Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information

Nano rod shaped and reusable basic Al_2O_3 catalyst for *N*-formylation of amines under solvent free condition: A novel, practical and convenient 'NOSE' approach

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(1) General Experimental Methods:

Rod shaped nano-Al_2O_3 (The average particle diameter 8.12 nm and average length 25.5 nm, S_{BET} =185.63 m^2g^{-1} and ρ =3.98 g cm^{-3}, purity, 99.99%) were purchased from Sigma Aldrich and used as received. The chemicals and reagents were purchased from Sigma-Aldrich, Merck, M/S S. D. Fine Chemicals Pvt. Ltd. and Loba chemical, and used without further purification. Transmission electron microscopy was performed by (TEM) [CM12, PHILIPS] with energy dispersive spectroscopy (EDS) [OXFORD] and sample preparation facility. The surface morphology and EDX were studied using JEOL scanning electron microscope (model JSM-6390LV SEM). The XRD pattern was recorded with Rigaku X-ray diffractometer. Melting points were determined in a Büchi 504 apparatus. IR spectra were recorded as KBr pallets in a Nicolet (Impact 410) FT-IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in a 400 MHz NMR spectrophotometer (JEOL, JNM ECS) using tetramethylsilane (TMS) as the internal standard and coupling constants are expressed in Hertz. Elemental analyses were carried out in a Perkin–Elmer CHN analyser (2400 series II). Mass spectra were recorded with a Waters Q-TOF Premier and Aquity UPLC spectrometer. Visualization was accomplished with UV lamp or I_2 stain. Reactions were monitored by thin-layer chromatography using aluminium sheets with silica gel 60 F_{254} (Merck).

(2) Characterization of the catalyst:

The SEM image of pure nano-Al_2O_3 is shown in figure 1 (manuscript). Small agglomerated particles of almost ordered surface morphology are observed in the SEM picture of the nano-alumina sample. EDX analyses were performed to determine the elemental constituents of pure nano- Al_2O_3 (figure 2, manuscript). It showed that the weight% of O and Al was found to

be 70.41 and 29.59 and atomic% was 80.05 and 19.95 respectively. Thus, the EDX suggests the presence of only O and Al in the nano-alumina sample.

The BET surface area of nano-Al_2O_3 was found to be 185.6 m^2g^{-1}, whereas the total pore volume was 0.9777 mLg^{-1}.

The X-ray diffractograms were obtained (XRD, MINI FLEX RIGAKU MODEL) with Cu K-α radiation (1.5418 Å) with scanning rate of 2^o per min from 2^o to 80^o. The X-ray diffraction spectrum (XRD) of Al_2O_3 is shown in figure 3 (manuscript). The diffraction peaks displayed almost all the characteristic diffraction of γ-alumina[1]. It was found that the Al_2O_3 nanoparticles show good crystallinity. The crystallite size of Al_2O_3 was determined by the use of Scherrer equation (i) by choosing the two highest peaks from XRD pattern. The crystallite sizes were found between 39.7 and 37.4 nm, calculated from the X-ray line broadening by applying full width half maximum (FWHM) of characteristic peaks (4 0 0) and (1 0 0) to the Scherrer equation.

$$D_{h\,k\,l} = \frac{0.9\lambda}{\beta \cos\theta} \quad \text{.....(i)}$$

The theoretical particle size was also calculated from the surface area assuming particles to be spherical. The equation for calculating the average particle diameter in nanometers is:

$$D_{BET} = \left(\frac{6000}{S_{BET} \times \rho} \right) \quad \text{.....(ii)}$$

where, D_{BET} is the equivalent particle diameter in nanometers, ρ is the density of the material in gcm^{-3}, and S is the specific surface area in m^2g^{-1}. The average particle diameter calculated from equation (ii) was 8.12 nm (S_{BET} =185.63 m^2g^{-1} and ρ =3.98 gcm^{-3}).

Particle size and external morphology of the prepared particles were observed on a Transmission Electron Microscope (TEM) (CM12, PHILIPS). It can be seen from the figure 4 that the shape of nano-alumina appears in the form of nano rod with an average length of 25.5 nm and average diameter of 7.18 nm. It can also be seen that some agglomeration was present and this was attributed to the large surface area of these rod shaped nano-Al_2O_3.

Typical SAED patterns of the Al_2O_3 nano rod generated as an inset in figure 5. It showed that the nano rods were well-crystallined. The SAED patterns were calculated and identified using JCPDS data card 10-425, indicating that most of these rings corresponded to the diffraction planes of γ-Al_2O_3. No un-assigned rings were left in the SAED patterns, endorsing the fact that formation of other types of metastable phases like δ-Al_2O_3, θ-Al_2O_3, etc were not observed.

To analyze the chemical structure, the FT-IR spectrum was recorded by using the Fourier Transform Infra-Red Spectroscopy (FT-IR) in the range of 400-4000 cm^{-1} frequency range on KBr pallets with a Nicolet (Impact 410) FT-IR spectrophotometer. As shown in figure 6, the peak at 3500 cm^{-1} is attributed to the atmospheric water vapour. An absorption band at ca. 1620 cm^{-1} was also observed which is in accordance with reported literature.[2] The peak at 1040 cm^{-1} corresponds to the Al-O stretching vibration.[3]

(3) General synthetic procedures

(A) General Procedure for the *N*-formylation of alky/aryl amines:

In an oven dried round bottomed flask (50 mL) nano rod shaped basic Al_2O_3 (5.0 mol%) were added and then alky/aryl amines (5.0 mmol) and formic acid (15.0 mmol) was added. The reaction was found to be mildly exothermic which required initial cooling on ice bath while formic acid was added to the reaction mixture containing alkyl/aryl amine and nano basic alumina. After that it was allowed to stir on a pre heated oil bath at 40^o C under aerobic condition

till the required time (the progress of the reaction was judged by TLC). The reaction mixture was brought to room temperature after its completion and ethyl acetate (3x10 mL) was added to it and then centrifuged at 3,500 rpm to recover the nano catalyst. Having done this, the reaction mixture was washed with water and brine, dried over Na_2SO_4, concentrated in a rotary evaporator and finally the crude product was charged to column chromatography (30% ethyl acetate: hexane as an eluent) for purification and wherever necessary the products were recrystallized from hot ethanol.

(B) General Procedure for the *N*-formylation of indole:

To a two neck round bottomed flask (50 mL) nano rod shaped basic Al_2O_3 (5.0 mol%, 5.0 mg) were added and then indole (1.0 mmol, 117 mg) and formic acid (98%, 3.0 mmol, 0.11 mL) was added. After that it was allowed to stir on a pre heated oil bath at 70° C till the required time (the progress of the reaction was judged by TLC). The reaction mixture was brought to room temperature after its completion and ethyl acetate (3x10 mL) was added to it and then centrifuged at 3,500 rpm to recover the nano catalyst. Having done this, the reaction mixture was washed with water and brine, dried over Na_2SO_4, concentrated in a rotary evaporator and finally the crude product was purified by column chromatography (30% ethyl acetate: hexane as an eluent).

(C) General Procedure for the synthesis of acetamide:

To a 50 mL round bottomed flask, nano-Al_2O_3 (5.0 mol%, 54.8 mg) were taken with aniline (10.7526 mmol, 1000 mg) and then acetic acid glacial (10.7526 mmol, 0.61 mL) was added to it. Then the reaction mixture was heated at 70° C on preheated oil bath till the product formation (monitored by TLC). The reaction mixture was brought to room temperature after its completion and ethyl acetate (3x10 mL) was added to it and then centrifuged at 3,500 rpm to recover the

nano alumina. Having done this, the reaction mixture was washed with water and brine, dried over Na_2SO_4, concentrated in a rotary evaporator and finally subjected column chromatography (30% ethyl acetate: hexane as an eluent) for purification.

(4) Recycling potential of nano- Al_2O_3

After carrying out the experiment, Ethyl acetate was poured and the reaction mixture was centrifuged to pellet out the nano Al_2O_3. The particles were then extracted by simple centrifugation (3,000 rpm) and washed with hot ethanol (3x10 mL) to remove all the organic impurities. Finally it was decanted and dried in vacuo. The recovered nano alumina rod was used directly in the next cycle. The nano-Al_2O_3 rod was found to be effective equally up to the fifth cycle and after that the yield of the product slightly decreased as shown in the figure 7.

(5) List of figures

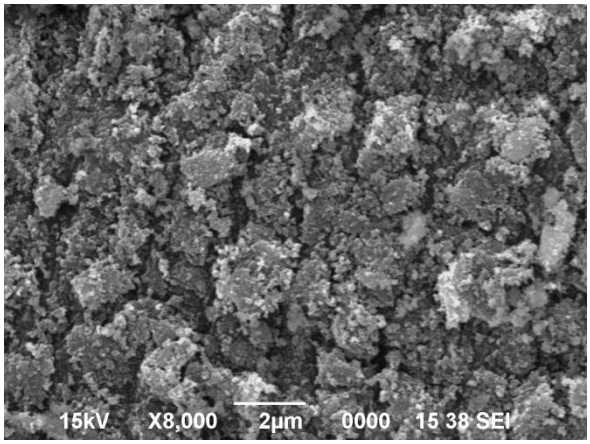


Figure 1. SEM photograph of fresh nano-Al_2O_3

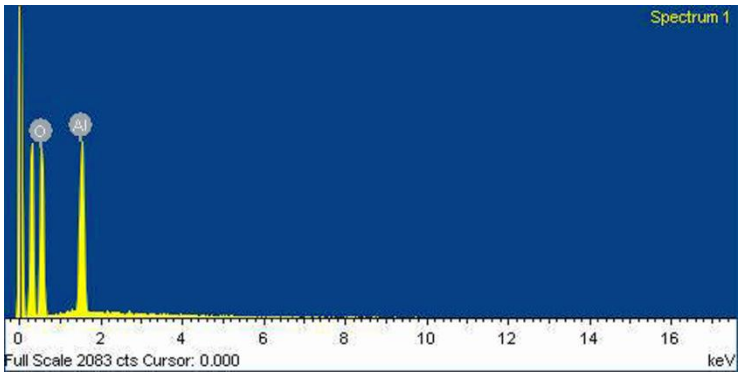


Figure 2. EDX of fresh nano- Al_2O_3

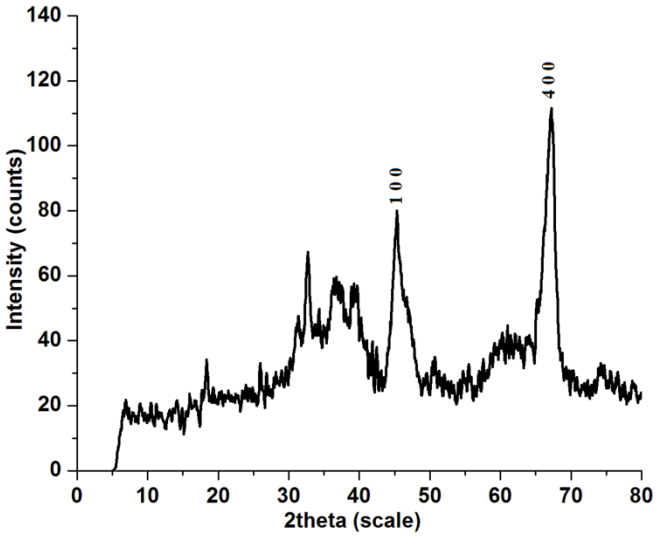


Figure 3. XRD pattern of fresh nano- Al_2O_3

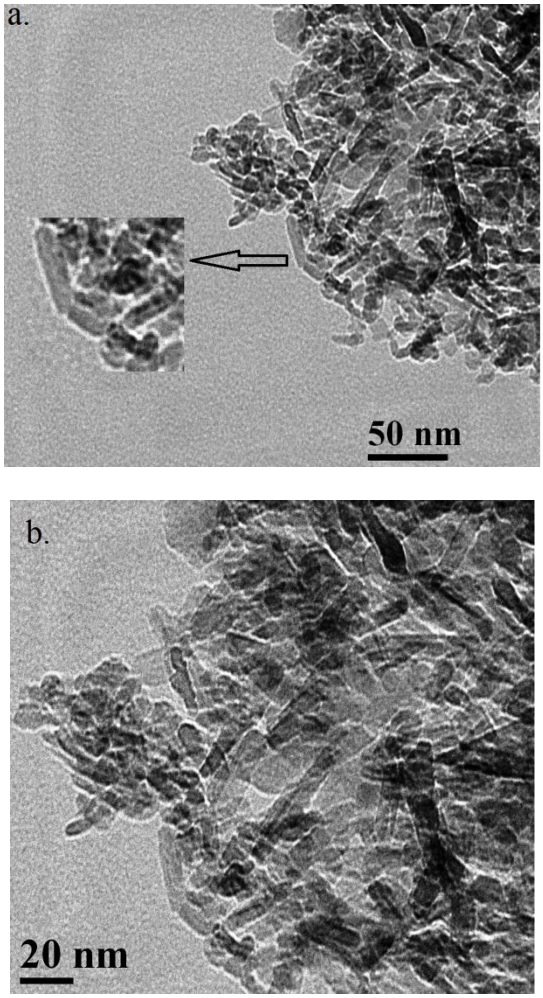


Figure 4. (a) TEM image of fresh nano-Al_2O_3 at 50 nm scale (b) TEM image of fresh nano-Al_2O_3 at 20 nm scale

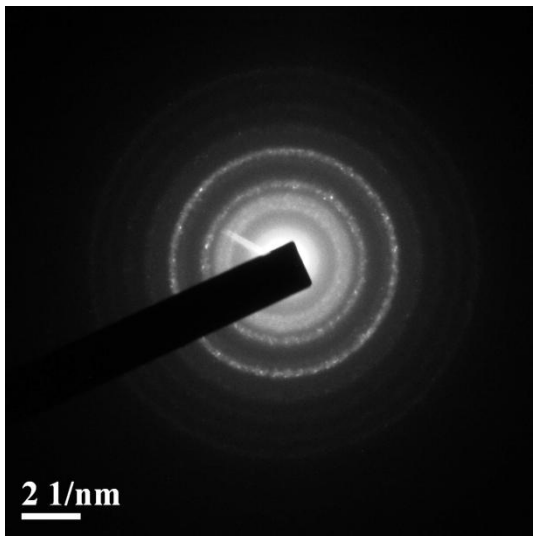


Figure 5. Corresponding size distribution with inset showing SAED patterns

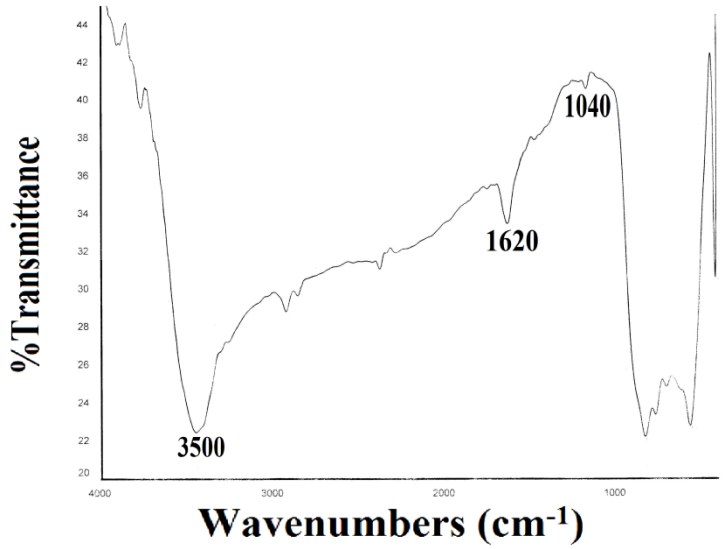


Figure 6. FTIR spectrum of fresh nano-Al_2O_3

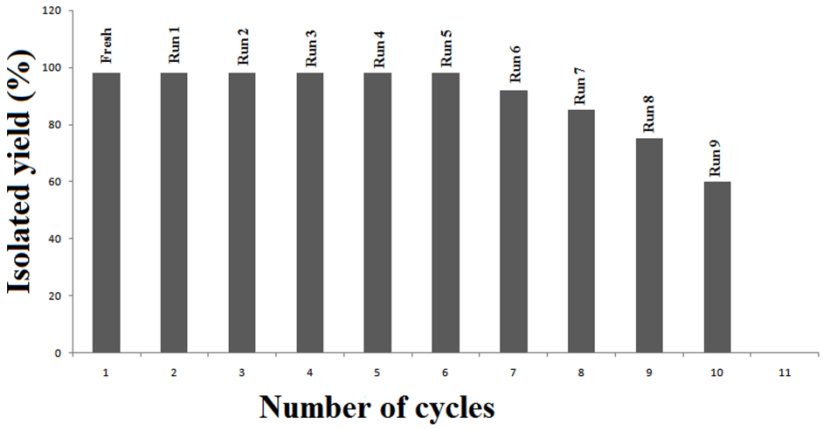
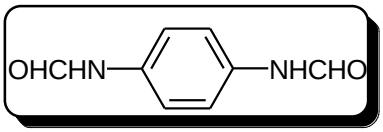


Figure 7. Catalyst recyclability chart

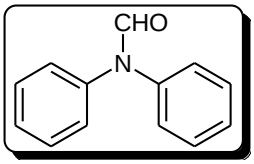
(6) Physical and Spectroscopic Data of Compounds:

***N*-(4-Formylamino-phenyl)-formamide (Table 4, entry 12[c])**



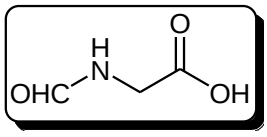
A light brown solid; R_f = 0.30 (30% AcOEt:hexane); mp 135-140 ^{0}C; ^{1}H NMR (400 MHz, DMSO, TMS): δ 8.22 (s, 1H), 7.53 (d, *J*=2.76, 2H, Ar-H), 7.13 (d, *J*=2.76, 2H, Ar-H); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 159.8, 134.8, 120.7, 120.1; IR (KBr pellets) ν_{max}: 3380 cm^{-1} (NH), 1710 cm^{-1} (CO), 2790 cm^{-1} (CH); m/z (GC-MS) 164.10 [M$^+$]; Anal. Calcd (%) for $C_8H_8N_2O_2$: C, 58.53; H, 4.91; N, 17.06. Found C, 58.52, H, 4.95, N, 17.08.

***N,N*-Diphenyl-formamide (Table 4, entry 14)**



A yellow solid; R_f = 0.76 (30% AcOEt:hexane); mp 68-73 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.69 (s, 1H), 7.16-7.7.39 (m, 10H, Ar-H); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 161.8, 141.8, 139.7, 129.7, 129.2, 127.1, 126.9, 126.2, 125.1; IR (KBr pellets) ν_{max}: 1700 cm^{-1} (CO), 2820 cm^{-1} (CH); m/z (GC-MS) 197.00 [M$^+$]; Anal. Calcd (%) for $C_{13}H_{11}NO$: C, 79.16; H, 5.62; N, 10.00. Found C, 79.15, H, 5.65, N, 9.97.

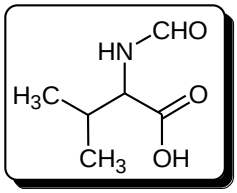
Formylamino-acetic acid (Table 4, entry 15)



A white solid; R_f = 0.53 (30% AcOEt:hexane); mp 133-138 ^{0}C; ^{1}H NMR (400 MHz, D_2O, TMS): δ 7.98 (s, 1H), 3.86 (s, 3H); ^{13}C NMR (100 MHz, D_2O, TMS): δ 173.1, 164.6, 40.6; IR (KBr

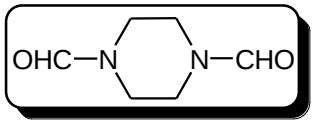
pellets) ν_{max}: 3400 cm^{-1} (NH), 1720 cm^{-1} (CO); 1690 (CO), 2800 cm^{-1} (CH); m/z (GC-MS) 103.03 [M^+]; Anal. Calcd (%) for $C_3H_5NO_3$: C, 34.96; H, 4.89; N, 13.59. Found C, 34.93, H, 4.85, N, 13.55.

2-Formyl amino-3-methyl-butyric acid (Table 4, entry 16)



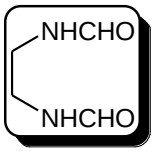
A white solid; R_f = 0.45 (30% AcOEt:hexane); mp 203-208 ^{0}C; ^{1}H NMR (400 MHz, D_2O, TMS): δ 8.17 (s, 1H), 3.99 (d, *J*=5.04, 3H), 3.41 (d, *J*=5.04, 3H), 1.96-2.09 (m, 1H); ^{13}C NMR (100 MHz, D_2O, TMS): δ 177.7, 169.6, 60.2, 29.7, 16.5, 16.4; IR (KBr pellets) ν_{max}: 3410 cm^{-1} (NH), 1725 cm^{-1} (CO); 1685 (CO), 2810 cm^{-1} (CH); m/z (GC-MS) 145.07 [M^+]; Anal. Calcd (%) for $C_6H_{11}NO_3$: C, 49.65; H, 7.64; N, 9.65. Found C, 49.63, H, 7.62, N, 9.62.

Piperazine-1,4-dicarbaldehyde (Table 4, entry 21[c])



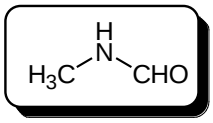
A light yellow tinted powder; R_f = 0.43 (30% AcOEt:hexane); mp 123-128 ^{0}C; ^{1}H NMR (400 MHz, DMSO, TMS): δ 8.30 (s, 1H), 3.10 (s, 8 H); ^{13}C NMR (100 MHz, DMSO-d_6, TMS): δ 167.9, 33.6; IR (KBr pellets) ν_{max}: 1735 cm^{-1} (CO); 2815 cm^{-1} (CH); m/z (GC-MS) 142.03 [M^+]; Anal. Calcd (%) for $C_6H_{10}N_2O_2$: C, 50.69; H, 7.09; N, 19.71. Found C, 50.64, H, 7.03, N, 19.73.

***N*-(2-Formylamino-ethyl)-formamide (Table 4, entry 22[c])**



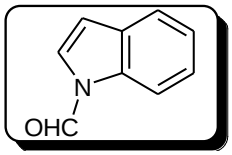
A off white powder; R_f = 0.48 (30% AcOEt:hexane); mp 110-115 ^{0}C; ^{1}H NMR (400 MHz, DMSO TMS): δ 8.14 (s, 1H), 3.42 (s, 4 H); ^{13}C NMR (100 MHz, DMSO- d_6, TMS): δ 167.9, 35.5; IR (KBr pellets) ν_{max}: 3435 cm^{-1} (NH), 1715 cm^{-1} (CO), 2825 cm^{-1} (CH); m/z (GC-MS) 116.00 [M$^+$]; Anal. Calcd (%) for $C_4H_8N_2O_2$: C, 41.37; H, 6.94; N, 24.12. Found C, 41.39, H, 6.92, N, 24.11.

_N_-Methyl-formamide (Table 4, entry 24)



A light yellow slightly viscous liquid; R_f = 0.84 (30% AcOEt:hexane); bp 195-200 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 8.45 (br, 1H), 8.26 (s, 1H), 2.78 (d, J=11.44, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 167.9, 24.6; IR (KBr pellets) ν_{max}: 3455 cm^{-1}(NH), 1738 cm^{-1} (CO), 2820 cm^{-1} (CH); m/z (GC-MS) 59.05 [M$^+$]; Anal. Calcd (%) for C_2H_5NO: C, 40.67; H, 8.53; N, 23.71. Found C, 40.63, H, 8.51, N, 23.73.

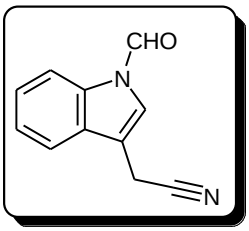
Indole-1-carbaldehyde (Table 5, entry 1)



A off white powder; R_f = 0.67 (30% AcOEt:hexane); mp 90-95 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$ TMS): δ 8.94 (s, 1H), 6.99-7.32 (m, 6H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 160.7, 137.0, 137.9, 127.9, 124.9, 124.7, 122.9, 122.7, 122.5, 120.3, 119.3, 119.2, 116.4, 111.7, ; IR

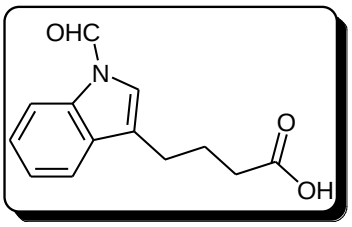
(KBr pellets) ν_{max}: 1727 cm^{-1} (CO), 2822 cm^{-1} (CH); m/z (GC-MS) 145.05 [M^+]; Anal. Calcd (%) for C_9H_7NO: C, 74.47; H, 4.86; N, 9.65. Found C, 74.43, H, 4.85, N, 9.62.

(1-Formyl-1*H*-indol-3-yl)-acetonitrile (Table 5, entry 5)



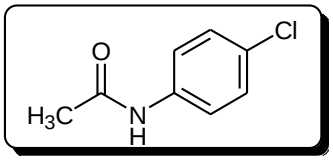
A brown oil; R_f = 0.24 (30% AcOEt:hexane); ^1H NMR (400 MHz, $CDCl_3$ TMS): δ 8.03 (s, 1H), 7.10-7.17 (m, 4H, Ar-H), 6.70 (s, 1H, Ar-H), 2.98 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 161.6, 136.4, 127.4, 122.0, 121.6, 119.3, 118.9, 115.4, 115.2, 111.2, 35.5; IR (KBr pellets) ν_{max}: 1705 cm^{-1} (CO), 2815 cm^{-1} (CH), 2200 (CN); m/z (GC-MS) 184.06 [M^+]; Anal. Calcd (%) for $C_{11}H_8N_2O$: C, 71.73; H, 4.38; N, 15.21. Found C, 71.74, H, 4.39, N, 15.26.

4-(1-Formyl-1*H*-indol-3-yl)-butyric acid (Table 5, entry 7)



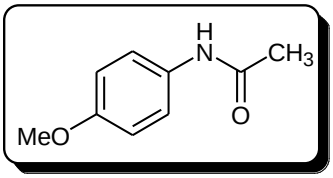
A light yellowish brown solid, R_f = 0.20 (30% AcOEt:hexane); mp 111-116 ^0C; ^1H NMR (400 MHz, $CDCl_3$ TMS): δ 9.3 (br, 1H), 9.0 (s, 1H), 7.11-7.59 (m, 4H, Ar-H), 6.97 (s, 1H, Ar-H), 2.81 (q, *J*=7.28, 2H), 2.42 (t, *J*=7.32, 2H), 2.06 (d, *J*=7.32, 2H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 180.0, 167.6, 136.4, 127.4, 122.0, 121.6, 119.3, 118.9, 115.4, 111.2, 33.6, 33.5, 25.1, 24.4; IR (KBr pellets) ν_{max}: 1720 cm^{-1} (CO), 1685 cm^{-1}(CO), 2807 cm^{-1} (CH), 3420 (OH); m/z (GC-MS) 231.09 [M^+]; Anal. Calcd (%) for $C_{13}H_{13}NO_3$: C, 67.52; H, 5.67; N, 6.06. Found C, 67.51, H, 5.62, N, 6.01.

***N*-(4-Chloro-phenyl)-acetamide (Table 6, entry 2)**



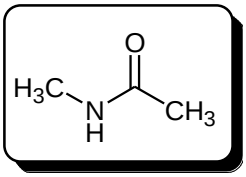
A off white crystalline needle; R_f = 0.26 (30% AcOEt:hexane); mp 177-182 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.45 (d, *J*=8.72,2H, Ar-H), 7.27 (d, *J*=8.72, 2H, Ar-H), 7.34 (br, 1H), 2.17 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 168.4, 136.4, 129.3, 129.0, 121.1, 29.7, 24.6; IR (KBr pellets) ν_{max}: 3406 cm^{-1} (NH), 1702 cm^{-1} (CO); m/z (GC-MS) 169.03 [M$^+$]; Anal. Calcd (%) for C_8H_8ClNO: C, 56.65; H, 4.75; N, 8.26. Found C, 56.62, H, 4.73, N, 8.25.

***N*-(4-Methoxy-phenyl)-acetamide (Table 6, entry 7)**



Light purple powder; R_f = 0.32 (30% AcOEt:hexane); mp 134-139 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 7.67 (br, 1H), 7.36 (d, *J*=7.80, 2H, Ar-H), 7.09 (d, *J*=7.76, 2H), 2.29 (s, 3H), 2.12 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ 168.5, 135.4, 133.9, 129.4, 120.1, 24.4, 20.8; IR (KBr **pellets**) ν_{max}: 3378 cm^{-1} (NH), 1674 cm^{-1} (CO); m/z (GC-MS) 165.08 [M$^+$]; Anal. Calcd (%) for $C_9H_{11}NO_2$: C, 65.44; H, 6.71; N, 8.48. Found C, 65.39, H, 6.73, N, 8.44.

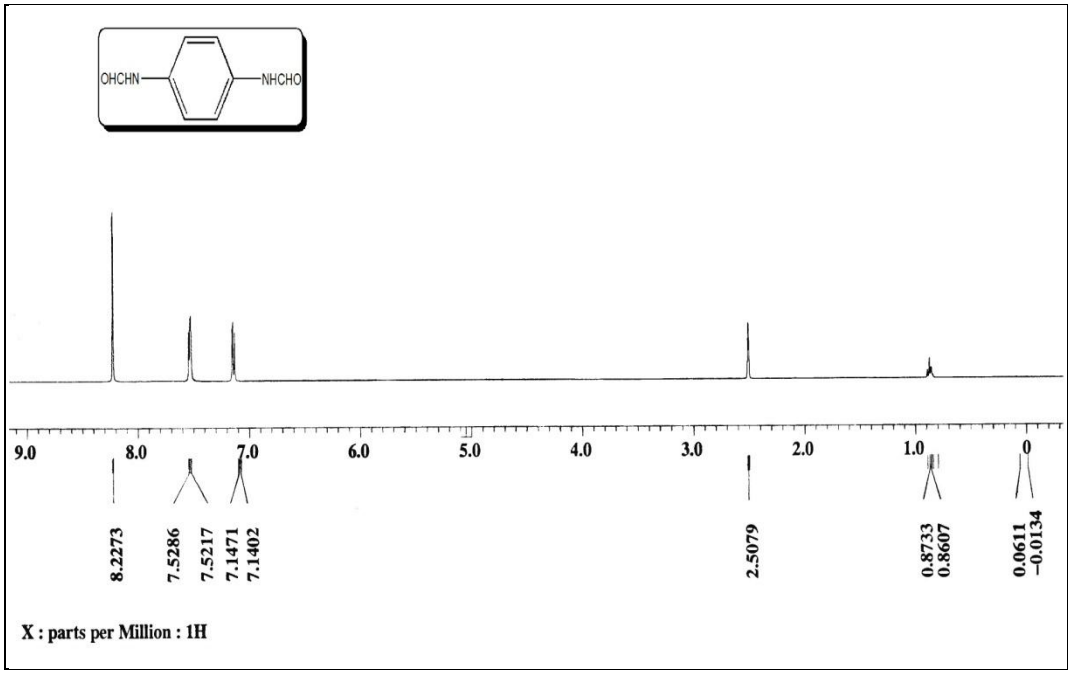
***N*-Methyl-acetamide (Table 6, entry 12)**



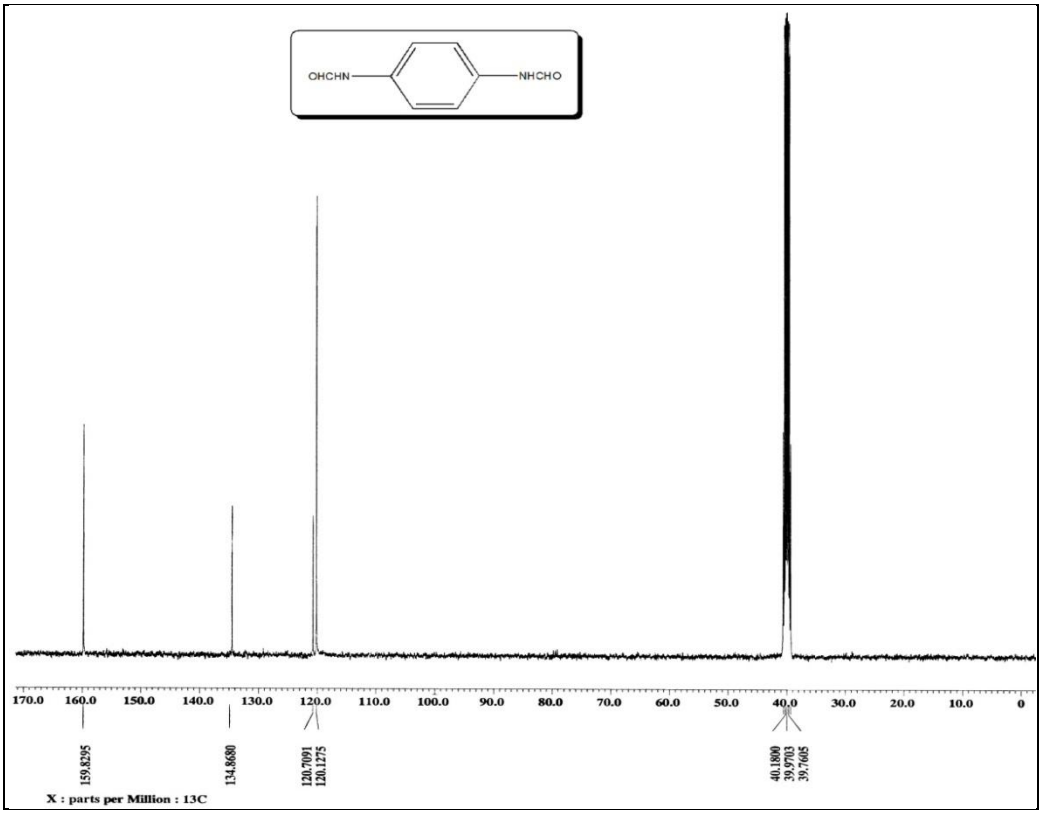
A colourless solid; R_f = 0.38 (30% AcOEt:hexane); mp 27-30 ^{0}C; ^{1}H NMR (400 MHz, $CDCl_3$, TMS): δ 5.52 (br, 1H), 2.82 (d, *J*=5.04, 3H), 2.04 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$, TMS): δ

170.8, 26.4, 23.1; IR (KBr pellets) ν_{max}: 3332 cm^{-1} (NH), 1690 cm^{-1} (CO); m/z (GC-MS) 73.05 [M^+]; Anal. Calcd (%) for C_3H_7NO: C, 49.30; H, 9.65; N, 19.16. Found C, 49.35, H, 9.63, N, 19.20.

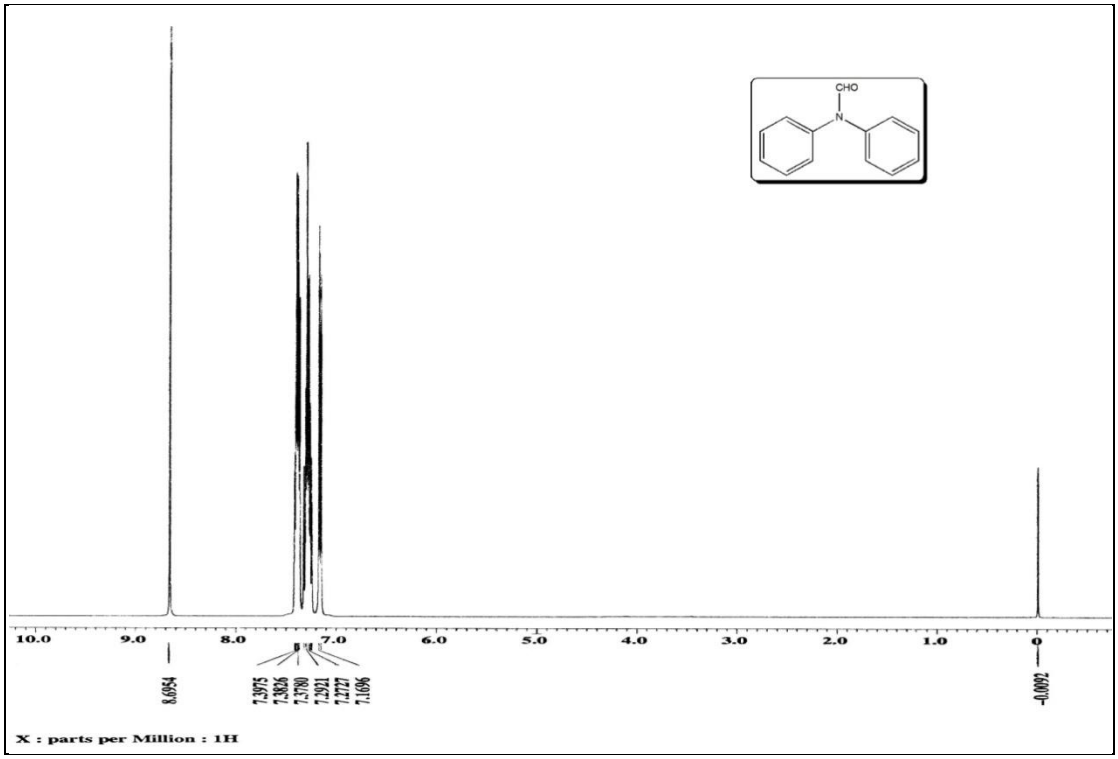
(7) (A) ^{1}H NMR (400 MHz, DMSO-d_6): *N*-(4-Formylamino-phenyl)-formamide (Table 4, entry 12)



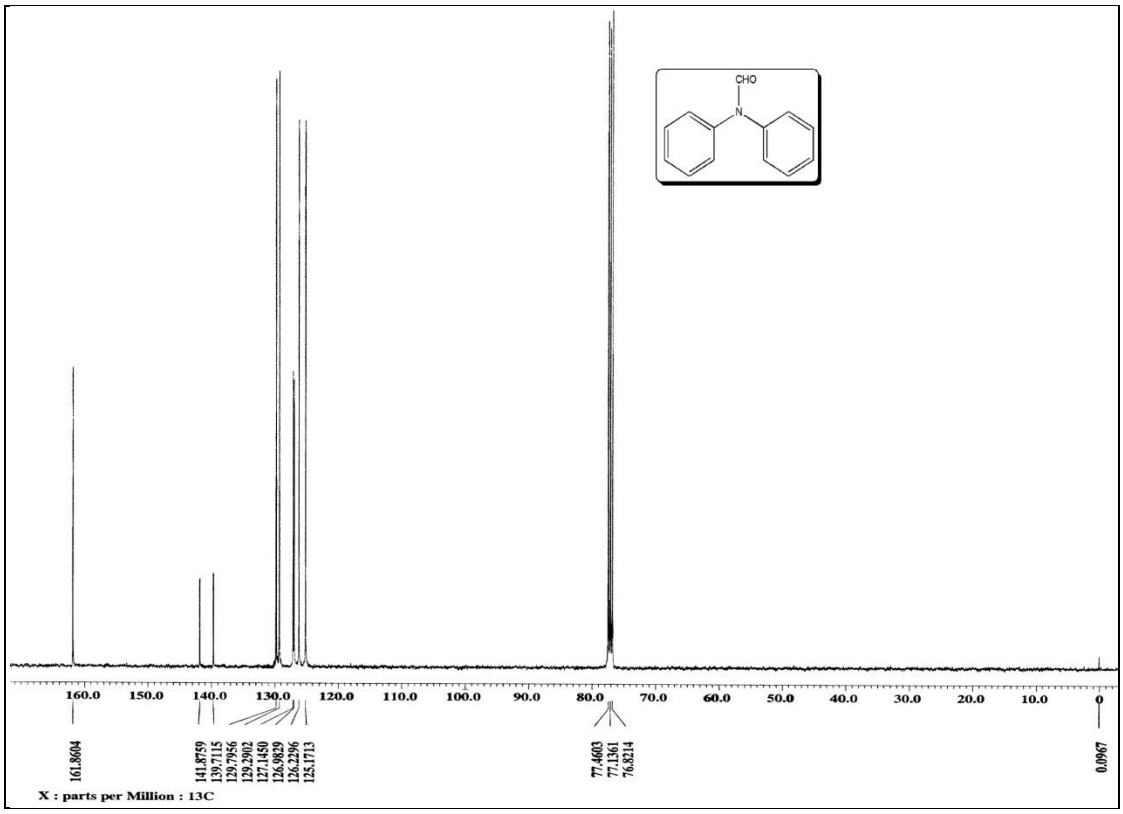
(B) ^{13}C NMR (100 MHz, DMSO-d_6): *N*-(4-Formylamino-phenyl)-formamide (Table 4, entry 12)



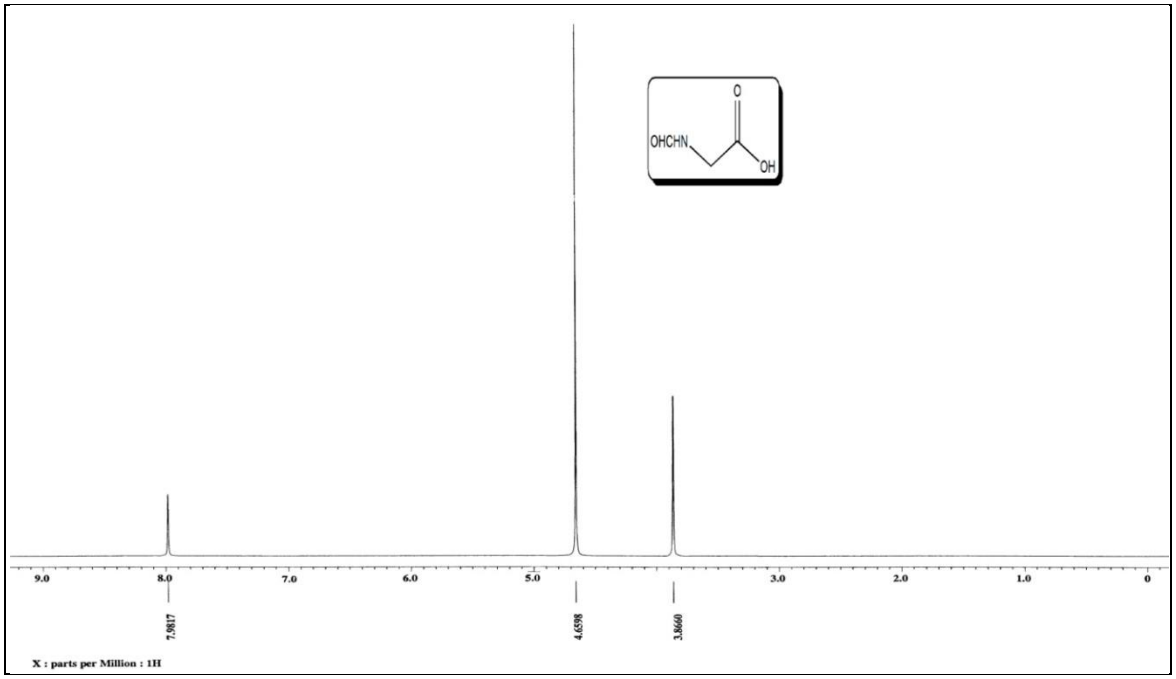
(C) ^{1}H NMR (400 MHz, $CDCl_3$): *N,N*-Diphenyl-formamide (Table 4, entry 14)



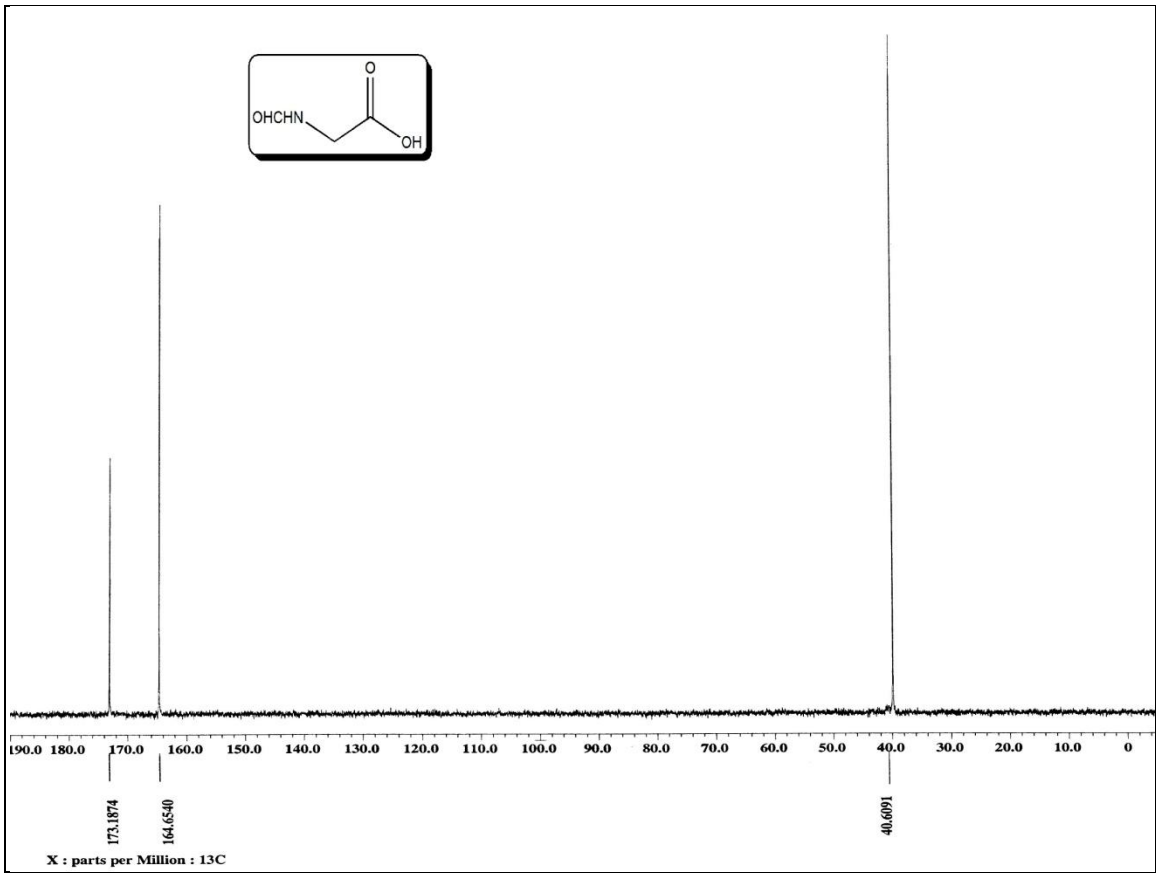
(D) ^{13}C NMR (100 MHz, $CDCl_3$): *N,N*-Diphenyl-formamide (Table 4, entry 14)



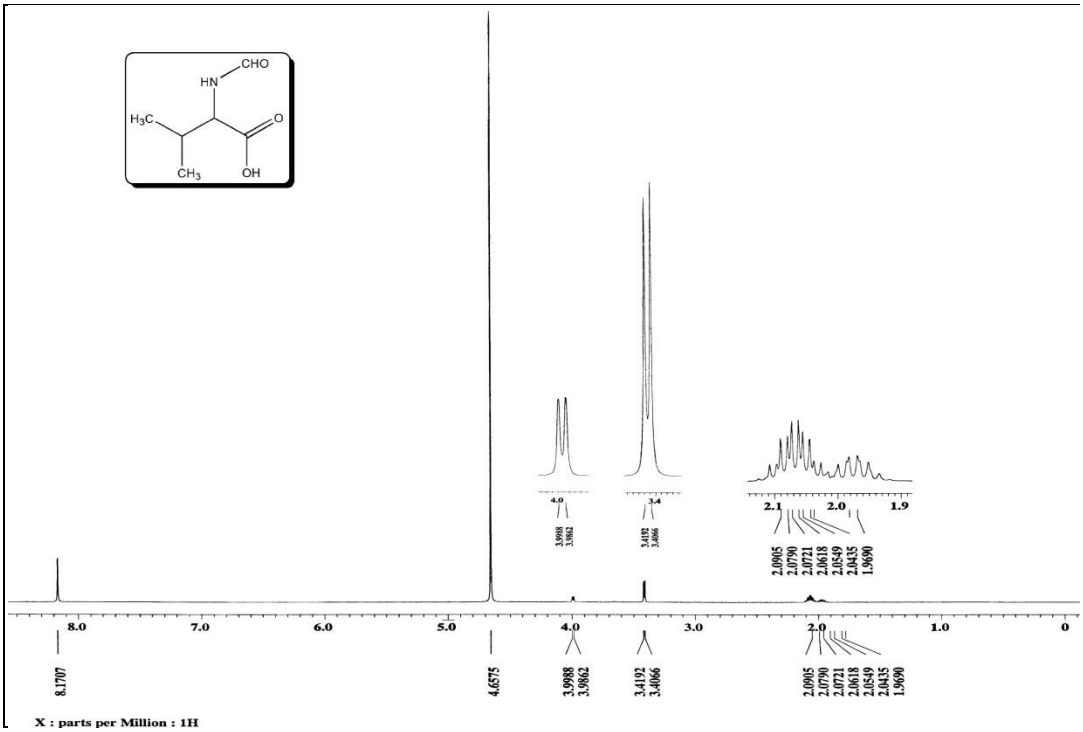
(E) ^{1}H NMR (400 MHz, D_2O): Formylamino-acetic acid (Table 4, entry 15)



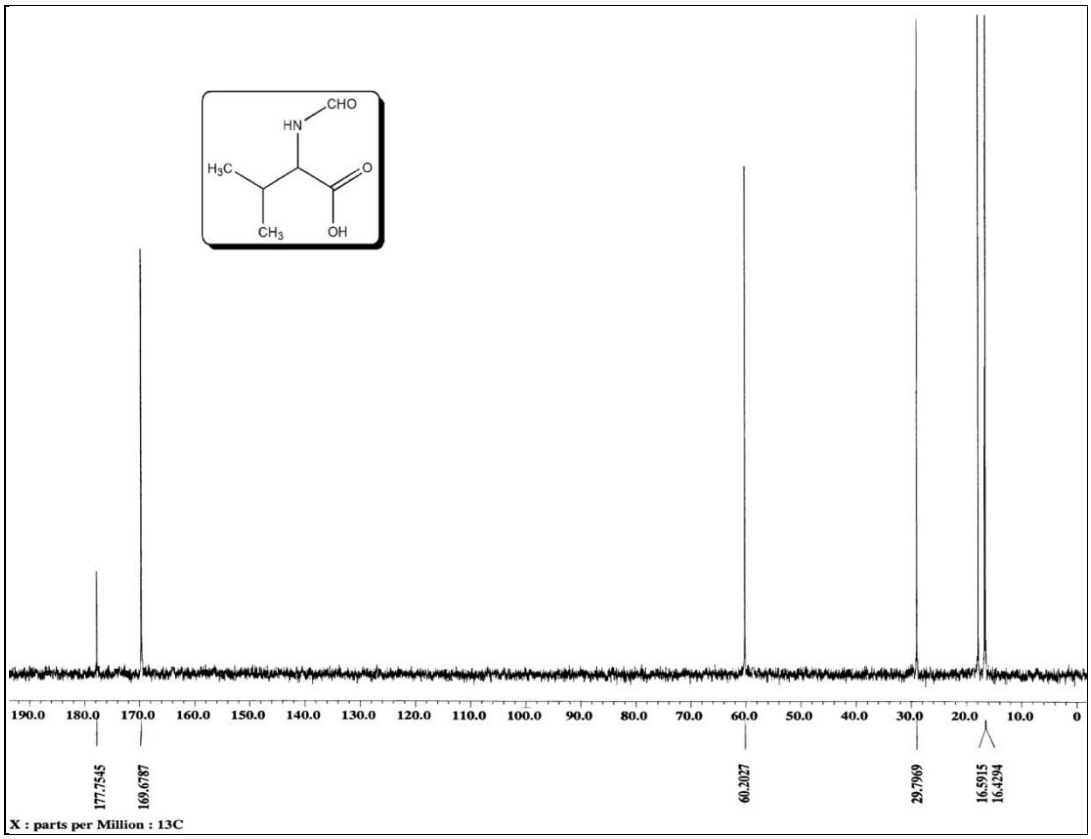
(F) ^{13}C NMR (100 MHz, D_2O): Formylamino-acetic acid (Table 4, entry 15)



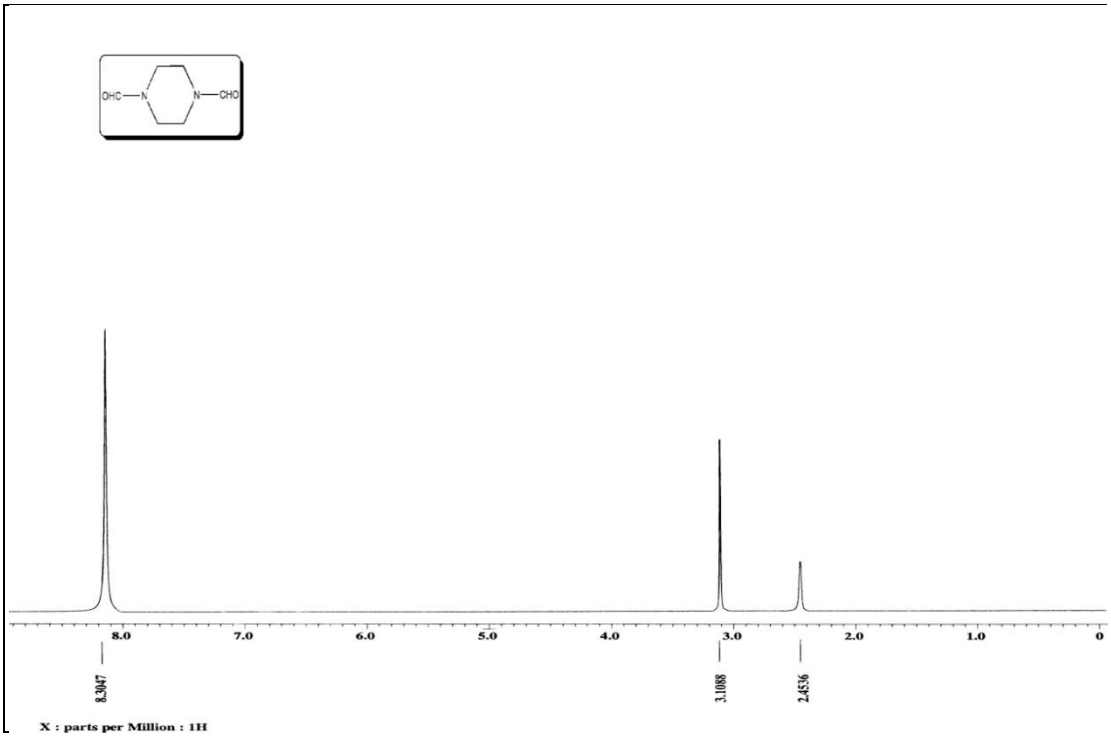
(G) ^{1}H NMR (400 MHz, D_2O): 2-Formyl amino-3-methyl-butyric acid (Table 4, entry 16)



(H) ^{13}C NMR (100 MHz, D_2O): 2-Formyl amino-3-methyl-butyric acid (Table 4, entry 16)

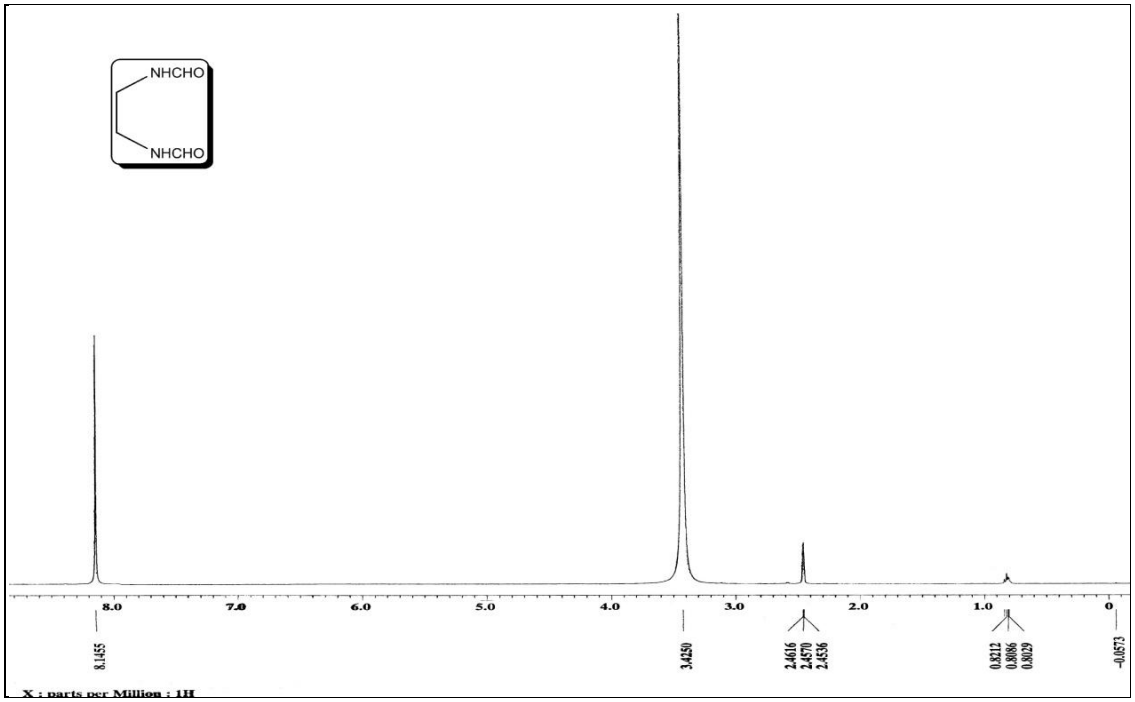


(I) ^{1}H NMR (400 MHz, DMSO-d_6): Piperazine-1,4-dicarbaldehyde (Table 4, entry 21)

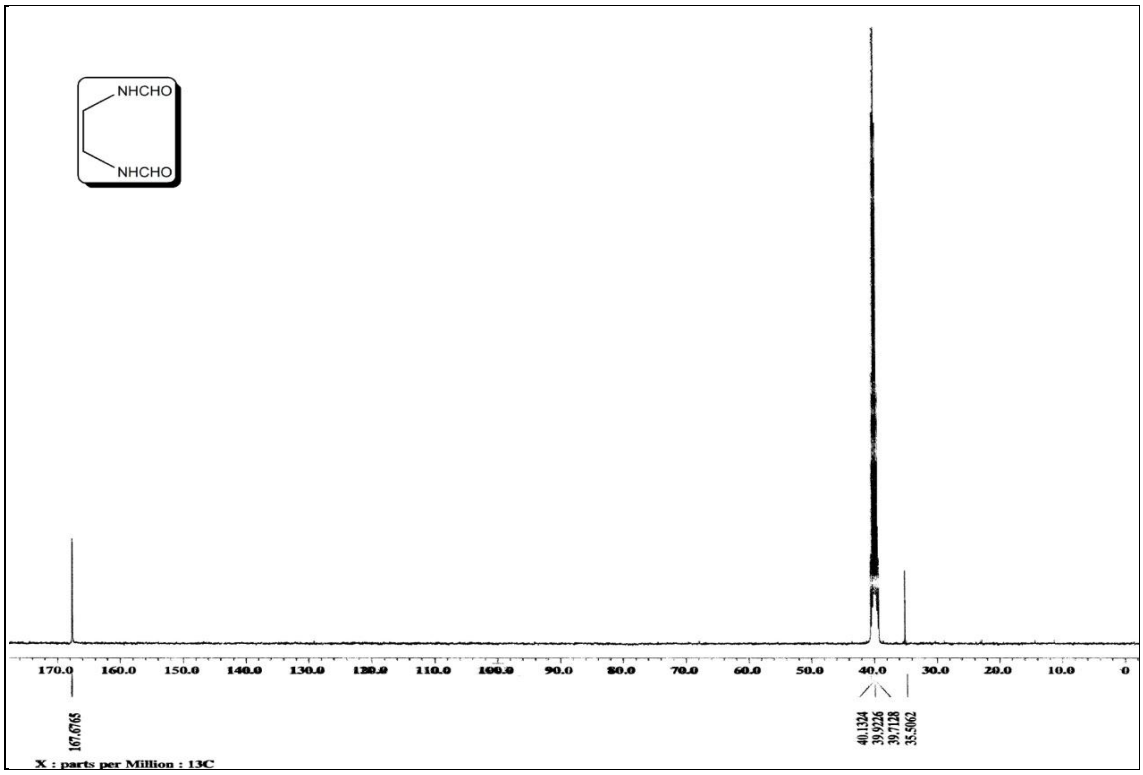


(J) ^{13}C NMR (100 MHz, DMSO-d_6): Piperazine-1,4-dicarbaldehyde (Table 4, entry 21)

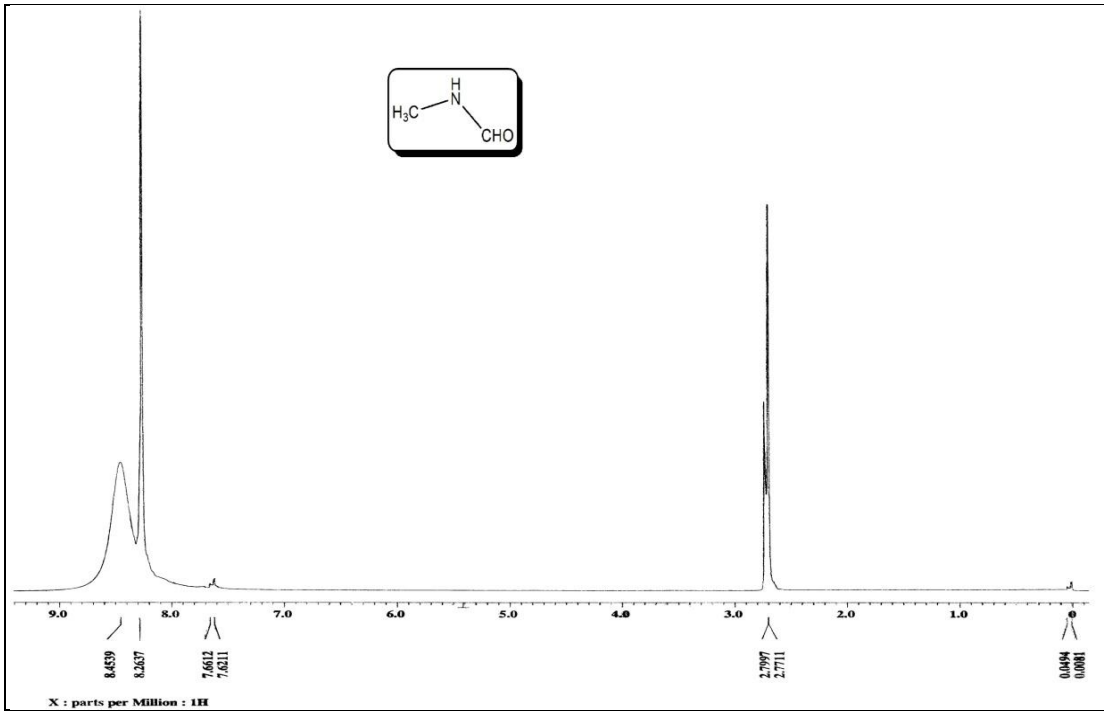
(K) ^{1}H NMR (400 MHz, DMSO-d_6): *N*-(2-Formylamino-ethyl)-formamide (Table 4, entry 22)



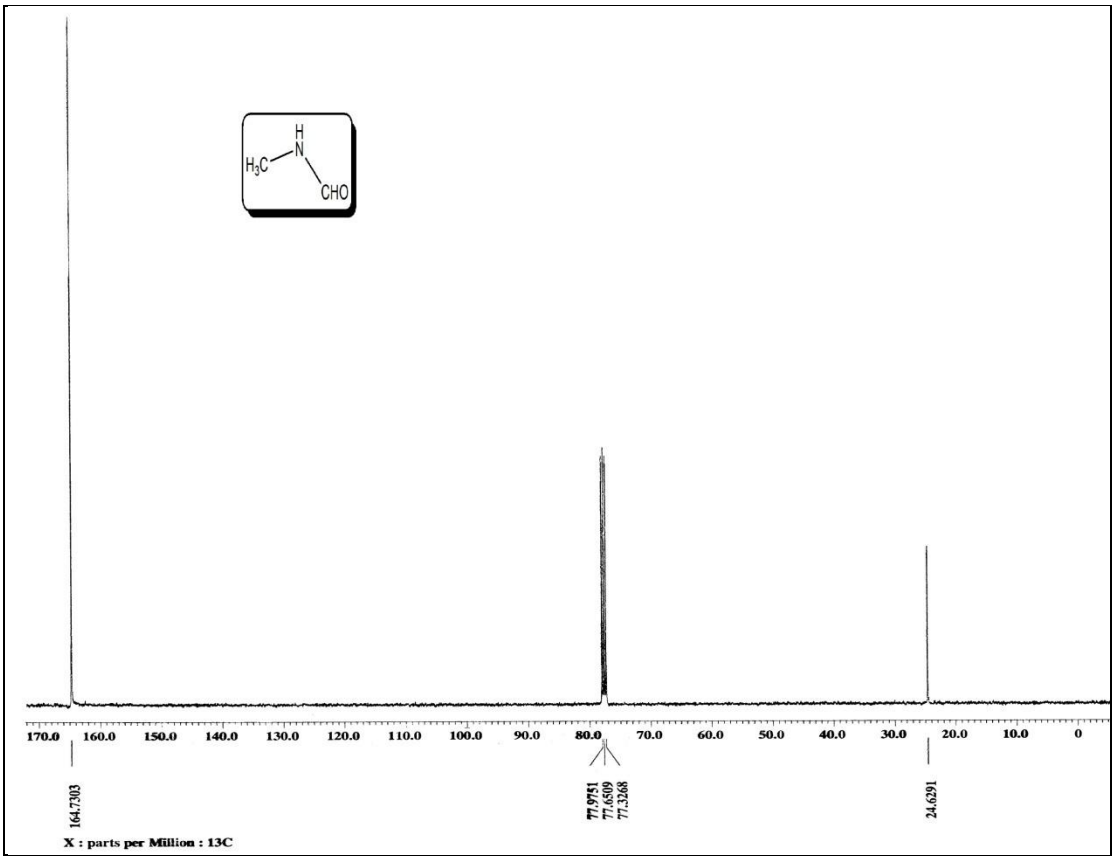
(L) ^{13}C NMR (100 MHz, DMSO-d_6): *N*-(2-Formylamino-ethyl)-formamide (Table 4, entry 22)



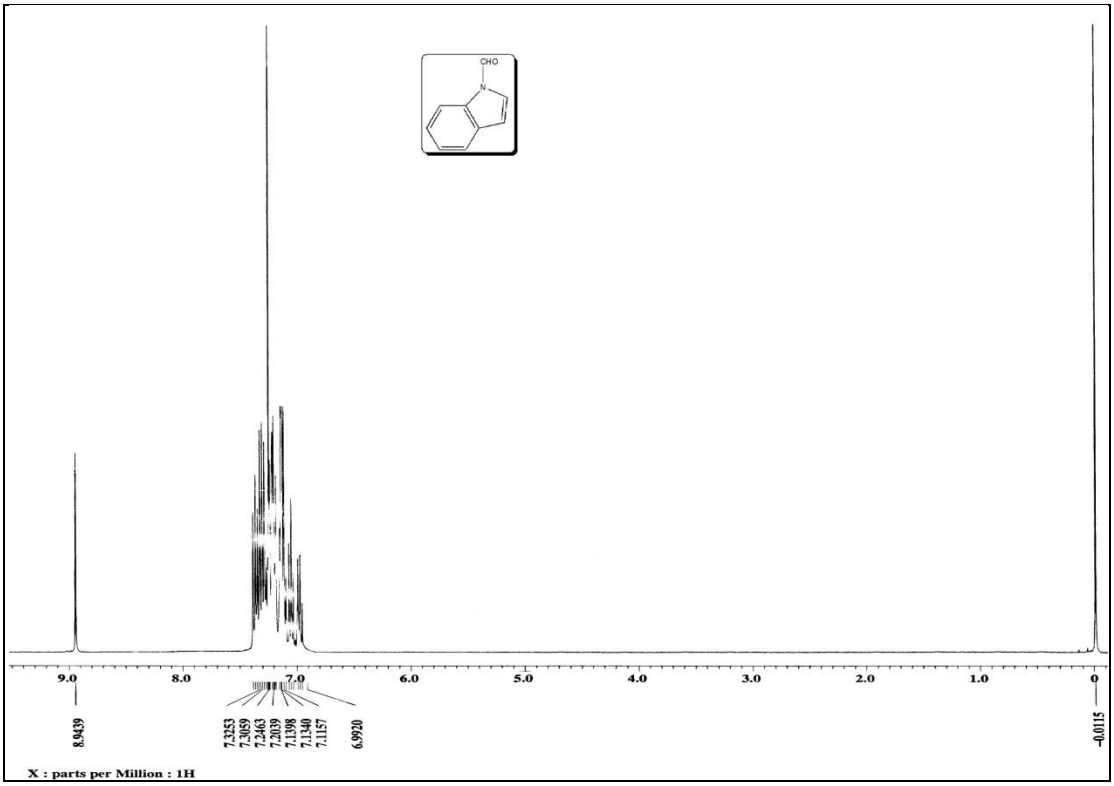
(M) ^{1}H NMR (400 MHz, $CDCl_3$): *N*-Methyl-formamide (Table 4, entry 24)



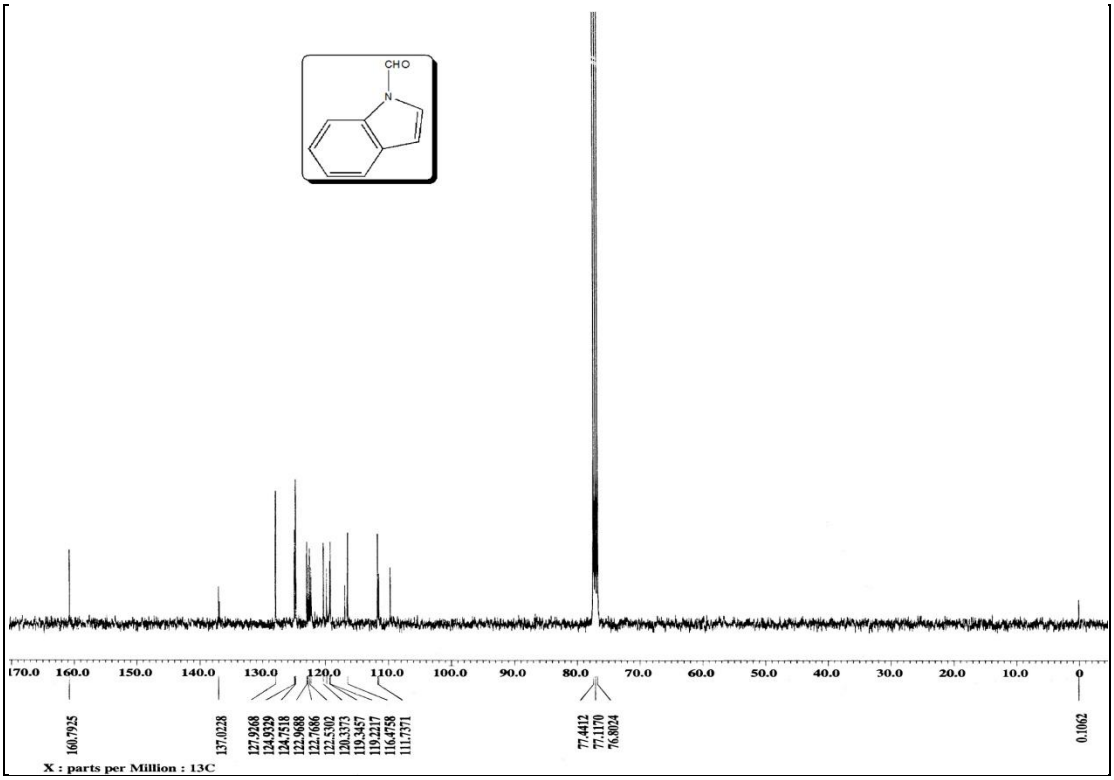
(N) ^{13}C NMR (100 MHz, $CDCl_3$): *N*-Methyl-formamide (Table 4, entry 24)



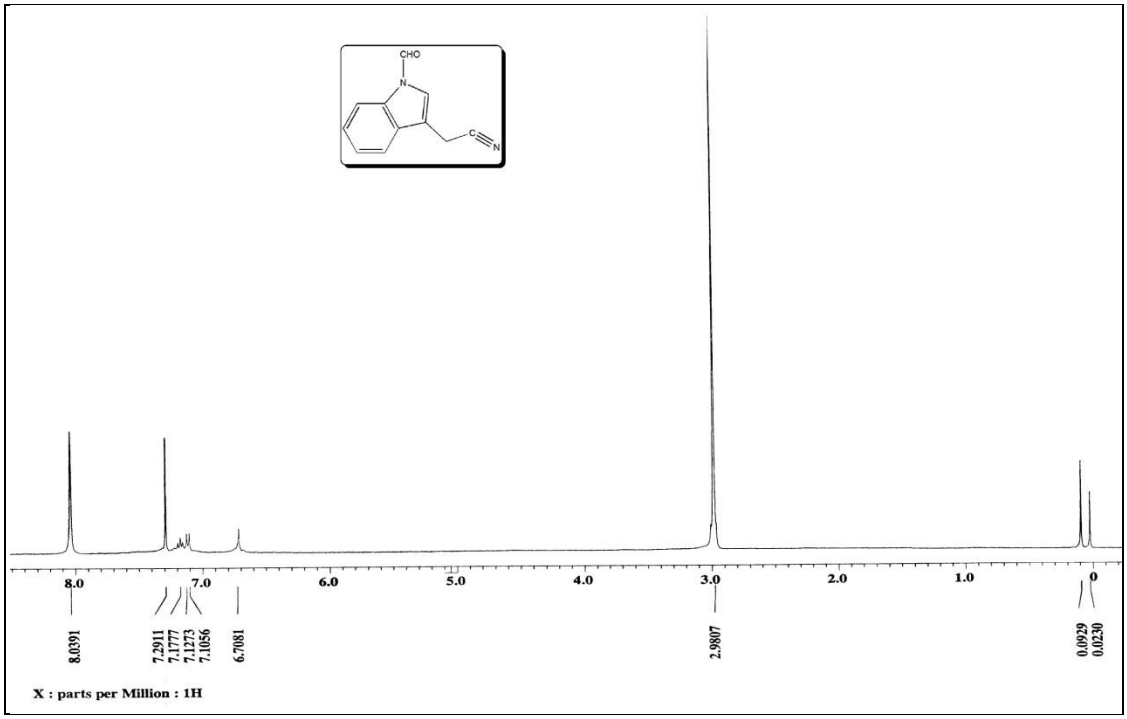
(O) ^{1}H NMR (400 MHz, $CDCl_3$): Indole-1-carbaldehyde (Table 5, entry 1)



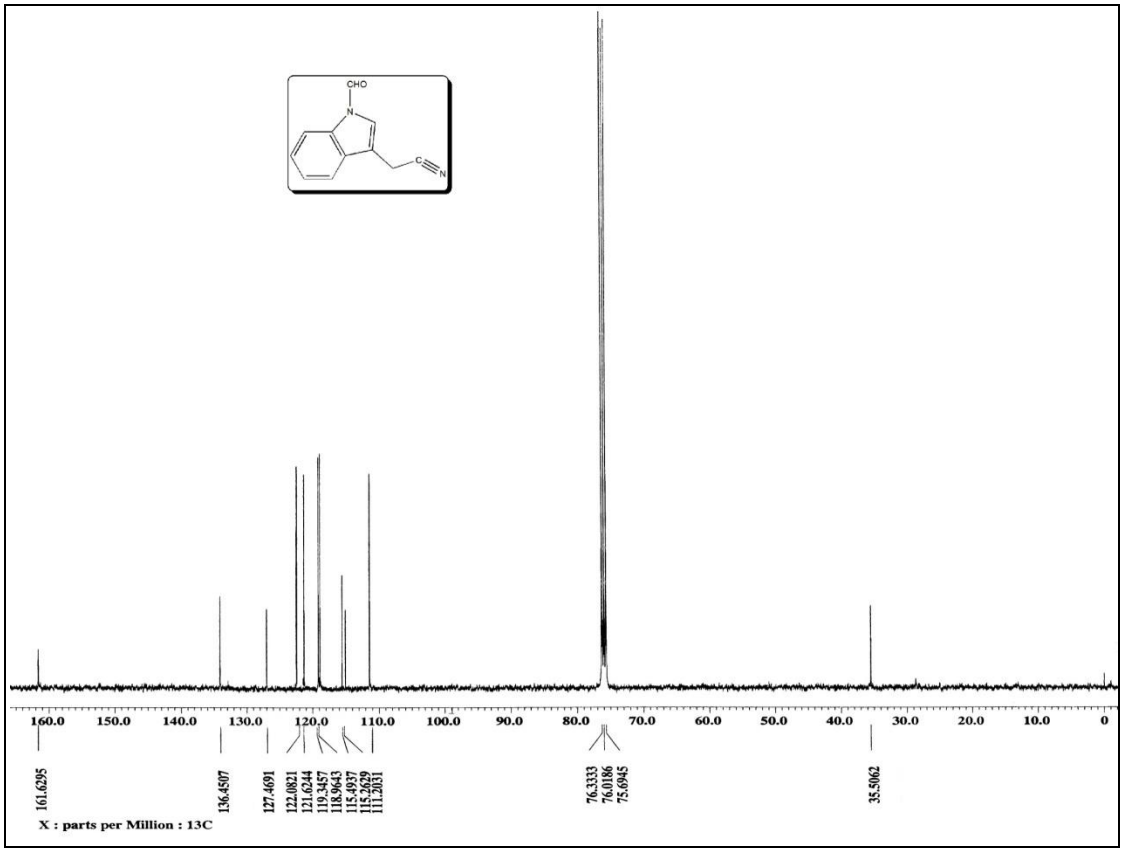
(P) ^{13}C NMR (100 MHz, $CDCl_3$): Indole-1-carbaldehyde (Table 5, entry 1)



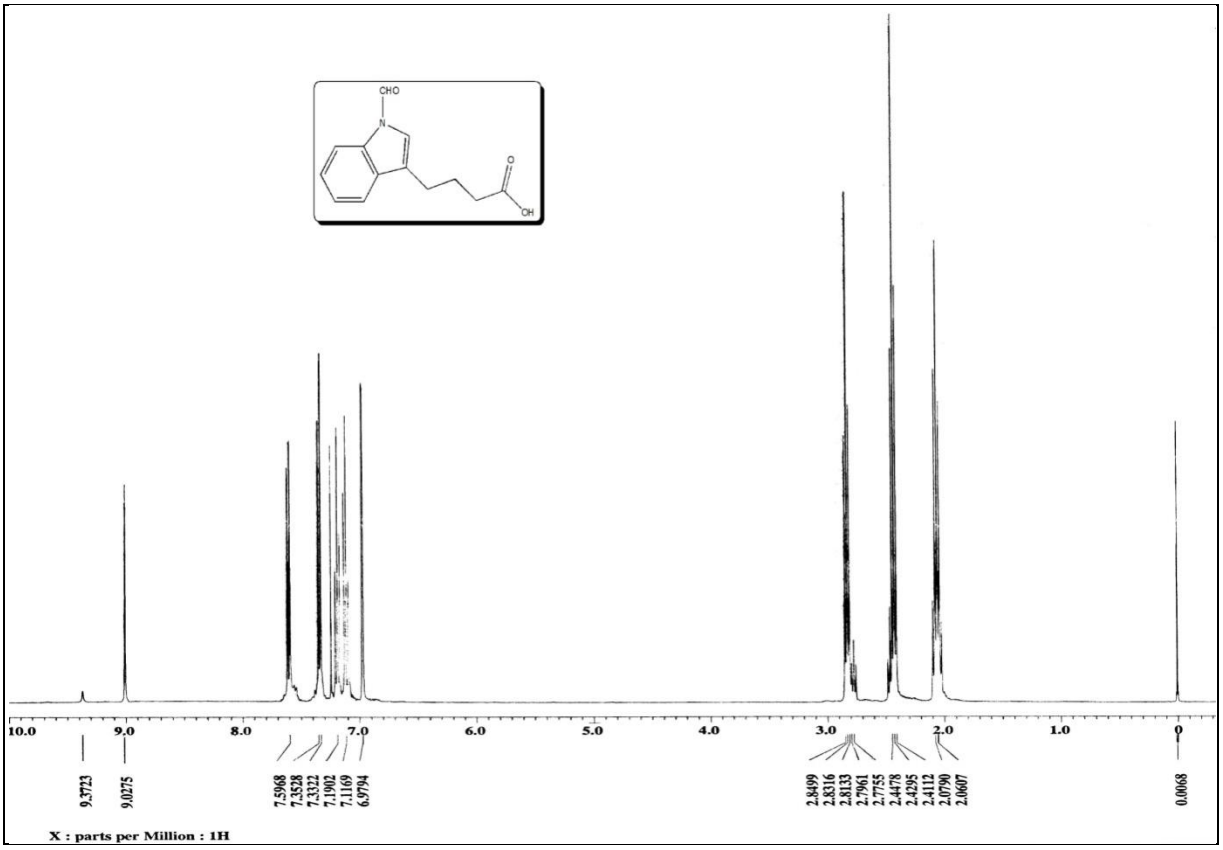
(Q) **^{1}H NMR (400 MHz, $CDCl_3$): (1-Formyl-1*H*-indol-3-yl)-acetonitrile (Table 5, entry 5)**



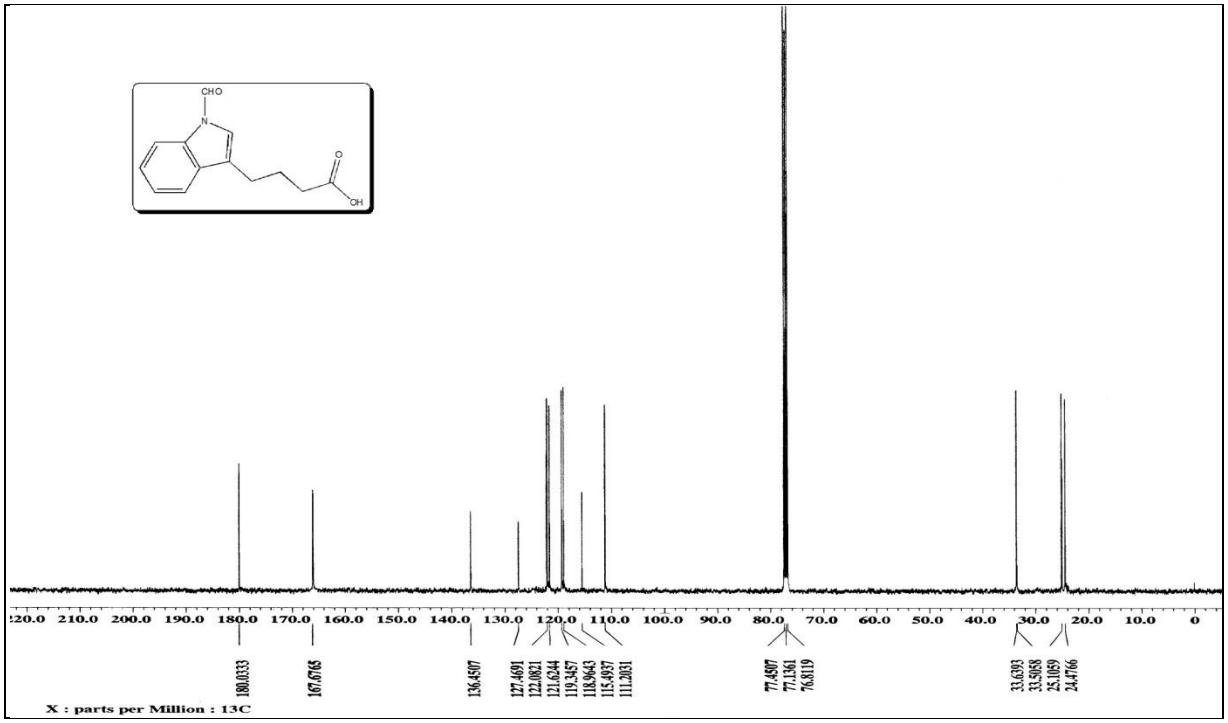
(R) **^{13}C NMR (100 MHz, $CDCl_3$): (1-Formyl-1*H*-indol-3-yl)-acetonitrile (Table 5, entry 5)**



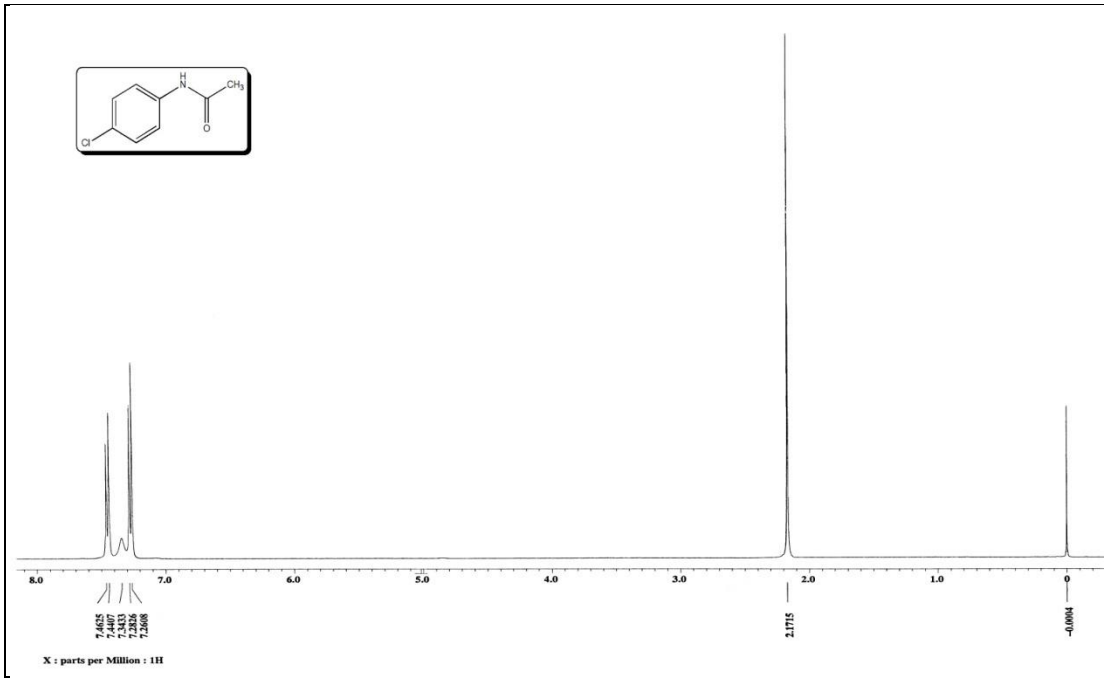
(S) **^{1}H NMR (400 MHz, $CDCl_3$): 4-(1-Formyl-1*H*-indol-3-yl)-butyric acid (Table 5, entry 7)**



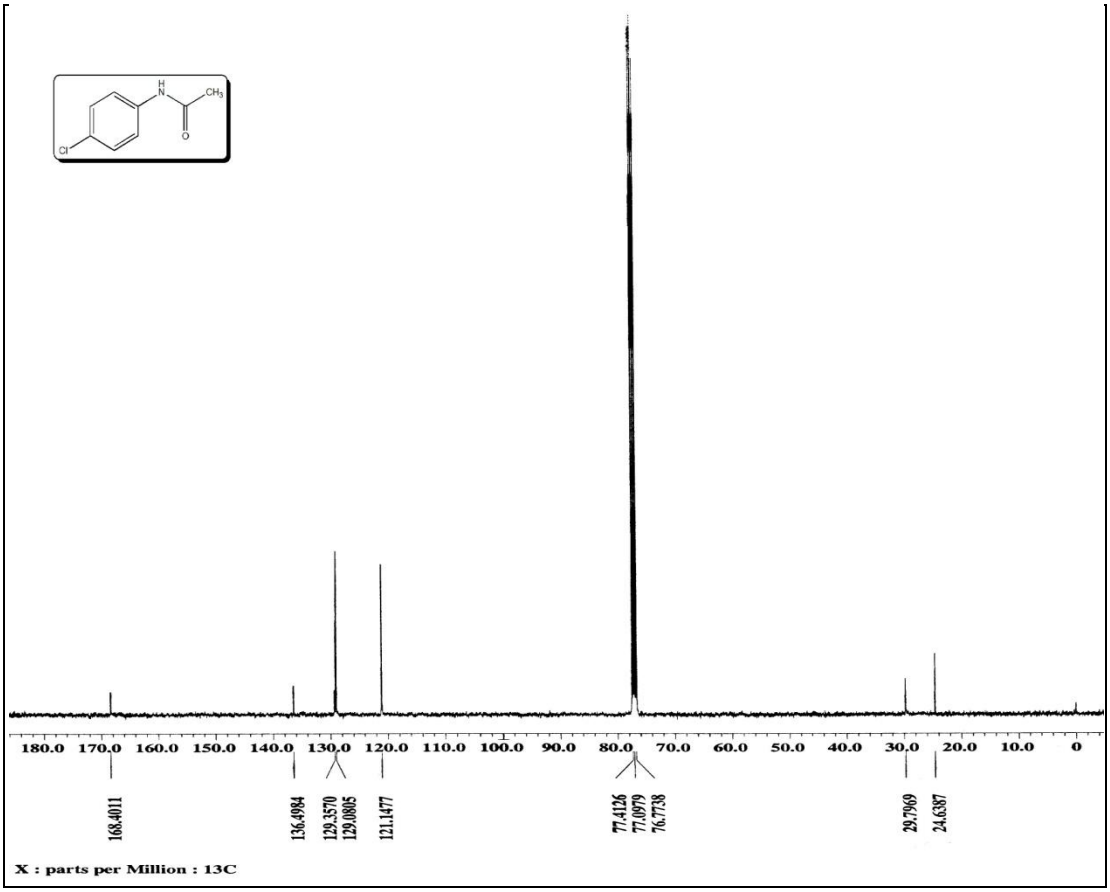
(T) ^{13}C NMR (100 MHz, $CDCl_3$): 4-(1-Formyl-1*H*-indol-3-yl)-butyric acid (Table 5, entry 7)



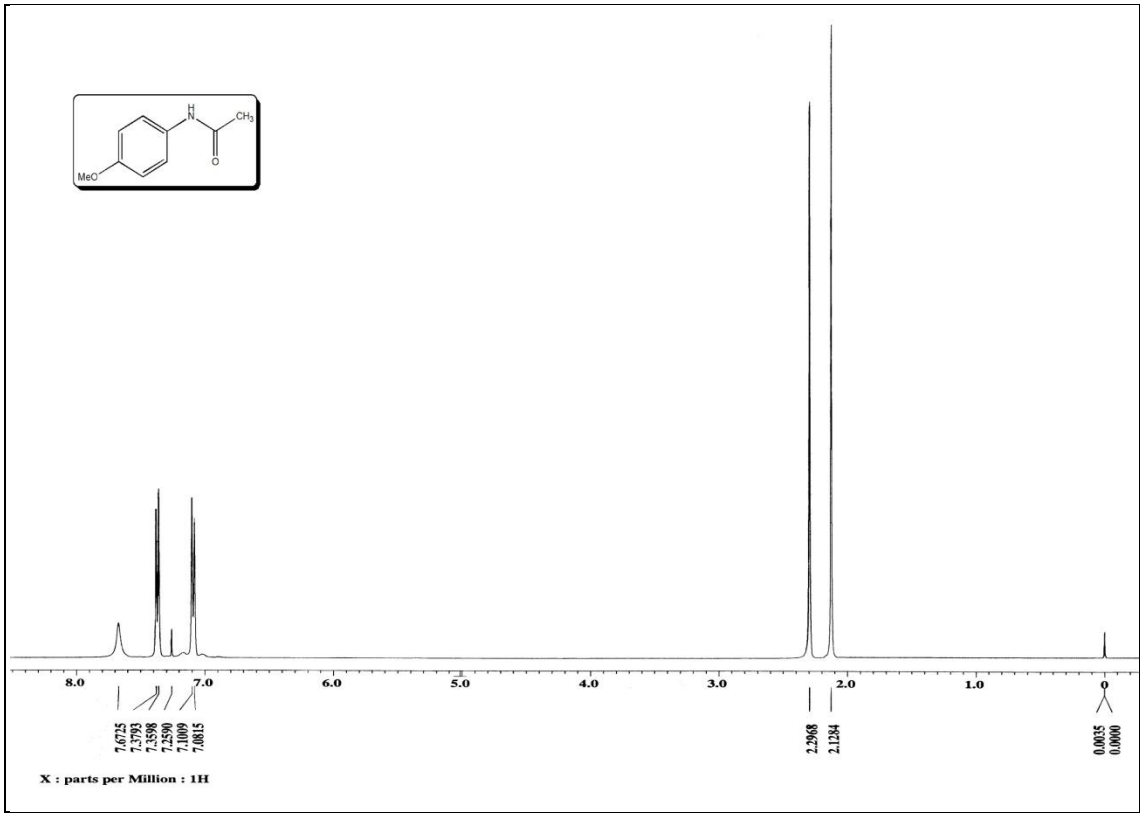
(U) ^{1}H NMR (400 MHz, $CDCl_3$): *N*-(4-Chloro-phenyl)-acetamide (Table 6, entry 2)



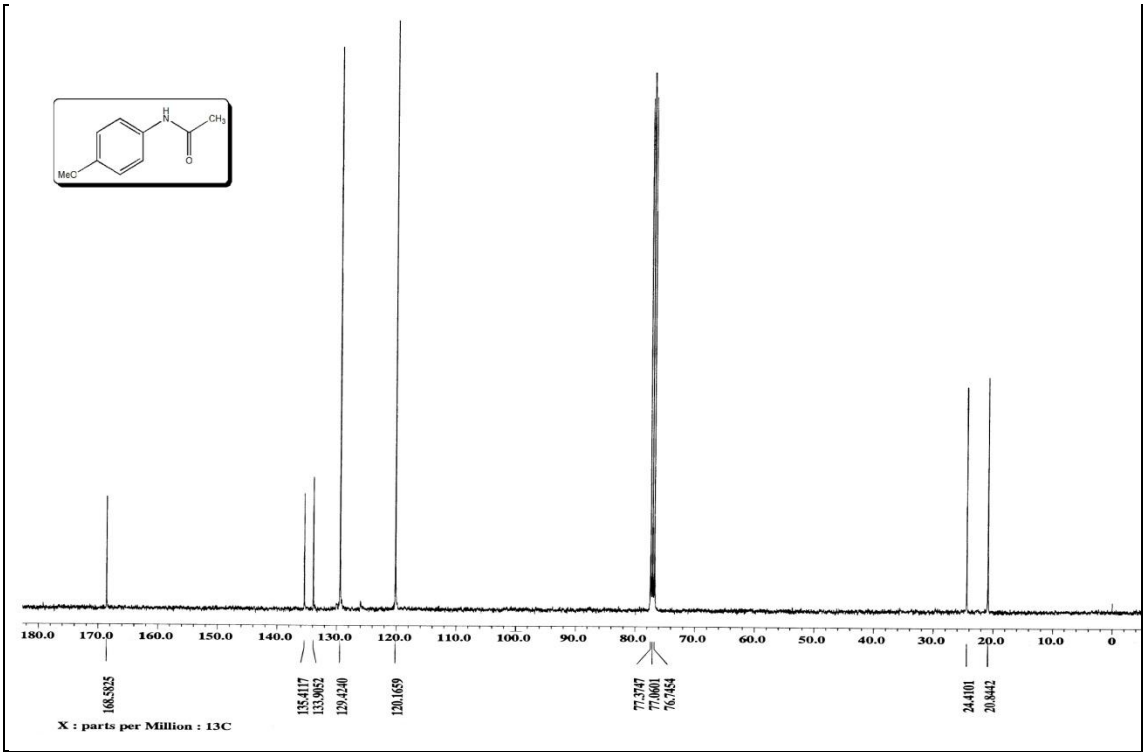
(V) ^{13}C NMR (100 MHz, $CDCl_3$): *N*-(4-Chloro-phenyl)-acetamide (Table 6, entry 2)



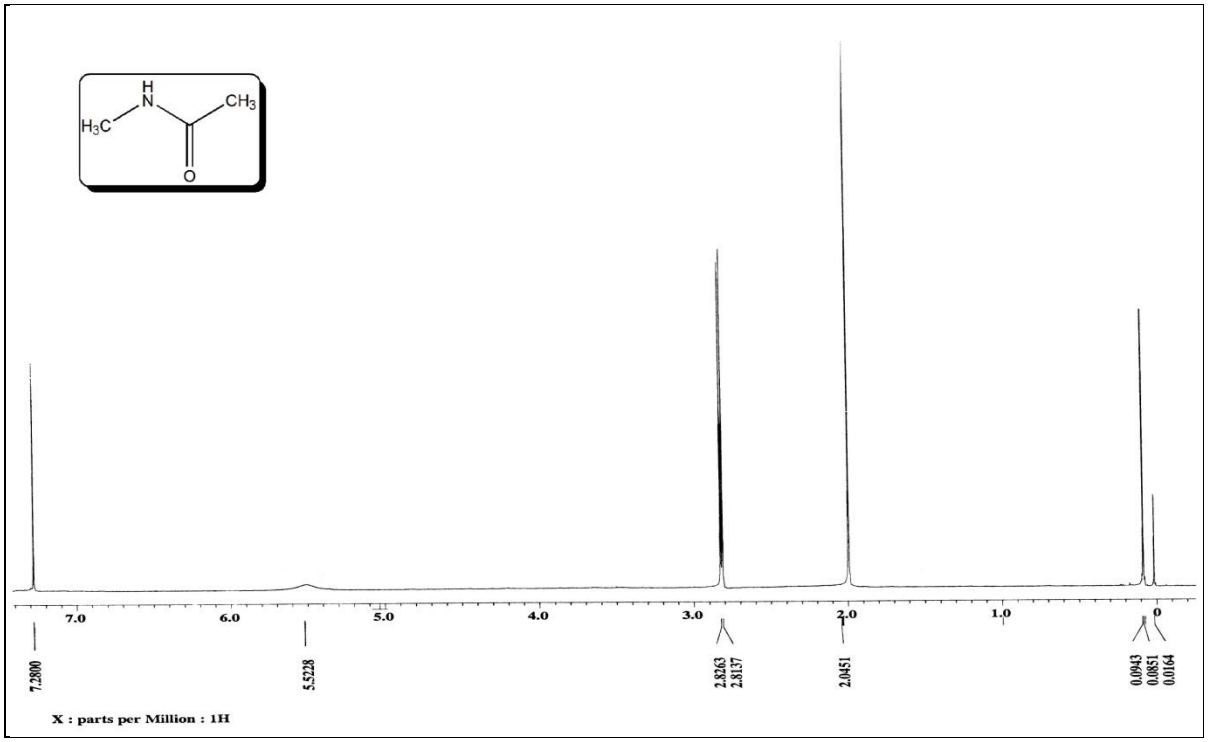
(W) ^{1}H NMR (400 MHz, $CDCl_3$): *N*-(4-Methoxy-phenyl)-acetamide (Table 6, entry 7)



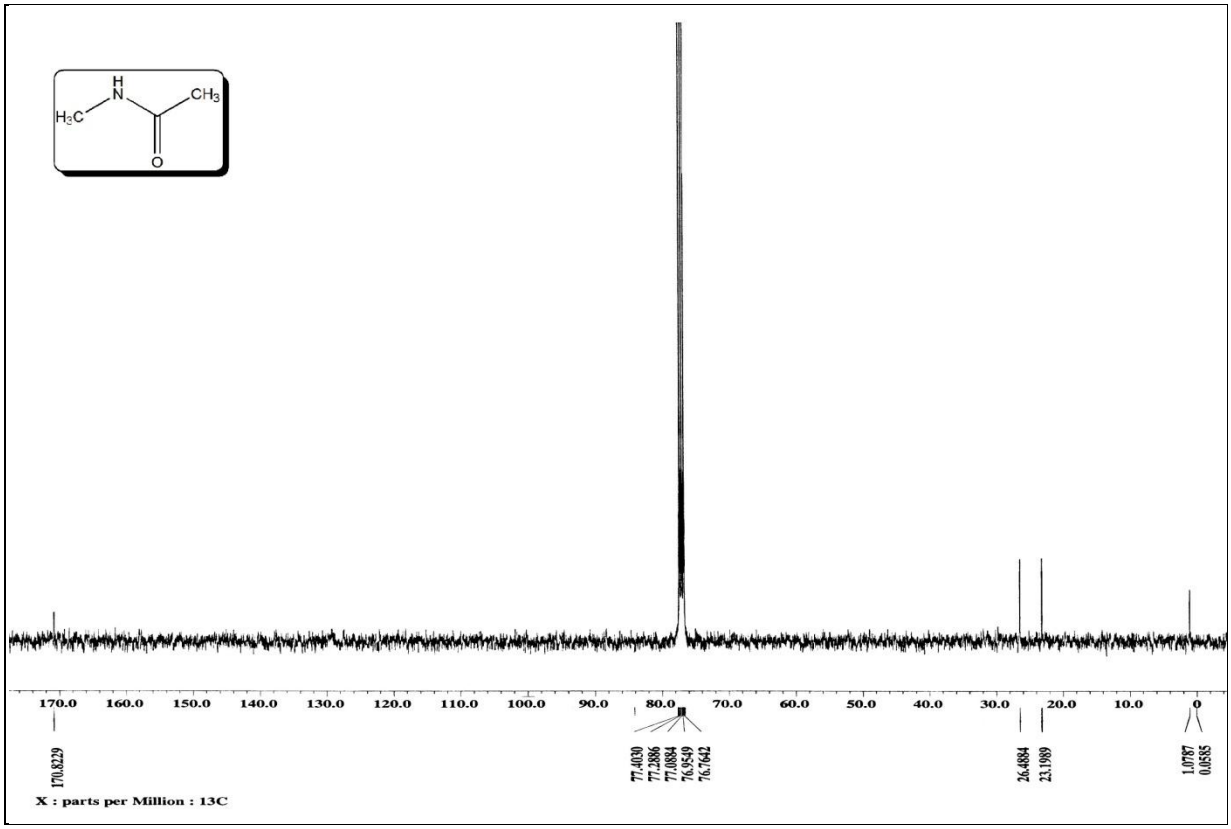
(X) **^{13}C NMR (100 MHz, $CDCl_3$): *N*-(4-Methoxy-phenyl)-acetamide (Table 6, entry 7)**



(Y) **^{1}H NMR (400 MHz, $CDCl_3$): *N*-Methyl-acetamide (Table 6, entry 12)**



(Z) **^{13}C NMR (100 MHz, $CDCl_3$): *N*-Methyl-acetamide (Table 6, entry 7)**



(8) References:

1. (a) A. Bhatnagar, E. Kumar and M. Sillanpaa, *Chem. Eng. J.* 2010, **163**, 317, (b) A. I. Y. Tok, F. Y. C. Boey and X. L. Zhao, *Journal of Materials Processing Technology* 2006, **178**, 270, (c) D. A. Fletcher, R. F. McMeeking and D. Parkin, *J. Chem. Inform. Compu. Sci*. 1996, **36**, 746.
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