

Constructing Two Dimensional Amide Porous Polymer to Promote Selective Oxidation Reactions

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Materials and methods

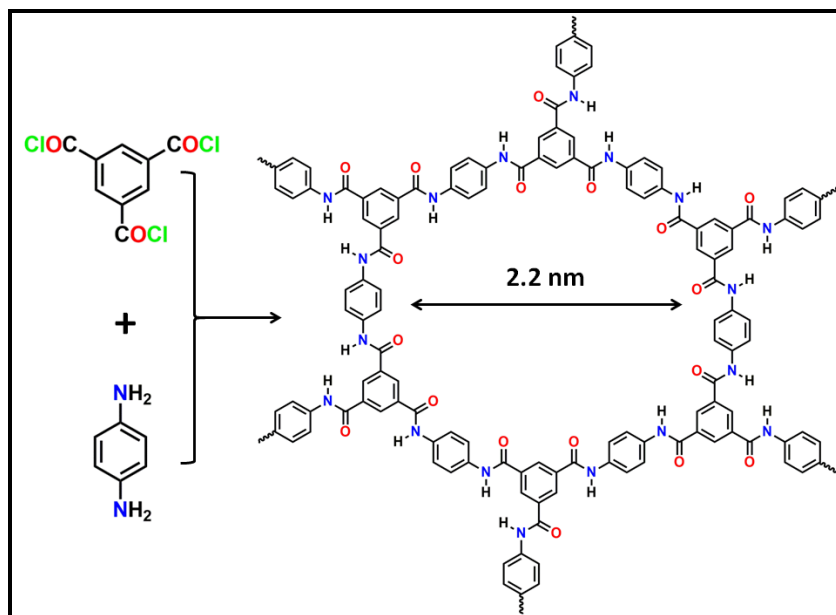
All chemicals and reagents utilized in the experiments were brought from commercial sources and used as received without further purification. 1,3,5-benzenetricarbonyl trichloride and *p*-phenylenediammine are brought from Alfa Aesar. The benzyl alcohols were imported from Himedia and the solvents employed are purchased from Merck.

Powder X-ray diffraction were recorded in Bruker diffractometer using monochromated Cu K α ($\lambda = 1.542 \text{ \AA}$) radiation. The FTIR spectra of starting and the synthesized COF-Am were obtained from Perkin Elmer spectrophotometer. Thermogravimetric analyses (TGA) was performed on Shimadzu 60 thermal analyzer under continuous nitrogen flow. TGA was recorded at heating rate of $10 \text{ }^{\circ}\text{C min}^{-1}$ under a nitrogen flow. The Quantchome Novawin (version 10.01) surface analyzer has been used to measure the N₂ adsorption isotherm and calculation of surface area. Ultra high purity nitrogen (99.999% pure) was considered for the measurement and the temperature during the process was controlled via refrigerated bath of liquid nitrogen (77K). Scanning electron microscope (SEM) images were recorded in JEOL JSM 6390 to examine the surface morphology of the material. Transmission electron microscope (TEM) images were recorded in JEOL JEM 2100 at the accelerating voltage of 200 kV. Solid UV-spectra was collected in Shimadzu UV-vis spectrophotometer. Solid state ¹³C CP-MAS NMR data has been recorded in Jeol 400 MHz spectrophotometer with spin rate of 5000 Hz employing 4mm MAS probe. The progress of the oxidation reactions of benzylalcohols was monitored by TLC using TLC silica gel F254 250 μm precoated-plates from Merck. Further product formation was confirmed via recording GC-MS spectrophotometer of the isolated reaction mixture. Theoretical calculation was obtained using Gaussian 9.0 programme suite.

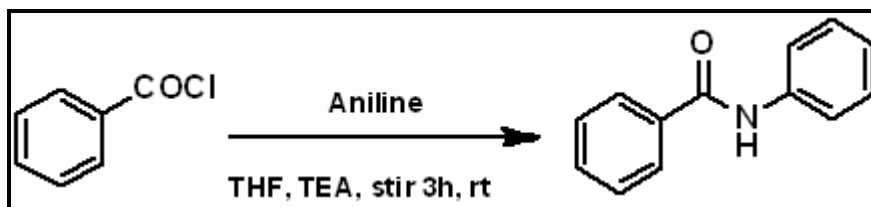
Synthetic procedures

A two neck round bottom flask was placed in ice cool condition and charged with *p*-phenylenediammine (1.5 mmol) solution in 5mL dry THF and added an excess amount of triethyl amine (TEA). Added to it 1,3,5-benzenetricarbonyl trichloride (1 mmol) solution in 2mL THF over a period of 2h maintaining the temperature at $0 \text{ }^{\circ}\text{C}$ (Scheme S1). The mixture was kept

in continuous stirring for another 12h under inert atmosphere at room temperature. The precipitate was filtered using vacuum filtration and further purified by solvent washing with acetone in which both the starting moieties are soluble whereas the desired COF is insoluble. The benzoyl chloride solution and aniline in 1:1 molar ratio were condensed following reported procedure in literature to synthesis the monomeric unit (*N*-phenyl benzamide) of COF-Am (Scheme S2).



Scheme S1 Schematic representation of COF-Am synthesis



Scheme S2 Schematic representation of *N*-phenyl benzamide synthesis

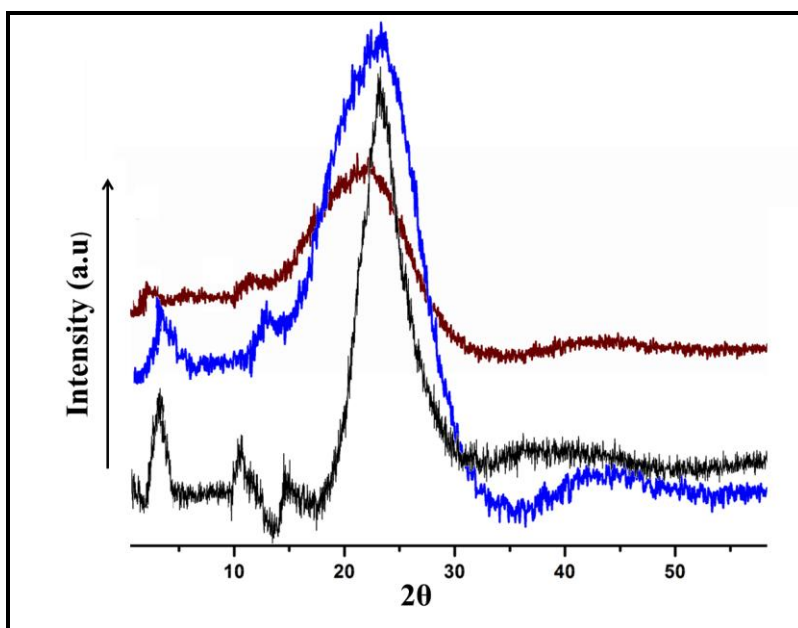
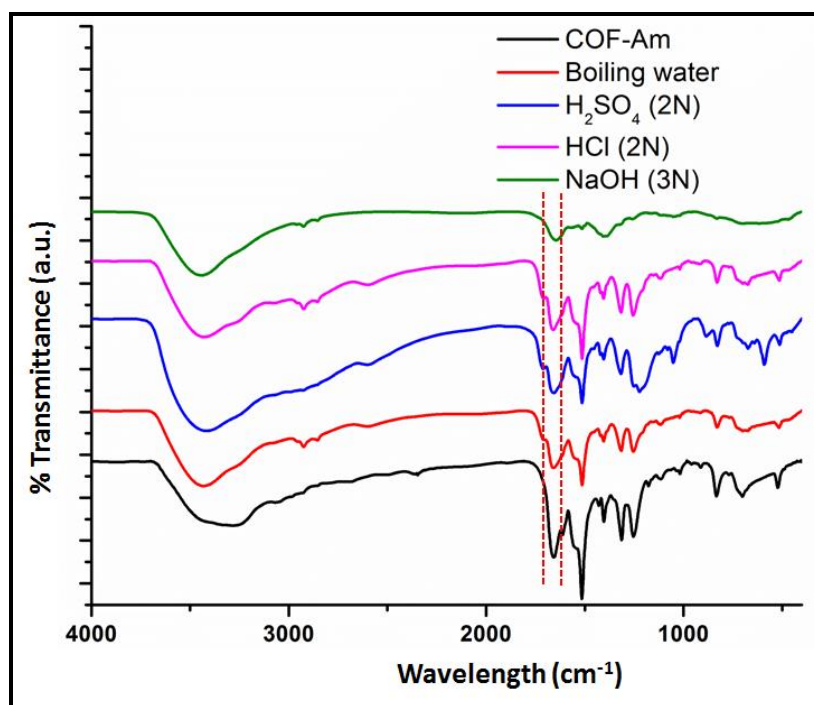
PXRD pattern of COF-Am under various conditions:

Figure S1 PXRD pattern of COF-Am as synthesized (brown), after antisolvent washing with acetone and vacuum dried (blue) and dried at 120°C for 24 h (black).

Stability Test:

Figure S2 FT-IR spectra of COF-Am at various environment; appearance of C=O frequency range in all cases (between red strip) reveals its stability.



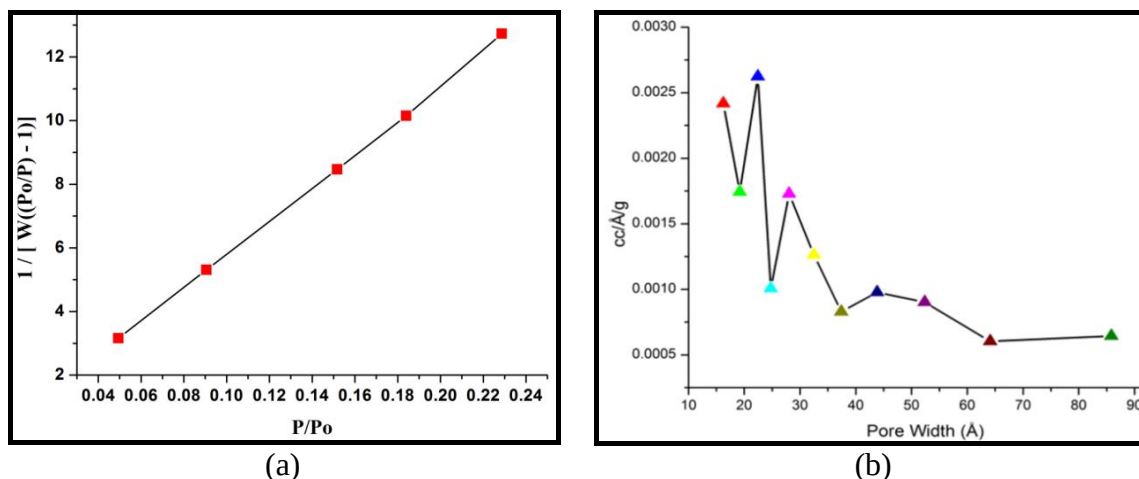
BET analysis:

Figure S3 BET surface area plot (a) and pore size distribution profile (b) of COF-Am.

Conformational geometry optimization using DMol3 for COF-Am:

The expected structure was optimized using DMol3¹ in Material Studio 7.0 package. However, we considered single ring of COF-Am by fixing the extended networking site of the building unit via hydrogen atom for our calculation. It attributes the framework to be planar and spherical in shape. Also the pore radius (2.0 nm) of the optimized ring almost matches to that obtained from BET analysis (i.e. 2.24 nm).

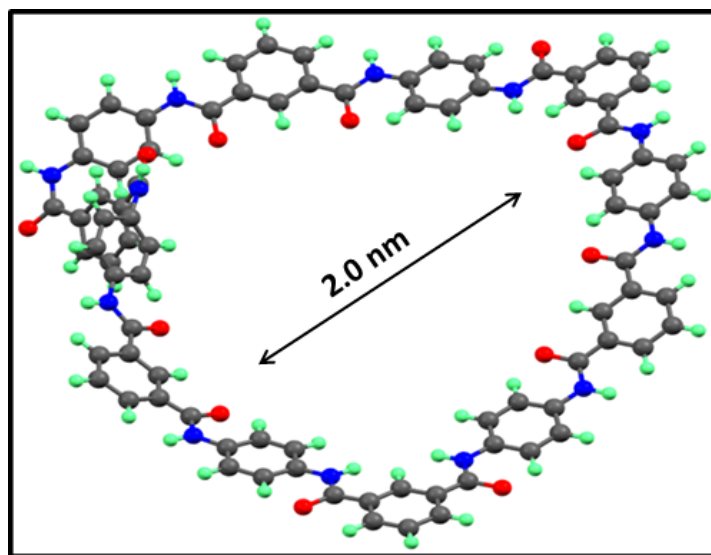
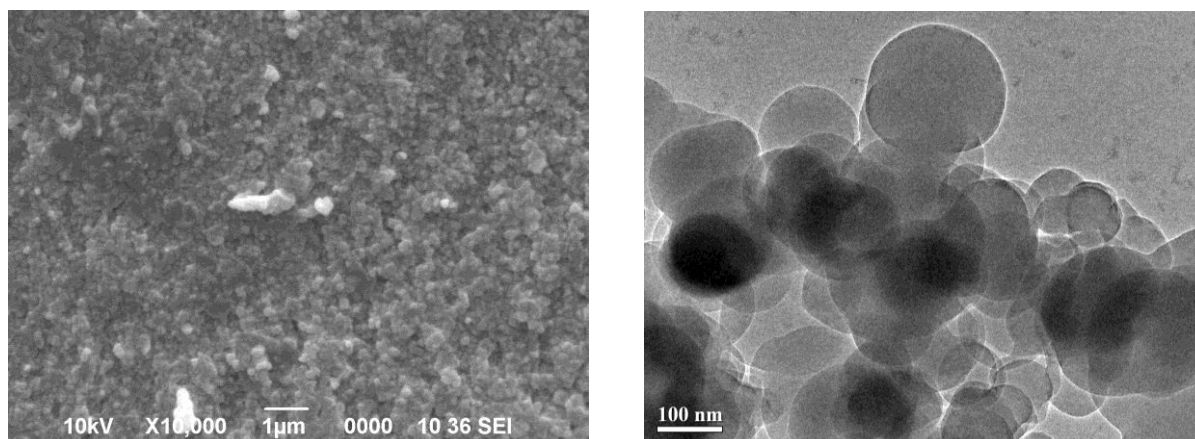
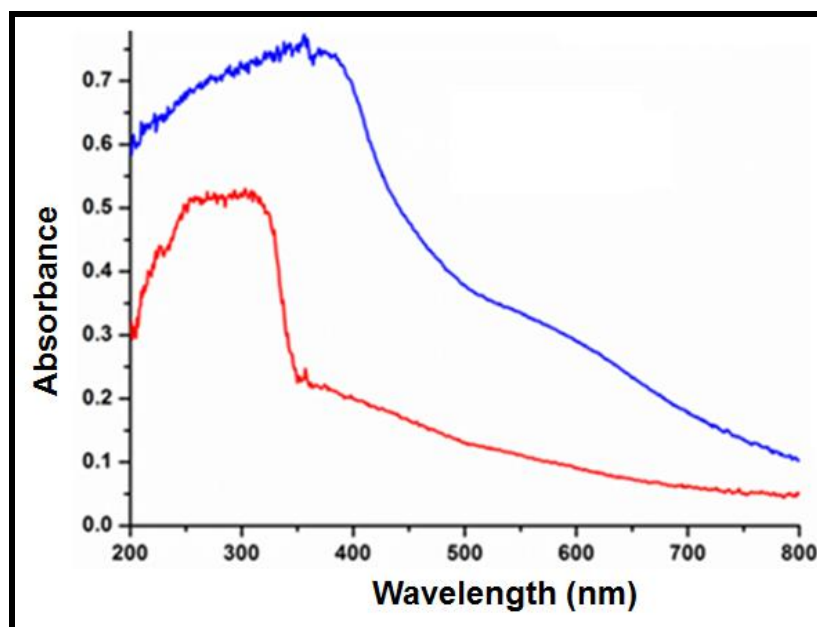


Figure S4 Optimized geometry of COF-Am by fixing the extended networking site of the building unit via hydrogen atom attributes nearly planar shape of COF-Am.

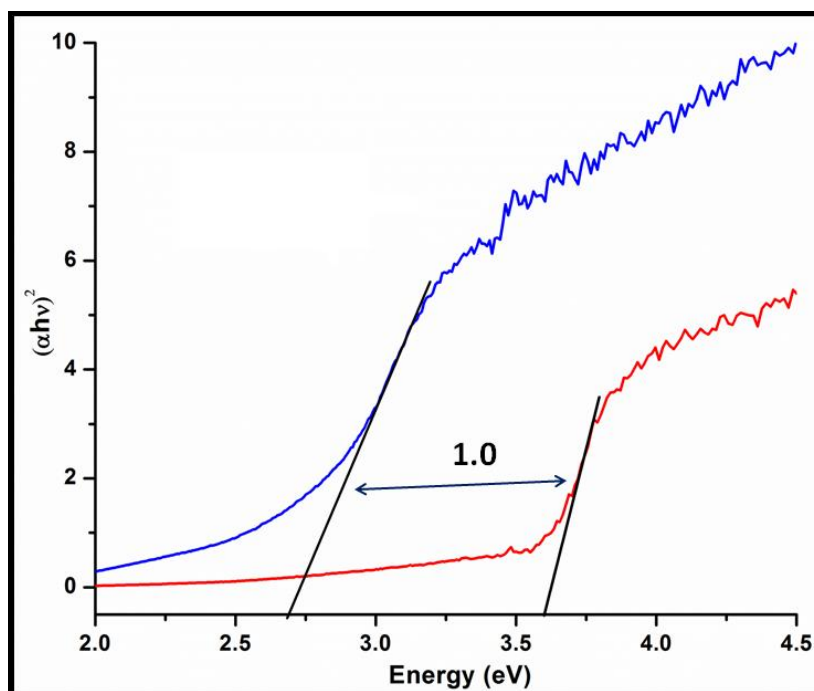
SEM and TEM analysis:

**Figure S5** SEM and TEM images of COF-Am.

Solid UV-Vis analysis:



(a)



(b)

Figure S6 Solid UV-Vis spectra depicting the difference in energy band gap between COF-Am (blue) and its monomeric unit, *N*-phenyl benzamide (red) in understanding the existence of extended π -cloud in COF-Am ((a) solid UV-vis absorption band).

Oxidant screening test:

Table S1 Screening of oxidants in selective oxidation of benzylalcohols to the corresponding benzaldehydes, TBHP has been found to be better in terms of yield (%) and selectivity

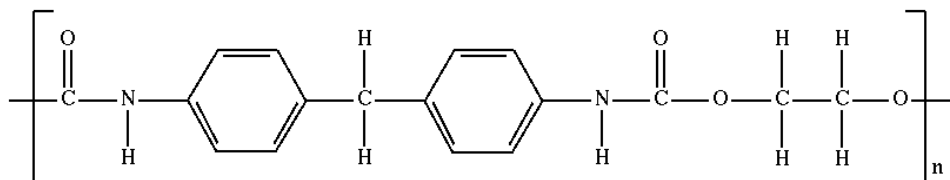
Entry	R ₁	R ₂	Time (h)	Oxidants	Yield (%)
1.	H	H	14	TBHP	63
				H ₂ O ₂	ND
2.	Cl	H	14	TBHP	44
				H ₂ O ₂	Trace
3	Br	H	14	TBHP	47
				H ₂ O ₂	Trace
4.	NO ₂	H	14	TBHP	>95
				H ₂ O ₂	Trace
5.	Me	H	14	TBHP	92
				H ₂ O ₂	Trace

6.	OMe	H	14	TBHP	78
				H ₂ O ₂	Trace
7.	H	Phenyl	10	TBHP	80
				H ₂ O ₂	ND
8.	H	Me	10	TBHP	54
				H ₂ O ₂	ND

*ND: Not detectable. Reaction conditions are identical as table 1 in the manuscript.

Catalytic role of π -conjugation: a comparison with other polymer

In order to generalise the catalytic activity of COF-Am for oxidation reactions of benzylalcohols we choose to consider polyurethane having other monomeric unit (carbamate) in lieu of COF-Am under identical reaction conditions with TBHP as oxidant (Table S2). But the progress of reaction is sluggish with trace amount of % yield. We speculate the reaction was initiated by the available amide functionality as in the case of COF-Am generating free radicals of TBHP. But the breakdown of extended π -conjugation in polyurethane might raise its band gap energy. As a consequence the easy electronic transition to the polymeric surface declines. Eventually the interaction energy of hydroxyl radicals with π -cloud via directional O-H $\cdots\pi$ interaction decreases thereby diminishing the stability of radicals on the catalyst surface. On the contrary in COF-Am the π -conjugation is propagated by carboxamide linkage and thus the free radicals generated by the breakdown of TBHP get stabilized to higher extent. In the process once the alcohol moiety comes in contact with the catalyst, probably the peroxide unit get detached from the catalyst surface and interact to give selectively benzaldehydes with good yield percent. Thus the presence of conjugated π -cloud in COF-Am plays an important role in the oxidation reactions with better yield.



Polyurethane consists of carbamate linkage

Table S2 Comparing the catalytic activity of COF-Am and polyurethane both having different monomeric unit in presence of TBHP as oxidant

Entry	R ₁	R ₂	Time (h)	Catalysts	Yield (%)
1.	H	H	14	COF-Am	63
				Polyurethane	5
2.	Cl	H	14	COF-Am	44
				Polyurethane	Trace
3	Br	H	14	COF-Am	47
				Polyurethane	2
4.	NO ₂	H	14	COF-Am	>95
				Polyurethane	3
5.	Me	H	14	COF-Am	92
				Polyurethane	5
6.	OMe	H	14	COF-Am	78
				Polyurethane	~2
7.	H	Phenyl	10	COF-Am	80
				Polyurethane	5
8.	H	Me	10	COF-Am	54
				Polyurethane	Trace

*Note: Reaction conditions are identical as in Table 1 in the manuscript

Catalytic role of amide functionality: We followed aforesaid procedure for the synthesis of below two compounds having one and three amide functionalities respectively in I and II.

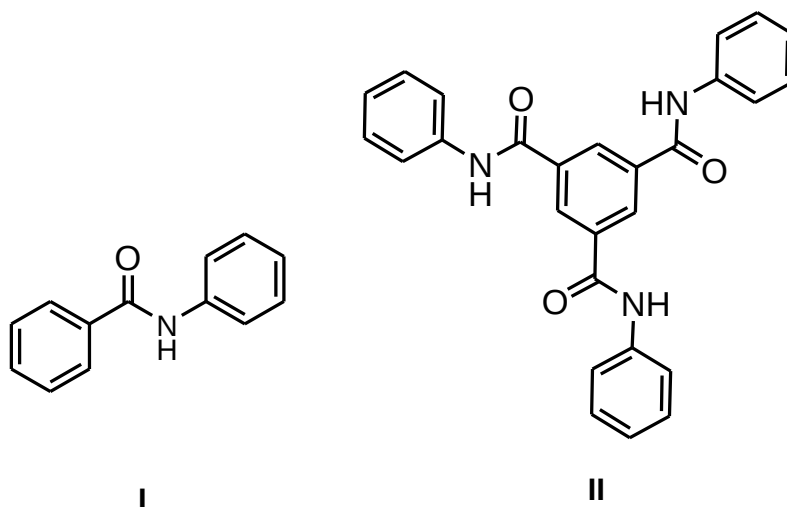


Table S3. Catalytic activity of amide functionality monomeric units with TBHP as oxidant for the oxidation of benzylalcohols

Entry	R ₁	R ₂	Time (h)	Monomers	Yield (%)
1.	H	H	14	I	ND
				II	2
2.	Cl	H	14	I	ND
				II	1
3	Br	H	14	I	ND
				II	Trace
4.	NO ₂	H	14	I	ND
				II	~ 2
5.	Me	H	14	I	ND
				II	Trace
6.	OMe	H	14	I	ND
				II	~ 2
7.	H	Phenyl	10	I	ND
				II	5
8.	H	Me	10	I	ND
				II	1

Note: **I** = *N*-phenyl benzamide and **II** = *N*¹*N*³*N*⁵-triphenylbenzene-1,3,5-tricarboxamide

*ND: Not detectable. Reaction conditions are identical as table 1 in the manuscript.

Reaction condition optimization:

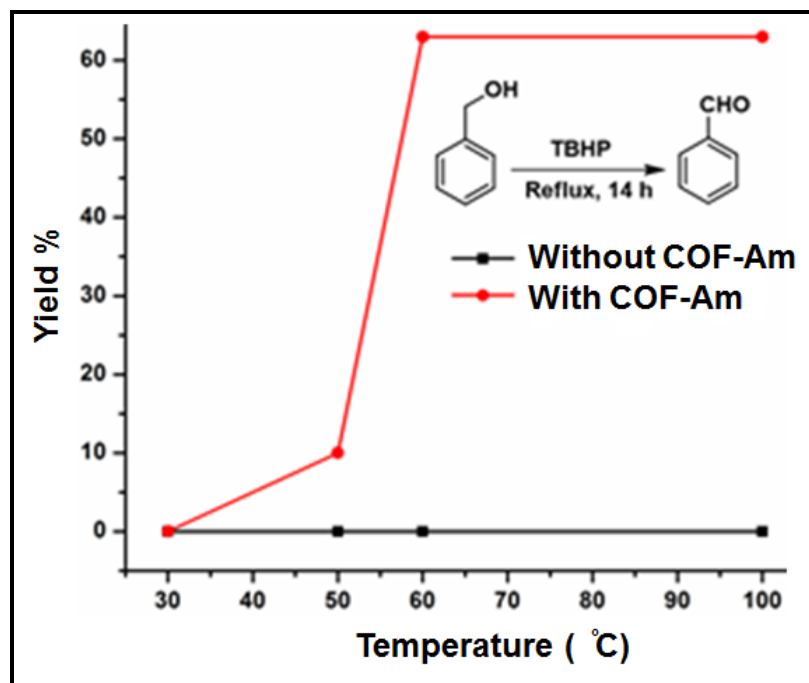


Figure S7 Temperature vs. yield (%) graph for optimization of utmost catalytic reaction conditions in the oxidation of benzylalcohols.

NMR analysis of products:

Benzaldehyde: ^1H -NMR (400MHz, CDCl_3): δ (ppm) = 9.8 (s, 1H), 7.8–7.5 (5H); ^{13}C -NMR (CDCl_3): δ (ppm) = 192.6, 136.4, 134.6, 129.8, 129.1.

p-Chlorobenzaldehyde: ^1H -NMR (400MHz, DMSO-d_6): δ (ppm) = 9.9 (s, 1H), 7.8 (d, 2H, J = 8.4), 7.6 (d, 2H, J = 8.4); ^{13}C -NMR (DMSO-d_6): δ (ppm) = 192.7, 139.9, 135.3, 131.7, 129.9.

p-Bromobenzaldehyde: ^1H -NMR (400MHz, CDCl_3): δ (ppm) = 9.9 (s, 1H), 7.7 (d, 2H, J = 8.4), 7.6 (d, 2H, J = 8.4); ^{13}C -NMR (CDCl_3): δ (ppm) = 191.2, 135.1, 132.5, 131.0, 129.8.

p-Nitrobenzaldehyde: ^1H -NMR (400MHz, CDCl_3): δ (ppm) = 10.1 (s, 1H), 8.3 (d, 2H, J = 8.4), 8.0 (d, 2H, J = 8.8); ^{13}C -NMR (CDCl_3): δ (ppm) = 190.4, 152.6, 140.1, 130.6, 124.4.

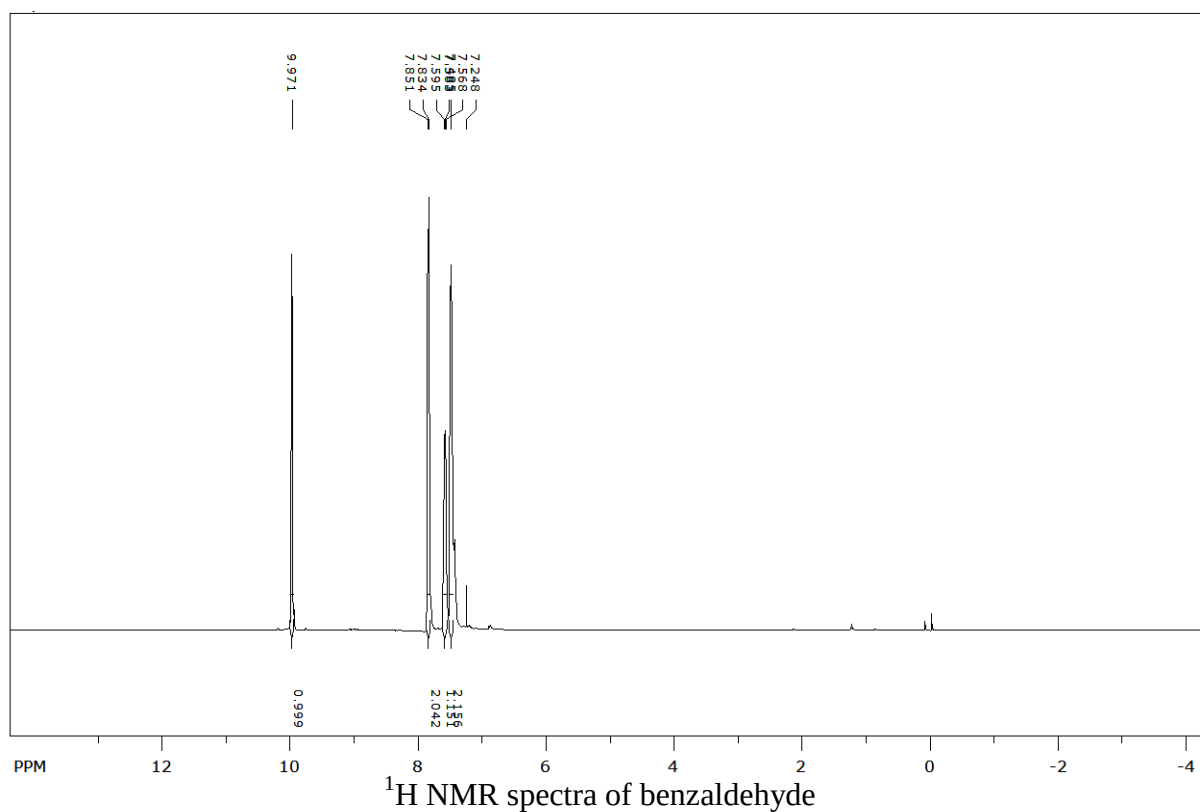
p-Methoxybenzaldehyde: ^1H -NMR (400MHz, CDCl_3): δ (ppm) = 9.7 (s, 1H), 7.7 (d, 2H, J = 8.8), 6.9 (d, 2H, J = 8.8), 3.7 (s, 3H); ^{13}C -NMR (CDCl_3): δ (ppm) = 190.9, 164.6, 132.0, 129.9, 114.3, 55.6.

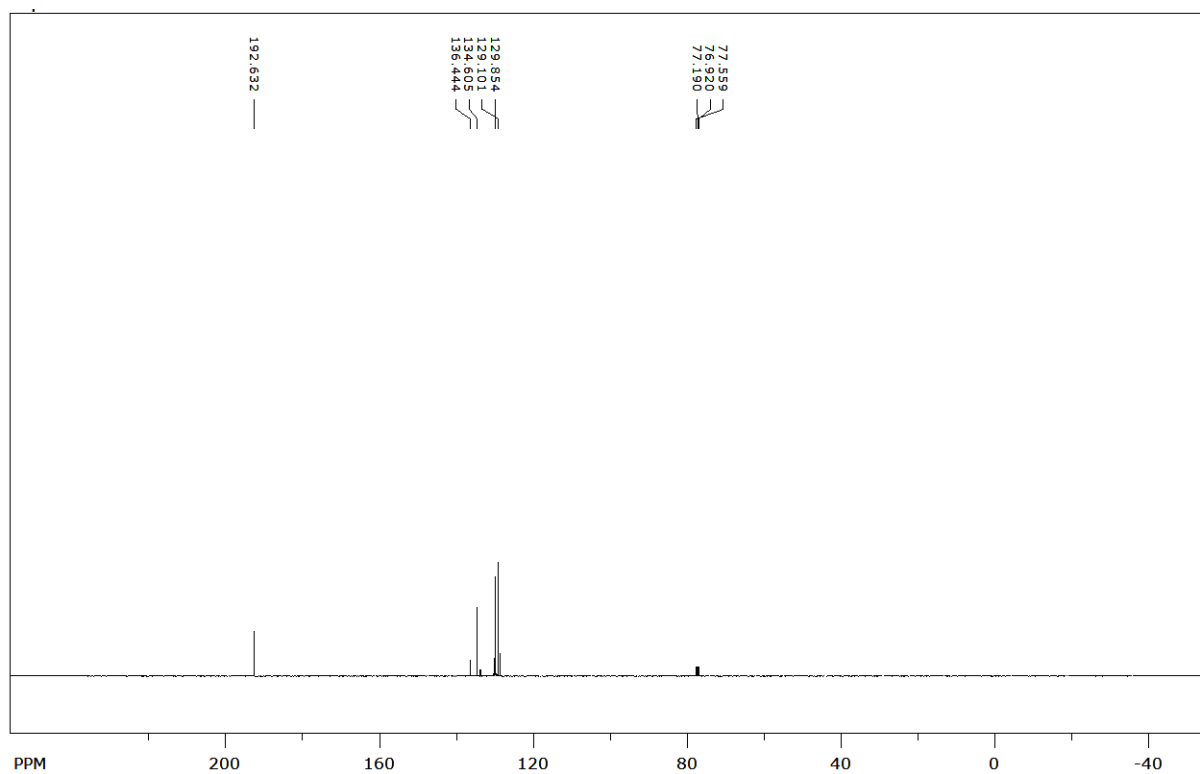
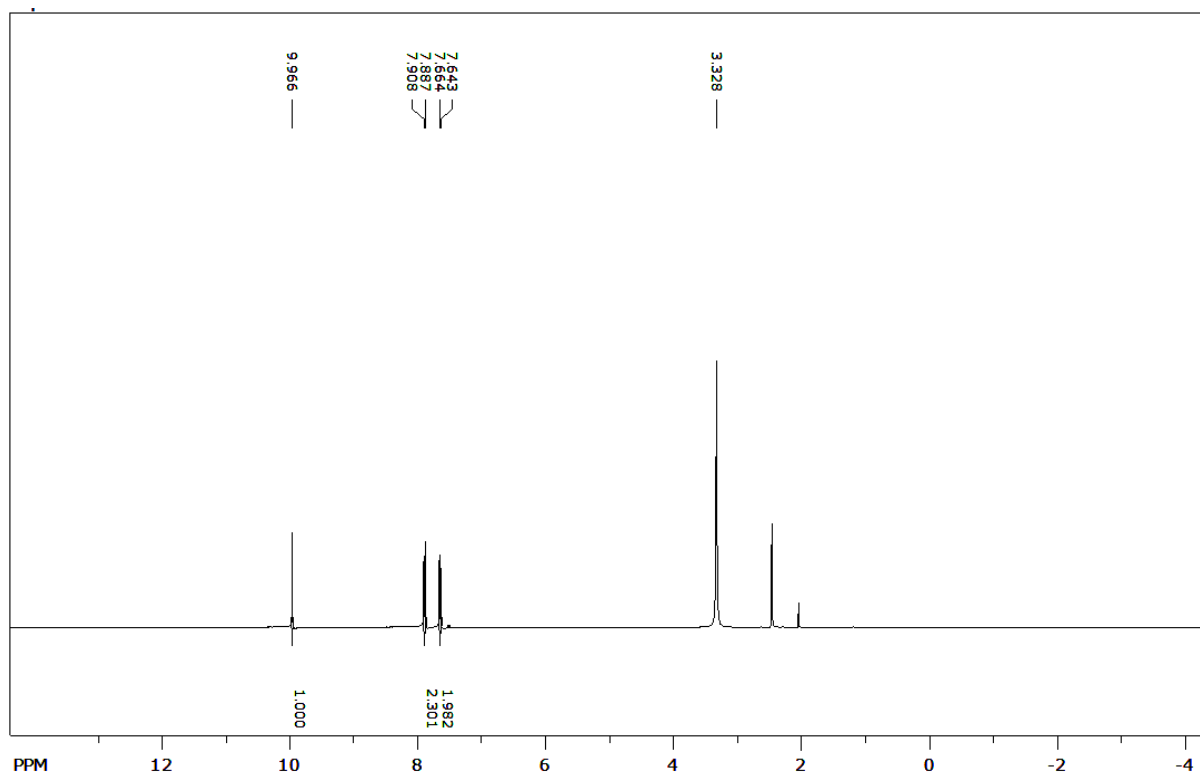
Tolualdehyde: ^1H -NMR (400MHz, CDCl_3): δ (ppm) = 9.9 (s, 1H), 7.7 (d, 2H, J = 8.0), 7.2 (d, 2H, J = 7.6), 2.3 (s, 3H); ^{13}C -NMR (CDCl_3): δ (ppm) = 192.1, 145.6, 134.2, 129.9, 129.8, 21.9.

Benzophenone: ^1H -NMR (400MHz, CDCl_3): δ (ppm) = 7.7 (d, 4H, J = 7.6), 7.5 (t, 2H, J = 7.6), 7.4 (t, 4H, J = 7.6); ^{13}C -NMR (CDCl_3): δ (ppm) = 196.8, 137.6, 132.5, 130.1, 128.3.

Acetophenone: ^1H -NMR (400MHz, CDCl_3): δ (ppm) = 7.9 (d, 2H, J = 7.6), 7.5 (t, 2H, J = 7.6), 7.4 (t, 2H, J = 7.6), 2.5 (s); ^{13}C -NMR (CDCl_3): δ (ppm) = 198.8, 137.0, 133.3, 128.7, 128.5, 26.6.

NMR Spectra (Figures S8):



¹³C NMR spectra of benzaldehyde¹H NMR spectra of *p*-chlorobenzaldehyde

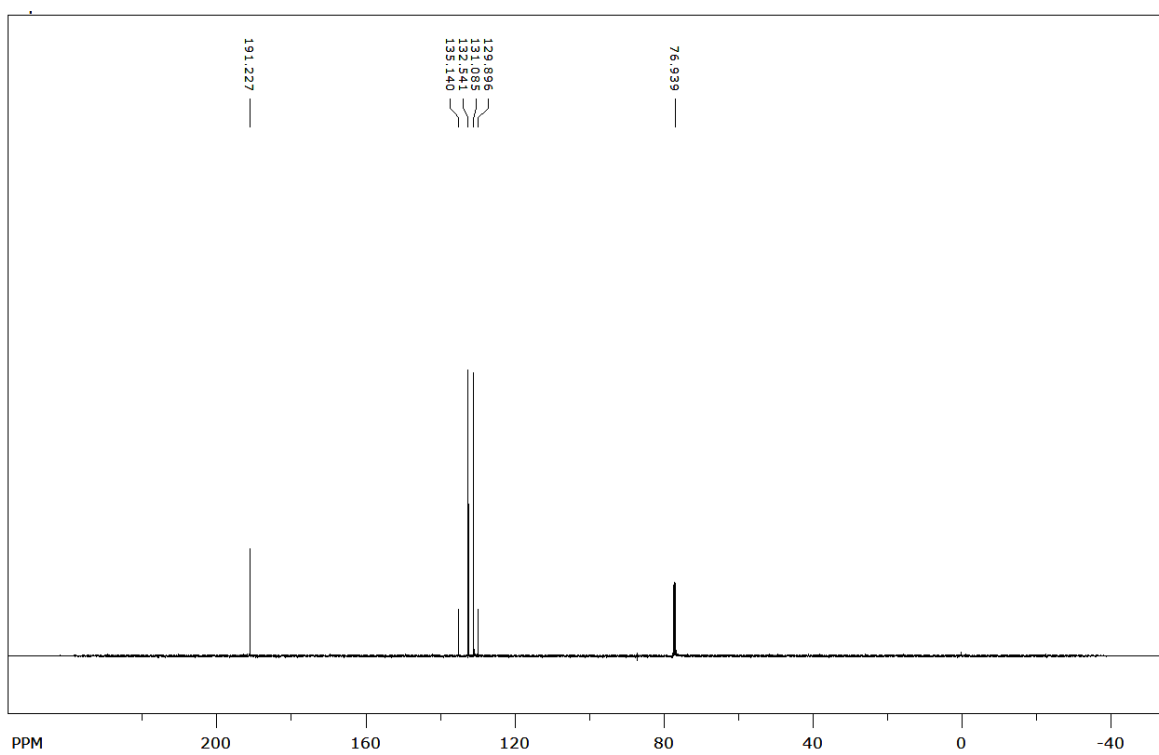
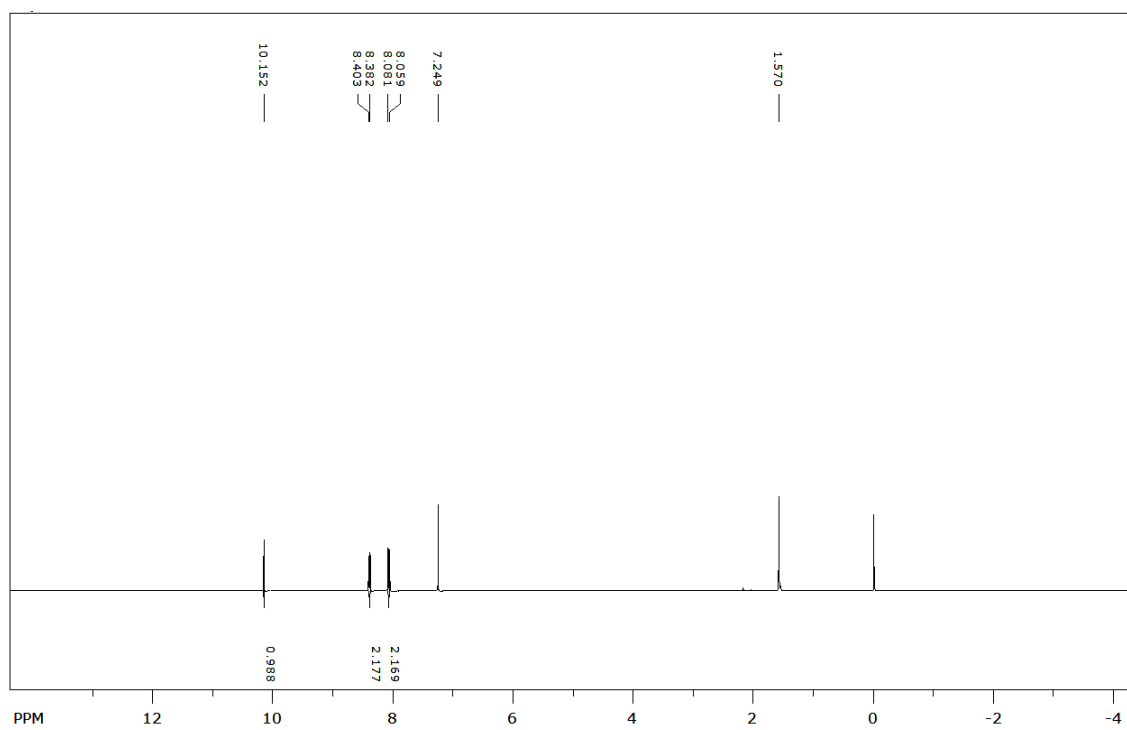
10

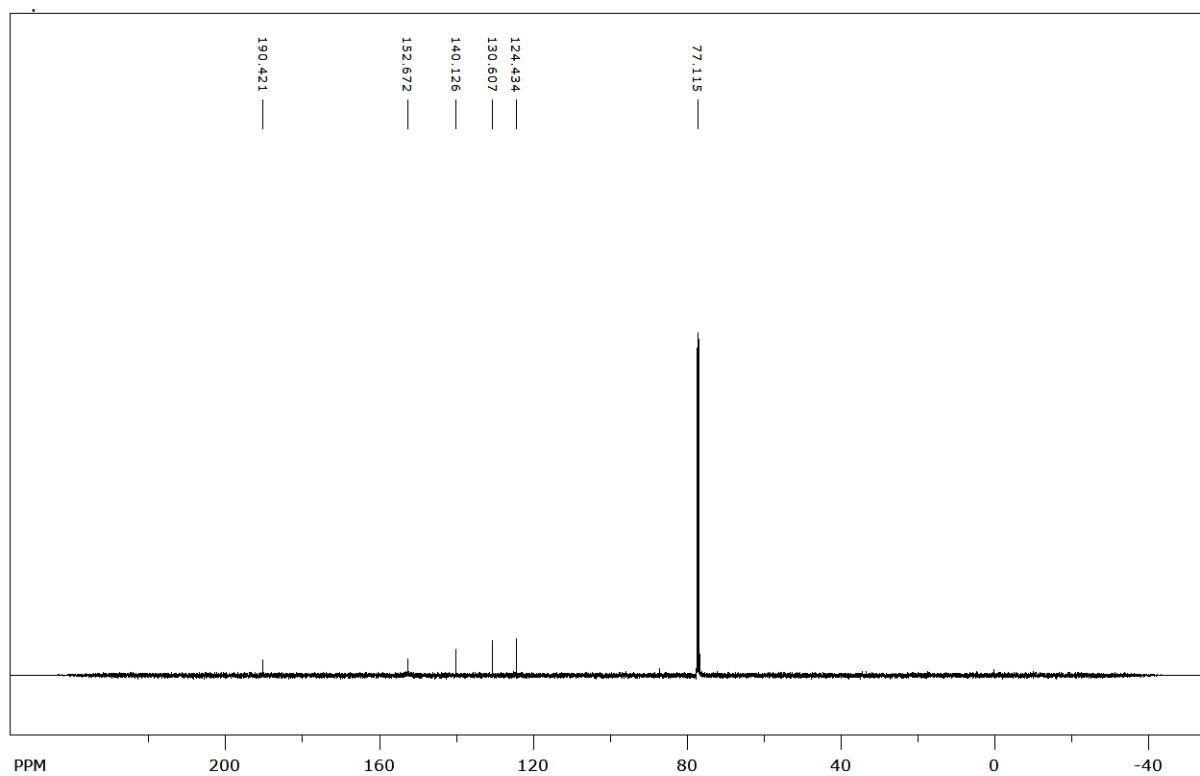
9.956

0.996

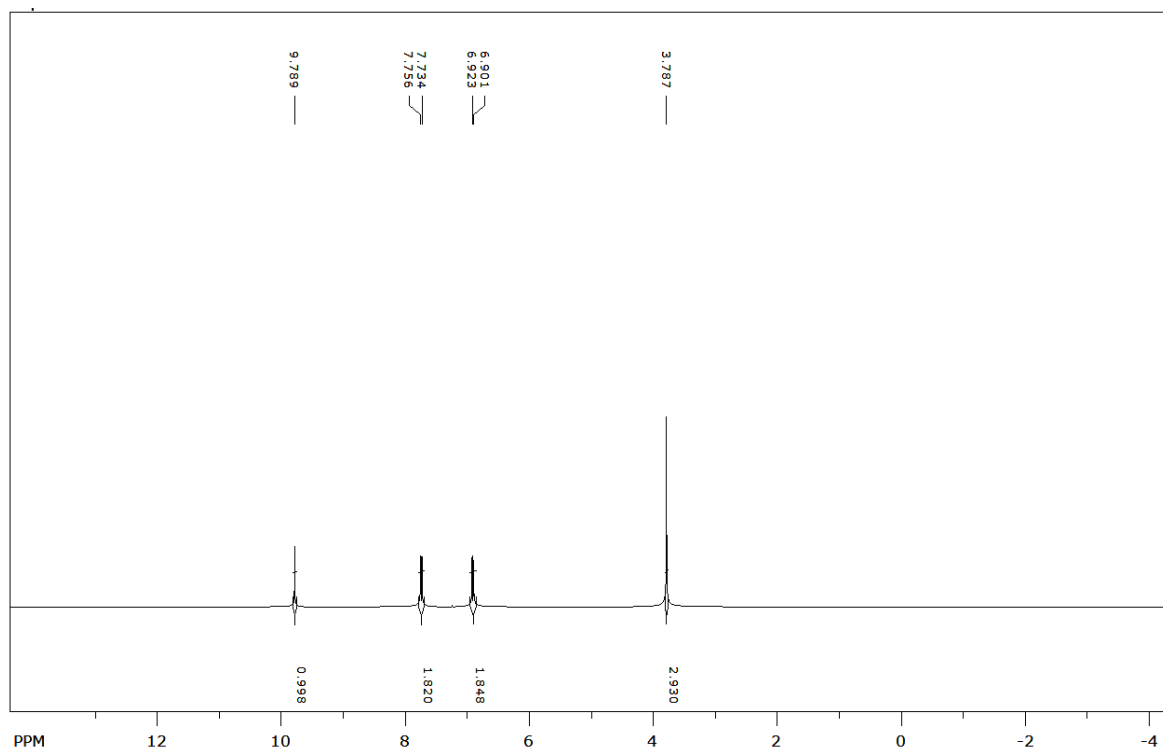
7.248
7.653
7.674
7.719
7.740

¹H NMR spectra of *p*-bromobenzaldehyde

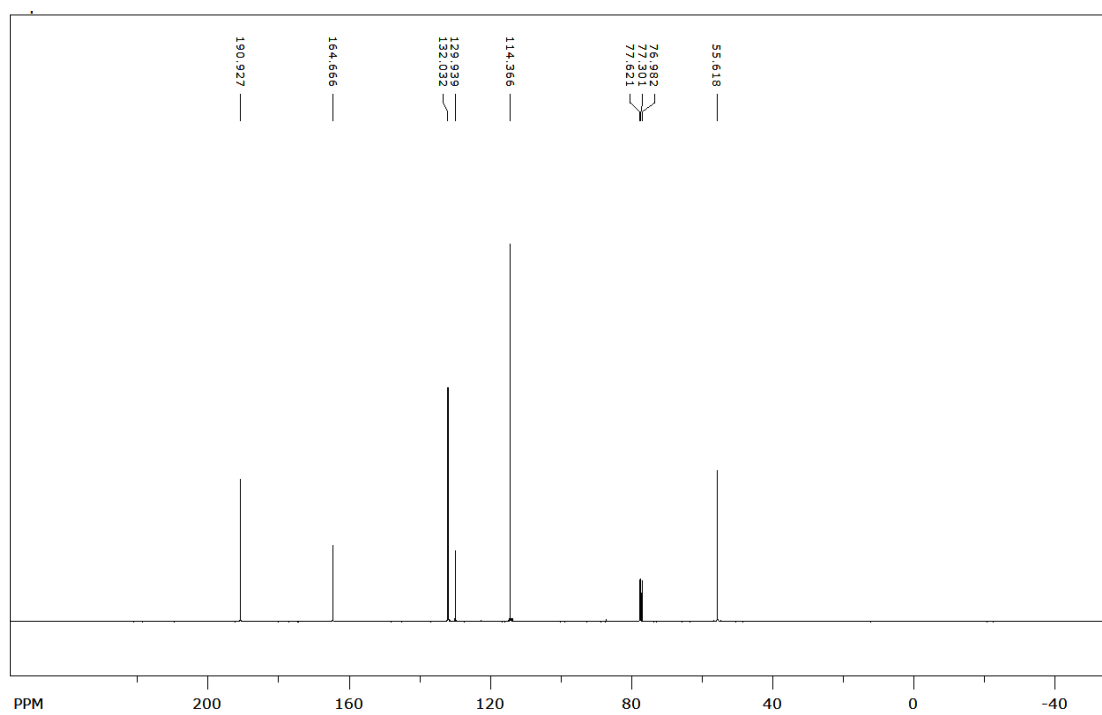
¹³C NMR spectra of *p*-bromobenzaldehyde¹H NMR spectra of *p*-nitrobenzaldehyde



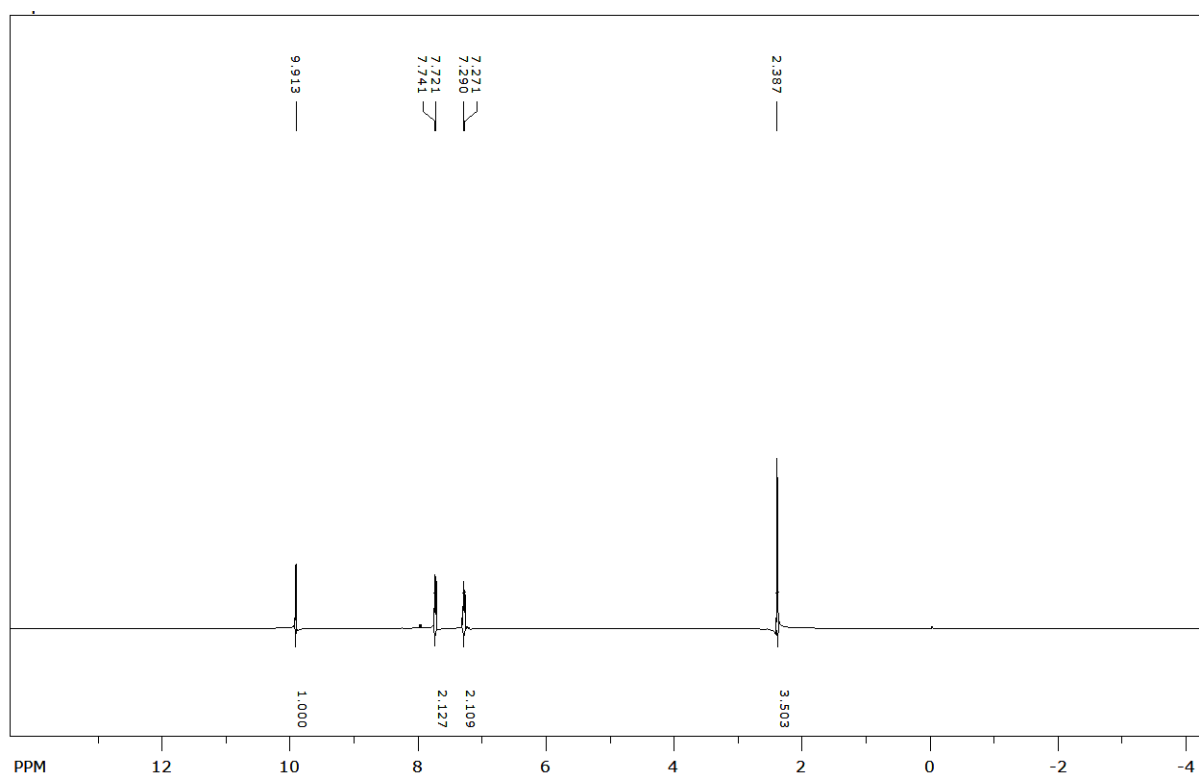
¹³C NMR spectra of *p*-nitrobenzaldehyde



¹H NMR spectra of *p*-methoxybenzaldehyde



¹³C NMR spectra of *p*-methoxybenzaldehyde



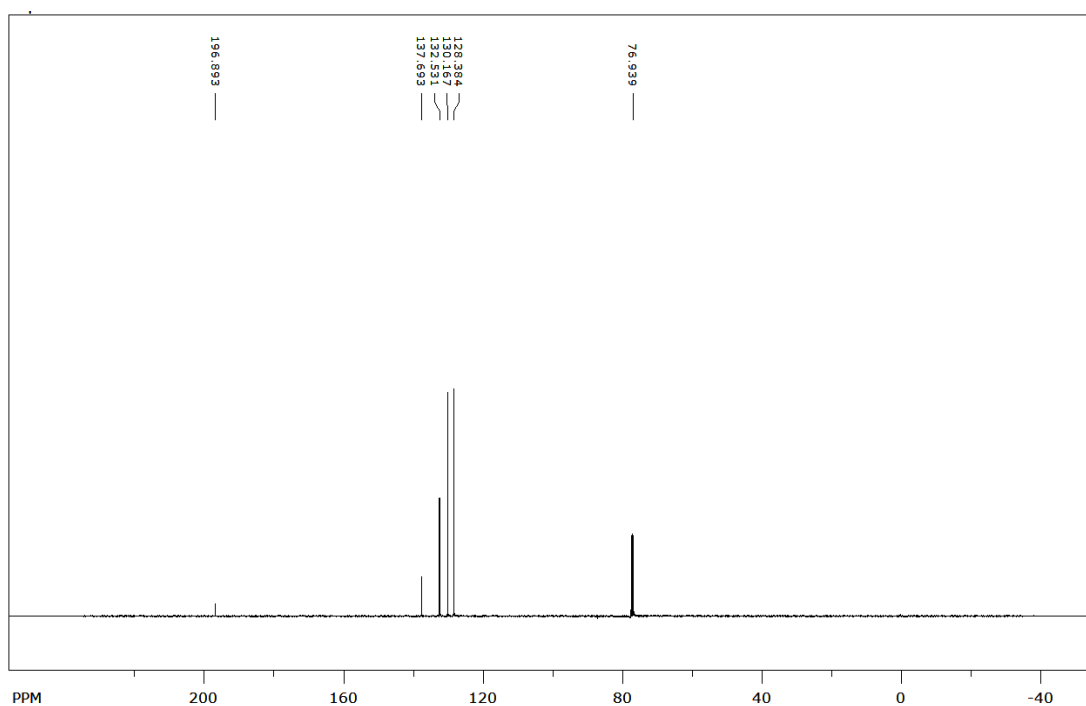
¹H NMR spectra of tolualdehyde

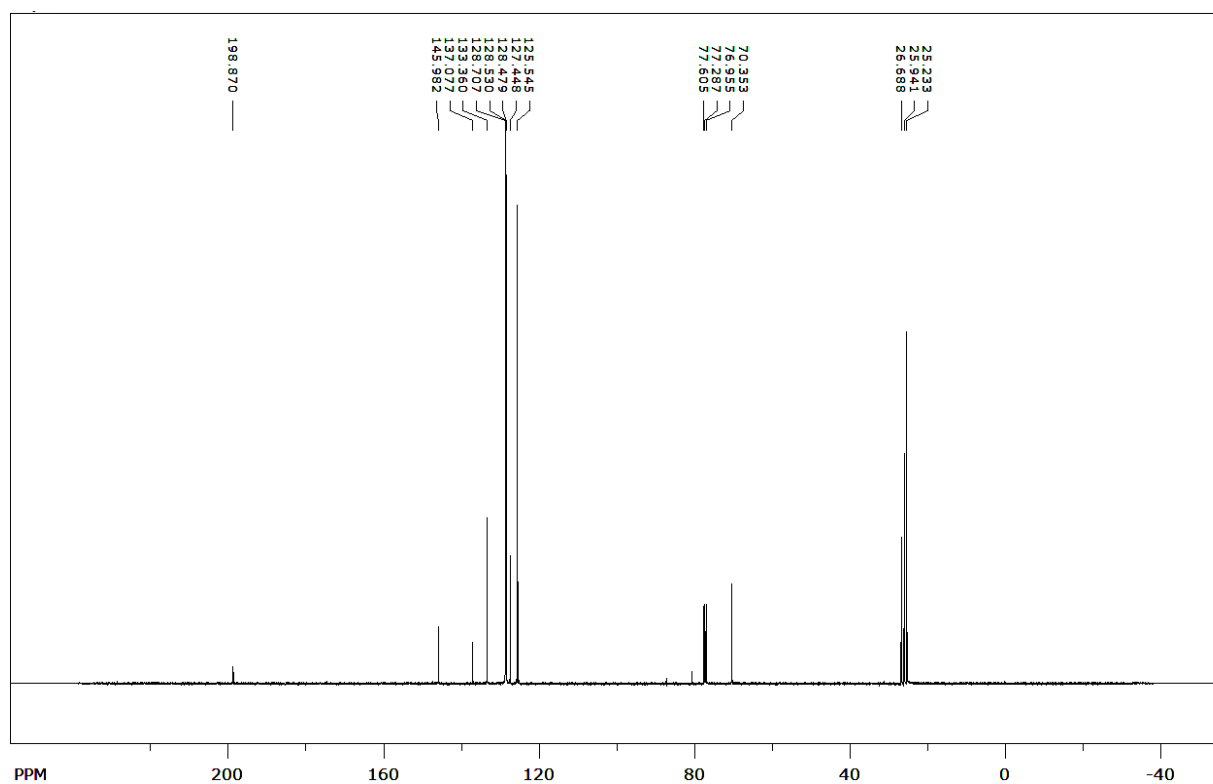
7.249
7.249
7.454
7.453
7.451
7.551
7.550
7.598
7.788
7.807

0.99
0.93
0.93

PPM

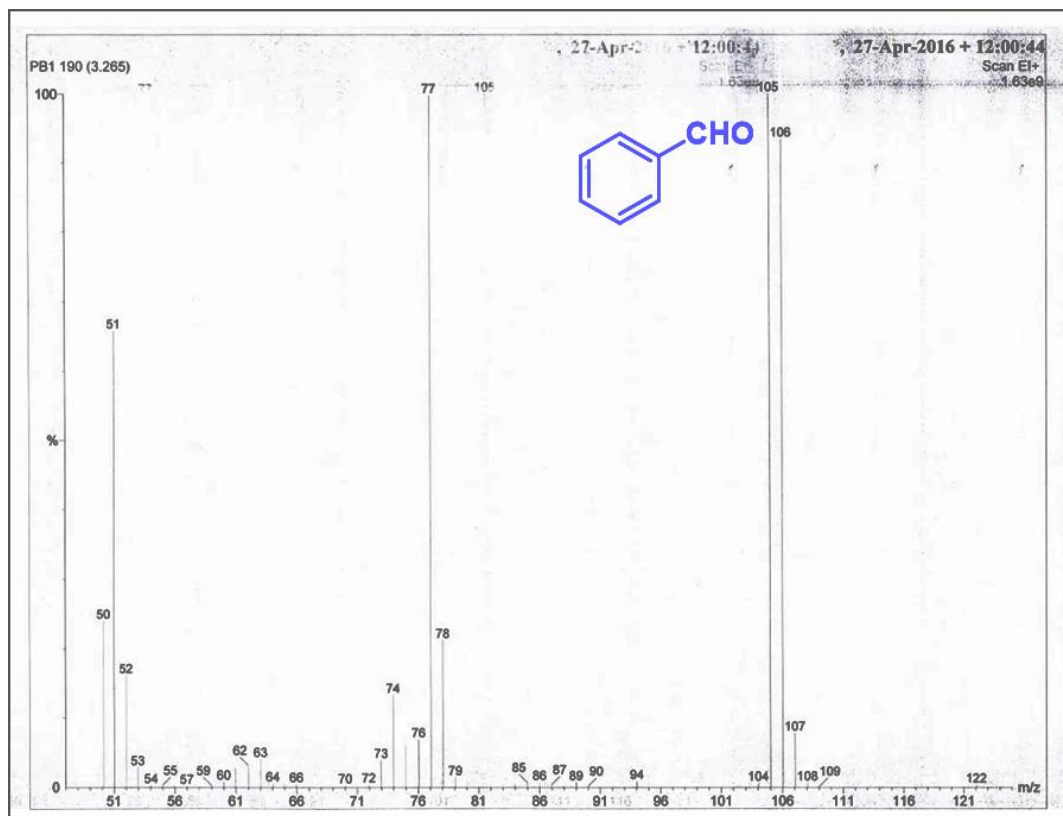
12 10 8 6 4 2 0 -2 -4

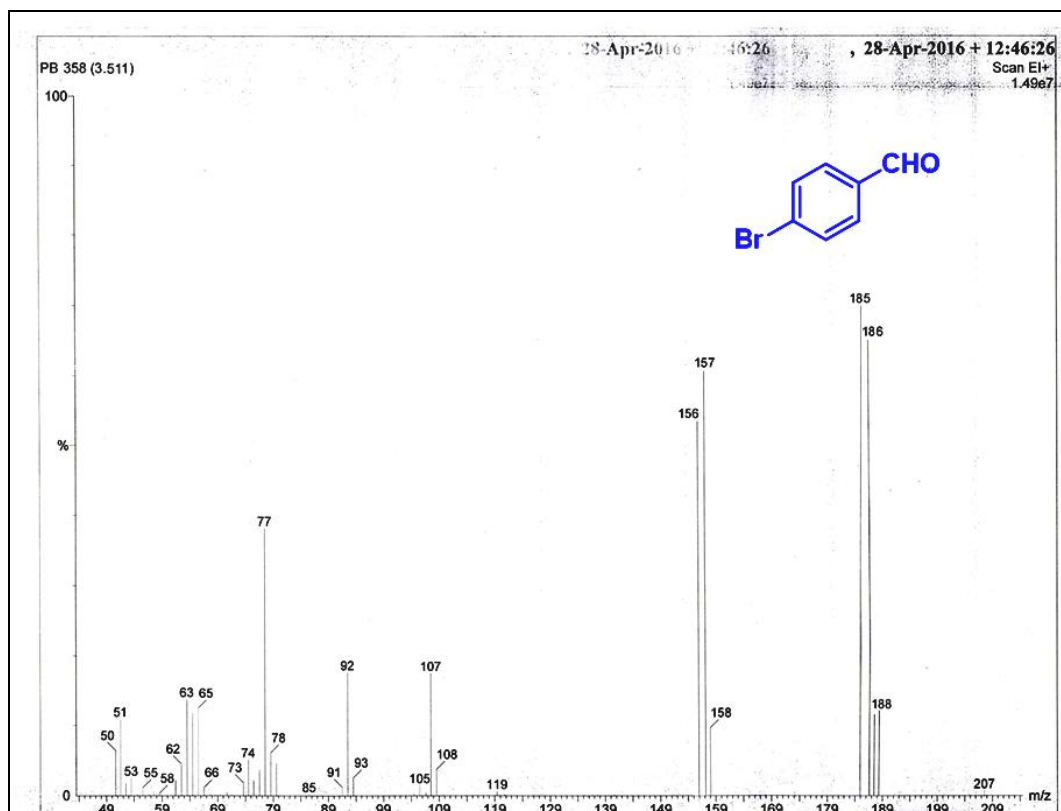
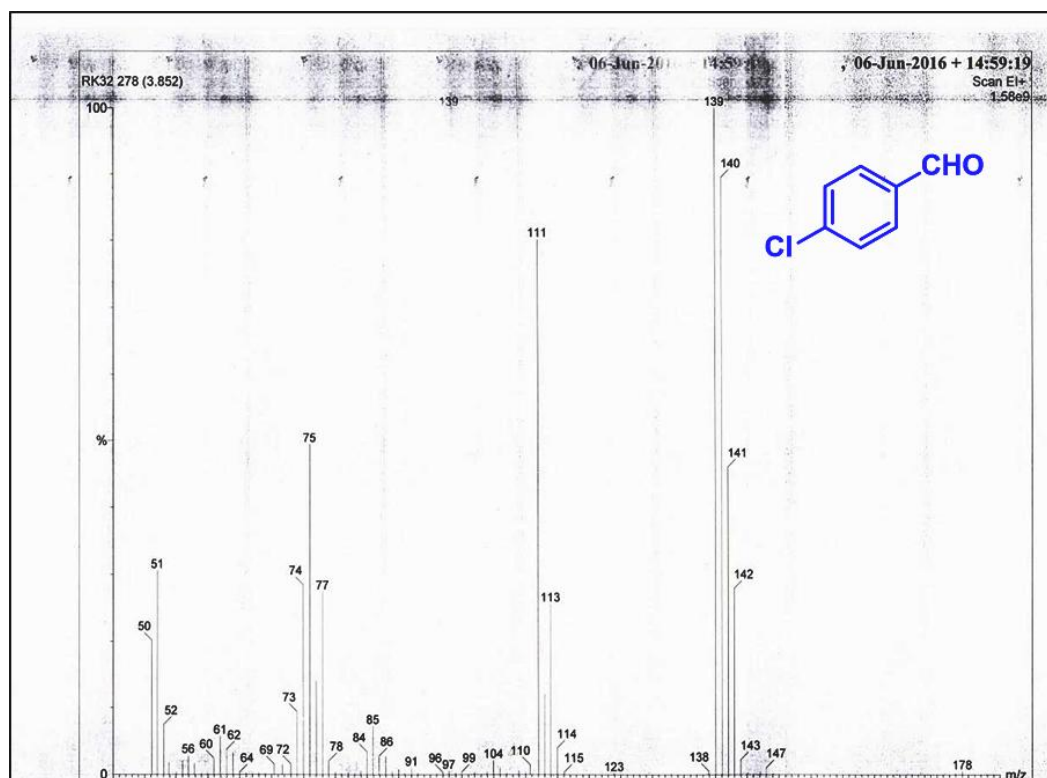


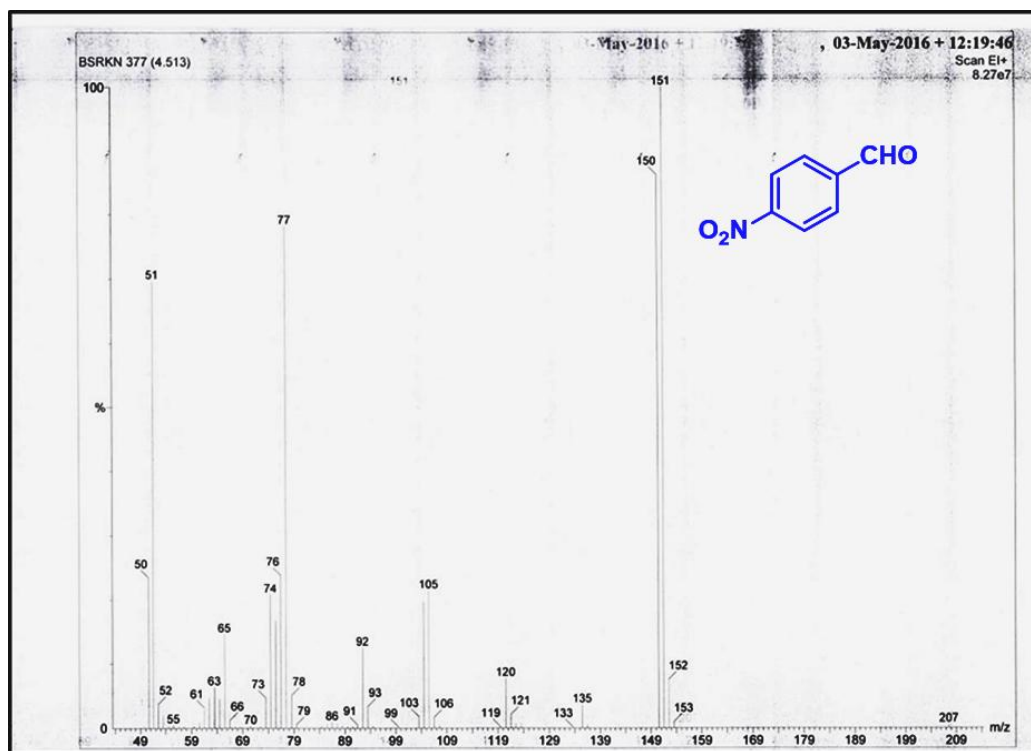
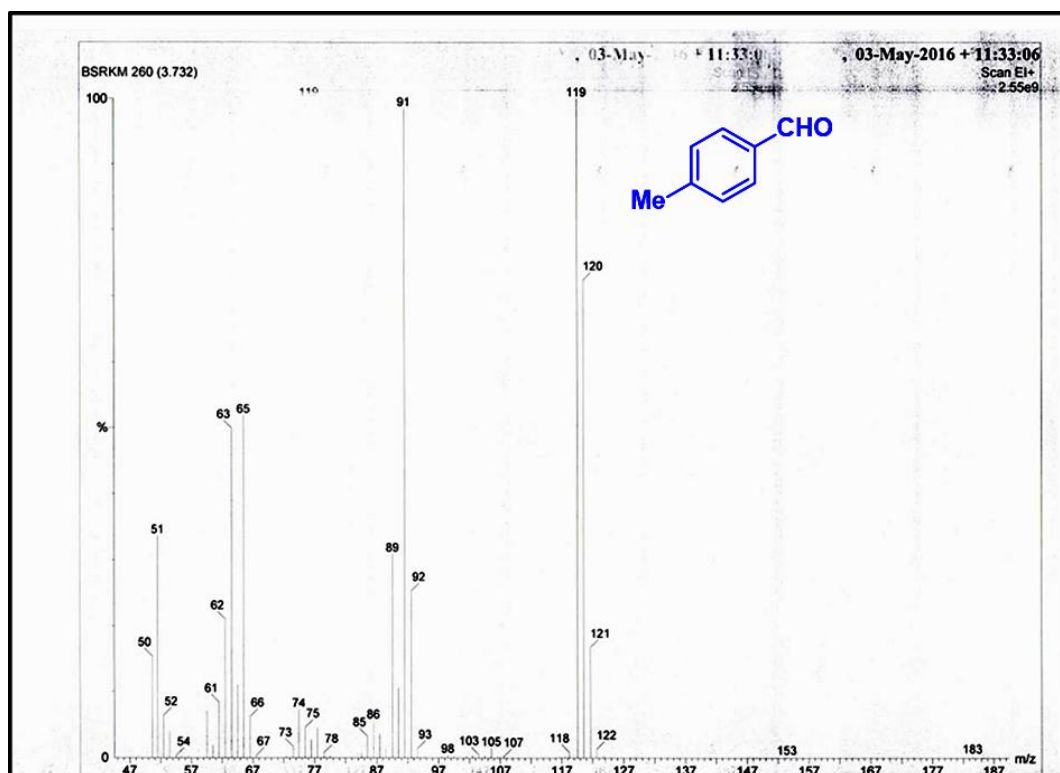


^{13}C NMR spectra of reaction mixture of acetophenone (peaks at 198.8, 137.0, 133.3, 128.7, 128.5 and 26.6 ppm are responsible for ^{13}C of acetophenone).

GC-mass spectra of the oxidized product (Figures S9):







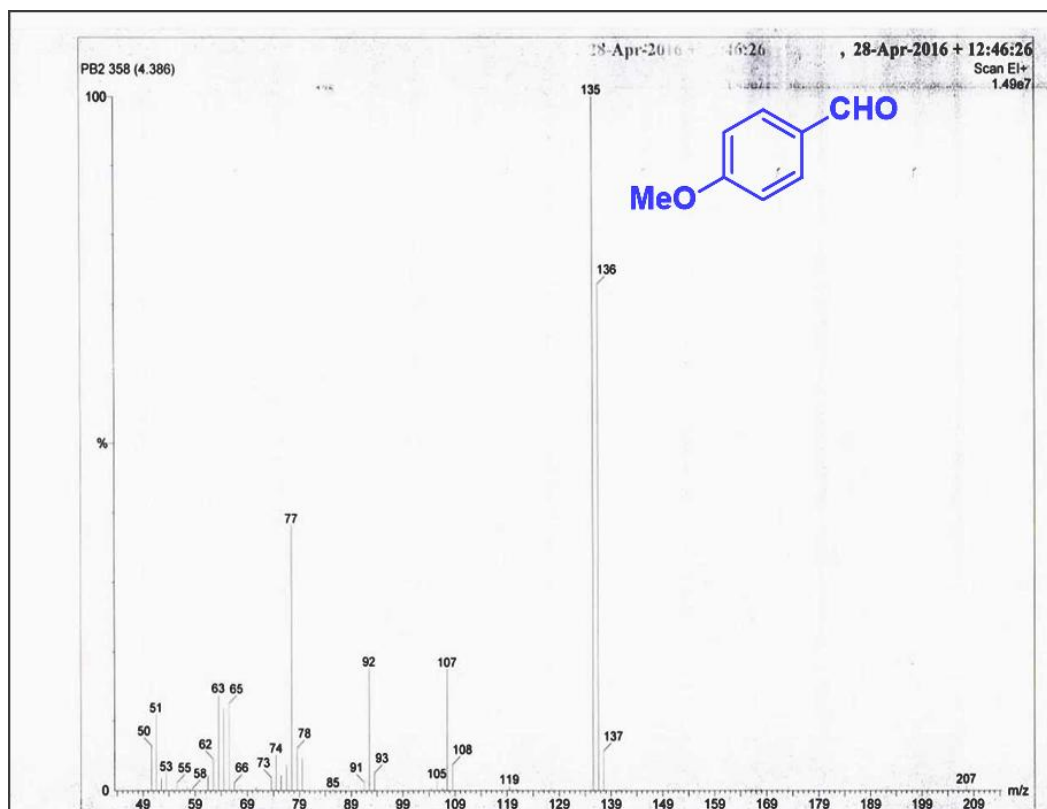
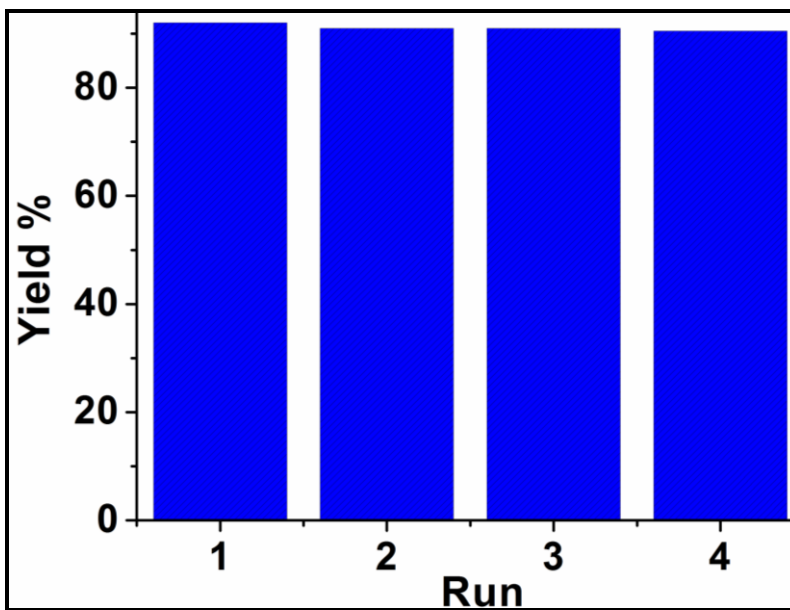
**Catalytic reusability test:**

Figure S10 Catalytic reusability of COF-Am and its yield % up to 4th cycle of oxidation of *p*-methyl benzylalcohol to corresponding benzaldehyde selectively.

PXRD analysis of COF-Am after 4th catalytic cycle:

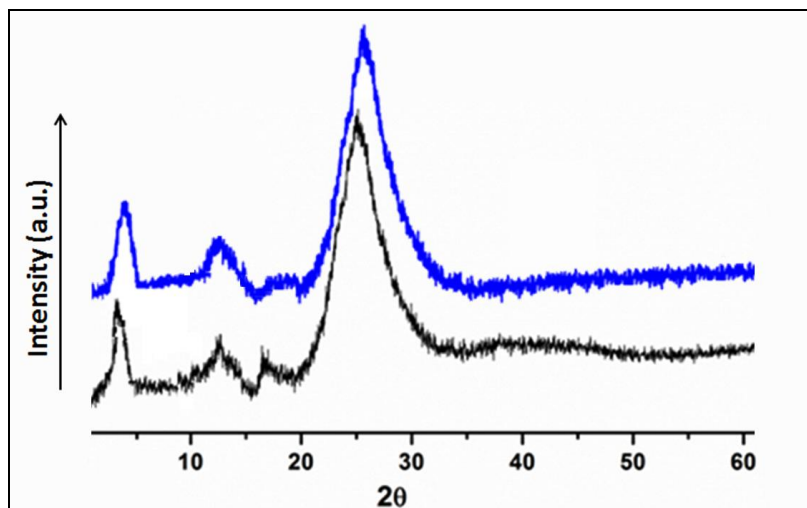


Figure S11 PXRD pattern of as synthesized (black) and after 4th catalytic cycle (blue) attributes the stability of COF-Am.

FT-IR spectra analysis for COF-Am after 4th catalytic cycle:

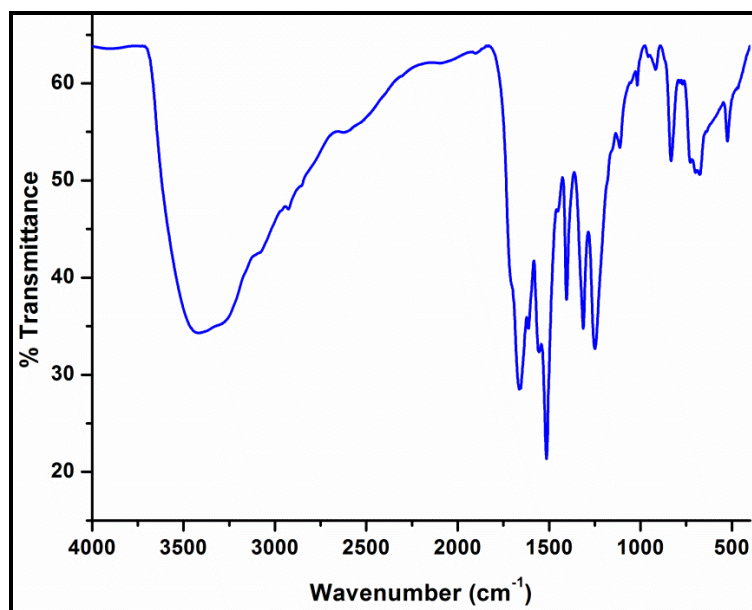


Figure S12 FTIR spectra of COF-Am after 4th catalytic cycle.

Reaction Mechanism Study: Computational details

The density functional theory (DFT)² calculations were performed using Gaussian09 programme.³ The functional used in this study was the B3LYP, consisting of a hybrid exchange functional as defined by Becke's three-parameter equation and the Lee-Yang-Parr correlation functional. The ground state geometry was obtained in the gas phase by full geometry optimization and the optimum structure located as stationary point on the potential energy surface was verified by the absence of imaginary frequencies. The basis set used in this study was 6-311++G (d,p).

References

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2. W. Kohn, A. D. Becke and R. G. Parr, *J. Chem. Phys.*, 1996, **100**, 12974–12980.
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