

Experimental

Part

1. Generalities

Solvents and reagents used in this work were purified according to standard literature techniques and stored under argon. Experiments which required an inert atmosphere were carried out under dry argon in a flame dried glass system. Flash chromatographies were run on silica gel (Merck 60, 230-400 mesh) with the solvent mixture indicated. Thin layer chromatography was performed on commercial silica plates that were developed by immersion in 5% phosphomolybdic acid in 95% ethanol. "Usual work up" means washing of the organic layer with brine, drying on anhydrous MgSO_4 , and evaporating *in vacuo* with a rotary evaporator at aspirator pressure.

Beilstein numerotation is given for the compounds, except for all compounds of iridals synthesis (iridals numerotation).

Melting points were determined on a Büchi B-540 apparatus and were uncorrected.

Optical rotations were measured (in CHCl_3) on a JASCO-P1010 polarimeter using a cell of 1 dm-length path.

IR spectra were recorded on a Perkin-Elmer Spectrum BX instrument with an FT-IR system, in chloroform solution. Absorption are given in cm^{-1} .

NMR spectra were run in CDCl_3 unless otherwise noted. They were recorded on either a Bruker Avance 300 NMR, 400 NMR or 500 NMR spectrometer (300, 400 and 500 MHz respectively). Gradients were used for the coherence transfert pathway selection in HMBC and HMQC experiments. In the latter, broadband decoupling was performed by using adiabatic WURST-40 pulses. For all compounds investigated, multiplicities of ^{13}C resonances were assigned by the SEFT technique¹³⁷. Experimental evidence favoring the structures investigated came from a comprehensive range of ^1H and ^{13}C NMR data (1D and 2D experiments) and corroborated by spatial proximity (n.O.e) studies using mainly the 1D NOEDIFF technique¹³⁸. ^1H chemical shifts are expressed in ppm downfield from TMS using the residual nondeuterated solvent as internal standard (CDCl_3 ^1H , 7.26 ppm; C_6D_6

¹³⁷ LeCocq, C.; Lallemand, J.-Y., *J. Chem. Soc. Chem. Commun.*, **1981**, 150-152.

¹H, 7.15 ppm, DMSO ¹H, 2.54 ppm). ¹³C spectra were measured at 75 and 125 MHz and the chemical shifts are reported relative to CDCl₃, C₆D₆ triplet or DMSO heptuplet centered respectively at 77.0 ppm, 128.0 ppm and 40.45 ppm. The NMR data are presented in the order:

δ value of the signal, peak multiplicity (abbreviations used are as follows: s, singlet; d, doublet; t, triplet; q, quartet; quint, quintet; m, multiplet), coupling constants in MHz and integrated number of protons.

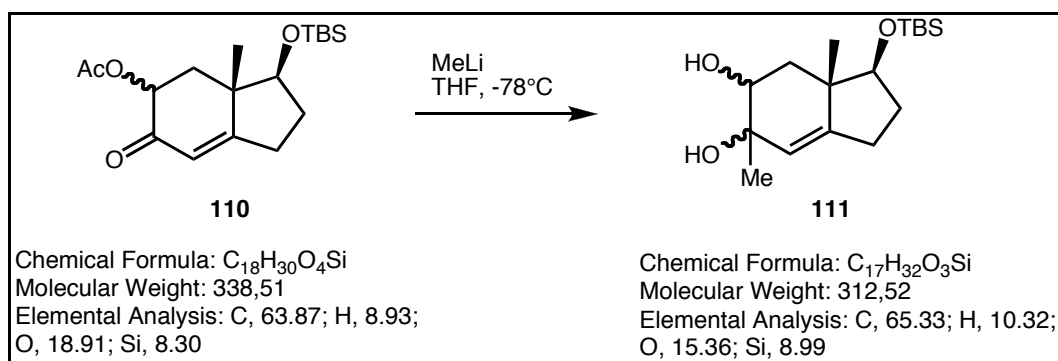
Low-resolution mass spectra were obtained with a Navigator LC/MS (AQA source) and acquired in the positive ion mode under electron spray ionization (ES⁺) using a mobil phase of methanol. They are abbreviated as ESIMS (MeOH). High-resolution mass spectra (HRESIMS) were performed with a LCT of Micromass[®] spectrometer.

Elemental analyses were performed with a CHN Perkin-Elmer analyzer.

Samples for XR structures were studied on a NONIUS Kappa CCD with graphite monochromatized MoK radiation.

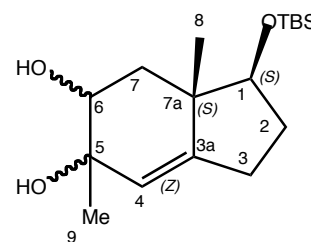
¹³⁸ Hall, L. D.; Sanders, J. K. M., *J. Am. Chem. Soc.*, **1980**, *102*, 5703-5711

2. Experimental part: Chapter 1.



To a stirred solution of **110** (518 mg, 1.53 mmol), in THF (10 mL), at -78°C, methyl lithium (3.48 mL, 2.2M in Et₂O) was slowly added. The solution was stirred 1 h at -78°C. Then the reaction mixture was diluted with ether, and a saturated solution of NH₄Cl was added until pH = 7. The aqueous layer was extract with Et₂O. The organic layer was worked up as usual and chromatographed on silica gel (ethyl acetate/heptane 4:6) to **111** yield (342 mg, 72%).

111: 3-(*tert*-Butyl-dimethyl-silyloxy)-3a,6-dimethyl-2,3,3a,4,5,6-hexahydro-1*H*-indene-5,6-diol.



Mp: colourless oil (characterized as a diastereomeric mixture).

$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

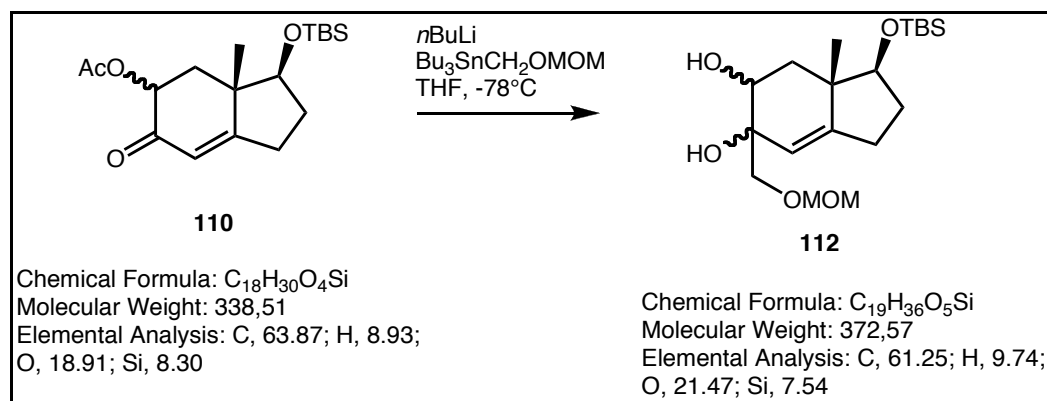
IR (film): ν = 3370, 2954, 1462, 1377, 1249, 1102, 1047, 909, 833, 773 cm⁻¹.

¹H-NMR (CDCl₃, 500 MHz): δ = characterized as a diastereomeric mixture.

¹³C-NMR (CDCl₃, 125 MHz): δ = characterized as a diastereomeric mixture.

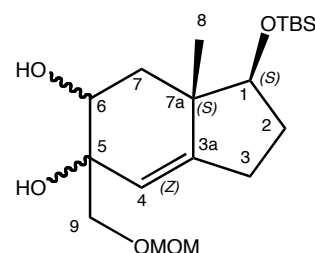
ESIMS (CH₂Cl₂ + MeOH): 335.2 ([*M* + Na]⁺, 100); 647.4 ([2*M* + Na]⁺, 100). HRESIMS: calcd. for C₁₇H₃₂O₃SiNa *m/z* 335.2018, found 335.1996.

Analysis calcd. for $C_{17}H_{32}O_3Si \cdot 0.9 H_2O$ (312.52): C 62.11, H 10.36; found C 62.09, H 9.81.



To a stirred solution of Bu_3SnCH_2OMOM **115** (783 mg, 2.15 mmol), in dry THF (5 mL), at $-78^\circ C$ under Argon, *n*-BuLi (1.35 mL, 1.6M in hexane) was slowly added (over 5 min). The reaction was stirred 5 min, and then a solution of **110** (297 mg, 0.88 mmol), in THF (5 mL) was slowly added. The reaction was stirred 20 min at $-78^\circ C$. The reaction mixture was diluted with diethyl ether, and a saturated solution of NH_4Cl was added until pH = 7. The aqueous layer was extract with ethyl acetate. The organic layer was worked up as usual and chromatographed on silica gel (ethyl acetate/heptane 2:8) to afford 276 mg of **112** (81%).

112: 3-(*tert*-Butyl-dimethyl-silyloxy)-6-methoxymethoxymethyl-3a-methyl-2,3,3a,4,5,6-hexahydro-1*H*-indene-5,6-diol.



Mp: colourless oil (characterized as a diastereomeric mixture).

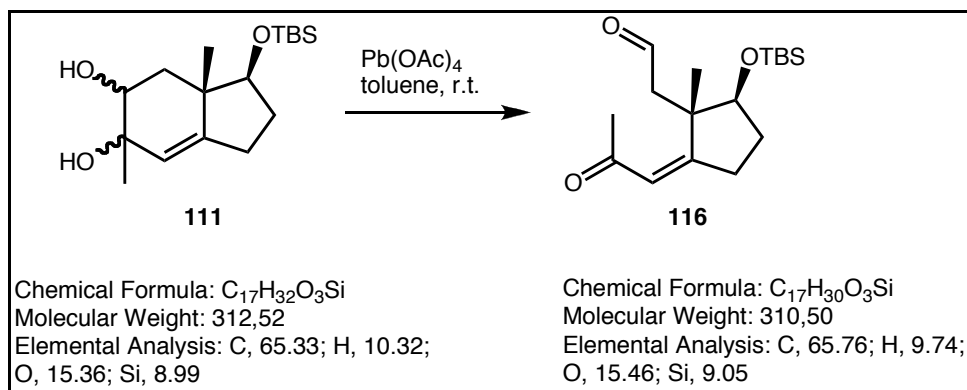
$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

IR (film): $\nu = 3420, 2929, 1743, 1463, 1378, 1250, 1148, 1106, 1041, 913, 836 \text{ cm}^{-1}$.

1H -NMR ($CDCl_3$, 500 MHz): δ = characterized as a diastereomeric mixture.

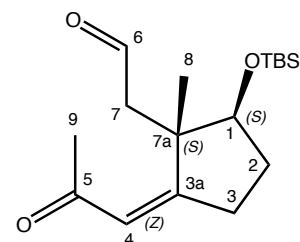
^{13}C -NMR ($CDCl_3$, 125 MHz): δ = characterized as a diastereomeric mixture.

ESIMS (MeOH + CH₂Cl₂): 395.2 ([M + Na]⁺, 100). HRESIMS: calcd. for C₁₉H₃₆O₅SiNa *m/z* 395.2230, found 395.2229.



A dry flask was charged with unsaturated diols **111** (26 mg, 0.083 mmol, diastereomeric mixture) and Pb(OAc)₄ (111 mg, 0.25 mmol, 3 eq.) vacuumed, flushed with argon and cooled to 0°C. Toluene (1 mL) was added, the cooling bath removed soon after and the reaction mixture was stirred for 15 h at room temperature, diluted with diethyl ether, filtered through MgSO₄/Celite/silica, the filtrate concentrated and purified by silica gel chromatography using diethyl ether-heptane, 1:1 as an eluent to give **116** (26 mg, 100%).

116: [2-(*tert*-Butyl-dimethyl-silanyloxy)-1-methyl-5-(2-oxo-propylidene)-cyclopentyl]-acetaldehyde.



Mp: colourless oil.

$[\alpha]_D^{20}$ = can't be obtained pure.

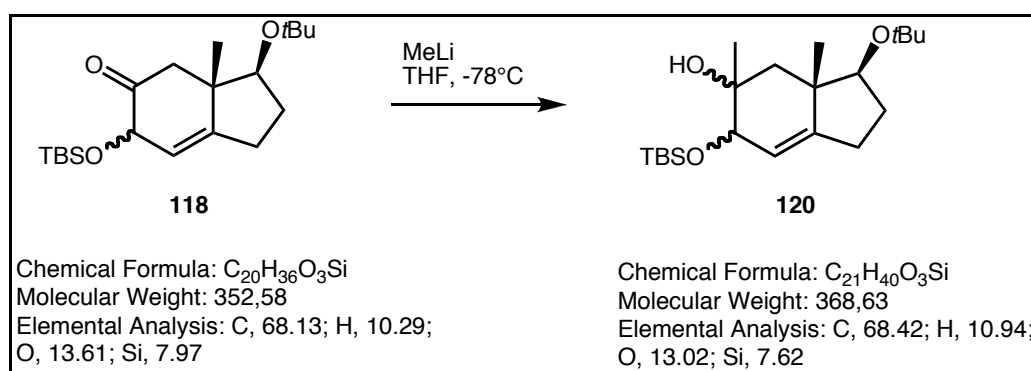
IR (film): ν = 2954, 1720, 1687, 1614, 1462, 1380, 1359, 1251, 1187, 1117, 885, 835 cm⁻¹.

¹H-NMR (CDCl₃, 500 MHz): δ = 0.02 (s, 3 H, SiMe), 0.03 (s, 3 H, SiMe), 0.88 (s, 9 H, Si*t*Bu), 1.10 (s, 3 H, H8), 1.23 (d, *J* = 10.6 Hz, 1 H, H3), 1.82 - 1.92 (m, 1 H, H3'), 2.13 (s, 3 H, H9), 2.40 - 2.66 (m, 2 H, H2), 2.73 (dd, *J* = 1.4, 18.0 Hz, 1 H, H7), 3.57 (dd, *J* = 1.3,

18.0 Hz, 1 H, H7'), 4.08 (dd, $J = 6.0, 10.1$ Hz, 1 H, H1), 6.16 (s, 1 H, H4), 9.57 (s, 1 H, H6).

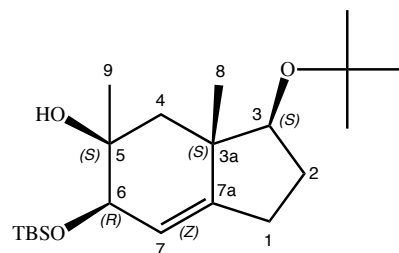
^{13}C -NMR (CDCl_3 , 125 MHz): $\delta = -5.1$ (SiMe), -4.8 (SiMe), 17.4 (C8), 18.0 (Cq-Si*t*Bu), 25.8 (3C-Si*t*Bu), 29.8 (C3), 31.9 (C9), 32.5 (C2), 47.5 (C7a), 49.7 (C7), 78.5 (C1), 121.5 (C4), 168.4 (C3a), 197.4 (C5), 201.9 (C6).

ESIMS ($\text{MeOH} + \text{CH}_2\text{Cl}_2$): 333.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{17}\text{H}_{30}\text{O}_3\text{SiNa}$ m/z 333.1862, found 333.1847.



To a stirred solution of **118** (105 mg, 0.3 mmol), in THF (10 mL), at -78°C , methyl lithium (0.6 mL, 1.6M in Et_2O) was slowly added. The solution was stirred 1 h at -78°C . Then the reaction mixture was diluted with ether, and a saturated solution of NH_4Cl was added until $\text{pH} = 7$. The aqueous layer was extract with Et_2O . The organic layer was worked up as usual and chromatographed on silica gel (ethyl acetate/heptane 1:9) to afford 87 mg of **120** (79%).

120: 3-*tert*-Butoxy-6-(*tert*-butyl-dimethyl-silanyloxy)-3a,5-dimethyl-2,3,3a,4,5,6-hexahydro-1*H*-inden-5-ol.



Mp: 57 - 58°C.

$[\alpha]_D^{20} = -68$ (c 0.8, CHCl_3).

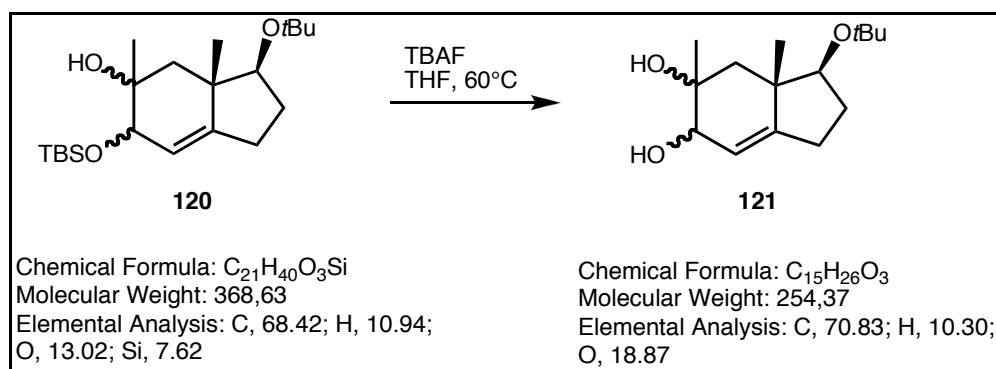
IR (film): $\nu = 2969, 2924, 2857, 1472, 1372, 1254, 1192, 1077, 1041, 886, 836 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 0.12$ (s, 3 H, SiMe), 0.13 (s, 3 H, SiMe), 0.93 (s, 9 H, Si*t*Bu), 1.16 (s, 9 H, O*t*Bu), 1.17 (s, 6 H, H8, H9), 1.40 and 1.95 (ABquartet, $J = 14.2$ Hz, 2 H, H4), 1.64 (tdd, $J = 6.1, 8.8, 13.0$ Hz, 1 H, H2), 1.89 (tdd, $J = 4.1, 8.3, 9.2$ Hz, 1 H, H2'), 2.04 (ddd, $J = 6.1, 9.7, 15.8$ Hz, 1 H, H1), 2.53 (ddd, $J = 4.2, 6.2, 15.5$ Hz, 1 H, H1'), 2.78 (s, 1 H, OH), 3.36 (t, $J = 8.6$ Hz, 1 H, H3), 3.98 (s, 1 H, H6), 5.16 (s, 1 H, H7).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = -4.8$ (SiMe), -3.8 (SiMe), 18.1 (Cq-Si*t*Bu), 18.6 (C8), 25.9 (3C-Si*t*Bu), 26.5 (C1), 28.6 (C9), 28.9 (3C-O*t*Bu), 30.3 (C2), 43.7 (C3a), 44.7 (C4), 70.0 (C5), 72.4 (Cq-O*t*Bu), 74.2 (C6), 80.2 (C3), 119.2 (C7), 148.5 (C7a).

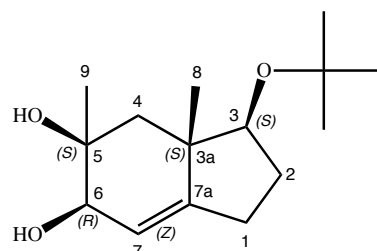
ESIMS (MeOH): 391.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{21}\text{H}_{40}\text{O}_3\text{NaSi}$ m/z 391.2644, found 391.2614.

Analysis calcd. for $\text{C}_{21}\text{H}_{40}\text{O}_3\text{Si}$ (368.63): C 68.42, H 10.94; found C 68.37, H 10.83.



TBAF (0.12 mL, 1M in THF) was added to **120** (39 mg, 0.11 mmol), at r.t. under Ar. The reaction mixture was stirred at 60°C for 2 h. Then the reaction mixture was diluted (at r.t.) with ethyl acetate (large amount) and worked up as usual. Flash chromatography (ethyl acetate/heptane 1:5) gives 22 mg (80%) of **121**.

121: 3-*tert*-Butoxy-3a,5-dimethyl-2,3,3a,4,5,6-hexahydro-1*H*-indene-5,6-diol.



Mp: 94 - 95°C.

$[\alpha]_D^{20} = -11$ (*c* 0.68, CHCl₃).

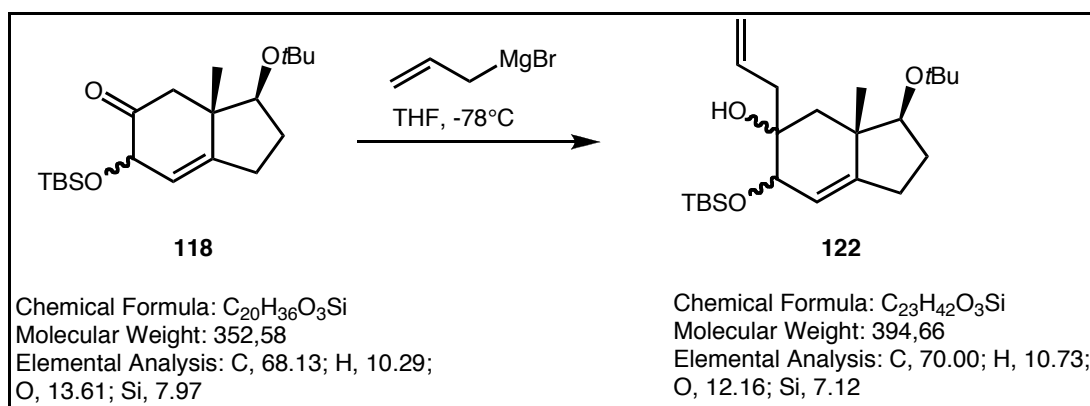
IR (film): $\nu = 3395, 2971, 2930, 1455, 1362, 1195, 1090, 1075, 1020, 882$ cm⁻¹.

¹H-NMR (CDCl₃, 400 MHz): $\delta = 1.15$ (s, 12 H, H8, OtBu), 1.26 (s, 3 H, H9), 1.45 and 1.92 (ABquartet, *J* = 14.4 Hz, 2 H, H4), 1.65 (tdd, *J* = 6.1, 8.8, 13.0 Hz, 1 H, H2), 1.82 - 1.95 (m, 1 H, H2'), 2.06 (dd, *J* = 6.2, 16.0 Hz, 1 H, H1), 2.52 (t, *J* = 14.5 Hz, 1 H, H1'), 3.36 (t, *J* = 8.6 Hz, 1 H, H3), 3.92 (s, 1 H, H6), 5.29 (s, 1 H, H7).

¹³C-NMR (CDCl₃, 75 MHz): $\delta = 19.0$ (C8), 26.5 (C1), 28.2 (C9), 28.9 (3C-OtBu), 30.2 (C2), 43.6 (C3a), 45.4 (C4), 70.8 (C5), 72.5 (Cq-OtBu), 73.0 (C6), 80.3 (C3), 119.4 (C7), 149.0 (C7a).

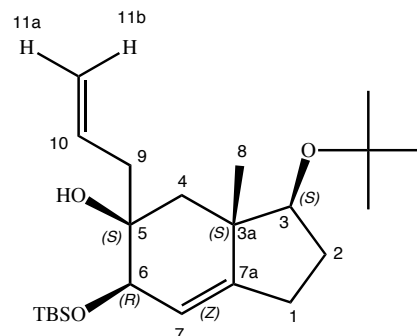
ESIMS (MeOH): 277.1 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₁₅H₂₆O₃Na *m/z* 277.1780, found 277.1770.

Analysis calcd. for C₁₅H₂₆O₃ (254.37): C 70.83, H 10.30; found C 71.01, H 10.28.



To a stirred solution of **118** (62 mg, 0.18 mmol), in THF (8 mL), at -78°C, allyl magnesiumbromide (0.72 mL, 1M in THF) was slowly added. The solution was stirred 1 h at -78°C. Then the reaction mixture was diluted with ether, and a saturated solution of NH₄Cl was added until pH = 7. The aqueous layer was extract with Et₂O. The organic layer was worked up as usual and chromatographed on silica gel (ethyl acetate/heptane 5:95) to afford 44 mg of **122** (64% and 27% of recovered SM).

122: 5-Allyl-3-*tert*-butoxy-6-(*tert*-butyl-dimethyl-silanyloxy)-3a-methyl-2,3,3a,4,5,6-hexahydro-1*H*-inden-5-ol.



Mp: colourless oil.

$[\alpha]_D^{20} = -21$ (*c* 0.785, CHCl₃).

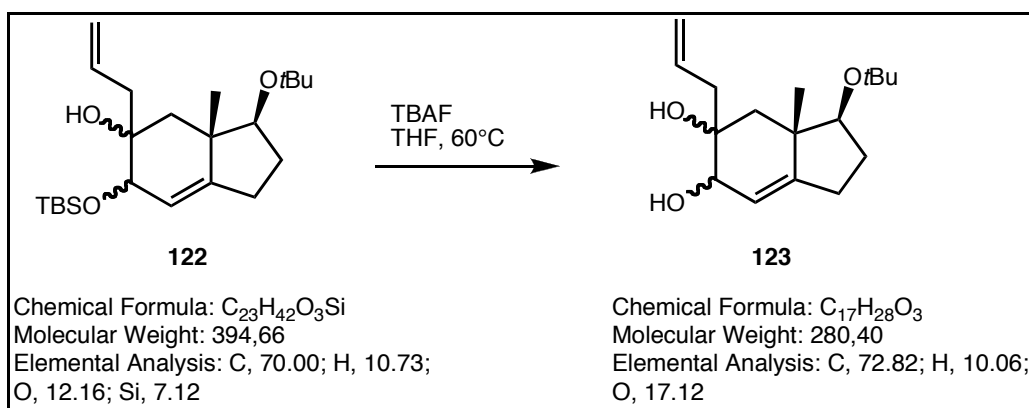
IR (film): $\nu = 3547, 2964, 2930, 2862, 1471, 1389, 1362, 1254, 1197, 1069, 1053, 885, 775$ cm⁻¹.

¹H-NMR (CDCl₃, 300 MHz): $\delta = 0.12$ (s, 3 H, SiMe), 0.14 (s, 3 H, SiMe), 0.93 (s, 9 H, Si*t*Bu), 1.15 (s, 9 H, O*t*Bu), 1.17 (s, 3 H, H8), 1.30 (d, *J* = 14.2 Hz, 1 H, H4), 1.64 (ddd, *J* = 2.5, 6.5, 12.3 Hz, 1 H, H2), 1.80 - 1.92 (m, 1 H, H2'), 1.94 (d, *J* = 14.2 Hz, 1 H, H4'), 2.02 (m, 1 H, H1), 2.12 (dd, *J* = 7.9, 13.7 Hz, 1 H, H9), 2.32 (dd, *J* = 6.7, 13.7 Hz, 1 H, H9'), 2.43 - 2.56 (m, 1 H, H1'), 2.84 (s, 1 H, OH), 3.33 (t, *J* = 8.5 Hz, 1 H, H3), 4.06 (s, 1 H, H6), 5.04 (dd, *J* = 2.1, 17.0 Hz, 1 H, H11a), 5.09 (dd, *J* = 2.1, 10.2 Hz, 1 H, H11b), 5.15 (s, 1 H, H7), 5.86 (dddd, *J* = 6.7, 7.9, 10.2, 17.0 Hz, 1 H, H10).

¹³C-NMR (CDCl₃, 75 MHz): $\delta = -4.7$ (SiMe), -3.6 (SiMe), 18.1 (Cq-Si*t*Bu), 18.4 (C8), 25.9 (3C-Si*t*Bu), 26.5 (C1), 28.8 (3C-O*t*Bu), 30.1 (C2), 42.2 (C4), 43.3 (C3a), 45.6 (C9), 72.0 (C6), 72.4 (C5), 72.5 (Cq-O*t*Bu), 80.7 (C3), 117.7 (C11), 118.9 (C7), 134.5 (C10), 148.5 (C7a).

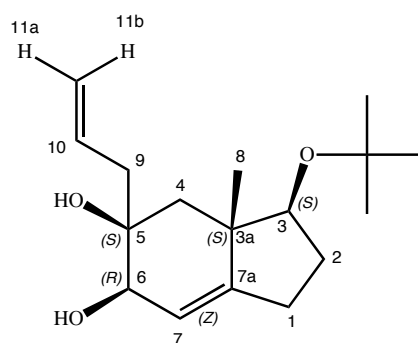
ESIMS (MeOH): 417.2 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₂₃H₄₂O₃NaSi *m/z* 417.2801, found 417.2791.

Analysis calcd. for C₂₃H₄₂O₃Si (394.66): C 70.00, H 10.73; found C 70.12, H 10.62.



TBAF (0.08 mL, 1M in THF) was added to **122** (26 mg, 0.07 mmol), at r.t. under Ar. The reaction mixture was stirred at 60°C for 2 h. Then the reaction mixture was diluted (at r.t.) with ethyl acetate (large amount) and worked up as usual. Flash chromatography (ethyl acetate/heptane 1:5) gives 16 mg (86%) of **123**.

123: 5-Allyl-3-*tert*-butoxy-3a-methyl-2,3,3a,4,5,6-hexahydro-1*H*-indene-5,6-diol.



Mp: 94 - 95°C.

$[\alpha]_D^{20} = -7$ (*c* 0.25, CHCl₃).

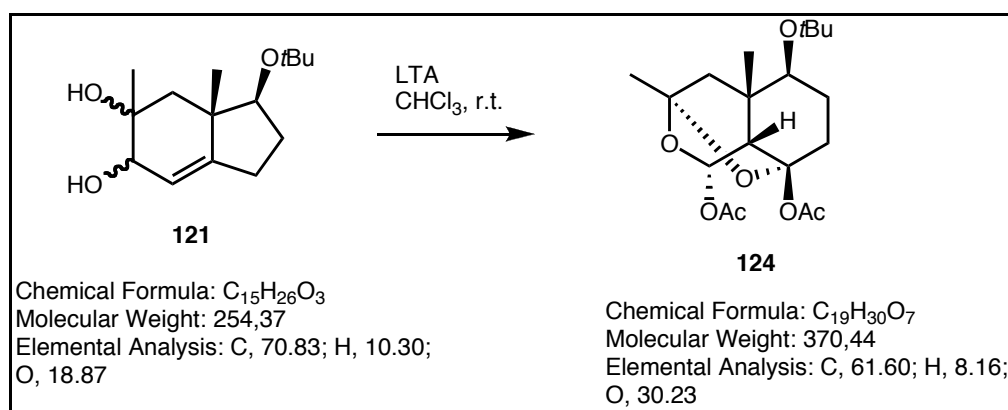
IR (film): $\nu = 3204, 2973, 2925, 2358, 2335, 1462, 1390, 1362, 1196, 1089$ cm⁻¹.

¹H-NMR (CDCl₃, 300 MHz): $\delta = 1.14$ (s, 9 H, *Ot*Bu), 1.15 (s, 3 H, H8), 1.35 (d, *J* = 14.2 Hz, 1 H, H4), 1.66 (tdd, *J* = 6.2, 8.7, 12.7 Hz, 1 H, H2), 1.92 (dddd, *J* = 4.0, 8.2, 9.6, 18.4 Hz, 1 H, H2'), 1.95 (d, *J* = 14.2 Hz, 1 H, H4'), 2.07 (m, 1 H, H1), 2.25 (dd, *J* = 7.2, 13.4 Hz, 1 H, H9), 2.37 (dd, *J* = 7.8, 13.5 Hz, 1 H, H9'), 2.51 (td, *J* = 3.0, 13.6 Hz, 1 H, H1'), 3.34 (t, *J* = 8.6 Hz, 1 H, H3), 4.02 (s, 1 H, H6), 5.14 (dd, *J* = 2.0, 11.0 Hz, 1 H, H11), 5.18 (d, *J* = 2.9 Hz, 1 H, H11), 5.25 (s, 1 H, H7), 5.95 (ddt, *J* = 7.2, 10.4, 17.2 Hz, 1 H, H10).

^{13}C -NMR (CDCl_3 , 75 MHz): $\delta = 18.5$ (C8), 26.4 (C1), 28.8 (3C-*Ot*Bu), 30.1 (C2), 43.3 (C3a), 43.7 (C4), 45.8 (C9), 71.6 (C6), 71.9 (C5), 72.6 (Cq-*Ot*Bu), 80.9 (C3), 119.1, 119.2 (C7, C11), 133.9 (C10), 148.8 (C7a).

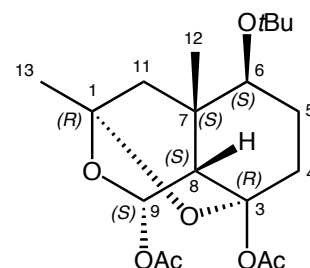
ESIMS (MeOH): 303.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{17}\text{H}_{28}\text{O}_3\text{Na}$ m/z 303.1936, found 303.1939.

Analysis calcd. for $\text{C}_{17}\text{H}_{28}\text{O}_3 \cdot 0.3 \text{H}_2\text{O}$ (280.40): C 71.44, H 10.09; found C 71.47, H 9.99.



A dry flask was charged with unsaturated diols **121** (30 mg, 0.12 mmol, diastereomeric mixture) and $\text{Pb}(\text{OAc})_4$ (160 mg, 0.36 mmol, 3 eq.) vacuumed, flushed with argon and cooled to 0°C . Chloroform (2 mL) was added, the cooling bath removed soon after and the reaction mixture was stirred for 15 h at room temperature, diluted with diethyl ether, filtered through $\text{MgSO}_4/\text{Celite}/\text{silica}$, the filtrate concentrated and purified by silica gel chromatography using diethyl ether-heptane, 2:1 as an eluent to give **124** (23 mg, 52%).

124: Acetic acid 3-acetoxy-6-*tert*-butoxy-1,7-dimethyl-2,10-dioxatricyclo[5.3.1.0^{0,0}]undec-9-yl ester.



Mp: 94 - 95°C .

$[\alpha]_D^{20} = -34$ (*c* 0.875, CHCl₃).

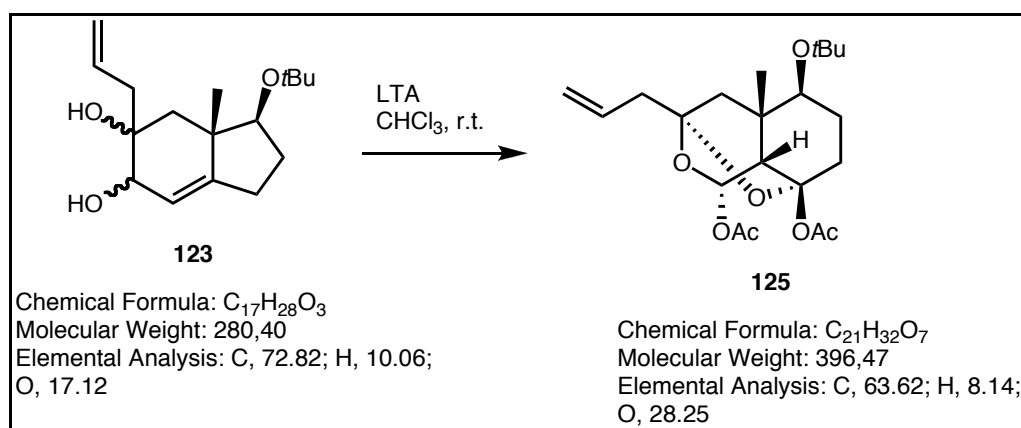
IR (film): $\nu = 2973, 1735, 1462, 1368, 1255, 1208, 1021, 1003$ cm⁻¹.

¹H-NMR (CDCl₃, 300 MHz): $\delta = 1.20$ (s, 9 H, *Ot*Bu), 1.27 (s, 3 H, H12), 1.44 (d, $J = 11.4$ Hz, 1 H, H11), 1.46 (s, 3 H, H13), 1.58 (ddd, $J = 2.2, 4.4, 12.8$ Hz, 1 H, H5), 1.64 (d, $J = 11.4$ Hz, 1 H, H11'), 1.70 - 1.74 (m, 1 H, H4), 1.88 (ddd, $J = 2.2, 4.6, 12.8$ Hz, 1 H, H5'), 2.09 (s, 3 H, Me-Ac), 2.10 (s, 3 H, Me-Ac), 2.72 (td, $J = 4.7, 13.0$ Hz, 1 H, H4), 3.14 (d, $J = 0.7$ Hz, 1 H, H8), 3.24 (s, 1 H, H6), 6.42 (d, $J = 0.8$ Hz, 1 H, H9).

¹³C-NMR (CDCl₃, 75 MHz): $\delta = 21.4$ (Me-Ac), 22.7 (Me-Ac), 24.7 (C13), 25.5 (C5), 25.9 (C12), 28.6 (C4), 28.9 (3C-*Ot*Bu), 36.3 (C8), 37.0 (C7), 44.4 (C11), 72.8 (C6), 73.6 (Cq-*Ot*Bu), 91.4 (C9), 98.3 (C3), 104.8 (C1), 169.5 (CO-Ac), 169.9 (CO-Ac).

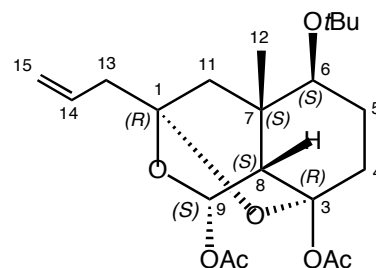
ESIMS (MeOH): 393.1 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₁₉H₃₀O₇Na *m/z* 393.1889, found 393.1867.

Analysis calcd. for C₁₉H₃₀O₇ (370.44): C 61.60, H 8.16; found C 61.82, H 8.36.



A dry flask was charged with unsaturated diols **123** (16 mg, 0.06 mmol, diastereomeric mixture) and Pb(OAc)₄ (76 mg, 0.17 mmol, 3 eq.) vacuumed, flushed with argon and cooled to 0°C. Chloroform (1 mL) was added, the cooling bath removed soon after and the reaction mixture was stirred for 15 h at room temperature, diluted with diethyl ether, filtered through MgSO₄/Celite/silica, the filtrate concentrated and purified by silica gel chromatography using diethyl ether-heptane, 1:1 as an eluent to give **125** (8 mg, 35%).

125: Acetic acid 9-acetoxy-1-allyl-6-*tert*-butoxy-7-methyl-2,10-dioxatricyclo[5.3.1.0^{0,0}]undec-3-yl ester.



Mp: colourless oil.

$[\alpha]_D^{20} = -28$ (c 0.48, CHCl_3).

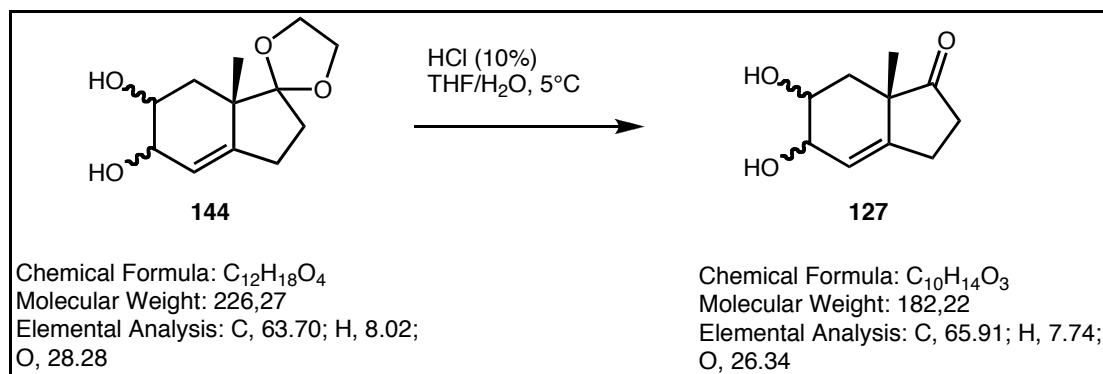
IR (film): $\nu = 2971, 2358, 2339, 1736, 1367, 1224, 1072, 1021 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 1.18$ (s, 9 H, *OrtBu*), 1.27 (s, 3 H, H12), 1.51 (d, $J = 14.1$ Hz, 1 H, H11), 1.60 (m, 2 H, H4, H5), 1.70 (d, $J = 14.1$ Hz, 1 H, H11), 1.84 (tdd, $J = 2.2, 4.7, 13.5$ Hz, 1 H, H5'), 2.09 (s, 3 H, Me-Ac), 2.10 (s, 3 H, Me-Ac), 2.50 (t, $J = 7.2$ Hz, 2 H, H13), 2.73 (td, $J = 4.7, 12.9$ Hz, 1 H, H4), 3.15 (s, 1 H, H8), 3.24 (s, 1 H, H6), 5.09 (dd, $J = 1.8, 5.0$ Hz, 1 H, H15), 5.14 (s, 1 H, H15'), 5.85 (m, 1 H, H14), 6.44 (d, $J = 0.8$ Hz, 1 H, H9).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 21.4$ (Me-Ac), 22.7 (Me-Ac), 25.6 (C5), 25.9 (C12), 28.7 (C4), 28.9 (3C-*OrtBu*), 36.7 (C8), 36.8 (C7), 42.0 (C11), 42.5 (C13), 72.9 (C6), 73.6 (Cq-*OrtBu*), 91.5 (C9), 99.3 (C1), 104.7 (C3), 118.7 (C15), 132.0 (C14), 169.79 (2CO-Ac).

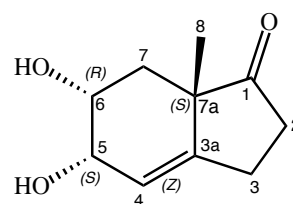
ESIMS (MeOH): 419.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{21}\text{H}_{32}\text{O}_7\text{Na}$ m/z 419.2046, found 419.2044.

Analysis calcd. for $\text{C}_{21}\text{H}_{32}\text{O}_7$ (396.47): C 63.62, H 8.14; found C 63.52, H 8.32.



To a stirred solution of alcohol **144** (18.2 g, 80.49 mmol) in THF (370 mL) at 0°C, HCl (10%, 370 mL) was added. The reaction mixture was stirred at 5°C (cold room) overnight. The reaction mixture was then diluted with ethyl acetate (large amount) and solid NaHCO₃ was added, at 0°C, until pH neutralisation. The aqueous layer was extracted with ethyl acetate. The organic layer was worked up as usual and chromatographed on silica gel (acetone/dichloromethane 1:4) to afford 13.66 g of **127** (93%).

127: 5,6-Dihydroxy-7a-methyl-2,3,5,6,7,7a-hexahydro-inden-1-one.



Mp: 110 - 110°C.

$[\alpha]_D^{20} = +188$ (*c* 1.08, CHCl₃).

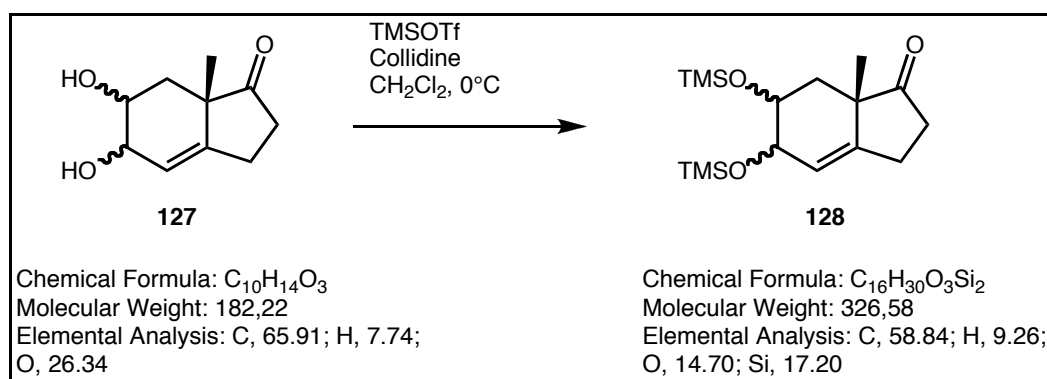
IR (film): $\nu = 3406, 2934, 2899, 1731, 1678, 1449, 1403, 1369, 1267, 1141, 1109, 1048, 937, 862, 715 \text{ cm}^{-1}$.

¹H-NMR (CDCl₃, 300 MHz): $\delta = 1.33$ (s, 3 H, H8), 1.84 (dd, *J* = 3.4, 14.4 Hz, 1 H, H7), 2.06 (dd, *J* = 6.0, 14.4 Hz, 1 H, H7'), 2.21 (dt, *J* = 9.3, 18.8 Hz, 1 H, H2), 2.46 - 2.52 (m, 1 H, H3), 2.62 - 2.71 (m, 1 H, H2'), 2.71 - 2.83 (m, 1 H, H3'), 3.98 (s, 1 H, H6), 4.20 (s, 1 H, H5), 5.61 (s, 1 H, H4).

¹³C-NMR (CDCl₃, 75 MHz): $\delta = 23.9$ (C8), 26.2 (C3), 32.9 (C7), 36.1 (C2), 48.2 (C7a), 67.9 (C5), 68.0 (C6), 120.5 (C4), 146.0 (C3a), 217.2 (C1).

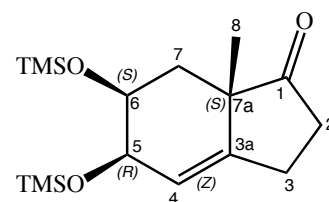
ESIMS (MeOH): 205.1 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₁₀H₁₄O₃Na *m/z* 205.0841, found 205.0818.

Analysis calcd. for C₁₀H₁₄O₃ (182.22): C 65.91, H 7.74; found C 65.85, H 7.71.



To a stirred solution of **127** (1.01 g, 5.55 mmol) in dry CH₂Cl₂ (20 mL) and collidine (2.22 mL, 16.65 mmol), chilled at 0°C, TMSOTf (2.36 mL, 18.27 mmol) was added under argon. The mixture was stirred at 0°C for 1 h 15 min (TLC monitoring). Upon disappearance of the starting material, dilution with heptane and usual workup afforded 1.39 g of **128** (77%), which was taken as such for the next step.

128: 7a-Methyl-5,6-bis-(trimethyl-silanyloxy)-2,3,5,6,7,7a-hexahydro-inden-1-one.



Mp: 44°C.

$[\alpha]_D^{20} = +79$ (*c* 1.04, CHCl₃).

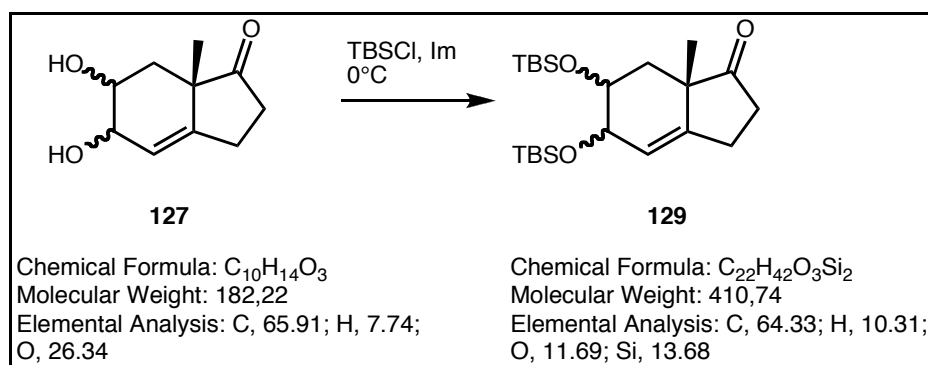
IR (film): $\nu = 2957, 1747, 1678, 1444, 1379, 1250, 1141, 1114, 1084, 1052, 1036, 994, 948, 892$ cm⁻¹.

¹H-NMR (CDCl₃, 300 MHz): $\delta = 0.00$ (s, 18 H, SiMe), 1.17 (s, 3 H, H8), 1.71 (dd, *J* = 3.9, 13.9 Hz, 1 H, H7), 1.78 (dd, *J* = 6.7, 13.9 Hz, 1 H, H7'), 2.07 (dt, *J* = 9.1, 18.5 Hz, 1 H, H2), 2.31 (dd, *J* = 10.4, 14.1 Hz, 1 H, H3), 2.49 (ddd, *J* = 1.3, 10.2, 18.7 Hz, 1 H, H2'), 2.55 - 2.70 (m, 1 H, H3'), 3.66 (dt, *J* = 3.7, 6.7 Hz, 1 H, H6), 3.95 (dt, *J* = 1.8, 3.7 Hz, 1 H, H5), 5.44 (dd, *J* = 2.2, 3.8 Hz, 1 H, H4).

¹³C-NMR (CDCl₃, 75 MHz): $\delta = 0.1$ (6C-SiMe), 24.0 (C8), 26.1 (C3), 33.4 (C7), 36.3 (C2), 48.9 (C7a), 68.9 (C5), 69.9 (C6), 122.3 (C4), 144.8 (C3a), 217.5 (C1).

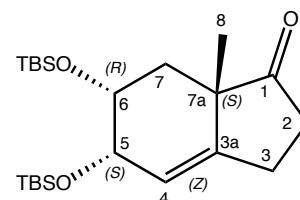
ESIMS (MeOH): 349.1 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₁₆H₃₀O₃Si₂Na *m/z* 349.1631, found 349.1654.

Analysis calcd. for C₁₆H₃₀O₃Si₂ (326.58): C 58.84, H 9.26; found C 59.06, H 9.32.



tert-butyldimethylsilyl chloride (1.09 g, 7.25 mmol) was added to a solution of imidazole (7.9 mg, 11.6 mmol) with diol **127** (530 mg, 2.9 mmol) in DMF (10 mL) at 0°C (TLC monitoring). After 3 h, one more equivalent of *tert*-butyldimethylsilyl chloride (504 mg) was added. The reaction mixture was stirred for 16 h then diluted with CH₂Cl₂, washed with 1N HCl and with a saturated solution of NaHCO₃. Usual work up followed by flash chromatography (heptane: AcOEt 9:1) of the residue gave 73% yield of the title compound **129**.

129: 5,6-Bis-(*tert*-butyl-dimethyl-silanyloxy)-7a-methyl-2,3,5,6,7,7a-hexahydro-inden-1-one.



Mp: yellow oil.

$[\alpha]_D^{20} = +29$ (*c* 1.22, CHCl₃).

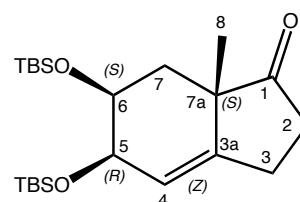
IR (film): 2930, 2857, 1749, 1472, 1362, 1254, 1140, 1036, 996, 875, 775 cm⁻¹.

¹H-NMR (CDCl₃, 300 MHz): δ = 0.02 (s, 3 H, SiMe), 0.03 (s, 3 H, SiMe), 0.04 (s, 3 H, SiMe), 0.06 (s, 3 H, SiMe), 0.87 (s, 9 H, Si*t*Bu), 0.88 (s, 9 H, Si*t*Bu), 1.21 (s, 3 H, H8), 1.82 (dd, *J* = 10.1, 13.5 Hz, 1 H, H7), 2.06 (dd, *J* = 5.4, 13.5 Hz, 1 H, H7'), 2.21 (dd, *J* = 9.0, 18.0 Hz, 1 H, H2 or H3), 2.41 (dd, *J* = 9.0, 14.0 Hz, 1 H, H2 or H3), 2.57 (dd, *J* = 1.7, 10.3 Hz, 1 H, H2 or H3), 2.63 (ddd, *J* = 9.0, 10.3, 18.0 Hz, 1 H, H2 or H3), 3.50 (ddd, *J* = 2.7, 5.8, 10.1 Hz, 1 H, H6), 3.97 (dd, *J* = 2.8, 5.8 Hz, 1 H, H5), 5.72 (dd, *J* = 2.3, 5.8 Hz, 1 H, H4).

^{13}C -NMR (CDCl_3 , 75 MHz): $\delta = -4.7$ (SiMe), -4.6 (SiMe), -4.5 (SiMe), -4.4 (SiMe), 18.2 (2Cq-Si*t*Bu), 25.5 (C8), 25.7 (C3), 25.9 (3C-Si*t*Bu), 26.0 (3C-Si*t*Bu), 31.9 (C7), 36.6 (C2), 50.1 (C7a), 68.6, 70.7 (C5, C6), 122.8 (C4), 145.7 (C3a), 217.5 (C1).

ESIMS (MeOH): 433.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{22}\text{H}_{42}\text{O}_3\text{Si}_2\text{Na}$ m/z 433.2570, found 433.2553.

129: 5,6-Bis-(*tert*-butyl-dimethyl-silanyloxy)-7a-methyl-2,3,5,6,7,7a-hexahydro-inden-1-one.



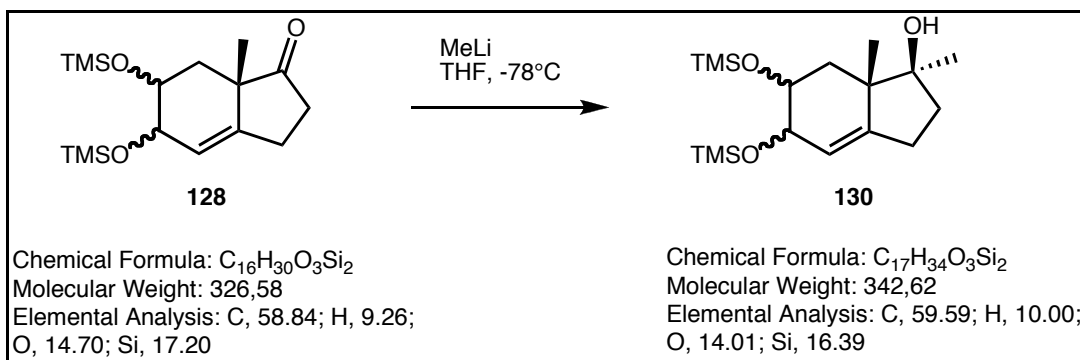
Mp: yellow oil.

IR (film): 2931, 1746, 1462, 1255, 1055, 838, 777 cm^{-1} .

^1H -NMR (CDCl_3 , 300 MHz): $\delta = 0.02$ (s, 3 H, SiMe), 0.03 (s, 3 H, SiMe), 0.04 (s, 3 H, SiMe), 0.07 (s, 3 H, SiMe), 0.87 (s, 9 H, Si*t*Bu), 0.88 (s, 9 H, Si*t*Bu), 1.20 (s, 3 H, H8), 1.82 (dd, $J = 10.2, 13.6$ Hz, 1 H, H7), 2.08 (dd, $J = 5.3, 13.4$ Hz, 1 H, H7'), 2.20 (dd, $J = 9.0, 18.3$ Hz, 1 H, H2), 2.40 (dd, $J = 10.3, 14.0$ Hz, 1 H, H3), 2.59 (dd, $J = 10.7, 18.6$ Hz, 1 H, H2'), 2.73 (dtd, $J = 2.3, 10.1, 13.6$ Hz, 1 H, H3'), 3.50 (ddd, $J = 2.7, 5.3, 10.2$ Hz, 1 H, H6), 3.97 (dd, $J = 2.5, 5.7$ Hz, 1 H, H5), 5.72 (dd, $J = 2.1, 5.9$ Hz, 1 H, H4).

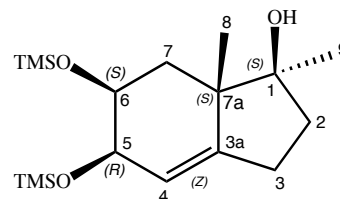
^{13}C -NMR (CDCl_3 , 75 MHz): $\delta = -4.7$ (SiMe), -4.6 (SiMe), -4.5 (SiMe), -4.4 (SiMe), 18.2 (2Cq-Si*t*Bu), 25.5 (C8), 25.7 (C3), 25.9 (Si*t*Bu), 26.0 (Si*t*Bu), 31.4 (C7), 36.6 (C2), 50.2 (C7a), 68.6, 70.8 (C5, C6), 122.9 (C4), 145.8 (C3a), 217.2 (C1).

ESIMS (MeOH): 433.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{22}\text{H}_{42}\text{O}_3\text{Si}_2\text{Na}$ m/z 433.2570, found 433.2510.



To a stirred solution of **128** (2.257 g, 6.91 mmol), in THF (30 ml), at -78°C, methyl lithium (15.7 mL, 1.6M in Et₂O) was slowly added. The solution was stirred 1 h at -78°C. Then the reaction mixture was diluted with ether, and a saturated solution of NH₄Cl was added until pH = 7. The aqueous layer was extract with Et₂O. The organic layer was worked up as usual and chromatographed on silica gel (ethyl acetate/heptane 2:8) to afford 1.75 g of **130** (74%).

130: 1,7a-Dimethyl-5,6-bis-(trimethyl-silanyloxy)-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-ol.



Mp: 122.5 - 130.0°C.

$[\alpha]_D^{20} = -54$ (*c* 1.08, CHCl₃).

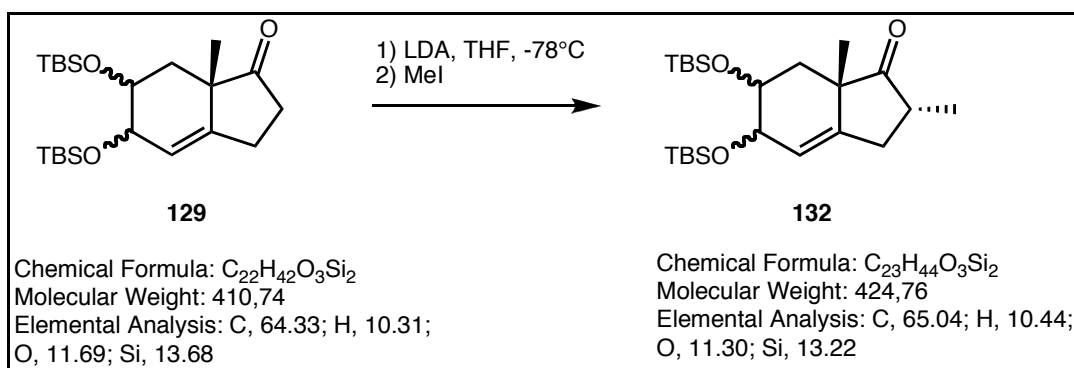
IR (film): $\nu = 3341, 2960, 2844, 2360, 2341, 1457, 1389, 1249, 1104, 1070, 1048, 899 \text{ cm}^{-1}$.

¹H-NMR (CDCl₃, 300 MHz): $\delta = 0.16$ (s, 18 H, SiMe), 1.14 (s, 3 H, H8), 1.18 (s, 3 H, H9), 1.51 (dd, *J* = 3.9, 12.5 Hz, 1 H, H7), 1.65 - 1.74 (m, 1 H, H2), 1.71 - 1.79 (m, 1 H, H7'), 1.92 - 2.04 (m, 1 H, H3), 2.05 - 2.13 (m, 1 H, H2'), 2.43 (tdd, *J* = 2.8, 8.9, 16.9 Hz, 1 H, H3'), 3.91 (dt, *J* = 3.9, 11.9 Hz, 1 H, H6), 4.04 - 4.10 (m, 1 H, H5), 5.12 (s, 1 H, H4).

¹³C-NMR (CDCl₃, 75 MHz): $\delta = 0.3$ (6C-SiMe), 20.6 (C9), 24.8 (C3), 25.3 (C8), 37.4 (C2), 37.5 (C7), 48.7 (C7a), 72.7 (C6), 74.9 (C5), 80.4 (C3a), 121.7 (C4), 147.6 (C1).

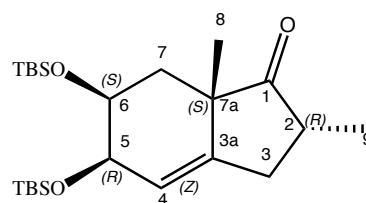
ESIMS (MeOH): 365.1 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₁₇H₃₄O₃Si₂Na *m/z* 365.1944, found 365.1932.

Analysis calcd. for C₁₇H₃₄O₃Si₂ (342.62): C 59.59, H 10.00; found C 59.97, H 9.83.



To a stirred solution of MeLi (0.83 mL, 1.6M) in dry THF (5 mL) at -40°C, was added freshly distilled *i*PrNH (0.19 mL, 1.33 mmol). After stirring for 30 min at -40°C, **129** (409 mg, 1.0 mmol) in THF (4 mL) was added dropwise over a period of 5 min at 0°C, and the mixture was stirred for 1 h, at 0°C. The mixture was cooled to -10°C, CH₃I (1.1 mL, 17.1 mmol) was added, and the reaction was stirred at r.t. for 1 h. The mixture was diluted with cold aqueous HCl (10%, 26 mL), extracted with ether. The organic layer was worked up as usual and chromatographed on silica gel (ethyl acetate/heptane 2:98) to **132** yield (355 mg, 84%).

132: 5,6-Bis-(*tert*-butyl-dimethyl-silanyloxy)-2,7a-dimethyl-2,3,5,6,7,7a-hexahydro-inden-1-one.



Mp: 59.0 - 60.0°C.

$[\alpha]_D^{20} = +42$ (*c* 0.8, CHCl₃).

IR (film): $\nu = 2956, 2358, 2342, 1748, 1255, 1096, 836, 775, 668$ cm⁻¹.

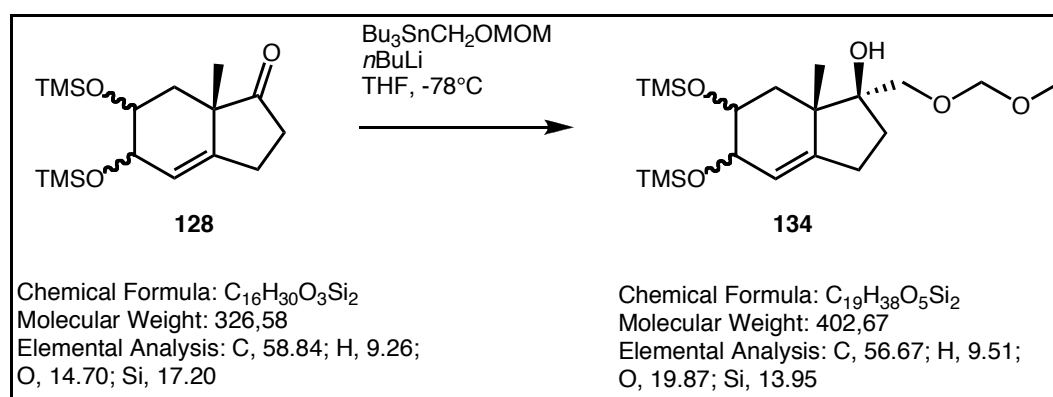
¹H-NMR (CDCl₃, 300 MHz): $\delta = 0.04$ (s, 3 H, SiMe), 0.05 (s, 3 H, SiMe), 0.06 (s, 3 H, SiMe), 0.08 (s, 3 H, SiMe), 0.89 (s, 9 H, Si*t*Bu), 0.90 (s, 9 H, Si*t*Bu), 1.03 (d, *J* = 7.6 Hz, 3 H, H9), 1.24 (s, 3 H, H8), 1.82 (dd, *J* = 10.3, 13.4 Hz, 1 H, H7), 1.99 (dd, *J* = 1.6, 14.8 Hz, 1 H, H3), 2.00 (dd, *J* = 5.3, 13.4 Hz, 1 H, H7), 2.62 (dq, *J* = 1.9, 7.5, 9.5 Hz,

1 H, H2), 2.93 (ddd, $J = 2.4, 9.9, 14.6$ Hz, 1 H, H3), 3.40 (ddd, $J = 2.6, 5.3, 10.3$ Hz, 1 H, H6), 3.91 (dd, $J = 2.5, 5.8$ Hz, 1 H, H5), 5.66 (dd, $J = 2.0, 5.9$ Hz, 1 H, H4).

^{13}C -NMR (CDCl_3 , 75 MHz): $\delta = -4.7$ (SiMe), -4.6 (SiMe), -4.5 (SiMe), -4.4 (SiMe), 16.9 (C9), 18.2 (2Cq-Si*t*Bu), 25.9 (C8, 6C-Si*t*Bu), 31.7 (C7), 34.4 (C3), 40.8 (C2), 50.5 (C7a), 68.7 (C5), 70.8 (C6), 123.7 (C4), 144.7 (C3a), 219.7 (C1).

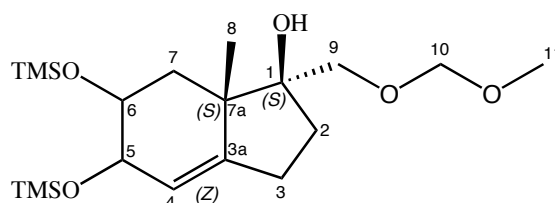
ESIMS (MeOH): 447.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{23}\text{H}_{44}\text{O}_3\text{Si}_2\text{Na}$ m/z 447.2727, found 447.2745.

Analysis calcd. for $\text{C}_{23}\text{H}_{44}\text{O}_3\text{Si}_2$ (424.76): C 65.04, H 10.44; found C 64.85, H 10.58.



To a stirred solution of $\text{Bu}_3\text{SnCH}_2\text{OMOM}$ **115** (1.102 g, 3.02 mmol), in dry THF (5 mL), at -78°C under Argon, $n\text{-BuLi}$ (1.84 mL, 2.34 mmol) was slowly added (over 5 min). The reaction was stirred 5 min, and then a solution of **128** (411 mg, 1.26 mmol), in THF (5 mL) was slowly added. The reaction was stirred 20 min at -78°C . The reaction mixture was diluted with diethyl ether, and a saturated solution of NH_4Cl was added until $\text{pH} = 7$. The aqueous layer was extract with ethyl acetate. The organic layer was worked up as usual and chromatographed on silica gel (ethyl acetate/heptane 5:95) to **134** yield (411 mg, 81%).

134: (1-Methoxymethoxymethyl-7a-methyl-5,6-bis-(trimethyl-silanyloxy)-2, 3,5,6,7,7a-hexahydro-1*H*-inden-1-ol).



Mp: colourless oil.

$[\alpha]_D^{20} = -66$ (*c* 0.62, CHCl₃).

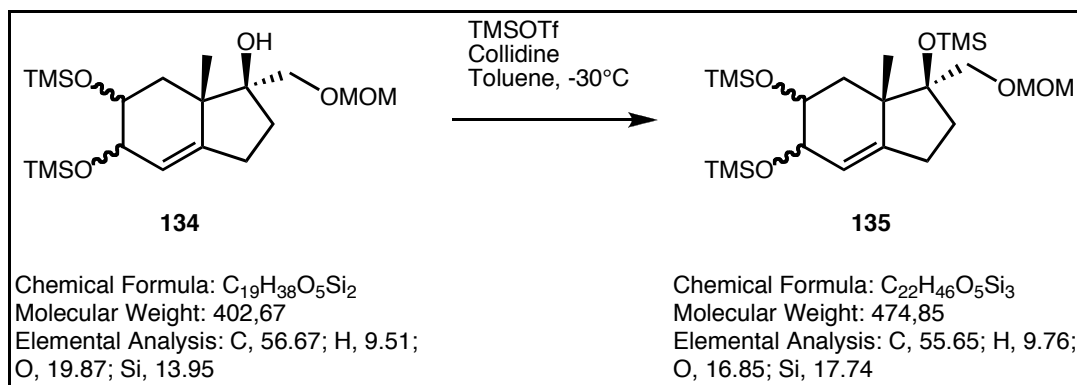
IR (film): $\nu = 3474, 2954, 1436, 1366, 1249, 1141, 1104, 1036, 1008, 974, 926, 840$ cm⁻¹.

¹H-NMR (CDCl₃, 300 MHz): $\delta = 0.97$ (s, 18 H, SiMe), 1.23 (s, 3 H, H8), 1.68 (dd, *J* = 9.5, 14.1 Hz, 1 H, H2), 1.80 (dd, *J* = 4.7, 14.0 Hz, 1 H, H2'), 2.02 (d, *J* = 9.6 Hz, 2 H, H7), 1.98 - 2.07 (m, 1 H, H3), 2.53 (t, *J* = 10.6 Hz, 1 H, H3'), 3.36 (s, 3 H, H11), 3.35 - 3.49 (m, 2 H, H9), 3.58 (ddd, *J* = 4.1, 4.2, 8.4 Hz, 1 H, H6), 3.97 (dd, *J* = 4.0 Hz, 1 H, H5), 4.65 (s, 2 H, H10), 5.39 (d, *J* = 5.0 Hz, 1 H, H4).

¹³C-NMR (CDCl₃, 75 MHz): $\delta = 0.1$ (3C-SiMe), 0.4 (3C-SiMe), 24.0 (C8), 25.3 (C3), 31.2 (C7), 32.1 (C2), 46.6 (C7a), 55.4 (C11), 68.4 (C5), 70.2 (C6), 72.3 (C9), 81.0 (C3a), 97.2 (C10), 120.3 (C4), 149.0 (C1).

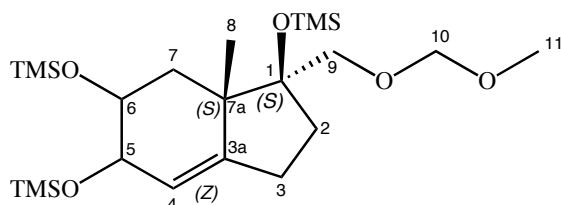
ESIMS (MeOH): 425.2 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₁₉H₃₈O₅Si₂Na *m/z* 425.2155, found 425.2156.

Analysis calcd. for C₁₉H₃₈O₅Si₂ · 0.1 C₇H₁₆ (402.67): C 57.33, H 9.67; found C 57.54, H 9.74.



To a stirred solution of **134** (125 mg, 0.31 mmol) in dry toluene (5 mL) and collidine (0.95 mL, 7.2 mmol), chilled at 0°C, TMSOTf (2.36 mL, 18.27 mmol) was added under argon. The mixture was stirred at 0°C for 20 min (TLC monitoring). Upon disappearance of the starting material, dilution with heptane and usual workup afforded 111 mg of **135** (75%), which was taken as such for the next step (20 mg of SM recovered 16%).

135: 3-Methoxymethoxymethyl-3a-methyl-3,5,6-tris-(trimethyl-silanyloxy)-2,3,3a,4,5,6-hexahydro-1*H*-indene.



Mp: 61.0 - 62.0°C.

$[\alpha]_D^{20} = -67$ (*c* 0.62, CHCl₃).

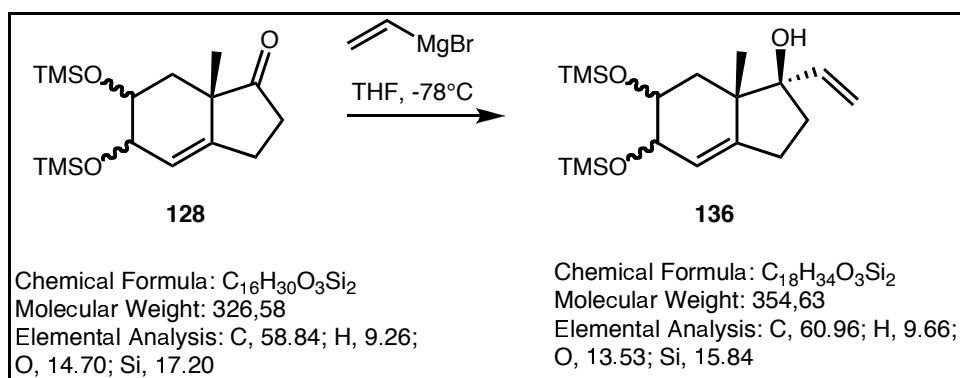
IR (film): $\nu = 2955, 1249, 1104, 1047, 874, 839$ cm⁻¹.

¹H-NMR (CDCl₃, 300 MHz): $\delta = 0.08$ (s, 18 H, SiMe), 0.14 (s, 9 H, SiMe), 1.10 (s, 3 H, H8), 1.48 (d, *J* = 6.6 Hz, 2 H, H7), 1.75 (dt, *J* = 8.3, 12.3 Hz, 1 H, H2), 2.01 (dt, *J* = 8.6, 15.4 Hz, 1 H, H3), 2.24 (ddd, *J* = 2.5, 9.5, 12.4 Hz, 1 H, H2'), 2.43 (ddd, *J* = 2.5, 12.2, 17.1 Hz, 1 H, H3'), 3.32 (s, 2 H, H9), 3.34 (s, 3 H, H11), 3.87 (dt, *J* = 6.7, 9.0 Hz, 1 H, H6), 4.02 (dd, *J* = 1.6, 7.0 Hz, 1 H, H5), 4.60 (s, 2 H, H10), 5.07 (d, *J* = 1.6 Hz, 1 H, H4).

¹³C-NMR (CDCl₃, 75 MHz): $\delta = 0.4$ (6C-SiMe), 2.2 (3C-SiMe), 21.5 (C8), 25.3 (C3), 30.7 (C2), 37.1 (C7), 49.1 (C7a), 55.4 (C11), 71.8 (C9), 72.7 (C6), 75.0 (C5), 84.2 (C3a), 96.8 (C10), 121.3 (C4), 147.3 (C1).

ESIMS (MeOH): 497.3 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₂₂H₄₆O₅Si₃Na *m/z* 497.2551, found 497.2528.

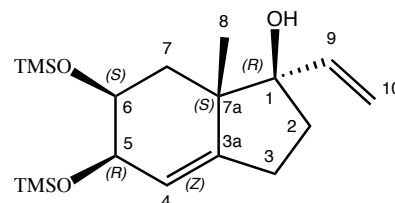
Analysis calcd. for C₂₂H₄₆O₅Si₃ · 0.15 C₇H₁₆ (474.85): C 56.51, H 9.96; found C 56.78, H 9.73.



To a stirred solution of **128** (506 mg, 1.55 mmol), in THF (7 mL), at -78°C, vinyl magnesiumbromide (9.3 mL, 1M in THF) was slowly added. The solution was stirred 1 h

at -78°C . Then the reaction mixture was diluted with ether, and a saturated solution of NH_4Cl was added until $\text{pH} = 7$. The aqueous layer was extract with Et_2O . The organic layer was worked up as usual and chromatographed on silica gel (ethyl acetate/heptane 2:8) to afford 198 mg of **136** (36%, 58% of recovered SM).

136: 7a-Methyl-5,6-bis-(trimethyl-silanyloxy)-1-vinyl-2,3,5,6,7,7a-hexahydro -1*H*-inden-1-ol.



Mp: colourless oil.

$[\alpha]_D^{20} = -33$ (c 0.9, CHCl_3).

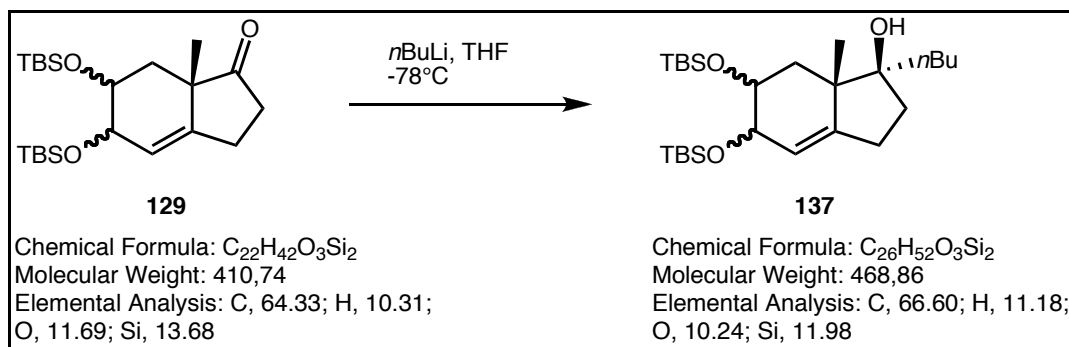
IR (film): $\nu = 3464, 2955, 2359, 2340, 1734, 1364, 1248, 1084, 889, 838 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 0.09$ (s, 9 H, SiMe), 0.43 (s, 9 H, SiMe), 1.24 (s, 3 H, H8), 1.56 - 1.64 (m, 2 H, H7), 1.86 (ddd, $J = 3.2, 9.6, 13.0$ Hz, 1 H, H2), 2.02 (td, $J = 7.3, 12.7$ Hz, 1 H, H2'), 2.16 (ddd, $J = 7.1, 9.4, 16.8$ Hz, 1 H, H3), 2.53 - 2.66 (m, 1 H, H3'), 3.59 (ddd, $J = 3.0, 5.6, 9.2$ Hz, 1 H, H6), 3.97 (dd, $J = 3.0, 5.5$ Hz, 1 H, H5), 5.08 (dd, $J = 1.4, 10.9$ Hz, 1 H, H10), 5.27 (dd, $J = 1.4, 17.3$ Hz, 1 H, H10'), 5.50 (ddd, $J = 1.4, 2.5, 5.6$ Hz, 1 H, H4), 5.87 (dd, $J = 10.9, 17.3$ Hz, 1 H, H9).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 0.0$ (3C-SiMe), 0.4 (3C-SiMe), 23.9 (C8), 25.4 (C3), 32.7 (C7), 35.2 (C2), 48.0 (C7a), 68.5 (C5), 70.2 (C6), 82.8 (C1), 110.8 (C10), 120.7 (C4), 141.8 (C9), 149.1 (C3a).

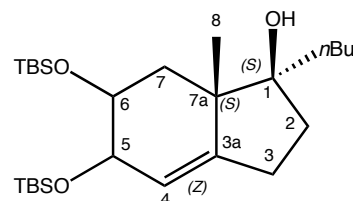
ESIMS (MeOH): 377.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{18}\text{H}_{34}\text{O}_3\text{Si}_2\text{Na}$ m/z 377.1944, found 377.1932.

Analysis calcd. for $\text{C}_{18}\text{H}_{34}\text{O}_3\text{Si}_2$ (354.63): C 60.96, H 9.66; found C 61.33, H 9.63.



To a stirred solution of **129** (100 mg, 0.24 mmol), in THF (2 mL), at $-78^{\circ}C$, methyl lithium (0.45 mL, 1.6M in Et₂O) was slowly added. The solution was stirred 1 h at $-78^{\circ}C$. Then the reaction mixture was diluted with ether, and a saturated solution of NH₄Cl was added until pH = 7. The aqueous layer was extracted with Et₂O. The organic layer was worked up as usual and chromatographed on silica gel (ethyl acetate/heptane 2:8) to afford 62 mg of **137** (55%, 45% of SM recovered).

137: 1-Butyl-5,6-bis-(tert-butyl-dimethyl-silanyloxy)-7a-methyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-ol.



Mp: yellow oil.

$[\alpha]_D^{20} = -54$ (*c* 1.4, CHCl₃).

IR (film): 3436, 2953, 2928, 2855, 1471, 1460, 1386, 1360, 1254, 1101, 1074, 1023, 876, 834, 773 cm⁻¹.

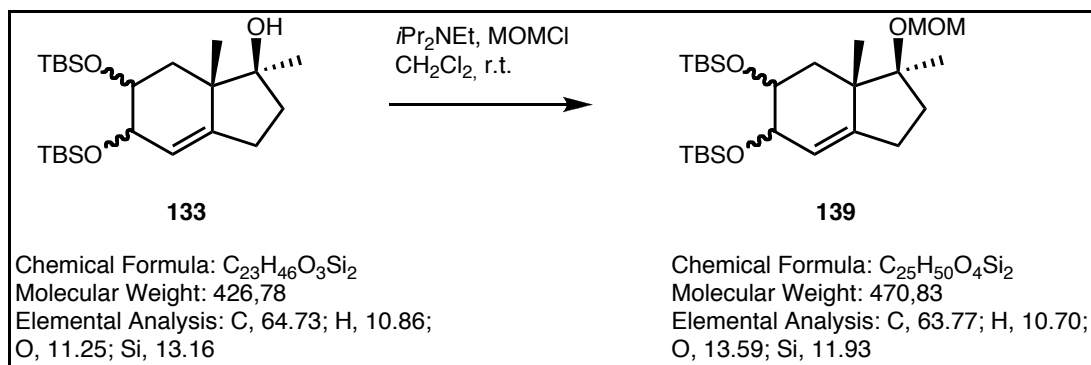
¹H NMR (CDCl₃, 500 MHz): δ = 0.09 (s, 6 H, SiMe), 0.10 (s, 6 H, SiMe), 0.91 (s, 21 H, Si*t*Bu, Me-*n*Bu), 1.17 (s, 3 H, H8), 1.25 - 1.46 (m, 6 H, Bu), 1.50 (dd, *J* = 3.4, 12.5 Hz, 1 H, H7), 1.69 (t, *J* = 12.5 Hz, 1 H, H7'), 1.71- 1.77 (m, 1 H, H2), 1.96 - 2.03 (m, 2 H, H2', H3), 2.39 (t, *J* = 13.6 Hz, 1 H, H3'), 3.82 (ddd, *J* = 3.5, 6.0, 10.5 Hz, 1 H, H6), 4.07 (d, *J* = 6.0 Hz, 1 H, H5), 5.12 (s, 1 H, H4).

¹³C NMR (CDCl₃, 125 MHz): -4.5 (SiMe), -4.4 (SiMe), -3.8 (SiMe), -3.7 (SiMe), 14.2 (Me-*n*Bu), 18.0 (Cq-Si*t*Bu), 18.2 (Cq-Si*t*Bu), 21.3 (C8), 23.4 (Bu), 24.9 (C3), 26.0 (3C-

SitBu), 26.1 (3C-SitBu, Bu), 32.1 (C2), 35.6 (Bu), 37.2 (C7), 49.4 (C7a), 73.2 (C6), 75.5 (C5), 82.1 (C1), 121.9 (C4), 147.2 (C3a).

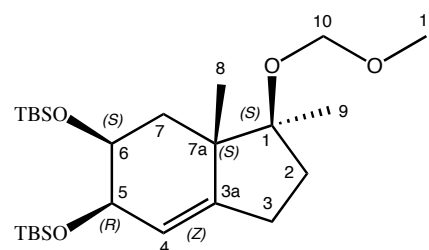
ESIMS (MeOH): 491.3 ($[M + Na]^+$, 100). HRESIMS: calcd. for $C_{26}H_{52}O_3Si_2Na$ m/z 491.3353, found 491.3361.

Analysis calcd. for $C_{26}H_{52}O_3Si_2 \cdot 0.5 H_2O$ (468.34): C 65.35, H 11.18; found C 65.42, H 11.08.



To an ice-cold solution of **133** (6.2 g, 14.53 mmol) in 55 mL of dry methylene chloride, under argon, was added chloromethyl methylether (6.62 mL, 87.18 mmol) and diisopropylethylamine (15.72 mL, 90.09 mmol). The reaction mixture was allowed to warm and stirred at r.t. for 16 h (while TLC-monitored), then quenched with water. The aqueous phase was extracted with methylene chloride and the combined organic layers were washed with dilute HCl, a saturated aq. solution of $NaHCO_3$ and brine. The combined organic extracts were dried over $MgSO_4$, concentrated and purified by column chromatography (ethyl acetate-heptane, 1:9) to give 6.73 g (98%) of **139**.

139: 5,6-Bis-(*tert*-butyl-dimethyl-silyloxy)-3-methoxymethoxy-3,3a-dimethyl-2,3,3a,4,5,6-hexahydro-1*H*-indene.



Mp: colourless oil.

$[\alpha]_D^{20} = -56$ (c 1.25, $CHCl_3$).

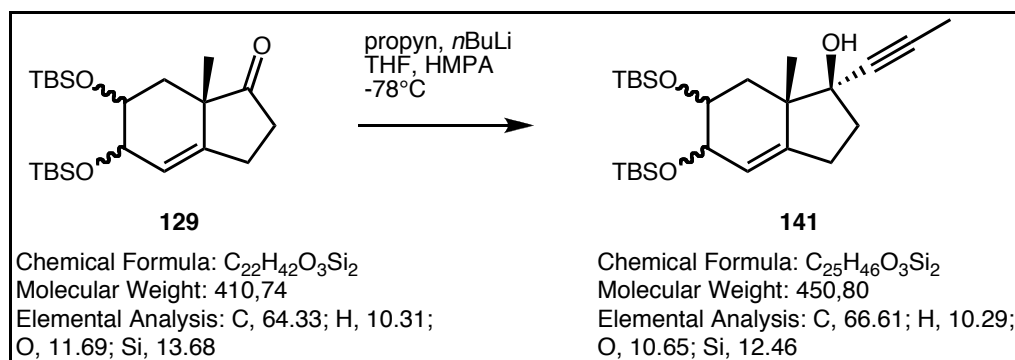
IR (film): $\nu = 2954, 1472, 1362, 1252, 1094, 1035, 1005, 833 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): $\delta = 0.03$ (s, 3 H, SiMe), 0.04 (s, 3 H, SiMe), 0.05 (s, 3 H, SiMe), 0.06 (s, 3 H, SiMe), 0.88 (s, 9 H, Si*t*Bu), 0.89 (s, 9 H, Si*t*Bu), 1.15 (s, 3 H, H9), 1.17 (s, 3 H, H8), 1.63 - 1.72 (m, 2 H, H2, H7), 1.83 (dd, $J = 6.0, 13.9 \text{ Hz}$, 1H, H7'), 2.02 - 2.13 (m, 2 H, H3, H2'), 2.49 (td, $J = 2.6, 5.0 \text{ Hz}$, 1 H, H3'), 3.38 (s, 3 H, H11), 3.59 (ddd, $J = 2.5, 6.0, 11.2 \text{ Hz}$, 1 H, H6), 3.94 (dd, $J = 2.4, 6.5 \text{ Hz}$, 1 H, H5), 4.72 and 4.77 (ABquartet, $J = 7.0 \text{ Hz}$, 2 H, H10), 5.51 (ddd, $J = 1.2, 2.3, 6.5 \text{ Hz}$, 1 H, H4).

$^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): $\delta = -4.5$ (2C-SiMe), -4.3 (2C-SiMe), 18.2 (2Cq-Si*t*Bu), 21.4 (C9), 25.3 (C3), 25.9 (C8), 26.1 (3C-Si*t*Bu), 26.2 (3C-Si*t*Bu), 32.5 (C7), 33.9 (C2), 49.6 (C7a), 55.2 (C11), 68.6 (C5), 71.6 (C6), 84.7 (C1), 92.2 (C10), 120.3 (C4), 149.8 (C3a).

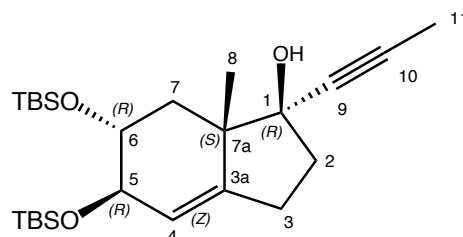
ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 493.3 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{25}\text{H}_{50}\text{O}_4\text{Si}_2\text{Na}$ m/z 493.3145, found 493.3141.

Analysis calcd. for $\text{C}_{25}\text{H}_{50}\text{O}_4\text{Si}_2$ (470.83): C 63.77, H 10.70; found C 63.84, H 10.81.



To a solution of propyne (0.32 mL, 5.7 mmol) in THF (4 mL) at -78°C under Ar, *n*BuLi (2.4 mL, 1.6 M in hexane) was added dropwise. The mixture was allowed to warm to -15°C and stirring was continued at this temperature. After 2 h, HMPA (1.2 mL) was added at -20°C and the resulting mixture was stirred for 10 min. A solution of **129** (155 mg, 0.38 mmol) in THF (2 mL) and HMPA (1.2 mL) was then added at -30°C and the mixture was left to stir overnight at room temperature. Then ether and a saturated solution of NH_4Cl were added and the organic layer was separated. The aqueous layer was extracted with ether, and the combined organic layers were washed with water, saturated aqueous NaHCO_3 solution and worked up as usual. Flash chromatography ethyl acetate/heptane (1:4) gives 141 mg (82%) of **141**.

141: 5,6-bis(*tert*-butyldimethylsilyloxy)-7a-methyl-1-(prop-1-ynyl)-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-ol.



Mp: 63.0°C.

$[\alpha]_D^{20} = -154$ (*c* 1.05, CHCl₃).

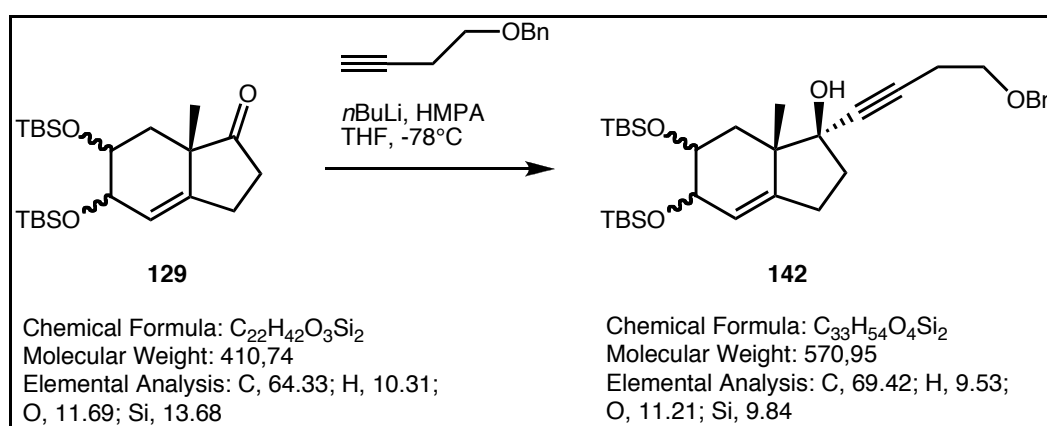
IR (film): $\nu = 2953, 2928, 2848, 1471, 1253, 1095, 1003, 830, 775$ cm⁻¹.

¹H-NMR (CDCl₃, 300 MHz): $\delta = 0.03, 0.05, 0.07$ (s, 12 H, SiMe), 0.89 (s, 9 H, Si*t*Bu), 0.90 (s, 9 H, Si*t*Bu), 1.13 (s, 3 H, H8), 1.64 (dd, *J* = 10.8, 13.3 Hz, 1 H, H7), 1.81 (s, 3 H, H11), 2.00 (dd, *J* = 6.2, 13.2 Hz, 1 H, H7'), 2.05 (dd, *J* = 3.2, 10.9 Hz, 1 H, H2), 2.06 - 2.12 (m, 1 H, H2'), 2.13 - 2.17 (m, 1 H, H3), 2.42 - 2.54 (m, 1 H, H3'), 3.82 (ddd, *J* = 2.5, 6.4, 10.6 Hz, 1 H, H6), 3.96 (dd, *J* = 2.3, 6.5 Hz, 1 H, H5), 5.58 (ddd, *J* = 1.4, 2.4, 6.5 Hz, 1 H, H4).

¹³C-NMR (CDCl₃, 75 MHz): $\delta = -4.5$ (2C-SiMe), -4.3 (2C-SiMe), 3.9 (C11), 18.2 (2Cq-Si*t*Bu), 24.0 (C8), 25.0 (C3), 25.9 (3C-Si*t*Bu), 26.0 (3C-Si*t*Bu), 33.3 (C7), 37.2 (C2), 49.8 (C7a), 68.6 (C5), 71.4 (C6), 78.6 (C1), 80.4 (C10), 82.7 (C9), 121.0 (C4), 148.9 (C3a).

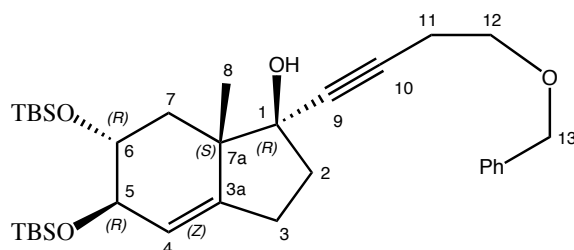
ESIMS (MeOH): 473.3 ([*M* + Na]⁺, 100). HRESIMS: calcd. for C₂₅H₄₆O₃Si₂Na *m/z* 473.2883, found 473.2882.

Analysis calcd. for C₂₅H₄₆O₃Si₂ · 0.3 H₂O (450.80): C 65.82, H 10.30; found C 65.78, H 10.09.



To a solution of 4-(benzyloxy)butyne (328 mg, 2.04 mmol) in THF (4 mL) at -78°C under Ar, *n*BuLi (1.22 mL, 1.6M in hexane) was added dropwise. The mixture was allowed to warm to -15°C and stirring was continued at this temperature. After 2 h, HMPA (0.6 mL) was added at -20°C and the resulting mixture was stirred for 10 min. A solution of **129** (389 mg, 0.95 mmol) in THF (1 mL) and HMPA (0.6 mL) was then added at -30°C and the mixture was left to stir overnight at room temperature. Then ether and a saturated solution of NH_4Cl were added and the organic layer was separated. The aqueous layer was extracted with ether, and the combined organic layers were washed with water, saturated aqueous NaHCO_3 solution and worked up as usual. A flash chromatography (ethyl acetate/heptane 5:95) gives 338 mg (62%) of **142**.

142: 1-(4-Benzyloxy-but-1-ynyl)-5,6-bis-(*tert*-butyl-dimethyl-silyloxy)-7a-methyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-ol.



Mp: 38.0°C .

$[\alpha]_D^{20} = -140$ (*c* 0.748, CHCl_3).

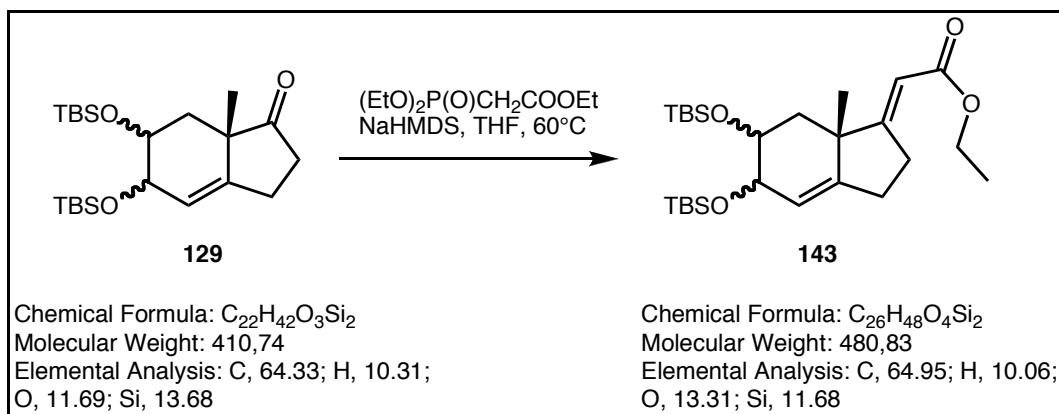
IR (film): $\nu = 3416, 2928, 2855, 1711, 1472, 1361, 1252, 1094, 1004, 883, 832, 775 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 0.00, 0.01, 0.03$ (s, 12 H, SiMe), 0.85 (s, 9 H, Si*t*Bu), 0.86 (s, 9 H, Si*t*Bu), 1.10 (s, 3 H, H8), 1.60 (dd, $J = 10.5, 13.4$ Hz, 1 H, H7), 1.96 (dd, $J = 6.3, 13.3$ Hz, 1 H, H7'), 2.02 (dd, $J = 3.7, 11.4$ Hz, 1 H, H2), 2.11 (dt, $J = 2.9, 9.0$ Hz, 1 H, H3), 2.18 (ddd, $J = 1.3, 7.6, 13.8$ Hz, 1 H, H2'), 2.42 (m, 1 H, H3'), 2.45 (t, $J = 7.2$ Hz, 2 H, H11), 3.52 (t, $J = 7.2$ Hz, 2 H, H12), 3.76 (ddd, $J = 2.5, 6.4, 10.4$ Hz, 1 H, H6), 3.90 (dd, $J = 2.5, 6.4$ Hz, 1 H, H5), 4.49 (s, 2 H, H13), 5.51 (ddd, $J = 1.3, 2.5, 6.4$ Hz, 1 H, H4), 7.22 - 7.35 (m, 5 H, Ph).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = -4.5, -4.4, -4.3$ (4C-SiMe), 18.2 (2Cq-Si*t*Bu), 20.4 (C11), 24.0 (C8), 25.0 (C3), 26.0 (3C-Si*t*Bu), 26.1 (3C-Si*t*Bu), 33.5 (C7), 37.4 (C2), 49.7 (C7a), 68.4 (C12), 68.7 (C5), 71.4 (C6), 73.0 (C13), 78.6 (C1), 81.4 (C10), 84.8 (C9), 121.1 (C4), 127.6, 127.8, 128.5 (5C-Ph), 138.1 (Cq-Ph), 148.7 (C3a).

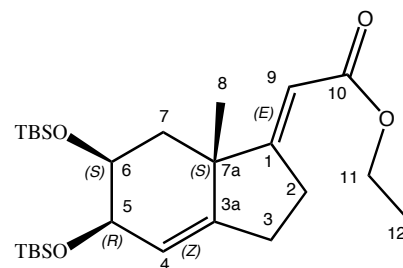
ESIMS (MeOH): 593.3 ($[M + Na]^+$, 100). HRESIMS: calcd. for $C_{33}H_{54}O_4Si_2Na$ m/z 593.3458, found 593.3458.

Analysis calcd. for $C_{33}H_{54}O_4Si_2 \cdot 0.45 H_2O$ (570.95): C 68.45, H 9.56; found C 68.47, H 9.43.



Over a solution of triethyl phosphonoacetate (0.61 mL, 3.06 mmol) in THF (4 mL) was added, at $-78^\circ C$, under Ar, NaHMDS (1.53 mL, 2M in THF). The media was stirred at $-78^\circ C$ for 1 h, then protected diol **129** (210 mg, 0.51 mmol) was added. The reaction mixture was stirred at $60^\circ C$ and TLC monitored. After 17 h, the reaction mixture was diluted with CH_2Cl_2 , washed with Na_2SO_3 (5%), saturated solution of $NaHCO_3$, water and brine, dried over $MgSO_4$ and concentrated under vacuum. Flash chromatography (AcOEt/heptane 5:95) of the crude product gives 220 mg (90%) of the desired compound **143**.

143: ethyl 2-(-5,6-bis(*tert*-butyldimethylsilyloxy)-7a-methyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-ylidene)acetate.



Mp: colourless oil.

$[\alpha]_D^{20} = -28$ (c 0.58, $CHCl_3$).

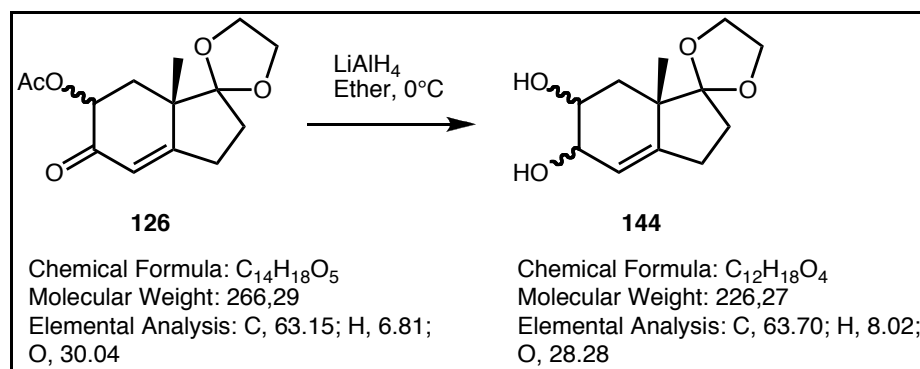
IR (film): $\nu = 2928, 2856, 1712, 1651, 1472, 1361, 1252, 1179, 1115, 1086, 877, 84, 774 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 0.06, 0.07, 0.08$ (s, 12 H, SiMe), 0.09 (s, 9 H, Si*t*Bu), 0.10 (s, 9 H, Si*t*Bu), 1.24 (s, 3 H, H8), 1.29 (t, $J = 7.1$ Hz, 3 H, H12), 1.82 (dd, $J = 4.2, 13.5$ Hz, 1 H, H7), 2.11 (dd, $J = 9.1, 13.5$ Hz, 1 H, H7'), 2.23 (ddd, $J = 1.9, 9.2, 14.6$ Hz, 1 H, H3), 2.56 (tdd, $J = 2.2, 2.4, 9.2$ Hz, 1 H, H3'), 2.89 (dtd, $J = 2.5, 9.2, 19.8$ Hz, 1 H, H2), 3.04 (ddt, $J = 2.3, 10.4, 19.9$ Hz, 1 H, H2'), 3.67 (ddd, $J = 3.1, 4.2, 9.0$ Hz, 1 H, H6), 4.03 (dd, $J = 3.2, 4.9$ Hz, 1 H, H5), 4.16 (q, $J = 7.2$ Hz, 2 H, H11), 5.48 (dd, $J = 1.8, 5.1$ Hz, 1 H, H4), 5.70 (t, $J = 2.5$ Hz, 1 H, H9).

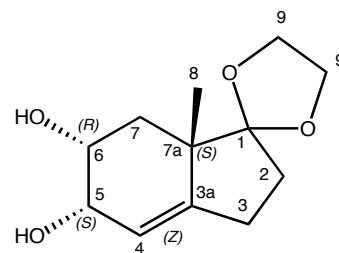
$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = -4.6$ (2C-SiMe), -4.5 (2C-SiMe), 14.3 (C12), 18.2 (2Cq-Si*t*Bu), 26.0 (6C-Si*t*Bu), 28.0 (C3), 30.3 (C8), 30.6 (C2), 36.2 (C7), 47.3 (C7a), 59.6 (C11), 69.2 (C5), 70.4 (C6), 109.6 (C9), 120.2 (C4), 148.2 (C3a), 167.2 (C10), 173.8 (C1).

ESIMS (MeOH): 503.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{26}\text{H}_{48}\text{O}_4\text{Si}_2\text{Na}$ m/z 503.2989, found 503.2974.

Analysis calcd. for $\text{C}_{26}\text{H}_{48}\text{O}_4\text{Si}_2$ (480.83): C 64.95, H 10.06; found C 64.61, H 10.18.



To a magnetically stirred suspension of LiAlH_4 (3.8 g, 99.2 mmol) in 150 mL of THF, cooled to nearly 0°C , was added dropwise a solution of acetoxyenone **126** (13.2 g, 49.6 mmol) in THF (50 mL). After stirring at this temperature for 30-40 min (TLC monitoring) the mixture was diluted with Et_2O and treated with a small amount of 6N NaOH solution (for each 1 g of LiAlH_4 1 mL of water, 1 mL of 6N NaOH and 3 mL more water were added). The organic layer was worked up as usual to give, after silica gel chromatography (ethyl acetate-heptane, 1:1), 98% (11 g) of the desired diols **144**.

144:

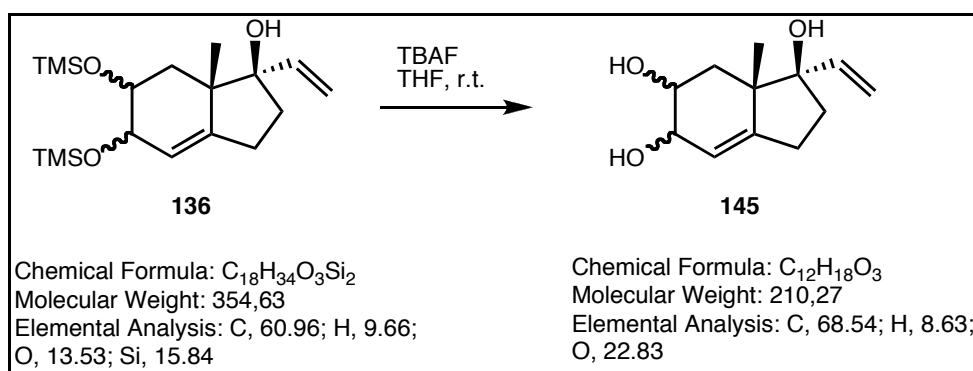
Mp: yellow oil.

 $[\alpha]_D^{20} = -90$ (c 0.8, CHCl_3)IR (film): 3401, 2945, 1308, 1125, 1041, 916, 856 cm^{-1} .

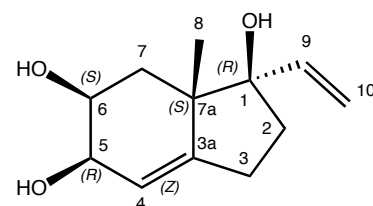
$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): 1.24 (s, 3 H, H8), 1.59 (dd, $J = 8.0, 13.8$ Hz, 1 H, H7), 1.81 (ddd, $J = 4.4, 9.9, 13.8$ Hz, 1 H, H2 or H3), 1.99 (dd, $J = 4.3, 13.8$ Hz, 1 H, H8), 2.05 (ddd, $J = 5.9, 12.4, 13.8$ Hz, 1 H, H2 or H3), 2.21 (ddd, $J = 5.9, 9.9, 16.5$ Hz, 1 H, H2 or H3), 2.36 - 2.47 (m, 2 H, 2OH), 1.59 (dddd, $J = 2.2, 4.3, 12.4, 16.5$ Hz, 1 H, H2 or H3), 3.83 - 4.00 (m, 5 H, H6, H9), 4.17 (t, $J = 5.0$ Hz, 1 H, H5), 5.51 (dd, $J = 2.5, 5.0$ Hz, 1 H, H4).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): 24.7 (C8), 25.6 (C3), 31.8, 32.5 (C2, C7), 46.6 (C7a), 64.3, 65.5, 67.7, 68.8 (C5, C6, 2C9), 117.5 (C1), 118.8 (C4), 150.1 (C3a).

ESIMS (MeOH): 249.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{12}\text{H}_{18}\text{O}_4\text{Na}$ m/z 249.1106, found 249.1103.



TBAF (0.68 mL, 1M in THF) was added to **136** (60 mg, 0.17 mmol), at r.t. under Ar. The reaction mixture was stirred at 60°C for 2 h. Then the reaction mixture was diluted (at r.t.) with ethyl acetate (large amount) and worked up as usual. Flash chromatography (ethyl acetate) give 34 mg (96%) of **145**.

145: 7a-Methyl-1-vinyl-2,3,5,6,7,7a-hexahydro-1*H*-indene-1,5,6-triol.

Mp: colourless oil.

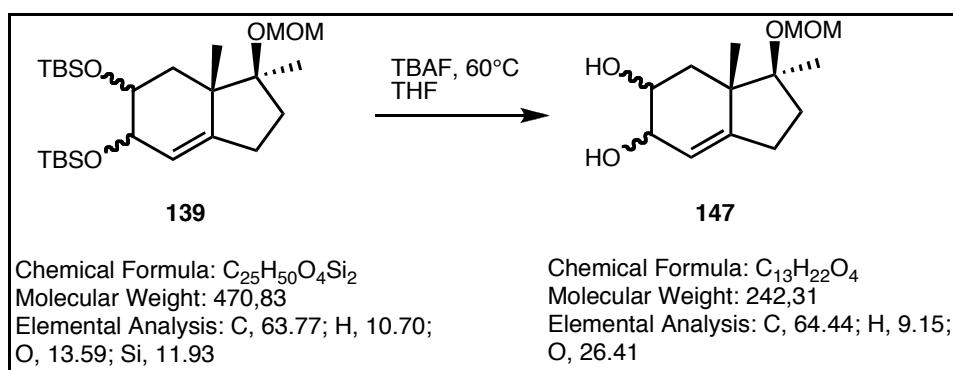
$[\alpha]_D^{20} = -97$ (*c* 1.6, CHCl₃).

IR (film): $\nu = 3372, 2359, 2339, 1053$ cm⁻¹.

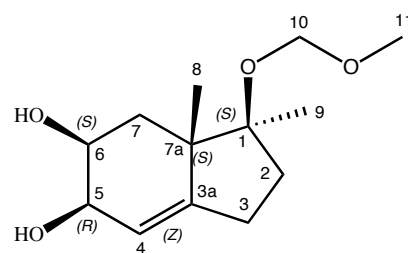
¹H-NMR (CDCl₃, 300 MHz): $\delta = 1.28$ (s, 3 H, H8), 1.59 (dd, *J* = 8.3, 14.1 Hz, 1 H, H7), 1.85 (dd, *J* = 4.6, 14.0 Hz, 1 H, H7'), 1.89 (dd, *J* = 3.3, 9.4 Hz, 1 H, H2), 2.02 (dd, *J* = 7.1, 12.6 Hz, 1 H, H2'), 2.11 - 2.24 (m, 1 H, H3), 2.62 (m, 1 H, H3'), 3.78 (ddd, *J* = 3.7, 4.8, 8.4 Hz, 1 H, H6), 4.13 (t, *J* = 3.9 Hz, 1 H, H5), 5.06 (dd, *J* = 1.2, 10.9 Hz, 1 H, H10), 5.24 (dd, *J* = 1.2, 17.3 Hz, 1 H, H10'), 5.52 (m, 1 H, H4), 5.82 (dd, *J* = 10.9, 17.3 Hz, 1 H, H9).

¹³C-NMR (CDCl₃, 75 MHz): $\delta = 24.0$ (C8), 25.7 (C3), 33.1 (C7), 35.1 (C2), 47.3 (C7a), 67.5 (C5), 68.5 (C6), 82.8 (C1), 111.4 (C10), 119.2 (C4), 141.8 (C9), 150.9 (C3a).

ESIMS (MeOH): 233.1 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₁₂H₁₈O₃Na *m/z* 233.1154, found 233.1156.



TBAF (57.18 mL, 57.18 mmol) was added to **139** (6.73 g, 14.29 mmol), at r.t. under Ar. The reaction mixture was stirred at 60°C for 2 h. Then the reaction mixture was diluted (at r.t.) with ethyl acetate (large amount) and worked up as usual. Flash chromatography (ethyl acetate/heptane 1:1) gives 3.46 g (100%) of **147**.

147: 3-Methoxymethoxy-3,3a-dimethyl-2,3,3a,4,5,6-hexahydro-1*H*-indene-5,6-diol.

Mp: colourless oil.

$[\alpha]_D^{20} = -104$ (*c* 1.25, CHCl₃).

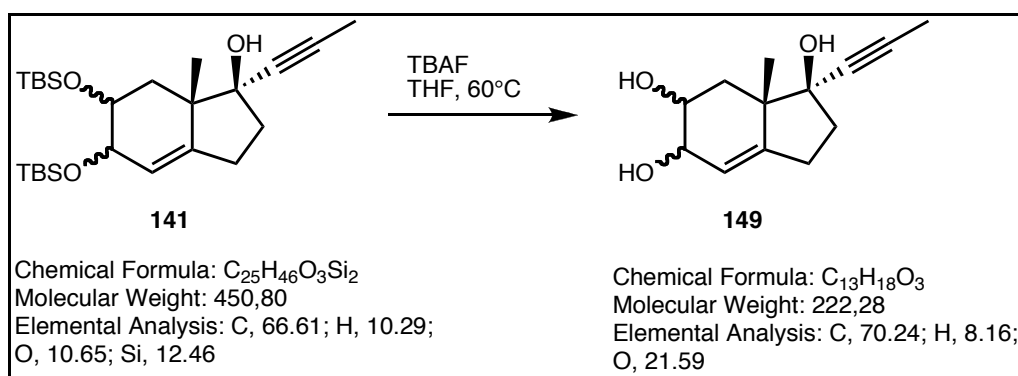
IR (film): $\nu = 3392, 2939, 1462, 1371, 1146, 1032, 918$ cm⁻¹.

¹H-NMR (CDCl₃, 500 MHz): $\delta = 1.13$ (s, 3 H, H₉), 1.23 (s, 3 H, H₈), 1.65 (dd, *J* = 9.0, 14.3 Hz, 1 H, H₇), 1.70 (t, *J* = 3.1 Hz, 1 H, H₂), 2.03 (dd, *J* = 5.1, 14.3 Hz, 1 H, H_{7'}), 2.06 - 2.16 (m, 2 H, H_{2'}, H₃), 2.28 (s, 1 H, OH), 2.37 (s, 1 H, OH), 2.51 - 2.58 (m, 1 H, H_{3'}), 3.37 (s, 3 H, H₁₁), 3.81 (qd, *J* = 4.5, 8.7 Hz, 1 H, H₆), 4.13 (s, 1 H, H₅), 4.70 and 4.75 (ABquartet, *J* = 7.1 Hz, 2 H, H₁₀), 5.50 (ddd, *J* = 1.3, 2.4, 5.4 Hz, 1 H, H₄).

¹³C-NMR (CDCl₃, 125 MHz): $\delta = 21.8$ (C₉), 24.7 (C₈), 25.6 (C₃), 33.2 (C₇), 33.9 (C₂), 48.6 (C_{7a}), 55.4 (C₁₁), 67.6 (C₅), 69.0 (C₆), 84.6 (C₁), 92.2 (C₁₀), 118.7 (C₄), 151.5 (C_{3a}).

ESIMS (CH₂Cl₂ + MeOH): 265.1 ([*M* + Na]⁺, 100). HRESIMS: calcd. for C₁₃H₂₂O₄Na *m/z* 265.1416, found 265.1432.

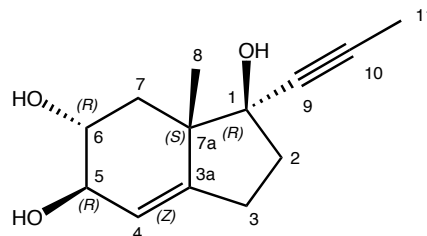
Analysis calcd. for C₁₃H₂₂O₄ · 0.22 H₂O (242.31): C 63.40, H 9.18; found C 63.39, H 9.19.



TBAF (0.78 mL, 1M in THF) was added to **141** (88 mg, 0.195 mmol), at r.t. under Ar. The reaction mixture was stirred at 60°C for 2 h. Then the reaction mixture was diluted

(at r.t.) with ethyl acetate (large amount) and worked up as usual. Flash chromatography (ethyl acetate/heptane 3:1) give 35 mg (81%) of **149**.

149: 7a-methyl-1-(prop-1-ynyl)-2,3,5,6,7,7a-hexahydro-1*H*-indene-1,5,6-triol.



Mp: colourless oil.

$[\alpha]_D^{20} = -192$ (*c* 1.05, CHCl₃).

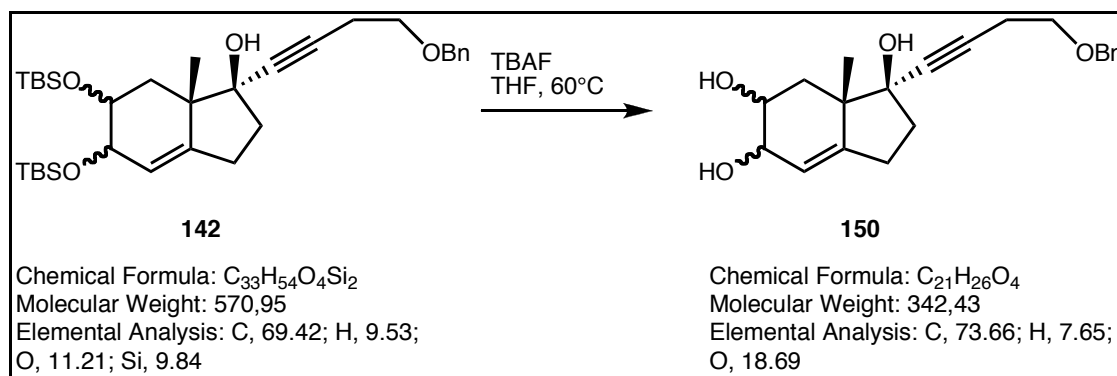
IR (film): $\nu = 3368, 2973, 2919, 1679, 1433, 1122, 1055, 1036, 940, 754$ cm⁻¹.

¹H-NMR (CDCl₃, 300 MHz): $\delta = 1.21$ (s, 3 H, H8), 1.72 (dd, *J* = 7.8, 14.0 Hz, 1 H, H7), 1.80 (s, 3 H, H11), 2.07 (dd, *J* = 4.9, 11.9 Hz, 1 H, H2), 2.18 (ddd, *J* = 4.6, 7.0, 9.0 Hz, 1 H, H3), 2.21 - 2.33 (m, 2 H, H2' and H7'), 2.45 - 2.59 (m, 1 H, H3'), 3.99 - 4.06 (m, 1 H, H6), 4.18 (t, *J* = 3.8 Hz, 1 H, H5), 5.50 (ddd, *J* = 1.2, 2.3, 4.9 Hz, 1 H, H4).

¹³C-NMR (CDCl₃, 75 MHz): $\delta = 3.7$ (C11), 22.8 (C8), 25.5 (C3), 34.3 (C7), 36.8 (C2), 48.5 (C7a), 67.8 (C5), 68.7 (C6), 78.6 (C1), 81.7 (C10), 82.1 (C9), 119.4 (C4), 150.0 (C3a).

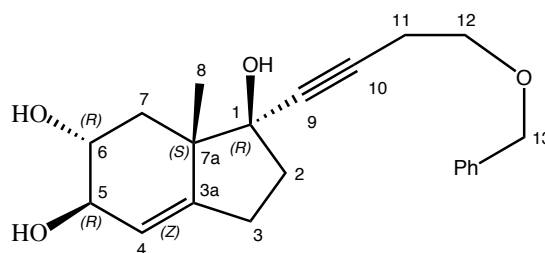
ESIMS (MeOH): 245.1 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₁₃H₁₈O₃Na *m/z* 245.1154, found 245.1156.

Analysis calcd. for C₁₃H₁₈O₃ · 1.5 H₂O (222.28): C 62.63, H 8.49; found C 62.48, H 7.51.



TBAF (3.64 mL, 1M in THF) was added to **142** (346 mg, 0.61 mmol), at r.t. under Ar. The reaction mixture was stirred at 60°C for 2 h. Then the reaction mixture was diluted (at r.t.) with ethyl acetate (large amount) and worked up as usual. Flash chromatography (ethyl acetate/heptane 3:1) gives 146 mg (70%) of **150**.

150: 1-(4-Benzyloxy-but-1-ynyl)-7a-methyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-1,5,6-triol.



Mp: colourless oil.

$[\alpha]_D^{20} = -133$ (*c* 0.87, CHCl₃).

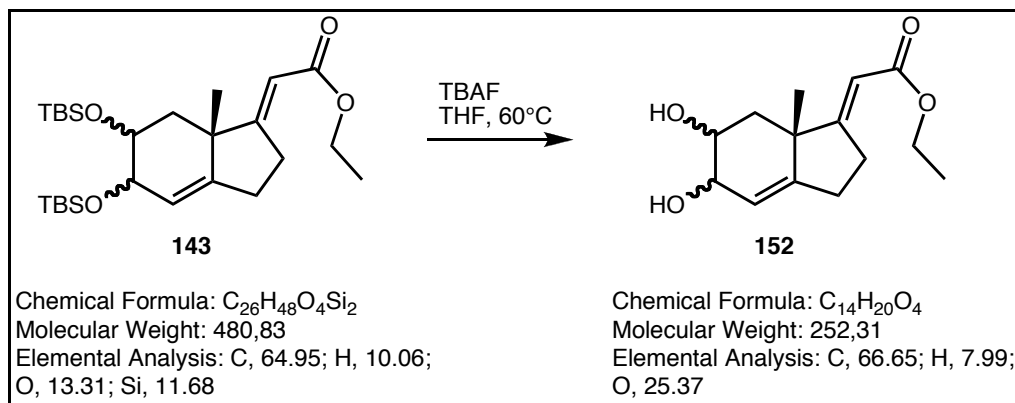
IR (film): $\nu = 3388, 2920, 1454, 1110, 939, 740, 698$ cm⁻¹.

¹H-NMR (CDCl₃, 300 MHz): $\delta = 1.12$ (s, 3 H, H8), 1.64 (dd, *J* = 7.7, 14.0 Hz, 1 H, H7), 1.98 (dd, *J* = 4.4, 11.5 Hz, 1 H, H2), 2.03 - 2.12 (m, 2 H, H2', H3), 2.18 (dd, *J* = 4.7, 14.0 Hz, 1 H, H7'), 2.39 (t, *J* = 6.7 Hz, 2 H, H11), 2.42 - 2.48 (m, 1 H, H3'), 2.88 (bs, 3 H, 3OH), 3.45 (t, *J* = 6.7 Hz, 2 H, H12), 3.89 - 3.94 (m, 1 H, H6), 4.02 (t, *J* = 3.9 Hz, 1 H, H5), 4.44 (s, 2 H, H13), 5.36 (ddd, *J* = 0.9, 2.2, 4.8 Hz, 1 H, H4), 7.21 - 7.28 (m, 5 H, Ph).

¹³C-NMR (CDCl₃, 75 MHz): $\delta = 20.0$ (C11), 22.6 (C8), 25.3 (C3), 34.1 (C7), 36.6 (C2), 48.4 (C7a), 67.7 (C5), 68.2 (C12), 68.6 (C6), 72.7 (C13), 78.3 (C1), 82.6 (C10), 84.2 (C9), 119.4 (C4), 127.6, 127.7, 128.4 (5C-Ph), 137.7 (Cq-Ph), 149.5 (C3a).

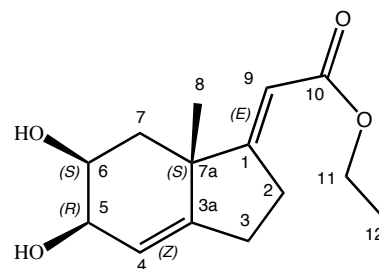
ESIMS (MeOH): 365.1 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₂₁H₂₆O₄Na *m/z* 365.1729, found 365.1749.

Analysis calcd. for C₂₁H₂₆O₄ · 1.0 H₂O (342.43): C 69.98, H 7.83; found C 69.83, H 7.67.



TBAF (1.74 mL, 1M in THF) was added to **143** (209 mg, 0.43 mmol) at r.t. under Ar. The reaction mixture was stirred at 60°C for 2 h. Then the reaction mixture was diluted (at r.t.) with ethyl acetate (large amount) and worked up as usual. Flash chromatography (ethyl acetate/heptane 1:1) give 98 mg (91%) of **152**.

152: (5,6-Dihydroxy-7a-methyl-2,3,5,6,7,7a-hexahydro-inden-1-ylidene)-acetic acid ethyl ester.



Mp: colourless oil.

$[\alpha]_D^{20} = -8$ (*c* 1.2, CHCl₃).

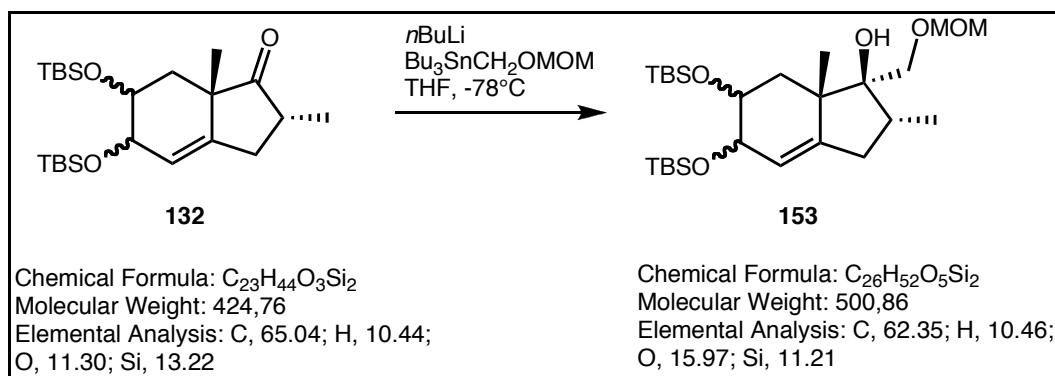
IR (film): $\nu = 3417, 2929, 1707, 1648, 1370, 1347, 1221, 1181, 1150, 1034, 859$ cm⁻¹.

¹H-NMR (CDCl₃, 300 MHz): $\delta = 1.27$ (t, *J* = 7.1 Hz, 3 H, H₁₂), 1.32 (s, 3 H, H₈), 1.74 (dd, *J* = 2.8, 14.0 Hz, 1 H, H₇), 2.25 (dd, *J* = 5.3, 14.1 Hz, 1 H, H_{7'}), 2.29 (ddd, *J* = 2.0, 9.4, 14.7 Hz, 1 H, H₃), 2.37 (bs, 1 H, OH), 2.57 - 2.62 (m, 1 H, H_{3'}), 2.85 (dtd, *J* = 2.6, 9.1, 19.9 Hz, 1 H, H₂), 3.03 (ddt, *J* = 2.4, 10.5, 19.9 Hz, 1 H, H_{2'}), 4.06 (bs, 1 H, H₆), 4.14 (q, *J* = 7.1 Hz, 2 H, H₁₁), 4.21 (bs, 1 H, H₅), 5.38 (td, *J* = 0.9, 2.2 Hz, 1 H, H₄), 5.61 (t, *J* = 2.6 Hz, 1 H, H₉).

¹³C-NMR (CDCl₃, 75 MHz): $\delta = 14.4$ (C₁₂), 28.4 (C₃), 28.9 (C₈), 29.8 (C₂), 37.6 (C₇), 45.5 (C_{7a}), 59.7 (C₁₁), 67.8 (C₆), 68.4 (C₅), 110.2 (C₉), 118.3 (C₄), 149.0 (C_{3a}), 167.1 (C₁₀), 174.0 (C₁).

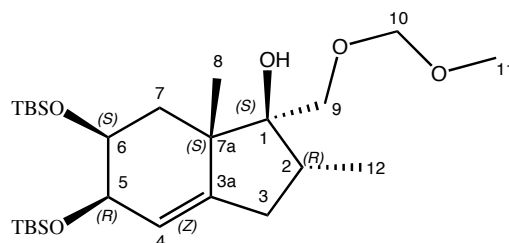
ESIMS (MeOH): 275.1 ($[M + Na]^+$, 100). HRESIMS: calcd. for $C_{14}H_{20}O_4Na$ m/z 275.1259, found 275.1237.

Analysis calcd. for $C_{14}H_{20}O_4 \cdot 0.9 H_2O$ (252.31): C 62.62, H 8.18; found C 62.61, H 7.54.



To a stirred solution of Bu_3SnCH_2OMOM **115** (186 mg, 0.51 mmol), in dry THF (1 mL), at $-78^\circ C$ under Argon, n -BuLi (0.3 mL, 1.6M in hexane) was slowly added (over 5 min). The reaction was stirred 5 min, and then a solution of **132** (45 mg, 0.1 mmol), in THF (1 mL) was slowly added. The reaction was stirred 20 min at $-78^\circ C$. The reaction mixture was diluted with diethyl ether, and a saturated solution of NH_4Cl was added until pH = 7. The aqueous layer was extract with ethyl acetate. The organic layer was worked up as usual and chromatographed on silica gel (ethyl acetate/heptane 1:9) to afford 46 mg of **153** (87%).

153: 5,6-Bis-(*tert*-butyl-dimethyl-silyloxy)-1-methoxymethoxymethyl-2,7a-dimethyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-ol.



Mp: colorless oil.

$[\alpha]_D^{20} = -106$ (c 0.8, $CHCl_3$).

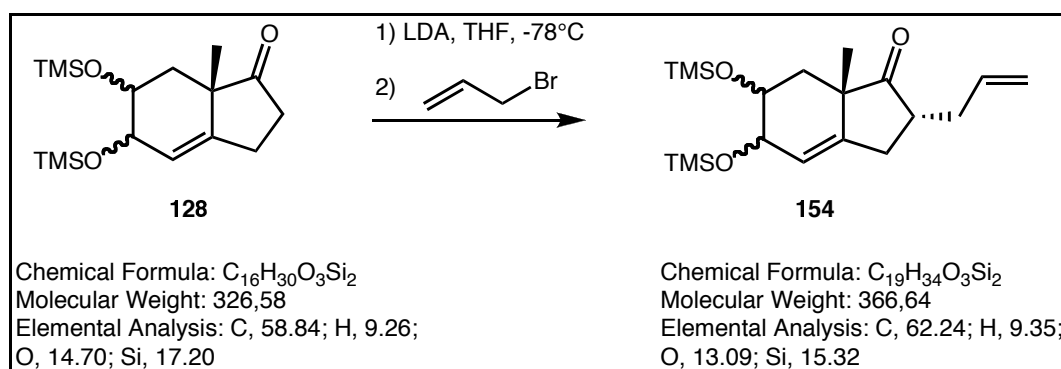
IR (film): $\nu = 3571, 2953, 2929, 2885, 2856, 1472, 1361, 1252, 1108, 1083, 1043, 1004, 835, 774$ cm^{-1} .

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 0.01$ (s, 3 H, SiMe), 0.03 (s, 3 H, SiMe), 0.04 (s, 3 H, SiMe), 0.05 (s, 3 H, SiMe), 0.88 (s, 9 H, Si*t*Bu), 0.89 (s, 9 H, Si*t*Bu), 1.00 (d, $J = 7.0$ Hz, 3 H, H12), 1.23 (s, 3 H, H8), 1.65 (dd, $J = 11.3, 14.0$ Hz, 1 H, H7), 1.66 (ddd, $J = 1.4, 8.7, 17.0$ Hz, 1 H, H3), 1.92 (dd, $J = 5.8, 14.0$ Hz, 1 H, H7), 2.35 - 2.49 (m, 1 H, H2), 2.71 (ddd, $J = 2.4, 11.0, 17.1$ Hz, 1 H, H3), 3.38 (s, 3 H, H11), 3.44 (d, $J = 2.0$ Hz, 2 H, H9), 3.48 (ddd, $J = 2.5, 5.8, 11.2$ Hz, 1 H, H6), 3.92 (dd, $J = 2.4, 6.4$ Hz, 1 H, H5), 4.59 and 4.65 (ABquartet, $J = 6.4$ Hz, 2 H, H10), 5.45 (ddd, $J = 1.7, 2.3, 6.5$ Hz, 1 H, H4).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = -4.5$ (2C-SiMe), -4.4 (2C-SiMe), 15.3 (C12), 18.2 (2Cq-Si*t*Bu), 25.8, 25.9, 26.0 (C8, 6C-Si*t*Bu), 32.5 (C7), 34.2 (C3), 39.1 (C2), 48.8 (C7a), 55.8 (C11), 68.6 (C5), 68.9 (C9), 71.5 (C6), 81.0 (C1), 97.5 (C10), 120.2 (C4), 148.1 (C3a).

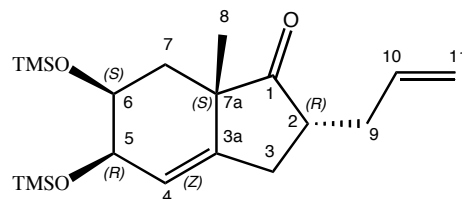
ESIMS (MeOH): 523.3 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{26}\text{H}_{52}\text{O}_5\text{Si}_2\text{Na}$ m/z 523.3251, found 523.3214.

Analysis calcd. for $\text{C}_{26}\text{H}_{52}\text{O}_5\text{Si}_2$ (500.86): C 62.35, H 10.46; found C 62.75, H 10.83.



To a solution of diisopropylamine (0.05 mL, 0.35 mmol) in dry THF (2 mL) under argon at -78°C was added 0.2 mL (0.31 mmol, 1.6M in hexane) of *n*-BuLi. After stirring the mixture at -78°C for 15 min, a solution of **128** (100 mg, 0.31 mmol) in dry THF (1 mL) was added, the mixture was stirred at -78°C for 1.5 h, quenched with saturated aqueous solution of ammonium chloride (2 mL/mmol), extracted with ether and following usual work up the residue was purified by flash chromatography on silica gel (ethyl acetate-heptane, 1:8) to afford 41 mg (40%) of **154** together with unreacted starting material (45 mg, 45%).

154: 2-Allyl-7a-methyl-5,6-bis-(trimethyl-silanyloxy)-2,3,5,6,7,7a-hexahydro-inden-1-one.



Mp: colourless oil.

$[\alpha]_D^{20} = -12$ (c 1.25, CHCl_3).

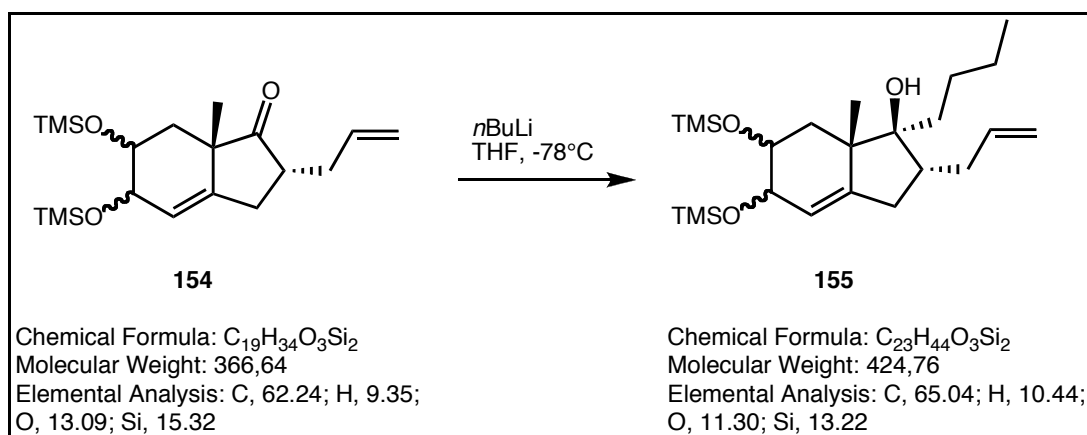
IR (film): $\nu = 2956, 1745, 1439, 1249, 1090, 893, 839 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 0.13$ (s, 9 H, SiMe), 0.15 (s, 9 H, SiMe), 1.33 (s, 3 H, H8), 1.85 - 1.89 (m, 2 H, H7), 1.92 - 2.04 (m, 1 H, H9), 2.20 (dd, $J = 1.8, 15.0$ Hz, 1 H, H3), 2.42 (dddt, $J = 1.5, 4.3, 5.8, 14.3$ Hz, 1 H, H9'), 2.71 (tdd, $J = 2.0, 4.2, 9.9$ Hz, 1 H, H2), 2.92 (ddt, $J = 2.1, 10.2, 14.9$ Hz, 1 H, H3'), 3.74 (dt, $J = 4.0, 7.2$ Hz, 1 H, H6), 4.07 (dt, $J = 1.7, 4.0$ Hz, 1 H, H5), 5.00 (s, 1 H, H11), 5.06 (d, $J = 8.1$ Hz, 1 H, H11'), 5.56 (dd, $J = 2.3, 4.0$ Hz, 1 H, H4), 5.70 (dddd, $J = 6.0, 7.8, 10.4, 16.5$ Hz, 1 H, H10).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 0.2$ (3C-SiMe), 0.3 (3C-SiMe), 24.6 (C8), 31.6 (C3), 33.5 (C7), 35.4 (C9), 45.2 (C2), 50.0 (C7a), 69.0 (C5), 70.0 (C6), 116.8 (C11), 123.2 (C4), 135.6 (C10), 143.9 (C3a), 218.6 (C1).

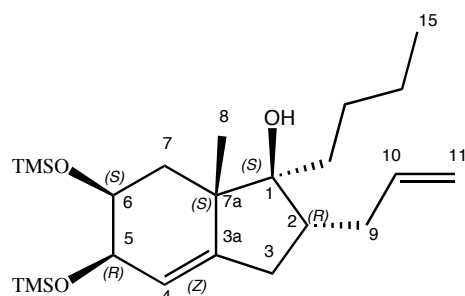
ESIMS (MeOH): 389.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{19}\text{H}_{34}\text{O}_3\text{Si}_2\text{Na}$ m/z 389.1944, found 389.1951.

Analysis calcd. for $\text{C}_{19}\text{H}_{34}\text{O}_3\text{Si}_2$ (366.64): C 62.24, H 9.35; found C 62.29, H 9.37.



To a stirred solution of **154** (79 mg, 0.22 mmol), in THF (5 mL), at -78°C , *n*-butyl lithium (0.41 mL, 1.6M in hexane) was slowly added. The solution was stirred 1 h at -78°C . Then the reaction mixture was diluted with ether, and a saturated solution of NH_4Cl was added until $\text{pH} = 7$. The aqueous layer was extract with Et_2O . The organic layer was worked up as usual and chromatographed on silica gel (ethyl acetate/heptane 2:8) to afford 86 mg of **155** (95%).

155: 2-Allyl-1-butyl-7a-methyl-5,6-bis-(trimethyl-silanyloxy)-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-ol.



Mp: 35.0°C .

$[\alpha]_D^{20} = -99$ (*c* 0.55, CHCl_3).

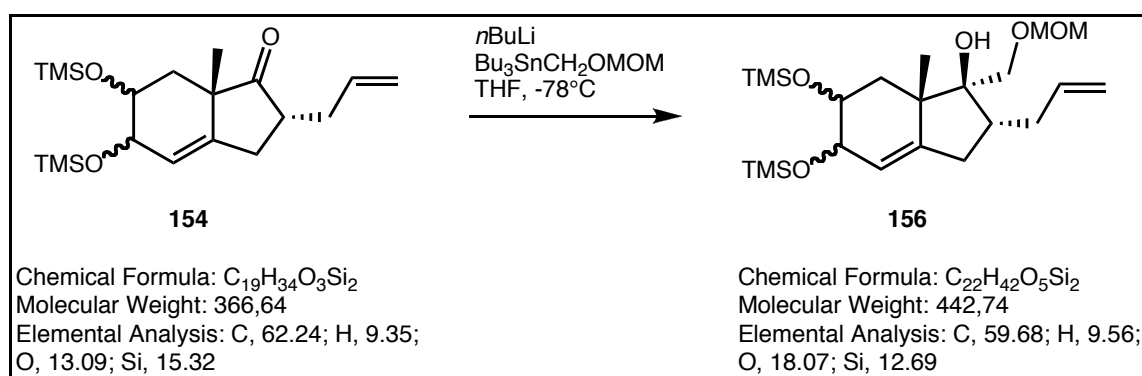
IR (film): $\nu = 2955, 2357, 1248, 1086, 896, 839 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 0.12$ (s, 18 H, SiMe), 1.93 (t, $J = 7.0$ Hz, 3 H, H15), 1.27 (s, 3 H, H8), 1.30 - 1.50 (m, 6 H, Bu), 1.62 (dd, $J = 5.0, 14.1$ Hz, 1 H, H7), 1.76 (dd, $J = 9.0, 17.0$ Hz, 1 H, H3), 1.83 (dd, $J = 5.0, 14.0$ Hz, 1 H, H7'), 1.89 - 1.98 (m, 1 H, H9), 2.26 (dtd, $J = 4.3, 9.3, 10.5$ Hz, 1 H, H2), 2.38 - 2.48 (m, 1 H, H9'), 2.67 (dd, $J = 10.7, 17.2$ Hz, 1 H, H3'), 3.73 (ddd, $J = 3.2, 5.1, 8.8$ Hz, 1 H, H6), 4.02 (dd, $J = 3.7, 4.4$ Hz, 1 H, H5), 4.98 (d, $J = 10.1$ Hz, 1 H, H11), 5.06 (dd, $J = 1.5, 17.1$ Hz, 1 H, H11'), 5.37 (dt, $J = 2.0, 5.4$ Hz, 1 H, H4), 5.79 (ddt, $J = 7.0, 10.1, 17.1$ Hz, 1 H, H10).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 0.0$ (3C-SiMe), 0.3 (3C-SiMe), 13.9 (C15), 24.0 (Bu), 25.0 (C8), 26.5 (Bu), 32.5 (C3), 32.9 (Bu), 33.3 (C7), 35.2 (C9), 46.0 (C2), 49.4 (C7a), 68.8 (C5), 70.6 (C6), 82.6 (C3a), 115.2 (C11), 119.7 (C4), 137.9 (C10), 148.3 (C1).

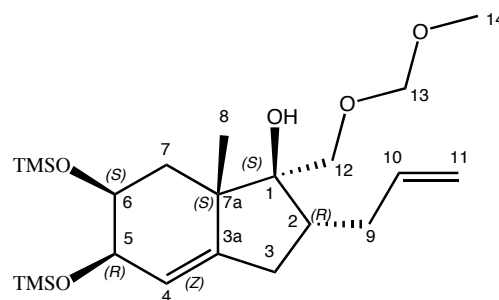
ESIMS (MeOH): 447.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{23}\text{H}_{44}\text{O}_3\text{Si}_2\text{Na}$ m/z 447.2727, found 447.2730.

Analysis calcd. for $\text{C}_{23}\text{H}_{44}\text{O}_3\text{Si}_2 \cdot 0.1 \text{ H}_2\text{O}$ (424.76): C 64.76, H 10.44; found C 64.68, H 10.38.



To a stirred solution of Bu₃SnCH₂OMOM **115** (215 mg, 0.59 mmol), in dry THF (1.5 mL), at -78°C under Argon, *n*-BuLi (0.36 mL, 1.6M in hexane) was slowly added (over 5 min). The reaction was stirred 5 min, and then a solution of **154** (70 mg, 0.19 mmol), in THF (2.5 mL) was slowly added. The reaction was stirred 20 min at -78°C. The reaction mixture was diluted with diethyl ether, and a saturated solution of NH₄Cl was added until pH = 7. The aqueous layer was extract with ethyl acetate. The organic layer was worked up as usual and chromatographed on silica gel (ethyl acetate/heptane 5:95) to afford 48 mg of **156** (57%).

156: 2-allyl-1-((methoxymethoxy)methyl)-7a-methyl-5,6-bis(trimethylsilyloxy)-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-ol.



Mp: colourless oil.

$[\alpha]_D^{20} = -93$ (*c* 0.45, CHCl₃).

IR (film): $\nu = 2953, 2360, 1248, 1081, 1039, 896, 839$ cm⁻¹.

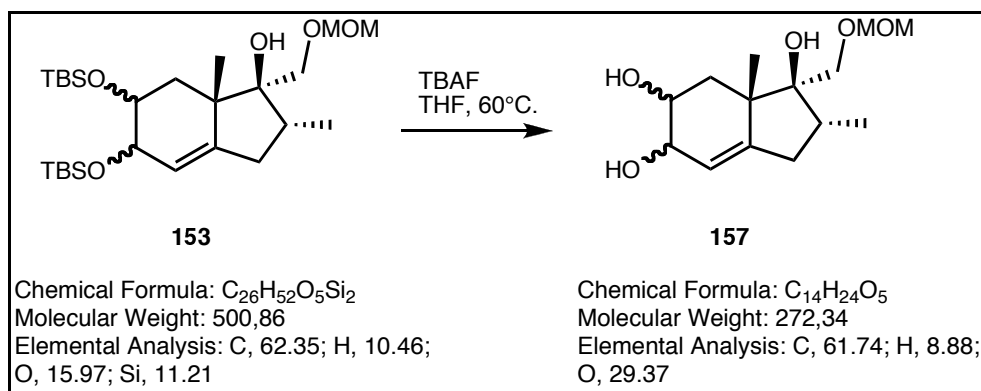
¹H-NMR (CDCl₃, 500 MHz): $\delta = 0.13$ (s, 18 H, SiMe), 1.30 (s, 3 H, H8), 1.69 (dd, *J* = 9.7, 14.0 Hz, 1 H, H7), 1.73 (dd, *J* = 8.5, 17.7 Hz, 1 H, H3), 1.85 (ddd, *J* = 7.6, 10.7, 13.7 Hz, 1 H, H9), 1.99 (dd, *J* = 5.0, 14.1 Hz, 1 H, H7), 2.38 - 2.45 (m, 1 H, H2), 2.46 - 2.48 (m, 1 H, H9), 2.72 (ddd, *J* = 2.4, 11.7, 17.6 Hz, 1 H, H3), 3.41 (s, 3 H, H14), 3.48 and 3.50

(ABquartet, $J = 9.9$ Hz, 2 H, H12), 3.63 (ddd, $J = 3.1, 4.9, 9.8$ Hz, 1 H, H6), 4.02 (dd, $J = 3.2, 5.4$ Hz, 1 H, H5), 4.65 and 4.68 (ABquartet, $J = 6.5$ Hz, 2 H, H13), 4.98 (dd, $J = 1.6, 10.4$ Hz, 1 H, H11), 5.05 (dd, $J = 1.6, 17.1$ Hz, 1 H, H11), 5.43 (d, $J = 5.5$ Hz, 1 H, H4), 5.80 (dddd, $J = 6.2, 7.4, 10.0, 17.1$ Hz, 1 H, H10).

^{13}C -NMR (CDCl_3 , 75 MHz): $\delta = 0.0$ (3C-SiMe), 0.3 (3C-SiMe), 24.6 (C8), 32.2 (C3), 32.9 (C7), 35.1 (C9), 43.8 (C2), 48.5 (C7a), 55.7 (C14), 68.5 (C5), 68.9 (C12), 70.4 (C6), 81.0 (C3a), 97.3 (C13), 115.1 (C11), 120.2 (C4), 137.9 (C10), 147.5 (C1).

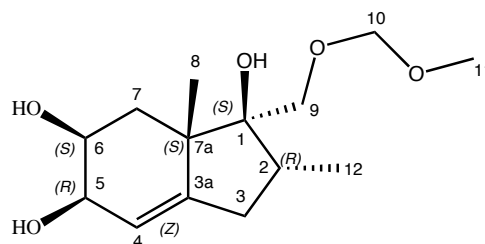
ESIMS (MeOH): 465.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{22}\text{H}_{42}\text{O}_5\text{Si}_2\text{Na}$ m/z 465.2468, found 465.2469.

Analysis calcd. for $\text{C}_{22}\text{H}_{42}\text{O}_5\text{Si}_2$ (442.74): C 59.68, H 9.56; found C 59.33, H 9.58.



TBAF (0.78 mL, 1M in THF) was added to **153** (88 mg, 0.195 mmol), at r.t. under Ar. The reaction mixture was stirred at 60°C for 2 h. Then the reaction mixture was diluted (at r.t.) with ethyl acetate (large amount) and worked up as usual. Flash chromatography (ethyl acetate/heptane 3:1) gives 35 mg (81%) of **157**.

157: 1-((methoxymethoxy)methyl)-2,7a-dimethyl-2,3,5,6,7,7a-hexahydro-1*H*-indene-1,5,6-triol.



Mp: colourless oil.

$[\alpha]_D^{20} = -82$ (c 0.675, CHCl_3).

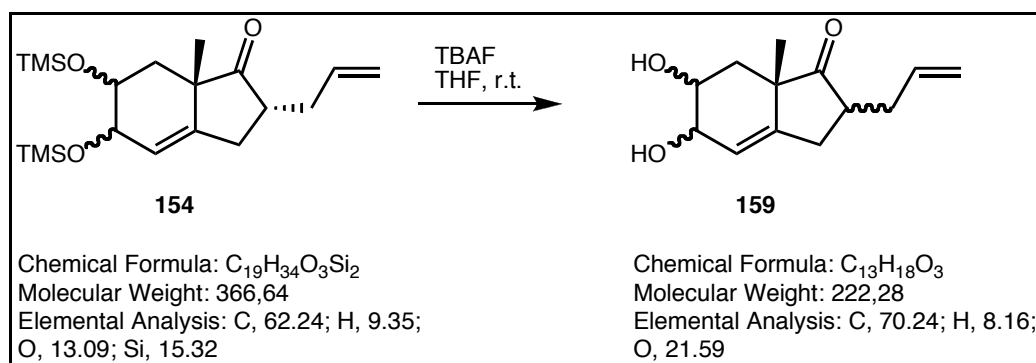
IR (film): $\nu = 3407, 2934, 2878, 1455, 1215, 1148, 1107, 1048 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): $\delta = 0.98$ (d, $J = 7.2 \text{ Hz}$, 3 H, H12), 1.29 (s, 3 H, H8), 1.62 (dd, $J = 9.0, 14.4 \text{ Hz}$, 1 H, H7), 1.68 (dd, $J = 8.5, 16.7 \text{ Hz}$, 1 H, H3), 2.23 (dd, $J = 4.8, 14.3 \text{ Hz}$, 1 H, H7), 2.47 (ddq, $J = 7.2, 8.5, 11.4 \text{ Hz}$, 1 H, H2), 2.78 (dddd, $J = 1.5, 2.3, 11.5, 17.2 \text{ Hz}$, 1 H, H3), 3.38 (s, 3 H, H11), 3.41 and 3.46 (ABquartet, $J = 10.0 \text{ Hz}$, 2 H, H9), 3.77 (ddd, $J = 4.1, 4.8, 8.8 \text{ Hz}$, 1 H, H6), 4.14 (t, $J = 4.5 \text{ Hz}$, 1 H, H5), 4.62 and 4.64 (ABquartet, $J = 6.5 \text{ Hz}$, 2 H, H10), 5.48 (dt, $J = 1.9, 5.3 \text{ Hz}$, 1 H, H4).

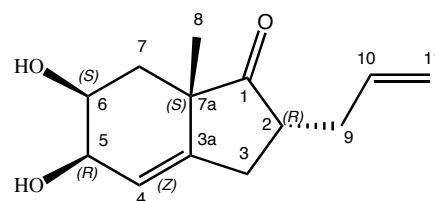
$^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): $\delta = 14.9$ (C12), 25.2 (C8), 33.4 (C3), 34.4 (C3), 38.2 (C2), 48.5 (C7a), 56.1 (C11), 67.5 (C5), 68.8 (C6), 69.2 (C9), 81.0 (C1), 97.7 (C10), 118.9 (C4), 150.5 (C3a).

ESIMS (MeOH): 295.1 ($[M + \text{Na}]^+$, 70). HRESIMS: calcd. for $\text{C}_{14}\text{H}_{24}\text{O}_5\text{Na}$ m/z 295.1521, found 295.1523.

Analysis calcd. for $\text{C}_{14}\text{H}_{24}\text{O}_5 \cdot 0.7 \text{ H}_2\text{O}$ (272.34): C 59.01, H 8.98; found C 58.87, H 8.96.



TBAF (1.04 mL, 1M in THF) was added to **154** (97 mg, 0.26 mmol), at r.t. under Ar. The reaction mixture was stirred at 60°C for 2 h. Then the reaction mixture was diluted (at r.t.) with ethyl acetate (large amount) and worked up as usual. Flash chromatography (ethyl acetate/heptane 1:1) gives 56 mg (97%) of a mixture of two diastereomer **159** (2:1).

159: 2-allyl-5,6-dihydroxy-7a-methyl-2,3,5,6,7,7a-hexahydro-inden-1-one.

Mp: characterized as a diastereomeric mixture.

$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

IR (film): $\nu = 3406, 2928, 1739, 1681, 1640, 1439, 1260, 1106, 1046, 917 \text{ cm}^{-1}$.

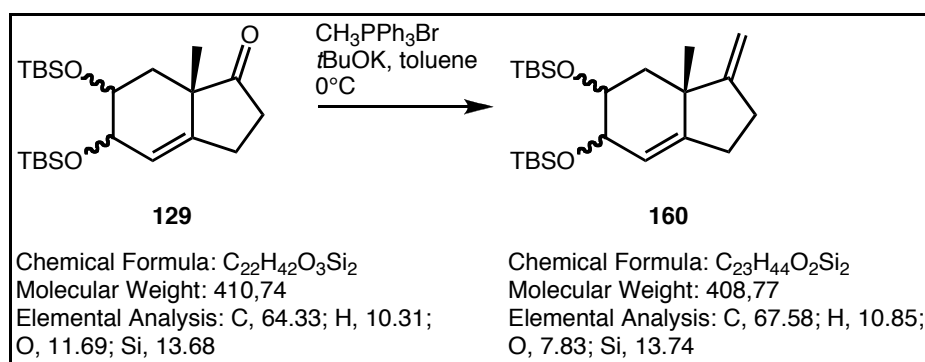
Major diastereomer:

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 1.27$ (s, 3 H, H8), 1.83 (ddd, $J = 3.6, 10.7, 14.3$ Hz, 1 H, H7), 2.06 (ddd, $J = 6.0, 14.3, 18.3$ Hz, 1 H, H7'), 2.21 - 2.24 (m, 1 H, H3), 2.25 - 2.29 (m, 1 H, H9), 2.46 - 2.48 (m, 1 H, H3'), 2.60 - 2.63 (m, 1 H, H9'), 2.95 (ddt, $J = 2.2, 10.2, 14.9$ Hz, 1 H, H2), 3.94 - 3.99 (m, 1 H, H6), 4.18 - 4.21 (m, 1 H, H5), 5.03 - 5.09 (m, 2 H, H11), 5.61 - 5.66 (m, 1 H, H4), 5.75 (ddt, $J = 7.0, 10.1, 17.0$ Hz, 1 H, H10).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 23.6$ (C8), 31.7 (C2), 33.2 (C3), 33.7 (C7), 35.6 (C9), 49.5 (C7a), 68.0 (C5), 68.1 (C6), 117.0 (C11), 120.4 (C4), 135.3 (C10), 145.2 (C3a), 218.5 (C1).

ESIMS (MeOH): 245.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_3\text{Na}$ m/z 245.1154, found 245.1156.

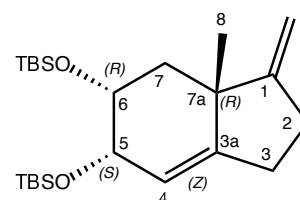
Analysis calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_3$ (222.28): C 70.24, H 8.16; found C 70.27, H 8.13.



A solution of potassium *tert*-butoxide (1.66 g, 14.85 mmol) in 35 mL of dry toluene was stirred under argon at room temperature as methyltriphenylphosphonium bromide (2.65 g, 7.42 mmol) was added. The resulting bright yellow solution was stirred for 1 h,

cooled to 0°C before ketone **129** (2.03 g, 4.95 mmol) was added in dry toluene (35 mL). The ice bath was removed and the solution was stirred at room temperature while the reaction progress was monitored by TLC. After 6 h stirring the reaction mixture was diluted with heptane and worked up as usual. Rapid filtration on silica gel with heptane-EtOAc as eluent afforded 1.91 g of product **160** (94%).

160: 5,6-Bis-(*tert*-butyl-dimethyl-silanyloxy)-3a-methyl-3-methylene-2,3,3a,4,5,6-hexahydro-1*H*-indene.



Mp: colourless oil.

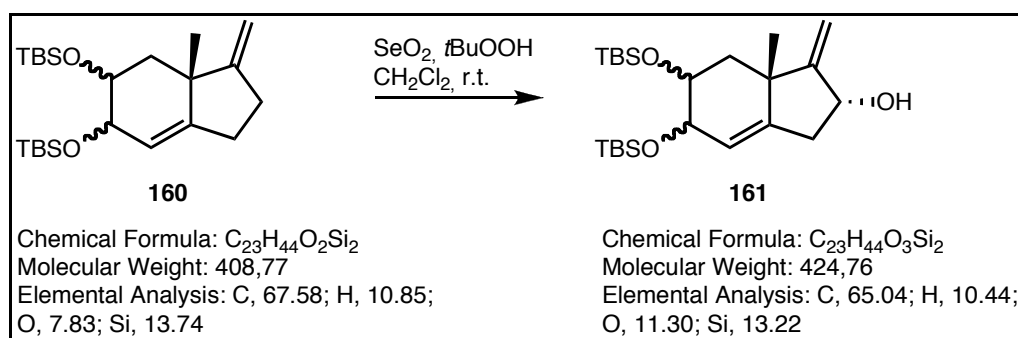
$[\alpha]_D^{20} = -37$ (*c* 0.88, CHCl₃).

IR (film): 2956, 2857, 1470, 1362, 1252, 1128, 1085, 996, 877, 833, 774 cm⁻¹.

¹H-NMR (CDCl₃, 300 MHz): 0.03 (s, 6 H, SiMe), 0.04 (s, 3 H, SiMe), 0.06 (s, 3 H, SiMe), 0.89 (s, 18 H, Si*t*Bu), 1.15 (s, 3 H, H8), 1.82 (dd, *J* = 4.8, 13.3 Hz, 1 H, H7), 2.02 (dd, *J* = 10.0, 13.3 Hz, 1 H, H7'), 2.10 (m, 1 H, H2 or H3), 2.32 (m, 1 H, H2 or H3), 2.43 - 2.67 (m, 2 H, H2 or H3), 3.60 (ddd, *J* = 2.7, 4.8, 10.0 Hz, 1 H, H6), 3.96 (dd, *J* = 2.7, 5.6 Hz, 1 H, H5), 4.73 (t, *J* = 2.0 Hz, 1 H, H9), 4.81 (t, *J* = 2.2 Hz, 1 H, H9'), 5.43 (dd, *J* = 2.2, 5.6 Hz, 1 H, H4).

¹³C-NMR (CDCl₃, 75 MHz): -4.4 (4C-SiMe), 18.3 (2Cq-Si*t*Bu), 26.1(6C-Si*t*Bu), 27.5 (C3), 29.7 (C2), 30.2 (C8), 35.2 (C7), 45.8 (C7a), 69.1, 70.6 (C5, C6), 102.4 (C9), 119.2 (C4), 150.4, 157.9 (C1, C3a).

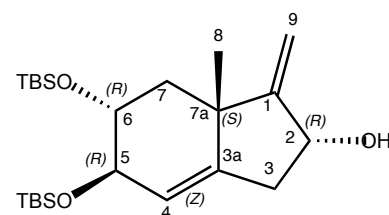
ESIMS (MeOH): 431.3 ([*M* + Na]⁺, 100). HRESIMS calcd. for C₂₃H₄₄O₂Si₂Na *m/z* 431.2776; found 431.2795.



160 (350 mg, 0.85 mmol) was dissolved in dry CH₂Cl₂ (5 mL), SeO₂ (95 mg, 0.85 mmol, 1 eq.) and (70%) *t*BuOOH (0.42 mL, 4.42 mmol, 5.2 eq.) were added at r.t. under argon. After 18 h stirring, dilution with CH₂Cl₂, usual work up and chromatography (heptane:ethyl acetate, 4:1) afforded 225 mg (63%) of the expected compound **161**.

Note: if the selenium oxydation is directly followed (without chromatography) by the MOM protection, the yield is 80% over the two reactions.

161: 3a-Methyl-3-methylene-5,6-bis-(1,1,2,2-tetramethyl-propylsilanyloxy)-2,3,3a,4,5,6-hexahydro-1H-inden-2-ol.



Mp: yellow oil.

$[\alpha]_D^{20} = -58$ (*c* 1.0, CHCl₃).

IR (film): $\nu = 3445, 2928, 2855, 1471, 1462, 1387, 1360, 1250, 1103, 1079, 1053, 848, 833, 772 \text{ cm}^{-1}$.

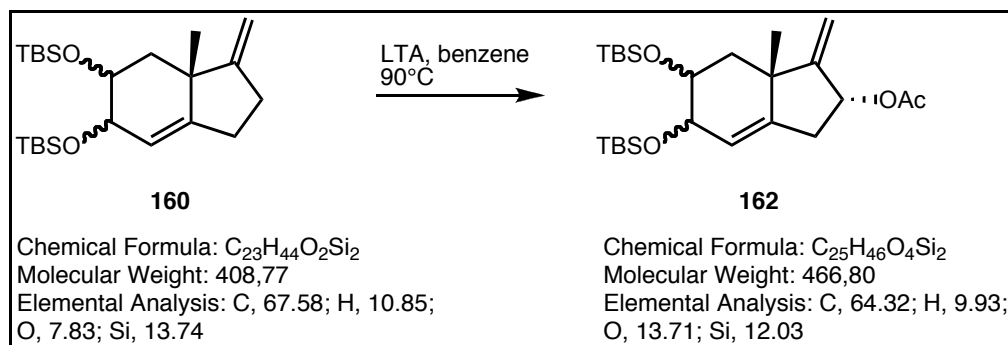
¹H NMR (CDCl₃, 500 MHz): $\delta = 0.08$ (s, 3 H, SiMe), 0.09 (s, 3 H, SiMe), 0.10 (s, 3 H, SiMe), 0.11 (s, 3 H, SiMe), 0.90 (s, 18 H, Si*t*Bu), 1.15 (s, 3 H, H8), 1.64 (t, *J* = 12.1 Hz, 1 H, H4), 1.76 (b, 1 H, OH), 1.94 (dd, *J* = 3.6, 12.6 Hz, 1 H, H4'), 2.15 (d, *J* = 15.8 Hz, 1 H, H1), 2.80 (ddt, *J* = 2.4, 7.5, 15.8 Hz, 1 H, H1'), 3.91 (ddd, *J* = 3.6, 6.8, 11.5 Hz, 1 H, H5), 4.11 (dt, *J* = 2.5, 6.8 Hz, 1 H, H6), 4.65 (dd, *J* = 1.5, 7.5 Hz, 1 H, H2), 4.94 (d, *J* = 1.8 Hz, 1 H, H9), 5.16 (d, *J* = 1.8 Hz, 1 H, H9), 5.30 (t, *J* = 2.6 Hz, 1 H, H7).

¹³C NMR (CDCl₃, 125 MHz): $\delta = -4.4$ (SiMe), -4.3 (SiMe), -3.9 (SiMe), -3.8 (SiMe), 18.0 (Cq-Si*t*Bu), 18.1 (Cq-Si*t*Bu), 26.0 (3C-Si*t*Bu), 26.1 (3C-Si*t*Bu), 27.4 (C8), 39.0 (C1), 43.1

(C4), 45.6 (C3a), 72.6 (C2), 72.7 (C5), 75.0 (C6), 106.9 (C9), 122.5 (C7), 145.7 (C7a), 163.6 (C3).

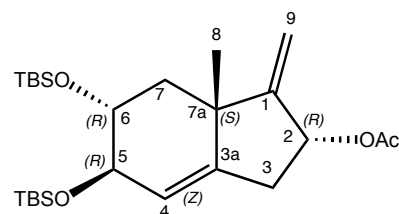
ESIMS (MeOH): 447.3 ($[M + Na]^+$, 100). HRESIMS: calcd. for $C_{23}H_{44}O_3Si_2Na$ m/z 447.2727, found 447.2694.

Analysis calcd. for $C_{23}H_{44}O_3Si_2$ (424.28): C 65.04, H 10.44; found C 65.17, H 10.53.



A dry three-necked flask, equipped with a Dean-Stark apparatus was charged with **160** (340 mg, 0.83 mmol) and $Pb(OAc)_4$ (1.47 g, 3.32 mmol, 4 eq.) vacuumed, flushed with argon before dry benzene (4.5 mL) was added and the reaction mixture was heated at 90°C (oil bath temperature should not exceed 100°C) for 1 h. After cooling a large volume of ether was added, and the reaction mixture stirred for an additional hour, filtered, and the filtrate washed with brine and water, dried on $MgSO_4$, concentrated and purified by chromatography on silica with heptane-EtOAc 96:4 as eluent afforded 133 mg (35%) of **162** (16% of SM recovered).

162: Acetic acid 5,6-bis-(*tert*-butyl-dimethyl-silyloxy)-3a-methyl-3-methylene-2,3,3a,4,5,6-hexahydro-1*H*-inden-2-yl ester.



Mp: 79 - 80°C.

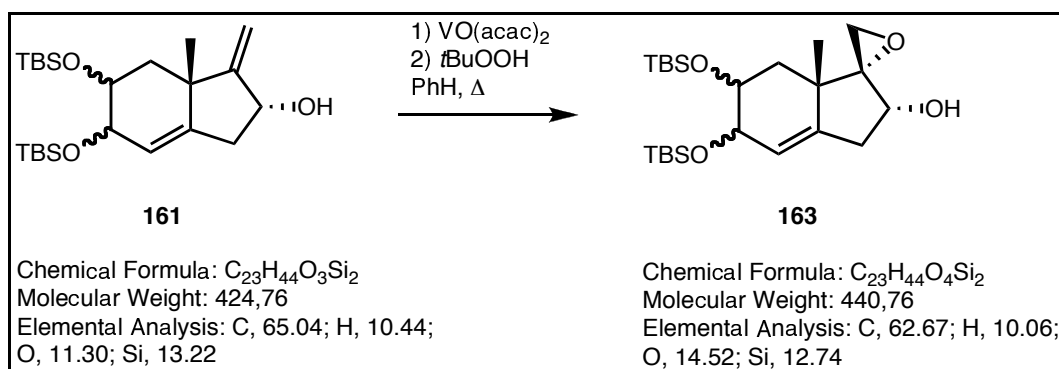
$[\alpha]_D^{20} = -26$ (c 0.5, $CHCl_3$).

IR (film): $\nu = 2956, 2925, 2852, 1739, 1245, 1103, 1077, 1052, 881, 837, 773$ cm^{-1} .

^1H NMR (CDCl_3 , 500 MHz): δ = 0.09 (s, 3 H, SiMe), 0.10 (s, 3 H, SiMe), 0.11 (s, 3 H, SiMe), 0.12 (s, 3 H, SiMe), 0.91 (s, 9 H, Si*t*Bu), 0.92 (s, 9 H, Si*t*Bu), 1.18 (s, 3 H, H8), 1.65 (t, J = 12.3 Hz, 1 H, H7), 1.92 (dd, J = 3.6, 12.5 Hz, 1 H, H7'), 2.05 (s, 3 H, Me-Ac), 2.16 (d, J = 16.7 Hz, 1 H, H3), 2.92 (ddt, J = 2.5, 8.2, 16.7 Hz, 1 H, H3'), 3.92 (ddd, J = 3.6, 7.0, 12.0 Hz, 1 H, H6), 4.13 (td, J = 2.4, 6.9 Hz, 1 H, H5), 4.97 (d, J = 1.8 Hz, 1 H, H9), 5.10 (d, J = 1.8 Hz, 1 H, H9'), 5.24 (t, J = 2.6 Hz, 1 H, H4), 5.68 (dd, J = 1.8, 8.2 Hz, 1 H, H2).

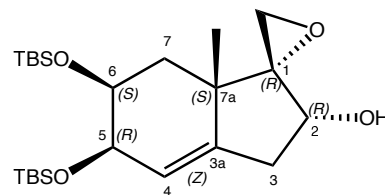
^{13}C NMR (CDCl_3 , 125 MHz): δ = -4.4 (SiMe), -4.4 (SiMe), -3.9 (SiMe), -3.8 (SiMe), 18.0 (Cq-Si*t*Bu), 18.2 (Cq-Si*t*Bu), 21.2 (Me-Ac), 26.0 (3C-Si*t*Bu), 26.1 (3C-Si*t*Bu), 27.2 (C8), 36.2 (C3), 42.9 (C7), 46.0 (C7a), 72.7 (C6), 74.1 (C2), 75.4 (C5), 108.2 (C9), 122.3 (C4), 144.7 (C3a), 158.1 (C1), 170.9 (CO-Ac).

ESIMS (MeOH): 489.3 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{25}\text{H}_{46}\text{O}_4\text{Si}_2\text{Na}$ m/z 489.2832, found 489.2850.



A mixture of alcohol **161** (158 mg, 0.37 mmol) and $\text{VO}(\text{acac})_2$ (1.5 mg, 5.66×10^{-3} mmol) in benzene (8 mL) was refluxed for 15 min under argon. Addition of *t*BuOOH (0.12 mL, 0.66 mmol, 5-6M in decane) followed and stirring continued at this temperature for 10 minutes. After cooling, the mixture was diluted with EtOAc washed with saturated aqueous NaHCO_3 , and worked up as usual. Chromatography of the residue on silica gel (heptane:ethyl acetate, 8:1 to 7:1) yielded the epoxide **163** (106 mg, 65%).

163: 5,6-bis(*tert*-butyldimethylsilyloxy)-7a-methyl-2,3,3a,6,7,7a-hexahydro spiro[indene-1,2'-oxiran]-2-ol.



Mp: colourless oil.

$[\alpha]_D^{20} = -94$ (*c* 0.4, CHCl₃).

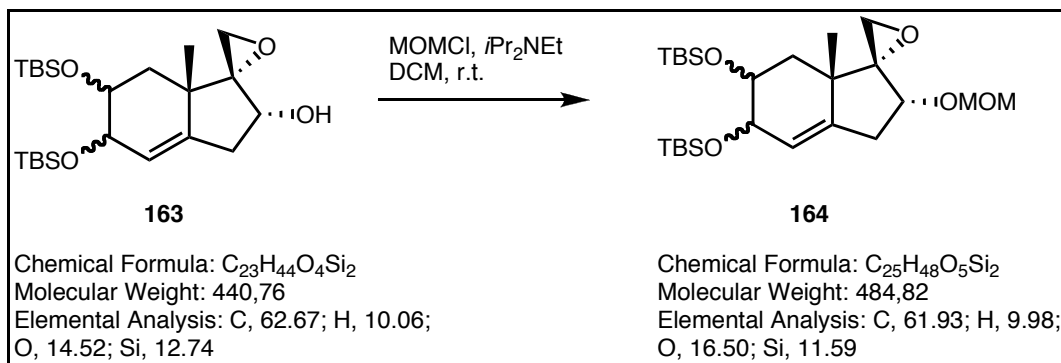
IR (film): $\nu = 3252, 1472, 1362, 1252, 1119, 1099, 1068, 1040, 834, 774, 679$ cm⁻¹.

¹H NMR (CDCl₃, 500 MHz): $\delta = 0.04$ (s, 6 H, SiMe), 0.04 (s, 3 H, SiMe), 0.06 (s, 3 H, SiMe), 0.88 (s, 9 H, Si*t*Bu), 0.88 (s, 9 H, Si*t*Bu), 1.16 (s, 3 H, H8), 1.26 (dd, *J* = 5.5, 13.1 Hz, 1 H, H7), 1.59 (dd, *J* = 10.5, 13.1 Hz, 1 H, H7'), 2.14 (ddd, *J* = 1.2, 3.2, 16.9 Hz, 1 H, H3), 2.27 (d, *J* = 7.6 Hz, 1 H, OH), 2.86 and 2.89 (ABquartet, *J* = 4.1 Hz, 2 H, H9), 2.98 (ddd, *J* = 2.5, 9.1, 16.9 Hz, 1 H, H3), 3.60 (ddd, *J* = 2.6, 5.4, 10.6 Hz, 1 H, H6), 3.96 (dd, *J* = 2.6, 6.2 Hz, 1 H, H5), 4.47 (ddd, *J* = 3.2, 7.2, 9.0 Hz, 1 H, H2), 5.64 (ddd, 1.2, 2.5, 6.2 Hz, 1 H, H4).

¹³C NMR (CDCl₃, 125 MHz): $\delta = -4.7$ (SiMe), -4.6 (SiMe), -4.5 (SiMe), -4.5 (SiMe), 18.2 (2Cq-Si*t*Bu), 25.9 (3C-Si*t*Bu), 26.0 (3C-Si*t*Bu), 26.2 (C8), 30.5 (C8), 37.6 (C3), 42.9 (C7a), 46.8 (C9), 68.5 (C2, C5), 69.2 (C1), 71.0 (C6), 122.1 (C4), 146.4 (C3a).

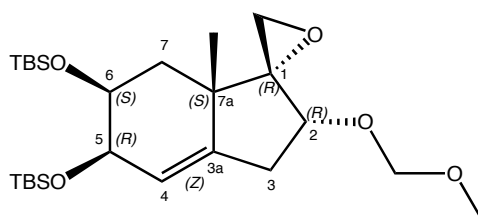
ESIMS (CH₂Cl₂ + MeOH): 463.3 ([*M* + Na]⁺, 100). HRESIMS: calcd. for C₂₃H₄₄O₄NaSi₂ *m/z* 463.2676, found 463.2662.

Analysis calcd. for C₂₃H₄₄O₄Si₂ (440.76): C 62.67, H 10.06; found C 62.64, H 9.82.



To a stirred solution of the alcohol **163** (2.5 g, 5.67 mmol) in dry CH₂Cl₂ (30 mL) at 0°C was added *i*Pr₂NEt (6.1 mL, 35.15 mmol) followed by addition of chloromethyl methyl ether (2.5 mL, 34.02 mmol). The mixture was stirred overnight at r.t. Then, it was quenched with water, and extracted with CH₂Cl₂. The combined extracts were washed with 1N HCl, aqueous saturated NaHCO₃ and worked up as usual. Chromatography of the residue on silica gel (heptane to heptane:ethyl acetate 2:1) yielded **164** (2.61 g, 95%).

164: (2-(methoxymethoxy)-7a-methyl-2,3,3a,6,7,7a-hexahydrospiro[indene-1,2'-oxirane]-5,6-diyl)bis(oxy)bis(*tert*-butyldimethylsilane).



Mp: Yellow oil.

$[\alpha]_D^{20} = -117$ (*c* 1.0, CHCl₃).

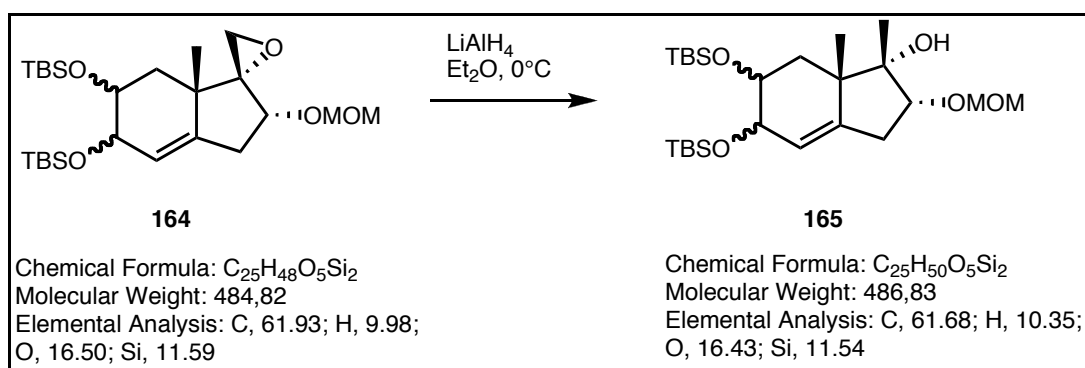
IR (film): 2949, 2928, 2855, 1471, 1362, 1252, 1146, 1117, 1084, 1050, 879, 834, 775 cm⁻¹.

¹H NMR (CDCl₃, 500 MHz): δ = 0.01 (s, 3 H, SiMe), 0.02 (s, 6 H, SiMe), 0.05 (s, 3 H, SiMe), 0.86 (s, 9 H, Si*t*Bu), 0.87 (s, 9 H, Si*t*Bu), 1.15 (s, 3 H, H8), 1.26 (dd, *J* = 5.3, 13.0 Hz, 1 H, H7), 1.53 (dd, *J* = 10.4, 13.0 Hz, 1 H, H7'), 2.26 (ddd, *J* = 1.2, 4.2, 16.7 Hz, 1 H, H3), 2.70 and 2.79 (ABquartet, *J* = 4.4 Hz, 2 H, H9), 2.98 (ddd, *J* = 2.5, 9.5, 16.7 Hz, 1 H, H3), 3.34 (s, 3 H, H11), 3.64 (ddd, *J* = 2.3, 5.3, 10.4 Hz, 1 H, H6), 3.95 (dd, *J* = 2.3, 6.3 Hz, 1 H, H5), 4.53 (dd, *J* = 4.2, 9.5 Hz, 1 H, H2), 4.56 and 4.64 (ABquartet, *J* = 6.8 Hz, 2 H, H10), 5.62 (ddd, *J* = 1.2, 2.5, 6.3 Hz, 1 H, H4).

¹³C NMR (CDCl₃, 125 MHz): -4.7 (SiMe), -4.6 (SiMe), -4.5 (SiMe), -4.4 (SiMe), 18.1 (2Cq-Si*t*Bu), 25.8 (3C-Si*t*Bu), 26.0 (3C-Si*t*Bu), 26.7 (C8), 30.3 (C7), 34.6 (C3), 43.2 (C7a), 45.2 (C9), 55.6 (C11), 67.6 (C1), 68.6 (C5), 71.1 (C6), 73.7 (C2), 96.2 (C10), 121.8 (C4), 146.4 (C3a).

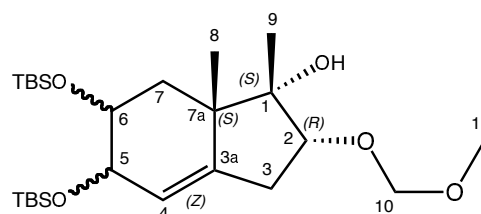
ESIMS (MeOH): 507.2 ([*M* + Na]⁺, 100). HRESIMS: calcd. for C₂₅H₄₈O₅Si₂Na *m/z* 507.2938, found 507.2928.

Analysis calcd. for C₂₅H₄₈O₅Si₂ (484.30): C 61.93, H 9.98; found C 61.78, H 9.97.



To a suspension of LiAlH₄ (40 mg, 1.05 mmol) in 3 mL of anhydrous ether, cooled at 0°C, was added dropwise a solution of epoxyde **164** (163 mg, 0.34 mmol, diastereomeric mixture) in 3 mL anhydrous ether. The reaction mixture was stirred at 0°C for 30 min at which point no starting material remained (TLC monitoring), diluted with wet ether and quenched with 0.04 mL of water, 0.04 mL of 6N NaOH, 0.12 mL of water, and stirring was continued at r.t. for 1 h. Filtration and concentration under reduced pressure yielded a mixture of alcohols **165** (144 mg, 94%).

165: 5,6-Bis-(*tert*-butyl-dimethyl-silanyloxy)-2-methoxymethoxy-1,7a-dimethyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-ol.



Mp: colourless oil (characterized as a diastereomeric mixture).

$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

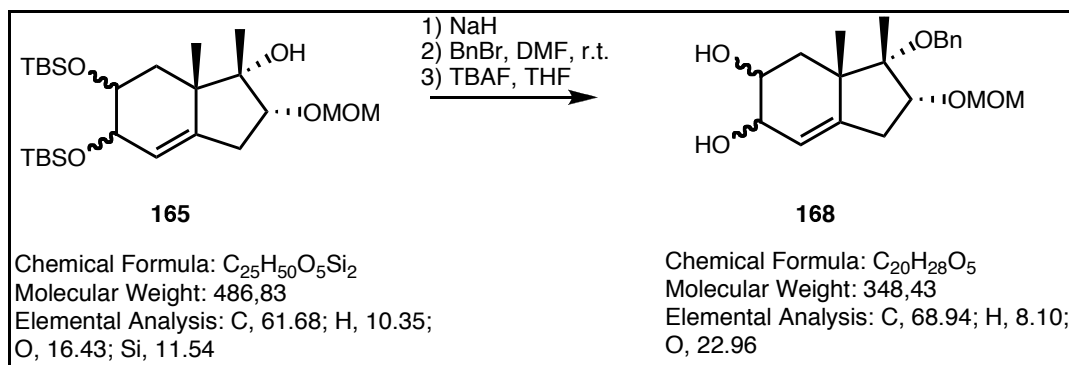
IR (film): $\nu = 2927, 2854, 1725, 1471, 1360, 1249, 1149, 1105, 1052, 1004, 879, 833, 773 \text{ cm}^{-1}$.

¹H-NMR (CDCl₃, 500 MHz): δ = characterized as a diastereomeric mixture.

¹³C-NMR (CDCl₃, 125 MHz): δ = characterized as a diastereomeric mixture.

ESIMS (CH₂Cl₂ + MeOH): 509.3 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for C₂₅H₅₀O₅Si₂Na m/z 509.3095, found 509.3090.

Analysis calcd. for C₂₅H₅₀O₅Si₂ (486.83): C 61.68, H 10.35; found C 61.76, H 10.04.

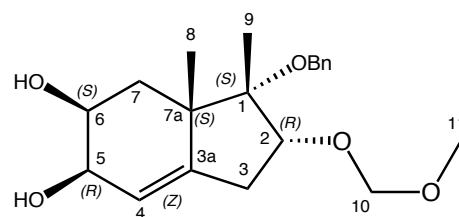


Sodium hydride (60% w/w in mineral oil; 187 mg, 4.3 mmol) was washed twice with dry hexane under argon atmosphere and the remainder of the hexane removed *via* syringe and the flask vacuumed then filled with argon. *N,N*-dimethylformamide (3 mL) and alcohol **165** (400 mg, 0.8 mmol) were added. After stirring for 0.5 h the reaction mixture was cooled to 0°C and BnBr (0.3 mL, 2.5 mmol) was added and the mixture was stirred for 20 h. Water and ether were added, the two phases separated and the organic phase was worked up as usual. The residue was chromatographed on silica (hexane-ethyl acetate, 9:1).

The product **167** is contaminated with BnBr so the yield was then done after TBAF deprotection.

To a magnetically stirred solution of **167** (474 mg, 0.8 mmol, 1 eq.) in dry THF (4 mL) was added tetrabutylammonium fluoride (3.2 mmol, 1M in THF). The reaction was kept at 60°C for 2 h (TLC monitoring). Ethyl acetate was then added and following extraction the crude mixture was worked up as usual. The residue was purified by chromatography (SiO₂, heptane-EtOAc, 2:1) to give the corresponding alcohol **168** (140 mg, 49% in two steps).

168: 3-Benzyloxy-2-methoxymethoxy-3,3a-dimethyl-2,3,3a,4,5,6-hexahydro-1*H*-indene-5,6-diol.



Mp: colourless oil.

$[\alpha]_D^{20} = -76$ (*c* 0.3, CHCl₃).

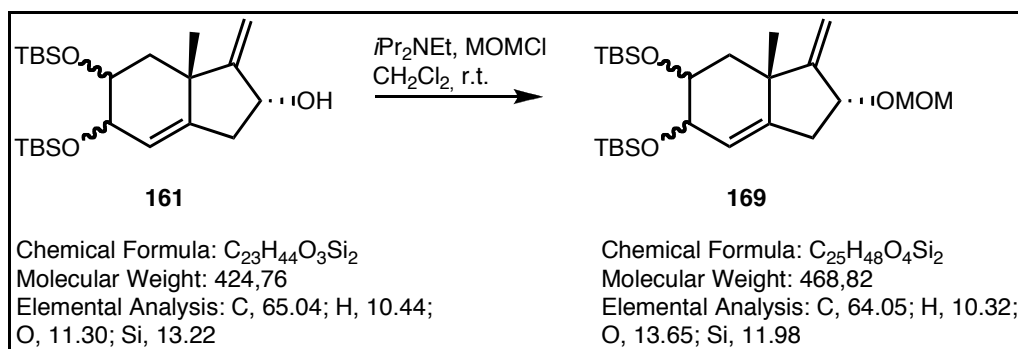
IR (film): $\nu = 3391, 2941, 2888, 1449, 1389, 1146, 1105, 1042, 917 \text{ cm}^{-1}$.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): $\delta = 1.12$ (s, 3 H, H8), 1.34 (s, 3 H, H9), 1.43 (dd, $J = 8.3, 13.5$ Hz, 1 H, H7), 2.23 (dd, $J = 5.5, 13.5$ Hz, 1 H, H7), 2.28 (dd, $J = 6.7, 17.0$ Hz, 1 H, H3), 2.88 (dd, $J = 9.4, 16.1$ Hz, 1 H, H3), 3.36 (s, 3 H, H11), 3.88 (td, $J = 3.5, 8.3$ Hz, 1 H, H6), 4.14 (t, $J = 4.4$ Hz, 1 H, H5), 4.24 (dd, $J = 6.9, 9.2$ Hz, 1 H, H2), 4.60 and 4.97 (ABquartet, $J = 12.0$ Hz, 2 H, CH_2Ph), 4.61 and 4.63 (ABquartet, $J = 6.4$ Hz, 2 H, H10), 5.53 (d, $J = 5.4$ Hz, 1 H, H4), 7.17 - 7.29 (m, 5 H, Ph).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): $\delta = 13.7$ (C9), 26.8 (C8), 32.4 (C7), 33.3 (C3), 49.1 (C7a), 55.4 (C11), 66.9 (CH_2Ph), 67.9 (C5), 69.5 (C6), 83.2 (C2), 85.0 (C1), 86.2 (C10), 117.9 (C4), 126.5 (Ph), 126.6 (2C-Ph), 128.0 (2C-Ph), 140.9 (Cq-Ph), 151.3 (C3a).

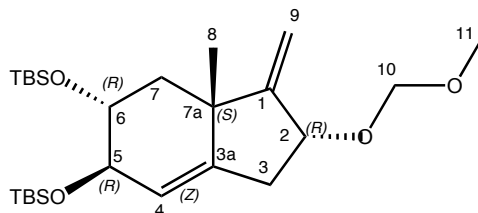
ESIMS (MeOH): 371.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{20}\text{H}_{28}\text{O}_5\text{Na}$ m/z 371.1834, found 371.1830.

Analysis calcd. for $\text{C}_{20}\text{H}_{28}\text{O}_5 \cdot 0.65 \text{ H}_2\text{O}$ (348.1): C 66.70, H 8.20; found C 66.69, H 7.73.



To an ice-cold solution of **161** (310 mg, 0.73 mmol) in 4 mL of dry methylene chloride, under argon, was added chloromethyl methylether (0.33 mL, 4.37 mmol) and diisopropylethylamine (0.78 mL, 4.52 mmol). The reaction mixture was allowed to warm and stirred at r.t. for 16 h (while TLC-monitored), then quenched with water. The aqueous phase was extracted with methylene chloride and the combined organic layers were washed with dilute HCl, a saturated aq. solution of NaHCO_3 and brine. The combined organic extracts were dried over MgSO_4 , concentrated and purified by column chromatography (ethyl acetate-heptane, 1:9) to give 303 mg (89%) of **169**.

169: 2-Methoxymethoxy-3a-methyl-3-methylene-5,6-bis-(1,1,2,2-tetramethyl-propyl silanyloxy)-2,3,3a,4,5,6-hexahydro-1*H*-indene.



Mp: yellow oil.

$[\alpha]_D^{20} = -88$ (*c* 0.9, CHCl₃).

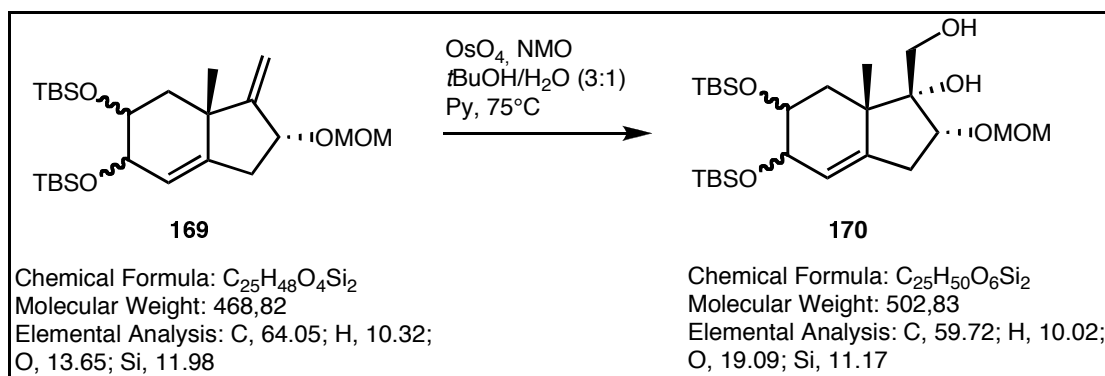
IR (film): $\nu = 2928, 2886, 2855, 1471, 1387, 1250, 1149, 1102, 1080, 1047, 877, 852, 835, 774$ cm⁻¹.

¹H NMR (CDCl₃, 500 MHz): $\delta = 0.08$ (s, 3 H, SiMe), 0.09 (s, 3 H, SiMe), 0.10 (s, 3 H, SiMe), 0.12 (s, 3 H, SiMe), 0.90 (s, 9 H, Si*t*Bu), 0.91 (s, 9 H, Si*t*Bu), 1.17 (s, 3 H, H8), 1.64 (t, *J* = 12.3 Hz, 1 H, H4), 1.90 (dd, *J* = 3.6, 12.4 Hz, 1 H, H4'), 2.24 (d, *J* = 15.6 Hz, 1 H, H1), 2.75 (ddt, *J* = 2.4, 7.6, 15.9 Hz, 1 H, H1'), 3.39 (s, 3 H, H11), 3.92 (ddd, *J* = 3.6, 6.9, 11.8 Hz, 1 H, H5), 4.12 (td, *J* = 2.8, 6.9 Hz, 1 H, H6), 4.62 (dd, *J* = 1.8, 7.6 Hz, 1 H, H2), 4.66 and 4.70 (ABquartet, *J* = 6.7 Hz, 2 H, H10), 4.99 (d, *J* = 1.8 Hz, 1 H, H9), 5.14 (d, *J* = 1.8 Hz, 1 H, H9'), 5.25 (t, *J* = 2.6 Hz, 1 H, H7).

¹³C NMR (CDCl₃, 125 MHz): $\delta = -4.4$ (SiMe), -4.3 (SiMe), -3.9 (SiMe), -3.7 (SiMe), 18.0 (Cq-Si*t*Bu), 18.2 (Cq-Si*t*Bu), 26.0 (3C-Si*t*Bu), 26.1 (3C-Si*t*Bu), 27.4 (C8), 36.3 (C1), 43.2 (C4), 45.6 (C3a), 55.4 (C11), 72.9 (C5), 75.6 (C6), 76.4 (C2), 94.8 (C10), 107.8 (C9), 122.1 (C7), 145.7 (C7a), 159.5 (C3).

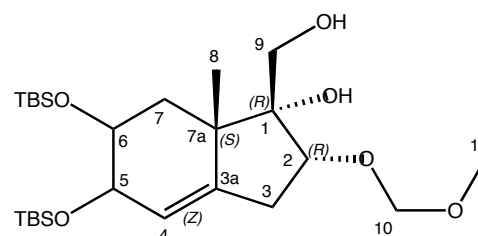
ESIMS (MeOH): 491.3 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₂₅H₄₈O₄Si₂Na *m/z* 491.2989, found 491.2975.

Analysis calcd. for C₂₅H₄₈O₄Si₂ (468.30): C 64.05, H 10.32; found C 64.27, H 10.15.



To a magnetically stirred solution of **169** (212 mg, 0.45 mmol) in *t*-BuOH-H₂O (3:1, 2.8 mL), in the presence of pyridine (0.04 mL, 0.49 mmol), *N*-methylnmorpholine *N*-oxide (54 mg, 0.46 mmol) and then a *t*-BuOH solution of OsO₄ (4.5 mL, 0.45 mmol) were added at room temperature under argon atmosphere. The mixture was stirred at room temperature overnight and treated with a 20% aqueous solution of NaHSO₃. After stirring for 2 h, the products were extracted with EtOAc twice, the combined organic layers were worked up as usual to give a crude residue which was chromatographed (eluent heptane-ethyl acetate 3:1 to 1:1) to afford 71 mg (31%) of **170**.

170: 5,6-Bis-(*tert*-butyl-dimethyl-silanyloxy)-1-hydroxymethyl-2-methoxymethoxy-7a-methyl-2,3,5,6,7,7a-hexahydro-1*H*-inden-1-ol.



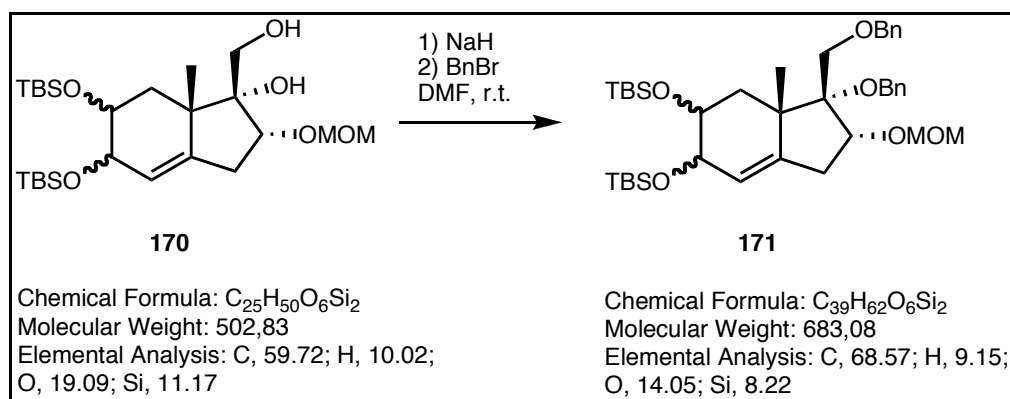
Mp: colourless oil.

IR (film): $\nu = 3482, 2953, 2929, 2855, 1471, 1361, 1251, 1107, 1039, 1004, 881, 835, 775 \text{ cm}^{-1}$.

¹H-NMR (CDCl₃, 500 MHz): $\delta = 0.03$ (s, 3 H, SiMe), 0.04 (s, 3 H, SiMe), 0.05 (s, 3 H, SiMe), 0.06 (s, 3 H, SiMe), 0.87 (s, 9 H, Si*t*Bu), 0.88 (s, 9 H, Si*t*Bu), 1.04 (s, 3 H, H8), 1.59 (dd, $J = 10.2, 13.0$ Hz, 1 H, H7), 2.06 (dd, $J = 5.7, 13.1$ Hz, 1 H, H7'), 2.14 (ddd, $J = 1.2, 4.6, 17.2$ Hz, 1 H, H3), 2.93 (ddd, $J = 2.3, 9.7, 17.2$ Hz, 1 H, H3'), 2.97 (s, 1 H, OH), 3.38 (s, 3 H, H11), 3.67 and 3.69 (ABquartet, $J = 11.9$ Hz, 2 H, H9), 3.83 (ddd, $J = 2.6, 5.8, 10.0$ Hz, 1 H, H6), 3.99 (dd, $J = 2.5, 6.0$ Hz, 1 H, H5), 4.24 (dd, $J = 4.7, 9.7$ Hz, 1 H, H2), 4.67 and 4.70 (ABquartet, $J = 6.4$ Hz, 2 H, H10), 5.58 (ddd, $J = 1.6, 2.3, 6.1$ Hz, 1 H, H4).

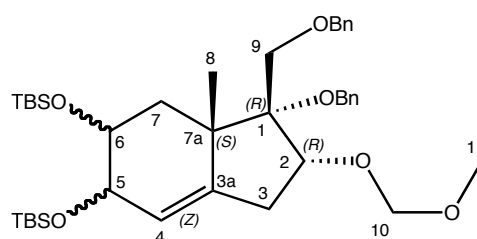
¹³C-NMR (CDCl₃, 75 MHz): $\delta = -4.6$ (SiMe), -4.5 (SiMe), -4.4 (2C-SiMe), 18.2 (2Cq-Si*t*Bu), 25.0 (C8), 25.9 (3C-Si*t*Bu), 26.1 (3C-Si*t*Bu), 32.4 (C7), 34.1 (C3), 48.5 (C7a), 55.8 (C11), 65.2 (C9), 68.7 (C5), 71.7 (C6), 79.6 (C2), 81.7 (C1), 96.2 (C10), 121.2 (C4), 148.2 (C3a).

ESIMS (CH₂Cl₂ + MeOH): 525.2 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₂₅H₅₀O₆Si₂Na m/z 525.3044, found 525.3082.



Sodium hydride (60% w/w in mineral oil; 74 mg, 1.7 mmol) was washed twice with dry hexane under argon atmosphere and the remainder of the hexane removed *via* syringe and the flask vacuumed then filled with argon. *N,N*-dimethylformamide (1 mL) and diol **170** (163 mg, 0.32 mmol) were added. After stirring for 0.5 h the reaction mixture was cooled to 0°C and BnBr (0.12 mL, 1.01 mmol) and *N,N*-dimethylformamide (1.5 mL) were added and the mixture was stirred for 16 h. Water and ether were added, the two phases separated and the organic phase was worked up as usual. Chromatography of the residue (hexane-EtOAc, 6:1) gave **171** (114 mg, 61%).

171: 3-Benzyloxy-3-benzyloxymethyl-5,6-bis-(*tert*-butyl-dimethyl-silyloxy)-2-methoxymethoxy-3a-methyl-2,3,3a,4,5,6-hexahydro-1*H*-indene.



Mp: colourless oil (characterized as a diastereomeric mixture).

$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

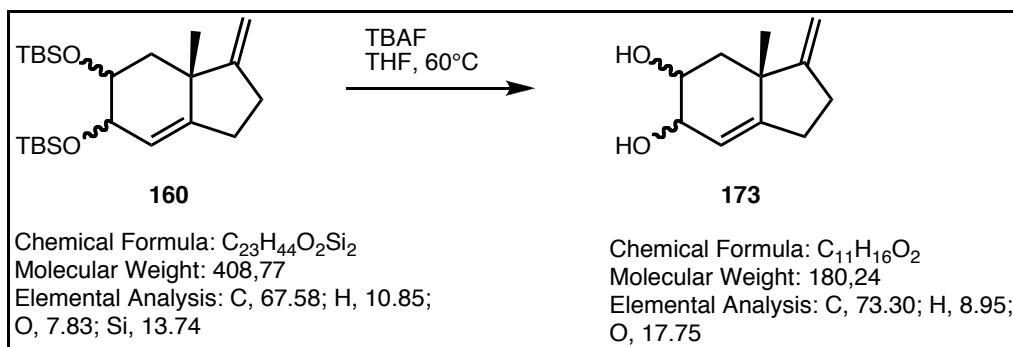
IR (film): ν = 2926, 1471, 1461, 1361, 1249, 1112, 1037, 996, 919, 882, 832, 773, 732, 695 cm⁻¹.

¹H-NMR (CDCl₃, 500 MHz): δ = characterized as a diastereomeric mixture.

¹³C-NMR (CDCl₃, 75 MHz): δ = characterized as a diastereomeric mixture.

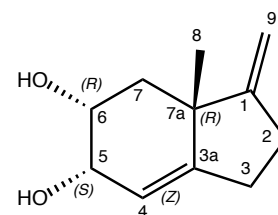
ESIMS (CH₂Cl₂ + MeOH): 705.4 ([M + Na]⁺, 100). HRESIMS: calcd. for C₃₉H₆₂O₆Si₂Na *m/z* 705.3983, found 705.3970.

Analysis calcd. for C₃₉H₆₂O₆Si₂ (683.08): C 68.58, H 9.15; found C 68.43, H 8.98.



Tetrabutylammonium fluoride (3.22 mL, 1M in THF) was added to the protected alcohol **160** (287 mg, 0.69 mmol) under argon, and the reaction mixture immediately heated at 60°C (oil-bath) for 2 h. After cooling to room temperature, the reaction mixture was diluted with EtOAc, and washed with brine till neutral pH. Usual work up and SiO₂ flash chromatography (heptane-EtOAc 3:2) of the residue gave the title compound **173** in 81% yield (100 mg).

173: 3a-Methyl-3-methylene-2,3,3a,4,5,6-hexahydro-1*H*-indene-5,6-diol.



Mp: colourless oil.

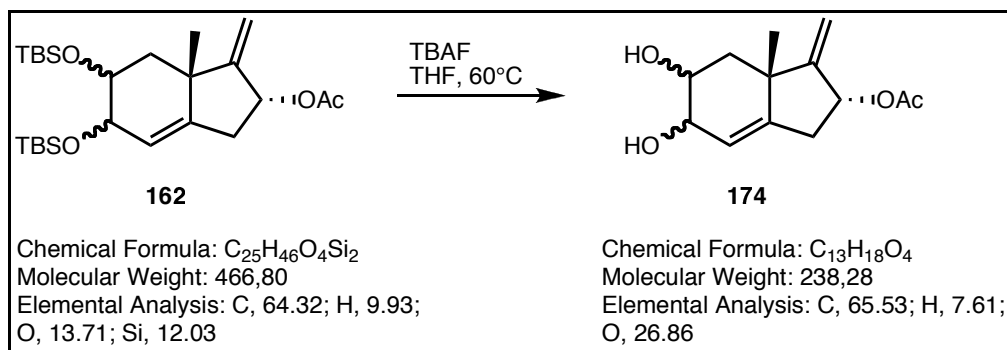
$[\alpha]_D^{20} = +22$ (*c* 1.28, CHCl₃)

IR (film): 3386, 2926, 1710, 1650, 1457, 1263, 1115, 1051, 879 cm⁻¹.

¹H-NMR (CDCl₃, 300 MHz): 1.35 (s, 3 H, H8), 1.86 (dd, *J* = 3.2, 14.3 Hz, 1 H, H7), 2.35 - 2.75 (m, 5 H, H2, H3, H7'), 3.95 (m, 1 H, H6), 4.25 (m, 1 H, H5), 4.80 (m, 2 H, H9), 5.45 (m, 1 H, H4).

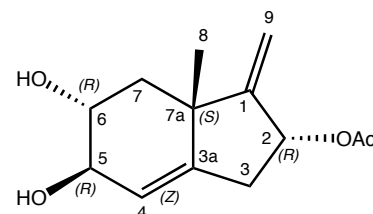
¹³C-NMR (CDCl₃, 75 MHz): 28.0 (C3), 29.0 (C8), 37.4 (C2, C7), 43.8 (C7a), 68.0, 68.5 (C5, C6), 103.0 (C9), 117.2 (C4), 151.3, 159.0 (C1, C3a).

ESIMS (MeOH): 203.2 ($[M + Na]^+$, 100). HRESIMS: calcd. for $C_{11}H_{16}O_2Na$ m/z 203.2387; found 203.2384.



TBAF (3.3 mL, 1M in THF) was added to **162** (260 mg, 0.55 mmol), at r.t. under Ar. The reaction mixture was stirred at 60°C for 4 h. Then the reaction mixture was diluted (at r.t.) with ethyl acetate (large amount) and worked up as usual. Flash chromatography (ethyl acetate/heptane 1:1) gives 110 mg (85%) of **174**.

174: Acetic acid 5,6-dihydroxy-3a-methyl-3-methylene-2,3,3a,4,5,6-hexahydro-1*H*-inden-2-yl ester.



Mp: yellow oil.

$[\alpha]_D^{20} = -34$ (c 1.0, $CHCl_3$).

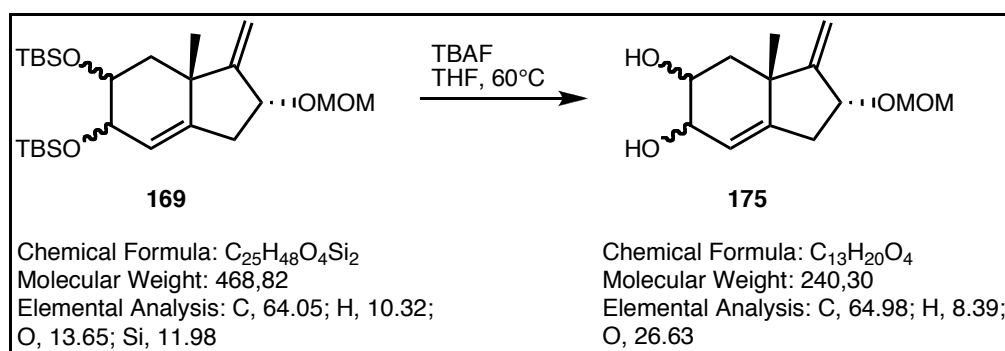
IR (film): $\nu = 3363, 2965, 2929, 1736, 1427, 1373, 1244, 1119, 1047, 918$ cm^{-1} .

1H NMR ($CDCl_3$, 300 MHz): $\delta = 1.19$ (s, 3 H, H8), 1.70 (t, $J = 12.4$ Hz, 1 H, H7), 2.03 - 2.09 (m, 1 H, H7'), 2.06 (s, 3 H, Me-Ac), 2.21 (d, $J = 16.7$ Hz, 1 H, H3), 2.92 (ddt, $J = 2.4, 8.3, 16.8$ Hz, 1 H, H3'), 3.93 (ddd, $J = 3.7, 7.4, 12.4$ Hz, 1 H, H6), 4.13 (ddd, $J = 3.7, 7.4, 12.4$ Hz, 1 H, H5), 5.00 (d, $J = 1.8$ Hz, 1 H, H9), 5.12 (d, $J = 1.8$ Hz, 1 H, H9'), 5.34 (m, 1 H, H1), 5.70 (ddd, $J = 2.0, 3.9, 8.3$ Hz, 1 H, H4).

^{13}C NMR (CDCl_3 , 75 MHz): δ = 21.2 (C8), 27.6 (Me-Ac), 36.1 (C3), 41.2 (C7), 46.2 (C7a), 72.2 (C6), 73.9 (C5), 75.1 (C2), 108.1 (C9), 120.1 (C4), 146.6 (C3a), 157.5 (C1), 170.9 (CO-Ac).

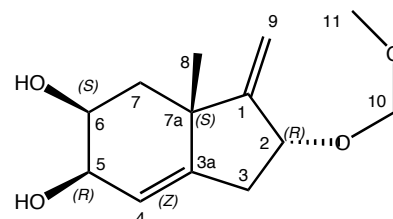
ESIMS (MeOH): 261.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_4\text{Na}$ m/z 261.1066, found 261.1103.

Analysis: calcd. for $\text{C}_{13}\text{H}_{18}\text{O}_4 \cdot 0.25 \text{H}_2\text{O}$ (238.12): C 64.31, H 7.68; found C 64.38, H 7.95.



TBAF (0.34 mL, 1M in THF) was added to **169** (40 mg, 0.085 mmol), at r.t. under Ar. The reaction mixture was stirred at 60°C for 2 h. Then the reaction mixture was diluted (at r.t.) with ethyl acetate (large amount) and worked up as usual. Flash chromatography (ethyl acetate/heptane 1:1) gives 16 mg (88%) of **175**.

175: 2-Methoxymethoxy-3a-methyl-3-methylene-2,3,3a,4,5,6-hexahydro-1*H*-indene-5,6-diol.



Mp: yellow oil.

$[\alpha]_D^{20} = -36$ (c 1.1, CHCl_3).

IR (film): ν = 3381, 2929, 1658, 1450, 1147, 1093, 1043, 915 cm^{-1} .

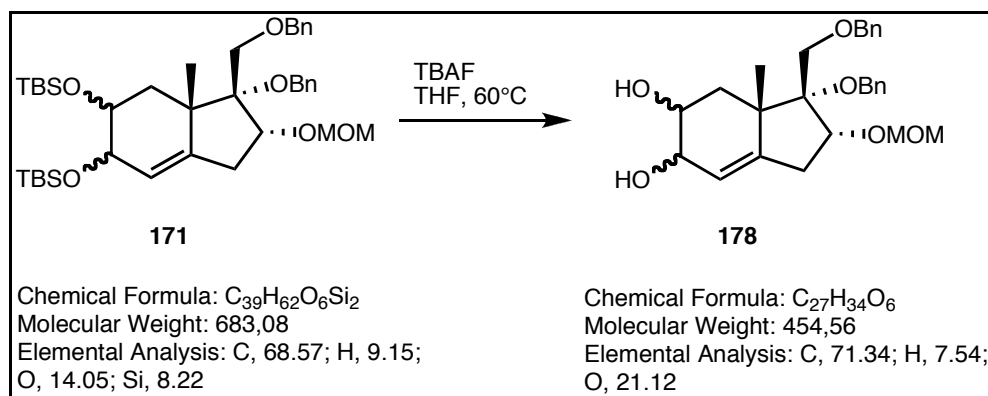
^1H NMR (CDCl_3 , 500 MHz): δ = 1.18 (s, 3 H, H8), 1.71 (td, J = 4.6, 12.2 Hz, 1 H, H7), 2.05 (dt, J = 3.8, 12.2 Hz, 1 H, H7'), 2.30 (d, J = 15.8 Hz, 1 H, H3), 2.70 (b, 1 H, OH), 2.76 (ddt, J = 2.5, 7.6, 15.7 Hz, 1 H, H3), 3.38 (s, 3 H, H11), 3.94 (ddd, J = 4.2, 7.8, 11.4

Hz, 1 H, H6), 4.13 (m, 1 H, H5), 4.66 (m, 1 H, H2), 4.66 and 4.69 (ABquartet, $J = 6.8$ Hz, 2 H, H10), 5.03 (d, $J = 1.8$ Hz, 1 H, H9), 5.16 (d, $J = 1.8$ Hz, 1 H, H9'), 5.35 (d, $J = 2.5$ Hz, 1 H, H4).

^{13}C NMR (CDCl_3 , 125 MHz): $\delta = 27.8$ (C8), 36.3 (C3), 41.4 (C7), 45.8 (C7a), 55.4 (C11), 72.4 (C6), 75.2 (C5), 76.3 (C2), 94.8 (C10), 108.3 (C9), 120.0 (C4), 147.7 (C3a), 159.0 (C1).

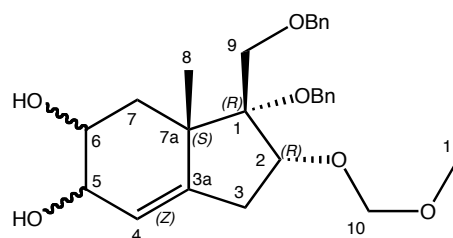
ESIMS (MeOH): 263.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{13}\text{H}_{20}\text{O}_4\text{Na}$ m/z 263.1259, found 263.1290.

Analysis: calcd. for $\text{C}_{13}\text{H}_{20}\text{O}_4 \cdot 0.35 \text{H}_2\text{O}$ (240.13): C 63.32, H 8.46; found C 63.34, H 8.57.



TBAF (1.0 mL, 1M in THF) was added to **171** (114 mg, 0.17 mmol), at r.t. under Ar. The reaction mixture was stirred at 60°C for 4.5 h. Then the reaction mixture was diluted (at r.t.) with ethyl acetate (large amount) and worked up as usual. Flash chromatography (ethyl acetate/ methanol 95:5) gives 66 mg (87%) of **178**.

178: 3-Benzyloxy-3-benzyloxymethyl-2-methoxymethoxy-3a-methyl-2,3,3a,4,5,6-hexahydro-1*H*-indene-5,6-diol.



Mp: colourless oil (characterized as a diastereomeric mixture).

$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

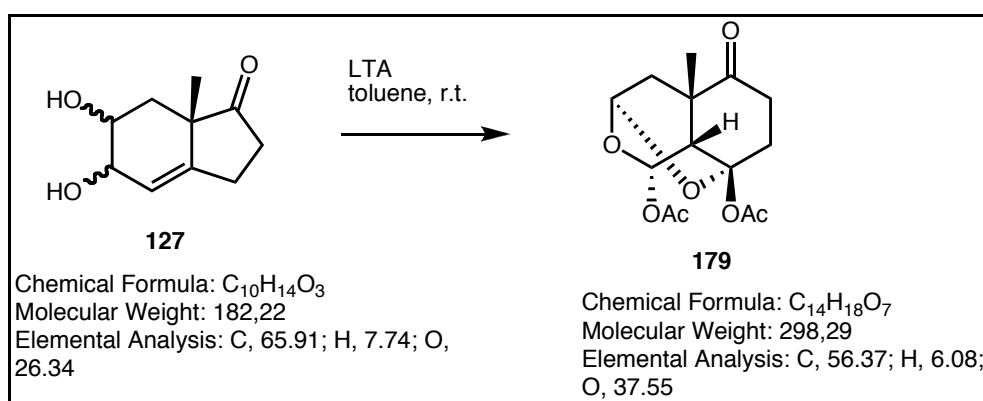
IR (film): $\nu = 3399, 2885, 1495, 1452, 1365, 1208, 1109, 1030, 916, 735, 696 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta =$ characterized as a diastereomeric mixture.

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta =$ characterized as a diastereomeric mixture.

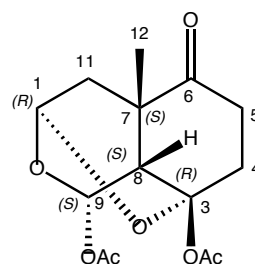
ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 477.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{27}\text{H}_{34}\text{O}_6\text{Na}$ m/z 477.2253, found 477.2271.

Analysis calcd. for $\text{C}_{27}\text{H}_{34}\text{O}_6 \cdot 0.85 \text{ H}_2\text{O}$ (454.56): C 69.02, H 7.66; found C 69.03, H 7.31.



A dry flask was charged with 180 mg of diol **127** (0.98 mmol) and 1.09 g of $\text{Pb}(\text{OAc})_4$ (2.33 mmol, 3 eq.) vacuumed, flushed with argon and cooled to nearly 0°C . Toluene (5 mL) was added, the ice bath removed soon after and the mixture was stirred at room temperature for 20 h, diluted with ether, filtered through Celite/Silica/Magnesium sulfate, the filtrate concentrated and purified by silica gel chromatography using ethyl acetate-heptane, 3:7 as an eluent to give the product **179** (115 mg, 39%) and 27mg (15%) of the half cascade (not characterized).

179: Acetic acid 3-acetoxy-7-methyl-6-oxo-2,10-dioxa-tricyclo[5.3.1.0^{0,0}]undec-9-yl ester.



Mp: $110 - 120^\circ\text{C}$.

$[\alpha]_D^{20} = +2$ (c 0.62, CHCl_3).

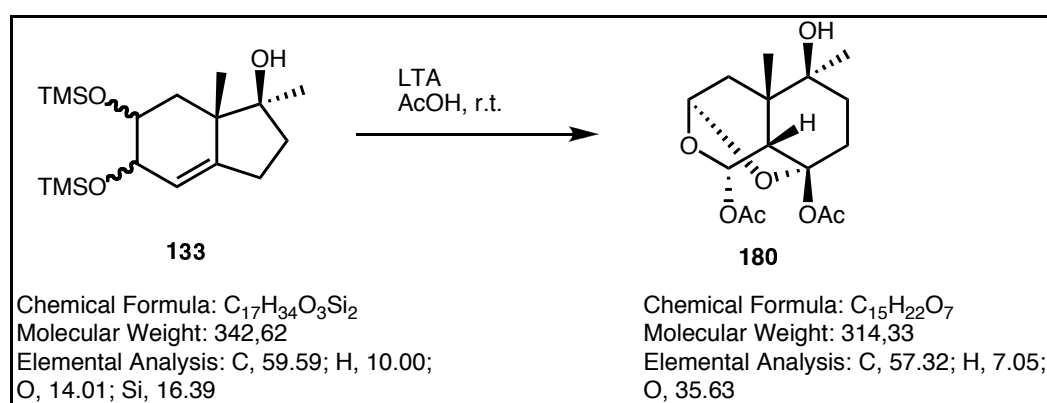
IR (film): 2978, 1740, 1448, 1371, 1251, 1073, 1029, 977 cm^{-1} .

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ = 1.29 (d, J = 14.6 Hz, 1 H, H11), 1.38 (s, 3 H, H12), 1.8 (dd, J = 1.2, 14.7 Hz, 1 H, H4 or H5 or H11), 2.05 (dd, J = 3.0, 14.0 Hz, 1 H, H4 or H5 or H11), 2.11 (s, 3 H, Me-Ac), 2.14 (s, 3 H, Me-Ac), 2.47 (ddd, J = 2.7, 5.5, 14.0 Hz, 1 H, H4 or H5 or H11), 2.69 - 2.95 (m, 2 H, H4, H5), 3.17 (s, 1 H, H8), 5.43 (d, J = 2.6 Hz, 1 H, H1), 6.41 (s, 1 H, H9).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ = 19.8 (C12), 21.0 (Me-Ac), 22.2 (Me-Ac), 31.8, 33.8, 39.9 (C4, C5, C11), 40.2 (C8), 43.0 (C7), 90.0 (C9), 91.9 (C1), 102.1 (C3), 169.1 (CO-Ac), 169.5 (CO-Ac), 208.4 (C6).

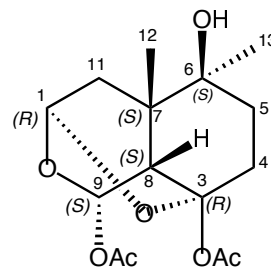
ESIMS (MeOH): 321.2 ($[M + \text{Na}]^+$, 100). HRESIMS calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_7\text{Na}$ m/z 321.0950, found 321.0949.

Analysis calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_7$ (298.29): C 56.37, H 6.08; found C 56.76, H 6.21.



A dry flask was charged with protected unsaturated diols **133** (2.3 g, 11.6 mmol, diastereomeric mixture) and $\text{Pb}(\text{OAc})_4$ (15.43 g, 34.8 mmol, 3 eq.) vacuumed, flushed with argon and cooled to 0°C . Acetic acid (25 mL) was added, the cooling bath removed soon after and the reaction mixture was stirred for 19 h at room temperature. The mixture was diluted with EtOAc and washed carefully with sat. NaHCO_3 solution until neutral pH and brine. The organic layer was concentrated under reduced pressure, dried over MgSO_4 and purified through flash chromatography using heptane-ether 1:1 as eluant afforded 3.01 g (85%) **180**.

180: Acetic acid 3-acetoxy-6-hydroxy-6,7-dimethyl-2,10-dioxatricyclo[5.3.1.0^{0,0}]undec-9-yl ester.



Mp: 129.0 - 130.0°C.

$[\alpha]_D^{20} = -44$ (*c* 0.965, CHCl₃).

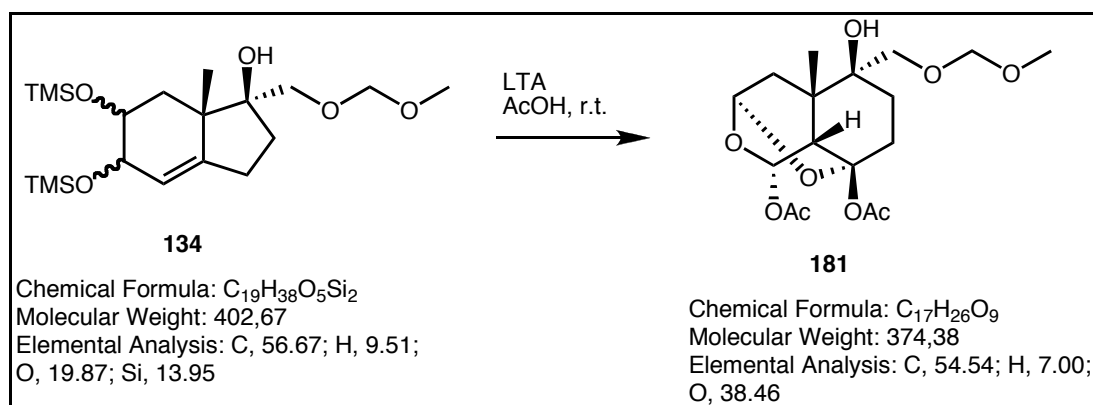
IR (film): $\nu = 3547, 2984, 2361, 1734, 1370, 1254, 1107, 1061, 1022, 979, 937$ cm⁻¹.

¹H-NMR (CDCl₃, 300 MHz): $\delta = 1.20$ (s, 3 H, H13), 1.31 (s, 1 H, H12), 1.53 (ddd, *J* = 2.0, 5.1, 14.4 Hz, 1 H, H5), 1.61 (dd, *J* = 1.5, 14.3 Hz, 1 H, H8), 1.69 (ddd, *J* = 1.9, 5.1, 13.2 Hz, 1 H, H4), 1.77 (dd, *J* = 2.6, 14.3 Hz, 1 H, H8'), 1.90 (ddd, *J* = 5.1, 13.3, 14.3 Hz, 1 H, H5'), 2.09 (s, 3 H, Me-Ac), 2.10 (s, 3 H, Me-Ac), 2.67 (dt, *J* = 5.1, 13.3 Hz, 1 H, H4'), 3.23 (s, 1 H, H2), 5.29 (s, 1 H, H1), 6.49 (s, 1 H, H9).

¹³C-NMR (CDCl₃, 75 MHz): $\delta = 20.3$ (C12), 21.3 (Me-Ac), 22.6 (Me-Ac), 24.6 (C13), 29.2 (C4), 33.5 (C5), 37.0 (C2), 38.8 (C7), 39.3 (C8), 72.6 (C6), 91.2 (C1), 92.7 (C9), 103.8 (C3), 169.5 (CO-Ac), 169.8 (CO-Ac).

ESIMS (MeOH): 337.1 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₁₅H₂₂O₇Na *m/z* 337.1263, found 337.1263.

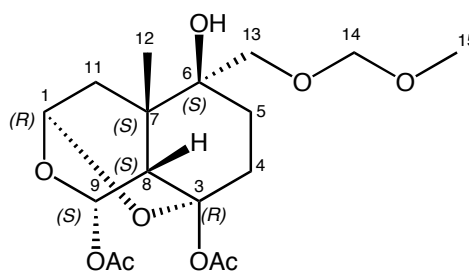
Analysis calcd. for C₁₅H₂₂O₇ (314.33): C 57.32, H 7.05; found C 57.47, H 7.11.



A dry flask was charged with unsaturated protected diols **134** (100 mg, 0.25 mmol, diastereomeric mixture) and Pb(OAc)₄ (360 mg, 0.81 mmol, 3 eq.) vacuumed, flushed with

argon and cooled to 0°C. Acetic acid (2 mL) was added, the cooling bath removed soon after and the reaction mixture was stirred for 19 h at room temperature. The mixture was diluted with EtOAc and washed carefully with sat. NaHCO₃ solution until neutral pH and brine. The organic layer was concentrated under reduced pressure, dried over MgSO₄ and purified through flash chromatography using heptane-ether 1:1 as eluent afforded 75 mg (80%) **181**.

181: Acetic acid 3-acetoxy-6-hydroxy-6-methoxymethoxymethyl-7-methyl-2,10-dioxatricyclo[5.3.1.0^{0,0}]undec-9-yl ester.



Mp: colourless oil.

$$[\alpha]_D^{20} = -37 (c 1.65, \text{CHCl}_3).$$

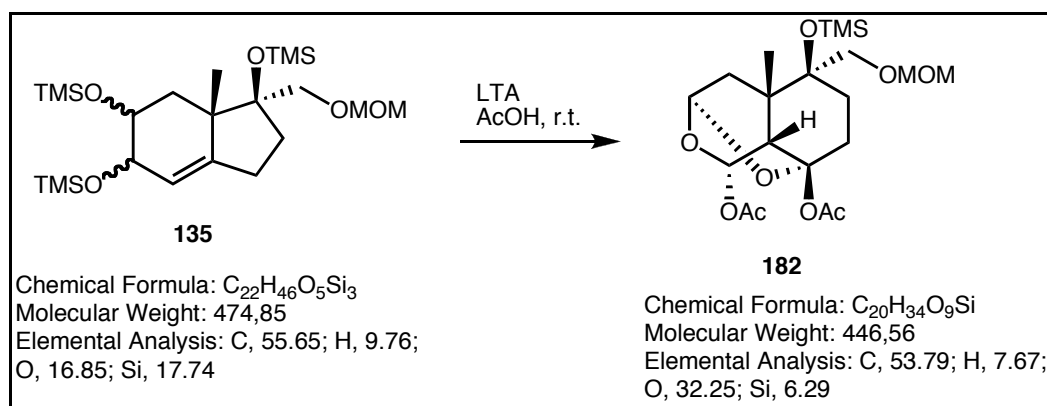
IR (film): $\nu = 3493, 2942, 1735, 1370, 1252, 1224, 1186, 1147, 1103, 1021, 937, 754 \text{ cm}^{-1}$.

¹H-NMR (CDCl₃, 300 MHz): $\delta = 1.19$ (s, 3 H, H12), 1.46 (d, $J = 14.3$ Hz, 1 H, H11), 1.58 - 1.70 (m, 3 H, H4, H5), 1.78 (d, $J = 14.2$ Hz, 1 H, H11'), 1.96 (s, 3 H, Me-Ac), 1.97 (s, 3 H, Me-Ac), 2.42 (s, 1 H, OH), 2.57 (dd, $J = 8.9, 18.4$ Hz, 1 H, H4'), 3.16 (s, 1 H, H8), 3.23 (s, 3 H, H15), 3.32 (d, $J = 10.0$ Hz, 1 H, H13), 3.48 (d, $J = 10.0$ Hz, 1 H, H13'), 4.52 (s, 2 H, H14), 5.16 (s, 1 H, H1), 6.37 (s, 1 H, H9).

¹³C-NMR (CDCl₃, 75 MHz): $\delta = 20.2$ (C12), 21.3 (Me-Ac), 22.6 (Me-Ac), 28.8 (C4, C5), 36.9 (C8), 38.0 (C7), 38.7 (C11), 55.7 (C15), 72.0 (C13), 76.1 (C6), 90.9 (C9), 92.4 (C1), 97.3 (C14), 103.8 (C3), 169.4 (CO-Ac), 169.8 (CO-Ac).

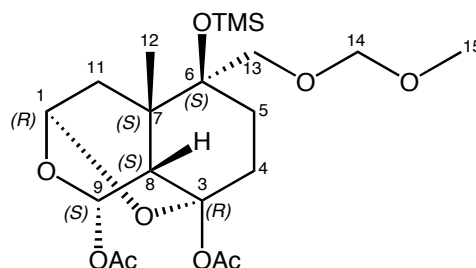
ESIMS (MeOH): 397.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for C₁₇H₂₆O₉Na m/z 397.1475, found 397.1478.

Analysis calcd. for C₁₇H₂₆O₉ · 0.95 H₂O (374.38): C 52.15, H 7.18; found C 52.14, H 6.91.



A dry flask was charged with unsaturated diols **135** (70 mg, 0.15 mmol, diastereomeric mixture) and $Pb(OAc)_4$ (200 mg, 0.45 mmol, 3 eq.) vacuumed, flushed with argon and cooled to 0°C. Acetic acid (1 mL) was added, the cooling bath removed soon after and the reaction mixture was stirred for 19 h at room temperature. The mixture was diluted with EtOAc and washed carefully with sat. $NaHCO_3$ solution until neutral pH and brine. The organic layer was concentrated under reduced pressure, dried over $MgSO_4$ and purified through flash chromatography using heptane-ether 1:1 as eluent afforded 27 mg (40%) **182**.

182: Acetic acid 3-acetoxy-6-methoxymethoxymethyl-7-methyl-6-(trimethyl-silanyloxy)-2,10-dioxatricyclo[5.3.1.0^{0,0}]undec-9-yl ester.



Mp: colourless oil.

$[\alpha]_D^{20} = -35$ (c 0.52, $CHCl_3$).

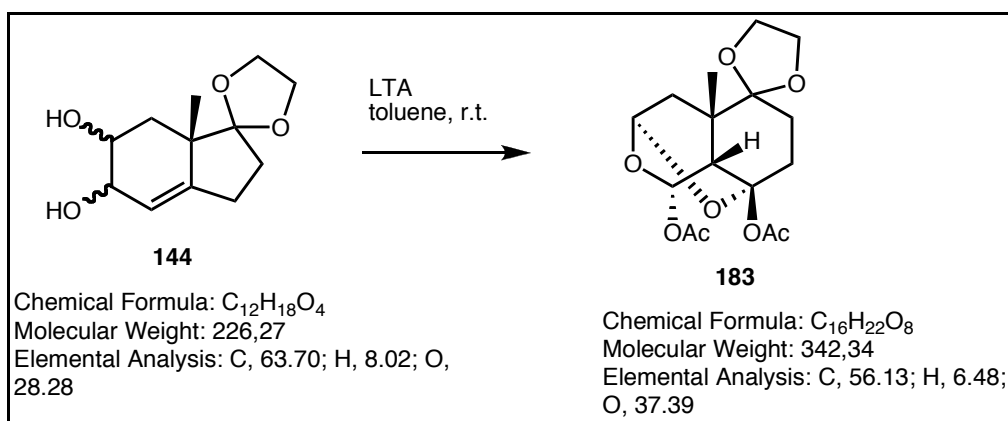
IR (film): $\nu = 2952, 2360, 1732, 1367, 1248, 1185, 1066, 1026, 983, 947, 841$ cm^{-1} .

1H -NMR ($CDCl_3$, 300 MHz): $\delta = 0.15$ (s, 9 H, SiMe), 1.23 (s, 3 H, H12), 1.26 - 1.36 (m, 2 H, H4), 1.57 (dd, $J = 4.0, 14.5$ Hz, 1 H, H11), 1.80 (td, $J = 4.7, 13.0$ Hz, 1 H, H5), 1.89 (td, $J = 3.2, 14.6$ Hz, 1 H, H5'), 2.07 (dd, $J = 3.0, 14.5$ Hz, 1 H, H11'), 2.09 (s, 3 H, Me-Ac), 2.11 (s, 3 H, Me-Ac), 3.27 (s, 1 H, H8), 3.35 (s, 3 H, H15), 3.47 and 3.57 (ABquartet, $J = 9.8$ Hz, 2 H, H13), 4.61 (s, 2 H, H14), 5.26 (s, 1 H, H1), 6.48 (s, 1 H, H9).

^{13}C -NMR (CDCl_3 , 75 MHz): $\delta = 1.9$ (3C-SiMe), 20.1 (C12), 21.4 (2Me-Ac), 27.2 (C5), 29.0 (C4), 36.6 (C8), 38.6 (C7), 39.4 (C11), 55.5 (C15), 71.4 (C13), 77.1 (C6), 90.9 (C9), 92.3 (C1), 96.6 (C14), 104.0 (C3), 169.4 (CO-Ac), 169.8 (CO-Ac).

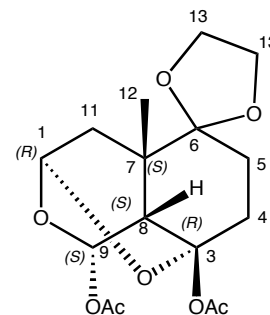
ESIMS (MeOH): 469.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for m/z $\text{C}_{20}\text{H}_{34}\text{O}_9\text{SiNa}$ 469.1870, found 469.1867.

Analysis calcd. for $\text{C}_{20}\text{H}_{34}\text{O}_9\text{Si} \cdot 0.45 \text{C}_7\text{H}_{16}$ (446.56): C 56.55, H 8.45; found C 56.55, H 8.16.



A dry flask was charged with 230 mg of diol **144** (1.0 mmol) and 1.10 g of $\text{Pb}(\text{OAc})_4$ (2.5 mmol, 3 eq.) vacuumed, flushed with argon and cooled to nearly 0°C . Toluene (5 mL) was added, the ice bath removed soon after and the mixture was stirred at room temperature for 20 h, diluted with ether, filtered through Celite/Silica/Magnesium sulfate, the filtrate concentrated and purified by silica gel chromatography using ethyl acetate-heptane, 3:7 as an eluent to give the product **183** (280 mg, 82%):

183:



Mp: 110-120°C.

$$[\alpha]_D^{20} = -40 \text{ (} c \text{ 1.04, CHCl}_3\text{)}$$

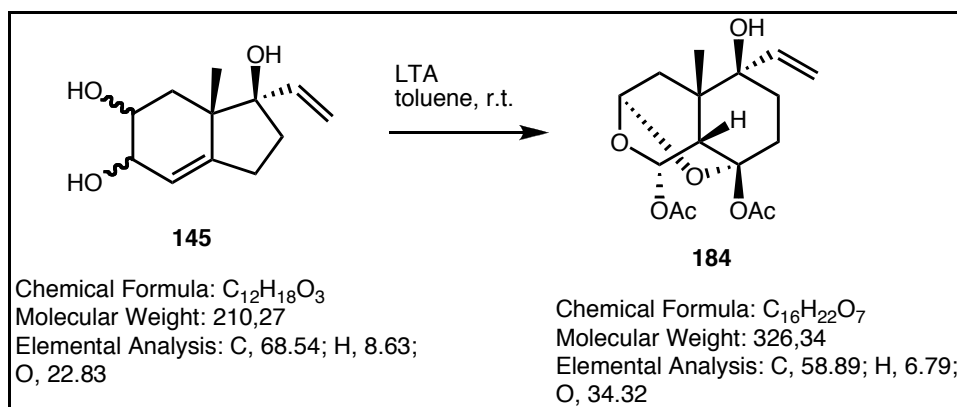
IR (film): 2982, 2880, 1736, 1445, 1370, 1261, 1223, 1078, 1039, 1007, 950 cm^{-1} .

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ = 1.18 (s, 3 H, H12), 1.66 (dd, J = 1.5, 14.7 Hz, 1 H, H11), 1.67 (ddd, J = 2.1, 5.2, 13.5 Hz, 1 H, H5), 1.78 (ddd, J = 2.0, 5.0, 13.0 Hz, 1 H, H4), 1.91 (td, J = 5.0, 13.5 Hz, 1 H, H5'), 2.09 (s, 3 H, Me-Ac), 2.10 (s, 3 H, Me-Ac), 2.13 (dd, J = 2.7, 14.7 Hz, 1 H, H11), 2.56 (td, J = 5.0, 13.0 Hz, 1 H, H4'), 3.14 (d, J = 1.2 Hz, 1 H, H8), 3.90 - 4.07 (m, 4 H, H13), 5.32 (dd, J = 1.3, 2.7 Hz, 1 H, H1), 6.43 (d, J = 1.2 Hz, 1 H, H9).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ = 19.3 (C12), 21.2 (Me-Ac), 22.5 (Me-Ac), 27.9, 30.5 (C4, C5), 38.8, 38.9 (C8, C11), 39.2 (C7), 65.4, 65.5 (2C13), 90.6, 92.6 (C1, C9), 103.1 (C3), 110.1 (C6), 169.2 (CO-Ac), 169.6 (CO-Ac).

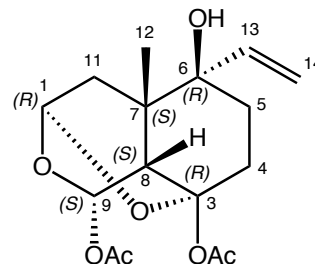
ESIMS (MeOH): 365.1 ($[M + \text{Na}]^+$, 100). HRESIMS calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_8\text{Na}$ m/z 365.1212, found 365.1215.

Analysis calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_8$ (342.34): C 56.13, H 6.48; found C 56.41, H 6.51.



A dry flask was charged with unsaturated diols **145** (20 mg, 0.095 mmol, diastereomeric mixture) and $\text{Pb}(\text{OAc})_4$ (129 mg, 0.29 mmol, 3 eq.) vacuumed, flushed with argon and cooled to 0°C . Toluene (1 mL) was added, the cooling bath removed soon after and the reaction mixture was stirred for 15 h at room temperature, diluted with diethyl ether, filtered through $\text{MgSO}_4/\text{Celite}/\text{silica}$, the filtrate concentrated and purified by silica gel chromatography using diethyl ether-heptane, 1:1 as an eluent to give **184** (16 mg, 51%).

184: Acetic acid 7-acetoxy-4-hydroxy-3-methyl-4-vinyl-10,11-dioxa-tricyclo[5.3.1.00,33]undec-9-yl ester.



Mp: colourless oil.

$[\alpha]_D^{20} = -21$ (c 0.8, CHCl_3).

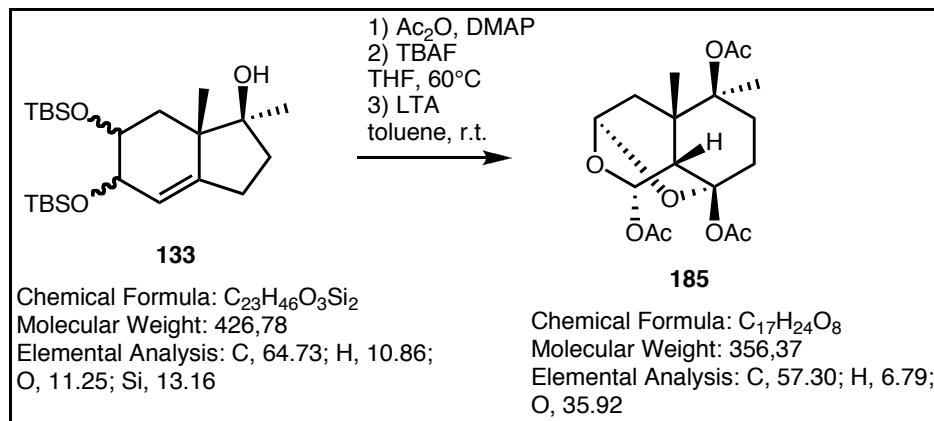
IR (film): $\nu = 3515, 2941, 1732, 1369, 1252, 1065, 949 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 1.27$ (s, 3 H, H12), 1.49 (ddd, $J = 1.9, 4.9, 14.6$ Hz, 1 H, H5), 1.61 (m, 1 H, H2), 1.76 (ddd, $J = 1.9, 5.1, 13.3$ Hz, 1 H, H6), 1.95 (dd, $J = 2.7, 14.4$ Hz, 1 H, H2'), 2.02 (dd, $J = 4.7, 13.4$ Hz, 1 H, H5'), 2.12 (s, 3 H, Me-Ac), 2.13 (s, 3 H, Me-Ac), 2.75 (td, $J = 5.1, 13.2$ Hz, 1 H, H6'), 3.30 (s, 1 H, H8), 5.28 (d, $J = 10.9$ Hz, 1 H, H14), 5.33 (s, 1 H, H1), 5.39 (d, $J = 17.2$ Hz, 1 H, H14'), 5.98 (dd, $J = 10.9, 17.2$ Hz, 1 H, H13), 6.48 (s, 1 H, H9).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 21.3$ (C12), 22.6 (2Me-Ac), 28.9 (C4), 32.0 (C5), 37.3 (C8), 38.4 (C7), 38.8 (C11), 75.1 (C6), 91.1 (C9), 92.5 (C1), 103.7 (C3), 115.5 (C14), 140.7 (C13), 169.5 (CO-Ac), 169.7 (CO-Ac).

ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 349.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_7\text{Na}$ m/z 349.1263, found 349.1228.

Analysis calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_7 \cdot 1.0 \text{ H}_2\text{O}$ (326.34): C 55.81, H 7.02; found C 55.65, H 6.46.

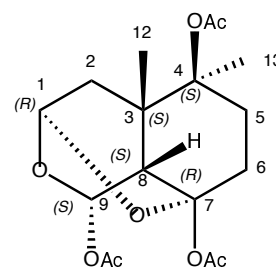


Acetic anhydride (14.8 mL, excess) was added to a stirring mixture of **133** (6.7 g, 15.76 mmol) and DMAP (1.9 g, 15.76 mmol) in dry pyridine (64 mL) under argon at 0°C. The reaction mixture was stirred for 3 h at 0°C (TLC monitoring), diluted with dichloromethane, washed with saturated sodium bicarbonate then 1N hydrochloric acid and worked up as usual to give, after silica gel flash column chromatography (eluent: heptane-EtOAc 95:5), 5.07 g (70%) of the corresponding acetate **140**.

TBAF (37.68 mL, 1M in THF) was added to **140** (4.4 g, 9.42 mmol), at r.t. under Ar. The reaction mixture was stirred at 60°C for 3 h. Then the reaction mixture was diluted (at r.t.) with ethyl acetate (large amount) and worked up as usual. Flash chromatography (ethyl acetate) gives 2.21 g (98%) of **146**.

A dry flask was charged with unsaturated diols **146** (96 mg, 0.4 mmol, diastereomeric mixture) and Pb(OAc)₄ (532 mg, 1.2 mmol, 3 eq.) vacuumed, flushed with argon and cooled to 0°C. Toluene (3 mL) was added, the cooling bath removed soon after and the reaction mixture was stirred for 19 h at room temperature, diluted with diethyl ether, filtered through MgSO₄/Celite/silica, the filtrate concentrated and purified by silica gel chromatography using diethyl ether-heptane, 1:1 as an eluent to give **185** (124 mg, 87%).

185: Acetic acid 6,9-diacetoxy-6,7-dimethyl-2,10-dioxa-tricyclo[5.3.1.0^{0,0}]undec-3-yl ester.



Mp: 147.0°C.

$[\alpha]_D^{20} = -6$ (*c* 1.00, CHCl₃).

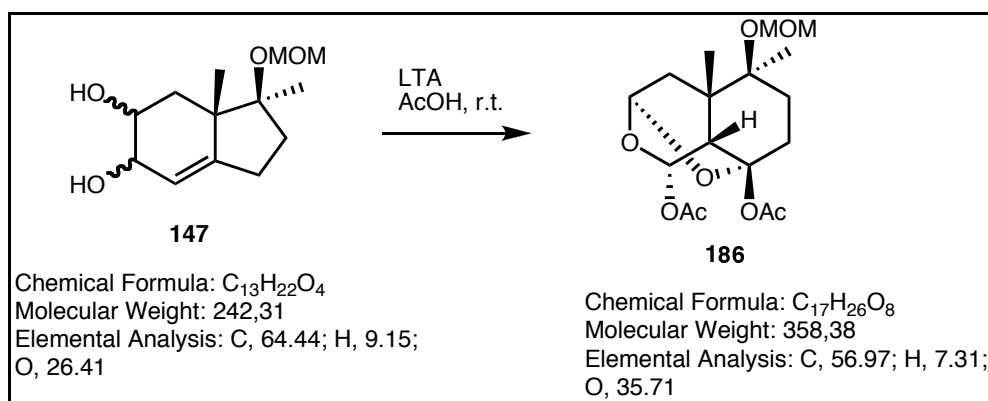
IR (film): $\nu = 2986, 1730, 1370, 1247, 1176, 1100, 1056, 1021, 951$ cm⁻¹.

¹H-NMR (CDCl₃, 300 MHz): $\delta = 1.28$ (s, 3 H, H12), 1.42 (s, 3 H, H13), 1.54 (dd, *J* = 1.3, 14.5 Hz, 1 H, H2), 1.53 - 1.56 (m, 1 H, H6), 1.67 (dd, *J* = 1.6, 4.8 Hz, 1 H, H5), 1.76 (dd, *J* = 2.6, 14.6 Hz, 1 H, H2), 2.02 (s, 3 H, Me-Ac), 2.05 (s, 3 H, Me-Ac), 2.06 (s, 3 H, Me-Ac), 2.33 (td, *J* = 3.8, 12.2 Hz, 1 H, H6), 2.70 - 2.80 (m, 1 H, H5), 3.26 (s, 1 H, H8), 5.25 (d, *J* = 1.1 Hz, 1 H, H1), 6.46 (s, 1 H, H9).

^{13}C -NMR (CDCl_3 , 75 MHz): $\delta = 20.3$ (C13), 20.5 (C12), 21.3 (Me-Ac), 22.1 (Me-Ac), 22.6 (Me-Ac), 27.0 (C5), 29.4 (C6), 36.8 (C8), 38.4 (C2), 39.8 (C3), 84.0 (C4), 90.8 (C9), 92.3 (C1), 103.4 (C7), 169.7 (CO-Ac), 170.2 (2CO-Ac).

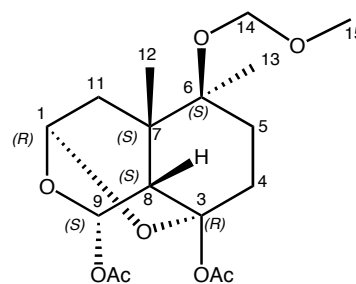
ESIMS (MeOH): 379.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{17}\text{H}_{24}\text{O}_8\text{Na}$ m/z 379.1369; found 379.1366.

Analysis calcd. for $\text{C}_{17}\text{H}_{24}\text{O}_8$ (356.37): C 57.30, H 6.79; found C 57.17, H 6.78.



A dry flask was charged with unsaturated diols **147** (3.23 g, 13.33 mmol, diastereomeric mixture) and $\text{Pb}(\text{OAc})_4$ (17.73 g, 39.99 mmol, 3 eq.) vacuumed, flushed with argon and cooled to 0°C . Acetic acid (25 mL) was added, the cooling bath removed soon after and the reaction mixture was stirred for 19 h at room temperature. The mixture was diluted with EtOAc and washed carefully with sat. NaHCO_3 solution till neutral pH and brine. The organic layer was concentrated under reduced pressure, dried over MgSO_4 and purified through flash chromatography using heptane-ether 1:1 as eluent afforded 4.0 g (84%) **186**.

186: Acetic acid 3-acetoxy-6-methoxymethoxy-6,7-dimethyl-2,10-dioxatricyclo [5.3.1.0^{0,0}]undec-9-yl ester.



Mp: 72.5-73.5°C.

$[\alpha]_D^{20} = -21$ (*c* 1.45, CHCl₃).

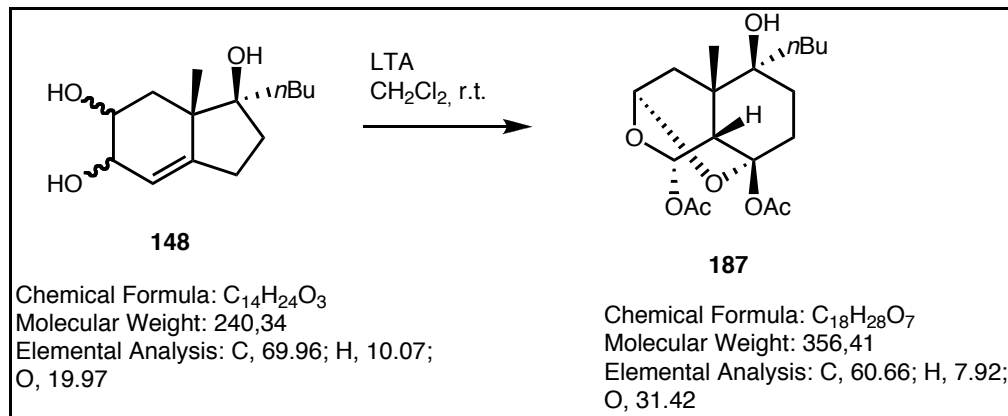
IR (film): $\nu = 2979, 1732, 1368, 1259, 1223, 1175, 1101, 1076, 1022, 978$ cm⁻¹.

¹H-NMR (CDCl₃, 300 MHz): $\delta = 1.11$ (s, 3 H, H13), 1.26 (s, 3 H, H12), 1.54 (dd, *J* = 1.4, 14.3 Hz, 1 H, H11), 1.57 - 1.84 (m, 4 H, H4, H5, H11'), 2.04 (s, 3 H, Me-Ac), 2.05 (s, 3 H, Me-Ac), 2.57 (td, *J* = 4.1, 10.8 Hz, 1 H, H4'), 3.31 (s, 1 H, H8), 3.38 (s, 3 H, H15), 4.63 and 4.72 (ABquartet, *J* = 4.6 Hz, 2 H, H14), 5.24 (dd, *J* = 1.5, 2.6 Hz, 1H, H1), 6.44 (d, *J* = 1.2 Hz, 1 H, H9).

¹³C-NMR (CDCl₃, 75 MHz): $\delta = 20.0$ (C13), 20.6 (C12), 21.3 (Me-Ac), 22.7 (Me-Ac), 29.3 (C4, C5), 36.7 (C8), 39.2 (C11), 39.8 (C7), 56.2 (C15), 78.0 (C6), 91.1, 91.2 (C9, C14), 92.5 (C1), 104.0 (C3), 169.5 (CO-Ac), 169.8 (CO-Ac).

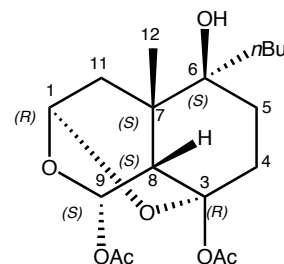
ESIMS (CH₂Cl₂ + MeOH): 381.1 ([*M*+Na]⁺, 100). HRESIMS: calcd. for C₁₇H₂₆O₈Na *m/z* 381.1525, found 381.1523.

Analysis calcd. for C₁₇H₂₆O₈ · 0.05 C₇H₁₆ (358.38): C 57.35, H 7.43; found C 57.32, H 7.37.



A dry flask was charged with diol **148** (40 mg, 0.17 mmol) and Pb(OAc)₄ (296 mg, 0.67 mmol, 4 eq.) vacuumed, flushed with argon and cooled to nearly 0°C. CH₂Cl₂ (1 mL) was added, the ice bath removed soon after and the mixture was stirred at room temperature for 5 h, diluted with ether, filtered through celite, the filtrate concentrated and purified by silica gel chromatography using ether-heptane, 1:1 as an eluent to give **187** (26 mg, 52%).

187: 1-[6-Butyl-6-hydroxy-7-methyl-3-(2-oxo-propyl)-2,10-dioxo-tricyclo [5.3.1.0^{0,0}] undec-9-yl]-propan-2-one.



Mp: 102°C.

$[\alpha]_D^{20} = -8$ (*c* 0.6, CHCl₃).

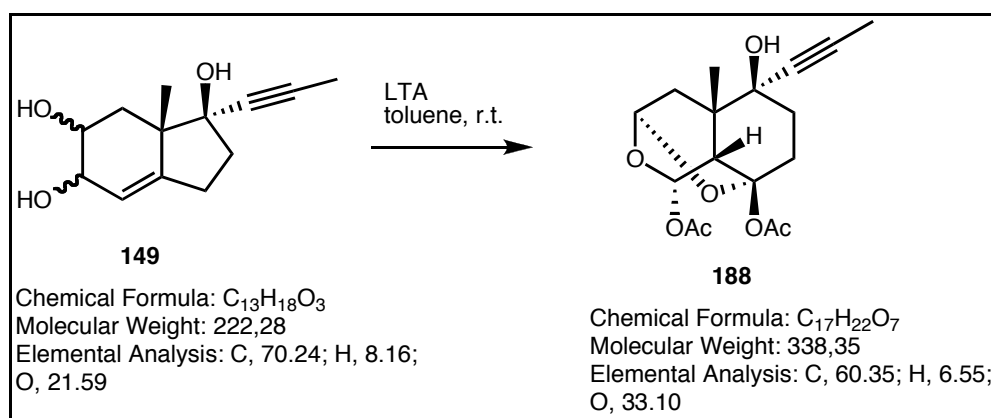
IR (film): 3529, 2955, 2935, 1728, 1457, 1368, 1251, 1221, 1285, 1104, 1061, 1022, 947 cm⁻¹.

¹H NMR (CDCl₃, 500 MHz): δ = 0.92 (t, *J* = 6.5 Hz, 3 H, Me-*n*Bu), 1.25 - 1.36 (m, 7 H, H5, Bu), 1.30 (s, 3 H, H12), 1.59 (dd, *J* = 1.4, 14.2 Hz, 1 H, H11), 1.60 - 1.64 (m, 1 H, H5'), 1.70 - 1.74 (m, 1 H, H4), 1.85 (dd, *J* = 2.8, 14.2 Hz, 1 H, H11'), 2.09 (s, 3 H, Me-Ac), 2.10 (s, 3 H, Me-Ac), 2.52 - 2.65 (m, 1 H, H4'), 3.26 (s, 1 H, H8), 5.22 (s, 1 H, H1), 6.52 (s, 1 H, H9).

¹³C NMR (CDCl₃, 125 MHz): δ = 14.0 (Me-*n*Bu), 19.7 (C12), 21.2 (Me-Ac), 22.6 (Me-Ac), 23.4 (Bu), 25.4 (Bu), 28.9, 29.1 (Bu, C4), 35.6 (C5), 37.1 (C8), 39.1 (C11), 39.6 (C7), 74.1 (C6), 91.3 (C9), 92.5 (C1), 103.7 (C3), 169.4 (CO-Ac), 169.7 (CO-Ac).

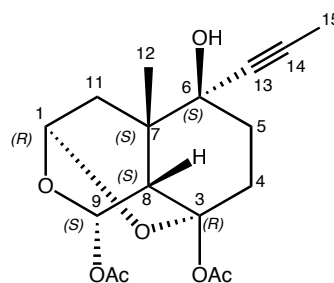
ESIMS (MeOH): 379.2 ([*M* + Na]⁺, 100). HRESIMS: calcd. for C₁₈H₂₈O₇Na *m/z* 379.1733, found 379.1729.

Analysis calcd. for C₁₈H₂₈O₇ (356.18): C 60.66, H 7.92; found C 61.12, H 8.45.



A dry flask was charged with unsaturated diols **149** (85 mg, 0.38 mmol, diastereomeric mixture) and $\text{Pb}(\text{OAc})_4$ (509 mg, 1.15 mmol, 3 eq.) vacuumed, flushed with argon and cooled to 0°C. Toluene (2 mL) was added, the cooling bath removed soon after and the reaction mixture was stirred for 15 h at room temperature, diluted with diethyl ether, filtered through $\text{MgSO}_4/\text{Celite}/\text{silica}$, the filtrate concentrated and purified by silica gel chromatography using diethyl ether-heptane, 1:1 as an eluent to give **188** (74 mg, 57%).

188: Acetic acid 3-acetoxy-6-hydroxy-7-methyl-6-prop-1-ynyl-2,10-dioxatricyclo [5.3.1.0^{0,0}]undec-9-yl ester.



Mp: 200.0°C.

$[\alpha]_D^{20} = -49$ (*c* 1.37, CHCl_3).

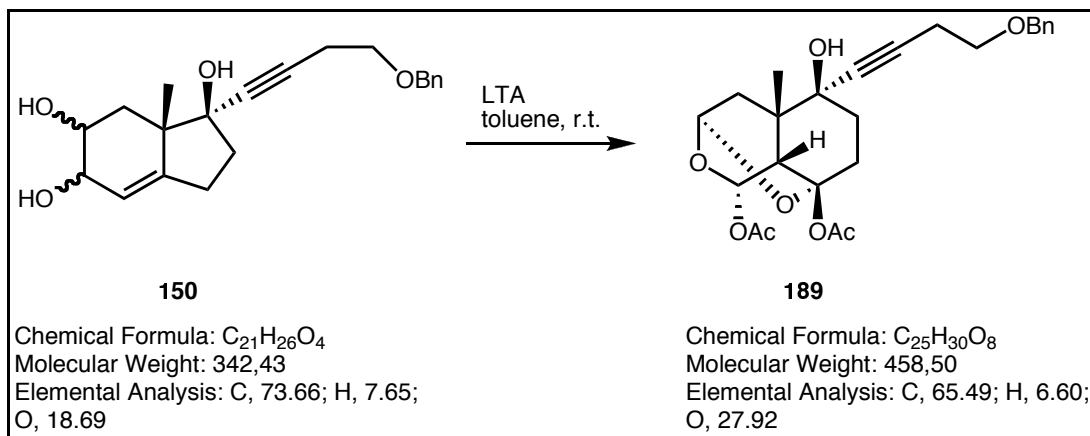
IR (film): $\nu = 3487, 2944, 1733, 1369, 1251, 1220, 1184, 1075, 1024, 952 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 1.43$ (s, 3 H, H12), 1.60 (dd, $J = 1.4, 14.7$ Hz, 1 H, H11), 1.63 (ddd, $J = 2.0, 5.0, 13.1$ Hz, 1 H, H4), 1.78 (s, 3 H, H15), 1.84 (ddd, $J = 2.0, 4.9, 14.5$ Hz, 1 H, H5), 1.96 (dd, $J = 2.7, 14.7$ Hz, 1 H, H11'), 2.04 (s, 6H, Me-Ac), 2.08 (dd, $J = 4.2, 13.9$ Hz, 1 H, H5'), 2.59 (td, $J = 4.9, 13.2$ Hz, 1 H, H4'), 3.10 (s, 1 H, H8), 5.25 (dd, $J = 1.2, 2.5$ Hz, 1 H, H1), 6.38 (d, $J = 0.7$ Hz, 1 H, H9).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 3.5$ (C15), 21.3 (Me-Ac), 22.3 (C12), 22.6 (Me-Ac), 28.6 (C4), 33.8 (C5), 37.0 (C8), 39.5 (C7), 39.8 (C11), 72.1 (C6), 80.7, 81.4 (C13, C14), 91.1 (C9), 92.7 (C1), 103.3 (C3), 169.7 (CO-Ac), 169.4 (CO-Ac).

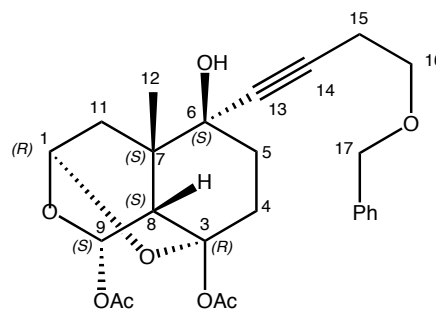
ESIMS (MeOH): 361.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{17}\text{H}_{22}\text{O}_7\text{Na}$ m/z 361.1263, found 361.1252.

Analysis calcd. for $\text{C}_{17}\text{H}_{22}\text{O}_7 \cdot 0.4 \text{ H}_2\text{O}$ (338.35): C 59.09, H 6.65; found C 59.08, H 6.68.



A dry flask was charged with unsaturated diols **150** (46 mg, 0.13 mmol, diastereomeric mixture) and Pb(OAc)₄ (179 mg, 0.40 mmol, 3 eq.) vacuumed, flushed with argon and cooled to 0°C. Acetic acid (1 mL) was added, the cooling bath removed soon after and the reaction mixture was stirred for 19 h at room temperature. The mixture was diluted with EtOAc and washed carefully with saturated NaHCO₃ solution till neutral pH and brine. The organic layer was concentrated under reduced pressure, dried over MgSO₄ and purified through flash chromatography using ether as eluant afforded 48 mg (80%) **189**.

189: 1-(4-Benzyloxy-but-1-ynyl)-7a-methyl-2,3,5,6,7,7a-hexahydro-1*H*-indene-1,5,6-triol.



Mp: 45.0 - 46.0°C.

$[\alpha]_D^{20} = -35$ (*c* 1.345, CHCl₃).

IR (film): $\nu = 2941, 1733, 1369, 1252, 1220, 1184, 1076, 1026, 951$ cm⁻¹.

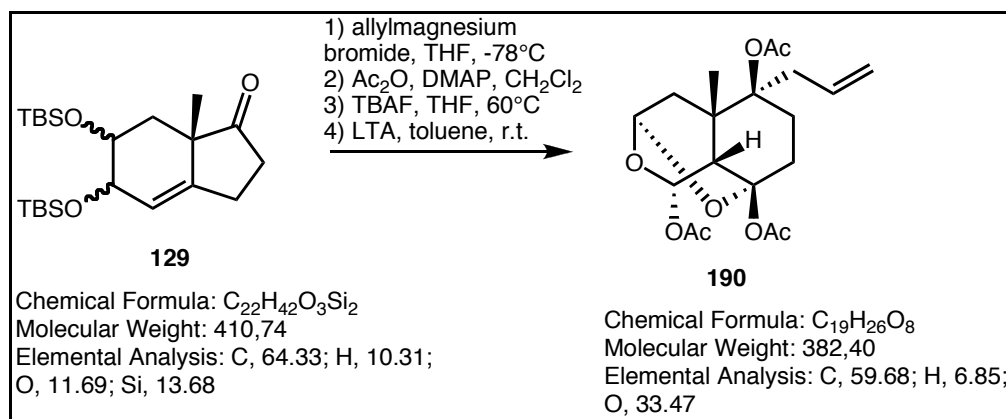
¹H-NMR (CDCl₃, 300 MHz): $\delta = 1.42$ (s, 3 H, H12), 1.57 (dd, *J* = 1.3, 14.7 Hz, 1 H, H11), 1.62 (ddd, *J* = 2.1, 4.9, 13.2 Hz, 1 H, H4), 1.83 (ddd, *J* = 2.1, 4.9, 14.5 Hz, 1 H, H5), 1.94 (dd, *J* = 2.7, 14.7 Hz, 1 H, H11), 2.03 (s, 3 H, Me-Ac), 2.04 (s, 3 H, Me-Ac), 2.05 - 2.12 (m, 1 H, H5), 2.45 (t, *J* = 6.8 Hz, 2 H, H15), 2.59 (dt, *J* = 4.9, 13.3 Hz, 1 H,

H4), 3.11 (s, 1 H, H8), 3.50 (t, $J = 6.8$ Hz, 2 H, H16), 4.47 (s, 2 H, H17), 5.23 (dd, $J = 1.2, 2.5$ Hz, 1 H, H1), 6.37 (d, $J = 0.8$ Hz, 1 H, H9), 7.21 - 7.29 (m, 5 H, Ph).

^{13}C -NMR (CDCl_3 , 75 MHz): $\delta = 20.1$ (C15), 21.3 (Me-Ac), 22.4 (C12), 22.6 (Me-Ac), 28.6 (C4), 33.8 (C5), 36.9 (C8), 39.5 (C7), 39.8 (C11), 68.2 (C16), 72.1 (C6), 73.0 (C17), 82.5, 82.8 (C13, C14), 91.1 (C9), 92.7 (C1), 103.3 (C3), 127.7, 127.8, 128.5 (5C-Ph), 137.9 (Cq-Ph), 169.4 (CO-Ac), 169.7 (CO-Ac).

ESIMS (MeOH): 481.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{25}\text{H}_{30}\text{O}_8\text{Na}$ m/z 481.1838, found 481.1865.

Analysis calcd. for $\text{C}_{25}\text{H}_{30}\text{O}_8 \cdot 1.2 \text{H}_2\text{O}$ (458.50): C 62.54, H 6.80; found C 62.44, H 6.62.



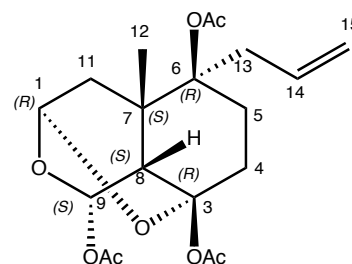
To a solution of **129** (880 mg, 2.14 mmol) in THF (32 mL) at -78°C under Ar, was added allylmagnesium bromide (10.73 mL, 1M in ether). The reaction mixture was stirred 1 h at -78°C . Then, the reaction mixture was diluted with ether, and a saturated solution of NH_4Cl was added. The aqueous layer was extracted with ether. The combined organic layers were worked up as usual. Flash chromatography (ethyl acetate/heptane 1:1) afforded 920 mg (95%) of alcohol, which was directly protected.

Acetic anhydride (14 mL, excess) was added to a stirring mixture of alcohol (857 mg, 1.89 mmol) and DMAP (276 mg, 2.26 mmol) in dry pyridine (15 mL) under argon at 0°C . The reaction mixture was stirred for 3 h at 0°C (TLC monitoring), diluted with dichloromethane, washed with saturated sodium bicarbonate then 1N hydrochloric acid and worked up as usual to give, after silica gel flash column chromatography (eluent: heptane-EtOAc 95:5), 232 mg (25%) of the corresponding acetate **138** (500 mg of SM recovered, 59%).

TBAF (1.7 mL, 1M in THF) was added to **138** (210 mg, 0.42 mmol), at r.t. under Ar. The reaction mixture was stirred at 60°C for 2 h. Then the reaction mixture was diluted (at r.t.) with ethyl acetate (large amount) and worked up as usual. Flash chromatography (ethyl acetate) gives 100 mg (88%) of **151**.

A dry flask was charged with 50 mg of diol (0.19 mmol) and 208 mg of Pb(OAc)₄ (0.47 mmol, 3 eq.) vacuumed, flushed with argon and cooled to nearly 0°C. Toluene (5 mL) was added, the ice bath removed soon after and the mixture was stirred at room temperature for 15h, diluted with ether, filtered through Celite/Silica/Magnesium sulfate, the filtrate concentrated and purified by silica gel chromatography using ethyl acetate-heptane, 3:7 as an eluent to give the product **190** (62 mg, 62%):

190: Acetic acid 3,6-diacetoxy-6-allyl-7-methyl-2,10-dioxatricyclo[5.3.1.0^{0,0}]undec-9-yl ester.



Mp: colourless oil.

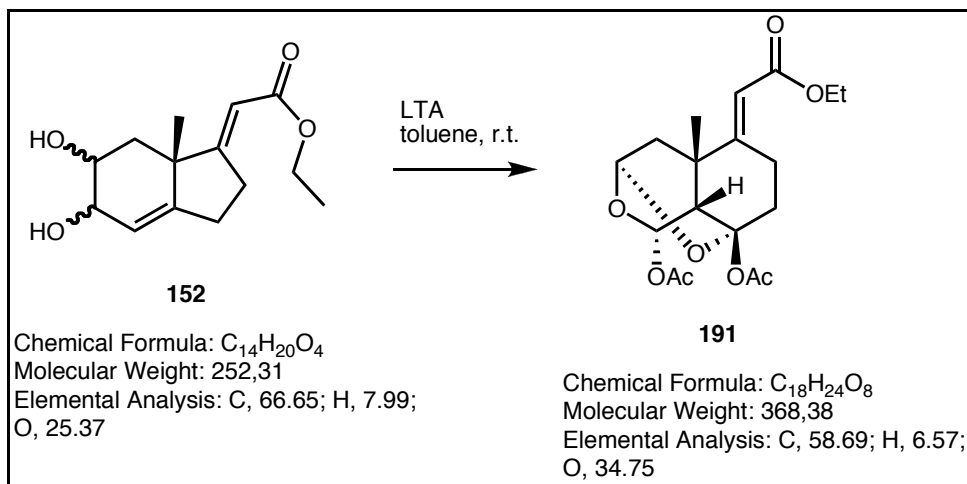
$$[\alpha]_D^{20} = +8 \text{ (} c \text{ 0.8, CHCl}_3\text{)}$$

IR (film): 2925, 2365, 1733, 1433, 1370, 1248, 1180, 1062, 1022, 956, 917 cm⁻¹.

¹H-NMR (CDCl₃, 300 MHz): 1.34 (s, 3 H, H12), 1.52 (dd, *J* = 1.5, 14.5 Hz, 1 H, H11), 1.63 (ddd, *J* = 2.2, 4.9, 13.2 Hz, 1 H, H4), 1.77 (ddd, *J* = 4.9, 13.3, 14.9 Hz, 1 H, H5), 1.95 (dd, *J* = 2.8, 14.5 Hz, 1 H, H11), 2.08 (s, 6 H, Me-Ac), 2.09 (s, 3 H, Me-Ac), 2.34 (td, *J* = 4.8, 13.2 Hz, 1 H, H4), 2.54 (dd, *J* = 8.2, 14.9 Hz, 1 H, H13), 2.75 (ddd, *J* = 2.2, 4.8, 14.9 Hz, 1 H, H5), 2.85 (ddt, *J* = 1.5, 6.8, 14.9 Hz, 1 H, H13), 3.31 (d, *J* = 1.3 Hz, 1 H, H8), 5.04 (dt, *J* = 1.5, 10.1 Hz, 1 H, H15), 5.05 (dq, *J* = 1.5, 18.0 Hz, 1 H, H15'), 5.25 (dd, *J* = 1.5, 2.8 Hz, 1 H, H1), 5.89 (dddd, *J* = 6.5, 8.2, 10.1, 18.0 Hz, 1 H, H14), 6.49 (d, *J* = 1.3 Hz, 1 H, H9).

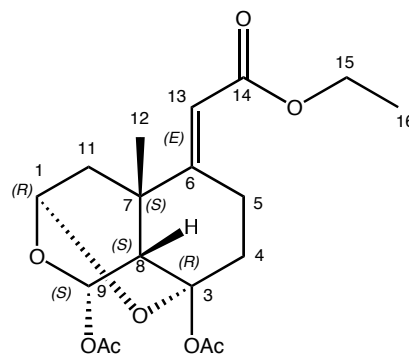
¹³C-NMR (CDCl₃, 75 MHz): 20.8 (C12), 21.3 (Me-Ac), 22.0 (Me-Ac), 22.5 (Me-Ac), 25.1 (C5), 29.6 (C4), 37.0 (C8), 38.9 (C11), 39.8 (C13), 40.6 (C7), 85.6 (C6), 90.6 (C9), 92.0 (C1), 103.2 (C3), 118.2 (C15), 133.9 (C14), 169.6 (CO-Ac), 169.7 (CO-Ac), 170.1 (CO-Ac).

ESIMS (MeOH): 405.1 ($[M + Na]^+$, 100). HRESIMS: calcd. for $C_{19}H_{26}O_8Na$ m/z 405.1525, found 405.1525



A dry flask was charged with unsaturated diols **152** (24 mg, 0.095 mmol, diastereomeric mixture) and $Pb(OAc)_4$ (129 mg, 0.29 mmol, 3 eq.) vacuumed, flushed with argon and cooled to $0^\circ C$. Toluene (1.5 mL) was added, the cooling bath removed soon after and the reaction mixture was stirred for 19 h at room temperature, diluted with diethyl ether, filtered through $MgSO_4$ /Celite/silica, the filtrate concentrated and purified by silica gel chromatography using diethyl ether-heptane, 1:1 as an eluent to give **191** (21 mg, 60%).

191: (3,9-Diacetoxy-7-methyl-2,10-dioxa-tricyclo[5.3.1.0^{0,0}]undec-6-ylidene)-acetic acid ethyl ester.



Mp: 102.0 - 103.0°C.

$[\alpha]_D^{20} = +36$ (c 0.65, $CHCl_3$).

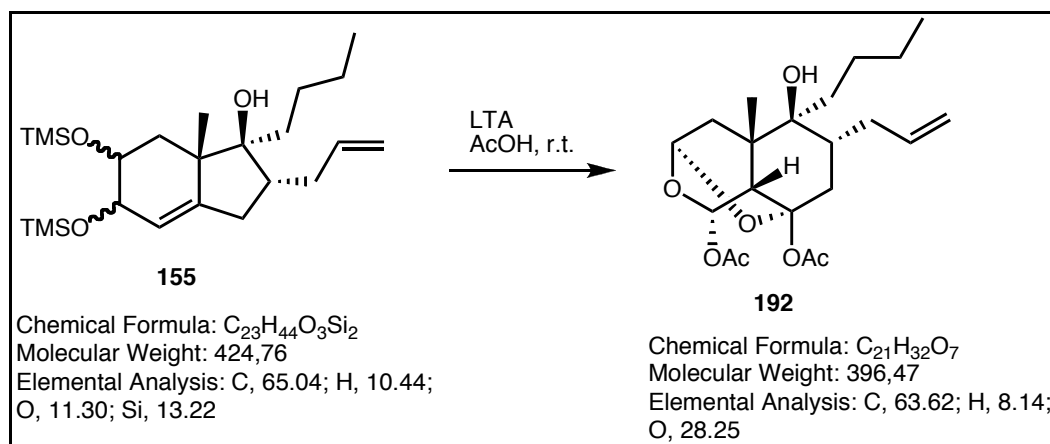
IR (film): $\nu = 2976, 1732, 1711, 1640, 1368, 1245, 1182, 1071, 1027 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 1.30$ (t, $J = 7.1$ Hz, 3 H, H16), 1.48 (s, 3 H, H12), 1.74 (dd, $J = 1.3, 14.4$ Hz, 1 H, H11), 1.95 (dd, $J = 2.7, 7.4$ Hz, 1 H, H4), 2.04 (dd, $J = 2.7, 14.5$ Hz, 1 H, H11'), 2.10 (s, 3 H, Me-Ac), 2.11 (s, 3 H, Me-Ac), 2.31 - 2.39 (m, 2 H, H4', H5), 2.91 (d, $J = 0.9$ Hz, 1 H, H8), 3.91 - 3.99 (m, 1 H, H5'), 4.18 (q, $J = 7.1$ Hz, 2 H, H15), 5.40 (dd, $J = 1.3, 2.6$ Hz, 1 H, H1), 5.88 (s, 1 H, H13), 6.56 (d, $J = 1.0$ Hz, 1 H, H9).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 14.3$ (C16), 21.3 (Me-Ac), 22.1 (C5), 22.5 (Me-Ac), 23.7 (C12), 33.4 (C4), 37.6 (C7), 41.1 (C8), 41.4 (C11), 60.2 (C15), 90.6 (C9), 92.1 (C1), 103.1 (C3), 115.4 (C13), 160.8 (C6), 166.6 (C14), 169.6 (2 CO-Ac).

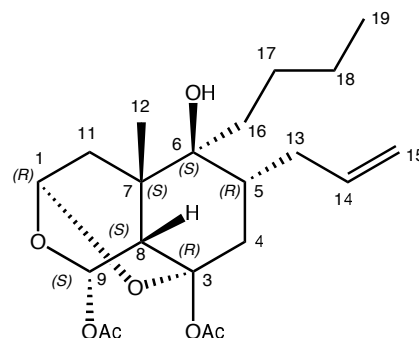
ESIMS (MeOH): 391.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{18}\text{H}_{24}\text{O}_8\text{Na}$ m/z 391.1369, found 391.1356.

Analysis calcd. for $\text{C}_{18}\text{H}_{24}\text{O}_8 \cdot 1.1 \text{ H}_2\text{O}$ (368.38): C 55.69, H 6.80; found C 55.41, H 6.41.



A dry flask was charged with unsaturated protected diols **155** (86 mg, 0.22 mmol, diastereomeric mixture) and $\text{Pb}(\text{OAc})_4$ (293 mg, 0.66 mmol, 3 eq.) vacuumed, flushed with argon and cooled to 0°C . Acetic acid (2 mL) was added, the cooling bath removed soon after and the reaction mixture was stirred for 15 h at room temperature. The mixture was diluted with EtOAc and washed carefully with saturated NaHCO_3 solution till neutral pH and brine. The organic layer was concentrated under reduced pressure, dried over MgSO_4 and purified through flash chromatography using heptane-ether 1:1 as eluent afforded 34 mg (40%) **192**.

192: Acetic acid 9-acetoxy-5-allyl-6-butyl-6-hydroxy-7-methyl-2,10-dioxatricyclo
[5.3.1.0^{0,0}]undec-3-yl ester.



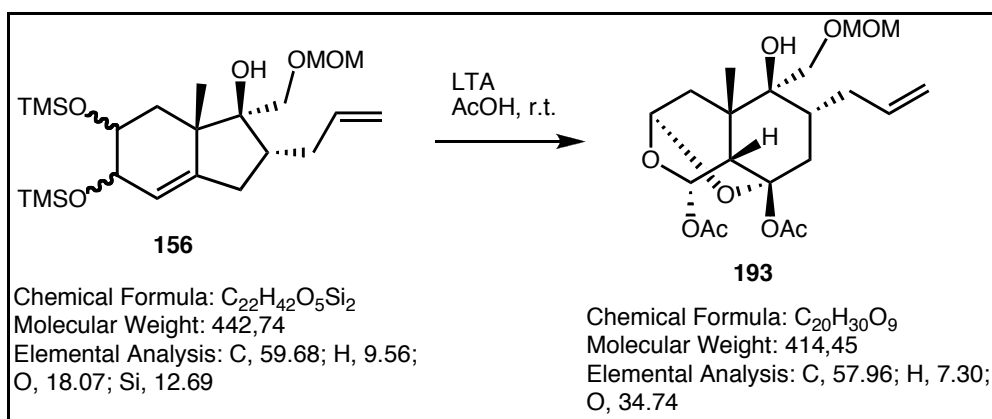
$[\alpha]_D^{20} = -84$ (c 0.68, CHCl_3).

IR (film): $\nu = 2956, 1735, 1369, 1245, 1180, 1026, 942 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): $\delta = 0.95$ (t, $J = 7.1$ Hz, 3 H, H19), 1.34 (s, 3 H, H12), 1.38 - 1.42 (m, 4 H, H17, H18), 1.53 (dd, $J = 1.1, 14.6$ Hz, 1 H, H11), 1.64 (t, $J = 4.5$ Hz, 2 H, H16), 1.84 (dd, $J = 7.1, 11.8$ Hz, 1 H, H5), 1.86 (d, $J = 14.1$ Hz, 1 H, H4), 2.10 (s, 3 H, Me-Ac), 2.11 (s, 3 H, Me-Ac), 2.10 - 2.14 (m, 1 H, H13), 2.14 (dd, $J = 2.9, 14.3$ Hz, 1 H, H11), 2.55 (td, $J = 7.9, 12.8$ Hz, 1 H, H13), 2.72 (dd, $J = 7.3, 14.2$ Hz, 1 H, H4), 3.37 (s, 1 H, H8), 5.05 - 5.08 (m, 2 H, H15), 5.27 (dd, $J = 1.0, 2.9$ Hz, 1 H, H1), 5.67 (dddd, $J = 5.5, 8.0, 10.1, 17.2$ Hz, 1 H, H14), 6.57 (s, 1 H, H9).

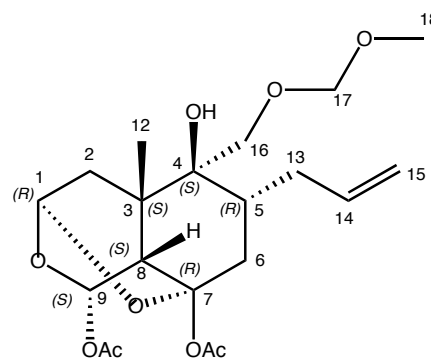
$^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): $\delta = 14.1$ (C19), 21.2 (C12), 21.3 (Me-Ac), 22.7 (Me-Ac), 23.3 (C17), 24.3 (C18), 29.9 (C4), 33.1 (C16), 35.3 (C13), 37.3 (C11), 37.5 (C8), 39.6 (C7), 42.3 (C5), 76.4 (C6), 91.5 (C9), 92.3 (C1), 104.6 (C3), 116.7 (C15), 137.5 (C14), 169.5 (CO-Ac), 169.8 (CO-Ac).

ESIMS (MeOH): 419.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{21}\text{H}_{32}\text{O}_7\text{Na}$ m/z 419.2046, found 419.2058.



A dry flask was charged with unsaturated protected diols **156** (20 mg, 0.067 mmol, diastereomeric mixture) and $\text{Pb}(\text{OAc})_4$ (89 mg, 0.2 mmol, 3 eq.) vacuumed, flushed with argon and cooled to 0°C. Acetic acid (1 mL) was added, the cooling bath removed soon after and the reaction mixture was stirred for 15 h at room temperature. The mixture was diluted with EtOAc and washed carefully with saturated NaHCO_3 solution till neutral pH and brine. The organic layer was concentrated under reduced pressure, dried over MgSO_4 and purified through flash chromatography using heptane-ether 1:1 as eluent afforded 7 mg (39%) **193**.

193: Acetic acid 9-acetoxy-5-allyl-6-hydroxy-6-methoxymethoxymethyl-7-methyl-2,10-dioxo-tricyclo[5.3.1.0^{0,0}]undec-3-yl ester.



Mp: colourless oil.

$[\alpha]_D^{20} = -8$ (c 0.95, CHCl_3).

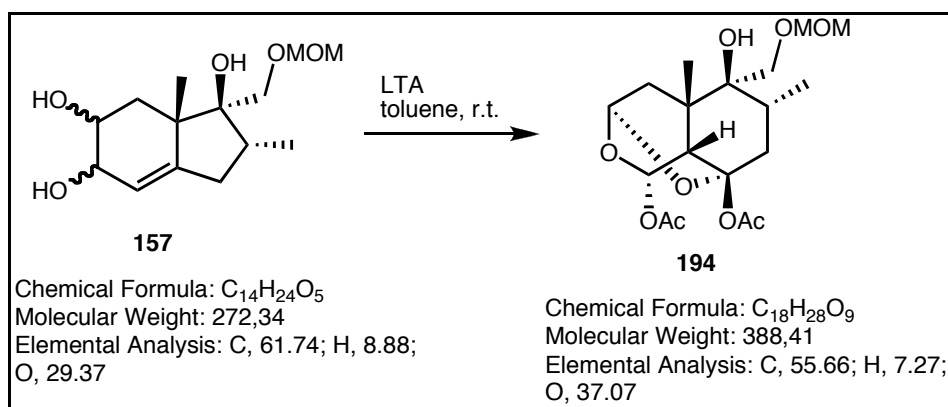
IR (film): $\nu = 2938, 1735, 1369, 1224, 1182, 1029, 982, 938 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): $\delta = 1.34$ (s, 3 H, H12), 1.53 - 1.57 (m, 1 H, H2), 1.88 (d, $J = 13.9$ Hz, 1 H, H6), 1.98 - 2.06 (m, 1 H, H5), 2.10 (s, 3 H, Me-Ac), 2.11 (s, 3 H, Me-Ac), 2.19 (dd, $J = 2.8, 14.5$ Hz, 1 H, H2), 2.20 - 2.27 (m, 1 H, H13), 2.48 (td, $J = 8.4,$

13.4 Hz, 1 H, H13), 2.77 (dd, $J = 7.3, 13.8$ Hz, 1 H, H6), 3.41 (s, 4 H, H8, H18), 3.67 and 3.85 (ABquartet, $J = 10.4$ Hz, 2 H, H16), 4.70 and 4.72 (ABquartet, $J = 6.7$ Hz, 2 H, H17), 5.05 (d, $J = 9.8$ Hz, 1 H, H15), 5.08 (d, $J = 17.1$ Hz, 1 H, H15), 5.28 (s, 1 H, H1), 5.67 (tdd, $J = 1.4, 5.4, 8.6$ Hz, 1 H, H14), 6.55 (s, 1 H, H9).

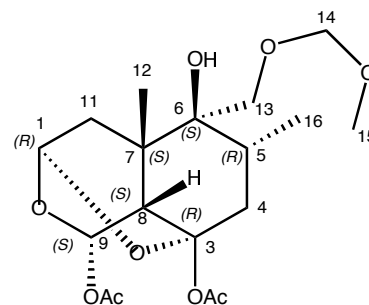
^{13}C -NMR (CDCl_3 , 125 MHz): $\delta = 21.3$ (Me-Ac), 21.5 (C12), 22.7 (Me-Ac), 30.0 (C6), 35.2 (C13), 36.9 (C8), 37.4 (C2), 37.9 (C3), 43.0 (C5), 56.0 (C18), 71.1 (C16), 75.4 (C4), 90.9 (C9), 92.1 (C1), 97.8 (C17), 104.7 (C7), 116.7 (C15), 137.7 (C14), 169.3 (CO-Ac), 169.7 (CO-Ac).

ESIMS (MeOH): 437.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{20}\text{H}_{30}\text{O}_9\text{Na}$ m/z 437.1788, found 437.1835.



A dry flask was charged with unsaturated diols **157** (36 mg, 0.13 mmol, diastereomeric mixture) and $\text{Pb}(\text{OAc})_4$ (178 mg, 0.36 mmol, 3 eq.) vacuumed, flushed with argon and cooled to 0°C . Toluene (1 mL) was added, the cooling bath removed soon after and the reaction mixture was stirred for 15 h at room temperature, diluted with diethyl ether, filtered through $\text{MgSO}_4/\text{Celite}/\text{silica}$, the filtrate concentrated and purified by silica gel chromatography using diethyl ether-heptane, 1:1 as an eluent to give **194** (26 mg, 51%).

194: Acetic acid 3-acetoxy-6-hydroxy-6-methoxymethoxymethyl-5,7-dimethyl-2,10-dioxa-tricyclo[5.3.1.0^{0,0}]undec-9-yl ester.



Mp: colourless oil.

$[\alpha]_D^{20} = -39$ (*c* 0.54, CHCl₃).

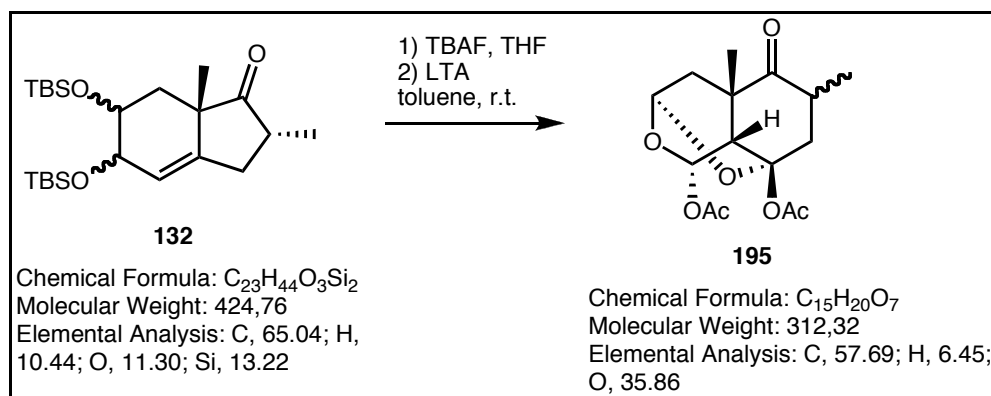
IR (film): $\nu = 3503, 2937, 2358, 2341, 1736, 1369, 1321, 1257, 1186, 1150, 1101, 1071, 1035, 987 \text{ cm}^{-1}$.

¹H-NMR (CDCl₃, 500 MHz): $\delta = 1.22$ (d, *J* = 7.8 Hz, 3 H, H16), 1.34 (s, 3 H, H12), 1.53 (dd, *J* = 1.1, 14.5 Hz, 1 H, H11), 1.68 (d, *J* = 13.7 Hz, 1 H, H4), 2.10 (s, 3 H, Me-Ac), 2.11 (s, 3 H, Me-Ac), 2.21 (quint, *J* = 7.9 Hz, 1 H, H5), 2.29 (dd, *J* = 2.8, 14.5 Hz, 1 H, H11), 2.96 (dd, *J* = 7.5, 13.7 Hz, 1 H, H4), 3.35 (s, 1 H, H8), 3.41 (s, 3 H, H15), 3.65 and 3.79 (ABquartet, *J* = 10.1 Hz, 2 H, H13), 4.68 and 4.70 (ABquartet, *J* = 6.6 Hz, 2 H, H14), 5.26 (d, *J* = 1.9 Hz, 1 H, H1), 6.54 (s, 1 H, H9).

¹³C-NMR (CDCl₃, 125 MHz): $\delta = 18.5$ (C16), 21.3 (Me-Ac), 21.7 (C12), 22.7 (Me-Ac), 34.8 (C4), 37.0 (C8), 37.5 (C11), 37.8 (C5), 38.1 (C7), 55.9 (C15), 70.8 (C13), 74.9 (C6), 91.1 (C9), 92.2 (C1), 97.7 (C14), 104.6 (C3), 169.4 (CO-Ac), 169.7 (CO-Ac).

ESIMS (MeOH): 411.2 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₁₈H₂₈O₉Na *m/z* 411.1631, found 411.1615.

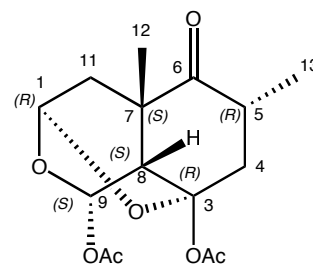
Analysis calcd. for C₁₈H₂₈O₉ · 0.7 H₂O (388.41): C 53.91, H 7.39; found C 53.77, H 7.23.



TBAF (0.84 mL, 1M in THF) was added to **132** (119 mg, 0.28 mmol), at r.t. under Ar. The reaction mixture was stirred at 60°C for 2 h. Then the reaction mixture was diluted (at r.t.) with ethyl acetate (large amount) and worked up as usual. Flash chromatography (ethyl acetate/heptane 2:1) gives 41 mg (75%) of a mixture of two diastereomer **158**, which are directly used in the next step.

A dry flask was charged with unsaturated diols **158** (41 mg, 0.2 mmol, diastereomeric mixture) and Pb(OAc)₄ (266 mg, 0.6 mmol, 3 eq.) vacuumed, flushed with argon and cooled to 0°C. Toluene (1 mL) was added, the cooling bath removed soon after and the reaction mixture was stirred for 19 h at room temperature, diluted with diethyl ether, filtered through MgSO₄/Celite/silica, the filtrate concentrated and purified by silica gel chromatography using diethyl ether-heptane, 1:1 as an eluent to give **195** (34 mg, 54%, two diastereomer 3:1).

195: Acetic acid 3-acetoxy-5,7-dimethyl-6-oxa-2,10-dioxa-tricyclo[5.3.1.0^{3,8}]undec-9-yl ester.



Mp: solid (characterized as a diastereomeric mixture).

$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

IR (film): $\nu = 2976, 1732, 1370, 1247, 1221, 1179, 1074, 1026, 958 \text{ cm}^{-1}$.

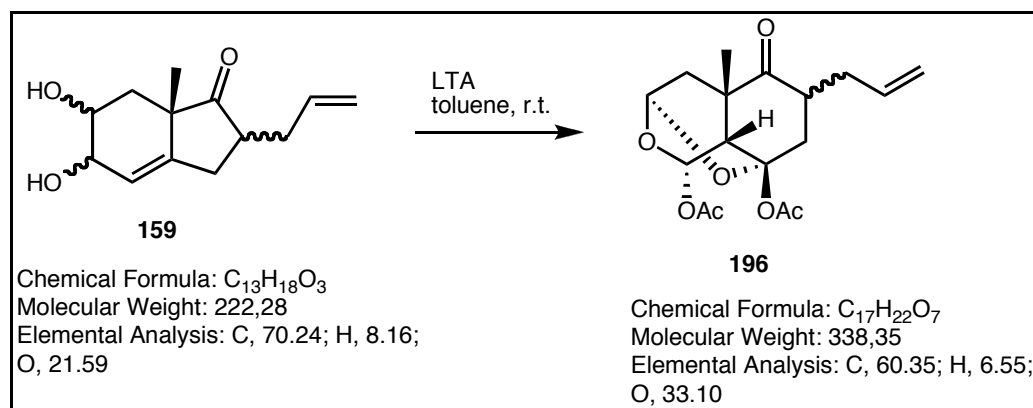
Major diastereomer:

¹H-NMR (CDCl₃, 500 MHz): $\delta = 1.08$ (d, $J = 6.5$ Hz, 3 H, H13), 1.39 (s, 3 H, H12), 1.78 (d, $J = 14.7$ Hz, 1 H, H11), 2.09 (dd, $J = 2.8, 14.8$ Hz, 1 H, H11'), 2.10 (s, 3 H, Me-Ac), 2.13 (s, 3 H, Me-Ac), 2.23 (dd, $J = 6.9, 13.4$ Hz, 1 H, H4), 2.44 (t, $J = 13.1$ Hz, 1 H, H4'), 3.04 (tt, $J = 6.5, 12.8$ Hz, 1 H, H5), 3.11 (s, 1 H, H8), 5.44 - 5.46 (m, 1 H, H1), 6.41 (s, 1 H, H9).

¹³C-NMR (CDCl₃, 125 MHz): $\delta = 13.9$ (C13), 20.3 (C12), 21.1 (Me-Ac), 22.4 (Me-Ac), 36.6 (C5), 40.1 (C11), 40.4 (C4), 40.9 (C8), 43.1 (C7), 90.2 (C9), 92.1 (C1), 102.0 (C3), 169.3 (CO-Ac), 169.6 (CO-Ac), 209.9 (C6).

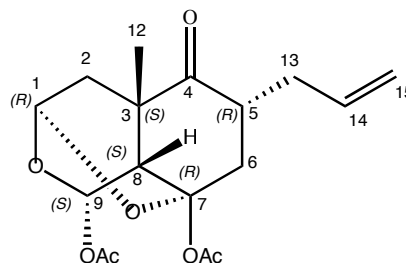
ESIMS (MeOH): 335.1 ($[M + Na]^+$, 100). HRESIMS: calcd. for $C_{15}H_{20}O_7Na$ m/z 335.1107, found 335.1098.

Analysis calcd. for $C_{15}H_{20}O_7$ (312.32): C 57.69, H 6.45; found C 57.18, H 6.43.



A dry flask was charged with unsaturated diols **159** (20 mg, 0.09 mmol, diastereomeric mixture) and $Pb(OAc)_4$ (120 mg, 0.27 mmol, 3 eq.) vacuumed, flushed with argon and cooled to 0°C. Toluene (2 mL) was added, the cooling bath removed soon after and the reaction mixture was stirred for 15 h at room temperature, diluted with diethyl ether, filtered through $MgSO_4$ /Celite/silica, the filtrate concentrated and purified by silica gel chromatography using diethyl ether-heptane, 1:1 as an eluent to give **196** (two diastereomer 2:1, 18 mg, 59%).

196: Acetic acid 7-acetoxy-5-allyl-3-methyl-4-oxo-10,11-dioxa-tricyclo[5.3.1.0^{0,0}]undec-9-yl ester.



Mp: mixture of diastereoisomere.

$[\alpha]_D^{20}$ = mixture of diastereoisomere.

IR (film): $\nu = 2938, 1732, 1441, 1370, 1249, 1217, 1070, 1029$ cm^{-1} .

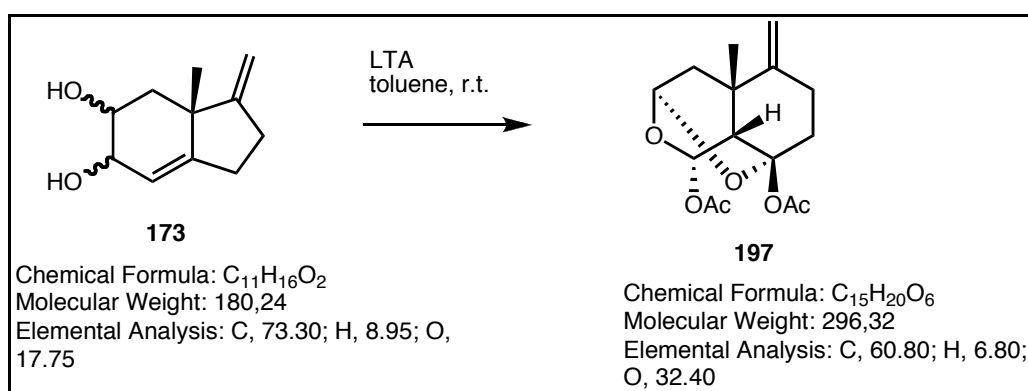
Major diastereomer:

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 1.40$ (s, 3 H, H12), 1.82 (t, $J = 13.3$ Hz, 1 H, H2), 2.04 - 2.09 (m, 1 H, H13), 2.12 (s, 3 H, Me-Ac), 2.14 (s, 3 H, Me-Ac), 2.13 - 2.18 (m, 1 H, H2'), 2.26 (dd, $J = 7.0, 13.4$ Hz, 1 H, H6), 2.41 (t, $J = 13.2$ Hz, 1 H, H6'), 2.47 - 2.63 (m, 1 H, H13), 2.93 - 3.04 (m, 1 H, H5), 3.14 (s, 1 H, H8), 5.04 (s, 1 H, H15), 5.08 (d, $J = 7.4$ Hz, 1 H, H15'), 5.47 (d, $J = 2.4$ Hz, 1 H, H1), 5.73 - 5.75 (m, 1 H, H14), 6.43 (s, 1 H, H9).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 20.3$ (C12), 21.2 (Me-Ac), 22.4 (Me-Ac), 33.0 (C13), 38.0 (C6), 40.0 (C2), 40.8 (C8), 41.3 (C5), 43.3 (C3), 90.1 (C9), 92.0 (C1), 102.2 (C7), 117.4 (C15), 135.2 (C14), 169.3 (CAc), 169.6 (CO-Ac), 208.9 (C4).

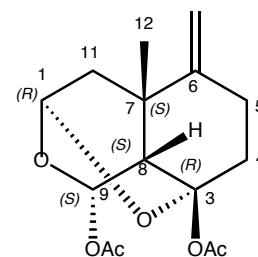
ESIMS (MeOH): 361.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{17}\text{H}_{22}\text{O}_7\text{Na}$ m/z 361.1263, found 361.1288.

Analysis calcd. for $\text{C}_{17}\text{H}_{22}\text{O}_7$ (338.35): C 60.35, H 6.55; found C 60.36, H 6.62.



A dry flask was charged with 245 mg of diol **173** (1.36 mmol) and 1.50 g of $\text{Pb}(\text{OAc})_4$ (3.40 mmol, 3 eq.) vacuumed, flushed with argon and cooled to nearly 0°C . Toluene (5 mL) was added, the ice bath removed soon after and the mixture was stirred at room temperature for 15 h, diluted with ether, filtered through Celite/Silica/Magnesium sulfate, the filtrate concentrated and purified by silica gel chromatography using ethyl acetate-heptane, 3:7 as an eluent to give the product **197** (325 mg, 80%).

197: Acetic acid 3-acetoxy-7-methyl-6-methylene-2,10-dioxa-tricyclo[5.3.1.0^{0,0}]undec-9-yl ester.



Mp: 110-115°C.

$[\alpha]_D^{20} = -28$ (*c* 1.5, CHCl₃).

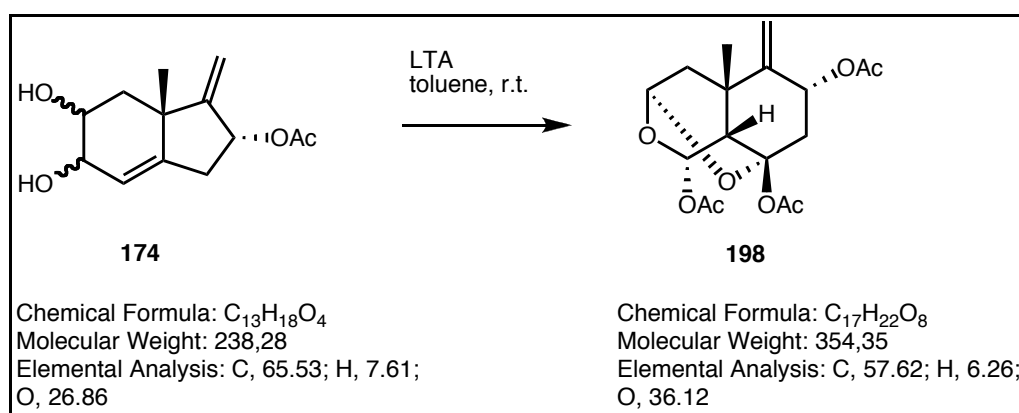
IR (film): 2980, 1730, 1380, 1200, 1080, 950 cm⁻¹.

¹H-NMR (CDCl₃, 300 MHz): 1.45 (s, 3 H, H12), 1.70 (dd, *J* = 1.4, 14.3 Hz, 1 H, H11), 1.86 - 1.90 (m, 1 H, H4 or H5), 1.95 (dd, *J* = 2.7, 14.3 Hz, 1 H, H11'), 2.09 (s, 6 H, Me-Ac), 2.18 - 2.38 (m, 2 H, H4 or H5), 4.47 (tdt, *J* = 1.6, 5.2, 12.3 Hz, 1 H, H4 or H5), 2.79 (d, *J* = 1.2 Hz, 1 H, H8), 4.87 (bs, 1 H, H13), 4.90 (bs, 1 H, H13'), 5.36 (dd, *J* = 1.4, 2.7 Hz, 1 H, H1), 6.54 (d, *J* = 1.2 Hz, 1 H, H9).

¹³C-NMR (CDCl₃, 75 MHz): 21.2 (Me-Ac), 22.5 (Me-Ac), 23.6 (C12), 29.5, 34.2 (C4, C5), 35.6 (C7), 41.0 (C11), 41.5 (C8), 90.7, 92.2 (C1, C9), 103.8 (C3), 109.8 (C13), 149.8 (C6), 169.5 (CO-Ac), 169.6 (CO-Ac).

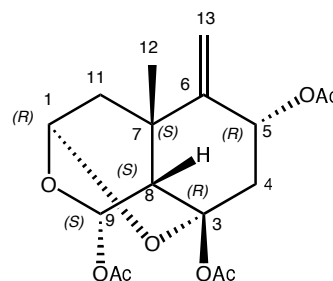
ESIMS (MeOH): 319.2 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₁₅H₂₀O₆Na *m/z* 319.1157; found 319.1155.

Analysis calcd. for C₁₅H₂₀O₆ (296.32): C 60.80, H 6.80; found C 60.57, H 6.74.



A dry flask was charged with $\text{Pb}(\text{OAc})_4$ (279 mg, 0.63 mmol) was vacuumed, flushed with argon and cooled to nearly 0°C . Then, it was suspended in dry toluene (0.5 mL) and a solution of diol **174** (50 mg, 0.21 mmol) in dry toluene (0.5 mL) was added dropwise at the same temperature. The mixture was stirred at r.t. for 15 h, diluted with Et_2O , filtered through a $\text{MgSO}_4/\text{Celite}/\text{SiO}_2$ pad and the filtrate concentrated. The residue was purified by silica gel chromatography using ethyl acetate-heptane, 1:3 as an eluent to give the product **198** (40 mg, 56%).

198: Acetic acid 3,5-diacetoxy-7-methyl-6-methylene-2,10-dioxatricyclo[5.3.1.0^{0,0}]undec-9-yl ester.



Mp: yellow oil.

$[\alpha]_D^{20} = -9$ (c 1.0, CHCl_3).

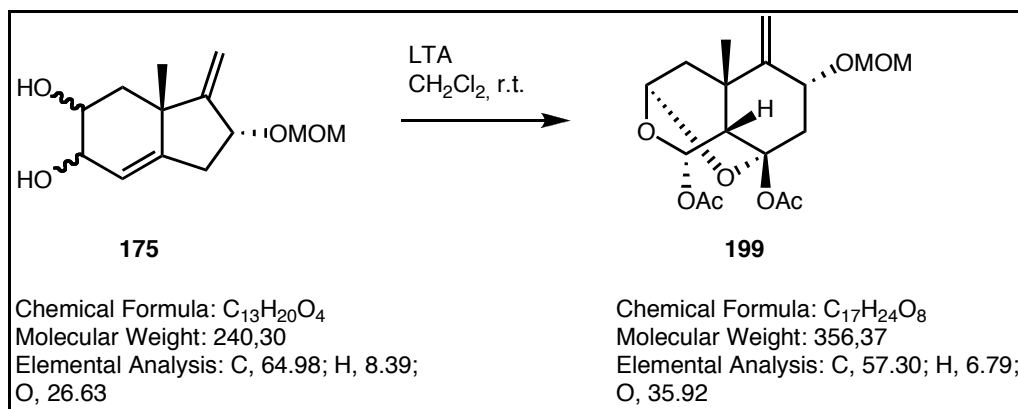
IR (film): $\nu = 2924, 1732, 1434, 1369, 1240, 1167, 1131, 1072, 1027, 968 \text{ cm}^{-1}$.

^1H NMR (300 MHz): $\delta = 1.49$ (s, 3 H, H12), 1.74 (dd, $J = 1.2, 14.0$ Hz, 1 H, H11), 2.03 (s, 3 H, Me-Ac), 2.10 (2s, 6 H, 2Me-Ac), 2.22 (dd, $J = 2.8, 14.8$ Hz, 1 H, H4), 2.55 (dd, $J = 2.8, 14.0$ Hz, 1 H, H11), 2.75 (dd, $J = 5.8, 14.8$ Hz, 1 H, H4), 2.90 (s, 1 H, H8), 5.28 (s, 1 H, H13), 5.31 (s, 1 H, H13), 5.33 (dd, $J = 1.0, 2.8$ Hz, 1 H, H1), 5.60 (dd, $J = 2.8, 5.6$ Hz, 1 H, H5), 6.56 (d, $J = 0.8$ Hz, 1 H, H9).

^{13}C NMR (75 MHz): $\delta = 21.2$ (Me-Ac), 21.4 (Me-Ac), 22.4 (Me-Ac), 24.8 (C12), 35.1 (C7), 38.6 (C4), 40.5 (C8), 41.2 (C11), 73.1 (C5), 90.6 (C9), 92.4 (C1), 102.6 (C3), 117.2 (C13), 147.1 (C6), 169.5 (CO-Ac), 169.8 (CO-Ac), 169.9 (CO-Ac).

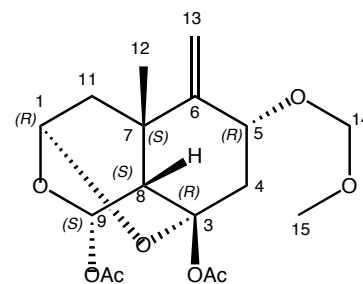
ESIMS (MeOH): 377.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{17}\text{H}_{22}\text{O}_8\text{Na}$ m/z 377.1212, found 377.1198.

Analysis: calcd. for $\text{C}_{17}\text{H}_{22}\text{O}_8 \cdot 0.1 \text{ C}_7\text{H}_{16}$ (354.13): C 58.34, H 6.53; found C 58.28, H 6.74.



A dry flask was charged with Pb(OAc)₄ (370 mg, 0.83 mmol) was vacuumed, flushed with argon and cooled to nearly 0°C. Then, it was suspended in dry toluene (0.5 mL) and a solution of diol **175** (50 mg, 0.21 mmol) in dry toluene (0.5 mL) was added dropwise at the same temperature. The mixture was stirred at r.t. for 15 h, diluted with Et₂O, filtered through a MgSO₄/Celite/SiO₂ pad and the filtrate concentrated. The residue was purified by silica gel chromatography using ethyl acetate-heptane, 1:3 as an eluent to give the product **199** (64 mg, 86%).

199: Acetic acid 3-acetoxy-5-methoxymethoxy-7-methyl-6-methylene-2,10-dioxatricyclo[5.3.1.0^{0,0}]undec-9-yl ester.



Mp: yellow oil.

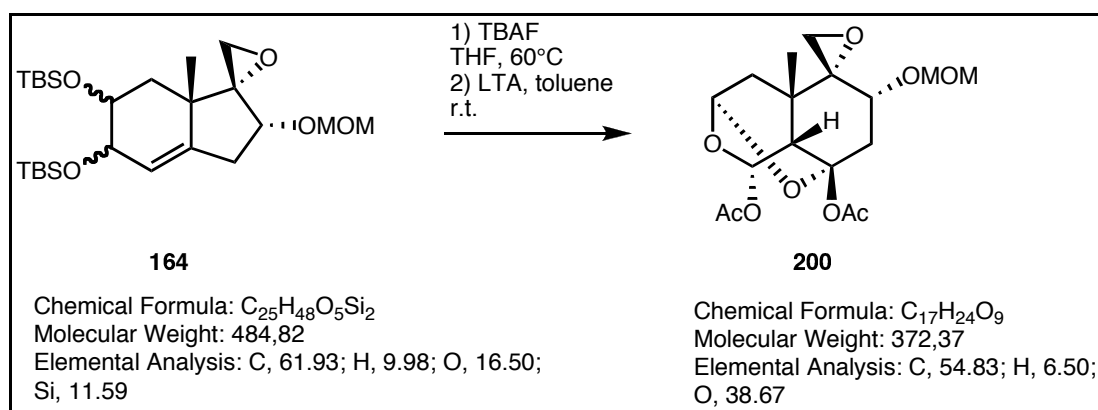
$[\alpha]_D^{20} = +14$ (*c* 0.5, CHCl₃).

IR (film): $\nu = 2939, 1730, 1369, 1248, 1229, 1213, 1168, 1075, 1022, 972$ cm⁻¹.

¹H NMR (500 MHz): $\delta = 1.47$ (s, 3 H, H12), 1.66 (d, *J* = 13.8 Hz, 1 H, H11), 2.10 (s, 3 H, Me-Ac), 2.11 (s, 3 H, Me-Ac), 2.22 (dd, *J* = 2.8, 14.3 Hz, 1 H, H4), 2.56 (dd, *J* = 2.6, 13.8 Hz, 1 H, H11), 2.75 (dd, *J* = 6.0, 14.3 Hz, 1 H, H4), 2.89 (s, 1 H, H8), 3.35 (s, 3 H, H15), 4.37 (dd, *J* = 2.9, 6.1 Hz, 1 H, H5), 4.55 and 4.66 (ABquartet, *J* = 6.8 Hz, 2 H, H14), 5.18 (s, 1 H, H13), 5.27 (s, 1 H, H13'), 5.31 (dd, *J* = 1.2, 2.8 Hz, 1 H, H1), 6.55 (d, *J* = 1.0 Hz, 1 H, H9).

^{13}C NMR (125 MHz): δ = 21.2 (Me-Ac), 22.5 (Me-Ac), 25.1 (C12), 34.8 (C7), 39.6 (C4), 40.8 (C8, C11), 55.4 (C15), 74.3 (C5), 90.7 (C9), 92.5 (C1), 93.0 (C14), 103.0 (C3), 115.9 (C13), 147.5 (C6), 169.5 (CO-Ac), 169.8 (CO-Ac).

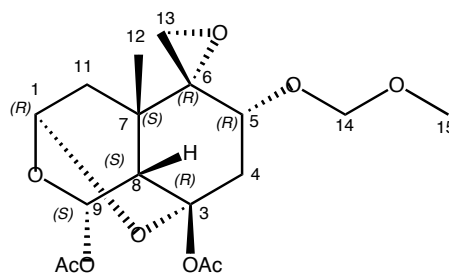
Analysis: calcd. for $\text{C}_{17}\text{H}_{24}\text{O}_8$ (356.14): C 57.30, H 6.79; found C 57.91, H 7.01.



TBAF (1.5 mL, 1M in THF) was added to **164** (180 mg, 0.37 mmol), at r.t. under Ar. The reaction mixture was stirred at 60°C for 3 h. Then the reaction mixture was diluted (at r.t.) with ethyl acetate (large amount) and worked up as usual. Flash chromatography (ethyl acetate/heptane 1:1) gives 85 mg (90%) of **176**.

A dry flask was charged with $\text{Pb}(\text{OAc})_4$ (1.12 g, 2.53 mmol) was vacuumed, flushed with argon and cooled to nearly 0°C. Then, it was suspended in dry toluene (1 mL) and a solution of diol **176** (128 mg, 0.5 mmol) in dry toluene (1 mL) was added dropwise at the same temperature. The mixture was stirred at r.t. for 15 h, diluted with Et_2O , filtered through a $\text{MgSO}_4/\text{Celite}/\text{SiO}_2$ pad and the filtrate concentrated. The residue was purified by silica gel chromatography using ethyl acetate-heptane, 1:2 as an eluent to give the product **200** (110 mg, 59%).

200:



Mp: 117°C.

$[\alpha]_D^{20} = -25$ (c 0.71, CHCl_3).

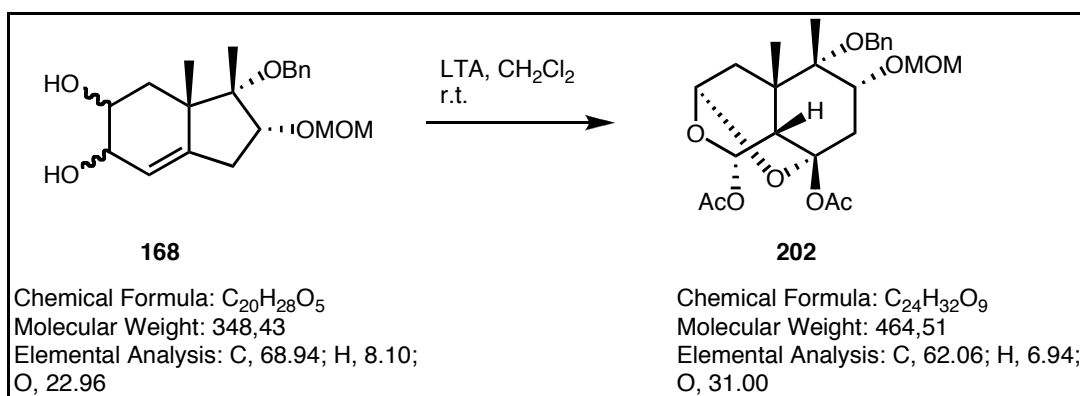
IR (film): $\nu = 2943, 1730, 1370, 1250, 1175, 1074, 1025, 976 \text{ cm}^{-1}$.

$^1\text{H NMR}$ (500 MHz, CDCl_3): $\delta = 1.15$ (s, 3 H, H12), 1.54 (dd, $J = 1.5, 14.0$ Hz, 1 H, H11), 2.12 (s, 3 H, Me-Ac), 2.14 (s, 3 H, Me-Ac), 2.32 (dd, $J = 2.0, 14.6$ Hz, 1 H, H4), 2.59 (d, $J = 4.3$ Hz, 1 H, H13), 2.76 (dd, $J = 5.1, 14.6$ Hz, 1 H, H4'), 2.96 (d, $J = 4.3$ Hz, 1 H, H13'), 3.07 (d, $J = 1.1$ Hz, 1 H, H8), 3.19 (dd, $J = 2.6, 14.0$ Hz, 1 H, H11'), 3.39 (s, 3 H, H15), 3.58 (dd, $J = 2.0, 5.1$ Hz, 1 H, H5), 4.66 and 4.74 (ABquartet, $J = 6.9$ Hz, 2 H, H14), 5.37 (dd, $J = 1.5, 2.6$ Hz, 1 H, H1), 6.50 (d, $J = 1.1$ Hz, 1 H, H9).

$^{13}\text{C NMR}$ (125 MHz, CDCl_3): $\delta = 21.3$ (C12, Me-Ac), 22.5 (Me-Ac), 33.6 (C7), 37.8 (C4), 38.4 (C11), 40.8 (C8), 50.7 (C13), 55.5 (C15), 60.6 (C6), 76.6 (C5), 90.5 (C9), 92.6 (C1), 96.1 (C14), 102.5 (C3), 169.5 (CO-Ac), 169.9 (CO-Ac).

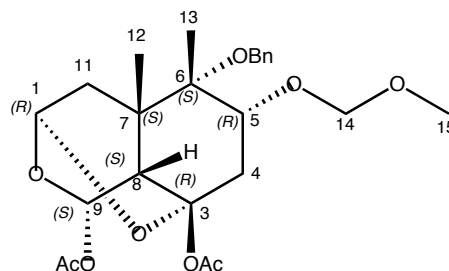
ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 395.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{17}\text{H}_{24}\text{O}_9\text{Na}$ m/z 395.1318, found 395.1322.

Analysis calcd. for $\text{C}_{17}\text{H}_{24}\text{O}_9 \cdot 0.1 \text{ H}_2\text{O}$ (372.37): C 55.60, H 6.75; found C 55.46, H 6.58.



A dry flask was charged with diol **168** (50 mg, 0.14 mmol) and $\text{Pb}(\text{OAc})_4$ (191 mg, 0.43 mmol, 3 eq.) vacuumed, flushed with argon and cooled to nearly 0°C . CH_2Cl_2 (0.8 mL) was added, the ice bath removed soon after and the mixture was stirred at room temperature for 5 h, diluted with ether, filtered through celite, the filtrate concentrated and purified by silica gel chromatography using ethyl acetate-heptane, 1:2 as an eluent to give **202** (46 mg, 70%).

202: Acetic acid 3-acetoxy-6-benzyloxy-5-methoxymethoxy-6,7-dimethyl-2,10-dioxatricyclo[5.3.1.0^{0,0}]undec-9-yl ester.



Mp: colourless oil.

$[\alpha]_D^{20} = -41$ (*c* 1.0, CHCl₃).

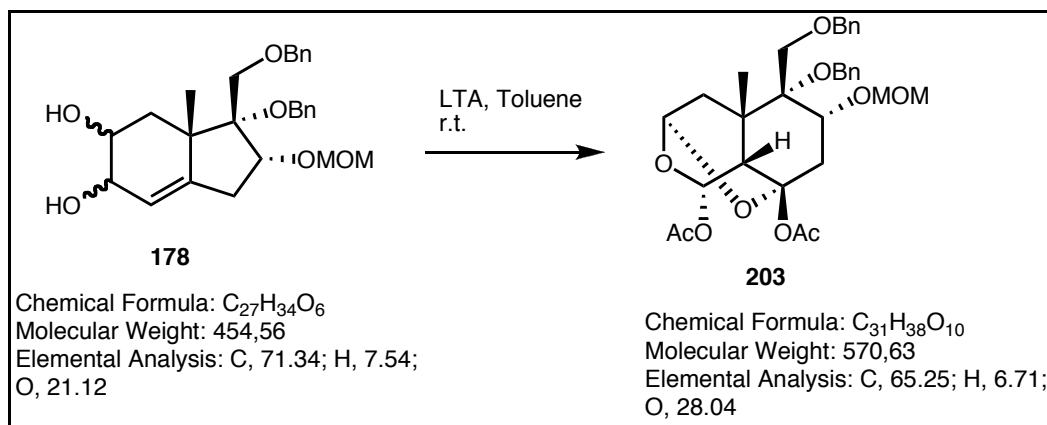
IR (film): $\nu = 2942, 1729, 1453, 1368, 1256, 1206, 1187, 1148, 1130, 1084, 1027, 998, 978 \text{ cm}^{-1}$.

¹H NMR (CDCl₃, 500 MHz): $\delta = 1.40$ (s, 1 H, H13), 1.41 (s, 3 H, H12), 1.40 - 1.43 (m, 1 H, H11), 2.11 (s, 3 H, Me-Ac), 2.13 (s, 3 H, Me-Ac), 2.36 (dd, *J* = 2.2, 15.1 Hz, 1 H, H4), 2.64 (dd, *J* = 2.2, 15.1 Hz, 1 H, H4), 3.14 (d, *J* = 1.4 Hz, 1 H, H8), 3.37 (s, 3 H, H15), 3.42 (dd, *J* = 2.6, 14.2 Hz, 1 H, H11), 4.04 (dd, *J* = 2.2, 4.2 Hz, 1 H, H5), 4.51 (s, 2 H, CH₂Ph), 4.60 and 4.74 (ABquartet, *J* = 6.7 Hz, 2 H, H14), 5.29 (dd, *J* = 4.3, 6.5 Hz, 1 H, H1), 6.51 (d, *J* = 1.4 Hz, 1 H, H9), 7.27 - 7.36 (m, 5 H, Ph).

¹³C NMR (CDCl₃, 125 MHz): $\delta = 18.5$ (C13), 21.2 (Me-Ac), 22.5 (Me-Ac), 22.8 (C12), 34.4 (C4), 37.3 (C11), 38.7 (C8), 39.0 (C7), 56.1 (C15), 63.0 (CH₂Ph), 77.1 (C6), 77.8 (C5), 91.0 (C9), 93.2 (C1), 96.8 (C14), 102.9 (C3), 126.7 (C-Ph), 127.1 (C-Ph), 128.2 (C-Ph), 139.2 (Cq-Ph), 169.6 (CO-Ac), 170.0 (CO-Ac).

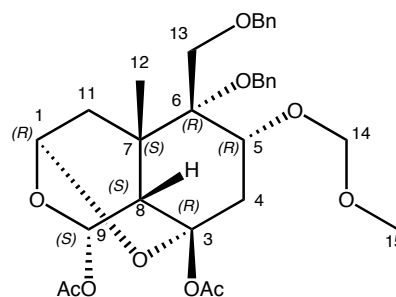
ESIMS (MeOH): 487.0 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₂₄H₃₂O₉Na *m/z* 487.1944, found 487.1922.

Analysis: calcd. for C₂₄H₃₂O₉ · 0.5 H₂O (464.2): C 60.88, H 7.02; found C 60.89, H 6.62.



A dry flask was charged with Pb(OAc)₄ (93 mg, 0.21 mmol, 3 eq.) was vacuumed, flushed with argon and cooled to nearly 0°C. Then, it was suspended in dry toluene (0.1 mL) and a solution of diol **178** (32 mg, 0.07 mmol) in dry toluene (0.3 mL) was added dropwise at the same temperature. The mixture was stirred at r.t. for 15 h, diluted with Et₂O, filtered through a MgSO₄/Celite/SiO₂ pad and the filtrate concentrated. The residue was purified by silica gel chromatography using ethyl acetate-heptane, 1:3 as an eluent to give the product **203** (24 mg, 60%).

203: Acetic acid 3-acetoxy-6-benzyloxy-6-benzyloxymethyl-5-methoxymethoxy-7-methyl-2,10-dioxo-tricyclo[5.3.1.0^{0,0}]undec-9-yl ester.

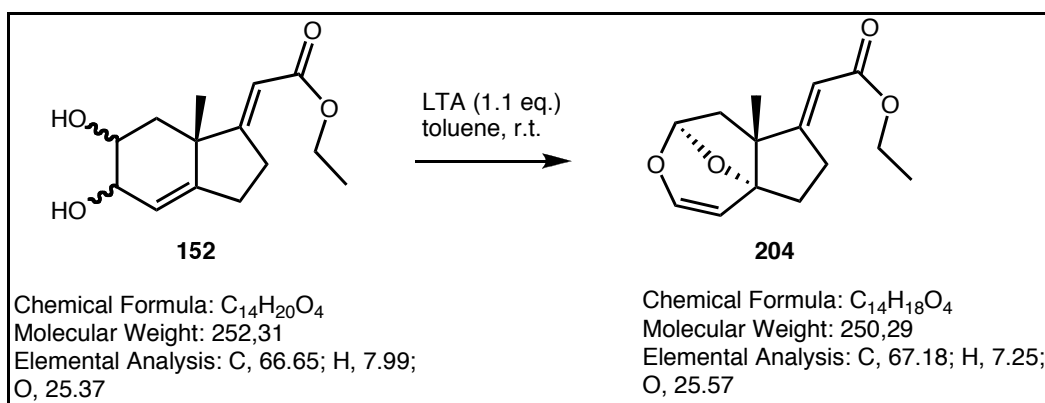


IR (film): $\nu = 2934, 1729, 1453, 1367, 1323, 1253, 1144, 1097, 1025, 974, 914, 733, 697 \text{ cm}^{-1}$.

¹H-NMR (CDCl₃, 300 MHz): $\delta = 1.33$ (s, 3 H, H12), 1.37 (dd, $J = 1.3, 14.6$ Hz, 1 H, H11), 2.10 (s, 3 H, Me-Ac), 2.13 (s, 3 H, Me-Ac), 2.41 (dd, $J = 2.4, 15.1$ Hz, 1 H, H4), 2.61 (dd, $J = 4.0, 15.1$ Hz, 1 H, H4'), 3.22 (d, $J = 1.1$ Hz, 1 H, H8), 3.39 (s, 3 H, H15), 3.48 (dd, $J = 2.7, 14.5$ Hz, 1 H, H11'), 3.83 (s, 2 H, H13), 4.49 and 4.56 (ABquartet, $J = 11.9$ Hz, 2 H, CH₂Ph), 4.62 - 4.75 (m, 5 H, H5, H14, CH₂Ph), 5.28 (dd, $J = 1.3, 2.7$ Hz, 1 H, H1), 6.46 (d, $J = 1.2$ Hz, 1 H, H9), 7.22 - 7.40 (m, 10 H, Ph).

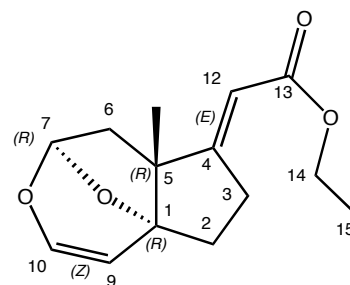
^{13}C -NMR (CDCl_3 , 75 MHz): $\delta = 21.3, 21.4$ (C12, Me-Ac), 22.6 (Me-Ac), 34.8 (C4), 38.3 (C11), 38.9 (C7), 39.1 (C8), 56.1 (C15), 65.6 (CH_2Ph), 72.5 (C13), 72.9 (C5), 73.8 (CH_2Ph), 78.4 (C6), 91.0 (C9), 93.1 (C1), 97.7 (C14), 102.9 (C3), 126.7, 127.0, 127.6, 127.8, 128.1, 128.5 (10C-Ph), 137.4 (Cq-Ph), 139.8 (Cq-Ph), 169.7 (CO-Ac), 169.9 (CO-Ac).

ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 593.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{31}\text{H}_{38}\text{O}_{10}\text{Na}$ m/z 593.2363, found 593.2371.



A dry flask was charged with unsaturated diols **152** (50 mg, 0.2 mmol, diastereomeric mixture) and $\text{Pb}(\text{OAc})_4$ (106 mg, 0.24 mmol, 1.1 eq.) vacuumed, flushed with argon and cooled to 0°C . Toluene (1 mL) was added, the cooling bath removed soon after and the reaction mixture was stirred for 15 h at room temperature, diluted with diethyl ether, filtered through $\text{MgSO}_4/\text{Celite}/\text{silica}$, the filtrate concentrated and purified by silica gel chromatography using diethyl ether-heptane, 1:1 as an eluent to give **204** (28 mg, 57%).

204: (5-Methyl-8,11-dioxo-tricyclo[5.3.1.0^{0,0}]undec-9-en-4-ylidene-acetic ethyl ester.



Mp: colourless oil.

$[\alpha]_D^{20} = +15$ (*c* 0.6, CHCl₃).

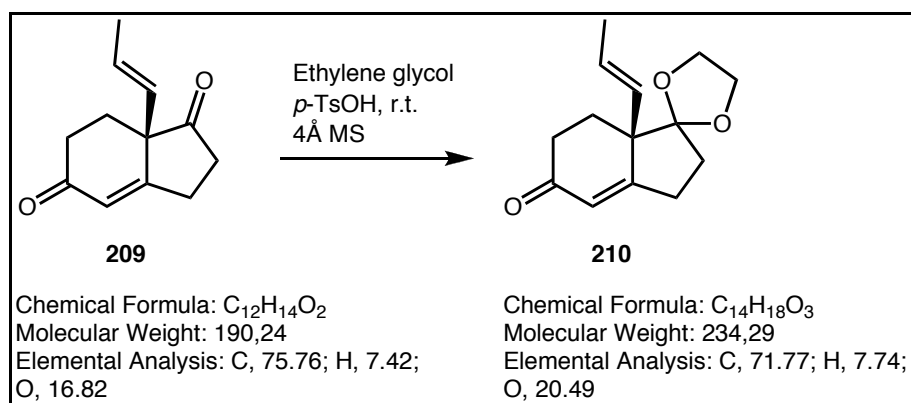
IR (film): $\nu = 2960, 1709, 1626, 1369, 1343, 1219, 1181, 1099, 1036, 948, 866$ cm⁻¹.

¹H-NMR (CDCl₃, 300 MHz): $\delta = 1.22$ (s, 3 H, H12), 1.27 (t, *J* = 7.1 Hz, 3 H, H16), 1.74 (dt, *J* = 10.0, 14.3 Hz, 1 H, H2), 2.26 (dt, *J* = 5.2, 14.3 Hz, 1 H, H2'), 2.37 (dd, *J* = 0.7, 13.9 Hz, 1 H, H6), 2.54 (dd, *J* = 5.2, 13.9 Hz, 1 H, H6'), 3.09 (dd, *J* = 2.6, 5.2 Hz, 1 H, H3), 3.12 (dd, *J* = 2.6, 5.2 Hz, 1 H, H3'), 4.14 (q, *J* = 7.1 Hz, 2 H, H15), 4.92 (d, *J* = 6.0 Hz, 1 H, H10), 5.60 (d, *J* = 5.2 Hz, 1 H, H7), 5.65 (t, *J* = 2.6 Hz, 1 H, H13), 6.29 (d, *J* = 6.0 Hz, 1 H, H9).

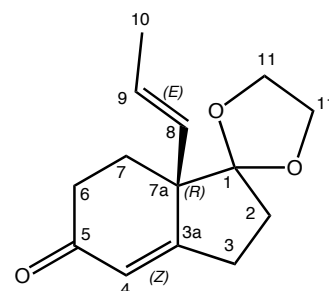
¹³C-NMR (CDCl₃, 75 MHz): $\delta = 14.4$ (C16), 22.1 (C12), 29.4 (C2), 30.4 (C3), 51.0 (C6), 59.8 (C15), 65.7 (C5), 91.8 (C1), 100.8 (C7), 104.4 (C10), 113.3 (C13), 141.6 (C9), 166.7 (C14), 175.4 (C4).

ESIMS (MeOH): 273.1 ($[M + Na]^+$, 20). HRESIMS: calcd. for C₁₄H₁₈O₄Na *m/z* 273.1103, found 273.1131.

Analysis calcd. for C₁₄H₁₈O₄ (250.29): C 67.18, H 7.25; found C 67.29, H 7.37.



209 (1.5 g, 7.8 mmol) was dissolved in ethylene glycol (37.5 mL). Molecular sieves (4Å) and *p*-TsOH (1.35 mg, 7.8 mmol, 1 eq.) were then added and the reaction mixture was refluxed at r.t. for 45 min. The reaction mixture was poured carefully into a mixture of ice+saturated aqueous NaHCO₃. This solution extracted with EtOAc. The organic layer worked up as usual to give 1.7 g (94%) of ketal **210**.

210:

Mp: colourless oil.

$[\alpha]_D^{20} = +27$ (c 1.03, CHCl_3).

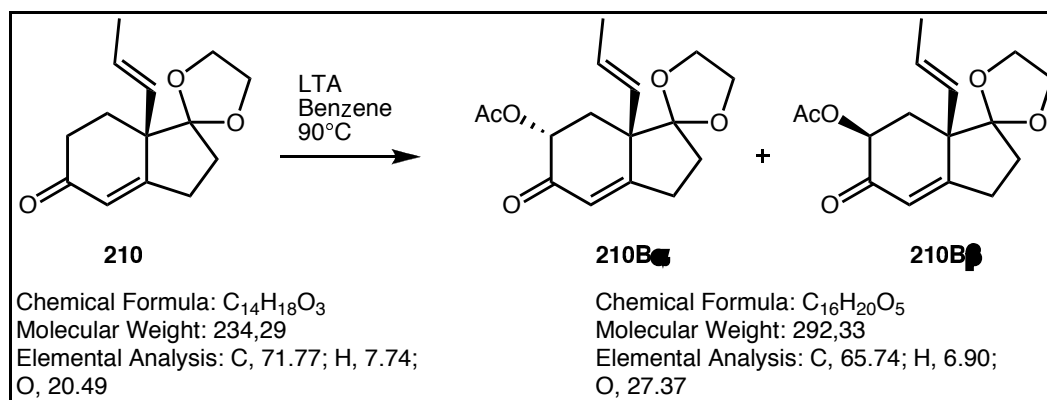
IR (film): $\nu = 2955, 2879, 1663, 1419, 1336, 1315, 1266, 1223, 1198, 1171, 1150, 1037, 972, 931, 897, 770 \text{ cm}^{-1}$.

$^1\text{H NMR}$ (CDCl_3 , 500 MHz): $\delta = 1.62$ (ddd, $J = 2.0, 4.9, 12.3 \text{ Hz}$, 1 H, H7) 1.70 (dd, $J = 1.4, 6.4 \text{ Hz}$, 3 H, H10), 1.77 (ddd, $J = 2.3, 8.3, 12.9 \text{ Hz}$, 1 H, H2), 2.02 (dt, $J = 10.5, 12.5 \text{ Hz}$, 1 H, H2'), 2.20 - 2.39 (m, 3 H, H7', H6), 2.46 - 2.59 (m, 2 H, H3), 3.95 - 3.99 (m, 4 H, H 11), 5.37 (dq, $J = 6.4, 15.7 \text{ Hz}$, 1 H, H9), 5.60 (dq, $J = 1.7, 15.7 \text{ Hz}$, 1 H, H8), 5.96 (s, 1 H, H4).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): $\delta = 18.0$ (C10), 25.7 (C7), 26.5 (C3), 31.6 (C2), 32.8 (C6), 54.8 (C7a), 64.7 (C11), 65.7 (C11), 117.0 (C1), 125.1 (C4), 127.6 (C9), 129.7 (C8), 170.1 (C3a), 199.5 (C5).

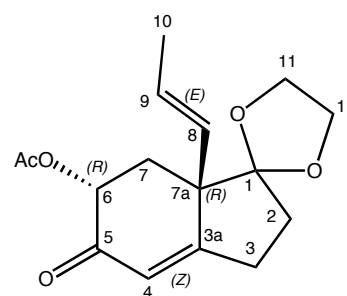
ESIMS (MeOH): 257.1 ($[M + H]^+$, 65). HRESIMS: calcd. for $\text{C}_{14}\text{H}_{19}\text{O}_3$ m/z 235.1312, found 235.1334.

Analysis: calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_3$ (234.13): C 71.77, H 7.74; found C 71.65, H 7.94.



A dry three-necked flask, equipped with a Dean-Stark apparatus was charged with **210** (300 mg, 1.2 mmol) and $\text{Pb}(\text{OAc})_4$ (2.27 g, 5.12 mmol, 4 eq.) vacuumed, flushed with argon before dry benzene (15 mL) was added and the reaction mixture was heated at 90°C (oil bath temperature should not exceed 100°C) for 4 days. After cooling a large volume of ether was added, and the reaction mixture stirred for an additional hour, filtered, and the filtrate washed with brine and water, dried on MgSO_4 , concentrated and purified by chromatography on silica with CH_2Cl_2 -Ether diethyl 30:1 as eluent afforded 298 mg (85%) of a mixture of **210B α** and **210B β** (1/1).

210B α :



Mp: 112-113°C.

$[\alpha]_D^{20} = +59$ (*c* 1.0, CHCl_3).

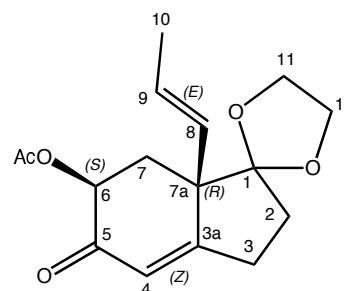
IR (film): $\nu = 2950, 1746, 1683, 1445, 1372, 1310, 1235, 1208, 1151, 1069, 1045, 976, 948, 902 \text{ cm}^{-1}$.

$^1\text{H NMR}$ (500 MHz): $\delta = 1.72$ (dd, $J = 1.5, 6.4$ Hz, 3 H, H10), 1.78 (ddd, $J = 2.1, 8.7, 13.1$ Hz, 1 H, H3), 1.92 (dd, $J = 5.3, 11.6$ Hz, 1 H, H7), 2.02 - 2.09 (m, 1 H, H3'), 2.13 (s, 3 H, Me-Ac), 2.37 (dd, $J = 11.7, 13.3$ Hz, 1 H, H7'), 2.46 - 2.53 (m, 1 H, H2), 2.56 - 2.63 (m, 1 H, H2'), 3.91 - 3.99 (m, 4 H, H11), 5.35 (dd, $J = 5.3, 13.4$ Hz, 1 H, H6), 5.44 (dq, $J = 6.4, 15.7$ Hz, 1 H, H9), 5.70 (dq, $J = 1.5, 15.7$ Hz, 1 H, H8), 6.01 (t, $J = 1.8$ Hz, 1 H, H4).

$^{13}\text{C NMR}$ (125 MHz): $\delta = 18.0$ (C10), 20.8 (Me-Ac), 26.5 (C2), 31.6 (C7), 32.1 (C3), 55.9 (C7a), 64.7, 65.8 (2C11), 71.1 (C6), 116.6 (C1), 123.9 (C4), 128.0 (C9), 129.5 (C8), 170.0, 170.1 (CO-Ac, C3a), 193.1 (C5).

ESIMS (MeOH): 315.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_5\text{Na}$ m/z 315.1208, found 315.1198.

Analysis: calcd. for $\text{C}_{16}\text{H}_{20}\text{O}_5$ (292.13): C 65.74, H 6.90; found C 65.26, H 7.04.

210B β :

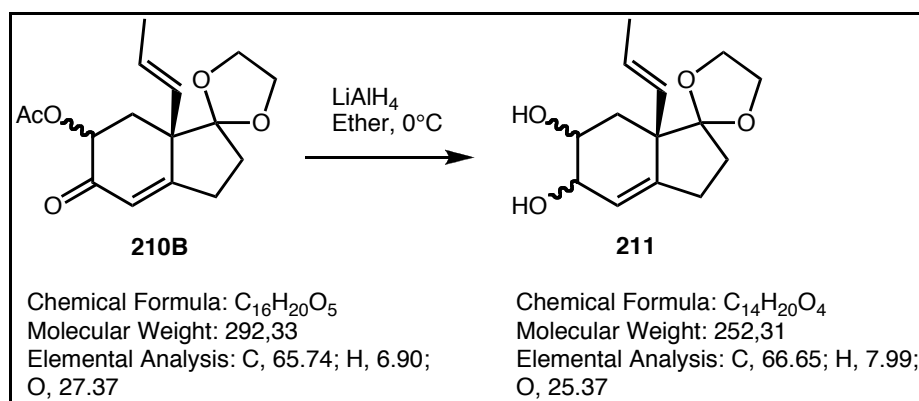
Mp: 57°C.

$[\alpha]_D^{20} = +36$ (*c* 0.9, CHCl₃).

IR (film): $\nu = 2953, 2878, 1739, 1675, 1641, 1440, 1370, 1310, 1229, 1152, 1035, 968, 948$ cm⁻¹.

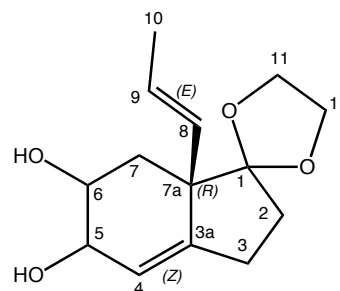
¹H NMR (500 MHz): $\delta = 1.68$ (dd, *J* = 1.6, 6.4 Hz, 3 H, H10), 1.77 (ddd, *J* = 2.0, 8.7, 13.0 Hz, 1 H, H3), 1.98 (s, 3 H, Me-Ac), 2.05 - 2.14 (m, 2 H, H3', H7), 2.38 (dd, *J* = 5.2, 14.7 Hz, 1 H, H7'), 2.52 - 2.60 (m, 1 H, H2), 2.63 - 2.70 (m, 1 H, H2'), 3.93 - 3.98 (m, 4 H, H11), 5.11 (dd, *J* = 2.3, 5.1 Hz, 1 H, H6), 5.33 (dq, *J* = 6.4, 15.7 Hz, 1 H, H9), 5.68 (dq, *J* = 1.5, 15.7 Hz, 1 H, H8), 6.12 (t, *J* = 1.4 Hz, 1 H, H4).

¹³C NMR (125 MHz): $\delta = 18.2$ (C10), 20.9 (Me-Ac), 27.1 (C2), 30.8 (C7), 31.2 (C3), 53.2 (C7a), 64.7, 65.8 (2C11), 70.2 (C6), 117.0 (C1), 124.1 (C4), 126.9 (C9), 132.7 (C8), 170.0 (CO-Ac), 172.0 (C3a), 192.8 (C5).



To a magnetically stirred suspension of LiAlH₄ (83 mg, 2.18 mmol, 4 eq.) in (1.5 mL) of anhydrous Et₂O, cooled to nearly 0°C, was added dropwise a solution of acetoxyenone **210B** (160 mg, 0.54 mmol) in anhydrous ether (1.5 mL). After stirring at this temperature for 30-40 min (TLC monitoring) the mixture was diluted with wet Et₂O and

treated with a small amount of 6N NaOH solution (for each 1 g of LiAlH_4 1 mL of water, 1 mL of 6N NaOH and 3 mL more water were added). The organic layer was worked up as usual to give, after silica gel chromatography (ethyl acetate-heptane, 4:1), 120 mg (98%) of the desired diols **211**.

211:

Mp: yellow oil.

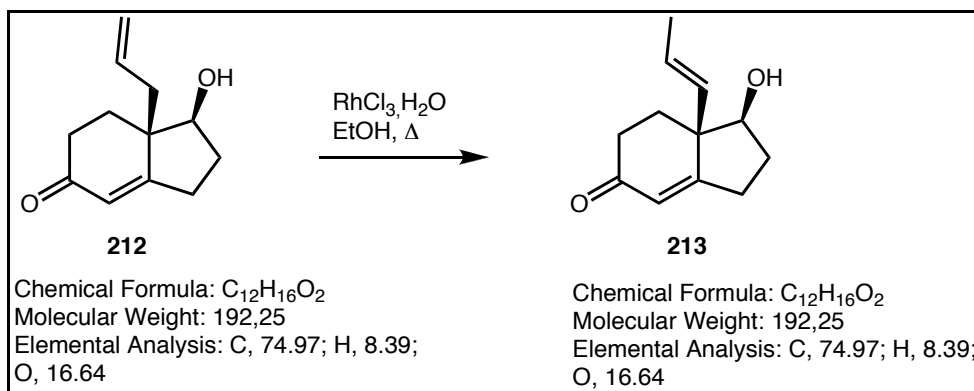
$[\alpha]_D^{20} = -61$ (*c* 1.8, CHCl_3).

IR (film): $\nu = 3403, 2939, 2880, 1441, 1306, 1252, 1155, 1035, 959, 914 \text{ cm}^{-1}$.

$^1\text{H NMR}$ (500 MHz): $\delta = 1.69$ (m, 1 H, H3), 1.71 (dd, $J = 1.4, 6.4$ Hz, 3 H, H10), 1.88 - 1.97 (m, 2 H, H3', H7), 2.05 (dd, $J = 3.0, 13.9$ Hz, 1 H, H7'), 2.28 (ddd, $J = 8.0, 9.5, 16.8$ Hz, 1 H, H2), 2.45 (ddd, $J = 2.5, 11.9, 16.8$ Hz, 1 H, H2'), 3.92 (m, 4 H, H11), 4.01 (dd, $J = 4.3, 8.5$ Hz, 1 H, H6), 4.16 (d, $J = 2.9$ Hz, 1 H, H5), 5.57 (dq, $J = 6.4, 15.8$ Hz, 1 H, H9), 5.66 (s, 1 H, H4), 5.86 (dd, $J = 1.4, 15.8$ Hz, 1 H, H8).

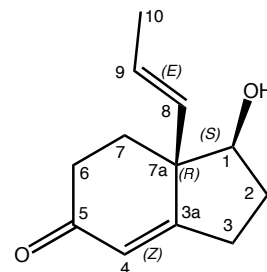
$^{13}\text{C NMR}$ (125 MHz): $\delta = 18.0$ (C10), 25.5 (C2), 31.3, 31.4 (C3, C7), 51.4 (C7a), 64.5, 65.6 (2C11), 68.6 (C5), 68.9 (C6), 117.1 (C1), 124.1 (C4), 126.4 (C9), 136.9 (C8), 143.0 (C3a).

ESIMS (MeOH): 275.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{14}\text{H}_{20}\text{O}_4\text{Na}$ m/z 275.1259, found 275.1244.



To a solution of **212** (5.96 g, 31.02 mmol, 1 eq.) in ethanol (220 mL), was added RhCl₃·3H₂O (324 mg, 1.55 mmol, 0.05 eq.). After refluxing the mixture for 1 h, the same amount of RhCl₃·3H₂O (324 mg, 1.55 mmol, 0.05 eq.) as above was added and the mixture was refluxed for one more hour. Evaporation under reduced pressure of the red solution gave an oil, which was diluted with diethyl ether (316 mL). The red suspension was stirred for 30 min at r.t. and then filtered. The supernatant was evaporated under reduced pressure to give 5.93 g of **213** (99%).

213: 1-Hydroxy-7a-propenyl-1,2,3,6,7,7a-hexahydro-inden-5-one.



Mp: 97°C.

$[\alpha]_D^{20} = +120$ (c 1.1, CHCl₃).

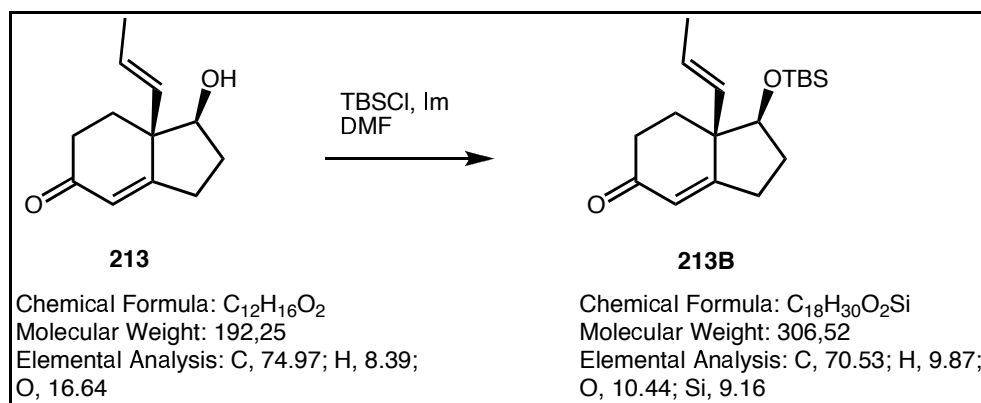
IR (film): $\nu = 3406, 2941, 1650, 1447, 1339, 1215, 1100, 976, 882 \text{ cm}^{-1}$.

¹H NMR (CDCl₃, 300 MHz): $\delta = 1.66$ (dt, $J = 1.3, 10.9$ Hz, 1 H, H2), 1.68 (dd, $J = 1.1, 6.1$ Hz, 3 H, H10), 1.80 (dd, $J = 4.6, 13.5$ Hz, 1 H, H7), 1.96 - 2.07 (m, 1 H, H2), 2.15 - 2.25 (m, 2 H, H6, H7), 2.26 - 2.35 (m, 1 H, H3), 2.36 - 2.45 (m, 1 H, H6'), 2.60 (dd, $J = 11.1, 19.6$ Hz, 1 H, H3'), 3.76 - 3.86 (m, 1 H, H1), 5.36 (qd, $J = 6.1, 15.8$ Hz, 1 H, H9), 5.50 (dd, $J = 1.1, 15.8$ Hz, 1 H, H8), 5.86 (s, 1 H, H4).

¹³C NMR (CDCl₃, 125 MHz): $\delta = 18.3$ (C10), 26.5 (C3), 29.7 (C2), 32.5 (C7), 33.4 (C6), 52.3 (C7a), 80.6 (C1), 125.1 (C4), 126.7 (C8), 129.2 (C9), 171.3 (C3a), 199.9 (C5).

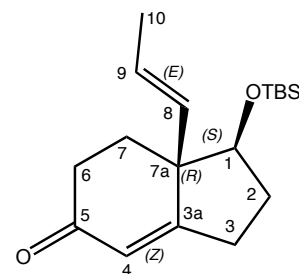
ESIMS (MeOH): 215.1 ($[M + Na]^+$, 100). HRESIMS: calcd. for $C_{12}H_{16}O_2Na$ m/z 215.1048, found 215.1094.

Analysis calcd. for $C_{12}H_{16}O_2 \cdot 0.35 H_2O$ (192.25): C 72.59, H 8.48; found C 72.46, H 8.24.



tert-butyldimethylsilyl chloride (9.28 g, 61.58 mmol, 3.2 equiv) was added to a solution of imidazole (8.38 g, 123.17 mmol, 6.4 eq.) and **213** (3.70 g, 19.24 mmol) in DMF (40 mL) at 0°C. The reaction mixture was allowed to warm to room temperature and stirred for 15 h (TLC monitoring). After cooling again at 0°C, extraction with methylene chloride, washing with 1N HCl and saturated $NaHCO_3$, the organic layer was worked up as usual and the residue was chromatographed (eluent heptane-EtOAc 9:1) to give **213B** (5.3 g, 90%).

213B: 1-(*tert*-Butyl-dimethyl-silyloxy)-7a-propenyl-1,2,3,6,7,7a-hexahydro-inden-5-one.



Mp: colourless oil.

$[\alpha]_D^{20} = +79$ (c 1.01, $CHCl_3$).

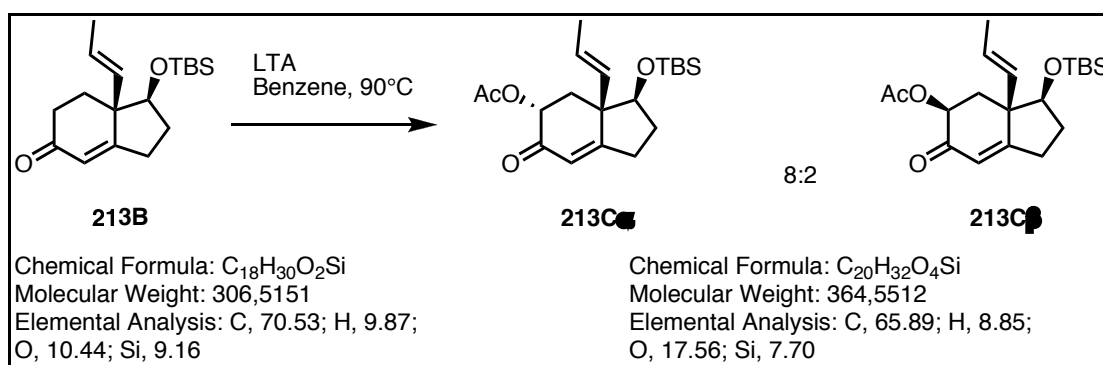
IR (film): $\nu = 2952, 2930, 2856, 1672, 1471, 1462, 1257, 1209, 1127, 976, 909, 871, 854, 836$ cm^{-1} .

^1H NMR (CDCl_3 , 500 MHz): $\delta = -0.15$ (s, 3 H, SiMe), -0.12 (s, 3 H, SiMe), 0.86 (s, 9 H, Si*t*Bu), $1.60 - 1.67$ (m, 1 H, H2), 1.65 (dd, $J = 1.5, 6.4$ Hz, 3 H, H10), $1.70 - 1.75$ (m, 1 H, H7), $1.78 - 1.85$ (m, 1 H, H2'), $2.00 - 2.05$ (m, 1 H, H7'), $2.18 - 2.25$ (m, 1 H, H6), 2.28 (dd, $J = 10.4, 19.9$ Hz, 1 H, H3), $2.32 - 2.40$ (m, 1 H, H6'), 2.51 (dd, $J = 10.9, 12.5$ Hz, 1 H, H3'), 3.68 (dd, $J = 6.7, 10.6$ Hz, 1 H, H1), 5.33 (qd, $J = 6.4, 15.8$ Hz, 1 H, H9), 5.60 (qd, $J = 1.5, 15.8$ Hz, 1 H, H8), 5.93 (s, 1 H, H4).

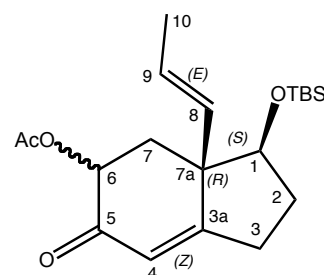
^{13}C -NMR (CDCl_3 , 125 MHz): $\delta = -4.8$ (SiMe), -4.4 (SiMe), 18.0 (Cq-Si*t*Bu), 18.2 (C10), 25.7 (3C-Si*t*Bu), 26.4 (C3), 29.8 (C2), 32.7 (C7), 33.2 (C6), 52.6 (C7a), 80.9 (C1), 125.1 (C4), $127.4, 127.5$ (C8, C9), 171.0 (C3a), 200.0 (C5).

ESIMS (MeOH): 329.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{18}\text{H}_{30}\text{O}_2\text{SiNa}$ m/z 329.1913 , found 329.1903 .

Analysis calcd. for $\text{C}_{18}\text{H}_{30}\text{O}_2\text{Si}$ (306.52): C 70.53, H 9.87; found C 70.04, H 9.81.



A dry three-necked flask, equipped with a Dean-Stark apparatus was charged with **213B** (3.7 g, 12.08 mmol) and $\text{Pb}(\text{OAc})_4$ (53.5 g, 120.83 mmol, 10 eq.) vacuumed, flushed with argon before dry benzene (145 mL) was added and the reaction mixture was heated at 90°C (oil bath temperature should not exceed 100°C) for 4 days. After cooling a large volume of ether was added, and the reaction mixture stirred for an additional hour, filtered, and the filtrate washed with brine and water, dried on MgSO_4 , concentrated and purified by chromatography on silica with heptane-diethyl ether 1:1 as eluent afforded 3.50 g (80%) of a mixture of **213C α** and **213C β** (8/2).

213C:

Mp: characterized as a diastereomeric mixture.

$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

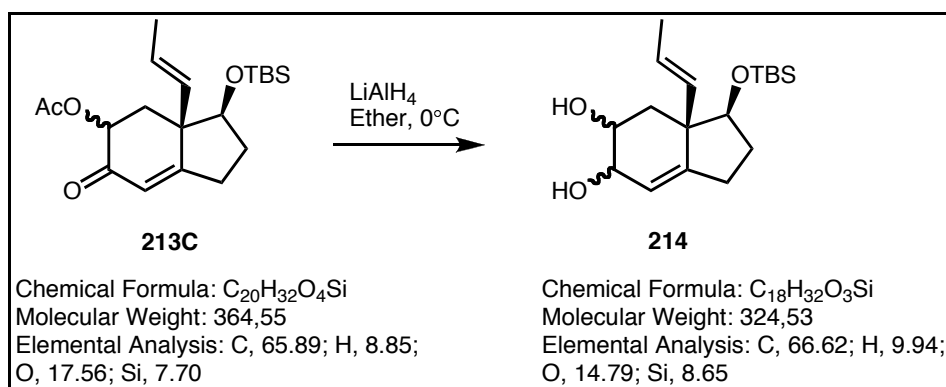
IR (film): ν = 2928, 2855, 1746, 1691, 1681, 1643, 1471, 1370, 1232, 1206, 1133, 1107, 1061, 1005, 974, 910, 857, 835, 775, 670 cm^{-1} .

^1H NMR (CDCl_3 , 500 MHz): δ = characterized as a diastereomeric mixture.

^{13}C NMR (CDCl_3 , 125 MHz): δ = characterized as a diastereomeric mixture.

ESIMS (MeOH): 387.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{20}\text{H}_{32}\text{O}_4\text{SiNa}$ m/z 387.1968, found 387.1955.

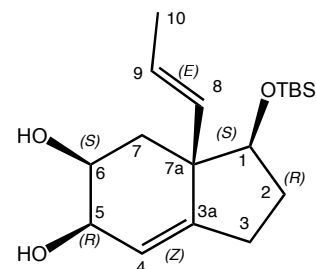
Analysis calcd. for $\text{C}_{20}\text{H}_{32}\text{O}_4\text{Si}$ (364.55): C 65.89, H 8.85; found C 65.44, H 8.77.



To a magnetically stirred suspension of LiAlH_4 (85.7mg, 2.26 mmol, 4 eq.) in (1.4 mL) of anhydrous Et_2O , cooled to nearly 0°C , was added dropwise a solution of acetoxyenone **213C** (214 mg, 0.56 mmol) in anhydrous ether (1.4 mL). After stirring at this temperature for 30-40 min (TLC monitoring) the mixture was diluted with wet Et_2O and treated with a small amount of 6N NaOH solution (for each 1 g of LiAlH_4 1 mL of water, 1 mL of 6N NaOH and 3 mL more water were added). The organic layer was

worked up as usual to give, after silica gel chromatography (ethyl acetate-heptane, 4:1), 98% (178 mg) of the desired diols **214**.

214a: 3-(tert-Butyl-dimethyl-silanyloxy)-3a-propenyl-2,3,3a,4,5,6-hexahydro-1*H*-inden-5,6-diol.



Mp: 67-68°C.

$[\alpha]_D^{20} = -36$ (*c* 1.7, CHCl₃).

IR (film): $\nu = 3392, 2954, 2928, 2855, 1471, 1433, 1360, 1249, 1129, 1104, 1052, 972, 863, 836, 774$ cm⁻¹.

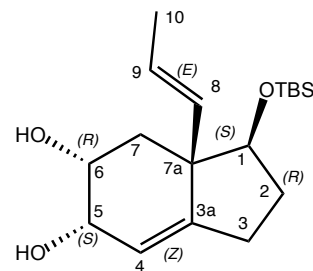
¹H NMR (CDCl₃, 500 MHz): $\delta = 0.00$ (s, 3 H, SiMe), 0.02 (s, 3 H, SiMe), 0.85 (s, 9 H, Si*t*Bu), 1.42 - 1.51 (m, 2 H, H2, H7), 1.67 (dd, *J* = 1.4, 6.3 Hz, 3 H, H10), 1.70 - 1.76 (m, 1 H, H2), 2.07 (dt, *J* = 8.6, 8.6 Hz, 1 H, H3), 2.34 - 2.41 (m, 1 H, H3), 2.35 (dd, *J* = 4.4, 14.1 Hz, 1 H, H7), 2.70 (d, *J* = 9.8 Hz, 1 H, OH6), 2.84 (d, *J* = 9.5 Hz, 1 H, OH5), 3.55 (dd, *J* = 7.1, 10.2 Hz, 1 H, H1), 3.91 - 3.96 (m, 1 H, H6), 4.04 - 4.09 (m, 1 H, H5), 5.46 (qd, *J* = 6.4, 16.0 Hz, 1 H, H9), 5.52 (s, 1 H, H4), 5.81 (dd, *J* = 1.4, 16.0 Hz, 1 H, H8).

¹³C-NMR (CDCl₃, 125 MHz): $\delta = -4.9$ (SiMe), -4.5 (SiMe), 17.9 (Cq-Si*t*Bu), 18.1 (C10), 25.5 (C3), 25.6 (3C-Si*t*Bu), 29.2 (C2), 36.1 (C7), 53.7 (C7a), 66.3 (C5), 67.3 (C6), 81.1 (C1), 121.3 (C4), 126.1 (C9), 130.4 (C8), 147.9 (C3a).

ESIMS (MeOH): 347.3 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₁₈H₃₂O₃NaSi *m/z* 347.2018, found 347.1996.

Analysis calcd. for C₁₈H₃₂O₃Si (364.207): C 66.62, H 9.94; found C 66.76, H 10.09.

214b: 3-(tert-Butyl-dimethyl-silanyloxy)-3a-propenyl-2,3,3a,4,5,6-hexahydro-1*H*-inden-5,6-diol.



Mp: 167-168°C.

$[\alpha]_D^{20} = +66$ (c 1.2, CHCl_3).

IR (film): $\nu = 3293, 2929, 2855, 1455, 1434, 1387, 1250, 1122, 1109, 1007, 978, 933, 862, 837, 775 \text{ cm}^{-1}$.

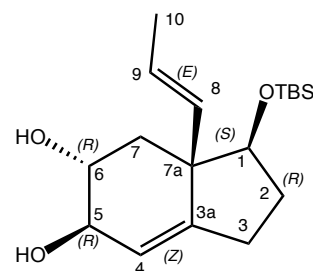
^1H NMR (CDCl_3 , 500 MHz): $\delta = 0.02$ (s, 3 H, SiMe), 0.05 (s, 3 H, SiMe), 0.90 (s, 9 H, Si*t*Bu), 1.22 - 1.33 (m, 1 H, H7), 1.55 (m, 1 H, H2), 1.67 (dd, $J = 1.5, 6.4$ Hz, 3 H, H10), 1.68 - 1.73 (m, 1 H, H2), 1.81 (dd, $J = 3.5, 11.7$ Hz, 1 H, H7), 2.15 (m, 1 H, H3), 2.34 (m, 1 H, H3), 3.65 (dd, $J = 7.1, 10.3$ Hz, 1 H, H1), 3.78 (td, $J = 3.7, 12.4$ Hz, 1 H, H6), 4.07 (m, 1 H, H5), 5.18 (qd, $J = 6.4, 15.7$ Hz, 1 H, H9), 5.59 (dd, $J = 1.5, 15.7$ Hz, 1 H, H8), 5.70 (m, 1 H, H4).

^{13}C -NMR (CDCl_3 , 125 MHz): $\delta = -4.8$ (SiMe), -4.4 (SiMe), 18.0 (Cq-Si*t*Bu), 18.1 (C10), 25.5 (C3), 25.8 (3C-Si*t*Bu), 30.0 (C2), 36.1 (C7), 53.6 (C7a), 66.3 (C5), 67.2 (C6), 81.1 (C1), 121.2 (C4), 126.0 (C9), 130.3 (C8), 147.8 (C3a).

ESIMS (MeOH): 347.3 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{18}\text{H}_{32}\text{O}_3\text{NaSi}$ m/z 347.2018, found 347.2003.

Analysis calcd. for $\text{C}_{18}\text{H}_{32}\text{O}_3\text{Si} \cdot 0.15 \text{ H}_2\text{O}$ (364.21): C 66.07, H 9.95; found C 66.05, H 10.25.

214c: 3-(tert-Butyl-dimethyl-silanyloxy)-3a-propenyl-2,3,3a,4,5,6-hexahydro-1*H*-inden-5,6-diol.



Mp: 123-124°C.

$[\alpha]_D^{20} = +16$ (*c* 1.04, CHCl₃).

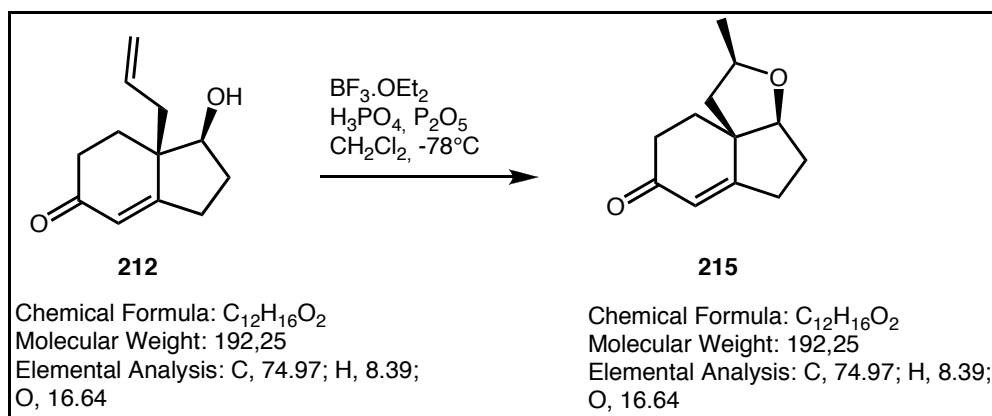
IR (film): $\nu = 3262, 2951, 2928, 2857, 1462, 1372, 1255, 1131, 1106, 1077, 1039, 975, 916, 864, 834, 774 \text{ cm}^{-1}$.

¹H NMR (CDCl₃, 500 MHz): $\delta = 0.00$ (s, 3 H, SiMe), 0.03 (s, 3 H, SiMe), 0.88 (s, 9 H, Si*t*Bu), 1.34 (t, *J* = 12.1 Hz, 1 H, H7), 1.52 -1.56 (m, 1 H, H2), 1.67 (dd, *J* = 1.4, 6.4 Hz, 3 H, H10), 1.73 - 1.76 (m, 1 H, H2'), 1.90 (dd, *J* = 3.4, 12.1 Hz, 1 H, H7'), 1.97 - 2.03 (m, 1 H, H3), 2.26 - 2.31 (m, 1 H, H3'), 3.57 (dd, *J* = 7.1, 10.2 Hz, 1 H, H1), 3.63 (bs, 1 H, OH), 3.64 - 3.69 (m, 1 H, H6), 3.77 (bs, 1 H, OH), 4.02 (bs, 1 H, H5), 5.29 (qd, *J* = 6.4, 15.7 Hz, 1 H, H9), 5.39 (s, 1 H, H4), 5.60 (dd, *J* = 1.4, 15.7 Hz, 1 H, H8).

¹³C-NMR (CDCl₃, 125 MHz): $\delta = -4.8$ (SiMe), -4.4 (SiMe), 18.0 (C_q-Si*t*Bu), 18.2 (C10), 24.9 (C3), 25.7 (3C-Si*t*Bu), 30.4 (C2), 39.9 (C7), 53.0 (C7a), 71.3 (C6), 75.0 (C5), 81.0 (C1), 122.6 (C4), 126.8 (C9), 130.7 (C8), 144.7 (C3a).

ESIMS (MeOH): 347.2 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₁₈H₃₂O₃NaSi *m/z* 347.2018, found 347.1994.

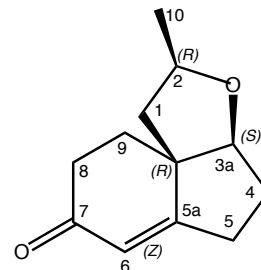
Analysis calcd. for C₁₈H₃₂O₃Si (364.207): C 66.62, H 9.94; found C 66.37, H 9.99.



A CH₂Cl₂ solution (5.8 mL) of **212** (910 mg, 4.73 mmol) was stirred and cooled at -78°C. To this was added 0.11 mL of H₃PO₄ (prepared by dissolving 480 mg of P₂O₅ in 1.32 mL of 84% H₃PO₄) and 0.23 mL of boron trifluoride etherate. The mixture was stirred for 1.5 h at -78°C and then for 2 days at room temperature. The mixture was then poured into 7 mL of 2N NH₄OH solution and the product was extracted with CH₂Cl₂, then the

solvent was evaporated under reduce pressure to give 646 mg (71%) of **215** (21% of SM recovered).

215: 2-Methyl-1,2,4,5,8,9-hexahydro-3a*H*-3-oxa-cyclopenta[*c*]inden-7-one.



Mp: yellow oil.

$[\alpha]_D^{20} = +163$ (*c* 1.81, CHCl₃).

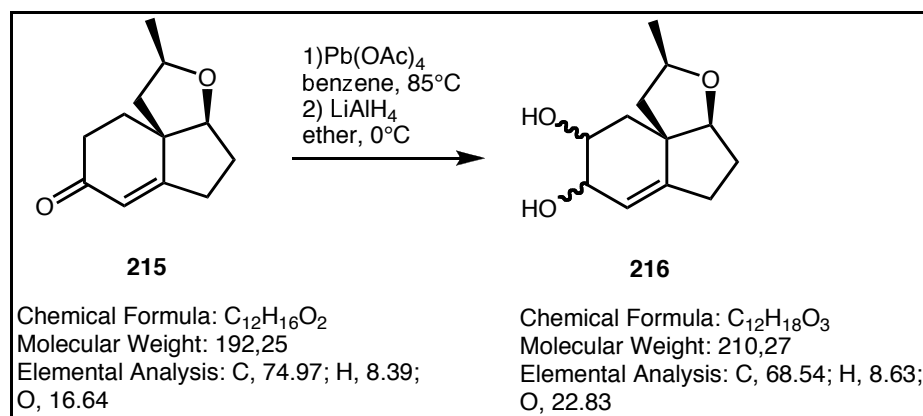
IR (film): $\nu = 2967, 2926, 2868, 1669, 1445, 1385, 1353, 1213, 1167, 1106, 1053, 961, 948, 908, 871, 850 \text{ cm}^{-1}$.

¹H-NMR (CDCl₃, 500 MHz): $\delta = 1.19$ (dd, *J* = 1.5, 5.9 Hz, 3 H, H10), 1.22 (dd, *J* = 4.5, 12.2 Hz, 1 H, H1), 1.54 (tdd, *J* = 1.1, 6.7, 13.4 Hz, 1 H, H4), 1.73 (tdd, *J* = 1.5, 5.8, 12.9 Hz, 1 H, H9), 1.89 (dd, *J* = 8.1, 13.7 Hz, 1 H, H4'), 2.01 (ddd, *J* = 2.3, 4.8, 13.0 Hz, 1 H, H9'), 2.16 (dd, *J* = 4.2, 12.3 Hz, 1 H, H1'), 2.23 (dd, *J* = 6.8, 15.0 Hz, 1 H, H5), 2.30 - 2.44 (m, 2 H, H8), 2.61 - 2.70 (m, 1 H, H5'), 3.79 - 3.85 (m, 1 H, H2), 3.97 (d, *J* = 5.7 Hz, 1 H, H3a), 5.66 (s, 1 H, H6)

¹³C-NMR (CDCl₃, 125 MHz): $\delta = 19.7$ (C10), 30.4 (C4), 31.3 (C5), 32.8 (C9), 35.5 (C8), 44.9 (C1), 53.7 (C9a), 75.6 (C2), 88.9 (C3a), 121.0 (C6), 174.8 (C5a), 199.3 (C7).

ESIMS (MeOH): 215.1 ($[M + Na]^+$, 55). HRESIMS: calcd. for C₁₂H₁₆O₂Na *m/z* 215.1048; found 215.1015.

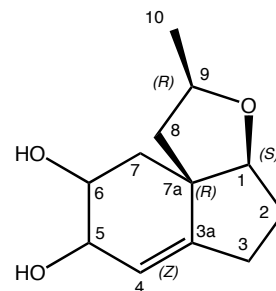
Analysis calcd. for C₁₂H₁₆O₂ · 0.25 H₂O (192.3): C 73.25, H 8.45; found C 73.25, H 8.33.



A dry three-necked flask, equipped with a Dean-Stark apparatus was charged with **215** (922 gm, 4.7 mmol) and $\text{Pb}(\text{OAc})_4$ (12.5 g, 28.2 mmol) vacuumed, flushed with argon before dry benzene (57 mL) was added and the reaction mixture was heated at 90°C (oil bath temperature should not exceed 100°C) for 4 days. After cooling a large volume of ether was added, and the reaction mixture stirred for an additional hour, filtered, and the filtrate washed with brine and water, dried on MgSO_4 , concentrated and purified by chromatography on silica with heptane- diethyl ether 1:1 as eluent afforded 624 mg (55%) of a mixture of product **215B**, which were directly used in the next step.

To a magnetically stirred suspension of LiAlH_4 (133 mg, 3.51 mmol) in (3 mL) of anhydrous Et_2O , cooled to nearly 0°C, was added dropwise a solution of acetoxyenone **215B** (220 mg, 0.88 mmol) in anhydrous ether (2 mL). After stirring at this temperature for 30-40 min (TLC monitoring) the mixture was diluted with wet Et_2O and treated with a small amount of 6N NaOH solution (for each 1 g of LiAlH_4 1 mL of water, 1 mL of 6N NaOH and 3 mL more water were added). The organic layer was worked up as usual to give, after silica gel chromatography (ethyl acetate-heptane, 4:1), 82% of the desired diols **216** (150 mg).

216: 2-Methyl-1,2,3a,4,5,7,8,9-octahydro-3-oxa-cyclopenta[*c*]indene-7,8-diol.



Mp: yellow oil.

$[\alpha]_D^{20} = +34$ (*c* 0.5, CHCl_3).

IR (film): 3400, 2962, 2924, 1434, 1384, 1278, 1172, 1103, 1046, 1028, 995, 970, 946 cm^{-1} .

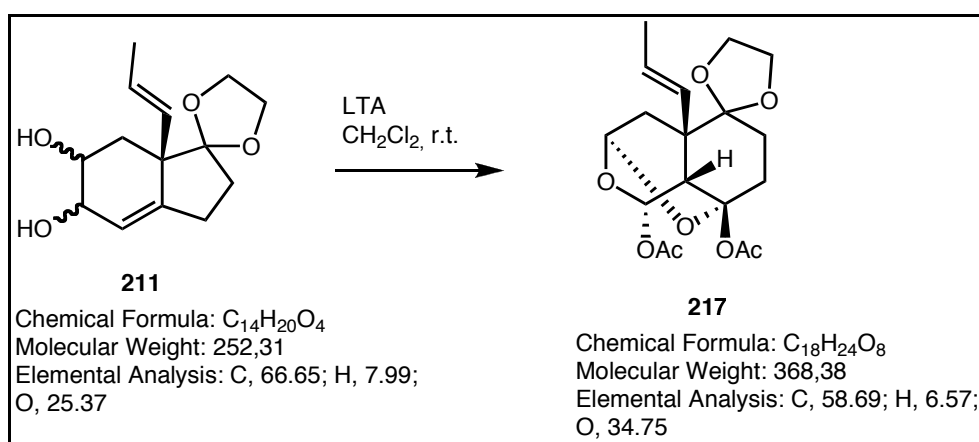
^1H NMR (CDCl_3 , 300 MHz): $\delta = 1.24$ (dd, $J = 5.9$ Hz, 3 H, H10), 1.29 - 1.33 (m, 1 H, H8), 1.48 (ddd, $J = 1.3, 2.5, 11.3$ Hz, 1 H, H2), 1.52 - 1.56 (m, 1 H, H7) 1.78 (dd, $J = 7.6, 13.4$ Hz, 1 H, H2'), 2.03 (dd, $J = 7.0, 14.0$ Hz, 1 H, H3), 2.32 (dd, $J = 3.9, 14.0$ Hz, 1 H, H7'), 2.44 - 2.56 (m, 1 H, H3'), 2.62 (dd, $J = 4.1, 12.5$ Hz, 1 H, H8'), 3.87 (ddd, $J = 4.1,$

5.9, 11.0 Hz, 1 H, H9), 3.94 (d, $J = 6.3$ Hz, 1 H, H1), 4.10 (m, 1 H, H6), 4.22 (m, 1 H, H5), 5.27 (t, $J = 1.4$ Hz, 1 H, H4).

^{13}C NMR (CDCl_3 , 125 MHz): $\delta = 19.5$ (C10), 29.6 (C3), 31.3 (C2), 37.4 (C7), 47.5 (C8), 49.7 (C7a), 67.8 (C6), 68.6 (C5), 75.3 (C9), 89.7 (C1), 117.4 (C4), 150.1 (C3a).

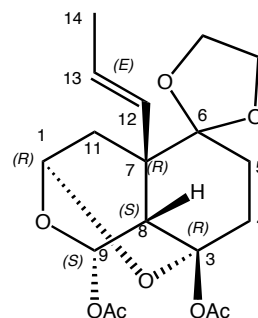
ESIMS (MeOH): 233.1 ($[M + \text{Na}]^+$, 56). HRESIMS: calcd. for $\text{C}_{12}\text{H}_{18}\text{O}_3\text{Na}$ m/z 233.1254, found 233.1159.

Analysis: calcd. for $\text{C}_{12}\text{H}_{18}\text{O}_3 \cdot 0.25 \text{ C}_7\text{H}_{16}$ (210.12): C 70.18, H 9.42; found C 70.11, H 9.64.



A dry flask was charged with diol **211** (35 mg, 0.138 mmol) and $\text{Pb}(\text{OAc})_4$ (246 mg, 0.554 mmol, 4 eq.) vacuumed, flushed with argon and cooled to nearly 0°C . CH_2Cl_2 (1 mL) was added, the ice bath removed soon after and the mixture was stirred at room temperature for 5 h, diluted with ether, filtered through celite, the filtrate concentrated and purified by silica gel chromatography using ethyl acetate-heptane, 1:3 as an eluent to give **217** (30 mg, 0.08 mmol, 66%).

217:



Mp: yellow oil.

$[\alpha]_D^{20} = -28$ (*c* 1.4, CHCl₃).

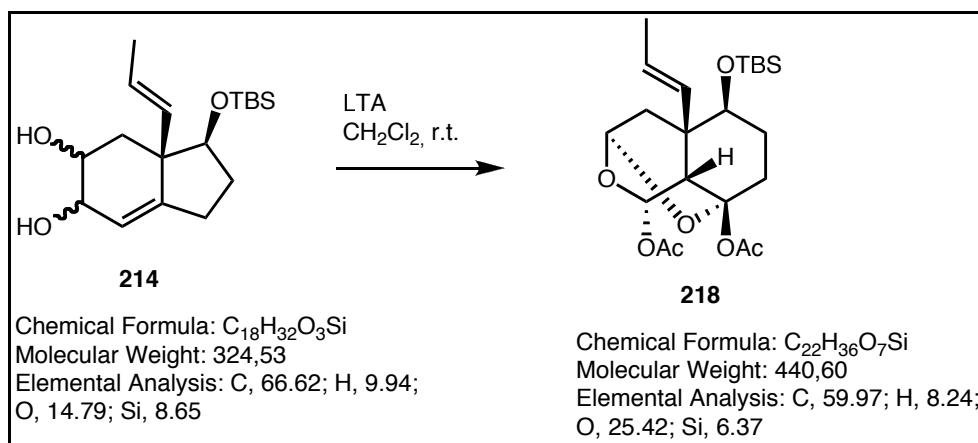
IR (film): $\nu = 2961, 2888, 1736, 1444, 1368, 1254, 1224, 1193, 1160, 1083, 1026, 994, 960$ cm⁻¹.

¹H-NMR (CDCl₃, 500 MHz): $\delta = 1.64$ (ddd, *J* = 2.0, 4.8, 13.7 Hz, 1 H, H5), 1.74 (dd, *J* = 1.5, 6.3 Hz, 3 H, H14), 1.82 (ddd, *J* = 2.0, 5.0, 13.1 Hz, 1 H, H4), 1.98 (td, *J* = 5.3, 13.7 Hz, 1 H, H5'), 2.07 (s, 3 H, Me-Ac), 2.10 (s, 3 H, Me-Ac), 2.08 - 2.13 (m, 2 H, H11), 2.60 (td, *J* = 4.8, 13.3 Hz, 1 H, H4'), 3.29 (s, 1 H, H8), 3.86 - 3.93 (m, 4 H, H15), 5.33 (t, *J* = 6.4, 15.8 Hz, 1 H, H1), 5.46 (dd, *J* = 1.5, 15.8 Hz, 1 H, H12), 5.67 (dq, *J* = 6.4, 15.8 Hz, 1 H, H13), 6.18 (s, 1 H, H9).

¹³C NMR (CDCl₃, 125 MHz): $\delta = 17.4$ (C14), 20.2 (Me-Ac), 21.5 (Me-Ac), 28.3 (C5), 29.7 (C4), 34.7 (C11), 37.2 (C8), 43.7 (C7), 64.7, 64.8 (C15, C15'), 90.4 (C9), 91.6 (C1), 102.1 (C3), 109.4 (C6), 128.2 (C13), 129.7 (C12), 168.2 (CO-Ac), 168.4 (CO-Ac).

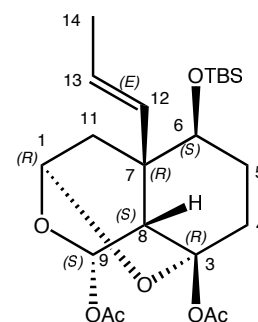
ESIMS (MeOH): 391.1 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₁₈H₂₄O₈Na *m/z* 391.1369, found 361.1373.

Analysis calcd. for C₁₈H₂₄O₈ · 0.9 H₂O (368.38): C 56.21, H 6.76; found C 56.19, H 6.53.



A dry flask was charged with 4.108 g of diol **214** (15.8 mmol) and 21 g of Pb(OAc)₄ (47.4 mmol, 3 eq.) vacuumed, flushed with argon and cooled to nearly 0°C. CH₂Cl₂ (60 mL) was added, the ice bath removed soon after and the mixture was stirred at r.t. for 15 h, diluted with acetonitrile, filtered through Celite, the filtrate concentrated and purified by silica gel chromatography using ethyl acetate-heptane, 1:3 as an eluent to give **218** (4.612 g, 12.9 mmol, 82%).

218: Acetic acid 3-acetoxy-6-(*tert*-butyl-dimethyl-silyloxy)-7-propenyl-2,10-dioxatricyclo[5.3.1.0^{0,0}]undec-9-yl ester.



Mp: yellow oil.

$[\alpha]_D^{20} = -17$ (*c* 1.31, CHCl₃).

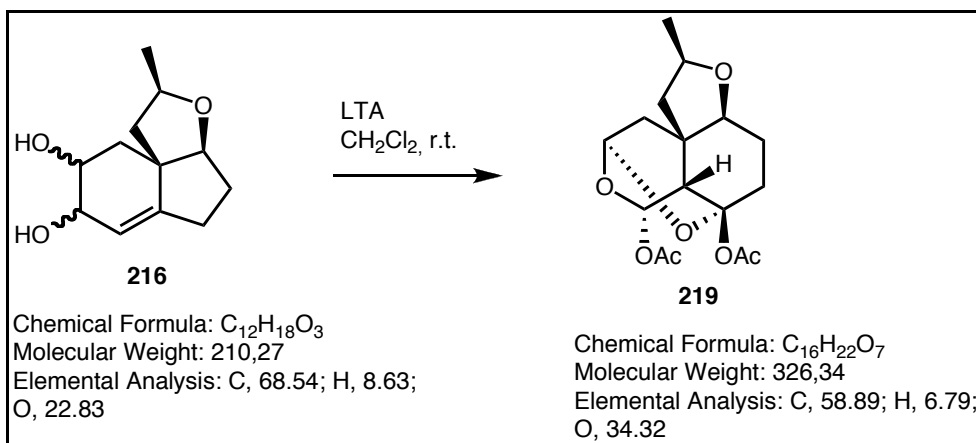
IR (film): $\nu = 2953, 2856, 1736, 1461, 1367, 1255, 1220, 1183, 1094, 1067, 1026, 974, 943, 878, 834, 774$ cm⁻¹.

¹H-NMR (CDCl₃, 500 MHz): $\delta = -0.01$ (s, 3 H, SiMe), 0.01 (s, 3 H, SiMe), 0.92 (s, 9 H, Si*t*Bu), 1.57 - 1.69 (m, 3 H, H4, H5, H11), 1.73 (d, *J* = 6.2 Hz, 3 H, H14), 1.95 (m, 1 H, H5'), 2.05 (d, *J* = 14.1 Hz, 1 H, H11'), 2.07 (s, 3 H, Me-Ac), 2.10 (s, 3 H, Me-Ac), 2.73 (ddd, *J* = 4.6, 13.1, 17.7 Hz, 1 H, H4'), 3.32 (s, 1 H, H8), 3.45 (t, *J* = 3.6 Hz, 1 H, H6), 5.30 (s, 1 H, H1), 5.52 (qd, *J* = 6.2, 16.0 Hz, 1 H, H13), 5.60 (d, *J* = 16.0 Hz, 1 H, H12), 6.16 (s, 1 H, H9).

¹³C-NMR (CDCl₃, 125 MHz): $\delta = -4.9$ (SiMe), -4.7 (SiMe), 17.9 (Cq-Si*t*Bu), 18.2 (C14), 21.2 (Me-Ac), 22.5 (Me-Ac), 25.7 (3C-Si*t*Bu), 27.0 (C5), 28.0 (C4), 35.5 (C8), 36.0 (C11), 42.1 (C7), 74.2 (C6), 91.6 (C9), 92.4 (C1), 103.9 (C3), 125.8 (C13), 135.7 (C12), 169.3 (CO-Ac), 169.5 (CO-Ac).

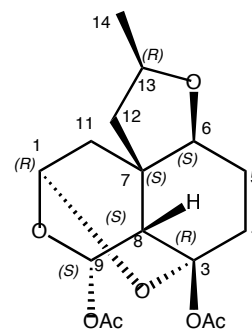
ESIMS (MeOH): 463.2 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₂₂H₃₆O₇SiNa *m/z* 463.2128, found 463.2117.

Analysis calcd. for C₂₂H₃₆O₇Si · 0.3 CH₂Cl₂ (440.6): C 57.47, H 7.92; found C 57.31, H 7.96.



A dry flask was charged with Pb(OAc)₄ (455 mg, 1.03 mmol, 4 eq.) was vacuumed, flushed with argon and cooled to nearly 0°C. Then, it was suspended in dry toluene (0.5 mL) and a solution of diol **216** (54 mg, 0.256 mmol) in dry toluene (0.5 mL) was added dropwise at the same temperature. The mixture was stirred at r.t. for 15 h, diluted with Et₂O, filtered through a MgSO₄/Celite/SiO₂ pad and the filtrate concentrated. Chromatography of the residue on silica gel (heptane:EtOAc, 1:0 to 4:1) yielded **219** (42 mg, 50%).

219:



Mp: colourless oil.

$[\alpha]_D^{20} = -29$ (*c* 1.01, CHCl₃).

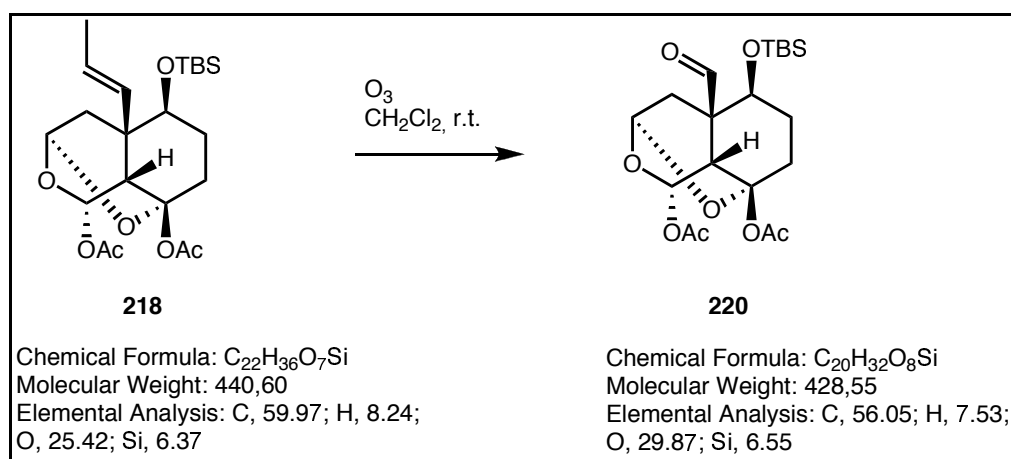
IR (film): $\nu = 2933, 2870, 1731, 1445, 1370, 1260, 1236, 1221, 1181, 1127, 1076, 1042, 1020, 960, 933, 882$ cm⁻¹.

¹H-NMR (CDCl₃, 500 MHz): 1.34 (d, *J* = 6.3 Hz, 3 H, H14), 1.72 - 1.78 (m, 2 H, H4, H11), 1.90 - 1.98 (m, 2 H, H5), 2.00 - 2.06 (m, 3 H, H11', H12), 2.10 (s, 3 H, Me-Ac), 2.10 (s, 3 H, Me-Ac), 2.60 (td, *J* = 5.4, 13.1 Hz, 1 H, H4'), 2.98 (s, 1 H, H8), 3.44 (dd, *J* = 1.6, 3.5 Hz, 1 H, H6), 4.18 (dq, *J* = 6.6, 6.6 Hz, 1 H, H13), 5.34 (d, *J* = 2.9 Hz, 1 H, H1), 6.28 (s, 1 H, H9).

^{13}C -NMR (CDCl_3 , 125 MHz): 21.2 (Me-Ac), 22.3 (Me-Ac), 22.6 (C5, C14), 28.3 (C4), 35.9 (C11), 37.9 (C8), 42.1 (C7), 42.8 (C12), 73.1 (C13), 81.4 (C6), 91.6 (C9), 93.5 (C1), 103.7 (C3), 169.4 (CO-Ac), 169.5 (CO-Ac).

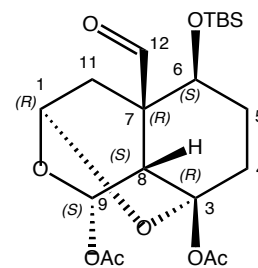
ESIMS (MeOH): 349.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_7\text{Na}$ m/z 349.1263; found 349.1252.

Analysis calcd. for $\text{C}_{16}\text{H}_{22}\text{O}_7 \cdot 0.25 \text{H}_2\text{O}$ (326.34): C 58.09, H 6.85; found C 58.01, H 6.76.



Ozone was passed into a stirred solution of **218** (500 mg, 1.13 mmol) in 41 mL of methylene chloride at -78°C until blue color persisted, stirred 5 additional minutes at this temperature after what 21 mL of Me_2S were added dropwise. The mixture was allowed to reach room temperature within approximately 30 min, concentrated under reduced pressure without heating, and purified through silica gel using heptane-ethyl acetate 4:1 as eluent, to give 348 mg (74%) of aldehyde **220**.

220: Acetic acid 3-acetoxy-6-(*tert*-butyl-dimethyl-silanyloxy)-7-formyl-2,10-dioxatricyclo[5.3.1.0^{0,0}]undec-9-yl ester.



Mp: 158°C .

$[\alpha]_D^{20} = -14$ (c 1.0, CHCl_3).

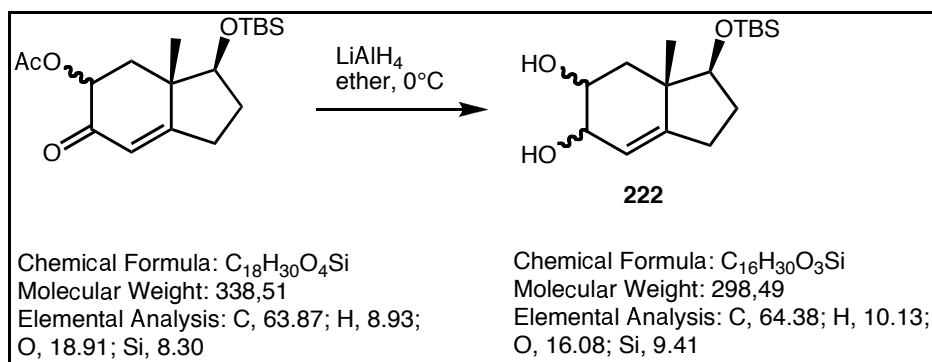
IR (film): $\nu = 2935, 1736, 1369, 1216, 1181, 1121, 1070, 1029, 972, 933, 869, 832 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): $\delta = 0.02$ (s, 3 H, SiMe), 0.06 (s, 3 H, SiMe), 0.90 (s, 9 H, Si*t*Bu), 1.61 (dd, $J = 2.6, 14.4 \text{ Hz}$, 1 H, H11), 1.70 (m, 2 H, H4, H5), 1.99 (m, 1 H, H5'), 2.09 (s, 3 H, Me-Ac), 2.13 (s, 3 H, Me-Ac), 2.24 (dd, $J = 1.0, 14.4 \text{ Hz}$, 1 H, H11), 2.76 (td, $J = 5.0, 13.3 \text{ Hz}$, 1 H, H4'), 3.89 (s, 1 H, H8), 3.94 (t, $J = 2.6 \text{ Hz}$, 1 H, H6), 5.35 (dd, $J = 1.5, 2.9 \text{ Hz}$, 1 H, H1), 6.01 (s, 1 H, H9), 9.62 (s, 1 H, H12).

$^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): -5.2 (SiMe), -4.4 (SiMe), 17.9 (Cq-Si*t*Bu) 21.2 (Me-Ac), 22.4 (Me-Ac), 25.6 (3C-Si*t*Bu) 26.5 (C5), 27.8 (C4), 31.9, 32.0 (C8, C11), 51.2 (C7), 70.6 (C6), 90.7 (C9), 92.2 (C1), 103.2 (C3), 169.2 (CO-Ac), 169.4 (CO-Ac), 201.9 (C12).

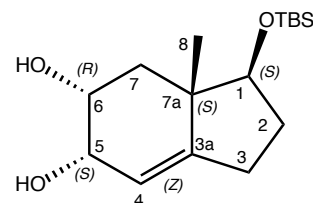
ESIMS (MeOH): 451.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{20}\text{H}_{32}\text{O}_8\text{NaSi}$ m/z 451.1764; found 451.1759.

Analysis calcd. for $\text{C}_{20}\text{H}_{32}\text{O}_8\text{Si}$ (438.63): C 56.05, H 7.53; found C 56.01, H 7.76.



To a magnetically stirred suspension of LiAlH_4 (3.77 g, 99.4 mmol) in 200 mL of THF, cooled to nearly 0°C , was added dropwise a solution of acetoxyenone (16.8 g, 49.7 mmol) in THF (100 mL). After stirring at this temperature for 30-40 min (TLC monitoring) the mixture was diluted with Et_2O and treated with a small amount of 6N NaOH solution (for each 1 g of LiAlH_4 1mL of water, 1 mL of 6N NaOH and 3 mL more water were added). The organic layer was worked up as usual to give, after silica gel chromatography (ethyl acetate-heptane, 3:7), 72% (10.5 g) of the desired diols **222**.

222: 3-(*tert*-Butyl-dimethyl-silanyloxy)-3a-methyl-2,3,3a,4,5,6-hexahydro-1*H*-indene-5,6-diol.



Mp: colourless oil.

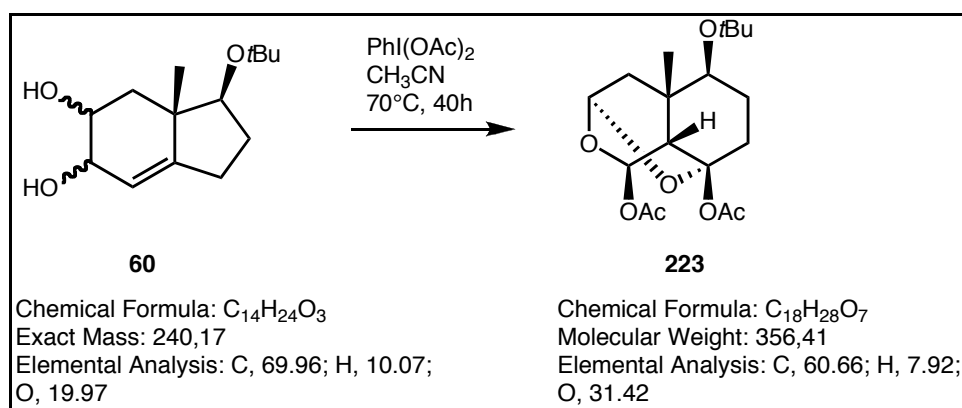
$$[\alpha]_D^{20} = -31 \text{ (} c \text{ 1.04, CHCl}_3 \text{)}$$

IR (film): 3380, 2956, 2857, 1463, 1360, 1256, 1107, 1055, 933, 861 cm^{-1} .

$^1\text{H-NMR}$ (300 MHz): 0.01 (s, 3 H, SiMe), 0.03 (s, 3 H, SiMe), 0.88 (s, 9 H, Si*t*Bu), 1.08 (s, 3 H, H8), 1.60 (dd, $J = 2.5, 14.0$ Hz, 1 H, H7), 1.63 (tdd, $J = 6.0, 8.7, 12.7$ Hz, 1 H, H2), 1.87 (dddd, $J = 4.0, 8.4, 9.6, 12.7$, 1 H, H2), 1.92 (dd, $J = 7.0, 14.0$ Hz, 1 H, H7), 2.06 (ddd, $J = 6.0, 9.6, 16.2$ Hz, 1 H, H3), 2.52 (dddt, $J = 2.0, 4.0, 12.7, 16.2$ Hz, 1 H, H3), 3.57 (t, $J = 8.7$ Hz, 1 H, H1), 3.91 (dt, $J = 4.0, 7.0$ Hz, 1 H, H6), 4.15 (td, $J = 2.0, 4.1$ Hz, 1 H, H5), 5.37 (t, $J = 3.2$ Hz, 1 H, H4).

$^{13}\text{C-NMR}$ (75 MHz): -4.8 (SiMe), -4.4 (SiMe), 18.0 (Cq-Si*t*Bu), 19.6 (C8), 25.7 (3C-Si*t*Bu), 26.3 (C3), 29.7, 37.5 (C2, C7), 43.9 (C7a), 67.9, 68.3, 79.9 (C1, C5, C6), 118.8 (C4), 150.2 (C3a).

ESIMS (MeOH): 321.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{16}\text{H}_{30}\text{O}_3\text{SiNa}$ m/z 321.1862; found 321.1847



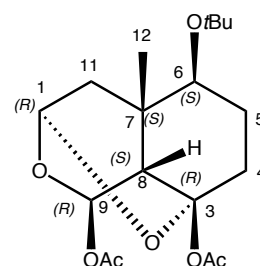
Over **60** (500 mg, 2.08 mmol) and PhI(OAc)_2 (3.35 g, 10.4 mmol, 5 eq.) vacuumed and flashed with argon, under argon dry CH_3CN (10 mL) was added and the reaction

mixture was stirred at 70°C for 20 h. After cooling, dilution with ether and washing with a saturated solution of Na₂S₂O₃, usual work up gives **223**.

Note: The yield is 55% after column chromatography over silicagel using ethyl acetate-heptane, 2/8 as an eluent.

Without chromatography, the NMR of the crude show the presence of the desired product which is contaminated with iodobenzene, this later can be removed under vacuum by heating at 30-35°C for 2 days.

223: Acetic acid 6-tert-butoxy-7-methyl-3-(2-oxo-propyl)-2,10-dioxa-tricyclo[5.3.1.0^{0,0}] undec-9-yl ester.



Mp: colourless oil.

$[\alpha]_D^{20} = +40$ (*c* 1.5, CHCl₃).

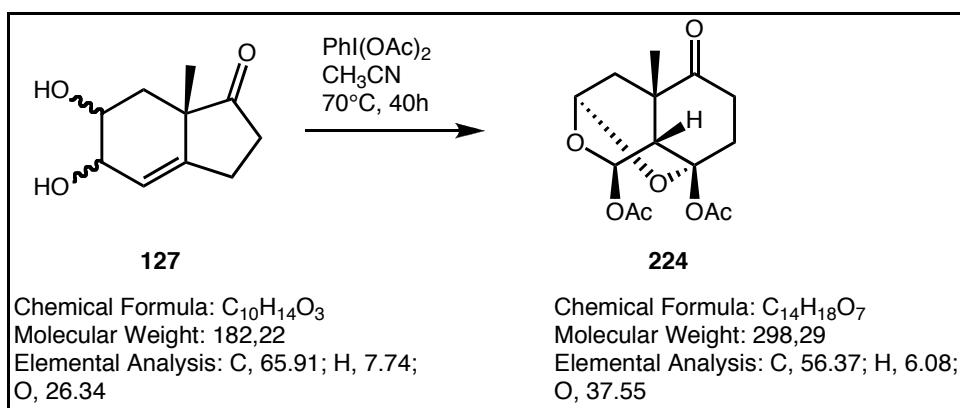
IR (film): $\nu = 2971, 1754, 1739, 1367, 1219, 1181, 1101, 1044, 1022, 1005, 965, 944$ cm⁻¹.

¹H NMR (CDCl₃, 500 MHz): $\delta = 1.19$ (s, 9 H, OtBu), 1.39 (s, 3 H, H12), 1.71 (ddt, *J* = 2.7, 4.3, 14.3 Hz, 1 H, H5), 1.76 (dd, *J* = 2.4, 4.3 Hz, 2 H, H11), 1.87 (tdd, *J* = 2.3, 4.8, 12.9 Hz, 1 H, H5), 2.06 (s, 3 H, Me-Ac), 2.10 (s, 3 H, Me-Ac), 2.28 (td, *J* = 4.4, 12.9 Hz, 1 H, H4), 2.35 (ddd, *J* = 2.6, 4.6, 12.9 Hz, 1 H, H4'), 2.69 (d, *J* = 2.3 Hz, 1 H, H8), 3.12 (t, *J* = 2.3 Hz, 1 H, H6), 5.33 (t, *J* = 2.4 Hz, 1 H, H1), 6.50 (d, *J* = 2.3 Hz, 1 H, H9).

¹³C NMR (CDCl₃, 125 MHz): $\delta = 21.5$ (Me-Ac), 22.3 (Me-Ac), 25.4 (C5), 27.0 (C4), 29.0 (C12, 3C-OtBu), 34.7 (C7), 38.7 (C11), 39.7 (C8), 73.5 (Cq-OtBu), 74.7 (C6), 90.9 (C9), 93.3 (C1), 104.7 (C3), 169.1 (CO-Ac), 169.5 (CO-Ac).

ESIMS (MeOH): 379.2 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₁₈H₂₈O₇Na *m/z* 379.1733, found 379.1722.

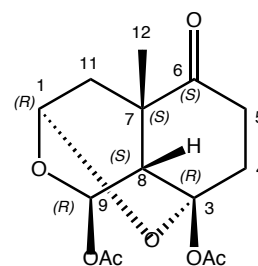
Analysis calcd. for C₁₈H₂₈O₇ · 0.35 (356.18): C 59.60, H 7.98; found C 59.64, H 8.04.



Over **127** (250 mg, 1.37 mmol) and PhI(OAc)₂ (2.2 g, 6.86 mmol, 5 eq.) vacuumed and flashed with argon, under argon dry CH₃CN (7 mL) was added and the reaction mixture was stirred at 70°C for 20 h. After cooling, dilution with ether and washing with a saturated solution of Na₂S₂O₃, usual work up gives **224**.

Note: The yield is 22% after column chromatography over silicagel using ethyl acetate-heptane, 1/2 as an eluent. Without chromatography, the NMR of the crude show the presence of the desired product which is contaminated with iodobenzene, this later can be removed under vacuum by heating at 30-35°C for 2 days.

224: Acetic acid 7-methyl-6-oxo-3-(2-oxo-propyl)-2,10-dioxa-tricyclo[5.3.1.0^{0,0}]undec-9-yl ester.



Mp: colourless oil.

$[\alpha]_D^{20} = +17$ (*c* 1.25, CHCl₃).

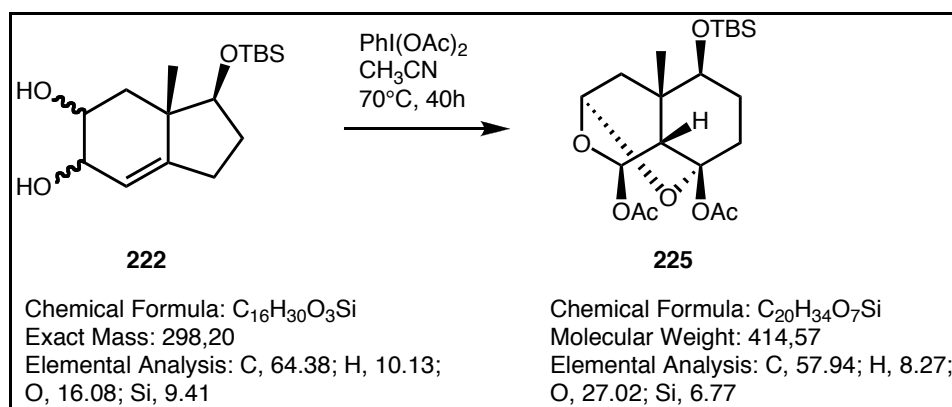
IR (film): $\nu = 2941, 1731, 1715, 1450, 1368, 1325, 1219, 1170, 1105, 1083, 1062, 1019, 996 \text{ cm}^{-1}$.

¹H NMR (CDCl₃, 500 MHz): $\delta = 1.47$ (s, 3 H, H12), 1.93 (d, *J* = 14.2 Hz, 1 H, H11), 2.11 (s, 3 H, Me-Ac), 2.12 (s, 3 H, Me-Ac), 2.30 (dd, *J* = 3.3, 14.2 Hz, 1 H, H11'), 2.51 (m, 1 H, H4), 2.61 (dd, *J* = 4.2, 12.9 Hz, 1 H, H5), 2.63 - 2.70 (m, 1 H, H4), 2.73 (dd, *J* = 5.3, 13.0 Hz, 1 H, H5), 3.03 (dd, *J* = 0.9, 3.0 Hz, 1 H, H8), 5.40 (d, *J* = 3.3 Hz, 1 H, H1), 6.40 (d, *J* = 3.0 Hz, 1 H, H9).

^{13}C NMR (CDCl_3 , 125 MHz): $\delta = 21.3$ (Me-Ac), 22.0 (Me-Ac), 22.8 (C12), 32.0 (C4), 34.5 (C5), 40.0 (C11), 41.5 (C8), 42.3 (C7), 90.0 (C9), 93.1 (C1), 102.9 (C3), 169.1 (CO-Ac), 169.4 (CO-Ac), 211.1 (C6).

ESIMS (MeOH): 321.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_7\text{Na}$ m/z 321.0950, found 321.0947.

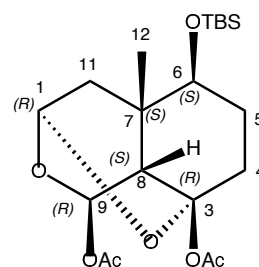
Analysis calcd. for $\text{C}_{14}\text{H}_{18}\text{O}_7 \cdot 0.35 \text{CH}_2\text{Cl}_2$ (298.10): C 52.57, H 5.93; found C 52.55, H 5.75.



Over **222** (100 mg, 0.33 mmol) and $\text{PhI}(\text{OAc})_2$ (531 mg, 1.65 mmol, 5 eq.) vacuumed and flashed with argon, under argon dry CH_3CN (2 mL) was added and the reaction mixture was stirred at 70°C for 20 h. After cooling, dilution with ether and washing with a saturated solution of $\text{Na}_2\text{S}_2\text{O}_3$, usual work up gives **225**.

Note: The yield is 18% after column chromatography over silicagel using ethyl acetate-heptane, 1/2 as an eluent. Without chromatography, the NMR of the crude show the presence of the desired product which is contaminated with iodobenzene, this later can be removed under vacuum by heating at $30\text{-}35^\circ\text{C}$ for 2 days.

225: Acetic acid 6-(tert-butyl-dimethyl-silyloxy)-7-methyl-3-(2-oxo-propyl)-2,10-dioxatricyclo[5.3.1.0^{0,0}]undec-9-yl ester.



Mp: colourless oil.

$[\alpha]_D^{20} = +3$ (c 1.5, CHCl_3).

IR (film): $\nu = 2953, 2856, 1754, 1737, 1462, 1366, 1247, 1220, 1182, 1082, 1004, 964, 945, 834, 774 \text{ cm}^{-1}$.

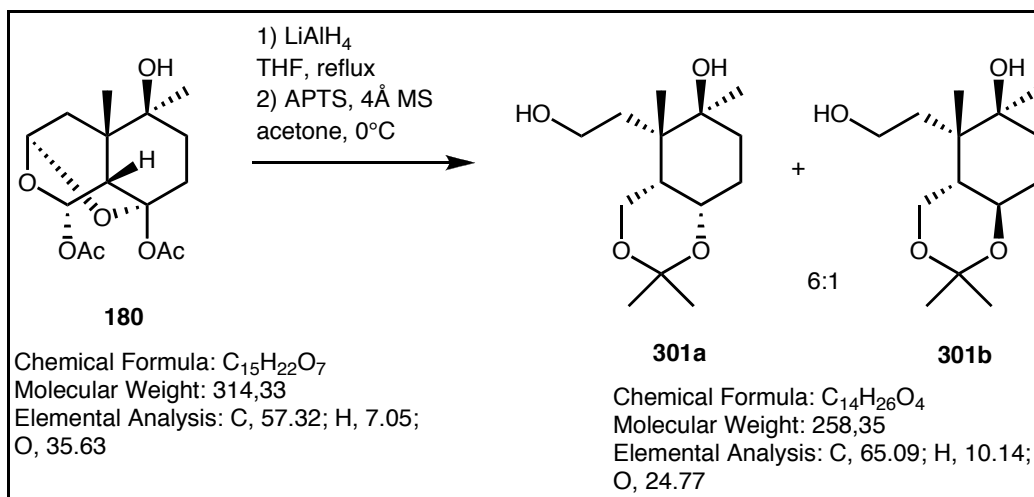
$^1\text{H NMR}$ (CDCl_3 , 500 MHz): $\delta = 0.06$ (s, 6 H, SiMe), 0.92 (s, 9 H, Si*t*Bu), 1.39 (s, 3 H, H12), 1.57 - 1.63 (m, 1 H, H5), 1.74 (d, $J = 2.2$ Hz, 2 H, H11), 1.92 - 1.99 (m, 1 H, H5'), 2.07 (s, 3 H, Me-Ac), 2.10 (s, 3 H, Me-Ac), 2.25 - 2.35 (m, 2 H, H4), 2.74 (d, $J = 2.5$ Hz, 1 H, H8), 3.28 (t, $J = 2.5$ Hz, 1 H, H6), 5.32 (t, $J = 2.2$ Hz, 1 H, H1), 6.47 (d, $J = 2.5$ Hz, 1 H, H9).

$^{13}\text{C NMR}$ (CDCl_3 , 125 MHz): $\delta = -4.8$ (SiMe), -4.4 (SiMe), 18.0 (Cq-Si*t*Bu), 21.4 (Me-Ac), 22.2 (Me-Ac), 25.8 (3C-Si*t*Bu), 26.7, 26.8 (C4, C5), 28.9 (C12), 35.1 (C7), 38.3 (C8), 39.3 (C11), 76.1 (C6), 90.6 (C9), 93.1 (C1), 104.6 (C3), 169.2 (CO-Ac), 169.4 (CO-Ac).

ESIMS (MeOH): 437.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{20}\text{H}_{34}\text{O}_7\text{SiNa}$ m/z 437.1971, found 437.1968.

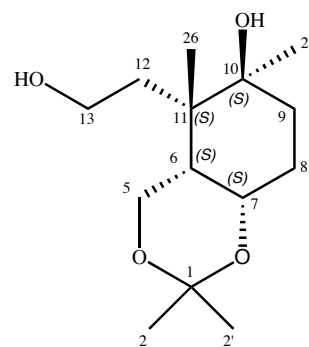
Analysis calcd. for $\text{C}_{20}\text{H}_{34}\text{O}_7\text{Si} \cdot 0.3 \text{ CH}_2\text{Cl}_2$ (414.20): C 57.47, H 7.92; found C 57.31, H 7.96.

3. Experimental part: Chapter 2.



To an ice cold magnetically stirred solution of **180** (1.4 g, 4.45 mmol) in 20 mL of dry THF, under argon atmosphere, LiAlH_4 (1.02 g, 26.7 mmol) was added. The mixture was stirred at reflux for 1 h. Upon disappearance of starting material, the reaction mixture was cooled to 0°C, diluted with ether, water (1.02 mL), 6N aq. NaOH (1.02 mL) and water (3.06 mL) again were added successively, and stirring continued at room temperature for 45 minutes. Rapid filtration on SiO_2 (eluent: EtOAc) and removal of solvent gave a residue, which was clean enough to be used without further purification (970 mg). The crude product was directly used in the next step.

The crude (970 mg, 4.45 mmol) was dissolved in dry acetone (15 mL) at 0°C under Ar. Molecular sieves (4Å) and APTS (85 mg, 0.45 mmol) were added. The reaction mixture was stirred 1 h, diluted with acetone and filtered over alumina (standard). The solvent was evaporated under reduce pressure and the crude product was purified through flash chromatography using heptane-ethyl acetate 1:1 as eluent afforded 744 mg (70% over two step) **301a** and **301b** (6:1).

301a: 5-(2-Hydroxy-ethyl)-2,2,5,6-tetramethyl-hexahydro-benzo[1,3]dioxin-6-ol.

Mp: colourless oil.

$[\alpha]_D^{20} = +26$ (*c* 2.75, CHCl₃).

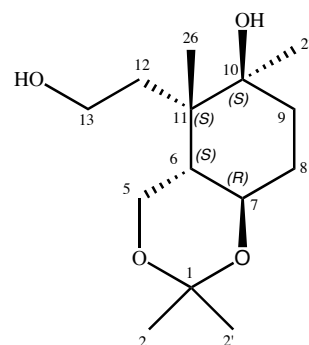
IR (film): $\nu = 3408, 2986, 1381, 1232, 1198, 1165, 1102$ cm⁻¹.

¹H-NMR (CDCl₃, 400 MHz): $\delta = 1.03$ (s, 3 H, H26), 1.25 (s, 3 H, H27), 1.27 - 1.34 (m, 1 H, H9), 1.41 (s, 3 H, H2), 1.47 (s, 3 H, H2'), 1.49 (d, *J* = 2.1 Hz, 1 H, H6), 1.56 - 1.61 (m, 1 H, H8), 1.62 - 1.66 (m, 1 H, H12), 1.96 (td, *J* = 4.0, 13.7 Hz, 1 H, H9'), 2.11 (tt, *J* = 4.7, 13.9 Hz, 1 H, H8'), 2.70 (quint, *J* = 7.2 Hz, 1 H, H12'), 3.75 (ddd, *J* = 5.8, 7.6, 10.3 Hz, 1 H, H13), 3.85 (dt, *J* = 7.5, 10.2 Hz, 1 H, H13'), 4.06 (d, *J* = 1.9 Hz, 2 H, H5), 4.18 (s, 1 H, H7).

¹³C-NMR (CDCl₃, 100 MHz): $\delta = 16.6$ (C26), 19.4 (C2), 26.1 (C27), 26.4 (C8), 29.6 (C2'), 30.6 (C9), 36.0 (C12), 38.7 (C6), 41.3 (C11), 60.7 (C13), 61.4 (C5), 67.4 (C7), 74.7 (C10), 98.5 (C1).

ESIMS (MeOH): 281.2 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₁₄H₂₆O₄Na *m/z* 281.1729, found 281.1721.

Analysis calcd. for C₁₄H₂₆O₄ · 0.15 H₂O (258.35): C 64.41, H 10.15; found C 64.44, H 9.86.

301b: 5-(2-Hydroxy-ethyl)-2,2,5,6-tetramethyl-hexahydro-benzo[1,3]dioxin-6-ol.

Mp: colourless oil.

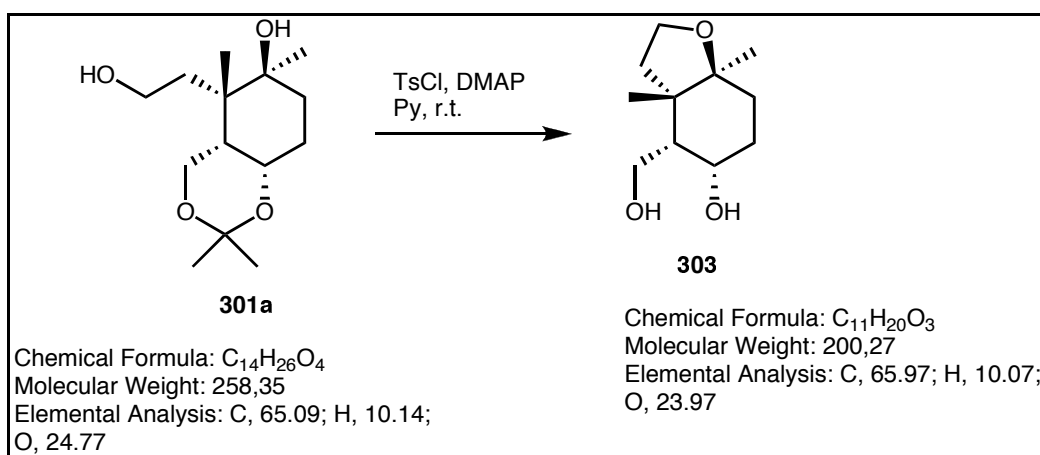
$[\alpha]_D^{20} = -25$ (c 1.15, CHCl_3).

IR (film): $\nu = 3390, 2928, 1373, 1211, 1023 \text{ cm}^{-1}$.

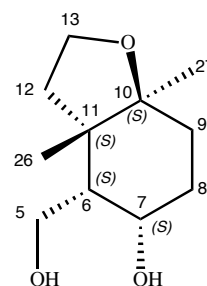
$^1\text{H-NMR}$ (CDCl_3 , 400 MHz): $\delta = 1.15$ (s, 3 H, H26), 1.14 - 1.18 (m, 1 H, H12), 1.17 (s, 3 H, H27), 1.24 (s, 3 H, H2), 1.36 (s, 3 H, H2'), 1.43 (s, 1 H, H6), 1.57 (dd, $J = 2.6, 12.8$ Hz, 1 H, H9), 1.89 (dd, $J = 1.9, 13.0$ Hz, 1 H, H9'), 1.94 - 1.97 (m, 2 H, H8), 2.88 (td, $J = 5.5, 14.6$ Hz, 1 H, H12'), 3.62 (td, $J = 4.6, 13.4$ Hz, 1 H, H13), 3.68 (dd, $J = 2.5, 12.4$ Hz, 1 H, H5), 3.80 (dd, $J = 5.4, 13.1$ Hz, 1 H, H13'), 4.15 (d, $J = 2.5$ Hz, 1 H, H7), 4.34 (d, $J = 12.4$ Hz, 1 H, H5'), 4.67 (s, 1 H, OH).

$^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): $\delta = 15.8$ (C26), 23.3 (C2), 25.8 (C27), 26.1 (C2'), 28.1 (C9), 30.6 (C8), 31.5 (C12), 42.3 (C11), 43.0 (C6), 61.4 (C13), 64.2 (C5), 73.5 (C7), 75.2 (C10), 100.2 (C1).

ESIMS (MeOH): 281.2 ($[M + \text{Na}]^+$, 50). HRESIMS: calcd. for $\text{C}_{14}\text{H}_{26}\text{O}_4\text{Na}$ m/z 281.1729, found 281.1729.



The alcohol **301a** (100 mg, 0.39 mmol) was dissolved in 2 mL of dry pyridine, DMAP (cat.) and *p*-toluenesulfonyl chloride (343 mg, 1.8 mmol) were added and the mixture was stirred from 0°C to room temperature for 4 h (TLC monitoring; excess of TsCl was added several times). The mixture was cooled to 0°C, diluted with methylene chloride, quenched with a saturated aqueous solution of sodium bicarbonate and worked up as usual. Chromatography (heptane-EtOAc 1:1) afforded 66 mg (85%) of **303** and 10 mg (10%) of recovered starting material.

303: 4-Hydroxymethyl-3a,7a-dimethyl-octahydro-benzofuran-5-ol.

Mp: 104.5 - 105.5°C.

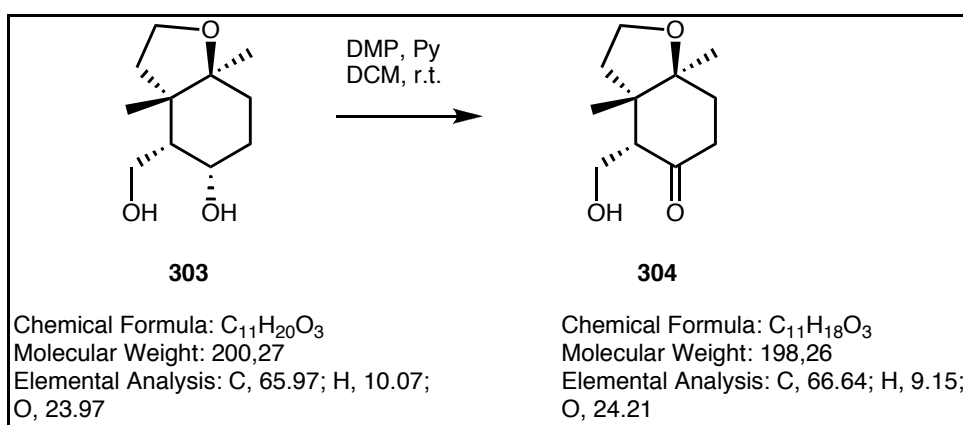
IR (film): $\nu = 3417, 3387, 2966, 2933, 2872, 1486, 1441, 1301, 1189, 1069, 1029 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz): $\delta = 1.14$ (s, 3 H, H27), 1.17 (s, 3 H, H26), 1.41 (s, 1 H, H6), 1.64 (dq, $J = 3.1, 13.8 \text{ Hz}$, 1 H, H8), 1.88 (tt, $J = 3.0, 13.8 \text{ Hz}$, 1 H, H8'), 2.21 - 2.24 (m, 4 H, H12, H9), 3.74 (td, $J = 2.9, 12.8 \text{ Hz}$, 1 H, H13), 3.96 (s, 2 H, H5), 3.98 (td, $J = 2.7, 12.1 \text{ Hz}$, 1 H, H13'), 4.17 (d, $J = 4.2 \text{ Hz}$, 1 H, H7).

$^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): 17.2 (C26), 24.6 (C27), 27.2 (C8), 30.0, 31.6 (C12, C9), 37.2 (C11), 40.0 (C6), 64.5 (C13), 69.7 (C5), 72.4 (C7), 73.6 (C10).

ESIMS (MeOH): 223.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{11}\text{H}_{20}\text{O}_3\text{Na}$ m/z 223.1310, found 223.1306.

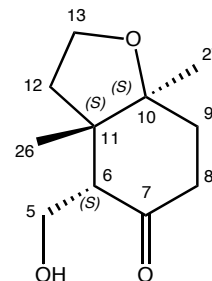
Analysis calcd. for $\text{C}_{11}\text{H}_{20}\text{O}_3$ (200.27): C 65.97, H 10.07; found C 66.39, H 10.02.



To a solution of the above alcohol **303** (79 mg, 0.4 mmol) in dry methylene chloride (2 mL) and pyridine (0.62 mL, 8.0 mmol) were added 1.0 g (2.4 mmol) of periodinane and stirring continued at room temperature for 2 h. The reaction was then diluted with methylene chloride quenched with a saturated aqueous solution of sodium bicarbonate and

washed with brine. Usual work up and chromatography (heptane-EtOAc, 3:1) afforded 61 mg (77%) of the desired ketone **304**.

304: 4-Hydroxymethyl-3a,7a-dimethyl-hexahydro-benzofuran-5-one.



Mp: 105.5-106.5°C.

$[\alpha]_D^{20} = +27$ (*c* 0.65, CHCl₃).

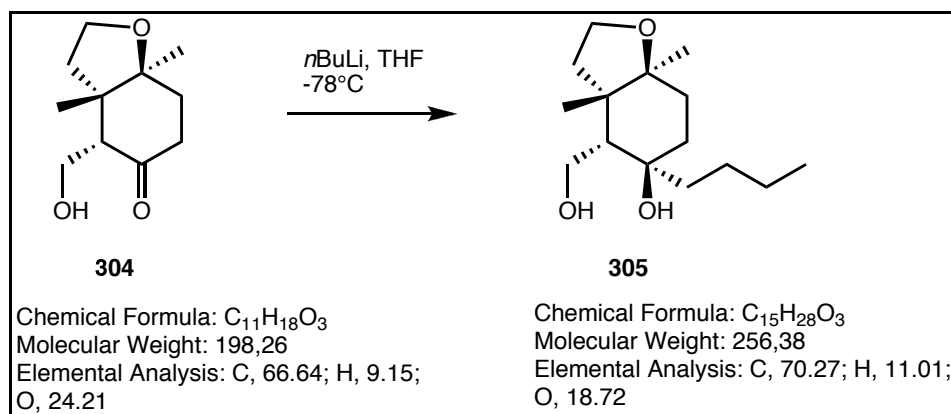
IR (film): $\nu = 3448, 2929, 1706, 1458, 1375, 1108, 1082, 1061 \text{ cm}^{-1}$.

¹H-NMR (CDCl₃, 300 MHz): $\delta = 1.19$ (dd, *J* = 1.9, 13.3 Hz, 1 H, H12), 1.25 (s, 3 H, H27), 1.33 (s, 3 H, H26), 1.66 (td, *J* = 5.3, 12.8 Hz, 1 H, H12'), 1.85 (ddd, *J* = 2.0, 6.9, 14.3 Hz, 1 H, H9), 2.19 (td, *J* = 5.0, 14.1 Hz, 1 H, H9'), 2.32 (s, 1 H, H6), 2.38 (dd, *J* = 2.0, 4.9 Hz, 1 H, H8), 2.79 (td, *J* = 7.0, 14.6 Hz, 1 H, H8'), 3.53 (dd, *J* = 2.6, 11.8 Hz, 1 H, H5), 3.66 (td, *J* = 2.4, 12.2 Hz, 1 H, H13), 3.83 (dd, *J* = 5.1, 11.6 Hz, 1 H, H13'), 4.51 (d, *J* = 11.8 Hz, 1 H, H5').

¹³C-NMR (CDCl₃, 75 MHz): 17.5 (C26), 24.2 (C27), 32.4 (C12), 34.9 (C9), 36.8 (C8), 42.2 (C11), 50.6 (C6), 61.7 (C5), 63.6 (C13), 73.1 (C10), 209.8 (C7).

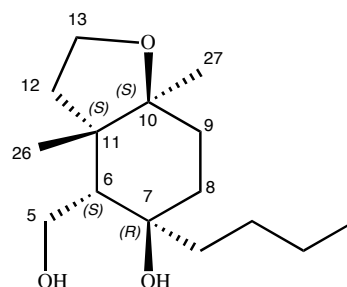
ESIMS (MeOH): 199.2 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₁₁H₁₉O₃Na *m/z* 199.1334, found 199.1339.

Analysis calcd. for C₁₁H₁₈O₃ · 0.1 C₇H₁₆ (198.26): C 67.47, H 9.49; found C 67.48, H 9.65.



To a solution of **304** (18 mg, 0.09 mmol) in THF (1 mL) at -78°C under Ar, was added *n*-BuLi (0.22 mL, 1.6M in hexane). The reaction mixture was stirred 1 h at -78°C . Then, the reaction mixture was diluted with ether, and a saturated solution of NH_4Cl was added. The aqueous layer was extracted with ether. The combined organic layers were worked up as usual. Flash chromatography (ethyl acetate/heptane 1:1) afforded 8 mg (35%) of **305**, and 9 mg (50%) of recovered starting material.

305: 5-Butyl-4-hydroxymethyl-3a,7a-dimethyl-octahydro-benzofuran-5-ol.



Mp: colourless oil.

$[\alpha]_D^{20} = +9$ (*c* 0.4, CHCl_3).

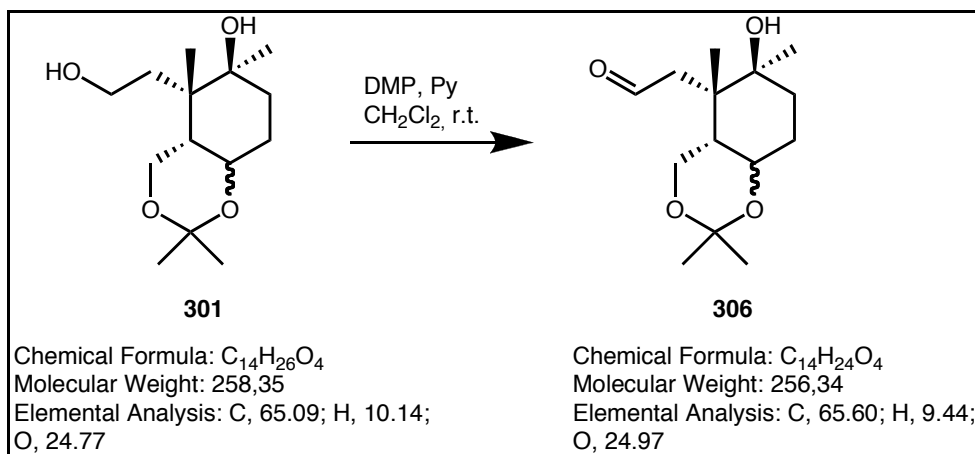
IR (film): $\nu = 3484, 2961, 2871, 1467, 1144, 1065, 956 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 0.88 - 1.92$ (m, 3 H, Bu), 1.05 (d, $J = 13.3$ Hz, 1 H, H12), 1.14 (s, 3 H, H27), 1.19 (s, 3 H, H26), 1.28 - 1.33 (m, 6 H, Bu), 1.35 - 1.38 (m, 1 H, H9), 1.48 (td, $J = 3.1, 13.6$ Hz, 1 H, H8), 1.59 (d, $J = 4.1$ Hz, 1 H, H6), 1.77 (td, $J = 2.5, 13.6$ Hz, 1 H, H8'), 2.25 (td, $J = 3.6, 13.8$ Hz, 1 H, H9'), 2.34 (td, $J = 5.9, 13.0$ Hz, 1 H, H12'), 3.74 (td, $J = 2.9, 11.9$ Hz, 1 H, H13), 3.81 (d, $J = 12.8$ Hz, 1 H, H5), 3.90 (dd, $J = 5.7, 11.4$ Hz, 1 H, H13'), 4.27 (d, $J = 12.6$ Hz, 1 H, H5').

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 14.1$ (MeBu), 18.0 (C26), 23.4 (Bu), 24.9 (C27), 26.4 (Bu), 30.5 (C8), 31.0 (C12), 31.4 (C9), 37.8 (C11), 41.7 (Bu), 42.8 (C6), 64.7 (C13), 65.3 (C5), 73.7 (C10), 74.5 (C7).

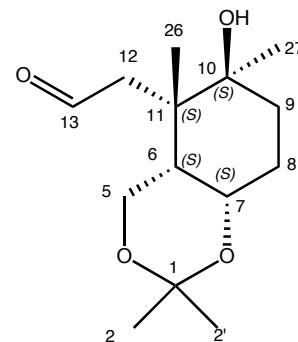
ESIMS (MeOH): 279.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{15}\text{H}_{28}\text{O}_3\text{Na}$ m/z 279.1936, found 279.1947.

Analysis calcd. for $\text{C}_{15}\text{H}_{28}\text{O}_3$ (256.38): C 70.27, H 11.01; found C 70.23, H 11.06.



To a solution of the above alcohol **301** (800 mg, 3.1 mmol) in dry methylene chloride (12 mL) and pyridine (2.44 mL, 30.9 mmol) were added 3.95 g (9.3 mmol) of periodinane and stirring continued at room temperature for 1.5 h. The reaction was then diluted with methylene chloride quenched with a saturated aqueous solution of sodium bicarbonate and washed with brine. Usual work up and chromatography (heptane-EtOAc, 3:1) afforded 675 mg (85%) of the desired aldehyde **306**.

306a: (6-hydroxy-2,2,5,6-tetramethyl-hexahydro-benzo[1,3]dioxin-5-yl)-acetaldehyde.



Mp: colourless oil.

$[\alpha]_D^{20} = +56$ (*c* 0.8, CHCl₃).

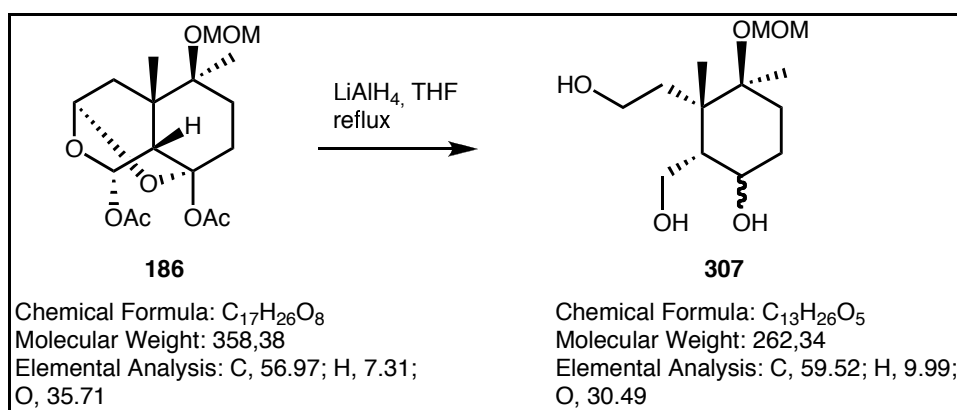
IR (film): $\nu = 3447, 2936, 1706, 1457, 1382, 1199, 1103, 1021$ cm⁻¹.

¹H-NMR (CDCl₃, 500 MHz): $\delta = 1.13$ (s, 3 H, H₂₇), 1.25 (s, 3 H, H₂₆), 1.28 (s, 3 H, H₂), 1.30 (m, 1 H, H₉), 1.39 (s, 3 H, H_{2'}), 1.49 (td, *J* = 1.5, 3.5 Hz, 1 H, H₆), 1.54 (m, 1 H, H₈), 1.89 (td, *J* = 3.5, 13.4 Hz, 1 H, H_{9'}), 2.03 (tt, *J* = 4.5, 13.9 Hz, 1 H, H_{8'}), 2.32 (dd, *J* = 3.0, 16.8 Hz, 1 H, H₁₂), 3.31 (dd, *J* = 1.7, 18.5 Hz, 1 H, H_{12'}), 4.01 (d, *J* = 3.4 Hz, 2 H, H₅), 4.11 (m, 1 H, H₇), 9.84 (dd, *J* = 3.0, 1.9 Hz, 1 H, H₁₃).

^{13}C -NMR (CDCl_3 , 75 MHz): $\delta = 18.2$ (C26), 19.0 (C2), 26.3 (C8, C27), 29.3 (C2'), 30.7 (C9), 38.5 (C6), 41.5 (C11), 49.2 (C12), 61.2 (C5), 67.1 (C7), 74.1 (C10), 99.0 (C1), 203.7 (C13).

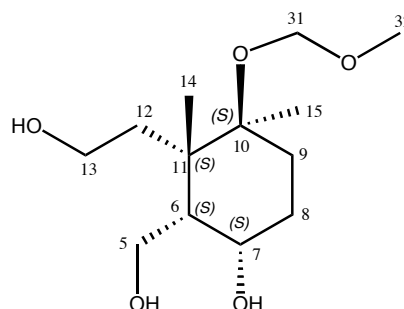
ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 279.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{14}\text{H}_{24}\text{O}_4\text{Na}$ m/z 279.1572, found 279.1578.

Analysis calcd. for $\text{C}_{14}\text{H}_{24}\text{O}_4$ (256.34): C 65.60, H 9.44; found C 65.52, H 9.56.



To an ice cold magnetically stirred solution of **186** (4.0 g, 11.16 mmol) in 40 mL of dry THF, under argon atmosphere, LiAlH_4 (2.54 g, 66.97 mmol) was added. The mixture was stirred at reflux for 1 h. Upon disappearance of starting material, the reaction mixture was cooled to 0°C , diluted with ether, water (2.54 mL), 6N aq. NaOH (2.54 mL) and water again (7.62 mL) were added successively, and stirring continued at room temperature for 45 minutes. Rapid filtration on SiO_2 (eluent: EtOAc) and removal of solvent gave a residue, which was clean enough to be used without further purification (2.64 g). Only for characterization, a sample was purified by chromatography (eluent Heptane-EtOAc 1:1) to yield **307** (90%).

307a: 3-(2-hydroxyethyl)-2-(hydroxymethyl)-4-(methoxymethoxy)-3,4-dimethylcyclohexanol.



Mp: 97.0-98.0°C.

$[\alpha]_D^{20} = +38$ (c 0.66, CHCl_3).

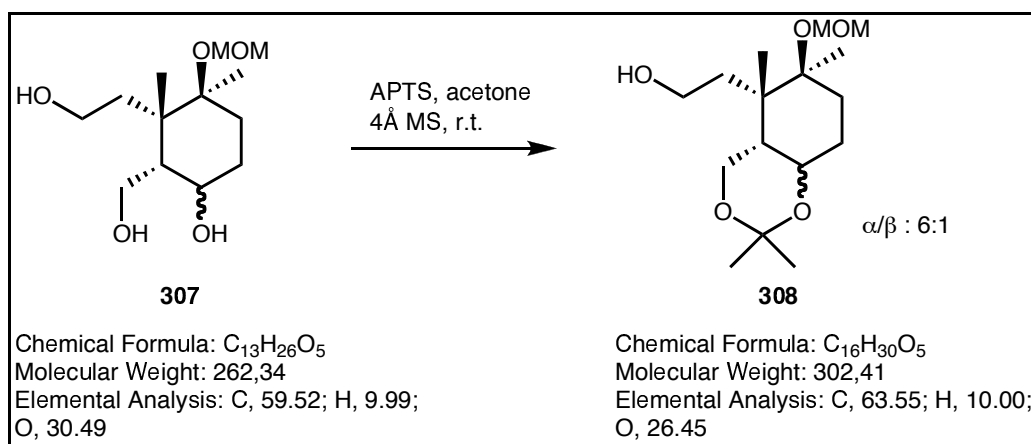
IR (film): $\nu = 3363, 2948, 1372, 1105, 1032, 916 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 1.09$ (s, 3 H, H26), 1.16 (s, 3 H, H27), 1.50 - 1.65 (m, 3 H, H8, H12), 1.73 (t, $J = 6.2$ Hz, 1 H, H9), 1.77 (dd, $J = 11.3, 14.2$ Hz, 1 H, H8'), 1.99 (td, $J = 3.2, 7.6$ Hz, 1 H, H6), 2.02 - 2.05 (m, 1 H, H9'), 3.28 (s, 3 H, H32), 3.63 (dt, $J = 2.2, 6.7$ Hz, 1 H, H13), 3.76 (dd, $J = 2.6, 10.9$ Hz, 2 H, H5, H13'), 3.92 (dd, $J = 8.0, 10.9$ Hz, 1 H, H5'), 4.25 (td, $J = 3.5, 6.6$ Hz, 1 H, H7), 4.59 and 4.63 (ABquartet, $J = 7.2$ Hz, 2 H, H31).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 19.6$ (C26), 20.4 (C27), 28.5 (C8), 37.0 (C9, C12), 43.1 (C11), 48.6 (C6), 55.5 (C32), 59.5 (C13), 60.8 (C5), 68.2 (C7), 80.0 (C10), 90.4 (C31).

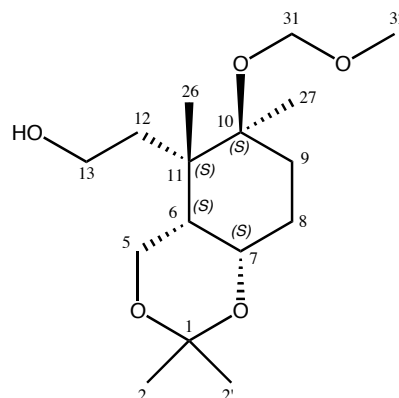
ESIMS (MeOH): 285.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{13}\text{H}_{26}\text{O}_5\text{Na}$ m/z 285.1678, found 285.1639.

Analysis calcd. for $\text{C}_{13}\text{H}_{26}\text{O}_5 \cdot 0.3 \text{ H}_2\text{O}$ (262.34): C 58.13, H 9.55; found C 58.35, H 9.75.



APTS (183 mg, 0.96 mmol) was added to a mixture of **307** (2.52 g, 9.61 mmol) in acetone (28 mL) with 4Å molecular sieves, at r.t. under Ar. The reaction mixture was stirred 30 min at room temperature. Then, the reaction mixture was diluted with acetone and filtered over alumina (acetone as eluant). The solvent was evaporated under reduced pressure, afforded 2.54 g (88%) of **308** (two diastereomer $\alpha/\beta : 6:1$).

308a: 2-(6-Methoxymethoxy-2,2,5,6-tetramethyl-hexahydro-benzo[1,3]dioxin-5-yl)-ethanol.



Mp: colourless oil.

$[\alpha]_D^{20} = +61$ (c 1.2, CHCl_3).

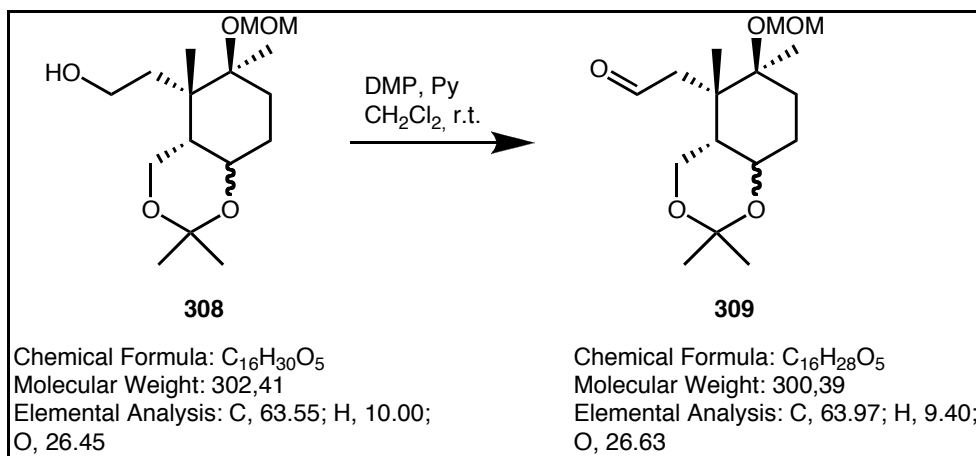
IR (film): $\nu = 2985, 1381, 1198, 1108, 1026 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 1.04$ (s, 3 H, H26), 1.22 (s, 3 H, H27), 1.41 (s, 3 H, H2), 1.46 (s, 3 H, H2'), 1.49 - 1.55 (m, 1 H, H9 or H8), 1.61 (dd, $J = 1.9, 3.6$ Hz, 1 H, H6), 1.67 (dd, $J = 5.9, 8.3$ Hz, 1 H, H12), 1.79 (dd, $J = 3.6, 13.6$ Hz, 1 H, H9 or H8), 1.85 - 1.96 (m, 2 H, H9 or H8), 2.73 (td, $J = 7.6, 15.1$ Hz, 1 H, H12'), 3.35 (s, 3 H, H32), 3.75 (ddd, $J = 5.6, 7.9, 10.4$ Hz, 1 H, H13), 3.86 (td, $J = 7.5, 10.4$ Hz, 1 H, H13'), 4.06 (d, $J = 3.2$ Hz, 2 H, H5), 4.19 (td, $J = 2.8, 4.9$ Hz, 1 H, H7), 4.62 and 4.72 (ABquartet, $J = 6.9$ Hz, 2 H, H31).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 16.3$ (C26), 19.1 (C2), 20.4 (C27), 26.4, 26.6 (C9, C8), 29.8 (C2'), 35.6 (C12), 38.2 (C6), 42.4 (C11), 55.4 (C32), 61.0, 61.6 (C5, C13), 67.4 (C7), 80.7 (C10), 90.4 (C31), 98.6 (C1).

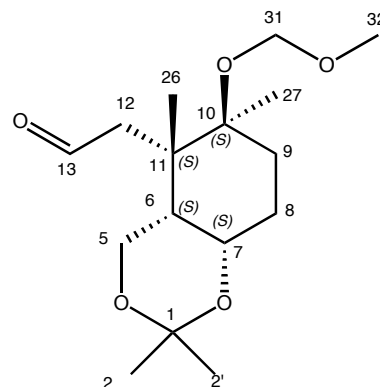
ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 325.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{16}\text{H}_{30}\text{O}_5\text{Na}$ m/z 325.1991, found 325.1978.

Analysis calcd. for $\text{C}_{16}\text{H}_{30}\text{O}_5 \cdot 0.65 \text{ H}_2\text{O}$ (302.41): C 61.18, H 10.04; found C 61.19, H 9.84.



To a solution of the above alcohol **308** (478 mg, 1.58 mmol) in dry methylene chloride (7 mL) and pyridine (1.28 mL, 15.81 mmol) were added 2.01 g (4.74 mmol) of periodinane and stirring continued at room temperature for 1.5 h. The reaction was then diluted with methylene chloride quenched with a saturated aqueous solution of sodium bicarbonate and washed with brine. Usual work up and chromatography (heptane-EtOAc, 3:1) afforded 448 mg (95%) of the desired aldehyde **309**.

309a: (6-Methoxymethoxy-2,2,5,6-tetramethyl-hexahydro-benzo[1,3]dioxin-5-yl)-acetaldehyde.



Mp: colourless oil.

$[\alpha]_D^{20} = +64$ (*c* 1.095, CHCl₃).

IR (film): $\nu = 2939, 1713, 1382, 1199, 1109, 1026$ cm⁻¹.

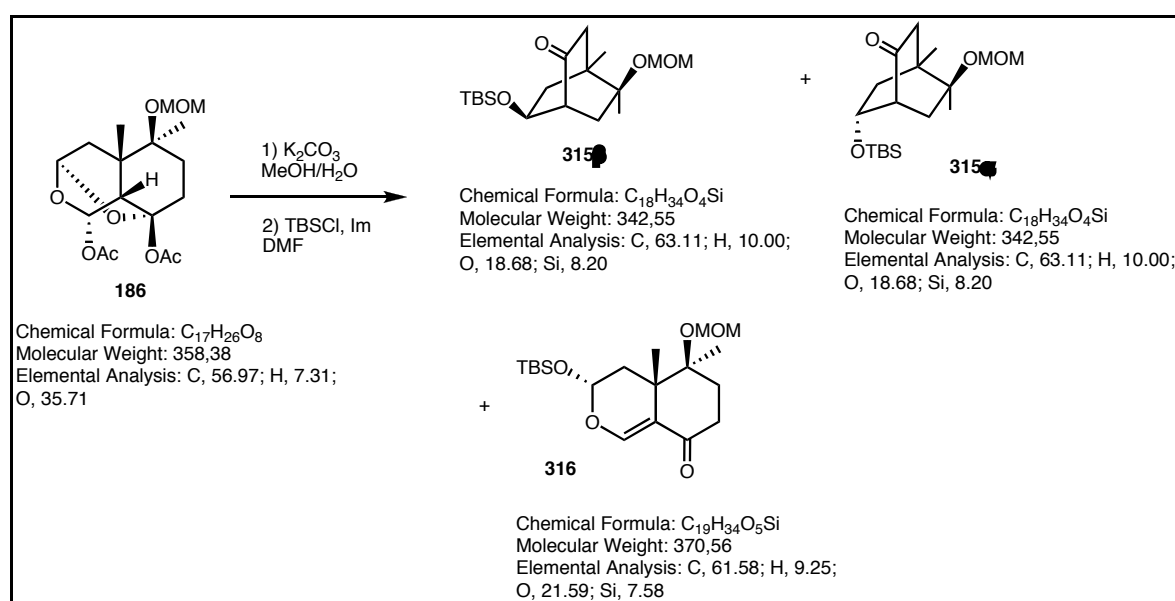
¹H-NMR (CDCl₃, 500 MHz): $\delta = 1.17$ (s, 3 H, H₂₆), 1.34 (s, 6 H, H₂₇, H₂), 1.45 (s, 3 H, H_{2'}), 1.48 - 1.58 (m, 2 H, H₉, H₈), 1.66 (dt, *J* = 1.7, 3.1 Hz, 1 H, H₆), 1.76 (dd, *J* = 4.0, 14.3 Hz, 1 H, H₁₂), 1.82 - 1.94 (m, 2 H, H_{9'}, H_{8'}), 2.43 (dd, *J* = 3.2, 16.9 Hz, 1 H, H_{12'}),

3.37 (s, 3 H, H32), 4.07 (d, $J = 3.2$ Hz, 2 H, H5), 4.17 (dt, $J = 2.1, 5.5$ Hz, 1 H, H7), 4.64 and 4.73 (ABquartet, $J = 7.1$ Hz, 2 H, H31), 9.92 (dd, $J = 1.8, 3.2$ Hz, 1 H, H13).

^{13}C -NMR (CDCl_3 , 75 MHz): $\delta = 18.4$ (C26), 19.0 (C27), 20.5 (C2), 26.5 (C9, C8), 29.4 (C2'), 38.3 (C6), 42.5 (C11), 49.1 (C12), 55.5 (C32), 61.3 (C5), 67.1 (C7), 79.8 (C10), 90.4 (C31), 99.0 (C1), 203.9 (C13).

ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 323.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{16}\text{H}_{28}\text{O}_5\text{Na}$ m/z 323.1834, found 323.1824.

Analysis calcd. for $\text{C}_{16}\text{H}_{28}\text{O}_5 \cdot 0.75 \text{H}_2\text{O}$ (300.39): C 61.22, H 9.47; found C 61.15, H 9.09.

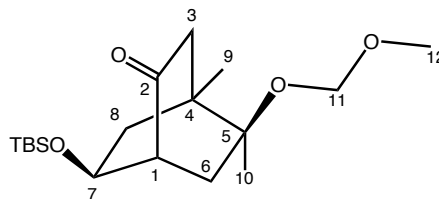


To a stirred solution of **186** (1 g, 2.79 mmol) in a 8:1 mixture of methanol (4 mL) and water (0.5 mL), chilled at 0°C was added potassium carbonate (1.92 mg, 13.95 mmol, 5 eq.). The resulting mixture was stirred at room temperature for 40 minutes. After removing the solvents without heating, dilution with EtOAc and washing with brine till neutral pH, the organic layers were dried over magnesium sulfate, concentrated under reduced pressure and the residue was filtered over silica (heptane-EtOAc 1:1) affording 570 mg (90%) of a mixture of three product. The crude product was directly protected.

tert-butyldimethylsilyl chloride (1.17 g, 7.77 mmol) was added to a solution of imidazole (1.05 g, 15.55 mmol) and the alcohol (555 mg, 2.43 mmol) in *N,N*-dimethylformamide (12 mL) at 0°C . The reaction mixture was stirred for 36 h then diluted with hexane, washed with brine and dried over MgSO_4 . Concentration under reduced

pressure and flash chromatography of the residue gave **315 β** (37%), **315 α** 19% and **316** 23%.

315 β : 7-(tert-Butyl-dimethyl-silanyloxy)-5-methoxymethoxy-4,5-dimethyl-bicyclo[2.2.2]octan-2-one.



Mp: 58.0°C.

$[\alpha]_D^{20} = +2$ (*c* 1.4, CHCl₃).

IR (film): $\nu = 2952, 2856, 1732, 1462, 1361, 1256, 1108, 1064, 1030, 920, 886, 836, 777 \text{ cm}^{-1}$.

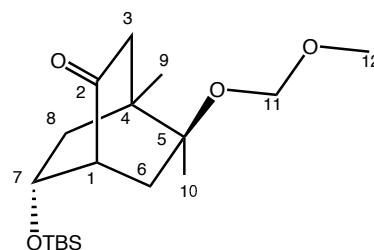
¹H NMR (CDCl₃, 500 MHz): $\delta = 0.00$ (s, 3 H, SiMe), 0.01 (s, 3 H, SiMe), 0.83 (s, 9 H, Si*t*Bu), 0.95 (s, 3 H, H9), 1.20 (s, 3 H, H10), 1.30 (d, *J* = 14.6 Hz, 1 H, H8), 1.40 (d, *J* = 14.7 Hz, 1 H, H6), 1.95 (d, *J* = 18.0 Hz, 1 H, H3), 2.07 (ddd, *J* = 3.0, 8.2, 14.6 Hz, 1 H, H8), 2.21 (dd, *J* = 4.4, 14.7 Hz, 1 H, H6), 2.37 (t, *J* = 4.5 Hz, 1 H, H1), 2.65 (dd, *J* = 2.9, 18.0 Hz, 1 H, H3), 3.28 (s, 3 H, H12), 4.01 (dd, *J* = 4.2, 8.2 Hz, 1 H, H7), 4.63 and 4.68 (ABquartet, *J* = 7.5 Hz, 2 H, H11).

¹³C NMR (CDCl₃, 125 MHz): $\delta = -4.8$ (SiMe), -4.7 (SiMe), 17.9 (C_q-Si*t*Bu), 20.2 (C9), 20.9 (C10), 25.7 (3C-Si*t*Bu), 36.5 (C6), 40.6 (C4), 41.3 (C8), 45.9 (C3), 51.3 (C1), 55.3 (C12), 69.2 (C7), 76.9 (C5), 90.9 (C11), 214.0 (C2).

ESIMS (MeOH): 365.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for C₁₈H₃₄O₄NaSi *m/z* 365.2124, found 365.2125.

Analysis calcd. for C₁₈H₃₄O₄Si · 0.1 CH₂Cl₂ (342.22): C 61.93, H 9.82; found C 61.91, H 9.77.

315 α : 7-(tert-Butyl-dimethyl-silanyloxy)-5-methoxymethoxy-4,5-dimethyl-bicyclo[2.2.2]octan-2-one.



Mp: yellow oil.

$[\alpha]_D^{20} = +5$ (*c* 1.4, CHCl₃).

IR (film): $\nu = 2953, 2885, 1726, 1462, 1377, 1251, 1154, 1120, 1069, 1032, 975, 917, 835$ cm⁻¹.

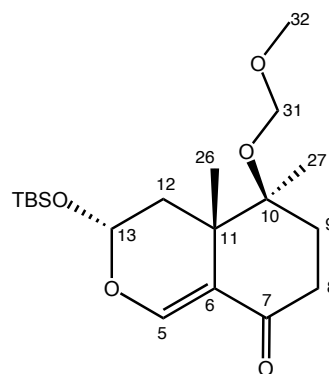
¹H NMR (CDCl₃, 500 MHz): $\delta = 0.01$ (s, 3 H, SiMe), 0.03 (s, 3 H, SiMe), 0.87 (s, 9 H, Si*t*Bu), 0.96 (s, 3 H, H9), 1.38 (s, 3 H, H10), 1.57 - 1.63 (m, 1 H, H8), 1.66 (d, *J* = 18.7 Hz, 1 H, H3), 1.80 (dd, *J* = 9.2, 14.6 Hz, 1 H, H8), 1.98 (dd, *J* = 3.0, 14.4 Hz, 1 H, H6), 2.21 (dd, *J* = 2.0, 14.4 Hz, 1 H, H6'), 2.34 (dd, *J* = 2.7, 5.6 Hz, 1 H, H1), 2.73 (dd, *J* = 3.5, 18.7 Hz, 1 H, H3), 3.31 (s, 3 H, H12), 4.05 (td, *J* = 3.2, 9.3 Hz, 1 H, H7), 4.70 (s, 2 H, H11).

¹³C NMR (CDCl₃, 125 MHz): $\delta = -4.8$ (2C-SiMe), 18.0 (Cq-Si*t*Bu), 20.0 (C9), 20.5 (C10), 25.7 (3C-Si*t*Bu), 32.6 (C6), 40.9 (C4), 42.4 (C8), 45.9 (C3), 53.1 (C1), 55.2 (C12), 65.6 (C7), 77.7 (C5), 90.8 (C11), 215.6 (C2).

ESIMS (MeOH): 365.2 ([*M* + Na]⁺, 100). HRESIMS: calcd. for C₁₈H₃₄O₄Na *m/z* 365.2124, found 365.2125.

Analysis calcd. for C₁₈H₃₄O₄Si (342.22): C 63.11, H 10.00; found C 63.03, H 10.01.

316: 3-(*tert*-Butyl-dimethyl-silanyloxy)-5-methoxymethoxy-4a,5-dimethyl-3,4,4a,5,6,7-hexahydro-isochromen-8-one.



Mp: yellow oil.

$[\alpha]_D^{20} = +57$ (*c* 2.0, CHCl₃).

IR (film): $\nu = 2952, 2888, 1679, 1589, 1253, 1189, 1134, 1092, 1034, 917, 840, 782$, cm⁻¹.

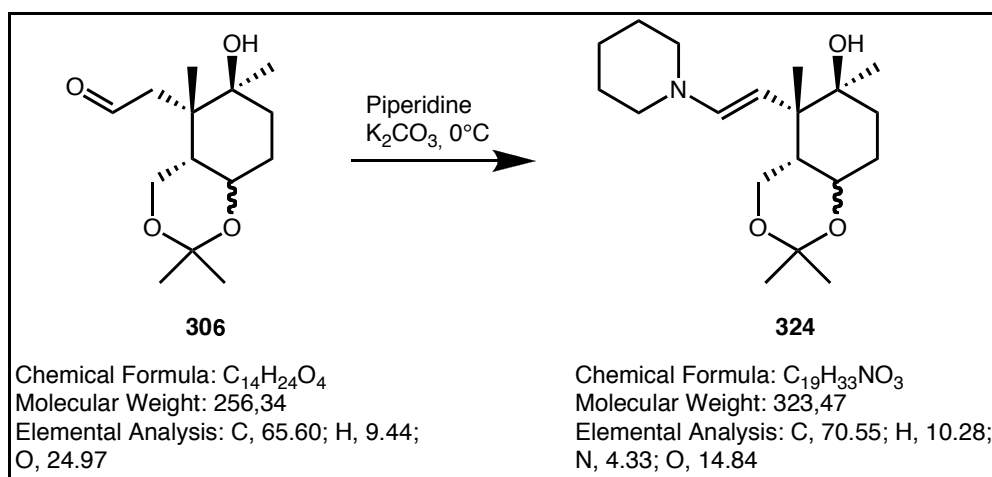
¹H NMR (CDCl₃, 500 MHz): $\delta = 0.15$ (s, 3 H, SiMe), 0.16 (s, 3 H, SiMe), 0.92 (s, 9 H, Si*t*Bu), 1.27 (s, 3 H, H26), 1.36 (s, 3 H, H27), 1.79 - 1.86 (m, 2 H, H12), 1.98 - 2.03 (m, 1 H, H9), 2.23 - 2.36 (m, 2 H, H9', H8), 2.47 - 2.53 (m, 1 H, H8), 3.38 (s, 3 H, H32), 4.71

and 4.81 (ABquartet, 7.5 Hz, 2 H, H31), 5.34 (dd, $J = 3.3, 8.6$ Hz, 1 H, H13), 7.30 (s, 1 H, H5).

^{13}C NMR (CDCl_3 , 125 MHz): $\delta = -5.2$ (SiMe), -4.3 (SiMe), 17.9 (Cq-SitBu), 19.4 (C27), 24.6 (C26), 25.6 (3C-SitBu), 29.8 (C9), 35.6 (C8), 36.3 (C12), 40.6 (C11), 55.3 (C32), 77.8 (C10), 91.0 (C31), 95.1 (C13), 119.1 (C6), 152.1 (C5), 197.9 (C7).

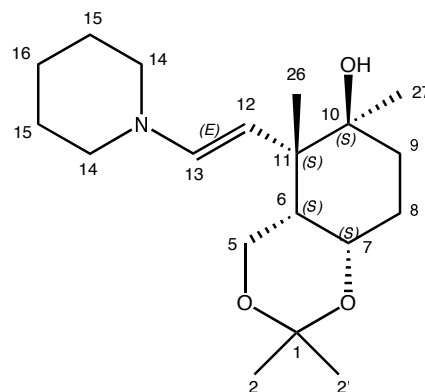
ESIMS (MeOH): 393.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{19}\text{H}_{34}\text{O}_5\text{SiNa}$ m/z 393.2073 , found 393.2062 .

Analysis calcd. for $\text{C}_{19}\text{H}_{34}\text{O}_5\text{Si} \cdot 0.1 \text{CH}_2\text{Cl}_2$ (370.21): C 60.52, H 9.09; found C 60.76, H 9.03.



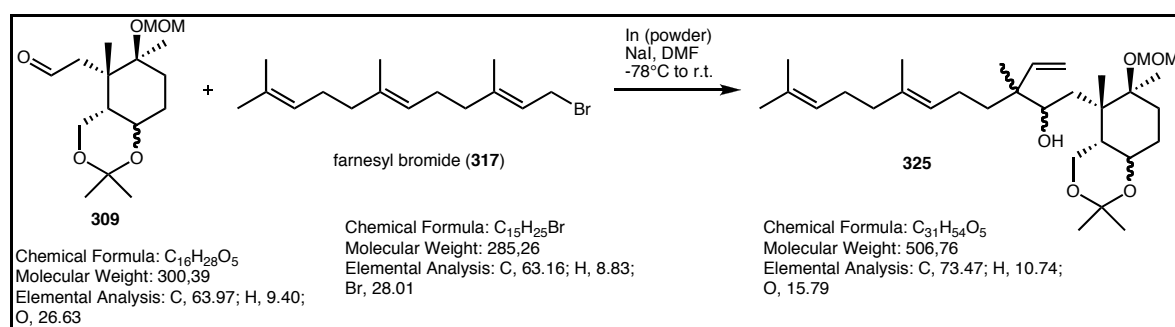
To a mixture of **306** (100 mg, 0.39) in piperidine (0.1 mL, 0.92 mmol), K_2CO_3 (22 mg, 0.16 mmol) was added at 0°C under Ar. The reaction mixture was stirred 18 h at room temperature, then the solution was filtered over silica (ether as eluant), and the solvent was evaporated under reduce pressure to afford 126 mg (100%) of **324**.

324: 2,2,5,6-Tetramethyl-5-(2-piperidin-1-yl-vinyl)-hexahydro-benzo[1,3]dioxin-6-ol.



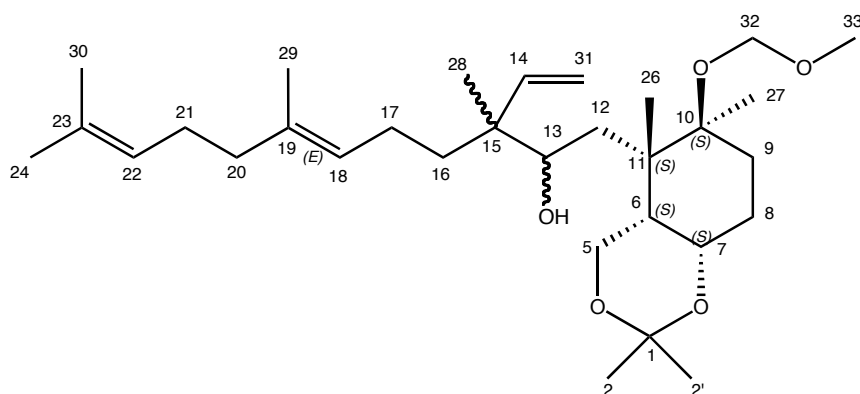
$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ = 0.95 (s, 3 H, H26 or H27), 1.04 (s, 3 H, H26 or H27), 0.98 - 1.25 (m, 3 H, H8, H9, H6), 1.30 (s, 3 H, H2), 1.33 (s, 3 H, H2'), 1.39 - 1.56 (m, 7 H, H9, H15, H16), 1.89 - 2.08 (m, 1 H, H8), 2.45 (bs, 1 H, OH), 2.67 - 2.76 (m, 4 H, H14), 3.69 (dd, J = 2.1, 12.2 Hz, 1 H, H5), 3.86 (dd, J = 5.3, 12.2 Hz, 1 H, H5), 4.06 - 4.11 (m, 1 H, H7), 5.03 (d, J = 14.5 Hz, 1 H, H12), 5.59 (d, J = 14.5 Hz, 1 H, H13).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ = 17.5 (C26), 20.0 (C27), 24.5, 24.9, 25.4, 26.8 (C8 or C9, 2C15, C16), 26.6 (C2), 28.8 (C2'), 31.1 (C8 or C9), 39.6 (C6), 44.0 (C11), 47.0 (C14), 50.5 (C14), 60.8 (C5), 66.2 (C7), 73.9 (C10), 98.4 (C1), 108.5 (C12), 138.2 (C13).



To a solution of farnesyl bromide **299Br** (2.6 mL, 9.54 mmol) in DMF (5.5 mL) at room temperature, under Ar, was added NaI (1.43 g, 9.54 mmol) and indium powder (864 mg, 7.53 mmol). The reaction mixture was stirred for 2 h. Then **309** (1.5 g, 5.02 mmol) in DMF (3.5 mL) was added. The reaction mixture was stirred at r.t. for 19 h. The reaction mixture was diluted with ethyl acetate, and a saturated solution of NH_4Cl was added. Usual work up and chromatography (ethyl acetate/heptane 1:2) afford 1.97 g of **325** (78%, diastereomeric mixture).

325: 1-(6-Methoxymethoxy-2,2,5,6-tetramethyl-hexahydro-benzo[1,3]dioxin-5-yl)-3,7,11-trimethyl-3-vinyl-dodeca-6,10-dien-2-ol.



Mp: colourless oil (characterized as a diastereomeric mixture).

$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

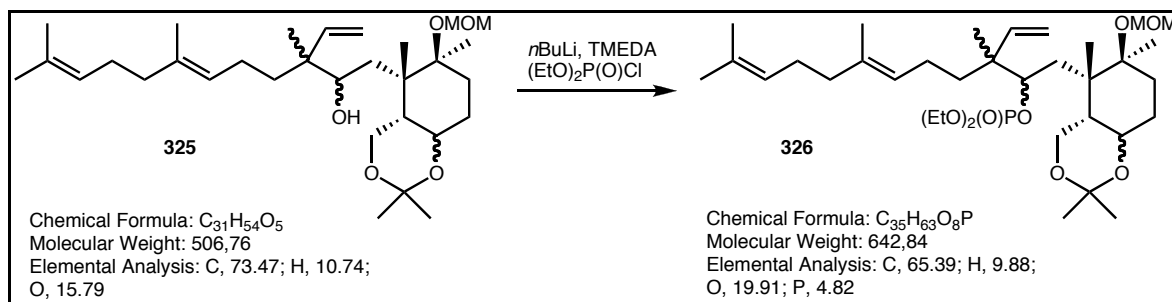
IR (film): $\nu = 2925, 1380, 1197, 1101, 1034, 913 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): δ = characterized as a diastereomeric mixture.

$^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): δ = characterized as a diastereomeric mixture.

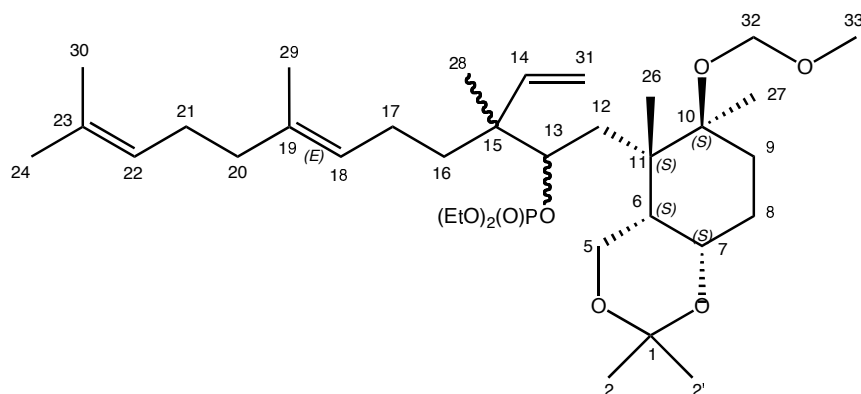
ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 529.3 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{31}\text{H}_{54}\text{O}_5\text{Na}$ m/z 529.3869, found 529.3848.

Analysis calcd. for $\text{C}_{31}\text{H}_{54}\text{O}_5 \cdot 0.25 \text{ H}_2\text{O}$ (506.77): C 72.83, H 10.74; found C 72.82, H 10.82.



To a solution of **325** (607 mg, 1.2 mmol) in THF (4 mL) at -78°C under Ar, TMEDA (0.49 mL, 3.23 mmol) and $n\text{BuLi}$ (0.83 mL, 1.32 mmol) were added. The reaction mixture was stirred 30 min and $(\text{EtO})_2\text{P(O)Cl}$ (0.2 mL, 1.32 mmol) was added. The reaction mixture was stirred at r.t. for 3 h. Water was added and the solvent was evaporated under vacuum. The crude product was diluted with ethyl acetate and washed with water. Usual work up and chromatography (ethyl acetate/heptane 1:6) afford 414 mg of **326** (68%, diastereomeric mixture) and 121 mg of **325** (16%).

326: Phosphoric acid diethyl ester 1-(6-methoxymethoxy-2,2,5,6-tetramethyl-hexahydro-benzo[1,3]dioxin-5-ylmethyl)-2,6,10-trimethyl-2-vinyl-undeca-5,9 -dienyl ester.



Mp: colourless oil (characterized as a diastereomeric mixture).

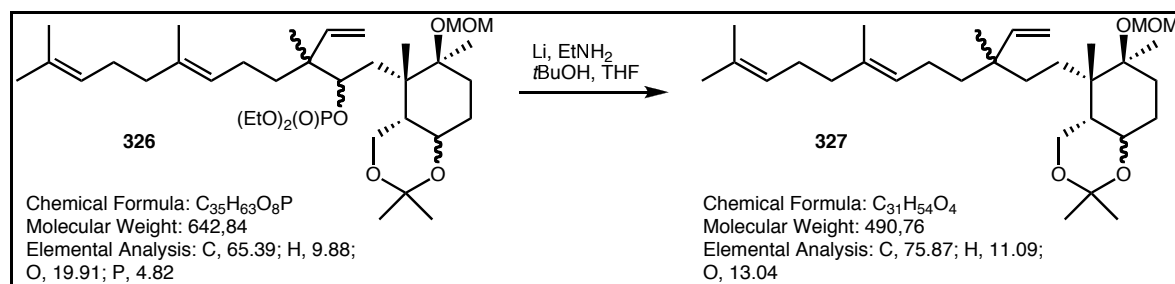
$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

IR (film): $\nu = 3424, 2929, 1454, 1379, 1261, 1198, 1167, 1101, 1033 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): δ = characterized as a diastereomeric mixture.

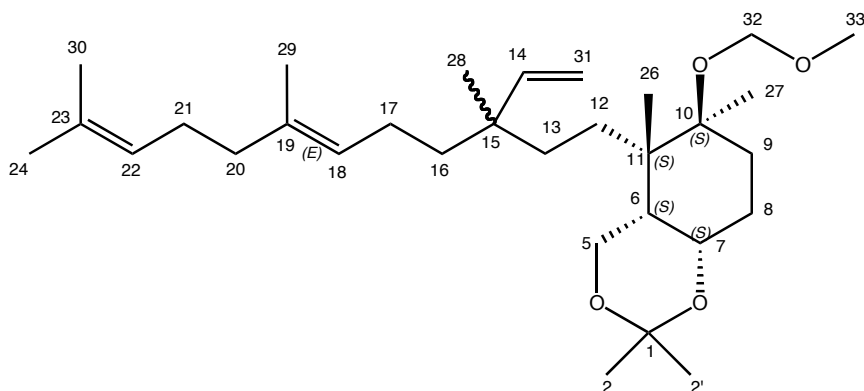
$^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): δ = characterized as a diastereomeric mixture.

ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 665.4 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{35}\text{H}_{63}\text{O}_8\text{PNa}$ m/z 665.4182, found 665.4151.



To a solution of **326** (1.6 g, 2.49 mmol) in THF (2 mL) at -78°C , EtNH_2 (20 mL), $t\text{BuOH}$ (6 mL) and lithium (173 mg, 24.89 mmol) were added. When lithium was added, blue colour appeared. When all the lithium was consumed, the reaction mixture was stirred at -78°C for 30 min. Then ether was added, and the reaction was stirred at r.t. for 1 h. All the solvents were evaporated under reduce pressure. The crude product was diluted with ether, washed with water. The aqueous layer was extracted with ether. Usual work up and chromatography (ethyl acetate/heptane 1:7) afford 1.12 g of **327** (91%, diastereomeric mixture).

327: 6-Methoxymethoxy-2,2,5,6-tetramethyl-5-(3,7,11-trimethyl-3-vinyl-dodeca-6,10-dienyl)-hexahydro-benzo[1,3]dioxine.



Mp: colourless oil (characterized as a diastereomeric mixture)

$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

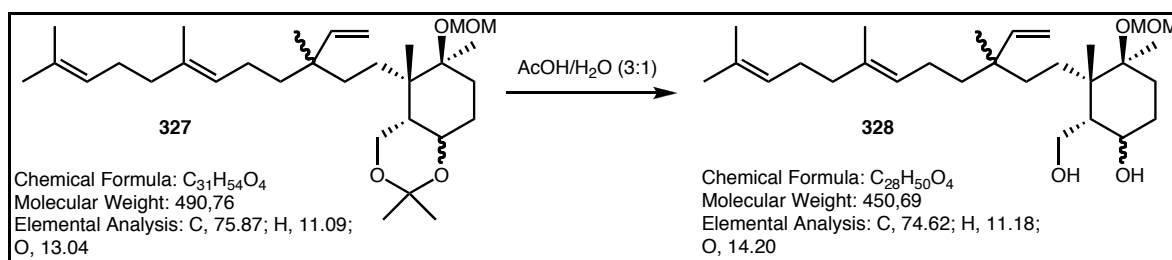
IR (film): ν = 2926, 1454, 1380, 1197, 1168, 1100, 1034, 918 cm^{-1} .

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ = characterized as a diastereomeric mixture.

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ = characterized as a diastereomeric mixture.

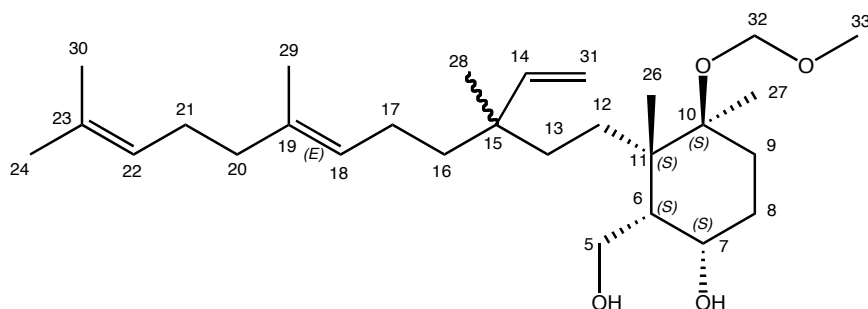
ESIMS (CH_2Cl_2 + MeOH): 513.4 ($[M + \text{Na}]^+$, 55). HRESIMS: calcd. for $\text{C}_{31}\text{H}_{54}\text{O}_4\text{Na}$ m/z 513.3920, found 513.3907.

Analysis calcd. for $\text{C}_{31}\text{H}_{54}\text{O}_4$ (490.76): C 75.87, H 11.09; found C 75.91, H 11.21.



327 (101 mg, 0.206 mmol) was diluted in a mixture of AcOH/ H_2O (1 mL, 3:1) at 0°C . The reaction mixture was stirred at r.t. for 2 h. The reaction mixture was diluted with ethyl acetate, washed with a saturated solution of NaHCO_3 (until pH = 7). Usual work up and chromatography (ethyl acetate/heptane 1:3) afford 79 mg of **328** (85%, diastereomeric mixture).

328: 2-Hydroxymethyl-4-methoxymethoxy-3,4-dimethyl-3-(3,7,11-trimethyl-3-vinyl-dodeca-6,10-dienyl)-cyclohexanol.



Mp: colourless oil (characterized as a diastereomeric mixture).

$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

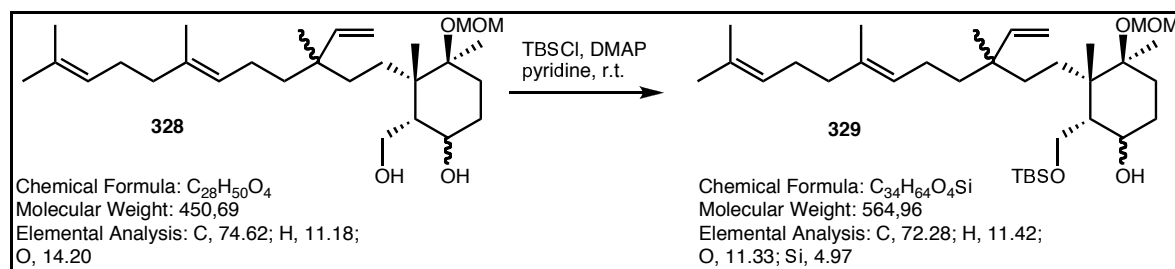
IR (film): $\nu = 3369, 2925, 1450, 1374, 1150, 1100, 1032, 916 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ = characterized as a diastereomeric mixture.

$^{13}\text{C-NMR}$ (CDCl_3 , 62,5 MHz): δ = characterized as a diastereomeric mixture.

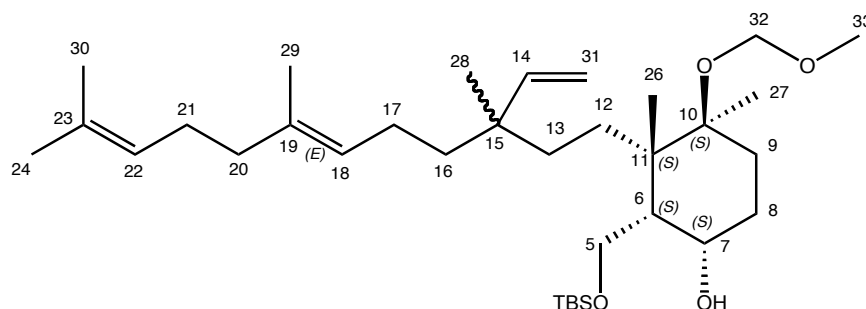
ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 473.3 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{28}\text{H}_{50}\text{O}_4\text{Na}$ m/z 473.3607, found 473.3625.

Analysis calcd. for $\text{C}_{28}\text{H}_{50}\text{O}_4 \cdot 0.5 \text{ H}_2\text{O}$ (450.70): C 73.16, H 11.18; found C 73.17, H 11.11.



To a solution of **328** (365 mg, 0.81 mmol) in CH_2Cl_2 (13 mL), DMAP (316 mg, 2.59 mmol) was added at 0°C . Then TBSCl (196 mg, 1.3 mmol) was added at 0°C under Ar. The reaction mixture was stirred at r.t. for 1.5 h. The reaction mixture was diluted with CH_2Cl_2 (large amount) washed with HCl (1N) and saturated solution of NaHCO_3 . Usual work up and chromatography (ethyl acetate/heptane 1:4) afford 287 mg of **329** (63%, diastereomeric mixture; 33% of SM recovered).

329: 2-(tert-Butyl-dimethyl-silyloxymethyl)-4-methoxymethoxy-3,4-dimethyl-3-(3,7,11-trimethyl-3-vinyl-dodeca-6,10-dienyl)-cyclohexanol.



Mp: colourless oil (characterized as a diastereomeric mixture).

$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

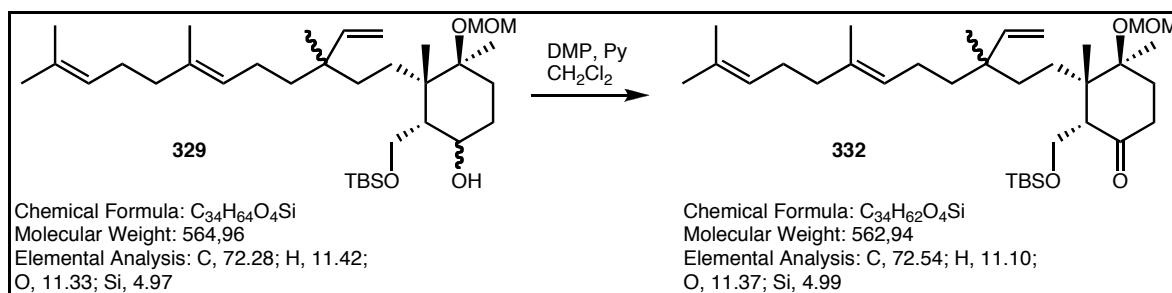
IR (film): $\nu = 2927, 1462, 1254, 1085, 1035, 837, 776 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): δ = characterized as a diastereomeric mixture.

$^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): δ = characterized as a diastereomeric mixture.

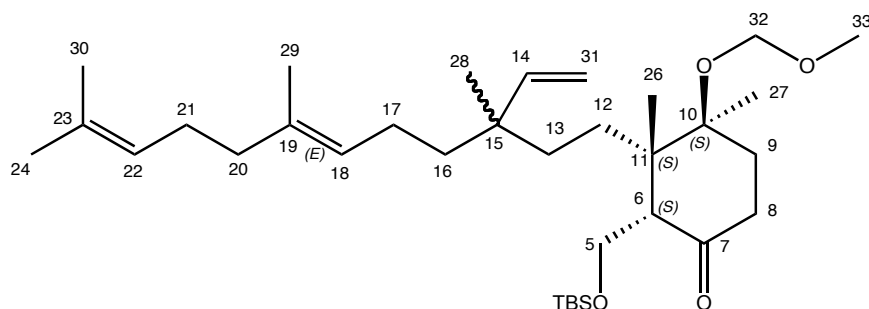
ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 587.4 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{34}\text{H}_{64}\text{O}_4\text{SiNa}$ m/z 587.4472, found 587.4488.

Analysis calcd. for $\text{C}_{34}\text{H}_{64}\text{O}_4\text{Si}$ (565.0): C 72.28, H 11.42; found C 72.41, H 11.62.



To a solution of alcohol **329** (60 mg, 0.106 mmol) in methylene chloride (1 mL) and pyridine (0.09 mL) were added 140 mg (0.329 mmol) of periodinane and stirring continued at room temperature for 1.5 h. The reaction was then diluted with methylene chloride quenched with a saturated aqueous solution of sodium bicarbonate and washed with brine. Usual work up and chromatography (heptane-EtOAc, 7:1) afforded 45 mg (75%) of the ketone **332** (5 mg, 8% of **329** recovered).

332: 2-(tert-Butyl-dimethyl-silyloxymethyl)-4-methoxymethoxy-3,4-dimethyl-3-(3,7,11-trimethyl-3-vinyl-dodeca-6,10-dienyl)-cyclohexanone.



Mp: colourless oil (characterized as a diastereomeric mixture).

$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

IR (film): $\nu = 2927, 2358, 1715, 1462, 1254, 1089, 1030, 836, 775 \text{ cm}^{-1}$.

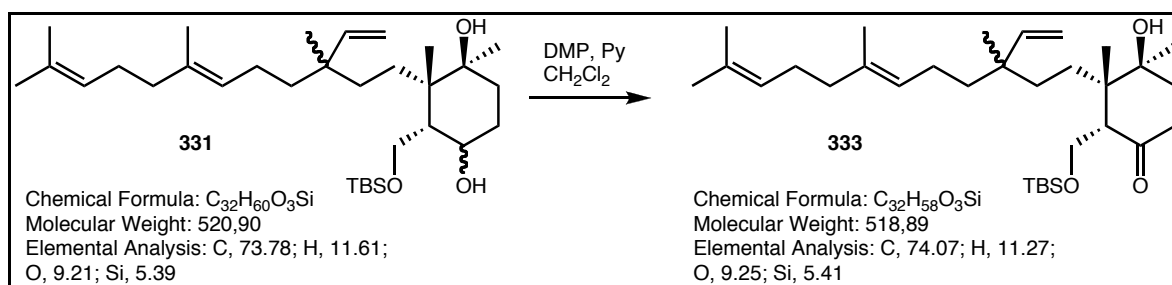
Major product:

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): $\delta = 0.05$ (s, 3 H, SiMe), 0.07 (s, 3 H, SiMe), 0.87 (s, 9 H, Si*t*Bu), 0.89 (s, 3 H, H28), 1.11 (s, 3 H, H26), 1.16 - 1.27 (m, 4 H, H12, H13), 1.20 (s, 3 H, H27), 1.58 (s, 3 H, H29), 1.60 (s, 3 H, H24/30), 1.68 (s, 3 H, H24/30), 1.80 - 1.91 (m, 3 H, H9, H17), 1.92 - 2.00 (m, 2 H, H20), 2.02 - 2.10 (m, 5 H, H9', H16, H21), 2.18 (dd, $J = 3.0, 12.9 \text{ Hz}$, 1 H, H8), 2.55 - 2.65 (m, 1 H, H8'), 3.23 (dd, $J = 3.2, 6.3 \text{ Hz}$, 1 H, H6), 3.43 (s, 3 H, H33), 3.57 (dd, $J = 3.3, 10.0 \text{ Hz}$, 1 H, H5), 4.19 (dd, $J = 7.2, 9.5 \text{ Hz}$, 1 H, H5'), 4.80 and 4.84 (ABquartet, $J = 7.5 \text{ Hz}$, 2 H, H32), 4.87 (d, $J = 1.4 \text{ Hz}$, 1 H, H31), 4.99 (d, $J = 11.2 \text{ Hz}$, 1 H, H31'), 5.06 - 5.11 (m, 2 H, H18, H22), 5.58 (ddd, $J = 6.4, 10.8, 17.4 \text{ Hz}$, 1 H, H14).

$^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): $\delta = -5.4$ (SiMe), -5.2 (SiMe), 16.0 (C29), 17.7 (C24/30), 18.0 (Cq-Si*t*Bu), 18.3 (C26), 19.7 (C27), 21.7 (C15), 22.2 (C28), 22.7 (C17), 25.7 (C24/30), 26.0 (3C-Si*t*Bu), 26.8 (C21), 27.8 (C16), 33.2 (C9), 36.0 (C12), 38.3 (C8), 39.7 (C20), 41.1 (C13), 49.2 (C11), 55.8 (C33), 58.2 (C6), 58.7 (C5), 80.2 (C10), 90.9 (C32), 112.4 (C31), 124.4, 124.7 (C18, C22), 131.3 (C23), 134.8 (C19), 146.5 (C14), 211.4 (C7).

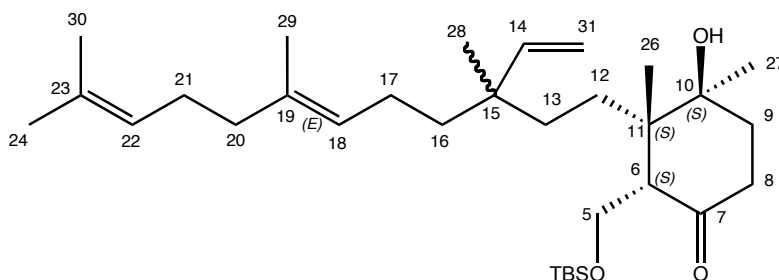
ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 585.4 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{34}\text{H}_{62}\text{O}_4\text{SiNa}$ m/z 585.4315, found 585.4327.

Analysis calcd. for $\text{C}_{34}\text{H}_{62}\text{O}_4\text{Si} \cdot 0.4 \text{ H}_2\text{O}$ (562.96): C 73.30, H 11.43; found C 73.37, H 11.36.



To a solution of alcohol **331** (122 mg, 0.23 mmol) in methylene chloride (1 mL) and pyridine (0.19 mL) were added 293 mg (0.69 mmol) of periodinane and stirring continued at room temperature for 1 h. The reaction was then diluted with methylene chloride quenched with a saturated aqueous solution of sodium bicarbonate and washed with brine. Usual work up and chromatography (heptane-EtOAc, 7:1) afforded 90 mg (76%) of the ketone **333** (two diastereomer, ed = 88%).

333: 2-(tert-Butyl-dimethyl-silyloxymethyl)-4-hydroxy-3,4-dimethyl-3-(3,7,11-trimethyl-3-vinyl-dodeca-6,10-dienyl)-cyclohexanone.



Mp: colorless oil (characterized as a diastereomeric mixture).

$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

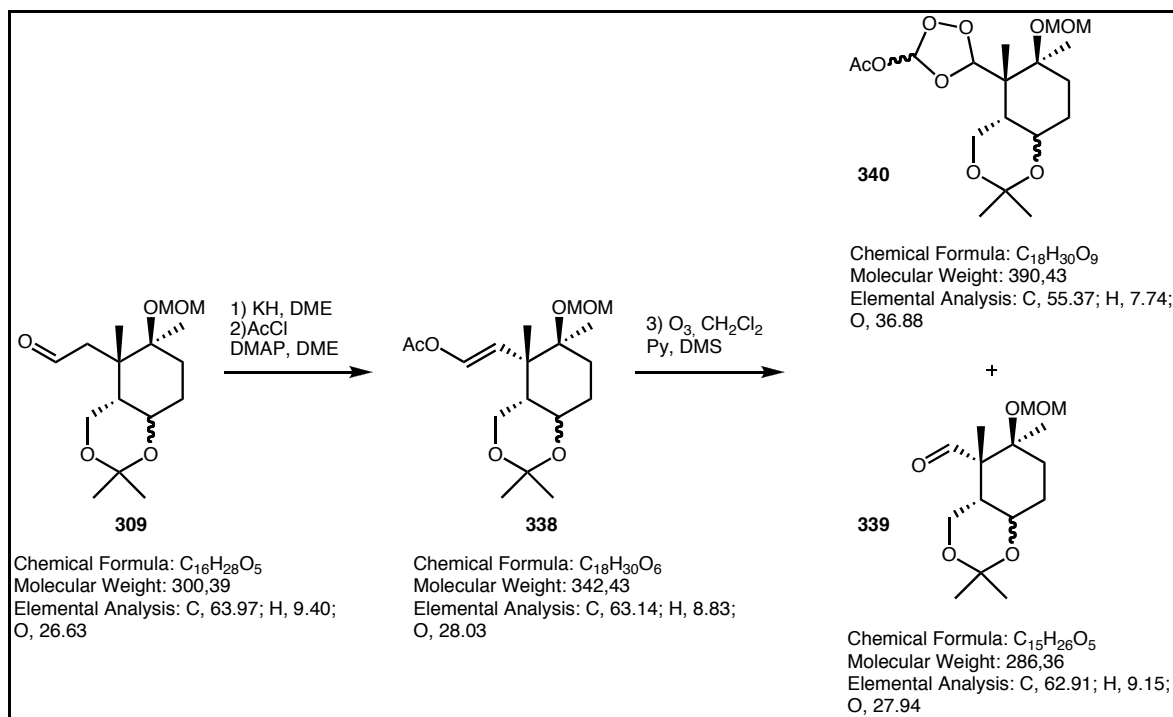
IR (film): $\nu = 3489, 2926, 2358, 1702, 1462, 1375, 1252, 1088, 1004, 911, 836 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ = characterized as a diastereomeric mixture.

$^{13}\text{C-NMR}$ (CDCl_3 , 62,5 MHz): δ = characterized as a diastereomeric mixture.

ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 541.4 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $C_{32}H_{58}O_3SiNa$ m/z 541.4053, found 541.4064.

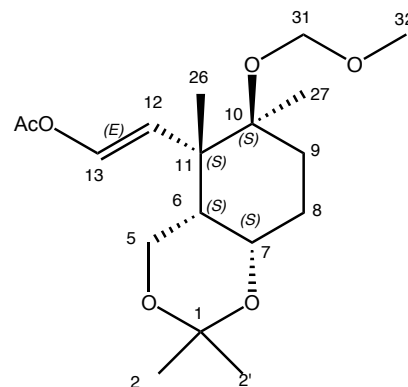
Analysis calcd. for $C_{32}H_{58}O_3Si$ (518.90): C 74.07, H 11.27; found C 74.04, H 11.22.



To a stirred solution of KH (640 mg, 5.59 mmol, 35% in oil, washing with pentane) in DME (5 mL), was added a solution of **309** (516 mg, 1.72 mmol) in DME (5 mL) at -5°C. The mixture was stirred at -5°C for 15 min, and added with a syringe to a suspension of AcCl (0.48 mL, 6.72 mmol) and DMAP (416 mg, 3.41 mmol) in DME (20 mL) at room temperature. The mixture was stirred at r.t. for 20 min, then poured into ice-water mixture, and extracted with heptane. The combined extracts were washed with a saturated solution of NaHCO₃, and worked up as usual to give **338**, which was directly used in the next step.

Ozone was passed into a stirred solution of **338** (550 mg, 1.62 mmol) in 10 mL of methylene chloride and 0.3 mL of pyridine at -78°C until blue color persisted, stirred five additional minutes at this temperature after what 5 mL of Me₂S were added dropwise. The mixture was allowed to reach room temperature within approximately 30 min, concentrated under reduced pressure without heating, and purified through silica gel using heptane-ethyl acetate 5:1 as eluent, to give 162 mg (33%) of aldehyde **339** and 109 mg of ozonide **340** (16%).

338a: Acetic acid 2-(6-Methoxymethoxy-2,2,5,6-tetramethyl-hexahydro-benzo[1,3]dioxin-5-yl)-vinyl ester.



Mp: colourless oil.

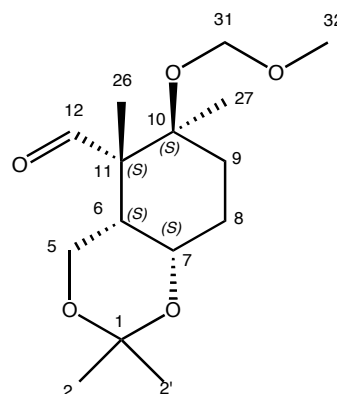
IR (film): $\nu = 2934, 1749, 1377, 1226, 1198, 1108, 1022 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 1.12$ (s, 3 H, H26 or H27), 1.14 (s, 3 H, H26 or H27), 1.37 (s, 3 H, H2), 1.40 (s, 3 H, H2'), 1.53 (dd, $J = 3.9, 6.4$ Hz, 1 H, H9), 1.58 (td, $J = 1.9, 3.8$ Hz, 1 H, H6), 1.63 (ddd, $J = 1.1, 3.4, 4.2$ Hz, 1 H, H8), 1.81 (td, $J = 3.2, 12.4$ Hz, 1 H, H9'), 1.93 (td, $J = 4.9, 9.2$ Hz, 1 H, H8'), 2.08 (s, 3 H, Me-Ac), 3.35 (s, 3 H, H32), 3.78 (d, $J = 12.4$ Hz, 1 H, H5), 3.95 (dd, $J = 4.1, 12.5$ Hz, 1 H, H5'), 4.16 (bs, 1 H, H7), 4.65 and 4.70 (ABquartet, $J = 7.0$ Hz, 2 H, H31), 6.21 (d, $J = 12.7$ Hz, 1 H, H12), 7.02 (d, $J = 12.7$ Hz, 1 H, H13).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 16.4$ (C26), 19.2 (C2), 20.9 (C27), 21.2 (Me-Ac), 26.4, 27.2 (C9, C8), 29.4 (C2'), 39.3 (C6), 44.4 (C11), 55.6 (C32), 61.0 (C5), 66.6 (C7), 78.9 (C10), 90.6 (C31), 98.2 (C1), 122.0 (C12), 134.5 (C13), 168.3 (CO-Ac).

ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 365.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{18}\text{H}_{30}\text{O}_6\text{Na}$ m/z 365.1940, found 365.1932.

339a: 6-methoxymethoxy-2,2,5,6-tetramethyl-hexahydro-benzo[1,3]dioxin-5-carbaldehyde.



Mp: colourless oil.

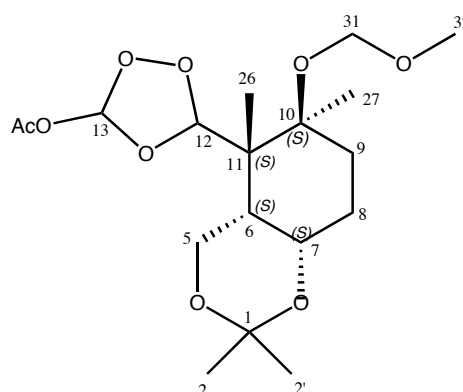
IR (film): $\nu = 3938, 1729, 1454, 1380, 1232, 1198, 1091, 1022, 916 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): $\delta = 1.14$ (s, 3 H, H27), 1.18 (s, 3 H, H26), 1.36 (s, 3 H, H2), 1.44 (s, 3 H, H2'), 1.70 (td, $J = 2.7, 10.1 \text{ Hz}$, 1 H, H9), 1.78 (dd, $J = 2.7, 9.6 \text{ Hz}$, 1 H, H8), 1.80 (d, $J = 3.0 \text{ Hz}$, 1 H, H6), 2.04 (dd, $J = 0.9, 13.2 \text{ Hz}$, 1 H, H8'), 2.07 (d, $J = 3.5 \text{ Hz}$, 1 H, H9'), 3.38 (s, 3 H, H32), 3.81 (ABquartet, $J = 12.6 \text{ Hz}$, 1 H, H5), 3.95 (dABquartet, $J = 3.2, 12.6 \text{ Hz}$, 1 H, H5'), 4.20 (dt, $J = 2.6, 2.9 \text{ Hz}$, 1 H, H7), 4.68 and 4.73 (ABquartet, $J = 7.1 \text{ Hz}$, 2 H, H31), 10.18 (s, 1 H, H12).

$^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): $\delta = 13.4$ (C26), 19.0 (C2), 21.8 (C27), 26.6 (C8), 28.3 (C9), 29.6 (C2'), 41.7 (C6), 55.7 (C32), 56.5 (C11), 60.8 (C5), 66.6 (C7), 90.0 (C31), 90.8 (C10), 98.9 (C1), 205.2 (C12).

ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 309.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{15}\text{H}_{26}\text{O}_5\text{Na}$ m/z 309.1678, found 309.1681.

340: Acetic acid 5-(6-methoxymethoxy-2,2,5,6-tetramethyl-hexahydro-benzo[1,3]dioxin-5-yl)-[1,2,4]trioxolan-3-yl ester.



Mp: colourless oil.

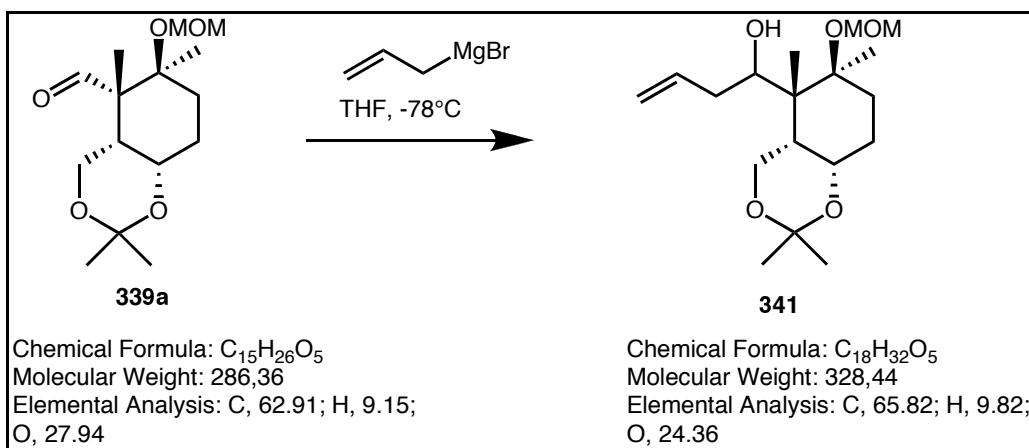
$[\alpha]_D^{20} = +29$ (c 0.72, CHCl_3).

IR (film): $\nu = 2939, 1753, 1456, 1381, 1228, 1132, 1025 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): $\delta = 0.87$ (s, 3 H, H26), 1.27 (s, 3 H, H27), 1.36 (s, 3 H, H2), 1.43 (s, 3 H, H2'), 1.56 (dtd, $J = 2.2, 3.5, 5.7 \text{ Hz}$, 1 H, H8), 1.64 (ddd, $J = 2.4, 3.4, 14.2 \text{ Hz}$, 1 H, H9), 1.68 (t, $J = 2.9 \text{ Hz}$, 1 H, H6), 1.90 - 1.97 (m, 1 H, H8' or H9'), 1.99 - 2.04 (m, 1 H, H8' or H9'), 2.06 (s, 3 H, Me-Ac), 3.34 (s, 3 H, H32), 3.77 (s, 1 H, H12), 3.89 (ABquartet, $J = 12.8 \text{ Hz}$, 1 H, H5), 3.99 (dABquartet, $J = 3.6, 12.8 \text{ Hz}$, 1 H, H5'), 4.14 (s, 1 H, H7), 4.65 and 4.70 (ABquartet, $J = 7.0 \text{ Hz}$, 2 H, H31), 5.58 (s, 1 H, H13).

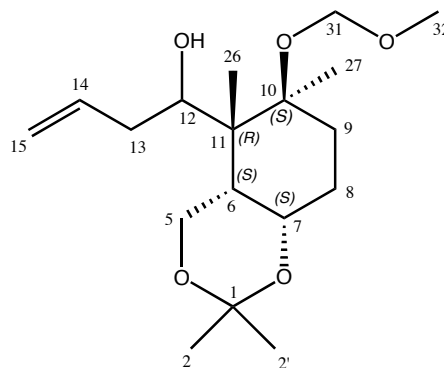
^{13}C -NMR (CDCl_3 , 125 MHz): δ = 12.1 (C26), 18.8 (C2), 21.1 (Me-Ac), 21.4 (C27), 26.5, 26.9 (C8, C9), 29.3 (C2'), 39.1 (C6), 43.5 (C11), 55.6 (C32), 59.5 (C12), 60.7 (C5), 66.6 (C7), 74.4 (C13), 79.4 (C10), 90.2 (C31), 98.5 (C1), 170.9 (CO-Ac).

Analysis calcd. for $\text{C}_{18}\text{H}_{30}\text{O}_9$. 0.45 C_7H_{16} (390.43): C 59.18, H 8.79; found C 59.21, H 8.15.



To a solution of **339a** (109 mg, 0.38 mmol) in THF (1.5 mL) at -78°C under Ar, was added allylmagnesium bromide (1.14 mL, 1M in ether). The reaction mixture was stirred 1 h at -78°C . Then, the reaction mixture was diluted with ether, and a saturated solution of NH_4Cl was added. The aqueous layer was extracted with ether. The combined organic layers were worked up as usual. Flash chromatography (ethyl acetate/heptane 1:4) afforded 65 mg (52%) of **341**.

341: 1-(6-(methoxymethoxy)-2,2,5,6-tetramethylhexahydro-4*H*-benzo[d][1,3]dioxin-5-yl)but-3-en-1-ol.



Mp: colourless oil.

$[\alpha]_D^{20} = +69$ (c 0.7, CHCl_3).

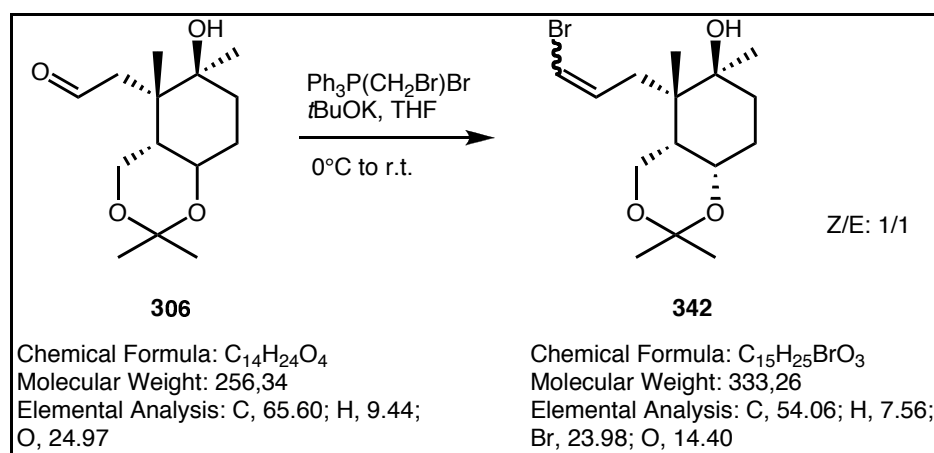
IR (film): $\nu = 3420, 2925, 1384, 1265, 1198, 1093, 1030, 950, 915 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 0.99$ (s, 3 H, H26), 1.22 - 1.30 (m, 1 H, H9), 1.33 (s, 3 H, H27), 1.43 (s, 3 H, H2), 1.47 (s, 3 H, H2'), 1.53 - 1.68 (m, 2 H, H8, H9'), 1.75 - 1.96 (m, 2 H, H6, H8'), 2.38 (s, 2 H, H13), 3.33 (s, 3 H, H32), 3.99 (s, 2 H, H5), 4.15 - 4.22 (m, 2 H, H7, H12), 4.60 and 4.69 (ABquartet, $J = 7.2 \text{ Hz}$, 2 H, H31), 4.88 - 5.11 (m, 2 H, H15), 5.94 (tdd, $J = 6.6, 10.1, 16.8 \text{ Hz}$, 1 H, H14).

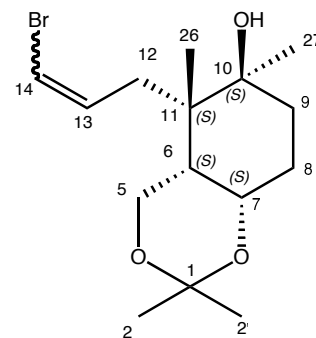
$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 18.7$ (C2), 20.9 (C26), 22.5 (C27), 25.8, 28.9 (C8, C9), 29.4 (C2'), 37.9 (C13), 41.0 (C6), 46.9 (C11), 55.4 (C32), 61.1 (C5), 67.3 (C7), 74.4 (C12), 80.1 (C10), 89.3 (C31), 99.4 (C1), 114.7 (C15), 139.2 (C14).

ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 351.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{18}\text{H}_{32}\text{O}_5\text{Na}$ m/z 351.2147, found 351.2133.

Analysis calcd. for $\text{C}_{18}\text{H}_{32}\text{O}_5$ (328.44): C 65.82, H 9.82; found C 65.91, H 9.94.



$t\text{BuOK}$ (53 mg, 0.47 mmol) and $\text{Ph}_3\text{P}(\text{CH}_2\text{Br})\text{Br}$ (204 mg, 0.47 mmol) was added in the same flask and dry under vacuum. THF (1.5 mL) was added and the yellow solution obtained was stirred 1 h at -50°C . Then the aldehyde **306** (100 mg, 0.39 mmol) in THF (1.5 mL) was added. The reaction mixture was stirred at r.t. for 2.5 h. Then, the mixture was hydrolysed using aqueous NaHCO_3 (5%, 2 mL) and extracted with ethyl acetate. The organic layers was combined, dried over MgSO_4 and evaporated. A flash chromatography (ethyl acetate/heptane 4:6) afforded 57 mg (44%) of **342** (35% of SM recovered).

342: 5-(3-Bromo-allyl)-2,2,5,6-tetramethyl-hexahydro-benzo[1,3]dioxin-6-ol.

Mp: colourless oil (characterized as a diastereomeric mixture).

$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

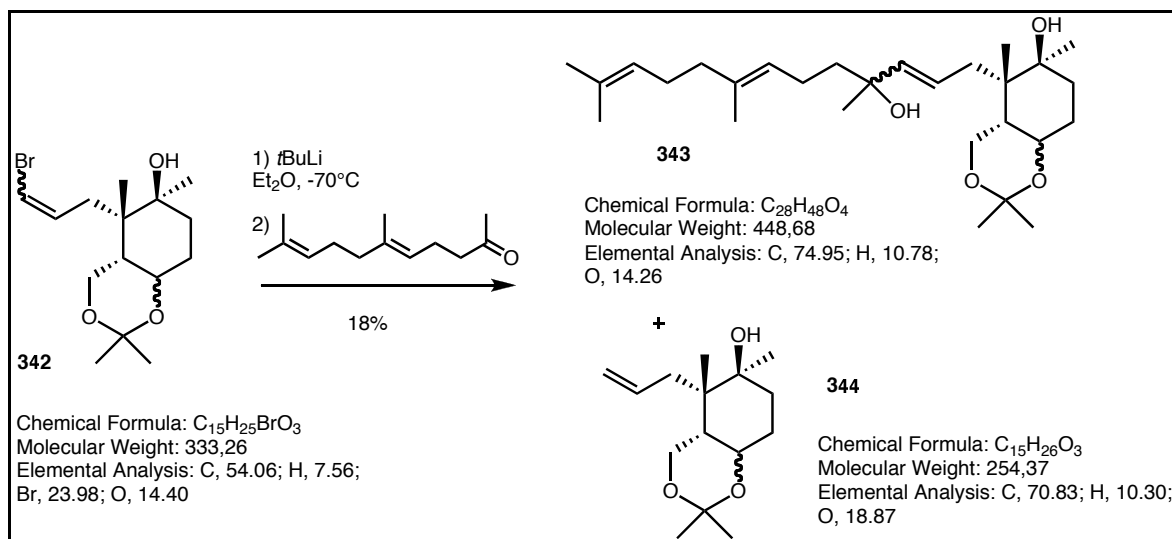
IR (film): ν = 3476, 2986, 2934, 1615, 1453, 1380, 1196, 1163, 1095, 1024, 902, 845 cm^{-1} .

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ = characterized as a diastereomeric mixture.

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ = characterized as a diastereomeric mixture.

Mass spectrum can be obtained only for the product without the acetone:

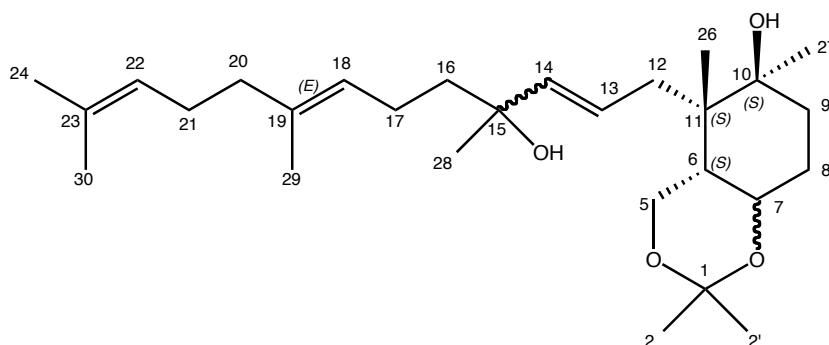
ESIMS ($\text{MeOH} + \text{CH}_2\text{Cl}_2$): 315.1 ($[M + \text{Na}]^+$, 100), 317.1 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{12}\text{H}_{21}\text{BrO}_3\text{Na}$ m/z 315.0572 and 315.0551, found 315.0573 and 317.0561.



To a solution of **342** (100 mg, 0.3 mmol) in anhydrous ether (1.5 mL) at -70°C , was added a solution of $t\text{BuLi}$ (0.37 mL, 0.63 mmol). After 1.5 h at -70°C , a solution of geranylacetone **300** (87 mg, 0.45 mmol) in anhydrous ether (1 mL) was added. The mixture was warmed to 0°C and stirred for 2 h. The solution was diluted with ether and

usual work up and chromatography (ethyl acetate/heptane 3:7) afford 24 mg of **343** (18%) and 10 mg of **GG344** (13%).

343: 5-(4-Hydroxy-4,8,12-trimethyl-trideca-2,7,11-trienyl)-2,2,5,6-tetramethyl-hexahydro-benzo[1,3]dioxin-6-ol.



Mp: colourless oil (characterized as a diastereomeric mixture).

$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

IR (film): $\nu = 3455, 2926, 2360, 1453, 1381, 1198, 1095, 1026, 668 \text{ cm}^{-1}$.

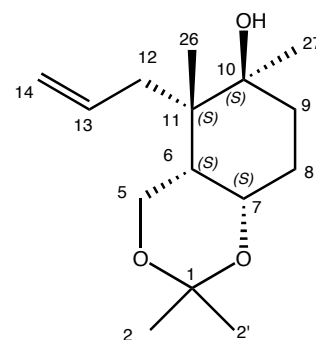
Major product.

$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): $\delta = 1.06$ (s, 3 H, H26), 1.27 (s, 3 H, H27), 1.30 (td, $J = 2.4, 7.5$ Hz, 1 H, H8), 1.35 (s, 3 H, H28), 1.40 (s, 3 H, H2), 1.45 (s, 3 H, H2'), 1.52 (t, $J = 3.6$ Hz, 1 H, H6), 1.60 (s, 6 H, H29, H30), 1.58 - 1.68 (m, 4 H, H9, H16), 1.68 (s, 3 H, H24), 1.97 (dd, $J = 6.6, 9.0$ Hz, 2 H, H20), 2.02 - 2.13 (m, 5 H, H8', H17, H21), 2.95 (dddd, $J = 1.5, 6.2, 9.2, 16.0$ Hz, 1 H, H12), 3.05 (ddd, $J = 2.5, 5.5, 16.7$ Hz, 1 H, H12), 4.02 (d, $J = 12.5$ Hz, 1 H, H5), 4.06 (dd, $J = 3.9, 12.6$ Hz, 1 H, H5'), 4.15 - 4.17 (m, 1 H, H7), 5.08 (t, $J = 6.8$, 1 H, H18 or H22), 5.14 (t, $J = 7.1$ Hz, 1 H, H18 or H22), 5.34 (dddd, $J = 1.5, 2.4, 5.3, 12.1$ Hz, 1 H, H14), 5.62 (dddd, $J = 1.5, 5.5, 9.3, 12.1$ Hz, 1 H, H13).

$^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): $\delta = 16.0, 17.7$ (C29, C30), 18.3 (C26), 19.0 (C2), 22.9 (C17), 25.7 (C24), 26.4 (C9), 26.7 (C19), 27.4 (C27), 29.2 (C28), 29.7 (C2'), 30.8 (C8), 32.7 (C12), 39.7 (C6, C20), 42.4 (C11), 43.8 (C16), 61.4 (C5), 67.0 (C7), 73.9 (C15), 75.1 (C10), 98.3 (C1), 124.3 (C18, C22), 130.3 (C13), 131.3 (C23), 134.8 (C14), 135.3 (C19).

ESIMS (CH_2Cl_2): 471.4 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{28}\text{H}_{48}\text{O}_4\text{Na}$ m/z 471.3450, found 471.3490.

Analysis calcd. for $\text{C}_{28}\text{H}_{48}\text{O}_4 \cdot 0.95 \text{ H}_2\text{O}$ (448.68): C 72.20, H 10.80; found C 72.17, H 10.49.

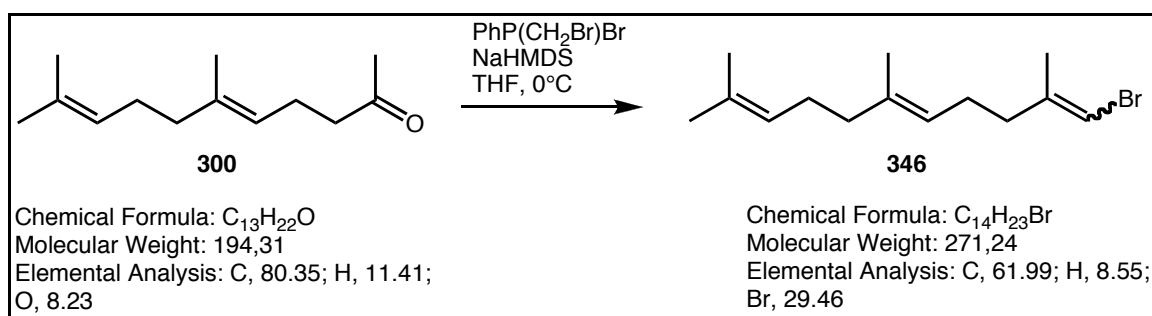
344: 5-Allyl-2,2,5,6-tetramethyl-hexahydro-benzo[1,3]dioxin-6-ol.

Mp: 112 - 113°C

[α]_D²⁰ = + 59 (*c* 1.1, CHCl₃).IR (film): ν = 3467, 2935, 1453, 1378, 1231, 1202, 1075, 1025, 907, 845 cm⁻¹.

¹H-NMR (CDCl₃, 500 MHz): δ = 0.93 (s, 3 H, H26), 1.18 (s, 3 H, H27), 1.25 (ddd, *J* = 2.6, 4.3, 13.7 Hz, 1 H, H9), 1.31 (s, 3 H, H2), 1.39 (s, 3 H, H2'), 1.48 (s, 1 H, H6), 1.53 (ddd, *J* = 2.2, 4.9, 5.8 Hz, 1 H, H8), 1.95 (dd, *J* = 4.2, 13.9 Hz, 1 H, H9'), 2.04 (tt, *J* = 4.5, 13.8 Hz, 1 H, H8'), 2.32 (dd, *J* = 8.9, 15.2 Hz, 1 H, H12), 2.94 (tdd, *J* = 1.8, 5.6, 15.2 Hz, 1 H, H12'), 3.92 (ABquartet, *J* = 12.6 Hz, 1 H, H5) and 3.98 (dABquartet, *J* = 3.9, 12.6 Hz, 1H, H5'), 4.09 (bs, 1 H, H7), 4.87 (dddd, *J* = 0.7, 1.7, 2.5, 10.1 Hz, 1 H, H14), 4.92 (dddd, *J* = 1.1, 2.0, 2.5, 17.0 Hz, 1 H, H14'), 6.04 (dddd, *J* = 5.6, 8.9, 10.0, 17.0 Hz, 1 H, H13).

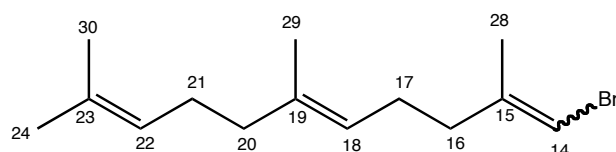
¹³C-NMR (CDCl₃, 125 MHz): δ = 18.6 (C26), 19.1 (C2), 26.5 (C8), 27.2 (C27), 29.7 (C2'), 30.9 (C9), 39.2 (C6), 39.9 (C12), 42.4 (C11), 61.2 (C5), 67.0 (C7), 74.9 (C10), 98.2 (C1), 115.5 (C14), 138.6 (C13).

Analysis calcd. for C₁₅H₂₆O₃ · 0.6 H₂O (254.37): C 67.94, H 10.34; found C 67.98, H 9.95.

To a suspension of Ph₃P(CH₂Br)Br (5.315 g, 12.19 mmol) in THF (10 mL) was added a solution of NaHMDS (12.19 mL, 1M in THF) at 0°C under Ar. The mixture was

stirred at the same temperature for 1 h. To the mixture was added a solution of geranyl acetone **300** (1.184 g, 6.09 mmol) in THF (5 mL) at 0°C, and the resulting mixture was stirred at the 0°C for 2.5 h. The solvent was evaporated. The crude product was diluted with pentane, filtrated and the solvent was evaporated under reduce pressure (many times) to afforded 1.5 g of an orange oil **346** (91%).

346: 1-Bromo-2,6,10-trimethyl-undeca-1,5,9-triene.



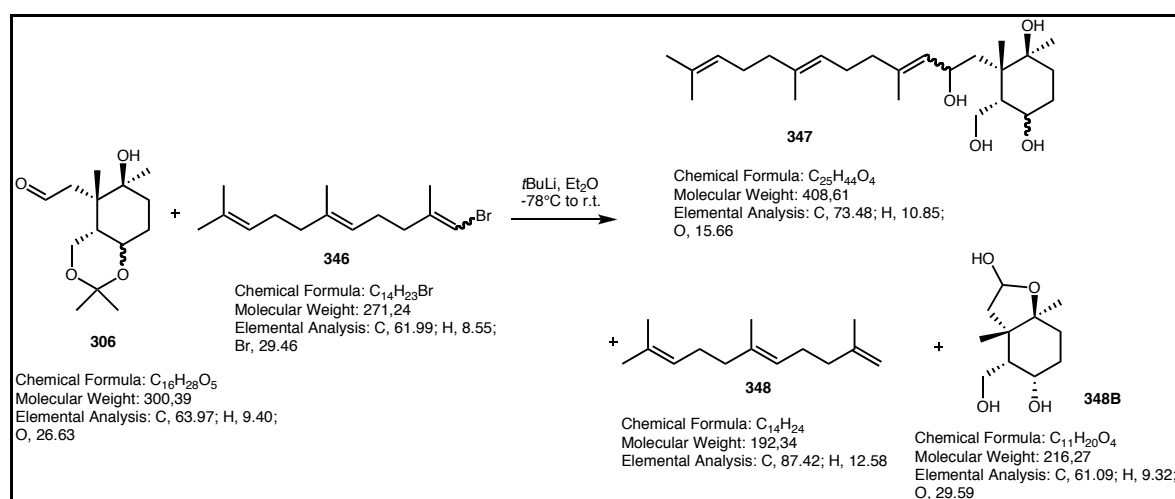
Mp: orange oil.

IR (film): 2915, 1438, 1376, 1281, 1108, 770, 714, 695 cm^{-1} .

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 1.60, 1.61, 1.69$ (s, 9 H, H24, H29, H30), 1.80 (s, 3 H, H28), 1.95 - 2.25 (m, 8 H, H16, H17, H20, H21), 5.05 - 5.15 (m, 2 H, H18, H22), 5.89 (s, 1 H, H14).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 16.0, 17.7$ (C24, C30), 19.1 (C28), 26.1 (C29), 25.7, 26.7, 38.4, 39.7 (C16, C17, C20, C21), 101.3 (C14), 123.0, 124.2 (C18, C22), 131.4, 136.1, 141.5 (C15, C19, C23).

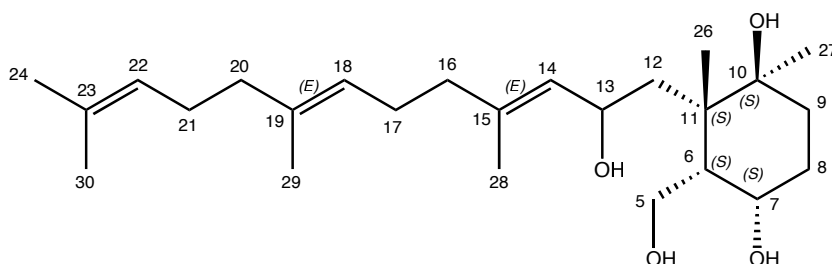
Analysis calcd. for $\text{C}_{14}\text{H}_{23}\text{Br}$ (271.24): C 61.99, H 8.55; found C 61.84, H 8.65.



To a solution of bromide **346** (633 mg, 2.73 mmol) in anhydrous ether (3 mL) at -70°C , was added a solution of *t*BuLi (3.22 mL, 1.7M in pentane). After 1.5 h at -70°C , a

solution of aldehyde **306** (200 mg, 0,78 mmol) in anhydrous ether (2 mL) was added. The mixture was warmed to 0°C and stirred for 2 h. Then TMSCl (1 mL, 7.8 mmol) was added and the reaction was stirred for 1 h. Usual work up and chromatography (heptane and then ethyl acetate/heptane 1:4) afford 13 mg of **347** (8%) (93 mg, 55% of lactol **348B** recovered).

347: 3-Hydroxymethyl-2-(2-hydroxy-4,8,12-trimethyl-trideca-3,7,11-trienyl)-1,2-dimethyl-cyclohexane-1,4-diol.



Mp: colourless oil (characterized as a diastereomeric mixture).

$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

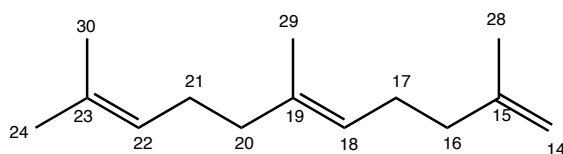
IR (film): $\nu = 3458, 2921, 1438, 1375, 1076, 1020 \text{ cm}^{-1}$.

Major product.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 1.14$ (s, 3 H, H27), 1.21 (s, 3 H, H26), 1.24 - 1.34 (m, 1 H, H8), 1.39 (s, 1 H, H6), 1.52 - 1.58 (m, 1 H, H9), 1.59 (s, 3 H, H29 or H24/30), 1.60 (s, 3 H, H29 or H24/30), 1.68 (s, 3 H, H24/30 or H28), 1.69 (s, 3 H, H24/30 or H28), 1.92 (dd, $J = 3.9, 13.1$ Hz, 1 H, H9'), 1.94 - 2.12 (m, 8 H, H16, H17, H20, H21), 2.22 (dt, $J = 3.8, 14.0$ Hz, 1 H, H8'), 3.15 - 3.17 (m, 1 H, H12), 3.36 - 3.42 (m, 1 H, H12'), 3.99 (dd, $J = 3.1, 8.6$ Hz, 1 H, H5), 4.10 (dd, $J = 3.0, 12.1$ Hz, 1 H, H5'), 4.17 (q, $J = 3.0$ Hz, 1 H, H7), 4.41 (ddd, $J = 3.1, 7.9, 11.3$ Hz, 1 H, H13), 5.07 - 5.11 (m, 2 H, H18, H22), 5.15 (dd, $J = 1.1, 8.0$ Hz, 1 H, H14).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 16.1, 16.9, 18.1, 25.7$ (C24, C28, C29, C30), 17.7 (C26), 24.7 (C27), 26.3, 26.8 (C20, C21), 27.3 (C9), 30.1 (C8), 38.2, 39.7 (C16, C17), 39.4 (C6), 41.9 (C11), 48.0 (C12), 69.6 (C5), 71.2 (C13), 72.3 (C7), 73.8 (C10), 123.7, 124.4, 125.2 (C14, C18, C22), 131.3 (C23), 135.4 (C19), 139.4 (C15).

ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 413.3 ($[M + \text{Na} - \text{H}_2\text{O}]^+$, 100). HRESIMS: calcd. for $\text{C}_{25}\text{H}_{42}\text{O}_3\text{Na}$ m/z 413.3032, found 413.3051.

348: 2,6,10-Trimethyl-undeca-1,5,9-triene.

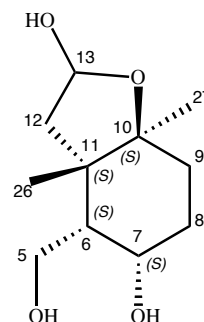
Mp: colourless oil.

IR (film): 2932, 1714, 1454, 1376, 1161, 1070 cm^{-1} .

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): δ = 1.62 (s, 6 H, H24/30, H29), 1.70 (s, 3 H, H24/30), 1.74 (s, 3 H, H28), 1.96 - 2.20 (m, 8 H, H16, H17, H20, H21), 4.70 (s, 1 H, H14), 4.72 (s, 1 H, H14'), 5.07 - 5.17 (m, 2 H, H18, H22).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): δ = 16.0 (C29), 17.7 (C24/30), 22.5 (C28), 25.7 (C24/30), 26.2 (C17), 26.7 (C21), 37.9 (C16), 39.7 (C20), 109.8 (C14), 124.1, 124.4 (C18, C22), 131.2 (C23), 135.1 (C19), 145.8 (C15).

Analysis calcd. for $\text{C}_{14}\text{H}_{24} \cdot 0.7 \text{H}_2\text{O}$ (192.34): C 82.04, H 12.49; found C 82.16, H 12.02.

348B: 4-Hydroxymethyl-3a,7a-dimethyl-octahydro-benzofuran-2,5-diol.

Mp: 82.0 - 83.0°C.

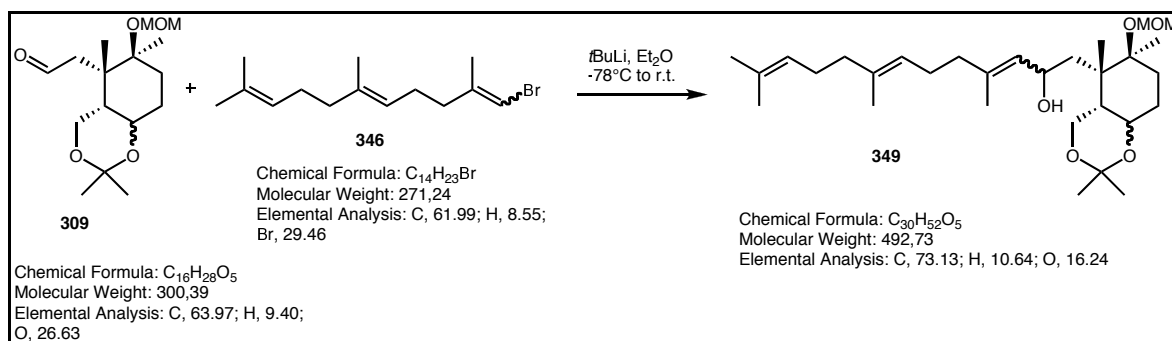
$[\alpha]_D^{20} = -13$ (c 0.82, CHCl_3).

IR (film): ν = 3418, 2938, 2887, 1453, 1376, 1326, 1177, 1102, 983, 966, 927, 839 cm^{-1} .

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz): δ = 1.20 (s, 3 H, H27), 1.21 (s, 3 H, H26), 1.40 (dd, J = 5.4, 14.0 Hz, 1 H, H9), 1.63 (d, J = 14.1 Hz, 1 H, H12), 1.72 (d, J = 13.8 Hz, 1 H, H8), 1.80 (dd, J = 4.2, 13.8 Hz, 1 H, H8'), 1.86 (s, 1 H, H6), 1.89 (d, J = 2.2 Hz, 1 H, H12'), 2.01 (td, J = 13.6, 5.3 Hz, 1 H, H9'), 3.94 (dd, J = 1.9, 9.2 Hz, 1 H, H5), 4.24 (s, 1 H, H7), 4.30 (d, J = 9.2 Hz, 1 H, H5'), 4.94 (s, 1 H, H13).

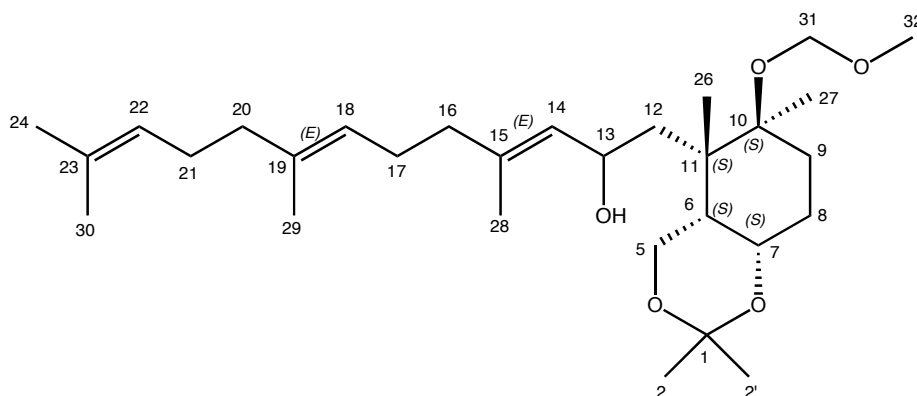
$^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz): 20.3 (C26), 24.7 (C27), 26.6 (C8), 31.7 (C9), 33.8 (C6), 35.7 (C11), 41.3 (C12), 65.7 (C5), 72.9 (C7), 73.7 (C10), 90.9 (C13).

Analysis calcd. for $\text{C}_{11}\text{H}_{20}\text{O}_4 \cdot 0.15 \text{C}_7\text{H}_{16}$ (216.27): C 62.57, H 9.76; found C 62.89, H 9.21.



To a solution of bromide **346** (2.8 g, 10.49 mmol) in ether (10 mL) at -78°C , under Ar, was added *t*BuLi (10.8 mL, 1.7M in pentane). The reaction mixture was stirred 1.5 h at -78°C , and aldehyde **309** (1.5 g, 4.99 mmol) in ether (5 mL) was added. The reaction mixture was stirred 2.5 h at r.t. At 0°C , ether was added and the reaction mixture was quenched with a saturated solution of ammonium chloride. Usual work up and chromatography (ethyl acetate/heptane 0:1 to 1:1) afford 1.37 g of **349** (56%).

349: 1-(6-Methoxymethoxy-2,2,5,6-tetramethyl-hexahydro-benzo[1,3]dioxin-5-yl)-4,8,12-trimethyl-trideca-3,7,11-trien-2-ol.



Mp: colourless oil (characterized as a diastereomeric mixture).

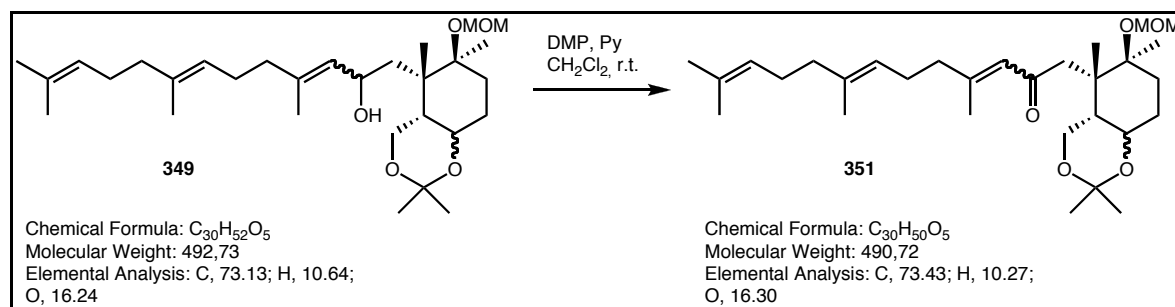
$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

IR (film): $\nu = 3483, 2926, 1455, 1376, 1211, 1149, 1098, 1035, 917 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl₃, 500 MHz): δ = characterized as a diastereomeric mixture.

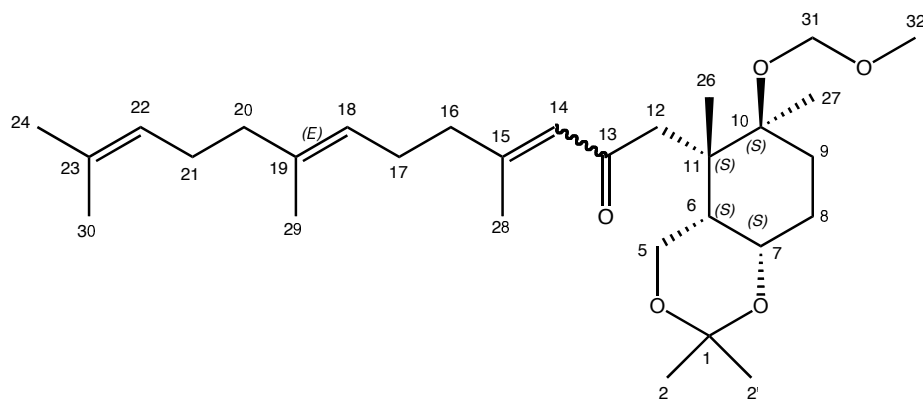
$^{13}\text{C-NMR}$ (CDCl₃, 125 MHz): δ = characterized as a diastereomeric mixture.

ESIMS (MeOH): 515.3 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for C₃₀H₅₂O₅Na m/z 515.3712, found 515.3722.



To a solution of alcohol **349** (585 mg, 1.19 mmol) in methylene chloride (5 mL) and pyridine (0.96 mL) were added 1.51 g (3.56 mmol) of periodinane and stirring continued at room temperature for 1 h. The reaction was then diluted with methylene chloride quenched with a saturated aqueous solution of sodium bicarbonate and washed with brine. Usual work up and chromatography (heptane-EtOAc, 7:1) afforded 234 mg (40%) of the ketone **351** (199 mg, 34% of SM recovered).

351: 1-(6-methoxymethoxy-2,2,5,6-tetramethyl-hexahydro-benzo[1,3]dioxin-5-yl)-4,8,12-trimethyl-trideca-3,7,11-trien-2-one.



Mp: colourless oil (characterized as a diastomeric mixture).

$[\alpha]_D^{20}$ = characterized as a diastomeric mixture.

IR (film): $\nu = 2927, 2360, 1698, 1616, 1456, 1381, 1197, 1168, 1103, 1034 \text{ cm}^{-1}$.

Major diastereomer:

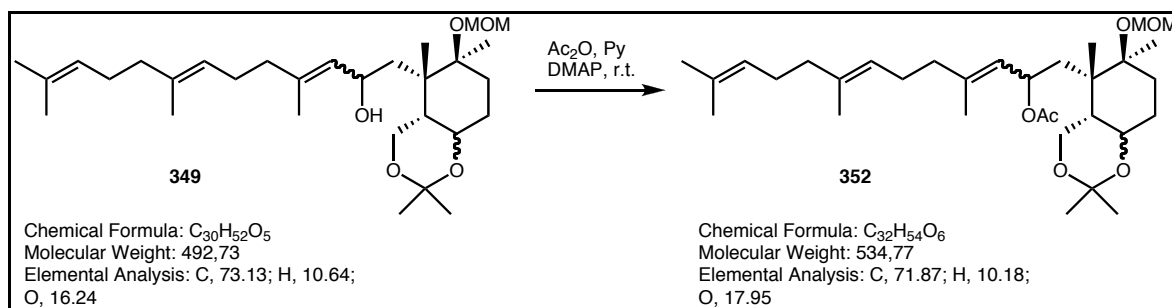
¹H-NMR (CDCl₃, 500 MHz): $\delta = 1.17$ (s, 3 H, H26), 1.35 (s, 3 H, H2), 1.37 (s, 3 H, H27), 1.44 (s, 3 H, H2'), 1.51 - 1.55 (m, 1 H, H9), 1.55 (d, $J = 3.9 \text{ Hz}$, 1 H, H6), 1.57 (s, 3 H, H24/30 or H29), 1.60 (s, 6 H, H28, H24/30 or H29), 1.68 (s, 3 H, H24/30 or H29), 1.88 - 1.93 (m, 2 H, H17), 2.05 (t, $J = 7.3 \text{ Hz}$, 1 H, H9'), 2.08 - 2.18 (m, 8 H, H8, H16, H20,

H21), 2.75 (d, $J = 16.7$ Hz, 1 H, H12), 3.35 (s, 3 H, H32), 3.36 (d, $J = 16.6$ Hz, 1 H, H12'), 4.00 (ddd, $J = 4.1, 12.5$ Hz, 1 H, H5), 4.14 (d, $J = 2.5$ Hz, 1 H, H7), 4.19 (d, $J = 12.7$ Hz, 1 H, H5'), 4.63 and 4.70 (ABquartet, $J = 7.0$ Hz, 2 H, H31), 5.06 - 5.11 (m, 2 H, H18, H22), 6.07 (s, 1 H, H14).

^{13}C -NMR (CDCl_3 , 125 MHz): $\delta = 16.0, 17.7, 25.7$ (C24, C30, C29), 18.1 (C27), 18.9 (C2), 19.2 (C28), 21.1 (C26), 25.8, 26.1 (C20, C21), 26.5 (C9), 26.7 (C8), 29.9 (C2'), 39.2 (C6), 39.7 (C17), 41.2 (C16), 44.2 (C11), 48.4 (C12), 55.4 (C32), 61.3 (C5), 67.1 (C7), 80.3 (C10), 90.5 (C31), 98.2 (C1), 123.1, 124.3 (C18, C22), 125.8 (C14), 131.4, 136.0 (C19, C23), 156.0 (C15), 201.3 (C13).

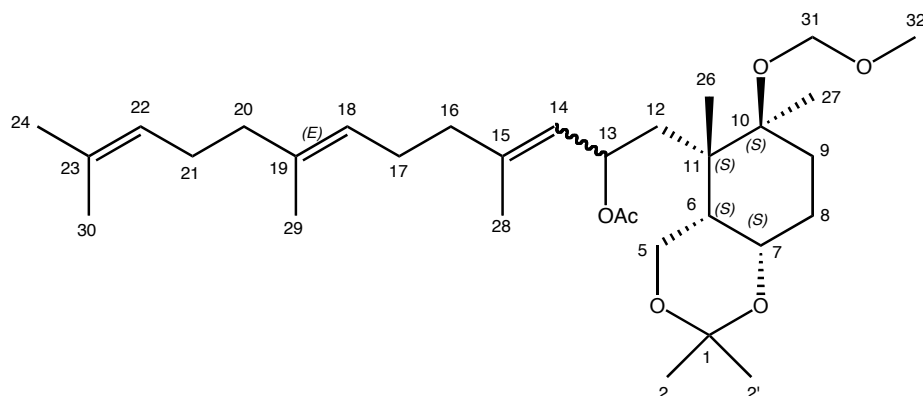
ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 513.3 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{30}\text{H}_{50}\text{O}_5\text{Na}$ m/z 513.3556, found 513.3541.

Analysis calcd. for $\text{C}_{30}\text{H}_{50}\text{O}_5$ (490.72): C 73.43, H 10.27; found C 73.11, H 10.21.



Anhydride acetic (1.23 mL) was added to a mixture of alcohol **349** (644 mg, 1.31 mmol) and DMAP (cat.) in pyridine (5.3 mL) at 0 °C under argon. After 1 h, the mixture was diluted with CH_2Cl_2 and washed with dilute hydrochloric acid, saturated sodium bicarbonate, water, brine and dried (MgSO_4). The solvent was evaporated under reduced pressure and the residue was chromatographed (SiO_2 , heptane-EtOAc, 7:1) to give 626 mg (89%) of **352**.

352: Acetic acid 1-(6-methoxymethoxy-2,2,5,6-tetramethyl-hexahydro-benzo[1,3]dioxin-5-ylmethyl)-3,7,11-trimethyl-dodeca-2,6,10-trienyl ester.



Mp: colourless oil (characterized as a diastereomeric mixture).

$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

IR (film): $\nu = 2926, 2360, 1728, 1452, 1370, 1240, 1197, 1114, 1023, 935 \text{ cm}^{-1}$.

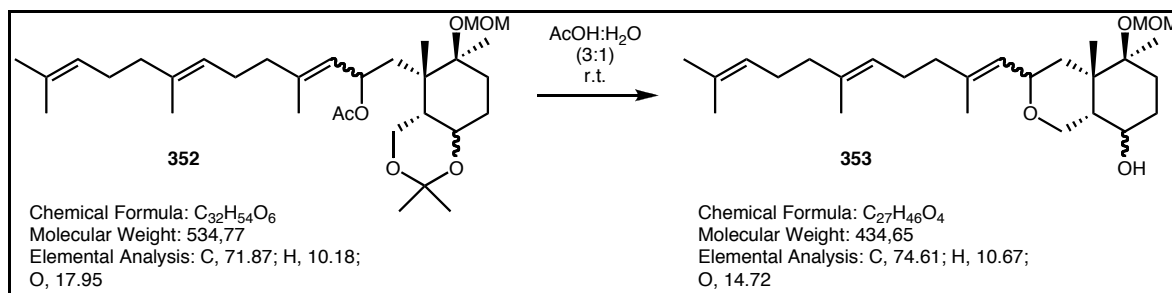
Major diastereomer:

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 0.99$ (s, 3 H, H26), 1.25 (s, 3 H, H2), 1.28 (s, 3 H, H27), 1.42 (s, 3 H, H2'), 1.48 - 1.53 (m, 1 H, H6), 1.57 - 1.60 (m, 1 H, H9), 1.60 (s, 3 H, H24/30), 1.61 (s, 3 H, H29), 1.67 (s, 6 H, H28, H24/30), 1.72 - 1.76 (m, 1 H, H12), 1.77 - 1.80 (m, 1 H, H9'), 1.82 - 2.10 (m, 10 H, H8, H16, H17, H20, H21), 1.97 (s, 3 H, H34), 2.80 (dd, $J = 2.5, 15.7 \text{ Hz}$, 1 H, H12), 3.35 (s, 3 H, H32), 4.05 and 4.10 (ABquartet, $J = 4.4 \text{ Hz}$, 2 H, H5), 4.14 (dt, $J = 4.0, 8.2 \text{ Hz}$, 1 H, H7), 4.61 and 4.72 (ABquartet, $J = 6.9 \text{ Hz}$, 2 H, H31), 5.05 - 5.20 (m, 3 H, H14, H18, H22), 5.78 (td, $J = 2.8, 9.2 \text{ Hz}$, 1 H, H13).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 15.8$ (C29), 16.2 (C26), 17.7 (C24/30), 19.0 (C2), 20.2 (C27), 21.8 (C34), 23.2, 25.7 (C28, C24/30), 26.4, 26.5, 26.6, 26.7 (C9, C17, C20, C21), 29.2 (C2'), 32.7 (C16), 37.8 (C12), 38.7 (C6), 39.8 (C8), 42.4 (C11), 55.4 (C32), 61.1 (C5), 67.1 (C7), 70.3 (C13), 80.5 (C10), 90.4 (C31), 98.4 (C1), 124.5, 124.7 (C18, C22), 125.9 (C14), 131.2 (C23), 134.8 (C19), 139.4 (C15), 170.2 (C33).

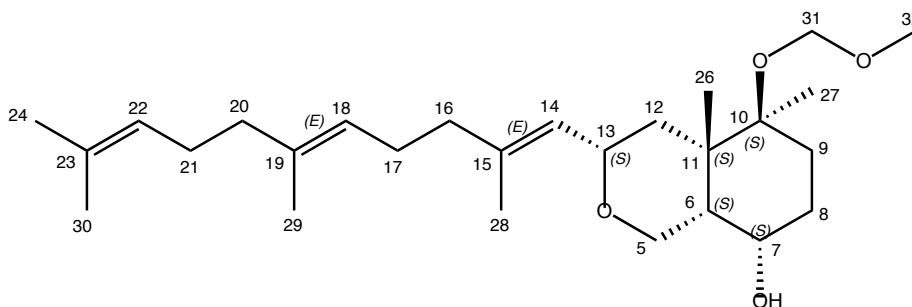
ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 557.3 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{32}\text{H}_{54}\text{O}_6\text{Na}$ m/z 557.3818, found 557.3814.

Analysis calcd. for $\text{C}_{32}\text{H}_{54}\text{O}_6 \cdot 0.5 \text{ H}_2\text{O}$ (534.77): C 70.68, H 10.19; found C 70.66, H 10.11.



A mixture of acetic acid and water (4 mL, 3:1) was added to the acetonide **352** (537 mg, 1.0 mmol) at 0°C. The reaction mixture was stirred at room temperature for 2.5 h. The media was diluted with ethyl acetate, washed with a saturated solution of NaHCO_3 (until pH = 7) and brine. The organic layer was dried with MgSO_4 , and the solvent was evaporated under reduce pressure. A flash chromatography gives 287 mg of alcohol **353** (66%) and 40 mg of **353B** (8%).

353: 5-Methoxymethoxy-4a,5-dimethyl-3-(2,6,10-trimethyl-undeca-1,5,9-trienyl)-octahydro-isochromen-8-ol.



Mp: colourless oil.

$[\alpha]_D^{20} = +7$ (c 0.58, CHCl_3).

IR (film): $\nu = 3484, 2922, 1450, 1375, 1150, 1096, 1076, 1035, 1020, 917 \text{ cm}^{-1}$.

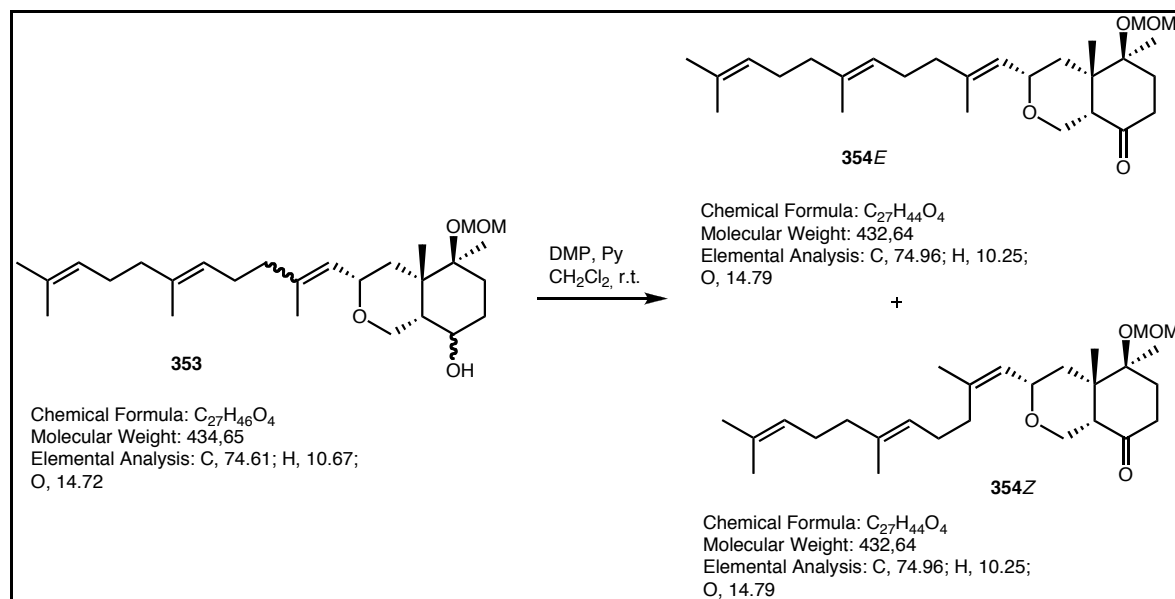
$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): $\delta = 1.12$ (s, 3 H, H27), 1.13 - 1.15 (m, 1 H, H12), 1.23 (s, 3 H, H26), 1.45 - 1.68 (m, 3 H, H6, H8, H9), 1.59 (s, 6 H, H29, H24/30), 1.67 (s, 3 H, H24/30), 1.69 (s, 3 H, H28), 1.87 - 2.13 (m, 11 H, H8', H9', H12', H16, H17, H20, H21), 3.38 (s, 3 H, H32), 3.98 and 4.11 (ABquartet, $J = 12.0$ Hz, 2 H, H5), 4.16 (s, 1 H, H7), 4.30 (s, 1 H, OH), 4.43 (t, $J = 8.9$ Hz, 1 H, H13), 4.65 and 4.77 (ABquartet, $J = 6.5$ Hz, 2 H, H31), 5.06 - 5.12 (m, 2 H, H18, H22), 5.15 (d, $J = 7.7$ Hz, 1 H, H14).

$^{13}\text{C-NMR}$ (CDCl_3 , 125 MHz): $\delta = 16.0, 17.7$ (C29, C24/30), 16.9 (C28), 18.3 (C26), 19.2 (C27), 25.7 (C24/30), 25.7, 26.8, 39.4, 39.7 (C16, C17, C20, C21), 26.3 (C8), 27.4 (C9),

37.7 (C12), 39.2 (C6, C11), 55.5 (C32), 69.6 (C5), 71.1 (C13), 72.4 (C7), 79.5 (C10), 90.4 (C31), 123.7, 124.4 (C18, C22), 125.3 (C14), 131.3 (C23), 135.4 (C19), 139.4 (C15).

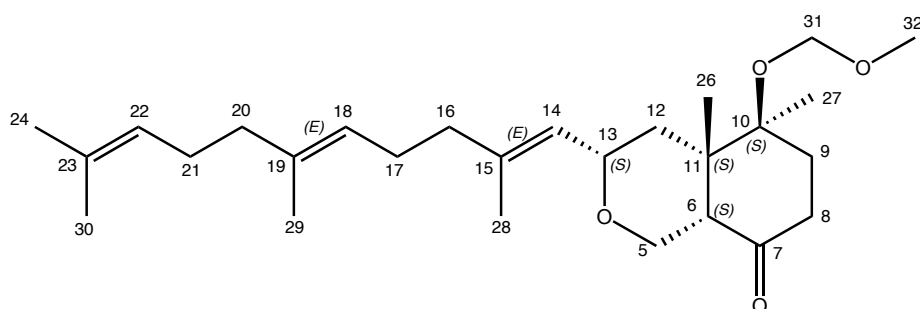
ESIMS (CH₂Cl₂ + MeOH): 457.2 ([M + Na]⁺, 100). HRESIMS: calcd. for C₂₇H₄₆O₄Na *m/z* 457.3294, found 457.3294.

Analysis calcd. for C₂₇H₄₆O₄ · 0.3 H₂O (434.65): C 73.69, H 10.67; found C 73.61, H 10.71.



To a solution of alcohol **353** (mixture of diastereomer, 214 mg, 0.49 mmol) in methylene chloride (2 mL) and pyridine (0.4 mL) were added 624 mg (1.47 mmol) of periodinane and stirring continued at room temperature for 1 h. The reaction was then diluted with methylene chloride quenched with a saturated aqueous solution of sodium bicarbonate and washed with brine. Usual work up and chromatography (heptane-EtOAc, 7:1) afforded 183 mg (86%) of the ketone **354E** and **354Z** (75/25).

354E: 5-Methoxymethoxy-4a,5-dimethyl-3-(2,6,10-trimethyl-undeca-1,5,9-trienyl)-octahydro-isochromen-8-one.



Mp: colourless oil.

$[\alpha]_D^{20} = -18$ (*c* 0.56, CHCl₃).

IR (film): $\nu = 2922, 2360, 1711, 1450, 1375, 1152, 1095, 1028, 918 \text{ cm}^{-1}$.

¹H-NMR (CDCl₃, 500 MHz): $\delta = 1.21$ (s, 3 H, H27), 1.23 - 1.33 (m, 2 H, H12), 1.37 (s, 3 H, H26), 1.58, 1.59, 1.67 (s, 9 H, H24, H29, H30), 1.66 (s, 3 H, H28), 1.96 - 2.04 (m, 4 H, H17, H21), 2.05 - 2.12 (m, 6 H, H9, H16, H20), 2.27 - 2.37 (m, 2 H, H6, H8), 2.59 (ddd, *J* = 8.7, 11.6, 15.5 Hz, 1 H, H8'), 3.42 (s, 3 H, H32), 3.63 (dd, *J* = 2.8, 11.9 Hz, 1 H, H5), 4.32 (ddd, *J* = 2.7, 7.7, 10.4 Hz, 1 H, H13), 4.56 (dd, *J* = 1.3, 11.9 Hz, 1 H, H5), 4.81 (s, 2 H, H31), 5.05-5.12 (m, 2 H, H18, H22), 5.14 (dd, *J* = 1.2, 2.5 Hz, 1 H, H14).

¹³C-NMR (CDCl₃, 125 MHz): $\delta = 16.0, 16.9, 17.7, 25.7$ (C24, C28, C29, C30), 18.5 (C26), 18.8 (C27), 26.4, 26.8 (C16, C20), 30.5 (C9), 36.6 (C8), 38.3 (C12), 39.4, 39.7 (C17, C21), 43.3 (C11), 50.0 (C6), 55.9 (C32), 62.1 (C5), 70.2 (C13), 78.7 (C10), 90.9 (C31), 123.9, 124.4 (C18, C22), 125.8 (C14), 131.3, 135.2 (C19, C23), 138.5 (C15), 209.8 (C7).

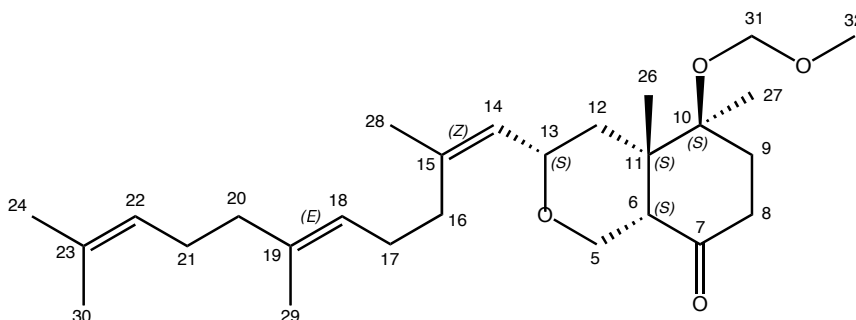
¹H-NMR (DMSO, 500 MHz): $\delta = 1.12$ (s, 3 H, H27), 1.18 - 1.23 (m, 2 H, H12), 1.29 (s, 3 H, H26), 1.55 (s, 6 H, H24/30, H29), 1.59 (s, 3 H, H28), 1.63 (s, 3 H, H24/30), 1.89 - 2.25 (m, 10 H, H9, H16, H17, H20, H21), 2.09 - 2.15 (m, 2 H, H8), 2.19 (s, 1 H, H6), 3.31 (s, 3 H, H32), 3.52 (dd, *J* = 2.6, 11.6 Hz, 1 H, H5), 4.20 - 4.28 (m, 2 H, H5', H13), 4.73 - 4.82 (m, 2 H, H31), 4.99 (d, *J* = 6.8 Hz, 1 H, H14), 5.06 (s, 2 H, H18, H22).

¹³C-NMR (DMSO, 125 MHz): $\delta = 15.8$ (C24/30 or C29), 16.4 (C28), 17.5 (C24/30 or C29), 18.1 (C26), 18.4 (C27), 25.4 (C24/30), 25.7, 26.2 (C17, C21), 29.2 (C9), 36.1 (C8), 37.7 (C12), 38.7, 39.1 (C16, C20), 42.6 (C11), 49.4 (C6), 55.1 (C32), 61.2 (C5), 69.4 (C13), 78.1 (C10), 90.2 (C31), 123.6, 124.0 (C18, C22), 126.4 (C14), 130.6 (C23), 134.5 (C19), 136.6 (C15), 208.9 (C7).

ESIMS (CH₂Cl₂ + MeOH): 455.3 ($[M + Na]^+$, 100). HRESIMS: calcd. for C₂₇H₄₄O₄Na *m/z* 455.3138, found 455.3127.

Analysis calcd. for C₂₇H₄₄O₄ · 0.95 H₂O (432.64): 72.10, H 10.29; found C 72.11, H 10.22.

354Z: 5-Methoxymethoxy-4a,5-dimethyl-3-(2,6,10-trimethyl-undeca-1,5,9-trienyl)-octahydro-isochromen-8-one.



Mp: colourless oil.

$[\alpha]_D^{20} = -30$ (c 0.8, CHCl_3).

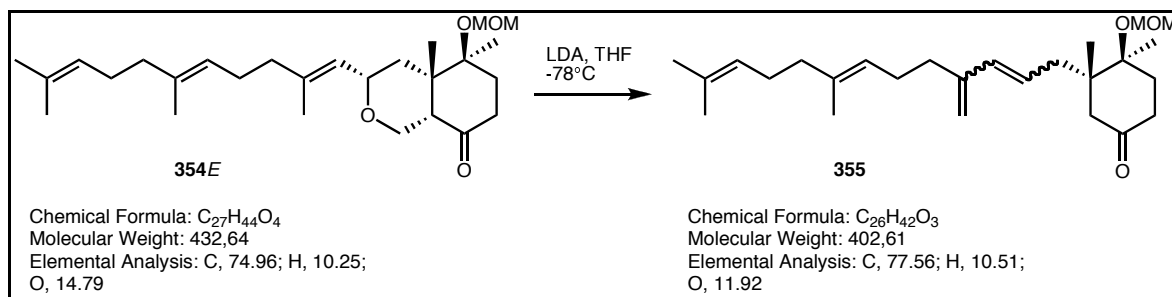
IR (film): $\nu = 2917, 2857, 1710, 1450, 1374, 1318, 1273, 1152, 1094, 1028, 917 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (C_6D_6 , 500 MHz): $\delta = 0.87$ (s, 3 H, H27), 1.09 (dd, $J = 13.1, 14.8$ Hz, 1 H, H12), 1.15 (s, 3 H, H26), 1.26 (dd, $J = 11.4, 12.9$ Hz, 1 H, H12'), 1.51 - 1.57 (m, 2 H, H9), 1.56 (s, 3 H, H24/30), 1.61 (s, 3 H, H29), 1.66 (s, 3 H, H24/30), 1.67 (s, 3 H, H28), 2.00 (s, 1 H, H6), 2.07 - 2.23 (m, 9 H, H8, H16, H17, H20, H21), 2.34 (ddd, $J = 8.3, 11.9, 15.8$ Hz, 1 H, H8'), 3.13 (s, 3 H, H32), 3.46 (dd, $J = 2.7, 11.7$ Hz, 1 H, H5), 4.48 (ddd, $J = 2.5, 7.7, 10.8$ Hz, 1 H, H13), 4.41 and 4.44 (ABquartet, $J = 7.4$ Hz, 2 H, H31), 4.87 (d, $J = 11.6$ Hz, 1 H, H5'), 5.23 (t, $J = 6.9$ Hz, 1 H, H18 or H22), 5.29 (t, $J = 5.3$ Hz, 1 H, H18 or H22), 5.33 (d, $J = 7.7$ Hz, 1 H, H14).

$^{13}\text{C-NMR}$ (C_6D_6 , 75 MHz): $\delta = 16.5$ (C29), 18.1 (C24/30), 18.9 (C26), 19.1 (C27), 23.7 (C28), 26.2 (C24/30), 27.5, 27.6 (C17, C21), 30.4 (C9), 33.4 (C16), 37.0 (C8), 39.4 (C12), 40.6 (C20), 43.5 (C11), 50.5 (C6), 55.9 (C32), 62.8 (C5), 70.5 (C13), 79.0 (C10), 91.1 (C31), 124.8, 125.2 (C18, C22), 128.7 (C14), 131.6 (C23), 135.9 (C19), 138.0 (C15), 207.6 (C7).

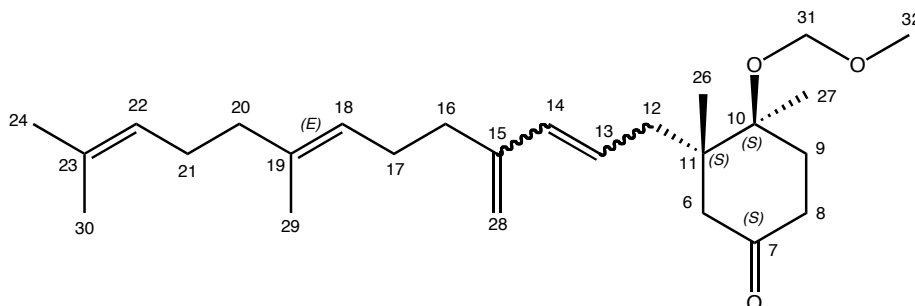
ESIMS (MeOH): 455.3 ($[M + \text{Na}]^+$, 100): HRESIMS calcd. for $\text{C}_{27}\text{H}_{44}\text{O}_4\text{Na}$ m/z 455.3137, found 455.3100.

Analysis calcd. for $\text{C}_{27}\text{H}_{44}\text{O}_4 \cdot 0.7 \text{ H}_2\text{O}$ (432.64): C 72.83, H 10.28; found C 72.85, H 10.05.



To a solution of iPr_2NH (0.05 mL, 0.348 mmol) in THF (0.2 mL), $nBuLi$ (0.22 mL, 1.6M in heptane) was added at $-78^\circ C$ under Ar. The reaction mixture was stirred 5 min and cetone **354E** (5 mg, 0.0116 mmol) in THF (0.3 mL) was added. The reaction mixture was stirred at r.t. for 3 h. The reaction mixture was diluted with ether and a saturated solution of NH_4Cl was added. Usual work up and flash chromatography (ethyl acetate/heptane 1:8) afford 2 mg of **355** (43%) and 2 mg of **354E** (40%).

355: 3-(8,12-Dimethyl-4-methylene-trideca-2,7,11-trienyl)-4-methoxy methoxy-3,4-dimethyl-cyclohexanone.



Mp: colourless oil (characterized as a diastereomeric mixture).

$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

IR (film): $\nu = 2928, 1716, 1456, 1153, 1089, 1031 \text{ cm}^{-1}$.

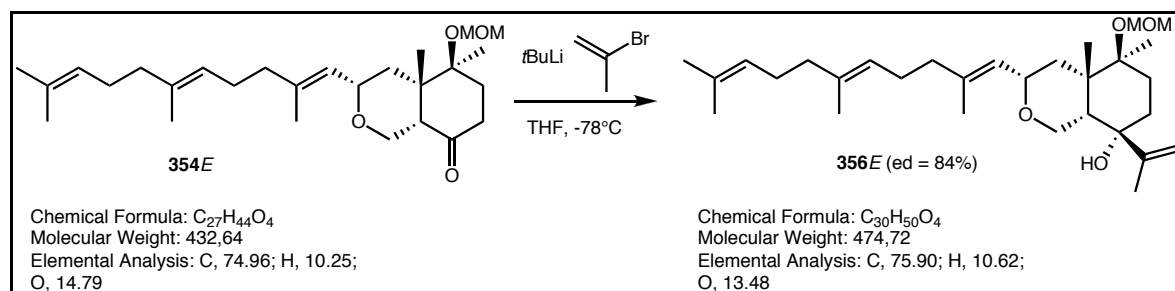
Major product.

1H -NMR ($CDCl_3$, 500 MHz): $\delta = 1.00$ (s, 3 H, H27), 1.30 (s, 3 H, H26), 1.61 (s, 6 H, H24/30, H29), 1.69 (s, 3 H, H24/30), 1.90 - 2.22 (m, 15 H, H6, H8, H9, H12, H16, H17, H20, H21), 2.67 (d, $J = 14.2$ Hz, 1 H, H8'), 3.42 (s, 3 H, H32), 4.79 and 4.84 (ABquartet, $J = 7.4$ Hz, 2 H, H31), 4.90 (s, 1 H, H28), 4.93 (s, 1 H, H28'), 5.08 - 5.18 (m, 2 H, H18, H22), 5.66 (td, $J = 7.5, 15.4$ Hz, 1 H, H13), 6.04 (d, $J = 15.7$ Hz, 1 H, H14).

^{13}C -NMR ($CDCl_3$, 125 MHz): $\delta = 16.1, 17.7$ (C24/30, C29), 18.7 (C26), 20.2 (C27), 25.7 (C24/30), 26.8 (C17, C21), 32.1, 32.3 (C6, C12), 37.6 (C16), 39.3 (C11), 39.7 (C20), 46.1

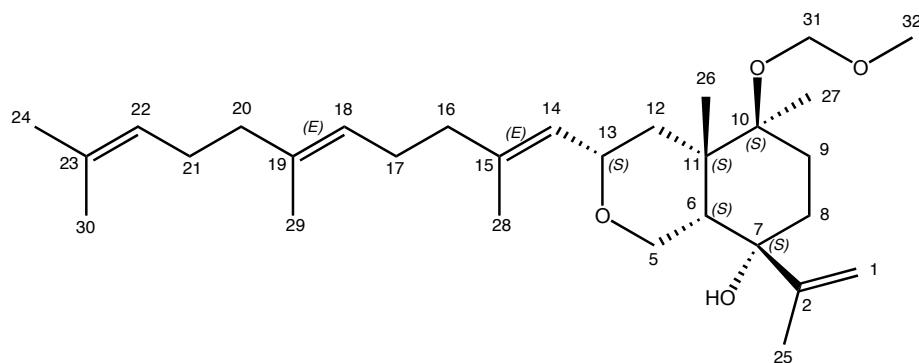
(C9), 47.7 (C8), 55.8 (C32), 78.5 (C10), 90.9 (C31), 114.3 (C28), 124.0, 124.4 (C18, C22), 131.3 (C23), 135.2 (C19), 136.1 (C14, C15), 145.6 (C13), 211.9 (C7).

ESIMS (CH₂Cl₂ + MeOH): 425.3 ([M + Na]⁺, 100). HRESIMS: calcd. for C₂₆H₄₂O₃Na *m/z* 425.3032, found 425.2997.



To a flame dried flask purged with Ar was added 2-bromopropene (0.1 mL, 1.12 mmol) dissolved in THF (0.5 mL). The flask was cooled to -78°C and *t*BuLi (1.3 mL, 2.24 mmol) was added slowly. The mixture was allowed to stir for 20 min. Ketone **354E** (60 mg, 0.14 mmol) in THF (0.5 mL) (dried over 4Å molecular sieves) was slowly added to the vinyl lithium reagent by syringe. The reaction was quenched with a saturated solution of NH₄Cl at -78°C after 20 min. The mixture was allowed to warm to room temperature. The aqueous layer was extracted with ether. The combined organic extracts were dried over MgSO₄, filtered and concentrated under reduce pressure. Flash chromatography (ethyl acetate/heptane 1:9) gives 43 mg of **356aE** and **356bE** (66%, ed = 84%) and 11 mg of starting material (18%).

356aE: 8-Isopropenyl-5-methoxymethoxy-4a,5-dimethyl-3-(2,6,10-trimethyl-undeca-1,5,9-trienyl)-octahydro-isochromen-8-ol.



Mp: colourless oil.

$[\alpha]_D^{20} = +11$ (*c* 1.5, CHCl₃).

IR (film): $\nu = 3463, 2925, 2362, 1450, 1383, 1261, 1095, 1031, 918, 804$ cm⁻¹.

¹H-NMR (CDCl₃, 300 MHz): $\delta = 1.09$ (d, *J* = 2.3 Hz, 1 H, H12), 1.13 (s, 3 H, H27), 1.22 (td, *J* = 3.0, 13.2 Hz, 1 H, H8), 1.26 (s, 3 H, H26), 4.59 (s, 6 H, H29, H24/30), 1.65 (s, 1 H, H6), 1.67 (s, 3 H, H24/30), 1.68 (s, 3 H, H28), 1.71 (s, 3 H, H25), 1.91 (td, *J* = 2.9, 13.5 Hz, 1 H, H8'), 1.95 - 2.17 (m, 11 H, H9, H12', H16, H17, H20, H21), 3.40 (s, 3 H, H31), 3.83 (dABquartet, *J* = 2.9, 12.2 Hz, 1 H, H5) and 4.03 (ABquartet, *J* = 12.2 Hz, 1 H, H5'), 4.39 (ddd, *J* = 3.1, 8.1, 10.8 Hz, 1 H, H13), 4.68 and 4.78 (ABquartet, *J* = 7.0 Hz, 2 H, H31), 4.92 (s, 1 H, H1), 5.05 - 5.12 (m, 2 H, H18, H22), 5.16 (d, *J* = 7.2 Hz, 1 H, H14), 5.26 (d, *J* = 1.8 Hz, 1 H, H1').

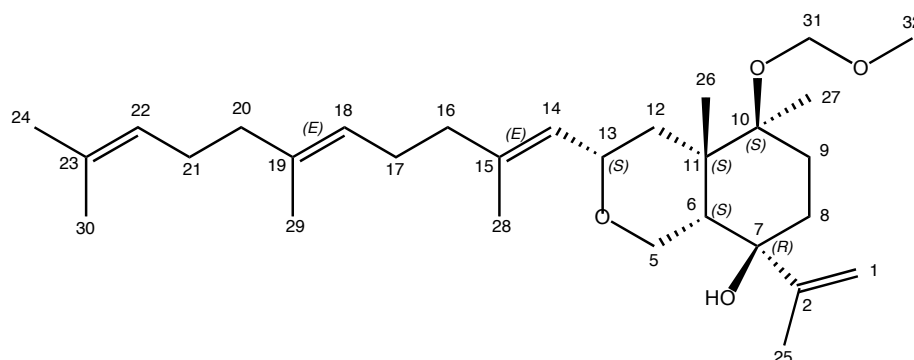
¹³C-NMR (CDCl₃, 75 MHz): $\delta = 16.2, 17.1, 17.9, 25.9$ (C24, C28, C29, C30), 19.2 (C26), 19.6 (C27), 20.1 (C25), 26.5 (C9), 26.9, 27.2 (C16, C20), 31.3 (C8), 37.1 (C12), 38.4 (C6), 39.6 (C11), 39.7, 39.9 (C17, C21), 55.7 (C32), 66.2 (C5), 71.2 (C13), 78.9 (C7), 79.6 (C10), 90.6 (C31), 111.9 (C1), 123.9, 124.5 (C18, C22), 125.5 (C14), 131.5 (C23), 135.6 (C19), 139.7 (C15), 151.4 (C2).

¹H-NMR (C₆D₆, 500 MHz): $\delta = 1.01$ (s, 3 H, H27), 1.09 (d, *J* = 12.0 Hz, 1 H, H12), 1.20 (s, 3 H, H26), 1.41 - 1.47 (m, 2 H, H8, H9), 1.56 (s, 3 H, H29), 1.57 (s, 3 H, H24/30), 1.59 (s, 3 H, H28), 1.56 - 1.60 (m, 1 H, H6), 1.68 (s, 6 H, H24/30, H25), 1.96 - 2.28 (m, 11 H, H8', H9', H12', H16, H17, H20, H21), 3.22 (s, 3 H, H32), 3.72 (dd, *J* = 1.7, 12.0 Hz, 1 H, H5), 4.13 (d, *J* = 12.1 Hz, 1 H, H5), 4.40 (ddd, *J* = 2.1, 8.3, 10.5 Hz, 1 H, H13), 4.49 and 4.61 (ABquartet, *J* = 7.1 Hz, 2 H, H31), 5.01 (s, 1 H, H1), 5.21 (t, *J* = 7.1 Hz, 1 H, H18 or H22), 5.22 (t, *J* = 7.1 Hz, 1 H, H18 or H22), 5.32 (d, *J* = 7.5 Hz, 1 H, H14), 5.64 (s, 1 H, H1'). ¹³C-NMR (C₆D₆, 125 MHz): $\delta = 16.5$ (C29), 17.2 (C28), 18.1 (C24/30), 19.5 (C26), 19.9 (C27), 20.5 (C25), 26.2 (C21), 27.1 (C24/30), 27.6 (C9), 27.7 (C17), 32.1 (C8), 37.8 (C12), 39.2 (C6), 40.1, 40.5 (C16, C20), 40.3 (C11), 55.7 (C32), 66.6 (C5), 71.7 (C13), 79.2 (C7), 79.9 (C10), 90.9 (C31), 112.4 (C1), 124.7, 125.3 (C18, C22), 127.2 (C14), 131.5 (C23), 135.7 (C15), 138.8 (C19), 152.5 (C2).

ESIMS (CH₂Cl₂ + MeOH): 497.3 ([*M* + Na]⁺, 100). HRESIMS: calcd. for C₃₀H₅₀O₄Na *m/z* 497.3607, found 497.3571.

Analysis calcd. for C₃₀H₅₀O₄ · 0.85 AcOEt (474.72): C 72.99, H 10.42; found C 73.07, H 10.43.

356bE: 8-Isopropenyl-5-methoxymethoxy-4a,5-dimethyl-3-(2,6,10-trimethyl-undeca-1,5,9-trienyl)-octahydro-isochromen-8-ol.



Mp: colourless oil.

$[\alpha]_D^{20} = -5$ (*c* 1.0, CHCl₃).

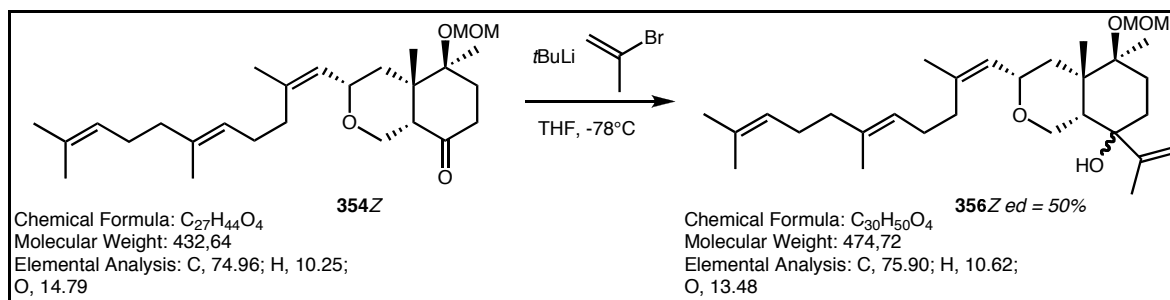
IR (film): $\nu = 3459, 2926, 2361, 1450, 1149, 1095, 1034, 897$ cm⁻¹.

¹H-NMR (CDCl₃, 500 MHz): $\delta = 1.11$ (s, 3 H, H27), 1.17 - 1.24 (m, 2 H, H8, H12), 1.27 (s, 3 H, H26), 1.54 (td, *J* = 2.9, 14.1 Hz, 1 H, H6), 1.60, 1.61, 1.68 (s, 9 H, H24, H29, H30), 1.64 (s, 3 H, H28), 1.72 (s, 3 H, H25), 1.92 (td, *J* = 3.1, 13.4 Hz, 1 H, H8'), 1.94 - 2.16 (m, 10 H, H9, H16, H17, H20, H21), 2.50 (dd, *J* = 7.9, 13.1 Hz, 1 H, H12'), 3.39 (s, 3 H, H32), 3.75 and 3.94 (ABquartet, *J* = 12.5 Hz, 2 H, H5), 4.67 and 4.78 (ABquartet, *J* = 7.0 Hz, 2 H, H31), 4.70 (s, 1 H, OH), 4.76 (t, *J* = 7.1 Hz, 1 H, H13), 4.93 (s, 1 H, H1), 5.08 (t, *J* = 6.2 Hz, 1 H, H18 or H22), 5.11 (t, *J* = 6.5 Hz, 1 H, H18 or H22), 5.28 (s, 1 H, H1'), 5.60 (d, *J* = 6.4 Hz, 1 H, H14).

¹³C-NMR (CDCl₃, 125 MHz): $\delta = 16.1, 17.7$ (C29, C24/30), 16.7 (C28), 19.2 (C27), 19.9 (C25), 20.9 (C26), 25.7 (C24/30), 26.3, 26.7, 27.0, 39.7, 39.8 (C9, C16, C17, C20, C21), 31.0 (C8), 34.4 (C12), 38.0 (C6), 38.1 (C11), 55.5 (C32), 59.8 (C5), 69.4 (C13), 78.6 (C7), 79.3 (C10), 90.4 (C31), 111.5 (C1), 123.8, 124.3 (C18, C22), 125.2 (C14), 131.3 (C23), 135.3 (C19), 138.1 (C15), 151.4 (C2).

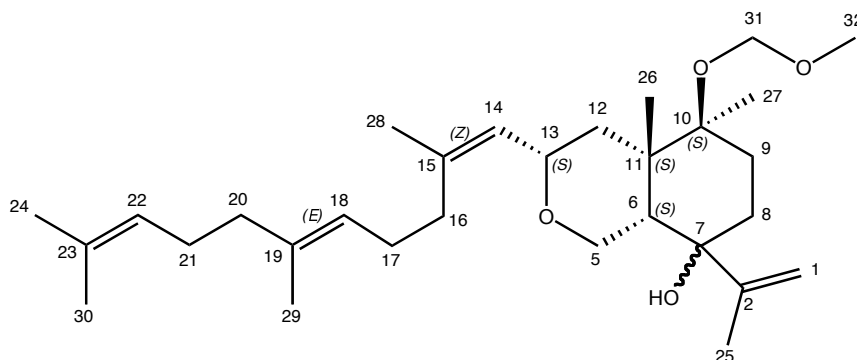
ESIMS (CH₂Cl₂ + MeOH): 497.3 ([*M* + Na]⁺, 100). HRESIMS: calcd. for C₃₀H₅₀O₄Na *m/z* 497.3607, found 497.3647.

Analysis calcd. for C₃₀H₅₀O₄ · 0.6 H₂O (474.72): C 74.21, H 10.63; found C 74.08, H 10.47.



To a flame dried flask purged with Ar was added 2-bromopropene (0.1 mL, 1.12 mmol) dissolved in THF (0.5 mL). The flask was cooled to -78°C and *t*BuLi (1.3 mL, 2.24 mmol) was added slowly. The mixture was allowed to stir for 20 min. Cetone **354Z** (50 mg, 0.116 mmol) in THF (0.5 mL) (dried over 4\AA molecular sieves) was slowly added to the vinyl lithium reagent by syringe. The reaction was quenched with a saturated solution of NH_4Cl at -78°C after 20 min. The mixture was allowed to warm to room temperature. The aqueous layer was extracted with ether. The combined organic extracts were dried over MgSO_4 , filtered and concentrated under reduce pressure. Flash chromatography (ethyl acetate/heptane 1:9) gives 27 mg of **356Z** (mixture of two diastereomere, 50%, ed: 50%) and 6 mg of the starting material (12%).

356Z: 8-Isopropenyl-5-methoxymethoxy-4a,5-dimethyl-3-(2,6,10-trimethyl-undeca-1,5,9-trienyl)-octahydro-isochromen-8-ol.



Mp: colourless oil (characterized as a diastereomeric mixture).

$[\alpha]_D^{20}$ = characterized as a diastereomeric mixture.

IR (film): $\nu = 3463, 2923, 1449, 1374, 1094, 1030, 918\text{ cm}^{-1}$.

Major product:

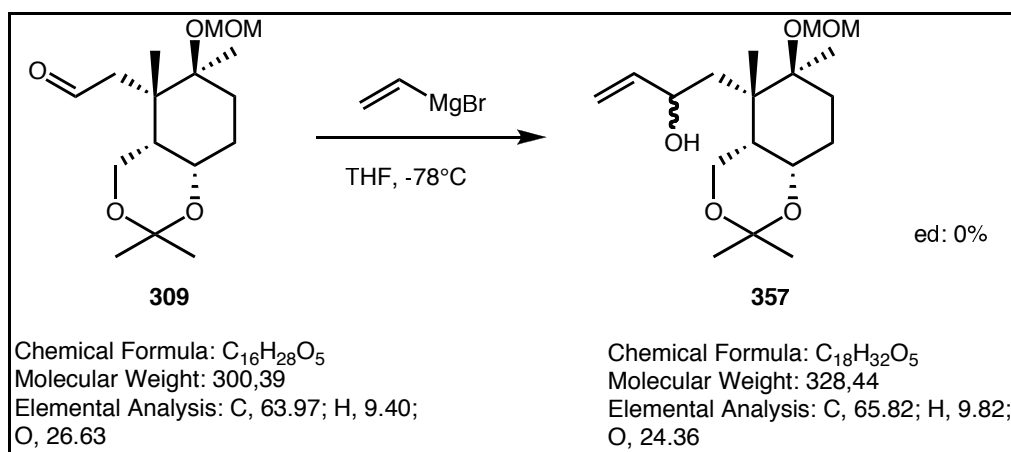
$^1\text{H-NMR}$ (CDCl_3 , 500 MHz): $\delta = 1.10$ (dd, $J = 3.2, 13.2$ Hz, 1 H, H12), 1.12 (s, 3 H, H27), 1.22 (td, $J = 3.2, 13.4$ Hz, 1 H, H8), 1.25 (s, 3 H, H26), 1.60 (s, 3 H, H24/30), 1.58 - 1.62 (m, 1 H, H6), 1.61 (s, 3 H, H29), 1.68 (s, 3 H, H24/30), 1.71 (s, 3 H, H25), 1.73 (s, 3 H,

H28), 1.92 (td, $J = 3.1, 13.5$ Hz, 1 H, H8), 1.95 - 2.17 (m, 11 H, H9, H12', H16, H17, H20, H21), 3.40 (s, 3 H, H32), 3.81 (dd, $J = 2.9, 12.2$ Hz, 1 H, H5), 4.02 (d, $J = 12.2$ Hz, 1 H, H5'), 4.38 (dt, $J = 3.0, 6.8$ Hz, 1 H, H13), 4.68 and 4.78 (ABquartet, $J = 7.0$ Hz, 2 H, H31), 4.92 (s, 1 H, H1), 5.06 - 5.18 (m, 3 H, H14, H18, H22), 5.26 (s, 1 H, H1').

^{13}C -NMR (CDCl_3 , 125 MHz): $\delta = 16.0$ (C29), 17.7 (C24/30), 19.0 (C26), 19.1 (C27), 19.4 (C25), 23.4 (C28), 25.7 (C24/30), 26.7 (C9, C17 or C21), 27.0 (C17 or C21), 31.1 (C8), 32.7 (C16), 37.7 (C12), 38.2 (C6), 39.5 (C11), 39.8 (C20), 55.5 (C32), 66.0 (C5), 70.6 (C13), 78.7 (C7), 79.4 (C10), 90.4 (C31), 111.6 (C1), 123.6 (C18), 124.3 (C22), 126.3 (C14), 131.4 (C23), 135.7 (C19), 140.0 (C15), 151.2 (C2).

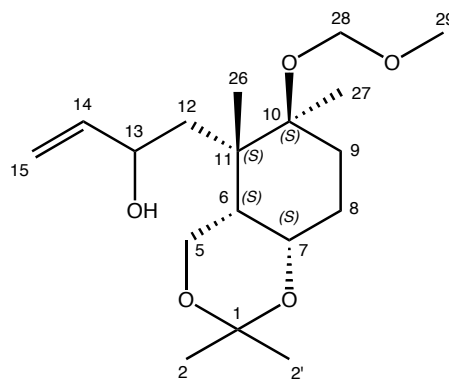
ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 497.3 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{30}\text{H}_{50}\text{O}_4\text{Na}$ m/z 497.3607, found 497.3633.

Analysis calcd. for $\text{C}_{30}\text{H}_{50}\text{O}_4 \cdot 0.1 \text{H}_2\text{O}$ (474.72): C 75.62, H 10.62; found C 75.57, H 10.46.



To a stirred solution of **309** (109 mg, 0.36 mmol), in THF (2 mL), at -78°C , vinyl magnesiumbromide (3.64 mL, 1M in THF) was slowly added. The solution was stirred 1 h at -78°C . Then the reaction mixture was diluted with ether, and a saturated solution of NH_4Cl was added until $\text{pH} = 7$. The aqueous layer was extract with Et_2O . The organic layer was worked up as usual and chromatographed on silica gel (ethyl acetate/heptane 1:1) to afford 108 mg of **357** (91%, ed: 0%).

357a: 1-(6-Methoxymethoxy-2,2,5,6-tetramethyl-hexahydro-benzo[1,3]dioxin-5-yl)-but-3-en-2-ol.



Mp: colourless oil.

$[\alpha]_D^{20} = +78$ (c 0.83, CHCl_3).

IR (film): $\nu = 3439, 2930, 1461, 1381, 1199, 1166, 1098, 1026, 916 \text{ cm}^{-1}$.

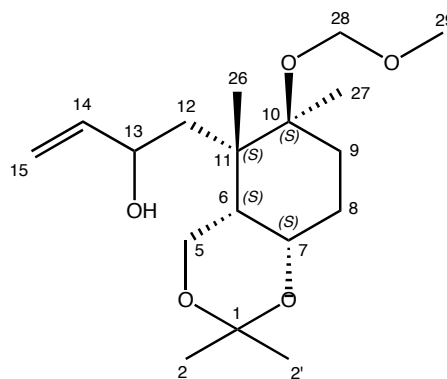
$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 1.22$ (s, 3 H, H27), 1.23 (s, 3 H, H26), 1.38 - 1.55 (m, 3 H, H8, H9, H12), 1.42 (s, 3 H, H2), 1.47 (s, 3 H, H2'), 1.66 (t, $J = 3.6$ Hz, 1 H, H6), 1.76 (dt, $J = 4.1, 14.0$ Hz, 1 H, H8' or H9'), 1.92 (ddt, $J = 4.4, 9.2, 13.5$ Hz, 1 H, H8' or H9'), 2.83 (dd, $J = 10.5, 16.2$ Hz, 1 H, H12), 3.36 (s, 3 H, H29), 4.07 (dABquartet, $J = 4.1, 12.6$ Hz, 1 H, H5), 4.20 (bs, 2 H, H7, H13), 4.31 (ABquartet, $J = 12.6$ Hz, 1 H, H5'), 4.63 and 4.73 (ABquartet, $J = 6.9$ Hz, 2 H, H28), 5.01 (d, $J = 6.9$ Hz, 1 H, H15), 5.25 (d, $J = 17.0$ Hz, 1 H, H15'), 5.90 (ddd, $J = 4.4, 10.4, 17.0$ Hz, 1 H, H14).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 15.5$ (C26), 19.1 (C2), 20.0 (C27), 26.3, 26.5 (C8, C9), 29.6 (C2'), 37.8 (C6), 38.6 (C12), 42.4 (C11), 55.4 (C29), 62.1 (C5), 67.7 (C7), 70.8 (C13), 81.0 (C10), 90.6 (C28), 99.3 (C1), 112.2 (C15), 143.7 (C14).

ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 351.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{18}\text{H}_{32}\text{O}_5\text{Na}$ m/z 351.2147, found 351.2118.

Analysis calcd. for $\text{C}_{18}\text{H}_{32}\text{O}_5$ (328.44) C 65.82, H 9.82; found C 65.71, H 9.76.

357b: 1-(6-Methoxymethoxy-2,2,5,6-tetramethyl-hexahydro-benzo[1,3]dioxin-5-yl)-but-3-en-2-ol.



Mp: colourless oil.

$[\alpha]_D^{20} = +53$ (c 1.13, CHCl_3).

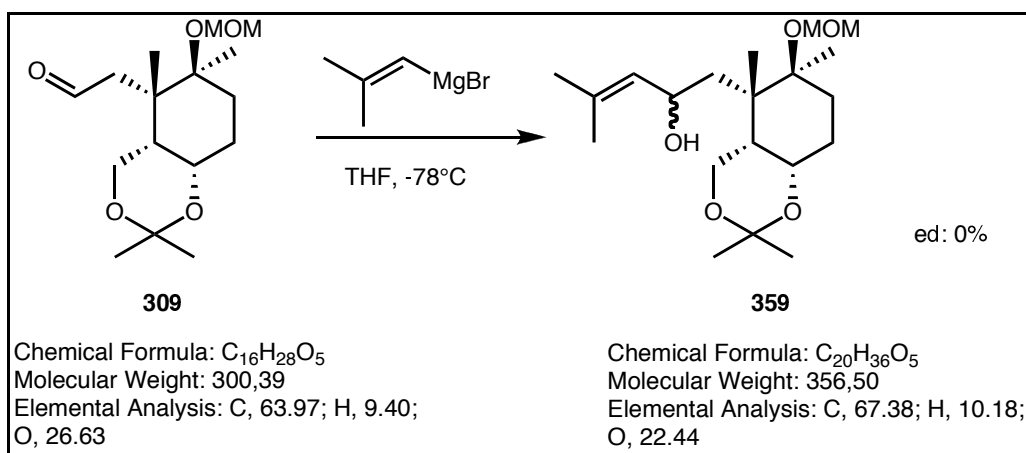
IR (film): $\nu = 3462, 2987, 1457, 1380, 1197, 1166, 1100, 1024, 915 \text{ cm}^{-1}$.

$^1\text{H-NMR}$ (CDCl_3 , 300 MHz): $\delta = 1.19$ (s, 3 H, H26), 1.30 (s, 3 H, H27), 1.36 (s, 3 H, H2), 1.45 (s, 3 H, H2'), 1.42 - 1.57 (m, 3 H, H8, H9, H12), 1.62 (s, 1 H, H6), 1.80 (dt, $J = 3.6, 13.0$ Hz, 1 H, H8' or H9'), 1.93 (tdd, $J = 4.4, 13.5, 18.3$, 1 H, H8' or H9'), 2.73 (d, $J = 15.9$ Hz, 1 H, H12'), 3.36 (s, 3 H, H29), 4.05 (dABquartet, $J = 4.1, 12.7$ Hz, 1 H, H5), 4.11 (dABquartet, $J = 1.9, 12.7$ Hz, 1 H, H5'), 4.17 (dd, $J = 4.1, 6.5$ Hz, 1 H, H7), 4.41 (t, $J = 6.4$ Hz, 1 H, H13), 4.64 and 4.72 (ABquartet, $J = 6.9$ Hz, 2 H, H28), 5.04 (td, $J = 1.4, 10.4$ Hz, 1 H, H15), 5.24 (td, $J = 1.5, 17.2$ Hz, 1 H, H15'), 6.01 (ddd, $J = 5.6, 10.4, 17.2$ Hz, 1 H, H14).

$^{13}\text{C-NMR}$ (CDCl_3 , 75 MHz): $\delta = 17.5$ (C26), 20.4 (C2, C27), 26.7 (C8, C9), 29.7 (C2'), 40.2 (C6, C12), 42.8 (C11), 55.4 (C29), 61.1 (C5), 67.3 (C7), 71.0 (C13), 80.6 (C10), 90.4 (C28), 98.6 (C1), 113.0 (C15), 143.2 (C14).

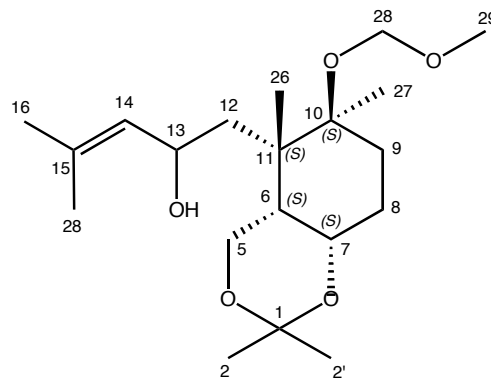
ESIMS ($\text{CH}_2\text{Cl}_2 + \text{MeOH}$): 351.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{18}\text{H}_{32}\text{O}_5\text{Na}$ m/z 351.2147, found 351.2115.

Analysis calcd. for $\text{C}_{18}\text{H}_{32}\text{O}_5 \cdot 0.25 \text{ H}_2\text{O}$ (328.44): C 64.93, H 9.84; found C 64.91, H 9.71.



To a stirred solution of **309** (84 mg, 0.27 mmol), in THF (2 ml), at -78°C, 2-methyl-1-propenylmagnesium bromide (5.5 mL, 0.5M in THF) was slowly added. The solution was stirred 1 h at -78°C. Then the reaction mixture was diluted with ether, and a saturated solution of NH₄Cl was added until pH = 7. The aqueous layer was extracted with Et₂O. The organic layer was worked up as usual and chromatographed on silica gel (ethyl acetate/heptane 1:9) to **359a** and **359b** yield (96 mg, 100%, ed: 0%).

359a: 1-(6-Methoxymethoxy-2,2,5,6-tetramethyl-hexahydro-benzo[1,3]dioxin-5-yl)-4-methyl-pent-3-en-2-ol.



Mp: colourless oil

$[\alpha]_D^{20} = +48$ (*c* 0.88, CHCl₃).

IR (film): $\nu = 3460, 2983, 2927, 1460, 1380, 1232, 1198, 1166, 1099, 1025, 987, 916$ cm⁻¹.

¹H-NMR (CDCl₃, 500 MHz): $\delta = 1.21$ (s, 6 H, H₂₆, H₂₇), 1.38 (dd, *J* = 2.7, 16.0 Hz, 1 H, H₁₂), 1.42 - 1.48 (m, 1 H, H₈), 1.46 (s, 3 H, H₂), 1.47 (s, 3 H, H_{2'}), 1.51 (dd, *J* = 3.8, 14.6 Hz, 1 H, H₉), 1.63 (d, *J* = 4.1 Hz, 1 H, H₆), 1.67 (s, 3 H, H_{16/28}), 1.69 (s, 3 H, H_{16/28}), 1.77 (dt, *J* = 4.2, 14.2 Hz, 1 H, H_{9'}), 1.91 (tt, *J* = 4.8, 14.1 Hz, 1 H, H_{8'}), 2.89

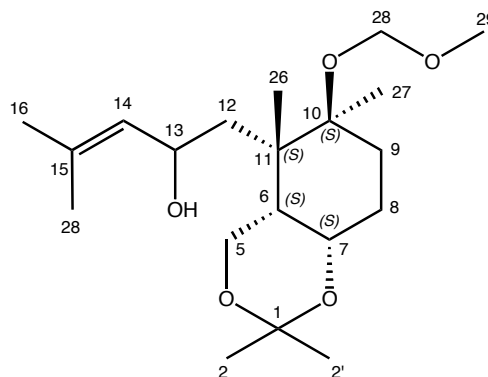
(dd, $J = 10.0, 16.0$ Hz, 1 H, H12'), 3.36 (s, 3 H, H32), 3.81 (d, $J = 6.7$ Hz, 1 H, OH), 4.06 (dd, $J = 4.1, 12.6$ Hz, 1 H, H5), 4.20 (s, 1 H, H7), 4.27 (d, $J = 12.6$ Hz, 1 H, H5'), 4.43 (dd, $J = 6.8, 13.8$ Hz, 1 H, H13), 4.62 and 4.72 (ABquartet, $J = 6.5$ Hz, 2 H, H31), 5.19 (d, $J = 8.5$ Hz, 1 H, H14).

^{13}C -NMR (CDCl_3 , 125 MHz): $\delta = 14.7$ (C26), 17.0 (C16/28), 18.1 (C2), 19.0 (C27), 24.7 (C16/28), 25.3, 25.6 (C8, C9), 28.8 (C2'), 36.9 (C6), 38.6 (C12), 41.5 (C11), 54.4 (C32), 61.1 (C5), 66.0 (C13), 66.6 (C7), 80.0 (C10), 89.6 (C31), 98.1 (C1), 129.9 (C14), 130.5 (C15).

ESIMS ($\text{MeOH} + \text{CH}_2\text{Cl}_2$): 379.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{20}\text{H}_{36}\text{O}_5\text{Na}$ m/z 379.2460, found 379.2449.

Analysis calcd. for $\text{C}_{20}\text{H}_{36}\text{O}_5$ (356.26): C 67.38, H 10.18; found C 66.95, H 9.93.

359b: 1-(6-Methoxymethoxy-2,2,5,6-tetramethyl-hexahydro-benzo[1,3]dioxin-5-yl)-4-methyl-pent-3-en-2-ol.



Mp: 91-92°C

$[\alpha]_D^{20} = +78$ (c 0.6, CHCl_3).

IR (film): $\nu = 3466, 2987, 2926, 1453, 1380, 1266, 1196, 1166, 1139, 1101, 1033, 986, 961, 918$ cm^{-1} .

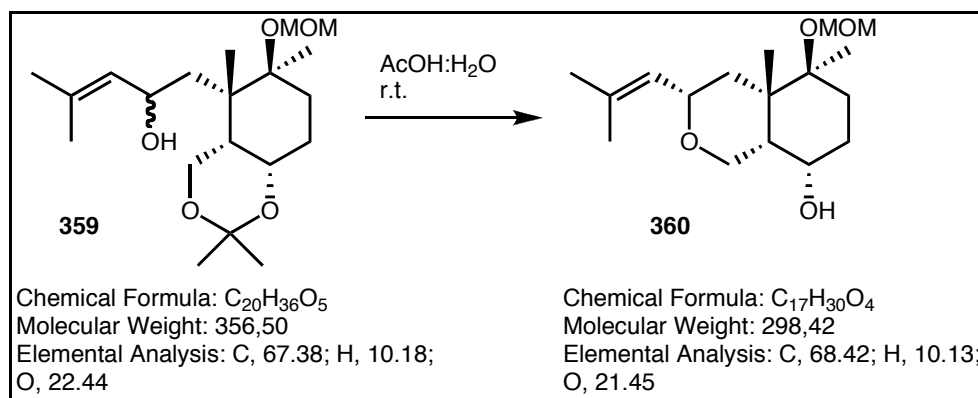
^1H -NMR (CDCl_3 , 500 MHz): $\delta = 1.16$ (s, 3 H, H26), 1.28 (s, 3 H, H2), 1.31 (s, 3 H, H27), 1.42 (s, 3 H, H2'), 1.47 - 1.58 (m, 3 H, H8, H9, H12), 1.60 (s, 1 H, H6), 1.68 (s, 3 H, H16/28), 1.70 (s, 3 H, H16/28), 1.80 - 1.94 (m, 2 H, H8', H9'), 2.60 - 2.70 (bs, 1 H, H12'), 3.36 (s, 3 H, H32), 4.03 (dd, $J = 4.3, 12.6$ Hz, 1 H, H5), 4.10 (d, $J = 12.6$ Hz, 1 H, H5'), 4.15 (s, 1 H, H7), 4.61 (dt, $J = 2.4, 8.4$ Hz, 1 H, H13), 4.64 and 4.72 (ABquartet, $J = 6.9$ Hz, 2 H, H31), 5.23 (d, $J = 8.8$ Hz, 1 H, H14).

^{13}C -NMR (CDCl_3 , 125 MHz): $\delta = 17.6$ (C26), 18.4 (C16/28), 19.8 (C2'), 20.5 (C27), 25.7 (C16/28), 26.7, 26.9 (C8, C9), 28.8 (C2), 39.5 (C6), 41.2 (C12), 42.7 (C11), 55.4 (C32),

61.8 (C5), 66.8 (C13), 67.3 (C7), 80.7 (C10), 90.5 (C31), 98.4 (C1), 129.9 (C14), 133.2 (C15).

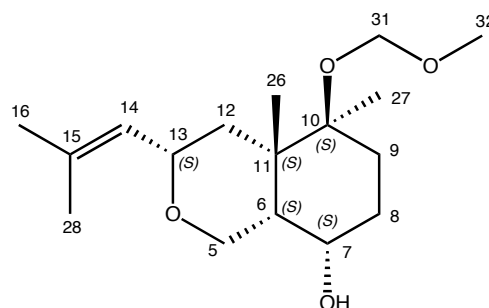
ESIMS (CH₂Cl₂ + MeOH): 379.2 ([M + Na]⁺, 100). HRESIMS: calcd. for C₂₀H₃₆O₅Na *m/z* 379.2460, found 379.2469.

Analysis calcd. for C₂₀H₃₆O₅ (356.26): C 67.38, H 10.18; found C 67.49, H 9.98.



A mixture of acetic acid and water (2 mL, 3:1) was added to the acetonide **359** (104 mg, 0.26 mmol) at 0°C. The reaction mixture was stirred at room temperature for 2 h. The media was diluted with ethyl acetate, washed with a saturated solution of NaHCO₃ (until pH = 7) and brine. The organic layer was dried with MgSO₄, and the solvent was evaporated under reduce pressure. A flash chromatography gives 71 mg of alcohol **360** (91%).

360: 5-Methoxymethoxy-4a,5-dimethyl-3-(2-methyl-propenyl)-octahydro-isochromen-8-ol.



Mp: yellow oil.

$[\alpha]_D^{20} = +1$ (*c* 1.2 CHCl₃).

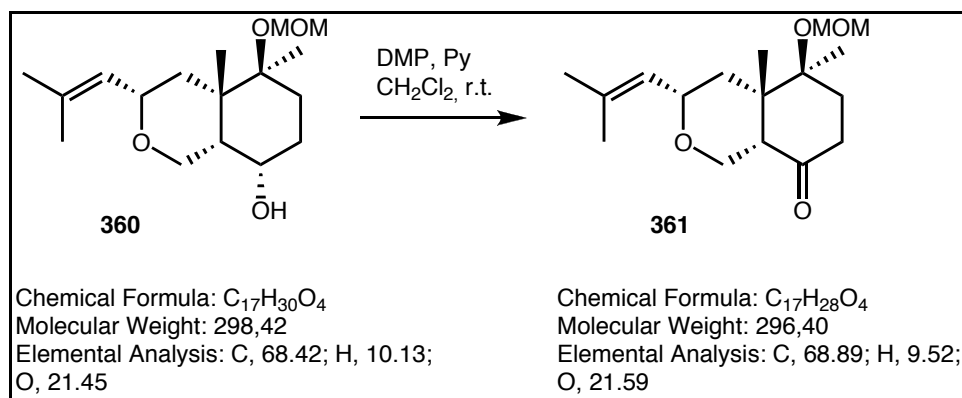
IR (film): $\nu = 3477, 2925, 1738, 1451, 1375, 1242, 1179, 1151, 1073, 1096, 1035, 1019, 916 \text{ cm}^{-1}$.

^1H NMR (300 MHz): $\delta = 1.11$ (s, 3 H, H27), 1.14 (m, 1 H, H12), 1.22 (s, 3 H, H26), 1.46 (s, 1 H, H6), 1.48 - 1.57 (m, 1 H, H9), 1.65 - 1.78 (m, 2 H, H8, H9), 1.68 (s, 3 H, H28), 1.71 (s, 3 H, H16), 1.90 (t, $J = 12.4$ Hz, 1 H, H12), 2.03 (td, $J = 14.0, 3.5$ Hz, 1 H, H8), 3.37 (s, 3 H, H32), 3.96 (ABquartet, $J = 12.1$ Hz, 1 H, H5), and 4.10 (dABquartet, $J = 2.7, 12.1$ Hz, 1 H, H5'), 4.15 (d, $J = 2.8$ Hz, 1 H, H7), 4.28 (b, 1 H, OH), 4.40 (ddd, $J = 3.0, 8.1, 11.3$ Hz, 1 H, H13), 4.64 and 4.75 (ABquartet, $J = 7.0$ Hz, 2 H, H31), 5.13 (d, $J = 8.0$ Hz, 1 H, H14).

^{13}C NMR (125 MHz): $\delta = 18.2$ (C26), 18.3 (C28), 19.1 (C27), 25.6 (C8, C16), 27.3 (C9), 37.6 (C12), 39.1 (C6, C11), 55.4 (C32), 69.6 (C5), 71.0 (C13), 72.3 (C7), 79.4 (C10), 90.3 (C31), 125.6 (C14), 136.0 (C15).

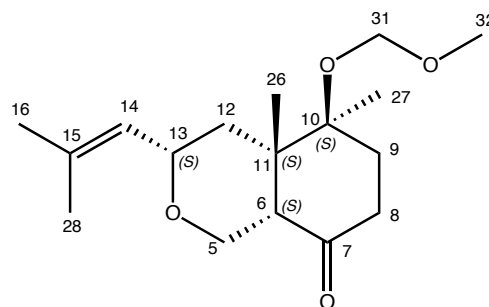
ESIMS (MeOH): 321.2 ($[M + \text{Na}]^+$, 100). HRESIMS: calcd. for $\text{C}_{17}\text{H}_{30}\text{O}_4\text{Na}$ m/z 321.2042, found 321.2026.

Analysis calcd. for $\text{C}_{17}\text{H}_{30}\text{O}_4$ (298.42): C 68.42, H 10.13; found C 68.18, H 9.81.



To a stirred solution of the alcohol **360** (71 mg, 0.24 mmol) in CH_2Cl_2 (2 mL) at 0°C were added pyridine (0.19 mL, 2.35 mmol) and Dess-Martin periodinane reagent (341 mg, 0.80 mmol). The reaction was monitored by TLC, occasional addition of further oxidant was necessary to complete the reaction. After the consumption of the starting material was checked, the reacting mixture was diluted with Et_2O and washed with aqueous 5% $\text{Na}_2\text{S}_2\text{O}_3$, aqueous saturated NaHCO_3 , and worked up as usual. Chromatography of the residue on silica gel (heptane:EtOAc, 3:1 to 2:1) yielded **361** (64 mg, 90%).

361: 5-(Methoxymethoxy)-4a,5-dimethyl-3-(2-methylprop-1-enyl)hexahydro-1*H*-isochromen-8(8*aH*)-one.



Mp: colourless oil.

$[\alpha]_D^{20} = -36$ (*c* 0.98 CHCl₃).

IR (film): $\nu = 2975, 2937, 1709, 1452, 1374, 1151, 1096, 1028, 918$ cm⁻¹.

¹H NMR (500 MHz, CDCl₃): $\delta = 1.21$ (s, 3 H, H27), 1.22 - 1.35 (m, 2 H, H9), 1.36 (s, 3 H, H26), 1.66 (s, 3 H, H18), 1.68 (s, 3 H, H16), 1.96 - 2.08 (m, 2 H, H12), 2.29 - 2.35 (m, 2 H, H6, H8), 2.58 (ddd, *J* = 8.0, 12.6, 15.1 Hz, 1 H, H8'), 3.41 (s, 3 H, H32), 3.62 (dd, *J* = 2.8, 11.9 Hz, 1 H, H5), 4.29 (ddd, *J* = 2.6, 7.9, 10.8 Hz, 1 H, H13), 4.55 (dd, *J* = 1.4, 11.9 Hz, 1 H, H5'), 4.81 (s, 2 H, H31), 5.10 (dd, *J* = 1.4, 7.9 Hz, 1 H, H14).

¹³C NMR (125 MHz, CDCl₃): $\delta = 18.4$ (C18, C26), 18.7 (C27), 25.6 (C16), 30.5 (C12), 36.6 (C8), 38.2 (C9), 43.3 (C11), 50.0 (C6), 55.9 (C32), 62.0 (C5), 70.1 (C13), 78.7 (C10), 90.8 (C31), 126.1 (C14), 135.3 (C15), 209.8 (C7).

ESIMS (CH₂Cl₂ + MeOH): 319.2 ([*M* + Na]⁺, 100). HRESIMS: calcd. for C₁₇H₂₈O₄Na *m/z* 319.1885, found 319.1871.

Analysis calcd. for C₁₇H₂₈O₄ · 0.5 H₂O (296.40): C 66.86, H 9.57; found C 66.81, H 9.29.

4. X-Ray data and results for 180.

A little needle of 0.50 x 0.10 x 0.10 mm was used for data collection. Empirical formula $C_{15}H_{22}O_7$, $M = 314.33$, $T = 293$ K. Orthorhombic system, space group $P 2_12_12_1$, $Z = 4$, $a = 6.768$ (3), $b = 9.411$ (6), $c = 24.089$ (12) Å, $V = 1534.3$ Å³, $d_{calc} = 1.361$ g cm⁻³, $F(000) = 672$, $\mu = 0.108$ mm⁻¹, $\lambda(\text{MoK}\alpha) = 0.71073$ Å. A total of 14648 intensity data was measured with a Nonius Kappa-CCD diffractometer up to $\theta = 27.86^\circ$, reduced to 3627 orthorhombic unique reflections.¹ The structure was solved with program *SHELXS86*.² Refinement of 205 parameters on F^2 , using program *SHELXL97*³, led to $R_1(F) = 0.0439$, calculated with the 2522 observed reflections having $I \geq 2$ sigma (I) and $wR_2(F^2) = 0.1059$ considering all the 3627 data. Goodness of fit = 1.049. Residual electronic density between -0.175 and 0.156 eÅ⁻³.

CCDC deposited number : CCDC 620080.

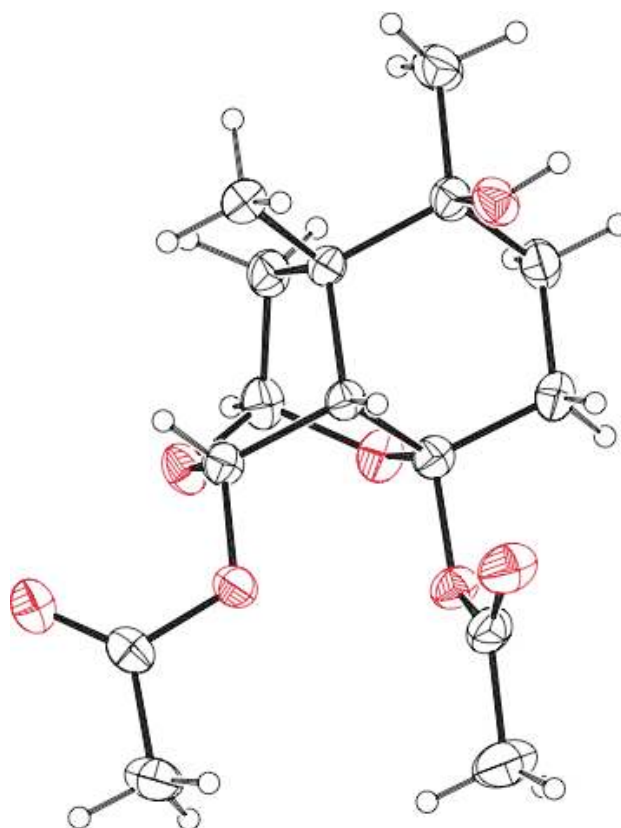


Table 1. Crystal data and structure refinement for **180**.

Identification code	'SIM063'	
Empirical formula	C ₁₅ H ₂₂ O	
Formula weight	314.33	
Temperature (K)	293(2) K	
Wavelength (Å)	0.71073	
Crystal system, space group	Orthorhombic, P 21 21 21	
Unit cell dimensions (Å, °)	a = 6.768(3)	α = 90
	b = 9.411(5)	β = 90
	c = 24.089(12)	γ = 90
Volume (Å ³)	1534.3(13)	
Z, Calculated density (mg/m ³)	4, 1.361	
Absorption coefficient (mm ⁻¹)	0.108	
F(000)	672	
Crystal size (mm)	0.50 x 0.10 x 0.10	
Theta range for data collection (°)	2.32 to 27.86	
Limiting indices	-8 ≤ h ≤ 8, -12 ≤ k ≤ 12, -31 ≤ l ≤ 31	
Reflections collected / unique	14648 / 3627 [R(int) = 0.0470]	
Completeness to θ = 27.86 Å	99.4%	
Absorption correction	None	
Refinement method	Full-matrix least-squares ^{F²}	
Data / restraints / parameters	3627 / 0 / 205	
Goodness-of-fit on F ²	1.049	
Final R indices [I > 2σ(I)]	R ₁ = 0.0439, wR ₂ = 0.0900 (2522 Fo)	
R indices (all data)	R ₁ = 0.0816, wR ₂ = 0.0159 (3627 data)	
Extinction coefficient	0.029(3)	
Largest diff. peak and hole (e.Å ⁻³)	0.156 and -0.175	

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å² x 10³) for **180**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	6339(3)	1515(2)	960(1)	40(1)
C(2)	4958(3)	2093(2)	1430(1)	36(1)
C(3)	3944(3)	3504(2)	1242(1)	32(1)

C(4)	5575(3)	4537(2)	1079(1)	38(1)
C(5)	6901(4)	4024(3)	618(1)	45(1)
C(6)	7846(4)	2621(3)	776(1)	48(1)
C(7)	2781(3)	4094(2)	1734(1)	37(1)
C(8)	7411(4)	157(3)	1132(1)	55(1)
C(9)	3396(4)	981(3)	1569(1)	50(1)
C(10)	6194(4)	2508(2)	1950(1)	44(1)
C(11)	6057(3)	4080(3)	2036(1)	44(1)
O(12)	5034(2)	1220(2)	505(1)	48(1)
O(13)	4097(2)	4483(2)	2164(1)	46(1)
O(14)	6736(2)	4819(2)	1555(1)	45(1)
O(15)	4873(2)	5973(2)	928(1)	43(1)
C(16)	3493(4)	6157(3)	536(1)	48(1)
O(17)	2744(3)	5211(2)	277(1)	61(1)
C(18)	3036(5)	7693(3)	457(1)	76(1)
O(19)	1732(2)	5359(2)	1567(1)	42(1)
C(20)	520(3)	5923(3)	1959(1)	43(1)
O(21)	211(2)	5362(2)	2398(1)	51(1)
C(22)	-313(4)	7306(3)	1772(1)	61(1)
H(3)	3062	3329	926	36
H(5A)	7921	4725	547	51
H(5B)	6135	3906	281	51
H(6A)	8780	2781	1075	54
H(6B)	8576	2256	460	54
H(7)	1845	3378	1870	42
H(8A)	6462	-585	1194	63
H(8B)	8140	327	1467	63
H(8C)	8304	-125	842	63
H(9A)	2609	793	1246	57
H(9B)	2565	1330	1861	57
H(9C)	4032	121	1687	57
H(10A)	5692	2015	2275	50
H(10B)	7563	2235	1897	50
H(11)	6905	4339	2350	49
HO12	5659	850	251	54
H(18A)	2411	7829	104	87
H(18B)	4239	8233	471	87
H(18C)	2166	8007	747	87
H(22A)	-1372	7581	2014	70
H(22B)	-806	7210	1400	70
H(22C)	702	8018	1780	70

Table 3. Bond lengths [Å] and angles [°].

C(1)-O(12)	1.434(3)
C(1)-C(6)	1.523(3)
C(1)-C(8)	1.527(3)
C(1)-C(2)	1.566(3)
C(2)-C(9)	1.524(3)
C(2)-C(10)	1.558(3)
C(2)-C(3)	1.562(3)
C(3)-C(4)	1.522(3)
C(3)-C(7)	1.529(3)
C(3)-H(3)	0.9800
C(4)-O(14)	1.415(2)
C(4)-O(15)	1.478(3)
C(4)-C(5)	1.507(3)
C(5)-C(6)	1.516(3)
C(5)-H(5A)	0.9700
C(5)-H(5B)	0.9700
C(6)-H(6A)	0.9700
C(6)-H(6B)	0.9700
C(7)-O(13)	1.413(2)
C(7)-O(19)	1.443(3)
C(7)-H(7)	0.9800
C(8)-H(8A)	0.9600
C(8)-H(8B)	0.9600
C(8)-H(8C)	0.9600
C(9)-H(9A)	0.9600
C(9)-H(9B)	0.9600
C(9)-H(9C)	0.9600
C(10)-C(11)	1.496(3)
C(10)-H(10A)	0.9700
C(10)-H(10B)	0.9700
C(11)-O(13)	1.413(3)
C(11)-O(14)	1.428(3)
C(11)-H(11)	0.9800
O(12)-HO12	0.8200
O(15)-C(16)	1.340(3)
C(16)-O(17)	1.200(3)
C(16)-C(18)	1.490(4)
C(18)-H(18A)	0.9600
C(18)-H(18B)	0.9600
C(18)-H(18C)	0.9600
O(19)-C(20)	1.360(3)
C(20)-O(21)	1.200(3)
C(20)-C(22)	1.488(3)
C(22)-H(22A)	0.9600
C(22)-H(22B)	0.9600

C(22)-H(22C)	0.9600
O(12)-C(1)-C(6)	108.84(17)
O(12)-C(1)-C(8)	109.72(18)
C(6)-C(1)-C(8)	109.4(2)
O(12)-C(1)-C(2)	104.59(17)
C(6)-C(1)-C(2)	111.88(18)
C(8)-C(1)-C(2)	112.22(17)
C(9)-C(2)-C(10)	111.56(17)
C(9)-C(2)-C(3)	110.05(18)
C(10)-C(2)-C(3)	104.83(16)
C(9)-C(2)-C(1)	109.57(17)
C(10)-C(2)-C(1)	110.40(18)
C(3)-C(2)-C(1)	110.36(15)
C(4)-C(3)-C(7)	109.98(16)
C(4)-C(3)-C(2)	107.38(17)
C(7)-C(3)-C(2)	108.04(15)
C(4)-C(3)-H(3)	110.5
C(7)-C(3)-H(3)	110.5
C(2)-C(3)-H(3)	110.5
O(14)-C(4)-O(15)	101.89(16)
O(14)-C(4)-C(5)	109.10(17)
O(15)-C(4)-C(5)	107.63(16)
O(14)-C(4)-C(3)	108.28(15)
O(15)-C(4)-C(3)	114.43(17)
C(5)-C(4)-C(3)	114.66(18)
C(4)-C(5)-C(6)	110.16(18)
C(4)-C(5)-H(5A)	109.6
C(6)-C(5)-H(5A)	109.6
C(4)-C(5)-H(5B)	109.6
C(6)-C(5)-H(5B)	109.6
H(5A)-C(5)-H(5B)	108.1
C(5)-C(6)-C(1)	112.7(2)
C(5)-C(6)-H(6A)	109.1
C(1)-C(6)-H(6A)	109.1
C(5)-C(6)-H(6B)	109.1
C(1)-C(6)-H(6B)	109.1
H(6A)-C(6)-H(6B)	107.8
O(13)-C(7)-O(19)	107.47(17)
O(13)-C(7)-C(3)	109.73(17)
O(19)-C(7)-C(3)	109.62(16)
O(13)-C(7)-H(7)	110.0
O(19)-C(7)-H(7)	110.0
C(3)-C(7)-H(7)	110.0
C(1)-C(8)-H(8A)	109.5
C(1)-C(8)-H(8B)	109.5
H(8A)-C(8)-H(8B)	109.5
C(1)-C(8)-H(8C)	109.5

H(8A)-C(8)-H(8C)	109.5
H(8B)-C(8)-H(8C)	109.5
C(2)-C(9)-H(9A)	109.5
C(2)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	109.5
C(2)-C(9)-H(9C)	109.5
H(9A)-C(9)-H(9C)	109.5
H(9B)-C(9)-H(9C)	109.5
C(11)-C(10)-C(2)	109.01(18)
C(11)-C(10)-H(10A)	109.9
C(2)-C(10)-H(10A)	109.9
C(11)-C(10)-H(10B)	109.9
C(2)-C(10)-H(10B)	109.9
H(10A)-C(10)-H(10B)	108.3
O(13)-C(11)-O(14)	110.32(18)
O(13)-C(11)-C(10)	110.7(2)
O(14)-C(11)-C(10)	110.46(18)
O(13)-C(11)-H(11)	108.4
O(14)-C(11)-H(11)	108.4
C(10)-C(11)-H(11)	108.4
C(1)-O(12)-HO12	109.5
C(7)-O(13)-C(11)	111.30(15)
C(4)-O(14)-C(11)	112.82(16)
C(16)-O(15)-C(4)	121.05(16)
O(17)-C(16)-O(15)	124.4(2)
O(17)-C(16)-C(18)	124.5(2)
O(15)-C(16)-C(18)	111.1(2)
C(16)-C(18)-H(18A)	109.5
C(16)-C(18)-H(18B)	109.5
H(18A)-C(18)-H(18B)	109.5
C(16)-C(18)-H(18C)	109.5
H(18A)-C(18)-H(18C)	109.5
H(18B)-C(18)-H(18C)	109.5
C(20)-O(19)-C(7)	115.15(16)
O(21)-C(20)-O(19)	123.1(2)
O(21)-C(20)-C(22)	125.9(2)
O(19)-C(20)-C(22)	111.0(2)
C(20)-C(22)-H(22A)	109.5
C(20)-C(22)-H(22B)	109.5
H(22A)-C(22)-H(22B)	109.5
C(20)-C(22)-H(22C)	109.5
H(22A)-C(22)-H(22C)	109.5
H(22B)-C(22)-H(22C)	109.5

Table 4. Torsion angles [°] for **180**

O(12)-C(1)-C(2)-C(9)	58.5(2)
C(6)-C(1)-C(2)-C(9)	176.2(2)
C(8)-C(1)-C(2)-C(9)	-60.4(2)
O(12)-C(1)-C(2)-C(10)	-178.2(2)
C(6)-C(1)-C(2)-C(10)	-60.6(2)
C(8)-C(1)-C(2)-C(10)	62.9(2)
O(12)-C(1)-C(2)-C(3)	-62.8(2)
C(6)-C(1)-C(2)-C(3)	54.8(2)
C(9)-C(2)-C(3)-C(4)	-176.9(2)
C(10)-C(2)-C(3)-C(4)	63.0(2)
C(1)-C(2)-C(3)-C(4)	-55.9(2)
C(9)-C(2)-C(3)-C(7)	64.5(2)
C(10)-C(2)-C(3)-C(7)	-55.6(2)
C(1)-C(2)-C(3)-C(7)	-174.5(2)
C(7)-C(3)-C(4)-O(14)	54.4(2)
C(2)-C(3)-C(4)-O(14)	-62.9(2)
C(7)-C(3)-C(4)-O(15)	-58.4(2)
C(2)-C(3)-C(4)-O(15)	-175.7(2)
C(7)-C(3)-C(4)-C(5)	176.5(2)
C(2)-C(3)-C(4)-C(5)	59.2(2)
O(14)-C(4)-C(5)-C(6)	64.1(2)
O(15)-C(4)-C(5)-C(6)	173.9(2)
C(3)-C(4)-C(5)-C(6)	-57.5(2)
C(4)-C(5)-C(6)-C(1)	52.5(3)
O(12)-C(1)-C(6)-C(5)	62.2(2)
C(8)-C(1)-C(6)-C(5)	-177.9(2)
C(2)-C(1)-C(6)-C(5)	-52.9(2)
C(4)-C(3)-C(7)-O(13)	-51.5(2)
C(2)-C(3)-C(7)-O(13)	65.4(2)
C(4)-C(3)-C(7)-O(19)	66.3(2)
C(2)-C(3)-C(7)-O(19)	-176.8(2)
C(9)-C(2)-C(10)-C(11)	-123.5(2)
C(3)-C(2)-C(10)-C(11)	-4.4(2)
C(1)-C(2)-C(10)-C(11)	114.4(2)
C(2)-C(10)-C(11)-O(13)	64.7(2)
C(2)-C(10)-C(11)-O(14)	-57.8(2)
O(19)-C(7)-O(13)-C(11)	-125.3(2)
C(3)-C(7)-O(13)-C(11)	-6.2(2)
O(14)-C(11)-O(13)-C(7)	63.5(2)
C(10)-C(11)-O(13)-C(7)	-59.1(2)
O(15)-C(4)-O(14)-C(11)	120.8(2)
C(5)-C(4)-O(14)-C(11)	-125.6(2)
C(3)-C(4)-O(14)-C(11)	-0.2(2)
O(13)-C(11)-O(14)-C(4)	-60.2(2)
C(10)-C(11)-O(14)-C(4)	62.5(2)

O(14)-C(4)-O(15)-C(16)	-170.9(2)
C(5)-C(4)-O(15)-C(16)	74.4(2)
C(3)-C(4)-O(15)-C(16)	-54.3(2)
C(4)-O(15)-C(16)-O(17)	-0.8(3)
C(4)-O(15)-C(16)-C(18)	-179.8(2)
O(13)-C(7)-O(19)-C(20)	-65.6(2)
C(3)-C(7)-O(19)-C(20)	175.2(2)
C(7)-O(19)-C(20)-O(21)	-5.6(3)
C(7)-O(19)-C(20)-C(22)	173.2(2)

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