

Supporting Information

Facile Asymmetric Synthesis of the Core Nuclei of Xanthanolides, Guaianolides, and Eudesmanolides

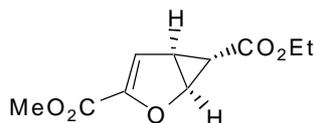
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General Remarks: Reactions with moisture-sensitive chemicals were performed under nitrogen in a flame-dried reaction flask. Solvents were dried by standard methods.

Chromatography: Macherey-Nagel silica gel (0.03-0.06 mm). Enantiomeric excesses were determined by analytical HPLC using a “Chiracel OD-H” column (flow: 1 ml/min) and a UV detector at 254 nm. Diastereomeric ratios were determined by integration of the respective diastereomeric peaks in ^{13}C NMR. TLC: commercially precoated aluminium sheets 60 F 254 (Merck). Uncorrected melting point: Büchi SMP 20. IR: Mattson Genesis series FT-IR, Perkin Elmer 298, Bruker IFS 66, ν in cm^{-1} . ^1H NMR and ^{13}C NMR: Bruker Avance 600, ARX 400, Avance 300, AC 250 F, δ in ppm, J in Hz. Multiplicities were determined by DEPT (distortionless enhancement by polarization transfer) measurements. MS: Finnigan MAT 95, Varian MAT 311A. Elemental analysis: Heraeus CHN-Rapid. XRD: Stoe Imaging Plate System, Siemens Stoe AED2. Optical rotation: Perkin-Elmer polarimeter PE 241.



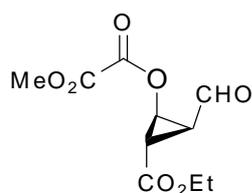
(1S,5S,6S)-(-)-2-Oxa-bicyclo[3.1.0]hex-3-ene-3,6-dicarboxylic acid 6-ethyl ester 3-methyl ester (6):¹

¹ Chhor, R. B.; Nosse, B.; Sörgel, S.; Böhm, C.; Seitz, M.; Reiser, O. *Chem. Eur. J.* **2003**, *9*, 260-270

Method A: To a mixture of furan-2-carboxylic acid methyl ester (**5**) (12.9 ml, 120 mmol, 3 equiv.), Cu(OTf)₂ (297 mg, 0.82 mmol, 2.0 mol%) and (*S,S*)-*t*Bu-box (303 mg, 1.02 mmol, 2.5 mol%) phenylhydrazine (89 mg, 0.82 mmol, 2.0 mol%) was added under nitrogen at 0 °C. After 30 min, a solution of ethyl diazoacetate (4.685 g, 41.1 mmol, 1 equiv.) in dry CH₂Cl₂ (70 ml) was added continuously *via* syringe-pump over 12 h in 4 equal amounts. After each addition, CH₂Cl₂ was expelled by passing nitrogen through the flask. Excess of furan-2-carboxylic methyl ester was evaporated under high vacuum at room temp. and the residue was purified by chromatography on silica (hexanes/ethylacetate 10:1) to provide **6** as a colorless oil (5.494 g, 63%). Enantiopure product **6** could be obtained by recrystallization from *n*-pentane (4.622 g, 53%).

Method B: To a solution of furan-2-carboxylic acid methyl ester (**5**) (37.0 g, 0.293 mol, 1.0 equiv.), Cu(OTf)₂ (700 mg, 1.94 mmol, 0.66 mol%) and (*S,S*)-*i*Pr-box (649 mg, 2.44 mmol, 0.83 mol%) phenylhydrazine (241 μ l, 2.44 mmol, 0.83 mol%) was added under nitrogen at 0 °C. After 20 min, a solution of ethyl diazoacetate (30.6 ml, 0.293 mol, 1.0 equiv.) in dry CH₂Cl₂ (200 ml) was added via dropping funnel over 13 h. The reaction mixture was filtered through a short pad of basic alumina and solvent was evaporated in vacuo. Unconverted furan-2-carboxylic acid methyl ester (**5**) was removed by distillation (5 mbar, b.p. 63-64 °C, 20.0 g, 54%) and the residue was purified by kugelrohr distillation (10⁻⁴–10⁻⁵ mbar, 88 °C) to provide **6** as a yellowish oil (22.0 g, 35% yield, 77% yield based on conversion of **5**, 81% *ee*) which after crystallization from *n*-pentane appeared as yellowish crystals (20.12 g, 32%, 99% *ee*).

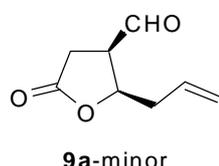
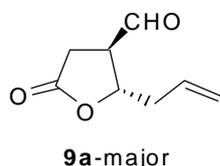
R_f (SiO₂, hexanes/ethylacetate 5:1) = 0.14; m.p. = 42 °C; $[\alpha]_D^{20} = -272$ (c = 1.0, CH₂Cl₂); ¹H NMR (250 MHz, CDCl₃): δ = 1.16 (dd, J = 2.7, 1.1 Hz, 1 H, 6-H), 1.23 (t, J = 7.1 Hz, 3 H, CH₃), 2.87 (ddd, J = 5.3, 2.9, 2.7 Hz, 1 H, 5-H), 3.78 (s, 3 H, OCH₃), 4.12 (q, J = 7.1 Hz, 2 H, CH₂), 4.97 (dd, J = 5.3, 1.1 Hz, 1 H, 1-H), 6.39 (d, J = 2.9 Hz, 1 H, 4-H); ¹³C NMR (62.9 MHz, CDCl₃): δ = 14.2 (+, CH₃), 21.5 (+, C-6), 31.9 (+, C-5), 52.1 (+, OCH₃), 61.0 (-, CH₂), 67.5 (+, C-1), 116.0 (+, C-4), 149.3 (Cquat, C-3), 159.5 (Cquat, CO), 171.7 (Cquat, CO); IR (KBr): $\tilde{\nu}$ = 3118, 2956, 1720, 1617, 1428, 1380, 1297, 1166, 1124, 1041, 954, 831, 725 cm⁻¹; MS (70 eV, ED): m/z (%) = 212.1 (9.8) [M⁺], 153.0 (11.5) [M⁺ – CO₂Me], 139.0 (100) [M⁺ – CO₂Et], 124.9 (24.4), 98.9 (28.6), 96.9 (31.7), 78.9 (11.3), 59.0 (13.5), 52.1 (11.5); elemental analysis calcd (%) for C₁₀H₁₂O₅ (212.2): C 56.60, H 5.70; found C 56.51, H 5.73.



(1*S*,2*S*,3*S*)-(-)-Oxalic acid 2-ethoxycarbonyl 3-formyl-cyclopropyl ester methyl ester (7):¹

A solution of **6** (2.50 g, 11.78 mmol) in dry CH₂Cl₂ (125 ml) was cooled to -78 °C and treated with ozone until the mixture turned blue. Excess ozone was expelled by passing oxygen through the solution, followed by addition of dimethyl sulfide (4.3 ml, 58.91 mmol, 5.0 equiv.). The reaction mixture was allowed to warm to room temp. and stirring was continued for 24 h. Saturated NaHCO₃ (10 ml) was added and layers were separated. The organic layer was washed with water (2 x 10 ml), dried, filtered and evaporated. The residue was recrystallized from Et₂O at -27 °C to yield **7** as a colorless solid (2.70 g, 94%).

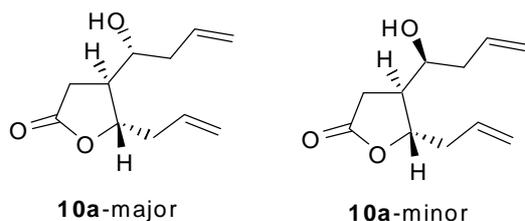
m.p. = 52 °C; $[\alpha]_{\text{D}}^{20} = -37.7$ (c = 1.0, CH₂Cl₂); ¹H NMR (250 MHz, CDCl₃): δ = 1.28 (t, *J* = 7.1 Hz, 3 H, CH₂CH₃), 2.79 (ddd, *J* = 7.3, 6.0, 4.0 Hz, 1 H, 2-H), 2.90 (dd, *J* = 6.0, 3.6 Hz, 1 H, 3-H), 3.91 (s, 3 H, CO₂CH₃), 4.19 (q, *J* = 7.1 Hz, 2 H, CH₂CH₃) 4.83 (dd, *J* = 7.3, 3.6 Hz, 1 H, 1-H), 9.45 (d, *J* = 4.0 Hz, 1 H, CHO); ¹³C NMR (62.9 MHz, CDCl₃): δ = 14.1 (+, CH₃), 26.4 (+, C-3), 34.9 (+, C-2), 54.0 (+, CO₂CH₃), 58.9 (+, C-1), 62.0 (-, CO₂CH₂CH₃), 156.6 (Cquat, CO), 156.9 (Cquat, CO), 168.1 (Cquat, CO₂CH₂CH₃), 192.7 (+, CHO); IR (KBr): $\tilde{\nu} = 3066, 3015, 2963, 2892, 1785, 1751, 1735, 1706, 1445, 1345, 1313, 1210, 1167, 1086, 1011, 963, 867, 790, 715, 613, 495$ cm⁻¹; MS (DCI, NH₃): *m/z* (%) = 262.0 (100) [M + NH₄⁺], 176.0 (20), 160.0 (55), 120.9 (15); elemental analysis calcd (%) for C₁₀H₁₂O₇ (244.2): calc. C 49.19, H 4.95; found C 49.22, H 4.99.



(2*R*/*S*,3*R*)-2-Allyl-5-oxo-tetrahydro-furan-3-carbaldehyde (9a):¹ A solution of **7** (5.00 g, 20.5 mmol) in dry CH₂Cl₂ (200 mL) was treated with BF₃·Et₂O (3.0 ml, 20.5 mmol) at -78 °C. After 10 minutes allyltrimethylsilane (5.0 ml, 30.75 mmol, 1.5 equiv.) was added and stirring was continued for 24 h. The reaction was quenched with saturated NaHCO₃ (6.0 ml) and the mixture was allowed to warm to 0 °C. After separation of the organic layer and drying

(MgSO₄), the solvent was evaporated under vacuo to yield the corresponding alcohol as a colorless oil (5.82 g, 100% crude yield, *dr* 95:5). The alcohol (5.78 g, 20.0 mmol) was dissolved in methanol (200 ml) at 0 °C and treated dropwise with a solution of Ba(OH)₂·8H₂O (3.15 g, 10.0 mmol, 0.5 equiv.) in MeOH (200 ml). CH₂Cl₂ (100 ml) and H₂O (100 ml) were added and the layers were separated. The aqueous layer was extracted with CH₂Cl₂ (10 x 100 ml). The combined organic layers were dried, filtered and concentrated in vacuo. Chromatography on silica gel (hexanes/ethylacetate 1:1) yielded **9a** as a colorless oil (2.02 g, 64%, *dr* = 95:5).

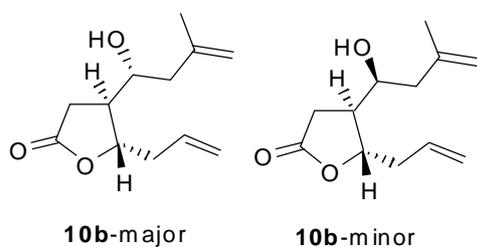
R_f (SiO₂, hexanes/ethylacetate 1:1) = 0.17; $[\alpha]_D^{20} = -31.7$ ($c = 1.35$, CH₂Cl₂); ¹H NMR (300 MHz, CDCl₃): $\delta = 2.35\text{--}2.59$ (m, 2 H, C1'-H), 2.71 (dd, $J = 18.2, 9.9$ Hz, 1 H, 3-H), 2.89 (dd, $J = 18.2, 7.5$ Hz, 1 H, 3-H, **9a**-major) and 3.00 (dd, $J = 17.7, 5.8$ Hz, **9a**-minor), 3.19 (dddd, $J = 10.0, 7.3, 6.0, 1.2$ Hz, 1 H, 4-H), 4.74 (dd, $J = 11.9, 6.2$ Hz, 1 H, 5-H), 5.10–5.27 (m, 2 H, 3'-H), 5.75 (dddd, $J = 17.3, 10.0, 7.0, 3.5$ Hz, 1 H, C2'-H), 9.69 (d, $J = 1.2$ Hz, 1 H, CHO, **9a**-major) and 9.82 (d, $J = 1.7$ Hz, CHO, **9a**-minor); ¹³C NMR (75.5 MHz, CDCl₃): $\delta = 28.67$ (-, C-3), 39.01 (-, C-1'), 51.06 (+, C-4), 77.87 (+, C-5), 120.30 (-, =CH₂), 130.82 (+, CH=CH₂), 174.07 (+, CHO); IR (film): $\tilde{\nu} = 3080, 2980, 2939, 2841, 1774, 1727, 1642, 1419, 1359, 1193, 1111, 1000, 924$ cm⁻¹; MS (EI, 70 eV): m/z (%) = 154.2 (5) [M⁺], 113.1 (100) [M - C₃H₅], 85.1 (95), 57.1 (95); elemental analysis calcd (%) for C₈H₁₀O₃ (154.2): C 62.33, H 6.54; found: C 62.36, H 6.83.



(1'R/S,4S,5S)-5-Allyl-4-(1'-hydroxy-but-3'-enyl)-dihydro-furan-2-one (10a): To a solution of the aldehyde **9a** (77 mg, 0.5 mmol) in dry CH₂Cl₂ (5 ml) at -40 °C BF₃·OEt₂ (190 μ l, 1.5 mmol, 3.0 equiv.) and allyl trimethylsilane (90 μ l, 0.55 mmol, 1.1 equiv.) were added. The solution was stirred for 12 h at -78 °C and then quenched with saturated NaHCO₃ solution (0.1 ml). The solution was allowed to warm to 0 °C and the mixture was dried (MgSO₄), filtered and concentrated in vacuo. The crude product was purified by chromatography on silica to give **10a** as a colorless oil (90 mg, 92%, *dr* = 78:22).

¹H NMR (300 MHz, CDCl₃): $\delta = 2.06\text{--}2.43$ (m, 4 H, CH₂), 2.44–2.50 (m, 1 H, 4-H), 2.48 (dd, $J = 17.4, 9.1$ Hz, 1 H, 3-H), 2.71 (dd, $J = 17.4, 8.1$ Hz, 1 H, 3-H), 3.64 (m, CHO, **10a**-

minor) and 3.72 (ddd, $J = 8.5, 3.8, 3.8$ Hz, 1 H, $CHOH$, **10a**-major), 4.54 (ddd, $J = 6.3, 6.2, 5.5$ Hz, 1 H, 5-H, **10a**-major) and 4.62 (ddd, $J = 6.5, 5.0, 5.0$ Hz, 5-H, **10a**-minor), 5.14–5.24 (m, 4 H, $=CH_2$), 5.68–5.91 (m, 2 H, $CH_2CH=CH_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 28.7$ (-, C-3, **10a**-minor: 32.0), 38.8 (-, C-2', **10a**-minor: 39.7), 40.4 (-, CH_2 , **10a**-minor: 40.1), 44.7 (+, C-4, **10a**-minor: 44.0), 68.6 (+, C-1', **10a**-minor: 72.0), 81.2 (+, C-5, **10a**-minor: 82.0), 119.1 (-, $HC=CH_2$, **10a**-minor: 119.0), 119.6 (-, $HC=CH_2$, **10a**-minor: 119.9), 132.2 (+, $HC=CH_2$, **10a**-minor: 132.5), 133.5 (+, $HC=CH_2$, **10a**-minor: 133.2), 176.5 (Cquat, CO, **10a**-minor: 176.1); IR (film): $\tilde{\nu} = 3461, 3078, 2979, 2933, 1774, 1419, 1195, 1046, 997, 918$ cm^{-1} ; MS (DCI, NH_3): m/z (%) = 214.1 (100) [$M + NH_4^+$]; elemental analysis calcd (%) for $C_{11}H_{16}O_8$ (196.2): C 67.32, H 8.22; found: C 67.40, H 6.35.

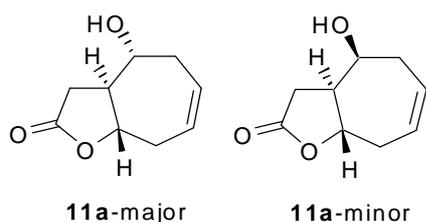


(1'*R/S*,4*S*,5*S*)-5-Allyl-4-(1'-hydroxy-3'-methyl-but-3'-enyl)-dihydro-furan-2-one (10b):

To a solution of the aldehyde **9a** (335 mg, 2.17 mmol) in dry CH_2Cl_2 (25 ml) at -78 °C trimethyl-(2-methylallyl)-silane (785 μ l, 4.35 mmol, 2.0 equiv.) was added, followed by the addition of $BF_3 \cdot OEt_2$ (300 μ l, 2.39 mmol, 1.1 equiv.) after 10 min. The solution was stirred for 11 h at -78 °C and then quenched with saturated $NaHCO_3$ solution (3.5 ml). The solution was allowed to warm to 0 °C and extracted with CH_2Cl_2 (3 x 25 ml). The combined organic layers were dried ($MgSO_4$), filtered and concentrated in vacuo. The crude product was purified by chromatography on silica (hexanes/ethylacetate 2:1) to give **10b** as a colorless oil (230 mg, 50%, $dr = 72:28$).

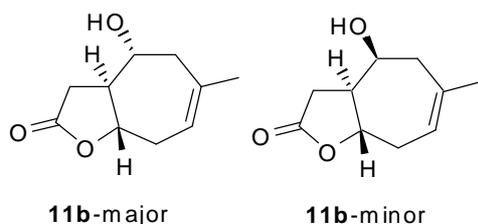
1H NMR (300 MHz, $CDCl_3$): $\delta = 1.76$ (bs, 3 H, CH_3 , **10b**-minor: 1.80), 2.06–2.62 (m, 5 H, 2 CH_2 , 4-H), 2.49 (dd, $J = 17.6, 9.2$ Hz, 1 H, 3-H, **10b**-major) and 2.66 (dd, $J = 17.5, 9.4$ Hz, 3-H, **10b**-minor), 2.72 (dd, $J = 17.6, 8.1$ Hz, 1 H, 3-H), 3.82 (m, 1 H, $CHOH$, **10b**-minor: 3.67–3.76), 4.57 (dd, $J = 11.9, 6.4$ Hz, 1 H, 5-H, **10b**-minor: 4.62–4.67), 4.82 (m, 1 H, $=CH_2$, **10b**-minor: 4.84), 4.94 (dt, $J = 3.1, 1.5$ Hz, 1 H, $=CH_2$, **10b**-major) and 4.96 (dt, $J = 3.1, 1.5$ Hz, $=CH_2$, **10b**-minor), 5.16–5.22 (m, 2 H, $=CH_2$), 5.71–5.98 (m, 1 H, $CH_2CH=CH_2$); ^{13}C NMR (75.5 MHz, $CDCl_3$): $\delta = 22.1$ (+, CH_3 , **10b**-minor: 22.2), 28.6 (-, C-3, **10b**-minor: 28.5), 38.8 (-, C-2', **10b**-minor: 39.6), 44.3 (-, CH_2 , **10b**-minor: 44.1), 44.7 (+, C-4, **10b**-minor: 44.3),

66.5 (+, C-1', **10b**-minor: 70.0), 81.1 (+, C-5, **10b**-minor: 81.9), 114.5 (-, HC=CH₂, **10b**-minor: 114.8), 119.0 (-, HC=CH₂, **10b**-minor: 118.9), 132.2 (+, HC=CH₂, **10b**-minor: 132.5), 141.2 (Cquat, CH₃C=CH₂, **10b**-minor: 141.1), 176.5 (Cquat, CO, **10b**-minor: 176.2); IR (film): $\tilde{\nu}$ = 3466, 3076, 2978, 2935, 1770, 1644, 1418, 1375, 1268, 1196, 1056, 983, 916 cm⁻¹; MS (DCI, NH₃): m/z (%) = 228.1 (100) [M + NH₄⁺]; MS (HR-EI, 70 eV): 210.1256 (C₁₂H₁₈O₃: calc. 210.1256 [M⁺]).



(3aS,4R/S,8aS)-4-Hydroxy-3,3a,4,5,8,8a-hexahydro-cyclohepta[b]furan-2-one (11a): The diene **10a** (97 mg, 0.494 mmol) was dissolved in dry CH₂Cl₂ (50 ml) under argon and (4,5-dihydroIMES)(PCy₃)Cl₂Ru=CHPh (**12**) (12.6 mg, 0.015 mmol, 3 mol%) was added. The reaction mixture was refluxed for 23 h and solvent was removed in vacuo. The crude product was purified by chromatography on silica (hexanes/ethylacetate 1:1) to give **11a** as a colorless oil (51 mg, 61%, *dr* = 81:19).

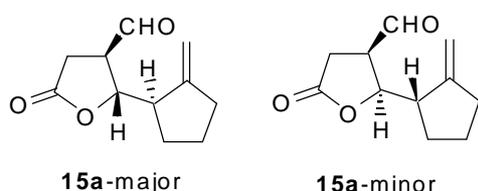
R_f (SiO₂, hexanes/ethylacetate 1:1) = 0.10; ¹H NMR (300 MHz, CDCl₃): δ = 2.19–2.55 (m, 4 H), 2.55 (dd, J = 16.9, 12.5 Hz, 1 H, 3-H), 2.70–2.82 (m, 1 H), 2.82 (dd, J = 16.9, 7.1 Hz, 1 H, 3-H), 3.60 (ddd, J = 9.9, 9.8, 3.6 Hz, 1 H, 4-H, **11a**-minor: 4.09–4.14), 4.01 (ddd, J = 10.5, 10.4, 3.0 Hz, 1 H, 8a-H, **11a**-major) and 4.47 (ddd, J = 10.6, 10.5, 3.0 Hz, 8a-H, **11a**-minor), 5.70–5.78 (m, 2 H, 6-H, 8-H); ¹³C NMR (75.5 MHz, CDCl₃): δ = 32.62 (-, CH₂, **11a**-minor: 33.25), 35.49 (-, CH₂, **11a**-minor: 33.56), 37.94 (-, CH₂, **11a**-minor: 35.66), 54.01 (+, CH, **11a**-minor: 51.37), 70.21 (+, CH, **11a**-minor: 64.94), 79.90 (+, CH, **11a**-minor: 76.65), 126.32 (+, =CH, **11a**-minor: 126.84), 127.24 (+, =CH, **11a**-minor: 127.09), 175.96 (Cquat, CO, **11a**-minor: 176.25); IR (film): $\tilde{\nu}$ = 3024, 2924, 1781, 1647, 1444, 1420, 1271, 1200, 1080, 986, 874, 804 cm⁻¹; MS (DCI, NH₃): m/z (%) = 186.1 (100) [M + NH₄⁺]; elemental analysis calcd (%) for C₉H₁₂O₃ (168.2): C 64.27, H 7.19; found: C 64.17, H 7.23.



(3aS,4R/S,8aS)-4-Hydroxy-6-methyl-3,3a,4,5,8,8a-hexahydro-cyclohepta[b]furan-2-one

(11b): The diene **10b** (101 mg, 0.48 mmol) was dissolved in dry CH₂Cl₂ (50 ml) under argon and (4,5-dihydroIMES)(PCy₃)Cl₂Ru=CHPh (**12**) (20.4 mg, 0.024 mmol, 5 mol%) was added. The reaction mixture was refluxed for 20 h and solvent was removed in vacuo. The crude product was purified by chromatography on silica (hexanes/ethylacetate 1:1) to give **11b** as a colorless solid (86 mg, 98%, *dr* = 78:22).

¹H NMR (400 MHz, CDCl₃): δ = 1.80 (s, 3 H, CH₃, **11b**-minor: 1.82), 2.21–2.38 (m, 3 H, 8-H, 5-H, 3a-H), 2.39–2.46 (m, 1 H, 5-H), 2.49 (dd, *J* = 16.9, 12.8 Hz, 1 H, 3-H), 2.65 (ddd, *J* = 14.9, 9.0, 2.9 Hz, 1 H, 8-H), 2.79 (dd, *J* = 16.9, 7.0 Hz, 1 H, 3-H), 3.61 (ddd, *J* = 9.9, 9.8, 3.2 Hz, 1 H, 4-H, **11b**-minor: 4.10–4.14), 3.94 (ddd, *J* = 10.7, 10.6, 2.8 Hz, 1 H, 8a-H, **11b**-major) and 4.43 (ddd, *J* = 10.9, 10.8, 2.9 Hz, 8a-H, **11b**-minor), 5.57–5.51 (m, 1 H, 7-H, **11b**-minor: 5.62–5.68); ¹³C NMR (100.6 MHz, CDCl₃): δ = 27.81 (+, CH₃, **11b**-minor: 28.78), 31.91 (-, CH₂, C-8, **11b**-minor: 32.72), 35.57 (-, CH₂, C-3, **11b**-minor: 33.22), 43.58 (-, CH₂, C-5, **11b**-minor: 40.81), 54.83 (+, CH, C-3a, **11b**-minor: 52.27), 69.98 (+, CH, C-4, **11b**-minor: 65.28), 80.11 (+, CH, C-8a, **11b**-minor: 76.81), 120.32 (+, =CH, C-7, **11b**-minor: 118.08), 135.70 (Cquat, C-6, **11b**-minor: 135.67), 175.60 (Cquat, C-2, **11b**-minor: 175.84); IR (KBr): $\tilde{\nu}$ = 3464, 3074, 2936, 1779, 1647, 1442, 1422, 1376, 1198, 1086, 1057, 981, 895 cm⁻¹; MS (EI, 70 eV): *m/z* (%) = 182.4 (25) [M⁺], 164.4 (10) [M⁺ – H₂O], 154.2 (10) [M⁺ – CO₂], 149.3 (25) [M⁺ – (H₂O + CH₃)], 113.2 (40), 85.2 (45), 69.2 (50), 57.1 (100), 43.1 (85), 28.1 (55); MS (HR-EI, 70 eV): 182.09420 (C₁₀H₁₄O₃: calc. 182.09430 [M⁺]).

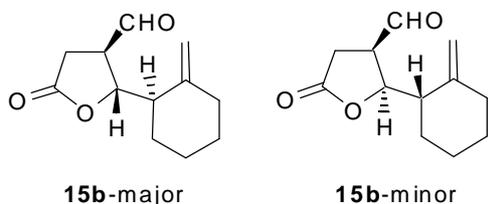


(1'R/S,2R/S,3S)-2-(2'-Methylene-cyclopentyl)-5-oxo-tetrahydro-furan-3-carbaldehyde

(15a): To a solution of (1*S*,2*S*,3*S*)-(-)-oxalic acid-2-ethoxycarbonyl-3-formyl-cyclopropyl-methyl ester (**7**) (4.84 g, 20 mmol) in dry CH₂Cl₂ (100 ml) at –78 °C BF₃·OEt₂ (2.64 ml, 21 mmol, 1.05 equiv.) was added. After 30 min cyclopent-1-enylmethyltrimethylsilane (3.70 g,

24 mmol, 1.2 equiv.) was added and the solution was stirred for 18 h. The reaction was quenched at $-78\text{ }^{\circ}\text{C}$ with saturated NaHCO_3 solution (6 ml), warmed to $0\text{ }^{\circ}\text{C}$, dried (MgSO_4), filtered and concentrated. The unpurified intermediate was dissolved in MeOH (60 ml), cooled to $0\text{ }^{\circ}\text{C}$ and a solution of $\text{Ba}(\text{OH})_2 \cdot 8\text{ H}_2\text{O}$ (6.62 g, 21 mmol, 1.05 equiv.) in MeOH (200 ml) was added dropwise. After additional stirring for 1.75 h at $0\text{ }^{\circ}\text{C}$, H_2O (350 ml) was added and the residue was removed by filtration. The solution then was extracted with CH_2Cl_2 (4 x 250 ml) and the combined organic layers were dried (MgSO_4). Concentration in vacuo afforded **15a** as a yellowish oil (3.228 g, 83%, $dr = 95:5$).

^1H NMR (300 MHz, CDCl_3): $\delta = 1.52\text{--}2.08$ (m, 4 H, 2 CH_2), 2.23–2.42 (m, 2 H), 2.70–2.85 (m, 1 H, C2'-H), 2.76 (dd, $J = 18.1, 10.2$ Hz, 1 H, 4-H), 2.92 (dd, $J = 18.1, 7.4$ Hz, 1 H, 4-H), 3.31 (dddd, $J = 10.2, 7.4, 6.4, 1.3$ Hz, 1 H, 3-H), 4.75 (dd, $J = 6.1, 6.0$ Hz, 1 H, 2-H), 4.98–5.02 (m, 1 H, = CH_2), 5.06–5.12 (m, 1 H, = CH_2), 9.70 (d, $J = 1.3$ Hz, CHO, **15a**-minor) and 9.74 (d, $J = 1.3$ Hz, 1 H, CHO, **15a**-major); ^{13}C NMR (75.4 MHz, CDCl_3): $\delta = 23.02$ (-, CH_2), 26.98 (-, CH_2), 28.45 (-, CH_2), 32.67 (-, CH_2), 46.82 (+, CH), 49.16 (+, CH), 79.58 (+, CH), 108.08 (-, = CH_2), 149.86 (Cquat), 173.25 (Cquat), 196.63 (+, CHO); IR (film): $\tilde{\nu} = 3426, 2955, 2873, 1771, 1653, 1435, 1198, 882\text{ cm}^{-1}$; MS (CI, NH_3): m/z (%) = 212.2 (100.0) [$\text{M}+\text{NH}_4^+$]; MS (HR-EI, 70 eV): 194.0943 ($\text{C}_{11}\text{H}_{14}\text{O}_3$: calc. 194.0943 [M^+]).

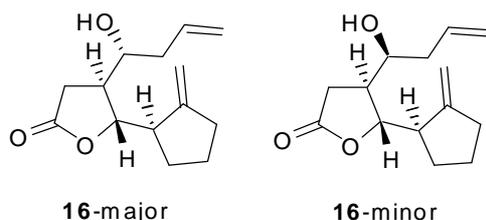


(1*R/S*,2*R/S*,3*S*)-2-(2'-Methylene-cyclohexyl)-5-oxo-tetrahydro-furan-3-carbaldehyde

(15b): To a solution of (1*S*,2*S*,3*S*)-(-)-oxalic acid-2-ethoxycarbonyl-3-formyl-cyclopropyl-methyl ester (**7**) (3.5 g, 14.3 mmol) in dry CH_2Cl_2 (100 ml) at $-78\text{ }^{\circ}\text{C}$ $\text{BF}_3 \cdot \text{OEt}_2$ (2.0 ml, 15.9 mmol, 1.1 equiv.) was added. After 10 min cyclohex-1-enylmethyl-trimethylsilane (4.0 g, 21.5 mmol, 1.5 equiv.) was added and the solution was stirred for 12 h. The reaction was quenched at $-78\text{ }^{\circ}\text{C}$ with saturated NaHCO_3 solution (40 ml), warmed to $0\text{ }^{\circ}\text{C}$ and extracted with CH_2Cl_2 (5 x 100 ml). The combined organic layers were dried (MgSO_4), filtered and concentrated. The unpurified intermediate was dissolved in MeOH (56 ml), cooled to $0\text{ }^{\circ}\text{C}$ and a solution of $\text{Ba}(\text{OH})_2 \cdot 8\text{ H}_2\text{O}$ (4.8 g, 15.1 mmol, 1.05 equiv.) in MeOH (26 ml) was added dropwise. After additional stirring for 2 h at $0\text{ }^{\circ}\text{C}$, H_2O (50 ml) was added and the layers were separated. The aqueous layer was extracted with CH_2Cl_2 (5 x 50 ml, 2 x 100 ml, 1 x 200 ml)

and the combined organic layers were dried (MgSO₄). Concentration in vacuo afforded **15b** as an oil (2.9 g, 13.9 mmol, 97 %) which was purified by chromatography on silica (CHCl₃) to give **15b** in 57% yield (1.7 g, *dr* = 91:9).

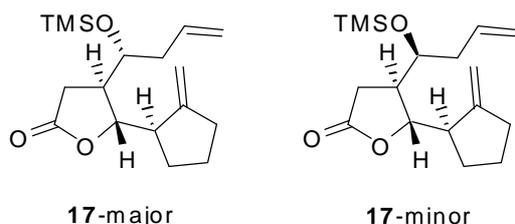
¹H NMR (300 MHz, CDCl₃): δ = 1.14–2.22 (m, 8 H, 4 CH₂), 2.36 (dt, *J* = 10.0, 3.9 Hz, 1 H, 1'-H), 2.73 (dd, *J* = 18.0, 10.0 Hz, 1 H, 4-H), 2.91 (dd, *J* = 18.0, 7.5 Hz, 1 H, 4-H), 3.30 (dddd, *J* = 9.8, 7.4, 6.3, 1.0 Hz, 1 H, 3-H), 4.79 (bs, 1 H, =CH₂), 4.88 (bs, 1 H, =CH₂), 4.92 (dd, *J* = 10.0, 6.2 Hz, 1 H, 2-H), 9.69 (d, *J* = 1.0 Hz, 1 H, CHO, **15b**-major) and 9.79 (d, *J* = 1.6 Hz, CHO, **15b**-minor); ¹³C NMR (75.4 MHz, CDCl₃): δ = 21.66 (-, CH₂), 27.95 (-, CH₂), 28.61 (-, CH₂), .29.55 (-, CH₂), 33.48 (-, CH₂), 49.13 (+, CH), 51.34 (+, CH), 78.70 (+, CH), 111.57 (-, =CH₂), 147.28 (Cquat), 174.28 (Cquat), 197.86 (+, CHO); IR (film): $\tilde{\nu}$ = 3435, 2934, 2859, 1645, 1771, 1448, 1020 cm⁻¹; MS (CI, NH₃): *m/z* (%) = 226.2 (100.0) [M+NH₄⁺]; MS (HR-EI, 70 eV): 208.1096 (C₁₂H₁₆O₃: calc. 208.1099 [M⁺]).



(1'R/S,1'R,4S,5R)-4-(1'-Hydroxy-but-3'-enyl)-5-(2''-methylene-cyclopentyl)-dihydrofuran-2-one (16): To a solution of the aldehyde **15a** (1.5 g, 7.68 mmol) in dry CH₂Cl₂ (90 ml) at -78 °C allyl trimethylsilane (2.44 ml, 15.36 mmol, 2.0 equiv.) was added followed by BF₃·OEt₂ (1.078 ml, 8.46 mmol, 1.1 equiv.) after 10 min. The solution was stirred for 12 h at -78 °C and then quenched with saturated NaHCO₃ solution (12 ml). The solution was allowed to warm to 0 °C and the layers were separated. The aqueous layer was extracted with CH₂Cl₂ (3 x 100 ml, 1 x 200 ml) and the combined organic layers were dried (Na₂SO₄) and filtered. After concentration in vacuo **16** was obtained as a colorless oil (1.20 g, 66%, *dr* = 80:20).

¹H NMR (300 MHz, CDCl₃): δ = 1.51–1.68 (m, 2 H, CH₂), 1.73–1.95 (m, 2 H, CH₂), 2.04–2.28 (m, 3 H, CH₂, 4-H), 2.31–2.45 (m, 2 H, CH₂), 2.51 (dd, *J* = 17.2, 9.3 Hz, 1 H, 3-H), 2.72 (dd, *J* = 17.2, 7.0 Hz, 1 H, 3-H), 2.60–2.74 (m, 1 H, CH), 3.71–3.80 (m, 1 H, CHOH), 4.62 (dd, *J* = 6.0, 4.7 Hz, 1 H, 5-H), 4.93–5.06 (m, 2 H, =CH₂), 5.18–5.24 (m, 2 H, =CH₂), 5.67–5.88 (m, 1 H, CH=CH₂); ¹³C NMR (75.4 MHz, CDCl₃): δ = 24.30 (-, CH₂, **16**-minor: 24.39), 27.11 (-, CH₂, **16**-minor: 26.67), 28.98 (-, CH₂, **16**-minor: 32.34), 33.90 (-, CH₂, **16**-minor: 34.04), 40.36 (-, CH₂, **16**-minor: 39.89), 43.27 (+, CH, **16**-minor: 42.89), 47.04 (+, CH, **16**-

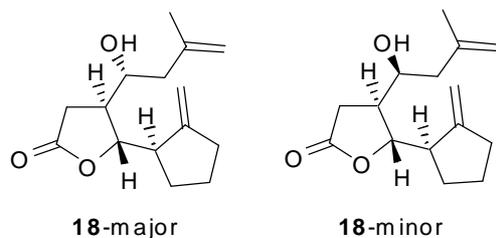
minor: 47.72), 70.12 (+, CH, **16**-minor: 72.31), 83.77 (+, CH, **16**-minor: 84.19), 107.44 (-, =CH₂, **16**-minor: 107.06), 119.32 (-, =CH₂, **16**-minor: 119.63), 133.64 (+, =CH, **16**-minor: 133.42), 151.90 (Cquat, **16**-minor: 152.35), 176.93 (Cquat, **16**-minor: 176.61); IR (film): $\tilde{\nu}$ = 3439, 2929, 1768, 1418, 1199 cm⁻¹; MS (CI, NH₃): m/z (%) = 254.2 (100.0) [M+NH₄⁺], 237.0 (11.7) [MH⁺]; MS (HR-EI, 70 eV): 236.1413 (C₁₄H₂₀O₃: calc. 236.1412 [M⁺]).



(1'*R*/S,1''*R*,4*S*,5*R*)-5-(2''-Methylene-cyclopentyl)-4-(1''-trimethylsilyloxy-but-3''-enyl)-dihydro-furan-2-one (17**):**

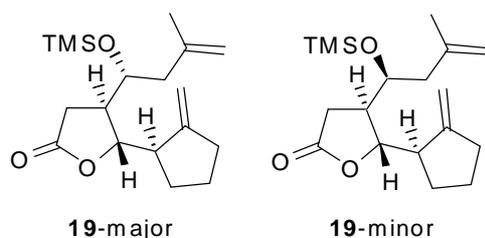
The alcohol **16** (450 mg, 1.90 mmol) was dissolved in CH₂Cl₂ (10 ml) and treated with trimethylamine (542 μ l, 3.90 mmol, 2.0 equiv.) and trimethylsilylchloride (436 μ l, 3.42 mmol, 1.8 equiv.). The reaction mixture was stirred for 20 min at room temp. and then quenched with saturated NaHCO₃ solution (10 ml). The aqueous layer was extracted with ethylacetate and the combined organic layers were washed with brine, dried (Na₂SO₄) and filtered. The solvent was removed in vacuo to obtain **17** as a colorless oil (433 mg, 74%, *dr* = 80:20).

¹H NMR (300 MHz, CDCl₃): δ = 0.08 (s, 9 H, SiMe₃), 1.50–1.70 (m, 2 H, CH₂), 1.72–1.87 (m, 2 H, CH₂), 2.04–2.48 (m, 6 H, 2 CH₂, 3-H, 4-H), 2.57–2.79 (m, 2 H, 3-H, 2'-H), 3.74–3.82 (m, 1 H, CHOH), 4.42 (dd, *J* = 5.7, 4.8 Hz, 1 H, 5-H), 4.86–5.18 (m, 4 H, =CH₂), 5.58–5.84 (m, 1 H, CH=CH₂); ¹³C NMR (75.4 MHz, CDCl₃): δ = 0.57 (+, 3 C, Si(CH₃)₃), 24.43 (-, CH₂, **17**-minor: 24.50), 27.23 (-, CH₂, **17**-minor: 26.68), 28.82 (-, CH₂, **17**-minor: 32.64), 34.03 (-, CH₂, **17**-minor: 34.19), 41.00 (-, CH₂, **17**-minor: 39.89), 43.08 (+, CH, **17**-minor: 42.35), 47.00 (+, CH, **17**-minor: 47.82), 71.15 (+, CH, **17**-minor: 74.47), 83.87 (+, CH, **17**-minor: 83.92), 107.45 (-, =CH₂, **17**-minor: 107.06), 118.30 (-, =CH₂, **17**-minor: 118.35), 133.85 (+, =CH, **17**-minor: 133.61), 152.07 (Cquat, **17**-minor: 152.39), 177.03 (Cquat, **17**-minor: 176.66).



(1′*R/S*,2′*R*,4*S*,5*R*)-4-(1′′-Hydroxy-3′′-methyl-but-3′′-enyl)-5-(2′-methylene-cyclopentyl)-dihydro-furan-2-one (18): To a solution of the aldehyde **15a** (620 mg, 3.192 mmol) in dry CH₂Cl₂ (30 ml) at −50 °C trimethyl-(2-methylallyl)-silane (820 mg, 6.384 mmol, 2.0 equiv.) was added followed by BF₃·OEt₂ (420 μl, 3.35 mmol, 1.05 equiv.) after 1.5 h. The solution was stirred for 16 h at −50 °C and then quenched with saturated NaHCO₃ solution (1 ml). After allowing to warm to 0 °C the reaction mixture was dried (Na₂SO₄), filtered and concentrated. Chromatography on silica (hexanes/ethylacetate) afforded **18** as a colorless oil (491 mg, 61%, *dr* = 71:29).

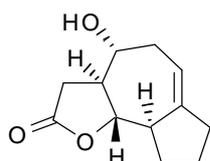
¹H NMR (300 MHz, CDCl₃): δ = 1.54–1.70 (m, 2 H, CH₂), 1.72–1.91 (m, 2 H, CH₂), 1.76 (s, 3 H, CH₃), 1.93–2.21 (m, 3 H, CH₂, 4-H), 2.31–2.44 (m, 2 H, CH₂), 2.51 (dd, *J* = 17.5, 9.4 Hz, 1 H, 3-H), 2.72 (dd, *J* = 17.5, 7.0 Hz, 1 H, 3-H), 2.65–2.77 (m, 1 H, CH), 3.78–3.89 (m, 1 H, CH), 4.64 (dd, *J* = 6.0, 4.7 Hz, 1 H, 5-H), 4.79–5.07 (m, 4 H, =CH₂); ¹³C NMR (75.4 MHz, CDCl₃): δ = 22.21 (+, CH₃, **18**-minor: 22.92), 24.29 (-, CH₂, **18**-minor: 24.43), 27.11 (-, CH₂, **18**-minor: 26.63), 28.88 (-, CH₂, **18**-minor: 32.37), 33.90 (-, CH₂, **18**-minor: 34.09), 43.43 (+, CH, **18**-minor: 43.28), 44.29 (-, CH₂, **18**-minor: 43.96), 47.05 (+, CH, **18**-minor: 47.67), 67.29 (+, CH, **18**-minor: 70.40), 83.78 (+, CH, **18**-minor: 84.23), 107.39 (-, CH₂, **18**-minor: 107.00), 114.40 (-, CH₂, **18**-minor: 114.65), 141.46 (Cquat, **18**-minor: 141.39), 151.94 (Cquat, **18**-minor: 152.33), 177.00 (Cquat, **18**-minor: 176.69); IR (film): $\tilde{\nu}$ = 3437, 2938, 1765, 1198, 887 cm⁻¹; MS (CI, NH₃): *m/z* (%) = 268.2 (100.0) [M + NH₄⁺]; MS (HR-EI, 70 eV): 250.1569 (C₁₅H₂₂O₃: calc. 250.1569 [M⁺]).



(1′*R/S*,2′*R*,4*S*,5*R*)-5-(2′-Methylene-cyclopentyl)-4-(3′′-methyl-1′′-trimethylsilyloxy-but-3′′-enyl)-dihydro-furan-2-one (19): The alcohol **18** (625 mg, 2.50 mmol) was dissolved in CH₂Cl₂ (10 ml), cooled to 0 °C and treated with trimethylamine (700 μl, 5.00 mmol, 2.0

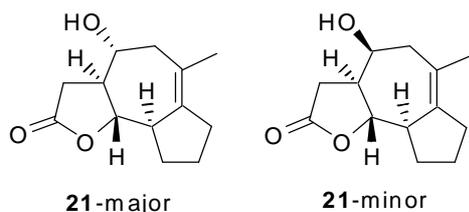
equiv.) and trimethylsilylchloride (400 μ l, 3.12 mmol, 1.25 equiv.). The reaction mixture was stirred for 3 h at room temp. and then quenched with saturated NaHCO₃ solution (10 ml). The aqueous layer was extracted with CH₂Cl₂ (3 x 25 ml) and the combined organic layers were dried (Na₂SO₄) and filtered. The solvent was removed in vacuo and the crude product was purified by chromatography on silica (hexanes/ethylacetate 2:1) to obtain **19** as a colorless oil (750 mg, 93%, *dr* = 70:30).

¹H NMR (300 MHz, CDCl₃): δ = 0.13 (s, 9 H, SiMe₃), 1.51–1.66 (m, 2 H, CH₂), 1.71 (s, 3 H, CH₃), 1.76–1.86 (m, 2 H, CH₂), 2.13–2.47 (m, 6 H, 2 CH₂, 4-H, 3-H), 2.59–2.67 (m, 1 H, C1'-H), 2.71 (dd, *J* = 20.7, 11.1 Hz, 1 H, 3-H), 3.90 (ddd, *J* = 8.8, 5.5, 1.6 Hz, 1 H, CHOTMS), 4.42 (dd, *J* = 5.5, 5.4 Hz, 1 H, 5-H), 4.69–4.74 (m, 1 H, =CH₂), 4.76–4.86 (m, 1 H, =CH₂), 4.86–4.92 (m, 1 H, =CH₂), 4.99–5.05 (m, 1 H, =CH₂); ¹³C NMR (75.4 MHz, CDCl₃): δ = 0.54 (+, 3 C, (CH₃)₃, **19**-minor: 0.56), 22.77 (+, CH₃, **19**-minor: 23.31), 24.42 (-, CH₂, **19**-minor: 24.50), 27.28 (-, CH₂, **19**-minor: 26.75), 28.45 (-, CH₂, **19**-minor: 32.95), 34.00 (-, CH₂, **19**-minor: 34.17), 42.66 (+, CH, **19**-minor: 42.57), 45.04 (-, CH₂, **19**-minor: 43.92), 47.02 (+, CH, **19**-minor: 48.04), 69.59 (+, CH, **19**-minor: 73.24), 83.89 (+, CH, **19**-minor: 83.38), 107.46 (-, CH₂, **19**-minor: 107.17), 114.08 (-, CH₂, **19**-minor: 114.30), 141.44 (Cquat, **19**-minor: 141.51), 152.08 (Cquat, **19**-minor: 152.28), 177.09 (Cquat, **19**-minor: 176.84).



(3a*S*,4*R*,9a*R*,9b*S*)-4-Hydroxy-3a,4,5,7,8,9,9a,9b-octahydro-3H-azuleno[4,5-*b*]furan-2-one (20): The diene **17** (295 mg, 0.954 mmol) was dissolved in dry CH₂Cl₂ (113 ml) under nitrogen and (4,5-dihydroIMES)(PCy₃)Cl₂Ru=CHPh (**12**) (40.5 mg, 0.0475 mmol, 5 mol%) was added. The solution was refluxed for 28 h and then treated with conc. HCl (52.2 mg, 1.5 equiv.). Refluxing was continued for 1 h, then the solution was cooled to room temp. and saturated NaHCO₃ solution (2.5 ml) was added. After 5 min the solution was dried (Na₂SO₄), filtered and concentrated. Chromatography on silica (hexanes/ethylacetate) afforded **20** as a colorless solid (68 mg, 34%, *dr* = 53:47). Crystallization to obtain the major diastereomer (4*R*) was done using a CH₂Cl₂ / *n*-hexane mixture.

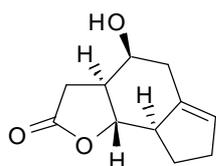
m.p. = 133-135 °C; $[\alpha]_D^{20} = -70.4$ ($c = 0.625$, CH_2Cl_2); $^1\text{H NMR}$ (600 MHz, CDCl_3): $\delta = 1.47\text{--}1.56$ (m, 1 H, 8-H), 1.63-1.68 (m, 1 H, 9-H), 1.69-1.75 (m, 1 H, 8-H), 2.12-2.19 (m, 1 H, 9-H), 2.20-2.33 (m, 2 H, 5-H, 7-H), 2.33-2.41 (m, 2 H, 3a-H, 7-H), 2.42 (ddd, $J = 14.5$, 9.3, 3.3 Hz, 1 H, 5-H), 2.51 (dd, $J = 17.0$, 12.8 Hz, 1 H, 3-H), 2.61-2.69 (m, 1 H, 9a-H), 2.80 (dd, $J = 17.0$, 7.3 Hz, 1 H, 3-H), 3.54 (ddd, $J = 10.2$, 10.1, 3.1 Hz, 1 H, 4-H), 3.74 (dd, $J = 10.1$, 10.1 Hz, 1 H, 9b-H), 5.58-5.66 (m, 1 H, 6-H); $^{13}\text{C NMR}$ (150.9 MHz, CDCl_3): $\delta = 25.02$ (-, CH_2 , C-8), 32.33 (-, CH_2 , C-9), 35.54 (-, 2 C, C-7, C-3), 38.07 (-, CH_2 , C-5), 47.10 (+, CH, C-9a), 54.23 (+, CH, C-3a), 70.66 (+, CH, C-4a), 84.21(+, CH, C-9b), 116.42 (+, =CH, C-6), 146.70 (Cquat, C-6a), 175.78 (Cquat, C-2); IR (KBr): $\tilde{\nu} = 3425$, 2958, 1757, 1438, 1227, 1192, 981, 953 cm^{-1} ; MS (EI, 70 eV): m/z (%) = 208.1 (69.3) [M^+], 190.1 (50.3) [$\text{M} - \text{H}_2\text{O}$], 131.1 (43.7) [$\text{M} - (\text{H}_2\text{O} + \text{CH}_2\text{CO}_2\text{H})$], 113.0 (36.6), 95.0 (100), 79.1 (60.5), 57.1 (46.3); MS (HR-EI, 70 eV): 208.1099 ($\text{C}_{12}\text{H}_{16}\text{O}_3$: calc. 208.1099).



(3a*S*,4*R/S*,9a*R*,9b*S*)-4-Hydroxy-6-methyl-3a,4,5,7,8,9,9a,9b-octahydro-3*H*-azuleno[4,5-*b*]furan-2-one (21): The diene **19** (200 mg, 0.62 mmol) was dissolved in dry toluene (13 ml) under argon and (4,5-dihydroIMES) $\text{Cl}_2\text{Ru}=\text{CH}-o\text{-OiPrC}_6\text{H}_4$ (**22**) (19.3 mg, 0.031 mmol, 5 mol%) was added. The solution was stirred for 24 h at 80 °C. Again 5 mol% of the ruthenium catalyst were added and stirring was continued for 5 d. The solvent was removed under reduced pressure, the residue was dissolved in CHCl_3 (20 ml) and treated with conc. HCl (140 mg, 2.3 equiv.). The reaction mixture was stirred for an additional hour at room temp. and saturated NaHCO_3 solution (3 ml) was added. After 5 min the solution was dried (MgSO_4), filtered and concentrated. Chromatography on silica (hexanes/ethylacetate) afforded **21** as a colorless solid (66 mg, 48%, $dr = 71:29$).

$^1\text{H NMR}$ (300 MHz, CDCl_3): $\delta = 1.41\text{--}1.70$ (m, 4 H, 2 CH_2), 1.75 (s, 3 H, CH_3), 2.07-2.40 (m, 5 H, 2 CH_2 , CH), 2.47 (dd, $J = 16.5$, 12.9 Hz, 1 H, 3-H), 2.59-2.70 (m, 1 H), 2.79 (dd, $J = 16.5$, 6.6 Hz, 1 H, 3-H), 3.54 (ddd, $J = 10.1$, 10.1, 2.5 Hz, 1 H, 4-H), 3.75 (dd, $J = 10.2$, 10.2 Hz, 1 H, 9b-H); $^{13}\text{C NMR}$ (75.4 MHz, CDCl_3): $\delta = 24.12$ (+, CH_3 , **21**-minor: 25.46), 24.83 (-, CH_2 , **21**-minor: 25.04), 32.06 (-, CH_2 , **21**-minor: 29.65), 32.95 (-, CH_2 , **21**-minor: 33.05),

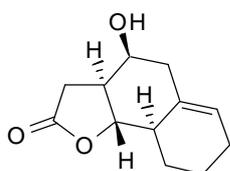
35.56 (-, CH₂, **21**-minor: 33.47), 45.56 (-, CH₂, **21**-minor: 42.05), 46.79 (+, CH, **21**-minor: 48.02), 54.67 (+, CH, **21**-minor: 52.11), 69.78 (+, CH, **21**-minor: 65.44), 84.06 (+, CH, **21**-minor: 81.09), 124.11 (Cquat, C-6, **21**-minor: 123.49), 139.05 (Cquat, C-6a, **21**-minor: 139.91), 175.73 (Cquat, C-2, **21**-minor: 175.90); IR (KBr): $\tilde{\nu}$ = 3438, 2930, 2855, 1774, 1379, 1186, 974, 704 cm⁻¹; MS (CI, NH₃): m/z (%) = 240.2 (100.0) [M + NH₄⁺], 222.9 (30.7) [MH⁺], 205.0 (15.4); MS (HR-EI, 70 eV): 222.1255 (C₁₂H₁₆O₃: calc. 222.1256).



(3a*S*,4*S*,8a*R*,8b*S*)-4-Hydroxy-3,3a,4,5,7,8,8a,8b-octahydro-1-oxa-as-indacen-2-one (24a**):**

A solution of **15a** (50 mg, 0.26 mmol) in dry CH₂Cl₂ (5 ml) was treated with BF₃·OEt₂ (0.99 ml, 7.8 mmol, 30 equiv.) under nitrogen and stirred for 12 h at room temp. After quenching with saturated NaHCO₃ solution (3.5 ml) the layers were separated and the aqueous layer was extracted with CH₂Cl₂ (3 x 15 ml). The combined organic layers were dried (Na₂SO₄) and filtered. Evaporation of the solvent in vacuo afforded **24a** as a solid (42 mg, 84%).

[α]_D²⁰ = -11.5 (c = 1.035, CH₂Cl₂); m.p. = 112-115 °C; ¹H NMR (300 MHz, CDCl₃): δ = 1.68–1.87 (m, 2 H, 7-H, 8-H), 2.18–2.48 (m, 4 H, 7-H, 8-H, 5-H), 2.43 (dd, J = 16.2, 6.6 Hz, 1 H, 3-H), 2.60–2.68 (m, 1 H), 8a-H), 2.64 (dd, J = 16.2, 13.4 Hz, 1 H, 3-H), 2.76–2.90 (m, 1 H), 4.02 (dd, J = 10.1, 10.0 Hz, 1 H, 8b-H), 4.18–4.29 (m, 1 H, 4-H), 5.64–5.69 (m, 1 H, 6-H); ¹³C NMR (75.4 MHz, CDCl₃): δ = 27.50 (-, CH₂), 31.32 (-, CH₂), 32.02 (-, CH₂), 36.70 (-, CH₂), 47.73 (+, CH), 51.13 (+, CH), 65.57 (+, CH), 84.21 (+, CH), 130.18 (+, =CH), 137.03 (Cquat, C-5a), 176.48 (Cquat, C-2); IR (KBr): $\tilde{\nu}$ = 3469, 2923, 2363, 1767, 1105, 1019 cm⁻¹; MS (EI, 70 eV): m/z (%) = 194.1 (16.6) [M⁺], 176.1 (9.8) [M - H₂O], 130.1 (15.2), 117.1 (100.0) [M - (CH₂CO₂H + H₂O)], 113.1 (28.0), 81.1 (66.8). MS (HR-EI, 70 eV): 194.0943 (C₁₁H₁₄O₃: calc. 194.0943 [M⁺]).



(3a*S*,4*S*,9a*R*,9b*S*)-4-Hydroxy-3a,4,5,7,8,9,9a,9b-octahydro-3H-naphtho[1,2-*b*]furan-2-one (24b): A solution of **15b** (338 mg, 1.62 mmol) in dry CH₂Cl₂ (30 ml) was treated with BF₃·OEt₂ (612 μl, 4.86 mmol, 3.0 equiv.) under nitrogen and stirred for 12 h at room temp. After quenching with saturated NaHCO₃ solution (7 ml) the layers were separated and the aqueous layer was extracted with CH₂Cl₂ (3 x 20 ml). The combined organic layers were dried (Na₂SO₄) and filtered. Evaporation of the solvent in vacuo afforded **24b** as a colorless oil (210 mg, 62%).

$[\alpha]_D^{20} = -28.1$ (c = 0.645, CH₂Cl₂); ¹H NMR (600 MHz, CDCl₃): δ = 1.36–1.54 (m, 2 H, 7-H, 9-H), 1.68–1.77 (m, 1 H, 9-H), 1.99–2.05 (m, 2 H, 8-H), 2.09–2.15 (m, 1 H, 7-H), 2.24 (dddd, *J* = 13.2, 11.1, 6.5, 1.9 Hz, 1 H, 3a-H), 2.32–2.43 (m, 3 H, 5-CH₂, 9a-H), 2.42 (dd, *J* = 16.2, 6.5 Hz, 1 H, 3-H), 2.63 (dd, *J* = 16.2, 13.2 Hz, 1 H, 3-H), 3.99 (dd, *J* = 11.0, 11.0 Hz, 1 H, 9b-H), 4.15–4.20 (m, 1 H, 4-H), 5.73 (bs, 1 H, 6-H); ¹³C NMR (100.6 MHz, CDCl₃): δ = 20.22 (-, CH₂), 25.40 (-, CH₂), 26.77(-, CH₂), 31.94 (-, CH₂, C-3), 42.43 (+, CH, C-9a), 42.94 (-, CH₂, C-5), 48.08 (+, CH, C-3a), 65.57 (+, CH, C-4), 83.18 (+, CH, C-9b), 129.16 (+, CH, C-6), 131.18 (Cquat, C-5a), 176.42 (Cquat, CO); IR (film): $\tilde{\nu} = 3438, 2928, 1770, 1423, 988$ cm⁻¹; MS (CI, NH₃): *m/z* (%) = 226.1 (100.0) [M + NH₄⁺]; MS (HR-EI, 70 eV): 208.1097 (C₁₂H₁₆O₃: calc. 208.1099 [M⁺]).