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SYNTHESIS OF 1-ARYL-1*H*-PYRROLO[2,3-*b*]PYRIDINES (1-ARYL-7-AZAINDOLES) BY A THERMAL DEHYDRATION-CYCLIZATION-DEHYDROGENATION SEQUENCE OF 2-ARYLAMINO-3-(1-HYDROXYALKYL)PYRIDINES

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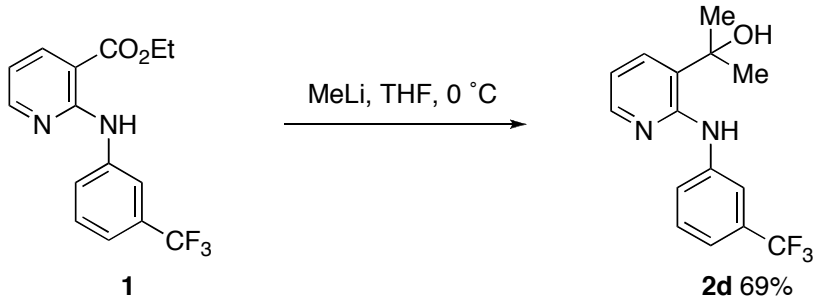
Abstract - 1-Aryl-1*H*-pyrrolo[2,3-*b*]pyridines (1-aryl-7-azaindoles) have been prepared in reasonable yields from the corresponding 2-arylamino-3-(1-hydroxyalkyl)pyridines, on heating at *ca*. 250 ˚C, through a successive dehydration/cyclization/dehydrogenation sequence.

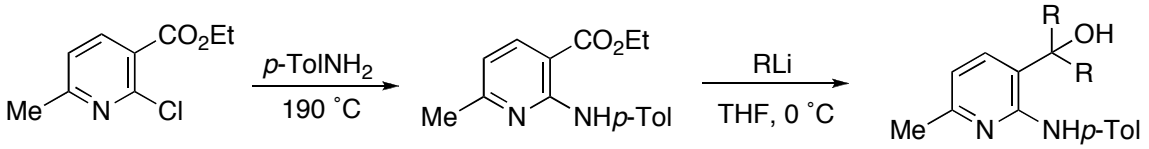
Previously, we demonstrated that 1-aryl-1*H*-indoles could be prepared by reactions of 2-(arylamino)styrene derivatives with iodine in the presence of sodium hydrogencarbonate under mild conditions.[1] As a continuation of this study, we became interested in synthesizing 1-aryl-1*H*-pyrrolo[2,3-*b*]pyridines utilizing the iodine-mediated cyclization of 2-arylamino-3-vinylpyridine derivatives. In order to prepare 2-arylamino-3-vinylpyridine derivatives, we conducted thermal dehydration of 2-arylamino-3-(1-hydroxyalkyl)pyridines (**2**). However, we found that the heating gave directly 1-aryl-1*H*-pyrrolo[2,3-*b*]pyridines (**10**). Herein, we wish to report the details of our studies on thermal reaction of 2-arylamino-3-(1-hydroxyalkyl)pyridines (**2**), which offers a new and facile route to 1-aryl-1*H*-pyrrolo[2,3-*b*]pyridines (**10**). In recent years, 1*H*-pyrrolo[2,3-*b*]pyridine derivatives has received considerable attention, because some of them exhibit a variety of biological activities.[2] For example, these have been reported to be useful as 5-HT_6 agonists and antagonists,[2i] antidiadetics,[2j] partial nicotinic agonists,[2k] and so on. Therefore, a number of works on the synthesis of this class of molecules have recently appeared.[3]

The starting materials, 2-arylamino-3-(1-hydroxyalkyl)pyridines (**2**), for the present 1*H*-pyrrolo[2,3-*b*]pyridine synthesis were prepared as follows. Compounds (**2a-c**) were prepared by a literature method[4] from commercially available 2-chloropyridine-3-carboxylic acid. Compounds (**2d-k**) could be easily prepared from known compounds. Thus, the reaction of ethyl 2-[3-(trifluoromethyl)phenylamino]-



1 **2d** 69%

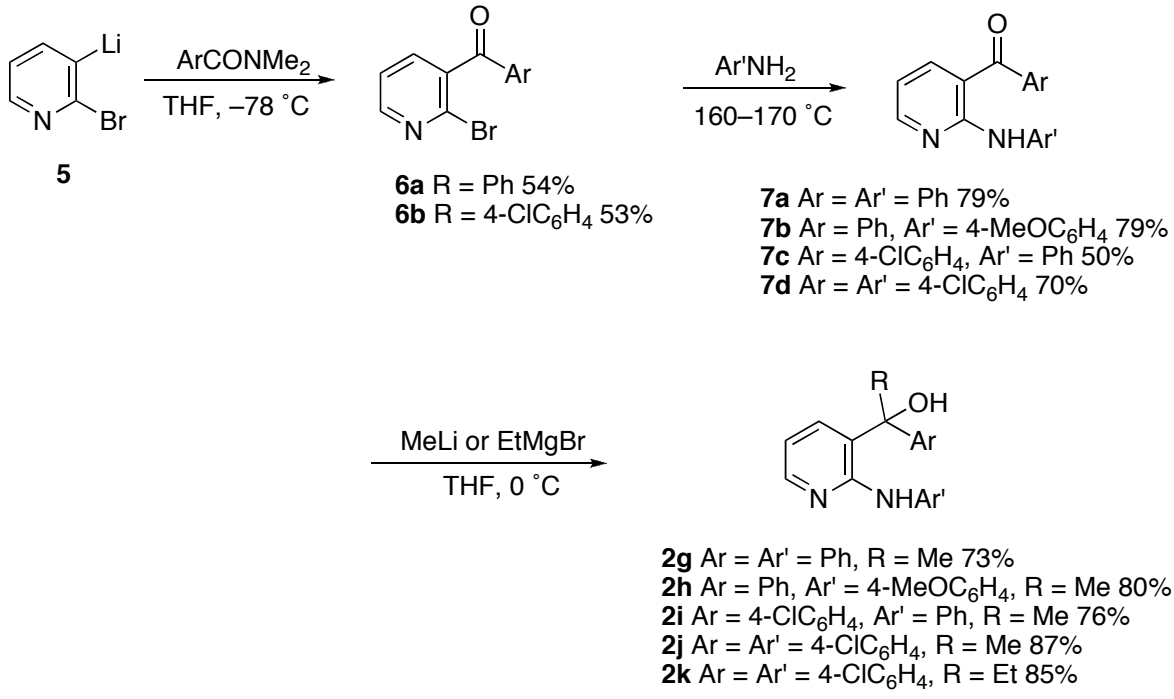
Scheme 1



3 **4** 66%

2e R = Me 76%
2f R = Et 73%

Scheme 2



5

6a R = Ph 54%
6b R = 4-ClC_6H_4 53%

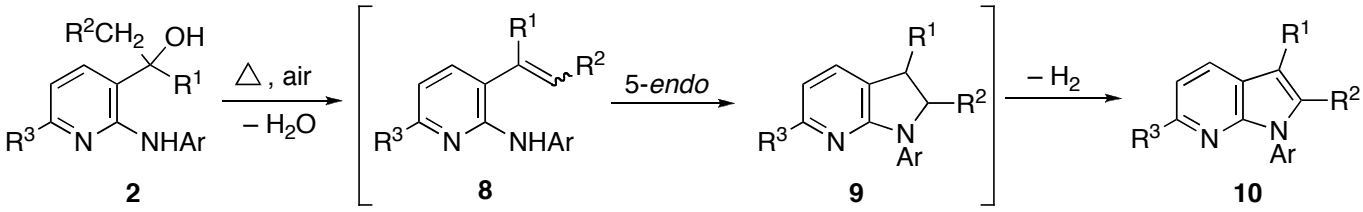
7a Ar = Ar' = Ph 79%
7b Ar = Ph, Ar' = 4-$MeOC_6H_4$ 79%
7c Ar = 4-ClC_6H_4, Ar' = Ph 50%
7d Ar = Ar' = 4-ClC_6H_4 70%

2g Ar = Ar' = Ph, R = Me 73%
2h Ar = Ph, Ar' = 4-$MeOC_6H_4$, R = Me 80%
2i Ar = 4-ClC_6H_4, Ar' = Ph, R = Me 76%
2j Ar = Ar' = 4-ClC_6H_4, R = Me 87%
2k Ar = Ar' = 4-ClC_6H_4, R = Et 85%

Scheme 3

pyridine-2-carboxylate (**1**)[5] with methyllithium afforded **2d** (Scheme 1). A mixture of ethyl 2-chloro-6-methylpyridine-2-carboxylate[6] and 4-methylaniline was heated at 190 ˚C to give ethyl 6-methyl-2-(4-methylphenyl)pyridine-2-carboxylate (**4**), which was allowed to react with methyllithium or ethyllithium to afford **2e** or **2f**, respectively (Scheme 2). The reaction of 2-bromo-3-lithiopyridine (**5**)[7]

with *N,N*-dimethylbenzamides gave 3-aroyl-2-bromopyridines (**6**), which were heated with aryl amines at 160–170 ˚C to give 3-aroyl-2-(arylamino)pyridines (**7**). These were allowed to react with methyllithium or ethylmagnesium bromide to afford **2g-k** (Scheme 3).



Scheme 4

Table 1. Preparation of 1-aryl-1*H*-pyrolo[2,3-*b*]pyridines (**10**)

Entry	**2**	Temp/°C	Time/h	**10** (Yield/%)[a]
1	**2a** (R^1 = Me, R^2 = R^3 = H, Ar = Ph)	270	2	**10a** (51)
2	**2b** (R^1 = Me, R^2 = R^3 = H, Ar = *p*-Tol)	270	2	**10b** (56)
3	**2c** (R^1 = Me, R^2 = R^3 = H, Ar = 4-$MeOC_6H_4$)	240	1	**10c** (60)
4	**2d** (R^1 = Me, R^2 = R^3 = H, Ar = 3-$CF_3C_6H_4$)	270	2	**10d** (34)
5	**2e** (R^1 = R^3 = Me, R^2 = H, Ar = *p*-Tol)	270	2	**10e** (57)
6	**2f** (R^1 = Et, R^2 = R^3 = Me, Ar = *p*-Tol)	250	2	**10f** (32)
7	**2g** (R^1 = Ar = Ph, R^2 = R^3 = H)	230	4	**10g** (61)
8	**2h** (R^1 = Ph, Ar = 4-$MeOC_6H_4$, R^2 = R^3 = H)	260	4	**10h** (68)
9	**2i** (R^1 = 4-ClC_6H_4, Ar = Ph, R^2 = R^3 = H)	240	2.5	**10i** (61)
10	**2j** (R^1 = Ar = 4-ClC_6H_4, R^2 = R^3 = H)	270	1	**10j** (71)
11	**2k** (R^1 = Ar = 4-ClC_6H_4, R^2 = Me, R^3 = H)	255	2.5	**10k** (45)

[a]Isolated yields.

The synthesis of 1-aryl-1*H*-pyrrolo[2,3-*b*]pyridines (**10**) from 2-arylamino-3-(1-hydroxyalkyl)pyridines (**2**) is illustrated in Scheme 4. Compounds (**2**), thus obtained, were subjected to the following thermal reaction sequence. Thus, when compounds (**2**) were heated, dehydration occurred to give 2-arylamino-3-vinylpyridine intermediates (**8**). These intermediates underwent the 5-*endo* ring closure to afford 2,3-dihydro-1*H*-pyrrolo[2,3-*b*]pyridine intermediates (**9**), dehydrogenation of which with oxygen gave rise to the desired products (**10**) in the yields summarized in Table 1. It shows that the sequence completes within 4 h at 230–270 ˚C to furnish the corresponding 1-aryl-1*H*-pyrrolo[2,3-*b*]pyridines (**10**) in generally moderate to fair yields, and that the yields of the 3-aryl derivatives (**10g-k**) (Entries 7–11) are slightly higher than those of the 3-alkyl derivatives (**10a-f**) (Entries 1–6). It also indicates that the 2-[(3-trifluoromethylphenyl)amino]pyridine derivative (**2d**) gave a poorer result, as can be seen from Entry 4. This is presumably attributed to the lower basicity of the nitrogen of the (3-trifluoromethylphenyl)amino group compared to those of other anilino groups due to the highly electron-withdrawing property of the trifluoromethyl group. The reaction using the substrates having a

methyl substituent at the β-position of the 3-vinyl moiety (*i.e.* R^2 = Me; **2f** and **2k**) also led to the desired pyrrolopyridine derivatives (**10f**) and (**10k**), but the yields were somewhat lower, presumably due to steric hindrance by the β-methyl group in the ring closure step (Entries 6 and 11). It should be noted that attempts to obtain 1-alkyl-1*H*-pyrrolo[2,3-*b*]pyridines by heating 1-[2-(alkylamino)pyridin-2-yl]-1-phenylethanols resulted in failure.

In summary, we have demonstrated that 1-aryl-1*H*-pyrrolo[2,3-*b*]pyridines can be prepared conveniently. This method may find some value in the synthesis of this type of heterocycles because of readily availability of the starting materials and the easiness of operations compared to previous methods.[3]

EXPERIMENTAL

The melting points were determined on a Laboratory Devices MEL-TEMP II melting-point apparatus and are uncorrected. The IR spectra were recorded on a Shimadzu FTIR-8300 spectrometer. The ^{1}H NMR spectra were determined using $SiMe_4$ as an internal reference in $CDCl_3$ with a JEOL ECP500 FT NMR spectrometer operating at 500 MHz. The ^{13}C NMR spectra were determined in $CDCl_3$ using TMS as an internal reference with a JEOL ECP500 FT NMR spectrometer operating at 125 MHz. Low-resolution mass spectra (EI, 70 eV) were recorded on a JEOL JMS-AX505 HA spectrometer. Thin-layer chromatography (TLC) was carried out on Merck Kieselgel 60 PF_{254}.

Starting Materials. 2-[2-(phenylamino)pyridin-3-yl]propan-2-ol (**2a**),[4] 2-[2-(4-methylphenylamino)-pyridin-3-yl]propan-2-ol (**2b**),[4] 2-[2-(4-methoxyphenylamino)pyridin-3-yl]propan-2-ol (**2c**),[4] ethyl 2-[3-(trifluoromethyl)phenyl]aminopyridine-3-carboxylate (**1**),[5] and ethyl 2-chloro-6-methylpyridine-3-carboxylate (**3**)[6] were prepared according to the appropriate reported procedures. All other chemicals used in this study were commercially available.

2-{2-[3-(Trifluoromethyl)phenyl]aminopyridin-3-yl}propan-2-ol (2d). This compound was prepared by reacting ethyl 2-[3-(trifluoromethyl)phenyl]aminopyridine-3-carboxylate (**1**)[5] with methyllithium at 0 °C in THF in 69% yield; a white solid; mp 96–98 °C (hexane); IR (KBr) 3421, 3303, 1617, 1610 cm^{-1}; ^{1}H NMR δ 1.69 (6H, s), 2.09 (1H, s), 6.75 (1H, dd, *J* = 7.8, 5.0 Hz), 7.18 (1H, d, *J* = 7.8 Hz), 7.38 (1H, t, *J* = 7.8 Hz), 7.43 (1H, dd, *J* = 7.8, 1.4 Hz), 7.77 (1H, d, *J* = 7.3 Hz), 7.89 (1H, s), 8.16 (1H, dd, *J* = 5.0, 1.4 Hz), 9.03 (1H, br s). Anal. Calcd for $C_{15}H_{15}F_3N_2O$: C, 60.81; H, 5.10; N, 9.45. Found: C, 60.80; H, 5.12; N, 9.44.

Ethyl 6-methyl-2-(4-methylphenylamino)pyridine-3-carboxylate (4). This compound was prepared by heating (190 °C) a mixture of ethyl 2-chloro-6-methylpyridine-3-carboxylate (**3**)[6] and 4-methylaniline for 25 min in 66% yield; a yellow solid; mp 85–86 °C (hexane); IR (KBr) 3267, 1684, 1620 cm^{-1}; ^{1}H NMR δ 1.40 (3H, t, *J* = 7.3 Hz), 2.32 (3H, s), 2.47 (3H, s), 4.36 (2H, q, *J* = 7.3 Hz), 6.54 (1H, d, *J* = 8.2 Hz), 7.12 (2H, d, *J* = 8.2 Hz), 7.65 (2H, d, *J* = 8.2 Hz), 8.11 (1H, d, *J* = 8.2 Hz), 10.15 (1H, br s). Anal. Calcd for $C_{16}H_{18}N_2O_2$: C, 71.09; H, 6.71; N, 10.36. Found: C, 70.87; H, 6.85; N, 10.55.

2-[6-Methyl-2-(4-methylphenylamino)pyridin-3-yl]propan-2-ol (2e). This compound was prepared by reacting **4** with MeLi at 0 ˚C in THF in 76% yield; a pale-yellow solid; mp 128–130 ˚C (hexane); IR (KBr) 3371, 3319, 1605 cm^{-1}; ^1H NMR δ 1.66 (6H, s), 1.91 (1H, s), 2.30 (3H, s), 2.42 (3H, s), 6.51 (1H, d, *J* = 7.8 Hz), 7.09 (2H, d, *J* = 8.2 Hz), 7.28 (2H, d, *J* = 8.2 Hz), 7.55 (1H, d, *J* = 7.8 Hz), 8.69 (1H, br s). Anal. Calcd for $C_{16}H_{20}N_2O$: C, 74.97; H, 7.86; N, 10.93. Found: C, 74.95; H, 8.05; N, 10.76.

2-[6-Methyl-2-(4-methylphenylamino)pyridin-3-yl]pentan-3-ol (2f). This compound was prepared by reacting **4** with EtLi at 0 ˚C in THF in 73% yield; a yellow solid; mp 93–94 ˚C (hexane); IR (KBr) 3304, 1609 cm^{-1}; ^1H NMR δ 0.85 (6H, t, *J* = 7.3 Hz), 1.55 (1H, s), 1.87–2.00 (4H, m), 2.30 (3H, s), 2.42 (3H, s), 6.51 (1H, d, *J* = 7.8 Hz), 7.08 (2H, d, *J* = 8.2 Hz), 7.12 (1H, d, *J* = 7.8 Hz), 7.56 (2H, d, *J* = 8.2 Hz), 8.99 (1H, br s). Anal. Calcd for $C_{18}H_{24}N_2O$: C, 76.02; H, 8.51; N, 9.85. Found: C, 75.98; H, 8.62; N, 9.82.

(2-Bromopyridin-3-yl)phenylmethanone (6a).[8] This compound was prepared by the reaction of 2-bromo-3-lithiopyridine (**5**), generated according to the procedure reported by Johnston *et al.*,[7] with *N*,*N*-dimethylbenzamide in 54% yield; an orange oil; R_f 0.43 (1:3 THF–hexane); IR (neat) 1672 cm^{-1}; ^1H NMR δ 7.42 (1H, dd, *J* = 7.3, 4.6 Hz), 7.50 (2H, dd, *J* = 8.2, 7.3 Hz), 7.65 (1H, t, *J* = 7.3 Hz), 7.67 (1H, dd, *J* = 7.3, 1.8 Hz), 7.82 (2H, d, *J* = 8.2 Hz), 8.53 (1H, dd, *J* = 4.6, 1.8 Hz).

Phenyl[2-(phenylamino)pyridin-3-yl]methanone (7a).[9] This compound was prepared by heating (170 ˚C) a mixture of **6a** and aniline for 45 min in 79% yield; a yellow solid; mp 87–90 ˚C (hexane). The spectral data for this compound were identical those reported previously.[9]

1-Phenyl-1-[2-(phenylamino)pyridine-3-yl]ethanol (2g). This compound was prepared by reacting **7a** with MeLi at 0 ˚C in THF in 73% yield; a pale-yellow solid; mp 147–148 ˚C (hexane–Et_2O); IR (KBr) 3409, 3334, 1607 cm^{-1}; ^1H NMR δ 1.96 (3H, s), 2.54 (1H, s), 6.75 (1H, dd, *J* = 7.8, 5.0 Hz), 6.89 (1H, tt, *J* = 7.3, 1.4 Hz), 7.16 (2H, dd, *J* = 7.8, 7.3 Hz), 7.25 (1H, tt, *J* = 7.3, 1.4 Hz), 7.30–7.33 (4H, m), 7.39 (2H, d, *J* = 7.3 Hz), 7.57 (1H, dd, *J* = 7.8, 1.8 Hz), 7.75 (1H, br s), 8.18 (1H, dd, *J* = 5.0, 1.8 Hz). Anal. Calcd for $C_{19}H_{18}N_2O$: C, 78.59; H, 6.25; N, 9.65. Found: C, 78.48; H, 6.21; N, 9.70.

[2-(4-Methoxyphenyl)aminopyridin-3-yl]phenylmethanone (7b). This compound was prepared by heating (170 ˚C) a mixture of **6a** and 4-methoxybenzenamine for 30 min in 79% yield; a yellow solid; mp 97–99 ˚C (hexane); IR (KBr) 3258, 1625, 1607 cm^{-1}; ^1H NMR δ 3.82 (3H, s), 6.64 (1H, dd, *J* = 7.8, 5.0 Hz), 6.93 (2H, d, *J* = 9.2 Hz), 7.50 (2H, t, *J* = 7.3 Hz), 7.58 (1H, t, *J* = 7.3 Hz), 7.59 (2H, d, *J* = 9.2 Hz), 7.64 (2H, d, *J* = 7.3 Hz), 7.85 (1H, dd, *J* = 7.8, 2.3 Hz), 8.36 (1H, dd, *J* = 5.0, 2.3 Hz), 10.70 (1H, s). Anal. Calcd for $C_{19}H_{16}N_2O_2$: C, 74.98; H, 5.30; N, 9.20. Found: C, 74.73; H, 5.33; N, 8.95.

1-[2-(4-Methoxyphenyl)aminopyridin-3-yl]-1-phenylethanol (2h). This compound was prepared by reacting **7b** with MeLi at 0 ˚C in THF in 80% yield; a pale-yellow solid; mp 138–140 ˚C (hexane–Et_2O); IR (KBr) 3410, 3308, 1601 cm^{-1}; ^1H NMR δ 1.96 (3H, s), 2.51 (1H, s), 3.74 (3H, s), 6.70 (1H, dd, *J* = 7.8, 5.0 Hz), 6.77 (2H, d, *J* = 8.7 Hz), 7.15 (2H, d, *J* = 8.7 Hz), 7.26 (1H, t, *J* = 7.3 Hz), 7.33 (2H, dd, *J*

= 7.8, 7.3 Hz), 7.40 (2H, d, *J* = 7.8 Hz), 7.46 (1H, br s), 7.55 (1H, dd, *J* = 7.8, 1.4 Hz), 8.13 (1H, dd, *J* = 5.0, 1.8 Hz). Anal. Calcd for $C_{20}H_{20}N_2O_2$: C, 74.98; H, 6.29; N, 8.74. Found: C, 74.97; H, 6.21; N, 8.71.

(2-Bromopyridin-2-yl)(4-chlorophenyl)methanone (6b).[8] This compound was prepared by the reaction of **5**[7] with *N,N*-dimethyl-4-chlorobenzamide in 53% yield; a yellow oil; R_f 0.29 (1:4 AcOEt–hexane); IR (neat) 1672 cm^{-1}; ^1H NMR δ 7.43 (1H, dd, *J* = 7.3, 5.0 Hz), 7.48 (2H, d, *J* = 8.7 Hz), 7.66 (1H, dd, *J* = 7.3, 1.8 Hz), 7.75 (2H, d, *J* = 8.7 Hz), 8.54 (1H, dd, *J* = 5.0, 1.8 Hz).

(4-Chlorophenyl)[2-(phenylamino)pyridine-2-yl]methanone (7c). This compound was prepared by heating (160 ˚C) a mixture of **6b** and aniline for 1 h in 50% yield; a yellow oil; R_f 0.66 (1:4 THF–hexane); IR (neat) 3283, 1628, 1601 cm^{-1}; ^1H NMR δ 6.70 (1H, dd, *J* = 7.8, 4.6 Hz), 7.10 (1H, t, *J* = 7.3 Hz), 7.37 (2H, dd, *J* = 7.8, 7.3 Hz), 7.49 (2H, d, *J* = 8.2 Hz), 7.60 (2H, d, *J* = 8.2 Hz), 7.73 (2H, d, *J* = 7.8 Hz), 7.82 (1H, dd, *J* = 7.8, 1.8 Hz), 8.42 (1H, dd, *J* = 4.6, 1.8 Hz), 10.76 (1H, br s). Anal. Calcd for $C_{18}H_{13}ClN_2O$: C, 70.02; H, 4.24; N, 9.07. Found: C, 70.00; H, 4.25; N, 9.07.

1-(4-Chlorophenyl)-1-[2-(phenylamino)pyridine-2-yl]ethanol (2i). This compound was prepared by reacting **7c** with MeLi at 0 ˚C in THF in 76% yield; a white solid; mp 133–135 ˚C (hexane–Et_2O); IR (KBr) 3396, 3277, 1603 cm^{-1}; ^1H NMR δ 1.93 (3H, s), 2.52 (1H, s), 6.76 (1H, dd, *J* = 7.3, 5.0 Hz), 6.91 (1H, t, *J* = 7.3 Hz), 7.21 (2H, dd, *J* = 7.8, 7.3 Hz), 7.26 (2H, d, *J* = 8.7 Hz), 7.32 (2H, d, *J* = 8.7 Hz), 7.34 (2H, d, *J* = 7.8 Hz), 7.56 (1H, dd, *J* = 7.3, 1.8 Hz), 7.81 (1H, br s), 8.19 (1H, dd, *J* = 5.0, 1.8 Hz). Anal. Calcd for $C_{19}H_{17}ClN_2O$: C, 70.26; H, 5.28; N, 8.62. Found: C, 69.98; H, 5.36; N, 8.58.

(4-Chlorophenyl)[2-(4-chlorophenyl)aminopyridin-2-yl]methanone (7d). This compound was prepared by heating (160 ˚C) a mixture of **6b** and 4-chlorobenzenamiine for 10 min in 70% yield; a yellow solid; mp 144–147 ˚C (hexane); IR (KBr) 3254, 1624, 1609 cm^{-1}; ^1H NMR δ 6.73 (1H, dd, *J* = 7.8, 5.0 Hz), 7.32 (2H, d, *J* = 8.7 Hz), 7.49 (2H, d, *J* = 8.7 Hz), 7.59 (2H, d, *J* = 8.7 Hz), 7.70 (2H, d, *J* = 8.7 Hz), 7.83 (1H, dd, *J* = 7.8, 2.3 Hz), 8.42 (1H, dd, *J* = 5.0, 2.3 Hz), 10.77 (1H, br s). Anal. Calcd for $C_{18}H_{12}Cl_2N_2O$: C, 62.99; H, 3.52; N, 8.16. Found: C, 62.74; H, 3.62; N, 8.06.

1-(4-Chlorophenyl)-1-[2-(4-chlorophenyl)aminopyridin-2-yl]ethanol (2j). This compound was prepared by reacting **7d** with MeLi at 0 ˚C in THF in 87% yield; a pale-yellow solid; mp 209–211 ˚C (hexane–Et_2O); IR (KBr) 3377, 3327, 1605 cm^{-1}; ^1H NMR δ 1.94 (3H, s), 2.49 (1H, s), 6.78 (1H, dd, *J* = 7.3, 5.0 Hz), 7.15 (2H, d, *J* = 8.7 Hz), 7.26–7.32 (6H, m), 7.56 (1H, dd, *J* = 7.3, 1.8 Hz), 7.88 (1H, br s), 8.19 (1H, dd, *J* = 5.0, 1.8 Hz). Anal. Calcd for $C_{19}H_{16}Cl_2N_2O$: C, 63.52; H, 4.49; N, 7.80. Found: C, 63.39; H, 4.62; N, 7.76.

1-(4-Chlorophenyl)-1-[2-(4-chlorophenyl)aminopyridin-2-yl]propan-1-ol (2k). This compound was prepared by reacting **7d** with EtMgBr at 0 ˚C in THF in 85% yield; a white solid; mp 152–154 ˚C (hexane); IR (KBr) 3380, 3331, 1605 cm^{-1}; ^1H NMR δ 0.93 (3H, t, *J* = 7.3 Hz), 2.17–2.35 (3H, m including s at 2.33), 6.78 (1H, dd, *J* =7.8, 5.0 Hz), 7.15 (2H, d, *J* = 8.7 Hz), 7.26 (4H, s), 7.31 (2H, d, *J* = 8.7 Hz), 7.59 (1H, d, *J* = 7.8, 1.8 Hz), 8.01 (1H, br s), 8.17 (1H, dd, *J* = 5.0, 1.8 Hz). Anal. Calcd for

$C_{20}H_{18}Cl_2N_2O$: C, 64.35; H, 4.86; N, 7.50. Found: C, 64.16; H, 4.90; N, 7.27.

Typical Procedure for the Preparation of Pyrrolopyridine Derivatives 10. 3-Methyl-1-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (10a). Compound **2a** (0.21 g, 1.0 mmol) was heated at 270 ˚C (neat) for 4 h in the air. After cooling to rt, the crude product was purified by preparative TLC on silica gel to give **10a** (0.11 g, 51%): a yellow oil; R_f 0.30 (1:9 Et_2O–hexane); IR (neat) 3051, 1599, 1504, 1427 cm^{-1}; ^1H NMR δ 2.38 (3H, d, *J* = 0.9 Hz), 7.12 (1H, dd, *J* = 7.8, 4.6 Hz), 7.30 (1H, t, *J* = 7.3 Hz), 7.31 (1H, s), 7.50 (2H, dd, *J* = 7.8, 7.3 Hz), 7.76 (2H, d, *J* = 7.8 Hz), 7.91 (1H, dd, *J* = 7.8, 1.4 Hz), 8.37 (1H, dd, *J* = 4.6, 1.4 Hz); MS *m/z* 208 (M^+, 100). Anal. Calcd for $C_{14}H_{12}N_2$: C, 80.74; H, 5.81; N, 13.45. Found: C, 80.61; H, 5.90; N, 13.25.

3-Methyl-1-(4-methylphenyl)-1*H*-pyrrolo[2,3-*b*]pyridine (10b): a yellow oil; R_f 0.24 (3:1 C_6H_6–hexane); IR (neat) 3056, 1601, 1516, 1429 cm^{-1}; ^1H NMR δ 2.37 (3H, d, *J* = 0.9 Hz), 2.40 (3H, s), 7.10 (1H, dd, *J* = 7.8, 5.0 Hz), 7.26 (1H, q, *J* = 0.9 Hz), 7.30 (2H, d, *J* = 7.8 Hz), 7.60 (2H, d, *J* = 7.8 Hz), 7.90 (1H, dd, *J* = 7.8, 1.4 Hz), 8.35 (1H, dd, *J* = 5.0, 1.4 Hz); MS *m/z* 222 (M^+, 100). Anal. Calcd for $C_{15}H_{14}N_2$: C, 81.05; H, 6.35; N, 12.60. Found: C, 81.00; H, 6.37; N, 12.58.

1-(4-Methoxyphenyl)-3-methyl-3-Methyl-1-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (10c): a yellow oil; R_f 0.30 (1:5 AcOEt–hexane); IR (neat) 3051, 1604, 1514, 1435 cm^{-1}; ^1H NMR δ 2.37 (3H, d, *J* = 0.9 Hz), 3.86 (3H, s), 7.03 (2H, d, *J* = 8.7 Hz), 7.10 (1H, dd, *J* = 7.8, 4.6 Hz), 7.23 (1H, q, *J* = 0.9 Hz), 7.60 (2H, d, *J* = 8.7 Hz), 7.91 (1H, dd, *J* = 7.8, 1.4 Hz), 8.34 (1H, dd, *J* = 4.6, 1.4 Hz); MS *m/z* (%) 238 (M^+, 100). Anal. Calcd for $C_{15}H_{14}N_2O$: C, 75.61; H, 5.92; N, 11.76. Found: C, 75.39; H, 6.00; N, 11.60.

3-Methyl-1-[3-(trifluoromethyl)phenyl]-1*H*-pyrrolo[2,3-*b*]pyridine (10d): a pale-yellow solid; mp 65–66 ˚C (hexane); IR (KBr) 3085, 1618, 1603, 1502, 1418 cm^{-1}; ^1H NMR δ 2.39 (3H, d, *J* = 0.9 Hz), 7.16 (1H, dd, *J* = 7.8, 4.6 Hz), 7.34 (1H, s), 7.53 (1H, d, *J* = 7.8 Hz), 7.63 (1H, t, *J* = 7.8 Hz), 7.93 (1H, dd, *J* = 7.8, 1.8 Hz), 8.04 (1H, s), 8.10 (1H, d, *J* = 7.8 Hz), 8.37 (1H, dd, *J* = 4.6, 1.8 Hz); MS *m/z* 276 (M^+, 100). Anal. Calcd for $C_{15}H_{11}F_3N_2$: C, 65.21; H, 4.01; N, 10.14. Found: C, 65.18; H, 4.02; N, 10.08.

3,6-Dimethyl-1-(4-methylphenyl)-1*H*-pyrrolo[2,3-*b*]pyridine (10e): a yellow oil; R_f 0.15 (1:9 C_6H_6–hexane); IR (neat) 3038, 1603, 1516, 1429 cm^{-1}; ^1H NMR δ 2.34 (3H, d, *J* = 1.4 Hz), 2.39 (3H, s), 2.62 (3H, s), 6.97 (1H, d, *J* = 7.8 Hz), 7.19 (1H, q, *J* = 1.4 Hz), 7.28 (2H, d, *J* = 8.2 Hz), 7.67 (2H, d, *J* = 8.2 Hz), 7.77 (1H, d, *J* = 7.8 Hz); MS *m/z* 236 (M^+, 100). Anal. Calcd for $C_{16}H_{16}N_2$: C, 81.32; H, 6.82; N, 11.85. Found: C, 81.35; H, 6.94; N, 11.65.

3-Ethyl-2,6-dimethyl-1-(4-methylphenyl)-1*H*-pyrrolo[2,3-*b*]pyridine (10f): a yellow oil; R_f 0.15 (1:9 Et_2O–hexane); IR (neat) 3038, 1603, 1516, 1427 cm^{-1}; ^1H NMR δ 1.25 (3H, t, *J* = 7.3 Hz), 2.22 (3H, s), 2.43 (3H, s), 2.52 (3H, s), 2.74 (2H, q, *J* = 7.3 Hz), 6.89 (1H, d, *J* = 8.2 Hz), 7.27 (2H, d, *J* = 8.2 Hz), 7.30 (2H, d, *J* = 8.2 Hz), 7.71 (1H, d, *J* = 8.2 Hz); ^{13}C NMR δ 11.01, 15.42, 17.63, 21.19, 24.57, 112.43, 115.49, 117.85, 125.75, 128.18, 129.65, 131.78, 134.46, 137.03, 148.75, 150.97; MS *m/z* 264 (M^+, 34), 249 (100). Anal. Calcd for $C_{18}H_{20}N_2$: C, 81.78; H, 7.63; N, 10.60. Found: C, 81.62; H, 7.83; N, 10.53.

1,3-Diphenyl-1*H*-pyrrolo[2,3-*b*]pyridine (10g): a yellow oil; R_f 0.16 (3:7 CH_2Cl_2–hexane); IR (neat) 3050, 1590, 1504, 1425 cm^{-1}; ^1H NMR δ 7.22 (1H, dd, *J* = 7.8, 4.6 Hz), 7.35 (1H, t, *J* = 7.3 Hz), 7.37 (1H, t, *J* = 7.3 Hz), 7.49 (2H, dd, *J* = 7.8, 7.3 Hz), 7.56 (2H, dd, *J* = 7.8, 7.3 Hz), 7.69 (2H, d, *J* = 7.8 Hz), 7.71 (1H, s), 7.81 (2H, dd, *J* = 7.8, 0.9 Hz), 8.28 (1H, dd, *J* = 7.8, 1.4 Hz), 8.43 (1H, dd, *J* = 4.6, 1.4 Hz); MS *m/z* 270 (M^+, 100). Anal. Calcd for $C_{19}H_{14}N_2$: C, 84.42; H, 5.22; N, 10.36. Found: C, 84.46; H, 5.36; N, 10.09.

1-(4-Methoxyphenyl)-3-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (10h): a yellow solid; mp 133–135 °C (hexane–Et_2O); IR (KBr) 3045, 1603, 1589, 1518, 1433 cm^{-1}; ^1H NMR δ 3.88 (3H, s), 7.07 (2H, d, *J* = 9.2 Hz), 7.19 (1H, dd, *J* = 7.8, 4.6 Hz), 7.33 (1H, t, *J* = 7.3 Hz), 7.48 (2H, dd, *J* = 7.8, 7.3 Hz), 7.65 (2H, d, *J* = 9.2 Hz), 7.67 (1H, s), 7.68 (2H, d, *J* = 7.8, 1.4 Hz), 8.28 (1H, dd, *J* = 7.8, 1.4 Hz), 8.41 (1H, dd, *J* = 4.6, 1.4 Hz); ^{13}C NMR δ 55.61, 114.67, 116.48, 116.84, 119.38, 125.27, 125.74, 126.47, 127.17, 128.27, 128.97, 131.31, 134.53, 143.95, 148.16, 158.29; MS *m/z* 300 (M^+, 100). Anal. Calcd for $C_{20}H_{16}N_2O$: C, 79.98; H, 5.37; N, 9.33. Found: C, 79.92; H, 5.38; N, 9.11.

3-(4-Chlorophenyl)-1-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (10i): a pale-yellow solid; mp 125–127 °C (hexane–Et_2O); IR (KBr disk) 3047, 1595, 1541, 1503, 1489 cm^{-1}; ^1H NMR δ 7.23 (1H, dd, *J* = 7.8, 4.6 Hz), 7.37 (1H, tt, *J* = 7.3, 1.4 Hz), 7.45 (2H, d, *J* = 8.7 Hz), 7.55 (2H, dd, *J* = 8.2, 7.3 Hz), 7.61 (2H, d, *J* = 8.7 Hz), 7.67 (1H, s), 7.79 (2H, dd, *J* = 8.2, 1.4 Hz), 8.22 (1H, dd, *J* = 7.8, 1.8 Hz), 8.43 (1H, dd, *J* = 4.6, 1.8 Hz); MS *m/z* 304 (M^+, 100). Anal. Calcd for $C_{19}H_{13}ClN_2$: C, 74.88; H, 4.30; N, 9.19. Found: C, 74.83; H, 4.31; N, 9.16.

1,3-Bis(4-chlorophenyl)-1*H*-pyrrolo[2,3-*b*]pyridine (10j): a pale-yellow solid; mp 186–189 °C (hexane–Et_2O); IR (KBr) 3044, 1589, 1545, 1499, 1489, 1431 cm^{-1}; ^1H NMR δ 7.23 (1H, dd, *J* = 7.8, 4.6 Hz), 7.45 (2H, d, *J* = 8.7 Hz), 7.51 (2H, d, *J* = 8.7 Hz), 7.60 (2H, d, *J* = 8.7 Hz), 7.64 (1H, s), 7.77 (2H, d, *J* = 8.7 Hz), 8.22 (1H, dd, *J* = 7.8, 1.4 Hz), 8.43 (1H, dd, *J* = 4.6, 1.4 Hz); ^{13}C NMR δ 116.38, 117.45, 119.60, 124.42, 125.09, 128.27, 128.37, 129.18, 129.52, 132.08, 132.52, 132.60, 136.62, 144.26, 147.90; MS *m/z* 338 (M^+, 100). Anal. Calcd for $C_{19}H_{12}Cl_2N_2$: C, 67.27; H, 3.57; N, 8.26. Found: C, 67.21; H, 3.69; N, 8.25.

1,3-Bis(4-chlorophenyl)-2-methyl-1*H*-pyrrolo[2,3-*b*]pyridine (10k): a pale-yellow solid; mp 184–186 °C (hexane); IR (KBr) 3047, 1593, 1551, 1491, 1423 cm^{-1}; ^1H NMR δ 2.37 (3H, s), 7.12 (1H, dd, *J* = 7.8, 4.6 Hz), 7.40 (2H, d, *J* = 8.7 Hz), 7.45 (2H, d, *J* = 8.7 Hz), 7.47 (2H, d, *J* = 8.7 Hz), 7.55 (2H, d, *J* = 8.7 Hz), 7.92 (1H, dd, *J* = 7.8, 1.8 Hz), 8.27 (1H, dd, *J* = 4.6, 1.8 Hz); MS *m/z* 352 (M^+, 100). Anal. Calcd for $C_{20}H_{14}ClN_2$: C, 68.00; H, 3.99; N, 7.93. Found: C, 67.71; H, 3.86, N, 7.72.

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