Synthesis of 2-Aryl-1-hydroxyazaindoles and 2-Arylazaindoles via Oxidation of *o*-Hydroxyaminostyrylpyridines

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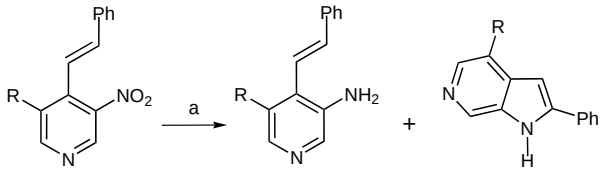
Abstract: 2-Aryl-1-hydroxyazaindoles (pyrrolopyridin-1-ols) are prepared via an oxidation/cyclization of *o*-hydroxyaminostyrylpyridines with DDQ. Reduction of the N–OH bond affords the corresponding 2-arylazaindoles (1*H*-pyrrolopyridines). The scope of the cyclization is explored via (i) the condensation of 4-methyl-3-nitropyridine with various aryl aldehydes to afford 2-aryl substituted 6-azaindoles and, (ii) the synthesis of 2-phenyl-4-, 5- and 7-azaindoles.

Key words: azaindoles, 1*N*-hydroxy azaindoles, cyclization, oxidation, 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ), pyrrolopyridines

The indole ring system is a common substructure of many natural products and pharmaceutical agents and various methods have been developed for the synthesis of indoles.[1] A structure-activity relationship (SAR) study of an indole pharmacophore often involves the preparation of synthetically challenging substituted azaindoles.[2] For example, the deoxygenation of 2-nitrostilbene in the presence of triethyl phosphite affords 2-phenylindole in 58% yield;[3] similar treatment of 3-nitro-4-[(*E*)-phenylethenyl]pyridine (**4a**) affords 2-phenyl-6-azaindole (**6a**) in only 14% yield.[4] Recently, acetylenic aminopyridines have proven useful for the synthesis of substituted azaindoles.[5] We now report the oxidation/cyclization of *o*-hydroxyaminostyrylpyridines with DDQ to afford 2-aryl substituted 1-hydroxyazaindoles[6] which can be readily reduced to the corresponding azaindoles.[7]

Our work in this area began with the observation shown in Scheme 1.

Treatment of 3-bromo-5-nitro-4[(*E*)-2-phenylethenyl]pyridine (**1**)[8,9] with iron filings in acetic acid–ethanol at reflux, surprisingly, gave a mixture of aniline **2** and 4-bromo-2-phenyl-6-azaindole (**3**) in 27% and 30% yield, respectively (Scheme 1). On the contrary, reduction of the desbromo compound **4a** gave aniline **5** in 84% yield and the formation of 2-phenyl-6-azaindole (**6a**) was not observed. Although, the difference in reactivity between **1** and **4a** is intriguing, it was clear that optimization of reductive conditions in favor of azaindole formation would be highly substrate dependent. Thus, we considered the mechanism of cyclization.



1 R=Br
4a R=H

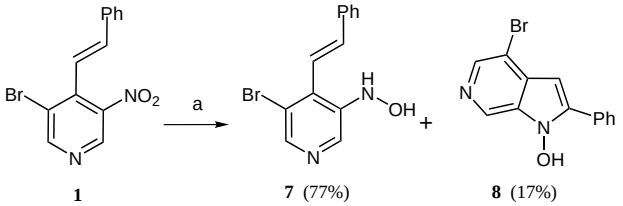
2 R=Br (27%)
5 R=H (84%)

3 R=Br (30%)
6a R=H (0%)

Scheme 1 *Reagents and conditions*: (a) Fe, HOAc–EtOH, Δ

The reduction of nitro compounds to amines is presumed to proceed through intermediate stages involving first conversion to the nitroso compound followed by formation of the hydroxylamine.[10] Initially, we considered that the hydroxylamine intermediate cyclized to afford azaindole **3** in a Michael type addition. It is known that 2- and 4-vinylpyridines can undergo conjugate addition reactions with amines and hydroxylamines.[11] Intramolecular addition of an intermediate *o*-arylhydroxylamine to a vinylpyridine followed by proton transfer, loss of water and tautomerization could account for azaindole **3**.

Alternatively, it is known that arylnitroso compounds can cyclize to afford 1-hydroxyindoles which can be reduced to the corresponding indoles. Hazard has reported a one-pot procedure for the preparation of 1-hydroxyindoles via an electrochemical reduction of *o*-nitrostyrenes to the corresponding hydroxylamines followed by an anodic oxidation in situ presumably to afford the arylnitroso compounds which cyclizes to the nitrones and then rearranges to the corresponding 1-hydroxyindoles.[12] Makosza has also reported the base-catalyzed cyclization of α,β-disubstituted *o*-nitroarylethanes to 2,3-disubstituted 1-hydroxindoles and has proposed that the cyclization occurs via a nitroso intermediate.[7] To identify which of these two cyclization precursors were responsible for azaindole formation we prepared the corresponding arylhydroxylamine of nitropyridine **1** (Scheme 2).



1 **7** (77%) **8** (17%)

Scheme 2 *Reagents and conditions*: (a) $SnCl_2 \cdot 2H_2O$, $NaOAc \cdot 3H_2O$, THF–MeOH, 0 °C

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A partial reduction of **1** with $SnCl_2 \cdot 2H_2O$ and $NaOAc \cdot 3H_2O$ in THF–MeOH at 0 °C gave arylhydroxylamine **7** and 4-bromo-1-hydroxy-2-phenyl-6-azaindole (**8**) in 77% and 17% yield, respectively.[13]

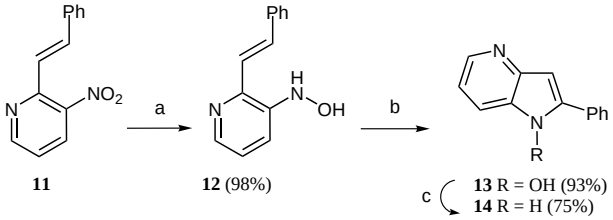
Formation of 1-hydroxyazaindole **8** suggests that the cyclization occurs via nitroso compound **1a** (Scheme 3). Thus, reduction of **1** affords nitroso intermediate **1a** which cyclizes to **1b** followed by rearrangement to 1-hydroxyazaindole **8**. Treatment of **8** with iron in acetic acid at reflux gave **3** in 98% yield. Furthermore, a proton NMR revealed a mixture of azaindoles **3** and **8** if the iron reduction of **1** was interrupted before completion.

We then concluded that compounds of type **7**, if treated with a suitable oxidant, could afford the indole nucleus. Except for the aforementioned electrochemical process to prepare 1-hydroxy-2-phenylindole reported by Hazard 30 years ago, there are no known examples of a chemical oxidation of either *o*-hydroxyaminostilbenes to afford indoles or *o*-hydroxyaminostyrylpyridines to afford azaindoles.[12] To explore this transformation **9a** → **10a** we optimized conditions for the preparation of arylhydroxylamine **9a**. Thus, condensation of 4-methyl-3-nitropyridine with benzaldehyde using catalytic piperidine in methanol at reflux gave *trans*-olefin **4a** in 66% yield.[9a] Reduction of the nitro group using $SnCl_2 \cdot 2H_2O$ and $NaOAc \cdot 3H_2O$ in MeOH–THF at 0 °C gave arylhydroxylamine **9a** in 93% yield. Formation of 1-hydroxy-2-phenyl-6-azaindole (**10a**) was not observed here, which is consistent with our earlier observation (Scheme 1, **4a** → **5**).

There are a number of reagents known to oxidize arylhydroxylamines to nitroso compounds, however many of these same oxidants are known to cause the decomposition of 1-hydroxyindoles.[10,14] In our hands oxidations with $FeCl_3$, MnO_2, DEAD, CAN, and CrO_2 gave complex mixtures of 1-hydroxyazaindoles and azaindoles in poor to moderate yields. To our knowledge DDQ has not been reported to convert arylhydroxylamines to arylnitroso compounds, however, it proved to be very useful for the conversion of pyridylhydroxylamine **9a** to 1-hydroxyazaindole **10a** (Table 1).

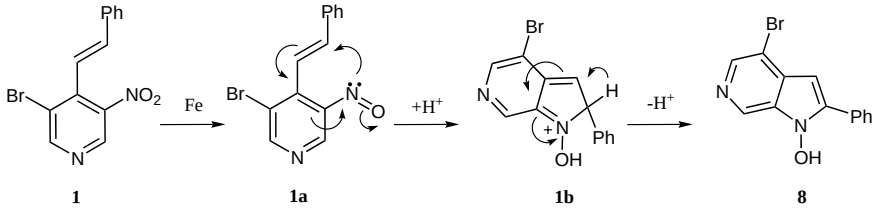
The scope of the cyclization was explored by treatment of hydroxylamines **9b–f** with DDQ (1 equiv) in MeCN–H_2O–HOAc to afford the corresponding 1-hydroxyazaindoles **10b–f** in good to excellent yields. Subsequent, reduction of the N–OH bond using iron filings in acetic acid–ethanol at reflux gave 2-aryl substituted 6-azaindoles **6a–f** in good to excellent yields (Table 1). For the oxidation/cyclization step, the addition of HOAc resulted in a substantial improvement in yield while use of excess DDQ resulted in lower yields. Also of interest, entry **9d** cyclized to **10d** upon stirring in MeCN–H_2O for 36 hours, presumably, via autoxidation of **9d** to the corresponding nitroso compound.[15] Finally, the hydroxyazaindoles **10a–f** and the corresponding azaindoles **6a–f** have quite similar ^1H and ^{13}C NMR spectra, however, a significant upfield shift is noted for the H-3 proton and the C-3 carbon in the oxygenated compounds.[6]

Application of this methodology to the synthesis of 2-phenyl-4-azaindole (**14**), 2-phenyl-5-azaindole (**18**) and 2-phenyl-7-azaindole (**21**) has been successful (Schemes 4, 5 and 6). Styrylpyridine **11** was prepared by known methods.[16] Stannous chloride reduction of **11** gave hydroxylamine **12** in 98% yield. Oxidation of **12** with DDQ furnished 1-hydroxy-2-phenyl-4-azaindole (**13**) in 93% yield and reduction of **13** afforded 2-phenyl-4-azaindole (**14**) in 75% yield.



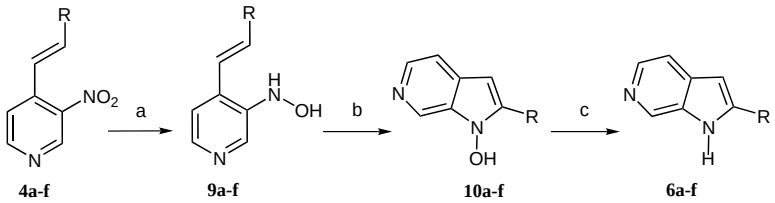
Scheme 4 Synthesis of 2-phenyl-4-azaindole. *Reagents and conditions*: (a) $SnCl_2 \cdot 2H_2O$, $NaOAc \cdot 3H_2O$, THF–MeOH, 0 °C (b) DDQ, MeCN–H_2O–HOAc, 0 °C (c) Fe, HOAc–EtOH, Δ

A synthesis of 2-phenyl-5-azaindole (**18**) began with styrylpyridine **15** which was prepared from commercially available 3-methyl-4-nitropyridine *N*-oxide by known methods.[17] Reduction of **15** gave the hydroxylamine **16** which was shown to exist as a mixture of tautomers by ^1H NMR (DMSO-d_6) spectroscopy. Fortunately, the major tautomer could be characterized by ^1H NMR spectroscopy in CD_3CO_2D. Treatment of **16** with DDQ gave an inseparable 2:1 mixture of 1-hydroxyazaindole **17** and azaindole **18** in 75% yield as shown by ^1H NMR spectroscopy. Reduction of the mixture gave 2-phenyl-5-azaindole[18] (**18**) in 60% overall yield from **16**.

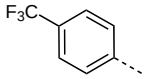
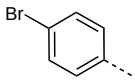
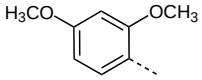


Scheme 3 Proposed mechanism: cyclization occurs via the nitroso intermediate **1a**

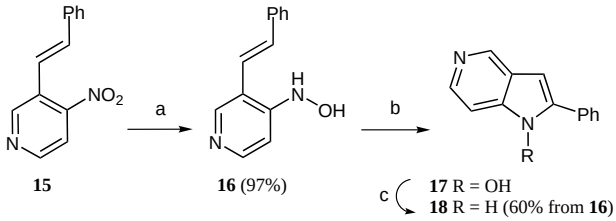
Table 1 Preparation of 2-Aryl-6-azaindoles[a]



4a-f **9a-f** **10a-f** **6a-f**

Entry	R	Yield (%) **9**	Yield (%) **10**	Yield (%) **6**
4a		93	91	85
4b		83	97	80
4c		92	94	99
4d		91	96	85
4e		90	88	98
4f		85	93	97

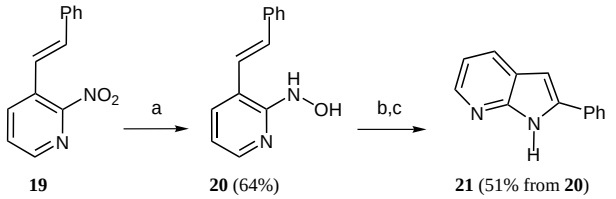
[a] *Reagents and conditions*: (a) $SnCl_2 \cdot 2H_2O$, $NaOAc \cdot 3H_2O$, THF–MeOH, 0 °C (b) DDQ, MeCN–H_2O–HOAc, 0 °C (c) Fe, HOAc–EtOH, Δ



15 **16** (97%)

Scheme 5 Synthesis of 2-phenyl-5-azaindole. *Reagents and conditions*: (a) $SnCl_2 \cdot 2H_2O$, $NaOAc \cdot 3H_2O$, THF–MeOH, 0 °C (b) DDQ, MeCN–H_2O–HOAc, 0 °C (c) Fe, HOAc–EtOH, Δ

Finally, 2-phenyl-7-azaindole[4,19] (**21**) was prepared from styrylpyridine **19**.[20] Reduction of **19** gave hydroxylamine **20** in 64% yield. Treatment of **20** with DDQ afforded 1-hydroxy-2-phenyl-7-azaindole which was reduced without purification to afford **21** in good yield (51% from **20**).



19 **20** (64%) **21** (51% from **20**)

Scheme 6 Synthesis of 2-phenyl-7-azaindole. *Reagents and conditions*: (a) $SnCl_2 \cdot 2H_2O$, $NaOAc \cdot 3H_2O$, THF–MeOH, 0 °C (b) DDQ, MeCN–H_2O–HOAc, 0 °C (c) Fe, HOAc–EtOH, Δ

In conclusion, we have described a general method for preparing 2-aryl substituted 4-, 5-, 6-, and 7-azaindoles via an oxidation/cyclization of *o*-hydroxyaminostyrylpyridines with DDQ. The cyclization provides access to 1-hydroxyazaindoles compounds for which there are few synthetic methods known. Extension of this methodology to other heterocycles and indoles is under investigation.

Melting points (uncorrected) were measured with a Büchi 510 apparatus. NMR spectra were recorded using a Bruker 400 spectrometer in ppm from internal $CHCl_3$, DMSO or HOAc on the δ scale and coupling constants *J* are given in Hz. Column chromatography was carried out on silica gel (70–230 mesh, E. Merck). Low resolution mass spectra were recorded using a Finnigan-SSQ7000 or a Micromass platform LCZ instrument. IR spectra were recorded on a Nicolet Impact 410 spectrometer.

4-Methyl-3-nitropyridine and 3-methyl-4-nitropyridine 1-oxide were obtained from Lancaster. *o*-Nitrostyrylpyridines **4a, 4d, 4e** and **11** are known compounds. Compounds **1, 4b, 4c** were prepared according to literature procedures by reaction of 4-methyl-3-nitropyridine with the appropriate aldehyde and 0.5 equivalent of piperidine in MeOH at reflux or in Ac_2O (for **4f**) at reflux. Compound **15** was obtained from 3-methyl-4-nitropyridine 1-oxide via condensation with benzaldehyde followed by deoxygenation with PCl_3 in CH_2Cl_2. Compound **19** was prepared from 3-hydroxy-2-nitropyridine via conversion to its triflate derivative followed by a Suzuki coupling with *trans*-4-vinylphenylboronic acid. The analytical and spectral data of the starting materials synthesized are given below.

3-Bromo-5-nitro-4-[(*E*)-2-phenylethenyl]pyridine (1)
Yield: 80%; mp 74–78 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.95 (s, 1 H), 8.92 (s, 1 H), 7.55 (m, 2 H), 7.46–7.38 (m, 3 H), 7.12 (d, *J* = 16.6 Hz, 1 H, C=CH), 6.98 (d, *J* = 16.6 Hz, 1 H, C=CH).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.0 (d), 143.4 (d), 139.9 (s), 139.4 (d), 129.7 (d), 128.9 (d), 127.3 (d), 122.4 (s), 119.6 (d), one aromatic singlet was not resolved.

3-Nitro-4-[(*E*)-2-phenylethenyl]pyridine (4a)
Yield: 67%; mp 111–113 °C (Lit.[9a] mp 114–116 °C).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 9.14 (s, 1 H), 8.82 (d, *J* = 5.3 Hz, 1 H), 8.02 (d, *J* = 5.3 Hz, 1 H), 7.67 (m, 3 H), 7.54 (d, *J* = 16.3 Hz, 1 H), 7.47–7.38 (m, 3 H).

3-Nitro-4-{[(*E*)-2-[4-(trifluoromethyl)phenyl]ethenyl}pyridine (4b)
Yield: 24%; mp 102–104 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.27 (s, 1 H), 8.84 (d, *J* = 5.3 Hz, 1 H), 7.78 (d, *J* = 16.2 Hz, 1 H, C=CH), 7.73 (d, coupling obscured by singlet at 7.72, 1 H), 7.72 (s, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.8 (d), 146.9 (d), 144.1 (s), 140.2 (s), 139.2 (s), 136.3 (d), 131.7 (q, $^2J_{CF}$ = 32 Hz), 128.2 (d), 124.3 (q, $^1J_{CF}$ = 270 Hz), 123.8 (d), 121.6 (d).

MS: *m*/*z* (%) = 295 (MH^+, 100).

Anal. Calcd for $C_{14}H_9F_3N_2O_2$: C, 57.15; H, 3.08; N, 9.52. Found: C, 56.89; H, 3.24; N, 9.42.

4-[(*E*)-2-(4-Bromophenyl)ethenyl]-3-nitropyridine (4c)
Yield: 53%; mp 115–119 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.23 (s, 1 H), 8.80 (d, *J* = 5.3 Hz, 1 H), 7.71 (d, *J* = 4.7 Hz, 1 H), 7.68 (d, *J* = 15.4 Hz, 1 H), 7.59 (d, *J* = 8.4 Hz, 2 H), 7.48 (d, *J* = 8.4 Hz, 2 H), 7.29 (d, *J* = 16.1 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.6 (d), 146.9 (d), 144.0 (s), 140.4 (s), 136.9 (d), 134.8 (s), 132.6 (d), 129.4 (d), 124.4 (s), 121.7 (d), 121.4 (d).

4-[(*E*)-2-(2,4-Dimethoxyphenyl)ethenyl]-3-nitropyridine (4d)
Yield: 56%; mp 85–86 °C (Lit.[9b] mp 98–99 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.16 (s, 1 H), 8.71 (d, *J* = 5.4 Hz, 1 H) 7.75 (d, *J* = 5.0 Hz, 1 H), 7.72 (d, *J* = 15.6 Hz, 1 H, C=CH), 7.62 (d, *J* = 16.2 Hz, 1 H, C=CH), 7.60 (d, *J* = 8.6 Hz, 1 H), 6.60 (dd, *J* = 8.6, 2.2 Hz, 1 H), 6.52 (d, *J* = 2.3 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.9, 159.6, 153.0, 146.8, 144.0, 141.6, 133.5, 129.5, 120.9, 118.3, 118.1, 105.9, 98.9, 56.0, 55.9.

3-Nitro-4-[(*E*)-2-(2-thienyl)ethenyl]pyridine (4e)
Yield: 84%; mp 103–105 °C (Lit.[4] mp 108–109 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.21 (s, 1 H), 8.75 (d, *J* = 5.3 Hz, 1 H), 7.68 (d, *J* = 5.3 Hz, 1 H), 7.54 (d, *J* = 15.9 Hz, 1 H, C=CH), 7.50 (d, *J* = 16.1 Hz, 1 H, C=CH), 7.44 (d, *J* = 5.0 Hz, 1 H), 7.31 (d, coupling obscured by $CDCl_3$ peak, 1 H), 7.12 (dd, *J* = 4.9, 3.9 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.3 (d), 147.0 (d), 143.8 (s), 141.3 (s), 140.3 (s), 131.1 (d), 130.0 (d), 128.5 (d), 128.4 (d), 120.8 (d), 119.7 (d).

MS: *m*/*z* (%) = 295 (MH^+, 100).

4-[(*E*)-2-(3-Furyl)ethenyl]-3-nitropyridine (4f)
Yield: 22%; mp 77–79 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.19 (s, 1 H), 8.75 (d, *J* = 5.3 Hz, 1 H), 7.71 (s, 1 H), 7.67 (d, *J* = 5.3 Hz, 1 H), 7.51 (s, 1 H), 7.39 (d, *J* = 16.0 Hz, 1 H), 7.30 (d, *J* = 16.0 Hz, 1 H), 6.75 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 153.4, 146.2, 145.44, 144.9, 144.0, 139.7, 128.7, 124.1, 121.2, 119.9, 108.1.

3-Nitro-2-[(*E*)-2-phenylethenyl]pyridine (11)
Yield: 35%; mp 104–106 °C (Lit.[16] mp 107–108 °C).

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.83 (dd, *J* = 4.5, 1.4 Hz, 1 H), 8.27 (dd, *J* = 8.3 Hz, 1 H), 8.09 (d, *J* = 15.5 Hz, 1 H), 7.78 (d, *J* = 15.5 Hz, 1 H), 7.66 (m, 2 H), 7.45–7.33 (m, 4 H).

4-Nitro-3-[(*E*)-2-phenylethenyl]pyridine (15)
2-Steps from 3-methyl-4-nitropyridine 1-oxide; overall yield: 44%.

Mp 84–85 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 9.12 (s, 1 H), 8.73 (d, *J* = 5.4 Hz, 1 H), 7.77 (d, *J* = 5.3 Hz, 1 H), 7.57 (m, 2 H), 7.52 (d, *J* = 16.3 Hz, HC=C), 7.39 (m, 3 H), 7.21 (d, *J* = 16.3 Hz, CH=C).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 150.7 (d), 149.6 (d), 135.9 (d), 135.8, 129.2 (d), 128.9 (d), 127.3 (d), 126.6, 119.7 (d), 116.7 (d), one aromatic singlet was not resolved.

2-Nitro-3-[(*E*)-2-phenylethenyl]pyridine (19)
Mp 76–77 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.44 (dd, *J* = 4.5, 1.3 Hz, 1 H), 8.22 (dd, *J* = 7.9, 0.8 Hz, 1 H), 7.59 (dd, *J* = 7.9, 4.5 Hz, 1 H), 7.53 (m, 2 H), 7.41–7.32 (m, 4 H), 7.16 (d, *J* = 16.2 Hz, CH=C).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 146.9 (d), 137.1 (d), 135.9 (d), 135.7 (s), 129.2 (d), 128.9 (d), 127.8 (d), 127.2 (d), 126.9 (s), 119.9 (d), one aromatic singlet was not resolved.

Reduction of 1 with Iron Filings; 5-Bromo-4-[(*E*)-2-phenylethenyl]pyridin-3-ylamine (2) and 4-Bromo-2-phenyl-1*H*-pyrrolo[2,3-*c*]pyridine (3); Typical Procedure
A mixture of **1** (305 mg, 1.0 mmol) and iron filings (336 mg, 6.0 mmol) in HOAc (5 mL) was refluxed for 40 min. The mixture was diluted with EtOAc (20 mL) and made basic with sat. aq $NaHCO_3$ (50 mL). The aqueous layer was separated and extracted with EtOAc (3 × 10 mL). The aqueous layer was filtered and extracted again with EtOAc (2 × 20 mL). The combined organic layers were washed with sat. aq $NaHCO_3$ (2 × 20 mL), brine (2 × 20 mL), dried (Na_2SO_4), filtered and concentrated in vacuo. The residue was adsorbed onto silica gel and chromatographed on silica gel using MeOH–CH_2Cl_2 (0:100, then 0.5:99.5, then 2:98) to afford 110 mg of **2** which was recrystallized from Et_2O–hexane to afford 75 mg (27%) of aniline **2** and 81 mg (30%) of azaindole **3**.

2
Mp 86–88 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 7.99 (s, 1 H), 7.89 (s, 1 H), 7.61 (d, *J* = 7.4 Hz, 1 H), 7.38 (dt, *J* = 7.1 Hz, 2 H), 7.31 (dt, *J* = 7.4 Hz, 1 H), 7.12 (d, *J* = 16.7 Hz, 1 H), 7.01 (d, *J* = 16.7 Hz, 1 H), 5.68 (s, 2 H, NH_2).

^{13}C (100 MHz, DMSO-d_6): δ = 144.2 (s), 138.9 (d), 137.0 (d), 136.9 (s), 136.2 (d), 129.1 (d), 128.8 (d), 127.3 (d), 126.9 (s), 123.0 (d), 121.6 (s).

MS: *m*/*z* (%) = 275/277 (MH^+, 100/85).

3
Mp 234–238 °C (dec.).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.4 (s, 1 H, NH), 8.70 (s, 1 H), 8.21 (s, 1 H), 7.98 (d, *J* = 7.2 Hz, 2 H), 7.51 (m, 2 H), 7.42 (m, 1 H), 6.96 (s, 1 H, H-3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 142.9 (s), 139.2 (d), 134.7 (s), 133.9 (s), 133.6 (d), 131.0 (s), 129.5 (d), 126.5 (d), 111.4 (s), 98.2 (d), one aromatic doublet was obscured.

MS: *m*/*z* (%) = 273/275 (MH^+, 100/97).

4-[(*E*)-2-Phenylethenyl]pyridin-3-ylamine (5)
Mp 185–188 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 8.14 (s, 1 H), 8.07 (d, *J* = 4.9 Hz, 1 H), 7.55 (d, *J* = 7.4 Hz, 2 H), 7.41 (t, *J* = 7.2 Hz, 2 H), 7.34 (t, *J* = 7.3 Hz, 1 H), 7.25 (1 H, partially obscured by $CDCl_3$), 7.18 (d, *J* = 16.2 Hz, 1 H), 7.08 (d, *J* = 16.2 Hz, 1 H), 3.83 (br s, 2 H, NH_2).

MS: *m*/*z* (%) = 197 (MH^+, 100).

Stannous Chloride Reduction of Nitrostyrylpyridines 1, 4a–f, 11, 15 and 19; *N*-{4-[(*E*)-2-(4-Bromophenyl)ethenyl]pyridin-3-yl}hydroxylamine (9c); Typical Procedure
To a solution of **4c** (1.0 g, 3.28 mmol) in THF–MeOH (1:1, 80 mL) cooled to 0 °C was added NaOAc·3H_2O (4.5 g, 33.08 mmol) followed by $SnCl_2$·2H_2O (3.7 g, 16.44 mmol). The reaction was monitored by TLC (MeOH–CH_2Cl_2, 5:95). After 5 h, the mixture was poured into ice cold sat. aq $NaHCO_3$ (pH 9), and extracted with EtOAc (3 × 80 mL). The combined organic layers were washed with sat. aq $NaHCO_3$ (2 × 80 mL), brine (3 × 80 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo to afford 963 mg of crude hydroxylamine **9c**, which was triturated with Et_2O to give 885 mg (92%) of **9c** as a yellow solid; mp 153–155 °C (dec.).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.70 (br s, 1 H), 8.58 (d, *J* = 1.5 Hz, 1 H), 8.41 (s, 1 H), 8.03 (d, *J* = 5.0 Hz, 1 H), 7.60 (s, 4 H), 7.47 (d, *J* = 5.0 Hz, 1 H), 7.36 (d, *J* = 16.3 Hz, 1 H), 7.30 (d, *J* = 16.2 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.6 (d), 141.8 (s), 137.3 (d), 136.9 (s), 132.5 (d), 131.5 (d), 129.7 (d), 129.2 (s), 123.2 (d), 122.1 (s), 119.2 (d).

MS: *m*/*z* (%) = 291/293 (MH^+, 100).

***N*-{5-Bromo-4-[(*E*)-2-phenylethenyl]pyridin-3-yl}hydroxylamine (7)**
Mp 125–129 °C (dec.).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.78 (s, 1 H, D_2O exchangeable), 8.67 (br s, 1 H, D_2O exchangeable), 8.38 (s, 1 H), 8.19 (s, 1 H), 7.60–7.58 (d, 2 H), 7.40 (t, 2 H), 7.34 (d, *J* = 7.2 Hz, 1 H), 7.13 (d, *J* = 16.8 Hz, 1 H, CH=C), 7.00 (d, *J* = 16.7 Hz, 1 H, CH=C).

MS: *m*/*z* (%) = 291/293 (MH^+, 100).

4-Bromo-2-phenyl-1*H*-pyrrolo[2,3-*c*]pyridin-1-ol (8)
Mp 230–233 °C (dec.).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.99 (s, 1 H, D_2O exchangeable), 8.78 (s, 1 H), 8.27 (s, 1 H), 7.96 (d, 2 H, *J* = 7.1 Hz), 7.55–7.51 (m, 3 H), 6.68 (s, 1 H, H-3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 141.2 (s), 139.4 (d), 132.5 (s), 131.6 (d), 129.7 (d), 129.6 (s), 129.3 (d), 128.9 (d), 127.8 (s), 111.7 (s), 95.5 (d).

MS: *m*/*z* (%) = 289/291 (MH^+, 100).

***N*-{4-[(*E*)-2-Phenylethenyl]pyridin-3-yl}hydroxylamine (9a)**
Yellow solid; mp 158–162 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.67 (s, 1 H, D_2O exchangeable), 8.53 (d, *J* = 1.8 Hz, 1 H), 8.38 (s, 1 H, D_2O exchangeable), 8.01 (d, *J* = 5.0 Hz, 1 H), 7.67 (d, *J* = 7.2 Hz, 2 H), 7.45 (d, *J* = 5.1 Hz, 1 H), 7.38 (m, 2 H), 7.31–7.29 (m, 3 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.1 (s), 141.4 (d), 137.2 (s), 136.8 (d), 132.4 (d), 129.1 (d), 128.7 (d), 127.4 (d), 121.9 (d), 118.6 (d), one aromatic singlet was not resolved.

MS: *m*/*z* (%) = 213 (MH^+, 100).

***N*-(4-{(*E*)-2-[4-(Trifluoromethyl)phenyl]ethenyl}pyridine-3-yl)hydroxylamine (9b)**
Mp 143–146 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.79 (s, 1 H, D_2O exchangeable), 8.63 (s, 1 H, D_2O, exchangeable), 8.43 (s, 1 H), 8.05 (d, *J* = 5.1 Hz, 1 H), 7.86 (d, *J* = 8.2 Hz, 2 H), 7.77 (d, *J* = 8.3 Hz, 2 H), 7.52 (d, *J* = 4.9 Hz, 1 H), 7.49 (d, coupling obscured by doublet at 7.52, 2 H), 7.42 (d, *J* = 16.2 Hz, 2 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.8 (s), 141.7 (s), 141.6 (d), 137.2 (d), 131.2 (d), 128.9, 128.3 (d), 126.4 (d), 125.1 (d), 123.8, 119.4 (d), one peak was not resolved.

MS: *m*/*z* (%) = 281 (MH^+, 100).

***N*-{4-[(*E*)-2-(2,4-Dimethoxyphenyl)ethenyl]pyridin-3-yl}hydroxylamine (9d)**
Mp 121–125 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.60 (s, 1 H, D_2O exchangeable), 8.50 (s, 1 H, D_2O exchangeable), 8.38 (s, 1 H), 8.00 (d, *J* = 5.1 Hz, 1 H), 7.66 (d, *J* = 9.2 Hz, 1 H), 7.41 (d, *J* = 16.3 Hz, 1 H), 7.36 (d, *J* = 5.1 Hz, 1 H), 7.12 (d, *J* = 16.3 Hz, 1 H), 6.60 (m, 2 H), 3.86 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 161.8 (s), 158.8 (s), 144.3 (s), 141.8 (d), 136.9 (d), 130.7 (s), 128.6 (d), 127.1 (d), 119.9 (d), 118.9 (s), 118.8 (d), 106.7 (d), 99.1 (d), 56.5 (q), 56.2 (q).

MS: *m*/*z* (%) = 271 (MH^+, 100).

***N*-{4-[(*E*)-2-(2-Thienyl)ethenyl]pyridin-3-yl}hydroxylamine (9e)**
Mp 131–134 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.69 (s, 1 H, D_2O exchangeable), 8.49 (br s, 1 H, D_2O exchangeable), 8.40 (s, 1 H), 8.01 (d, *J* = 5.0 Hz, 1 H), 7.54 (d, *J* = 4.5 Hz, 1 H), 7.51 (d, *J* = 15.8 Hz, 1 H), 7.43 (d, *J* = 5.0 Hz, 1 H), 7.29 (d, *J* = 3.3 Hz, 1 H), 7.09 (dd, *J* = 4.8, 3.7 Hz, 1 H), 7.02 (d, *J* = 16.0 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.3 (s), 142.9 (s), 141.9 (d), 137.2 (d), 129.5 (s), 128.9 (d), 128.6 (d), 127.4 (d), 126.1 (d), 121.5 (d), 119.0 (d).

MS: *m*/*z* (%) = 219 (MH^+, 10), 203 (100), 201 (40).

***N*-{4-[(*E*)-2-(3-Furyl)ethenyl]pyridin-3-yl}hydroxylamine (9f)**
Mp 136–139 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.56 (s, 1 H), 8.55 (s, 1 H), 8.38 (s, 1 H), 7.99 (d, *J* = 5.0 Hz, 1 H), 7.88 (s, 1 H), 7.71 (s, 1 H), 7.38 (d, *J* = 5.0 Hz, 1 H), 7.20 (d, *J* = 16.1 Hz, 1 H), 7.01 (d, *J* = 16.1 Hz, 1 H), 6.89 (s, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 145.2 (d), 144.2 (s), 143.2 (d), 141.9 (d), 137.6 (d), 129.8 (s), 125.3 (s), 123.0 (d), 121.8 (d), 118.8 (d), 108.6 (d).

***N*-{2-[(*E*)-2-Phenylethenyl]pyridin-3-yl}hydroxylamine (12)**
Mp 159–162 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 8.80 (s, 1 H), 8.53 (s, 1 H), 8.02 (d, *J* = 4.4 Hz, 1 H), 7.66 (d, *J* = 7.7 Hz, 2 H), 7.62 (d, *J* = 15.6 Hz, 1 H), 7.47 (d, *J* = 8.0 Hz, 1 H), 7.41 (d, *J* = 14.5 Hz, 1 H), 7.40 (dd, *J* = 7.3, 7.3 Hz, 2 H), 7.30 (t, *J* = 7.3 Hz, 1 H), 7.17 (d, *J* = 8.1, 4.5 Hz, 1 H).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 145.8 (s), 140.8 (d), 140.4 (s), 137.9 (s), 131.8 (d), 129.6 (d), 128.8 (d), 127.9 (d), 123.8 (d), 123.5 (d), 121.0 (d).

MS: *m*/*z* (%) = 213 (MH^+, 5), 197 (100), 195 (50).

***N*-{3-[(*E*)-2-Phenylethenyl]pyridin-4-yl}hydroxylamine (16)**
Yellow oil.

^{1}H NMR (400 MHz, CD_3CO_2D, major tautomer): δ = 9.06 (br, partially CD_3CO_2D exchanged), 8.51 (br, partially CD_3CO_2D exchanged), 8.37 (s, 1 H), 8.24 (d, *J* = 7.0 Hz, 1 H) 7.66 (d, *J* = 7.2 Hz, 1 H), 7.60 (d, *J* = 7.3 Hz, 2 H), 7.48–7.31 (m, 5 H), 7.19 (d, *J* = 16.0 Hz, 1 H), 7.02 (d, *J* = 16.1 Hz, 1 H).

***N*-{3-[(*E*)-2-Phenylethenyl]pyridin-2-yl}hydroxylamine (20)**
Orange solid; mp 141–146 °C (dec.).

^{1}H NMR (400 MHz, CD_3CO_2D, single tautomer): δ = 8.11 (d, *J* = 7.3 Hz, 1 H), 8.00 (d, *J* = 6.1 Hz, 1 H), 7.59 (d, *J* = 7.3 Hz, 2 H), 7.40–7.31 (m, 3 H), 7.23 (d, *J* = 16.0 Hz, CH=C), 7.06 (d, *J* = 16.0 Hz, 1 H), 7.00 (t, *J* = 6.9 Hz, 1 H).

^{13}C NMR (100 MHz, CD_3CO_2D): δ = 151.26 (s), 137.85 (d), 135.96 (s), 135.25 (d), 133.39 (d), 128.93 (d), 128.70 (d), 127.17 (d), 121.46 (s), 117.25 (d), 113.79 (d).

MS: *m*/*z* (%) = 213 (MH^+, 100).

DDQ Oxidation/Cyclization; 2-(4-Bromophenyl)-1*H*-pyrrolo[2,3-*c*]pyridin-1-ol (10c); Typical Procedure
To a solution of arylhydroxylamine **9c** (145 mg, 0.50 mmol) in a mixture of MeCN–H_2O–HOAc (10:2:1, 19.5 mL) cooled to –10 °C was added DDQ (110 mg, 0.48 mmol) in one portion. The mixture turned a deep red and the reaction was monitored by TLC (MeOH–CH_2Cl_2, 1:9). After 20 min, the yellow reaction mixture was diluted with 1 N aq HCl (10 mL) and Et_2O (20 mL). The acidic aqueous phase was separated and the organic layer extracted with 1 N aq HCl (3 × 5 mL). The combined acidic aqueous layers were washed with 1:1 Et_2O–hexane (3 × 5 mL), made basic with $NaHCO_3$ and extracted with EtOAc (3 × 15 mL). The combined organic layers were dried (Na_2SO_4), filtered and concentrated in vacuo to afford 136 mg (94%) of 1-hydroxy-6-azaindole **10c** as a yellow solid; mp 184–188 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ= 11.84 (br, 1 H, OH), 8.82 (s, 1 H, H-7), 8.16 (d, *J* = 5.5 Hz, 1 H, H-5), 7.90 (d, *J* = 8.5 Hz, 2 H, ArH), 7.74 (d, *J* = 8.5 Hz, 2 H, ArH), 7.56 (d, *J* = 5.5 Hz, 1 H, H-4), 6.79 (s, 1 H, H-3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 139.5 (s), 139.1 (d), 132.9 (s), 132.8 (d), 132.6 (d), 130.9 (d), 129.9 (s), 127.8 (s), 123.1 (s), 115.4 (d), 96.7 (d).

MS: *m*/*z* (%) = 291/289 (MH^+, 42/42), 274 (100), 272 (88), 194 (50).

Anal. Calcd for $C_{13}H_9BrN_2O$: C, 54.00; H, 3.14; N, 9.69. Found: C, 53.85; H, 3.02; N, 9.45.

2-Phenyl-1*H*-pyrrolo[2,3-*c*]pyridin-1-ol (10a)
Mp 172–175 °C (dec.).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.79 (br s, 1 H), 8.75 (br, 1 H), 8.12 (br, 1 H), 7.91 (d, *J* = 7.1 Hz, 2 H), 7.53–7.40 (m, 4 H), 6.69 (s, 1 H, H-3).

MS: *m*/*z* (%) = 211 (MH^+, 100).

2-(4-Trifluoromethylphenyl)-1*H*-pyrrolo[2,3-*c*]pyridin-1-ol (10b)
Mp 192–198 °C (dec.).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.01 (br, 1 H), 8.81 (br, 1 H), 8.13 (d, *J* = 8.2 Hz, 3 H), 7.85 (d, *J* = 8.3 Hz, 2 H), 7.52 (br, 1 H), 6.83 (s, 1 H, H-3).

MS: *m*/*z* (%) = 278 (M^+, 34), 262 (100).

2-(2,4-Dimethoxyphenyl)-1*H*-pyrrolo[2,3-*c*]pyridin-1-ol (10d)
Mp 95–100 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.18 (br s, 1 H, OH), 8.72 (s, 1 H), 8.10 (d, *J* = 5.4 Hz, 1 H), 7.53 (d, *J* = 8.4 Hz, 1 H), 7.47 (d, *J* = 5.4 Hz, 1 H), 6.73 (d, *J* = 2.0 Hz, 1 H), 6.68 (dd, *J* = 8.5, 2.1 Hz, 1 H), 6.46 (s, 1 H), 3.86 (s, 3 H, OCH_3), 3.82 (s, 3 H, OCH_3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 162.2 (s), 159.4 (s), 138.7 (d), 138.3 (s), 133.0 (d), 132.2 (d), 127.9 (s), 115.0 (d), 111.9 (s), 105.9 (d), 99.6 (d), 97.8 (d), 56.5 (q), 56.3 (q), one aromatic doublet was not resolved.

2-(2-Thienyl)-1*H*-pyrrolo[2,3-*c*]pyridin-1-ol (10e)
Mp 190–195 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.04 (br, 1 H), 8.72 (s, 1 H), 8.10 (d, *J* = 5.4 Hz, 1 H), 7.82 (d, *J* = 3.6 Hz, 1 H), 7.73 (d, *J* = 5.0 Hz, 1 H), 7.47 (d, *J* = 5.4 Hz, 1 H), 7.23 (dd, *J* = 4.9, 3.8 Hz, 1 H), 6.77 (s, 1H, H-3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 138.5 (d), 135.5 (s), 132.1 (d), 131.5 (s), 129.0 (d), 128.5 (d), 128.4 (d), 128.0 (s), 115.0 (d), 94.1 (d), one aromatic singlet was not resolved.

MS: *m*/*z* (%) = 216 (M^+, 60), 200 (100).

2-(3-Furyl)-1*H*-pyrrolo[2,3-*c*]pyridin-1-ol (10f)
Mp 194–197 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.80 (br s, 1 H), 8.73 (s, 1 H), 8.35 (s, 1 H), 8.10 (d, *J* = 5.2 Hz, 1 H), 7.85 (s, 1 H), 7.47 (d, *J* = 5.2 Hz, 1 H), 7.09 (d, *J* = 1.8 Hz, 1 H), 6.67 (s, 1 H, H-3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 144.8 (d), 142.2 (d), 138.8 (d), 134.1 (s), 132.1 (d), 128.2 (s), 116.5 (s), 115.1 (d), 110.5 (d), 94.4 (d), one aromatic doublet was not resolved.

MS: *m*/*z* (%) = 201 (MH^+, 25), 185 (100).

2-Phenyl-1*H*-pyrrolo[3,2-*b*]pyridin-1-ol (13)
Mp 194–196 °C (dec.).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.48 (s, 1 H, OH), 8.36 (dd, *J* = 4.5, 1.1 Hz, 1 H), 7.93 (d, *J* = 7.2 Hz, 2 H), 7.83 (d, *J* = 8.2 Hz, 1 H), 7.52 (td, *J* = 7.5, 7.3 Hz, 2 H), 7.43 (td, *J* = 7.3, 7.3 Hz, 1 H), 7.18 (dd, *J* = 8.1, 4.6 Hz, 1 H), 6.79 (s, 1 H, H-3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 143.7 (d), 141.2 (s), 140.4 (s), 130.6 (s), 129.1 (d), 128.9 (d), 128.6 (d), 117.3 (d), 116.5 (d), 97.3 (d), one aromatic singlet was not resolved.

MS: *m*/*z* (%) = 211 (MH^+, 20), 209 (32), 195 (100).

Iron Reduction of 1-Hydroxyazaindoles; 2-(4-Bromophenyl)-1*H*-pyrrolo[2,3-*c*]pyridine (6c); Typical Procedure

A mixture of hydroxyindole **10c** (52 mg, 0.180 mmol) and iron filings (200 mg, 3.58 mmol) was refluxed in HOAc–EtOH (1:2, 12 mL). The reaction was monitored by TLC in MeOH–CH_2Cl_2 (5:95) for disappearance of the yellow starting material to afford a slightly less polar product, which has a blue fluorescence under UV light. After 45 min, the excess iron was removed with a magnetic bar. The mixture was made basic with sat. aq $NaHCO_3$ (25 mL) and extracted with EtOAc (3 × 20 mL). The combined organic layers were washed with sat. aq $NaHCO_3$ (20 mL), brine (3 × 20 mL), dried (Na_2SO_4), filtered, and concentrated in vacuo to afford the crude product in quantative yield; mp 264–266 °C. Chromatography on silica gel using MeOH–CH_2Cl_2 (1:9, then 2:98, then 3:97, then 4:96, then 5:95, then 6:94) gave 40.1 mg (81%); mp 264–266 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.13 (br s, 1 H), 8.76 (s, 1 H, H-7), 8.10 (d, *J* = 5.5 Hz, 1 H, H-5), 7.90 (d, *J* = 8.5 Hz, 2 H), 7.73 (d, *J* = 8.5 Hz, 2 H), 7.53 (d, *J* = 5.5 Hz, 1 H, H-4), 7.03 (s, 1 H, H-3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 141.0 (s), 139.1 (d), 135.2 (d), 133.6 (s), 132.9 (d), 131.4 (s), 128.6 (d), 122.6 (s), 115.4 (d), 99.4 (d).

MS: *m*/*z* (%) = 273/275 (MH^+, 100/100).

2-Phenyl-1*H*-pyrrolo[2,3-*c*]pyridine (6a)

Mp 222–224 °C (Lit.[4] mp 223–225 °C).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.03 (s, 1 H, NH), 8.76 (s, 1 H), 8.10 (d, *J* = 5.3 Hz, 1 H), 7.94 (d, *J* = 7.6 Hz, 2 H), 7.51 (m, 3 H), 7.41 (m, 1 H), 6.98 (s, 1 H, H-3).

2-(4-Trifluoromethylphenyl)-1*H*-pyrrolo[2,3-*c*]pyridine (6c)

Mp 239–242 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.23 (s, 1 H), 8.80 (s, 1 H), 8.16 (d, *J* = 8.2 Hz, 2 H), 8.13 (d, *J* = 5.5 Hz, 1 H), 7.88 (d, *J* = 8.3 Hz, 2 H), 7.56 (d, *J* = 5.4 Hz, 1 H), 7.15 (s, 1 H, H-3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 140.3 (s), 139.2 (d), 136.0 (s), 135.5 (d), 129.9 (q, $^2J_{CF}$ = 31 Hz), 127.2 (d), 126.8 (d), 125.0 (q, $^1J_{CF}$ = 270 Hz), 100.6 (d), one aromatic doublet and one aromatic singlet was not resolved.

MS: *m*/*z* (%) = 263 (MH^+, 100).

2-(2,4-Dimethoxyphenyl)-1*H*-pyrrolo[2,3-*c*]pyridine (6d)

Yield: 85%; mp 142–145 °C (Lit.[9b] mp 150–152 °C).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.51 (br s, 1 H, NH), 8.73 (s, 1 H), 8.05 (d, *J* = 5.4 Hz, 1 H), 7.78 (d, *J* = 8.6 Hz, 1 H), 7.45 (d, *J* = 5.4 Hz, 1 H), 6.85 (s, 1 H), 6.74 (d, *J* = 2.2 Hz, 1 H), 6.69 (dd, *J* = 8.6, 2.3 Hz, 1 H), 3.95 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 161.4 (s), 158.2 (s), 139.3 (s), 138.1 (d), 134.2 (d), 132.9 (s), 129.9 (d), 112.9 (s), 106.3 (d), 99.5 (d), 56.2 (q), 55.9 (q), two aromatic doublets and one aromatic singlet was not resolved.

MS: *m*/*z* (%) 254 (M^+, 100), 253 (68).

2-(2-Thienyl)-1*H*-pyrrolo[2,3-*c*]pyridine (6e)

Mp 208–211 °C (dec.) (Lit.[4] mp 235–236 °C).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.08 (s, 1 H), 8.71 (s, 1 H), 8.09 (d, *J* = 5.4 Hz, 1 H), 7.65 (m, 2 H), 7.48 (d, *J* = 5.4 Hz, 1 H), 7.20 (dd, *J* = 4.0, 4.6 Hz, 1 H), 6.75 (s, 1 H, H-3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 139.1 (d), 136.9 (s), 135.2 (s), 134.7 (d), 133.7 (s), 129.2 (d), 127.7 (d), 126.2 (d), 98.7 (d), one aromatic doublet and one aromatic singlet was not resolved.

MS: *m*/*z* (%) = 201 (M^+, 100).

2-(3-Furyl)-1*H*-pyrrolo[2,3-*c*]pyridine (6f)

Mp 218–220 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.88 (br s, 1 H, NH), 8.70 (s, 1 H), 8.28 (s, 1 H), 8.07 (d, *J* = 5.4 MHz, 1 H), 7.82 (br s, 1 H), 7.47 (d, *J* = 5.4 Hz, 1 H), 7.05 (br s, 1 H), 6.73 (s, 1 H).

2-Phenyl-1*H*-pyrrolo[3,2-*b*]pyridine (14)

Mp 235–242 °C (Lit.[4] mp 255–256 °C).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.80 (s, 1 H, NH), 8.31 (d, *J* = 4.1 Hz, 1 H), 7.93 (d, *J* = 7.6 Hz, 2 H), 7.75 (d, *J* = 8.1 Hz, 1 H), 7.50 (m, 2 H), 7.38 (m, 1 H), 7.10 (dd, *J* = 8.1, 4.6 Hz, 1 H), 7.06 (s, 1 H, H-3).

2-Phenyl-1*H*-pyrrolo[3,2-*c*]pyridine (18)[4]

Mp 271–274 °C (dec.) (Lit.[19] mp 274–276 °C).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 11.97 (s, 1 H, NH), 8.82 (s, 1 H), 8.17 (d, *J* = 5.5 Hz, 1 H), 7.90 (d, *J* = 7.8 Hz, 2 H), 7.49 (t, *J* = 7.4 Hz, 2 H), 7.38 (m, 2 H), 7.05 (s, 1H, H-3).

^{13}C NMR (100 MHz, DMSO-d_6): δ = 143.8 (d), 141.3 (d), 141.2 (s), 139.7 (s), 132.3 (s), 129.9 (d), 129.0 (d), 126.6 (s), 126.2 (d), 107.5 (d), 98.5 (d).

MS: *m*/*z* (%) = 194 (M^+, 100).

2-Phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (21)[19]

Mp 195–198 °C (Lit.[4] mp 204–205 °C).

^{1}H NMR (400 MHz, DMSO-d_6): δ = 12.20 (br s, 1 H, NH), 8.19 (dd, *J* = 4.7, 1.57 Hz, 1 H), 7.93–7.90 (m, 3 H), 7.45 ('t', *J* = 7.7 Hz, 2 H), 7.33 (t, *J* = 7.4 Hz, 1 H), 7.04 (dd, *J* = 7.8, 4.68 Hz, 1 H), 6.91 (d, *J* = 2.1 Hz, H-3).

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