# Supporting information

## First application of Core-Shell Ag@Ni magnetic nanocatalyst for transfer hydrogenation reactions of aromatic nitro and carbonyl compounds

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General methods and experimental procedures……..……..2
Preparation of Ag–Ni core–shell nanoparticles ……..…….……2
General method for the reduction of nitroarenes and carbonyl compounds…….……...3
Proton Interpretation of synthesized compound…….……..3
Optimization of reaction conditions with 4-hydroxy nitrobenzene ……...…….....4
TEM and Histogram of Ag@Ni core-shell nanocatalysts…..……..……..……..…….5
Comparison of reduction of nitrobenzene with existing protocol…….6
$^1$H NMR spectra of compounds……..…..……..…….……7
References…….17

## General methods and experimental procedures

### Experimental Techniques

All commercial reagents were used as received unless otherwise mentioned. For analytical and preparative thin-layer chromatography, Merck, 0.2 mm and 0.5 mm Kieselgel GF 254 percoated plates were used, respectively. The spots were visualized using UV light.

X-ray diffraction (XRD) patterns of the as-synthesized nanoparticles were recorded using a PANalytical X'pert PRO x-ray diffractometer with Cu-K$\alpha$ radiation. Transmission electron microscopy (TEM) was performed on a TECNAI F-30 transmission electron microscope operating at 300 kV. Energy dispersive x-ray spectroscopy (EDS) analyses in both spot and line-scan mode were used to identify the chemical components of single nanoparticles. The TEM samples were prepared by dropping the particle suspensions in toluene onto a copper grid coated with carbon film before drying at room temperature under ambient conditions.

Proton NMR spectra were recorded on a Bruker, 300, 5 mm probe at 300 MHz. $^{1}$H shifts are reported relative to internal TMS.

### Preparation of Ag–Ni core–shell nanoparticles

Ag–Ni core–shell nanoparticles were prepared via the thermal decomposition of nickel(acetylacetonate)$_2$(Ni(acac)$_2$, 96%, Acros) and $AgNO_3$ (99.8%, SCRC) in oleylamine (80–90%, Acros) using a one-pot seed-growth method. In a typical synthesis, a mixture of 6 ml of oleylamine, 0.1 mmol of triphenylphosphine (TPP; CP grade, SCRC), 0.4 mmol of Ni(acac)$_2$ and 0.1 mmol of $AgNO_3$ was decanted into a three necked flask and kept under a flow of high-purity argon gas at room temperature for 20 min. After that the mixture was heated to 80 $^{o}$C and kept at this temperature for 15 min with strong magnetic stirring. The resulting solution was then slowly heated up to a temperature of 190 $^{o}$C (the reaction temperature may range from 180 to 230 $^{o}$C) directly and aged for 40 min. After cooling down to room temperature naturally, excess acetone was added to the black solution to give a black precipitate which was isolated via centrifugation. The precipitate was then washed fully with a mixture of hexane and acetone, and dried in a vacuum.

**General method for the reduction of nitroarenes and carbonyl compounds**

The nitroarene **1** or the carbonyl compound **3** (1 mmol), isopropyl alcohol (3 mL), KOH (1.5 mmol) and Ag@Ni (50 mg), were stirred at 80 $^{o}$C for an appropriate time. After completion of the reaction (monitored by TLC), the catalyst was separated magnetically. The resultant product extracted with ethyl acetate and repeatedly washed with water (5 to 7 times) to remove KOH. Then the organic solvent was evaporated in vacuo. The crude product was purified by column chromatography on silica gel using n-hexane and ethyl acetate as eluent.

**Proton Interpretation of synthesized compound**

**Aniline (2a):** Obtained in 95% yield**;** $^{1}$H NMR (300 MHz, $CDCl_3$) δ: 7.14 (t, *J* = 7.6 Hz, 2H), 6.74 (t, 1H, *J* = 7.2 Hz), 6.66 (d, 2H, *J* = 7.5 Hz), 3.53 (br s, 2H).

**2-Methoxy aniline (2b):** Obtained in 91% yield**;** $^{1}$H NMR (300 MHz, DMSO) δ: 6.78 (d, 1H, *J* = 7.8Hz), 6.69-6.61 (m, 2H), 6.54-6.48 (m, 1H), 4.65 (br s, 2H), 3.73 (s, 3H).

**2-Chloro aniline (2c):** Obtained in 86 % yield**;** $^{1}$H NMR (300 MHz, $CDCl_3$) δ: 7.22 (d, 1H, *J* = 8.1Hz), 7.04 (t, 1H, *J* = 7.6 Hz), 6.70-6.62 (m, 2H), 3.99 (br s, 2H).

**4-Bromo aniline (2d):** Obtained in 94% yield**;** $^{1}$H NMR (300 MHz, $CDCl_3$) δ: 7.23 (d, 2H, *J* = 8.7 Hz), 6.55 (d, 2H, *J* = 8.7 Hz), 3.65 (br s, 2H).

**3-Bromo aniline (2 e):** Obtained in 93% yield**;** $^{1}$H NMR (300 MHz, $CDCl_3$) δ: 7.01-6.96 (t, 1H, *J* = 7.6 Hz), 6.86-6.80 (t, 2H, *J* = 8.5 Hz), 6.57 (d, 1H, *J* = 7.8 Hz), 3.67 (br s, 2H).

**4-Fluro aniline (2f):** Obtained in 89% yield**;** $^{1}$H NMR (300 MHz, $CDCl_3$) δ: 6.87-6.81 (m, 2H), 6.62-6.57 (m, 2H), 3.54 (br s, 2H).

**2, 5-dichloro aniline (2g):** Obtained in 88% yield**;** $^{1}$H NMR (300 MHz, $CDCl_3$) δ: 7.13-7-10 (m, 1H), 6.71 (d, 1H, *J* = 1.5 Hz), 6.65-6.62 (m, 1H), 4.09 (br s, 2H).

**3-Methyl aniline (2h):** Obtained in 93% yield**;** $^{1}$H NMR (300 MHz, DMSO) δ: 6.87 (t, 1H, *J* = 7.5Hz), 6.37 (s, 1H), 6.32-6.29 (m, 1H), 4.90 (s, 2H), 2.13 (s, 3H).

**4-hydroxy aniline (2i):** Obtained in 90% yield**;** $^{1}$H NMR (300 MHz, DMSO) δ: 8.31 (br, s, 1H), 6.49-6.40 (q, 4H), 4.35 (br s, 2H).

**1-Amino naphthalene (2j):** Obtained in 85% yield**;** $^{1}$H NMR (400 MHz, $CDCl_3$) δ: 7.81-7.78 (m, 2H), 7.45-7.43 (m, 2H), 7.32-7.22 (m, 2H), 6.77-6.75 (dd, 1H, *J* = 6.6 and 1.8 Hz), 4.12 (s, 2H).

***Ortho*-phenylenediammine (2k):** Obtained in 93% yield**;** $^{1}$H NMR (300 MHz, $CDCl_3$) δ: 6.72 (m, 4H), 3.36 (br s, 4H).

**3-Nitro aniline (2l) :** Obtained in 94 % yield**;** $^{1}$H NMR (300 MHz, $CDCl_3$) δ: 7.59-7.56 (dd, 1H, *J* = 8.1 and 1.2 Hz), 7.49 (s, 1H), 7.30-7.26 (m, 1H), 6.96-6.93 (dd, 1H, *J* = 7.8 and 1.5 Hz), 4.00 (br s, 2H).

**4-Amino benzonitrile (2m):** Obtained in 91% yield**;** $^1$H NMR (300 MHz, $CDCl_3$) δ: 7.41 (d, 1H, *J* = 7.6 Hz), 6.66 (d, 1H, *J* = 7.5 Hz), 4.22 (br s, 1H).

**4-Ethyl 4-amino benzoate (2n):** Obtained in 93% yield**;** $^1$H NMR (300 MHz, $CDCl_3$) δ: 7.87 (d, 2H, *J* = 8.7 Hz), 6.64 (d, 2H, *J* = 8.7 Hz), 4.34-4.27 (q, 2H, *J* = 7.0 Hz), 4.08 (br s, 2H), 1.38 (t, 3H, *J* = 7.0 Hz).

**4-Amino acetophenone (2o):** Obtained in 94% yield**;** $^1$H NMR (300 MHz, $CDCl_3$) δ: 7.81 (d, 2H, *J* = 7.8 Hz), 6.65 (d, 2H, *J* = 7.8 Hz), 4.19 (s, 2H), 2.50 (s, 3H).

**1-Phenylethanol (4a):** Obtained in % yield**;** $^1$H NMR (300 MHz, DMSO) δ: 7.33-7.27 (m, 4H), 7.22-7.18 (m, 1H), 5.16 (br s, 1H), 4.74-4.72 (m, 1H), 1.33 (d, 3H, *J*=6.0Hz).

**1-(4-Chlorophenyl) ethanol (4b):** Obtained in % yield**;** $^1$H NMR (300 MHz, DMSO) δ: 7.35 (s, 4H), 5.22 (s, 1H), 4.75-4.68 (m, 1H), 1.31 (d, 3H, *J* = 6.3 Hz).

**1-(4-Bromophenyl) ethanol (4c):** Obtained in 91% yield**;** $^1$H NMR (300 MHz, DMSO) δ: 7.50 (d, 2H, *J* = 8.1 Hz), 7.31 (d, 2H, *J* = 7.8 Hz), 5.23 (br, 1H, -OH), 4.72-4.68 (m, 1H), 1.31 (d, 3H, *J* = 6.3Hz).

**Cyclohexanol (4d):** Obtained in 90 % yield**;** $^1$H NMR (400 MHz, $CDCl_3$) δ: 4.45 (d, 1H, *J* = 2.7 Hz), 3.39 (br, 1H), 1.74-1.63 (m, 4H), 1.48-1.45 (m, 1H), 1.25-1.07 (m, 5H).

**Optimization of reaction conditions with 4-hydroxy nitrobenzene**

First we performed reaction without catalyst and base, and after 12 hours no corresponding product was observed (Table 1, entry 1). Either KOH or nanocatalyst is also not enough to perform hydrogen transfer reaction as well (Table 1, entries 2 and 3). Depending on the amount of Ag@Ni core shell NPs yield increased from 35 to 90% (Table 1, entries 4 to 6). Indeed, increasing the quantity of catalyst from 10 mg to 50 mg lead to an increase in the yield of reaction. The reduction reactions were also carried out in NaOH, but the results were less satisfactory (Table 1, entry 7).

**Table 1**. Optimization of reaction conditions for the reduction of 4-hydroxy nitrobenzene.[a]

| Entry | Catalyst | Base | Time (h) | Isolated yield % |
|---|---|---|---|---|
| 1 | ---- | ------ | 12 | NR[b] |
| 2 | ---- | KOH | 12 | NR[b] |
| 3 | Ag@Ni core shell NPs | ------ | 12 | NR[b] |
| 4 | Ag@Ni core shell NPs | KOH | 2 | 35[c] |
| 5 | Ag@Ni core shell NPs | KOH | 2 | 65[d] |
| 6 | Ag@Ni core shell NPs | KOH | 2 | 90[e] |
| 7 | Ag@Ni core shell NPs | NaOH | 2 | 78 |

[a] Reaction conditions: Nitrocompound (1 mmol), Base (1.5 mmol), Temp. 80 °C, IPA (3 mL), catalyst = 50 mg
[b] NR= No reaction
[c] 10 mg catalyst used
[d] 30 mg catalyst used
[e] 50 mg catalyst used

## TEM and Histogram of Ag@Ni core-shell nanocatalysts

Transmission emission micrograph and histogram are depicted in Figure 1. These NPs have a very narrow size distribution with a standard deviation of 1.14 nm.

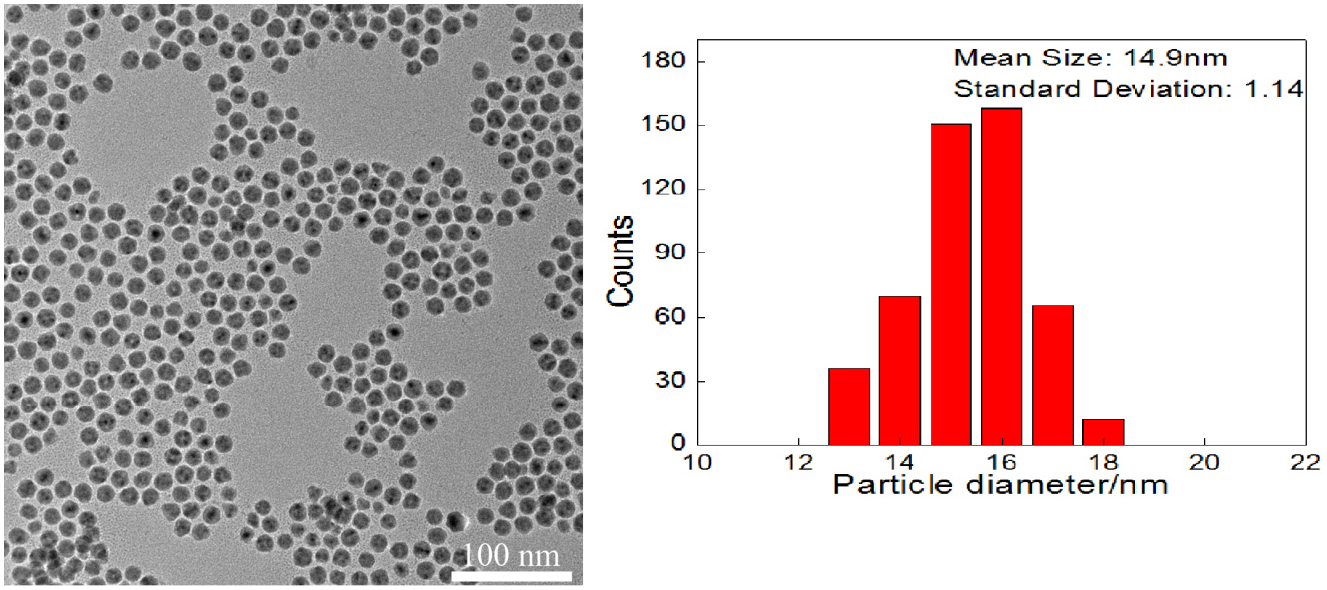



Figure 1: TEM at 100 nm (Right) and particle size distribution of core-shell nano catalysts (left).

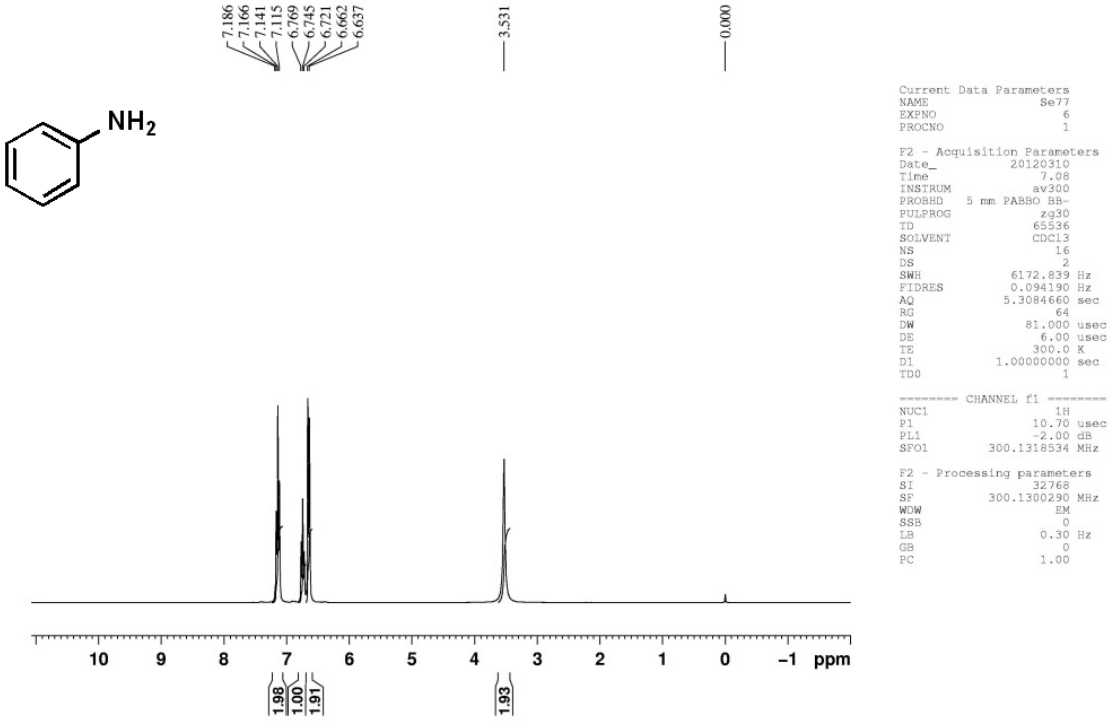
**Table 2.** Comparison of reduction of nitrobenzene with existing protocol

| Entries | Reaction conditions | Time (h) | Yield (%) |
|---|---|---|---|
| 1 | γ-$Fe_2O_3$, KOH, IPA | 6 | 80[1] |
| 2 | Mesoporous COHMA , KOH, IPA | 2 | 91[2] |
| 3 | NanoMgO-$ZrO_2$ | 2 | 94[3] |
| 4 | Ni-MCM41, KOH, IPA | 4 | 93[4] |
| 5 | Pd-DNA nanohybrids, $H_2$ balloon, | 4 | 95[5] |
| 6 | $Fe_3O_4$-Ni, glycerol, KOH | 3 | 94[6] |
| 7 | Core-shell Ag@Ni, KOH, IPA (present work) | **2** | **96** |

a) IPA- Isopropyl alcohol,

From above table, it is clear that present protocol is superior to existing protocol, in terms of yield of aniline. Pd-DNA nanohybrids catalyst found to be comparable to present protocol, but the main drawback of this protocol is that use of expensive Pd metal.

# Proton NMR Spectra of compounds

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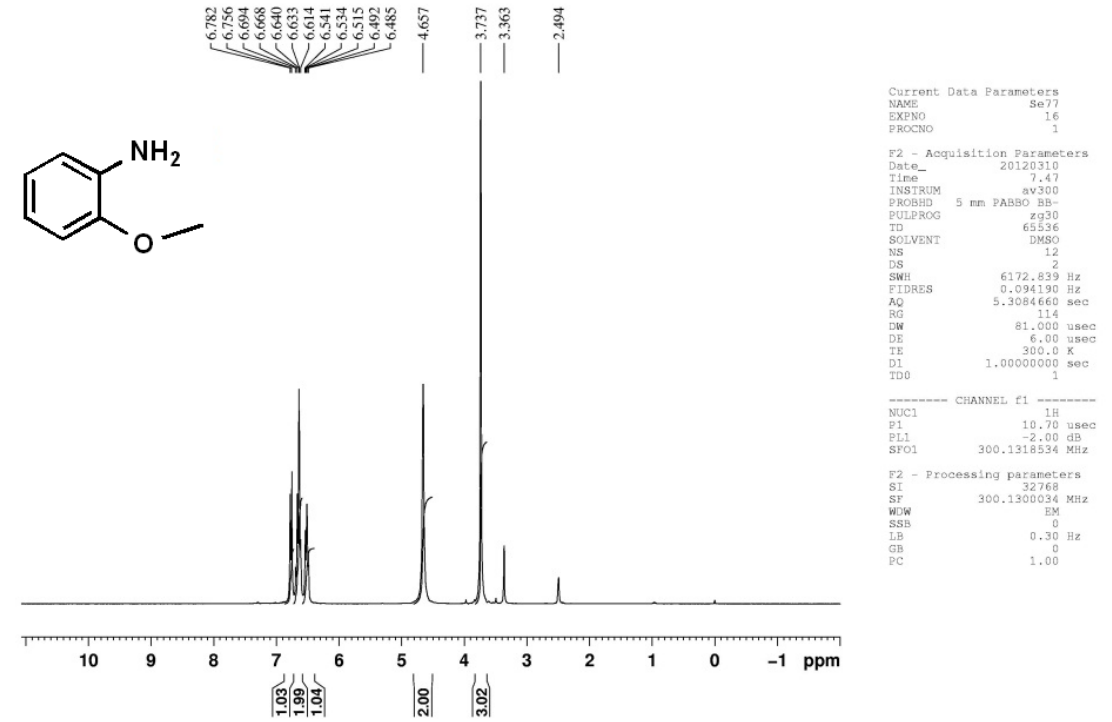
**Proton NMR spectra of aniline (2a)**

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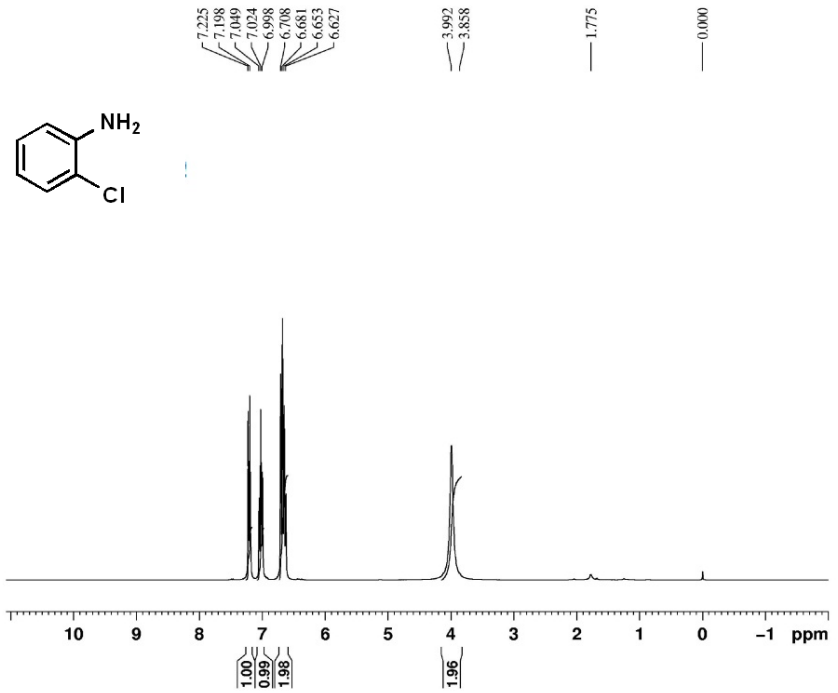


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AQ                5.3084660 sec
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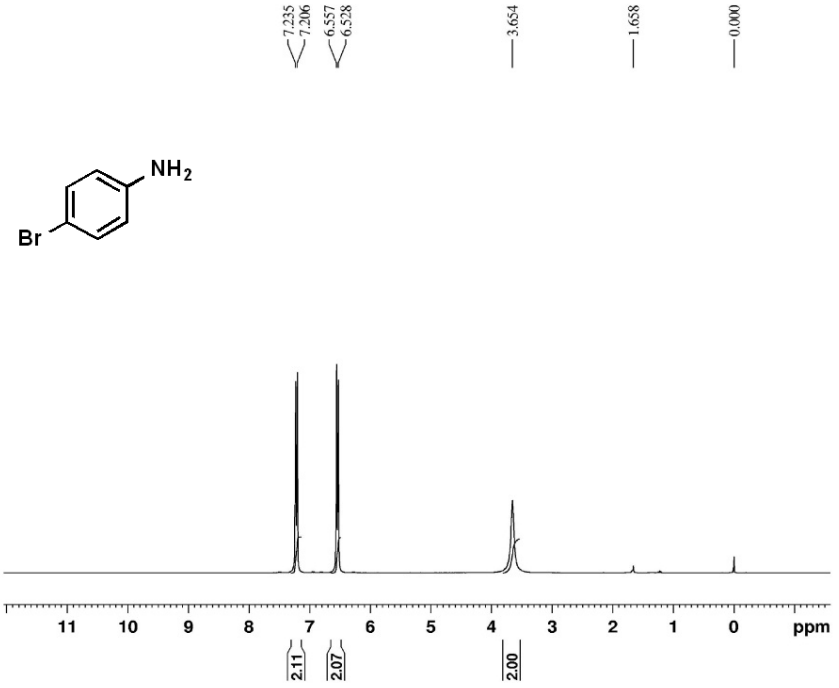
**Proton NMR of 2-chloro aniline (2c)**

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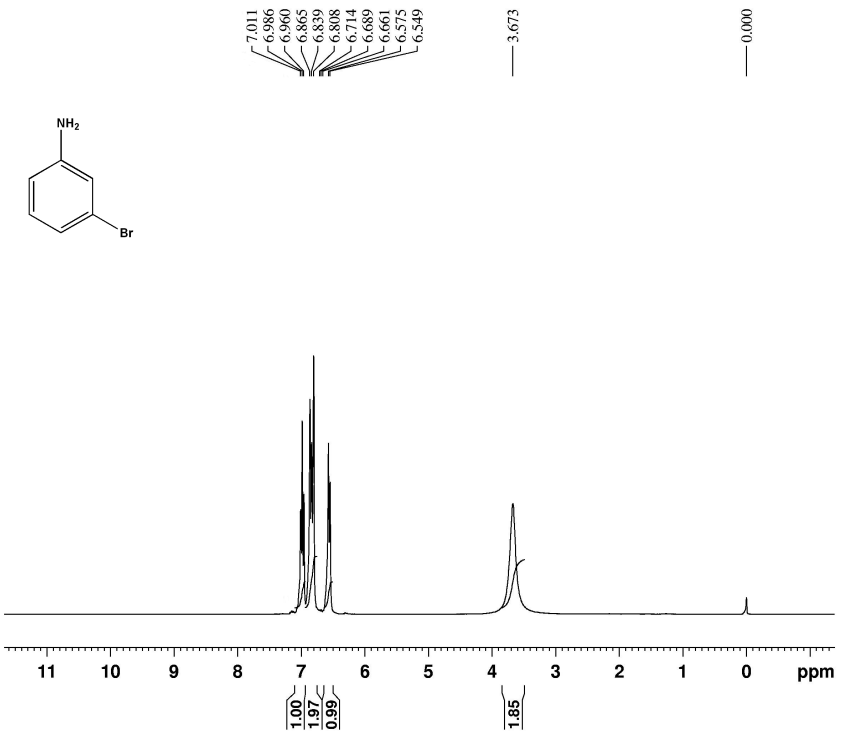
**Proton NMR of 4-bromo aniline (2d)**

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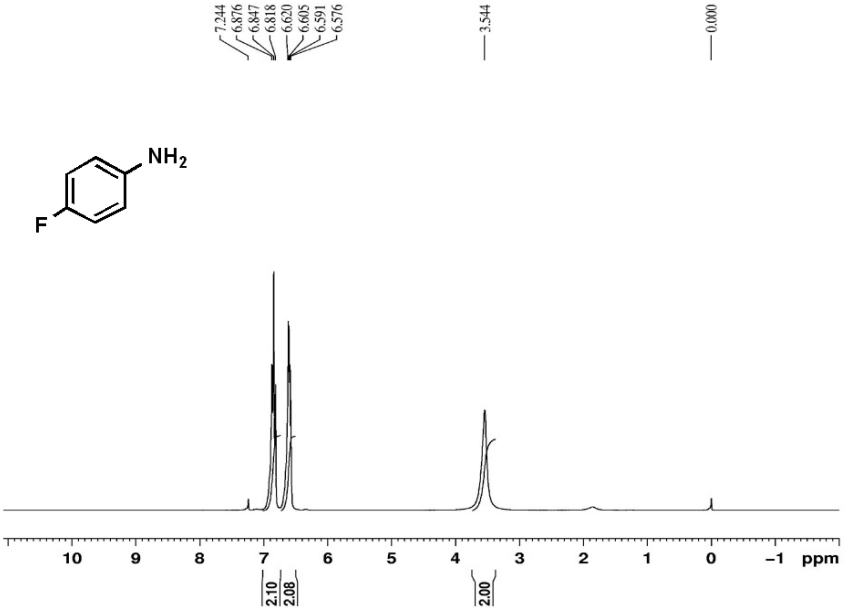


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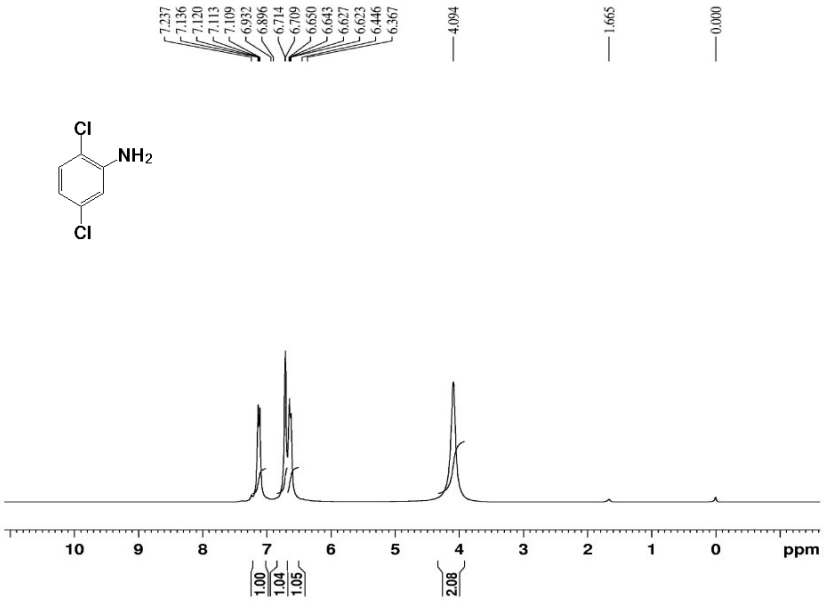
**Proton NMR of 4-fluro aniline (2f)**

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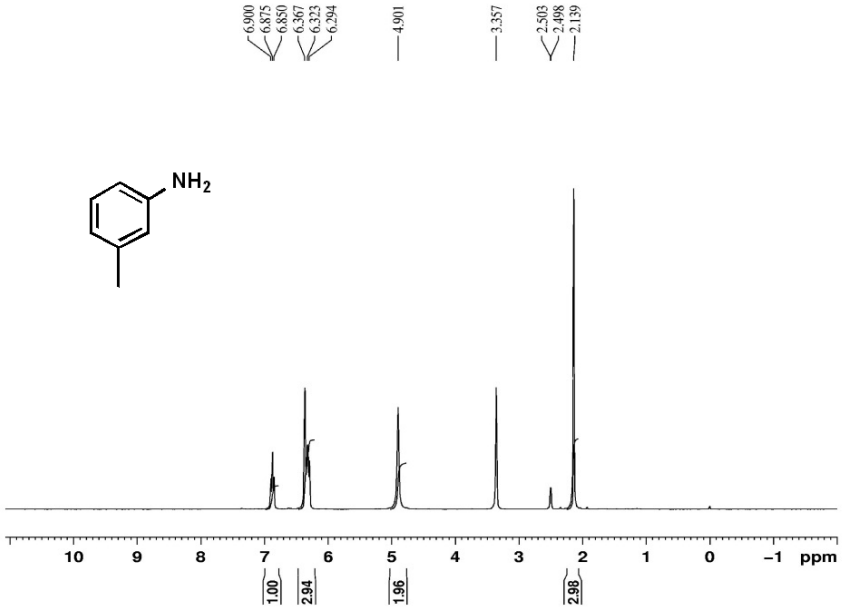
**Proton NMR of 2, 5-dichloro aniline (2g)**

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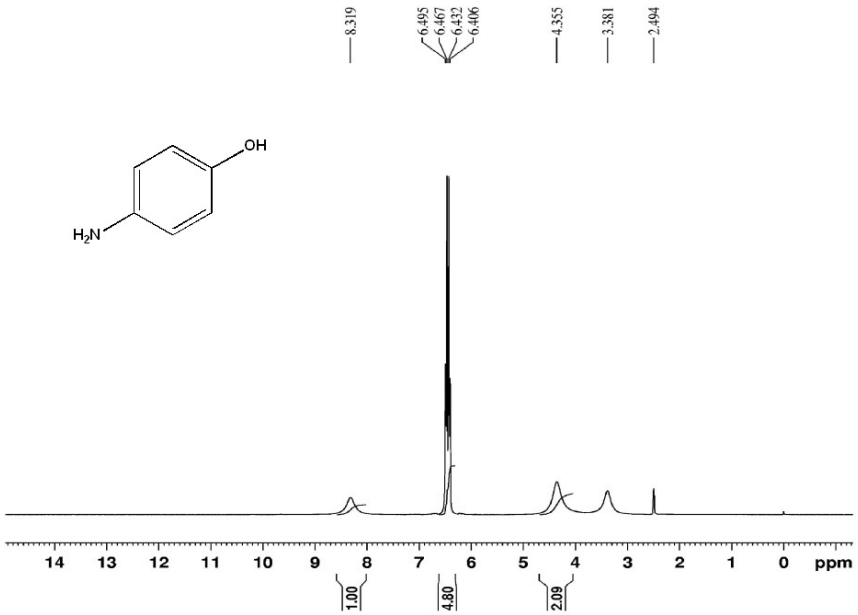
**Proton NMR of 3-methyl aniline (2h)**

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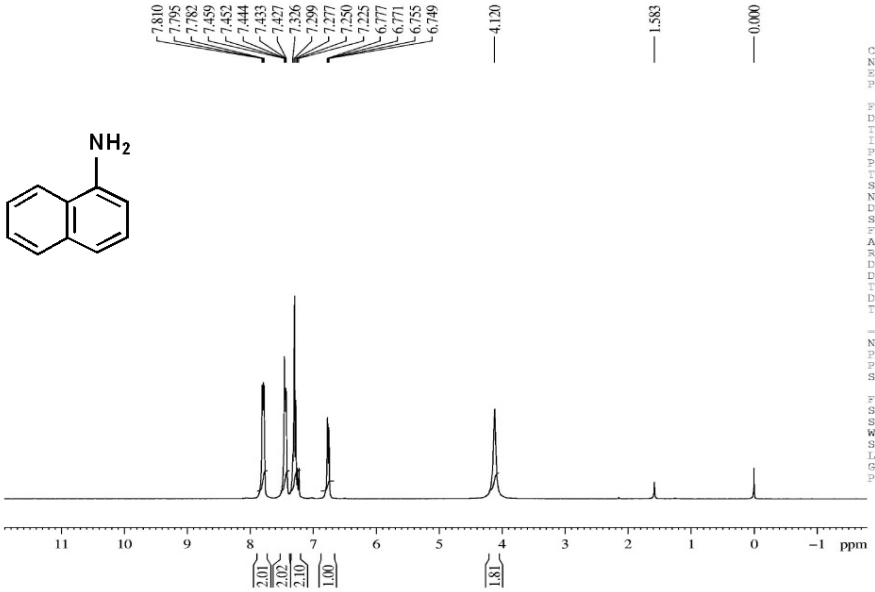
**Proton NMR of 4-hydroxy aniline (2i)**

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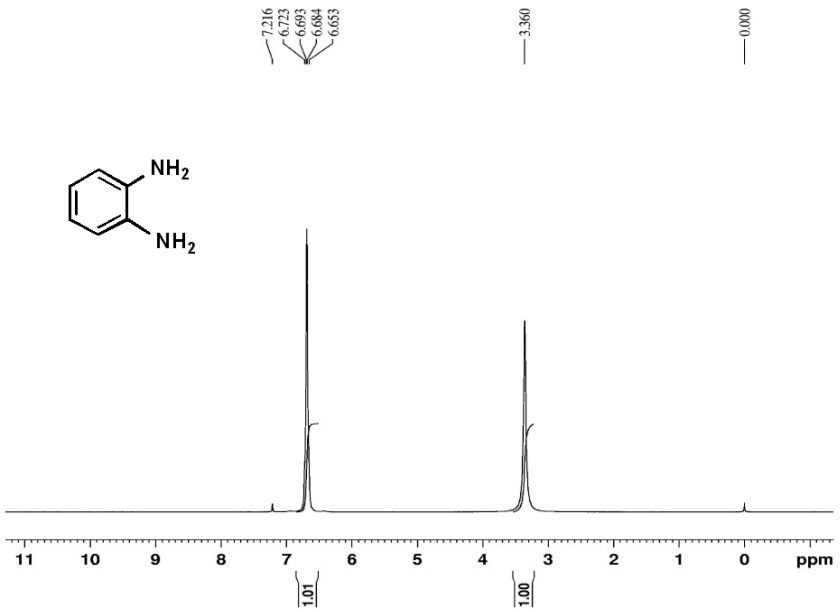
DW                81.000 usec
DE                 6.00 usec
TE                300.0 K
D1             1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.70 usec
PL1                -2.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF            300.1300169 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

**Proton NMR of naphthyl amine (2j)**

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Current Data Parameters
NAME                  March-09-2012
EXPNO                            43
PROCNO                            1

F2 - Acquisition Parameters
Date_                      20120309
Time                          15.24
INSTRUM                       av300
PROBHD     5 mm PABBO BB-
PULPROG                        zg30
TD                            65536
SOLVENT                       CDCl3
NS                                8
DS                                2
SWH                        6172.839 Hz
FIDRES                     0.094190 Hz
AQ                         5.3084660 sec
RG                             101.6
DW                          81.000 usec
DE                           6.00 usec
TE                           300.0 K
D1                      1.00000000 sec
TD0                               1

======== CHANNEL f1 ========
NUC1                             1H
P1                           10.70 usec
PL1                          -2.00 dB
SFO1                  300.1318534 MHz

F2 - Processing parameters
SI                            32768
SF                    300.1300197 MHz
WDW                              EM
SSB                               0
LB                            0.30 Hz
GB                                0
PC                             1.00
```
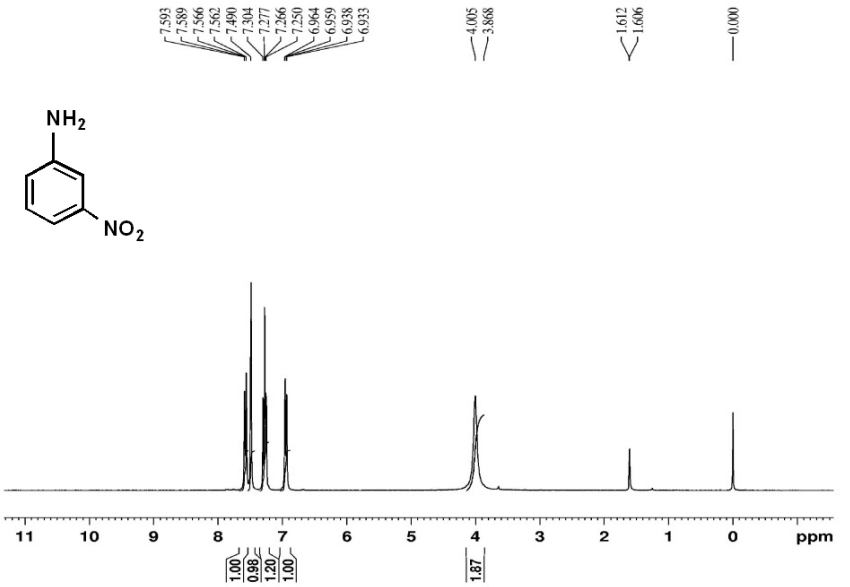
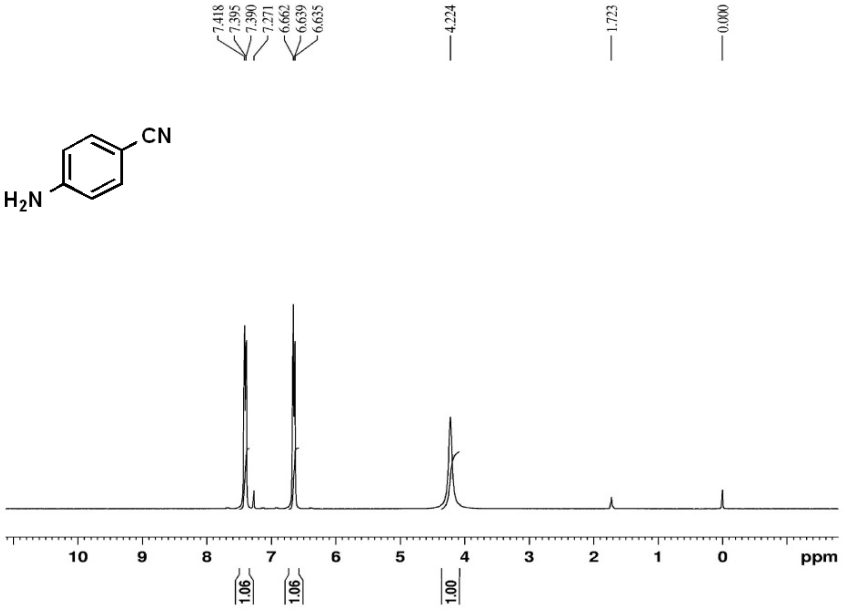

**Proton NMR of *ortho*-phenylene diamine (2k)**



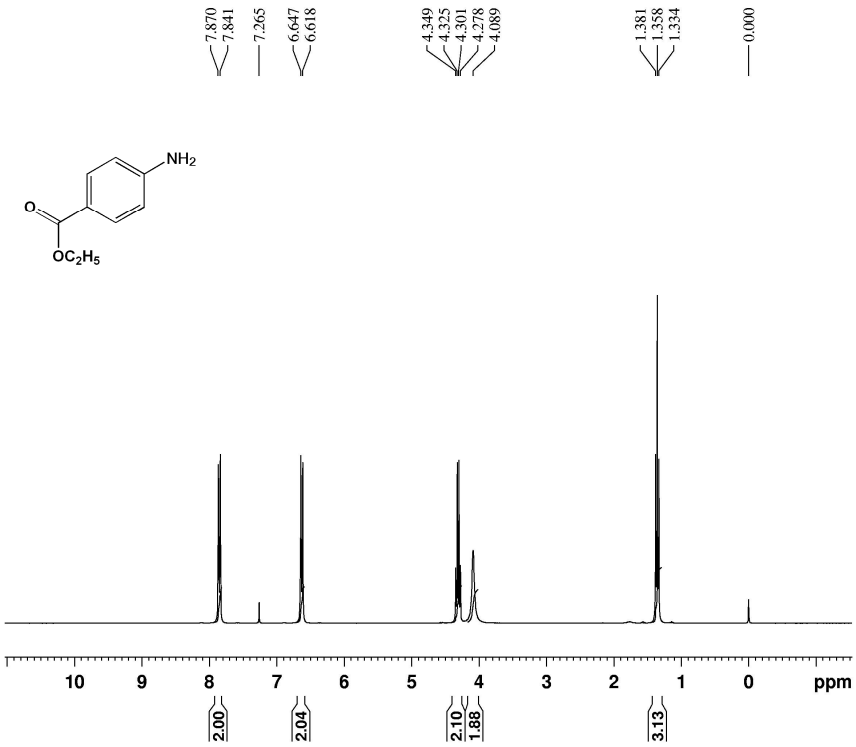

```
Current Data Parameters
NAME                  March-09-2012
EXPNO                            47
PROCNO                            1

F2 - Acquisition Parameters
Date_                      20120309
Time                          15.59
INSTRUM                       av300
PROBHD     5 mm PABBO BB-
PULPROG                        zg30
TD                            65536
SOLVENT                       CDCl3
NS                               12
DS                                2
SWH                        6172.839 Hz
FIDRES                     0.094190 Hz
AQ                         5.3084660 sec
RG                             287.4
DW                          81.000 usec
DE                           6.00 usec
TE                           300.0 K
D1                      1.00000000 sec
TD0                               1

======== CHANNEL f1 ========
NUC1                             1H
P1                           10.70 usec
PL1                          -2.00 dB
SFO1                  300.1318534 MHz

F2 - Processing parameters
SI                            32768
SF                    300.1300053 MHz
WDW                              EM
SSB                               0
LB                            0.30 Hz
GB                                0
PC                             1.00
```

**Proton NMR of 3-nitro aniline (2l)**



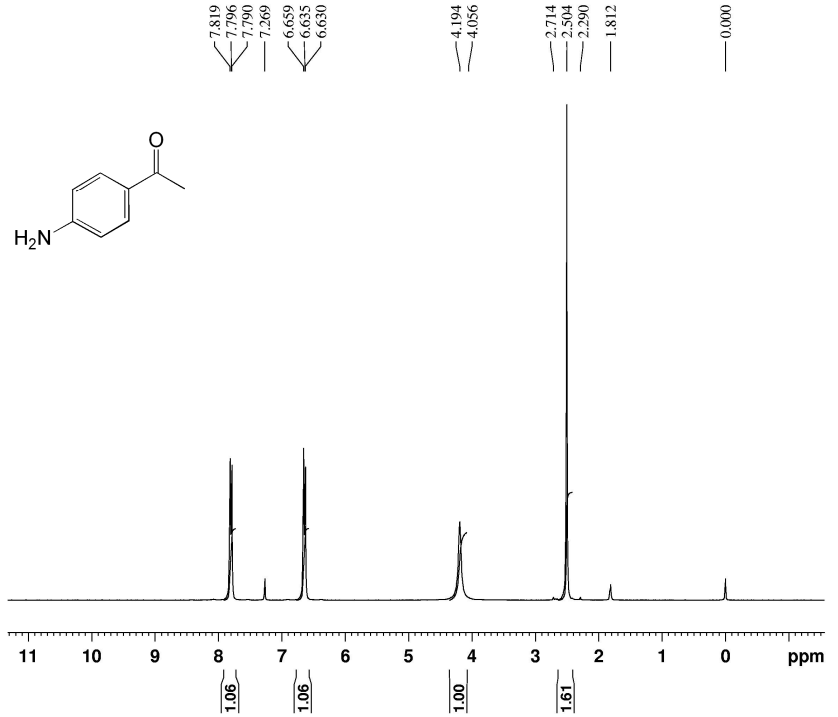

```
Current Data Parameters
NAME        March-09-2012
EXPNO                  44
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120309
Time                15.27
INSTRUM             av300
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     11
DS                      2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ              5.3084660 sec
RG                  203.2
DW                 81.000 usec
DE                  6.00 usec
TE                 300.0 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  10.70 usec
PL1                 -2.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300025 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

**Proton NMR 4-amino benzonitrile (2m)**



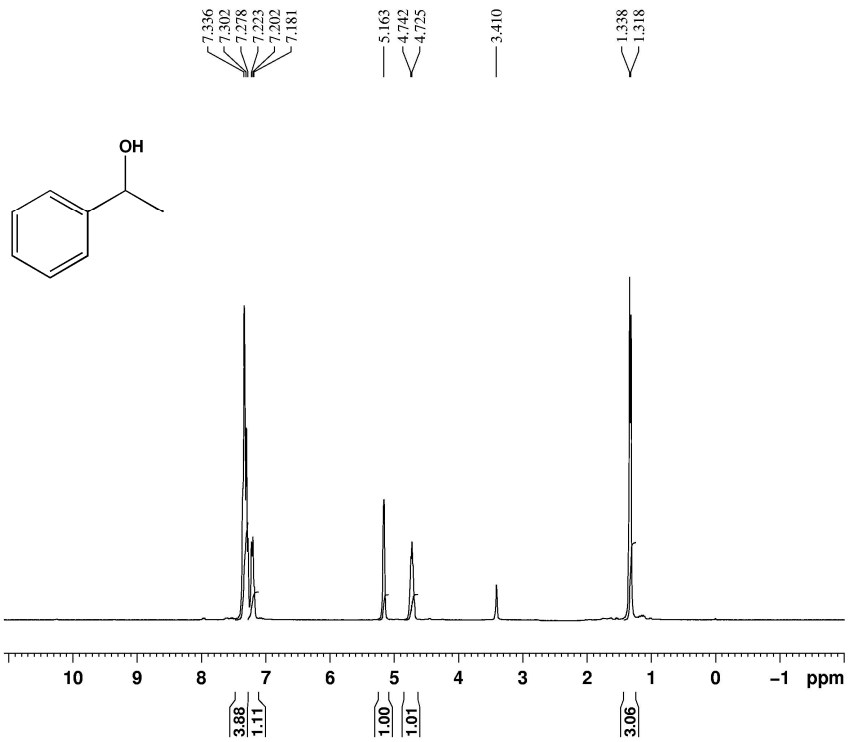

```
Current Data Parameters
NAME        March-09-2012
EXPNO                  25
PROCNO                  1

F2 - Acquisition Parameters
Date_            20120309
Time                12.51
INSTRUM             av300
PROBHD   5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT             CDCl3
NS                     16
DS                      2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ              5.3084660 sec
RG                    128
DW                 81.000 usec
DE                  6.00 usec
TE                 300.0 K
D1              1.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  10.70 usec
PL1                 -2.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                  32768
SF            300.1300054 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   1.00
```

**Proton NMR of 4-ethyl ester aniline (2n)**



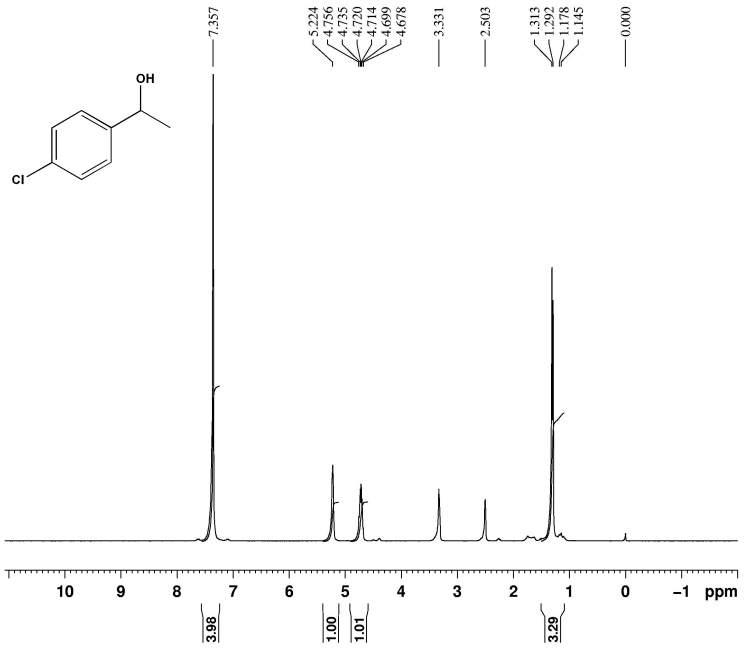

```
Current Data Parameters
NAME       March-09-2012
EXPNO                 53
PROCNO                 1

F2 - Acquisition Parameters
Date_           20120309
Time               16.30
INSTRUM            av300
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT            CDCl3
NS                    16
DS                     2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ              5.3084660 sec
RG                   181
DW                81.000 usec
DE                 6.00 usec
TE                300.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.70 usec
PL1                -2.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300038 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

**Proton NMR of 4-amino acetophenone (2o)**



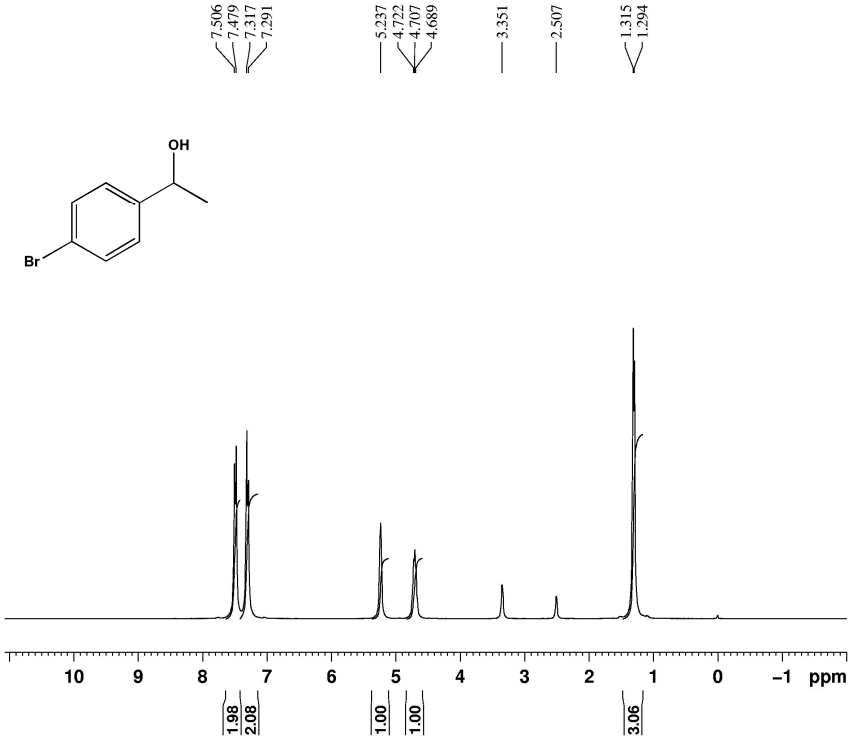

```
Current Data Parameters
NAME                 Se77
EXPNO                  12
PROCNO                  1

F2 - Acquisition Parameters
Date_           20120310
Time               7.36
INSTRUM            av300
PROBHD   5 mm PABBO BB-
PULPROG             zg30
TD                 65536
SOLVENT             DMSO
NS                    12
DS                     2
SWH             6172.839 Hz
FIDRES          0.094190 Hz
AQ              5.3084660 sec
RG                  45.3
DW                81.000 usec
DE                 6.00 usec
TE                300.0 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 10.70 usec
PL1                -2.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                 32768
SF           300.1300053 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```

**Proton NMR of 1-phenyl ethanol (4a)**



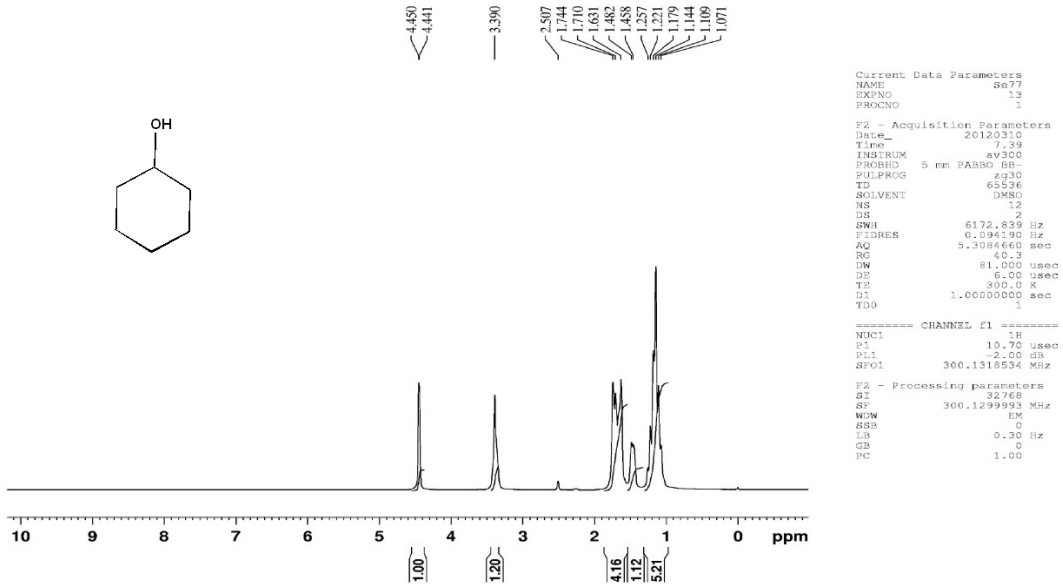

```
Current Data Parameters
NAME                  Se77
EXPNO                   14
PROCNO                   1

F2 - Acquisition Parameters
Date_              20120310
Time                  7.42
INSTRUM              av300
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT              DMSO
NS                      11
DS                       2
SWH              6172.839 Hz
FIDRES           0.094190 Hz
AQ               5.3084660 sec
RG                   203.2
DW                81.000 usec
DE                 6.00 usec
TE                 300.0 K
D1            1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                  10.70 usec
PL1                 -2.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                   32768
SF            300.1300005 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

**Proton NMR of 1-(4-Chlorophenyl)ethanol ( 4b)**




```
Current Data Parameters
NAME                  Se77
EXPNO                   11
PROCNO                   1

F2 - Acquisition Parameters
Date_              20120310
Time                  7.33
INSTRUM              av300
PROBHD    5 mm PABBO BB-
PULPROG              zg30
TD                  65536
SOLVENT              DMSO
NS                      11
DS                       2
SWH              6172.839 Hz
FIDRES           0.094190 Hz
AQ               5.3084660 sec
RG                   181
DW                81.000 usec
DE                 6.00 usec
TE                 300.0 K
D1            1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                  10.70 usec
PL1                 -2.00 dB
SFO1          300.1318534 MHz

F2 - Processing parameters
SI                   32768
SF            300.1299998 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

**Proton NMR of 1-(4-Bromophenyl)ethanol (4c)**




```
Current Data Parameters
NAME                  Se77
EXPNO                   13
PROCNO                   1

F2 - Acquisition Parameters
Date_              20120310
Time                  7.39
INSTRUM             av300
PROBHD    5 mm PABBO BB-
PULPROG               zg30
TD                  65536
SOLVENT              DMSO
NS                      12
DS                       2
SWH               6172.839 Hz
FIDRES            0.094190 Hz
AQ                5.3084660 sec
RG                     40.3
DW                81.000 usec
DE                 6.00 usec
TE                 300.0 K
D1              1.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                   1H
P1                 10.70 usec
PL1                -2.00 dB
SFO1         300.1318534 MHz

F2 - Processing parameters
SI                   32768
SF              300.1299993 MHz
WDW                     EM
SSB                      0
LB                  0.30 Hz
GB                       0
PC                    1.00
```

**Proton NMR of Cyclohexanol (4d)**

## References

1. S. U. Sonavane, M. B. Gawande, S. S. Deshpande, A. Venkataraman, R. V. Jayaram, *Catal. Commun.* **2007**, *8*, 1803-1806;

2. S.K. Mohapatra, S. U. Sonavane, R. V. Jayaram, P. Selvam, *Tetrahedron Lett.*, 2002, 43, 8527-8529.

3. M. B. Gawande, P. S. Branco, K. Parghi, J. J. Shrikhande, R. K. Pandey, C. A. A. Ghumman, N. Bundaleski, O. Teodoro, R. V. Jayaram, *Catal. Sci. Technol.* **2011**, *1*, 1653-1664

4. S.K. Mohapatra, S. U. Sonavane, R. V. Jayaram, P.Selvam, *Org. Lett*., Vol. 4, No. 24

5. Y. Wang, G. Ouyang, J. Zhang, Z. Wang, *Chem. Commun.,* 2010, **46**, 7912–7914

6. M. B. Gawande, A. K. Rathi, P. S. Branco, I. D. Nogueira, A. Velhinho, J. J. Shrikhande, U. U. Indulkar, R. V. Jayaram, C. A. A. Ghumman, N. Bundaleski, O. M. N. D. Teodoro, *Chem. Eur. J.* **2012**, *18,* 12628-12632