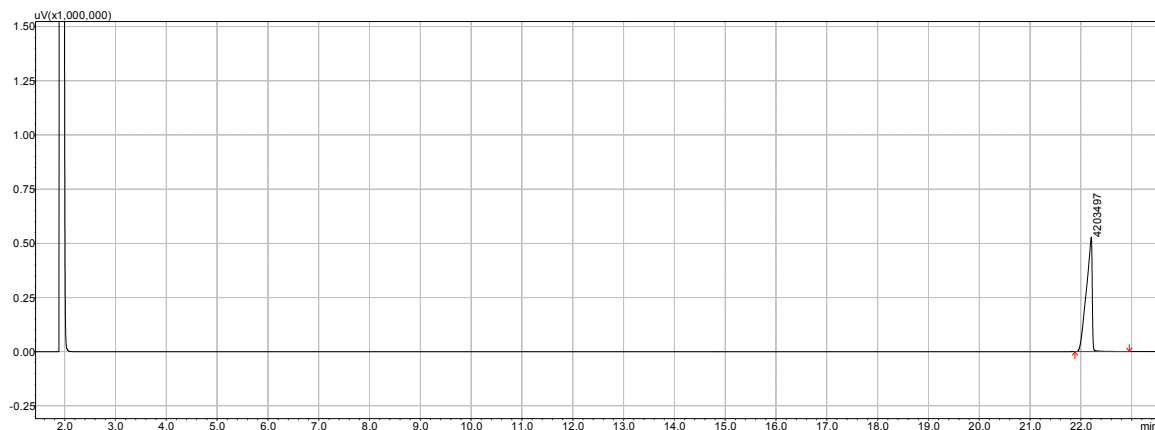
Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	22.5066					Diphenylmethanol

1	22.786	1225865.6	26074.4	100.0000	100.0000	diphenylmethanol
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Gas chromatogram for standard benzophenone



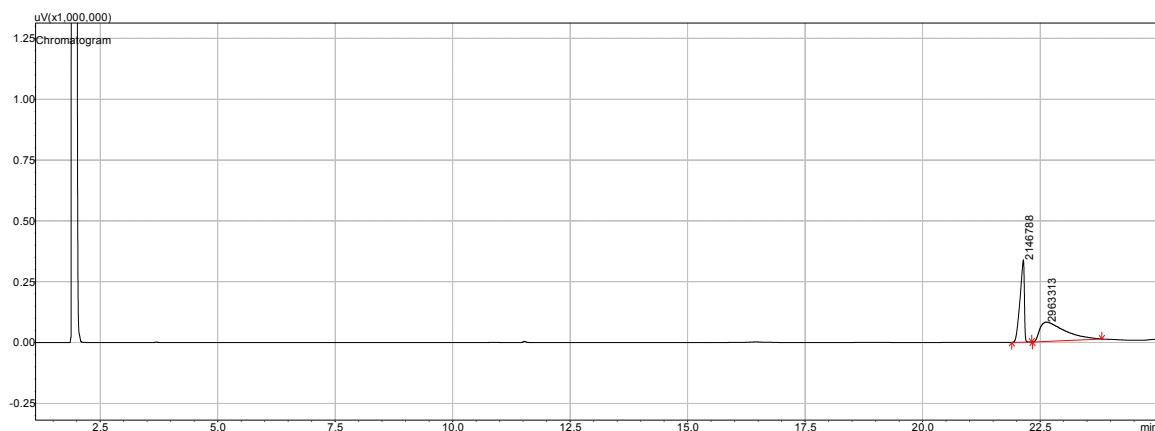
GC conditions are same as standard diphenylmethanol.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	22.204	4203496.7	526314.4	100.0000	100.0000	benzophenone

Gas chromatogram for the oxidation of diphenylmethanol to benzophenone product

GC conditions are same as standard diphenylmethanol.

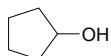


Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	22.143	2146788.2	337944.3	42.01068	42.0107	benzophenone
2	22.623	2963313.5	80008.4	57.98932	57.9893	diphenylmethanol

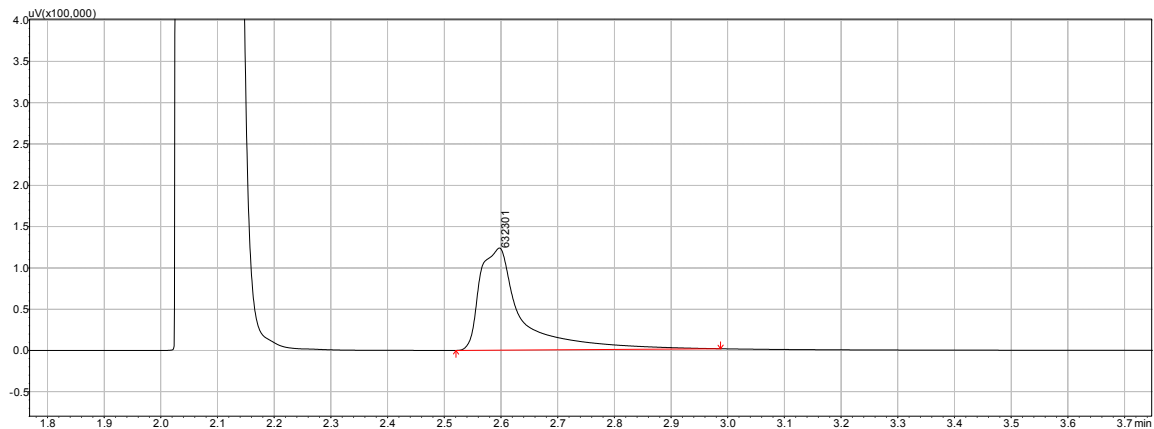


Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	22.056	464004.3	87811.3	90.15991	90.1599	benzophenone
2	23.113	50641.6	1236.2	9.84009	9.8401	diphenylmethanol

Gas chromatogram for standard cyclopentanol



GC conditions for standard cyclopentanol. Column information Rtx-5, L = 30m, 0.25mmID, injector temperature 220 °C, column flow rate 0.90 ml/min, column temperature 100 – 120 °C, temperature program 5 °C/min, detector temperature 250 °C.

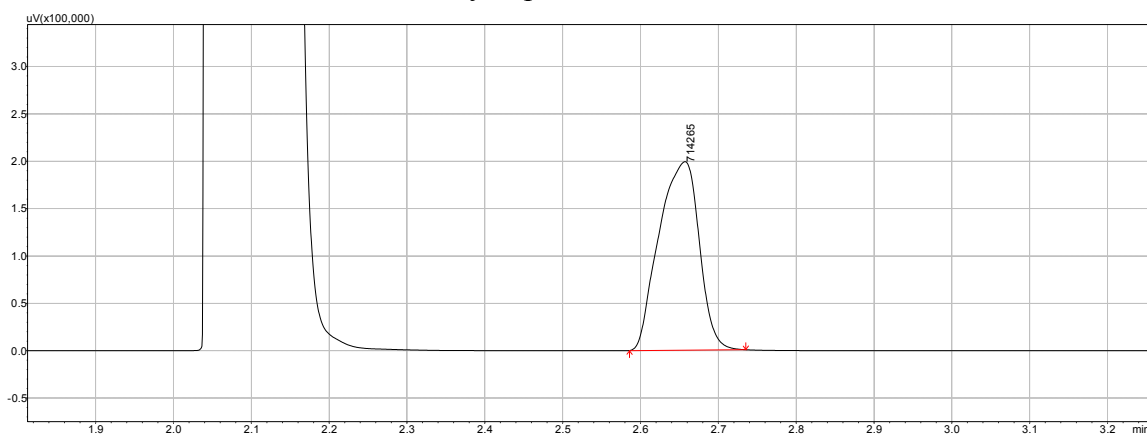


Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	2.597	632301.1	123262.0	100.00000	100.0000	cyclopentanol

Gas chromatogram for standard cyclopentanone



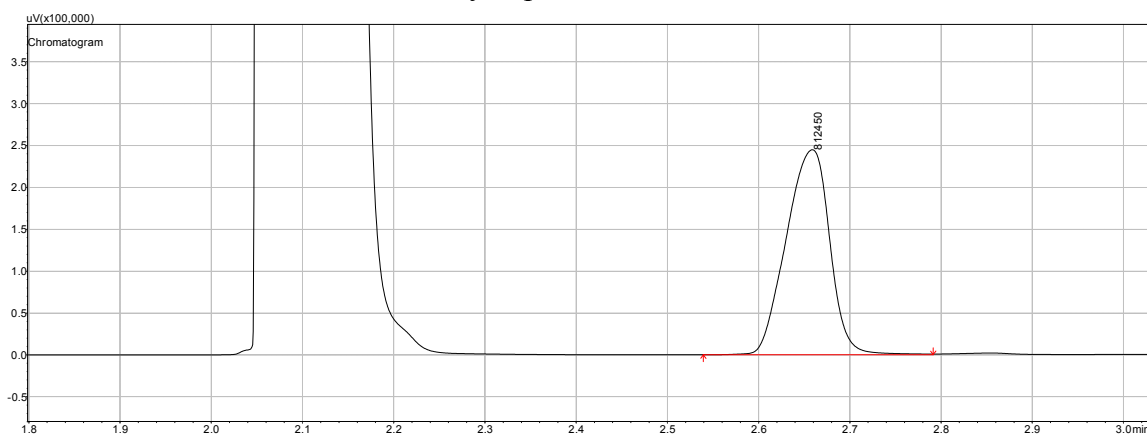
GC conditions are same as standard cyclopentanol.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	2.657	714264.9	198326.7	100.00000	100.0000	cyclopentanone

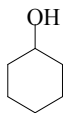
Gas chromatogram for the oxidation of cyclopentanol to cyclopentanone product

GC conditions are same as standard cyclopentanol.

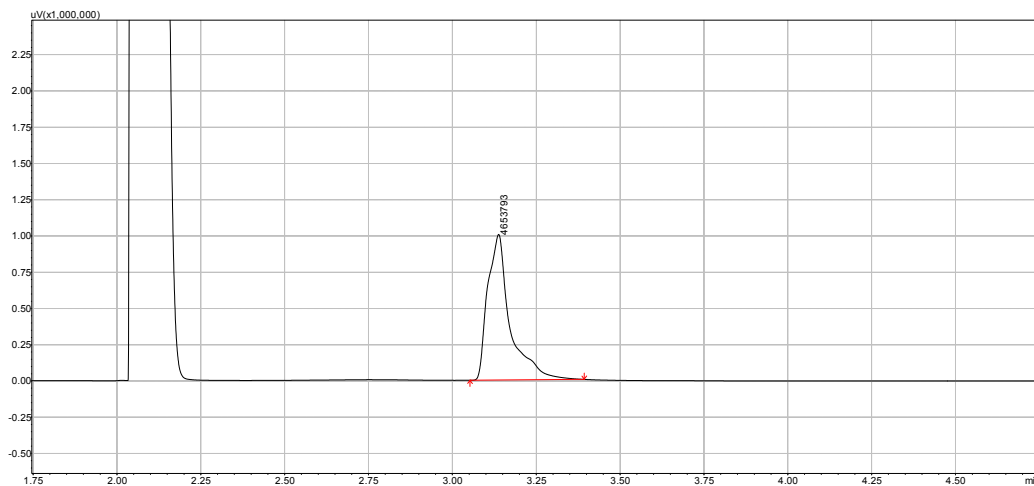


Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	2.658	812449.9	244344.7	100.00000	100.0000	cyclopentanone

Gas chromatogram for standard cyclohexanol

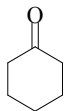


GC conditions for standard cyclohexanol. Column information Rtx-5, L = 30m, 0.25mmID, injector temperature 220 °C, column flow rate 0.90 ml/min, column temperature 100 – 120 °C, temperature program 5 °C/min, detector temperature 250 °C.

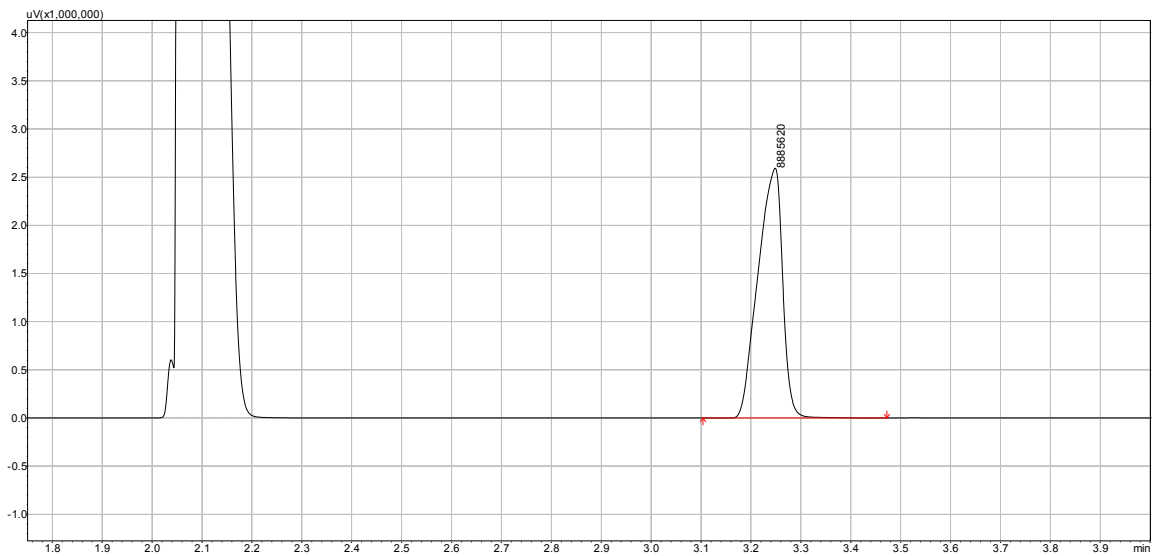


Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	3.138	4653792.8	999269.3	100.00000	100.0000	Cyclohexanol

Gas chromatogram for standard cyclohexanone



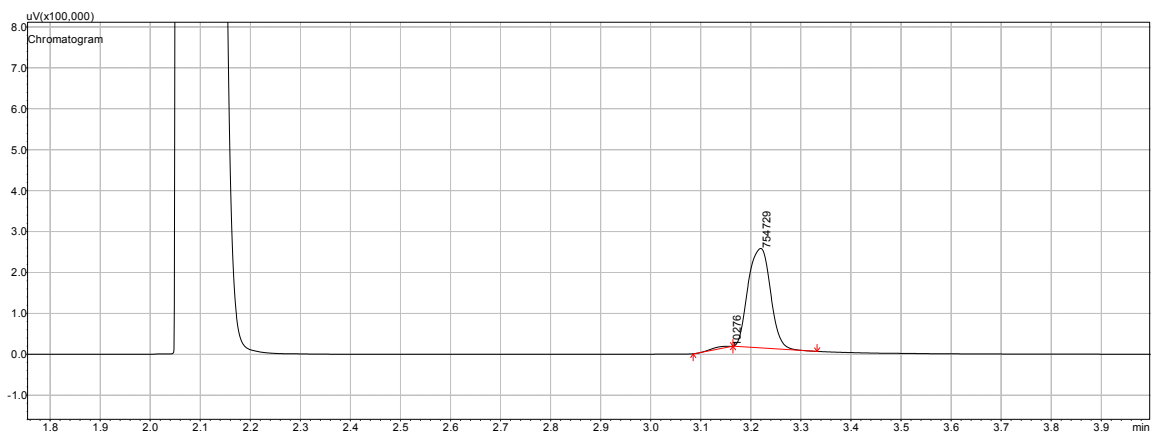
GC conditions are same as standard cyclohexanol.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	3.248	8885619.7	2558822.3	100.00000	100.0000	Cyclohexanone

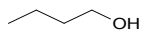
Gas chromatogram for the oxidation of cyclohexanol to cyclohexanone product

GC conditions are same as standard cyclohexanol.

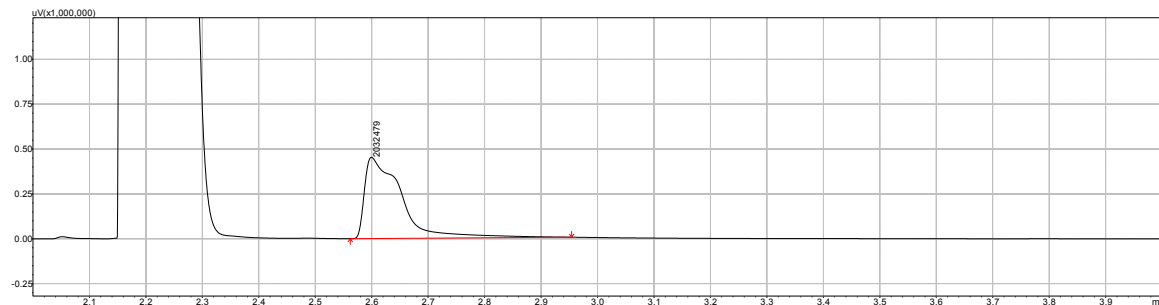


Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	3.160	10276.0	1021.0	1.34326	1.3433	cyclohexanol
2	3.219	754729.3	240360.1	98.65674	98.6567	cyclohexanone

Gas chromatogram for standard n-butanol

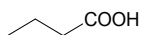


GC conditions for standard n-butanol. Column information Rtx-5, L = 30m, 0.25mmID, injector temperature 220 °C, column flow rate 0.96 ml/min, column temperature 70 – 120 °C, temperature program 3 °C/min, detector temperature 250 °C.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	2.600	2032479.3	447332.2	100.00000	100.0000	n-butanol

Gas chromatogram for standard butyric acid

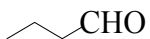


GC conditions are same as standard n-butanol.

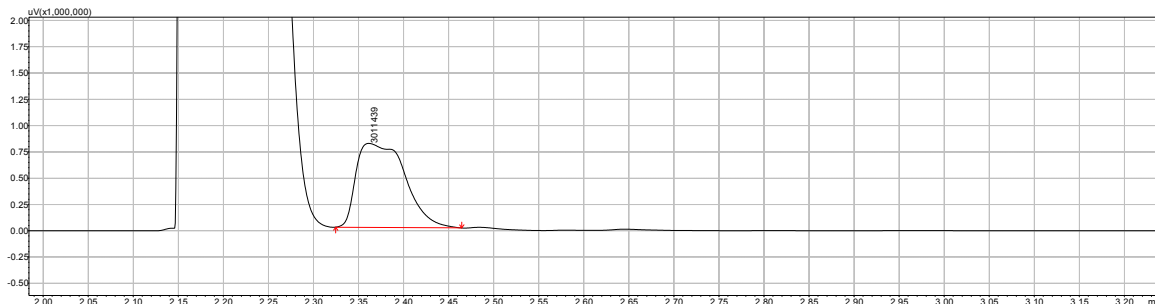


Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	3.947	2771521.8	164376.2	100.00000	100.0000	Butyric acid

Gas chromatogram for standard butyraldehyde



GC conditions are same as standard n-butanol.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	2.362	3011438.9	793325.7	100.00000	100.0000	Butyraldehyde

Gas chromatogram for the n-butanol oxidation product

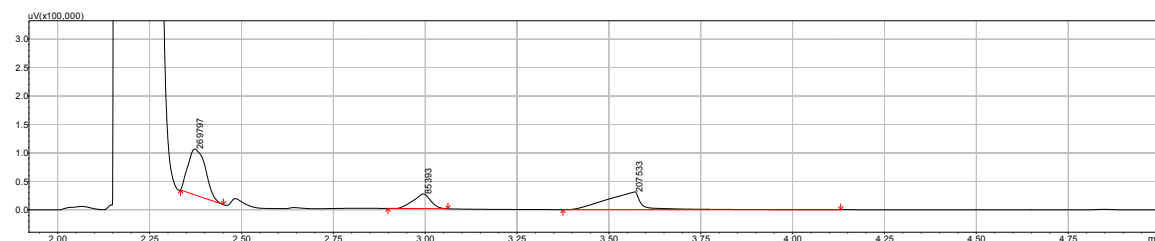
GC conditions are same as standard n-butanol.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	4.006	2964944.6	174506.4	100.00000	100.0000	Butyric acid

Gas chromatogram for the n-butanol oxidation product at 3h.

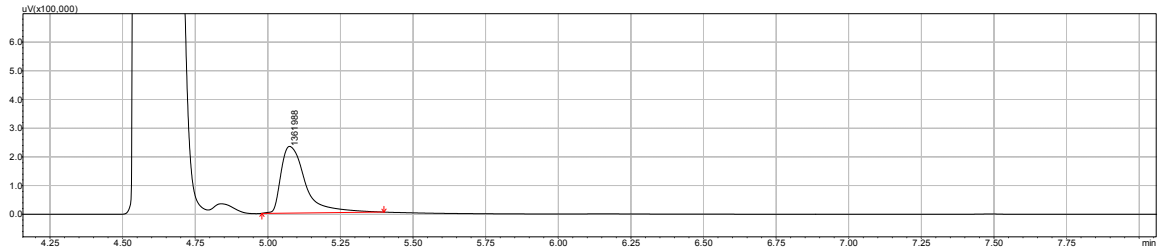
GC conditions are same as standard n-butanol.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	2.373	269797.4	80337.4	47.94493	47.9449	Butyraldehyde
2	2.995	85393.2	25701.9	15.17498	15.1750	n-butanol
3	3.569	207533.0	30959.9	36.88009	36.8801	Butyric acid

Gas chromatogram for standard n-butanol (GC column was damaged due to this GC conditions were reset)

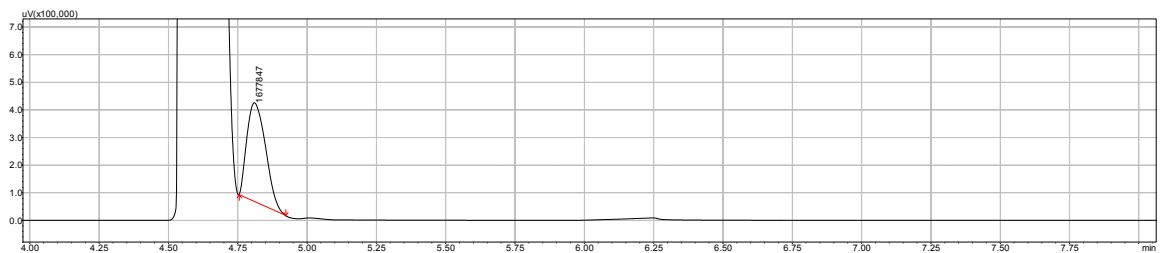
GC conditions for standard n-butanol. Column information Rtx-5, L = 30m, 0.25mmID, injector temperature 220 °C, column flow rate 0.35 ml/min, column temperature 60 – 90 °C, temperature program 3 °C/min, detector temperature 250 °C.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	5.075	1361987.6	232244.4	100.00000	100.0000	n-butanol

Gas chromatogram for standard butyraldehyde

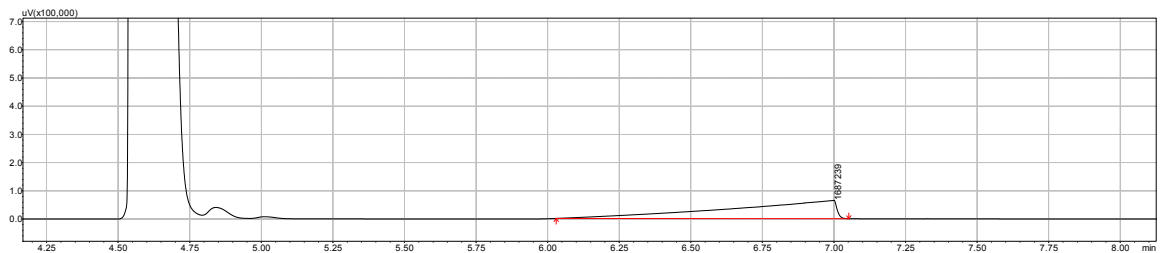
GC conditions are same as above standard n-butanol.



Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	4.810	1677847.3	353799.8	100.00000	100.0000	Butyraldehyde

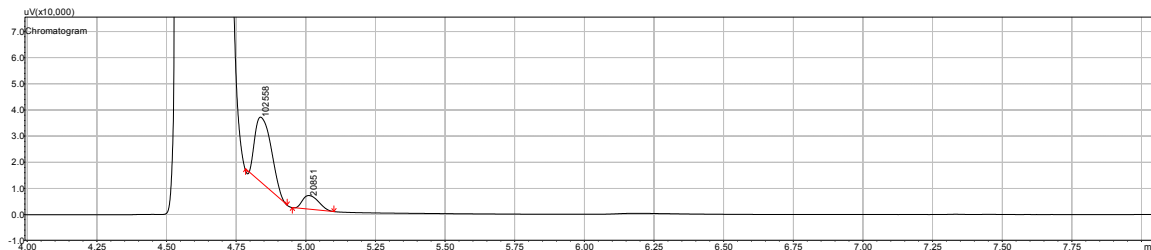
Gas chromatogram for standard butyric acid

GC conditions are same as above standard n-butanol.



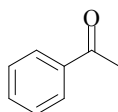
Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	6.997	1687238.8	64675.3	100.00000	100.0000	Butyric acid

Gas chromatogram for the n-butanol oxidation product (under N₂-atm) at 3 h.
 GC conditions are same as above standard n-butanol.

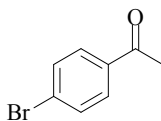


Peak#	Ret. time	Area	Height	Conc.	Area%	Compound name
1	4.838	102558.3	24713.4	83.10415	83.1041	Butyraldehyde
2	5.010	20851.1	5184.4	16.89585	16.8959	n-butanol

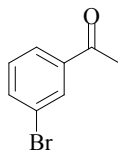
IV) ¹H NMR data for all the catalytic products



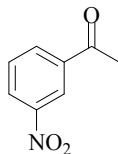
¹H NMR (400 MHz, CDCl₃): δ 7.94 – 7.91 (m, 2H, ArH); 7.55 – 7.52 (m, 1H, ArH); 7.45 – 7.41 (m, 2H, ArH); 2.57 (s, 3H, CH₃) ppm.



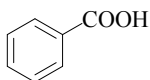
¹H NMR (400 MHz, CDCl₃) δ 7.81 – 7.78 (m, 2H, ArH); 7.59 – 7.57 (m, 2H, ArH); 2.56 (s, 3H, CH₃) ppm.



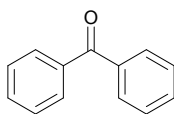
¹H NMR (400 MHz, CDCl₃) δ 7.99 – 7.98 (t, 1H, ArH); 7.79 – 7.77 (m, 1H, ArH); 7.60 – 7.59 (m, 1H, ArH); 7.27 – 7.24 (t, 1H, ArH); 2.50 (s, 3H, CH₃) ppm.



$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 8.75 – 8.74 (s, 1H, ArH); 8.41 – 8.39 (m, 1H, ArH); 8.28 – 8.25 (m, 1H, ArH); 7.68 – 7.64 (t, 1H); 2.67 (s, 3H) ppm.



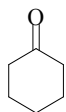
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 10.00 (s, 1H, COOH); 8.11 – 8.09 (d, 2H, ArH); 7.87 – 7.85 (t, 1H, ArH); 7.63 – 7.57 (t, 2H, ArH) ppm.



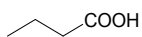
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 7.81 – 7.79 (m, 4H, ArH); 7.61 – 7.57 (m, 2H, ArH); 7.50 – 7.46 (m, 4H, ArH) ppm.



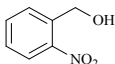
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.14 – 2.08 (t, 4H, 2CH₂); 1.94 – 1.87 (m, 4H, 3CH₂) ppm.



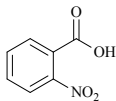
$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 2.33 – 2.27 (t, 4H, 2CH₂); 1.84 – 1.61 (m, 6H, 3CH₂) ppm.



$^1\text{H NMR}$ (400 MHz, CDCl_3) δ 9.99 (s, 1H, COOH); 2.32 – 2.28 (t, 2H, CH₂); 1.66 – 1.61 (m, 2H, CH₂); 0.96 – 0.91 (t, 3H, CH₃) ppm.



$^1\text{H NMR}$ (400 MHz, DMSO) δ 8.03 – 8.01 (d, 1H, ArH); 7.83 – 7.81 (d, 1H, ArH); 7.77 – 7.73 (t, 1H, ArH); 7.53 – 7.49 (t, 1H, ArH); 5.55 – 5.53 (t, 1H, OH); 4.81 – 4.80 (d, 2H, CH₂OH) ppm.



^1H NMR (400 MHz, DMSO) δ 10.2 (s, 1H, COOH); 7.73 – 7.68 (m, 2H, ArH); 7.65 – 7.57 (m, 2H, ArH) ppm.

Impurity

^1H NMR (400 MHz, DMSO) δ 7.92 – 7.90 (m, 1H, ArH); 7.81 – 7.79 (d, 1H, ArH), 7.73 – 7.71 (t, 2H, ArH); 7.49 – 7.45 (t, 1H, ArH); 7.41 – 7.37 (m, 2H, ArH); 5.45 – 5.42 (t, 1H, OH); 5.25 – 5.22 (t, 1H, OH); 4.75 – 4.74 (d, 2H, CH₂); 4.60 – 4.58 (d, 2H, CH₂) ppm.

Recycling and recovery of the catalyst

After completion of reaction the organic product was separated by diethyl ether and the catalyst remain in aqueous phase. The separated aqueous phase was reused for further catalysis without adding of extra catalyst and the catalyst was also recovered by the following procedure. The aqueous phase was evaporated at room temperature. A solid material obtained was washed with ethanol and the precipitate was air-dried. Then a solid compound was collected and characterized with FT-IR. The FT-IR spectrum of used catalyst after 5th cycle was same as fresh catalyst (see figure S2). The same procedure was applied for all POM catalysts.

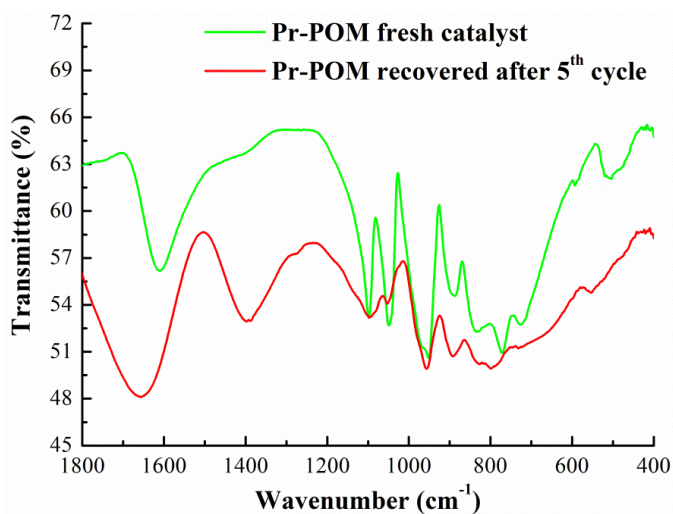


Figure S2 Comparison of FT-IR spectra of fresh **Pr-POM** and recovered solid **Pr-POM** catalyst after 5th cycle.

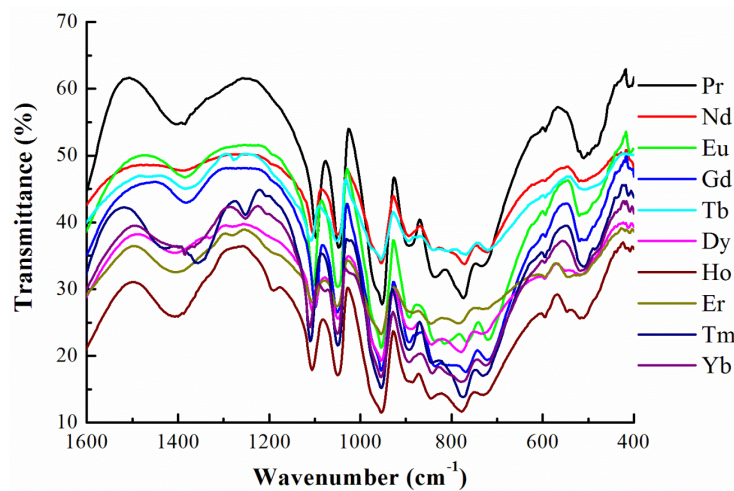


Figure S3 The FT-IR spectra of **Pr – Yb** recovered POM catalysts after 1st cycle.