Supporting Information.

1-(3-Tributylstannyl-1-tritylaziridin-2-ylmethyl)indole-3-carboxylic acid ethyl ester (11a).

To a solution of 10 (0.105 g, 0.56 mmol) in 2:1 THF/DMPU (3.0 mL) at -78 °C was added a solution of NaN(TMS)_2 (0.75 mL of a 1 M solution in THF, 0.75 mmol) via syringe. To the resulting yellow solution was added a solution of mesylate 9^8,9 (0.375 g, 0.55 mmol) in anhydrous THF (4.7 mL) via cannula. The solution was warmed to rt and then maintained at 60 °C (oil bath temperature) for 4 days. The resulting brown reaction mixture was cooled to rt, poured into H_2O (25 mL), and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were washed with brine (1 x 20 mL) and dried (MgSO_4). Filtration and solvent removal (aspirator, then vacuum pump) afforded 2.149 g of a crude, brown oil that was purified by flash chromatography on silica gel (14 x 5 cm) using 1:9 ethyl acetate/hexanes eluent, 20 x 40 mL fractions collected. Fractions 11-13 were combined to yield 0.200 g (47%) of 11a as a clear, colorless oil.; analytical TLC on silica gel, 1:5 ethyl acetate/hexanes, Rf=0.47. No parent ion for C_{45}H_{56}N_2O_2Sn; M-C_4H_9, 719.2658, error=0 ppm; base peak=243 amu; IR(CH_2Cl_2, cm^{-1}) 1695, 1730, 1717, 3026, 2926, 1600, 1505, 1474, 1442, 1357, 1257, 1193, 1119, 1085, 1038, 995, 911, 876, 811, 611, C=O; 300 MHz NMR(CDCl_3, ppm) δ 8.17-8.11 (1H, m) 7.73 (1H, s) 7.40-7.35 (6H, m) 7.26-7.23 (3H, m) 7.19-7.13 (9H, m) 4.35 (2H, q, J= 7.2 Hz) 4.29 (1H, ABX, J= 14.0, 6.6 Hz) 4.12 (1H, ABX, J= 14.0, 5.2 Hz) 1.76 (1H, ddd, J= 6.6, 6.6, 5.2 Hz) 1.52-1.41 (6H, m) 1.40 (3H, t, J= 7.2 Hz) 1.35-1.21 (6H, m) 1.09 (1H, d, J= 6.6 Hz) 1.05-0.91 (6H, m) 0.86 (9H, t, J= 7.2 Hz) ^{13}C NMR (75 MHz, CDCl_3, ppm) δ 164.9, 143.9, 136.7, 133.6, 129.4, 129.3, 127.3, 126.7, 126.6, 122.6, 121.8, 109.8, 107.5, 75.6, 59.5, 50.9, 35.4, 29.2, 27.4, 25.8, 14.6, 13.6, 10.2.

1-(3-Tributylstannyl-1-tritylaziridin-2-ylmethyl)-2-deutero-indole-3-carboxylic acid ethyl ester (11b). To a solution of 11a (0.124 g, 0.16 mmol) in anhydrous THF (7.5 mL) at -78 °C was added a solution of phenyllithium (0.36 mL of a 1.8 M solution in 70:30
cyclohexane/diethyl ether, 0.65 mmol) via syringe. The resulting light-yellow colored solution was stirred at -78 °C for 20 min and d<sub>4</sub>-ethanol (2.0 mL, 34.00 mmol) was added via syringe. The resulting reaction was warmed to rt and stirred for 30 min. The reaction was poured into H<sub>2</sub>O (25 mL) and extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 x 25 mL). The combined organic layers were washed with brine (1 x 20 mL) and dried (MgSO<sub>4</sub>). Filtration and solvent removal (aspirator, then vacuum pump) afforded 0.136 g of a light-yellow oil that was purified by flash chromatography on silica gel (19 x 2.5 cm) using 1:9 ether/hexanes eluent, 25 x 8 mL fractions collected. Fractions 14-21 were combined to yield 0.111 g (89%) of 11b as a clear, colorless oil; analytical TLC on silica gel, 1:5 ethyl acetate/hexanes, Rf=0.47; No parent ion for C<sub>45</sub>H<sub>22</sub>DN<sub>2</sub>O<sub>2</sub>Sn; M-C<sub>4</sub>H<sub>9</sub>, 720.2721, error=0 ppm; base peak=243 amu; IR (CHCl<sub>3</sub>, cm<sup>-1</sup>) 1695, 1708, 1666, 1232, 1162, 1029, 748, 696 cm<sup>-1</sup>.<sup>1</sup>H NMR (CDCl<sub>3</sub>, ppm) δ 8.17-8.11 (1H, m) 7.40-7.34 (6H, m) 7.28-7.23 (3H, m) 7.21-7.13 (9H, m) 4.35 (2H, q, J= 7.1 Hz) 4.29 (1H, ABX, J= 14.0, 6.6 Hz) 4.12 (1H, ABX, J= 14.0, 5.0 Hz) 1.76 (1H, ddd, J= 6.6, 6.6, 5.0 Hz) 1.55-1.38 (6H, m) 1.40 (3H, t, J= 7.1 Hz) 1.34-1.21 (6H, m) 1.09 (1H, d, J= 6.6 Hz) 1.03-0.92 (6H, m) 0.86 (9H, t, J= 7.3 Hz) <sup>13</sup>C NMR (75 MHz, {<sup>1</sup>H}, CDCl<sub>3</sub>, ppm) δ 165.0, 143.9, 136.7, 133.8, 129.3 (two partly overlapping signals), 127.3, 126.7-126.6 (two partly overlapping signals), 122.6, 121.8, 109.8, 107.3, 75.6, 59.5, 50.9, 35.4, 29.2, 27.4, 25.8, 14.6, 13.6, 10.1.

9a-Deutero-1,2-(N-tritylaziridino)-2,3,9a-tetrahydro-1H-pyrrolo[1,2-a] indole-9-carboxylic acid ethyl ester (18). To a solution of 11b (0.077 g, 0.099 mmol) in anhydrous THF (5.0 mL) at -78 °C was added methyllithium (4.0 mL of a 0.10 M solution in ether, 0.40 mmol) via syringe. The resulting solution was maintained at -78 °C for 5 min, and then warmed to -65 °C. The reaction was stirred for 15 min, and quenched at -65 °C with EtOH (0.60 mL, 10.2 mmol), warmed to rt, poured into H<sub>2</sub>O (20 mL), and the aqueous layer extracted with CH<sub>2</sub>Cl<sub>2</sub>
(3x20 mL). The combined organic layers were washed with brine (1x15 mL), dried (MgSO₄).

Filtration and solvent removal (aspirator, then vacuum pump) afforded 0.0840 g of a yellow residue that was purified by PLC (20x20x0.2 cm, 1:5 EtOAc/hexanes eluent, 5 elutions) to yield 0.0467 g of 18 containing 18% of 12; analytical TLC on silica gel, 1:4 CH₂Cl₂/hexane, Rf= 0.15;

300 MHz NMR (CDCl₃, ppm) δ 7.52 (7H, d, J = 7.4 Hz overlapping 1H m) 7.34-7.17 (9H, m)
7.14 (1H, dd, J = 7.9, 7.4 Hz) 6.78 (1H, ddd, J = 7.4, 7.4, 1.0 Hz) 6.65 (1H, d, J = 7.9 Hz) 4.30-4.16 (2H, m) 4.04 (1H, bs) 3.85 (1H, d, J = 11.3 Hz) 3.25 (1H, dd, J = 11.3, 4.1 Hz) 2.34 (1H, dd, J = 5.1, 4.1 Hz) 2.12 (1H, d, J = 5.1 Hz) 1.29 (3H, t, J = 7.2 Hz).

(1S, 2S)-1,2-(N-Tritylaziridino)-2,3-dihydro-1H-pyrrolo[1,2-a]indole-9-carboxylic acid ethyl ester (19). To a solution of 11b (0.121 g, 0.155 mmol) in anhydrous THF (8.0 mL) at -78 °C was added a solution of methylolithium (2.40 mL of a 0.26 M solution in ether, 0.624 mmol) slowly via syringe. The resulting yellow solution was stirred at -78 °C for 5 min, warmed to -65 °C (CHCl₃/CO₂ bath), and stirred an additional 20 min at -65 °C. Next, a solution of phenylselenenyl chloride (0.136 g, 0.713 mmol) in anhydrous THF (8.0 mL) was added via cannula. The resulting yellow reaction mixture was stirred an additional 20 min at -65 °C, and slowly warmed to rt. The reaction was next poured into H₂O (40 mL) and extracted with CH₂Cl₂ (3 x 40 mL). The combined organic layers were washed with brine (1 x 60 mL) and dried (MgSO₄). Filtration and solvent removal (aspirator, then vacuum pump) afforded 0.195 g of a yellow residue that was purified by flash chromatography on silica gel (4 x 18 cm) using 1:3 ether/hexanes eluent, 30 x 20 mL fractions collected. Fractions 12-18 were combined to yield 0.0601 g (80%) of 19 as a light-yellow oil; analytical TLC on silica gel 60 F₂₅₄, 1:1 ether/hexanes, Rf= 0.50; [α]D25⁰ -16 (c 1.3, CH₂Cl₂). Molecular ion calcd for C₃₉H₃₉N₂O₂: 484.21510; found m/e= 484.2151, error= 0 ppm; base peak= 243 amu; IR (neat, cm⁻¹) 1691, 300 MHz NMR (CDCl₃, ppm) δ 7.52 (7H, d, J = 7.4 Hz overlapping 1H m) 7.34-7.17 (9H, m)
7.14 (1H, dd, J = 7.9, 7.4 Hz) 6.78 (1H, ddd, J = 7.4, 7.4, 1.0 Hz) 6.65 (1H, d, J = 7.9 Hz) 4.30-4.16 (2H, m) 4.04 (1H, bs) 3.85 (1H, d, J = 11.3 Hz) 3.25 (1H, dd, J = 11.3, 4.1 Hz) 2.34 (1H, dd, J = 5.1, 4.1 Hz) 2.12 (1H, d, J = 5.1 Hz) 1.29 (3H, t, J = 7.2 Hz).

(1S, 2S)-1,2-(N-Tritylaziridino)-2,3-dihydro-1H-pyrrolo[1,2-a]indole-9-carboxylic acid ethyl ester (19). To a solution of 11b (0.121 g, 0.155 mmol) in anhydrous THF (8.0 mL) at -78 °C was added a solution of methylolithium (2.40 mL of a 0.26 M solution in ether, 0.624 mmol) slowly via syringe. The resulting yellow solution was stirred at -78 °C for 5 min, warmed to -65 °C (CHCl₃/CO₂ bath), and stirred an additional 20 min at -65 °C. Next, a solution of phenylselenenyl chloride (0.136 g, 0.713 mmol) in anhydrous THF (8.0 mL) was added via cannula. The resulting yellow reaction mixture was stirred an additional 20 min at -65 °C, and slowly warmed to rt. The reaction was next poured into H₂O (40 mL) and extracted with CH₂Cl₂ (3 x 40 mL). The combined organic layers were washed with brine (1 x 60 mL) and dried (MgSO₄). Filtration and solvent removal (aspirator, then vacuum pump) afforded 0.195 g of a yellow residue that was purified by flash chromatography on silica gel (4 x 18 cm) using 1:3 ether/hexanes eluent, 30 x 20 mL fractions collected. Fractions 12-18 were combined to yield 0.0601 g (80%) of 19 as a light-yellow oil; analytical TLC on silica gel 60 F₂₅₄, 1:1 ether/hexanes, Rf= 0.50; [α]D25⁰ -16 (c 1.3, CH₂Cl₂). Molecular ion calcd for C₃₉H₃₉N₂O₂: 484.21510; found m/e= 484.2151, error= 0 ppm; base peak= 243 amu; IR (neat, cm⁻¹) 1691,
C=O; 400 MHz NMR (CDCl₃, ppm) δ 8.25-8.20 (1H, m) 7.49 (6H, d, J= 7.2 Hz) 7.32-7.20 (12H, m) 4.44 (1H, d, J= 11.5 Hz) 4.26 (1H, ABX₃, J= 10.6, 7.3 Hz) 4.19 (1H, ABX₃, J= 10.6, 7.3 Hz) 4.08 (1H, dd, J= 11.5, 4.0 Hz) 3.32 (1H, d, J= 4.4 Hz) 3.06 (1H, dd, J= 4.4, 4.0 Hz) 1.08 (3H, t, J= 7.3 Hz). ¹³C NMR (100 MHz, {H}, CDCl₃, ppm) δ 164.8, 149.4, 133.4, 130.4, 129.3, 127.7, 127.6, 127.1, 122.5, 121.9, 121.7, 109.6, 100.9, 74.4, 59.4, 47.7, 41.6, 36.8, 14.1.

(1S, 25)-1,2-Aziridino-2,3-dihydro-1H-pyrrolo[1,2-a]indole-9-carboxylic acid ethyl ester (20). To a solution of ester 19 (0.0363 g, 0.075 mmol) in anhydrous CH₂Cl₂ (3.0 mL) at 0 °C was added triethylsilane (36 mL, 0.225 mmol) via microliter syringe. To the resulting solution was added a solution of methanesulfonic acid (0.45 mL of a 0.5 M solution in CH₂Cl₂, 0.225 mmol) dropwise via syringe (the yellow color of the resulting solution gradually faded over 5 min). The resulting solution was stirred at 0 °C for 15 min, quenched via addition of i-Pr₂NEt (65 mL, 0.373 mmol), stirred for 30 min at 0 °C, warmed to rt, and stirred an additional 2 h at rt. The reaction was next diluted with CH₂Cl₂ (10 mL) and washed with brine (2 x 10 mL). The combined washings were extracted with CH₂Cl₂ (1 x 10 mL) and the combined organic layers dried (Na₂SO₄). Filtration and solvent removal (aspirator, then vacuum pump) afforded 0.0461 g of a white solid that was purified by PLC (silica gel washed with 1:1 hexanes/NEt₃ and dried before using; 20x20x0.1 cm; EtOAc eluent). Isolation of the band with Rf= 0.17 yielded 0.0119 g (65%) of 20 as a colorless oil; analytical TLC on washed (1:1 hexanes/NEt₃) silica gel 60 F₂₅₄, EtOAc, Rf= 0.13. Molecular ion calcld for C₁₄H₁₄N₂O₂: 242.10550; found m/e= 242.1045, error= 4 ppm; base peak= 241 amu; IR (neat, cm⁻¹) 3273, N-H; 1687, C=O; 400 MHz NMR (CDCl₃, ppm) δ 8.14-8.08 (1H, m) 7.25-7.15 (3H, m) 4.44 (1H, ABX₃, J= 10.8, 7.2 Hz) 4.38 (1H, ABX₃, J= 10.8, 7.2 Hz) 4.26 (1H, br d, J= 11.7 Hz) 4.20-4.10 (1H, m) 4.00-3.80 (1H, br s) 3.64-3.50 (1H, br s) 1.44 (3H, t, J= 7.2 Hz) 0.60 (1H, br s). ¹³C NMR (100 MHz, {H}, C₆D₆, ppm) δ
164.7, 150.5, 133.6, 130.7, 122.8, 122.7, 122.0, 109.6, 94.8, 59.5, and 14.6; in addition, strong signals attributed to N-C carbons were observed at 46.5 and 32.9 ppm, while weak, broadened signals were seen at 39.2 and 30.2 ppm. Tentatively, the weak signals are assigned to one of the aziridine carbons with two resonances resulting from the presence of aziridine invertomers.

(1S, 2S)-9-Hydroxymethyl-1,2-(N-tritylaziridino)-2,3-dihydro-1H-pyrrolo[1,2-a]indole (21). To a solution of ester 19 (0.0056 g, 0.012 mmol) in anhydrous ether (1.50 mL) at 0 °C was added LiAlH₄ (0.12 mL of a 0.5 M solution in 50:50 ether/THF, 0.060 mmol) slowly via syringe. The resulting reaction was stirred at 0 °C for 4 h, diluted with anhydrous ether (2.0 mL), and quenched with a saturated solution of Na\(^+\)K\(^+\) tartrate (2.0 mL). The reaction was warmed to rt and stirred vigourously at rt for 3.5 h (long stirring time ensures complete formation of the water soluble aluminum by-products). The resulting biphasic mixture was separated and the aqueous layer extracted with CH₂Cl₂ (3 x 10 mL). The combined organic layers were then washed with brine (1 x 15 mL) and dried (Na₂SO₄). Filtration and solvent removal (aspirator, then vacuum pump) afforded 0.0073 g of a yellow residue that was purified by PLC (silica gel washed with 1:1 hexanes/NEt₃ and dried before using; 20x20x0.025 cm; 3:1 ether/hexanes eluent). Isolation of the major band with Rf= 0.34 yielded 0.0037 g (72%) of 21 as a colorless oil; analytical TLC on washed (1:1 hexanes/NEt₃) silica gel 60 F₂₅₄, 3:1 ether/hexanes, Rf= 0.22. Molecular ion calcd for C₅₁H₃₆N₂O: 442.20460; found m/e = 442.2050, error= 1 ppm; base peak= 243 amu; IR (neat, cm⁻¹) 3370, O-H; 400 MHz NMR (CDCl₃, ppm) δ 7.72 (1H, dt, J= 7.7, 1.1 Hz) 7.54-7.47 (6H, m) 7.33-7.19 (11H, m) 7.18-7.12 (1H, m) 4.97 (1H, AB, J= 12.5 Hz) 4.87 (1H, AB, J= 12.5 Hz) 4.39 (1H, d, J= 11.0 Hz) 4.05 (1H, dd, J= 11.0, 4.0 Hz) 3.00 (1H, d, J= 4.8 Hz) 2.96 (1H, dd, J= 4.8, 4.0 Hz) 1.40 (1H, br s). \(^{13}\)C NMR (100 MHz, CDCl₃, ppm) δ 144.2, 141.4, 133.5, 130.7, 129.2, 127.8, 127.1, 121.8, 119.5, 119.3, 109.4, 108.1, 74.4, 56.5, 46.8, 42.7, 34.2.