Supporting information

Biogenic $CuFe_2O_4$ Magnetic Nanoparticles as a green, reusable and excellent nanocatalyst for the acetylation reaction under solvent free conditions

Rituparna Chutia and Bolin Chetia*

*Department of Chemistry, Dibrugarh University, Dibrugarh-786004, Assam, India

*Email: bolinchetia@dibru.ac.in

Tel.: +91-373-237-0210; fax: +91-373-237-0323;

1. General Information

Chemicals and reagents were purchased from commercial suppliers and used without further purification. Reactions were monitored by thin layer chromatography (TLC) on silica gel plates (60 F254), visualizing with ultraviolet light. ^{1}H-NMR and ^{13}C-NMR spectra was determined in $CDCl_3$ solution by using 400 MHz spectrometer taking tetramethylsilane (TMS, $\delta = 0.00$) as internal standard and expressed in ppm. Spin multiplicities are given as s (singlet), d (doublet), t (triplet) and m (multiplet) as well as b (broad). Infrared spectra were recorded on a FT-IR spectrometer. Melting points were determined using melting point apparatus and are uncorrected.

2. Characterization methods for $CuFe_2O_4$ NPs:

Powder X-ray diffraction pattern of the NPs were measured at Rigaku/Ultima-IV with Cu Kα X-ray source of λ= 1.54056 Å. The morphology of the synthesized NPs were obtained by scanning electron microscope (SEM) images using scanning electron microscope (model: JSM-6360 JEOL) with accelerating voltage 20 kV and magnification range 10,000X to 27,000X. Transmission electron microscope (TEM) and high resolution-TEM images were recorded with transmission electron microscope (Model: JEM-100 CX II) with accelerating voltage 20-100kV. The presence of elemental copper, iron and oxygen were further determined through energy dispersive spectroscopy (EDS). The magnetic measurements were done by Vibrating Sample Magnetometer (VSM)(Model:7410 series).X-ray photoelectron spectra (XPS) were recorded on an XPS-AES Module, Model: PHI 5000 Versa Prob II

3. Characterization of the products:

N-phenylacetamide: Silvery brown**,**^{1}H-NMR (400 MHz, *CDCl$_3$*): δ 7.80(brs, 1H),7.44 (d, 2H),7.23 (t, 2H), 7.03 (t, 1H), 2.07 (s, 3H); ^{13}C-NMR (100 MHz, *CDCl$_3$*): δ168.88, 137.97, 128.83, 124.30, 120.07, 24.48 ppm; m/z = 135.07.

4-Bromophenyl acetamide: Grey, ^{1}H-NMR (400 MHz, *CDCl$_3$*): δ 7.42 (m, 4H), 7.35 (br, 1H), 2.18 (s, 3H) ppm; ^{13}C NMR (100 MHz, *CDCl$_3$*): δ 168.36, 136.91, 131.95, 121.36, 116.86, 24.63 ppm; m/z = 212.98.

1-Napthyl acetamide: light pink,; ^{1}H NMR (400 MHz, *CDCl$_3$*): δ 8.03 (s, br, 1H), 7.89 (d, 2H), 7.73 (d, 2H), 7.48 (m, 3H), 2.33 (s, 3H) ppm; ^{13}C NMR (100 MHz, *CDCl$_3$*): δ 168.8, 134.4, 132.1, 128.6, 127.2,126.6, 125.8,122.1,121.8, 120.6, 24.2 ppm; m/z = 185.08

2-Napthyl acetamide: Grey, ^{1}H-NMR (400 MHz, *CDCl$_3$*): δ 8.18 (br, 1H), 7.7 (d, 1H), 7.6 (s, 1H), 7.4 (m, 5H), 2.02 (s, 3H) ppm; ^{13}C NMR (100 MHz, *CDCl$_3$*): δ 168.8, 135.97, 133.94, 127.83, 126.5, 121.4, 118.1, 108.4, 22.9 ppm. m/z = 185.22.

N,N-diphenylacetamide: black; ^{1}H-NMR (400 MHz, *CDCl$_3$*): δ 7.34-6.9 (m, 10H), 2.06 (s, 3H) ppm; ^{13}C NMR (100 MHz, *CDCl$_3$*): δ 170.57, 143.19, 129.76, 128.52, 120.90, 117.77, 23.89 ppm. m/z =211.27

N-acetyl-4-chloroaniline: Grey; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.05 (s, 1H), 7.38-7.21 (m, 4H), 2.10 (s, 3H) ppm; ^{13}C NMR(100MHz, $CDCl_3$): 168.9, 137.30, 128.52, 120.91, 22.01 ppm; m/z= 169.03.

N-acetyl-3-nitroaniline: White; ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.97 (s, 1H), 8.8 (d, 1H,), 8.73 (s, 1H), 8.66 (d, 1H), 7.55 (t, 1H), 2.27 (s, 3H) ppm; ^{13}C NMR (100MHz, $CDCl_3$): 168.98, 136.97, 135.83, 134.76, 125.94, 123.83, 122.30, 25.483 ppm; m/z=180.05.

N-acetyl-2-nitroaniline: White**; ^{1}**H NMR (400 MHz, $CDCl_3$): 9.6 (s, 1H), 8.57 (d, 1H), 8.42 (d, 1H), 8.23 (t, 1H), 7.9 (t, 1H), 2.07 (s, 3H) ppm; ^{13}C-NMR (100 MHz, *CDCl$_3$*): 168.71, 140.17, 135.9, 135.1, 125.6, 122.8, 121.2, 22.9 ppm; m/z=180.05.

2,4dinitrophenylacetamide: yellow; ^{1}H-NMR (400 MHz, *$CDCl_3$*): δ 9.12 (s, 1H), 8.4 (s, 1H), 8.24 (d, 1H), 7.5 (d, 1H), 2.03 (s, 3H) ppm; ^{13}C NMR (100 MHz, *$CDCl_3$*): δ 168.96, 144.3, 142.1,141.9, 127.9, 123.8, 118.9, 22.9 ppm; m/z = 124.05.

4-nitrophenyl acetate: White, ^{1}H-NMR (400 MHz, *$CDCl_3$*): δ 8.16 (d, 2H), 7.44 (d, 2H), 2.06(s, 3H) ppm; ^{13}C-NMR (100 MHz, *$CDCl_3$*): δ 169.68, 157.97, 145.43, 122.76, 121.53, 20.05 ppm; m/z = 181.06.

2-Nitrophenyl acetate: Brown; ^{1}H NMR (400 MHz, *$CDCl_3$*): δ 8.12 (d, 1H), 7.66 (t, 1H), 7.61 (t, 1H), 7.4 (d, 1H), 2.38(s, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): 168.71, 144.13, 137.57, 126.66, 120.24, 119.97, 20.83 ppm; m/z= 195.17.

3-acetamidophenyl acetate: white, ^{1}H-NMR (400 MHz, *$CDCl_3$*): δ7.47 (s, 1H), 7.30-7.26 (m, 2H), 6.85 (d, 1H), 2.3 (s, 3H), 2.17 (s, 3H) ppm: ^{13}C-NMR (100 MHz, *$CDCl_3$*): δ 154.5, 130.2, 127.3, 124.9, 121.3, 115.7, 14.9 ppm. m/z = 108.058.

2-acetamidobenzyl acetate: Creamy, ^{1}H NMR (400 MHz, *$CDCl_3$*): δ 8.8 (s, 1H), 7.99 (d, 1H), 7.4 (d, 1H), 7.3 (m, 1H), 7.14(m, 1H), 5.1(s, 2H), 2.2 (s, 3H), 2.1 (s, 3H) ppm; ^{13}C-NMR (100 MHz, *$CDCl_3$*): 136.66, 131.76, 125.87, 123.72, 24.39, 20.99 ppm; m/z = 207.23.

Octyl Acetate: White, ^{1}H NMR (400 MHz, *$CDCl_3$*): δ 4.054 (t, 2H), 2.053 (s, 3H), 1.61 (m, 3H), 1.25 (m, 2H), 0.884 (t, 3H); ^{13}C NMR (100 MHz, *$CDCl_3$*): δ 170.08, 65,083, 31.94, 28.97, 25.94, 22.83, 20.30, 14.07 ppm; m/z = 172.15

Cyclohexyl acetate: white; ^{1}H NMR (400 MHz, *$CDCl_3$*): δ 4.07 (m, 1H), 2.01(s, 3H), 1.89-1.28(m, 10H) ppm; ^{13}C-NMR (100 MHz, *$CDCl_3$*): 170.31, 75.25, 33.25, 28.03, 21.02 ppm; m/z = 142.10.

4-Methoxybenzyl acetate: oily yellow; ^{1}H-NMR (400 MHz, *CDCl3*): δ 7.69 (d, 1H), 7.35 (d, 1H), 7.18(d, 1H), 6.83(d, 2H), 4.98 (s, 2H), 3.70(s, 3H), 1.98 (s, 3H) ppm; ^{13}C-NMR (100 MHz, $CDCl_3$): δ 171.05, 159.62, 130.16, 128.01, 113.93, 55.29, 21.11ppm; m/z = 180.08

4-Chloro benzylacetate: White; ^{1}H NMR (400 MHz, *$CDCl_3$*): δ 7.26 (s, 4H), 5.06 (s, 2H), 2.10 (s, 3H) ppm; ^{13}CNMR (100 MHz, $CDCl_3$): 170.61, 139.82, 133.3, 129.06, 128.76, 68.49, 20.19 ppm; m/z= 170.01.

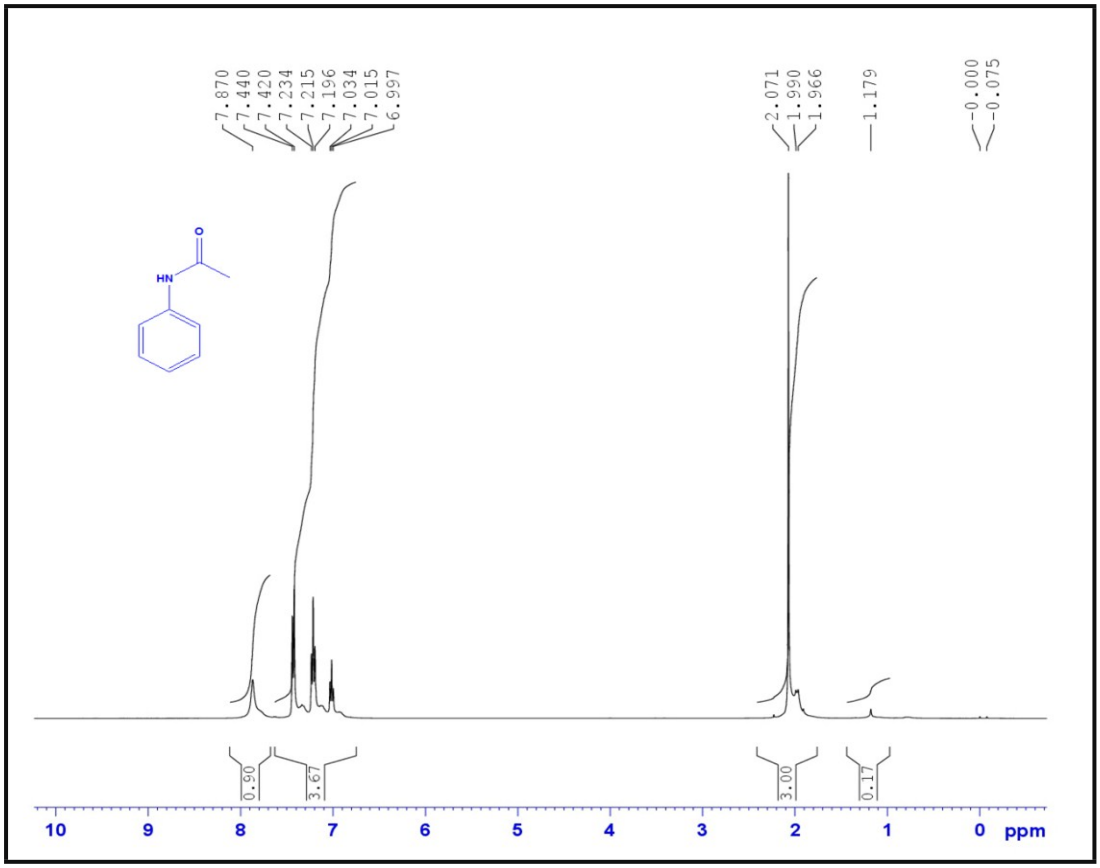
Cinnamyl acetate: White; ^{1}H NMR (400 MHz, *$CDCl_3$*): δ 7.40 (d, 2H), 7.33-7.31 (t, 2H), 7.27-7.25 (t, 1H), 6.66 (d, 1H), 6.31-6.24 (m, 1H), 4.73 (d, 2H), 2.09 (s, 3H) ppm; ^{13}C NMR(100MHz, $CDCl_3$): 170.88, 136.18, 134.21, 131.01, 128.61, 127.67, 123.14, , 65.1, 21.02 ppm; m/z= 176.21.

4-Nitro benzylacetate: White; ^{1}H NMR (400 MHz, *$CDCl_3$*): δ 8.23 (d, 2H), 7.53(d, 2H), 5.20(s, 2H), 2.16(s, 3H) ppm; ^{13}C NMR(100MHz, $CDCl_3$): 170.51, 148.16,147.53, 128.26, 126.63, 123.91, 64.9, 20.73 ppm; m/z= 195.17.

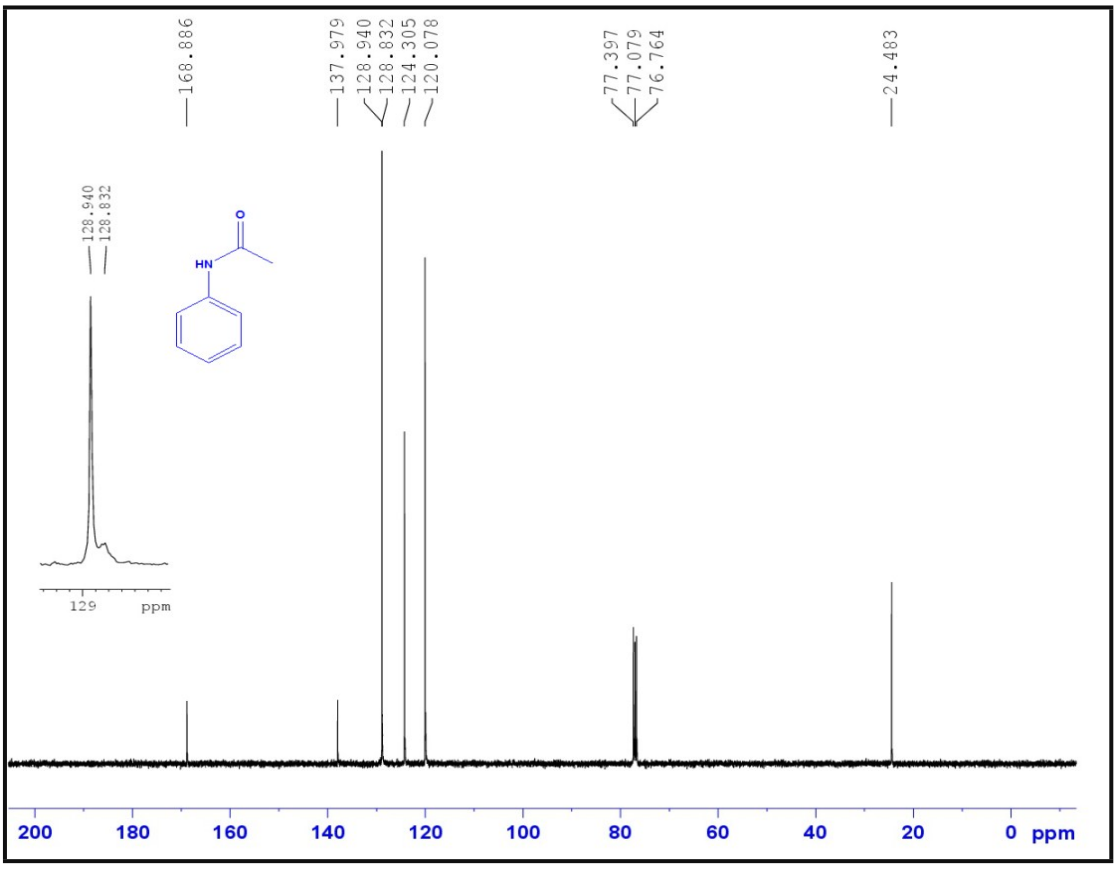
S-2 Acetamidophenylethanethioate: Black; ^{1}H NMR (400 MHz, *$CDCl_3$*): δ 8.08 (s, 1H), 7.77(m, 2H), 7.12 (d, 1H), 6.68 (d, 1H), 2.46 (s, 3H), 2.05 (s, 3H) ppm; ^{13}C NMR(100MHz, $CDCl_3$): 197.23, 172.43, 144.24, 133.82, 130.68, 130.21, 129.34, 128.49, 30.37, 26.33 ppm; m/z= 209.05.

NMR Spectra of Some Compounds:

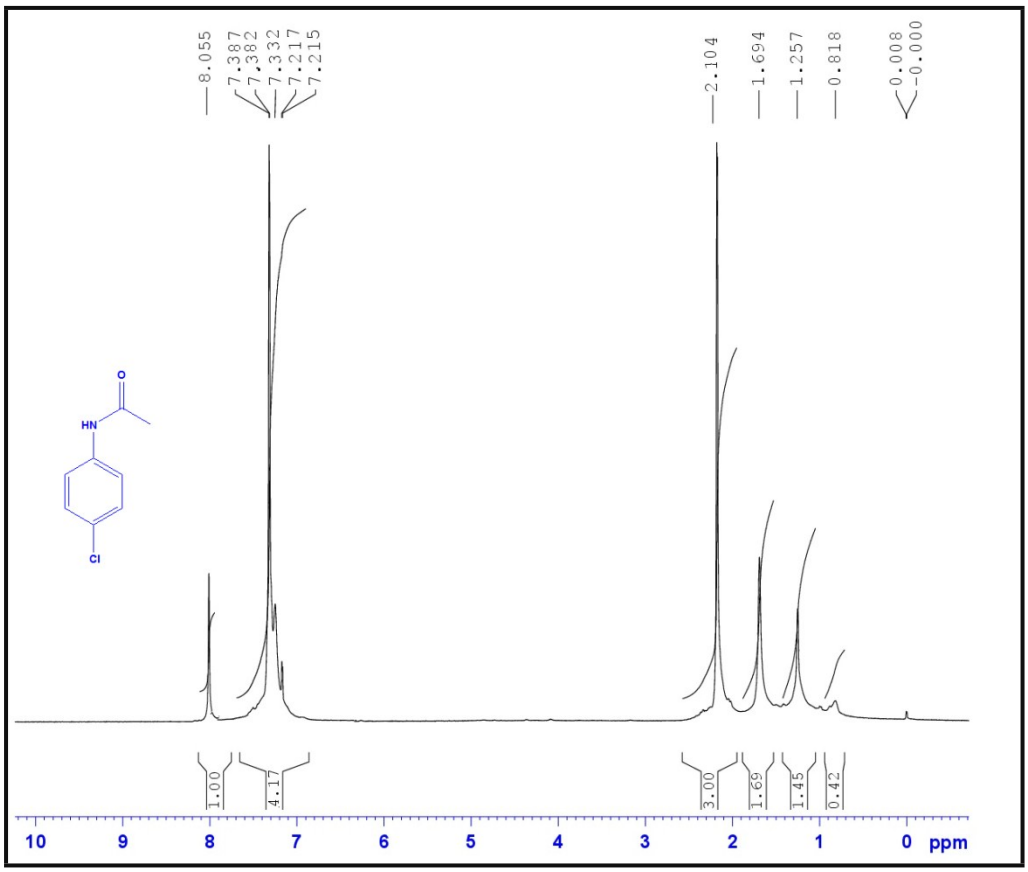
^{1}H NMR Spectra of N-phenylacetamide:



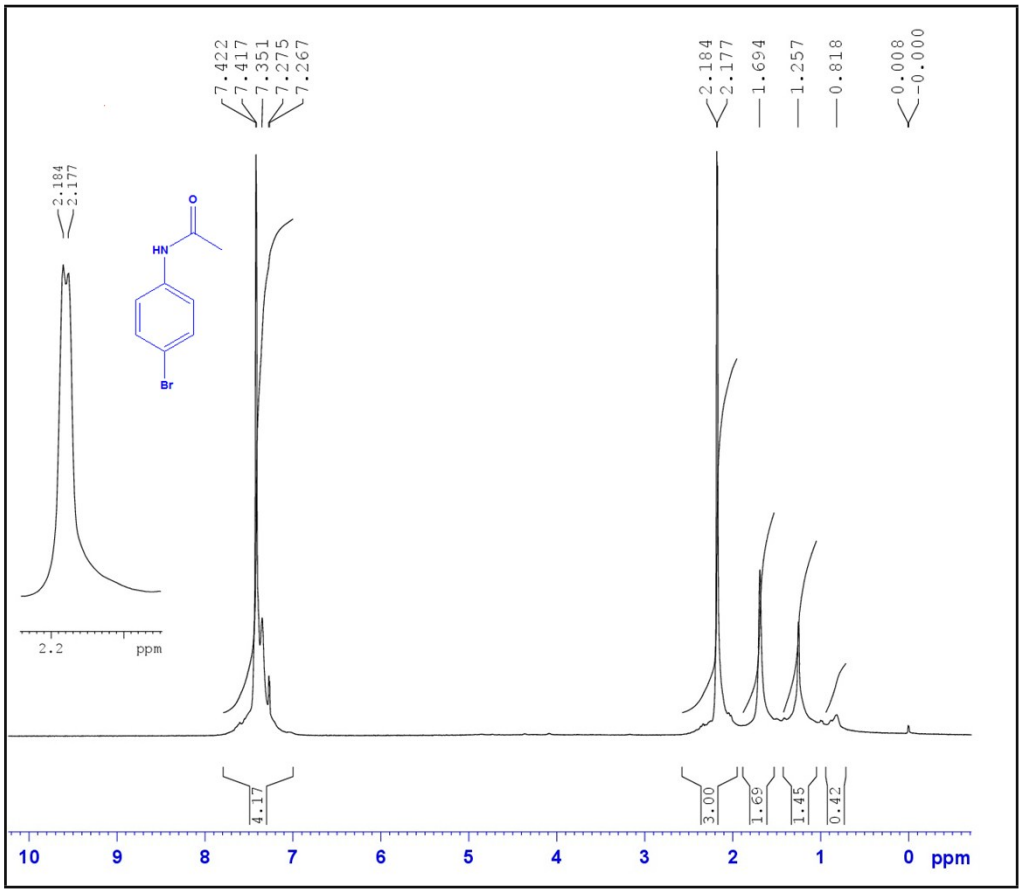
^{13}C of N-phenylacetamide:



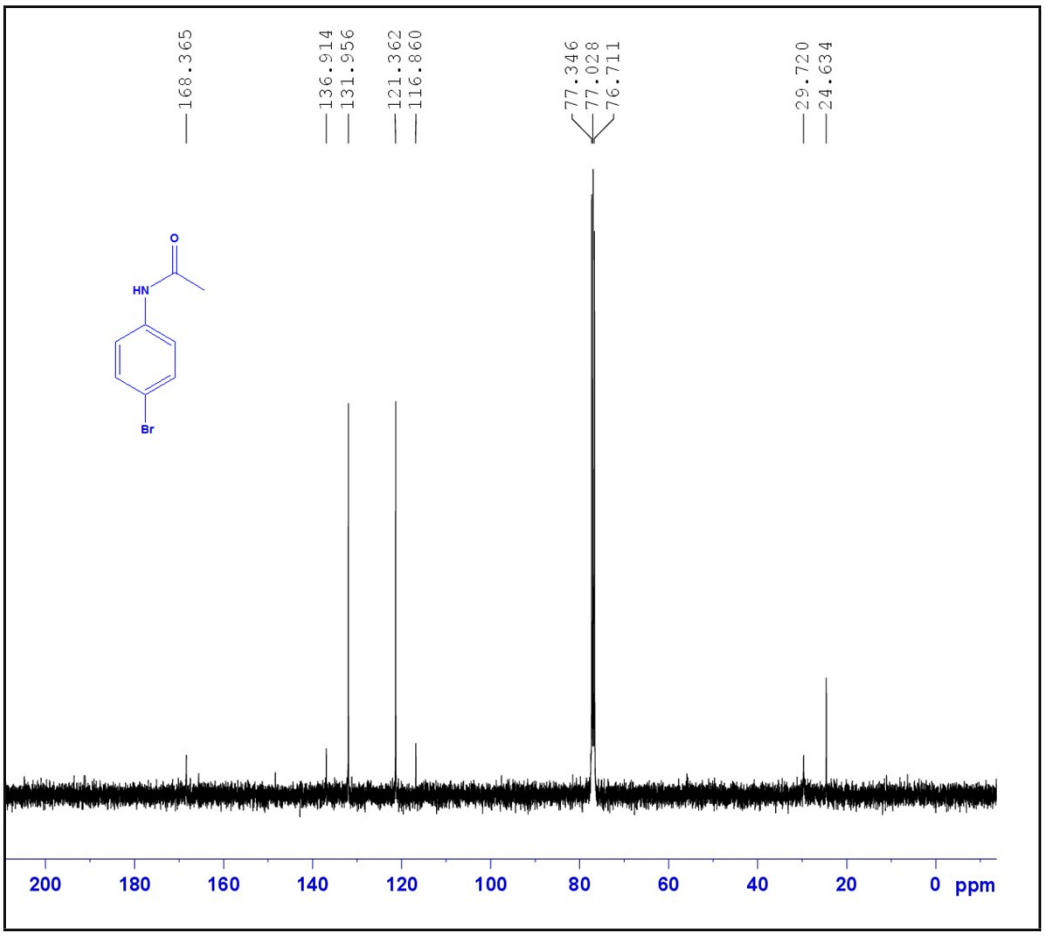
[1]H NMR of N-acetyl-4-chloroaniline



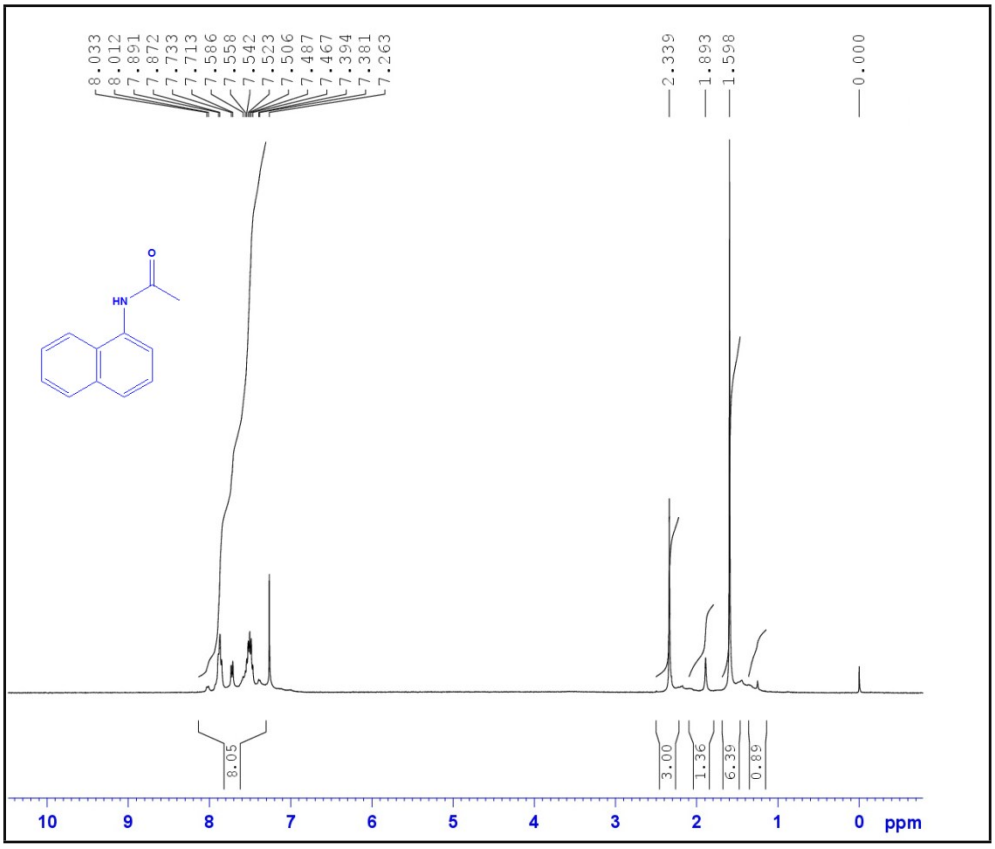
[1]H NMR of 4-Bromophenyl acetamide:



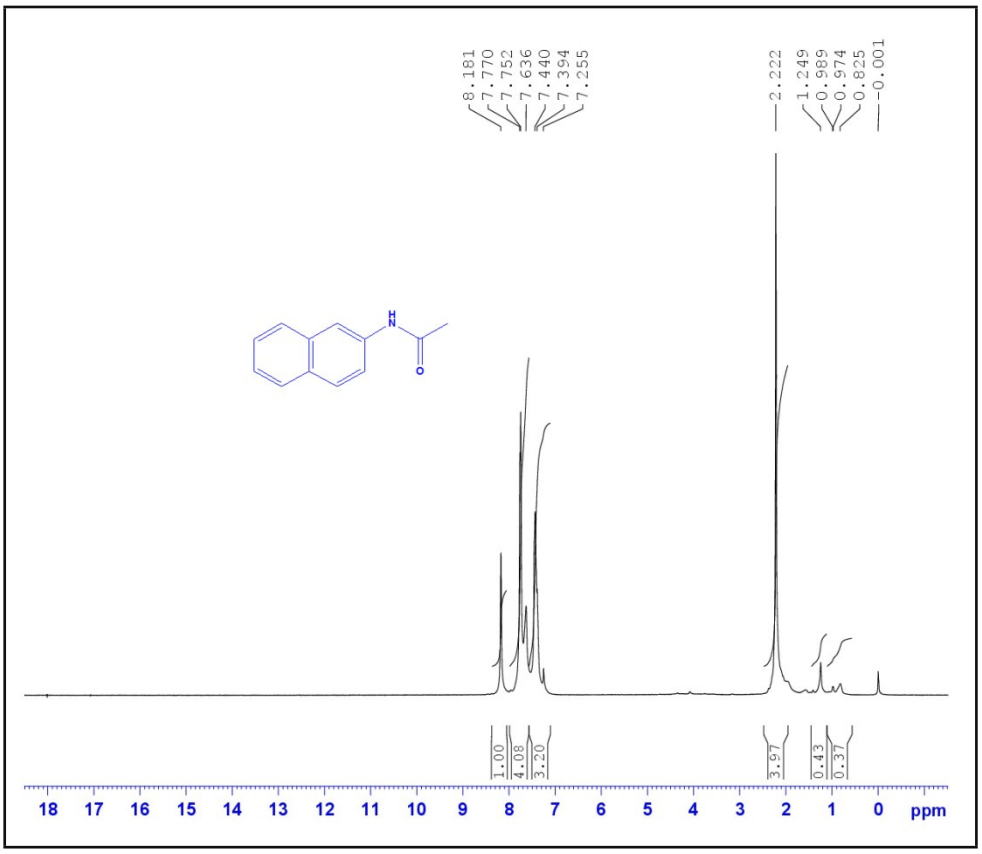
^{13}C NMR of 4-Bromophenyl acetamide:



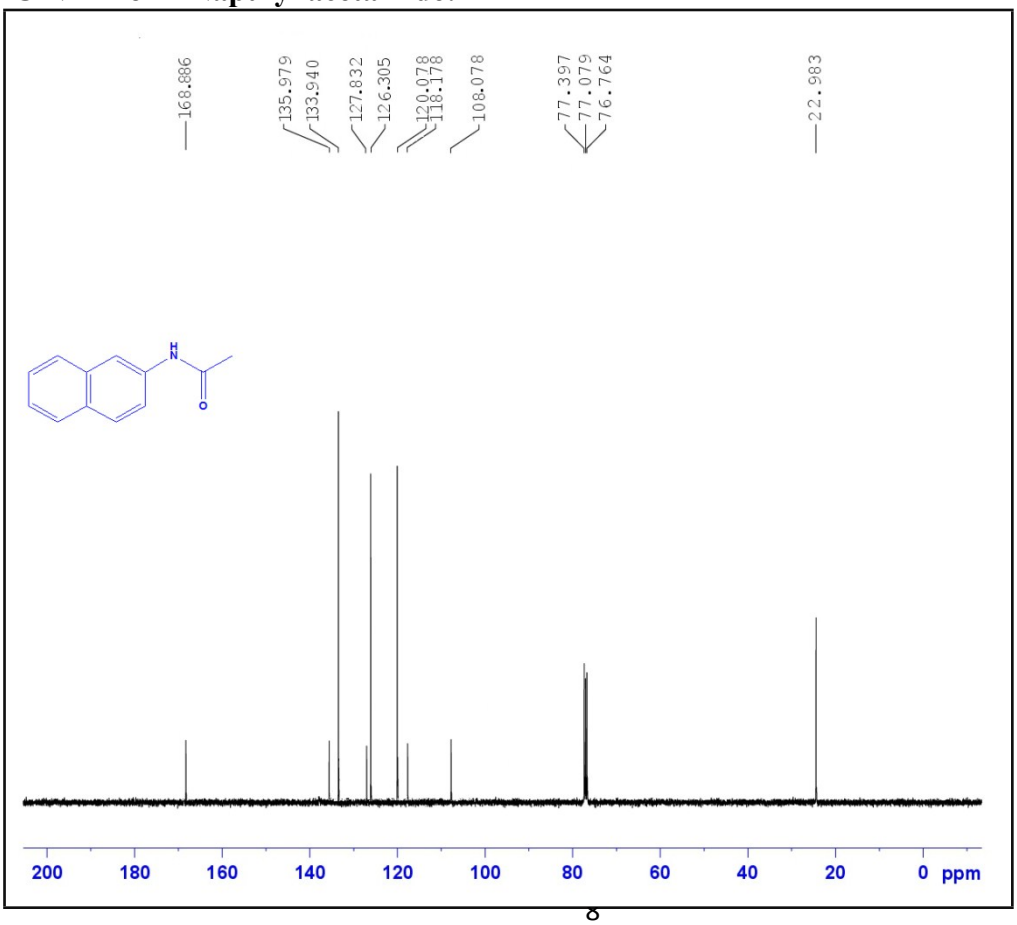
^{1}H NMR of 1-Napthyl acetamide:



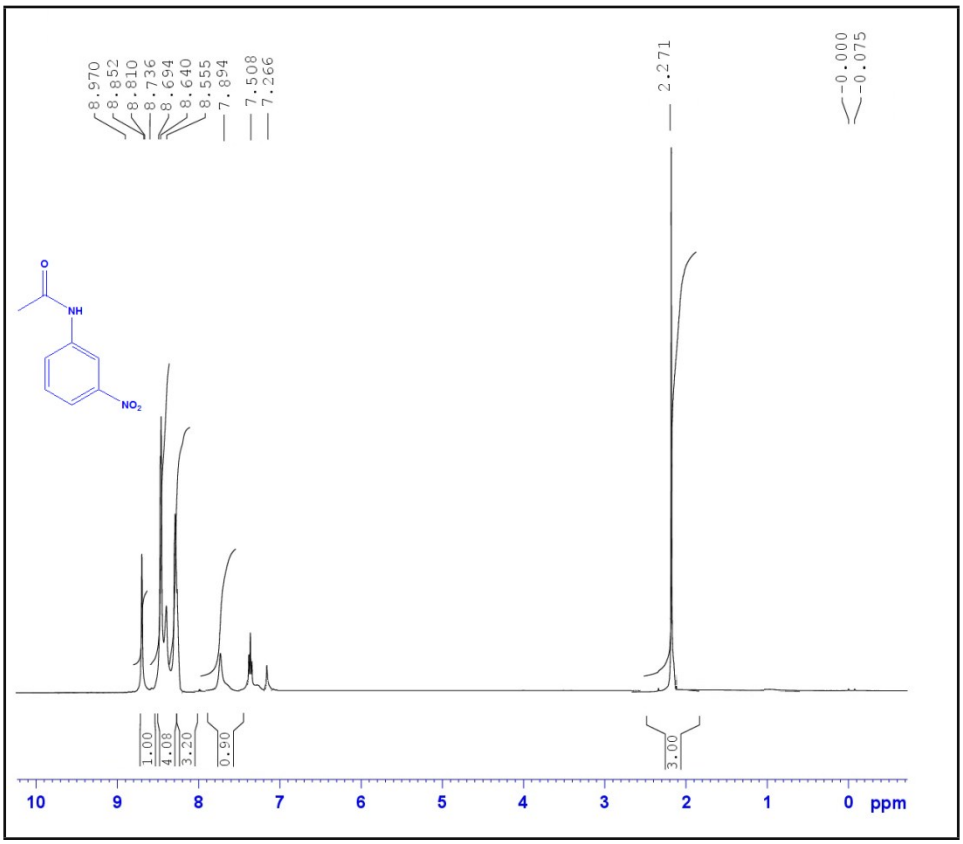
^{1}H NMR of 2-Napthyl acetamide:



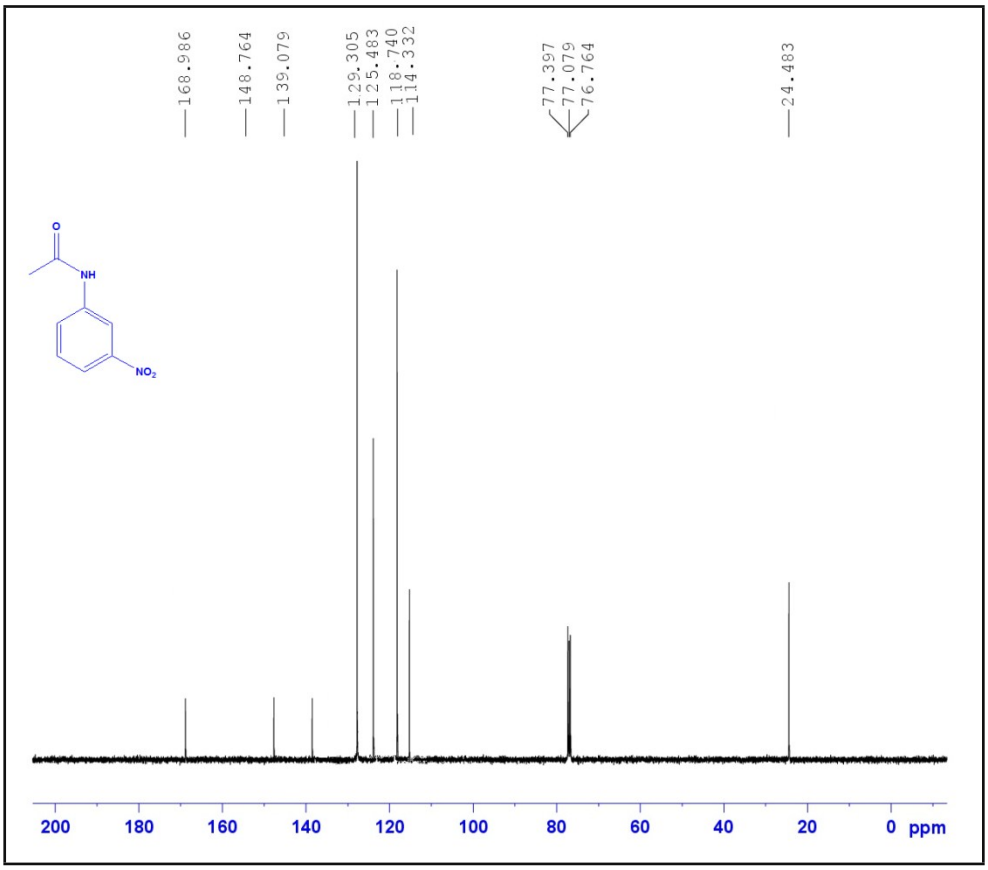
^{13}C NMR of 2-Napthyl acetamide:



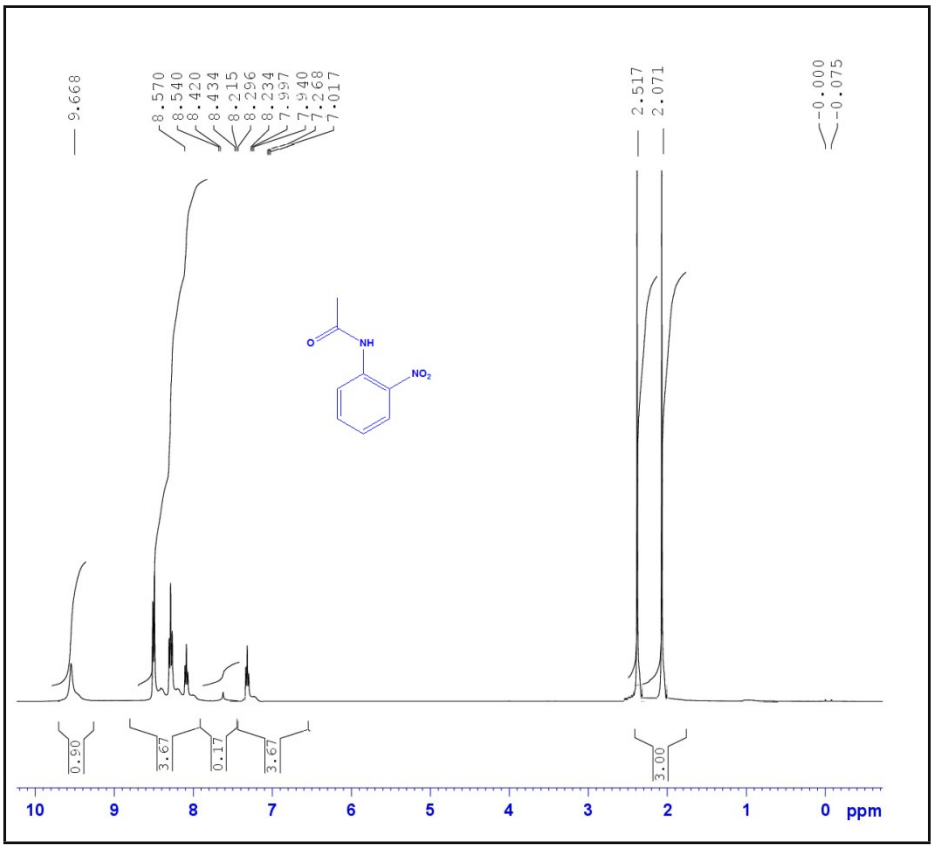
^{1}H NMR of N-acetyl-3-nitroaniline:



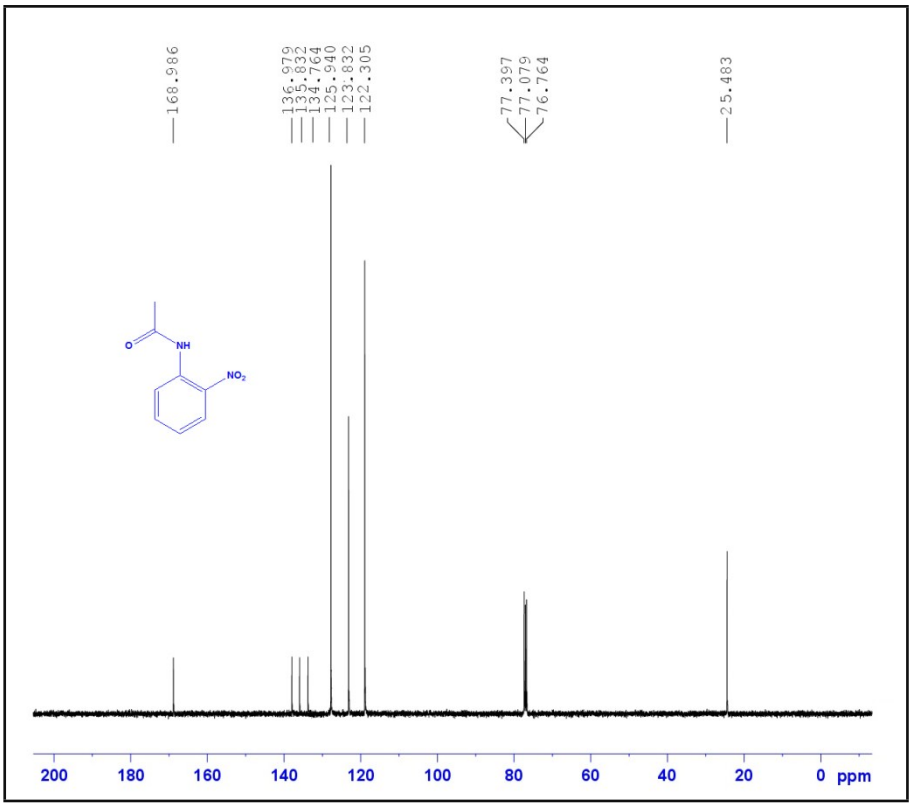
^{13}C NMR of N-acetyl-3-nitroaniline:



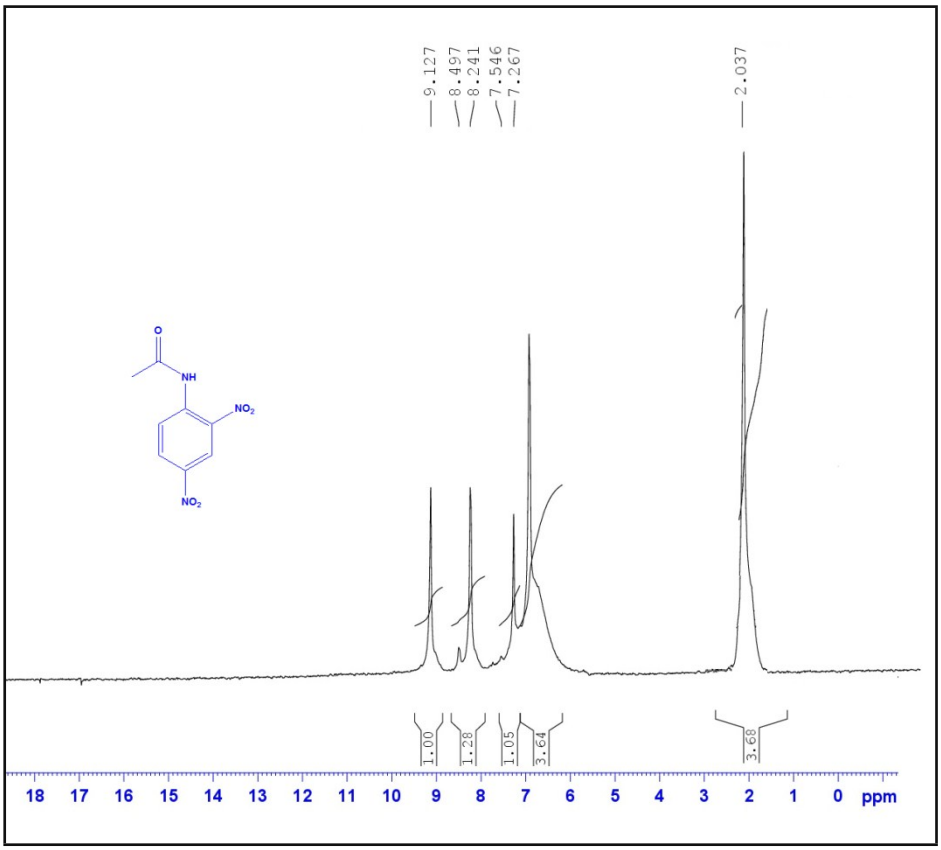
^{1}H NMR of N-acetyl-2-nitroaniline:



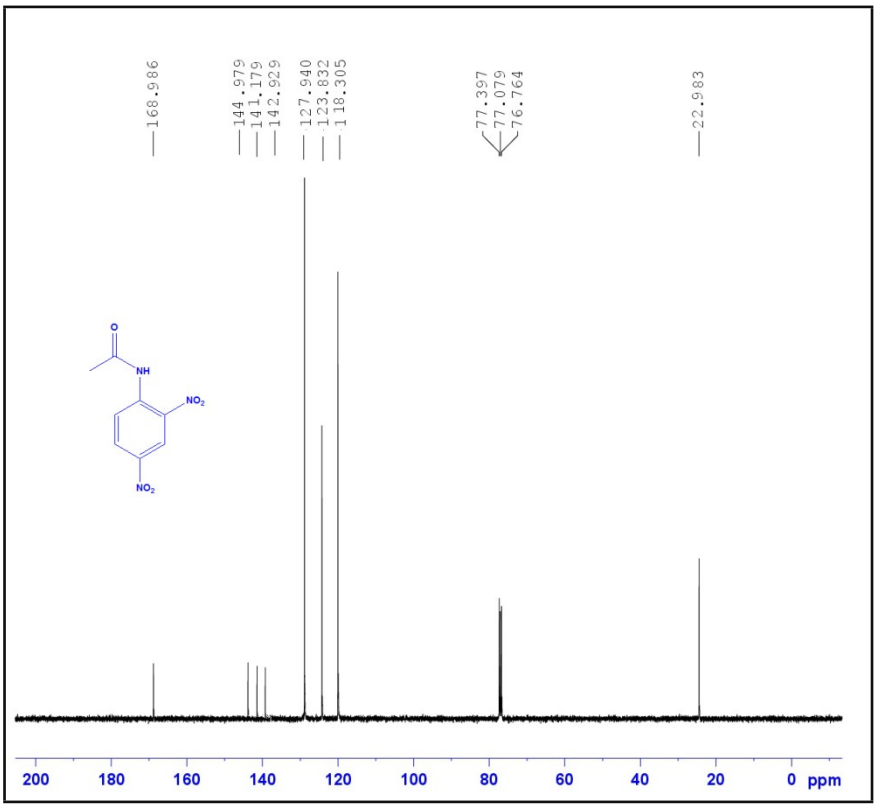
^{13}C NMR of N-acetyl-2-nitroaniline:



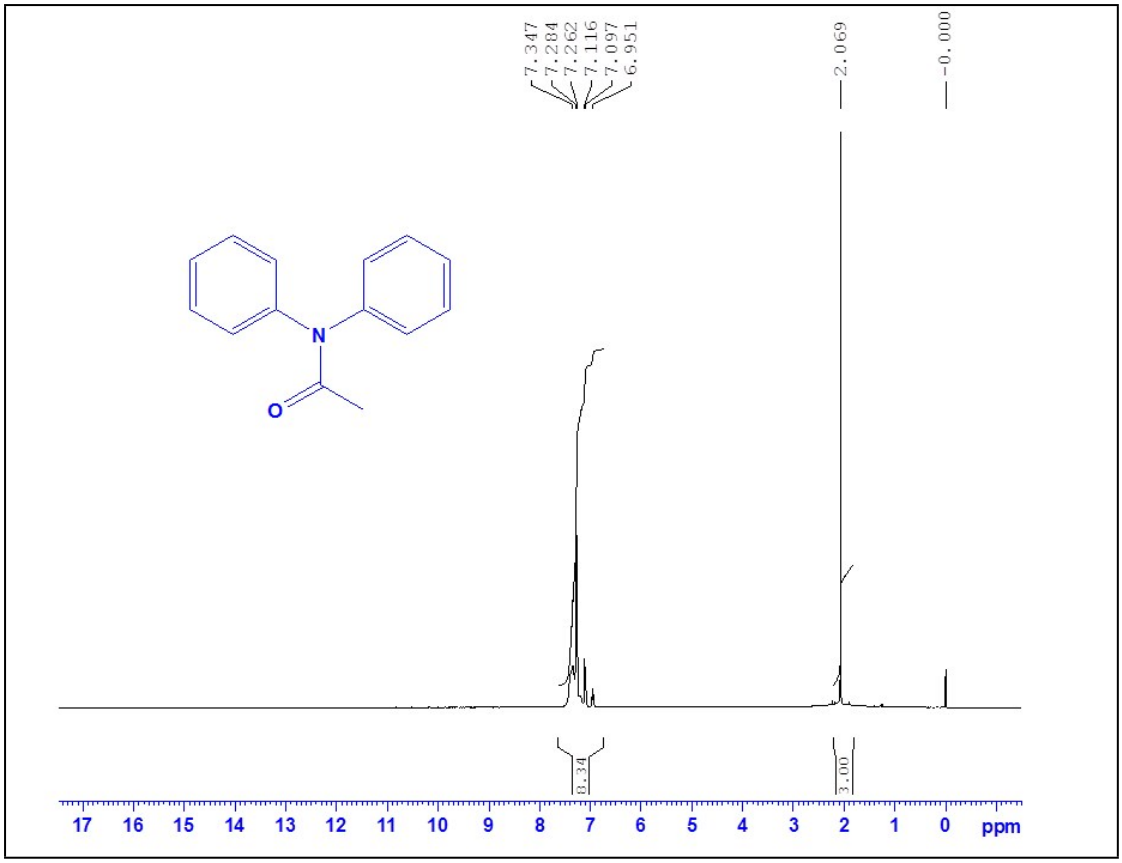
^{1}H NMR of 2,4dinitrophenylacetamide:



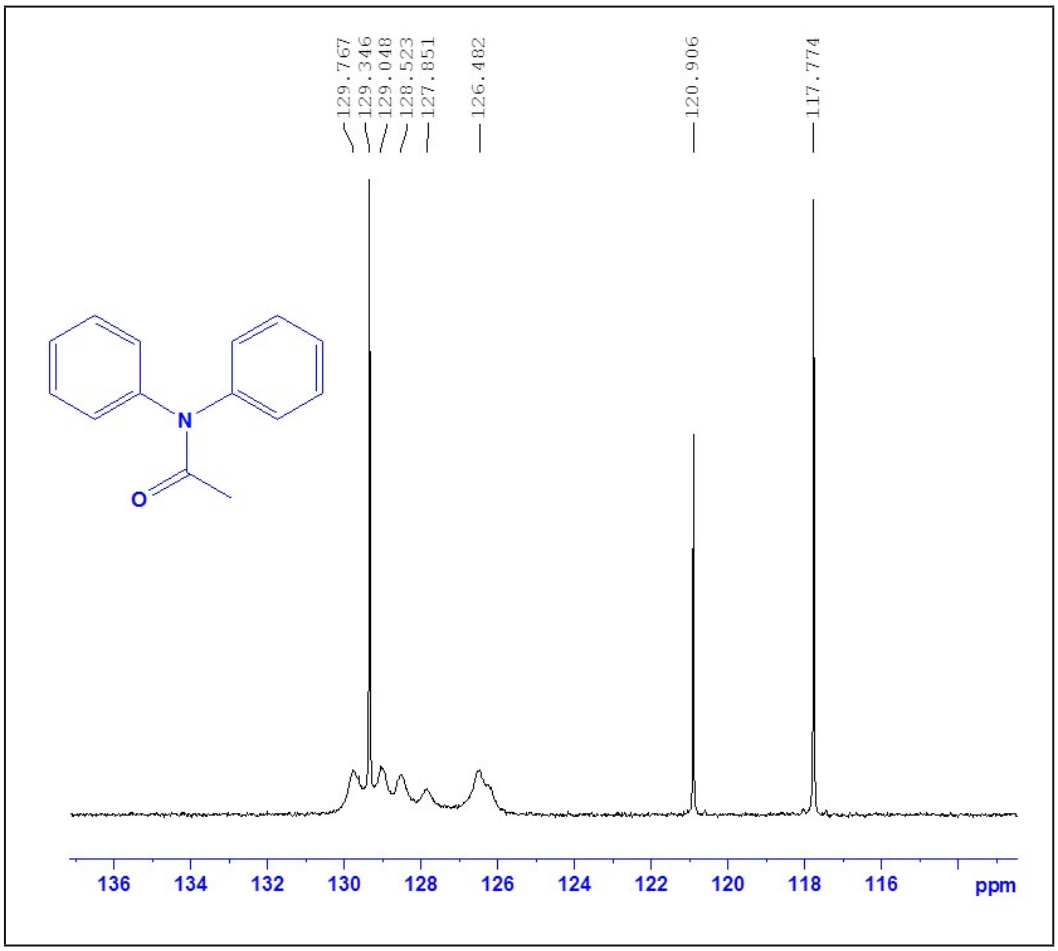
^{13}C NMR of 2,4dinitrophenylacetamide:



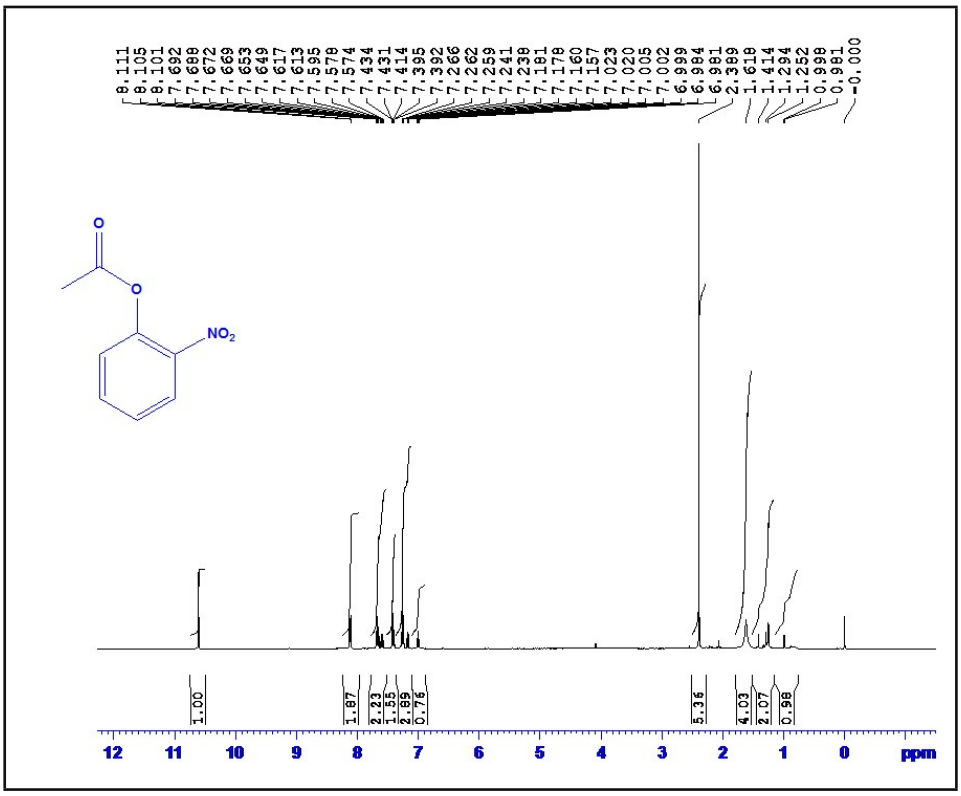
^{1}H NMR ofN,N-diphenylacetamide:



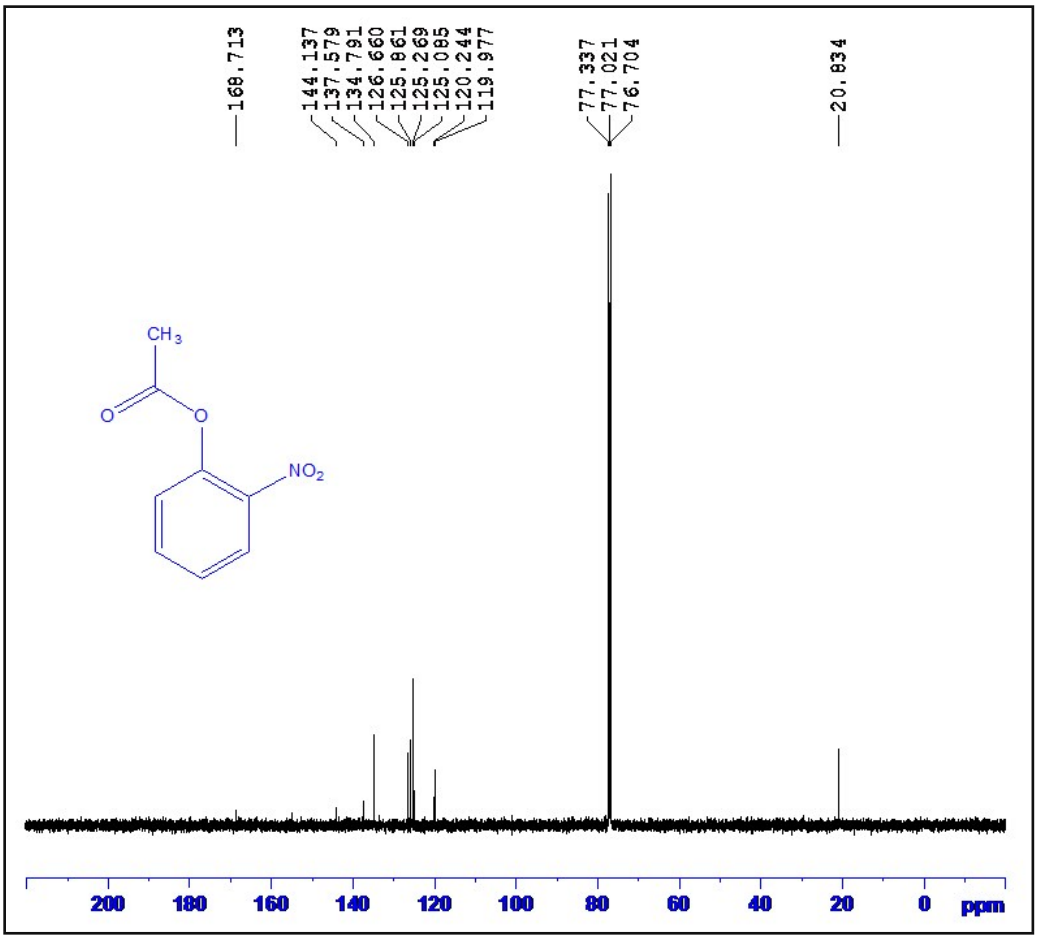
^{13}C NMR of N,N-diphenylacetamide:



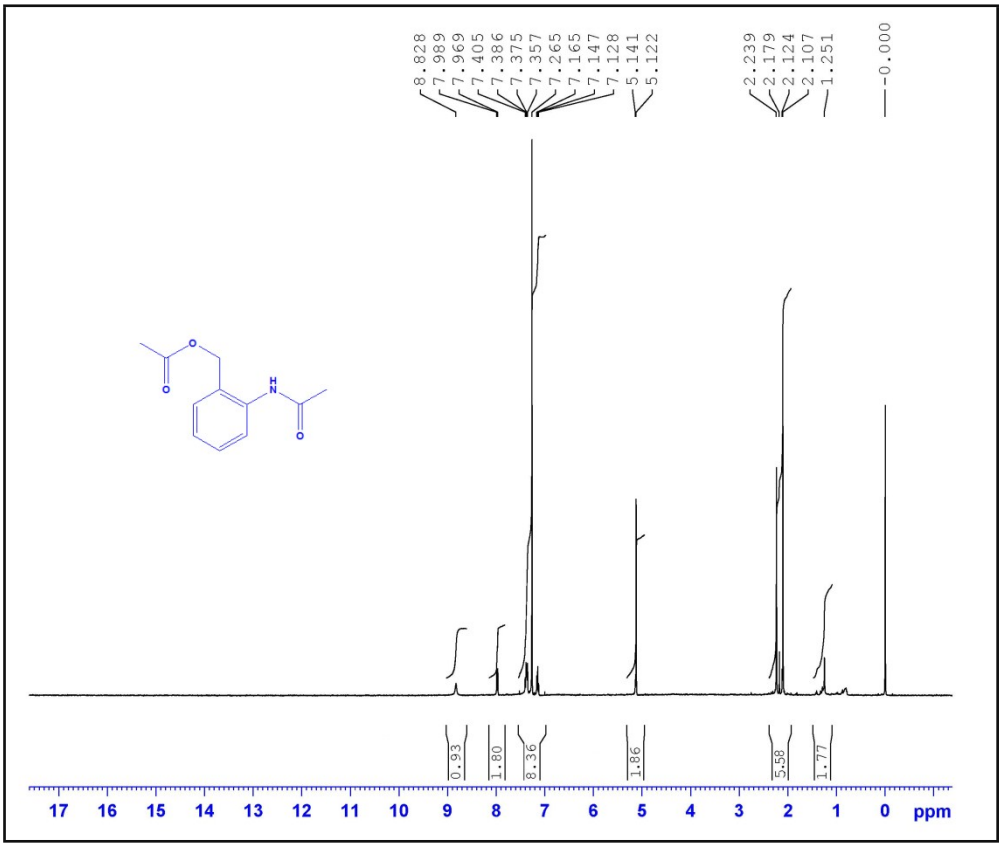
[1]H NMR of 2-Nitrophenyl acetate



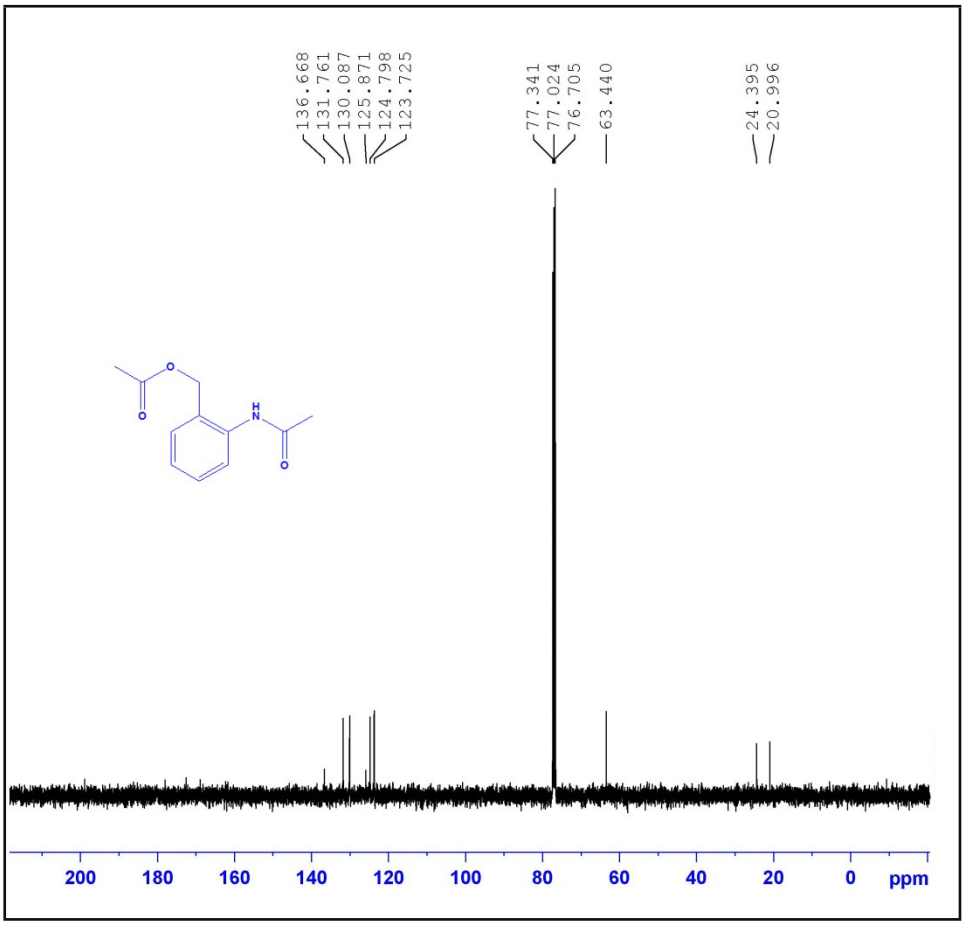
[13]NMR of 2-Nitrophenyl acetate



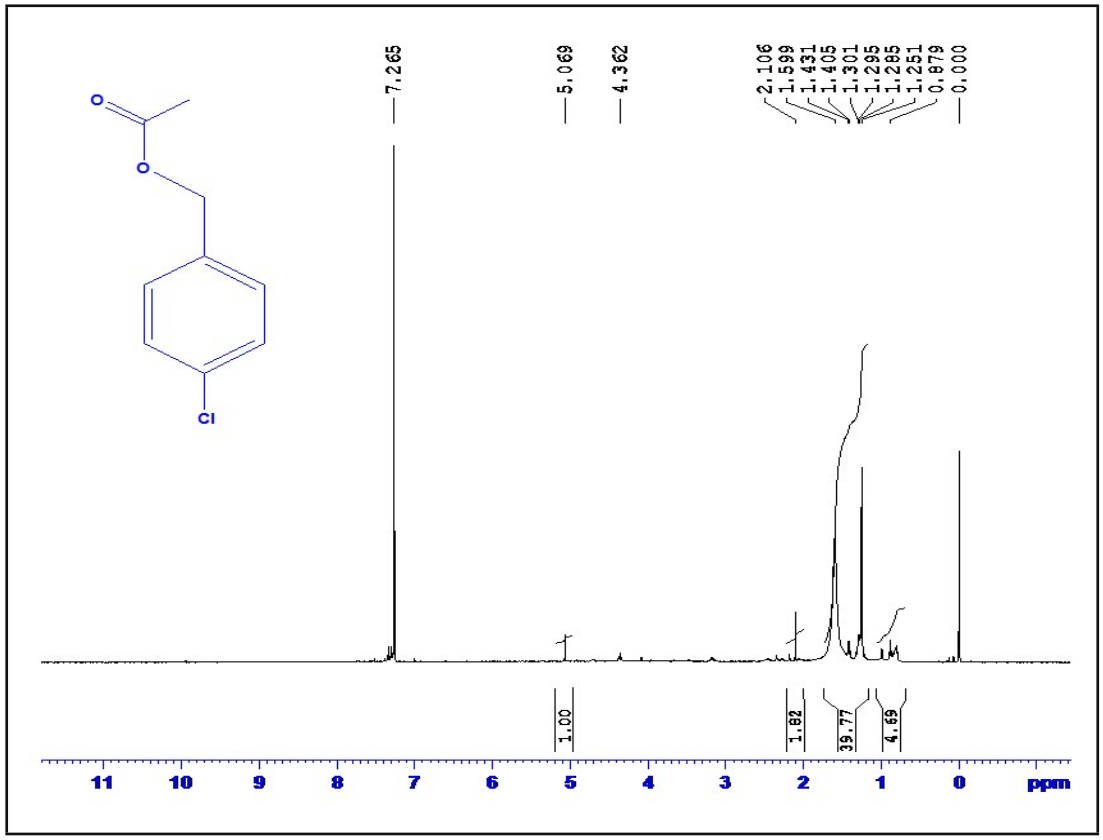
^{1}H NMR of **2-acetamidobenzyl acetate:**



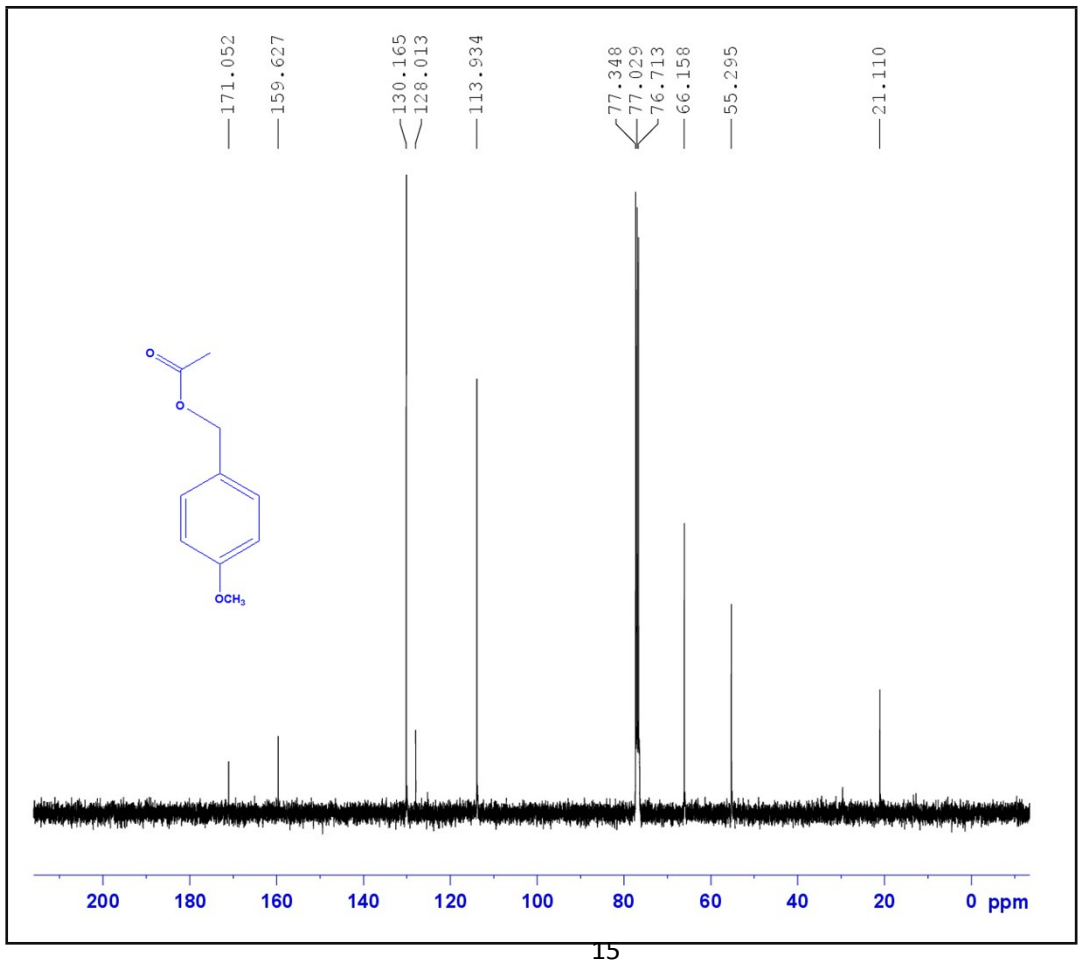
^{13}C NMR of 2-acetamidobenzyl acetate:



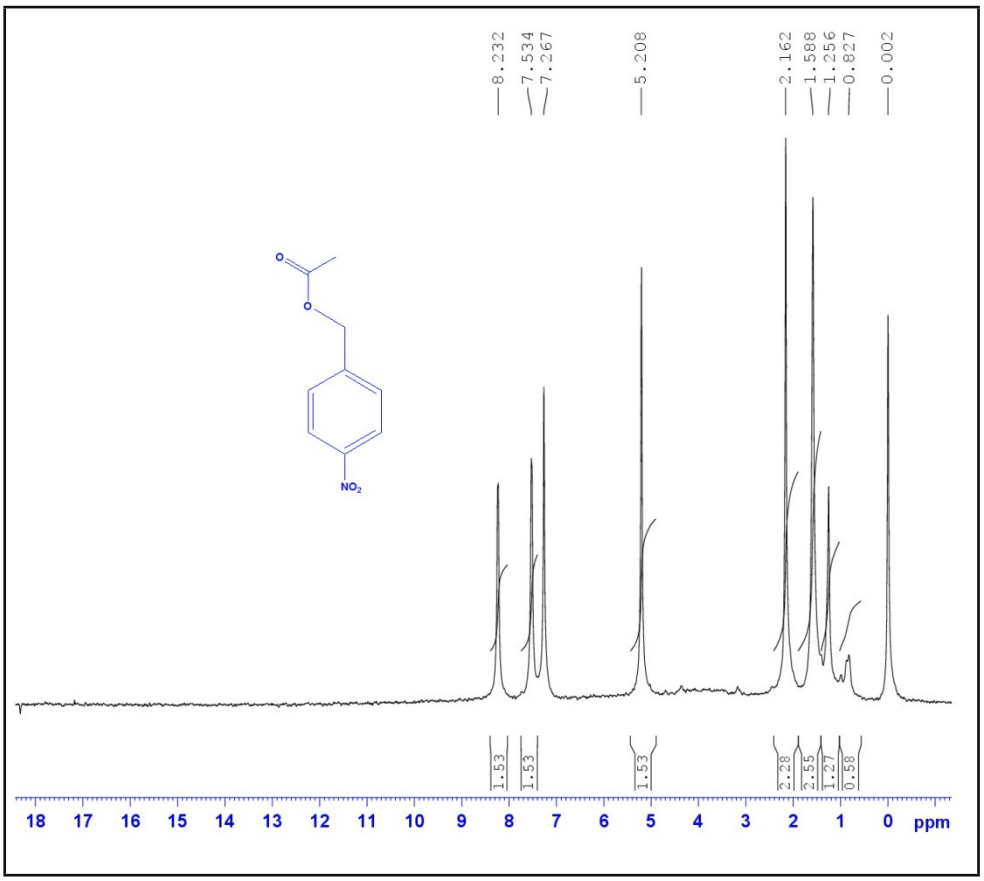
^{1}H NMR of 4-Chloro benzylacetate:



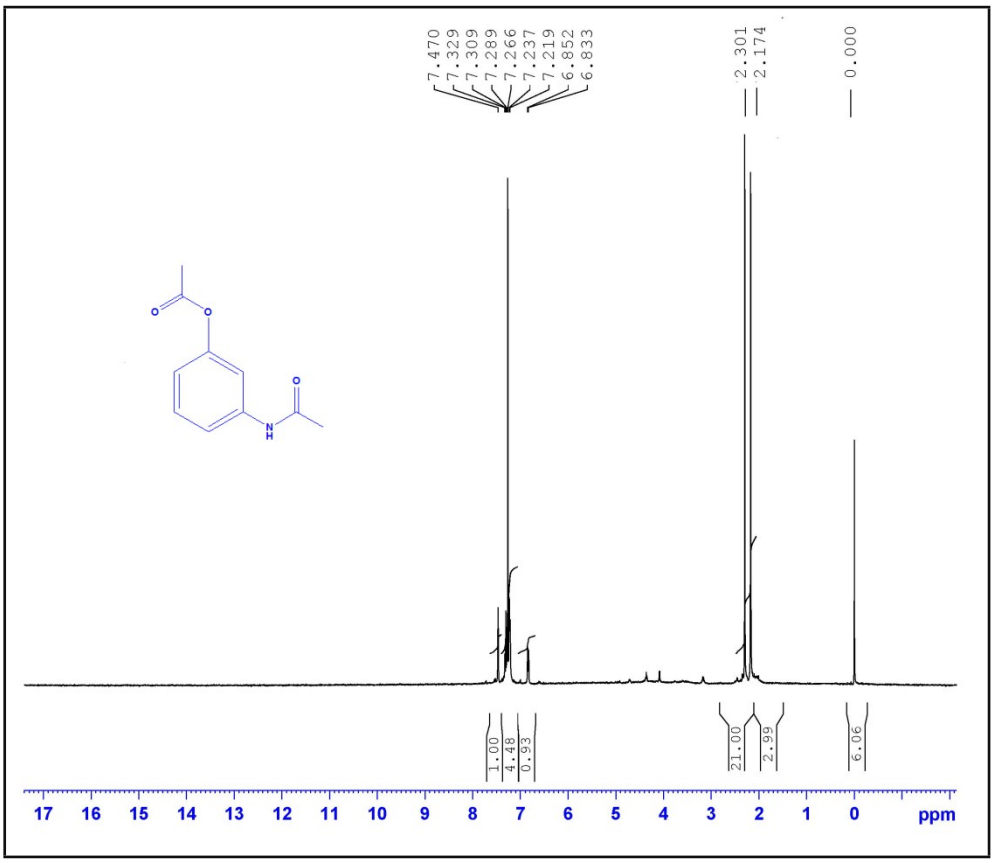
^{13}C NMR of 4-Methoxybenzyl acetate:



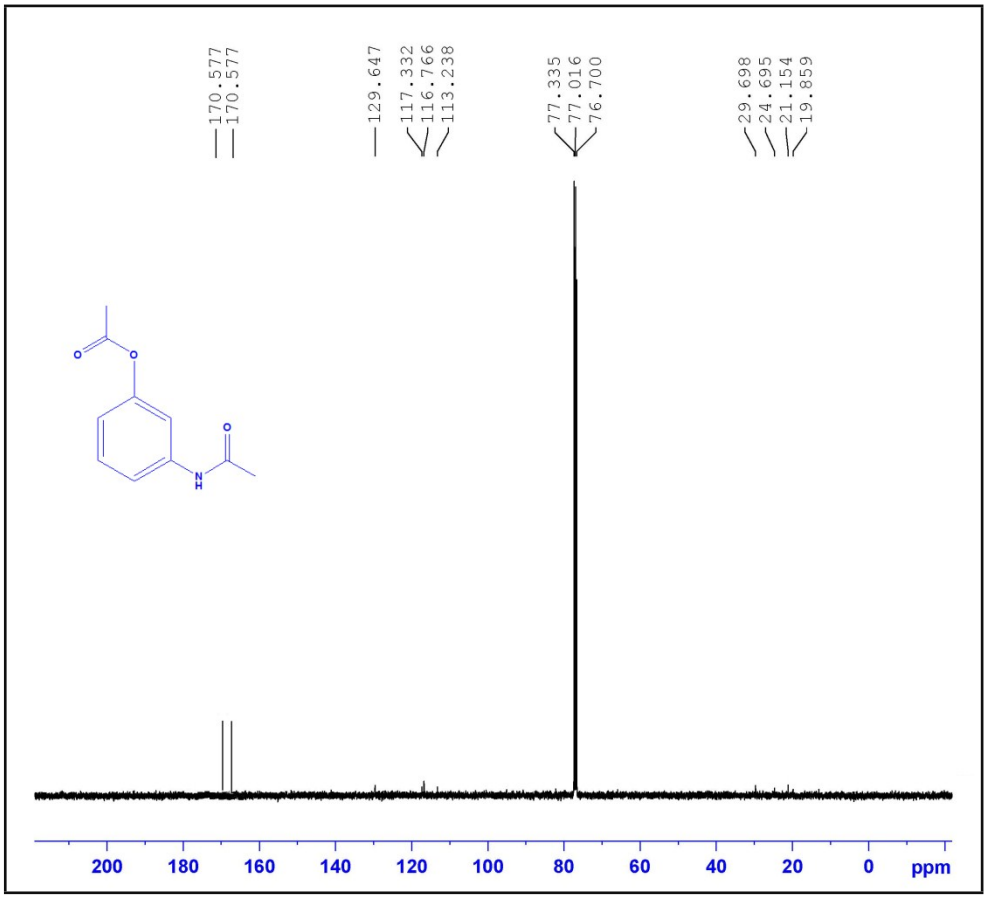
^{1}H NMR of 4-Nitro benzylacetate:



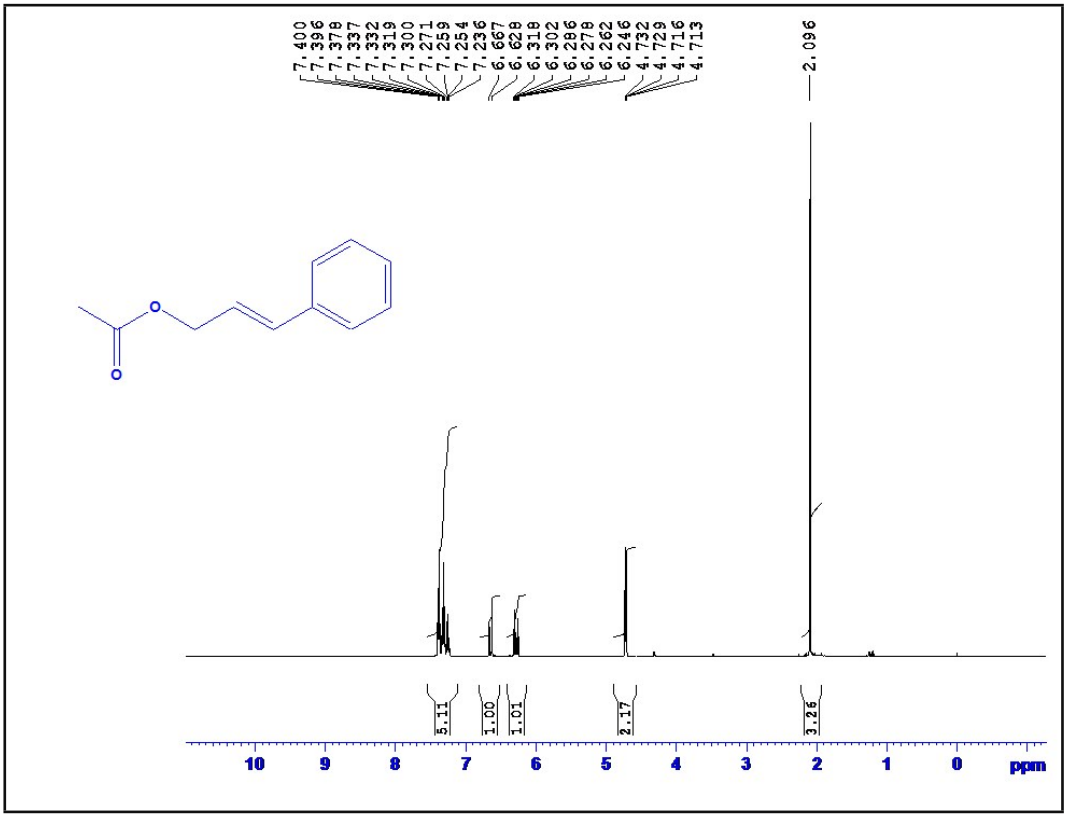
^{1}H NMR of 3-acetamidophenyl acetate:



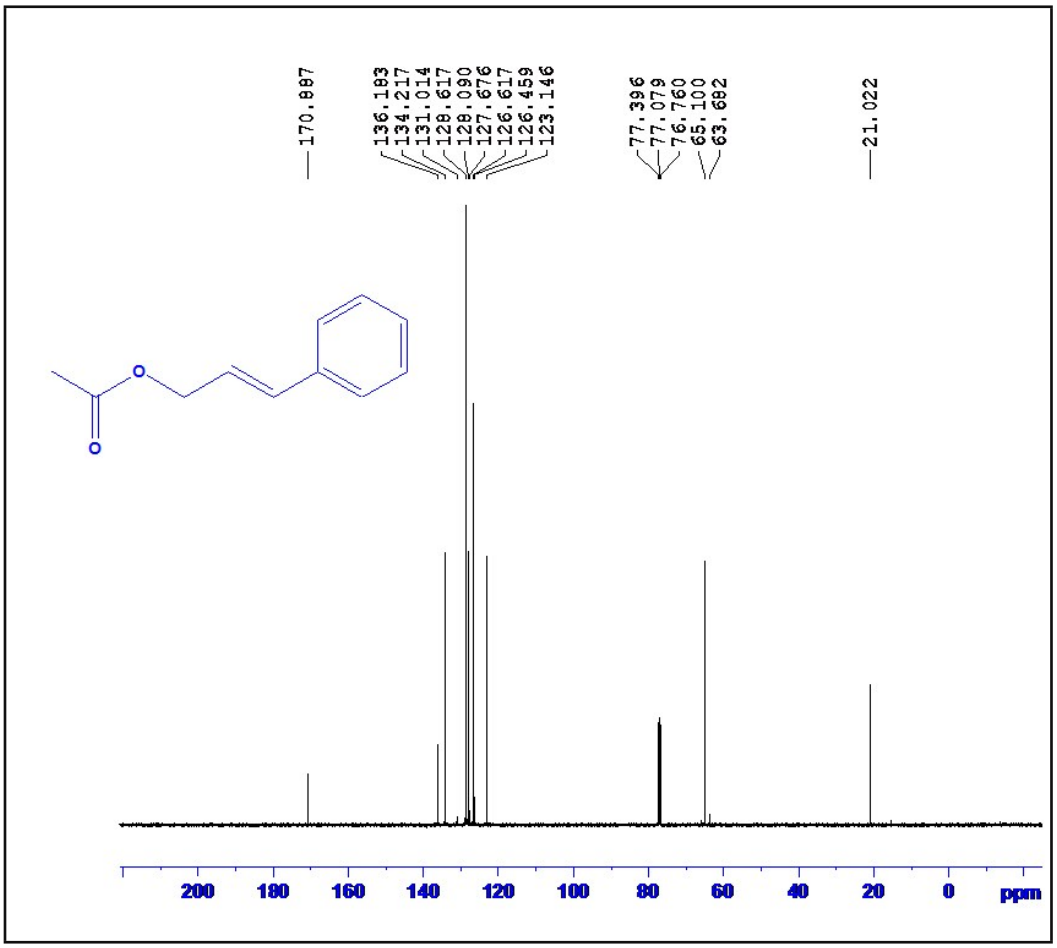
^{13}C NMR of **3-acetamidophenyl acetate:**



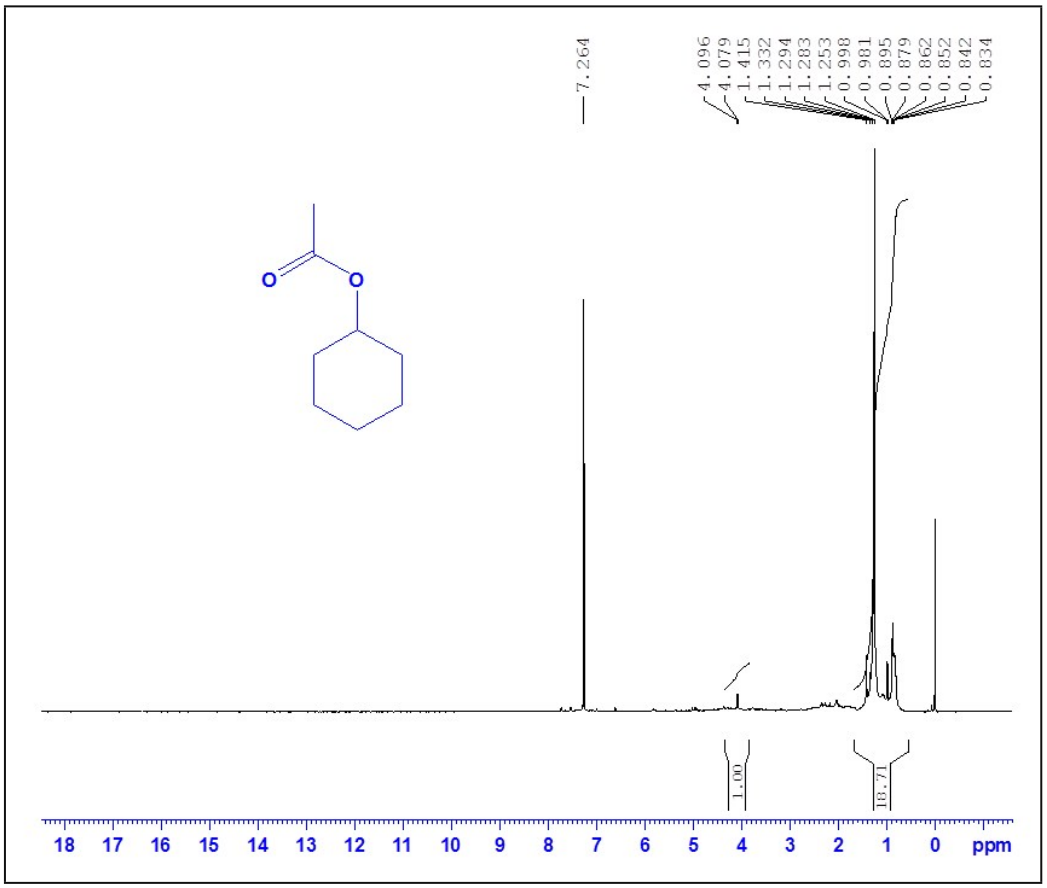
^{1}H NMR of Cinnamyl acetate:



^{13}C NMR of Cinnamyl acetate:



^{1}H NMR of Cyclohexyl acetate:



^{1}H NMR of Octyl Acetate: