Electronic Supplementary Material (ESI) for Green Chemistry

Supporting Information

Zinc phthalocyanine with PEG-400 as a recyclable catalytic system for selective reduction of aromatic nitro compounds

Upendra Sharma, Neeraj Kumar,* Praveen Kumar Verma, Vishal Kumar and Bikram Singh*

Natural Plant Products Division, CSIR-Institute of Himalayan Bioresource Technology (Council of Scientific and Industrial research), Palampur, Himachal Pradesh-176 061, INDIA

Table of Contents

1. General Information

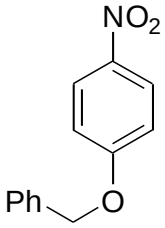
High grade solvents were used for all reactions. Flash chromatography was carried out with 230-400 mesh silica gel. 230-400 mesh silica gel, TLC silica gel 60 F254 plates were purchased from Merck India Ltd. Nitro compounds, NMR solvent were purchased from sigma Aldrich and spectrochem. The GC-MS analysis was carried out on a Shimadzu (QP 2010) series Gas Chromatogram-Mass Spectrometer (Tokyo, Japan), AOC-20i auto-sampler coupled, and a DB-5 MS capillary column, (30 m x 0.25 mm i.d., 0.25µm). The initial temperature of column was 70°C held for 4 min. and was programmed to 230 °C at 4°C/min., then held for 15 min. at 230°C; the sample injection volume was 2 µl in GC grade dichloromethane. Helium was used as carrier gas at a flow rate of 1.1 ml min^{-1} on split mode (1:50).

The IR spectra were recorded on a a NICOLET-6700 FT-IR spectrometer with KBr disc.and the ν_{max} are expressed in cm^{-1}. The electronic spectra were recorded on a Perkin Elmer Lambda-35 UV/Vis spectrophotometer and the λ_{max} are expressed in nanometers. ^{1}H NMR and ^{13}C NMR experiments were performed on Bruker Avance-300 spectrometer. Chemical shifts are reported in parts per million (ppm) downfield from an internal standard. Mass spectra were recorded on QTOF-Micro of Waters Micromass.

2. General procedure

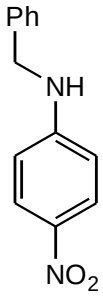
Synthesis of zinc (II) phthalocyanine: Zinc (II) phthalocyanine was prepared by following the literature procedure from $ZnCl_2$.[1]

Benzyl 4-nitrophenyl ether is prepared by the literature procedure.[2]



^{1}H NMR (300 MHz, $CDCl_3$): δ 5.18 (s, 2H), 7.04 (d, *J* = 9.0 Hz, 2H), 7.28-7.44 (m, 5H), 8.21 (d, *J* = 9.0 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 71.1, 115.3, 126.3, 127.9, 128.9, 129.2, 135.9, 142.1, 164.1. HRMS calculated for $[M+H]^+$ is 230.0817 and found 230.0842.

***N*-benzyl-4-nitroaniline** is prepared by following the literature procedure.[3]



^{1}H NMR (300 MHz, $CDCl_3$): δ 4.40 (s, 2H), 5.11 (bs, 1H), 6.55 (d, *J* = 6.5 Hz, 2H), 7.32 (m, 5H), 8.04 (d, *J* = 6.6 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 48.3, 112.0, 127.1, 128.0, 128.5, 129.6, 138.2, 139.0, 153.9. HRMS calculated for $[M+H]^+$ is 229.0997 and found 229.0954.

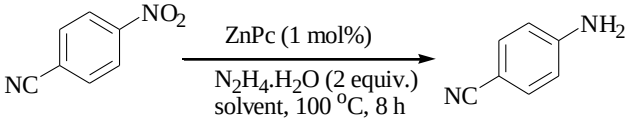
Representative experimental procedure for reduction of nitro compounds: To a mixture of nitro compound (1.34 mmol) and catalyst (1 mol %) in PEG-400 (3 mL) was added hydrazine hydrate (2 equiv.). The reaction mixture was stirred at 100 ºC for 8 h. Time was not optimized separately for all substrates. After completion of reaction as monitored by TLC (silica gel, hexane/ethyl acetate), the reaction mixture was cooled to ambient temperature and 20 ml of ethyl acetate was added. PEG-400 was removed by washing with distilled water and ethyl acetate layer was dried under reduced pressure using rotatory evaporator and analyzed by GC-MS. In cases (Table 2, entries 9, 12, 15 and 32) where the products are partially soluble in water the reaction mixture was dissolved in ethyl acetate and directly analyzed by GC-MS. The initial temperature of column was 70 ºC held for 4 min. and was programmed to 230 ºC at 4 ºC/min., then held for 15 min. at 230 ºC, the sample injection volume was 2 µl in GC grade dichloromethane. Helium was used as carrier gas at a flow rate of 1.1 ml min^{-1} on split mode (1: 50). Whenever necessary, crude products were purified by column chromatography (silica 230-400, *n*-hexane/ethyl acetate mixture).

Representative experimental procedure for reduction of carbonyl compounds: To a mixture of carbonyl compound (1.34 mmol) and catalyst (1 mol%) in PEG-400 (3 mL) was added sodium borohydride (0.5 equiv.). The reaction mixture was stirred at room temperature for

appropriate time. After completion of reaction as monitored by TLC (silica gel, hexane/ethyl acetate) the crude product was extracted with diethyl ether (3x10 ml). Diethyl ether fractions were combined and dried under reduced pressure using rotatory evaporator. Crude products were purified by column chromatography (silica 60-120, *n*-hexane/ethyl acetate mixture).

Representative experimental procedure for reductive amination of nitro-substituted benzaldehydes: To a mixture of nitrobenzaldehyde (1 mmol), 4-methoxyaniline (1 mmol) and catalyst (1 mol %) in ethanol (5 ml) was added sodium borohydride (1.0 equiv.). The reaction mixture was stirred at room temperature for 1 h. After completion of reaction as monitored by TLC (silica gel, hexane/ethyl acetate) the reaction mixture was filtered and passed through anhydrous Na_2SO_4. The filtrate was dried under vacuum and the crude products obtained were purified by column chromatography (silica 60-120, *n*-hexane/ethyl acetate mixture).

Table S1 Evaluation of different solvents for reduction of 4-nitrobenzonitrile.



Entry	Catalyst	Solvent	Yield (%)[a]
1	ZnPc	Water	8[b]
2	ZnPc	Ethanol	92
3	ZnPc	Ethylacetate	No reaction
4	ZnPc	THF	6
5	ZnPc	[Bmim]BF_4	97
6	ZnPc	[Bmim]HSO_4	87
7	ZnPc	Water: Ethanol (1: 1)	46
8	ZnPc	Ethylene glycol	93
9	ZnPc	Toluene	8
10	ZnPc	PEG-400	99
11	ZnPc	DMF	52

[a]Yield is calculated on the basis of GC-MS analysis.
[b]4-nitrobezamide was observed as major side product with yield 86%.

Optimization of the amount of catalyst: The minimum amount of catalyst which can be used for the reaction was optimized (Table S2) by initially starting with 0.025 mol% of catalyst and gradually increased the

amount upto 0.50 mol%. Full conversion was not observed with 0.025 mol% of the catalyst whereas 98% yield was observed with 0.050 mol % of catalyst (Table S2, entry 2). Which indicates that the amount of catalyst can be reduced to 0.050 mol %.

Table S2. Optimization of the amount of catalyst.

Entry	1	2	3	4	5
Catalyst (mol%)	0.025	0.050	0.128	0.257	0.50
Yield (%)[a]	84	98	95	>99	>99

[a] GC-MS yield is reported.

Recyclability of the catalyst: The recyclability of catalytic system was evaluated by using 4-nitrobenzonitrile as test substrate. After completion of reaction the product was extracted with Et_2O and remaining residue was used as such after drying over rotary evaporator. Successive reactions were carried out by sequential addition of fresh substrate and hydrazine hydrate to the crude remains after extracting the product. The catalytic system can be reused upto four cycles (Figure S1). However, the reduction of the substrate was not complete in the fifth cycle.

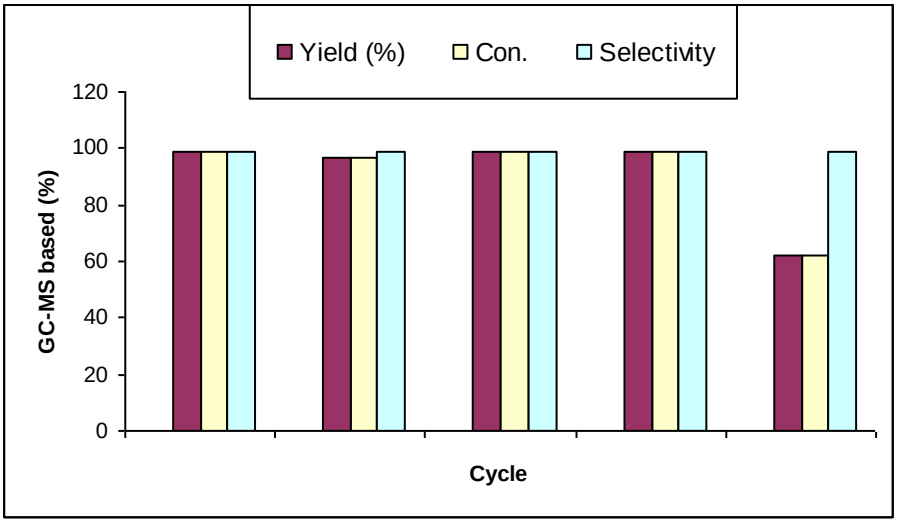


Figure S1. Recyclability of the catalyst.

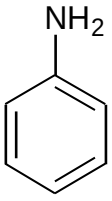
3. Characterization of catalyst and products:[4]

Zinc phthalocyanine: (Figure S2 for FT-IR and Figure S3 for UV-vis) Obtained as a blue product from $ZnCl_2$, IR (KBr) cm^{-1}; 2927 (υC-H), 1637, 1621, 1401 (υC-N), 1317 (υC-C), 1116, (υC-H), 892, (γC-H), 615, 477 (ΦC-C). UV-vis (THF) λ_{max} nm; 666, 602.

Characterization of nitro reduction products:

All compounds were identified by spectral comparison with literature data.[5, 6]

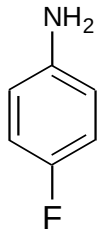
Aniline (Table 2, entry 1):



^{1}H NMR (300 MHz, $CDCl_3$): δ 3.68 (bs, 2H), 6.72-6.76 (m, 2H), 6.82-6.87 (m, 1H), 7.21-7.27 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 115.1,

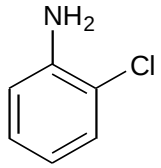
119.3, 129.7, 146.9. HRMS calculated for $[M+H]^+$ is 94.0657 and found 94.0691.

2-Fluroaniline (Table 2, entry 2):



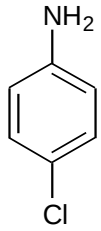
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.60 (s, 2H), 6.59-6.65 (m, 2H), 6.86-6.93 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 115.9, 116.2, 116.4, 116.5, 143.1, 155.2, 158.3. HRMS calculated for $[M+H]^+$ is 112.0563 and found 112.0537.

2-Chloroaniline (Table 2, entry 3):



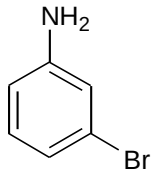
^{1}H NMR (300 MHz, CD_3COCD_3): δ 4.07 (bs, 2H), 6.69-6.72 (m, 1H), 6.75-6.79 (m, 1H), 7.04-7.07 (m, 1H), 7.22-7.26 (m, 1H), ^{13}C NMR (75 MHz, CD_3COCD_3): δ 116.2, 119.3, 119.6, 128.0, 129.7, 143.3. HRMS calculated for $[M+H]^+$ is 128.0267 and found 128.0264.

4-Chloroaniline (Table 2, entry 4):



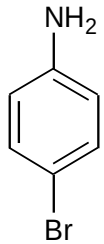
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.59 (bs, 2H), 6.62 (d, *J* = 14.8 Hz, 2H), 7.11 (d, *J* = 14.8 Hz, 2H), ^{13}C NMR (75 MHz, $CDCl_3$): δ 116.6, 123.5, 129.5, 145.3. HRMS calculated for $[M+H]^+$ is 128.0267 and found 128.0249.

3-Bromoaniline (Table 2, entry 5):



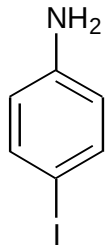
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.74 (bs, 2H), 6.59-7.06 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 114.1, 118.2, 121.7, 123.4, 131.0, 148.2. HRMS calculated for $[M+H]^+$ is 171.9762 and found 171.9798.

4-Bromoaniline (Table 2, entry 6):



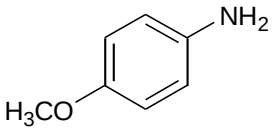
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.70 (bs, 2H) 6.57 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.4 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 110.5, 117.1, 132.02, 145.9. HRMS calculated for $[M+H]^+$ is 171.9762 and found 171.9793.

4-Iodoaniline (Table 2, entry 7):



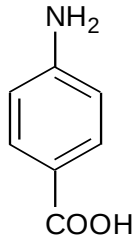
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.50 (bs, 2H), 6.48 (d, *J* = 11.3, 2H), 7.41 (d, *J* = 11.3, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 79.8, 117.7, 138.3, 146.3. HRMS calculated for $[M+H]^+$ is 219.9623 and found 219.9664.

4-Methoxyaniline (Table 2, entry 8):



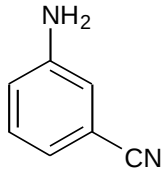
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.39 (bs, 2H), 3.77 (s, 3H), 6.65-6.79 (m, 4H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.1, 115.2, 116.8, 140.3, 153.2. HRMS calculated for $[M+H]^+$ is 124.0762 and found 124.0736.

4-Amino-benzoic acid (Table 2, entry 9):



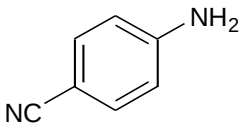
^{1}H NMR (300 MHz, CD_3COCD_3): δ 6.67-6.72 (m, 2H), 7.76-7.81 (m, 2H); ^{13}C NMR (75 MHz, CD_3COCD_3): δ 114.1, 118.7, 132.8, 154.4, 168.2. HRMS calculated for $[M+H]^+$ is 138.0555 and found 138.573.

3-Aminobenzonitrile (Table 2, entry 10):



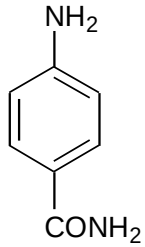
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.96 (bs, 2H), 6.85-6.88 (m, 1H), 6.90 (s, 1H), 6.99-7.02 (m, 1H), 7.19-7.24 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 113.2, 117.8, 119.5, 122.2, 130.4, 147.4. HRMS calculated for $[M+H]^+$ is 119.0609 and found 119.0624.

4-Aminobenzonitrile (Table 2, entry 11):



^{1}H NMR (300 MHz, $CDCl_3$): δ 4.23 (bs, 2H), 6.65 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 100.4, 114.8, 120.5, 134.1, 150.9. HRMS calculated for $[M+H]^+$ is 119.0609 and found 119.0658.

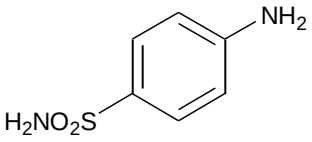
4-Aminobenzamide (Table 2, entry 12):



^{1}H NMR (300 MHz, DMSO-d_6): δ 3.62 (s, 2H), 4.88 (s, 2H, merged with methanol signal), 6.67 (d, *J* = 7.9 Hz, 2H), 7.66 (d, *J* = 7.9 Hz, 2H); ^{13}C

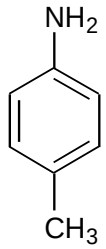
NMR (75 MHz, DMSO-d_6): δ 114.5, 122.1, 130.3, 153.3, 172.6. HRMS calculated for $[M+H]^+$ is 137.0715 and found 137.0746.

4-Amino-benzene-1-sulphonamide (Table 2, entry 13):



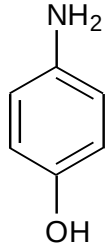
^{1}H NMR (300 MHz, CD_3OD): δ 6.70 (d, J = 14.0 Hz, 2H), 7.59 (d, J = 14.0 Hz, 2H); ^{13}C NMR (75 MHz, CD_3OD): δ 113.4, 127.9, 130.3, 152.5. HRMS calculated for $[M+H]^+$ is 173.0385 and found 173.0354.

4-Methylaniline (Table 2, entry 14):



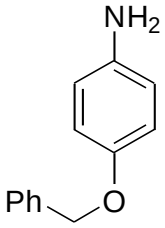
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.29 (s, 3H), 3.52 (bs, 2H), 6.65 (d, J = 8.0 Hz, 2H), 7.01 (d, J = 7.3 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 20.8, 115.6, 128.1, 130.1, 144.2. HRMS calculated for $[M+H]^+$ is 108.0813 and found 108.0842.

4-Aminophenol (Table 2, entry 15):



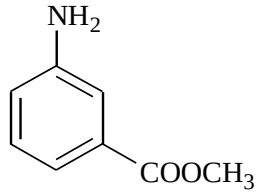
^{1}H NMR (300 MHz, CD_3OD): δ 6.60-6.67 (m, 4H); ^{13}C NMR (75 MHz, CD_3OD): δ 115.7, 117.5, 139.2, 150.2. HRMS calculated for $[M+H]^+$ is 110.0606 and found 110.0575.

Benzyl-4-aminophenyl ether (Table 2, entry 16):



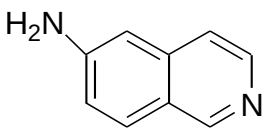
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.33 (bs, 2H), 5.02 (s, 2H), 6.66 (d, *J* = 8.7 Hz, 2H), 6.84 (d, *J* = 8.7 Hz, 2H), 7.35-7.46 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 71.2, 116.5, 116.7, 127.9, 128.2, 128.9, 137.9, 140.6, 152.4.

Methyl- 3-Amino-benzoate (Table 2, entry 19):



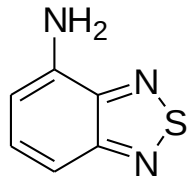
^{1}H NMR (300 MHz, $CDCl_3$): δ 6.85-6.88 (m, 1H), 7.19-7.24 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 114.1, 118.7, 132.8, 154.4, 168.2. HRMS calculated for $[M+H]^+$ is 152.0712 and found 152.0715.

6-Aminoisoquinoline (Table 2, entry 26):



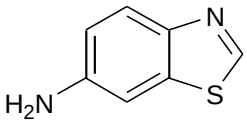
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.32 (bs, 2H), 6.93 (bs, 1H), 7.36 (s, 3H), 7.58 (d, *J* = 5.3, 1H), 8.44 (d, *J* = 4.98, 1H) 9.15 (s, 1H) ^{13}C NMR (75 MHz, $CDCl_3$): δ 113.4, 114.7, 118.1, 126.3, 128.2, 129.8, 142.1, 153.1. HRMS calculated for $[M+H]^+$ is 145.0766 and found 145.0731.

4-Amino-2, 1, 3-benzothiadiazole (Table 2, entry 28):



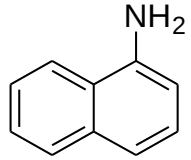
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.71 (bs, 2H) 6.62 (d, *J* = 6.8, 1H), 7.33-7.43 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 107.0 110.4, 131.6, 139.2, 148.1, 156.1. HRMS calculated for $[M+H]^+$ is 152.0282 and found 152.0257.

6-Aminobenzothiazole (Table 2, entry 29):



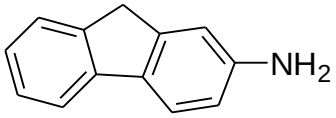
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.91 (bs, 2H), 6.85-6.88 (m, 1H), 7.15 (s, 1H), 7.89 (d, *J* = 8.6, 1H), 8.70 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 106.0, 116.1, 124.3, 135.8, 145.2, 147.1, 150.2. HRMS calculated for $[M+H]^+$ is 151.0330 and found 151.0352.

1-Aminonaphthalene (Table 2, entry 30):



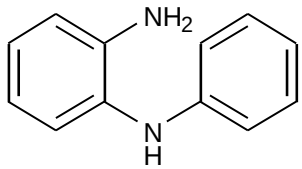
^{1}H NMR (300 MHz, $CDCl_3$): δ 4.12 (bs, 2H), 6.81 (d, *J* = 6.084 Hz, 1H), 7.33-7.51 (m, 3H), 7.75-7.84 (m, 2H), ^{13}C NMR (75 MHz, $CDCl_3$): δ 110.1, 119.4, 121.3, 124.1, 125.3, 126.3, 126.8, 129.0, 134.8, 142.6. HRMS calculated for $[M+H]^+$ is 144.0813 and found 144.837.

2-Aminofullrene (Table 2, entry 31):



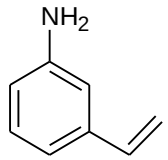
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.74 (brs, 2H), 3.85(s, 2H), 6.73-6.76 (m, 1H), 6.8 (s, 1H), 7.24-7.29 (m, 1H), 7.37-7.41 (m, 1H), 7.50 (d, *J* = 7.3, 1H), 7.62 (d, *J* = 8.0, 1H), 7.70 (d, *J* = 7.5, 1H),; ^{13}C NMR (75 MHz, $CDCl_3$): δ 37.2, 112.2, 114.4, 119.0, 121.0, 125.2, 125.5, 127.1, 133.3, 142.6, 142.7, 145.6, 146.2. HRMS calculated for $[M+H]^+$ is 182.0970 and found 182.0953.

2-Aminodiphenylamine (Table 2, entry 31):



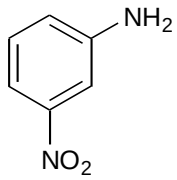
^{1}H NMR (300 MHz, CD_3OD): δ 5.30 (brs, 1H), 6.67-6.74 (m, 4H), 6.82-6.85 (m, 1H), 6.91-6.96 (m, 1H), 7.05-7.15 (m, 3H); ^{13}C NMR (75 MHz, CD_3OD): δ 116.4, 117.9, 119.9, 120.2, 126.1, 126.5, 130.4, 130.9, 143.8, 148.0. HRMS calculated for $[M+H]^+$ is 185.1079 and found 185.1054.

3-Aminostyrene (Table 2, entry 33):



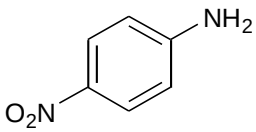
^{1}H NMR (300 MHz, $CDCl_3$) δ 5.22 (d, *J* = 10.8 Hz, 1H), 5.72 (d, *J* = 17.6 Hz, 1H), 6.60-6.63 (m, 2H), 6.76 (s, 1H), 6.85 (d, *J* = 7.4 Hz, 1H), 7.11-7.16 (m, 1H), ^{13}C NMR (300 MHz, $CDCl_3$) δ 113.1, 113.9, 115.1, 117.3, 129.8, 137.4, 139.1, 146.9. HRMS calculated for $[M+H]^+$ is 120.0813 and found 120.0801.

3-Nitroaniline (Table 2, entry 35):



^{1}H NMR (300 MHz, $CDCl_3$): δ 4.05 (bs, 2H), 6.95 (d, *J* = 9.3 Hz, 1H), 7.24-7.29 (m, 1H), 7.48 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 1H),; ^{13}C NMR (75 MHz, $CDCl_3$): δ 109.3, 113.4, 121.0, 130.3, 147.9, 149.6. HRMS calculated for $[M+H]^+$ is 139.0508 and found 139.0563.

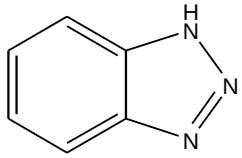
4-Nitroaniline (Table 2, entry 36):



^{1}H NMR (300 MHz, $CDCl_3$): δ 4.43 (bs, 2H), 6.63 (d, *J* = 8.7 Hz, 2H), 8.08 (d, *J* = 8.7 Hz, 2H),; ^{13}C NMR (75 MHz, $CDCl_3$): δ 113.7, 126.7,

139.4, 152.9. HRMS calculated for $[M+H]^+$ is 139.0508 and found 139.0531.

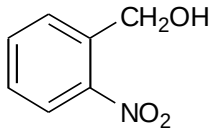
Benzotriazole



^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40-7.43 (m, 2H), 7.92-7.95 (m, 2H),; ^{13}C NMR (75 MHz, $CDCl_3$): δ 115.3, 126.4, 139.2; HRMS calculated for $[M+H]^+$ is 120.0562 and found 120.0562.

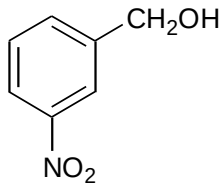
Characterization of carbonyl reduction products:

2-Nitro-benzylalchol (Table 3, entry 1)



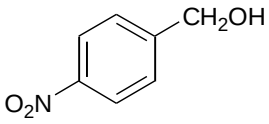
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.58 (brs, 1H), 4.99 (s, 2H), 7.47-7.52 (m, 1H), 7.67-7.77 (m, 2H), 8.12 (d, *J* = 8.17 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 62.9, 125.4, 128.9, 130.3, 134.5, 137.1, 148.0.

3-Nitro-benzylalchol (Table 3, entry 2)



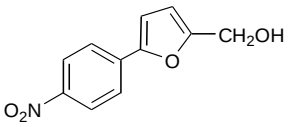
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.12 (brs, 1H), 4.76 (s, 2H), 7.46-7.51 (m, 1H), 7.64-7.66 (m, 1H), 8.05-8.08 (m, 1H), 8.17 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 64.1, 121.7, 122.7, 129.8, 133.1, 143.3, 148.6.

4-Nitro-benzylalchol (Table 3, entry 3)



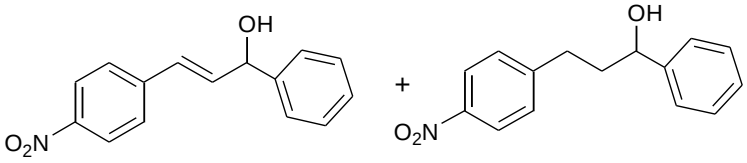
^{1}H NMR (300 MHz, $CDCl_3$): δ 2.55 (brs, 1H), 4.82 (s, 2H), 7.52 (d, *J* = 8.3Hz, 2H), 8.18 (d, *J* = 8.6 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 64.3, 124.0, 127.3, 147.5, 148.7.

4-(4-Nitrophenyl)-furfural alcohol (Table 3, entry 5)



^{1}H NMR (300 MHz, CD_3COCD_3): δ 4.75 (brs, 1H), 4.65 (s, 2H), 6.51 (d, *J* = 3.3Hz, 1H), 7.12 (d, *J* = 3.3 Hz, 1H), 7.94 (d, *J* = 11.1Hz, 2H), 8.28 (d, *J* = 11.2 Hz, 1H); ^{13}C NMR (75 MHz, CD_3COCD_3): δ 56.8, 110.0, 110.7, 124.1, 124.5, 136.9, 146.7, 151.2, 158.2.

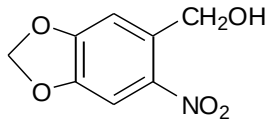
(Table 3, entry 6)



^{1}H NMR (300 MHz, CD_3COCD_3): δ 2.04-2.09 (m, 2H), 2.87-2.91 (m, 2H), 4.73 (t, *J* =7.1, 1H), 5.46 (d, *J* =5.3, 1H), 6.74-6.76 (m, 1H), 6.87-6.89 (m, 1H), 7.24-7.42 (m, 7H), 7.46-7.55 (m, 5H), 7.69-7.72 (m, 2H), 8.13-8.19 (m, 4H); ^{13}C NMR (75 MHz, CD_3COCD_3): δ 33.3, 42.1, 73.8,

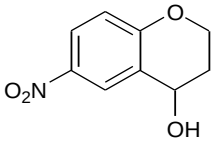
75.3, 124.9, 125.3, 127.3, 127.9, 128.2, 128.4, 128.7, 128.8, 129.6, 129.8, 131.0, 139.7, 145.1, 145.4, 147.3, 147.8, 148.3, 152.3.

3,4-methylenedioxy-6-nitrobenzylalchol (Table 3, entry 7)



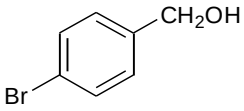
^{1}H NMR (300 MHz, CD_3OD): δ 4.86 (s, 2H), 6.15 (s, 2H), 7.29 (s, 1H), 7.58 (s, 1H); ^{13}C NMR (75 MHz, CD_3OD): δ 61.2, 103.6, 105.0, 106.8, 136.4, 140.9, 147.2, 153.1.

(Table 3, entry 8)



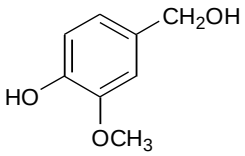
^{1}H NMR (300 MHz, CD_3OD): δ 1.89-1.98 (m, 1H), 2.01-2.10 (m, 1H), 3.54 (brs, 1H), 4.25-4.29 (m, 2H), 4.69 (overlapped with MeOD signal), 6.81 (d, *J* = 10.8, 1H), 7.95 (d, *J* = 11.6, 1H), 8.18 (s, 1H); ^{13}C NMR (75 MHz, CD_3OD): δ 31.9, 63.9, 65.2, 118.9, 126.2, 127.3, 127.6, 142.7, 161.9

4-Bromo-benzylalchol (Table 3, entry 10)



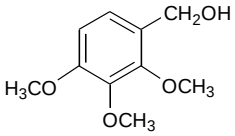
^{1}H NMR (300 MHz, CD_3OD): δ 4.56 (s, 2H), 7.25 (d, *J* = 8.2Hz, 2H), 7.47 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (75 MHz, CD_3OD): δ 63.4, 120.9, 128.8, 131.4, 141.0.

3-Metoxy-4-hydroxybenzylalchol (Table 3, entry 11)



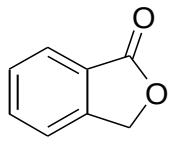
^{1}H NMR (300 MHz, CD_3OD): δ 3.84 (s, 3H), 4.51 (s, 2H), 6.78 (s, 2H), 6.94 (s, 1H); ^{13}C NMR (75 MHz, CD_3OD): δ 55.3, 64.3, 111.1, 115.0, 120.1, 133.2, 145.9, 147.9.

2,3,4-Trimethoxybenzylalchol (Table 3, entry 12)



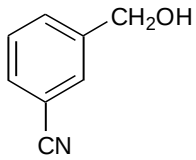
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.76 (s, 3H), 3.78 (s, 3H), 3.83 (s, 3H), 4.51 (s, 2H), 6.56 (d, *J* = 8.4Hz, 2H), 6.92 (d, *J* = 8.4 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 56.3, 61.0, 61.4, 107.5, 123.6, 127.4, 142.3, 151.9, 153.7.

Thalide (Table 3, entry 13)



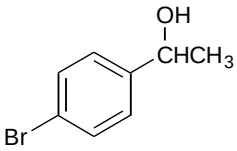
^{1}H NMR (300 MHz, $CDCl_3$): δ 5.33 (s, 2H), 7.53 (t, *J* = 8.4, 2H), 7.69 (t, *J* = 7.5, 1H), 7.91 (d, *J* = 7.4, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 69.7, 122.2, 125.8, 129.1, 134.1, 146.6, 171.2.

3-Cyano-benzylalchol (Table 3, entry 14)



^{1}H NMR (300 MHz, CD_3OD): δ 4.66 (s, 2H), 7.50-7.55 (m, 1H), 7.61-7.71 (m, 3H); ^{13}C NMR (75 MHz, CD_3OD): δ 62.9, 112.3, 118.7, 129.4, 130.1, 130.8, 131.3, 143.8.

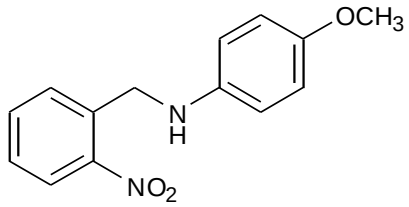
1-(4-Bromophenyl)ethanol (Table 3, entry 16)



^{1}H NMR (300 MHz, $CDCl_3$): δ 1.40 (d, *J* = 6.4Hz, 3H), 4.75 (q, *J* = 19.3Hz, 2H), 7.17 (d, *J* = 8.3Hz, 2H), 7.43 (d, *J* = 8.3 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 25.5, 69.9, 121.4, 127.6, 131.8, 145.2.

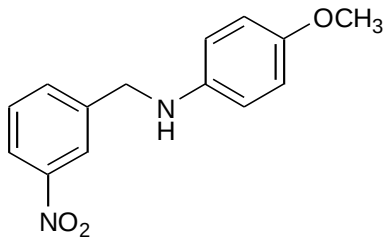
Characterization of carbonyl reductive amination products:

4-Methoxy-*N*-(2′-nitrobenzyl)aniline



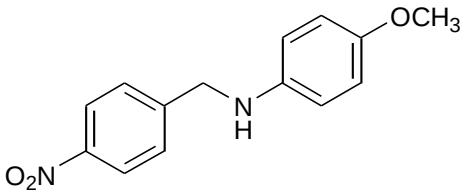
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.74 (s, 3H), 4.67 (s, 2H), 6.54 (d, *J* = 8.9 Hz, 2H), 6.76 (d, *J* = 8.9 Hz, 2H), 7.39-7.44 (m, 1H), 7.54-7.59 (m, 1H), 7.68 (d, *J* = 7.7 Hz, 1H), 8.05 (d, *J* = 8.1 Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 47.0, 56.1, 114.6, 115.3, 125.4, 128.3, 130.3, 133.9, 136.2, 142.0, 148.7, 152.8.

4-Methoxy-*N*-(3′-nitrobenzyl)aniline



^{1}H NMR (300 MHz, $CDCl_3$): δ 3.74 (s, 3H), 4.41 (s, 2H), 6.58 (d, *J* = 8.9 Hz, 2H), 6.78 (d, *J* = 8.9 Hz, 2H), 7.47-7.52 (m, 1H), 7.72 (d, *J* = 7.6 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.24 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 48.8, 56.1, 114.7, 115.4, 122.5, 129.8, 133.7, 142.0, 142.8, 149.0, 153.0.

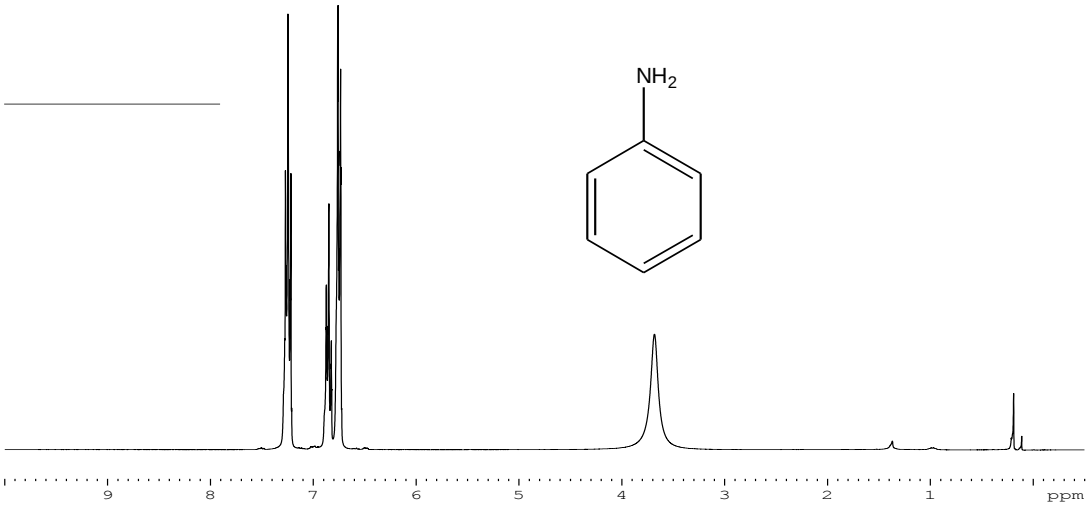
4-Methoxy-*N*-(4′-nitrobenzyl)aniline

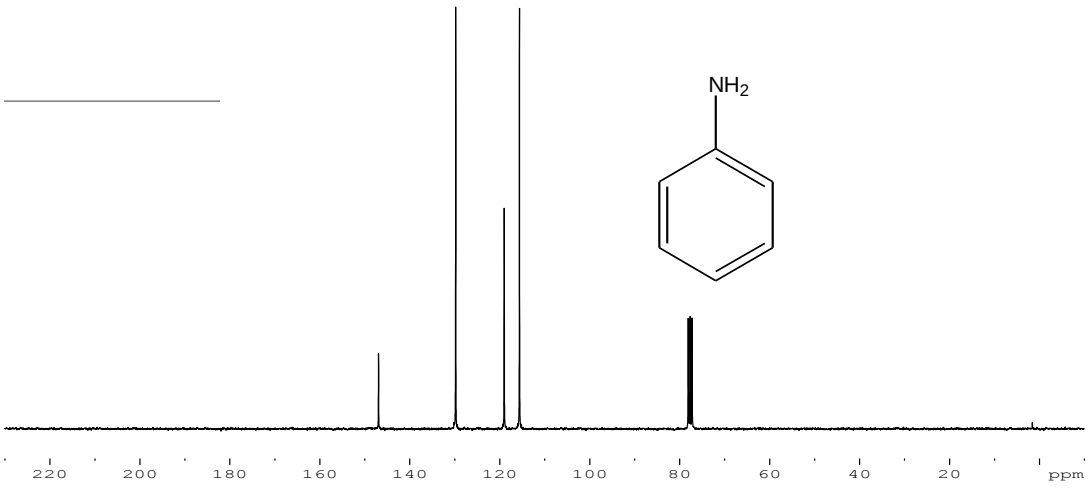


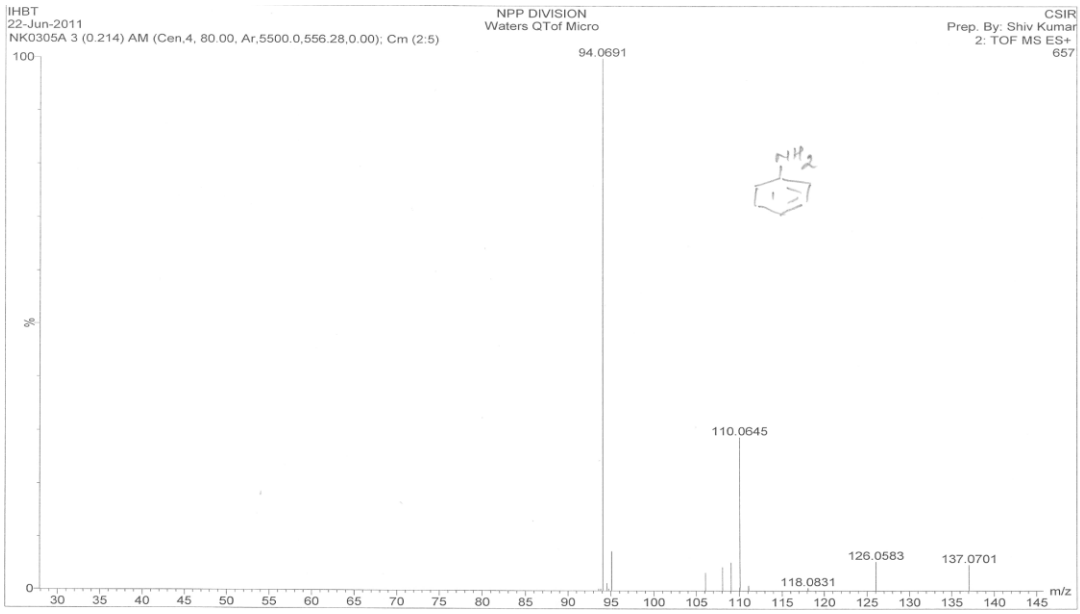
^{1}H NMR (300 MHz, $CDCl_3$): δ 3.74 (s, 3H), 4.44 (s, 2H), 6.55 (d, *J* = 8.9 Hz, 2H), 6.78 (d, *J* = 8.9 Hz, 2H), 7.54 (d, *J* = 8.5 Hz, 2H), 8.18 (d, *J* = 8.5 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 48.9, 56.1, 114.6, 115.4, 124.2, 128.1, 141.9, 147.5, 148.2, 152.9.

4. Spectra of Compounds

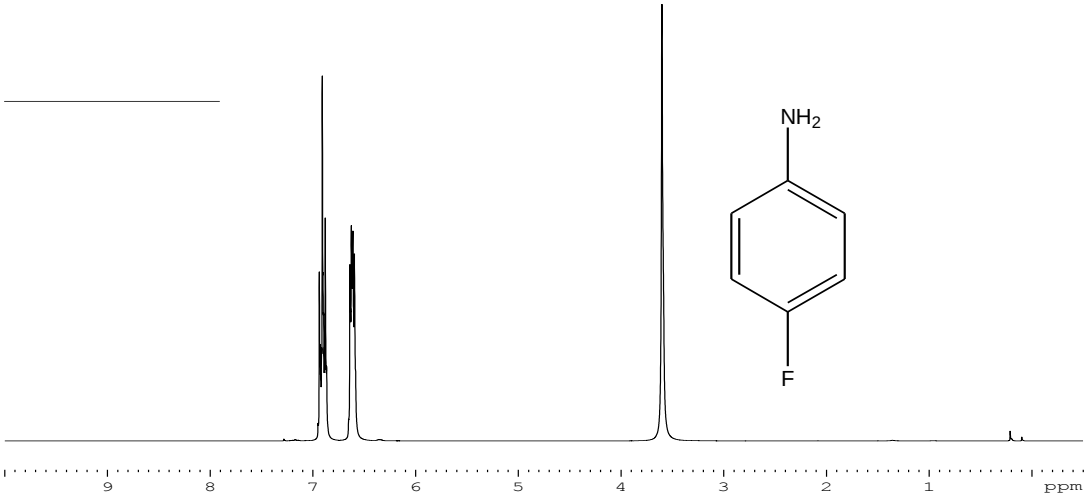
Aniline (Table 2, entry 1)

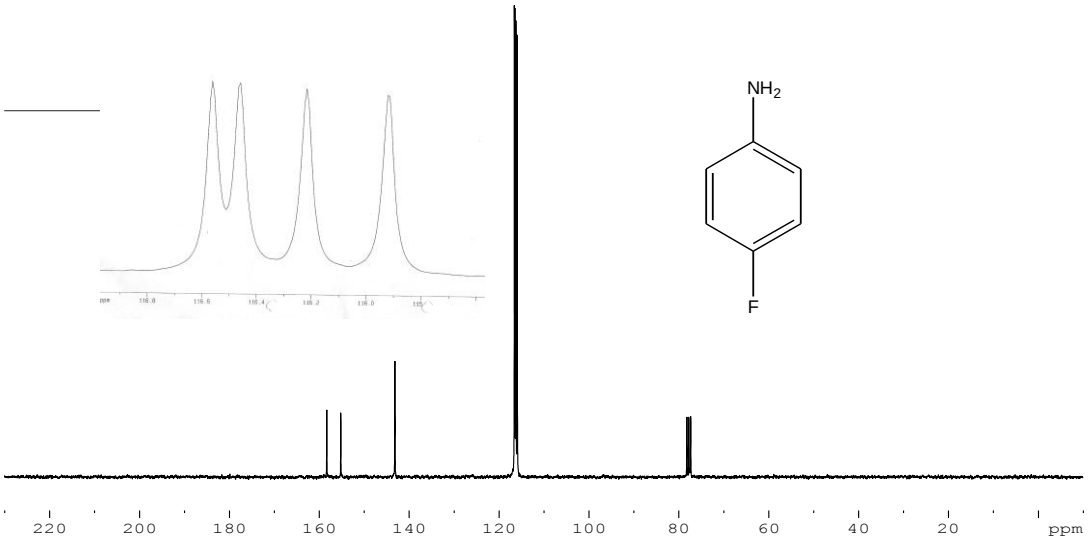


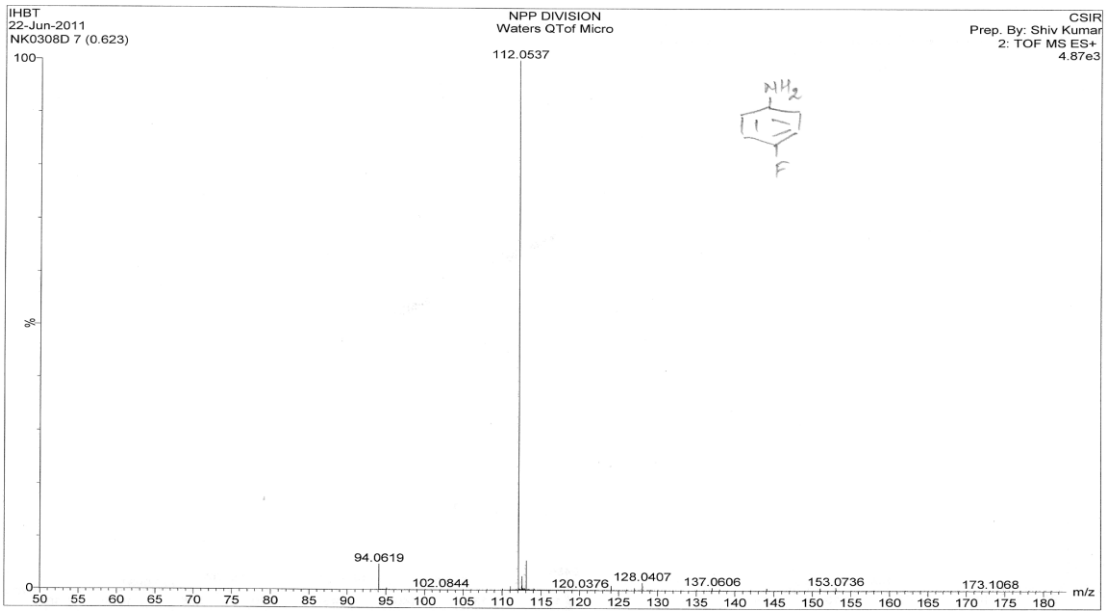




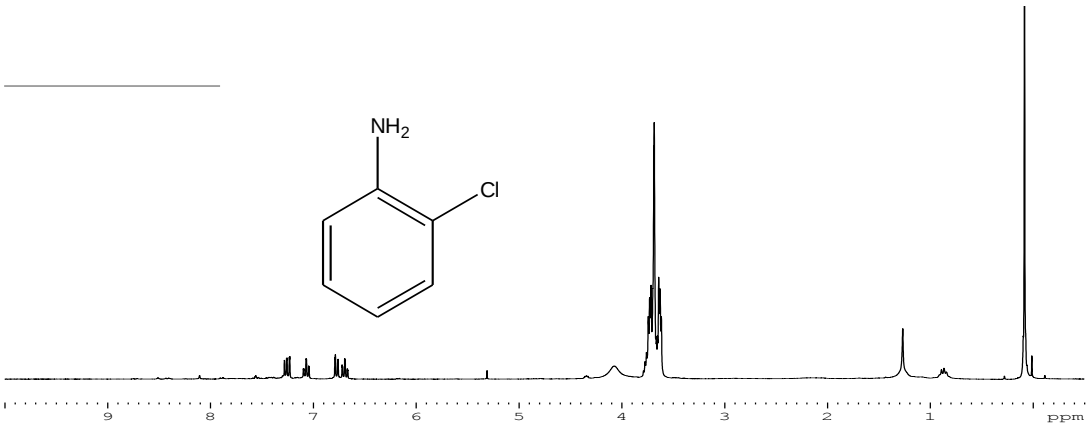
2-Floroaniline (Table 2, entry 2)

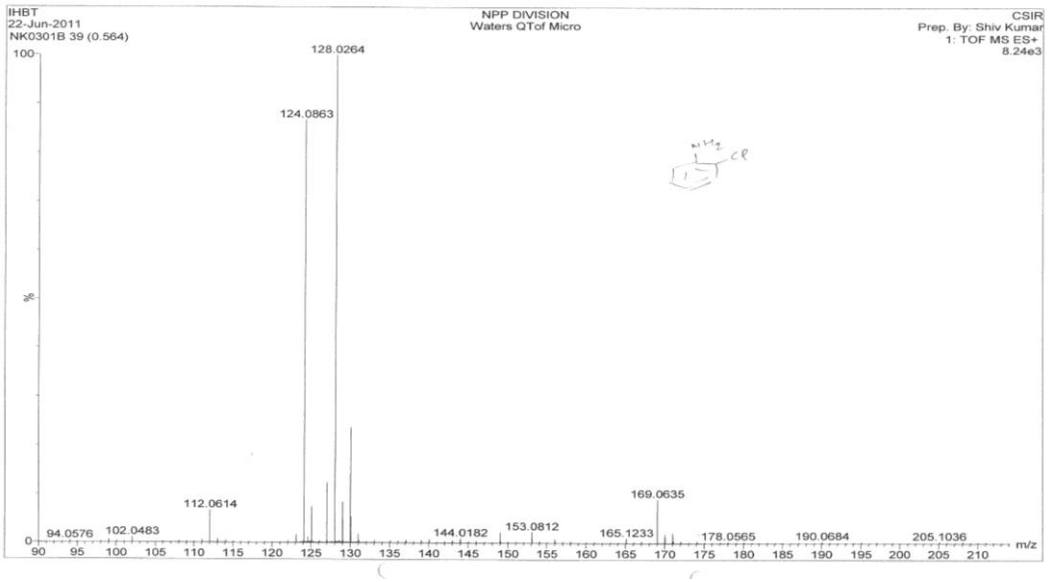




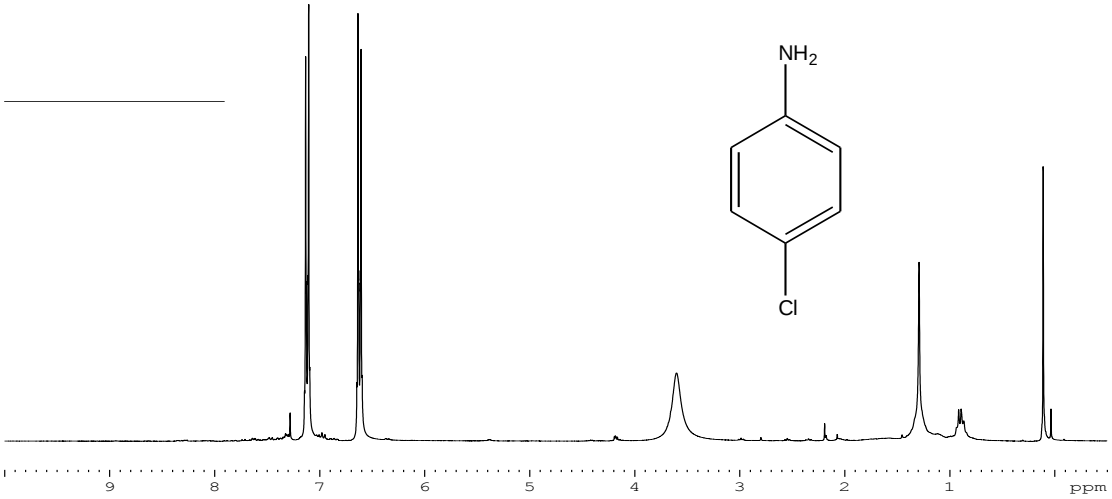


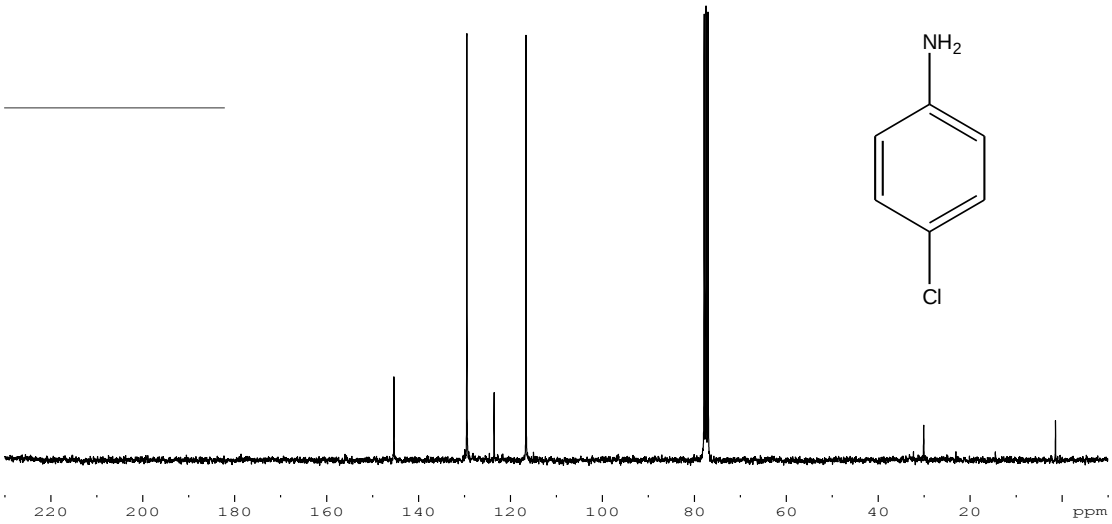
2-Chloroaniline (Table 2, entry 3)

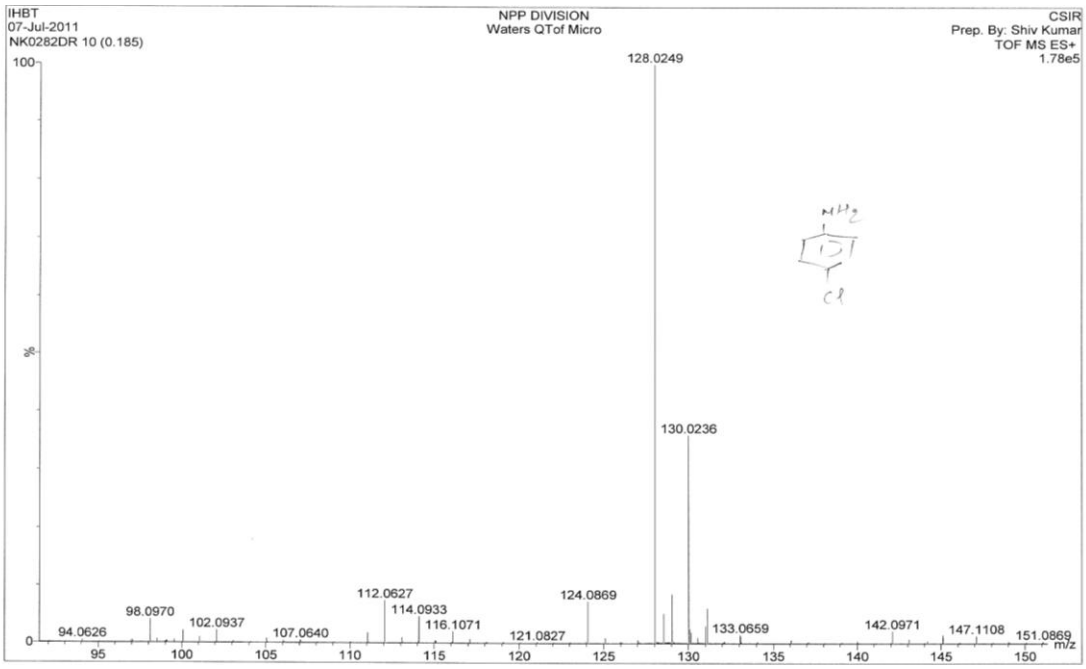




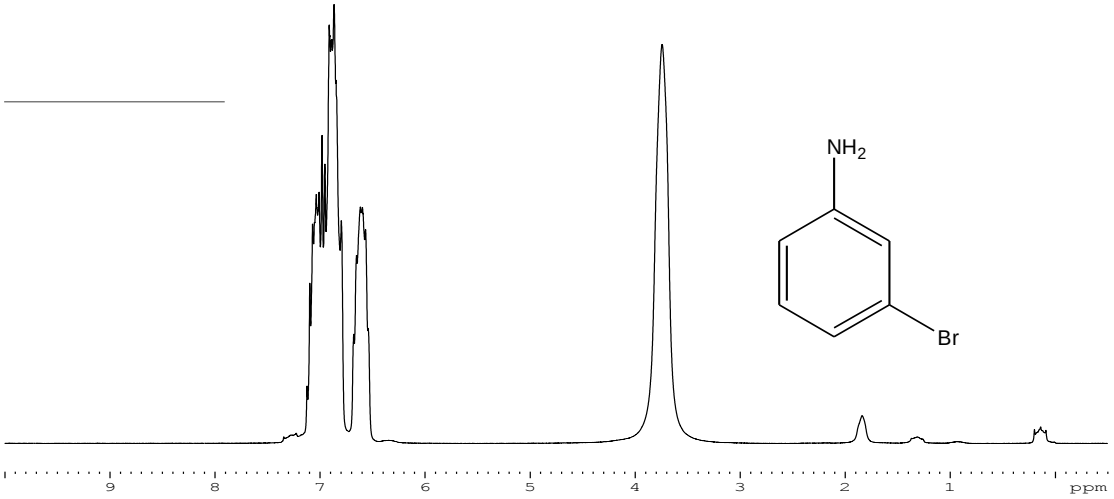
4-Chloroaniline (Table 2, entry 4)

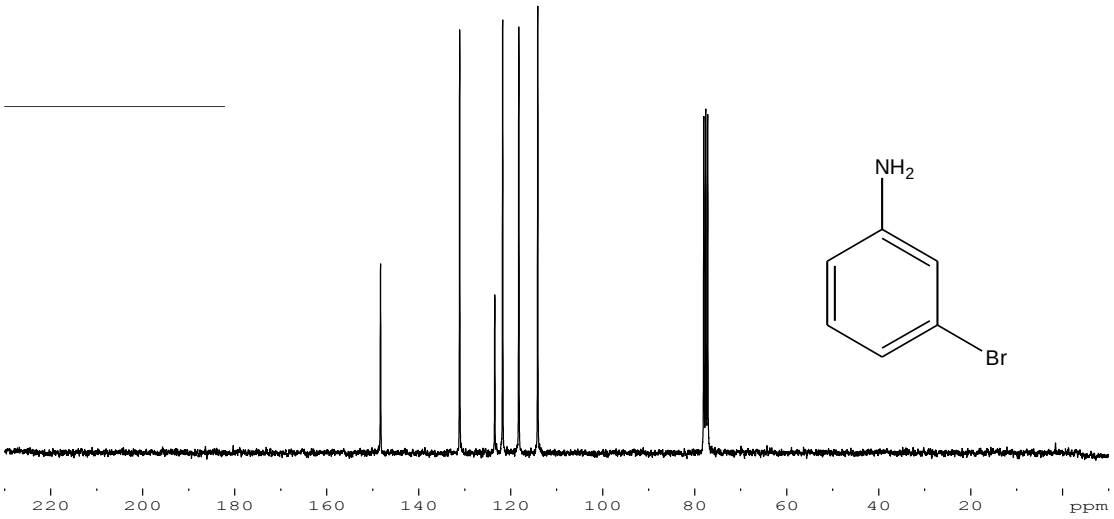


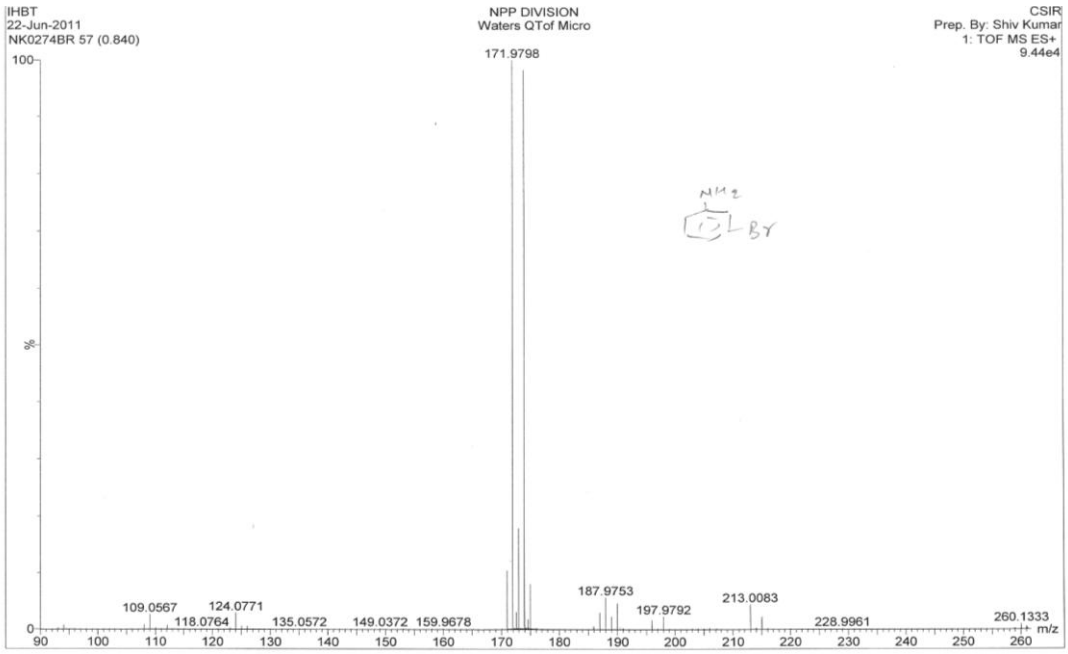




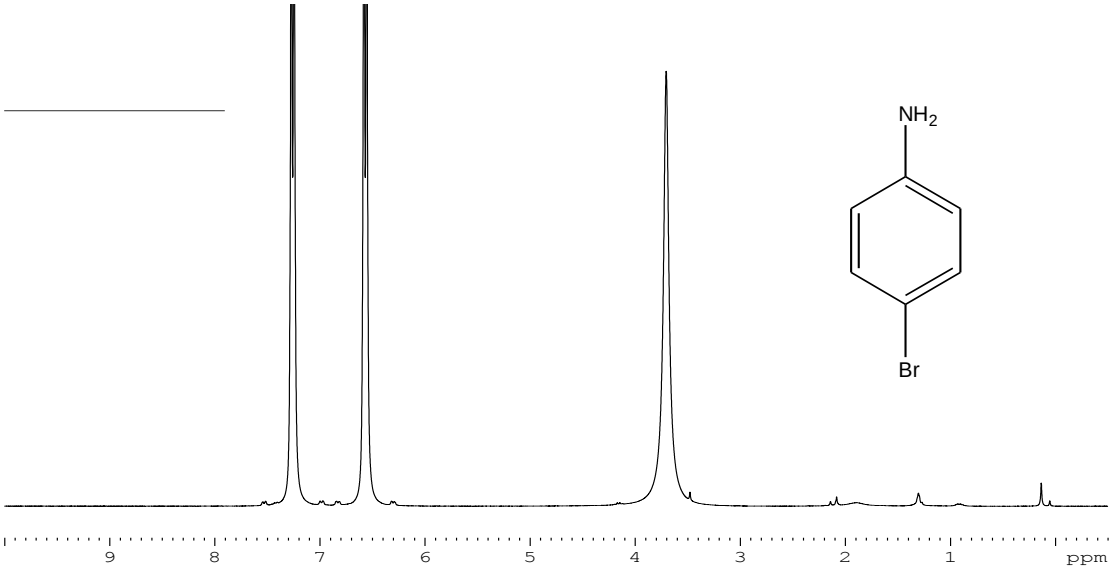
3-Bromoaniline (Table 2, entry 5)

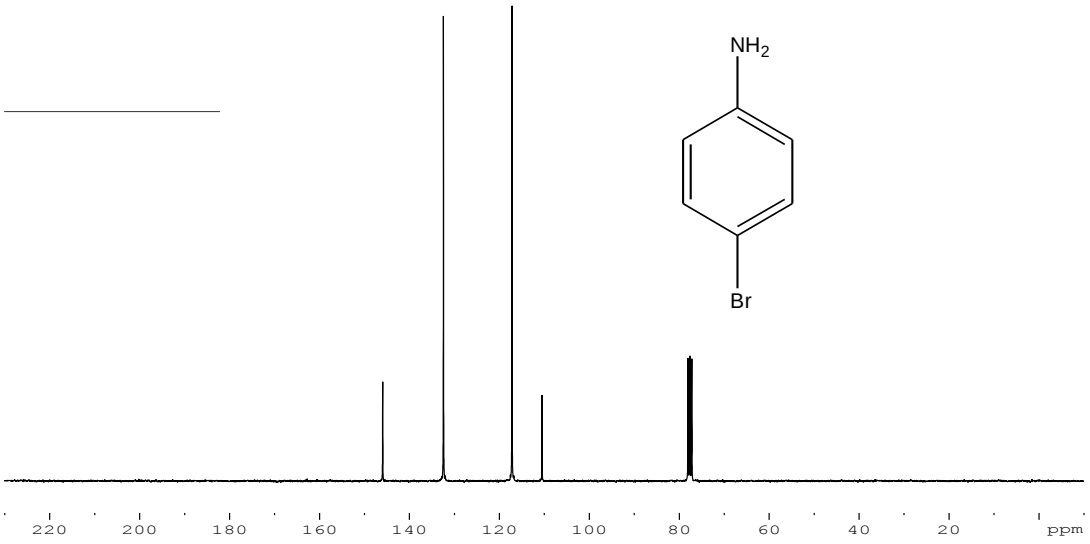


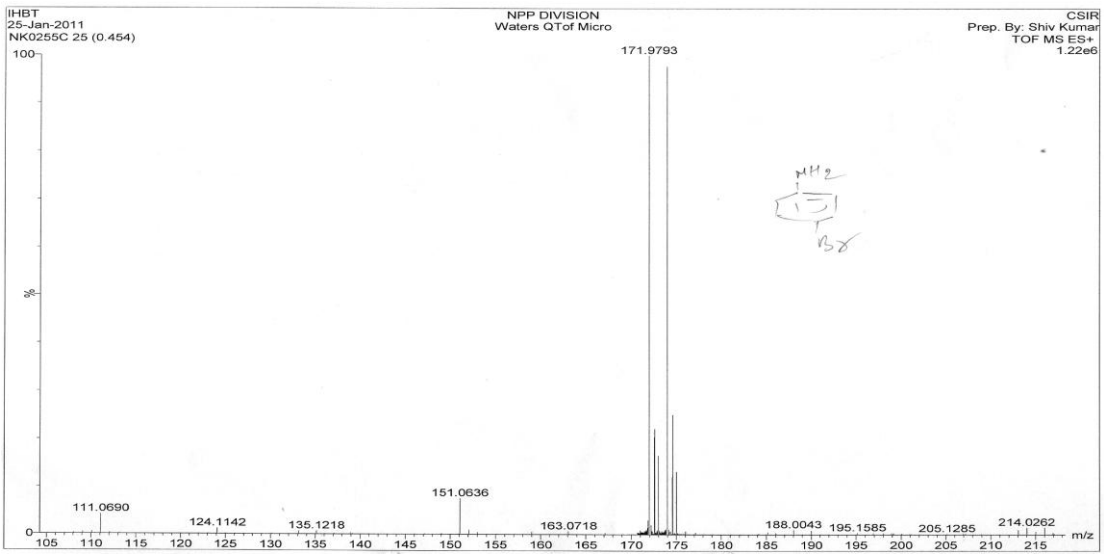




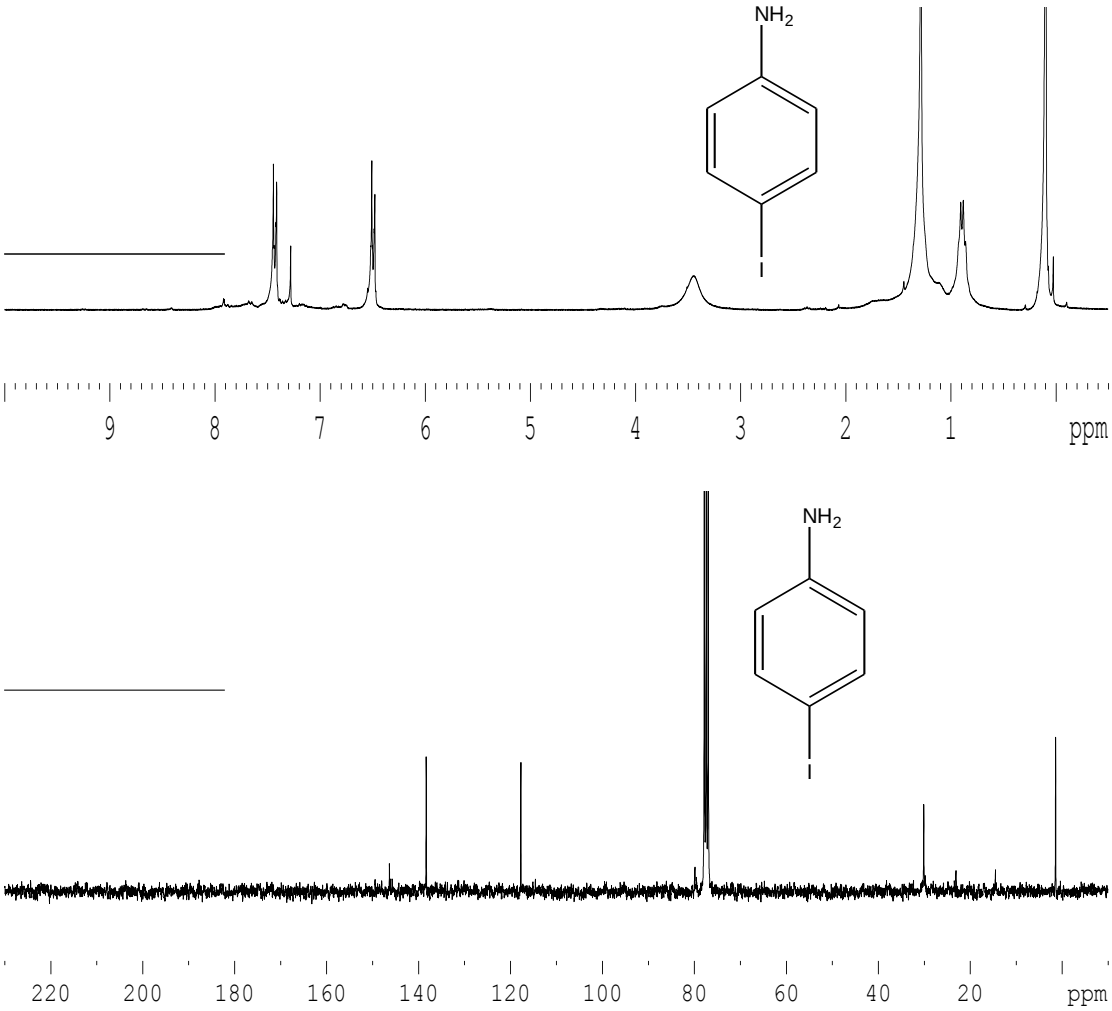
4-Bromoaniline (Table 2, entry 6)

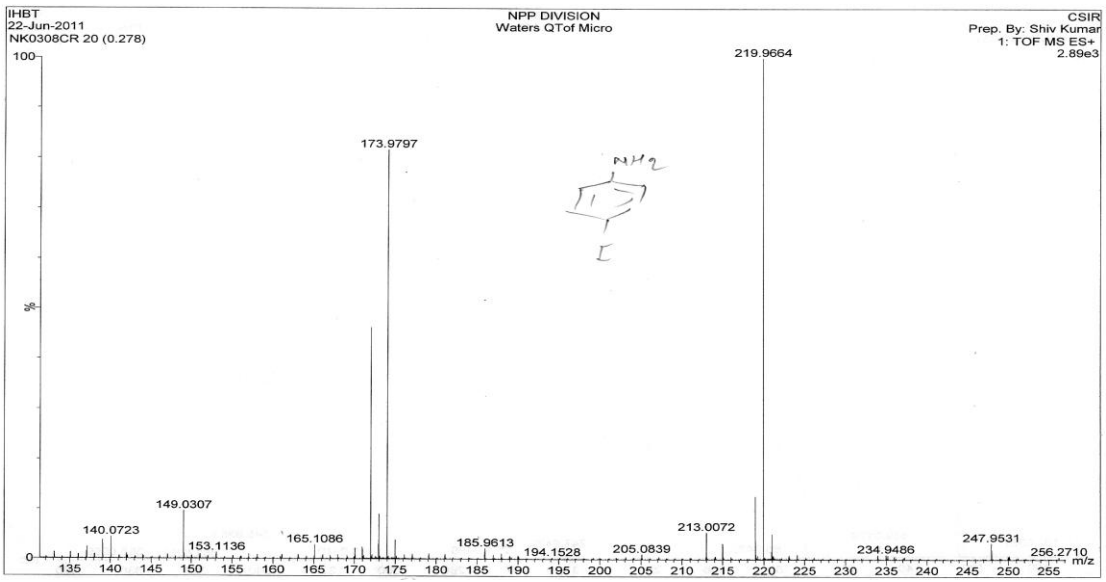




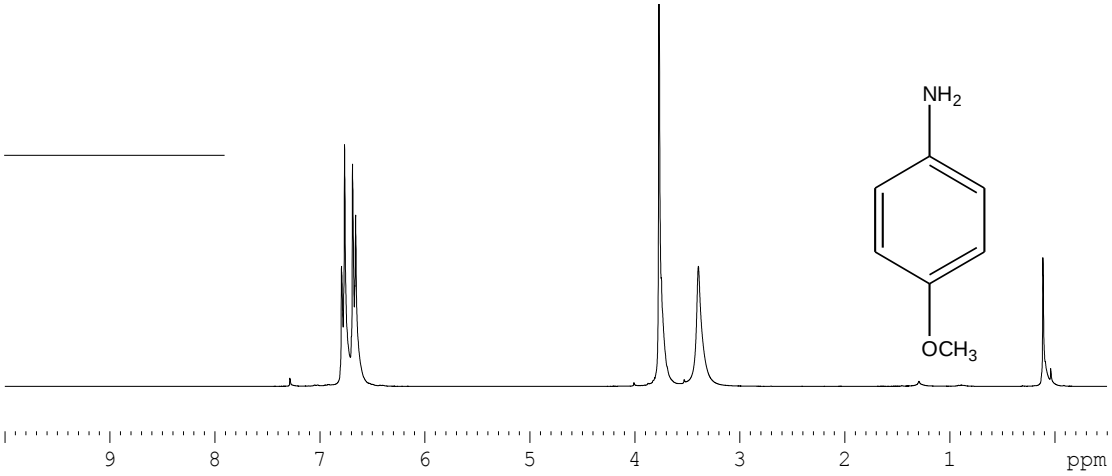


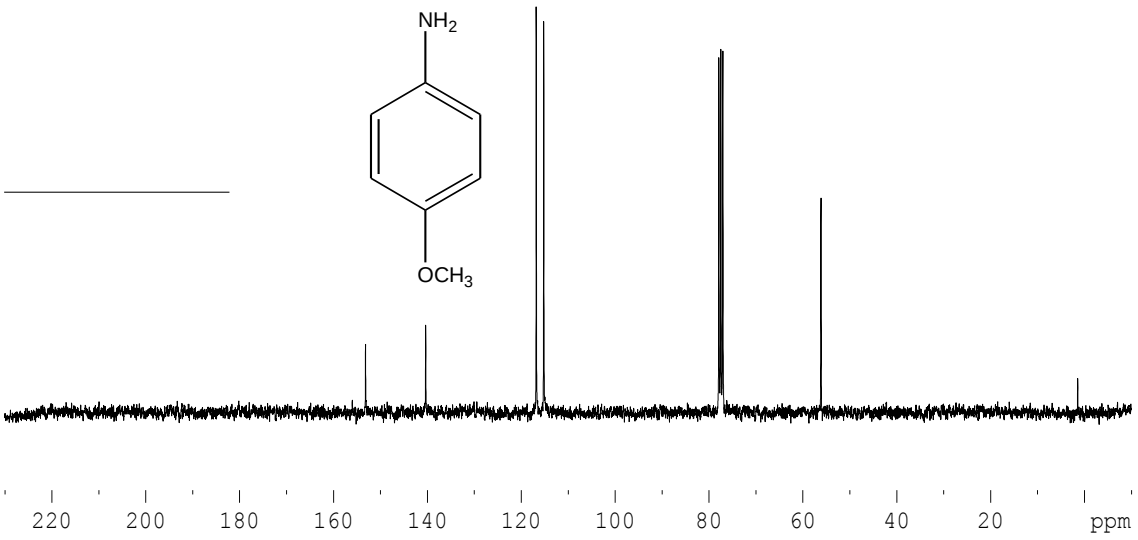
4-Iodoaniline (Table 2, entry 7)

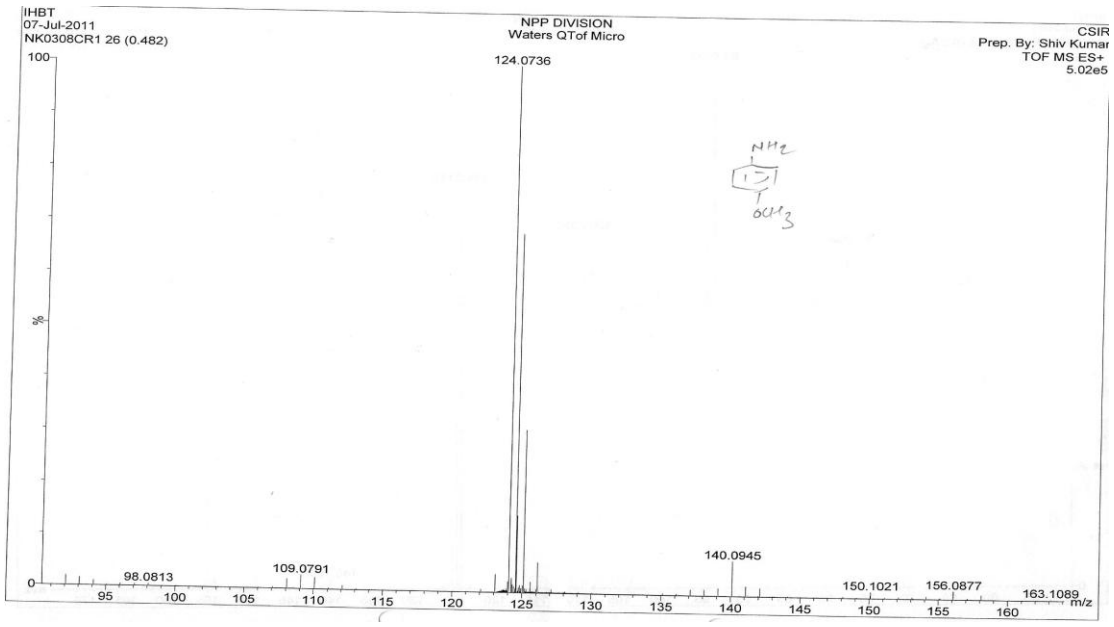




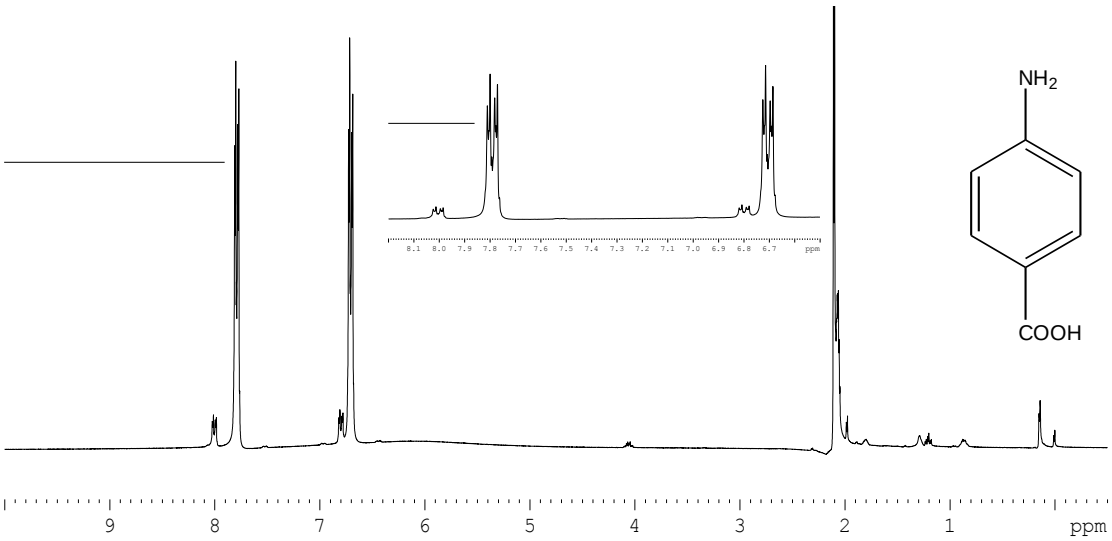
4-Methoxyaniline (Table 2, entry 8)

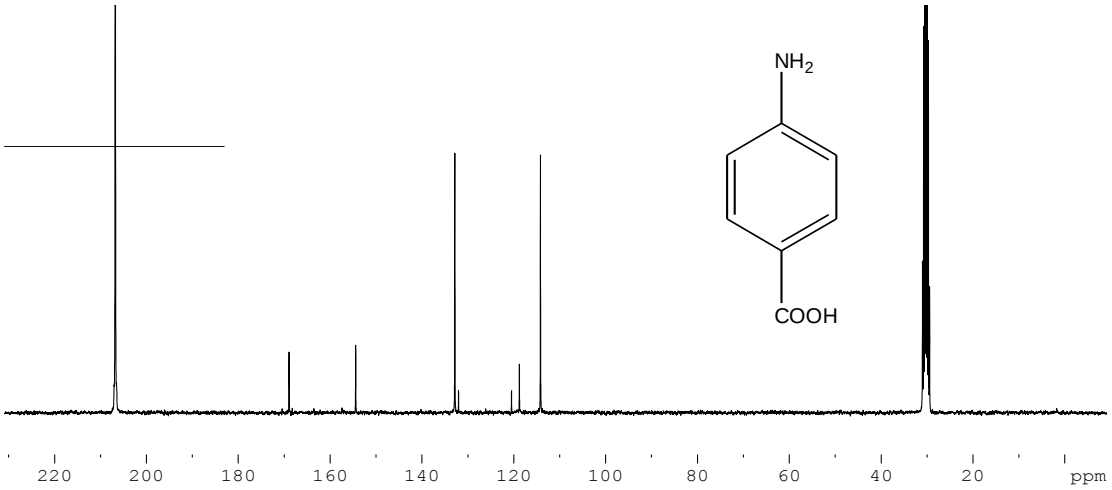


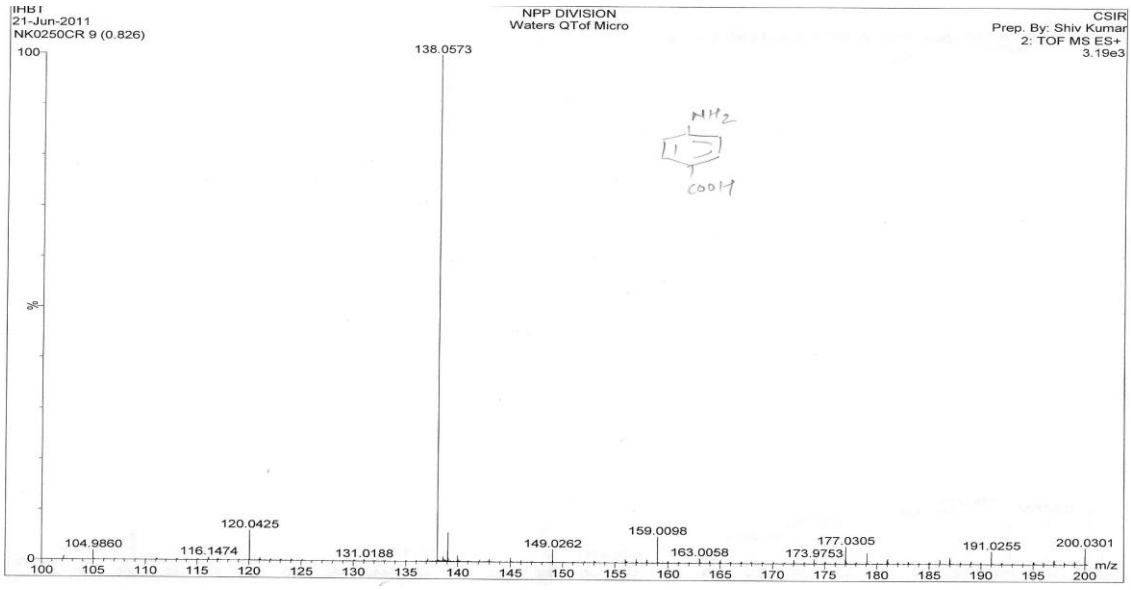




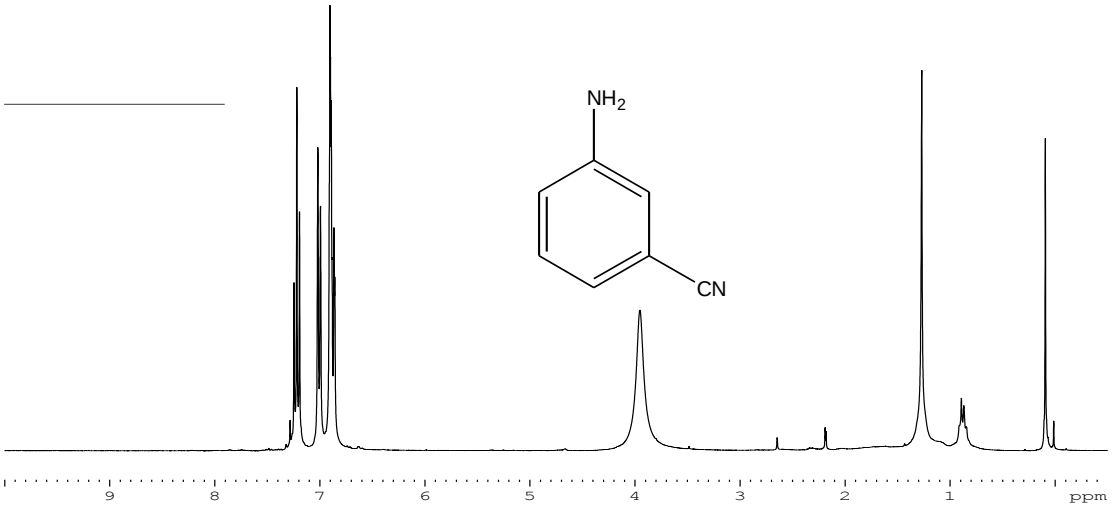
4-Aminobenzoic acid (Table 2, entry 9)

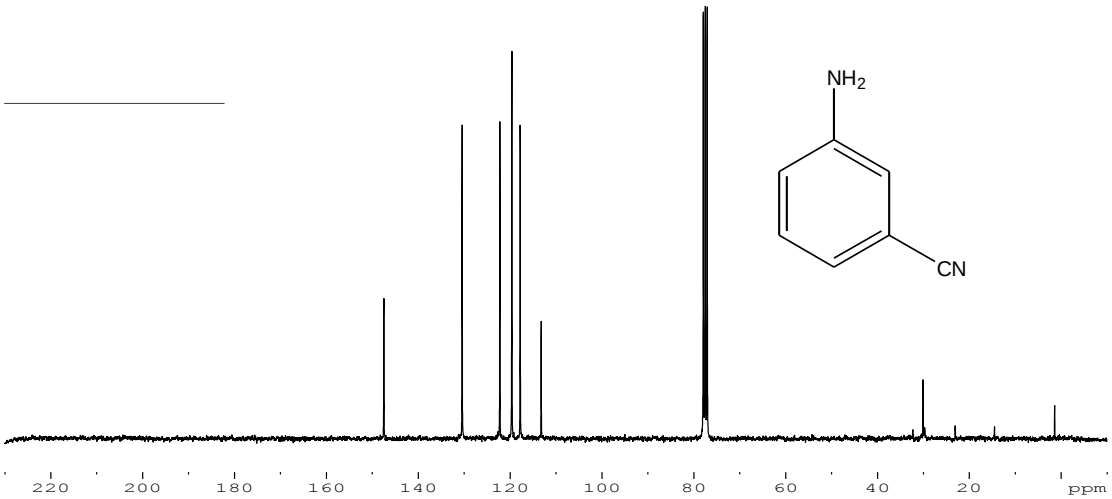


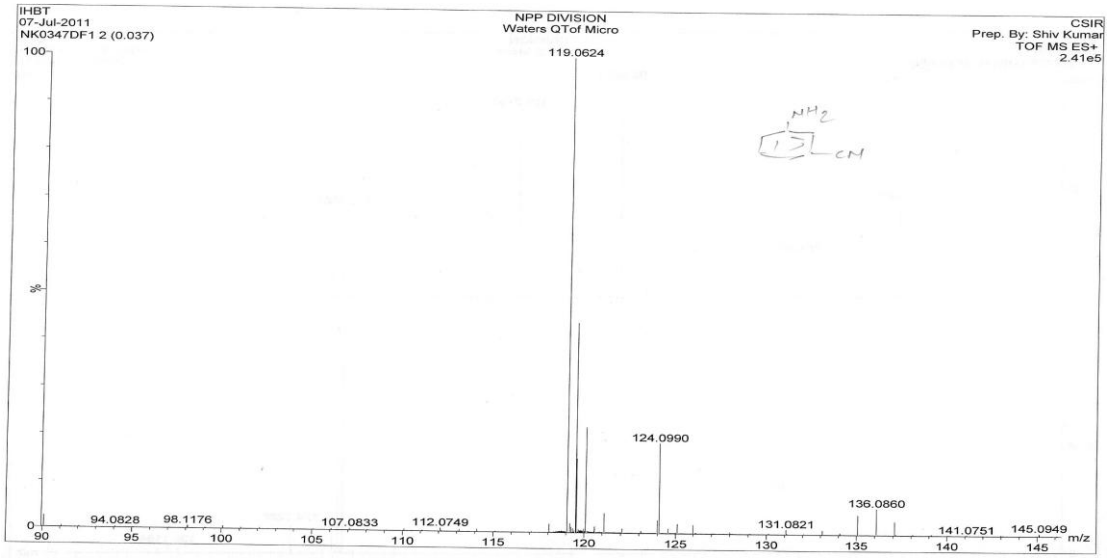




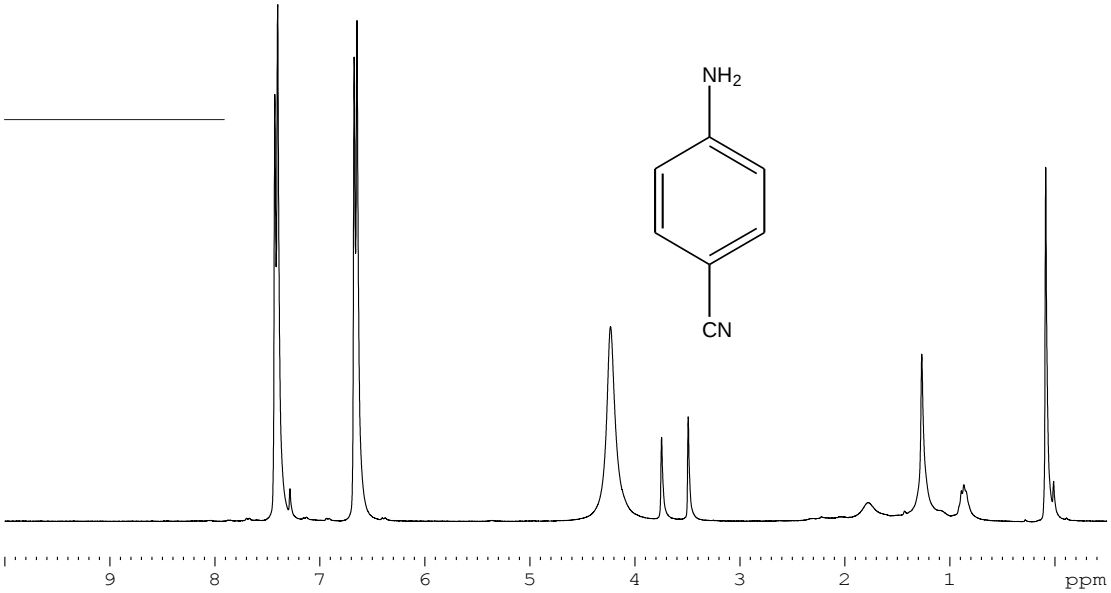
3-aminobenzonitrile (Table 2, entry 10)

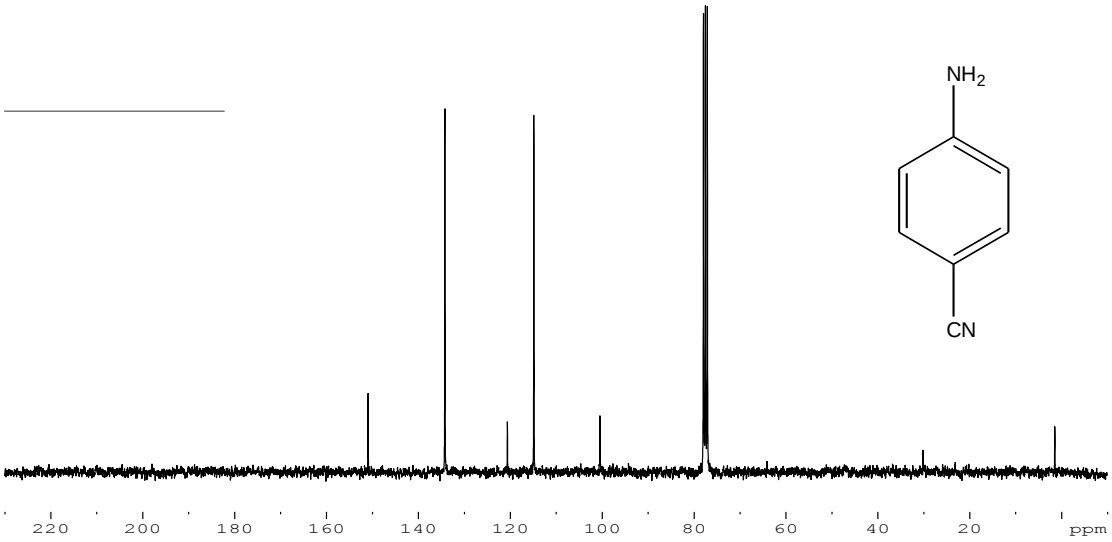


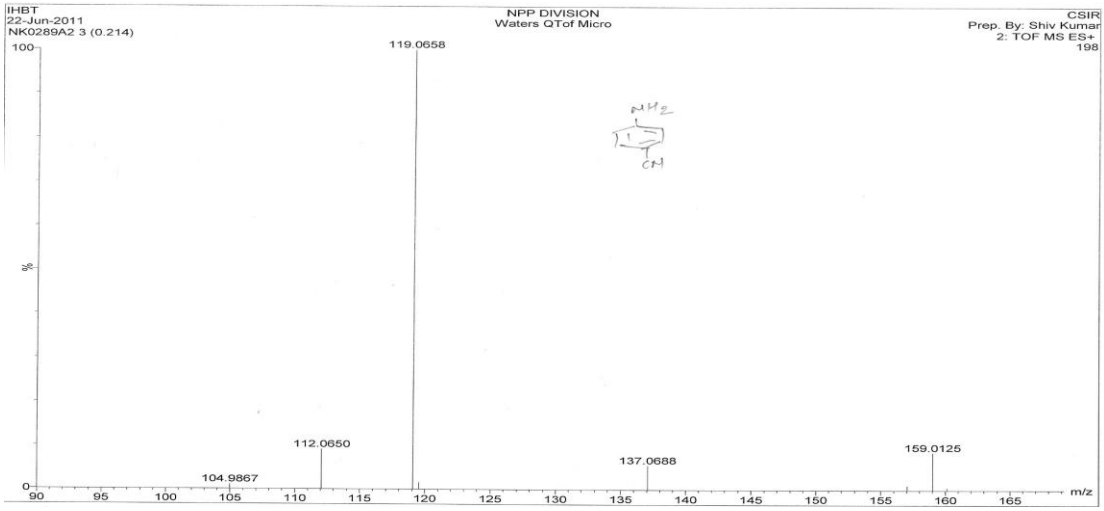




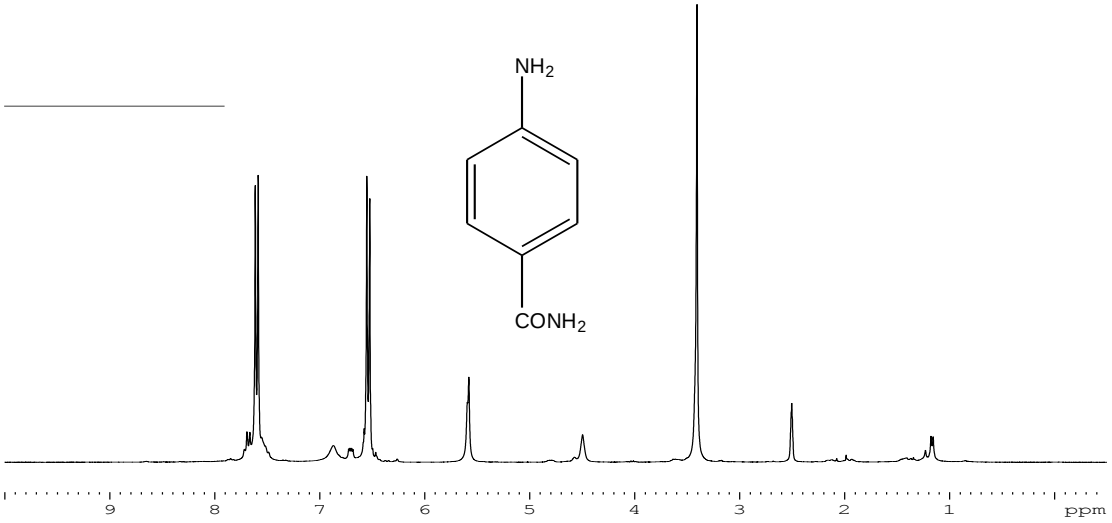
4-aminobenzonitrile (Table 2, entry 11)

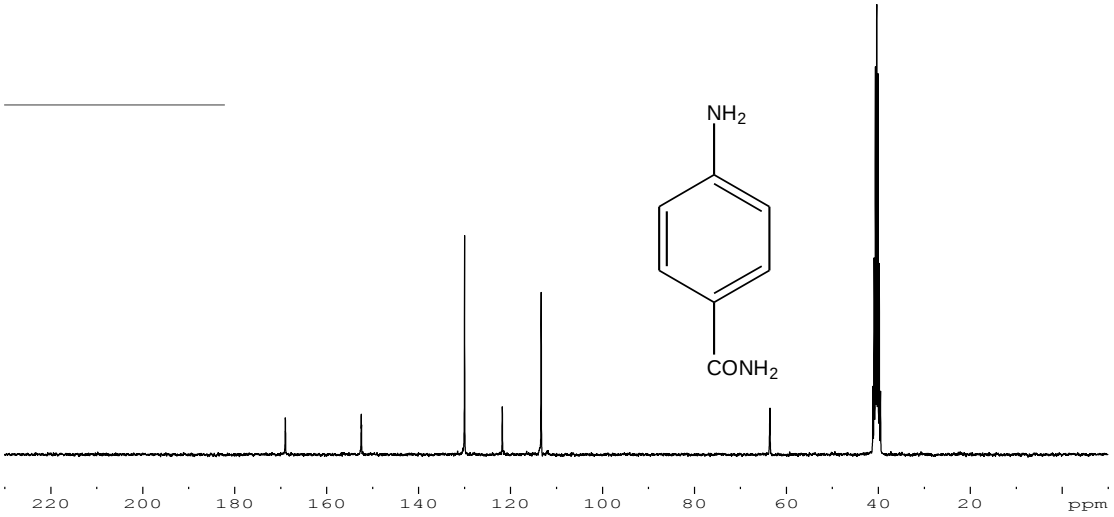


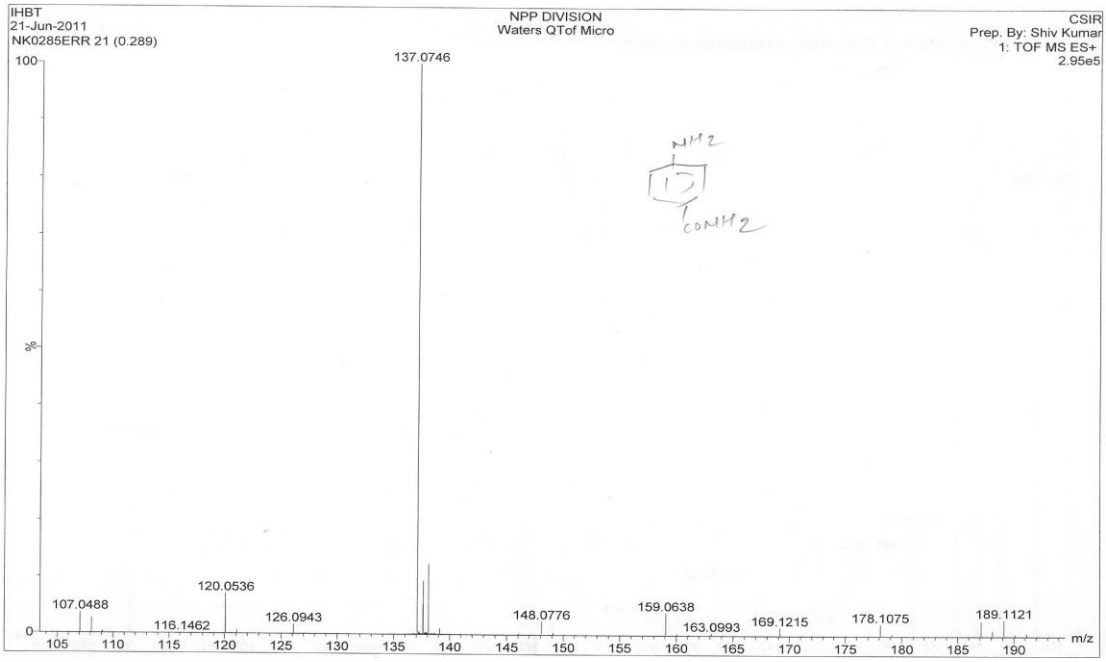




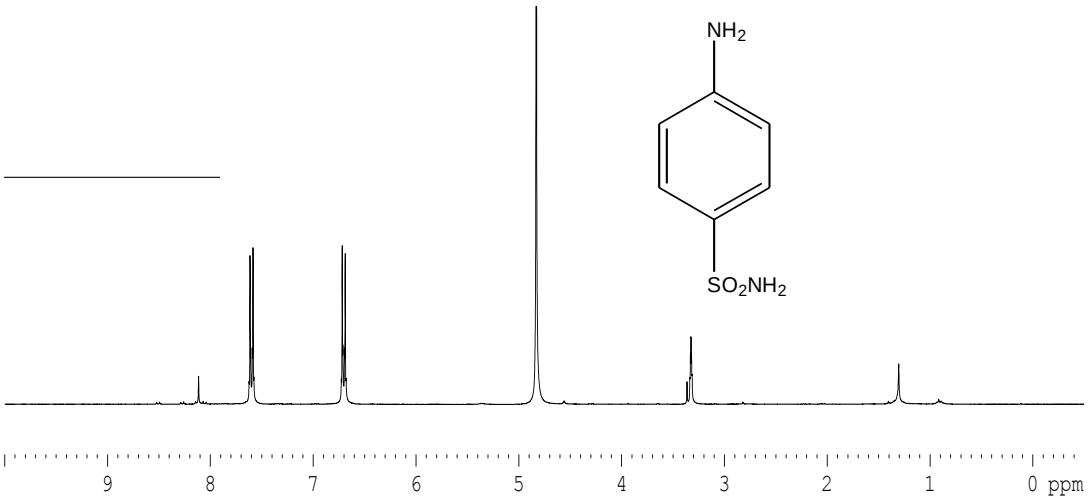
4-Aminobenzamide (Table 2, entry 12)

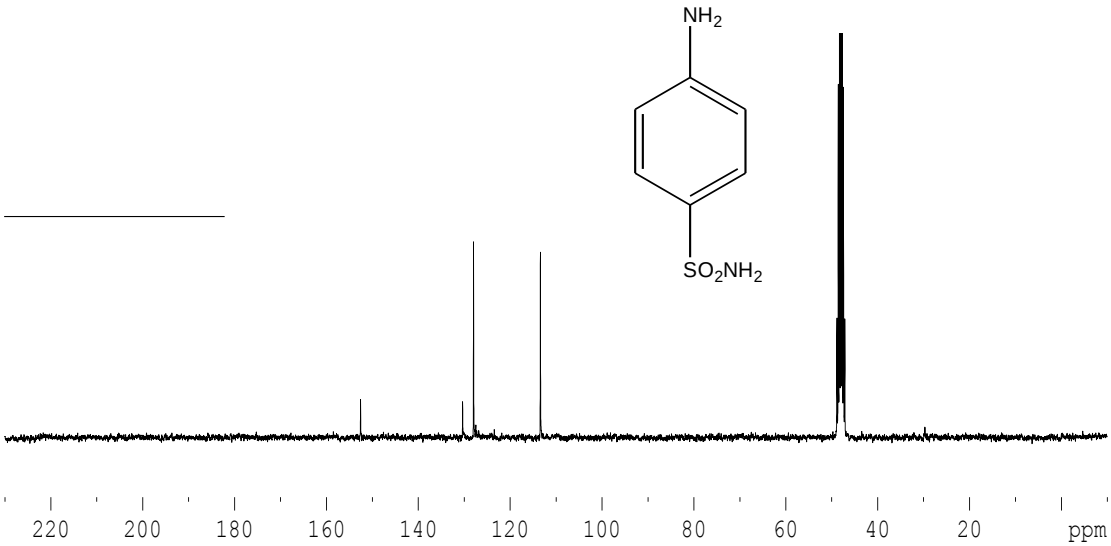


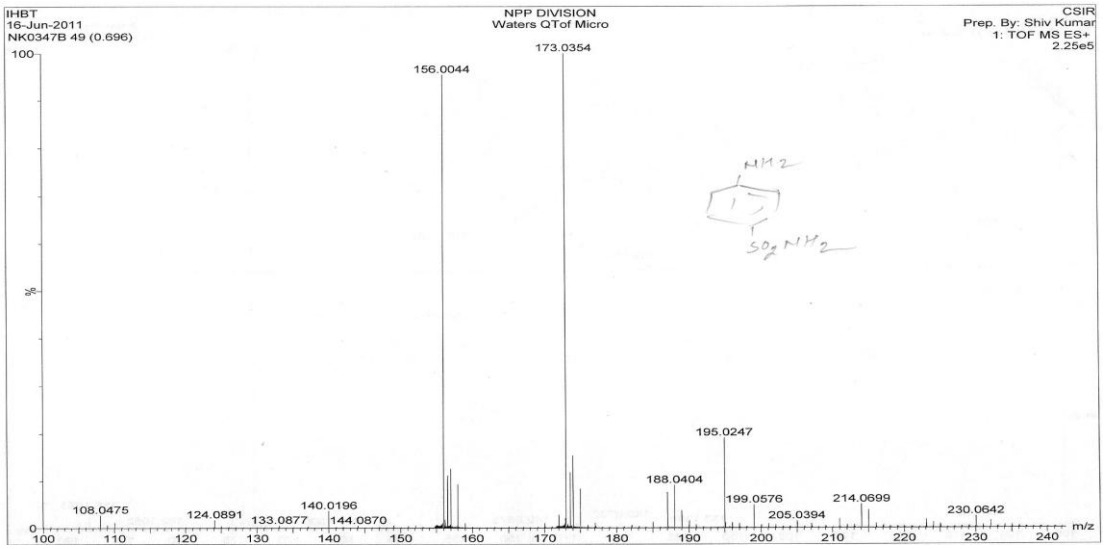




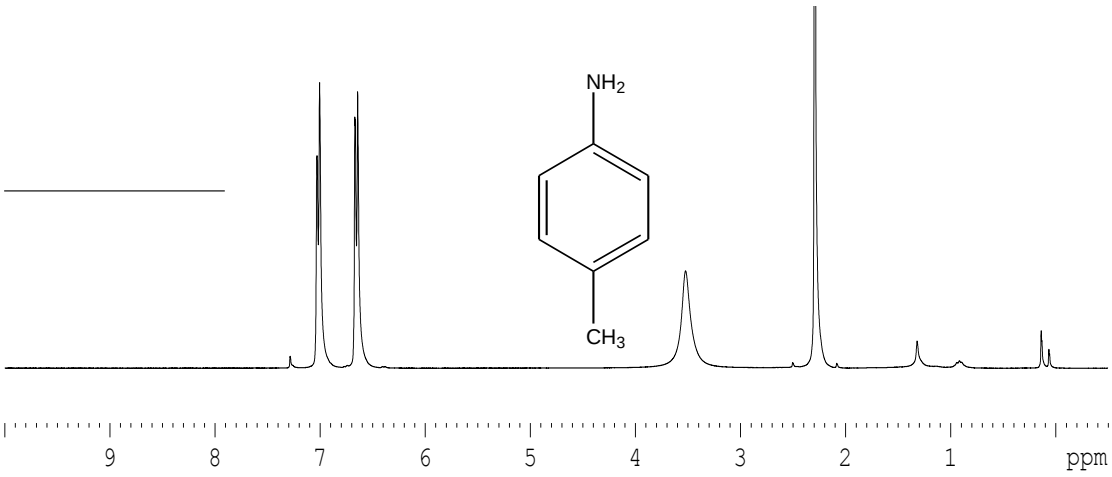
4-Aminosulphonamide (Table 2, entry 13)

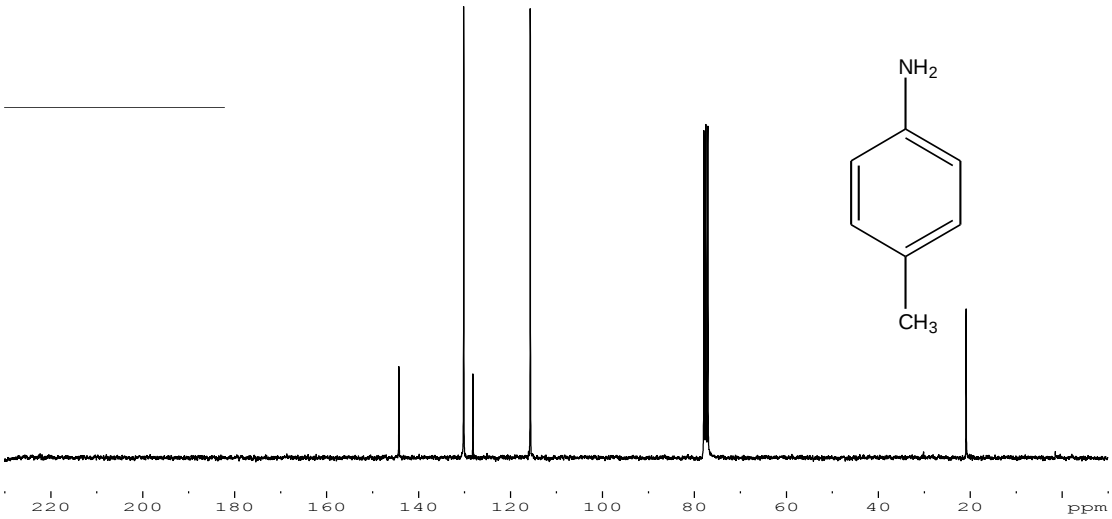


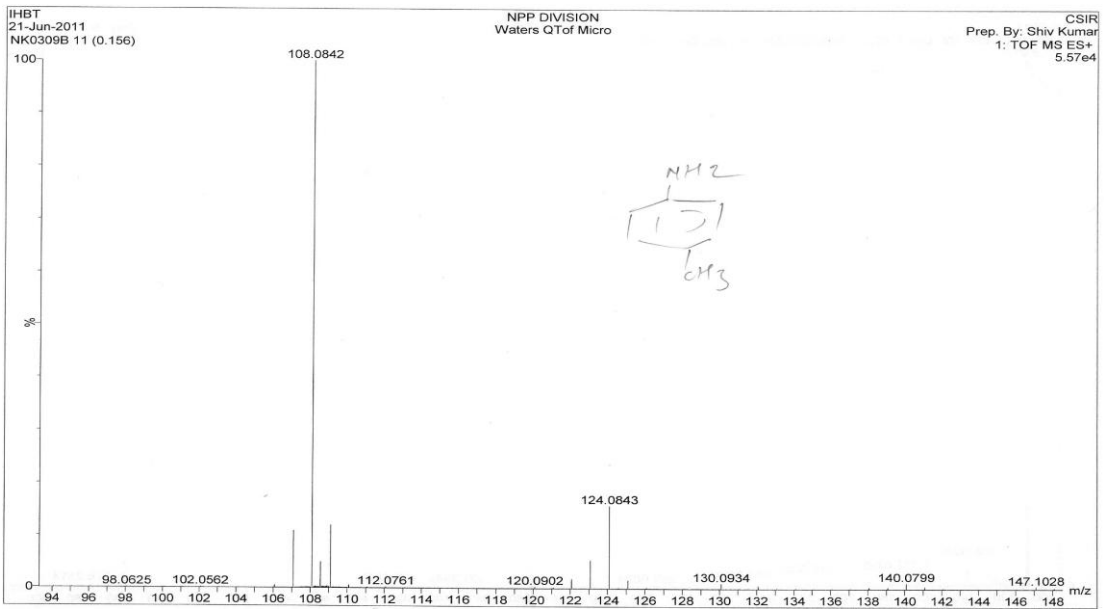




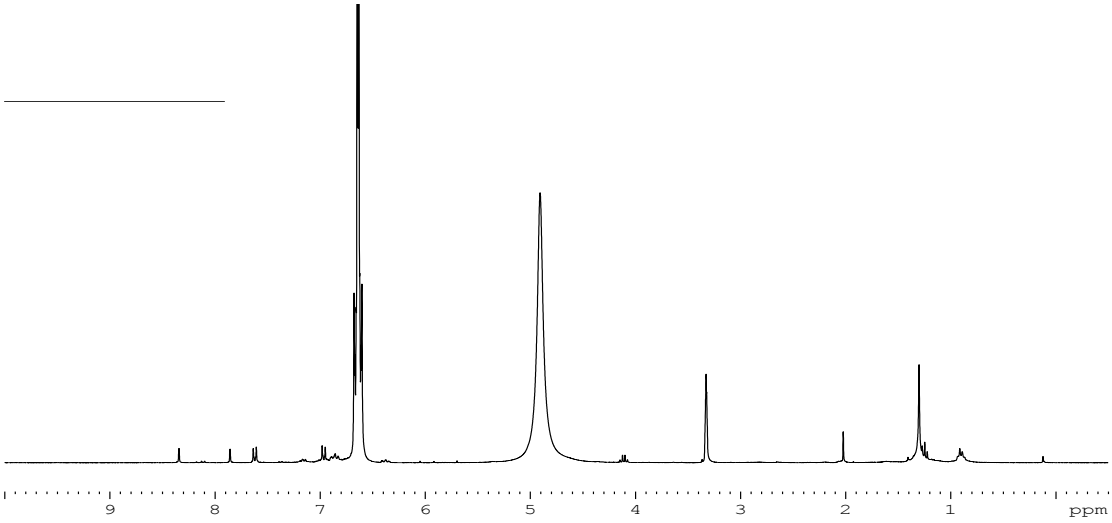
4-Methylaniline (Table 2, entry 14)

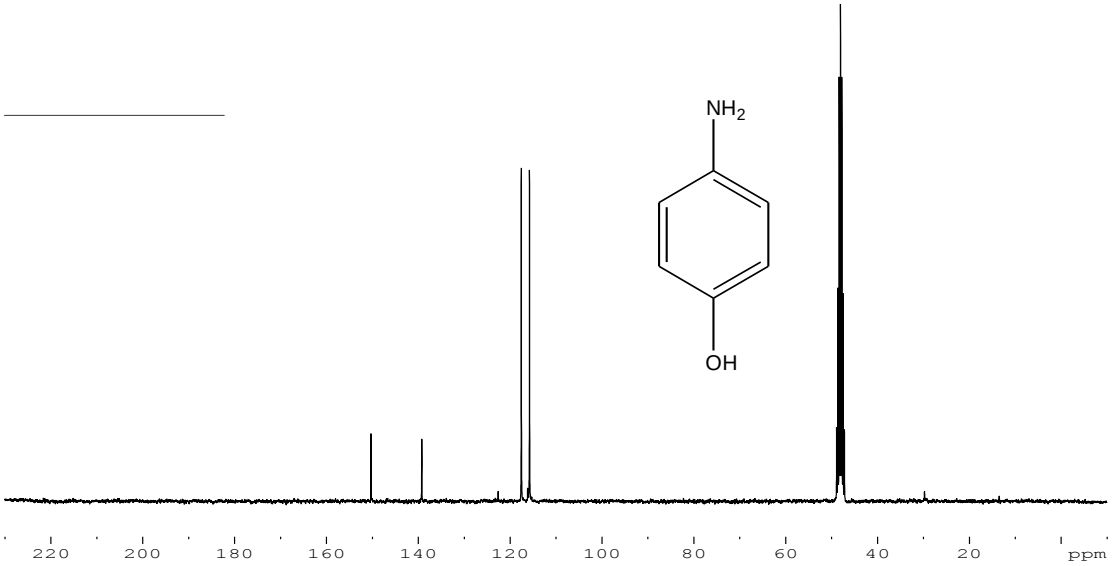


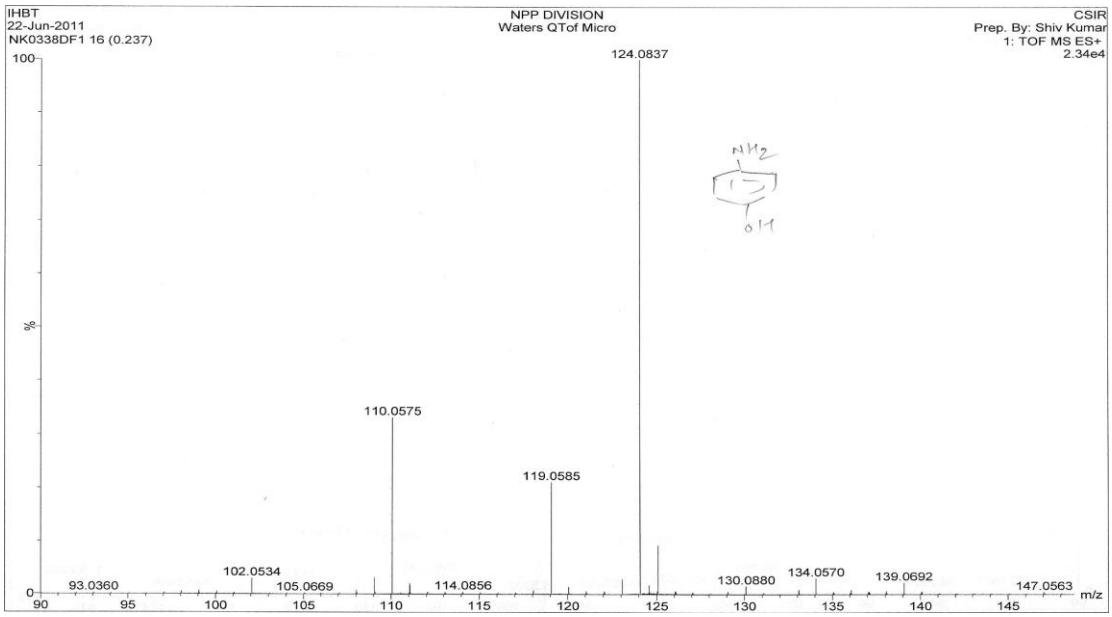




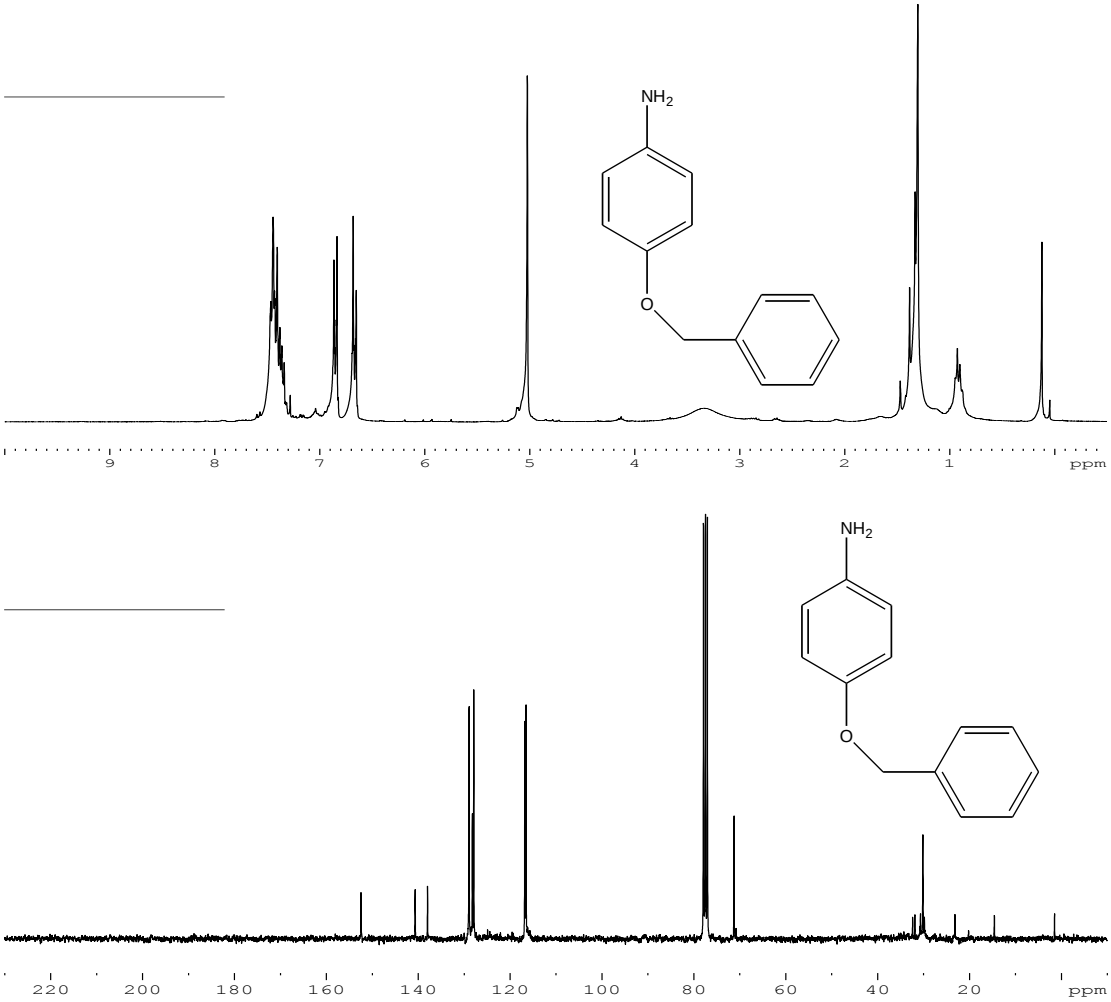
4-Aminophenol (Table 2, entry 15)



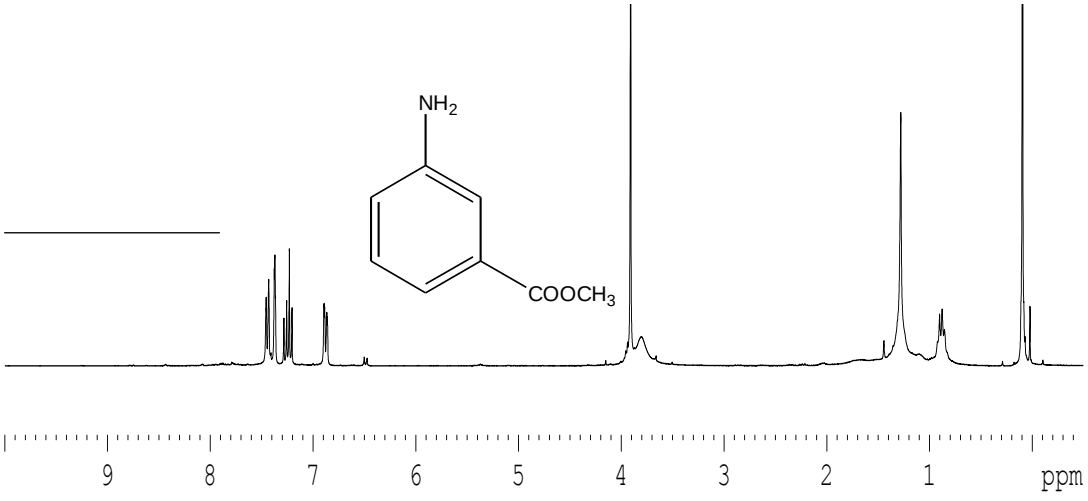


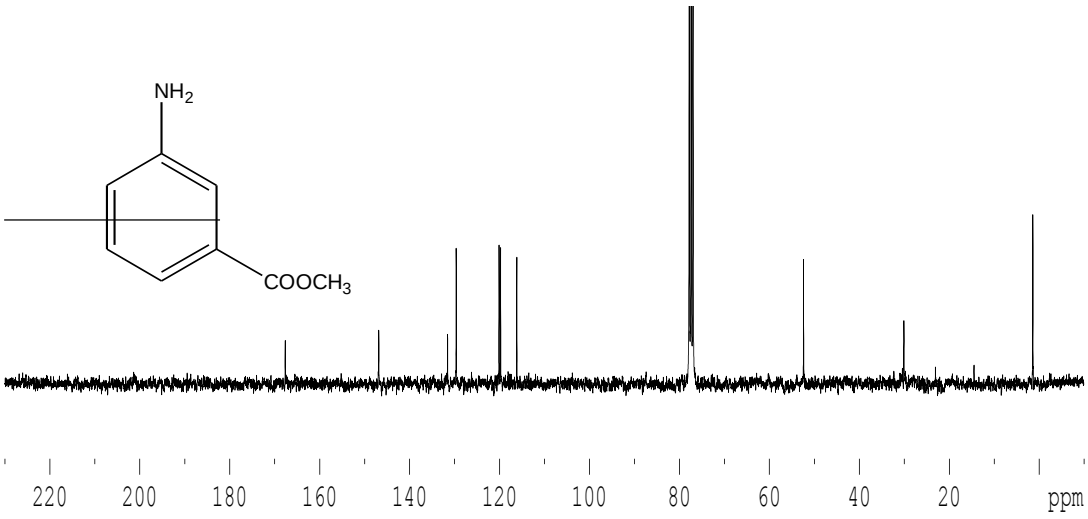


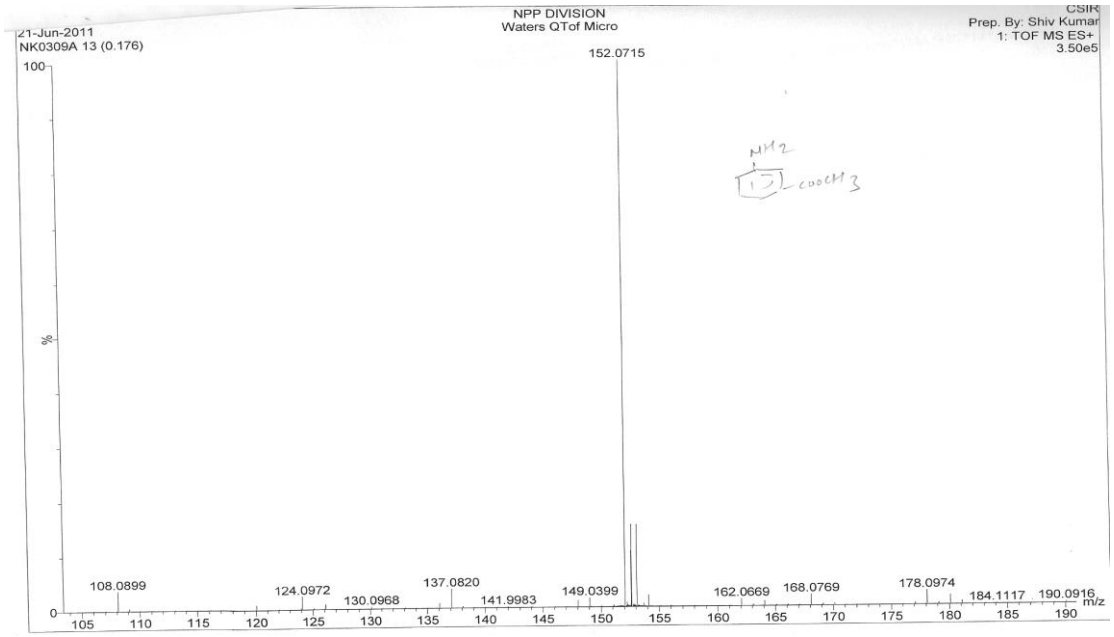
Benzyl-4-aminophenyl ether (Table 2, entry 16)



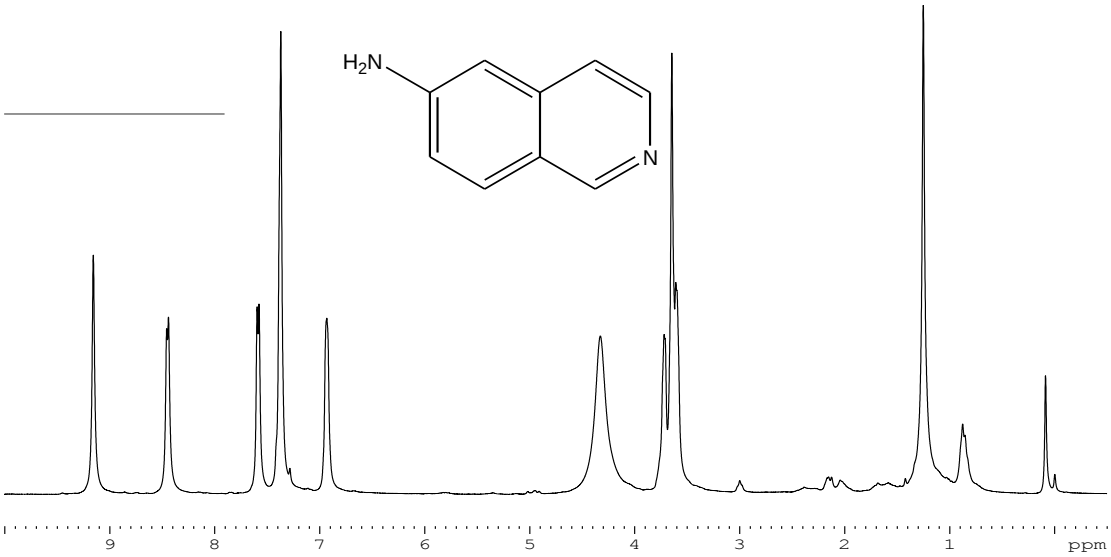
Methy-3-aminobenzoate (Table 2, entry 19)

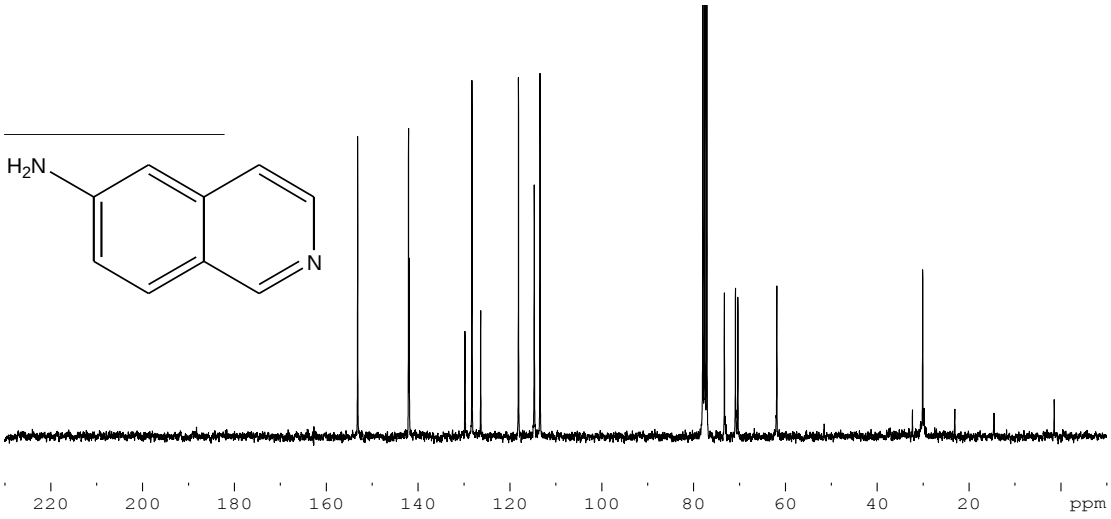






6-Aminoisoquinoline (Table 2, entry 28)





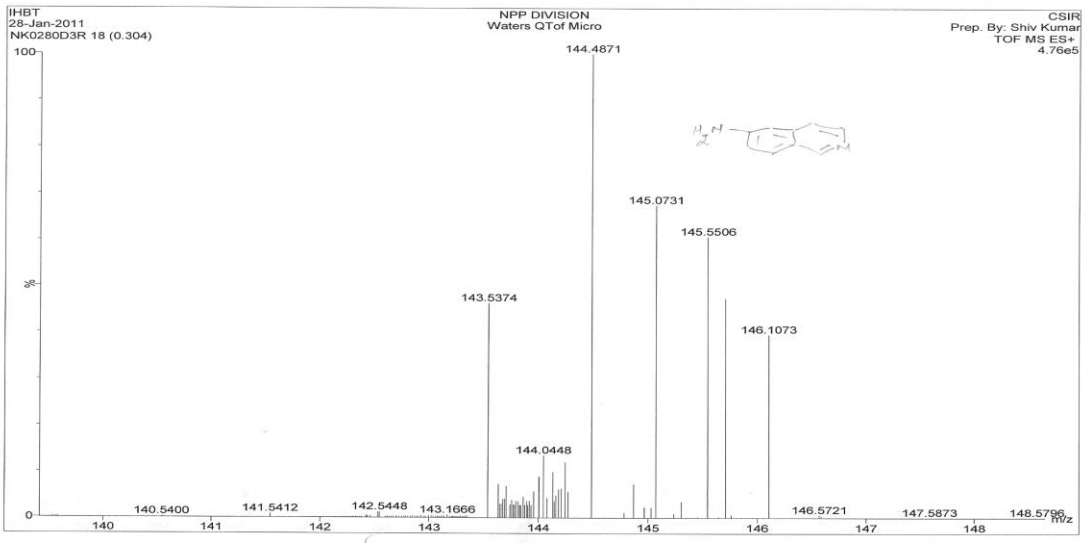
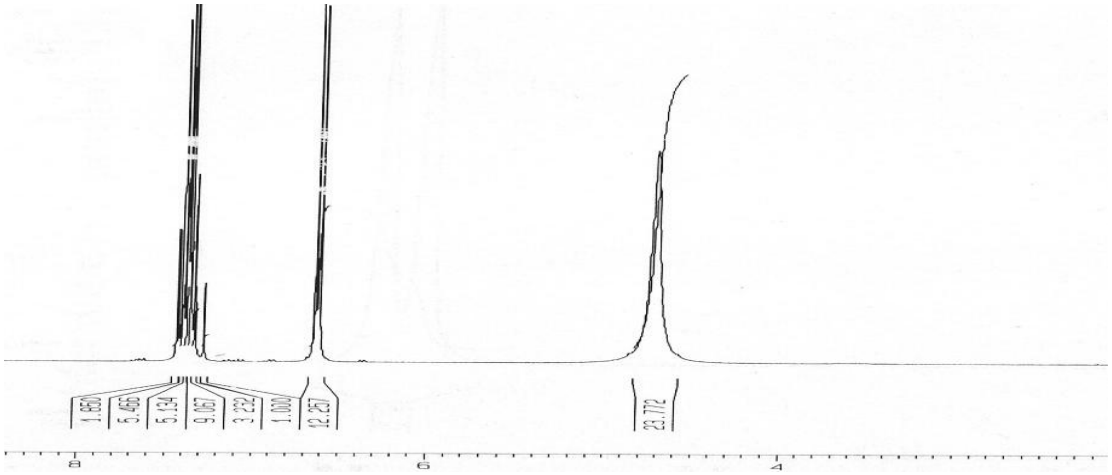
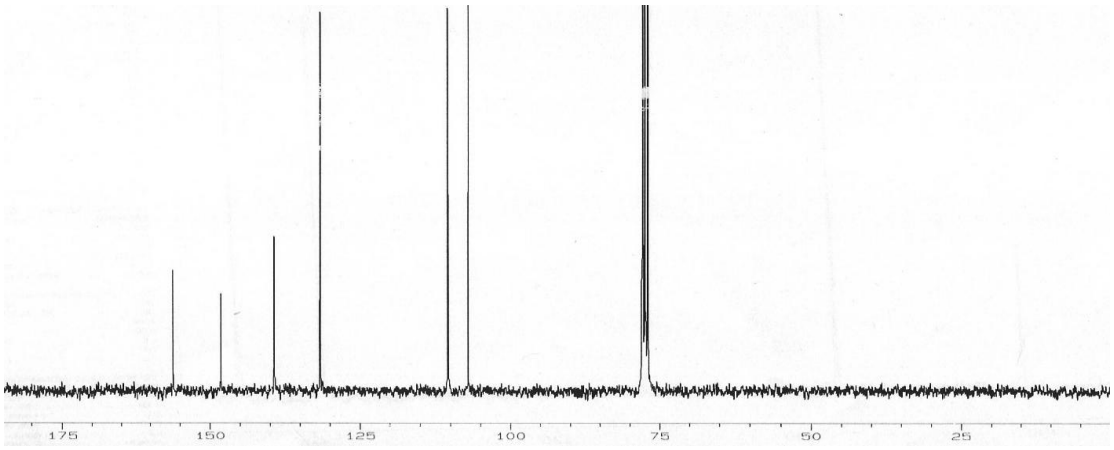
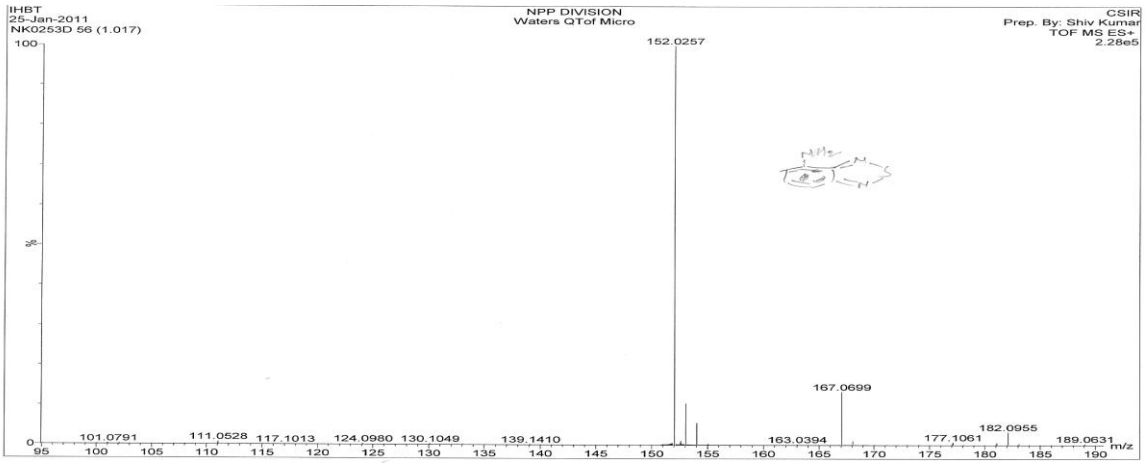


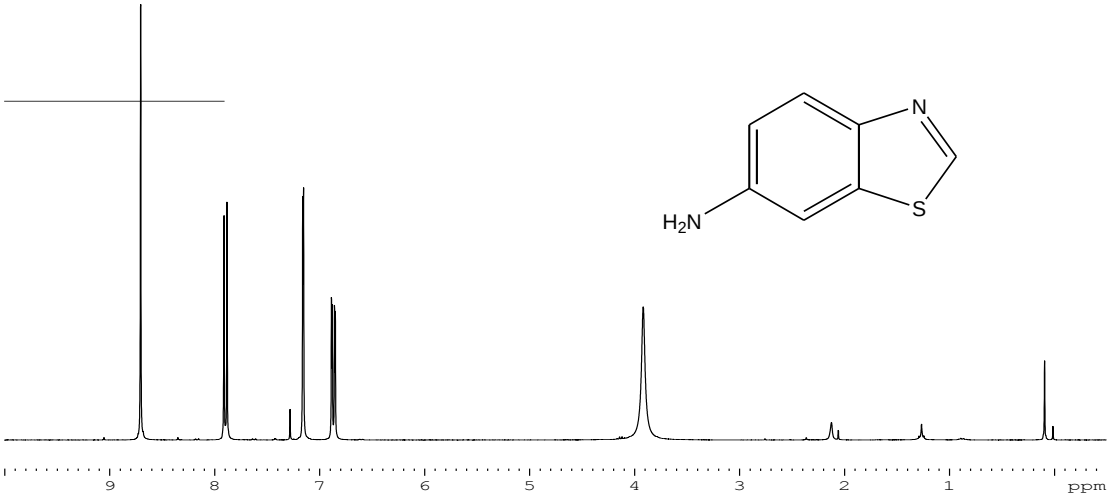
Table 2, entry 30

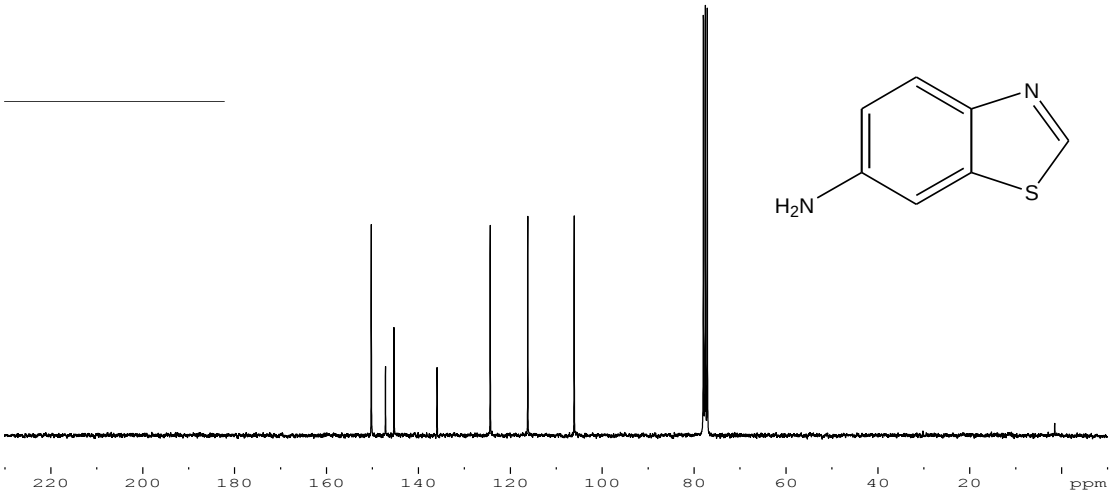


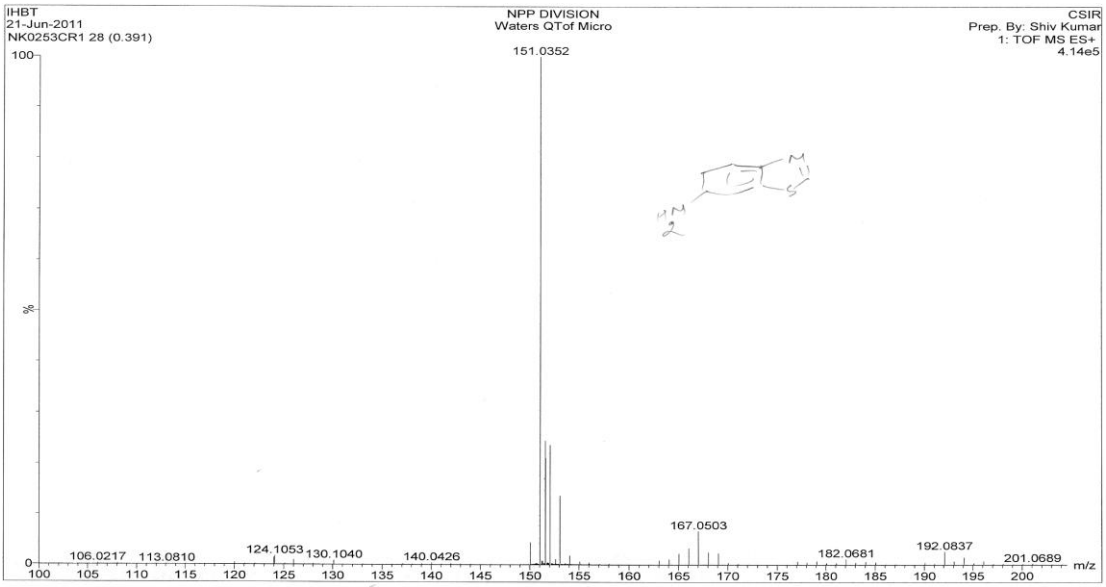




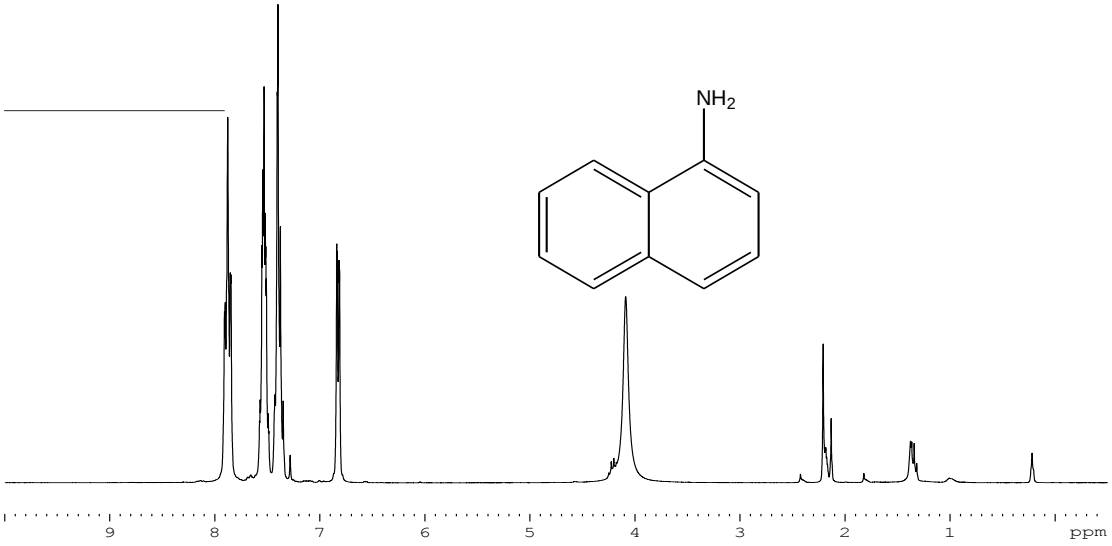
6-Aminobenzothiazole (Table 2, entry 31)

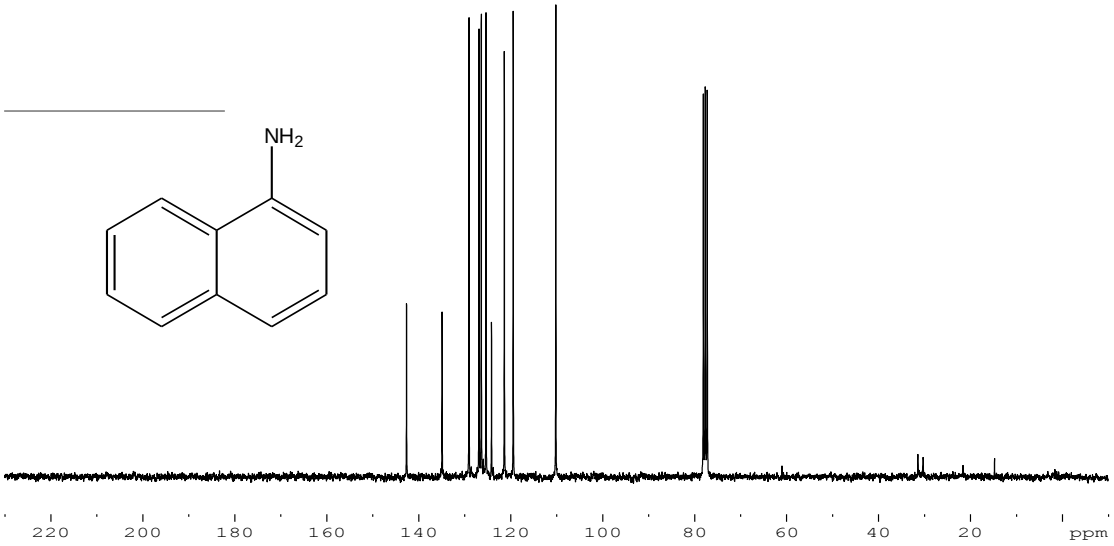


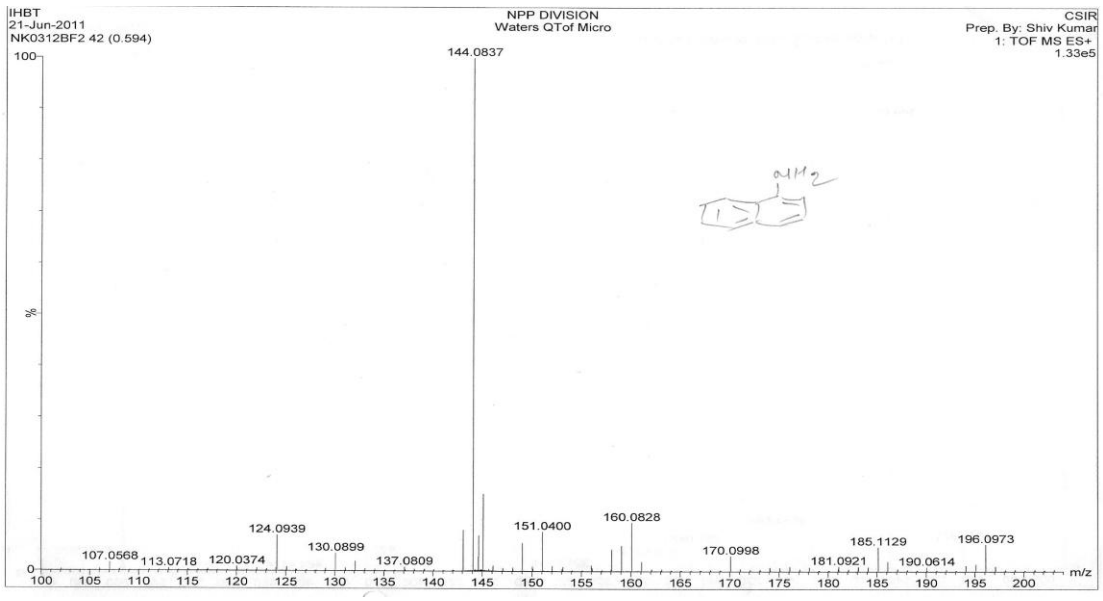




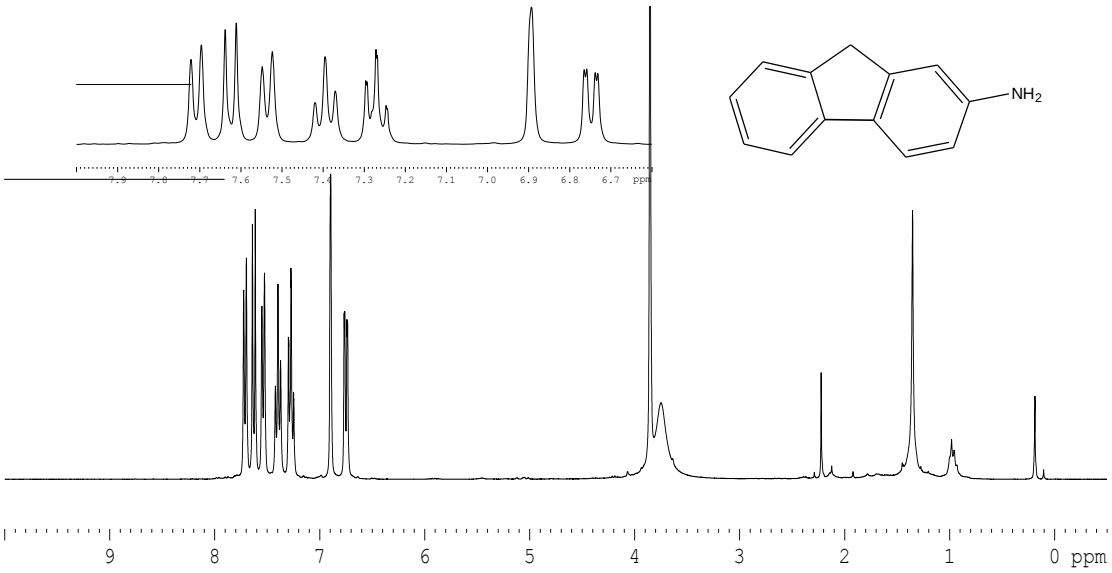
1-Aminonaphthalene (Table 2, entry 32)

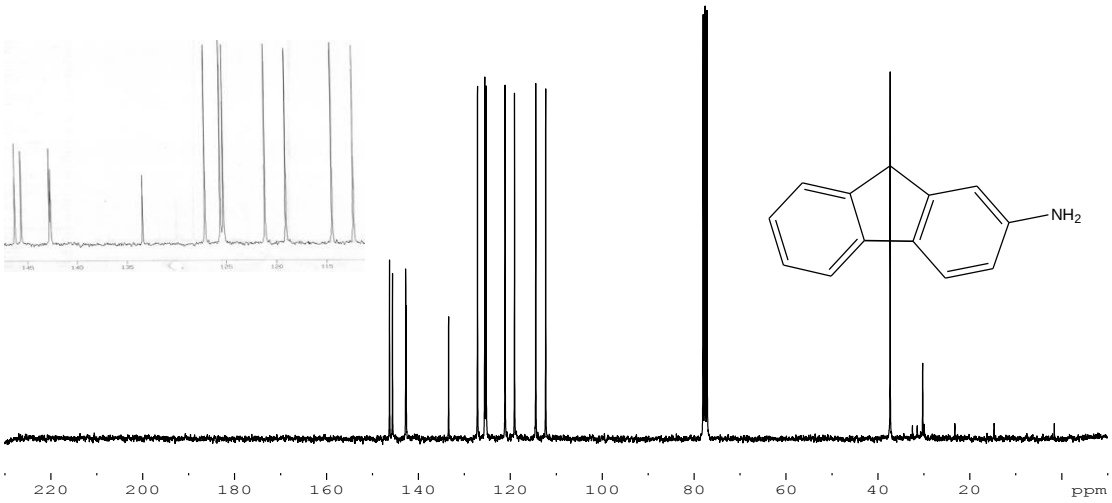


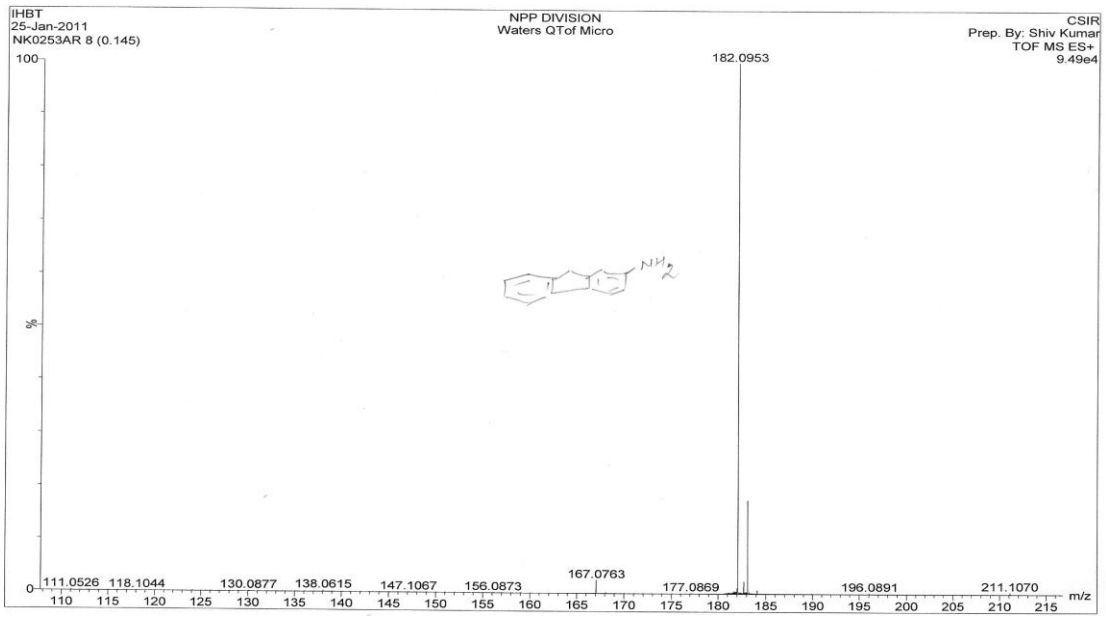




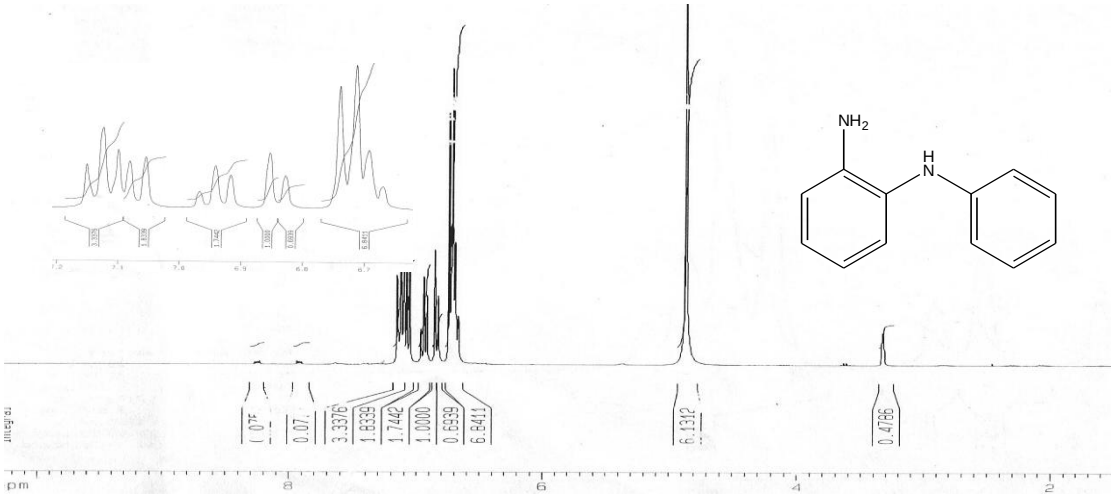
2-Aminofluorene (Table 2, entry 33)

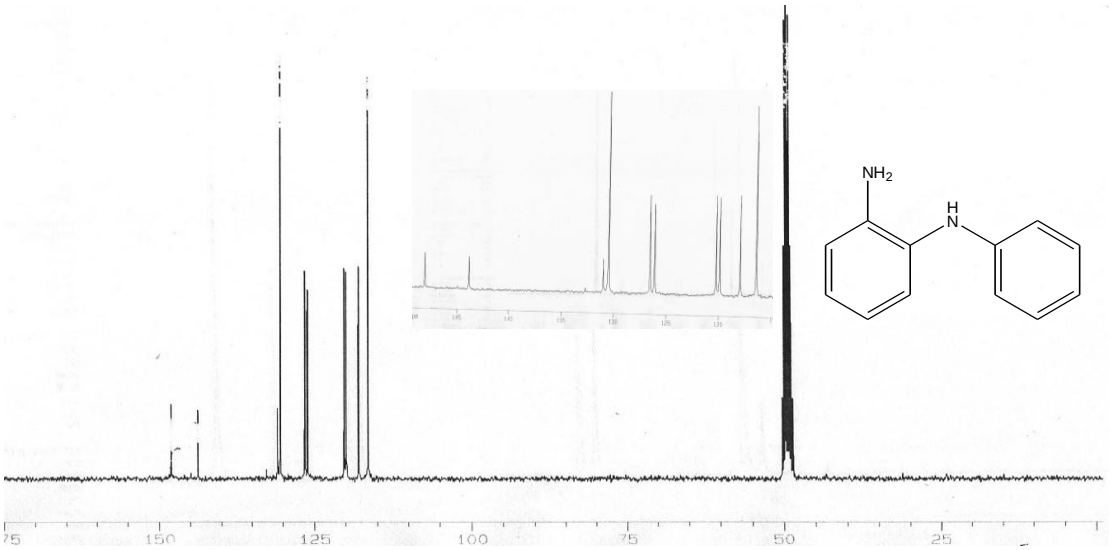


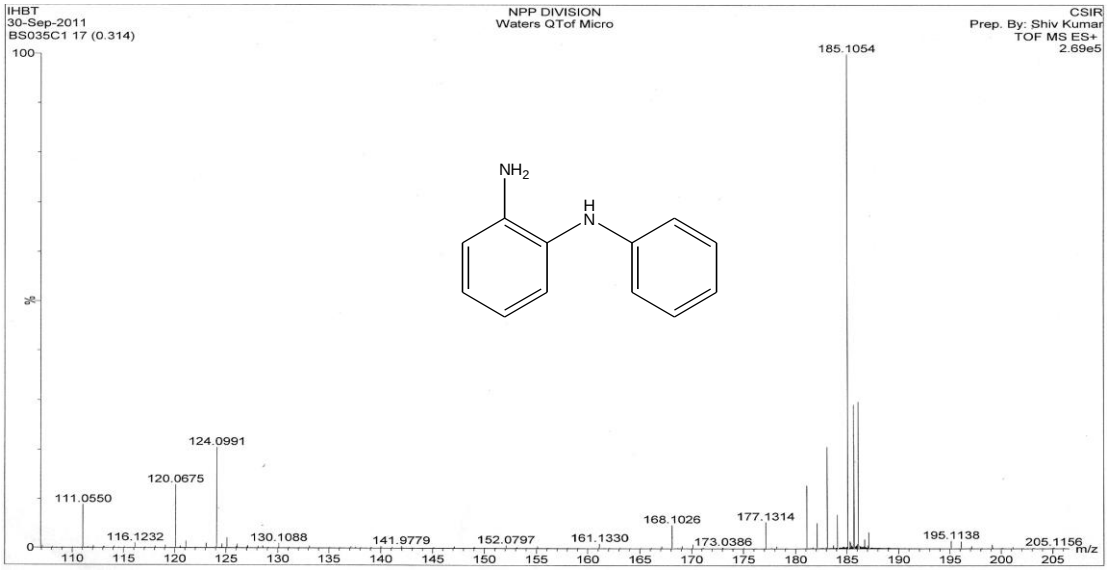




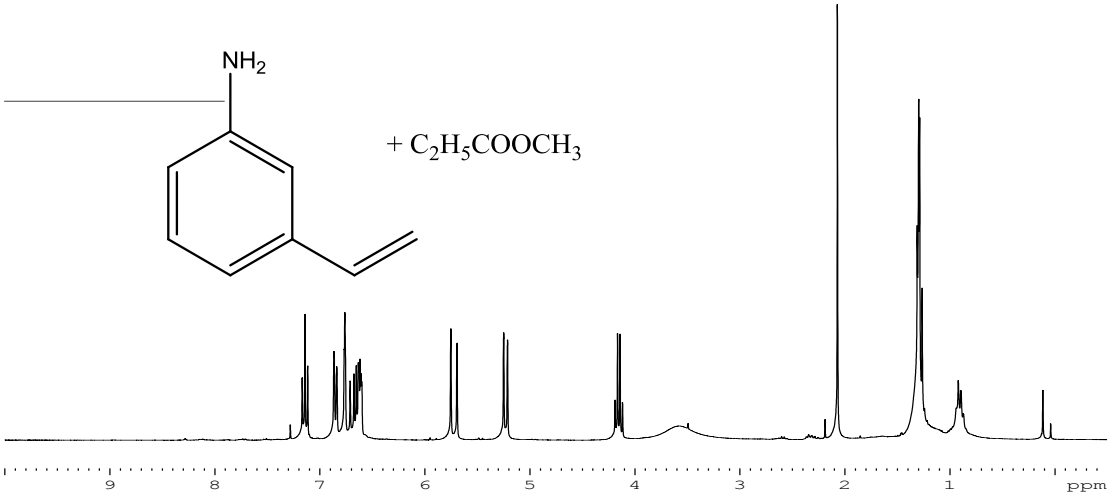
2-Aminobiphenylamine (Table 2, entry 34)

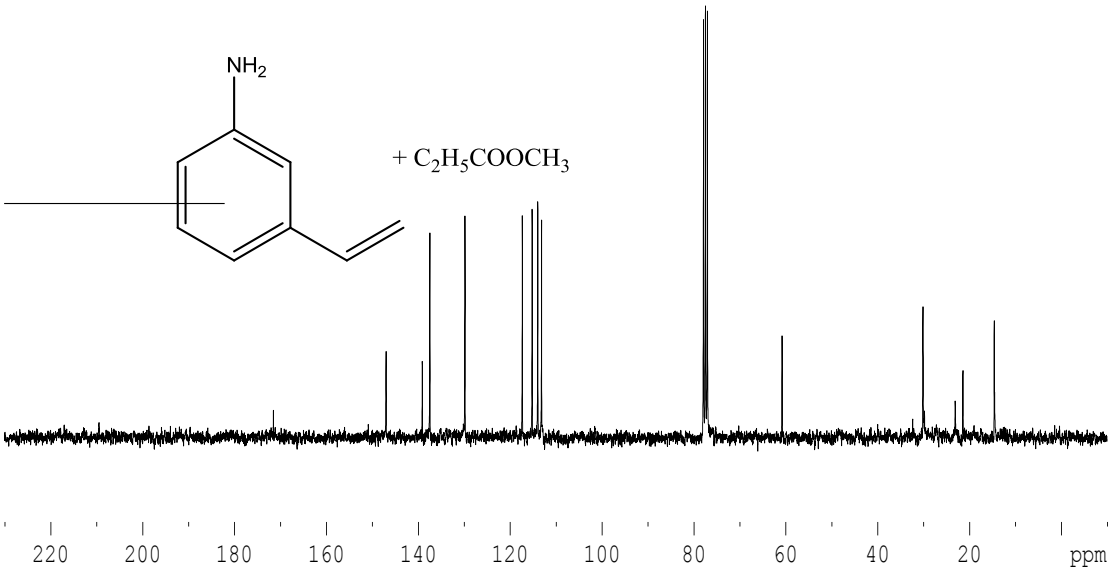


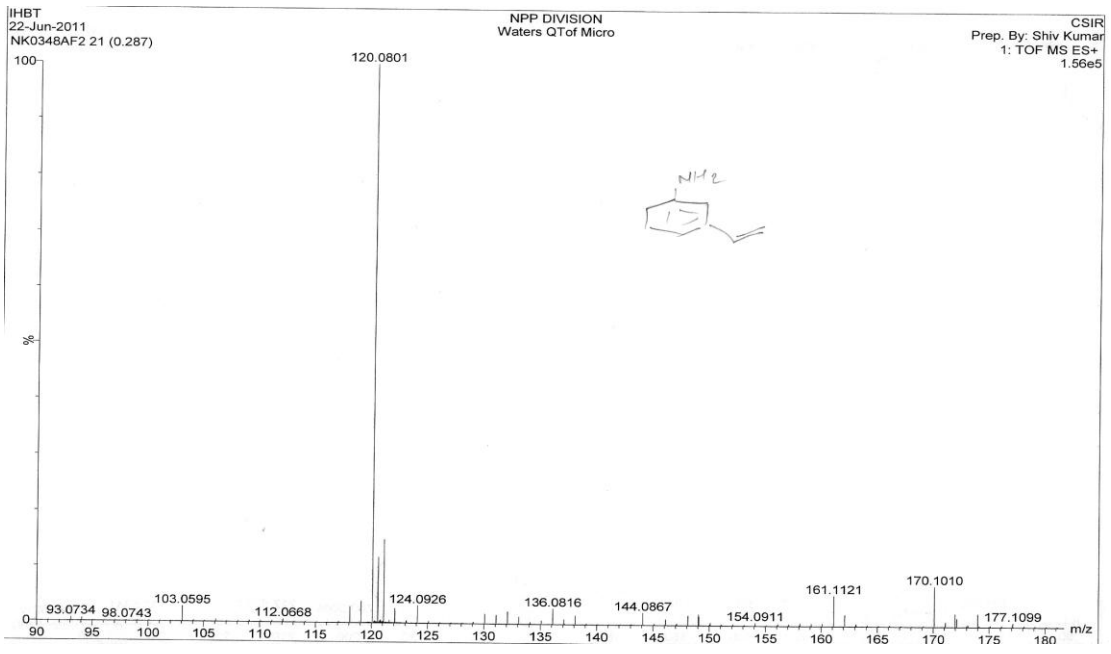




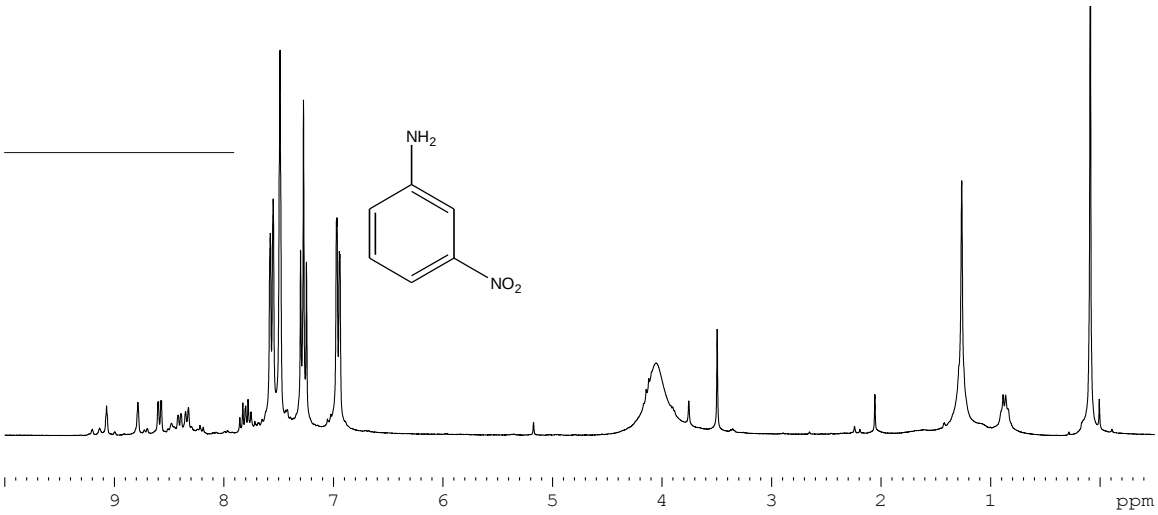
3-Aminostyrene (Table 2, entry 35)

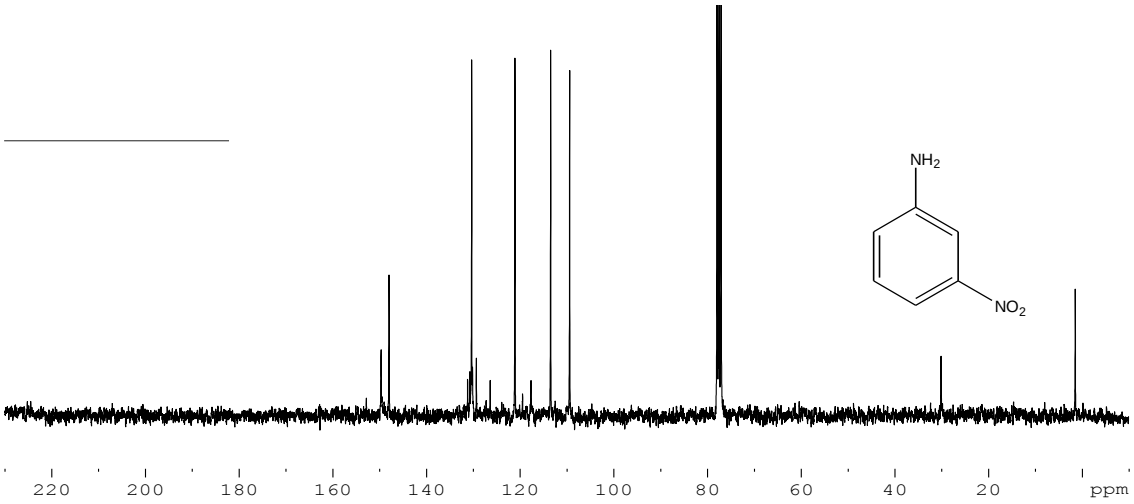


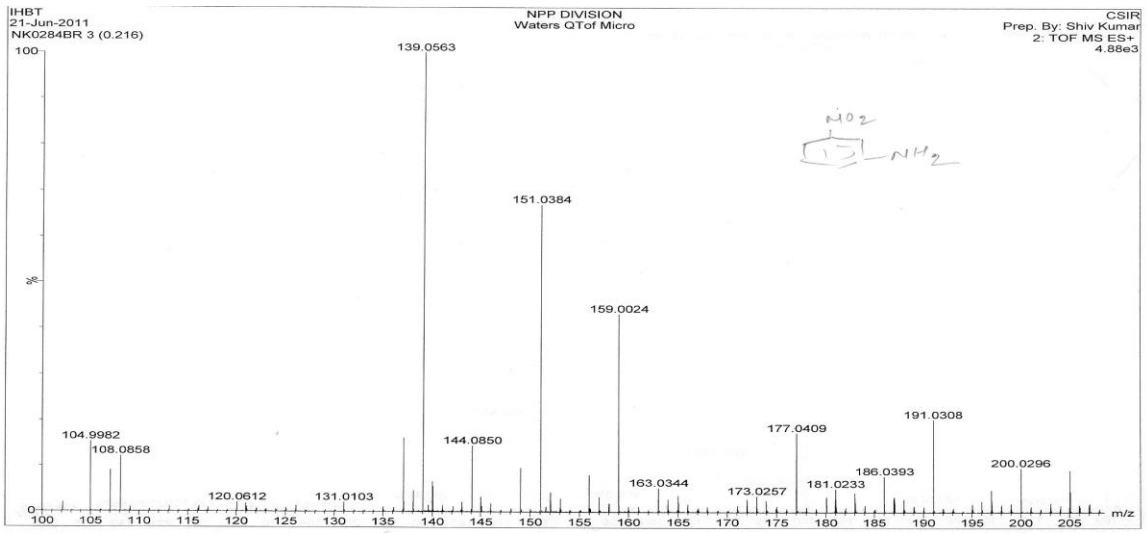




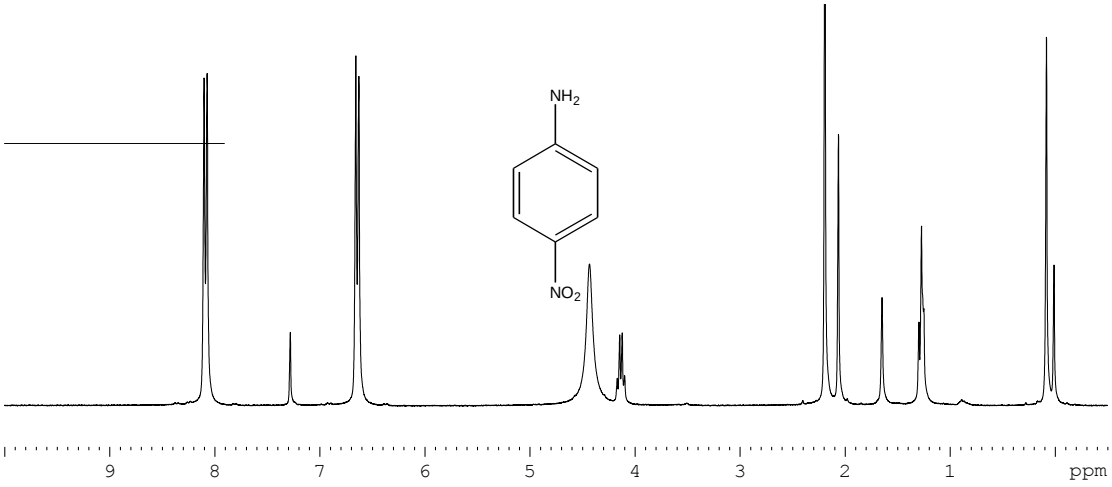
3-Nitroaniline (Table 2, entry 37)

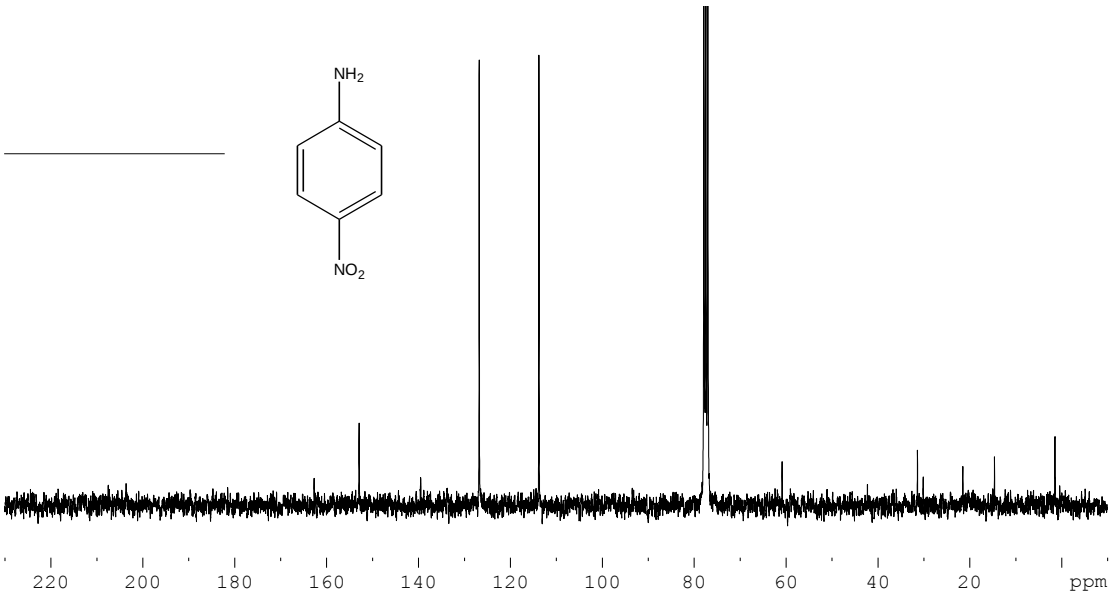


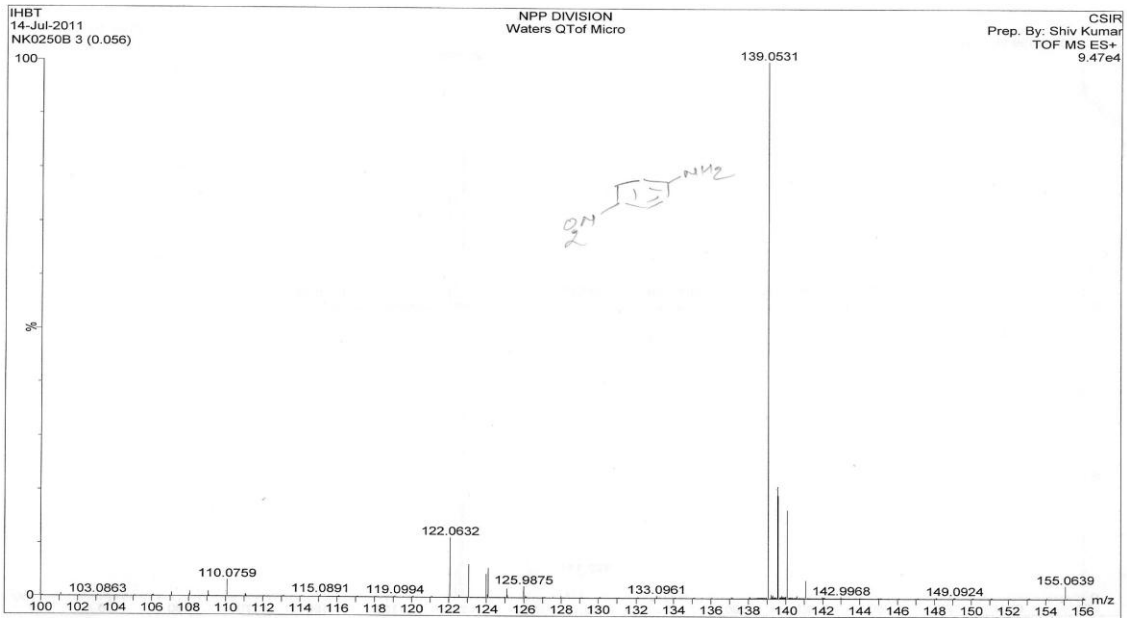




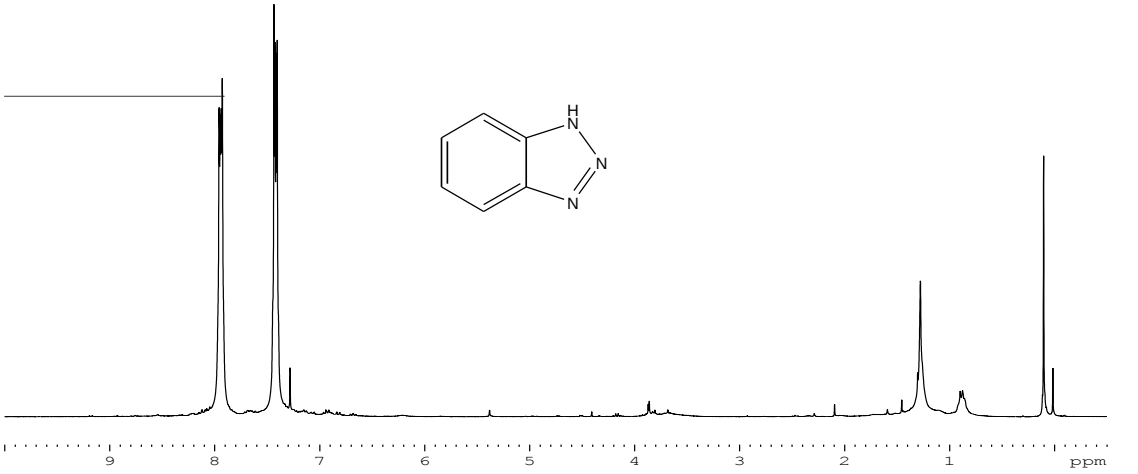
4-Nitroaniline (Table 2, entry 38)

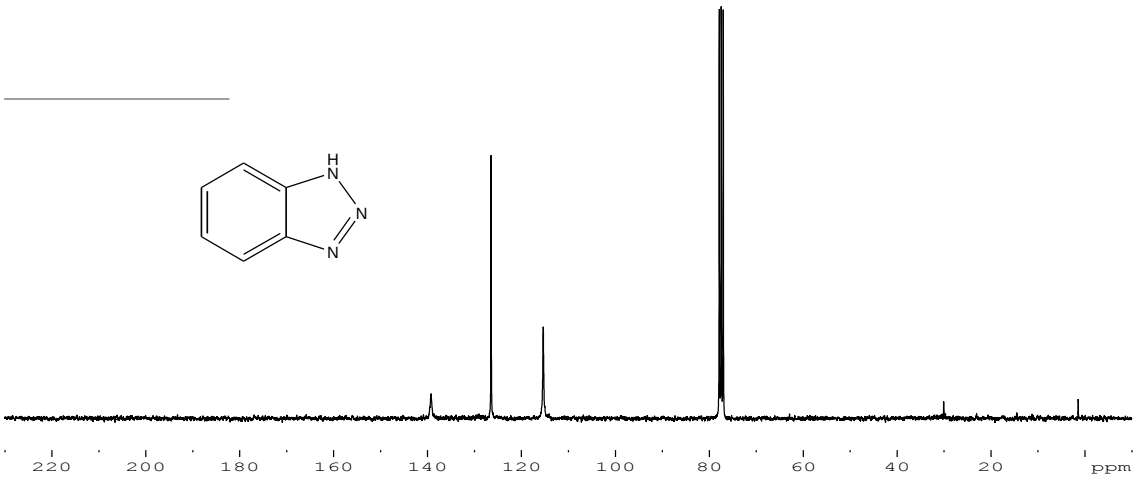


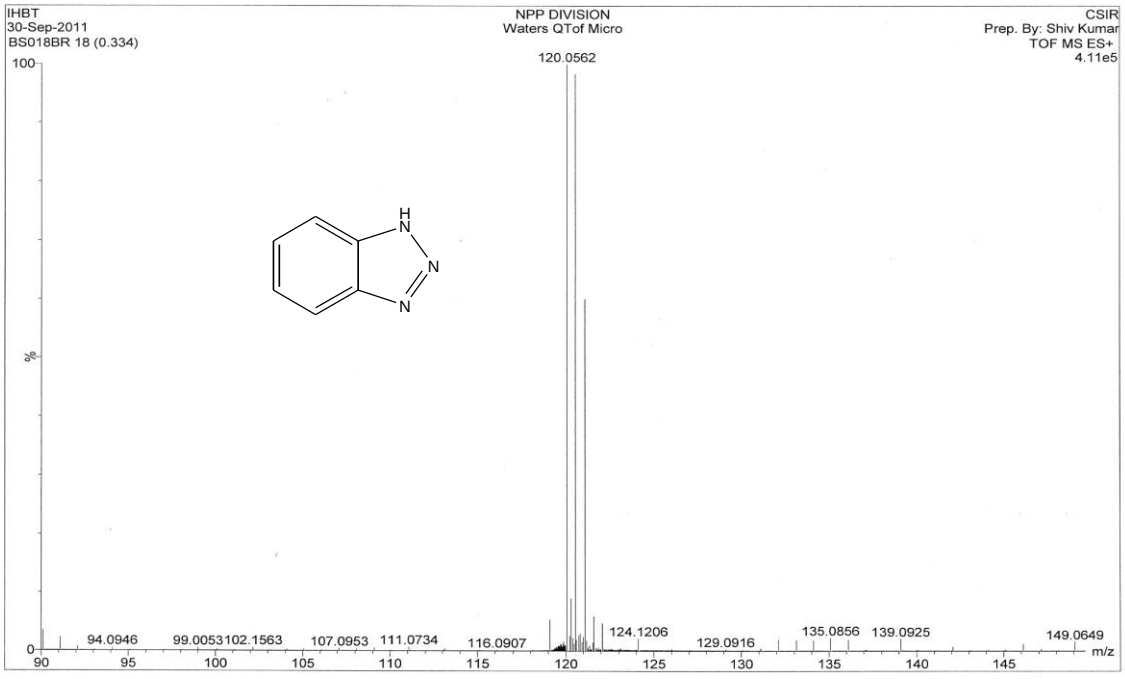




Benzotriazole

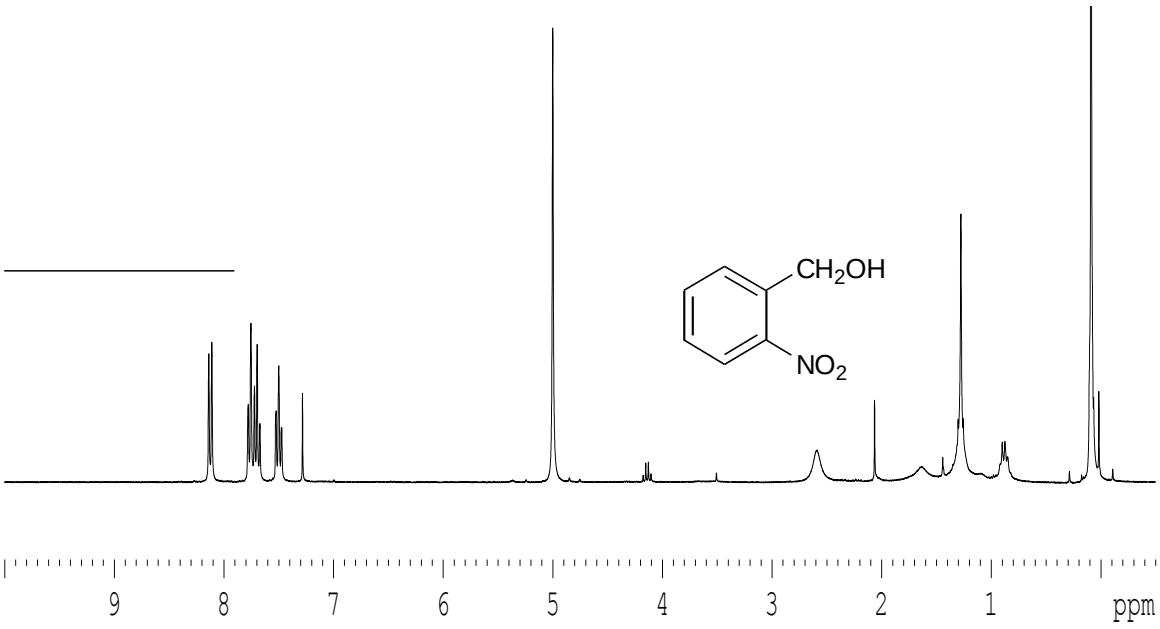


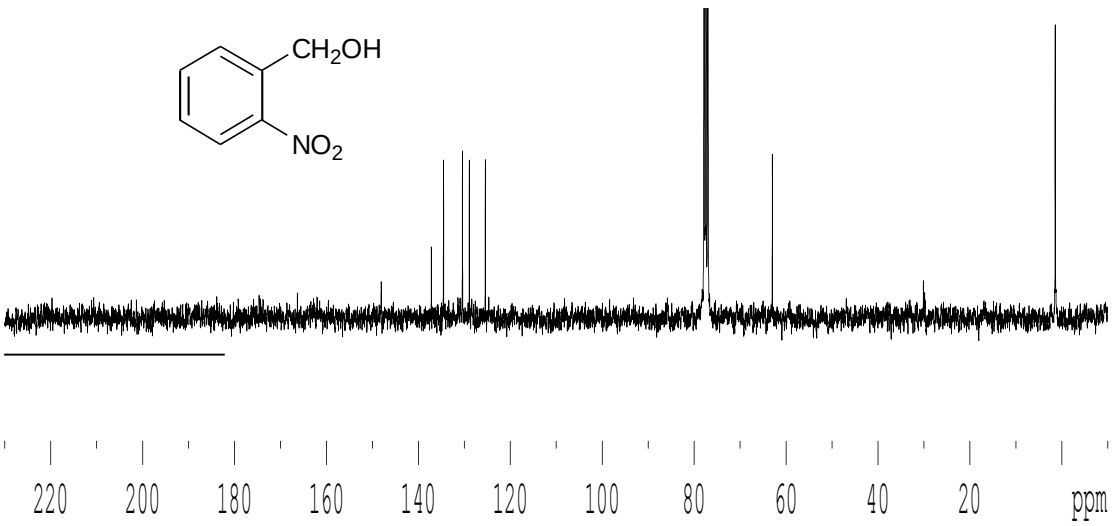




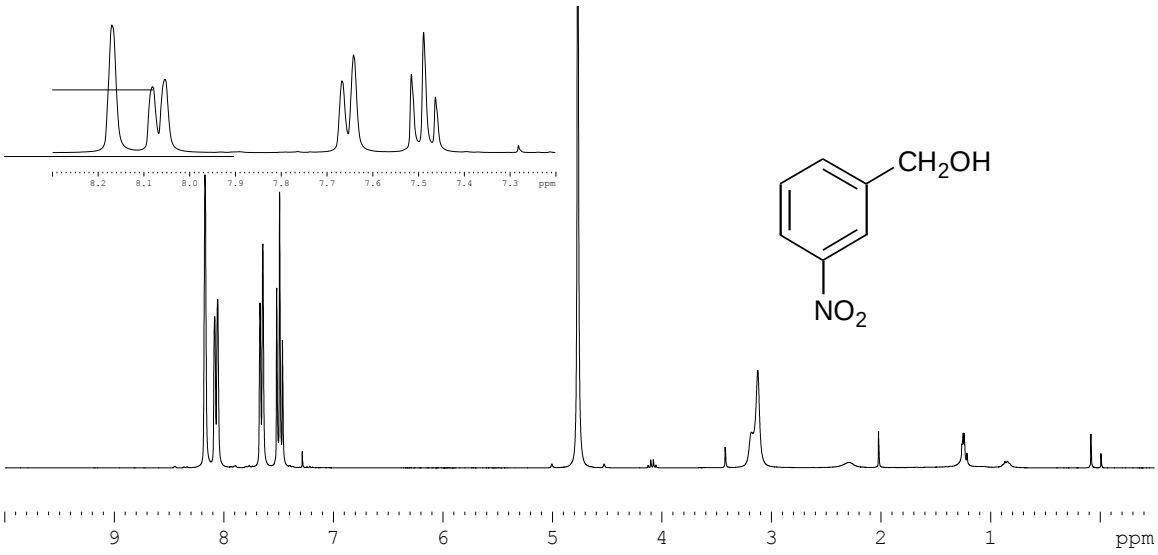
Spectra of carbonyl reduction products

2-Nitro-benzylalchol (Table 3, entry 1)

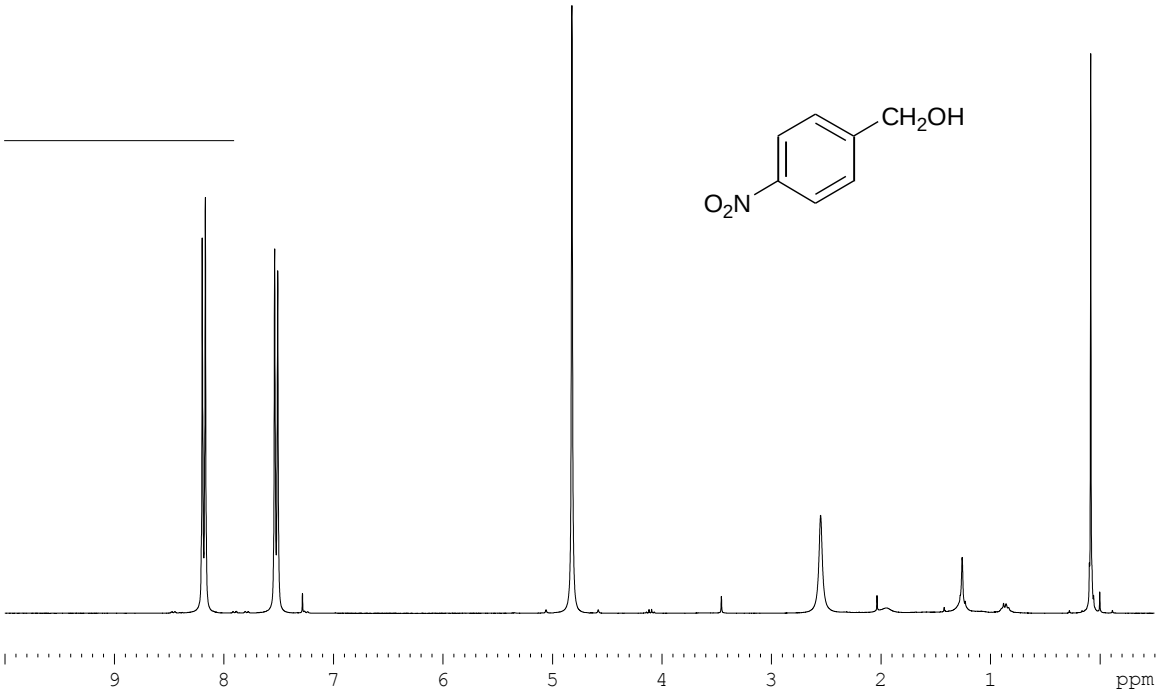


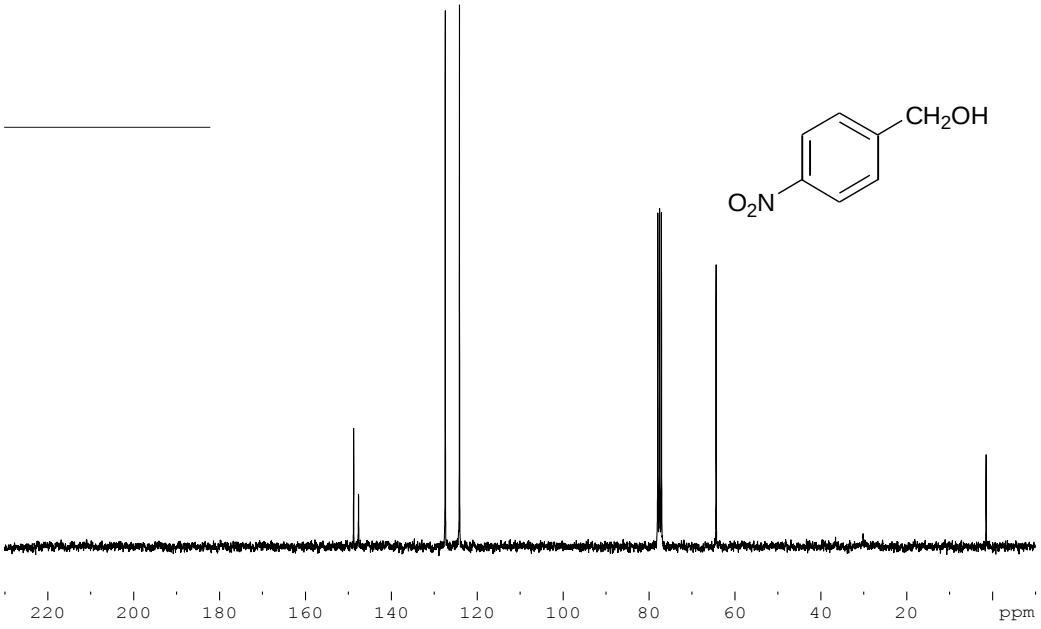


3-Nitro-benzylalchol (Table 3, entry 2)

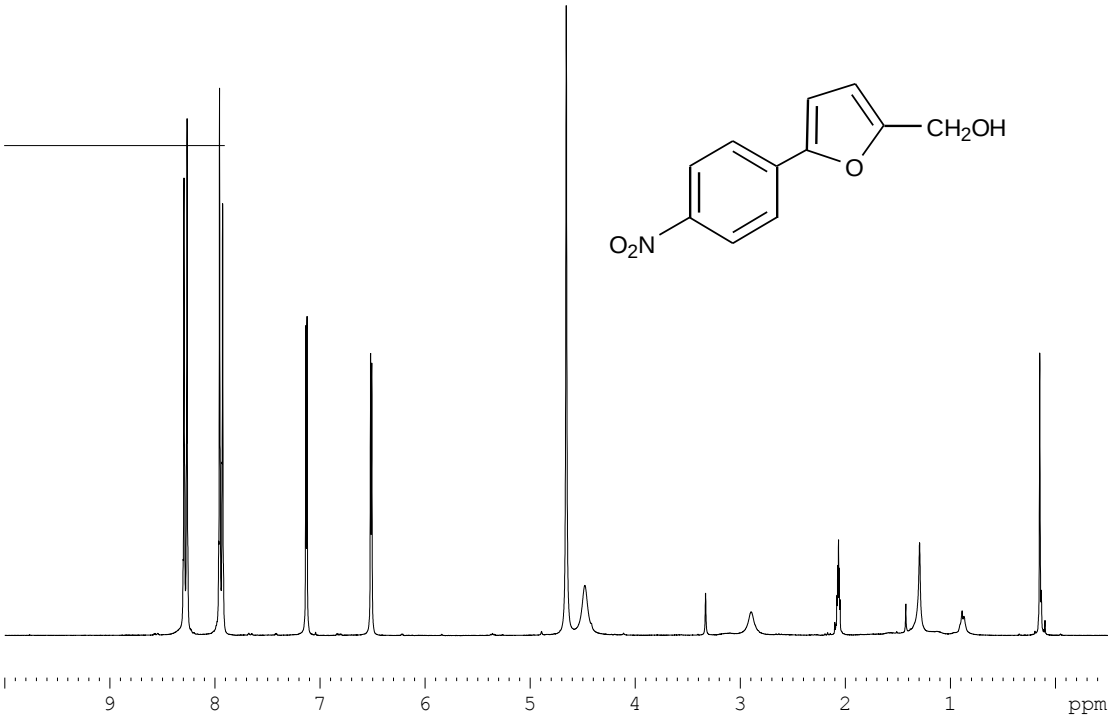


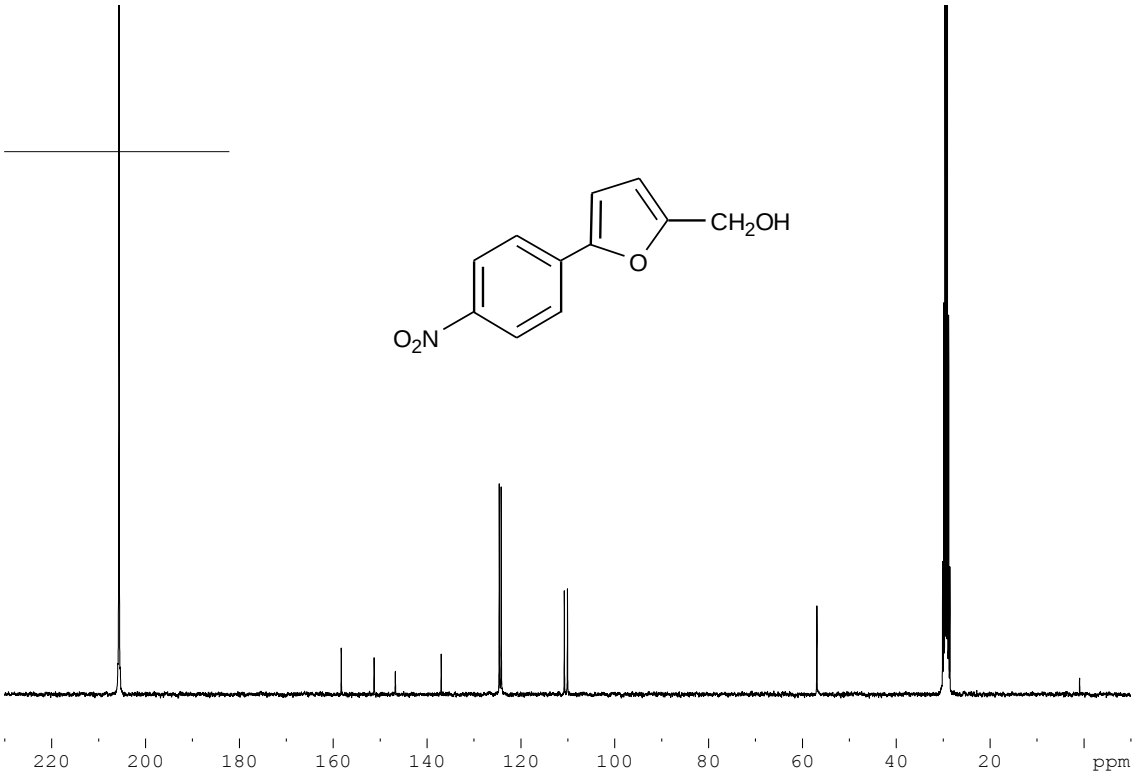
4-Nitro-benzylalchol (Table 3, entry 3)



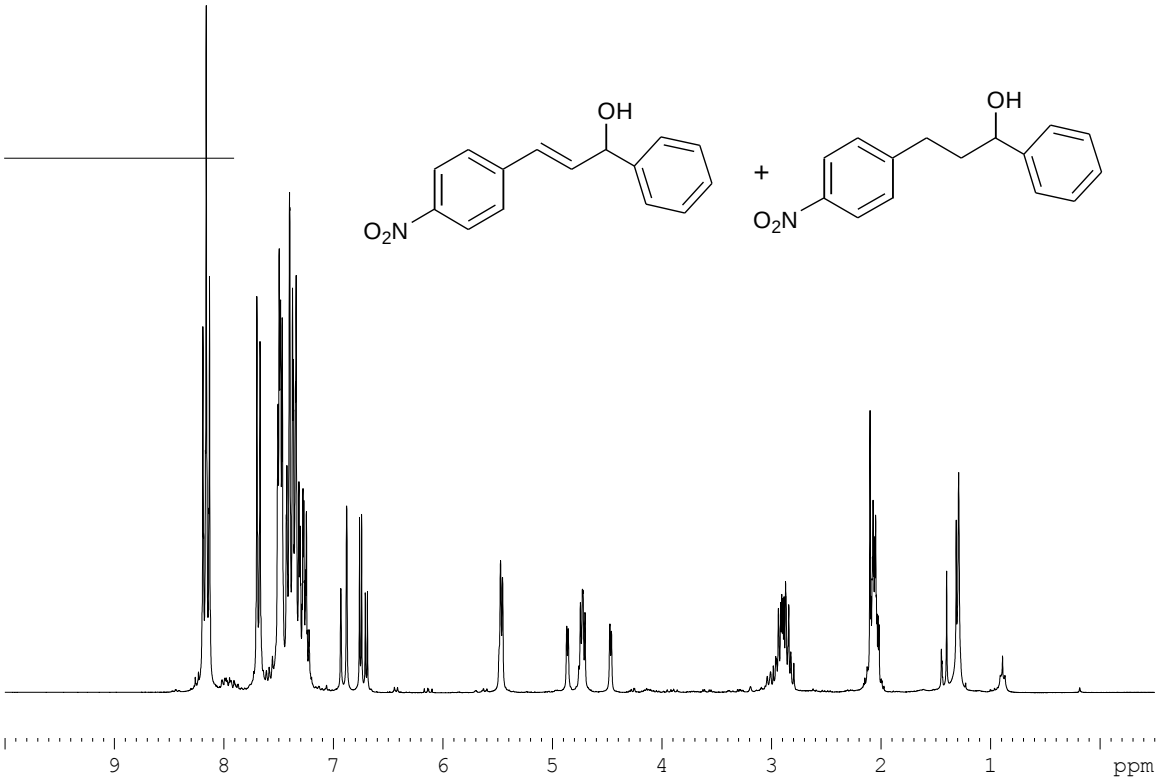


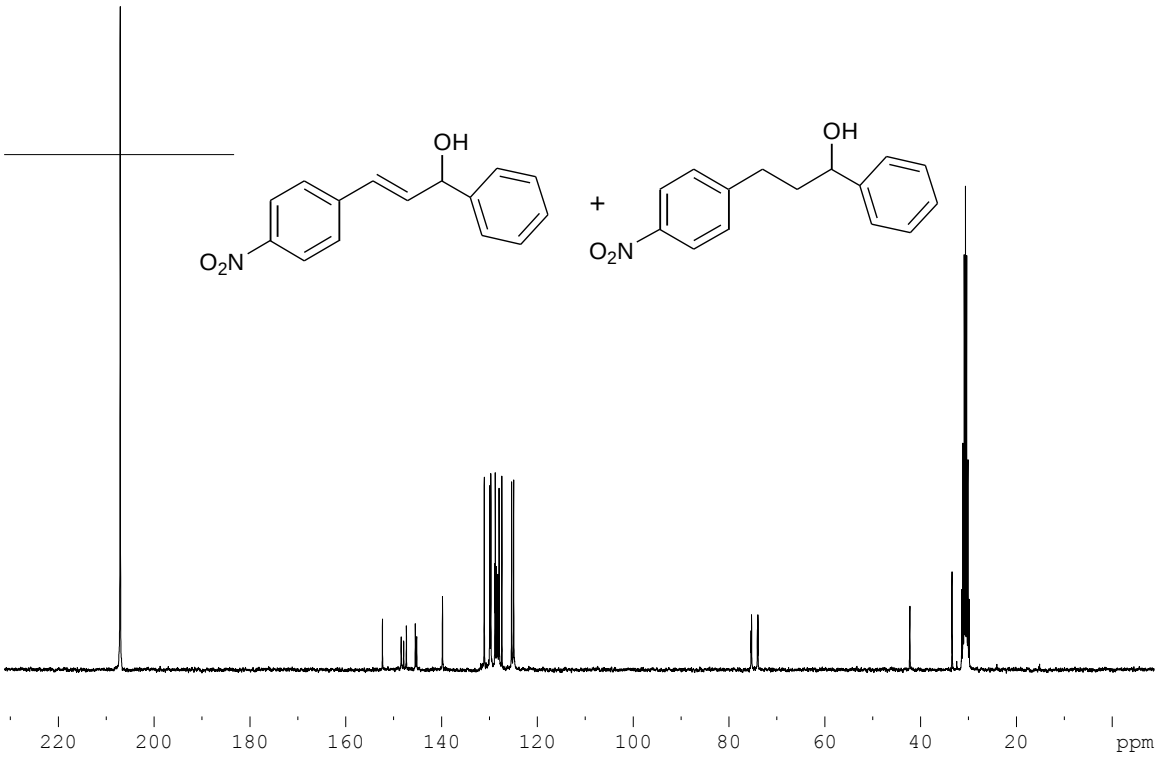
4-(4-Nitrophenyl) furfural alcohol (Table 3, entry 5)



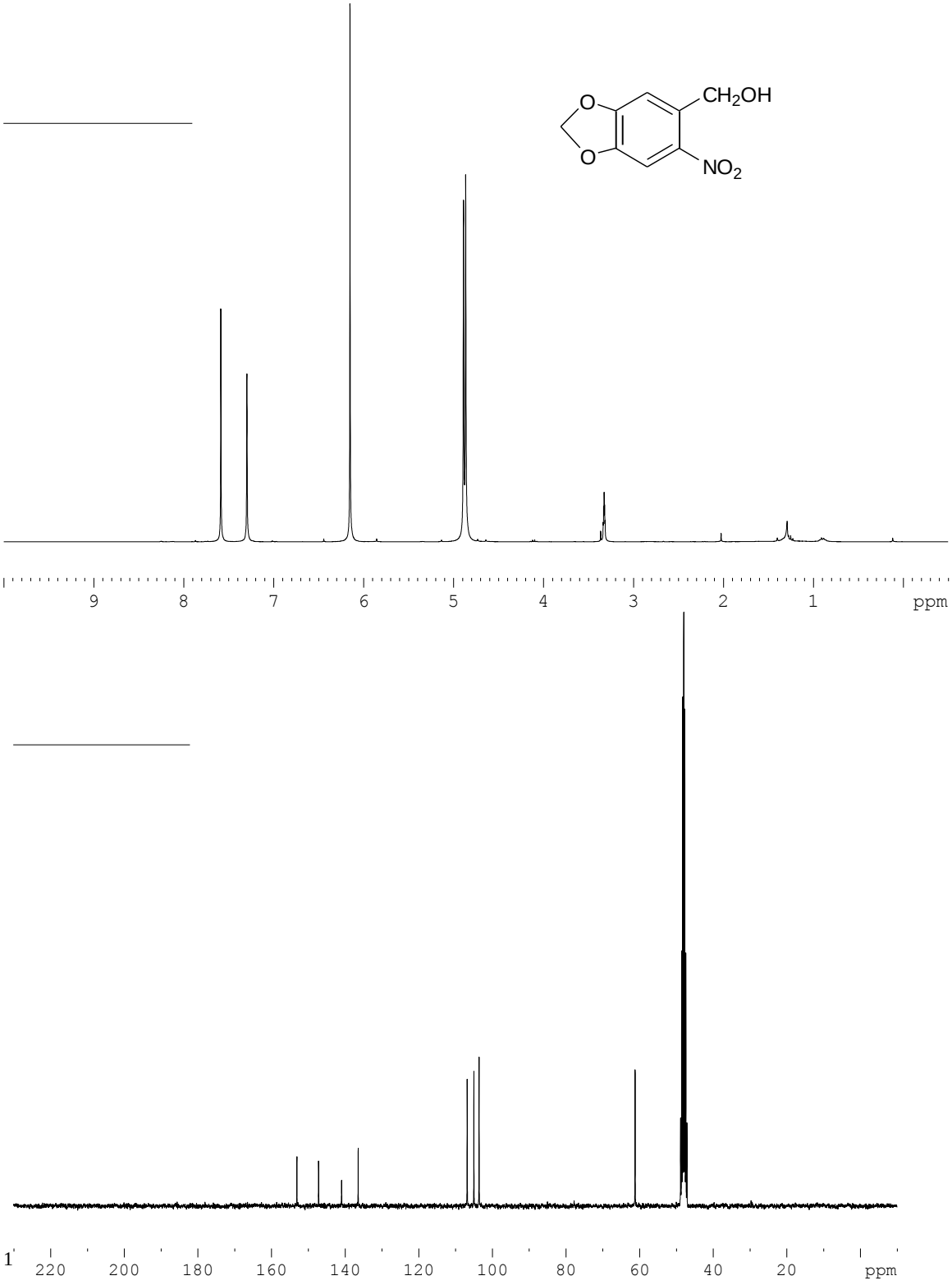


(Table 3, entry 6)

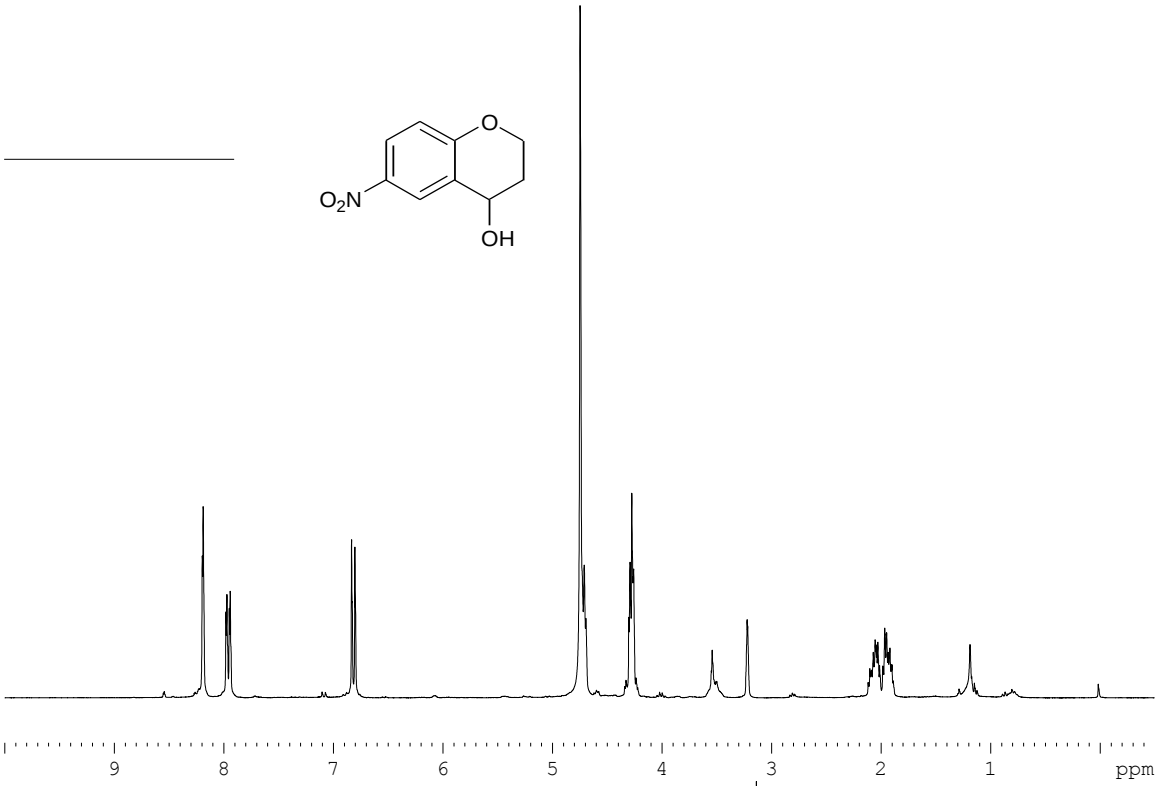


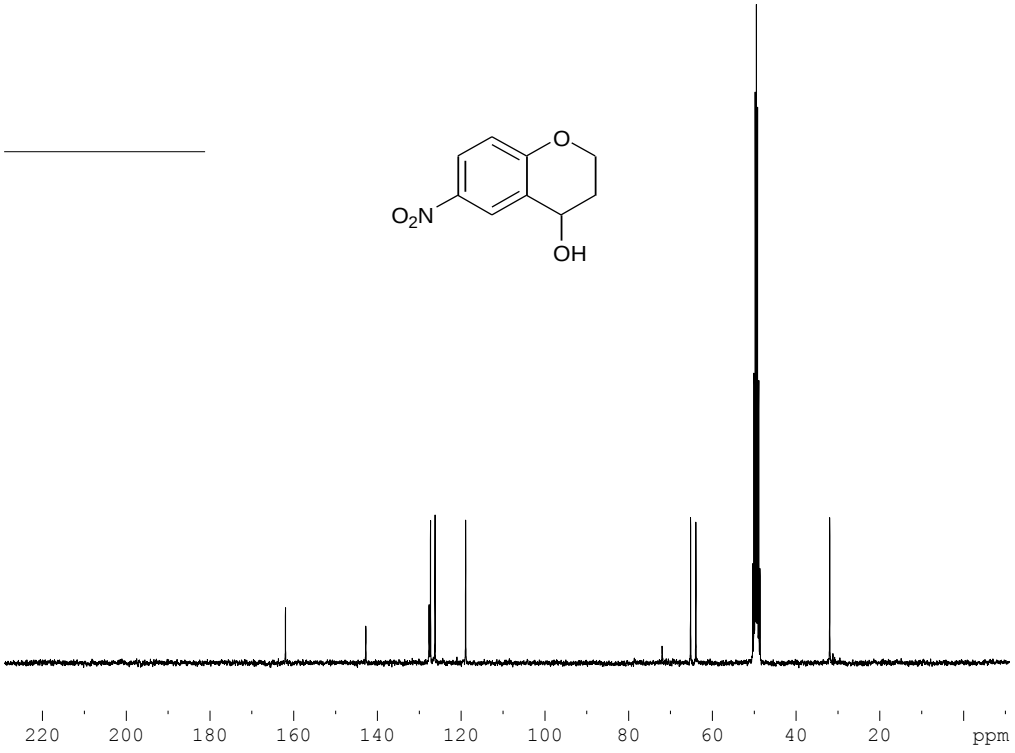


3,4-methylenedioxy-6-nitrobenzylalchol (Table 3, entry 7)

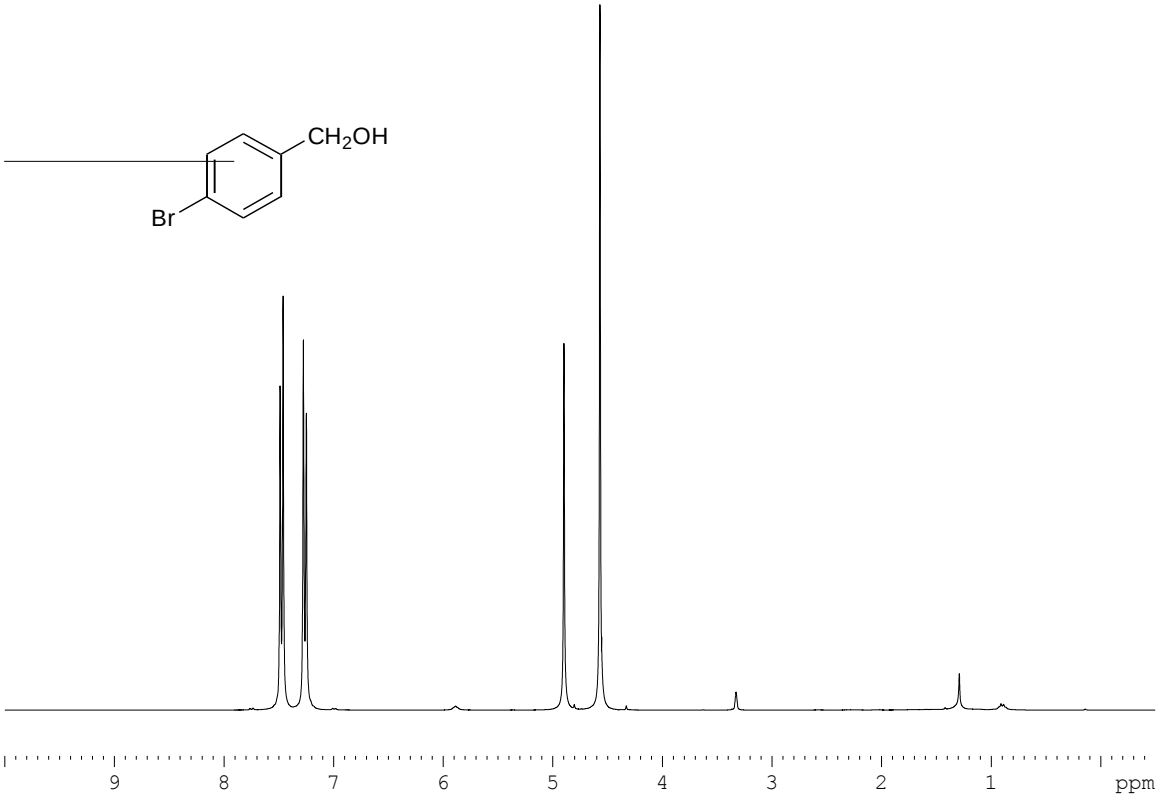


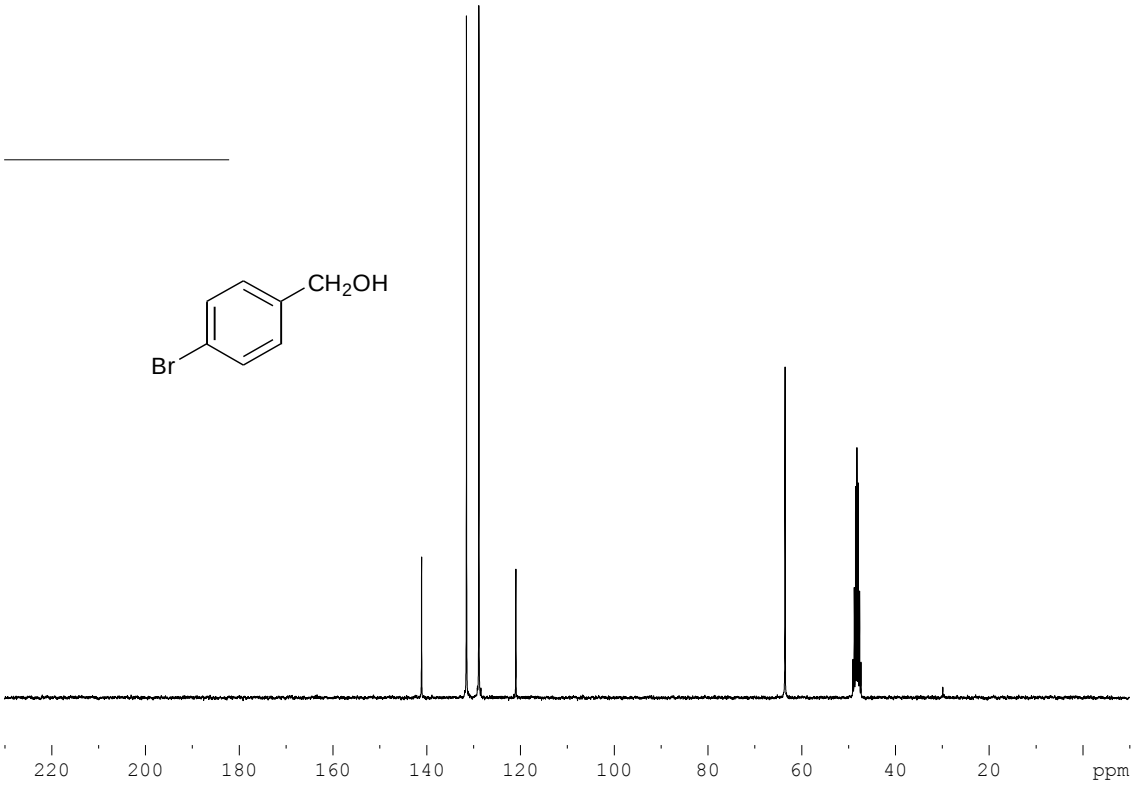
(Table 3, entry 8)



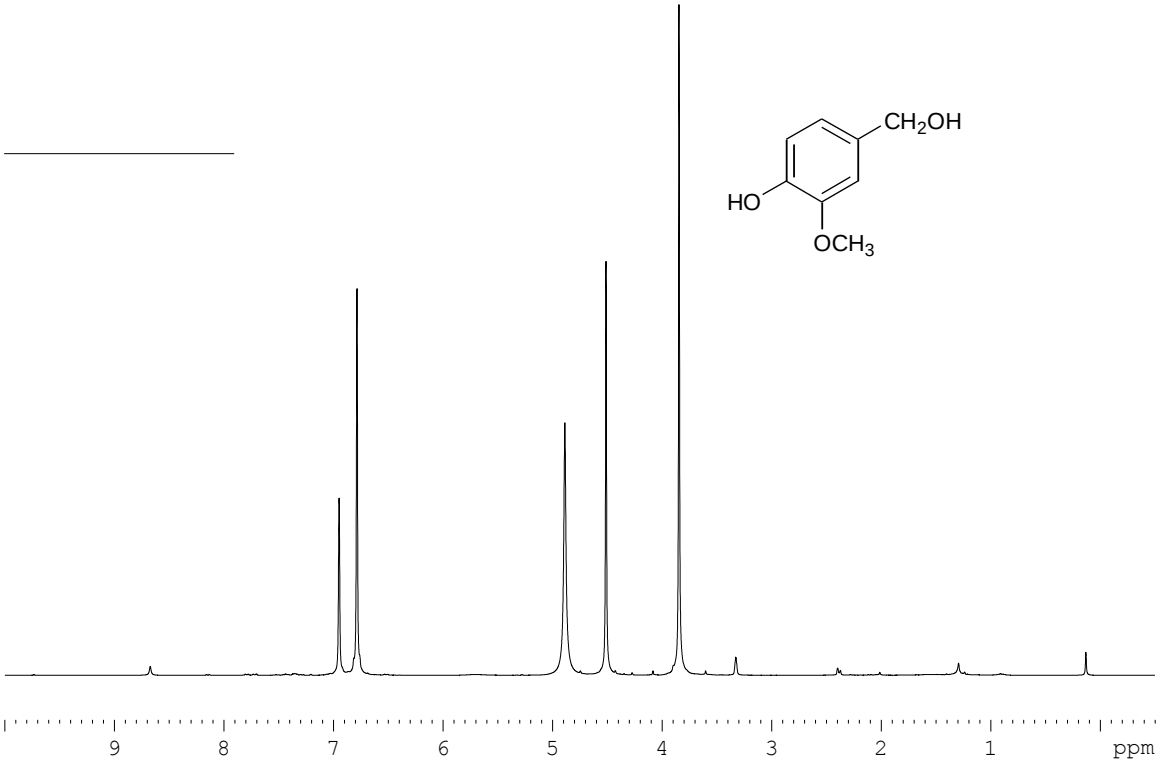


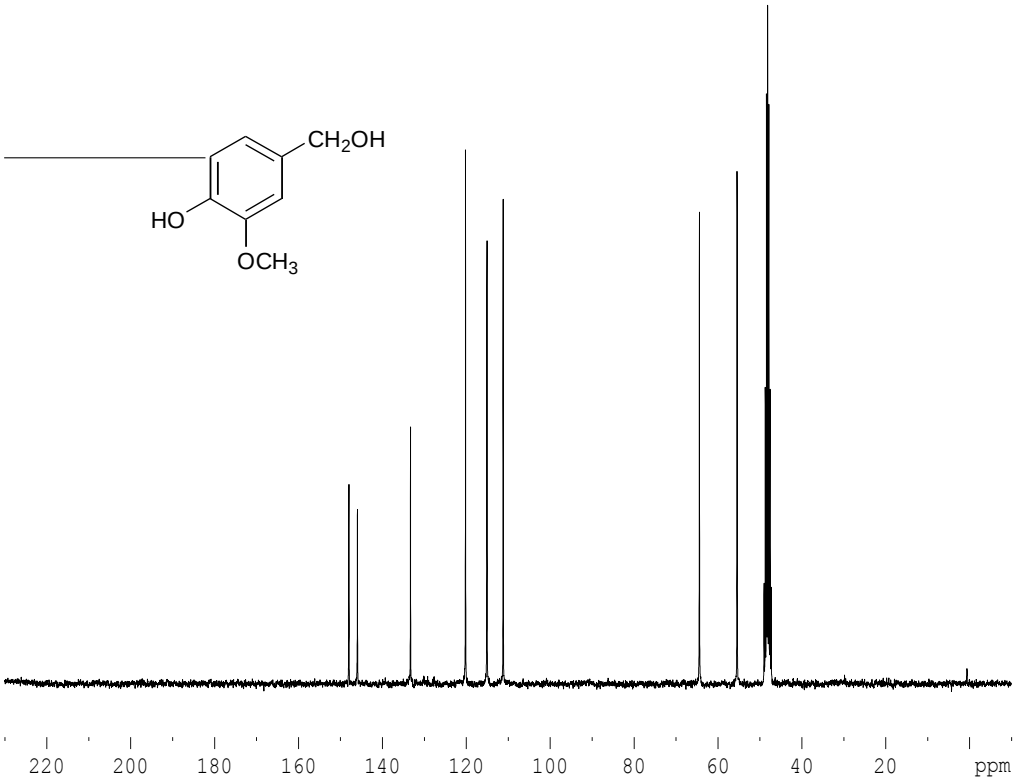
4-Bromo-benzylalchol (Table 3, entry 10)



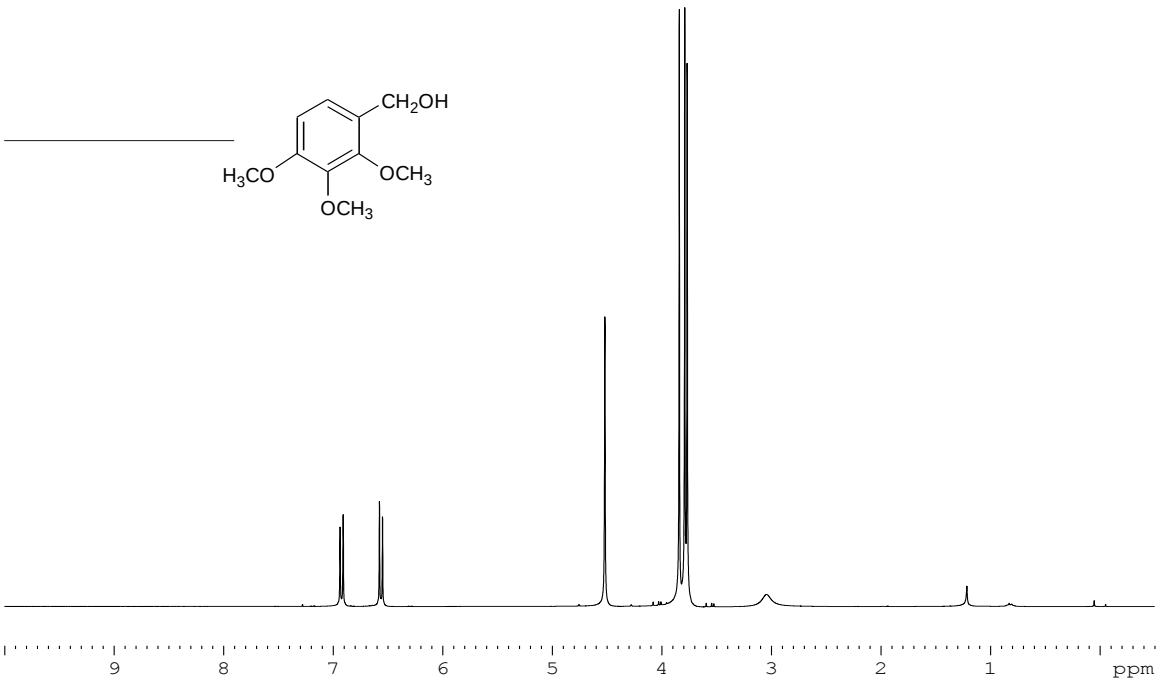


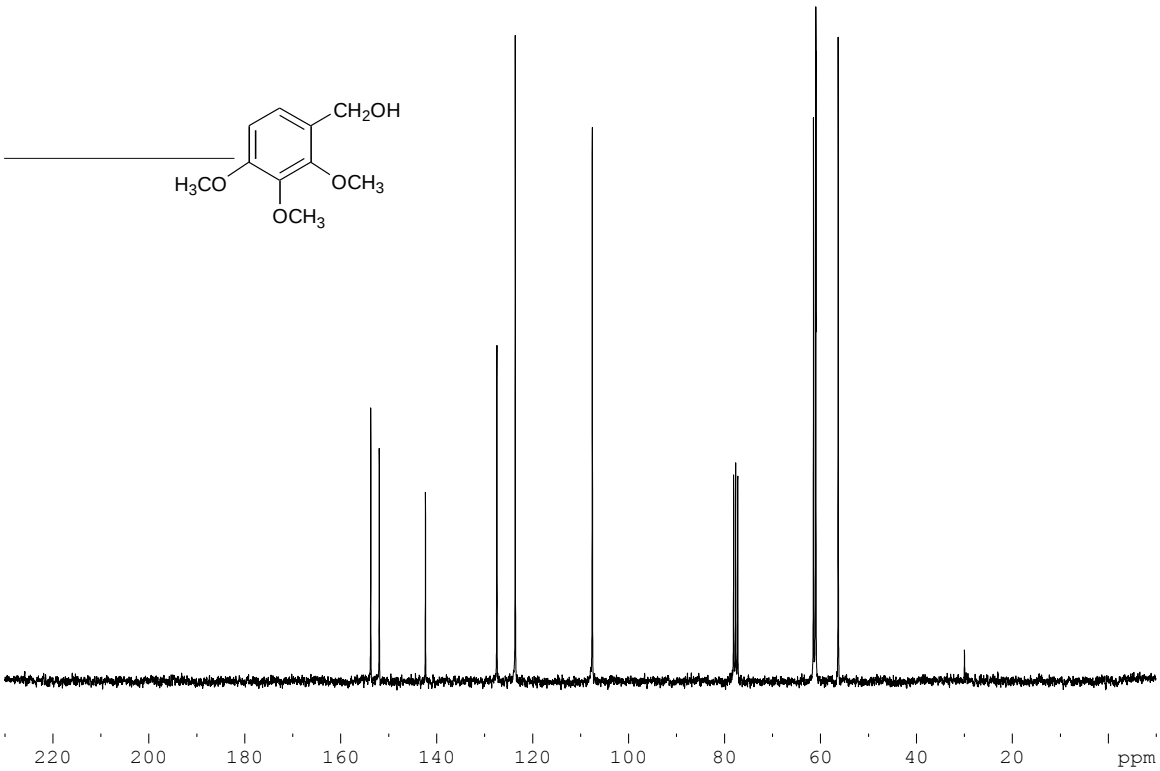
3-Metoxy-4-hydroxybenzylalchol (Table 3, entry 11)



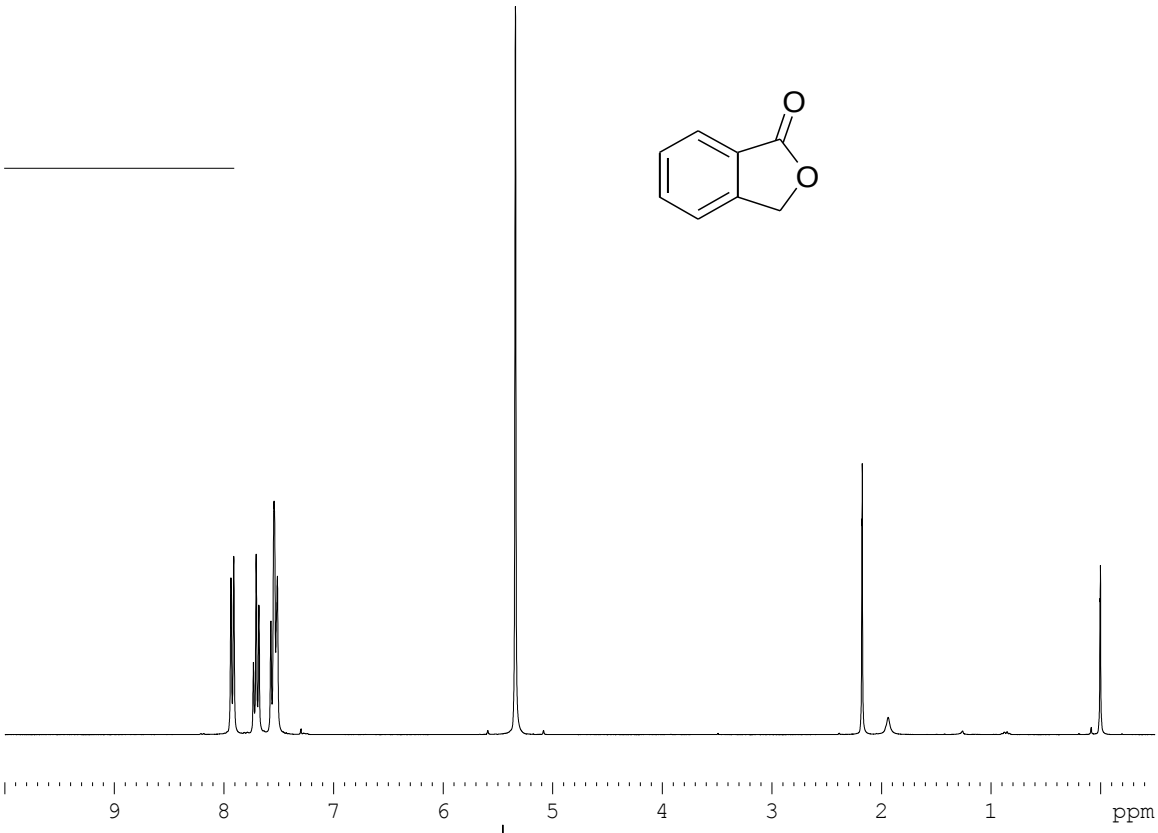


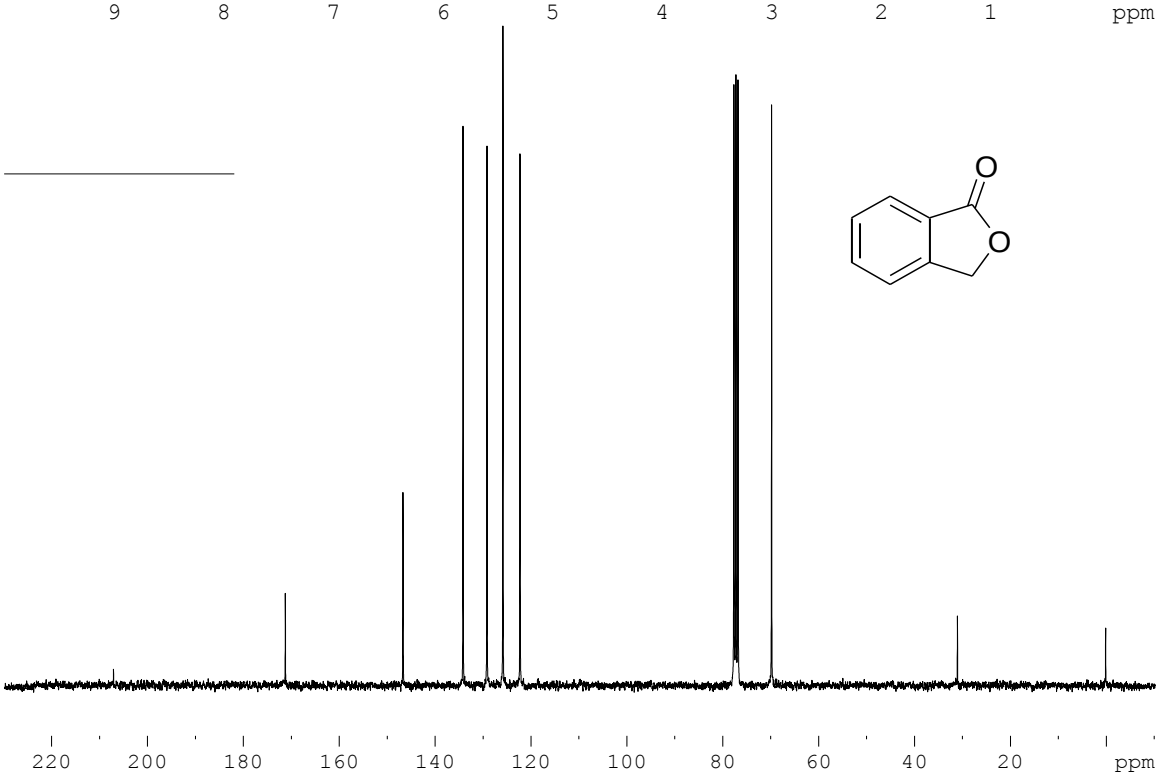
2,3,4-Trimethoxy-benzylalchol (Table 3, entry 12)



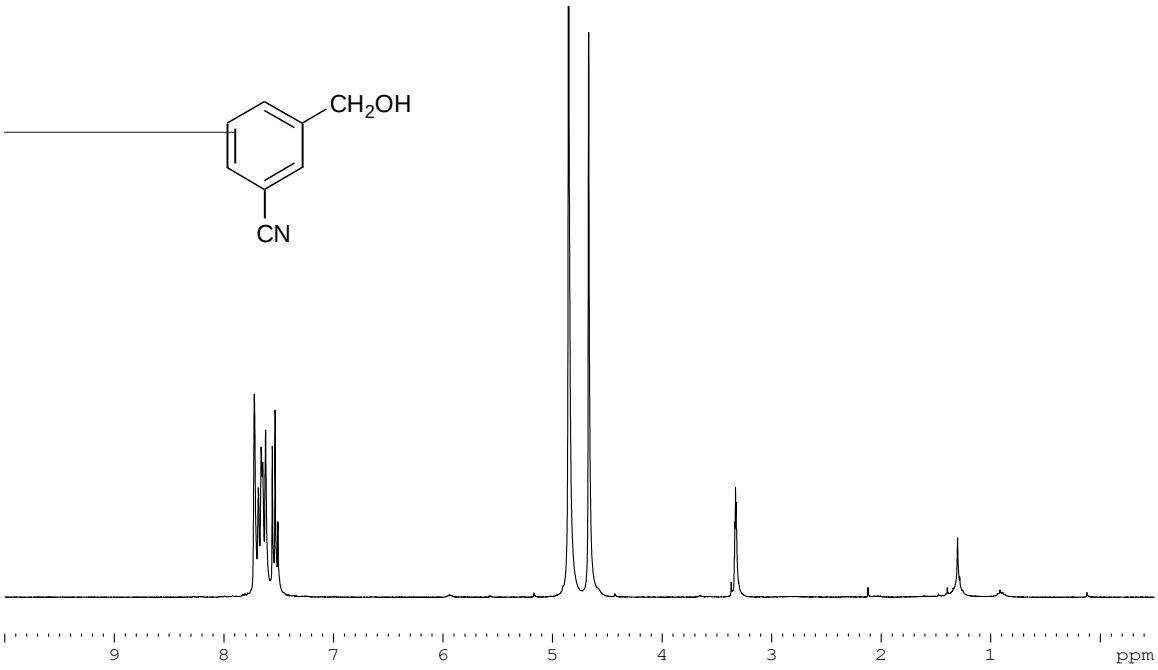


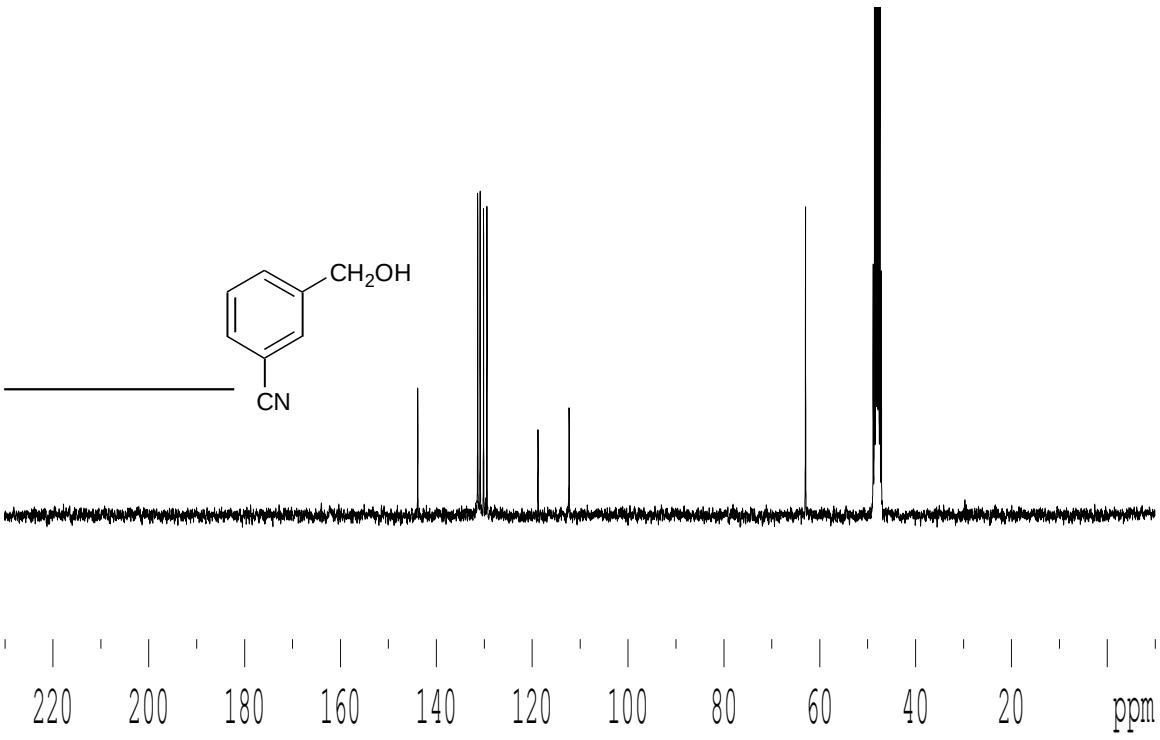
Thalide (Table 3, entry 13)



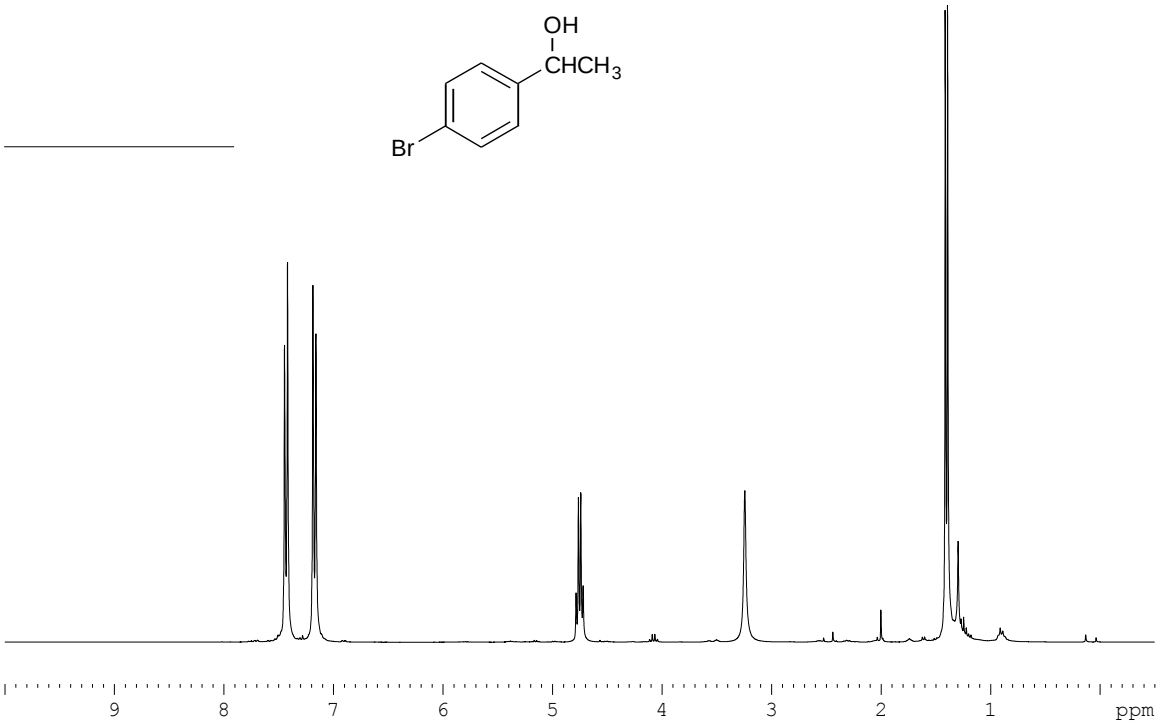


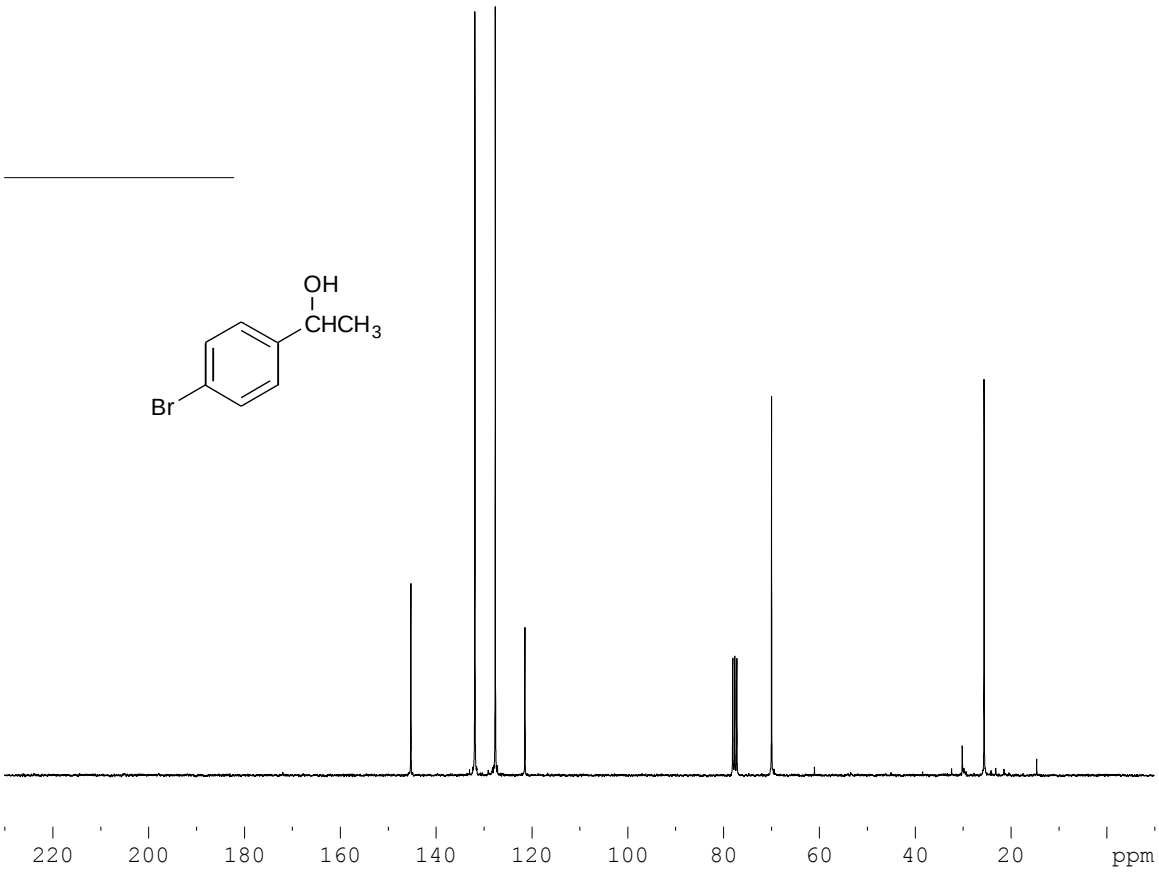
3-Cyano-benzylalchol (Table 3, entry 14)





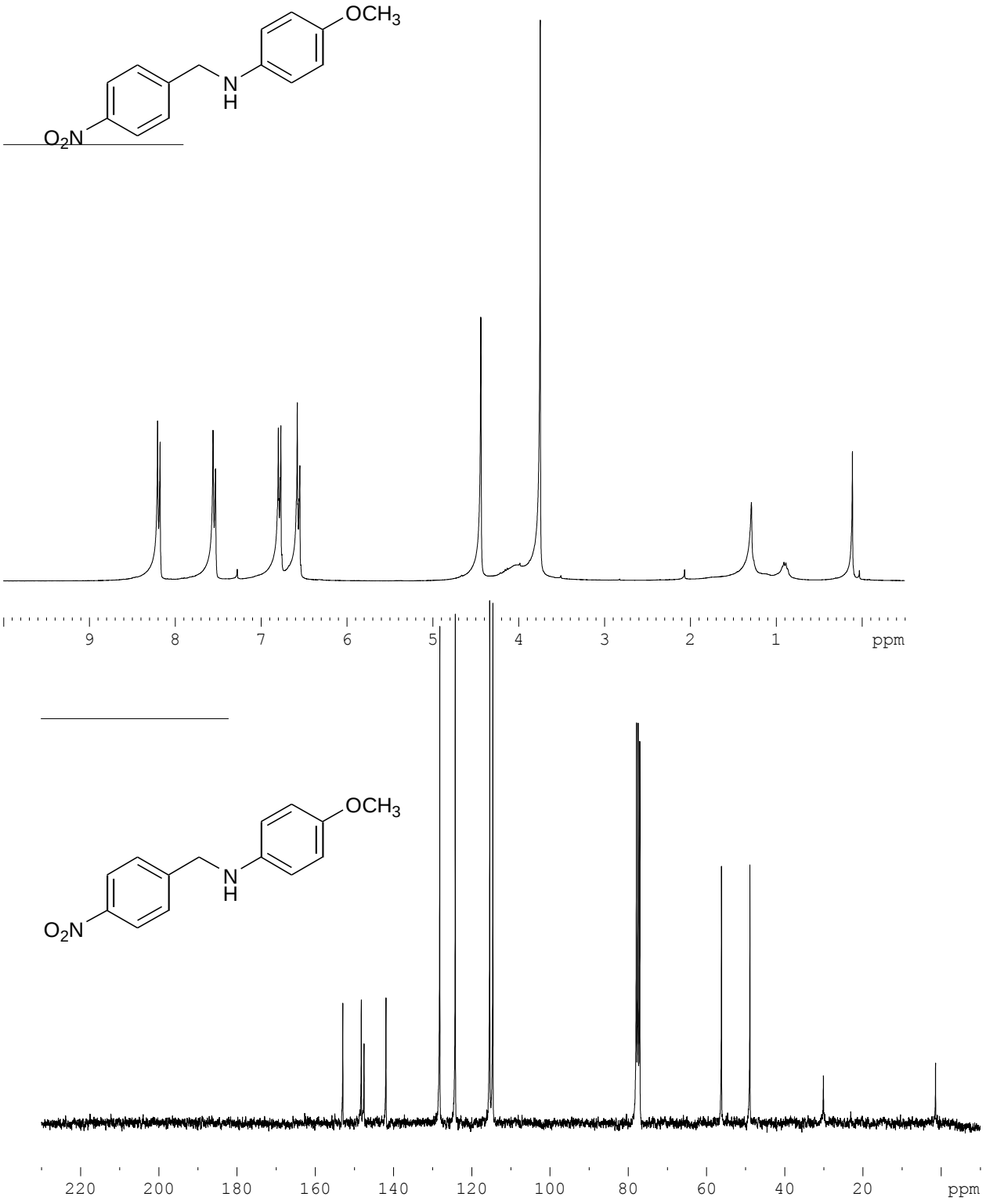
1-(4-Bromophenyl)ethanol (Table 3, entry 16)





Spectra of reductive amination product

4-Methoxy-*N*-(4′-nitrobenzyl)aniline



5. IR of Zinc Phthalocyanine

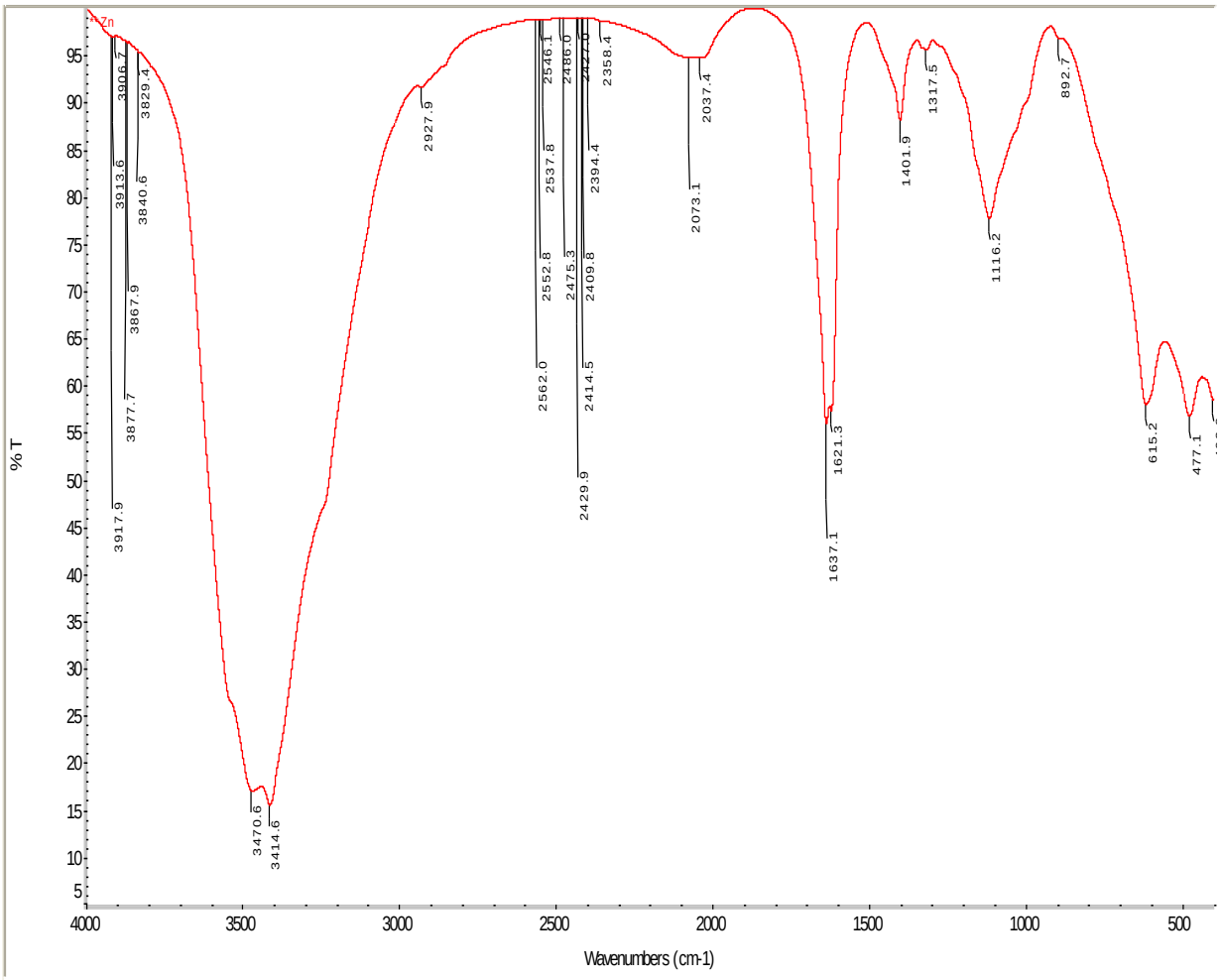


Fig. S2 IR spectra of ZnPc.

6. UV-vis spectra of ZnPc

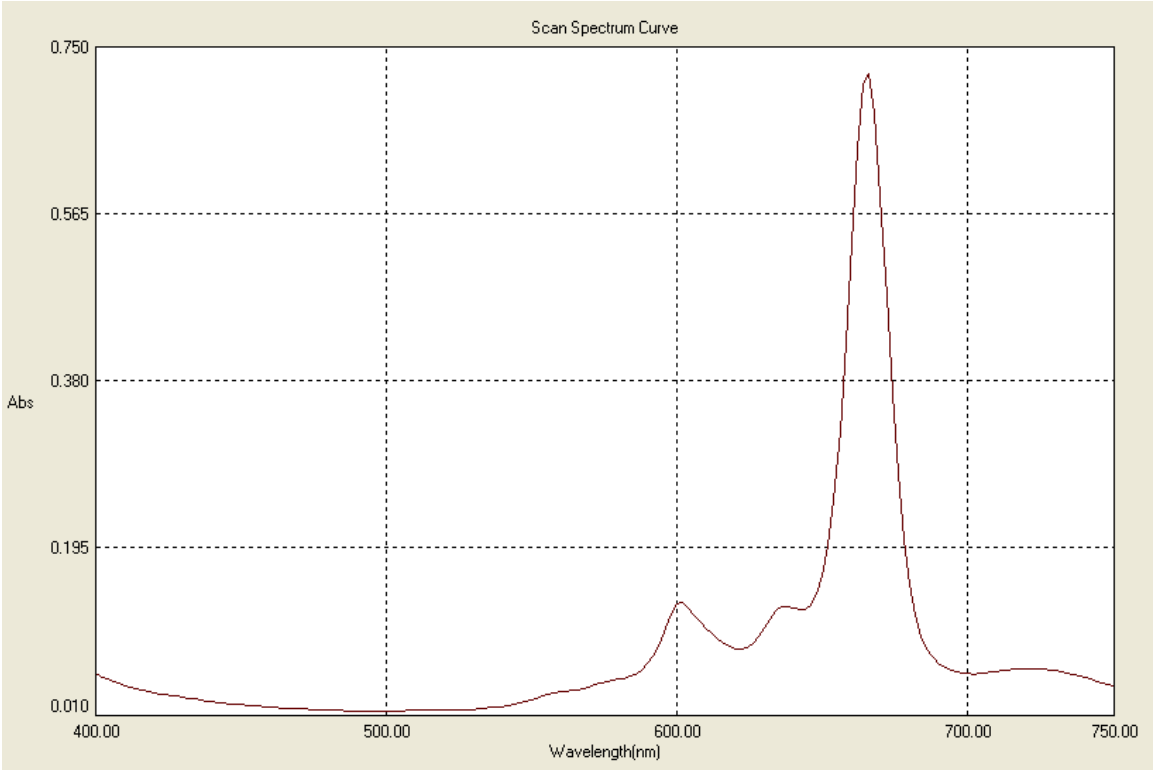


Fig. S2 Uv-vis spectra of ZnPc in THF.

7. References

1. K. S. Jung, J. H. Kwon, S. M. Shon, J. P. Ko, J. S. Shin, S. S. Park, *J. Mater. Sci.* **2004,** *39,* 723.
2. N. M. T.Lourenco, C. A. M. Afonso, *Tetrahedron* **2003**, *59,* 789.
3. J. L. Romera, J. M. Cid, A. A. Trabanco *Tetrahedron Lett*. **2004**, *45*, 8797.
4. D. Villemin, M. Hammadi2, M. Hachemi, N. Bar, *Molecules* **2001**, 6, 831.
5. M. Takasaki, Y. Motoyama, K. Higashi, S. H. Yoon, I. Mochida, H. Nagashima, *Org. Lett.* **2008**, *10*, 1601.
6. G. de Noronha, C. C. Romao, A. C. Fernandes *J. Org. Chem.* **2009**, *74*, 6960