

## Electronic Supplementary Information

### An unconventional iron oxide catalyst for 5-hydroxymethylfurfural oxidation to 2,5-diformylfuran

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## 1. Materials and methods

### 1.1. Chemicals and materials

All chemicals and solvents used under present work were of high purity grade (AR) and straightforwardly utilized as received without any further purification. The used  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and xylene (mixture of ortho-, meta- and para forms) were purchased from Sigma Aldrich and Central Drug Health (P) Ltd. respectively. Sodium sulphate (anhydrous) and silica gel 60-120 were purchased from SD Fine Chem. Ltd. The used molecular oxygen was supplied from an oxygen cylinder through balloon. A high-pressure autoclave reactor (made of stainless steel, 250 mL) connected with oxygen cylinder was utilized for the activation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> at particular temperature and oxygen pressure.

### 1.2. Analytical instruments and methods

The Bruker Advance 600/300 MHz (<sup>1</sup>H) and 150/75 MHz (<sup>13</sup>C) Nuclear Magnetic Resonance (NMR) spectrometer was used for recording <sup>1</sup>H and <sup>13</sup>C NMR spectra for all synthesised compounds. The spectra of synthesised molecules were recorded at 25 °C under CDCl<sub>3</sub> solvent [residual CHCl<sub>3</sub> ( $\delta_H$  7.26 ppm) or CDCl<sub>3</sub> ( $\delta_C$  77.00 ppm)]. The chemical shifts were recorded in  $\delta$  (ppm) relative to the TMS and NMR solvent signal. The coupling constants (J) were given in Hz, and multiplicities were reported as s, singlet; d, doublet; m, multiplet. The mass spectrum for some of prepared compounds were performed on Waters micro mass Q-TOF Ultima spectrometer and Agilent high resolution 6560 Ion Mobility Q-TOF LC/MS spectrometer using electron spray ionization (ESI) technique. The mass spectra of some of other remaining compounds were also recorded on Gas Chromatography Mass Spectrometry using electron ionization (EI) technique (Shimadzu (QP 2010) series GC-MS (Tokyo, Japan), equipped with FID, AOC 5000 autosampler, DB-5MS capillary column (30m $\times$  0.25mm i.e. width film thickness 0.25 $\mu$ m)). The size of nano particles of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> catalyst before and after performing the reaction, and thereafter its activation was analysed through Transmission Electron Microscope (TEM; FEI, Technai G2sTwin). The phase transition occurring before and after performing the reaction and thereafter its activation was analysed by Fourier Transform Infrared Spectroscopy (FTIR; Shimadzu) in range between 4000-400 cm<sup>-1</sup>. On the same note, the change in oxidation state of iron (Fe) in  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (following phase transition) before and after performing the reaction, and thereafter its activation was analysed through using X-ray photoelectron spectroscopy (XPS; Thermofisher scientific, Nexsa base, ). The alteration in crystalline structure of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> before and after performing the reaction, and thereafter its activation was analysed by using Powder X-ray Diffractometer (P-XRD; Rigaku Corporation,

Smart Lab 9kW rotating anode x-ray diffractometer). In addition, the thin layer chromatography (TLC) using Merck pre-coated silica gel plates 60F254 under UV light detector was utilized for monitoring the reaction progress.

### 1.3. Yield calculations

The following two equations were used for calculating the conversion of the reaction and selectivity of desired compounds:

$$\text{Conversion of the reaction} = (M_{RC} / M_{RI}) \times 100 \quad \dots\dots(1)$$

where  $M_{RC}$  stands for number of millimoles of the reactant consumed and  $M_{RI}$  stands for number of millimoles of reactant initially taken of.

$$\text{Selectivity of desired oxidised product} = (M_P / M_{RC}) \times 100 \quad \dots\dots(2)$$

where  $M_P$  stands for number of millimoles of the product formed and  $M_{RC}$  stands for number of millimoles of reactant consumed.

### 1.4. Experimental methods

#### General experimental description

An oven dried round bottomed flask/Pyrex<sup>®</sup> reaction tube was charged with 5-hydroxymethylfurfural (5HMF) and iron oxide (2 equiv.) in xylene as solvent medium. The round bottomed flask was then tightly packed by rubber septum over which the oxygen balloon was inserted with the help of a long needle. Then the reaction mixture was allowed to stir at 135 °C reaction temperature for 12 hrs under vigorous stirring. After that, the progress of the reaction was monitored on thin layer chromatography (TLC). The targeted compounds were extracted by ethyl acetate, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure system. The crude reaction mass was then purified by performing column chromatography in hexane:ethyl acetate (7:3) as eluent. Finally, the oxidized products were analyzed and confirmed by NMR and ESI-MS/GC-MS analytical techniques.

#### 1.4.1. Experimental procedure for 5-HMF conversion to DFF synthesis

An oven dried Pyrex<sup>®</sup> reaction tube (40 mL) was charged with 5-hydroxymethylfurfural (5-HMF) (0.397 mmol, 50.00 mg) and iron oxide (0.794 mmol 126.73 mg) in xylene (3 mL) solvent system. The Pyrex<sup>®</sup> tube was then tightly packed by a rubber septum through which an oxygen balloon was inserted with the help of a long cannula, and allowed to flow continuously within the reaction media. Then the reaction mixture was allowed to stir at 135 °C reaction temperature (oil temperature of hot

plate = 145 °C) for 12 hrs reaction time. The progress of the reaction was monitored by thin layer chromatography (TLC). After the completion of the reaction, the crude was extracted by ethyl acetate in repetitive iterations, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure system. The desired compound diformylfuran (DFF) then isolated through column chromatography and weighed to 38.00 mg (82% conversion, 94% selectivity). Finally, the desired product (DFF) was analyzed and confirmed by NMR and GC-MS analytical techniques.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 9.79 (s, 2H), 7.29 (s, 2H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 178.24, 153.17, 118.42; m/z MS (EI) [M]<sup>+</sup> = 124, [M-H]<sup>+</sup> = 123, [M-CHO]<sup>+</sup> = 95.

#### **1.4.2. Experimental procedure for scale-up synthesis of DFF from 5-HMF**

An oven dried two neck round bottomed flask (100 mL) was charged with 5-hydroxymethylfurfural (5HMF) (3.968 mmol, 500.00 mg) and iron oxide (7.936 mmol, 1267.46 mg) in xylene (13 mL) solvent medium. The round bottomed flask was then tightly packed by rubber septum through which an oxygen balloon was inserted with the help of a long cannula, and allowed to flow constantly. Then, the reaction mixture was allowed to stir at 135 °C for 12 hrs. The progress of the reaction was monitored on TLC. After completion of reaction, the reaction crude was extracted by ethyl acetate, dried over Na<sub>2</sub>SO<sub>4</sub>, and evaporated using rotary evaporator. The reaction crude then purified through column chromatography to isolate DFF in 275.00 mg amount (68% conversion, 83% selectivity). Finally, the product was analyzed and confirmed by NMR and GC-MS analytical techniques. The spectral data was same as mentioned in experimental description 1.4.1.

#### **1.4.3. Experimental procedure for gram scale synthesis of DFF from 5-HMF**

An oven dried round bottomed flask (100 mL) was charged with 5-hydroxymethylfurfural (5HMF) (7.936 mmol, 1.00 g) and iron oxide (15.873 mmol, 2.53 g) in xylene (26 mL) solvent media. Further, the same experimental procedure was followed as described in experimental section 1.4.2. to yield DFF as final product. The product was weighed to 450.00 mg (65% conversion, 71% selectivity), and analyzed and confirmed by NMR and GC-MS analytical techniques. The spectral data was same as mentioned in experimental description 1.4.1.

#### **1.4.4. Experimental procedure for 3-methoxybenzaldehyde synthesis from 3-methoxybenzylalcohol**

An oven dried Pyrex<sup>®</sup> reaction tube (40 mL) was charged with 3-methoxybenzylalcohol (0.362 mmol, 50.00 mg) and iron oxide (0.724 mmol, 115.62 mg) in xylene (3 mL) solvent. The Pyrex<sup>®</sup> tube was then tightly packed by a rubber septum through which an oxygen balloon was inserted

with the help of a long cannula, and allowed to flow continuously within the reaction media. Then the reaction mixture was allowed to stir at 135 °C reaction temperature for 12 hrs reaction time. The progress of the reaction was monitored by thin layer chromatography (TLC). After the completion of the reaction, the crude was extracted by ethyl acetate in repetitive iterations, dried over Na<sub>2</sub>SO<sub>4</sub> and evaporated under reduced pressure system. The desired oxidized compound 3-methoxybenzaldehyde then isolated through column chromatography and weighed to 45.00 mg (92% conversion, 99% selectivity). Finally, the oxidized product was analyzed and confirmed by NMR and ESI-MS analytical techniques.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 9.90 (s, 1H), 7.38-7.35 (m, 2H), 7.32-7.31 (d, *J* = 1.8 Hz, 1H), 7.11-7.09 (m, 1H), 3.79 (s, 3H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 191.10, 159.15, 136.81, 129.01, 122.51, 120.50, 111.06, 54.45; m/z MS (EI) [M]<sup>+</sup> = 136, [M-H]<sup>+</sup> = 135, [M-CHO]<sup>+</sup> = 107.

#### **1.4.5. Experimental procedure for 3,4-dimethylbenzaldehyde synthesis from 3,4-dimethylbenzylalcohol**

An oven dried Pyrex<sup>®</sup> reaction tube (40 mL) was charged with 3,4-dimethylbenzylalcohol (0.367 mmol, 50.00 mg) and iron oxide (0.734 mmol, 117.26 mg) in xylene (3 mL) solvent. After that, the same experimental procedure was followed as described in experimental section 1.4.4. to yield 3,4-dimethylbenzaldehyde as oxidized product. The oxidized product was weighed to 45.00 mg (94% conversion, 97% selectivity), and analyzed and confirmed by NMR and GC-MS analytical techniques.

<sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>) δ 9.84 (s, 1H), 7.55 (s, 1H), 7.52 (d, *J* = 7.7 Hz, 1H), 7.20 (d, *J* = 7.7 Hz, 1H), 2.25 (d, *J* = 4.1 Hz, 6H); <sup>13</sup>C NMR (150 MHz, CDCl<sub>3</sub>) δ 191.23, 143.28, 136.47, 133.60, 129.54, 129.22, 126.71, 19.21, 18.61; m/z MS (EI) [M]<sup>+</sup> = 134, [M-H]<sup>+</sup> = 133, [M-CHO]<sup>+</sup> = 105.

#### **1.4.6. Experimental procedure for 4-methylbenzaldehyde synthesis from 4-methylbenzylalcohol**

An oven dried Pyrex<sup>®</sup> reaction tube (40 mL) was charged with 4-methylbenzylalcohol (0.409 mmol, 50.00 mg) and iron oxide (0.818 mmol, 130.73 mg) in xylene (3 mL) solvent. After that, the same experimental procedure was followed as described in experimental section 1.4.4. to yield 4-methylbenzaldehyde as oxidized product. The oxidized product was weighed to 47.00 mg (100% conversion, 96% selectivity), and analyzed and confirmed by NMR and GC-MS analytical techniques.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.91 (s, 1H), 7.73 (d,  $J = 8.0$  Hz, 2H), 7.27 (d,  $J = 8.0$  Hz, 2H), 2.38 (s, 3H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  190.99, 144.52, 133.16, 128.82, 128.68, 20.85; m/z MS (EI)  $[\text{M}]^+ = 120$ ,  $[\text{M}-\text{H}]^+ = 119$ ,  $[\text{M}-\text{CHO}]^+ = 91$ .

#### **1.4.7. Experimental procedure for 4-chlorobenzaldehyde synthesis from 4-chlorobenzylalcohol**

An oven dried Pyrex<sup>®</sup> reaction tube (40 mL) was charged with 4-chlorobenzylalcohol (0.351 mmol, 50.00 mg) and iron oxide (0.701 mmol, 111.51 mg) in xylene (3 mL) solvent. After that, the same experimental procedure was followed as described in experimental section 1.4.4. to yield 4-chlorobenzaldehyde as oxidized product. The oxidized product was weighed to 45.00 mg (94% conversion, 97% selectivity), and analyzed and confirmed by NMR and GC-MS analytical techniques.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.91 (s, 1H), 7.75 (d,  $J = 8.4$  Hz, 2H), 7.44 (d,  $J = 8.4$  Hz, 2H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  190.84, 140.96, 134.74, 130.90, 129.46; m/z MS (EI)  $[\text{M}]^+ = 140$ ,  $[\text{M}-\text{H}]^+ = 139$ ,  $[\text{M}-\text{CHO}]^+ = 111$ .

#### **1.4.8. Experimental procedure for 3-bromobenzaldehyde synthesis from 3-bromobenzylalcohol**

An oven dried Pyrex<sup>®</sup> reaction tube (40 mL) was charged with 3-bromobenzylalcohol (0.267 mmol, 50.00 mg) and iron oxide (0.534 mmol, 85.00 mg) in xylene (3 mL) solvent. After that, the same experimental procedure was followed as described in experimental section 1.4.4. to yield 3-bromobenzaldehyde as oxidized product. The oxidized product was weighed to 46.00 mg (94% conversion, 99% selectivity), and analyzed and confirmed by NMR and GC-MS analytical techniques.

$^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ )  $\delta$  9.87 (s, 1H), 7.92 (s, 1H), 7.72 (d,  $J = 7.6$  Hz, 1H), 7.66 (d,  $J = 8.0$  Hz, 1H), 7.33 (t,  $J = 7.6$  Hz, 1H);  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ )  $\delta$  190.73, 138.00, 137.29, 132.32, 130.63, 128.38, 123.37; m/z MS (EI)  $[\text{M}]^+ = 184$  (Exact Mass),  $[\text{M}-\text{H}]^+ = 183$ ,  $[\text{M}-\text{CHO}]^+ = 155$ .

#### **1.4.9. Experimental procedure for conversion of 5-methylfurfuryl alcohol to 5-methylfurfuraldehyde**

An oven dried Pyrex<sup>®</sup> reaction tube (40 mL) was charged with 5-methylfurfuryl alcohol (0.446 mmol, 50.00 mg) and iron oxide (0.892 mmol, 142.58 mg) in xylene (3 mL) solvent. After that, the same experimental procedure was followed as described in experimental section 1.4.4. to yield 5-methylfurfuraldehyde as oxidized product although obtained in very trace amount with

100% conversion of reaction. The oxidized product was analyzed by GC-MS analytical technique.

m/z MS (EI)  $[M]^+ = 110$ ,  $[M-H]^+ = 109$ ,  $[M-CHO]^+ = 81$ .

#### **1.5.0. Experimental procedure for conversion of 2,5-Bis(hydroxymethyl)furan to 5-hydroxymethylfurfural**

An oven dried Pyrex<sup>®</sup> reaction tube (40 mL) was charged with 2,5-bis(hydroxymethyl)furan (0.391 mmol, 50.00 mg) and iron oxide (0.781 mmol, 124.75 mg) in xylene (3 mL) solvent. After that, the same experimental procedure was followed as described in experimental section 1.4.4. to yield 5-hydroxymethylfurfural as oxidized product. The oxidized product was weighed to 10.00 mg (96% conversion, 21% selectivity), and analyzed and confirmed by ESI-MS analytical technique.

m/z MS (ESI)  $[M+1]^+ = 127$ ,  $[M-H_2O]^+ = 109$ .

#### **1.5.1. Experimental procedure for conversion of methyl-5-(hydroxymethyl)furan-2-carboxylate to methyl-5-formyl-2-furoate**

An oven dried Pyrex<sup>®</sup> reaction tube (40 mL) was charged with methyl-5-(hydroxymethyl)furan-2-carboxylate (0.321 mmol, 50.00 mg) and iron oxide (0.641 mmol, 102.36 mg) in xylene (3 mL) solvent. After that, the same experimental procedure was followed as described in experimental section 1.4.4. to yield methyl-5-formyl-2-furoate as oxidized product. The oxidized product was weighed to 10.00 mg (52% conversion, 39% selectivity), and analyzed and confirmed by ESI-MS analytical technique.

m/z MS (EI)  $[M]^+ = 154$ ,  $[M-H]^+ = 153$ ,  $[M-CHO]^+ = 125$ ,  $[M-OMe]^+ = 123$ ,  $[M-CO_2Me]^+ = 95$ ,  $[M-CO_2Me-CO]^+ = 67$ .

## **2. Recyclability test for used $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> catalyst**

### **2.1. Method optimization for activation of used iron oxide catalyst**

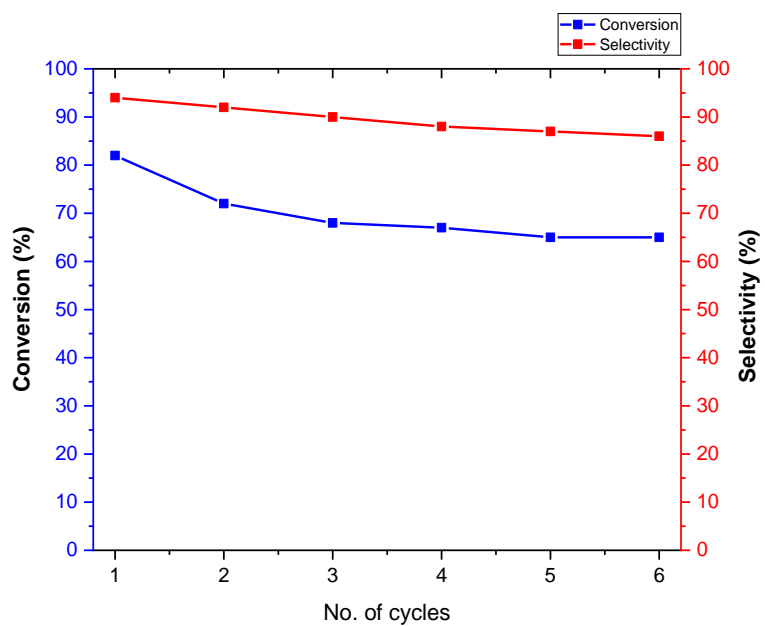
A high-pressure autoclave reactor connected to O<sub>2</sub> cylinder was utilized for optimizing the best suitable conditions for the activation of used  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. Initially, we optimized the temperature for this purpose starting from 150 to 350 °C through 250 °C at 12 hrs operational time, and found that 250 °C temperature was suitable to perform the action. Similarly, the O<sub>2</sub> pressure was optimized initiating from 10-20 bar range and then subsequently enhancing to 70-80 bar through 30-40 bar range. It was noticed that at high temperature 350 °C and pressure 70-80 bar,

the used iron oxide became reddish in color and when implemented to standard reaction conditions for DFF synthesis then yielded it only in trace amount. Although, when the same used  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was allowed to keep in high-pressure reactor at operational conditions of 250 °C and 30-40 bar (O<sub>2</sub> pressure) for 12 hrs then the resulted  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> was obtained in brownish color, and on further implementing under the standard reaction conditions interestingly afforded DFF in good conversion and selectivity. Hence, through this study the best optimized operational conditions for activation of used  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> were set to 250 °C temperature and 30-40 bar O<sub>2</sub> pressure for 12 hrs.

## 2.2. Recyclability experiments

Once the methodology was well optimized to yield maximum 5-HMF conversion and DFF selectivity, and found to perform well in gram scale, then after that we performed recyclability test for used catalyst. In the beginning, when we directly utilized one cycle older Fe<sub>2</sub>O<sub>3</sub> catalyst in the next consecutive cycle without any prior activation, then the applied reaction conditions did not give DFF as final product and almost whole 5-HMF remained as such. Thereby, we then activated the used Fe<sub>2</sub>O<sub>3</sub> catalyst at optimized temperature 250 °C and 30-40 bar O<sub>2</sub> pressure in a high-pressure autoclave reactor for 12 hrs. After activating the catalyst, we observed a decrease in its weight by 17 mg and finally we obtained 110 mg catalyst, which was to be used for next cycle (initially it was 127 mg). Now as per the obtained amount of catalyst (110 mg), accordingly we took 5-HMF (43 mg) as initial feed and then performed the next cycle at standard reaction conditions. To our fortune, the reaction performed well in this case, and we ended up with DFF in 92% selectivity and 72% conversion. Although, 10% decrease in conversion was still noticed whereas the selectivity almost remained the same. In the same manner, when we further activated the catalyst following the same parameters after reaction work-up then this time we ended up with 94 mg  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. Now, further accordingly we took 5-HMF (37 mg) as per catalyst amount for third cycle and performed the reaction. Interestingly, this time we also obtained DFF in 90% selectivity with 68% conversion. Therefore, following this procedure first we activated catalyst and then according to the reduced weight of catalyst we took 5-HMF as initial feed and then performed the reaction up to six cycles. In this way, the catalyst was recycled upto six cycles with almost slight loss in DFF selectivity meanwhile 5-HMF conversion reduced to 65% (**Fig. 1**). It was also noticed that after 6<sup>th</sup> cycle we ended up with 74 mg iron oxide. The loss in crystalline structure of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> NPs (XRD analysis) along with the enhancement in particle size (TEM analysis) due to agglomeration might be the cause for the reduction in 5-HMF conversion.

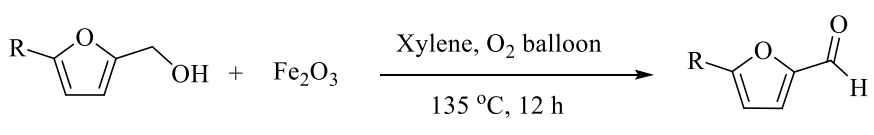
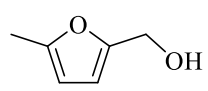
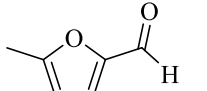
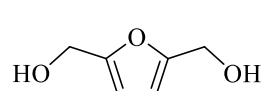
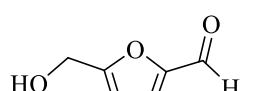
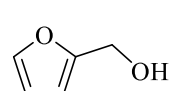
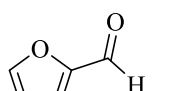
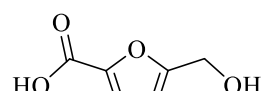
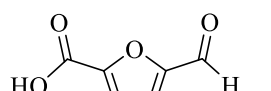
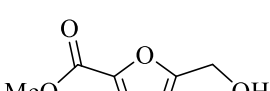
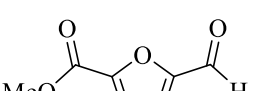




**Figure 1.** Recyclability test for  $\text{Fe}_2\text{O}_3$

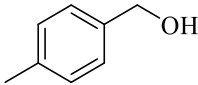
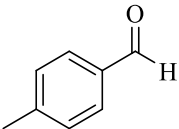
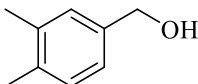
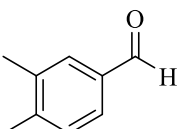
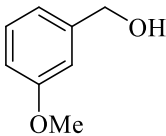
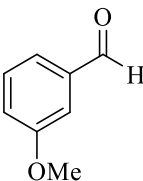
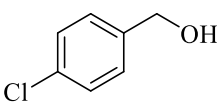
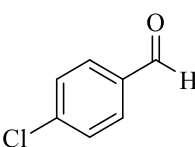
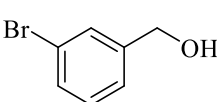
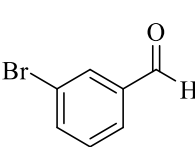
#### 4. Analytical and spectral data

**Table 1.** Substrate scope for established methodology in furfuryl alcohol derivatives<sup>a</sup>

Entry	Reactant	Product	Conversion	Selectivity
				
1.			100	Trace
2.			96	21
3.			64	0
4.			70	0
5.			52	39

<sup>a</sup>Reaction conditions: Entry 1-5 (50 mg), Fe<sub>2</sub>O<sub>3</sub> (2 equiv.), xylene (3 mL), O<sub>2</sub> balloon at 135 °C and 12 h.

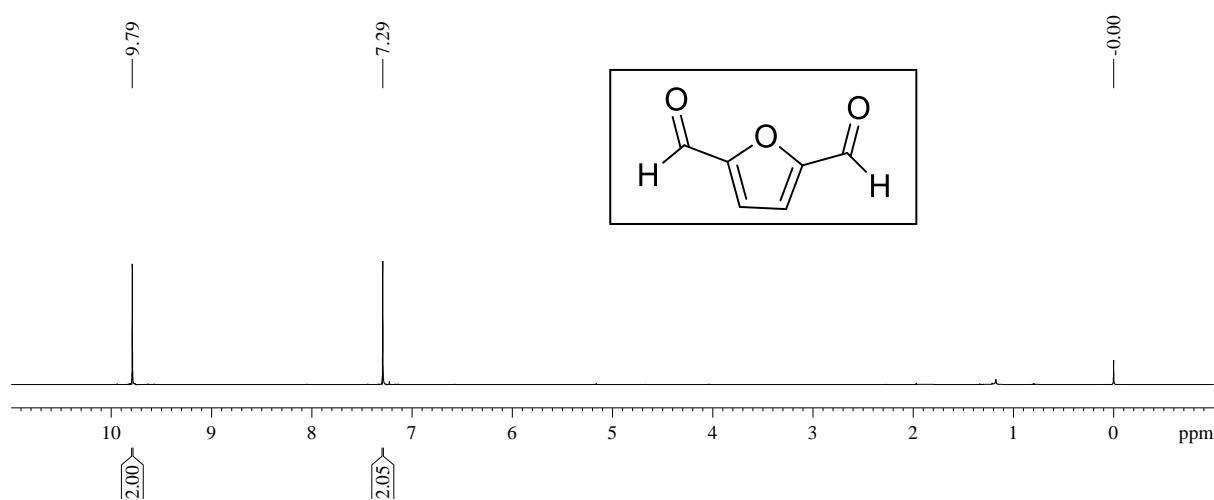
**Table 2.** Substrate scope for established methodology in benzyl alcohol derivatives<sup>a</sup>

Entry	Reactant	Product	Conversion	Selectivity
1.			100	96
2.			94	97
3.			92	99
4.			94	97
5.			94	99

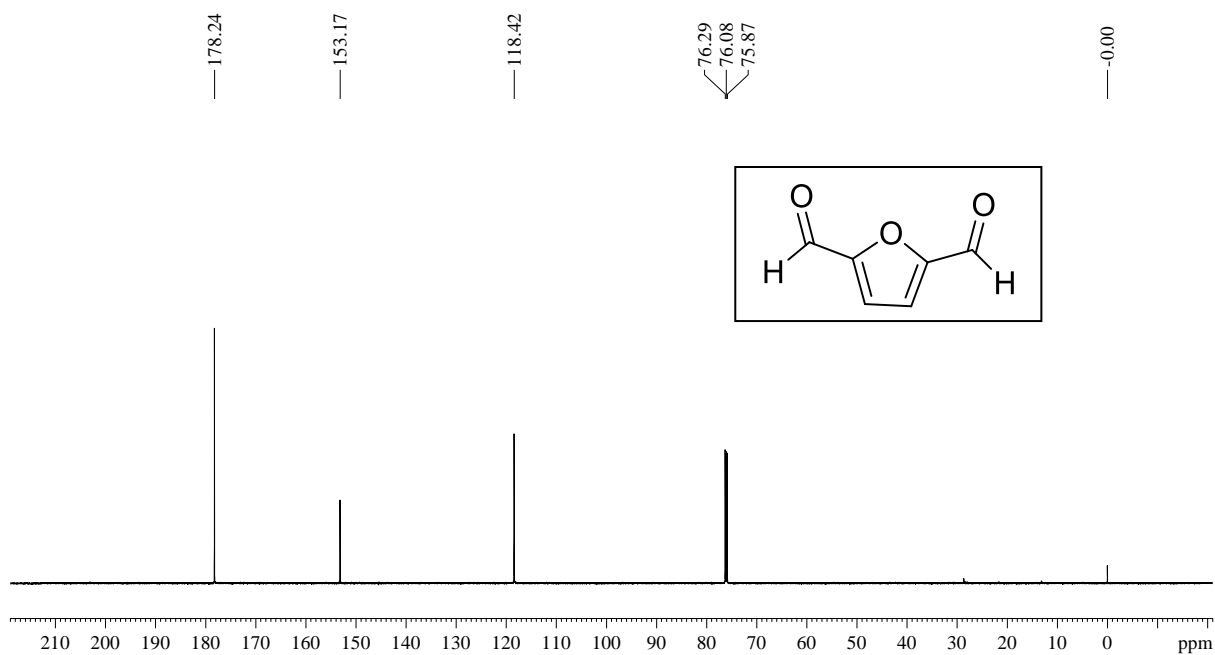
<sup>a</sup>Reaction conditions: Entry 1-5 (50 mg), Fe<sub>2</sub>O<sub>3</sub> (2 equiv.), xylene (3 mL), O<sub>2</sub> balloon at 135 °C and 12 h.

**Table 3.** Atomic concentration percentage of each constituent for fresh, used and activated  $\gamma$ - $\text{Fe}_2\text{O}_3$  catalyst

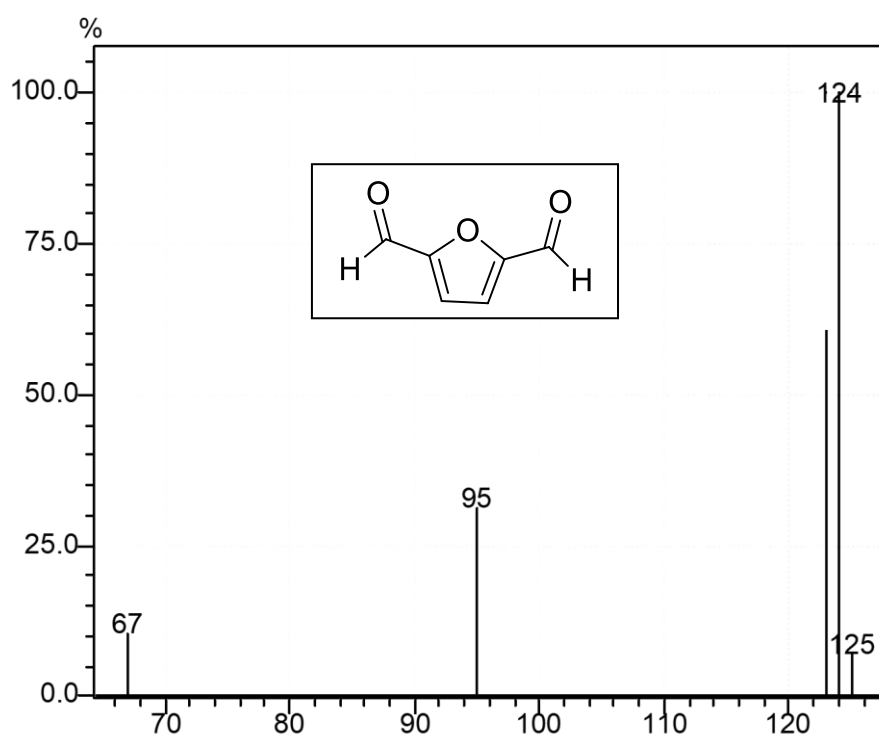
Core levels	Fresh catalyst	Used catalyst after 1 <sup>st</sup> cycle	Activated catalyst
Atomic % for Fe2p	13.83	9.05	26.18
Atomic % for O1s	44.85	38.13	48.60
Atomic % for C1s	41.32	52.48	25.22



**Figure 1.**  $^1\text{H}$  NMR spectra of DFF



**Figure 2.** <sup>13</sup>C NMR spectra of DFF



**Figure 3.** EI-MS Spectra of DFF

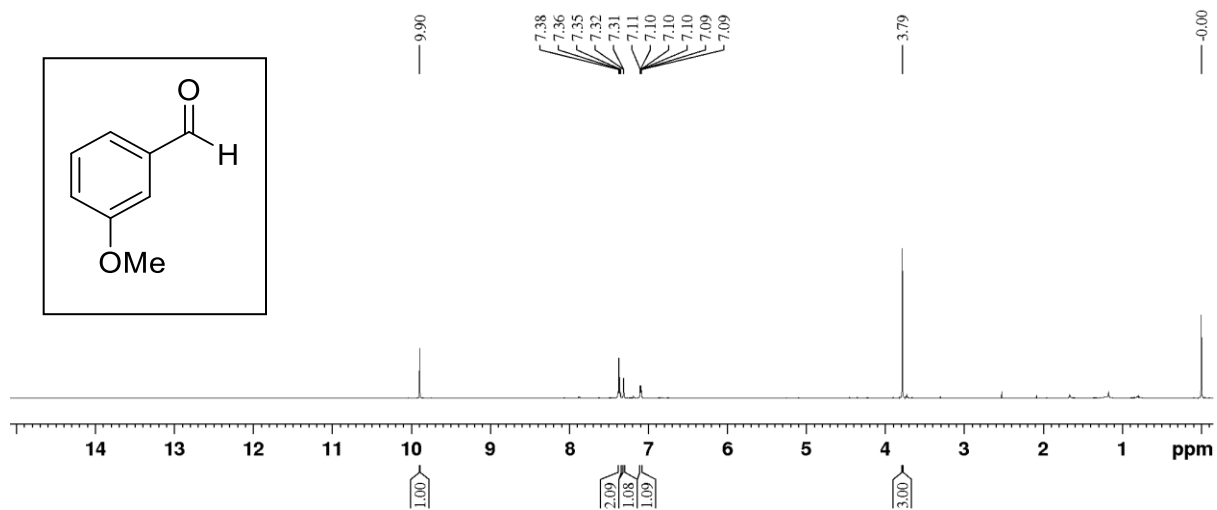


Figure 4.  $^1\text{H}$  NMR spectra of 3-methoxybenzaldehyde

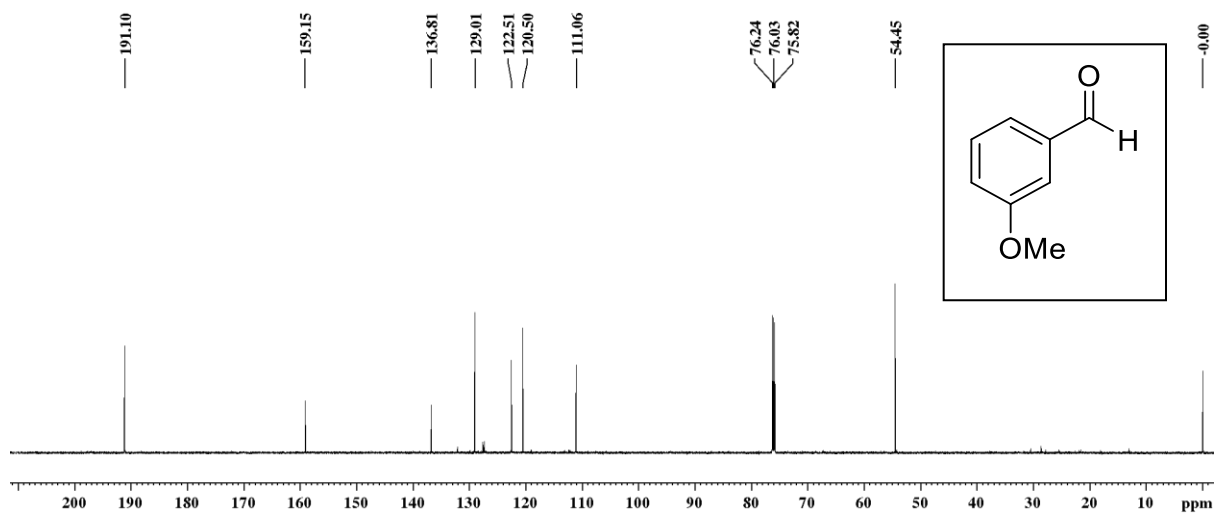


Figure 5.  $^{13}\text{C}$  NMR spectra of 3-methoxybenzaldehyde

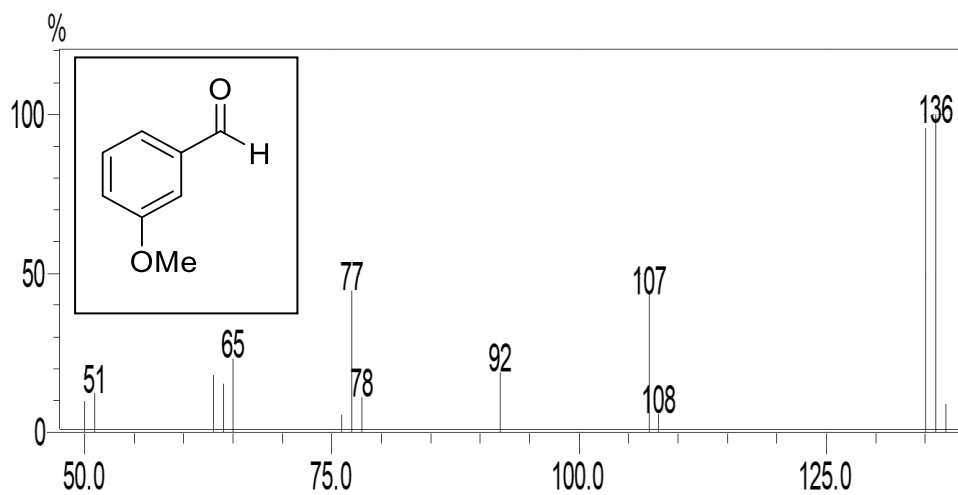


Figure 6. EI-MS spectra of 3-methoxybenzaldehyde

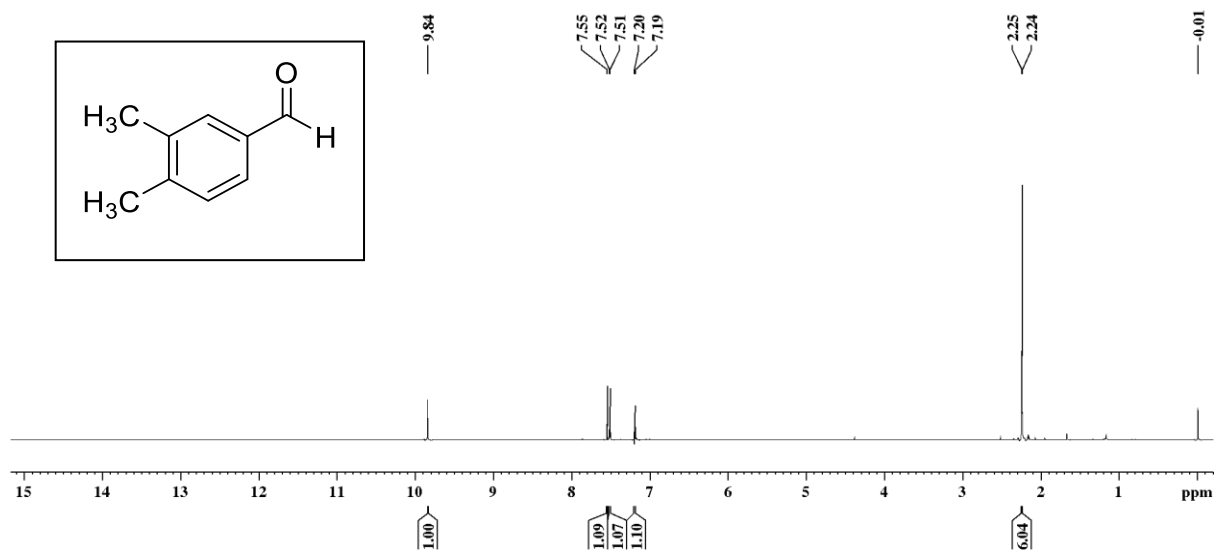
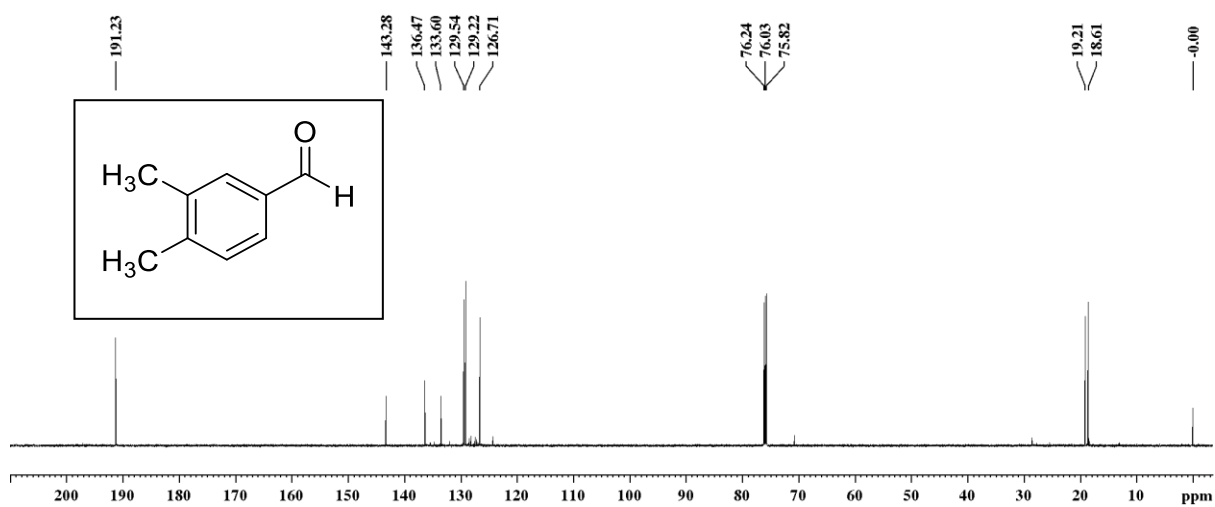
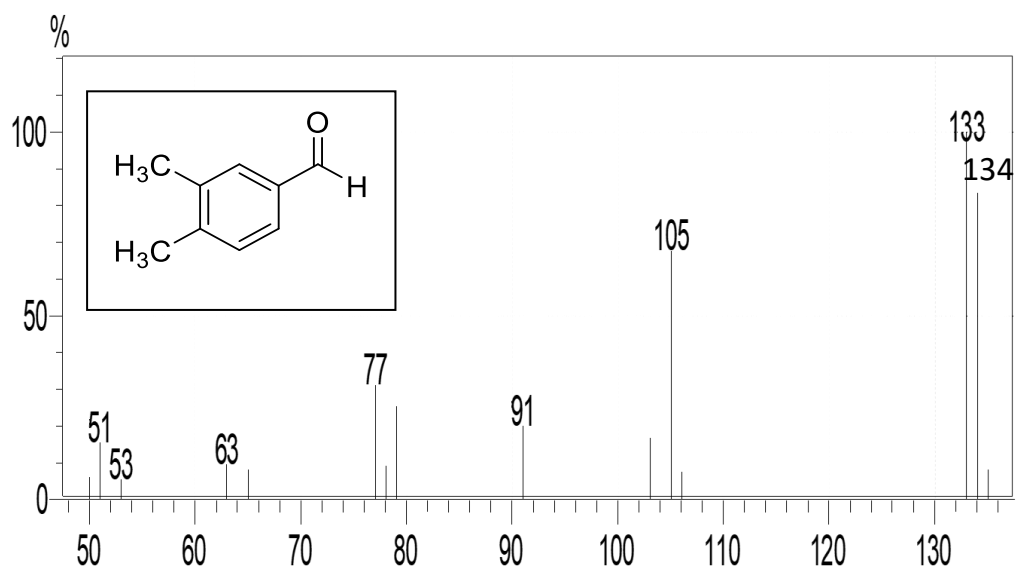


Figure 7.  $^1\text{H}$  NMR spectra of 3,4-dimethylbenzaldehyde



**Figure 8.**  $^{13}\text{C}$  NMR spectra of 3,4-dimethylbenzaldehyde



**Figure 9.** EI-MS spectra of 3,4-dimethylbenzaldehyde



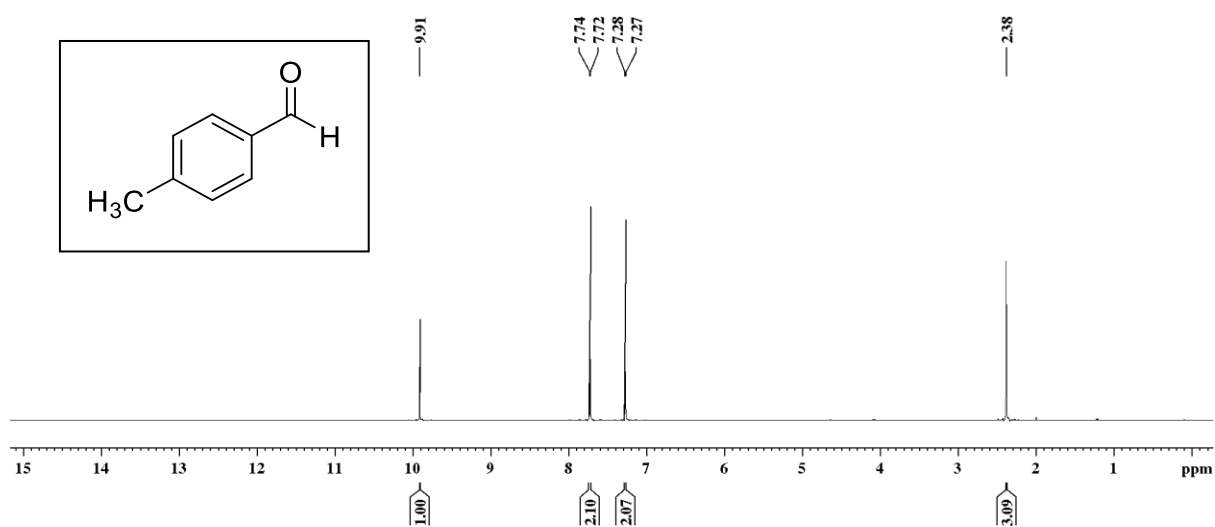


Figure 10.  $^1\text{H}$  NMR spectra of 4-methylbenzaldehyde

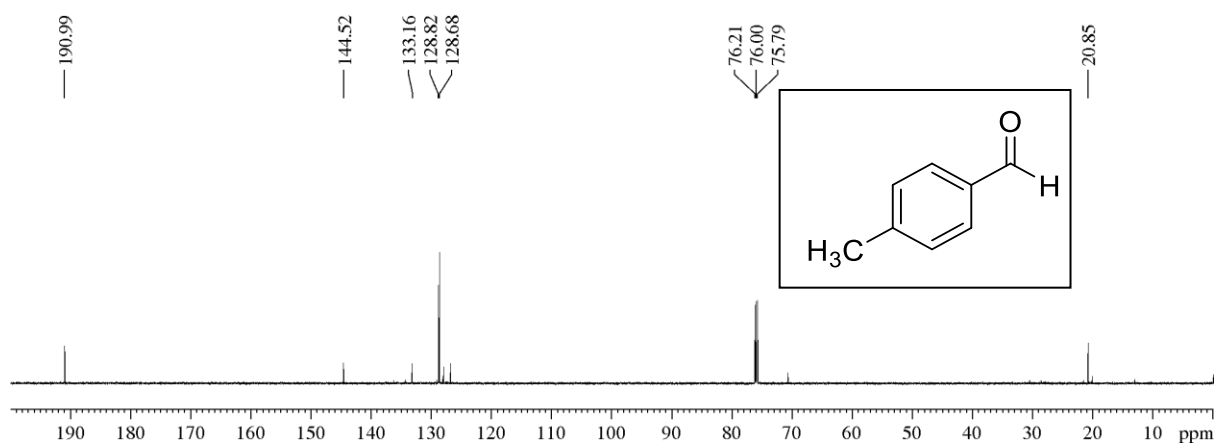


Figure 11.  $^{13}\text{C}$  NMR spectra of 4-methylbenzaldehyde

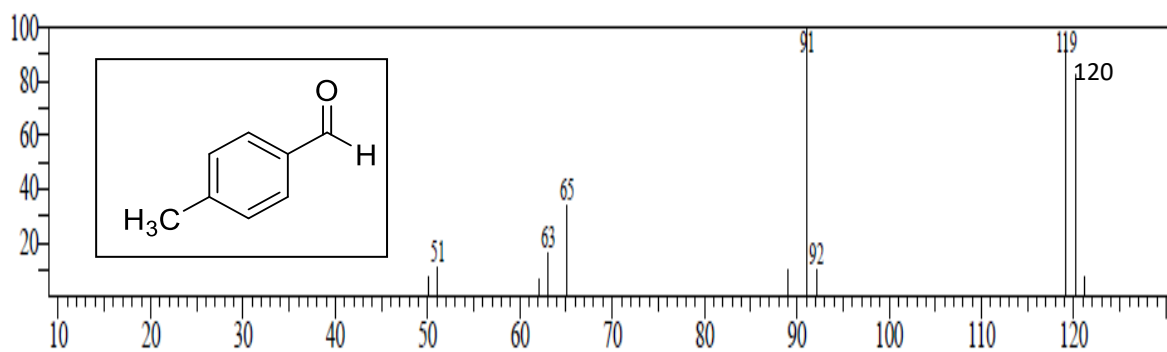


Figure 12. EI-MS spectra of 4-methylbenzaldehyde

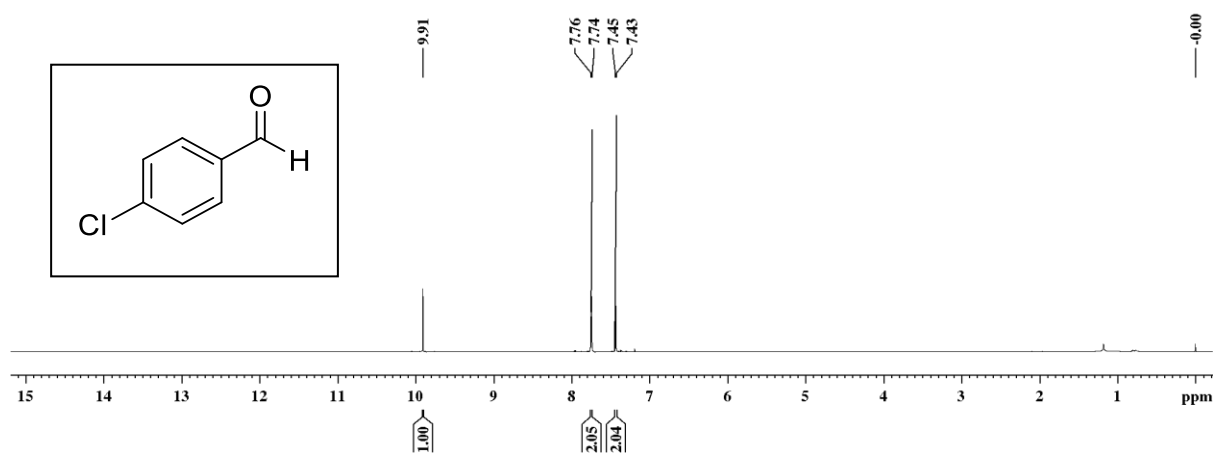


Figure 13.  $^1\text{H}$  NMR spectra of 4-chlorobenzaldehyde

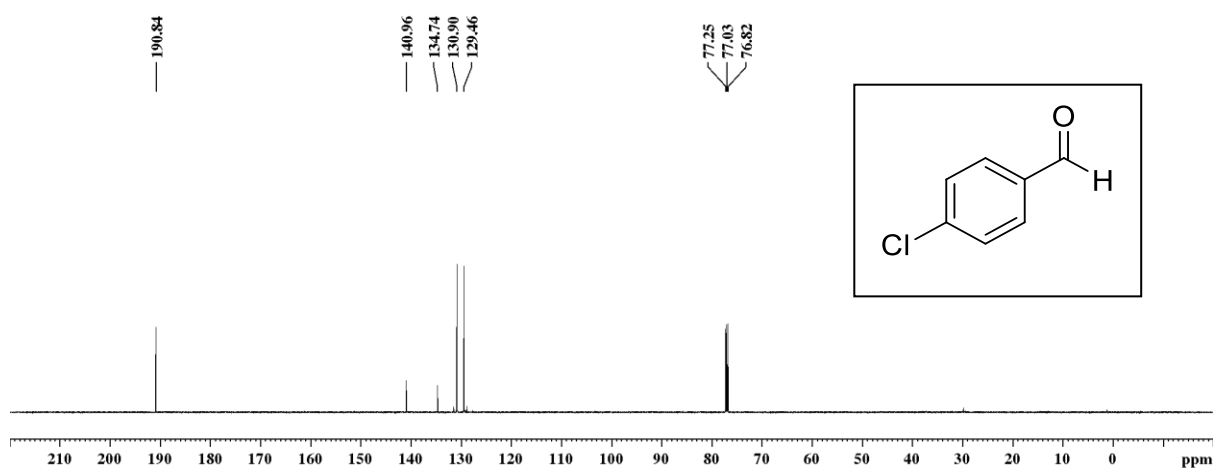


Figure 14.  $^{13}\text{C}$  NMR spectra of 4-chlorobenzaldehyde

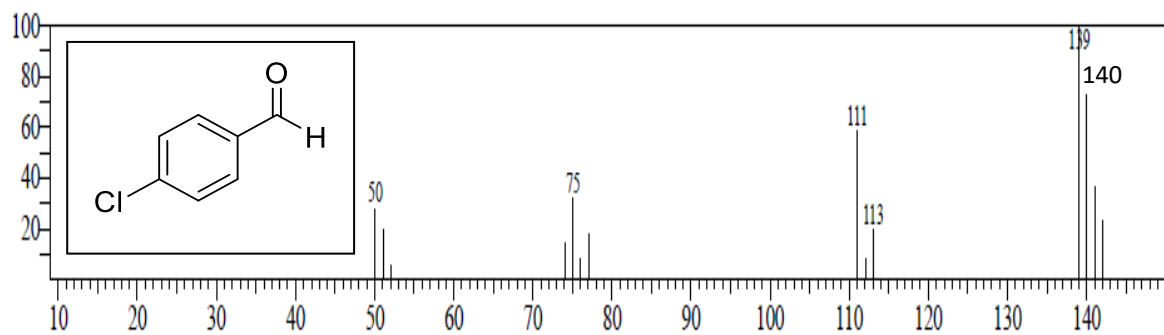
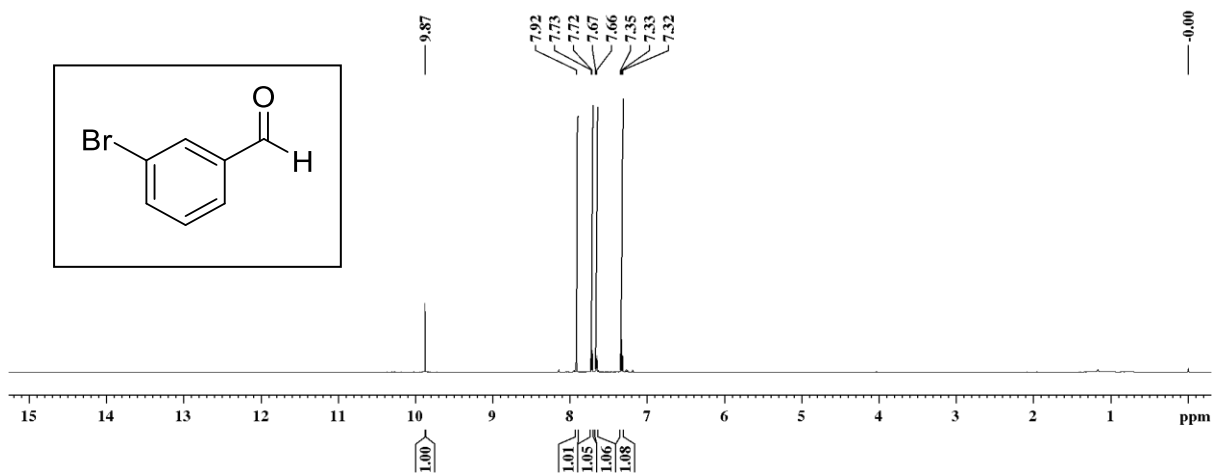
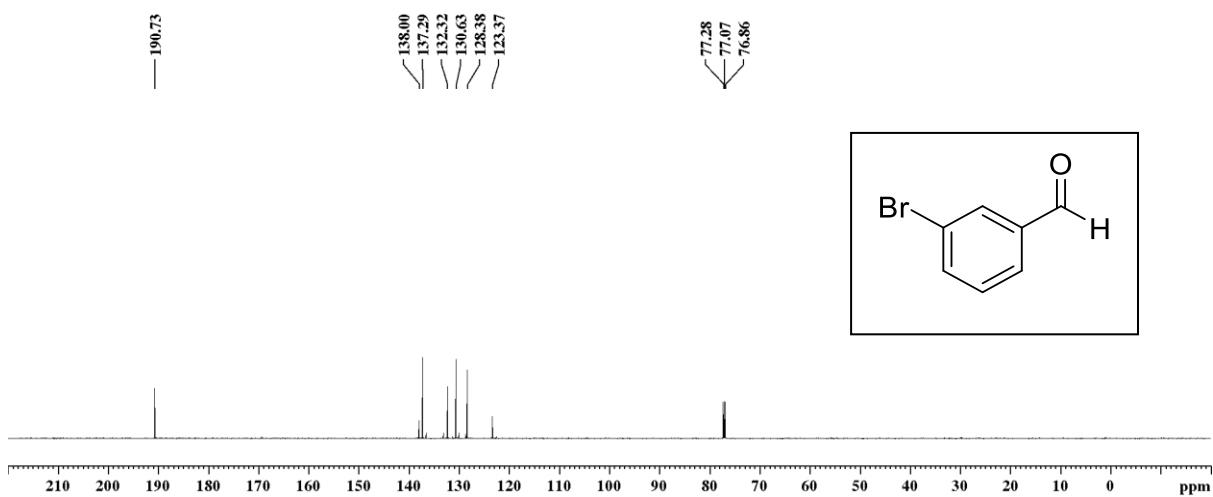


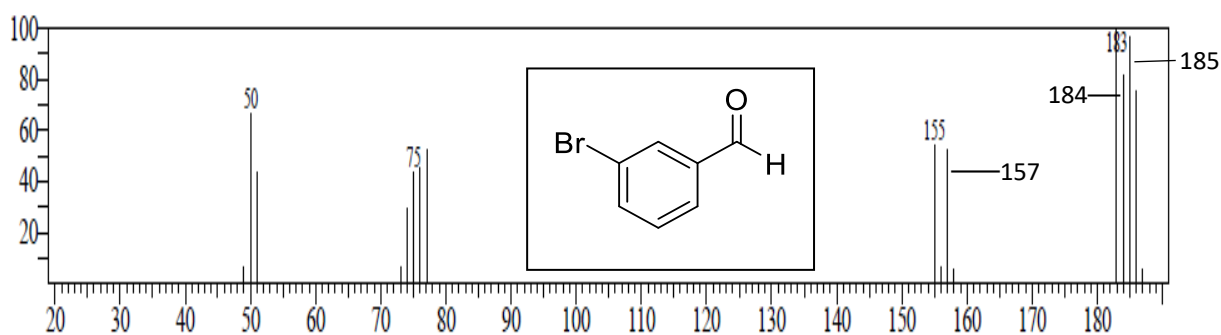
Figure 15. EI-MS spectra of 4-chlorobenzaldehyde



**Figure 16.**  $^1\text{H NMR}$  spectra of 3-bromobenzaldehyde



**Figure 17.**  $^{13}\text{C NMR}$  spectra of 3-bromobenzaldehyde



**Figure 18.** EI-MS spectra of 3-bromobenzaldehyde

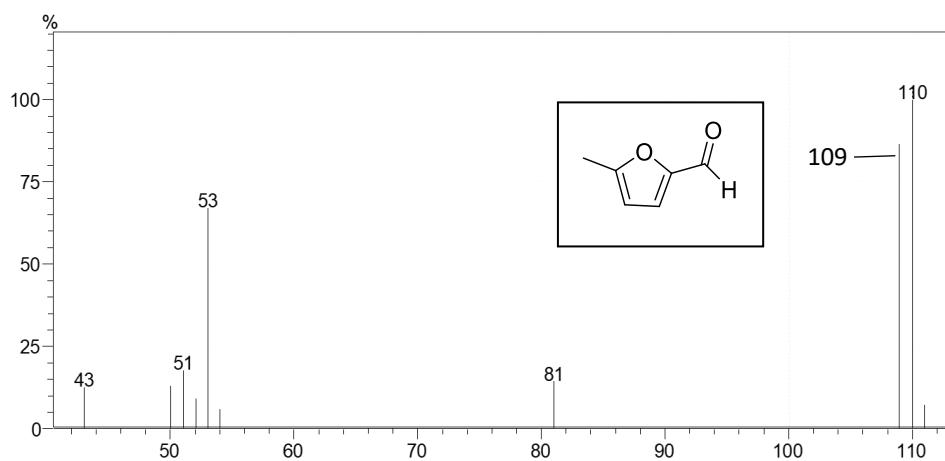


Figure 19. EI-MS spectra of 5-methylfurfuryl alcohol

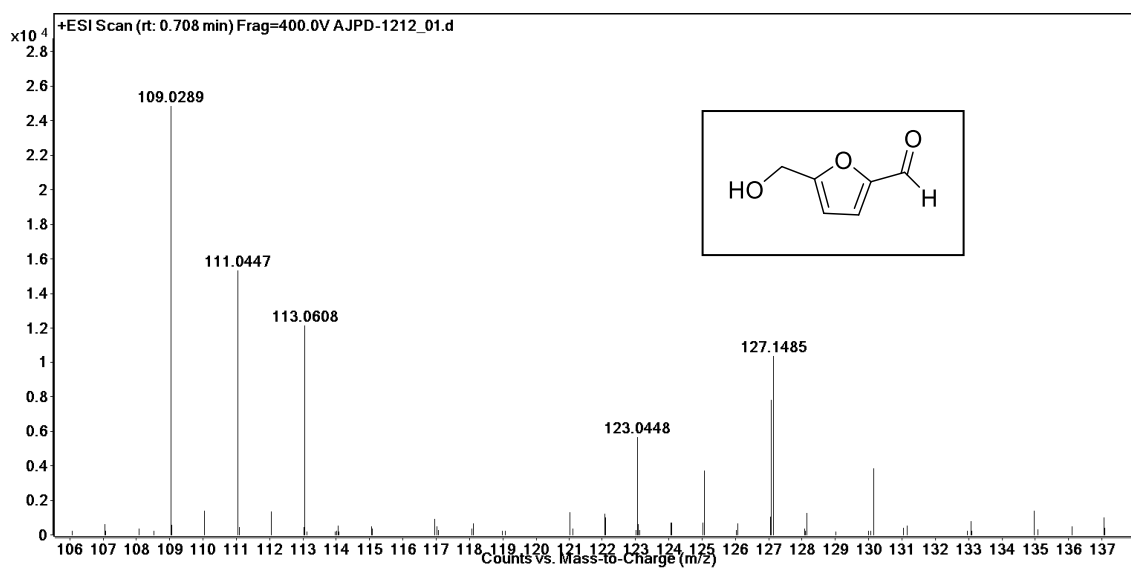


Figure 20. ESI-MS spectra of 5-hydroxymethylfurfural

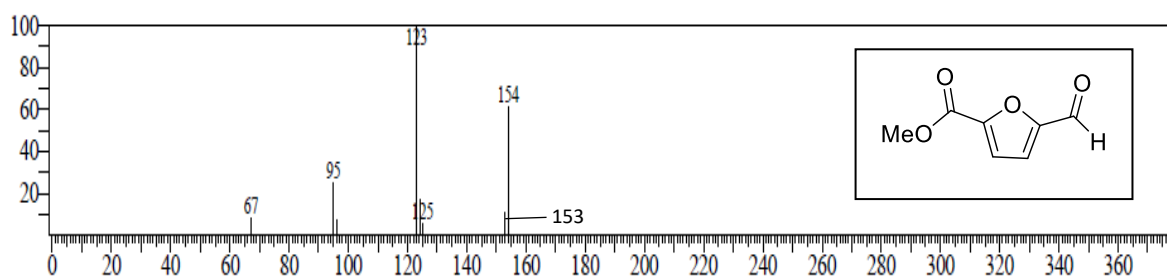


Figure 21. EI-MS spectra of methyl-5-formyl-2-furoate