

## Electronic Supplementary Information

### Ultrasonic irradiation-assisted $\text{MnFe}_2\text{O}_4$ nanoparticles catalyzed solvent-free selective oxidation of benzyl alcohol to benzaldehyde at room temperature

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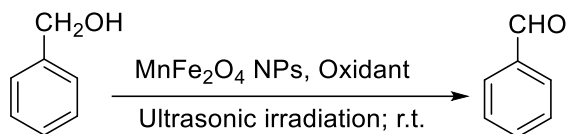
## Characterization of the product

The synthesized  $\text{MnFe}_2\text{O}_4$  NPs were characterized by different spectroscopic, microscopic, and diffractometric techniques. X-ray diffraction (XRD) study of the dried powder samples was carried out on a Phillips X'Pert Pro Powder X-ray diffractometer using  $\text{Cu } k\alpha$  radiation with a wavelength of 0.154 nm at an accelerating voltage of 40 kV with 35 mA current. For the scanning electron microscopic (SEM) study, a small amount of the dry powder samples was spread on carbon tape pasted on an aluminum stub, and then sputter-coated with gold to minimize the charging effect. The micrographs were then recorded in a field emission scanning electron microscope (FESEM) (Carl ZEISS Sigma supra 55 FESEM) at an accelerating voltage of 5 kV. For transmission electron microscopic (TEM) studies, a drop of an aqueous suspension of an individual powder sample was cast on a carbon-coated copper grid. The excess solutions were soaked with tissue paper followed by drying in the air. The micrographs were then recorded in a high-resolution Technai electron microscope (F30 S-Twin) at an accelerating voltage of 200 kV. The  $\text{N}_2$  gas adsorption-desorption isotherms of the products were recorded at 77 K (Quantachrome Nova 1000 Instrument) after degassing the powder samples at 110 °C for 4 h in an inert atmosphere. The dried powder of the samples was subjected to magnetic measurements at room temperature using a Quantum Design 7T SQUID magnetometer (MPMS@3). X-ray photoelectron spectroscopy (XPS) analyses of the dried powder samples were performed in SPECS Germany made ESCA spectrometer.  $^{57}\text{Fe}$  Mössbauer spectroscopy measurement was performed in transmission mode using a PC-based Mossbauer spectrometer. Atomic absorption spectroscopy study was performed on a Thermo Scientific ICE 3000 Series Atomic Absorption Spectrometer (AAS) in Flame mode using air and acetylene.  $^1\text{H}$  and  $^{13}\text{C}$   $\{^1\text{H}\}$  NMR spectra were recorded in a JNM ECS 400 MHz NMR spectrophotometer (JEOL) and an Advance NEO 500 MHz NMR spectrophotometer (Bruker) using tetramethylsilane (TMS) as the internal standard. Chemical shift values and coupling constants are expressed in ppm and Hertz (Hz) respectively.

## Leaching study

For the leaching study, the reaction mixture was filtered after the completion of the reaction. The filtrate was then evaporated in a heating mantle and the residue was dissolved in a solution of  $\text{HNO}_3$  (1 mL  $\text{HNO}_3$  in 12 mL water) for quantitative analysis of Mn and Fe in an atomic absorption spectrometer.

**Table S1.** Optimization of reaction condition for oxidation of benzyl alcohol to benzaldehyde using sample MnF-1 <sup>a</sup>

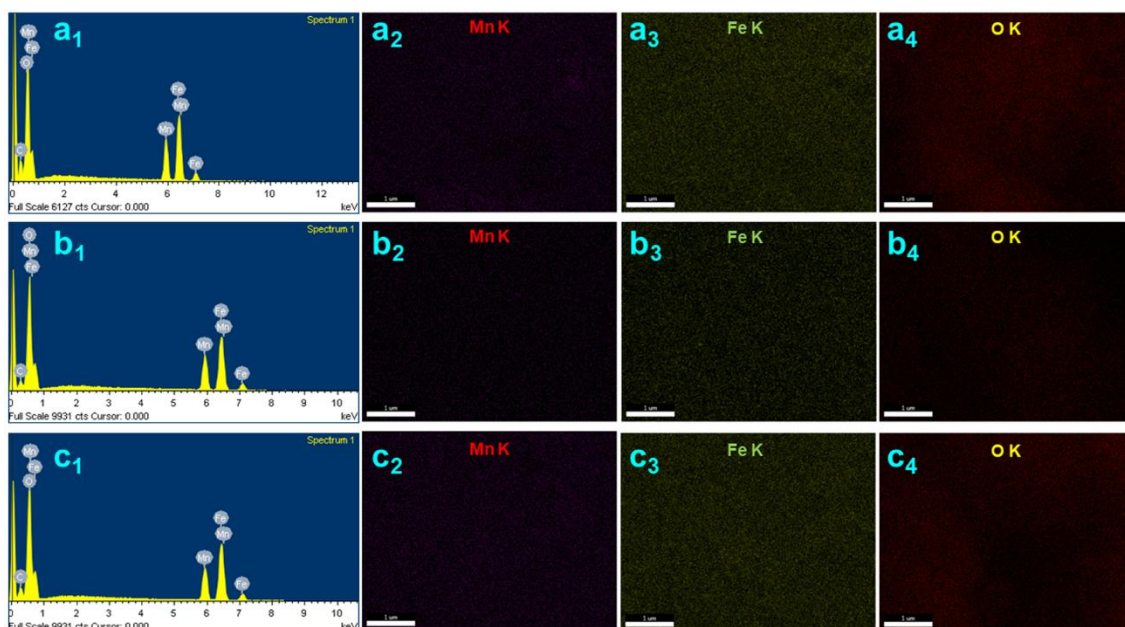


Entry	Catalyst loading (mg)	Solvent (mL)	Oxidant (mmol)	Time (h)	Temperature (°C)	Yield <sup>b</sup> (%)
1	10	-	TBHP (1.5)	3	r.t	85
2	10	CH <sub>3</sub> CN (2.0)	TBHP (1.5)	3	r.t	72
3	10	H <sub>2</sub> O (2.0)	TBHP (1.5)	3	r.t	33
4	10	Toluene (2.0)	TBHP (1.5)	3	r.t	63
5	10	Acetone (2.0)	TBHP (1.5)	3	r.t	21
6	10	CH <sub>3</sub> CN+H <sub>2</sub> O (v/v=1:1; 2.0 mL)	TBHP (1.5)	3	r.t	trace
7	10	CH <sub>3</sub> CN+toluene (v/v=1:1; 2.0 mL)	TBHP (1.5)	3	r.t	30
8	15	-	TBHP (1.5)	2	r.t	90
9	20	-	TBHP (1.5)	2	r.t	92
10	15	-	TBHP (1.0)	2	r.t	80
11	15	-	TBHP (2.0)	2	r.t	91
12	15	-	TBHP (1.5)	2	40	86
13	15	-	TBHP (1.5)	4	r.t	93
14	15	-	H <sub>2</sub> O <sub>2</sub> (1.5)	4	r.t	30
15 <sup>c</sup>	15	-	O <sub>2</sub>	4	r.t	trace

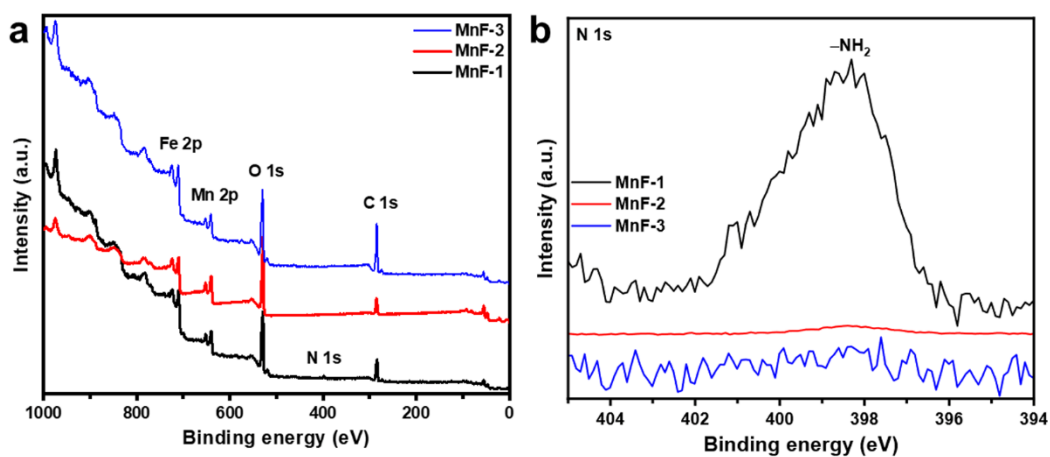
<sup>a</sup> Reaction conditions: benzyl alcohol (1.0 mmol)

<sup>b</sup> isolated yield

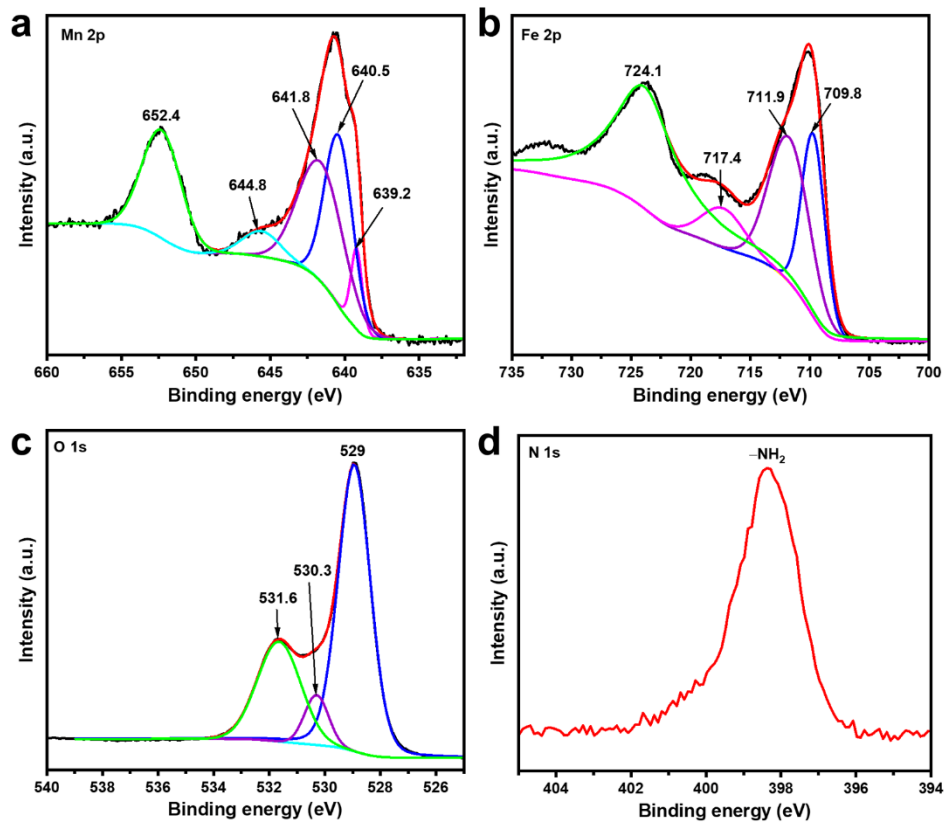
<sup>c</sup> the reaction was performed by placing an O<sub>2</sub> gas filled balloon into the round bottom flask fitted with standard joint.



**Figure S1.** EDX spectra of different samples (a<sub>1</sub>) MnF-1, (b<sub>1</sub>) MnF-2 and (c<sub>1</sub>) MnF-3. The elemental mapping image of samples (a<sub>2</sub>-a<sub>4</sub>) MnF-1, (b<sub>2</sub>-b<sub>4</sub>) MnF-2, and (c<sub>2</sub>-c<sub>4</sub>) MnF-3.



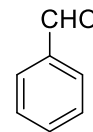
**Figure S2.** (a) XPS survey scan spectra and (b) high resolution XPS spectra of N 1s region recorded from of different samples of MnFe<sub>2</sub>O<sub>4</sub> NPs.



**Figure S3.** High-resolution XPS spectra of (a) Mn 2p, (b) Fe 2p, (c) O 1s, and (d) N 1s regions of sample MnF-1 after catalysis.

## Characterization of the catalytic products

**Entry 1, Table 4:** Benzaldehyde

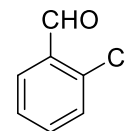


**Physical appearance:** Colourless liquid

**$^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz):**  $\delta$  9.87 (*s*, 1H), 7.74 (*d*, *J*=8 Hz, 2H), 7.48 (*t*, *J*=8 Hz, 2H), 7.38 (*t*, *J*=8 Hz, 1H) ppm

**$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 100 MHz):** 192.45, 136.37, 134.47, 129.72, 128.99 ppm

**Entry 2, Table 4:** 2-chlorobenzaldehyde

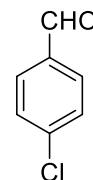


**Physical appearance:** Yellow coloured liquid

**$^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz):**  $\delta$  10.48 (*s*, 1H), 7.93-7.91 (*m*, 1H), 7.55-7.50 (*m*, 1H), 7.48-7.40 (*m*, 1H), 7.37 (*d*, *J*=8 Hz, 1H) ppm

**$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 100 MHz):** 189.91, 135.16, 133.39, 132.34, 131.44, 130.65, 126.71 ppm

**Entry 3, Table 4:** 4-chlorobenzaldehyde

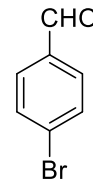


**Physical appearance:** Pale yellow powder; melting point (mp) = 45 °C

**$^1\text{H}$  NMR (CDCl<sub>3</sub>, 400 MHz):**  $\delta$  9.93 (*s*, 1H), 7.77 (*d*, *J*=8 Hz, 2H), 7.46 (*d*, *J*=8 Hz, 2H) ppm

**$^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 100 MHz):** 190.97, 141.02, 134.85, 131.03, 129.54 ppm

**Entry 5, Table 4:** 4-bromobenzaldehyde

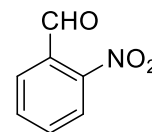


**Physical appearance:** White solid; mp= 57 °C

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):** δ 9.97 (*s*, 1H), 7.74 (*d*, *J*=8 Hz, 2H), 7.68 (*d*, *J*=8 Hz, 2H) ppm

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):** 191.26, 135.20, 132.67, 131.12, 129.86 ppm

**Entry 6; Table 4:** 2-nitrobenzaldehyde

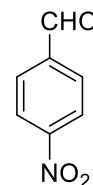


**Physical appearance:** White solid, mp= 43-46 °C

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):** δ 10.40 (*s*, 1H), 8.09 (*t*, *J*=4.5 Hz, 1H), 7.94-7.93 (*m*, 1H), 7.80-7.73 (*m*, 2H) ppm

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):** δ 188.13, 149.93, 134.06, 133.68, 131.23, 129.59, 124.46 ppm

**Entry 8; Table 4:** 4-nitrobenzaldehyde



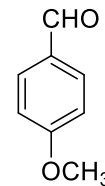
**Physical appearance:** Pale yellow solid; mp= 104-106 °C

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):** δ 10.17 (*s*, 1H), 8.41 (*d*, *J*=8.8 Hz, 2H), 8.08 (*d*, *J*=8.8 Hz, 2H) ppm

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):** δ 190.38, 151.22, 140.12, 130.57, 124.40 ppm



**Entry 10, Table 4:** 4-methoxybenzaldehyde

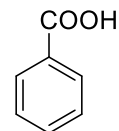


**Physical appearance:** Light yellow liquid

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 500 MHz):** δ 9.87 (*s*, 1H), 7.83 (*t*, *J*=4.25 Hz, 2H), 6.99 (*t*, *J*=4.25 Hz, 2H), 3.88 (*s*, 3H) ppm

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 125 MHz):** δ 191.10, 164.86, 132.51, 130.12, 114.59, 55.83 ppm

Benzoic acid<sup>1</sup>



**Physical appearance:** white crystals; mp= 121-122 °C

**<sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz):** δ 8.13 (*d*, *J*= 8 Hz, 2H), 7.62 (*t*, *J*= 8 Hz), 7.49 (*t*, *J*= 8 Hz, 2H) ppm

**<sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz):** δ 171.90, 133.81, 130.23, 129.32, 128.52 ppm

## $^1\text{H}$ and $^{13}\text{C}$ NMR spectra of selected isolated products

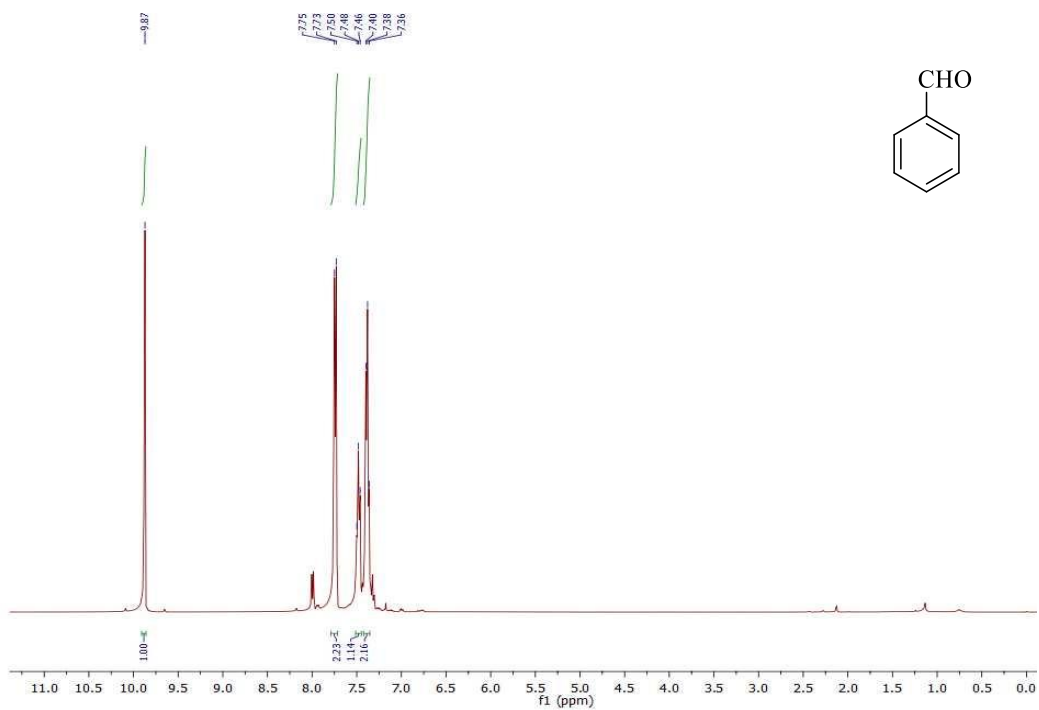


Figure S4.  $^1\text{H}$  NMR spectrum of benzaldehyde.

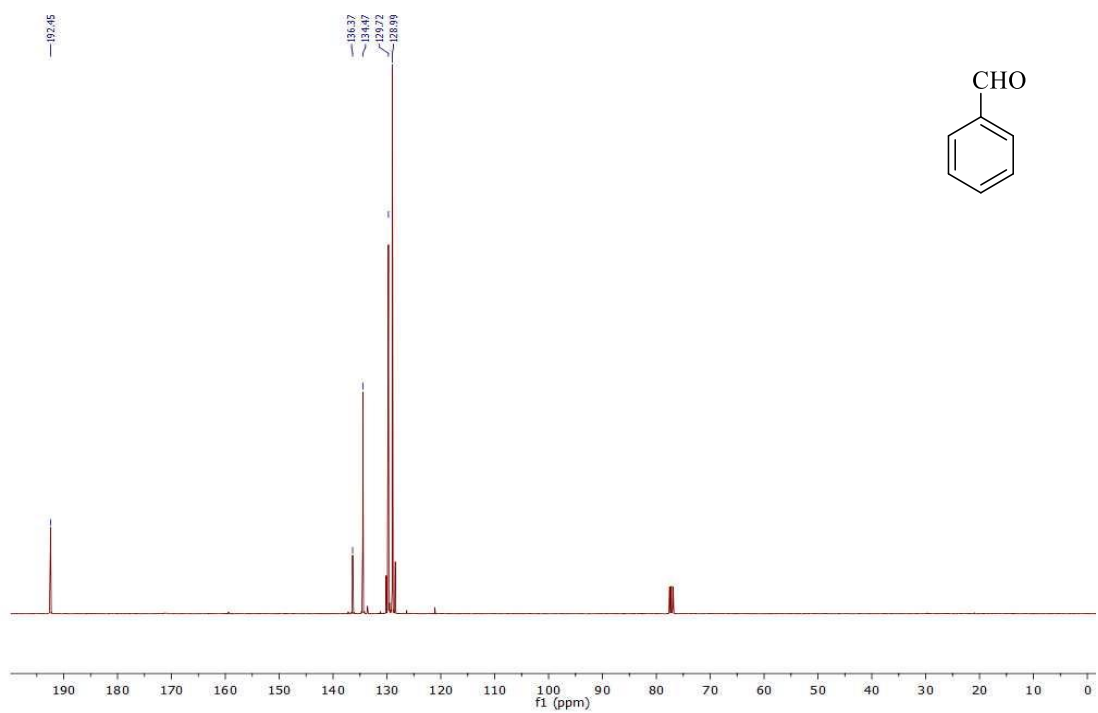
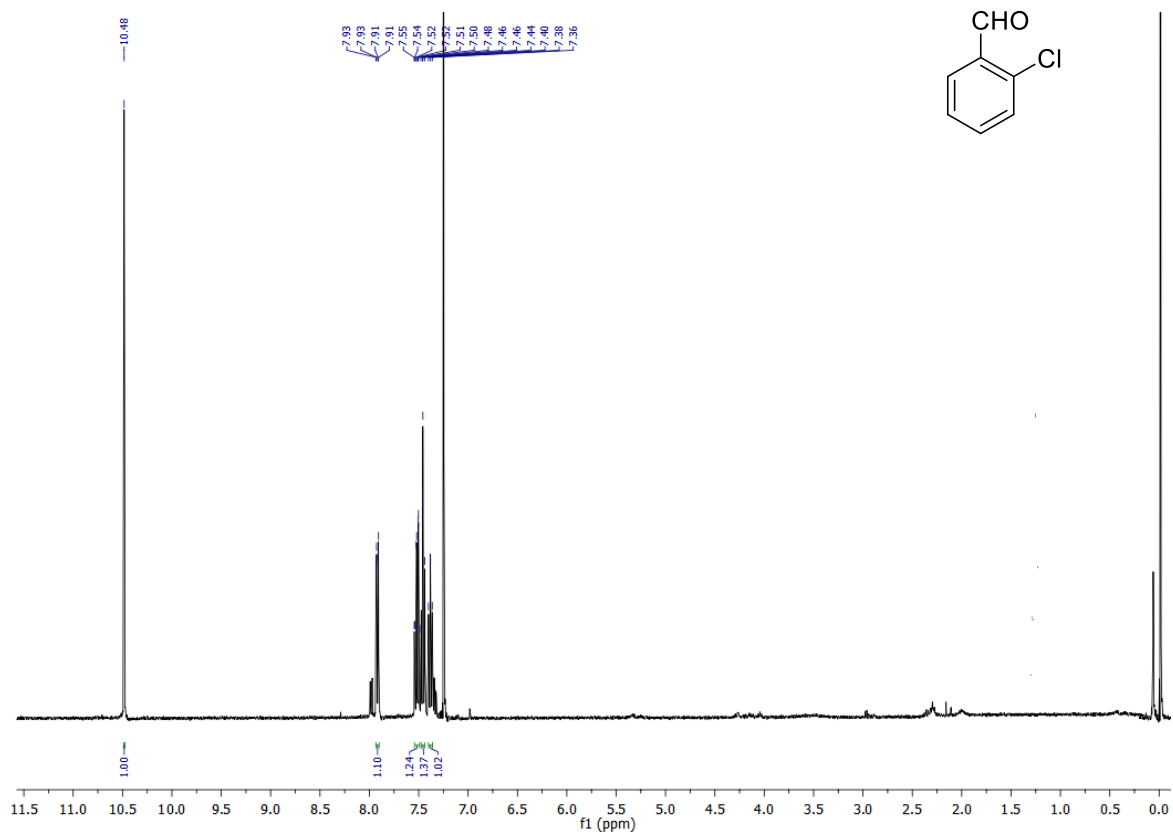
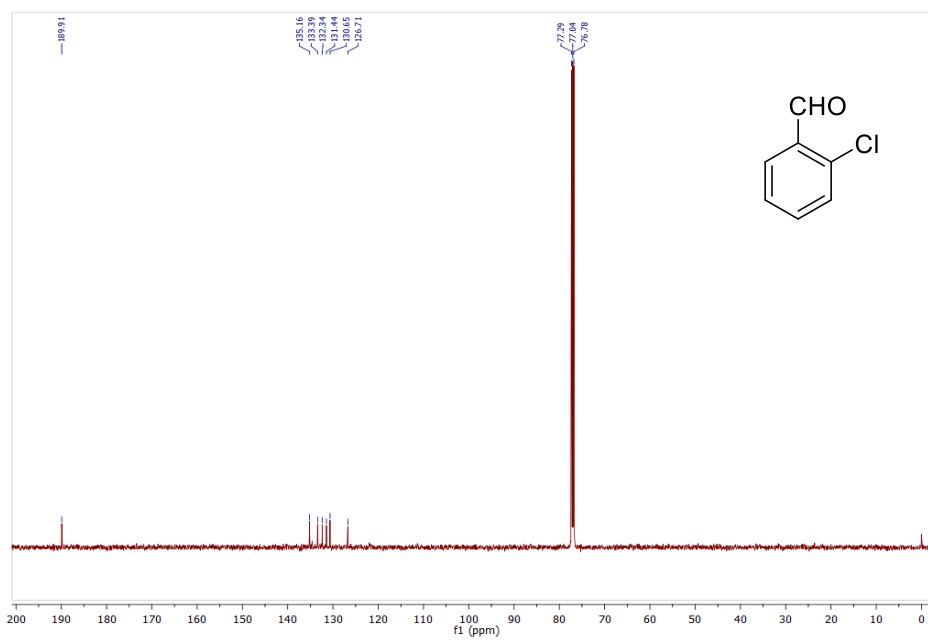


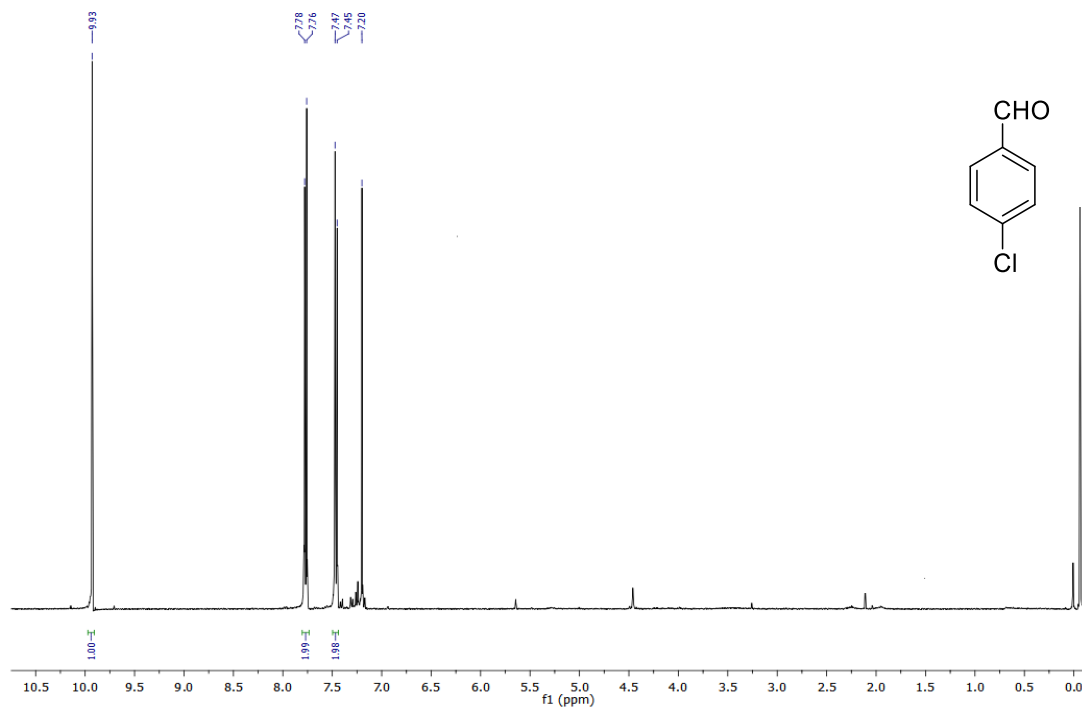
Figure S5.  $^{13}\text{C}$  NMR spectrum of benzaldehyde.



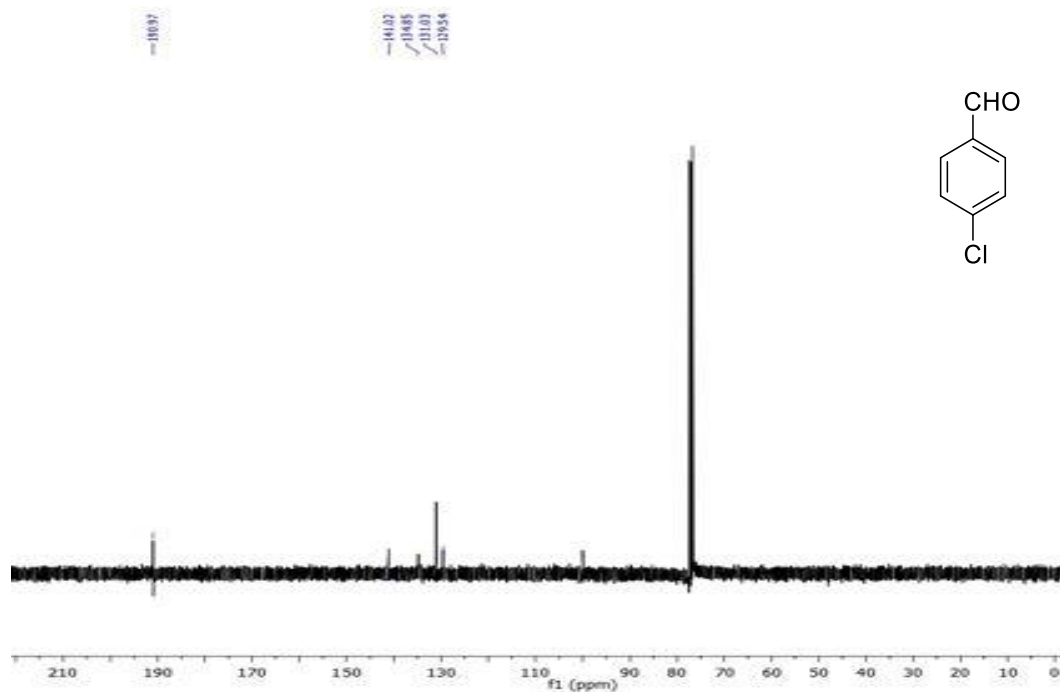
**Figure S6.**  $^1\text{H}$  NMR spectrum of 2-chlorobenzaldehyde.



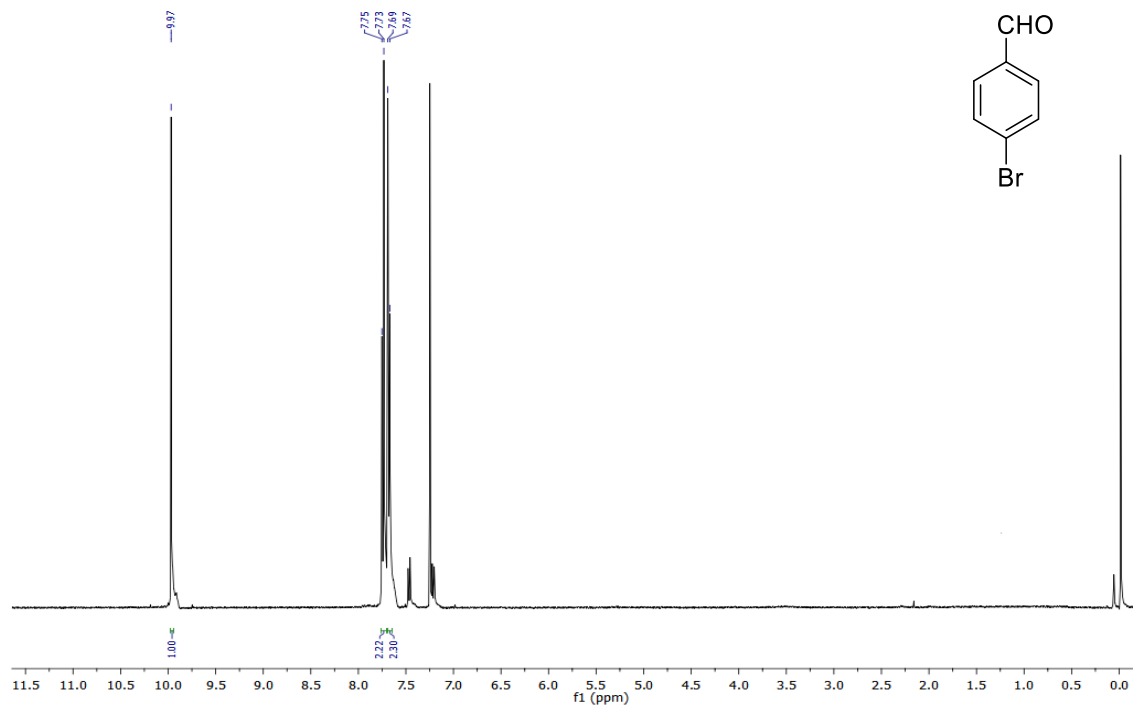
**Figure S7.**  $^{13}\text{C}$  NMR spectrum of 2-chlorobenzaldehyde.



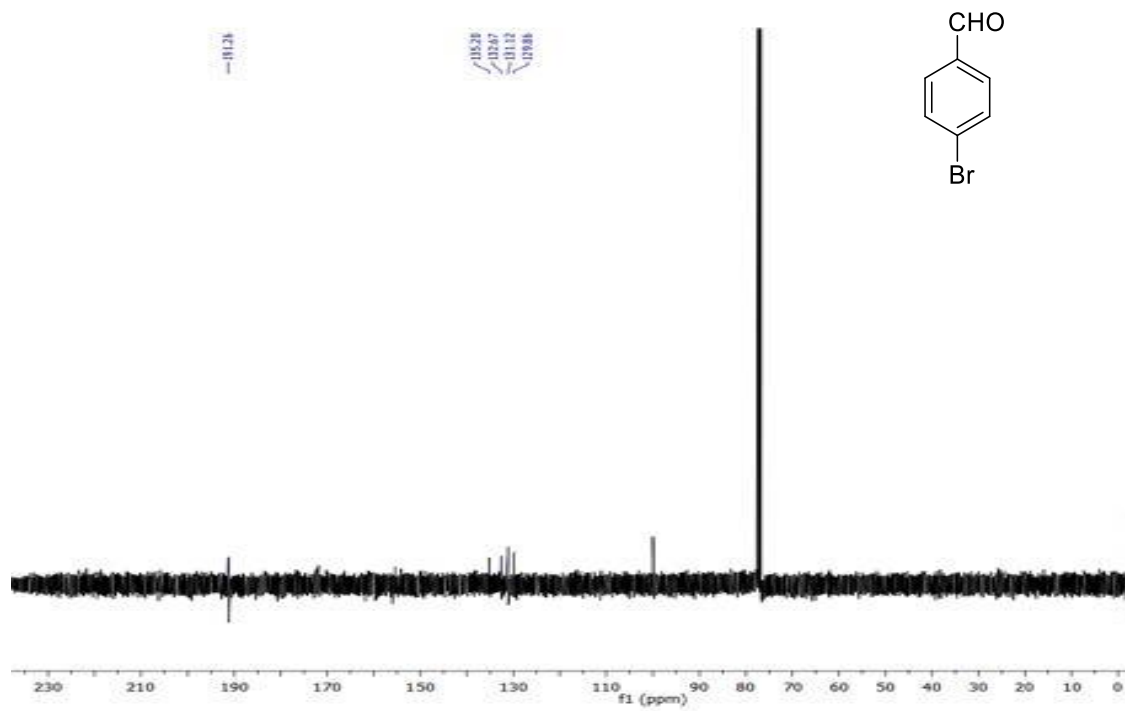
**Figure S8.**  $^1\text{H}$  NMR spectrum of 4-chlorobenzaldehyde.



**Figure S9.**  $^{13}\text{C}$  NMR spectrum of 4-chlorobenzaldehyde.



**Figure S10.**  $^1\text{H}$  NMR spectrum of 4-bromobenzaldehyde.



**Figure S11.**  $^{13}\text{C}$  NMR spectrum of 4-bromobenzaldehyde.

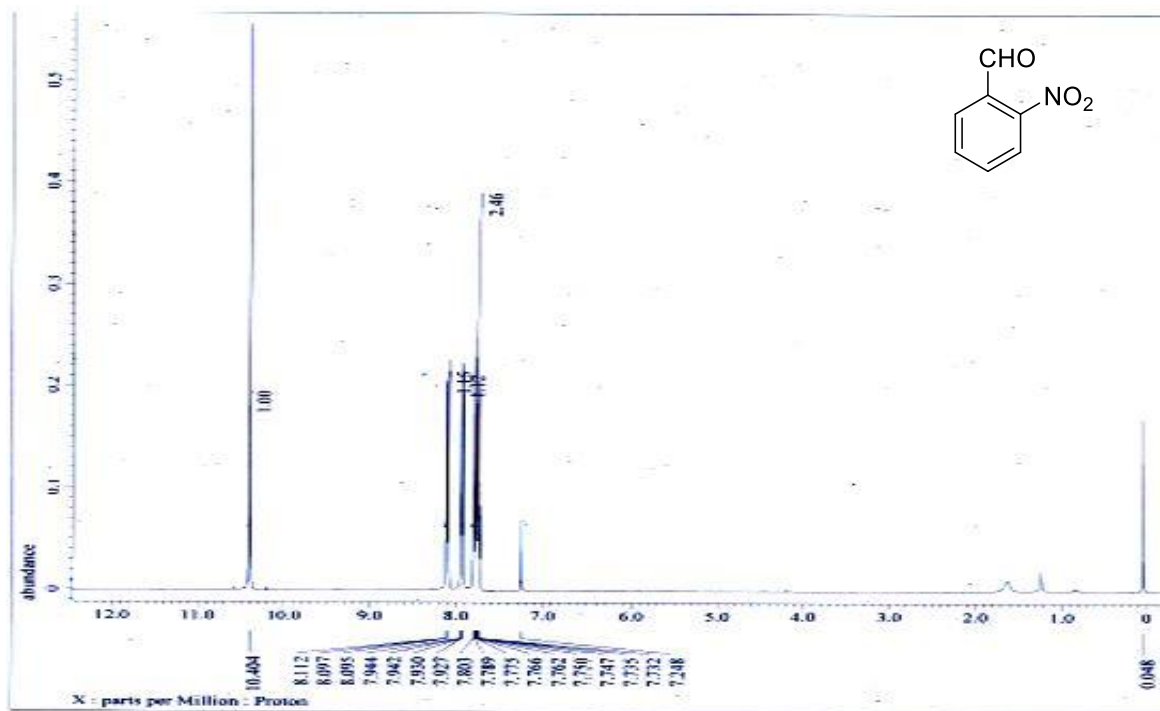


Figure S12.  $^1\text{H}$  NMR spectrum of 2-nitrobenzaldehyde.

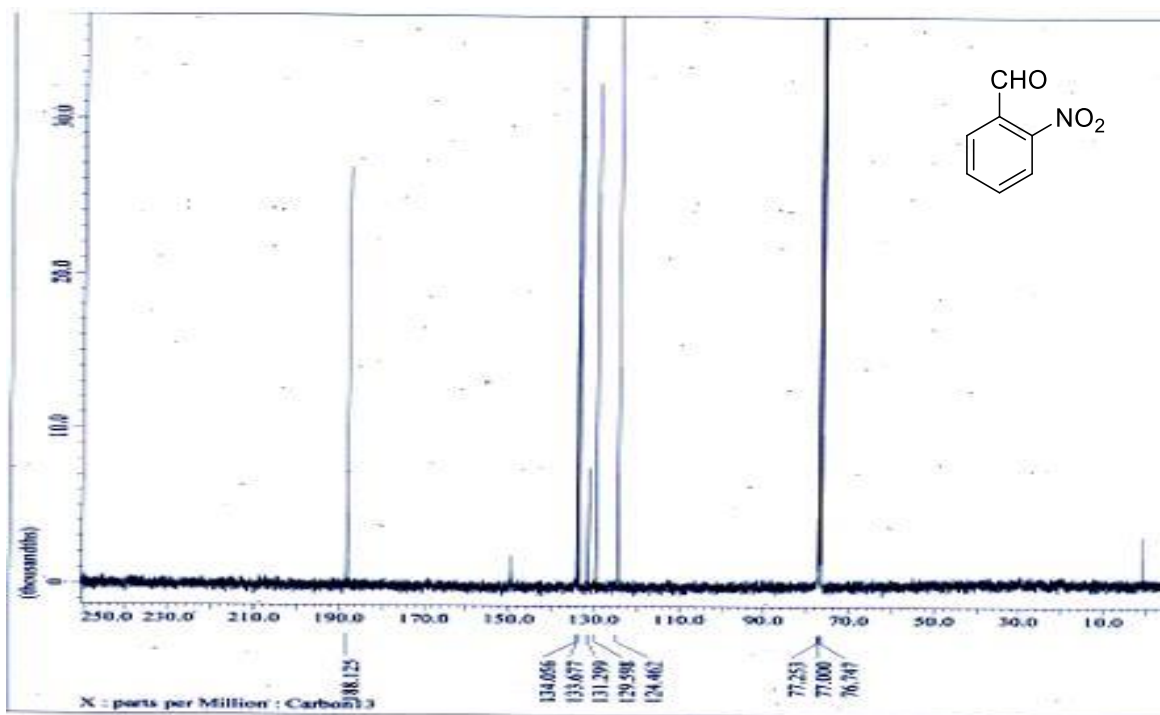


Figure S13.  $^{13}\text{C}$  NMR spectrum of 2-nitrobenzaldehyde.

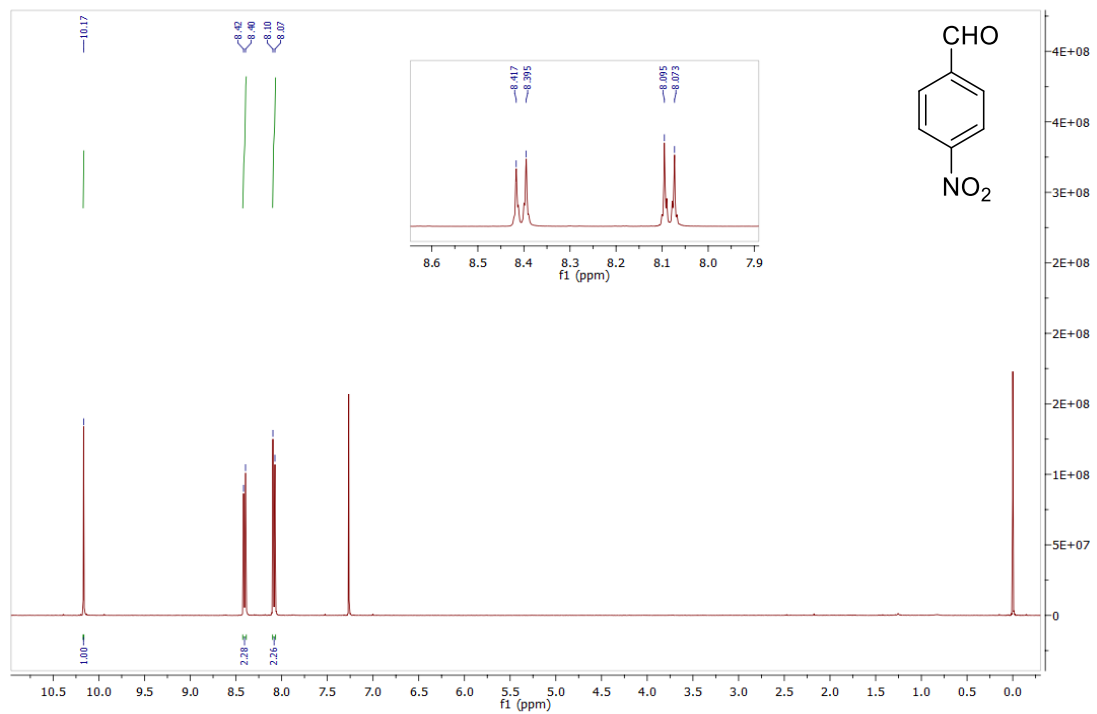


Figure S14.  $^1\text{H}$  NMR spectrum of 4-nitrobenzaldehyde.

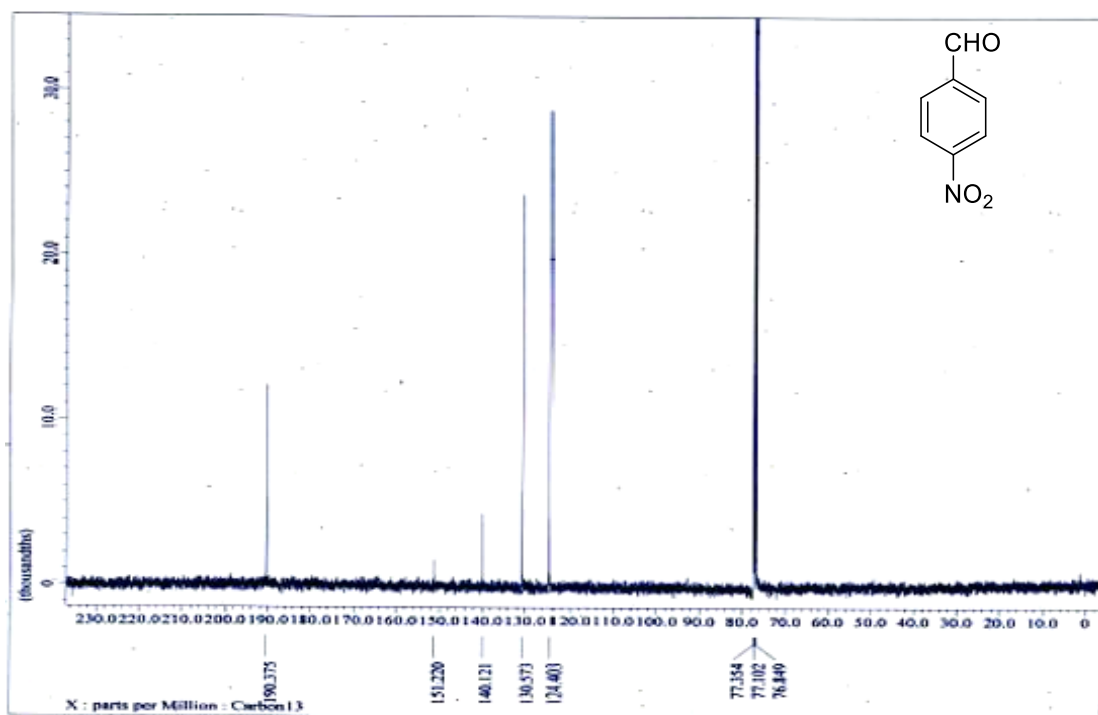


Figure S15.  $^{13}\text{C}$  NMR spectrum of 4-nitrobenzaldehyde.

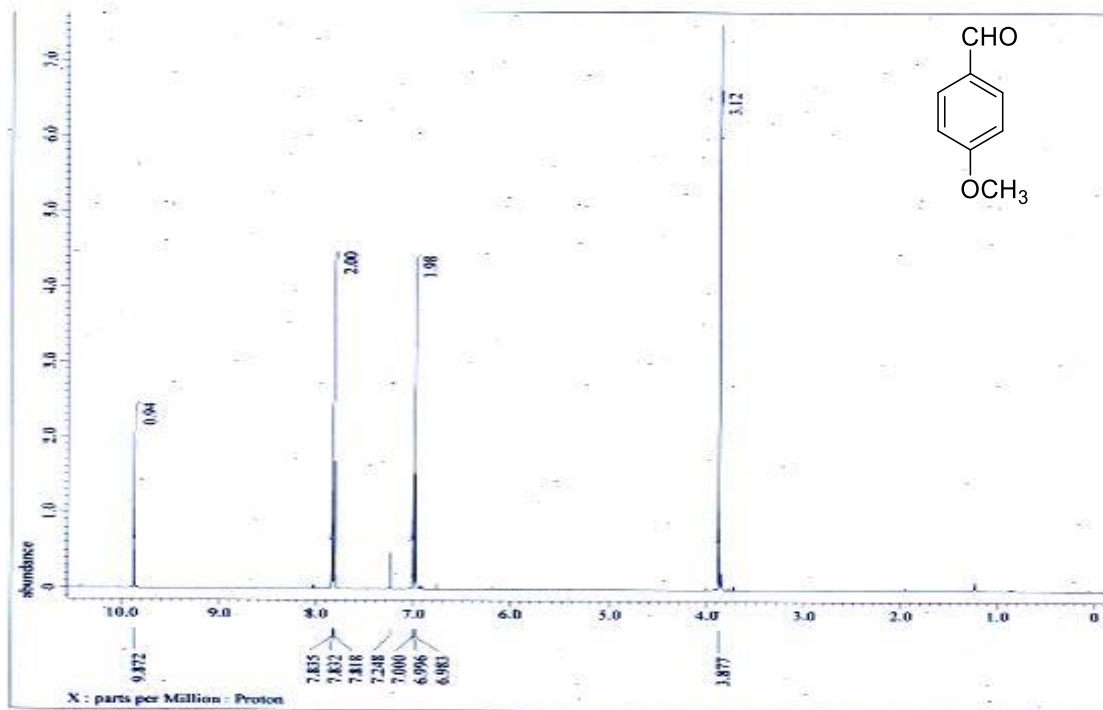


Figure S16.  $^1\text{H}$  NMR spectrum of 4-methoxybenzaldehyde.

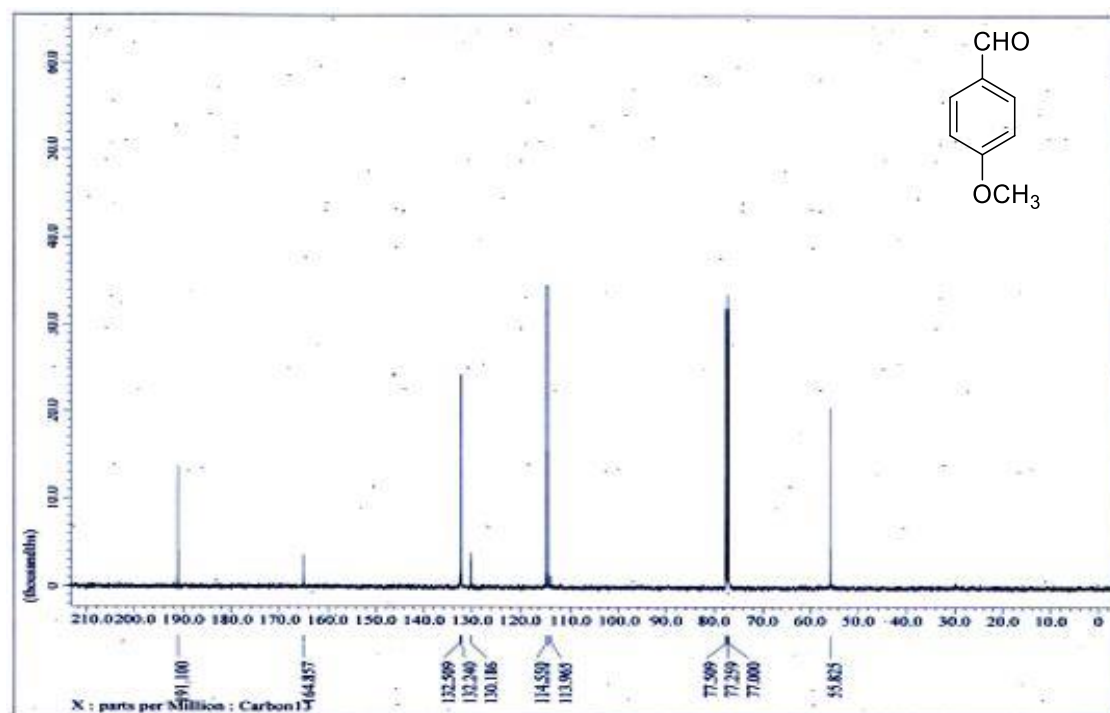
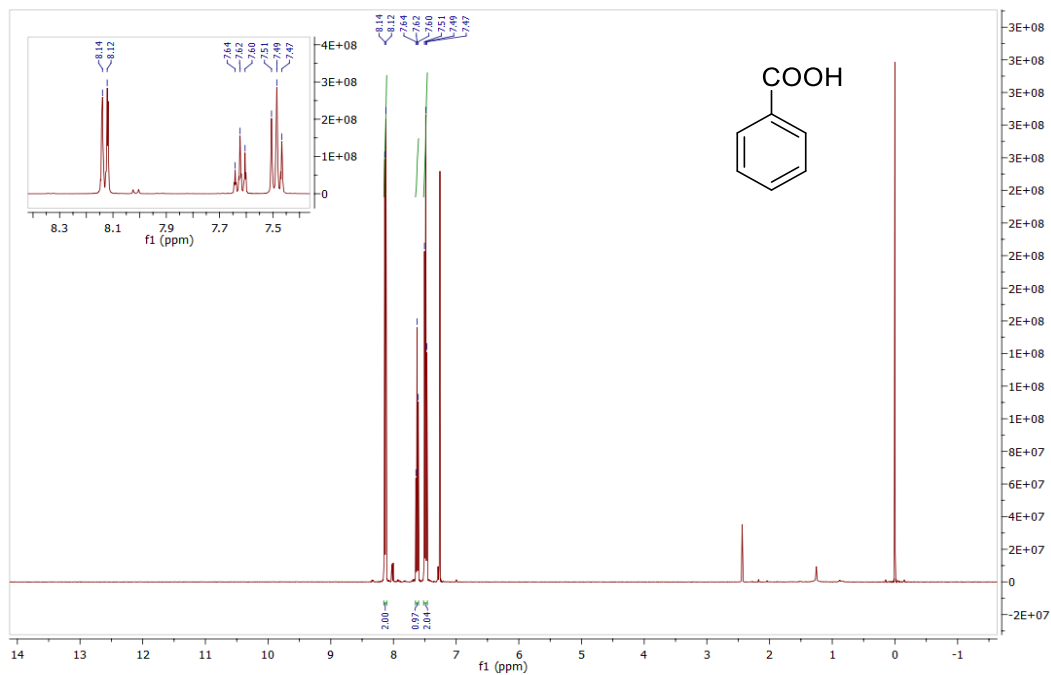
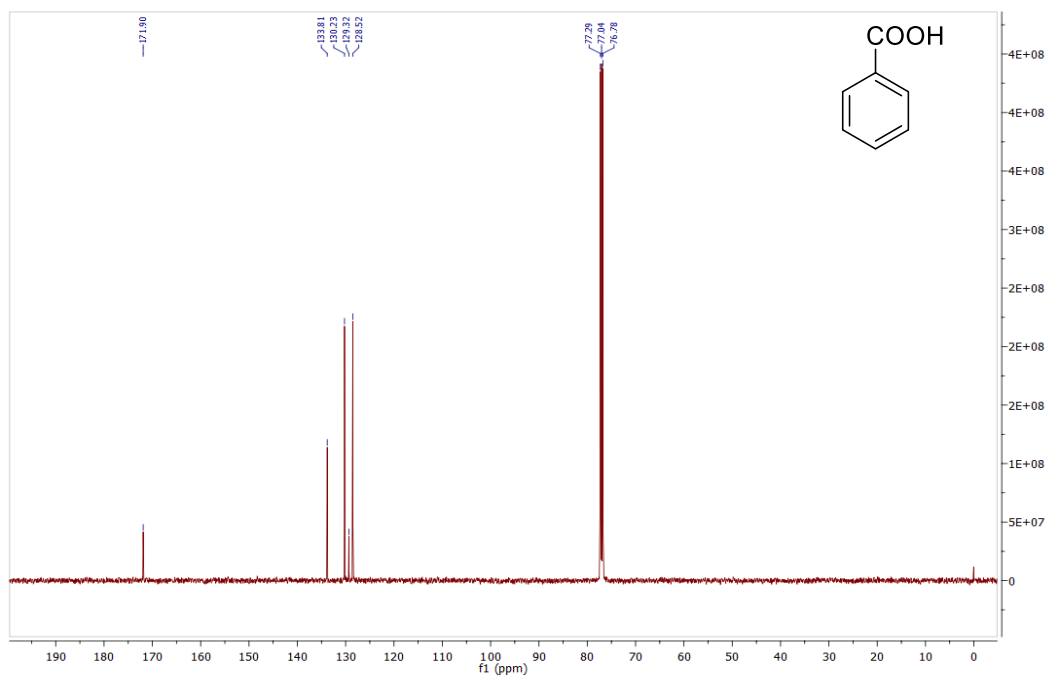


Figure S17.  $^{13}\text{C}$  NMR spectrum of 4-methoxybenzaldehyde.





**Figure S18.** <sup>1</sup>H NMR spectrum of benzoic acid.



**Figure S19.** <sup>13</sup>C NMR spectrum of benzoic acid.

**Reference.**

1. Guan, X. et al. *New J. Chem.*, 2021, 45, 18192. DOI: 10.1039/D1NJ03145G