acidic solution was basified with solid KOH, extracted with ether, dried ($CaSO_4$), and concentrated. The residue was purified by preparative TLC (silica gel, 10:1 $CHCl_3$–ethyl acetate) to give 8.8 mg of 1 (32% from 18) as a colorless oil and 6.3 mg (22%) of N-acylated product. 1: ^1H NMR ($CDCl_3$)[29] δ 8.96 (br s, NH), 7.10 (d, J = 7.8 Hz, H-14), 6.42–6.37 (m, H-15 and H-17), 5.82–5.68 (m, CH=CH), 3.78 (s, MeO), 3.76 (s, MeO), 2.63 (d, J = 1.5 Hz, CHN), 0.64 (t, J = 7.4 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$) 169.2 (s), 167.4 (s), 160.3 (s), 144.7 (s), 133.4 (d), 130.8 (s), 125.1 (d), 122.0 (d), 105.3 (d), 96.9 (d), 92.7 (s), 70.4 (d), 55.7 (q), 54.8 (s), 51.2 (2C, q and t), 50.8 (t), 44.8 (t), 41.7 (s), 28.8 (t), 27.2 (t), 7.7 ppm (q); IR ($CHCl_3$) 3397, 2795, 1675, 1618 cm^{-1}; MS(CI), m/e 367 (MH^+), 366. All spectral (250-MHz ^1H NMR, 63-MHz ^{13}C NMR, solution IR, and mass) and chromatographic data (TLC in three solvent systems) of synthetic 1 were indistinguishable from those of an authentic sample of 16-methoxytabersonine.

***dl*-16-Methoxy-1-(methoxycarbonyl)-2,3,6,7-tetradehydroaspidospermidine:** ^1H NMR ($CDCl_3$) δ 7.49 (d, J = 2.2 Hz, H-17), 7.09 (d, J = 8.2 Hz, H-14), 6.56 (dd, J = 8.2, 2.3 Hz, H-15), 5.92 (dd, J = 8.5, 3.1 Hz, H-3), 5.6–5.85 (m, HC=CH), 3.93 (s, MeO), 3.82 (s, MeO), 2.58 (d, J = 1.6 Hz, CHN), 0.65 (t, J = 7.5 Hz, CH_2CH_3).

Acknowledgment. Financial support from the National Institutes of Health (Grant No. NS-12389) and the Camille and Henry Dreyfus Foundation (teacher-scholar award to L.E.O.) is gratefully acknowledged. NMR and mass spectra were determined at Irvine with spectrometers purchased with the assistance of NSF departmental instrumentation grants. High-resolution mass spectra were determined at the NSF-sponsored MCMS at the University of Nebraska—Lincoln. We particularly wish to thank Dr. A. J. Hannart of Omnichem, Louvain-La-Neuve, Belgium, and Professor Martin Kuehne of the University of Vermont for generous samples of natural 16-methoxytabersonine.

Registry No. (±)-1, 86116-70-3; 4, 81903-99-3; (±)-5 (isomer 1), 86045-65-0; (±)-5 (isomer 2), 86045-79-6; 5 iodide derivative, 86045-77-4; (±)-6 (isomer 1), 86045-66-1; (±)-6 (isomer 2), 86045-80-9; 6 (R = H), 86045-78-5; (±)-10, 86045-67-2; 11, 86045-68-3; 13, 86045-69-4; (±)-14, 86045-70-7; (±)-15, 86064-56-4; (±)-16, 86045-71-8; (±)-17, 86064-57-5; (±)-18, 86045-73-0; (±)-18 oxazolidine derivative, 86045-75-2; (±)-19, 86045-72-9; (±)-20, 86045-74-1; 1-chloro-3-(phenylthio)propane, 4911-65-3; (±)-1,3-chloro-1-(phenylthio)propane, 86045-76-3; 2-bromo-4-methoxyaniline, 32338-02-6; trimethylacetyl chloride, 3282-30-2; trimethylsilyl cyanide, 7677-24-9; methyltriphenylphosphonium bromide, 1779-49-3; methyl chloroformate, 79-22-1.

Supplementary Material Available: Experimental and spectral data for the preparation of 10 via intermediates 7–9 (3 pages). Ordering information is given on any current masthead.

(29) Lounasmaa, M.; Kan, S.-K. *Acta Chem. Scand., Ser. B* **1980**, *B34*, 379–381.

Efficient Construction of the 10*H*-Pyrido[3,4-*b*]carbazole Ring System. Syntheses of Isoellipticine and 7-Methoxyisoellipticine

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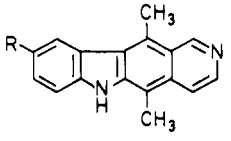
Received January 12, 1983

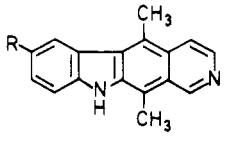
Practical syntheses of isoellipticine (**2a**) (5,11-dimethyl-10*H*-pyrido[3,4-*b*]carbazole) and 7-methoxyisoellipticine (**2b**) are described in which the key steps are regioselective acylation of a 3-lithio-1-(phenylsulfonyl)indole (**12** or **25**) with 3,4-pyridinedicarboxylic anhydride (**7**) and strong-base-mediated cyclization to the corresponding quinone (**5** or **28**). Further manipulation affords **2a** and **2b** in 20% and 21% overall yield from indole (**10**) and 5-methoxyindole (**23**), respectively. Keto acid **20** was also converted to isoellipticine (**2a**) in 85% yield.

The Ochrosia and Aspidosperma plant alkaloids ellipticine (**1a**) (5,11-dimethyl-6*H*-pyrido[4,3-*b*]carbazole) and, particularly, 9-methoxyellipticine (**1b**) are potent anticancer agents, and a derivative of **1b** is currently in clinical use in France.[2] Since the isolation of these two alkaloids[3] and the discovery of their anticancer activity,[4] many synthetic approaches to the pyrido[4,3-*b*]carbazole ring system have been reported.[5-7] Our own work in this area has recently culminated in a highly efficient synthesis of ellipticine (**1a**), proceeding in ca. 55% overall yield from indole (six steps).[7]

In contrast to the intense activity directed toward the synthesis of pyrido[4,3-*b*]carbazoles, very little attention has been focused on the isomeric pyridocarbazoles, such as 5,11-dimethyl-10*H*-pyrido[3,4-*b*]carbazole (**2a**) (hereafter referred to as "isoellipticine"). In fact, only one total synthesis of isoellipticine (**2a**)[8] and the preparation of isoellipticine quinone **5**[6a] have been described. Herein we delineate a new approach for the construction of the pyrido[3,4-*b*]carbazole ring system, resulting in syntheses of isoellipticine (**2a**) and the previously unknown 7-methoxyisoellipticine (**2b**).



1a (R = H)
1b (R = OCH_3)



2a (R = H)
2b (R = OCH_3)

Our synthetic approach to isoellipticine (**2a**) parallels that which we devised to fashion ellipticine (**1a**),[7] and both strategies are outlined in Scheme I. One obvious attractive

(1) Work done in partial fulfillment of the requirements for the Ph.D., Dartmouth College, 1982.

(2) Van-Bac, N.; Moisand, C.; Gouyette, A.; Muzard, G., Dat-Xuong, N.; Le Pecq, J. B.; Paoletti, C. *Cancer Treat. Rep.* **1980**, *64*, 879 and references cited therein.

(3) (a) Goodwin, S.; Smith, A. F.; Horning, E. C. *J. Am. Chem. Soc.* **1959**, *81*, 1903. (b) Woodward, R. B.; Iacobucci, G. A.; Hochstein, F. A. *Ibid.* **1959**, *81*, 4434.

(4) (a) Svoboda, G. H.; Poore, G. A.; Montfort, M. L. *J. Pharm. Sci.* **1968**, *57*, 1720. (b) Dalton, L. K.; Demerac, S.; Elmes, B. C.; Loder, J. W.; Swan, J. M.; Teitei, T. *Aust. J. Chem.* **1967**, *20*, 2715.

(5) For reviews, see: (a) Sainsbury, M. *Synthesis* **1977**, 437. (b) Barone, R.; Chanon, M. *Heterocycles* **1981**, *16*, 1357.

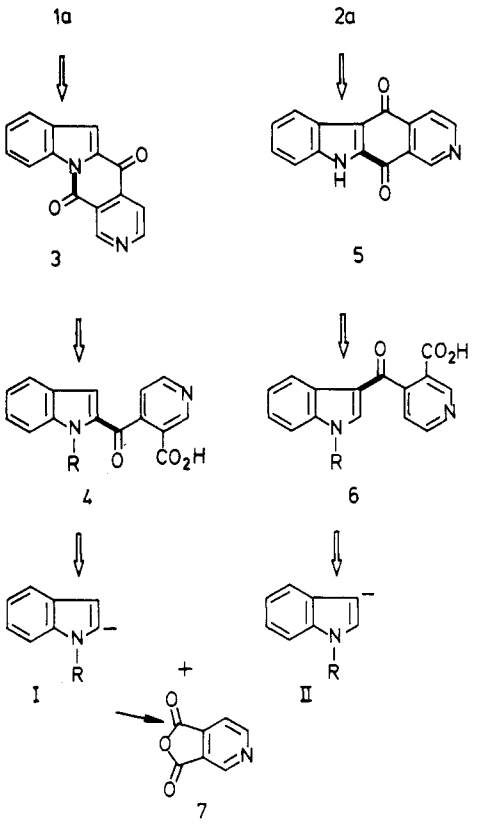
(6) For post 1980 syntheses of **1a**, see: (a) Ashcroft, W. R.; Beal, M. G.; Joule, J. A. *J. Chem. Soc., Chem. Commun.* **1981**, 994. (b) Kano, S.; Sugino, E.; Shibuya, S.; Hibino, S. *J. Org. Chem.* **1981**, *46*, 2979. (c) Reference 7.

(7) Saulnier, M. G.; Gribble, G. W. *J. Org. Chem.* **1982**, *47*, 2810.

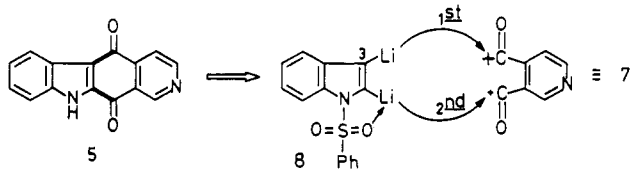
(8) Fujiwara, A. N.; Acton, E. M.; Goodman, L. *J. Med. Chem.* **1967**, *10*, 126.

0022-3263/83/1948-2690$01.50/0

Scheme I



Scheme II



feature of these synthetic routes is that 3,4-pyridinedicarboxylic anhydride (7; cinchomeronic anhydride) is common to both.

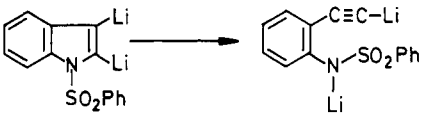
Our ellipticine (**1a**) synthesis proceeded according to this plan (Scheme I), and the crucial acylation of I (as 2-lithio-1-(phenylsulfonyl)indole) with **7** was highly regioselective (92:8) in the expected sense.[7] The resulting keto acid **4** was converted, via keto lactam **3**, to **1a** in excellent overall yield from indole. Similarly, our projected synthesis of the pyrido[3,4-*b*]carbazole ring system (**2a**) is contingent upon the regioselective acylation of anion II (as 3-lithio-1-(phenylsulfonyl)indole[9]) with **7**.

A bolder approach to isoellipticine quinone **5** was envisaged in the diacylation of indole dianion **8** with **7** (cf. Scheme II), with the anticipation that the presumed more reactive indole-3 anion would guide the reaction in the desired direction.

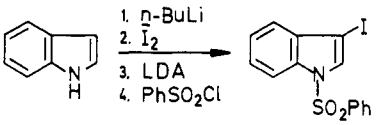
Unfortunately, this direct approach to isoellipticine quinone **5** was thwarted by the facile ring opening of 2,3-dilithio-1-(phenylsulfonyl)indole (**8**) to lithium (2-(*N*-lithiophenylsulfonamido)phenyl)acetylide (**9**). The synthesis of **8** and details of this cleavage process, which occurs even at −120 °C, have been reported separately.[10]

Results and Discussion

Synthesis of Isoellipticine (2a). Following our earlier work,[9] the requisite 1-(phenylsulfonyl)-3-iodoindole (**11**)

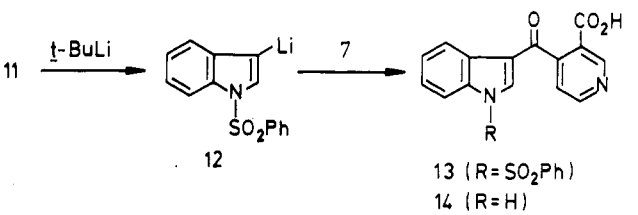


was prepared in one pot from indole (**10**) in 88% yield.

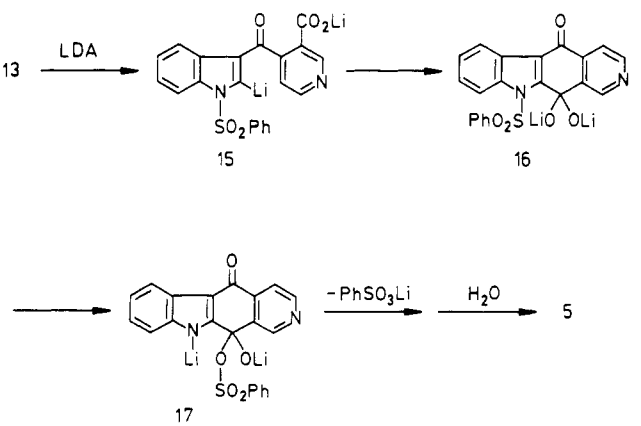


This very efficient procedure avoids the isolation of unstable 3-iodoindole.

Reaction of **11** with 2 equiv of *tert*-butyllithium (−100 °C, tetrahydrofuran (THF), to generate 3-lithio-1-(phenylsulfonyl)indole[9] (**12**), followed by the addition of pyridine anhydride **7**[11] at −100 °C[12] produced keto acid **13** in 57% yield after recrystallizaton with complete regioselectivity. The isomeric keto acid could not be detected by thin layer chromatography (TLC) or carbon magnetic resonance (^{13}C NMR) analysis of the crude product. Removal of the phenylsulfonyl protecting group in **13** was accomplished with aqueous methanolic potassium carbonate (reflux, 6.5 h) to afford keto acid **14** in virtually quantitative yield.

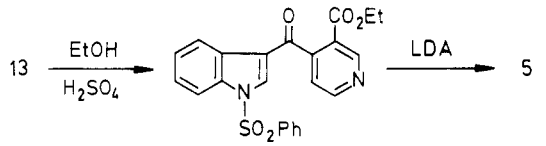


After an unsuccessful attempt to cyclize **14** to the desired isoellipticine quinone **5** using relatively mild Friedel–Crafts conditions (hot neat acetic anhydride), we examined strong base methodology as a means with which to effect this ring closure. Thus, the addition of keto acid **13** to a solution of 3.5 equiv of lithium diisopropylamide (LDA) in THF (40 °C) yielded quinone **5** in 41% yield. This transformation is envisioned to proceed via lithiation at the indole-2 position to give **15** followed by intramolecular addition to the lithium carboxylate carbonyl, affording **16**. Transfer of the phenylsulfonyl group from nitrogen to oxygen, perhaps intramolecularly, would give **17**, and loss of lithium phenylsulfonate leads to quinone **5**.



(9) Saulnier, M. G.; Gribble, G. W. *J. Org. Chem.* **1982**, *47*, 757.
(10) Gribble, G. W.; Saulnier, M. G. *J. Org. Chem.* **1983**, *48*, 607.
(11) This material is readily prepared from the commercially available diacid using the procedure of: Bachman, G. B.; Barker, R. S. *J. Org. Chem.* **1949**, *14*, 97.
(12) This low temperature is necessary to prevent the rearrangement[9] of **12** to the more stable 2-lithio isomer.

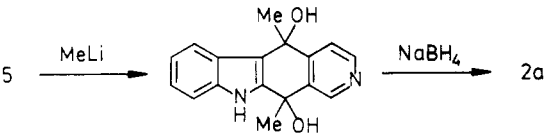
This anionic cyclization leading to **5** was substantially improved by employing keto ester **18**, which was prepared in 89% yield from **13** by using a Fisher esterification. Thus, the LDA-induced cyclization of **18** proceeded smoothly at 0 °C to afford **5** in 66% yield after flash chromatography over silica gel. Presumably, the in situ



18

generated lithium ethoxide is responsible for the removal of the phenylsulfonyl group.

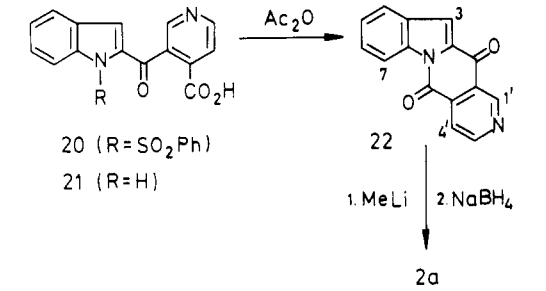
In accord with expectations, quinone **5** reacted with methyllithium (THF, reflux, 3.5 h) to give diol **19** as a mixture of diastereomers that, without purification, was reduced with sodium borohydride (ethanol, reflux) to yield isoellipticine (**2a**) in 67% yield after purification.



19

This material was identical in all aspects with a sample of isoellipticine provided to us by Dr. E. M. Acton[8] and with material synthesized in the following manner.

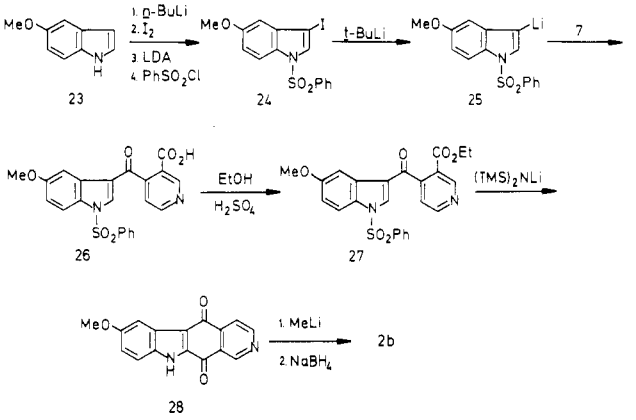
As described in our ellipticine (**1a**) synthesis,[7] the reaction of pyridine anhydride **7** with 2-lithio-1-(phenylsulfonyl)indole affords a mixture of keto acids in 78% yield in a 92:8 ratio. The major isomer (cf. Scheme I) was converted to **1a**. We have now transformed the minor keto acid **20** into isoellipticine (**2a**) in 85% overall yield. Thus,



treatment of **20** with aqueous methanolic potassium carbonate (reflux, 4.5 h) gave keto acid **21** (95% yield), which, upon exposure to hot acetic anhydride (85 °C, 24 h), cyclized to keto lactam **22** (98% yield). The structure of **22** is supported by its reconversion to **21** with aqueous base at room temperature and by spectral data. Thus, the infrared spectrum shows carbonyl absorption at 1711 and 1671 cm^{-1}, and the 360-MHz ^1H NMR spectrum displays the expected deshielded signals for protons C-3, C-7, C-1′, and C-4′ (7.80, 8.50, 9.34, and 8.18 ppm, respectively) due to the magnetic anisotropy of the proximate carbonyl groups. Finally, reaction of keto lactam **22** with methyllithium (2 equiv, THF, −100 °C) followed by reduction of the derived diols with sodium borohydride (aqueous ethanol, reflux) gave isoellipticine (**2a**) in 91% yield after purification by flash chromatography. This material was identical in all aspects with that obtained from quinone **5** (vide supra).

Synthesis of 7-Methoxyisoellipticine (2b). Prompted by the extraordinary biological activity of the A-ring-oxygenated ellipticine derivatives (e.g. **1b**), we sought to

Scheme III



apply our methodology to the synthesis of an A-ring-oxygenated isoellipticine. The target molecule, 7-methoxyisoellipticine (**2b**), represented a tough test of our strong base technology due to the propensity for the anisole ring to undergo ortho metalation.[13]

Our synthesis of **2b** is summarized in Scheme III. The required 5-methoxyindole (**23**) was readily prepared by the procedure of Leimgruber and Batcho.[14] A one-pot iodination/phenylsulfonation sequence transformed **23** into 1-(phenylsulfonyl)-3-iodo-5-methoxyindole (**24**) in 75% yield. Generation of 3-lithio-1-(phenylsulfonyl)-5-methoxyindole (**25**) with 2 equiv of *tert*-butyllithium (−100 °C, THF) was achieved without any detectable methoxy-directed lithiation, and upon quenching with pyridine anhydride **7** the desired keto acid **26** was isolated in 77% yield after crystallization from acetone. As with the reaction of **12**, this ring opening of **7** with **25** appears to be completely regioselective in the expected[7] sense. The ethyl ester **27** was prepared in nearly quantitative yield but, unfortunately, LDA-mediated cyclization of **27** to methoxy quinone **28** proceeded in only 33% yield. However, this deprotonation–cyclization sequence was greatly improved by using the hindered base lithium bis(trimethylsilyl)amide (25 °C, THF). In this manner, **28** was obtained in 60% yield following flash chromatography. Treatment of **28** with methyllithium and then sodium borohydride gave 7-methoxyisoellipticine (**2b**) in 62% yield. The structures of **28** and **2b** are supported by analytical and spectral data, including 360-MHz ^1H NMR spectra (cf. Experimental Section).

In summary, we have described a convenient, efficient, and versatile synthesis of the pyrido[3,4-*b*]carbazole ring system. The synthetic path is complementary to our previously reported[7] construction of the pyrido[4,3-*b*]-carbazole (ellipticine) ring system, and both methodologies should find utility in the preparation of other heterocyclic ring systems.

Experimental Section

Melting points were determined in open capillaries with a Mel-Temp Laboratory Devices apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlabs, Atlanta, GA. Infrared spectra were recorded on a Perkin-Elmer 599 instrument. ^1H NMR spectra were routinely obtained at 60 MHz with a Hitachi Perkin-Elmer R-24 spectrometer and, in certain cases, with a JEOL-FX60Q Fourier transform NMR spectrometer. Chemical shifts are reported in parts per million downfield from

(13) Gschwend, H. W.; Rodriguez, H. R. *Org. React.* (*N.Y.*) **1979**, *26*, 1.

(14) Batcho, A. D.; Leimgruber, W. *Chem. Abstr.* **1977**, *86*, 29624; Batcho, A. D., private communication.

tetramethylsilane as the internal reference. ^{13}C NMR spectra were measured on a JEOL-FX60Q Fourier transform NMR spectrometer operating at 15 MHz. Low-resolution mass spectra were determined on a Finnigan EI-CI gas chromatograph–mass spectrometer. Ultraviolet (UV) spectra were recorded on a Unicam SP-800A spectrophotometer or on a Cary 15 or 219 instrument. "Flash chromatography" refers to the technique developed by Still[15] and the grade of silica used was 230–400 mesh. Thin layer chromatography (TLC) was performed on precoated (0.2 mm) silica gel 60 F_{254} plastic sheets (E. Merck). Spots were visualized under 254-nm ultraviolet light and/or by spraying with a solution of 3% aqueous ceric ammonium sulfate in 10% sulfuric acid followed by brief heating. The alkyllithium reagents were purchased from Aldrich and rigorously standardized by titration against 2,5-dimethoxybenzyl alcohol.[16] Tetrahydrofuran was distilled from sodium/benzophenone and diisopropylamine was distilled over sodium hydride. For many of the lithiation procedures, a three-neck round-bottomed flask fitted with an internal thermometer, magnetic stirring bar, argon inlet adapter, and rubber serum cap was found to be most convenient. All reactions were performed in oven-dried (130 °C) glassware under prepurified argon or nitrogen.

1-(Phenylsulfonyl)indol-3-yl 3-Carboxy-4-pyridyl Ketone (13). A magnetically stirred solution of iodoindole 11[9] (4.11 g, 10.7 mmol) in dry THF (135 mL) was cooled to −105 °C under argon and treated rapidly via syringe with 2 equiv of *tert*-butyllithium (1.95 M in pentane, 11.0 mL, 21.5 mmol). The yellow–orange suspension that resulted was stirred for 12 min at −100 °C, cooled to −105 °C, and quenched rapidly via syringe with a solution of 3,4-pyridinedicarboxylic acid anhydride (7) (1.76 g, 11.8 mmol) in dry THF (30 mL), with very efficient mixing being maintained throughout the addition. The internal temperature rose to −85 °C, with the initially resulting dark color becoming light yellow–orange. The mixture was kept at −100 °C for 1 h and then allowed to warm slowly to room temperature overnight. After the solvent was removed by rotary evaporation, the resulting dark oil was dissolved in H_2O (325 mL) and slowly acidified to pH 2 with 20% HCl with efficient stirring and cooling. The resulting white precipitate was collected by filtration after 15 min at 5 °C, washed with H_2O, and thoroughly dried in vacuo to give 4.25 g (97%) of **13** as a colorless solid which appeared pure by TLC (R_f 0.15, THF). Crystallization from acetone gave 2.46 g (57%) of analytically pure **13** in two crops: mp 228–229 °C dec; IR (KBr) 3425 (br s), 2450 (br s), 1713 (s), 1664 (s), 1538 (s), 1450 (s), 1388 (s), 1296 (s), 1216 (s), 1185 (m), 978 (s), 744 (s), 581 cm^{-1} (m); 360-MHz ^1H NMR (Me_2SO-d_6) δ 9.18 (s, 1 H), 8.96 (d, 1 H, J = 5.0 Hz), 8.24 (m, 1 H), 8.17–8.10 (m, 3 H), 8.00 (m, 1 H), 7.78 (m, 1 H), 7.69–7.61 (m, 3 H), 7.54–7.44 (m, 2 H); ^{13}C NMR (Me_2SO-d_6) δ 189.5, 165.8, 153.3, 150.9, 147.9, 136.3, 135.3, 134.7, 134.3, 130.1, 127.3, 127.0, 126.2, 125.1, 124.7, 122.3, 121.6, 120.5, 113.2; UV (95% EtOH) λ_{max} 218, 268 (sh), 275 (sh), 293 nm.

Anal. Calcd for $C_{21}H_{14}N_2O_5S$: C, 62.06; H, 3.47; N, 6.89; S, 7.89. Found: C, 61.87; H, 3.49; N, 6.86; S, 7.83.

3-Carboxy-4-pyridyl 3-Indolyl Ketone (14). A mixture of keto acid **13** (1.50 g, 3.69 mmol), K_2CO_3 (2.04 g, 14.7 mmol), methanol (45 mL), and H_2O (15 mL) was refluxed under N_2 with magnetic stirring for 6.5 h. The mixture was cooled and the solvent was removed in vacuo to give a viscous oil. This material was dissolved in H_2O (100 mL) and slowly acidified to pH 2–3 with 20% HCl with efficient cooling and stirring. The aqueous layer was partitioned with ethyl acetate (1 × 250 mL), saturated with solid NaCl, and then further extracted with ethyl acetate (3 × 75 mL). The combined extracts were washed with H_2O (2 × 175 mL) and brine (2 × 200 mL), dried (Na_2SO_4), and concentrated in vacuo to give 0.97 g (99%) of pure **14** as a white solid after further drying at 20 °C (0.5 torr) (R_f 0.10, THF), mp 226–228 °C dec. Crystallization from acetone gave the analytical sample as pure white fluffy crystals: mp 241–243 °C dec; IR (KBr) 3350 (s), 1717 (s), 1636 (s), 1515 (s), 1423 (s), 1233 (s), 1207 (s), 896 (s), 750 (s), 630 cm^{-1} (s); ^1H NMR (Me_2SO-d_6) δ 9.10 (s, 1 H), 8.88 (d, 1 H, J = 5.5 Hz), 8.14 (m, 1 H), 7.75–7.10 (m, 6 H); ^{13}C NMR (Me_2SO-d_6) δ 188.3, 166.1, 152.7, 150.6, 149.4, 136.9, 136.0, 125.5, 124.9, 123.3, 122.1, 121.8, 121.3, 115.9, 112.4; mass spectrum, m/e 266 (M^+) 221, 158, 144 (100%), 116, 89; UV (95% EtOH) λ_{max} 243, 264 (sh), 308 nm.

Anal. Calcd for $C_{15}H_{10}N_2O_3 \cdot {}^1/_2C_3H_6O$: C, 67.11; H, 4.44; N, 9.49. Found: C, 67.49; H, 4.76; N, 9.42.

1-(Phenylsulfonyl)indol-3-yl 3-Carbethoxy-4-pyridyl Ketone (18). A mixture of keto acid **13** (0.60 g, 1.47 mmol), absolute ethanol (50 mL), and concentrated sulfuric acid (25 drops, ca. 5 mmol) was refluxed for 96 h in a Soxhlet apparatus containing activated 3-Å molecular sieves. The total volume was concentrated in vacuo by two thirds and the mixture was poured into 5% aqueous sodium bicarbonate (150 mL). After extraction with ethyl acetate (4 × 75 mL), the combined extracts were washed with brine (2 × 75 mL), dried (Na_2SO_4), and concentrated in vacuo to afford 0.57 g (89%) of pure **18** as an off-white solid (R_f 0.52, THF). Flash chromatography over silica gel with 2:1 methylene chloride–ethyl acetate afforded 0.55 g of analytically pure **18** as a colorless solid: mp 163–165 °C; IR (KBr) 1720 (s), 1662 (s), 1537 (s), 1447 (s), 1381 (s), 1299 (s), 1180 (m), 971 (s), 737 (s), 578 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 9.30 (s, 1 H), 9.00 (d, 1 H), 8.50–7.15 (m, 11 H), 4.08 (q, 2 H, J = 7.5 Hz), 0.94 (t, 3 H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 188.6, 164.0, 153.0, 151.4, 148.7, 137.2, 135.0, 134.6, 133.6, 129.6, 129.5, 127.1, 127.0, 126.3, 125.2, 122.9, 121.0, 113.1, 61.9, 13.5; mass spectrum, m/e 434 (M^+) 389, 284, 237, 141, 115, 77 (100%); UV (95% EtOH) λ_{max} 267 (sh), 273 (sh), 295 nm.

Anal. Calcd for $C_{23}H_{18}N_2O_5S$: C, 63.58; H, 4.18; N, 6.45; S, 7.38. Found: C, 63.31; H, 4.23; N, 6.40; S, 7.30.

10*H*-Pyrido[3,4-*b*]carbazole-5,11-quinone (5). A solution of the keto ester **18** (200.0 mg, 0.4603 mmol) in dry THF (25 mL) was slowly added at 0 °C over 15 min to a magnetically stirred solution of lithium diisopropylamide (LDA) (1.10 mmol) prepared from diisopropylamine (0.12 g, 1.2 mmol) and *n*-butyllithium (1.73 M in hexane; 0.61 mL, 1.10 mmol) in dry THF (10 mL) under argon. There immediately resulted an orange–brown color which soon became a persistent deep red–brown. After 15 min at 0 °C, the reaction mixture was refluxed overnight. The mixture was cooled, poured into saturated aqueous sodium bicarbonate (150 mL), and extracted with ethyl acetate (3 × 75 mL). The combined extracts were washed with H_2O (1 × 50 mL) and brine (2 × 100 mL), dried (Na_2SO_4), and concentrated in vacuo to afford 100.0 mg of a dark brown solid. This material was dissolved in minimal THF and adsorbed onto silica gel. Flash chromatography over silica gel with ethyl acetate elution gave 75 mg (66%) of pure quinone **5** as an orange–brown solid after drying at 50 °C (0.3 torr), mp 312–316 °C dec (lit.[6a] mp 317–320 °C). This material was identical in all respects (TLC, IR, UV, mass spectrum, mmp 314–318 °C dec) with an authentic sample of **5** (R_f 0.59, EtOAc) kindly provided by Professor J. A. Joule: IR (KBr) 1660 (s), 1645 (s), 1520 (s), 1475 (s), 1328 (s), 1252 (m), 1220 (s), 1020 (s), 918 (s), 740 cm^{-1} (m); mass spectrum, m/e 248 (M^+, 100%), 220, 192, 164, 138, 124 (M^{2+}); UV (EtOH) λ_{max} 260 (sh), 275, 297 (sh) nm.

A 41% crude yield (one spot by TLC) of quinone **5** was obtained when a dilute solution of keto acid **13** (200 mg, 0.492 mmol) in dry THF was slowly added over 75 min to a solution of LDA (3.5 equiv) in dry THF at 35–40 °C under argon with magnetic stirring. After refluxing the resulting reddish–brown mixture for 28 h, the reaction was worked up (vide supra) to afford 50.0 mg of **5**.

5,11-Dimethyl-10*H*-pyrido[3,4-*b*]carbazole (2a, Isoellipticine) from Quinone 5. The quinone **5** (27.6 mg, 0.111 mmol) in dry THF (40 mL) was treated at 20 °C under argon with methyllithium (1.62 M in Et_2O, 0.46 mL, 0.75 mmol). The mixture was stirred at 25 °C for 10 min and then refluxed for 3.5 h. The resulting reddish-brown mixture was cooled, and the THF was removed in vacuo to give a brown solid. This material was immediately treated under argon with absolute ethanol (50 mL) and sodium borohydride (two pellets, ca. 0.5 g) and refluxed with stirring for 1 h. After an additional sodium borohydride pellet was added, reflux was maintained for 3 h. The resulting yellow–orange highly fluorescent mixture was cooled and the EtOH was removed in vacuo. The residue was partitioned between H_2O (150 mL) and $CHCl_3$ (100 mL) and stirred overnight. The aqueous layer was then extracted with additional $CHCl_3$ (4 × 75 mL), and the combined organic extracts were washed with H_2O (1 × 150 mL) and brine (2 × 250 mL), dried (K_2CO_3), and concentrated in vacuo to afford a yellow solid. Flash chromatography on silica gel with THF elution gave 18.3 mg (67%) of pure **2a** as a yellow

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solid, mp 243–250 °C dec (lit.[8] mp 270–286 °C dec (MeOH)). This material was identical (IR, UV, TLC, MS) with a sample supplied by Dr. E. M. Acton: IR (KBr) 1615 (m), 1500 (s), 1463 (s), 1400 (m), 1320 (m), 1280 (s), 1225 (m), 1012 (s), 740 cm^{-1} (m); 360-MHz ^1H NMR (Me_2SO-d_6) δ 11.4 (s, 1 H), 9.59 (s, 1 H), 8.41 (d, 1 H, J = 6.1 Hz), 8.41 (m, 1 H), 8.13 (d, 1 H, J = 6.1 Hz), 7.58–7.55 (m, 2 H), 7.28–7.24 (m, 1 H), 3.15 (s, 3 H), 2.96 (s, 3 H); 90-MHz ^{13}C NMR (Me_2SO-d_6) δ 148.6, 143.1, 143.0, 138.4, 128.7, 127.5, 125.5, 125.2, 124.7, 124.0, 122.8, 118.8, 116.7, 110.6, 110.5, 14.4, 11.7; mass spectrum, m/e 246 (M^+, 100%), 231, 217, 123 (M^{2+}, 50%); UV (EtOH) λ_{max} 228, 272 (sh), 281, 301 (sh), 317, 331 nm; (EtOH + 1% of added 20% HCl) λ_{max} 233, 263, 298, 349 nm.

4-Carboxy-3-pyridyl 2-Indolyl Ketone (21). A magnetically stirred mixture of keto acid **20** (3.20 g, 7.87 mmol), K_2CO_3 (3.60 g, 26.0 mmol), methanol (90 mL), and H_2O (30 mL) was refluxed under N_2 for 4.5 h. The mixture was cooled and the solvent removed in vacuo to give a light tan solid. This material was dissolved in H_2O (150 mL) and slowly acidified to pH 2–3 with 20% HCl while maintaining efficient cooling and stirring. The resulting precipitate was collected, washed several times with H_2O, and thoroughly dried at 30 °C (0.5 torr) to give 2.03 g (95%) of **21** which was pure by TLC (R_f 0.40, THF), mp 247–250 °C dec. This material was not further purified but used directly in the following reaction: IR (KBr) 3355 (s), 1717 (s), 1635 (s), 1520 (s), 1260 (m), 907 (s), 739 (s), 666 (s), 443 cm^{-1} (s); 360-MHz ^1H NMR (Me_2SO-d_6) δ 12.10 (s, 1 H), 8.94 (d, 1 H, J = 5.2 Hz), 8.87 (s, 1 H), 7.87 (d, 1 H, J = 4.9 Hz), 7.65 (d, 1 H, J = 8.2 Hz), 7.49 (d, 1 H, J = 8.7 Hz), 7.32 (m, 1 H), 7.08 (m, 1 H), 6.75 (s, 1 H); 90-MHz ^{13}C NMR (Me_2SO-d_6) δ 185.8, 166.3, 151.9, 148.5, 138.6, 138.3, 135.9, 134.4, 127.2, 126.1, 123.0, 122.9, 120.7, 113.0, 112.1; UV (95% EtOH) λ_{max} 226 (sh), 318 nm; mass spectrum, m/e 266 (M^+), 248, 220, 192, 144, 89 (100%); exact mass calcd for $C_{15}H_{10}N_2O_3$: 266.0691. Found: 266.0680.

Indolo[1,2-*b*][2,6]naphthyridine-5,12-quinone (22). Keto acid **21** (1.83 g, 6.87 mmol) was heated under N_2 with magnetic stirring in neat acetic anhydride (175 mL) at ca. 85 °C for 24 h. The acetic anhydride was then nearly completely removed by distillation at 50–60 °C (10–20 torr). The residue was cooled and treated with H_2O (150 mL). After the ice-cooled mixture was stirred for 0.5 h, the product was collected by filtration, washed several times with H_2O, and dried at 50 °C (0.5 torr) to afford 1.67 g (98%) of pure keto lactam **22** as a greenish-yellow solid which was pure by TLC (R_f 0.67, THF), mp 187–190 °C. Recrystallization from acetone gave the analytical sample as green prisms: mp 216–218.5 °C dec; IR (KBr) 1711 (s), 1671 (s), 1554 (s), 1379 (s), 1342 (s), 1244 (s), 1021 (s), 749 (s), 728 (s), 685 (s), 370 cm^{-1} (s); 360-MHz ^1H NMR (Me_2SO-d_6) δ 9.34 (s, 1 H), 9.15 (d, 1 H, J = 5.0 Hz), 8.50 (d, 1 H, J = 8.7 Hz), 8.18 (d, 1 H, J = 5.0 Hz), 7.90 (d, 1 H, J = 7.9 Hz), 7.80 (s, 1 H), 7.66 (m, 1 H), 7.45 (m, 1 H); 90-MHz ^{13}C NMR (Me_2SO-d_6) δ 174.8, 157.9, 155.4, 147.9, 137.6, 136.5, 133.5, 129.8, 128.4, 126.5, 125.4, 124.1, 121.0, 116.3, 115.8; UV (95% EtOH) λ_{max} 234, 277, 310 (sh), 380 nm (log ϵ 4.36, 4.11, 3.81, 3.96); mass spectrum, m/e 248.0571 (M^+, calcd 248.0586).

Anal. Calcd for $C_{15}H_8N_2O_2$: C, 72.58; H, 3.25; N, 11.28. Found: C, 72.42; H, 3.28; N, 11.24.

Isoellipticine (2a) from Keto Lactam 22. A magnetically stirred suspension of the keto lactam **22** (166.3 mg, 0.6699 mmol) in dry THF (33 mL) was heated under argon at 40 °C for 20–30 min to effect dissolution, and the resulting yellow-orange solution was then rapidly cooled to −103 °C and treated via syringe over 20 sec with methyllithium (1.48 M in Et_2O, 0.91 mL, 1.35 mmol). The resulting yellow-brown mixture was stirred at −100 °C for 20 min and then maintained at −80 °C to −90 °C for an additional 45 min. After warming to 10 °C over 1.5 h, H_2O (5 mL) was added and the reaction mixture was stirred for 5 min. The solvent was removed in vacuo with minimal heating to afford the derived diols as a tannish gummy residue. This material was immediately treated under argon with absolute ethanol (100 mL) and excess sodium borohydride (4 pellets, ca. 1.0 g) and then refluxed with magnetic stirring for 21 h. The sodium borohydride was added in portions: two pellets initially, one more after 1 h, and the last pellet after 4 h. After approximately 1 h at reflux, the reaction mixture became bright yellow-orange and highly fluorescent. At the end of the 21 h reflux period, the reaction mixture was cooled and the solvent was removed in vacuo. The resulting bright yellow solid residue was partitioned between H_2O (100 mL) and $CHCl_3$ (150 mL) and stirred for 0.5 h. After further extraction with $CHCl_3$ (3 × 100 mL), the aqueous layer was slowly acidified with concentrated HCl to pH 2, basified to pH 9–10 with aqueous 2 N NaOH, and extracted again with $CHCl_3$ (2 × 50 mL). The combined organic portions were washed with H_2O (1 × 100 mL) and brine (2 × 200 mL), dried (K_2CO_3), and evaporated in vacuo to give a canary yellow solid which was exceptionally clean by TLC (R_f 0.41, THF). Flash chromatography over silica gel with 1:1 ethyl acetate–THF afforded 150.3 mg (91%) of pure **2a** as a bright yellow solid, mp 270–283 °C dec (lit.[8] mp 270–286 °C dec). This material was identical in all respects with a sample provided by Dr. E. M. Acton (mmp 270–283 °C dec) and with that prepared from quinone **5** (vide supra).

1-(Phenylsulfonyl)-3-iodo-5-methoxyindole (24). A magnetically stirred solution of 5-methoxyindole (**23**) (7.54 g, 51.2 mmol) in dry THF (80 mL) was cooled to −78 °C under argon and treated with *n*-butyllithium (1.70 M in hexane, 30.7 mL, 52.2 mmol) via syringe over 5 min. The milky white suspension that resulted was warmed to 15 °C over 1 h and then transferred (via a wide bore needle attached to a 50 mL syringe) dropwise over 10 min into a −78 °C solution of iodine (13.3 g, 52.2 mmol) in dry THF (75 mL) with vigorous magnetic stirring maintained in this second (500 mL) three-neck round-bottomed flask. This solution was stirred under argon at −78 °C for 1 h and then slowly warmed to 5 °C over an additional 1 h. Methanol (1–2 drops) was added, and the mixture was cooled to −78 °C over 45 min and then treated via syringe over 5 min with a solution of lithium diisopropylamide (LDA) prepared in the original flask from diisopropylamine (5.35 g, 52.9 mmol) and *n*-butyllithium (1.70 M in hexane; 30.7 mL, 52.2 mmol) in dry THF (25 mL). The resulting yellow-orange cloudy mixture was stirred at −78 °C for 0.5 h and quenched with benzenesulfonyl chloride (9.50 g, 53.8 mmol) neat via syringe over 1 min. The mixture was kept at −78 °C for 2 h and then allowed to warm slowly to room temperature overnight. The resulting dark colored contents were cooled to 5 °C, poured into 2% aqueous sodium bicarbonate (500 mL), and extracted with Et_2O (3 × 300 mL). The combined extracts were washed with 3% aqueous sodium thiosulfate (2 × 250 mL), H_2O (2 × 200 mL), and brine (2 × 250 mL), dried (Na_2SO_4), and concentrated in vacuo to afford 25.9 g of light purple crystalline material. Recrystallization from 5:1 ether–methylene chloride gave 11.8 g (56%) of pure **24** as off-white crystals after washing with hexane, mp 149–150 °C. The mother liquor was chromatographed over Florisil with 1:1 ether–hexane to give an additional 4.15 g (75% combined yield) of pure **24**. Crystallization from 4:1 Et_2O–CH_2Cl_2 gave the analytical sample: mp 153–154 °C; IR (KBr) 1600 (m), 1475 (s), 1445 (s), 1365 (s), 1170 (m), 1032 (s), 828 (m), 805 (s), 725 (s), 685 (s), 600 cm^{-1} (m); ^1H NMR ($CDCl_3$) δ 7.98–7.20 (m, 7 H), 7.09–6.70 (m, 2 H), 3.78 (s, 3 H); ^{13}C NMR ($CDCl_3$) δ 157.0, 137.8, 133.9, 133.4, 130.3, 129.2, 128.8, 126.6, 115.1, 114.3, 104.0, 67.1, 55.7; UV (95% EtOH) λ_{max} 221, 262, 294 (sh), 300, 307 (sh) nm.

Anal. Calcd for $C_{15}H_{12}NO_3SI$: C, 43.60; H, 2.93; N, 3.39; S, 7.76; I, 30.71. Found: C, 43.66; H, 2.93; N, 3.37; S, 7.81; I, 30.81.

1-(Phenylsulfonyl)-5-methoxyindol-3-yl 3-Carboxy-4-pyridyl Ketone (26). A magnetically stirred solution of the iodoindole **24** (6.70 g, 16.2 mmol) in dry THF (215 mL) under argon was cooled to −105 °C and treated rapidly via syringe with 2 equiv of *tert*-butyllithium (2.10 M in pentane; 15.5 mL, 32.5 mmol). The resulting light yellow cloudy mixture was stirred at −100 °C for 10 min, cooled to −108 °C, and then quenched very rapidly via syringe with a solution of 3,4-pyridinedicarboxylic acid anhydride (**7**) (2.66 g, 17.8 mmol) in dry THF (55 mL) with very efficient cooling and stirring being maintained throughout the addition. The resulting reddish-brown solution was kept at approximately −100 °C for 1 h and then allowed to warm to room temperature overnight. The solvent was removed in vacuo to give a tan residue, which was dissolved in H_2O (400 mL) and slowly acidified to pH 2–3 with 20% HCl with efficient stirring and cooling. The resulting milky white precipitate was stirred at 5–10 °C for 1 h, collected by filtration, thoroughly washed with H_2O, and dried at 60 °C (0.5 torr). The resulting white solid material was digested with boiling acetone (450 mL) for 45 min, cooled to room temperature, and suction filtered to afford 2.05 g of pure **26** as a white solid, mp 260–263 °C dec (R_f 0.44, THF). The filtrate was concentrated to 60 mL and allowed to cool slowly. This gave

an additional 3.39 g (77% combined yield) of pure keto acid **26**, mp 238–241 °C dec. Recrystallization from acetone gave the analytical sample: mp 259–260 °C dec; IR (KBr) 3450 (br s), 2490 (br s), 1714 (s), 1658 (s), 1536 (s), 1485 (s), 1456 (s), 1389 (s), 1225 (s), 1170 (m), 984 (s), 690 (s), 608 cm^{-1} (s); 360-MHz ^1H NMR (Me_2SO-d_6) δ 9.16 (s, 1 H), 8.93 (d, 1 H, J = 4.9 Hz), 8.10–8.03 (m, 2 H), 7.88 (d, 1 H, J = 9.2 Hz), 7.80–7.73 (m, 1 H), 7.69 (d, 1 H, J = 2.5 Hz), 7.66–7.58 (m, 4 H), 7.07 (dd, 1 H, J = 9.2 and 2.5 Hz), 3.81 (s, 3 H); ^{13}C NMR (Me_2SO-d_6) δ 189.4, 165.7, 157.3, 153.2, 150.8, 147.9, 136.3, 135.2, 135.1, 130.0, 128.8, 128.2, 127.1, 124.6, 121.6, 120.3, 115.1, 114.1, 104.4, 55.5; UV (95% EtOH) λ_{max} 215, 266 (sh), 273 (sh), 286 (sh) nm.

Anal. Calcd for $C_{22}H_{16}N_2O_6S$·C_3H_6O: C, 60.72; H, 4.48; N, 5.66; S, 6.48. Found: C, 60.63; H, 4.50; N, 5.62; S, 6.43.

1-(Phenylsulfonyl)-5-methoxyindol-3-yl 3-Carbethoxy-4-pyridyl Ketone (27). The keto acid **26** (1.95 g, 4.47 mmol), absolute ethanol (260 mL), and concentrated sulfuric acid (110 drops, ca. 22 mmol) were refluxed for 96 h with a Soxhlet apparatus containing activated molecular sieves. The reaction mixture was worked up as for **18** to afford 2.02 g (98%) of pure **27** as a light tan solid (R_f 0.55, EtOAc). Flash chromatography as for **18** gave 1.76 g of analytically pure **27** as colorless crystals: mp 160–161.5 °C; IR (KBr) 1716 (s), 1656 (s), 1537 (s), 1452 (s), 1383 (s), 1305 (s), 1170 (m), 979 (s), 728 cm^{-1} (s); ^1H NMR ($CDCl_3$) δ 9.32 (s, 1 H), 8.95 (d, 1 H), 8.03–7.25 (m, 9 H), 7.03 (dd, 1 H), 4.08 (q, 2 H, J = 7.5 Hz), 3.87 (s, 3 H), 0.99 (t, 3 H, J = 7.5 Hz); ^{13}C NMR ($CDCl_3$) δ 189.0, 164.3, 157.8, 153.2, 151.6, 148.2, 137.2, 134.4, 133.9, 129.5, 129.4, 128.3, 126.8, 123.9, 121.1, 120.9, 116.1, 113.9, 104.4, 61.7, 55.7, 13.5; UV (95% EtOH) λ_{max} 216, 266 (sh), 275 (sh), 290 (sh) nm.

Anal. Calcd for $C_{24}H_{20}N_2O_6S$: C, 62.06; H, 4.34; N, 6.03; S, 6.90. Found: C, 61.99; H, 4.38; N, 6.00; S, 6.90.

7-Methoxy-10*H*-pyrido[3,4-*b*]carbazole-5,11-quinone (28). A solution of lithium bis(trimethylsilyl)amide (3.57 mmol) in dry THF (10 mL) was prepared under argon from freshly distilled 1,1,1,3,3,3-hexamethyldisilazane (0.60 g, 3.7 mmol) and *n*-butyllithium (1.70 M in hexane; 2.10 mL, 3.57 mmol). To this magnetically stirred solution at 25 °C was slowly added dropwise a solution of the keto ester **27** (552.6 mg, 1.189 mmol) in dry THF (40 mL) over 70 min. The resulting red-orange solution was stirred at room temperature for an additional 30 min, refluxed for 30 min, and then allowed to stir at room temperature under argon overnight. The reaction mixture was then treated with 20% HCl (20 mL) and stirred at room temperature for 1 h. The mixture was poured into saturated aqueous sodium bicarbonate (150 mL) and diluted with H_2O (50 mL), and the resulting dark reddish-brown mixture was partitioned with ethyl acetate (400 mL) and subjected to continuous extraction (refluxing ethyl acetate in the reservoir) for 48 h. The brine-washed (1 × 200 mL) and dried (Na_2SO_4) extracts contained most of the material, but continuous extraction for an additional 7 days provided considerably more quinone **28** which was nearly pure by TLC (R_f 0.50, EtOAc). The combined extracts were adsorbed onto silica gel and flash chromatographed with 1:1 ethyl acetate–methylene chloride to provide 198.0 mg (60%) of pure quinone **28** as a reddish-brown solid, mp 300–304 °C. Recrystallization from 4:1 ethyl acetate–THF gave the analytical sample as bright red-orange crystals: mp 310–313 °C dec; IR (KBr) 3425 (br s), 1662 (s), 1656 (s), 1589 (s), 1515 (m), 1480 (s), 1266 (s), 1098 (m), 1017 (s), 702 (s), 500 cm^{-1} (m); 360-MHz ^1H NMR (Me_2SO-d_6) δ 13.2–12.9 (br s, 1 H), 9.16 (s, 1 H), 9.04 (d, 1 H, J = 5.0 Hz), 7.87 (d, 1 H, J = 5.0 Hz), 7.49 (d, 1 H, J = 2.4 Hz), 7.44 (d, 1 H, J = 9.0 Hz), 7.04 (dd, 1 H, J = 2.4 and 9.0 Hz), 3.84 (s, 3 H); UV (EtOH) λ_{max} 269 (sh), 279, 324 (sh), 442 nm (log ϵ 4.20, 4.25, 3.28, 3.68); mass spectrum, m/e 278 (M^+, 100%), 263, 235, 152, 139 (M^{2+}), 125; exact mass calcd for $C_{16}H_{10}N_2O_3$: 278.0692. Found: 278.0697.

Anal. Calcd for $C_{16}H_{10}N_2O_3$: C, 69.06; H, 3.62; N, 10.07. Found: C, 68.78; H, 3.68; N, 10.03.

5,11-Dimethyl-7-methoxy-10*H*-pyrido[3,4-*b*]carbazole (2b, 7-Methoxyisoellipticine). Quinone **28** (258.9 mg, 0.9303 mmol) in dry THF (140 mL) was treated at 20 °C under argon with methyllithium (1.48 M in Et_2O; 4.00 mL, 5.92 mmol). The mixture was stirred at 25 °C for 5 min and then refluxed for 3.5 h. The resulting reddish-brown mixture was cooled and treated with H_2O (15 mL), and the solvent was removed in vacuo to give the derived diol as a reddish viscous residue. This material was immediately treated under argon with sodium borohydride (6 pellets, ca. 1.5 g) and absolute ethanol (250 mL) and then refluxed with magnetic stirring for 21 h. The sodium borohydride was added in portions: three pellets initially, one more after 1 h, and one after 19 and 20 h at reflux. The highly fluorescent mixture was cooled and worked up as for **2a**. The resulting yellow-brown solid was dissolved in dry THF and adsorbed onto silica gel. Flash chromatography over silica gel with 3:1 ethyl acetate–THF elution afforded 141.4 mg (55%) of pure **2b** as a yellow-orange solid (62% based on 28.5 mg of pure recovered quinone **28**), mp 230–235 °C dec (R_f 0.43, THF). Crystallization from ethyl acetate gave the analytical sample: mp 250–253 °C dec; IR (KBr) 3460 (br s), 1606 (s), 1490 (m), 1385 (s), 1280 (m), 1227 (s), 1148 (s), 1021 (m), 853 (s), 836 (s), 804 (m), 460 cm^{-1} (s); 360-MHz ^1H NMR (Me_2SO-d_6) δ 11.16 (s, 1 H), 9.59 (s, 1 H), 8.39 (d, 1 H, J = 6.1 Hz), 8.12 (d, 1 H, J = 6.1 Hz), 7.90 (d, 1 H, J = 2.1 Hz), 7.50 (d, 1 H, J = 8.7 Hz), 7.23 (dd, 1 H, J = 8.7 and 2.1 Hz), 3.91 (s, 3 H), 3.15 (s, 3 H), 2.94 (s, 3 H); 90-MHz ^{13}C NMR (Me_2SO-d_6) δ 152.9, 148.7, 142.7, 139.0, 138.2, 137.8, 127.8, 125.6, 124.8, 116.7, 116.0, 111.1, 110.4, 107.8, 98.3, 55.7, 14.4, 11.7; mass spectrum, m/e 276 (M^+, 100%), 261 (97%), 233, 218, 138 (M^{2+}, 24%); UV (EtOH) λ_{max} 234, 280 (sh), 287, 306 (sh), 324 (sh), 338 (sh), 430 (sh), 440 nm (log ϵ 4.26, 4.63, 4.63, 4.08, 3.84, 3.44, 3.54, 3.56).

Anal. Calcd for $C_{18}H_{16}N_2O$·($^1/_8$)$C_4H_8O_2$: C, 77.33; H, 5.96; N, 9.75. Found: C, 77.30; H, 5.80; N, 9.64.

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Registry No. **2a**, 13799-49-0; **2b**, 86335-34-4; **5**, 80757-41-1; **7**, 4664-08-8; **11**, 80360-14-1; **13**, 86335-35-5; **14**, 86335-36-6; **18**, 86335-37-7; **19**, 86335-38-8; **20**, 81940-22-9; **21**, 86335-39-9; **22**, 86335-40-2; **22** (diol derivative), 86335-41-3; **23**, 1006-94-6; **24**, 86335-42-4; **26**, 86335-43-5; **27**, 86335-44-6; **28**, 86335-45-7; **28** (diol derivative), 86335-46-8.