Preparation and Study of Tautomers Derived from 2-(2′-Pyridyl)indole and Related Compounds

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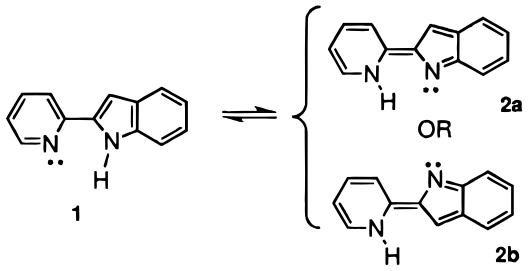
Methylation of 2-(2′-pyridyl)indole provides the corresponding N-methylated salt that undergoes deprotonation with mild base to provide the tautomeric (*E*)-1-methyl-2-(2′-indolenylidene)-1,2-dihydropyridine, whose geometry is established through a NOE experiment. Bridging at the 3,3′-positions leads to tautomers having the opposite stereochemistry. A benzo-fused analogue exhibits similar behavior as does 2-(2′-quinolinyl)pyrrole. The importance of the connectivity to pyridine is examined by considering three possible regioisomers, only two of which show tautomeric behavior. The tautomers show strong solvatochromic dependence and good linear behavior. The indoles absorb at shorter wavelengths and are strongly emitting while the tautomers show a strong bathochromic shift and emit only weakly; the salts exhibit intermediate behavior. NMR properties are consistent with contributions from a dipolar and uncharged resonance form while MO calculations indicate that the indole is about 40 kcal/mol more stable than its tautomer.

Introduction

The photophysical behavior of a number of heteroaromatic systems is dominated by changes in the acid and base character of the excited state. One manifestation of this behavior is photoinduced proton transfer, and we have recently been studying these effects as they apply to the 2-(2′-pyridyl)indole molecule (**1**).[1] Intramolecular proton transfer can be assisted by alcohol solvents, and the involvement of indole tautomers such as **2** became of interest. This ring system appears to be as yet unreported, although related species involving 4′-pyridyl substituents[2] or 3-substituted indoles[3] are known.

Molecules such as **1** are of particular interest because of the complementary juxtaposition of the pyridine and pyrrole rings. Pyridine is π-deficient but exhibits Lewis basicity because of its available lone-pair electrons. As such, it is a good H-bond acceptor. Pyrrole or indole, on the other hand, is π-excessive and exhibits increased reactivity toward electrophiles. It is comparably nonbasic and a good H-bond donor. The juxtaposition of these two nuclei in a 1,4-relationship is particularly interesting in that the two centers can potentially be interacting. To inhibit the tautomerization between **1** and **2**, we chose to investigate the corresponding *N*-methylpyridinium compounds that could lead to methylated analogues of **2** incapable of simple tautomeric reversion. This paper will report the results of that study.



Results and Discussion

Treatment of **1** with excess methyl iodide in acetonitrile leads to formation of the corresponding pyridinium salt **3** in 73% yield. When **3** is treated with ammonium hydroxide, a red solid is obtained in 53% yield, which showed an ^{1}H NMR similar to the starting salt but with a general upfield shift of all resonances. In accordance with the appearance of 13 signals in the ^{13}C NMR, the material was identified as the indole tautomer **4**. Possible ambiguity with respect to stereochemistry about the double bond was resolved by an NOE experiment in which irradiation of the *N*-methyl peak at 4.56 ppm showed an enhancement of H_3 at 7.23 ppm, which would only be possible for the trans isomer. This result implies that deprotonation occurs from the transoid conformer of **3** in which the N−H is sterically more accessible to the base.

The tautomeric analogue of **4** was prepared from the 1-methyl-1-phenylhydrazone of 2-acetylpyridine (**5**) by a straightforward application of the Fisher indole synthesis.[4] If methyl group migration were possible, one might imagine that **4** could revert back to the indole form and

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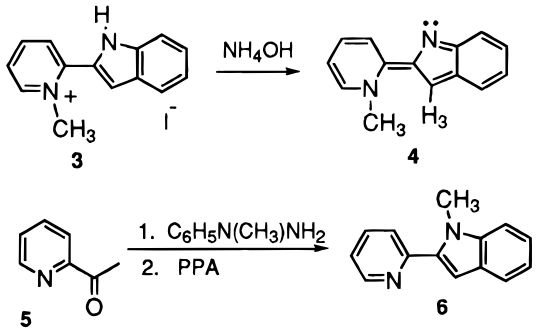
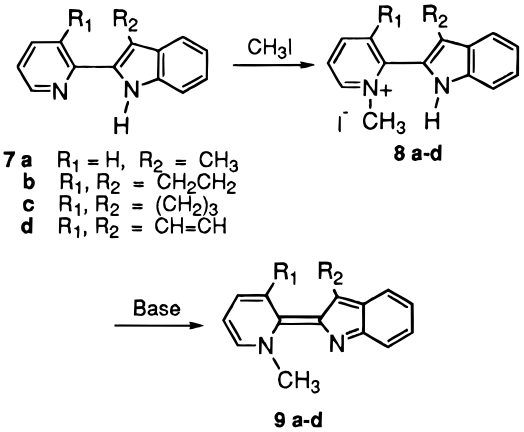
thus provide the tautomeric structure **6**. No evidence for such tautomeric reversion has been observed under thermal or photochemical conditions.



3 **4** **5** **6**

To better evaluate the factors influencing formation of the trans isomer as well as the propensity for tautomeric reversion, 3-methyl-2-(2′-pyridyl)indole (**7a**) was next prepared by treatment of the phenylhydrazone of 2-propionylpyridine with PPA.[5] Steric interaction between the methyl groups of the corresponding *N*-methylpyridinium salt (**8a**) should favor the cisoid conformation of this species. Thus, deprotonation of **8a** led to a 51% yield of **9a** having the opposite stereochemistry from **4** as determined by the upfield shift of $H_{3'}$ as compared with the same resonance for **4** where this proton is deshielded by the lone pair electrons of the indolylidene nitrogen (see Table 3).

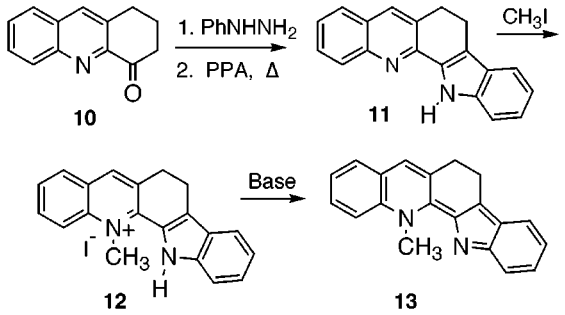
Bridging the 3,3′-positions of 2-(2′-pyridyl)indole can accomplish the same geometric restriction. We have previously reported the preparation of 3,3′-polymethylene-bridged indoles **7b**,**c**,[6] which can be methylated to afford the salts **8b**,**c**. Deprotonation of these salts then provides the indole tautomers **9b**,**c**. Additional conjugation between the pyridine and indole, which results from incorporating an unsaturated bridge, does not alter the course of the reaction. The dimethylene-bridged indole **7b** may be dehydrogenated by refluxing with 10% Pd/C in nitrobenzene. The resulting pyridocarbazole **7d**[7] may be methylated to **8d**, and deprotonation with ammonium hydroxide provides a 79% yield of the fully conjugated indole tautomer **9d**.



7 a $R_1 = H$, $R_2 = CH_3$
b $R_1, R_2 = CH_2CH_2$
c $R_1, R_2 = (CH_2)_3$
d $R_1, R_2 = CH{=}CH$

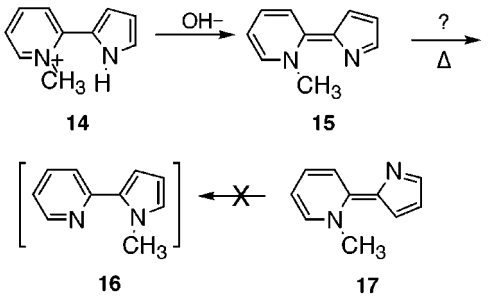
8 a-d **9 a-d**

A benzo-fused analogue of **7b** was prepared by Fischer indolization of 1,2,3,4-tetrahydroacridin-4-one,[8] affording 12,13-dihydro-5*H*-indolo[3,2-*c*]acridine (**11**) in 70% yield. Methylation of **11** provided the quinolinium salt **12**, which upon deprotonation gave the indole tautomer **13** in 48% yield.



10 **11** **12** **13**

It became of interest to see if the same tautomerism would be evidenced by pyridylpyrrole derivatives. There is a brief report that indicates that the *N*-methylpyridinium salt **14** of the parent system, 2-(2′-pyridyl)pyrrole, deprotonates to form the corresponding tautomer **15**.[9] The Russian workers further indicate that heating this tautomer promotes methyl migration to provide the *N*-methylpyrrole derivative **16**. This migration would require the *cis*-geometry as they indicate for **15**, which is, however, not in accord with what we have observed for **4**. The more favorable proton abstraction from the less hindered transoid conformation of **14** should lead to the trans isomer **17** for which methyl migration would be even more unlikely.



14 **15** **16** **17**

The described synthesis of the 2-(2′-pyridyl)pyrrole precursor to **14** appeared quite tedious.[10] Instead, we prepared the analogous 2-(2′-quinolinyl)pyrrole (**20a**) by the direct Friedländer condensation of 2-aminobenzaldehyde with 2-acetylpyrrole.[11] Subsequent methylation provided the salt **21**, which underwent deprotonation to the pyrrole tautomer **23**. The question of stereochemistry in **23** was established by a NOE experiment in which irradiation of the *N*-methyl group showed enhancement of both H_8 and $H_{3'}$. Thus, we are inclined to believe that the deprotonation product from **14** was, in fact, **17** and that thermal isomerization to **16** did not occur. We have not observed thermal or photochemical methyl migration even in systems such as **9a**−**d**, which are constrained to a cis conformation.

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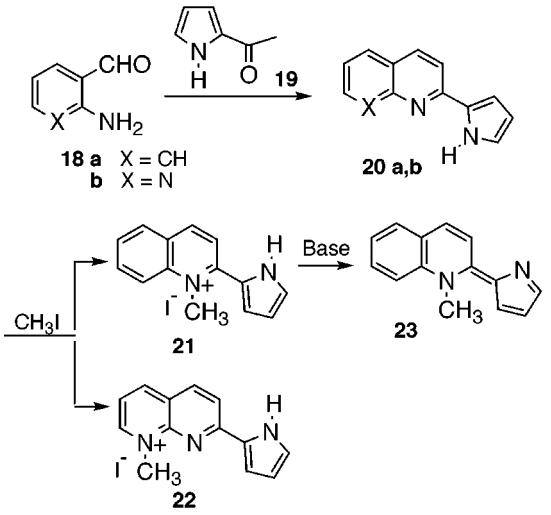
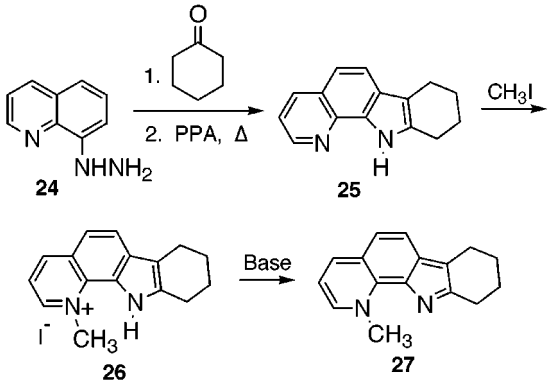
An analogous Friedländer condensation using 2-aminonicotinaldehyde provided the 2-(2′-[1,8]naphthyridyl) derivative **20b**, which preferentially methylated at the 8-position, providing the salt **22**. Attempted deprotonation of this salt led to unstable material that could not be characterized.

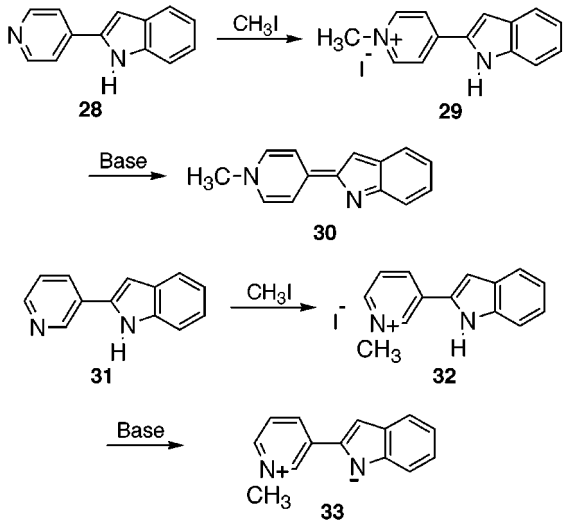


A tetrahydro derivative of **7d** could be prepared from the PPA-promoted Fisher indolization of the 8-quinolinehydrazone of cyclohexanone, thus affording **25**. The aromatic nucleus of **25** is related to 2-(2′-pyridyl)pyrrole in the same way that 1,10-phenanthroline is related to 2,2′-bipyridine. Methylation provided the salt **26**, and deprotonation led smoothly to the tautomer **27**.



The position of substitution on the pyridine ring of **1** is important in determining the tautomeric nature of the corresponding pyridyl indole. Previous workers have examined the 4-pyridyl and 3-pyridyl isomers **28** and **31** and observed that the former tautomerizes readily[2] while the latter does not. We repeated their work to have information on the series of three isomers, **1**, **28**, and **31**. Fisher indolization of the phenylhydrazones derived from 4- and 3-acetylpyridine provided the pyridylindoles **28** and **31**, which could be methylated with methyl iodide to the corresponding pyridinium salts **29** and **32**. Deprotonation of **29** proceeded smoothly to afford the tautomer **30**, but similar reaction of **32** could only be accomplished under more severe conditions and the dipolar product **33** was stable only for minutes in DMSO-d_6 where its NMR spectrum could be determined.

The electronic absorption spectra of the pyridylindoles, their pyridinium salts, and the indole tautomers are of



interest since they exhibit a progressive bathochromic shift of the longest wavelength band (Figure 1). This shift can be associated with a decrease in the $\pi-\pi^*$ HOMO−LUMO gap reflected by an increase in the total energy of the system. More subtle structural influences on the stability of the indole tautomers are reflected by their absorption maxima as recorded in Table 1. The two methyl groups in **9a** cause a slight twisting about the 2,2′-bond, diminishing delocalization and shifting the band to higher energy relative to **4**. The dimethylene bridge in **9b** forces coplanarity and has the opposite effect. Dehydrogenation of the bridge considerably increases delocalization and flattening of the system to cause a 30 nm bathochromic shift for **9d**, while approximately the same shift is observed for **13**, which is a benzo-fused analogue of **9b**.

The indole tautomers exhibit solvatochromic behavior. In less polar solvents, the uncharged form of the tautomer is favored. This species exhibits a lower energy or longer wavelength electronic absorption. For **9b** in hexane, this value is about 446 nm. In more polar solvents, the dipolar resonance form assumes greater importance and the absorption maximum shifts to higher energy or shorter wavelength, around 408 nm for **9b** in DMSO. Plotting the absorption maxima vs the polarity index of the solvent shows approximately linear behavior (Figure 2).

A unique and important property of the indole nucleus is its ability to fluoresce. Table 2 lists the emission

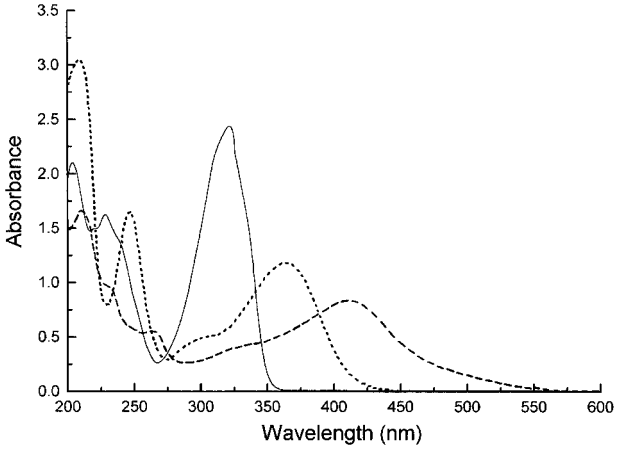


Figure 1. Electronic absorption spectra for **1**, **3**, and **4** (8×10^{-5} M in CH_3CN): **1** (—), **3** (···), **4** (- -).

Table 1. Long-Wavelength Electronic Absorption Maxima for Pyridylindole Derivatives[a]

indole	λ_{max}	salt	λ_{max}	tautomer	λ_{max}
1	321 (4.36)	**3**	364 (4.10)	**4**	411 (3.96)
7a	328 (4.24)	**8a**	360 (3.82)	**9a**	389 (3.65)
7b	337 (4.36)	**8b**	389 (4.39)	**9b**	414 (4.35)
7c	328 (4.39)	**8c**	374 (4.10)	**9c**	410 (3.94)
7d	339 (3.67)	**8d**	383 (3.98)	**9d**	444 (3.76)
11	377 (4.38)	**12**	432 (4.51)	**13**	450 (4.39)
20a	350 (4.36)	**21**	401 (4.32)	**23**	444 (4.28)
20b	364 (4.37)	**22**	429 (4.32)		
25	350 (3.57)	**26**	408 (4.01)	**27**	486 (3.93)
28	321 (4.42)	**29**	381 (4.44)	**30**	432 (4.21)
31	311 (4.36)	**32**	324 (4.29)		

[a] 8×10^{-5} M in CH_3CN; λ_{max} in nm and log ϵ in parentheses.

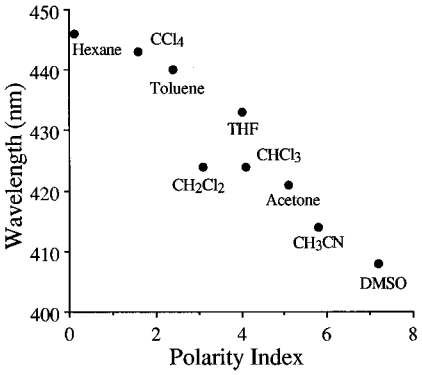


Figure 2. Solvatochromic behavior for indole tautomer **9b** (8×10^{-5} M).

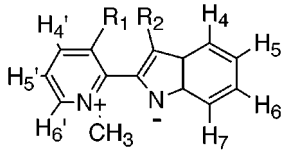
Table 2. Emission Maxima for Pyridylindole Derivatives[a]

indole[b]	λ_{max}	salt	λ_{max}
1	376 (676)[c]	**3**	506 (s)[e]
7a	399 (247)	**8a**	419 (m)
7b	404 (711)	**8b**	543 (w)
7c	389 (85)	**8c**	541 (m)
7d	423 (110)	**8d**	551 (m)
11	434 (449)	**12**	541 (s)
20a	424 (371)	**21**	447 (m)
20b	452 (267)	**22**	515 (m)
25	422 (10)	**26**	504 (s)
28	384[d]	**29**	508 (w)
31	385 (722)	**32**	424 (w)

[a] 8×10^{-5} M in CH_3CN. [b] Excited at long-wavelength band where absorbance = 1.00. [c] λ in nm and relative intensity in parentheses. [d] Relative intensity more than 1000. [e] λ in nm; due to wide variation, relative intensities are qualitative.

maxima for the indoles and their salts. The emission intensity is strongest for the parent indoles, less for the salts, and very weak for the tautomers. Of the indoles, the most intense emissions are for the 2-pyridylindoles, **1**, **28**, and **31**. The weakest emission is for **25**, which could also be viewed as a pyrroloquinoline derivative.

Table 3 presents a comparison of the ^{1}H NMR chemical shift data for indole tautomers **4** and **9a**−**d**. Two interesting features are in evidence. The $H_{3'}$ proton of **4** is shifted downfield due to deshielding by the lone pair electrons on the indole nitrogen. The indole tautomers are expected to evidence considerable double-bond character for the 2−2′ bond, which connects the two cyclic portions of the molecule. One can write a dipolar resonance form **34** for this species, which would decrease



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this double bond character while accumulating positive charge on the pyridinium ring and negative charge on the indole. It is expected that factors that tend to force the two rings out of coplanarity would favor the contribution of this resonance form, and such an increased contribution might be reflected in the chemical shifts of the protons on the respective rings. In comparing the tautomers **4** and **9a**, this effect becomes evident in that the pyridine ring protons, $H_{4'}$−$H_{6'}$, are shifted downfield 0.06−0.10 ppm while the indole protons, H_4−H_7, are shifted upfield 0.13−0.18 ppm. Furthermore, as we proceed along the series **9b**, **9c**, **9a**, we expect the dihedral angle between the rings to increase and we do observe a downfield trend for all four protons in the pyridine ring along this series. A corresponding upfield shift is not as clearly evidenced for the indole protons possibly due to the greater localization of the negative charge on the pyrrole moiety.

Molecular orbital calculations[12] were carried out at the Hartree−Fock level using the 3-21G basis set[13] on the isomeric structures **4** and **6** to assess the importance of resonance stabilization in **6** versus the planarity and delocalization exhibited by **4**. The difference in total energies between these two isomers was 39.84 kcal/mol, favoring the pyridylindole. The cisoid form of **4** was found to be more stable than the transoid isomer by about 2.96 kcal/mol, indicating that the deprotonation is kinetically controlled. This difference is comparable to the difference in energies between the two planar conformers of **6** where the transoid species is 4.26 kcal/mol higher in energy.

Experimental Section

Nuclear magnetic resonance spectra were obtained at 300 MHz for ^{1}H and 75 MHz for ^{13}C. Melting points were measured with a capillary melting point apparatus and are not corrected. Elemental analyses were performed by National Chemical Consulting, Inc., Tenafly, NJ. The indole tautomers were not sufficiently stable to allow combustion analysis; their NMR (excepting ^{13}C for **9a**,**c**) spectra are contained in the Supporting Information.

The pyridylindoles **1**, **6**, and **7b**,**c**,[1a,6] 4-oxo-1,2,3,4-tetrahydroacridine (**10**),[8] and 8-hydrazinoquinoline (**24**)[14] were prepared according to previously described procedures. The 2-(2′-pyridyl)-3-methylindole (**7a**) was prepared according to the method of Bradsher and Litzinger,[5] the 2-aminobenzaldehyde (**18a**) was prepared according to the method of Opie and Smith,[15] and the 2-aminonicotinaldehyde (**18b**) was prepared according to the method of Majewicz and Caluwe.[16]

(12) Gaussian 94, Rev. B.1: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Kieth, T.; Peterson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Comperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A. Gaussian, Inc., Pittsburgh, PA, 1995.

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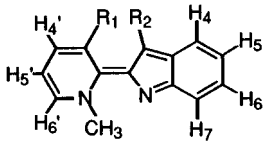
(15) Opie, J. W.; Smith, L. I. *Organic Syntheses*; Wiley: New York, 1955; Collect. Vol. III, p 56.

Table 3. ^{1}H NMR Chemical Shift Data for Indole Tautomers[a]



compd	H3′	H4′	H5′	H6′	H3	H4	H5	H6	H7	NCH_3	bridge
4,[b] R_1 = H3′, R_2 = H3	8.52	8.22	7.59	8.66	7.23	7.53	6.81	6.99	7.41	4.56	
9a, R_1 = H3′, R_2 = CH_3	8.00	8.28	7.66	8.76		7.38	6.68	6.81	7.28	4.52	2.43 (CH_3)
9b, R_1, R_2 = CH_2CH_2		7.90	7.19	8.21		7.36	6.65	6.82	7.31	4.79	3.03, 2.97
9c, R_1, R_2 = $(CH_2)_3$		8.23	7.57	8.64		7.42	6.69	6.85	7.33	4.59	2.80, 2.58, 2.21
9d, R_1, R_2 = CH═CH		8.98	7.77	8.98		7.76	7.06	7.32	7.47	5.39	8.53, 8.21

[a] Recorded in DMSO-d_6 at 25 °C. Chemical shifts reported in ppm downfield from Me_4Si. [b] Reverse stereochemistry about NC═CN.

1-Methyl-2-(2′-indolyl)pyridinium Iodide (3). A mixture of 2-(2′-pyridyl)indole (**1**, 4.0 g, 20.6 mmol) and methyl iodide (8.8 g, 61.8 mmol) in acetonitrile (50 mL) was refluxed for 19 h. After cooling, a precipitate was collected and dried to afford **3** as a brown solid (5.1 g, 73%), which was recrystallized from water: mp 227−9 °C; ^{1}H NMR (DMSO-d_6) δ 12.13 (s, 1H, NH), 9.10 (d, 1H, J = 5.7 Hz, H_6), 8.63 (t, 1H, J = 7.7 Hz, H_4), 8.31 (d, 1H, J = 8.1 Hz, H_3), 8.04 (t, 1H, J = 6.6 Hz, H_5), 7.74 (d, 1H, J = 8.1 Hz, $H_{4'}$), 7.56 (d, 1H, J = 8.4 Hz, $H_{7'}$), 7.38 (s, 1H, $H_{3'}$), 7.33 (t, 1H, J = 7.7 Hz, $H_{6'}$), 7.16 (t, 1H, J = 7.5 Hz, $H_{5'}$), 4.47 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6) δ 147.1, 147.0, 144.5, 137.7, 128.7, 127.3, 126.6, 125.3, 124.9, 121.7, 120.6, 112.2, 110.0, 47.9. Anal. Calcd for $C_{14}H_{13}N_2I$: C, 50.00; H, 3.87; N, 8.33. Found: C, 50.12; H, 3.83; N, 8.20.

1-Methyl-2-(2′-indolenylidene)-1,2-dihydropyridine (4). A mixture of 1-methyl-2-(2′-indolyl)pyridinium iodide (**3**, 1.0 g, 3.0 mmol) and sodium acetate (2.0 g) in water (40 mL) was heated to dissolve completely. After the mixture was cooled to room temperature, ammonium hydroxide (10 mL) was added, and the solution was stirred for 10 min. The solution was then extracted with CH_2Cl_2 (3 × 50 mL). The organic layer was dried over anhydrous Na_2CO_3, and the solvent was evaporated to afford **4** as a red solid (0.33 g, 53%): mp 56 °C dec; ^{1}H NMR (DMSO-d_6) δ 8.66 (d, 1H, J = 6.0 Hz, H_6), 8.52 (d, 1H, J = 8.4 Hz, H_3), 8.22 (t, 1H, J = 7.7 Hz, H_4), 7.59 (t, 1H, J = 6.5 Hz, H_5), 7.53 (d, 1H, J = 7.8 Hz, $H_{4'}$), 7.41 (d, 1H, J = 8.1 Hz, $H_{7'}$), 7.23 (s, 1H, $H_{3'}$), 6.99 (t, 1H, J = 7.5 Hz, $H_{6'}$), 6.81 (t, 1H, J = 7.4 Hz, $H_{5'}$), 4.56 (s, 3H, CH_3); ^{13}C NMR (DMSO-d_6) δ 151.1, 145.5, 142.0, 133.7, 129.8, 128.1, 121.9, 121.13, 121.06, 118.3, 116.6, 108.3, 108.2, 47.8; MS *m*/*z* 208 (M^+), 193 (M − 15).

11*H*-Pyrido[2,3-*a*]carbazole (7d). A mixture of 10,11-dihydro-5*H*-pyrido[2,3-*a*]carbazole (**7b**, 0.78 g, 3.5 mmol) and 10% Pd/C (0.10 g) in nitrobenzene (6 mL) was heated to 170−5 °C for 4 h. An additional 10% Pd/C (0.10 g) and nitrobenzene (3 mL) were added and the mixture was stirred overnight at 170−5 °C. The reaction mixture was cooled to room temperature and filtered. The filtered solid was washed with CH_2Cl_2 (5 × 5 mL), and the filtrate and washings were combined. The solvent was evaporated, and the residue was chromatographed on alumina (24 g), eluting with benzene and then EtOAc. Nitrobenzene and aniline were eluted with the benzene fraction. A slightly brown solid (0.59 g, 77%), obtained from the EtOAc fraction, was recrystallized from EtOH to afford **7d**: mp 164−5 °C (lit.[7] mp 172−3 °C); ^{1}H NMR ($CDCl_3$) δ 10.93−10.77 (bs, 1H, NH), 8.96 (dd, 1H, H_2), 8.37 (d, 1H, J = 8.1 Hz, H_4), 8.25 (d, 1H, J = 8.4 Hz, H_6), 8.18 (d, 1H, J = 7.8 Hz, H_7), 7.62 (d, 1H, J = 8.4 Hz, H_{10}), 7.54−7.48 (overlapping, 2H, H_3 and H_5), 7.46 (t, 1H, J = 7.8 Hz, H_9), 7.33 (t, 1H, J = 7.4 Hz, H_8).

1-Methyl-2-[2′-(3′-methylindolyl)]pyridinium Iodide (8a). Following the procedure described for **3**, 2-(2′-pyridyl)-3-methylindole (**7a**, 2.4 g, 11.5 mmol) was treated with methyl iodide (4.9 g, 34.5 mmol) for 22 h to afford **8a** as a brown solid (1.29 g, 32%): mp 207−9 °C; ^{1}H NMR (DMSO-d_6) δ 11.50 (s, 1H, NH), 9.21 (d, 1H, J = 6.0 Hz, H_6), 8.67 (t, 1H, J = 7.8 Hz, H_4), 8.24 (d, 1H, J = 7.8 Hz, H_3), 8.19 (t, 1H, J = 6.9 Hz, H_5), 7.69 (d, 1H, J = 8.1 Hz, $H_{4'}$), 7.50 (d, 1H, J = 8.1 Hz, $H_{7'}$), 7.30 (t, 1H, J = 7.7 Hz, $H_{6'}$), 7.14 (t, 1H, J = 7.4 Hz, $H_{5'}$), 4.23 (s, 3H, N−CH_3), 2.31 (s, 3H, C−CH_3); ^{13}C NMR (DMSO-d_6) δ 147.4, 147.3, 145.0, 136.9, 131.1, 127.5, 126.7, 124.3, 123.8, 119.9, 119.8, 115.2, 112.0, 47.0, 9.2. Anal. Calcd for $C_{14}H_{13}N_2I\cdot 0.25H_2O$: C, 50.77; H, 4.37; N, 7.90. Found: C, 50.79; H, 4.09; N, 7.53.

1-Methyl-3,3′-dimethylene-2-(2′-indolyl)pyridinium Iodide (8b). Following the procedure described for **3**, 3,3′-dimethylene-2-(2′-pyridyl)indole (**7b**, 1.51 g, 6.9 mmol) was treated with methyl iodide (2.94 g, 20.7 mmol) for 20 h to afford **8b** as a brown solid (1.99 g, 80%): mp 280−2 °C; ^{1}H NMR (DMSO-d_6) δ 11.61 (s, 1H, NH), 8.67 (d, 1H, J = 6.0 Hz, H_6), 8.34 (d, 1H, J = 7.5 Hz, H_4), 7.75−7.69 (overlapping, 2H, H_5 and $H_{4'}$), 7.62 (d, 1H, J = 8.4 Hz, $H_{7'}$), 7.36 (t, 1H, J = 7.7 Hz, $H_{6'}$), 7.16 (t, 1H, J = 7.5 Hz, $H_{5'}$), 4.56 (s, 3H, N−CH_3), 3.16 (t, 2H, J = 6.6 Hz, 3-CH_2), 3.06 (t, 2H, J = 6.9 Hz, 3′-CH_2); ^{13}C NMR (DMSO-d_6) δ 144.1, 143.6, 142.0, 139.8, 137.7, 126.4, 126.2, 124.3, 124.1, 123.0, 120.8, 120.5, 113.0, 47.2, 28.9, 18.2. Anal. Calcd for $C_{16}H_{15}N_2I$: C, 53.04; H, 4.14; N, 7.73. Found: C, 53.05; H, 4.38; N, 7.63.

1-Methyl-3,3′-trimethylene-2-(2′-indolyl)pyridinium Iodide (8c). Following the procedure described for **3**, 3,3′-trimethylene-2-(2′-pyridyl)indole (**7c**, 0.20 g, 0.85 mmol) was treated with methyl iodide (2.0 g, 14 mmol) for 20 h to afford **8c** as a brown solid (0.15 g, 49%): mp 245−7 °C; ^{1}H NMR (DMSO-d_6) δ 11.67 (s, 1H, NH), 9.00 (d, 1H, J = 5.7 Hz, H_6), 8.56 (d, 1H, J = 7.8 Hz, H_4), 7.98 (t, 1H, J = 6.9 Hz, H_5), 7.77 (d, 1H, J = 7.8 Hz, $H_{4'}$), 7.56 (d, 1H, J = 8.4 Hz, $H_{7'}$), 7.33 (t, 1H, J = 7.7 Hz, $H_{6'}$), 7.16 (t, 1H, J = 7.4 Hz, $H_{5'}$), 4.38 (s, 3H, N−CH_3), 2.81 (t, 2H), 2.64 (t, 2H), 2.31 (quintet, 2H); ^{13}C NMR (DMSO-d_6) δ 147.7, 145.4, 145.0, 144.8, 142.5, 127.7, 126.0, 124.9, 123.3, 123.0, 120.0, 119.5, 112.4, 47.6, 33.2, 31.3, 19.3. Anal. Calcd for $C_{17}H_{17}N_2I$: C, 54.26; H, 4.52; N, 7.45. Found: C, 54.05; H, 4.48; N, 7.85.

1-Methyl-11*H*-pyrido[2,3-*a*]carbazolium Iodide (8d). Following the procedure described for **3**, 11*H*-pyrido[2,3-*a*]-carbazole (**7d**, 0.44 g, 2 mmol) was treated with methyl iodide (0.85 g, 6 mmol) for 20 h to afford **8d** as a brown-yellow solid (0.51 g, 71%): mp 254−6 °C; ^{1}H NMR (DMSO-d_6) δ 12.33 (s, 1H, NH), 9.37 (d, 1H, J = 5.7 Hz, H_2), 9.32 (d, 1H, J = 8.1 Hz, H_4), 8.83 (d, 1H, J = 8.7 Hz, H_6), 8.45 (d, 1H, J = 7.8 Hz, H_7), 8.13 (overlapping, 2H, H_5 and H_3), 7.92 (d, 1H, J = 8.1 Hz, H_{10}), 7.67 (t, 1H, J = 7.6 Hz, H_9), 7.43 (t, 1H, J = 7.6 Hz, H_8), 5.08 (s, 3H, N−CH_3); ^{13}C NMR (DMSO-d_6) δ 147.7, 147.6, 146.2, 140.5, 129.1, 128.9, 128.1, 126.8, 126.0, 123.4, 120.9, 120.8, 120.5, 120.1, 112.8, 48.9. Anal. Calcd for $C_{16}H_{13}N_2I$: C, 53.33; H, 3.61; N, 7.78. Found: C, 53.34; H, 3.49; N, 7.40.

1-Methyl-2-[2′-(3′-methylindolenylidene)]-1,2-dihydropyridine (9a). To a solution of 1-methyl-2-[2′-(3′-methylindolyl)]pyridinium iodide (**8a**, 0.35 g, 1.0 mmol) in water (10 mL) was added cold 5% KOH solution (40 mL), and the mixture was stirred for 10 min. The solution was extracted with CH_2Cl_2 (3 × 50 mL), and the organic layer was dried over anhydrous Na_2CO_3. The solvent was evaporated to afford a red solid **9a** (0.11 g, 51%): mp 55 °C dec; ^{1}H NMR (DMSO-d_6) δ 8.76 (d, 1H, J = 6.3 Hz, H_6), 8.28 (t, 1H, J = 7.7 Hz, H_4),

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8.00 (d, 1H, J = 8.1 Hz, H_3), 7.66 (t, 1H, J = 6.6 Hz, H_5), 7.38 (d, 1H, J = 8.1 Hz, $H_{4'}$), 7.28 (d, 1H, J = 8.1 Hz, $H_{7'}$), 6.81 (t, 1H, J = 7.4 Hz, $H_{6'}$), 6.68 (t, 1H, J = 7.2 Hz, $H_{5'}$), 4.52 (s, 3H, NCH_3), 2.43 (s, 3H, CCH_3); MS m/z 222 (M^+), 208 (M − 14).

1-Methyl-3,3′-dimethylene-2-(2′-indolenylidene)-1,2-dihydropyridine (9b). Following the procedure described for **4**, 1-methyl-3,3′-dimethylene-2-(2′-indolyl)pyridinium iodide (**8b**, 0.30 g, 0.8 mmol) was treated with ammonium hydroxide (10 mL) to afford **9b** as a red solid (0.12 g, 62%): mp 45 °C dec; ^{1}H NMR (DMSO-d_6) δ 8.21 (d, 1H, J = 6.3 Hz, H_6), 7.90 (d, 1H, J = 7.5 Hz, H_4), 7.36 (d, 1H, J = 8.1 Hz, $H_{4'}$), 7.31 (d, 1H, J = 8.1 Hz, $H_{7'}$), 7.19 (t, 1H, J = 6.9 Hz, H_5), 6.82 (t, 1H, J = 7.4 Hz, $H_{6'}$), 6.65 (t, 1H, J = 7.4 Hz, $H_{5'}$), 4.79 (s, 3H, NCH_3), 3.03 (t, 2H, J = 6.6 Hz, 3-CH_2), 2.97 (t, 2H, J = 6.9 Hz, 3′-CH_2); ^{13}C NMR (DMSO-d_6) δ 151.0, 148.7, 142.0, 138.4, 137.1, 135.5, 126.9, 122.8, 121.3, 119.6, 119.4, 118.4, 116.3, 47.0, 30.5, 19.8; MS m/z 234 (M^+).

1-Methyl-3,3′-trimethylene-2-(2′-indolenylidene)-1,2-dihydropyridine (9c). Following the procedure described for **4**, 1-methyl-3,3′-trimethylene-2-(2′-indolyl)pyridinium iodide (**8c**, 75 mg, 0.2 mmol) was treated with ammonium hydroxide (10 mL) to afford **9c** as a red solid (31 mg, 63%): mp 43 °C dec; ^{1}H NMR (DMSO-d_6) δ 8.64 (d, 1H, J = 6.0 Hz, H_6), 8.23 (d, 1H, J = 7.5 Hz, H_4), 7.57 (t, 1H, J = 6.9 Hz, H_5), 7.42 (d, 1H, J = 7.8 Hz, $H_{4'}$), 7.33 (d, 1H, J = 8.1 Hz, $H_{7'}$), 6.85 (t, 1H, J = 7.4 Hz, $H_{6'}$), 6.69 (t, 1H, J = 7.4 Hz, $H_{5'}$), 4.59 (s, 3H, NCH_3), 2.80 (t, 2H), 2.58 (t, 2H), 2.21 (quintet, 2H); MS m/z 248 (M^+), 234 (M − 14).

1-Methyl-3,3′-ethenyl-2-(2′-indolenylidene)-1,2-dihydropyridine (9d). Following the procedure described for **4**, 1-methyl-11*H*-pyrido[2,3-*a*]carbazolium iodide (**8d**, 0.22 g, 0.6 mmol) was treated with ammonium hydroxide (10 mL) to afford **9d** as a red solid (0.11 g, 79%): mp 162 °C dec; ^{1}H NMR (DMSO-d_6) δ 8.99−8.96 (overlapping, 2H, H_4 and H_6), 8.53 (d, 1H, J = 8.1 Hz, 3′-CH), 8.21 (d, 1H, J = 8.1 Hz, $H_{4'}$), 7.80−7.74 (overlapping, 2H, H_5 and 3-CH), 7.47 (d, 1H, J = 8.1 Hz, $H_{7'}$), 7.32 (t, 1H, J = 7.5 Hz, $H_{6'}$), 7.06 (t, 1H, J = 7.4 Hz, $H_{5'}$), 5.39 (s, 3H, NCH_3); ^{13}C NMR (DMSO-d_6) δ 152.2, 143.2, 142.9, 139.7, 132.4, 129.0, 127.2, 123.9, 123.6, 123.3, 119.8, 118.5, 116.7, 116.3, 111.2, 49.7; MS m/z 232 (M^+), 218 (M − 14).

12,13-Dihydro-5*H*-indolo[3,2-*c*]acridine (11). A mixture of 1,2,3,4-tetrahydroacridin-4-one (**10**, 1.10 g, 5.6 mmol), phenylhydrazine (0.65 g, 6.0 mmol), and acetic acid (1 drop) in absolute EtOH (50 mL) was refluxed for 2 h. After cooling, the phenylhydrazone as an orange solid was collected (1.02 g, 64%): mp 92−3 °C; ^{1}H NMR ($CDCl_3$) δ 8.03 (d, 1H, J = 8.4 Hz, H_5), 7.93 (s, 1H, H_9), 7.72 (d, 1H, J = 7.8 Hz, H_8), 7.68 (t, 1H, J = 6.9 Hz, H_6), 7.51 (t, 1H, J = 7.4 Hz, H_7), 7.32 (d, 2H, J = 4.2 Hz, *o*-Ph), 7.31 (t, 2H, J = 4.2 Hz, *m*-Ph), 7.35−7.31 (bs, 1H, NH), 6.87 (m, 1H, *p*-Ph), 3.03 (t, 2H, J = 6.0 Hz, H_3), 2.93 (t, 2H, J = 6.0 Hz, H_1), 2.06 (m, 2H, H_2).

After polyphosphoric acid (PPA, 15 g) was heated at 150 °C for 10 min and cooled to 120 °C, the phenylhydrazone of 1,2,3,4-tetrahydroacridin-4-one (7.20 g, 25.0 mmol) was added, and the mixture was stirred for 30 min. The mixture was then cooled, made basic with 50% NaOH solution, and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$. The solvent was evaporated to afford **11** as a brown yellow solid (4.76 g, 70%), which was recrystallized from EtOH: mp 202−3 °C; ^{1}H NMR ($CDCl_3$) δ 10.07 (bs, 1H, NH), 8.02 (d, 1H, J = 8.4 Hz, H_7), 7.91 (s, 1H, H_{11}), 7.73 (d, 1H, J = 8.4 Hz, H_{10}), 7.61−7.54 (overlapping, 2H, H_8 and H_1), 7.44 (t, 1H, J = 7.8 Hz, H_9), 7.21−7.09 (overlapping, 3H, H_4, H_3 and H_2), 3.31 (t, 2H, J = 6.9 Hz, H_{12}), 3.15 (t, 2H, J = 6.9 Hz, H_{13}). Anal. Calcd for $C_{19}H_{14}N_2$: C, 84.44; H, 5.19; N, 10.37. Found: C, 84.69; H, 5.30; N, 10.17.

6-Methyl-12,13-dihydro-5*H*-indolo[3,2-*c*]acridinium Iodide (12). A mixture of 12,13-dihydro-5*H*-indolo[3,2-*c*]acridine (**11**, 0.35 g, 1.3 mmol) and methyl iodide (2.5 g, 17.6 mmol) in CH_3CN (10 mL) was refluxed for 24 h. Additional methyl iodide (2.5 g, 17.6 mmol) was added, and reflux was continued an additional 24 h. A brown solid formed (0.11 g, 21%), which was recrystallized from H_2O to afford **12**: mp 264−6 °C; ^{1}H NMR (DMSO-d_6) δ 12.00 (bs, 1H, NH), 8.84 (s, 1H, H_{11}), 8.49 (d, 1H, J = 8.7 Hz, H_7), 8.19 (d, 1H, J = 7.8 Hz, H_{10}), 8.07 (t, 1H, J = 7.7 Hz, H_8), 7.89−7.83 (overlapping, 2H, H_1 and H_9), 7.66 (d, 1H, J = 8.4 Hz, H_4), 7.46 (t, 1H, J = 7.7 Hz, H_3), 7.22 (t, 1H, J = 7.4 Hz, H_2), 4.68 (s, 3H, N−CH_3), 3.26−3.18 (overlapping, 4H, H_{12} and H_{13}); ^{13}C NMR (DMSO-d_6) δ 147.5, 140.8, 140.6, 138.7, 133.8, 133.5, 131.5, 129.0, 128.6, 128.0, 126.8, 125.2, 124.5, 121.3, 121.2, 118.9, 113.2, 41.9, 28.8, 18.7. Anal. Calcd for $C_{20}H_{17}N_2I$: C, 58.25; H, 4.13; N, 6.80. Found: C, 58.59; H, 4.04; N, 7.07.

1-Methyl-3,3′-dimethylene-2-(2′-indolenylidene)-1,2-dihydroquinoline (13). Following the procedure described for **4**, 6-methyl-12,13-dihydro-5*H*-indolo[3,2-*c*]acridinium iodide (**12**, 89 mg, 0.22 mmol) was treated with ammonium hydroxide (10 mL) to afford **13** as a red solid (29 mg, 48%): mp 72−4 °C dec; ^{1}H NMR (DMSO-d_6) δ 8.28 (s, 1H, H_4), 8.10 (d, 1H, J = 8.7 Hz, H_8), 7.91 (d, 1H, J = 7.5 Hz, H_5), 7.83 (t, 1H, J = 8.0 Hz, H_7), 7.60 (t, 1H, J = 7.5 Hz, H_6), 7.41 (d, 1H, J = 8.1 Hz, $H_{4'}$), 7.33 (d, 1H, J = 8.7 Hz, $H_{7'}$), 6.91 (t, 1H, J = 7.4 Hz, $H_{6'}$), 6.68 (t, 1H, J = 7.4 Hz, $H_{5'}$), 5.22 (s, 3H, N−CH_3), 3.13−3.05 (overlapping, 4H, CH_2CH_2); ^{13}C NMR (DMSO-d_6) δ 154.2, 151.0, 139.7, 136.1, 135.5, 135.3, 132.2, 131.4, 128.1, 127.2, 126.0, 125.7, 125.4, 120.8, 120.1, 118.5, 119.4, 116.5, 40.4, 31.5, 20.7; MS m/z 284 (M^+), 268 (M − 16).

2-(2′-Pyrrolyl)quinoline (20a). A mixture of 2-aminobenzaldehyde (**18a**, 1.21 g, 10.0 mmol) and 2-acetylpyrrole (1.09 g, 10.0 mmol) was dissolved in absolute EtOH (50 mL). Saturated ethanolic KOH (1 mL) was added, and the mixture was refluxed for 36 h under Ar. After cooling, H_2O (20 mL) was added, and the mixture was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic layers were washed with water and dried over anhydrous $MgSO_4$. The solvent was evaporated, and the residue was purified by chromatography on alumina (18 g), eluting with CH_2Cl_2/hexane (1:1), to afford **20a** as a slightly brown solid (1.26 g, 65%), which was recrystallized from hexane: mp 129−130 °C (lit.[10] mp 133−135 °C); ^{1}H NMR (acetone-d_6) δ 10.93 (bs, 1H, NH), 8.20 (d, 1H, J = 8.7 Hz, H_4), 7.89 (d, 1H, J = 8.4 Hz, H_8), 7.83 (d, 2H, J = 8.7 Hz, H_5 and H_3), 7.66 (t, 1H, J = 7.7 Hz, H_7), 7.44 (t, 1H, J = 7.2 Hz, H_6), 7.04 (q, 1H), 6.95 (q, 1H), 6.25 (q, 1H); ^{13}C NMR ($CDCl_3$) δ 150.2, 147.7, 136.4, 131.7, 129.6, 128.1, 127.5, 126.6, 125.2, 121.3, 117.7, 110.2, 109.4.

2-(2′-Pyrrolyl)-1,8-naphthyridine (20b). Following the procedure described for **20a**, a mixture of 2-aminonicotinaldehyde (**18b**, 2.44 g, 20.0 mmol), 2-acetylpyrrole (2.18 g, 20.0 mmol), and saturated ethanolic KOH (1 mL) was refluxed for 2 d under Ar to afford a crude product that was purified by chromatography on alumina (18 g). The first fraction eluted by CH_2Cl_2/hexane (1:1) was unreacted 2-acetylpyrrole. The second fraction, eluting with CH_2Cl_2/EtOAc (1:1), afforded **20b** as a brown solid (2.43 g, 62%): mp 157−9 °C; ^{1}H NMR ($CDCl_3$) δ 10.52 (s, 1H, NH), 9.01 (dd, 1H, H_7), 8.08 (m, 1H, H_5), 8.07 (d, 1H, H_4), 7.76 (d, 1H, H_3), 7.38 (dd, 1H, H_6), 7.07 (s, 1H), 6.97 (s, 1H), 6.35 (q, 1H). Anal. Calcd for $C_{19}H_{14}N_2$: C, 73.85; H, 4.61; N, 21.54. Found: C, 73.77; H, 4.30; N, 21.28.

1- Methyl-2-(2′-pyrrolyl)quinolinium Iodide (21). Following the procedure described for **3**, 2-(2′-pyrrolyl)quinoline (**20a**, 1.82 g, 9.4 mmol) was treated with methyl iodide (6.66 g, 46.9 mmol) for 3 d to afford **21** as a brown solid (0.79 g, 25%): mp 174−5 °C; ^{1}H NMR (DMSO-d_6) δ 12.58 (s, 1H, NH), 8.90 (d, 1H, J = 9.0 Hz, H_4), 8.44 (d, 1H, J = 9.0 Hz, H_8), 8.30 (d, 1H, J = 8.1 Hz, H_5), 8.16 (t, 1H, J = 6.3 Hz, H_7), 8.15 (d, 1H, J = 9.0 Hz, H_3), 7.91 (t, 1H, J = 7.5 Hz, H_6), 7.61 (q, 1H), 7.34 (q, 1H), 6.61 (q, 1H), 4.54 (s, 3H, NCH_3); ^{13}C NMR (DMSO-d_6) δ 150.6, 142.9, 139.7, 135.5, 130.3, 130.1, 128.7, 126.6, 124.5, 122.8, 121.8, 118.6, 113.0, 43.6. Anal. Calcd for $C_{14}H_{13}N_2I$: C, 50.00; H, 3.87; N, 8.33. Found: C, 50.04; H, 3.69; N, 8.20.

1-Methyl-2-(2′-pyrrolyl)-1,8-naphthyridinium Iodide (22). Following the procedure described for **3**, 2-(2′-pyrrolyl)-1,8-naphthyridine (**20b**, 1.62 g, 8.3 mmol) was treated with methyl iodide (3.54 g, 24.9 mmol) for 1 h to afford **22** as an orange solid (2.80 g, 100%): mp 287−9 °C (270 °C, turns black); ^{1}H NMR (DMSO-d_6) δ 12.17 (s, 1H, NH), 9.36 (d, 1H, J = 5.4 Hz, H_7), 9.02 (d, 1H, J = 7.8 Hz, H_5), 8.63 (d, 1H, J = 9.0 Hz, H_4), 8.29 (d, 1H, J = 8.7 Hz, H_3), 7.93 (dd, 1H, J = 6.0, 7.8 Hz, H_6), 7.39 (s, 1H), 7.33 (s, 1H), 6.37 (s, 1H), 4.56 (s, 3H,

NCH_3). Anal. Calcd for $C_{13}H_{12}N_3I$: C, 46.29; H, 3.56; N, 12.46. Found: C, 46.29; H, 3.38; N, 12.29.

***N*-Methyl-2-(2′-pyrrolylidenyl)-1,2-dihydroquinoline (23).** Following the procedure described for **4**, 1-methyl-2-(2′-pyrrolyl)quinolinium iodide (**21**, 168 mg, 0.5 mmol) was treated with ammonium hydroxide (10 mL) to afford **23** as a violet solid (70 mg, 67%): mp 90 °C dec; ^{1}H NMR (DMSO-d_6) δ 8.23 (d, 1H, J = 8.4 Hz, H_3), 7.87 (d, 1H, J = 8.1 Hz, H_4), 7.84 (d, 1H, J = 8.7 Hz, H_8), 7.78 (d, 1H, J = 7.8 Hz, H_5), 7.71 (t, 1H, J = 7.8 Hz, H_7), 7.44−7.40 (overlapping, 2H, H_6 and $H_{5'}$), 7.38 (d, 1H, J = 3.3 Hz, $H_{3'}$), 6.39 (d, 1H, J = 3.6 Hz, $H_{4'}$), 4.44 (s, 3H, NCH_3); ^{13}C NMR (DMSO-d_6) δ 149.0, 145.2, 140.1, 134.9, 134.3, 131.7, 128.5, 125.1, 124.8, 124.2, 116.9, 116.8, 40.6; MS m/z 208 (M^+).

7,8,9,10-Tetrahydro-11*H*-pyrido[2,3-*a*]carbazole (25). A mixture of 8-hydrazinoquinoline (**24**, 0.95 g, 6 mmol), cyclohexanone (0.59, 6 mmol), and acetic acid (1 drop) in absolute ethanol (15 mL) was refluxed for 20 h. The solvent was evaporated to afford a dark oil. Chromatography on alumina (20 g), eluting with CH_2Cl_2/hexane (1:1), provided the quinolylhydrazone as an orange oil (1.16 g, 81%).

A mixture of the quinolylhydrazone of cyclohexanone (1.15 g, 4.8 mmol) and PPA (6.5 g) was heated at 150 °C for 1 h. The mixture was cooled, made basic with 10% NaOH, and extracted with CH_2Cl_2. The organic layer was dried over anhydrous $MgSO_4$. The solvent was evaporated to afford a sticky solid. Chromatography on alumina (25 g), eluting with CH_2Cl_2/hexane (1:1), provided **25** as a yellow solid (0.68 g, 64%), which was recrystallized from hexane: mp 147−8 °C (lit.[17] mp 151 °C); ^{1}H NMR ($CDCl_3$) δ 10.47 (bs, 1H, NH), 8.79 (m, 1H, H_2), 8.26 (dd, 1H, J = 8.1 Hz, 1.2 Hz, H_4), 7.69 (d, 1H, J = 8.4 Hz, H_5), 7.42 (d, 1H, J = 8.7 Hz, H_6), 7.34 (dd, 1H, J = 8.1 Hz, 4.5 Hz, H_3), 2.81 (b, 2H, CH_2), 2.76 (b, 2H, CH_2), 1.92 (t, 4H, CH_2CH_2).

7,8,9,10-Tetrahydro-11*H*-pyrido[2,3-*a*]carbazolium Iodide (26). Following the procedure described for **3**, 7,8,9,10-tetrahydro-11*H*-pyrido[2,3-*a*]carbazole (**25**, 0.30 g, 1.4 mmol) was treated with methyl iodide (2.0 g, 14 mmol) for 20 h to afford **26** as a yellow solid (0.36 g, 73%): mp 283−5 °C; ^{1}H NMR (DMSO-d_6) δ 11.93 (s, 1H, NH), 9.13−9.07 (overlapping, 2H, H_2 and H_4), 8.01 (d, 1H, J = 8.7 Hz, H_5), 7.86 (t, 1H, J = 6.3 Hz, H_3), 7.84 (d, 1H, J = 8.7 Hz, H_6), 4.79 (s, 3H, N−CH_3), 2.95 (t, 2H, CH_2), 2.78 (t, 2H, CH_2), 1.90 (quintet, 4H, CH_2-CH_2). Anal. Calcd for $C_{16}H_{17}N_2I$: C, 52.75; H, 4.67; N, 7.69. Found: C, 52.63; H, 4.54; N, 7.51.

1-Methyl-4′,5′,6′,7′-tetrahydro-3,3′-ethenyl-2-(2′-indolenylidene)-1,2-dihydropyridine (27). Following the procedure described for **4**, 7,8,9,10-tetrahydro-11*H*-pyrido[2,3-*a*]-carbazolium iodide (**26**, 150 mg, 0.4 mmol) was treated with ammonium hydroxide (10 mL) to afford **27** as a red solid (55 mg, 59%): mp 85−7 °C; ^{1}H NMR (DMSO-d_6) δ 8.52−8.48 (overlapping, 2H, H_2 and H_4), 7.69 (d, 1H, J = 7.8 Hz, H_5), 7.23 (t, 1H, J = 6.9 Hz, H_3), 7.17 (d, 1H, J = 8.4 Hz, H_6), 4.94 (s, 3H, N−CH_3), 2.92 (t, 2H, CH_2), 2.83 (t, 2H, CH_2), 1.84 (quintet, 4H, CH_2CH_2); MS m/z 236 (M^+), 218 (M − 18).

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Supporting Information Available: ^{1}H NMR spectra of **9a**,**c** and **33** and ^{1}H and ^{13}C NMR spectra of **4**, **9b**,**d**, **13**, **23**, **27**, and **30** (17 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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