Using a Temporary Silicon Connection in Stereoselective Allylation with Allylsilanes: Application to the Synthesis of Stereodefined 1,2,4-Triols

Julien Beignet, Liam R. Cox*

School of Chemistry, University of Birmingham, Edgbaston, Birmingham, B15 2TT, UK.

Email: l.r.cox@bham.ac.uk

Supporting information:

General experimental procedures for the allylation of aldehydes 6, Tamao oxidation of the cyclization products 7 and acetonide formation from triols 9.

Characterization data for allylation products, triols and acetonide derivatives (^{1}H-NMR and ^{13}C-NMR only)

General Information

All characterizations were carried out at the School of Chemistry, University of Birmingham, UK.

Elemental analyses were recorded on a Carlo Erba EA1110 simultaneous CHNS analyser. Infrared spectra were recorded neat as thin films between sodium chloride discs on a Perkin Elmer 1600 FTIR spectrometer. The intensity of each band is described as s (strong), m (medium) or w (weak) and with the prefix v (very) and suffix br (broad) where appropriate. ^{1}H-NMR and ^{13}C-NMR spectra were recorded at 500 and 125 MHz, 400 and 100 MHz or 300 and 75 MHz, respectively, using Bruker DRX 500, Bruker AMX 400, Bruker AV 400, Bruker AV 300 and Bruker AC 300 spectrometers. Chemical shifts are reported as δ values (ppm) referenced to the following solvent signals: $CHCl_3$, δ 7.26; $CDCl_3$, δ 77.0. Acetonides **11** and **12** were recorded in d_6-benzene: C_6H_6, δ 7.16; C_6D_6, δ 128.0. The term, 'stack' is used to describe a region where resonances arising from non-equivalent nuclei are coincident, and multiplet, m, to describe a region where resonances arising from a single nucleus (or equivalent nuclei) are coincident but coupling constants cannot be readily assigned. Connectivities were deduced from COSY90, HSQC and HMBC experiments. GOESY and NOESY experiments were used to elucidate relative stereochemistry. Mass spectra were recorded on a Micromass LCT spectrometer utilizing electrospray ionization (and a methanol mobile phase), and Micromass Prospec and Zabspec spectrometers utilizing electron impact and/or chemical ionization (ammonia as the carrier gas). HRMS were recorded on a Micromass LCT spectrometer using a lock mass incorporated into the mobile phase.

Preparative HPLC was performed on a reverse phase Phenomenex Luna 10u C18(2)100A 50 × 21, 20 mm × 10 micron fitted with a Dionex P580 pump and a Dionex UVD170S detector (used at 210 and 225 nm) using a helium-degassed HPLC grade water/acetonitrile gradient, without acidic additives. Elution was monitored and spectra were recorded on Dionex Chromeleon 6.11 software.

Reactions

All reactions were conducted in oven-dried (140 °C) or flame-dried Schlenk glassware under a nitrogen atmosphere, and at ambient temperature (20 to 25 °C) unless otherwise stated, with magnetic stirring. Volumes of 5 cm^3 or less were measured and dispensed with Hamilton gastight syringes. Reactions were monitored by thin layer chromatography using pre-coated glass-backed ICN silica-rapid plates (60A F_{254}) and visualized by UV detection (254 nm) and potassium manganate(VII) and/or ammonium molybdate(IV) - cerium(IV) sulfate dips. Column chromatography was performed on Merck silica gel (particle size 40-63 μm mesh) or Fluka 60 (40-60 μm mesh) silica gel. Evaporation and concentration under reduced pressure was performed at 50 - 500 mbar. Residual solvent was removed under high vacuum (1 mbar).

Materials

All reagents were obtained from commercial sources and used without further purification unless stated otherwise. 2,4,6-Tri-*tert*-butylprimidine (TTBP) was synthesized following a known procedure.[1] Trimethylsilyl chloride was distilled under nitrogen from CaH_2 and stored under nitrogen at 4 °C. Trimethylsilyl trifluoromethanesulfonate (triflate) was stored in a Schlenk tube under nitrogen at 4 °C and used whilstever the compound was colorless. Over time a pink coloration was observed whereupon fresh TMSOTf was used. Diethylamine and *N*,*N*,*N'*,*N'*- tetramethylethylenediamine were distilled under a nitrogen atmosphere from KOH and stored under nitrogen at room temperature over activated 4 Å molecular sieves (activated by heating under a vacuum for 15 min with a bunsen flame immediately before use). Dichloromethane and acetonitrile were freshly distilled under nitrogen from CaH_2. Tetrahydrofuran and diethyl ether were freshly distilled under nitrogen from sodium benzophenone ketyl. All solutions are aqueous and saturated unless stated otherwise.

General procedure for allylation reaction: synthesis of oxasilacycles 7a-i and 8a-i.

TMSOTf (1.0 equiv.) was added dropwise (approximately one drop per second) *via* syringe to a solution of *aldehyde* **6a-i** (1.0 equiv.) and 2,6-di-*tert*-butyl-4-methylpyridine (2,6-DTBMP) (1.2 equiv.) in CH_2Cl_2 (0.1 M reaction concentration) at –78 °C. The reaction mixture was stirred at –78 °C. TLC indicated consumption of starting material within 8-16 h. The reaction was then quenched by adding

[1] Crich, D.; Smith, M.; Yao, Q.; Picione, J, *Synthesis* **2001**, 323-326.

an equivalent volume of $NaHCO_3$ solution at –78 °C and allowed to warm to room temperature over 30 min. The two phases were separated and the aqueous phase extracted with CH_2Cl_2 (2 × volume of aqueous phase). The combined organic extracts were successively washed with water (1/3 volume of organic phase) and brine (1/3 volume of organic phase) and dried over $MgSO_4$. Filtration and evaporation of the volatiles under reduced pressure on a rotary evaporator provided a yellow oil (quantitative mass recovery). This was used in the following Tamao oxidation without further purification. Analytically pure samples of each oxasilacycle were obtained by preparative HPLC. This allylation reaction was performed on scales ranging from 0.15 mmol to 15 mmol of aldehyde without any noticeable changes in rates, yields or ratios of products. All reactions were carried out a minimum of two times.

General procedure for Tamao oxidation: formation of triols 9.

H_2O_2 (20 equiv., 60% in H_2O), $KHCO_3$ (3.0 equiv.) and KF (5.0 equiv.) were added to a solution of the products from the allylation of *aldehyde* **6a-i** (1 equiv.) in MeOH:THF (1:1) (0.1 M reaction concentration) and the resulting mixture was stirred at room temperature in a round-bottom flask. The reaction was monitored by TLC and consumption of the starting material occurred within 4 to 7 days (an additional 5 equiv. of H_2O_2 were sometimes added after a few days to drive the reaction to completion). The mixture was then poured into an equal volume of $Na_2S_2O_3$ solution and stirred for 30 min. The resulting mixture was extracted with EtOAc (3 × 2 volumes) and the combined organic extracts were washed with brine (~1/6 volume of EtOAc) and dried over $MgSO_4$. Filtration and evaporation of the volatiles under reduced pressure on a rotary evaporator afforded the triol **9** as a yellow oil which was further purified by flash column chromatography. A short column and gradient elution were used to minimize losses of the *triol* **9a-h** on the silica.

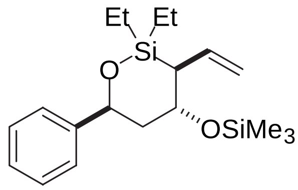
General procedure for Acetonide formation: formation of acetonides 11 and 12.

Na_2SO_4 (40 mg) and *p*TsOH•H_2O (2 mg, 16 μmol) were added to a solution of *triol* **9a-h** (30 mg) in acetone (non redistilled, 1.0-2.0 mL) and the resulting mixture was stirred overnight. The reaction mixture was poured over a $NaHCO_3$ solution (3 mL) and the layer was extracted with EtOAc (3 × 10 mL). The combined organic extracts were washed with brine (5 mL) and dried over $MgSO_4$. Filtration and evaporation of the volatiles under reduced pressure on a rotary evaporator left a mixture of acetonides **11** and **12** as a pale yellow oil in quantitative yield. The mixture was then used without further purification for NMR spectroscopic studies (in C_6D_6).

Allylation reaction of Aldehyde 6a:

TMSOTf (2.37 mL, 13.1 mmol) was added to a solution of *aldehyde* **6a** (4.60 g, 13.1 mmol) and TTBP (2.96 g, 14.4 mmol) in CH_2Cl_2 (131 mL) at –78 °C and the reaction mixture was stirred for 8 h. Aqueous work-up and removal of the solvent afforded compounds **7a** and **8a** (70:18; inseparable mixture) as a colorless liquid (7.51 g, 88%, resulting mass being diene products). This was used in the following step without any further purification. Analytically pure samples of each compound could not be obtained by preparative HPLC (t = 0 → 50 min, 0 → 100% MeCN in H_2O); **7a** t_R = 68.3 min (contaminated with diene **5a**) and **8a** t_R = 70.4 min (contaminated with residual TTBP).

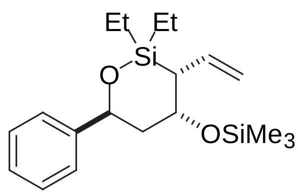
(3*S, 4*R**, 6*S**) oxasilinane 7a**



$C_{19}H_{32}O_2Si_2$
Exact Mass: 348.19408
Mol. Wt.: 348.62718
C, 65.46; H, 9.25; O, 9.18; Si, 16.11%

HPLC: t_R = 68.3 min; ν_{max}(film)/cm^{-1} 3075w, 3029w, 2956s, 2916m, 2877s, 1627m (C=C), 1494w, 1453m, 1415m, 1364w, 1328w, 1309w, 1252s, 1200w, 1146m, 1003s, 939m, 887m, 871m, 842s, 800m, 745m, 698s; δ_H(300 MHz) 0.14 (9H, s, Si(C*H*$_3$)$_3$), 0.62-0.75 (2H, m, OSi(C*H*$_2$CH$_3$)), 0.80-0.93 (2H, m, OSi(C*H*$_2$CH$_3$)), 1.01 (3H, t, *J* 8.1, OSi(CH$_2$C*H*$_3$)), 1.04 (3H, t, *J* 8.1, OSi(CH$_2$C*H*$_3$)), 1.82 (1H, ddd, *J* 14.1, 5.4, 2.7, 5-$H_{pseudoeq.}$), 1.91-2.03 (2H, stack, 3-*H*, 5-$H_{pseudoax.}$), 4.13 (1H, app. t, *J* 4.4, 4-*H*), 4.96 (1H, d, *J* 10.5, 1-H_{cis}), 4.98 (1H, d, *J* 16.2, 1-H_{trans}), 5.29 (1H, dd, *J* 9.6, 2.7, 6-*H*), 5.87 (1H, app. dt, *J* 16.2, 10.5, 2-*H*), 7.12-7.42 (5H, stack, Ph*H*); δ_C(75 MHz) 0.1 (CH$_3$, Si(*C*H$_3$)$_3$), 5.0 (2 × CH$_2$, OSi(*C*H$_2$CH$_3$)$_2$), 6.7 (CH$_3$, OSi(CH$_2$*C*H$_3$)), 6.9 (CH$_3$, OSi(CH$_2$*C*H$_3$)), 38.5 (CH, *C*-3), 42.1 (CH$_2$, *C*-5), 70.1 (CH, *C*-4), 71.4 (CH, *C*-6), 113.8 (CH$_2$, *C*-1), 125.4 (CH, Ph), 126.8 (CH, Ph), 128.2 (CH, Ph), 137.2 (CH, *C*-2), 145.3 (quat. C, *ipso*Ph); *m/z* (TOF ES+) 371.2 [(M+Na)$^+$, 100%]; HRMS *m/z* (TOF ES+) 371.1843 ([M+Na]$^+$. $C_{19}H_{32}NaO_2Si_2$ requires 371.1839).

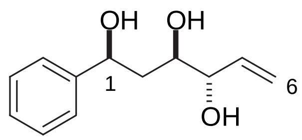
(3R*, 4R*, 6S*) oxasilinane 8a



$C_{19}H_{32}O_2Si_2$
Exact Mass: 348.19408
Mol. Wt.: 348.62718
C, 65.46; H, 9.25; O, 9.18; Si, 16.11%

HPLC: t_R = 70.4 min; ν_{max}(film)/cm^{-1} 2956s, 2876m, 1626w (C=C), 1584w, 1564w, 1455w, 1453m, 1363w, 1252m, 1120m, 1067s, 1050m, 1004m, 963m, 880m, 844s, 802w, 787w, 727m, 698m, 661m; δ_H(300 MHz) 0.09 (9H, s, Si(C*H*$_3$)$_3$), 0.50-0.85 (4H, stack, OSi(C*H*$_2$CH$_3$)$_2$), 0.90 (3H, t, *J* 7.5, OSi(CH$_2$C*H*$_3$)), 0.98 (3H, t, *J* 7.9, OSi(CH$_2$C*H*$_3$)), 1.56 (1H, app. d, *J* 13.9, 5-*H*$_a$), 1.80 (1H, ddd, *J* 13.9, 5.0, 2.0, 5-*H*$_b$), 1.89 (1H, dd, *J* 10.1, 2.4, 3-*H*), 4.17-4.26 (1H, m, 4-*H*), 4.78-4.90 (2H, stack, 1-C*H*$_2$), 5.17 (1H, dd, *J* 11.0, 1.6, 6-*H*), 5.84 (1H, app. dt, *J* 17.3, 10.1, 2-*H*), 7.09-7.30 (5H, stack, Ph*H*); δ_C(75 MHz) 0.3 (CH$_3$, Si(*C*H$_3$)$_3$), 4.8 (CH$_2$, OSi(*C*H$_2$CH$_3$)), 5.9 (CH$_2$, OSi(*C*H$_2$CH$_3$)), 6.7 (CH$_3$, OSi(CH$_2$*C*H$_3$)), 6.8 (CH$_3$, OSi(CH$_2$*C*H$_3$)), 38.3 (CH, *C*-3), 45.9 (CH$_2$, *C*-5), 69.5 (CH, *C*-4), 71.5 (CH, *C*-6), 112.8 (CH$_2$, *C*-1), 125.3 (CH, Ph), 126.9 (CH, Ph), 128.2 (CH, Ph), 137.9 (CH, *C*-2), 145.6 (quat. C, *ipso*Ph); *m/z* (TOF ES+) 371.2 [(M+Na)$^+$, 100%]; HRMS *m/z* (TOF ES+) 371.1837 ([M+Na]$^+$. $C_{19}H_{32}NaO_2Si_2$ requires 371.1839).

(1*S**, 3*R**, 4*S**) 1-Phenyl-hex-5-ene-1,3,4-triol 9a



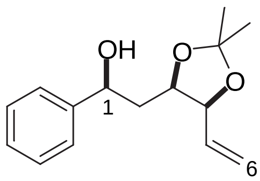
$C_{12}H_{16}O_3$
Exact Mass: 208.10995
Mol. Wt.: 208.25364
C, 69.21; H, 7.74; O, 23.05%

H_2O_2 (4.63 g, 60% in H_2O, 81.8 mmol), $KHCO_3$ (1.23 g, 12.3 mmol) and KF (1.19 g, 20.4 mmol) were added to a solution of the products from the allylation of *aldehyde* **6a** (2.42 g, 2.5 mmol of *oxasilinane* **7a**) in MeOH:THF (1:1, 41 mL) and the resulting mixture was stirred for 5 days. Aqueous work-up and purification by flash column chromatography (70 → 80% EtOAc in hexane) afforded *triol* **9a** as a colorless viscous oil (383 mg, 73%); R_f = 0.25 (70% EtOAc in hexane); (Found: C, 69.05; H, 7.91. $C_{12}H_{16}O_3$ requires C, 69.21; H, 7.74%); ν_{max}(film)/cm^{-1} 3380br vs (OH), 3086s, 3030s, 2981s, 2919s, 1954w, 1882w, 1723m, 1644m (C=C), 1604w (C=C), 1494s, 1454s, 1434s, 1258s, 1204s, 1063s, 995s, 928s, 853m, 821m, 761s, 701s; δ_H(300 MHz) 1.79 (1H, app. dt, *J* 14.7, 3.0, 1 × 2-C*H*$_a$H$_b$), 1.80-1.97 (1H, m, 2-CH$_a$*H*$_b$), 2.30 (1H, br s, O*H*), 3.10 (1H, br s, O*H*), 3.50 (1H, br s, O*H*), 3.99 (1H, dt, *J* 9.9, 3.0, 3-*H*), 4.12-4.16 (1H, m, 4-*H*), 4.94 (1H, dd, *J* 9.9, 3.0, 1-*H*), 5.24 (1H, d, *J* 10.7, 6-*H*$_{cis}$), 5.32 (1H, d, *J* 16.9, 6-*H*$_{trans}$), 5.88 (1H, ddd, *J* 16.9, 10.7, 6.2, 5-*H*), 7.24-7.41 (5H, stack, Ph*H*); δ_C(75 MHz) 39.5 (CH$_2$, *C*-2), 74.3 (CH, *C*HOH), 74.4 (CH, *C*HOH), 75.7 (CH, *C*HOH), 117.4 (CH$_2$, *C*-6), 125.7 (CH, Ph), 127.6 (CH, Ph), 128.4 (CH, Ph), 135.9 (CH, *C*-5), 144.1 (quat. C, *ipso*Ph); *m/z* (TOF ES+) 231 [(M+Na)$^+$, 100%]; HRMS *m/z* (TOF ES+) 231.0991 ([M+Na]$^+$. $C_{12}H_{16}NaO_3$ requires 231.0997).

Acetonide protection of *triol* 9a (and trace 10a)

Na_2SO_4 (40 mg) and *p*TsOH•H_2O (3 mg, 16 μmol) were added to a solution of *triol* **9a** (30 mg, 0.14 mmol) in acetone (non redistilled, 1.4 mL) and the resulting mixture was stirred overnight. Aqueous work-up afforded *alcohols* **11a**, **12a** and **13a** as an inseparable mixture (14:8:1 by ^{1}H NMR) (34 mg, quantitative).

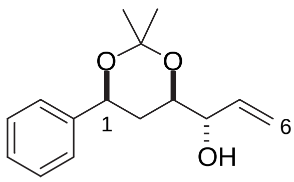
(1*S, 3*R**, 4*S**) 2-(2,2-Dimethyl-5-vinyl-[1,3]dioxolan-4-yl)-1-phenyl-ethanol 11a**



$C_{15}H_{20}O_3$
Exact Mass: 248.14125
Mol. Wt.: 248.31750
C, 72.55; H, 8.12; O, 19.33%

δ_H(C_6D_6, 400 MHz) 1.21 (3H, s, (C*H*$_3$)$_{pseudoax.}$), 1.43 (3H, s, (C*H*$_3$)$_{pseudoeq.}$), 1.53 (1H, ddd, *J* 14.0, 4.6, 2.9, 2-C*H*$_a$H$_b$), 1.93 (1H, ddd, *J* 14.0, 10.4, 8.7, 2-CH$_a$*H*$_b$), 3.15 (1H, br s, 1 × O*H*), 3.97 (1H, ddd, *J* 10.4, 6.9, 2.9, 3-*H*), 4.20 (1H, app. t, *J* 6.9, 4-*H*), 4.84 (1H, dd, *J* 8.7, 4.6, 1-*H*), 4.92 (1H, ddd, *J* 10.4, 1.7, 1.1, 6-*H*$_{cis}$), 5.05-5.11 (1H, m, 6-*H*$_{trans}$), 5.52 (1H, ddd, *J* 17.3, 10.4, 6.9, 5-*H*), 7.07-7.29 (3H, stack, Ph*H*), 7.44 (2H, d, *J* 7.2, *o*Ph*H*); δ_C(C_6D_6, 100 MHz) 25.6 (CH_3, (*C*H$_3$)$_{pseudoax.}$), 28.2 (CH_3, (*C*H$_3$)$_{pseudoeq.}$), 40.8 (CH_2, *C*-2), 73.6 (CH, *C*-1), 77.8 (CH, *C*-3), 79.7 (CH, *C*-4), 108.8 (quat. C, *C*(CH_3)$_2$), 117.6 (CH_2, *C*-6), 126.25 (CH, *o*Ph), 126.7-131.1 (CH and CD, stack, Ph, *C*$_6$D$_6$), 134.6 (CH, *C*-5), 145.2 (quat. C, *ipso*Ph).

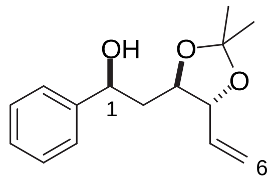
(1*S, 3*R**, 4*S**) 1-(2,2-Dimethyl-6-phenyl-[1,3]dioxan-4-yl)-prop-2-en-1-ol 12a**



$C_{15}H_{20}O_3$
Exact Mass: 248.14125
Mol. Wt.: 248.31750
C, 72.55; H, 8.12; O, 19.33%

δ_H(C_6D_6, 400 MHz) 1.29 (3H, s, (C*H3*)*pseudoax.*), 1.46-1.50 (1H, m, 2-C*H*$_a$H$_b$), 1.51 (3H, s, (C*H3*)*pseudoeq.*), 1.70 (1H, app. q, *J* 12.0, 2-CH$_a$*H*$_b$), 2.01 (1H, br s, OH), 3.73 (1H, ddd, *J* 12.0, 4.1, 2.5, 3-*H*), 4.07-4.12 (1H, m, 4-*H*), 4.65 (1H, dd, *J* 12.0, 2.7, 1-*H*), 5.05-5.11 (1H, m, 6-*H*$_{cis}$), 5.35 (1H, app. dt, *J* 17.3, 1.9, 6-*H*$_{trans}$), 5.79 (1H, ddd, *J* 17.3, 10.7, 5.2, 5-*H*), 7.07-7.29 (3H, stack, Ph*H*), 7.34 (2H, d, *J* 7.2, *o*Ph*H*); δ_C(C_6D_6, 100 MHz) 19.8 (CH_3, (*C*H$_3$)*pseudoax.*), 30.3 (CH_3, (*C*H$_3$)*pseudoeq.*), 33.3 (CH_2, *C*-2), 71.2 (CH, *C*-1), 72.5 (CH, *C*-3), 74.3 (CH, *C*-4), 99.1 (quat. C, *C*(CH_3)$_2$), 116.0 (CH_2, *C*-6), 126.17 (CH, *o*Ph), 126.7-131.1 (CH and CD, stack, Ph, C_6D_6), 136.7 (CH, *C*-5), 143.1 (quat. C, *ipso*Ph).

(1*S, 3*R**, 4*R**) 2-(2,2-Dimethyl-5-vinyl-[1,3]dioxolan-4-yl)-1-phenyl-ethanol 13a**



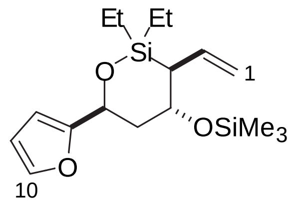
$C_{15}H_{20}O_3$
Exact Mass: 248.14125
Mol. Wt.: 248.31750
C, 72.55; H, 8.12; O, 19.33%

δ_H(C_6D_6, 400 MHz) -identifiable resonances- 1.37 (3H, s, C*H3*), 1.38 (3H, s, C*H3*), 1.82-1.88 (1H, m, 2-C*H*$_a$H$_b$), 3.93-3.98 (1H, stack, 4-*H*), 4.96 (1H, br d (+ unresolved fine coupling), *J* 10.5, 6-*H*$_{cis}$), 5.16 (1H, dm, *J* 16.9, 6-*H*$_{trans}$), 5.66 (1H, ddd, *J* 16.9, 10.5, 6.7, 5-*H*); δ_C(C_6D_6, 100 MHz) 27.1 (CH_3, *C*H$_3$), 27.5 (CH_3, *C*H$_3$), 41.3 (CH_2, *C*-2), 77.9 (CH, *C*-3), 82.7 (CH, *C*-4), 109.0 (quat. C, *C*(CH_3)$_2$), 117.9 (CH_2, *C*-6), 125.9 (CH, *o*Ph), 135.7 (CH, *C*-5), 145.6 (quat. C, *ipso*Ph).

Allylation reaction of Aldehyde 6b:

TMSOTf (324 µL, 1.8 mmol) was added to a solution of *aldehyde* **6b** (607 mg, 1.8 mmol) and 2,6-DTBMP (443 mg, 2.2 mmol) in CH_2Cl_2 (18 mL) at –78 °C and the reaction mixture was stirred for 8 h. Aqueous work-up and removal of the solvent afforded compounds **7b** and **8b** (69:17; inseparable mixture) as a yellow liquid (1.003 g, 86%, resulting mass being diene products). This was used in the following step without any further purification. Analytically pure samples of compounds **7b** and **8b** were obtained as colorless oils by preparative HPLC (5% H_2O in MeCN); **7b** t_R = 35.6 min and **8b** t_R = 43.0 min.

(3*S, 4*R**, 6*S**) oxasilinane 7b**



$C_{17}H_{30}O_3Si_2$

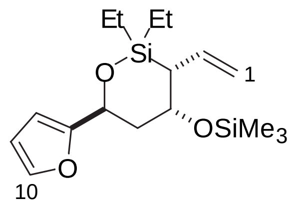
Exact Mass: 338.17335

Mol. Wt.: 338.58930

C, 60.30; H, 8.93; O, 14.18; Si, 16.59%

HPLC: t_R = 35.6 min; ν_{max}(film)/cm^{-1} 3077w, 2956s, 2878m, 1628w (C=C), 1505w, 1460w, 1414w, 1351w, 1252s, 1156m, 1070s, 1005m, 956w, 876m, 840s, 727m, 628m; δ_H(400 MHz) 0.10 (9H, s, Si(C*H*$_3$)$_3$), 0.55 (2H, q, *J* 7.8, OSi(C*H*$_2$CH$_3$)), 0.76 (2H, q, *J* 7.8, OSi(C*H*$_2$CH$_3$)), 0.86 (3H, t, *J* 7.8, OSi(CH$_2$C*H*$_3$)), 1.01 (3H, t, *J* 7.8, OSi(CH$_2$C*H*$_3$)), 1.90 (1H, ddd, *J* 14.1, 8.1, 4.0, 5-C*H*$_a$H$_b$), 1.98 (1H, dd, *J* 10.3, 7.3, 3-*H*), 2.20 (1H, ddd, *J* 14.1, 6.6, 2.4, 5-CH$_a$*H*$_b$), 4.18 (1H, app. td, *J* 7.7, 2.2, 4-*H*), 4.90-4.98 (2H, stack, 1-C*H*$_2$), 5.23 (1H, dd, *J* 6.5, 4.0, 6-*H*)), 5.74 (1H, dt, *J* 16.9, 10.4, 2-*H*), 6.22 (1H, d, *J* 3.2, 8-*H*), 6.32 (1H, dd, *J* 3.2, 2.0, 9-*H*), 7.36 (1H, dd, *J* 2.0, 0.7, 10-*H*); δ_C(100 MHz) 0.1 (CH$_3$, Si(*C*H$_3$)$_3$), 5.1 (CH$_2$, OSi(*C*H$_2$CH$_3$)), 5.5 (CH$_2$, OSi(*C*H$_2$CH$_3$)), 6.1 (CH$_3$, OSi(CH$_2$*C*H$_3$)), 6.5 (CH$_3$, OSi(CH$_2$*C*H$_3$)), 39.1 (CH$_2$, *C*-5), 40.1 (CH, *C*-3), 66.0 (CH, *C*-6), 70.1 (CH, *C*-4), 105.6 (CH, *C*-8), 110.1 (CH, *C*-9), 114.0 (CH$_2$, *C*-1), 137.1 (CH, *C*-2), 141.5 (CH, *C*-10), 156.9 (quat. C, *C*-7); *m/z* (TOF ES+) 361.2 [(M+Na)$^+$, 100%]; HRMS *m/z* (TOF ES+) 361.1627 ([M+Na]$^+$. $C_{17}H_{30}NaO_3Si_2$ requires 361.1631).

(3*R, 4*R**, 6*S**) oxasilinane 8b**



$C_{17}H_{30}O_3Si_2$

Exact Mass: 338.17335

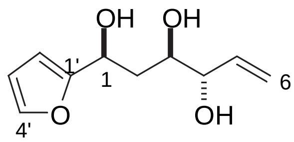
Mol. Wt.: 338.58930

C, 60.30; H, 8.93; O, 14.18; Si, 16.59%

HPLC: t_R = 43.0 min; ν_{max}(film)/cm^{-1} 2956s, 2877m, 1626w (C=C), 1460w, 1350w, 1322w, 1252m, 1150w, 1117m, 1073m, 1049m, 1004w, 963w, 880w, 840m, 806w, 784w, 727m; δ_H(400 MHz) 0.13

(9H, s, Si(CH_3)$_3$), 0.53-0.92 (4H, stack, OSi(CH_2CH$_3$)$_2$), 0.98 (3H, t, *J* 7.8, OSi(CH$_2$CH_3)), 0.99 (3H, t, *J* 7.8, OSi(CH$_2$CH_3)), 1.83-1.99 (3H, stack, 3-*H*, 5-CH_2), 4.28-4.34 (1H, m, 4-*H*), 4.89 (1H, dd, *J* 10.2, 2.2, 1-H_{cis}), 4.92 (1H, dd, *J* 17.2, 1.5, 1-H_{trans}), 5.24 (1H, dd, *J* 10.6, 2.8, 6-*H*), 5.89 (1H, dt, *J* 17.2, 10.2, 2-*H*), 6.20 (1H, d, *J* 3.2, 8-*H*), 6.30 (1H, dd, *J* 3.2, 2.0, 9-*H*), 7.33-7.37 (1H, m, 10-*H*); δ_C(100 MHz) 0.2 (CH$_3$, Si(*C*H$_3$)$_3$), 4.8 (CH$_2$, OSi(*C*H$_2$CH$_3$)), 5.7 (CH$_2$, OSi(*C*H$_2$CH$_3$)), 6.5 (CH$_3$, OSi(CH$_2$*C*H$_3$)), 6.7 (CH$_3$, OSi(CH$_2$*C*H$_3$)), 38.4 (CH, *C*-3), 41.2 (CH$_2$, *C*-5), 63.6 (CH, *C*-6), 71.1 (CH, *C*-4), 105.0 (CH, *C*-8), 110.0 (CH, *C*-9), 113.0 (CH$_2$, *C*-1), 137.8 (CH, *C*-2), 141.5 (CH, *C*-10), 157.6 (quat. C, *C*-7); *m/z* (TOF ES+) 361.2 [(M+Na)$^+$, 100%]; HRMS *m/z* (TOF ES+) 361.1636 ([M+Na]$^+$. $C_{17}H_{30}NaO_3Si_2$ requires 361.1631).

(1*S, 3*R**, 4*S**) 1-Furan-2-yl-hex-5-ene-1,3,4-triol 9b**



$C_{10}H_{14}O_4$
Exact Mass: 198.08921
Mol. Wt.: 198.21576
C, 60.59; H, 7.12; O, 32.29%

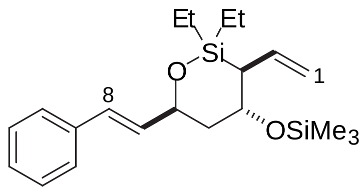
H_2O_2 (3.06 g, 60% in H_2O, 54.0 mmol), $KHCO_3$ (811 mg, 8.1 mmol) and KF (784 mg, 15.5 mmol) were added to a solution of the products from the allylation of *aldehyde* **6b** (1.578 g, 1.61 mmol of *oxasilinane* **7b**) in MeOH:THF (1:1, 27 mL) and the resulting mixture was stirred for 5 days. Aqueous work-up and purification by flash column chromatography (70 $\rightarrow$ 90% EtOAc in hexane) afforded *triol* **9b** as a yellow viscous oil (201 mg, 61%); R_f = 0.27 (70 % EtOAc in hexane); (Found: C, 60.81; H, 7.16. $C_{10}H_{14}O_4$ requires C, 60.59; H, 7.12%); ν_{max}(film)/cm^{-1} 3346br s (OH), 2918m, 1706w, 1640w, 1504m, 1425m, 1314m, 1229m, 1173w, 1146m, 1068s, 1009s, 929m, 884m, 854w, 816w and 742s; δ_H(300 MHz) 1.88-2.08 (2H, stack, CH_2), 3.10 (1H, br s, O*H*), 3.82 (1H, br s, O*H*), 3.87-3.98 (2H, stack, C*H*OH, O*H*), 4.11-4.19 (1H, m, C*H*OH), 4.90 (1H, dd, *J* 9.2, 4.1, C*H*OH), 5.23 (1H, d, *J* 10.3, =CHH_{cis}), 5.32 (1H, d, *J* 17.3, =CHH_{trans}), 5.87 (1H, ddd, *J* 17.3, 10.3, 6.2, C*H*=CH$_2$), 6.22 (1H, d, *J* 2.9, 2'-*H*), 6.29-6.32 (1H, m, 3'-*H*), 7.34 (1H, app. s, 4'-*H*); δ_C(75 MHz) 35.9 (CH$_2$), 67.5 (CH, *C*HOH), 73.9 (CH, *C*HOH), 75.6 (CH, *C*HOH), 105.9 (CH, *C*-2' or *C*-3'), 110.2 (CH, *C*-3' or *C*-2'), 117.6 (CH$_2$, =*C*H$_2$), 135.9 (CH, =*C*H), 142.0 (CH, *C*-4') and 155.9 (quat. C, *C*-1'); *m/z* (TOF ES+) 221.1 ([M+Na]$^+$, 100 %); HRMS *m/z* (TOF ES+) 221.0786 ([M+Na]$^+$. $C_{10}H_{14}NaO_4$ requires 221.0790).

Allylation reaction of Aldehyde 6c:

TMSOTf (145 μL, 0.80 mmol) was added to a solution of *aldehyde* **6c** (297 mg, 0.80 mmol) and 2,6-DTBMP (197 mg, 0.96 mmol) in CH_2Cl_2 (8 mL) at –78 °C and the reaction mixture was stirred for 8 h.

Aqueous work-up and removal of the solvent afforded compounds **7c** and **8c** (64:18; inseparable mixture) as a yellow liquid (524 mg, 82%, remaining mass being diene products). This was used in the following step without any further purification. Analytically pure samples of compounds **7c** and **8c** were obtained as colorless oils by preparative HPLC (3% H_2O in MeCN); **7c** t_R = 48.3 min and **8c** t_R = 83.9 min.

(3*S, 4*R**, 6*S**, 7*E*) oxasilinane 7c**



$C_{21}H_{34}O_2Si_2$

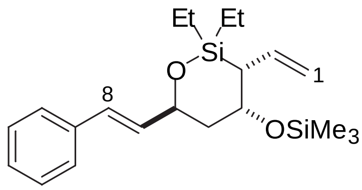
Exact Mass: 374.20973

Mol. Wt.: 374.66446

C, 67.32; H, 9.15; O, 8.54; Si, 14.99%

HPLC: t_R = 48.3 min; ν_{max}(film)/cm^{-1} 3079w, 3040w, 3027w, 2956s, 2915m, 2876s, 1942w, 1872w, 1798w, 1739, 1627m (C=C), 1600w, 1578w, 1496m, 1459m, 1448m, 1414m, 1364m, 1340m, 1328m, 1303w, 1251s, 1201w, 1159m, 1120m, 1071s, 998s, 967m, 942m, 885m, 869m, 842s, 780m, 745s, 725m, 692m, 658w, 626m; δ_H(500 MHz) 0.12 (9H, s, OSi(C*H*$_3$)$_3$), 0.61-0.71 (2H, m, OSi(C*H*$_2$CH$_3$)), 0.76-0.82 (2H, m, OSi(C*H*$_2$CH$_3$)), 0.99 (3H, t, *J* 8.0, OSi(CH$_2$C*H*$_3$)), 1.03 (3H, t, *J* 7.5, OSi(CH$_2$C*H*$_3$)), 1.81 (1H, ddd, *J* 14.0, 7.3, 3.7, 5-C*H$_a$*H$_b$), 1.91 (1H, ddd, *J* 14.0, 7.3, 2.1, 5-CH$_a$*H$_b$*), 1.97 (1H, dd, *J* 10.3, 6.8, 3-*H*), 4.13 (1H, app. t, *J* 6.9, 4-*H*), 4.83-4.88 (1H, m, 6-*H*), 4.93 (1H, d, *J* 10.3, 1-*H$_{cis}$*), 4.95 (1H, d, *J* 17.5, 1-*H$_{trans}$*), 5.75 (1H, dt, *J* 17.5, 10.3, 2-*H*), 6.26 (1H, dd, *J* 15.9, 5.4, 7-*H*), 6.60 (1H, d, *J* 15.9, 8-*H*), 7.22 (1H, t, *J* 7.5, *p*Ph*H*), 7.31 (2H, t, *J* 7.5, 2 × *m*Ph*H*), 7.37 (2H, d, *J* 7.5, 2 × *o*Ph*H*); δ_C(125 MHz) 0.2 (CH$_3$, Si(CH$_3$)$_3$), 5.4 (CH$_2$, OSi(*C*H$_2$CH$_3$)), 5.7 (CH$_2$, OSi(*C*H$_2$CH$_3$)), 6.0 (CH$_3$, OSi(CH$_2$*C*H$_3$)), 6.6 (CH$_3$, OSi(CH$_2$*C*H$_3$)), 39.8 (CH, *C*-3), 40.8 (CH$_2$, *C*-5), 70.1 (CH, *C*-6), 70.3 (CH, *C*-4), 113.9 (CH$_2$, *C*-1), 126.4 (CH, *o*Ph), 127.3 (CH, *p*Ph), 128.5 (CH, *m*Ph), 129.1 (CH, *C*-8), 132.5 (CH, *C*-7), 137.1 (quat. C, *ipso*Ph), 137.2 (CH, *C*-2); *m/z* (TOF ES+) 397.0 ([M+Na]$^+$, 100 %); HRMS *m/z* (TOF ES+) 397.2005 ([M+Na]$^+$. $C_{21}H_{34}NaO_2Si_2$ requires 397.1995).

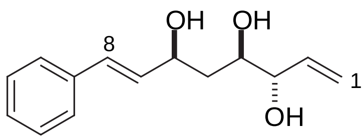
(3*R, 4*R**, 6*S**, 7*E*) oxasilinane 8c**



$C_{21}H_{34}O_2Si_2$
Exact Mass: 374.20973
Mol. Wt.: 374.66446
C, 67.32; H, 9.15; O, 8.54; Si, 14.99%

HPLC: t_R = 83.9 min; ν_{max}(film)/cm^{-1} 3077w, 3027w, 2956s, 2913s, 2876s, 1626w (C=C), 1601w, 1495w, 1449w, 1416w, 1362w, 1341w, 1321w, 1301w, 1252s, 1120w, 1170w, 1140m, 1088s, 1057s, 1003m, 962s, 899m, 868m, 841s, 809w, 777w, 743m, 722m, 692m, 666m; δ_H(400 MHz) 0.14 (9H, s, OSi(C*H₃*)₃), 0.54-0.91 (4H, stack, OSi(C*H₂*CH₃)₂), 0.99 (3H, t, *J* 7.8, OSi(CH₂C*H₃*)), 1.02 (3H, t, *J* 8.0, OSi(CH₂C*H₃*)), 1.55 (1H, dd, *J* 13.9, 11.7, 5-$H_{pseudoax.}$), 1.80 (1H, ddd, *J* 13.9, 5.1, 2.2, 5-$H_{pseudoeq.}$), 1.90 (1H, dd, *J* 10.0, 2.7, 3-*H*), 4.25-4.31 (1H, m, 4-*H*), 4.81-4.87 (1H, m, 6-*H*), 4.87 (1H, d, *J* 10.3, 1-H_{cis}), 4.91 (1H, d, *J* 16.5, 1-H_{trans}), 5.90 (1H, dt, *J* 16.5, 10.3, 2-*H*), 6.22 (1H, dd, *J* 15.7, 5.7, 7-*H*), 5.59 (1H, d, *J* 15.7, 8-*H*), 7.19 (1H, t, *J* 7.3, *p*Ph*H*), 7.27 (2H, t, *J* 7.3, 2 × *m*Ph*H*), 7.37 (2H, d, *J* 7.3, 2 × *o*Ph*H*); δ_C(100 MHz) 0.2 (CH₃, Si(*C*H₃)₃), 4.9 (CH₂, OSi(*C*H₂CH₃)), 5.7 (CH₂, OSi(*C*H₂CH₃)), 6.6 (CH₃, OSi(CH₂*C*H₃)), 6.7 (CH₃, OSi(CH₂*C*H₃)), 38.5 (CH, *C*-3), 43.1 (CH₂, *C*-5), 68.0 (CH, *C*-6), 71.3 (CH, *C*-4), 112.8 (CH₂, *C*-1), 126.4 (CH, *o*Ph), 127.2 (CH, *p*Ph), 128.4 (CH, *m*Ph), 128.5 (CH, *C*-8), 133.1 (CH, *C*-7), 137.2 (quat. C, *ipso*Ph), 137.9 (CH, *C*-2); *m/z* (TOF ES+) 397.1 ([M+Na]$^+$, 100 %); HRMS *m/z* (TOF ES+) 397.1991 ([M+Na]$^+$. $C_{21}H_{34}NaO_2Si_2$ requires 397.1995).

(3*S, 4*R**, 6*S**, 7*E*) 8-Phenyl-octa-1,7-diene-3,4,6-triol 9c**

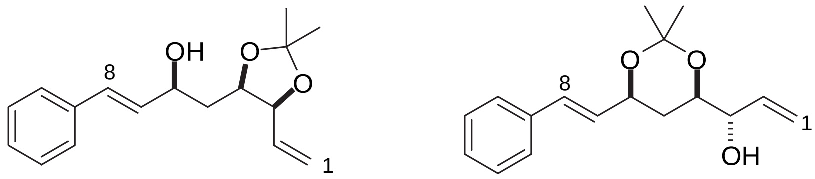


$C_{14}H_{18}O_3$
Exact Mass: 234.12560
Mol. Wt.: 234.29092
C, 71.77; H, 7.74; O, 20.49%

H_2O_2 (1.130 g, 60% in H_2O, 40.00 mmol), $KHCO_3$ (600 mg, 6.00 mmol) and KF (581 mg, 10.00 mmol) were added to a solution of the crude products from the allylation of *aldehyde* **6c** (1.244 g, 1.28 mmol of *oxasilinane* **7c**) in MeOH:THF (1:1, 20 mL) and the resulting mixture was stirred for 5 days.

Aqueous work-up and purification by flash column chromatography (70 $\rightarrow$ 90% EtOAc in hexane) afforded *triol* **9c** as a colorless viscous oil (254 mg, 85%); R_f = 0.28 (70% EtOAc in hexane); ν_{max}(film)/cm^{-1} 3367vs br (OH), 3082s, 3060s, 3026s, 2982m, 2916m, 1951w, 1878w, 1807w, 1646m (C=C), 1599m, 1578m, 1494s, 1449s, 1426s, 1315s, 1183m, 1110s, 1070s, 994s, 969s, 930s, 857m, 750s, 694s; δ_H(300 MHz) 1.72-1.79 (2H, stack, CH_2), 2.50-3.70 (3H, br, 3 $\times$ O*H*), 3.93-4.01 (1H, m, 4-*H*), 4.16 (1H, app. t, *J* 4.5, 3-*H*), 4.57 (1H, app. q, *J* 6.6, 6-*H*), 5.26 (1H, d, *J* 10.7, =CH_{cis}H$_{trans}$), 5.35 (1H, d, *J* 17.3, =CH$_{cis}$$H_{trans}$), 5.89 (1H, ddd, *J* 17.3, 10.7, 6.3, C*H*=CH$_2$), 6.21 (1H, dd, *J* 15.8, 6.6, PhCH=C*H*), 6.60 (1H, d, *J* 15.8, PhC*H*=CH), 7.20-7.40 (5H, stack, Ph*H*); δ_C(75 MHz) 37.6 (CH$_2$, *C*-5), 72.8 (CH, 1 $\times$ *C*HOH), 74.2 (CH, 1 $\times$ *C*HOH), 75.7 (CH, 1 $\times$ *C*HOH), 117.5 (CH$_2$, =*C*H$_2$), 126.5 (CH), 127.7 (CH), 128.6 (CH), 130.2 (CH), 131.5 (CH), 136.1 (CH), 136.4 (quat. C, *ipso*Ph); *m/z* (TOF ES+) 257.1 ([M+Na]$^+$, 100 %); HRMS *m/z* (TOF ES+) 257.1161 ([M+Na]$^+$. $C_{14}H_{18}NaO_3$ requires 257.1154).

Acetonide protection of triol 9c: 1-(2,2-dimethyl-5-vinyl-[1,3]dioxolan-4-yl)-4-phenyl-but-3-en-2-ol 11c and 1-(2,2-dimethyl-6-styryl-[1,3]dioxan-4-yl)-prop-2-en-1-ol 12c



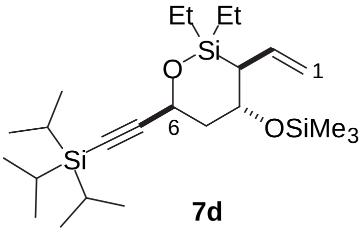
11c **12c**

$C_{17}H_{22}O_3$
Exact Mass: 274.15689
Mol. Wt.: 274.35478
C, 74.42; H, 8.08; O, 17.49 %

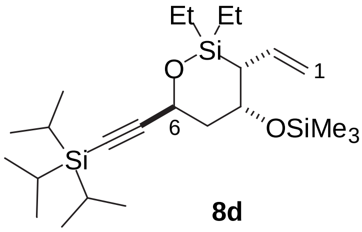
Na_2SO_4 (40 mg) and *p*TsOH•H_2O (2 mg, 16 μmol) were added to a solution of *triol* **9c** (30 mg, 0.13 mmol) in acetone (1.3 mL) and the resulting mixture was stirred overnight. Aqueous work-up afforded *acetonides* **11c** and **12d** as colorless oils and an inseparable mixture (73:27 **11c**:**12c** by ^{1}H NMR) (35 mg, quantitative mass recovery). ^{1}H-NMR revealed the presence of other compounds that severely complicated spectral analysis. However, the two major acetonide products **11c** and **12c** still predominated and readily permitted assignment of the 1,2- and 1,3-relative stereochemistry of triol **9c**); δ_H(C_6D_6, 300 MHz) -identifiable resonances- 1.22 (3H, s, 1 $\times$ CH_3), 1.29 (3H, s, 1 $\times$ CH_3), 1.44 (3H, s, 1 $\times$ CH_3), 1.51 (3H, s, 1 $\times$ CH_3), 5.55-5.70 (1H, m, 2-*H* **11c**), 5.71-5.86 (1H, m, 2-*H* **12c**); δ_H(C_6D_6, 75 MHz) -identifiable resonances- 19.9 (CH$_3$, 1 $\times$ *C*H$_3$ **12c**), 25.7 (CH$_3$, 1 $\times$ *C*H$_3$ **11c**), 28.2 (CH$_3$, 1 $\times$ *C*H$_3$ **11c**), 30.3 (CH$_3$, 1 $\times$ *C*H$_3$ **12c**), 38.3 (CH$_2$, *C*-5 **12c**), 38.5 (CH$_2$, *C*-5 **11c**), 71.8 (CH, 1 $\times$ *C*H(O) **11c**), 77.5 (CH, 1 $\times$ *C*H(O) **11c**) 79.8 (CH, 1 $\times$ *C*H(O) **11c**), 98.8 (quat. C, *C*(CH$_3$)$_2$ **12c**), 108.8 (quat. C, *C*(CH$_3$)$_2$ **11c**).

Allylation reaction of Aldehyde 6d:

TMSOTf (100 μL, 0.55 mmol) was added to a solution of *aldehyde* **6d** (249 mg, 0.55 mmol) and 2,6-DTBMP (137 mg, 0.66 mmol) in CH_2Cl_2 (6 mL) at –78 °C and the reaction mixture was stirred for 16 h. Aqueous work-up and removal of the solvent afforded oxasilinanes **7d** and **8 d** (80:12; inseparable mixture) as a yellow liquid (385 mg, 92%, remaining mass being diene products). This was used in the following oxidation step without any further purification. We were unable to separate the two diastereoisomers by preparative HPLC.



7d



8d

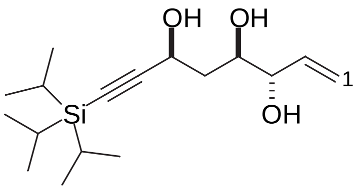
$C_{24}H_{48}O_2Si_2$

Exact Mass: 374.20973

Mol. Wt.: 374.66446

C, 67.32; H, 9.15; O, 8.54; Si, 14.99%

(3*S, 4*R**, 6*S**) 8-Triisopropylsilanyl-oct-1-en-7-yne-3,4,6-triol 9d**



$C_{17}H_{32}O_3Si$

Exact Mass: 312.21207

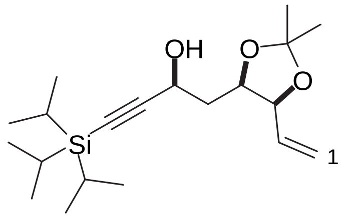
Mol. Wt.: 312.51968

C, 65.33; H, 10.32; O, 15.36; Si, 8.99%

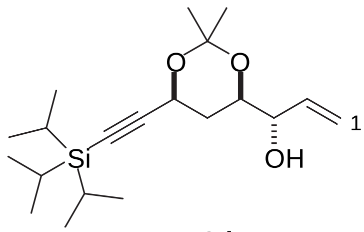
H_2O_2 (623 mg, 60% in H_2O, 11.00 mmol), $KHCO_3$ (132 mg, 1.32 mmol) and KF (128 mg, 2.20 mmol) were added to a solution of the crude products from the allylation of *aldehyde* **6d** (385 mg, 0.44 mmol of *oxasilinane* **7d**) in MeOH:THF (1:1, 6 mL) and the resulting mixture was stirred for 5 days. Aqueous work-up and purification by flash column chromatography (70 → 90% EtOAc in hexane) afforded *triol* **9d** as a colorless viscous oil (47 mg, 34%); R_f = 0.30 (50% EtOAc in hexane); ν_{max}(film)/cm^{-1} 3368s br (OH), 2944s, 2893s, 2868s, 2735m, 2171m (C≡C), 1723w, 1645w (C=C), 1464s, 1427m, 1384m, 1367m, 1316m, 1245m, 1187w, 1061s, 1018s, 996s, 925s, 883s, 849m, 733m, 678s; δ_H(300 MHz)

1.05 (21H, br s, Si(C*H*(C*H*$_3$)$_2$)$_3$), 1.80-1.98 (2H, stack, C*H*$_2$), 3.15-3.49 (3H, br, 3 × O*H*), 3.89-3.98 (1H, m, 1 × C*H*OH), 4.12-4.20 (1H, m, 1 × C*H*OH), 4.64 (1H, dd, *J* 7.7, 5.5, 1 × C*H*OH), 5.25 (1H, d, *J* 10.8, =CH_{cis}H$_{trans}$), 5.34 (1H, d, *J* 17.3, =CH$_{cis}$$H_{trans}$), 5.86 (1H, ddd, *J* 17.3, 10.8, 6.1, 2-*H*); δ_C(75 MHz) 10.7 (CH, Si(*C*H(CH$_3$)$_2$)$_3$), 18.1 (CH$_3$, Si(CH(*C*H$_3$)$_2$)$_3$), 38.7 (CH$_2$, *C*-5), 61.8 (CH, 1 × *C*HOH), 73.2 (CH, 1 × *C*HOH), 75.6 (CH, 1 × *C*HOH), 86.1 (quat. C, 1 × C≡C), 108. 1 (quat. C, 1 × C≡C), 117.7 (CH$_2$, =*C*H$_2$), 136.4 (CH, *C*H=CH$_2$); *m/z* (TOF ES+) 335.1 ([M+Na]$^+$, 100 %); HRMS *m/z* (TOF ES+) 335.2020 ([M+Na]$^+$. C$_{17}$H$_{32}$NaO$_3$Si requires 335.2018).

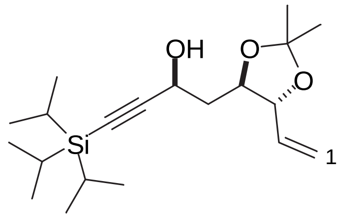
Acetonide protection of triol 9d (and trace 10d): 1-(2,2-dimethyl-5-vinyl-[1,3]dioxolan-4-yl)-4-triisopropylsilanyl-but-3-yn-2-ol 11d and 1-{2,2-dimethyl-6-[(triisopropylsilanyl)-ethynyl]-[1,3]dioxan-4-yl}-prop-2-en-1-ol 12d and 1-(2,2-dimethyl-5-vinyl-[1,3]dioxolan-4-yl)-4-triisopropylsilanyl-but-3-yn-2-ol 13d



11d



12d



13d

C$_{20}$H$_{36}$O$_3$Si
Exact Mass: 352.24337
Mol. Wt.: 352.58354
C, 68.13; H, 10.29; O, 13.61; Si, 7.97 %

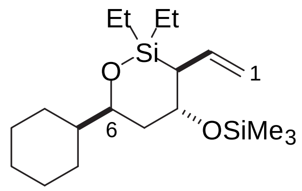
Na$_2$SO$_4$ (40 mg) and *p*TsOH•H$_2$O (2 mg, 16 μmol) were added to a solution of *triol* **9d** (30 mg, 0.10 mmol) in acetone (1.0 mL) and the resulting mixture was stirred overnight. Aqueous work-up afforded *acetonides* **11d**, **12d** and **13d** as a colorless oil and an inseparable mixture (~90% **11d** by ^{1}H NMR) (35 mg, quantitative); due to resonance overlaps and the small relative proportions of **12d** and **13d**, only resonances for **11d** could be completely assigned in the ^{1}H NMR spectrum; δ_H(C$_6$D$_6$, 300 MHz for **11d**) 1.23 (21H, s, Si(C*H*(C*H*$_3$)$_2$)$_3$), 1.37 (3H, s, 1 × C(C*H*$_3$)$_2$), 1.51 (3H, s, 1 × C(C*H*$_3$)$_2$), 1.80 (1H, ddd, *J* 13.7, 7.8, 2.6, 5-H_aH$_b$), 2.02-2.17 (1H, m, 5-H$_a$$H_b$), 2.42-2.70 (1H, br, O*H*), 4.42-4.53 (2H, stack, 3-*H*, 4-*H*), 4.73 (1H, dd, *J* 7.8, 6.6, 6-*H*), 5.05 (1H, dd, *J* 10.4, 1.3, 1-H_{cis}), 5.21 (1H, d, *J* 16.9, 1-H_{trans}), 5.70 (1H, ddd, *J* 16.9, 10.3, 2.6, 2-*H*); δ_C(C$_6$D$_6$, 75 MHz; those resonances that are not specifically assigned belong to either **12d** or **13d**) 10.6 (CH, Si(*C*H(CH$_3$)$_2$)$_3$), 10.8 (CH, Si(*C*H(CH$_3$)$_2$)$_3$ **11d**), 11.2 (CH, Si(*C*H(CH$_3$)$_2$)$_3$), 18.21 (CH$_3$, Si(CH(*C*H$_3$)$_2$)$_3$), 18.24 (CH$_3$, Si(CH(*C*H$_3$)$_2$)$_3$ **11d**), 18.4 (CH$_3$, Si(CH(*C*H$_3$)$_2$)$_3$), 18.8 (CH$_3$, (*C*H$_3$)$_{pseudoax.}$ **12d**), 25.0 (CH$_3$, (*C*H$_3$)$_{pseudoax.}$ **11d**), 26.5 (CH$_3$, 1 × *C*H$_3$ **13d**), 26.8 (CH$_3$, 1 × *C*H$_3$ **13d**), 27.7 (CH$_3$, (*C*H$_3$)$_{pseudoeq.}$ **11d**), 29.5 (CH$_3$, (*C*H$_3$)$_{pseudoeq.}$ **12d**), 38.9 (CH$_2$, *C*-5 **11d**), 39.8 (CH$_2$, 1 × *C*-5), 60.6 (CH, 1 × CH), 61.0 (CH, 1 × CH), 61.4 (CH, 1 × CH **11d**), 71.7 (CH, 1 ×

CH), 73.9 (CH, 1 × CH), 76.1 (CH, 1 × CH **11d**), 78.5 (CH, 1 × CH), 79.5 (CH, 1 × CH **11d**), 82.5 (CH, 1 × CH), 84.8 (quat. C, 1 × SiC≡C), 85.1 (quat. C, 1 × SiC≡C **11d**), 85.2 (quat. C, 1 × SiC≡C), 99.1 (quat. C, $C(CH_3)_2$ **12d**), 107.5 (quat. C, $C(CH_3)_2$ **13d**), 108.7 (quat. C, $C(CH_3)_2$ **11d**), 109.1 (quat. C, 1 × SiC≡C), 109.5 (quat. C, 1 × SiC≡C), 109.6 (quat. C, 1 × SiC≡C **11d**), 116.2 (CH_2, 1 × *C*-1), 117.7 (CH_2, *C*-1 **11d**), 118.1 (CH_2, 1 × *C*-1), 135.0 (CH, C-2 **11d**), 135.7 (CH, 1 × *C*-2), 136.6 (CH, 1 × *C*-2).

Allylation reaction of Aldehyde 6e:

TMSOTf (324 µL, 1.8 mmol) was added to a solution of *aldehyde* **6e** (607 mg, 1.8 mmol) and 2,6-DTBMP (443 mg, 2.2 mmol) in CH_2Cl_2 (18 mL) at –78 °C and the reaction mixture was stirred for 8 h. Aqueous work-up and removal of the solvent afforded compounds **7e** and **8e** (69:14; inseparable mixture) as a yellow liquid (1.003 g, 83%, remaining mass being diene products). This was used in the following step without any further purification. Samples of compounds **7e** and **8e** were obtained as colorless oils by preparative HPLC (5% H_2O in MeCN); **7e** t_R = 74.9 min (contaminated with residual diene **5e**) and **8e** t_R = 85.2 min.

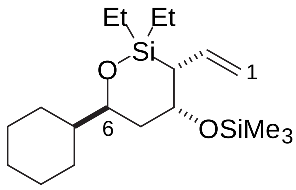
(3*S, 4*R**, 6*S**) oxasilinane 7e**



$C_{19}H_{38}O_2Si_2$
Exact Mass: 354.24103
Mol. Wt.: 354.67482
C, 64.34; H, 10.80; O, 9.02; Si, 15.84%

HPLC: t_R = 74.9 min; ν_{max}(film)/cm^{-1} 3075w, 2954s, 2926s, 2876s, 2853s, 1626m (C=C), 1450m, 1414m, 1378w, 1347w, 1306w, 1251s, 1152m, 1002s, 969m, 939m, 896m, 872m, 841s, 810w, 749m, 724m, 685w; δ_H(300 MHz) 0.10 (9H, s, $Si(CH_3)_3$), 0.44-0.86 (4H, stack, $OSi(CH_2CH_3)_2$), 0.85-1.42 (12H, stack including [0.92 (3H, t, *J* 7.7, $OSi(CH_2CH_3)$), 0.97 (3H, t, *J* 7.7, $OSi(CH_2CH_3)$)], $OSi(CH_2CH_3)_2$, 6 × cyclohexyl*H*), 1.51-2.01 (8H, stack, 5-CH_2, 3-*H*, 5 × cyclohexyl*H*), 3.78 (1H, app. td, *J* 7.7, 3.1, C*H*(OSi)), 4.07 (1H, app. td, *J* 6.6, 2.2, C*H*(OSi)), 4.90 (1H, d, *J* 11.4, 1-H_{cis}), 4.91 (1H, d, *J* 15.8, 1-H_{trans}), 5.67-5.83 (1H, m, 2-*H*); δ_C (75 MHz) 0.2 (CH_3, $Si(CH_3)_3$), 5.2 (CH_2, $Si(CH_2CH_3)$), 5.5 (CH_2, $Si(CH_2CH_3)$), 6.3 (CH_3, $Si(CH_2CH_3)$), 6.6 (CH_3, $Si(CH_2CH_3)$), 26.1 (CH_2, cyclohexylCH_2), 26.3 (CH_2, cyclohexylCH_2), 26.6 (CH_2, cyclohexylCH_2), 29.1 (CH_2, 2 × cyclohexylCH_2), 36.7 (CH_2, *C*-5), 39.7 (CH, *C*-3), 43.8 (CH, *C*-7), 71.0 (CH, *C*H(OSi)), 73.3 (CH, *C*H(OSi)), 113.4 (CH_2, *C*-1), 137.6 (CH, *C*-2); *m/z* (TOF ES+) 377.3 ([M+Na]$^+$, 100 %); HRMS *m/z* (TOF ES+) 377.2312 ([M+Na]$^+$. $C_{19}H_{38}NaO_2Si_2$ requires 377.2308).

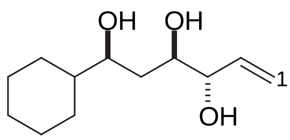
(3*R, 4*R**, 6*S**) oxasilinane 8e**



$C_{19}H_{38}O_2Si_2$
Exact Mass: 354.24103
Mol. Wt.: 354.67482
C, 64.34; H, 10.80; O, 9.02; Si, 15.84%

HPLC: t_R = 85.2 min; ν_{max}(film)/cm^{-1} 3075w, 2955s, 2927s, 2875m, 2854m, 1626w, 1451m, 1416w, 1378w, 1349w, 1325w, 1302w, 1273w, 1251m, 1205w, 1170w, 1132m, 1103m, 1082m, 1058m, 1047m, 1003m, 963m, 921w, 898m, 865m, 841s, 815m, 794w, 772w, 722m, 665m; δ_H(400 MHz) 0.10 (9H, s, Si(CH_3)$_3$), 0.47-0.86 (4H, stack, OSi(C*H*$_2$CH$_3$)$_2$), 0.91-1.42 (13H, stack including [0.94 (3H, t, *J* 7.9, OSi(CH$_2$C*H*$_3$)), 0.97 (3H, t, *J* 7.9, OSi(CH$_2$C*H*$_3$)), 1.35-1.41 (1H, m, 5-$H_{pseudoax.}$)], OSi(CH$_2$C*H*$_3$)$_2$, 5-$H_{pseudoax.}$, 6 × cyclohexyl*H*), 1.61-1.85 (7H, stack including [1.83 (1H, dd, *J* 9.9, 2.6, 3-*H*)], 5-$H_{pseudoeq.}$, 3-*H*, 5 × cyclohexyl*H*), 3.91 (1H, dd, *J* 10.2, 5.6, 6-*H*), 4.22-4.28 (1H, m, 4-*H*), 4.84 (1H, d, *J* 10.4, 1-H_{cis}), 4.87 (1H, d, *J* 17.5, 1-H_{trans}), 5.87 (1H, app. dt, *J* 17.5, 10.2, 2-*H*); δ_C (100 MHz) 0.2 (CH$_3$, Si(*C*H$_3$)$_3$), 4.8 (CH$_2$, OSi(*C*H$_2$CH$_3$)), 5.4 (CH$_2$, OSi(*C*H$_2$CH$_3$)), 6.60 (CH$_3$, OSi(CH$_2$*C*H$_3$)), 6.63 (CH$_3$, OSi(CH$_2$*C*H$_3$)), [26.4, 26.8, 28.5, 28.7 (CH$_2$, cyclohexyl*C*H$_2$, some overlap), 38.7 (CH$_2$, *C*-5), 38.8 (CH, *C*-3), 44.3 (CH, *C*-7), 70.9 (CH, *C*-6), 71.6 (CH, *C*-4), 112.3 (CH$_2$, *C*-1), 138.4 (CH, *C*-2); *m/z* (TOF ES+) 377.3 ([M+Na]$^+$, 100 %); HRMS *m/z* (TOF ES+) 377.2299 ([M+Na]$^+$. $C_{19}H_{38}NaO_2Si_2$ requires 377.2308).

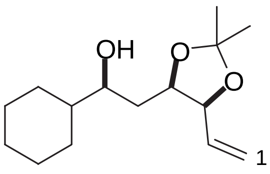
(1*S, 3*R**, 4*S**) 1-Cyclohexyl-hex-5-ene-1,3,4-triol 9e**



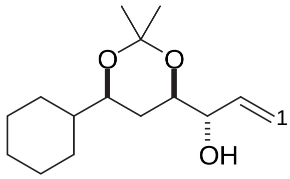
$C_{12}H_{22}O_3$
Exact Mass: 214.15689
Mol. Wt.: 214.30128
C, 67.26; H, 10.35; O, 22.40%

H_2O_2 (1.133 g, 60% in H_2O, 20.00 mmol), $KHCO_3$ (300 mg, 3.00 mmol) and KF (291 mg, 5.00 mmol) were added to a solution of the products from the allylation of *aldehyde* **6e** (663 mg, 0.72 mmol of *oxasilinane* **7e**) in MeOH:THF (1:1, 10 mL) and the resulting mixture was stirred for 5 days. Aqueous work-up and purification by flash column chromatography (50 $\rightarrow$ 70% EtOAc in hexane) afforded *triol* **9e** as a colorless viscous oil (78 mg, 51%); R_f = 0.30 (50% EtOAc in hexane); ν_{max}(film)/cm^{-1} 3368br s (OH), 2926s, 2852s, 1645w (C=C), 1450s, 1318m, 1180m, 1065m, 994m, 926m, 893m, 847m; δ_H(300 MHz) 0.80-1.84 (13H, stack, 3-CH_2, 11 $\times$ cyclohexyl*H*), 2.90-3.78 (4H, stack including [3.58-3.67 (1H, m, 1 $\times$ C*H*OH)], 1 $\times$ C*H*OH, 3 $\times$ O*H*), 3.88 (1H, app. dt, *J* 9.7, 3.1, 1 $\times$ C*H*OH), 4.12 (1H, app. t, *J* 4.6, 1 $\times$ C*H*OH), 5.23 (1H, d, *J* 10.7, =CH_{cis}H$_{trans}$), 5.32 (1H, d, *J* 17.2, =CH$_{cis}$$H_{trans}$), 5.87 (1H, ddd, *J* 17.2, 10.7, 6.3, C*H*=CH_2); δ_C(75 MHz) 26.1 (CH_2), 26.2 (CH_2), 26.5 (CH_2), 27.8 (CH_2), 28.8 (CH_2), 33.7 (CH_2, *C*-2), 44.4 (CH, cyclohexyl*C*H), 75.2 (CH, 1 $\times$ *C*HOH), 75.7 (CH, 1 $\times$ *C*HOH), 76.8 (CH, 1 $\times$ *C*HOH), 117.2 (CH_2, =CH_2), 136.3 (CH, *C*H=CH_2); *m/z* (TOF ES+) 237.2 ([M+Na]$^+$, 100%). HRMS *m/z* (TOF ES+) 237.1460 ([M+Na]$^+$. $C_{12}H_{22}NaO_3$ requires 237.1467).

Acetonide protection of Triol 9e: 1-cyclohexyl-2-(2,2-dimethyl-5-vinyl-[1,3]dioxolan-4-yl)-ethanol 11e and 1-(6-cyclohexyl-2,2-dimethyl-[1,3]dioxan-4-yl)-prop-2-en-1-ol 12e



11e



12e

$C_{15}H_{26}O_3$
Exact Mass: 254.18820
Mol. Wt.: 254.36514
C, 70.83; H, 10.30; O, 18.87 %

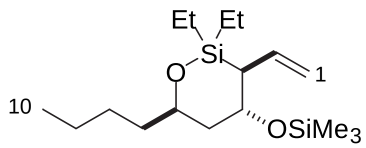
Na_2SO_4 (40 mg) and *p*TsOH•H_2O (2 mg, 16 μmol) were added to a solution of *triol* **9e** (30 mg, 0.14 mmol) in acetone (1.4 mL) and the resulting mixture was stirred overnight. Aqueous work-up afforded *acetonides* **11e** and **12e** as a colorless oil and an inseparable mixture (40:60 **11e**:**12e** by ^{1}H NMR) (36 mg, quantitative); Data reported on the mixture of **11e** and **12e**: δ_H(300 MHz) 0.80-2.09 (38H, stack including [1.21 (3H, s, 1 $\times$ CH_3), 1.26 (3H, s, 1 $\times$ CH_3), 1.40 (3H, s, 1 $\times$ CH_3), 1.46 (3H, s, 1 $\times$ CH_3)], 4 $\times$ CH_3, 22 $\times$ cyclohexyl*H*, 2 $\times$ 5-H_2), 3.27-3.37 (1H, m), 3.51-3.59 (1H, m), 3.60-3.70 (1H, m), 4.00-4.09 (1H, m), 4.13-4.21 (1H, m), 4.29 (1H, t, *J* 6.4), 5.01 (1H, d, *J* 10.3, 1-H_{cis} **11e**), 5.13 (1H, d, *J* 10.3, 1-H_{cis} **12e**), 5.15 (1H, d, *J* 17.5, 1-H_{trans} **11e**), 5.44 (1H, d, *J* 16.8, 1-H_{trans} **12e**), 5.66 (1H, ddd, *J* 17.5, 10.3, 7.0, 2-*H* **11e**), 5.84 (1H, ddd, *J* 16.8, 10.3, 5.0, 2-*H* **12e**), OH resonances not observed; δ_C(100 MHz) 19.9 (CH_3, 1 $\times$ CH_3 **12e**), 25.6 (CH_3, 1 $\times$ CH_3 **11e**), 26.4 (CH_2), 26.5 (CH_2), 26.7 (CH_2), 26.8 (CH_2), 27.01 (CH_2), 27.8 (CH_2), 28.1 (CH_3, 1 $\times$ CH_3 **11e**), 28.2 (CH_2), 28.4 (CH_2), 28.9 (CH_2), 29.5

(CH_2), 30.2 (CH_2), 30.3 (CH_3, 1 × C*H_3* **12e**), 34.8 (CH_2), 43.3 (CH, 1 × cyclohexyl*C*H), 44.4 (CH, 1 × cyclohexyl*C*H), 72.5 (CH, 1 × CH(O)), 73.0 (CH, 1 × CH(O)), 74.5 (CH, 1 × CH(O)), 75.5 (CH, 1 × CH(O)), 79.1 (CH, 1 × CH(O)), 80.0 (CH, 1 × CH(O)), 98.5 (quat. C, *C*(CH_3)$_2$ **12e**), 108.4 (quat. C, *C*(CH_3)$_2$ **11e**), 115.8 (CH_2, 1 × *C*-1), 117.6 (CH_2, 1 × *C*-1), 134.9 (CH, 1 × *C*-2), 136.9 (CH, 1 × *C*-2).

Allylation reaction of Aldehyde 6f:

TMSOTf (202 µL, 1.12 mmol) was added to a solution of *aldehyde* **6f** (369 mg, 1.12 mmol) and 2,6-DTBMP (277 mg, 1.35 mmol) in CH_2Cl_2 (12 mL) at –78 °C and the reaction mixture was stirred for 8 h. Aqueous work-up and removal of the solvent afforded compounds **7f** and **8f** (68:8; inseparable mixture) as a colorless liquid (630 mg, 76%, remaining mass being diene products). This was used in the following step without any further purification. Analytically pure samples of each compound were obtained as colorless oils by preparative HPLC (t = 0 → 40 min, 50 → 100% MeCN in H_2O); **7f** t_R = 66.9 min and **8f** t_R = 69.0 min.

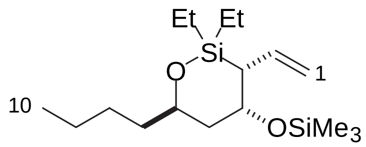
(3*S, 4*R**, 6*R**) oxasilinane 7f**



$C_{17}H_{36}O_2Si_2$
Exact Mass: 328.22538
Mol. Wt.: 328.63754
C, 62.13; H, 11.04; O, 9.74; Si, 17.09%

HPLC: t_R = 66.9 min; ν_{max}(film)/cm^{-1} 2957s, 2876s, 1628m (C=C), 1462m, 1378w, 1252s, 1152m, 1115m, 1067s, 998m, 946w, 871w, 841s, 748w, 725m; δ_H(400 MHz) 0.09 (9H, s, Si(C*H_3*)$_3$), 0.58 (2H, q, *J* 7.8, OSi(C*H_2*CH_3)), 0.65-0.80 (2H, m, OSi(C*H_2*CH_3)), 0.90 (3H, t, *J* 7.0, 10-C*H_3*), 0.91 (3H, t, *J* 7.9, OSi(CH_2C*H_3*)), 0.96 (3H, t, *J* 7.8, OSi(CH_2C*H_3*)), 1.23-1.45 (5H, stack, 9-C*H_2*, 8-C*H_2*, 7-C*H_a*H_b), 1.49-1.56 (1H, m, 7-CH_a*H_b*), 1.61 (1H, ddd, *J* 14.1, 7.6, 3.7, 5-C*H_a*H_b), 1.70 (1H, ddd, *J* 14.1, 6.8, 2.8, 5-CH_a*H_b*), 1.88 (1H, dd, *J* 10.4, 6.9, 3-*H*), 4.03-4.11 (2H, stack, 4-*H*, 6-*H*), 4.88-4.94 (2H, stack, 1-C*H_2*), 5.71 (1H, dt, *J* 16.5, 10.4, 2-*H*); δ_C(100 MHz) 0.1 (CH_3, Si(CH_3)$_3$), 5.2 (CH_2, OSi(*C*$H_2$$CH_3$)), 5.4 ($CH_2$, OSi(*C*$H_2$$CH_3$)), 6.3 ($CH_3$, OSi($CH_2$*C*$H_3$)), 6.5 ($CH_3$, OSi($CH_2$*C*$H_3$)), 14.1 ($CH_3$, *C*-10), 22.6 ($CH_2$), 28.2 ($CH_2$), 37.3 ($CH_2$), 40.1 (CH, *C*-3), 40.4 (CH_2), 69.8 (CH, *C*H(O)), 70.4 (CH, *C*H(O)), 113.5 (CH_2, *C*-1), 137.5 (CH, *C*-2); *m/z* (TOF ES+) 351.3 ([M+Na]$^+$, 100 %); HRMS *m/z* (TOF ES+) 351.2151 ([M+Na]$^+$. $C_{17}H_{36}NaO_2Si_2$ requires 351.2152).

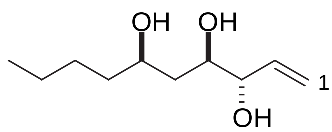
(3R*, 4R*, 6R*) oxasilinane 8f



$C_{17}H_{36}O_2Si_2$
Exact Mass: 328.22538
Mol. Wt.: 328.63754
C, 62.13; H, 11.04; O, 9.74; Si, 17.09%

HPLC: t_R = 69.0 min; ν_{max}(film)/cm^{-1} 2957s, 1626w (C=C), 1456m, 1252m, 1057m, 963w, 897w, 841m, 725w; δ_H(400 MHz) 0.10 (9H, s, Si(CH_3)$_3$), 0.48-0.84 (4H, stack, OSi(CH_2CH$_3$)$_2$), 0.89 (3H, t, J 7.0, 10-CH_3), 0.95 (3H, t, J 7.8, OSi(CH$_2$CH_3)), 0.96 (3H, t, J 7.8, OSi(CH$_2$CH_3)), 1.23-1.41 (6H, stack, 9-CH_2, 8-CH_2, 7-CH_aH$_b$, 5-$H_{pseudoax.}$), 1.43-1.49 (1H, m, 7-CH$_a$$H_b$), 1.65 (1H, ddd, J 13.9, 4.9, 1.7, 5-$H_{pseudoeq.}$), 1.83 (1H, dd, J 10.2, 2.8, 3-H), 4.08-4.16 (1H, m, 6-H), 4.19-4.23 (1H, m, 4-H), 4.84 (1H, dd, J 10.2, 2.2, 1-H_{cis}), 4.88 (1H, dd, J 17.1, 2.2, 1-H_{trans}), 5.88 (1H, dt, J 17.1, 10.2, 2-H); δ_C(100 MHz) 0.2 (CH$_3$, Si(CH$_3$)$_3$), 6.6 (2 × CH$_3$, 2 × CH$_2$, OSi(CH$_2$$CH_3$)$_2$), 14.1 (CH$_3$, C-10), 22.7 (CH$_2$), 27.6 (CH$_2$), 38.0 (CH$_2$), 38.8 (CH, C-3), 42.3 (CH$_2$), 67.0 (CH, CH(O)), 71.6 (CH, CH(O)), 112.5 (CH$_2$, C-1), 138.3 (CH, C-2); m/z (TOF ES+) 351.3 ([M+Na]$^+$, 100 %); HRMS m/z (TOF ES+) 351.2151 ([M+Na]$^+$. $C_{17}H_{36}NaO_2Si_2$ requires 351.2152).

(3S*, 4R*, 6R*) Dec-1-ene-3,4,6-triol 9f

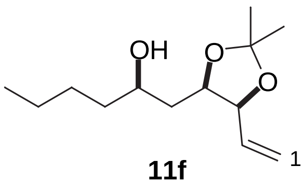


$C_{10}H_{20}O_3$
Exact Mass: 188.14125
Mol. Wt.: 188.26400
C, 63.80; H, 10.71; O, 25.50%

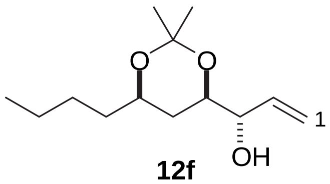
H_2O_2 (1.207 g, 60% in H_2O, 21.30 mmol), $KHCO_3$ (320 mg, 3.20 mmol) and KF (309 mg, 5.32 mmol) were added to a solution of the products from the allylation of *aldehyde* **6f** (663 mg, 0.72 mmol of *oxasilinane* **7f**) in MeOH:THF (1:1, 11 mL) and the resulting mixture was stirred for 5 days. Aqueous work-up and purification by flash column chromatography (70 → 90% EtOAc in hexane) afforded *triol* **9f** as a colorless viscous oil (89 mg, 65%); R$_f$ = 0.30 (70% EtOAc in hexane); ν_{max}(film)/cm^{-1} 3368br s

(OH), 2956s, 2930s, 2861s, 1645w (C=C), 1431s, 1379m, 1318m, 1189m, 1126s, 1054s, 995s, 925s, 847m, 731m; δ_H(300 MHz) 0.86 (3H, t, *J* 6.8, C*H*$_3$), 1.20-1.65 (8H, stack, 4 × C*H*$_2$), 3.15-3.92 (4H, stack including [3.77-3.84 (1H, m, C*H*OH), 3.88 (1H, dt, *J* 9.6, 3.1, C*H*OH)], 2 × O*H*, 2 × C*H*OH), 4.07-4.22 (2H, stack including [4.10 (1H, app. t, *J* 5.9, C*H*OH)], C*H*OH, O*H*), 5.23 (1H, d, *J* 10.3, =CH*H*$_{cis}$), 5.31 (1H, *J* 17.3, =CH*H*$_{trans}$), 5.86 (1H, ddd, 17.3, 10.3, 5.9, C*H*=CH$_2$); δ_C(75 MHz) 13.6 (CH$_3$, *C*-10), 22.3 (CH$_2$), 27.2 (CH$_2$), 36.7 (CH$_2$), 37.6 (CH$_2$), 72.3 (CH, *C*HOH), 74.9 (CH, *C*HOH), 75.7 (CH, *C*HOH), 117.5 (CH$_2$, =*C*H$_2$), 136.6 (CH, *C*H=CH$_2$); *m/z* (CI+) 206 [(M+NH$_4$)$^+$, 100%], 188 (M)$^+$ (26), 148 (10), 172 (8); HRMS *m/z* (CI+) 206.175561 ([M+NH$_4$]$^+$. $C_{10}H_{24}NO_3$ requires 206.175619).

Acetonide protection of triol 9f: 1-(2,2-dimethyl-5-vinyl-[1,3]dioxolan-4-yl)-hexan-2-ol 11f and 1-(6-butyl-2,2-dimethyl-[1,3]dioxan-4-yl)-prop-2-en-1-ol 12f



11f



12f

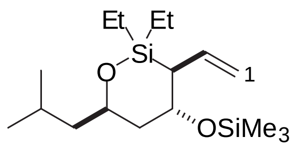
$C_{13}H_{24}O_3$
Exact Mass: 228.17255
Mol. Wt.: 228.32786
C, 68.38; H, 10.59; O, 21.02 %

Na$_2$SO$_4$ (40 mg) and *p*TsOH•H$_2$O (3 mg, 16 μmol) were added to a solution of *triol* **9f** (30 mg, 0.16 mmol) in acetone (1.6 mL) and the resulting mixture was stirred overnight. Aqueous work-up afforded *alcohols* **11f** and **12f** as a colorless oil and an inseparable mixture (1:1 by ^{1}H NMR) (35 mg, quantitative); Data reported on the mixture of **11f** and **12f**: δ_H(C$_6$D$_6$, 300 MHz) 0.82 (3H, t, *J* 7.0, 1 × C*H*$_3$(CH$_2$)$_3$), 0.92 (3H, t, *J* 7.4, 1 × C*H*$_3$(CH$_2$)$_3$), 1.12-1.65 (28H, stack including [1.22 (3H, s, 1 × CC*H*$_3$), 1.27 (3H, s, 1 × CC*H*$_3$), 1.40 (3H, s, 1 × CC*H*$_3$), 1.46 (3H, s, 1 × CC*H*$_3$)], 8 × C*H*$_2$, 2 × C(C*H*$_3$)$_2$), 2.25-2.42 (1H, br s, 1 × O*H*), 2.96 (1H, br s, 1 × O*H*), 3.49-3.60 (1H, m, 1 × *n*BuC*H*), 3.66 (1H, ddd, *J* 11.8, 4.0, 3.0, 1 × C*H*(O)CH(O)CH=CH$_2$), 3.69-3.79 (1H, m, 1 × *n*BuC*H*), 4.06 (1H, ddd, *J* 10.0, 6.2, 2.9, 1 × C*H*(O)CH(O)CH=CH$_2$), 4.16 (1H, app. t, *J* 5.0, 1 × C*H*(O)CH=CH$_2$), 4.30 (1H, app. t, *J* 6.9, 1 × C*H*(O)CH=CH$_2$), 5.01 (1H, d, *J* 10.3, 1 × 1-*H*$_{cis}$), 5.14 (1H, app. dt, *J* 10.3, 1.8, 1 × 1-*H*$_{cis}$), 5.15 (1H, d, *J* 17.3, 1 × 1-*H*$_{trans}$), 5.43 (1H, app. dt, *J* 17.3, 1.8, 1 × 1-*H*$_{trans}$), 5.65 (1H, ddd, *J* 17.3, 10.3, 6.9, 1 × 2-*H*), 5.85 (1H, ddd, *J* 17.3, 10.3, 5.0, 1 × 2-*H*); δ_C(C$_6$D$_6$, 75 MHz) 13.6 (CH$_3$, 1 × *C*H$_3$(CH$_2$)$_3$), 13.7 (CH$_3$, 1 × *C*H$_3$(CH$_2$)$_3$), 19.3 (CH$_3$, 1 × *C*CH$_3$ **12f**), 22.5 (CH$_2$), 22.6 (CH$_2$), 25.1 (CH$_3$, 1 × *C*CH$_3$ **11f**), 27.0 (CH$_2$), 27.5 (CH$_2$), 27.6 (CH$_3$, 1 × *C*CH$_3$ **11f**), 29.8 (CH$_3$, 1 × *C*CH$_3$ **12f**), 30.2 (CH$_2$), 36.2 (CH$_2$), 37.3 (CH$_2$), 37.5 (CH$_2$), 68.5 (CH, 1 × *C*H(O)), 70.9 (CH, 1 × *C*H(O)), 72.1 (CH, 1 × *C*H(O)), 74.1 (CH, 1 × *C*H(O)), 78.4 (CH, 1 × *C*H(O)), 79.7 (CH, 1 × *C*H(O)), 98.5 (quat. C, *C*(CH$_3$)$_2$ **12f**), 108.7 (quat. C, *C*(CH$_3$)$_2$ **11f**), 115.8 (CH$_2$, 1 × *C*-1), 117.5 (CH$_2$, 1 × *C*-1), 135.0 (CH, 1 × *C*-2), 137.1 (CH, 1 × *C*-2).

Allylation reaction of Aldehyde 6g:

TMSOTf (217 µL, 1.20 mmol) was added to a solution of *aldehyde* **6g** (394 mg, 1.20 mmol) and 2,6-DTBMP (296 mg, 1.40 mmol) in CH_2Cl_2 (12 mL) at –78 °C and the reaction mixture was stirred for 8 h. Aqueous work-up and removal of the solvent afforded compounds **7g** and **8 g** (40:15; inseparable mixture) as a yellow liquid (687 mg, 55%, remaining material being diene products). This was used in the following step without any further purification. Analytically pure samples of compounds **7g** and **8g** were obtained as colorless oils by preparative HPLC (t = 0 → t = 40 min, 50 → 100% MeCN in H_2O); **7g** t_R = 66.9 min and **8g** t_R = 76.0 min.

(3*S, 4*R**, 6*R**) oxasilinane 7g**



$C_{17}H_{36}O_2Si_2$

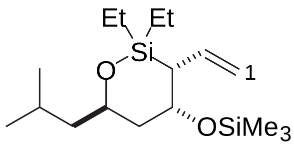
Exact Mass: 328.22538

Mol. Wt.: 328.63754

C, 62.13; H, 11.04; O, 9.74; Si, 17.09%

HPLC: t_R = 66.9 min; ν_{max}(film)/cm^{-1} 3077w, 2956s, 2877s, 1628m (C=C), 1468m, 1415w, 1375m, 1347w, 1330w, 1304w, 1252s, 1154m, 1116m, 1073s, 990m, 959m, 935m, 893m, 867m, 841s, 747m, 724m, 656w, 631m; δ_H(400 MHz) 0.09 (9H, s, Si(C*H*$_3$)$_3$), 0.56 (2H, q, *J* 7.6, OSi(C*H*$_2$CH$_3$)), 0.67-0.78 (2H, m, OSi(C*H*$_2$CH$_3$)), 0.89 (6H, d, *J* 6.6, CH(C*H*$_3$)$_2$), 0.91 (3H, t, *J* 7.8, OSi(CH$_2$C*H*$_3$)), 0.97 (3H, t, *J* 7.8, OSi(CH$_2$C*H*$_3$)), 1.15 (1H, ddd, *J* 13.4, 8.3, 4.9, 7-C*H*$_a$H$_b$), 1.50 (1H, ddd, *J* 13.4, 8.8, 5.6, 7-CH$_a$*H*$_b$), 1.61 (1H, ddd, *J* 13.9, 7.1, 3.7, 5- C*H*$_a$H$_b$), 1.68 (1H, ddd, *J* 13.9, 6.9, 2.8, 5-CH$_a$*H*$_b$), 1.73-1.83 (1H, m, 8-*H*), 1.89 (1H, dd, *J* 10.4, 7.0, 3-*H*), 4.07 (1H, td, *J* 7.0, 2.7, 4-*H*), 4.16-4.22 (1H, m, 6-*H*), 4.86-4.95 (2H, stack, 1-C*H*$_2$), 5.72 (1H, dt, *J* 16.3, 10.5, 2-*H*); δ_C(100 MHz) 0.1 (CH$_3$, Si(*C*H$_3$)$_3$), 5.30 (CH$_2$, OSi(*C*H$_2$CH$_3$)), 5.34 (CH$_2$, OSi(*C*H$_2$CH$_3$)), 6.2 (CH$_3$, OSi(CH$_2$*C*H$_3$)), 6.5 (CH$_3$, OSi(CH$_2$*C*H$_3$)), 22.1 (CH$_3$, *C*-9), 23.1 (CH$_3$, *C*-9'), 24.6 (CH, *C*-8), 39.9 (CH, *C*-3), 40.8 (CH$_2$, *C*-5), 46.8 (CH$_2$, *C*-7), 67.5 (CH, *C*-6), 70.6 (CH, *C*-4), 113.5 (CH$_2$, *C*-1), 137.5 (CH, *C*-2); *m/z* (TOF ES+) 351.1 ([M+Na]$^+$, 100 %); HRMS *m/z* (TOF ES+) 351.2146 ([M+Na]$^+$. $C_{17}H_{36}NaO_2Si_2$ requires 351.2152).

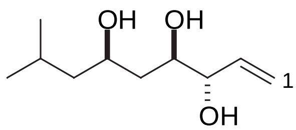
(3*R, 4*R**, 6*R**) oxasilinane 8g**



$C_{17}H_{36}O_2Si_2$
Exact Mass: 328.22538
Mol. Wt.: 328.63754
C, 62.13; H, 11.04; O, 9.74; Si, 17.09%

HPLC: t_R = 76.0 min; ν_{max}(film)/cm^{-1} 3076w, 2957s, 2877m, 1627w (C=C), 1462m, 1416w, 1370w, 1324w, 1252s, 1170w, 1126m, 1084s, 1058s, 1004m, 968m, 938w, 898m, 868m, 841s, 808w, 757m, 723m, 658w; δ_H(500 MHz) 0.09 (9H, s, Si(C*H*$_3$)$_3$), 0.47-0.86 (4H, stack, OSi(C*H*$_2$CH$_3$)$_2$), 0.800 (3H, d, *J* 6.5, 9-C*H*$_3$), 0.805 (3H, d, *J* 6.5, 9'-C*H*$_3$), 0.93 (6H, t, *J* 7.9, OSi(CH$_2$C*H*$_3$)$_2$), 1.10 (1H, ddd, *J* 13.5, 8.3, 4.8, 7-C*H*$_a$H$_b$), 1.35 (1H, dd, *J* 13.8, 11.1, 5-C$H_{pseudoax.}$), 1.43 (1H, ddd, *J* 13.5, 8.2, 5.7, 7-CH$_a$*H*$_b$), 1.62 (1H, ddd, *J* 13.8, 5.0, 1.8, 5-C$H_{pseudoeq.}$), 1.73-1.82 (1H, m, 8-*H*), 1.82 (1H, dd, *J* 10.1, 2.7, 3-*H*), 4.16-4.25 (2H, stack, 4-*H*, 6-*H*), 4.80-4.92 (2H, stack, 1-C*H*$_2$), 5.86 (1H, dt, *J* 17.3, 10.2, 2-*H*); δ_C(125 MHz) 0.2 (CH$_3$, Si(*C*H$_3$)$_3$), 4.8 (CH$_2$, Si(*C*H$_2$CH$_3$)), 5.4 (CH$_2$, OSi(*C*H$_2$CH$_3$)), 6.6 (2 $\times$ CH$_3$, OSi(CH$_2$*C*H$_3$)$_2$), 22.2 (CH$_3$, *C*-9), 23.2 (CH$_3$, *C*-9'), 24.4 (CH, *C*-8), 38.9 (CH, *C*-3), 42.9 (CH$_2$, *C*-5), 47.5 (CH$_2$, *C*-7), 65.0 (CH), 71.6 (CH), 112.4 (CH$_2$, *C*-1), 138.3 (CH, *C*-2); *m/z* (TOF ES+) 351.3 ([M+Na]$^+$, 100 %); HRMS *m/z* (TOF ES+) 351.2154 ([M+Na]$^+$. $C_{17}H_{36}NaO_2Si_2$ requires 351.2152).

(3*S, 4*R**, 6*R**) 8-Methyl-non-1-ene-3,4,6-triol 9g**

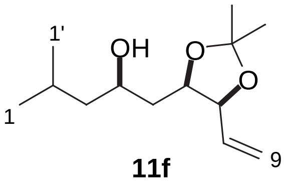


$C_{10}H_{20}O_3$
Exact Mass: 188.14125
Mol. Wt.: 188.26400
C, 63.80; H, 10.71; O, 25.50%

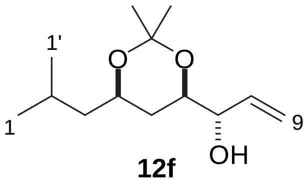
H_2O_2 (1.247 g, 60% in H_2O, 22.00 mmol), $KHCO_3$ (330 mg, 3.30 mmol) and KF (320 mg, 5.50 mmol) were added to a solution of the products from the allylation of *aldehyde* **6g** (684 mg, 0.77 mmol of *oxasilinane* **7g**) in MeOH:THF (1:1, 11 mL) and the resulting mixture was stirred for 5 days. Aqueous work-up and purification by flash column chromatography (70 $\rightarrow$ 90% EtOAc in hexane) afforded *triol* **9g** as a colorless viscous oil (87 mg, 60%); R_f = 0.29 (70% EtOAc in hexane); ν_{max}(film)/cm^{-1} 3315br s

(OH), 2954s, 1645m (C=C), 1469s, 1434s, 1368s, 1311s, 1192m, 1171m, 1147s, 1077s, 995s, 924s, 881m, 852m, 813m, 738s; δ_H(300 MHz) 0.89 (6H, d, *J* 6.6, (C*H*3)$_2$CH), 1.13-1.28 (1H, m, 7-H_aH$_b$), 1.36-1.63 (3H, stack, 7-H$_a$$H_b$, 5-*H*), 1.66-1.80 (1H, m, (CH$_3$)$_2$C*H*), 3.22 (1H, br s, 1 × O*H*), 3.32 (1H, br s, 1 × O*H*), 3.85-4.20 (4H, stack including [3.86-3.95 (2H, stack, 2 × C*H*OH), 4.08-4.15 (1H, m, 1 × C*H*OH)], 1 × O*H*, 3 × C*H*OH), 5.24 (1H, d, *J* 10.7, =CH_{cis}H$_{trans}$), 5.31 (1H, d, *J* 17.3, =CH$_{cis}$$H_{trans}$), 5.86 (1H, ddd, *J* 17.3, 10.7, 6.1, C*H*=CH$_2$); δ_C(75 MHz) 21.8 (CH$_3$, 1 × (*C*H$_3$)$_2$CH), 22.9 (CH$_3$, 1 × (*C*H$_3$)$_2$CH), 23.9 (CH, (CH$_3$)$_2$*C*H), 37.2 (CH$_2$), 47.1 (CH$_2$), 70.4 (CH, 1 × *C*HOH), 74.9 (CH, 1 × *C*HOH), 75.7 (CH, 1 × *C*HOH), 117.5 (CH$_2$, =*C*H$_2$), 136.6 (CH, =*C*H); *m/z* (CI+) 206 [(M+NH$_4$)$^+$, 100%], 188 (M)$^+$ (19), 153 (6); HRMS *m/z* (CI+) 206.175418 ([M+NH$_4$]$^+$. $C_{10}H_{24}NO_3$ requires 206.175619).

Acetonide protection of triol 9g: 1-(2,2-dimethyl-5-vinyl-[1,3]dioxolan-4-yl)-4-methyl-pentan-2-ol 11g and 1-(6-isobutyl-2,2-dimethyl-[1,3]dioxan-4-yl)-prop-2-en-1-ol 12g



11f



12f

$C_{13}H_{24}O_3$
Exact Mass: 228.17255
Mol. Wt.: 228.32786
C, 68.38; H, 10.59; O, 21.02 %

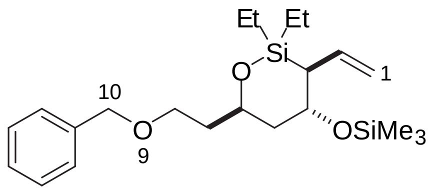
Na$_2$SO$_4$ (40 mg) and *p*TsOH•H$_2$O (3 mg, 16μmol) were added to a solution of *triol* **9g** (32 mg, 0.17 mmol) in acetone (1.7 mL) and the resulting mixture was stirred overnight. Aqueous work-up afforded *acetonides* **11g** and **12g** as a colorless oil and an inseparable mixture (53:47 by ^{1}H NMR) (36 mg, quantitative); Data reported on the mixture of **11g** and **12g**: δ_H(C$_6$D$_6$, 300 MHz) 0.86 (3H, d, *J* 2.9, 1 × (C*H*3)$_2$CH), 0.89 (3H, d, *J* 2.9, 1 × (C*H*3)$_2$CH), 1.06 (3H, d, *J* 7.0, 1 × (C*H*3)$_2$CH), 1.09 (3H, d, *J* 6.6, 1 × (C*H*3)$_2$CH), 1.09-1.73 (20H, stack including [1.31 (3H, s, 1 × (C*H*3)$_{pseudoax.}$), 1.35 (3H, s, 1 × (C*H*3)$_{pseudoax.}$), 1.50 (3H, s, 1 × (C*H*3)$_{pseudoeq.}$), 1.54 (3H, s, 1 × (C*H*3)$_{pseudoeq.}$)], 2 × 3-H_2, 2 × 5-H_2, 2 × CH(C*H*3)$_2$), 1.90-2.02 (1H, m, 1 × 2-*H*), 2.03-2.18 (1H, m, 1 × 2-*H*), 2.18 (1H, br s, 1 × O*H*), 3.08 (1H, br s, 1 × O*H*), 3.61-3.73 (2H, stack, 1 × 4-*H*, 1 × 6-*H*), 3.85 (1H, tdd, *J* 12.1, 3.7, 2.6, 1 × 4-*H*), 4.03 (1H, ddd, *J* 10.7, 7.0, 2.9, 1 × 6-*H*), 4.15 (1H, app. t, *J* 4.4, 1 × 7-*H*), 4.29 (1H, app. t, *J* 6.6, 1 × 7-*H*), 5.00 (1H, d, *J* 10.3, 1 × 9-H_{cis}), 5.14 (1H, d, *J* 10.3, 1 × 9-H_{cis}), 5.15 (1H, d, *J* 17.6, 1 × 9-H_{trans}), 5.43 (1H, td, *J* 17.3, 1.8, 1 × 9-H_{trans}), 5.63 (1H, ddd, *J* 17.6, 10.3, 5.1, 7.0, 1 × 8-*H*), 5.83 (1H, ddd, *J* 17.3, 10.3, 5.1, 1 × 8-*H*); δ_C(C$_6$D$_6$, 75 MHz) 19.2 (CH$_3$, (*C*H$_3$)$_{pseudoax.}$**12g**), [21.7, 22.9, 23.2, 24.1 (CH and CH$_3$, (*C*H$_3$)$_2$CH **11g**, (*C*H$_3$)$_2$*C*H **12g**), some overlap], 25.0 (CH$_3$, (*C*H$_3$)$_{pseudoax.}$**11g**), 27.6 (CH$_3$, (*C*H$_3$)$_{pseudoeq.}$**11g**), 29.8 (CH$_3$, (*C*H$_3$)$_{pseudoeq.}$**12g**), 30.6 (CH$_2$), 38.1 (CH$_2$), 45.5 (CH$_2$), 47.0 (CH$_2$), 66.4

(CH), 69.0 (CH), 72.1 (CH), 74.1 (CH), 78.4 (CH), 79.7 (CH), 98.4 (quat. C, $(CH_3)_2C$ **12g**), 108.7 (quat. C, $(CH_3)_2C$ **11g**), 115.8 (CH_2, *C*-9), 117.5 (CH_2, *C*-9), 135.0 (CH, *C*-8), 137.0 (CH, *C*-8).

Allylation reaction of Aldehyde 6h:

TMSOTf (145 µL, 0.80 mmol) was added to a solution of *aldehyde* **6h** (325 mg, 0.80 mmol) and 2,6-DTBMP (203 mg, 0.96 mmol) in CH_2Cl_2 (8 mL) at –78 °C and the reaction mixture was stirred for 8 h. Aqueous work-up and removal of the solvent afforded compounds **7h** and **8h** (40:15; inseparable mixture) as a yellow liquid (532 mg, 55%, remaining material being diene products). This was used in the following step without any further purification. Analytically pure samples of compounds **7h** and **8h** were obtained as colorless oils by preparative HPLC (t = 0 → t = 40 min, 50 → 100% MeCN in H_2O); **7h** t_R = 38.6 min and **8h** t_R = 48.7 min.

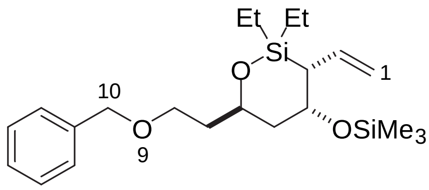
(3*S, 4*R**, 6*R**) oxasilinane 7h**



$C_{22}H_{38}O_3Si_2$
Exact Mass: 406.23595
Mol. Wt.: 406.70632
C, 64.97; H, 9.42; O, 11.80; Si, 13.81%

HPLC: t_R = 38.6 min; ν_{max}(film)/cm^{-1} 3074w, 3031w, 2954s, 2915m, 2876m, 1805w, 1627w (C=C), 1496w, 1455m, 1414w, 1363w, 1251s, 1204w, 1152m, 1114s, 1075s, 1028m, 996m, 933m, 873m, 840s, 745m, 733m, 697m; δ_H(500 MHz) 0.10 (9H, s, Si(C*H*$_3$)$_3$), 0.56 (2H, q, *J* 7.9, OSi(C*H*$_2$CH$_3$)), 0.66-0.80 (2H, m, OSi(C*H*$_2$CH$_3$)), 0.91 (3H, t, *J* 7.9, OSi(CH$_2$C*H*$_3$)), 0.98 (3H, t, *J* 7.9, OSi(CH$_2$C*H*$_3$)), 1.65 (1H, ddd, *J* 13.8, 7.0, 3.5, 5-C*H*$_a$H$_b$), 1.71-1.86 (3H, stack, 5-CH$_a$*H*$_b$, 7-C*H*$_2$), 1.88 (1H, dd, *J* 10.3, 6.7, 3-*H*), 3.59-3.64 (2H, m, 8-C*H*$_2$), 4.08 (1H, app. td, *J* 6.8, 2.2, 4-*H*), 4.27-4.33 (1H, m, 6-*H*), 4.50 (1H, A of AB, *J* 12.1, PhC*H*$_A$H$_B$), 4.52 (1H, B of AB, *J* 12.1, PhCH$_A$*H*$_B$), 4.92 (1H, d, *J* 11.3, 1-*H*$_{cis}$), 4.93 (1H, d, *J* 16.0, 1-*H*$_{trans}$), 5.68-5.77 (1H, m, 2-*H*), 7.26-7.36 (5H, stack, Ph*H*); δ_C(125 MHz) 0.12 (CH$_3$, Si(*C*H$_3$)$_3$), 5.3 (CH$_2$, OSi(*C*H$_2$CH$_3$)), 5.4 (CH$_2$, OSi(*C*H$_2$CH$_3$)), 6.3 (CH$_3$, OSi(CH$_2$*C*H$_3$)), 6.5 (CH$_3$, OSi(CH$_2$CH$_3$)), 37.9 (CH$_2$, *C*-7), 39.8 (CH, *C*-3), 40.6 (CH$_2$, *C*-5), 66.7 (CH, *C*-6), 67.4 (CH$_2$, *C*-8), 70.5 (CH, *C*-4), 73.1 (CH$_2$, Ph*C*H$_2$), 113.7 (CH$_2$, *C*-1), 127.5 (CH, Ph), 127.6 (CH, Ph), 128.3 (CH, Ph), 137.4 (CH, *C*-2), 138.6 (quat. C, *ipso*Ph); *m/z* (TOF ES+) 429.1 ([M+Na]$^+$, 100 %); HRMS *m/z* (TOF ES+) 429.2277 ([M+Na]$^+$. $C_{22}H_{38}NaO_3Si_2$ requires 429.2257).

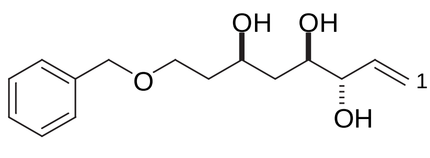
(3*R, 4*R**, 6*R**) oxasilinane 8h**



$C_{22}H_{38}O_3Si_2$
Exact Mass: 406.23595
Mol. Wt.: 406.70632
C, 64.97; H, 9.42; O, 11.80; Si, 13.81%

HPLC: t_R = 48.7 min; ν_{max}(film)/cm^{-1} 3073w, 3031w, 3044w, 2955s, 2914m, 2875s, 1626w (C=C), 1416w, 1363w, 1316w, 1251s, 1204w, 1170w, 1112m, 1080s, 1054s, 1028m, 1003m, 962m, 897w, 879w, 860m, 841s, 807w, 731m, 696m; δ_H(400 MHz) 0.10 (9H, s, Si(C*H*$_3$)$_3$), 0.45-0.59 (2H, m, OSi(C*H*$_2$CH$_3$)), 0.53-0.90 (2H, m, OSi(C*H*$_2$CH$_3$)), 0.95 (3H, t, *J* 7.8, OSi(CH$_2$C*H*$_3$)), 0.96 (3H, t, *J* 7.9, OSi(CH$_2$C*H*$_3$)), 1.44 (1H, ddd, *J* 14.0, 11.2, 1.2, 5-$H_{pseudoax.}$), 1.66 (1H, ddd, *J* 14.0, 4.9, 2.0, 5-$H_{pseudoeq.}$), 1.71-1.77 (2H, stack, 7-C*H*$_2$), 1.84 (1H, dd, *J* 10.0, 2.9, 3-*H*), 3.63 (2H, t, *J* 6.7, 8-C*H*$_2$), 4.19-4.25 (1H, m, 4-*H*), 4.30-4.38 (1H, m, 6-*H*), 4.50 (2H, s, PhC*H*$_2$), 4.85 (1H, dd, *J* 10.2, 2.2, 1-H_{cis}), 4.89 (1H, dd, *J* 17.3, 1.5, 1-H_{trans}), 5.88 (1H, app. dt, *J* 17.3, 10.1, 2-*H*), 7.26-7.36 (5H, stack, Ph*H*); δ_C(100 MHz) 0.12 (CH$_3$, Si(*C*H$_3$)$_3$), 4.8 (CH$_2$, OSi(*C*H$_2$CH$_3$)), 5.4 (CH$_2$, OSi(*C*H$_2$CH$_3$)), 6.6 (2 $\times$ CH$_3$, OSi(CH$_2$*C*H$_3$)$_2$), 38.3 (CH$_2$, *C*-7), 38.7 (CH, *C*-3), 42.7 (CH$_2$, *C*-5), 64.4 (CH, *C*-6), 67.3 (CH$_2$, *C*-8), 71.5 (CH, *C*-4), 73.0 (CH$_2$, Ph*C*H$_2$), 112.5 (CH$_2$, *C*-1), 127.4 (CH, Ph), 127.5 (CH, Ph), 128.3 (CH, Ph), 138.2 (CH, *C*-2), 138.8 (quat. C, *ipso*Ph); *m/z* (TOF ES+) 429.2 ([M+Na]$^+$, 100 %); HRMS *m/z* (TOF ES+) 429.2273 ([M+Na]$^+$. $C_{22}H_{38}NaO_3Si_2$ requires 429.2257).

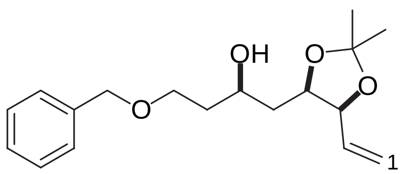
(3*S, 4*R**, 6*R**) 8-Benzyloxy-oct-1-ene-3,4,6-triol 9h**



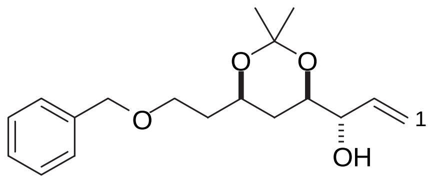
$C_{15}H_{22}O_4$
Exact Mass: 266.15181
Mol. Wt.: 266.33278
C, 67.64; H, 8.33; O, 24.03%

H_2O_2 (623 mg, 60% in H_2O, 11.0 mmol), $KHCO_3$ (165 mg, 1.65 mmol) and KF (160 mg, 2.75 mmol) were added to a solution of the products from the allylation of *aldehyde* **6h** (356 mg, 0.37 mmol of *oxasilinane* **7h**) in MeOH:THF (1:1, 8 mL) and the resulting mixture was stirred for 5 days. Aqueous work-up and purification by flash column chromatography (70 → 90% EtOAc in hexane) afforded *triol* **9h** as a colorless viscous oil (92 mg, 63%); R_f = 0.28 (80% EtOAc in hexane); ν_{max}(film)/cm^{-1} 3392s br (OH), 3088m, 3031m, 2919s, 2866s, 1874w, 1737w, 1644w (C=C), 1496m, 1454s, 1428s, 1365m, 1312m, 1207m, 1094s, 1028s, 996s, 927m, 849w, 799s, 737s; δ_H(300 MHz) 1.50-1.90 (4H, stack, 2 × C*H₂*), 3.59-3.78 (2H, stack), 3.83-3.95 (1H, m, 1 × C*H*OH), 4.04-4.18 (2H, stack), 4.52 (2H, s, PhC*H₂*), 5.22 (1H, d, *J* 10.7, =C$H_{cis}$$H_{trans}$), 5.32 (1H, d, *J* 17.3, =C$H_{cis}$$H_{trans}$), 5.85 (1H, ddd, *J* 17.3, 10.7, 5.9, C*H*=CH_2), 7.25-7.42 (5H, stack, Ph*H*), the resonance for the 3 × OHs v br and not resolved; δ_C(75 MHz) 36.8 (CH_2), 36.9 (CH_2), 68.9 (CH_2), 71.9 (CH, 1 × *C*HOH), 73.4 (CH_2), 74.5 (CH, 1 × *C*HOH), 75.4 (CH, 1 × *C*HOH), 116.7 (CH_2, =CH_2), 127.7 (CH, Ph), 127.8 (CH, Ph), 128.5 (CH, Ph), 136.5 (CH, *C*H=CH_2), 137.6 (quat. C, *ipso*Ph); *m/z* (TOF ES+) 289.1 ($[M+Na]^+$, 100%); HRMS *m/z* (TOF ES+) 289.1 ($[M+Na]^+$. $C_{15}H_{22}NaO_4$ requires 289.1416).

Acetonide protection of triol 9h: 4-benzyloxy-1-(2,2-dimethyl-5-vinyl-[1,3]dioxolan-4-yl)-butan-2-ol 11h and 1-[6-(2-benzyloxy-ethyl)-2,2-dimethyl-[1,3]dioxan-4-yl]-prop-2-en-1-ol 12h



11h



12h

$C_{18}H_{26}O_4$
Exact Mass: 306.18311
Mol. Wt.: 306.39664
C, 70.56; H, 8.55; O, 20.89 %

Na_2SO_4 (40 mg) and *p*TsOH•H_2O (3 mg, 16 μmol) were added to a solution of *triol* **9h** (30 mg, 0.11 mmol) in acetone (1.6 mL) and the resulting mixture was stirred overnight. Aqueous work-up afforded *acetonides* **11h** and **12h** as a colorless oil and as an inseparable mixture (56:44 by ^{1}H NMR) (33 mg, quantitative); Data reported on the mixture of **11h** and **12h**: δ_H(C_6D_6, 300 MHz) 1.20-1.53 (16H, stack including [1.25 (3H, s, $(CH_3)_{pseudoax.}$ **11h**), 1.30 (3H, s, $(CH_3)_{pseudoax.}$ **12h**), 1.46 (3H, s, $(CH_3)_{pseudoeq.}$ **11h**), 1.48 (3H, s, $(CH_3)_{pseudoeq.}$ **12h**)], $C(CH_3)_2$ **11h**, $C(CH_3)_2$ **12h**, 1 × C*H₂* **11h**, 1 × C*H₂* **12h**), 1.67-1.93 (4H, stack, BnOCH₂C*H₂* **11h**, BnOCH₂C*H₂* **12h**), [(3.37-3.49), (3.50-3.61), (3.61-3.73), (3.90-4.01), (4.02-4.21), (4.28-4.41) 14H, 6 × stack / m, 4 × C*H₂*O, 6 × C*H*O], 5.04 (1H, d, *J* 10.3, 1-H_{cis} **11h**), 5.16 (1H, app. dt, *J* 10.3, 1.7, 1-H_{cis} **12h**), 5.18 (1H, d, *J* 15.8, 1-H_{trans} **11h**), 5.45 (1H, app. dt, *J* 17.3, 1.7 1-H_{trans} **12h**), 5.69 (1H, ddd, *J* 15.8, 10.3, 7.0, 2-*H* **11h**), 5.83 (1H, ddd, *J* 17.3, 10.3, 5.1, 2-*H* **12h**), 7.09-7.37 (10H, stack, Ph*H* **11h**, Ph*H* **12h**), resonances for OH not observed; δ_C(C_6D_6, 75 MHz) 20.0 (CH_3, (CH_3)$_{pseudoax.}$ **12h**), 25.7 (CH_3, (CH_3)$_{pseudoax.}$ **11h**), 28.3 (CH_3, (CH_3)$_{pseudoeq.}$ **11h**), 30.4 (CH_3, (CH_3)$_{pseudoeq.}$ **12h**), 30.7 (CH_2), 37.2 (CH_2), 37.8 (CH_2), 38.2 (CH_2), 66.0 (CH), 66.4 (CH_2), 68.1 (CH_2), 69.2 (CH), 72.3 (CH), 73.1 (CH_2), 73.2 (CH_2), 74.4 (CH), 78.0 (CH), 80.0 (CH), 98.8 (quat. C, *C*(CH_3)$_2$ **12h**), 108.7 (quat. C, *C*(CH_3)$_2$ **11h**), 115.9 (CH_2, *C*-1), 117.5 (CH_2, *C*-1), 127.66 (CH, Ph), 127.68 (CH, Ph), 127.74 (CH, Ph), 127.78 (CH, Ph), 128.56 (CH, Ph), 128.58 (CH, Ph), 135.1 (CH, *C*-2), 136.9 (CH, *C*-2), 139.2(quat. C, *ipso*Ph), 139.4 (quat. C, *ipso*Ph).