Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Light induced carboxylation of Aryl derivatives with cooperative COF as active photocatalyst and Ni(II) co-catalyst

PekhamChakrabortty,[a]Anjan Das,[a] Arpita HazraChowdhury,[a]Swarbhanu Ghosh, [a] Aslam Khan,[b]Sk. ManirulIslam[a*]

[a]Department of Chemistry, Kalyani University, Kalyani, West Bengal, 741235, India

[b]King Abdullah Institute for Nanotechnology, King Saud University, Riyadh, 11451, Saudi Arabia

Contents

Instrumentation

NMR Spectra: ^{1}HNMRspectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts for protons is reported in parts per million (ppm).

PXRD: The PXRD analysis was performed by using an X-ray diffractometer (BRUKER, Powder X-Ray ecoD8 ADVANCE) equipped with Ni-filtered Cu Kα (λ= 0.15406 nm) radiation.

SEM: FESEM images of the catalyst were acquired by using Scanning Electron Microscope (SEM) [JEOL JSM IT 300], was done to know about the morphological information of the sample.

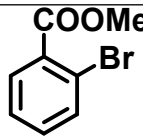
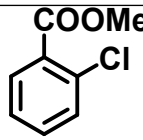
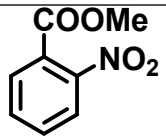
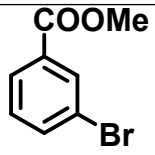
TEM: Transmission Electron Microscope (TEM) [JEOL JEM 2100] was used obtain the morphological information of the sample.

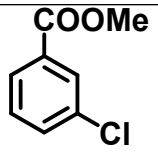
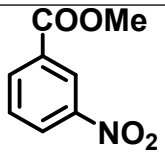
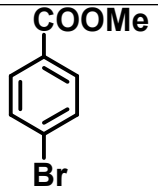
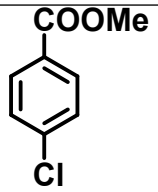
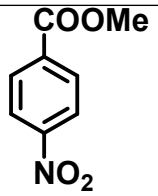
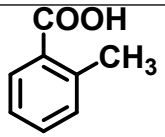
BET: The N_2 adsorption-desorption analysis of TFPG-DAAQ COF sample was conducted by using a BET Surface Analyzer [QUANTACHROME ASIQCOV602-5].

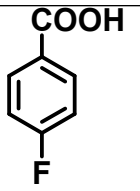
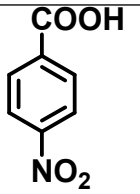
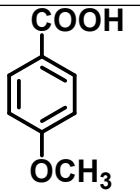
Fluorescence Spectroscopy: The Fluorescence Emission spectra was recorded by using Horiba Fluoro Max 4 spectrometer.

Reaction setup:

^{1}H &^{13}C-NMR data of products:

Entry	Compound	NMR analysis
1		Yellowish oil, yield 83%, ^{1}H- NMR ($CDCl_3$, 400MHz): 7.80-7.77 (1H, m), 7.67-7.65 (1H, m), 7.38-7.26 (2H, m), 3.93 (3H, s). ^{13}C-NMR ($CDCl_3$, 100MHz): 166.63, 134.34, 132.60, 132.07, 131.31, 127.17, 121.65, 52.51.
2		Yellowish oil, yield 81%, ^{1}H- NMR ($CDCl_3$, 400MHz): 7.71-7.67 (1H, m), 7.58-7.53 (1H, m), 7.27-7.19 (2H, m), 3.85-3.82 (3H, d, J=12Hz). ^{13}C-NMR ($CDCl_3$, 100MHz): 166.72, 134.43, 132.63, 132.32, 131.38, 127.24, 121.74, 52.53
3		Yellowish oil, yield 85%, ^{1}H- NMR ($CDCl_3$, 400MHz): 7.79-7.77 (1H, m), 7.66-7.64 (1H, m), 7.38-7.27 (2H, m), 3.93 (3H, s). ^{13}C-NMR ($CDCl_3$, 100MHz): 166.63, 134.36, 132.58, 132.24, 131.32, 127.18, 121.67, 52.46.
4		Yellowish oil, yield 85%, ^{1}H- NMR ($CDCl_3$, 400MHz): 8.09 (1H, s), 7.89-7.88 (1H, d, J=4Hz), 7.61-7.59 (1H, d, J=8Hz), 7.26-7.19 (1H, m), 3.84 (3H, s). ^{13}C-NMR ($CDCl_3$, 100MHz): 165.80, 135.89,132.62, 132.03, 129.97, 128.17, 122.46, 52.46.

5		Yellowish oil, yield 81%, ^{1}H- NMR ($CDCl_3$, 400MHz): 8.15-8.14 (1H, m), 7.95-7.92 (1H, m), 7.66-7.63 (1H, m),7.30-7.28(1H, m) 3.90-3.89 (3H, d, J=4Hz).
6		Yellowish oil, yield 86%, ^{1}H- NMR ($CDCl_3$, 400MHz): 8.14 (1H, s), 7.94-7.92 (1H, d, J=8Hz), 7.65-7.63 (1H, m), 7.30-7.26 (1H, m), 3.89 (3H, s). ^{13}C-NMR ($CDCl_3$, 100MHz): 165.79, 135.92, 132.68, 132.17, 130.01, 128.22, 122.53, 52.46.
7		Yellowish solid, yield 93%, ^{1}H- NMR ($CDCl_3$, 400MHz): 7.84-7.82 (1H, d, J=4Hz), 7.52-7.50 (1H, d, J=4Hz), 3.84 (3H, s).
8		Yellowish solid, yield 95%, ^{1}H- NMR ($CDCl_3$, 400MHz): 8.28-8.31 (1H, m), 8.20-8.23 (1H, m), 3.98 (3H, s). ^{13}C-NMR ($CDCl_3$, 100MHz): 165.20, 150.52, 135.47, 130.73, 123.57, 52.88.
9		Yellowish solid, yield 95%, ^{1}H- NMR ($CDCl_3$, 400MHz): 8.28-8.31 (1H, m), 8.20-8.23 (1H, m), 3.98 (3H, s). ^{13}C-NMR ($CDCl_3$, 100MHz): 165.20, 150.52, 135.47, 130.73, 123.57, 52.88.
10		white solid, ^{1}H- NMR ($CDCl_3$, 400MHz): 7.80-7.78 (1H, d, J=8Hz), 7.22-7.21 (2H, d, J=4Hz), 6.85 (1H, s), 2.41 (3 H). ^{13}C-NMR ($CDCl_3$, 100MHz): 172.45, 133.86, 130.38 129.89, 128.60, 128.28, 127.50, 28.28.

11		white solid, ^{1}H- NMR (DMSO-d_6, 400MHz): 13.07(1H) ,8.01-7.98 (1H, m,), 7.31-7.27 (1H, m). ^{13}C-NMR (DMSO-d_6, 100MHz): 166.34-166.10 (d, J = 24 Hz, C-F), 163.62, 132.11-132.01 (d, J = 10 Hz, C-H), 127.27, 115.69-115.47 (d, J= 22 Hz, C-H).
12		white solid, ^{1}H- NMR (DMSO-d_6 400MHz): 8.33-8.31 (1H, d, J=8Hz), 8.17-8.15 (1H, d, J=8Hz). ^{13}C-NMR (DMSO-d_6, 100MHz): 166.27, 150.49, 136.81, 131.16, 124.21.
13		white solid, ^{13}C-NMR (DMSO-d_6, 100MHz): 167.79, 159.59, 138.38, 129.73, 117.18, 55.64

^{1}H &^{13}C spectra of products:

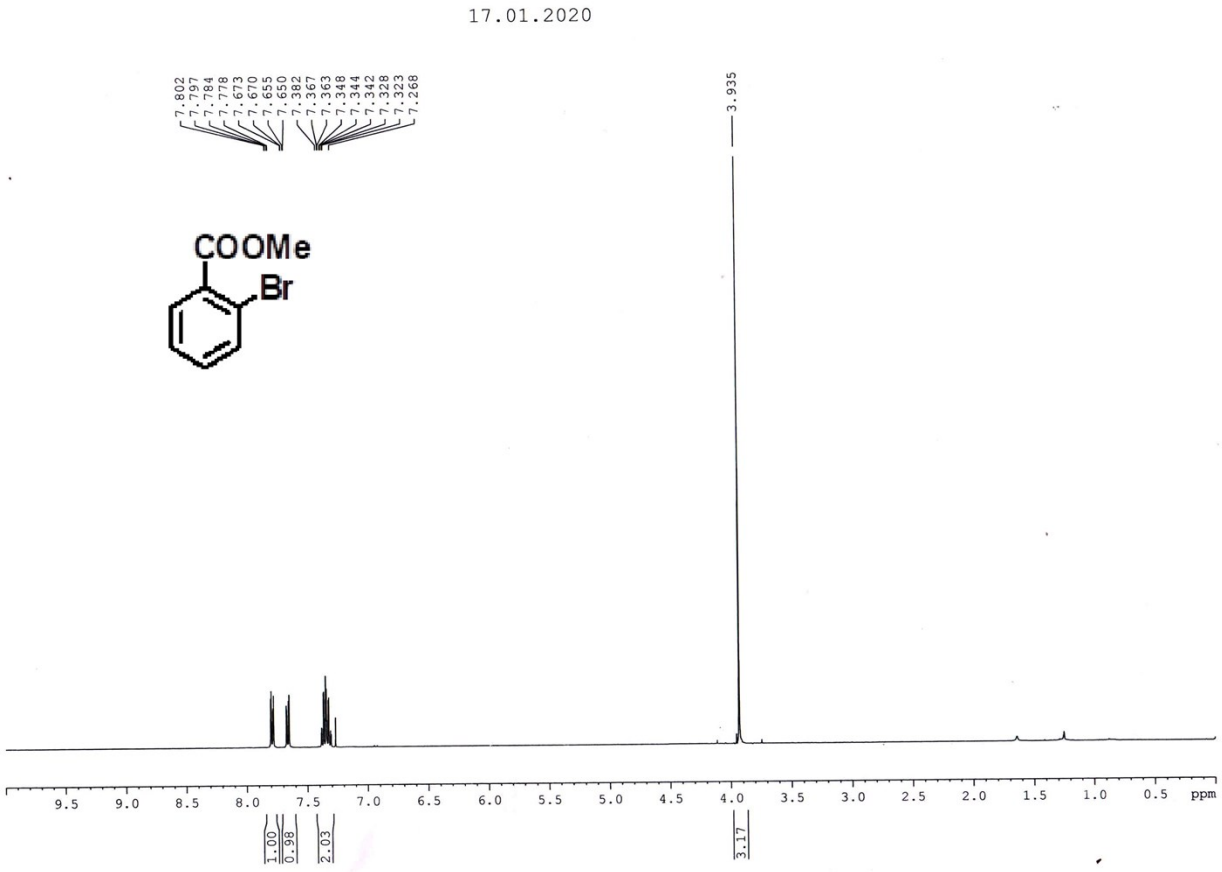


Figure 1: ^{1}H NMR spectra of 2-Bromo-benzoic acid methyl ester (1)

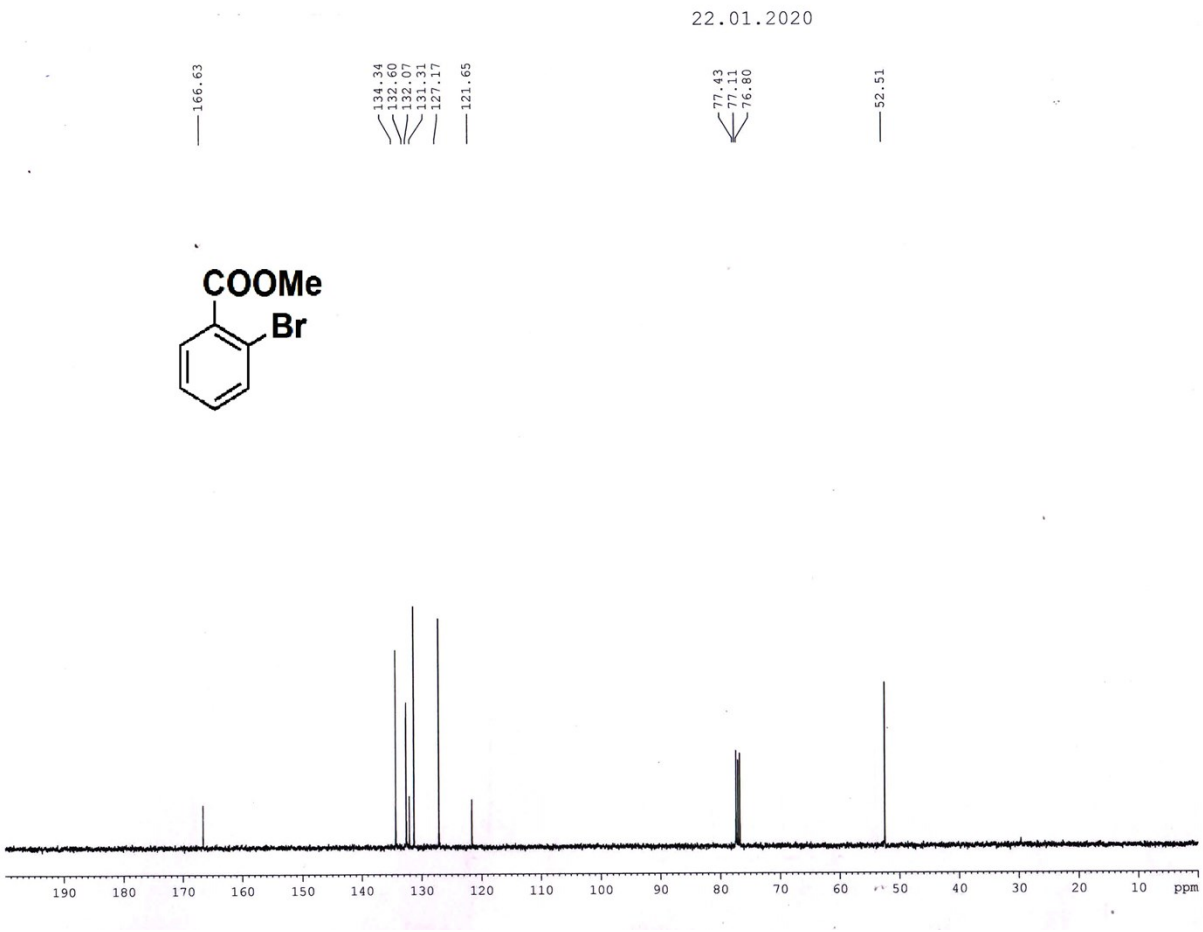


Figure 2: ^{13}C NMR spectra of 2-Bromo-benzoic acid methyl ester (1)

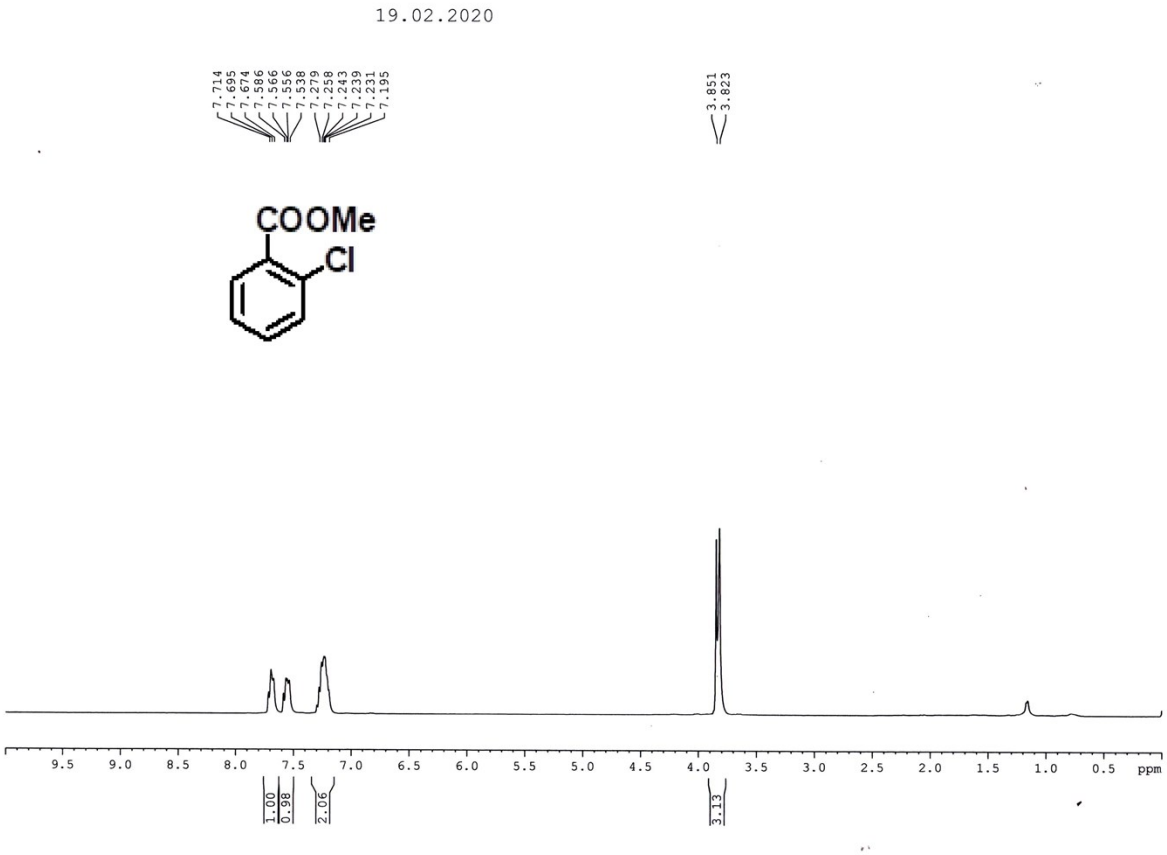


Figure 3: ^{1}H NMR spectra of 2-Chloro-benzoic acid methyl ester (2)

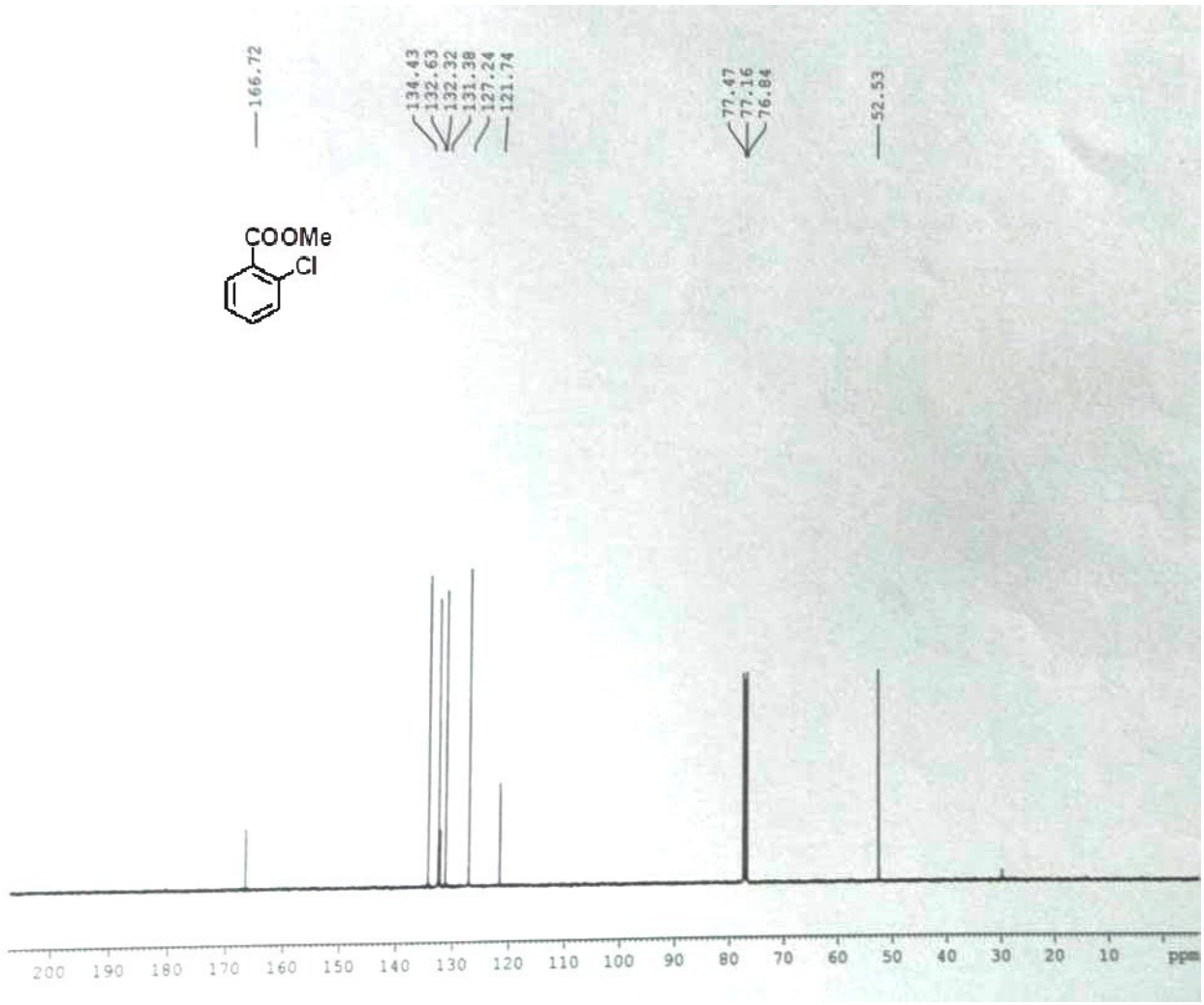


Figure 4: ^{13}C NMR spectra of 2-Chloro-benzoic acid methyl ester (2)

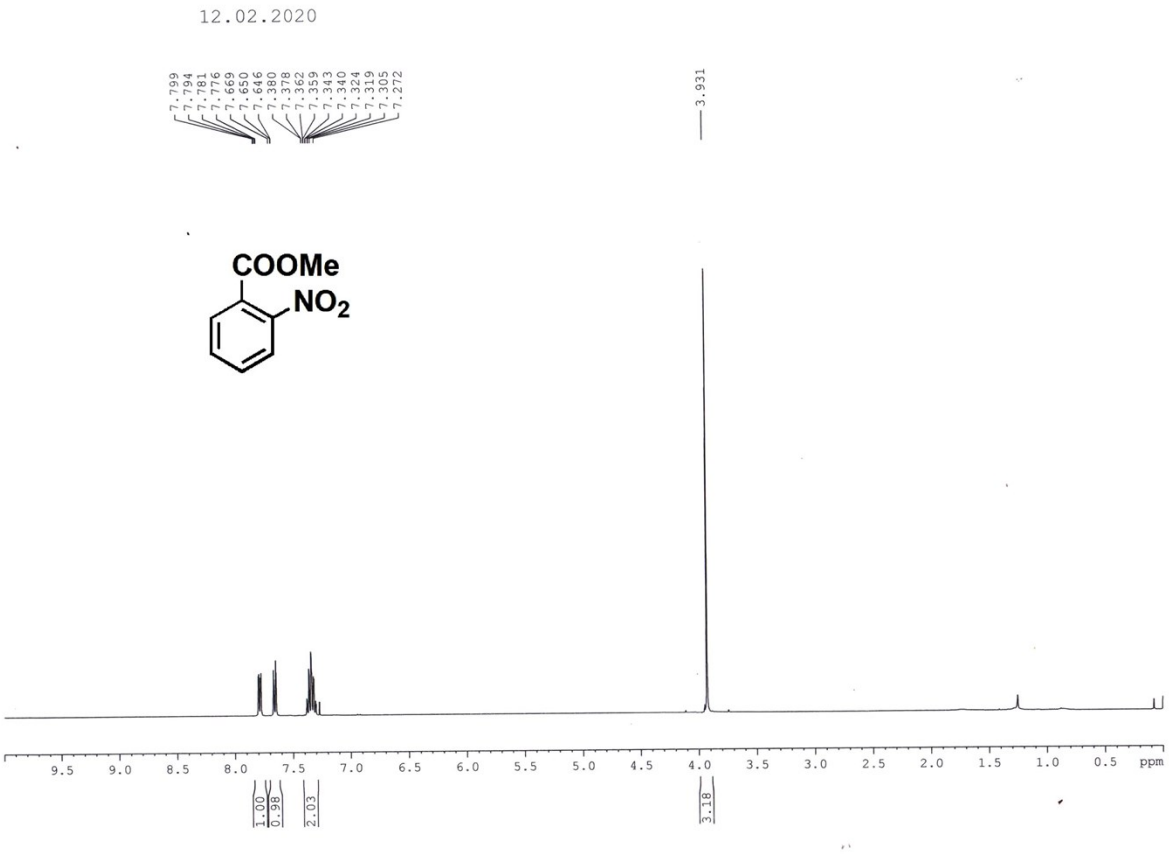


Figure 5: ^{1}H NMR spectra of 2-Nitro-benzoic acid methyl ester (3)

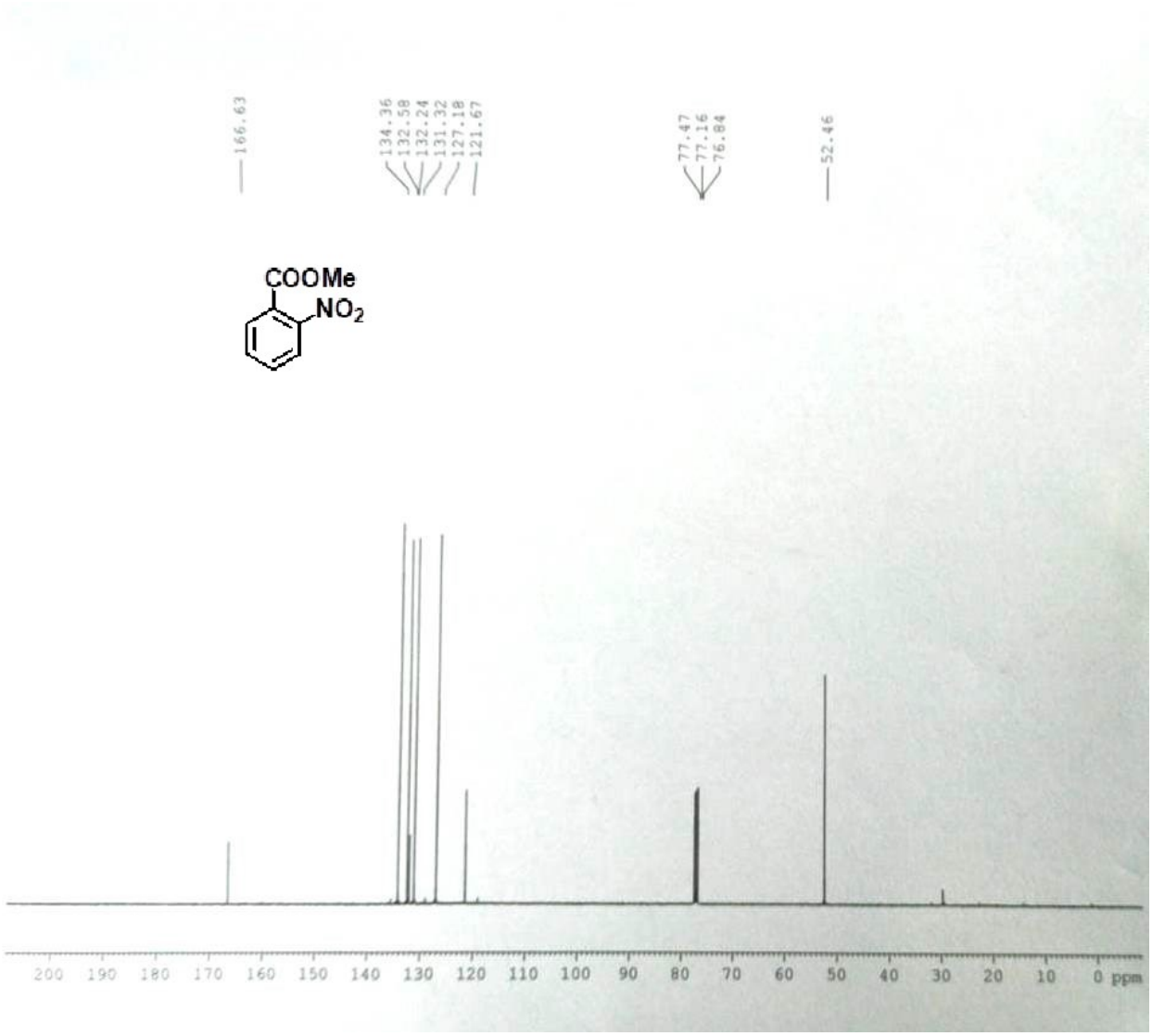


Figure 6: ^{13}C NMR spectra of 2-Nitro-benzoic acid methyl ester (3)

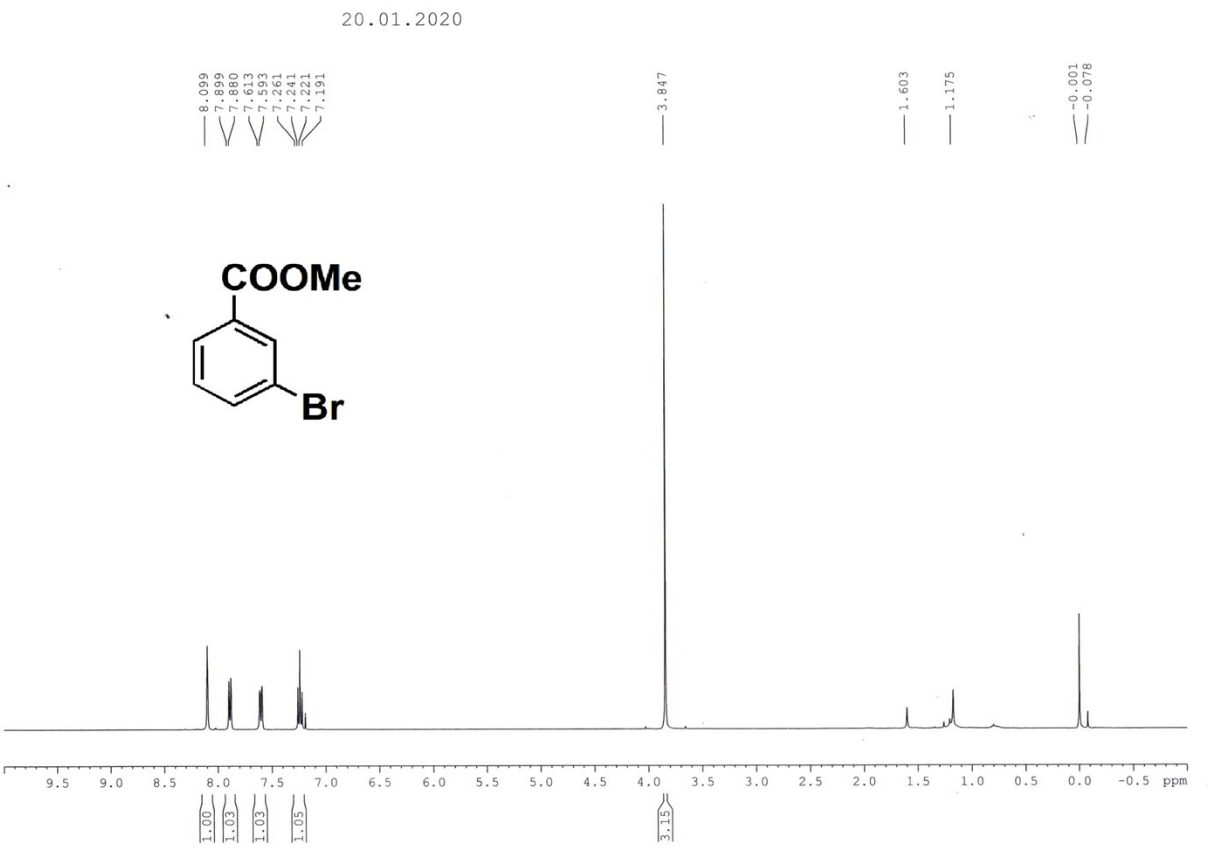


Figure 7: ^{1}H NMR spectra of 3-Bromo-benzoic acid methyl ester (4)

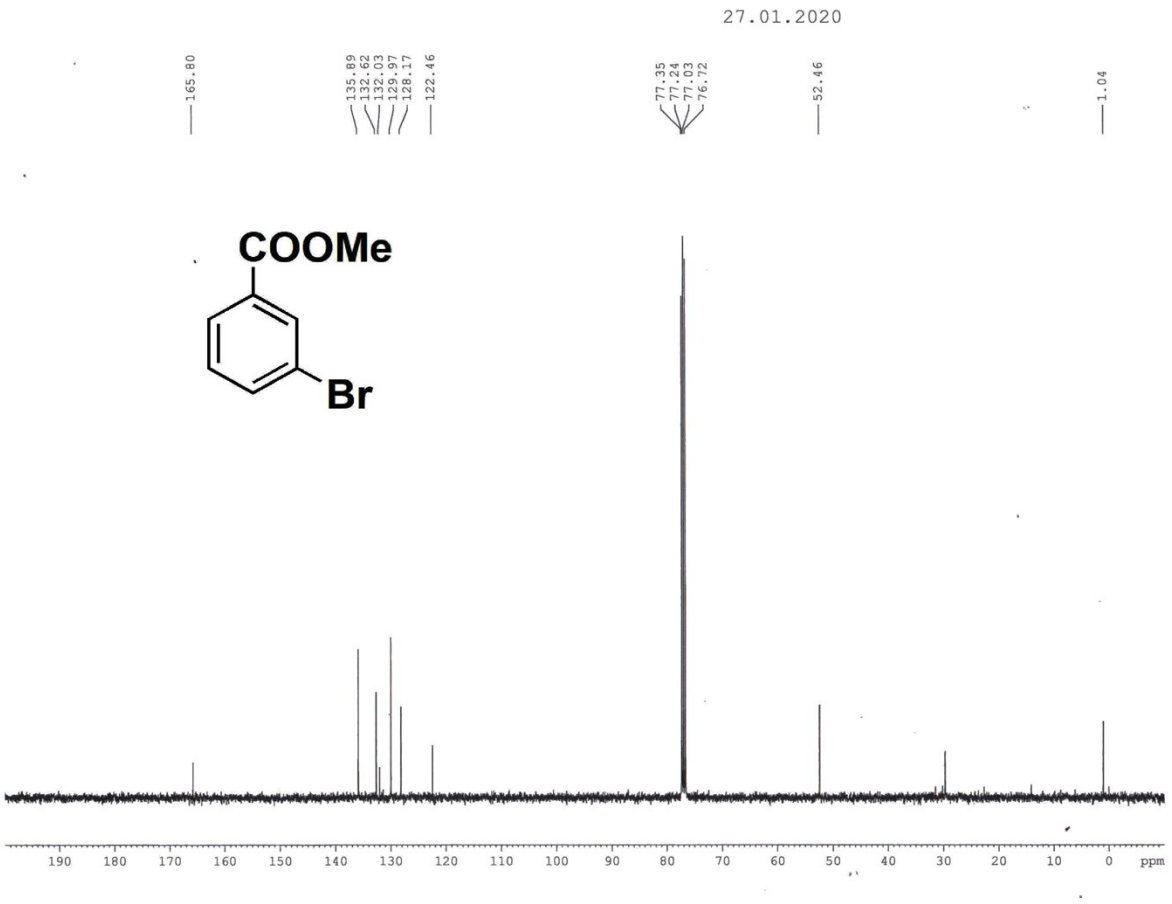


Figure 8: ^{13}C NMR spectra of 3-Bromo-benzoic acid methyl ester (4)

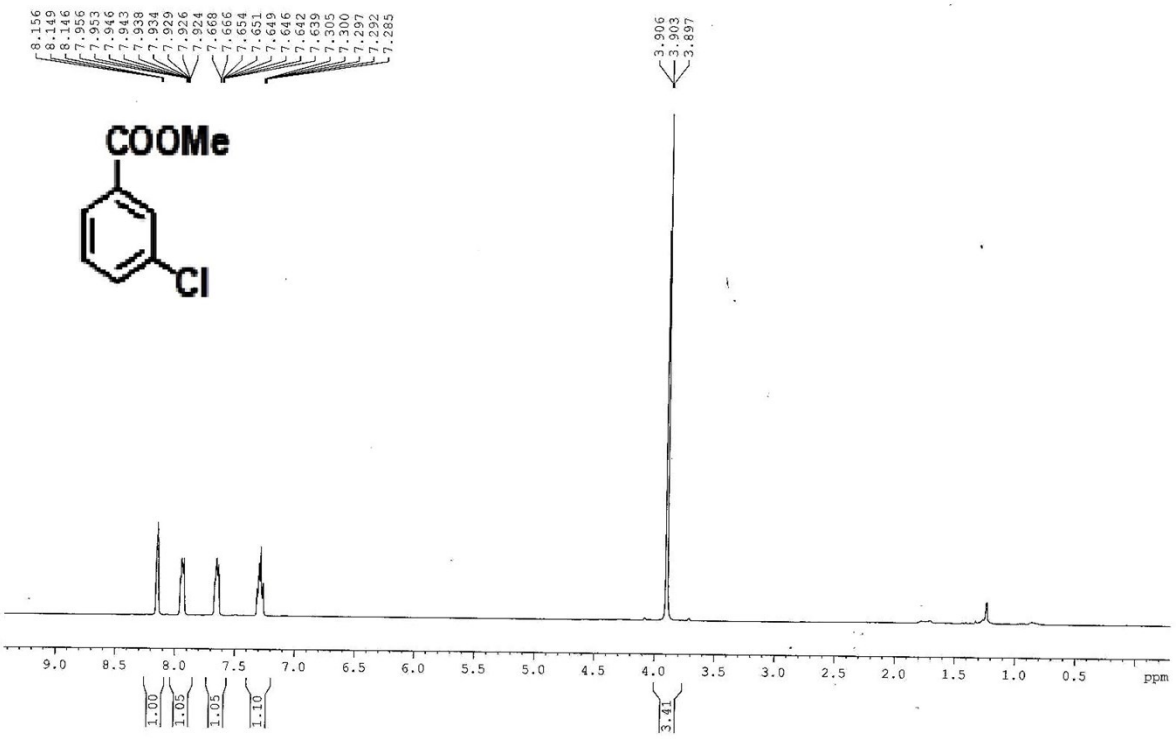


Figure 9: ^{1}H NMR spectra of 3-Chloro-benzoic acid methyl ester (5)

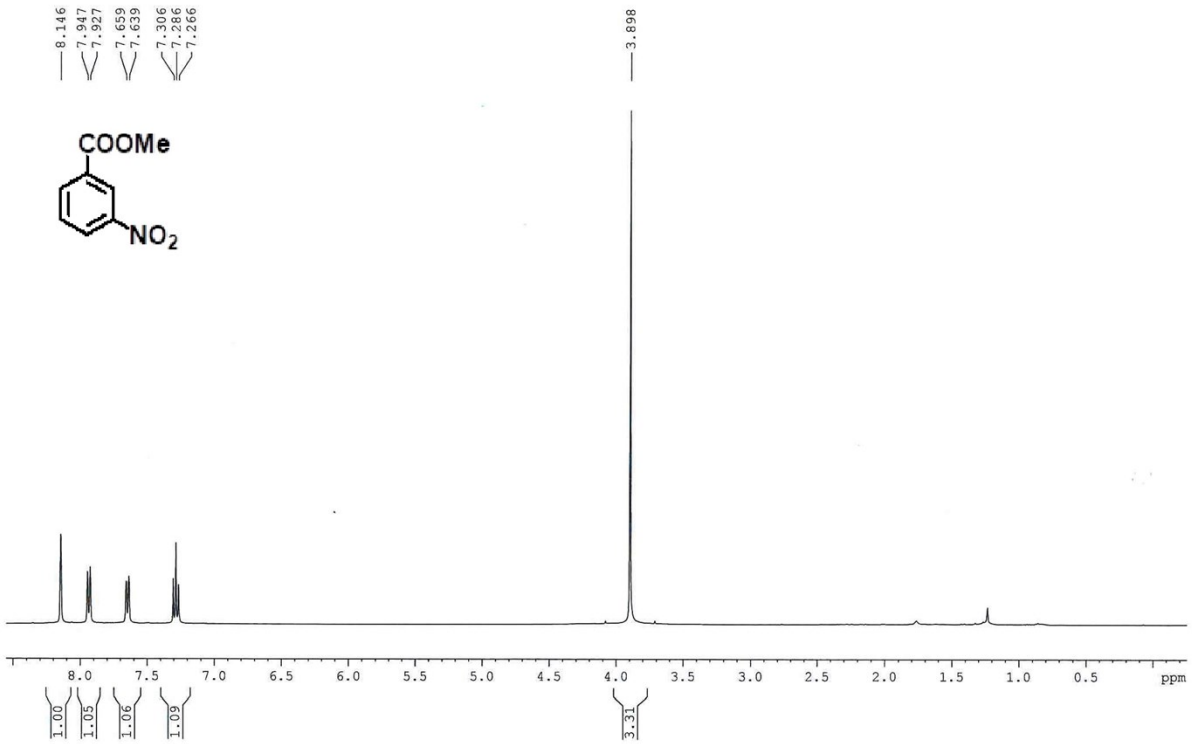


Figure 10: ^{1}H NMR spectra of 3-Nitro-benzoic acid methyl ester (6)

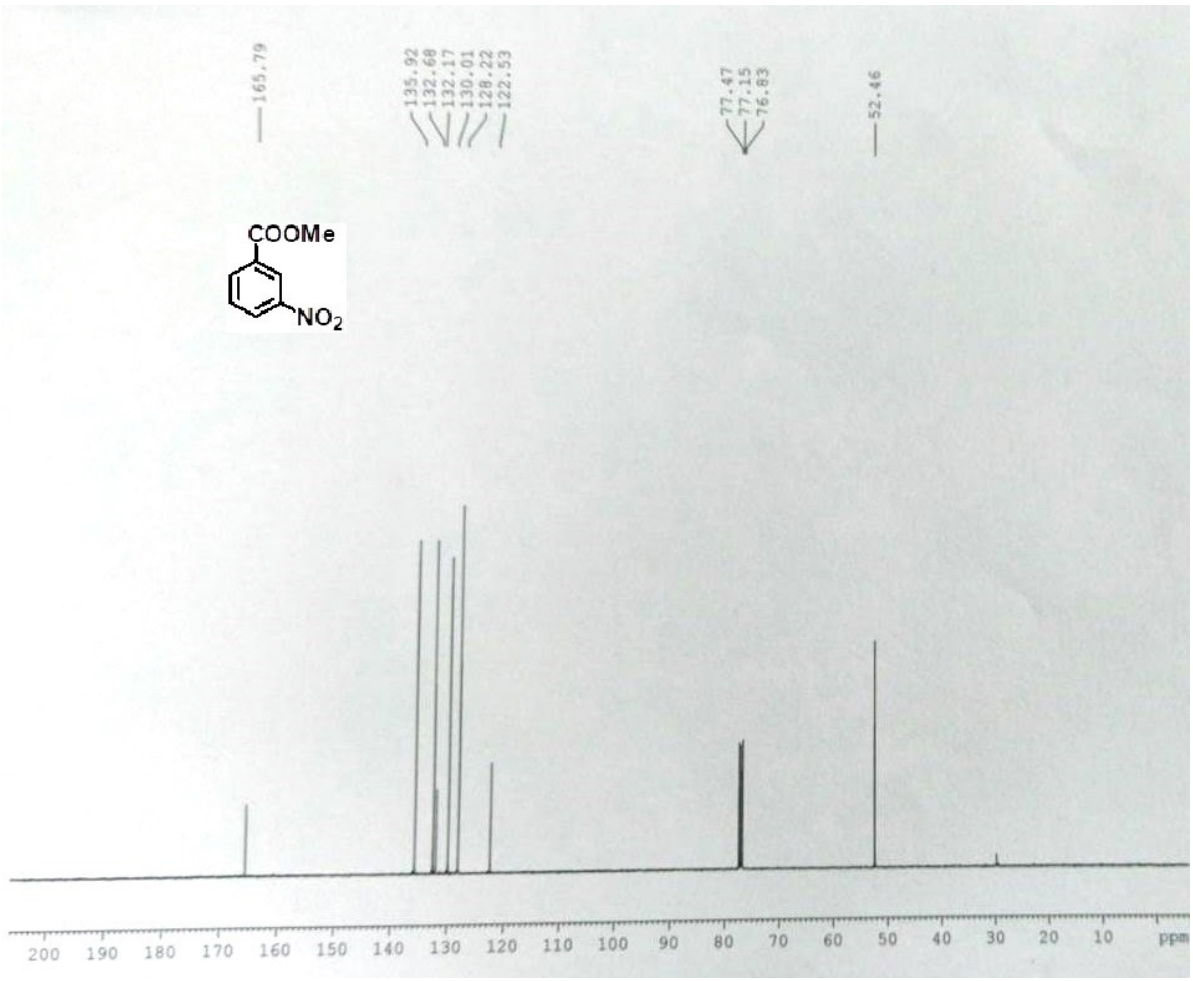


Figure 11: ^{13}C NMR spectra of 3-Nitro-benzoic acid methyl ester (6)

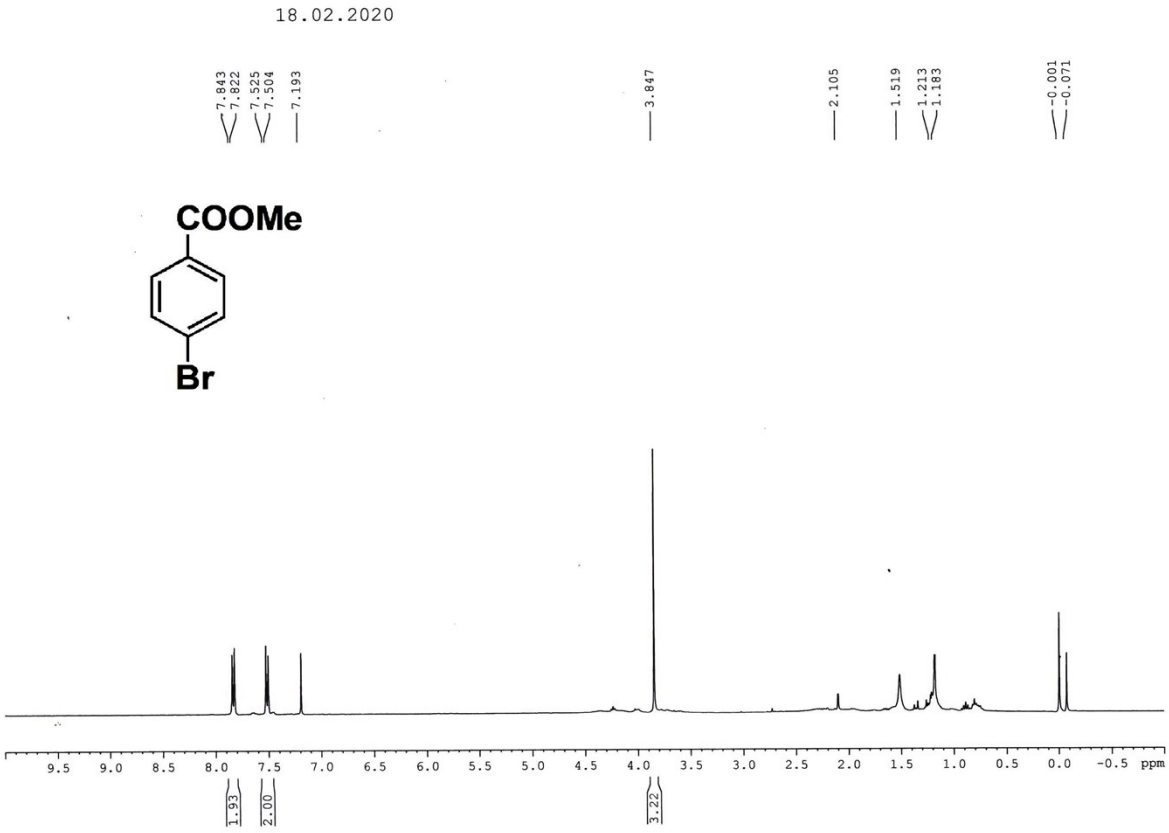


Figure 12: ^{1}H NMR spectra of 4-Bromo-benzoic acid methyl ester (7)

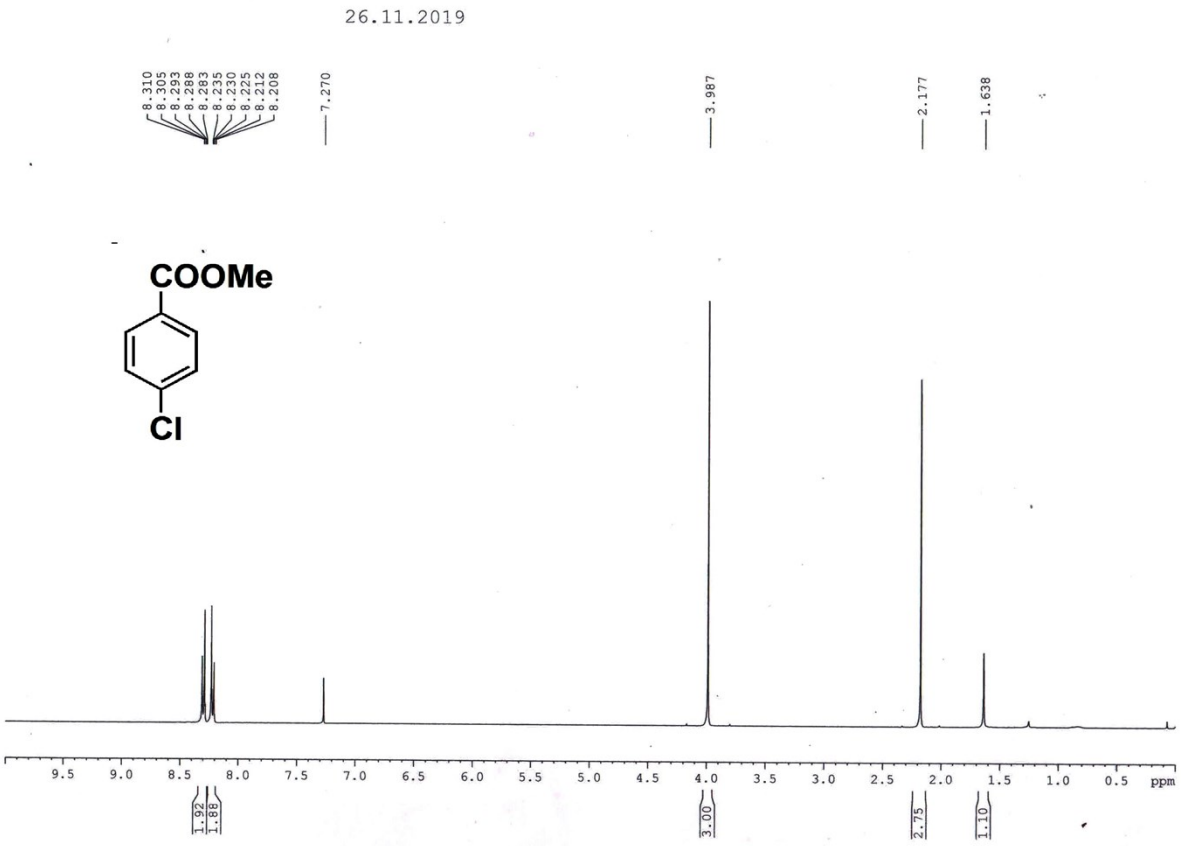


Figure 13: ^{1}H NMR spectra of 4-Chloro-benzoic acid methyl ester (8)

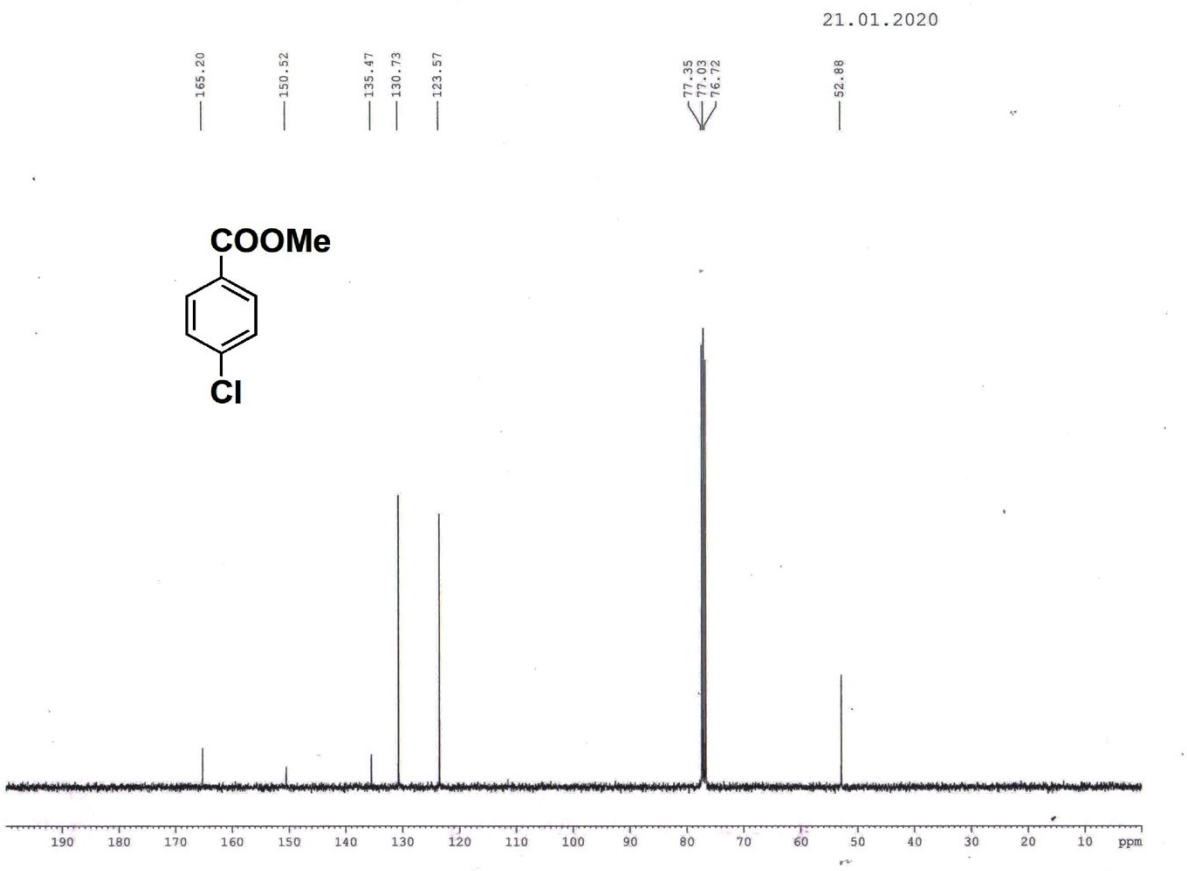


Figure 14: ^{13}C NMR spectra of 4-Chloro-benzoic acid methyl ester (8)

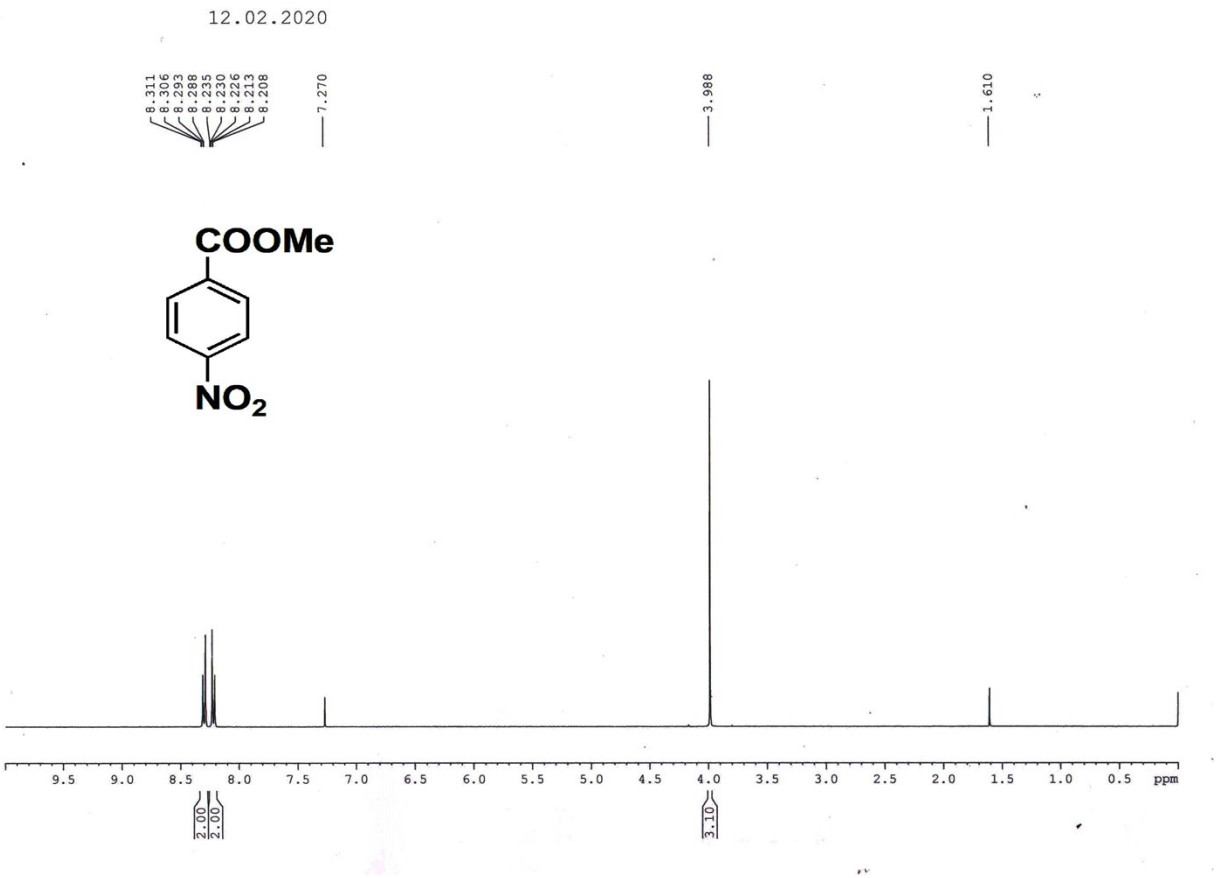


Figure 15: ^{1}H NMR spectra of 4-Nitro-benzoic acid methyl ester (9)

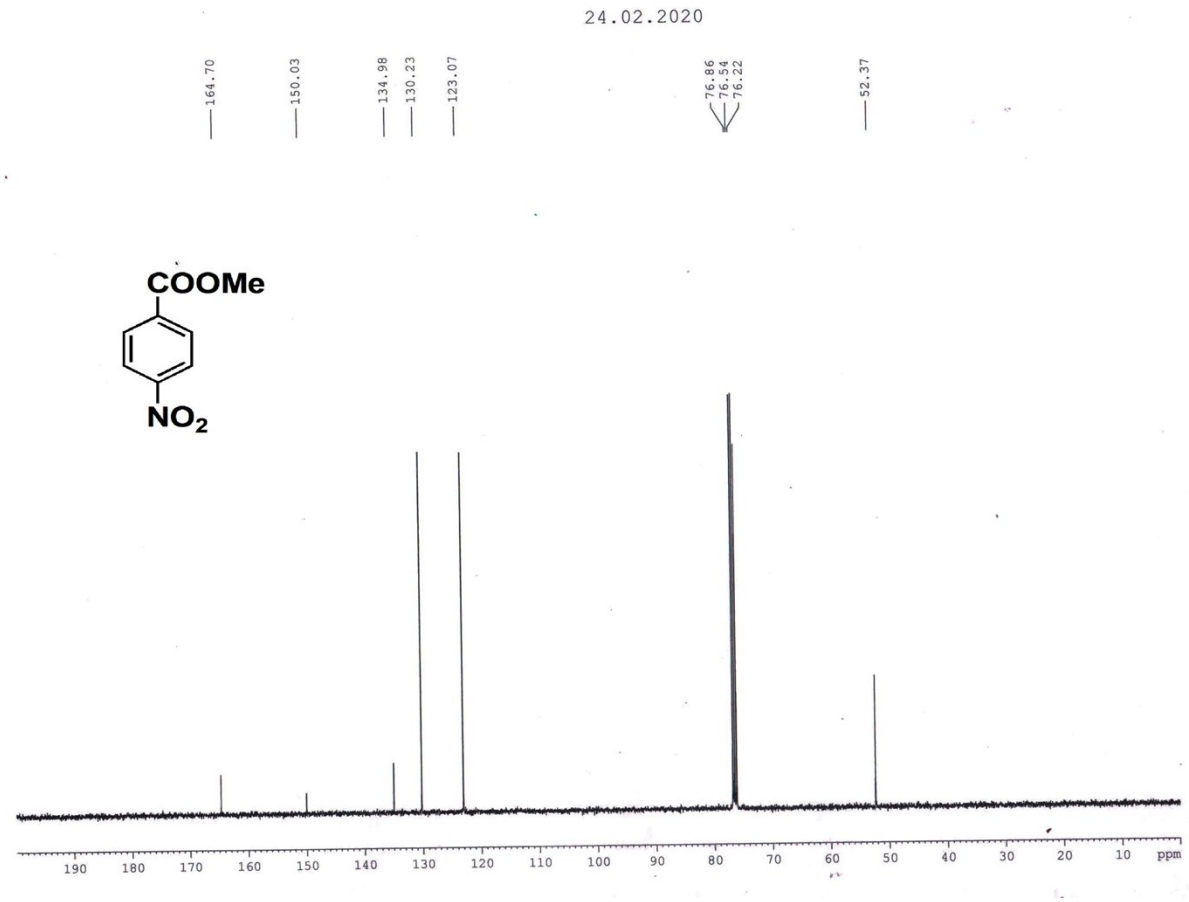


Figure 16: ^{13}C NMR spectra of 4-Chloro-benzoic acid methyl ester (9)

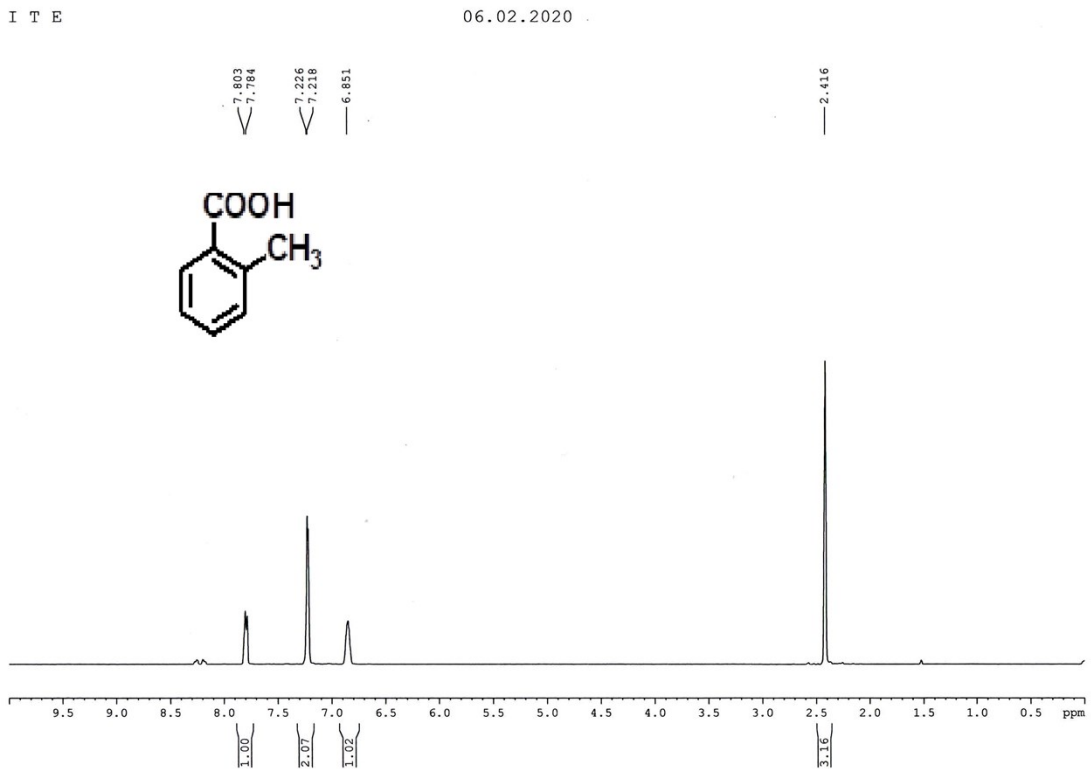


Figure 17: ^{1}H NMR spectra of 2-Methyl-benzoic acid (10)

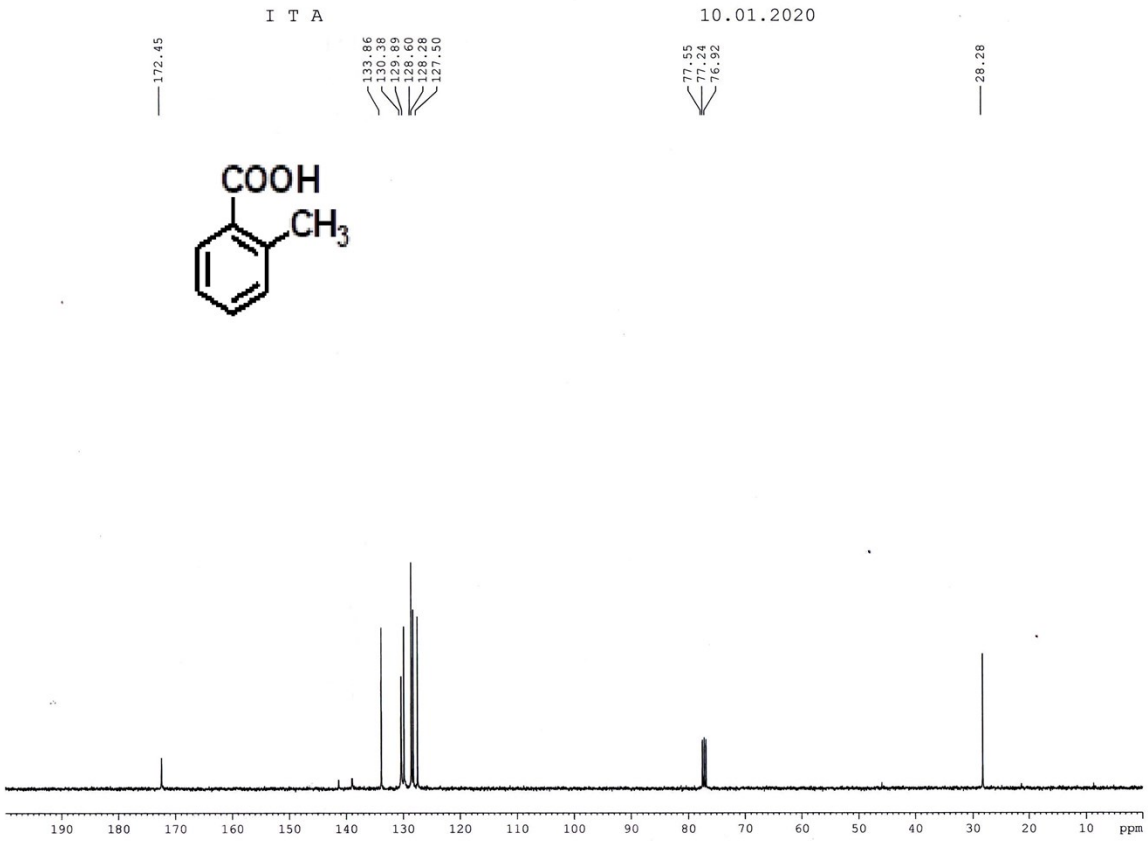


Figure 18: ^{13}C NMR spectra of 2-Methyl-benzoic acid (10)

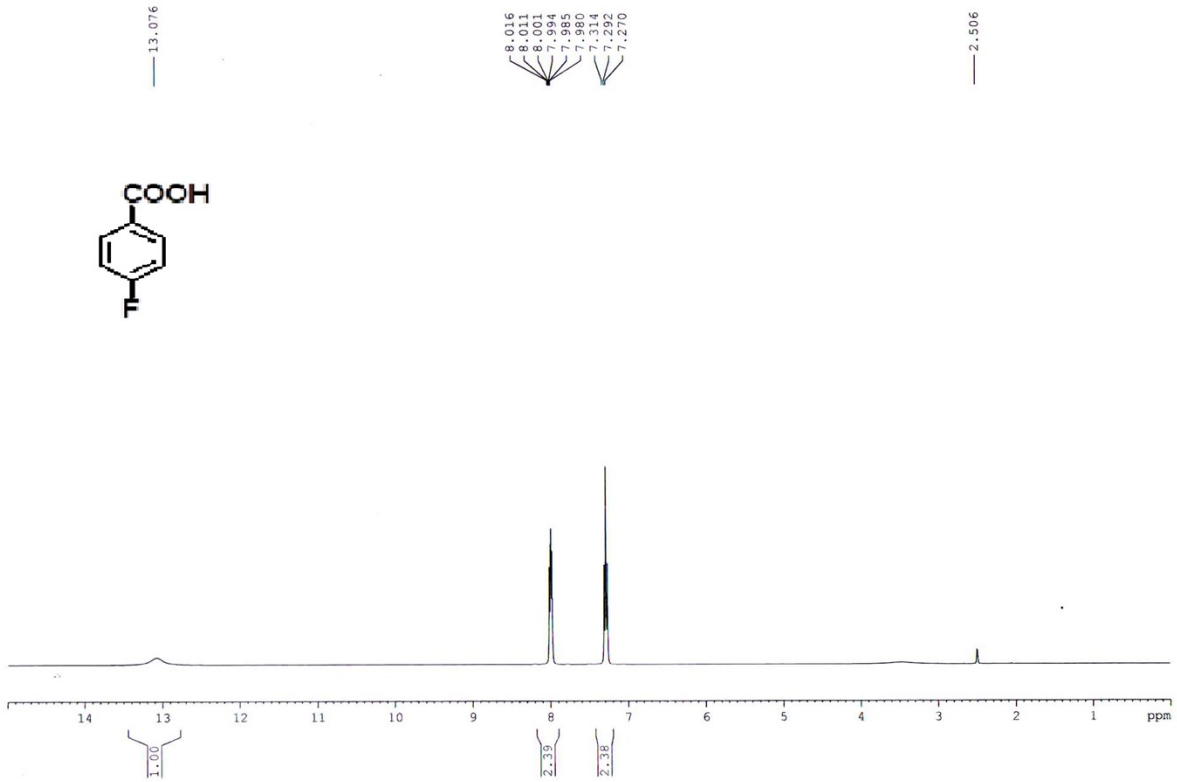


Figure 19: 1H NMR spectra of 4- Fluoro- benzoic acid (11)

Figure 20: ^{13}C NMR spectra of 4- Fluoro- benzoic acid(11)

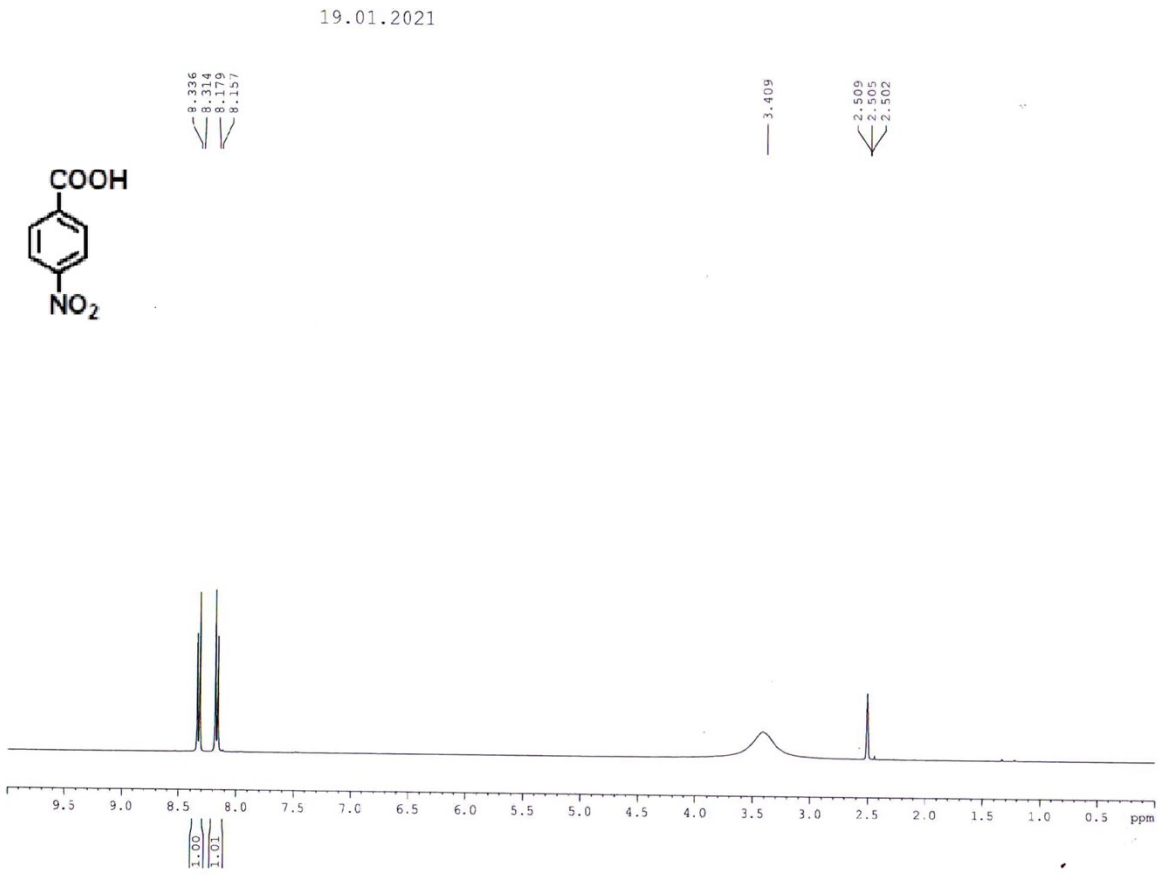


Figure 21: ^{1}H NMR spectra of 4- Nitro- benzoic acid (12)

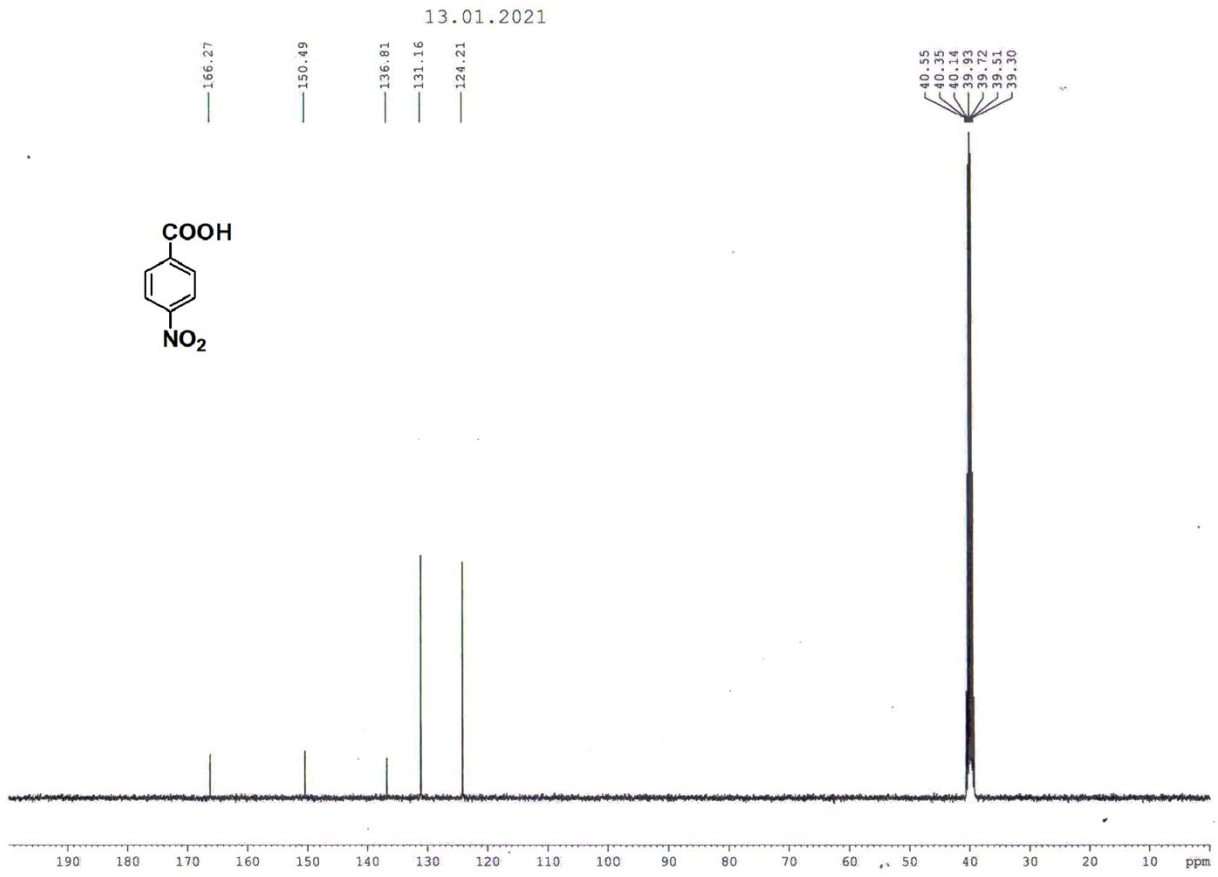


Figure 22: ^{13}C NMR spectra of 4- Nitro- benzoic acid(12)

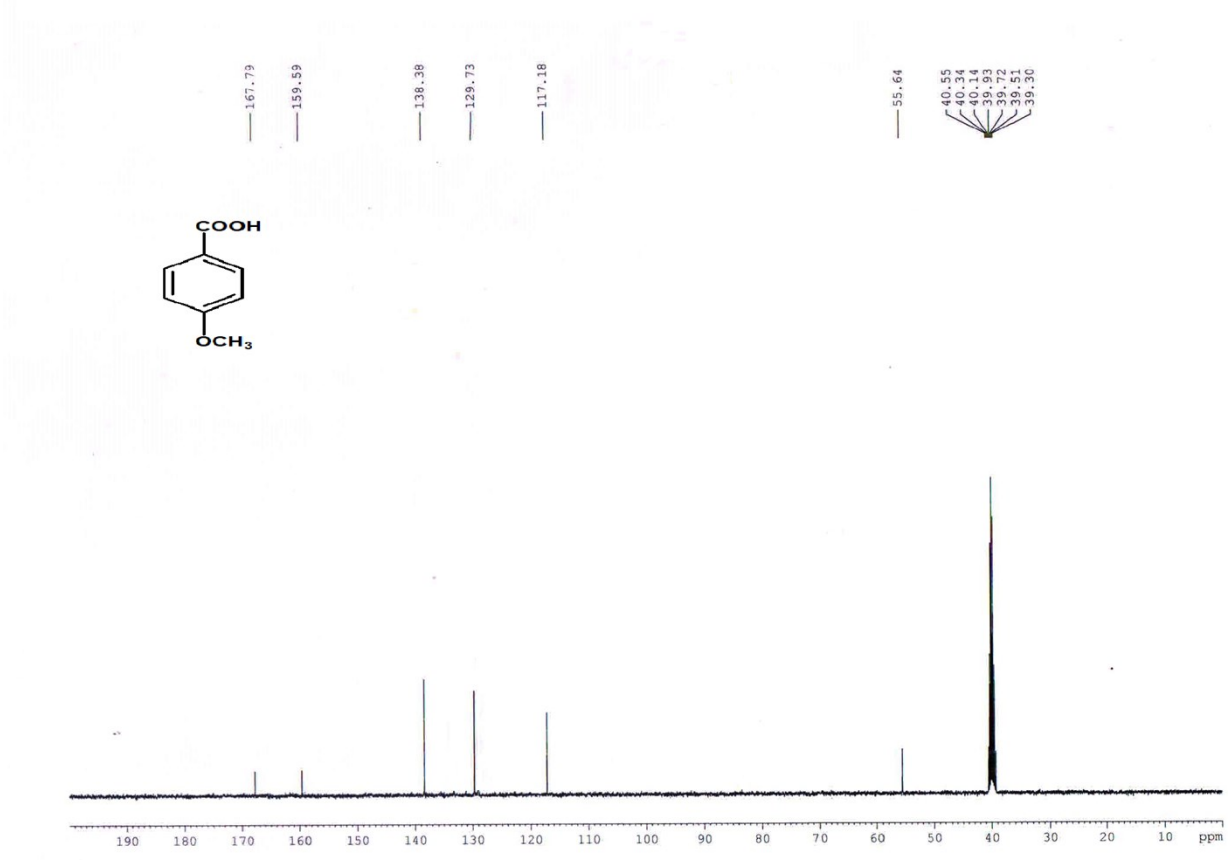


Figure 23: ^{13}C NMR spectra of 4-Methoxy-benzoic acid (13)