Supporting Information

for

Formation of substituted Tetrahydropyrans Through Oxetane Ring Opening: Application to the Synthesis of C1-C17 Fragment of Salinomycin

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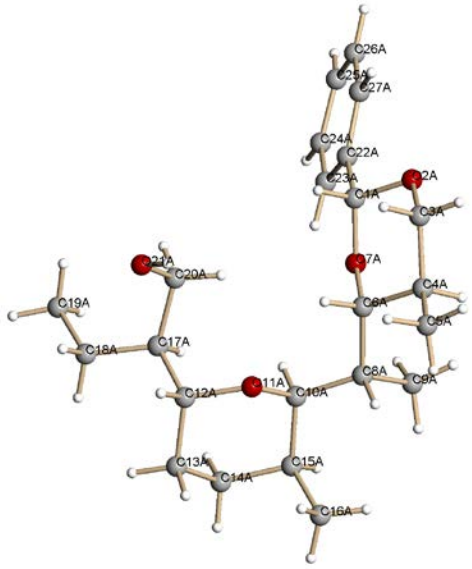
1. General methods:

All reactions requiring anhydrous conditions were conducted in flame dried glass apparatus under an atmosphere of nitrogen. THF and Et_2O were freshly distilled from sodium/benzophenone ketyl prior to use. 1,2-Dichloroethane, dichloromethane were freshly distilled on CaH_2, toluene and benzene were distilled on molten sodium metal. Anhydrous *t*-BuOH was obtained by drying with $MgSO_4$ followed by distillation on CaH_2 and stored under nitrogen over activated 4 Å molecular sieves. Reactions were monitored by TLC analysis using silica plates with fluorescent indicator (254 nm) and Visualization of the spots on TLC plates was achieved either by exposure to iodine vapor or UV light or by dipping the plates to sulphuric acid-β-naphthol or to ethanolic anisaldehyde-sulphuric acid-acetic acid or to Phosphomolybdic acid-sulphuric acid solution and heating the plates at 120 °C. All commercially available reagents were purchased from Sigma-Aldrich, and used without further purification. Infrared spectra were recorded using a thin film supported between NaCl plates or as a solid embedded in a KBr disc. ^{1}H and ^{13}C NMR spectra were recorded in Fourier transform mode at the field strength specified either on 300 MHz or 400 MHz or 500 MHz spectrometer. Chemical shifts in ppm are quoted relative to the residual signals of chloroform (δ_H 7.26 ppm or δ_C 77.0 ppm). Multiplicities in the ^{1}H NMR spectra are described as s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet, br = broad and coupling constants are reported in Hz. For low (MS) and high (HRMS) resolution mass spectra ion mass/charge (*m/z*) ratios are reported as values in atomic mass units. Optical rotations were determined with a polarimeter at 589 nm. Data are reported as follows: $[\alpha]_\lambda^{temp}$, concentration (c in g/100 mL), and solvent.

2. **X-ray information for compound 29:** X-ray data for the compound was collected at room temperature using a Bruker Smart Apex CCD diffractometer with graphite monochromated MoKα radiation (λ=0.71073Å) with ω-scan method.[1] Preliminary lattice parameters and orientation matrices were obtained from four sets of frames. Integration and scaling of intensity data were accomplished using SAINT program.[1] The structure was solved by direct methods using SHELXS97[2] and refinement was carried out by full-matrix least-squares technique using SHELXL97.[2] Anisotropic displacement parameters were included for all non-hydrogen atoms. All H atoms were positioned geometrically and treated as riding on their parent O and C atoms [O-H = 0.82 Å amd C-H = 0.93-0.97 Å and U_{iso}(H) = 1.5U_{eq}(C and O) for methyl H or 1.2U_{eq}(c)

for other H atoms]. The methyl groups were allowed to rotate but not to tip. In the absence of significant anomalous scattering efforts, Friedel pairs were merged. The absolute configuration of the procured material was known in advance.



ORTEP structure of compound **29**

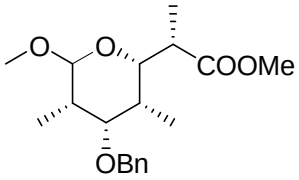
A view of **29**, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are represented by circles of arbitrary radii. The asymmetric unit contains two molecules (same numbering labeled with suffixes A and B) and molecule B has been omitted for clarity.

Crystal data for compound **29**: $C_{23}H_{36}O_4$, M = 376.52, colorless block, 0.21 × 0.18 × 0.09 mm^3, orthorhombic, space group $P2_12_12_1$ (No. 19), a = 10.5288(6), b = 15.9360(9), c = 25.9755(15) Å, V = 4358.4(4) Å^3, Z = 8, D_c = 1.148 g/cm^3, F_{000} = 1648, CCD Area Detector, MoKα radiation, λ = 0.71073 Å, T = 294(2)K, $2\theta_{max}$ = 50.0º, 42238 reflections collected, 4295 unique (R_{int} = 0.0543). Final *GooF* = 1.362, *R1* = 0.0868, *wR2* = 0.1738, *R* indices based on 3947 reflections with I>2σ(I) (refinement on F^2), 497 parameters, 0 restraints, μ = 0.077 mm^{-1}. CCDC 934894 contains supplementary Crystallographic data for the structure.

References:

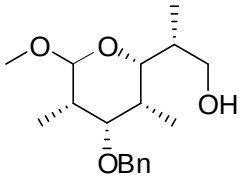
1. Bruker (2001). SAINT (Version 6.28a) & SMART (Version 5.625). Bruker AXS Inc., Madison, Wisconsin, USA.
2. Sheldrick GM. (2008**)** Acta Crystallogr A64: 112-122.

(*S*)-Methyl-2-((2*S*,3*R*,4*S*,5*S*)-4-(benzyloxy)-6-methoxy-3,5-dimethyltetrahydro-2H-pyran-2-yl)propanoate (11).



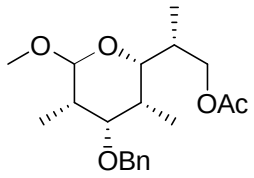
The compound **11** was obtained as pale yellow oil. R_f = 0.45 (hexane: EtOAc, 9:1); $[\alpha]_D^{28}$ = + 88.7 (*c* 0.7, $CHCl_3$); IR (neat) $\upsilon_{max:}$ 2976, 2925, 1718, 1455, 1274, 1176, 968 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.34-7.20 (m, 5H), 4.50 (s, 2H), 4.45 (s, 1H) 3.96-3.88 (m, 1H), 3.83 (t, *J* = 5.5 Hz, 1H), 3.68 (s, 3H), 3.24 (s, 3H), 2.73-2.60 (m, 1H), 2.23-2.03 (m, 2H), 1.11-1.04 (m, 6H), 0.97 (d, *J* = 7.2 Hz, 3H). ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 176.1, 138.8, 128.2, 127.3, 127.1, 104.3, 75.0, 71.7, 69.4, 54.8, 51.6, 41.7, 36.4, 32.5, 13.1, 13.0, 7.6 ppm; HRMS calculated for $C_{19}H_{28}O_5Na$ $[M + Na]^+$ 359.1815, found 359.1842.

(2*R*)-2-((2*R*,3*R*,4*S*,5*S*)-4-(Benzyloxy)-6-methoxy-3,5-dimethyltetrahydro-2H-pyran-2-yl) propan-1-ol (14).



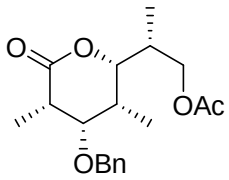
To an ice cooled suspension of $LiAlH_4$ (1.36 g, 35.71 mmol) in anhydrous THF (40 mL), was added a solution of ester **11** (8.0 g, 23.81 mmol) in anhydrous THF (40 mL) under nitrogen atmosphere. The reaction mixture was stirred for 4 h at room temperature and quenched with aq. saturated Na_2SO_4 solution (3 mL). The precipitate formed was filtered through a pad of celite and washed with ethyl acetate (2 x 50 mL). The filtrate was dried over anhydrous Na_2SO_4, filtered and evaporated under reduced pressure. The resulting crude product was purified by silica gel column chromatography utilizing ethyl acetate and hexane (1:9) as an eluent to obtain alcohol **14** (6.82 g, 93%) as colorless oil. R_f = 0.5 (hexane: EtOAc, 7:3); $[\alpha]_D^{28}$ = +46 (*c* 0.9, $CHCl_3$); IR (neat) $\upsilon_{max:}$ 3425, 2926, 1720, 1605, 1454, 1247, 1075 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.32-7.20 (m, 5H), 4.53 (s, 1H), 4.49 (s, 2H), 3.79 (t, *J* = 5.2 Hz, 1H), 3.66-3.58 (m, 2H), 3.57-3.50 (m, 1H), 3.33 (s, 3H), 3.12-3.05 (bs, 1H), 2.25-2.15 (m, 1H), 2.14-2.04 (m, 1H), 2.02-1.92 (m, 1H), 1.05 (d, *J* = 7.5 Hz, 3H), 1.00 (d, *J* = 7.6 Hz, 3H), 0.79 (d, *J* = 7.5 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.8, 128.2, 127.3, 127.1, 104.3, 75.8, 74.8, 69.3, 68.5, 54.7, 36.3, 35.9, 33.4, 13.0, 12.0, 7.8 ppm; HRMS calculated for $C_{18}H_{28}O_4Na$ $[M + Na]^+$ 331.1885, found 331.1875.

(*R*)-2-((2*R*,3*R*,4*S*,5*S*,6*S*)-4-(Benzyloxy)-6-methoxy-3,5-dimethyltetrahydro-2H-pyran-2-yl) propyl acetate (15).



To a stirred solution of alcohol **14** (1.2 g, 3.90 mmol) in anhydrous CH_2Cl_2 (20 mL), Et_3N (1.1 mL, 7.80 mmol), acetic anhydride (0.55 mL, 5.85 mmol) and catalytic amount of DMAP (50 mg) were added at 0 ^oC and stirred at room temperature for 4 h. The reaction mixture was quenched with H_2O (5 mL) and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (2 x 20 mL). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure and purified by silica gel column chromatography using ethyl acetate and hexane (1:19) as mobile phase to obtain the acetate derivative **15** (1.29 g, 95%) as colorless liquid. R_f = 0.6 (hexanes:EtOAc, 8:2); $[\alpha]_D^{28}$ = +40 (*c* 0.6, $CHCl_3$); IR (neat) $\upsilon_{max:}$ 3448, 2924, 2854, 1734, 1458, 1371, 1245, 1077, 1021 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.32-7.20 (m, 5H), 4.49 (s, 3H), 4.29 (dd, *J* = 3.7, 10.5 Hz, 1H), 4.04 (dd, *J* = 6.0, 10.5 Hz, 1H), 3.80 (t, *J* = 5.2, 1H), 3.56 (dd, *J* = 2.2, 10.5 Hz, 1H), 3.25 (s, 3H), 2.26-2.06 (m, 2H), 2.04 (s, 3H), 2.03-1.95 (m, 1H), 1.05 (d, *J* = 7.5 Hz, 3H), 0.97 (d, *J* = 6.7 Hz, 3H), 0.91 (d, *J*= 6.7 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.2, 139.0, 128.3, 127.3, 127.2, 104.4, 75.4, 70.2, 69.4, 66.6, 54.6, 36.4, 34.0, 33.1, 20.9, 13.2, 12.9, 7.6 ppm; MS (ESI) calculated for $C_{20}H_{31}O_5$ $[M + H]^+$ 351, found 351.

(*R*)-2-((2*R*,3*R*,4*S*,5*S*)-4-(Benzyloxy)-3,5-dimethyl-6-oxotetrahydro-2H-pyran-2-yl)propyl acetate (17).

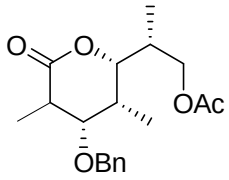


A solution of acetal **15** (10.0 g, 28.6 mmol) in CH_3COOH:H_2O:THF (6:3:2, 110 mL) was stirred at 60 ^oC for 8 h. The reaction mixture was diluted with ethyl acetate (10 mL) and solid $NaHCO_3$ was added. After the effervescence stopped, the organic layer was separated and the aqueous layer was extracted with ethyl acetate (2 x 100 mL). The combined organic layer was dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude compound was passed through a small pad of silica gel to give compound **16** (8.63 g, 90%) as colorless viscous liquid. R_f = 0.5 (hexanes:EtOAc, 7:3). The compound was utilized directly without further purification.

To a solution of lactol **16** (4.0 g, 11.9 mmol) in CH_2Cl_2 (40 mL) at 0 ^oC was added TEMPO (185 mg, 1.19 mmol) followed by iodobenzene diacetate (5.75 g, 17.85 mmol) and allowed the reaction mixture to stirred at ambient temperature for 4 h. After conversion of the diol completely to lactone, reaction mixture was quenched with saturated solution of Sodium

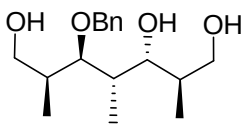
thiosulfate (5 mL) and extracted with CH_2Cl_2 (3 x 50 mL). The combined organic layers were dried over Na_2SO_4 and evaporation of solvent under reduced pressure led to the crude lactone which was purified on silica gel column chromatography to furnish the lactone **17** as colorless viscous liquid (3.57 g, 90%). R_f = 0.40 (hexanes:EtOAc, 7:3); $[\alpha]_D^{28}$ = -38.5 (*c* 1, $CHCl_3$); IR (neat) υ_{max}: 3461, 2922, 2852, 1723, 1458, 1273, 1110~~, 988, 715~~ cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.36-7.22 (m, 5H), 4.53 (ABq, *J* = 11.3 Hz, 2H), 4.32 (m, 1H), 4.10 (dd, *J* = 5.2, 11.3 Hz, 1H), 4.0-3.9 (m, 2H), 2.92-2.82 (m, 1H), 2.48-2.37 (m, 1H), 2.20-2.09 (m, 1H), 2.04 (s, 3H), 1.31 (d, *J* = 7.5 Hz, 3H), 0.98-0.92 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 174.1, 170.9, 137.6, 128.3, 127.7, 127.3, 78.7, 75.8, 72.4, 65.5, 38.2, 33.8, 32.7, 20.8, 12.8, 12.2, 6.1 ppm; HRMS calculated for $C_{19}H_{26}O_5Na$ $[M + Na]^+$ 357.1688, found 357.1677.

(*R*)-2-((2*R*,3*R*,4*S*,5*R*)-4-(Benzyloxy)-3,5-dimethyl-6-oxotetrahydro-2H-pyran-2-yl) propyl acetate (10).



To a stirred solution of lactone **17** (3.6 g, 10.78 mmol) in anhydrous CH_2Cl_2 (20 mL), at 0 °C was added DBU (diazabicyclo [5.4.0] undec-7-ene, 1.61 mL, 10.78 mmol) and the resulting solution was stirred at room temperature for 4 h. Then the reaction mixture was diluted with water (5 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic layers were washed with brine, dried over Na_2SO_4 and evaporated to give crude 3-*epi*-lactone which was purified on silica gel using to furnish the 3-*epi*-lactone **10** as colorless liquid (3.35 g, 92%). R_f = 0.49 (hexanes:EtOAc, 7:3); $[\alpha]_D^{28}$ = -54.4 (*c* 0.6, $CHCl_3$); IR (neat) υ_{max}: 3465, 2975, 2932, 1735, 1457, 1270, 1109~~, 986, 714~~ cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.35-7.18 (m, 5H), 4.48 (ABq, *J* = 11.5 Hz, 2H), 4.31-4.23 (m, 1H), 4.05 (dd, *J* = 5.4, 10.9 Hz, 1H), 3.91-3.84 (m, 1H), 3.40 (dd, *J* = 4.1, 10.3 Hz, 1H), 2.52-2.40 (m, 1H), 2.34-2.24 (m, 1H), 2.10-2.02 (m, 1H), 1.99 (s, 3H), 1.30 (d, *J* = 6.9 Hz, 3H), 0.93-0.85 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.0, 171.0, 137.6, 128.5, 128.0, 127.6, 80.8, 79.4, 70.8, 65.5, 38.4, 34.5, 30.6, 20.8, 14.6, 12.7, 4.2 ppm; HRMS calculated for $C_{19}H_{26}O_5Na$ $[M + Na]^+$ 357.1662, found 357.1677.

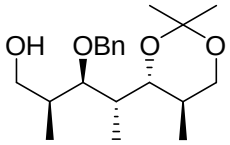
(2*R*,3*R*,4*S*,5*R*,6*S*)-5-(Benzyloxy)-2,4,6-trimethylheptane-1,3,7-triol (18).



To an ice cooled suspension of $LiAlH_4$ (0.54 g, 14.08 mmol) in anhydrous THF (15 mL), was added a solution of lactone **10** (2.35 g, 7.04 mmol) in anhydrous THF (15 mL) under nitrogen

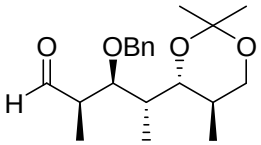
atmosphere. The reaction mixture was stirred for 4 h at room temperature and quenched with aq. saturated Na_2SO_4 solution. The precipitate formed was filtered through a pad of celite and washed with ethyl acetate. The filtrate was dried over anhydrous Na_2SO_4, concentrated to dryness under reduced pressure. The resulting crude product was purified by silica gel column chromatography utilizing ethyl acetate and hexane (50:50) as an eluent to obtain alcohol **18** (1.97 g, 95%) as colorless oil. R_f = 0.49 (EtOAc) $[\alpha]_D^{28}$ = -8.8 (*c* 0.8, $CHCl_3$); IR (neat) υ_{max}: 3508, 1462, 1036 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.34-7.23 (m, 5H), 4.64 (s, 2H), 3.82 (d, *J* = 9.8 Hz, 1H), 3.63-3.48 (m, 5H), 2.06-1.94 (m, 1H), 1.91-1.76 (m, 2H), 1.03-0.96 (m, 6H), 0.73 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.1, 128.3, 127.6, 127.6, 84.3, 76.3, 75.4, 68.5, 65.1, 38.1, 37.3, 36.5, 13.1, 12.1, 10.4 ppm; HRMS calculated for $C_{17}H_{28}O_4Na$ $[M + Na]^+$ 319.1837, found 319.1833.

(2*S*,3*R*,4*R*)-3-(Benzyloxy)-2-methyl-4-((4*R*,5*R*)-2,2,5-trimethyl-1,3-dioxan-4-yl)pentan-1-ol (19).



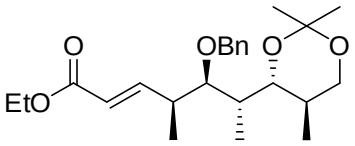
To a stirred solution of compound **18** (1.2 g, 4.05 mmol) in anhydrous CH_2Cl_2 (12 mL) was added 2,2-dimethoxypropane (0.74 mL, 6.07 mmol) followed by a catalytic amount of ±camphor sulphonic acid (47 mg, 0.20 mmol) at 0 °C. The reaction mixture was stirred for 2 h at room temperature and quenched with saturated $NaHCO_3$ (2 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated under reduced pressure, and purified by silica gel chromatography to afford compound **19** (1.25 g, 93%) as viscous liquid. R_f = 0.49 (hexanes:EtOAc, 7:3) $[\alpha]_D^{28}$ = -14.5 (*c* 0.85, $CHCl_3$); IR (neat)υ_{max}: 3484, 2967, 2879, 1458, 1382, 1068~~, 699~~ cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.32-7.20 (m, 5H), 4.61 (s, 2H), 3.85 (d, *J* = 11.0 Hz, 1H), 3.63 (dd, *J* = 5.0, 12.0 Hz, 2H), 3.56 (d, *J* = 6.0 Hz, 2H), 3.45 (t, *J* = 11.0 Hz, 1H), 1.94-1.81 (m, 3H), 1.37 (s, 6H), 0.88 (d, *J* = 7.0 Hz, 3H), 0.84 (d, *J* = 7.0 Hz, 3H), 0.72 (d, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.2, 128.3 (2C), 127.2, 126.9 (2C), 98.0, 79.1, 74.1, 73.3, 66.2 (2C), 37.8, 36.6, 30.3, 29.8, 19.5, 12.4, 9.6, 9.4 ppm; HRMS calculated for $C_{20}H_{32}O_4Na$ $[M + Na]^+$ 359.2198, found 359.2210.

(2*R*,3*S*,4*R*)-3-(Benzyloxy)-2-methyl-4-((4*R*,5*R*)-2,2,5-trimethyl-1,3-dioxan-4-yl)pentanal (20)



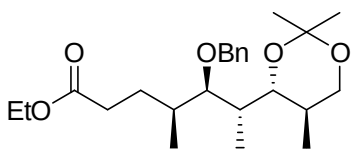
Iodoxybenzoic acid (1.25 g, 4.47 mmol) was taken in anhydrous DMSO (2 mL) and stirred for 30 min. Alcohol **19** (1.0 g, 2.98 mmol) in anhydrous CH_2Cl_2 (10 mL) was added to the reaction mixture at room temperature and stirred for 4 h. After completion of the reaction (monitored by TLC), the reaction mixture was quenched with water (7 mL) and the solid formed was filtered through celite. The organic layer was separated and aqueous layer extracted with ether (3 x 15 mL). The combined organic layers were washed with brine (6 mL), dried over anhydrous Na_2SO_4, concentrated under reduced pressure and purified by silica gel column chromatography using ethyl acetate and hexane (1:19) as mobile phase to obtain aldehyde **20** (0.92 g, 93%) as colorless liquid. R_f = 0.50 (hexanes:EtOAc, 9:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ 9.76 (d, *J* = 1.7 Hz, 1H), 7.36-7.23 (m, 5H), 4.67-4.48 (ABq, *J* = 11.3 Hz, 2H), 3.93-3.84 (m, 1H), 3.76-3.61 (m, 2H), 3.50-3.40 (m, 1H), 2.73-2.64 (m, 1H), 2.04-1.75 (m, 2H), 1.34 (s, 6H), 1.21 (d, *J* = 6.9 Hz, 3H), 0.81 (d, *J* = 6.9 Hz, 3H), 0.71 (d, *J* = 6.6 Hz, 3H) ppm. MS (ESI) calculated for $C_{20}H_{31}O_4$ $[M + H]^+$ 335, found 335.

(4*S*,5*R*,6*R*,*E*)-Ethyl-5-(benzyloxy)-4-methyl-6-((4*R*,5*R*)-2,2,5-trimethyl-1,3-dioxan-4-yl)hept-2-enoate (21).



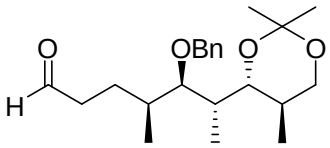
The aldehyde **20** (0.92 g, 2.74 mmol) obtained from above was treated with the stabilized C2-Wittig ylide (1.24 g, 3.56 mmol) in benzene (20 mL) at reflux temperature for 4 h. After completion of the reaction (TLC analysis), benzene was removed under vacuum, and the crude ester was subjected to silica gel column chromatography using EtOAc and hexane (4:96) as an eluent to afford *α,β*-unsaturated ester **21** (1.05 g, 95%) as colorless liquid. R_f = 0.50 (hexanes:EtOAc, 9:1); $[\alpha]_D^{28}$ = +21.1 (*c* 0.7, $CHCl_3$); IR (neat) υ_{max}: 3438, 2977, 2931, 1718, 1649, 1262, 1179, 1058~~, 956, 739~~ cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$: δ 7.34-7.09 (m, 6H), 5.83 (d, *J* = 15.8, 1H), 4.47 (ABq, 11.3 Hz, 2H), 4.16 (dd, *J* = 7.5, 14.3 Hz, 2H), 3.87 (dd, *J* =1.5, 10.5 Hz, 1H), 3.65 (dd, *J* = 5.2, 11.3 Hz, 1H), 3.53-3.41 (m, 2H), 2.60 (q, *J* = 5.2 Hz, 1H), 1.91-1.77 (m, 2H), 1.34 (s, 6H), 1.31-1.25 (t, *J* = 7.5 Hz, 3H), 1.09 (d, *J* = 6.7 Hz, 3H), 0.86 (d, *J* = 6.7 Hz, 3H), 0.71 (d, *J* = 6.0 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 153.3, 138.7, 128.2, 127.2, 127.1, 120.2, 97.9, 82.0, 74.4, 73.1, 66.2, 60.0, 38.5, 36.8, 30.3, 29.7, 19.4, 14.2, 12.3, 11.0, 9.4 ppm; HRMS calculated for $C_{24}H_{36}O_5Na$ $[M + Na]^+$ 427.2440, found 427.2443.

(4*S*,5*R*,6*R*)-Ethyl 5-(benzyloxy)-4-methyl-6-((4*R*,5*R*)-2,2,5-trimethyl-1,3-dioxan-4-yl) heptanoate (22).



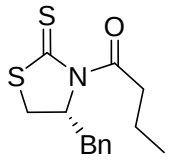
$NiCl_2.6H_2O$ (0.45 g, 1.90 mmol).was added to a stirred solution of conjugated alkene **21** (3.50 g, 8.66 mmol) in MeOH (30 mL) at 0 ^oC. Then was added $NaBH_4$ (0.66 g, 17.32 mmol) in portions. The reaction mixture was stirred for another 4 h and quenched with saturated NH_4Cl (10 mL). The reaction mixture was concentrated to get the residue, which was extracted with EtOAc (3 x 30 mL). The organic extract was washed with brine (10 mL), and dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The crude reaction mixture was purified by silica gel column chromatography using EtOAc and hexane (5:95) as an eluent to provide the corresponding saturated ester compound **22** (3.20 g, 91%) as clear oil. R_f = 0.50 (hexanes:EtOAc, 9:1); $[\alpha]_D^{28}$ = -20.0 (*c* 0.7, $CHCl_3$); IR (neat) υ_{max}: 3450, 2925, 2854, 1734, 1377, 1175, 1007 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.31-7.18 (m, 5H), 4.66-4.55 (ABq, *J* = 12.1 Hz, 2H), 4.02 (q, *J* = 6.7 Hz, 2H), 3.83 (d, *J* = 9.0 Hz, 1H), 3.66-3.59 (m, 1H), 3.48-3.35 (m, 2H), 2.42-2.22 (m, 2H), 1.91-1.76 (m, 3H), 1.73-1.61 (m, 2H), 1.34 (s, 3H), 1.32 (s, 3H), 1.25 (t, *J* = 7.5 Hz, 3H), 0.91 (d, *J* = 6.7 Hz, 3H), 0.81 (d, *J* = 7.5 Hz, 3H), 0.71 (d, *J* = 7.5 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.7, 139.2, 128.2, 127.1, 126.7, 97.9, 82.2, 74.5, 73.3, 66.2, 60.2, 36.8, 35.1, 32.8, 30.3, 30.2, 29.8, 19.4, 14.2, 12.4, 12.2, 9.5 ppm; HRMS calculated for $C_{24}H_{38}O_5Na$ $[M + Na]^+$ 429.2609, found 429.2616.

(4*S*,5*R*,6*R*)-5-(Benzyloxy)-4-methyl-6-((4*R*,5*R*)-2,2,5-trimethyl-1,3-dioxan-4-yl)heptanal (9).



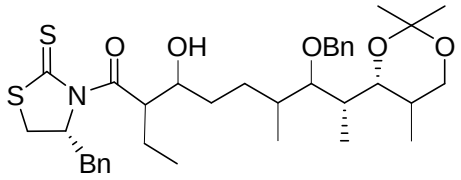
A solution of saturated ester **22** (6.0 g, 14.78 mmol) in 50 mL of CH_2Cl_2 was cooled to -78 ^oC DIBAL-H (10.4 mL, 17.74 mmol; 25% solution in toluene) was added drop wise over a period of 5 minutes. The resulting mixture was stirred for 0.5 h at -78 ^oC and quenched with saturated aqueous sodium-potassium tartrate solution (20 mL). The mixture was warmed to room temperature and stirred for 2.5 h. Organic layer was separated and aqueous layer extracted with CH_2Cl_2 (2 x 80 mL). Combined organic layer was dried over Na_2SO_4 and evaporated. Silica gel column chromatography of the crude product using EtOAc and hexane (5:95) as an eluent afforded the aldehyde **9** (4.42 g, 90%) as colorless liquid. R_f = 0.50 (hexanes:EtOAc, 9:1); ^1H NMR (300 MHz, $CDCl_3$): δ 9.79 (d, *J* = 1.7 Hz, 1H), 7.43-7.29 (m, 5H), 4.65 (s, 2H), 3.90 (d, *J* = 10.5 Hz, 1H), 3.71 (dd, *J* = 5.28, 10.5 Hz, 1H), 3.51 (t, *J* = 11.3 Hz, 1H), 3.43-3.33 (m, 1H), 2.64-2.25 (m, 2H), 2.01-1.75 (m, 4H), 1.74-1.50 (m, 1H), 1.40 (s, 3H), 1.38 (s, 3H), 1.09 (d, *J* = 6.8 Hz, 3H), 0.88 (d, *J* = 6.8 Hz, 3H), 0.72 (d, *J* = 6.8 Hz, 3H) ppm; MS (ESI) calculated for $C_{22}H_{35}O_4$ $[M + H]^+$ 335, found 335.

1-(4-Benzyl-2-thioxothiazolidin-3-yl)butan-1-one (23).



To a stirred solution of 4-benzyl-2-thioxothiazolidine (2.2 g, 10.5 mmol) in anhydrous CH_2Cl_2 (20 mL) was added Et_3N (1.9 mL, 13.65 mmol) followed by *n*-butyryl chloride (1.2 mL, 11.5 mmol) at 0 °C. The reaction mixture was stirred for 1 h at room temperature and quenched with saturated ammonium chloride solution (5 mL). The aqueous layer was extracted with CH_2Cl_2 (2 x 25 mL). The combined organic layer was dried over anhydrous Na_2SO_4, concentrated to dryness under reduced pressure, and purified by silica gel chromatography using EtOAc and hexane (5: 95) as an eluent to afford compound **23** (2.64 g , 90%) as a solid. M.P. = 101 ^oC; R_f = 0.50 (hexanes:EtOAc, 9:1); $[\alpha]_D^{28}$ = -204.0 (*c* 1, $CHCl_3$); IR (KBr): 2958, 2925, 1694, 1162, 1062, 1034 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.35-7.20 (m, 5H), 5.37-5.29 (m, 1H), 3.41-3.28 (m, 2H), 3.25-3.17 (m, 1H), 3.13-2.97 (m, 2H), 2.86 (d, *J* = 11.3 Hz, 1H), 2.45-2.29 (m, 1H), 1.80-1.62 (m, 2H), 1.0 (t, *J* = 7.4 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 200.1, 173.8, 136.5, 129.3, 128.7, 127.1, 68.5, 40.2, 36.7, 31.8, 18.1, 13.5 ppm; HRMS calculated for $C_{14}H_{18}NOS_2$ $[M + H]^+$ 280.0827, found 280.0824.

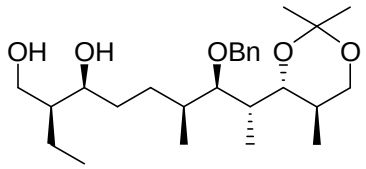
1-(4-Benzyl-2-thioxothiazolidin-3-yl)-7-(benzyloxy)-2-ethyl-3-hydroxy-6-methyl-8-(2,2,5-trimethyl-1,3-dioxan-4-yl)nonan-1-one (24).



To the solution of thione **23** (2.47 g, 8.84 mmol) in anhydrous CH_2Cl_2 (20 mL) at 0 °C was added neat $TiCl_4$ (1.0 mL, 9.11 mmol) dropwise, and the resulting slurry was stirred for 15 min. DIPEA (1.67 mL, 9.67 mmol) was added dropwise, and the resultant deep red solution was stirred for 15 min. *N*-methyl pyrrolidinone (1.69 mL, 17.68 mmol) was added and stirred for 15 min. at 0 °C. The resulting mixture was added by aldehyde (1.6 g, 4.42 mmol) **9** dropwise in CH_2Cl_2 (10 mL) at -78 ^oC. The reaction was stirred at -78 ^oC for another 1 h. Temperature was gradually increased to 0 °C and stirred for another 1h, quenched by the addition of a saturated $NaHCO_3$ solution. The layers were separated and the aqueous layer was then extracted into CH_2Cl_2 (3 x 30 mL). The organic extracts were dried (Na_2SO_4) and evaporated to give a crude yellow oil, which was purified by flash chromatography using EtOAc and hexane (5:95) as an eluent to provide the compound **24** (2.42 g, 86%) as yellow oil. R_f = 0.50 (hexanes:EtOAc, 7:3); $[\alpha]_D^{28}$ = -69.5 (*c* 2.4, $CHCl_3$); IR (neat) υ_{max}: 3442, 2922, 2855, 1724, 1636, 1033 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.38-7.16 (m, 10H), 5.39-5.29 (m, 1H), 4.94-4.86 (m, 1H), 4.67-4.52 (m,

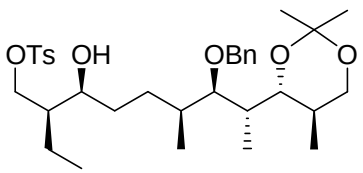
2H), 3.87-3.74 (m, 2H), 3.67-3.58 (m, 1H), 3.49-3.18 (m, 5H), 3.09-2.98 (m, 1H), 2.87-2.78 (m, 1H), 2.07-1.77 (m, 2H) 1.74-1.57 (m, 1H), 1.51-1.22 (m, 11H), 0.99 (t, *J* = 7.5 Hz, 3H), 0.89 (d, *J* = 6.0 Hz, 3H), 0.79 (d, *J* = 7.5 Hz, 3H), 0.70 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 201.8, 176.5, 139.5, 136.4, 129.3, 128.8, 128.2, 127.2, 127.0, 126.7, 97.9, 82.6, 74.5, 73.4, 72.9, 69.1, 66.2, 49.5, 36.9, 36.8, 35.4, 32.8, 31.6, 31.5, 30.3, 29.8, 19.5, 19.4, 12.6, 12.4, 11.9, 9.6 ppm; HRMS calculated for $C_{36}H_{51}NO_5S_2Na$ $[M + Na]^+$ 664.3095, found 664.3106.

(2*S*,3*S*,6*S*,7*R*,8*R*)-7-(Benzyloxy)-2-ethyl-6-methyl-8-((4*R*,5*R*)-2,2,5-trimethyl-1,3-dioxan-4-yl)nonane-1,3-diol (25).



A solution of sodium borohydride (0.7 g, 18.50 mmol) in water (10 mL) was added drop wise to a cooled (0 ^{o}C) solution of amide **24** (6.0 g, 9.35 mmol) in THF (90.0 mL). Stirring was continued for 2 h with concomitant warming of the mixture to room temperature. The solution was treated with saturated aqueous NH_4Cl solution (40 mL), stirred for 1 h, The layers were separated and the aqueous layer was then extracted into CH_2Cl_2 (30 x 20 mL). The organic extracts were dried over anhydrous Na_2SO_4 and evaporated to give a crude oil which was purified by silica gel chromatography using ethyl acetate and hexane (2:8) as an eluent to yield a viscous diol **25** (3.7 g, 90%) as colorless viscous liquid. R_f = 0.50 (hexanes:EtOAc, 6:4); $[\alpha]_D^{28}$ = -20.9 (*c* 2, $CHCl_3$); IR (neat) υ_{max}: 3413, 2931, 2877, 1457, 1377, 1196, 1060, 1013 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.34-7.17 (m, 5H), 4.60 (s, 2H), 3.86-3.58 (m, 5H), 3.49-3.32 (m, 2H), 1.90-1.74 (m, 2H), 1.73-1.57 (m, 2H), 1.56-1.39 (m, 2H), 1.34 (s, 3H), 1.32 (s, 3H), 1.26-1.07 (m, 4H), 0.98 (m, 9H), 0.71 (d, *J* = 6.0 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.5, 128.2, 127.1, 126.8, 97.9, 82.8, 75.5, 74.5, 73.5, 66.2, 64.4, 45.9, 36.9, 35.5, 31.8, 31.5, 30.3, 29.9, 19.5, 18.0, 12.6, 12.4, 12.2, 9.6 ppm; HRMS calculated For $C_{26}H_{44}O_5Na$ $[M + Na]^+$ 459.3103, found 459.3086.

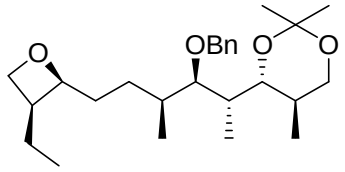
(2*S*,3*S*,6*S*,7*R*,8*R*)-7-(Benzyloxy)-2-ethyl-3-hydroxy-6-methyl-8-((4*R*,5*R*)-2,2,5-trimethyl-1,3-dioxan-4-yl)nonyl 4-methylbenzenesulfonate (26).



p-Toluenesulfonyl chloride (1.73 g, 9.11 mmol) was added to a stirred solution of alcohol **25** (4.0 g, 9.17 mmol) in pyridine: CH_2Cl_2 (1:1) (38 mL) at 0 ^{o}C. And stirred for 8 h, the reaction was

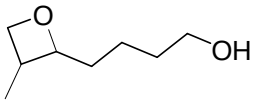
quenched by addition of ice (0.5 g). The mixture was diluted with CH_2Cl_2 (2 x 35 mL) and washed with aq. saturated copper sulfate solution (7 mL) followed by aq. saturated $NaHCO_3$ solution (7 mL) and brine (10 mL). The organic layer was filtered, dried over (Na_2SO_4) and concentrated under vacuum. The residue was purified by silica gel chromatography using ethyl acetate and hexane (1:9) as an eluent to give tosylated product **26** (4.33 g, 80%) as colorless oil. R_f = 0.50 (hexanes:EtOAc, 8:2); $[\alpha]_D^{28}$ = -4.2 (*c* 1.3, $CHCl_3$); IR (neat) υ_{max}: 3456, 2962, 2927, 2855, 1726, 1458, 1362, 1176, 1098~~, 949~~ cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.80 (d, *J* = 8.3 Hz, 2H), 7.38-7.30 (m, 5H), 7.28-7.24 (m, 3H), 4.67-4.56 (m, 2H), 4.14-4.0 (m, 2H), 3.89 (d, *J* = 10.3 Hz, 1H), 3.72-3.61 (m, 2H), 3.49 (t, *J* = 11.3 Hz, 1H), 3.38 (d, *J* = 9.6 Hz, 1H), 2.44 (s, 3H), 1.94-1.80 (m, 1H) 1.69-1.53 (m, 5H), 1.39 (s, 3H), 1.37 (s, 3H), 1.31-1.22 (m, 4H), 0.92-0.79 (m, 9H), 0.71 (d, *J* = 7.5 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 144.8, 139.5, 133.0, 129.8, 128.2, 127.9, 127.2, 126.9, 98.0, 82.9, 74.6, 73.5, 71.2, 70.4, 66.3, 44.9, 36.9, 35.5, 32.2, 31.7, 30.3, 29.9, 21.6, 19.5, 18.3, 12.6, 12.4, 11.9, 9.7 ppm; HRMS calculated for $C_{33}H_{51}O_7S$ $[M + H]^+$ 591.3355, found 591.3335.

(4*R*,5*R*)-4-((2*R*,3*R*,4*S*)-3-(Benzyloxy)-6-((2*S*,3*S*)-3-ethyloxetan-2-yl)-4-methylhexan-2-yl)-2,2,5-trimethyl-1,3-dioxane (27).



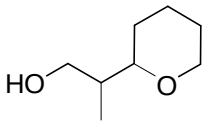
To an ice cooled suspension of NaH (60% dispersion in mineral oil) (0.32 g, 8.12 mmol) in THF (20 mL) was added to stirred solution of tosylate **26** (4.0 g, 6.67 mmol) under nitrogen atmosphere. The reaction mixture was stirred for 3 h at room temperature and quenched with saturated aqueous NH_4Cl solution (3 mL). Organic layer separated and aqueous layer extracted with EtOAc (2 x 10 mL). Combined organic layer dried over Na_2SO_4 and evaporated under reduced pressure. The crude product was purified by flash chromatography (using ethyl acetate and hexane (2:8) as an eluent to afford the oxetane **27** (2.6 g, 92%) as colorless liquid. R_f = 0.60 (hexanes:EtOAc, 8:2); IR (neat) υ_{max}: 2931, 2868, 1458, 1062~~, 734~~ cm^{-1}; $[\alpha]_D^{28}$ = -10.1 (*c* 1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.35-7.23 (m, 5H), 4.79-4.70 (m, 2H), 4.61 (ABq, *J* = 11.7 Hz, 2H), 4.16-4.11 (m, 1H), 3.88 (d, *J* = 10.7 Hz, 1H), 3.67 (dd, *J* = 4.8, 11.7 Hz, 1H), 3.48 (t, *J* = 11.7 Hz, 1H), 3.39 (d, *J* = 9.7 Hz, 1H), 2.83-2.74 (m, 1H), 1.91-1.81 (m, 3H) 1.74-1.53 (m, 3H), 1.50-1.41 (m, 4H), 1.38 (s, 3H), 1.36 (s, 3H), 0.92 (d, *J* = 6.8 Hz, 3H), 0.85-0.79 (m, 6H), 0.70 (d, *J* = 6.8 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.5, 128.2 (2C), 127.0, 126.8 (2C), 98.0, 84.9, 82.6, 74.4, 74.2, 73.5, 66.3, 39.4, 36.9, 35.5, 30.3 (2C) 30.2, 29.9, 21.5, 19.5, 12.6, 12.4, 11.6, 9.6 ppm; HRMS calculated for $C_{26}H_{43}O_4$ $[M + H]^+$ 419.31610, found 419.31559.

4-((2*S*,3*S*)-3-Methyloxetan-2-yl)butan-1-ol (1a).



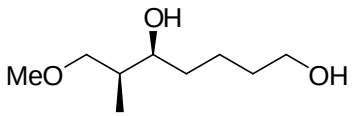
(70 mg, 0.3 mmol) benzyl ether of alcohol **1a** treated by with $Pd(OH)_2$ (10 mg, 20 wt% on activated charcoal) under hydrogen atmosphere to yield in **1a** (56 mg, 92%) yield as a colorless liquid. R_f = 0.25 (hexanes:EtOAc, 5:5); $[\alpha]_D^{28}$ = -1.3 (*c* 0.3, $CHCl_3$); IR (neat) υ_{max}: 3418, 2924, 2864 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.86-4.81 (m, 1H), 4.78-4.74 (m, 1H), 4.07 (t, *J* = 5.64 Hz, 1H), 3.66-3.61 (m, 2H), 3.06-2.97 (m, 1H), 1.86-1.77 (m, 1H), 1.65-1.53 (m, 4H), 1.47-1.37 (m, 1H), 1.16 (d, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 85.1, 75.6, 62.6, 32.2, 31.6, 31.1, 20.8, 13.2 ppm; HRMS calculated for $C_8H_{17}O_2$ $[M + H]^+$ 145.1220, found 145.1223.

(*S*)-2-((*R*)-Tetrahydro-2H-pyran-2-yl)propan-1-ol (1b).



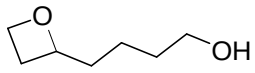
A solution of oxetane **1a** (20 mg, 0.138 mmol), in CH_2Cl_2:*i*-PrOH (15:1) 1 mL was cooled to 0 ^oC. To this CSA (3.2 mg, 0.138 mmol) was added the reaction mixture was allowed to warm to room temperature and stirred for 2 h before quenching with solid $NaHCO_3$. CH_2Cl_2 layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic layer was washed with brine (3 mL), dried over Na_2SO_4 and the solvent was evaporated under reduced pressure to obtain the crude product which was purified by flash column chromatography with ethyl acetate and hexane (5:5) as an eluent to afford the primary alcohol **1b** (18.8 mg, 94 %) as colorless liquid. R_f = 0.5 (hexanes:EtOAc, 5:5); $[\alpha]_D^{28}$ = -1.4 (*c* 1.0, $CHCl_3$); IR (neat) υ_{max}: 2958, 2926, 2855, 1725, 1460, 1272 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.04-3.95 (m, 1H), 3.65-3.57 (m, 2H), 3.48-3.37 (m, 1H), 3.26-3.17 (m, 1H), 1.90-1.80 (m, 1H), 1.79-1.64 (m, 2H), 1.59-1.42 (m, 3H), 1.40-1.20 (m, 1H), 0.83 (d, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 84.4, 68.6, 68.2, 40.3, 30.0, 25.9, 23.2, 13.4 ppm; HRMS calculated for $C_8H_{16}O_2Na$ $[M + Na]^+$ 167.1038, found 167.1042.

(5*S*,6*S*)-7-Methoxy-6-methylheptane-1,5-diol (1c).



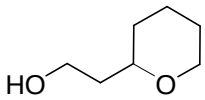
Colorless liquid **1c** (8 mg, 93%). R_f = 0.35 (hexanes:EtOAc, 5:5); $[\alpha]_D^{28}$ = +1.4 (*c* .05, $CHCl_3$); IR (neat) υ_{max}: 3448, 2924, 2854, 1734, 1458, 1371, 1245, 1077, 1021 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.76-3.72 (m, 1H), 3.66 (t, *J* = 6.2 Hz, 2H), 3.45-3.43 (m, 2H), 3.34 (s, 3H), 1.88-1.82 (m, 1H), 1.68-1.47 (m, 5H), 1.45-1.38 (m, 1H), 0.91 (d, *J* = 7.01 Hz, 3H) ppm; MS (ESI) calculated for $C_9H_{21}O_3$ $[M + H]^+$ 177, found 177.

(*S*)-4-(Oxetan-2-yl)butan-1-ol (2a).



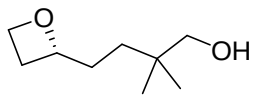
Colorless liquid **2a**. R_f = 0.2 (hexanes:EtOAc, 5:5); $[\alpha]_D^{28}$ = +2.1 (*c* 0.8, $CHCl_3$); IR (neat) υ_{max}: 3417, 2922, 2854 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.91-4.79 (m, 1H), 4.67 (m, 1H), 4.55-4.46 (m, 1H), 3.65 (t, *J* = 6.42 Hz, 2H), 2.73-2.61 (m, 1H), 2.41-2.28 (m, 1H), 1.93-1.76 (m, 2H), 1.74-1.54 (m, 2H), 1.50-1.32 (m, 2H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 82.8, 68.1, 62.5, 37.5, 32.3, 27.5, 20.3 ppm; HRMS calculated for $C_7H_{15}O_2$ $[M + H]^+$ 131.1064, found 131.1066.

(*R*)-2-(Tetrahydro-2H-pyran-2-yl)ethanol (2b).



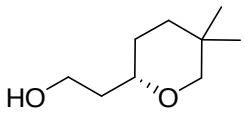
A solution of oxetane (**2a)** (20 mg, 0.153 mmol), in CH_2Cl_2:*i*-PrOH (15:1) 1 mL was cooled to 0 ^oC. To this CSA (3.5 mg, 0.153 mmol) was added the reaction mixture was allowed to warm up to room temperature and stirred for 2 h before quenching with solid $NaHCO_3$. CH_2Cl_2 layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 5 mL). The combined organic layer was washed with brine (3 mL), dried over anhydrous Na_2SO_4 and solvent was evaporated under reduced pressure to obtain the crude product which was purified by flash column chromatography with ethyl acetate and hexane (5:5) as an eluent to afford the alcohol **2b** (18.8 mg, 94 %) as colorless liquid. R_f = 0.6 (hexanes:EtOAc, 5:5); $[\alpha]_D^{28}$ = -7.9 (*c* 0.9, $CHCl_3$); IR (neat) υ_{max}: 2959, 2926, 1754, 1458, 1271 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.03-3.94 (m, 1H), 3.78 (t, *J* = 6.4 Hz, 2H), 3.58-3.48 (m, 2H), 1.86-1.30 (m, 8H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 78.6, 68.4, 61.6, 38.1, 31.9, 25.8, 23.3 ppm; HRMS calculated for $C_7H_{14}O_2Na$ $[M + Na]^+$ 153.0882, found 153.0886.

(R)-2,2-dimethyl-4-(oxetan-2-yl)butan-1-ol (3a).



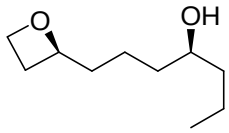
Colorless liquid **3a**. R_f = 0.3 (hexanes:EtOAc, 6:4); $[\alpha]_D^{28}$ = -7.9 (*c* 1.2, $CHCl_3$); IR (neat) ν_{max}: 3414, 2924, 2854, 1729, 1458, 1068 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.84-4.73 (m, 1H), 4.71-4.62 (m, 1H), 4.56-4.46 (m, 1H), 3.33 (q, *J* = 10.7 Hz, 2H), 2.72-2.59 (m, 1H), 2.39-2.26 (m, 1H), 1.82-1.55 (m, 2H), 1.35-1.13 (m, 2H), 0.89 (s, 6H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 83.3, 71.2, 68.1, 34.7, 32.2, 32.1, 27.4, 24.0, 23.8 ppm; HRMS calculated for $C_9H_{19}O_2$ $[M + H]^+$ 159.1379, found 159.1378

(S)-2-(5,5-dimethyltetrahydro-2H-pyran-2-yl)ethanol (3b).



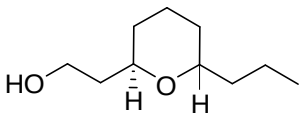
Primary alcohol **3b** (9.3 mg, 93 %) was obtained from corresponding oxetane **3a** (10 mg, 0.06 mmol). R_f = 0.3 (hexanes:EtOAc, 8:2); $[\alpha]_D^{28}$ = -6.2 (*c* 2.0, $CHCl_3$); IR (neat) ν_{max}: 3412, 2920, 2851, 1720, 1451, 1063 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.78 (s, 2H), 3.49-3.38 (m, 2H), 3.16 (d, *J* = 11.3 Hz, 1H), 2.86 (bs, 1H), 1.84-1.64 (m, 2H), 1.61-1.10 (m, 4H), 1.03 (s, 3H), 0.80 (s, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 78.2, 78.1, 61.2, 37.4, 36.4, 29.8, 28.2, 27.1, 23.3 ppm; HRMS calculated for $C_9H_{19}O_2$ $[M + H]^+$ 159.1379, found 159.1373.

(S)-1-((S)-oxetan-2-yl)heptan-4-ol (4a).



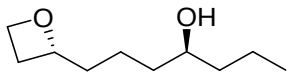
Colorless liquid **4a**. R_f = 0.5 (hexanes:EtOAc, 7:3); $[\alpha]_D^{28}$ = +8.2 (*c* 2, $CHCl_3$); IR (neat) ν_{max}: 3412, 2927, 2853, 1729, 1452, 1061 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.98-4.78 (m, 1H), 4.71-4.62 (m, 1H), 4.55-4.46 (m, 1H), 3.66-3.56 (m, 1H), 2.72-2.59 (m, 1H), 2.41-2.27 (m, 1H), 1.91-1.57 (m, 3H), 1.55-1.26 (m, 7H), 0.93 (t, *J* = 6.0 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 82.7, 71.2, 68.0, 39.6, 37.7, 37.0, 27.5, 20.0, 18.8, 14.0 ppm; HRMS calculated for $C_{10}H_{21}O_2$ $[M + H]^+$ 173.1536, found 173.1530.

2-((2R,6S)-6-propyltetrahydro-2H-pyran-2-yl)ethanol (4b).



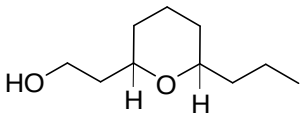
Primary alcohol **4b** (11 mg, 92 %) was obtained from corresponding oxetane **4a** (12 mg, 0.07 mmol). R_f = 0.5 (hexanes:EtOAc, 8:2); $[\alpha]_D^{28}$ = -36.5 (*c* 1.5, $CHCl_3$); IR (neat) ν_{max}: 3411, 2920, 2855, 1726, 1459, 1055 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.93-3.87 (m, 1H), 3.85-3.74 (m, 3H), 2.89-2.84 (m, 1H), 1.97-1.88 (m, 1H), 1.81-1.59 (m, 5H), 1.57-1.50 (m, 1H), 1.47-1.25 (m, 5H), 0.93 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 71.4, 70.9, 61.8, 36.0, 34.4, 30.9, 29.4, 19.0, 18.4, 14.0 ppm; HRMS calculated for $C_{10}H_{20}O_2Na$ $[M + Na]^+$ 195.1340, found 195.1338

(S)-1-((R)-oxetan-2-yl)heptan-4-ol (5a).



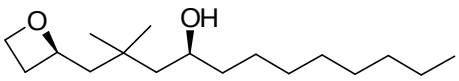
Colorless liquid **5a**. R_f = 0.5 (hexanes:EtOAc, 7:3); $[\alpha]_D^{28}$ = -2.8 (*c* 2, $CHCl_3$); IR (neat) ν_{max}: 3412, 2927, 2853, 1729, 1452, 1061 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.88-4.78 (m, 1H), 4.70-4.63 (m, 1H), 4.54-4.47 (m, 1H), 3.66-3.57 (m, 1H), 2.71-2.61 (m, 1H), 2.39-2.29 (m, 1H), 1.91-1.78 (m, 1H), 1.75-1.61 (m, 1H), 1.54-1.28 (m, 8H), 0.93 (t, *J* = 7.1 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 82.7, 71.3, 68.0, 39.7, 37.8, 37.1, 27.6, 20.4, 18.8, 14.0 ppm; HRMS calculated for $C_{10}H_{21}O_2$ $[M + H]^+$ 173.1536, found 173.1530.

2-((2S,6S)-6-propyltetrahydro-2H-pyran-2-yl)ethanol (5b).



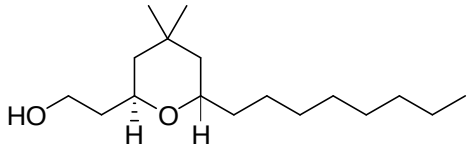
Primary alcohol **5b** (13.9 mg, 93 %) was obtained from corresponding oxetane **5a** (15 mg, 0.08 mmol). R_f = 0.45 (hexanes:EtOAc, 7:3); $[\alpha]_D^{28}$ = -0.5 (*c* 0.5, $CHCl_3$); IR (neat) ν_{max}: 3411, 2920, 2855, 1726, 1459, 1055 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 3.84-3.75 (m, 1H), 3.60-3.54 (m, 1H), 3.36-3.30 (m, 1H), 3.18-3.12 (bs, 1H), 1.85-1.71 (m, 2H), 1.70-1.63 (m, 2H), 1.60-1.45 (m, 4H), 1.44-1.25 (m, 4H), 1.24-1.14 (m, 1H), 0.90 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 78.8, 77.8, 62.0, 38.5, 37.8, 31.6, 31.3, 23.4, 18.8, 14.0 ppm; HRMS calculated for $C_{10}H_{20}O_2Na$ $[M + Na]^+$ 195.1354, found 195.1340.

(S)-2,2-dimethyl-1-((S)-oxetan-2-yl)dodecan-4-ol (6a).



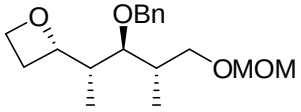
Colorless liquid **6a**. R_f = 0.4 (hexanes:EtOAc, 7:3); $[\alpha]_D^{28}$ = +6.7 (*c* 1.1, $CHCl_3$); IR (neat) ν_{max}: 3418, 2920, 2853, 1721, 1453, 1065 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 5.12-5.10 (m, 1H), 4.69-4.60 (m, 1H), 4.50-4.49 (m, 1H), 3.81-3.69 (m, 1H), 2.71-2.59 (m, 1H), 2.46-2.31 (m, 1H), 1.93 (dd, *J* = 6.8, 14.3 Hz, 1H), 1.66-1.53 (m, 3H), 1.44-1.35 (m, 3H), 1.34-1.21 (m, 11H), 0.96 (m, 3H), 0.95 (m, 3H), 0.88 (t, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 80.6, 69.1, 68.0, 50.8, 50.0, 39.7, 32.6, 31.9, 29.6 (2C), 29.6, 29.2, 28.7, 27.7, 25.6, 22.6, 14.1 ppm; HRMS calculated for $C_{17}H_{34}O_2Na$ $[M + Na]^+$ 293.2447, found 293.2439.

2-((2R,6S)-6-heptyl-4,4-dimethyltetrahydro-2H-pyran-2-yl)ethanol (6b).



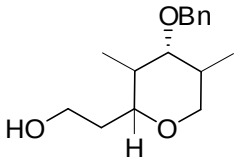
Primary alcohol **6b** (15.4 mg, 91 %) was obtained from corresponding oxetane **6a** (17 mg, 0.06 mmol). R_f = 0.4 (hexanes:EtOAc, 7:3); $[\alpha]_D^{28}$ = -14.8 (*c* 1.3, $CHCl_3$); IR (neat) ν_{max}: 3410, 2912, 2850, 1727, 1455, 1060 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.03-3.96 (m, 1H), 3.83-3.75 (m, 3H), 3.04-2.99 (bs, 1H), 1.93-1.83 (m, 1H), 1.63-1.53 (m,1H), 1.47-1.22 (m, 18H) 1.02 (s, 3H), 1.00 (s, 3H), 0.88 (t, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 70.3, 70.1, 62.2, 43.3, 42.3, 37.1, 35.2, 31.8, 31.3, 30.7, 29.7, 29.5, 29.2, 28.3, 26.2, 22.6, 14.1 ppm; HRMS calculated for $C_{17}H_{35}O_2$ $[M + H]^+$ 271.2631, found 271.2629.

(*R*)-2-((2*S*,3*R*,4*R*)-3-(Benzyloxy)-5-(methoxymethoxy)-4-methylpentan-2-yl)oxetane (7a).



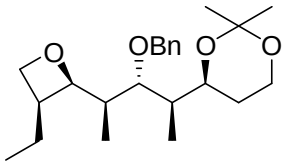
Colorless liquid **7a**. (89 mg, 92 %). R_f = 0.3 (hexanes:EtOAc, 8:2); $[\alpha]_D^{28}$ = +1.2 (*c* 0.8, $CHCl_3$); IR (neat) υ_{max}: 3448, 2924, 1458, 1045 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.39-7.27 (m, 5H), 5.02-4.93 (m, 1H) 4.70-4.58 (m, 3H), 4.54 (s, 2H), 4.47-4.39 (m, 1H), 3.71 (dd, *J* = 4.5, 9.4 Hz, 1H), 3.46 (dd, *J* = 7.5, 9.4 Hz, 1H), 3.36 (s, 3H), 3.22 (dd, *J* = 4.5, 7.5 Hz, 1H), 2.66-2.48 (m, 2H), 2.18-2.00 (m, 2H), 1.08 (d, *J* = 7.0 Hz, 3H), 1.07 (d, *J* = 7.0 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.7, 129.7, 128.5, 127.8, 96.7, 86.7, 75.7, 69.7, 68.2, 66.2, 55.3, 37.7, 36.6, 34.2, 14.9, 11.8 ppm; HRMS calculated for $C_{18}H_{28}O_4Na$ $[M + Na]^+$ 331.1872, found 331.1879.

2-((2*S*,3*S*,4*S*,5*R*)-4-(Benzyloxy)-3,5-dimethyltetrahydro-2H-pyran-2-yl)ethanol (7b).



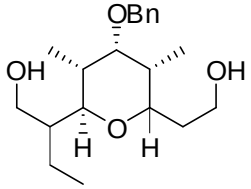
Primary alcohol **7b** (30 mg, 70 %) was obtained from the corresponding oxetane (50 mg, 0.16 mmol) as colorless liquid. R_f = 0.5 (hexanes:EtOAc, 6:4); $[\alpha]_D^{28}$ = +11.4 (*c* 0.75, $CHCl_3$); IR (neat) υ_{max}: 3424, 2924, 2854, 1729, 1068 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.37-7.28 (m, 5H), 4.74 (s, 2H), 4.72-4.68 (m, 1H), 3.87-3.78 (m, 3H), 3.60 (dd, *J* = 4.4, 11.1 Hz, 1H), 3.55 (dd, *J* = 2.0, 9.9 Hz, 1H), 2.09-2.01 (m, 2H), 1.99-1.92 (m, 1H), 1.90-1.82 (m, 1H), 1.25 (d, *J* = 7.1 Hz, 3H), 0.94 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 137.9, 128.5, 127.9, 127.8, 86.5, 76.4, 64.2, 61.7, 60.0, 42.7, 39.4, 35.8, 16.4, 10.4 ppm; HRMS calculated for $C_{16}H_{24}O_3Na$ $[M + Na]^+$ 287.1611, found 287.1617.

(*S*)-4-((2*R*,3*R*,4*S*)-3-(Benzyloxy)-4-((2*R*,3*S*)-3-ethyloxetan-2-yl)pentan-2-yl)-2,2-dimethyl-1,3-dioxane (8a).



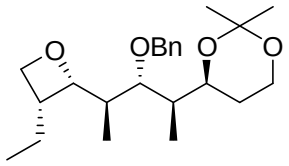
Colorless liquid **8a**. R_f = 0.3 (hexanes:EtOAc, 8:2); $[\alpha]_D^{28}$ = + 26.5 (*c* 0.7, $CHCl_3$); IR (neat) $\upsilon_{max:}$ 3450, 2960, 2930, 1721, 1021 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.38-7.27 (m, 5H), 4.80-4.76 (m, 1H), 4.69-4.65 (m, 1H), 4.53 (ABq, *J* = 11.3 Hz, 2H), 4.19-4.15 (m, 1H), 3.98-3.92 (m, 2H), 3.86-3.81 (m, 1H), 3.18 (t, *J* = 6.2 Hz, 1H), 2.58-2.51 (m, 1H), 2.41-2.33 (m, 1H), 1.86-1.75 (m, 2H), 1.74-1.65 (m, 2H), 1.40 (s, 3H), 1.37 (s, 3H), 1.33-1.23 (m, 1H), 0.99 (d, *J* = 7.0 Hz, 3H), 0.97 (d, *J* = 6.9 Hz, 3H) 0.75 (t, *J* = 7.3 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.8, 128.1, 127.2, 127.1, 98.1, 86.3, 84.5, 73.7, 73.3, 68.2, 60.1, 41.2, 41.1, 37.4, 29.9, 29.1, 22.4, 19.3, 12.6, 11.6, 11.2 ppm; HRMS calculated for $C_{23}H_{36}O_4Na$ $[M + Na]^+$ 399.2499, found 399.2505.

2*R*,3*R*,4*S*)-4-((2*R*,3*S*,6*R*)-6-((*S*)-1-Hydroxybutan-2-yl)-3-methyltetrahydro-2H-pyran-2-yl)-2-methylpentane-1,3-diol (8b).



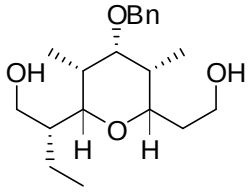
Diol **8b** (28.5 mg, 80%) obtained as colorless liquid from corresponding oxetane (40 mg, 0.106 mmol). R_f = 0.35 (hexanes:EtOAc, 6:4); $[\alpha]_D^{28}$ = -4.3 (*c* 0.6, $CHCl_3$); IR (neat) υ_{max}: 3414, 2924, 2854, 1729, 1458, 1068 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.38-7.27 (m, 5H), 4.63 (s, 2H), 4.24-4.19 (m, 1H), 3.87-3.77 (m, 2H), 3.72 (dd, *J* = 4.6, 11.0 Hz, 1H), 3.66-3.64 (m, 1H), 3.56-3.52 (m, 1H), 3.49-3.43 (m, 1H), 1.99-1.86 (m, 2H), 1.73-1.53 (m, 3H), 1.45-1.36 (m, 2H), 1.07 (d, *J* = 7.2 Hz, 3H), 0.97-0.90 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.9, 128.3, 127.5, 127.2, 82.9, 80.0, 75.6, 70.6, 68.0, 62.2, 44.7, 38.5, 36.5, 29.7, 20.8, 14.6, 11.7, 11.4 ppm; HRMS calculated for $C_{20}H_{32}O_4Na$ $[M + Na]^+$ 359.2187, found 359.2192.

(*S*)-4-((2*R*,3*R*,4*S*)-3-(Benzyloxy)-4-((2*S*,3*R*)-3-ethyloxetan-2-yl)pentan-2-yl)-2,2-dimethyl-1,3-dioxane (9a).



Colorless liquid **9a**. R_f = 0.3 (hexanes:EtOAc, 8:2); $[\alpha]_D^{28}$ = -0.9 (*c* 0.5, $CHCl_3$); IR (neat) υ_{max}: 3450, 2960, 2930, 1721, 1021 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.41-7.23 (m, 5H), 4.94 (dd, *J* = 6.8, 11.0 Hz, 1H), 4.73-4.57 (m, 3H), 4.39-4.31 (m, 1H), 4.00-3.88 (m, 2H), 3.85-3.77 (m, 1H), 3.41 (d, *J* = 10.2 Hz, 1H), 2.67-2.54 (m, 1H), 2.47-2.34 (m, 1H), 1.96-1.65 (m, 4H), 1.39 (s, 3H), 1.36 (s, 3H), 1.20-1.12 (m, 1H), 0.96 (d, *J* =7.0 Hz, 3H), 0.88-0.79 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.2, 128.1, 127.1, 127.0, 97.9, 85.1, 83.1, 74.6, 73.2, 67.1, 60.2, 41.1, 40.0, 35.9, 30.0, 28.2, 20.9, 19.5, 13.2, 11.0, 10.5 ppm; HRMS calculated for $C_{23}H_{36}O_4Na$ $[M + Na]^+$ 399.2495, found 399.2505.

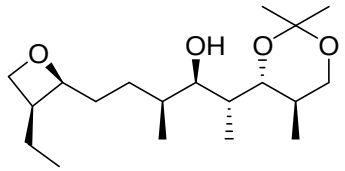
(*R*)-2-((2*R*,3*R*,4*R*,5*R*,6*S*)-4-(Benzyloxy)-6-(2-hydroxyethyl)-3,5-dimethyltetrahydro-2H-pyran-2-yl)butan-1-ol (9b).



Diol **9b** (32 mg, 80% yield) a colorless liquid was obtained from the corresponding oxetane (45 mg, 0.12 mmol). R_f = 0.35 (hexanes:EtOAc, 6:4); $[\alpha]_D^{28}$ = -5.6 (*c* 0.7, $CHCl_3$); IR (neat) $\upsilon_{max:}$ 3414, 2924, 2854, 1729, 1458, 1068 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.33-7.17 (m, 5H), 4.47 (s, 2H), 4.18-4.12 (m, 1H), 3.79-3.65 (m, 2H), 3.58-3.38 (m, 3H), 3.30-3.21 (m, 1H), 2.41-2.19 (m, 1H), 2.18-2.03 (m, 1H), 2.01-1.89 (m, 1H), 1.87-1.74 (m, 1H), 1.72-1.44 (m, 3H), 0.94-0.74 (m, 9H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.8, 128.3, 127.4, 127.2, 83.6, 79.7, 78.1,

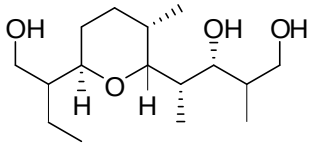
69.1, 64.1, 60.3, 42.4, 36.2, 35.0, 33.5, 19.6, 11.3, 8.8, 8.7 ppm; HRMS calculated for $C_{20}H_{32}O_4Na$ $[M + Na]^+$ 359.2183, found 359.2192.

(2*R*,3*R*,4*S*)-6-((2*S*,3*S*)-3-Ethyloxetan-2-yl)-4-methyl-2-((4*R*,5*R*)-2,2,5-trimethyl-1,3-dioxan-4-yl)hexan-3-ol (8).



To a solution of compound **27** (2.0 g, 4.78 mmol) in ethyl acetate (10 mL) was added $Pd(OH)_2$ (200 mg, 20 wt% on activated charcoal) under H_2 atmosphere with stirring at room temperature for 4 h. The reaction mixture was filtered on a small pad of celite, concentrated under reduced pressure, and was purified by silica gel chromatography using ethyl acetate and hexane (2:8) as an eluent to afford the secondary alcohol **8** (1.49 g, 95%) as a colorless liquid. R_f = 0.30 (hexane:EtOAc, 8:2); $[\alpha]_D^{28}$ = -13.8 (*c* 1, $CHCl_3$); IR (neat) υ_{max}: 3427, 2961, 2874, 1459, 1382, 1198~~, 868~~ cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 4.84-4.76 (m, 1H), 4.73 (dd, *J* = 6.0, 7.5 Hz, 1H), 4.14 (t, *J* = 6.0 Hz, 1H), 3.91 (dd, *J* = 2.2, 10.7 Hz, 1H), 3.73-3.66 (m, 1H), 3.53 (t, *J* = 11.3 Hz, 1H), 3.32 (q, *J* = 6.0 Hz, 1H), 2.87-2.73 (m, 1H), 2.54 (d, *J* = 6.7 Hz, 1H), 1.99-1.78 (m, 3H) 1.75-1.51 (m, 4H), 1.46 (s, 3H), 1.37 (s, 3H), 1.34-1.17 (m, 1H), 1.01-0.93 (m, 6H), 0.87-0.79 (m, 3H), 0.71 (d, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 98.0, 84.6, 77.5, 75.0, 74.2, 66.3, 39.2, 35.6, 30.4 (2C), 29.6, 28.9, 28.5, 21.4, 19.0, 14.0, 12.0, 11.5, 10.7 ppm; HRMS calculated For $C_{19}H_{37}O_4$ $[M + H]^+$ 329.2687, found 329.2686.

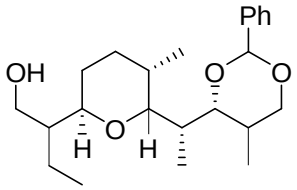
(2*R*,3*R*,4*S*)-4-((2*R*,3*S*,6*R*)-6-((*S*)-1-Hydroxybutan-2-yl)-3-methyltetrahydro-2H-pyran-2-yl)-2-methylpentane-1,3-diol (28).



A solution of oxetane **8** (1.40 g, 4.27 mmol), in CH_2Cl_2:*i*-PrOH (15:1) 12 mL was cooled to 0 ^oC. To this CSA (97 mg, 0.42 mmol) was added the reaction mixture was allowed to warm up to room temperature and stirred for 2 h before quenching with solid $NaHCO_3$. CH_2Cl_2 layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 x 10 mL). The combined organic layer was washed with brine (5 mL), dried over Na_2SO_4 and the solvent was evaporated under reduced pressure to get the crude product which was purified by flash column chromatography with ethyl acetate and hexane (5:5) as an eluent to afford the alcohol **28** as colorless liquid (1.13 g, 92 %). R_f = 0.5 (EtOAc); IR (neat) υ_{max}: 3379, 2929, 1655, 1461, 1026~~, 768~~ cm^{-1}. $[\alpha]_D^{28}$ = -36.1 (*c* 1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 3.92 (dd, *J* = 1.5, 9.8 Hz, 1H), 3.77 (d, *J* = 4.5

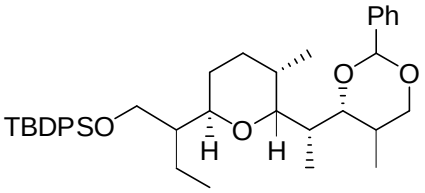
Hz, 2H), 3.73-3.61 (m, 4H), 3.35-3.15 (bs, 4H), 2.07-1.97 (m, 1H), 1.94-1.78 (m, 3H), 1.73-1.60 (m, 1H) 1.53-1.11 (m, 5H), 1.01-0.88 (m, 6H), 0.82-0.72 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 75.6, 74.4, 71.8, 68.7, 63.8, 40.7, 36.8, 36.6, 28.5, 26.4, 22.1, 20.9, 13.0, 11.9, 10.8, 7.6 ppm; HRMS calculated For $C_{16}H_{33}O_4$ $[M + H]^+$ 289.2357, found 289.2374.

(2*S*)-2-((2*R*,5*S*,6*R*)-5-Methyl-6-((1*R*)-1-((4*R*,5*R*)-5-methyl-2-phenyl-1,3-dioxan-4-yl) ethyl)tetrahydro-2H-pyran-2-yl) butan-1-ol (29).



To a solution of triol **28** (0.52 mg, 1.80 mmol) in anhydrous CH_2Cl_2 (20 mL) was added the benzaldehyde dimethyl acetal (0.29 mL, 2.16 mmol) at 0 ^oC. To the reaction mixture was added a catalytic amount of CSA (20 mg, 0.09 mmol) and the reaction mixture was stirred at rt for 1 h. After completion of the reaction, the reaction mixture was quenched by adding a saturated solution of $NaHCO_3$ at 0 ^oC and the product was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. Crude product was purified by column chromatography to obtain alcohol using ethyl acetate and hexane (1:9) as an eluent to afford the alcohol **29** as a crystalline solid (0.61 g, 90 %). M.P. = 109 ^oC; R_f = 0.50 (hexanes:EtOAc, 7:3); $[\alpha]_D^{28}$ = -68.2 (*c* 1, $CHCl_3$); IR (KBr): 3448, 2960, 1638, 102~~11, 759~~ cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.54-7.48 (m, 2H), 7.40- 7.31 (m, 3H), 5.55 (s, 1H), 4.11 (dd, *J* = 4.5, 11.3 Hz, 1H), 3.85-3.71 (m, 3H), 3.69-3.47 (m, 3H), 2.19-2.02 (m, 1H), 1.98-1.72 (m, 5H), 1.55-1.41 (m, 2H), 1.40-1.20 (m, 2H), 0.98 (d, *J* = 6.8 Hz, 3H), 0.92-0.83 (m, 6H), 0.76 (d, *J* = 6.7 Hz, 3H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ 139.0, 128.6, 128.1, 126.2 , 101.2, 80.7, 73.9, 73.3, 71.2, 60.7, 39.9, 35.5, 30.2, 28.3, 26.4, 20.7, 20.5, 12.1, 11.5, 11.3, 8.5 ppm; HRMS calculated For $C_{23}H_{37}O_4$ $[M + H]^+$ 377.2688, found 377.2686.

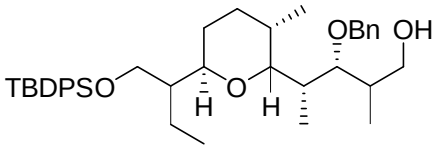
***Tert*-Butyl((2*S*)-2-((2*R*,5*S*,6*R*)-5-methyl-6-((1*R*)-1-((4*R*,5*R*)-5-methyl-2-phenyl-1,3-dioxan-4-yl) ethyl)tetrahydro-2H-pyran-2-yl)butoxy)diphenylsilane (30).**



Alcohol **29** (0.48 g, 1.27 mmol) was dissolved in anhydrous CH_2Cl_2 (5 mL) and treated with imidazole (0.12 g, 1.9 mmol) at 0 °C. After 30 minutes TBDPSCl (0.50 mL, 1.53 mmol) was added via syringe. The reaction mixture was allowed to warm to room temperature and stirred

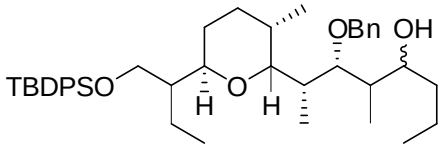
for 2 h and quenched with saturated aqueous solution of NH_4Cl (10 mL) and extracted with CH_2Cl_2 (1 x 10 mL). The combined organic phases were washed with brine (3 mL), dried over Na_2SO_4 and the solvent was removed under reduced pressure. Crude product was purified by column chromatography using ethyl acetate and hexane (2:98) as an eluent to afford the compound **30** as colorless liquid (0.72 g, 92 %). R_f = 0.40 (hexanes:EtOAc, 95:5); IR (neat) υ_{max}: 3449, 2957, 2857, 1460, 1110~~, 70 2~~ cm^{-1}; $[\alpha]_D^{28}$ = -31.7 (*c* 1, $CHCl_3$); ^1H NMR (300 MHz, $CDCl_3$): δ 7.76-7.71 (m, 2H), 7.66-7.61 (m, 2H), 7.45-7.34 (m, 4H), 7.33- 7.27 (m, 2H), 7.24-7.12 (m, 3H), 7.05-7.00 (m, 2H), 4.75 (s, 1H), 4.12 (dd, *J* = 4.5, 11.3 Hz, 1H), 3.91-3.84 (m, 2H), 3.72 (dd, *J* = 1.5, 9.8 Hz, 1H), 3.61-3.55 (m, 1H), 3.45-3.39 (m, 1H), 3.02 (t, *J* = 11.3 Hz, 1H), 2.02-1.82 (m, 3H), 1.80-1.65 (m, 3H), 1.53-1.34 (m, 3H), 1.32-1.18 (m, 1H), 1.04-0.95 (m, 12H), 0.81-0.75 (m, 6H), 0.68 (d, *J* = 6.7 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.8, 135.9, 135.8, 134.0, 133.5, 129.5, 129.4, 128.2, 127.8, 127.7, 127.6, 125.9, 100.5, 80.0, 72.7, 72.6, 69.2, 59.8, 38.4, 35.5, 30.2, 28.2, 26.8, 26.4, 20.0, 19.4, 19.3, 11.8, 11.6, 11.3, 8.2 ppm; HRMS calculated For $C_{39}H_{54}O_4NaSi$ $[M + Na]^+$ 637.3686, found 637.3683.

(2*R*,3*R*,4*S*)-3-(Benzyloxy)-4-((2*R*,3*S*,6*R*)-6-((*S*)-1-(*tert*-butyldiphenylsilyloxy)butan-2-yl)-3-methyltetrahydro-2H-pyran-2-yl)-2-methylpentan-1-ol (31).



To a solution of compound **30** (0.90 g, 1.46 mmol) in anhydrous CH_2Cl_2 (10 mL) was added DIBAL-H (3 mL, 1 M in toluene) at -15 ^oC and the reaction mixture was stirred at same temperature while monitoring the reaction. After completion, the reaction was quenched by the addition of aq. saturated solution of sodium potassium tartrate (5 mL). The mixture was stirred for 2.5 h at room temperature. Then the product was extracted with CH_2Cl_2 (2 x 10 mL) and washed with brine (5 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. Crude product was purified by column chromatography using ethyl acetate and hexane (2:98) as an eluent to afford the compound **31** as colorless liquid (0.81 g, 90 %). R_f = 0.60 (hexanes:EtOAc, 8:2); $[\alpha]_D^{28}$ = -30.5 (*c* 1, $CHCl_3$); IR (neat) υ_{max}: 3449, 2929, 2860, 1108~~, 701~~ cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.69-7.63 (m, 4H), 7.45-7.31 (m, 6H), 7.30-7.21 (m, 3H), 7.16-7.12 (m, 2H), 4.29 (ABq, *J* = 11.3 Hz, 2H), 3.90-3.80 (m, 2H), 3.73 (dd *J* = 3.5, 9.8 Hz, 1H), 3.62 (d, *J* = 7.7 Hz, 1H), 3.52-3.44 (m, 3H), 3.00-2.90 (m, 1H), 1.96-1.78 (m, 4H), 1.77-1.64 (m, 2H), 1.54-1.32 (m, 4H), 1.05 (s, 9H), 0.96 (d, *J* = 6.9 Hz, 3H), 0.86 (d, *J* = 6.9 Hz, 3H), 0.78-0.71 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.7, 135.7, 135.7, 134.8, 133.9, 133.8, 129.6, 128.2, 127.7, 127.6, 127.3, 127.2, 82.7, 74.5, 73.8, 72.4, 66.8, 61.9, 40.8, 38.8, 36.7, 29.4, 27.0, 26.8, 26.5, 21.4, 19.4, 13.9, 12.9, 10.7, 10.1 ppm; HRMS calculated For $C_{39}H_{56}O_4NaSi$ $[M + Na]^+$ 639.3853, found 639.3840.

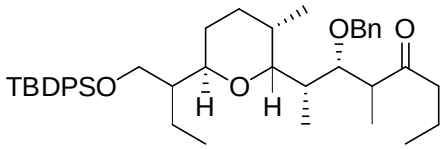
(5*R*,6*R*,7*S*)-6-(Benzyloxy)-7-((2*R*,3*S*,6*R*)-6-((*S*)-1-(*tert*-butyldiphenylsilyloxy)butan-2-yl)-3-methyltetrahydro-2H-pyran-2-yl)-5-methyloctan-4-ol (32).



To a solution of alcohol **31** (0.30 g, 0.487 mmol) in anhydrous CH_2Cl_2 (4 mL) under argon atmosphere, Dess-Martin periodinane (2.4 mL, 0.30 M in CH_2Cl_2) and $NaHCO_3$ (50 mg, 0.58 mmol) were added. After stirring for 2 h at room temperature, aqueous saturated sodium thiosulfate (5 mL) and CH_2Cl_2 (5 mL) were added. The organic phase was separated and washed with brine. The organic layer was dried over anhydrous Na_2SO_4 filtered, and concentrated under reduced pressure. Crude product was purified over small pad of silica gel column to afford the product aldehyde as colorless liquid (0.28 g, 93 %). R_f = 0.45 (hexanes:EtOAc, 95:5).

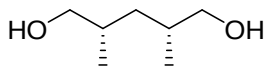
To a stirred solution of aldehyde (0.28 g, 0.39 mmol) in anhydrous THF (3 mL) was cooled to -78 ^oC, a solution (0.6 mL, 0.5M of *n*-propyl magnesium bromide in THF {prepared from magnesium (120 mg) and *n*-propyl bromide (0.50 mL) in THF (5 mL)} was added drop wise. After 1 h at -78 ^oC the reaction mixture was quenched by the addition of a saturated aqueous solution of NH_4Cl (5 mL). The product was extracted with diethyl ether (2 x 5 mL) and washed with brine (3 mL). The organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Crude product was purified by column chromatography using ethyl acetate and hexane (2:98) an eluent to afford the compound **32** (0.28 g, 95 %) as colorless liquid (88% yield for two steps). R_f = 0.40 (hexanes:EtOAc, 95:5); $[\alpha]_D^{28}$ = -25.6 (*c* 1, $CHCl_3$); IR (neat) υ_{max}: 3457, 3069, 2959, 2856, 1460, 1110~~, 702~~ cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.74-7.63 (m, 4H), 7.43-7.31 (m, 6H), 7.29- 7.21 (m, 3H), 7.16-7.10 (m, 2H), 4.27 (ABq, *J* = 11.4 Hz, 2H), 3.89-3.73 (m, 4H), 3.63-3.58 (m, 1H), 3.42 (dd, *J* = 2.4, 10.1 Hz, 1H), 2.98-2.92 (m, 1H), 1.99-1.90 (m, 1H), 1.88-1.77 (m, 2H), 1.64-1.54 (m, 2H), 1.52-1.34 (m, 4H), 1.31-1.18 (m, 4H), 1.05 (s, 9H), 0.95 (d, *J* = 6.9 Hz, 3H), 0.92-0.84 (m, 6H), 0.81-0.71 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 138.7, 135.7, 134.0, 133.9, 129.6, 129.5, 128.2, 127.6, 127.3, 127.2, 83.5, 75.6, 74.4, 72.5, 71.6, 62.2, 41.7, 40.6, 37.5, 36.8, 29.3, 26.9, 26.8, 21.3, 19.6, 19.5, 19.4, 14.1, 12.8, 10.7, 10.6, 10.5 ppm; HRMS calculated For $C_{42}H_{62}O_4NaSi$ $[M + Na]^+$ 681.43099, found 681.43096.

(5*S*,6*S*,7*S*)-6-(Benzyloxy)-7-((2*R*,3*S*,6*R*)-6-((*S*)-1-(*tert*-butyldiphenylsilyloxy)butan-2-yl)-3-methyltetrahydro-2H-pyran-2-yl)-5-methyloctan-4-one (6).



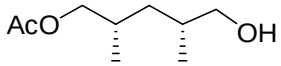
To a solution of alcohol **32** (0.20 g, 0.30 mmol) in CH_2Cl_2 (3 mL) under argon, Dess-Martin periodinane (1.5 mL, 0. 30 M in CH_2Cl_2) and $NaHCO_3$ (40 mg, 0.45 mmol) were added. After stirring for 2 h at room temperature, aqueous saturated sodium thiosulfate (2 mL) and CH_2Cl_2 (5 mL) were added. The organic phase was separated and washed with brine. The organic layer was dried over anhydrous Na_2SO_4, and concentrated under reduced pressure. Crude product was purified by column chromatography using ethyl acetate and hexane (2:98) as an eluent to afford the compound **6** as colorless liquid. (0.18 g, 90%). R_f = 0.40 (hexane:EtOAc, 95:5); $[\alpha]_D^{28}$ = -14.9 (*c* 1, $CHCl_3$); IR (neat) υ_{max}: 2961, 2856, 1726, 1458, 1282, 1119~~, 977~~ cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.74-7.61 (m, 4H), 7.43-7.32 (m, 6H), 7.27- 7. 17 (m, 3H), 7.11-7.05 (m, 2H), 4.36-4.21 (m, 2H), 4.03 (d, *J* = 9.4 Hz, 1H), 3.94-3.85 (m, 2H), 3.72-3.66 (m, 1H), 3.56 (dd, *J* = 3.0, 10.0 Hz, 1H), 2.88-2.77 (m, 1H), 2.42-2.33 (m, 2H), 1.90-1.63 (m, 5H), 1.55-1.22 (m, 6H), 1.07 (s, 9H), 0.97-0.89 (m, 6H), 0.87-0.78 (m, 6H), 0.75-0.68 (t, *J* = 9.4 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 213.8, 139.3, 135.7 (2C), 135.6 (2C), 134.2, 133.9, 129.4 (2C), 127.9 (2C), 127.6 (2C), 127.5 (2C), 126.9 (3C), 80.4, 73.7, 73.3, 72.0, 62.1, 48.6, 45.7, 42.2, 36.2, 29.9, 29.7, 27.0 (4C), 22.2, 19.5, 16.7, 13.9 (2C), 13.7, 11.1, 9.4 ppm; HRMS calculated For $C_{42}H_{60}O_4NaSi$ $[M + Na]^+$ 679.4151, found 679.4153.

(2*R*,4*S*)-2,4-Dimethylpentane-1,5-diol (33)



^1H NMR (300 MHz, $CDCl_3$): δ 3.53-3.38 (m, 4H), 1.80-1.66 (m, 2H), 1.31-1.18 (m, 2H), 0.97-0.83 (m, 6H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 67.1, 36.7, 32.8, 17.6 ppm. MS (ESI) calculated for $C_7H_{17}O_2$ $[M + H]^+$ 133, found 133.

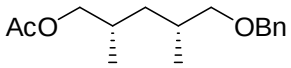
(2*S*,4*R*)-5-Hydroxy-2,4-dimethylpentyl acetate (34).



To a stirred solution of *meso*-diol **33** (4.0 g, 22.9 mmol) in THF (130 mL) and water (170 μL) was added PPL (Porcine Pancreatic Lipase) enzyme (11.6 g) and vinyl acetate (8.4 mL, 91.6 mmol) at room temperature. The reaction mixture was stirred for 12 h at room temperature. After complete conversion of the starting material (as indicated by TLC), the reaction mixture was filtered off through a pad of celite, washed with ethyl acetate, dried over Na_2SO_4, concentrated under reduced pressure and purified by column chromatography using ethyl acetate and hexane (4:96) as an eluent afford the mono acetate compound **34** (2.47 g, 47%) as a colorless liquid. R_f =

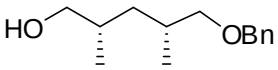
0.5 (hexane:EtOAc, 9:1); $[\alpha]_D^{28}$ = +9.8 (*c* 0.6, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 3.97 (dd, *J* = 5.2, 10.7 Hz, 1H), 3.84 (dd, *J* = 6.9, 10.7 Hz, 1H), 3.49 (dd, *J* = 5.4, 10.5 Hz, 1H), 3.40 (dd, *J* = 6.4, 10.5 Hz, 1H), 2.06 (s, 3H), 1.96-1.83 (m, 1H), 1.79-1.67 (m, 1H), 1.50-1.38 (m, 1H), 1.30-1.15 (m, 1H), 0.97 (d, *J* = 3.2 Hz, 3H), 0.95 (d, *J* = 3.0 Hz, 3H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.5, 69.2, 67.4, 37.1, 32.8, 29.8, 20.8, 17.7, 17.2 ppm. MS (ESI) calculated for $C_9H_{18}O_3Na$ $[M+Na]^+$ 197, found 197.

(2*S*,4*R*)-5-(Benzyloxy)-2,4-dimethylpentyl acetate (35).



A solution of monoacetate compound **34** (100 mg, 0.63 mmol) dissolved in CH_2Cl_2 (2 mL) was added to the solution of benzyl imidate (240 mg, 0.95 mmol) in cyclohexane (2 mL). The reaction was cooled to 0 ^oC and treated with TfOH (3 μL, 0.03 mmol). The reaction mixture was warmed to room temperature, stirred for 24 h. After completion of the reaction, the reaction mixture was quenched by adding a saturated solution of $NaHCO_3$ at 0 ^oC and the product was extracted with CH_2Cl_2. The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. Crude product was purified by column chromatography using ethyl acetate and hexane (2:98) as an eluent to afford the alcohol **35** (134 mg, 80 %) as colorless liquid R_f = 0.55 (hexanes:EtOAc, 95:5); $[\alpha]_D^{28}$ = +5.1 (*c* 1.8, $CHCl_3$); IR (neat) υ_{max}: 2919, 2851, 1738, 1240~~, 769~~ cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.38-7.29 (m, 5H), 4.50 (s, 2H), 3.96 (dd, *J* = 5.2, 10.5 Hz, 1H), 3.82 (dd, *J* = 6.7, 10.5 Hz, 1H), 3.33 (dd, *J* = 6.0, 9.0 Hz, 1H), 3.23 (dd, *J* = 6.7, 9.0 Hz, 1H), 2.04 (s, 3H), 1.95-1.81 (m, 2H), 1.52-1.41 (m, 1H), 1.30-1.15 (m, 1H), 0.99-0.91 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 171.2, 138.7, 128.2 (2C), 127.4 (3C), 75.6, 72.9, 69.3, 37.8, 30.8, 30.0, 20.8, 17.8, 17.7 ppm; HRMS calculated For $C_{16}H_{24}O_3Na$ $[M+Na]^+$ 287.1616, found 287.1617.

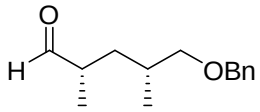
(2*S*,4*R*)-5-(Benzyloxy)-2,4-dimethylpentan-1-ol (36).



To an ice cooled suspension of $LiAlH_4$ (86 mg, 2.27 mmol) in anhydrous THF (2 mL), was added a solution of compound **35** (300 mg, 1.13 mmol) in anhydrous THF (2 mL) under nitrogen atmosphere. The reaction mixture was stirred for 2 h at room temperature and quenched with saturated Na_2SO_4 solution. The precipitate formed was filtered through a pad of celite and washed with ethyl acetate. The filtrate was dried over anhydrous Na_2SO_4, concentrated to dryness under reduced pressure. The resulting crude product was purified by silica gel column chromatography utilizing ethyl acetate and hexane (1:9) as an eluent to obtain alcohol **36** (227

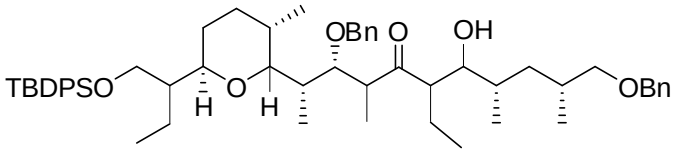
mg, 90%) as colorless oil. R_f = 0.5 (hexanes:EtOAc, 3:7); $[\alpha]_D^{28}$ = -2.6 (*c* 1, $CHCl_3$); IR (neat) υ_{max}: 3416, 2923, 2856, 1457, 1098, 1031~~,770~~ cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$): δ 7.45-7.26 (m, 5H), 4.50 (s, 2H), 3.54-3.38 (m, 2H), 3.35-3.21 (m, 2H), 1.95-1.80 (m, 1H), 1.77-1.60 (m, 2H), 1.53-1.39 (m, 1H), 1.0-0.87 (m, 6H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 138.5, 128.3, 127.5, 127.4, 75.8, 73.0, 67.8, 37.6, 33.1, 30.9, 18.1, 17.6 ppm; HRMS calculated For $C_{14}H_{22}O_2Na$ $[M + Na]^+$ 245.1511, found 245.1512.

(2*S*,4*R*)-5-(Benzyloxy)-2,4-dimethylpentanal (7).



To a solution of alcohol **36** (40 mg, 0.18 mmol) in CH_2Cl_2 (1.5 mL) under argon, Dess-Martin periodinane (0.72 mL, 0.21 mmol, 0.3 M in CH_2Cl_2) and $NaHCO_3$ (17 mg, 0.21 mmol) were added. After stirring for 2 h at room temperature, saturated aqueous sodium thiosulfate (1 mL) and ether (5 mL) were added. The organic phase was separated and washed with brine (2 mL). The organic layer was dried ($MgSO_4$), filtered, and concentrated under reduced pressure. The residue was purified by flash chromatography (hexanes:EtOAc, 95:5) on silica gel to give the desired aldehyde **7** (36 mg, 90%) as colourless oil. R_f = 0.4 (hexanes:EtOAc, 9:1); ^1H NMR (300 MHz, $CDCl_3$): δ 9.49 (s, 1H) 7.31-7.17 (m, 5H), 4.41 (s, 2H), 3.23 (d, *J* = 5.4 Hz, 2H), 2.43-2.36 (m, 1H), 1.86-1.75 (m, 2H), 1.61-1.43 (m, 1H) 1.03 (d, *J* = 6.9 Hz, 3H), 0.89 (d, *J* = 6.2 Hz, 3H) ppm; ^{13}C NMR (100 MHz, $CDCl_3$): δ 205.2, 138.5, 128.3, 127.5, 75.3, 73.0, 44.2, 35.0, 31.2, 17.5, 14.3 ppm; HRMS calculated For $C_{14}H_{20}O_2Na$ $[M + Na]^+$ 243.1354, found 243.1355.

(2*S*,3*S*,4*S*,6*R*,7*S*,8*S*,10*R*)-3,11-Bis(benzyloxy)-2-((2*R*,3*S*,6*R*)-6-((*S*)-1-(*tert*-butyldiphenyl silyloxy)butan-2-yl)-3-methyltetrahydro-2H-pyran-2-yl)-6-ethyl-7-hydroxy-4,8,10-trimethylundecan-5-one (4).



To a solution of ketone **6** (90 mg, 0.13 mmol) in anhydrous CH_2Cl_2 (2 mL) was added solution of (0.30 mL, 0.50 M) *i*-$PrOTiCl_3$ dropwise at -78 °C under argon. The pale yellow solution was stirred for 5 min, and DIPEA (0.30 mL, 0.50 M) was added dropwise at -78 °C. The resulting orange-red solution was stirred for 30 min at -78 °C, then aldehyde **7** (40 mg, 0.18 mmol) dissolved in anhydrous CH_2Cl_2 (1 mL) was added. After 3 h at -78 °C the reaction was quenched by addition of saturated NH_4Cl (5 mL) and vigorously stirred at room temperature. The mixture was diluted with CH_2Cl_2 the organic layer was successively washed with brine. The organic layer was dried over anhydrous Na_2SO_4 filtered and concentrated under reduced pressure. Crude

product was purified by silica gel column chromatography using ethyl acetate and hexane (4:96) as an eluent to afford the product **4** as colorless liquid. (90 mg, (94:6 dr), 85% based on recovered starting material) recovered ketone (10 mg, 11%). R_f = 0.45 (hexanes:EtOAc, 9:1); $[\alpha]_D^{28}$ = -17.2 (*c* 1, $CHCl_3$); IR (neat) υ_{max}: 3448, 2927, 2855, 1458, 1260, 1091~~, 802~~ cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$): δ 7.67-7.60 (m, 5H), 7.35-7.28 (m, 7H), 7.27- 7.23 (m, 4H), 7.16-7.07 (m, 2H), 7.04-7.01 (m, 2H), 4.44-4.34 (m, 3H), 4.14 (d, *J* = 11.3 Hz, 1H), 4.0 (d, *J* = 9.8 Hz, 1H), 3.86 (dd, *J* = 4.9, 9.9 Hz, 1H), 3.82-3.76 (m, 1H), 3.72-3.66 (m, 1H), 3.51-3.47 (m, 1H), 3.29 (dd, *J* = 4.7, 9.1 Hz, 1H), 3.25 (d, *J* = 9.1 Hz, 1H), 3.04 (t, *J* = 8.7 Hz, 1H), 2.87-2.89 (m, 1H), 2.56-2.52 (m, 1H), 1.83-1.78 (m, 1H), 1.76-1.60 (m, 7H), 1.51-1.30 (m, 7H) 1.01 (s, 9H), 0.89 (d, *J* = 6.9 Hz, 3H), 0.87-0.79 (m, 12H), 0.68-0.63 (t, *J* = 7.3 Hz, 3H), 0.53 (d, *J* = 6.6 Hz, 3H) ppm; ^{13}C NMR (125 MHz, $CDCl_3$): δ 217.9, 139.0, 138.9, 135.8, 135.7, 134.2, 133.9, 129.5, 129.4, 128.2, 128.1, 127.6, 127.5, 127.4, 127.3, 127.2, 127.1, 80.3, 75.8, 74.3, 74.0, 73.8, 72.9, 71.9, 62.3, 55.9, 48.8, 42.6, 38.4, 36.3, 33.5, 31.1, 30.1, 29.7, 27.1, 22.5, 19.5, 19.4, 19.3, 16.7, 15.9, 14.3, 14.0, 13.2, 11.1, 9.7 ppm; HRMS calculated For $C_{56}H_{80}O_6NaSi$ $[M + Na]^+$ 899.5615, found 899.5640.