Nitroarylstannanes as Synthons for the Preparation of Phenanthridine and Benzo[*i*]phenanthridine Derivatives

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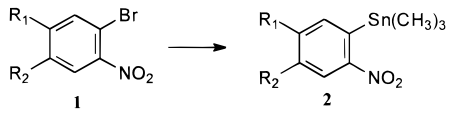
Received August 19, 1999

Substituted benzo[*c*]phenanthridine alkaloids and, more recently, benzacridine derivatives have demonstrated activity as topoisomerase I poisons and were shown to possess antitumor activity.[1,2] In view of our interest in furthering the structure activity associated with these antitumor compounds, we explored synthetic methods to provide for variously substituted phenanthridine and benzo[*i*]phenanthridines. Preparation of the *N*-oxide of phenanthridine has been accomplished by reductive cyclization of 2-formyl-2′-nitrobiphenyl using ferrous sulfate in aqueous ammonia.[3] 2-Formyl-3-(*o*-nitrophenyl)thiophene, 2-formyl-3-(*o*-nitrophenyl)furan, and 4-formyl-3-(*o*-nitrophenyl)thiophene have been similarly treated to form thieno[2,3-*c*]quinoline-*N*-oxide, furo-[2,3-*c*]quinoline-*N*-oxide, and thieno[3,4-*c*]quinoline-*N*-oxide, respectively.[3,4] A similar reductive cyclization has recently been used in the preparation of 3-phenanthridin-6-ylpropionic acid ethyl ester and its *N*-oxide.[5] The formation of the requisite 2-formyl-2′-nitroaryl intermediates was frequently accomplished by reaction of the appropriate formyl boronic acid with *o*-nitrobenzene.[3,4] 3-Formyl-2-tributylstannaylfuran, however, has been coupled to *o*-bromobenzene with subsequent reductive cyclization to form furo[3,2-*c*]quinoline *N*-oxide.[6] More recently, coupling of 7-stannylated indoline with *o*-bromobenzaldehyde derivatives proved to be an effective method for the preparation of pyrrolophenanthridone alkaloids.[7] Using a similar approach, we envisioned that the use of *o*-nitrostannanes could serve as an efficient method for the preparation of a variety of substituted phenanthridine and benzo[*i*]phenanthridine derivatives.

The Stille coupling reaction for the formation of biaryl compounds has been used extensively in organic synthesis.[8,9] However, only a limited number of *o*-nitroarylstannanes have been synthesized,[10] and there are no reports of an *o*-nitrostannane being coupled with an *o*-bromobenzaldehyde derivative. In the present study, we investigated the ease of formation of several *o*-nitroarylstannanes (**2a**−**f**) with varying electron-donating and electron-withdrawing substituents. We also evaluated these *o*-nitroarylstannanes for their utility in forming the requisite 2-(*o*-nitrophenyl)benzaldehyde and 2-(*o*-nitrophenyl)-1-naphthaldehyde intermediates needed for the preparation of phenanthridine and benzo[*i*]phenanthridine derivatives, respectively.

Scheme 1



	R_1	R_2	Yield
2a	OCH_3	OCH_3	70%
2b	OCH_2O		65%
2c	H	H	75%
2d	H	OCH_3	55%
2e	H	CH_3	65%
2f	H	CF_3	60%

Various trimethyl-*o*-nitrophenylstannane derivatives (**2a**−**f**) were synthesized from the appropriately substituted 2-bromonitrobenzene by reaction with hexamethylditin and $Pd(PPh_3)_4$ in THF at reflux (Scheme 1) in yields ranging from 55 to 75%.

Reaction of **2a**, **2b**, **2d**, and **2f** with 2-bromobenzaldehyde in the presence of tetrakis(triphenylphosphine)-palladium(0) and cuprous bromide in refluxing THF resulted in the formation of the 2-(*o*-nitrophenyl)benzaldehyde derivatives **3a**, **3b**, **3d**, and **3f**. Treatment of these biphenyl derivatives with zinc dust in acetic acid provided the phenanthridine derivatives, **4a**, **4b**, **4d**, and **4f** in yields ranging from 55 to 83% (Scheme 2).

Compound **4d** has previously been synthesized by decomposition and subsequent rearrangement of 9-azido-2-methoxyfluorene to provide a mixture of **4d** together with 8-methoxyphenanthridine in low yield.[11] This same method resulted in the formation of a mixture tentatively characterized as **4e** and 8-methylphenanthridine. An alternative method for the preparation of **4e** involved reduction of 3-methyl-5*H*-phenanthridin-6-one with zinc dust.[12] There are several additional methods for the preparation of phenanthridines.[13] These methods, however, generally provide product in low yield and lack the flexibility that would make them suitable for preparation of many substituted phenanthridines. The coupling of *o*-nitroarylstannanes to *o*-bromobenzaldehydes offers a convenient route that allows for the preparation of a wide variety of substituted phenanthridines.

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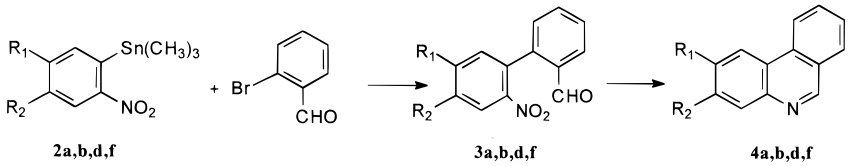
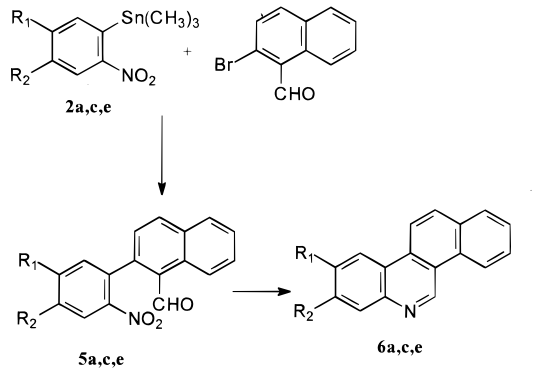
10.1021/jo991318g CCC: $19.00
Published on Web 03/30/2000

Scheme 2



Scheme 3



This general synthetic approach was extended to the preparation of several benzo[*i*]phenanthridine derivatives. Reaction of **2a**, **2c**, or **2e** with 2-bromo-1-naphthaldehyde provided a convenient route for the formation of 2-(2-nitrophenyl)-1-naphthaldehydes **5a**, **5c**, and **5e**, respectively (Scheme 3). Treatment of these 2-(2-nitrophenyl)-1-naphthaldehydes with zinc dust in acetic acid at reflux provided 8,9-dimethoxybenzo[*i*]phenanthridine (**6a)**, benzo[*i*]phenanthridine (**6c**), and 8-methylbenzo[*i*]-phenanthridine (**6e)** in good yield.

There are several methods for the preparation of benzo[*i*]phenanthridine, **6c**. These involve (1) the decomposition and rearrangement of 11-azido-11*H*-benzo[*a*]-fluorene,[14] (2) reduction of benzo[*i*]phenanthridone,[15] (3) benzyne cyclizations of either *N*-(2-chloro-1-naphthylmethylene)aniline or *N*-phenyl-(2-chloro-1-naphthyl)-methylamine,[16] as well as (4) cyclization of *N*-[2-cyclohexyl-1-(naphth-2-yl)]formamide followed by dehydrogenation with Pd/C.[17] Compounds **6a** and **6e** have not been previously synthesized. The use of 11-azido-11*H*-benzo-[*a*]fluorene was shown to result in the formation of a mixture of **6c** and benzo[*a*]phenanthridine. The synthetic methods for the preparation of either benzo[*i*]phenanthridone or *N*-[2-cyclohexyl-1-(naphth-2-yl)]formamide are multistep and are not amenable to the synthesis of a variety of substituted benzo[*i*]phenanthridines. It is not surprising, therefore, that there are limited reports on the synthesis of substituted benzo[*i*]phenanthridines in the literature. The coupling of *o*-nitroarylstannanes with appropriately substituted 2-bromo-1-naphthaldehydes should provide a practical method for the preparation of benzo[*i*]phenanthridine derivatives.[18]

In summary, we have developed an effective method for the preparation of 2-formyl-2′-nitrobiaryl derivatives that can serve as effective intermediates for a variety of substituted heterocycles that incorporate the phenanthridine ring system.

Experimental Section

General Methods. Proton (^{1}H) and carbon (^{13}C) nuclear magnetic resonance were recorded using a 200 Fourier transform spectrometer. NMR spectra (200 MHz ^{1}H and 50 MHz ^{13}C) are reported with chemical shifts shown in δ units downfield from tetramethylsilane (TMS). Coupling constants are reported in hertz (Hz). Mass spectra were obtained from Washington University Resource for Biomedical and Bio-organic Mass Spectroscopy within the Department of Chemistry at Washington University, St. Louis, MO. Infrared spectral data (IR) are reported in cm^{-1}. Melting points were determined using a capillary melting point apparatus and are uncorrected. Column chromatography refers to flash chromatography conducted on SiliTech 32−63 μm (ICN Biomedicals, Eschwegge, Ger.) using the solvent system indicated. Compound **1a** and **1b** were prepared by nitration of 4-bromoveratrole and 4-bromo-1,2-(methylenedioxy)benzene as previously described.[19,20] Intermediates **1c**−**f** were purchased from Aldrich Chemical Co. (Milwaukee, WI). 2-Bromo-1-naphthaldehyde was prepared by treatment of 2-bromo-3,4-dihydro-1-naphthaldehyde[21] with DDQ. All reactions were carried out under nitrogen.

2-Bromo-1-naphthaldehyde. Dimethylformamide (0.8 mL, 10 mmol) was added dropwise to a solution of phosphorus tribromide (0.8 mL, 8.4 mmol) in dry chloroform (20 mL) at 0 °C. The mixture was stirred at 0 °C for 1 h to give a pale yellow suspension. A solution of β-tetralone (500 mg, 3.4 mmol) in dry chloroform (20 mL) was added to the yellow suspension, and the mixture was heated at reflux for 1 h. The reaction mixture was cooled to 0 °C and made basic with saturated aqueous $NaHCO_3$ solution. The resulting mixture was extracted with dichloromethane, dried (anhyd Na_2SO_4), and evaporated in vacuo. The residue was chromatographed over 100 g of silica gel using a 1:3 mixture of ethyl acetate/hexanes to give 2-bromo-3,4-dihydro-1-naphthaldehyde in 83% yield.[21] 2-Bromo-3,4-dihydro-1-naphthaldehyde (160 mg, 0.68 mmol) and DDQ (154 mg, 0.68 mmol) was refluxed in toluene (20 mL) for 12 h. After being cooled to room temperature, the mixture was filtered through a Celite bed and the filtrate was evaporated to dryness. The residue obtained was chromatographed on 75 g silica gel using a 1:3 mixture of ethyl acetate/hexanes to give 2-bromo-1-naphthaldehyde in 90% yield: mp = 80−2 °C; ^{1}H NMR ($CDCl_3$) δ 7.53−7.71 (3H, m), 7.85 (1H, dd, J = 7.8, 1.5), 7.88 (1H, d, J = 8.8), 9.10 (1H, d, J = 8.8), 10.77 (1H, s); ^{13}C NMR ($CDCl_3$) δ 125.2, 127.7, 128.9, 130.1, 131.0, 131.2, 132.2, 133.4, 135.8, 195.3; HRMS calcd for $C_{11}H_7BrO$ 233.9680, found 233.9682.

General Procedure for the Preparation of Trimethylnitroarylstannanes (2). Trimethyl(3,4-dimethoxy-6-nitrophenyl)stannane (2a). A mixture of hexamethylditin (3 g, 9.2 mmol), compound **1a** (1.6 g, 6.1 mmol), and $Pd(PPh_3)_4$ (200 mg) in anhydrous THF (30 mL) was heated to reflux under nitrogen

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for 10 h. After the mixture was cooled to room temperature, THF was evaporated and methylene chloride (30 mL) was added to the residue. To this mixture was added dropwise aqueous potassium fluoride (7.0 M, 2 mL) with vigorous stirring. The mixture was passed through a Celite bed, and the filtrate was washed with brine. The methylene chloride layer was dried (anhyd Na_2SO_4), filtered, and evaporated in vacuo. The residue was chromatographed over 100 g of silica gel using 1:6 ethyl acetate/hexanes to give **2a** in 70% yield: mp 115−7 °C; ^{1}H NMR ($CDCl_3$) δ 0.32 (9H, s [^{119}Sn−H, d, $^2J_{Sn-H}$ = 54]), 3.94 (3H, s), 3.99 (3H, s), 7.03 (1H, s), 7.88 (1H, s); ^{13}C NMR ($CDCl_3$) δ −7.2, 56.7, 107.7, 117.3, 134.0, 146.8, 149.8, 154.1; HRMS calcd for $C_{11}H_{17}NO_4Sn - CH_3$ 329.9937, found 329.9939.

Trimethyl(3,4-methylenedioxy-6-nitrophenyl)stannane (2b). Prepared from **1b** (1.6 g, 6.5 mmol) in 65% yield: ^{1}H NMR ($CDCl_3$) δ 0.32 (9H, s [^{119}Sn−H, d, $^2J_{Sn-H}$ = 52]), 6.12 (2H, s), 7.04 (1H, s), 7.82 (1H, s); ^{13}C NMR ($CDCl_3$) δ −6.9, 103.3, 105.8, 114.5, 137.2, 147.9, 149.4, 153.4; HRMS calcd for $C_{10}H_{13}NO_4Sn - CH_3$ 315.9632, found 315.9638.

Trimethyl(2-nitrophenyl)stannane (2c). Prepared from **1c** (1.3 g, 6.4 mmol) in 75% yield: ^{1}H NMR ($CDCl_3$) δ 0.35 (9H, s [^{119}Sn−H, d, $^2J_{Sn-H}$ = 54]), 7.47−7.75 (3H, m), 8.34 (1H, dd, J = 8.1, 1.2); ^{13}C NMR ($CDCl_3$) δ −7.2, 124.5, 129.9, 134.0, 137.6, 140.3, 153.7; HRMS calcd for $C_9H_{13}NO_2Sn-CH_3$ 271.9734, found 271.9744.

Trimethyl(4-methoxy-2-nitrophenyl)stannane (2d). Prepared from **1d** (1.6 g, 6.9 mmol) in 55% yield: mp 93−5 °C; ^{1}H NMR ($CDCl_3$) δ 0.32 (9H, s [^{119}Sn−H, d, $^2J_{Sn-H}$ = 54]), 3.89 (3H, s), 7.21 (1H, dd, J = 8.0, 2.6), 7.57 (1H, d, J = 8.0), 7.86 (1H, d, J = 2.6); ^{13}C NMR ($CDCl_3$) δ −7.1, 56.7, 107.7, 117.3, 133.9, 146.8, 149.6, 154.1; HRMS calcd for $C_{10}H_{15}NO_3Sn - CH_3$ 301.9839, found 301.9832.

Trimethyl(4-methyl-2-nitrophenyl)stannane (2e). Prepared from **1e** (1.1 g, 5.1 mmol) in 65% yield: ^{1}H NMR ($CDCl_3$) δ 0.31 (9H, s [^{119}Sn−H, d, $^2J_{Sn-H}$ = 52]), 2.43 (3H, s), 7.43 (1H, d, J = 7.0), 7.56 (1H, d, J = 7.0), 8.14 (1H, s); ^{13}C NMR ($CDCl_3$) δ −7.3, 21.5, 124.9, 135.0, 136.5, 137.4, 140.4, 153.9; HRMS calcd for $C_{10}H_{15}NO_2Sn - CH_3$ 285.9890, found 285.9890.

Trimethyl(4-trifluoromethyl-2-nitrophenyl)stannane (2f). Prepared from **1f** (1.4 g, 5.2 mmol) in 60% yield: ^{1}H NMR ($CDCl_3$) δ 0.38 (9H, s [^{119}Sn−H, d, $^2J_{Sn-H}$= 56]), 7.88 (2H, s), 8.58 (1H, s); ^{13}C NMR ($CDCl_3$) δ −7.1, 121.2, 126.3, 129.9, 132.8, 138.6, 145.7, 153.9; HRMS calcd for $C_{10}H_{12}NO_2F_3Sn - CH_3$ 339.9607, found 315.9604.

General Procedure for the Preparation of 2-Formyl-2′-nitrobiphenyl Derivatives (3a,b,d,f) and 2-(2-Nitrophenyl)-1-naphthaldehydes (5a,c,e). 2-(4,5-Dimethoxy-2-nitrophenyl)benzaldehyde (3a). Tetrakis(triphenylphosphine)palladium (0) (60 mg, 0.05 mmol) and cuprous bromide (10 mg, 0.07 mmol) were added to a solution of **2a** (345 mg, 1.0 mmol) and 2-bromobenzaldehyde (150 mg, 0.8 mmol) in THF (15 mL) at room temperature. The mixture was refluxed under N_2 for 15 h. After cooling, THF was evaporated and ethyl acetate (30 mL) was added to the residue. The solution was washed with water (20 mL). The organic layer was separated and passed through a Celite bed to remove suspended particles. The organic layer was then washed with brine, dried (anhyd Na_2SO_4), and evaporated in vacuo. The residue was chromatographed using 75 g of silica gel and a 1:3 mixture of ethyl acetate/hexanes to give **3a** in 70% yield: mp 118−120 °C; ^{1}H NMR ($CDCl_3$) δ 3.92 (3H, s), 4.03 (3H, s), 6.69 (1H, s), 7.24 (1H, dd, J = 7.1, 1.9), 7.53−7.69 (2H, m), 7.75 (1H, s), 7.99 (1H, dd, J = 7.1, 1.9), 9.86 (1H, s); ^{13}C NMR ($CDCl_3$) δ 56.9, 57.0, 108.2, 114.1, 128.9, 130.1, 130.2, 134.2, 141.3, 141.8, 149.1, 153.2, 191.7; HRMS calcd for $C_{15}H_{13}NO_5 - NO_2$ 241.0865, found 241.0855.

2-(4,5-Methylenedioxy-2-nitrophenyl)benzaldehyde (3b). Prepared from **2b** (320 mg, 1.0 mmol) and 2-bromobenzaldehyde (150 mg, 0.8 mmol) in 60% yield: ^{1}H NMR ($CDCl_3$) δ 6.18 (2H, s), 6.70 (1H, s), 7.22 (1H, dd, J = 6.9, 1.8), 7.30−7.36 (1H, m), 7.56−7.63 (1H, m), 7.65 (1H, s), 7.97 (1H, dd, J = 7.0, 2.0), 9.89 (1H, s); ^{13}C NMR ($CDCl_3$) δ 103.8, 105.9, 111.5, 129.1, 130.1, 130.7, 131.1, 134.1, 134.3, 141.3, 142.7, 148.4, 151.9, 191.6.

2-(4-Methoxy-2-nitrophenyl)benzaldehyde (3d). Prepared from **2d** (300 mg, 1.0 mmol) and 2-bromobenzaldehyde (150 mg, 0.8 mmol) in 60% yield: ^{1}H NMR ($CDCl_3$) δ 3.94 (3H, s), 7.21−7.27 (3H, m), 7.52−7.66 (3H, m), 7.98 (1H, dd, J = 7.1, 2.0), 9.86 (1H, s); ^{13}C NMR ($CDCl_3$) δ 56.5, 109.7, 119.7, 126.3, 129.0, 130.3, 130.7, 133.8, 134.1, 134.4, 141.0, 149.8, 160.3, 191.8; HRMS calcd for $C_{14}H_{11}NO_4 - NO_2$ 211.0759, found 211.0753.

2-(4-Trifluoromethyl-2-nitrophenyl)benzaldehyde (3f). Prepared from **2f** (425 mg, 1.2 mmol) and 2-bromobenzaldehyde (185 mg, 1.0 mmol) in 95% yield: mp = 115−7 °C; ^{1}H NMR ($CDCl_3$) δ 7.24 (1H, dd, J = 6.7, 2.0), 7.47 (1H, d, J = 8.1), 7.64−7.69 (2H, m), 7.91 (1H, dd, J = 8.1, 1.1), 7.97 (1H, d, J = 6.7), 8.39 (1H, s), 9.87 (1H, s); ^{13}C NMR ($CDCl_3$) δ 120.6, 122.2, 122.3, 126.0, 129.7, 130.2, 132.0, 132.9, 133.4, 133.8, 134.4, 138.5, 148.9, 191.6; HRMS calcd for $C_{14}H_8NO_3F_3 - NO_2$ 249.0527, found 249.0531.

2-(3,4-Dimethoxy-6-nitrophenyl)-1-naphthaldehyde (5a). Prepared from **2a** (350 mg, 1.0 mmol) and 2-bromo-1-naphthaldehyde (235 mg, 1.0 mmol) in 90% yield: mp = 136−8 °C; ^{1}H NMR ($CDCl_3$) δ 3.94 (3H, s), 4.02 (3H, s), 6.74 (1H, s), 7.28 (1H, d, J = 8.4), 7.58−7.70 (2H, m), 7.78 (1H, s), 7.85−7.91 (1H, m), 8.04 (1H, d, J = 8.4), 9.21 (1H, d, J = 8.4), 10.24 (1H, s); ^{13}C NMR ($CDCl_3$) δ 57.0, 57.1, 108.3, 114.8, 126.0, 127.1, 127.3, 128.4, 128.8, 129.4, 129.8, 130.7, 133.8, 134.7, 141.0, 145.5, 148.3, 153.1, 193.4; HRMS calcd for $C_{19}H_{15}NO_5 - NO_2$ 291.1021, found 291.1012.

2-(*o*-Nitrophenyl)-1-naphthaldehyde (5c). Prepared from **2c** (345 mg, 1.2 mmol) and 2-bromo-1-naphthaldehyde (235 mg, 1.0 mmol) in 97% yield: ^{1}H NMR ($CDCl_3$) δ 7.31 (1H, d, J = 8.4), 7.42 (1H, dd, J = 7.0, 2.0), 7.60−7.79 (4H, m), 7.95 (1H, dd, J = 8.0, 1.3), 8.08 (1H, d, J = 8.4), 8.18 (1H, dd, J = 7.0, 2.0), 9.20 (1H, d, J = 9.1), 10.28 (1H, s); ^{13}C NMR ($CDCl_3$) δ 125.2, 126.0, 127.2, 127.7, 128.8, 129.0, 129.9, 130.1, 131.1, 133.2, 133.7, 133.9, 134.7, 135.0, 144.2, 148.9, 193.1. HRMS calcd for $C_{17}H_{11}NO_3$ 277.0739, found 277.0748.

2-(4-Methyl-2-nitrophenyl)-1-naphthaldehyde (5e). Prepared from **2e** (300 mg, 1.0 mmol) and 2-bromo-1-naphthaldehyde (150 mg, 0.64 mmol) in 70% yield: ^{1}H NMR ($CDCl_3$) δ 2.55 (3H, s), 7.30 (1H, s), 7.43 (1H, d, J = 7.8), 7.50 (1H, d, J = 7.8), 7.57−7.78 (2H, m), 7.93 (1H, d, J = 7.5), 7.98 (1H, s), 8.06 (1H, d, J = 8.4), 9.23 (1H, d, J = 8.4), 10.26 (1H, s); ^{13}C NMR ($CDCl_3$) δ 21.9, 125.5, 126.1, 127.4, 127.6, 129.0, 130.0, 131.1, 132.0, 133.5, 133.9, 134.0, 134.7, 140.7, 144.5, 148.8, 193.4; HRMS calcd for $C_{18}H_{13}NO_3 - NO_2$ 245.0966, found 245.0959.

General Procedure for the Preparation of Phenanthridine (4a,b,d,f) and Benzo[*i*]phenanthridine Derivatives (6a,c,e). 2,3-Dimethoxyphenanthridine (4a). Compound **3a** (100 mg, 0.35 mmol) was dissolved in glacial acetic acid (20 mL) and heated to reflux with zinc dust (200 mg, 3.1 mmol) for 3 h. Acetic acid was evaporated in vacuo, and the residue was dissolved in chloroform. The solution was filtered through a Celite bed and the filtrate washed successively with saturated sodium bicarbonate solution and brine. The organic layer was dried (anhyd Na_2SO_4) and evaporated in vacuo. The residue was chromatographed using 75 g of silica gel and a 1:1 mixture of ethyl acetate/hexanes to give **4a** in 55% yield: mp 127−9 °C; ^{1}H NMR ($CDCl_3$) δ 4.01(3H, s), 4.12 (3H, s), 7.59 (1H, s), 7.65 (1H, d, J = 7.9), 7.80 (1H, dd, J = 8.3, 1.4), 7.84 (1H, s), 8.02 (1H, d, J = 7.7), 8.44 (1H, d, J = 8.1), 9.17 (1H, s); ^{13}C NMR ($CDCl_3$) δ 56.6, 102.2, 110.6, 118.8, 121.8, 126.2, 126.8, 129.3, 131.0, 132.6, 141.1, 150.0, 151.4, 151.9; IR (KBr) 1611, 1492, 1438; HRMS calcd for $C_{15}H_{13}NO_2$ 239.0947, found 239.0944.

2,3-Methylenedioxyphenanthridine (4b). Prepared from **3b** (80 mg, 0.29 mmol) in 67% yield: mp = 186−8 °C; ^{1}H NMR ($CDCl_3$) δ 6.15 (2H, s), 7.54 (1H, s), 7.63 (1H, t, J = 7.0), 7.80 (1H, t, J = 7.0), 7.87 (1H, s), 7.98 (1H, d, J = 8.0), 8.39 (1H, d, J = 8.0), 9.16 (1H, s); ^{13}C NMR ($CDCl_3$) δ 99.9, 102.3, 108.3, 120.6, 122.1, 126.2, 127.1, 129.1, 131.1, 133.0, 142.3, 148.7, 149.7, 151.8; IR (KBr) 1619, 1470; HRMS calcd for $C_{14}H_9NO_2$ 223.0633, found 223.0633.

3-Methoxyphenanthridine (4d). Prepared from **3d** (90 mg, 0.35 mmol) in 83% yield: mp = 58−60 °C (lit.[11] mp = 57−8 °C); ^{1}H NMR ($CDCl_3$) δ 3.99 (3H, s), 7.31 (1H, dd, J = 9.0, 2.7), 7.59−7.66 (2H, m), 7.81 (1H, t, J = 7.5), 8.01 (1H, d, J = 7.7), 8.45 (1H, d, J = 9.0), 8.49 (1H, d, J = 8.1), 9.25 (1H, s); ^{13}C NMR ($CDCl_3$) δ 56.0, 110.5, 118.6, 121.8, 123.9, 126.0, 126.9, 129.3, 131.5, 133.2, 146.6, 154.5, 155.3, 160.5; IR (KBr): 1673, 1611, 1467; HRMS calcd for $C_{14}H_{11}NO$ 209.0841, found 209.0839.

3-Trifluoromethylphenanthridine (4f). Prepared from **3f** (100 mg, 0.34 mmol) in 60% yield: mp = 120−2 °C; ^{1}H NMR ($CDCl_3$) δ 7.76−7.97 (3H, m), 8.10 (1H, d, J = 7.8), 8.47 (1H, s), 8.62 (1H, d, J = 7.7), 8.66 (1H, d, J = 8.5), 9.35 (1H, s); ^{13}C

NMR ($CDCl_3$) δ 121.8, 122.7, 123.5, 123.8, 127.3, 127.4, 128.2, 129.2, 129.4, 131.0, 132.1, 132.2, 144.3, 155.4; IR (KBr) 1672, 1328; HRMS calcd for $C_{14}H_8NF_3$ 247.0609, found 247.0604.

8,9-Dimethoxybenzo[*i*]phenanthridine (6a). Prepared from **5a** (100 mg, 0.30 mmol) in 90% yield: mp 164−6 °C; ^{1}H NMR ($CDCl_3$) δ 4.09 (3H, s), 4.14 (3H, s), 7.62 (1H, s), 7.65−7.76 (2H, m), 7.84 (1H, s), 7.96 (1H, d, J = 8.0), 8.09 (1H, d, J = 8.0), 8.39 (1H, d, J = 8.0), 8.87 (1H, d, J = 8.0), 10.06 (1H, s); ^{13}C NMR ($CDCl_3$) δ 56.6, 56.7, 102.0, 109.6, 119.4, 120.2, 121.4, 122.4, 127.2, 128.4, 129.4, 130.7, 131.6, 131.8, 141.1, 142.4, 146.0, 150.2, 151.6; IR (KBr) 1611, 1513, 1485; HRMS calcd for $C_{19}H_{15}NO_2$ 289.1103, found 289.1113.

Benzo[*i*]phenanthridine (6c). Prepared from **5c** (80 mg. 0.29 mmol) in 95% yield: mp 180−2 °C (lit.[14] mp = 182 °C); ^{1}H NMR (DMSO) δ 7.75−7.94 (4H, m), 8.20 (1H, d, J = 6.5), 8.24 (1H, d, J = 6.5), 8.41 (1H, d, J = 9.0), 8.90 (1H, d, J = 9.0), 8.94 (1H, d, J = 8.0), 9.20 (1H, d, J = 8.0), 10.40 (1H, s); ^{13}C NMR (DMSO) δ 120.5, 121.6, 123.0, 123.7, 124.0, 127.5, 127.6, 128.5, 129.2, 129.3, 129.7, 129.9, 131.7, 132.1, 132.5, 145.2, 148.5; IR (KBr) 1655, 1593, 1506; HRMS calcd for $C_{17}H_{11}N$ 229.0891, found 229.0895.

8-Methylbenzo[*i*]phenanthridine (6e). Prepared from **5e** (80 mg. 0.27 mmol) in 60% yield: mp = 162−4 °C; ^{1}H NMR (DMSO) δ 2.60 (3H, s), 7.63 (1H, d, J = 8.0), 7.72−7.89 (2H, m), 8.01 (1H, s), 8.18 (1H, d, J = 7.5), 8.35 (1H, d, J = 8.4), 8.79 (1H, d, J = 7.5), 8.82 (1H, d, J = 8.0), 9.16 (1H, d, J = 8.0), 10.34 (1H, s); ^{13}C NMR (DMSO) δ 21.4, 120.5, 121.2, 121.8, 122.8, 123.4, 127.4, 128.4, 129.1, 129.2, 129.4, 129.8, 131.7, 131.9, 132.3, 139.1, 145.4, 148.4; IR (KBr) 1651, 1614, 1589; HRMS calcd for $C_{18}H_{13}N$ 243.1048, found 243.1038.

Acknowledgment. Mass spectrometry was provided by the Washington University Mass Spectrometry Resource, an NIH Research Resource (Grant No. P41RR0954). This study was supported by Grant CA 39662 from the National Cancer Institute (L.F.L.) and a fellowship grant from the Johnson & Johnson Discovery Research Fund (E.J.L.).

Supporting Information Available: ^{1}H and ^{13}C NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

JO991318G