

Supplementary Information

Catalyst-Free Water Mediated Reduction of Nitroarenes Using Glucose as Hydrogen Source

**Manoranjan Kumar, Upendra Sharma, Sushila Sharma, Vishal Kumar, Bikram Singh,
Neeraj Kumar***

*Natural Plant Products Division, CSIR-Institute of Himalayan Bioresource
Technology, Palampur, Himachal Pradesh-176 061, INDIA*

Table of Contents

- 1. General Information**
- 2. General procedures**
- 3. Characterization of products**
- 4. ^1H and ^{13}C NMR spectra of isolated compounds**
- 5. NMR spectra for alkaline degradation of glucose**
- 6. HRMS (ESI) spectra of isolated compounds**
- 7. References**

1. General Information

High grade solvents were used for all reactions. Column chromatography was carried out with 60-120 mesh silica gel. Silica gel, TLC plates (silica gel 60 F254) were purchased from Merck India Ltd. Nitro compounds, NMR solvent were purchased from Sigma-Aldrich and Spectrochem. The GC-MS analysis was carried out using DB-5 MS capillary column, (30 m x 0.25 mm i.d., 0.25 μ m) on a Shimadzu (QP 2010) series Gas Chromatogram-Mass Spectrometer (Tokyo, Japan) coupled with AOC-20i auto-sampler. The initial temperature of column was 70 °C held for 4 min. and was programmed upto 230 °C at 4°C/min., then held for 15 min. at 230 °C; the sample injection volume was 2 μ L 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).

¹H NMR and ¹³C NMR experiments were performed on Bruker Avance-300 and 600 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

(a) Representative experimental procedure for reduction of nitro compounds

D-glucose (2 mmol) was added to the mixture of nitroarene (1 mmol) and KOH (4 mmol) in H₂O: DMSO (1: 1, 4 mL) and refluxed at 110 °C for 24 h. After completion of the reaction (as monitored by TLC and GC-MS), reaction vessel was kept at room temperature and product was extracted with ethyl acetate (3 x 5 mL). Combined organic layer was washed with brine and distilled water (3 x 5 mL), dried on anhydrous sodium sulphate and solvent was evaporated under vacuum. Crude product was analyzed directly using GC-MS. In case of large scale (10 mmol of substrate)

reaction, product was purified using column chromatography (silica gel 60-120 mesh, *n*-hexane/ ethylacetate) (Table 2, entries 5, 13, 15 and 22).

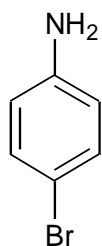
(b) Experimental procedure for the study of alkaline degradation of

glucose: D-glucose (2 mmol) was added to the mixture of nitroarene (1 mmol) and KOH (4 mmol) in H₂O: DMSO-d₆ (1: 1, 4 mL) and refluxed at 110 °C for 24 h. After completion of the reaction, the reaction vessel was kept at room temperature and product was directly analyzed by NMR.

3. Characterization of nitro reduction products:

All compounds were identified by comparison of spectral data with literature.¹

4-Bromoaniline (Table 2, entry 5)¹

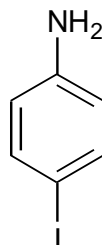


¹H NMR (600 MHz, CD₃OD): δ 6.59 (d, *J* = 7.8 Hz, 2H), 7.15 (d, *J* = 7.8 Hz, 2H);

¹³C NMR (150 MHz, CD₃OD): δ 108.9, 116.7, 131.4, 146.7; HRMS calculated for

[M+H]⁺ is 171.9762 and found 171.9753.

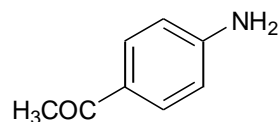
4-Iodoaniline (Table 2, entry 6)¹



^1H NMR (300 MHz, CD_3OD): δ 6.50 (d, $J = 8.7$ Hz, 2H), 7.34 (d, $J = 8.7$ Hz, 2H);

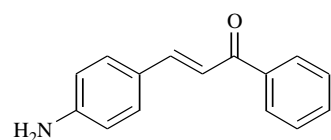
^{13}C NMR (75 MHz, CD_3OD): δ 79.1, 118.6, 138.8, 148.6; HRMS calculated for $[\text{M}+\text{H}]^+$ is 219.9623 and found 219.9611.

4-Aminoacetophenone (Table 2, entry 13)¹



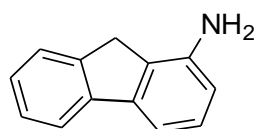
^1H NMR (300 MHz, CD_3OD): δ 2.47 (s, 2.47, 3H), 6.65 (s, 2H), 7.76 (s, 2H); ^{13}C NMR (75 MHz, CD_3OD): δ 26.6, 114.9, 127.6, 132.9, 156.1, 199.9. HRMS calculated for $[\text{M}+\text{H}]^+$ is 136.0762 and found 136.0755.

4-Aminochalcone (Table 2, entry 15):



^1H NMR (300 MHz, CD_3OD): δ 6.70 (d, $J = 8.5$ Hz, 2H), 7.45-7.61 (m, 6H), 7.74 (d, $J = 15.4$, 1H), 8.04 (d, $J = 8.5$, 2H); ^{13}C NMR (75 MHz, CD_3OD): δ 115.7, 117.4, 124.9, 129.5, 129.9, 132.2, 133.8, 140.2, 148.4, 152.0, 193.1; HRMS calculated for $[\text{M}+\text{H}]^+$ is 224.1075 and found 224.1086.

2-Aminofluorene (Table 2, entry 19)¹

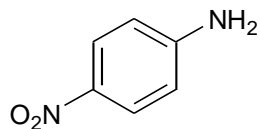


^1H NMR (300 MHz, CD_3OD): δ 3.75 (s, 2H), 6.75 (dd, $J = 8.1$ Hz, $J = 1.9$ Hz, 1H), 6.92 (s, 1H), 7.13 (t, $J = 7.3$ Hz, 1H), 7.25 (t, $J = 7.3$ Hz, 1H), 7.43 (d, $J = 7.4$, 1H), 7.52 (d, $J = 8.1$, 1H), 7.60 (d, $J = 7.5$, 1H); ^{13}C NMR (75 MHz, CD_3OD): δ 37.4,

113.0, 115.4, 119.1, 121.2, 125.5, 125.8, 127.5, 129.2, 133.7, 143.4, 146.0, 148.0;

HRMS calculated for $[M+H]^+$ is 182.0970 and found 182.0958.

4-Nitroaniline (Table 2, entry 22)¹

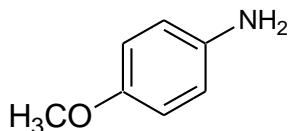


¹H NMR (300 MHz, CD₃OD): δ 6.62 (d, *J* = 9.0 Hz, 2H), 7.98 (d, *J* = 9.0 Hz, 2H);

¹³C NMR (75 MHz, CD₃OD): δ 114.1, 127.7, 138.7, 157.2. HRMS calculated for

$[M+H]^+$ is 139.0508 and found 139.0521.

4-Methoxyaniline (Table 2, entry 7)¹

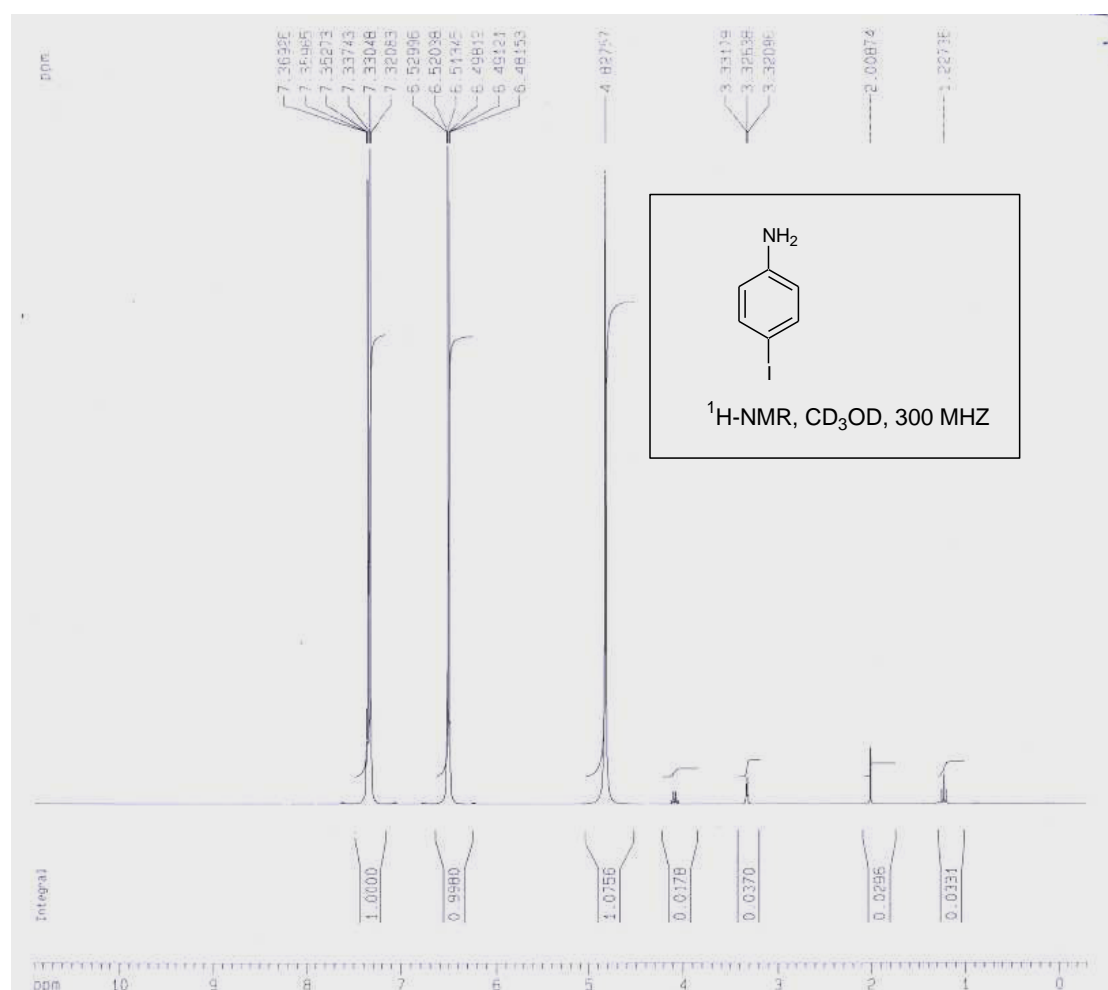


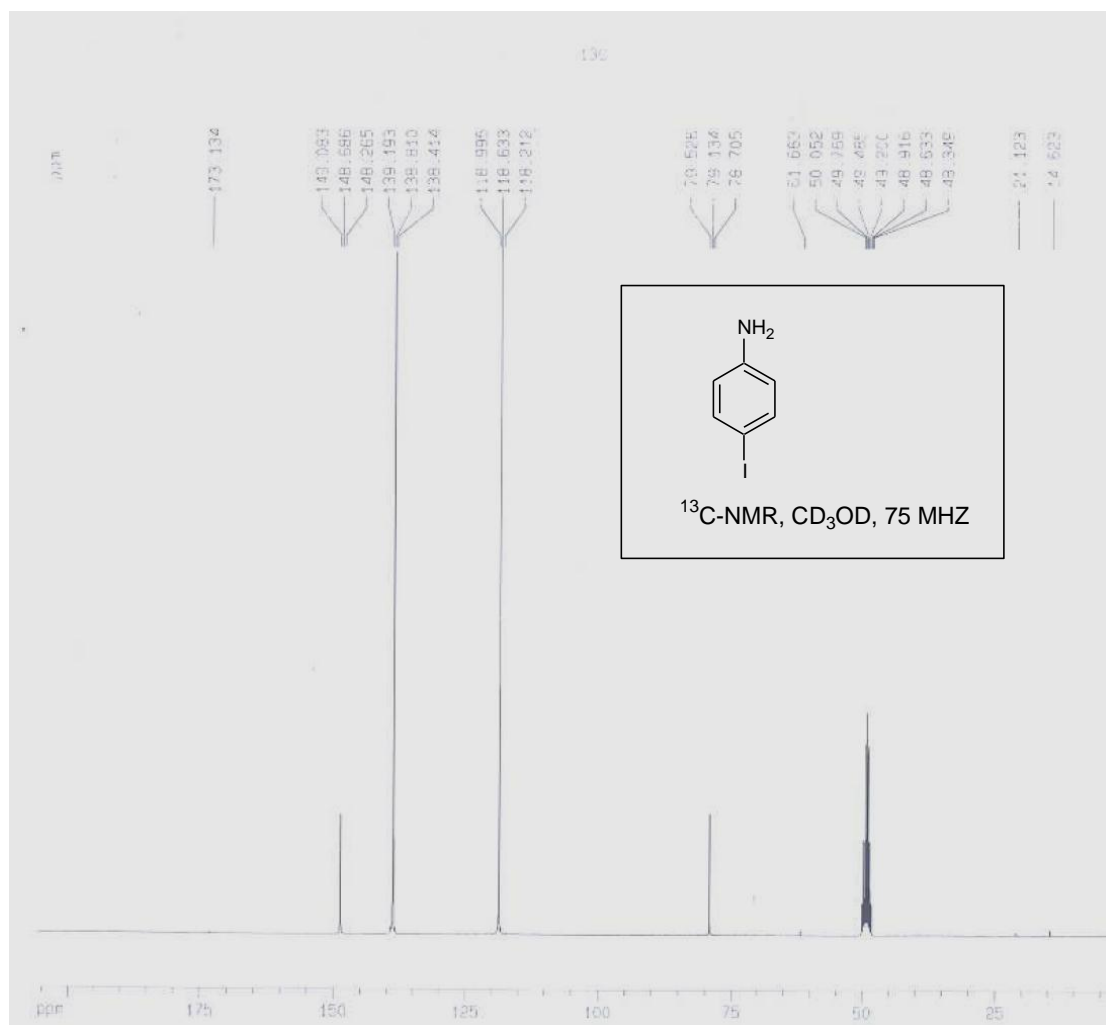
¹H NMR (600 MHz, CD₃OD): δ 6.71 (s, 4H), 3.68 (s, 3H); ¹³C NMR (150 MHz,

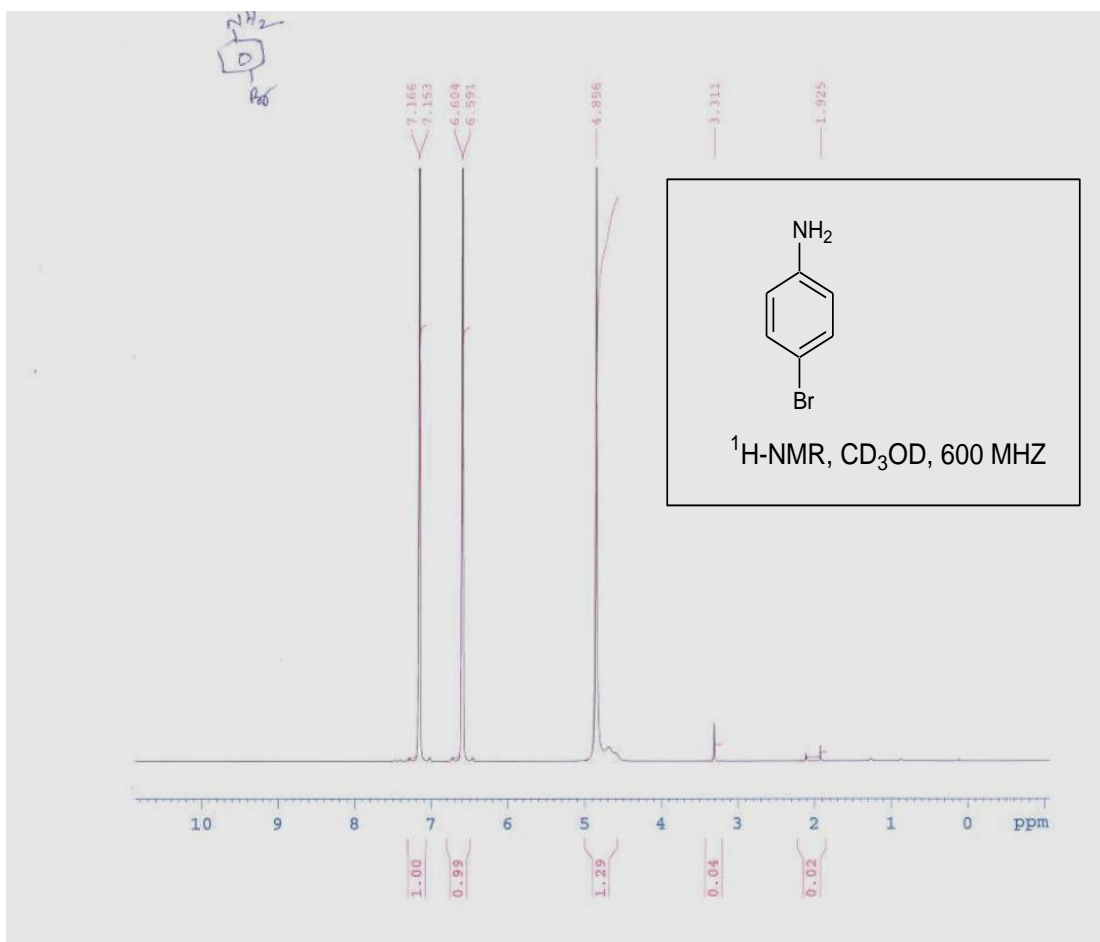
CD₃OD): δ 56.24, 115.81, 118.32, 141.64, 154.52; HRMS calculated for $[M+H]^+$ is

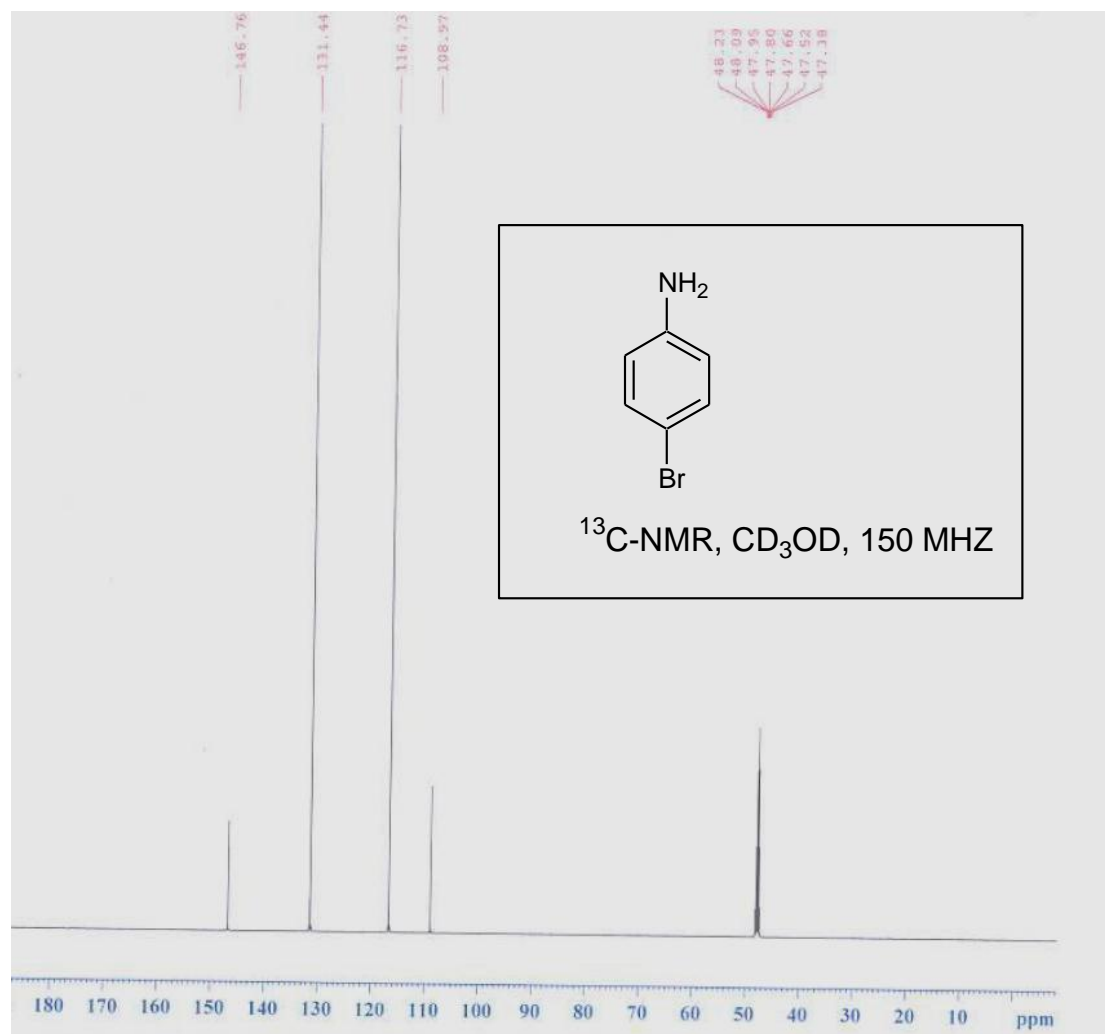
124.0762 and found 124.0751.

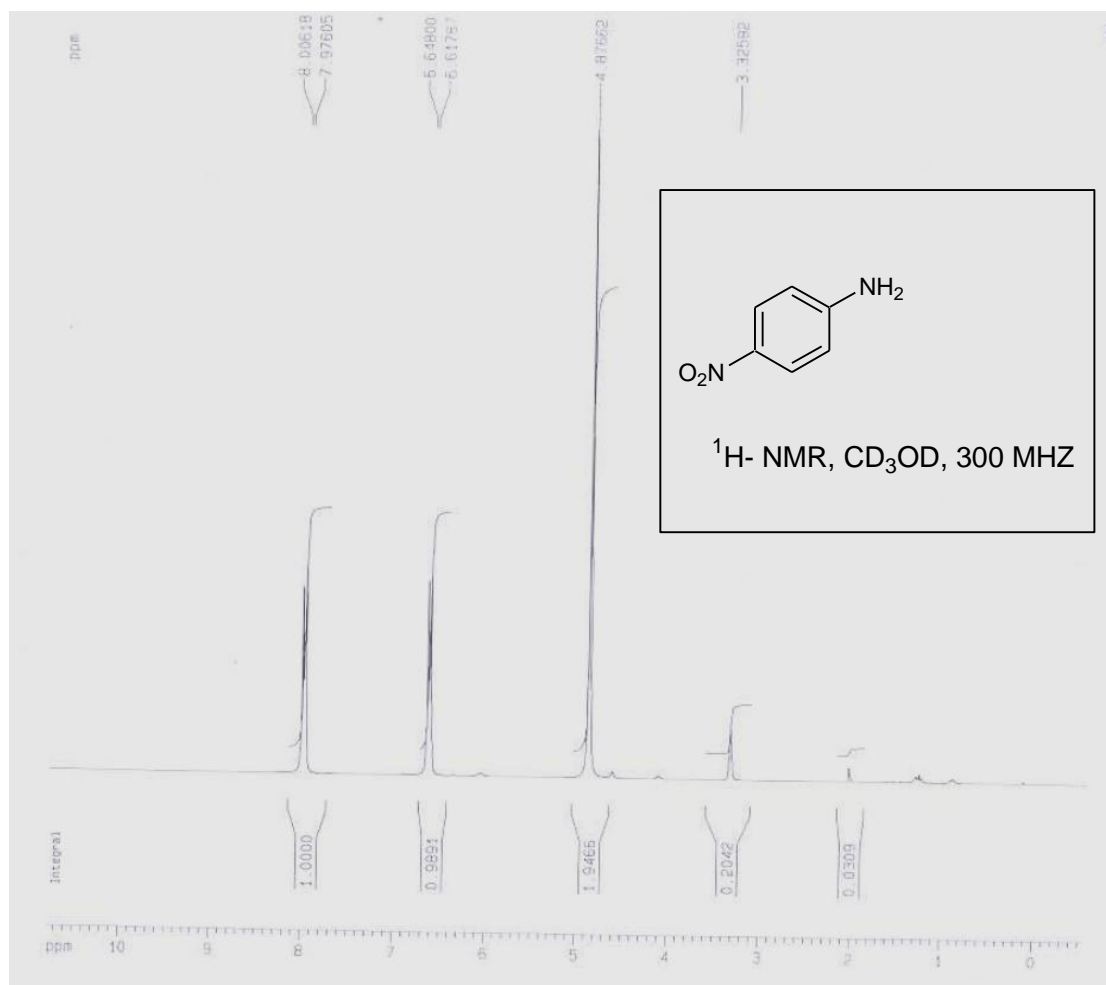
4. ^1H and ^{13}C NMR spectra of isolated compounds

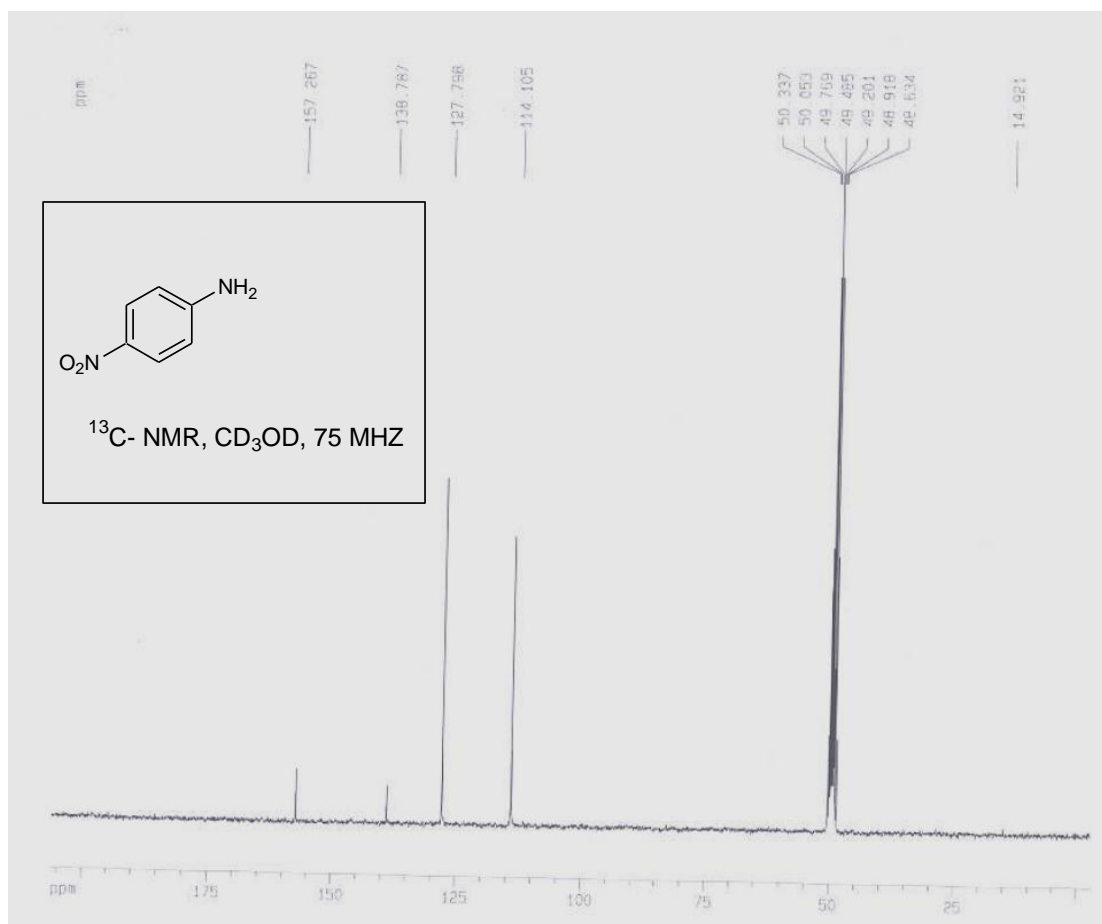


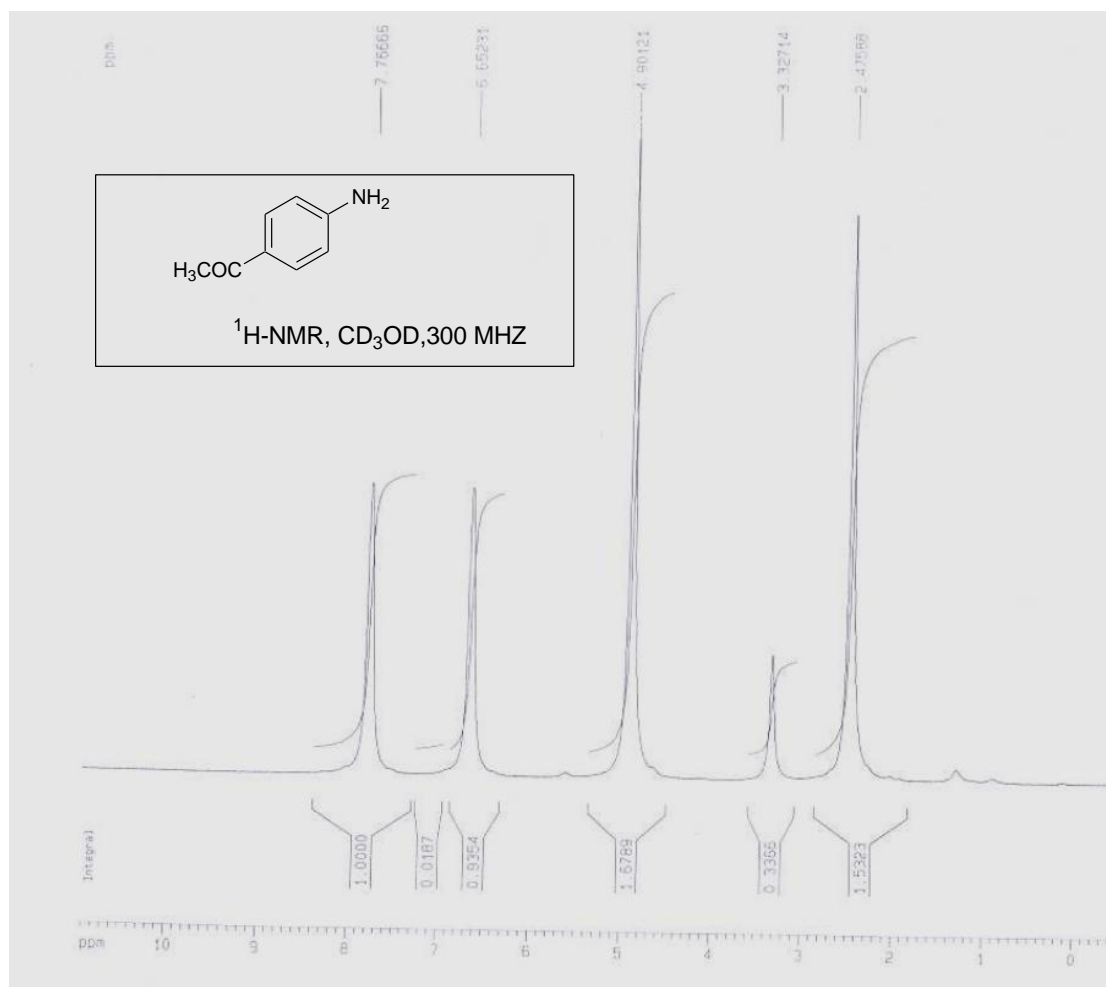


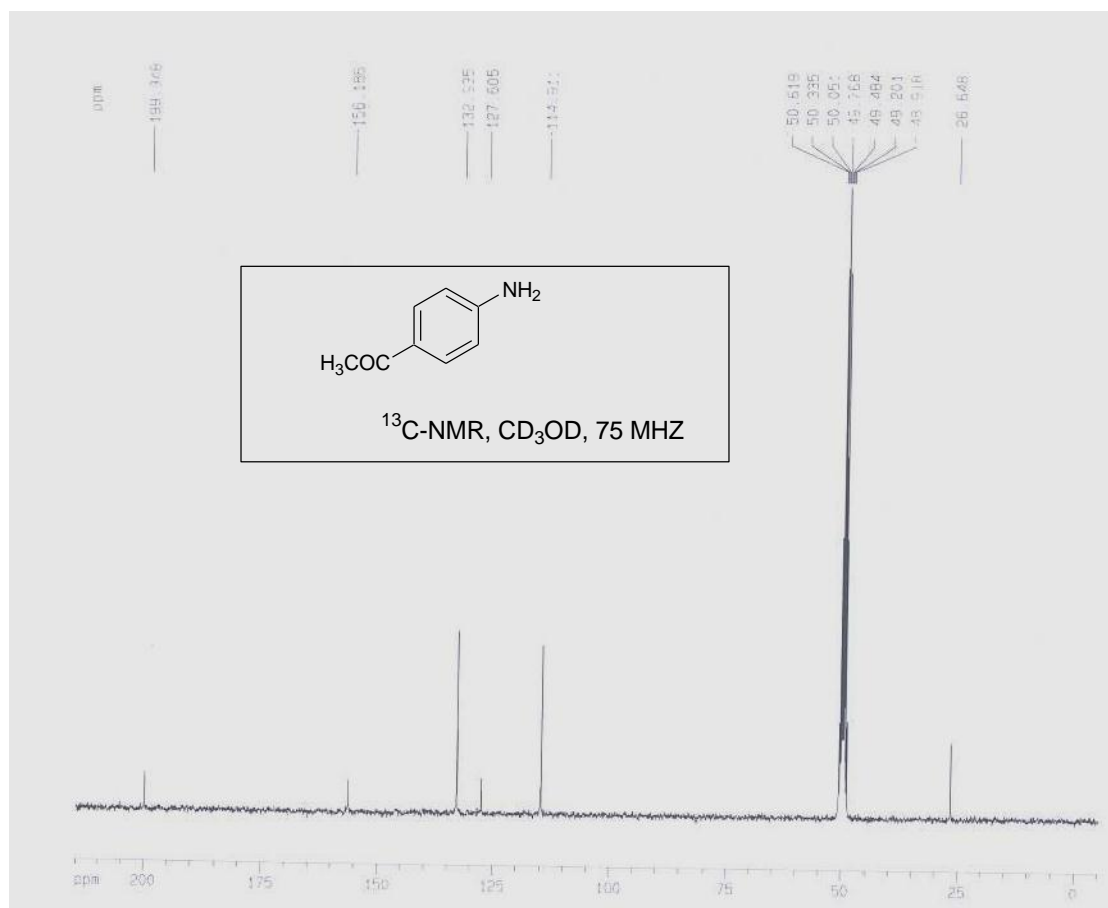


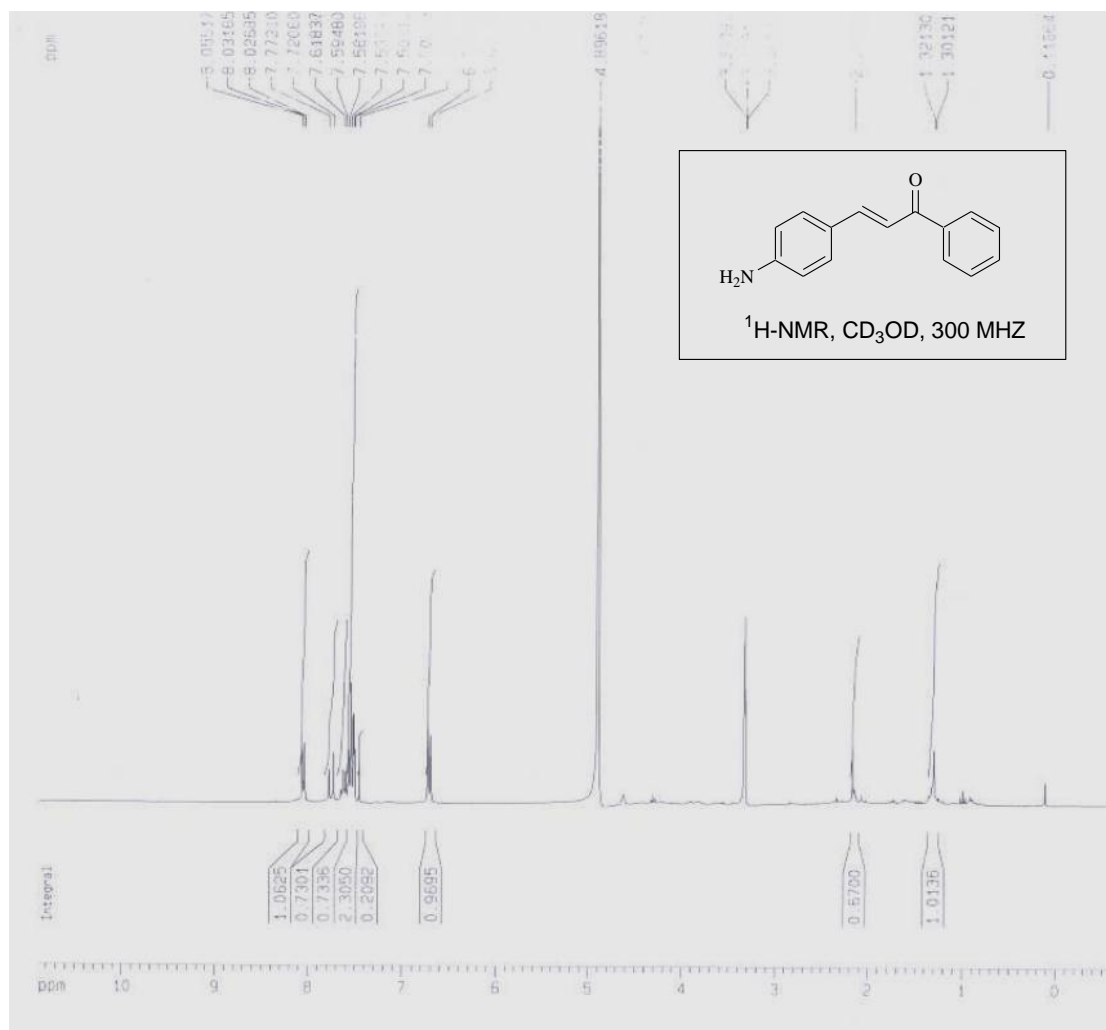


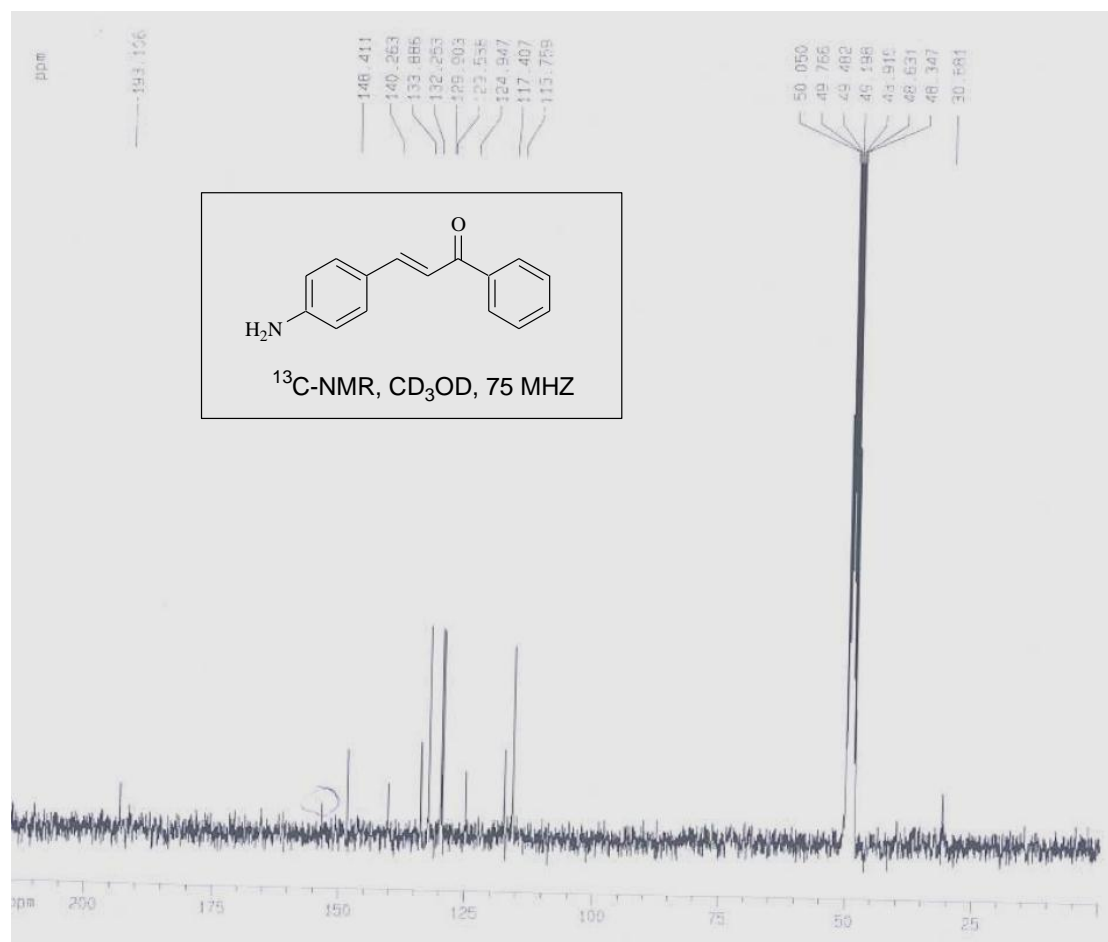


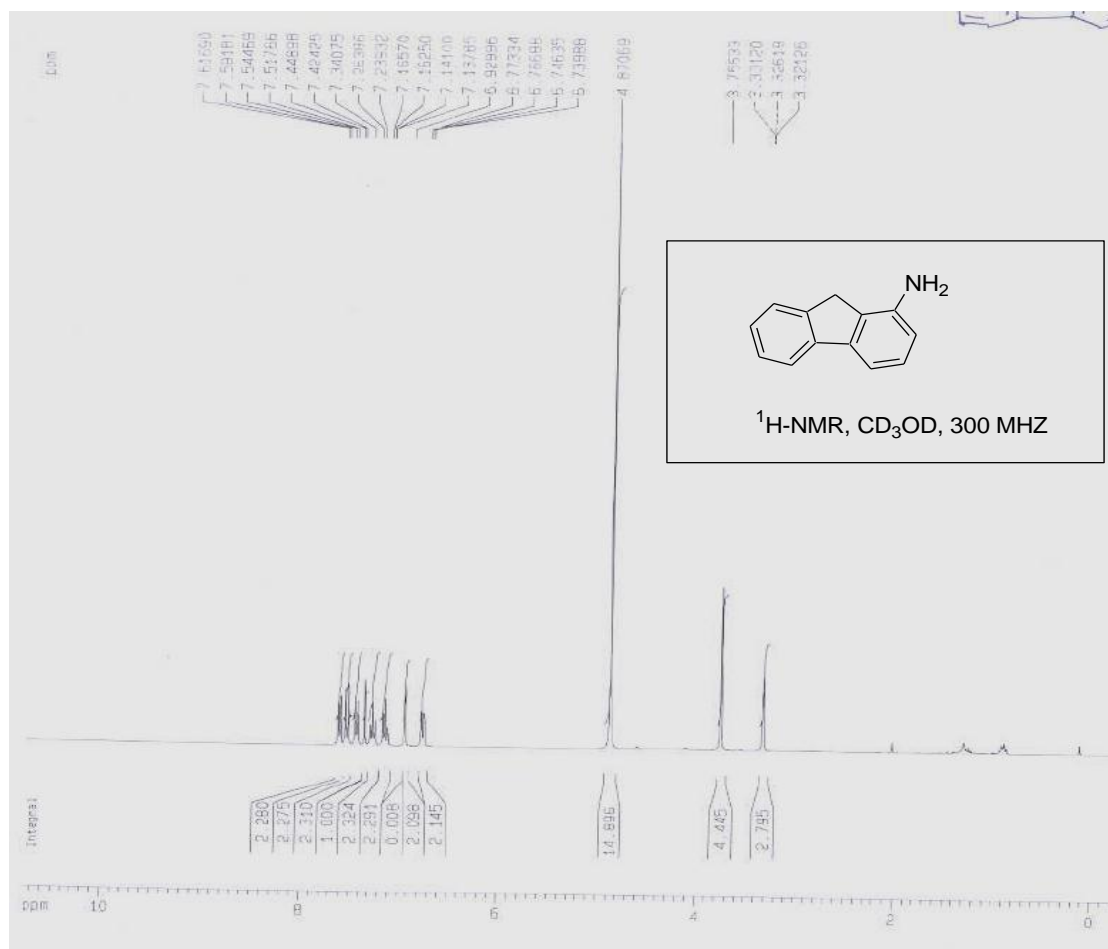


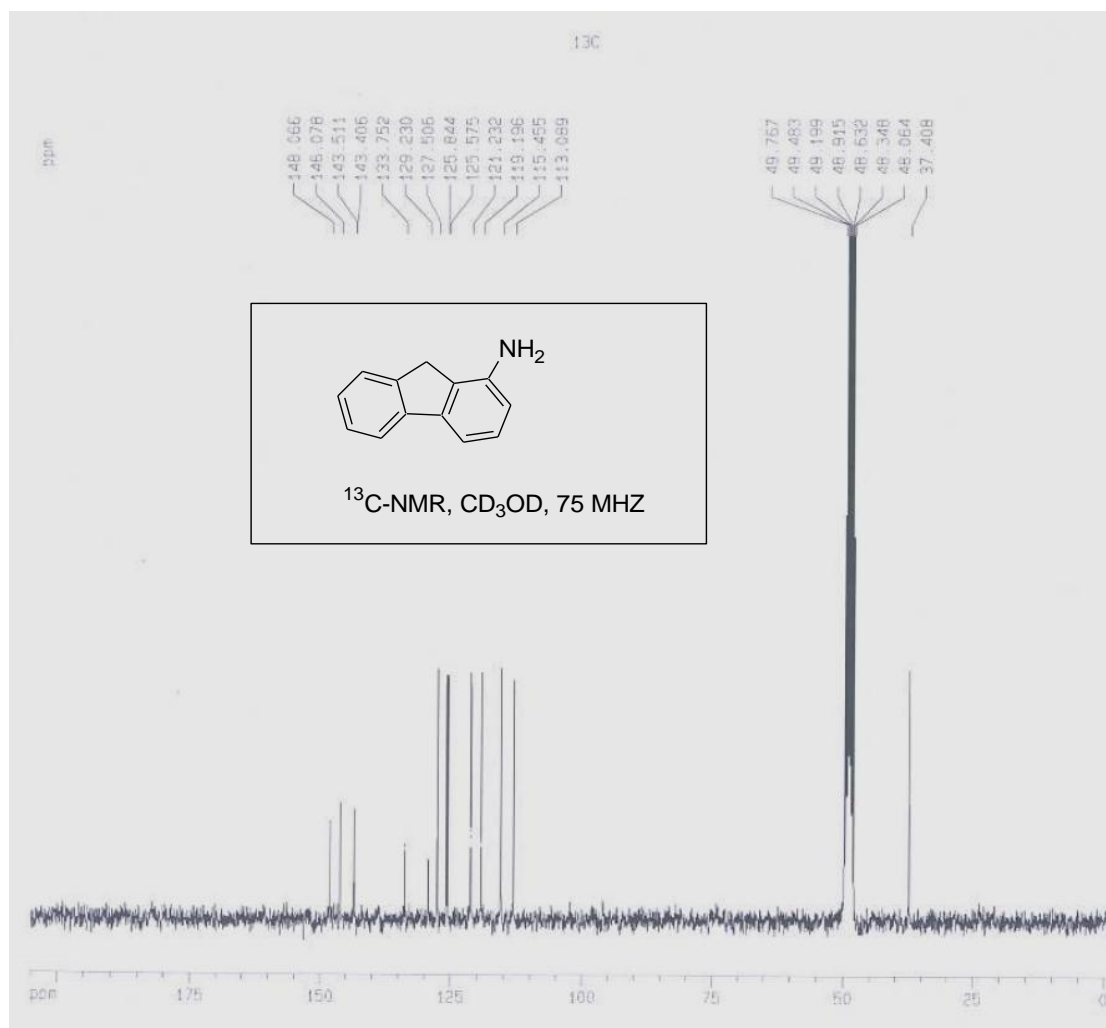


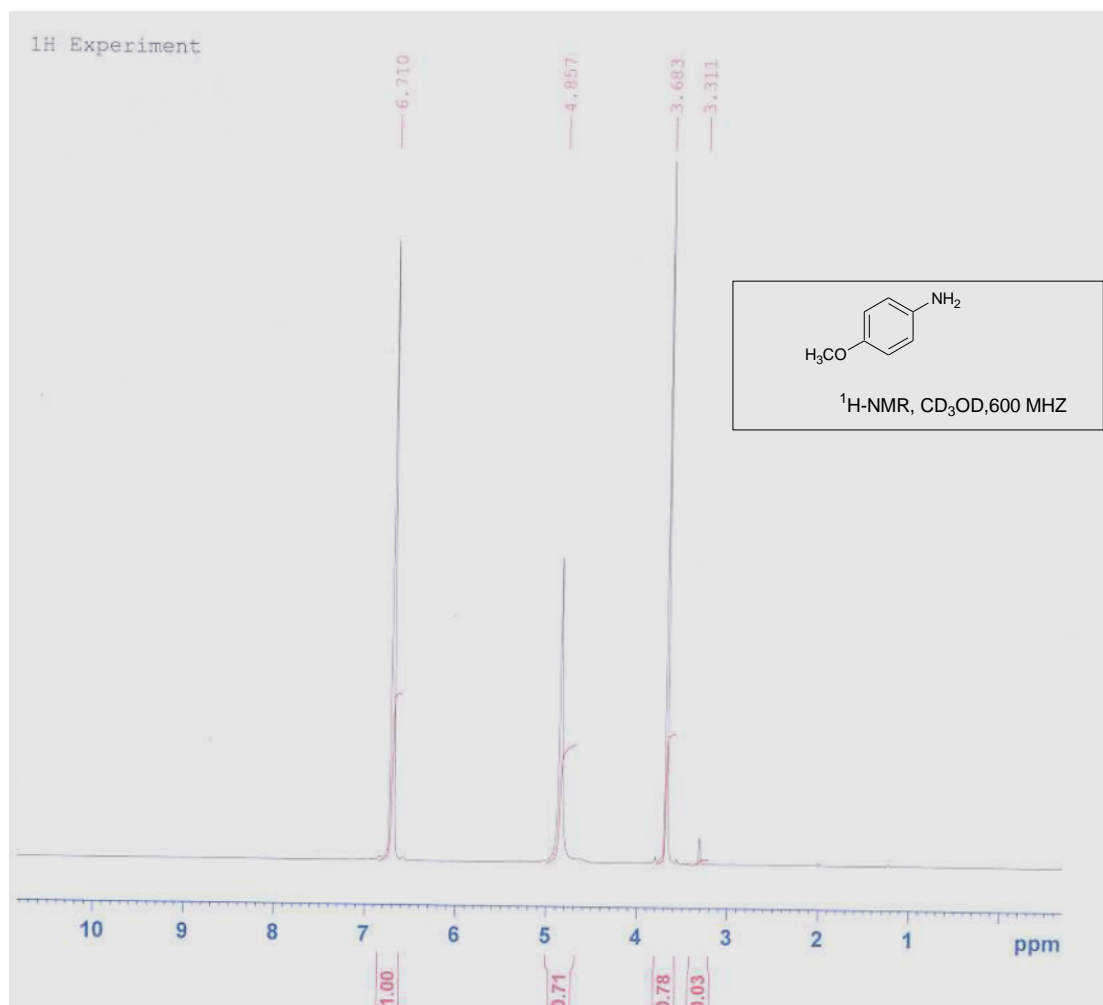


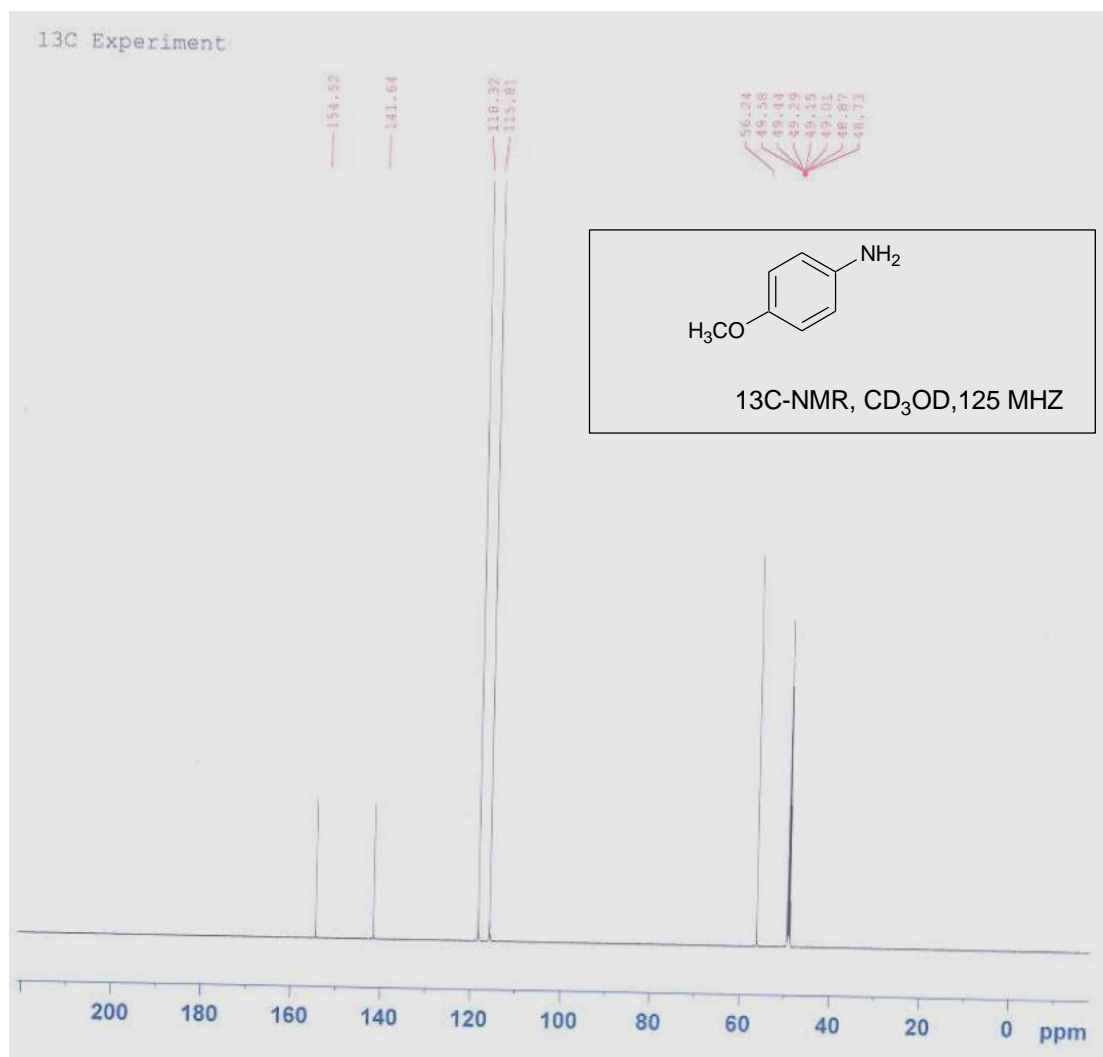






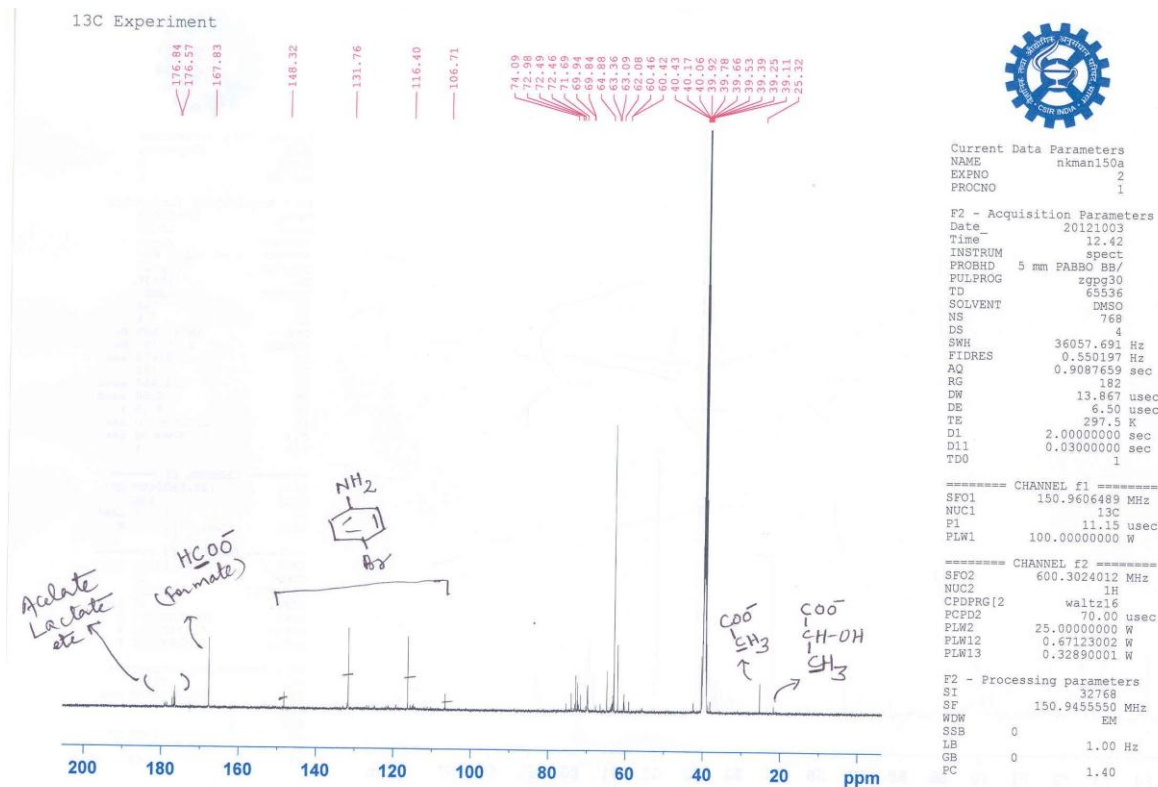




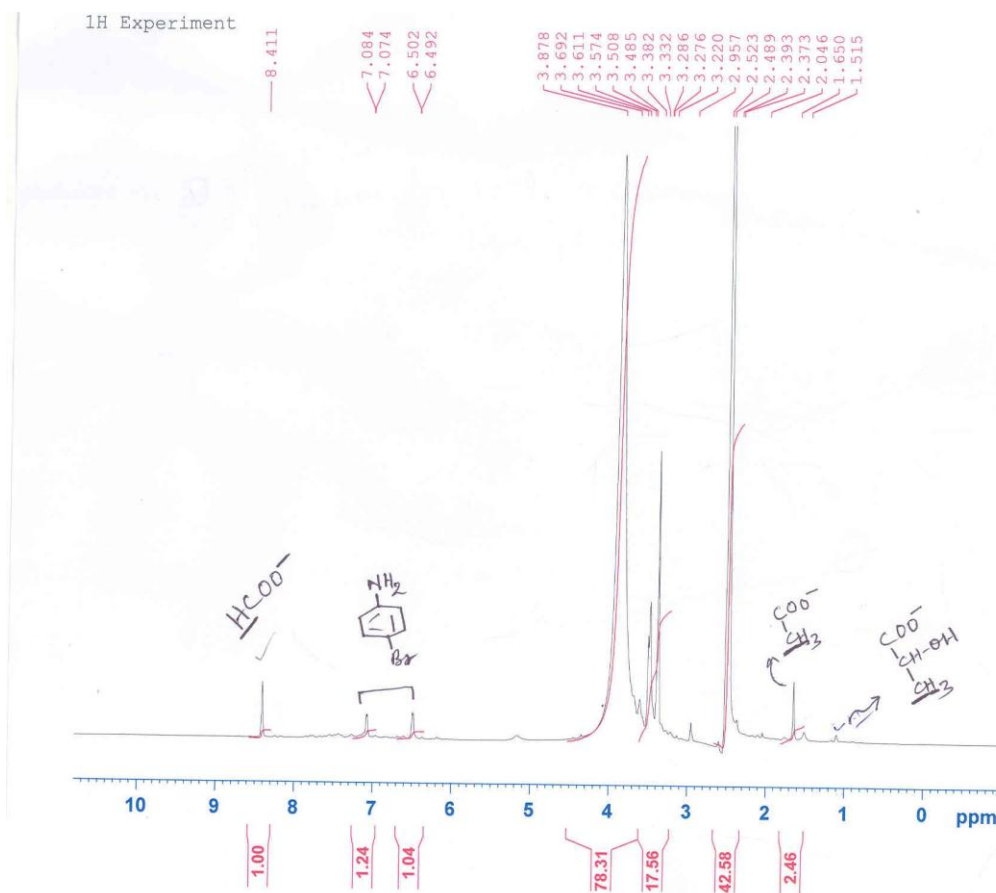


5. NMR spectra for alkaline degradation of glucose

¹³C NMR Spectra of Reaction mixture carried out in DMSO-d₆ / H₂O and KOH



¹H NMR Spectra of reaction mixture carried out in DMSO-d₆ / H₂O and KOH



Current Data Parameters
NAME nkman150a
EXPNO 1
PROCNO 1

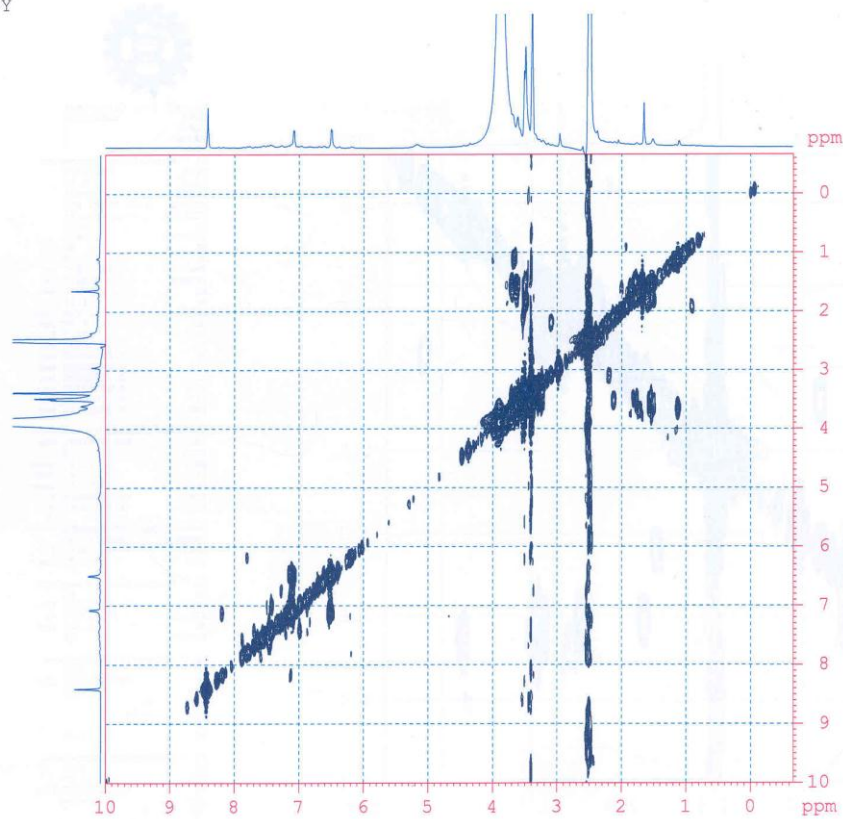
F2 - Acquisition Parameters
Date_ 20121003
Time 12.03
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 65536
SOLVENT DMSO
NS 16
DS 2
SWH 12019.230 Hz
FIDRES 0.183399 Hz
AQ 2.7262976 sec
RG 8.81
DW 41.600 usec
DE 6.50 usec
TE 295.9 K
D1 1.0000000 sec
TDO 1

===== CHANNEL f1 =====
SF01 600.3029254 MHz
NUC1 1H
P1 11.47 usec
PLW1 25.0000000 W

F2 - Processing parameters
SI 65536
SF 600.3000140 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.40

COSY Spectra of reaction mixture carried out in DMSO-d₆ / H₂O and KOH

COSY



```
Current Data Parameters
NAME      nkman150a
EXPNO    6
PROCNO   1

F2 - Acquisition Parameters
Date_    20121009
Time     6.18
INSTRUM spect
PROBHD   5 mm PABBO BB/
PULPROG  cosypppgpf
TD       2048
SOLVENT  DMSO
NS       64
DS       2
SWH      8012.820 Hz
FIDRES   3.912510 Hz
AQ       0.1277952 sec
RG       4.91
DW       62.400 usec
DE       6.50 usec
TE       296.7 K
D0       0.00000300 sec
D1       2.00000000 sec
D11      0.03000000 sec
D12      0.00020000 sec
D13      0.00004000 sec
D16      0.00020000 sec
IN0      0.00012480 sec

----- CHANNEL f1 -----
SF01    600.3036091 MHz
NUC1    1H
P0      11.47 usec
P1      11.47 usec
P17     2500.00 usec
PLW1    25.00000000 W
PLW10   4.86539984 W

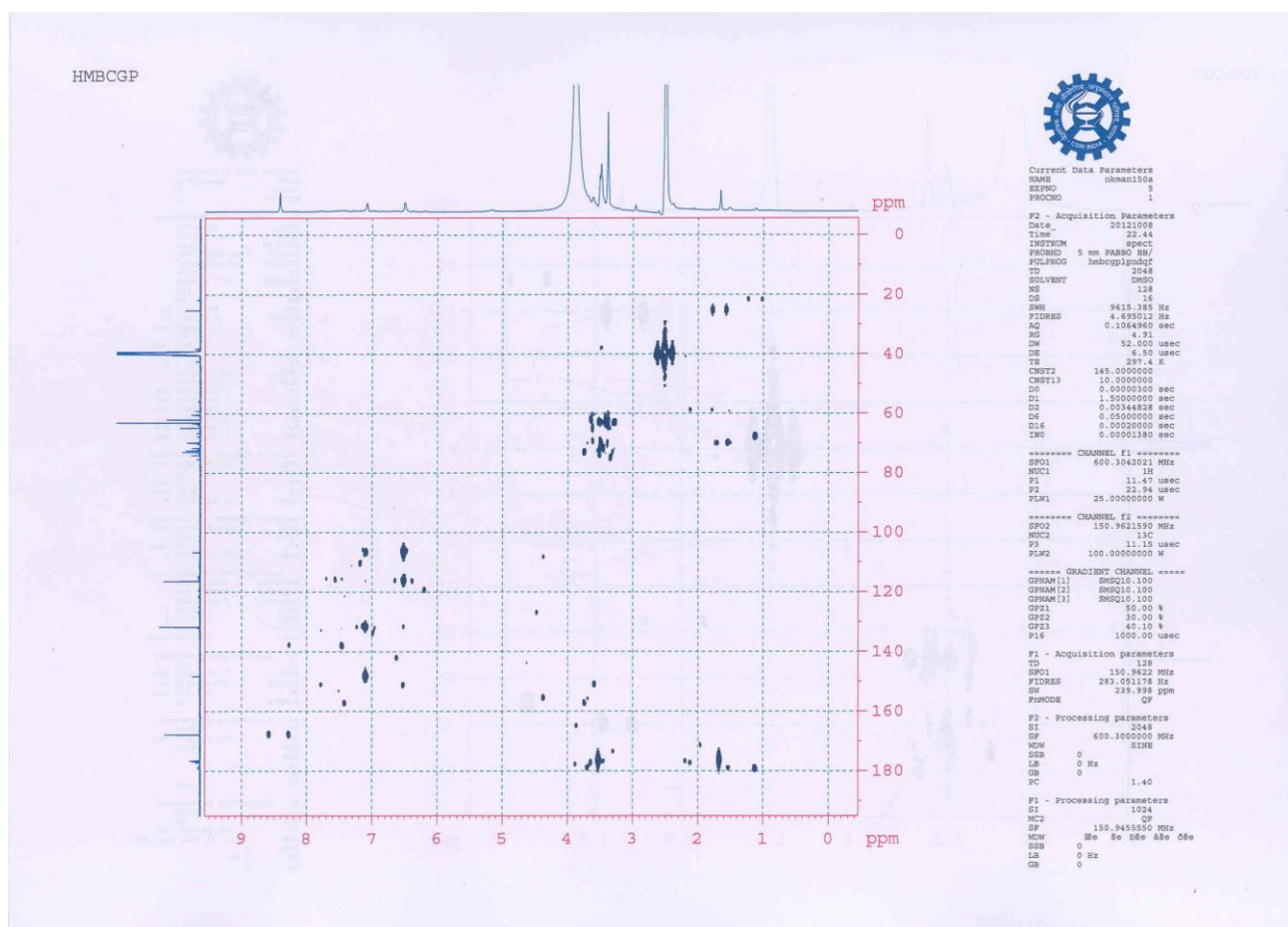
----- GRADIENT CHANNEL -----
GENAM[1] SMSQ10.100
GP21    10.00 %
F15     1000.00 usec

F1 - Acquisition parameters
TD      82
SF01    600.3036 MHz
FIDRES   97.717323 Hz
SW       13.348 ppm
F0CODE   GF

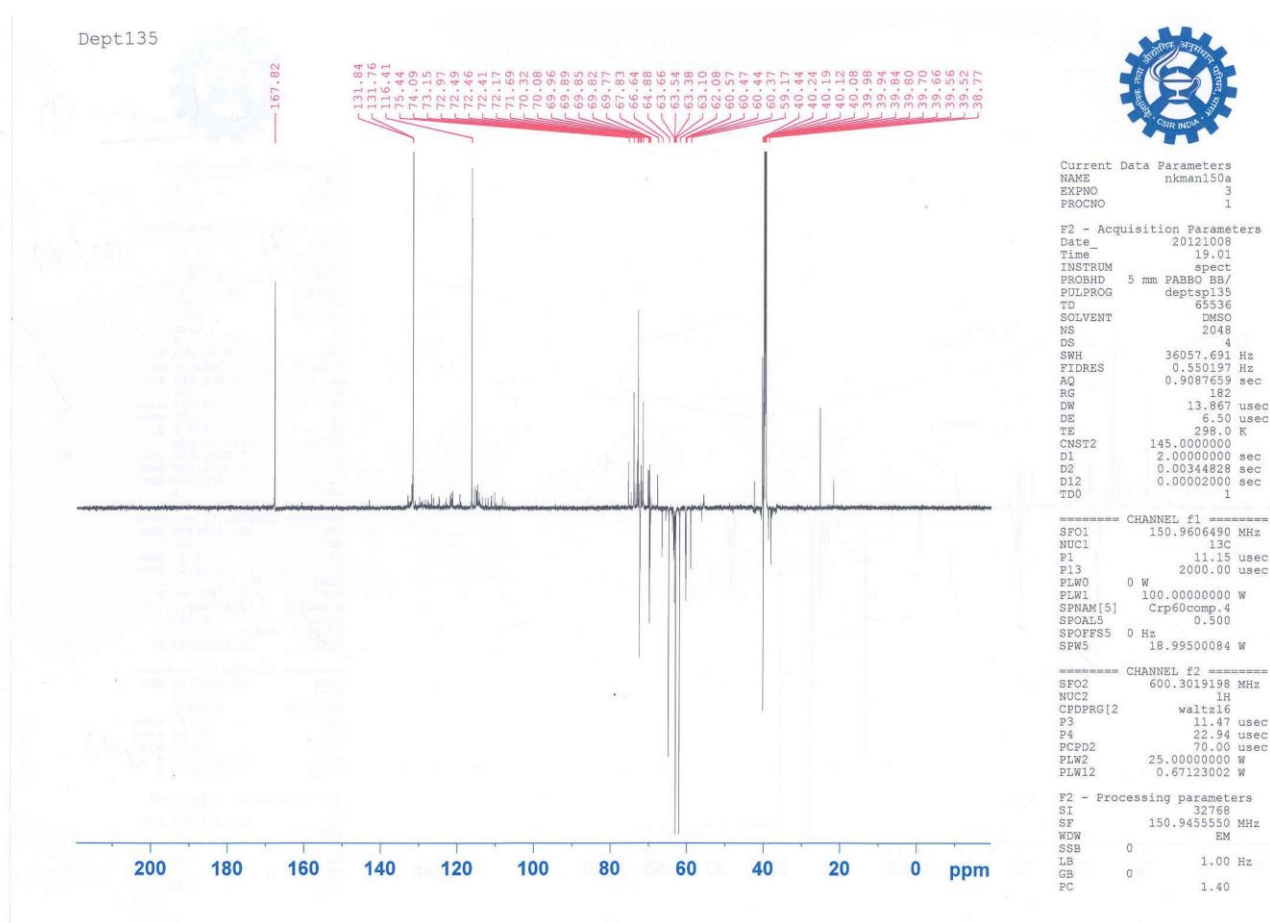
F2 - Processing parameters
SI       1024
SF       600.3000000 MHz
WDW      QSIINE
SSB      0
LB       0 Hz
GB       0
FC       1.40

F1 - Processing parameters
SI       1024
MC2      GF
SF       600.3000000 MHz
WDW      States
SSB      0
LB       0 Hz
GB       0
```

HMBC Spectra of reaction mixture carried out in DMSO-d₆ / H₂O and KOH

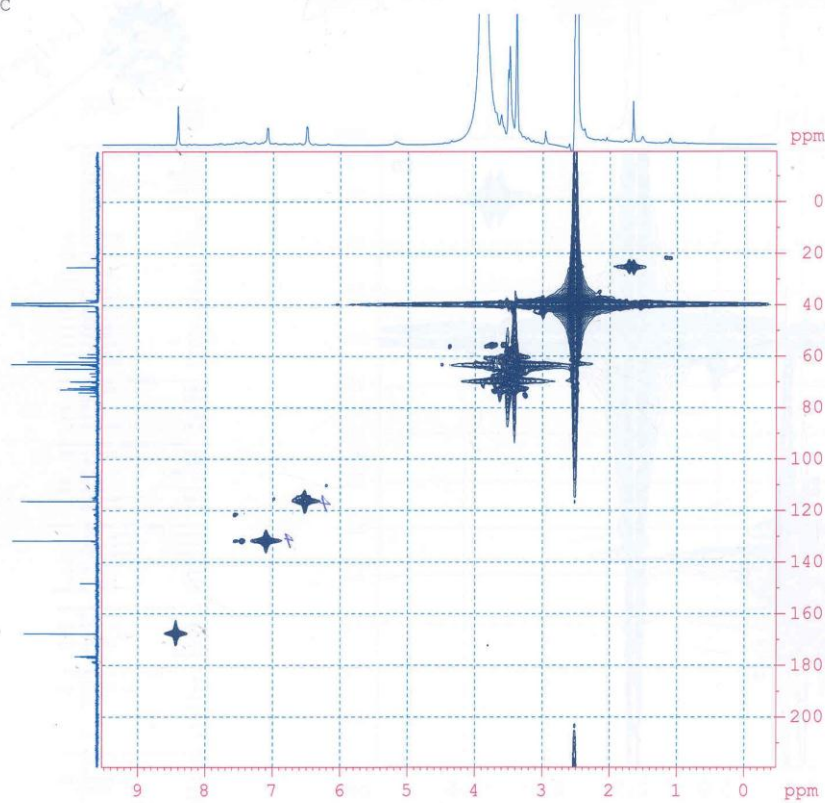


DEPT-135 spectra of reaction mixture carried out in DMSO-d₆ / H₂O and KOH



HMQC Spectra of reaction mixture carried out in DMSO-d₆ / H₂O and KOH

HMQC



```
Current Data Parameters
NAME          nman150a
EXPNO        4
PROCNO       1

F2 - Acquisition Parameters
Date_        201108
Time         18.03
INSTRUM      spect
PROBHD       5 mm PABBO BBI
PULPROG      hmqcpuf
TD           1024
SOLVENT      DMSO
NS           64
DS           16
SWH          6005.615 Hz
FIDRES       3.889783 Hz
AQ           0.0851968 sec
RG           31.91
DW           83.200 usec
DE           6.30 usec
TE           298.0 K
CHFT2       148.000000 sec
D0           0.0000000 sec
D1           1.5000000 sec
D2           0.0044828 sec
D12          0.0002000 sec
D13          0.0000400 sec
D16          0.0002000 sec
D10          0.00001365 sec

===== CHANNEL f1 =====
SFO1         600.3021199 MHz
NUC1         1H
P1           11.47 usec
F2           22.94 usec
PLW1        25.00000000 W

===== CHANNEL f2 =====
SFO2         150.9664490 MHz
NUC2         13C
PROBHD2      13C
P2           11.15 usec
PLW2        100.00000000 W
PLW12       3.45339990 W

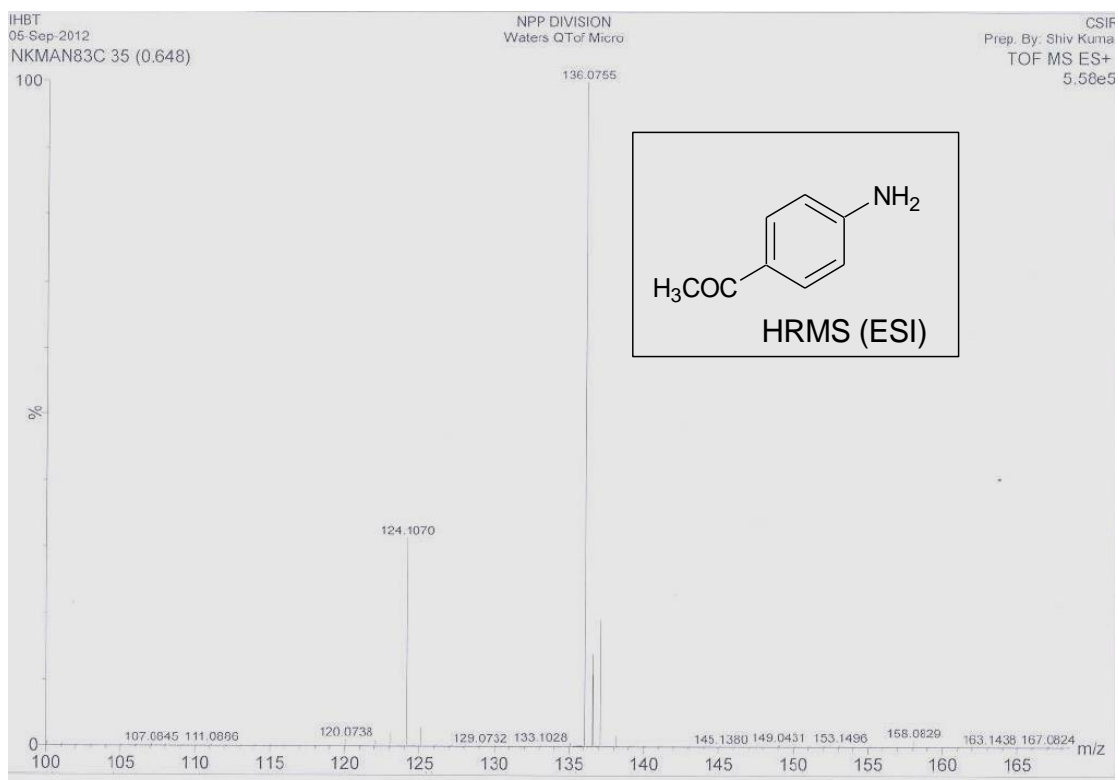
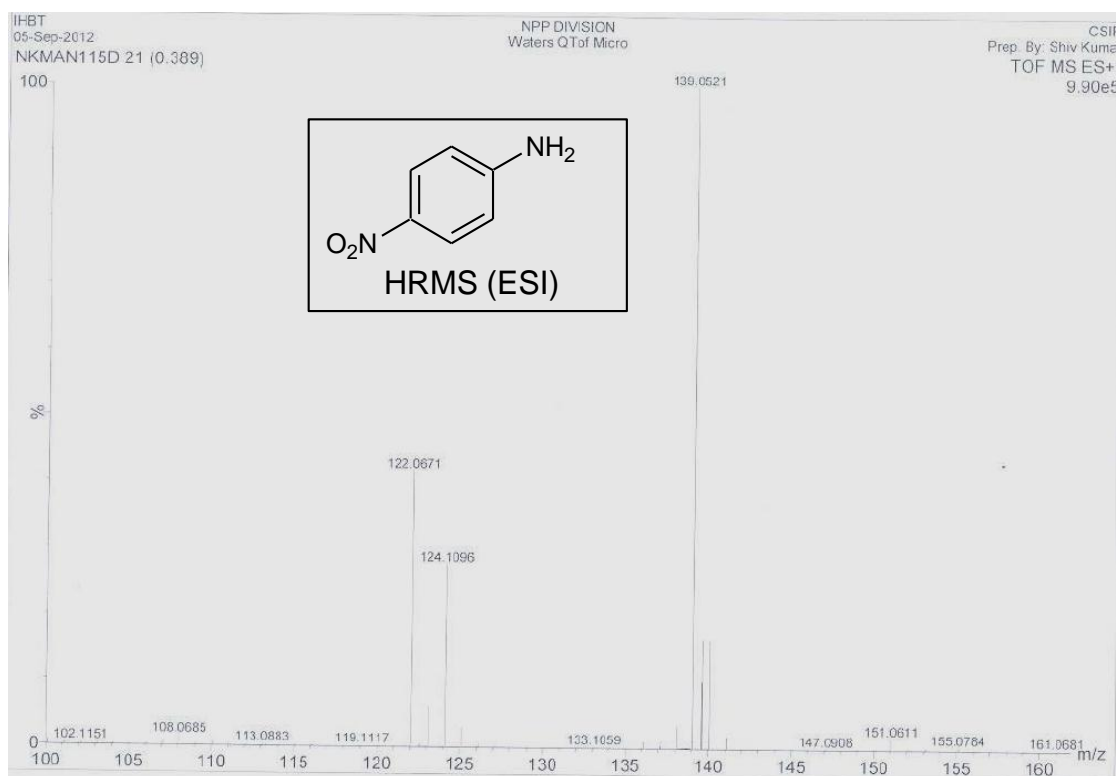
===== GRADIENT CHANNEL =====
GPNAM[1]     SMSG10.100
GPNAM[2]     SMSG10.100
GPNAM[3]     SMSG10.100
GPR1         30.00 u
GPR2         30.00 u
GPR3         40.10 u
PL6          1000.00 usec

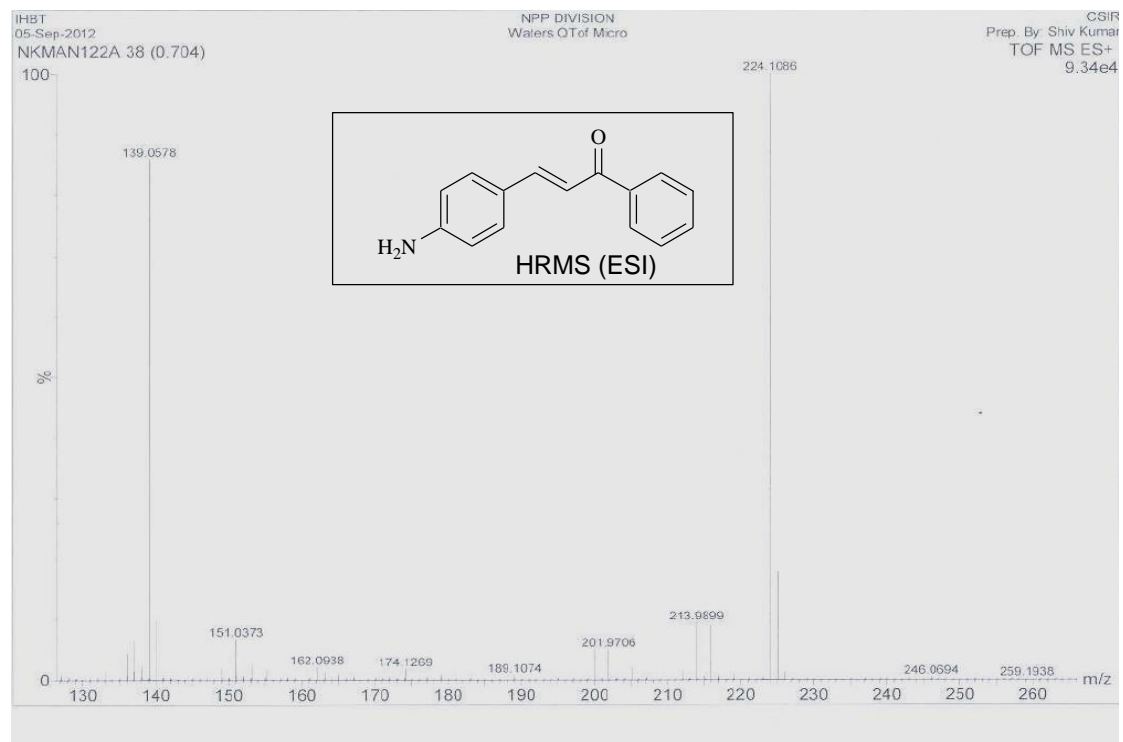
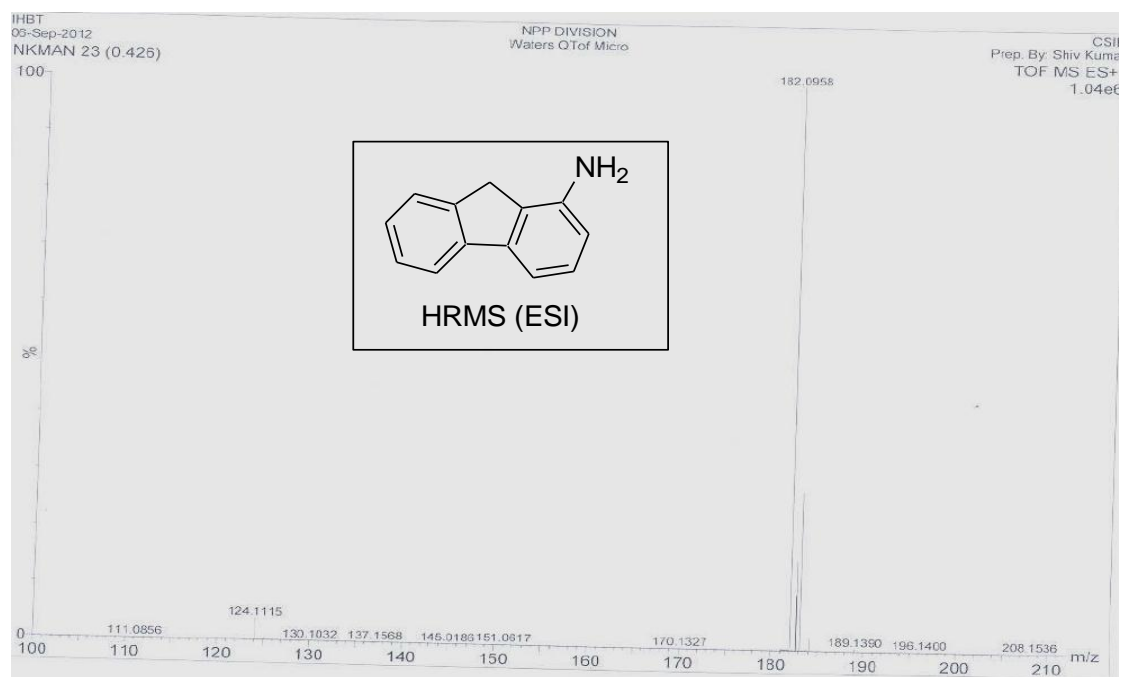
F1 - Acquisition parameters
TD           128
SFO1         150.9666 MHz
FIDRES       281.653665 Hz
SW           238.849 ppm
PRMODE       QF

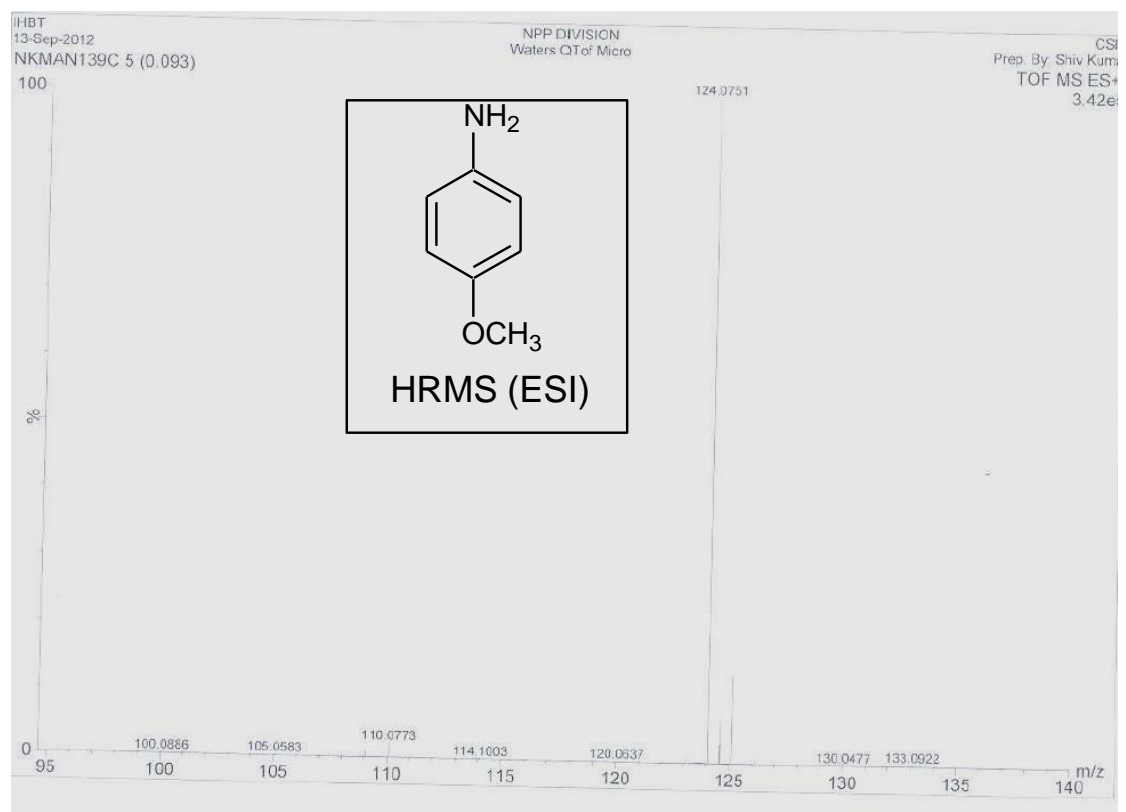
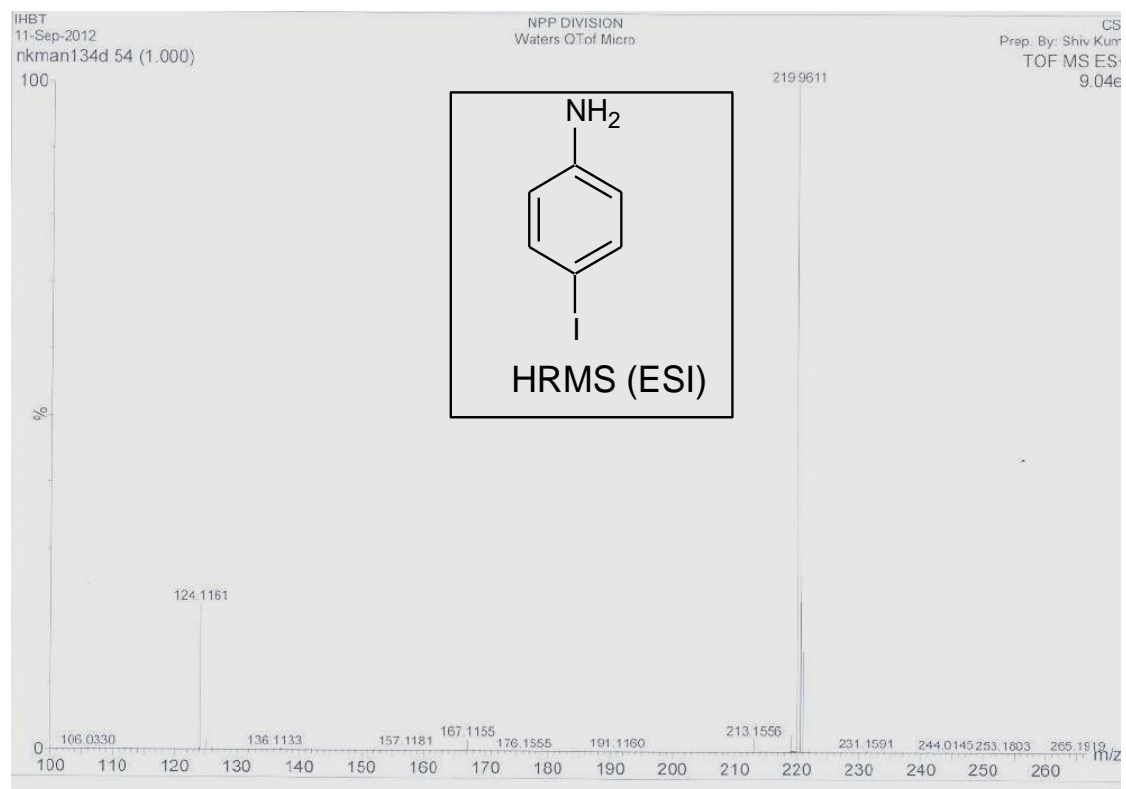
F2 - Processing parameters
SI           1024
SF           600.3060000 MHz
WVW         0 Hz
SFB         2
GB           0 Hz
PC           1.40

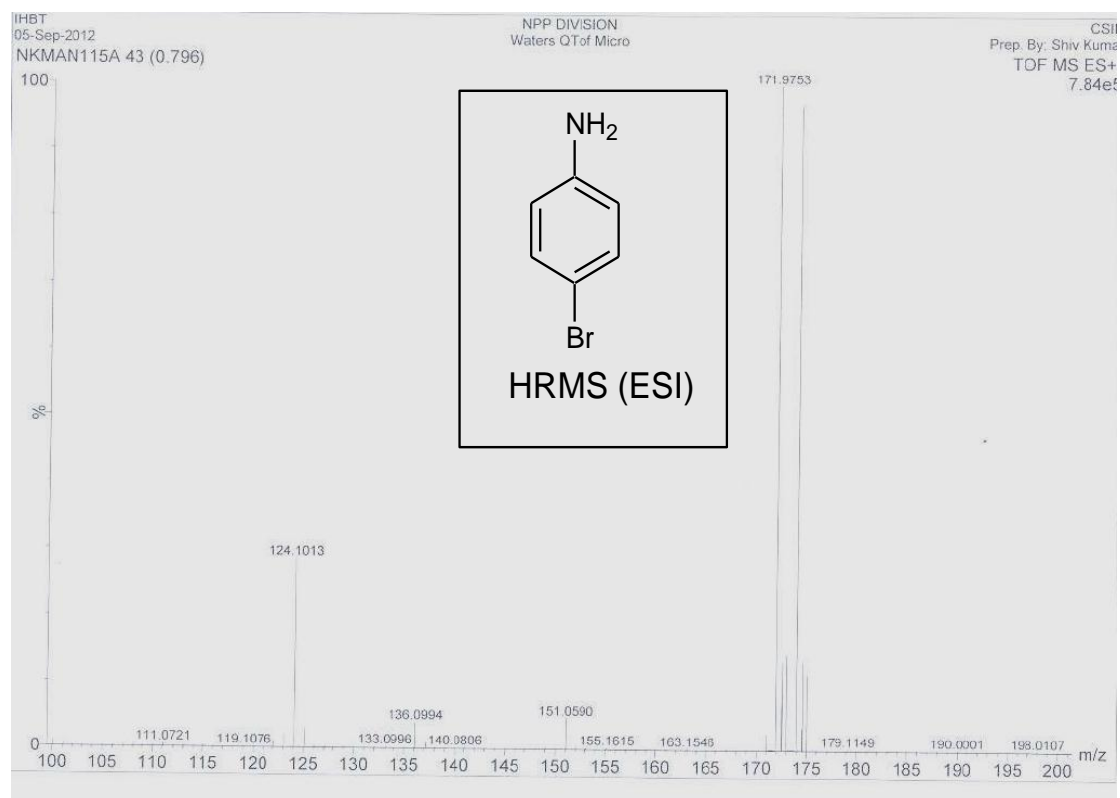
F1 - Processing parameters
SI           1024
MC2         0F
SF           150.9455550 MHz
WVW         0 Hz
SFB         2
GB           0 Hz
```

HRMS (ESI) spectra of isolated compounds









4. References

1. U. Sharma, P. K. Verma, N. Kumar, V. Kumar, M. Bala and B. Singh, *Chem. Eur. J.*, 2011, **17**, 5903-4907.