

**Supporting Information: Synthesis, Characterization and Application of γ -
 MnO_2 /Graphene Oxide for Selective Aerobic Oxidation of Benzyl Alcohols to
Corresponding Carbonyl Compounds**

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Table of Contents

Sr. No.	Contents	Page No.
S1	General information	3
S2	Spectral data for selected compounds	3
S3	Copies of ^1H ^{13}C NMR, MS spectra of selected compounds	5
S4	References	23

S1. General information

All reagents were purchased from commercial sources and used as received. Natural graphite flakes (325 mesh, Alfa Aesar), potassium carbonate (S D Fine Chem. Ltd., Mumbai), sulphuric acid (99%, Merck), nitric acid (99%, Merck), hydrogen peroxide (30%, S D Fine Chem. Ltd., Mumbai), potassium carbonate (99% Sigma Aldrich), toluene (99%, Merck), benzyl alcohols (Sigma Aldrich) and used without any further purification. The progress of reaction was monitored by gas chromatography Perkin Elmer Clarus 400 GC equipped with flame ionization detector with a capillary column (Elite-1, 30 m x 0.32 mm x 0.25 μ m). Representative products were purified by column chromatography on silica gel (100-200) mesh. All the products are well known compounds and also confirmed by ^1H NMR, ^{13}C NMR, and GC-MS. The chemical shifts are reported in parts per million (δ) relative to tetramethylsilane as an internal standard. Mass spectra were obtained on Shimadzu GCMS-QP 2010 instrument (Rtx-17, 30 m \times 25mmID, film thickness 0.25 μ m) (column flow- 2 mL/min, 80 $^\circ\text{C}$ to 240 $^\circ\text{C}$ at 10 $^\circ$ /min. rise.).

S2. Spectral data for selected compounds

Compound 1a: MF = $\text{C}_6\text{H}_4\text{CHOBr}$ Yellow liquid; IR (KBr) : ν_{max} 2816 (-CH), 2779 (-CH), 1711 (C=O), 528 (C-Br); ^1H NMR(200MHz, CDCl_3 , TMS): δ = δ 7.33-7.41 (t, 1H), 7.73-7.78 (m, 1H), 8.25-8.26 (m, 1H), 10.0 (s, 1H); ^{13}C NMR(50MHz, CDCl_3 , TMS): δ = δ ^{13}C NMR (50 MHz, CDCl_3) δ 122.59 (C), 128.36 (CH), 128.76 (CH), 130.07 (CH), 133.20 (CH), 136.81 (C), 170.77 (CH).

GC-MS (EI) m/z (%) = 185(64) $[\text{M}]^+$, 155, 75, 65, 50. 78.

Compound 2b: MF = C₆H₄NO₂CHO Yellow solid; IR (KBr): ν_{\max} 2733 (-CH), 2866 (-CH), 1702 (-C=O); ¹H NMR (200MHz,CDCl₃,TMS): δ = δ 7.73-7.81 (t, 1H), 8.22-8.25 (d, 1H), 8.47-8.51 (d, 1H), 8.71 (s, 1H), 10.12 (s, 1H); ¹³C NMR(50MHz,CDCl₃,TMS): δ = δ 114.56 (CH), 131.43 (CH), 131.62 (CH), 131.78 (C), 168.38 (C), 189.83 (CH). [1]

GC-MS (EI) m/z (%) = 124(100) [M]⁺, 95, 75, 50.

Compound 3c: MF = C₆H₄CHO F White solid; IR (KBr): ν_{\max} 2860 (-CH), 2764 (-CH), 1786 (-C=O) 1040 (C-F); ¹H NMR (200MHz,CDCl₃,TMS): δ = δ 7.12-7.17 (m,1H), 7.23-7.29 (m, 1H), 7.89-7.95 (m,1H), 8.07-8.14 (m,1H), 9.97 (s, 1H); ¹³C NMR(50MHz,CDCl₃,TMS): δ = 115.87 (CH), 131.43 (CH), 131.62 (CH), 132.75 (C), 189.83 (CH). [1]

GC-MS (EI) m/z (%) = 124(100) [M]⁺, 95, 75, 50.

Compound 4d: MF = C₆H₄CHOCl colourless liquid; IR (KBr): ν_{\max} 2831 (-CH), 2866 (-CH), 1694 (-C=O), 610 (-C-Cl); ¹H NMR (200MHz,CDCl₃,TMS): δ = δ 7.38-7.52 (m, 1H), 7.56-7.63 (m, 1H), 7.74-7.86 (m, 1H), 7.98-8.02 (d, 1H), 10.06 (s, 1H); ¹³C NMR (50MHz,CDCl₃,TMS): δ = 124.51 (CH), 128.63 (CH), 130.43 (CH), 134.69 (C), 189.79 (CH).

MS (ESI): m/z [M] = 136.13

Compound 6f: MF = C₈H₈O₂ Light Brown liquid; IR (KBr): ν_{\max} 2970 (-CH), 2863 (-CH), 2761 (-CH) 1689 (-C=O); ¹H NMR (200MHz,CDCl₃,TMS): δ = δ 3.80 (s, 3H), 6.91-6.98 (d, 2H), 7.44-7.77 (d, 2H), 9.80 (s, 1H); ¹³C NMR (50MHz,CDCl₃,TMS): δ = 55.6 (-CH₃), 114.3 (CH), 129.9 (-C), 132.0 (CH), 164.6 (-C), 190.9 (CH).

GC-MS (EI) m/z (%) = 135(100) [M]⁺, 107, 92, 77, 63.

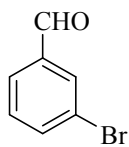
Compound 7g: MF = C₇H₆O₂ Yellowish Solid; IR (KBr): ν_{\max} 2869 (-CH), 1676 (C=O); ¹H NMR(200MHz,CDCl₃,TMS): δ = δ 6.96-6.98 (d, 2H), 7.80-7.83 (d, 2H), 9.83 (s, 1H); ¹³C NMR(50MHz,CDCl₃,TMS): δ 116.21 (CH), 129.73 (-C), 132.68 (CH), 161.92 (-C), 191.5 (CH).
GC-MS (EI) m/z (%) = 122(100) [M]⁺, 93, 65.

Compound 8h: MF = C₇H₆O₂ Colourless liquid; IR (KBr): ν_{\max} 2845 (-CH), 1660 (-C=O); ¹H NMR(200MHz,CDCl₃,TMS): δ = δ 6.91-6.98 (m, 2H), 7.44-7.50 (m, 2H), 9.81 (s, 1H), 10.99 (s, 1H); ¹³C NMR(50MHz,CDCl₃,TMS): δ = δ 117.6 (CH), 119.9 (CH), 120.1 (-C), 133.8 (CH), 137.0 (CH), 161.6 (-C), 196.7 (CH).

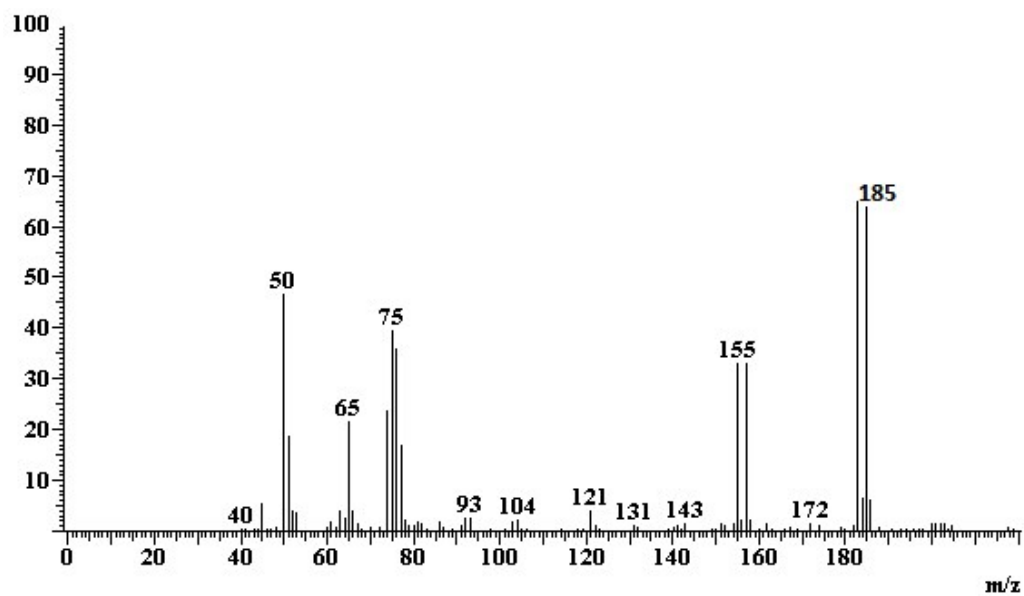
GC-MS (EI) m/z (%) = 122(100) [M]⁺, 93, 65.

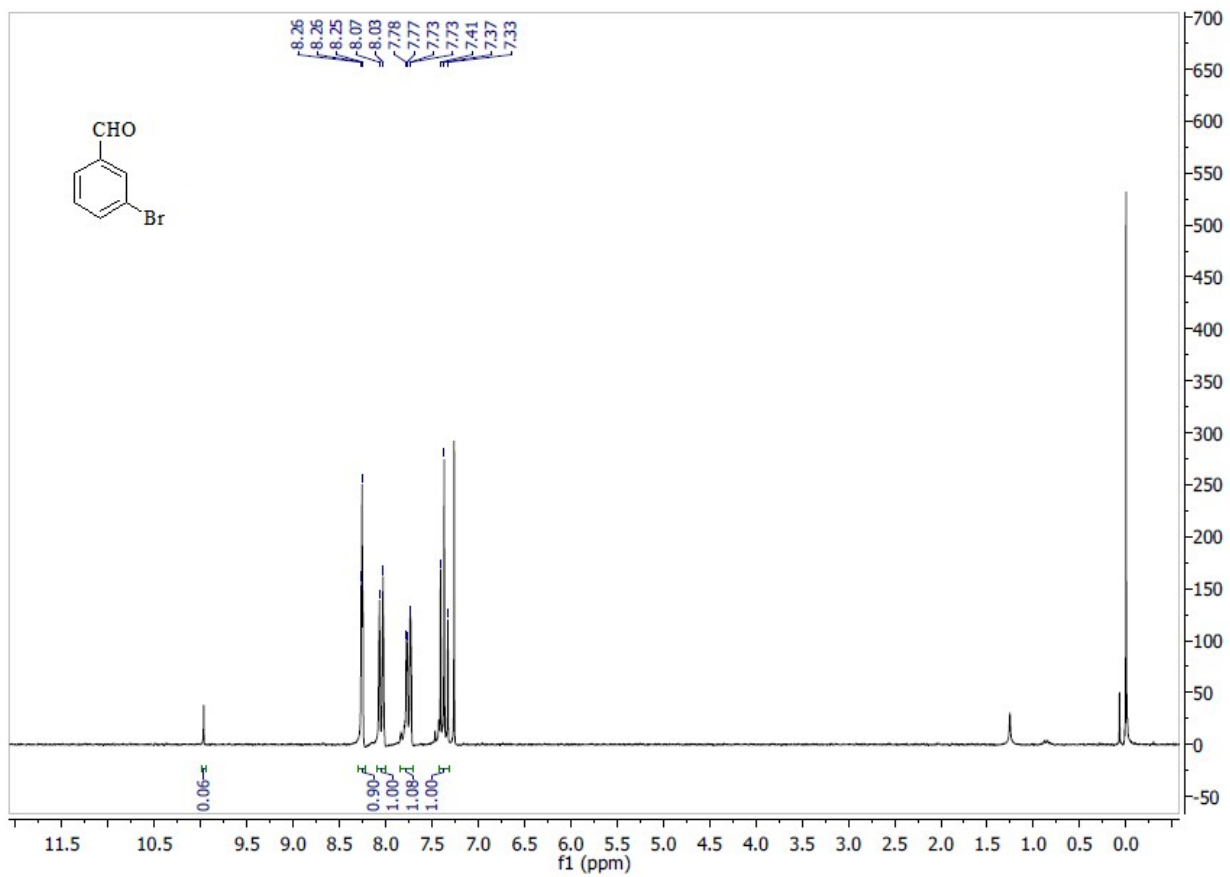
S3. Copies of ^1H ^{13}C NMR, MS spectra of selected products

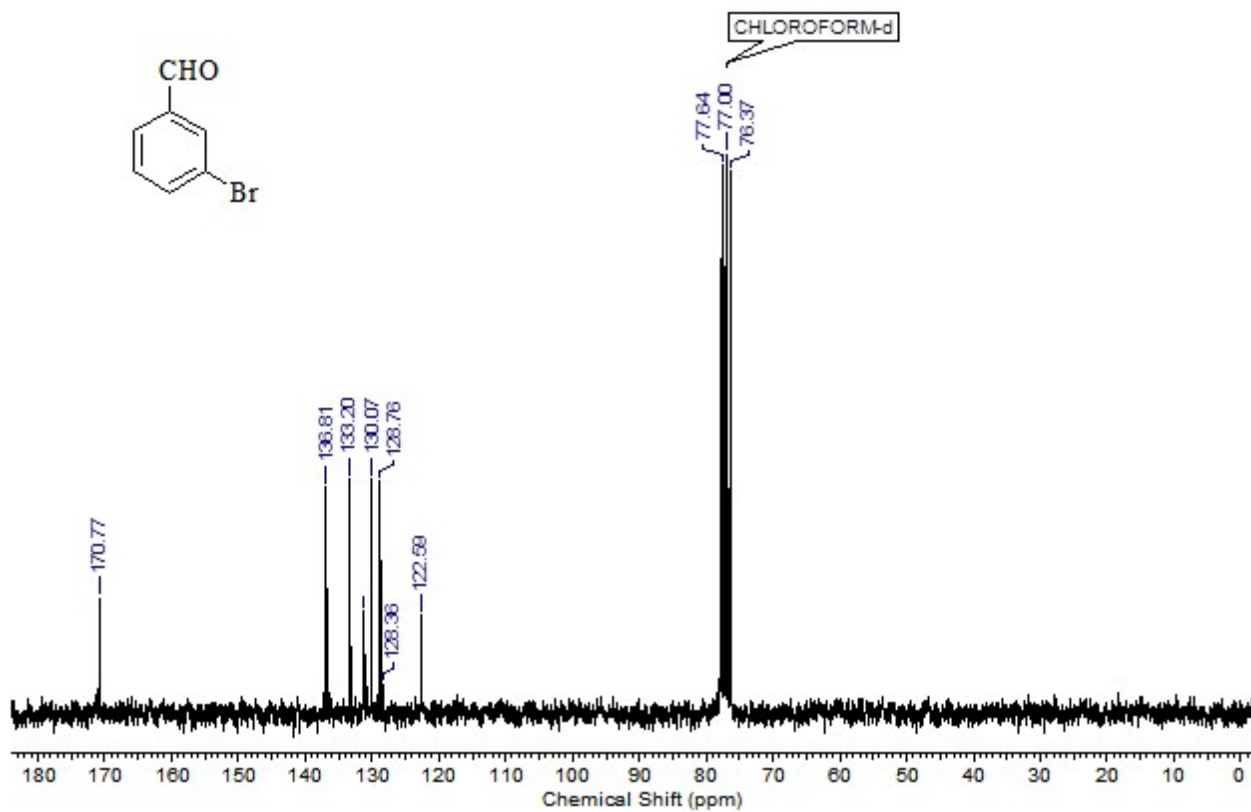
1a. 3-Bromobenzaldehyde



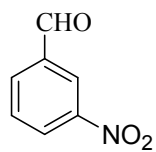
Mol. Wt.: 185.02



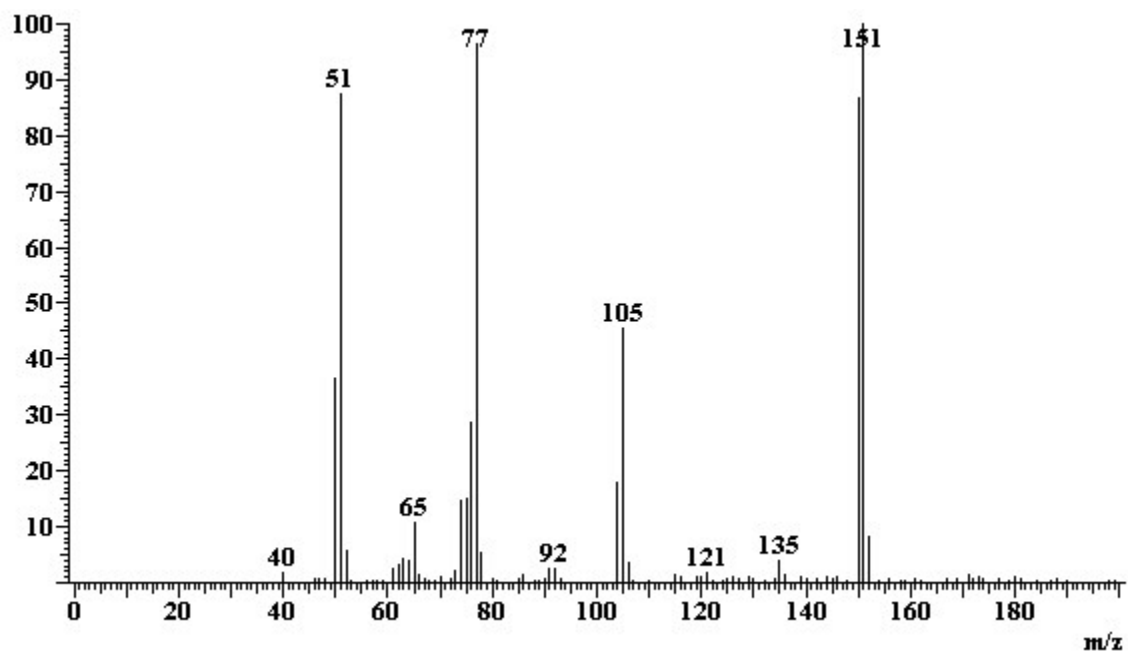


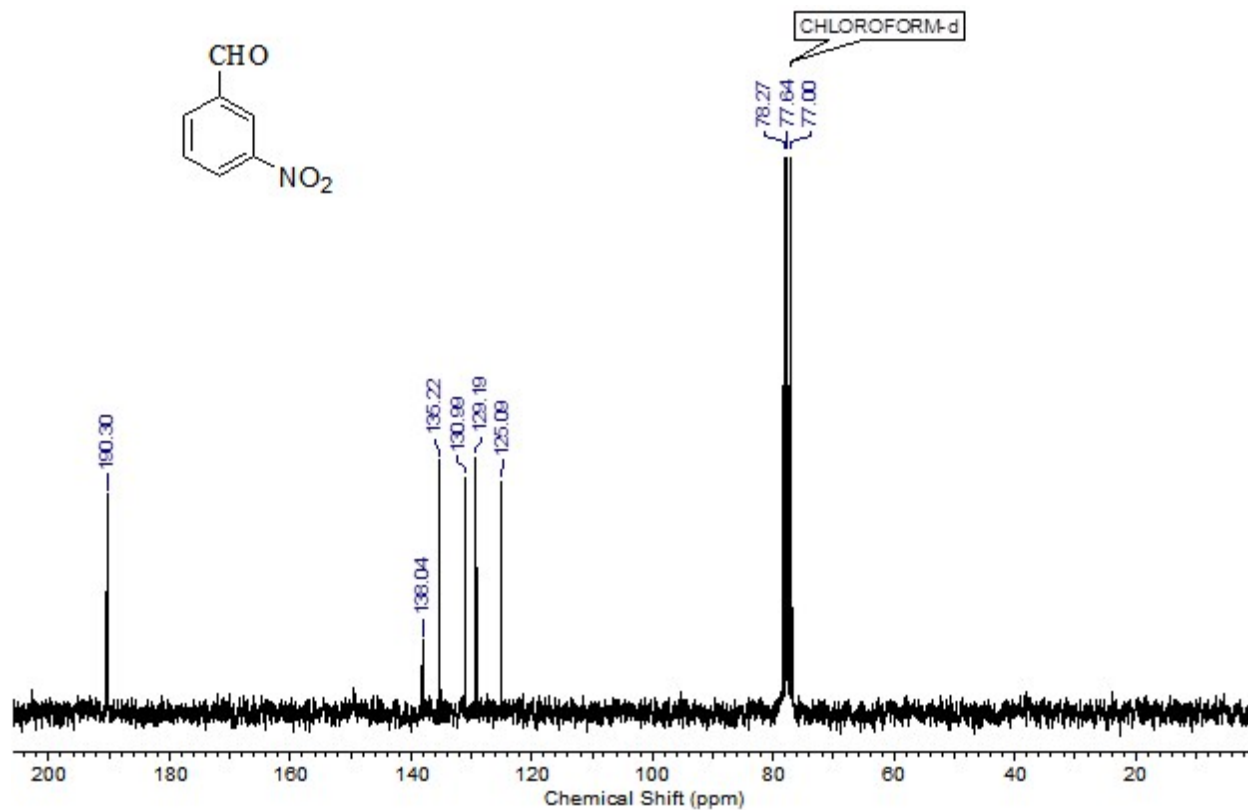
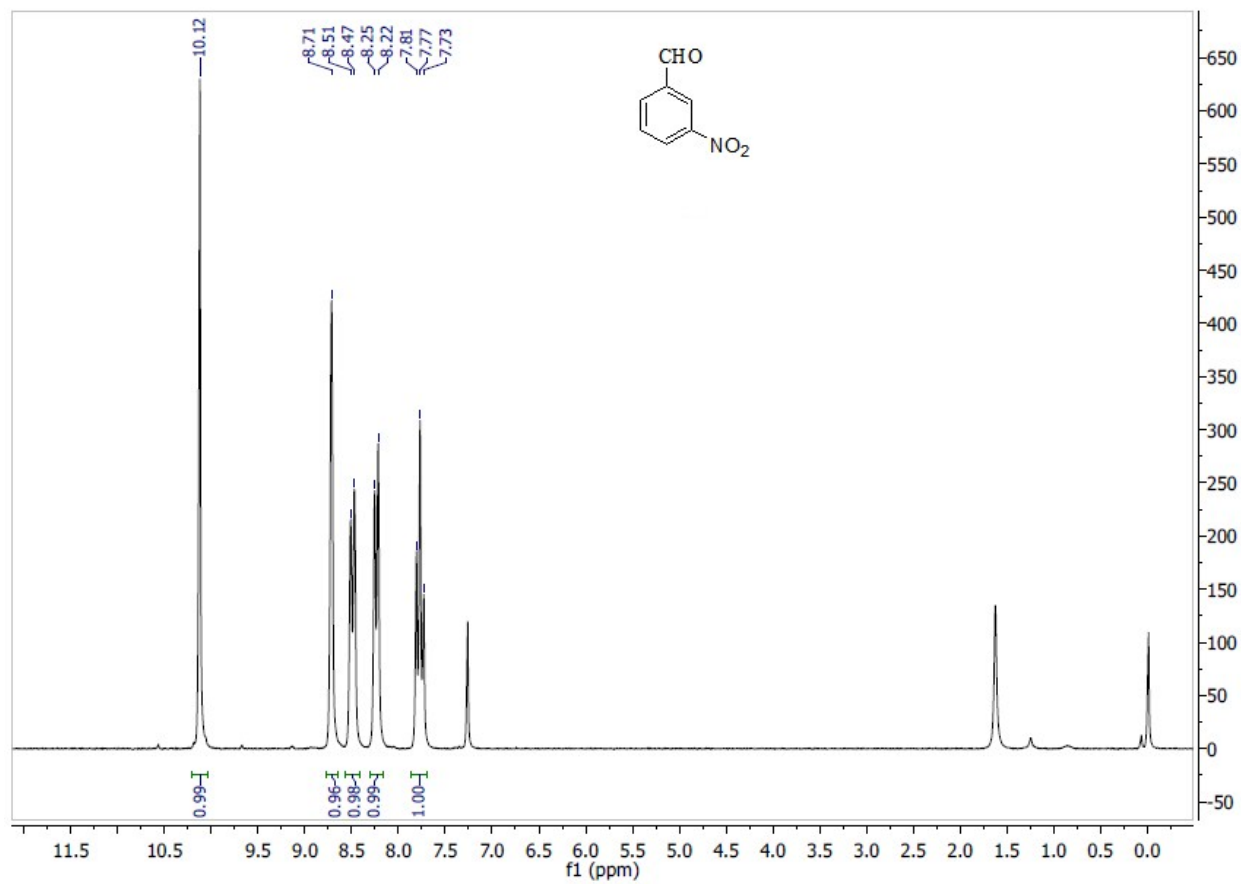


2b. 3-Nitrobenzaldehyde

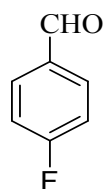


Mol. Wt.: 151.12

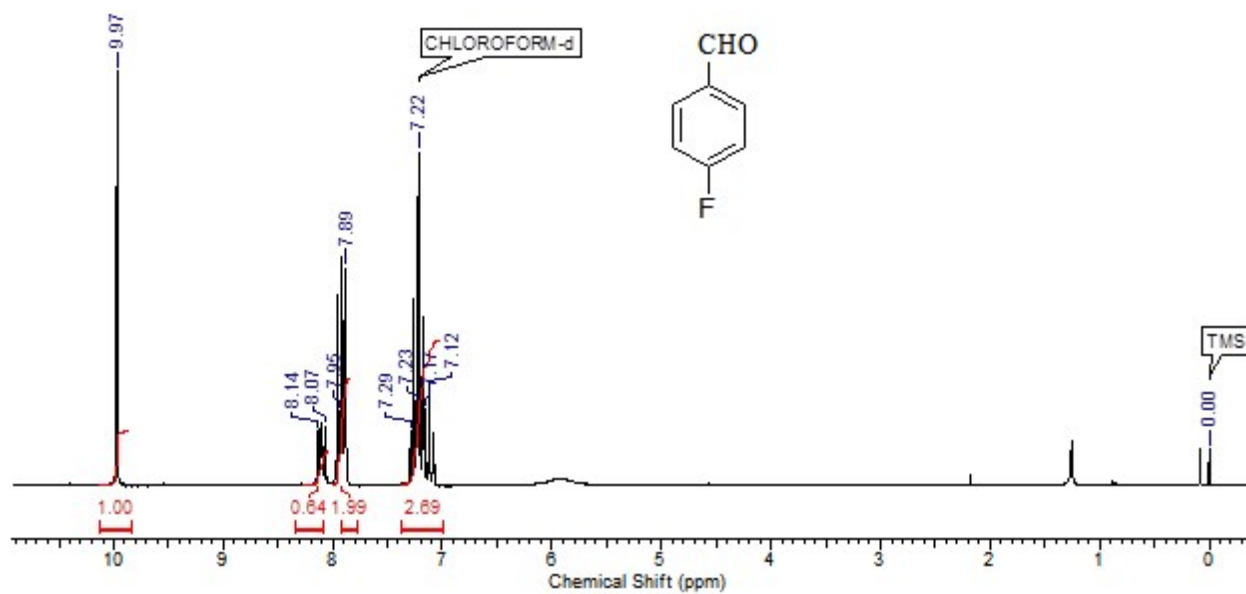
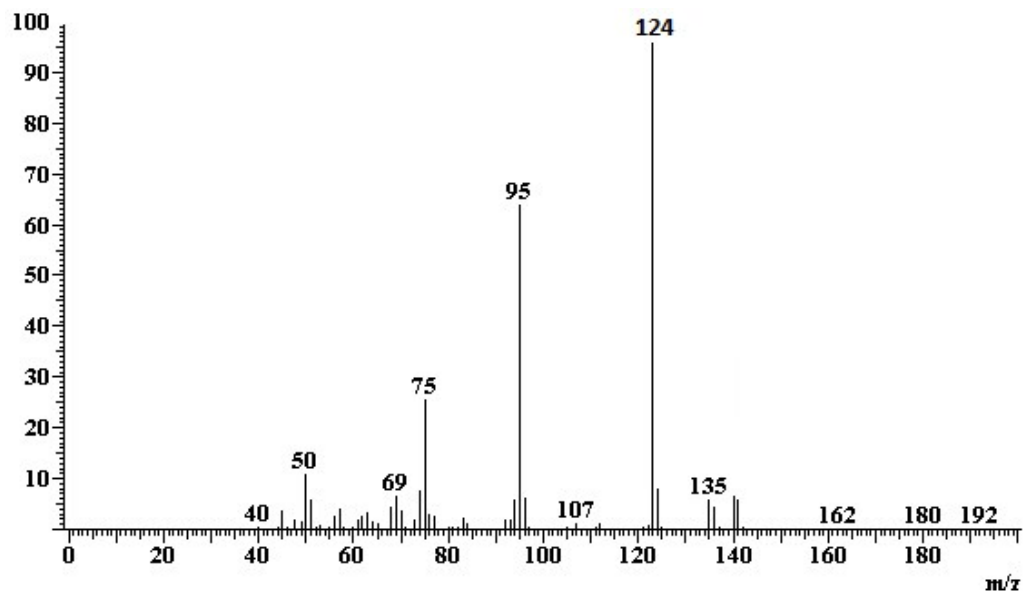


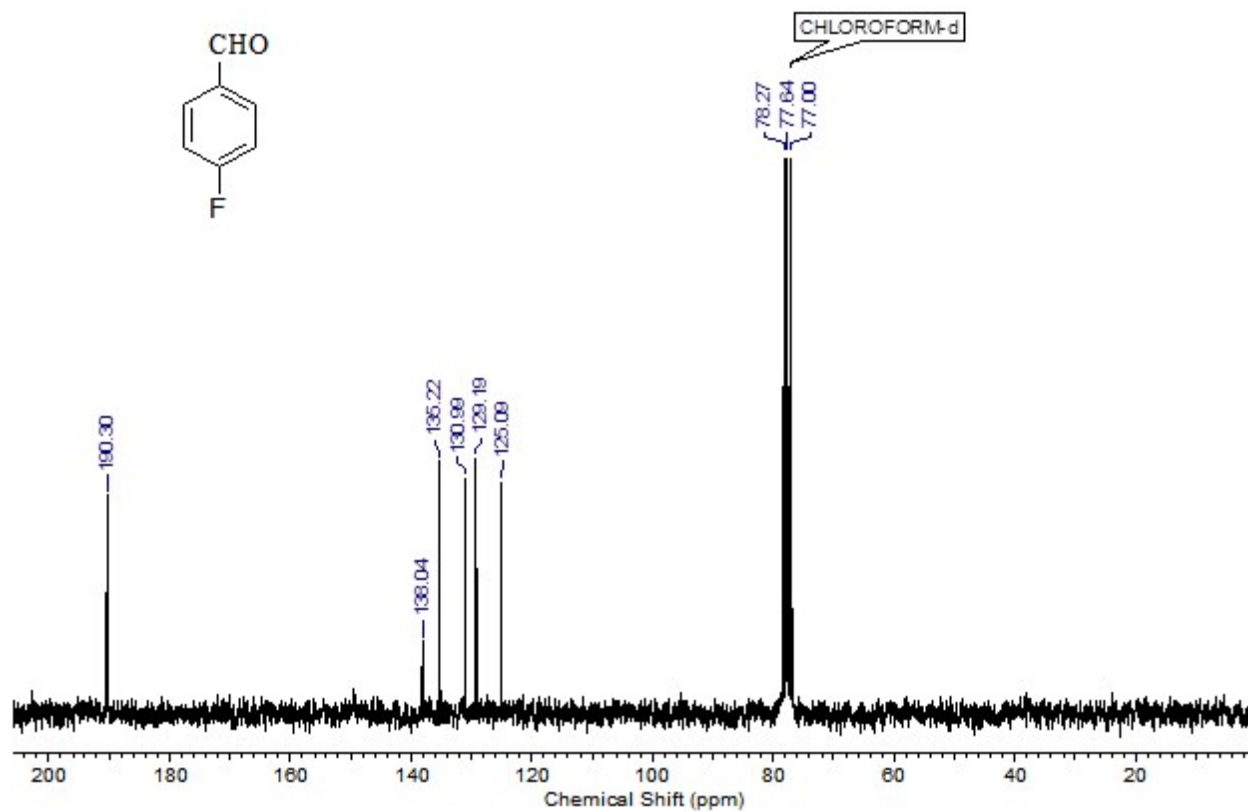


3c. 4-Florobenzaldehyde

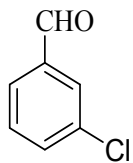


Mol. Wt.: 124.11

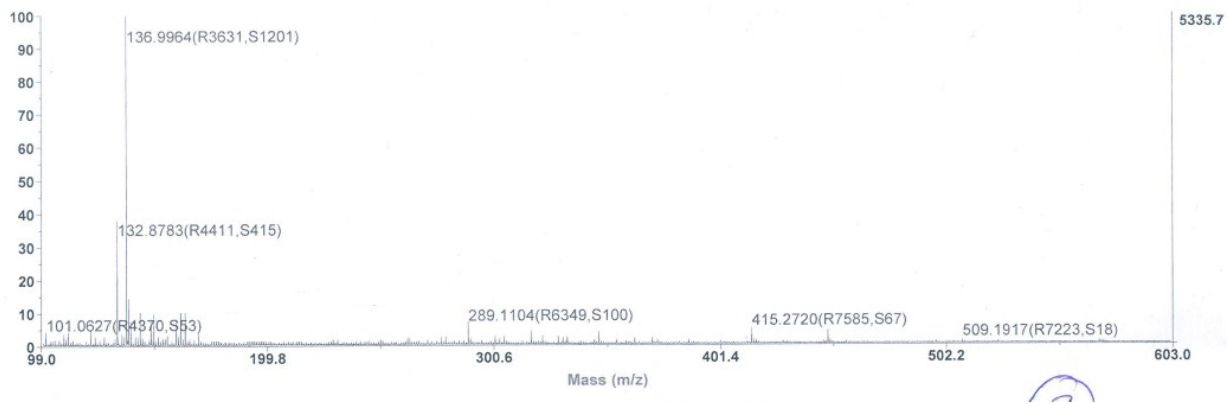


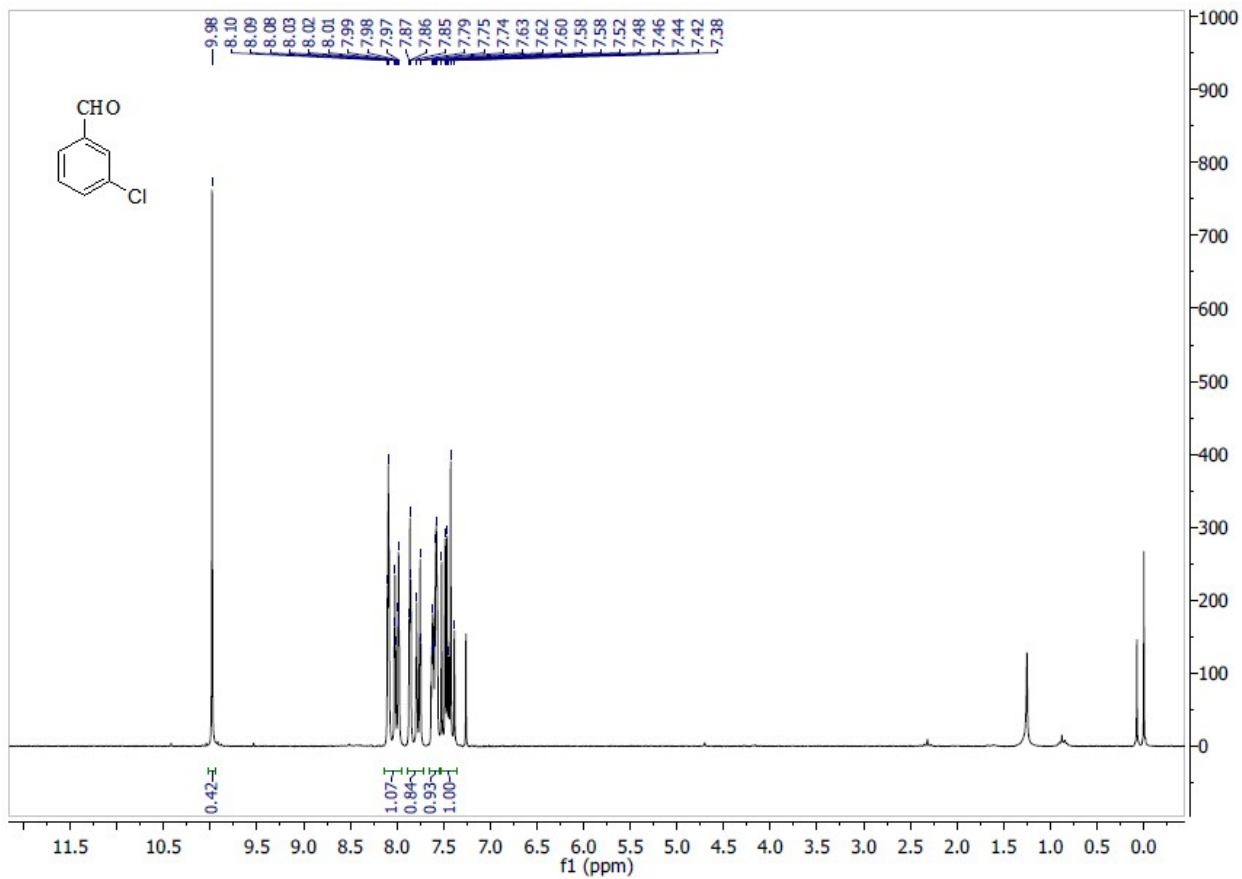


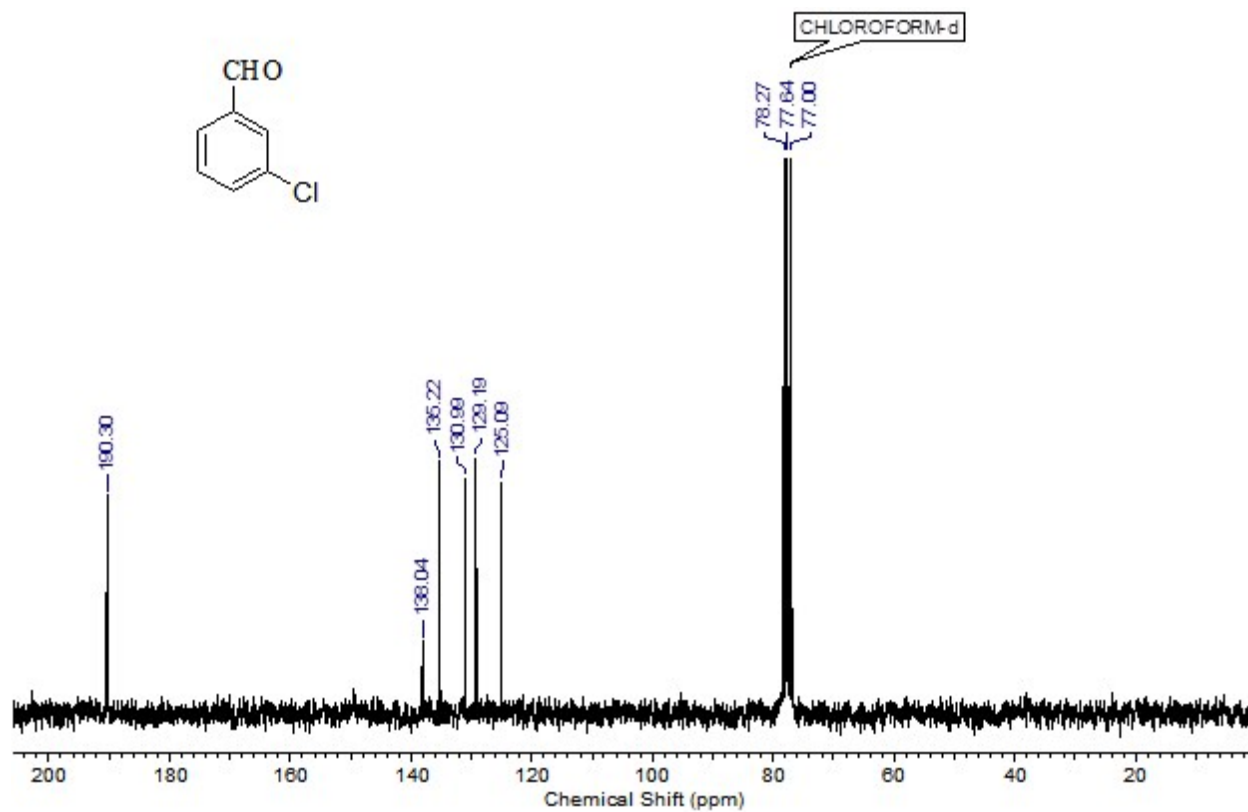
4d. 3-Chlorobenzaldehyde



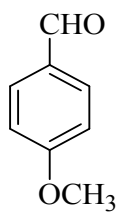
Mol. Wt.: 140.57







6f. 4-Methoxybenzaldehyde



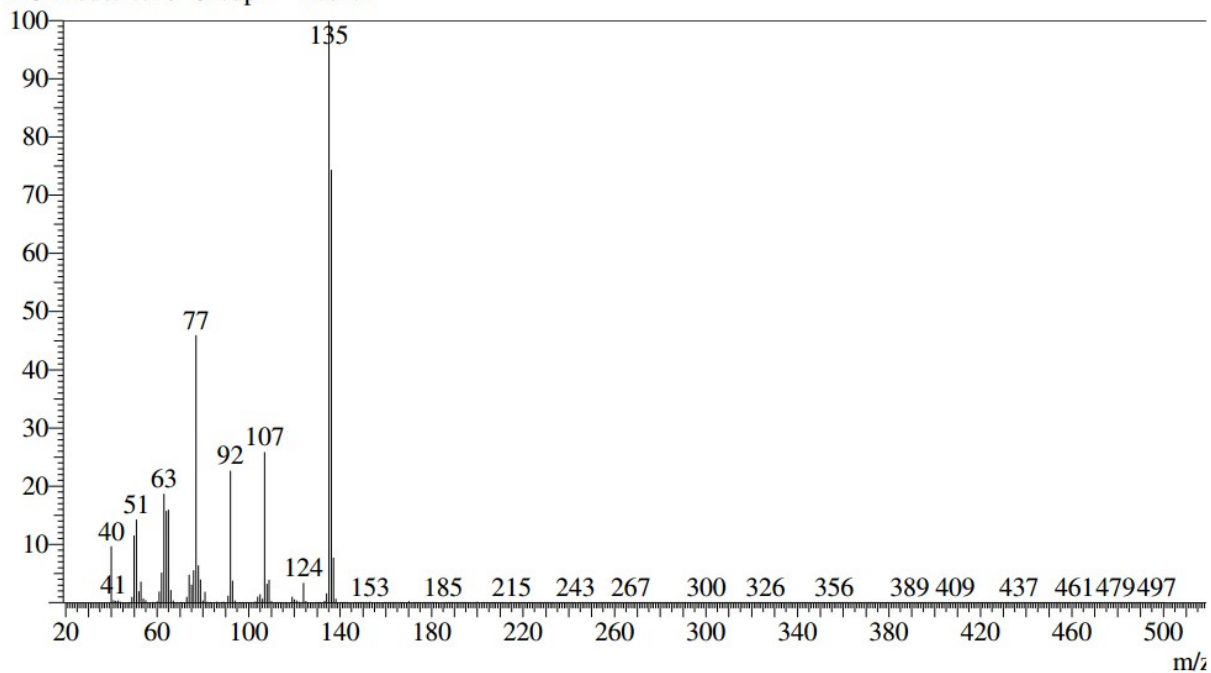
Mol. Wt.: 136.15

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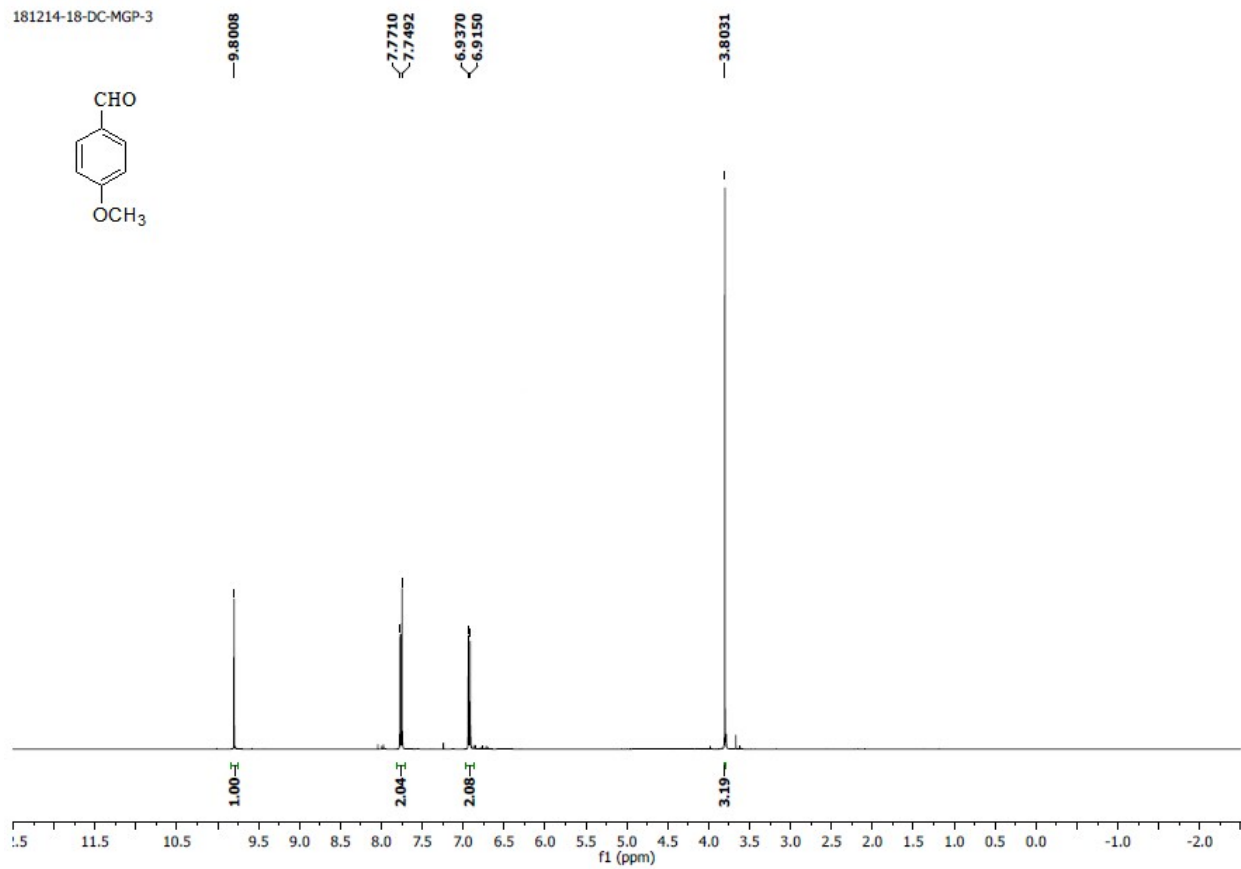
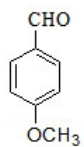
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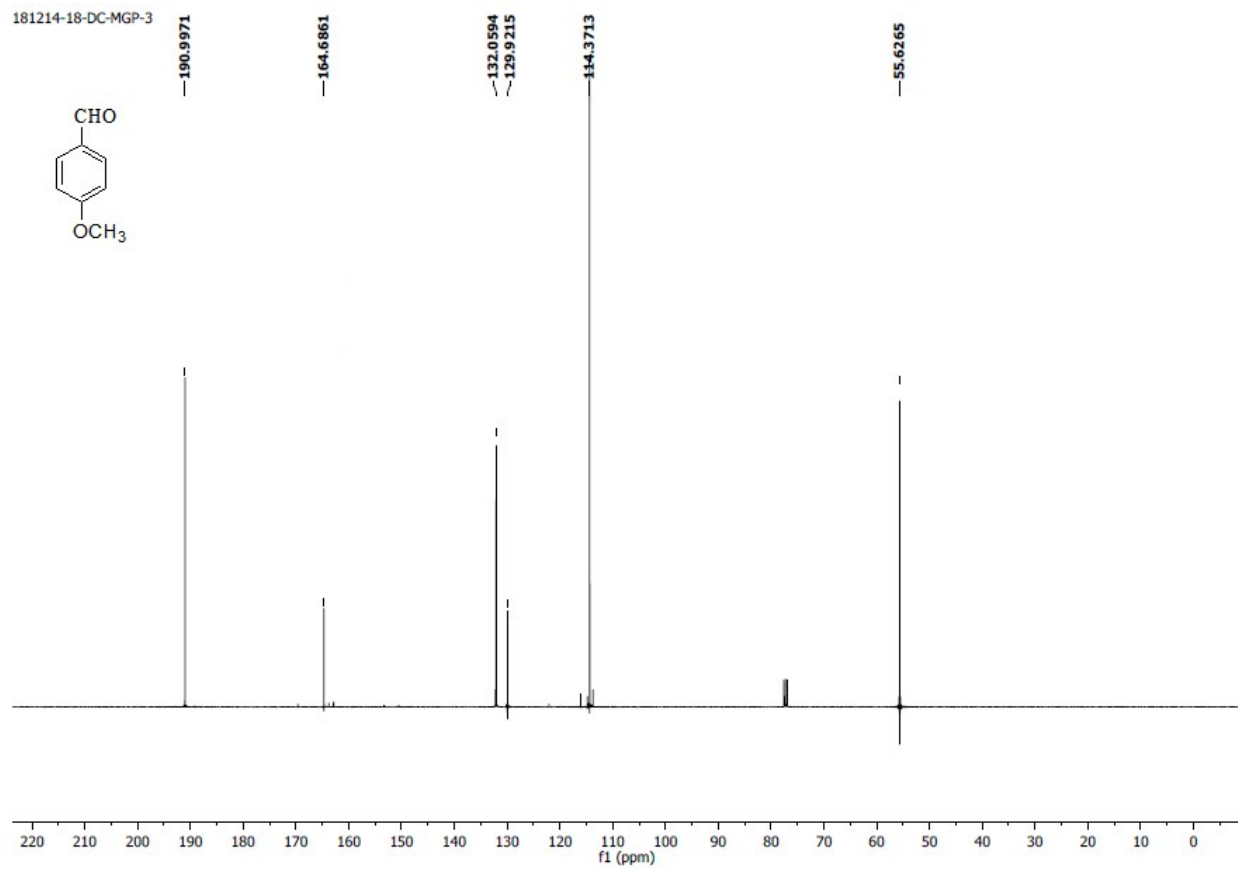
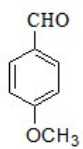
BG Mode:None Group 1 - Event 1



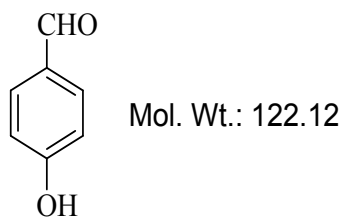
181214-18-DC-MGP-3



181214-18-DC-MGP-3



7g. 4-Hydroxybenzaldehyde

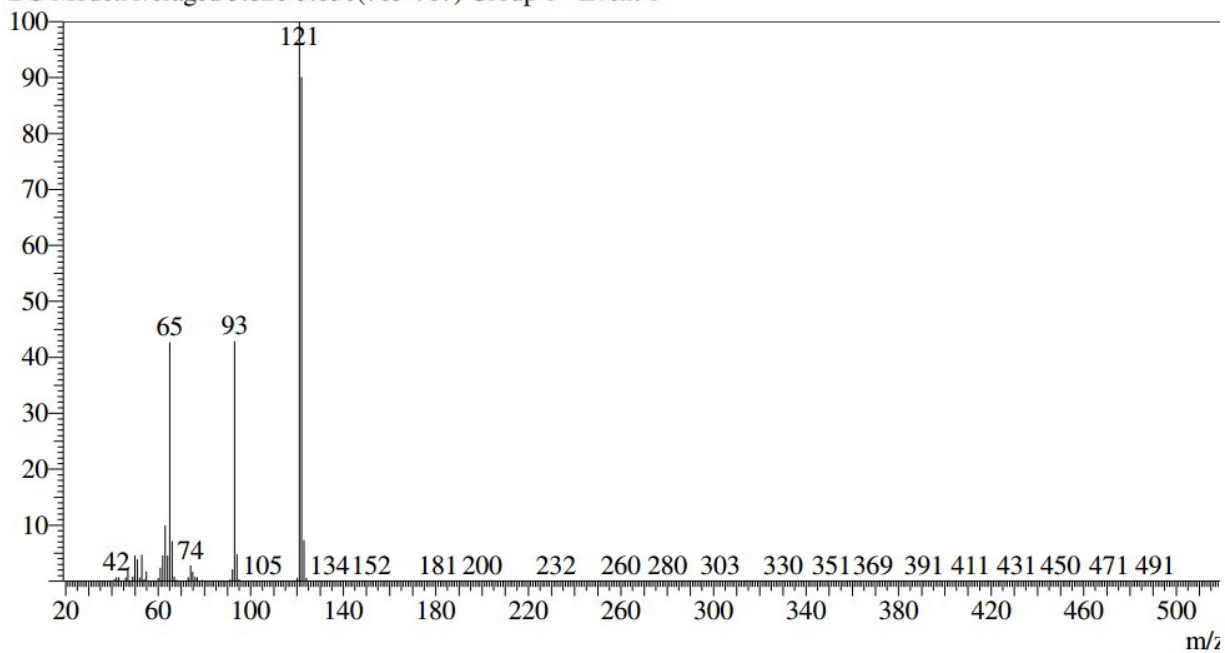


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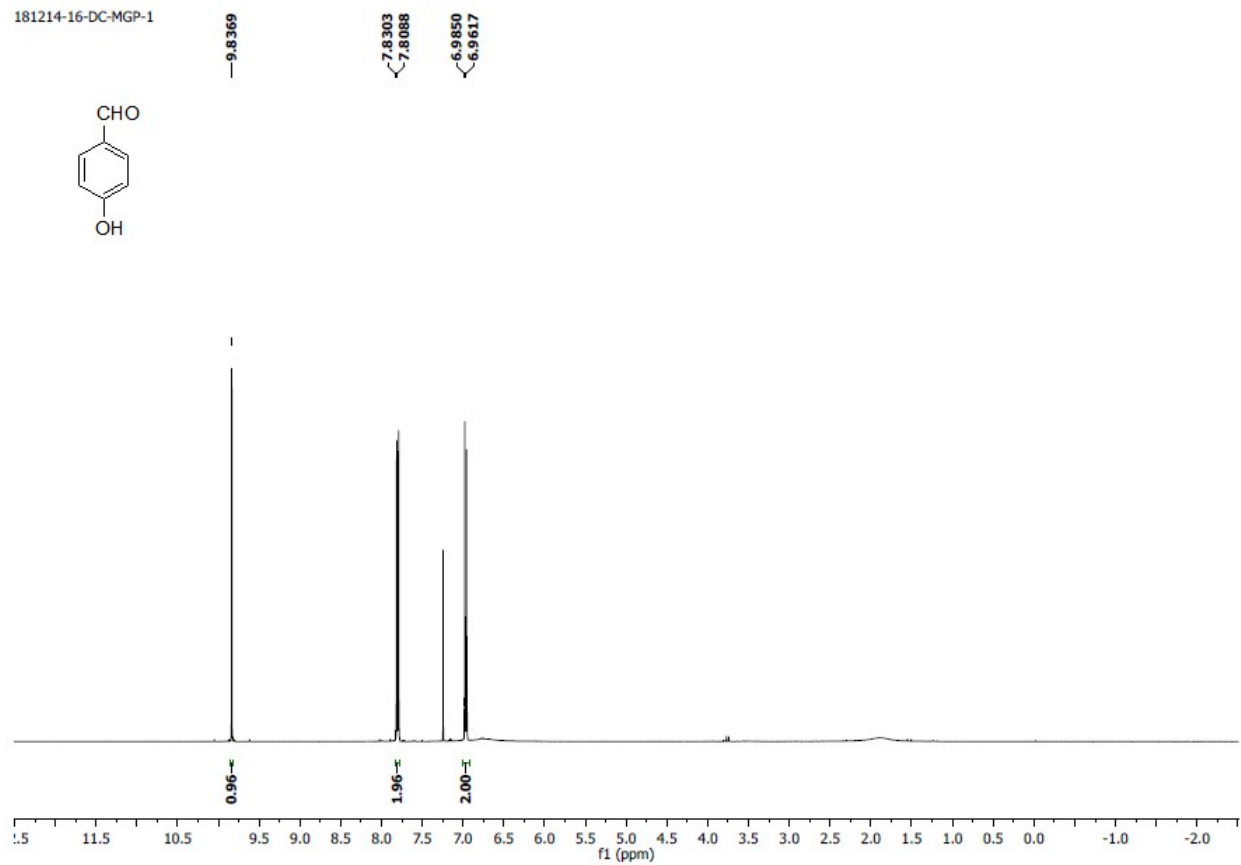
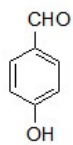
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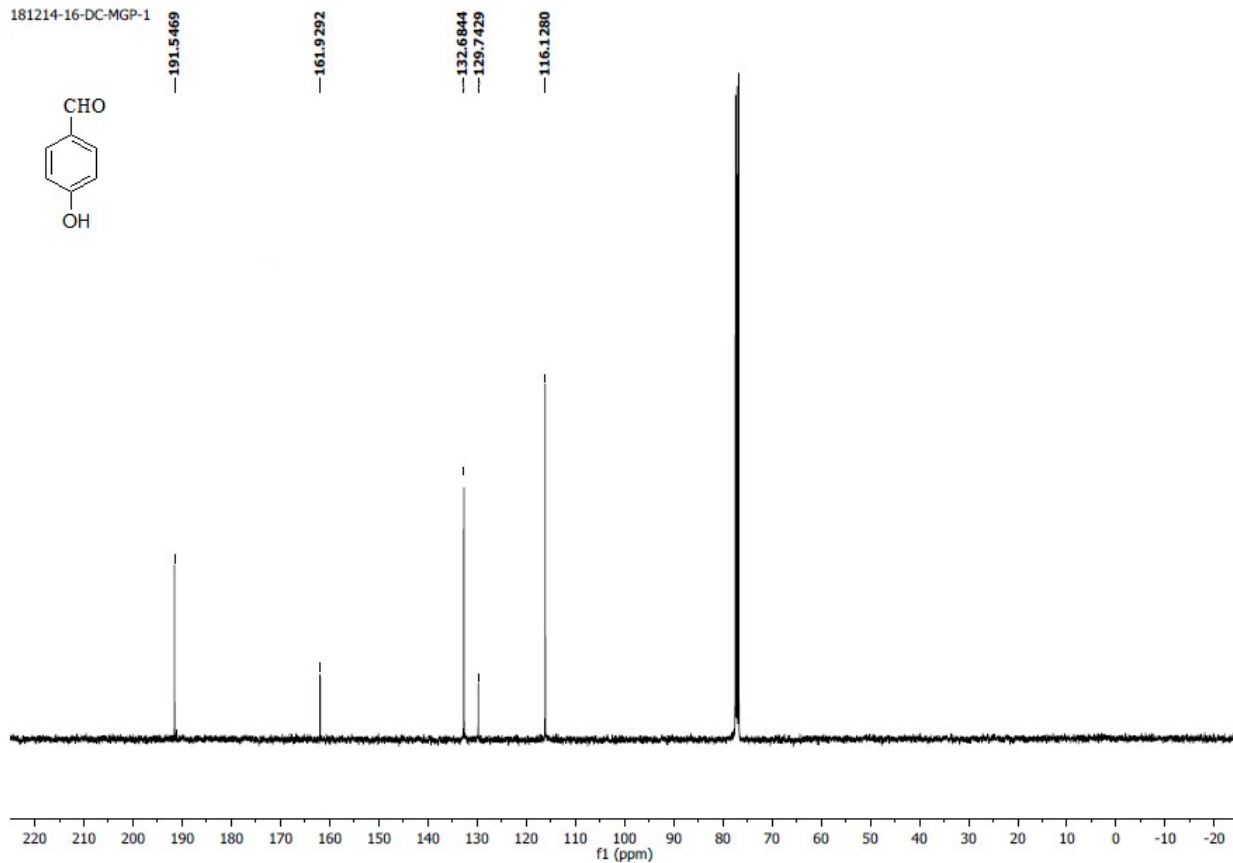
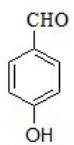
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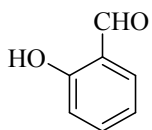
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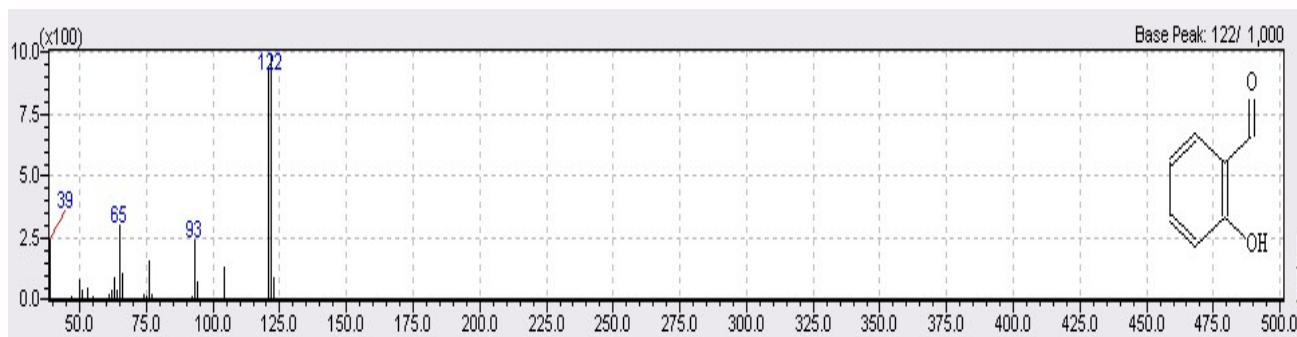
181214-16-DC-MGP-1



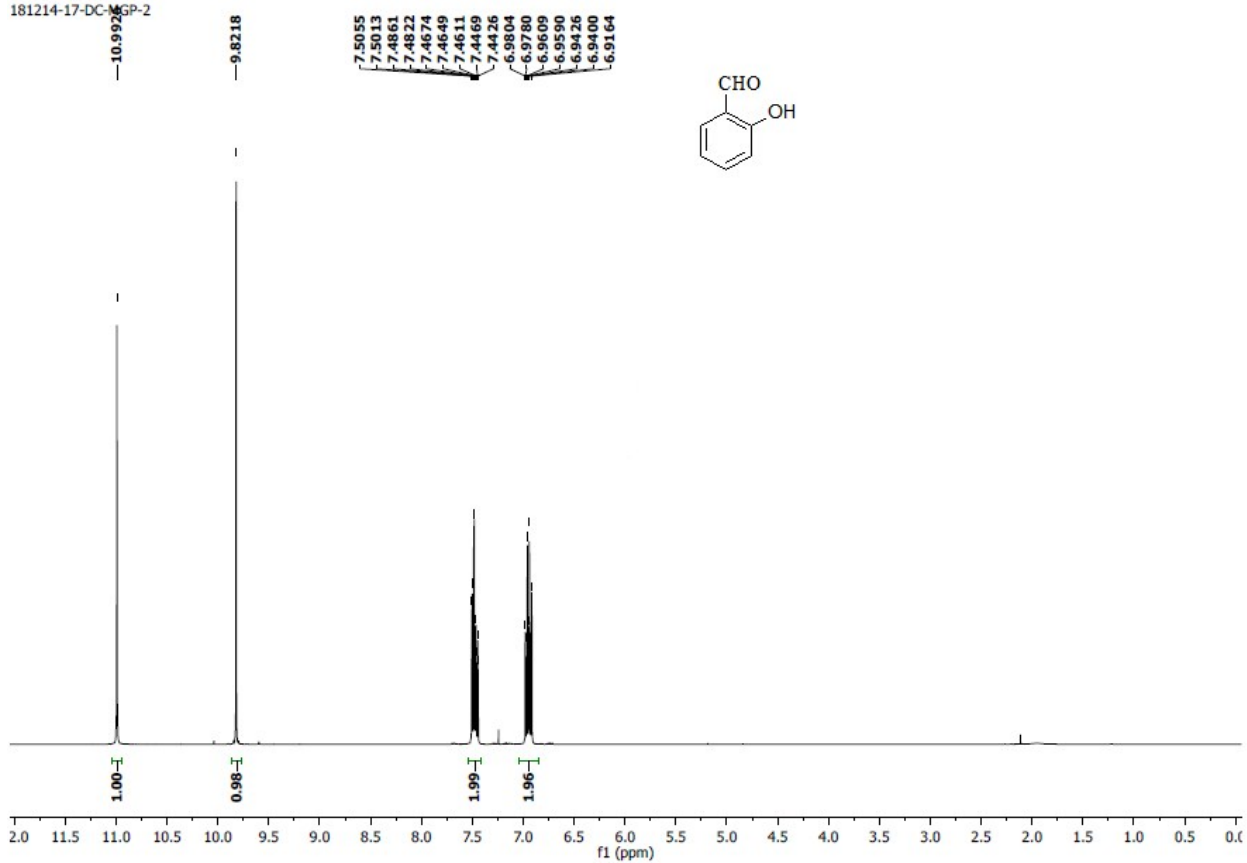
8h. 2-Hydroxybenzaldehyde



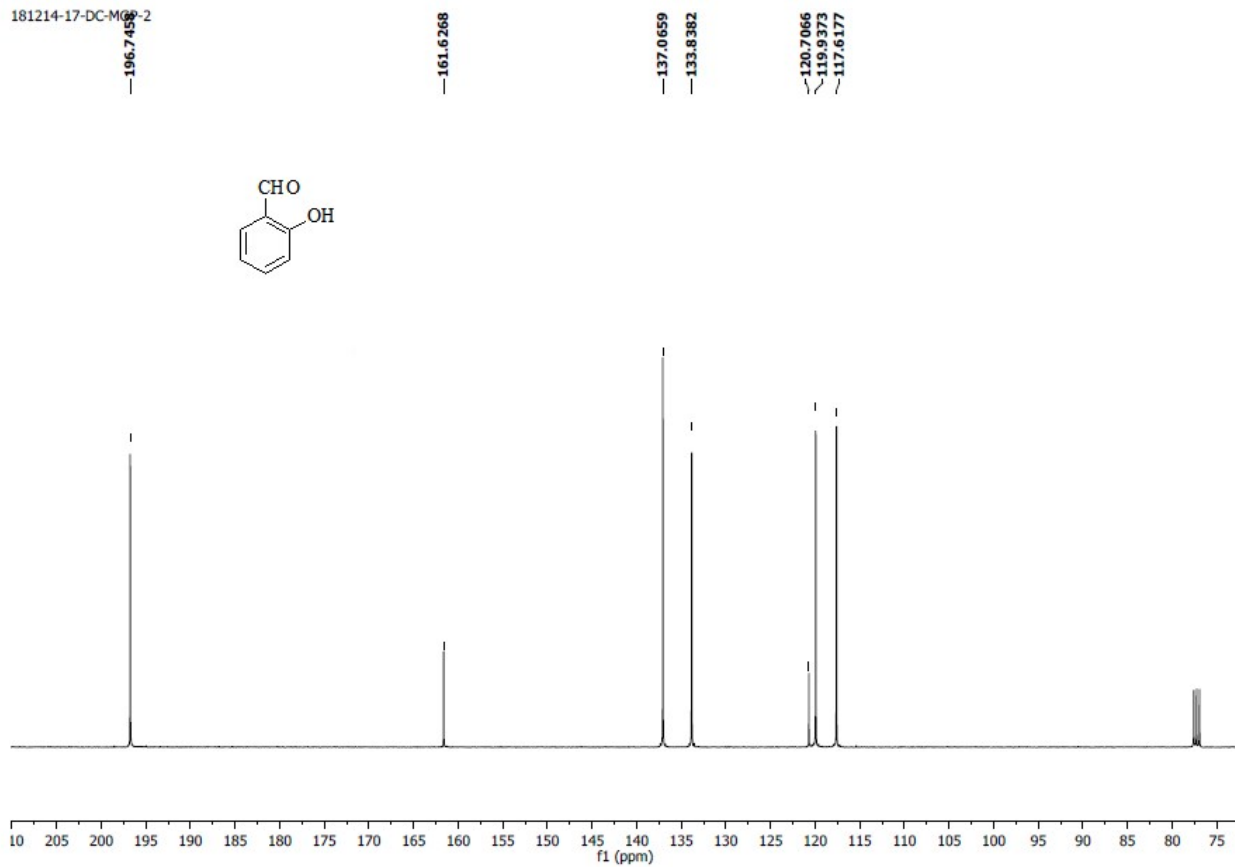
Mol. Wt.: 122.12



181214-17-DC-MGP-2



181214-17-DC-M06-2



S4. References:

- [1] P. Das, N. Aggarwal, N.R. Guha, *Tetrahedron Lett.* 54 (2013) 2924.