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Direct Access to 4-Carboxy-1,8-naphthyridines and Related Compounds through Pfitzinger-Type Chemistry

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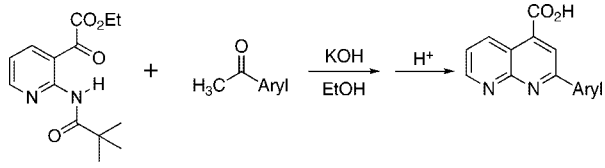
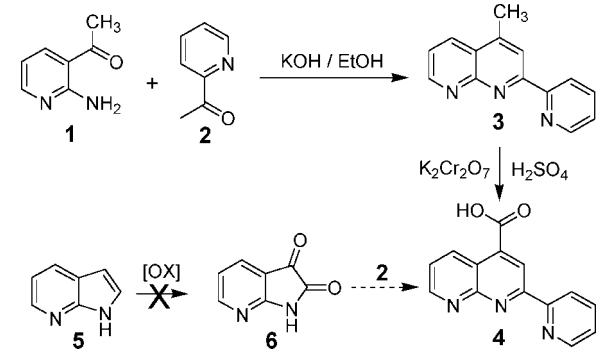
Received February 29, 2008



The 4-carboxy-1,8-naphthyrid-2-yl moiety is a useful ligand component in that it promotes lower energy electronic absorption in its metal complexes and also provides a useful tether for anchoring the ligand to a semiconductor surface. The synthon [2-(pivaloylamino)pyrid-3-yl]oxoacetic acid ethyl ester can be easily obtained in two steps from 2-aminopyridine. The Pfitzinger-type condensation of this molecule with a 2-acetylazaaromatic species in ethanolic KOH, after acidification, directly provides bi- and tridentate ligands containing the 4-carboxy-1,8-naphthyrid-2-yl moiety.

The strategic design of new photosensitizers is becoming an area of increasing importance both for energy conversion[1] and therapeutic applications.[2] For transition metal-based sensitizers, the structure of the ligands often dictates such critical features as absorption energy and intensity and excited state lifetimes. From this point of view we have discovered that the use of 1,8-naphthyridine (nap) as a ligand can show some distinct advantages over the more traditional pyridine or quinoline.[3] Since 1,8-naphthyridine is more electronegative and more delocalized than pyridine, transition metal complexes involving this moiety show longer wavelength, lower energy absorptions than their pyridine counterparts.[4] We have recently used this effect to advantage in the design of new photosensitizer dyes for TiO_2-based solar cells where the incident photon-to-current efficiency (IPCE) remains strong even beyond 750 nm.[3] This paper describes a simple method for the introduction of the 4-carboxy-1,8-naphthyrid-2-yl moiety into a variety of polypyridine-type multidenate ligand systems.

SCHEME 1



The parent 1,8-naphthyridine nucleus can be readily synthesized by the Friedländer condensation between 2-aminonicotinaldehyde[5] and an enolizable ketone such as 2-acetylpyridine (**2**).[6] To attach the ligand and its derivative metal complexes to a semiconductor surface such as TiO_2, the incorporation of an anchoring group, such as a carboxy substituent, at the 4- or 5-position is desirable. To accomplish this modification one can use 3-acetyl-2-aminopyridine (**1**) in the Friedländer reaction but the self-condensation of **1** is a serious complication. Oxidation of the resulting 4-methyl-1,8-naphthyridine **3** to convert the methyl group to a carboxlic acid can be accomplished with chromic acid but the yields are often quite poor, as degradation of the molecule under the harsh oxidation conditions is sometimes difficult to avoid (Scheme 1).

In seeking an alternative route to these systems, we investigated the closely related Pfitzinger reaction[7] in which isatin leads smoothly to 4-carboxy-substituted quinolines in good yields. Preparation of the analogous 1,8-naphthyridine derivative would require 7-azaisatin (**6**) as the synthon. Although this molecule has been reported,[8] our attempts to prepare **6** by the oxidation of commercially available 7-azaindole (**5**) under a variety of conditions were unsuccessful (Scheme 1). The closely related 5-azaisatin[9] is known and it reacts readily with enolizable ketones to provide 4-carboxy-1,6-naphthyridine derivatives. However, the coordination chemistry of these species is sometimes difficult to control.

A more accessible synthon for the formation of **4**, which could react in much the same manner as azaisatin **6**, is the 2-aminopyridine ethyl glyoxalate derivative **11**. This species is too

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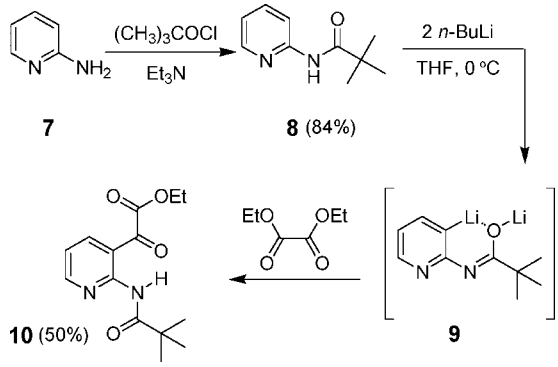
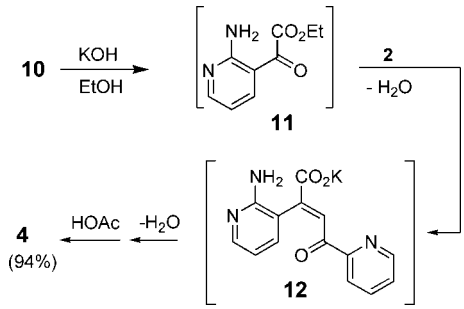
10.1021/jo800456r CCC: $40.75
Published on Web 05/08/2008

SCHEME 2



SCHEME 3

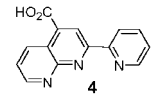
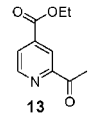
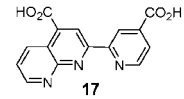
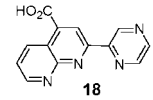
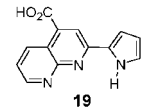
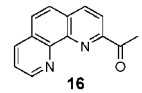
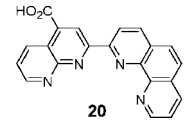


reactive to be useful and is better handled as the protected amide **10**.[10] The reaction of 2-aminopyridine with trimethylacetyl chloride proceeds smoothly in 84% yield to provide **8**.[11] This species may then be ortho-metalated specifically at the 3-position by using 2 equiv of *n*-butyllithium. Reaction of the dianion **9** with diethyl oxalate incorporates the α-ketoester moiety in 50% yield (Scheme 2). This material is an easily purified solid (mp 118−119 °C) that can be stored without difficulty. In principle, deprotection of the amide function of **10** would give the 2-amino-3-α-ketoester **11**, which might then cyclize to provide 7-azaisatin (**6**). This conversion proved both difficult and unnecessary.

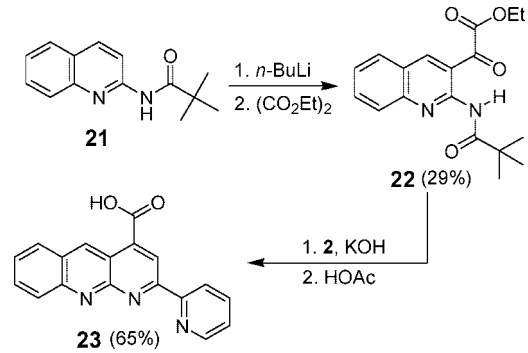
The direct treatment of **10** and 2-acetylpyridine with ethanolic KOH would result in the hydrolysis of the protecting group to provide **11**, which then directly undergoes Claisen-type condensation with the enolate anion of **2** to provide **12**. This species cyclodehydrates to form the naphthyridine ring followed by hydrolysis of the ester group (Scheme 3). Final acidification with acetic acid gives a 94% isolated yield of 2-(pyrid-2′-yl)-4-carboxy-1,8-naphthyridine (**4**) by simple precipitation. The same protocol may be applied by using **10** and other 2-acetyl-azaaromatics in place of **2** to provide other bi- and tridentate ligands or ligand precursors and the results for several systems are summarized in Table 1.

The same protocol used to prepare **10** from 2-aminopyridine can be applied to other similar 2-amino-azaaromatic systems. Thus 2-aminoquinoline may be protected with trimethylacetyl chloride to afford a nearly quantitative yield of **21**, which may then be converted to **22** in 29% yield by treatment with *n*-butyllithium and diethyl oxalate. Condensation of **22** with 2-acetylpyridine afforded a 65% yield of the 4-carboxybenzo[*b*]-1,8-naphthyridine derivative **23** (Scheme 4). A similar approach was attempted with 2-aminopyrazine and 2-aminoquinoxaline but these systems are more difficult to functionalize in the 3-position.

TABLE 1. Preparation of 4-Carboxy-1,8-naphthyridines with Use of 10

acetyl aromatic	product	yield
 2	 4	94%
 13	 17	53%
 14	 18	79%
 15	 19	59%
 16	 20	83%

SCHEME 4



If one uses a diacetyl azaaromatic in the condensation step, tridentate bis-4-carboxy-1,8-naphthyridines can be prepared without any diminishment in the overall yield. Several such reactions are summarized in Table 2. The bridging ligand **31** is closely related to one that has been recently used to prepare a diruthenium complex which is effective in water oxidation.[12]

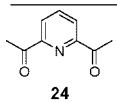
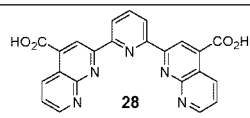
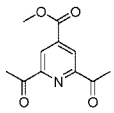
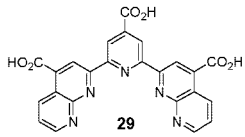
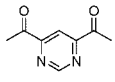
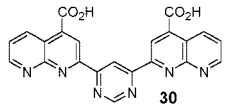
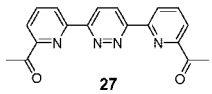
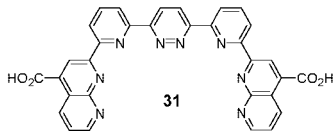
The [2-(pivaloylamino)pyrid-3-yl]oxoacetic acid ethyl ester (**10**) is an excellent substitute for the relatively unavailable 7-azaisatin in the Pfitzinger synthesis of ligands incorporating the 4-carboxy-1,8-naphthyridine moiety. The reagent **10** is stable, the reaction and product isolation are simple, and the yields are good. The resulting ligands are expected to find considerable utility in the immobilization of photosensitizer catalysts on semiconductor surfaces such as titanium dioxide and such systems will be reported in future work.

(10) This reagent has been reported in a patent but the NMR characterization is incorrect: Grootenhuis, P. D. J.; Garcia-Guzman, B. M.; Makings, L. R.; Londo, P. M. U.S. Patent 2005056552 A1, 2005.

(11) Turner, J. A. *J. Org. Chem.* **1983**, *48*, 3401–3408.

(12) Zong, R.; Thummel, R. P. *J. Am. Chem. Soc.* **2005**, *127*, 12802–12803.

TABLE 2. Preparation of Bis-4-carboxy-1,8-naphthyridines with Use of 10

acetyl aromatic	product	yield
 **24**	 **28**	80%
 **25**	 **29**	81%
 **26**	 **30**	69%
 **27**	 **31**	98%

Experimental Section

The ^{1}H NMR and ^{13}C NMR spectra were obtained at 300 and 75 MHz (200 MHz for **31**), respectively. Chemical shifts were reported in parts per million (ppm) relative to TMS and the *J* values are ±0.3 Hz. Melting points were measured on a Thomas-Hoover capillary melting point apparatus and were not corrected. Commercial 2-aminopyridine, 2-acetylpyridine, 2,6-diacetylpyridine, 2-acetylpyrazine, and 2-acetylpyrrole were used as received. The 2-(pivaloylamino)pyridine (**8**),[11] ethyl 2-acetylpyridine-4-carboxylate (**13**),[13] 2-acetyl-1,10-phenanthroline (**16**),[14] 4,6-diacetylpyrimidine (**26**),[15] 3,6-di(6′-acetylpyrid-2′-yl)pyridazine (**27**),[16] 2-aminoquinoline,[17] and 2-(pivaloylamino)quinoline (**21**)[18] were prepared according to literature procedures. For the combustion analyses, it is not unusual for strong polydentate chelators to retain water even after rigorous drying.

[2-(Pivaloylamino)pyrid-3-yl]oxoacetic Acid Ethyl Ester (10). The compound was prepared following the protocol developed by Turner[11] and Hewawasam and Meanwell.[19] The 2-(pivaloylamino)pyridine (**8**, 7.60 g, 42.7 mmol) in dry THF (100 mL) was treated with *n*-butyllithium (1.6 M in hexane, 53 mL, 84.8 mmol) at −70 °C for 1 h, yielding a light yellow solution. The mixture was allowed to warm to ice-bath temperature, and some precipitate was observed. The mixture was stirred at 0 °C for 3 h, and more precipitate formed. After the mixture was cooled to −70 °C, diethyl oxalate (16 mL in 10 mL of dry THF) was added dropwise. The mixture was allowed to warm to room temperature and stirred for 20 min. The reaction was quenched with acidic ice−water (1 mL of concentrated HCl and 100 mL of ice). The product was extracted with ether (3 × 50 mL) and dried over Na_2SO_4. Evaporation of the solvents gave a red oil (9.0 g) that was chromatogaphed on silica gel eluting with a mixture of 1:1 ethyl acetate and hexanes to provide **10** as light yellow crystals (6.0 g, 50%), mp 118−119 °C: ^{1}H NMR ($CDCl_3$) δ 9.92 (s, 1H), 8.61 (dd, J = 2.1, 7.5 Hz, 1H), 8.08 (dd, J = 1.5, 7.5 Hz, 1H), 7.17(dd, J = 1.8, 7.5 Hz, 1H), 4.41 (q, J = 6.9 Hz, 2H), 1.42 (t, J = 6.9 Hz, 3H), 1.33 (s, 9H); ^{13}C NMR ($CDCl_3$) δ 185.0, 176.8, 161.5, 153.0, 150.5, 140.8, 118.7, 117.3, 62.8, 40.0, 27.3, 14.0; IR (ATR, cm^{-1}) ν 1731, 1709, 1673. Anal. Calcd for $C_{14}H_{18}N_2O_4$ (278.30): C, 60.42; H, 6.52; N, 10.07. Found: C, 60.43; H, 6.51; N, 10.04.

2-(Pyrid-2′-yl)-1,8-naphthyridine-4-carboxylic Acid (4).[3] A mixture of **10** (202 mg, 0.73 mmol), 2-acetylpyridine (70 mg, 0.58 mmol), and ethanol (10 mL) was treated with KOH (116 mg, 2.07 mmol) under reflux for 48 h. The alcohol was removed and water (3 mL) was added to the residue to give a solution. The aqueous solution was extracted with CH_2Cl_2 (3 × 3 mL), acidified with HOAc (0.4 mL) to produce a white precipitate. The precipitate was collected, washed with water, ethanol, and ether, and dried to give **4** as a white solid (137 mg, 94%), mp >250 °C: ^{1}H NMR (DMSO-d_6) δ 9.21 (dd, J = 2.1, 8.4 Hz, 1H), 9.19 (dd, J = 2.1, 4.2 Hz, 1H), 9.10 (s, 1H), 8.80 (ddd, J = 0.9, 4.2, 6.9 Hz, 1H), 8.64 (d, J = 8.1 Hz, 1H), 8.08 (dt, J = 1.5, 7.8 Hz, 1H), 7.75 (dd, J = 4.2, 8.7 Hz, 1H), 7.60 (ddd, J = 1.2, 4.5, 7.2 Hz, 1H); ^{13}C NMR (D_2O/CD_3OD/KOH) δ 174.2, 159.2, 155.3, 154.8, 154.6, 149.7, 149.6, 139.2, 137.7, 126.3, 124.1, 123.8, 120.4, 118.2; IR (ATR, cm^{-1}) ν 1716, 1597; MS (MALDI-TOF) *m*/*z* 252.27 [M + H]$^+$, 274.27 [M + Na]$^+$.

2-(4′-Carboxypyrid-2′-yl)-1,8-naphthyridine-4-carboxylic Acid (17).[3] A solution of **10** (150 mg, 0.54 mmol), ethyl 2-acetylisonicotinate (**13**, 100 mg, 0.52 mmol), and KOH (113 mg, 2.0 mmol) in EtOH (15 mL) was refluxed for 8 h. The precipitate was collected, washed with EtOH (5 mL), and dried to provide a light brown solid as the potassium salt of **17** (145 mg, 75%), mp >280 °C: ^{1}H NMR (D_2O/CD_3OD) δ 9.03 (dd, J = 1.5, 4.8 Hz, 1H), 8.74 (d, J = 4.8 Hz, 1H), 8.69 (dd, J = 1.5, 8.1 Hz, 1H), 8.65 (s, 1H), 8.36 (s, 1H), 7.84 (dd, J = 0.9, 5.1 Hz, 1H), 7.66 (dd, J = 4.5, 8.1 Hz, 1H); ^{13}C NMR (D_2O/CD_3OD) δ 174.4, 173.6, 159.6, 156.0, 155.6, 155.2, 150.8, 150.1, 147.4, 137.7, 125.2, 124.4, 122.9, 120.5, 118.3; IR (ATR, cm^{-1}) ν 1611, 1586, 1547. The salt (145 mg, 0.39 mmol) in water (5 mL) was treated with HOAc (0.5 mL) to give a gray precipitate that was separated by centrifugation and washed with water (3 × 5 mL), EtOH (5 mL), and a 1:1 mixture of EtOH−Et_2O, then dried to give a gray solid (81 mg, 53%), mp >300 °C: ^{1}H NMR (DMSO-d_6) δ 9.24 (dd, J = 2.1, 8.1 Hz, 1H), 9.21 (dd, J = 1.8, 4.5 Hz, 1H), 9.09 (s, 1H), 9.07 (s, 1H), 8.99 (d, J = 4.8 Hz, 1H), 8.00 (dd, J = 1.5, 4.8 Hz, 1H), 7.77 (dd, J = 4.2, 8.1 Hz, 1H); IR (ATR, cm^{-1}) ν 1709; MS (MALDI-TOF) *m*/*z* 296.24 [M + H]$^+$, 318.21 [M + Na]$^+$, 340.21 [M + 2Na]$^+$.

[2-(Pivaloylamino)quinolin-3-yl]oxoacetic Acid Ethyl Ester (22). Under Ar, 2-(pivaloylamino)quinoline (**21**, 364 mg, 1.59 mmol) was dissolved in dry THF (4 mL) and the solution was cooled at −78 °C. *n*-BuLi (1.6 M in hexanes, 2.49 mL) was added dropwise. After addition, the mixture was stirred at −10 °C for 3 h. Then at −78 °C, diethyl oxalate (0.57 mL, 4.14 mmol) was added dropwise. After 15 min at −78 °C, then 15 min at room temperature, the mixture was quenched by adding water. The mixture was extracted with EtOAc (3 × 20 mL). The organic phase was dried over $MgSO_4$. Evaporation of the EtOAc gave an oil that was purified by column chromatography on silica gel eluting with $CHCl_3$/MeOH (200:1, then 100:1) to afford **22** as a light-yellow waxy solid (370 mg, 29%): ^{1}H NMR ($CDCl_3$) δ 9.91 (s, 1 H), 8.59 (s, 1 H), 7.96 (d, J = 7.8 Hz, 1 H), 7.78−7.83 (m, 2 H), 7.48−7.51 (m, 1 H), 4.43 (q, J = 7.2 Hz, 2 H), 1.43 (t, J = 7.2 Hz, 3 H), 1.35 (s, 9 H); ^{13}C NMR ($CDCl_3$) δ 184.8, 177.2, 161.8, 148.5, 147.8, 143.8, 133.3, 129.0, 128.2, 126.3, 124.4, 118.4, 62.8, 40.1, 21.3, 14.1; IR (ATR, cm^{-1}) ν 1731, 1708, 1669, 1620; MS (MALDI-TOF) *m*/*z* 329.32 [M + H]$^+$, 351.32 [M + Na]$^+$.

2-(Pyrid-2′-yl)benzo[*b*]-1,8-naphthyridine-4-carboxylic Acid (23). A solution of **22** (400 mg, 1.22 mmol) and KOH (271 mg, 4.87 mmol) in EtOH/H_2O (20 mL, 4:1) was heated at reflux for 1 h. After addition of 2-acetylpyridine, the reaction mixture was heated at reflux overnight. EtOH was evaporated. The residue was diluted with water (5 mL) and extracted with CH_2Cl_2 (2 × 10 mL).

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The aqueous phase was acidified with acetic acid to pH ~3. The precipitate was collected then washed with water and EtOH to give **23** as a light-brown solid (240 mg, 65%), mp >280 °C: ^{1}H NMR (DMSO-d_6) δ 9.98 (s, 1 H), 9.14 (s, 1 H), 8.85 (d, J = 4.5 Hz, 1 H), 8.76 (d, J = 7.8 Hz, 1 H), 8.34 (d, J = 7.8 Hz, 1 H), 8.25 (d, J = 9.3 Hz, 1 H), 8.10−8.17 (m, 1 H), 7.96−8.02 (m, 1 H), 7.70−7.76 (m, 1 H), 7.62−7.68 (m, 1 H); ^{13}C NMR (D_2O/CD_3OD/KOH) δ 174.0, 160.2, 153.9, 153.2, 149.7, 149.2, 148.7, 138.9, 138.8, 133.0, 129.5, 127.9, 127.2, 126.4 (2C), 123.9, 118.1, 116.8; IR (ATR, cm^{-1}) ν 1699, 1600; MS (MALDI-TOF) m/z 302.29 [M + H]$^+$, 324.28 [M + Na]$^+$, 346.27 [M + 2Na]$^+$. Anal. Calcd for $C_{18}H_{11}N_3O_2\cdot 0.25H_2O$ (305.81): C, 70.70; H, 3.79; N, 13.74. Found: C, 71.28; H, 3.87; N, 13.19.

Methyl 2,6-Diacetylisonicotinate (25). To a solution of H_2SO_4 (0.4 M, 400 mL) was added methyl isonicotinate (5.50 g, 40 mmol), pyruvic acid (14.1 g, 140 mmol), and $AgNO_3$ (0.54 g in 5 mL of water). Ammonium persulfate (36.5 g, 160 mmol) was added in small portions to the mixture.[20] The mixture was stirred at room temperature overnight and extracted with chloroform (3 × 80 mL). The organic phase was washed with a saturated Na_2CO_3 solution (100 mL) and brine (100 mL), then dried over $MgSO_4$. Evaporation of the solvent gave **25** as a yellow solid. Recrystallization from ethyl acetate and hexanes gave crystalline needles of methyl 2,6-diacetylisonicotinate (2.1 g, 24%), mp 131−132 °C: ^{1}H NMR ($CDCl_3$) δ 8.74 (s, 2H), 4.01 (s, 3H), 2.83 (s, 6H); ^{13}C NMR ($CDCl_3$) δ 198.4, 164.4, 153.7, 140.0, 124.0, 53.1, 25.7; IR (ATR, cm^{-1}) ν 1727, 1701, 1250, 949, 770. Anal. Calcd for $C_{11}H_{11}NO_4$ (221.21): C, 59.73; H, 5.01; N, 6.33. Found: C, 59.68; H, 4.87; N, 6.33.

2,6-Di(4′-carboxy-1′,8′-naphthyrid-2′-yl)pyridine (28). The synthetic procedure as described for **4** was followed. The overnight reaction of 2,6-diacetylpyridine (84 mg, 0.50 mmol), **10** (370 mg, 1.33 mmol), and KOH (200 mg, 3.57 mmol) in ethanol (20 mL) afforded a suspension. Treatment of the crude product with water, CH_2Cl_2, and HOAc gave **28** as a colorless solid (170 mg, 80%), mp >280 °C: ^{1}H NMR (DMSO-d_6) δ 9.28 (dd, J = 1.5, 8.4 Hz, 2H), 9.16 (m, 4H), 8.82 (d, J = 7.5 Hz, 2H), 8.34 (t, J = 7.5 Hz, 1H), 7.73 (dd, J = 4.5, 8.4 Hz, 2H); ^{13}C NMR (D_2O/CD_3OD/KOH) δ 174.6, 158.4, 154.9, 154.0, 153.8, 148.9, 139.6, 137.8, 124.8, 123.8, 120.7, 118.2; IR (ATR, cm^{-1}) ν 1699, 1590. Anal. Calcd for $C_{23}H_{13}N_5O_4\cdot 1.25H_2O$ (445.90): C, 61.95; H, 3.50; N, 15.71. Found: C, 61.72; H, 3.05; N, 15.39.

2,6-Di(4′-carboxy-1′,8′-naphthyrid-2′-yl)pyridine-4-carboxylic Acid (29). The synthetic procedure as described for **4** was followed. The reaction of **10** (278 mg, 1.0 mmol), **25** (73 mg, 0.33 mmol), and KOH (200 mg, 3.57 mmol) for 24 h afforded a suspension. Treatment of the crude product with water, CH_2Cl_2, and HOAc gave **29** as a colorless solid (125 mg, 81%), mp >280 °C: ^{1}H NMR (DMSO-d_6) δ 9.28 (dd, J = 1.5, 8.1 Hz, 2H), 9.22 (s, 2H), 9.18 (dd, J = 1.5, 4.2 Hz, 2H), 9.15 (s, 2H), 7.73 (dd, J = 4.2, 8.7 Hz, 2H); ^{13}C NMR (D_2O/CD_3OD/KOH) δ 174.7, 173.6, 159.7, 156.5, 155.7, 155.3, 150.2, 148.5, 137.8, 124.4, 123.6, 120.7, 118.6; IR (ATR, cm^{-1}) ν 1701, 1592. Anal. Calcd for $C_{24}H_{13}N_5O_6\cdot 2H_2O$ (503.43): C, 57.26; H, 3.40; N, 13.91. Found: C, 56.78; H, 2.80; N, 13.69.

4,6-Di(4′-carboxy-1′,8′-naphthyrid-2′-yl)pyrimidine (30). A solution of **10** (407 mg, 1.46 mmol) and KOH (164 mg, 2.92 mmol) in EtOH/H_2O (6 mL, 5:1) was heated at reflux for 1 h. To the resulting solution was added **26** (100 mg, 0.61 mmol). The solution was heated at reflux for 24 h, during which a very thick precipitate formed. The reaction mixture was cooled and water (10 mL) was added and the EtOH was evaporated under vacuum. The precipitate dissolved slowly to give a clear solution. The aqueous solution was extracted with CH_2Cl_2 (3 × 50 mL). Acidification of the aqueous solution with 10% HCl led to precipitation. The precipitate was collected and triturated with EtOH, followed by filtration and drying to give **30** as a light-yellow solid (179 mg, 69%), mp >280 °C: ^{1}H NMR (DMSO-d_6/D_2O/NaOD) δ 9.67 (s, 1 H), 9.55 (s, 1 H), 9.10−9.12 (m, 2 H), 9.05 (dd, J = 1.5, 8.4 Hz, 2 H), 8.73 (s, 2 H), 7.66−7.71 (m, 2 H); ^{13}C NMR (D_2O/CD_3OD/KOH) δ 173.6, 163.6, 159.2, 156.6, 155.4 (2C), 150.1, 137.8, 124.9, 121.5, 118.3, 116.4; IR (ATR, cm^{-1}) ν 1715, 1585. Anal. Calcd for $C_{22}H_{12}N_6O_4\cdot H_2O\cdot 0.5$EtOH (465.23) C, 59.36; H, 3.68; N, 18.06. Found: C, 59.82; H, 3.82; N, 18.00.

3,6-Di(6′-[4″-carboxy-1″,8″-naphthyrid-2″-yl]pyrid-2′-yl)pyridazine (31). The synthetic procedure as described for **4** was followed. A mixture of **10** (115 mg, 0.41 mmol), 3,6-di(6′-acetylpyrid-2′-yl)pyridazine (**27**, 41 mg, 0.13 mmol), and KOH (120 mg, 2.14 mmol) in ethanol (10 mL) was refluxed overnight. Treatment of the crude product with water, NaOH (2M, 0.2 mL), CH_2Cl_2, and HOAc gave a gel-like mixture. The mixture was separated by centrifugation. The solid was washed with water (twice) and ethanol (twice), then dried to give **31** as a colorless material (74 mg, 98%), mp >280 °C: ^{1}H NMR (DMSO-d_6) δ 9.06 (dd, J = 1.8, 4.5 Hz, 2H), 9.00−8.95 (m, 6H), 8.68 (d, J = 8.1 Hz, 2H), 8.58 (d, J = 7.2 Hz, 2H), 8.20 (t, J = 7.8 Hz, 2H), 7.54 (dd, J = 4.5, 8.4 Hz, 2H); ^{13}C NMR (200 MHz, DMSO-d_6) δ 168.1, 157.9, 157.2, 155.7, 155.6, 153.2, 152.7, 152.6, 139.0, 137.4, 125.6, 122.8, 122.1, 121.8, 120.9, 116.9; IR (ATR, cm^{-1}) ν 1713, 1584; MS (MALDI-TOF) m/z 579.5 [M + H]$^+$, 601.5 [M + Na]$^+$, 617.5 [M + K]$^+$, 623.5 [M + 2Na]$^+$, 639.5 [M + K + Na]$^+$, 655.5 [M + 2K]$^+$.

Acknowledgment. We would like to thank the Robert A. Welch Foundation (E-621) and the National Science Foundation (CHE-0352617) for financial support of this work.

Note Added after ASAP Publication. In the version published ASAP May 8, 2008 the abstract and toc graphic contained errors; the corrected version was published May 14, 2008.

Supporting Information Available: The synthesis of compounds **18**−**20** and the ^{1}H and ^{13}C NMR spectra of compounds **4**, **10**, **17**−**20**, **22**, **23**, **25**, and **28**−**31**. This material is available free of charge via the Internet at http://pubs.acs.org.

JO800456R

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