Supplementary Information

Choline chloride based eutectic solvent: an efficient and reusable solvent system for the synthesis of primary Amides from aldehydes and from Nitriles

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1. Experimental section:

Preparation of deep eutectic solvent (choline chloride: zinc chloride)

Choline chloride (1 mmol) and zinc chloride (2 mmol) were taken in a round bottom flask and heated up to 100 ºC for 30 min. to give colourless transparent liquid. This was used as a eutectic solvent after cooling.

General process for the synthesis of amides from aldehydes

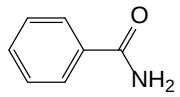
Aldehyde 0.106 gm. (1 mmol), hydroxyl amine hydrochloride 0.069 gm. (1 mmol) and choline chloride: 2 zinc chloride based DES (4 gm) were added in 50 ml round bottom flask and the reaction mixture was stirred at 100 ºC temperatures. The progress of the reaction was monitored by TLC. The product was extracted in ethyl acetate. The solid product was obtained after evaporation of ethyl acetate. The obtained solid was purified by column chromatography over silica (ethyl acetate/n-hexane, 1:2). The pure product was characterized by GC-MS, ^{1}H NMR and ^{13}C NMR.

General process for the synthesis of amides from nitriles

Nitriles 0.103 gm. (1 mmol), water (1 ml) and choline chloride: zinc chloride based DES (4 gm) was added in 50 ml round bottom flask and the reaction mixture was stirred at 100 ºC temperatures. The progress of the reaction was monitored by TLC. The product was extracted in ethyl acetate. The solid product was obtained after evaporation of ethyl acetate. The obtained solid was purified by column chromatography over silica (ethyl acetate/n-hexane, 1:2). The pure product was characterized by GC-MS, ^{1}H NMR and ^{13}C NMR.

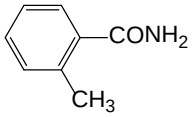
3. Analytical data of products:

1) Benzamide[2] (3a):



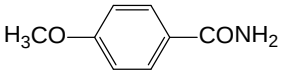
(Off-white solid); mp 127-128 ºC (lit mp 127-128 ºC); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.92 (d, 2 H, 3*J* = 7.2 Hz, HAr), 7.55-7.52(m, 1H, HAr), 7.45-7.42 (m, 2 H, HAr), 3.40 (br, s, 2H, NH). **^{13}C NMR** (100 MHz, $CDCl_3$): δ169.8, 133.4, 132.0, 128.7, 127.35 ppm. **GC-MS** m/z (% relative intensity): 121 (M^+, 74), 105 (99), 77 (100), 51 (37).

2) 2-Methyl Benzamide[2] (3b):



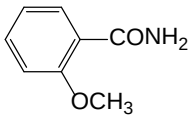
(Off-white solid); 141-142 ºC (lit mp 141-142 ºC); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.47-7.37 (m, 3 H), 7.31-7.22 (m, 2 H), 2.50 (s, 3 H). δ 5.88 (br, s, 1 H, NH). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 171.9, 136.4, 135.0, 130.5, 127.0, 125.8, 20.0 ppm. **GC-MS** m/z (% relative intensity): 135 (M^+, 81, 119 (88), 91 (100), 65 (35), 44 (30).

3) P-Methoxy benzamide[2] (3c):



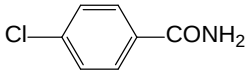
(White solid); mp 166-167 ºC (lit mp 166 ºC); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.80-7.77 (m, 1H), 6.95-6.92 (d, 2H, 3*J* = 8.8 Hz, HAr), 6.0 (br, s, 1H, NH), 3.80 (s, 3 H, OCH3). **^{13}C NMR** (100 MHz, $CDCl_3$): δ168.9, 162.6, 129.3, 125.5, 113.8, 55.0 ppm. **GC-MS** m/z (% relative intensity):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

4) O-Methoxy benzamide[3] (3d):



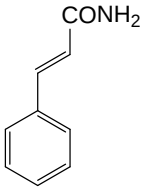
(White solid); mp 127-128 ºC (lit mp 127-128 ºC); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 8.2 (dd, *J* = 8.0, 2.0 Hz, 1H),7.74 (br s, 1H), 7.50-7.45 (m, 1H), 7.09 (dt, *J* = 7.6, 0.8 Hz, 1H), 7.01 (dd, *J* = 8.4, 0.8 Hz, 1H), 6.04 (br s, 1H), 3.97 (s, 3H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ167.0, 157.8, 133.4, 132.6, 121.3, 120.7, 111.3, 56.0 ppm. **GC-MS** m/z (% relative intensity): 151 (M^+, 24), 134 (87), 105 (86), 77 (81), 63 (26).

5) 4-Chlorobenzamide[3] (3f):



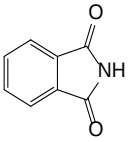
(White solid); mp 171-172 ºC (lit mp 172-173 ºC); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.77 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 8.8 Hz, 2H), 6.00 (br s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ168.4, 133.7, 131.9, 130.5, 127.2 ppm. **GC-MS** m/z (% relative intensity): 155 (M^+, 53), 139 (100), 111(58), 75 (44), 50 (26), 44 (51).

6) Cinnamide[2] (3g):



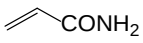
(White solid); mp 149-151 ºC (lit mp 149-150 ºC); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.51-7.48 (m, 3H), 7.37-7.26 (m, 4H), 5.99 (br, s, 1H, NH), 6.48 (d, 1H, 3*J* = 16.0Hz, C=CH). **^{13}C NMR** (100 MHz, $CDCl_3$): δ167.7, 142.6, 134.5, 130.0, 128.9, 127.9, 119.4 ppm. **GC-MS** m/z (% relative intensity): 146 (M^+, 100), 131 (49), 103 (78), 77 (86), 51 (46).

7) Phthalimide[1] (3h):



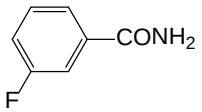
(White solid); mp 237-238 ºC (lit mp 238 ºC); **^{1}H NMR** (300 MHz, DMSO): δ 7.82 (S, 4H), 11.35 (bs, 1H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ 169.46, 134.5, 132.3, 123.1 ppm. **GC-MS** m/z (% relative intensity): 147 (M^+, 100), 104 (70), 103 (32), 76 (93). 50 (37).

8) Acryl amide (3i):



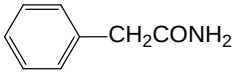
(White solid); mp 84-85 ºC (lit mp 84.5 ºC); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 6.35 -6.15 (m *J* = 8.4 Hz, 2H), 5.74-5.68 (2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ168.0, 130.2, 127.6 ppm. **GC-MS** m/z (% relative intensity): 71 (M^+, 100), 55 (67), 44 (87), 30 (11).

9) 3- Fluoro benzamide (3j):



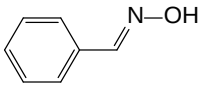
(White solid); mp 115-117 ºC (lit mp 115-117 ºC**), ^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.58-7.53 (d, 2H), 7.46-7.23 (d, 2H). 6.10 (br s, 2H). **^{13}C NMR** (100 MHz, $CDCl_3$): δ168.2, 130.4, 130.3, 114.9, 114.6, ppm. **GC-MS** m/z (% relative intensity): 139 (M^+, 75), 123 (100), 95 (90), 75 (34), 44 (19).

10) 2-Phenylacetamide[2] (3l):



(White solid); mp 155-156 ºC (lit mp 156-157 ºC); **^{1}H NMR** (300 MHz, $CDCl_3$): δ 7.40-7.26 (m, 5H, HAr), 5.57 (br, s, 1H, NH), 3.59(s, 2H, CH2). **^{13}C NMR** (100 MHz, $CDCl_3$): δ173.4, 134.8, 129.2, 127.5, 43.3 ppm. **GC-MS** m/z (% relative intensity): 135 (M^+, 20), 91 (100), 92 (99), 65 (28), 44 (34).

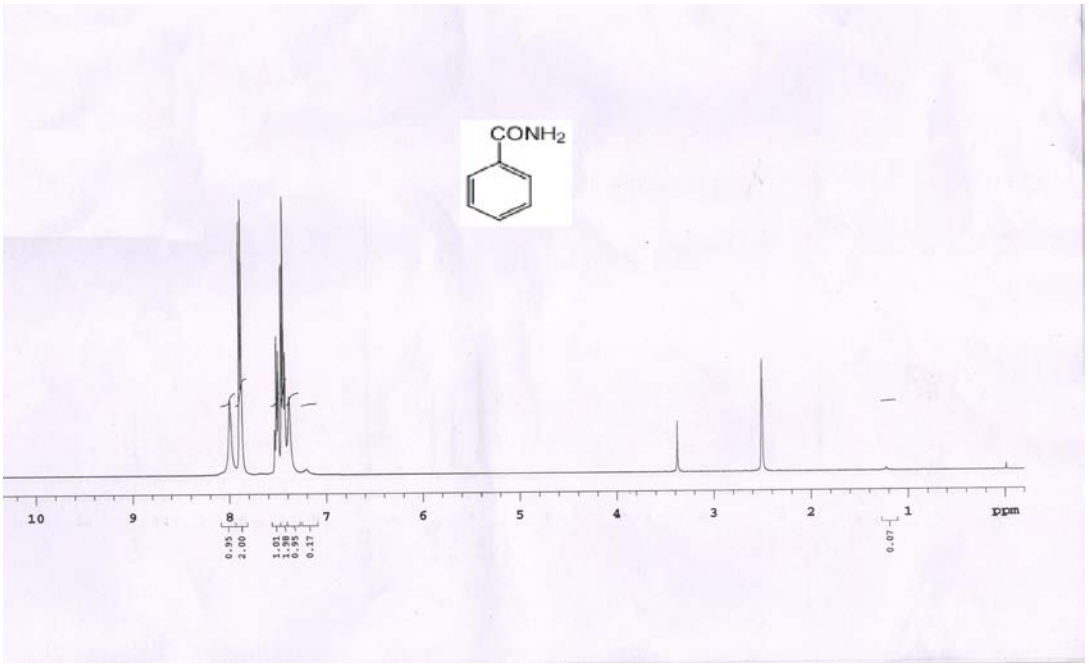
11) Benzaldoxime (5a) :



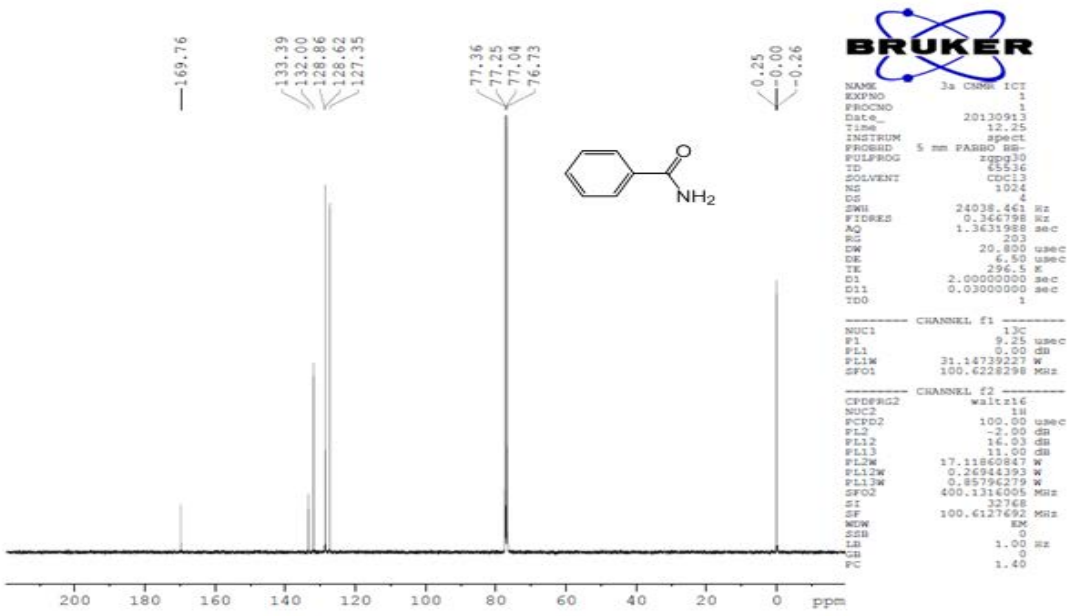
^{1}H NMR (300 MHz, $CDCl_3$): δ 8.20 (s, CH), δ 7.60 (d, 2H), δ 7.40 (d, 3H), δ 2.05 (s OH). **GC-MS** m/z (% relative intensity): 121 (M^+, 100), 103 (21), 94 (26), 78 (70), 51 (48).

1) Benzamide (3a):

^{1}H NMR



^{13}C NMR



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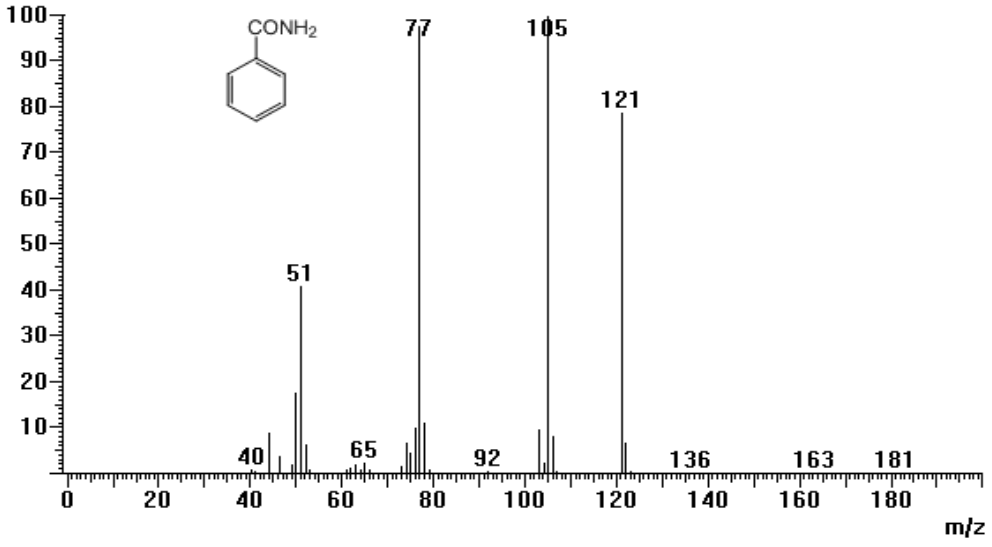
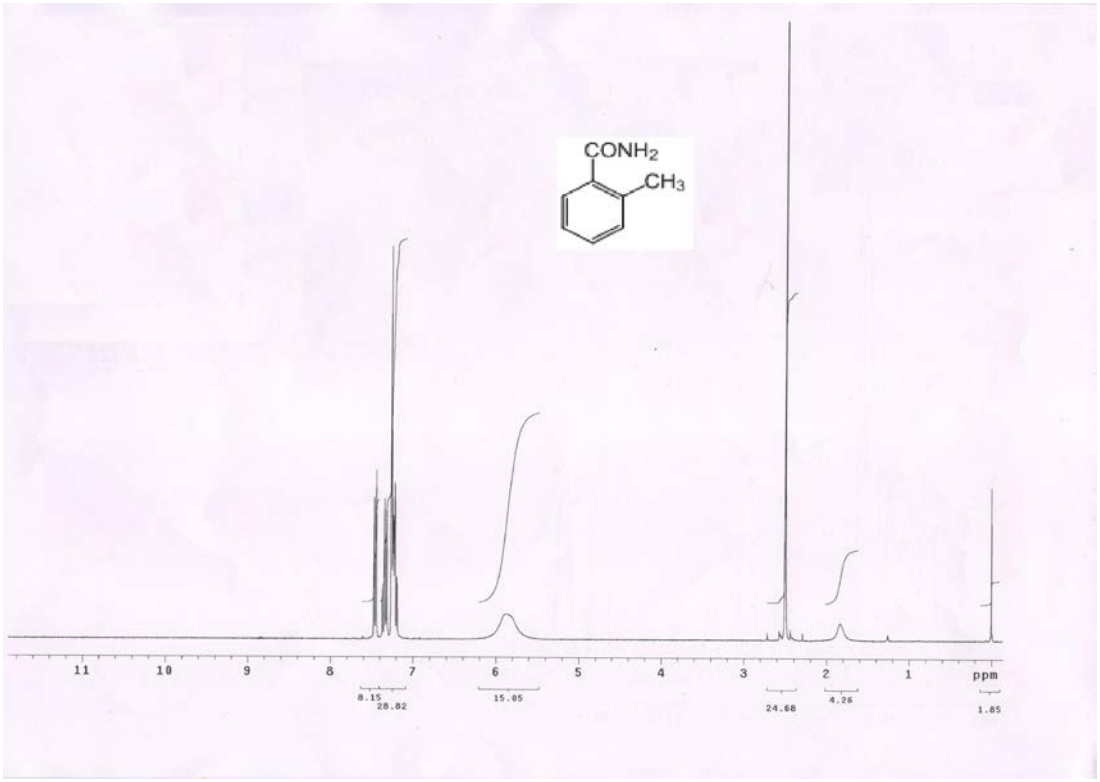
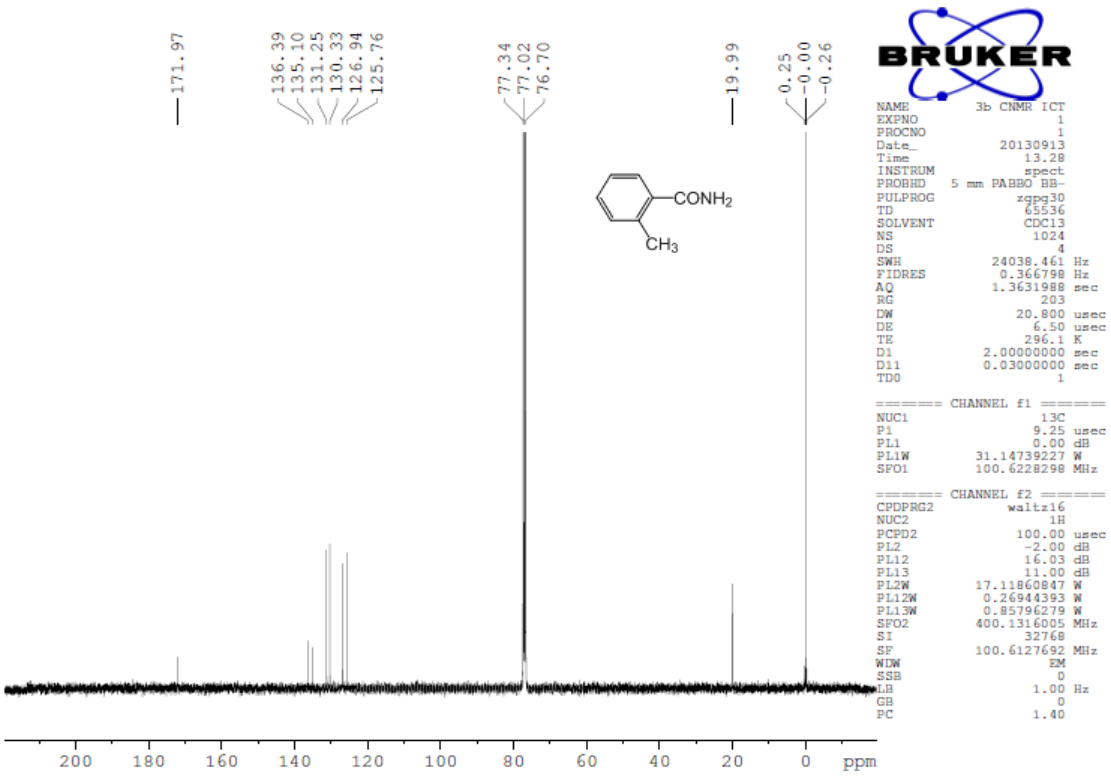


2) 2-Methyl benzamide (3b):

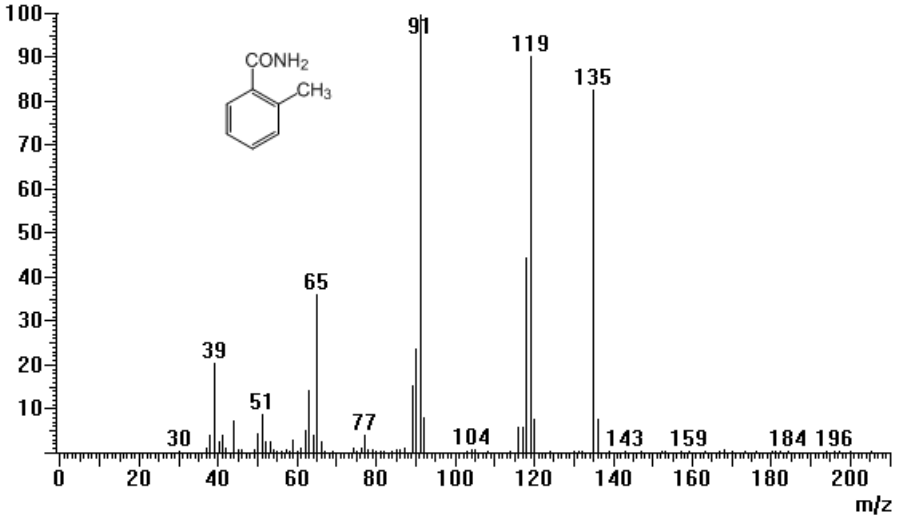
^{1}H NMR



^{13}C NMR

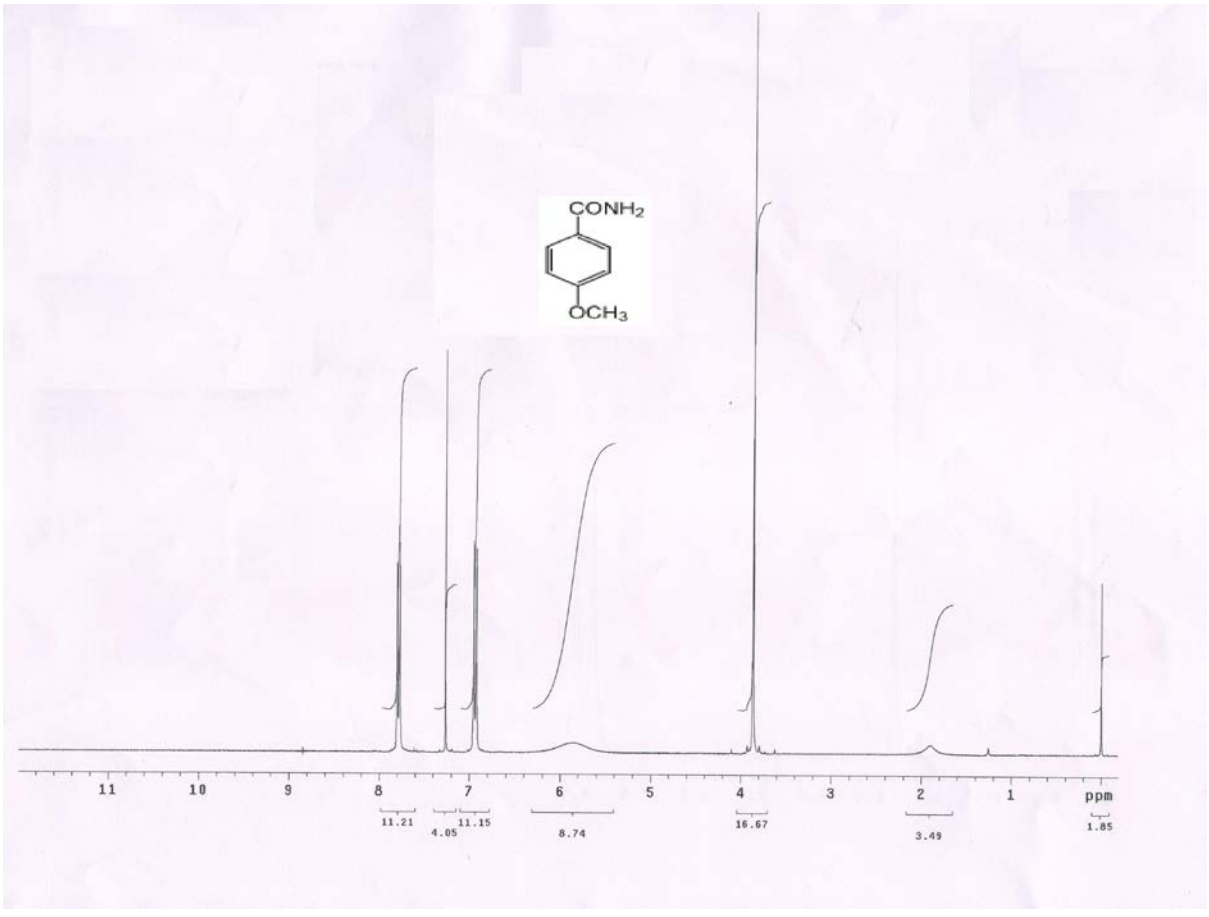


MS

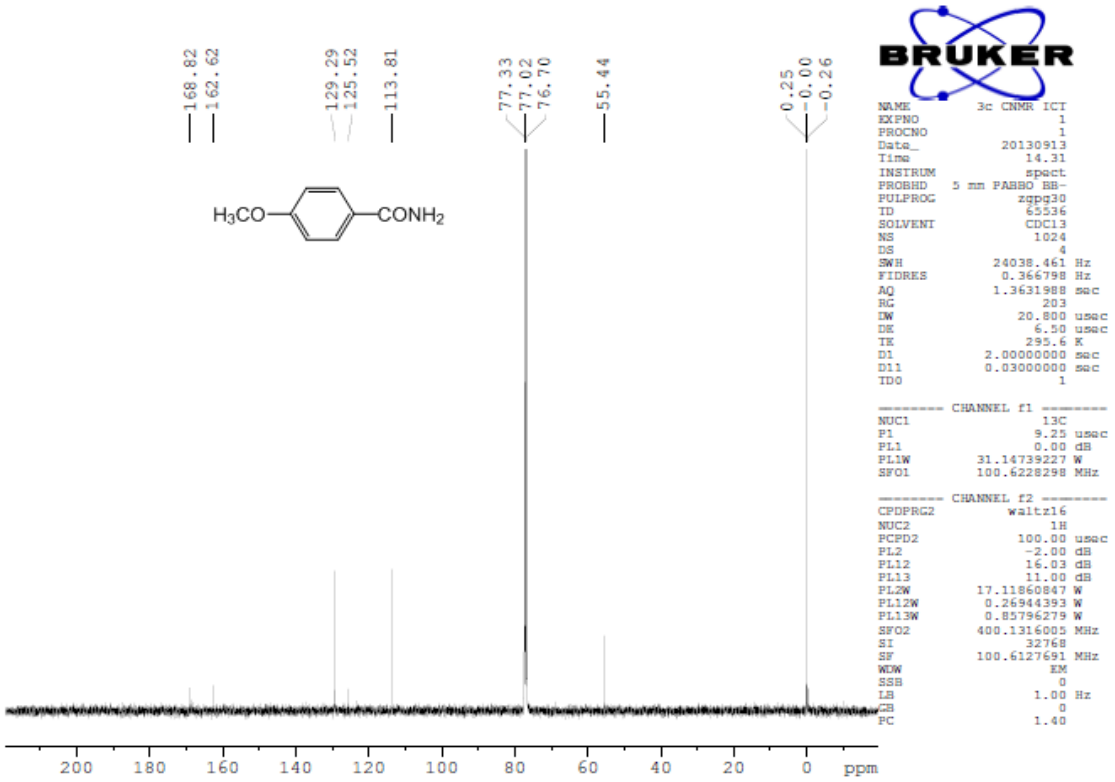


3) P- Methoxy benzamide (3c):

^{1}H NMR



^{13}C NMR



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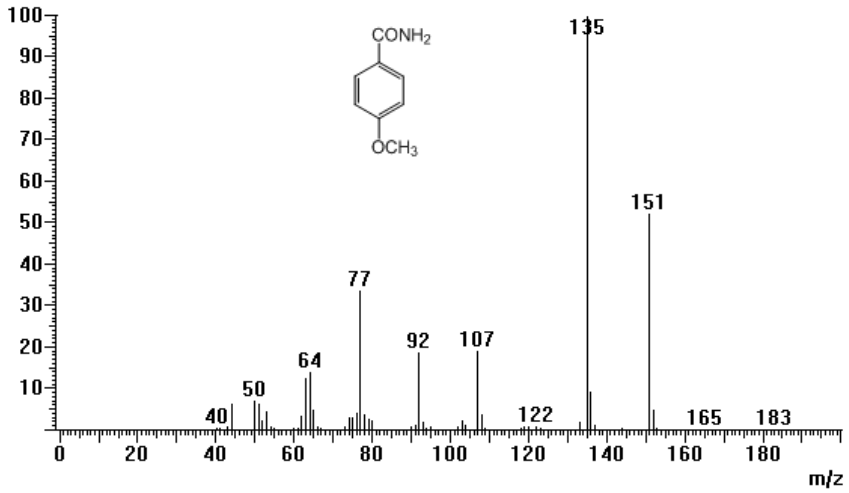
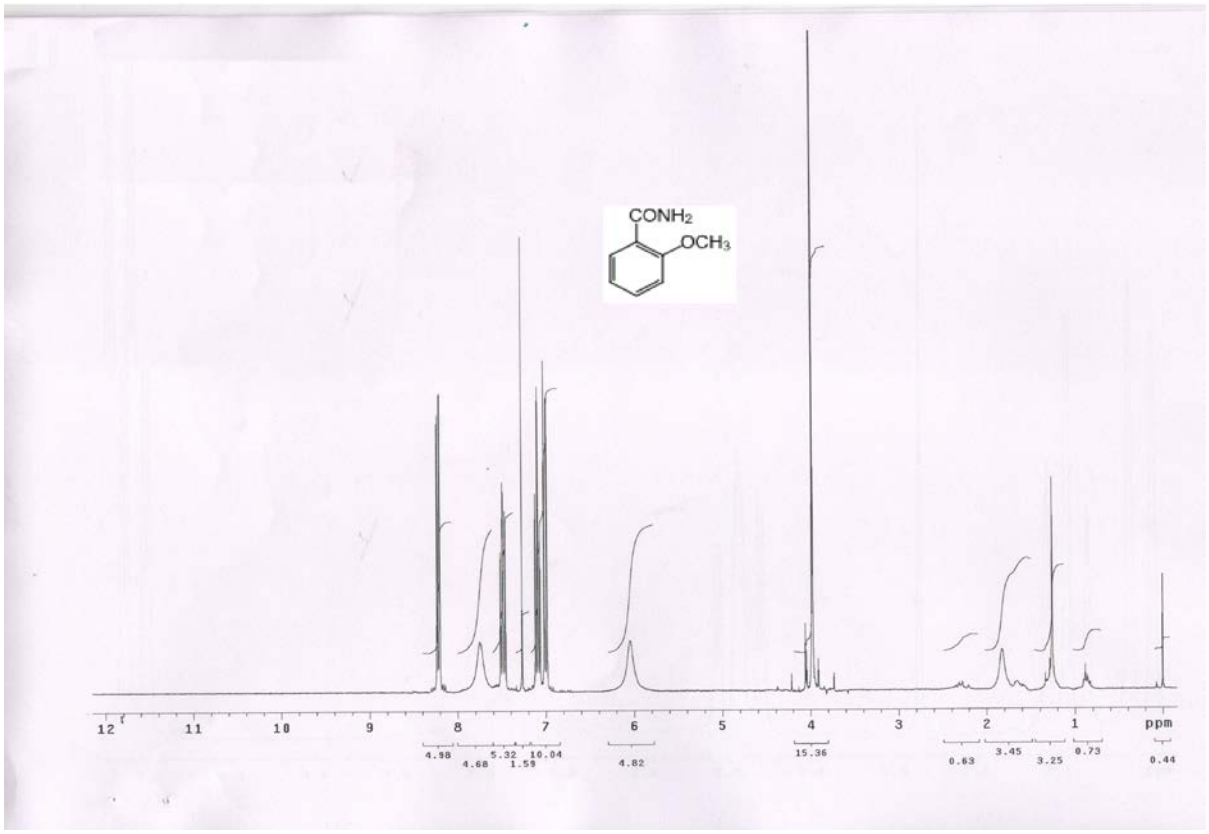
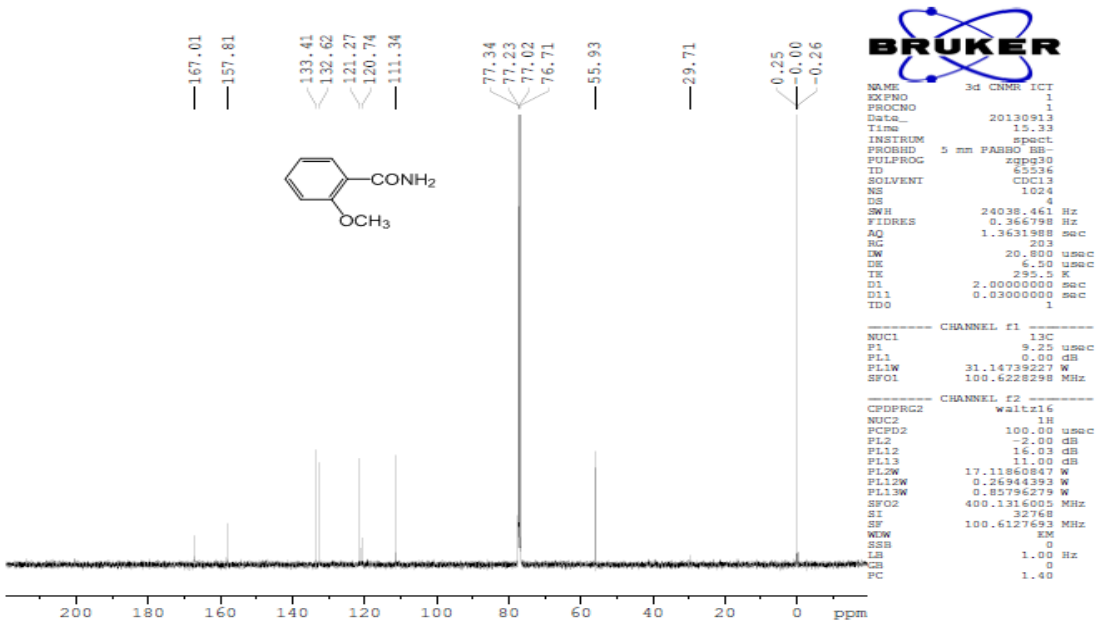


4) O- Methoxy benzamide (3d):

^{1}H NMR



^{13}C NMR



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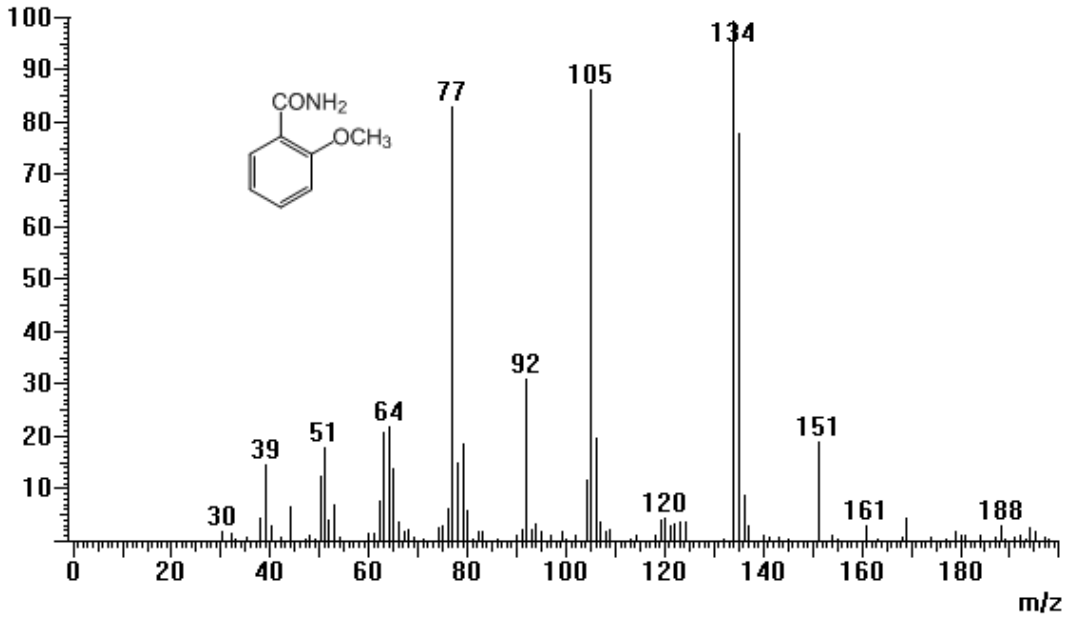
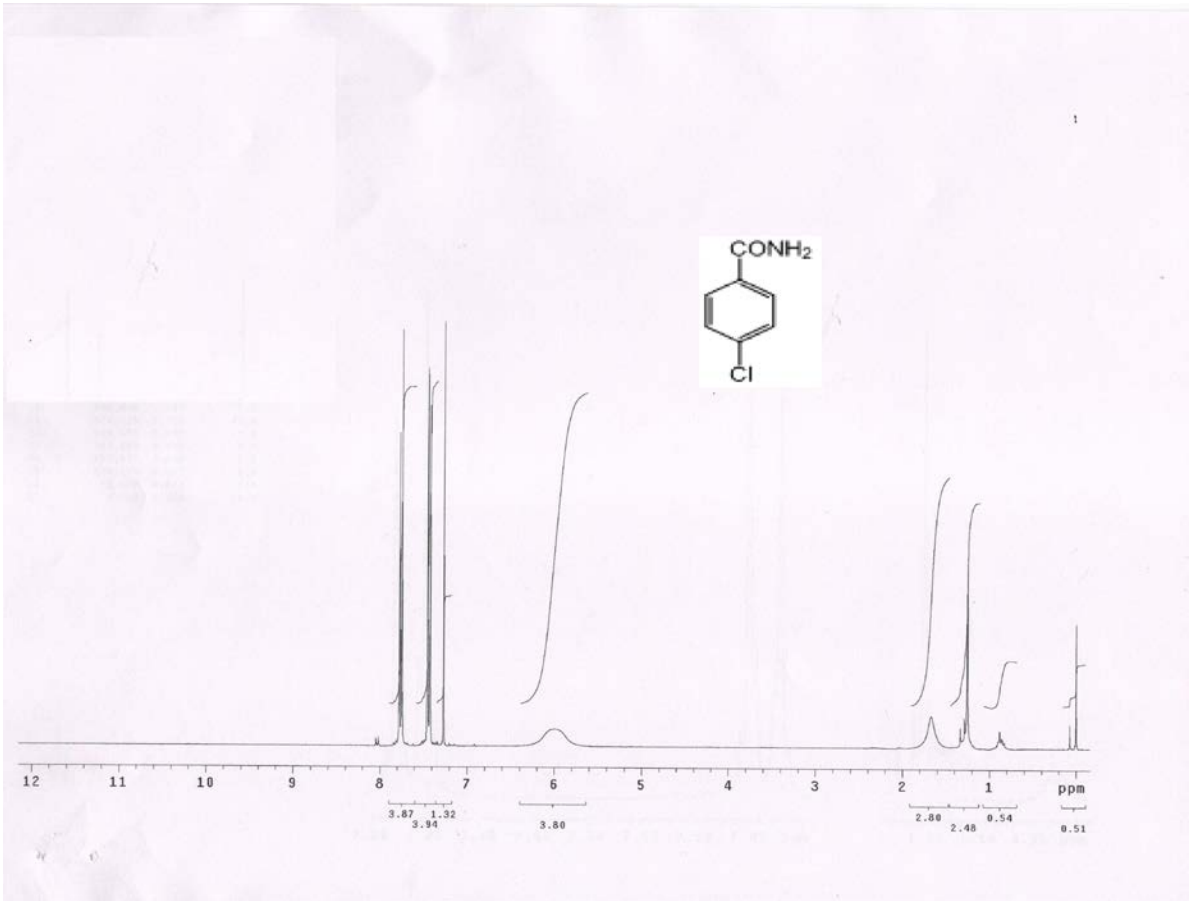


5) P- chloro benzamide (3f):

^{1}H NMR



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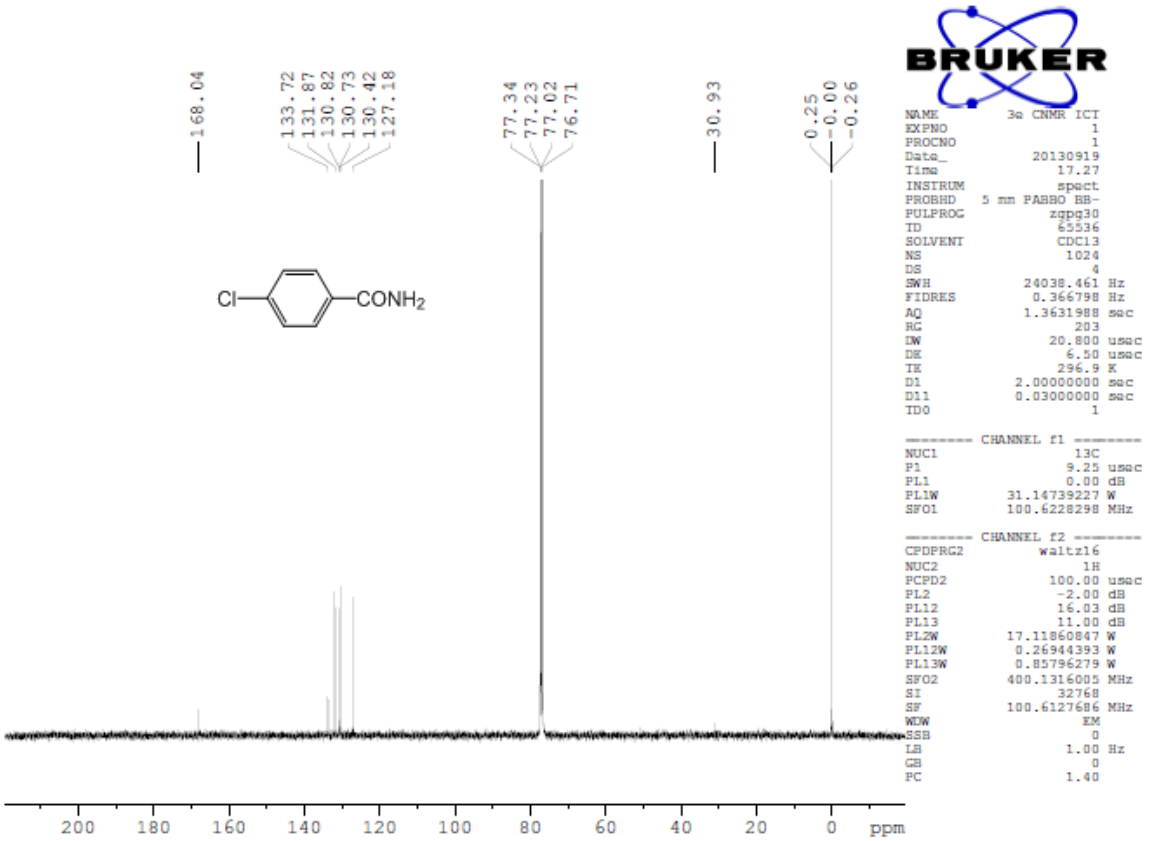

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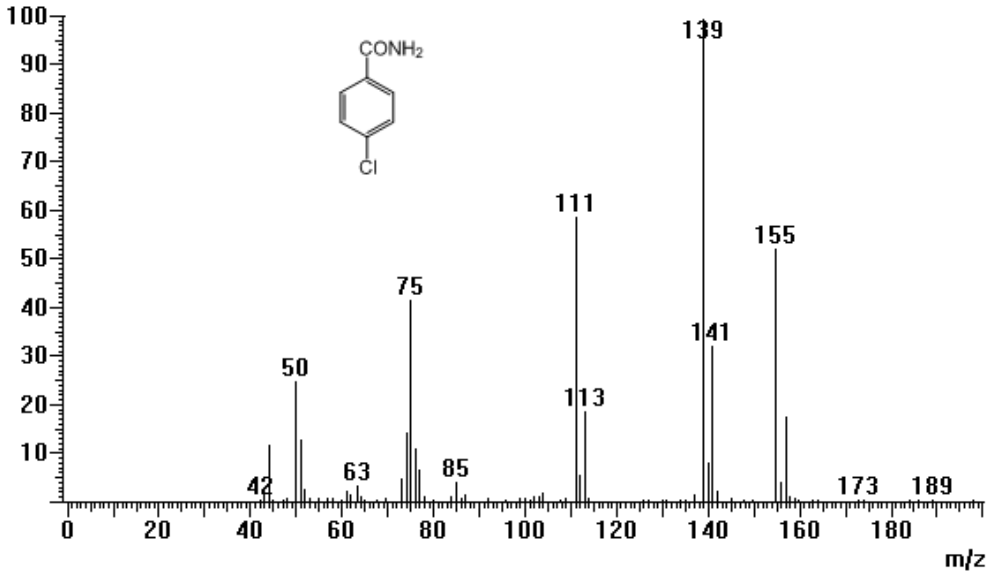
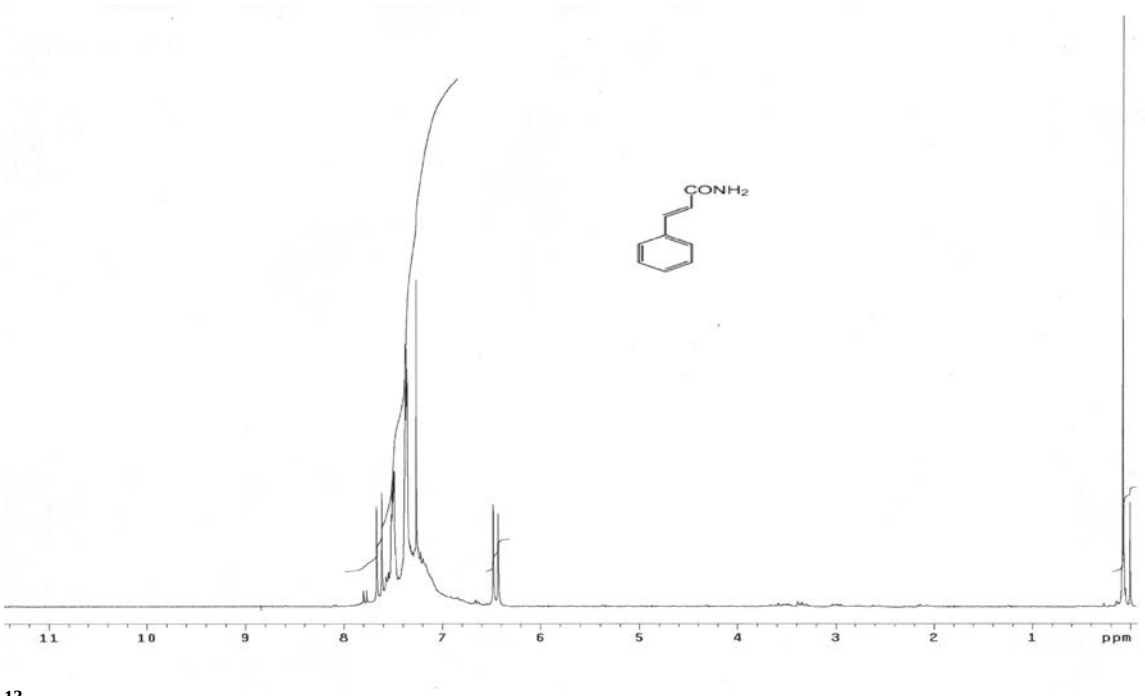
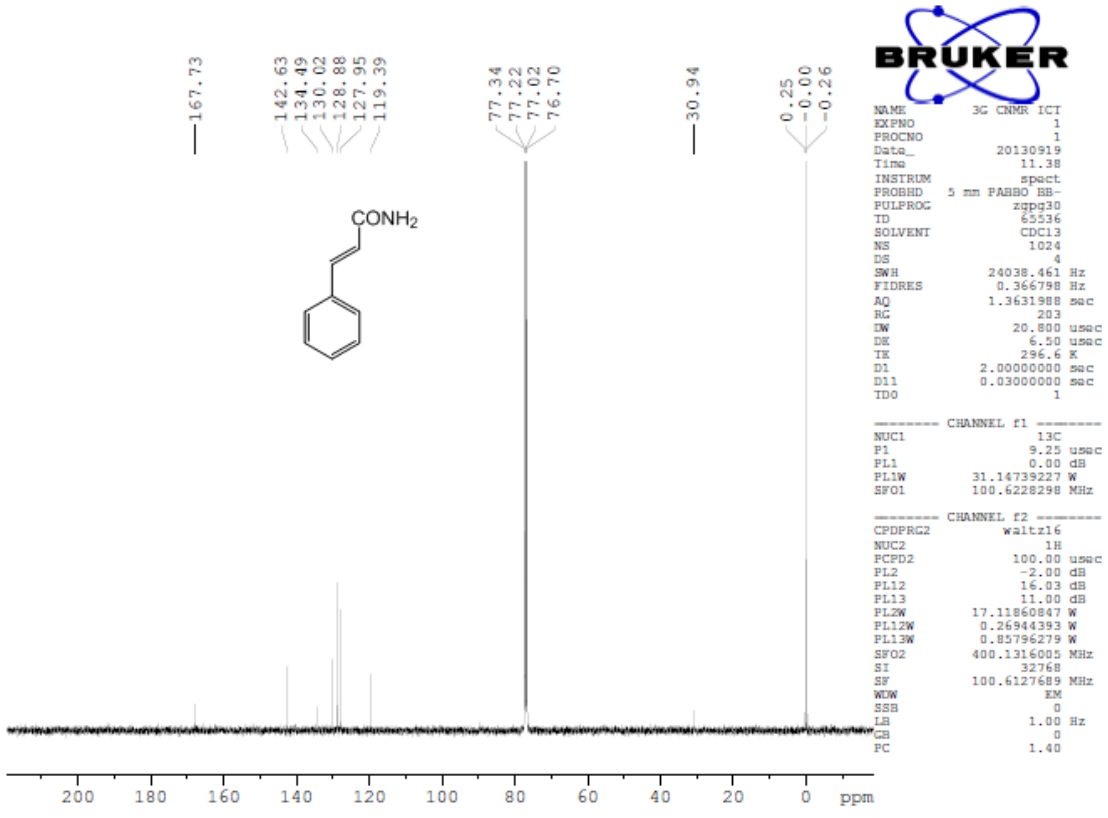


6) Cinnamide (3g):

^{1}H NMR



^{13}C NMR



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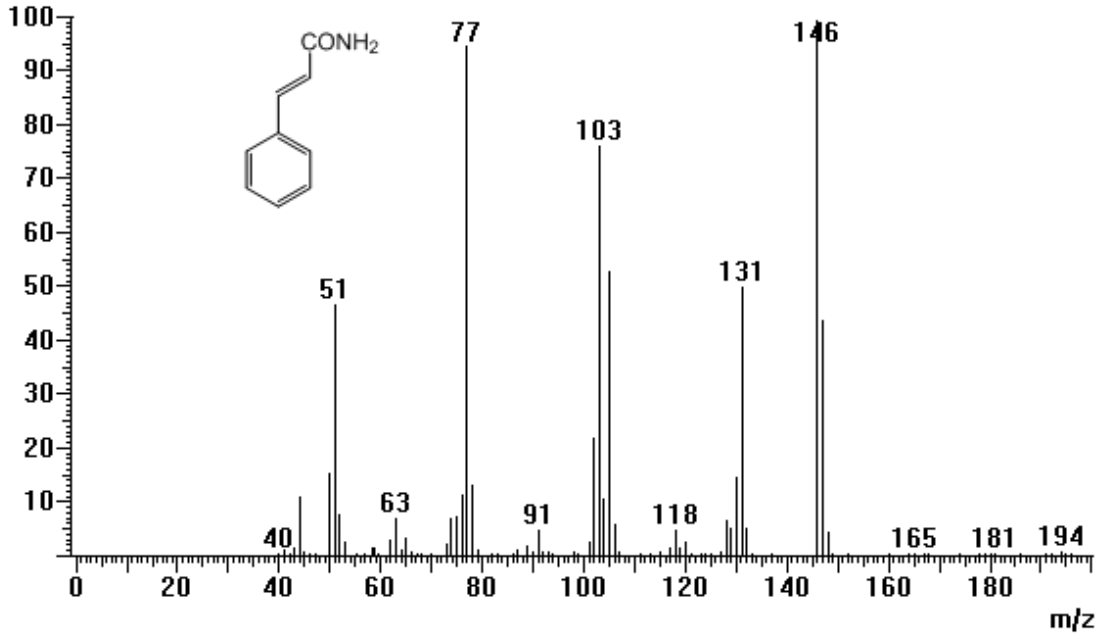
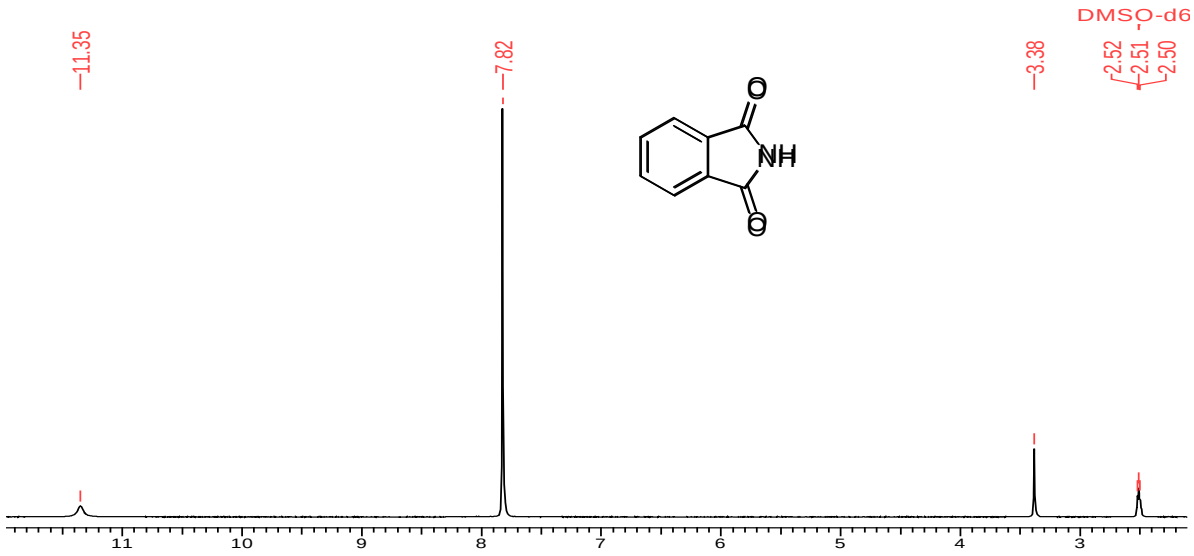
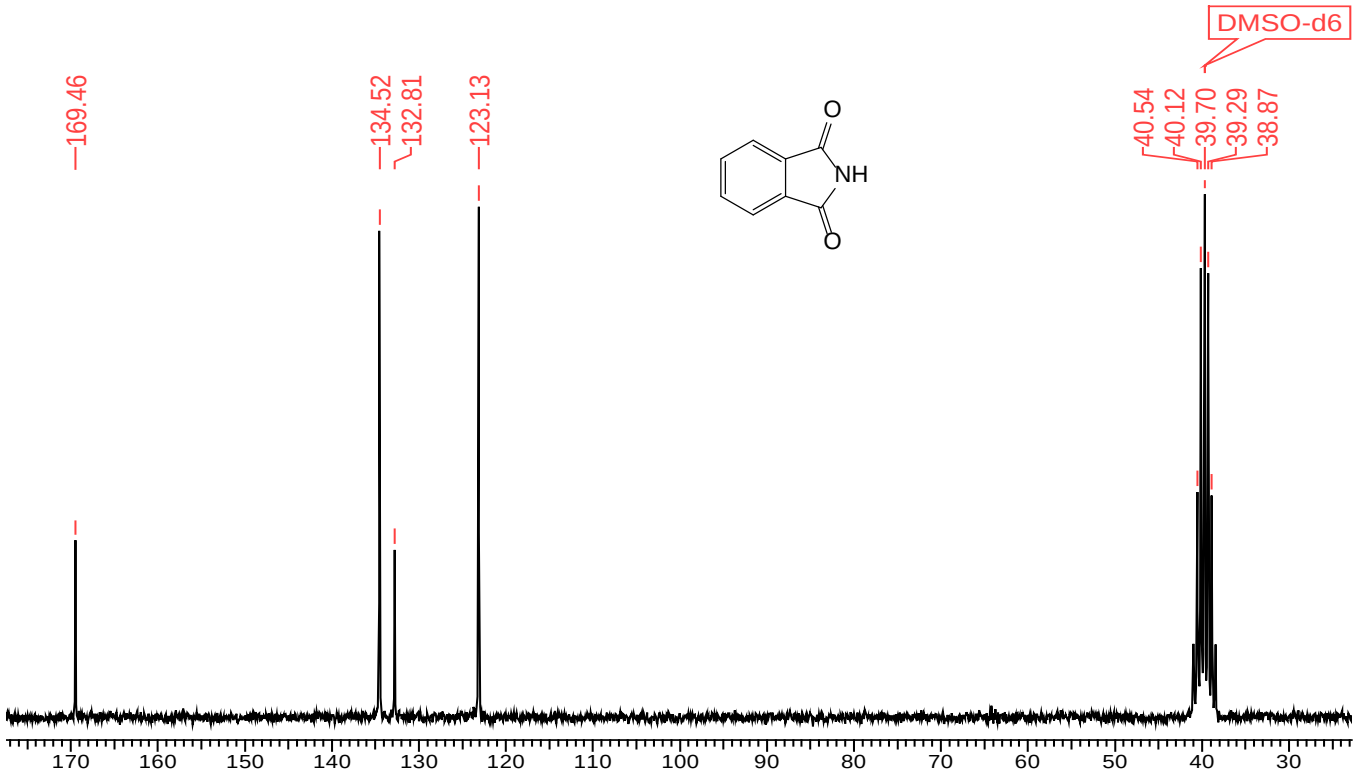


7) Phthalimide (3h):

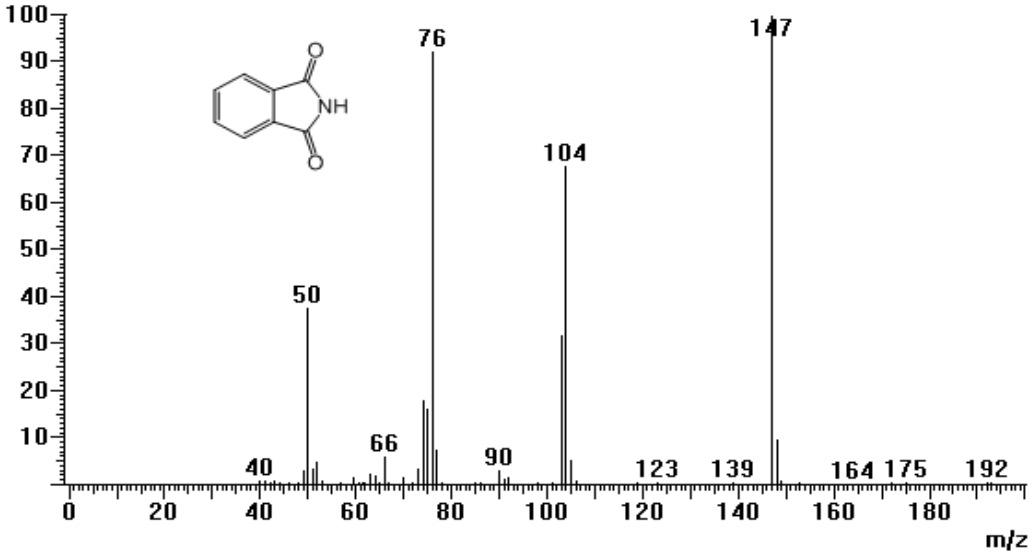
^{1}H NMR



^{13}C NMR

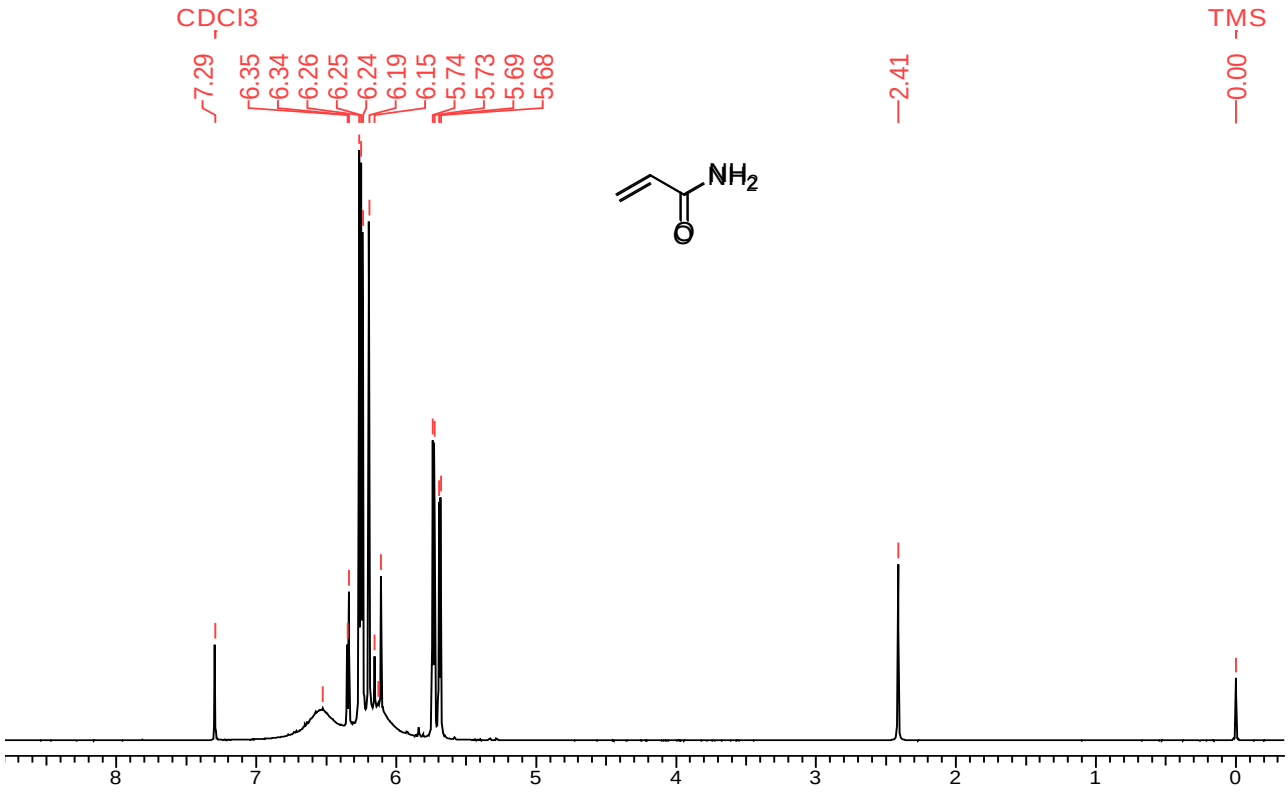


MS

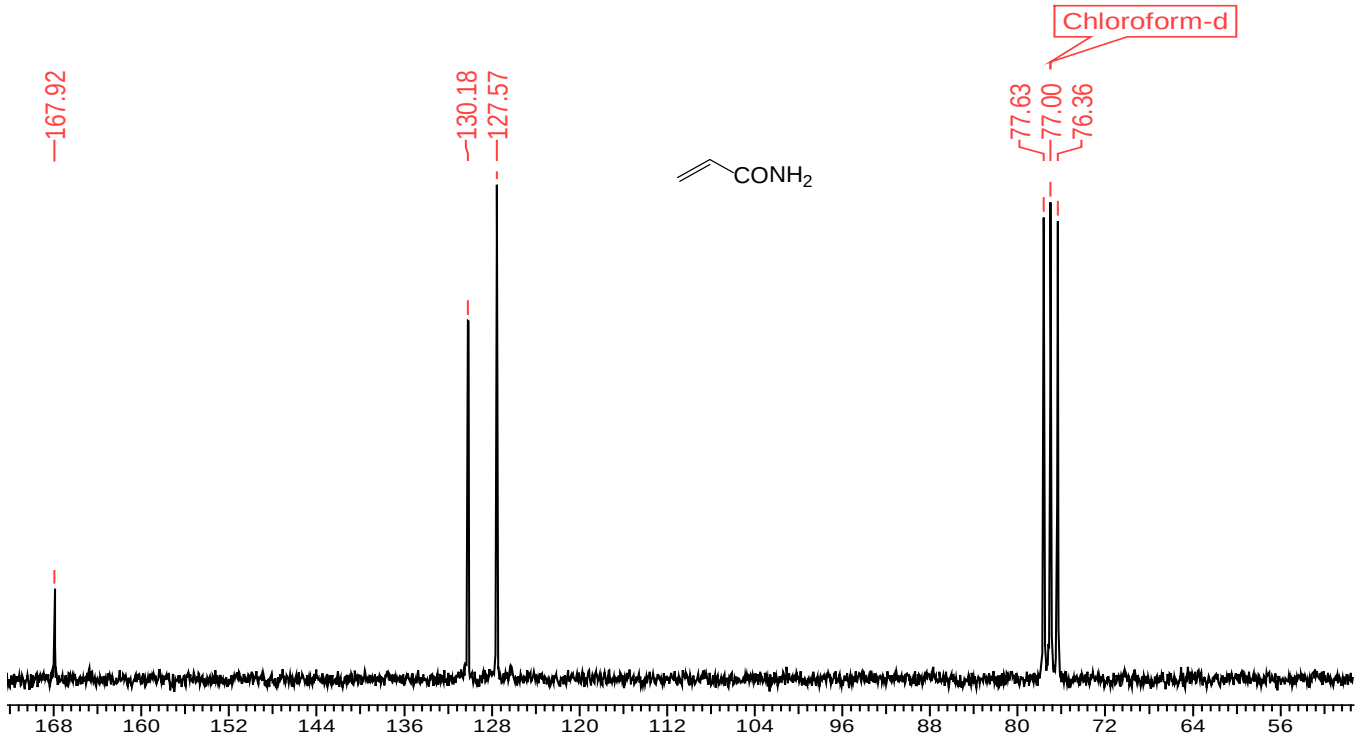


8) Acryl amide (3i):

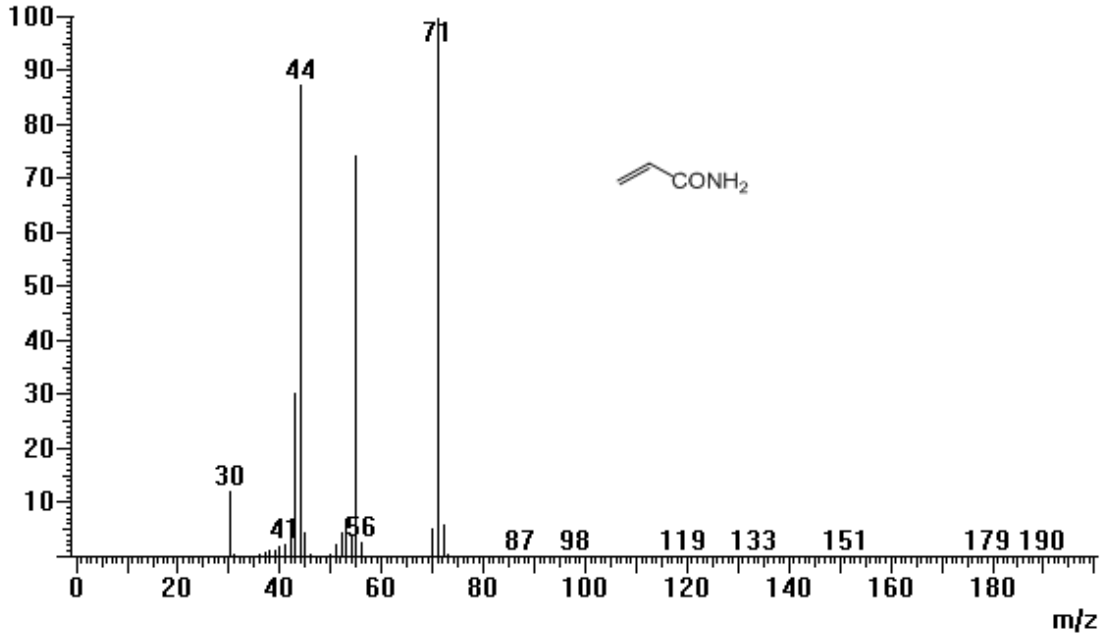
^{1}H NMR



13C NMR

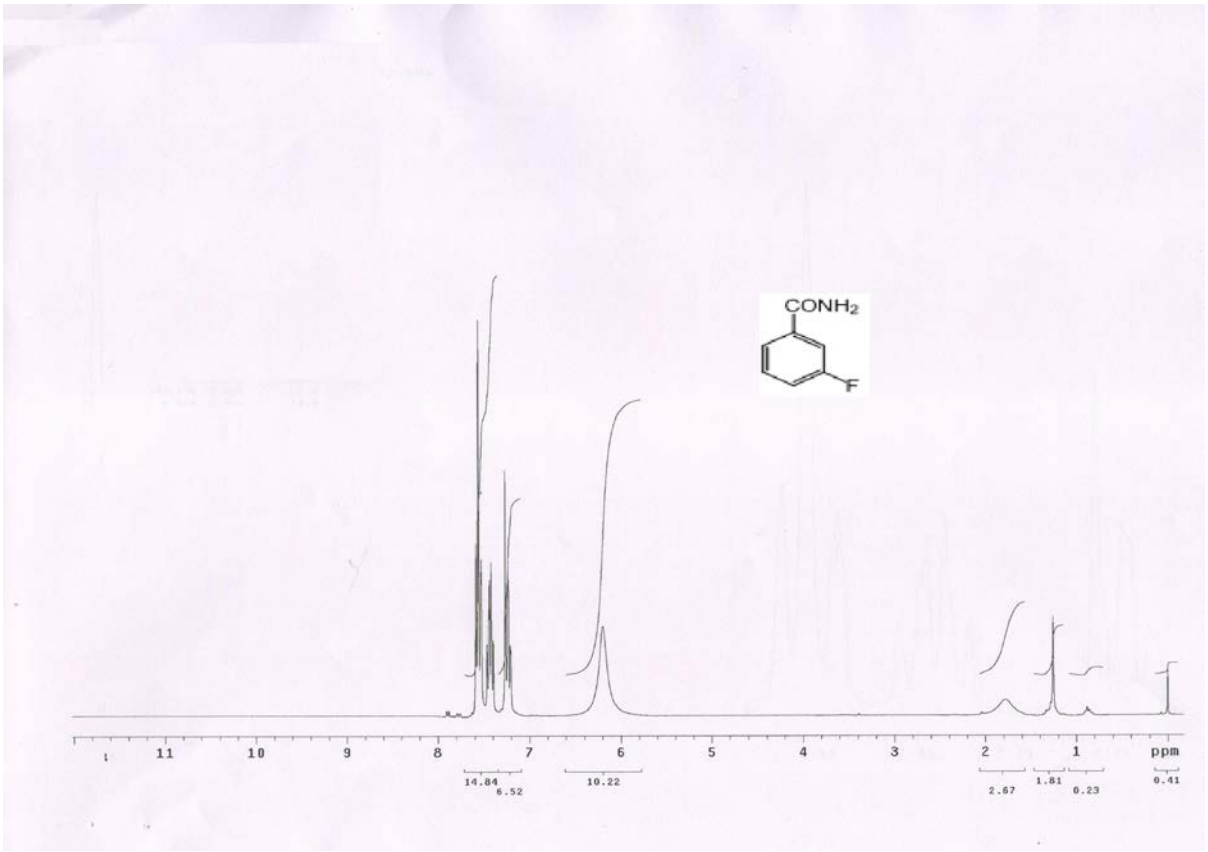


MS

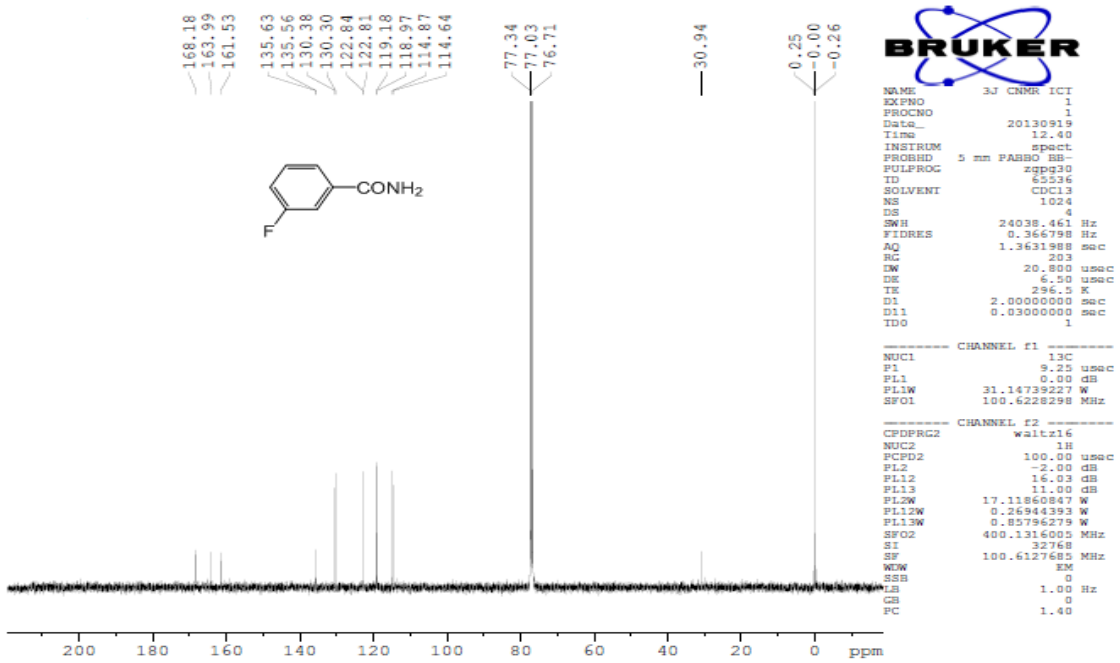


9) 3-Fluorobenzamide (4j):

^{1}H NMR



^{13}C NMR



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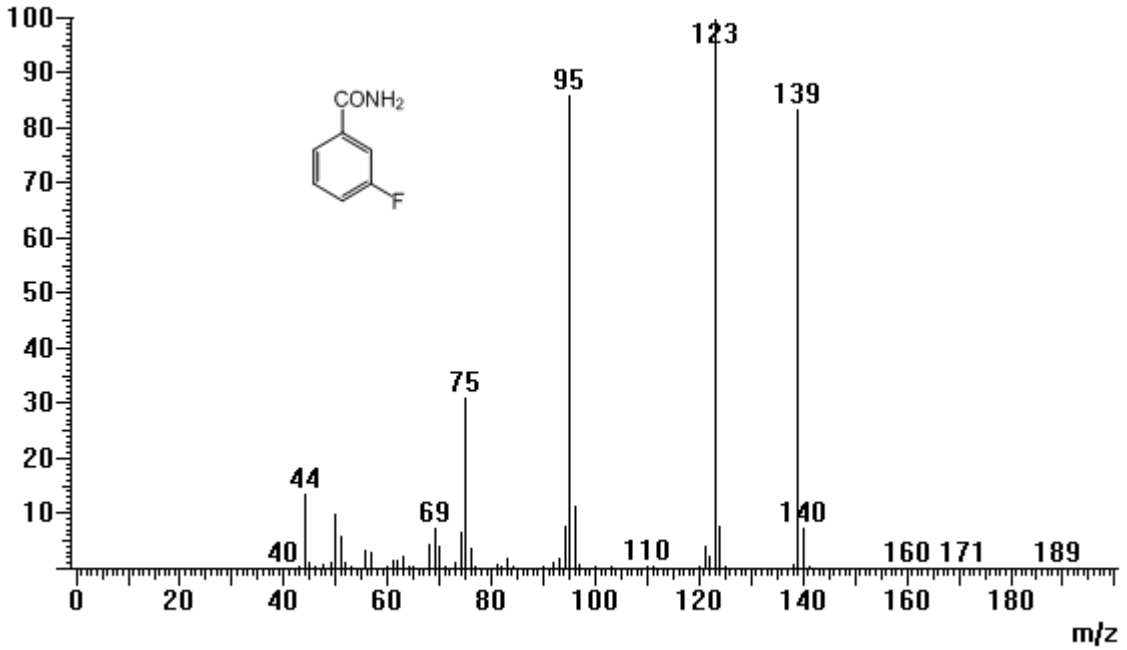
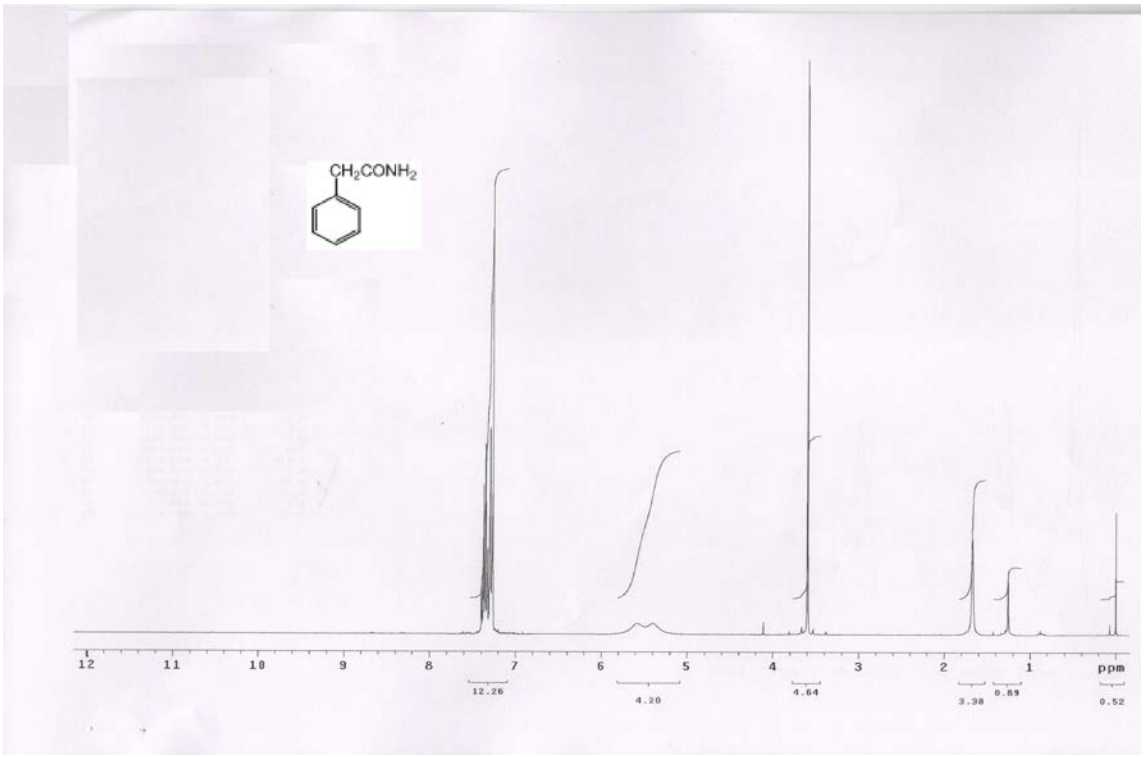
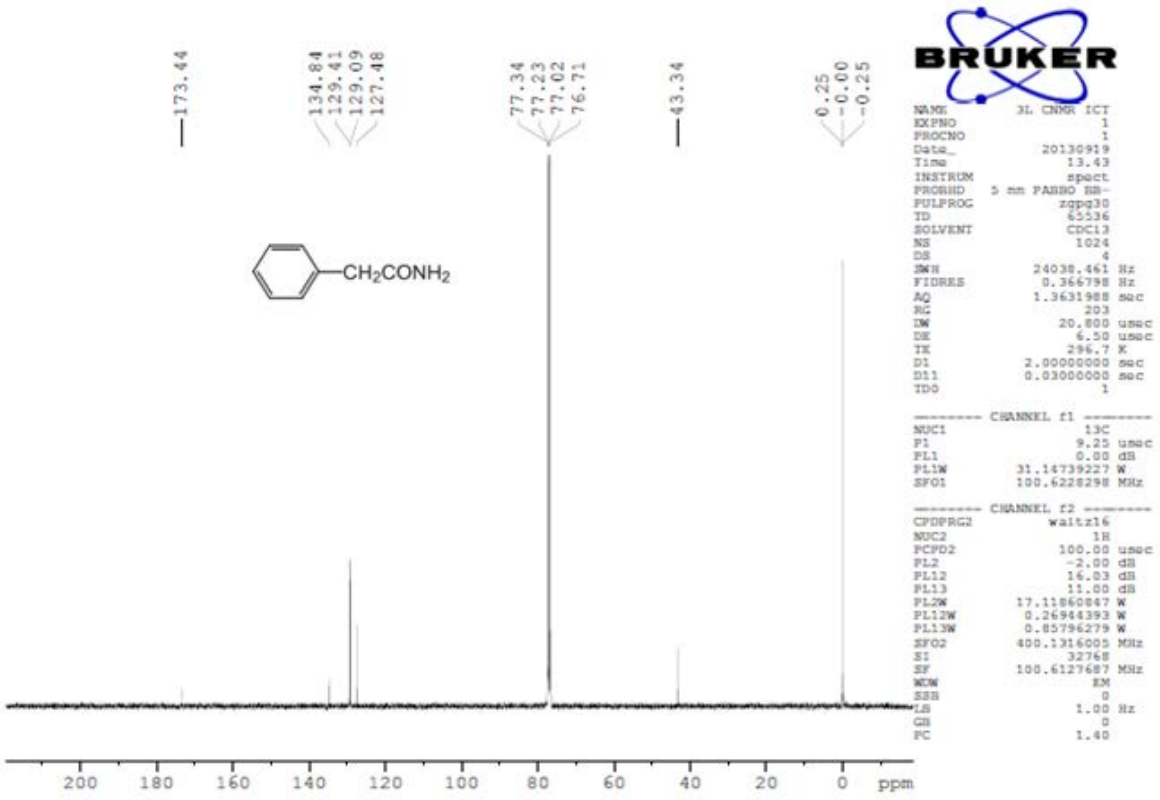


10) 2-Phenylacetamide (4l):

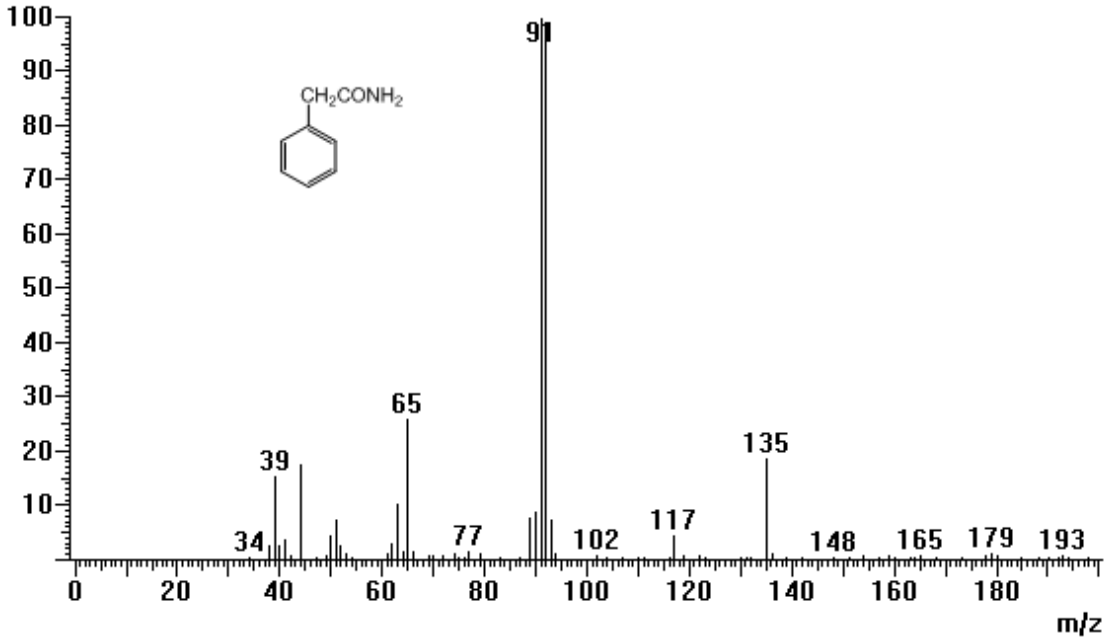
^{1}H NMR



^{13}C NMR

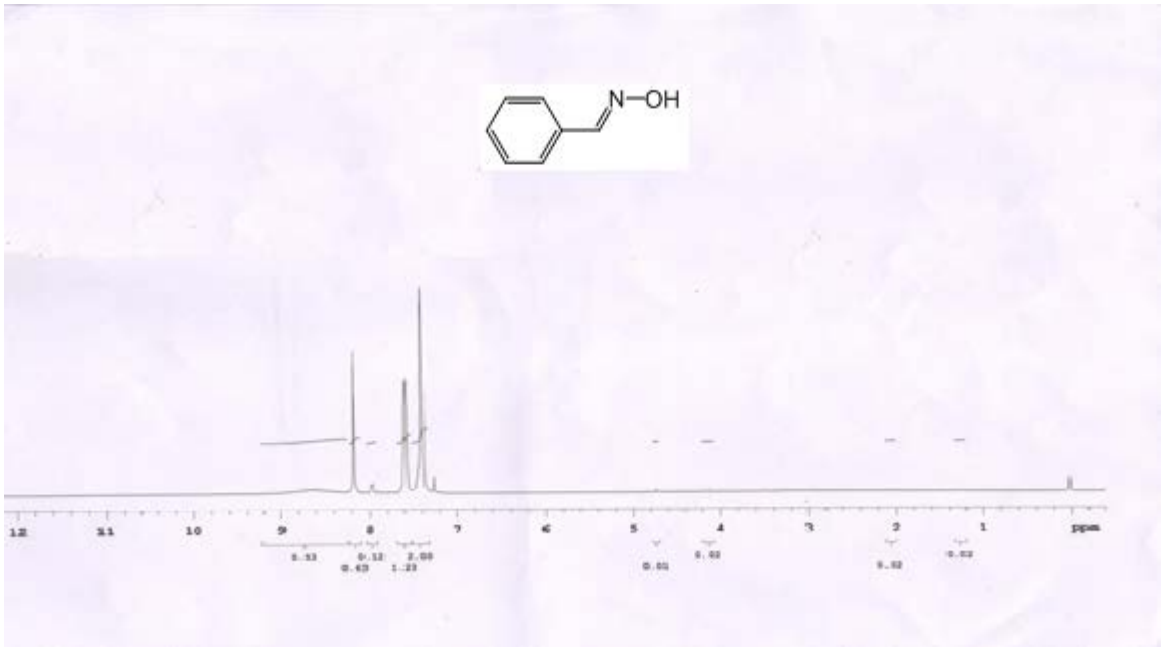


MS



11) Benzaldoxime (5a) :

^{1}H NMR



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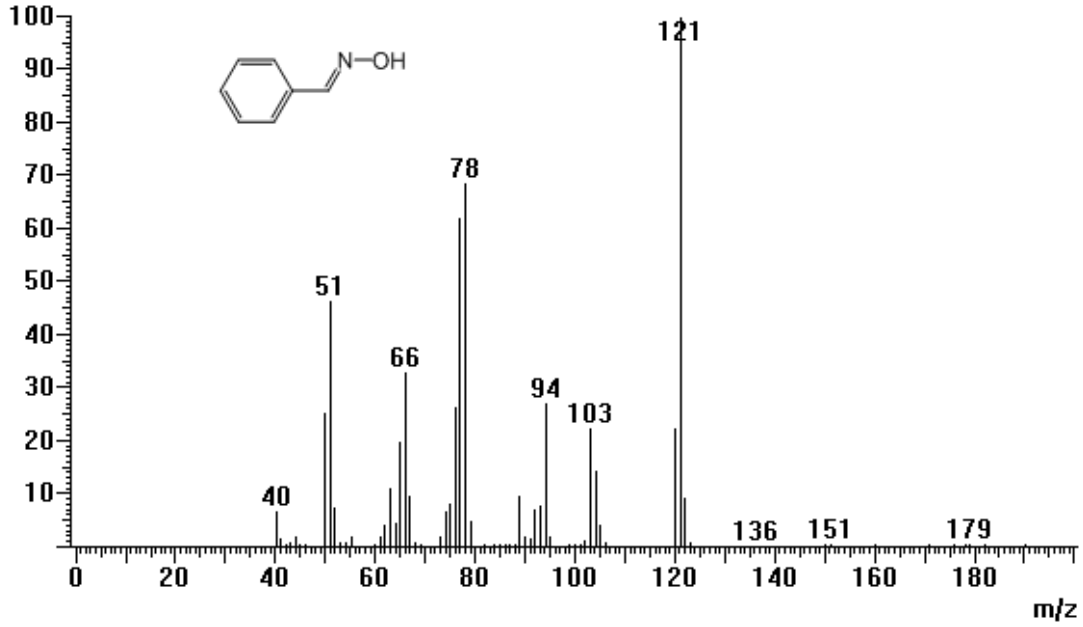

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