Supporting Information

Solvent-free and Melt Aerobic Oxidation of Benzyl Alcohols Using Pd@Cu2(BDC)2DABCO Prepared Through Reduction by Dimethylformamide

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Materials and instruments

All reagents including organic linker H2BDC, metal salt Cu(OAc)2.H2O, 1,4-benzenedicarboxylate (BDC, 99%), 1,4-diazabicyclo[2.2.2]octane (DABCO), Palladium (II) chloride (PdCl2), benzyl alcohols and solvent were obtained from commercially available sources such as Sigma–Aldrich and Merck without any purification. X-ray powder diffraction (XRD) measurements were performed using an X'pert MPD. Philips diffractometer with Cu radiation source (λ = 1.54050˚A) at 40 Kv voltage and 40 mA current. BET (Brunauer-Emmett-Teller) surface area of the samples was determined from N2 adsorption–desorption isotherms using a micromeritics ASAP 2020 analyzer. The sample was characterized using a scanning electron microscope (SEM) with a ZEISS at 30 kV with gold coating. Transmission electron microscopy (TEM) was carried out using an EM10C-100kV series microscope from the Zeiss Company, Germany. The actual loading of palladium was determined by Inductively Coupled Plasma (ICP) analysis on sequential plasma spectrometer, Shimadzu (ICPS-7000 ver. 2). X-ray photoelectron spectroscopy (XPS) measurements were conducted on a PHI Quantum 2000 XPS system equipped with an Al Xray source (1486.6 eV). 1H-NMR spectra were measured (CDCl3) with a Bruker DRX-500 AVANCE spectrometer at 400.13. Melting points were measured on an Electrothermal 9100 apparatus and GC analysis of determination of conversions and selectivities was performed on an Agilent 6890N.

One-step Supporting of Palladium Nanoparticle ($Pd@Cu_2(BDC)_2(DABCO)$)

[$Cu_2(BDC)_2DABCO$] was synthesis by that are reported in our previous work [44]. A mixture of $Cu(OAc)_2.H_2O$ (0.6 mmol), H_2BDC (0.6 mmol) and DABCO (0.3 mmol) with molar ratio of 2:2:1 were ball-milled vigorously at 28 Hz at room temperature for 2 hours. The obtained green powder was washed with DMF (3 × 10 mL). Solvent exchange was carried out with methanol (3 × 10 mL) at room temperature. To remove the guest molecules of MOFs, obtained powder was treated by heating under vacuum at 130 °C for 12 hours, resulting in 1.6 g of pure product which corresponds to 94% isolated yield. 0.1 g of the synthesized MOF was dissolved in 2 cc of DMF and then 3 mg of $PdCl_2$ with purity of 99.9% were added to the mixture. The solution was sonicated for 20 min, then stirred at 80˚ C for 20 h and finally it was stirred at 130˚C with the purpose of reduction of Pd(II) to Pd (0) and encapsulation in MOF. Finally, the product (Pd NPs@$Cu_2(BDC)_2$(DABCO) was centrifuged, washed with DMF and methanol and dried in vacuum at 120 °C for 12 h.

Catalyst Usage for the oxidation of benzyl alcohols

In a typical oxidation, 0.5 ml substrate (grams for the solid benzyl alcohols), catalysts and base used as described in the manuscript and were added into a 10-ml three-neck round-bottom flask, which was fitted with a magnetic stirrer and an air inlet tube. The reaction was performed at 120 °C in an oil bath with magnetic stirring. A stream of air produced by air pump was conducted into the reaction mixture and controlled by a flow meter at a constant flow rate (5 ml min^{-1}). After completion of the reaction that monitored by TLC, ethyl acetate was added to the reaction mixture and catalyst was filtered. Then, the filtrate was analyzed by GC. Solvent was evaporated under reduced pressure. All of the aldehydes characterized by melting point (for solids) and ^1H-NMR spectroscopy and confirmed with what is reported in the literature [48-52].

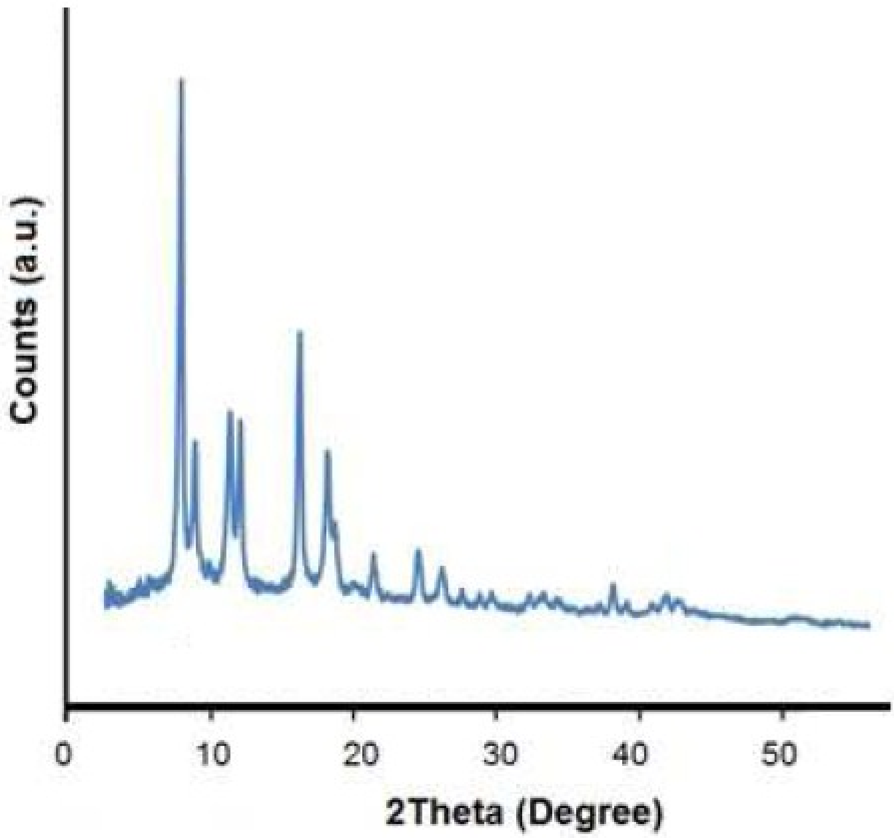


Fig S1. a) XRD pattern of recycling PdNPs@$Cu_2(BDC)_2$(DABCO)

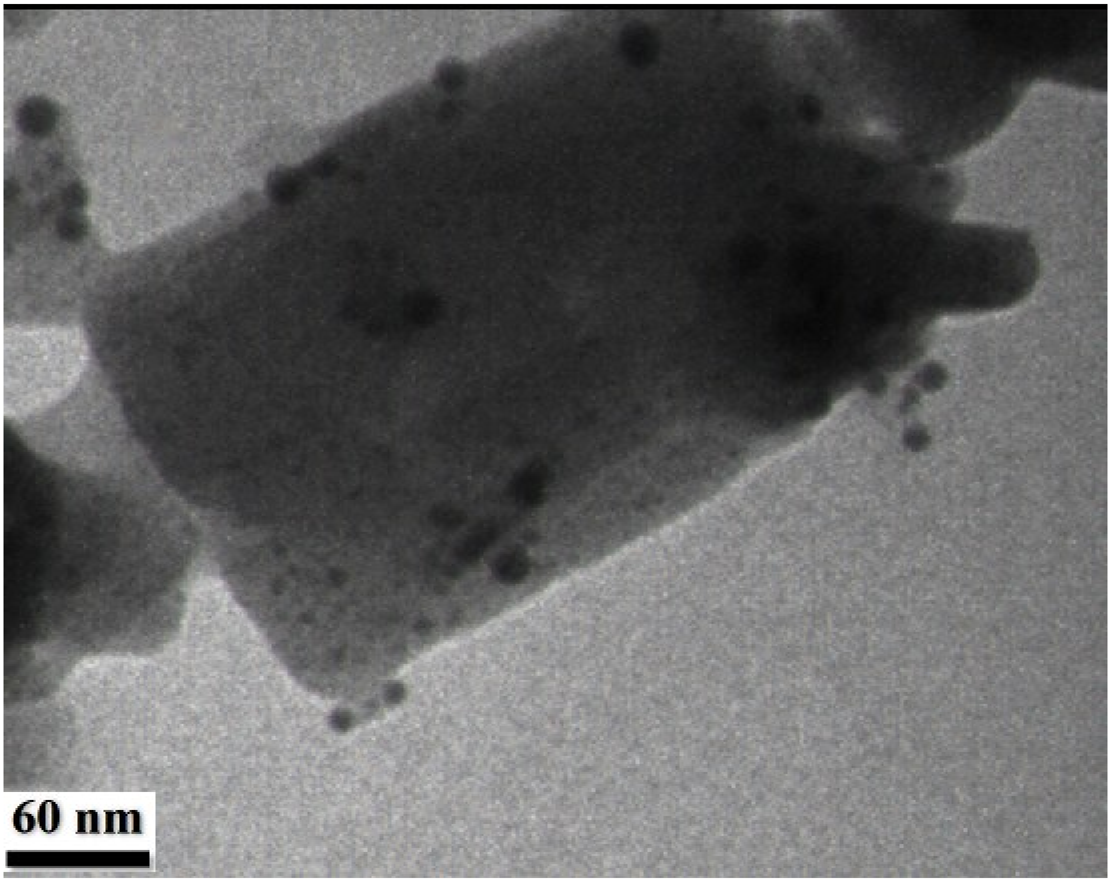


Fig S2. TEM micrograph of the recycled PdNPs/$Cu_2(BDC)_2$DABCO

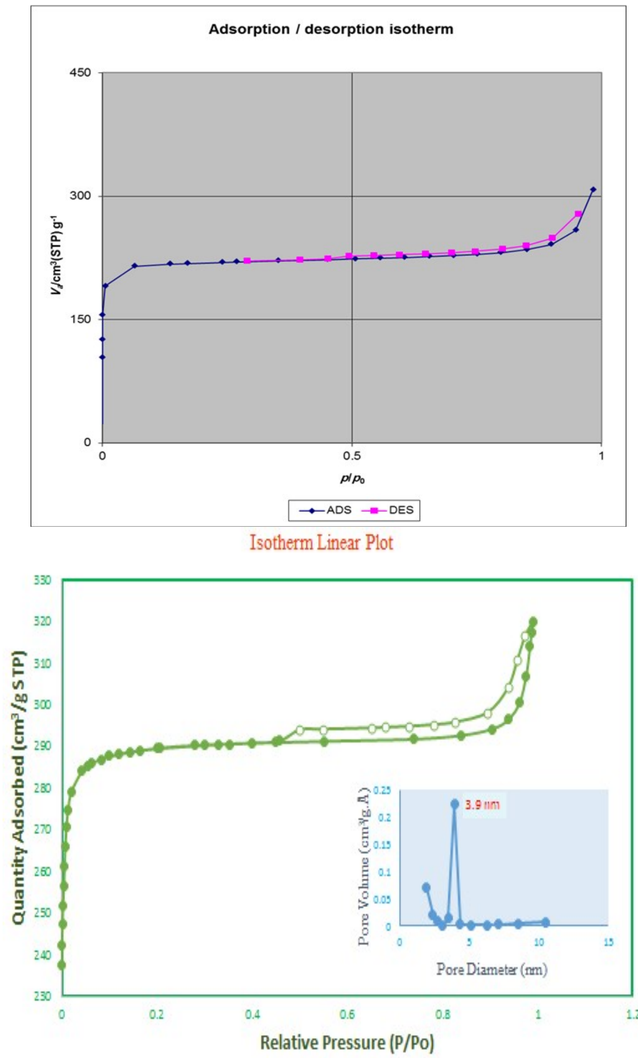


Fig S3. The N_2 adsorption–desorption isotherms of the nanoporous [$Cu_2(BDC)_2(DABCO)$] (Right) and PdNPs@[$Cu_2(BDC)_2(DABCO)$] (Left)

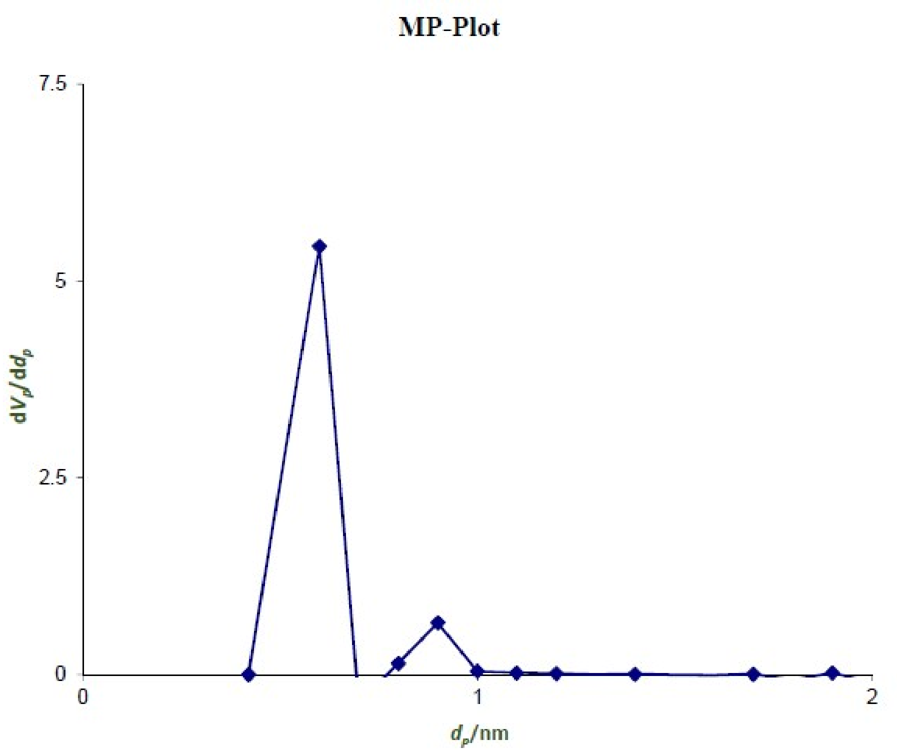


Fig S4. MP-Plot of the as-synthesized $Cu_2(BDC)_2(DABCO)$

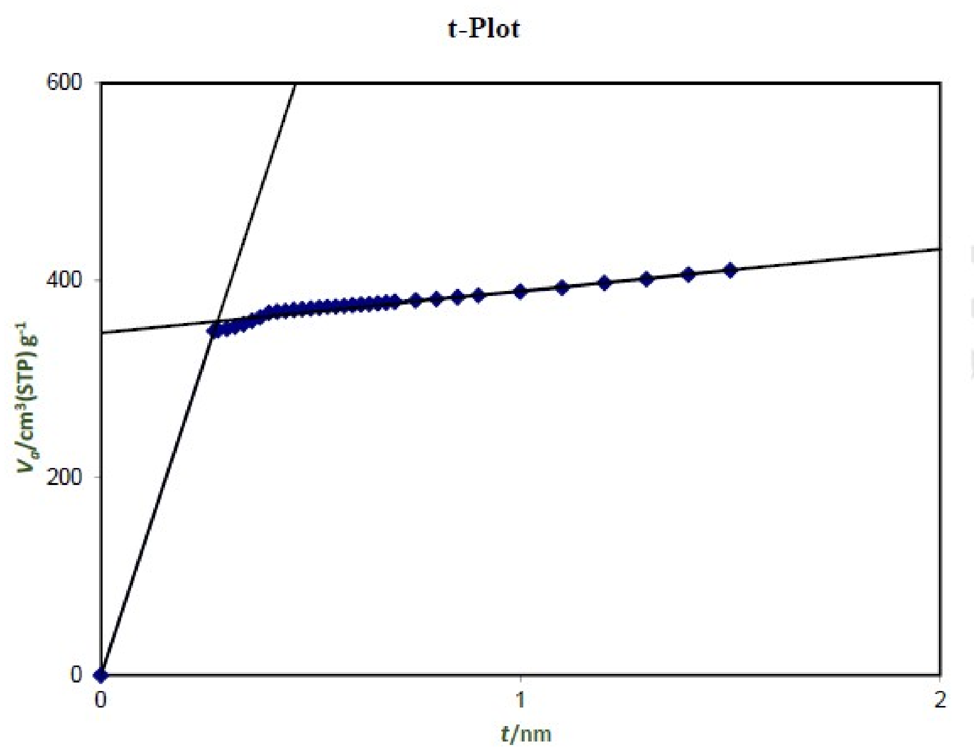


Fig S5. t-Plot of the as-synthesized $Cu_2(BDC)_2(DABCO)$

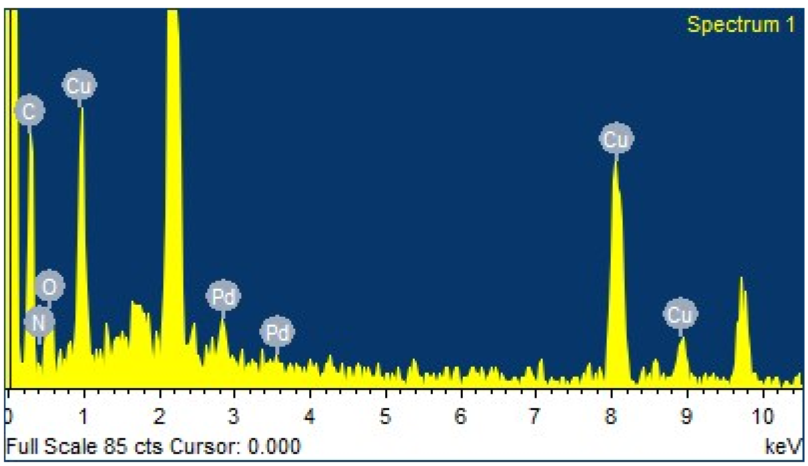


Fig S7. EDX analysis of Pd-NPs@$Cu_2(BDC)_2$DABCO

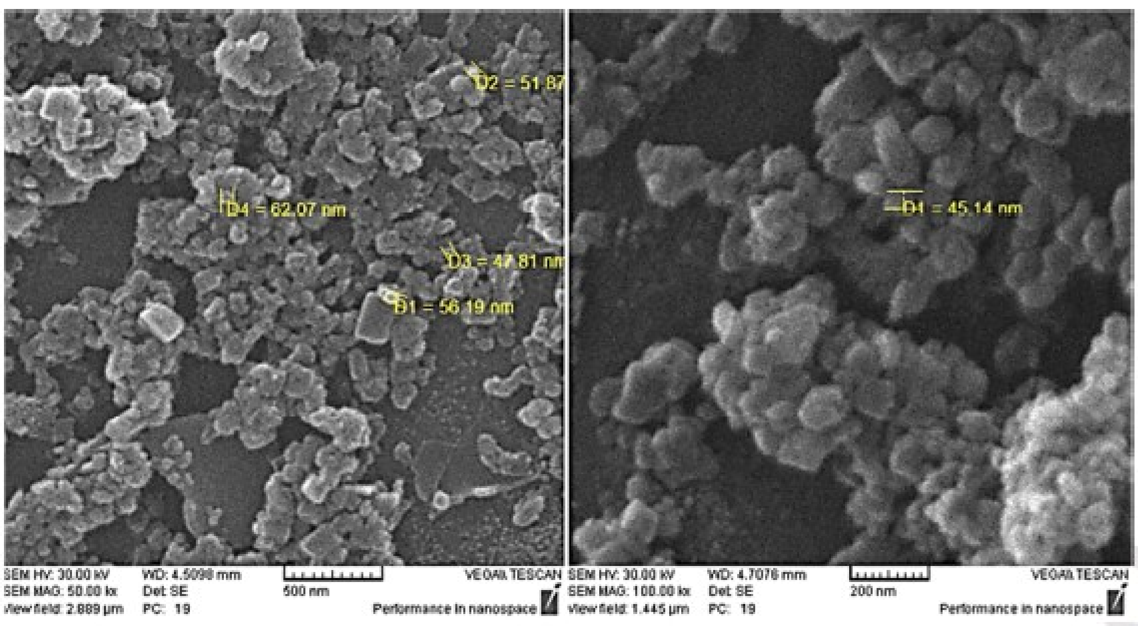
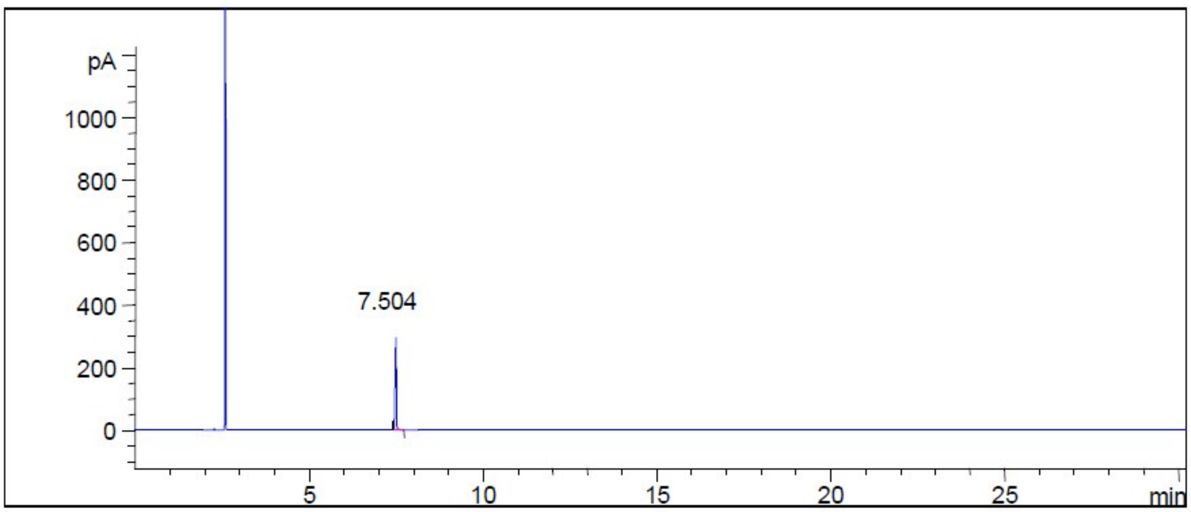


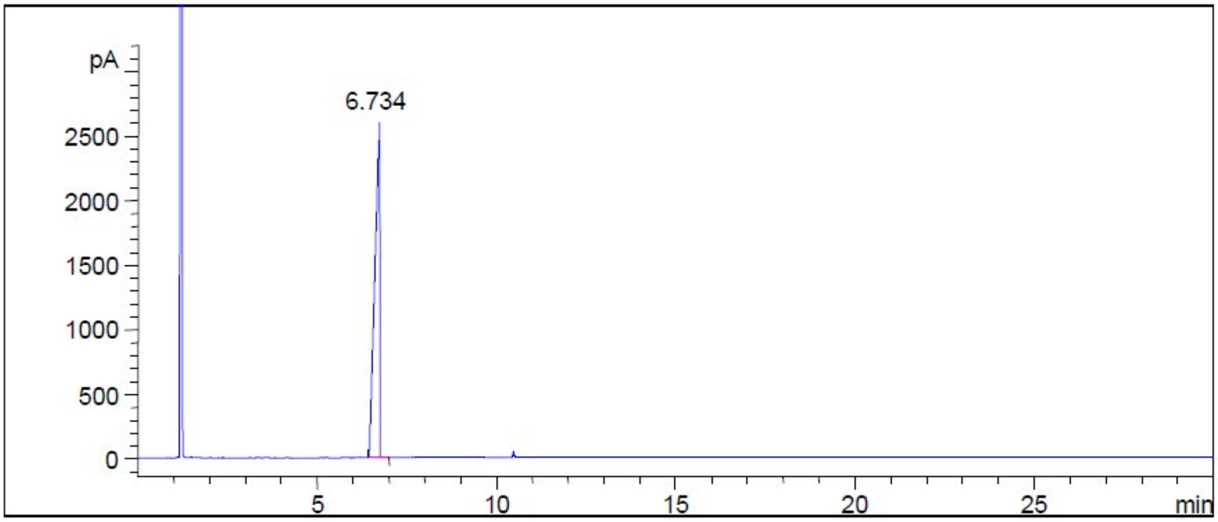
Fig S8. SEM image of $Cu_2(BDC)_2DABCO$

GC diagrams of Benzyl alcohols and Benzaldehydes:



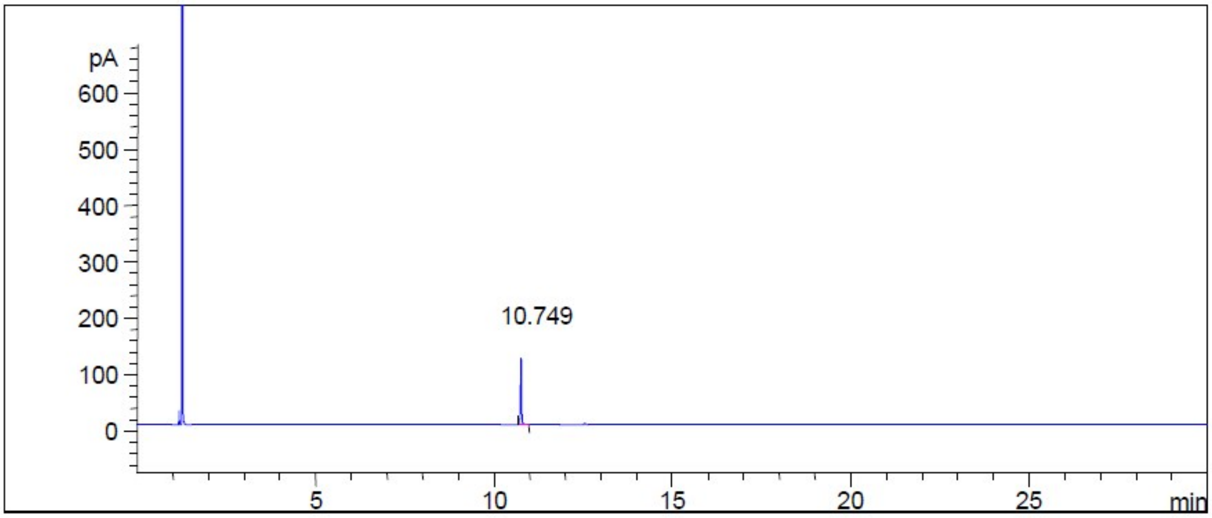
Peak	Ret. Time(min)	Area	Height	Width	Area(%)	Symmetry
1	7.504	806.4	295.1	0.0384	100.00	1.867
	Totals:	806.4	295.1		100.000	

Fig S9. GC of benzyl alcohol



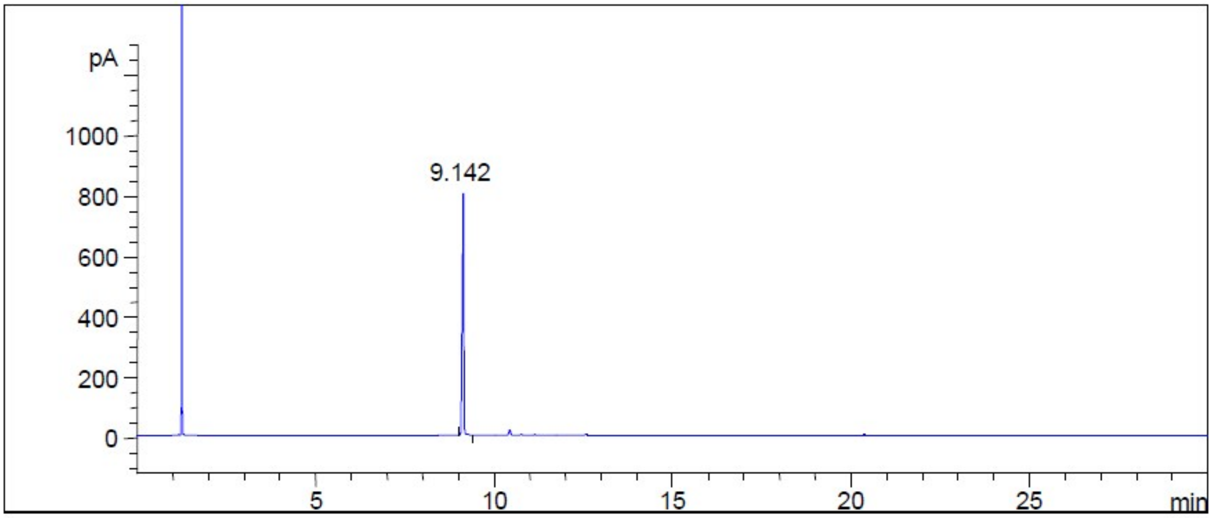
Peak	Ret. Time(min)	Area	Height	Width	Area(%)	Symmetry
1	6.734	23741.0	2593.5	0.1108	100.000	15.867
	Totals:	23741.0	2593.5		100.000	

Fig S10. GC of oxidation of benzyl alcohol



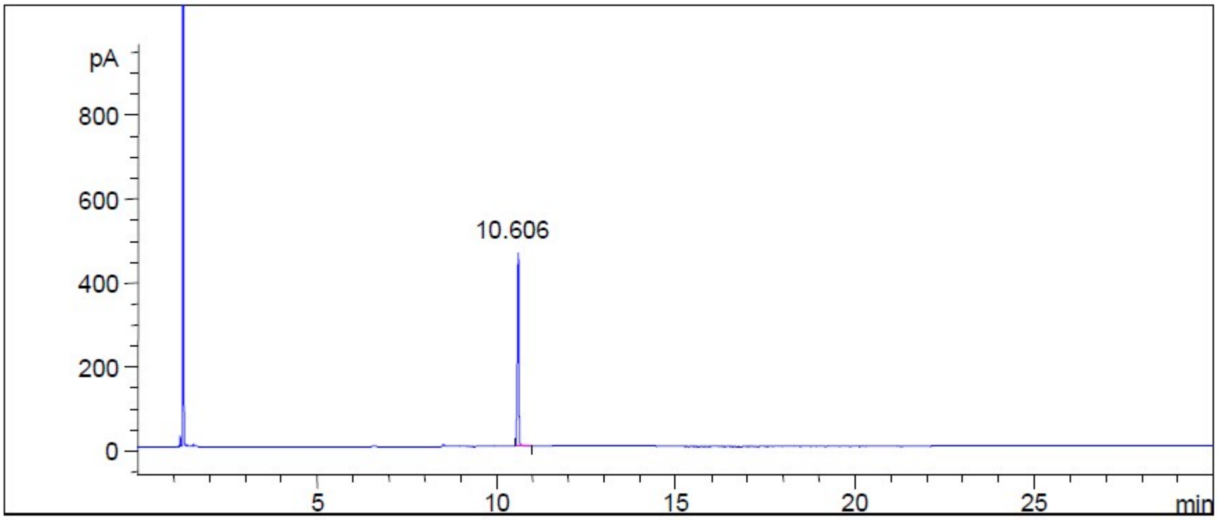
Peak	Ret. Time(min)	Area	Height	Width	Area(%)	Symmetry
1	10.749	309.3	118.6	0.0399	100.000	0.981
	Totals:	309.3	118.6		100.000	

Fig S11. GC of 2-methylbenzyl alcohol



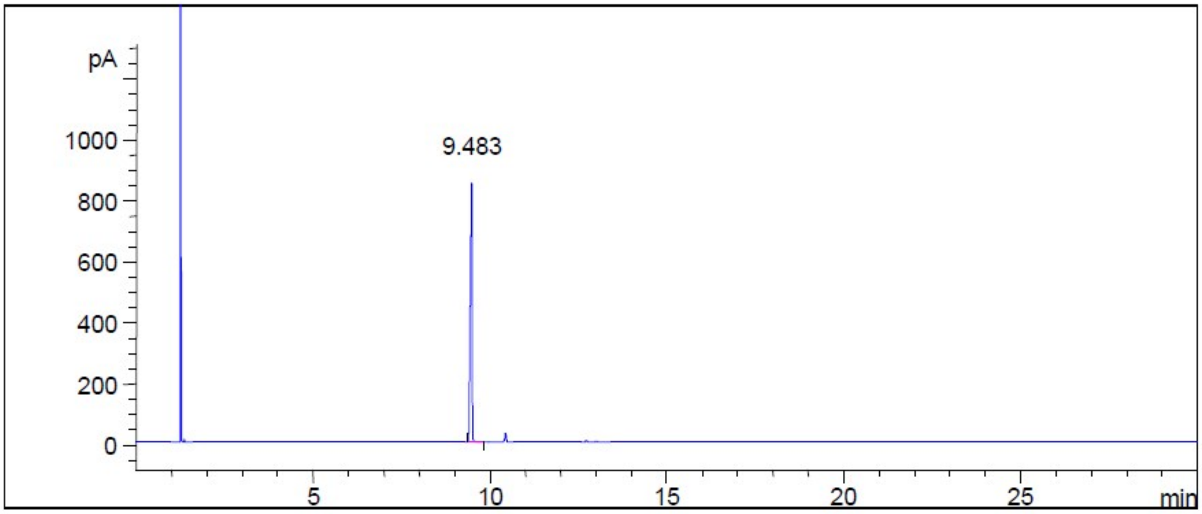
Peak	Ret. Time(min)	Area	Height	Width	Area(%)	Symmetry
1	9.142	2631.7	799.8	0.0484	100.000	2.070
	Totals:	2631.7	799.8		100.000	

Fig S12. GC of oxidation of 2-methylbenzyl alcohol



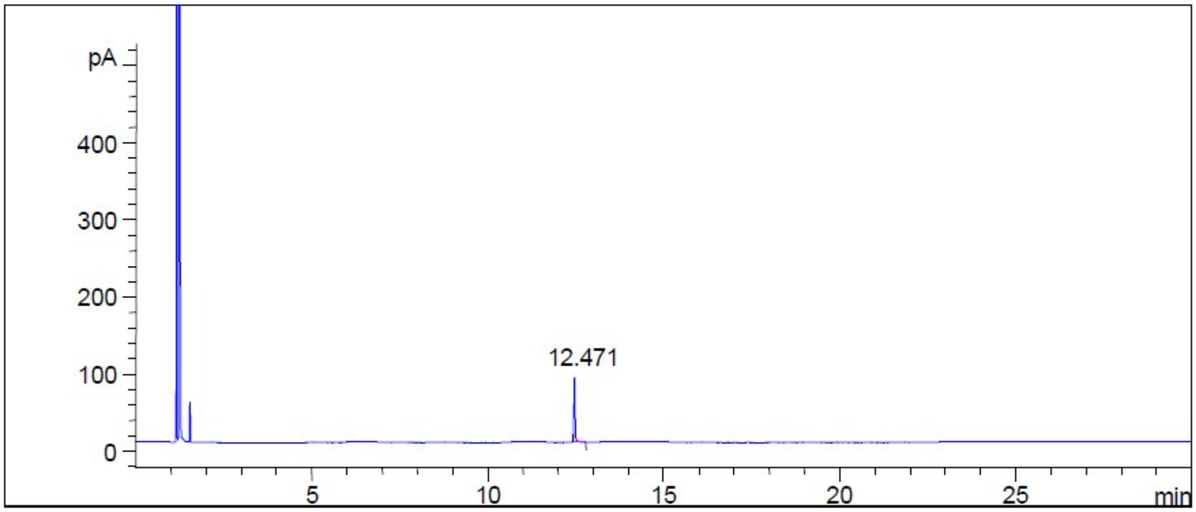
Peak	Ret. Time(min)	Area	Height	Width	Area(%)	Symmetry
1	10.606	1413.5	460.9	0.0413	100.000	2.207
	Totals:	1413.5	460.9		100.000	

Fig S13. GC of 4-methylbenzyl alcohol



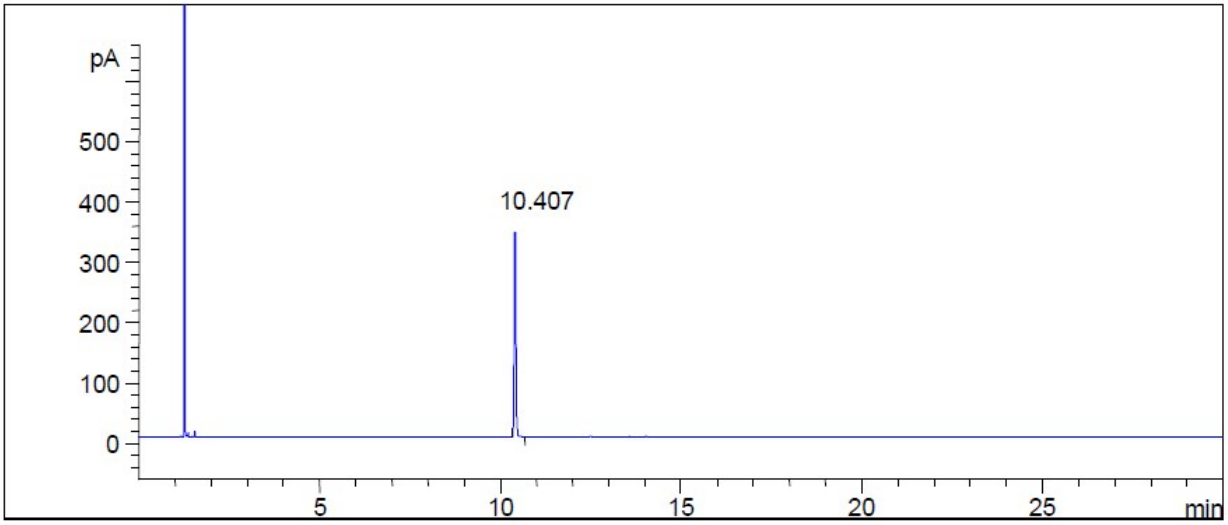
Peak	Ret. Time(min)	Area	Height	Width	Area(%)	Symmetry
1	9.483	2843.2	849.9	0.0470	100.000	2.571
	Totals:	2843.2	849.9		100.000	

Fig S14. GC of oxidation of 4-methylbenzyl alcohol



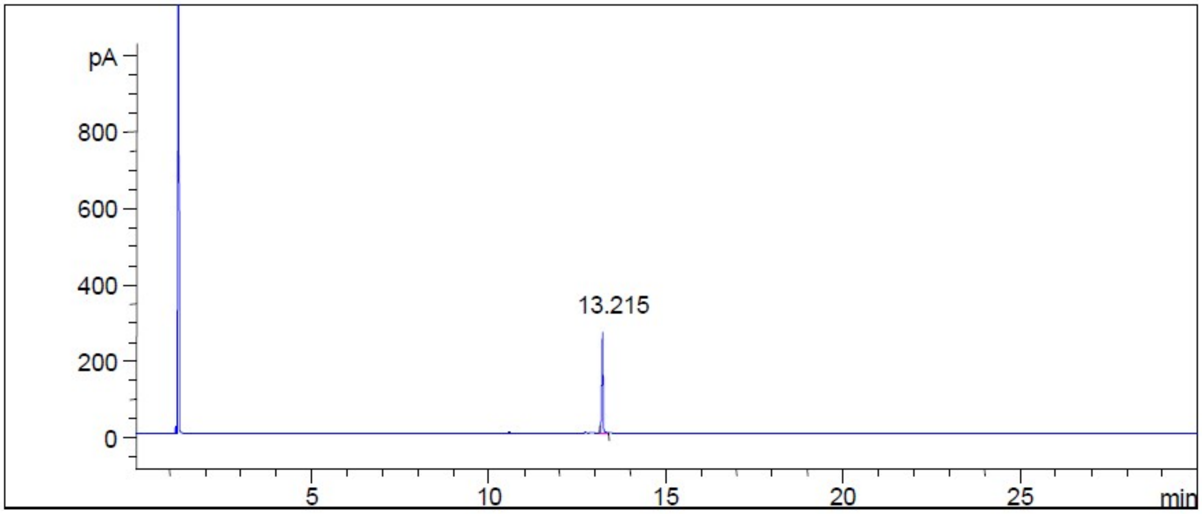
Peak	Ret. Time(min)	Area	Height	Width	Area(%)	Symmetry
1	12.471	223.5	83.9	0.0401	100.000	0.887
	Totals:	223.5	83.9		100.000	

Fig S15. GC of 4-bromobenzyl alcohol



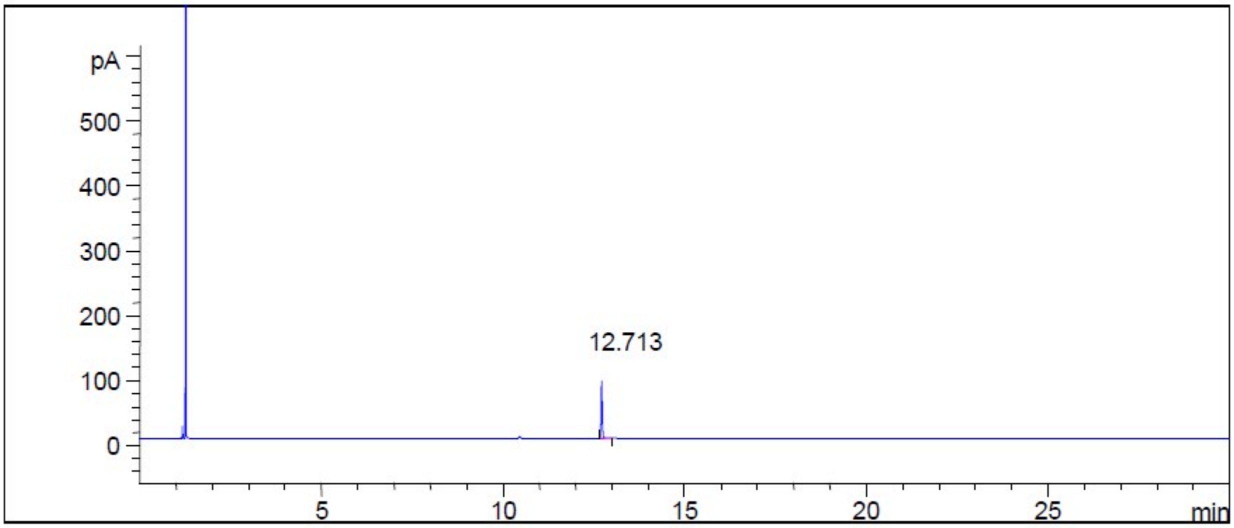
Peak	Ret. Time(min)	Area	Height	Width	Area(%)	Symmetry
1	10.407	993.3	339.5	0.0441	100.000	1.096
	Totals:	993.3	339.5		100.000	

Fig S16. GC of oxidation of 4-bromobenzyl alcohol



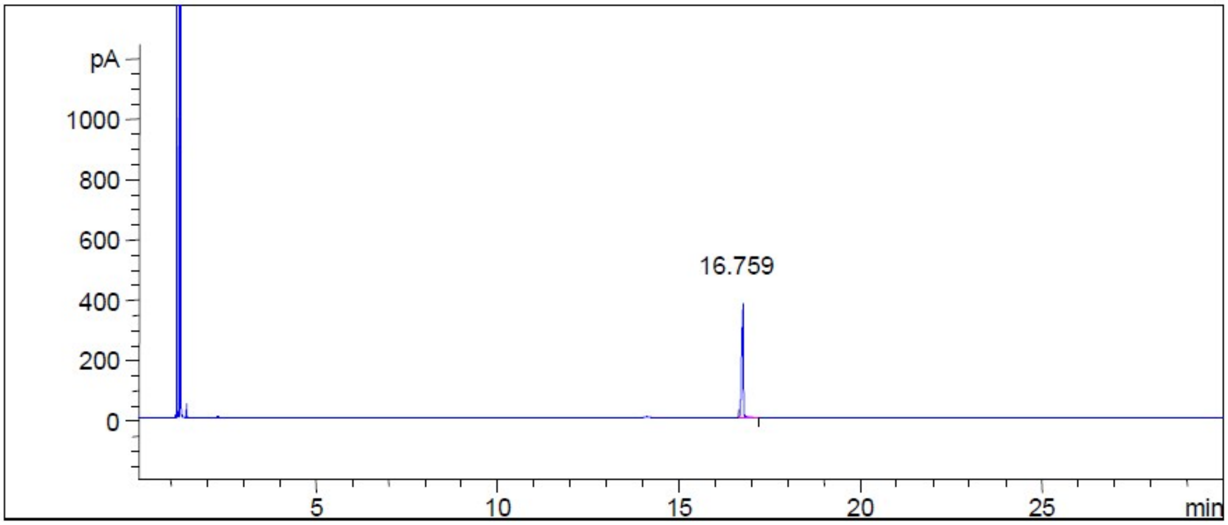
Peak	Ret. Time(min)	Area	Height	Width	Area(%)	Symmetry
1	13.215	711.0	264.0	0.0404	100.000	1.526
	Totals:	711.0	264.0		100.000	

Fig S17. GC of 4-methoxybenzyl alcohol



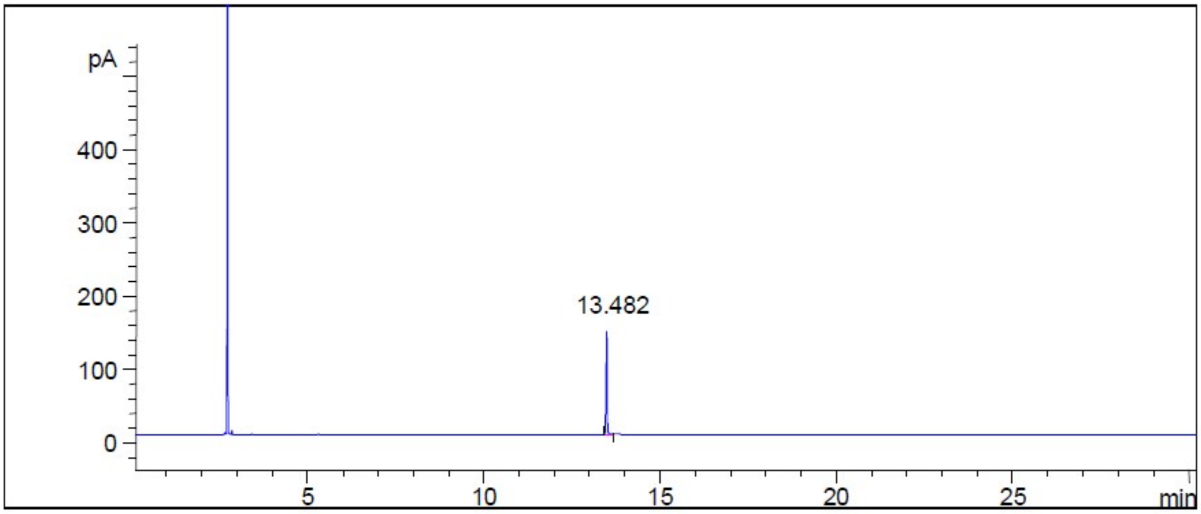
Peak	Ret. Time(min)	Area	Height	Width	Area(%)	Symmetry
1	13.215	216.8	87.8	0.0383	100.000	0.930
	Totals:	216.8	87.8		100.000	

Fig S18. GC of oxidation of 4-methoxybenzyl alcohol



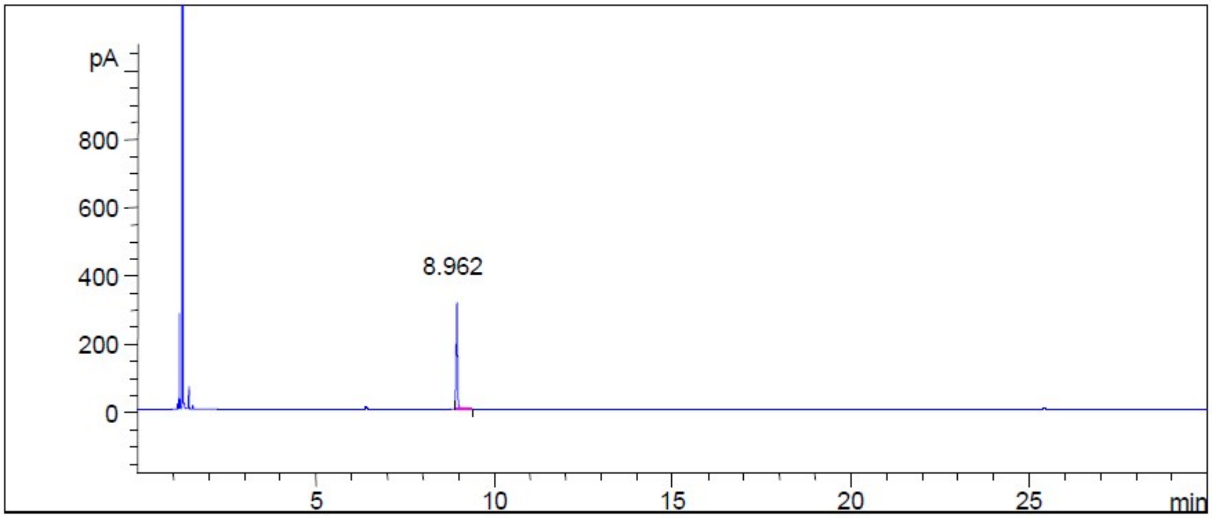
Peak	Ret. Time(min)	Area	Height	Width	Area(%)	Symmetry
1	16.759	1215.0	377.6	0.0430	100.000	2.900
	Totals:	1215.0	377.6		100.000	

Fig S19. GC of 4-nitrobenzyl alcohol



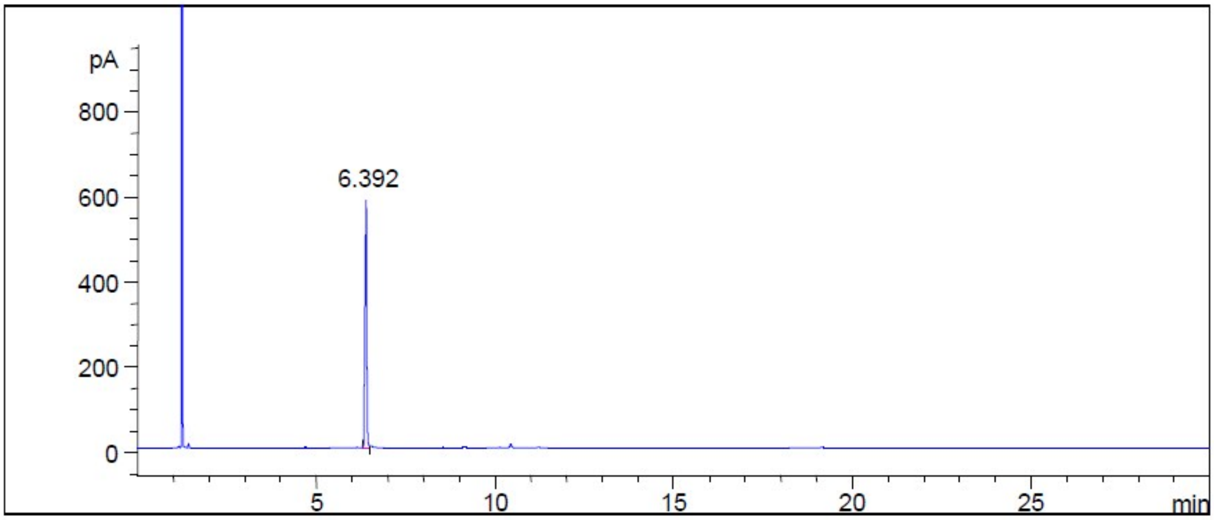
Peak	Ret. Time(min)	Area	Height	Width	Area(%)	Symmetry
1	13.482	341.4	140.7	0.0363	100.000	1.418
	Totals:	341.4	140.7		100.000	

Fig S20. GC of oxidation of 4-nitrobenzyl alcohol



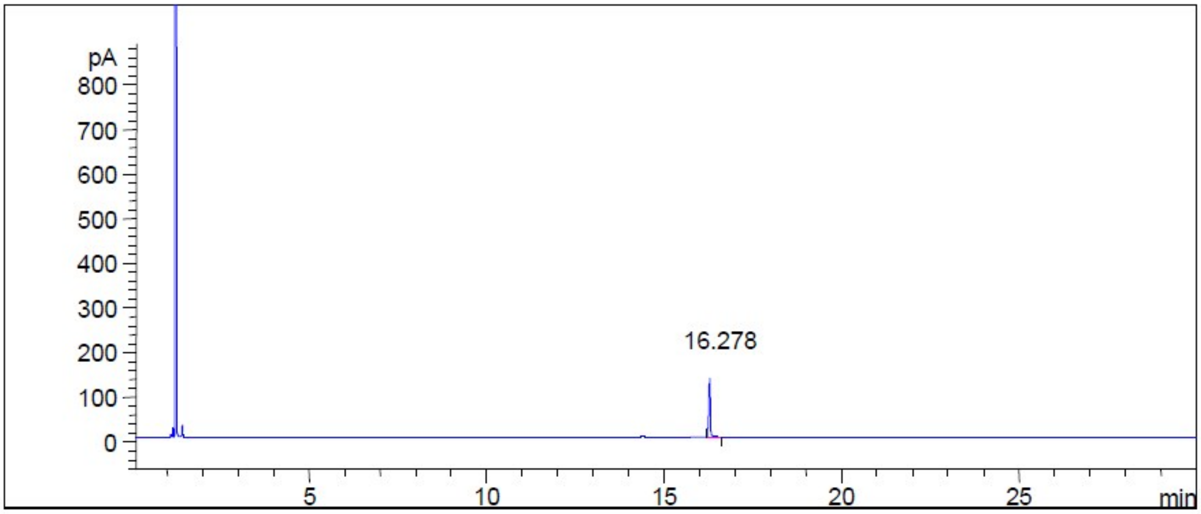
Peak	Ret. Time(min)	Area	Height	Width	Area(%)	Symmetry
1	8.962	927.5	310.9	0.0433	100.000	1.258
	Totals:	927.5	310.9		100.000	

Fig S21. GC of 4-chlorobenzyl alcohol



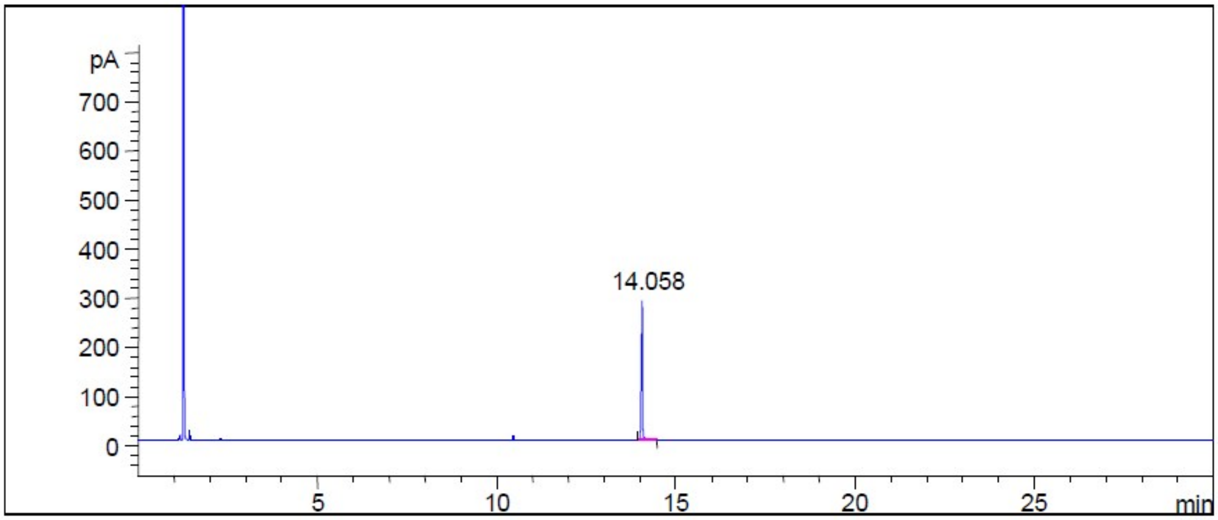
Peak	Ret. Time(min)	Area	Height	Width	Area(%)	Symmetry
1	6.392	2166.0	581.0	0.0535	100.000	1.795
	Totals:	2166.0	581.0		100.000	

Fig S22. GC of oxidation of 4-chlorobenzyl alcohol



Peak	Ret. Time(min)	Area	Height	Width	Area(%)	Symmetry
1	16.278	341.4	140.7	0.0363	100.000	1.418
	Totals:	341.4	140.7		100.000	

Fig S23. GC of 2-nitrobenzyl alcohol



Peak	Ret. Time(min)	Area	Height	Width	Area(%)	Symmetry
1	14.058	789.7	284.0	0.0399	100.000	1.580
	Totals:	789.7	284.0		100.000	

Fig S24. GC of oxidation of 2-nitrobenzyl alcohol

Selected ^{1}H-NMR spectra:

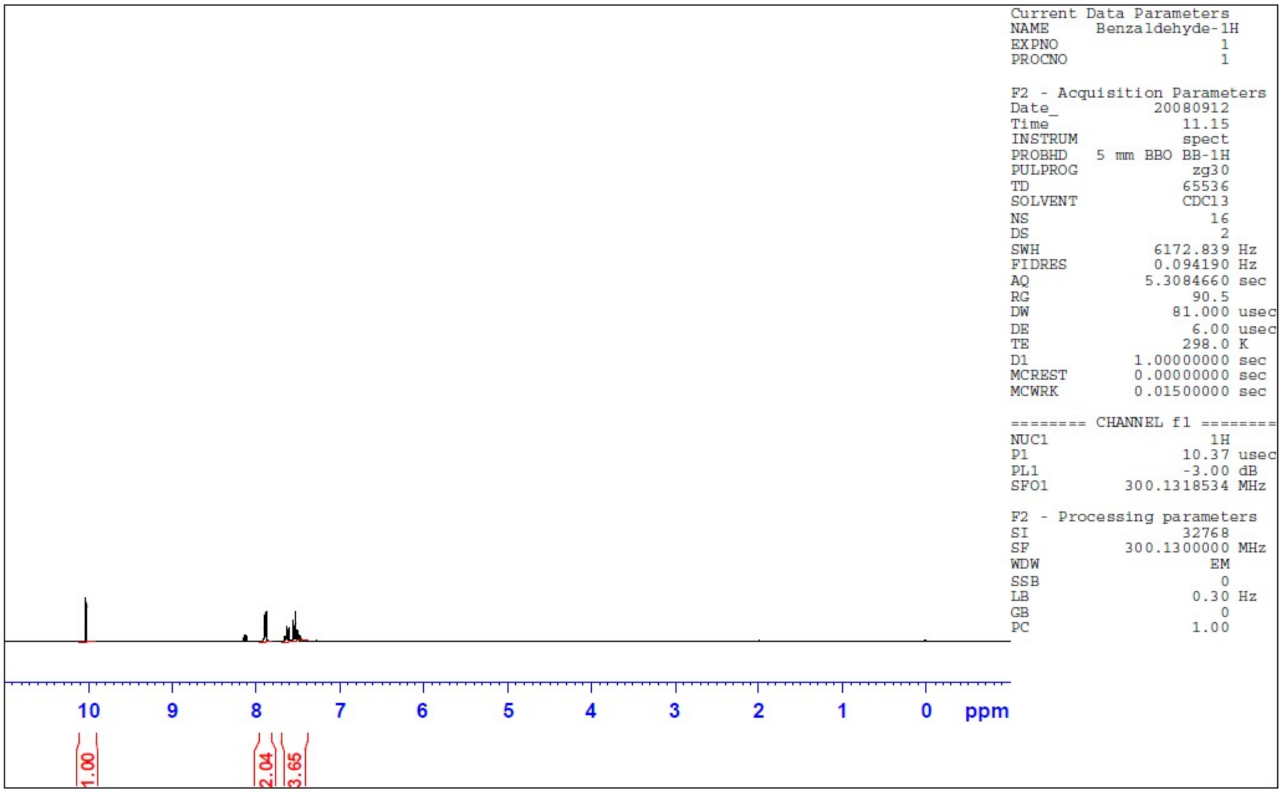


Fig S25. ^{1}H-NMR of Benzaldehyde

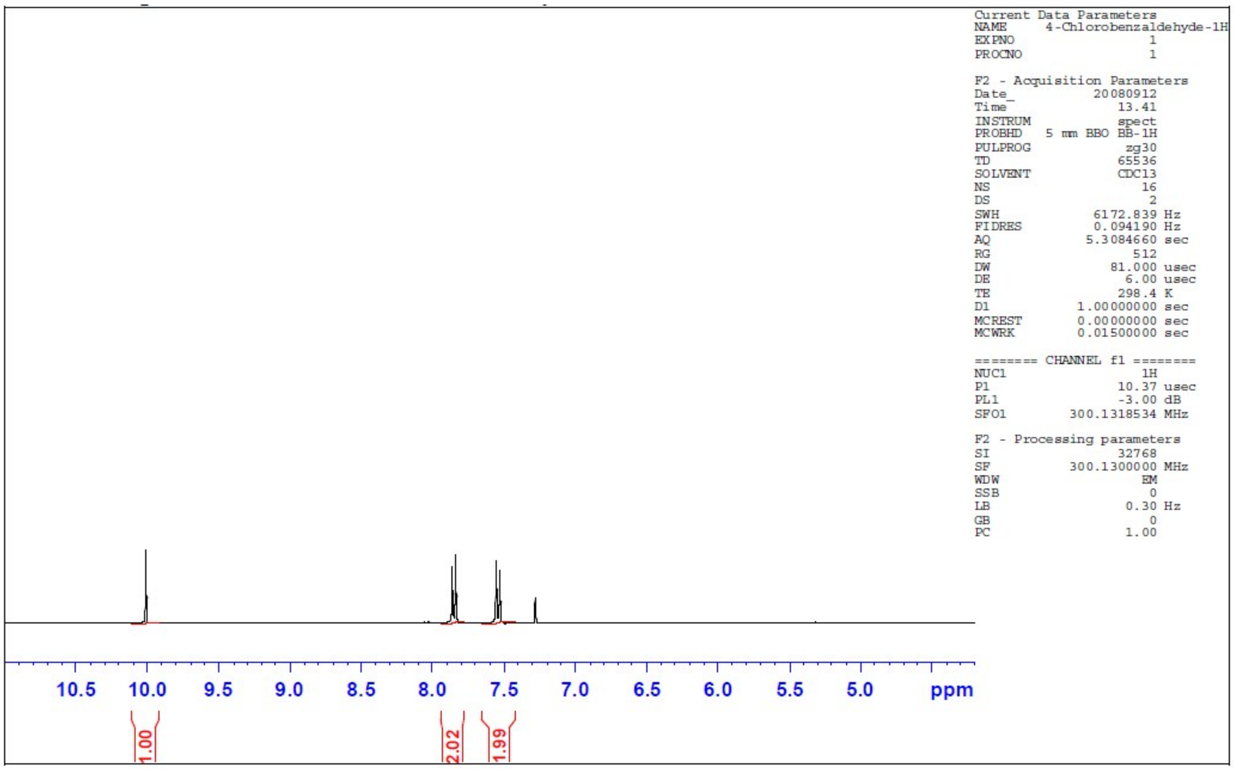


Fig S26. ^{1}H-NMR of 4-chlorobenzaldehyde