

Supporting Information

Photochemistry of tosylstilbenoids in the preparation of complex heterocyclic compounds. Synthesis of a cyclopropafuroindolone analogue of the DNA-alkylating section of the antitumor compound CC-1065

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Organic Letters

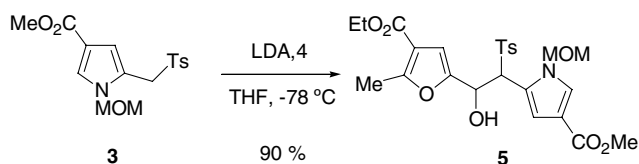
General Procedures. Air- and moisture-sensitive reactions were performed in flame-dried round bottom flasks fitted with rubber septa under a positive pressure of argon. Air- and moisture-sensitive liquids and solutions were transferred via syringe or stainless steel cannula. Organic solutions were concentrated by rotary evaporation below 35 °C at ca. 20 mm Hg. Flash column chromatography was performed as described by Still *et al.* employing silica gel Merck 60 (230-400 mesh).¹ Thin layer chromatography was performed using aluminum plates with silica gel Merck 60 F₂₅₀.

Materials. Commercial reagents and solvents were used as received with the following exceptions: THF and benzene were distilled from sodium/benzophenone; dichloromethane and chlorobenzene were distilled from P₂O₅; methanol was distilled from Mg/I₂; triethylamine and diisopropylamine were distilled from calcium hydride; pyridine was distilled from KOH. The molarity of *n*-butyllithium solutions was determined by titration using diphenylacetic acid as an indicator.

Instrumentation. Infrared (IR) spectra were obtained using a MIDAC PRS 124 spectrometer. Ultraviolet (UV) spectra were obtained in the noted solvents using a Hewlett Packard 8452A spectrometer. Proton and carbon-13 nuclear magnetic resonance (¹H NMR or ¹³C NMR) spectra were recorded with a Bruker AM500 (500 MHz), a Bruker AM300 (300 MHz) or a Bruker WM250 (250 MHz) NMR spectrometer; chemical shifts are expressed in parts per million (δ scale) downfield from tetramethylsilane and are referenced to residual protium in the NMR solvent. Melting points were recorded with a Büchi apparatus and are uncorrected. Mass spectra (MS) and High Resolution Mass Spectra (HRMS) were recorded with a Kratos MS-50 and a Hewlett Packard 59970MS spectrometer, using Electronic Impact (EI, 75 eV) or Fast Atom Bombardment (FAB, bis(2-hydroxyethyl) disulfide matrix).

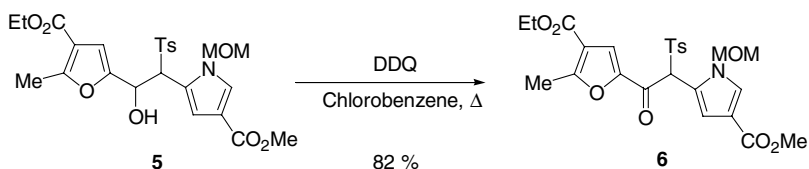
¹ Still, W. C.; Kahn, M.; Mitra, A. *J. Org. Chem.* **1978**, *43*, 2923.

Methyl 5-[2-(4-ethoxycarbonyl-5-methylfuran-2-yl)-2-hydroxy-1-tosylethyl]-*N*-methoxymethylpyrrol-3-carboxylate (5).



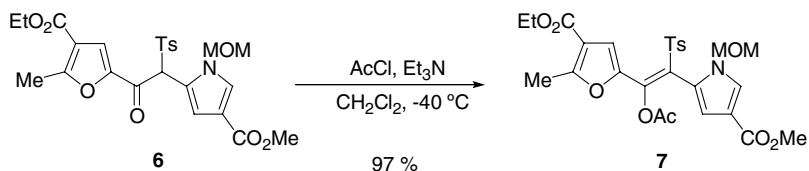
n-BuLi (1.92 M in hexanes, 7.40 mL, 14.23 mmol) was added to a cold (-78 °C) solution of diisopropylamine (2.00 mL, 14.33 mmol) in dry THF (80 mL). The resulting solution was stirred at 0 °C for 15 min and after cooling to -78 °C sulfone **3** (4.00 g, 11.86 mmol) was added and temperature was increased to -50 °C over 3 h. Aldehyde **4** (2.38 g, 13.05 mmol) was added to the resulting red solution and the mixture was stirred at -50 °C for 1 h. HCl 10 % (50 mL) was added and the mixture was extracted with CH₂Cl₂ (3x100 mL). The combined organic layers were dried (Na₂SO₄), evaporated and purified by flash chromatography (hexanes/EtOAc 7:3) to give the desired β-hydroxysulfone **5** (5.57 g, 91 %) as a single diastereoisomer: mp 184 °C (hexanes/EtOAc) (desc.); ¹H NMR (CDCl₃) δ 7.55 (d, 2H, *J* = 8.1 Hz, ArH), 7.28 (d, 2H, *J* = 8.4 Hz, ArH), 7.19 (d, 1H, *J* = 1.7 Hz, ArH), 6.43 (s, 1H, ArH), 6.42 (s, 1H, ArH), 5.26 (dd, 1H, *J* = 9.9 Hz, 2.9 Hz, CHOH), 5.21 (d, 1H, *J* = 11.3 Hz, CH₂OMe), 5.09 (d, 1H, *J* = 9.9 Hz, CHTs), 4.81 (d, 1H, *J* = 11.3 Hz, CH₂OMe), 4.37 (d, 1H, *J* = 2.9 Hz, OH), 4.19 (c, 2H, *J* = 7.1 Hz, CO₂CH₂CH₃), 3.78 (s, 3H, CO₂CH₃), 2.87 (s, 3H, CH₂OCH₃), 2.44 (s, 3H, ArCH₃), 2.42 (s, 3H, ArCH₃), 1.29 (t, 3H, *J* = 7.1 Hz, CO₂CH₂CH₃); ¹³C NMR δ 164.40, 163.57, 158.74, 150.05, 145.59, 133.83, 129.62 (CH), 129.57 (CH), 128.46 (CH), 122.55, 115.69, 114.34, 114.25 (CH), 109.62 (CH), 78.83 (CH₂), 67.47 (CH), 65.77 (CH), 60.03 (CH₂), 55.65 (CH₃), 51.06 (CH₃), 21.52 (CH₃), 14.13 (CH₃), 13.45 (CH₃); MS (FAB, *m/z*) 520 (MH⁺, 18), 502 (MH⁺-H₂O, 3.8), 488 (M⁺-OMe, 8.6), 347 (M⁺-H₂O -Ts, 100). HRMS (IE) C₂₅H₂₇NO₈S (M⁺-H₂O) requires 501.14574; found 501.14577.

Methyl 5-[2-(4-ethoxycarbonyl-5-methylfuran-2-yl)-2-oxo-1-tosylethyl]-*N*-methoxymethylpyrrol-3-carboxylate (6).



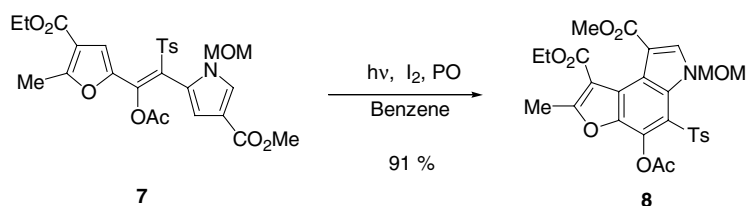
A solution of β -hydroxysulfone **5** (5.57 g, 10.72 mmol) and DDQ (7.30 g, 32.16 mmol) in dry chlorobenzene (100 mL) was refluxed for 2 h. A 40 % aqueous solution of $\text{Na}_2\text{S}_2\text{O}_3$ (100 mL) was added and the mixture was stirred vigorously for 5 min. The formed precipitate was filtered through a celite pad and washed with CH_2Cl_2 (500 mL). The filtrate was washed with water (100 mL) and brine (100 mL) and dried (Na_2SO_4). The solvent was evaporated and the residue was purified by flash chromatography (hexanes/EtOAc 7:3) to give the desired ketone **6** (4.54 g, 82 %): mp 159-161 °C (hexanes/EtOAc); ^1H NMR (CDCl_3) δ 7.60 (s, 1H, ArH), 7.52 (d, 2H, $J = 8.2$ Hz, ArH), 7.45 (d, 1H, $J = 1.5$ Hz, ArH), 7.26 (d, 2H, $J = 8.2$ Hz, ArH), 6.43 (d, 1H, $J = 1.1$ Hz, ArH), 6.24 (s, 1H, CHTs), 6.11 (d, 1H, $J = 11.1$ Hz, CH_2OMe), 4.97 (d, 1H, $J = 11.1$ Hz, CH_2OMe), 4.30 (c, 2H, $J = 7.1$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$), 3.74 (s, 3H, CO_2CH_3), 3.25 (s, 3H, CH_2OCH_3), 2.64 (s, 3H, ArCH_3), 2.43 (s, 3H, ArCH_3), 1.35 (t, 3H, $J = 7.1$ Hz, $\text{CO}_2\text{CH}_2\text{CH}_3$); ^{13}C NMR δ 176.20, 164.97, 164.21, 162.27, 148.35, 145.60, 132.25, 130.61 (CH), 129.83 (CH), 128.93 (CH), 121.50, 120.50, 116.69, 115.76 (CH), 115.58, 79.58 (CH_2), 66.96 (CH), 60.79 (CH_2), 55.90 (CH_3), 55.15 (CH_3), 21.70 (CH_3), 14.29 (CH_3), 14.20 (CH_3); MS (IE, m/z) 517 (M^+ , 1.8), 486 ($\text{M}^+ - \text{OMe}$, 2.1), 472 ($\text{M}^+ - \text{CH}_2\text{OMe}$, 2.1), 362 ($\text{M}^+ - \text{Ts}$, 100). Anal. Calc. for $\text{C}_{25}\text{H}_{27}\text{NO}_9\text{S}$: C, 58.02; H, 5.26; N, 2.71. Found: C, 57.81; H, 5.05; N, 2.77.

Methyl 5-[2-acetoxy-2-(4-ethoxycarbonyl-5-methylfuran-2-yl)-1-tosylethenyl]-*N*-methoxymethylpyrrol-3-carboxylate (7).



To a cooled (-40 °C) solution of ketone **6** (4.00 g, 7.73 mmol) and Et₃N (10.00 mL, 71.74 mmol) in dry CH₂Cl₂ (80 mL), acetyl chloride (4.00 mL, 56.25 mmol) was added dropwise over 20 min. The temperature was allowed to rise to -10 °C over 3 h and the reaction mixture was poured into an HCl solution (10%, 50 mL) at 0 °C. The aqueous layer was extracted with CH₂Cl₂ (3x50 mL) and the combined organic layers were dried (Na₂SO₄), evaporated and purified by flash chromatography (hexanes/EtOAc 8:1 to 7:3) to give heterostilbene **7** (4.20 g, 97 %) as a single isomer of unknown stereochemistry: ¹H NMR (CDCl₃) δ 7.66 (d, 2H, *J* = 8.3 Hz, ArH), 7.60 (d, 1H, *J* = 1.6 Hz, ArH), 7.28 (d, 2H, *J* = 8.3 Hz, ArH), 6.35 (d, 1H, *J* = 1.6 Hz, ArH), 6.23 (s, 1H, ArH), 5.12 (d, 1H, *J* = 10.5 Hz, CH₂OMe), 4.98 (d, 1H, *J* = 10.5 Hz, CH₂OMe), 4.19 (c, 2H, *J* = 7.1 Hz, CO₂CH₂CH₃), 3.79 (s, 3H, CO₂CH₃), 3.15 (s, 3H, CH₂OCH₃), 2.45 (s, 3H, ArCH₃), 2.42 (s, 3H, ArCH₃), 2.37 (s, 3H, ArCH₃), 1.25 (t, 3H, *J* = 7.1 Hz, CO₂CH₂CH₃); ¹³C NMR δ 168.25, 164.50, 162.42, 161.78, 146.60, 144.74, 143.61, 137.30, 129.51 (CH), 128.20 (CH), 127.95 (CH), 122.09, 119.78, 117.19, 116.54, 116.30, 114.44, 78.83 (CH₂), 60.49 (CH₂), 56.59 (CH₃), 51.09 (CH₃), 21.58 (CH₃), 20.82 (CH₃), 14.03 (CH₃), 13.87 (CH₃); MS (IE, *m/z*) 559 (M⁺, 3.5), 528 (M⁺-OMe, 1.6), 517 (MH⁺-Ac, 37), 485 (M⁺-OMe -Ac, 42), 404 (M⁺-Ts, 5.5); UV (EtOH) 304, 226. HRMS (IE) C₂₇H₂₉NO₁₀S requires 559.15122; found 559.15143.

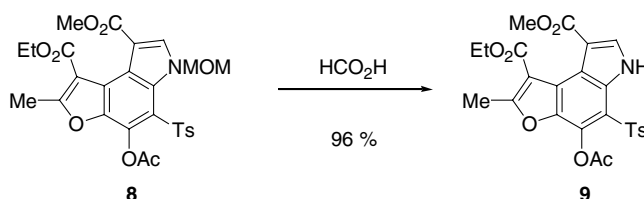
Ethyl 4-acetoxy-2-methyl-8-methoxycarbonyl-*N*-methoxymethyl-5-tosyl-6*H*-furo[3,2-*e*]indole-1-carboxylate (8**).**



A deoxygenated solution of heterostilbene **7** (108 mg, 0.19 mmol), I₂ (49 mg, 0.19 mmol) and propylene oxide (2.10 mL, 30.0 mmol) in dry benzene (200 mL) was irradiated (Hanovia Lamp, 450 W) for 1 h in a Pyrex reactor. An aqueous solution of Na₂S₂O₃ was added until decoloration of the mixture and the solvent was removed under reduced pressure. Water was added (20 mL) and the mixture extracted with EtOAc (3x50 mL). The

combined organic layers were dried (Na₂SO₄), evaporated and purified by flash chromatography (hexanes/EtOAc 3:2 to 1:1) to give furoindole **8** (108 mg, 91 %) as a white foam: ¹H NMR (CDCl₃) δ 8.02 (s, 1H, ArH), 7.75 (d, 2H, *J* = 8.6 Hz, ArH), 7.28 (d, 2H, *J* = 8.6 Hz, ArH), 5.85 (s, 2H, CH₂OMe), 4.31 (c, 2H, *J* = 7.1 Hz, CO₂CH₂CH₃), 3.84 (s, 3H, CO₂CH₃), 2.96 (s, 3H, CH₂OCH₃), 2.67 (s, 3H, ArCH₃), 2.42 (s, 3H, ArCH₃), 2.29 (s, 3H, OCOCH₃), 1.31 (t, 3H, *J* = 7.1 Hz, CO₂CH₂CH₃); ¹³C NMR δ 167.16, 164.82, 164.11, 163.56, 144.09, 141.98, 140.87, 136.56 (CH), 132.79, 130.37, 129.45 (CH), 126.53 (CH), 124.45, 118.97, 115.75, 113.12, 110.91, 83.67 (CH₂), 60.87 (CH₂), 56.38 (CH₃), 51.44 (CH₃), 21.52 (CH₃), 20.575 (CH₃), 13.85 (CH₃), 13.83 (CH₃); MS (IE, *m/z*) 557 (M⁺, 14), 515 (MH⁺-Ac, 100), 483 (M⁺-Ac -OMe, 67), 453 (M⁺-Ac -OMe -OMe, 12).; UV (EtOH) 318, 234. HRMS (IE) C₂₇H₂₇NO₁₀S requires 557.13557; found 557.13551.

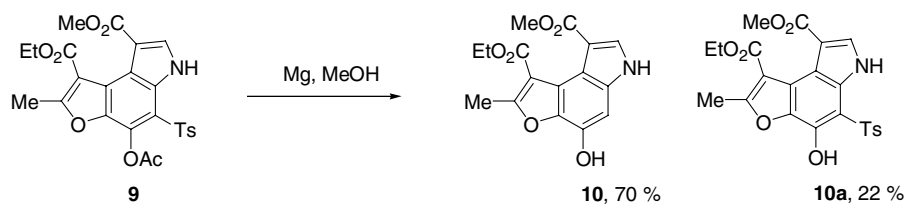
Ethyl 4-acetoxy-2-methyl-8-methoxycarbonyl-5-tosyl-6*H*-furo[3,2-*e*]indole-1-carboxylate (9**).**



A solution of furoindole **8** (2.82 g, 5.06 mmol) in formic acid (98 %, 20 mL) was stirred at rt for 20 h. After addition of water (50 mL), the mixture was extracted with CH₂Cl₂ (3x50 mL), the combined organic layers were washed with saturated aqueous NaHCO₃ (2x50 mL), dried (Na₂SO₄) and the solvent removed. Flash chromatography (hexanes/EtOAc 3:2 to 2:3) provided the *N*-demethoxymethylated furoindole **9** (2.49 g, 96 %) as a light-yellow solid: mp 194-196 °C (hexanes/EtOAc); ¹H NMR (CDCl₃) δ 10.72 (broad s, 1H, NH), 7.98 (d, 1H, *J* = 2.8 Hz, ArH), 7.83 (d, 2H, *J* = 7.3 Hz, ArH), 7.27 (d, 2H, *J* = 7.7 Hz, ArH), 4.29 (c, 2H, *J* = 7.1 Hz, CO₂CH₂CH₃), 3.83 (s, 3H, CO₂CH₃), 2.65 (s, 3H, ArCH₃), 2.46 (s, 3H, ArCH₃), 2.38 (s, 3H, OCOCH₃), 1.28 (t, 3H, *J* = 7.1 Hz, CO₂CH₂CH₃); ¹³C NMR δ 167.46, 164.94, 164.21, 163.16, 144.91, 141.86, 139.11, 131.55 (CH), 131.12, 129.81, 129.70 (CH), 126.75 (CH), 124.48, 116.55, 113.11, 112.92, 110.97,

60.87 (CH₂), 51.35 (CH₃), 21.535 (CH₃), 20.591(CH₃), 13.82 (CH₃), 13.73 (CH₃); MS (IE, m/z) 513 (M⁺, 5.6), 471 (MH⁺-Ac, 100), 439 (M⁺-Ac -OMe), 425 (M⁺-Ac -CH₂OMe, 21), 412 (M⁺-Ac -CO₂Me, 7.6), 367 (M⁺-Ac -OMe -CO₂Et, 11). Anal. Calc. for C₂₅H₂₃NO₉S: C, 58.47; H, 4.51; N, 2.73. Found: C, 58.71; H, 4.34; N, 2.87.

Ethyl 4-hydroxy-2-methyl-8-methoxycarbonyl-6H-furo[3,2-e]indole-1-carboxylate (10).

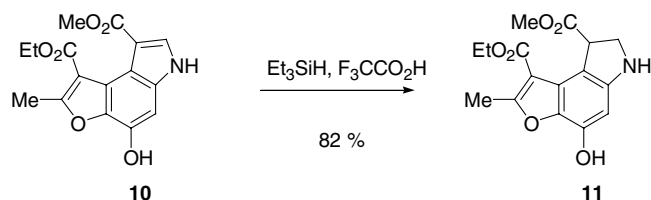


A mixture of furoindol **9** (2.00 g, 3.89 mmol), Mg (ribbon cut up into pieces, 1.47 g, 61.25 mmol) in dry MeOH (70 mL) was stirred for 1 h at rt (water bath). HCl 10 % (60 mL) was added and the mixture was extracted with CH₂Cl₂ (3x40 mL). The combined organic layers were dried (Na₂SO₄), evaporated and purified by flash chromatography (hexanes/EtOAc 6:4 to 1:1) to give the desired furoindol **10** (870 mg, 70 %) as a white solid: mp 206-208 °C (hexanes/EtOAc) (desc.); ¹H NMR (MeOD-*d*₄) δ 7.72 (s, 1H, ArH), 6.85 (s, 1H, ArH), 4.25 (c, 2H, *J* = 7.2 Hz, CO₂CH₂CH₃), 3.77 (s, 3H, CO₂CH₃), 2.63 (s, 3H, ArCH₃), 1.26 (t, 3H, *J* = 7.2 Hz, CO₂CH₂CH₃); ¹³C NMR δ 168.24, 167.65, 159.32, 142.20, 140.99, 135.81, 130.48 (CH), 119.85, 113.97, 111.94, 110.14, 95.62 (CH), 61.81 (CH₂), 51.58 (CH₃), 14.25 (CH₃), 13.38 (CH₃); MS (IE, m/z) 317 (M⁺, 83.7), 285 (M⁺ - MeOH, 18.5), 271 (M⁺ - EtOH, 50.4), 258 (M⁺ - CO₂Me, 52.4), 213 (M⁺ - CO₂Me - OEt, 100.0). HRMS (IE) C₁₆H₁₅NO₆ requires 317.089937; found 317.089677.

Phenol **10a** was also obtained (402 mg, 22 %): mp 171-172 °C (hexanes/EtOAc); ¹H NMR (CDCl₃) δ 9.91 (broad s, 1H, NH), 9.39 (s, 1H, OH), 7.82 (d, 2H, *J* = 8.3 Hz, ArH), 7.79 (d, 1H, *J* = 3.1 Hz, ArH), 7.23(d, 2H, *J* = 8.3 Hz, ArH), 4.29 (c, 2H, *J* = 7.1 Hz, CO₂CH₂CH₃), 3.8 (s, 3H, CO₂CH₃), 2.70 (s, 3H, ArCH₃), 2.34 (s, 3H, ArCH₃), 1.26 (t, 3H, *J* = 7.1 Hz, CO₂CH₂CH₃); ¹³C NMR δ 165.08, 164.37, 163.00, 145.30, 140.21, 139.13, 138.63, 130.08 (CH), 129.46 (CH), 128.93, 125.85 (CH), 125.46, 113.07, 111.43, 111.07,

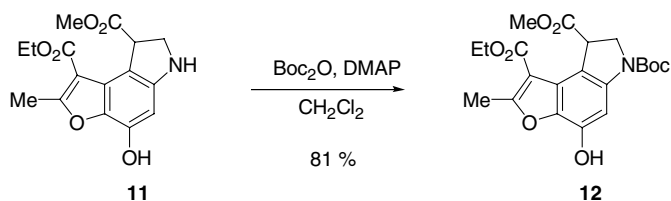
102.97, 60.88 (CH₂), 51.33 (CH₃), 21.49 (CH₃), 13.85 (CH₃), 13.75 (CH₃); MS (IE, m/z) 471 (M⁺, 100), 440 (M⁺-OMe, 14), 426 (M⁺-CO₂Et, 30), 412 (M⁺-CO₂Me, 18), 367 (M⁺-OMe -CO₂Et, 23). HRMS (IE) C₂₃H₂₁NO₈S requires 471.09879; found 471.09884.

Ethyl 4-hydroxy-8-methoxycarbonyl-2-methyl-7,8-dihydro-6*H*-furo[3,2-*e*]indole-1-carboxylate (11**).**



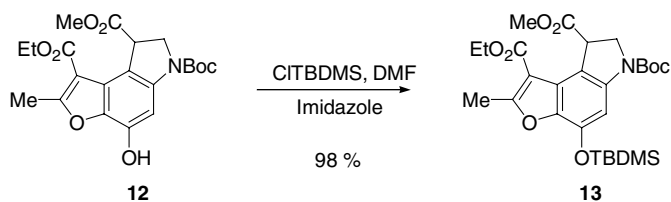
A mixture of pyrroloindole **10** (420 mg, 1.32 mmol), Et₃SiH (1.6 mL, 10.73 mmol) and F₃CCO₂H (8.0 mL, 103.84 mmol) was stirred at rt for 1.70 h. The volatiles were removed under reduced pressure and the resulting solid washed (EtOAc) to provide furoindoline **11** (345 mg, 82 %) as an air sensitive white solid: ¹H NMR (MeOD-*d*₄) δ 6.80 (s, 1H, ArH), 4.98 (dd, 1H, *J* = 7.7 Hz, 4.4 Hz), 4.36 (m, 2H, CO₂CH₂CH₃), 4.09 (m, 2H), 3.67 (s, 3H, CO₂CH₃), 2.76 (s, 3H, ArCH₃), 1.39 (t, 3H, *J* = 7.1 Hz, CO₂CH₂CH₃); ¹³C NMR δ 173.57, 166.16, 164.94, 145.29, 144.33, 136.07, 126.39, 116.09, 111.18, 102.01 (CH), 62.05 (CH₂), 53.11 (CH₃), 50.45 (CH₂), 48.56 (CH), 14.80 (CH₃), 14.68 (CH₃); MS (IE, m/z) 319(M⁺, 12.0), 287 (M⁺-MeOH, 4.6), 273 (M⁺-EtOH, 2.6), 260 (M⁺-CO₂Me, 22.0), 231 (M⁺-CO₂Me -Et, 10.3), 214 (M⁺-CO₂Me -EtOH, 100.0). HRMS (IE) C₁₆H₁₇NO₆ requires 319.105588; found 319.106337.

Ethyl *N*-(*t*-butyloxycarbonyl)-4-hydroxy-8-methoxycarbonyl-2-methyl-7,8-dihydro-6*H*-furo[3,2-*e*]indole-1-carboxylate (12**).**



To a mixture of indolone **11** (175 mg, 0.55 mmol) in dry CH₂Cl₂ (5 mL), di-*t*-butyl dicarbonate (0.4 mL, 1.74 mmol) and a catalytic amount of 4-dimethylaminopyridine were added. The reaction was stirred overnight and the solvent was removed under reduced pressure. Flash chromatography (hexanes/EtOAc 8:2) provided the desired *N*-Boc protected pyrroloindoline **12** (188 mg, 81 %) as a white solid: mp 196-197 °C (hexanes-EtOAc); ¹H NMR (CDCl₃) δ 7.66 (broad s, 1H, ArH), 4.73 (t, 1H, *J* = 7.7 Hz), 4.30 (m, 4H), 3.66 (s, 3H, CO₂CH₃), 2.65 (s, 3H, ArCH₃), 1.54 (s, 9H, CO₂C(CH₃)₃), 1.36 (t, 3H, *J* = 7.2 Hz, CO₂CH₂CH₃); ¹³C NMR δ 173.87, 164.22, 163.84, 152.36, 141.22, 140.32, 139.05, 124.48, 109.83, 109.67, 99.48 (CH), 81.28, 60.52 (CH₂), 52.29 (CH₃), 51.69 (CH₂), 44.71 (CH), 28.42 (CH₃), 14.85 (CH₃), 14.25 (CH₃); MS (IE, *m/z*) 419 (M⁺, 2.4), 363 (MH⁺ -C(CH₃)₃, 7.7), 331 (MH⁺ -C(CH₃)₃ -MeOH, 21.3), 317 (MH⁺ -C(CH₃)₃ -EtOH, 19.2), 304 (MH⁺ -C(CH₃)₃ -CO₂Me, 45.1), 260 (MH⁺ -C(CH₃)₃ -CO₂Me -CO₂, 30.9), 214 (MH⁺ -C(CH₃)₃ -CO₂Me -CO₂ -EtOH, 100.0), 57 (C(CH₃)₃⁺, 30.2). Anal. Calc. for C₂₁H₂₅NO₈: C, 60.14; H, 6.01; N, 3.34. Found: C, 60.03; H, 5.89; N, 3.32.

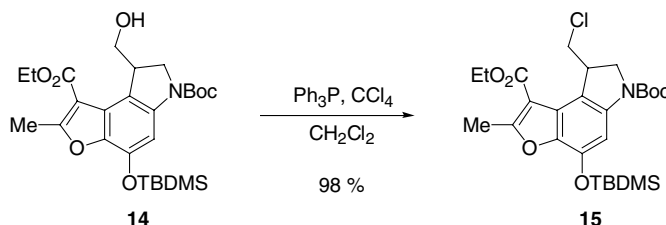
Ethyl 4-(*t*-butyldimethyl)silyloxy-*N*-(*t*-butyloxycarbonyl)-8-methoxycarbonyl-2-methyl-7,8-dihydro-6*H*-furo[3,2-*e*]indole-1-carboxylate (13**).**



A solution of phenol **12** (441 mg, 1.05 mmol), *t*-butyldimethylsilyl chloride (792 mg, 5.26 mmol) and imidazole (715 mg, 10.5 mmol) in dry DMF was stirred overnight. Water (30 mL) was added and the resulting mixture extracted with Et₂O (3x20 mL). The organic layers were dried (Na₂SO₄), evaporated and purified by flash chromatography (hexanes/EtOAc 9:1) to give the desired silylether **13** (550 mg, 98 %) as a white solid: mp 115-116 °C (hexanes/EtOAc); ¹H NMR (CDCl₃) δ 7.60 (broad s, <1H, ArH), 7.18 (broad s, <1H, ArH), 4.75 (t, 1H, *J* = 7.6 Hz), 4.31 (m, 4H), 3.67 (s, 3H, CO₂CH₃), 2.71 (s, 3H,

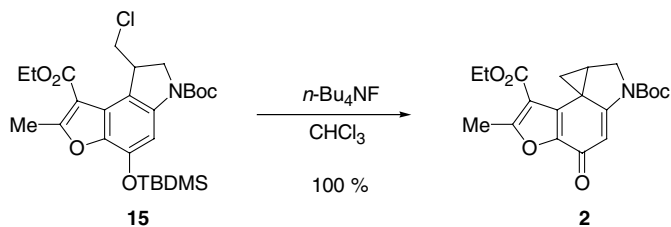
CH₂OH, 100.0), 374 (MH⁺ -C(CH₃)₃ -CH₂OH -CO₂, 8.9), 372 (MH⁺ -C(CH₃)₃ -CH₂OH -EtOH, 15.1), 328 (MH⁺ -C(CH₃)₃ -CH₂OH -EtOH -CO₂, 17.8), 57 (C(CH₃)₃⁺, 26.9). HRMS (IE) C₂₆H₃₉NO₇Si requires M⁺ 505.249581; found 505.251398.

Ethyl 4-(*t*-butyldimethyl)silyloxy-*N*-(*t*-butyloxycarbonyl)-8-chloromethyl-2-methyl-7,8-dihydro-6*H*-furo[3,2-*e*]indole-1-carboxylate (15**).**



A solution of alcohol **14** (192 mg, 0.38 mmol), triphenylphosphine (300 mg, 1.14 mmol) and dry CCl₄ (0.36 mL, 3.76 mmol) in dry CH₂Cl₂ (5 mL) was stirred for 4 h. The solvent was removed under reduced pressure and the crude was purified by flash chromatography (hexanes/EtOAc 95:5) to give the chloro derivative **15** (195 mg, 98 %) as a white solid: mp 113-115 °C (hexanes/EtOAc); ¹H NMR (CDCl₃) δ 7.49 (broad s, 1H, ArH), 4.43 (dc, 2H, *J* = 7.2 Hz, 1.9 Hz, CO₂CH₂CH₃), 4.18 (m, 2H), 3.96 (dd, 1H, *J* = 11.3 Hz, 8.8 Hz), 3.78 (dd, 1H, *J* = 10.4 Hz, 2.8 Hz), 3.30 (t, 1H, *J* = 10.4 Hz), 2.73 (s, 3H, ArCH₃), 1.58 (s, 9H, CO₂(CH₃)₃), 1.44 (t, 3H, *J* = 7.2 Hz, CO₂CH₂CH₃), 1.03 (s, 9H, ArOSi(CH₃)₂C(CH₃)₃), 0.23 (s, 6H, ArOSi(CH₃)₂C(CH₃)₃); ¹³C NMR δ 164.58, 163.95, 152.49, 141.94, 140.33, 123.36, 114.34, 109.17, 104.42 (CH), 80.86, 60.69 (CH₂), 52.28 (CH₂), 47.63 (CH₂), 42.28 (CH), 28.51 (CH₃), 25.61 (CH₃), 18.32, 15.22 (CH₃), 14.48 (CH₃), -4.45 (CH₃); MS (IE, *m/z*) 523 (M⁺, 4.8), 467 (MH⁺ -C(CH₃)₃, 21.5), 431 (MH⁺ -C(CH₃)₃ -HCl, 6.3), 418 (MH⁺ -C(CH₃)₃ -CH₂Cl, 100.0), 374 (MH⁺ -C(CH₃)₃ -CH₂Cl -CO₂, 8.2), 372 (MH⁺ -C(CH₃)₃ -CH₂Cl -EtOH, 13.4), 328 (MH⁺ -C(CH₃)₃ -CH₂Cl -EtOH -CO₂, 14.9), 57 (C(CH₃)₃⁺, 32.9).

Ethyl *N*-(*t*-butyloxycarbonyl)-2-methyl-8-oxo-4a,5,6,8-tetrahydro-4*H*-cyclopropa[*c*]furo[3,2-*e*]indole-3-carboxylate (2**).**



n-Bu₄NF·3H₂O (5 mg, 0.01 mmol) was added to a solution of furoindoline **15** (4 mg, 0.008 mmol) in CHCl₃ (0.5 mL). Five min later the resulting yellow solution was filtered through a pad of flash silica gel (hexanes/EtOAc 3:7 to 0:1) to give cyclopropafuroindolone **2** (3 mg, 100 %) as a pale-yellow oil: ¹H NMR (CDCl₃) δ 6.75 (s, 1H, ArH), 4.31 (c, 2H, *J* = 7.2 Hz, CO₂CH₂CH₃), 4.00 (t, 1H, *J* = 11.3 Hz, CHCH₂N), 3.92 (dd, 1H, *J* = 11.3 Hz, 4.7 Hz, CHCH₂N), 3.38 (m, 1H, CHCH₂N), 2.68 (s, 3H, ArCH₃), 2.20 (dd, 1H, *J* = 3.4 Hz, 7.5 Hz, CH₂RR'), 1.54 (s, 9H, CO₂C(CH₃)₃), 1.38 (t, 3H, *J* = 7.2 Hz, CO₂CH₂CH₃), 1.29 (m, 1H, CH₂RR'); IR (KBr) 3420, 2924, 1707, 0637, 0385, 1150 cm⁻¹; MS (IE, *m/z*) 373 (M⁺, 19.5), 317 (MH⁺ -C(CH₃)₃, 89.5), 273 (MH⁺ -CO₂C(CH₃)₃, 80.2), 244 (MH⁺ -CO₂C(CH₃)₃ -Et, 98.7), 227 (MH⁺ -CO₂C(CH₃)₃ -EtOH, 51.8), 199 (MH⁺ -CO₂C(CH₃)₃ -EtOH -CO, 66.4), 57 (C(CH₃)₃⁺, 100.0); UV (EtOH) 326, 280, 226. HRMS (IE) C₂₀H₂₃NO₆ requires M⁺ 373.152538; found 373.151267.