Supporting information

Solid Supported Platinum(0) Nanoparticles Catalyzed Chemo-selective Reduction of Nitroarenes to N-Arylhydroxylamines

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CONTENTS **Pages**

1. Preparation of solid supported platinum (0) catalyst (SS-Pt)

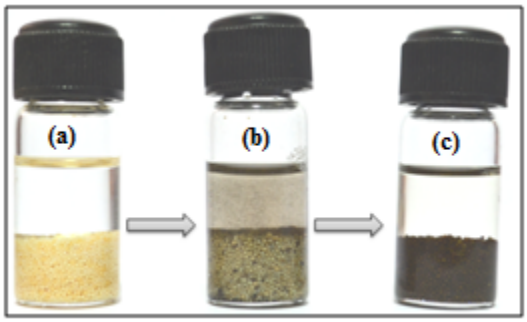
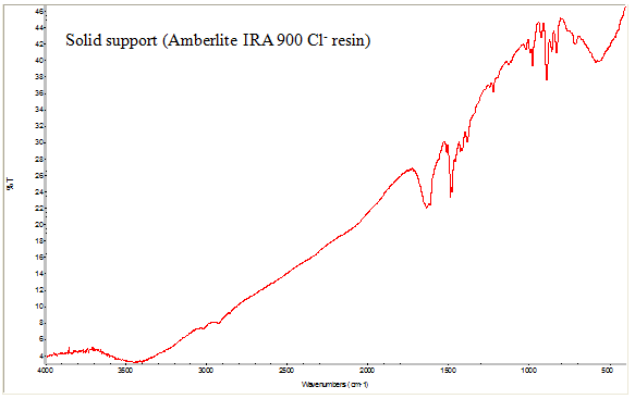
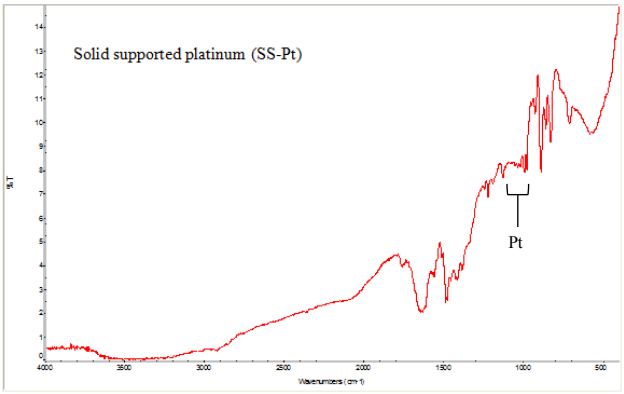


Figure 1. (a) Suspension of $^{-}BH_4$ exchanged resin beads in DMF, (b) During the *in situ* reduction (Pt(II) →Pt(0)) and deposition on solid support, (c) After the deposition of Pt(0) on resin surface

2. FT-IR spectra of solid support and solid supported platinum (0) catalyst



(A)



(B)

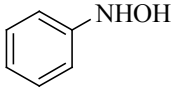
Figure 2. **(A)**FTIR spectra of Amberlite IRA 900 Cl^- resin (Solid support), (B) FTIR spectra of solid supported platinum catalyst

3. ICP-MS analysis of reaction mixture

In the recyclability experiments we have used 390 mg of SS-Pt (1 mol% Pt) for 200 mg of substrate (4-nitrotoluene). 390 mg SS-Pt contains 2.84 mg platinum metal as 10 mg $PtCl_2$ was bound in 1 gm of borohydride exchanged resin matrix. The reaction mixture was analyzed for ICP-MS after proper acidic digestion. The results are summarized below.

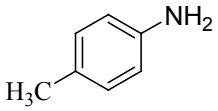
No. of Cycles	Amount of Pt metal leached (ppm)	% age of Pt leached with respect to initial metal content
3rd	0.1977	0.52
7th	0.3707	1.02
10th	0.4233	1.16

4. Typical experimental Procedure for reduction of Nitrobenzene to phenylhydroxylamine



A mixture of nitrobenzene (150 mg, 1.21 mmol), SS-Pt (323 mg, 1 mol% Pt) and PEG-400 (2 ml) were taken in a 25 ml round bottomed flask. N_2H_4. H_2O (hydrazine hydrate) (176 µl, 3.63 mmol) was added to the mixture under stirring condition. The reaction mixture was then put in a water bath of 60 ^oC and magnetically stirred for 70 minutes. The progress of the reaction was monitored by TLC. On completion, 2 ml of distilled water was added to the reaction mixture and extracted with ethylacetate (3×3 ml) and dried over anhydrous Na_2SO_4. Evaporation of the combined organic layer followed by column chromatography (Hexane:EtOAc = 85:15) over silica gel (60-120 mesh) afforded N-phenylhydroxylamine **1** as a white crystalline solid (122.29 mg, 92%); mp 87-89 ^oC; ^{1}HNMR (300 MHz, MeOD) δ 4.84 (brs, 1H, NH), 6.88-6.93 (m, 1H), 7.01-7.04 (m, 2H), 7.20-7.26 (m, 2H), 8.63 (brs, 1H, N-OH); ^{13}C NMR (75 MHz, MeOD) δ 115.10 (2C), 122.11, 129.47 (2C), 151.90. ESIMS data; m/z calc. for $[M+H]^+$ C_6H_8NO 110.0600 obsd. 110.0619.

5. Typical experimental procedure for reduction of 4-nitrotoluene to 4-toluedine

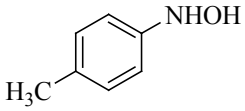


A mixture of nitrobenzene (150 mg, 1.21 mmol), SS-Pt (646 mg, 2 mol% Pt) and PEG-400 (2 ml.) were taken in a 25 ml round bottomed flask. N_2H_4. H_2O (hydrazine hydrate) (412 µl, 8.47 mmol) was added to the mixture under stirring condition. The reaction mixture was then put in a water bath of 100 ^oC and magnetically stirred for 120 minutes. The progress of the reaction was monitored by TLC. On completion, 2 ml of distilled water was added to the reaction mixture and extracted with ethylacetate (3×3 ml) and dried over anhydrous Na_2SO_4. Evaporation of the combined organic layer followed by column chromatography (Hexane:EtOAc = 80:20) over silica gel (60-120 mesh) afforded 4-toluedine **28** as a white crystalline solid (76.36 mg, 75%); mp 40-41 ^oC; ^{1}HNMR (300 MHz, $CDCl_3$) δ 2.25 (s, 3H), 3.54 (br, N-H), 6.62 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 8.1 Hz, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.34, 115.13 (2C), 127.66, 129.63 (2C), 143.69.

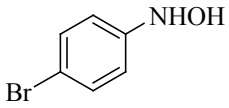
6. General experimental Procedure for the reduction of nitroarenes to N-arylhydroxylamine in 10 gm scale

A mixture of nitroarene (10 gm), SS-Pt (0.5 mol% Pt) and 25 ml of PEG-400 were taken in a 250 ml round bottom flask. The reaction mixture was set into a 60 ^oC water bath and stirred magnetically. N_2H_4. H_2O (3 mmol) was added portion wise into the reaction mixture at least for 30 minutes. Extra precaution was taken to remove excess H_2 gas evolution. Progress of reaction was monitored by TLC. On completion, 10 ml of distilled water was added to the reaction mixture and extracted with ethylacetate (15×3 ml) and dried over anhydrous Na_2SO_4. Evaporation of the combined organic layer and followed by column chromatography over silica gel (60-120 mesh) afforded desired corresponding N-arylhydroxylamine. This procedure was applied to prepare compounds **1**, **2**, **4**, **8** and **9**.

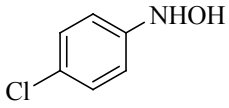
7. Experimental and spectral data of N-arylhydroxylamine derivatives



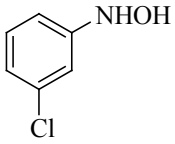
N-Hydroxy-4-methylbenzenamine (**2**) Prepared as described the method for **1**, starting form 4-methylnitrobenzene (150 mg, 1.09 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 90:10) **2** as colourless crystalline solid (129.28 mg, 96%); mp 91-93 ^oC; ^{1}HNMR (300 MHz, MeOD) δ 2.25 (s, 3H), 4.89 (brs, 1H, NH), 6.89-6.92 (m, 2H), 7.02-7.05 (m, 2H); ^{13}C NMR (75 MHz, MeOD) δ 116.06 (2C), 130.06 (2C), 131.68, 149.76.



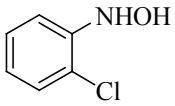
4-Bromo-N-hydroxybenzenamine (**3**) Prepared as described the method for **1**, starting form 4-bromonitrobenzene (150 mg, 0.742 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 85:15) **3** as colourless semi solid (136.81 mg, 98%); ^{1}HNMR (300 MHz, MeOD) δ 4.85 (brs, 1H, NH), 6.82-6.89 (m, 2H), 7.25-7.33 (m, 2H); ^{13}C NMR (75 MHz, MeOD) δ 113.38, 116.56 (2C), 132.38 (2C), 152.04.



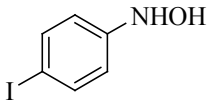
4-Chloro-N-hydroxybenzenamine (**4**) Prepared as described the method for **1**, starting form 4-chloronitrobenzene (150 mg, 0.952 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 90:10) **4** as light yellow crystalline solid (129.89 mg, 95%); mp 88-90 ^{o}C; ^{1}HNMR (300 MHz, MeOD) δ 6.91-6.96 (m, 2H), 7.16-7.21 (m, 2H); ^{13}C NMR (75 MHz, MeOD) δ 115.9 (2C), 126.14, 129.06 (2C), 150.75. ESIMS data; *m/z* calc. for $[M+H]^{+}$ C_6H_7ClNO 144.5783 obsd. 144.5757.



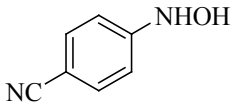
3-Chloro-N-hydroxybenzenamine (**5**) Prepared as described the method for **1**, starting form 3-chloronitrobenzene (150 mg, 0.952 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 90:10) **5** as light yellow liquid (118.92 mg, 87%); ^{1}HNMR (300 MHz, MeOD) δ 4.88 (brs, 1H, NH), 6.79-6.84 (m, 2H), 6.99-7.00 (m, 1H), 7.11-7.14 (m, 1H), 8.62 (brs, 1H, N-OH); ^{13}C NMR (75 MHz, MeOD) δ 112.87, 114.46, 121.17, 130.79 (2C), 135.49, 154.34.



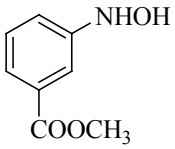
2-Chloro-N-hydroxybenzenamine (**6**) Prepared as described the method for **1**, starting from 2-chloronitrobenzene (150 mg, 0.952 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 90:10) **6** as light brown semi solid (124.42 mg, 91%); ^{1}HNMR (300 MHz, MeOD) δ 4.91 (brs, 1H, NH), 6.79-6.84 (m, 1H), 7.18-7.30 (m, 3H); ^{13}C NMR (75 MHz, MeOD) δ 116.19, 119.44, 124.24, 128.5, 129.65, 148.42.



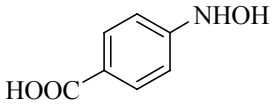
N-Hydroxy-4-iodobenzenamine (**7**) Prepared as described the method for **1**, starting form 4-iodonitrobenzene (150 mg, 0.602 mmol) and purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 85:15) afforded **7** (127.40 mg, 90%) as brown semi solid; ^{1}HNMR (300 MHz, MeOD) δ 4.86 (brs, 1H, NH), 6.75-6.76 (d, 2H, *J*= 8.4 Hz), 7.48-7.50 (d, 2H, *J*= 8.4 Hz); ^{13}C NMR (75 MHz, MeOD) δ 82.75, 116.94 (2C), 138.38 (2C), 152.66. ESIMS data; *m/z* calc. for $[M+H]^+$ C_6H_7INO 236.0298 obsd. 235.9549.



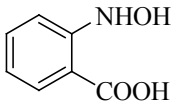
4-(Hydroxyamino)benzonitrile (**8**) Prepared as described the method for **1**, starting from 4-nitrobenzonitrile (150 mg, 1.013 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 70:30) **8** as orange crystalline solid (134.45 mg, 99%); ^{1}HNMR (300 MHz, MeOD) δ 4.83 (brs, 1H, NH), 6.94-6.97 (d, 2H, *J*= 8.4 Hz), 7.46-7.49 (d, 2H, *J*= 9); ^{13}C NMR (75 MHz, MeOD) δ 98.26, 113.55 (2C), 120.96, 134.12 (2C), 156.86. ESIMS data; *m/z* calc. for $[M+H]^+$ $C_7H_7N_2O$ 135.0552 obsd. 135.0529.



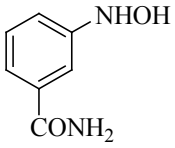
Methyl 3-(hydroxyamino)benzoate (**9**) Prepared as described the method for **1**, starting from methyl-3-nitrobenzoate (150 mg, 0.828 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 60:40) **9** as orange crystalline solid (127.32 mg, 92%); ^{1}HNMR (300 MHz, MeOD) δ 3.86 (s, 3H), 4.84 (brs, 1H, NH), 7.15-7.19 (m, 1H), 7.27-7.32 (m, 1H), 7.48-7.51 (m, 1H), 7.63-7.64 (m, 1H); ^{13}C NMR (75 MHz, MeOD) δ 52.52, 115.44, 119.34, 122.62, 129.72 (2C), 153.12, 168.84. ESIMS data; *m/z* calc. for $[M+H]^+$ $C_8H_{10}NO_3$ 168.0655 obsd. 168.0637.



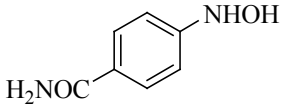
4-(Hydroxyamino)benzoic acid (**10**) Prepared as described the method for **1**, starting from 4-nitrobenzoic acid (150 mg, 0.898 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 30:70) **10** as light brown crystalline solid (118.18 mg, 86%); mp 170-172 ^{o}C; ^{1}HNMR (300 MHz, MeOD) δ 4.90 (brs, 1H, NH), 6.92-6.96 (m, 2H), 7.86-7.90 (m, 2H); ^{13}C NMR (75 MHz, MeOD) δ 112.96 (2C), 122.49, 132.04 (2C), 157.42, 170.31. ESIMS data; *m/z* calc. for $[M+H]^+$ $C_7H_8NO_3$ 154.0498 obsd. 154.0476.



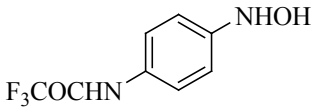
2-(Hydroxyamino)benzoic acid (**11**) Prepared as described the method for **1**, starting from 2-nitrobenzoic acid (150 mg, 0.898 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 30:70) **11** as light brown crystalline solid (119.55 mg, 87%); mp 143-144 ^{o}C; ^{1}HNMR (300 MHz, DMSO-d_6) δ 6.73-6.78 (m, 1H), 7.23-7.26 (d, 1H, *J*= 7.5 Hz), 7.43-7.49 (m, 1H), 7.77-7.80 (d, 1H, *J*= 7.8 Hz), 8.86 (brs, 1H, N-OH); ^{13}C NMR (75 MHz, DMSO-d_6) δ 111.37, 113.61, 117.64, 130.90, 134.11, 153.75, 169.03. ESIMS data; *m/z* calc. for $[M+H]^+$ $C_7H_8NO_3$ 154.0498 obsd. 154.0467.



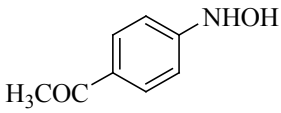
3-(Hydroxyamino)benzamide (**12**) Prepared as described the method for **1**, starting from 3-nitrobenzamide (150 mg, 0.903 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 40:60) **12** as white crystalline solid (126.36 mg, 92%); mp chrred at 130 ^{o}C; ^{1}HNMR (300 MHz, MeOD) δ 4.85 (brs, 1H, NH), 7.09-7.13 (m, 1H), 7.24-7.32 (m, 2H), 7.46-7.47 (m, 1H); ^{13}CNMR (75 MHz, MeOD) δ 121.99, 116.30, 118.79, 127.93, 133.56, 151.30, 170.98. ESIMS data; *m/z* calc. for $[M+H]^+$ $C_7H_9N_2O_2$ 153.0658 obsd. 153.0668.



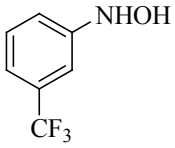
4-(Hydroxyamino)benzamide (**13**) Prepared as described the method for **1**, starting from 4-nitrobenzamide (150 mg, 0.903 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 30:70) **13** as white crystalline solid (123.61 mg, 90%); mp 181-183 ^{o}C; ^{1}HNMR (300 MHz, MeOD) δ 4.83 (brs, 1H, NH), 6.92-6.97 (m, 2H), 7.72-7.77 (m, 2H); ^{13}CNMR (75 MHz, MeOD) δ 113.61 (2C), 126.0, 130.09 (2C), 156.79 (2C), 172.78. ESIMS data; *m/z* calc. for $[M+H]^+$ $C_7H_9N_2O_2$ 153.0658 (exact mass) obsd. 153.0636.



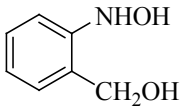
2,2,2-Trifluoro-N-(4-(hydroxyamino)phenyl)acetamide (**14**) Prepared as described the method for **1**, starting from 4-nitrobenzamide (150 mg, 0.641 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 40:60) **14** as yellow crystalline solid (138.20 mg, 98%); mp 147-149 ^{o}C; ^{1}HNMR (300 MHz, MeOD) δ 2.19 (brs, 1H, N-OH), 4.84 (brs, 1H, NH), 6.59-6.63 (d, 2H, *J*= 7.5 Hz), 7.94-7.97 (d, 2H, *J*= 9.3); ^{13}C NMR (75 MHz, MeOD) δ 30.67, 113.98 (2C), 127.32 (2C), 138.26, 156.74.



1-(4-(Hydroxyamino)phenyl)ethanone (**15**) Prepared as described the method for **1**, starting from 4-nitroacetophenone (150 mg, 0.909 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 60:40) **15** as orange crystalline solid (107.07 mg, 78%); mp 111-113 ^{o}C; ^{1}HNMR (300 MHz, MeOD) δ 2.48 (s, 3H), 4.83 (brs, 1H, NH), 6.92-6.95 (d, 2H, *J*= 8.7), 7.83-7.86 (d, 2H, *J*= 8.7); ^{13}C NMR (75 MHz, MeOD) δ 26.11, 112.7 (2C), 129.79, 131.20 (2C), 157.57, 199.53. ESIMS data; *m/z* calc. for $[M+H]^{+}$ $C_8H_{10}NO_2$ 152.0706 (exact mass) obsd. 152.0719.

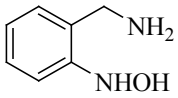


3-(Trifluoromethyl)-N-hydroxybenzenamine (**16**) Prepared as described the method for **1**, starting from 3-trifluoromethylnitrobenzene (150 mg, 0.785 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 80:20) **16** as colourless liquid (129.27 mg, 93%); ^{1}HNMR (300 MHz, MeOD) δ 4.86 (brs, 1H, NH), 7.08-7.15 (m, 2H), 7.27-7.35 (m, 2H), 8.72 (brs, 1H, N-OH); ^{13}C NMR (75 MHz, MeOD) δ 110.91, 117.85 (2C), 130.21 (3C), 153.40. ESIMS data; *m/z* calc. for $[M+H]^{+}$ $C_7H_7F_3NO$ 178.0474 obsd. 178.0451.

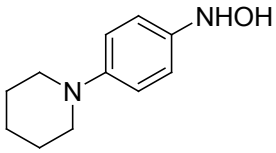


(2-(Hydroxyamino)phenyl)methanol (**17**) Prepared as described the method for **1**, starting from 2-nitrobenzylalcohol (150 mg, 1.111 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 50:50) **17** as orange crystalline solid (152.90 mg, 99%); mp 131-133 ^{o}C; ^{1}HNMR (300 MHz, MeOD) δ 4.58 (s, 2H), 4.88 (brs,

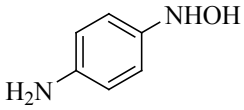
1H, NH), 6.85-6.90 (m, 1H), 7.15-7.30 (m, 3H), 8.48 (brs, 1H, N-OH); ^{13}C NMR (75 MHz, MeOD) δ 62.88, 114.78, 121.53, 127.09, 128.84, 129.41, 150.39.



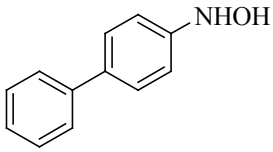
2-(Aminomethyl)-N-hydroxybenzenamine (**18**) Prepared as described the method for **1**, starting from 2-nitrobenzylamine (150 mg, 0.986 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 70:30) **18** as light yellow crystalline solid (113.03 mg, 83%); mp 143-145 ^{o}C; ^{1}HNMR (300 MHz, MeOD/$CDCl_3$ (1:1)) δ 4.44 (s, 2H), 4.50 (brs, NH), 7.06-7.11 (m, 1H), 7.29-7.34 (t, 1H, *J*= 7.6 Hz), 7.46-7.49 (d, 1H, *J*= 8.4 Hz), 7.68-7.71 (d, 1H, *J*= 8.4), 7.07 (brs, 1H, N-OH); ^{13}C NMR (75 MHz, MeOD/$CDCl_3$ (1:1)) δ 29.99, 110.45, 121.12, 123.22, 127.09, 134.12, 140.56.



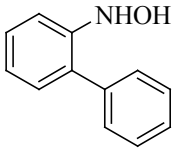
N-Hydroxy-4-(piperidine-1-yl)benzenamine (**19**) Prepared as described the method for **1**, starting from 1-(4-nitrophenyl)pyrrolidine (150 mg, 0.781 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 40:60) **20** as dark brown semi solid (138.13 mg, 92%); ^{1}HNMR (300 MHz, MeOD) δ 1.51-1.57 (m, 2H), 1.67-1.74 (m, 4H), 2.93 (brs, 4H), 4.88 (brs, 1H, NH), 6.62-6.70 (m, 2H), 6.84-6.86 (m, 2H); ^{13}C NMR (75 MHz, MeOD) δ 25.08 (2C), 27.03, 54.50 (2C), 117.68 (2C), 120.92 (2C), 142.77, 146.40.



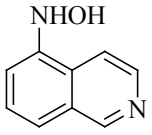
4-Amino-N-hydroxybenzenamine (**20**) Prepared as described the method for **1**, starting from 4-nitroaniline (150 mg, 1.086 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 30:70) **20** as dark brown crystalline solid (119.95 mg, 89%); mp 127-130 ^{o}C; ^{1}HNMR (300 MHz, MeOD) δ 4.85 (brs, 1H, NH), 6.63 (s, 4H); ^{13}C NMR (75 MHz, MeOD) δ 118.44 (4C), 140.13 (2C).



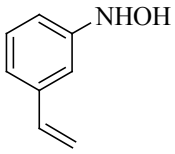
4-Phenyl-N-hydroxybenzamine (**21**) Prepared as described the method for **1**, starting from 4-nitrobiphenyl (150 mg, 0.753 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 80:20) **21** as yellow crystalline solid (135.26 mg, 83%); mp 151-153 ^{o}C; ^{1}HNMR (300 MHz, MeOD) δ 4.90 (brs, 1H, NH), 7.04-7.07 (m, 2H), 7.23-7.28 (m, 2H), 7.36-7.41 (m, 2H), 7.48-7.57 (m, 3H); ^{13}C NMR (75 MHz, MeOD) δ 115.39 (2C), 127.39 (3C), 129.70 (2C), 135.07, 142.45, 152.18. ESIMS data; *m/z* calc. for $[M+H]^{+}$ $C_{12}H_{12}NO$ 186.0913 obsd. 186.0928.



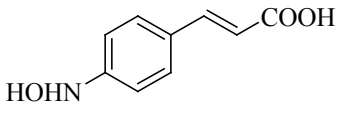
2-Phenyl-N-hydroxybenzamine (**22**) Prepared as described the method for **1**, starting from 2-nitrobiphenyl (150 mg, 0.753 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 80:20) **22** as yellow liquid (131.08 mg, 94%); ^{1}HNMR (300 MHz, MeOD) δ 4.89 (brs, 1H, NH), 6.92-6.95 (m, 2H), 7.07-7.10 (m, 2H), 7.29-7.41 (m, 4H), 8.62 (brs, 1H, N-OH); ^{13}C NMR (75 MHz, MeOD) δ 116.09, 122.10, 128.34, 128.99, 129.17, 129.56 (2C), 129.97 (2C), 131.18, 139.66, 148.66. ESIMS data; *m/z* calc. for $[M+H]^{+}$ $C_{12}H_{12}NO$ 186.0913 obsd. 186.0859.



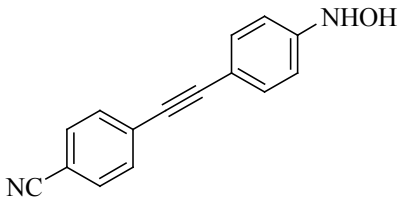
N-Hydroxyisoquinolin-5-amine (**23**) Prepared as described the method for **1**, starting form 5-nitroisoquinoline (150 mg, 0.862 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 70:30) **23** as brown crystalline solid (125.51 mg, 91%); mp 133-135 ^{o}C; ^{1}HNMR (300 MHz, DMSO-d_6) δ 7.32-7.34 (m, 1H), 7.45-7.56 (m, 2H), 7.81-7.83 (d, 1H, *J*= 6 Hz), 8.42-8.44 (d, 1H, *J*= 6 Hz), 8.67 (brs, 1H, N-OH), 9.20-9.21 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 109.81, 114.89, 117.70, 124.31, 128.02, 128.46, 141.57, 146.09, 152.15. ESIMS data; *m/z* calc. for $[M+H]^{+}$ $C_9H_9N_2O$ 161.0709 obsd. 161.0719.



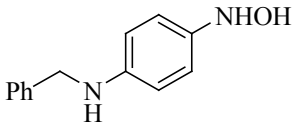
N-Hydroxy-3-vinylbenzenamine (**24**) Prepared as described the method for **1**, starting from 3-nitrostyrene (150 mg, 1.006 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 80:20) **24** as white crystalline solid (118.23 mg, 87%); ^{1}HNMR (300 MHz, MeOD) δ 4.87 (brs, 1H, NH), 5.17-5.21 (d, 1H, *J*= 12 Hz), 5.70-5.76 (d, 1H, *J*= 17.7 Hz), 6.63-6.73 (m, 1H), 6.87-6.96 (m, 2H), 7.09 (s, 1H), 7.15-7.20 (m, 1H); ^{13}C NMR (75 MHz, MeOD) δ 112.55, 113.78, 114.75, 120.23, 129.75, 183.29, 139.37, 152.66. ESIMS data; *m/z* calc. for $[M+H]^+$ $C_8H_{10}NO$ 136.0756 obsd. 136.0733.



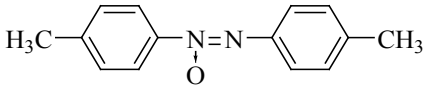
3-(4-(Hydroxyamino)phenyl)acrylic acid (**25**) Prepared as described the method for **1**, starting from 4-nitrocinnamic acid (150 mg, 0.777 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 30:70) **25** as yellow crystalline solid (108.51 mg, 78%); mp decomposed at 133 ^{o}C; ^{1}HNMR (300 MHz, DMSO-d_6) δ 6.24-6.29 (d, 1H, *J*= 15.9 Hz), 6.80-6.83 (d, 2H, *J*= 8.4 Hz), 7.45-7.50 (m, 3H), 8.55 (brs,1H, NH), 8.72 (brs, 1H, N-OH), 12.09 (brs, 1H, COOH); ^{13}C NMR (75 MHz, DMSO-d_6) δ 112.35 (2C), 114.29, 124.83, 129.28 (2C), 144.57, 154, 168.11. ESIMS data; *m/z* calc. for $[M+H]^+$ $C_9H_{10}NO_3$ 180.0655 obsd. 180.0632.



4-(2-(4-(Hydroxyamino)phenyl)ethynyl)benzonitrile (**26**) Prepared as described the method for **1**, starting form 4-(2-(4-nitrophenyl)ethynyl)benzonitrile (150 mg, 0.528 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 60:40) **26** as yellow crystalline solid (117.41 mg, 95%); mp 193-195 ^{o}C; ^{1}HNMR (300 MHz, MeOD/ $CDCl_3$ (1:1)) δ 4.24 (brs, 1H, NH), 6.64-6.67 (m, 2H), 7.10-7.13 (m, 2H), 7.29-7.38 (m, 4H); ^{13}C NMR (75 MHz, DMSO-d_6) δ 86.14, 95.16, 110.04, 112.36 (2C), 118.56, 128.04, 131,63 (3C), 132.47 (4C), 152.98. ESIMS data; *m/z* calc. for $[M+H]^+$ $C_{15}H_{11}N_2O$ 235.0865 obsd. 235.0849.



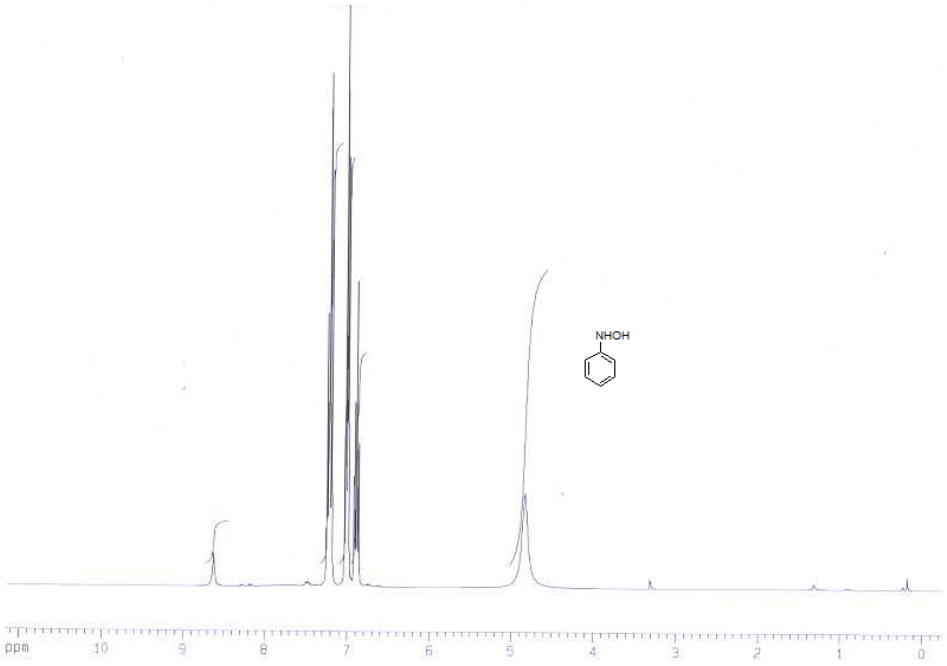
4-(Benzylamino)-N-hydroxybenzenamine (**27**) Prepared as described the method for **1**, starting form **1**, starting from 4-benzylaminonitrobenzene (150 mg, 0.657 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane:EtOAc = 50:50) **26** as yellow crystalline solid (123.89 mg, 88%); mp 129-131 ^{o}C; ^{1}HNMR (300 MHz, DMSO-d_6/ MeOD (1:1)) δ 4.86 (s, 2H), 4.10 (brs, 1H, NH), 6.75-6.81 (m, 2H), 7.16-7.27 (m, 3H), 7.32-7.37 (m, 2H), 7.97-8.01 (m, 2H); ^{13}C NMR (75 MHz, DMSO-d_6/ MeOD (1:1)) δ 54.26, 111.53, 125.87, 126.54 (3C), 127.21, 128.78 (3C), 136.51, 137.26, 153.49.



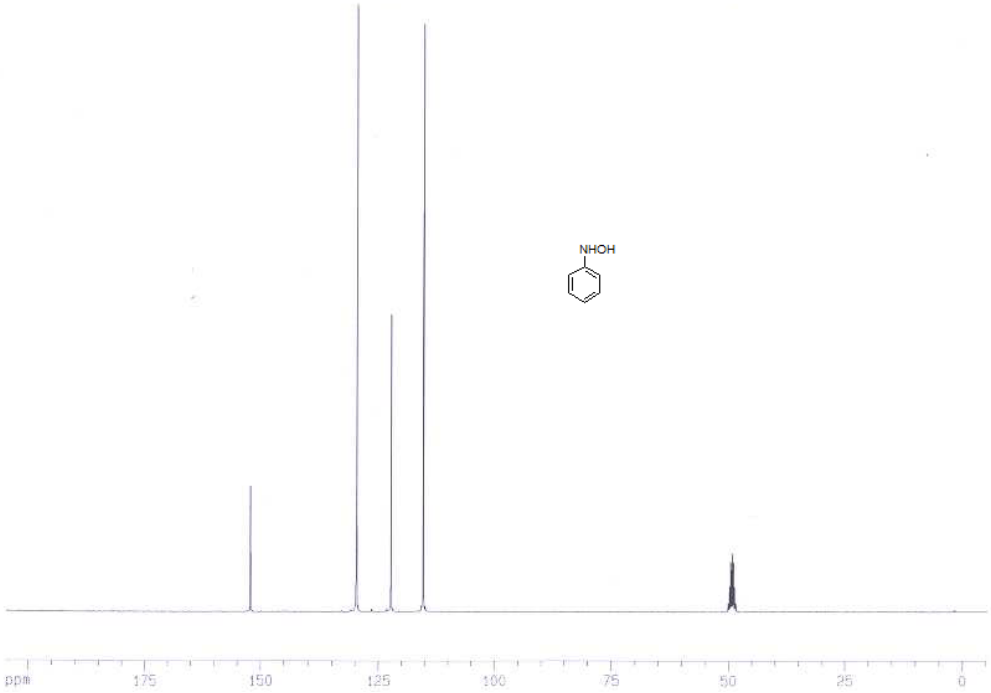
4, 4'-Dimethylazoxybenzene (**30**) Prepared as described the method for **28**, starting from N-hydroxy-4-methylbenzenamine (200 mg, 1.626 mmol) gave, after purification with silica gel (60-120 mesh) column chromatography (Hexane) **30** as light yellow crystalline solid (312.35 mg, 85%); mp 129-131 ^{o}C; ^{1}HNMR (300 MHz, $CDCl_3$) δ 2.44 (s, 3H), 2.46 (s, 3H), 7.28-7.32 (m, 4H), 8.15-8.18 (d, 2H, *J*= 8.4 Hz), 8.20-8.23 (d, 2H, *J*= 8.7 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.22, 21.49, 122.06 (2C), 125.60 (2C), 129.22 (4C), 139.94, 141.78, 141.84, 146.15. ESIMS data; *m/z* calc. for $[M+H]^+$ $C_{14}H_{15}N_2O$ 227.1178 obsd. 227.1162.

8. ^{1}H, ^{13}C NMR and selected ESIMS spectra of N-aryl hydroxylamines

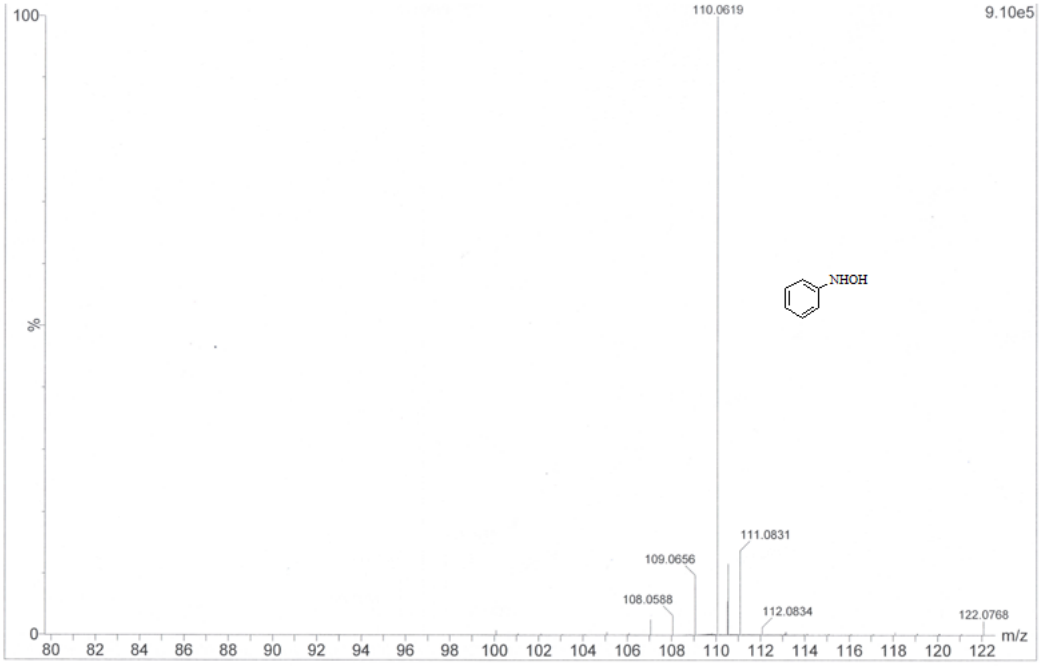
Phenylhydroxylamine (**1**) (^{1}H NMR in MeOD)



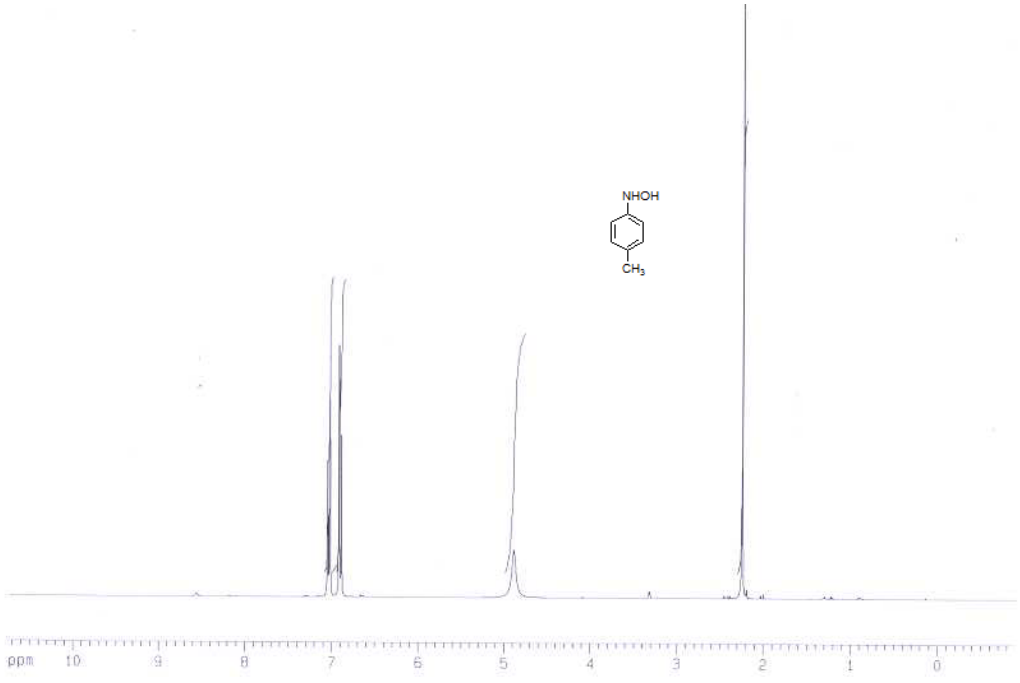
Phenylhydroxylamine (**1**) (^{13}C NMR in MeOD)



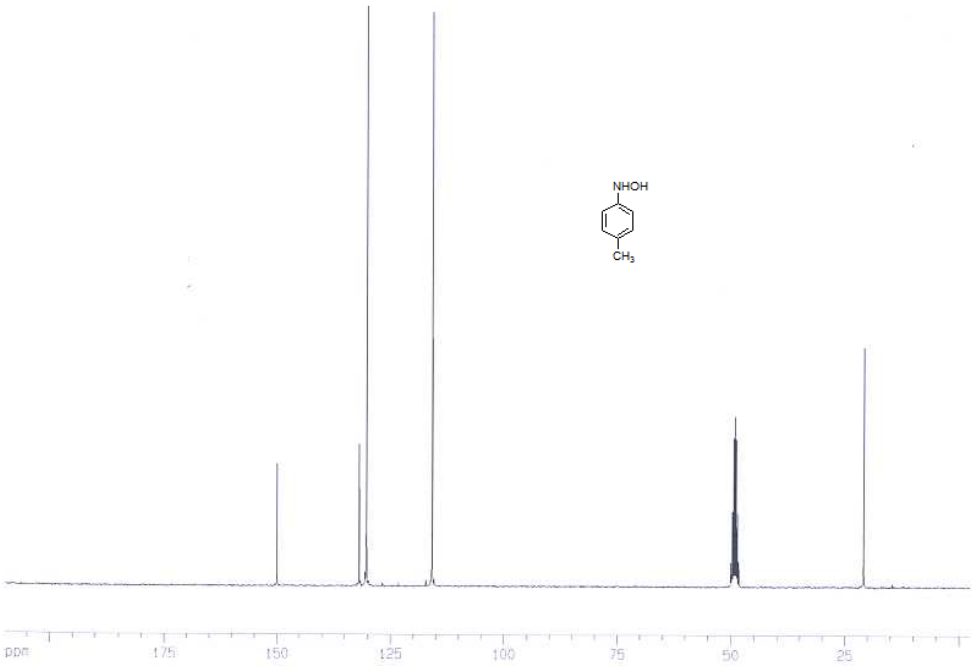
Phenylhydroxylamine (**1**) (ESIMS in CH_3CN/H_2O (1:1))



4-methylphenylhydroxylamine (**2**) (^{1}H NMR in MeOD)

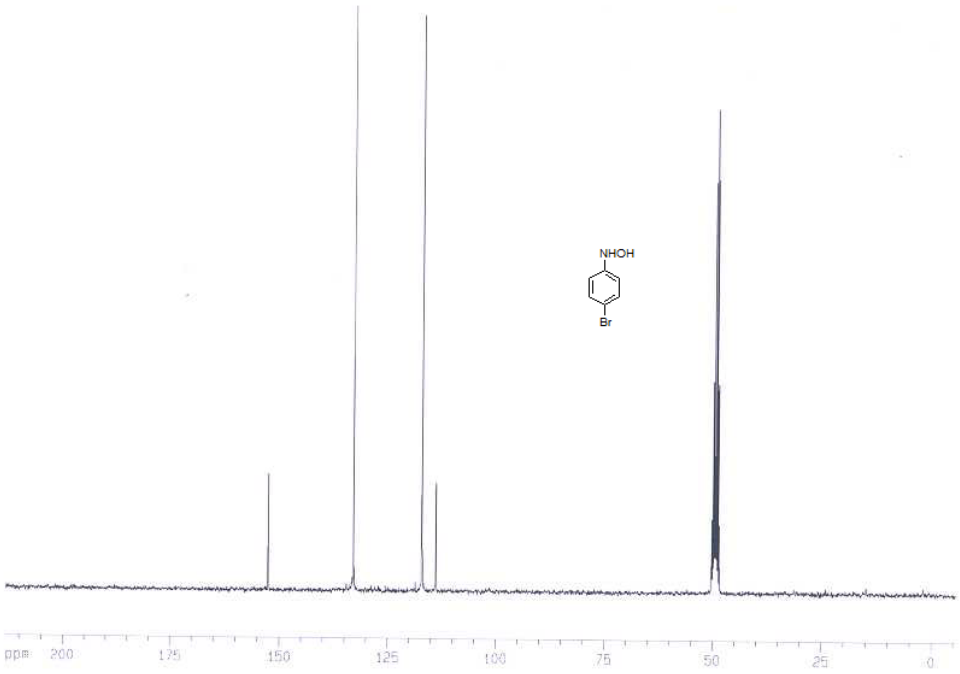


4-methylphenylhydroxylamine (**2**) (^{13}C NMR in MeOD)

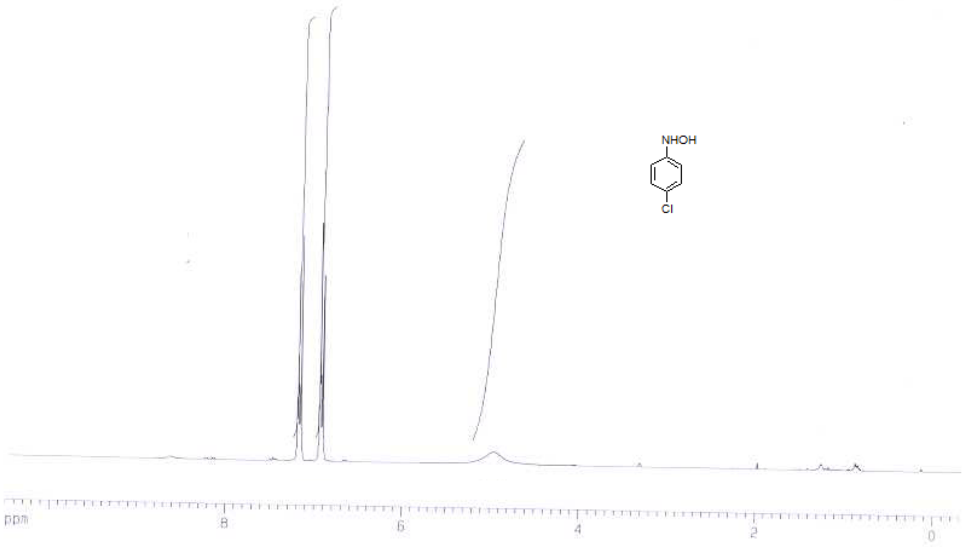


4-Bromophenylhydroxylamine (**3**) (^{1}H NMR in MeOD)

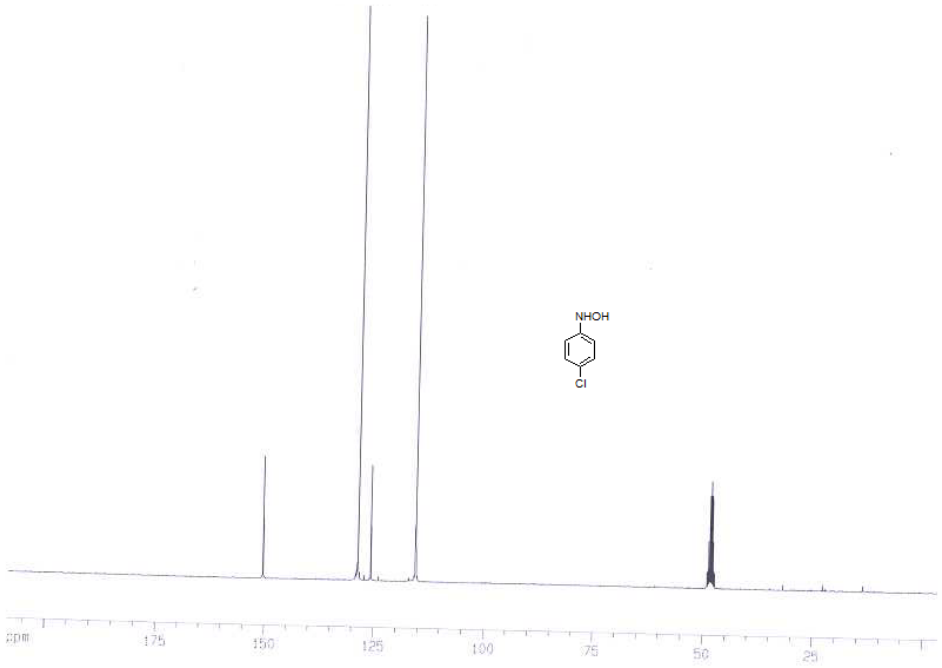
4-Bromophenylhydroxylamine (**3**) (^{13}C NMR in MeOD)



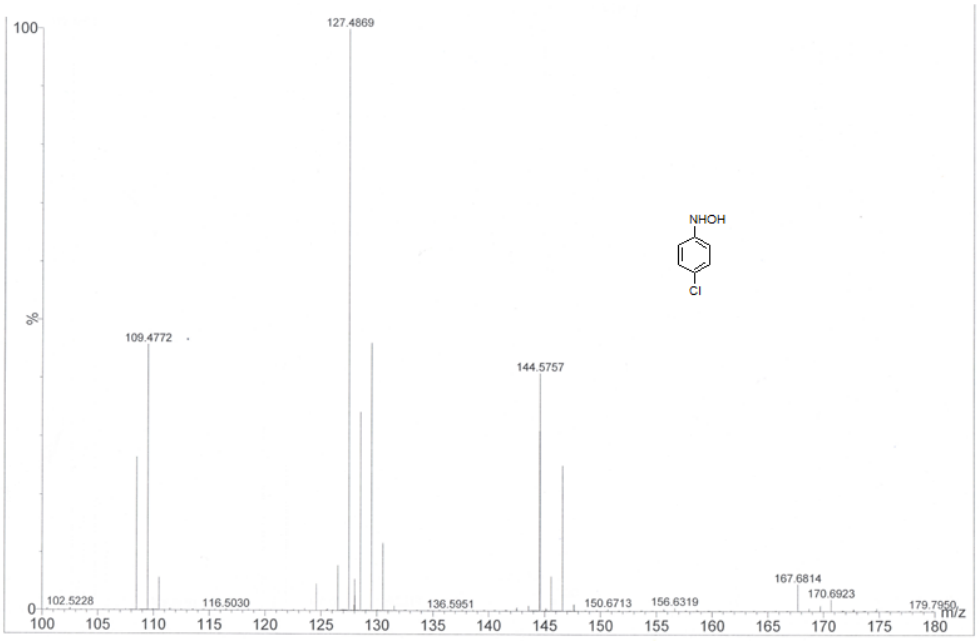
4-chlorophenylhydroxylamine (**4**) (^{1}H NMR in MeOD)



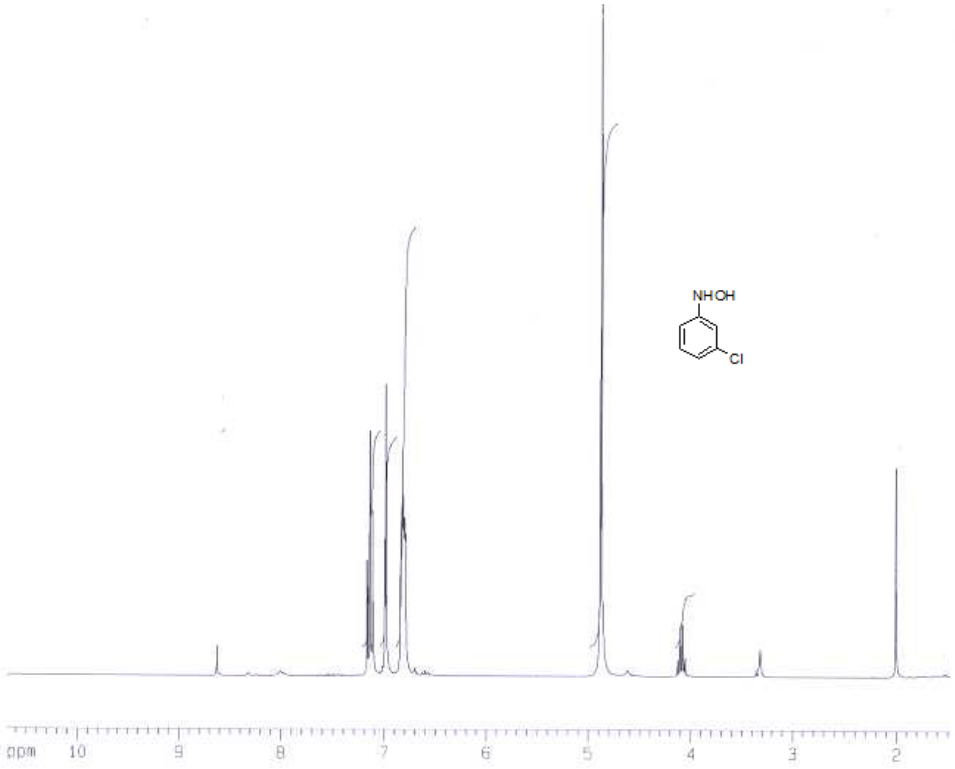
4-chlorophenylhydroxylamine (**4**) (^{13}C NMR in MeOD)



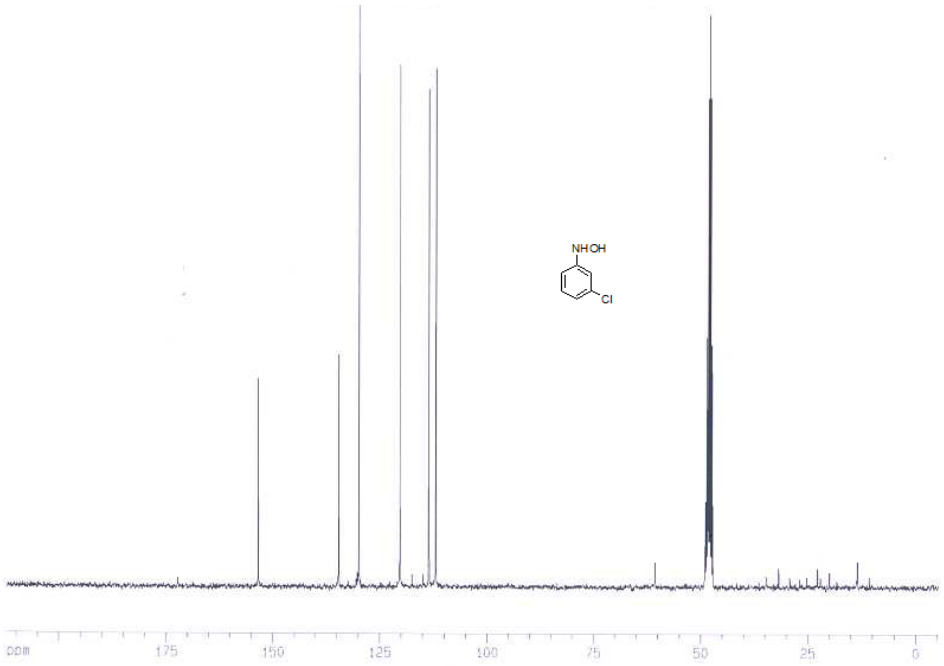
4-chlorophenylhydroxylamine (**4**) (ESIMS in CH_3CN/H_2O (1:1))



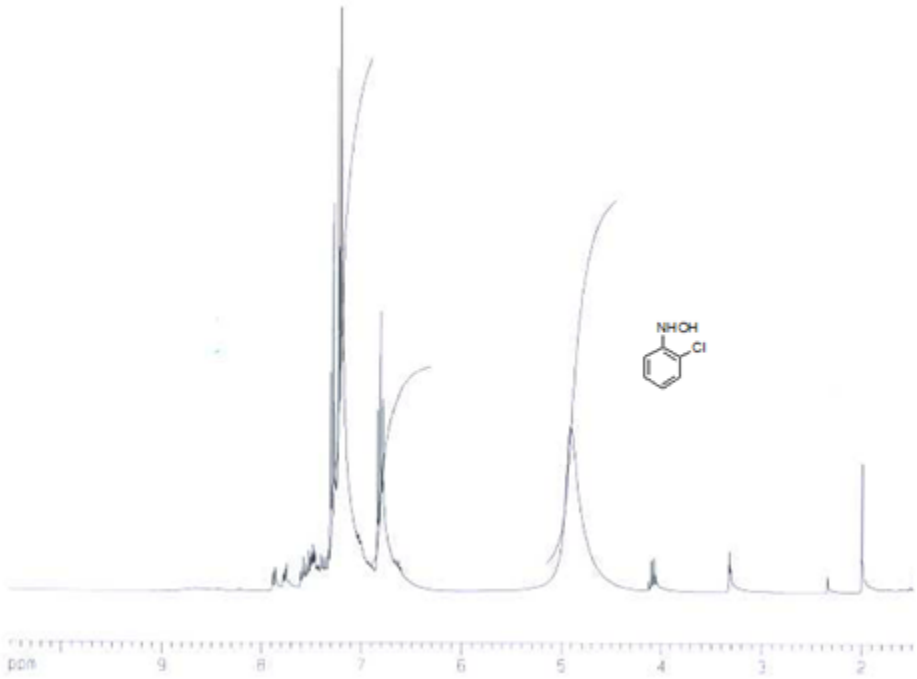
3-chlorophenylhydroxylamine (**5**) (^{1}H NMR in MeOD)



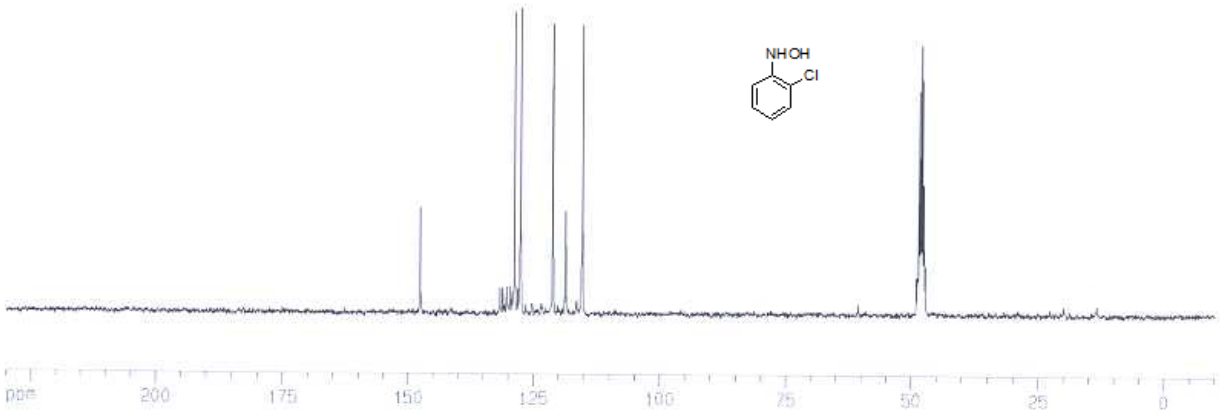
3-chlorophenylhydroxylamine (**5**) (^{13}C NMR in MeOD)



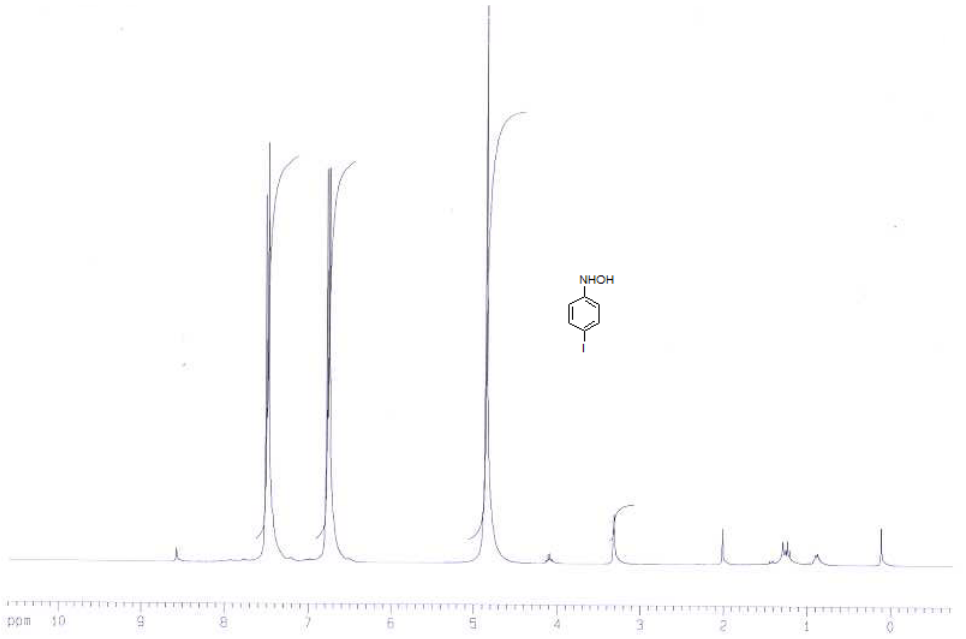
2-chlorophenylhydoxylamine (**6**) (^{1}H NMR in MeOD)



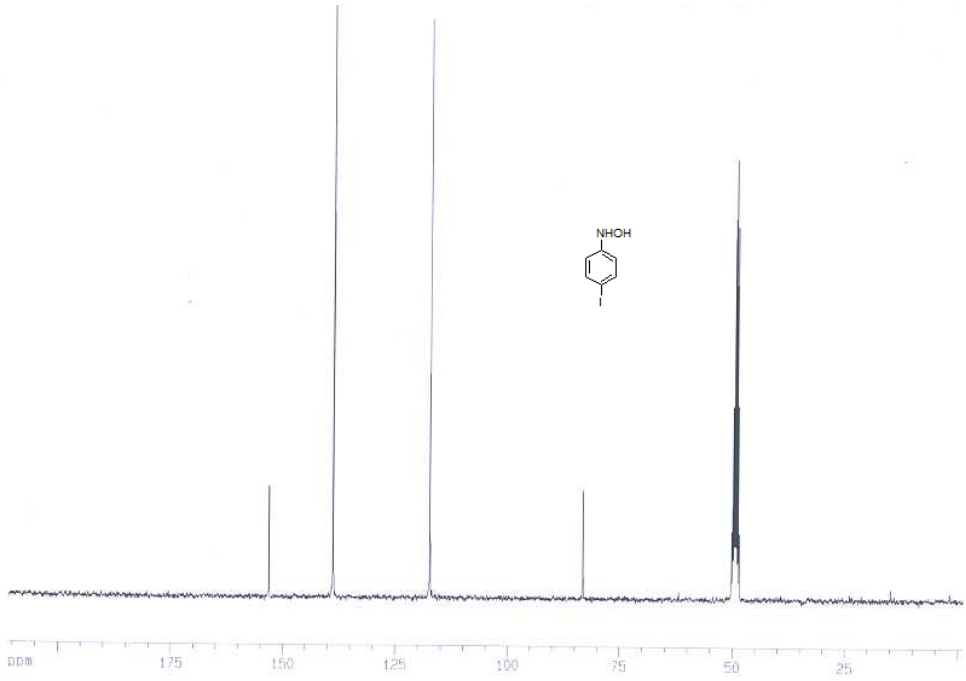
2-chlorophenylhydoxylamine (**6**) (^{13}C NMR in MeOD)



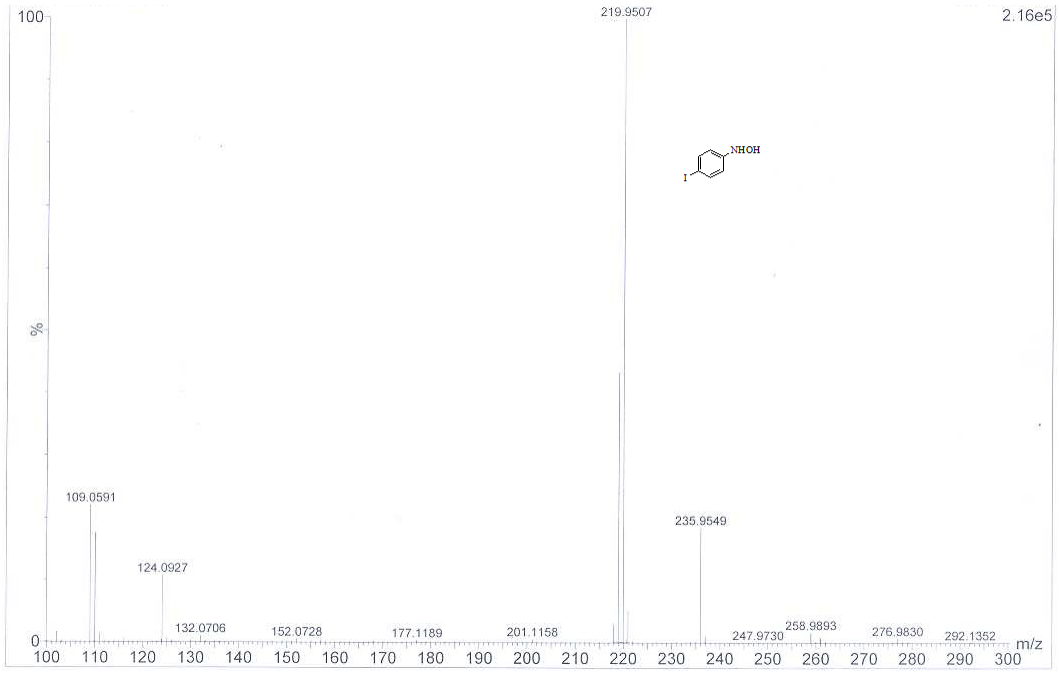
4-Iodophenylhydroxylamine (**7**) (^{1}H NMR in MeOD)



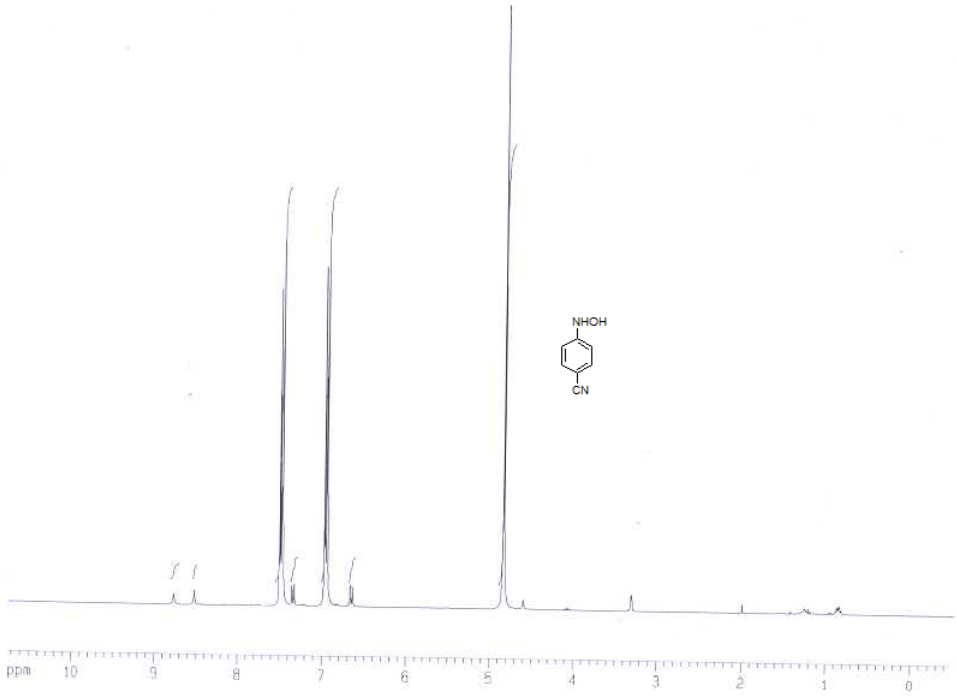
4-Iodophenylhydroxylamine (**7**) (^{13}C NMR in MeOD)



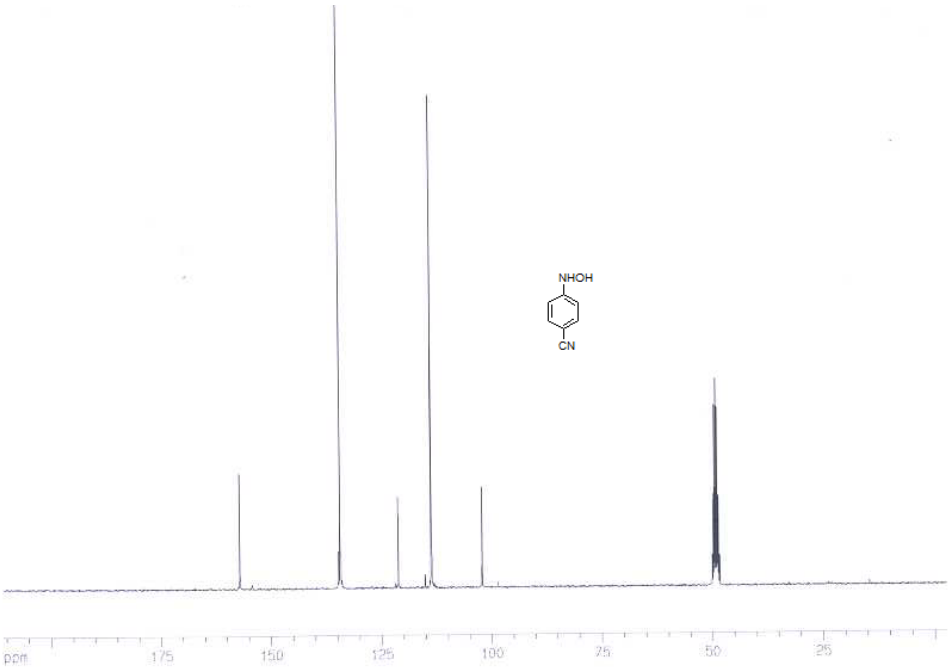
4-Iodophenylhydroxylamine (**7**) (ESIMS in CH_3CN/H_2O (1:1))



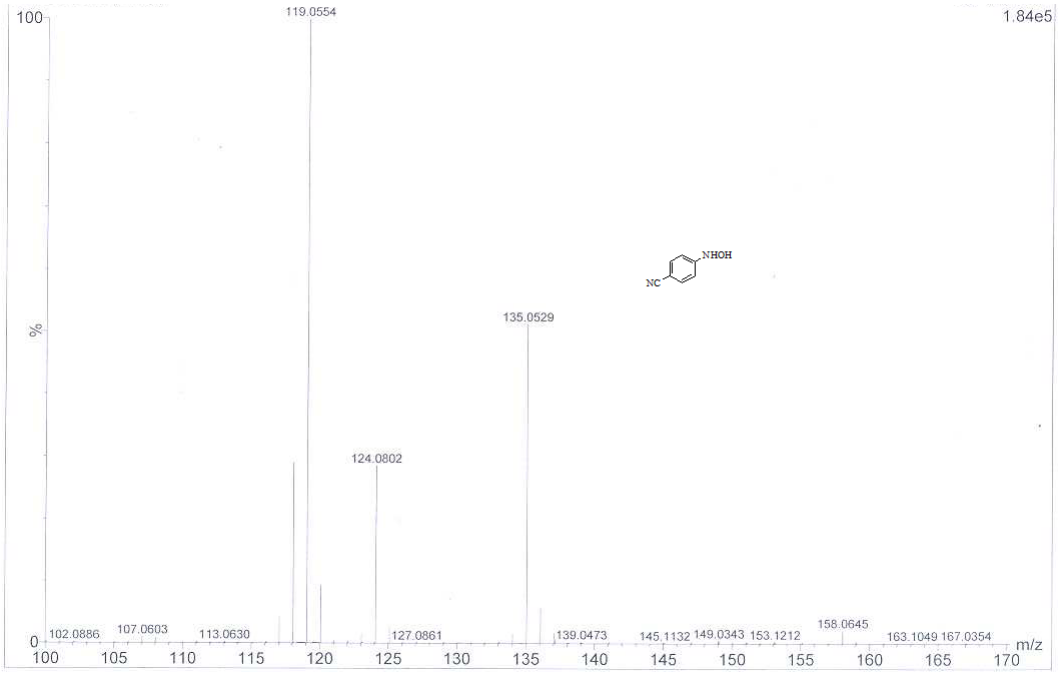
4-Cyanophenylhydroxylamine (**8**) (^{1}H NMR in MeOD)



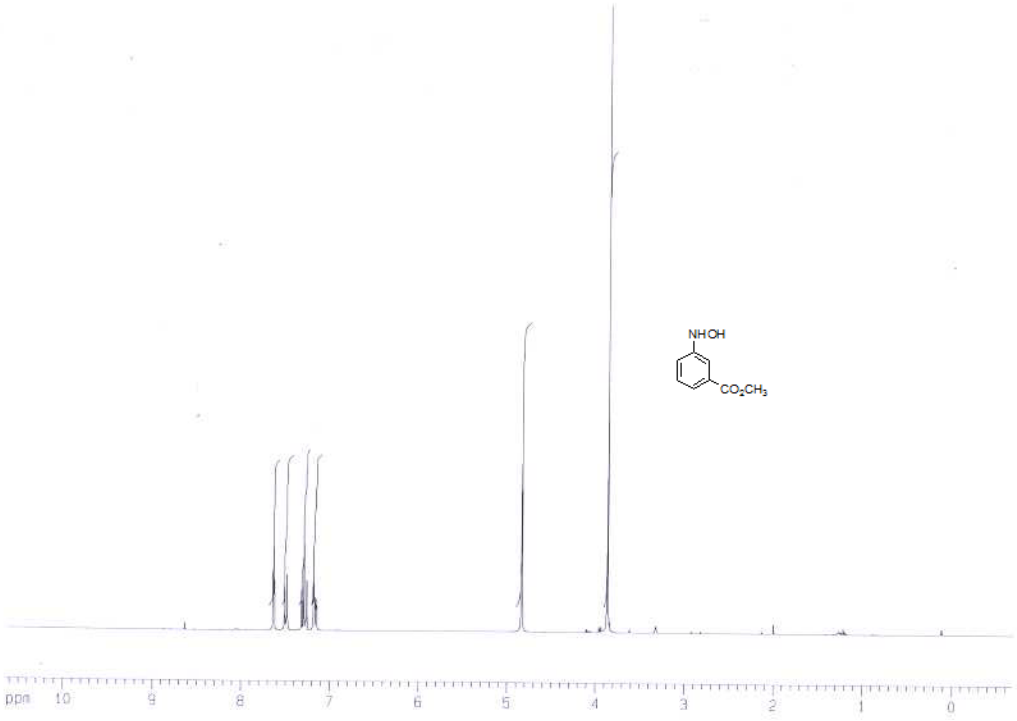
4-Cyanophenylhydroxylamine (**8**) (^{13}C NMR in MeOD)



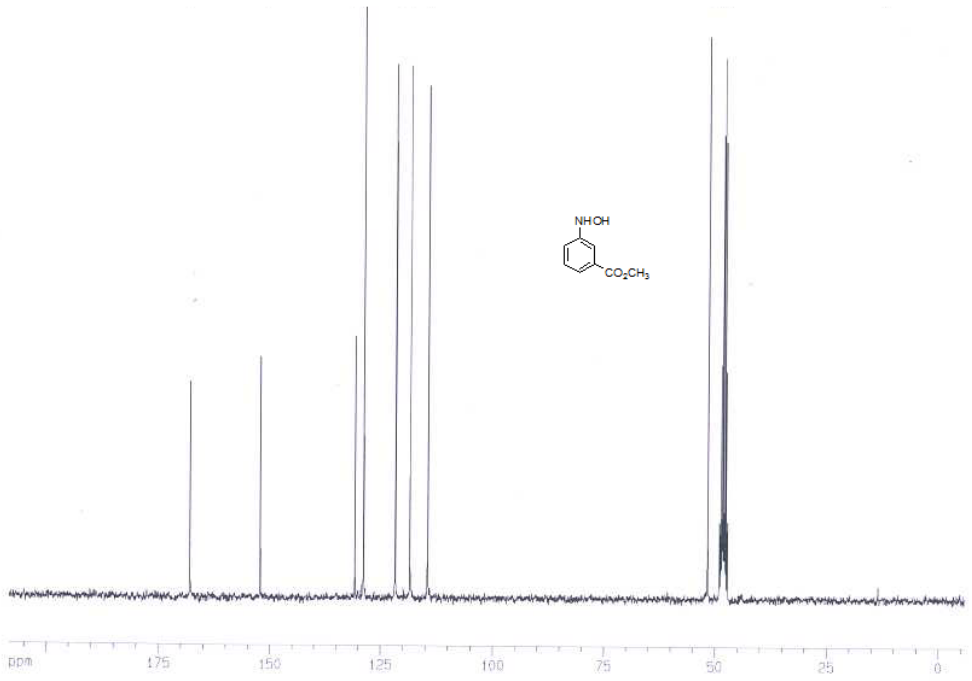
4-Cyanophenylhydroxylamine (**8**) (ESIMS in CH_3CN/H_2O (1:1))



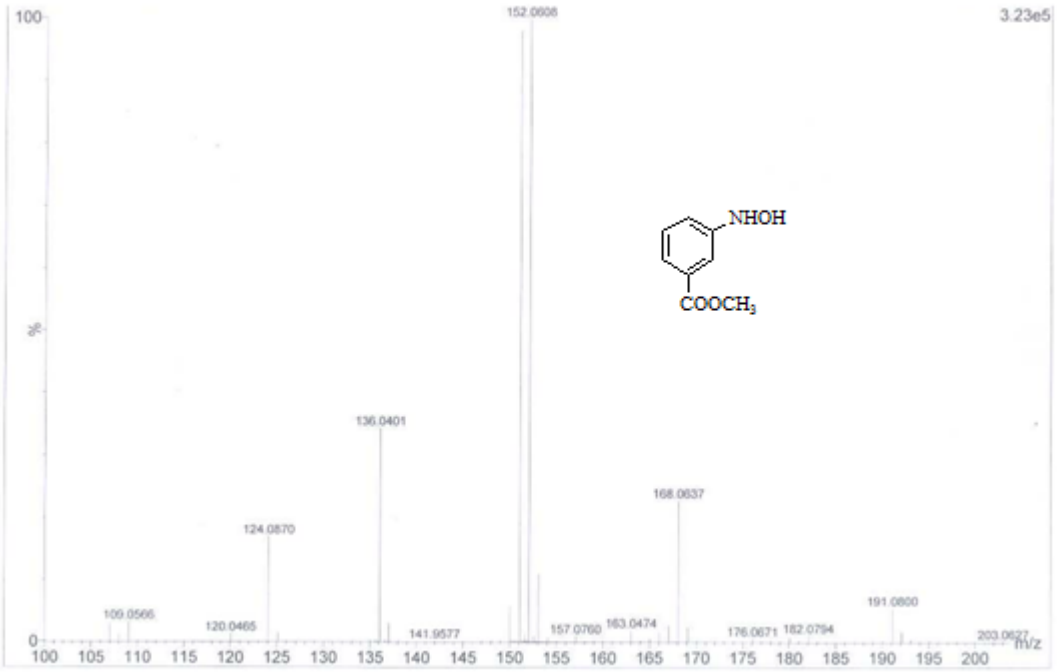
3-carbomethoxyphenylhydroxylamine (**9**) (^{1}H NMR in MeOD)



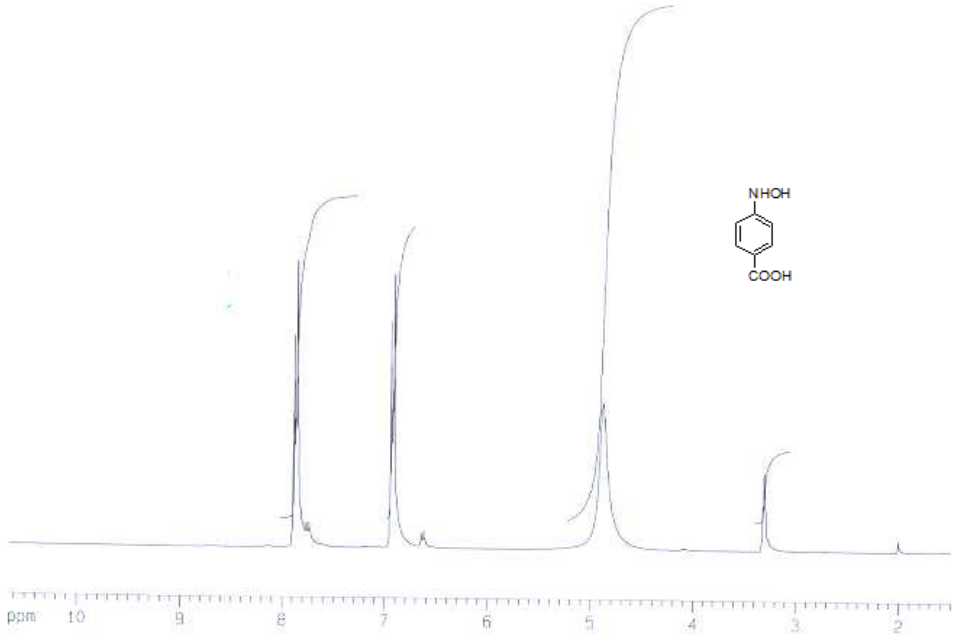
3-carbomethoxyphenylhydroxylamine (**9**) (^{13}C NMR in MeOD)



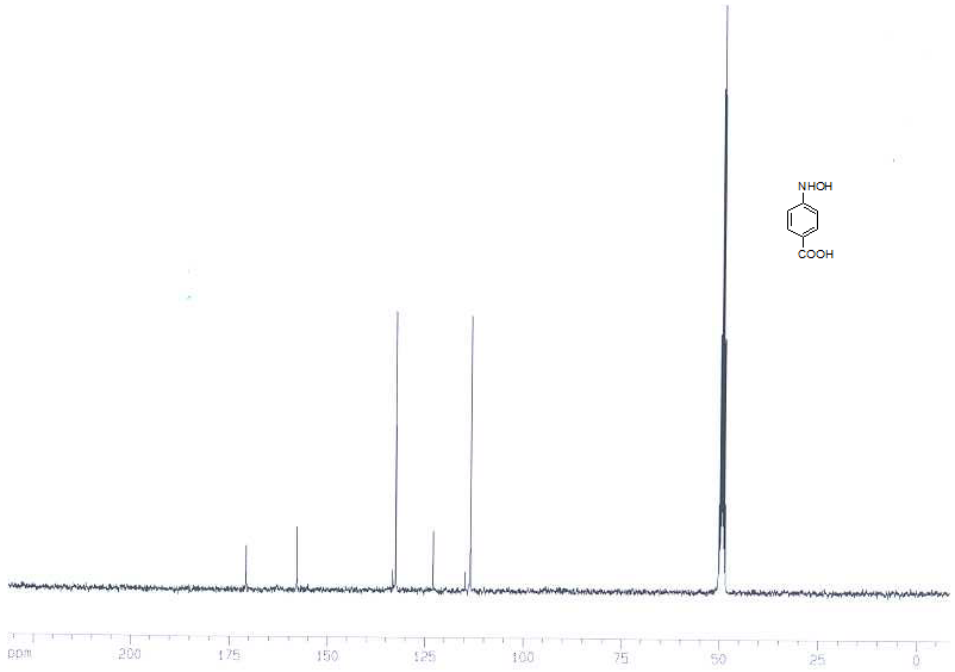
3-carbomethoxyphenylhydroxylamine (**9**) (ESIMS in CH_3CN/H_2O (1:1))



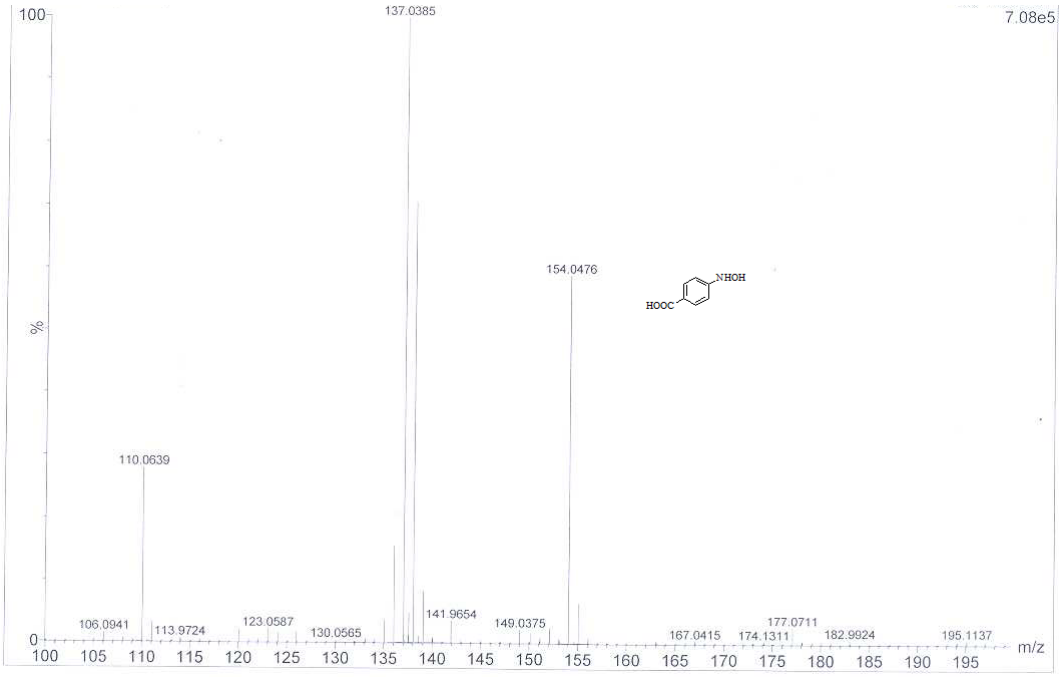
4-carboxyphenylhydroxylamine (**10**) (^{1}H NMR in MeOD)



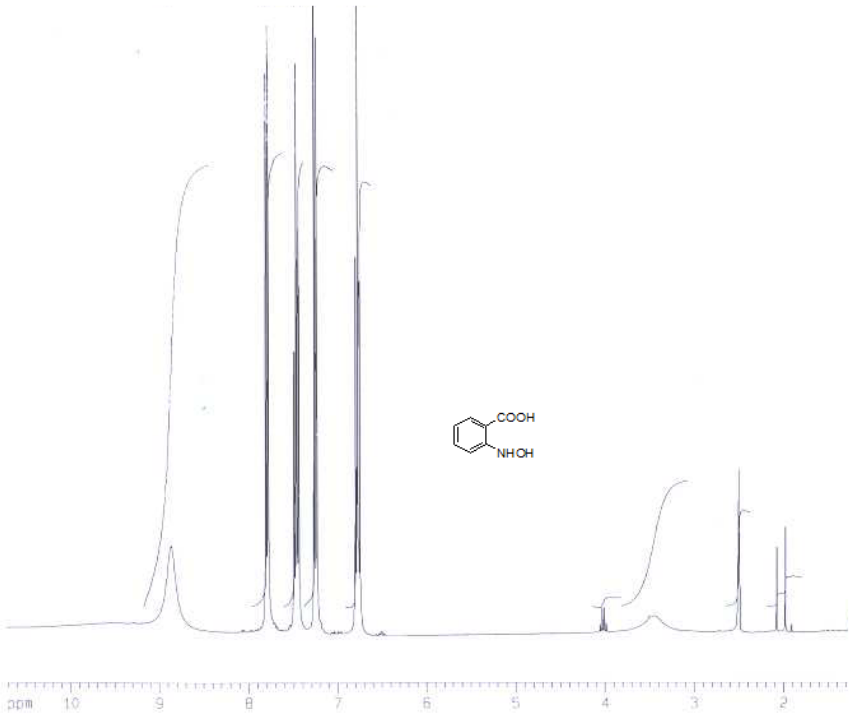
4-carboxyphenylhydroxylamine (**10**) (^{13}C NMR in MeOD)



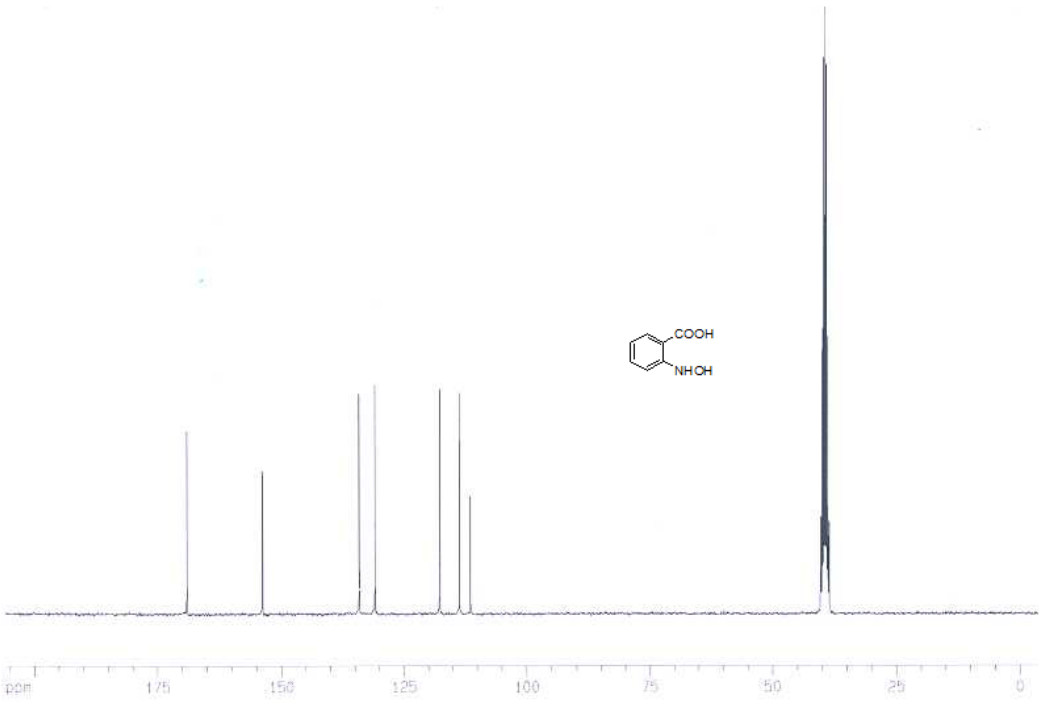
4-carboxyphenylhydroxylamine (**10**) (ESIMS in CH_3CN/H_2O (1:1))



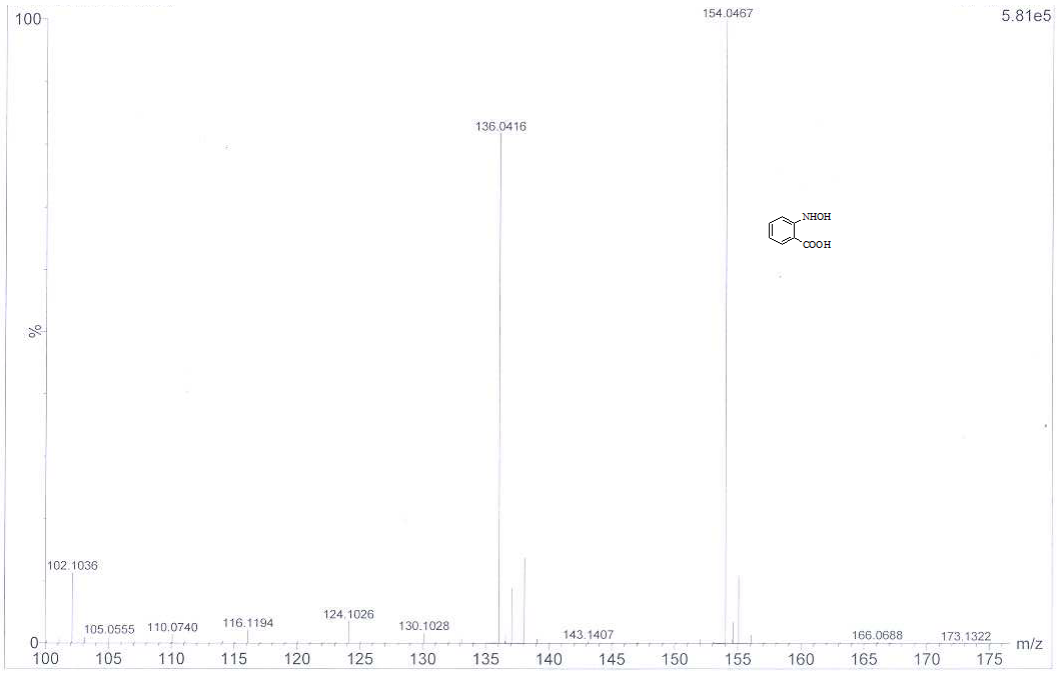
2-(hydroxyamino)benzoic acid (**11**) (^{1}H NMR in DMSO-d_6)



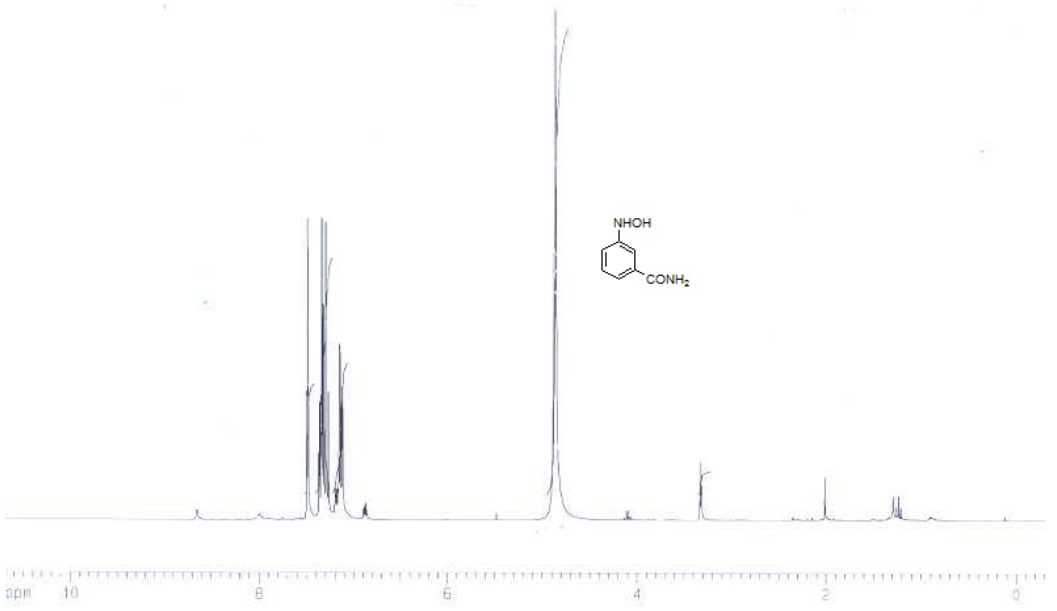
2-(hydroxyamino)benzoic acid (**11**) (^{13}C NMR in DMSO-d_6)



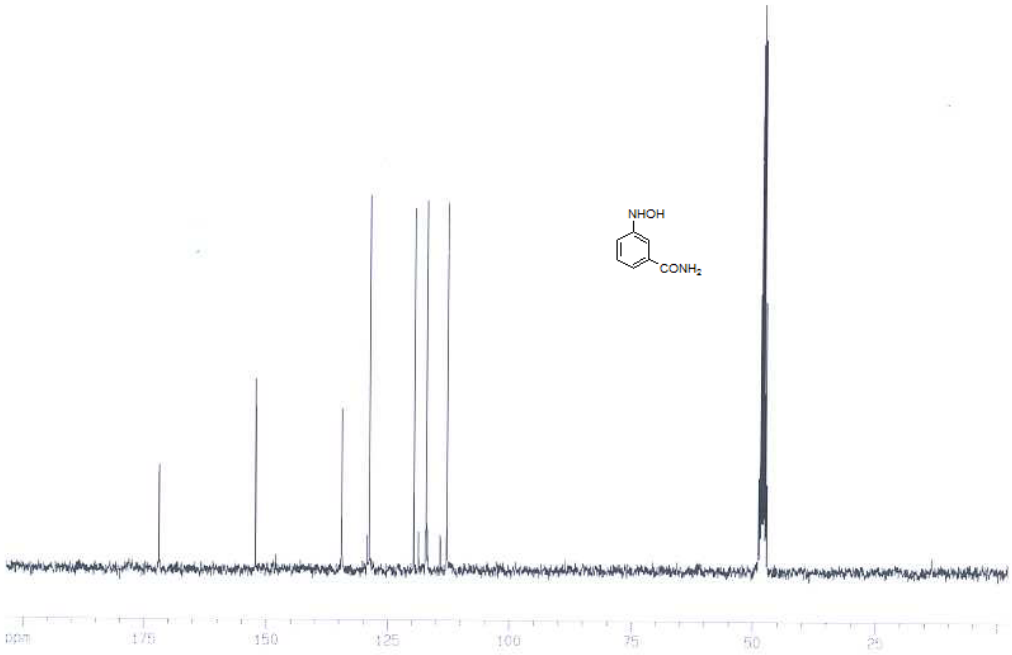
2-(hydroxyamino)benzoic acid (**11**) (ESIMS in CH_3CN/H_2O (1:1))



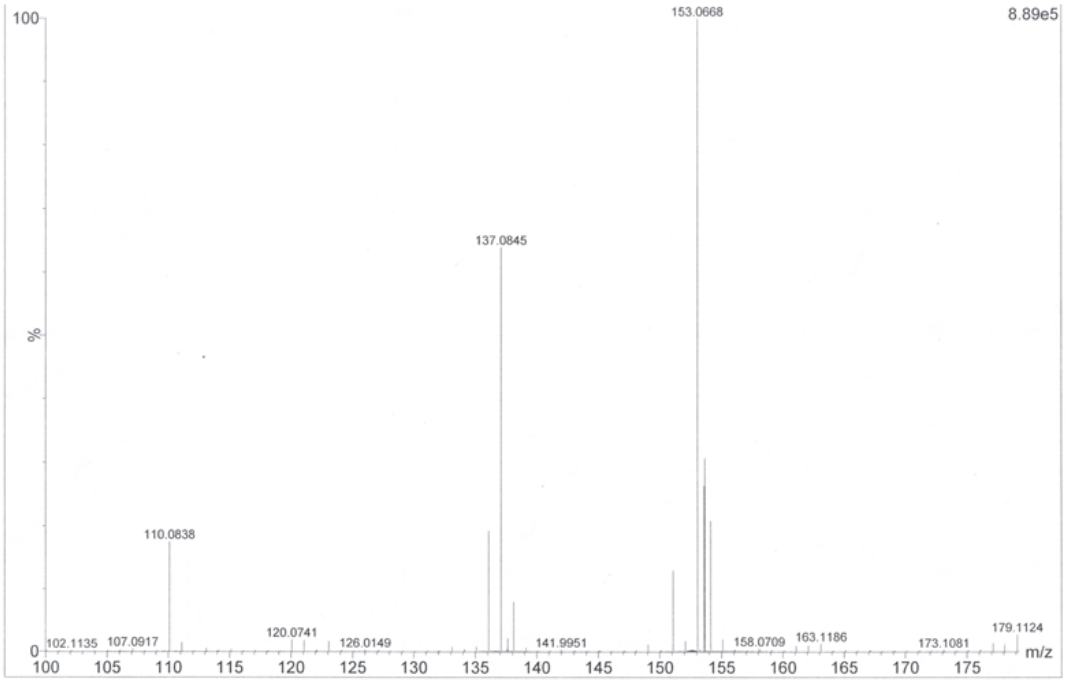
3-(hydroxyamino)benzamide (**12**) (^{1}H NMR in MeOD)



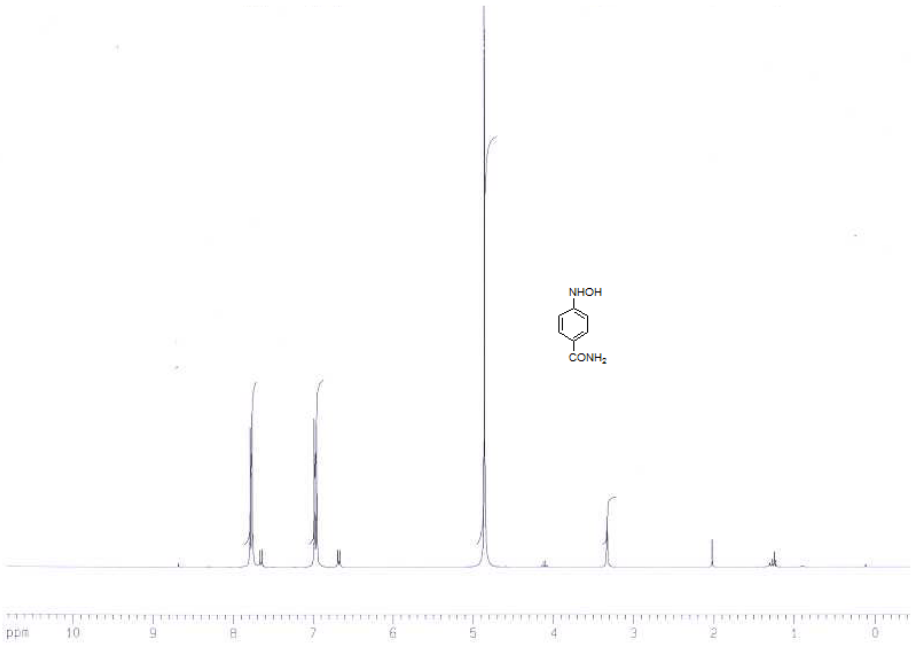
3-(hydroxyamino)benzamide (**12**) (^{13}C NMR in MeOD)



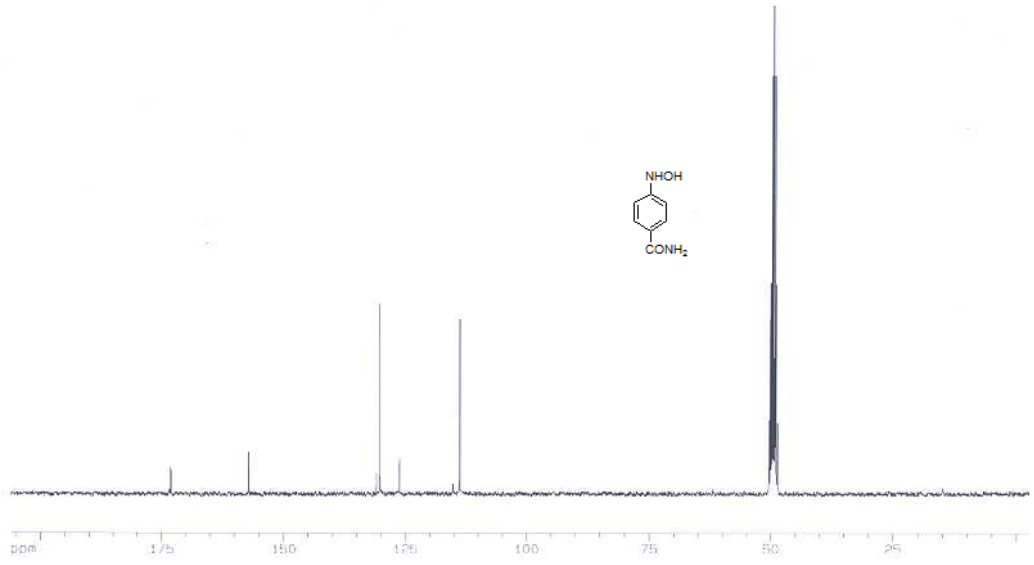
3-(hydroxyamino)benzamide (**12**) (ESIMS in CH_3CN/H_2O (1:1))



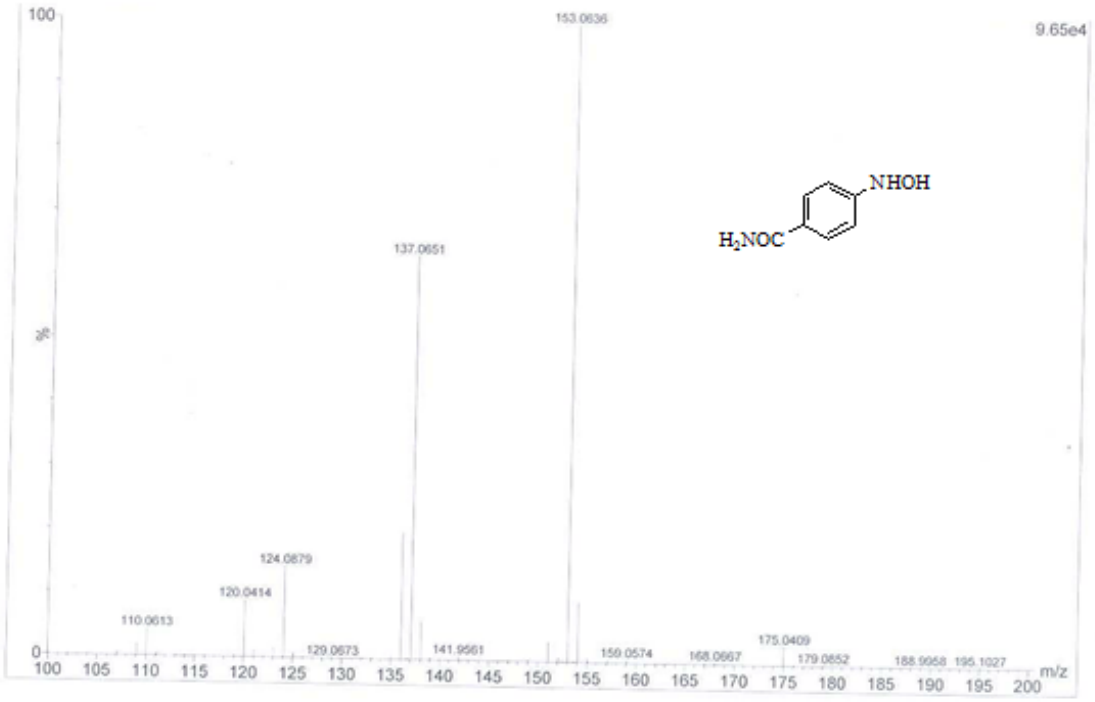
4-Carbaminophenylhydroxylamine (**13**) (^{1}H NMR in MeOD)



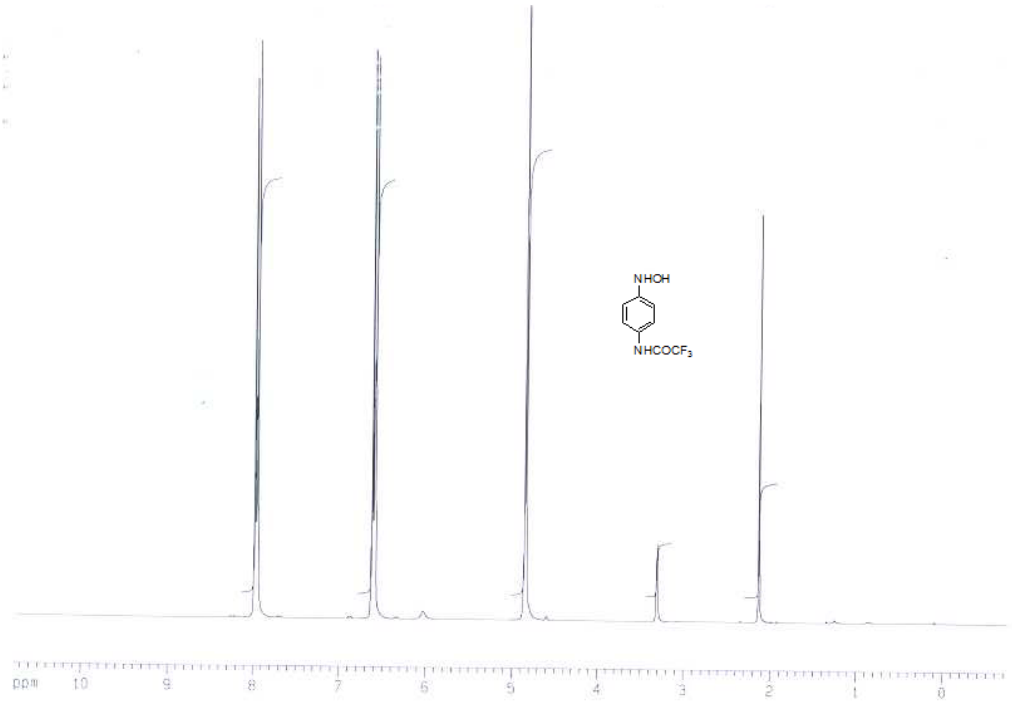
4-Carbaminophenylhydroxylamine (**13**) (^{13}C NMR in MeOD)



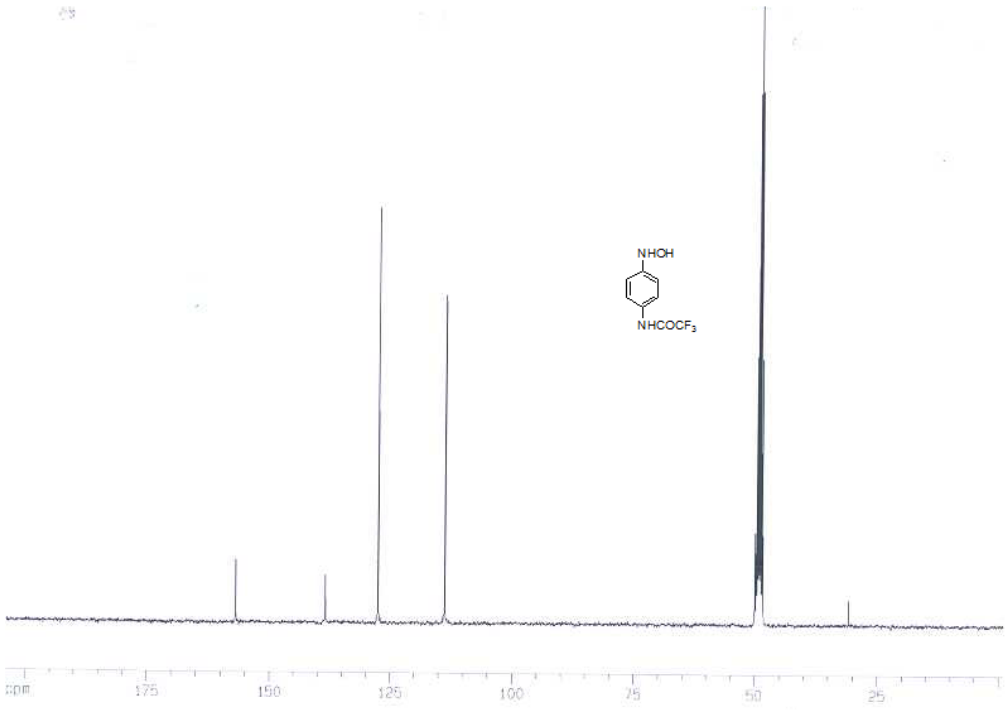
4-Carbaminophenylhydroxylamine (**13**) (ESIMS in CH_3CN/H_2O (1:1))



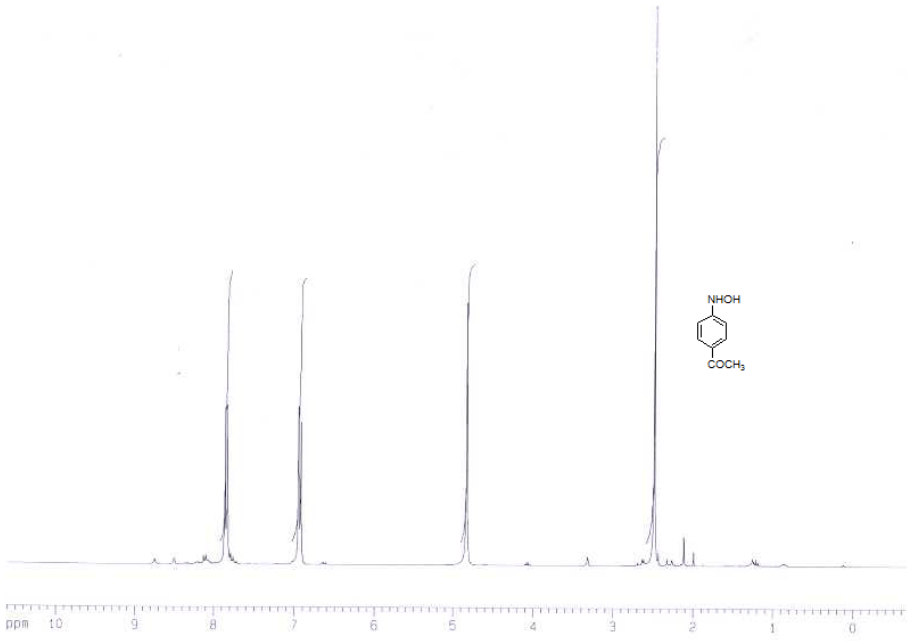
2,2,2-trifluoro-N-(4-(hydroxyamino)phenyl)acetamide (**14**) (^{1}H NMR in MeOD)



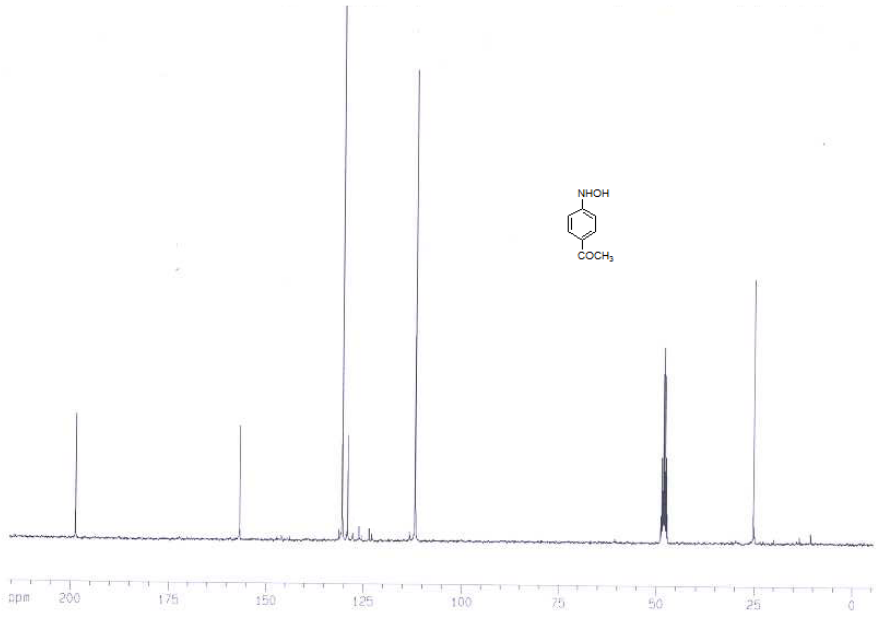
2,2,2-trifluoro-N-(4-(hydroxyamino)phenyl)acetamide (**14**) (^{13}C NMR in MeOD)



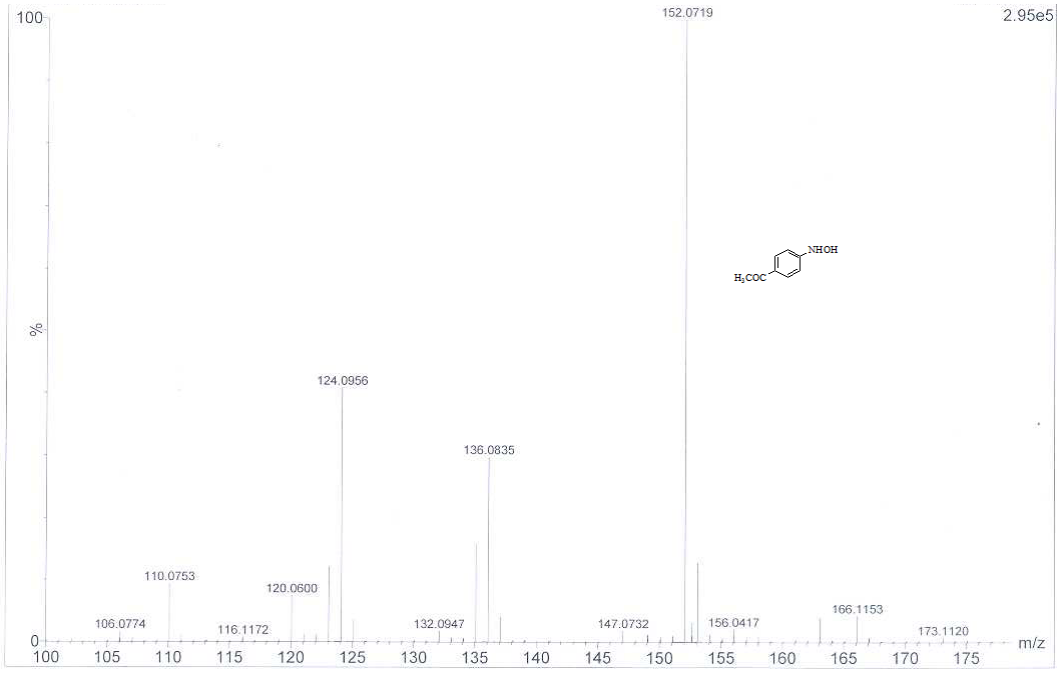
4-acetylphenylhydroxylamine (**15**) (^{1}H NMR in MeOD)



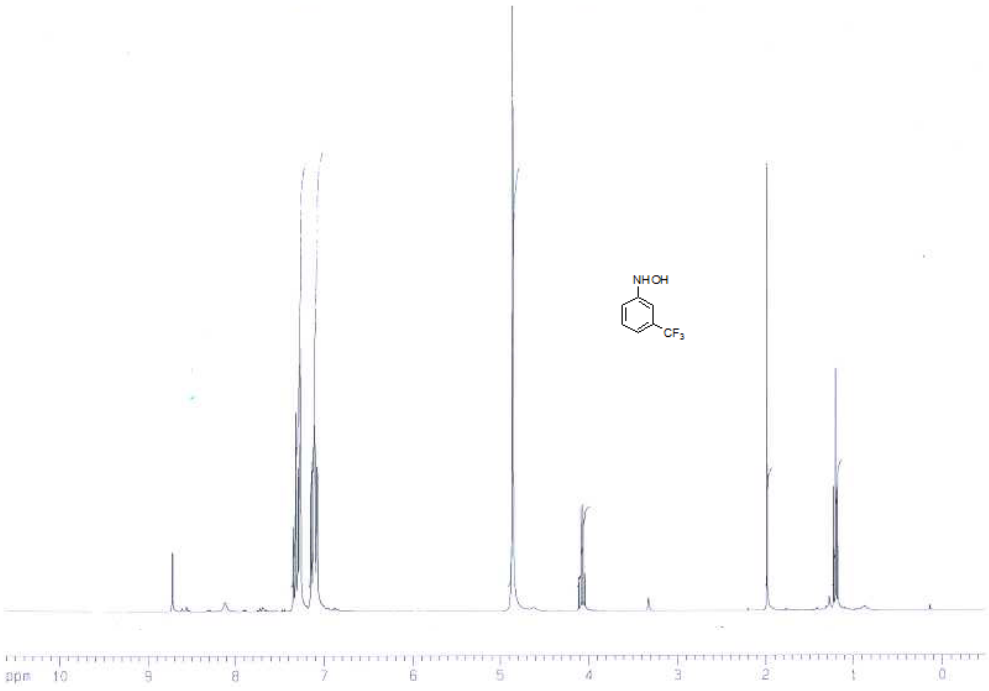
4-acetylphenylhydroxylamine (**15**) (^{13}C NMR in MeOD)



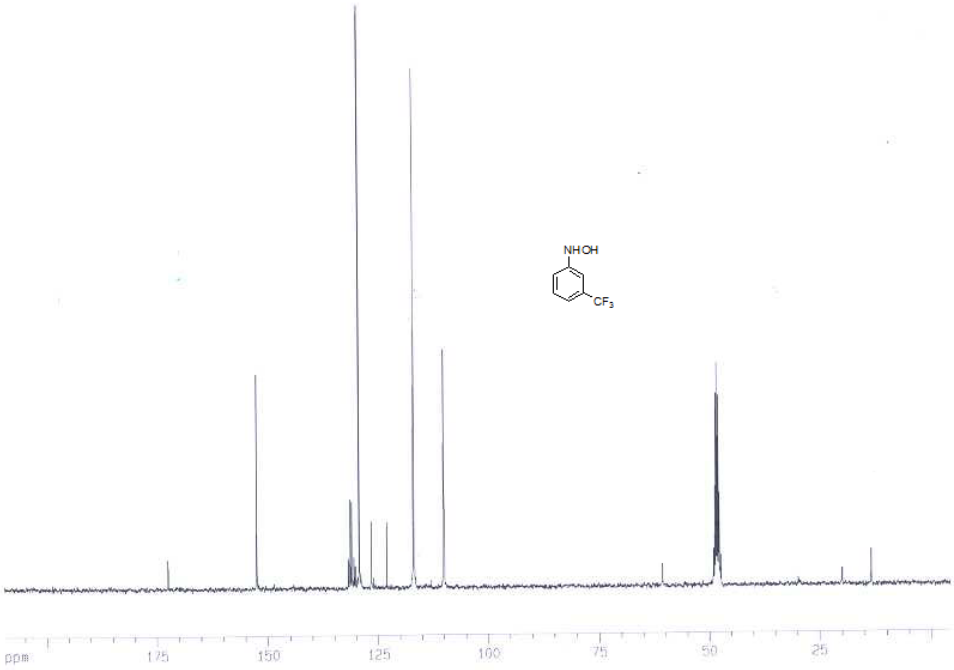
4-acetylphenylhydroxylamine (**15**) (ESIMS in CH_3CN/H_2O (1:1))



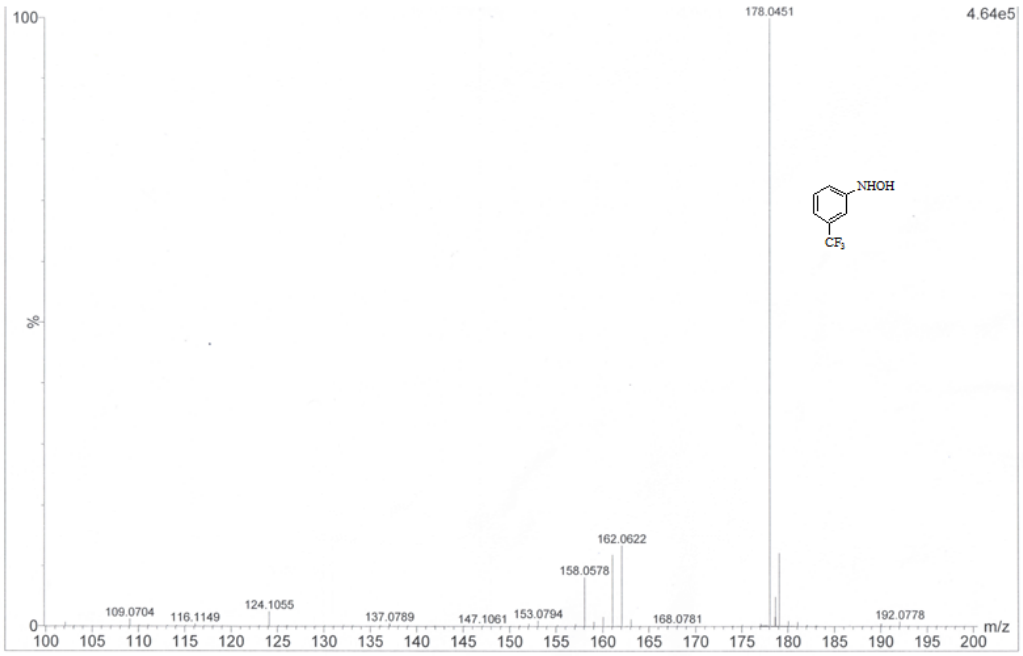
3-trifluoromethylphenylhydroxylamine (**16**) (^{1}H NMR in MeOD)



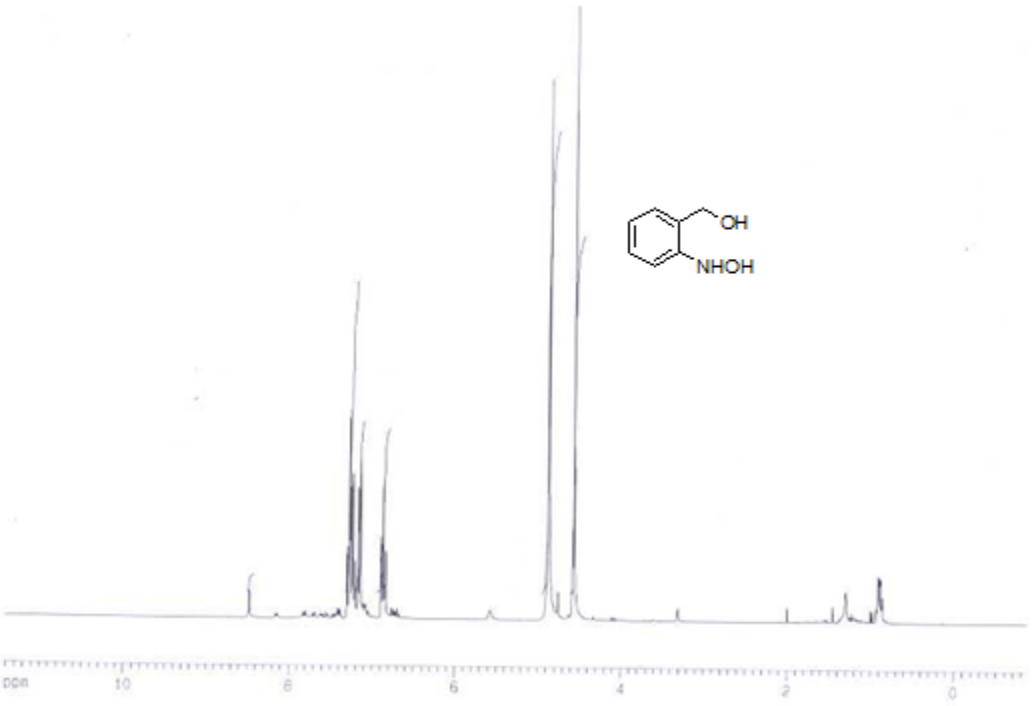
3-trifluoromethylphenylhydroxylamine (**16**) (^{13}C NMR in MeOD)



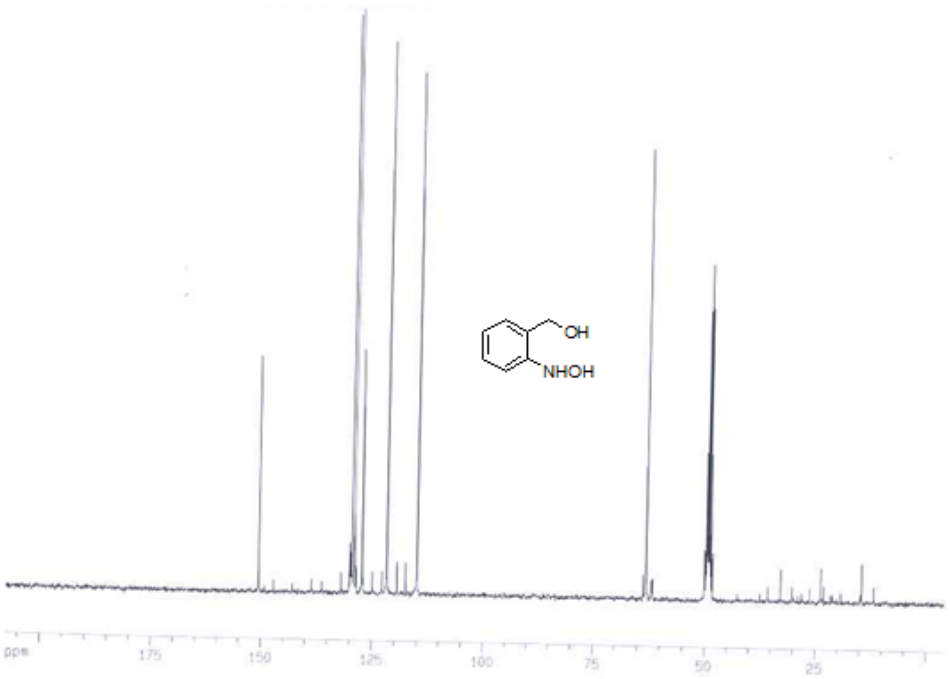
3-trifluoromethylphenylhydroxylamine (**16**) (ESIMS in CH_3CN/H_2O (1:1))



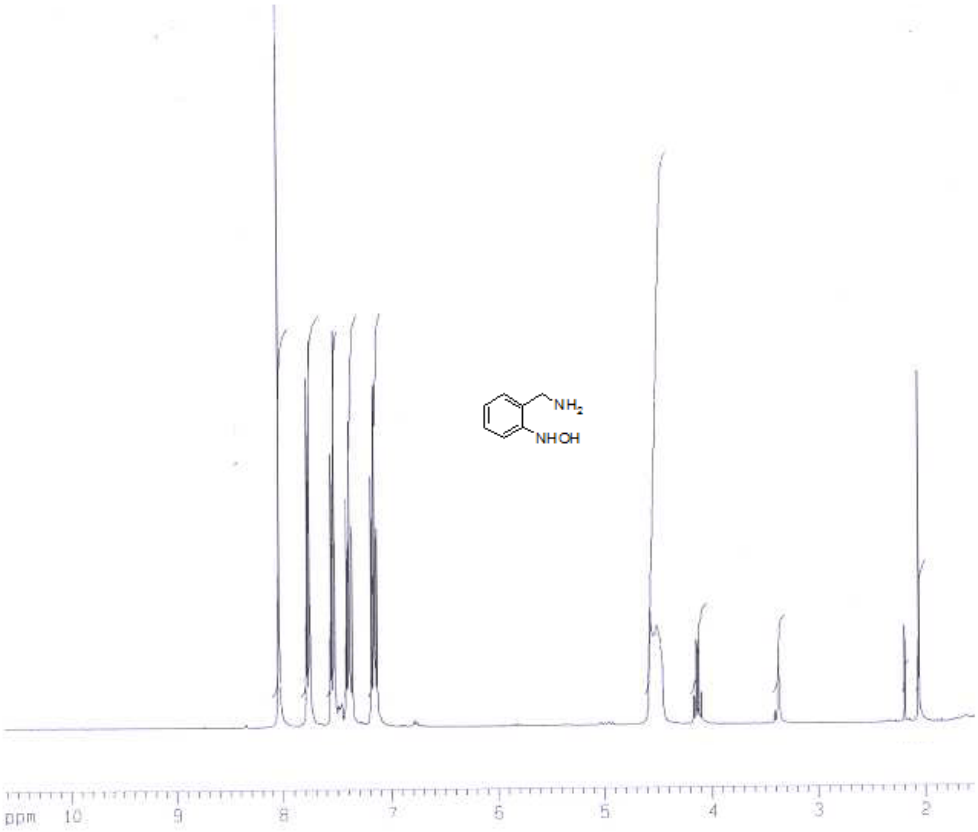
2-hydroxymethylphenylhydroxylamine (**17**) (^{1}H NMR in MeOD)



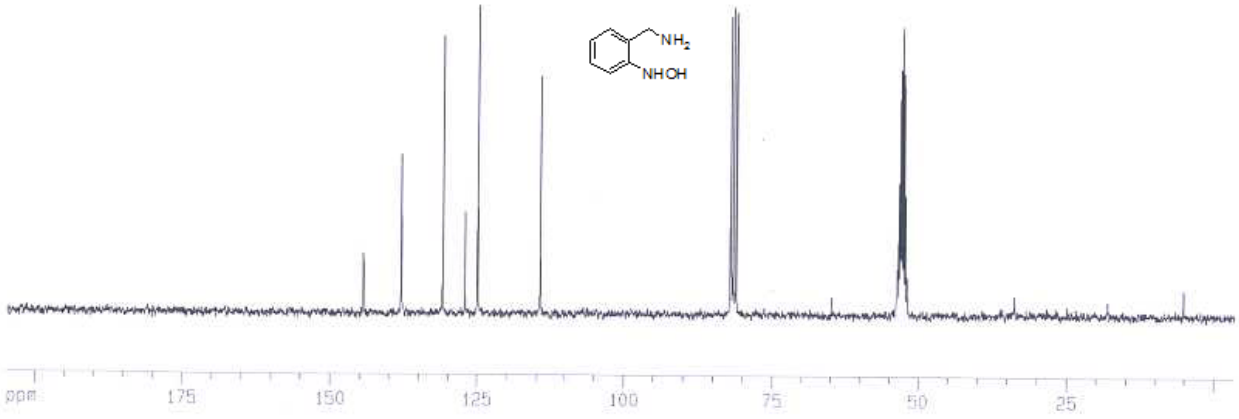
2-hydroxymethylphenylhydroxylamine (**17**) (^{13}C NMR in MeOD)



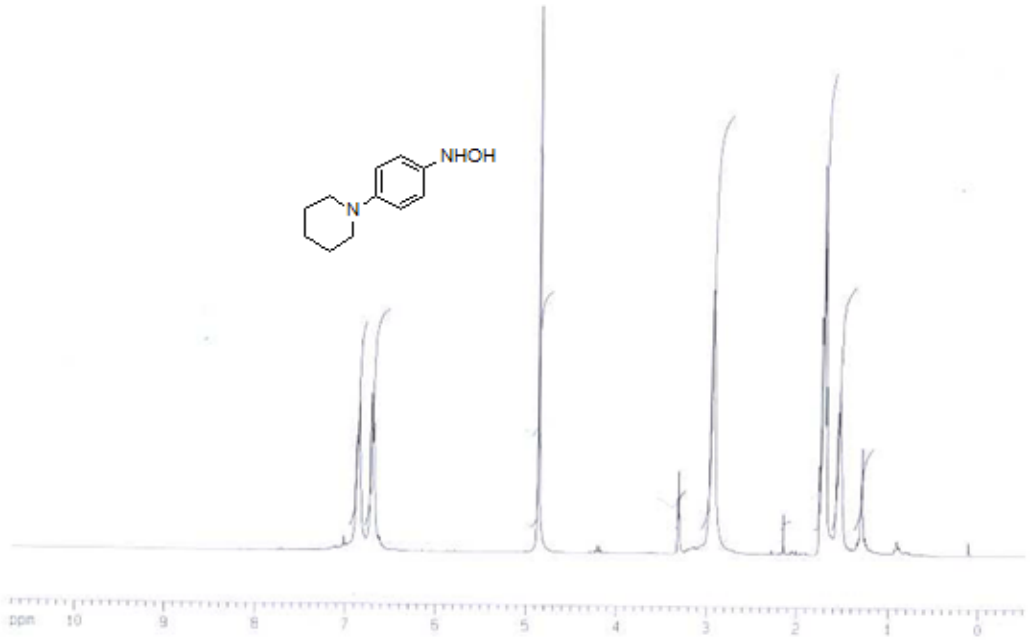
2-(aminomethyl)-N-hydroxybenzenamine (**18**) (^{1}H NMR in $CDCl_3$/MeOD (1:1))



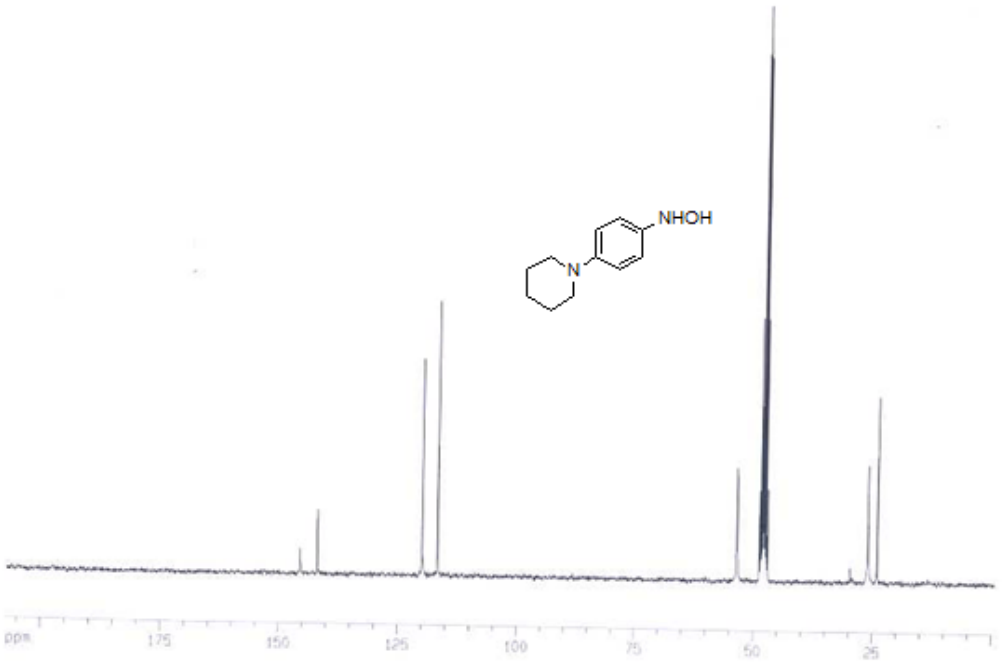
2-(aminomethyl)-N-hydroxybenzenamine (**18**) (^{13}C NMR in $CDCl_3$/MeOD (1:1))



N-hydroxy-4-(piperidin-1-yl)benzenamine (**19**) (^{1}H NMR in MeOD)

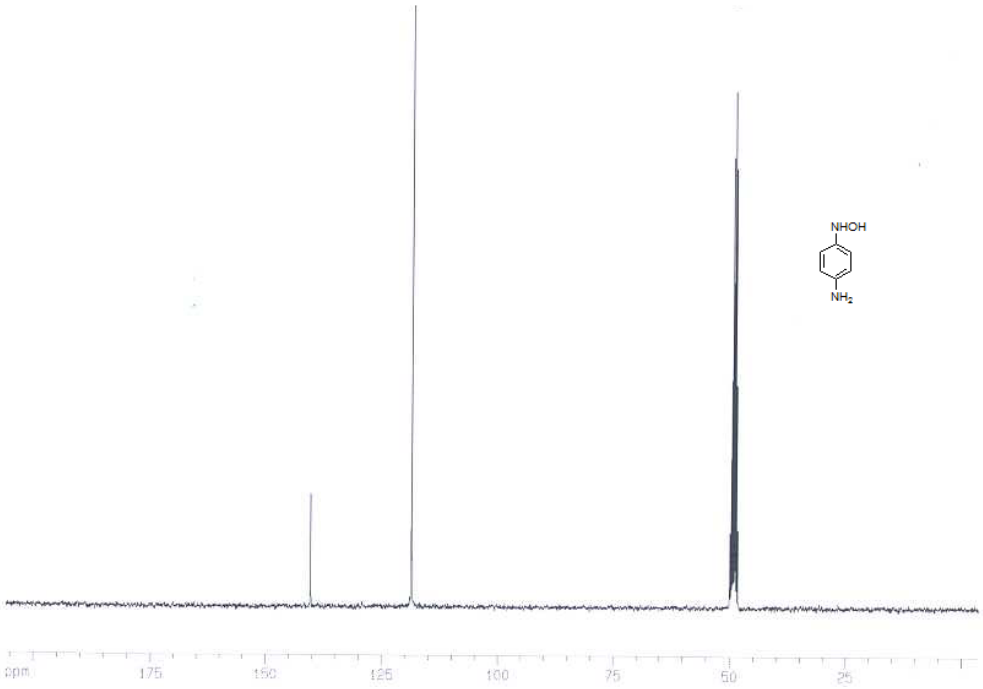


N-hydroxy-4-(piperidin-1-yl)benzenamine (**19**) (^{13}C NMR in MeOD)

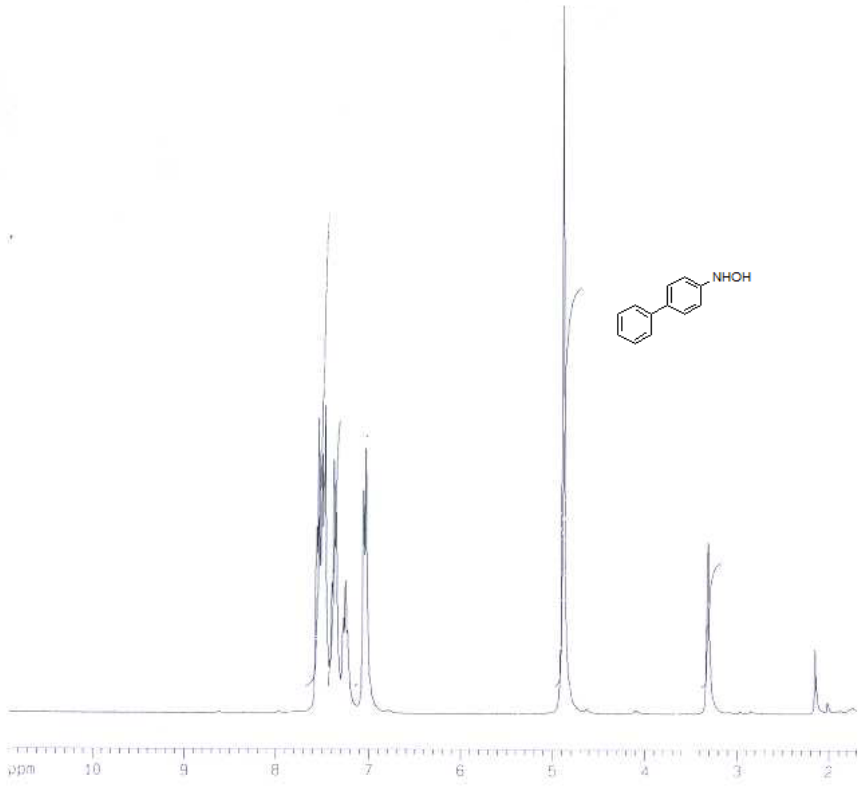


4-aminophenylhydroxylamine (**20**) (^{1}H NMR in MeOD)

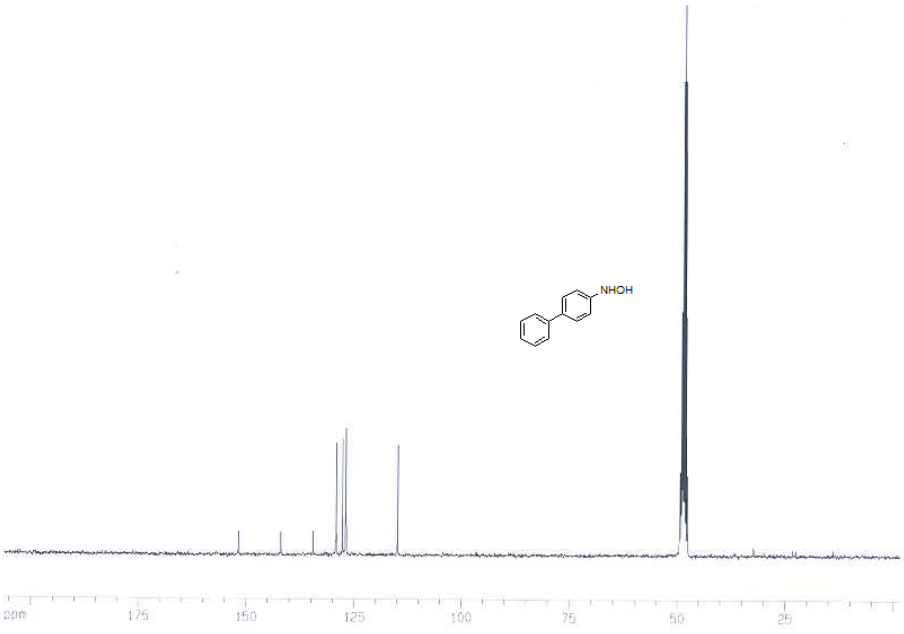
4-aminophenylhydroxylamine (**20**) (^{13}C NMR in MeOD)



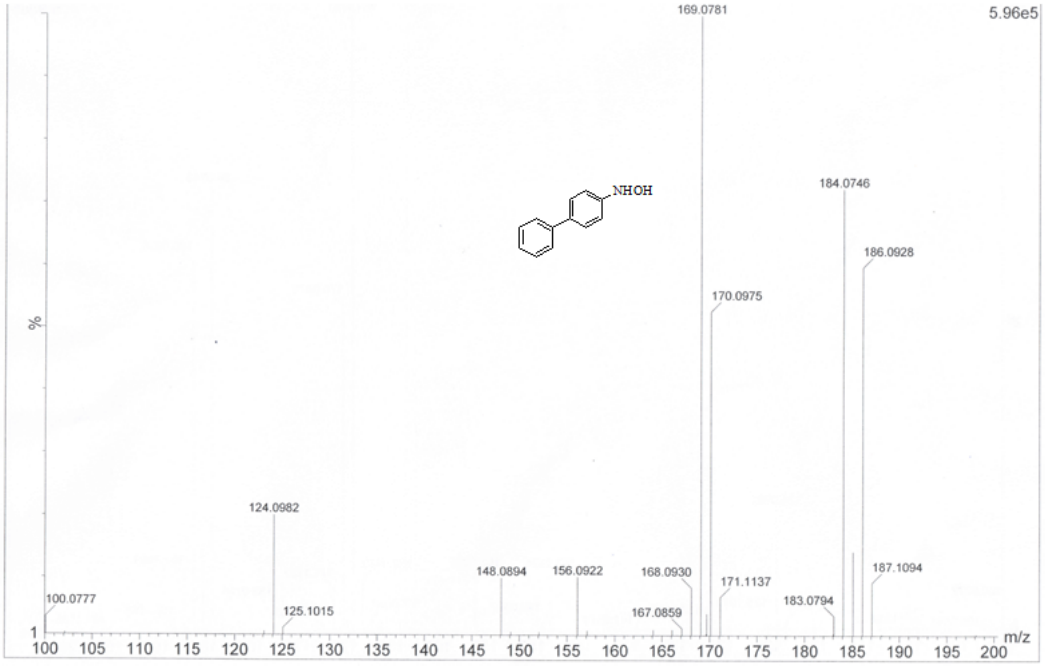
4-Phenylphenylhydroxylamine (**21**) (^{1}H NMR in MeOD)



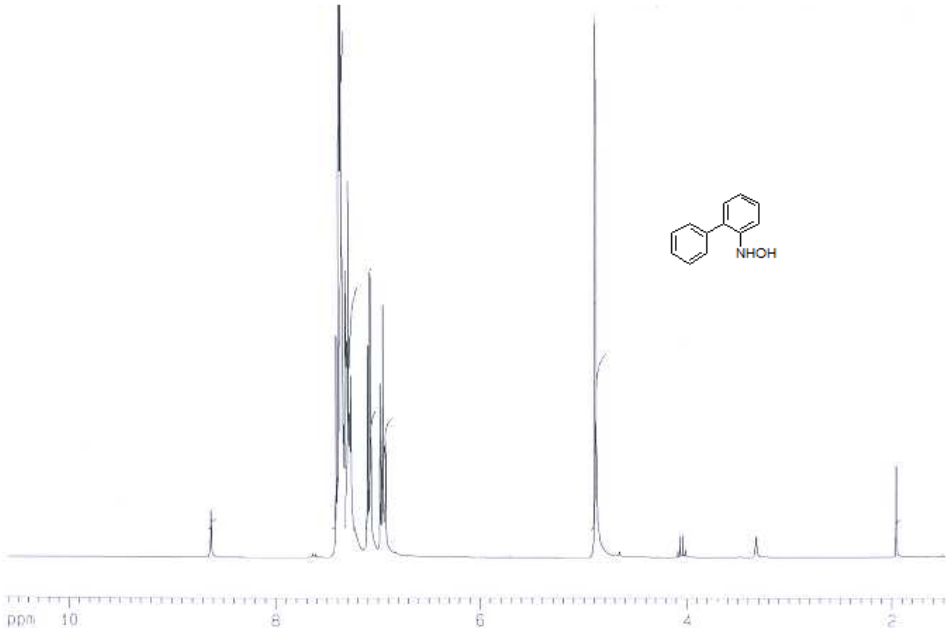
4-Phenylphenylhydroxylamine (**21**) (^{13}C NMR in MeOD)



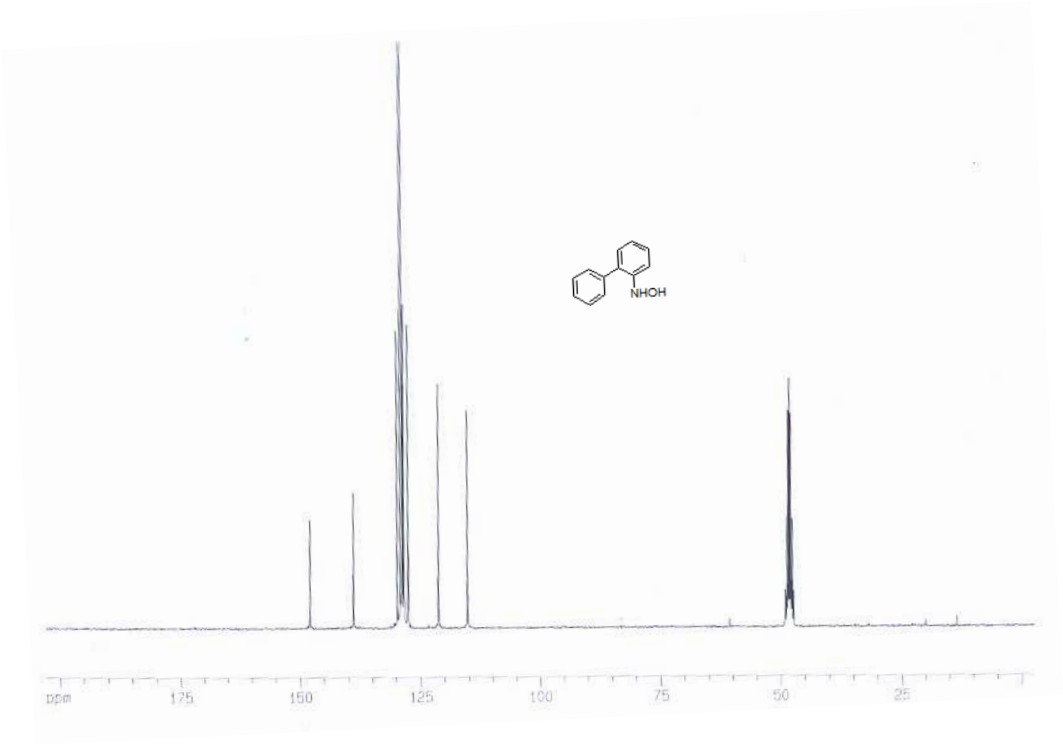
4-Phenylphenylhydroxylamine (**21**) (ESIMS in CH_3CN/H_2O (1:1))



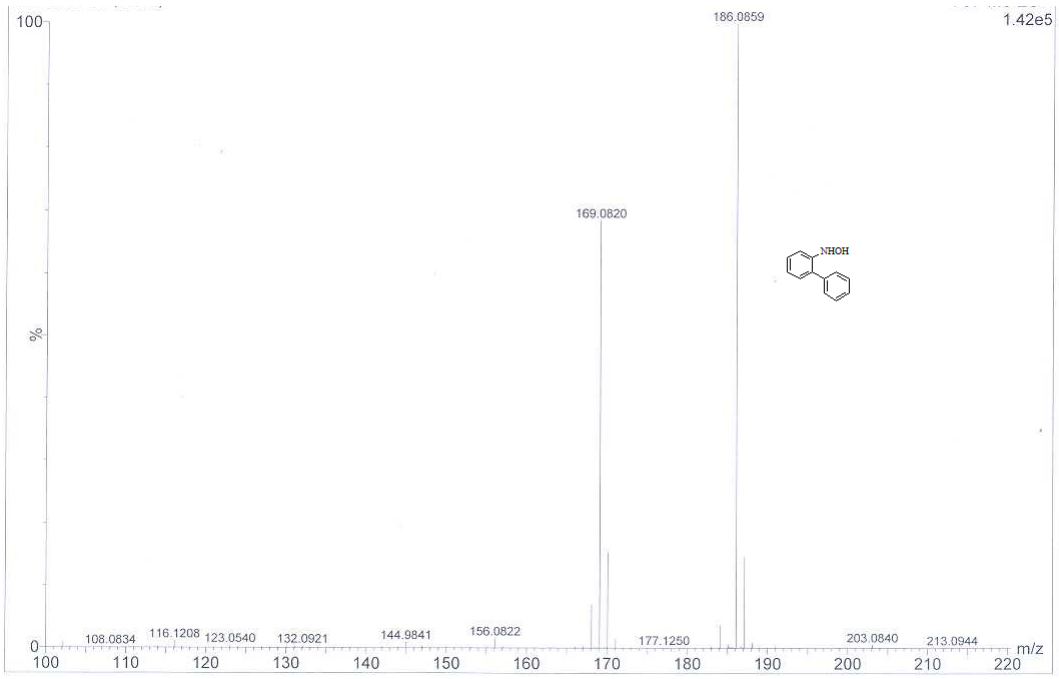
2-phenylphenylhydroxylamine (**22**) (^{1}H NMR in MeOD)



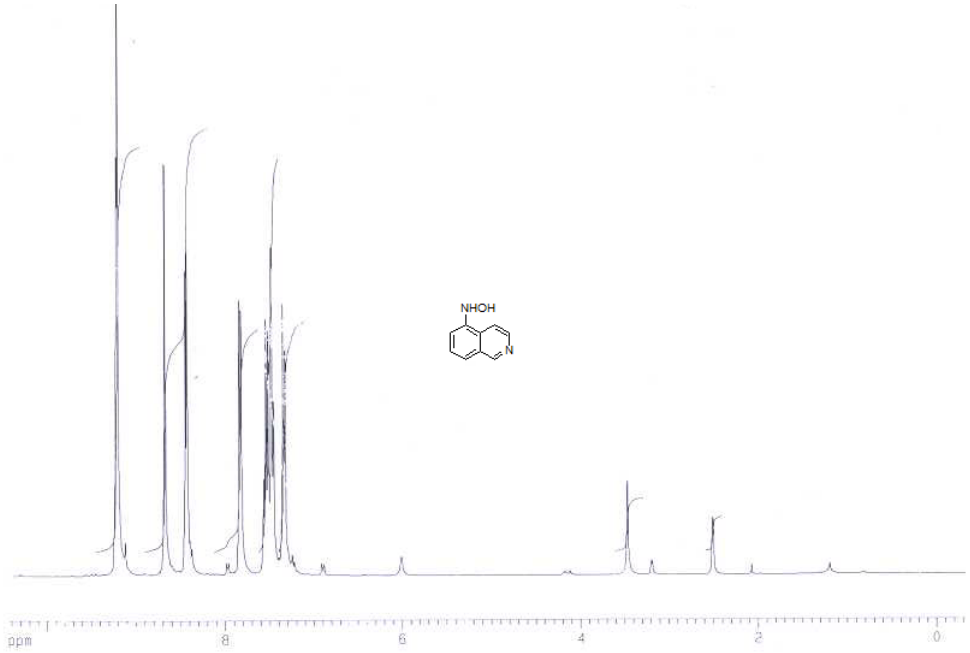
2-phenylphenylhydroxylamine (**22**) (^{13}C NMR in MeOD)



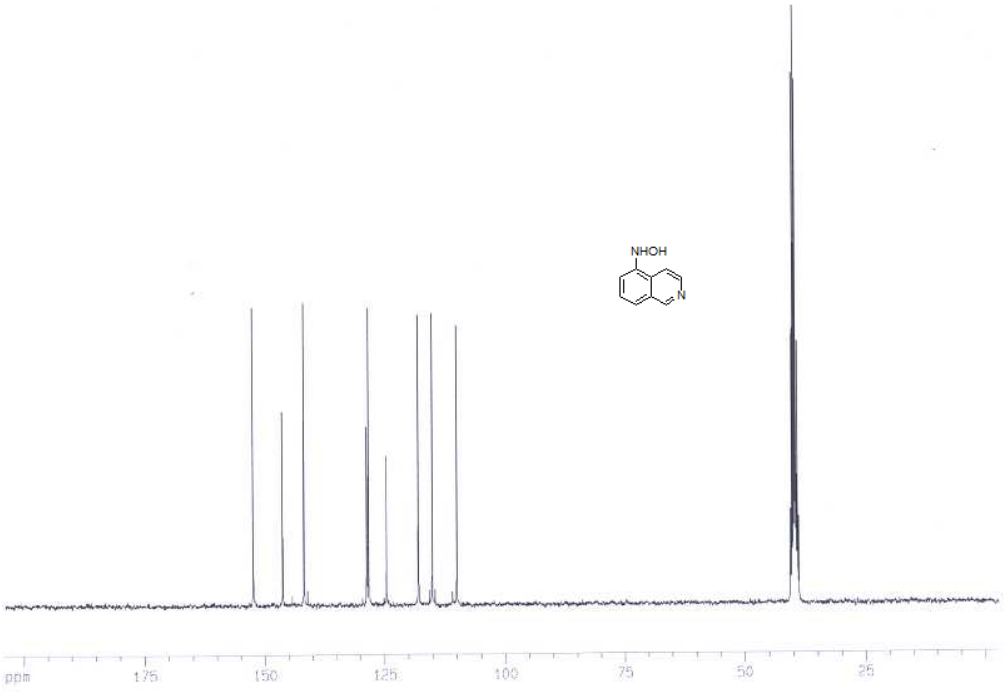
2-phenylphenylhydroxylamine (**22**) (ESIMS in CH_3CN/H_2O (1:1))



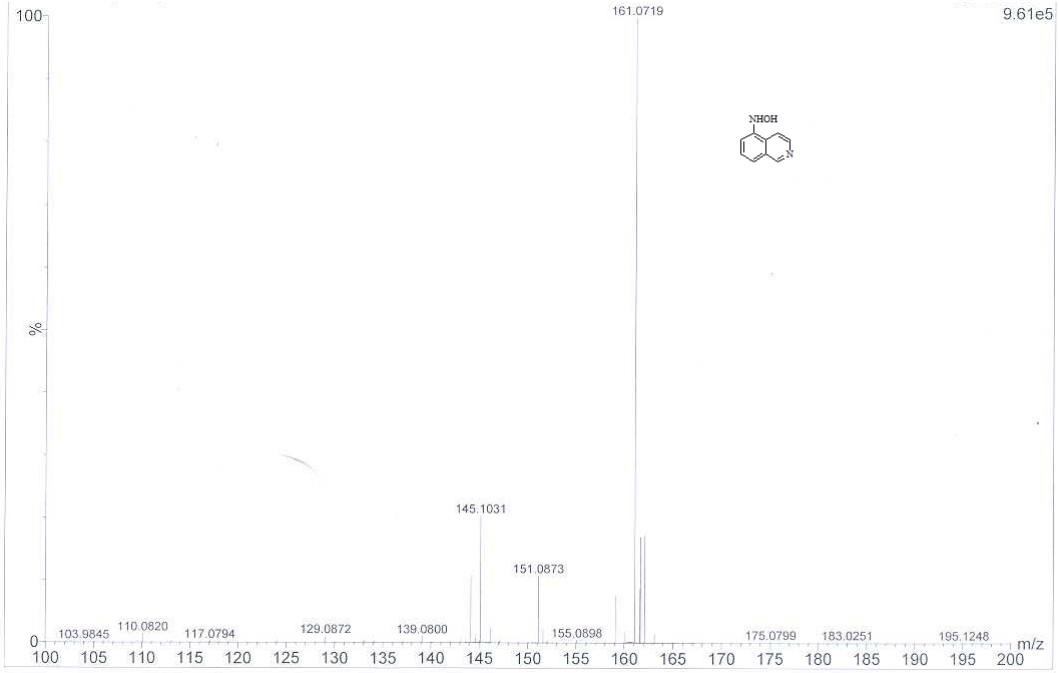
N-hydroxyisoquinolin-5-amine (**23**) (^{1}H NMR in DMSO-d_6)



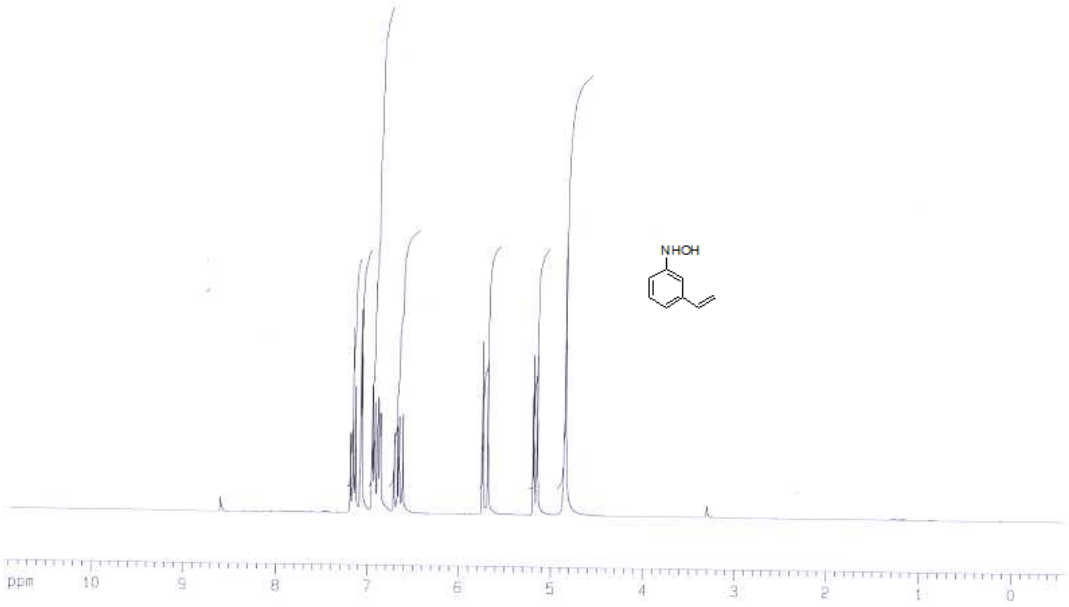
N-hydroxyisoquinolin-5-amine (**23**) (^{13}C NMR in DMSO-d_6)



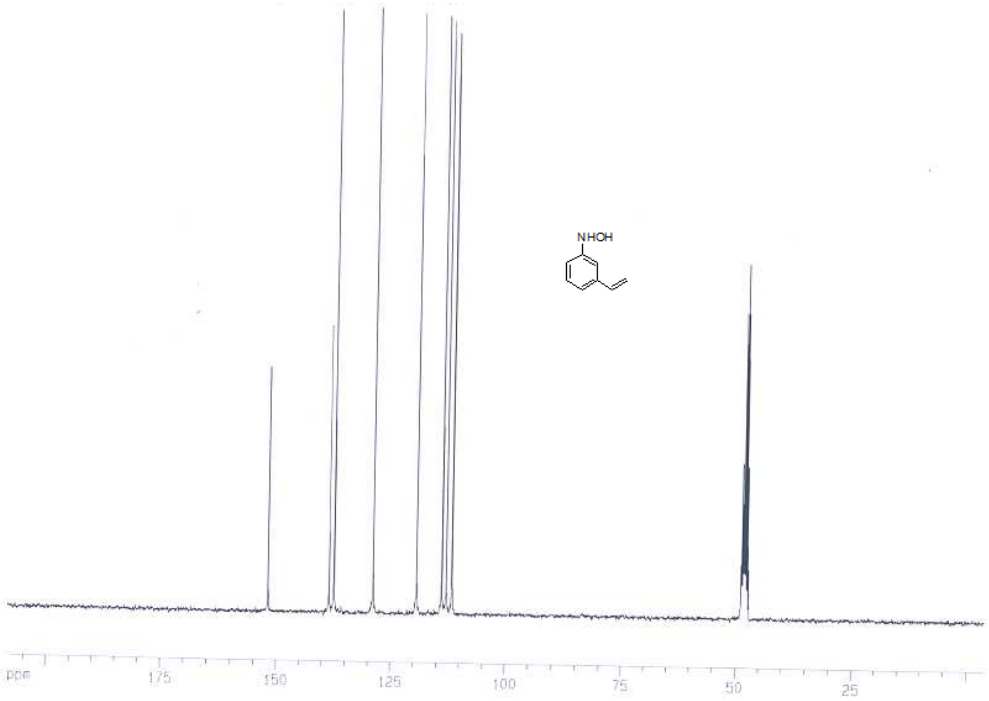
N-hydroxyisoquinolin-5-amine (**23**) (ESIMS in CH_3CN/H_2O (1:1))



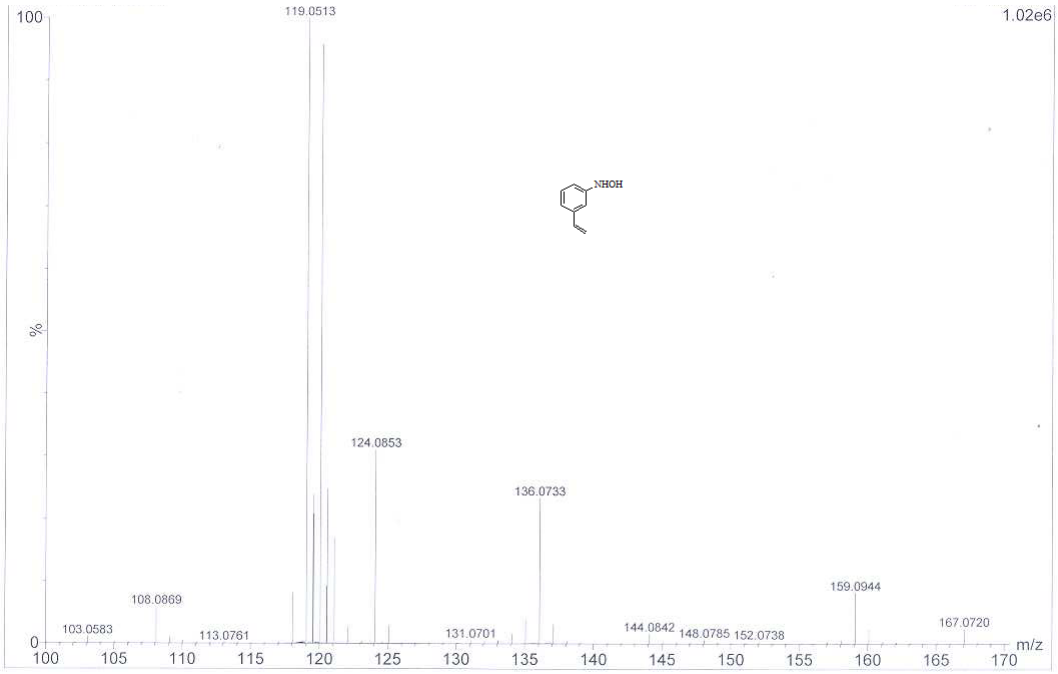
4-alkenylphenylhydroxylamine (**24**) (^{1}H NMR in MeOD)



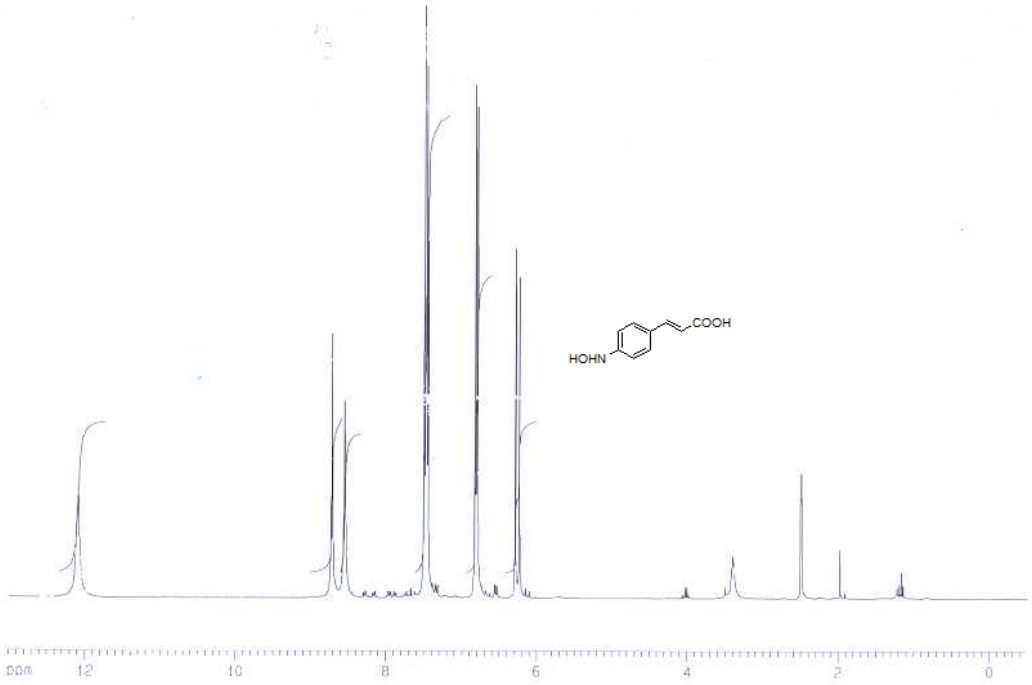
4-alkenylphenylhydroxylamine (**24**) (^{13}C NMR in MeOD)



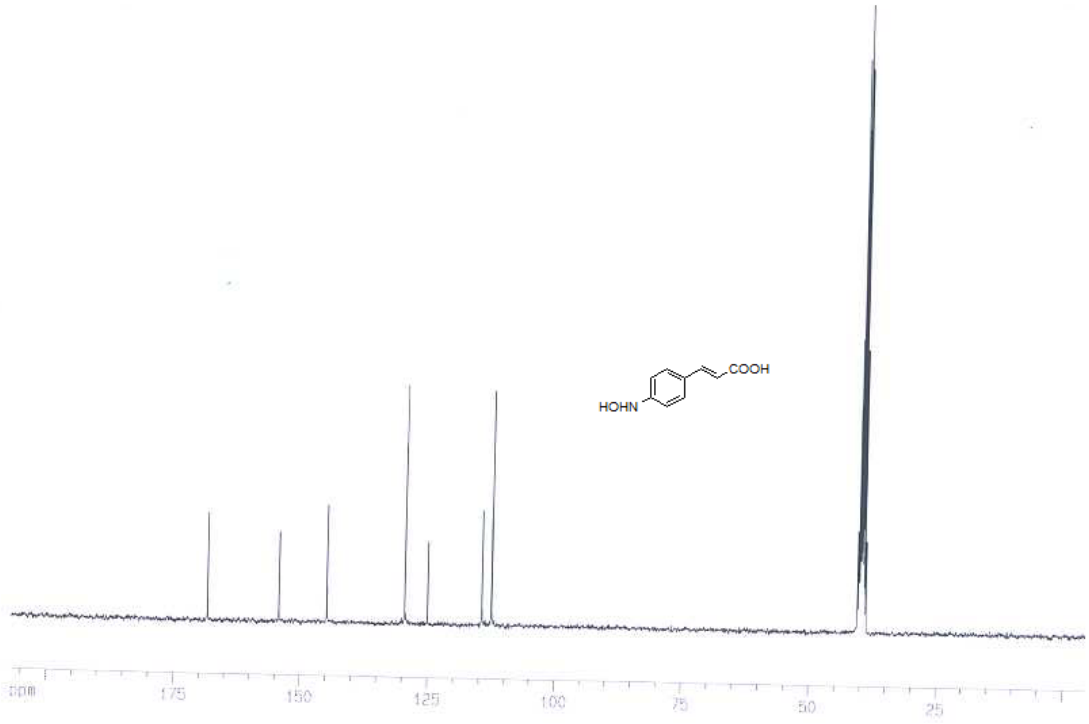
4-alkenylphenylhydroxylamine (**24**) (ESIMS in CH_3CN/H_2O (1:1))



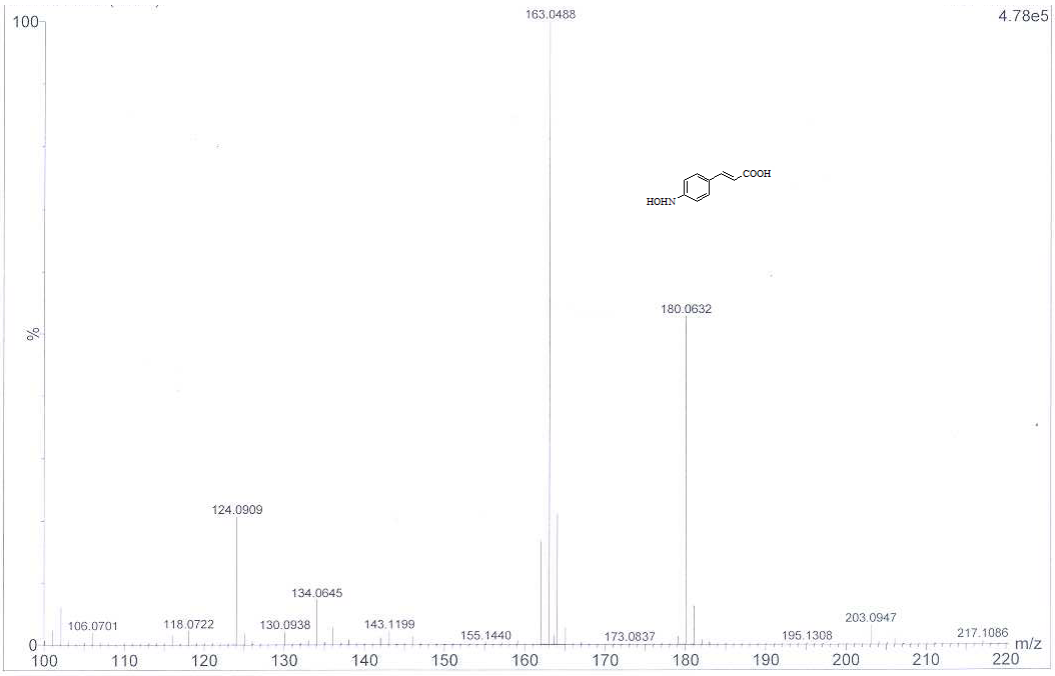
3-(4-(hydroxyamino)phenyl)acrylic acid (**25**) (^{1}H NMR in DMSO-d_6)



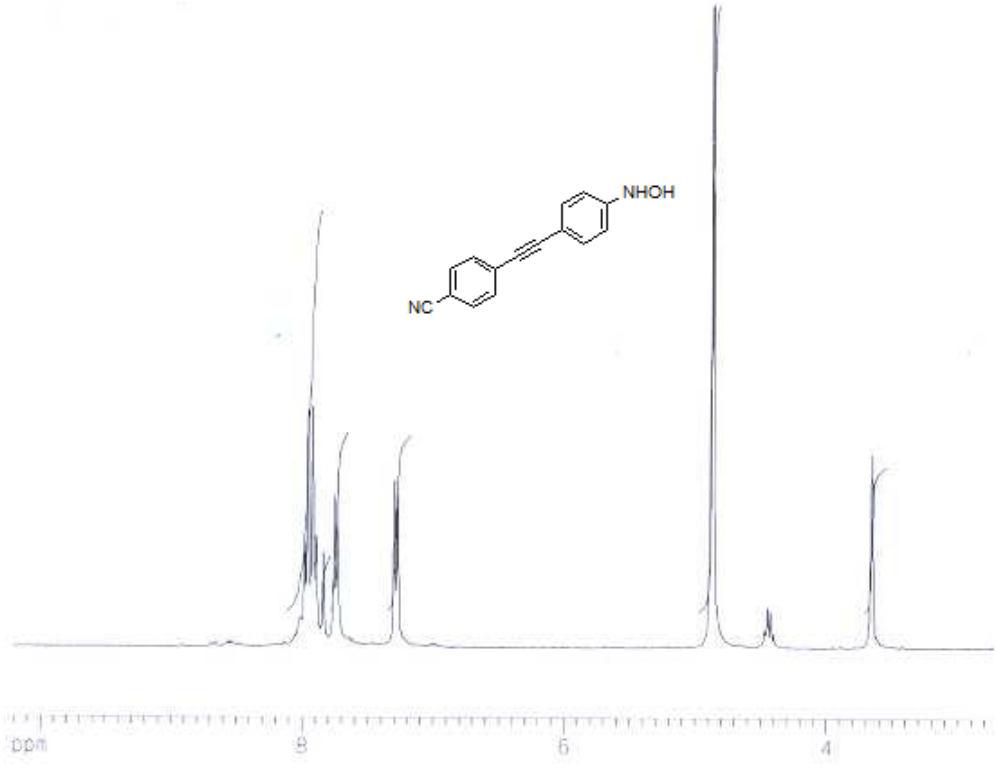
3-(4-(hydroxyamino)phenyl)acrylic acid (**25**) (^{13}C NMR in DMSO-d_6)



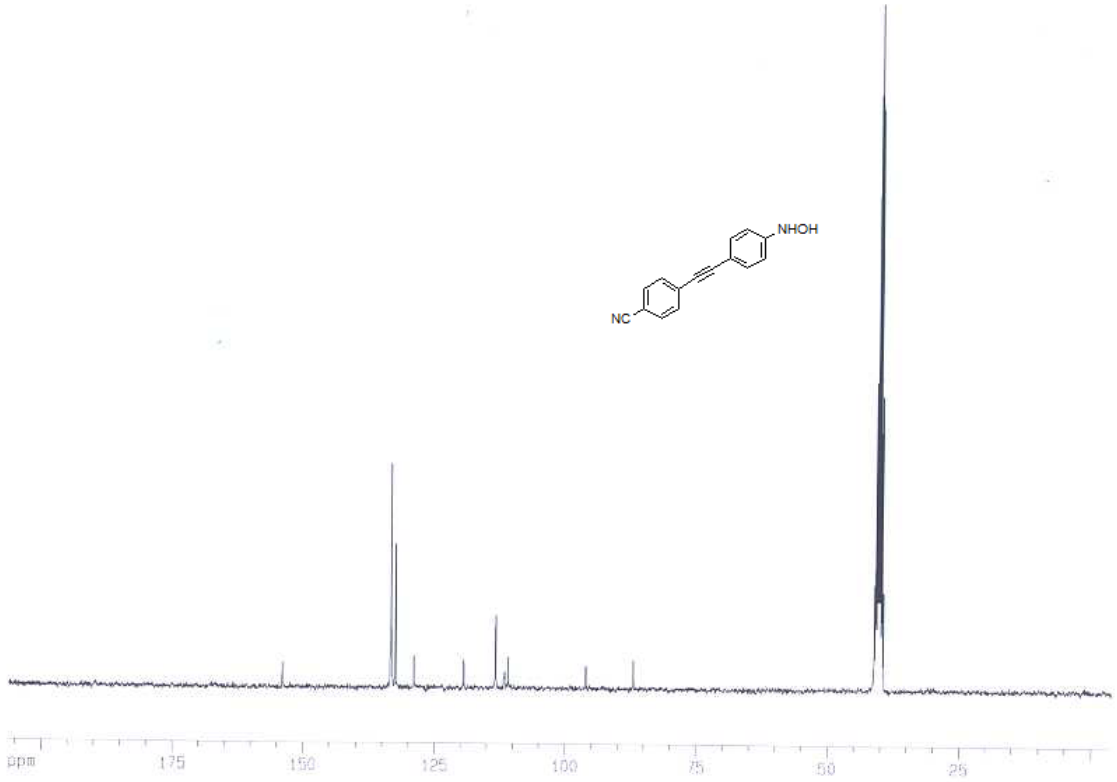
3-(4-(hydroxyamino)phenyl)acrylic acid (**25**) (ESIMS in CH_3CN/H_2O (1:1))



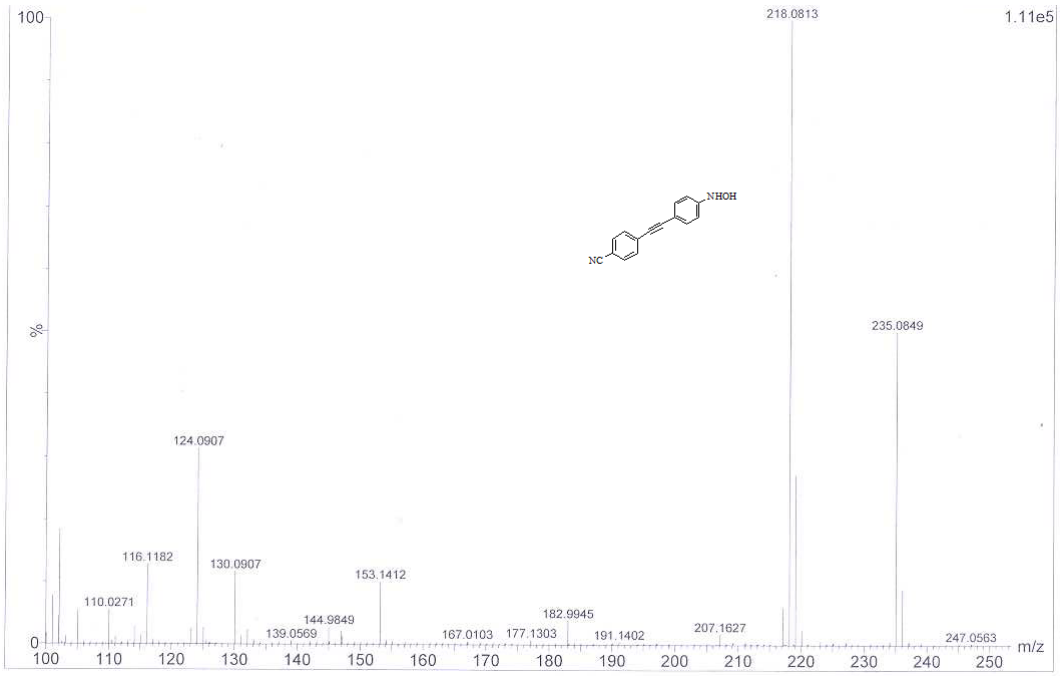
4-(2-(4-(hydroxyamino)phenyl)ethynyl)benzonitrile (**26**) (^{1}H NMR in MeOD/ $CDCl_3$ (1:1))



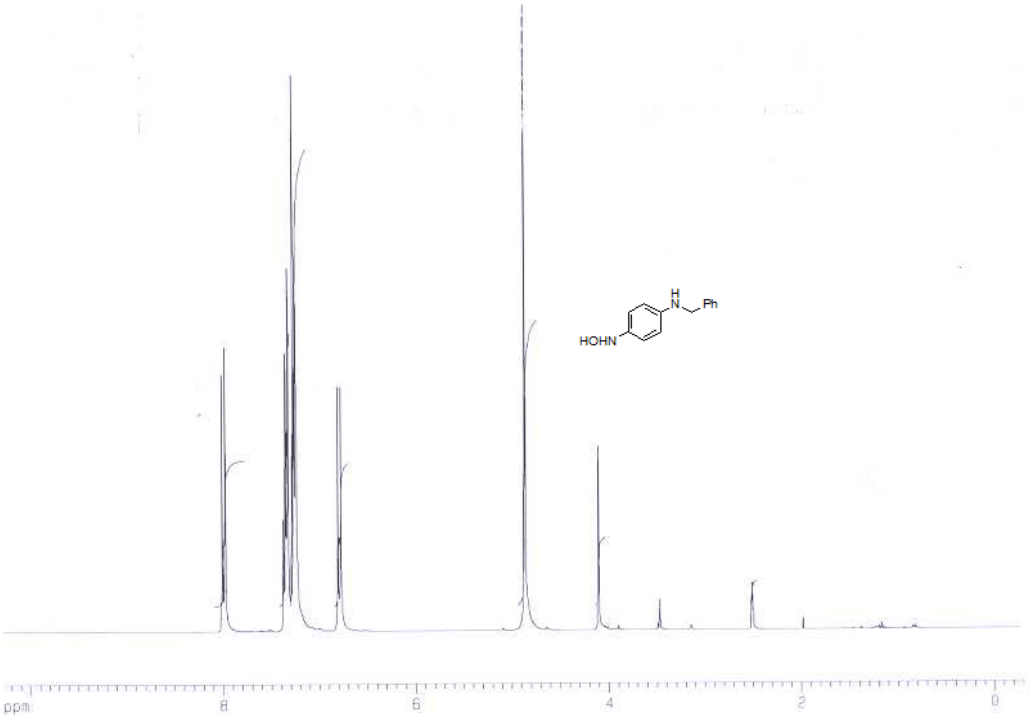
4-(2-(4-(hydroxyamino)phenyl)ethynyl)benzonitrile (**26**) (^{13}C NMR in DMSO-d_6)



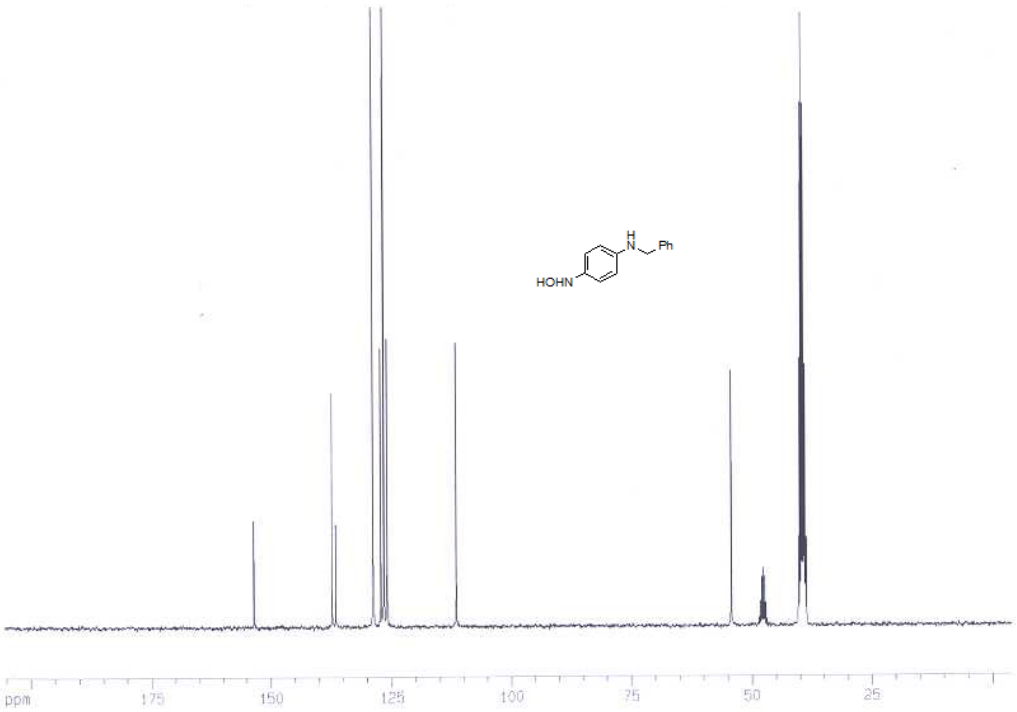
4-(2-(4-(hydroxyamino)phenyl)ethynyl)benzonitrile (**26**) (ESIMS in CH_3CN/H_2O (1:1))



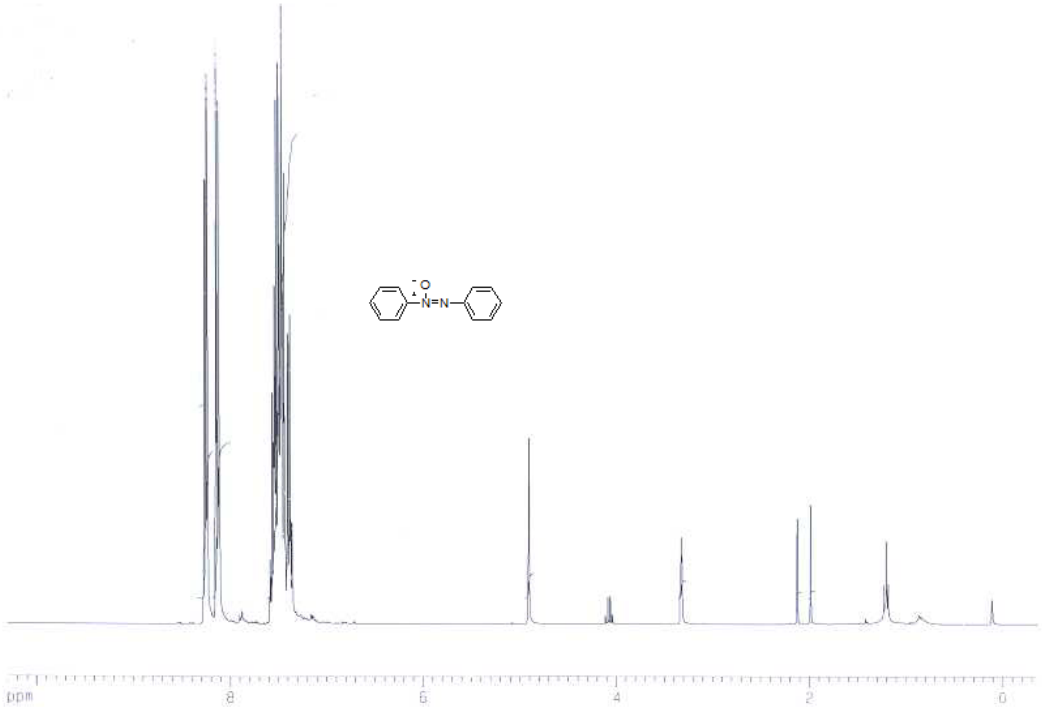
4-(benzylamino)-N-hydroxybenzenamine (**27**) (^{1}H NMR in DMSO-d_6/ MeOD (1:1))



4-(benzylamino)-N-hydroxybenzenamine (**27**) (^{13}C NMR in DMSO-d_6/ MeOD (1:1))

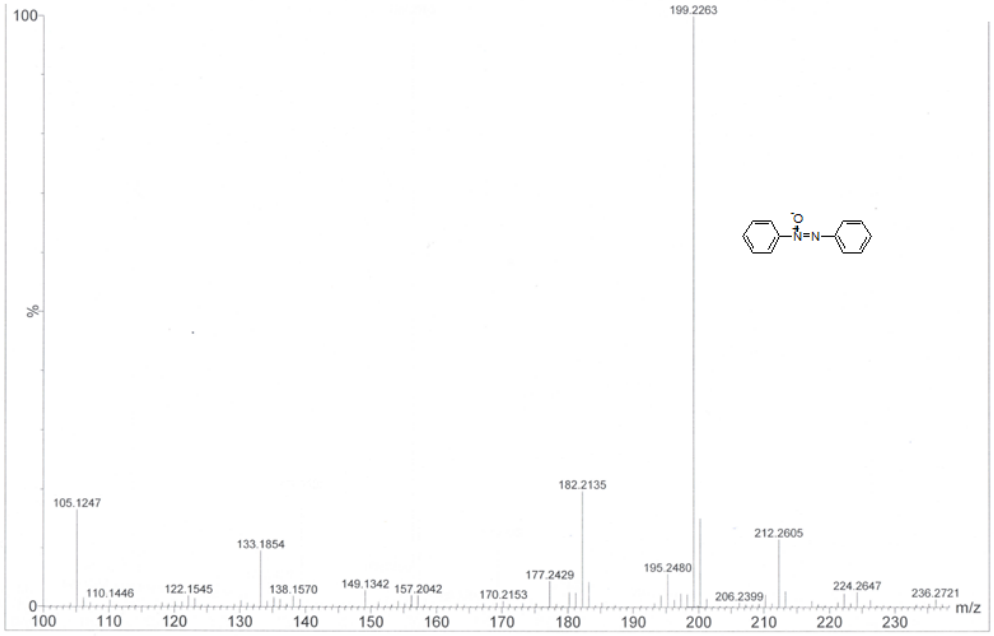


Azoxybenzene (**29**) (^{1}H NMR in MeOD)

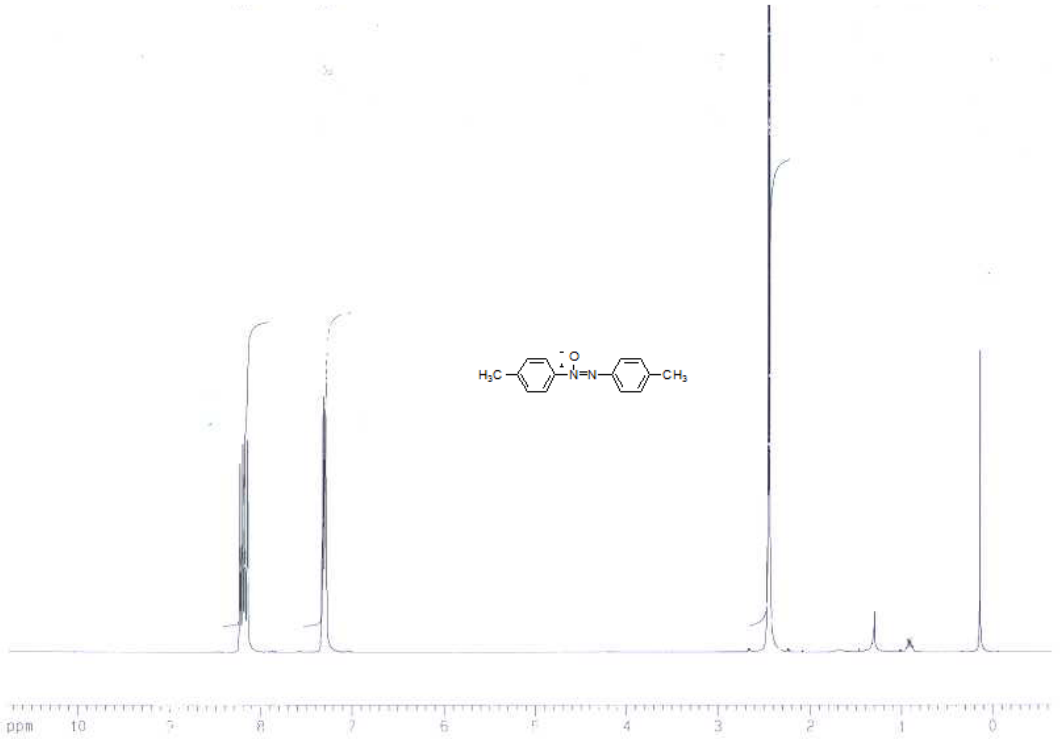


Azoxybenzene (**29**) (^{13}C NMR in MeOD)

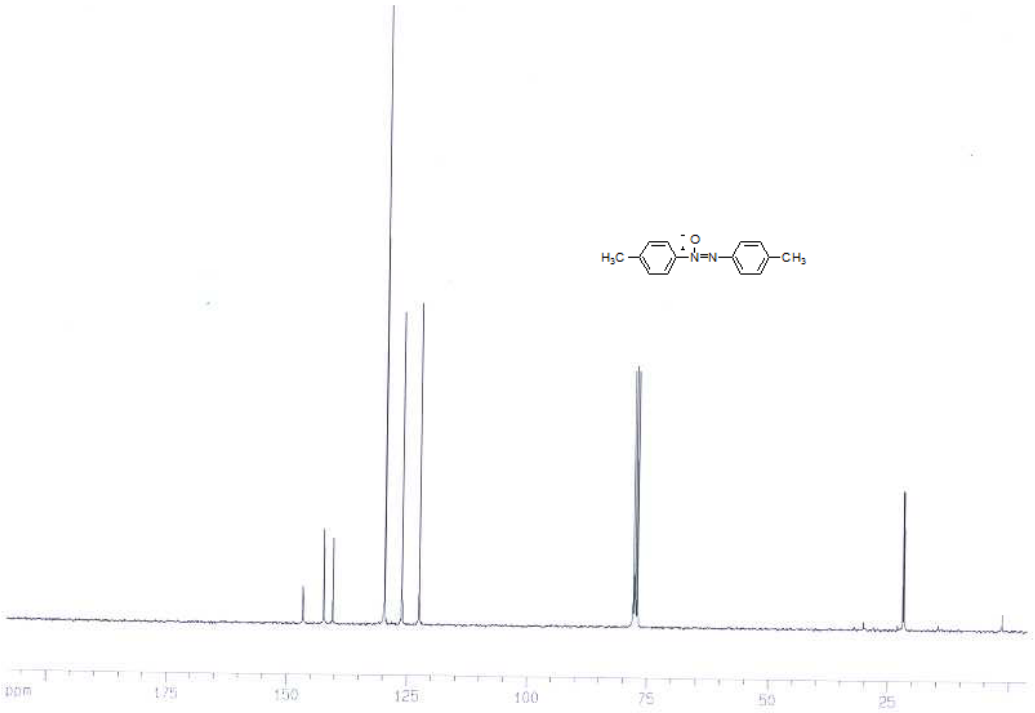
Azoxybenzene (**29**) (ESIMS in CH_3CN/H_2O (1:1))



4, 4'-dimethylazoxybenzene (**30**) (^1H NMR in $CDCl_3$)



4, 4'-dimethylazoxybenzene (**30**) (^{13}C NMR in $CDCl_3$)



4, 4'-dimethylazoxybenzene (**30**) (ESIMS in CH_3CN/H_2O (1:1))