Stereoselective Formation of Tri- and Tetracycles by Samarium Diiodide-Induced Cyclizations of Naphthyl Substituted Ketones

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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 SmI₂ 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 (18 equiv.) was added. The ketone and *tert*-butanol (2.0 equiv.), dissolved in THF (20 mL), were then added in one portion to the deep purple solution. After 16 h the reaction mixture 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.

rac-(1*S*,4*aS*,10*aS*)-1-Methyl-1,2,3,4,4*a*,10*a*-hexahydrophenanthren-1-ol (**8**)

Analytical data: colorless oil; ¹H NMR (CDCl₃, 500 MHz): δ = 7.16-7.09 (m, 3 H, Ar), 7.06-7.01 (m, 1 H, Ar), 6.46 (dd, *J* = 3.2, 9.7 Hz, 1 H, 9-H), 5.68 (br. d, *J* = 9.7 Hz, 1 H, 10-H), 3.11 (td, *J* = 5.4, 12.1 Hz, 1 H, 4*a*-H), 2.57 (m, 1 H, 10*a*-H), 1.75-1.44 (m, 6 H, CH₂, OH), 1.38-1.31 (m, 1 H, CH₂), 1.34 (s, 3 H, CH₃); ¹³C NMR (CDCl₃, 126 MHz): δ = 140.6, 132.7 (2 s, C-4*b*, C-8*a*), 128.8, 128.7, 128.3, 128.2, 127.6, 126.3 (6 d, C-5, C-6, C-7, C-8, C-9, C-10), 71.5 (s, C-1), 46.4 (d, C-10*a*), 36.7 (d, C-4*a*), 35.0, 27.3, 20.0 (3 t, CH₂), 28.7 (q, CH₃); IR (film): ν = 3420 cm⁻¹ (br. s, OH), 3100-2900 (=C-H, C-H), 1600 (C=C); C₁₅H₁₈O (214.3) calcd.: C 84.07, H 8.47; found: C 84.22, H 8.22.

***rac*-(1*S*,9*aS*)-1-Methyl-1,2,3,4,9,9*a*-hexahydroanthracen-1-ol (10*a*)**

Analytical data: colorless oil; ^1H NMR (CDCl_3 , 500 MHz): δ = 7.39 (d, J = 7.3 Hz, 1 H, Ar), 7.20-7.12 (m, 3 H, Ar), 5.63 (s, 1 H, 10-H), 3.44-3.24 (m, 3 H, 9-H, 9*a*-H), 2.33-2.28, 2.07-1.98 (2 m, 1 H each, 4-H), 1.93-1.74 (m, 4 H, 2-H, 3- H_A , OH), 1.52-1.41 (m, 1 H, 3- H_B), 0.84 (s, 3 H, CH_3); ^{13}C NMR (CDCl_3 , 126 MHz): δ = 137.8, 135.0, 133.7 (3 s, C-4*a*, C-8*a*, C-10*a*), 129.4, 128.3, 126.2, 125.5 (4 d, C-5, C-6, C-7, C-8), 117.9 (d, C-10), 76.5 (s, C-1), 53.0 (d, C-9*a*), 41.0 (t, C-2), 35.4 (t, C-4), 30.3 (t, C-9), 25.6 (t, C-3), 20.9 (q, CH_3); IR (film): ν = 3450 cm^{-1} (br. s, OH), 3100-2850 (=C-H, C-H), 1600 (C=C); $\text{C}_{15}\text{H}_{18}\text{O}$ (214.3) calcd.: C 84.07, H 8.47; found: C 84.34, H 8.47.

***rac*-(1*R*,9*aS*)-1-Methyl-1,2,3,4,9,9*a*-hexahydroanthracen-1-ol (10*b*)**

Analytical data: colorless oil; ^1H NMR (CDCl_3 , 500 MHz): δ = 7.09-7.04 (m, 3 H, Ar), 6.91 (d, J = 6.5 Hz, 1 H, Ar), 6.17 (s, 1 H, 10-H), 3.19 (dd, J = 3.5, 17.3 Hz, 1 H, 9- H_A), 3.08 (dd, J = 10.4, 17.3 Hz, 1 H, 9- H_B), 2.47 (dd, J = 3.5, 10.4 Hz, 1 H, 9*a*-H), 2.39-2.34 (m, 1 H, 4- H_A), 2.15 (dt, J = 5.0, 13.2 Hz, 1 H, 4- H_B), 1.86-1.75 (m, 3 H, 3- H_A , 2- H_A , OH), 1.61 (dt, J = 5.2, 13.2 Hz, 1 H, 2- H_B), 1.45 (tq, J = 4.4, 13.2 Hz, 1 H, 3- H_B), 1.01 (s, 3 H, 1- CH_3); ^{13}C NMR (CDCl_3 , 126 MHz): δ = 140.8, 133.4, 133.4 (3 s, C-4*a*, C-8*a*, C-10*a*), 127.2, 126.5, 126.0, 125.5 (4 d, C-5, C-6, C-7, C-8), 75.2 (s, C-1), 48.3 (d, C-9*a*), 42.8 (t, C-2), 35.0 (t, C-4), 26.2 (t, C-9), 25.0 (t, C-3), 20.6 (q, CH_3); IR (film): ν = 3450 cm^{-1} (br. s, OH), 3100-2850 (=C-H, C-H), 1600 (C=C); $\text{C}_{15}\text{H}_{18}\text{O}$ (214.3) calcd.: C 84.07, H 8.47; found: C 84.08, H 8.25.

***rac*-(1*S*,2*S*,11*S*,13*S*)-1-Isopropyl-15-oxatetracyclo[11.2.1.0^{2,11}.0^{5,10}]hexadeca-3,5(10),6,8-tetraen-14-one (15)**

Analytical data: colorless solid; mp 132-136 $^{\circ}\text{C}$; ^1H NMR (CDCl_3 , 500 MHz): δ = 7.21-7.16, 7.11-7.05 (2 m, 2 H each, Ar), 6.53 (dd, J = 3.0, 9.8 Hz, 1 H, 3-H), 5.61 (br. d, J = 9.8 Hz, 1 H, 4-H), 3.29-3.24 (m, 1 H, 2-H), 3.08 (ddd, J = 6.2, 6.3, 13.0 Hz, 1 H, 11-H), 2.68 (m, 1 H, 13-H), 2.35-2.30 (m, 1 H, 16-H), 2.13 (quint., J = 6.9 Hz, 1 H, 17-H), 1.90-1.83 (m, 2 H, 12-H, 16-H), 1.58 (dt, J = 2.0, 13.0 Hz, 1 H, 12-H), 1.08, 1.05 (2 d, J = 6.9 Hz, 3 H each, CH_3); ^{13}C NMR (CDCl_3 , 126 MHz): δ = 178.5 (s, C=O), 136.9, 132.1 (2 s, Ar), 128.9, 128.2, 128.0, 127.3, 126.7, 124.6 (6 d, Ar, C-3, C-4), 90.6 (s, C-1), 39.3 (d, C-13), 39.0 (d, C-2), 35.3 (d, C-11), 34.9 (t, C-16), 32.2 (t, C-12), 30.8 (d, C-17), 17.0, 16.4 (2 q, CH_3); IR (KBr): ν = 3040-2850 cm^{-1} (=C-H, C-H), 1775 (C=O); MS (EI, 180 $^{\circ}\text{C}$, 80 eV): m/z (%) = 268 (60)

[M⁺], 251 (13) [M⁺ - OH], 223 (6) [M⁺ - CO₂H], 128 (100) [C₁₀H₈⁺]; C₁₈H₂₀O₂ (268.4) calcd.: C 80.56, H 7.51; found: C 80.01, H 7.56.

***rac*-(2a*R*,2b*R*,8b*R*,10a*R*)-1,2b,8b,9,10,10a-Hexahydrocyclobuta[*a*]phenanthren-2a(2*H*)-ol (21)**

Analytical data: colorless oil; ¹H NMR (CDCl₃, 500 MHz): δ = 7.17-7.13 (m, 3 H, Ar), 7.03 (d, *J* = 7.5 Hz, 1 H, Ar), 6.47 (dd, *J* = 2.5, 9.6 Hz, 1 H, 4-H), 6.18 (dd, *J* = 4.9, 9.6 Hz, 1 H, 3-H), 3.02 (m_c, 1 H, 8b-H), 2.67 (m_c, 1 H, 2b-H), 2.26 (m_c, 1 H, 10a-H), 2.14-2.06 (m, 2 H, 2-H, 9-H), 1.91-1.78 (m, 2 H, 1-H, 10-H), 1.74-1.67 (m, 1 H, 2-H), 1.63 (br. s, 1 H, OH), 1.52-1.45 (m, 1 H, 10-H), 1.39 (m_c, 1 H, 9-H), 1.27-1.20 (m, 1 H, 1-H); ¹³C NMR (CDCl₃, 125 MHz): δ = 139.0, 133.4 (2 s, C-4a, C-8a), 128.4 (d, C-3), 128.0 (d, C-4), 127.5, 126.4, 126.3, 126.2 (4 d, Ar), 75.2 (s, C-2a), 43.5 (d, C-2b), 43.3 (d, C-10a), 36.3 (d, C-8b), 33.2 (t, C-2), 24.5 (t, C-10), 23.0 (t, C-9), 18.9 (C-1); IR (film): ν = 3380 cm⁻¹ (br. s, OH), 3035-2830 (=C-H, C-H), 1630 (C=C); MS (EI, 70 °C, 80 eV): *m/z* (%) = 226 (20) [M⁺], 196 (100) [M⁺ - CH₂O], 181 (16) [M⁺ - C₂H₅O]; HRMS (70 °C, 80 eV): [M⁺]: C₁₆H₁₈O calcd.: 226.1358; found: 242.1366; C₁₆H₁₈O (226.3) calcd.: C 84.91, H 8.02; found: C 84.71, H 7.97.

***rac*-(3a*R*,3b*R*,9b*R*,11a*S*)-1,2,3,3b,9b,10,11,11a-Octahydro-3a*H*-cyclopenta[*a*]phenanthren-3a-ol (22)**

Analytical data: colorless solid; mp 114-116 °C; ¹H NMR (CDCl₃, 500 MHz): δ = 7.22-7.09 (m, 3 H, Ar), 7.02 (d, *J* = 7.7 Hz, 1 H, Ar), 6.52 (d, *J* = 9.5 Hz, 1 H, 5-H), 6.18 (dd, *J* = 5.2, 9.5 Hz, 1 H, 4-H), 3.30-3.22 (m, 1 H, 9b-H), 2.65 (dd, *J* = 5.2, 7.0 Hz, 1 H, 3b-H), 2.42-2.28 (m, 1 H, 10-H), 2.04-1.89 (m, 1 H, 1-H), 1.80-1.70 (m, 1 H, 11a-H), 1.65-1.60 (m, 1 H, 10-H), 1.60-1.55 (m, 2 H, 11-H, 2-H), 1.55-1.20 (m, 5 H, 11-H, 3-H, 2-H, 1-H); ¹³C NMR (CDCl₃, 125 MHz): δ = 137.2, 134.4 (2 s, C-5a, C-9a), 129.9 (d, C-4), 128.5 (d, C-5), 127.4, 126.2, 126.0, 124.1 (4 d, Ar), 84.1 (s, C-3a), 47.6 (d, C-11a), 44.2 (d, C-3b), 36.5 (d, C-9b), 33.2 (t, C-3), 29.1 (t, C-1), 28.0 (t, C-11), 24.4 (t, C-10), 19.8 (t, C-2); IR (KBr): ν = 3380 cm⁻¹ (br. s, OH), 3050-2800 (=C-H, C-H); MS (EI, 100 °C, 80 eV): *m/z* (%) = 240 (52) [M⁺], 223 (3) [M⁺ - H₂O], 154 (49), 129 (62), 128 (100) [C₁₀H₈⁺]; HRMS (100 °C, 80 eV): [M⁺]: C₁₇H₂₀O calcd.: 240.1514; found: 240.1537; C₁₇H₂₀O (240.4) calcd.: C 84.96, H 8.39; found: 84.67, H 8.25.

***rac*-(4a*R*,4b*R*,10b*R*,12a*S*)-1,3,4,4b,10b,11,12,12a-Octahydrobenzo[*a*]phenanthren-4a(2*H*)-ol (23)**

Analytical data: colorless solid; mp 106-108 °C; ¹H NMR (CDCl₃, 500 MHz): δ = 7.20-7.10 (m, 3 H, Ar), 7.01 (d, *J* = 7.5 Hz, 1 H, Ar), 6.51 (d, *J* = 9.8 Hz, 1 H, 6-H), 6.18 (dd, *J* = 5.7, 9.8 Hz, 1 H, 5-H), 3.25 (m_c, 1 H, 10b-H), 2.63 (dd, *J* = 5.7, 7.0 Hz, 1 H, 4b-H), 2.37-2.30 (m, 1 H, 11-H), 2.00-1.90 (m, 1 H, CH₂), 1.79-1.72 (m, 1 H, 12a-H), 1.68-1.54 (m, 5 H, CH₂, OH), 1.46-1.20 (m, 6 H, CH₂); ¹³C NMR (CDCl₃, 125 MHz): δ = 137.2, 134.4 (2 s, Ar), 129.9 (d, C-5), 128.4 (d, C-6), 127.3, 126.2, 125.9, 124.1 (4 d, Ar), 84.0 (s, C-4a), 47.5 (d, C-12a), 44.1 (d, C-4b), 36.5 (d, C-10b), 33.2, 29.0, 26.4, 24.4, 19.8, 19.7 (6 t, CH₂); IR (KBr): ν = 3365 cm⁻¹ (br. s, OH), 3000-2800 (=C-H, C-H); MS (EI, 80 °C, 80 eV): *m/z* (%) = 254 (1) [M⁺], 222 (33) [M⁺ - CH₃OH], 154 (88), 128 (100) [C₁₀H₈⁺]; C₁₈H₂₂O (254.4) calcd.: C 84.99, H 8.72; found: C 84.90, H 8.58.

***rac*-(4b*R*,6a*S*,11a*R*,11b*R*)-4b,5,6,6a,7,8,9,10,11,11b-Decahydro-11a*H*-cyclohepta[*a*]phenanthren-11a-ol (24)**

Analytical data: colorless solid; mp 109-111 °C; ¹H NMR (CDCl₃, 500 MHz): δ = 7.16-7.08 (m, 3 H, Ar), 7.03-6.98 (m, 1 H, Ar), 6.45 (dd, *J* = 2.7, 9.9 Hz, 1 H, 13-H), 6.06 (dd, *J* = 3.3, 9.9 Hz, 1 H, 12-H), 3.17 (m_c, 1 H, 4b-H), 2.53 (m_c, 1 H, 11b-H), 1.97-1.15 (m, 16 H, CH, CH₂, OH); ¹³C NMR (CDCl₃, 125 MHz): δ = 139.9, 133.1 (2 s, Ar), 129.0, 127.8, 127.4, 126.2*, 125.9 (5 d, Ar, C-12, C-13), 76.5 (s, C-11a), 46.5 (d, C-6a), 44.6 (d, C-11b), 37.3 (d, C-4b), 33.3, 29.8, 29.5, 29.1, 24.4, 20.8, 19.7 (7 t, CH₂) *signal with higher intensity; IR (KBr): ν = 3435 cm⁻¹ (br. s, OH), 3060-2800 (=C-H, C-H); MS (EI, 90 °C, 80 eV): *m/z* (%) = 268 (38) [M⁺], 250 (16) [M⁺ - H₂O], 154 (100), 128 (49) [C₁₀H₈⁺]; HRMS (90 °C, 80 eV): [M⁺]: C₁₉H₂₄O calcd.: 268.1827; found: 268.1842; C₁₉H₂₄O (268.4) calcd.: C 85.03, H 9.01; found: C 84.90, H 8.58.

***rac*-(4b*R*,6a*S*,11a*R*,12b*R*)-4b,6,6a,7,8,9,10,11,12,12b-Decahydrocycloocta[*a*]phenanthren-12(5*H*)-ol (25)**

Analytical data: colorless oil; (purity • 90 %); ¹H NMR (CDCl₃, 500 MHz): δ = 7.26 (br. d, *J* • 7.5 Hz, 1 H, Ar), 7.16 (dt, *J* = 1.3, 7.5 Hz, 1 H, Ar), 7.09 (tt, *J* = 1.3, 7.3 Hz, 1 H, Ar), 6.99 (dd, *J* = 1.3, 7.3 Hz, 1 H, Ar), 6.56 (d, *J* = 9.8 Hz, 1 H, 14-H), 6.12 (dd, *J* = 6.0, 9.8 Hz, 1 H, 13-H), 3.19 (m_c, 1 H, 4b-H), 2.56-2.50 (m, 2 H, CH₂), 2.38 (m_c, 1 H, 12b-H), 1.85-0.86 (m, 16 H, CH, CH₂, OH); ¹³C NMR (CDCl₃, 125 MHz): δ = 138.9, 135.4 (2 s, Ar), 131.2, 129.8,

127.5, 125.9, 125.5, 122.9 (6 d, Ar, C-13, C-14), 63.1 (s, C-12a), 42.8 (d, C-6a), 42.0 (d, C-12b), 35.6 (d, C-4b), 32.3, 30.0, 29.6, 28.4, 26.6, 26.2, 26.0, 23.1 (8 t, CH₂); IR (film): ν = 3435 cm⁻¹ (br. s, OH), 3025-2850 (=C-H, C-H); MS (EI, 130 °C, 80 eV): m/z (%) = (6) [M⁺ - H₂O], 207 (100), 128 (70) [C₁₀H₈⁺].

***rac*-(3a*R*,3b*R*,9b*R*,11a*S*)-1,2,3,3b,4,5,9b,10,11,11a-Decahydro-3a*H*-cyclopenta[*a*]phenanthren-3a-ol (26)**

0.240 g (1.00 mmol) **22** and 0.100 g Pd(10%)/C in 12 mL methanol were stirred for 24 h under hydrogen atmosphere. Filtration on celite and evaporation gave 0.238 g (98 %) of **26**.

Analytical data: colorless solid; mp 108-111 °C; ¹H NMR (CDCl₃, 270 MHz): δ = 7.24-7.09 (m, 4 H, Ar), 3.14 (m, 1 H, 9b-H), 2.96-2.74 (m, 3 H, 11a-H, 5-H), 2.19-1.48 (m, 14 H, CH, CH₂, OH); ¹³C NMR (CDCl₃, 67.9 MHz): δ = 141.2, 137.1 (2 s, Ar), 128.4, 127.7, 125.8, 125.6 (4 d, Ar), 82.6 (s, C-3a), 46.1, 44.2, 37.2 (3 d, CH), 36.8, 30.0, 28.3, 26.7, 25.2, 22.0, 20.5 (7 t, CH₂); IR (KBr): ν = 3380 cm⁻¹ (br. s, OH), 3050-2800 (=C-H, C-H); MS (EI, 70 °C, 80 eV): m/z (%) = 242 (45) [M⁺], 224 (100) [M⁺ - H₂O], 200 (26) [M⁺ - C₂H₂O]; HRMS (70 °C, 80 eV): [M⁺]: C₁₇H₂₂O calcd.: 242.1670; found: 242.1666.

***rac*-(3a*R*,11a*S*)-1,2,3,10,11,11a-Hexahydro-3a*H*-cyclopenta[*a*]phenanthren-3a-ol (27)**

A suspension of 0.100 g (0.420 mmol) **22** and 0.869 g (10.0 mmol) MnO₂ in 25 mL THF was refluxed. Conversion was monitored by TLC. After 2 h 0.869 g (10.0 mmol) MnO₂ were added, the suspension refluxed for again 2 h. After cooling to room temperature the mixture was filtrated on celite, evaporated and diluted with CH₂Cl₂. The solution was washed with 1 N HCl and water, dried over anhydrous magnesium sulfate, filtered and evaporated. Chromatography of the resulting crude product on silica gel using hexane/ethyl acetate mixture (90:10) afforded 0.073 g (73 %) of **27**.

Analytical data: colorless solid; mp 93-95 °C; ¹H NMR (CDCl₃, 270 MHz): δ = 7.97, 7.79 (2 d, J = 8.1 Hz, 1 H each, Ar), 7.73-7.63, 7.54-7.42 (2 m, 2 H each, Ar), 3.72 (m, 1 H, 11a-H), 3.31 (td, J = 4.6, 16.7 Hz, 1 H, 10-H), 2.97 (ddd, J = 5.5, 10.7, 16.7 Hz, 1 H, 10-H), 2.35-1.22 (m, 9 H, CH₂, OH); ¹³C NMR (CDCl₃, 67.9 MHz): δ = 138.7, 132.4, 131.5, 131.2 (4 s, Ar), 128.3, 126.7, 126.0, 125.4*, 123.7 (5 d, Ar), 82.2 (s, C-3a), 47.9 (d, C-11a), 40.5, 30.3, 28.4, 24.8, 22.1 (5 t, CH₂) *signal with higher intensity; IR (KBr): ν = 3380 cm⁻¹ (br. s, OH), 3050-2800 (=C-H, C-H); MS (EI, 70 °C, 80 eV): m/z (%) = 238 (100) [M⁺], 209 (99) [M⁺ -

C₂H₅], 196 (90) [M⁺ - C₂H₂O]; C₁₇H₁₈O (238.3) calcd.: C 85.67, H 7.61; found: C 85.15, H 7.47.

***rac*-(1a*S*,5b*R*,7a*S*,10a*R*,10b*S*,10c*R*)-1a,5b,6,7,7a,8,9,10,10b,10c-Decahydro-10a*H*-cyclopenta[1,2]phenanthro[9,10-*b*]oxiren-10a-ol (28)**

A solution of 0.240 g (1.00 mmol) **22** and 0.257 g (1.05 mmol) *m*-CPBA (70%) in 1.5 mL CH₂Cl₂ was stirred first at 0 °C, then at room temperature. The conversion was monitored by TLC. After 8 h the solution was diluted with 10 mL CH₂Cl₂, washed with 4 N NaOH solution and water. The organic layer was dried over anhydrous magnesium sulfate, filtered and evaporated to afford 0.256 g (quant.) **28**.

Analytical data: colorless solid; mp 109-110 °C; ¹H NMR (CDCl₃, 500 MHz): δ = 7.37 (d, *J* = 7.4 Hz, 1 H, Ar), 7.31-7.24 (m, 1 H, Ar), 7.23-7.15 (m, 2 H, Ar), 4.00 (dd, *J* = 2.6, 4.3 Hz, 1 H, 10c-H), 3.85 (d, *J* = 4.3 Hz, 1 H, 1a-H), 3.17-3.10 (m, 1 H, 5b-H), 2.75 (dd, *J* = 2.6, 7.0 Hz, 1 H, 10b-H), 2.45 (qd, *J* = 3.2, 14.0 Hz, 1 H, 6-H), 2.01-1.91 (m, 1 H, 8-H), 1.79-0.94 (m, 8 H, 6-H, 7-H, 7a-H, 10-H, 9-H, 8-H, OH), 0.82-0.69 (m, 1 H, 9-H); ¹³C NMR (CDCl₃, 126 MHz): δ = 137.0, 133.1 (2 s, Ar), 129.7, 128.8, 125.6, 124.3 (4 d, Ar), 82.9 (s, C-10a), 55.6 (d, C-10c), 53.9 (d, C-1a), 49.5 (d, C-7a), 42.8 (d, C-10b), 31.8 (t, C-9), 31.1 (d, C-5b), 29.5 (t, C-8), 28.3 (t, C-7), 24.6 (t, C-6), 20.0 (t, C-10); IR (KBr): ν = 3365 cm⁻¹ (br. s, OH), 3065-2850 (=C-H, C-H); MS (EI, 70 °C, 80 eV): *m/z* (%) = 256 (16) [M⁺], 238 (16) [M⁺ - H₂O], 154 (35), 145 (41), 86 (44), 84 (66), 49 (100); C₁₇H₂₀O₂ (256.4) calcd.: C 79.65, H 7.86; found: C 79.88, H 7.84.

***rac*-(3a*S*,3b*R*,9b*R*,11*S*,11a*S*)-Methyl 3a-Hydroxy-2,3,3a,3b,9b,10,11,11a-octahydro-1*H*-cyclopenta[*a*]phenanthren-11-carboxylate (30)**

Analytical data: foamy resin; ¹H NMR (CDCl₃, 500 MHz): δ = 7.14 (m_c, 2 H, 8-H, 7-H), 7.08 (m_c, 1 H, 9-H), 7.01 (m_c, 1 H, 6-H), 6.42 (br. d, *J* • 9.7 Hz, 1 H, 5-H), 5.74 (d, *J* = 9.7 Hz, 1 H, 4-H), 3.61 (s, 3 H, OCH₃), 3.13-3.07 (m, 1 H, 9b-H), 2.96 (td, *J* = 5.2, 13.4 Hz, 1 H, 11-H), 2.69 (br. s, 1 H, 3b-H), 2.36 (m_c, 1 H, 11a-H), 2.15 (m_c, 1 H, 3-H_B), 1.98 (q, *J* = 13.4 Hz, 1 H, 10-H_B), 1.92-1.49 (m, 6 H, 2-H, 3-H_A, 1-H, OH), 1.46 (td, *J* = 3.4, 13.4 Hz, 1 H, 10-H_A); ¹³C NMR (CDCl₃, 126 MHz): δ = 175.3 (s, C=O), 139.3, 132.4 (2 s, C-5a, C-9a), 127.7, 127.5*, 127.2 (3 d, C-8, C-7, C-5, C-4), 126.8 (d, C-9), 126.1 (d, C-6), 81.2 (s, C-3a), 51.5 (q, OCH₃), 47.0 (d, C-11a), 44.6 (d, C-3b), 39.4 (d, C-11), 38.0 (t, C-3), 36.9 (d, C-9b), 25.0 (t, C-10), 24.1 (t, C-1), 20.8 (t, C-2) *signal with higher intensity; IR (KBr): ν = 3440 cm⁻¹ (br. s,

OH), 3100-2900 (=C-H, C-H), 1735 (C=O), 1630 (C=C); MS (EI, 120 °C, 80 eV): m/z (%) = 298 (37) [M^+], 280 (22) [$M^+ - H_2O$], 220 (10) [$M^+ - H_2O - HCO_2CH_3$]; HRMS (120 °C, 80 eV): [M^+]: $C_{19}H_{22}O_3$ calcd.: 298.1569; found: 298.1538.

***rac*-(3a*S*,3b*R*,9b*R*,11*R*,11a*S*)- Methyl 3a-Hydroxy-2,3,3a,3b,9b,10,11,11a-octahydro-1*H*-cyclopenta[*a*]phenanthren-11-carboxylate (32)**

Analytical data: foamy resin; 1H NMR ($CDCl_3$, 500 MHz): δ = 7.22-7.10 (m, 3 H, 7-H, 8-H, 9-H), 7.02 (d, J = 6.5 Hz, 1 H, 6-H), 6.51 (br. d, J • 9.8 Hz, 1 H, 5-H), 6.17 (dd, J = 5.1, 9.8 Hz, 1 H, 4-H), 3.72 (s, 3 H, OCH_3), 3.36 (td, J = 4.0, 7.7 Hz, 1 H, 9b-H), 2.69 (m_c, 1 H, 3b-H), 2.54 (td, J = 4.0, 14.0 Hz, 1 H, 10-H), 2.41 (br. s, 1 H, OH), 2.35 (dt, J = 4.0, 10.6 Hz, 1 H, 11-H), 2.13-1.81 (m, 3 H, 1-H, 10-H, 11a-H), 1.68-1.54 (m, 1 H, 2-H), 1.50-1.19 (m, 4 H, 1-H, 2-H, 3-H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 177.7 (s, C=O), 136.0, 134.1 (2 s, C-5a, C-9a), 129.4, 128.5, 127.6, 126.3, 126.3, 123.9 (6 d, C-4, C-5, C-6, C-7, C-8, C-9), 80.7 (s, C-3a), 51.7 (q, OCH_3), 48.7 (d, C-11a), 43.8 (d, C-3b), 42.3 (d, C-11), 35.3 (t, C-3), 33.5 (d, C-9b), 27.8 (t, C-10), 27.8 (t, C-1), 19.6 (t, C-2); IR (KBr): ν = 3435 cm^{-1} (br. s, OH), 3055-2850 (=C-H, C-H), 1730 (C=O), 1630 (C=C); MS (EI, 120 °C, 80 eV): m/z (%) = 298 (8) [M^+], 280 (12) [$M^+ - H_2O$], 220 (6) [$M^+ - H_2O - HCO_2CH_3$], 128 (17) [$C_{10}H_8^+$]; $C_{19}H_{22}O_3$ (298.4) calcd.: C 76.48, H 7.43; found: C 76.62, H 7.49.

***rac*-(4b*R*,6*R*,6a*S*,10a*R*,10b*R*)-Methyl 10a-Hydroxy-4b,5,6,6a,7,8,9,10,10a,10b-decahydrobenzo[*a*]phenanthren-6-carboxylate (34)**

Analytical data: colorless solid; mp = 163-165 °C; 1H NMR ($CDCl_3$, 500 MHz): δ = 7.25-7.21, 7.18-7.15 (2 m, 3 H, Ar), 7.03 (d, J = 7.1 Hz, 1 H, Ar), 6.63 (d, J = 9.6 Hz, 1 H, 12-H), 6.15 (dd, J = 6.0, 9.6 Hz, 1 H, 11-H), 3.74 (s, 3 H, OCH_3), 3.41-3.38 (m, 1 H, 4b-H), 2.83 (ddd, J = 2.5, 9.3, 12.9 Hz, 1 H, 6-H), 2.64 (td, J = 2.5, 14 Hz, 1 H, 5-H), 2.50 (dd, J = 6.0, 7.4 Hz, 1 H, 10b-H), 2.06 (ddd, J = 5.5, 12.9, 14.0 Hz, 1 H, 5-H), 1.58 (br.s, 1 H, OH), 1.88-1.80, 1.41-1.17, 0.89-79 (3 m, 9 H, 6a-H, 7-H, 8-H, 9-H, 10-H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 175.7 (s, CO), 136.7, 134.8 (2 s, Ar), 130.3 (d, C-12), 129.1 (d, C-11), 127.9, 126.6, 126.3, 122.9 (4 d, Ar), 73.9 (s, C-10a), 51.7 (q, OCH_3), 47.6 (d, C-10b), 45.6 (d, C-6a), 40.6 (d, C-6), 36.1 (d, C-4b), 28.9 (t, C-5), 27.7, 24.4, 21.2, 20.3 (4 t, C-7, C-8, C-9, C-10); IR (KBr): ν = 3510 cm^{-1} (O-H), 2950-2865 (=C-H, C-H), 1720 (C=O); MS (EI, 80 eV, 40 °C) m/z (%) = 312 (22) [M^+], 294 (100) [$M^+ - H_2O$], 280 (12) [$M^+ - CH_3O/H$], 141 (56) [$C_{11}H_9^+$],

128 (59) [$C_{10}H_8^+$], 98 (94), 54 (19); HRMS (80 eV, 40 °C): [M^+]: $C_{20}H_{24}O_3$ calcd.: 312.1725; found 312.1742.

***rac*-(1*R*,2*R*/*S*,11*R*/*S*,13*S*,14*S*)-18-Oxapentacyclo[11.5.2.0^{1,14}.0^{2,11}.0^{5,10}]jicosa-3,5,7,9-tetraen-20-one (35)**

Analytical data: colorless solid; mp = 108-110 °C; 1H NMR ($CDCl_3$, 500 MHz): δ = 7.16-7.15, 7.06-7.04, 7.02-7.00 (3 m, 4 H, Ar), 6.38 (dd, J = 3.3, 10.2 Hz, 1 H, 4-H), 6.18 (br. d, J = 10.2 Hz, 1 H, 3-H), 3.27-3.26 (m, 1 H, 2-H), 3.24-3.19 (m, 1 H, 11-H), 2.68 (t, J = 5.0 Hz, 1 H, 13-H), 2.20-2.12 (m, 1 H, 14-H), 2.52-2.22, 2.10-2.04, 2.02-1.95, 1.61-1.55 (4 m, 8 H, 15-H, 16-H, 17-H, 18-H), 1.80 (ddd, J = 1.1, 13.2, 14.3 Hz, 1 H, 12-H), 1.69 (td, J = 5.5, 13.2 Hz, 12-H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 178.8 (s, CO), 136.8, 131.5 (2 s, Ar), 128.1, 128.1, 127.3, 126.4 (4 d, Ar), 126.9, 126.3 (2 d, C-3, C-4), 87.2 (s, C-1), 49.8 (d, C-14), 43.5 (d, C-2), 43.1 (d, C-13), 35.7 (d, C-11), 26.7 (t, C-12), 34.9, 24.9, 22.8, 20.5 (4 t, C-15, C-16, C-17, C-18); IR (KBr): ν = 2920-2855 (=C-H, C-H), 1775 (C=O), 1490-1450 (C-H); MS (EI, 80 eV, 100 °C) m/z (%) = 280 (56) [M^+], 234 (10), 182 (61), 165 (22) [$C_{13}H_9^+$], 141 (48) [$C_{11}H_9^+$], 128 (100) [$C_{10}H_8^+$], 98 (12); HRMS (80 eV, 100 °C): [M^+]: $C_{19}H_{20}O_2$ calcd.: 280.1463; found: 280.1457.

***rac*-(4*bR*,6*R*,6*aS*,10*aR*,10*bR*)-Methyl 8-Ethyleneacetal-10*a*-hydroxy-4*b*,5,6,6*a*,7,8,9,10*a*,10*b*-decahydrobenzo[*a*]phenanthren-6-carboxylate (37)**

Analytical data: colorless solid; mp = 173-175 °C; 1H NMR ($CDCl_3$, 500 MHz): δ = 7.29-7.23 (2 m, 2 H, Ar), 7.16 (t, J = 7.1 Hz, 1 H, Ar), 7.03 (t, J = 7.1 Hz, 1 H, Ar), 6.64 (d, J = 9.6 Hz, 1 H, 12-H), 6.15 (dd, J = 6.0, 9.6 Hz, 1 H, 11-H), 3.82-3.79, 3.78-3.74 (2 m, 4 H, OCH_2CH_2O), 3.76 (s, 3 H, OCH_3), 3.40-3.36 (m, 1 H, 4*b*-H), 3.13 (ddd, J = 2.5, 10.2, 13.5 Hz, 1 H, 6-H), 2.67-2.64 (m, 1 H, 5-H), 2.53 (dd, J = 6.6 Hz, 1 H, 10*b*-H), 2.07-2.02 (m, 2 H, 6*a*-H, 7-H), 1.91 (ddd, J = 5.0, 13.5, 18.7 Hz, 1 H, 5-H), 1.75 (ddd, J = 4.4, 13.7, 18.1 Hz, 1 H, 9-H), 1.51-1.45 (m, 2 H, 7-H, 10-H), 1.39 (br. s, 1 H, OH), 1.28-1.25 (m, 1 H, 9-H), 1.09 (ddd, J = 4.1, 14.3, 18.1 Hz, 1 H, 10-H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 176.1 (s, CO), 136.5, 134.5 (2 s, Ar), 130.6 (d, C-12), 128.3 (d, C-11), 128.3, 126.6, 126.4, 123.2 (4 d, Ar), 108.2 (s, C-8), 73.4 (s, C-10*a*), 64.5, 63.8 (2 t, OCH_2CH_2O), 51.7 (q, OCH_3), 47.2 (d, C-10*b*), 45.6 (d, C-6*a*), 41.6 (d, C-6), 36.2 (d, C-4*b*), 32.0 (t, C-7), 30.3 (t, C-9), 29.8 (t, C-5), 26.1 (t, C-10); IR (KBr): ν = 3485 cm^{-1} (O-H), 2950-2875 (=C-H, C-H), 1730 (C=O), 1450-1435 (C-H); MS (EI, 80 eV, 150 °C): m/z (%) = 370 (57) [M^+], 352 (49) [$M^+ - H_2O$], 212 (24), 156 (60)

[C₈H₁₂O₃⁺], 141 (69) [C₁₁H₉⁺], 128 (88) [C₁₀H₈⁺], 86 (100), 55 (64), 43 (57) [OCH₂CH⁺], 28 (41) [CH₂CH₂⁺]; HRMS (EI, 80 eV, 150-160 °C): [M⁺]: C₂₂H₂₆O₅ calcd.: 370.1780, found: 370.1765.

***rac*-(1*R*,2*R*/*S*,11*R*/*S*,13*S*,14*S*)-16-Ethyleneacetal-19,20-dioxapentacyclo[11.5.3.0^{1,14}.0^{2,11}.0^{5,10}]henicosa-3,5,7,9-tetraen-20-one (38)**

Analytical data: colorless solid; mp = 193-194 °C; ¹H NMR (CDCl₃, 500 MHz): δ = 7.17, 7.16 (2 d, *J* = 5.5 Hz, 2 H, Ar), 7.05 (dd, *J* = 3.3, 5.5 Hz, 1 H, Ar), 7.01 (dd, *J* = 3.6, 5.5 Hz, 1 H, Ar), 6.42 (dd, *J* = 3.3, 10.2 Hz, 1 H, 4-H), 6.12 (br. d, *J* = 10.2 Hz, 1 H, 3-H), 4.02-3.94 (m, 4 H, OCH₂CH₂O), 3.29-3.27 (m, 1 H, 2-H), 3.25-3.20 (m, 1 H, 11-H), 2.70-2.66, 2.64-2.63 (2 m, 2 H, 13-H, 14-H), 2.41 (t, *J* = 13.2 Hz, 1 H, 12-H), 2.29-2.15, 2.09-2.04, 1.79-1.70 (3 m, 7 H, 12-H, 15-H, 17-H, 18-H); ¹³C NMR (CDCl₃, 126 MHz): δ = 178.5 (s, CO), 136.6, 131.4 (2 s, Ar), 128.3, 15.0 (2 s, C-3, C-4), 128.1, 127.9, 127.3, 126.5 (4 d, Ar), 108.9 (s, C-16), 85.9 (s, C-1), 64.8, 64.4 (2 t, OCH₂CH₂O), 45.4, 42.6 (2 d, C-13, C-14), 43.4, 35.7 (2 d, C-2, C-11), 32.9 (t, C-12), 34.1, 31.3, 26.6 (3 t, C-15, C-17, C-18); IR (KBr): ν = 3485 cm⁻¹ (O-H), 3035-2880 (=C-H, C-H), 1775 (C=O), 1460-1430 (C-H); MS (EI, 80 eV, 150 °C): *m/z* (%) = 338 (7) [M⁺], 279 (2), 183 (34), 156 (100) [C₈H₁₂O₃⁺], 141 (35) [C₁₁H₉⁺], 128 (7) [C₁₀H₈⁺], 86 (9), 43 (2) [OCH₂CH⁺]; HRMS (80 eV, 150-160 °C): [M⁺]: C₂₁H₂₂O₄ calcd.: 338.1517, found: 338.1532.

***rac*-(4*bR*,6*S*,6*aS*,10*aR*,10*bR*)-Methyl 10*a*-Hydroxy-4*b*,5,6,6*a*,7,8,9,10,10*a*,10*b*-decahydrobenzo[*a*]phenanthren-6-carboxylate (40)**

Analytical data: colorless solid; mp = 171-174 °C; ¹H NMR (CDCl₃, 500 MHz): δ = 7.37 (d, *J* = 7.4 Hz, 1 H, Ar), 7.23 (dt, *J* = 1.5, 7.4 Hz, 1 H, Ar), 7.19 (dt, *J* = 1.1, 7.4 Hz, 1 H, Ar), 7.07 (dd, *J* = 1.5, 7.4 Hz, 1 H, Ar), 6.62, 6.09 (2 dd, *J* = 3.0, 9.9 Hz, *J* = 2.0, 9.9 Hz 2 H, 11-H, 12-H), 3.72 (s, 3 H, OCH₃), 3.34 (td, *J* = 4.0, 13.2 Hz, 1 H, 6-H), 3.05 (ddd, *J* = 4.1, 12.6, 15.2 Hz, 1 H, 4*b*-H), 2.58 (td, *J* = 2.0, 15.2 Hz, 1 H, 10*b*-H), 2.39 (td, *J* = 4.0, 13.5 Hz, 1 H, 5-H), 2.09 (td, *J* = 4.0, 12.1 Hz, 1 H, 6*a*-H), 1.87 (td, *J* = 13.2, 13.5 Hz, 1 H, 5-H), 1.56 (br. s, 1 H, OH), 2.34-2.31, 1.71-1.68, 1.65-1.61, 1.45-1.17 (4 m, 8 H, 7-H, 8-H, 9-H, 10-H); ¹³C NMR (CDCl₃, 126 MHz): δ = 175.8 (s, CO), 138.7, 133.9 (2 s, Ar), 130.3, 128.1 (2 d, C-11, C-12), 127.6, 126.4, 125.9, 123.9 (4 d, Ar), 72.6 (s, C-10*a*), 51.7 (q, OCH₃), 46.1 (d, C-6*a*), 41.3 (d, C-6), 38.4 (d, C-10*b*), 35.8 (d, C-4*b*), 25.7 (t, C-5), 37.5, 24.4, 24.1, 23.3 (4 t, C-7, C-8, C-9, C-10); IR (KBr): ν = 3480 cm⁻¹ (O-H), 2930-2855 (=C-H, C-H), 1715 (C=O), 1450-1440 (C-

H); MS (EI, 80 eV, 100 °C): m/z (%) = 312 (18) [M^+], 294 (55) [$M^+ - H_2O$], 280 (41) [$M^+ - CH_3O/H$], 234 (100) [$M^+ - H_2O/CH_3O/H$], 183 (49), 165 (41) [$C_{13}H_9^+$], 141 (64) [$C_{11}H_9^+$], 98 (30); HRMS (EI, 80 eV, 100 °C): [M^+]: $C_{20}H_{24}O_3$ calcd.: 312.1725, found: 312.1735.

***rac*-(1*R*,2*R*/*S*,12*R*,13*S*)-18-Oxapentacyclo[10.5.2.1^{2,6}.0^{1,13}.0^{10,20}]icosa-3,6(20),7,9-tetraen-19-one (41)**

Analytical data: colorless solid (92% purity from 1H NMR); 1H NMR ($CDCl_3$, 500 MHz): δ = 7.16 (dd, J = 7.4, 7.7 Hz, 1 H, Ar), 7.05 (d, J = 7.7 Hz, 1 H, Ar), 6.98 (d, J = 7.4 Hz, 1 H, Ar), 6.09-6.02 (m, 2 H, 3-H, 4-H), 3.75 (dd, J = 4.8, 9.1 Hz, 1 H, 2-H), 3.42-3.37, 3.33-3.27 (2 m, 2 H, 5-H), 3.21 (dd, J = 12.1, 15.9 Hz, 1 H, 11-H), 3.12 (dd, J = 3.6, 15.9 Hz, 1 H, 11-H), 2.59 (dd, J = 3.6, 12.1 Hz, 1 H, 12-H), 2.21-2.18, 1.62-1.51, 1.45-1.38, 1.21-1.07, 1.00-0.92 (5 m, 9 H, 13-H, 14-H, 15-H, 16-H, 17-H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 181.5 (s, CO), 137.4, 134.7, 134.0 (3 s, Ar), 127.3, 127.1, 126.9 (3 d, Ar), 126.3, 124.9 (2 d, C-3, C-4), 88.0 (s, C-1), 50.1 (d, C-2), 45.3 (d, C-12), 41.9 (d, C-13), 33.9 (t, C-11), 31.1 (t, C-3), 29.5, 28.5, 23.4, 21.1 (4 t, C-14, C-15, C-16, C-17); IR (KBr): ν = 2930-2860 cm^{-1} (=C-H, C-H), 1760 (C=O), 1460-1440 (C-H); MS (EI, 80 eV, 80 °C): m/z (%) = 280 (63) [M^+], 262 (9) [$M^+ - H_2O$], 183 (100), 182 (75), 165 (35) [$C_{13}H_9^+$], 141 (47) [$C_{11}H_9^+$], 84 (9); HRMS (80 eV, 80 °C): [M^+]: $C_{19}H_{20}O_2$ calcd.: 280.1463, found: 280.1474.

***rac*-(1*R*,2*R*/*S*,12*R*,13*S*)-16-Ethyleneacetal-18-oxapentacyclo[10.5.2.1^{2,6}.0^{1,13}.0^{10,20}]icosa-4,6(20),7,9-tetraen-19-one (43)**

Analytical data: colorless solid; mp = 190-192 °C; 1H NMR ($CDCl_3$, 500 MHz): δ = 7.16 (dd, J = 7.4, 7.7 Hz, 1 H, Ar), 6.98 (d, J = 7.7 Hz, 1 H, Ar), 6.97 (d, J = 7.7 Hz, 1 H, Ar), 6.40 (dd, J = 3.3, 9.4 Hz, 1 H, 5-H), 5.95 (ddd, J = 2.7, 6.3, 9.4 Hz, 1 H, 4-H), 3.87-3.74 (m, 4 H, OCH_2CH_2O), 3.26-3.21 (m, 2H, 2-H, 11-H), 3.16 (dd, J = 11.5, 16.2 Hz, 1 H, 11-H), 2.84 (ddd, J = 1.4, 6.3, 18.1 Hz, 1 H, 3-H), 2.65-2.59 (m, 1 H, 3-H), 2.56 (dd, J = 3.6, 11.8 Hz, 1 H, 12-H), 2.42-2.37 (m, 1 H, 17-H), 1.85-1.82 (m, 1 H, 17-H), 1.74 (dd, J = 5.8, 12.0 Hz, 1 H, 13-H), 1.68 (dd, J = 4.4, 13.7 Hz, 1 H, 15-H), 1.61-1.56 (m, 2 H, 14-H, 15-H), 1.37 (dd, J = 12.0, 13.2 Hz, 1 H, 14-H); ^{13}C NMR ($CDCl_3$, 126 MHz): δ = 181.1 (s, CO), 137.1, 134.1, 132.5 (3 s, Ar), 128.1, 127.7, 125.6 (3 d, Ar), 127.5 (d, C-5), 126.6 (d, C-4), 107.1 (s, C-16), 86.6 (s, C-1), 64.5, 64.3 (2 t, OCH_2CH_2O), 45.4 (d, C-2), 45.1 (d, C-12), 40.7 (d, C-13), 36.1 (t, C-14), 33.5 (t, C-11), 29.6 (t, C-15), 27.9 (t, C-17), 23.4 (t, C-3); IR (KBr): ν = 3000-2920 cm^{-1} (=C-H, C-H), 1775 (C=O), 1450-1435 (C-H); MS (EI, 80 eV, 140 °C): m/z (%) = 338 (5)

[M⁺], 320 (4), [M⁺ - H₂O], 182 (61), 156 (100) [C₈H₁₂O₃⁺], 141 (76) [C₁₁H₉⁺], 128 (14) [C₁₀H₈⁺], 99 (26), 43 (2) [OCH₂CH⁺]; HRMS (80 eV, 140 °C): [M⁺]: C₂₁H₂₂O₄ calcd.: 338.1517, found: 338.1536.

***rac*-(1*R*,2*R*/*S*,12*R*,13*S*)-16-Ethyleneacetal-18-oxapentacyclo[10.5.2.1^{2,6}.0^{1,13}.0^{10,20}]jicosa-3,6(20),7,9-tetraen-19-one (44)**

Analytical data: colorless solid; mp = 264-266 °C; ¹H NMR (CDCl₃, 500 MHz): δ = 7.15 (dd, *J* = 7.4, 7.7 Hz, 1 H, Ar), 7.05 (d, *J* = 7.7 Hz, 1 H, Ar), 6.96 (d, *J* = 7.4 Hz, 1 H, Ar), 6.09-6.01 (m, 2 H, 3-H, 4-H), 3.87-3.83, 3.82-3.73 (2 m, 5 H, 1-H, OCH₂CH₂O), 3.45-3.40, 3.32-3.26 (2 m, 2 H, 5-H), 3.22 (dd, *J* = 12.1, 15.9 Hz, 1 H, 11-H), 3.13 (dd, *J* = 3.6, 15.9 Hz, 1 H, 11-H), 2.63 (dd, *J* = 3.6, 12.1 Hz, 1 H, 12-H), 2.22 (ddd, *J* = 2.2, 4.4, 14.8 Hz, 1 H, 17-H), 1.88 (dd, *J* = 6.0, 12.1 Hz, 1 H, 13-H), 1.72 (ddd, *J* = 4.7, 13.2, 13.5 Hz, 1 H, 15-H), 1.62 (ddd, *J* = 2.7, 6.0, 13.2 Hz, 1 H, 14-H), 1.57-1.49 (m, 2 H, 15-H, 17-H), 1.42 (dd, *J* = 12.4, 13.2 Hz, 1 H, 14-H); ¹³C NMR (CDCl₃, 126 MHz): δ = 180.9 (s, CO), 137.1, 134.3 (3 s, Ar), 127.6, 127.2, 126.9 (3 d, Ar), 126.7, 124.6 (2 d, C-3, C-4), 107.0 (s, C-16), 87.0 (s, C-1), 64.5, 64.3 (2 t, OCH₂CH₂O), 49.5 (d, C-2), 45.2 (d, C-13), 41.5 (d, C-12), 36.3 (t, C-14), 33.9 (t, C-11), 29.7 (t, C-15), 29.5 (t, C-5), 29.1 (t, C-17); IR (KBr): ν = 2975-2860 cm⁻¹ (=C-H, C-H), 1775 (C=O), 1445-1425 (C-H); MS (EI, 80 eV, 130 °C): *m/z* (%) = 338 (30) [M⁺], 156 (100) [C₈H₁₂O₃⁺], 141 (31) [C₁₁H₉⁺], 121 (38), 55 (30), 43 (53) [OCH₂CH⁺], 28 (56) [CH₂CH₂⁺]; HRMS (80 eV, 130 °C): [M⁺]: C₂₁H₂₂O₄ calcd.: 338.1517, found: 338.1525.