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DISSYMMETRY OF CERTAIN SUBSTITUTED DIPYRIDOTETRAAZAPENTALENES†

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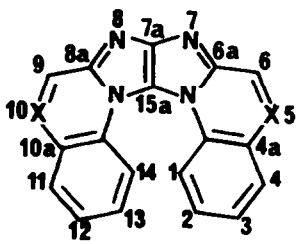
Abstract: In a two-step synthesis from starting amines, a series of compounds has been prepared in which steric crowding (**1b,c,d,f**) was introduced into the "bay region" of pyrido[1",2":1',2']imidazo[4',5':4,5]imidazo[1,2-a]pyridine (**1a**). This forces the tetracyclic ring system into non-planarity. Two hexaheterohelicenes **2a** and **b** were prepared that incorporate the 1,3,4,6-tetraazapentalene ring system and provide molecular crowding in the "bay region" due to the terminal rings, which similarly distort the hexacyclic ring system from planarity. Single crystal X-ray structure determinations revealed that the compounds (**1b,c,d,f,2a** and **b**) exist as enantiomeric pairs in the crystalline state.

The availability of a new heterocyclic ring system such as dipyrido-[1,2-a:2',1'-f]-1,3,4,6-tetraazapentalene (**1a**),[1-4] which has a "bay region", invites substitution that, because of steric crowding, could produce dissymmetry. For example, 1,10-dialkyl substitution might be expected to cause increasing distortion from the planarity[5] of the parent ring system (**1a**) through the series 1,10-dimethyl- (**1b**), 1,10-diethyl- (**1c**), 1,10-diisopropyl- (**1d**), and 1,10-di-t-butyldipyrido[1,2-a:2',1'-f]-1,3,4,6-tetraazapentalene (**1e**).[4] Similar distortion might also be expected of the 1,10-dibromo-substituted compound **1f** and the diquinolino and diquinoxalino derivatives **2a** and **2b**. The latter two compounds would fall within the category of heterohelicenes, introduced and thoroughly investigated by Wynberg.[6-9] As hexacyclic compounds, they also bear a direct relationship to the original hexahelicene of Newman.[10-12]

1a R=H **d** R=*i*-Pr
b R=Me **e** R=*t*-Bu
c R=Et **f** R=Br

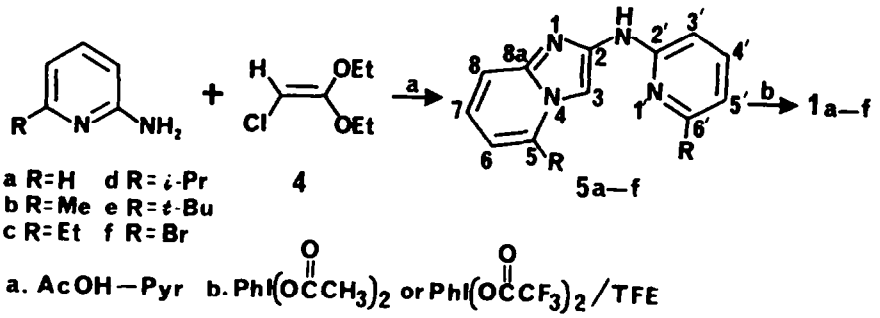


2a X=CH
b X=N

†This article is dedicated to Hans Wynberg, Professor of Organic Chemistry, University of Groningen, The Netherlands, on the occasion of his sixty-fifth birthday.

The synthesis of the tetracyclic ring system **1a** has been described briefly.[1] The synthesis of the homologously substituted compounds **1b,c,d,f** and of the related 3,8-dimethyl- and 1,3,8,10-tetramethyl-substituted **1a** followed the same general route (Scheme I) with some modifications in the reaction conditions. Each example required the availability of the appropriately substituted 2-aminopyridine, and some innovation was required to obtain several of these simple starting materials in sufficient purity and quantity.

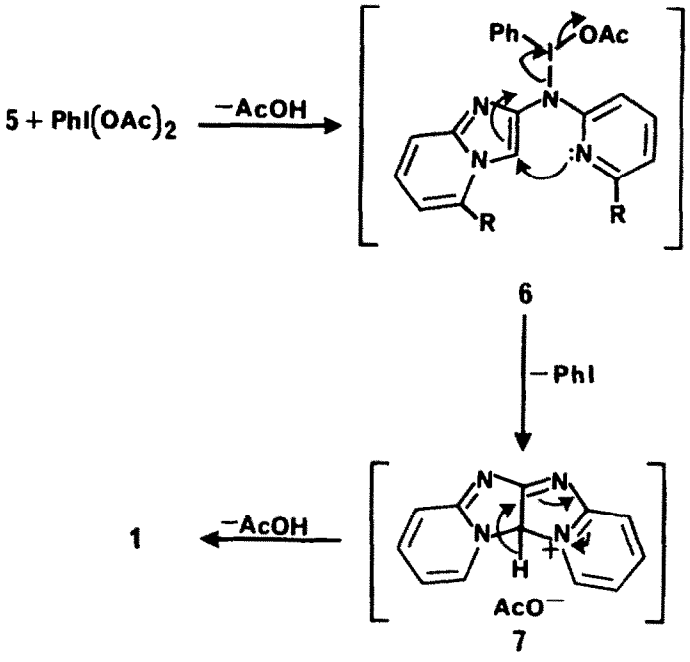
Scheme I



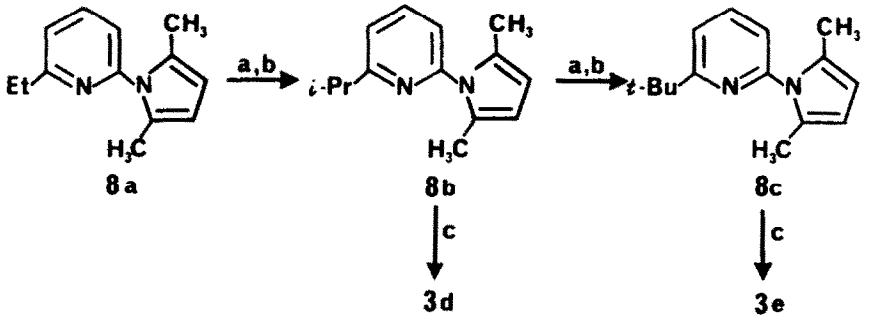
The first step (Scheme I) in the two-step synthesis of **1b–f** was the formation of the substituted N-(2-pyridinyl)imidazo[1,2-a]pyridin-2-amine (**5b–f**) from the appropriately substituted pyridin-2-amine (**3b–f**) and chloroketene diethyl acetal (**4**). The literature procedures[1,13] for the preparation of **5** were improved by treating **3** with **4** in a 1:1 (v/v) solution of pyridine-acetic acid at 60 °C. Removal of the solvent gave an oily residue which, when treated with aqueous sodium bicarbonate, resulted in the precipitation of nearly pure **5** (moderate yields). The pyridinylimidazopyridinamines (**5**) were treated with the versatile reagent iodobenzene diacetate[14–16] under the conditions developed in this Laboratory[1] with the intent of effecting oxidative cyclization to yield the 1,10-disubstituted dipyrido-1,3,4,6-tetraazapentalenes (**1b–f**). The yields of **1** decreased with increase in the size of the alkyl group (Me to i-Pr), and in the case of the di-t-butyl compound **5e** the tetraazapentalene **1e** was not formed at all. The relative yields reveal that the increased bulk of the alkyl substituents interfered with the cyclization. The ^{1}H NMR spectrum of one of the major products of the oxidation of **5e** showed that solvent (2,2,2-trifluoroethanol, TFE) addition had occurred at carbon 3 of **5e**. This competing reaction can be explained if one considers a feasible reaction pathway for the oxidative cyclization (Scheme II). The first step probably involves ligand exchange at the iodine atom of iodobenzene diacetate by the secondary amine of **5** with loss of acetate to form intermediate **6**. Nucleophilic attack at carbon 3 of the imidazopyridine ring system, concurrent with or following fragmentation of **6** gives intermediate **7**, which can lose a proton to give **1**. If the cyclization step is retarded due to the bulk of the t-butyl group(s), the solvent could act as a competing nucleophile to produce a solvent-addition product, for which there is evidence. In an attempt to avoid such addition, the oxidation of **5e** was carried out in the less nucleophilic 1,1,1,3,3,3-hexafluoro-2-propanol (HFP)[17] or the bulkier 2-methyl-1,1,1,3,3,3-hexafluoro-2-propanol; nevertheless, the desired product **1e** was still not formed.

Compound **5f** was found to be unreactive towards iodobenzene diacetate. However, compound **1f** could be synthesized by treating **5f** with iodobenzene bis(trifluoroacetate), which is a more powerful dehydrogenating agent than iodobenzene diacetate.[10,17]

Scheme II



Scheme III



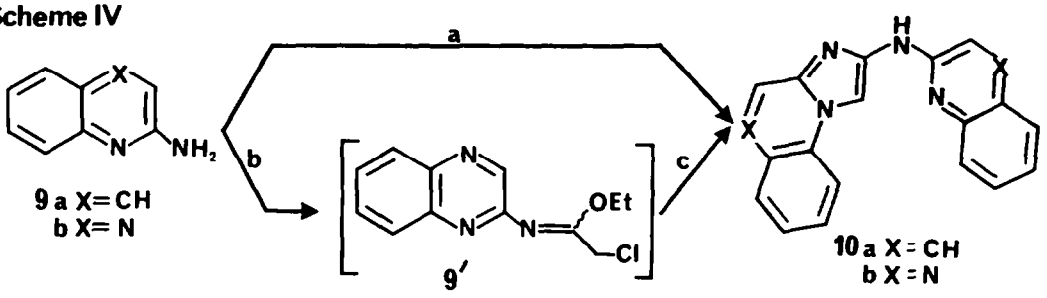
a. *n*-BuLi/THF b. MeI c. $NH_2OH \cdot HCl$/EtOH—H_2O, reflux

Although the starting amines (**3b–e**) were known compounds, problems were encountered with their synthesis. The literature synthesis[20] of **3e** was not amenable to a large scale preparation. In our hands, the treatment of either 2-ethyl- or 2-isopropylpyridine with sodium amide in xylene at reflux[21] failed to give **3c** or **3d**. Our successful approach to the preparation of these alkylpyridinamines on a reasonable scale was based on the work of Breukelman and coworkers for the preparation of **3c**.[22] The amine-protected 6-ethylpyridin-2-

amine (**8a**)[22] (obtained by the alkylation of the protected 6-methylpyridin-2-amine) was treated with n-BuLi followed by quenching of the anion with methyl iodide (Scheme III) to give **8b** in quantitative yield. The amine-protected 6-t-butylpyridin-2-amine (**8c**) was prepared by the alkylation of **8b** under similar conditions. Compounds **3d** and **3e** were then obtained by the deprotection of **8b** and **8c** by hydroxylamine hydrochloride in refluxing aqueous ethanol. 6-Bromopyridin-2-amine was prepared by the method of Johnson and coworkers.[23]

We hoped to synthesize the hexaheterohelicenes **2a** and **2b** using the same strategy as outlined above. However, compounds **10a** and **10b** could not be obtained using the conditions under which **5a–f** were prepared. Instead, the method of Kato and coworkers[13] (chloroketene diethyl acetal and **9a** in a melt) was used to obtain **10a** in low yield (Scheme IV). Compound **10a** upon treatment with iodobenzene diacetate in TFE gave the hexaheterohelicene **2a** (Scheme V). To prepare **10b** from **9b**, we again had to alter the reaction conditions. 2-Aminoquinoxaline and chloroketene diethyl acetal were caused to react in acetonitrile which contained a catalytic amount of p-toluenesulfonic acid to give intermediate **9'** (Scheme IV). A second equivalent of **9b** was added to the reaction solution containing **9'**, which was then brought to reflux. After 3 hours, the product, **10b**, precipitated from the reaction solution.

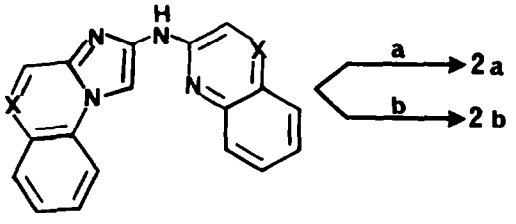
Scheme IV



a. 4,Δ b. 4/CH_3CN c. 9b,Δ

Attempts at oxidative cyclization of **10b** using iodobenzene diacetate or iodobenzene bis(trifluoroacetate) in TFE failed to provide **2b**. ^1H NMR spectra of the crude reaction mixture at different stages indicated that solvent addition had occurred. We therefore resorted to using the more bulky and less nucleophilic 1,1,1,3,3,3-hexafluoro-2-propanol (HFP)[17] as the solvent instead of

Scheme V



a. $PhI(OAc)_2$/TFE b. $PhI(OAc)_2$/HFP/0°C

TFE in order to retard solvent addition and promote cyclization. In fact, under these conditions, compound **2b** was obtained in 20% yield (Scheme V). The yield of **2b** from **10b** could be increased to 51% by reversing the order of addition, that is, by addition of **10b** to a solution containing iodobenzene diacetate (2 equiv) at 0 °C.

Although numerous preparations of 2-aminoquinoline (**9a**) are described,[24-26] none of these methods could provide the desired amount of the amine. We found that by heating 2-chloroquinoline with ammonia dissolved in formamide in a steel bomb at 175-180 °C for 24 hours, followed by continuous extraction of the reaction solution with chloroform, **9a** could be obtained in reasonable amounts in greater than 65% yield. 2-Aminoquinoxaline was prepared by the method of Pfister and coworkers.[27]

Single crystal X-ray structure determinations[28] were obtained on **1a**,**b**,**c**,**d**, and **f**. The ORTEP drawings (Figures 1-2) showed that the substituent in the bay region forced the molecule out of the planarity exhibited by the unsubstituted **1a**.[8] Further analysis of the data revealed the following. (1) Although the molecules **1b**,**c**,**d**,**f** are predicted to possess a plane of symmetry through the 5a-11a bond (ignoring the helicity for the moment), none of the compounds is symmetrical according to the X-ray data. This finding is attributed to intermolecular forces within the crystal lattice as well as intramolecular distortion. (2) The bond lengths are surprisingly constant, suggesting that the distortions are accommodated by slight changes throughout each structure. (3) The angles within the 5-5 ring system are fairly constant. (4) The Van der Waals distance between the C1 and C10 substituents increases monotonically through the series **1b**,**c**,**d**,**f**. (5) As predicted by MMPMI molecular mechanics calculations,[29] there

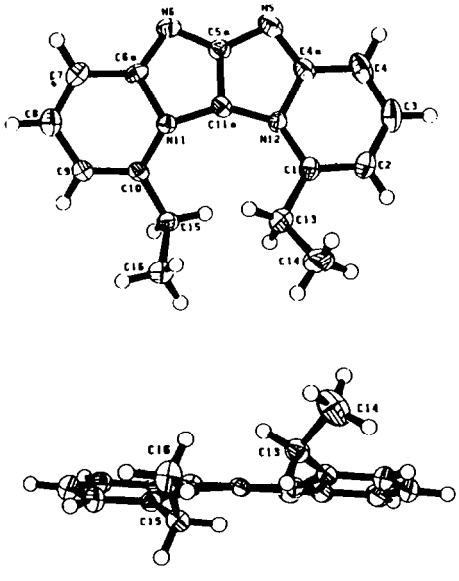


Figure 1. ORTEP drawings of the "top" and "side" view of **1c** as determined by X-ray analysis.

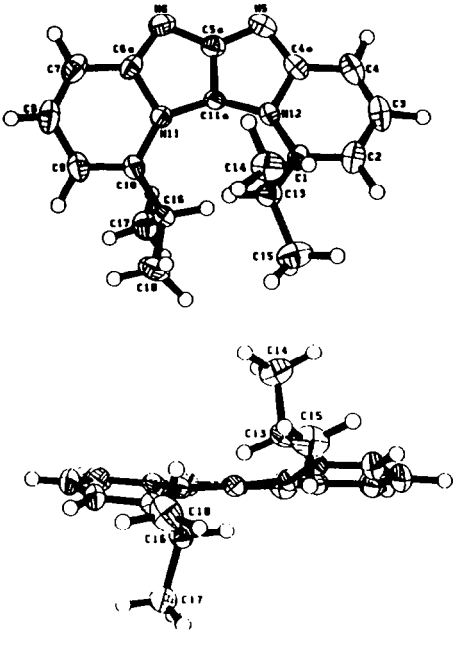
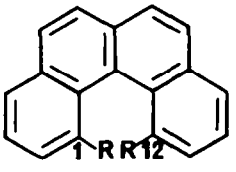


Figure 2. ORTEP drawings of the "top" and "side" view of **1d** as determined by X-ray analysis.

are significant differences in the dihedral (torsional) angles[27] between the unsubstituted **1a** and each of the bay-substituted compounds. The dihedral angle which shows the greatest deviation from that in **1a** is that formed by the atoms 5a-11a-11-10 (5a-11a-12-1): **1a**, 178.6° (178.0°); **1b**, 161.7° (164.1°); **1c**, 160.2° (164.6°); **1d**, 160.7° (162.0°); **1f**, 158.0° (157.0°). The dialkyl derivatives **1b-d** are all distorted from planarity to the same degree, although the bulk of the substituent increases. The conformational orientation of the alkyl groups in relation to the bay region probably accounts for this. The ethyl (**1c**, Figure 1) and isopropyl (**1d**, Figure 2) groups are arranged so that the component methyl groups are out of the bay region and the α-hydrogens are tucked into the bay region, providing for least crowding. Molecular mechanics calculations using MMPMI[27] predict an increase in strain energy with an increase in bulk of the substituent: **1a**, 46.712; **1b**, 49.482; **1c**, 50.769; **1d**, 55.559; **1f**, 53.518 kcal.

A comparison of the tetracyclic ring systems, benzo[c]phenanthrene (**11a**) and **1a-f** reveals that the bay region of the dipyrido-1,3,4,6-tetraazapentalene (**1**) is obviously wider than that of **11**. In the unsubstituted **11a** the bay region angles are 119°, 131°, and 119°,[30] whereas that of **1a**[2] has bay region angles of 133°, 143°, and 133°. This results in less steric crowding in **1a**; hence, it is planar. The steric crowding in **1b** is sufficient to force the structure to become non-planar.[31] The magnitude of the difference in size of the bay region can be seen by the large difference in the distance between atoms 1 and 12 in **11a** and atoms 1 and 10 in **1a**. The distance between C1 and C12 in **11a** is 3.00 A, but if the molecule were planar, the calculated distance would be 2.4 A.[30] In the virtually planar **1a**, the distance between C1 and C10 is 3.77 A.[2]

The dipyrido-1,3,4,6-tetraazapentalene ring system is distorted from planarity by the introduction of substituents at positions 1 and 10. The substitution causes a slight increase in the bay region angles (angles are almost equivalent in **1b-d,f**) from **1a**, and the distance between C1 and C10 is increased to just over 4 A regardless of the substituent. The 1,12-dimethylbenzo[c]phenanthrene (**11b**) was resolved and found to be optically stable up to 250 °C, at which point decomposition occurs.[32] Resolution of the enantiomers of **1b-d,f** has not yet been attempted. It is presumed that racemization of enantiomers will occur at a much lower temperature.



11 a R=H
b R=CH_3

There are several other interesting features of these compounds. All of the compounds are fluorescent except for **1f**, in which heavy-atom quenching exerts its effect. The quantum yields of **1c** and **1d** are much lower than those of **1a** and **1b**. The quantum yield of the 3,8-dimethyl-substituted **1a** is greater than that for the 1,10-dimethyl compound **1b**, but the quantum yield of **1b** and the 1,3,8,10-tetramethyl-substituted **1a** are almost equal. Therefore, the deviation from planarity, caused by steric crowding of the "bay region" substitu-

ents, is the cause of the decrease in the quantum yield. The melting points of the dialkyl compounds are as follows: **1b**, 230-240 °C; **1c**, 95-97 °C; and **1d**, 182-184 °C. Thus, the melting point of the diethyl compound **1c** is lower than the melting points of **1b** and **1d**. Examination of the ORTEP drawing (Figure 1) reveals that both methyl components of the ethyl groups lie above the approximate plane of the ring system unlike the methyl groups in either **1b** and **1d** (Figure 2) which are clearly on opposite sides. Molecular mechanics calculations (MMPMI) predict that the terminal methyl groups in **1c** are on opposite sides of the ring system, so it is supposed that the conformation shown in Figure 1 is the result of crystal-packing forces. In the case of the diisopropyl compound **1d**, there is great similarity between the observed X-ray structure and the derived MMPMI structure.

The ORTEP drawing (Figure 2) from the X-ray structure determination of **1d** suggests that the two methyl groups comprising each isopropyl group might be magnetically non-equivalent since one lies in the plane of the ring and the other lies out of the plane. Thus, if the structure were sterically congested enough to hinder rotation about the C1(10)-α-CH bond, it might be possible to observe two methyl resonances in the ^{1}H NMR spectrum. However, the spectrum observed for a solution of **1c** in $CDCl_3$ at room temperature showed only one broadened methyl doublet. When a variable temperature ^{1}H NMR study[31] was conducted, the resonance broadened as the temperature was decreased. The resonance then split into two peaks which were separated by 285 Hz at -90 °C. The process by which the methyls are interconverting is not clear. There could be simple rotation about the C1(10)-α-CH bond, inversion of the ring system, or a combination of the two. This suggests that the barrier of racemization is low.

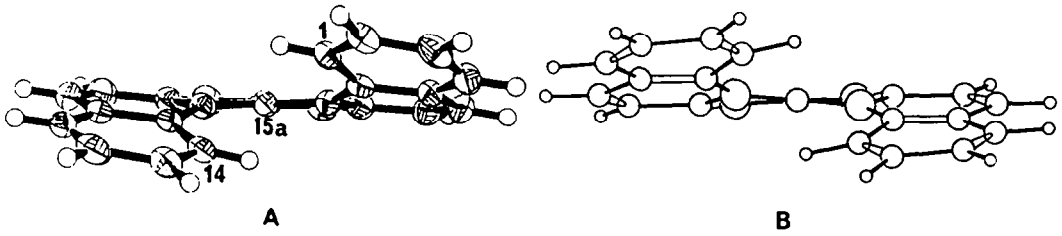
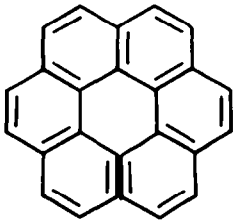
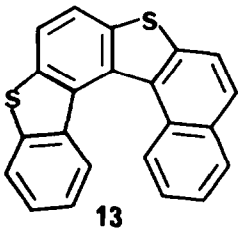


Figure 3. A. ORTEP drawings of the "side" view of **2a** as determined by X-ray analysis. B. MM2 derived ORTEP drawing of the "side" view of **2a**.

The hexaheterohelicene **2a** and **b** are conformationally similar to **1b-d, f** (**2a**, Figure 3) due to molecular crowding of the bay region by the terminal rings. The angles and dihedral angles are very similar. When compared with the hexahelicene **12**[10-12] and the hexaheterohelicene **13**,[5] there are some differences. An MM2 energy minimization calculation of **12** predicted that 1-H and 16-H would



12



13

overlap each other. The ORTEP drawing of the X-ray-determined structure of **2a** (Figure 3) clearly shows that the corresponding 1-H and 14-H do not overlap. Also, the distance between C1 and C14 of **13** is 2.91 Å[8] compared with 3.095 and 3.190 for **2a** and **2b**, respectively. Not surprisingly, the bay regions of **2a** and **2b** are wider than those in **12** and **13**.

Resolution of **2a** and **2b** has not been attempted since we expect optically active forms to racemize at a temperature at or below room temperature. Compound **13** has a $t_{1/2}$ of racemization at 25 °C of 241 min.[8] An MM2 energy minimization calculation showed that extension of the ring system of **2a** by two rings would give an octaheterohelicene in which the terminal rings would clearly overlap. During the preparation of this manuscript, an octaheterohelicene incorporating the central 1,3,4,6-tetraazapentalene ring system was successfully synthesized and will be the subject of a sequel.

Finally, compounds **1b-d,f** and **2a,b** constitute a new series of heterohelicenes which incorporate the 1,3,4,6-tetraazapentalene ring system. The compounds owe their helicity to steric repulsion between substituents in the bay region. Compounds **2a** and **b** are similar to Wynberg's hexaheterohelicene, dibenzo[e:e']bis[1]benzothieno[2,3-*b*][2]benzothiophene.[33] The bay regions of the 6,6,5,5,6,6 and 6,6,5,6,5,6[8] examples are wider than those of the all-six-membered hexahelicenes.

EXPERIMENTAL

Chemicals, Materials, and Techniques. Tetrahydrofuran (THF) was purified by distillation from Na-benzophenone. MeOH and EtOH were of anhydrous grade; all other solvents and reagents were of reagent grade unless specified otherwise. Petroleum ether was of bp 30-60 °C. 6-Methyl-2-pyridinamine was distilled from CaH_2 prior to use. All reactions were carried out under nitrogen and stirred magnetically unless stated otherwise. Removal of solvent was done by rotary evaporation under reduced pressure unless indicated otherwise. Dichloroacetaldehyde diethyl acetal, 2,5-hexanedione, hydroxylamine hydrochloride, iodobenzene diacetate, 2,2,2-trifluoroethanol (Gold Label), 4,6-dimethyl-2-pyridinamine, 2-chloroquinoline, methyl iodide (MeI), and *n*-BuLi in hexane were purchased from the Aldrich Chemical Company, Milwaukee, WI. 2-(2,5-Dimethyl-1*H*-pyrrol-1-yl)-6-methylpyridine was prepared by the procedure of Broadbent and coworkers[34] with slight modification in the proportion of the reagents. Thin-layer chromatography (TLC) was performed on E. Merck silica gel 60 F_{254} precoated (0.2 mm with fluorescent indicator) plastic-backed plates. The solvent system used was $CHCl_3$-MeOH (10:1, v/v). Column chromatography was performed on silica gel (large pore, 58 microns) from Alfa.

Instrumentation. Melting points were determined on a Büchi melting point apparatus and are uncorrected. ^1H Nuclear magnetic resonance (NMR) spectra were recorded on a Varian XL-200 (200.06 MHz) or a General Electric QE-300 (300.15 MHz) Fourier transform spectrometer using tetramethylsilane as an internal standard. ^{13}C NMR spectra were recorded at 50.3 or 75.5 MHz, using the deuterated solvent as an internal reference.[35] Complete NMR spectral assignments on some of the compounds prepared were based on proton-proton spin-decoupling, nOe, and proton-coupled carbon experiments, and short and long range heteronuclear correlation (HETCOR) spectroscopy. The HETCOR experiments provided unequivocal confirmation of tentative assignments. Infrared spectra were recorded on an IBM IR-32 Fourier transform spectrophotometer. Ultra-

violet/visible spectra were obtained on a Beckman Acta MVI spectrophotometer. Fluorescence excitation and emission spectra were recorded on a Spex Fluorolog 111C spectrofluorometer coupled with a Datamate microprocessor. Mass spectra were obtained on a Varian MAT CH-5 instrument in the Mass Spectrometry Laboratory, School of Chemical Sciences. Elemental analyses were performed by Josef Nemeth and his staff at the University of Illinois.

Chloroketene Diethyl Acetal (2-Chloro-1,1-Diethoxyethene) (4). CAUTION! Chloroketene diethyl acetal is a mutagen and should be handled with caution in a well-ventilated hood, with suitable trapping. A modification of the literature procedure[36a] gave improved yields of product in a much shorter reaction time. Dichloroacetaldehyde diethyl acetal (150.17 g, 0.803 mol) in THF (120 mL) was added slowly to a cooled (0 °C, ice-water bath) suspension of potassium tert-butoxide (105.20 g, 0.937 mol) in THF (400 mL) with vigorous mechanical stirring. The cooling bath was then replaced with a heating mantle and the mixture was refluxed for 12 h. After cooling to room temperature, the brown reaction mixture was centrifuged in 250 mL polypropylene vials in a Dupont Instruments Sorvall™ RC-5B Refrigerated Superspeed Centrifuge. The pellets were washed with THF (ca 80 mL) and centrifuged again. The combined supernatants were concentrated and the residue (quantitative yield) was fractionally distilled to give 98.7 g (82%) of analytically pure 4: bp 73-76 °C at 10 torr (lit.[37] 166 °C at 732-740 torr). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 158.58 (C-1), 74.58 (C-2), 64.21 (two -O$\underline{C}H_2CH_3$), 14.65 and 14.06 (-OCH$_2\underline{C}H_3$). Calcd for $C_6H_{11}ClO_2$: C, 47.85; H, 7.36; Cl, 23.54. Found: C, 47.66; H, 7.37; Cl, 23.47.

Alkylation of Protected Alkylpyridinamines. General Procedure. The literature procedure[38] was used with the modification that n-BuLi was employed as the base in place of LDA. The temperature at which the reaction was performed depended on the substrate.

2-(2,5-Dimethyl-1H-pyrrol-1-yl)-6-(1-methylethyl)pyridine (8b). The reaction temperature was maintained between 0 ° and -30 °C (quantitative crude yield): bp 150-152 °C at 3.2 torr. ^{1}H-NMR (200.06 MHz, $CDCl_3$) δ 7.71 (m, 1, H-4), 7.14 (d, $\underline{J}$ = 7.8 Hz, 1, H-5), 7.00 (d, $\underline{J}$ = 7.7 Hz, 1, H-3), 5.89 (s, 2, H-3' and 4'), 3.09 (m, $\underline{J}$ = 7.0 Hz, 1, 6-C$\underline{H}$(CH$_3$)$_2$), 2.15 (s, 6, 2' and 5'-C$\underline{H}_3$), 1.31 (d, $\underline{J}$ = 7.0 Hz, 6, 6-CH(C$\underline{H}_3$)$_2$). ^{13}C-NMR (50.3 MHz, $CDCl_3$) δ 166.74 (C-6), 150.79 (C-2), 137.70 (C-4), 127.95 (C-2' and 5'), 118.60 (C-5), 118.29 (C-3), 106.43 (C-3' and 4'), 35.68 (6-$\underline{C}$H(CH$_3$)$_2$), 21.95 (6-CH($\underline{C}$H$_3$)$_2$), 12.90 (2' and 5'-$\underline{C}$H$_3$). Calcd for $C_{14}H_{18}N_2$: C, 78.46; H, 8.47; N, 13.07. Found: C, 78.45; H, 7.90; N, 12.28.

2-(2,5-Dimethyl-1H-pyrrol-1-yl)-6-(1,1-dimethylethyl)pyridine (8c) was obtained in quantitative crude yield. After addition of n-BuLi at -40 °C, the temperature was allowed to warm to 20 °C. MeI was added in portions while the temperature was maintained below 25 °C. ^{1}H-NMR (200.06 MHz, $CDCl_3$) δ 7.72 (m, $\underline{J}$ = 7.84 Hz and 7.77 Hz, 1, H-4), 7.30 (dd, $\underline{J}$ = 7.84 and 0.59 Hz, 1, H-5), 6.99 (dd, $\underline{J}$ = 7.77 and 0.59 Hz, 1, H-3), 5.91 (s, 2, H-3' and 4'), 2.17 (s, 6, 2' and 5'-C$\underline{H}_3$), 1.37 (s, 9, 6-C(C$\underline{H}_3$)$_3$). ^{13}C-NMR (50.3 MHz, $CDCl_3$) δ 169.25 (C-6), 150.54 (C-2), 137.76 (C-4), 128.61 (C-2' and 5'), 118.15 (C-3), 117.04 (C-5), 106.58 (C-3' and 4'), 37.68 (6-$\underline{C}$H(CH$_3$)$_2$), 29.99 (6-CH(C$\underline{H}_3$)$_2$), 13.45 (2' and 5'-C$\underline{H}_3$). Calcd for $C_{15}H_{20}N_2$: C, 78.90; H, 8.83; N, 12.27. Found: C, 78.52; H, 8.52; N, 12.34.

Deprotection of 2,5-Dimethyl-1-Pyrrolylalkylpyridines. General Procedure. The literature procedure[38] was used with the following details for the workup:

the dark red reaction mixture was poured into 250 mL of 3 N HCl, extracted with ether (3 x 200 mL), and the ether layer was discarded; the aqueous layer was then poured onto solid $NaHCO_3$ (60 g) with vigorous hand stirring, made alkaline (pH 13) with saturated NaOH, and extracted with ether (2 x 150 mL); the combined ether extracts were dried (Na_2SO_4), filtered, decolorized, and filtered again; after solvent removal the resulting oil was distilled under high vacuum to give the product, which was characterized by ^1H and ^{13}C NMR spectroscopy.

6-(1-Methylethyl)-2-pyridinamine (3d) (49%): bp 90-95 °C at 1.8 torr. ^1H-NMR (300.15 MHz, $CDCl_3$) δ 7.34 (m, 1, H-4), 6.52 (d, J = 7.4 Hz, 1, H-5), 6.30 (d, J = 8.1 Hz, 1, H-3), 4.57 (br s, 2, NH_2), 2.85 (m, J = 6.9 Hz, 1, 6-CH(CH_3)$_2$), 1.24 (d, J = 6.9 Hz, 6, 6-CH(CH_3)$_2$). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 166.08 (C-6), 157.83 (C-2), 138.00 (C-4), 109.94 (C-5), 105.71 (C-3), 36.00 (6-CH(CH_3)$_2$), 22.43 (6-CH(CH_3)$_2$). FT-IR (neat) 3470, 3327, 2964 (s), 1617 (vs), 1577 (vs), 1462 (vs), 1340, 1174, 1052, 987, 799 (vs), 742, 641, 581 cm^{-1}. EI-Mass spectrum (70 eV) m/z (rel intensity): 136 (82, M^+), 135 (34), 121 (100), 108 (44), 104 (13), 94 (14), 32 (10) amu.

6-(1,1-Dimethylethyl)-2-pyridinamine (3e) (35%): bp 78-80 °C at 1.7 torr (lit.[20] mp 38-39 °C). ^1H-NMR (300.15 MHz, $CDCl_3$) δ 7.29 (m, 1, H-4), 6.63 (d, J = 7.6 Hz, 1, H-5), 6.24 (d, J = 8.1 Hz, 1, H-3), 4.68 (br s, 2, NH_2), 1.29 (s, 9, 6-C(CH_3)$_3$). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 167.73 (C-6), 157.50 (C-2), 137.55 (C-4), 108.42 (C-5), 105.38 (C-3), 36.73 (6-C(CH_3)$_3$), 29.88 (6-C(CH_3)$_3$). Calcd for $C_9H_{14}N_2$: C, 71.95; H, 9.39; N, 18.65. Found: C, 71.97; H, 9.29; N, 18.58.

Preparation of N-Pyridinylimidazo[1,2-a]pyridines. General Procedure. Chloroketene diethyl acetal (4) (12.0 mmol) was added to a stirred solution of alkylpyridinamine (26.5 mmol) in 60 mL of acetic acid/pyridine (1:1 v/v) at 60 °C (oil bath temperature). The reaction time varied depending on starting material. After removal of most of the solvent under high vacuum, the viscous oily residue, still containing some AcOH, was poured into a saturated solution of $NaHCO_3$ with vigorous stirring by hand. Additional bicarbonate was added, if necessary, to obtain a final pH of 7-8. The solid which precipitated from the mixture was filtered and dried in a vacuum oven at room temperature (in the case of **5d** and **5e**, the product oiled out and required an extractive (Et_2O) workup). The crude product was sufficiently pure by ^1H-NMR analysis to be taken to the next step, and an analytically pure sample could be obtained by recrystallization from EtOH.

5-Methyl-N-(6-methyl-2-pyridinyl)imidazo[1,2-a]pyridin-2-amine (5b) (49%): mp 187-189 °C (dec.) (from EtOH). TLC, R_f = 0.45. ^1H-NMR (200.06 MHz, $(CD_3)_2SO$) δ 9.65 (s, 1, NH), 8.02 (s, 1, H-3), 7.47 (m, 1, H-4'), 7.29 (d, J = 8.9 Hz, 1, H-8), 7.15 (m, 1, H-7), 6.91 (d, J = 8.3 Hz, 1, H-3'), 6.72 (d, J = 7.0 Hz, 1, H-6), 6.62 (d, J = 7.0 Hz, 1, H-5'), 2.59 (s, 3, 5-CH_3), 2.45 (s, 3, 6'-CH_3). ^{13}C-NMR (50.3 MHz, $(CD_3)_2SO$) δ 155.69 (C-6'), 153.93 (C-2'), 144.77 (C-2), 141.48 (C-8a), 137.23 (C-4'), 134.00 (C-5), 123.65 (C-7), 112.88 (C-5'), 111.82 (C-8), 110.26 (C-6), 107.14 (C-3'), 95.11 (C-3), 24.19 (6'-CH_3), 18.29 (5-CH_3). FT-IR (KBr) 3250, 3195, 3029, 1615, 1549 (vs), 1510, 1457, 1331, 1228, 1145, 782, 766, 659, 504, 426 cm^{-1}. EI-Mass spectrum (70 eV) m/z (rel intensity): 239 (16), 238 (100, M^+), 237 (27), 146 (10), 119 (18), 93 (15), 92 (29), 65 (23), 39 (11) amu. Calcd for $C_{14}H_{14}N_4$: C, 70.56; H, 5.92; N, 23.51. Found: C, 70.42; H, 5.93; N, 23.30.

5-Ethyl-N-(6-ethyl-2-pyridinyl)imidazo[1,2-a]pyridin-2-amine (5c) (40%): mp

168-170 °C (dec.). TLC, R_f = 0.52. ^{1}H-NMR (300.15 MHz, $(CD_3)_2SO$) δ 9.73 (s, 1, NH), 8.20 (s, 1, H-3), 7.48 (m, 1, H-4'), 7.30 (d, J = 8.8 Hz, 1, H-8), 7.18 (m, 1, H-7), 6.89 (d, J = 8.3 Hz, 1, H-3'), 6.69 (d, J = 6.8 Hz, 1, H-6), 6.62 (d, J = 7.2 Hz, 1, H-5'), 2.91 (m, J = 7.3 Hz, 2, 5-CH_2CH_3), 2.75 (m, J = 7.5 Hz, 2, 6'-CH_2CH_3), 1.37 (t, 3, 5-CH_2CH_3), 1.35 (t, 3, 6'-CH_2CH_3). ^{13}C-NMR (75.5 MHz, $(CD_3)_2SO$) δ 160.46 (C-6'), 153.94 (C-2'), 144.79 (C-2), 141.49 (C-8a), 138.72 (C-5), 137.16 (C-4'), 123.63 (C-7), 111.95 (C-8), 111.77 (C-5'), 108.07 (C-6), 107.47 (C-3'), 94.95 (C-3), 30.45 (6'-CH_2CH_3), 24.64 (5-CH_2CH_3), 13.13 (6'-CH_2CH_3), 9.96 (5-CH_2CH_3). FT-IR (KBr) 3196, 3033, 2969, 1610(s), 1538 (vs), 1456(vs), 1330(s), 1218, 1147, 982, 800(s), 759(s), 734, 700, 646, 500 cm^{-1}. UV λ_{max} nm (ϵ x 10^3, L mol^{-1} cm^{-1}): (EtOH) 339 (13.5), 302 (8.8), 257 (28.9), 230 (sh). EI-Mass spectrum (10 eV) m/z (rel intensity): 267 (20), 266 (100, M$^+$), 265 (51), 252 (11), 238 (7), 160 (4), 145 (12), 134 (8) amu. Calcd for $C_{14}H_{14}N_4$: C, 72.15; H, 6.81; N, 21.04. Found: C, 72.24; H, 6.93; N, 20.99.

5-(1-Methylethyl)-N-(6-(1-methylethyl)-2-pyridinyl)imidazo[1,2-a]pyridin-2-amine (5d) (47%): mp 138-141 °C (dec.). TLC, R_f = 0.59. ^{1}H-NMR (300.15 MHz, $(CD_3)_2SO$) δ 9.82 (s, 1, NH), 8.38 (s, 1, H-3), 7.49 (m, 1, H-4'), 7.32 (d, J = 8.7 Hz, 1, H-8), 7.20 (m, 1, H-7), 6.88 (d, J = 8.2 Hz, 1, H-3'), 6.70 (d, J = 7.0 Hz, 1, H-6), 6.63 (d, J = 7.2 Hz, 1, H-5'), 3.24 (m, J = 6.7 Hz, 1, 5-$CH(CH_3)_2$), 2.99 (m, J = 6.8 Hz, 1, 6'-$CH(CH_3)_2$), 1.41 (d, J = 6.7 Hz, 3, 5-$CH(CH_3)_2$), 1.34 (d, J = 6.8 Hz, 3, 6'-$CH(CH_3)_2$). ^{13}C-NMR (75.5 MHz, $(CD_3)_2SO$) δ 164.36 (C-6'), 153.91 (C-2'), 144.78 (C-2), 142.75 (C-5), 141.63 (C-8a), 137.22 (C-4'), 123.72 (C-7), 112.11 (C-8), 110.74 (C-5'), 107.81 (C-3'), 106.17 (C-6), 95.39 (C-3), 35.40 (6'-$CH(CH_3)_2$), 29.85 (5-$CH(CH_3)_2$), 22.50 (6'-$CH(CH_3)_2$), 19.30 (5-$CH(CH_3)_2$). FT-IR (KBr) 3206, 3040, 2959, 2929, 1612 (s), 1540 (vs), 1457 (s), 1325, 1292, 1219, 1157, 1099, 991, 801, 774, 735 (s), 708, 665, 642, 502 cm^{-1}. UV λ_{max} nm (ϵ x 10^3, L mol^{-1} cm^{-1}): (EtOH) 340 (br) (15.9), 331 (br) (15.9), 258 (62.6). EI-Mass spectrum (70 eV) m/z (rel intensity): 295 (22), 294 (100, M$^+$), 293 (44), 280 (23), 279 (64), 267 (16), 266 (88), 263 (18), 147 (16), 133 (22), 104 (16), 77 (15), 32 (35) amu. Calcd for $C_{18}H_{22}N_4$: C, 73.43; H, 7.53; N, 19.03. Found: C, 73.14; H, 7.59; N, 19.07.

5-(1,1-Dimethylethyl)-N-(6-(1,1-dimethylethyl)-2-pyridinyl)imidazo-[1,2-a]pyridin-2-amine (5e) (52%): mp 221-223 °C. TLC, R_f = 0.52. ^{1}H-NMR (300.15 MHz, $(CD_3)_2SO$) δ 9.75 (s, 1, NH), 8.59 (s, 1, H-3), 7.51 (m, 1, H-4'), 7.33 (d, J = 8.5 Hz, 1, H-8), 7.19 (m, 1, H-7), 6.83 (d, J = 8.2 Hz, 1, H-3'), 6.76 (two d, J = 7.5 Hz, 2, H-6 and H-5'), 1.55 (s, 9, 5-$C(CH_3)_3$), 1.39 (s, 9, 6'-$C(CH_3)_3$). ^{13}C-NMR (75.5 MHz, $(CD_3)_2SO$) δ 166.55 (C-6'), 153.26 (C-2'), 144.52 (C-5), 142.01 (C-2), 142.64 (C-8a), 137.13 (C-4'), 123.78 (C-7), 112.76 (C-8), 108.51 (C-5'), 107.90 (C-3'), 107.53 (C-6), 98.33 (C-3), 37.09 (6'-$C(CH_3)_3$), 34.96 (5-$C(CH_3)_3$), 30.12 (6'-$C(CH_3)_3$), 26.58 (5-$C(CH_3)_3$). FT-IR (KBr) 3268, 3049, 2951, 2916, 2860, 1613 (s), 1542 (vs), 1507, 1454 (vs), 1420, 1322 (s), 1243 (s), 1157 (s), 989, 799, 776 (s), 739, 704, 679, 525 cm^{-1}. UV λ_{max} nm (ϵ x 10^3, L mol^{-1} cm^{-1}): (EtOH) 341 (br) (16.7), 334 (br) (16.4), 303 (10.8), 257 (35.8), 238 (sh) (21.9). EI-Mass spectrum (70 eV) m/z (rel intensity): 323 (11), 322 (49, M$^+$), 321 (28), 308 (10), 307 (22), 291 (14), 281 (22), 280 (100), 266 (11), 265 (18), 161 (8), 147 (11), 132.5 (8), 118 (9), 91 (9) amu. Calcd for $C_{22}H_{26}N_4$: C, 74.49; H, 8.13; N, 17.38. Found: C, 74.26; H, 8.21; N, 17.25.

5-Bromo-N-(6-bromo-2-pyridinyl)imidazo[1,2-a]pyridin-2-amine (5f): (57%) mp > 250 °C. TLC, R_f = 0.40. ^{1}H-NMR (300.15 MHz,((($CD_3)_2SO$): δ 10.30 (s, 1),

8.19 (s, 1), 7.55 (dd, 1), 7.49 (d, J = 8.5 Hz, 1), 7.24 (m, 2), 7.09 (d, J = 8.2 Hz, 1), 7.01 (d, J = 7.4 Hz, 1). FT-IR (KBr) 3230, 3180, 3040, 1610, 1595, 1550, 1542, 1520, 1460, 1400, 1325, 1155, 1125, 980, 755, 745, 710 cm^{-1}. UV λ_{max} nm (ϵ x 10^3, L mol^{-1} cm^{-1}): (EtOH) 351 (22.0), 340 (2.11), 302 (17.5), 261 (44.3), 242 (sh) (32.0), 205 (sh) (46.7). EI-Mass spectrum (70 eV) m/z (rel intensity): 370 (11), 368 (25), 366 (12, M^+), 215 (11), 214 (11), 213 (12), 175 (43), 174 (100), 173 (47), 172 (100), 156 (11), 147 (20), 145 (21) amu. Calcd for $C_{18}H_8N_4Br_2$: C, 39.16; H, 2.19; N, 15.22; Br, 43.42. Found: C, 39.15; H, 2.19; N, 14.91; Br, 43.24.

Preparation of Dialkypyrido[1",2":1',2']imidazo[4',5':4,5]imidazo[1,2-a]-pyridines. General Procedure. The literature procedure[1] employing iodobenzene diacetate in CF_3CH_2OH was used. The crude product was either triturated with EtOAc and then recrystallized from EtOAc or EtOH, or was purified by chromatography on silica gel.

1,10-Dimethylpyrido[1",2":1',2']imidazo[4',5':4,5]imidazo[1,2-a]pyridine (1b) (67%): mp 230–240 °C (dec.). TLC, R_f = 0.38. ^{1}H-NMR (200.06 MHz, $CDCl_3$) δ 7.59 (d, J = 9.1 Hz, 2, H-4 and 7), 7.20 (m, 2, H-3 and 8), 6.64 (d, J = 6.8 Hz, 2, H-2 and 9), 3.02 (s, 6, 1,10-CH_3); (200.06 MHz, $CD_3OD^{[3a]}$) δ 7.28 (H-4 and 7), 7.21 (H-3 and 8), 6.73 (H-2 and 9), 3.01 (1 and 10-CH_3). ^{13}C-NMR (50.3 MHz, CD_3OD) δ 154.47 (C-5a), 151.12 (C-4a and 6a), 138.11 (C-1 and 10), 127.67 (C-3 and 8), 116.82 (C-11a), 114.61 (C-4 and 7), 113.97 (C-2 and 9), 24.42 (1 and 10-CH_3). FT-IR (KBr) 1533, 1508, 1462, 1413, 1385, 1337, 1211, 1141, 1122, 1092, 1017, 776, 765, 708, 582 cm^{-1}. UV λ_{max} nm (ϵ x 10^3, L mol^{-1} cm^{-1}): (EtOH) 370 (12.4), 353 (16.3), 266 (21.7), 258 (22.7), 245.5 (38.6). Fluorescence: λ^{em}_{max} 414 nm, Φ = 0.41 (absolute ethanol) (relative to coumarin in absolute ethanol, Φ = 0.51 at λ^{ex} = 350 nm (measured relative to the reported value of Φ = 0.64 at λ^{ex} = 366 nm[3a])) (all excitations at 350 nm). EI-Mass spectrum (70 eV) m/z (rel intensity): 237 (18), 236 (100, M^+), 235 (39), 221 (72), 118 (13), 92 (49), 65 (45), 39 (24) amu. Calcd for $C_{14}H_{12}N_4$: C, 71.16; H, 5.12; N, 23.72. Found: C, 71.21; H, 5.07; N, 23.62.

1,10-Diethylpyrido[1",2":1',2']imidazo[4',5':4,5]imidazo[1,2-a]pyridine (1c) (53%): mp 95–97 °C. TLC, R_f = 0.25. ^{1}H-NMR (200.06 MHz, $CDCl_3$) δ 7.61 (d, J = 9.1 Hz, 2, H-4 and 7), 7.29 (m, 2, H-3 and 8), 6.77 (d, J = 7.0 Hz, 2, H-2 and 9), 3.23 (m, J = 7.4 Hz, 4, 1 and 10-CH_2CH_3), 1.24 (t, J = 7.4 Hz, 6, 1 and 10-CH_2CH_3). ^{13}C-NMR (50.3 MHz, CD_3OD) δ 155.18 (C-5a), 149.51 (C-4a and 6a), 141.95 (C-1 and 10), 125.40 (C-3 and 8), 115.72 (C-11a), 115.08 (C-4 and 7), 110.24 (C-2 and 9), 28.61 (1 and 10-CH_2CH_3), 14.37 (1 and 10-CH_2CH_3). FT-IR (KBr) 2990, 2940, 1540, 1515, 1445, 1415, 1400, 1350, 1200, 1120, 1030, 820, 780, 765, 710 cm^{-1}. UV λ_{max} nm (ϵ x 10^3 L mol^{-1} cm^{-1}): (EtOH) 372 (14.1), 356 (16.6), 270 (18.4), 262 (19.6), 245 (38.7), 240 (sh) (35.0). Fluorescence: λ^{em}_{max} 416.5 nm, Φ = 0.21 (absolute ethanol) (relative to coumarin in absolute ethanol, Φ = 0.51 at λ^{ex} = 350 nm (measured relative to the reported value of Φ = 0.64 at λ^{ex} = 366 nm[3a])) (all excitations at 350 nm). EI-Mass spectrum (70 eV) m/z (rel intensity): 264 (100, M^+), 249 (30), 236 (18), 235 (72). Calcd for $C_{16}H_{16}N_4$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.58; H, 6.14; N, 21.27.

1,10-Bis(1-methylethyl)pyrido[1",2":1',2']imidazo[4',5':4,5]imidazo[1,2-a]-pyridine (1d) (34%): mp 182–184 °C (dec.) (from EtOAc). TLC, R_f = 0.44. ^{1}H-NMR (300.15 MHz, $CDCl_3$) δ 7.68 (d, J = 9.0 Hz, 2, H-4 and 7), 7.35 (dd, J = 9.0 and 7.1 Hz , 2, H-3 and 8), 6.85 (d, J = 7.1 Hz, 2, H-2 and 9), 3.38 (m,

J = 6.7 Hz, 2, 1 and 10-CH(CH$_3$)$_2$), 1.20 (d, J = 6.7 Hz, 12, 1 and 10-CH(CH$_3$)$_2$); (300.15 MHz, CD$_3$OD) δ 7.61 (dd, ^{4}J = 0.9 Hz, 2, H-4 and 7), 7.52 (dd, 2, H-3 and 8), 7.08 (dd, ^{4}J = 0.9 Hz, 2, H-2 and 9), 3.43 (1 and 10-CH(CH$_3$)$_2$), 1.24 (d, J = 6.7 Hz, 12, 1 and 10-CH(CH$_3$)$_2$). ^{13}C-NMR (75.5 MHz, CD$_3$OD) δ 154.98 (C-5a), 150.97 (C-4a and 6a), 148.91 (C-1 and 10), 128.54 (C-3 and 8), 116.81 (C-11a), 115.66 (C-4 and 7), 110.21 (C-2 and 9), 35.00 (1 and 10-CH(CH$_3$)$_2$), 22.66 (1 and 10-CH(CH$_3$)$_2$). FT-IR (KBr) 2965, 1626, 1531 (s), 1506 (vs), 1459, 1411 (s), 1341, 1202 (vs), 1115, 1058, 858, 765 (vs), 709 (vs) cm^{-1}. UV λ_{max} nm (ϵ x 10^3, L mol^{-1} cm^{-1}): (EtOH) 373.5 (17.0), 357.5 (21.0), 307.5 (11.5), 295.0 (14.2), 272.5 (22.4), 265.0 (23.1), 245.5 (44.8). Fluorescence: λ^{em}_{max} 418 nm, Φ = 0.19 (absolute ethanol) (relative to coumarin in absolute ethanol, Φ = 0.51 at λ^{ex} = 350 nm (measured relative to the reported value of Φ = 0.64 at λ^{ex} = 366 nm[39])) (all excitations at 350 nm). EI-Mass spectrum (70 eV) m/z (rel intensity): 293 (17), 292 (83, M$^+$), 291 (15), 277 (51, M$^+$ - CH$_3$), 264 (10), 250 (58), 249 (100, M$^+$ - C$_3$H$_7$), 235 (38), 234 (26), 233 (15), 221 (13), 104 (16), 91 (14), 78 (17), 77 (25), 41 (10) amu. Calcd for $C_{18}H_{20}N_4$: C, 73.94; H, 6.90; N, 19.16. Found: C, 73.81; H, 6.74; N, 19.39.

3,8-Dimethylpyrido[1",2":1',2']imidazo[4',5':4,5]imidazo[1,2-a]pyridine (49%): mp 290 °C (dec.) (from EtOH). TLC, R_f = 0.32. ^{1}H-NMR (200.06 MHz, CD$_3$OD) δ 8.19 (d, J = 7.0 Hz, 2, H-1 and 10), 6.99 (s, 2, H-4 and 7), 6.60 (d, J = 7.0 Hz, 2, H-2 and 9), 2.25 (s, 6, 3 and 8-CH$_3$). ^{13}C-NMR (50.3 MHz, CD$_3$OD) δ 152.84 (C-5a), 147.78 (C-4a and 6a), 138.10 (C-3 and 8), 124.24 (C-1 and 10), 115.07 (C-2 and 9), 115.03 (C-11a), 114.86 (C-4 and 7), 21.62 (3 and 8-CH$_3$). FT-IR (KBr) 1639, 1587, 1510, 1482, 1395, 1299, 1231, 1198, 1161, 1148, 1058, 788, 772, 738, 650, 605 cm^{-1}. UV λ_{max} nm (ϵ x 10^3, L mol^{-1} cm^{-1}): (EtOH) 360.5 (19.6), 344 (21.4), 304 (12.0), 291 (13.9). Fluorescence: λ^{em}_{max} 394 nm, Φ = 0.58 (absolute ethanol) (relative to coumarin in absolute ethanol, Φ = 0.51 at λ^{ex} = 350 nm (measured relative to the reported value of Φ = 0.64 at λ^{ex} = 366 nm[39])) (all excitations at 350 nm). EI-Mass spectrum (70 eV) m/z (rel intensity): 237 (18), 236 (100, M$^+$), 235 (61), 221 (39), 118 (12), 92 (34), 65 (24), 32 (17) amu. Calcd for $C_{14}H_{12}N_4$: C, 71.16; H, 5.12; N, 23.72. Found: C, 70.80; H, 5.19; N, 23.54.

1,3,8,10-Tetramethylpyrido[1",2":1',2']imidazo[4',5':4,5]imidazo[1,2-a]-pyridine (38%): mp 240 °C (dec.) (from EtOH). TLC, R_f = 0.40. ^{1}H-NMR (200.06 MHz, CD$_3$OD) δ 6.87 (s, 2, H-4 and 7), 6.48 (s, 2, H-2 and 9), 2.91 (s, 6, 1 and 10-CH$_3$), 2.24 (s, 6, 3 and 8-CH$_3$). ^{13}C-NMR (50.3 MHz, CD$_3$OD) δ 154.35 (C-5a), 151.03 (C-4a and 6a), 138.59 (C-3 and 8), 136.88 (C-1 and 10), 116.25 (C-2 and 9), 115.95 (C-11a), 113.06 (C-4 and 7), 24.72 (1 and 10-CH$_3$), 20.99 (3 and 8-CH$_3$). FT-IR (KBr) 1639, 1525, 1507, 1476, 1444, 1408, 1385, 1317, 1209, 1190, 1157, 1057, 1028, 971, 964, 846, 824, 600, 565 cm^{-1}. UV λ_{max} nm (ϵ x 10^3, L mol^{-1} cm^{-1}): (EtOH) 360.5 (19.6), 344 (21.4), 304 (12.0), 291 (13.9). Fluorescence: λ^{em}_{max} 417 nm, Φ = 0.38 (absolute ethanol) (relative to coumarin in absolute ethanol, Φ = 0.51 at λ^{ex} = 350 nm (measured relative to the reported value of Φ = 0.64 at λ^{ex} = 366 nm[39])) (all excitations at 350 nm). EI-Mass spectrum (70 eV) m/z (rel intensity): 265 (24), 264 (100, M$^+$), 263 (27), 250 (18), 249 (98), 131 (12), 106 (28), 79 (25), 77 (21), 39 (11) amu. Calcd for $C_{16}H_{16}N_4$: C, 72.70; H, 6.10; N, 21.20. Found: C, 72.32; H, 6.12; N, 21.05.

1,10-Dibromopyrido[1",2":1',2']imidazo[4',5':4,5]imidazo[1,2-a]pyridine (1f). The above general procedure was used except that iodobenzene bis(trifluoroacetate) was used instead of iodobenzene diacetate, (58%): mp

195-200 °C (dec). TLC, R_f = 0.36. ^{1}H-NMR (300.15 MHz, $CDCl_3$) δ 7.72 (d, J = 8.9 Hz, 2), 7.19 (m, 4). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 155.1, 150.1, 126.1, 117.8, 117.4, 116.8, 116.2. FT-IR (KBr) 3050, 1610, 1595, 1515, 1485, 1465, 1400, 1325, 1215, 1160, 1100, 1070, 780, 765 cm^{-1}. UV λ_{max} nm (ϵ x 10^3 L mol^{-1} cm^{-1}): (EtOH) 392 (7.9), 374 (9.5), 304 (6.8), 251 (29.0). Fluorescence: No fluorescence detected (EtOH) λ^{ex} = 350.0 nm. EI-Mass spectrum (70 eV) m/z (rel intensity): 368 (17), 366 (37), 364 (17, M$^+$), 288 (16), 287 (C4), 286 (16), 285 (100), 206 (23), 158 (65), 156 (69), 144 (13), 142 (13), 115 (17), 103 (34) amu. Calcd for $C_{12}H_6N_4Br_2$: C, 39.38; H, 1.65; N, 15.31; Br, 43.66. Found: C, 39.44; H, 1.61; N, 15.12; Br, 43.30.

N-(2-Quinoxalinyl)imidazo[1,2-a]quinoxalin-2-amine (**10b**). Compound **9b** (2.0 g, 138 mmol), chloroketene diethyl acetal (4) (3.12 g, 20.7 mmol) and *p*-toluenesulfonic acid (200 mg) were combined in dry CH_3CN and stirred at room temperature for 6 h. An additional 2.0 g of **9a** was added to the reaction solution and the solution was heated to reflux for 4 h. The mixture was cooled in an ice bath and the precipitate was collected and washed with hot MeOH to afford 1.80 g (42%) of **10b**, mp > 250 °C. TLC, R_f = 0.41. ^{1}H-NMR (300.15 MHz, $(CD_3)_2SO$) δ 11.03 (s, 1, NH), 9.26 (s, 1), 9.02 (s, 1), 8.72 (s, 1), 8.59 (d, J = 8.1 Hz, 1), 8.17 (d, J = 8.2 Hz, 1), 8.06 (d, J = 8.1 Hz, 1), 7.88 (d, J = 7.9 Hz, 1), 7.78 (m, 1), 7.71 (m, 1), 7.64 (m, 1), 7.49 (m, 1). FT-IR (KBr) 3210, 3100, 3050, 3040, 3010, 1580, 1555, 1545, 1535, 1495, 1450, 1410, 1400, 1360, 1290, 1020, 880, 750 cm^{-1}. UV λ_{max} nm (ϵ x 10^3, L mol^{-1} cm^{-1}): (EtOH) 394 (17.7), 380 (sh) (16.7), 333 (9.7), 320 (9.2), 280 (28.5), 260 (25.3), 239 (28.5), 217 (34.5). EI-Mass spectrum (70 eV) m/z (rel intensity): 312 (100, M$^+$), 311 (49), 285 (17), 294 (63), 184 (21), 169 (29), 168 (17) 156 (44), 130 (30), 129 (100), 103 (70), 102 (100), 90 (74) amu. Calcd for $C_{18}H_{12}N_6$: C, 69.22; H, 3.87; N, 26.91. Found: C, 68.91; H, 3.98; N, 27.00.

Quinolino[1",2":1',2']imidazo[4',5':4,5]imidazo[1,2-a]quinoline (**2a**). Compound **2a** was prepared from **10a** by the procedure used to synthesize **1b-f**, (55%): mp > 250 °C. TLC, R_f = 0.25. ^{1}H-NMR (300.15 MHz, $CDCl_3$) δ 7.94 (m, 2), 7.75 (d, 1), 7.65 (d, 1), 7.54 (m, 2). ^{13}C-NMR (75.5 MHz, $CDCl_3$) δ 153.5, 146.5, 133.2, 128.7, 126.9, 126.7, 124.5, 124.0, 121.3, 119.2, 118.4. FT-IR (KBr) 3200, 1600, 1545, 1515, 1470, 1440, 1350, 1290, 1270, 1210, 1120, 1040, 1000, 950, 865, 800, 795, 755 cm^{-1}. UV λ_{max} nm (ϵ x 10^3, L mol^{-1} cm^{-1}): (EtOH) 400 (14.0), 379 (15.8), 358 (12.3), 250 (32.5), 228 (37.7), 208 (36.8). Fluorescence: λ^{em}_{max} 428 nm, Φ = 0.31 (absolute ethanol) (relative to coumarin in absolute ethanol, Φ = 0.51 at λ^{ex} = 350 nm (measured relative to the reported value of Φ = 0.64 at λ^{ex} = 366 nm[39]) (all excitations at 350 nm). EI-Mass spectrum (70 eV) m/z (rel intensity): 308 (100, M$^+$), 154 (28), 128 (26) amu. Calcd for $C_{20}H_{12}N_4 \cdot 0.5\ H_2O$: C, 75.70; H, 4.13; N, 17.65. Found: C, 75.49; H, 3.89; N, 17.51.

Quinoxalino[1",2":1',2']imidazo[4',5':4,5]imidazo[1,2-a]quinoxaline (**2b**). A solution of **10b** (1.0 g, 3.2 mmol in 75 mL 1,1,1,3,3,3-hexafluoro-2-propanol (HFP)) was added dropwise over 4 h to a solution of iodobenzene diacetate (2.25 g, 7.0 mmol in 75 mL of HFP) cooled to 0 °C. After the solution was stirred an additional 1 h, the solvent was removed to afford an oily red residue. Trituration of the residue with EtOAc gave a solid which was collected and washed with EtOAc to afford 510 mg (51%) of **2b**: mp > 250 °C. TLC, R_f = 0.27. ^{1}H-NMR (300.15 MHz, $CDCl_3$) δ 9.36 (s, 1), 8.29 (m, 1), 8.14 (m, 1), 7.74 (m, 2). ^{13}C-NMR (75.5 MHz, $CDCl_3$): 145.6, 141.7, 126.4, 121.1, 130.9, 128.1,

127.2, 126.6, 121.1, 120.0. IR (KBr) 3160, 1605, 1590, 1550, 1505, 1495, 1460, 1455, 1315, 1305, 1285, 1225, 1150, 1120, 1010, 910, 810, 780, 765, 750 cm^{-1}. UV λ_{max} nm ($\epsilon \times 10^3$, L mol^{-1} cm^{-1}): (EtOH) 397 (163), 380 (23.6), 364 (sh) (17.0), 254 (31.8), 244 (sh) (28.8), 228 (35.4), 208 (32.5). Fluorescence: λ^{em}_{max} 427.5 nm, Φ = 0.51 (absolute ethanol) (relative to coumarin in absolute ethanol, Φ = 0.51 at λ^{ex} = 350 nm (measured relative to the reported value of Φ = 0.64 at λ^{ex} = 366 nm[27])) (all excitations at 350 nm). EI-Mass spectrum (70 eV) m/z (rel intensity): 310 (100, M^+), 156 (17), 155 (14), 130 (13), 129 (23), 103 (20), 102 (37), 76 (18), 75 (11) amu. Calcd for $C_{18}H_{10}N_4$: C, 69.67; H, 3.25; N, 27.09. Found: C, 69.44; H, 3.30; N, 26.92.

2-Aminoquinoline (9a). 2-Chloroquinoline (10.0 g, 61.2 mmol) was placed in a steel bomb and 100 mL of formamide saturated with ammonia at 0 °C was added. The mixture was heated to 175-180 °C for 24 h. The solution was cooled to room temperature and continuously extracted with $CHCl_3$ for 24 h. The $CHCl_3$ extract was concentrated and the residue was recrystallized from H_2O to give 6.1 g (69%) of 9a, mp 128.5-130 °C (lit.[28] 129-130 °C). Calcd for $C_9H_8N_2$: C, 74.97; H, 5.59; N, 19.43. Found: C, 74.96; H, 5.49; N, 19.59.

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