Efficient Synthesis of 2-Substituted 7-Azaindole Derivatives via Palladium-Catalyzed Coupling and C–N Cyclization Using 18-Crown-6

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Received 26 April 2007

Abstract: A practical and straightforward preparation of various novel 2-substituted 7-azaindole derivatives from 2-amino-3-iodopyridine by a two-step procedure is described that gives the desired compounds in good overall yields.

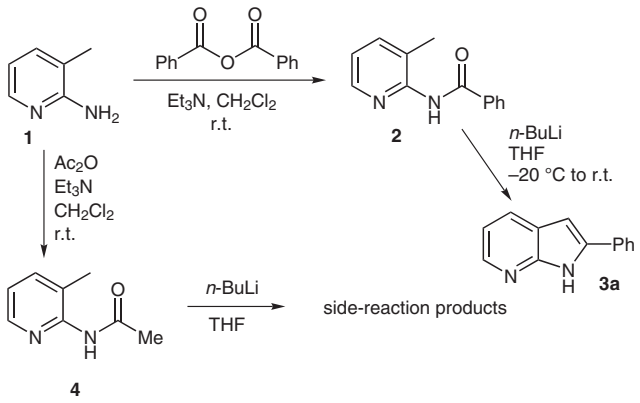
Key words: alkynes, 7-azaindoles, 18-crown-6, heterocycles, palladium catalysis

The indole core is present in a wide variety of biologically active natural and unnatural compounds with important applications in medicinal chemistry due to their capability of binding to many receptors with excellent affinities.[1] Because of their wide range of applications, the preparation and functionalization of indoles is a major area of focus for organic synthetic chemists and numerous approaches for the synthesis of their analogues have been described during the last few decades.[2] Although the 7-azaindole (1*H*-pyrrolo[2,3-*b*]pyridine) nucleus is present in a few natural products, these compounds have attracted much attention due to their interesting physicochemical properties as they are known as efficient fluorescent chromophores,[3] but mainly because of their pharmacological activity.[4]

Numerous methods have been described for the synthesis of 7-azaindoles.[5] Among them, ring-closure reactions in which a carbon–nitrogen bond is formed constitutes a common approach; in this manner Clemo and Swan described the first preparation of 2-substituted 7-azaindoles, such as 2-methyl-7-azaindole and 2-ethyl-7-azaindole, which were obtained from the corresponding amides under drastic reaction conditions.[6] Later, the Madelung synthesis involving an intramolecular cyclization under much milder conditions led to 2-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine, however, the isolated yield was poor.[7] Since that time, many other approaches have been developed for the preparation of a limited number of 2-substituted 7-azaindoles,[8] and many of them require N-protection of the intermediate pyrrole nitrogen fragment in the cyclization reactions to reach the desired 7-azaindoles in good yields.[9]

Herein, we describe a simple and efficient synthesis by an easy two-step sequence that involves a palladium-catalyzed Sonogashira coupling followed by cyclization to give various 2-substituted 7-azaindoles in high overall yields.

In our initial attempts we focused our efforts on the preparation of 2-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (**3a**). We applied a modified procedure from that described by Houlihan and co-workers using commercially available 2-amino-3-methylpyridine (**1**),[7] which allowed the formation of the amide **2** with benzoic anhydride in quantitative yield (Scheme 1). Cyclization of the amide **2** gave **3a** in low yield (25%). We decided to extend this methodology to the preparation of 2-methyl-1*H*-pyrrolo[2,3-*b*]pyridine employing acetic anhydride, but the use of butyllithium led to the formation of side reaction products due to the acidity of the hydrogens α to the carbonyl group. To confirm this behavior, we next reacted **1** with pivaloyl anhydride, intramolecular cyclization led to 2-*tert*-butyl-1*H*-pyrrolo[2,3-*b*]pyridine in 60% yield. Based on these results we questioned if this strategy could be of general value for the preparation of 2-substituted 7-azaindoles without compound structure limitations.

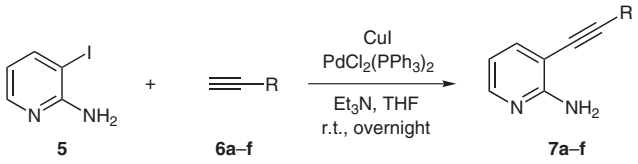


Scheme 1 Initial attempts for the synthesis of 7-azaindoles

In this manner, we decided to investigate different approaches for the preparation of 2-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (**3a**) that have previously been satisfactorily employed for the synthesis of indole homologues. The best results achieved in the synthesis of **3a** could then be extended to the preparation of other interesting 7-azaindoles. Thus, we initially considered the sequence based on the palladium-catalyzed Sonogashira coupling of an alkyne to 2-amino-3-iodopyridine (**5**) for later study of the

SYNTHESIS 2007, No. 14, pp 2149–2152
Advanced online publication: 18.06.2007
DOI: 10.1055/s-2007-983730; Art ID: Z10607SS

cyclization process. Phenylacetylene (**6a**) was used then as a model alkyne and the reaction with **5** in the presence of copper(I) iodide and dichlorobis(triphenylphosphine)palladium with triethylamine as base in tetrahydrofuran, gave 2-amino-3-(phenylethynyl)pyridine (**7a**) in near quantitative yield (Scheme 2).



5 **6a–f** **7a–f**

Scheme 2

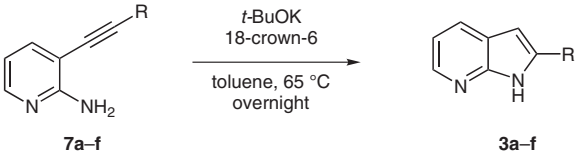
Table 1 Preparation of **7a–f** from 2-Amino-3-iodopyridine (**5**) by Palladium-Catalyzed Sonogashira Coupling

Entry	Compound	R	Isolated yield (%)
1	**7a**	Ph	97
2	**7b**	Pr	83
3	**7c**	Bu	88
4	**7d**	$(CH_2)_4Me$	89
5	**7e**	*i*-Bu	81
6	**7f**	Cy	83

The same reaction was extended to alkyl derivatives **6b–e** and also to a cycloalkyl structure **6f**, all gave the corresponding pyridine derivatives **7b–f** in high yields (Table 1).

Different approaches were then used in the intramolecular cyclization step, for example, we performed this process using **7a** as starting material in the presence of indium bromide as catalyst in refluxing toluene, unfortunately no reaction was observed.[10] Next, the amino group was subjected to mesyl monoprotection using pyridine as base in tetrahydrofuran at room temperature so that the cyclization of the *N*-mesyl derivative could be attempted, however, in the presence of tetrabutylammonium fluoride in refluxing tetrahydrofuran, only starting material was recovered.[11] Using potassium *tert*-butoxide as base and *N*-methylpyrrolidine (NMP) as solvent, we did not observe the formation 2-phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (**3a**) either at room temperature or at 40 °C.[8c,d] At this point, we decided to use 18-crown-6, due to its ability to form a potassium complex in its cavity, which is more soluble in the reaction media than the corresponding free salt and, moreover, its use will increase the potential of the base. We carried out the process in anhydrous toluene as solvent, observing poor reactivity at room temperature, however, when the reaction mixture was heated to 65 °C no starting material was detected and the final product **3a** was recovered in 94% yield after flash chromatography (Scheme 3).

The cyclization step was later performed with alkynes **7b–f** observing in all cases high yields of the isolated 7-azaindoles **3b–f** (Table 2).



7a–f **3a–f**

Scheme 3

Table 2 Synthesis of 2-Substituted 1*H*-Pyrrolo[2,3-*b*]pyridine **3a–f** by Intramolecular Cyclization of **7a–f**

Entry	Compound	Isolated yield (%)
1	**3a**	94
2	**3b**	84
3	**3c**	87
4	**3d**	82
5	**3e**	80
6	**3f**	81

In conclusion, we have developed a versatile and efficient route for the preparation of 2-substituted 7-azaindoles, most of which have not previously been described in the literature, using a simple two-step synthesis that involves a palladium-catalyzed coupling and followed by intramolecular cyclization using catalytic amounts of 18-crown-6, to give 2-substituted 1*H*-pyrrolo[2,3-*b*]pyridines in high overall yields.

Chemical reagents were purchased from Aldrich, Fluka, Lancaster, or Prolabo, and were used without further purification. Solvents were distilled from a desiccant under N_2. Flash chromatography was performed using silica gel 60 (230–240 mesh). Melting points were taken on samples in open capillary tubes and are uncorrected. IR spectra were recorded on using NaCl plates or KBr pellets in a Perkin-Elmer 1720-X F7. ^1H, ^{13}C NMR, DEPT, and ^1H–^{13}C heteronuclear experiments were obtained using AV-300 (^1H, 300.13 MHz and ^{13}C, 75.5 MHz) or DPX 300 (^1H, 300.13 MHz and ^{13}C, 75.5 MHz) spectrometers. ESI$^+$ using a HP1100 chromatograph mass detector, or EI with a Finigan MAT 95 spectrometer were used to record mass spectra (MS). Microanalyses were performed on a Perkin-Elmer model 2400 instrument.

2-Amino-3-(alk-1-ynyl)pyridines 7a–f; General Procedure

To a suspension of 2-amino-3-iodopyridine (**5**, 250 mg, 1.14 mmol), CuI (11.0 mg, 0.057 mmol), and $PdCl_2(PPh_3)_2$ (39.9 mg, 0.057 mmol) in anhyd THF (4.6 mL) under a N_2 atmosphere were added successively Et_3N (0.48 mL, 3.41 mmol) and the alkyne **6a–f** (1.48 mmol), and the mixture was stirred overnight at r.t. The mixture was diluted with Et_2O (5 mL) and filtered through Celite, the solvents were evaporated under reduced pressure, and the crude residue purified by flash chromatography (silica gel, hexane to 40% EtOAc–hexane) to afford the corresponding alkynes **7a–f** (Table 1).

2-Amino-3-(phenylethynyl)pyridine (7a)

Eluent gradient: hexane to 40% EtOAc–hexane; white solid; yield: 97%; mp 121–123 °C; R_f = 0.18 (20% EtOAc–hexane).

IR (KBr): 3467, 3289, 3136, 1633, 1564, 1452, 1246 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 5.20 (br s, 2 H), 6.68 (dd, *J* = 7.4, 5.1 Hz, 1 H), 7.38 (t, *J* = 3.0 Hz, 3 H), 7.52–7.55 (m, 2 H), 7.62–7.65 (m, 1 H), 8.04 (d, *J* = 4.0 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 77.1, 95.7, 103.5, 113.5, 122.4, 128.4 (2 C), 128.7, 131.5 (2 C), 140.2, 147.1, 158.4.

MS (ESI$^+$, 60 eV): *m*/*z* (%) = 195 [(M + H)$^+$, 100], 196 [(M + 2 H)$^{2+}$, 20], 217 [(M + Na)$^+$, 18].

Anal. Calcd for $C_{13}H_{10}N_2$: C, 80.39; H, 5.19; N, 14.42. Found: C, 80.39; H, 5.19; N, 14.42.

2-Amino-3-(pent-1-ynyl)pyridine (7b)
Eluent gradient: hexane to 40% EtOAc–hexane; colorless oil; yield: 83%; R_f = 0.28 (40% EtOAc–hexane).

IR (NaCl): 3472, 3297, 3164, 2962, 1604, 1571, 1453, 1222 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.04 (t, *J* = 7.3 Hz, 3 H), 1.57–1.69 (m, 2 H), 2.42 (t, *J* = 7.0 Hz, 2 H), 5.10 (br s, 2 H), 6.56 (dd, *J* = 7.4, 5.0 Hz, 1 H), 7.45 (d, *J* = 7.4 Hz, 1 H), 7.96 (d, *J* = 4.6 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.5, 21.4, 22.1, 75.8, 96.5, 103.9, 113.2, 139.6, 146.9, 158.9.

MS (ESI$^+$, 60 eV): *m*/*z* (%) = 161 [(M + H)$^+$, 100], 162 [(M + 2 H)$^{2+}$, 16], 183 [(M + Na)$^+$, 11].

Anal. Calcd for $C_{10}H_{12}N_2$: C, 74.97; H, 7.55; N, 17.48. Found: C, 74.99; H, 7.56; N, 17.45.

2-Amino-3-(hex-1-ynyl)pyridine (7c)
Eluent gradient: hexane to 40% EtOAc–hexane; colorless oil; yield: 88%; R_f = 0.28 (40% EtOAc–hexane).

IR (NaCl): 3472, 3330, 3167, 2957, 1605, 1571, 1452, 1223 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.93 (t, *J* = 7.1 Hz, 3 H), 1.39–1.63 (m, 4 H), 2.44 (t, *J* = 7.1 Hz, 2 H), 5.10 (br s, 2 H), 6.55 (dd, *J* = 7.5, 5.0 Hz, 1 H), 7.44 (dd, *J* = 7.4, 2.0 Hz, 1 H), 7.95 (dd, *J* = 5.0, 2.0 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.5, 19.1, 21.9, 30.6, 75.7, 96.6, 103.9, 113.1, 139.5, 146.8, 158.9.

MS (ESI$^+$, 60 eV): *m*/*z* (%) = 175 [(M + H)$^+$, 100], 176 [(M + 2 H)$^+$, 15].

Anal. Calcd for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.79; H, 8.11; N, 16.10.

2-Amino-3-(hept-1-ynyl)pyridine (7d)
Eluent gradient: hexane to 40% EtOAc–hexane; colorless oil; yield: 89%; R_f = 0.27 (40% EtOAc–hexane).

IR (NaCl): 3474, 3300, 3167, 2931, 1604, 1570, 1454, 1223 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.90 (t, *J* = 7.1 Hz, 3 H), 1.27–1.46 (m, 4 H), 1.54–1.64 (m, 2 H), 2.42 (t, *J* = 7.1 Hz, 2 H), 5.15 (br s, 2 H), 6.54 (dd, *J* = 7.5, 5.0 Hz, 1 H), 7.44 (dd, *J* = 7.4, 2.0 Hz, 1 H), 7.94 (dd, *J* = 5.1, 1.7 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8, 19.4, 22.0, 28.3, 31.0, 75.7, 96.7, 103.9, 113.1, 139.5, 146.8, 158.9.

MS (ESI$^+$, 60 eV): *m*/*z* (%) = 188 [M$^+$, 100], 189 [(M + H)$^+$, 19].

Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.55; H, 8.59; N, 14.86.

2-Amino-3-(4-methylpent-1-ynyl)pyridine (7e)
Eluent gradient: hexane to 40% EtOAc–hexane; colorless oil; yield: 81%; R_f = 0.22 (40% EtOAc–hexane).

IR (NaCl): 3470, 3382, 3303, 3166, 2950, 1607, 1567, 1450, 1219 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.03 (d, *J* = 6.8 Hz, 6 H), 1.84–1.97 (m, 1 H), 2.34 (d, *J* = 6.5 Hz, 2 H), 5.10 (br s, 2 H), 6.56 (t, *J* = 5.4 Hz, 1 H), 7.46 (d, *J* = 7.4 Hz, 1 H), 7.96 (d, *J* = 3.7 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.9 (2 C), 28.0, 28.6, 76.6, 95.6, 104.0, 113.2, 139.6, 146.8, 158.9.

MS (ESI$^+$, 60 eV): *m*/*z* (%) = 175 [(M + H)$^+$, 100], 176 [(M + 2 H)$^{2+}$, 17].

Anal. Calcd for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.82; H, 8.10; N, 16.08.

2-Amino-3-(cyclohexylethynyl)pyridine (7f)
Eluent gradient: hexane to 40% EtOAc–hexane; white solid; yield: 83%; mp 75–77 °C; R_f = 0.24 (40% EtOAc–hexane).

IR (KBr): 3468, 3290, 3143, 2928, 2851, 1626, 1569, 1453, 1222 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.35–1.48 (m, 3 H), 1.51–1.58 (m, 3 H), 1.72–1.76 (m, 2 H), 1.86–1.90 (m, 2 H), 2.59–2.64 (m, 1 H), 5.10 (br s, 2 H), 6.56 (dd, *J* = 7.5, 5.0 Hz, 1 H), 7.46 (dd, *J* = 7.4, 1.7 Hz, 1 H), 7.94 (dd, *J* = 5.0, 1.4 Hz, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 24.7, 25.7 (2 C), 29.7, 32.6 (2 C), 75.6, 100.9, 104.0, 113.2, 139.5, 146.8, 158.8.

MS (ESI$^+$, 60 eV): *m*/*z* (%) = 200 [M$^+$, 100], 201 [(M + H)$^+$, 19].

Anal. Calcd for $C_{13}H_{16}N_2$: C, 77.96; H, 8.05; N, 13.99. Found: C, 77.98; H, 8.02; N, 14.00.

2-Substituted 1*H*-Pyrrolo[2,3-*b*]pyridines 3a–f; General Procedure
To a soln of the pyridine **7a**–**f** (0.86 mmol) in anhyd toluene (14 mL) were added successively *t*-BuOK (203 mg, 1.81 mmol) and 18-crown-6 (22.8 mg, 0.086 mmol), and the mixture was stirred overnight at 65 °C. The solvent was evaporated under reduced pressure and the residue suspended in H_2O (5 mL) and extracted with CH_2Cl_2 (3 × 5 mL). The organic phases were combined and dried (Na_2SO_4) and the organic solvent was removed under reduced pressure. The crude mixture was purified by flash chromatography (silica gel, 10–60% EtOAc–hexane) to afford the corresponding 7-azaindoles **3a**–**f** (Table 2).

2-Phenyl-1*H*-pyrrolo[2,3-*b*]pyridine (3a)
Eluent gradient: 10–60% EtOAc–hexane; white solid; yield: 94%; mp 204–206 °C; R_f = 0.56 (60% EtOAc–hexane).

IR (KBr): 3163, 2362, 1870, 1588, 1541, 1458, 1282 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.81 (s, 1 H), 7.12 (dd, *J* = 7.7, 4.8 Hz, 1 H), 7.39–7.45 (m, 1 H), 7.52–7.56 (m, 2 H), 7.91–8.00 (m, 3 H), 8.33 (d, *J* = 4.3 Hz, 1 H), 12.78 (br s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 97.3, 116.2, 122.5, 125.9 (2 C), 128.1, 128.6, 128.9 (2 C), 132.4, 139.6, 141.8, 149.8.

MS (ESI$^+$, 60 eV): *m*/*z* (%) = 195 [(M + H)$^+$, 100], 196 [(M + 2 H)$^{2+}$, 19], 217 [(M + Na)$^+$, 13].

Anal. Calcd for $C_{13}H_{10}N_2$: C, 80.39; H, 5.19; N, 14.42. Found: C, 80.42; H, 5.18; N, 14.40.

2-Propyl-1*H*-pyrrolo[2,3-*b*]pyridine (3b)
Eluent gradient: 10–60% EtOAc–hexane; white solid; yield: 84%; mp 73–75 °C; R_f = 0.47 (60% EtOAc–hexane).

IR (KBr): 2958, 1587, 1545, 1412, 1276 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.07 (t, *J* = 7.5 Hz, 3 H), 1.83–1.96 (m, 2 H), 2.89 (t, *J* = 7.5 Hz, 2 H), 6.20 (s, 1 H), 7.07 (dd, *J* = 7.6, 4.8 Hz, 1 H), 7.87 (dd, *J* = 7.8, 1.5 Hz, 1 H), 8.24 (d, *J* = 4.1 Hz, 1 H), 12.30 (br s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9, 22.3, 30.7, 97.1, 115.3, 121.8, 127.5, 140.1, 141.6, 149.1.

MS (ESI$^+$, 60 eV): *m*/*z* (%) = 161 [(M + H)$^+$, 100], 162 [(M + 2 H)$^{2+}$, 15], 183 [(M + Na)$^+$, 38].

Anal. Calcd for $C_{10}H_{12}N_2$: C, 74.97; H, 7.55; N, 17.48. Found: C, 74.95; H, 7.56; N, 17.49.

2-Butyl-1*H*-pyrrolo[2,3-*b*]pyridine (3c)
Eluent gradient: 10–60% EtOAc–hexane; white solid; yield: 87%; mp 48–49 °C; R_f = 0.37 (60% EtOAc–hexane).

IR (KBr): 3472, 3297, 3164, 2930, 1588, 1544, 1416, 1278 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.01 (t, *J* = 7.4 Hz, 3 H), 1.44–1.57 (m, 2 H), 1.82–1.92 (m, 2 H), 2.94 (t, *J* = 7.4 Hz, 2 H), 6.25 (s, 1 H), 7.08 (dd, *J* = 7.7, 4.8 Hz, 1 H), 7.88 (dd, *J* = 7.7, 1.4 Hz, 1 H), 8.26 (dd, *J* = 4.8, 1.4 Hz, 1 H), 12.70 (br s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.8, 22.4, 28.4, 31.1, 96.9, 115.2, 121.9, 127.5, 139.9, 141.9, 149.2.

MS (ESI$^+$, 60 eV): *m*/*z* (%) = 175 [$(M + H)^+$, 100], 176 [$(M + 2 H)^{2+}$, 18].

Anal. Calcd for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.79; H, 8.11; N, 16.10.

2-Pentyl-1*H*-pyrrolo[2,3-*b*]pyridine (3d)
Eluent gradient: 10–60% EtOAc–hexane; white solid; yield: 82%; mp 83–85 °C; R_f = 0.52 (60% EtOAc–hexane).

IR (KBr): 2930, 1588, 1542, 1427, 1278 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.99 (t, *J* = 7.1 Hz, 3 H), 1.40–1.55 (m, 4 H), 1.89–1.99 (m, 2 H), 2.97 (t, *J* = 7.7 Hz, 2 H), 6.30 (br s, 1 H), 7.15 (br s, 1 H), 7.94 (d, *J* = 6.2, 1 H), 8.32 (br s, 1 H), 13.05 (br s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 13.9, 22.4, 28.7, 28.8, 31.5, 96.8, 115.2, 122.0, 127.4, 139.7, 142.0, 149.1.

MS (ESI$^+$, 60 eV): *m*/*z* (%) = 188 [M^+, 100], 189 [$(M + H)^+$, 18].

Anal. Calcd for $C_{12}H_{16}N_2$: C, 76.55; H, 8.57; N, 14.88. Found: C, 76.58; H, 8.57; N, 14.85.

2-Isobutyl-1*H*-pyrrolo[2,3-*b*]pyridine (3e)
Eluent gradient: 10–60% EtOAc–hexane; white solid: yield: 80%; mp 82–84 °C; R_f = 0.53 (60% EtOAc–hexane).

IR (KBr): 3215, 3128, 3081, 2958, 1609, 1588, 1420, 1281 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.06 (t, *J* = 6.8 Hz, 6 H), 2.13–2.27 (m, 1 H), 2.78 (d, *J* = 7.1 Hz, 2 H), 6.25 (s, 1 H), 7.07 (dd, *J* = 8.0, 4.8 Hz, 1 H), 7.87 (dd, *J* = 7.7, 1.4 Hz, 1 H), 8.23 (dd, *J* = 4.8, 1.7 Hz, 1 H), 12.45 (br s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 22.5 (2 C), 28.8, 38.2, 97.9, 115.3, 121.8, 127.5, 140.0, 140.8, 149.1.

MS (ESI$^+$, 60 eV): *m*/*z* (%) = 175 [$(M + H)^+$, 100], 176 [$(M + 2 H)^{2+}$, 13].

Anal. Calcd for $C_{11}H_{14}N_2$: C, 75.82; H, 8.10; N, 16.08. Found: C, 75.81; H, 8.13; N, 16.06.

2-Cyclohexyl-1*H*-pyrrolo[2,3-*b*]pyridine (3f)
Eluent gradient: 10–60% EtOAc–hexane; white solid; yield: 81%; mp 170–172 °C; R_f = 0.38 (60% EtOAc–hexane).

IR (KBr): 3126, 3071, 3015, 2922, 2849, 1609, 1587, 1423, 1277 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.25–1.60 (m, 5 H), 1.64–1.95 (m, 3 H), 2.17–2.22 (m, 2 H), 2.83–2.93 (m, 1 H), 6.21 (s, 1 H), 7.06 (dd, *J* = 6.8, 4.8 Hz, 1 H), 7.87 (d, *J* = 7.7 Hz, 1 H), 8.24 (s, 1 H), 12.08 (br s, 1 H).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 26.1, 26.3 (2 C), 32.7 (2 C), 37.8, 95.0, 115.3, 121.6, 127.6, 140.3, 146.9, 149.0.

MS (ESI$^+$, 60 eV): *m*/*z* (%) = 200 [M^+, 100], 201 [$(M + H)^+$, 19].

Anal. Calcd for $C_{13}H_{16}N_2$: C, 77.96; H, 8.05; N, 13.99. Found: C, 77.97; H, 8.05; N, 13.98.

Acknowledgment

Financial support of this work by the Principado de Asturias (IB-05-109) is gratefully acknowledged. V.G.-F. thanks Spanish MEC for a personal grant (Juan de la Cierva Program), S.A.-S. thanks Mexican CONACYT for a pre-doctoral fellowship and M.C.M thanks Brazilian Agency CAPES for a post-doctoral fellowship.

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