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Synthesis of sarcodictyin A analogue containing 14-methyl group and C(12)=C(13) bond in ring A from levoglucosenone

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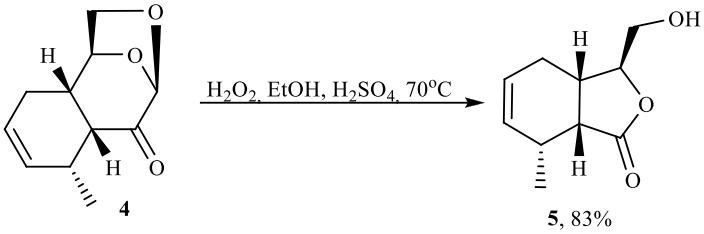
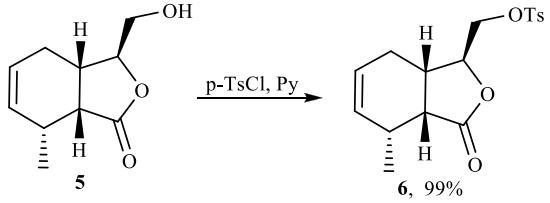
The spectral and analytical data were obtained using the equipment of the *Khimiya* Joint Center at the Institute of Organic Chemistry, Ufa Research Center, Russian Academy of Sciences. ^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker AM-300 (300 MHz for ^{1}H and 75.47 MHz for ^{13}C) and on a spectrometer Bruker Avance III, (500.13 MHz for ^{1}H and 125.47 MHz for ^{13}C). IR spectra were recorded on spectrophotometers Shimadzu IRPrestige-21 or Bruker Tensor 27 (neat or mulls in mineral oil). Mass spectra were measured on a GC-MS instrument Hewlett Packard, chromatograph HP 6890 with a mass-selective detector HP 5973. The elemental compositions were determined on a Euro-2000 CHNS(O) analyzer. Optical rotation was determined on a polarimeter Perkin Elmer-341. Analytic TLC was carried out on Sorbfil plates of the grade PTSKh-AF-A ("Sorbpolymer" Co., Krasnodar). The melting points were measured on a Boëtius 05 heating block.



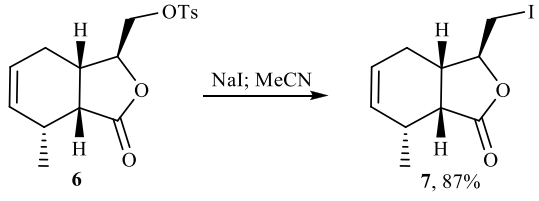
(3*S*,3a*S*,7*R*,7a*R*)-3-Hydroxymethyl-7-methyl-3a,4,7,7a-tetrahydroisobenzofuran-1(3*H*)-one (5). Ketone **4** (1.67 g, 8.6 mmol), was dissolved in 30 ml of ethanol, 7 ml of 30% hydrogen peroxide and 0.051 ml of sulfuric acid were added, and the mixture was stirred for 4 h at 70–75°C. The mixture was then treated with a saturated solution of Na_2SO_3 until peroxide compounds disappeared, ethanol was distilled off on a rotary evaporator, and the aqueous phase was extracted with ethyl acetate. The combined extracts were dried over $MgSO_4$, the solvent was removed on a rotary evaporator, and the residue was subjected to chromatography on silica gel. Yield 1.30 g (83%), white crystals, mp. 105-110ºC, $[\alpha]_D^{20}$ -31.8º (*c* 1.0, $CHCl_3$), R_f 0.5 (hexane- EtOAc, 1:1). IR ($CHCl_3$, ν/cm^{-1}): 3466, 2850, 1751, 1460, 1365, 1197, 1031. ^{1}H NMR ($CDCl_3$) δ: 1.22 (d, 3H, CH_3, *J* 7.24 Hz), 2.02 (ddd, 1H, CH_2,

J 16.67, 4.09, 2.83 Hz), 2.23 (ddd, 1H, CH_2, *J* 16.67, 7.23, 1.58 Hz), 2.7 (m, 1H, CH), 2.78 (m, 1H, CH), 2.89 (tdd, , 1H, CH, *J* 7.24, 2.83, 2.2 Hz), 3.52 (dd, 1H, CH_2, *J* 12.58, 3.46 Hz), 3.56 (dd, 1H, CH_2, *J* 12.58, 2.2 Hz), 4.02 (m, 1H, CH_2, *J* 3.46, 2.2 Hz), 5.54–5.56 (m, 2H, CH=). ^{13}C NMR ($CDCl_3$) *δ*: 17.21 (CH_3), 25.06 (C^4), 28.48 (C^7), 34.56 (C^{3a}), 43.51 (C^{7a}), 63.02 ($C^{1'}$), 86.02 (C^3), 125.39 (C^5), 133.93 (C^6), 178.26 (CO). Found, %: C 65.84; H 7.86. MS: *m/z*: 182.0937 $[M]^+$. Calc. for $C_{10}H_{14}O_3$: C 65.91; H 7.74.



5 **6**, 99%

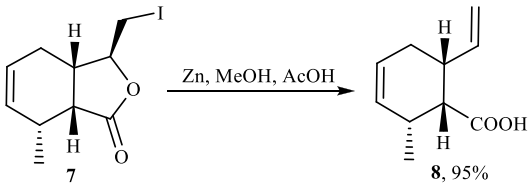
[(1*S*,3a*R*,4*R*,7a*S*)-4-Methyl-3-oxo-1,3,3a,4,7,7a-hexahydroisobenzofuran-1-yl]methyl 4-methylbenzenesulfonate (6). A solution of 0.824 g (4.53 mmol) of alcohol **5** in 20 ml of pyridine was cooled to 0°C, 1.04 g (5.43 mmol) of *p*-TsCl was added, and the mixture was stirred for 5 h at room temperature. The mixture was then diluted with water and extracted with ethyl acetate, the combined extracts were washed with 5% aqueous HCl, brine, and water, dried over $MgSO_4$, concentrated, and the residue was purified by chromatography on silica gel. Yield 1.51 g (99%), white crystals, mp. 55-57ºC, $[\alpha]_D^{20}$ -4.º (*c* 1.0, $CHCl_3$), R_f 0.5 (hexane- EtOAc, 3:1). IR ($CHCl_3$, *ν*/cm^{-1}): 2968, 1770, 1361, 1176, 975, 815, 665. ^{1}H NMR ($CDCl_3$) *δ*: 1.25 (d, 3H, CH_3, *J* 7.3 Hz), 2.03 (ddd, 1H, CH_2, *J* 17.25, 4.65, 3.32 Hz), 2.24 (ddd, 1H, CH_2, *J* 17.25, 9.29, 3.32 Hz), 2.45 (s, 3H, CH_3), 2.48 (dd, 1H, C^{3a}H, 7.29, 7.29 Hz), 2.77 (m, 1H, C^4H), 2.86 (dd, 1H, C^{7a}H, *J* 9.29, 7.29 Hz), 4.07-4.20 (m, 3H, CH, CH_2), 5.73–5.85 (m, 2H, CH=), 7.35 (d, 2H, CH^{ar}, *J* 8.62 Hz), 7.76 (d, 2H, CH^{ar}, *J* 8.62 Hz). ^{13}C NMR ($CDCl_3$) *δ*: 14.12 (CH_3), 17.04 (CH_3), 25.23 (C^7), 28.64 (C^4), 35.37 (C^{7a}), 43.03 (C^{3a}), 69.40 ($C^{1'}$), 81.64 (C^1), 125.22(C^6), 127.90 (C^{ar}), 130.02 (C^{ar}), 132.21 (C^{ar}), 134.62 (C^5), 145.35 (C^{ar}), 176.59 (CO). Found, %: C 60.85; H 5.90; S 9.43. MS: *m/z*: 336.1026 $[M]^+$. Calc. for $C_{17}H_{20}O_5S$: C 60.70; H 5.99; S 9.53.



6 **7**, 87%

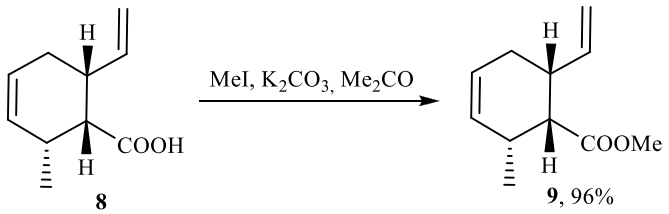
(3*S*,3a*S*,7*R*,7a*R*)-3-Iodomethyl-7-methyl-3a,4,7,7a-tetrahydroisobenzofuran-1(3*H*)-one (7). Sodium iodide (1.90 g, 12.71 mmol), was added to a solution of 1.423 g (4.24 mmol) of compound **6**

in 25 ml of acetonitrile, and the mixture was boiled for 3 h. The mixture was then cooled to room temperature and diluted with water, the organic phase was separated and washed with a saturated solution of $Na_2S_2O_3$, the aqueous phase was extracted with ethyl acetate, the extracts were combined with the organic phase and dried over $MgSO_4$. The solvent was distilled off under reduced pressure, and the residue was purified by chromatography on silica gel. Yield 1.072 g (87%), white crystals, mp 43-45ºC, $[\alpha]_D^{20}$ -50.3º (*c* 1.0, $CHCl_3$), R_f 0.55 (hexane - EtOAc, 5:1). IR ($CHCl_3$, ν/cm^{-1}): 2931, 1757, 1454, 1356, 1201, 1114, 975, 646. ^{1}H NMR ($CDCl_3$) δ: 1.30 (d, 3H, CH_3, *J* 7.3 Hz), 2.10 (td, 1H, CH_2, *J* 17.25, 3.32 Hz), 2.28 (ddt, 1H, CH_2, *J* 17.25, 9.29, 1.99 Hz), 2.50 (t, 1H, CH, *J* 7.29 Hz), 2.72 (m, 1H, CH), 2.94 (dd, 1H, CH, *J* 7.29, 9.29 Hz), 3.35 (dd, 2H, CH_2, *J* 10.62, 5.31 Hz), 4.02 (dd, 1H, CH, *J* 5.31, 5.31 Hz), 5.82 (br.s, 2H, CH=). ^{13}C NMR ($CDCl_3$) δ: 7.53 (C$^{1'}$), 16.84 (CH_3), 25.81 (C^4), 28.79 (C^7), 39.66 (C^{3a}), 43.58 (C^{7a}), 83.24 (C^3), 125.54 (C^5), 134.41 (C^6), 176.46 (CO). Found, %: C 41.35; H 4.52; I 43.32. MS: *m/z*: 291.9955 $[M]^+$. Calc. for $C_{10}H_{13}IO_2$: C 41.12; H 4.49; I 43.44.



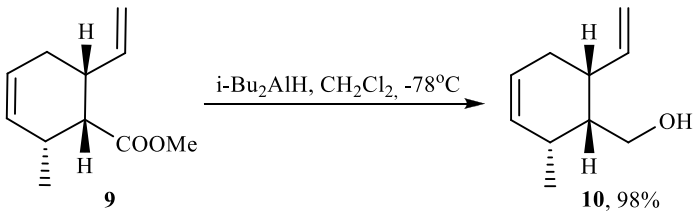
7 **8**, 95%

(1*R*,2*R*,6*R*)-2-Methyl-6-vinylcyclohex-3-ene-1-carboxylic acid (8). Iodide **7** (2.5 g, 8.56 mmol), was dissolved in 20 ml of methanol, 2.82 g (42.8 mmol) of zinc powder and 0.1 ml of acetic acid were added, and the mixture was vigorously stirred for 3 h. The mixture was filtered, the precipitate was washed with methanol, and the filtrate was combined with the washings and evaporated on a rotary evaporator. The residue was dissolved in ethyl acetate, the solution was washed with brine and dried over $MgSO_4$. The solvent was distilled off, and the residue was purified by chromatography on silica gel. Yield 1.35 g (95%), white crystals, mp 71-73ºC, $[\alpha]_D^{20}$ -64.º (*c* 1.0, $CHCl_3$), R_f 0.3-0.5 (hexane - EtOAc, 3:1). IR ($CHCl_3$, ν/cm^{-1}): 2922, 1703, 1454, 1232, 956, 688. ^{1}H NMR ($CDCl_3$) δ: 1.03 (d, 3H, CH_3, *J* 7.4 Hz), 2.0 (ddd, 1H, CH_2, *J* 17.6, 4.7, 4.7 Hz), 2.28 (ddd, 1H, CH_2, *J* 17.6, 10.8, 2.3 Hz), 2.50-2.60 (m, 2H, C^{6}H, C^{2}H), 2.78 (dd, 1H, C^{1}H, *J* 5.7, 4.5 Hz), 4.95 (d, 1H, CH_2=, *J* 10.4 Hz), 5.05 (d, 1H, CH_2=, *J* 17.2), 5.38 (d, 1H, C^{3}H, *J* 10.1 Hz), 5.69 (ddd, 1H, C^{4}H, *J* 10.1, 4.7, 2.3 Hz), 5.75 (ddd, 1H, CH=, *J* 17.2, 10.4, 6.9 Hz). ^{13}C NMR ($CDCl_3$) δ: 18.02 (CH_3), 27.10 (C^5), 32.40 (C^2), 39.59 (C^6), 48.48 (C^1), 114.78 (C$^{2'}$), 126.00 (C^4), 129.43 (C^3), 140.27 (C$^{1'}$), 178.87 (CO). Found, %: C 72.38; H 8.42. MS: *m/z*: 166.0988 $[M]^+$. Calc. for $C_{10}H_{14}O_2$: C 72.26; H 8.49.



8 **9**, 96%

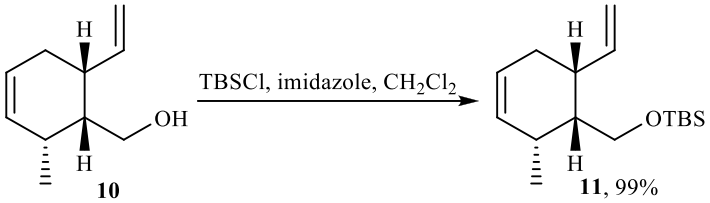
Methyl (1*R*,2*R*,6*R*)-2-methyl-6-vinylcyclohex-3-ene-1-carboxylate (9). A mixture of 4.50 g (27.11 mmol) of acid **8**, 6.75 ml (108.44 mmol) of iodomethane, and 9.36 g (67.78 mmol) of anhydrous potassium carbonate in 40 ml of anhydrous acetone was stirred at room temperature until the reaction was complete. The mixture was filtered, the precipitate was washed with diethyl ether, the filtrate was combined with the washings and evaporated on a rotary evaporator, and the residue was purified by chromatography on silica gel. Yield 4.27 g (96%), colorless oil, $[\alpha]_D^{20}$ -97.5º (*c* 1.0, $CHCl_3$), R_f 0.2 (hexane). IR ($CHCl_3$, *v*/cm^{-1}): 2960, 1735, 1435, 1382, 1149, 997, 916, 690. ^{1}H NMR ($CDCl_3$) δ: 1.03 (d, 3H, CH_3, *J* 7.63 Hz), 2.05 (td, 1H, CH_2, *J* 17.39, 5.19 Hz), 2.35 (m, 1H, CH_2), 2.53-2.64 (m, 2H, H^6, H^2), 2.85 (dd, 1H, CH, *J* 6.1, 3.96 Hz), 3.06 (s, 3H, CH_3), 5.01 (d, 1H, CH_2=, *J* 10.38, 1.22 Hz), 5.08 (d, 1H, CH_2=, *J* 17.39, 1.22 Hz), 5.42 (dd, 1H, CH, *J* 10.07, 1.83 Hz), 5.75 (dd, 1H, CH, *J* 10.07, 6.82 Hz), 5.78 (ddd, 1H, CH=, *J* 17.39, 10.07, 6.71 Hz). ^{13}C NMR ($CDCl_3$) δ: 18.05 (CH_3), 27.16 (C^5), 32.67 (C^2), 39.71 (C^6), 48.37 (C^1), 50.64 (CH_3), 114.42 ($C^{2'}$), 125.98 (C^4), 129.40 (C^3), 140.56 ($C^{1'}$), 172.77 (CO). Found, %: C 73.38; H 8.89. MS: *m/z*: 180.1145 $[M]^+$. Calc. for $C_{11}H_{16}O_2$: C 73.30; H 8.95.



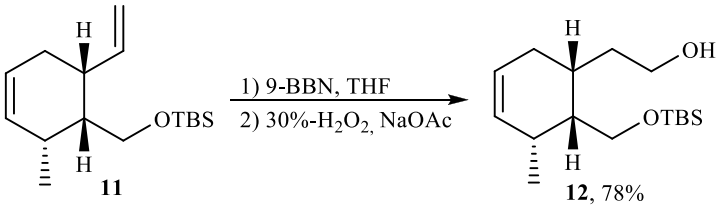
9 **10**, 98%

[(1*R*,2*R*,6*R*)-2-Methyl-6-vinylcyclohex-3-en-1-yl]methanol (10). A solution of 2.85 g (15.83 mmol) of ester **9** in 70 ml of dichloromethane was cooled to –78°C, 8.5 ml (34.83 mmol) of a 73% solution of DIBAL-H in toluene was added dropwise, and the mixture was stirred for 30 min at this temperature. The mixture was treated with 10 ml of ethyl acetate, allowed to warm up to 0°C, and treated with 3% aqueous HCl to destroy gel. The organic phase was separated, the aqueous phase was extracted with dichloromethane, the extracts were combined with the organic phase, washed with water, and dried over $MgSO_4$. The solvent was distilled off, and the residue was subjected to chromatography on silica gel. Yield 2.36 g (98%), oily substance, colorless oil, $[\alpha]_D^{20}$ -13.3º (*c* 1.0, $CHCl_3$), R_f 0.42 (hexane - EtOAc, 6:1). IR ($CHCl_3$, *v*/cm^{-1}): 3334, 3014, 2889, 1456, 1215, 1157, 1031, 914, 758. ^{1}H NMR ($CDCl_3$) δ: 1.05 (d, 3H, CH_3, *J* 7.6 Hz), 1.49 (br.s, 1H, OH), 1.94-2.07 (m, 2H, CH,

CH_2), 2.15 (m, 1H, CH_2), 2.48-2.60 (m, 2H, CH), 3.55 (dd, 2H, CH_2, *J* 11.4, 5.8 Hz), 5.04 (dd, 1H, CH_2=, *J* 10.1, 1.7 Hz), 5.05 (dd, 1H, CH_2=, *J* 17.7, 1.7 Hz), 5.46 (dd, 1H, CH, *J* 9.9, 1.8 Hz), 5.65 (ddd, 1H, CH, *J* 9.9, 3.9, 2.8 Hz), 6.04 (ddd, 1H, CH=, *J* 17.7, 10.1, 6.1 Hz). ^{13}C NMR ($CDCl_3$) δ: 18.17 (CH_3), 27.10 (C^5), 33.86 (C^2), 40.31 (C^6), 44.23 (C^1), 60.62 (CH_2O), 113.76 ($C^{2'}$), 125.23 (C^4), 132.27 (C^3), 142.31 ($C^{1'}$). Found, %: C 78.63; H 10.78. Calc. for $C_{10}H_{16}O$: C 78.90; H 10.59.

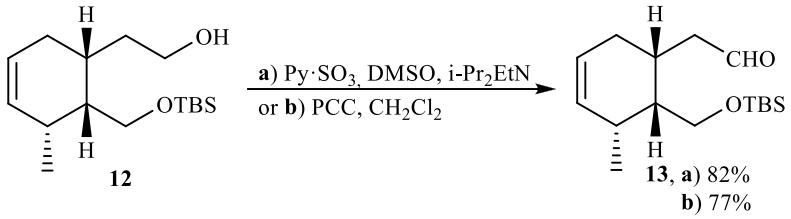


***tert*-Butyldimethyl{[(1*R*,2*R*,6*R*)-2-methyl-6-vinylcyclohex-3-en-1-yl]methoxy}silane (11).** A solution of 2.12 g (13.95 mmol) of alcohol **10**, 2.32 g (15.34 mmol) of *tert*-butyldimethylsilyl chloride, and 1.04 g (15.34 mmol) of imidazole in 30 ml of dichloromethane was stirred at room temperature until the initial compound disappeared (TLC). The mixture was treated with 30 ml of water and extracted with dichloromethane, the combined extracts were dried over $MgSO_4$. The solvent was distilled off, and the residue was purified by chromatography on silica gel. Yield 3.67 g (99%), colorless oil, $[\alpha]_D^{20}$ -5.5º (*c* 1.0, $CHCl_3$), R_f 0.63 (hexane). IR ($CHCl_3$, ν/cm^{-1}): 3018, 2929, 2857, 1638, 1472, 1361, 1256, 1096, 837, 676. ^{1}H NMR ($CDCl_3$) δ: 0.01 (s, 6H, CH_3), 0.88 (s, 9H, CH_3), 1.03 (d, 3H, CH_3, *J* 7.5 Hz), 1.88 (m, 1H, CH_2), 1.95 (m, 1H, CH), 2.12 (m, 1H, CH_2), 2.43-2.54 (m, 2H, CH), 3.56 (dd, 1H, CH_2, *J* 10.2, 5.3 Hz), 3.61 (dd, 1H, CH_2, *J* 10.2, 6.8), 4.98 (dd, 1H, CH_2=, *J* 10.1, 1.7 Hz), 4.99 (dd, 1H, CH_2=, *J* 17.7, 1.7 Hz), 5.48 (dd, 1H, CH, *J* 9.9, 2.0 Hz), 5.62 (ddd, 1H, CH, *J* 9.9, 6.0, 3.6 Hz), 5.98 (ddd, 1H, CH=, *J* 17.7, 10.1, 6.9 Hz). ^{13}C NMR ($CDCl_3$) δ: -5.38 (CH_3), 18.15 (CH_3), 18.53 (**C**CH_3), 25.90 (CH_3), 28.14 (C^5), 33.78 (C^2), 40.31 (C^6), 43.90 (C^1), 60.59 (CH_2O), 113.37 ($C^{2'}$), 124.75 (C^4), 132.57 (C^3), 142.09 ($C^{1'}$). Found, %: C 72.23; H 11.49. MS: *m/z*: 209.1 [*M*-CMe_3]$^+$. Calc. for $C_{16}H_{30}OSi$: C 72.11; H 11.35.



2-[(1*R*,2*R*,6*S*)-6-(*tert*-Butyldimethylsiloxymethyl)-5-methylcyclohex-3-en-1-yl]ethanol (12). A solution of 0.744 g (6.08 mmol) of 9-borabicyclo[3.3.1]nonane in 25 ml of anhydrous THF was

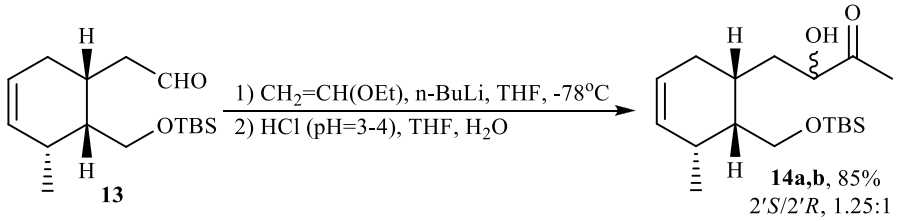
added to a solution of 1.470 g (5.53 mmol) of olefinic ester **11** in 25 ml of anhydrous THF, the mixture was vigorously stirred for 1 h. Then 7.4 ml of a 3 *M* solution of sodium acetate and 2.53 ml of 30% hydrogen peroxide were added, and the mixture was vigorously stirred for 4 h at room temperature. The mixture was then treated with 5% aqueous HCl to reach weakly acidic pH, and with a saturated solution of Na_2SO_3 until peroxide compounds disappeared. The mixture was extracted with ethyl acetate, the combined extracts were washed with water, dried over $MgSO_4$, and evaporated, and the residue was subjected to chromatography on silica gel. Yield 1.22 g (78%), colorless oil, $[\alpha]_D^{20}$ -9.9º (*c* 1.0, $CHCl_3$), R_f 0.3 (hexane - EtOAc, 4:1). IR ($CHCl_3$, ν/cm^{-1}): 2927, 1741, 1699, 1469, 1373, 1247, 1089, 1049, 837, 775. ^{1}H NMR ($CDCl_3$) δ: 0.00 (s, 6H, CH_3), 0.82 (s, 9H, CH_3), 0.98 (d, 3H, CH_3, *J* 7.6 Hz), 1.47-1.65 (m, 2H, CH, CH_2), 1.70-1.96 (m, 4H, CH, CH_2), 2.48 (m, 1H, CH), 2.42 br.s(1H, CH), 3.55 (m, 2H, CH_2), 3.68 (m, 2H, CH_2), 5.33 (d, 1H, CH, *J* 9.8 Hz), 5.52 (dd, 1H, CH, *J* 9.8, 3.8 Hz). ^{13}C NMR ($CDCl_3$) δ: -5.48 (CH_3), 18.14 (**C**CH_3), 18.56 (CH_3), 25.92 (CH_3), 29.22 (C^2), 34.55 (C^5), 34.73 (C^1), 36.80 (C$^{2'}$), 42.79 (C^6), 59.65 (C$^{1'}$), 61.73 (CH_2OTBS), 125.59 (C^3), 132.15 (C^4). Found, %: C 67.32; H 11.25. MS: *m/z*: 227.1 [*M*-CMe_3]$^+$. Calc. for $C_{16}H_{32}O_2Si$: C 67.54; H 11.34.



2-[(1*R*,5*R*,6*S*)-6-(*tert*-Butyldimethylsilyloxymethyl)-5-methylcyclohex-3-en-1-yl]ethanal (13). *a*. *Oxidation with Py·SO$_3$–DMSO*. A solution of 0.105 g (0.37 mmol) of alcohol **12** in 5 ml of dichloromethane was cooled to 0°C, 0.11 ml (1.47 mmol) of DMSO, 0.14 ml (0.74 mmol) of *i*-Pr_2NEt, and 0.116 g (0.74 mmol) of Py·SO_3 were added, and the mixture was stirred for 3 h. The mixture was then treated with saturated aqueous solutions of $Na_2S_2O_3$ (5 ml) and $NaHCO_3$ (5 ml), stirred for 10 min at 0°C, and extracted with dichloromethane. The extract was evaporated on a rotary evaporator, and the residue was subjected to silica gel chromatography. Yield of **13** 0.086 g (82%).

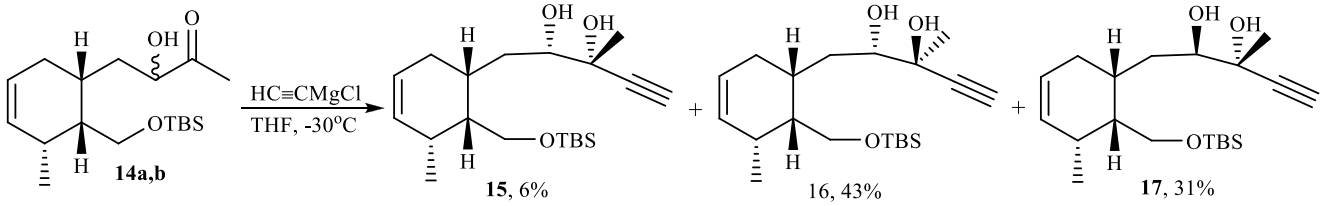
b. *Oxidation with pyridinium chlorochromate*. Pyridinium chlorochromate, 0.920 g (4.24 mmol), was added at 25°C to a solution of 0.550 g (1.93 mmol) of alcohol **12** in 30 ml of dichloromethane. The mixture was stirred for 45 min, 30 ml of petroleum ether (bp 40–70°C) was added, and the precipitate was filtered off and washed with petroleum ether. The filtrate was evaporated on a rotary evaporator, and the residue was subjected to silica gel chromatography. Yield 0.420 g (77%), colourless oil, $[\alpha]_D^{20}$ -29.2º (*c* 1.0, $CHCl_3$), R_f 0.62 (hexane - EtOAc, 6:1). IR ($CHCl_3$, ν/cm^{-1}): 2929, 2857, 1723, 1472, 1257, 1216, 1094, 910, 760, 668. ^{1}H NMR ($CDCl_3$) δ: 0.03 (s, 6H, CH_3), 0.88 (s,

9H, CH_3), 0.99 (d, 3H, CH_3, *J* 7.6 Hz), 1.74-1.95 (m, 2H, CH, CH_2), 2.09 (m, 1H, H^2), 2.40-2.58 (m, 3H, CH, CH_2), 2.75 (m, 1H, CH_2), 3.61 (m, 2H, CH_2OTBS), 5.39 (d, 1H, H^3, *J* 10.0 Hz), 5.55 (dd, 1H, H^4, *J* 10.0, 2.6 Hz), 9.78 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$) δ: -5.49 (CH_3), 18.14 (**C**CH_3), 18.23 (CH_3), 25.91 (CH_3), 28.78 (C^2), 32.00 (C^1), 34.01 (C^5), 42.76 (C^6), 48.51 ($C^{1'}$), 59.72 (CH_2OTBS), 124.96 (C^3), 132.07 (C^4), 202.96 (CHO). Found, %: C 68.13; H 10.62. MS: *m/z* 225.1 [*M*-CMe_3]$^+$. Calc. for $C_{16}H_{30}O_2Si$: C 68.03; H, 10.70.



(3*RS*)-4-[(1*R*,5*R*,6*S*)-6-(*tert*-Butyldimethylsilyloxymethyl)-5-methylcyclohex-3-en-1-yl]-3-hydroxybutan-2-one (14a/14b). A solution of 0.94 ml (9.92 mmol) of ethyl vinyl ether in 5 ml of THF was cooled to –78°C, 1.24 ml of a 2 *M* solution of butyllithium (2.48 mmol) in hexane was added in an inert atmosphere. The mixture was allowed to warm up to room temperature, stirred for 1.5 h, and cooled again to –78°C. A solution of 0.350 g (1.24 mmol) of aldehyde **13** in 3 ml of THF was added dropwise. When the reaction was complete (TLC), the mixture was treated with 3% aqueous HCl to pH 3–4 to hydrolyze intermediate enol ether (TLC), and the solution was neutralized with a saturated aqueous solution of sodium hydrogen carbonate and extracted with ethyl acetate. The combined extracts were dried over $MgSO_4$ and evaporated on a rotary evaporator, and the residue was subjected to silica gel chromatography. Yield 0.344 g (85%), ratio 2′*S*-**14a**/2′*R*-**14b** 1.25 (according to the 1H NMR data), colorless oil, R_f 0.5 (hexane - EtOAc, 6:1). IR ($CHCl_3$, ν/cm^{-1}): 2956, 2929, 1714, 1359, 1253, 1093, 910, 837, 734. 2′*S*-Epimer **14a:** ^{1}H NMR ($CDCl_3$) δ: 0.05 (s, 6H, CH_3), 0.87 (s, 9H, CH_3), 1.04 (d, 3H, CH_3, *J* 7.1 Hz), 1.28 (m, 1H, CH_2), 1.40 (m, 1H, CH_2), 1.75-2.20 (m, 4H, CH, CH_2), 2.20 (s, 3H, CH_3), 2.50 (m, 1H, H^5), 3.62 (m, 2H, CH_2OTBS), 4.37 (d, 1H, $H^{3'}$, *J* 9.7 Hz), 5.37 (d, 1H, H^4, *J* 9.9 Hz), 5.56 (m, 1H, H^3). ^{13}C NMR ($CDCl_3$) δ: -5.38 (CH_3), 18.17 (**C**CH_3), 18.65 (CH_3), 25.93 (CH_3), 26.02 (CH_3), 29.64 (C^2), 34.40 (C^1), 34.59 (C^5), 37.67 ($C^{4'}H_2$), 41.71 (C^6), 59.84 (CH_2OTBS), 76.10 ($C^{3'}$), 125.67 (C^3), 132.04 (C^4), 210.79 (CO). 2′*R*-Epimer **14b**: ^{1}H NMR ($CDCl_3$) δ: 0.05 (s, 6H, CH_3), 0.89 (s, 9H, CH_3), 0.99 (d, 3H, CH_3, *J* 7.5 Hz), 1.28 (m, 1H, CH_2), 1.58 (m, 1H, CH_2), 1.75-2.20 (m, 4H, CH, CH_2), 2.20 (s, 3H, CH_3), 2.50 (m, 1H, H^5), 3.62 (m, 2H, CH_2OTBS), 3.77 (d, 1H, $H^{3'}$, *J* 3.7 Hz), 5.36 (d, 1H, H^4, *J* 9.8 Hz), 5.56 (m, 1H, H^3). ^{13}C NMR ($CDCl_3$) δ: -5.26 (CH_3), 18.35 (**C**CH_3), 18.52 (CH_3), 25.93 (CH_3), 26.02 (CH_3), 28.17 (C^2), 34.20 (C^1), 35.01 (C^5), 38.50

($C^{4'}H_2$), 43.74 (C^6), 59.56 (CH_2OTBS), 75.53 ($C^{3'}$), 125.18 (C^3), 132.04 (C^4), 211.21 (CO). Found, %: C 66.30; H 10.58. MS: *m/z* 269.2 [*M*-CMe_3]$^+$. Calc. for $C_{18}H_{34}O_3Si$: C 66.21; H 10.49.



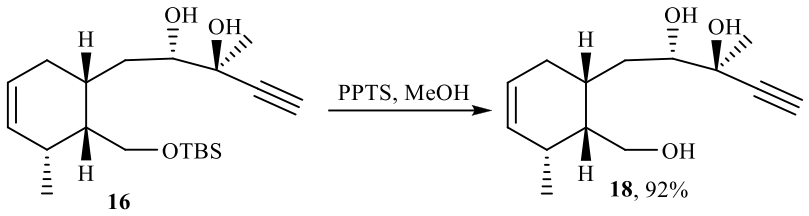
(2*S*,3*R*)-1-[(1*R*,5*R*,6*S*)-6-(*tert*-Butyldimethylsilyloxymethyl)-5-methylcyclohex-3-en-1-yl]-3-methylpent-4-yne-2,3-diol (15), (2*S*,3*S*)-1-[(1*R*,5*R*,6*S*)-6-(*tert*-butyldimethylsilyloxymethyl)-5-methylcyclohex-3-en-1-yl]-3-methylpent-4-yne-2,3-diol (16), and (2*R*,3*R*)-1-[(1*R*,5*R*,6*S*)-6-(*tert*-butyldimethylsilyloxymethyl)-5-methylcyclohex-3-en-1-yl]-3-methylpent-4-yne-2,3-diol (17). A solution of 5.4 mmol of ethynylmagnesium chloride in 30 ml of THF was cooled to –78°C, a solution of 0.320 g (0.98 mmol) of epimer mixture **14a**/**14b** in 10 ml of THF was added, and the mixture was allowed to warm up to –30°C over a period of 1 h. When the reaction was complete (TLC), the mixture was neutralized with 3% aqueous HCl and extracted with ethyl acetate. The extract was dried over $MgSO_4$ and evaporated, and the residue was subjected to silica gel chromatography to isolate diols: 0.021 g (6%) of **15**, 0.148 g (43%) of **16**, and 0.107 g (31%) of **17**.

15: colorless oil, $[\alpha]_D^{20}$ -0.9º (*c* 1.0, $CHCl_3$), R_f 0.34 (hexane - EtOAc, 3:1). IR ($CHCl_3$, *ν*/cm^{-1}): 2929, 2857, 1463, 1257, 1082, 836, 775. ^{1}H NMR ($CDCl_3$) *δ*: 0.09 (s, 6H, CH_3), 0.92 (s, 9H, CH_3), 0.99 (d, 3H, CH_3, *J* 7.6 Hz), 1.42 (s, 3H, CH_3), 1.76 (m, 1H, $H^{1'}$), 1.87 (m, 1H, H^2), 2.08 (m, 2H, H^1, $H^{1'}$), 2.10 (m, 1H, H^2), 2.27 (m, 2H, H^6), 2.36 (s, 1H, ≡CH), 2.51 (m, 1H, H^5), 3.38 (s, 1H, OH), 3.43 (d, 1H, $H^{2'}$, *J* 8.1 Hz), 3.68 (m, 2H, CH_2OTBS), 4.09 (s, 1H, OH), 5.35 (d, 1H, H^4, *J* 9.8 Hz), 5.56 (m, 1H, H^3). ^{13}C NMR ($CDCl_3$) *δ*: -5.41 (CH_3), -5.29 (CH_3), 18.46 (**C**CH_3), 18.55 (CH_3), 25.44 (CH_3), 26.15 (CH_3), 29.06 (C^2), 34.41 (C^5), 36.94 ($C^{1'}$), 37.43 (C^1), 41.77 (C^6), 60.11 (CH_2OTBS), 71.32 ($C^{3'}$), 72.42 (≡CH), 77.71 ($C^{2'}$), 85.78 (≡C), 125.61 (C^3), 131.79 (C^4). Found, %: C 68.09; H 10.34. MS: *m/z* 319 [*M*-Me-H_2O]$^+$. Calc. for $C_{20}H_{36}O_3Si$: C 68.13; H 10.29.

16: colorless oil, $[\alpha]_D^{20}$ -34.7º (*c* 1.0, $CHCl_3$), R_f 0.34 (hexane - EtOAc, 3:1). IR ($CHCl_3$, *ν*/cm^{-1}): 2929, 2857, 1463, 1257, 1082, 836, 775. ^{1}H NMR ($CDCl_3$) *δ*: 0.01 (s, 6H, CH_3), 0.88 (s, 9H, CH_3), 1.03 (d, 3H, CH_3, *J* 7.6 Hz), 1.41 (m, 1H, $H^{1'}$), 1.33 (s, 3H, CH_3), 1.76 (m, 1H, H^2), 1.85 (dd, 1H, $H^{1'}$, *J* 13.9, 9.7 Hz), 1.94 (m, 1H, H^6), 2.06 (m, 2H, H^1, H^2), 2.47 (s, 1H, ≡CH), 2.50 (m, 1H, H^5), 2.85 (br.s, 1H, OH), 3.59 (m, 2H, CH_2OTBS), 3.78 (d, 1H, $H^{2'}$, *J* 9.7 Hz), 5.37 (d, 1H, H^4, *J* 10.0 Hz), 5.57 (ddd, 1H, H^3, *J* 10.0, 5.0, 2.8 Hz). ^{13}C NMR ($CDCl_3$) *δ*: -5.41 (CH_3), -5.37 (CH_3), 18.26 (**C**CH_3), 18.88

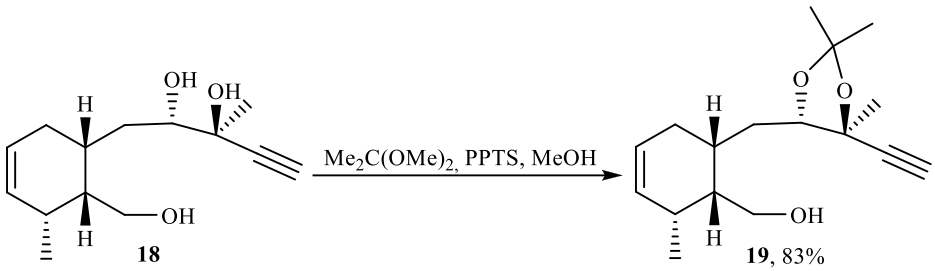
(CH_3), 23.64 (CH_3), 25.98 (CH_3), 30.09 (C^2), 34.32 ($C^{1'}$), 34.92 (C^1), 35.00 (C^5), 42.00 (C^6), 59.36 (CH_2OTBS), 70.95 ($C^{3'}$), 72.72 (≡CH), 75.67 ($C^{2'}$), 86.37 (≡C), 125.94 (C^3), 132.12 (C^4). Found, %: C 68.20; H 10.28. MS: *m/z*($I_{отн,}$ %): 319 (51) [*M*-Me-H_2O]$^+$, 277 (53), 195 (33), 157 (34), 119 (72), 105 (56), 75 (100). Calc. for $C_{20}H_{36}O_3Si$: C 68.13; H 10.29.

17: colorless oil, $[\alpha]_D^{20}$ -11.6º (*c* 1.0, $CHCl_3$), R_f 0.34 (hexane - EtOAc, 3:1). IR ($CHCl_3$, *ν*/cm^{-1}): 2929, 2857, 1463, 1256, 1086, 836, 775. ^{1}H NMR ($(CD_3)_2CO$), *δ*: 0.06 (s, 6H, CH_3), 0.89 (s, 9H, CH_3), 1.03 (d, 3H, CH_3, *J* 7.6 Hz), 1.38 (s, 3H, CH_3), 1.52 (ddd, 1H, $H^{1'}$, *J* 14.0, 10.6, 3.4 Hz), 1.73 (m, 1H, H^2), 1.87 (m, 1H, H^6), 1.93 (dd, 1H, $H^{1'}$, *J* 14.0, 4.7 Hz), 2.10 (m, 1H, H^1), 2.14 (m, 1H, H^2), 2.51 (m, 1H, H^5), 2.81 (s, 1H, ≡CH), 2.85 (br.s, 1H, OH), 3.53 (dd, 1H, $H^{2'}$, *J* 10.6, 4.7 Hz), 3.68 (m, 2H, CH_2OTBS), 5.39 (d, 1H, H^4, *J* 9.8 Hz), 5.58 (ddd, 1H, H^3, *J* 9.8, 3.9, 2.5 Hz). ^{13}C NMR ($(CD_3)_2CO$) *δ*: -6.08 (CH_3), -6.03 (CH_3), 17.82 (**C**CH_3), 18.20 (CH_3), 23.80 (CH_3), 25.47 (CH_3), 28.14 (C^2), 34.49 (C^1), 34.77 (C^5), 36.55 ($C^{1'}$), 42.95 (C^6), 59.72 (CH_2OTBS), 70.23 ($C^{3'}$), 72.36 (≡CH), 75.19 ($C^{2'}$), 87.14 (≡C), 125.58 (C^3), 131.93 (C^4). Found, %: C 68.16; H 10.36. MS: *m/z* (%): 319 (1) [*M*-Me-H_2O]$^+$, 277 (34), 195 (22), 157 (26), 119 (48), 105 (50), 75 (100). Calc. for $C_{20}H_{36}O_3Si$: C 68.13; H 10.29.

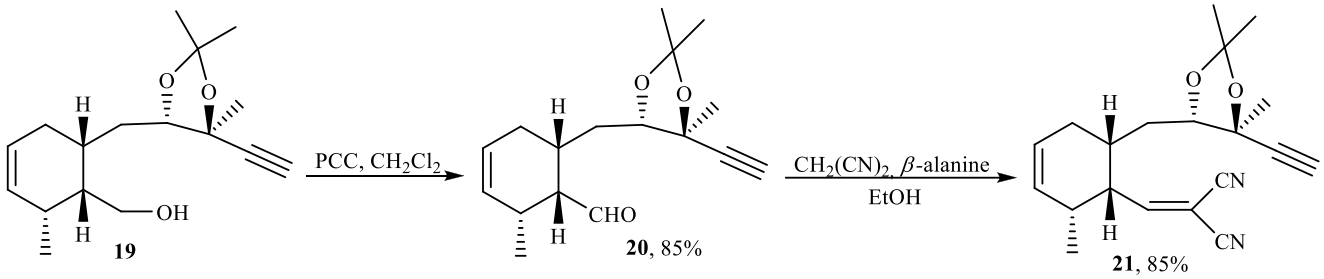


16 **18**, 92%

(2*S*,3*S*)-1-[(1*R*,5*R*,6*S*)-6-Hydroxymethyl-5-methylcyclohex-3-en-1-yl]-3-methylpent-4-yne-2,3-diol (18). Pyridinium *p*-toluenesulfonate, 0.026 g (5 wt %), was added to a solution of 0.520 g (1.48 mmol) of compound **16** in 5 ml of methanol. The mixture was stirred for 18 h and evaporated, and the residue was purified by silica gel chromatography. Yield 0.323 g (92%). colorless oil, $[\alpha]_D^{20}$ -26.5º (*c* 1.0, $CHCl_3$), R_f 0.33 (hexane - EtOAc, 1:1). IR ($CHCl_3$, *ν*/cm^{-1}): 2929, 1558, 1374, 1079, 756, 678. ^{1}H NMR ($CDCl_3$) *δ*: 1.07 (d, 3H, CH_3, *J* 7.5 Hz), 1.40 (ddd, 1H, $H^{1'}$, *J* 13.6, 4.5, 1.2 Hz), 1.45 (s, 3H, CH_3), 1.79 (m, 1H, H^2), 1.93 (m, 2H, $H^{1'}$, H^6), 2.05 (m, 1H, H^2), 2.10 (m, 1H, H^1), 2.50 (m, 1H, H^5), 2.51 (s, 1H, ≡CH), 2.80 (br.s, 1H, OH), 3.65 (m, 2H, CH_2OH), 3.76 (dd, 1H, $H^{2'}$, *J* 10.1, 1.2 Hz), 5.40 (d, 1H, H^4, *J* 10.0 Hz), 5.60 (m, 1H, H^3). ^{13}C NMR ($CDCl_3$) *δ*: 18.78 (CH_3), 23.94 (CH_3), 30.18 (C^2), 34.31 (C^1), 34.57 (C^5), 34.93 ($C^{1'}$), 41.76 (C^6), 59.19 (CH_2OH), 71.03 ($C^{3'}$), 73.11 (≡CH), 74.94 ($C^{2'}$), 86.12 (≡C), 126.41 (C^3), 132.10 (C^4). Found, %: C 70.66; H 9.36. MS: *m/z* 220.0 [*M*-H_2O]$^+$. Calc. for $C_{14}H_{22}O_3$: C 70.56; H 9.30.

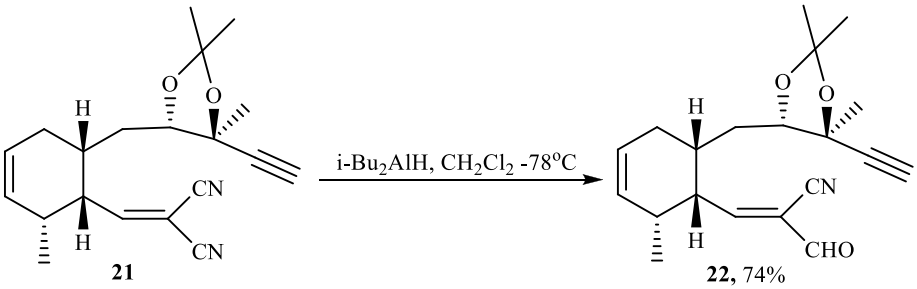


[(1*S*,2*R*,6*R*)-6-{[(4*S*,5*S*)-5-Ethynyl-2,2,5-trimethyl-1,3-dioxolan-4-yl]methyl}-2-methylcyclohex-3-en-1-yl]methanol (19). Triol **18** (0.300 g, 1.26 mmol) was dissolved in 3 ml of methanol, 1.55 ml (12.6 mmol) of 2,2-dimethoxypropane and 0.015 g (5 wt%) of PPTS were added, and the mixture was stirred until the reaction was complete (TLC). The solvent was distilled off, and the residue was purified by silica gel chromatography. Yield 0.290 g (83%), colorless oil, $[\alpha]_D^{20}$ -7.9° (*c* 1.0, $CHCl_3$), R_f 0.38 (hexane - EtOAc, 5:1). IR ($CHCl_3$, ν/cm^{-1}): 2935, 1373, 1187, 1085, 680. ^{1}H NMR ($CDCl_3$) δ: 1.08 (d, 3H, CH_3, *J* 7.6 Hz), 1.34 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.63 (ddd, 1H, H$^{1''}$, *J* 13.9, 9.1, 7.5 Hz), 1.74 (ddd, 1H, H$^{1''}$, *J* 13.9, 7.0, 3.8 Hz), 1.82 (m, 1H, H^5), 1.87 (m, 1H, H^1), 2.05 (m, 1H, H^6), 2.16 (m, 1H, H^5), 2.47 (s, 1H, ≡CH), 2.53 (m, 1H, H^2), 3.70 (m, 2H, CH_2OH), 4.28 (dd, 1H, H$^{4'}$, *J* 9.1, 3.8 Hz), 5.43 (d, 1H, H^3, *J* 9.5 Hz), 5.62 (m, 1H, H^4). ^{13}C NMR ($CDCl_3$) δ: 18.61 (CH_3), 23.27 (CH_3), 25.94 (CH_3), 28.36 (CH_3), 29.69 (C^5), 32.91 (C$^{1''}$), 34.38 (C^2), 35.06 (C^6), 43.12 (C^1), 59.70 (CH_2O), 72.43 (≡CH), 74.03 (C$^{5'}$), 81.10 (C$^{4'}$), 85.23 (≡C), 108.60 (C$^{2'}$), 126.30 (C^4), 132.15 (C^3). Found, %: C 73.28; H 9.39. MS: *m/z* 277.2 [*M*-H]$^+$. Calc. for $C_{17}H_{26}O_3$: C 73.34; H 9.41.



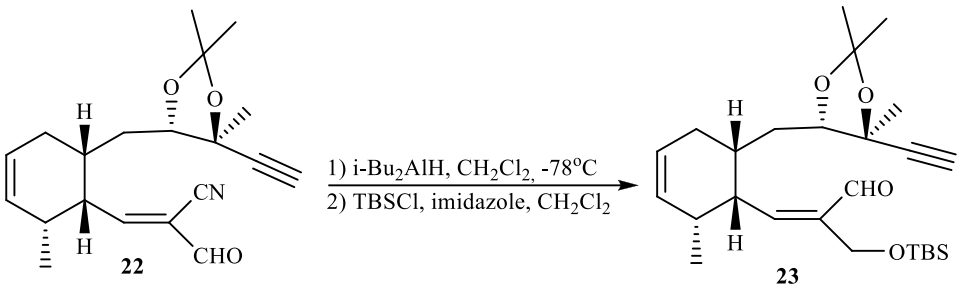
2-{[(1*S*,2*R*,6*R*)-6-{[(4*S*,5*S*)-2,2,5-Trimethyl-5-ethynyl-1,3-dioxolan-4-yl]methyl}-2-methylcyclohex-3-en-1-yl]methylidene}propanedinitrile (21). Pyridinium chlorochromate, 0.470 g (2.18 mmol), was added at 15°C to a solution of 0.275 g (0.99 mmol) of alcohol **19** in 15 ml of dichloromethane. The mixture was stirred for 30 min and diluted with 30 ml of petroleum ether (bp 40–70°C), the precipitate was filtered off and washed with petroleum ether, and the solvent was removed from the filtrate to isolate 0.232 g (85%) of aldehyde **20**. To a solution of 0.610 g (2.20 mmol) of aldehyde **20** in 10 ml of EtOH was added 0.656 g (9.95 mmol) of propanedinitrile and 0.118 g (1.32 mmol) of *β*-alanine. The reaction mixture was stirred for 60 h at 10°C, then 10 ml of EtOH and

10 ml of H_2O were added. The products were extracted with petroleum ether, the extract was dried with $MgSO_4$, evaporated, and the residue was chromatographed on SiO_2. Yield 0.625 g (87%), colorless oil, $[\alpha]_D^{20}$ -87.8º (*c* 1.0, $CHCl_3$), R_f 0.3 (hexane - EtOAc, 10:1). IR ($CHCl_3$, ν/cm^{-1}): 3300, 2936, 1374, 1187, 1095, 1003, 936, 685. ^{1}H NMR ($CDCl_3$) δ: 0.96 (d, 3H, CH_3, *J* 7.5 Hz), 1.34 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.45 (s, 3H, CH_3), 1.47 (m, 2H, H$^{1''}$), 1.78 (m, 1H, H^5), 2.33 (m, 1H, H^6), 2.36 (m, 1H, H^5), 2.53 (s, 1H, ≡CH), 2.77 (m, 1H, H^2), 3.14 (m, 1H, H^1), 4.27 (t, 1H, H$^{4'}$, *J* 6.5 Hz), 5.48 (d, 1H, H^3, *J* 10.1 Hz), 5.76 (ddd, 1H, H^4, *J* 10.1, 4.4, 2.4 Hz), 7.23 (d, 1H, H$^{3'}$, *J* 11.9 Hz). ^{13}C NMR ($CDCl_3$) δ: 19.07 (CH_3), 23.24 (CH_3), 25.89 (CH_3), 28.24 (CH_3), 28.94 (C^5), 33.74 (C$^{1''}$), 35.05 (C^2), 36.48 (C^6), 47.02 (C^1), 72.87 (≡CH), 75.19 (C$^{5''}$), 80.01 (C$^{4''}$), 84.52 (≡C), 92.08 (C$^{2'}$), 109.02 (C$^{2''}$), 110.90 (CN), 112.03 (CN), 126.08 (C^4), 129.92 (C^3), 169.20 (C$^{3'}$). Found, %: C 74.06; H 7.49; N 8.61. MS: *m/z*: 309.2 [*M*-Me]$^+$. Calc. for $C_{20}H_{24}N_2O_2$: C 74.04; H 7.46; N 8.64.

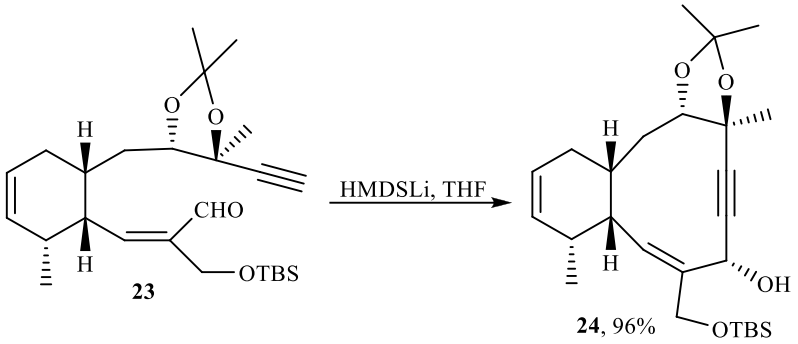


21 **22**, 74%

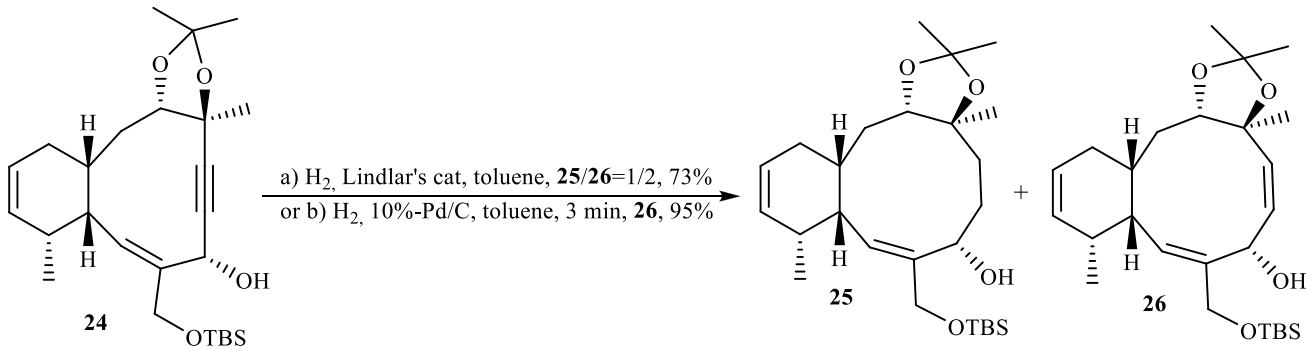
2(*E*)-3-[(1*S*,2*R*,6*R*)-6-{[(4*S*,5*S*)-2,2,5-Trimethyl-5-ethynyl-1,3-dioxolan-4-yl]methyl}-2-methylcyclohex-3-en-1-yl]-2-formylprop-2-enenitrile (22). To a solution of 0.625 g (1.93 mmol) of compound **21** in 75 ml of CH_2Cl_2 cooled to –95°C was added dropwise 0.75 ml (4.24 mmol) of 100% (*i*-Bu)$_2$AlH, and the mixture was stirred at this temperature for 1 min. Then to the reaction mixture 1 ml of *i*-PrOH and 2 ml of EtOAc were added, the reaction mixture was warmed to 0°C, 5 ml of H_2O was added, and the reaction mixture was treated with 3% solution of HCl till the disappearance of gel. Reaction products were extracted with CH_2Cl_2, the extract was dried with $MgSO_4$, evaporated, and the residue was chromatographed on SiO_2. Yield 0.467 g (74%), colorless oil, R_f 0.3 (hexane - EtOAc, 3:1). ^{1}H NMR ($CDCl_3$) δ: 0.96 (d, 3H, CH_3, *J* 7.6 Hz), 1.32 (s, 3H, CH_3), 1.40 (s, 3H, CH_3), 1.50 (m, 2H, H$^{1''}$), 1.56 (s, 3H, CH_3), 1.82 (m, 1H, H^5), 2.37 (m, 1H, H^6), 2.38 (m, 1H, H^5), 2.49 (s, 1H, ≡CH), 2.80 (m, 1H, H^2), 3.27 (m, 1H, H^1), 4.30 (dd, 1H, H$^{4'}$, *J* 9.2, 3.6 Hz), 5.50 (d, 1H, H^3, *J* 10.0 Hz), 5.78 (ddd, 1H, H^4, *J* 10.0, 4.4, 2.4 Hz), 7.39 (d, 1H, H$^{3'}$, *J* 11.7 Hz), 9.45 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$) δ: 19.03 (CH_3), 23.21 (CH_3), 25.96 (CH_3), 28.25 (CH_3), 29.01 (C^5), 33.80 (C$^{1''}$), 35.09 (C^2), 36.63 (C^6), 46.41 (C^1), 72.85 (≡CH), 75.20 (C$^{5''}$), 80.18 (C$^{4''}$), 84.52 (≡C), 108.94 (C$^{2''}$), 112.56 (CN), 123.02 (C$^{2'}$), 125.93 (C^4), 130.23 (C^3), 167.23 (C$^{3'}$), 185.64 (CHO). Found, %: C 73.45; H 7.64; N 4.34. Calc. for $C_{20}H_{25}NO_3$: C 73.37; H 7.70; N 4.28.



(2*Z*)-2-(*tert*-Butyldimethylsilyloxymethyl)-3-[(1*S*,2*R*,6*R*)-6-{[(4*S*,5*S*)-2,2,5-trimethyl-5-ethynyl-1,3-dioxolan-4-yl]methyl}-2-methylcyclohex-3-en-1-yl]prop-2-enal (23). To a solution of 0.460 g (1.41 mmol) of aldehyde **22** in 60 ml of CH_2Cl_2 cooled to –78°C was added dropwise 2.75 ml (11.25 mmol) of 73% toluene solution of (*i*-Bu)$_2$AlH. The reaction mixture was warmed to –40°C and was stirred for 3 h. Then 5 ml of *i*-PrOH and 5 ml of EtOAc were added dropwise, the reaction mixture was warmed to 0°C, 15 ml of H_2O was added, and the reaction mixture was treated with 3% solution of HCl till the disappearance of gel. Reaction products were extracted with CH_2Cl_2, the extract was dried with $MgSO_4$ and evaporated. The residue was dissolved in 5 ml of CH_2Cl_2, cooled to 0°C, and 0.213 g (1.41 mmol) of TBSCl and 0.096 g (1.41 mmol) of imidazole was added. The reaction mixture was stirred at room temperature till the disappearance of the initial compound (TLC monitoring), diluted with water (10 ml). Reaction products were extracted with CH_2Cl_2, the extract was dried with $MgSO_4$, evaporated, and the residue was chromatographed on SiO_2. Yield 0.450 g (72%), colorless oil, $[\alpha]_D^{20}$ -50.8º (*c* 1.0, $CHCl_3$), R_f 0.7 (hexane - EtOAc, 5:1). IR ($CHCl_3$, ν/cm^{-1}): 2926, 1668, 1463, 1374, 1254, 1184, 1108, 838. ^{1}H NMR ($CDCl_3$) δ: 0.04 (s, 3H, CH_3), 0.05 (s, 3H, CH_3), 0.88 (s, 9H, CH_3), 0.89 (m, 3H, CH_3), 1.29 (s, 3H, CH_3), 1.41 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.44 (m, 2H, C$^{1''}$H$_2$), 1.85 (m, 1H, H^5), 2.23 (m, 1H, H^6), 2.25 (m, 1H, H^5), 2.45 (s, 1H, ≡CH), 2.69 (m, 1H, H^2), 3.44 (d, 1H, H^1, *J* 12.3 Hz), 4.24 (dd, 1H, H$^{4'}$, *J* 8.3, 3.8 Hz), 4.36 (s, 2H, OCH_2), 5.42 (d, 1H, H^3, *J* 10.0 Hz), 5.71 (m, 1H, H^4), 6.72 (d, 1H, H$^{3'}$, *J* 12.3 Hz), 10.15 (s, 1H, CHO). ^{13}C NMR ($CDCl_3$) δ: -5.42 (CH_3), 14.12 (CH_3), 18.17 (**C**Me$_3$), 19.37 (CH_3), 23.09 (CH_3), 25.78 (CH_3), 25.94 (CH_3), 28.27 (CH_3), 28.83 (C^5), 33.36 (C$^{1''}$), 34.79 (C^2), 35.67 (C^6), 38.46 (C^1), 60.16 (CH_2OTBS), 72.76 (≡CH), 75.19 (C$^{5''}$), 80.34 (C$^{4''}$), 84.63 (≡C), 108.74 (C$^{2''}$), 125.69 (C^4), 130.52 (C^3), 142.30 (C$^{2'}$), 145.00 (C$^{3'}$), 190.03 (CO). Found, %: C 69.93; H 9.53. MS: *m/z* 431.2612 [*M*-Me]$^+$. Calc. for $C_{26}H_{42}O_4Si$: C 69.91; H 9.48.



(1*R*,3*S*,7*S*,10*S*,11*Z*,13*S*,14*R*)-11-(*tert*-Butyldimethylsilyloxymethyl)-5,5,7,14-tetramethyl-4,6-dioxatricyclo[11.4.0.0^{3,7}]heptadeca-11,15-dien-8-yn-10-ol (24). A 1.06 *M* solution of lithium hexamethyldisilazide in THF (1 ml, 1.02 mmol) was added at 0°C to a solution of 0.230 g (0.51 mmol) of aldehyde **23** in 5 ml of THF. The mixture was stirred for 15 min, treated with a saturated aqueous solution of ammonium chloride, and extracted with ethyl acetate. The extract was dried over $MgSO_4$ and evaporated, and the residue was purified by silica gel chromatography. Yield 0.220 g (96%). colorless oil, $[\alpha]_D^{20}$ -13.9º (*c* 1.0, $CHCl_3$), R_f 0.55 (hexane - EtOAc, 5:1). IR ($CHCl_3$, ν/cm^{-1}): 2926, 1457, 1374, 1246, 1047, 759. ^{1}H NMR ($CDCl_3$) δ: 0.09 (s, 3H, CH_3), 0.10 (s, 3H, CH_3), 0.90 (s, 6H, CH_3), 0.91 (m, 3H, CH_3), 1.23 (s, 3H, CH_3), 1.32 (s, 3H, CH_3), 1.42 (s, 3H, CH_3), 1.43 (s, 3H, CH_3), 1.47 (ddd, 1H, H^{2A}, *J* 14.9, 12.1, 2.8, Hz), 1.62 (m, 1H, H^{2B}), 1.79 (m, 1H, H^{17}), 2.04 (m, 1H, H^{1}), 2.06 (m, 1H, H^{17}), 2.51 (m, 1H, H^{14}), 2.87 (d, 1H, H^{1}, *J* 11.6 Hz), 3.99 (d, 1H, OH, *J* 8.7 Hz), 4.12 (dd, 1H, H^{3}, *J* 3.5, 2.8 Hz), 4.21 (d, 1H, CH_2OTBS, *J* 11.9 Hz), 4.49 (d, 1H, CH_2OTBS, *J* 11.9 Hz), 5.20 (d, 1H, H^{12}, *J* 11.6 Hz), 5.34 (m, 2H, H^{10}, H^{15}), 5.62 (m, 1H, H^{16}). ^{13}C NMR ($CDCl_3$) δ: -5.34 (CH_3), -5.14 (CH_3), 18.08 (**C**Me_3), 18.45 (CH_3), 22.39 (CH_3), 23.47 (CH_3), 25.74 (CH_3), 26.53 (CH_3), 28.41 (CH_3), 29.43 (C^{17}), 31.52 (C^{2}), 35.42 (C^{14}), 37.87 (C^{1}), 38.81 (C^{13}), 61.88 (C^{10}), 67.53 (CH_2OTBS), 76.05 (C^{7}), 83.87 (C^{3}), 87.75 (C^{8}), 93.34 (C^{9}), 108.87 (C^{5}), 124.38 (C^{12}), 125.42 (C^{16}), 131.43 (C^{15}), 144.29 (C^{11}). Found, %: C 69.89; H 9.54. MS: *m/z* 431.2618 [*M*-Me]$^+$. Calc. for $C_{26}H_{42}O_4Si$: C 69.91; H 9.48.



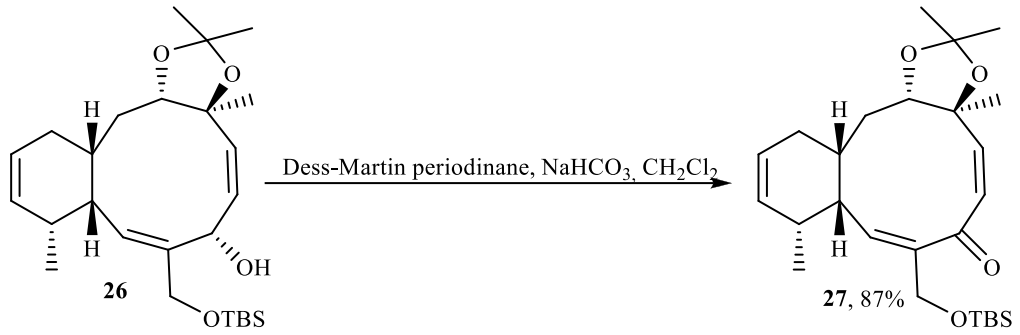
(1*R*,3*S*,7*S*,10*S*,11*Z*,13*S*,14*R*)-11-(*tert*-Butyldimethylsilyloxymethyl)-5,5,7,14-tetramethyl-4,6-dioxatricyclo[11.4.0.0^{3,7}]heptadeca-11,15-dien-10-ol (25) and **(1*R*,3*S*,7*S*,8*Z*,10*S*,11*Z*,13*S*,14*R*)-11-(*tert*butyldimethylsilyloxymethyl)-5,5,7,14-tetramethyl-4,6-dioxatricyclo[11.4.0.0^{3,7}]-heptadeca-8,11,15-trien-10-ol (26).** *a*. To 2 ml of toluene was added 0.023 g of Lindlar catalyst, and the solution was stirred for 30 min in a hydrogen atmosphere at a pressure of 1 bar. Then 0.015 g (0.034 mmol) of alcohol **24** in 2 ml of toluene was added, the reaction mixture was stirred for 6 h in a hydrogen atmosphere at a pressure of 1 bar. The precipitate was filtered off, washed with EtOAc, the filtrate was evaporated, and the residue was chromatographed on SiO_2. Yield 0.011 g (73%) of dienol **25** and trienol **26** (1 : 2).

b. To 2 ml of toluene was added 0.008 g of 10% Pd/C, and the solution was stirred for 30 min in a hydrogen atmosphere at a pressure of 1 bar. Then 0.020 g (0.045 mmol) of alcohol **24** in 2 ml of toluene was added, the reaction mixture was stirred for 3 min in a hydrogen atmosphere at a pressure of 1 bar. The precipitate was filtered off, washed with EtOAc, the filtrate was evaporated, and the residue was chromatographed on SiO_2. Yield 0.019 g (95%) of trienol **26**.

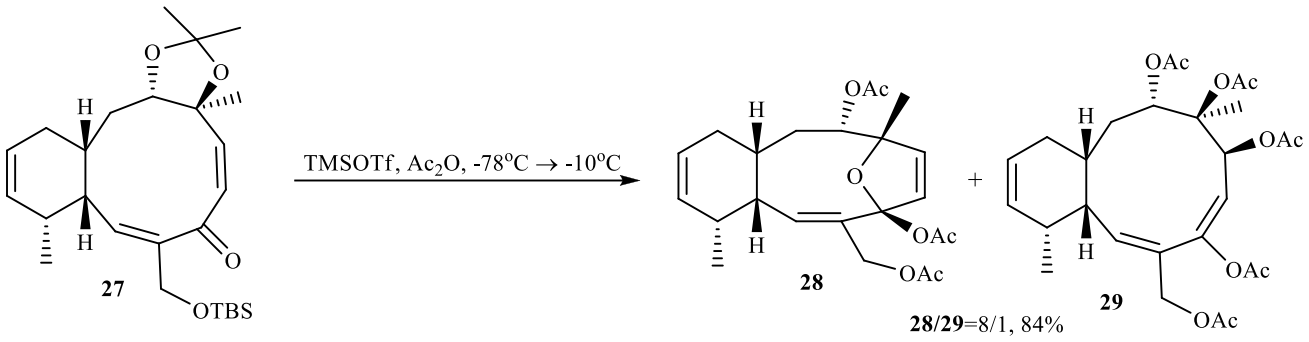
25 (from the mixture with **26**): colorless oil, R_f 0.25 (hexane - EtOAc, 5:1). ^{1}H NMR (C_6D_6) δ: -0.03 (s, 3H, CH_3), 0.00 (s, 3H, CH_3), 0.88 (s, 9H, CH_3), 0.91 (m, 3H, CH_3), 1.25 (m, 2H, H^{8}), 1.26 (s, 3H, CH_3), 1.30 (s, 3H, CH_3), 1.32 (m, 1H, H^{17}), 1.39 (s, 3H, CH_3), 1.45 (m, 3H, H^{2}, H^{9}), 1.78 (m, 1H, H^{2}), 1.83 (m, 1H, H^{17}), 2.04 (m, 1H, H^{14}), 2.22 (m, 1H, H^{1}), 2.73 (m, 1H, H^{13}), 4.08 (d, 1H, CH_2O, *J* 12.5 Hz), 4.27 (d, 1H, H^{3}, *J* 5.6 Hz), 4.48 (d, 1H, CH_2O, *J* 12.5 Hz), 5.00 (d, 1H, H^{10}, *J* 10.8 Hz), 5.40 (m, 1H, H^{15}), 5.44 (d, 1H, H^{12}, *J* 10.2 Hz), 5.56 (m, 1H, H^{16}). ^{13}C NMR (C_6D_6) δ: 1.04 (CH_3), 18.04 (**C**CH_3), 18.96 (CH_3), 22.76 (CH_3), 25.65 (CH_3), 26.23 (CH_3), 28.32 (CH_3), 29.69 (C^{17}), 30.34 (C^{9}), 31.98 (C^{8}), 34.22 (C^{1}), 36.73 (C^{2}), 37.94 (C^{13}), 38.48 (C^{14}), 65.38 (C$^{1'}$), 67.92 (C^{10}), 83.46 (C^{3}), 86.06 (C^{7}), 108.10 (C^{5}), 125.88 (C^{16}), 125.98 (C^{12}), 131.31 (C^{15}), 135.48 (C^{11}). Found, %: C 69.25; H 10.31. MS: *m/z*: 435.3 [*M*-Me]$^+$. Calc. for $C_{26}H_{46}O_4Si$: C 69.28; H 10.29.

26: colorless oil, $[\alpha]_D^{20}$ -32.2º (*c* 1.0, CH_2Cl_2), R_f 0.25 (hexane - EtOAc, 5:1). IR ($CHCl_3$, ν/cm^{-1}): 2957, 1372, 1265, 1048, 838, 759, 500. ^{1}H NMR (C_6D_6) δ: -0.04 (s, 3H, CH_3), -0.01 (s, 3H, CH_3), 0.88 (s, 9H, CH_3), 0.91 (d, 3H, CH_3, *J* 6.9 Hz), 1.16 (s, 3H, CH_3), 1.26 (m, 1H, H^{17}), 1.27 (m, 1H, H^{2}), 1.32 (s, 3H, CH_3), 1.48 (s, 3H, CH_3), 1.58 (ddd, 1H, H^{2}, *J* 14.9, 9.0, 3.0 Hz), 1.83 (m, 1H, H^{17}), 2.22 (m, 1H, H^{1}), 2.25 (m, 1H, H^{14}), 3.06 (dt, 1H, H^{13}, *J* 11.6, 3.6 Hz), 4.06 (d, 1H, CH_2O, *J* 12.6 Hz), 4.50 (dd, 1H, CH_2O, *J* 12.6, 1.4 Hz), 4.91 (d, 1H, H^{3}, *J* 9.0 Hz), 5.35 (d, 1H, H^{12}, *J* 11.6 Hz), 5.40 (d, 1H, H^{15}, *J* 10.1 Hz), 5.50 (dd, 1H, H^{8}, *J* 13.2, 1.4 Hz), 5.56 (ddd, 1H, H^{16}, *J* 10.1, 5.1, 2.4 Hz), 5.78 (dd, 1H, H^{9}, *J* 13.2, 7.5 Hz), 5.87 (d, 1H, H^{10}, *J* 7.5 Hz). ^{13}C NMR (C_6D_6) δ: -5.76 (CH_3), 17.95 (**C**CH_3), 19.36 (CH_3), 23.89 (CH_3), 25.65 (CH_3), 26.88 (CH_3), 28.56 (CH_3), 29.50 (C^{17}), 34.22 (C^{1}, C^{2}), 32.92 (C^{14}), 38.21 (C^{13}), 65.26 (C$^{1'}$), 67.18 (C^{10}), 73.81 (C^{3}), 82.87 (C^{7}), 107.04 (C^{5}), 123.66 (C^{12}), 125.25

(C^{16}), 130.31 (C^{8}), 131.10 (C^{15}), 132.94 (C^{9}), 142.20 (C^{11}). Found, %: C 69.61; H 9.90. MS: *m/z*: 433.3 [*M*-Me]$^+$. Calc. for $C_{26}H_{44}O_4Si$: C 69.59; H 9.88.



(1*R*,3*S*,7*S*,8*Z*,11*Z*,13*S*,14*R*)-11-(*tert*-Butyldimethylsilyloxymethyl)-5,5,7,14-tetramethyl-4,6-dioxatricyclo[11.4.0.0^{3,7}]heptadeca-8,11,15-trien-10-one (27). To a solution of 0.028 g (0.06 mmol) of triol **26** in 3 ml of CH_2Cl_2 at 0°C was added 0.051 g (0.62 mmol) of $NaHCO_3$, 0.031 g (0.07 mmol) of Dess–Martin reagent, and the reaction mixture was stirred for 3 h at 0°C. The mixture was treated with 3 ml of saturated $Na_2S_2O_3$ solution and 3 ml of saturated $NaHCO_3$ solution, diluted with 5 ml of H_2O, reaction products were extracted with petroleum ether, the extract was dried with $MgSO_4$, evaporated, the residue was chromatographed on SiO_2. Yield 0.024 g (87%), colorless oil, $[\alpha]_D^{20}$ -96.4º (*c* 1.0, CH_2Cl_2), R_f 0.55 (hexane - EtOAc, 3:1). IR ($CHCl_3$, ν/cm^{-1}): 2956, 1615, 1249, 1078, 1005, 838, 777. ^{1}H NMR (C_6D_6) δ: -0.01 (s, 3H, CH_3), 0.00 (s, 3H, CH_3), 0.71 (d, 3H, CH_3, *J* 7.5 Hz), 0.91 (s, 9H, CH_3), 1.31 (s, 3H, CH_3), 1.36 (s, 3H, CH_3), 1.37 (s, 3H, CH_3), 1.52 (ddd, 1H, H^2, *J* 15.0, 11.2, 7.1 Hz), 1.68 (m, 1H, H^{17}), 1.69 (m, 1H, H^1), 1.77 (m, 1H, H^2), 1.78 (m, 1H, H^{17}), 2.23 (m, 1H, H^{14}), 3.66 (dt, 1H, H^{13}, *J* 12.9, 2.2 Hz), 3.71 (d, 1H, H^3, *J* 7.1 Hz), 4.53 (dd, 1H, CH_2O, *J* 14.7, 1.3 Hz), 4.58 (dd, 1H, CH_2O, *J* 14.7, 1.6 Hz), 5.32 (d, 1H, H^{15}, *J* 10.1 Hz), 5.56 (m, 1H, H^{16}), 5.68 (d, 1H, H^9, *J* 14.0 Hz), 5.94 (d, 1H, H^8, *J* 14.0 Hz), 6.45 (d, 1H, H^{12}, *J* 12.9 Hz). ^{13}C NMR (C_6D_6) δ: -5.76 (CH_3), -5.73 (CH_3), 17.99 (**C**CH_3), 19.29 (CH_3), 22.12 (CH_3), 25.66 (CH_3), 26.35 (CH_3), 28.34 (CH_3), 28.66 (C^{17}), 33.58 (C^2), 34.27 (C^{14}), 38.04 (C^1), 39.00 (C^{13}), 62.60 ($C^{1'}$), 80.99 (C^3), 83.05 (C^7), 106.18 (C^5), 125.25 (C^{16}), 130.31 (C^{15}), 131.37 (C^8), 139.04 (C^{12}), 139.05 (C^9), 142.37 (C^{11}), 194.66 (C^{10}). Found, %: C 69.87; H 9.54. MS: *m/z*: 389.2 [*M*-CMe_3]$^+$. Calc. for $C_{26}H_{42}O_4Si$: C 69.91; H 9.48.

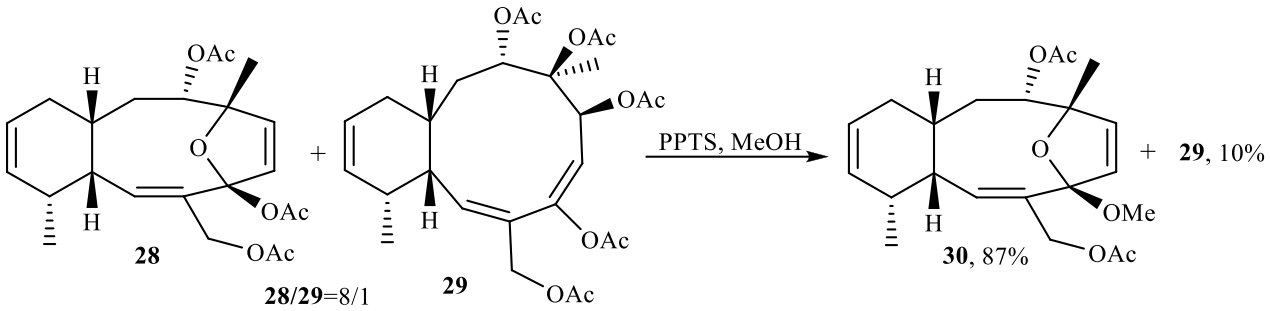


{(1*S*,2*Z*,4*S*,5*R*,9*R*,11*S*,12*S*)-1,11-Diacetoxy-5,12-dimethyl-15-oxatricyclo[10.2.1.0^{4,9}]-pentadeca-2,6,13-trien-2-yl}methyl acetate (28) and **{(4*R*,4a*S*,9*S*,10*R*,11*S*,12a*R*)-7,9,10,11-tetraacetoxy-4,10-dimethyl-4,4a,9,11,12,12a-hexahydro-1*H*-benzo[10]annulen-6-yl}methyl acetate (29).** To a solution of 0.083 g (0.186 mmol) of ketone **16** in 10 ml of a mixture CH_2Cl_2-Ac_2O, 4 : 1, was added 0.14 ml (0.744 mmol) of TMSOTf at –78°C. The reaction mixture was warmed to –10°C, and it was stirred at this temperature till the disappearance of the initial compound (TLC monitoring). The reaction mixture was treated with a saturated solution of $NaHCO_3$, the reaction products were extracted with ethyl acetate, the extract was dried with $MgSO_4$, evaporated, and the residue was chromatographed on SiO_2. Yield 0.065 g (84%) of triacetate **28** and pentaacetate **29** in a ratio 8 : 1.

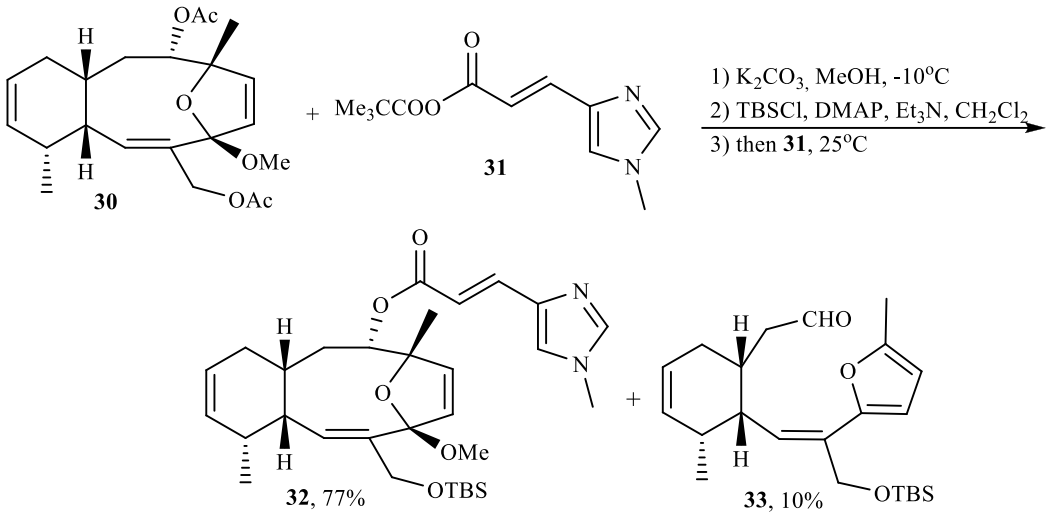
28: colorless oil, $[\alpha]_D^{20}$ -3.3º (*c* 0.5, CH_2Cl_2), R_f 0.6 (hexane - EtOAc, 1:1). IR ($CHCl_3$, ν/cm^{-1}): 2957, 1729, 1373, 1230, 1039, 736, 372. ^{1}H NMR ($CDCl_3$) δ: 0.93 (d, 3H, CH_3, *J* 7.5 Hz), 1.10 (dd, 1H, H^{10}, *J* 15.1, 3.2 Hz), 1.35 (ddd, 1H, H^{10}, *J* 15.1, 8.0, 3.6 Hz), 1.40 (m, 1H, H^8), 1.46 (s, 3H, CH_3), 1.81 (m, 1H, H^8), 1.99 (s, 3H, CH_3), 2.03 (s, 3H, CH_3), 2.14 (s, 3H, CH_3), 2.17 (m, 1H, H^9), 2.45 (m, 1H, H^5), 3.85 (dt, 1H, H^4, *J* 9.5, 3.6 Hz), 4.60 (d, 1H, CH_2O, *J* 12.5 Hz), 4.62 (d, 1H, CH_2O, *J* 12.5 Hz), 4.86 (d, 1H, H^{11}, *J* 8.0 Hz), 5.39 (d, 1H, H^6, *J* 10.0 Hz), 5.49 (d, 1H, H^3, *J* 9.5 Hz), 5.60 (ddd, 1H, H^7, *J* 10.0, 4.9, 2.5 Hz), 6.07 (d, 1H, H^{14}, *J* 5.8 Hz), 6.14 (d, 1H, H^{13}, *J* 5.8 Hz). ^{13}C NMR ($CDCl_3$) δ: 18.86 (CH_3), 20.82 (CH_3), 21.03 (CH_3), 21.25 (CH_3), 25.51 (CH_3), 29.36 (C^8), 34.03 (C^5), 36.59 (C^{10}), 37.91 (C^4), 39.20 (C^9), 66.71 (C$^{1'}$), 78.64 (C^{11}), 90.44 (C^{12}), 112.22 (C^1), 126.02 (C^7), 130.90 (C^6), 132.15 (C^{13}), 133.40 (C^{14}), 133.45 (C^3), 135.69 (C^2), 168.39 (CO), 169.87 (CO), 170.82 (CO). Found, %: C 65.93; H 7.25. MS: *m/z*: 375.2 [*M*-CH_3CO]$^+$. Calc. for $C_{23}H_{30}O_7$: C 66.01; H 7.23.

29: colorless oil, $[\alpha]_D^{20}$ -54.1º (*c* 0.5, CH_2Cl_2), R_f 0.6 (hexane - EtOAc, 1:1). IR ($CHCl_3$, ν/cm^{-1}): 2959, 1743, 1373, 1231, 1023, 737. ^{1}H NMR (C_6D_6) δ: 0.86 (d, 3H, CH_3, *J* 7.4 Hz), 1.30 (ddd, 2H, H^{12}, *J* 15.3, 8.0, 2.8 Hz), 1.40 (m, 2H, H^1, H^{12}), 1.58 (m, 1H, H^1), 1.56 (s, 3H, CH_3), 1.65 (s, 3H, CH_3), 1.66 (s, 3H, CH_3), 1.71 (s, 3H, CH_3), 1.77 (s, 3H, CH_3), 1.82 (s, 3H, CH_3), 1.97 (m, 1H, H^{12a}), 2.46 (m, 1H, H^4), 3.20 (ddd, 1H, H^{4a}, *J* 11.8, 4.5, 3.9 Hz), 4.12 (dd, 1H, CH_2O, *J* 13.9, 1.4 Hz), 5.20 (dd, 1H,

CH_2O, *J* 13.9, 1.3 Hz), 5.38 (m, 1H, H^3, *J* 9.9 Hz), 5.52 (ddd, 1H, H^2, *J* 9.9, 4.7, 2.4 Hz), 5.68 (d, 1H, H^5, *J* 11.8 Hz), 5.75 (d, 1H, H^{11}, *J* 8.0 Hz), 5.86 (d, 1H, H^9, *J* 10.5 Hz), 6.04 (d, 1H, H^8, *J* 10.5 Hz). ^{13}C NMR (C_6D_6) δ: 15.70 (CH_3), 18.83 (CH_3), 19.81 (CH_3), 20.05 (CH_3), 20.11 (CH_3), 20.36 (CH_3), 21.79 (CH_3), 29.07 (C^1), 33.56 (C^4), 34.55 (C^{12a}), 35.76 (C^{12}), 40.46 (C^{4a}), 65.65 ($C^{1'}$), 72.22 (C^{11}), 73.53 (C^9), 87.14 (C^{10}), 116.77 (C^8), 124.99 (C^2), 131.40 (C^3), 133.01 (C^5), 134.29 (C^6), 148.40 (C^7), 167.68 (CO), 168.69 (CO), 169.29 (CO), 169.41 (CO), 170.01 (CO). Found, %: C 62.36; H 7.03. MS: *m/z*: 538.25 $[M+H_2O]^+$. Calc. for $C_{27}H_{36}O_{10}$: C 62.30; H 6.97.



{(1*R*,2*Z*,4*S*,5*R*,9*R*,11*S*,12*S*)-11-Acetoxy-5,12-dimethyl-1-methoxy-15-oxatricyclo[10.2.1.0^{4,9}]-pentadeca-2,6,13-trien-2-yl}methyl acetate (30). To a solution of 0.044 g of a mixture of acetates **28** and **29** in 3 ml of MeOH at 25°C was added 0.003 g of PPTS. On completion of the reaction (TLC monitoring) the solvent was distilled off, the residue was chromatographed on SiO_2. We obtained 0.032 g (88%) of compound **30** and 0.007 g (10%) of initial pentaacetate **29**. Compound **30**: colorless oil, $[\alpha]_D^{20}$ +13.8º (*c* 0.5, CH_2Cl_2), R_f 0.5 (hexane - EtOAc, 2:1). IR ($CHCl_3$, ν/cm^{-1}): 2956, 1738, 1446, 1373, 1238, 1040. ^{1}H NMR (C_6D_6) δ: 0.88 (d, 3H, CH_3, *J* 7.5 Hz), 1.16 (dd, 1H, H^{10}, *J* 15.0, 3.1 Hz), 1.34 (s, 3H, CH_3), 1.45 (m, 1H, H^8), 1.54 (ddd, 1H, H^{10}, *J* 15.0, 11.5, 7.9 Hz), 1.62 (s, 3H, CH_3), 1.64 (s, 3H, CH_3), 1.70 (m, 1H, H^8), 2.28 (m, 1H, H^5), 2.30 (m, 1H, H^9), 3.11 (s, 3H, OCH_3), 3.97 (ddd, 1H, H^4, *J* 9.6, 4.8, 3.4 Hz), 4.62 (d, 1H, CH_2O, *J* 15.1 Hz), 4.64 (d, 1H, CH_2O, *J* 15.1 Hz), 5.04 (d, 1H, H^{11}, *J* 7.9 Hz), 5.36 (d, 1H, H^6, *J* 10.0 Hz), 5.55 (ddd, 1H, H^7, *J* 10.0, 4.5, 2.2 Hz), 5.66 (d, 1H, H^3, *J* 9.6 Hz), 5.81 (d, 1H, H^{14}, *J* 5.9 Hz), 5.96 (d, 1H, H^{13}, *J* 5.9 Hz). ^{13}C NMR (C_6D_6) δ: 18.76 (CH_3), 20.26 (CH_3), 20.39 (CH_3), 24.06 (CH_3), 29.35 (C^8), 34.06 (C^5), 36.79 (C^{10}), 37.88 (C^4), 39.29 (C^9), 49.13 (CH_3), 66.09 ($C^{1'}$), 78.71 (C^{11}), 90.23(C^{12}), 115.92 (C^1), 125.96 (C^7), 130.84 (C^6), 131.16 (C^{13}), 132.62 (C^3), 133.32 (C^{14}), 135.25 (C^2), 168.92 (CO), 169.39 (CO). Found, %: C 67.65; H 7.76. MS: *m/z*: 359.05 $[M-CH_3O]^+$. Calc. for $C_{22}H_{30}O_6$: C 67.67; H 7.74.



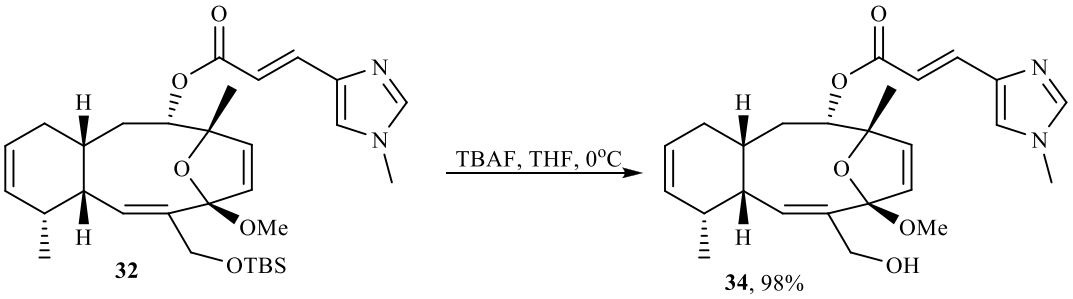
(1*S*,2*S*,4*R*,8*R*,9*S*,10*Z*,12*R*)-11-(*tert*-Butyldimethylsilyloxymethyl)-1,8-dimethyl-12-methoxy-15-oxatricyclo[10.2.1.0^{4,9}]pentadeca-6,10,13-trien-2-yl (2*E*)-3-(1-methyl-1*H*-imidazol-4-yl)prop-2-enoate (32) and **2-{(1*R*,5*R*,6*S*)-6-[(*Z*)-3-(*tert*-butyldimethylsilyloxy)-2-(5-methylfuran-2-yl)prop-1-enyl]-5-methylcyclohex-3-enyl}acetaldehyde (33).** To a solution of 0.080 g (0.58 mmol) of K_2CO_3 in 15 ml of MeOH cooled to –10°C was added a solution of 0.091 g (0.23 mmol) of diacetate **30** in 5 ml of MeOH. The obtained mixture was stirred at –10°C till total consumption of the initial compound (TLC monitoring). The solvent was distilled off, the obtained precipitate was washed with 15 ml of CH_2Cl_2, and the filtrate was evaporated.

To a solution of obtained crude diol in 6 ml of CH_2Cl_2 at 0°C was added 1 ml (6.90 mmol) of Et_3N, 0.040 g (0.33 mmol) of DMAP, and 0.088 g (0.58 mmol) of TBSCl. After complete consumption of the initial compound (TLC monitoring) to the reaction mixture 0.045 g (0.37 mmol) of DMAP was charged and dropwise was added 5.82 ml of (1.16 mmol) 0.2 *M* CH_2Cl_2 solution of mixed anhydride **31**. The mixture was stirred at room temperature for 24 h. The solvent was distilled off, and the residue was chromatographed on SiO_2. Yield 0.010 g (10%) of aldehyde **33** and 0.099 g (77%) of urocanate **32**.

32: colorless oil, $[\alpha]_D^{20}$ -39.7º (*c* 1.0, CH_2Cl_2), R_f 0.4 (EtOAc). ^{1}H NMR ($CDCl_3$) δ: 0.04 (s, 3H, CH_3), 0.05 (s, 3H, CH_3), 0.89 (s, 9H, CH_3), 0.96 (d, 3H, CH_3, *J* 7.5 Hz), 1.16 (dd, 1H, H^3, *J* 15.3, 3.2 Hz), 1.43 (m, 1H, H^5), 1.45 (s, 3H, CH_3), 1.50 (m, 1H, H^3), 1.81 (m, 1H, H^5), 2.21 (m, 1H, H^4), 2.47 (m, 1H, H^8), 3.22 (s, 3H, OCH_3), 3.72 (s, 3H, NCH_3), 3.84 (m, 1H, H^9), 4.03 (d, 1H, CH_2O, *J* 13.1 Hz), 4.17 (d, 1H, **C**CH_2O, *J* 13.1 Hz), 4.97 (d, 1H, H^2, *J* 8.0 Hz), 5.40 (d, 1H, H^7, *J* 9.9 Hz), 5.53 (d, 1H, H^{10}, *J* 9.7 Hz), 5.59 (ddd, 1H, H^6, *J* 9.9, 4.6, 2.4 Hz), 6.08 (d, 1H, H^{14}, *J* 6.0 Hz), 6.10 (d, 1H, H^{13}, *J* 6.0 Hz), 6.56 (d, 1H, H$^{2'}$, *J* 15.5 Hz), 7.10 (s, 1H, H^{5ar}), 7.49 (s, 1H, H^{2ar}), 7.52 (d, 1H, H$^{3'}$, *J* 15.5 Hz). ^{13}C NMR ($CDCl_3$) δ: - 5.37 (CH_3), 18.86 (**C**CH_3), 18.99 (CH_3), 24.42 (CH_3), 25.88 (CH_3), 29.67 (C^5), 33.63 (NCH_3), 34.24 (C^8), 36.53 (C^3), 37.64 (C^9), 39.31 (C^4), 49.48 (OCH_3), 64.79 (CH_2O), 78.96

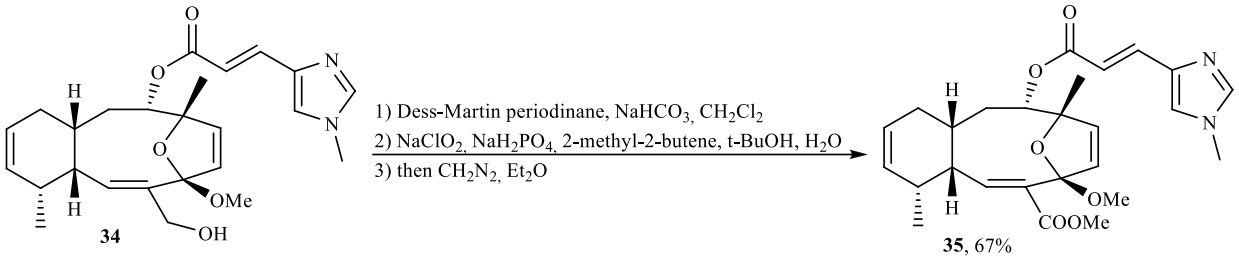
(C^{2}), 90.24 (C^{1}), 116.06 (C^{12}), 116.36 ($C^{2'}$), 123.63 (C^{5ar}), 126.00 (C^{6}), 128.28 (C^{10}), 131.03 (C^{13}), 131.16 (C^{7}), 133.54 (C^{14}), 138.08 ($C^{3'}$), 138.34 (C^{4ar}), 139.11 (C^{11}), 139.26 (C^{2ar}), 166.68 (CO). Found, %: C 67.15; H 8.05; N 5.01. Calc. for $C_{31}H_{46}N_2O_5Si$: C 67.11; H 8.36; N 5.05.

33: colorless oil, $[\alpha]_D^{20}$ –26.9° (*c* 0.5, $CHCl_3$), R_f 0.52 (hexane–EtOAc, 10:1). IR ($CHCl_3$, ν/cm^{-1}): 2928, 1726, 1361, 1254, 1133, 1047, 837, 776. ^{1}H NMR (C_6D_6) δ: 0.03 (s, 6H,CH_3), 0.93 (d, 3H, CH_3, *J* 7.5 Hz), 0.95 (s, 9H, CH_3), 1.69–1.76 (m, 2H, H_2), 1.79 (ddd, 1H, CHCHO, *J* 17.7, 5.5, 1.0 Hz), 2.05 (s, 3H, CH_3), 2.30 (ddd, 1H, CHCHO, *J* 17.7, 8.3, 1.0 Hz), 2.43 (m, 1H, H^{1}), 2.51 (m, 1H, H^{5}), 3.51 (dt, 1H, H^{6}, *J* 11.7, 3.6 Hz), 4.38 (dd, 1H, $H^{3'}$, *J* 13.2, 1.5 Hz), 4.41 (dd, 1H, $H^{3'}$, *J* 13.2, 1.5 Hz), 5.41 (d, 1H, H^{4}, *J* 9.9 Hz), 5.60 (ddd, 1H, H^{3}, *J* 9.9, 4.8, 2.6 Hz), 5.70 (d, 1H, $H^{1'}$, *J* 11.7 Hz), 5.78 (dt, 1H, H^{4ar}, *J* 3.2, 1.0 Hz), 6.16 (d, 1H, H^{3ar}, *J* 3.2 Hz), 9.34 (s, 1H, CHO). ^{13}C NMR (C_6D_6) δ: -5.52 (CH_3), -5.51 (CH_3), 13.13 (CH_3), 18.14 (CCH_3), 18.73 (CH_3), 25.68 (CH_3), 28.15 (C^{2}), 32.88 (C^{1}), 34.98 (C^{5}), 39.73 (C^{6}), 48.14 (CHCHO), 65.08 ($C^{3'}$), 106.79 (C^{4ar}), 108.99 (C^{3ar}), 123.35 ($C^{1'}$), 125.28 (C^{3}), 127.97 ($C^{2'}$), 131.67 (C^{4}), 132.06 (C^{5ar}), 151.03 (C^{2ar}), 200.08 (CO). Found, %: C 71.15; H 9.27. MS: *m/z* 388.2 $[M]^+$. Calc. for $C_{23}H_{36}O_3Si$: C 71.08; H 9.34.



(1*S*,2*S*,4*R*,8*R*,9*S*,10*Z*,12*R*)-11-Hydroxymethyl-1,8-dimethyl-12-methoxy-15-oxatricyclo-[10.2.1.0$^{4.9}$]pentadeca-6,10,13-trien-2-yl (2*E*)-3-(1-methyl-1*H*-imidazol-4-yl)prop-2-enoate (34). To a solution of 0.047 g (0.08 mmol) of compound **32** in 6 ml of anhydrous THF cooled to 0°C was added 0.040 g (0.12 mmol) of $Bu_4NF{\cdot}3H_2O$. After a complete consumption of the initial compound (TLC monitoring) the reaction mixture was evaporated. The residue was chromatographed on SiO_2. Yield 0.036 g (97%), colorless oil, $[\alpha]_D^{20}$ -24.7º (*c* 1.0, $CHCl_3$), R_f 0.35 ($CHCl_3$ – MeOH, 15:1). IR ($CHCl_3$, ν/cm^{-1}): 2957, 1700, 1640, 1272, 1161, 980. ^{1}H NMR ($(CD_3)_2CO$) δ: 0.99 (d, 3H, CH_3, *J* 7.6 Hz), 1.17 (dd, 1H, H^{3}, *J* 15.1, 3.1 Hz), 1.37 (m, 1H, H^{5}), 1.40 (ddd, 1H, H^{3}, *J* 15.1, 7.9, 3.7 Hz), 1.46 (s, 3H, CH_3), 1.81 (m, 1H, H^{5}), 2.21 (m, 1H, H^{4}), 2.46 (m, 1H, H^{8}), 3.29 (s, 3H, OCH_3), 3.70 (s, 3H, NCH_3), 3.85 (m, 1H, H^{9}), 3.96 (d, 1H, CH_2O, *J* 12.1 Hz), 4.14 (d, 1H, CH_2O, *J* 12.1 Hz), 4.96 (d, 1H, H^{2}, *J* 7.9 Hz), 5.39 (d, 1H, H^{7}, *J* 9.8 Hz), 5.44 (d, 1H, H^{10}, *J* 9.7 Hz), 5.58 (ddd, 1H, H^{6}, *J* 9.8, 4.5, 2.1 Hz), 6.09 (d, 1H, H^{13}, *J* 5.9 Hz), 6.18 (d, 1H, H^{14}, *J* 5.9 Hz), 6.55 (d, 1H, $H^{2'}$, *J* 15.6 Hz), 7.10 (s, 1H, H^{5ar}), 7.48 (s, 1H, H^{2ar}), 7.52 (d, 1H, $H^{3'}$, *J* 15.6 Hz). ^{13}C NMR ($CDCl_3$) δ: 18.96 (CH_3), 23.85 (CH_3),

29.30 (C^5), 33.67 (NCH_3), 34.00 (C^8), 36.49 (C^3), 37.62 (C^9), 39.04 (C^4), 49.65 (OCH_3), 66.76 (CH_2O), 78.69 (C^2), 90.66 (C^1), 115.98 ($C^{2'}$), 116.95 (C^{12}), 122.72 (C^{5ar}), 125.89 (C^6), 129.88 (C^{13}), 131.04 (C^7), 131.67 (C^{10}), 135.17 (C^{14}), 136.32 ($C^{3'}$), 138.28 (C^{4ar}), 138.88 (C^{11}), 139.21 (C^{2ar}), 166.68 (CO). Found, %: C 68.12; H 7.39; N 6.26. MS: *m/z*: 441.25 $[M+H]^+$. Calc. for $C_{25}H_{32}N_2O_5$: C 68.16; H 7.32; N 6.36.



Methyl (1*R*,2*E*,4*S*,5*R*,9*R*,11*S*,12*S*)-1-methoxy-5,12-dimethyl-11-{[(2*E*)-3-(1-methyl-1*H*-imidazol-4-yl)prop-2-enyl]oxy}-15-oxatricyclo[10.2.1.0^{4,9}]pentadeca-2,6,13-triene-2-carboxylate or 12,13-dedihydro-14-deisopropyl-11-demethyl-11,12-dihydro-4-methoxy-14(*R*)-methyl-sarcodictyin A (35). To a solution of 0.036 g (0.08 mmol) of alcohol **34** in 3 ml of CH_2Cl_2 was added 0.067 g (0.82 mmol) of $NaHCO_3$, 0.043 g (0.1 mmol) of Dess–Martin reagent, and the reaction mixture was stirred at room temperature. After a complete consumption of the initial compound 0.1 ml of 2-propanol was added, and the stirring was continued for 10 min. The solvent was evaporated, and the residue was chromatographed on SiO_2. The obtained aldehyde without purification was dissolved in 2.4 ml of a mixture *t*-BuOH–H_2O, 5 : 1, cooled to 0°C, 0.43 ml (4.09 mmol) of 2-methylbut-2-ene, 0.045 g (0.29 mmol) of NaH_2PO_4, and 0.022 g (2.45 mmol) of $NaClO_2$ was added. After a complete consumption of the initial compound (TLC monitoring) a saturated solution of diazomethane in Et_2O was added to the reaction mixture. The reaction mixture was diluted with water, the reaction products were extracted with EtOAc, the extract was dried with $MgSO_4$, evaporated, the residue was chromatographed on SiO_2. Yield 0.025 g (67%), colorless oil, $[\alpha]_D^{20}$ -31.3º (*c* 1.0, CH_2Cl_2), R_f 0.25 (EtOAc). IR ($CHCl_3$, ν/cm^{-1}): 3305, 2953, 1695, 1644, 1516, 1410, 1311, 1214, 1156, 1079. ^{1}H NMR ($CDCl_3$) δ: 0.98 (d, 3H, CH_3, *J* 7.5 Hz), 1.21 (dd, 1H, H^{10}, *J* 15.1, 3.1 Hz), 1.38 (m, 1H, H^8), 1.40 (m, 1H, H^{10}), 1.46 (s, 3H, CH_3), 1.86 (m, 1H, H^8), 2.24 (m, 1H, H^9), 2.54 (m, 1H, H^5), 3.16 (s, 3H, OCH_3), 3.68 (s, 3H, OCH_3), 3.76 (s, 3H, NCH_3), 4.11 (d.t, 1H, H^4, *J* 10.0, 3.8 Hz), 4.93 (d, 1H, H^{11}, *J* 7.8 Hz), 5.46 (d, 1H, H^6, *J* 10.0 Hz), 5.66 (ddd, 1H, H^7, *J* 10.0, 4.45, 2.2 Hz), 6.33 (d, 1H, H^{13}, *J* 6.0 Hz), 6.46 (d, 1H, $H^{2'}$, *J* 15.6 Hz), 6.53 (d, 1H, H^{14}, *J* 6.0 Hz), 6.60 (d, 1H, H^3, *J* 10.0 Hz), 7.44 (s, 1H, H^{5ar}), 7.57 (d, 1H, $H^{3'}$, *J* 15.6 Hz), 7.59 (s, 1H, H^{2ar}). ^{13}C NMR ($(CD_3)_2CO$) δ: 18.55 (CH_3), 23.62 (CH_3), 29.20 (C^8), 32.74 (NCH_3), 33.99 (C^5), 36.42 (C^{10}), 38.27 (C^4), 39.21 (C^9), 49.18 (OCH_3), 51.07 (OCH_3), 77.99 (C^{11}), 89.88 (C^{12}), 114.31 ($C^{2'}$), 115.54 (C^1), 123.92 (C^{5ar}), 126.18 (C^7), 130.49 (C^6), 131.54 (C^{14}), 134.63 (C^{13}), 134.73 (C^2), 137.44 ($C^{3'}$), 137.86 (C^{4ar}), 139.77 (C^{2ar}), 142.37 (C^3), 166.05 (CO),

166.25 (CO). Found, %: C 66.71; H 6.85; N 5.89. MS: *m/z*: 469.25 $[M+H]^+$. Calc. for $C_{26}H_{32}N_2O_6$: C 66.65; H 6.88; N 5.98.