Novel Stereoselective Syntheses of Highly Functionalized Benzannulated Pyrrolizidines and Indolizidines by Samarium Diiodide-Induced Cyclizations of Indole Derivatives

Steffen Gross and Hans-Ulrich Reissig*

Institut für Chemie – Organische Chemie, Freie Universität Berlin, Takustr. 3, D-14195 Berlin, Germany

hans.reissig@chemie.fu-berlin.de

Experimental Conditions: All reactions were performed under argon atmosphere in flame dried flasks. Unless otherwise stated, materials were obtained from commercial suppliers and were used without further purification. Hexamethylphosphoramide was distilled and kept under argon. Tetrahydrofuran was freshly distilled from sodium/benzophenone under argon for each of the SmI_2 reactions.

General experimental procedure: Samarium (2.4 - 2.5 equiv) and 1,2-diiodoethane (2.2 equiv) were suspended in freshly distilled anhydrous THF (10 mL per mmol samarium) under an argon atmosphere and stirred for 2 h at room temperature. To the resulting dark blue solution HMPA (10 equiv.) was added if necessary. The ketone and phenol (2.0 equiv.), dissolved in THF (20 mL), were then added in one portion to the deep blue solution. After 16 h the reaction was quenched with saturated aqueous solution of sodium bicarbonate, the organic layer was separated and the aqueous layer was extracted with diethyl ether (3 x 25 mL). The combined ether extracts were washed with brine (25 mL), dried over anhydrous magnesium sulfate, filtered and evaporated. The resulting crude product was purified by flash chromatography on silica gel using hexane/ethyl acetate mixtures.

4-(9*H*-Carbazol-9-yl)butan-2-ol (2)

Analytical data: colorless solid; mp 84-88 °C; ^{1}H NMR ($CDCl_3$, 270 MHz): δ = 1.15 (d, *J* = 5.9 Hz, 3H, 1-H), 1.64 (s, br, 1H, OH), 1.76-1.91 (m, 1H, 3-H), 1.96-2.08 (m, 1H, 3-H), 3.72 (m_c, 1H, 2-H), 4.36 (ddd, *J* = 4.6, 7.3, 14.9 Hz, 1H, 4-H), 4.50 (ddd, *J* = 6.6, 8.5, 14.9 Hz, 1H, 1-H), 7.25 (m_c, 2H, Ar), 7.48 (d, *J* = 3.9 Hz, 4H, Ar), 8.12 (d, *J* = 7.8 Hz, 2H, Ar); ^{13}C NMR ($CDCl_3$, 68 MHz): δ = 24.12 (q, C-1), 37.6, 39.4 (2t, C-3, C-4), 65.2 (d, C-2), 108.6, 118.7, 120.3 (3d, Ar), 122.7 (s, C_{ipso}), 125.6 (d, Ar), 140.3 (s, C_{ipso}); IR (Film): ν = 3345 cm^{-1} (OH), 3045 (ArH), 2970-2875 (CH), 1595 (C=C); MS (EI, 120 °C, 80 eV): *m/z* (%) = 239 [M^+] (43),

194 [M^+ - C_2H_5O] (1), 180 [M^+ - C_3H_7O] (100); HRMS (120 °C, 80 eV): [M^+]: $C_{16}H_{17}NO$ calcd.: 239.13101; found: 239.13066; $C_{16}H_{17}NO$ (239.3) calcd.: C 80.41, H 7.17, N 5.86; found: C 79.72, H 6.64, N 5.57.

(1*R,9a*S**)-1-Methyl-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indol-1-ol (5)**

Analytical data: colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.04 (s, 3H, 1-CH_3), 1.81 (ddd, *J* = 4.3, 8.0, 12.3 Hz, 1H, 2-H), 2.04 (td, *J* = 8.0, 12.3 Hz, 1H, 2-H), 2.84 (s, br, 1H, OH), 3.05-3.10 (m, 3H, 9-H, 3-H), 3.60 (ddd, *J* = 4.2, 8.0, 10.6 Hz, 1H, 3-H), 3.91 (dd, *J* = 5.6, 8.1 Hz, 1H, 9a-H), 6.56 (d, *J* = 7.8 Hz, 1H, 5-H), 6.74 (dt, *J* = 1.0, 7.3 Hz, 1H, 7-H), 7.04 (d* *J* = 7.4 Hz, 1H, 8-H), 7.08 (t, *J* = 7.8 Hz, 1H, 6-H); * with further splitting; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.9 (q, 1-CH_3), 29.5, 41.1, 50.5 (3t, C-9, C-2, C-3), 72.9 (d, C-9a), 77.3 (s, C-1), 109.9, 119.5, 124.1, 127.5, 129.9 (4d, C-5, C-7, C-8, C-6), 129.9, 154.0 (2s, C_{ipso}); IR (film): ν = 3365 cm^{-1} (OH), 3070-3025 (=CH), 2970-2870 (CH), 1605 (C=C); MS (EI, 100 °C, 80 eV): *m/z* (%) = 189 [M^+] (57), 169 [M^+ - H_2 - H_2O] (16), 154 (37), 131 (100); $C_{12}H_{15}NO$ (189.3) calcd.: C 76.16, H 7.99, N 7.40; found: C 75.90, H 8.14, N 7.33.

(9*R,9a*S**)-9-Methyl-6,7,8,9,9a,10-hexahydropyrido[1,2-*a*]indol-9-ol (6)**

Analytical data: colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.30 (s, 3H, 9-CH_3), 1.46 (dt, *J* = 5.1, 12.6 Hz, 1H, 8-H), 1.60 (s, br, 1H, OH), 1.68-1.80 (m, 2H, 7-H), 1.93 (td*, *J* = 4.0, 12.6 Hz, 1H, 8-H), 2.47 (dt*, *J* = 4.0, 11.5 Hz, 1H, 6-H), 2.81 (dd*, *J* = 12.1, 15.2 Hz, 1H, 10-H), 2.94 (dd, *J* = 7.9, 15.2 Hz, 1H, 10-H), 3.08 (dd, *J* = 7.9, 12.1 Hz, 1H, 9a-H), 3.58 (dd*, *J* = 4.8, 11.5 Hz, 1H, 6-H), 6.45 (d, *J* = 7.8 Hz, 1H, 4-H), 6.68 (dt, *J* = 1.0, 7.2 Hz, 1H, 2-H), 7.07 (t, br, *J* = 7.8 Hz, 1H, 3-H), 7.11 (d*, *J* = 7.2 Hz, 1H, 1-H); * with further splitting; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 20.9 (q, 9-CH_3), 23.5, 29.4, 40.8, 45.1 (4t, C-7, C-10, C-8, C-6), 71.0 (s, C-9), 73.7 (d, C-9a), 106.6, 118.1, 124.6, 127.3 (4d, C-4, C-2, C-3, C-1), 128.7, 151.7 (2s, C_{ipso}); IR (film): ν = 3430 cm^{-1} (OH), 3050-3025 (=CH), 2940-2690 (CH), 1610 (C=C); MS (EI, 100 °C, 80 eV): *m/z* (%) = 203 [M^+] (46), 186 [M^+ - OH] (4), 170 [M^+ - CH_3 - H_2O] (5), 145 (11), 132 [Indole-N-CH_3^+] (100); $C_{13}H_{17}NO$ (203.3) calcd.: C 76.80, H 8.43, N 6.89; found: C 77.28, H 8.49, N 6.34.

(9*R,9a*S**)-9-Hydroxy-9-methyl-8,9,9a,10-tetrahydropyrido[1,2-*a*]indol-6(7*H*)-one (9)**

Analytical data: colorless solid; mp 152-153 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.28 (s, 3H, 9-CH_3), 1.95-2.06 (m, 2H, 8-H), 2.53 (ddd, *J* = 2.8, 11.0, 18.3 Hz, 1H, 7-H), 2.69 (ddd, *J* = 2.8, 7.6, 18.3 Hz, 1H, 7-H), AB-part of ABX-system (δ_A = 3.10, δ_B = 3.14, dd, J_{AB} = 16.1 Hz, J_{AX} = 9.2 Hz, J_{BX} = 9.9 Hz, 2H, 10-H), 3.39 (s, br, 1H, OH), 4.25 (dd, *J* = 9.2, 9.9 Hz, 1H, 9a-H), 7.04 (dt, *J* = 1.1, 7.6 Hz, 1H, 1-H), 7.18 (m_c, 2H, 2-H, 3-H), 8.12 (d, br, *J* = 7.9 Hz, 1H, 4-H); ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 20.0 (q, 9-CH_3), 29.9, 31.1, 36.4 (3t, C-10, C-7, C-8), 67.5 (d, C-9a), 69.8 (s, C-9), 116.8, 124.3, 124.6, 127.4 (4d, C-4, C-1, C-2, C-3), 129.8, 142.3 (2s, C_{ipso}), 167.8 (s, C-6); IR (film): ν = 3315 cm^{-1} (OH), 3070-3040 (=CH), 2965 (CH), 1625 (CO), 1590 (C=C); MS (EI, 100 °C, 80 eV): *m/z* (%) = 217 [M^+] (45), 131 [Indole-N=CH_2^+] (13), 118 [Indole + H^+] (100); $C_{13}H_{15}NO_2$ (217.3) calcd.: C 71.20, H 6.84, N 6.39; found: C 71.38 , H 6.82, N 6.35.

(9*R,9a*S**)-9-Hydroxy-8,9,9a,10-tetrahydropyrido[1,2-*a*]indol-6(7*H*)-one (10)**

Analytical data: colorless solid; mp 191-192 °C (sublimation at 169 °C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.90 (dddd, *J* = 7.3, 10.3, 10.7, 13.1 Hz, 1H, 8-H), 2.20 (m_c, 1H, 8-H), 2.59 (ddd, *J* = 7.3, 10.7, 18.0 Hz, 1H, 7-H), 2.73 (ddd, *J* = 3.1, 7.3, 18.0 Hz, 1H, 7-H), 3.06 (dd, *J* = 10.4, 15.6 Hz, 1H, 10-H), 3.32 (dd, *J* = 8.2, 15.6 Hz, 1H, 10-H), 3.97 (ddd, *J* = 4.5, 9.3, 10.3 Hz, 1H, 9-H), 4.06 (ddd, *J* = 8.2, 9.3, 10.4 Hz, 1H, 9a-H), 7.05 (dt, *J* = 1.1, 7.5 Hz, 1H, 3-H), 7.20 (m_c, 2H, 1-H, 2-H), 8.10 (d^*, *J* = 8.6 Hz, 1H, 4-H); * with further splitting; ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 30.1, 31.1, 34.3 (3t, C-8, C-7, C-10), 65.4, 71.2 (2d, C-9a, C-9), 117.0, 124.3, 124.6, 127.6 (4d, C-4, C-1, C-2, C-3), 130.1, 142.6, 167.6 (3s, C_{ipso}, C_{ipso}, C-6); IR (film): ν = 3235 cm^{-1} (OH), 2955-2840 (CH), 1625 (CO), 1590 (C=C); MS (EI, 100 °C, 80 eV): *m/z* (%) = 203 [M^+] (40), 184 [M^+ - H_2O - H] (2), 131 [Indole-N=CH_2^+] (11), 118 (100); $C_{12}H_{13}NO_2$ (203.2) calcd.: C 70.93, H 6.45, N 6.89; found: C 70.94 , H 6.70, N 5.96.

Methyl (1*R,9a*S**,9*R**)-1-Hydroxy-1-methyl-2,3,9,9a-tetrahydro-1*H*-pyrrolo[1,2-*a*]indol-9-carboxylate (12a) and Methyl (1*S**,9a*R**,9*R**)-1-Hydroxy-1-methyl-2,3,9,9a-tetrahydro-1H-pyrrolo[1,2-a]indol-9-carboxylate (12b) and Methyl 6-Hydroxy-6-methyl-5,6-dihydro-4H-pyrrolo[3,2,1-*ij*]chinolin-1-carboxylate (13)**

Analytical data of **12a**: colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.06 (s, 3H, 1-CH_3), 1.88 (ddd, *J* = 3.6, 7.3, 12.5 Hz, 1H, 2-H), 2.16 (td, *J* = 8.2, 12.5 Hz, 1H, 2-H), 2.53 (s, br, 1H, OH), 3.06 (ddd, *J* = 7.3, 9.1, 10.4 Hz, 1H, 3-H), 3.66 (ddd, *J* = 3.6, 8.2, 4.5 Hz, 1H, 3-H), 3.74 (s, 3H, OCH_3), 4.19 (d, *J* = 3.7 Hz, 1H, 9-H), 4.29 (d, *J* = 3.7 Hz, 1H, 9a-H), 6.57 (dd, *J* = 0.5, 7.9 Hz, 1H, 5-H), 6.76 (dt, *J* = 1.0, 7.5, Hz, 1H, 7-H), 7.14 (dddd, *J* = 0.5, 7.5, 7.9 Hz, 1H, 6-H), 7.23 (d, br, *J* = 7.5 Hz, 1H, 8-H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 21.8 (q, 1-CH_3), 41.0 (t, C-2), 47.8 (d, C-9), 50.1 (t, C-3), 52.6 (q, OCH_3), 75.6 (d, C-9a), 76.8 (s, C-1), 110.3, 119.5, 125.0 (3d, C-5, C-7, C-8), 127.0 (s, C-8a), 129.2 (d, C-6), 153.8, 173.2 (2s, C-4a, CO); IR (film): ν = 3410 cm^{-1} (OH), 3070-3000 (=CH), 2970-2875 (CH), 1740 (CO), 1665, 1600 (C=C); MS (EI, 70 °C, 80 eV): *m/z* (%) = 247 [M^+] (35), 189 [M^+ - C_3H_6O) (23), 130 (100), 84 [M^+ - C_4H_7O] (93); HRMS (70 °C, 80 eV): [M^+]: $C_{14}H_{17}NO_3$ calcd.: 247.12084; found: 247.12324; $C_{14}H_{17}NO_3$ (247.3) calcd.: C 67.99, H 6.93, N 5.66; found: C 67.24, H 6.73, N 5.23.

Analytical data of **12b**: colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.81 (s, 3H, 1-CH_3), 1.90 (dddd, *J* = 0.5, 1.3, 7.5, 12.3 Hz, 1H, 2-H), 2.25 (m_c, 1H, 2-H), 3.04 (ddd, *J* = 7.5, 10.6, 11.0 Hz, 1H, 3-H), 3.63 (m_c, 1H, 3-H), 3.91 (s, 3H, OCH_3), 4.17 (d, *J* = 9.7 Hz, 1H, 9a-H), 4.50 (d, *J* = 9.7 Hz, 9-H), 6.52 (d, *J* = 7.9 Hz, 1H, 5-H), 6.77 (ddt, *J* = 0.4, 1.0, 7.5 Hz, 1H, 7-H), 7.15 (m_c, 1H, 6-H), 7.43 (dddd, *J* = 0.6, 1.3, 7.5 Hz, 1H, 8-H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 22.2 (q, 1-CH_3), 40.5 (t, C-2), 47.1 (d, C-9), 49.3 (t, C-3), 52.7 (q, OCH_3), 73.5 (d, C-9a), 76.0 (s, C-1), 109.0, 119.0 (2d, C-5, C-7), 124.1 (s, C-8a), 124.7, 128.7 (2d, C-8 C-6), 154.3, 173.0 (2s, C-4a, CO); IR (film): ν = 3425 cm^{-1} (OH), 3050 (=CH), 2950-2900 (CH), 1700 (CO), 1665, 1555 (C=C); MS (EI, 110 °C, 80 eV): *m/z* (%) = 247 [M^+] (3), 245 [M^+ - 2H] (28), 198 (100); HRMS (110 °C, 80 eV): [M^+ - 2H]: $C_{14}H_{15}NO_3$ calcd.: 245.11869; found: 245.10569.

Analytical data of **13**: colorless solid; mp 86 ºC; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.70 (s, 3H, 6-CH_3), 2.66 (ddd, *J* = 1.7, 7.0, 12.7 Hz, 1H, 5-H), 2.86 (dtd, *J* = 0.8, 9.3, 12.7 Hz, 1H, 5-H), 3.97 (s, 3H, OCH_3), 4.02 (ddd, *J* = 7.0, 9.3, 10.7 Hz, 1H, 4-H), 4.27 (ddd, *J* = 1.7, 9.3, 10.7 Hz, 1H, 4-H), 5.28 (s, br, 1H, OH), 7.21-7.27 (m_c, 3H, 2-H, 7-H, 8-H), 8.00-8.02 (m, 1H,

9-H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 27.1 (q, 6-CH_3), 42.7 (t, C-4), 43.4 (t, C-5), 51.3 (q, OCH_3), 75.1 (s, C-6), 98.1 (s, C-1), 110.2 (d, C-2), 121.7, 122.1, 122.4 (3d, C-7, C-8, C-9), 129.8 (s, C-9a), 132.0 (s, C-6a), 157.2 (s, C-9b), 167.3 (s, CO); IR (film): ν = 3435 cm^{-1} (OH), 3050 (=CH), 2950-2900 (CH), 1665 (CO), 1615, 1555 (C=C); MS (EI, 60 °C, 80 eV): *m/z* (%) = 245 [M^+] (38), 230 [M^+ - CH_3] (3), 198 [M^+ - CH_3 - CH_3OH] (100), 170 [M^+ - CH_3 - CH_3OH - CO_2] (10); HRMS (60 °C, 80 eV): [M^+]: $C_{14}H_{15}NO_3$ calcd.: 245.10519; found: 245.10733; $C_{14}H_{15}NO_3$ (245.3) calcd.: C 68.55, H 6.16, N 5.71; found: C 69.58, H 5.77, N 4.83.

Methyl (9*R,9a*S**,10*R**)-9-Hydroxy-9-methyl-6,7,8,9,9a,10-hexahydropyrido[1,2-*a*]indol-10-carboxylate (15)**

Analytical data: colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.28 (s, 3H, 9-CH_3), 1.53 (dt, *J* = 4.8, 13.0 Hz, 1H, 8-H), 1.66-1.81 (m, 2H, 7-H), 1.98 (m_c, 1H, 8-H), 2.55 (dt, *J* = 3.6, 11.5 Hz, 1H, 6-H), 2.65 (s, br, 1H, OH), 3.46 (dd, *J* = 1.0, 11.5 Hz, 1H, 9a-H), 3.60 (dd, *J* = 4.5, 11.5 Hz, 1H, 6-H), 3.84 (s, 3H, OCH_3), 4.03 (dd, *J* = 1.0, 11.5 Hz, 1H, 10-H), 6.49 (d, *J* = 7.7 Hz, 1H, 4-H), 6.71 (tt, *J* = 1.0, 7.5 Hz, 1H, 2-H), 7.13 (qt, *J* = 1.0, 7.7 Hz, 1H, 3-H), 7.24 (m_c, 1H, 1-H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 20.9 (q, 9-CH_3), 23.3 (t, C-7), 40.7 (t, C-8), 45.0 (t, C-6), 47.3 (d, C-10), 52.6 (q, OCH_3), 70.4 (s, C-9), 75.2 (d, C-9a), 107.0 (d, C-4), 118.3 (d, C-2), 124.6 (d, C-1), 125.2 (s, C-10a), 128.6 (d, C-3), 150.7 (s, C-4a), 173.5 (s, CO); IR (film): ν = 3430 cm^{-1} (OH), 3050 (=CH), 2950-2700 (CH), 1740 (CO), 1665, 1605 (C=C); MS (EI, 40 °C, 80 eV): *m/z* (%) = 261 [M^+] (53), 222 (21), 190 [M^+ - C_4H_7O] (100); HRMS (40 °C, 80 eV): [M^+]: $C_{15}H_{19}NO_3$ calcd.: 261.13649; found: 261.13821; $C_{15}H_{19}NO_3$ (261.3) calcd.: C 68.90, H 7.33, N 5.36; found: C 68.56, H 7.14, N 5.17.

Methyl (9*R,9a*S**,10*R**)-9-Hydroxy-9-methyl-6-oxo-7,8,9,9a,10-hexahydropyrido[1,2-*a*]indol-10-carboxylate (17)**

Analytical data : colorless solid; mp 58-61 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.24 (s, 3H, 9-CH_3), 2.00 (ddd, *J* = 3.0, 8.2, 13.0 Hz, 1H, 8-H), 2.04-2.09 (m, 1H, 8-H), 2.56 (ddd, *J* = 8.2, 10.5, 18.5 Hz, 1H, 7-H), 2.74 (ddd, *J* = 3.0, 7.6, 18.5 Hz, 1H, 7-H), 2.87 (s, br, 1H, OH), 3.83 (s, 3H, OCH_3), 4.29 (d, *J* = 9.6 Hz, 1H, 10-H), 4.64 (d, *J* = 9.6 Hz, 1H, 9a-H), 7.06 (dt, *J* = 1.0, 7.5 Hz, 1H, 3-H), 7.26 (m_c, 1H, 2-H), 7.34 (d, br, *J* = 7.5 Hz, 1H, 1-H), 8.17 (d, J = 8.1 Hz, 1H, 4-H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 20.0 (q, 9-CH_3), 31.1, 36.5 (2t, C-7, C-8), 47.6 (d, C-10), 52.9 (q, OCH_3), 69.2 (d, C-9a), 69.8 (s, C-9), 117.0, 124.3, 124.4 (3d, C-4, C-1, C-3), 126.5 (s, C_{ipso}), 129.0 (d, C-2), 142.0 (s, C_{ipso}), 167.5, 172.2 (2s, NCO, CO_2CH_3); IR

(film):

ν = 3375 cm^{-1} (OH), 3020 (=CH), 2950-2885 (CH), 1745, 1635 (CO), 1590 (C=C); MS (EI, 120 °C, 80 eV): *m/z* (%) = 275 [M^+] (52), 257 [M^+ - H_2O] (53), 198 (100), 176 (51); $C_{15}H_{17}NO_4$ (275.3) calcd.: C 65.44, H 6.22, N 5.09; found: C 65.09, H 6.20, N 4.95.

Methyl (9*R,9a*S**,10*R**)-10-Allyl-9-hydroxy-9-methyl-6-oxo-7,8,9,9a,10-hexahydro-pyrido-[1,2-*a*]indol-10-carboxylate (18)**

Analytical data: colorless oil; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.20 (s, 3H, 9-CH_3), 1.74 (s, br, 1H, OH), 1.86 (ddd, *J* = 2.6, 7.7, 13.1 Hz, 1H, 8-H), 1.99 (dddd, *J* = 0.9, 7.7, 13.1 Hz, 1H, 8-H), 2.56 (ddd, *J* = 7.7, 11.0, 18.5 Hz, 1H, 7-H), 2.70 (ddd, *J* = 2.6, 7.7, 18.5 Hz, 1H, 7-H), 2.87 (dd, *J* = 9.2, 14.2 Hz, 1H, 10-CH_2), 3.02 (tdd, *J* = 1.9, 5.2, 14.2 Hz, 1H, 10-CH_2), 3.69 (s, 3H, OCH_3), 4.31 (s, 1H, 9a-H), 5.15 (dtd, *J* = 0.4, 1.5, 10.1 Hz, 1H, =CH_2), 5.20 (dtd, *J* = 0.9, 1.9, 17.1 Hz, 1H, =CH_2), 5.48 (dddd, *J* = 5.2, 9.2, 10.1, 17.1 Hz, 1H, =CH-), 7.09 (dt, *J* = 1.1, 7.6 Hz, 1H, 2-H), 7.21 (ddd, *J* = 0.6, 1.4, 7.7 Hz, 1H, 1-H), 7.28 (ddd, *J* = 1.4, 7.6, 8.2 Hz, 1H, 3-H), 8.28 (ddd, *J* = 0.6, 1.1, 8.2 Hz, 1H, 4-H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 20.3 (q, 9-CH_3), 30.9, 37.8, 44.0 (3t, C-7, C-8, 10-C), 53.1 (q, OCH_3), 56.6, 70.6 (2s, C-10, C-9), 72.9 (d, C-9a), 116.8 (d, C-4), 121.0 (t, =CH_2), 124.0, 124.9, 128.9 (3d, C-2, C-1, C-3), 129.7 (s, C_{ipso}), 132.2 (d, =CH-), 142.6 (s, C_{ipso}), 167.8, 175.3 (2s, NCO, CO_2CH_3); IR (film): ν = 3430 cm^{-1} (OH), 3075 (=CH), 2975-2885 (CH), 1730, 1660 (CO), 1595 (C=C); MS (EI, 100 °C, 80 eV): *m/z* (%) = 315 [M^+] (33), 274 [M^+ - CHO] (5), 176 (100); $C_{15}H_{17}NO_4$ (315.4) calcd.: C 68.55, H 6.71, N 4.44; found: C 68.34, H 6.67, N 4.28.

Methyl (9*R,9a*S**,10*R**)-10-Allyl-9-{[*tert*-butyl(dimethyl)siloxy]ethyl}-9-hydroxy-6-oxo-6,7,8,9,9a,10-hexahydropyrido[1,2-*a*]indol-10-carboxylate (20)**

Analytical data: colorless crystals; mp 127-131 °C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.05 (s, 6H, Si-CH_3), 0.86 [s 9H, C(CH_3)$_3$], 1.64 (td, *J* = 3.8, 14.6, Hz, 1H, 9-CH_2), 1.79 (ddd, *J* = 5.5, 9.7, 14.6 Hz, 1H, 9-CH_2), 1.85-1.88 (m, 1H, 8-H), 2.16 (ddd, *J* = 3.5, 7.0, 13.8 Hz, 1H, 8-H), 2.46 (ddd, *J* = 7.0, 10.9, 18.1 Hz, 1H, 7-H), 2.69 (ddd, *J* = 3.5, 7.6, 18.1 Hz, 1H, 7-H), 2.93 (dd, *J* = 9.0, 14.3 Hz, 1H, 10-CH_2), 3.02 (tdd, *J* = 1.5, 5.5, 14.3 Hz, 1H, 10-CH_2), 3.60 (s, 3H, OCH_3), 3.77-3.87 (m, 2H, OCH_2), 4.28 (s, 1H, 9a-H), 4.34 (s, 1H, OH), 5.08 (d, *J* = 10.2 Hz, 1H, =CH_2), 5.14 (d, J = 17.0 Hz, 1H, =CH_2), 5.49 (ddd, *J* = 5.5, 9.0, 10.2, 17.0 Hz, 1H, =CH-), 7.05 (dt, *J* = 1.1, 7.7 Hz, 1H, 1-H), 7.13 (dd, *J* = 1.4, 7.8 Hz, 1H, 3-H), 7.24 (dt, *J* =

1.1, 7.7 Hz, 1H, 2-H), 8.22 (d, *J* = 7.8 Hz, 1H, 4-H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = -5.7, -5.6 (2s, Si-CH_3), 18.0, 25.7 [s, q, C(CH_3)$_3$], 30.9, 31.7, 33.1, 41.4 (4t, 9-C, C-7, C-8, 10-C), 52.3 (q, OCH_3), 55.9 (s, C-10), 59.7 (t, OCH_2), 73.0 (d, C-9a), 73.2 (s, C-9), 116.8 (d, C-4), 120.5 (t, =CH_2), 124.0, 124.1, 128.7 (3d, C-1, C-3, C-2), 131.1 (s, C_{ipso}), 132.7 (d, =CH-), 142.7, 168.1, 173.7 (s, C_{ipso}, NCO, CO_2CH_3); IR (KBr): ν = 3455 cm^{-1} (OH), 3065(=CH), 2955-2855 (CH), 1730, 1665 (CO), 1595 (C=C); MS (EI, 135 °C, 80 eV): *m/z* (%) = 459 [M^+] (16), 402 [M^+ - C_3H_5O] (99), 286 (90), 144 (86), 111 (100); $C_{25}H_{37}NO_5Si$ (445.7) calcd.: C 65.33, H 8.04, N 3.05; found: C 65.16, H 8.11, N 2.88.

Methyl (2a*R,10b*S**,10c*R**)-2a-Hydroxy-5-oxo-1,2,2a,4,5,10c-hexahydrobenzo[*b*]pentacyclo[*hi*]indol-10b(3*H*)-carboxylate (22)**

Analytical data: colorless solid; mp 167-169 °C (sublimation at 150 °C); ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.64 (ddd, *J* = 7.4, 12.8, 13.0 Hz, 1H, 1-H), 1.95 (dt, *J* = 4.4, 14.1 Hz, 1H, 3-H), 2.06 (dddd, *J* = 0.6, 1.9, 6.7, 13.7 Hz, 1H, 1-H), 2.15 (ddd, *J* = 1.9, 7.3, 13.1 Hz, 1H, 2-H), 2.21 (ddd, *J* = 2.6, 5.7, 14.6 Hz, 1H, 3-H), 2.44 (dddd, *J* = 0.5, 2.6, 4.1, 14.6 Hz, 1H, 4-H), 2.71 (m_c, 2H, 2-H, 4-H), 3.00 (s, 1H, OH), 3.80 (s, 3H, OCH_3), 4.75 (d, *J* = 1.6 Hz, 1H, 10c-H), 7.09 (ddt, *J* = 0.7, 1.1, 7.6 Hz, 1H, 8-H), 7.28 (t*, *J* = 8.1 Hz, 1H, 9-H), 7.43 (d*, *J* = 7.6 Hz, 1H, 10-H), 8.05 (d*, *J* = 8.1 Hz, 1H, 7-H); * with further splitting; ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 32.8, 33.7, 39.0, 39.6 (4t, C-4, C-3, C-2, C-1), 53.0 (q, OCH_3), 61.6 (s, C-10b), 75.8 (d, C-10c), 81.7 (s, C-2a), 115.6, 124.3, 124.4, 129.2 (4d, Ar), 131.5, 141.7, 170.6, 174.0 (4s, C-10a, C-6a, C-5, CO_2CH_3); IR (film): ν = 3300 cm^{-1} (OH), 3080 (=CH), 2975-2855 (CH), 1730, 1640 (CO), 1590 (C=C); MS (EI, 140 °C, 80 eV): *m/z* (%) = 287 [M^+] (61), 269 [M^+ - H_2O] (10), 228 [M^+ - CH_3 - CO_2] (4), 210 [M^+ - H_2O - CH_3 - CO_2] (100); HRMS (140 °C, 80 eV): [M^+]: $C_{16}H_{17}NO_4$ calcd.: 287.11576; found: 287.11734.

Diethyl (1*R,7*R**,7a*S**)-7-Hydroxy-7-methyl-5,6,7,7a-tetrahydro-1*H*-pyrrolizin-1,2-dicarboxylate (25) and Diethyl 7-Hydroxy-7-methyl-5,6,7,7a-tetrahydro-1H-pyrrolizin-1,2-dicarboxylate (mixture of minor stereo isomers)**

Analytical data of **25**: yellow oil; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.16, 1.18 (2t, *J* = 7.1 Hz, je 3H, CH_2CH_3), 1.21 (s, 3H, 7-CH_3), 1.76 (ddd, *J* = 5.3, 7.5, 12.7 Hz, 1H, 6-H), 1.99 (td, *J* = 8.0, 12.7 Hz, 1H, 6-H), 3.13-3.18 (m, 1H, 5-H), 3.35 (ddd, *J* = 5.3, 8.0, 10.8 Hz, 1H, 5-H), 3.87 (dd, *J* = 1.0, 4.5 Hz, 1H, 1-H), 3.90 (d, *J* = 4.5 Hz, 1H, 7a-H), 4.04, 4.10 (2q, *J* = 7.1 Hz, je 2H, CH_2CH_3), 7.00 (d, *J* = 1.0, Hz, 1H, 3-H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.0, 14.3

(2q, CH_2CH_3), 22.2 (q, 7-CH_3), 40.4 (t, C-6), 46.9 (t, C-5), 47.5 (d, C-1), 59.3, 61.1 (2t, OCH_2), 76.7 (s, C-7), 77.9 (d, C-7a), 105.4 (s, C-2), 152.7 (d, C-3), 165.0, 174.2 (2s, CO); IR (film): ν = 3445 cm^{-1} (OH), 2980-2905 (CH), 1735, 1690 (CO), 1590 (C=C); MS (EI, 120 °C, 80 eV): *m/z* (%) = 283 [M^+] (22), 238 [M^+ - C_2H_5O] (19), 220 [M^+ - C_2H_5O - H_2O] (5), 210 (56), 164 (100); HRMS (100 °C, 80 eV):[M^+]: $C_{14}H_{21}NO_5$ calcd.: 283.14197; found: 283.14346; $C_{15}H_{15}NO_4$ (273.3) calcd.: C 59.35, H 7.47, N 4.94; found: C 59.39, H 7.22, N 4.37.

Analytical data of minor stereo isomers (yellow oil): Main component: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.21, 1.24 (2t, *J* = 7.1 Hz, je 3H, CH_2CH_3), 1.36 (s, 3H, 7-CH_3), 1.93 (dt, *J* = 9.9, 13.3 Hz, 1H, 6-H), 2.04 (ddd, *J* = 2.6, 6.6, 13.3 Hz, 1H, 6-H), 3.33-3.40 (m, 2H, 5-H), 3.79 (d, *J* = 4.8 Hz, 1H, 7a-H), 4.04 (dd, *J* = 1.2, 4.8 Hz, 1H, 1-H), 4.05-4.29 (m, 4H, CH_2CH_3, overlap with signal of the minor component), 7.14 (d, *J* = 1.2 Hz, 1H, 3-H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.1, 14.4 (2q, CH_2CH_3), 22.6 (q, 7-CH_3), 39.9 (t, C-6), 46.1 (d, C-1), 46.6 (t, C-5), 59.3, 61.0 (2t, OCH_2), 74.2 (s, C-7), 77.6 (d, C-7a), 105.7 (s, C-2), 153.5 (d, C-3), 165.3, 168.6, 169.5, 169.6 (4s, CO for both components).

Minor component: ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.24, 1.25 (2t, *J* = 7.1 Hz, each 3H, CH_2CH_3), 1.45 (s, 3H, 7-CH_3), 2.17-2.21 (m, 2H, 6-H), 3.23 (ddd, *J* = 4.8, 7.0, 11.7 Hz, 1H, 5-H), 3.67-3.72 (m, 1H, 5-H), 3.65, 4.00 (2d, *J* = 7.4 Hz, je 1H, 7a-H, 1-H), 4.05-4.29 (m, 4H, CH_2CH_3, overlap with signal of the minor component), 7.14 (s, 1H, 3-H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 13.9, 14.0 (2q, CH_2CH_3), 23.7 (q, 7-CH_3), 40.2, 40.9 (2t, C-5, C-6), 50.1 (d, C-7a), 61.4, 62.8 (2t, OCH_2), 67.2 (d, C-1), 76.6 (s, C-7), 105.7* (s, C-2), 153.5* (d, C-3), 165.3, 168.6, 169.5, 169.6 (4s, CO for both components). * overlap with signal of the main component. IR (film): ν = 3450 cm^{-1} (OH), 2980-2905 (CH), 1735, 1690 (CO), 1590 (C=C); MS (EI, 120 °C, 80 eV): *m/z* (%) = 283 [M^+] (16), 238 [M^+ - C_2H_5O] (12), 220 [M^+ - C_2H_5O - H_2O] (4), 210 (6), 164 (100); HRMS (120 °C, 80 eV): [M^+]: $C_{14}H_{21}NO_5$ calcd.: 283.14197; found: 283.14355.

Diethyl (1*R,8*R**,8a*S**)-8-Hydroxy-8-methyl-1,5,6,7,8,8a-hexahydro-1,2-indolizidindi-carboxylate (26)**

Analytical data: colorless solid; mp 93-95°C; ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 1.14 (t, *J* = 7.1 Hz, 3H, CH_2CH_3), 1.15 (s, 3H, 8-CH_3), 1.19 (t, *J* = 7.1 Hz, 3H, CH_2CH_3), 1.38-1.63 (m, 3H, 6-H, 7-H), 1.79-1.85 (m, 1H, 7-H), 2.48 (s, 1H, br, OH), 2.84-2.95 (m, 1H, 5-H), 3.33-

3.41 (m, 1H, 5-H), 3.51 (d, *J* = 8.9 Hz, 1H, 8a-H), 3.82 (dd, *J* = 1.0, 8.9 Hz, 1H, 1-H), 4.02 (m_c, 2H, CH_2CH_3), 4.11 (q, *J* = 7.1 Hz, 2H, CH_2CH_3), 7.05 (d, *J* = 1.0 Hz, 1H, 3-H); ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 14.0, 14.4 (2q, CH_2CH_3), 20.4 (q, 8-CH_3), 23.4 (t, C-6), 39.0 (t, C-7), 46.4 (t, C-5), 47.3 (d, C-1), 58.9, 61.1 (2t, CH_2CH_3), 70.1 (s, C-8), 74.8 (d, C-8a), 98.1 (s, C-2), 150.1 (d, C-3), 165.6, 174.4 (2s, CO); IR (KBr): ν = 3445 cm^{-1} (OH), 3075 (=CH), 2980-2860 (CH), 1720 (CO), 1655, 1580 (C=C); MS (EI, 80 °C, 80 eV): *m/z* (%) = 297 [M^+] (8), 279 [M^+ - H_2O] (6), 252 [M^+ - C_2H_5O] (4), 224 [M^+ - $C_4H_5O_2$] (100); $C_{15}H_{23}NO_5$ (297.4) calcd.: C 60.59, H 7.79, N 4.71; found: C 60.50, H 7.51, N 4.59.