Electronic Supplementary Material (ESI) for RSC Advances.

Supporting Information for

Palladium on Manganese ferrite: an efficient catalyst for one pot synthesis of primary amides from iodobenzene.

Vilas Gangadhar Jadhav,[a] Jeevan Manohar Bhojane,[a] and Jayashree Milind Nagarkar[b]

e-mail : jm.nagarkar@ictmumbai.edu.in

Experimental Section.

Materials.

All Chemicals purchased were of analytical grade. $FeCl_3.6H_2O$ and $MnCl_2.4H_2O$ was purchased from MS/ S.D fine Chemicals, iodobenzene derivatives were purchased from Alfa Aesar and used without further purifications.

1. Synthesis of Pd-$MnFe_2O_4$

The catalyst is prepared by sonochemical coprecipitation method with little modification without addition of any capping agent [1]. The Pd incorporated MnFe2O4 nanoparticles were prepared by adding $PdCl_2$ and KCl [2] as electrolytes in to the reaction mixture of $MnFe_2O_4$. The $MnFe_2O_4$NPs were prepared by sonochemical assisted co-precipitation method. The aqueous solutions of iron (III) chloride (9.5 mmol, 50 mL) and manganese (II) chloride tetrahydrate (4.4 mmol, 50 mL) in distilled water were mixed together and placed in an ultrasonic bath (frequency 30 kHz and power of 150 Watts) . To this we added solution (50mL) of $PdCl_2$ (60 mg) and KCl(0.5 g). The temperature of the bath was initially maintained at 27°C. 30 ml of 3M NaOH was added drop wise to this solution, with continuous ultrasound irradiation. The temperature of the bath was then increased up to 60°C and maintained for 30 min and open to the atmosphere which resulted in the blackish brown colored precipitate. The reaction temperature was slowly brought to 80°C, maintained for 1h and then aged overnight at room temperature. The blackish brown colored precipitate was then separated by filtration, washed several times with distilled water and finally with ethanol. The solid product was then further dried in an oven at 120°C for nearly two hour and

finally dried at 200°C for 4h to yield the ferrite catalyst. The synthesized sample by this method was named as Pd–$MnFe_2O_4$ MNPs.

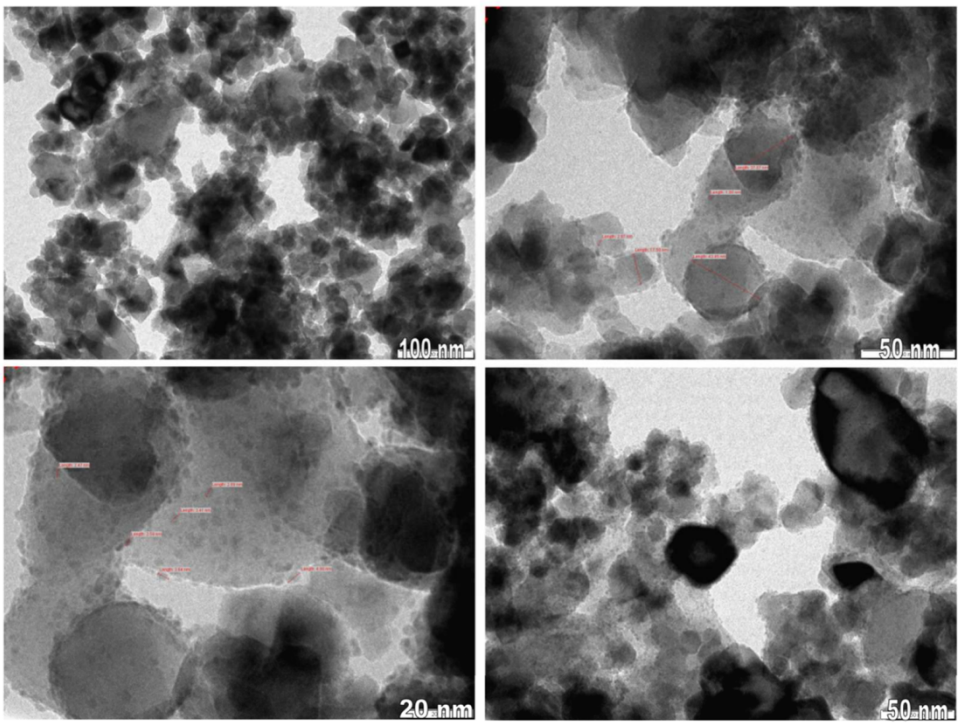


Figure 1: TEM images for Pd-$MnFe_2O_4$ magnetic nanoparticles with different magnifications

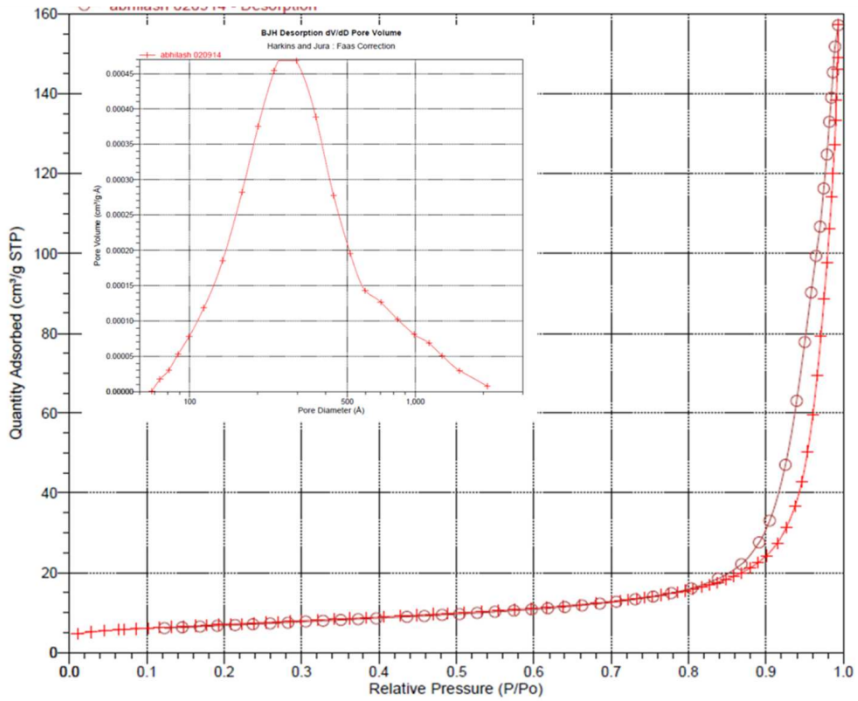


Figure 2: BET surface area and inset corresponding BJH desorption dV/dD pore volume distribution plots.

2. General procedure for one pot synthesis of amides from iodobenene

A clean and dry glass vial charged with iodobenzene (1 mmol), $K_4Fe(CN)_6$ (0.25 mmol), K_2CO_3 (1.2mmol) and DMSO: H_2O (2:1) as a solvent system and Pd-$MnFe_2O_4$ (30 mg,

1mol% Pd). Then vial was screw capped with silicon septum and placed in a oil bath at

110°C and stirred for 18h. After completion of the reaction vial was cooled to room temperature, catalyst was separated magnetically. Water was (5ml) added to reaction mixture and extracted with ethyl acetate (10mL X 2 times). The organic layer is then dried over sodium sulphate. The crude product was purified by column chromatography

(Silica 60-120 mesh) using ether / ethyl acetate (20%) as eluent to give the pure product. Purified product

was characterized by mass spectroscopy and ^{1}H NMR techniques.

3. Spectral Data

[1]HNMR spectras were recorded on Agilent 400MHz, Bruker 300 MHz instrument and 13C were on recorded on 100MHz.

Benzamide: (Table 2 Entry 1) (white solid); mp 126-128 °C GC-MS (EI, 70 eV) m/z (%): 121 (M^+, 74), 105 (99), 77 (100), 51 (37).[1]H NMR (300 MHz, $CDCl_3$): δ 7.92 (d, 2 H, 3*J* = 7.2 Hz, HAr), 7.55-7.52(m,1H, HAr), 7.45-7.42 (m, 2 H, HAr), 3.40 (br, s, 2H, NH). 13C (100 MHz, $CDCl_3$): δ169.8, 133.4, 132.0, 128.7, 127.35 ppm.

2-Methyl Benzamide: (Table 2 Entry 3)

(Off-white solid); 140-142 ºC, GC-MS (EI, 70 eV) m/z (%): 135 (M^+, 81,) 119 (88), 91 (100), 65 (35), 44 (30). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.47-7.37 (m, 3 H), 7.31-7.22 (m, 2 H), 2.50 (s, 3 H). δ 5.88 (br, s, 1 H, NH). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.9, 136.4, 135.0, 130.5, 127.0, 125.8, 20.0 ppm.

4-Nitro, 3- Methyl benzamide: (Table 2 Entry 4)

(Off white solid mp 166-168 ºC,) 1H NMR (400 MHz, DMSO D6): 8.59-8.39 (S, 1H), 8.1-8.3 (d, 1H), 7.73-7.46 (d, 1H), 2.44-2.57 (S, 3H) 13C(100 MHz): 166.06, 149.15, 136.34, 133.74, 133.4, 132.28, 123.84, 19.97 ppm.

GC-MS (EI, 70 eV) m/z (%): 163 (M^+, 100), 147(16.2), 118(36.7), 117(16.1), 89(38.2), 63(23.5), 44(26.8).

2-Methoxy Benzamide (Table 2 Entry 5)

(White solid); mp 126-127 ºC GC-MS (EI, 70 eV) m/z (%): 151 (M^+, 24), 134 (87), 105 (86), 77 (81), 63 (26). **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.2 (dd, *J* = 8.0, 2.0 Hz, 1H),7.74 (br s, 1H), 7.50-7.45 (m, 1H), 7.09 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.01 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.04 (br s, 1H), 3.97 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ167.0, 157.8, 133.4, 132.6, 121.3, 120.7, 111.3, 56.0 ppm.

2- Fluoro benzamide: (Table 2 Entry 6)

(Light brown solid mp 116-118 ºC); GC-MS (EI, 70 eV) m/z (%): 139 (M^+, 75), 123 (100), 95 (90), 75 (34), 44 (19) **^{1}H NMR** (300 MHz, DMSO D_6): δ 7.8 -7.5 (d, 2H), 7.6-7.4 (t, 1H). 7.1-7.3 (t 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 165.7, 160.9, 158.4, 132.93, 132.85, 130.6, 130.64, 124.8, ppm. 19F(DMSO 100 MHz) δ109.01 ppm

4-Methyl Benzamide (Table 2 Entry 7)

(White solid mp 158-160 ºC);**^{1}H NMR** (400 MHz, DMSO D6): δ 7.78-7.62 (dd, 2H), 7.38-7.15 (q, 2H) 2.3(s, 3H);). **^{13}C NMR** (100 MHz, DMSO D6): δ 168.15, 141.1, 131.2, 129, 127.1, 21.3.

GC-MS (EI, 70 eV) m/z (%): 135 (M^+, 81,) 119 (88), 91 (100), 65 (35), 44 (30).

4-Methoxybenzamide (Table 2 Entry 8)

(White solid); mp 166-167 ºC (lit mp 166 ºC); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.80-7.77 (m, 1H), 6.95-6.92 (d, 2H, 3*J* = 8.8 Hz, HAr), 6.0 (br, s, 1H, NH), 3.80 (s, 3 H, OCH3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ168.9, 162.6, 129.3, 125.5, 113.8, 55.0 ppm. GC-MS (EI, 70 eV) m/z (%): 151 (M^+, 51), 135 (100), 107 (18), 92 (19), 77 (34), 64 (14), 44 (12).

4-nitrobenzamide: (Table 2 Entry 9)

(White solid); mp 198-200 ºC **^{1}H NMR** (400 MHz, DMSO D6): δ 8.4-8.2 (d, 2H), 8.2-8.0 (d 2H) 7.8-7.6 (2H NH) **^{13}C NMR** (100 MHz, DMSO D6): δ 167, 149, 141, 129, 124 ppm. GC-MS (EI, 70 eV) m/z (%): 166 (M^+, 61.1), 167(29), 150(100), 120(17.5), 104(35.3),75(27.5), 65(54), 50(32).

3,5 dimethoxy benzamide: (Table 2 Entry 10)

(off white solid 146-148 ºC) **^{1}H NMR** (400 MHz, DMSO D6): δ 8.1-7.78 (S, 1H), 7.5-7.2 (s, 1H), 7.15-6.8 (S, 2H) 6.15-.45 (S, 1H), 3.89 (s , 6H).**^{13}C NMR** (100 MHz, DMSO D6): 167.7, 161.1, 137.4, 105.8, 103.5, 56.1; GC-MS (EI, 70 eV) m/z (%): 181 (M^+, 100), 165(75.4), 137(39), 122(28.9), 107(22.4),
77(18.4), 63(14.7), 44(10.3)

4-Bromobenzamide: (Table 2 Entry 11)

(off white solid); mp 192-193 ºC

^{1}H NMR (400 MHz, DMSO D6): δ 8.1-7.7 (d, 2H), 7.7-7.3(d, 2H)

^{13}C NMR (100 MHz, DMSO D6): 167.3, 133.8, 131.6, 130, 125.4 ppm.

GC-MS (EI, 70 eV) m/z (%): 201 (M^+, 49.4), 199(50.4), 184(94.6), 182(100), 157(40.9),

77(16.1), 75(41).

4-Chlorobenzamide: (Table 2 Entry 12)

(White solid); mp 170-172 ºC GC-MS (EI, 70 eV) m/z (%): 155 (M^+, 53), 139 (100), 111(58), 75 (44), 50 (26), 44 (51) ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 6.00 (br s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ168.4, 133.7, 131.9, 130.5, 127.2 ppm.

3-Flurobenzamide: (Table 2 Entry 13)

(White solid); mp 115-117 ºC GC-MS (EI, 70 eV) m/z (%): 139 (M^+, 75), 123 (100), 95 (90), 75 (34), 44 (19).^{1}H NMR (300 MHz, CDCl3): δ 7.58-7.53 (d, 2H), 7.46-7.23 (d, 2H). 6.10 (br s, 2H).

2-chlorobenzamide:

(off white solid); mp 140-141 ºC **^{1}H NMR** (400 MHz, DMSO D6) 8-7.5 (d, 2H), 7.5- 7.19(m, 2H)

^{13}C NMR (100 MHz, DMSO D6):168.9, 138.1, 130.04, 130.02, 126.9. GC-MS (EI, 70 eV) m/z (%): - 155(M^+, 48), 139(100), 141(35), 113(42) 111(12), 75(25), 50(15)

Nicotinamide.

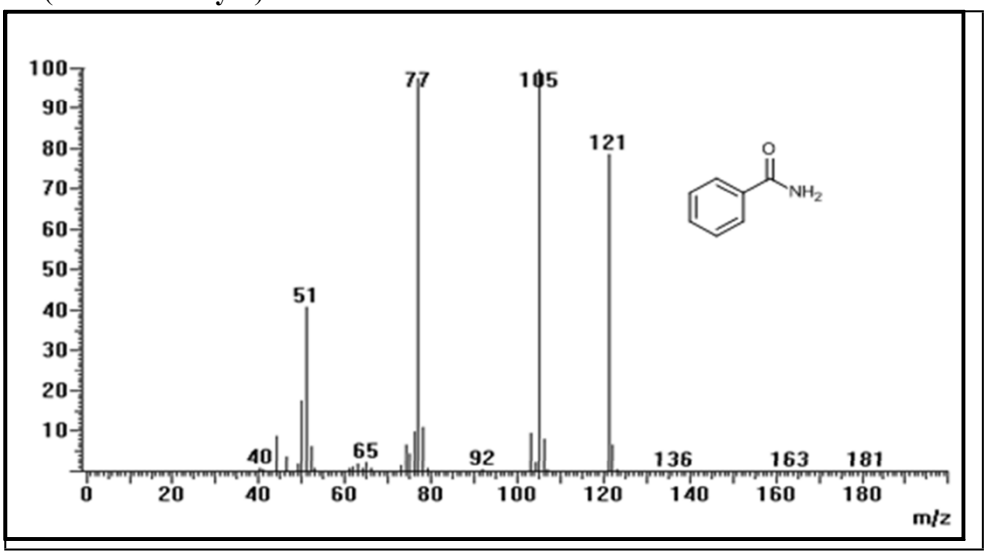
(White solid); mp 127-128 ºC

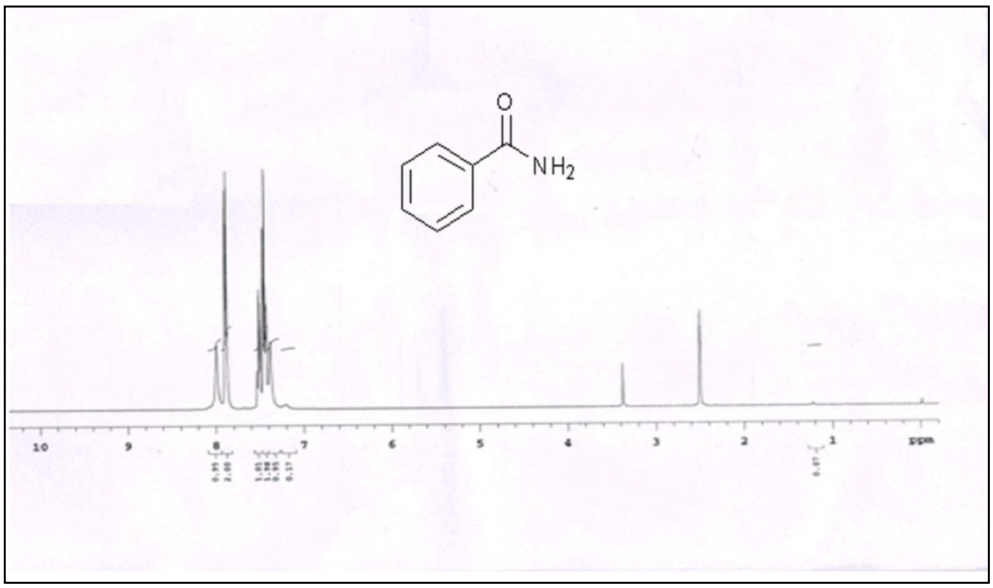
^{1}H NMR (400 MHz, DMSO D6) : 8.1(s, 1H), 8.7-8.6(d, 1H), 8.3-8.2(d, 1H), 7.8-7.4(dd, 1H)

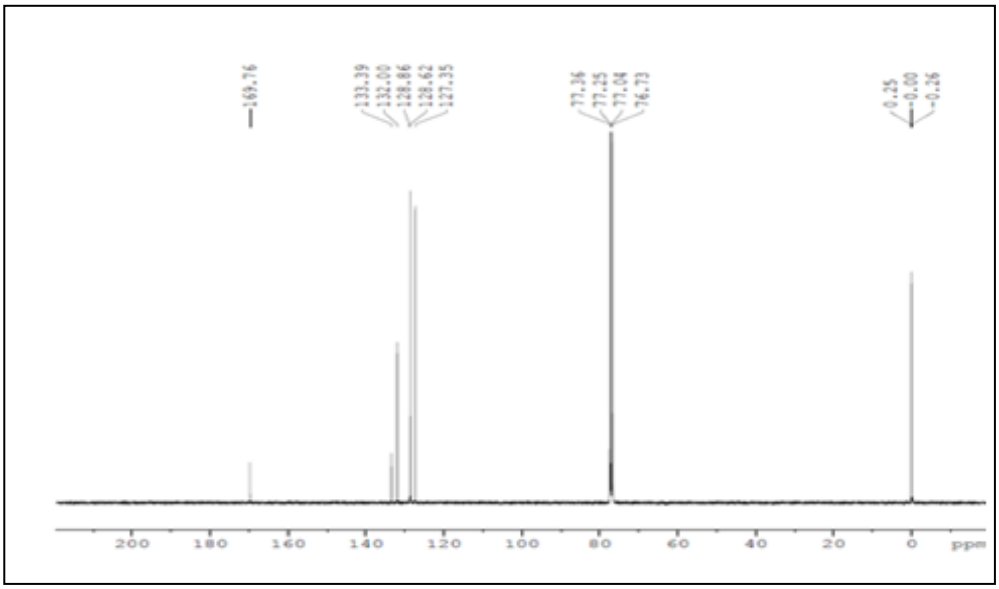
^{13}C NMR (100 MHz, DMSO D6): 166.63, 152.2, 149.4, 140.3, 129.3, 123.88, GC-MS (EI, 70 eV) m/z (%): - 122(M^+ 100), 106(72), 78(83), 94(8.9) 51(45)

4. Mass Spectrum, ^{1}H NMR and 13C NMR spectrum.

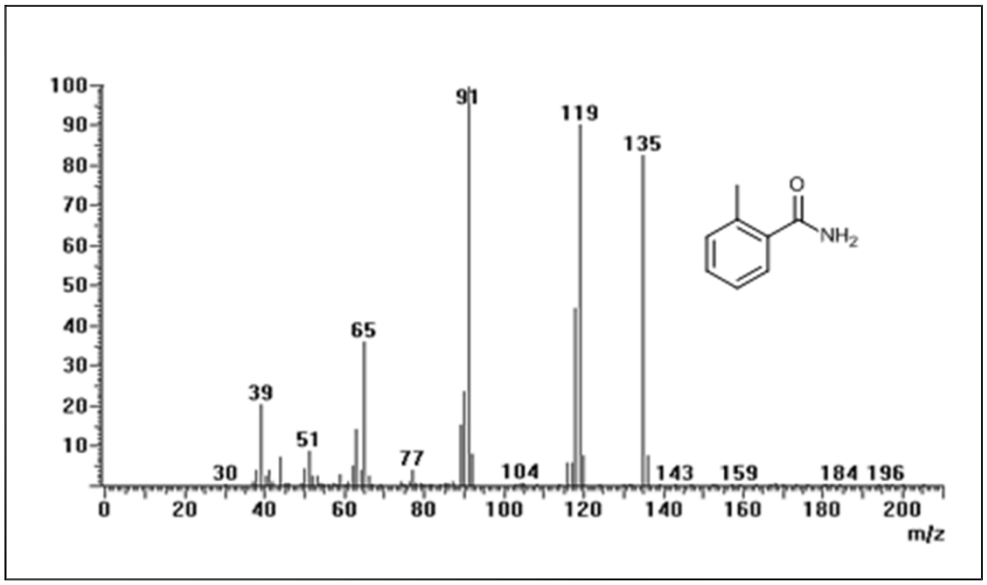
Benzamide: (Table 2 Entry 1)

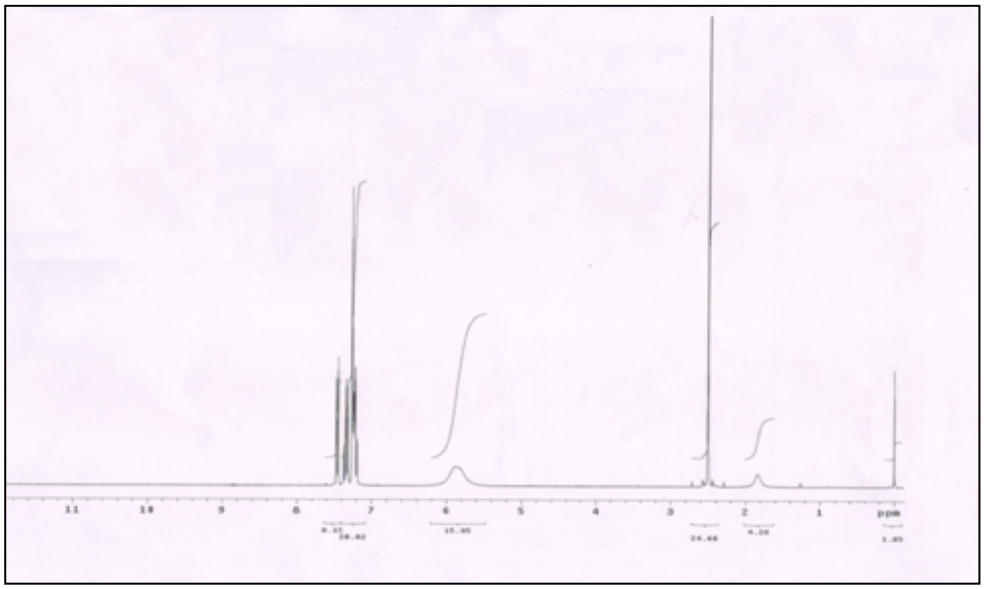


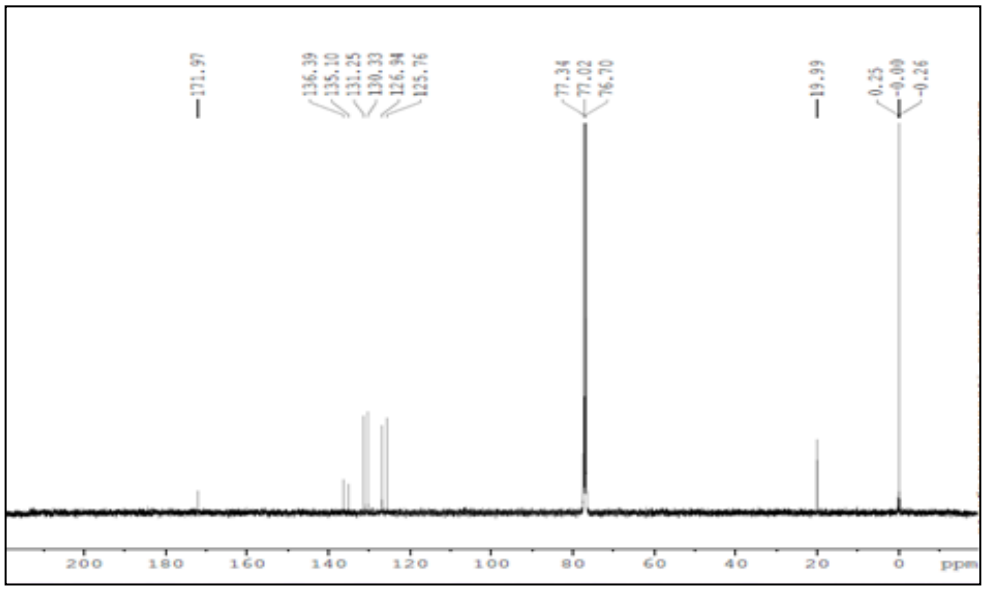




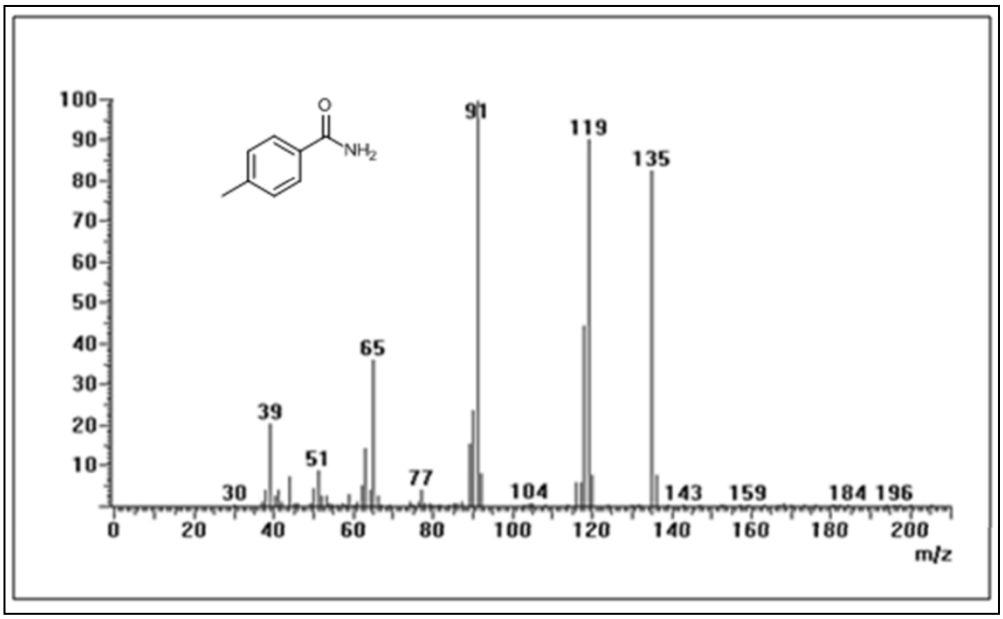
2-Methyl benzamide: (Table 2 Entry 5)

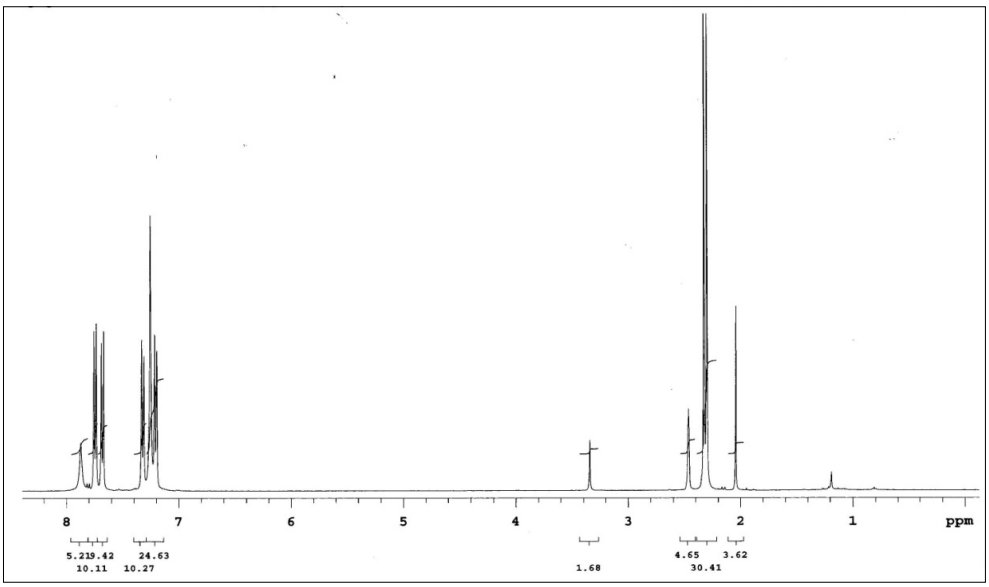


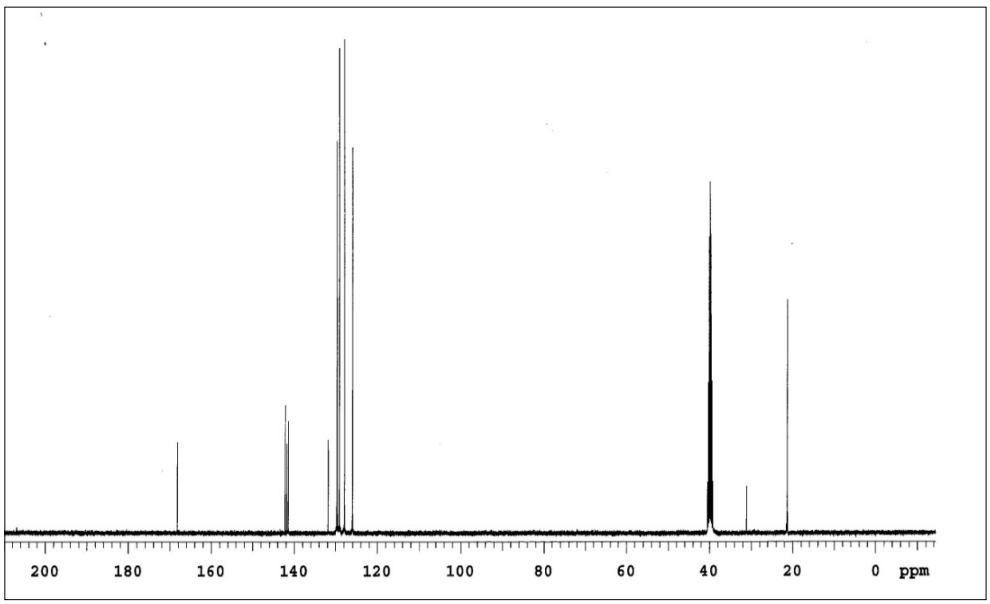




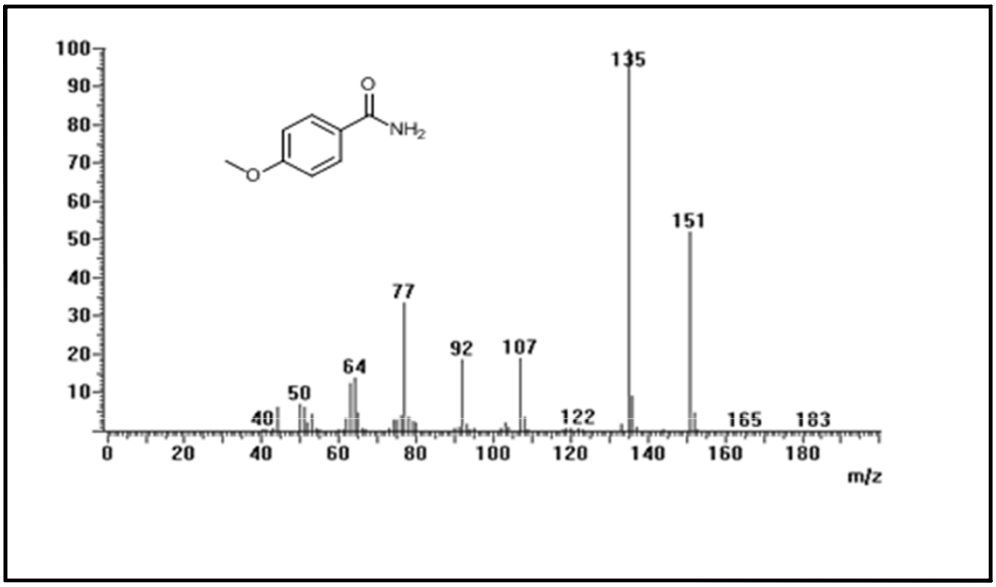
4-Methylbenzamide: (Table 2 Entry 9)

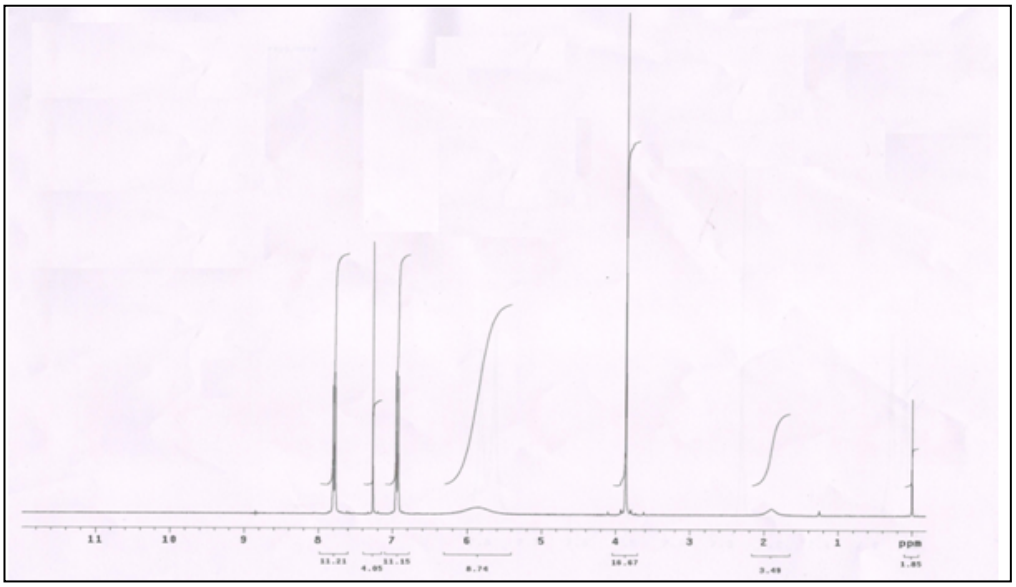


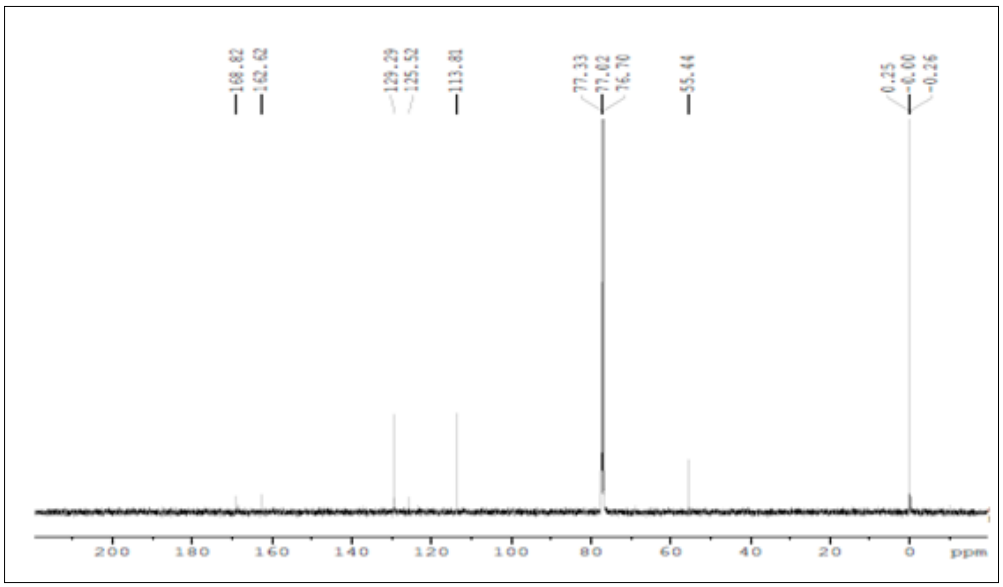




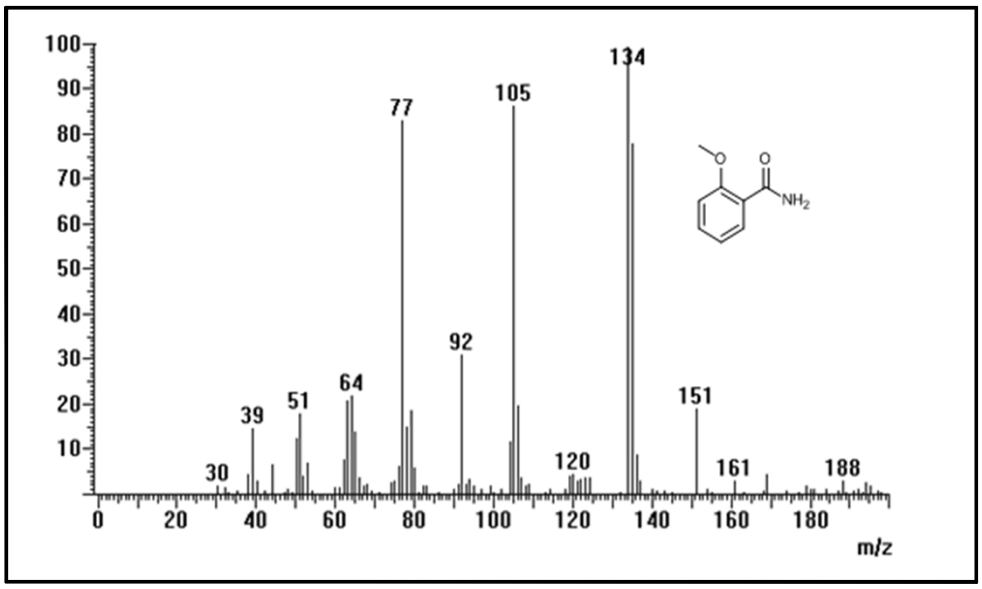
4-Methoxybenzamide (Table 2 Entry 10)

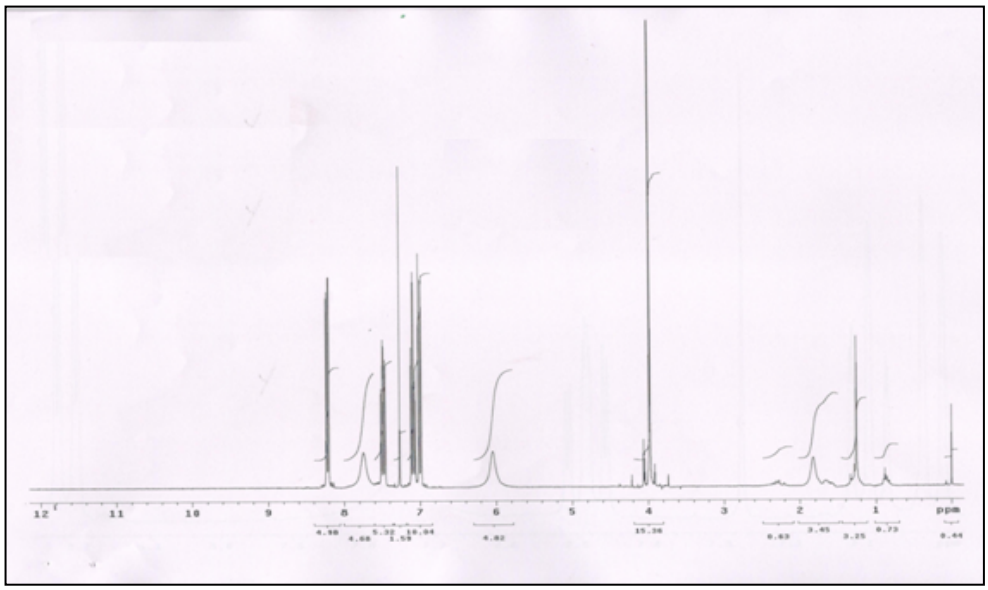


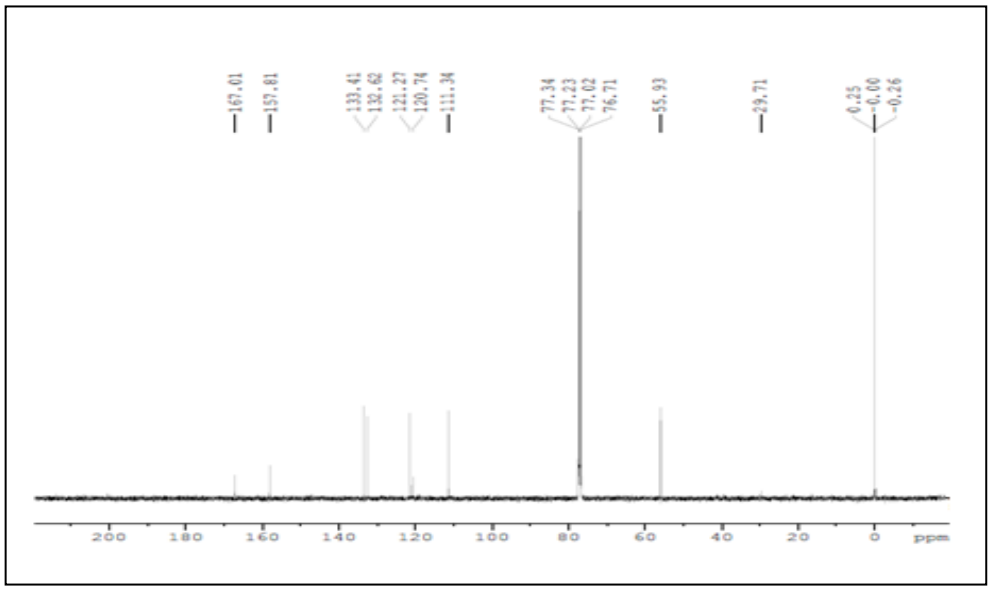




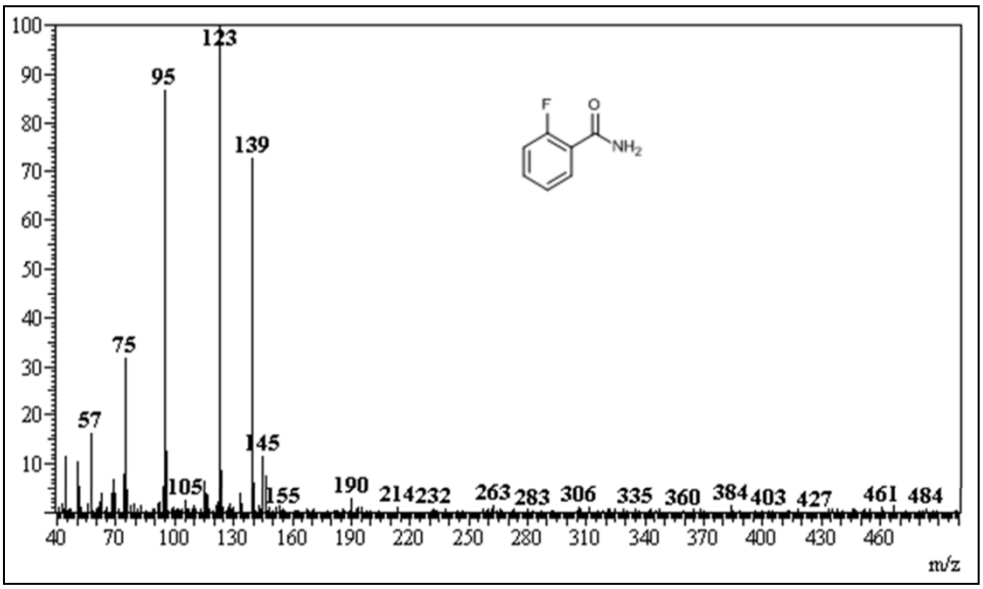
2-Methoxy Benzamide (Table 2 Entry 7)

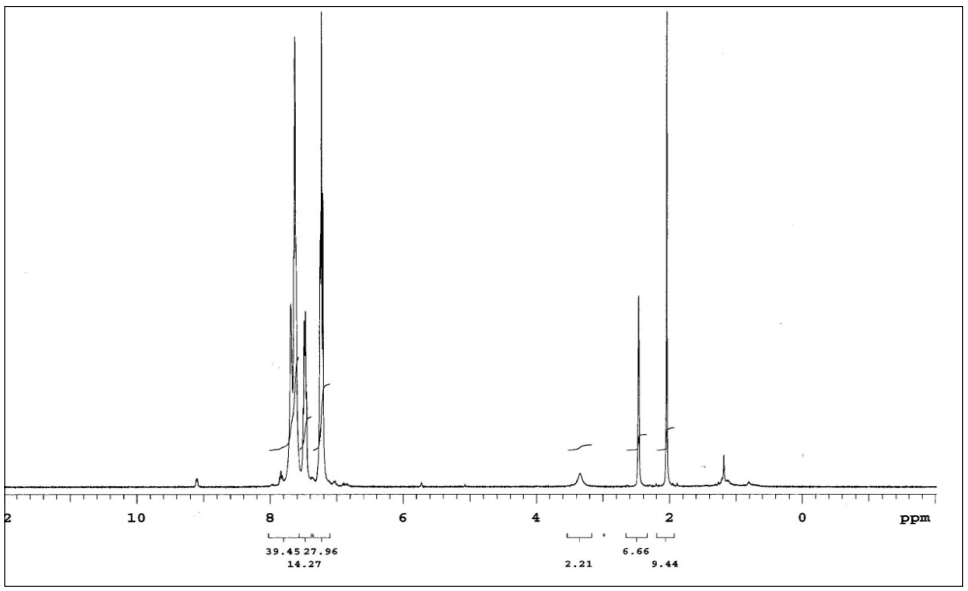


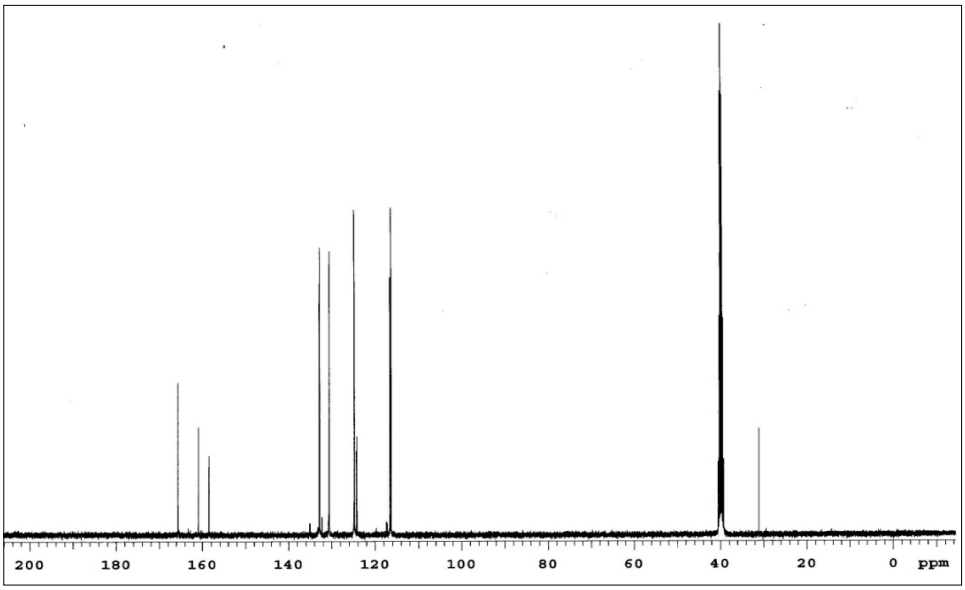




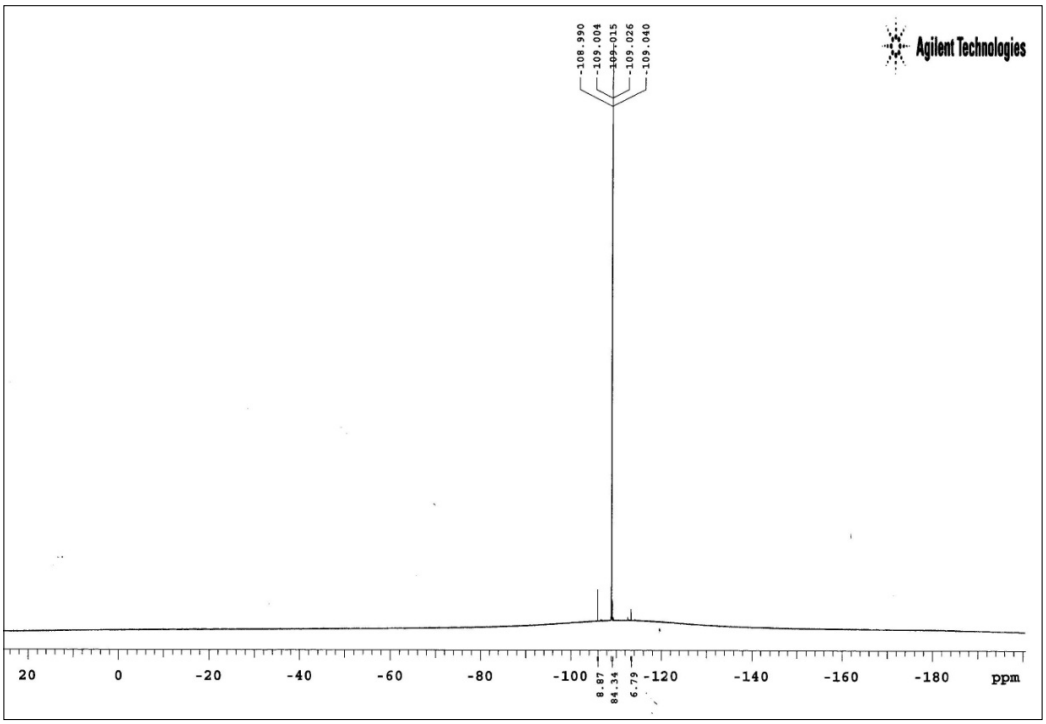
2- Fluoro benzamide: (Table 2 Entry 8)



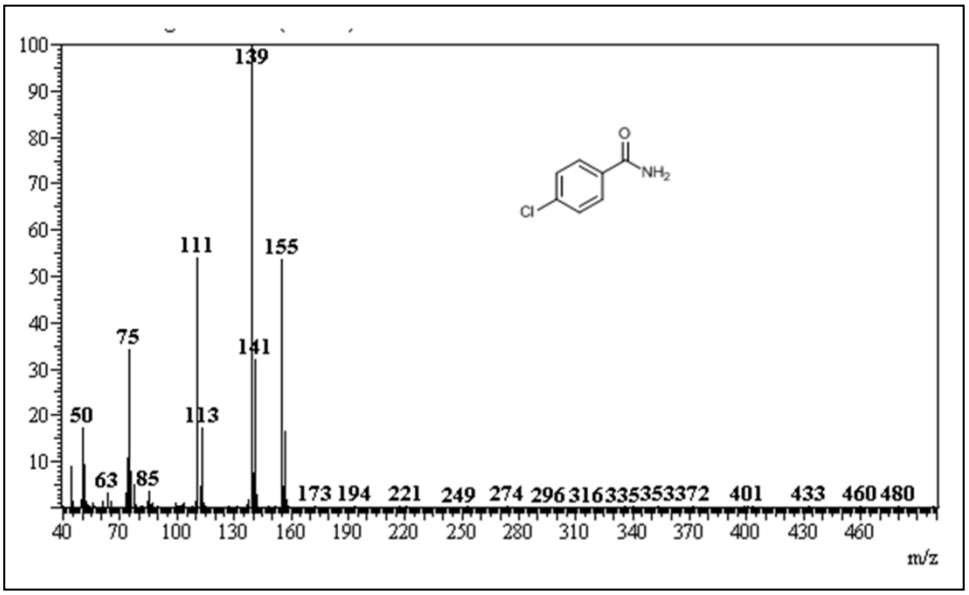


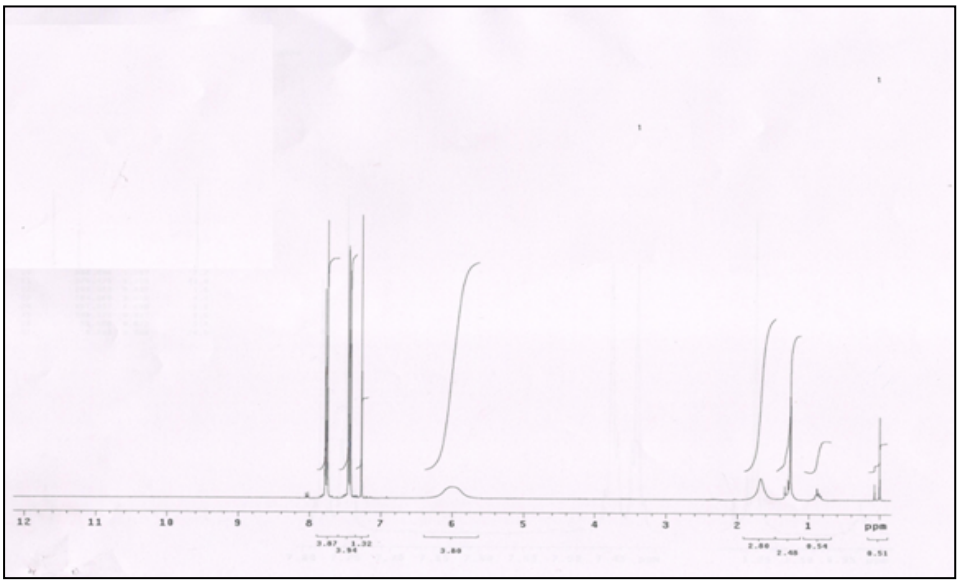

200
180
160
140
120
100
80
60
40
20
0
ppm

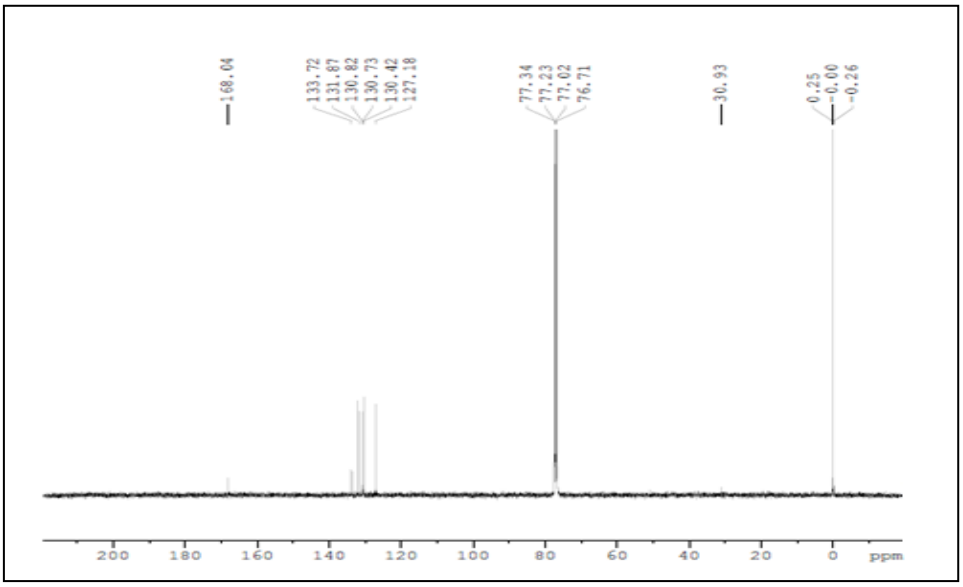
19F NMR


-108.990
-109.004
-109.015
-109.026
-109.040
Agilent Technologies
20
0
-20
-40
-60
-80
-100
-120
-140
-160
-180
ppm
8.87
84.34
6.79

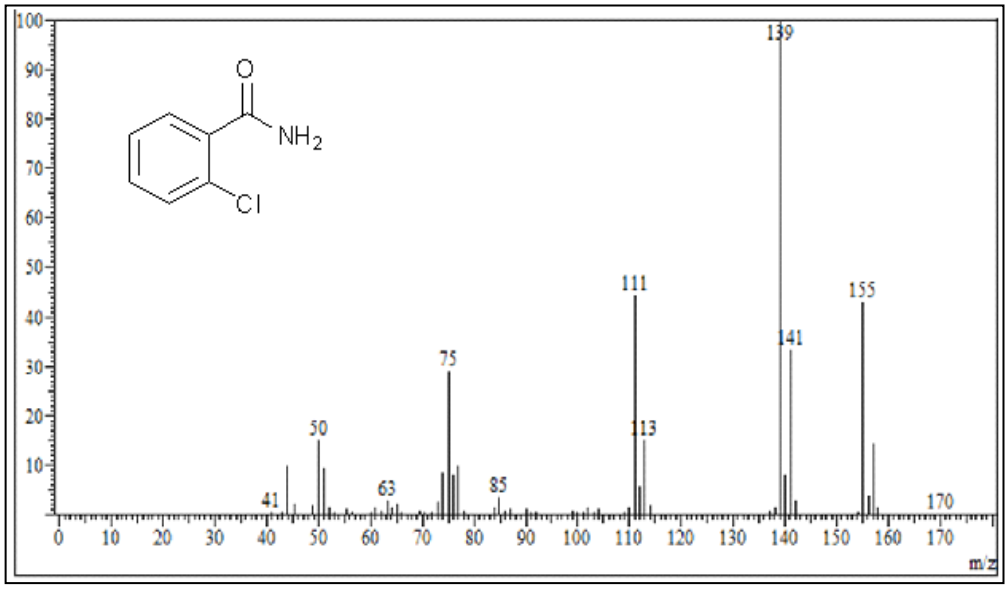
4-Chlorobenzamide: (Table 2 Entry 14)

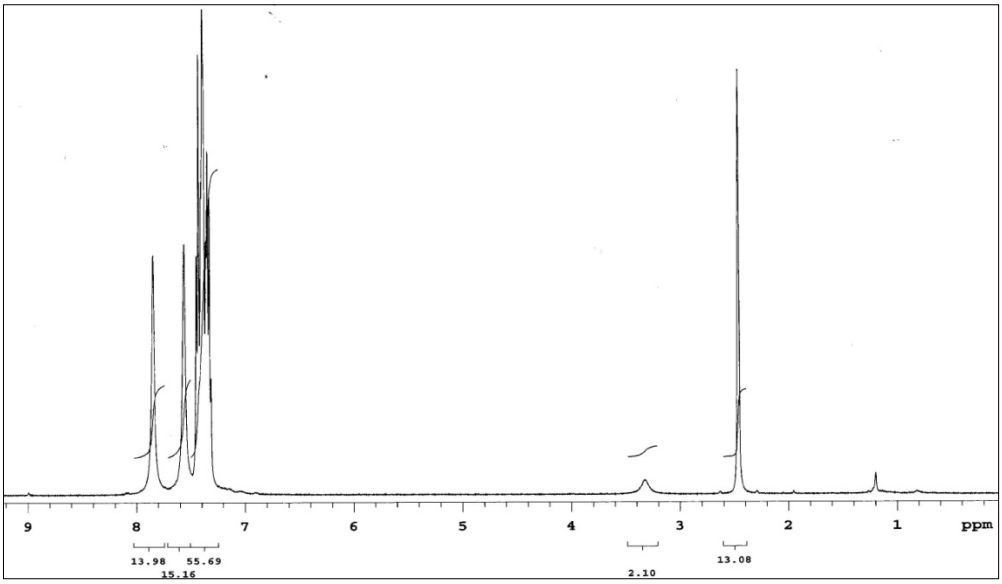


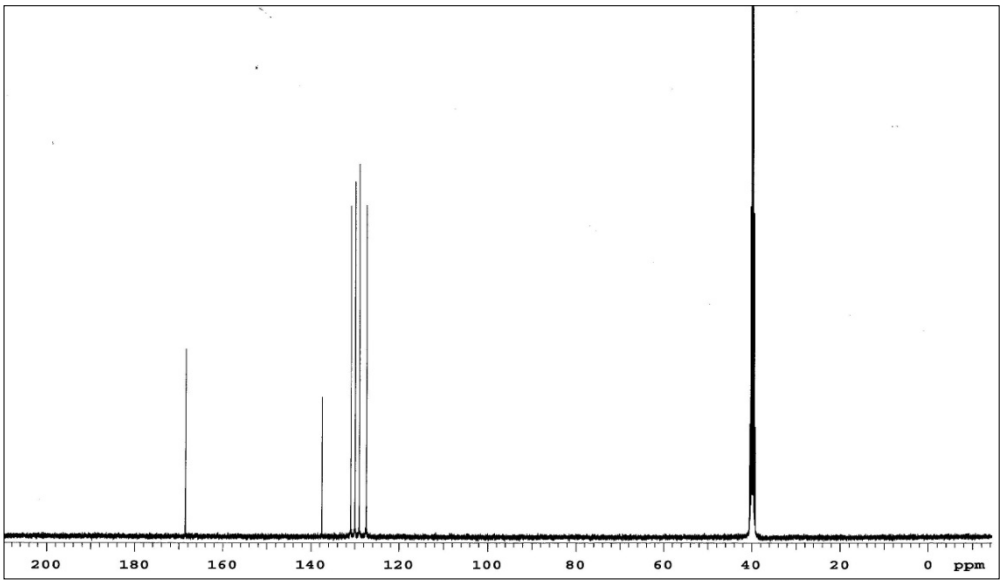




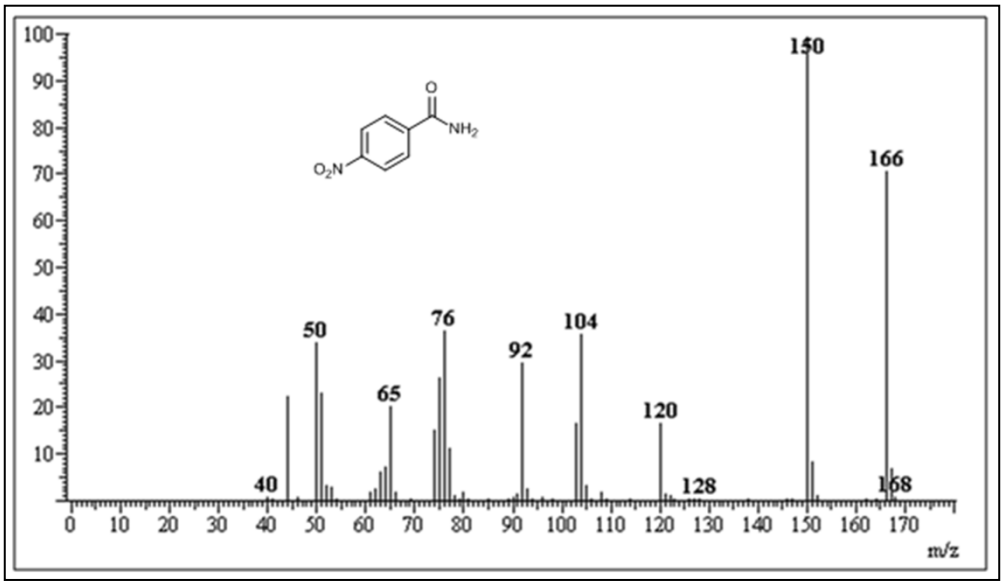
2-chlorobenzamide: (Table 2 Entry 4)

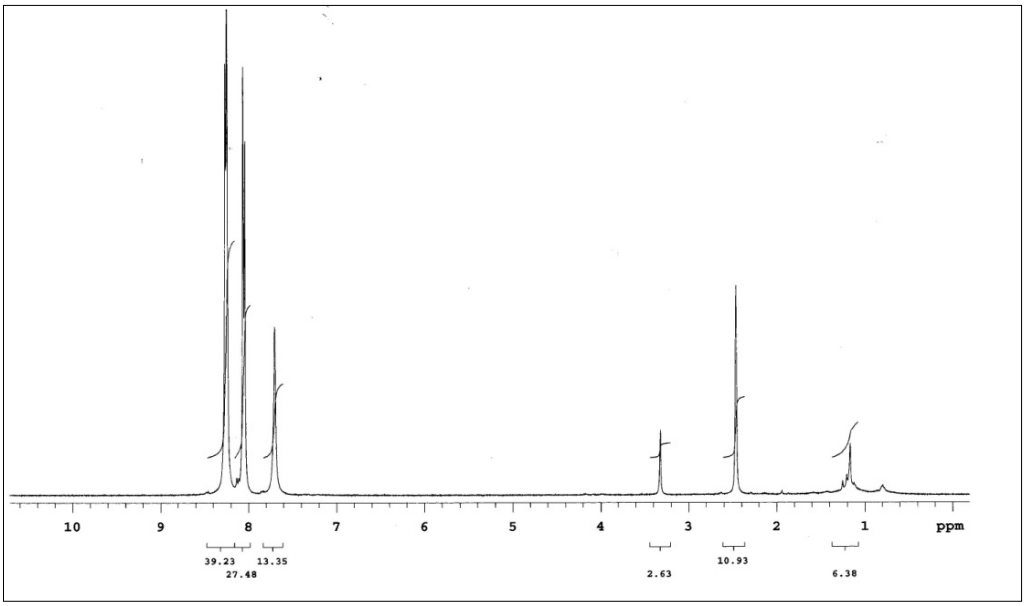


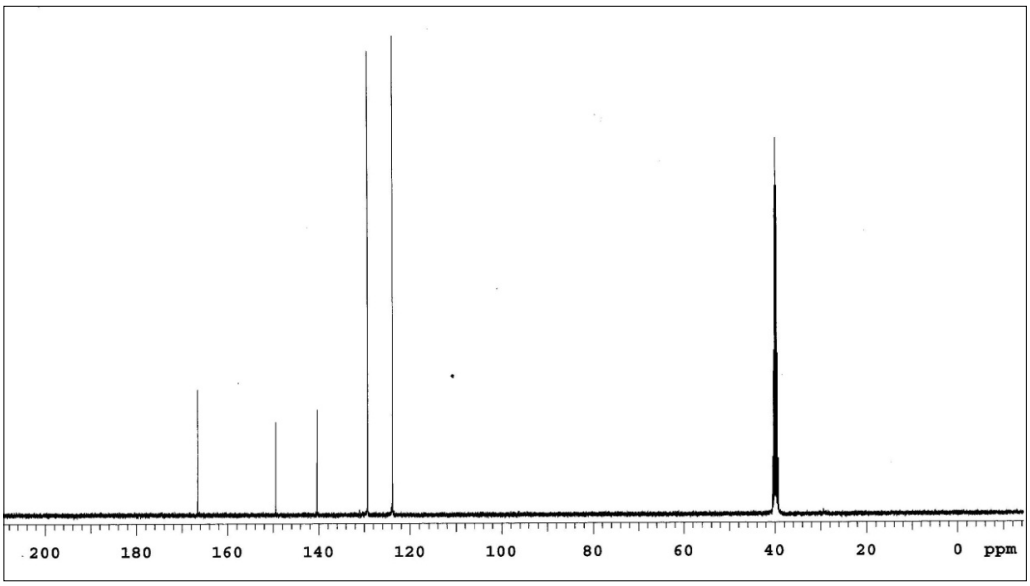




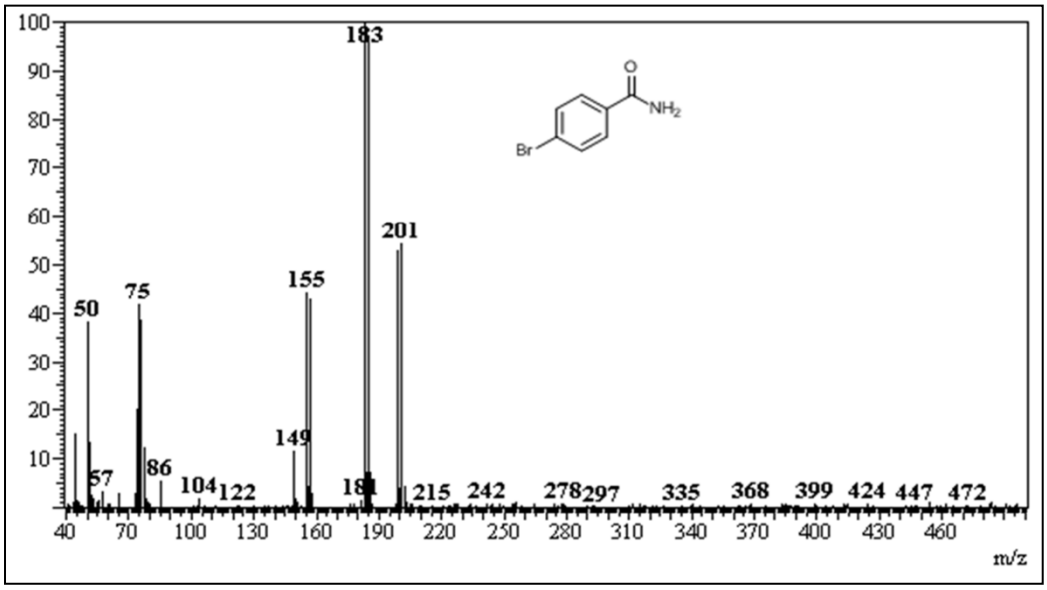
4-nitrobenzamide: (Table 2 Entry 11)

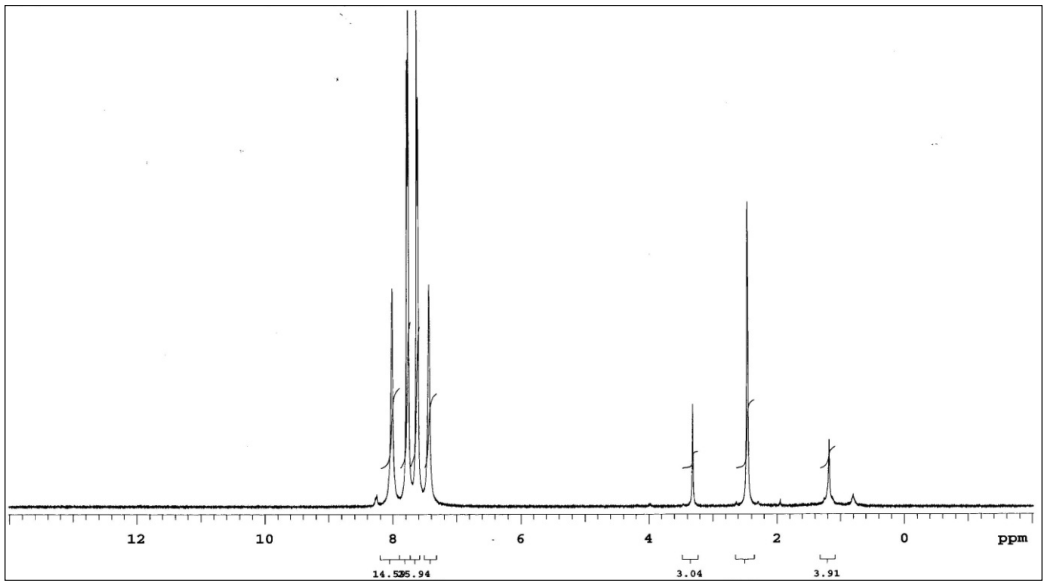


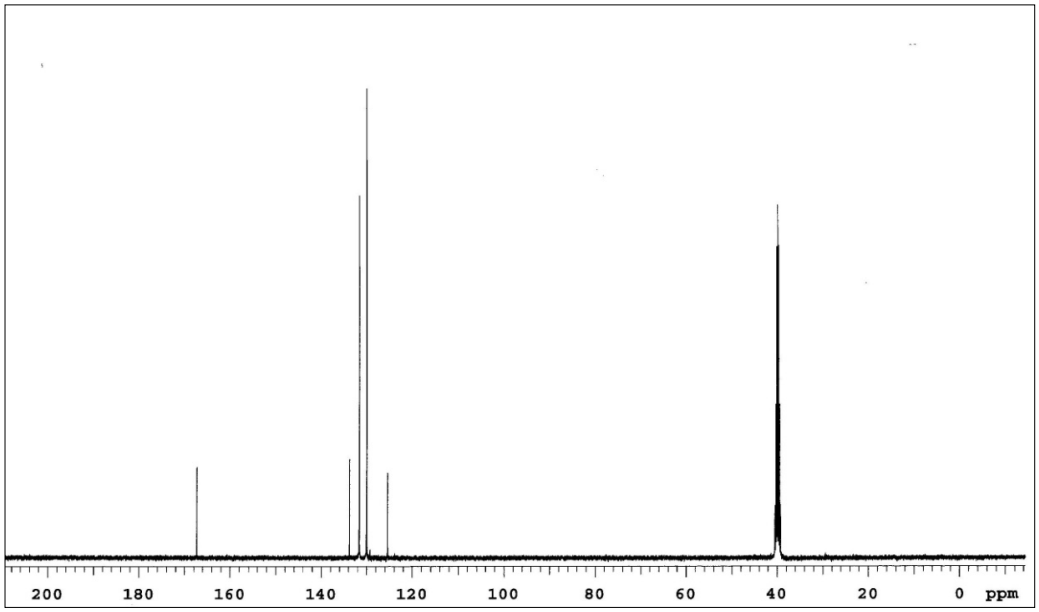




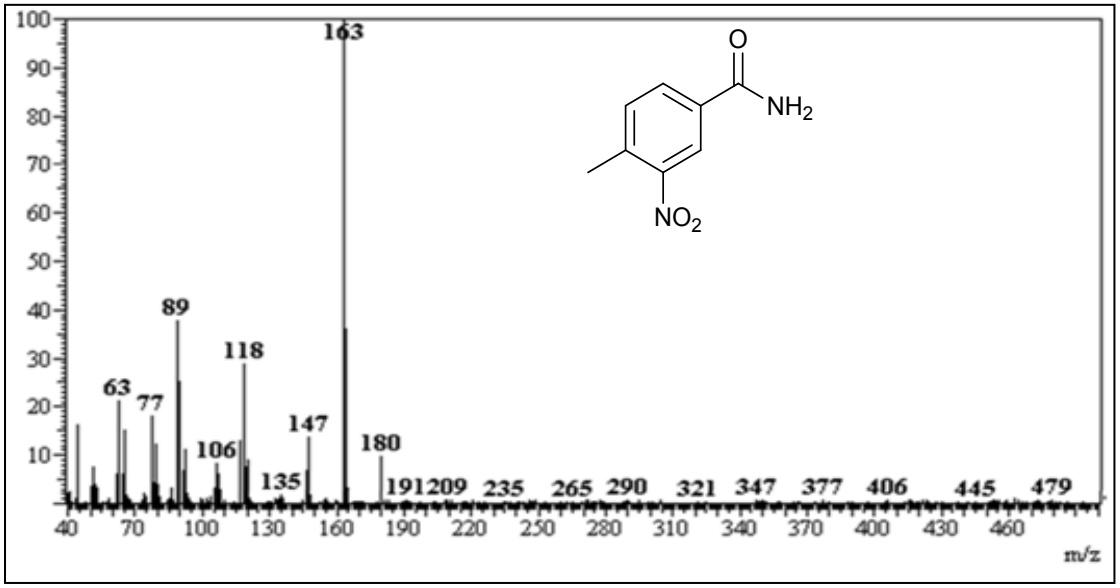
4-Bromobenzamide: (Table 2 Entry 13)

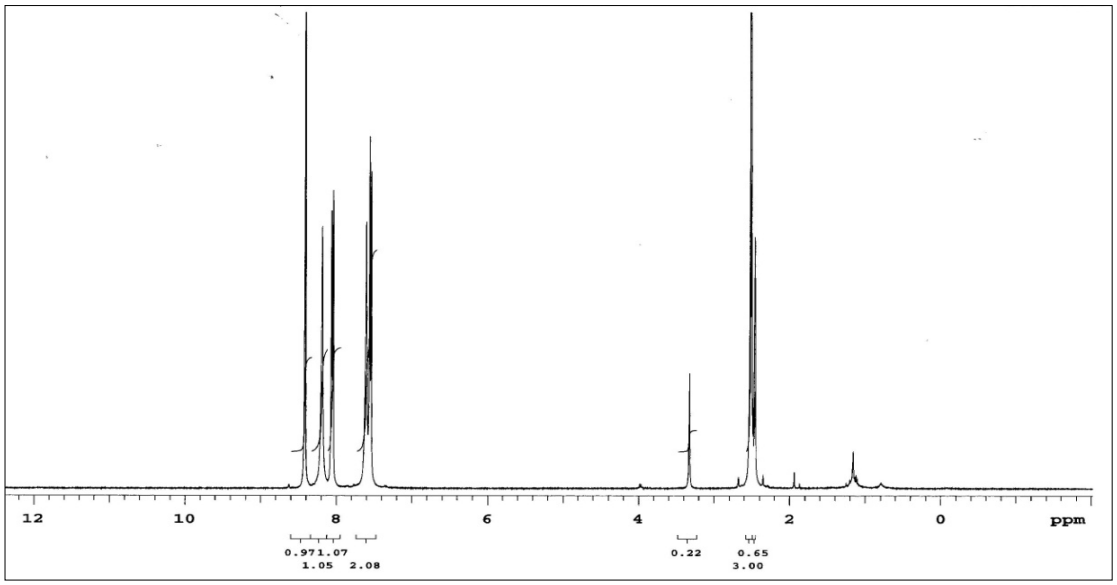


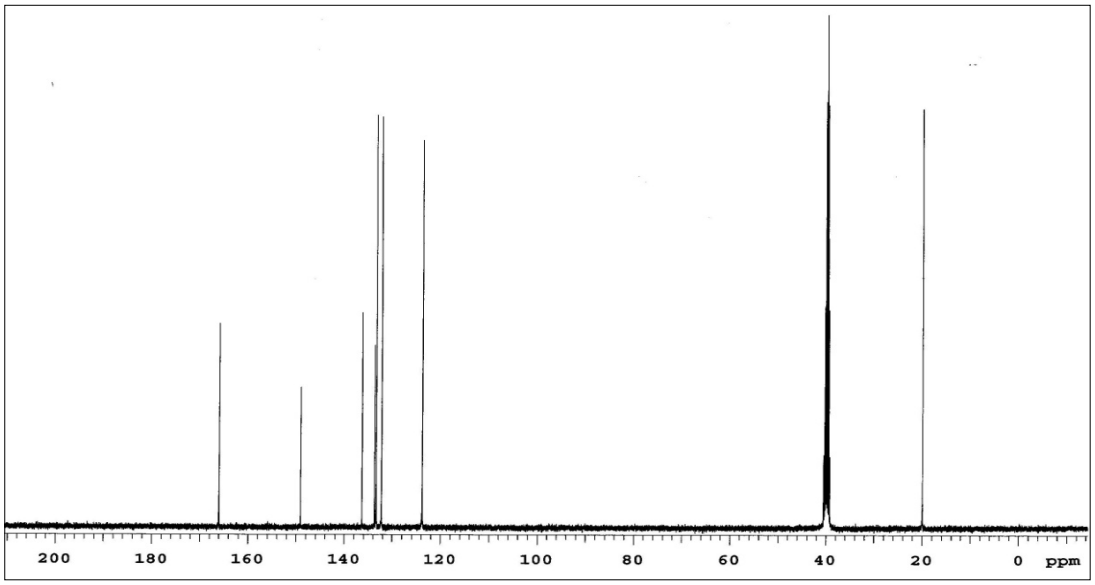




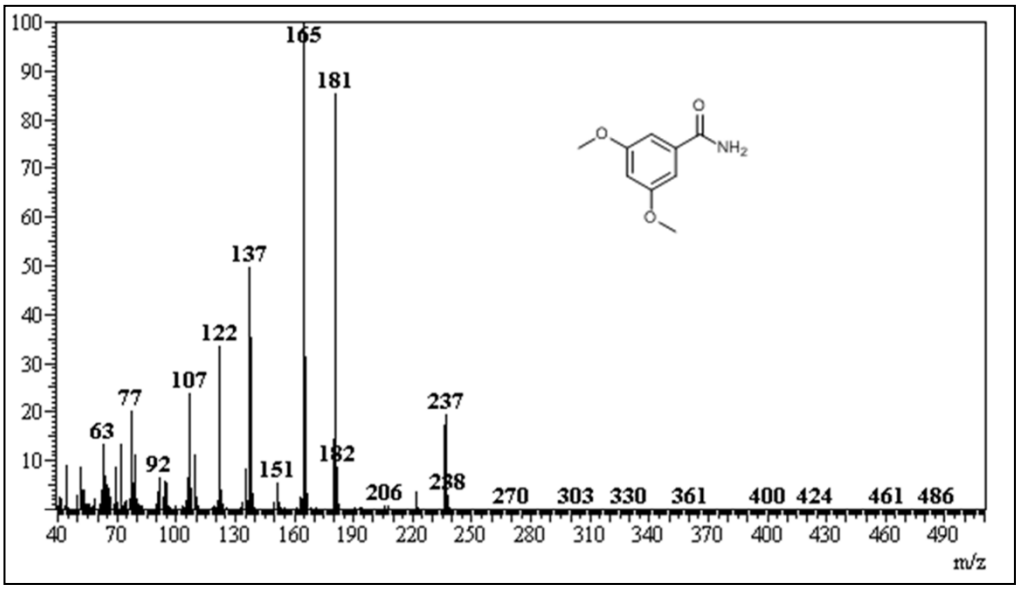
4- Methyl 3-Nitro benzamide: (Table 2 Entry 6)

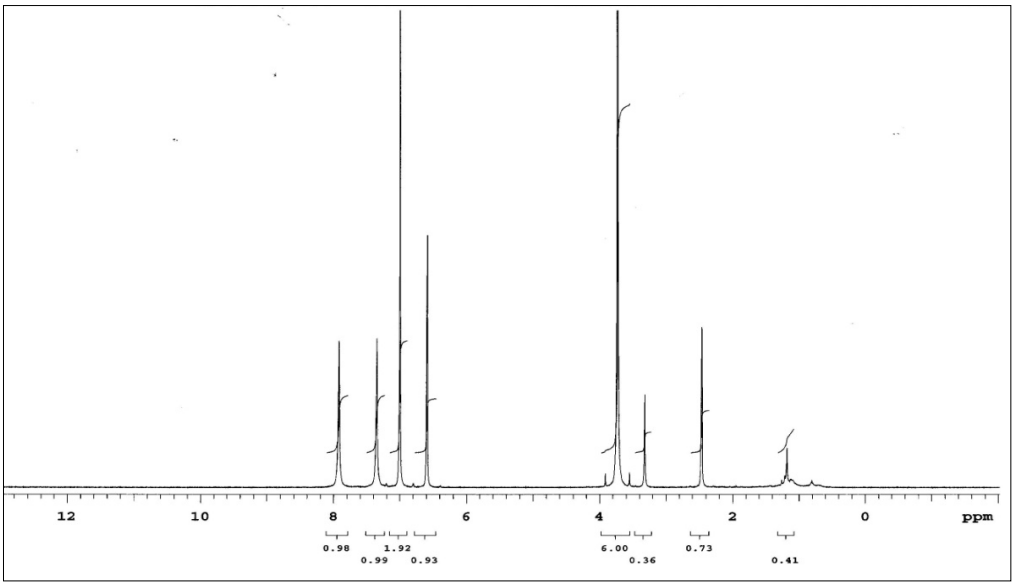


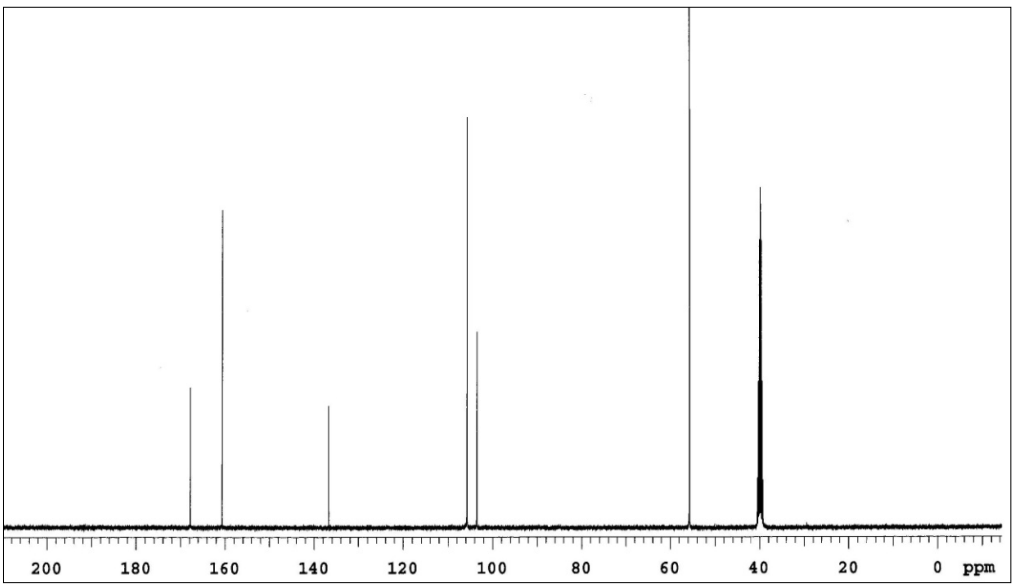




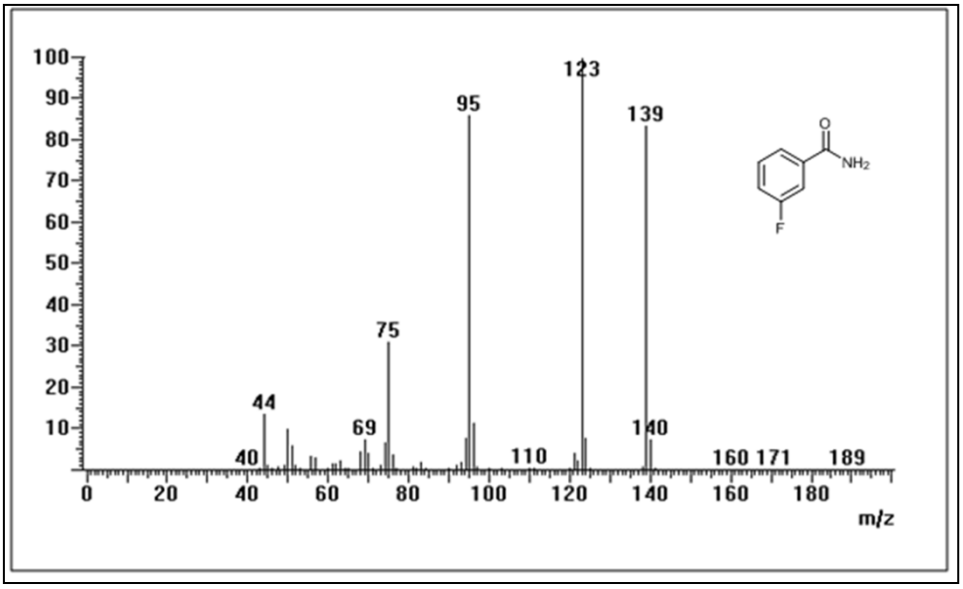
3,5 dimethoxy benzamide: (Table 2 Entry 12)

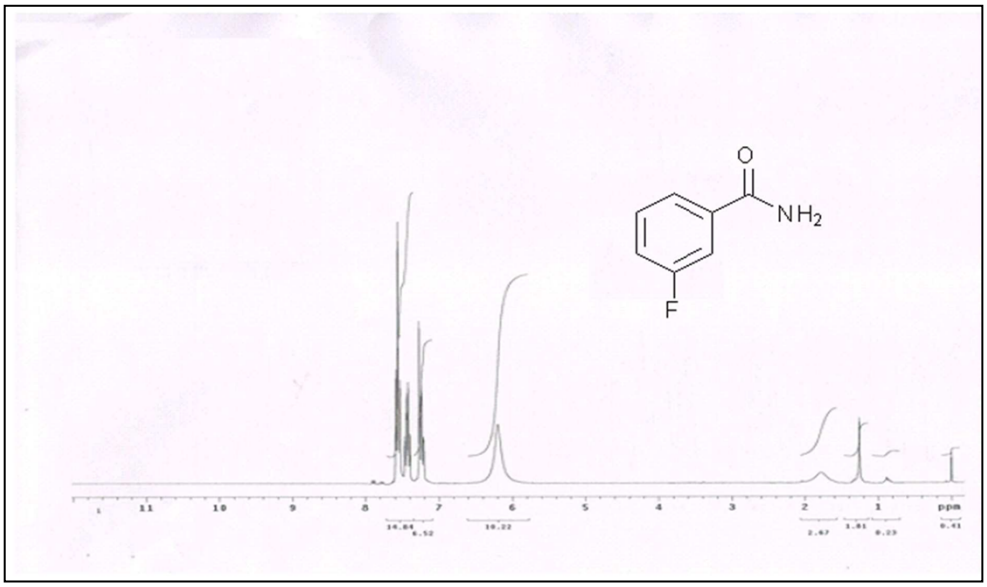


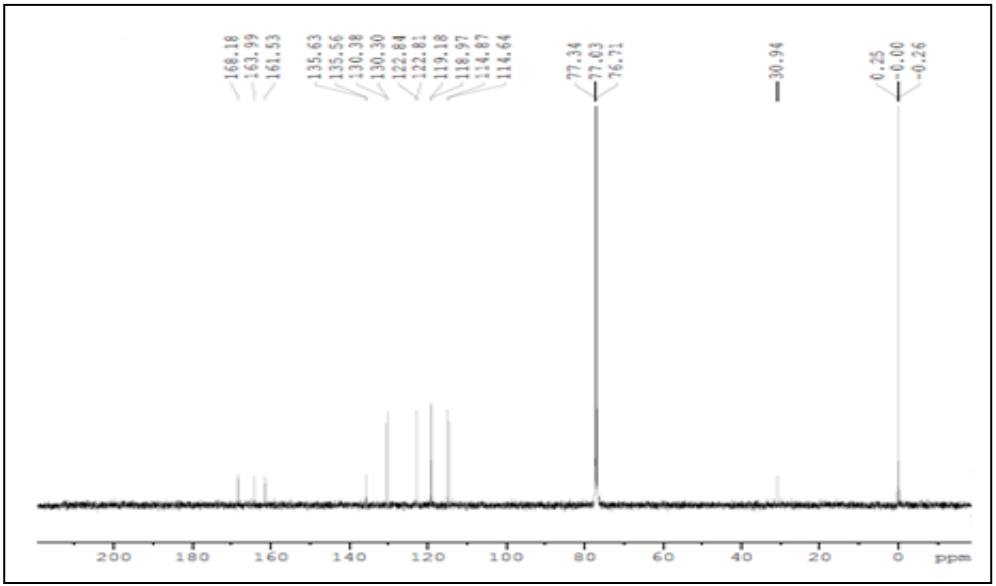




3-Flurobenzamide: (Table 2 Entry 15)







Nicotinamide(Table 2 entry 16)