# Supporting Information for

# Minimisation of E-Factor in the Synthesis of *N*-Hydroxylamines: The Role of Silver (I)-based Coordination Polymers in Green Chemistry

Mehdi Sheykhan, Zohreh Rashidi Ranjbar, Ali Morsali, Akbar Heydari*

Chemistry Department, Tarbiat Modares University, P. O. Box 14155-4838 Tehran, Iran

E-mail: akbar.heydari@gmx.de

**Table of contents:**

E-Factor, [S1-S6] defined as the mass ratio of waste to desired product. Therefore, as the E-Factor increases the amount of waste increases and, lead to greater negative environmental impact. The ideal E-Factor is 0. Put quite simply, it is kilograms (of raw materials) in, minus kilograms of desired product, divided by kilograms.[7]

Following the important role of environmental acceptability in organic synthesis, our work based on invention of a method to minimize the E-Factor. Calculation of this factor and comparison with literature review show this is achieved.

**For entry e:**

$$\mathrm{E} = \frac{0.208\ \mathrm{g\ (UHP)} + 1\ \mathrm{mL}\left(0.71\,\frac{\mathrm{g}}{\mathrm{mL}}\right)\mathrm{(ether)} + 0.358\ \mathrm{g\ (entry\ \mathbf{e})} - 0.81 * 0.390\ \mathrm{g}}{0.81 * 0.390\ \mathrm{g}} = 3.04$$

**Same calculation for other entries lead to E-Factors = 2.36-4.29**
**(entries a:4.29, b:4.21, c:4.00, d:3.15, e:3.04, f:2.36)**

- **Ref 5 (***J. Org. Chem.*, 1990, **55**, 1981-1983)

$$\mathrm{E} = \frac{41\ \mathrm{g\ (amine)} + (2 + 1.2)\left(0.79\,\frac{\mathrm{g}}{\mathrm{mL}}\right)\mathrm{(acetone)} + 0.074\ \mathrm{g\ (dioxirane)} - 0.76(0.335\ \mathrm{g})}{0.76 * 0.335\ \mathrm{g}} = 170.2$$

**S1-**R. A. Sheldon, *Chem. Ind. (London)*, **1992**, 903–906
**S2-**R. A. Sheldon, in *Precision Process Technology*, M.P. C. Weijnen, A. A.H. Drinkenburg (Eds.), Kluwer, Dordrecht, 1993, pp. 125–138.
**S3-**R. A. Sheldon, in *Industrial Environmental Chemistry*, D.T. Sawyer, A. E. Martell (Eds.), Plenum, New York, 1992, pp. 99–119.
**S4-**R. A. Sheldon, *J. Chem. Technol. Biotechnol.*, 1997, **68**, 381–388.
**S5-**R. A. Sheldon, *J. Mol. Catal. A: Chemical*, 1996, **107**, 75–83.
**S6-**R. A. Sheldon, *Pure Appl. Chem.*, 2000, **72**, 1233–1246.
**S7-**R. A. Sheldon, I. Arends and U. Hanefeld, *Green Chemistry and Catalysis*, 2007, p. 2.

- **Ref 6 (***J. Org. Chem*., 1999, **64**, 7451-7458)

For step 1:

$$\frac{2.6\ \mathrm{g\ (amine)} + 40\mathrm{mL}\left(0.86\,\frac{\mathrm{g}}{\mathrm{mL}}\right)\mathrm{(toluene)} + 2.12\ \mathrm{g\ (benzaldehyde)} - 4\ \mathrm{g\ (imine)}}{4\ \mathrm{g}} = 8.78$$

For step 2:

$$\frac{4\ \mathrm{g\ (imine)} + (20 + 50)\ \mathrm{mL}\left(1.33\,\frac{\mathrm{g}}{\mathrm{mL}}\right)\mathrm{(CH2Cl2)} + 4.1\ \mathrm{g\ (mCPBA)} - 3.5\ \mathrm{g(oxaziridine)}}{3.5\ \mathrm{g}} = 27.88$$

For step 3:

$$\frac{0.47\ \mathrm{g\ (oxaziridine)} + (30)\mathrm{mL}\left(1.33\,\frac{\mathrm{g}}{\mathrm{mL}}\right)\mathrm{(CH2Cl2)} + 8\ \mathrm{mL}\ (1.49\,\frac{\mathrm{g}}{\mathrm{mL}})\mathrm{(TFA)} - 0.3\ \mathrm{g}}{0.3\ \mathrm{g}} = 173$$

**Therefore net E-Factor = 173+27.88+8.78 = 209.66**

- **Ref 7 (***J. Org. Chem*., 2000, 65, 5937-5941)

$$\mathrm{E} = \frac{0.388\ \mathrm{g\ (amine)} + 15\ \mathrm{mL}\left(0.87\,\frac{\mathrm{g}}{\mathrm{mL}}\right)\mathrm{(benzene)} + 1.39\ \mathrm{g\ (oxone)} + 150\ \mathrm{mL}\left(0.79\,\frac{\mathrm{g}}{\mathrm{mL}}\right)\mathrm{(MeOH)} - 0.331\ \mathrm{g}}{0.331\ \mathrm{g}} = 401.83$$

- **Ref 9** (*Chem. Commun.*, 2000, 5, 409-410)

$$\frac{0.0068\ \mathrm{g\ (BINAP)} + 2.5\ \mathrm{mL}\left(0.89\,\frac{\mathrm{g}}{\mathrm{mL}}\right)\mathrm{(THF)} + 0.0026\ \mathrm{g\ (NBu4BH4)} + 0.092\ \mathrm{(N.oxide)} - 0.076\ \mathrm{g}}{0.076\ \mathrm{g}}$$

$$= 29.6$$

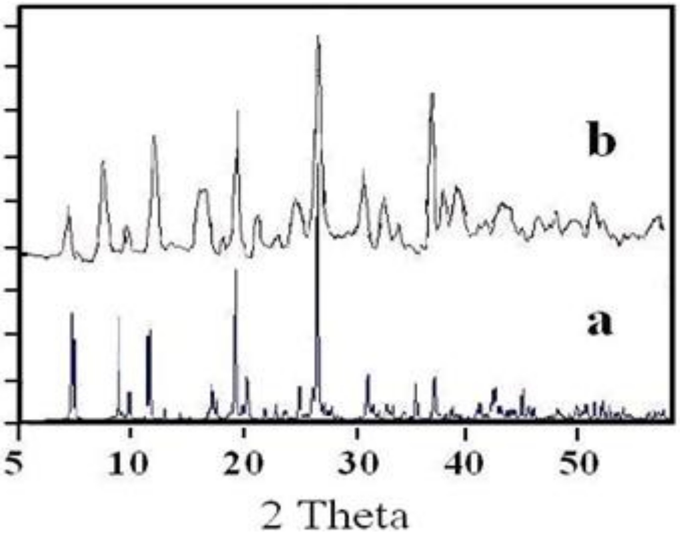
**E-Factor = 29.6** (only in hydrogenation step, 2 to 3, without regarding transformation to nitrone)

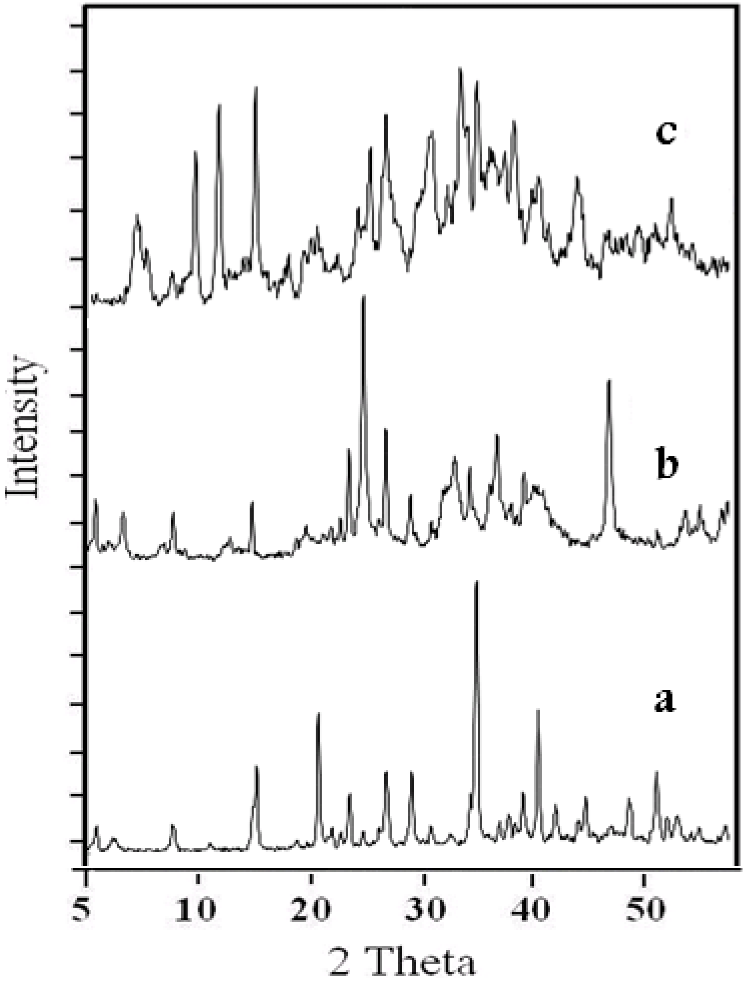
- **Ref 10** (*J. Org. Chem.* 1994, **59**, 4858-4861)

$$\frac{0.183\ \mathrm{g\ (imine)} + 20\ \mathrm{mL}\left(0.79\,\frac{\mathrm{g}}{\mathrm{mL}}\right)\mathrm{(acetone)} + 0.074\ \mathrm{g\ (dioxirane)} - 0.107\ \mathrm{g}}{0.107\ \mathrm{g}} = 149$$

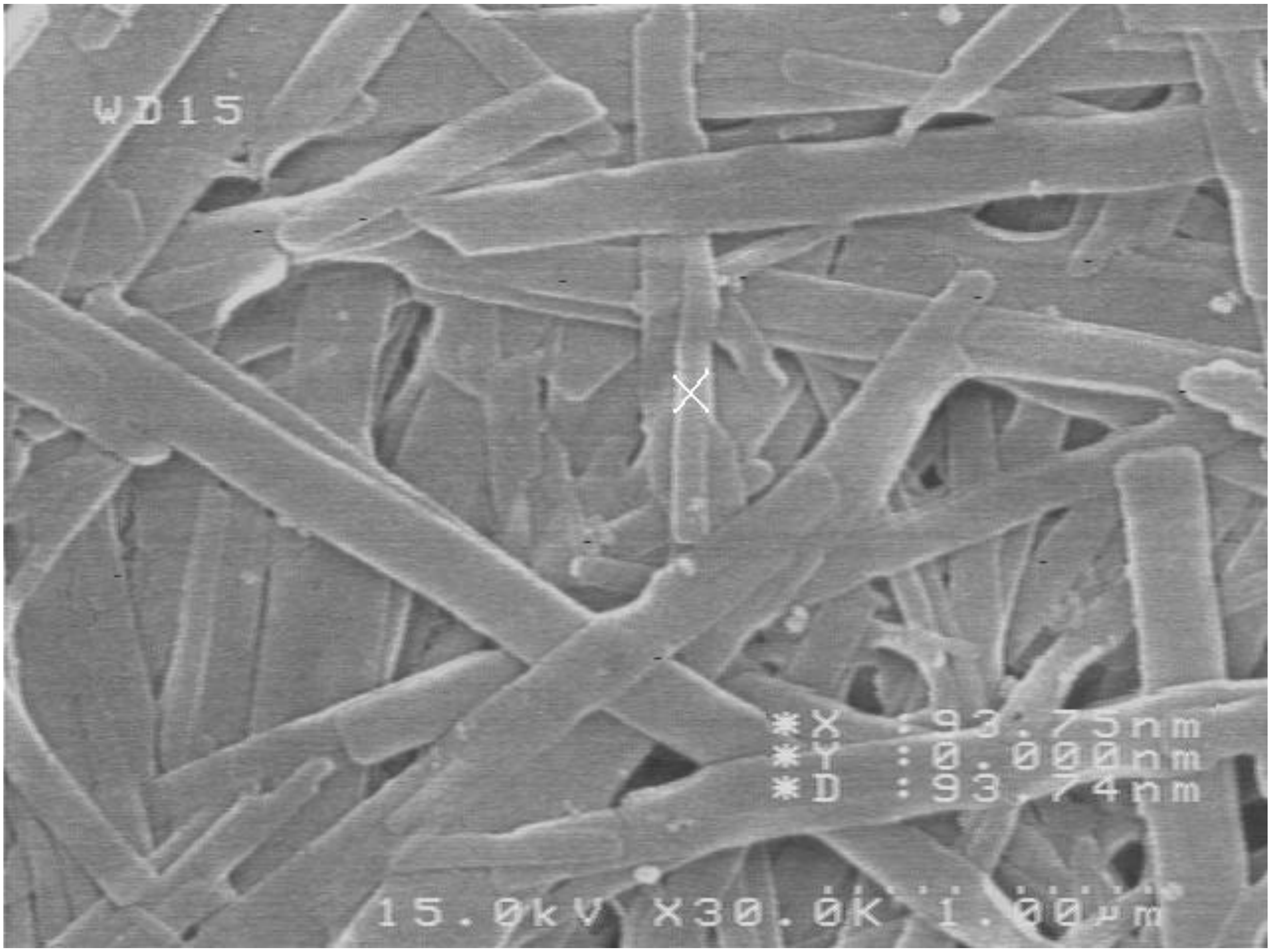
**E-Factor = 149 (**until syhthesis of nitrone 11 and without regarding its aqueous hydrolysis step by HCl to N-hydroxylamine 12)

**1. XRD patterns of [Ag(μ-bpfb)($NO_3$)]$_n$ (top) and [Ag(μ-bpfb)(X)]$_n$ (X$^-$= $NO_3^-$, SCN$^-$, $N_3^-$ and $ClO_4^-$) 4a-d nano-structures (down)**

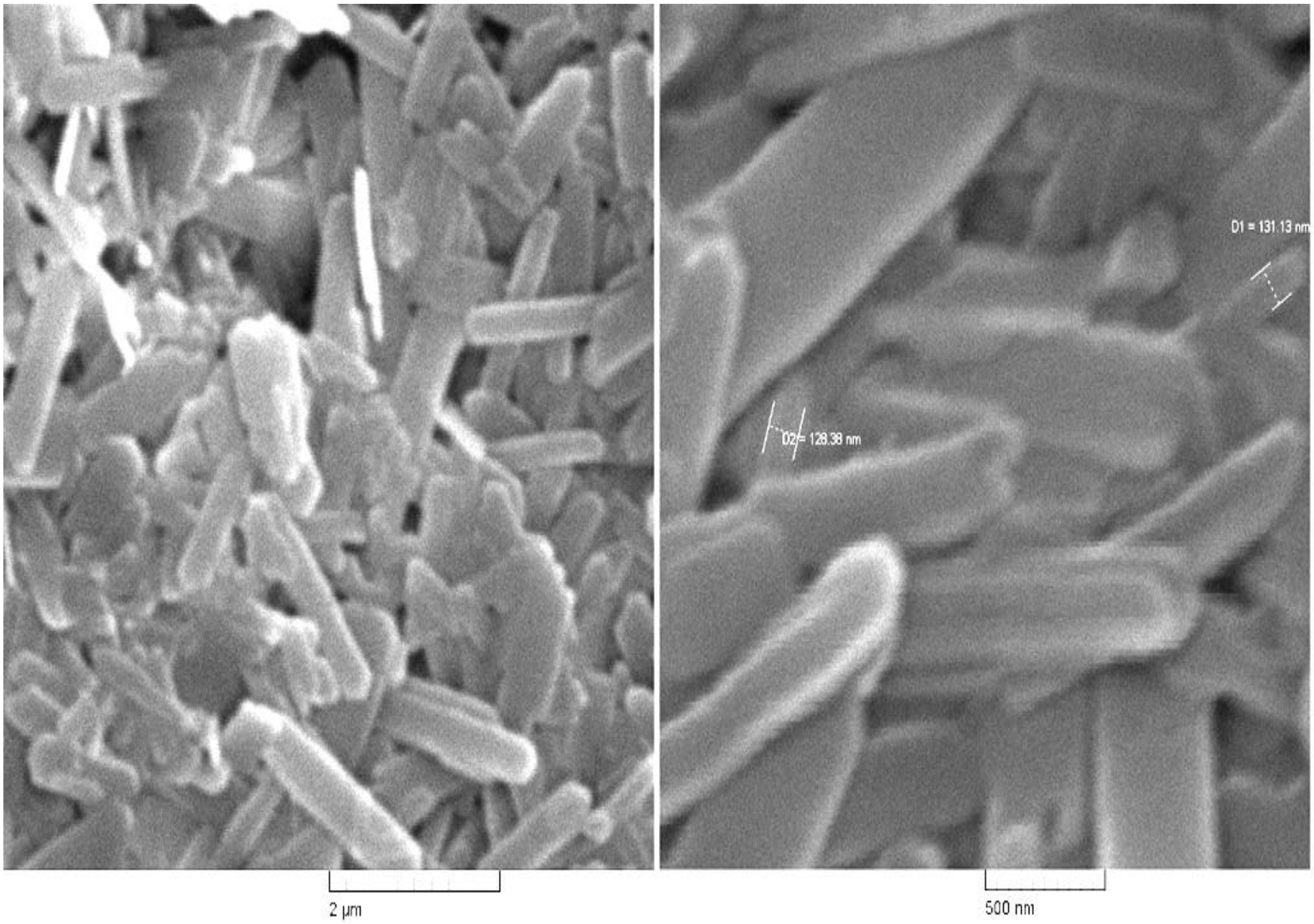




## 2. SEM images

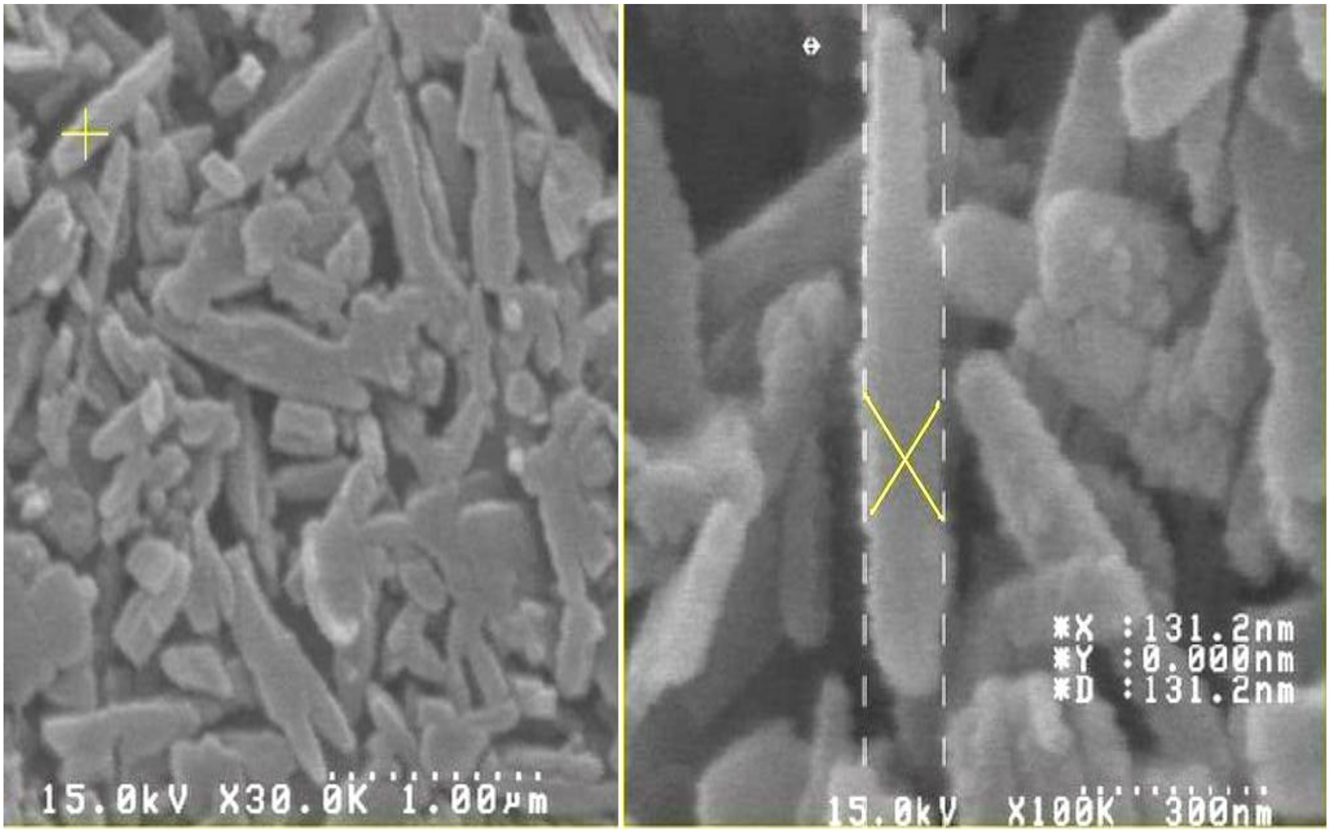


[Ag(μ-bpfb)($NO_3$)]$_n$ **(4a)**



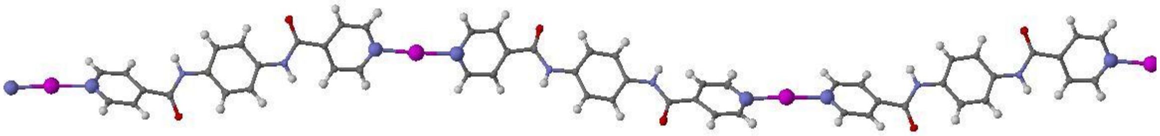
$[Ag(\mu\text{-bpfb})(SCN)]_n$ **(4b)**

[Ag(μ-bpfb)($N_3$)]$_n$ **(4c)**

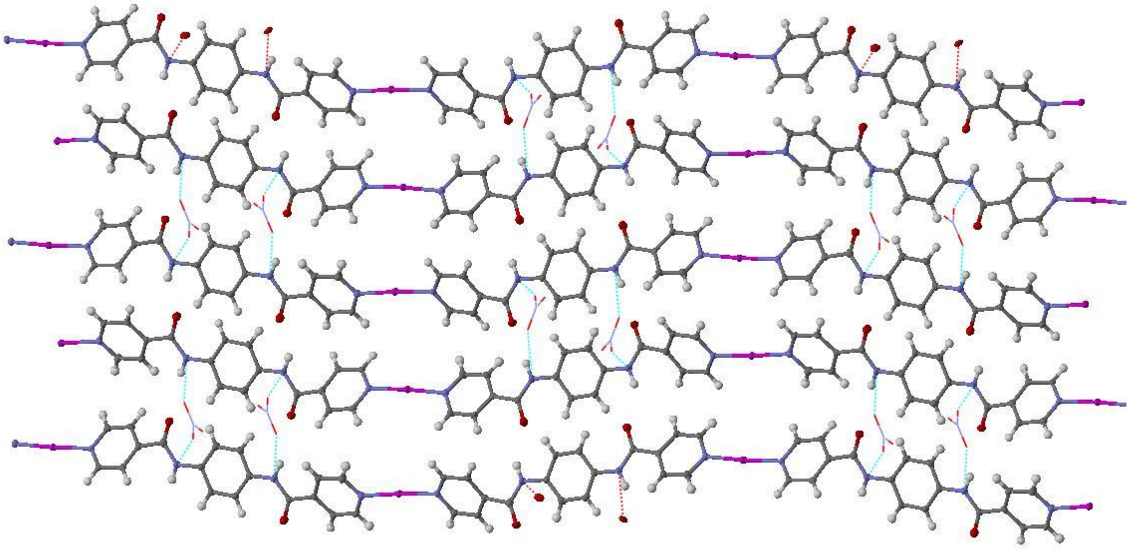


[Ag(μ-bpfb)($ClO_4$)]$_n$ **(4d)**

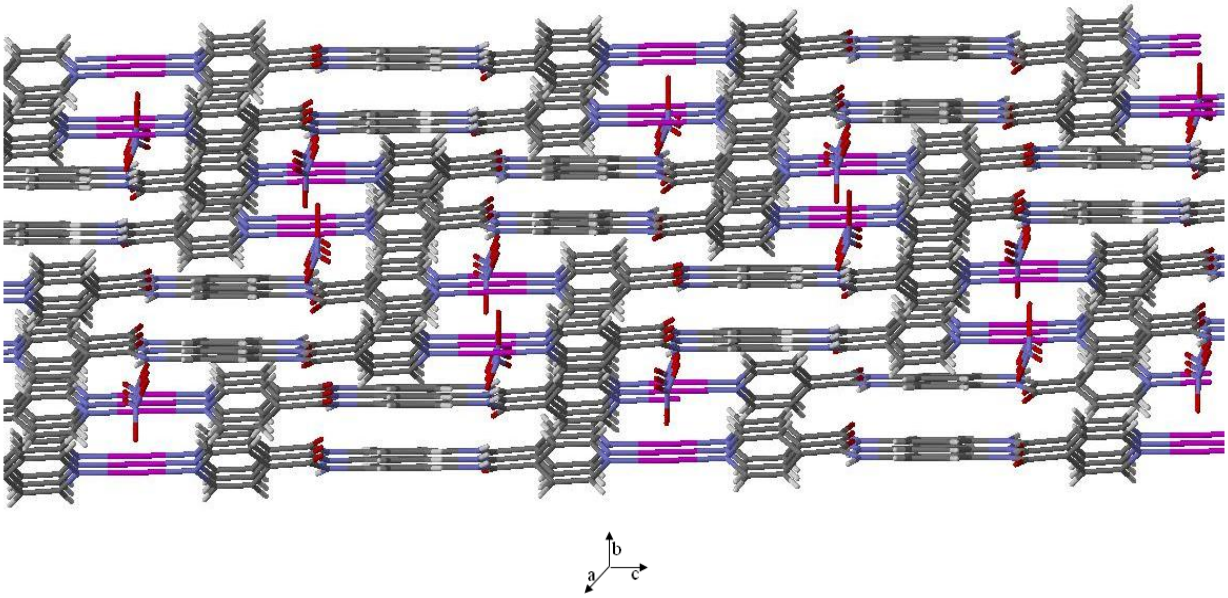
## 3. X-ray crystallographic results



A fragment of the one-dimensional chain in compound **4a** along crystallographic c axis [001] (Ag = violet, O = red, C = gray, N = blue).

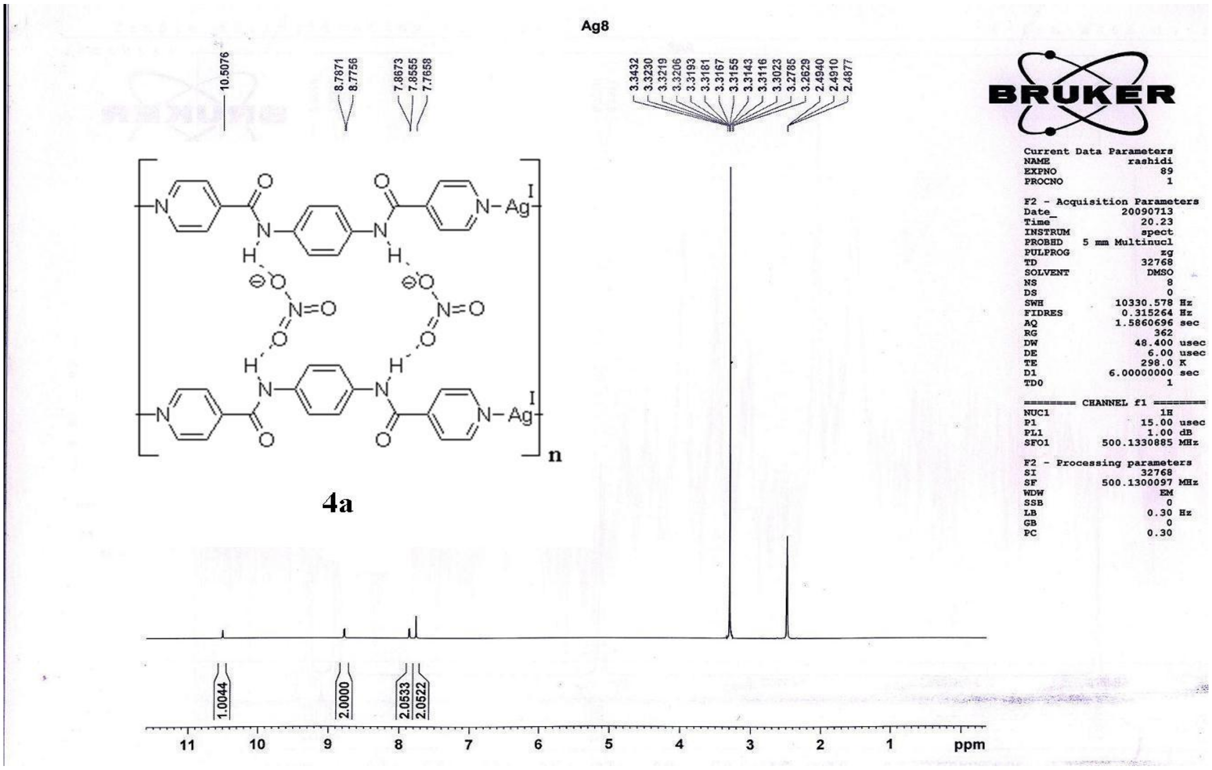


Hydrogen bonds form the 2D coordination polymer (Ag = violet, O = red, C = gray, N = blue).

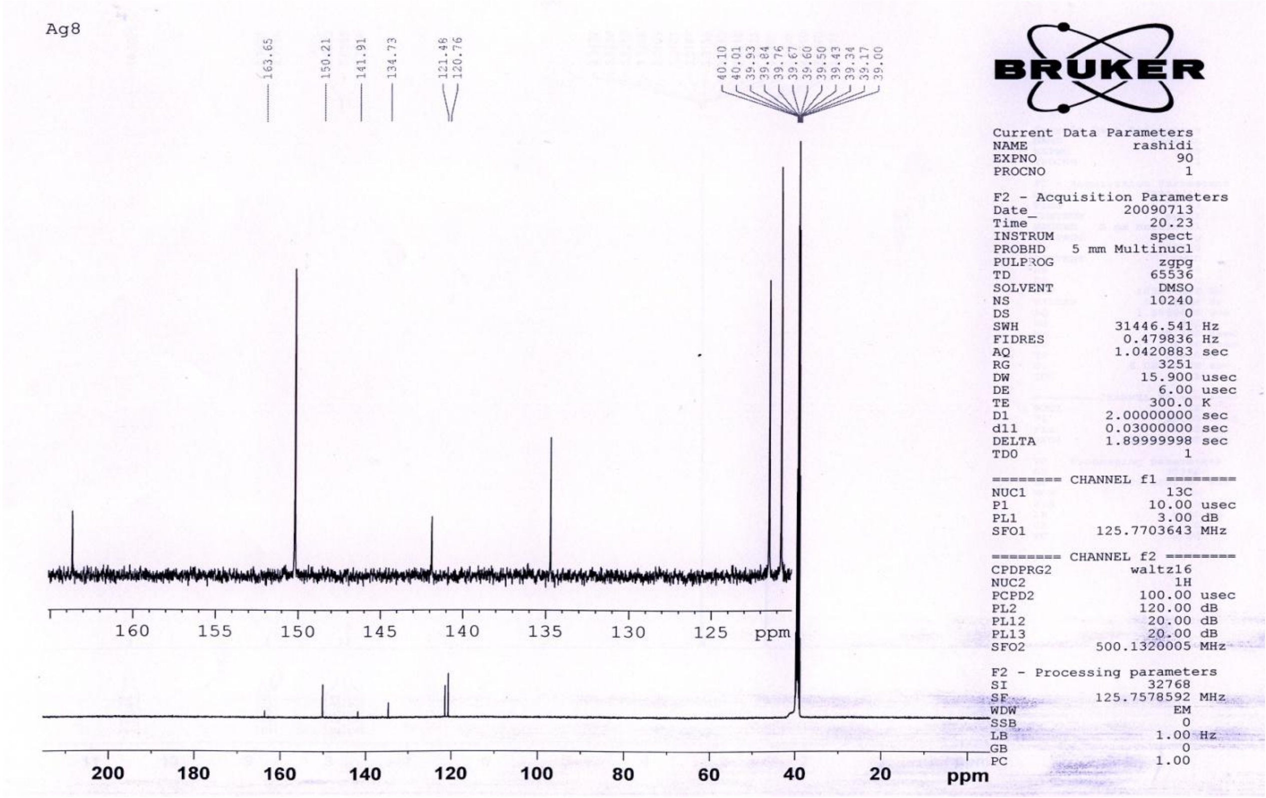


The π-π stacking interaction in supermolecule structure (Ag = violet, O = red, C = gray, N = blue).

## 4. $^{1}$H and $^{13}$C-NMR of $[Ag(\mu\text{-bpfb})(NO_3)]_n$ (4a)

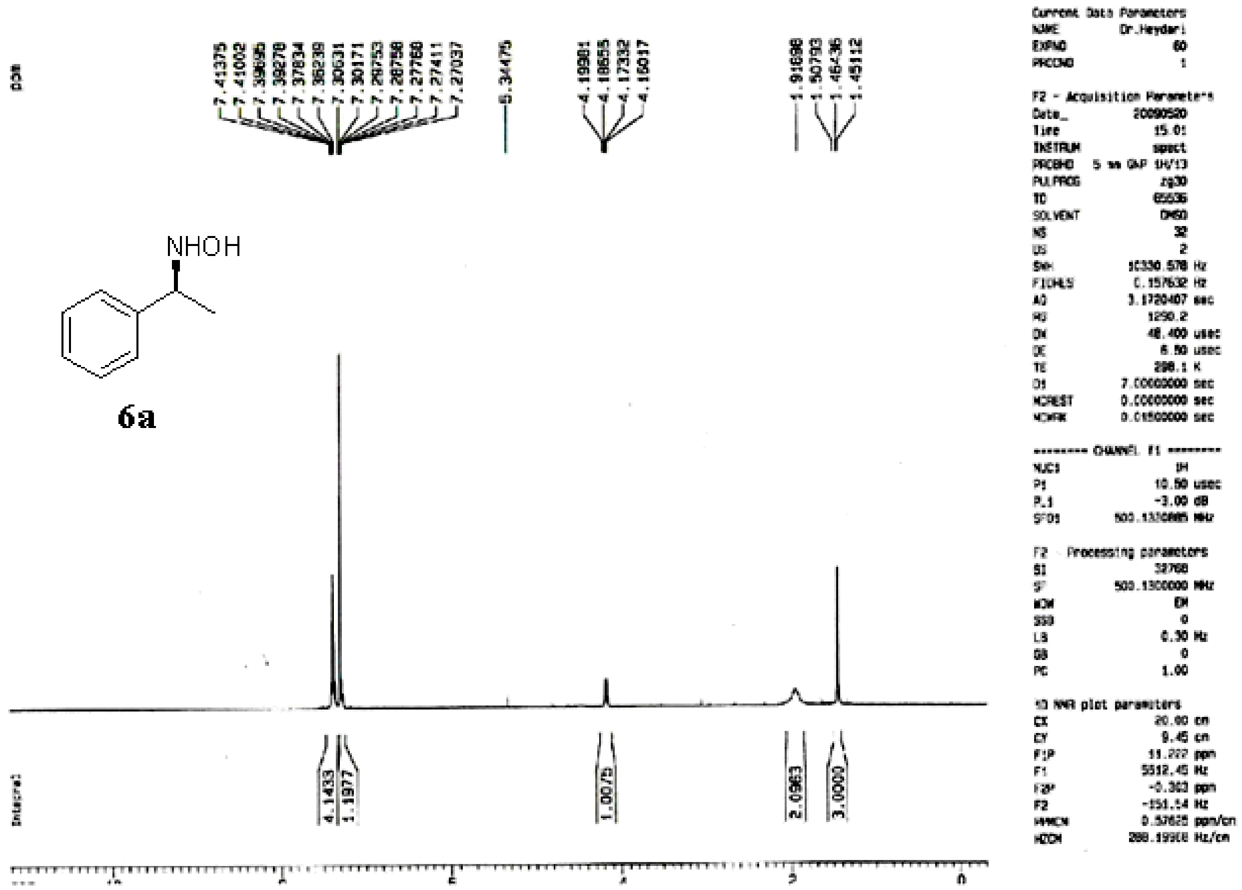


```
Current Data Parameters
NAME              rashidi
EXPNO                  89
PROCNO                  1

F2 - Acquisition Parameters
Date_            20090713
Time                20.23
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG                zg
TD                  32768
SOLVENT              DMSO
NS                      8
DS                      0
SWH            10330.578 Hz
FIDRES          0.315264 Hz
AQ             1.5860696 sec
RG                    362
DW                 48.400 usec
DE                   6.00 usec
TE                  298.0 K
D1             6.00000000 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                   1H
P1                  15.00 usec
PL1                  1.00 dB
SFO1          500.1330885 MHz

F2 - Processing parameters
SI                  32768
SF            500.1300097 MHz
WDW                    EM
SSB                     0
LB                   0.30 Hz
GB                      0
PC                   0.30
```



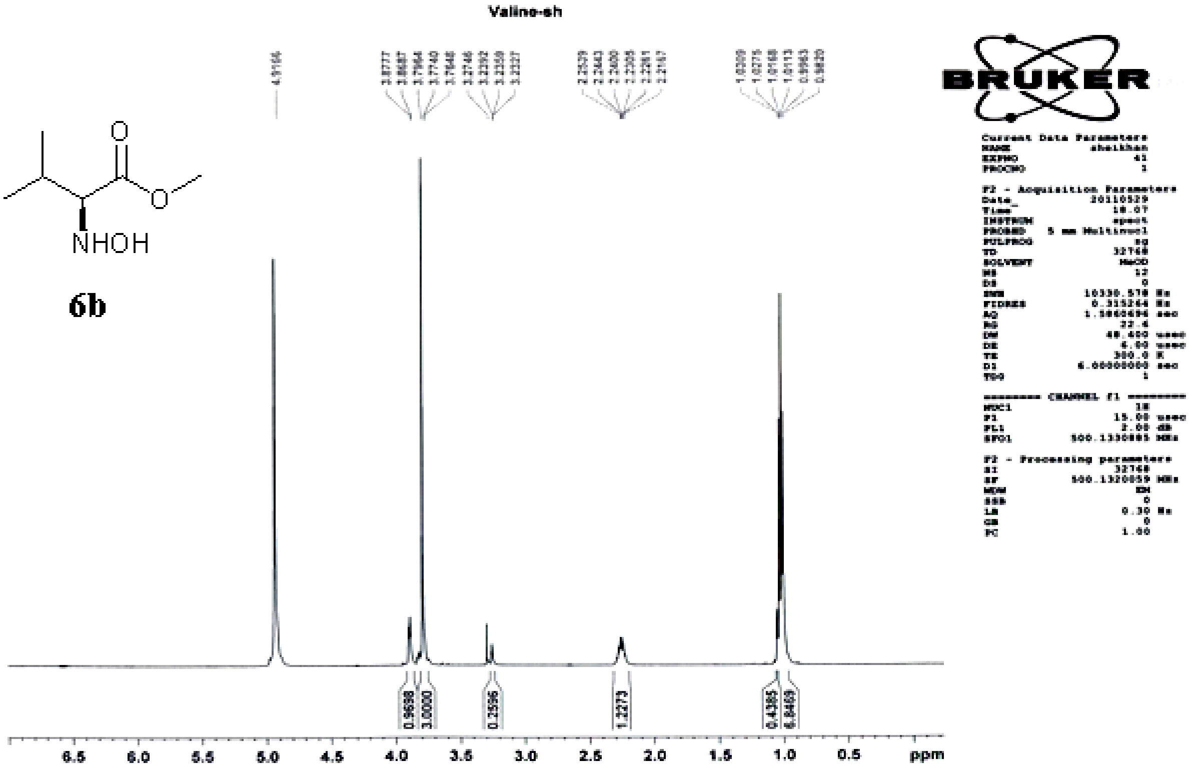
```
Current Data Parameters
NAME              rashidi
EXPNO                  90
PROCNO                  1

F2 - Acquisition Parameters
Date_            20090713
Time                20.23
INSTRUM             spect
PROBHD   5 mm Multinucl
PULPROG              zgpg
TD                  65536
SOLVENT              DMSO
NS                  10240
DS                      0
SWH            31446.541 Hz
FIDRES          0.479836 Hz
AQ             1.0420883 sec
RG                   3251
DW                 15.900 usec
DE                   6.00 usec
TE                  300.0 K
D1             2.00000000 sec
d11            0.03000000 sec
DELTA          1.89999998 sec
TD0                     1

======== CHANNEL f1 ========
NUC1                  13C
P1                  10.00 usec
PL1                  3.00 dB
SFO1          125.7703643 MHz

======== CHANNEL f2 ========
CPDPRG2           waltz16
NUC2                   1H
PCPD2              100.00 usec
PL2                120.00 dB
PL12                20.00 dB
PL13                20.00 dB
SFO2          500.1320005 MHz

F2 - Processing parameters
SI                  32768
SF            125.7578592 MHz
WDW                    EM
SSB                     0
LB                   1.00 Hz
GB                      0
PC                   1.00
```

## 5. $^1$H NMR of *N*-monoalkylated hydroxylamines derivatives

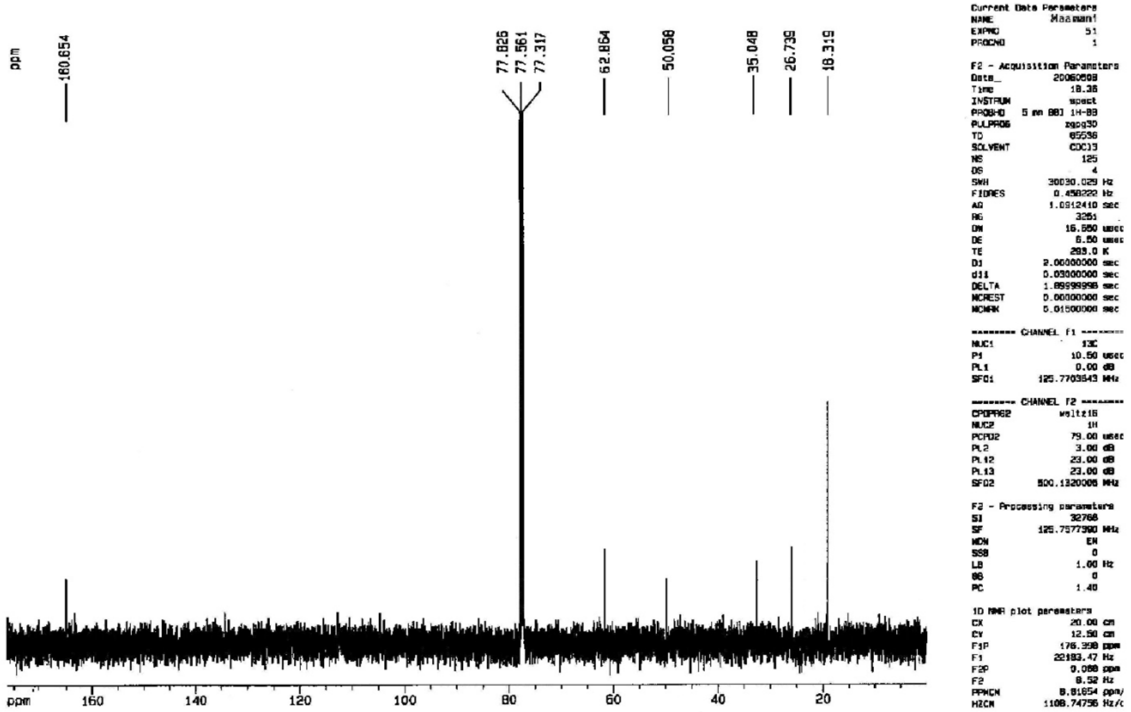


**6a**

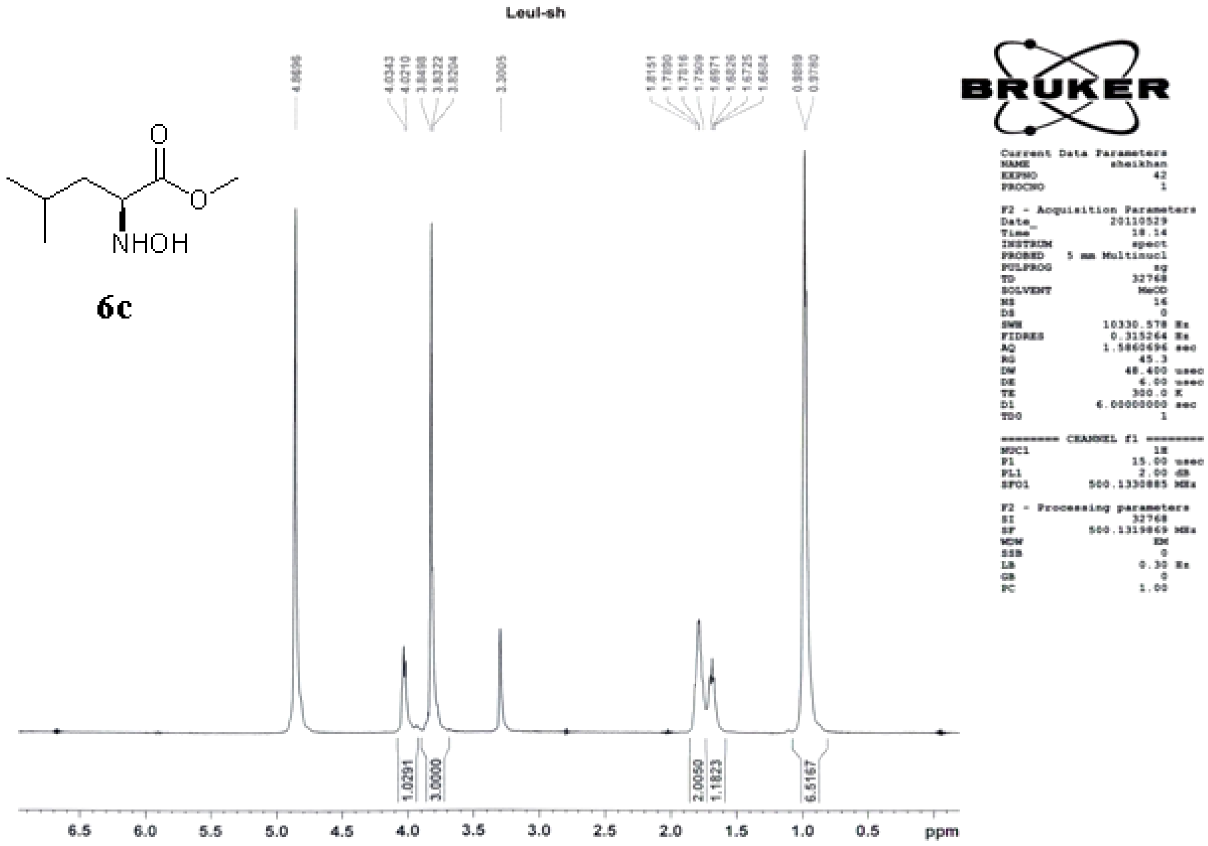
White crystals, mp 69–71 $^{o}$C [ref 20]



**6b**



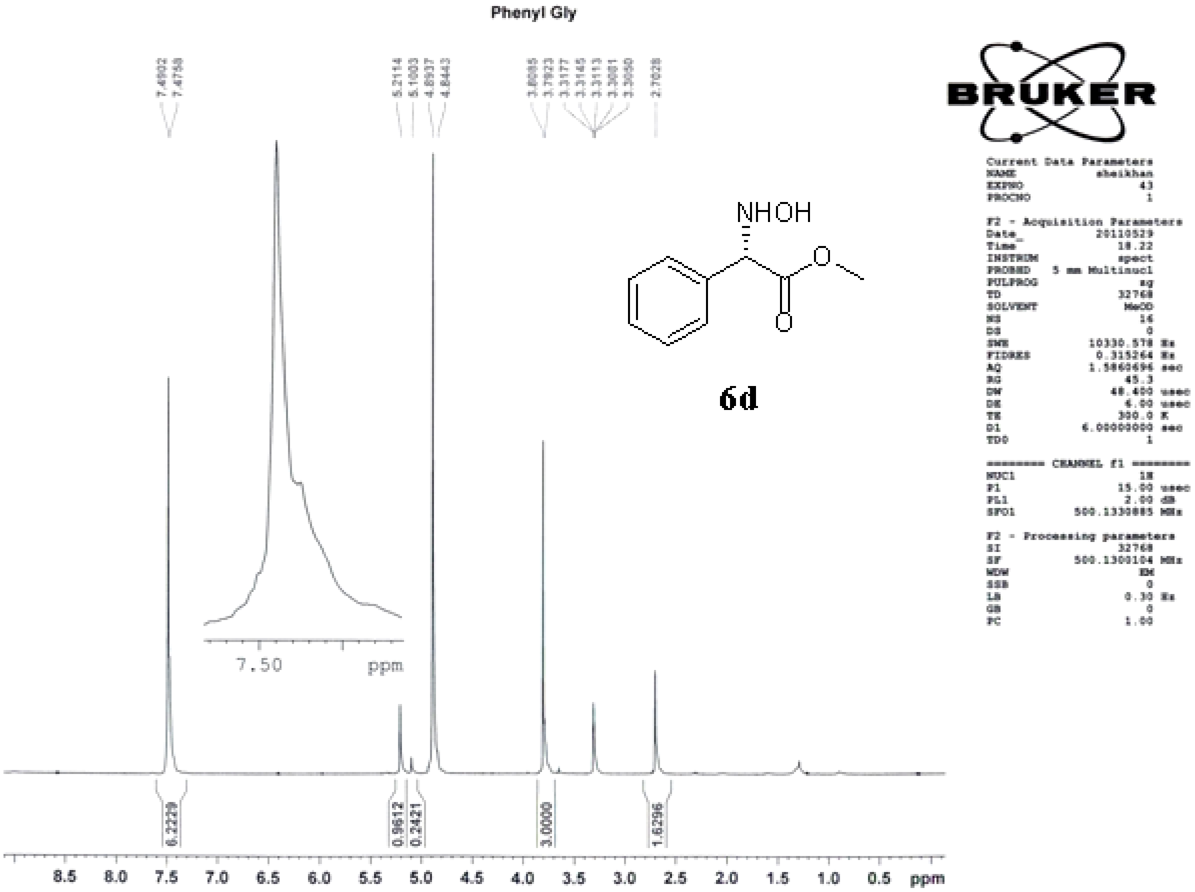
White crystals, mp 158–159 $^{o}$C [ref 5]



**6c**

```
Current Data Parameters
NAME              sheikhan
EXPNO                   42
PROCNO                   1

F2 - Acquisition Parameters
Date_             20110529
Time                 18.14
INSTRUM              spect
PROBHD    5 mm Multinucl
PULPROG                 zg
TD                   32768
SOLVENT               MeOD
NS                      16
DS                       0
SWH             10330.578 Hz
FIDRES           0.315264 Hz
AQ              1.5860696 sec
RG                    45.3
DW                  48.400 usec
DE                    6.00 usec
TE                   300.0 K
D1             6.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   15.00 usec
PL1                   2.00 dB
SFO1          500.1330885 MHz

F2 - Processing parameters
SI                   32768
SF            500.1319869 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

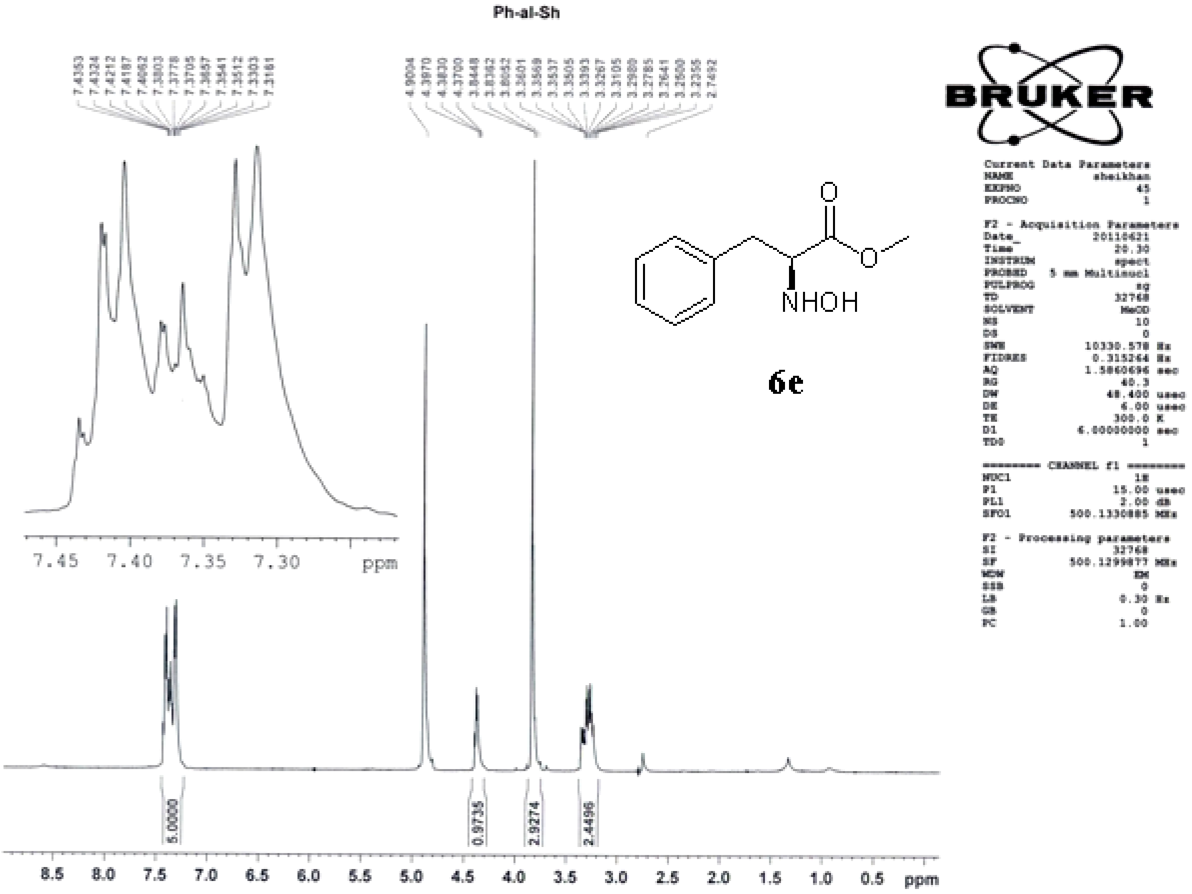
White crystals, mp 65–67 $^{o}$C [ref 19]



```
Current Data Parameters
NAME              sheikhan
EXPNO                   43
PROCNO                   1

F2 - Acquisition Parameters
Date_             20110529
Time                 18.22
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG                 zg
TD                   32768
SOLVENT               MeOD
NS                      16
DS                       0
SWH            10330.578 Hz
FIDRES          0.315264 Hz
AQ             1.5860696 sec
RG                    45.3
DW                  48.400 usec
DE                    6.00 usec
TE                   300.0 K
D1             6.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   15.00 usec
PL1                   2.00 dB
SFO1           500.1330885 MHz

F2 - Processing parameters
SI                   32768
SF             500.1300104 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

**6d**

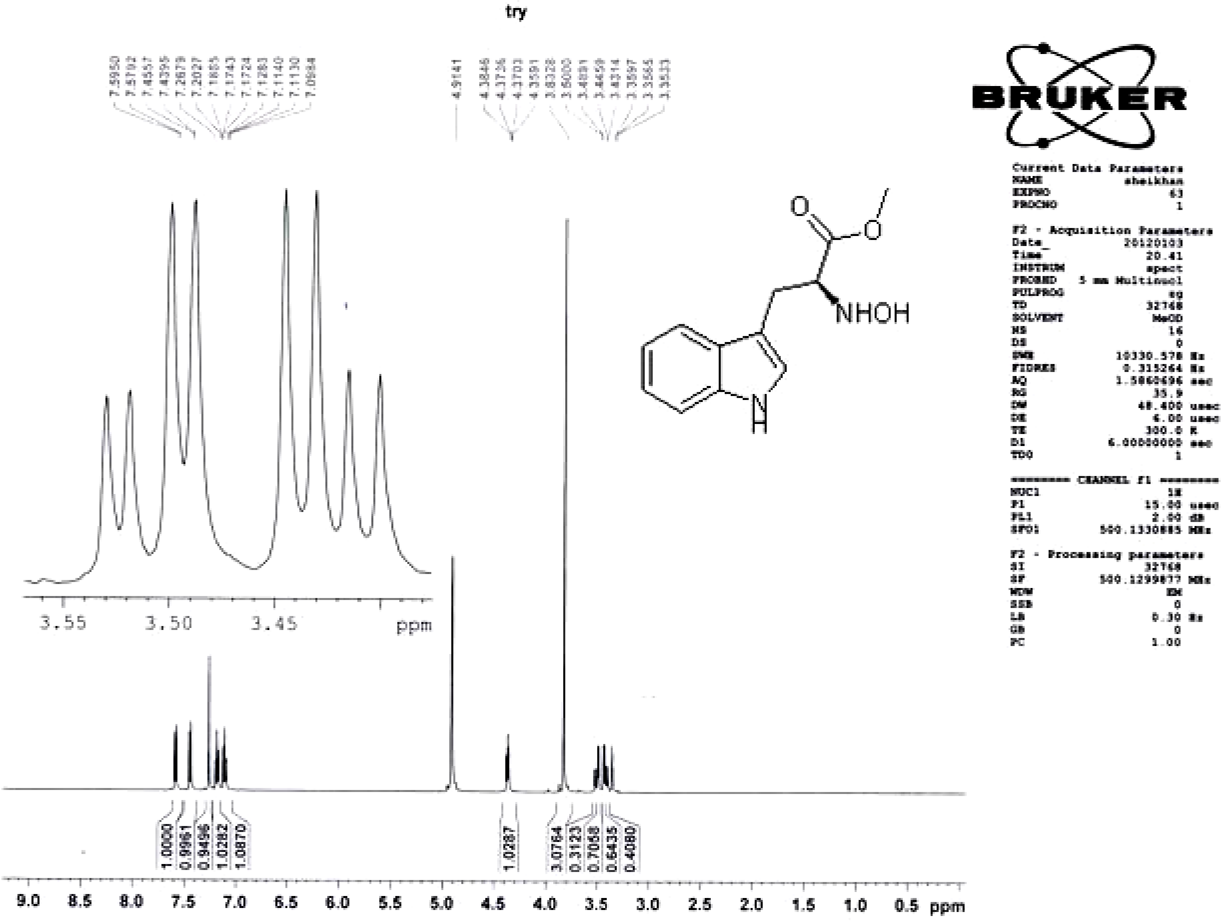
Pale yellow crystals, mp 140–142 °C [ref 4]



**6e**

```
Current Data Parameters
NAME              sheikhan
EXPNO                   45
PROCNO                   1

F2 - Acquisition Parameters
Date_             20110621
Time                 20.30
INSTRUM              spect
PROBHD   5 mm Multinucl
PULPROG                 zg
TD                   32768
SOLVENT               MeOD
NS                      10
DS                       0
SWH             10330.578 Hz
FIDRES           0.315264 Hz
AQ              1.5860696 sec
RG                    40.3
DW                  48.400 usec
DE                    6.00 usec
TE                   300.0 K
D1              6.00000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   15.00 usec
PL1                   2.00 dB
SFO1           500.1330885 MHz

F2 - Processing parameters
SI                   32768
SF             500.1299877 MHz
WDW                     EM
SSB                      0
LB                    0.30 Hz
GB                       0
PC                    1.00
```

White crystals, mp 69–71 $^{o}$C [ref 5,6]



```
Current Data Parameters
NAME                sheikhan
EXPNO                     63
PROCNO                     1

F2 - Acquisition Parameters
Date_               20120103
Time                   20.41
INSTRUM                spect
PROBHD   5 mm Multinucl
PULPROG                   zg
TD                     32768
SOLVENT                 MeOD
NS                        16
DS                         0
SWH                10330.578 Hz
FIDRES              0.315264 Hz
AQ                 1.5860696 sec
RG                      35.9
DW                    48.400 usec
DE                      6.00 usec
TE                     300.0 K
D1                6.00000000 sec
TD0                        1

======== CHANNEL f1 ========
NUC1                      1H
P1                     15.00 usec
PL1                     2.00 dB
SFO1             500.1330885 MHz

F2 - Processing parameters
SI                     32768
SF               500.1299877 MHz
WDW                       EM
SSB                        0
LB                      0.30 Hz
GB                         0
PC                      1.00
```

Pale yellow crystals, mp 82 $^{o}$C [ref 21]