(R = H, R[1] = OMe), 90381-62-7; **6e** (R = OMe, R[1] = H), 90381-63-8; **7**, 62924-93-0; **8**, 51674-10-3; **10**, 101402-93-1; **11**, 101402-94-2; **11a**, 101402-98-6; **12**, 101402-95-3; **14**, 101402-96-4; **15**, 101402-97-5; **17**, 4664-08-8; **18**, 101402-90-8; **19**, 101402-89-5; **20**, 699-98-9; **21**, 101402-92-0; **22**, 101402-91-9; **23**, 59414-23-2; **24**, 61539-61-5; **25** (R = H), 101402-69-1; **25** (R = Ac), 101402-70-4; **26** (R = H), 101402-73-7; **26** (R = Ac), 101402-74-8; **27**, 101402-77-1; **28** (R = Ac), 101402-76-0; **29** (R = H), 101402-71-5; **29** (R = Ac), 101402-72-6; **30** (R = H), 101402-75-9; **31** (R = H), 101402-78-2; **31** (R = Ac), 101402-79-3; **32b**, 513-81-5; **32c**, 3588-31-6; **33b** (R[5] = Ac), 101402-80-6; **33b** (R[5] = H), 101402-81-7; **34a**, 101402-83-9; **34b**, 13785-28-9; **35b**, 101402-85-1; **35c**, 101402-87-3; **36a**, 101402-86-2; **37a**, 101402-82-8; **37b**, 2768-65-2; **38a**, 101402-84-0; **38b**, 2893-08-5; **41**, 101402-99-7; isoquinoline, 119-65-3; 5-nitroisoquinoline, 607-32-9; 5-aminoisoquinoline, 1125-60-6; 5,8-diaminoisoquinoline, 1127-49-7; 5,8-dimethoxyquinazoline, 17944-05-7; 2-chloro-5,8-dimethoxy-4-methylquinoline, 58868-27-2; 2-chloro-5,8-dihydroxy-4-methylquinoline, 101402-57-7; 2-chloro-4-methyl-5,8-quinolinedione, 101402-58-8; 1-acetoxy-1,3-butadiene, 1515-76-0; 1,4-diacetoxy-1,3-butadiene, 3817-40-1; pyridine-2-carboxaldehyde, 1121-60-4; pyridine-4-carboxaldehyde, 872-85-5; *o*-bromoanisole, 578-57-4.

A Facile Synthesis of 7-Halo-5*H*-indeno[1,2-*b*]pyridines and -pyridin-5-ones

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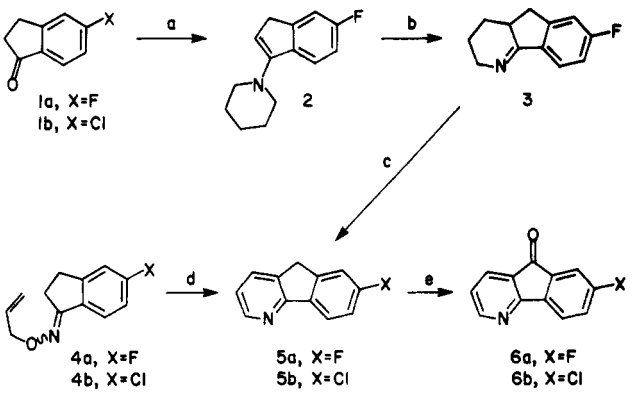
The 2-aryl-3-methylpyridines **7a–c** were obtained in good yield by the addition of the corresponding aryllithium to 2-fluoro-3-methylpyridine. Permanganate oxidation provided the 2-aryl-3-pyridinecarboxylic acids **8a–c** which were cyclized to 5*H*-indeno[1,2-*b*]pyridin-5-ones **6a–c** in hot polyphosphoric acid. The 5*H*-indeno[1,2-*b*]pyridines **5a–c** were readily obtained from the ketones **6a–c** by treatment with hydrazine in hot diethylene glycol.

Recently, we required as intermediates various 7-halo-5*H*-indeno[1,2-*b*]pyridines and the corresponding pyridin-5-ones. While the bromo-substituted compounds are readily obtained by bromination of 5*H*-indeno[1,2-*b*]-pyridin-5-one,[1] to our knowledge the 7-chloro and 7-fluoro compounds have not been reported. Our attempts to chlorinate either the unsubstituted azafluorene or the ketone with a variety of chlorinating agents were unsatisfactory, as were our efforts to introduce a fluoro substituent proceeding from the 7-nitro ketone by reduction to the amine followed by a Schiemann reaction. Thus, our attention turned to finding a route of synthesis that would be applicable to both the 7-chloro and the 7-fluoro compounds. A review of the reported syntheses[2] of 4-azafluorene and 4-azafluorenone suggested several routes that might be modified to provide the 7-halo derivatives.

The procedure described by Parcell and Hauck for the preparation of 4-azafluorene from 1-indanone[2b] provided the first sample of 7-fluoro-5*H*-indeno[1,2-*b*]pyridine (**5a**). Thus, the piperidine enamine **2** of 5-fluoro-1-indanone[3] (**1a**) was reacted with 3-bromopropylamine hydrobromide to furnish the tetrahydroindenopyridine **3** which was then dehydrogenated to provide **5a** in 75% yield (Scheme I). It proved necessary to purify **3** by distillation prior to the dehydrogenation reaction, as attempts using crude or only partially purified material failed. The yield of **3** from the distilled enamine **2** was 46%; however, the enamine was obtained in only 29% yield as distillation resulted in substantial decomposition. Therefore, **2** was typically used without purification, increasing the overall yield of **3** from **1a** to 28%. Oxidation of **5a** to the azafluorenone **6a** was

Scheme I[a]



[a] (a) Piperidine, catalytic TSOH, toluene, reflux; (b) $Br(CH_2)_3NH_2 \cdot HBr$, DMF, 100 °C; (c) 10% Pd/C, nitrobenzene, xylene, reflux; (d) sealed tube, 190–200 °C; (e) O_2, Triton B, pyridine.

accomplished in 36% yield by bubbling oxygen into a pyridine solution of the azafluorene and Triton B.[4] Unfortunately, the 7-chloro compounds were not readily accessible via this route as the chloro-substituted tetrahydroindenopyridine decomposed upon distillation.

A second route from 5-halo-1-indanones investigated was based on Irie's synthesis of substituted pyridines by the thermolysis of *O*-allyl oxime ethers.[5] Both 5-fluoro- (**1a**) and 5-chloro-1-indanone (**1b**) were readily converted to the oxime ethers **4a** and **4b** by O-alkylation (NaOEt/EtOH, allyl bromide, 95%) of the corresponding oxime ($H_2NOH \cdot HCL$, EtOH, pyridine, 72–86%). Thermolysis of **4a** and **4b** at 190–200 °C in a sealed tube did indeed produce **5a** and the first sample of **5b**, but the yields (14% and 15%, respectively) were too low to be useful. As with **5a**, oxidation of **5b** with oxygen and Triton B in pyridine furnished the azafluorenone **6b** in 33% yield.

(1) Mlochowski, J.; Szulc, Z. *J. Prakt. Chem.* **1980**, *322*, 971.
(2) (a) Chatterjea, J. N; Prasad, K. *Indian J. Chem. Soc.* **1955**, *32*, 371. (b) Parcell, R. F.; Hauck, F. P., Jr. *J. Org. Chem.* **1963**, *28*, 3468. (c) Skraup, Z.; Cobenzl, A. *Monatsh. Chem.* **1883**, *4*, 436. (d) Prostakov, N. S. et. al. *Zh. Org. Khim.* **1977**, *13*, 1484. (e) Abramovitch, R. A.; Notation, A. D; Seng, G. C. *Tetrahedron Lett.* **1959**, 1. (f) Abramovitch, R. A.; Notation, A. D.; Seng, G. C. *Can. J. Chem.* **1960**, *38*, 761. (g) Abramovitch, R. A.; Tertzakian, G. *Tetrahedron Lett.* **1963**, 1511.
(3) Olivier, M.; Maréchal, E. *Bull. Soc. Chim. Fr.* **1973**, 3092.
(4) Sprinzak, Y. *J. Am. Chem. Soc.* **1958**, *80*, 5440.
(5) (5) Irie, H.; Katayama, I.; Mizuno, Y. *Heterocycles* **1979**, *12*, 771.

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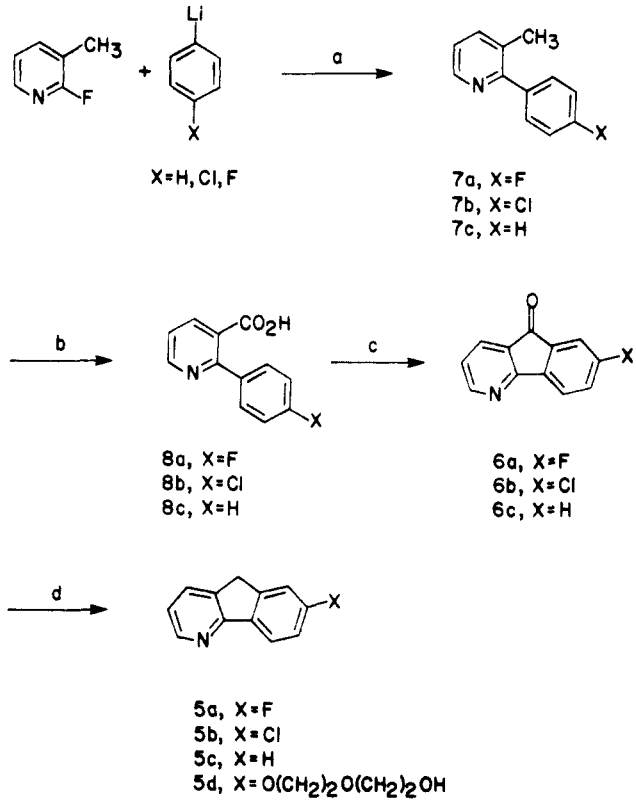
Scheme II[a]



[a] (a) Et_2O, −40 to 0 °C; (b) $KMnO_4$, water, reflux; (c) PPA, 200–215 °C; (d) $(NH_2)_2$, diethylene glycol, 180 °C.

Arylation of 3-picoline with phenyllithium has been reported to afford a mixture of 2- and 6-phenyl-3-methylpyridine;[2e,f] however, the reaction with (4-chlorophenyl)lithium, generated from 4-bromochlorobenzene using *n*-butyllithium,[6] was unsuccessful. To increase the reactivity and avoid the formation of the undesired isomer, the use of commercially available 2-fluoro-3-methylpyridine was investigated. Indeed, the reaction of 2-fluoro-3-methylpyridine with phenyllithium did provide **7c** in 82% yield, and in this case the corresponding reaction with (4-chlorophenyl)lithium was successful, providing 2-(4-chlorophenyl)-3-methylpyridine (**7b**) in 80% yield as a waxy solid (Scheme II). Initial attempts with (4-fluorophenyl)lithium at comparable temperatures produced low yields (40–50%) of the desired product **7a** and considerable amounts of 4-bromo-4′-fluorobiphenyl which was difficult to separate from **7a** by distillation due to their similar boiling points. Performing the lithium halide exchange at −65 °C followed by addition of the fluoropicoline at −35 to −30 °C minimized formation of the biphenyl and increased the yield of **7a** to 78%.[7]

With an efficient synthesis of the 2-(4-substituted-phenyl)-3-methylpyridines **7a** and **7b** in hand, the successful preparation of the desired 7-halo-5*H*-indeno[1,2-*b*]pyridines and pyridin-5-ones was assured. Though the direct cyclization of **7c** to the indenopyridine **5c** using a catalyst called K-16 has been reported,[2d] the unavailability of this catalyst led us to utilize a three-step procedure. Potassium permanganate oxidation[2f] produced the substituted 3-nicotinic acids **8a–c** which could be readily isolated by Celite filtration to remove the manganese dioxide followed by acidification with acetic acid and continuous extraction with methylene chloride. Cyclization to the ketones occurred smoothly in hot polyphosphoric acid providing high yields (82–99%) of the azafluorenones **6a–c**. Treatment of the ketones with excess hydrazine in diethylene glycol[8] at 180 °C cleanly produced 80–98% yields of the azafluorenes **5a–c**. The usual Wolff–Kishner procedure including potassium hydroxide gave a comparable yield of **5b** (75%), but when applied to **5a** produced exclusively **5d**, as the result of fluoride displacement by the potassium salt of diethylene glycol.

In conclusion, 5*H*-indeno[1,2-*b*]pyridin-5-one and the 7-chloro and 7-fluoro derivatives are available in three steps from 2-fluoro-3-methylpyridine. The ketones can be cleanly reduced to 5*H*-indeno[1,2-*b*]pyridines in high yield by using hydrazine in diethylene glycol. The conversion of these 7-halo-4-azafluorenones and azafluorenes to spiroimidazolidinediones and spiropyrrolidinediones along with the activity of such compounds as aldose reductase inhibitors will be reported at a later date.

Experimental Section

General Methods. All melting points are uncorrected. Infrared spectra were obtained on a Beckman IR4230 spectrometer. Proton NMR spectra were determined either at 60 MHz on a Varian EM-360 instrument or at 270 MHz on a JOEL GX270 spectrometer with tetramethylsilane as an internal standard. Gas chromatography was performed on a Hewlett Packard 5840A gas chromatograph on a 3% OV-17 column. J. T. Baker anhydrous ether and Aldrich Chemical Co. gold label anhydrous tetrahydrofuran were used as received. Elemental analyses were performed by Galbraith Laboratories, Knoxville, TN.

2-Phenyl-3-methylpyridine (7c). Under nitrogen, a solution of 2-fluoro-3-methylpyridine (14.5 g, 0.131 mol) in 50 mL of dry diethyl ether was added over 45 min to a stirred, −10 to 0 °C solution of phenyllithium (1.1 equiv, 60 mL of a 2.4 M 7:3 cyclohexane/ether solution) in 60 mL of dry ether. The mixture was then stirred for 30 min at −10 to 0 °C and for 30 min at room temperature before it was poured into 300 mL of 20% aqueous ammonium chloride. The partially emulsified organic layer was separated, and the aqueous phase was extracted with ether (2 × 20 mL). The combined extracts were then filtered through Celite, separated from the water layer, dried ($MgSO_4$), and concentrated to leave an oily residue which was distilled to provide 18.0 g (82%) of **7c**: bp 78–84 °C/0.07 mmHg (lit.[2f] 159–160 °C/31 mmHg); ^1H NMR ($CDCl_3$) δ 8.45 (dd, 1 H), 7.2–7.6 (m, 6 H), 7.0 (dd, 1 H), 2.25 (s, 3 H).

Anal. Calcd for $C_{12}H_{11}N$: C, 85.17; H, 6.55; N, 8.28. Found: C, 85.36; H, 6.70; N, 8.38.

2-(4-Chlorophenyl)-3-methylpyridine (7b). Under nitrogen, *n*-butyllithium (1.05 equiv, 200 mL of a 2.6 M hexane solution) was added over 1.5 h to a stirred, −20 °C solution of 4-bromochlorobenzene (1.25 equiv, 0.621 mol, 118 g) in 450 mL of dry diethyl ether. After 1 h, 2-fluoro-3-methylpyridine (1.0 equiv, 0.500 mol, 55.0 g) was added at −20 °C over a 1-h period. After having stirred at −20 °C for another hour, the reaction was quenched by the addition of 500 mL of 20% aqueous ammonium chloride, and the mixture was transferred to a separatory funnel. The organic layer was separated, and the aqueous phase was extracted with ether (2 × 200 mL). The combined organic layers were then dried ($MgSO_4$) and concentrated to provide an oil which solidified on standing. After trituration with hexane (about 60 mL) and chilling in a dry ice–acetone bath, 80 g (80%) of **7b** was collected by filtration: mp 57–59 °C; ^1H NMR ($CDCl_3$) δ 8.50 (m, 1 H), 7.40–7.70 (m, 5 H), 7.15 (dd, 1 H), 2.40 (s, 3 H).

Anal. Calcd for $C_{12}H_{10}ClN$: C, 70.77; H, 4.95; N, 6.88. Found: C, 70.73; H, 5.03; N, 6.71.

2-(4-Fluorophenyl)-3-methylpyridine (7a). Under nitrogen, *n*-butyllithium (1.15 equiv, 265 mL of a 2.6 M hexane solution)

(6) (6) Jones, R. G.; Gilman, H. In *Organic Reactions*; Adams, R., Ed.; Robert E. Krieger: New York, 1975, Vol. 6, Chapter 7.

(7) The reaction of 2-fluoro-3-methylpyridine with (4-fluorophenyl)-magnesium bromide was also investigated. With this less reactive reagent, reaction times of several hours in refluxing toluene were required to obtain 50–60% yields of **7a**.

(8) Todd, D. In *Organic Reactions*; Adams, R., Ed.; John Wiley: New York, 1949; Vol. 4, Chapter 8. p 378.

was added over 1 h to a mechanically stirred, −60 to −70 °C solution of 4-bromofluorobenzene (1.1 equiv, 0.66 mol, 115.5 g, 72.5 mL) in 1 L of dry diethyl ether. The mixture was stirred at −65 °C for an additional hour and was then allowed to warm over 10–15 min to −40 °C at which temperature the addition of 2-fluoro-3-methylpyridine (0.60 mol, 66.6 g) was commenced. The majority of the fluoropicoline was added over 50 min at −35 to −30 °C. The mixture was then stirred for 30 min at −40 to −30 °C and then allowed to warm to 7 °C over 1 h, at which time 500 mL of 20% aqueous ammonium chloride was added. The mixture was transferred to a separatory funnel where the organic layer was separated, and the aqueous phase was extracted with ether (2 × 250 mL). The combined extracts were dried ($MgSO_4$), concentrated, and distilled at 0.03–0.05 mmHg, collecting 99 g in a single fraction of bp 35–150 °C. This material was then redistilled through a 6-in., 24/40 Vigreux column to provide 87.5 g (78%) of **7a** of 95% purity as determined by GLC analysis: bp 77–82 °C/0.03 mmHg; ^{1}H NMR ($CDCl_3$) δ 8.5 (dd, 1 H), 7.3–7.6 (m, 3 H), 6.9–7.25 (m, 3 H), 2.3 (s, 3 H).

Anal. Calcd for $C_{12}H_{10}FN$: C, 76.99; H, 5.38; N, 7.48. Found: C, 76.83; H, 5.58; N, 7.50.

2-Phenyl-3-pyridinecarboxylic Acid (8c). A mixture of **7c** (10.0 g, 0.059 mol) and potassium permanganate (3 equiv, 0.178 mol, 28.1 g) in 250 mL of water was heated to reflux over 1 h 45 min and maintained at reflux until all the permanganate was consumed (2 h). The mixture was filtered hot through Celite, and the filter pad was washed with hot water (100 mL). The filtrate was acidified with glacial acetic acid and then continuously extracted with methylene chloride for 18 h. The methylene chloride extract was dried ($MgSO_4$) and concentrated to leave 12.7 g of a thick, viscous syrup which, upon trituration with cold diethyl ether, crystallized to provide, after filtration and air drying, 7.23 g (61%) of **8c**: mp 166–168 °C (lit.[2f] 167–169 °C); ^{1}H NMR ($CDCl_3$/Me_2SO-d_6) δ 10.2 (br, 1 H), 8.7 (dd, 1 H), 8.1 (dd, 1 H), 7.2–7.7 (m, 6 H); IR (KBr) 1710 cm^{-1}.

Anal. Calcd for $C_{12}H_9NO_2$: C, 72.35; H, 4.55; N, 7.03. Found: C, 72.22; H, 4.68; N, 6.88.

2-(4-Chlorophenyl)-3-pyridinecarboxylic Acid (8b). Prepared from **7b** using the procedure described for **8c** above: 40% yield; mp 173–175 °C (from ethyl acetate); ^{1}H NMR (Me_2SO-d_6) δ 11.5 (br, 1 H), 8.6 (dd, 1 H), 8.0 (dd, 1 H), 7.2–7.5 (m, 5 H); IR (KBr) 1690 cm^{-1}.

Anal. Calcd for $C_{12}H_8ClNO_2$: C, 61.69; H, 3.45; N, 5.99. Found: C, 61.47; H, 3.38; N, 6.19.

2-(4-Fluorophenyl)-3-pyridinecarboxylic Acid (8a). Prepared from **7a** by using the procedure described for **8c** above: 60% yield; mp 159–162 °C; ^{1}H NMR (Me_2SO-d_6) δ 11.5 (br, 1 H), 8.6 (dd, 1 H), 8.0 (dd, 1 H), 7.0–7.7 (m, 5 H); IR (KBr) 1710 cm^{-1}.

Anal. Calcd for $C_{12}H_8FNO_2$: C, 66.36; H, 3.71; N, 6.45. Found: C, 66.23; H, 3.72; N, 6.45.

5*H*-Indeno[1,2-*b*]pyridin-5-one (6c). A mixture of **8c** (7.50 g, 0.038 mol) and 125 g of polyphosphoric acid was heated over 20 min to 225 °C and maintained at 210–215 °C for 2 h, after which time the hot mixture was poured into 625 mL of ice–cold 3 M sodium hydroxide. Some additional sodium hydroxide was added to make the solution basic. The mixture was cooled in ice, and the solid that separated was collected by filtration and thoroughly dried to provide 6.6 g (98%) of **6c**: mp 138–140 °C (from ethanol) (lit.[2f] 139.5–141.5 °C); ^{1}H NMR ($CDCl_3$) δ 8.5 (dd, 1 H), 7.0–7.9 (m, 6 H); IR (KBr) 1710 cm^{-1}.

Anal. Calcd for $C_{12}H_7NO$: C, 79.55; H, 3.89; N, 7.73. Found: C, 79.35; H, 4.01; N, 7.69.

7-Chloro-5*H*-indeno[1,2-*b*]pyridin-5-one (6b). A mixture of **8b** (22.9 g, 0.098 mol) and 500 g of polyphosphoric acid was heated at 200 °C for 10 h. The mixture, at ca. 80 °C, was slowly poured into 200 mL of water. Ice was added to bring the volume up to about 4 L, and after 1 h the solid that had separated was collected by filtration. The moist solid was dissolved in methylene chloride (about 700 mL), treated with $MgSO_4$ and charcoal, and filtered through Celite. Solvent removal left 17.5 g (82%) of **6b**: mp 156–158 °C; ^{1}H NMR ($CDCl_3$) δ 8.6 (dd, 1 H), 7.1–8.0 (m, 5 H); IR (KBr) 1715 cm^{-1}.

Anal. Calcd for $C_{12}H_6ClNO$: C, 66.84; H, 2.80; N, 6.50. Found: C, 67.18; H, 2.90; N, 6.43.

7-Fluoro-5*H*-indeno[1,2-*b*]pyridin-5-one (6a). A mixture of **8a** (98.7 g, 0.455 mol) and 1.5 kg of polyphosphoric acid was heated over 30 min to 210 °C and maintained at that temperature for 4 h. After the mixture had cooled to 180 °C, it was poured into a mixture of 4 L of 3.75 M sodium hydroxide and 3.5 kg of ice. After an additional liter of water and 2 L of ethyl acetate were added to achieve clean-phase separation, the organic layer was removed, and the aqueous layer was extracted with additional ethyl acetate (2 × 1 L). The combined extracts were washed with water (500 mL) and brine (500 mL), dried ($MgSO_4$), filtered through Celite and decolorizing carbon, and concentrated to provide 76.9 g (85%) of **6a** as a bright yellow solid: mp 156–158 °C (from ethanol); ^{1}H NMR ($CDCl_3$, 270 MHz) δ 8.6 (dd, 1 H), 7.9 (dd, 1 H), 7.8 (dd, 1 H), 7.4 (dd, 1 H), 7.3 (ddd, 1 H), 7.2 (dd, 1 H); IR (KBr) 1725 cm^{-1}.

Anal. Calcd for $C_{12}H_6FNO$: C, 72.36; H, 3.04; N, 7.03. Found: C, 72.40; H, 3.15; N, 7.01.

5*H*-Indeno[1,2-*b*]pyridine (5c). A mixture of **6c** (5.00 g, 0.028 mol) and hydrazine monohydrate (4 equiv, 5.4 mL) in 180 mL of diethylene glycol was heated to 180 °C and maintained at that temperature for 4 h. After having been cooled to room temperature, the mixture was poured into 500 mL of water and 100 mL of brine and was extracted with ethyl acetate (3 × 100 mL). The combined extracts were washed with water (2 × 100 mL), dried ($MgSO_4$), and concentrated to leave 4.53 g (98%) of **5c**: mp 93–95 °C; ^{1}H NMR ($CDCl_3$) δ 8.5 (dd, 1 H), 8.0 (m, 1 H), 7.65 (dd, 1 H), 7.2–7.5 (m, 3 H), 7.0 (dd, 1 H), 3.7 (s, 2 H).

Anal. Calcd for $C_{12}H_9N$: C, 86.20; H, 5.43; N, 8.38. Found: C, 86.21; H, 5.63; N, 8.34.

7-Chloro-5*H*-indeno[1,2-*b*]pyridine (5b). A mixture of **6b** (47.0 g, 0.219 mol) and hydrazine monohydrate (4 equiv, 42 mL) in 1 L of diethylene glycol was refluxed with vigorous stirring for 2.5 h. After the reaction mixture had cooled to 100 °C, it was poured onto crushed ice bringing the total volume to about 3 L. The white solid that separated was collected by filtration, washed well with water, and dried to provide 35 g (80%) of **5b** homogeneous by TLC: mp 97–101 °C; ^{1}H NMR ($CDCl_3$) δ 8.5 (dd, 1 H), 7.0–8.0 (m, 5 H), 3.8 (s, 2 H).

Anal. Calcd for $C_{12}H_8ClN$: C, 71.47; H, 4.00; N, 6.95. Found: C, 71.54; H, 3.99; N. 6.91.

7-Fluoro-5*H*-indeno[1,2-*b*]pyridine (5a). A mixture of **6a** (18.0 g, 0.090 mol) and hydrazine monohydrate (4 equiv, 18 mL) in 600 mL of diethylene glycol was heated to 180 °C and maintained at that temperature for 4 h. The mixture was cooled to room temperature and poured into 1200 mL of water. The yellow solid that separated was collected by filtration and dried to provide 13.2 g (80%) of **5a**. An additional 3.2 g of material was recovered from the filtrate by extraction with ethyl acetate: mp 90–93 °C (from hexane); ^{1}H NMR ($CDCl_3$) δ 8.5 (dd, 1 H), 7.95 (ddd, 1 H), 7.7 (dd, 1 H), 6.9–7.3 (m, 3 H), 3.75 (s, 2 H).

Anal. Calcd from $C_{12}H_8FN$: C, 77.82; H, 4.35; N, 7.56. Found: C, 78.03; H, 4.42; N, 7.52.

Registry No. **5a**, 97677-23-1; **5b**, 101419-82-3; **5c**, 244-99-5; **6a**, 101419-80-1; **6b**, 101419-81-2; **6c**, 3882-46-0; **7a**, 101419-76-5; **7b**, 101419-77-6; **7c**, 10273-90-2; **8a**, 101419-78-7; **8b**, 101419-79-8; **8c**, 33421-39-5; PhLi, 591-51-5; 4-BrC_6H_4Cl, 106-39-8; 4-BrC_6H_4F, 460-00-4; 2-fluoro-3-methylpyridine, 2369-18-8.