Supporting information

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

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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) $\rightarrow$ 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

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 PtCl₂ 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.

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<tr>
<th>No. of Cycles</th>
<th>Amount of Pt metal leached (ppm)</th>
<th>% age of Pt leached with respect to initial metal content</th>
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<td>3&lt;sup&gt;rd&lt;/sup&gt;</td>
<td>0.1977</td>
<td>0.52</td>
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<td>7&lt;sup&gt;th&lt;/sup&gt;</td>
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<td>1.16</td>
</tr>
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4. **Typical experimental Procedure for reduction of Nitrobenzene to phenylhydroxylamine**

\[
\text{[NHOH]} \quad \text{[N-OH]}
\]

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. N₂H₄.H₂O (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 °C 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 Na₂SO₄. 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 °C; ¹H NMR (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); ¹³C NMR (75 MHz, MeOD) δ 115.10 (2C), 122.11, 129.47 (2C), 151.90. ESIMS data; m/z calc. for [M+H]+ C₆H₈NO 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. N₂H₄. H₂O (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 °C 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 Na₂SO₄. Evaporation of the combined organic layer followed by column chromatography (Hexane:EtOAc = 80:20) over silica gel (60-120 mesh) afforded 4-toluedine as a white crystalline solid (76.36 mg, 75%); mp 40-41 °C; ¹H NMR (300 MHz, CDCl₃) 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); ¹³C NMR (75 MHz, CDCl₃) 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 °C water bath and stirred magnetically. N₂H₄. H₂O (3 mmol) was added portion wise into the reaction mixture at least for 30 minutes. Extra precaution was taken to remove excess H₂ 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 Na₂SO₄. Evaporation of the combined organic layer 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 from 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 °C; ¹H NMR (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); ¹³C 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 from 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%); $^1$H NMR (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 from 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 °C; $^1$H NMR (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$_6$H$_7$ClNO 144.5783 obsd. 144.5757.

3-Chloro-N-hydroxybenzenamine (5) Prepared as described the method for 1, starting from 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%); $^1$H NMR (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%); $^1$H NMR (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 from 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) $\delta$ 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) $\delta$ 82.75, 116.94 (2C), 138.38 (2C), 152.66. ESIMS data; m/z calc. for [M+H]$^+$ C$_6$H$_7$INO 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) $\delta$ 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) $\delta$ 98.26, 113.55 (2C), 120.96, 134.12 (2C), 156.86. ESIMS data; m/z calc. for [M+H]$^+$ C$_7$H$_7$N$_2$O 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) $\delta$ 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) $\delta$ 52.52, 115.44, 119.34, 122.62, 129.72 (2C), 153.12, 168.84. ESIMS data; m/z calc. for [M+H]$^+$ C$_8$H$_{10}$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 °C; $^1$HNMR (300 MHz, MeOD) $\delta$ 4.90 (brs, 1H, NH), 6.92-6.96 (m, 2H), 7.86-7.90 (m, 2H); $^{13}$C NMR (75 MHz, MeOD) $\delta$ 112.96 (2C), 122.49, 132.04 (2C), 157.42, 170.31. ESIMS data; m/z calc. for [M+H]$^+$ C$_7$H$_8$NO$_3$ 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 °C; \(^1\)HNMR (300 MHz, DMSO-\(d_6\)) \(\delta\) 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-\(d_6\)) \(\delta\) 111.37, 113.61, 117.64, 130.90, 134.11, 153.75, 169.03. ESIMS data; \(m/z\) calc. for [M+H]\(^{+}\) C\(_7\)H\(_8\)NO\(_3\) 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 °C; \(^1\)HNMR (300 MHz, MeOD) \(\delta\) 4.85 (brs, 1H, NH), 7.09-7.13 (m, 1H), 7.24-7.32 (m, 2H), 7.46-7.47 (m, 1H); \(^{13}\)C NMR (75 MHz, MeOD) \(\delta\) 121.99, 116.30, 118.79, 127.93, 133.56, 151.30, 170.98. ESIMS data; \(m/z\) calc. for [M+H]\(^{+}\) C\(_7\)H\(_9\)N\(_2\)O\(_2\) 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 °C; \(^1\)HNMR (300 MHz, MeOD) \(\delta\) 4.83 (brs, 1H, NH), 6.92-6.97 (m, 2H), 7.72-7.77 (m, 2H); \(^{13}\)C NMR (75 MHz, MeOD) \(\delta\) 113.61 (2C), 126.0, 130.09 (2C), 156.79 (2C), 172.78. ESIMS data; \(m/z\) calc. for [M+H]\(^{+}\) C\(_7\)H\(_9\)N\(_2\)O\(_2\) 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 °C; ¹H NMR (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); ¹³C 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 °C; ¹H NMR (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); ¹³C 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]^+ C₈H₁₀NO₂ 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%); ¹H NMR (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); ¹³C NMR (75 MHz, MeOD) δ 110.91, 117.85 (2C), 130.21 (3C), 153.40. ESIMS data; m/z calc. for [M+H]^+ C₇H₇F₃NO 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 °C; ¹H NMR (300 MHz, MeOD) δ 4.58 (s, 2H), 4.88 (brs,
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 °C; \(^1\)HNMR (300 MHz, MeOD/CDCl\(_3\) (1:1)) \(\delta\) 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)) \(\delta\) 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) \(\delta\) 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) \(\delta\) 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 °C; \(^1\)HNMR (300 MHz, MeOD) \(\delta\) 4.85 (brs, 1H, NH), 6.63 (s, 4H); \(^13\)C NMR (75 MHz, MeOD) \(\delta\) 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 °C; \(^1\)HNMR (300 MHz, MeOD) \(\delta\) 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) \(\delta\) 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) \(\delta\) 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) \(\delta\) 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,N-Hydroxyisoquinolin-5-amine (23) Prepared as described the method for 1, starting from 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 °C; \(^1\)HNMR (300 MHz, DMSO-d\(_6\)) \(\delta\) 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\(_6\)) \(\delta\) 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\(_9\)H\(_9\)N\(_2\)O 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%); $^1$H NMR (300 MHz, MeOD) $\delta$ 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) $\delta$ 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$_8$H$_{10}$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 °C; $^1$H NMR (300 MHz, DMSO-d$_6$) $\delta$ 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$_6$) $\delta$ 112.35 (2C), 114.29, 124.83, 129.28 (2C), 144.57, 154, 168.11. ESIMS data; $m/z$ calc. for [M+H]$^+$ C$_9$H$_{10}$NO$_3$ 180.0655 obsd. 180.0632.

4-(2-(4-(Hydroxyamino)phenyl)ethynyl)benzonitrile (26) Prepared as described the method for 1, starting from 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 °C; $^1$H NMR (300 MHz, MeOD/CDCl$_3$ (1:1)) $\delta$ 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$_6$) $\delta$ 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$_2$O$_2$ 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 °C; \( ^1 \)HNMR (300 MHz, DMSO-d$_6$/MeOD (1:1)) \( \delta \) 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)) \( \delta \) 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 °C; \( ^1 \)HNMR (300 MHz, CDCl$_3$) \( \delta \) 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$_3$) \( \delta \) 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$_2$O 227.1178 obsd. 227.1162.
8. $^1\text{H}, ^{13}\text{C}$ NMR and selected ESIMS spectra of N-aryl hydroxylamines

Phenylhydroxylamine (1) ($^1\text{H}$ NMR in MeOD)

Phenylhydroxylamine (1) ($^{13}\text{C}$ NMR in MeOD)
Phenylhydroxylamine (1) (ESIMS in CH₃CN/H₂O (1:1))

4-methylphenylhydroxylamine (2) (¹H 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 CH₃CN/H₂O (1:1))

3-chlorophenylhydroxylamine (5) (¹H NMR in MeOD)
3-chlorophenylhydroxylamine (5) ($^{13}$C NMR in MeOD)

2-chlorophenylhydroxylamine (6) ($^1$H NMR in MeOD)
2-chlorophenylhydroxylamine (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$_3$CN/H$_2$O (1:1))
4-Cyanophenylhydroxylamine (8) ($^1$H NMR in MeOD)

4-Cyanophenylhydroxylamine (8) ($^{13}$C NMR in MeOD)
4-Cyanophenylhydroxylamine (8) (ESIMS in CH$_3$CN/H$_2$O (1:1))

3-carbethoxyphenylhydroxylamine (9) (¹H NMR in MeOD)
3-carbethoxyphenylhydroxylamine (9) ($^{13}$C NMR in MeOD)
3-carbomethoxyphenylhydroxylamine (9) (ESIMS in CH$_3$CN/H$_2$O (1:1))

4-carboxyphenylhydroxylamine (10) ($^1$H NMR in MeOD)

4-carboxyphenylhydroxylamine (10) ($^{13}$C NMR in MeOD)
4-carboxyphenylhydroxylamine (10) (ESIMS in CH$_3$CN/H$_2$O (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$_3$CN/H$_2$O (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$_3$CN/H$_2$O (1:1))

4-Carbaminophenylhydroxylamine (13) ($^1$H NMR in MeOD)
4-Carbaminophenylhydroxylamine (13) \(^{13}\text{C}\) NMR in MeOD

4-Carbaminophenylhydroxylamine (13) (ESIMS in CH\(_3\)CN/H\(_2\)O (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) (**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 CH₃CN/H₂O (1:1))

3-trifluoromethylphenylhydroxylamine (16) (¹H NMR in MeOD)
3-trifluoromethylphenylhydroxylamine (16) ($^{13}$C NMR in MeOD)

3-trifluoromethylphenylhydroxylamine (16) (ESIMS in CH$_3$CN/H$_2$O (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) \(^{13} \text{C NMR in MeOD}\)

4-aminophenylhydroxylamine (20) \(^{1} \text{H NMR in MeOD}\)
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$_3$CN/H$_2$O (1:1))
2-phenylphenylhydroxylamine (22) ($^1$H NMR in MeOD)

2-phenylphenylhydroxylamine (22) ($^{13}$C NMR in MeOD)
2-phenylphenylhydroxylamine (22) (ESIMS in CH$_3$CN/H$_2$O (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 CH₃CN/H₂O (1:1))

4-alkenylphenylhydroxylamine (24) (¹H NMR in MeOD)
4-alkenylphenylhydroxylamine (24) \(^{13}\text{C}\) NMR in MeOD)

![13C NMR in MeOD]

4-alkenylphenylhydroxylamine (24) (ESIMS in CH\(_3\)CN/H\(_2\)O (1:1))

![ESIMS in CH\(_3\)CN/H\(_2\)O (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$_3$CN/H$_2$O (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$_3$CN/H$_2$O (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) (1H NMR in MeOD)

Azoxybenzene (29) (13C NMR in MeOD)
Azoxybenzene (29) (ESIMS in CH$_3$CN/H$_2$O (1:1))

4, 4’-dimethylazoxybenzene (30) (\textsuperscript{1}H NMR in CDCl$_3$)
4, 4’-dimethylazoxybenzene (30) \( ^{13} \text{C NMR in CDCl}_3 \)