(relative intensity) 779 (**12a** M^+, 5), 777 (**13** M^+, 2.5); HRMS (FAB), exact mass observed 778.2408 ($C_{45}H_{36}N_3O_{10}$ $(M + 1)^+$, 778.2415). A mixed sample containing **12a** and **13** in $CHCl_3$/hexane solution displays a fluorescence emission maximum at 495 nm with an excitation maximum at 399.5 nm.[25]

Acknowledgment. Financial support was provided by PHS Grant GM 05829-26. Fast atom bombardment and field desorption mass spectra were obtained in the Mass Spectrometry Laboratory, School of Chemical Sciences, University of Illinois, supported in part by a grant from the National Institute of General Medical Sciences (Grant GM 27029). The ZAB-HF mass spectrometer was purchased in part with grants from the Division of Research Resources, National Institutes of Health (Grant RR 01575), and the National Science Foundation (Grant PCM-8121494). We appreciate the assistance of Keith Carriker (2-D FT NMR) and Susan Morris (cyclic voltammetry). We also thank Dr. Milan R. Uskoković of Hoffmann-La Roche Inc. for a generous gift of 1,3-dibenzyl-2-oxoimidazoldine-4,5-*cis*-dicarboxylic acid.

Registry No. **4a**, 26339-42-4; **4b**, 96666-59-0; **5a**, 26511-17-1; **5b**, 96666-45-4; **5c**, 96666-46-5; **5d**, 96666-47-6; **6a**, 96666-48-7; **6b**, 96666-49-8; **7**, 96666-50-1; **9a**, 96666-51-2; **9b**, 96666-52-3; **9c**, 96666-53-4; **9d**, 96666-54-5; **10**, 96666-55-6; **11**, 14215-97-5; **12a**, 96666-56-7; **12b**, 96666-57-8; **13**, 96666-58-9; $NH_2CH_2C_6H_5$, 100-46-9; $NH_2CH_2C_6H_4$-4-OCH_3, 2393-23-9.

Supplementary Material Available: Tables of atomic coordinates, anisotropic thermal parameters, and torsion angles from X-ray structure determination of **9a** (10 pages). Ordering information is given on any current masthead page.

(25) Since **12a** and **13** proved to be difficult to separate, methods for the preparation of **13** by another route are being explored, one that would not require such a separation in the final step.

Synthesis of Imidazo[4,5-*h*]-1,3-diazabiphenylene (*lin*-Benzocyclobutadienopurine), a Ring System Having a Benzocyclobutadieno Spacer between the Terminal Rings of Purine[1]

Marc d'Alarcao, Venkatesalu Bakthavachalam, and Nelson J. Leonard*

Roger Adams Laboratory, School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

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Two distinct syntheses of the pyrimido[6,5-*i*]imidazo[4,5-*g*]cinnoline ring system have been accomplished. The first of these began with 2-acetamido-4-chloro-5-nitroacetophenone, which was elaborated sequentially by fusion of the imidazole, pyridazine, and pyrimidine rings to provide the tetracyclic system. The second synthesis made use of a Pd-catalyzed cross-coupling reaction of (4,6-dimethoxypyrimidin-5-yl)zinc chloride and 3,4-dinitrobromobenzene, followed by closure of the imidazole and pyridazine rings. The flash vacuum pyrolysis (810–860 °C, 10^{-3} torr) of the unsubstituted tetracyclic compound, pyrimido[4,5-*i*]imidazo[4,5-*g*]cinnoline, resulted in the extrusion of nitrogen to provide imidazo[4,5-*h*]-1,3-diazabiphenylene (*lin*-bcb-purine), the parent molecule to a new class of linearly extended purine analogues.

Recent work in this laboratory has suggested that the dimensional probe *lin*-naphthoadenine (Figure 1), widened by 4.8 Å with respect to adenine, exceeds the space limitations of the active site in calf adenosine deaminase.[2] The related *lin*-naphthohypoxanthine, which is only monooxidized in the buttermilk xanthine oxidase system, exceeds the limits for the usual second stage oxidation (of hypoxanthine).[3] By contrast, *lin*-benzoadenine (Figure 1) and *lin*-benzoadenosine, in which the lateral extension with respect to adenine is 2.4 Å, are readily accepted within the active site of adenosine deaminase. Moreover, *lin*-benzohypoxanthine and *lin*-benzoinosine are oxidized in both terminal rings in the xanthine oxidase system.[4] To define more precisely the spatial restrictions on the activity of these enzymes it remains a desirable goal to prepare a dimensional probe having a lateral extension intermediate between 2.4 Å and 4.8 Å. For this purpose, derivatives of *lin*-benzocyclobutadienopurine (*lin*-bcb-purine) (**2**)[1] such as *lin*-bcb-adenine (Figure 1), in which the benzocyclobutadieno spacer separates the terminal rings by 3.9 Å, were chosen. In this paper, we report two independent syntheses of the pyrimido[6,5-*i*]imidazo[4,5-*g*]cinnoline ring system (e.g., **3**) and the gas-phase thermolysis of the unsubstituted parent to produce *lin*-bcb-purine (**2**).

Results and Discussion

Previous experience has shown[5] that the synthesis of **2** by elaboration of a 1,3-diazabiphenylene such as **1** (Figure 2, path a) may be complicated by facile rearrangement of this ring system to an isoquinoline upon attempted electrophilic or nucleophilic substitution. Accordingly, we decided to follow path b, which utilizes a thermal, gas-phase nitrogen-extrusion reaction of a fused pyridazine precursor **3** in the ultimate step.

Two distinct synthetic strategies leading to the requisite pyridazine precursors were employed, one utilizing a sequential ring-elaboration approach, and the other, a ring-coupling, ring-elaboration approach. The first of these, diagrammed in Scheme I, began with the substituted acetophenone **4**, prepared by an improvement[6] of the lit-

(1) *lin*-bcb-Purine (*lin*-benzocyclobutadienopurine) is the trivial name we are suggesting for the imidazo[4,5-*h*]-1,3-diazabiphenylene ring system having a benzocyclobutadiene spacer between the pyrimidine and imidazole rings of purine (e.g., **2**). This choice is consistent with the names of the other nucleoside base analogues, e.g., *lin*-benzoadenine and *lin*-naphthoadenine, in which the terminal rings are separated by benzo and naphtho spacers, respectively.

(2) Stevenson, T. M.; Leonard, N. J. *J. Org. Chem.* **1984**, *49*, 2158.

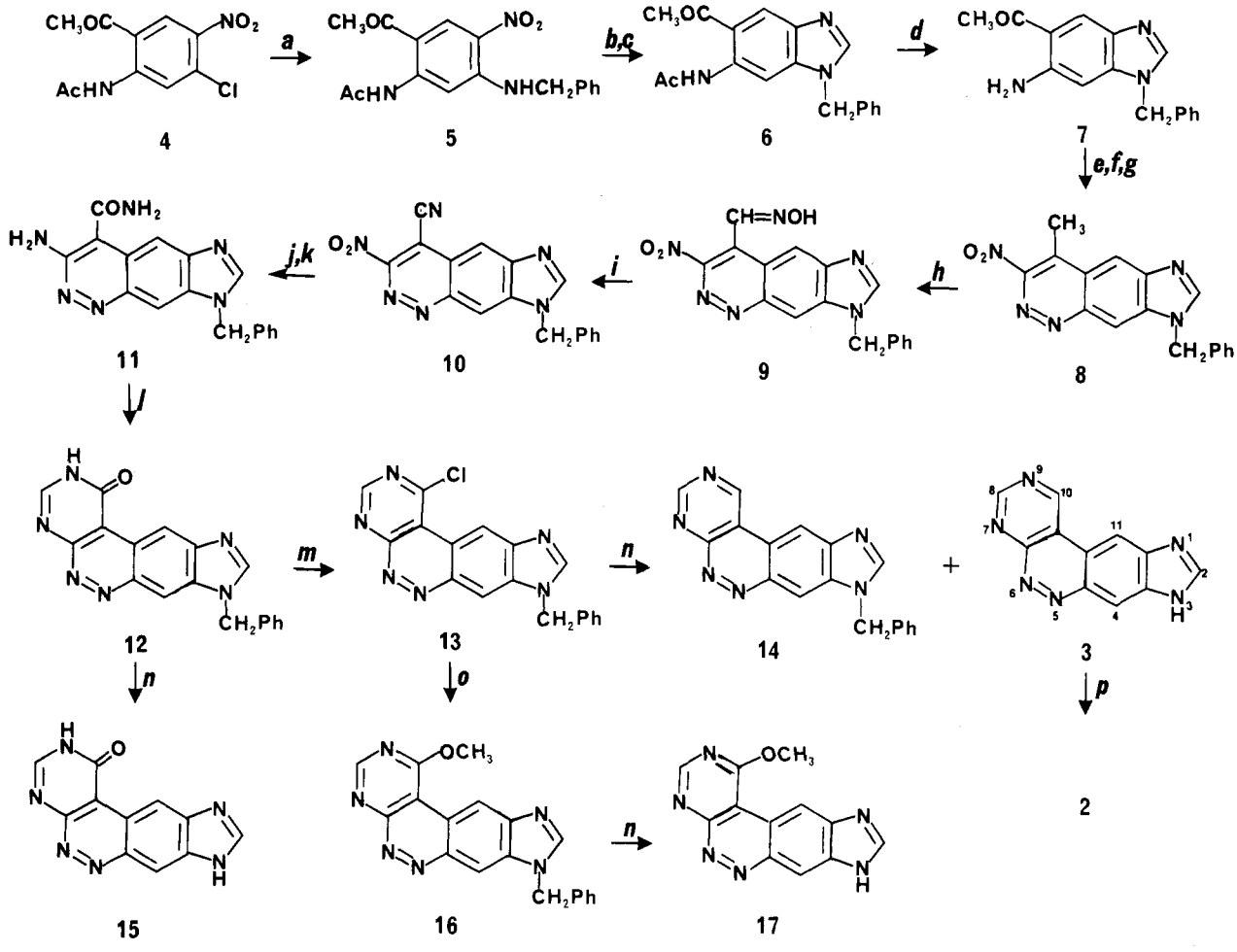
(3) Moder, K. P.; Leonard, N. J. *J. Am. Chem. Soc.* **1982**, *104*, 2613.

(4) Leonard, N. J. *Acc. Chem. Res.* **1982**, *15*, 128 and references cited therein.

(5) (a) d'Alarcao, M.; Leonard, N. J. *J. Am. Chem. Soc.* **1983**, *105*, 5958. (b) Bakthavachalam, V.; d'Alarcao, M.; Leonard, N. J. *J. Org. Chem.* **1984**, *49*, 289.

0022-3263/85/1950-2456$01.50/0

Scheme I[a]



[a] (a) $PhCH_2NH_2$, *n*-BuOH; (b) H_2, RaNi, DMF; (c) $HC(OMe)_3$, HCOOH; (d) HCl, EtOH, H_2O; (e) $NaNO_2$, HCl; (f) CH_3NO_2, KOH; (g) Dabco, H_2O; (h) *i*-$C_5H_{11}ONO$, HCl; (i) Ac_2O; (j) $SnCl_2$, HCl; (k) KOH, EtOH, H_2O; (l) HCOOEt, NaOEt, EtOH; (m) $POCl_3$, $Et_4N^+Cl^-$, $PhNEt_2$, CH_3CN; (n) Na/NH_3; (o) NaOMe, MeOH; (p) 810-860 °C.

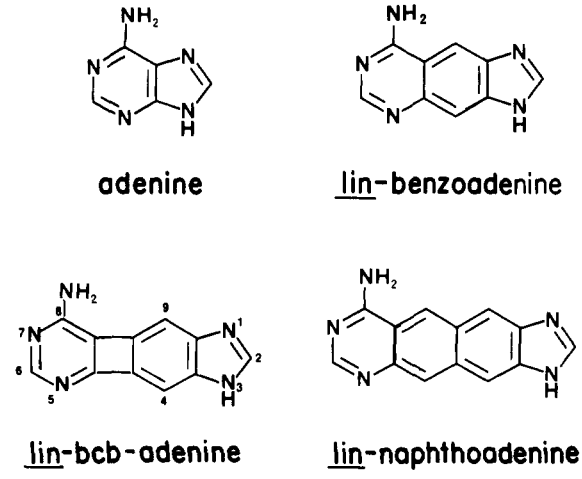


Figure 1. Dimensional probes related to adenine.

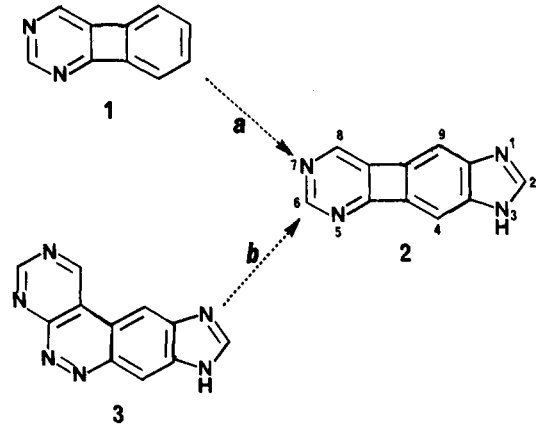


Figure 2. Synthetic approaches to *lin*-bcb-purine.

erature procedure[7] from 4-chloro-2-nitrobenzoic acid in 70% overall yield and continued with the sequence **5** (86% yield) → **6** (80%) → **7** (92%) → **8** (74%) by the general method of Baumgarten and DeBrunner,[8] modified by using diazabicyclooctane (Dabco)[9] → **9** (80%) → **10** (76%) → **11** (86%).

The final pyrimidine ring in **12** was formed by treatment of **11** with ethyl formate in ethanolic NaOEt. Substitution by chlorine under conditions described by Robins and Uznański[10] gave **13** in 68% yield from **11**. Catalytic hy-

(6) Bakthavachalam, V. Ph.D. Thesis, University of Illinois, 1984.
(7) Atkinson, C. M.; Simpson, J. C. E. *J. Chem. Soc.* **1947**, 232.
(8) Baumgarten, H. E.; DeBrunner, M. R. *J. Am. Chem. Soc.* **1954**, *76*, 3489.
(9) The smooth cyclization of nitroformaldehyde *o*-acetylphenylhydrazone to 4-methyl-3-nitrocinnoline was carried out in H_2O in the presence of Dabco, a modification reported by Kanoktanaporn, S.; MacBride, J. A. H. *Tetrahedron Lett.* **1977**, 1817.

drogenation of **13** resulted in unwanted reduction of the cinnoline nucleus, but Na/NH_3 reduction provided the hydrogenolyzed product **3** in 53% yield together with 3% of **14**, still possessing a benzyl group. Reduction of the oxo compound **12** by Na/NH_3 gave clean debenzylation to **15** in 77% yield, and identical reductive treatment of methoxy-substituted **16** (prepared from **13** by the action of NaOMe) gave **17** in 30% yield based on **13**.

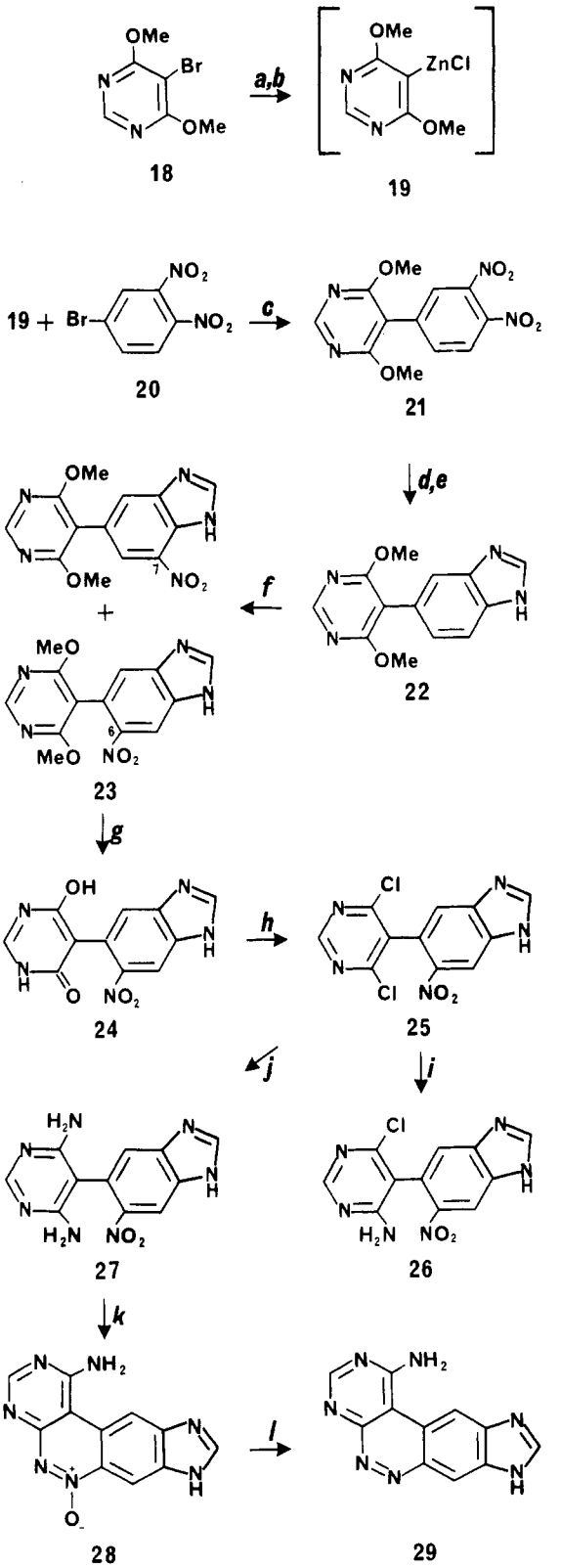
The second approach to the pyrimido[6,5-*i*]imidazo-[4,5-*g*]cinnoline ring system is illustrated in Scheme II. In this route, substituted pyrimidine and benzene rings are coupled and the imidazole and pyridazine rings are formed subsequently. 5-Bromo-4,6-dimethoxypyrimidine (**18**)[11] was lithiated with *n*-butyllithium, then converted to the organozinc derivative **19** with $ZnCl_2$. Intermediate **19** was cross-coupled successfully with 3,4-dinitrobromobenzene (**21**)[12] without interference from the nitro groups[13] in a Pd-catalyzed reaction to provide **21** (51% yield based on **18**). The sequence continued with **21** → **22** (76%) → **23** (49%) (and 16% of the 7-nitro isomer); **23** → **24** → **25** (66%).

Nucleophilic displacement of the chlorines in **25** with NH_3 occurred in a stepwise manner. Since the replacement of the first Cl by NH_2 deactivates the ring, replacement of the second Cl required more forcing conditions than the first. Thus, treatment of **25** with ethanolic NH_3 at 100 °C for 4 h provided the monoamino compound **26** cleanly (88%), whereas reaction at 180 °C for 48 h was used to obtain the diamino compound **27** (67%). The intramolecular base-catalyzed condensation of the amino group with the nitro group to form the final pyridazine ring was accomplished most efficiently in the absence of H_2O and of hydroxide ion. Thus, treatment of **27** with refluxing ethanolic NaOEt provided the *N*-oxide **28** which was readily reduced to **29** with Fe in acetic acid in 88% yield from **27**.

The gas-phase pyrolysis of the fused pyridazine derivatives was performed in a specially constructed apparatus described earlier.[5b] Even when compounds **13**, **16**, and **17** were subjected to carefully selected pyrolysis conditions within the ranges 600–800 °C and $1–5 \times 10^{-3}$ torr, extensive decomposition occurred before sublimation into the pyrolysis zone. An attempt to enhance the volatility of **15** and **17** by trimethylsilylation with bis(trimethylsilyl)-acetamide before pyrolysis did not improve the outcome. Pyrolysis of **29** at 800 °C produced a discernible product, but high-resolution mass spectral analysis revealed that HCN rather than N_2 had been extruded from **29** during the course of the reaction. A bis(trifluoroacetyl) derivative of **29** underwent decomposition before vaporization.

By contrast, the unsubstituted compound **3** was converted successfully, albeit in low yield, to *lin*-bcb-purine (**2**) by gas-phase pyrolysis at 810–860 °C. The temperature range of pyrolysis was crucial. The yellow solid product has resonances in the ^1H NMR spectrum in the region of 7.34–8.40 ppm, considerably upfield from those in **3** (8.91–10.78 ppm), consistent with the induced paramagnetic ring current in the newly formed four-membered ring. The UV spectrum is marked by strong absorbances at 245, 275, 345, and 362 nm, and the mass spectrum indicates that the molecular ion fragments by sequential loss of up to three molecules of HCN. This compound, which is the first example of the tetracyclic ring system, an imidazo-[4,5-*h*]-1,3-diazabiphenylene, at least establishes the preparability of this ring system and encourages us to pursue the synthesis of *lin*-bcb-adenine and other *lin*-bcb-

Scheme II[a]



[a] (a) *n*-BuLi, THF, −78 °C; (b) $ZnCl_2$, −78 °C → 20 °C; (c) $(Ph_3P)_2PdCl_2$-Dibah, THF; (d) Pd/C, H_2; (e) HCOOH; (f) KNO_3, H_2SO_4; (g) Me_3SiCl-NaI, CH_3CN; (h) $POCl_3$, $Et_4N^+Cl^-$, $PhNEt_2$, CH_3CN; (i) NH_3, EtOH, 100 °C; (j) NH_3, EtOH, 180 °C; (k) NaOEt, EtOH; (l) Fe, HOAc, H_2O.

(10) Robins, M. J.; Uznański, B. *Can. J. Chem.* **1981**, *59*, 2601.
(11) Caton, M. P.; Grant, M. S.; Pain, D. L.; Slack, R. *J. Chem. Soc.* **1965**, 5467.
(12) *Beilstein* **1922**, *5*, 266.
(13) The use of organozinc compounds in Pd-catalyzed cross-coupling reactions was introduced by Negishi, E.-I.; King, A. O.; Okukado, N. *J. Org. Chem.* **1977**, *42*, 1821.

purine-based derivatives as potential dimensional probes in biochemical systems.

Experimental Section

Tetrahydrofuran (THF) was purified by distillation from Na benzophenone. Methanol and ethanol used were of anhydrous grade. Dibah, $(Ph_3P)_2PdCl_2$, and 4-chloro-2-nitrobenzoic acid were obtained from Aldrich Chemical Company. $ZnCl_2$ was dried by heating with an open flame in an evacuated vessel until bubbling ceased. Petroleum ether was of bp 30–60 °C. Thin-layer chromatography (TLC) was performed on Brinkmann silica gel (0.25 mm with fluorescent indicator) plates. Column chromatography was performed on silica gel (0.05–0.2 mm) or neutral alumina (activity I) from Brinkmann. Melting points were determined on a Büchi capillary melting point apparatus and are uncorrected. Ultraviolet spectra (UV) were obtained on a Beckman Acta MVI spectrophotometer. Infrared (IR) spectra were recorded on a Perkin-Elmer 1320 spectrophotometer. ^1H nuclear magnetic resonance (NMR) spectra were recorded on a Varian EM-390 (90 MHz), a Varian XL-200 (200 MHz), or a Nicolet NTC-360 (360 MHz) spectrometer by using tetramethylsilane as an internal standard. Low-resolution electron-impact mass spectra (MS) were obtained on a Varian MAT CH-5 instrument while high-resolution electron-impact mass spectra (HRMS) were obtained on a Varian MAT-731 spectrometer coupled with a 620i computer and a STATOS recorder by J. Carter Cook and his staff. Microanalyses were performed by Josef Nemeth and his staff at the University of Illinois.

2-Acetamido-4-(benzylamino)-5-nitroacetophenone (5). A mixture of 2-acetamido-4-chloro-5-nitroacetophenone (4) (105 g, 0.41 mol), benzylamine (98 mL, 0.91 mol), and *n*-BuOH (1500 mL) was heated at reflux for 4 h. The reaction mixture was transferred to a beaker and cooled. The precipitated yellow solid was filtered, washed with *n*-BuOH (100 mL) and C_2H_5OH (200 mL), and dried. An analytically pure sample was obtained by recrystallization from *n*-BuOH: 115 g (86%); mp 130–132 °C; ^1H NMR (90 MHz, $CDCl_3$) δ 2.26 (s, 3, CH_3), 2.63 (s, 3, CH_3), 4.50–4.56 (d, 2, benzylic H) (becomes a singlet on D_2O shake), 7.4 (s, 5, C_6H_5), 8.40 (s, 1, ArH), 8.76 (br s, 1, NH), 8.80 (s, 1, ArH); MS (10 eV), *m/e* (relative intensity) 327 (M^+, 100), 267 (74), 105 (59), 91 (15). Anal. Calcd for $C_{17}H_{17}N_3O_4$: C, 62.37; H, 5.24; N, 12.84. Found: C, 62.27; H, 5.20; N, 12.70.

6-Acetamido-5-acetyl-1-benzylbenzimidazole (6). A mixture of the nitro compound **5** (12 g, 37 mmol), DMF (110 mL), and concentrated NH_4OH (5 mL) was hydrogenated over Raney Ni (2 g) at 3 atm and 25 °C for 2 h. The catalyst was filtered and washed with DMF (25 mL). The filtrate was evaporated under reduced pressure, and the dark green residue was taken up in trimethyl orthoformate (100 mL) and HCOOH (1 mL). The mixture was heated at reflux for 3 h and then concentrated to half the volume. Addition of water (400 mL) precipitated a colorless solid, which was filtered, washed with water, and dried. Recrystallization from aqueous C_2H_5OH twice gave an analytically pure sample of **6** as colorless needles: 9.0 g (80%); mp 165–167 °C; ^1H NMR (90 MHz, $CDCl_3$) δ 2.28 (s, 3, CH_3), 2.79 (s, 3, CH_3), 5.31 (s, 2, benzylic H), 7.20–7.36 (m, 5, C_6H_5), 7.96 (s, 1, ArH), 8.40 (s, 1, ArH), 8.90 (s, 1, ArH); MS (10 eV), *m/e* (relative intensity) 307 (M^+, 100), 265 (71), 250 (14), 91 (15). Anal. Calcd for $C_{18}H_{17}N_3O_2$: C, 70.34; H, 5.58; N, 13.67. Found: C, 70.29; H, 5.46; N, 13.73.

5-Acetyl-6-amino-1-benzylbenzimidazole (7). A stirred solution of **6** (27 g, 88 mmol) in C_2H_5OH (225 mL) and concentrated HCl (225 mL) was heated at reflux for 1.5 h and cooled. The reaction mixture was diluted with water (750 mL) and neutralized with NaOH. The precipitated solid was separated by filtration and recrystallized from aqueous C_2H_5OH to give fine greenish yellow needles of **7**: 21.5 g (92%); mp 195–196 °C; ^1H NMR (90 MHz, $CDCl_3$) δ 2.68 (s, 3, CH_3), 5.20 (s, 2, benzylic H), 6.34 (s, 1, ArH), 7.10–7.31 (m, 5, C_6H_5), 7.76 (s, 1, ArH), 8.20 (s, 1, ArH); MS (10 eV), *m/e* (relative intensity) 265 (100), 250 (32), 174 (9), 91 (25). Anal. Calcd for $C_{16}H_{15}N_3O$: C, 72.43;, H, 5.70; N, 15.84. Found: C, 72.58; H, 5.68; N, 16.15.

3-Benzyl-8-methyl-7-nitroimidazo[4,5-*g*]cinnoline (8). A slurry of amine **7** (14 g, 53 mmol) and $NaNO_2$ (3.7 g, 53 mmol) in water (120 mL) was stirred at 0 °C. To this, concentrated HCl (8.83 mL, 106 mmol) was added in drops to give a clear diazonium salt solution, which was immediately added to a solution of CH_3NO_2 (3.2 g, 53 mmol) and KOH (3.5 g, 53 mmol) in ice–water (600 mL). An orange precipitate appeared immediately, and the mixture was stirred at 25 °C for 30 min. Dabco (11.9 g, 106 mmol) was added to this, and the stirring was continued at 100 °C for an additional 4 h. The cooled reaction mixture was filtered and the brown solid obtained was washed with water and dried. Recrystallization from acetone (decolorizing carbon) gave light brown flakes of **8**: 12.5 g (74%); mp 256–257 °C, ^1H NMR (90 MHz, CD_3COOD) 5.93 (s, 2, benzylic H), 7.56 (s, 5, C_6H_5), 9.23 (s, 1, ArH), 9.37 (s, 1, ArH), 9.70 (s, 1, ArH); MS (10 eV), *m/e* (relative intensity) 319 (28), 273 (3), 91 (100). Anal. Calcd for $C_{17}H_{13}N_5O_2$: C, 63.94; H, 4.10; N, 21.93. Found: C, 63.99; H, 4.05; N, 22.11.

3-Benzyl-7-nitroimidazo[4,5-*g*]cinnoline-8-aldehyde Oxime (9). To a stirred suspension of compound **8** (12.5 g, 39 mmol) in ethanolic HCl (4.3 g of anhydrous HCl in 40 mL of absolute EtOH) at 0 °C was added dropwise a solution of isoamyl nitrite (4.7 g, 42 mmol) in EtOH (5 mL). The resulting mixture was stirred at 0 °C for 30 min and at 25 °C for 16 h. The precipitated product was filtered, washed with EtOH, and dried. The solid was extracted repeatedly with hot acetone (5 × 750 mL), and the acetone extract was concentrated to give yellow needles of oxime **9**: (10.9 g, 80%). An analytically pure sample was prepared by recrystallization from CH_3OH: mp 212–213 °C dec; ^1H NMR (90 MHz, $(CD_3)_2SO$) δ 5.78 (s, 2, benzylic H), 7.34–7.49 (m, 5, C_6H_5), 8.80 (s, 1, CH=N), 8.84 (s, 1, ArH), 8.90 (s, 1, ArH), 9.00 (s, 1, ArH), 12.60 (s, 1, OH); MS (10 eV), *m/e* (relative intensity) 330 (32), 91 (100). Anal. Calcd for $C_{17}H_{12}N_6O_3$: C, 58.62; H, 3.47; N, 24.13. Found: C, 58.41; H, 3.52; N, 23.98.

3-Benzyl-8-cyano-7-nitroimidazo[4,5-*g*]cinnoline (10). A solution of oxime **9** (12.5 g, 36 mmol) in acetic anhydride (120 mL) was heated at 140 °C for 1 h. The reaction mixture was cooled to 0 °C to precipitate a yellow solid which was separated by filtration. Recrystallization from EtOH provided bright yellow needles of **10**: 9 g (76%); mp 243–245 °C dec; ^1H NMR (200 MHz, $(CD_3)_2SO$) δ 5.83 (s, 2, benzylic H), 7.31–7.50 (m, 5, C_6H_5), 8.62 (s, 1, ArH), 9.08 (s, 1, ArH), 9.15 (s, 1, ArH); MS (10 eV), *m/e* (relative intensity) 330 (46), 91 (100). Anal. Calcd for $C_{17}H_{10}N_6O_2$: C, 61.82; H, 3.05; N, 25.44. Found: C, 61.90; H, 3.11; N, 25.08.

7-Amino-3-benzylimidazo[4,5-*g*]cinnoline-8-carboxamide (11). To a stirred suspension of **10** (9 g, 27 mmol) in H_2O (150 mL) and 12 N HCl (60 mL) at 0 °C was added dropwise a solution of $SnCl_2 \cdot 2H_2O$ (18.2 g, 81 mmol) in 12 N HCl (35 mL) and H_2O (15 mL). The resulting mixture was stirred at 0 °C for 2 h and at 25 °C for 16 h, then diluted with water (150 mL), and basified (to pH 12) with 35% KOH. The reddish brown precipitate formed was filtered, washed with water, and dried. The solid was treated with KOH (20 g) in H_2O–EtOH (500 mL each) at reflux for 2 h. The reaction mixture was cooled, and the yellow solid that precipitated was separated by filtration, washed with H_2O and EtOH, and dried: 7.5 g (86%); mp >300 °C (CH_3OH); ^1H NMR (200 MHz, $(CD_3)_2SO$) δ 5.63 (s, 2, benzylic H), 6.2 (s, 2, amine), 7.27–7.52 (m, 5, C_6H_5), 7.88–8.13 (br s, 2, amide NH_2), 8.01 (s, 1, ArH), 8.34 (s, 1, ArH), 8.79 (s, 1, ArH); MS (10 eV), *m/e* (relative intensity) 318 (50), 290 (7), 273 (10), 91 (100). Anal. Calcd for $C_{17}H_{14}N_6O$: C, 64.14; H, 4.43; N, 26.40. Found: C, 63.86; H, 4.27; N, 26.20.

3-Benzylpyrimido[6,5-*i*]imidazo[4,5-*g*]-9*H*-cinnolin-10-one (12). Compound **11** (5.5 g, 17 mmol) and HCOOEt (6.3 g, 85 mmol) were added to a solution of Na (3.9 g, 170 mmol) in EtOH (600 mL), and the mixture was heated at reflux for 3 h. The resulting mixture was diluted with H_2O (200 mL) to give a clear solution and was acidified with 6 N HCl to pH 3. The yellow precipitate obtained on cooling was filtered and washed with small amounts of H_2O and EtOH and dried: 4.8 g (85%); mp >300 °C (DMF–H_2O); ^1H NMR (200 MHz, $(CD_3)_2SO$) δ 5.78 (s, 2, benzylic H), 7.35–7.49 (m, 5, C_6H_5), 8.48 (s, 1, ArH), 8.8 (s, 1, ArH), 8.98 (s, 1, ArH), 9.89 (s, 1, ArH); MS (10 eV), *m/e* (relative intensity) 328 (100), 91 (56). Anal. Calcd for $C_{18}H_{12}N_6O$: C, 65.84; H, 3.68; N, 25.60. Found: C, 65.98; H, 3.49; N, 25.33.

3-Benzyl-10-chloropyrimido[6,5-*i*]imidazo[4,5-*g*]cinnoline (13). A mixture of compound **12** (3.0 g, 9.2 mmol), $Et_4N^+Cl^-$ (1.68 g, 9.2 mmol), $PhNEt_2$ (1.4 g, 9.2 mmol), CH_3CN (distilled from CaH_2) (25 mL), and freshly distilled $POCl_3$ (40 mL) was heated at 100 °C for 4 h and was then concentrated to 20 mL by dis-

tillation under reduced pressure. The residue was poured slowly into aqueous $NaHCO_3$ (75 g in 800 mL) at 5 °C with stirring and the resultant mixture was left at room temperature for 3 h. The precipitated chloro compound **13** was filtered, washed with H_2O, and dried. Recrystallization from benzene provided light green needles: 2.6 g (80%); mp 258–260 °C dec; ^1H NMR (200 MHz, $(CD_3)_2SO$) δ 5.80 (s, 2, benzylic H), 7.31–7.50 (m, 5, C_6H_5), 8.48 (s, 1, ArH), 8.86 (s, 1, ArH), 9.06 (s, 1, ArH), 9.90 (s, 1, ArH); MS (10 eV), *m/e* (relative intensity) 348 (M^+ + 2, 31), 346 (M^+, 100), 91 (79). Anal. Calcd for $C_{18}H_{11}ClN_6$: C, 62.34; H, 3.20; Cl, 10.22; N, 24.23. Found: C, 62.47; H, 3.14; Cl, 10.44; N, 24.23.

Reduction of 3-Benzyl-10-chloropyrimido[6,5-*i*]imidazo-[4,5-*g*]cinnoline (13) with Na in Liquid NH_3. A mixture of compound **13** (400 mg, 1.2 mmol) and liquid NH_3 (80 mL) was stirred at −75 °C for 15 min. To this was added Na (160 mg, 7 mmol) and the resulting deep blue mixture was stirred at −75 °C for 2.5 h. NH_4Cl crystals (750 mg) were added to the reaction mixture, and the stirring was continued for an additional 15 min. Ammonia was allowed to evaporate and the residue was extracted with warm $CHCl_3$/MeOH (1:1, 300 mL). The extract was evaporated onto a small amount of silica gel and dry-loaded onto a column of silica gel packed in $CHCl_3$–CH_3OH (8.5:1.5). Elution with the same solvent gave 3-benzylpyrimido[6,5-*i*]imidazo[4,5-*g*]cinnoline (**14**) (R_f 0.4) and pyrimido[6,5-*i*]imidazo[4,5-*g*]cinnoline (**3**) (R_f 0.2).

3-Benzylpyrimido[4,5-*i*]imidazo[4,5-*g*]cinnoline (14). Yield: 10 mg (3%); mp 286–288 °C dec; ^1H NMR (360 MHz, $CDCl_3$) δ 5.65 (s, 2, benzylic H), 7.34–7.43 (m, 5, C_6H_5), 8.49 (s, 1, ArH), 8.87 (s, 1, ArH), 9.12 (s, 1, ArH), 9.75 (s, 1, ArH), 10.37 (s, 1, ArH); MS (10 eV), *m/e* (relative intensity) 312 (M^+, 58), 257 (6), 91 (100); HREIMS exact mass calcd for $C_{18}H_{12}N_6$ (M^+) 312.1123, obsd 312.1124.

Pyrimido[4,5-*i*]imidazo[4,5-*g*]cinnoline (3). Yield: 130 mg (53%); mp >300 °C; ^1H NMR (360 MHz, $CDCl_3$) δ 8.91 (s, 1, ArH), 9.08 (s, 1, ArH), 9.33 (s, 1, ArH), 9.70 (s, 1, ArH), 10.78 (s, 1, ArH); MS (10 eV), *m/e* (relative intensity) 222 (M^+, 100), 194 (M^+ − N_2, 1), 167 (72), 140 (17), 113 (7); HRMS calcd for $C_{11}H_6N_6$ *m/e* 222.0653, found *m/e* 222.0656.

Pyrimido[6,5-*i*]imidazo[4,5-*g*]-9*H*-cinnolin-10-one (15). Compound **12** (1.2 g, 3.6 mmol) was placed in a three-necked flask fitted with a dry ice condenser, NH_3 inlet, and N_2 line. Ammonia (75 mL) was condensed, and the mixture was stirred at −75 °C for 30 min. To this was added Na (340 mg, 14.6 mmol) in small pieces. The resulting dark blue mixture was stirred at −75 °C for 2 h. Ammonium chloride was added until the mixture turned yellow, and then NH_3 was allowed to evaporate. The residue was transferred onto a filter with CH_2Cl_2, washed with water (20 mL), and dried. Recrystallization from DMF (200 mL) gave **15** as a yellow solid: 670 mg (77%); mp >300 °C; ^1H NMR (200 MHz, $(CD_3)_2SO$) δ 8.54 (s, 1, ArH), 8.84 (s, 1, ArH), 8.97 (s, 1, ArH), 9.81 (s, 1, ArH); MS (10 eV), *m/e* (relative intensity) 238 (M^+, 84), 183 (23), 155 (55), 128 (60), 101 (20), 28 (100). Anal. Calcd for $C_{11}H_6N_6O$: C, 55.36; H, 2.39; N, 35.28. Found: C, 55.10;, H, 2.56; N, 34.95.

3-Benzyl-10-methoxypyrimido[6,5-*i*]imidazo[4,5-*g*]-cinnoline (16). The chloro compound **13** (350 mg, 1 mmol) was added to a solution of Na (460 mg, 20 mmol) in CH_3OH (70 mL), and the mixture was stirred under dry N_2 at 25 °C for 3 h and at reflux for 15 min. The reaction mixture was diluted with H_2O (100 mL) and acidified with 3 N HCl. The precipitated solid was filtered, washed with H_2O, and dried. Recrystallization from hexane–$CHCl_3$ gave green fibrous crystals of **16**: 260 mg (75%); mp 228–230 °C dec; ^1H NMR (200 MHz, $CDCl_3$) δ 4.43 (s, 3, OCH_3), 5.63 (s, 2, benzylic H), 7.35–7.40 (m, 5, C_6H_5), 8.45 (s, 1, ArH), 8.81 (s, 1, ArH), 9.19 (s, 1, ArH), 9.61 (s, 1, ArH); MS (10 eV), *m/e* (relative intensity) 342 (M^+, 100), 328 (9), 91 (13). Anal. Calcd for $C_{19}H_{14}N_6O$: C, 66.66; H, 4.12; N, 24.55. Found: C, 66.96; H, 3.91; N, 24.35.

10-Methoxypyrimido[6,5-*i*]imidazo[4,5-*g*]cinnoline (17). A mixture of **16** (100 mg, 0.3 mmol) and liquid NH_3 (20 mL) was stirred at −75 °C for 30 min. Sodium (30 mg, 1.3 mmol) was added, and the mixture was stirred at −75 °C for 2 h. NH_4Cl crystals were added until the reaction mixture turned orange and then NH_3 was allowed to evaporate. The residue was recrystallized from EtOH to give **17** as a yellow solid: 30 mg (40%); mp >260 °C; ^1H NMR (200 MHz, $(CD_3)_2SO$) δ 4.45 (s, 3, OCH_3), 8.48 (s, 1, ArH), 8.88 (s, 1, ArH), 9.05 (s, 1, ArH), 9.75 (s, 1, ArH). This compound and the related **10-methoxy-3-(trimethylsilyl)pyrimido[6,5-*i*]imidazo[4,5-*g*]cinnoline**, made by the action of bis(trimethylsilyl)acetamide on **17** at reflux in anhydrous CH_3CN under an atmosphere of dry N_2, were characterized by NMR alone before attempted pyrolysis. 3-(Trimethylsilyl)-**17**: mp 228–230 °C dec; ^1H NMR (220 MHz) ($CDCl_3$) δ 0.65 (s, 9, $Si(CH_3)_3$), 4.38 (s, 3, OCH_3), 8.42 (s, 1, ArH), 8.75 (s, 1, ArH), 9.10 (s, 1, ArH), 9.65 (s, 1, ArH).

4,6-Dimethoxy-5-(3,4-dinitrophenyl)pyrimidine (21). 5-Bromo-4,6-dimethoxypyrimidine (**18**)[11] (10.0 g, 45.9 mmol) in 100 mL of THF was cooled to −63 °C (dry ice–$CHCl_3$ bath) under dry N_2 and 29.6 mL (47.0 mmol) of 1.59 M *n*-butyllithium in hexane was added. This was stirred at −63 °C for 20 min, then a solution of dry $ZnCl_2$ (6.82 g, 50.0 mmol) in 50 mL of was added and the reaction mixture containing **19** was allowed to warm to room temperature (30 min). In a separate vessel a solution of catalyst was prepared under N_2 by addition of 1.4 mL (1.4 mmol) of 1.0 M diisobutylaluminum hydride in hexane to a suspension of $(Ph_3P)_2PdCl_2$ (0.50 g, 0.70 mmol) in 90 mL of THF. To this catalyst solution was added a solution of 3,4-dinitrobromobenzene (**20**)[12] (11.0 g, 44.7 mmol) in 40 mL of THF followed by the pyrimidine solution described above. The resulting dark reaction was stirred at room temperature for 42 h, and then 1 M H_2SO_4 (100 mL) was added. The layers were separated, the aqueous portion was extracted with ether (2 × 75 mL), and the combined organic extracts were dried (Na_2SO_4) and evaporated to dryness. Recrystallization of the residue from EtOH (450 mL) afforded 7.0 g (51%) of pale yellow product: mp 208–209 °C dec; ^1H NMR (90 MHz, $(CD_3)_2SO$) δ 3.94 (s, 6, OCH_3), 8.04 (dd, 1, H-6′, ^3J = 8 Hz, ^4J = 2 Hz), 8.25 (d, 1, H-1′, ^4J = 2 Hz), 8.28 (d, 1, H-5′, ^3J = 8 Hz), 8.55 (s, 1, H-2); MS (10 eV), *m/e* (relative intensity) 306 (100, M^+). Anal. Calcd for $C_{12}H_{10}N_4O_6$: C, 47.07; H, 3.29; N, 18.29. Found: C, 47.05; H, 3.25; N, 17.96.

5-(4,6-Dimethoxypyrimidin-5-yl)benzimidazole (22). A suspension of **21** (3.00 g, 9.80 mmol) and 10% Pd on carbon (0.20 g) in 200 mL of HCOOH was shaken in a Parr hydrogenation apparatus under 3 atm of H_2 for 3 h. This was filtered through Celite to remove the catalyst, and the filtrate was warmed on a steam bath under N_2 for 5 h. The resulting yellow solution was allowed to cool, poured into H_2O (300 mL), and adjusted to pH 8 with concentrated NH_4OH. After standing overnight the product was collected by filtration: 1.90 g (76%); mp 260–261 °C. A portion of this was recrystallized from CCl_4–acetone to give an analytical sample: mp 261–262 °C; ^1H NMR (90 MHz, $(CD_3)_2SO$) δ 3.92 (s, 6, OCH_3), 7.11 (d, 1, H-6 or H-7, $J_{6,7}$ = 8 Hz), 7.47–7.66 (superimposed d and s, 2, H-6 or H-7 and H-4), 8.24 (s, 1, H-2), 8.50 (s, 1, H-2′); MS (10 eV), *m/e* (relative intensity) 256 (100, M^+). Anal. Calcd for $C_{13}H_{12}N_4O_2$: C, 60.93; H, 4.72; N, 21.86. Found: C, 60.68; H, 4.80; N, 21.78.

5-(4,6-Dimethoxypyrimidin-5-yl)-6-nitrobenzimidazole (23). To a flask containing concentrated H_2SO_4 (10 mL) which was chilled in an ice bath was added KNO_3 (606 mg, 6.00 mmol) followed by **22** (1.50 g, 5.86 mmol). The reaction mixture was allowed to warm to room temperature, stoppered, and stirred for 4 h. The resulting red solution was poured into H_2O (50 mL) and made slightly basic with concentrated NH_4OH. After cooling overnight the solid was collected by filtration, dissolved in acetone, and evaporated onto silica gel (ca. 2 g). This powder was dry-loaded onto a 75-g silica gel column and eluted with 7% EtOH–$CHCl_3$ to obtain the 7-nitro isomer (280 mg, 16%, R_f 0.3) followed by the desired 6-nitro isomer **23** as a monoethanol complex (1.0 g, 49%, R_f 0.2): mp 236–236.5 °C (transitory liquefaction at 131–136 °C upon loss of ethanol); ^1H NMR (90 MHz, $(CD_3)_2SO$) δ 1.11 (t, 3, CH_3CH_2OH), 3.55 (q, 2, CH_3CH_2OH), 3.87 (s, 6, OCH_3), 7.69 (s, 1, H-4), 8.40–8.47 (m, 3, H-2, H-7, H-2′); MS (10 eV), *m/e* (relative intensity) 301 (100, $M^+ - C_2H_6O$), 255 (14, $M^+ - NO_2 - C_2H_6O$). Anal. Calcd for $C_{13}H_{11}N_5O_4 \cdot C_2H_6O$: C, 51.87; H, 4.93; N, 20.16. Found: C, 51.80; H, 5.03; N, 20.30.

The monoethanol complex was suitable for use in the subsequent reaction. Warming this material in an oven at 160 °C effected complete loss of EtOH. Anal. Calcd for $C_{13}H_{11}N_5O_4$: C, 51.83; H, 3.68; N, 23.25. Found: C, 51.65; H, 3.68; N, 23.20.

5-(4,6-Dihydroxypyrimidin-5-yl)-6-nitrobenzimidazole (24). A solution of **23** (as its monoethanol complex, 5.0 g, 14.4 mmol) and anhydrous NaI (11.5 g, 76.7 mmol) in dry CH_3CN (375 mL)

was prepared under N_2, and Me_3SiCl (15.0 mL, 118 mmol) was added via syringe. The reaction was warmed at reflux for 6 h, allowed to cool to room temperature, and evaporated to dryness. The dark residue was suspended in H_2O (150 mL) and a saturated aqueous solution of $Na_2S_2O_3$ was added dropwise, with vigorous stirring, until all the I_2 had been consumed (as judged by a color change from brown to pale yellow). The resulting suspension was carefully adjusted to pH 4.5 with concentrated NH_4OH and the solid product was collected by filtration. This was dried in vacuo at 111 °C for 20 h to give 3.75 g (95%) of hygroscopic yellow solid: mp >250 °C; ^1H NMR (90 MHz, $(CD_3)_2SO$) δ 7.60 (s, 1), 8.11 (s, 1), 8.21 (s, 1), 8.45 (s, 1). Anal. Calcd for $C_{11}H_{17}N_5O_4$: C, 48.36; H, 2.58; N, 25.63. Found: C, 48.16; H, 2.68; N, 25.38.

5-(4,6-Dichloropyrimidin-5-yl)-6-nitrobenzimidazole (25). To a solution of **24** (1.00 g, 3.66 mmol) and Et_4NCl (2.66 g, 16.1 mmol) in CH_3CN was added *N,N*-diethylaniline (1.33 mL, 8.29 mmol) and $POCl_3$ (11 mL). The solution was stirred at reflux under N_2 for 3 h, allowed to cool, and poured into 130 mL of ice–H_2O. The aqueous solution was adjusted to pH 8 with concentrated NH_4OH (ice cooling) and extracted with EtOAc (3 × 50 mL). The extracts were dried ($MgSO_4$), evaporated to 15 mL, and 250 mL of petroleum ether was added. The white precipitate which formed was redissolved in 15 mL of EtOAc and reprecipitated with 250 mL of petroleum ether twice more. The solid was air dried and crystallized from 10% EtOH–H_2O (165 mL) to give in two crops a greyish-white solid: 770 mg (68%); mp 205–207 °C; ^1H NMR (360 MHz, $(CD_3)_2SO$) δ 7.93 (br s, 1, NH), 8.69 (br s, 2), 9.02 (s, 1); MS (10 eV), *m/e* (relative intensity) 313 (2), 311 (10), 276 (36), 274 (100). Anal. Calcd for $C_{11}H_5Cl_2N_5O_2$: C, 42.61; H, 1.63; N, 22.58; Cl, 22.87. Found: C, 42.63; H, 1.72; N, 22.36; Cl, 22.90.

5-(4-Amino-6-chloropyrimidin-5-yl)-6-nitrobenzimidazole (26). A solution of **25** (400 mg, 1.29 mmol) in 50 mL of EtOH was saturated with anhydrous NH_3 at 0 °C. This was sealed in a steel pressure vessel and warmed at 100 °C for 3.5 h. After cooling to room temperature, the vessel was opened and the contents were evaporated onto ~2 g silica gel. This was dry-loaded onto a 50-g silica gel column packed in 20% EtOH–$CHCl_3$. Elution with the same solvent and collection of the major product gave 330 mg of crude **26** (88%). Recrystallization from 50% EtOH–H_2O afforded a yellow crystalline hydrate: mp 270 °C; ^1H NMR ($(CD_3)_2SO$) δ 6.85 (br s, 2, NH_2), 7.57 (s, 1), 8.20 (s, 1), 8.50 (s, 1), 8.53 (s, 1); MS (10 eV), *m/e* (relative intensity) 290, 292 (36, 12, M^+), 273, 275 (100, 358, $M^+ - NH_3$). Anal. Calcd for $C_{11}H_7ClN_6O_2 \cdot H_2O$: C, 42.80; H, 2.94; N, 27.22; Cl, 11.49 Found: C, 42.47; H, 2.91; N, 27.01; Cl, 11.33.

5-(4,6-Diaminopyrimidin-5-yl)-6-nitrobenzimidazole (27). A solution of **25** (600 mg, 1.94 mmol) in 100 mL of EtOH was saturated with anhydrous NH_3 at 0 °C and the resulting solution was sealed in a steel pressure vessel and warmed at 180 °C. After 48 h the bomb was allowed to cool to room temperature and the contents were evaporated onto a small amount of neutral alumina. This solid was dry-loaded onto a column of neutral alumina packed in 5% H_2O–acetone. Elution with the same solvent and collection of the major product provided an orange-yellow solid suitable for use in the next reaction: 350 mg (67%). An analytical sample was obtained by recrystallization from H_2O: mp >265 °C; ^1H NMR (90 MHz, $(CD_3)_2SO$) δ 4.46 (br s, 4, NH_2's), 7.40 (s, 1), 7.82 (s, 1), 8.39 (s, 1), 8.48 (s, 1); MS (10 eV), *m/e* (relative intensity) 271 (12), 255 (19), 254 (100). Anal. Calcd for $C_{11}H_9N_7O_2$: C, 48.71; H, 3.34; N, 36.15. Found: C, 48.52; H, 3.31; N, 35.89.

10-Aminopyrimido[6,5-*i*]imidazo[4,5-*g*]cinnoline 5-Oxide (28). To a solution of Na (2.6 g, 113 mmol) in 70 mL of dry EtOH was added **27** (346 mg, 1.28 mmol) and the solution was warmed at reflux for 44 h and protected from moisture by a $CaSO_4$ drying tube. The resulting deep red solution was evaporated to dryness, the residue was dissolved in 75 mL of H_2O, and this was adjusted to pH 7 with 3 N HCl. The yellow precipitate was collected by filtration, washed with H_2O and a small amount of MeOH, and dried to give crude product suitable for use in the next reaction: 333 mg (100%); mp >260 °C; ^1H NMR (200 MHz, $(CD_3)_2SO$ + D_2O) δ 8.62 (s, 1), 8.80 (s, 1), 8.88 (s, 1), 8.93 (s, 1); MS (70 eV), *m/e* (relative intensity) 253 (62), 237 (100), 182 (74), 155 (53), 154 (39), 128 (81), 44 (60); HRMS calcd for $C_{11}H_7N_7O$ *m/e* 253.07121, found *m/e* 253.07115.

10-Aminopyrimido[6,5-*i*]imidazo[4,5-*g*]cinnoline (29). A suspension of **28** (100 mg, 0.40 mmol) in 50 mL of 50% aqueous HOAc was purged of oxygen by vigorous bubbling of Ar beneath the surface of the liquid for 30 min. To this was added Fe powder (200 mg, 3.58 mmol) and the reaction was stirred magnetically for 2 h under Ar. The excess Fe was removed by withdrawal of the magnetic stir bar and the remaining solution was evaporated to dryness. The residue was redissolved in H_2O and allowed to stand at room temperature to afford the solid product as a precipitate: 82 mg (88%); mp >260 °C; ^1H NMR (200 MHz, $(CD_3)_2SO$ + D_2O + $(NH_4)_2SO_4$) δ 8.70 (s, 1), 8.77 (s, 1), 8.90 (br s, 1), 8.97 (s, 1); MS (10 eV), *m/e* (relative intensity) 237 (100), 182 (43); HRMS calcd for $C_{11}H_7N_7$ *m/e* 237.07629, found *m/e* 237.07674.

***lin*-bcb-Purine, Imidazo[4,5-*h*]-1,3-diazabiphenylene (2).** Compound **3** (40 mg, 0.18 mmol) was pyrolyzed[5b] at 810–860 °C and 10^{-3} torr. The pyrolysate was extracted thoroughly with acetone (30 mL), and the filtered extracts were evaporated onto a small amount of silica gel. This was dry-loaded onto a silica gel column packed in 10% EtOH–$CHCl_3$. Elution with the same solvent and collection of the nonfluorescent product (R_f 0.39, TLC, 20% EtOH–$CHCl_3$), eluting just after a minor component exhibiting bright blue fluorescence, gave **2** as a yellow solid: 4 mg (11%); ^1H NMR (200 MHz, $(CD_3)_2SO$) δ 7.34 (s, 1), 7.45 (s, 1), 7.65 (s, 1), 8.14 (s, 1), 8.40 (s, 1); UV (EtOH, relative absorbance) λ_{max} 245 (1.00), 275 (0.96), 345 sh (0.32), 362 nm (0.41); IR (KBr) 800, 860, 920, 1020, 1085, 1200, 1255, 1280, 1375, 1445, 1560, 1655 cm^{-1}; MS (10 eV), *m/e* (relative intensity) 194 (51, M^+), 167 (100, $M^+ - HCN$), 140 (21, $M^+ - 2HCN$), 113 (7, $M^+ - 3HCN$); HRMS calcd for $C_{11}H_6N_4$ *m/e* 194.0593, found *m/e* 194.0597.

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