Utilization of 1-Oxa-2,2-(dimesityl)silacyclopentane Acetals in the Stereoselective Synthesis of Polyols

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A. Synthesis of Starting Materials	
i) Synthesis of Silyl Anion	S-2
ii) Synthesis of Enoates	S-3
B. Conjugate Addition Reactions	S-12
C. Enolate Alkylation	S-17
D. Intramolecular Hydrosilylation Reactions	S-18
E. Lewis acid-mediated Nucleophilic Substitution Reactions	S-24
F. Oxidation of C–Si Bond	S-27
G. Reactions of 1,3–Diols	S-31
H. One Flask Formation of Oxasilacyclopentane Acetal	S-37
I. X-Ray Crystallographic Data	S-39
J. GCMS and Spectra Data for Stereochemical Proofs	S-70

Experimental Section

General: ¹H NMR and ¹³C NMR spectra were recorded at ambient temperature at 400 or 500 MHz, and 100 or 125 MHz, respectively, using a Bruker DRX400 or DRX500 spectrometer. The data are reported as follows: chemical shift in ppm from internal tetramethylsilane on the δ scale, multiplicity (br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, and m = multiplet), coupling constants in Hz, and integration. High resolution mass spectra were acquired on a VG Analytical 7070E or Fisons Autospec spectrometer and were obtained by peak matching. Microanalyses were performed by Atlantic Microlab, Atlanta, GA. Analytical gas-liquid chromatography (GLC) was performed on a Hewlett Packard 5890 Level 4 chromatograph equipped with a split mode injection system and a flame ionization detector. Fused silica capillary columns (30 m \times 0.32 mm) wall-coated with DB-1 (J & W Scientific) was used with helium as the carrier gas (16 psi column head pressure). GC-MS analyses were conducted on a Finnigan Trace-MS from 50 °C for 1 min then ramped 10 °C / min to 270 °C. Fused silica capillary columns ($30 \times$ 0.32 mm) wall-coated with DB-5 (J&W Scientific) were used with ammonia as the reagent gas for chemical impact (CI) analysis. Unless otherwise stated, all reactions were carried out under an atmosphere of nitrogen in glassware which had been flame-dried under a stream of nitrogen. Air sensitive compounds were stored in an Innovative Technologies nitrogen atmosphere drybox. THF, CH₂Cl₂, Et₂O, and toluene were purified by filtration through activated alumina according to the method of Grubbs.¹ Hexane, benzene, trichlorosilane, and $BF_3 \cdot Et_2O$ were purified by distillation from CaH₂. NaH and Li^o were washed with hexanes and dried under reduced pressure prior to use. Ethyl crotonate, crotonaldehyde, and isobutyraldehyde were purified by distillation over CaCl₂. All other reagents were used as received.

A-i. Synthesis of Silyl Anion.



Dimesitylchlorosilane. To a mixture of mesityllithium etherate² (19.96 g, 99.7 mmol) in 84 mL of benzene was added a solution of trichlorosilane (5.0 mL, 50 mmol) in 20 mL of benzene dropwise over 1 h. After 20 h, the mixture was filtered through Celite, yielding a yellow filtrate. The yellow solid was washed with benzene (4 × 100 mL). The washes were combined and concentrated *in vacuo* to afford an orange oil. The oil was purified by bulb-to-bulb distillation (165–170 °C / 0.1 Torr) to give the known compound as a white solid² (7.79 g, 70%): ¹H NMR (500 MHz, CDCl₃) δ 6.83 (s, 4H), 6.12 (s, 1H), 2.42 (s, 12H), 2.27 (s, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 144.3, 140.6, 129.4, 128.0, 23.1, 21.1; IR (KBr) 3021, 2966, 2921, 2197, 1606, 1077, 836 cm⁻¹; HRMS (CI/isobutane) *m* / *z* calcd for C₁₈H₂₃ClSi (M⁺) 302.1258, found 302.1251. Anal. Calcd for C₁₈H₂₃ClSi: C, 71.37; H, 7.65. Found: C, 71.33; H, 7.79.

Mes Mes_Si_H • 3 THF Li

Dimesitylsilyllithium (4). Lithium powder (0.58 g, 84 mmol, 30% dispersion in mineral oil, washed with hexanes) was suspended in 7 mL of THF. To the cooled (0 °C) suspension, a cooled (0 °C) solution of dimesitylchlorosilane (4.0 g, 13 mmol) in 20 mL of THF was added dropwise and stirred for 4 h. Using Schlenk glassware, the THF was removed *in vacuo* and the brown residue was dissolved in 20 mL of toluene. The solution was filtered through an enclosed glass frit into a Schlenk flask and concentrated *in vacuo* until a white precipitate began to appear. To the mixture was added 15 mL of *n*-pentane. The precipate was filtered and washed with 5 mL of cold *n*-pentane. The filtrate was concentrated *in vacuo*, and the addition of *n*-pentane and filtration were

carried out three more times to afford an off-white solid as product in purity sufficient for further transformations^{3,4} (2.04 g, 50%): ¹H NMR (500 MHz, C_6D_6) δ 6.93 (s, 4H), 4.77 (s, 1H), 3.38 (br s, 12H), 2.71 (s, 12 H), 2.27 (s, 6H), 1.23 (br s, 12H).

A-ii. Synthesis of Enoates.



Ethyl ($2R^*, 3R^*$)-3-benzyloxy-2,4-dimethyl-pentanoate. To a solution of ethyl (2R, 3R)-2,4-dimethyl-3-hydroxypentanoate⁵ (1.0 g, 5.8 mmol) in 13 mL of 2:1 CH₂Cl₂/cyclohexane was added benzyl trichloroacetimidate (1.3 mL, 7.0 mmol), followed by TfOH (0.11 mL, 1.2 mmol). After 3h at 22 °C, the mixture was filtered through Celite and washed with cyclohexane. The filtrate was washed with 20 mL of sodium bicarbonate (saturated aqueous), 20 mL of H₂O, and 20 mL of brine. The organic layer was dried over sodium sulfate, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (2:98 to 4:96 EtOAc/hexanes) to afford the product as a colorless oil (0.76 g, 51%): ¹H NMR (500 MHz, CDCl₃) δ 7.32 (m, 3H), 7.26 (m, 2H), 4.56 (m, 2H), 4.13 (q, *J* = 7.1, 2H), 3.55 (m, 1H), 2.67 (dq, *J* = 7.0, 5.6, 1H), 1.81 (dq, *J* = 13.4, 6.7, 1H), 1.26 (t, *J* = 7.1, 3H), 1.23 (d, *J* = 7.0, 3H), 1.00 (d, *J* = 6.7, 3H), 0.96 (d, *J* = 6.8, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 175.6, 138.7, 128.2, 127.5, 127.4, 85.7, 74.7, 60.3, 42.4, 31.6, 19.7, 18.2, 14.1, 11.7; IR (thin film) 3030, 2963, 1731, 1455, 1065 cm⁻¹; HRMS (CI+/NH₃) *m* / *z* calcd for C₁₆H₂₅O₃ (M+H)⁺ 265.1804, found 265.1801. Anal. Calcd for C₁₆H₂₄O₃: C, 72.69; H, 9.15. Found: C, 72.48; H 9.04.



Ethyl (4*R**,5*R**)-*E*-5-benzyloxy-4,6-dimethyl-hept-2-eneoate (1a). To a cooled (-78 °C) solution of ethyl (2*R**,3*R**)-3-benzyloxy-2,4-dimethyl-pentanoate (0.67 g, 2.5 mmol) in 25 mL of Et₂O was added dropwise over 5 min *i*-Bu₂AlH (2.5 mL, 3.8 mmol, 1.5 M in toluene). After 10 min, 1 mL of MeOH was added, followed by 2 mL of H₂O. The solution was warmed to 22 °C

over 1h. The solution was diluted with 40 mL of sodium potassium tartrate (saturated aqueous), and the organic layer was separated. The aqueous layer was extracted with Et₂O (3×30 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated in vacuo to afford the aldehyde. In a separate flask, triethyl phosphonoacetate (0.75 mL, 3.8 mmol) was added to a slurry of NaH (0.15 g, 3.8 mmol, 60% dispersion in oil, washed with hexanes) in 19 mL of THF. The reaction mixture was stirred for 1h at 22 °C. A solution of the aldehyde in 8 mL of THF was added to the reaction mixture. After 45 min at 22 °C, 7 mL of ammonium chloride (saturated aqueous) was added and the mixture was diluted with 20 mL of H₂O. The organic layer was separated and the aqueous layer was extracted with EtOAc (2×30 mL). The combined organic layers were washed with brine $(2 \times 50 \text{ mL})$, dried over sodium sulfate, filtered, and concentrated in vacuo to give a 97:3 mixture of E/Z isomers as determined by GCMS-EI. The pale yellow oil was purified by flash chromatography (5:95 EtOAc:hexanes) to give the product, a pale yellow oil, as a single diastereomer by ¹H NMR spectroscopy (0.57 g, 78%): ¹H NMR (500 MHz, CDCl₃) δ 7.33 (m, 4H), 7.27 (m, 1H), 7.00 (dd, J = 15.7, 8.1, 1H), 5.84 (dd, J = 15.7, 1.2, 1H), 4.55 (d, J = 1.6, 2H), 4.19 (q, J = 7.1, 2H), 3.10 (t, J = 5.6, 1H), 2.63 (m, 1H), 1.83 (m, 1H), 1.29 (t, J = 7.1, 3H), 1.13 (d, J = 6.7, 3H, 0.97 (d, J = 6.9, 3H), 0.96 (d, J = 6.7, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 166.7, 152.2, 138.7, 128.3, 127.6, 127.5, 120.5, 87.8, 75.1, 60.2, 39.8, 31.3, 20.3, 17.5, 14.7, 14.3; IR (thin film) 3029, 2964, 1718, 1651, 1454, 1181 cm⁻¹; HRMS (CI+/NH₃) m / z calcd for C₁₈H₂₇O₃ (M+H)⁺ 291.1960, found 291.1963. Anal. Calcd for C₁₈H₂₆O₃: C, 74.45; H, 9.02. Found: C, 74.64; H 8.87.

Ethyl (4 R^* ,5 R^*)-*E*-5-(*tert*-butyl-dimethylsiloxy)-4,6-dimethyl-hept-2-eneoate (1d). To a solution of Dess-Martin periodinane (0.98 g, 2.3 mmol) in 4.3 mL of 10:1 pyridine/CH₂Cl₂ was added a solution of (2 R^* ,3 R^*)-3-(*tert*-buty-dimethylsiloxy)-2,4-dimethyl-1-pentanol⁶ (0.52 g, 2.1 mmol) in 1 mL of 10:1 pyridine/CH₂Cl₂ and the solution was stirred for 45 min. The solution was diluted with 20 mL of Et₂O and poured into 25 mL of 1:1 Na₂S₂O₃/NaHCO₃ (saturated aqueous).

The organic layer was separated, and the aqueous layer was extracted with Et₂O (3×20 mL). The combined organic layers were washed with NaHCO₃ (2×30 mL) and brine (2×30 mL), dried over Mg₂SO₄, filtered, and concentrated *in vacuo* to give the aldehyde. In a separate flask, triethyl phosphonoacetate (0.42 mL, 2.1 mmol) in 4.2 mL of THF was added dropwise to a mixture of NaH (0.084 g, 2.1 mmol, 60% dispersion in mineral oil, washed with hexanes) in 4.2 mL of THF. After 1h, the aldehyde in 1 mL of THF was added and the mixture was stirred for 1.25h. To the solution was added 5 mL of NH₄Cl (saturated aqueous) and the mixture was diluted with 25 mL of H₂O. The organic layer was separated and the aqueous layer was extracted with EtOAc (3×30) mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated in vacuo to give a pale yellow oil as an 80:20 mixture of diastereomers. The resulting oil was purified by flash column chromatography (0.5:99.5 to 1:99 EtOAc/hexanes) to give the product, a colorless oil, as a single diastereomer by ¹H NMR spectroscopy (0.34 g, 52%): ¹H NMR (500 MHz, CDCl₃) δ 6.98 (dd, J = 15.8, 7.8, 1H), 5.78 (dd, J = 15.8, 1.3, 1H), 4.18 (dq, J = 7.1, 1.6, 2H), 3.38 (t, J = 4.9, 1H),3H), 0.91 (s, 9H), 0.89 (d, J = 6.9, 3H), 0.85 (d, J = 6.8, 3H), 0.05 (s, 3H), 0.03 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 166.8, 153.0, 120.1, 80.1, 60.1, 40.8, 32.0, 26.2, 20.3, 18.4, 17.6, 14.9, 14.2, -3.76, -3.84; IR (thin film) 2958, 1721, 1652, 1464, 1254, 1179 cm⁻¹; HRMS (CI+/NH₃) m / z calcd for C₁₆H₃₁O₃Si (M-CH₃)⁺ 299.2042, found 299.2040. Anal. Calcd for C₁₇H₃₄O₃Si: C, 64.92; H, 10.90. Found: C, 64.88; H, 11.09.

Ethyl (4*R**,5*R**)-*E*-5-(2,2-dimethylpropionyloxy)-4,6-dimethylhept-2-eneoate. To a cooled (0 °C) solution of ethyl (4*R*,5*R*)-*E*-4,6-dimethyl-5-hydroxy-hept-2-eneoate⁷ (1.0 g, 5.0 mmol) in 20 mL of CH₃CN was added pivalic anhydride (1.5 mL, 7.5 mmol), followed by a solution of Sc(OTf)₃ (0.025 g, 0.050 mmol) in 0.5 mL CH₃CN. After the solution was warmed to 22 °C for 2h, 10 mL of sodium bicarbonate (saturated aqueous) was added. The mixture was diluted with 50 mL of H₂O and 50 mL of Et₂O. The organic layer was separated, and the aqueous layer was

extracted with Et₂O (3 × 50 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash column chormatography (1:99 to 3:97 EtOAc/hexanes) to yield the product as a colorless oil (1.1 g, 79%): ¹H NMR (500 MHz, CDCl₃) δ 6.80 (dd, J = 15.7, 8.3, 1H), 5.81 (d, J = 15.7, 1H), 4.76 (dd, J = 7.3, 4.9, 1H), 4.16 (q, J = 7.1, 2H), 2.63 (m, 1H), 1.84 (m, 1H), 1.27 (t, J = 7.1, 3H), 1.19 (s, 9H), 1.01 (d, J = 6.7, 3H), 0.86 (d, J = 6.8, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 177.9, 166.3, 149.9, 121.5, 78.7, 60.3, 38.7, 30.0, 27.29, 27.26, 19.7, 16.3, 14.9, 14.2; IR (thin film) 2973, 1731, 1651, 1281, 1158 cm⁻¹; HRMS (CI+/NH₃) *m* / *z* calcd for C₁₄H₂₃O₃ (M-OC₂H₅)⁺ 239.1647, found 239.1644.



D-1,2,5,6-*O***-(3-pentylidene)-mannitol**. To a solution of D-mannitol (6.2 g, 34 mmol) in 15 mL of DMF was added camphorsulfonic acid (0.25 g, 1.0 mmol). The reaction mixture was heated to 40 °C and 3,3-dimethoxypentane (9.5 g, 72 mmol) was added dropwise over 15 min. Complete dissolution occurred after 45 min. The solution was stirred for another 4h at 40 °C. The solution was cooled to 25 °C and a few drops of Et₃N were added. The solution was diluted with 100 mL of MTBE and washed with brine (4 × 100 mL). The combined organic layers were filtered through sodium sulfate and concentrated *in vacuo* to give a white solid⁸ (9.03 g, 83%): ¹H NMR (500 MHz, CDCl₃) δ 4.15 (m. 4H), 3.92 (m, 2H), 3.77 (t, *J* = 6.2, 2H), 2.85 (d, *J* = 6.8, 2H), 1.65 (m, 8H), 0.89 (m, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 113.2, 76.1, 71.5, 67.3, 29.5, 28.9, 8.2, 8.0; IR (KBr) 3422, 2975, 2883, 1464, 1086, 916 cm⁻¹; HRMS (FAB+) *m* / *z* calcd for C₁₆H₃₁O₆ (M+H)⁺ 319.2120, found 319.2117.



Ethyl (R)-E-4,5-O-(3-pentylidene)-4,5-dihydroxy-2-pentenoate (1c). To a mixture of KHCO₃ (0.28 g, 2.8 mmol) and KIO₄ (7.2 g, 31 mmol) in 44 mL of H₂O was added a solution of D-1,2,5,6-O-(3-pentilidene)-mannitol (9.0 g, 28 mmol) in 18 mL of THF dropwise over 5 min. The reaction mixture was stirred at 25 °C for 5h and then cooled to 5 °C. The mixture was filtered through Celite and the solids were washed with 20 mL of EtOAc. The filtrate was warmed to 25 °C and saturated with sodium chloride. The mixture was filtered again and the solids were washed with 20 mL of EtOAc. The organic layer was removed, and the aqueous layer was extracted with EtOAc (2×20 mL). The combined organic layers were filtered through sodium sulfate and concentrated *in vacuo*. The resulting oil was purified by bulb-to-bulb distillation (50 °C, 0.1 Torr) to yield the aldehyde. In a separate flask, triethylphosphonoacetate (6.5 mL, 33 mmol), *i*-Pr₂NEt (6.5 mL, 37 mmol), and the aldehyde (4.9 g, 31 mmol) were added to LiCl (1.7 g, 37 mmol) in 31 mL of CH₃CN. The solution was stirred at 25 °C for 1.5h. The mixture was diluted with 60 mL of H_2O and the organic layer was separated. The aqueous layer was extracted with Et₂O (4 × 50 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated *in vacuo* to give a colorless oil as a 98:2 mixture of E/Z isomers as determined by GCMS-CI/NH₄Cl. The oil was purified by flash chromatography (1:99 to 10:90 EtOAc/hexanes) to yield as product a colorless oil⁸ (3.8 g, 54%): ¹H NMR (400 MHz, CDCl₃) δ 6.87 (dd, J = 15.6, 6.0, 1H), 6.11 (dd, J = 15.6, 1.2, 1H), 4.66 (m, 1H), 4.20 (q, J = 7.0, 2H and m, 1H), 3.62 (t, J = 8.0, 1H), 1.68 (m, 4H), 1.30 (t, J = 7.0, 3H), 0.92 (q, J = 7.6, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 165.9, 144.2, 122.4, 114.1, 75.3, 69.3, 60.5, 53.4, 29.7, 29.4, 14.1, 8.0; IR (thin film): 2977, 1723, 1663, 1465, 1175, 1079 cm⁻¹; HRMS (LSIMS) m / z calcd for $C_{12}H_{21}O_2$ (M+H)⁺ 229.1440, found 229.1442. Anal. Calcd for C₁₂H₂₀O₂: C, 63.14; H, 8.83. Found: C, 63.04; H, 8.76.



(*R*)-*E*-4,5-*O*-isopropylidine-4,5-dihydroxy-2-pentenoate. To a cooled (0 °C) mixture of 1,2,5,6-diisopropylidine-D-mannitol (2.5 g, 9.7 mmol) in 25 mL of sodium bicarbonate (saturated aqueous) was added dropwise a solution of NaIO₄ (2.5 g, 12 mmol) in 20 mL of H₂O. The reaction mixture was warmed to 22 °C for 1h. Triethyl phosphonoacetate (4.4 mL, 20 mmol) was added, followed by a solution of K₂CO₃ (28 g, 200 mmol) in 35 mL of H₂O, and the mixture was stirred for 18h. The reaction mixture was extracted with CH₂Cl₂ (3 × 75 mL). The combined organic layers were washed with 100 mL of brine, dried over sodium sulfate, filtered, and concentrated *in vacuo* to give a 98:2 mixture of E/Z isomers as a colorless oil by GCMS-CI/NH₄CI. The resulting oil was purified by flash column chromatography (10:90 EtOAc/hexanes) to give the product as a colorless oil⁹ (2.8 g, 72%): ¹H NMR (500 MHz, CDCl₃) δ 6.88 (dd, *J* = 15.6, 5.7, 1H), 6.10 (dd, *J* = 15.6, 1.4, 1H), 4.67 (dq, *J* = 7.0, 1.3, 1H), 4.20 (q, *J* = 7.1, 2H and dd, *J* = 8.3, 6.8, 1H), 3.68 (dd, *J* = 8.2, 7.2, 1H), 1.45 (s, 3H), 1.41 (s, 3H), 1.30 (t, *J* = 7.1, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 165.7, 144.5, 122.2, 109.9, 74.7, 68.6, 60.3, 26.2, 25.5, 14.0; HRMS (CI+/NH₃) *m* / *z* calcd for C₁₀H₁₇O₄ (M+H)⁺ 201.1127, found 201.1122. [α]²⁵_D 24.1 (*c* 0.220, CHCl₃).



(*S*)-4-Benzyl-3-[(2*R*,3*S*)-3-hydroxy-2-methyl-3-phenyl-propionyl]-oxazolidin-2-one. To a mixture of (*S*)-4-benzyl-3-propionyl-oxazolidin-2-one (0.98 g, 4.3 mmol) and MgCl₂ (0.046 g, 0.43 mmol) in 8.6 mL of EtOAc was added Et₃N (1.2 mL, 8.6 mmol), benzaldehyde (0.48 mL, 4.7 mmol), and (CH₃)₃SiCl (0.81 mL, 6.4 mmol), respectively. The mixture was stirred for 24h at 22 °C. The reaction mixture was filtered through a silica gel column with 200 mL of Et₂O. The solution was concentrated *in vacuo* and dissolved in 100 mL of MeOH. To the solution was added

1 mL of 1:9 TFA/MeOH and the solution was concentrated *in vacuo* to yield a white solid as a 24:1 mixture of diastereomers as determined by GCMS-EI.¹⁰ The solid was purified by flash chromatography (10:90 EtOAc:hexanes) to give a white solid¹¹ (1.3 g, 93%): ¹H NMR (500 MHz, CDCl₃) δ 7.43 (m, 2H), 7.38 (m, 2H), 7.33–7.27 (m, 4H), 7.15 (m, 2H), 4.82 (t, J = 7.7, 1H), 4.69 (m, 1H), 4.35 (dq, J = 7.0, 1H), 4.19 (m, 1H), 4.14 (dd, J = 9.1, 2.8, 1H), 3.19 (dd, J = 13.6, 3.4, 1H), 3.12 (d, J = 7.3, 1H), 2.67 (dd, J = 13.6, 9.3, 1H), 1.11 (d, J = 6.9, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 176.5, 153.4, 142.0, 133.1, 129.3, 128.8, 128.4, 127.9, 127.1, 126.6, 77.2, 65.8, 55.2, 44.2, 37.4, 14.7; HRMS (CI+/NH₃) *m* / *z* calcd for C₂₀H₂₁NO₄ (M⁺) 339.1471, found 339.1464; $[\alpha]_{D}^{25}$ -9.43 (*c* 0.795, CHCl₃).



(4S,5S)-5-Methyl-2,4-diphenyl-1,3-dioxane. To a cooled (0 °C) solution of (*S*)-4-Benzyl-3-[(2*R*,3*S*)-3-hydroxy-2-methyl-3-phenyl-propionyl]-oxazolidin-2-one (0.54 g, 1.6 mmol) and MeOH (0.065 mL, 1.6 mmol) in 5.3 mL of THF was added LiBH₄ (0.035 g, 1.6 mmol). The reaction mixture was stirred at 0 °C for 1 h, and 10 mL of sodium potassium tartrate (saturated aqueous) was added and stirred for 30 min. The mixture was diluted with 30 mL of CH₂Cl₂ and 30 mL of sodium potassium tartrate (saturated aqueous). The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (2 × 50 mL). The organic layers were combined and washed with brine (2 × 70 mL), dried over sodium sulfate, filtered, and concentrated *in vacuo* to give a pale yellow oil. The oil was dissolved in 3.5 mL of DMF and charged with benzaldehyde dimethyl acetal (0.24 mL, 1.6 mmol) and CSA (0.015 g), respectively at 22 °C. The reaction mixture was stirred at 22 °C for 38 h and 10 mL of sodium carbonate (saturated aqueous) was added. The mixture was diluted with 30 mL of MTBE. The organic layer saturated aqueous) was added. The mixture was diluted with 30 mL of MTBE. The organic layer saturated aqueous was added. The mixture was diluted with 30 mL of MTBE. The organic layer saturated aqueous was added. The mixture was diluted with 30 mL of MTBE. The organic layer saturated aqueous was added. The mixture was diluted with 30 mL of MTBE. The organic layer saturated aqueous was added. The mixture was diluted with 30 mL of MTBE. The organic layer saturated aqueous was added in *vacuo* to give a pale yellow oil as a 97:3 mixture of diastereomers as determined by ¹H NMR spectroscopy. The resulting oil was purified by flash column chromatography (1:99 EtOAc:hexanes) to yield the product, a pale yellow oil, as a single diastereomer as determined by ¹H NMR spectroscopy (0.25 g, 63%): ¹H NMR (500 MHz, CDCl₃) δ 7.55 (m, 2H), 7.42 (m, 2H), 7.34 (m, 6H), 5.68 (s, 1H), 4.38 (d, J = 10.0, 1H), 4.26 (dd, J = 11.4, 4.6, 1H), 3.69 (t, J = 11.3, 1H), 2.16 (m, 1H), 0.66 (d, J = 6.7, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 139.6, 138.4, 128.7, 128.2, 128.1, 128.0, 127.4, 126.2, 101.5, 86.3, 73.3, 35.8, 12.2; IR (thin film) 3063, 2958, 1454, 1111, 754 cm⁻¹; HRMS (CI+/NH₃) *m* / *z* calcd for C₁₇H₁₉O₂ (M+H)⁺ 255.1385, found 255.1390. Anal. Calcd for C₁₇H₁₈O₂: C, 80.28; H, 7.13. Found: C, 80.41; H 7.15. [α]²⁵_D –38.7 (*c* 0.315, CHCl₃).



(2S,3S)-3-Benzyloxy-2-methyl-3-phenyl-propan-1-ol: To a cooled (-78 °C) solution of (4S,5S)-5-Methyl-2,4-diphenyl-1,3-dioxane (0.25 g, 0.98 mmol) in 5 mL of CH₂Cl₂ was added dropwise over 5 min i-Bu₂AlH (3.3 mL, 4.9 mmol, 1.5 M in toluene). The solution was warmed to 22 °C for 18h. The reaction mixture was cooled to 0 °C and 2 mL of MeOH was added. The mixture was diluted with 20 mL of sodium potassium tartrate (saturated aqueous) and stirred for 2h. The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (3×50 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo to afford a 97:3 mixture of regioisomers. The pale yellow oil was purified by flash column chromatography (4:96 to 10:90 EtOAc:hexanes) to afford the product, a pale yellow oil, as a single diastereomer as determined by ¹H NMR spectroscopy (0.22 g, 89%): ¹H NMR (500 MHz, CDCl₃) δ 7.39 (m, 2H), 7.34 (m, 5H), 7.28 (m, 3H), 4.42 (d, J = 11.6, 1H), 4.21 (d, J = 11.6, 1H), 4.19 (d, J = 11.6, 1H= 8.8, 1H), 3.68 (m, 2H), 3.23 (m, 1H), 2.11 (m, 1H), 0.66 (d, J = 7.0, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 140.3, 137.7, 128.4, 128.3, 127.9, 127.8, 127.7, 127.4, 87.1, 70.4, 67.4, 41.9, 13.7; IR (thin film) 3419, 3029, 2875, 1494, 1454, 1063 cm⁻¹; HRMS (CI+/NH₃) m / z calcd for C₁₇H₂₁O₂ (M+H)⁺ 257.1541, found 257.1540. Anal. Calcd for C₁₇H₂₀O₂: C, 79.65; H, 7.86. Found: C, 79.67; H 8.05. $[\alpha]_{D}^{25}$ –180 (*c* 0.120, CHCl₃).



Ethyl (4R,5S)-E-5-benzyloxy-4-methyl-5-phenyl-pent-2-eneoate (1e). To a cooled (-78 °C) solution of (COCl)₂ (0.43 mL, 0.86 mmol) in 2.9 mL of CH₂Cl₂ was added 0.12 mL of DMSO. The solution was stirred for 15 min at -40 °C and then cooled to -78 °C. A solution of (2S,3S)-3-Benzyloxy-2-methyl-3-phenyl-propan-1-ol (0.20 g, 0.78 mmol) in 0.35 mL of CH₂Cl₂ was added dropwise to the reaction mixture, followed by triethylamine (0.54 mL, 3.9 mmol). The mixture was slowly warmed to 0 °C over 3h and then poured into 30 mL of sodium bicarbonate (saturated aqueous). The organic layer was washed with 30 mL of 1 N NaHSO₄, sodium bicarbonate (saturated aqueous, 2×30 mL), and brine (2×30 mL). The organic layer was dried over sodium sulfate, filtered, and concentrated in vacuo to give the aldehyde. In a separate flask, triethyl phosphonoacetate (0.24 mL, 1.2 mmol) was added to a mixture of NaH (0.054 g, 1.2 mmol, 60% dispersion in oil, washed with hexanes) in 6 mL of THF. The mixture was stirred at 22 °C for 1 h. A solution of the unpurified aldehyde in 2.6 mL of THF was added to the reaction mixture and the resulting mixture was stirred for 1 h. To the mixture was added 5 mL of NH₄Cl (saturated aqueous), and the mixture was diluted with 30 mL of H₂O. The organic layer was separated, and the aqueous layer was extracted with EtOAc $(3 \times 75 \text{ mL})$ and the combined organic layers were dried over MgSO₄, filtered, and concentrated in vacuo to give a 91:9 mixture of E/Z isomers as determined by GCMS-EI. The pale yellow oil was purified by flash column chromatography (2:98 EtOAc:hexanes) to afford the product, a colorless oil, as a single diastereomer as determined by ¹H NMR spectroscopy (0.19 g, 76%): ¹H NMR (500 MHz, CDCl₃) δ 7.38-7.27 (m, 10H), 7.10 (dd, J = 15.8, 7.8, 1H), 5.80 (dd, J = 15.8, 1.1, 1H), 4.45 (d, J = 12.0, 1H), 4.20 (q, J = 7.1, 2H and m, 1H), 4.14 (d, J = 7.6, 1H), 2.71 (m, 1H), 1.30 (t, J = 7.1, 3H), 0.88 (d, J = 6.9, 3H); ¹³C NMR (125) MHz, CDCl₃) δ 166.5, 151.2, 139.8, 138.2, 128.3, 128.2, 127.9, 127.6, 127.5, 127.41, 127.39, 121.2, 84.6, 70.3, 60.0, 43.2, 16.0, 14.2; IR (thin film) 3063, 2979, 1717, 1653, 1453, 1272 cm⁻¹; HRMS (CI+/NH₃) m/z calcd for C₂₁H₂₅O₃ (M+H)⁺ 325.1803, found 325.1791. Anal. Calcd for $C_{21}H_{24}O_3$: C, 77.75; H, 7.46. Found: C, 77.50; H 7.44. $[\alpha]_{D}^{25}$ -81.6 (*c* 0.255, CHCl₃).

B. Conjugate Addition Reactions



Ethyl $(3R^*, 4S^*, 5R^*)$ -5-benzyloxy-3-(dimesitylsilyl)-6,4-dimethyl-heptanoate (2a). To a cooled (-78 °C) solution of Me₂Zn (1.8 mL, 3.5 mmol, 2.0 M in toluene) in 23 mL of THF, was added a cooled (0 °C) solution of silvilithium 4 (1.5 g, 3.5 mmol) in 3.5 mL of THF. The solution was warmed to 0 °C for 5 min and then re-cooled to -78 °C. To a separate flask, MeLi (0.30 mL, 0.35 mmol, 1.2 M in Et₂O) was added to a cooled (-78 °C) slurry of CuCN (0.016 g, 0.18 mmol) in 4.5 mL of THF. The slurry was warmed to -30 °C, stirred for 5 min, cooled to -78 °C, and stirred for 5 min. The cuprate solution was added to the zincate solution, and the mixture was stirred at -78 °C for 10 min. To the reaction solution was added (CH₃)₃SiCl (1.3 mL, 10.5 mmol) followed by a cooled (-78 °C) solution of enoate **1a** (1.0 g, 3.4 mmol) in 2.0 mL of THF. After 5h at -78 °C, 5 mL NH₄Cl (saturated aqueous) was added, and the mixture was warmed to 25 °C. The mixture was diluted with 50 mL of water and acidified with 3 mL of 1 N HCl. The organic layer was separated and the aqueous layer was extracted with Et₂O (3×30 mL). The combined organic layers were dried with MgSO₄, filtered, and concentrated *in vacuo* to yield a colorless oil as a >99:1 mixture of diastereomers as determined by GCMS-EI. The oil was purified by flash column chromatography (hexanes to 1:99 EtOAc/hexanes) to give the product as a white solid (1.5 g, 83%): mp 125 – 127 °C. ¹H NMR (500 MHz, CDCl₃) δ 7.26 (m, 4H), 7.20 (m, 1H), 6.78 (s, 2H), 6.73 (s, 2H), 5.17 (d, J = 6.8, 1H), 4.65 (d, J = 11.0, 1H), 4.60 (d, J = 11.0, 1H), 3.67 (dq, J = 10.7, 7.1, 1.1)1H), 3.44 (dq, J = 10.7, 7.2, 1H), 3.19 (dd, J = 6.8, 4.2, 1H), 2.97 (dd, J = 17.1, 4.6, 1H), 2.62 (m, 1H), 2.42 (s, 6H), 2.40 (s, 6H), 2.29 (m, 1H), 2.22 (s, 3H), 2.19 (s, 3H), 2.06 (m, 1H), 1.95 (dq, J =13.5, 6.7, 1H), 1.07 (d, J = 7.0, 3H), 0.95 (t, J = 7.1, 3H), 0.90 (d, J = 6.7, 3H), 0.87 (d, J = 6.8, 3H); ¹³C NMR (125 MHz, CDCl₂) δ 173.9, 145.1, 144.6, 139.2, 139.0 138.8, 129.2, 129.1, 128.8, 128.7, 128.1, 127.2, 127.1, 92.2, 75.1, 59.9, 34.0, 32.3, 31.5, 24.3, 23.8, 23.5, 20.9, 20.2, 18.5, 13.8, 10.4; IR (KBr pellet) 3029, 2966, 1721, 1604, 1464, 1109 cm⁻¹; HRMS (TOF MS ES+/Na) m / z

calcd for C₃₆H₅₀O₃SiNa (M+Na)⁺ 581.3427, found 581.3422. Anal. Calcd for C₃₆H₅₀O₃Si: C, 77.37; H, 9.02. Found: C, 77.45; H, 9.10.



Ethyl (3*R**,4*R**,5*R**)-3-(dimesitylsilyl)-5-(2,2-dimethylpropionyloxy)-4,6-dimethylhept-2-eneoate. To a cooled (-78 °C) solution of Me₂Zn (0.18 mL, 0.35 mmol, 2.0 M in toluene) in 2.3 mL of THF was added a cooled (0 °C) solution of silvllithium 4 (0.15 g, 0.35 mmol) in 0.4 mL of THF. The solution was warmed to 0 °C for 5 min and then re-cooled to -78 °C. In a separate flask, MeLi (0.029 mL, 0.035 mmol, 1.2 M in Et₂O) was added to a cooled (-78 °C) slurry of CuCN (0.0016 g, 0.018 mmol) in 0.45 mL of THF. The slurry was warmed to -30 °C, stirred for 5 min, cooled to -78 °C, and stirred for 5 min. The cuprate solution was added to the zincate solution and the mixture was stirred at -78 °C for 10 min. To the reaction solution was added (CH₃)₃SiCl (0.13 mL, 1.0 mmol) followed by a cooled (-78 °C) solution of ethyl ($4R^*, 5R^*$)-E-5-(2,2-dimethylpropionyloxy)-4,6-dimethylhept-2-eneoate (0.097 g, 0.34 mmol) in 0.2 mL of THF. After 18 h at -78 °C, 5 mL of NH₄Cl (saturated aqueous) was added and the mixture was warmed to 25 °C. The mixture was diluted with 50 mL of H₂O. The organic layer was separated, and the aqueous layer was extracted with Et₂O (3 \times 30 mL). The combined organic layers were dried with MgSO₄, filtered, and concentrated in vacuo to yield a colorless oil as a 98:2 mixture of diastereomers as determined by GCMS-EI. The oil was purified by flash chromatography (hexanes to 1:99 EtOAc/hexanes) to give the product as a white solid (0.12 g, 64%): mp 128-130 °C. ¹H NMR (500 MHz, CDCl₃) δ 6.80 (s, 2H), 6.77 (s, 2H), 5.15 (d, J = 6.7, 1H), 4.76 (dd, J = 7.6, 4.1, 1H), 3.96 (dq, J = 14.3, 7.1, 1H), 3.81 (dq, J = 14.3, 7.1, 1H), 2.59 (dd, J = 16.7, 7.5, 1H), 2.50 (m, 2H), 2.43(s, 6H), 2.39 (s, 6H), 2.23 (s, 3H), 2.21 (s, 3H), 2.05 (m, 2H), 1.18 (s, 9H), 1.12 (t, J = 7.1, 3H), 0.95 (d, J = 7.0, 3H), 0.76 (d, J = 6.8, 3H), 0.64 (d, J = 6.7, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 178.0, 173.8, 145.1, 144.7, 139.1, 139.0, 129.04, 128.96, 128.86, 128.4, 80.9, 60.4, 39.2, 34.0, 31.9, 29.7, 29.3, 27.4, 23.7, 23.6, 22.2, 21.0, 20.9, 20.1, 16.0, 13.9, 11.9; IR (KBr pellet) 2969, 2929, 1727, 1605, 1461, 1160 cm⁻¹; HRMS (CI+/NH₃) m / z calcd for C₃₄H₅₁O₄Si (M-H)⁺

551.3556, found 551.3553. Anal. Calcd for C₃₄H₅₂O₄Si: C, 73.86; H, 9.48. Found: C, 73.89; H, 9.63.



(3S,4R)-3-(dimesitylsilyl)-4,5-O-(3-pentilidene)-4,5-dihydroxypentanoate 2c. To a cooled (0 °C) solution of Me₂Zn (1.0 mL, 2.0 mmol, 2.0 M in toluene) in 13 mL of THF was added a cooled (0 °C) solution of 15 (0.83 g, 2.0 mmol) in 2.2 mL of THF. The solution was stirred at 0 °C for 20 min and then cooled to -78 °C. In a separate flask, MeLi (0.075 mL, 0.11 mmol, 1.45 M in Et₂O) was added to a cooled (-78 °C) slurry of CuCN (0.005 g, 0.06 mmol) in 1.5 mL of THF. The slurry was warmed to -30 °C, stirred for 5 min, cooled to -78 °C, and stirred for 5 min. The cuprate solution was added to the zincate solution and the mixture was stirred at -78 °C for 10 min. To the reaction solution was added a cooled (-78 °C) solution of enoate 1c (0.43 g, 1.9 mmol) in 1.3 mL of THF. After 2.5h at -78 °C, 3 mL NH₄Cl (saturated aqueous) was added, and the mixture was warmed to 25 °C. The mixture was diluted with 50 mL of NaCl (saturated aqueous) and the metal salts were dissolved with 3 mL of 1 N HCl. The aqueous layer was extracted with Et₂O (3 \times 70 mL). The combined organic layers were dried with MgSO₄, filtered, and concentrated in vacuo to yield a yellow oil as a 98:2 mixture of diastereomers as determined by GCMS-EI. The oil was purified by flash chromatography (hexanes to 2:98 EtOAc/hexanes) to give the product as a viscous yellow oil (0.77 g, 82%): ¹H NMR (500 MHz, CDCl₃) δ 6.79 (s, 2H), 6.77 (s, 2H), 5.08 (d, J = 6.0, 1H), 4.12 (dt, J = 8.2, 6.0, 1H), 4.05 (dq, J = 10.8, 7.2, 1H), 3.95 (dq, J = 10.8, 7.2, 1H), 3.44 (dd, J = 10.8, 10.8, 10.8, 10.8, 10.8, 10.8, 10.8, 10.8, 10.8, 10.8, 10.8, 10.8, 10.8, 10.8, 10.8, 10.8, 10.8, 10.8, 10.8 = 8.3, 5.9, 1H), 3.27 (t, J = 8.4, 1H), 2.64 (m, 2H), 2.41 (s, 6H and m, 1H), 2.37 (s, 6H), 2.22 (s, 6H), 1.49 (m, 4H), 1.17 (t, J = 7.2, 3H), 0.84 (t, J = 7.4, 3H), 0.77 (t, J = 7.4, 3H); ¹³C NMR (125) MHz, CDCl₃) δ 173.8, 144.9, 144.4, 139.4, 139.3, 129.2, 129.0, 128.8, 127.6, 78.4, 77.2, 69.0, 60.3, 33.6, 29.7, 29.3, 25.8, 23.7, 23.5, 21.0, 20.9, 14.0, 8.1, 8.0; IR (thin film) 3023, 2973, 2151, 1732, 1605, 1076, 846 cm⁻¹; HRMS (LSI) *m* / *z* calcd for $C_{30}H_{43}O_4Si$ (M-H)⁺ 495.2930, found 495.2929. Anal. Calcd for C₃₀H₄₄O₄Si: C, 72.54; H, 8.93. Found: C, 72.75; H, 8.97.



(3S*,4R*)-3-(dimesitylsilyl)-4,5-O-isopropylidine-4,5-dihydroxypentanoate. To a cooled (-78 °C) solution of Me₂Zn (0.36 mL, 0.72 mmol, 2.0 M in toluene) in 4.8 mL of THF, was added a cooled (0 °C) solution of silvilithium 4 (0.30 g, 0.72 mmol) in 0.7 mL of THF. The solution was stirred at 0 °C for 5 min and then cooled to -78 °C. In a separate flask, MeLi (0.063 mL, 0.076 mmol, 1.2 M in Et₂O) was added to a cooled (-78 °C) slurry of CuCN (0.003 g, 0.036 mmol) in 0.9 mL of THF. The slurry was warmed to -30 °C, stirred for 5 min, cooled to -78 °C, and stirred for 5 min. The cuprate solution was added to the zincate solution and stirred at -78 °C for 10 min. To the reaction solution was added a cooled (-78 °C) solution of (*R*)-*E*-4,5-*O*-dimethylacetonide-4,5-dihydroxy-2-pentenoate (0.14 g, 0.70 mmol) in 0.4 mL of THF. After 3h at -78 °C, 3 mL of NH₄Cl (saturated aqueous) was added and the mixture was warmed to 25 °C. The organic layer was separated and the aqueous layer was extracted with Et_2O (3 \times 50 mL). The combined organic layers were dried with MgSO₄, filtered, and concentrated *in vacuo* to yield a yellow oil as a 98:2 mixture of diastereomers as determined by GCMS-EI. The oil was purified by flash column chromatography (hexanes to 2:98 EtOAc/hexanes) to give the product as a colorless oil (0.19 g, 59%): ¹H NMR (500 MHz, CDCl₃) δ 6.79 (s, 2H), 6.77 (s, 2H), 5.06 (d, J = 6.1, 1H), 4.14 (q, J = 7.1, 1H), 4.06 (dq, J = 10.8, 7.1, 1H), 3.95 (dq, J = 14.3, 7.1, 1H), 3.49 (dd, J = 8.5, 6.0, 1H), 3.33 (t, J = 8.1, 1H), 2.63 (m, 2H), 2.41 (m, 1H and s, 6H), 2.37 (s, 6H), 2.23 (s, 6H), 1.32 (s, 3H), 1.21 (s, 3H), 1.18 (t, J = 7.1, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 173.9, 144.9, 144.5, 139.4, 139.3, 129.2, 129.0, 128.7, 127.6, 108.2, 77.9, 68.6, 60.3, 33.0, 26.4, 25.7, 25.5, 23.7, 23.5, 21.0, 20.9, 14.0; IR (thin film) 2983, 1732, 1604, 1453, 1056, 846 cm⁻¹; HRMS (CI+/NH₃) m / z calcd for C₂₈H₃₉O₄Si (M-H)⁺ 467.2617, found 467.2619. Anal. Calcd for C₂₈H₄₀O₄Si: C, 71.75; H, 8.60. Found: C, 71.47; H, 8.56. [α]²⁵_D –72.5 (*c* 0.120, CHCl₃).

Ethyl (3S,4R,5S)-5-benzyloxy-3-(dimesitylsilyl)-4-methyl-5-phenyl-pentanoate (2e). To a cooled (-78 °C) solution of Me₂Zn (0.48 mL, 0.96 mmol, 2.0 M in toluene) in 6 mL of THF was added a cooled (0 °C) solution of silvilithium 4 (0.40 g, 0.96 mmol) in 1.2 mL of THF. The solution was stirred at 0 °C for 5 min and then cooled to -78 °C. In a separate flask, MeLi (0.080 mL, 0.096 mmol, 1.2 M in Et₂O) was added to a cooled (-78 °C) slurry of CuCN (0.004 g, 0.048 mmol) in 1.2 mL of THF. The slurry was warmed to -30 °C, stirred for 5 min, cooled to -78 °C, and stirred for 5 min. The cuprate solution was added to the zincate solution, and the mixture was stirred at -78 °C for 10 min. To the mixture was added (CH₃)₃SiCl (0.38 mL, 2.9 mmol) followed by a cooled (-78 °C) solution of enoate 1e (0.30 g, 0.92 mmol) in 0.7 mL of THF. After 18 h at -78 °C, 5 mL of NH₄Cl (saturated aqueous) was added, and the mixture was warmed to 25 °C. The mixture was diluted with 50 mL of water and acidified with 3 mL of 1 N HCl. The aqueous layer was extracted with Et₂O (3 \times 30 mL). The combined organic layers were dried with MgSO₄, filtered, and concentrated in vacuo to yield a yellow oil as a 93:7 mixture of diastereomers as determined by ¹H NMR spectroscopy. The oil was purified by flash chromatography (hexanes to 0.5:99.5 EtOAc/hexanes) to give the product as a viscous, pale yellow oil (0.41 g, 76%): ¹H NMR $(500 \text{ MHz}, \text{CDCl}_3) \delta 7.34-7.22 \text{ (m, 10H)}, 6.73 \text{ (s, 2H)}, 6.72 \text{ (s, 2H)}, 5.20 \text{ (d, } J = 7.0, 1\text{H)}, 4.34 \text{ (d, } J = 7.0, 1\text{H)}, 4.34$ J = 11.4, 1H, 4.18 (d, J = 11.5, 1H), 4.03 (d, J = 9.0, 1H), 3.76 (dq, J = 14.2, 7.1, 1H), 3.51 (dq, J = 14.2, 1H), = 14.3, 7.1, 1H, 3.42 (m, 1H), 2.41 (s, 6H), 2.39 (s, 6H), 2.27 (d, <math>J = 7.2, 2H), 2.23 (s, 3H), 2.20 (s, 3H3H), 2.19 (m, 1H), 1.02 (t, J = 7.1, 3H), 0.72 (d, J = 7.0, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 173.5, 145.1, 141.4, 138.8, 129.1, 129.0, 128.9, 128.6, 128.2, 128.0, 127.9, 127.7, 127.5, 127.2, 84.0, 70.4, 60.0, 39.4, 31.5, 23.7, 23.4, 20.9, 19.8, 13.8, 12.7; IR (thin film) 3027, 2976, 1730, 1604, 1453, 840 cm⁻¹; HRMS (CI+/NH₃) m / z calcd for C₃₀H₄₇O₃Si (M-H)⁺ 591.3295, found 591.3289. Anal. Calcd for C₃₉H₄₈O₃Si: C, 79.01; H, 8.16. Found: C, 78.80; H, 8.37. [α]²⁵_D 29.9 (*c* 0.405, CHCl₃).

C. Enolate Alkylation

Ethyl $(2R^*, 3R^*, 4S^*, 5R^*)$ -5-benzyloxy-3-(dimesitylsilyl)-2,4,6-trimethyl-heptanoate (5a). To a cooled (-78 °C) solution of diisopropylamine (0.35 mL, 2.5 mmol) in 1.2 mL of THF was added n-BuLi (0.95 mL, 2.3 mmol, 2.4 M in hexanes). The solution was warmed to 0 °C for 30 min and then re-cooled to -78 °C. To the solution was added ester 2a (1.1 g, 2.0 mmol) in 2 mL of THF followed by 1.7 mL of HMPA. After 1.5h at -78 °C, MeI (1.2 mL, 20 mmol) was added. The reaction mixture was warmed to 22 °C for 18h, 5 mL of NH₄Cl (saturated aqueous) was added, and the mixture was diluted with 70 mL of MTBE. The organic layer was washed with H_2O (4 × 50 mL) and brine (4 \times 50 mL). The organic layer was dried over sodium sulfate, filtered, and concentrated in vacuo to afford a pale yellow oil as a 97:3 mixture of diastereomers as determined by GCMS-EI. The resulting oil was purified by flash column chromatography (hexanes to 0.5:99.5 EtOAc/hexanes) to afford the product as a pale yellow oil (0.96 g, 87%): ¹H NMR (500 MHz, CDCl₃) δ 7.30 (m, 4H), 7.23 (m, 1H), 6.77 (s, 2H), 6.73 (s, 2H), 5.30 (d, J = 6.1, 1H), 4.52 (d, J = 10.9, 1H), 4.45 (d, J = 11.0, 1H), 4.10 (tdd, J = 10.8, 7.1, 3.7, 2H), 3.01 (dd, J = 9.0, 2.2, J)1H), 2.97 (m, 1H), 2.73 (m, 1H), 2.47 (br s, 6H), 2.42 (br s, 6H), 2.22 (s, 3H), 2.19 (s, 3H), 2.06 (m, 1H), 1.87 (m, 1H), 1.27 (m, 6H), 1.09 (d, J = 7.0, 3H), 0.93 (d, J = 6.8, 3H), 0.64 (d, J = 6.8, 3H) 3H); ¹³C NMR (125 MHz, CDCl₃) δ 178.2, 144.5, 144.2, 139.1, 138.9, 138.6, 130.8, 129.6, 129.4, 129.0, 128.2, 127.5, 127.3, 87.8, 75.5, 60.5, 38.9, 37.0, 30.0, 28.8, 24.4, 24.0, 21.3, 21.0, 20.9, 17.4, 15.6, 14.1, 13.4; IR (thin film) 3027, 2967, 1727, 1604, 1453, 909 cm⁻¹; HRMS (CI+/NH₃) m / z

calcd for C₄₀H₅₁O₃Si (M-H)⁺ 571.3608, found 571.3611. Anal. Calcd for C₄₀H₅₂O₃Si: C, 77.57; H,

9.15. Found: C, 77.64; H, 9.34.

D. Intramolecular Hydrosilylation Reactions



(3R*)-1-Oxa-3-[(1S*,2R*)-2-benzyloxy-1,3-dimethylbutyl]-5-ethoxy-2,2-

(dimesityl)silacyclopentane (3a). To a cooled (0 °C) solution of silvl ester 2a (0.40 g, 0.72 mmol) in 5 mL of THF was added *n*-Bu₄NF (0.072 mL, 0.072 mmol, 1.0 M in THF). The solution was stirred for 5 min at 0 °C. To the mixture was added 3 mL of sodium bicarbonate (saturated aqueous) and the mixture was partitioned between 30 mL of CH_2Cl_2 and 30 mL of sodium bicarbonate (saturated aqueous). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo to yield a viscous, yellow oil as an 85:15 mixture of diastereomers as determined by GCMS-EI. The oil was purified by flash column chromatography (hexanes to 1:99 EtOAc:hexanes) to give the mixture of diastereomers as a pale yellow oil (0.33 g, 82%): Mixture: IR (thin film) 3026, 2968, 1605, 1453, 1064, 756 cm⁻¹; HRMS (CI+/NH₃) m / z calcd for C₃₆H₄₉O₃Si (M-H)⁺ 557.3451, found 557.3441. Anal. Calcd for C₃₆H₅₀O₃Si: C, 77.37; H, 9.02. Found: C, 77.10; H, 9.02. Major isomer, characteristic peaks: ¹H NMR (500 MHz, CDCl₃) δ 7.31 (m, 4H), 7.23 (m, 1H), 6.77 (s, 2H), 6.71 (s, 2H), 5.07 (m, 1H), 4.61 (d, J = 11.1, 1H), 4.56 (d, J = 11.2, 1H), 3.93 (dq, J = 9.4, 7.2, 1H), 3.51 (dq, J = 9.3, 7.0, 1H), 2.98 (t, J = 5.3, 1H), 2.41(s, 6H), 2.39 (s, 6H), 2.23 (s, 3H), 2.21 (s, 3H), 1.92 (m, 1H), 1.22 (t, J = 7.1, 3H), 0.93 (d, J = 6.8, 1.23 (s, 6H), 2.23 (s, 6H), 2.23 (s, 6H), 2.24 (3H), 0.85 (d, J = 6.8, 3H), 0.73 (d, J = 6.8, 3H); Minor product, characteristic peaks: δ 5.30 (m, 0.19H), 3.34 (m, 0.21H), 0.66 (d, J = 6.9, 0.66H); Major product: ¹³C NMR (125 MHz, CDCl₂) δ 144.0, 139.2, 139.1, 129.2, 128.9, 128.2, 127.34, 127.26, 102.0, 90.9, 75.5, 63.6, 33.9, 33.5, 31.5, 30.5, 23.82, 23.75, 21.0, 20.9, 20.7, 17.8, 15.2, 12.0; Minor product, characteristic peaks: δ 143.4, 138.6, 134.0, 131.3, 128.8, 128.2, 127.4, 127.3, 100.8, 90.8, 75.3, 62.4, 33.7, 33.6, 30.6, 29.7, 39.0, 23.4, 20.6, 14.9, 11.8.



(3S)-1-Oxa-3-[(R)-1-benzyloxy-2-methylpropyl]-5-ethoxy-2,2-(dimesityl)silacyclopentane (3b). To a cooled (-78 °C) solution of Me₂Zn (1.2 mL, 2.4 mmol, 2.0 M in toluene) in 16 mL of THF was added a cooled (0 °C) solution of silvilithium 4 (1.0 g, 2.4 mmol) in 3.0 mL of THF. The solution was warmed to 0 °C for 5 min and then re-cooled to -78 °C. In a separate flask, MeLi (0.20 mL, 0.24 mmol, 1.2 M in Et₂O) was added to a cooled (-78 °C) slurry of CuCN (0.011 g, 0.12 mmol) in 3.0 mL of THF. The slurry was warmed to -30 °C, stirred for 5 min, cooled to -78 °C, and stirred for 5 min. The cuprate solution was added to the zincate solution and the mixture was stirred at -78 °C for 10 min. To the mixture was added a cooled (-78 °C) solution of ethyl (R)-E-4-benzyloxy-5-methyl-hex-2-eneoate^{12,13} (0.60 g, 2.3 mmol) in 1.9 mL of THF. After 18h at -78 °C, 5 mL of NH₄Cl (saturated aqueous) was added, and the mixture was warmed to 25 °C and diluted with 50 mL of water. The organic layer was separated, and the aqueous layer was extracted with Et₂O (3 \times 40 mL). The combined organic layers were dried with MgSO₄, filtered, and concentrated in vacuo to yield a colorless oil as a 96:4 mixture of diastereomers as determined by ¹H NMR spectroscopy. To a cooled (0 °C) solution of the oil in 9.3 mL of THF was added *n*-Bu₄NF (0.28 mL, 0.28 mmol, 1 M in THF). The solution was stirred for 40 min at 0 °C. To the reaction mixture was added 3 mL of sodium bicarbonate (saturated aqueous) was added, and the mixture was partitioned between 30 mL of CH₂Cl₂ and 30 mL of sodium bicarbonate (saturated aqueous). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated in *vacuo* to yield a viscous, yellow oil as an 80:20 mixture of diastereomers as determined by ¹H NMR spectroscopy. The oil was purified by flash chromatography (hexanes to 0.5:99.5 EtOAc:hexanes) to give the product as a pale yellow oil (0.47 g, 63%): Mixture: IR (thin film) 3027, 2969, 1605, 1454, 1070 cm⁻¹; HRMS (CI+/NH₃) m / z calcd for C₃₁H₃₉O₃Si (M-C₃H₇)⁺ 487.2668, found 487.2667. Anal. Calcd for C₃₄H₄₆O₃Si: C, 76.93; H, 8.73. Found: C, 76.97; H, 8.79. Major isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.27 (m, 1H), 7.22 (m, 4H), 6.76 (s, 2H), 6.67

(s, 2H), 5.16 (dd, J = 5.0, 3.7, 1H), 4.37 (d, J = 10.9, 1H), 4.29 (d, J = 10.9, 1H), 3.98 (dq, J = 14.2, 7.1, 1H), 3.52 (m, 2H), 2.54 (m, 1H), 2.39 (s, 6H), 2.34 (s, 6H), 2.30 (m, 1H), 2.22 (s, 3H), 2.19 (s, 3H), 2.15 (m, 1H), 1.58 (m, 1H), 1.24 (t, J = 7.1, 3H), 0.95 (d, J = 6.8, 3H), 0.72 (d, J = 6.9, 3H); Minor isomer, characteristic peaks: δ 7.08 (d, J = 7.1, 0.58H), 6.72 (s, 0.59H), 5.32 (t, J = 4.1, 0.26H), 4.15 (d, J = 11.8, 0.30H), 3.30 (dq, J = 14.1, 7.1, 0.25H), 3.21 (dd, J = 6.5, 3.8, 0.28H), 3.14 (d, J = 11.5, 0.25H), 2.61 (m, 0.19H), 1.98 (m, 0.61H), 0.96 (m, 3.3H); Major product: ¹³C NMR (125 MHz, CDCl₃) δ 144.2, 143.3, 139.6, 139.1, 139.0, 133.9, 130.2, 129.12, 129.08, 127.9, 127.4, 126.9, 102.1, 82.8, 73.6, 63.8, 33.5, 32.8, 30.8, 23.84, 23.79, 23.2, 21.0, 20.8, 16.8, 15.3; Minor product, characteristic peaks: δ 143.8, 139.7, 138.7, 138.6, 133.7, 131.2, 128.8, 127.8, 126.69, 126.66, 101.9, 82.2, 70.8, 62.5, 34.0, 31.7, 29.7, 27.3, 24.1, 19.3, 18.5, 14.8.



(3S,4R)-1-Oxa-3-(1,2-O-(3-pentilidene)-1,2-dihydroxyethyl)-5-ethoxy-2,2-

(dimesityl)silacyclopentane (3c). To a cooled (0 °C) solution of activated 4 Å molecular sieves (0.10 g) and *n*-Bu₄NF (0.44 mL, 0.44 mmol, 1 M in THF) in 11 mL of CH₂Cl₂ was added a solution of silane ester 2c (0.66 g, 1.3 mmol) in 7.4 mL of CH₂Cl₂. The solution was warmed to 25 °C and stirred for 3 h. To the reaction solution was added 3 mL of sodium carbonate (saturated aqueous), and the mixture was partitioned between 50 mL of CH₂Cl₂ and 90 mL of sodium carbonate (saturated aqueous). The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 40 mL). The combined organic layers were filtered through sodium sulfate and concentrated *in vacuo* to yield a colorless oil as an 80:20 mixture of diastereomers as determined by GCMS-CI/NH₄Cl. The oil was purified by flash chromatography (hexanes to 3:97 EtOAc:hexanes) to give each diastereomer as a colorless oil (0.60 g, 91%, combined yield): Mixture: IR (thin film) 3025, 2880, 2246, 1605, 1455, 1075, 980, 734 cm⁻¹; HRMS (LSIMS) *m* / *z* calcd for C₃₀H₄₄O₄Si (M-H)⁺ 495.2931, found 495.2927. Major isomer: ¹H NMR (500 MHz, CDCl₃) δ 6.76 (s, 2H); 6.72 (s, 2H); 5.22 (dd, *J* = 5.3, 1.0, 1H), 4.32 (ddd, *J* = 10.8, 8.8, 5.6, 1H), 3.90 (dq, *J* = 9.1, 7.0, 1H), 3.49 (dq, *J* = 9.1, 7.1, 1H), 3.11 (t, *J* = 7.8, 1H), 2.97 (dd, *J* = 7.7, 5.6,

1H), 2.58 (m, 1H), 2.41 (s, 6H), 2.34 (s, 6H), 2.22 (d, J = 5.0, 6H and m, 1H), 2.08 (ddd, J = 10.8, 6.5, 2.2, 1H), 1.57 (m, 2H), 1.49 (m, 2H), 1.19 (t, J = 7.0, 3H), 0.87 (t, J = 7.5, 3H), 0.83 (t, J = 7.5, 3H); ¹³C NMR (125 MHz CDCl₃) δ 143.9, 143.2, 139.6, 139.3, 132.6, 129.5, 129.23, 129.19, 110.9, 102.2, 77.3, 69.4, 63.6, 34.4, 31.7, 30.4, 29.7, 23.3, 21.0, 20.9, 15.0, 8.05, 8.00; Minor isomer: ¹H NMR (500 MHz, CDCl₃) δ 6.76 (s, 2H), 6.70 (s, 2H), 5.37 (dd, J = 5.9, 4.2, 1H), 3.89 (m, 1H), 3.64 (dq, J = 9.6, 7.1, 1H), 3.42 (m, 3H), 2.47 (m, 1H), 2.40 (s, 6H), 2.33 (m, 1H), 2.29 (s, 6H), 2.21 (d, J = 5.0, 6H), 2.02 (m, 1H), 1.57 (m, 2H), 1.33 (q, J = 7.5, 2H), 1.03 (t, J = 7.0, 3H), 0.87 (t, J = 7.4, 3H), 0.59 (t, J = 7.4, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 143.6, 143.0, 139.2, 138.9, 132.8, 130.2, 129.0, 128.9, 111.9, 101.3, 77.2, 76.5, 69.2, 63.2, 34.3, 30.4, 30.0, 29.2, 23.6, 23.3, 23.0, 20.94, 20.93, 14.9, 8.1, 7.8.



(3*R**)-1-Oxa-3-[(1*S**,2*R**)-2-(*tert*-butyl-dimethylsiloxy)-1,3-dimethylbutyl]-5-ethoxy-2,2-(dimesityl)silacyclopentane (3d). To a cooled (-78 °C) solution of Me₂Zn (0.50 mL, 0.99 mmol, 2.0 M in toluene) in 6.6 mL of THF was added a cooled (0 °C) solution of silyllithium 4 (0.44 g, 1.0 mmol) in 1.0 mL of THF. The solution was warmed to 0 °C for 5 min and then cooled to -78 °C. In a separate flask, MeLi (0.085 mL, 0.1 mmol, 1.2 M in Et₂O) was added to a cooled (-78 °C) slurry of CuCN (0.006 g, 0.05 mmol) in 1.3 mL of THF. The slurry was warmed to -30 °C, stirred for 5 min, cooled to -78 °C, and stirred for 5 min. The cuprate solution was added to the zincate solution and the mixture was stirred at -78 °C for 10 min. To the reaction solution was added (CH₃)₃SiCl (0.40 mL, 3.0 mmol) followed by a cooled (-78 °C) solution of enoate 1d (0.30 g, 0.95 mmol) in 0.6 mL of THF. After 18h at -78 °C, 5 mL of NH₄Cl (saturated aqueous) was added, and the mixture was warmed to 25 °C and diluted with 50 mL of water. The aqueous layer was extracted with Et₂O (3 × 30 mL). The combined organic layers were dried with MgSO₄, filtered, and concentrated *in vacuo* to yield a colorless oil as a 96:4 mixture of diastereomers as determined by GCMS-EI. To a cooled (0 °C) solution of the oil in 3.4 mL of THF was added *n*-Bu₄NF (0.10 mL, 0.10 mmol, 1 M in THF). The solution was stirred for 40 min at 0 °C. To the solution was added 3 mL of sodium bicarbonate (saturated aqueous) and the mixture was partitioned between 30 mL of CH_2Cl_2 and 30 mL of sodium bicarbonate (saturated aqueous). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to yield a viscous, yellow oil as an 83:17 mixture of diastereomers as determined by GCMS-EI. The oil was purified by flash chromatography (hexanes to 5:95 CH_2Cl_2 :hexanes) to give the product as a pale yellow oil (0.19 g, 63%): ¹H NMR (500 MHz, CDCl₃) δ 6.78 (s, 2H), 6.72 (s, 2H), 5.08 (m, 1H), 3.96 (dq, *J* = 14.2, 7.1, 1H), 3.53 (dq, *J* = 14.2, 7.1, 1H), 3.33 (dd, *J* = 6.8, 2.1, 1H), 2.44 (m, 1H), 2.42 (s, 6H), 2.41 (s, 6H), 2.24 (s, 3H), 2.23 (s, 3H), 2.15 (dd, *J* = 10.6, 5.2, 1H), 2.01 (m, 2H), 1.81 (dtd, *J* = 13.6, 6.8, 2.1, 1H), 1.24 (t, *J* = 7.0, 3H), 0.90 (s, 9H), 0.86 (d, *J* = 6.9, 3H), 0.83 (d, *J* = 6.7, 3H), 0.65 (d, *J* = 6.8, 3H), 0.04 (s, 3H), 0.01 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 144.0, 143.4, 139.1, 139.0, 134.0, 131.7, 129.2, 128.9, 101.8, 81.7, 63.6, 34.6, 33.1, 31.6, 30.8, 26.4, 23.9, 23.8, 21.2, 21.01, 20.95, 18.7, 16.1, 15.2, 13.5, -3.2, -3.3; IR (thin film) 3024, 2954, 1606, 1462, 1045 cm⁻¹; HRMS (CI+/NH₃) *m* / *z* calcd for C₃₅H₅₇O₃Si₂ (M-H)⁺ 581.3846, found 581.3850. Anal. Calcd for C₃₅H₅₅O₃Si₂: C, 72.10; H, 10.03. Found: C, 72.18; H, 10.11.



(3S)-1-Oxa-3-[(1R,2S)-2-benzyloxy-1-methyl-2-phenyl-ethyl]-5-ethoxy-2,2-

(dimesityl)silacyclopentane (3e). To a cooled (0 °C) solution of silyl ester 2e (0.19 g, 0.32 mmol) in 2 mL of THF was added *n*-Bu₄NF (0.032 mL, 0.032 mmol, 1 M in THF). The solution was stirred for 30 min at 0 °C. To the reaction mixture was added 3 mL of sodium carbonate (saturated aqueous) and the mixture was partitioned between 30 mL of CH_2Cl_2 and 30 mL of sodium bicarbonate (saturated aqueous). The organic layer was separated, and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to yield a pale yellow oil as an 85:15 mixture of diastereomers as determined by ¹H NMR spectroscopy. The oil was purified by flash column chromatography (hexanes to 0.5:99.5 EtOAc:hexanes) to give the mixture of diastereomers as a

pale yellow oil (0.15 g, 79%): Mixture: IR (thin film) 3027, 2972, 1604, 1453, 1064, 908 cm⁻¹; HRMS (TOF MS ES+/Na) *m* / *z* calcd for $C_{39}H_{48}O_3SiNa$ (M+Na)⁺ 615.3270, found 615.3262. Anal. Calcd for $C_{39}H_{48}O_3Si$: C, 79.01; H, 8.16. Found: C, 78.82; H, 8.42. Major isomer, characteristic peaks: ¹H NMR (500 MHz, CDCl₃) δ 7.34-7.23 (m, 10H), 6.76 (s, 2H), 6.65 (s, 2H), 5.07 (dd, *J* = 8.2, 4.0, 1H), 4.41 (d, *J* = 11.9, 1H), 4.13 (d, *J* = 11.9, 1H), 3.95 (m, 2H), 3.53 (m, 1H), 2.78 (m, 1H), 2.38 (s, 6H), 2.37 (br s, 6H), 2.22 (s, 3H), 2.15 (s, 3H), 1.22 (t, *J* = 7.1, 3H), 0.32 (d, *J* = 6.9, 3H); Minor product, characteristic peaks: δ 5.31 (m, 0.17H), 4.15 (d, *J* = 12.0, 0.24H), 3.33 (dq, *J* = 14.1, 7.1, 0.17H), 3.15 (m, 0.15H), 0.95 (t, *J* = 7.1, 0.61H); Major product: ¹³C NMR (125 MHz, CDCl₃) δ 144.0, 143.9, 141.7, 139.0, 138.9, 138.8, 133.8, 131.7, 129.12, 128.8, 128.24, 128.19, 127.64, 127.5, 127.3, 102.1, 85.3, 70.6, 63.7, 38.4, 32.8, 28.0, 23.6, 20.9, 15.3, 13.2; Minor product, characteristic peaks: δ 141.8, 138.7, 138.4, 133.5, 129.06, 128.6, 128.15, 127.67, 127.2, 101.0, 85.7, 70.7, 62.1, 38.7, 33.0, 29.7, 24.6, 23.2, 15.0, 13.5.



($3R^*, 4R^*$)-1-Oxa-3-[($1S^*, 2R^*$)-2-benzyloxy-1,3-dimethylbutyl]-5-ethoxy-4-methyl-2,2-(dimesityl)silacyclopentane (6a). To a cooled (0 °C) solution of ester 5a (0.96 g, 1.7 mmol) in 11 mL of THF was added *n*-Bu₄NF (0.17 mL, 0.17 mmol, 1.0 M in THF). After 45 min at 0 °C, additional *n*-Bu₄NF (0.17 mL, 0.17 mmol, 1.0 M in THF) was added, and the solution was stirred for 1h at 0 °C. To the solution was added 3 mL of sodium bicarbonate (saturated aqueous) and the THF was removed *in vacuo*. The resulting oil was partitioned between 30 mL of CH₂Cl₂ and 30 mL of sodium bicarbonate (saturated aqueous). The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (3 × 30 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to yield a viscous, yellow oil as an 84:16 mixture of diastereomers as determined by GCMS-EI. The oil was purified by flash chromatography (hexanes to 0.5:99.5 EtOAc:hexanes) to give the mixture of diastereomers as a pale yellow oil (0.86 g, 90%): Mixture: IR (thin film) 3025, 2971, 1605, 1452, 977 cm⁻¹; HRMS (TOF MS ES+/Na) *m* / *z* calcd for C₁₇H₅₂O₃SiNa (M+Na)⁺ 595.3583, found 595.3580. Major isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.29 (m, 3H), 7.21 (m, 2H), 6.73 (s, 2H), 6.71 (s, 2H), 5.01 (d, *J* = 4.3, 1H), 4.30 (d, *J* = 11.8, 1H), 4.07 (m, 1H), 3.89 (dq, *J* = 14.2, 7.1, 1H), 3.50 (dq, *J* = 14.0, 7.0, 1H), 3.08 (t, *J* = 5.1, 1H), 2.41 (s, 6H), 2.31 (br s, 6H and m, 1H), 2.22 (s, 3H), 2.21 (s, 3H), 2.11 (dd, *J* = 7.8, 5.6, 1H), 1.96 (dq, *J* = 13.5, 6.5, 1H), 1.20 (t, *J* = 7.1, 3H), 1.13 (d, *J* = 7.1, 3H), 1.05 (d, *J* = 6.9, 3H), 0.95 (m, 1H), 0.90 (d, *J* = 6.7, 3H), 0.84 (d, *J* = 6..9, 3H); minor product, characteristic peaks: δ 4.59 (m, 0.29H), 4.54 (d, *J* = 11.2, 0.19H), 4.51 (d, *J* = 11.0, 0.19H), 3.69 (dq, *J* = 14.1, 7.0, 0.16H), 3.45 (m, 0.12H), 3.38 (dd, *J* = 8.9, 2.1, 0.21H), 3.18 (m, 0.10H); major product, characteristic peaks: ¹³C NMR (125 MHz, CDCl₃) δ 139.7, 138.75, 138.72, 133.9, 129.4, 128.3, 128.1, 127.3, 127.2, 126.5, 102.9, 89.0, 88.8, 63.7, 40.0, 35.3, 31.4, 23.6, 21.05, 20.99, 20.4, 18.4, 15.1, 14.6; minor product, characteristic peaks: δ 106.4, 75.7, 74.6, 63.2, 42.1, 36.3, 32.8, 30.1, 21.3, 16.2, 15.7, 12.7.

E. Lewis acid-mediated Nucleophilic Substitution Reactions



(3*R**,5*S**)-1-Oxa-3-[(1*S**,2*R**)-2-benzyloxy-1,3-dimethylbutyl]-5-(3-propenyl)-2,2-

(dimesityl)silacyclopentane. To a cooled (-78 °C) solution of acetal **3a** (0.23 g, 0.41 mmol) in 14 mL of CH₂Cl₂ was added allyltrimethylsilane (0.13 mL, 0.82 mmol) followed by BF₃•OEt₂ (0.052 mL, 0.41 mmol). The solution was warmed to 22 °C for 2h, and 10 mL of sodium bicarbonate (saturated aqueous) was added. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (3×50 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to yield a colorless oil as a >99:1 mixture of diastereomers as determined by GCMS-EI. The oil was purified by flash column chromatography (hexanes to 0.5:99.5 EtOAc:hexanes) to give the product as a viscous oil (0.21 g, 91%): ¹H NMR (500 MHz, CDCl₃) δ 7.33 (m, 5H), 6.73 (s, 2H), 6.71 (s, 2H), 5.76 (ddt, *J* = 17.1, 10.1, 6.9, 1H), 4.97 (m, 2H), 4.62 (s, 2H), 4.16 (m, 1H), 2.88 (m, 1H), 2.38 (s, 6H), 2.34 (br s, 6H), 2.29-2.11 (m, 4H), 2.22 (s, 3H), 2.21 (s, 3H), 1.94 (m, 1H), 1.80 (dq, *J* = 13.2, 6.6, 1H), 1.68 (m, 1H), 0.88 (d, *J* = 6.6, 3H), 0.78 (d, *J* = 6.9, 3H), 0.62 (d, *J* = 6.8, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 139.3, 138.9,

138.6, 135.7, 134.0, 131.7, 129.1, 128.9, 127.3, 127.2, 116.1, 90.5, 75.5, 75.4, 42.7, 34.0, 32.7, 31.2, 30.2, 23.7, 20.98, 20.95, 19.9, 18.4, 11.9; IR (thin film) 2963, 1605, 1453, 1067 cm⁻¹; HRMS (TOF MS ES+/Na) m / z calcd for $C_{37}H_{50}O_2SiNa$ (M+Na)⁺ 577.3478, found 577.3480. Anal. Calcd for $C_{37}H_{50}O_2Si$: C, 80.09; H, 9.08. Found: C, 79.90; H, 9.25.



(3*R**,5*S**)-1-Oxa-3-[(1*S**,2*R**)-2-(*tert*-butyl-dimethylsiloxy)-1,3-dimethylbutyl]-5-(3-

propenyl)-2,2-(dimesityl)silacyclopentane. To a cooled solution (-78 °C) of acetal 3d (0.15 g, 0.26 mmol) in 8.7 mL of CH₂Cl₂ was added allyltrimethylsilane (0.083 mL, 0.52 mmol) followed by BF₃•OEt₂ (0.033 mL, 0.26 mmol). The solution was warmed to 0 °C for 1 h and quenched with 10 mL of sodium bicarbonate (saturated aqueous). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 30 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo to yield a colorless oil as a >99:1 mixture of diastereomers as determined by GCMS-EI. The oil was purified by flash chromatography (hexanes to 0.5:99.5 CH₂Cl₂:hexanes) to give the product, a viscous oil, as a single diastereomer as determined by ¹H NMR spectroscopy (0.13 g, 87%): ¹H NMR (500 MHz, CDCl₂) δ 6.78 (s, 2H), 6.76 (s, 2H), 5.82 (ddt, J = 17.3, 10.2, 7.0, 1H), 5.01 (m, 2H), 4.21 (m, 1H), 3.29 (t, J = 3.9, 1H), 2.46 (s, 6H), 2.39 (br s, 6H), 2.26 (s, 3H), 2.25 (s, 3H and m, 1H), 2.20 (m, 3H), 1.86 (m, 1H), 1.69 (dt, J = 15.6, 7.0, 1H), 1.49 (m, 1H), 0.94 (s, 9H), 0.77 (d, J = 5.3, 3H), 0.75 (d, J = 5.1, 3H), 0.69(d, J = 6.9, 3H), 0.11 (s, 3H), 0.10 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 143.8, 143.3, 138.8, 138.6, 135.7, 134.0, 131.8, 129.0, 128.9, 116.1, 81.8, 75.4, 42.7, 35.0, 32.8, 32.5, 31.0, 26.3, 23.8, 23.1, 21.01, 20.97, 20.5, 18.7, 16.9, 13.1, -3.2, -3.4; IR (thin film) 2957, 2856, 1605, 1472, 1048 cm⁻¹ ¹; HRMS (CI+/NH₃) m / z calcd for C₃₃H₅₁O₂Si₂ (M-C₃H₇)⁺ 535.3427, found 535.3427. Anal. Calcd for C₃₆H₅₈O₂Si₂: C, 74.68; H, 10.10. Found: C, 74.90; H, 10.23.



(3S,5R)-1-Oxa-3-[(1R,2S)-2-benzyloxy-1-methyl-2-phenyl-ethyl]-5-(3-propenyl)-2,2-

(dimesityl)silacyclopentane. To a cooled (-78 °C) solution of acetal 3e (0.14 g, 0.24 mmol) in 8 mL of CH₂Cl₂ was added allyltrimethylsilane (0.076 mL, 0.48 mmol) followed by BF₃•OEt₂ (0.030 mL, 0.24 mmol). After the solution was warmed to 22 °C for 2h, 5 mL of sodium bicarbonate (saturated aqueous) was added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 40 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo to yield a pale yellow oil as a 99:1 mixture of diastereomers as determined by ¹H NMR spectroscopy. The oil was purified by flash column chromatography (hexanes to 0.5:99.5 EtOAc:hexanes) to give the product as a pale yellow oil (0.12 g, 86%): ¹H NMR (500 MHz, CDCl₃) δ 7.35-7.24 (m, 10H), 6.71 (s, 2H), 6.66 (s, 2H), 5.75 (ddt, J = 17.0, 10.4, 7.0, 1H, 4.95 (m, 2H), 4.42 (d, J = 12.0, 1H), 4.22 (m, 1H), 4.14 (d, J = 11.9, 1H), 4.04 (d= 7.6, 1H), 2.84 (m, 1H), 2.34 (s, 6H), 2.28 (br s, 6H), 2.21 (s, 3H and m, 1H), 2.17 (s, 3H), 2.15-2.03 (m, 3H), 1.68 (m, 1H), 0.42 (d, J = 7.0, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 143.6, 141.6, 138.9, 138.6, 138.5, 135.9, 133.8, 132.1, 128.9, 128.8, 128.17, 128.15, 127.51, 127.46, 127.36, 127.2, 85.8, 76.2, 70.7, 42.7, 39.2, 31.4, 25.3, 23.8, 22.7, 20.99, 20.95, 13.8; IR (thin film) 3027, 2927, 1604, 1453, 1065, 909 cm⁻¹; HRMS (TOF MS ES+/Na) m / z calcd for C₄₀H₄₈O₂SiNa (M+Na)⁺ 611.3322, found 611.3318. Anal. Calcd for C₄₀H₄₈O₂Si: C, 81.58; H, 8.22. Found: C, 81.31; H, 8.39. $[\alpha]_{D}^{25}$ –213.1 (*c* 0.130, CHCl₃).



(3R*,4R*,5S*)-1-Oxa-3-[(1S*,2R*)-2-benzyloxy-1,3-dimethylbutyl]-4-methyl-5-(3-

propenyl)-2,2-(dimesityl)silacyclopentane. To a cooled (-78 °C) solution of acetal 6a (0.86 g, 1.5 mmol) in 50 mL of CH₂Cl₂ was added allyltrimethylsilane (0.48 mL, 3.0 mmol) followed by BF₃•OEt₂ (0.19 mL, 1.5 mmol). The solution was warmed to 0 °C for 1.5 h, and 10 mL of sodium bicarbonate (saturated aqueous) was added. The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated in vacuo to yield a pale yellow oil as a 98:2 mixture of diastereomers as determined by GCMS-EI. The oil was purified by flash chromatography (hexanes to 0.5:99.5 EtOAc:hexanes) to give the product as a colorless, viscous oil (0.71 g, 84%): ¹H NMR (500 MHz, CDCl₃) δ 7.29 (m, 5H), 6.71 (m, 4H), 5.77 (ddt, J = 17.0, 10.1, 6.8, 1H), 4.93 (m, 2H), 4.57 (s, 2H), 3.99 (m, 1H), 3.39 (dd, J = 9.1, 2.2, 1H), 2.38 (m, 12H), 2.20 (s, 3H), 2.19 (s, 2H), 2.20 (s, 2H), 2.23H), 2.15 (m, 4H), 1.92 (dt, J = 14.3, 7.2, 1H), 1.85 (m, 1H), 1.25 (d, J = 7.2, 3H), 1.01 (d, J = 7.2, 2H), 1.01 3H), 0.99 (d, J = 6.9, 3H), 0.89 (d, J = 6.9, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 139.1, 138.8, 138.4, 135.9, 133.6, 130.8, 128.2, 127.4, 127.3, 115.8, 88.9, 81.4, 76.0, 41.5, 40.4, 37.2, 32.8, 30.1, 22.9, 21.2, 21.0, 20.9, 16.6, 15.5, 15.1; IR (thin film) 3026, 2964, 1605, 1453, 758 cm⁻¹; HRMS (TOF MS ES+/Na) *m* / *z* calcd for $C_{38}H_{52}O_2SiNa$ (M+Na)⁺ 591.3634, found 591.3628.

F. Oxidation of C-Si Bond



 $(3R^*,4S^*,5R^*,7S^*)$ -3-benzyloxy-2,4-dimethyl-dec-9-ene-5,7-diol (7a). To a mixture of CsOH•H₂O (0.76 g, 4.7 mmol) in 5.2 mL of NMP was added *tert*-butylhydroperoxide (0.53 mL, 3.8 mmol, 70% aqueous). A solution of $(3R^*,5S^*)$ -1-oxa-3-[($1S^*,2R^*$)-2-benzyloxy-1,3-dimethylbutyl]-5-(3-propenyl)-2,2-(dimesityl)silacyclopentane (0.26 g, 0.47 mmol) in 2.9 mL of NMP was added, followed by CsF (0.37 g, 2.6 mmol). After 10h, 15 mL of Na₂S₂O₃ (saturated aqueous) was added. The mixture was diluted with 100 mL of MTBE and washed with H₂O (4

× 30 mL) and brine (3 × 30 mL). The organic layer was dried over sodium sulfate, filtered, and concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (10:90 EtOAc/hexanes) to yield the product as a yellow oil (0.097 g, 69%): ¹H NMR (500 MHz, CDCl₃) δ 7.33 (m, 4H), 7.26 (m, 1H), 5.80 (ddt, *J* = 17.4, 10.4, 7.2, 1H), 5.10 (m, 2H), 4.63 (q, *J* = 11.4, 2H), 3.97 (m, 1H), 3.89 (tt, *J* = 8.0, 4.0, 1H), 3.50 (d, *J* = 4.2, 1H), 3.45 (dd, *J* = 7.4, 2.5, 1H), 2.95 (d, *J* = 3.3, 1H), 2.25 (m, 2H), 1.94 (dq, *J* = 13.6, 6.8, 1H), 1.87 (m, 1H), 1.65 (m, 2H), 1.05 (d, *J* = 6.7, 3H), 0.91 (d, *J* = 6.8, 3H), 0.85 (d, *J* = 7.0, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 138.9, 134.7, 128.3, 127.6, 127.4, 117.7, 85.5, 73.9, 71.3, 68.3, 42.0, 40.0, 39.6, 30.6, 20.2, 19.6, 11.3; IR (thin film) 3406, 3030, 2958, 1641, 1454, 1068 cm⁻¹; HRMS (CI+/NH₃) *m* / *z* calcd for C₁₉H₃₁O₃ (M+H)⁺ 307.2273, found 307.2274. Anal. Calcd for C₁₉H₃₀O₃: C, 74.47; H, 9.87. Found: C, 74.88; H, 10.02.



(3*R**,4*S**,5*R**,7*S**)-2,4-dimethyl-dec-9-ene-3,5,7-triol (7d). From 7a: To a cooled (–78 °C) flask containing ~5 mL of condensed ammonia was added Na⁰ metal (0.015 g, 0.64 mmol) until the solution retained a blue color. After 10 min at –78 °C, a solution of diol 7a (0.050 g, 0.16 mmol) in 2 mL of THF was added. If the blue color faded, more Na⁰ metal (0.015 g, 0.64 mmol) was added. After 10 min at –78 °C, 5 mL of MeOH was added and the mixture was stirred for 30 min at –78 °C. The mixture was warmed to 25 °C, stirred for 30 min, and partitioned between 10 mL of NaH₂PO₄ (saturated aqueous) and 20 mL of CH₂Cl₂. The organic layer was separated and the aqueous layer was extracted with CH₂Cl₂ (2 × 20 mL). The combined organic layers were dried over sodium sulfate, filtered, and concentrated *in vacuo* to yield a yellow oil. The resulting oil was purified by flash column chromatography.(10:90 to 30:70 EtOAc/hexanes) to yield the product as a yellow oil (0.035 g, >99%): ¹H NMR (500 MHz, CDCl₃) δ 5.83 (ddt, *J* = 17.4, 10.4, 7.0, 1H), 5.15 (m, 2H), 4.00 (m, 2H), 3.83 (br s, 1H), 3.57 (d, *J* = 8.6, 1H), 3.06 (br s, 1H), 2.93 (br s, 1H), 2.30 (t, *J* = 6.7, 2H), 1.85 (ddd, *J* = 13.7, 9.9, 3.0, 1H), 1.69 (m, 2H), 1.55 (ddd, *J* = 14.3, 8.0, 2.3, 1H), 1.02 (d, *J* = 6.5, 3H), 0.96 (d, *J* 7.1, 3H), 0.81 (d, *J* = 6.6, 3H); ¹³C NMR (125 MHz, CDCl₃)

δ 134.7, 118.1, 77.0, 72.7, 68.4, 41.8, 40.4, 39.0, 31.2, 19.8, 18.9, 10.2; IR (thin film) 3362, 2963, 1641, 1462, 1070 cm⁻¹; HRMS (CI+/NH₃) *m* / *z* calcd for C₁₂H₂₅O₃ (M+H)⁺ 217.1804, found 217.1800. Anal. Calcd for C₁₂H₂₄O₃: C, 66.63; H, 11.18. Found: C, 66.87; H, 11.20. *From* (3*R**,5*S**)-1-Oxa-3-[(1*S**,2*R**)-2-(tert-butyl-dimethylsiloxy)-1,3-dimethylbutyl]-5-(3-propenyl)-2,2-(dimesityl)silacyclopentane: To a mixture of CsOH•H₂O (0.36 g, 2.1 mmol) in 2.3 mL of

NMP was added cumene hydroperoxide (0.30 mL, 1.7 mmol, 88% aqueous). A solution of $(3R^*, 5S^*)$ -1-oxa-3-[$(1S^*, 2R^*)$ -2-(*tert*-butyl-dimethylsiloxy)-1,3-dimethylbutyl]-5-(3-propenyl)-

2,2-(dimesityl)silacyclopentane (0.12 g, 0.21 mmol) in 1.5 mL of NMP was added, followed by CsF (0.19 g, 1.2 mmol). After 18h, solid Na₂S₂O₃ (0.30 g) was added and stirred for 2h. The mixture was diluted with 20 mL of CH₂Cl₂, filtered through a fritted glass funnel, and washed with CH₂Cl₂ (2 × 20 mL). The solution was concentrated *in vacuo*, and the remaining NMP was removed by bulb-to-bulb distillation (60 °C/0.1 Torr). The resulting oil was purified by flash column chromatography (10:90 to 30:70 EtOAc/hexanes) to yield the product as a yellow oil (0.036 g, 80%): ¹H NMR (500 MHz, CDCl₃) δ 5.83 (ddt, *J* = 17.5, 10.4, 7.1, 1H), 5.14 (m, 2H), 3.99 (br s, 2H), 3.87 (br s, 1H), 3.56 (d, *J* = 9.2, 1H), 3.11 (br s, 1H), 2.96 (br s, 1H), 2.30 (t, *J* = 6.8, 2H), 1.85 (m, 1H), 1.68 (m, 2H), 1.56 (m, 1H), 1.02 (d, *J* = 6.5, 3H), 0.96 (dd, *J* = 7.9, 1.9, 3H), 0.82 (d, *J* = 6.7, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 134.7, 118.0, 77.0, 72.6, 68.4, 41.8, 40.4, 38.9, 31.1, 19.8, 18.9, 10.2; HRMS (CI+/NH₃) *m* / *z* calcd for C₁₂H₂₅O₃ (M+H)⁺ 217.1804, found 217.1794.





(3*R**,4*S**,5*R**,7*S**)-2,4-dimethyl-dec-9-ene-3,5,7-triol (7d) Note: Removal of the benzyl group of protected triol 7a by dissolving metal reduction leads to triol 7d. This is spectroscopically identical to the triol obtained from oxidation of oxasilacyclopentane derived from 3d (despite containing an unknown contaminant).



(1*S*,2*S*,3*S*,5*R*)-1-benzyloxy-2-methyl-1-phenyl-oct-7-ene-3,5-diol (7e). To a mixture of CsOH•H₂O (1.6 g, 9.3 mmol) in 10 mL of NMP was added cumenehydroperoxide (1.2 mL, 7.4 mmol, 88% aqueous). A solution of (3S,5R)-1-Oxa-3-[(1R,2S)-2-benzyloxy-1-methyl-2-phenylethyl]-5-(3-propenyl)-2,2-(dimesityl)silacyclopentane (0.55 g, 0.93 mmol) in 4.7 mL of NMP was added, followed by CsF (0.77 g, 5.1 mmol). After 10 h, 15 mL of Na₂S₂O₃ (saturated aqueous) was added and the mixture was stirred for 1h. The mixture was diluted with 50 mL of H₂O and extracted with MTBE (3×50 mL). The organic layer was washed with H₂O (4×30 mL) and brine (3 \times 30 mL). The organic layer was dried over sodium sulfate, filtered, and concentrated *in* vacuo. The resulting oil was purified by flash column chromatography (10:90 EtOAc/hexanes) to yield the product as a yellow oil (0.17 g, 53%): ¹H NMR (500 MHz, CDCl₃) δ 7.34 (m, 10H), 5.82 (ddt, J = 17.2, 10.1, 7.1, 1H), 5.07 (m, 2H), 4.99 (br s, 1H), 4.37 (d, J = 11.5, 1H), 4.24 (d, J = 9.3, 1H)1H), 4.20 (d, J = 11.5, 1H), 4.02 (m, 2H), 3.61 (br s, 1H), 2.31 (dt, J = 13.9, 7.0, 1H), 2.22 (dt, J = 13.9, 7.0, 1H), 2.23 (dt, J = 13.9, 7.0, 1H), 2 13.4, 6.7, 1H), 2.11 (m, 1H), 1.67 (m, 2H), 0.52 (d, J = 6.9, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 139.9, 137.2, 135.1, 128.44, 128.42, 128.1, 127.9, 127.8, 117.2, 87.8, 74.0, 70.4, 68.0, 44.1, 42.0, 38.6, 12.9; IR (thin film) 3421, 3030, 2922, 1641, 1453, 1061 cm⁻¹; HRMS (CI+/NH₃) m / z calcd for C₂₂H₂₉O₃ (M+H)⁺ 341.2117, found 341.2109. Anal. Calcd for C₂₂H₂₈O₃: C, 77.61; H, 8.29. Submitted. $[\alpha]_{D}^{25}$ -69.6 (*c* 0.135, CHCl₃).



 $(3R^*,4S^*,5R^*,6R^*,7S^*)$ -3-benzyloxy-2,4,6-trimethyl-dec-9-ene-5,7-diol (8a). To a mixture of CsOH•H₂O (2.1 g, 12 mmol) in 14 mL of NMP was added *tert*-butylhydroperoxide (1.4 mL, 9.8 mmol, 70% aqueous). A solution of $(3R^*,4R^*,5S^*)$ -1-oxa-3-[$(1S^*,2R^*)$ -2-benzyloxy-1,3-dimethylbutyl]-4-methyl-5-(3-propenyl)-2,2-(dimesityl)silacyclopentane (0.69 g, 1.2 mmol) in 6.2 mL of NMP was added, followed by CsF (1.0 g, 6.8 mmol). After 10 h at 70 °C, 15 mL of Na₂S₂O₃ (saturated aqueous) was added. The mixture was diluted with 100 mL of MTBE and

washed with H_2O (4 × 30 mL) and brine (3 × 30 mL). The organic layer was dried over sodium sulfate, filtered, and concentrated *in vacuo* to yield a colorless oil. The resulting oil was purified by flash column chromatography (10:90 EtOAc/hexanes) to yield the product as a yellow oil (0.32 g, 84%): ¹H NMR (500 MHz, CDCl₃) δ 7.36 (m, 4H), 7.28 (m, 1H), 5.80 (m, 1H), 5.11 (m, 2H), 4.80 (d, *J* = 11.5, 1H), 4.65 (d, *J* = 11.6, 1H), 4.02 (d, *J* = 10.1, 1H), 3.68 (dq, *J* = 9.2, 4.6, 1H), 3.45 (dd, *J* = 8.1, 1.9, 1H), 3.29 (s, 1H), 2.53 (d, *J* = 4.2, 1H), 2.30 (m, 2H), 1.92 (m, 2H), 1.65 (m, 1H), 1.09 (d, *J* = 6.6, 3H), 1.01 (d, *J* = 7.1, 3H), 0.91 (d, *J* = 6.8, 3H), 0.77 (d, *J* = 7.0, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 139.1, 135.0, 128.3, 127.6, 127.3, 117.6, 85.4, 75.5, 74.5, 71.3, 40.1 37.4, 37.0, 30.7, 20.2, 20.1, 10.2, 10.1; IR (thin film) 3386, 3030, 2971, 1641, 1454, 1068 cm⁻¹; HRMS (CI+/NH₃) *m* / *z* calcd for C₁₇H₂₇O₃ (M-C₃H₅)⁺ 279.1960, found 279.1957. Anal. Calcd for C₂₀H₃₂O₃: C, 74.96; H, 10.06. Found: C, 75.94; H, 9.96.

G. Reactions of 1,3-Diols



(4*S**,6*R**)-4-Allyl-6-[(1*S**,2*R**)-2-benzyloxy-1,3-dimethyl-butyl]-2,2-dimethyl-1,3dioxane. To a solution of diol 7a (0.034 g, 0.11 mmol) and 2,2-dimethoxypropane (1.5 mL, 12 mmol) in 1 mL of acetone was added CSA (<0.005 g). After 5 min, a few drops of Et₃N were added. The solution was concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (hexanes to 0.5:99.5 EtOAc/hexanes) to yield the product as a colorless oil (0.034 g, 89%): ¹H NMR (500 MHz, CDCl₃) δ 7.33 (m, 4H), 7.25 (m, 1H), 5.80 (ddt, *J* = 17.1, 10.8, 6.8, 1H), 5.07 (m, 2H), 4.62 (s, 2H), 3.84 (dq, *J* = 9.2, 6.3, 1H), 3.77 (ddd, *J* = 9.0, 6.2, 1H), 3.41 (dd, *J* = 8.1, 1.9, 1H), 2.30 (dt, *J* = 13.8, 6.9, 1H), 2.19 (dt, *J* = 13.7, 7.0, 1H), 1.89 (dq, *J* = 13.6, 6.8, 1H), 1.73 (m, 1H), 1.63 (m, 2H), 1.34 (s, 3H), 1.31 (s, 3H), 1.02 (d, *J* = 6.7, 3H), 0.90 (d, *J* = 6.9, 3H), 0.88 (d, *J* = 7.0, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 139.7, 134.6, 128.2, 127.1, 127.0, 116.7, 100.2, 83.6, 74.2, 68.1, 66.3, 41.4, 40.2, 36.9, 31.6, 25.2, 25.1, 19.8, 19.7, 8.9; IR (thin film) 3067, 2981, 1642, 1454, 1377, 1224 cm⁻¹; HRMS (CI+/NH₃) *m* / *z* calcd for C₂₁H₃₁O₃ (M-CH₃)⁺ 331.2273, found 331.2273. Anal. Calcd for C₂₂H₃₄O₃: C, 76.26; H, 9.89. Found: C, 76.05; H, 9.90.





(4*S*,5*R*)-4-(dimesitylsilyl)-5-hydroxymethyl-dihydro-furan-2-one. To a solution of (3*S*,4*R*)-3-(dimesitylsilyl)-4,5-*O*-isopropylidine-4,5-dihydroxypentanoate (0.24 g, 0.51 mmol) in 2 mL of EtOH was added 0.23 mL of concentrated HCl, and the solution was stirred for 2h. The EtOH was removed *in vacuo*, and the resulting oil was diluted with 30 mL of CH₂Cl₂. The organic layer was washed with sodium bicarbonate (saturated aqueous, 2×50 mL), dried over sodium sulfate, filtered, and concentrated *in vacuo*. The resulting white solid was purified by flash column chromatography (10:90 to 30:70 EtOAc/hexanes) to afford the product as a white solid (0.20 g, >99%): mp 62-64 °C. ¹H NMR (500 MHz, CDCl₃) δ 6.84 (s, 2H), 6.82 (s, 2H), 5.19 (d, *J* = 5.2, 1H), 4.45 (ddd, *J* = 9.2, 4.1, 2.4, 1H), 3.63 (ddd, *J* = 12.7, 5.7, 2.1, 1H), 3.13 (ddd, *J* = 11.8, 7.4, 4.4, 1H), 2.94 (dd, *J* = 16.2, 7.8, 1H), 2.66 (m, 1H), 2.61 (m, 1H), 2.39 (s, 6H), 2.37 (s, 6H), 2.26 (s, 3H), 2.25 (s, 3H), 1.72 (m, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 177.3, 144.3, 144.0, 139.81, 139.78, 129.2, 129.1, 127.5, 126.6, 84.6, 63.0, 33.6, 23.4, 23.1, 22.7, 20.9, 20.8; IR (KBr pellet) 3434, 3022, 2959, 1774, 1605, 1450 cm⁻¹; HRMS (CI+/NH₃) *m* / *z* calcd for C₂₃H₃₄NO₃Si (M+NH₄)⁺ 400.2308, found 400.2318. Anal. Calcd for $C_{23}H_{30}O_{3}Si$: C, 72.21; H, 7.90. Found: C, 71.96; H, 7.90. $[\alpha]_{D}^{25}$ –116.8 (*c* 0.0950, CHCl₃).

Relative Stereochemistry between C-4 and C-5 proven by DPFGSE-NOE data



 $\begin{array}{ll} (4S,5R)-4-(dimesityIsilyI)-5-hydroxymethyl-dihydro-furan-2-one.\\ H_a irradiated: & H_b (1.4\%)\\ H_c irradiated: H_d (1.0\%)\\ Note: There was no NOE observed between H_a and H_c or H_b and H_d.\\ (Mixing time was 0.5 s.)\\ & & & & & \\ & & & H_3C \ CH_3 \end{array}$



(4R,6S)-4-Allyl-6-[(1S,2S)-2-benzyloxy-1-methyl-2-phenyl-ethyl]-2,2-dimethyl-1,3-

dioxane. To a solution of **7e** (0.035 g, 0.10 mmol), 1.2 mL of 2,2-dimethoxypropane, and 0.7 mL of acetone was added CSA (<0.005 g). After 5 min, a few drops of Et₃N were added. The solution was concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (hexanes to 0.5:99.5 EtOAc/hexanes) to yield the product as a colorless oil (>99%): ¹H NMR (500 MHz, CDCl₃) δ 7.31 (m, 10H), 5.77 (ddt, *J* = 17.1, 10.2, 6.9, 1H), 5.06 (m, 2H), 4.39 (d, *J* = 11.8, 1H), 4.30 (d, *J* = 7.4, 1H), 4.19 (d, *J* = 11.8, 1H), 3.95 (dt, *J* = 9.3, 6.4, 1H), 3.80 (dq, *J* = 9.7, 6.3, 1H), 2.26 (m, 2H), 2.15 (dt, *J* = 13.7, 6.9, 1H), 1.69 (ddd, *J* = 12.7, 9.4, 5.8, 1H), 1.39 (s, 3H), 1.35 (s, 3H and m, 1H), 0.67 (d, *J* = 7.0, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 139.9, 138.6, 134.6, 128.3, 128.1, 127.8, 127.6, 127.4, 116.7, 100.2, 81.8, 70.3, 66.6, 66.4, 43.7, 40.2, 33.4, 25.1, 10.1; HRMS (CI+/NH₃) *m* / *z* calcd for C₂₄H₂₉O₃ (M-CH₃)⁺ 365.2117, found 365.2111. [α]²⁵_D -51.1 (*c* 0.235, CHCl₃).



(4R,6S)-4-Allyl-6-[(1S,2S)-2-benzyloxy-1-methyl-2-phenyl-ethyl]-2,2-dimethyl-1,3-dioxane. C.: $\delta 25.1$

 C_b^{a} : δ 25.1 Note: C_a and C_b have the same chemical shift in the ¹³C NMR spectrum according to correlation in the HMQC. The 1,3-cis diol results in chemical shifts of 19 and 30 ppm for the acetonide methyl groups.



(4R,6S)-4-Allyl-6-[(1S,2S)2-benzyloxy-1-methyl-2-phenyl-ethyl]-2-(4-nitro-phenyl)-1,3-

dioxane. A round bottom flask fitted with a Dean-Stark trap and reflux condenser was charged with **7e** (0.098 g, 0.29 mmol) and 4-nitrobenzaldehyde (0.058 g, 0.38 mmol) in 14 mL of benzene. CSA (<0.020g) was added and the solution was heated to reflux for 12 h. The solution was cooled to 22 °C and a few drops of Et₃N were added. The solution was concentrated *in vacuo* to afford a yellow oil as a 60:40 mixture of diastereomers. The resulting oil was purified by flash column chromatography (hexanes to 0.5:99.5 EtOAc/hexanes) to yield separate samples of both diastereomers as yellow oils (0.076 g, 54%): Major isomer: ¹H NMR (500 MHz, CDCl₃) δ 8.19 (d, J = 8.8, 2H), 7.61 (d, J = 8.7, 2H), 7.34 (m, 10H), 5.83 (m, 1H and s, 1H), 5.12 (m, 2H), 4.45 (d, J = 11.8, 1H), 4.39 (d, J = 7.5, 1H), 4.31 (dd, J = 14.8, 6.6, 1H), 4.23 (m, 2H), 4.19 (d, J = 11.7, 1H), 2.82 (dt, J = 15.2, 7.6, 1H), 2.38 (dt, J = 13.1, 6.5, 1H), 2.06 (dt, J = 13.0, 6.0, 1H), 1.41 (d, J = 12.4, 1H), 0.76 (d, J = 7.0, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 148.0, 145.8, 139.6, 138.3, 134.4, 128.3, 127.9, 127.8, 127.7, 127.6, 127.1, 123.4, 117.4, 92.8, 81.1, 72.5, 72.2, 70.4, 43.6, 35.2, 28.1, 10.2; IR (thin film) 3064, 2930, 1607, 1522, 1454, 1347 cm⁻¹; HRMS (TOF MS ES+/Na) *m* / *z*

calcd for C₂₉H₃₁NO₅Na (M+Na)⁺ 496.2100, found 496.2109. [α]²⁵_D 1.0 (*c* 0.10, CHCl₃). Minor isomer: ¹H NMR (500 MHz, CDCl₃) δ 8.15 (d, *J* = 8.8, 2H), 7.37 (d, *J* = 8.7, 2H), 7.34 (m, 4H), 7.29 (m, 5H), 7.23 (m, 1H), 5.84 (ddt, *J* = 17.2, 10.2, 7.0, 1H), 5.73 (s, 1H), 5.12 (m, 2H), 4.78 (d, *J* = 3.8, 1H), 4.64 (d, *J* = 12.4, 1H), 4.25 (d, *J* = 12.4, 1H), 4.04 (dtd, *J* = 12.1, 6.4, 2.3, 1H), 3.65 (dd, *J* = 11.3, 5.4, 1H), 2.94 (m, 1H), 2.41 (dt, *J* = 13.7, 6.6, 1H), 2.26 (dt, *J* = 13.8, 6.9, 1H), 1.78 (ddd, *J* = 14.0, 11.6, 6.1, 1H), 1.64 (d, *J* = 13.7, 1H), 0.81 (d, *J* = 6.8, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 147.9, 145.5, 138.5, 137.4, 133.5, 128.4, 128.1, 128.0, 127.8, 127.63, 127.55, 127.1, 123.3, 117.7, 93.2, 78.2 74.1, 72.0, 70.1, 40.4, 36.8, 30.2, 10.8; IR (thin film) 3064, 2927, 1608, 1523, 1348, 1107 cm⁻¹; HRMS (TOF MS ES+/Na) *m* / *z* calcd for C₂₉H₃₁NO₅Na (M+Na)⁺ 496.2100, found 496.2118. [α]²⁵_D -0.66 (*c* 0.305, CHCl₃).

Absolute Stereochemistry of 1,3-trans diol proven by DPFGSE-NOE data



 $(2R,4R^*,6S^*)$ -4-Allyl-6-[(1S*,2S*)-2-benzyloxy-1-methyl-2-phenylethyl)-2-(4-nitro-phenyl)-1,3-dioxane H_b irradiated: H_c (5.1%)

 $H_a^{(3.9\%)}$ $H_e^{(3.9\%)}$ $H_e^{(3.9\%)}$ Note: In order to minimize unfavorable gauche and diaxial interactions, the 1,3-dioxane adopts the above pictured conformer, in which an NOE is observed between H_e and H_d . If the other 1,3-trans diol were obtained, the methyl group would be pointed away from the C-5 methylene and no NOE should be observed. (Mixing time was 0.5s)



(2S,4R,6S)-4-Allyl-6-[(1S,2S)-2-benzyloxy-1-methyl-2-phenyl-ethyl]-2-(4nitro-phenyl)-1,3-dioxane. H_a irradiated: H_b (1.3%)

H_d irradiated:

adiated: $H_{e}^{i}(1.8\%)$ $H_{f}(0.9\%)$

 H_{b} , (3.0%) H_{c} (4.8%)

Note: In order to minimize unfavorable gauche and diaxial interactions, the 1,3-dioxane adopts the above pictured conformer, in which an NOE is observed between H_e and H_d . If the other 1,3-trans diol were obtained, the methyl group would be pointed away from the C-5 methylene and no NOE should be observed. (Mixing time was 0.5 s.)



(2R*,4S*,5R*,6R*)-4-Allyl-6-[(1S*,2R*)-2-benzyloxy-1,3-dimethylbutyl]-2-(4-nitro-

phenyl)-5-methyl-1,3-dioxane. A round bottom flask fitted with a Dean-Stark trap and reflux condenser was charged with diol 8a (0.050 g, 0.16 mmol) and 4-nitrobenzaldehyde (0.032 g, 0.21 mmol) in 8 mL of benzene. CSA (<0.005 g) was added and the solution was heated to reflux for 12 h. After the solution was cooled to 22 °C, a few drops of Et₃N were added, and the solution was concentrated *in vacuo*. The resulting oil was purified by flash column chromatography (hexanes to 0.5:99.5 EtOAc/hexanes) to yield the product as a yellow oil (0.063 g, 86%): ¹H NMR (500 MHz, CDCl₃) δ 8.21 (d, *J* = 8.6, 2H), 7.57 (d, *J* = 8.8, 2H), 7.33 (m, 4H), 7.28 (m, 1H), 5.78 (ddt, *J* = 17.1, 10.2, 6.9, 1H), 5.30 (s, 1H), 5.08 (m, 2H), 4.82 (d, *J* = 12.2, 1H), 4.42 (d, *J* = 12.2, 1H), 3.92 (br t, *J* = 7.8, 1H), 3.86 (dd, *J* = 10.1, 2.0, 1H), 3.45 (dd, *J* = 9.2, 2.5, 1H), 2.62 (dt, *J* = 15.1, 7.5, 1H), 2.31 (dt, *J* = 14.1, 7.0, 1H), 1.93 (m, 2H), 1.58 (m, 1H), 1.15 (d, *J* = 7.0, 3H), 1.10 (d, *J* = 6.6, 2H)

3H), 0.87 (d, J = 6.3, 3H), 0.83 (d, J = 6.9, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 148.0, 145.9, 139.7, 134.4, 128.4, 127.4, 127.3, 127.0, 123.4, 117.3, 93.0, 84.1, 79.7, 75.14, 75.09, 36.2, 34.6, 31.4, 31.2, 20.5, 19.4, 12.7, 7.8; IR (thin film) 3067, 2973, 1609, 1524, 1348, 1104 cm⁻¹; HRMS (CI+/NH₃) m / z calcd for C₂₇H₃₄NO₅ (M-H)⁺ 452.2437, found 452.2442. Anal. Calcd for C₂₇H₃₅NO₅: C, 71.50; H, 7.78. Submitted.





H. One flask Formation of Oxasilacyclopentane Acetal



(3*R*,4*S*)-1-Oxa-3,4-dimethyl-5-ethoxy-2,2-di(mesityl)silacyclopentane (6f). To a cooled ($-78 \,^{\circ}$ C) solution of Me₂Zn (0.12 mL, 0.24 mmol, 2.0 M in toluene) in 1.6 mL of THF was added a cooled (0 $^{\circ}$ C) solution of silyllithium 4 (0.10 g, 0.24 mmol) in 0.25 mL of THF. The solution was warmed to 0 $^{\circ}$ C for 5 min and then re-cooled to $-78 \,^{\circ}$ C. In a separate flask, MeLi (0.020 mL, 0.024 mmol) in 0.3 mL of THF. The slurry was warmed to $-30 \,^{\circ}$ C, stirred for 5 min, cooled to $-78 \,^{\circ}$ C, and stirred for 5 min. The resulting solution was added to the reaction solution and stirred at $-78 \,^{\circ}$ C for 10 min. To the reaction solution was added a cooled ($-78 \,^{\circ}$ C) solution of ethyl *trans*-crotonate (0.026 g, 0.23 mmol) in 0.2 mL of THF. After 5 min at $-78 \,^{\circ}$ C, CH₃I (0.088 mL, 1.4 mmol) was added, and the mixture was warmed to 22 $^{\circ}$ C for 12h. The mixture was cooled to 0 $^{\circ}$ C,

n-Bu₄NF (0.24 mL, 0.24 mmol, 1.0 M in THF) was added, and the mixture was warmed to 22 °C for 1h. The reaction mixture was quenched with 5 mL of sodium bicarbonate (saturated aqueous). The organic layer was separated and the aqueous layer was extracted with Et₂O (3×25 mL). The combined organic layers were dried over MgSO₄, filtered, and concentrated in vacuo to give the product as a 70:30 mixture of diastereomers as determined by ¹H NMR spectroscopy. The resulting oil was purified by flash column chromatography (hexanes to 1:99 EtOAc/hexanes) to give the product as a pale yellow oil (0.072 g, 79%): ¹H NMR (500 MHz, CDCl₃) major isomer δ 6.79 (s, 2H), 6.73 (s, 2H), 4.64 (d, J = 7.9, 1H), 3.94 (dq, J = 9.7, 7.1, 1H), 3.53 (dq, J = 9.7, 7.0, 1H), 2.44 (s, 6H), 2.39 (s, 6H), 2.23 (s, 3H), 2.22 (s, 3H), 1.70 (m, 1H), 1.42 (m, 1H), 1.23 (t, J = 7.1, 3H), 1.07 (d, J = 6.8, 6H); minor isomer, characteristic peaks: δ 5.04 (d, J = 3.2, 0.15H), 3.44 (dq, J = 9.5, 7.1, 0.16H), 3.28 (dq, J = 9.7, 6.9, 0.13H), 2.41 (s, 1.2H), 2.30 (s, 1.1H), 1.75 (m, 1.2H), 10.36H), 0.88 (m, 1.3H); major product: ¹³C NMR (125 MHz, CDCl₃) δ 144.6, 143.6, 139.2, 139.0, 133.2, 129.1, 128.8, 107.6, 64.1, 45.8, 30.1, 23.5, 23.4, 21.01, 20.99, 15.5, 15.3, 11.8; minor product, characteristic peaks: δ 144.1, 143.4, 138.7, 138.6, 133.3, 129.3, 128.4, 102.8, 62.0, 45.5, 29.7, 26.3, 23.6, 23.3, 14.9, 13.8, 12.0; HRMS (CI+/NH₃) m / z calcd for C₂₅H₃₆O₂Si submitted. Characterization data for material obtained from three separate steps: HRMS (EI-GCMS) m / zcalcd for C₂₅H₃₅O₂Si (M-H)⁺ 395.2405, major anomer: found 395.2408; minor anomer: found 395.2418. Anal. Calcd for C₂₅H₃₆O₂Si: C, 75.70; H, 9.15. Found: C, 75.53; H, 9.18.

I. X-Ray Crystallographic Data



X-ray Data Collection, Structure Solution and Refinement for (2'*R**,3'S*,4S*)-4-Benzyl-3-(3'-hydroxy-2'-methyl-3'-phenyl-propionyl)-oxazolidin-2-one:

A colorless crystal of approximate dimensions $0.17 \times 0.26 \times 0.37$ mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART¹ program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT² and SADABS³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴ program. The diffraction symmetry was 2/m and the systematic absences were consistent with the monoclinic space groups C2, Cm or C2/m. It was later determined that the noncentrosymmetric space group C2 was correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵ for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined (x,y,z and U_{iso}) or included were included using a riding model. The crystal was grown from a mixture of hexanes. There appeared to be _ molecule of hexane(s) present per formula unit. The solvent molecule was disordered and included with partial site-occupancy-factors. The hexane(s) formed polymeric chains and could not be unambiguously identified. Hydrogen atoms associated with the hexane(s) were not included in the refinement.

At convergence, wR2 = 0.2052 and Goof = 1.072 for 247 variables refined against 4782 data. As a comparison for refinement on F, R1 = 0.0629 for those 4092 data with I > $2.0\sigma(I)$. The absolute structure could not be assigned by inversion of the model or by refinement of the Flack parameter⁶.



Table 1. Crystal data and structure refinement for $(2'R^*, 3'S^*, 4S^*)$ -4-Benzyl-3-(3'-hydroxy-2'-methyl-3'-phenyl-propionyl)-oxazolidin-2-one.Identification codekaw30Empirical formula C_{20} H $_{21}$ N O $_4$ (C $_6$ H $_{14}$)Formula weight382.46Temperature173(2) KWavelength0.71073 ÅCrystal systemMonoclinic

Space group Unit cell dimensions Volume Ζ Density (calculated) Absorption coefficient F(000) Crystal size Theta range for data collection Index ranges Reflections collected Independent reflections Completeness to theta = 28.27° Absorption correction Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F² Final R indices [I > 2sigma(I)] R indices (all data) Absolute structure parameter Extinction coefficient Largest diff. peak and hole

*C*2 $\alpha = 90^{\circ}$. a = 25.012(6) Åb = 5.5115(13) Å $\beta = 106.141(4)^{\circ}$. c = 15.991(4) Å $\gamma = 90^{\circ}$. 2117.5(8) Å³ 4 1.200 Mg/m³ 0.082 mm⁻¹ 820 0.37 x 0.26 x 0.17 mm³ 1.84 to 28.27°. $-33 \le h \le 32, -7 \le k \le 7, -21 \le l \le 21$ 11335 4782 [R(int) = 0.0286]97.2% None 0.9863 and 0.9705 Full-matrix least-squares on F² 4782 / 2 / 247 1.072 R1 = 0.0629, wR2 = 0.1926R1 = 0.0739, wR2 = 0.2052-0.2(16)0.0027(17)0.945 and -0.227 e.Å-3

	Х	У	Z	U(eq)	· · · · · · · · · · · · · · · · · · ·
N(1)	3486(1)	8655(4)	5213(1)	27(1)	
O(1)	2657(1)	9993(4)	5267(1)	34(1)	
O(2)	2765(1)	9353(4)	3941(1)	31(1)	
O(3)	4322(1)	6884(5)	5493(1)	41(1)	
O(4)	4613(1)	9674(4)	4082(1)	36(1)	
C(1)	3565(1)	9117(5)	6142(2)	28(1)	
C(2)	2962(1)	9433(6)	6161(2)	33(1)	
C(3)	2950(1)	9324(5)	4718(2)	28(1)	
C(4)	3907(1)	7526(6)	4933(2)	30(1)	
C(5)	3824(1)	7085(5)	3974(2)	28(1)	
C(6)	4391(1)	7333(5)	3780(2)	28(1)	
C(7)	4329(1)	7072(5)	2813(2)	30(1)	
C(8)	4036(1)	8813(6)	2234(2)	37(1)	
C(9)	3982(1)	8605(7)	1346(2)	43(1)	
C(10)	4223(1)	6689(7)	1034(2)	45(1)	
C(11)	4522(2)	4959(7)	1608(2)	47(1)	
C(12)	4573(1)	5147(6)	2499(2)	37(1)	
C(13)	3924(1)	11386(6)	6455(2)	38(1)	
C(14)	4039(1)	11617(6)	7430(2)	35(1)	
C(15)	4393(1)	9980(7)	7975(2)	41(1)	
C(16)	4484(1)	10095(7)	8873(2)	46(1)	
C(17)	4230(2)	11849(8)	9239(2)	48(1)	
C(18)	3875(2)	13488(7)	8702(2)	49(1)	
C(19)	3779(2)	13376(6)	7803(2)	44(1)	
C(20)	3578(1)	4554(6)	3750(2)	39(1)	
C(21)	2672(2)	8690(12)	8254(4)	75(1)	
C(22)	2446(2)	8751(13)	9052(4)	79(2)	
C(23)	2600(4)	6310(20)	9603(7)	86(3)	
C(24)	2607(4)	11189(19)	9562(6)	80(2)	

Table 2. Atomic coordinates $(x \ 10^4)$ and equivalent isotropic displacement parameters (Å²x 10³) for(**2**'*R**,**3**'*S**,**4***S**)-**4**-Benzyl-3-(**3**'-hydroxy-2'-methyl-3'-phenyl-propionyl)-oxazolidin-2-one. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

1.399(3)
1.404(3)
1.465(3)
1.341(3)
1.455(3)
1.199(3)
1.220(3)
1.434(4)
1.526(3)
1.539(4)
1.510(3)
1.527(4)
1.538(3)
1.517(3)
1.387(4)
1.392(4)
1.393(4)
1.377(5)
1.389(5)
1.397(4)
1.509(3)
1.389(5)
1.390(5)
1.392(4)
1.374(5)
1.385(6)
1.391(4)
1.534(8)
1.566(12)
1.597(13)
1.562(12)
1.562(12)

Table 3. Bond lengths [Å] and angles [°] for $(2^{R*}, 3^{S*}, 4S^{*})$ -4-Benzyl-3- $(3^{-hydroxy-2^{-methyl-3^{-hydroxy-2^{-methyl-3^{-hydroxy-2^{-methyl-3^{-hydroxy-2^{-methyl-3^{-hydroxy-2^{-methyl-3^{-hydroxy-2^{-methyl-3^{-hydroxy-3^{-hydrox-3^{-hydrox-3^{-hydrox3^{-hydrox3^{-hydrox3^{-hydrox3^{-hydrox3^{-hydrox3^{-hydrox3^{-hydrox3^{-hydrox3^{-hy$

C(4)-N(1)-C(3)	128.5(2)
C(4)-N(1)-C(1)	120.0(2)
C(3)-N(1)-C(1)	111.4(2)
C(3)-O(1)-C(2)	110.6(2)
N(1)-C(1)-C(2)	100.58(19)
N(1)-C(1)-C(13)	111.9(2)
C(2)-C(1)-C(13)	113.0(3)
O(1)-C(2)-C(1)	104.88(19)
O(2)-C(3)-O(1)	123.4(2)
O(2)-C(3)-N(1)	128.3(2)
O(1)-C(3)-N(1)	108.2(2)
O(3)-C(4)-N(1)	117.2(2)
O(3)-C(4)-C(5)	123.1(2)
N(1)-C(4)-C(5)	119.6(2)
C(4)-C(5)-C(20)	108.5(2)
C(4)-C(5)-C(6)	108.50(19)
C(20)-C(5)-C(6)	111.6(2)
O(4)-C(6)-C(7)	110.4(2)
O(4)-C(6)-C(5)	107.7(2)
C(7)-C(6)-C(5)	111.0(2)
C(12)-C(7)-C(8)	119.3(3)
C(12)-C(7)-C(6)	120.8(3)
C(8)-C(7)-C(6)	119.9(3)
C(7)-C(8)-C(9)	120.3(3)
C(10)-C(9)-C(8)	120.3(3)
C(9)-C(10)-C(11)	119.7(3)
C(10)-C(11)-C(12)	120.2(3)
C(7)-C(12)-C(11)	120.1(3)
C(14)-C(13)-C(1)	109.4(2)
C(15)-C(14)-C(19)	118.5(3)
C(15)-C(14)-C(13)	119.9(3)
C(19)-C(14)-C(13)	121.6(3)
C(14)-C(15)-C(16)	120.8(3)
C(17)-C(16)-C(15)	120.5(3)
C(16)-C(17)-C(18)	119.2(3)
C(17)-C(18)-C(19)	120.6(3)
C(14)-C(19)-C(18)	120.5(3)
C(21)-C(22)-C(24)	110.6(6)
C(21)-C(22)-C(23)	110.6(6)
C(24)-C(22)-C(23)	116.7(6)
C(24)#1-C(23)-C(22)	114.9(8)
C(23)#2- $C(24)$ - $C(22)$	112.5(8)

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,y-1/2,-z+2 #2 -x+1/2,y+1/2,-z+2

displace	ement facto	or exponent t	akes the form	n: $-2\pi^{2}$ [n ² a	$+20^{11} + \dots +$	- 2 n k a* b* U	12
	U ¹¹	U ²²	U ³³	U ²³	U ¹³	U ¹²	
N(1)	23(1)	36(1)	21(1)	-2(1)	6(1)	-1(1)	
O(1)	28(1)	47(1)	28(1)	-4(1)	9(1)	6(1)	
O(2)	27(1)	39(1)	25(1)	0(1)	4(1)	4(1)	
O(3)	26(1)	72(2)	26(1)	4(1)	6(1)	10(1)	
O(4)	31(1)	49(1)	28(1)	-7(1)	7(1)	-7(1)	
C(1)	28(1)	35(1)	20(1)	-1(1)	8(1)	-4(1)	
C(2)	32(1)	45(2)	23(1)	0(1)	10(1)	1(1)	
C(3)	26(1)	32(1)	28(1)	1(1)	10(1)	2(1)	
C(4)	23(1)	41(2)	25(1)	-1(1)	7(1)	-1(1)	
C(5)	23(1)	40(2)	22(1)	-2(1)	8(1)	2(1)	
C(6)	25(1)	38(1)	24(1)	-1(1)	8(1)	0(1)	
C(7)	28(1)	38(2)	25(1)	-2(1)	10(1)	-2(1)	
C(8)	42(2)	43(2)	29(1)	0(1)	13(1)	5(1)	
C(9)	51(2)	47(2)	30(1)	5(1)	9(1)	2(1)	
C(10)	57(2)	56(2)	26(1)	-10(1)	15(1)	-9(2)	
C(11)	55(2)	50(2)	40(2)	-13(2)	21(1)	2(2)	
C(12)	40(2)	39(2)	34(2)	-4(1)	13(1)	3(1)	
C(13)	49(2)	42(2)	23(1)	-3(1)	11(1)	-15(1)	
C(14)	38(1)	44(2)	24(1)	-6(1)	11(1)	-15(1)	
C(15)	35(1)	59(2)	29(1)	-10(1)	8(1)	-4(1)	
C(16)	43(2)	64(2)	26(1)	-3(1)	1(1)	-2(2)	
C(17)	58(2)	61(2)	24(1)	-6(2)	11(1)	-10(2)	
C(18)	68(2)	47(2)	36(2)	-8(2)	21(2)	$1(2)^{2}$	
C(19)	59(2)	38(2)	34(2)	-3(1)	10(1)	-4(1)	
C(20)	34(1)	45(2)	42(2)	-9(1)	16(1)	-8(1)	

Table 4. Anisotropic displacement parameters (Å²x 10³) for (**2**'*R**,**3**'*S**,**4***S**)-**4-Benzyl-3-(3'-hydroxy-2'-methyl-3'-phenyl-propionyl)-oxazolidin-2-one**. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h² a*²U¹¹ + ... + 2 h k a* b* U¹²]

	Х	У	Z	U(eq)	
H(1A)	3735	7669	6493	33	
H(2A)	2820	7924	6358	39	
H(2B)	2930	10774	6556	39	
H(5A)	3560	8321	3630	34	
H(6A)	4648	6048	4104	34	
H(8A)	3872	10150	2446	45	
H(9A)	3777	9790	955	52	
H(10Å)	4186	6551	428	54	
H(11A)	4691	3643	1395	56	
H(12A)	4776	3955	2889	45	
H(13A)	4279	11250	6300	45	
H(13B)	3725	12848	6167	45	
H(15A)	4575	8768	7732	49	
H(16A)	4725	8950	9237	55	
H(17A)	4297	11936	9852	57	
H(18A)	3696	14699	8949	59	
H(19A)	3534	14509	7441	53	
H(20A)	3218	4458	3881	59	
H(20B)	3832	3344	4097	59	
H(20C)	3525	4234	3130	59	
H(1)	4961(4)	9430(100)	4270(30)	71(14)	

Table 5. Hydrogen coordinates ($x \ 10^4$) and isotropic displacement parameters (Å²x 10³) for (**2**'*R**,**3**'*S**,**4***S**)-**4**-**Benzyl-3**-(**3**'-**hydroxy-2**'-**methyl-3**'-**phenyl-propionyl**)-**oxazolidin-2-one**.

Table 6. Torsion angles [°] for $(2^{*}R^{*}, 3^{*}S^{*}, 4S^{*})$ -4-Benzyl-3- $(3^{*}-hydroxy-2^{*}-methyl-3^{*}-phenyl-propionyl)$ -oxazolidin-2-one.

C(4)-N(1)-C(1)-C(2)	-160.0(3)
C(3)-N(1)-C(1)-C(2)	16.0(3)
C(4)-N(1)-C(1)-C(13)	79.8(3)
C(3)-N(1)-C(1)-C(13)	-104.2(3)
C(3)-O(1)-C(2)-C(1)	18.8(3)
N(1)-C(1)-C(2)-O(1)	-20.0(3)
C(13)-C(1)-C(2)-O(1)	99.5(3)
C(2)-O(1)-C(3)-O(2)	171.8(3)
C(2)-O(1)-C(3)-N(1)	-8.9(3)
C(4)-N(1)-C(3)-O(2)	-10.5(5)
C(1)-N(1)-C(3)-O(2)	174.0(3)
C(4)-N(1)-C(3)-O(1)	170.2(3)
C(1)-N(1)-C(3)-O(1)	-5.3(3)
C(3)-N(1)-C(4)-O(3)	-172.6(3)
C(1)-N(1)-C(4)-O(3)	2.6(4)
C(3)-N(1)-C(4)-C(5)	5.5(4)
C(1)-N(1)-C(4)-C(5)	-179.2(2)
O(3)-C(4)-C(5)-C(20)	85.6(3)
N(1)-C(4)-C(5)-C(20)	-92.4(3)
O(3)-C(4)-C(5)-C(6)	-35.8(4)
N(1)-C(4)-C(5)-C(6)	146.2(3)

C(4)-C(5)-C(6)-O(4)	-55.3(3)
C(20)-C(5)-C(6)-O(4)	-174.8(2)
C(4)-C(5)-C(6)-C(7)	-176.3(2)
C(20)-C(5)-C(6)-C(7)	$64.2(3)^{\prime}$
O(4)-C(6)-C(7)-C(12)	125.1(3)
C(5)-C(6)-C(7)-C(12)	-115.5(3)
O(4)-C(6)-C(7)-C(8)	-53.2(3)
C(5)-C(6)-C(7)-C(8)	66.2(3)
C(12)-C(7)-C(8)-C(9)	1.0(4)
C(6)-C(7)-C(8)-C(9)	179.3(3)
C(7)-C(8)-C(9)-C(10)	-0.8(5)
C(8)-C(9)-C(10)-C(11)	0.0(5)
C(9)-C(10)-C(11)-C(12)	0.5(5)
C(8)-C(7)-C(12)-C(11)	-0.4(4)
C(6)-C(7)-C(12)-C(11)	-178.7(3)
C(10)-C(11)-C(12)-C(7)	-0.4(5)
N(1)-C(1)-C(13)-C(14)	-174.3(2)
C(2)-C(1)-C(13)-C(14)	73.1(3)
C(1)-C(13)-C(14)-C(15)	70.2(3)
C(1)-C(13)-C(14)-C(19)	-106.8(3)
C(19)-C(14)-C(15)-C(16)	0.1(5)
C(13)-C(14)-C(15)-C(16)	-177.0(3)
C(14)-C(15)-C(16)-C(17)	-0.7(5)
C(15)-C(16)-C(17)-C(18)	0.8(5)
C(16)-C(17)-C(18)-C(19)	-0.4(6)
C(15)-C(14)-C(19)-C(18)	0.3(5)
C(13)-C(14)-C(19)-C(18)	177.4(3)
C(17)-C(18)-C(19)-C(14)	-0.1(5)
C(21)-C(22)-C(23)-C(24)#1	179.4(6)
C(24)-C(22)-C(23)-C(24)#1	51.9(10)
C(21)-C(22)-C(24)-C(23)#2	-178.3(6)
C(23)-C(22)-C(24)-C(23)#2	-50.7(10)

Symmetry transformations used to generate equivalent atoms: #1 -x+1/2,y-1/2,-z+2 #2 -x+1/2,y+1/2,-z+2 References.

- 1. SMART Software Users Guide, Version 5.1, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
- SAINT Software Users Guide, Version 6.0, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
- 3. Sheldrick, G. M. SADABS, Version 2.03, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 2000.
- 4. Sheldrick, G. M. SHELXTL Version 5.10, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
- 5. International Tables for X-Ray Crystallography 1992, Vol. C., Dordrecht: Kluwer AcademicPublishers.
- 6. Flack, H. D. Acta. Cryst., A39, 876-881, 1983.

Definitions:

 $wR2 = \left[\Sigma[w(F_0^2 - F_0^2)^2] / \Sigma[w(F_0^2)^2]^{1/2}\right]$

 $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

Goof = S = $[\Sigma[w(F_o^2-F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

The thermal ellipsoid plot is shown at the 50% probability level.

X-ray Data Collection, Structure Solution and Refinement for Ester 2a.

A colorless crystal of approximate dimensions 0.11 x 0.28 x 0.31 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART¹ program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT² and SADABS³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴ program. The diffraction symmetry was 2/m and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$ which was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵ for neutral atoms were used throughout the analysis. Hydrogen atoms were either located from a difference-Fourier map and refined (x,y,z and U_{iso}) or were included using a riding model. At convergence, wR2 = 0.1367 and GOF = 1.022 for 366 variables refined against 8020 data. As a comparison for refinement on F, R1 = 0.0486 for those 5683 data with I > 2.0 σ (I).



Table 1. Crystal data and structure refinement for ester 2a.Identification codekaw26 (Jason Tenenbaum)Empirical formula C_{36} H₅₀ O₃ Si

Formula weight	558.85	
Temperature	173(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	$P2_1/n$	
Unit cell dimensions	a = 12.6902(5) Å	<i>α</i> = 90°.
	b = 12.2857(5) Å	$\beta = 96.2520(10)^{\circ}$.
	c = 21.1888(8) Å	$\gamma = 90^{\circ}$.
Volume	3283.9(2) Å ³	•
Z	4	
Density (calculated)	1.130 Mg/m^3	
Absorption coefficient	0.104 mm ⁻¹	
F(000)	1216	
Crystal size	0.31 x 0.28 x 0.11 mm ³	
Theta range for data collection	1.79 to 28.31°.	
Index ranges	$-16 \le h \le 16, -15 \le k \le 16$	$-28 \le l \le 28$
Reflections collected	34702	, ,
Independent reflections	8020 [R(int) = 0.0478]	
Completeness to theta = 28.31°	98.0%	
Absorption correction	None	
Max. and min. transmission	0.9887 and 0.9685	
Refinement method	Full-matrix least-squares of	on F ²
Data / restraints / parameters	8020 / 0 / 366	
Goodness-of-fit on F ²	1.022	
Final R indices [I>2sigma(I)]	R1 = 0.0486, wR2 = 0.117	70
R indices (all data)	R1 = 0.0802, $wR2 = 0.130$	67
Extinction coefficient	0.0015(4)	
Largest diff. peak and hole	0.389 and -0.352 e.Å ⁻³	
-		

	Х	У	Z	U(eq)	
Si(1)	5175(1)	8339(1)	1296(1)	21(1)	<u> </u>
O(1)	3977(1)	9771(1)	3223(1)	28(1)	
O(2)	5861(1)	7060(1)	2954(1)	29(1)	
O(3)	4551(1)	5889(1)	2630(1)	35(1)	
C(1)	4814(1)	8711(1)	2119(1)	22(1)	
C(2)	4141(1)	9779(1)	2092(1)	23(1)	
C(3)	4311(1)	10425(1)	2717(1)	25(1)	
C(4)	3716(2)	11514(2)	2710(1)	33(1)	
C(5)	3990(2)	12108(2)	3339(1)	43(1)	
C(6)	3942(2)	12237(2)	2155(1)	44(1)	
C(7)	2961(1)	9578(2)	1898(1)	30(1)	
C(8)	4244(1)	7737(1)	2391(1)	26(1)	
C(9)	4991(2)	6881(1)	2683(1)	26(1)	
C(10)	5192(2)	4993(2)	2910(1)	42(1)	
C(11)	5068(2)	4873(2)	3603(1)	45(1)	
C(12)	4793(2)	9511(2)	3718(1)	32(1)	
C(13)	4288(2)	8907(2)	4220(1)	31(1)	
C(14)	3655(2)	9453(2)	4612(1)	46(1)	
C(15)	3148(2)	8885(2)	5055(1)	54(1)	
C(16)	3282(2)	7781(2)	5127(1)	49(1)́	

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for Ester **2a**. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

C(17)	3918(2)	7237(2)	4748(1)	57(1)
C(17)	4415(2)	7237(2) 7801(2)	4740(1)	$\frac{37(1)}{46(1)}$
C(10)	4413(2)	7001(2)	4290(1)	40(1)
C(19)	56/3(1)	6883(1)	1286(1)	24(1)
C(20)	5023(2)	6023(2)	1028(1)	31(1)
C(21)	5429(2)	4967(2)	1021(1)	35(1)
C(22)	6453(2)	4717(2)	1262(1)	34(1)
C(23)	7088(2)	5560(2)	1517(1)	29(1)
C(24)	6725(1)	6629(1)	1537(1)	24(1)
C(25)	3881(2)	6179(2)	751(1)	43(1)
C(26)	6875(2)	3571(2)	1239(1)	51(1)
C(27)	7471(1)	7479(2)	1839(1)	28(1)
C(28)	6075(1)	9295(1)	897(1)	22(1)
C(29)	6711(1)	10132(1)	1195(1)	23(1)
C(30)	7355(1)	10761(1)	846(1)	24(1)
C(31)	7405(1)	10597(2)	202(1)	27(1)
C(32)	6779(2)	9778(2)	-92(1)	27(1)
C(33)	6118(1)	9134(1)	236(1)	24(1)
C(34)	6752(2)	10399(2)	1891(1)	29(1)
C(35)	8122(2)	11286(2)	-155(1)	38(1)
C(36)	5473(2)	8271(2)	-137(1)	29(1)

Table 3.	Bond lengths	[Å]	and angles	[°]	for	Ester 2a
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Si(1)-C(19)	1.8979(18)
Si(1)-C(28)	1.8993(18)
Si(1)-C(1)	1.9065(18)
O(1) - C(12)	1.428(2)
O(1)-C(3)	1.439(2)
O(2)-C(9)	1.208(2)
O(3)-C(9)	1.341(2)
O(3) - C(10)	1.456(2)
C(1) - C(8)	1.541(2)
C(1)-C(2)	1.563(2)
C(2)-C(7)	1.529(2)
C(2)-C(3)	1.540(2)
C(3)-C(4)	1.536(3)
C(4)-C(6)	1.524(3)
C(4)-C(5)	1.527(3)
C(8)-C(9)	1.504(3)
C(10)-C(11)	1.500(3)
C(12)-C(13)	1.497(3)
C(13)-C(18)	1.376(3)
C(13)-C(14)	1.389(3)
C(14)-C(15)	1.384(3)
C(15)-C(16)	1.372(4)
C(16)-C(17)	1.372(4)
C(17)-C(18)	1.387(3)
C(19)-C(20)	1.414(3)
C(19)-C(24)	1.417(2)
C(20)-C(21)	1.396(3)
C(20)-C(25)	1.515(3)
C(21)-C(22)	1.379(3)
C(22)-C(23)	1.385(3)

C(22) $C(2C)$	1.509(2)
C(22)-C(20)	1.508(3)
C(23) - C(24)	1 394(3)
C(23) - C(24)	1.574(5)
C(24)-C(27)	1.506(3)
ငက်လ် ငက်က်	1 412(2)
C(20)- $C(29)$	1.413(2)
C(28)-C(33)	1421(2)
C(20) C(33)	1.121(2)
C(29)-C(30)	1.394(2)
C(20) = C(34)	1.506(2)
C(2) - C(3+)	1.500(2)
C(30)-C(31)	1.388(2)
C(21) $C(22)$	1 207(2)
C(31)-C(32)	1.38/(3)
C(31)-C(35)	1 506(3)
C(22) $C(22)$	1.202(2)
C(32)-C(33)	1.393(3)
C(33) - C(36)	1.509(2)
C(33) - C(30)	1.505(2)
$C(19)-S_1(1)-C(28)$	111.16(8)
C(1) $S(1)$ $C(1)$	110 45(9)
C(19) - SI(1) - C(1)	110.45(8)
C(28)-Si(1)-C(1)	118.40(8)
C(12) O(1) C(2)	115.02(14)
C(12)-O(1)-C(3)	115.02(14)
C(9)-O(3)-C(10)	116 35(16)
C(3) C(3) C(10)	110.00(14)
C(8)-C(1)-C(2)	112.88(14)
$C(\hat{s}) = C(\hat{1}) = S(\hat{1})$	108.00(12)
C(0) - C(1) - SI(1)	100.99(12)
C(2)-C(1)-Si(1)	110.61(11)
C(t) C(t) C(t)	110.92(14)
C(7) - C(2) - C(3)	110.05(14)
C(7)-C(2)-C(1)	112.93(14)
C(2) $C(2)$ $C(1)$	112 09(14)
C(3)-C(2)-C(1)	112.08(14)
O(1)-C(3)-C(4)	108.04(14)
O(1) C(2) C(2)	100.12(14)
U(1) - U(3) - U(2)	109.13(14)
C(4)-C(3)-C(2)	114 66(15)
C(t) C(t) C(t)	110 59(19)
C(0) - C(4) - C(3)	110.38(18)
C(6)-C(4)-C(3)	112 46(16)
C(5) C(4) C(2)	110.00(17)
C(5)-C(4)-C(3)	110.00(17)
C(9)-C(8)-C(1)	11335(15)
	102.70(17)
O(2)-C(9)-O(3)	123./9(1/)
O(2) - C(9) - C(8)	124 83(16)
O(2) - O(3) - O(0)	124.05(10)
O(3)-C(9)-C(8)	111.32(16)
O(3) - C(10) - C(11)	111.07(18)
O(3)-O(10)-O(11)	111.07(18)
O(1)-C(12)-C(13)	107.50(15)
C(18) C(12) C(14)	1184(2)
C(10) - C(13) - C(14)	110.4(2)
C(18)-C(13)-C(12)	121.26(19)
C(14) C(12) C(12)	120.25(10)
C(14) - C(13) - C(12)	120.55(19)
C(15)-C(14)-C(13)	120.2(2)
C(10) C(15) C(14)	120.9(2)
C(10) - C(13) - C(14)	120.8(2)
C(15)-C(16)-C(17)	1194(2)
C(10) C(10) C(10)	120.0(2)
C(16)-C(17)-C(18)	120.0(2)
C(13) - C(18) - C(17)	1212(2)
C(15) C(10) C(17)	121.2(2)
C(20)-C(19)-C(24)	11/.82(16)
C(20) = C(10) = Si(1)	121.88(14)
C(20) - C(10) - SI(1)	121.00(14)
$C(24)-C(19)-S_1(1)$	120.30(13)
C(21) C(20) C(10)	110 88(18)
C(21) - C(20) - C(19)	119.00(10)
C(21)-C(20)-C(25)	116.85(17)
C(1)	123 27(17)
C(19) - C(20) - C(23)	123.27(17)
C(22)-C(21)-C(20)	122.50(19)
$\dot{c}\dot{c}\dot{1}\dot{1}\dot{1}\dot{c}\dot{c}\dot{1}\dot{2}\dot{1}\dot{1}$	117 55(19)
C(21) - C(22) - C(23)	117.55(18)
C(21)-C(22)-C(26)	121.3(2)
\dot{c}	121 1(2)
U(23) - U(22) - U(20)	121.1(2)
C(22)-C(23)-C(24)	122.38(18)
, , - (−-, ~(−·)	

C(23)-C(24)-C(19)	119.86(17)
C(23)-C(24)-C(27)	118.10(16)
C(19)-C(24)-C(27)	122.03(16)
C(29)-C(28)-C(33)	117.37(16)
C(29)-C(28)-Si(1)	126.37(13)
C(33)-C(28)-Si(1)	116.25(13)
C(30)-C(29)-C(28)	120.43(16)
C(30)-C(29)-C(34)	116.01(16)
C(28)-C(29)-C(34)	123.56(16)
C(31)-C(30)-C(29)	122.22(17)
C(32)-C(31)-C(30)	117.51(17)
C(32)-C(31)-C(35)	122.00(17)
C(30)-C(31)-C(35)	120.50(17)
C(31)-C(32)-C(33)	122.32(17)
C(32)-C(33)-C(28)	120.15(16)
C(32)-C(33)-C(36)	117.40(16)
C(28)-C(33)-C(36)	122.45(16)

Table 4. Anisotropic displacement parameters $(Å^2 x \ 10^3)$ for Ester **2a**. The anisotropic displacement factor exponent takes the form: $-2\pi^2 [h^2 a^{*2} U^{11} + ... + 2 h k a^* b^* U^{12}]$

	T T 1 1	I 122	T 133	I 123	T 113	I 112	
	U^{11}	U^{22}	033	U^{23}	015	U^{12}	
$\overline{\mathrm{Si}(1)}$	22(1)	20(1)	21(1)	-1(1)	1(1)	1(1)	
O(1)	24(1)	34(1)	24(1)	2(1)	4(1)	0(1)	
O(2)	$\frac{27(1)}{27(1)}$	29(1)	$\frac{21(1)}{31(1)}$	$\frac{2(1)}{4(1)}$	2(1)	-1(1)	
O(3)	$\frac{27(1)}{37(1)}$	24(1)	43(1)	6(1)	2(1)	-5(1)	
C(1)	21(1)	22(1)	24(1)	1(1)	3(1)	0(1)	
C(2)	23(1)	23(1)	24(1)	1(1)	4(1)	2(1)	
C(3)	23(1)	26(1)	27(1)	-1(1)	6(1)	0(1)	
C(4)	$\frac{23(1)}{34(1)}$	30(1)	35(1)	-3(1)	8(1)	6(1)	
C(5)	53(1)	34(1)	44(1)	-10(1)	9(1)	10(1)	
C(6)	61(2)	27(1)	46(1)	2(1)	13(1)	11(1)	
C(7)	25(1)	$\frac{2}{33(1)}$	31(1)	-1(1)	2(1)	2(1)	
C(8)	23(1)	25(1)	29(1)	3(1)	$\frac{2(1)}{2(1)}$	-2(1)	
C(9)	30(1)	24(1)	$\frac{1}{24(1)}$	2(1)	$\frac{2(1)}{8(1)}$	-4(1)	
C(10)	44(1)	23(1)	58(1)	$\frac{1}{6(1)}$	4(1)	0(1)	
C(11)	37(1)	$\frac{10}{40(1)}$	58(2)	16(1)	-2(1)	-5(1)	
C(12)	27(1)	42(1)	26(1)	3(1)	2(1)	1(1)	
C(13)	$\frac{1}{28(1)}$	42(1)	$\frac{1}{23(1)}$	0(1)	$\frac{1}{2(1)}$	0(1)	
C(14)	55(1)	50(1)	38(1)	2(1)	18(1)	11(1)	
C(15)	52(2)	76(2)	37(1)	3(1)	21(1)	11(1)	
C(16)	44(1)	72(2)	33(1)	10(1)	10(1)	-10(1)	
C(17)	71(2)	49(2)	55(2)	12(1)	22(1)	$1(1)^{'}$	
C(18)	56(1)	46(1)	39(1)	4(1)	20(1)	7(1)	
C(19)	27(1)	23(1)	22(1)	-1(1)	4(1)	1(1)	
C(20)	32(1)	28(1)	32(1)	-3(1)	1(1)	-1(1)	
C(21)	44(1)	23(1)	37(1)	-5(1)	2(1)	-2(1)	
C(22)	47(1)	26(1)	28(1)	0(1)	5(1)	9(1)	
C(23)	33(1)	31(1)	23(1)	3(1)	5(1)	9(1)	
C(24)	28(1)	27(1)	17(1)	2(1)	6(1)	3(1)	
C(25)	35(1)	30(1)	61(2)	-11(1)	-7(1)	-4(1)	
C(26)	72(2)	27(1)	51(1)	-4(1)	-1(1)	16(1)	

C(27) C(28) C(29) C(30) C(31) C(32) C(32) C(33) C(34) C(35)	25(1) 22(1) 22(1) 23(1) 24(1) 30(1) 26(1) 30(1) 38(1)	31(1)22(1)23(1)24(1)31(1)32(1)25(1)32(1)47(1)	26(1) 22(1) 23(1) 27(1) 25(1) 20(1) 21(1) 25(1) 29(1)	$ \begin{array}{c} 1(1) \\ 0(1) \\ -1(1) \\ 1(1) \\ 4(1) \\ 1(1) \\ 0(1) \\ -6(1) \\ 3(1) \end{array} $	2(1) 2(1) 2(1) 2(1) 3(1) 4(1) 1(1) 5(1) 7(1)	2(1) 3(1) 3(1) 2(1) 2(1) 4(1) 6(1) -7(1) -9(1)
C(35) C(36)	38(1) 33(1)	47(1) 32(1)	29(1) 29(1) 23(1)	3(1) -5(1)	7(1) 0(1)	-9(1) -1(1)

Table 5. Hydrogen coordinates ($x \ 10^4$) and isotropic displacement parameters (Å²x 10³) for Ester **2a**.

	Х	У	Z	U(eq)	
 II(1 A)	5106	0015	2401	26	
$\Pi(1A)$ $\Pi(2A)$	3480	004 <i>3</i> 10249	2401	20	
$\Pi(2A)$ $\Pi(2A)$	4400	10246	2914	20	
$\Pi(3A)$	2020	10374	2014	30	
$\Pi(4A)$ $\Pi(5A)$	2939	17801	2004	59	
$\Pi(SA)$ $\Pi(SB)$	5000 4754	12001	2404	03 65	
$\Pi(3D)$ $\Pi(5C)$	2785	12247	2687	03 65	
$\Pi(3C)$ $\Pi(6A)$	3783	12018	2160	05 66	
$\Pi(0A)$ $\Pi(6D)$	2776	12910	2109	00 66	
$\Pi(0D)$	3720	12207	2185	00 66	
$\Pi(0C)$ $\Pi(7A)$	2580	12397	2103	44	
$\Pi(7\mathbf{A})$ $\Pi(7\mathbf{D})$	2580	0002	2207	44	
H(7C)	2062	9092	2207	44	
$\Pi(7C)$ $\Pi(8A)$	2805	9241	2717	21	
$\Pi(0A)$ $\Pi(0A)$	3803	7403	2/1/ 2046	21	
$\Pi(0D)$ $\Pi(10A)$	5046	7403 5127	2040	50	
U(10R)	<i>4</i> 075	/200	2637	50	
$\Pi(10D)$ $\Pi(11A)$	4975	4309	2080	50	
$\mathbf{U}(11\mathbf{R})$	4222	4270	3780	68	
H(11C)	5288	4723 5548	3825	68	
H(12A)	5134	10185	3823	38	
H(12R)	53/1	0053	3551	38	
H(12D) H(14A)	3560	10220	<i>4575</i>	56	
H(14A)	2703	0263	5313	50	
H(16A)	2703	7308	5/35	59	
$H(17\Delta)$	4018	6474	4795	69	
$H(18\Delta)$	4010	7416	4035	55	
$H(21\Delta)$	4050	4400	843	42	
$H(23\Delta)$	7796	5403	1686	35	
$H(25\Lambda)$	3583	5478	601	55 64	
H(25R)	3852	6690	394	64	
H(25C)	3469	6470	1078	64	
$H(26\Delta)$	6316	3090	1044	76	
H(26R)	7105	3377	1672	76	
H(26C)	7478	3558	987	76	
H(274)	8157	7142	1980	41	
11(2/11)	0157	/174	1700	71	

H(27B)	7173	7795	2206	41	
H(27C)	7569	8052	1530	41	
H(30A)	7774	11320	1056	29	
H(32A)	6803	9652	-533	33	
H(34A)	7241	11007	1992	43	
H(34B)	6999	9761	2142	43	
H(34C)	6042	10603	1991	43	
H(35A)	8058	11059	-601	57	
H(35B)	8858	11195	32	57	
H(35C)	7917	12053	-129	57	
H(36A)	5621	8293	-581	44	
H(36B)	4717	8407	-114	44	
H(36C)	5661	7553	43	44	
H(1)	4219(15)	8388(15)	930(9)	25(5)	

Table 6. Torsion angles [°] for Ester 2a.

C(19)-Si(1)-C(1)-C(8)	-40.78(14)
C(28)-Si(1)-C(1)-C(8)	-170.55(11)
C(19)-Si(1)-C(1)-C(2)	-165.45(11)
C(28)-Si(1)-C(1)-C(2)	64.79(14)
C(8)-C(1)-C(2)-C(7)	-38.7(2)
Si(1)-C(1)-C(2)-C(7)	83.68(16)
C(8)-C(1)-C(2)-C(3)	87.31(18)
Si(1)-C(1)-C(2)-C(3)	-150.28(12)
C(12)-O(1)-C(3)-C(4)	-116.78(17)
C(12)-O(1)-C(3)-C(2)	117.95(16)
C(7)-C(2)-C(3)-O(1)	65.48(18)
C(1)-C(2)-C(3)-O(1)	-61.69(18)
C(7)-C(2)-C(3)-C(4)	-55.8(2)
C(1)-C(2)-C(3)-C(4)	176.98(15)
O(1)-C(3)-C(4)-C(6)	-175.20(17)
C(2)-C(3)-C(4)-C(6)	-53.3(2)
O(1)-C(3)-C(4)-C(5)	61.1(2)
C(2)-C(3)-C(4)-C(5)	-177.00(17)
C(2)-C(1)-C(8)-C(9)	-154.89(15)
Si(1)-C(1)-C(8)-C(9)	81.79(16)
C(10)-O(3)-C(9)-O(2)	-1.3(3)
C(10)-O(3)-C(9)-C(8)	-178.56(16)
C(1)-C(8)-C(9)-O(2)	33.1(3)
C(1)-C(8)-C(9)-O(3)	-149.70(15)
C(9)-O(3)-C(10)-C(11)	85.5(2)
C(3)-O(1)-C(12)-C(13)	175.79(15)
O(1)-C(12)-C(13)-C(18)	105.5(2)
O(1)-C(12)-C(13)-C(14)	-73.0(2)
C(18)-C(13)-C(14)-C(15)	-1.5(3)
C(12)-C(13)-C(14)-C(15)	177.0(2)
C(13)-C(14)-C(15)-C(16)	1.6(4)
C(14)-C(15)-C(16)-C(17)	-0.7(4)
C(15)-C(16)-C(17)-C(18)	-0.3(4)
C(14)-C(13)-C(18)-C(17)	0.6(4)
C(12)-C(13)-C(18)-C(17)	-177.9(2)

C(16)-C(17)-C(18)-C(13)	0.3(4)
C(28)-Si(1)-C(19)-C(20)	-124.87(15)
C(1)-Si(1)-C(19)-C(20)	101.61(16)
C(28)-Si(1)-C(19)-C(24)	54.57(16)
C(1)-Si(1)-C(19)-C(24)	-78.95(15)
C(24)-C(19)-C(20)-C(21)	-0.6(3)
Si(1)-C(19)-C(20)-C(21)	178.84(15)
C(24)-C(19)-C(20)-C(25)	179.39(19)
Si(1)-C(19)-C(20)-C(25)	-1.2(3)
C(19)-C(20)-C(21)-C(22)	0.4(3)
C(25)-C(20)-C(21)-C(22)	-179.6(2)
C(20)-C(21)-C(22)-C(23)	-0.1(3)
C(20)-C(21)-C(22)-C(26)	-1792(2)
C(21)-C(22)-C(23)-C(24)	0.0(3)
C(26)-C(22)-C(23)-C(24)	$179\ 10(19)$
C(22)-C(22)-C(23)-C(24)	-0.2(3)
C(22)-C(23)-C(24)-C(17)	-0.2(5) 178 57(17)
C(22)- $C(23)$ - $C(24)$ - $C(27)$	1/8.5/(1/)
S(1) C(19) C(24) C(23)	(0.5(5))
SI(1)-C(19)-C(24)-C(25) C(20)-C(10)-C(24)-C(27)	-1/0.93(13) 179.21(17)
C(20)-C(19)-C(24)-C(27)	-1/8.21(1/)
SI(1)-C(19)-C(24)-C(27)	2.3(2)
C(19)-S1(1)-C(28)-C(29)	-113./6(15)
C(1)-S1(1)-C(28)-C(29)	15.68(18)
C(19)-Si(1)-C(28)-C(33)	65.25(15)
C(1)-Si(1)-C(28)-C(33)	-165.31(12)
C(33)-C(28)-C(29)-C(30)	-0.4(2)
$S_1(1)-C(28)-C(29)-C(30)$	178.56(13)
C(33)-C(28)-C(29)-C(34)	-179.91(16)
Si(1)-C(28)-C(29)-C(34)	-0.9(3)
C(28)-C(29)-C(30)-C(31)	-0.2(3)
C(34)-C(29)-C(30)-C(31)	179.33(16)
C(29)-C(30)-C(31)-C(32)	0.4(3)
C(29)-C(30)-C(31)-C(35)	-179.24(18)
C(30)-C(31)-C(32)-C(33)	0.1(3)
C(35)-C(31)-C(32)-C(33)	179.68(18)
C(31)-C(32)-C(33)-C(28)	-0.7(3)
C(31)-C(32)-C(33)-C(36)	179.82(17)
C(29)-C(28)-C(33)-C(32)	0.9(2)
Si(1)-C(28)-C(33)-C(32)	-178.24(13)
C(29)-C(28)-C(33)-C(36)	-179.68(16)
Si(1)-C(28)-C(33)-C(36)	1.2(2)
	(-)

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Definitions:

wR2 = $[\Sigma[w(F_o^2-F_o^2)^2] / \Sigma[w(F_o^2)^2]^{1/2}$

 $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

 $GOF = S = [\Sigma[w(F_o^2 - F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

The thermal ellipsoid plot is shown at the 50% probability level.



X-ray Data Collection, Structure Solution and Refinement for Ethyl (3*R*,4*R*,5*R*)-3-(dimesitylsilyl)-5-(2,2-dimethyl-propionyloxy)-4,6-dimethyl-hept-2-eneoate.

A colorless crystal of approximate dimensions 0.28 x 0.30 x 0.37 mm was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART¹ program package was used to determine the unit-cell parameters and for data collection (25 sec/frame scan time for a sphere of diffraction data). The raw frame data was processed using SAINT² and SADABS³ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL⁴ program. The diffraction symmetry was 2/m and the systematic absences were consistent with the centrosymmetric monoclinic space group $P2_1/n$ which was later determined to be correct.

The structure was solved by direct methods and refined on F^2 by full-matrix least-squares techniques. The analytical scattering factors⁵ for neutral atoms were used throughout the analysis. Hydrogen atoms were either located from a difference-Fourier map and refined (x,y,z and U_{iso}) or were included using a riding model. Carbon atoms C(10), C(11) and C(12) were disordered and included using multiple components with partial site-occupancy-factors. At convergence, wR2 = 0.1660 and Goof = 1.030 for 357 variables refined against 7948 data. As a comparison for refinement on F, R1 = 0.0568 for those 6075 data with I > 2.0 σ (I).



Table 1. Crystal data and structure refinemed dimethyl-propionyloxy)-4,6-dimethyl-hept-2 Identification code Empirical formula Formula weight Temperature Wavelength Crystal system Space group Unit cell dimensions	ent for Ethyl $(3R,4R,5R)$ -3-6 2-eneoate. kaw33 (Jason Tenenbaum C ₃₄ H ₅₂ O ₄ Si 552.85 173(2) K 0.71073 Å Monoclinic $P2_1/n$ a = 12.7614(5) Å	(dimesitylsilyl)-5-(2,2-)) $\alpha = 90^{\circ}$.
Volume	b = 12.5893(5) Å c = 20.3324(8) Å $3263.6(2) \text{ Å}^{3}$	$\beta = 92.4460(10)^{\circ}.$ $\gamma = 90^{\circ}.$
Density (calculated) Absorption coefficient F(000) Crystal size Theta range for data collection Index ranges Reflections collected Independent reflections Completeness to theta = 28.30° Absorption correction Max. and min. transmission Refinement method Data / restraints / parameters Goodness-of-fit on F ² Final R indices [I>2sigma(I)] R indices (all data) Extinction coefficient Largest diff. peak and hole	7 1.125 Mg/m ³ 0.106 mm ⁻¹ 1208 0.37 x 0.30 x 0.28 mm ³ 1.85 to 28.30°. -17 $\le h \le 16$, -16 $\le k \le 15$ 34367 7948 [R(int) = 0.0347] 98.1% None 0.9710 and 0.9619 Full-matrix least-squares of 7948 / 0 / 357 1.030 R1 = 0.0568, wR2 = 0.148 R1 = 0.0777, wR2 = 0.166 0.0008(5) 0.668 and -0.458 e.Å ⁻³	, -27 ≤ <i>l</i> ≤ 26 on F ² 82 60

	Х	У	Z	U(eq)	
$\overline{\mathrm{Si}(1)}$	5213(1)	8088(1)	1303(1)	22(1)	
O(1)	3786(1)	9218(1)	3371(1)	$\frac{1}{33(1)}$	
O(2)	5324(1)	9133(2)	3936(1)	63(1)	
O(3)	5839(1)	6618(1)	2901(1)	37(1)	
O(4)	4540(1)	5501(1)	2570(1)	45(1)	
C(1)	4795(1)	8330(1)	2181(1)	22(1)	
C(2)	4104(1)	9353(2)	2204(1)	25(1)	
C(3)	4217(2)	9914(2)	2874(1)	30(1)	
C(4)	3642(2)	10982(2)	2912(1)	45(1)	
C(5)	3863(2)	11492(2)	3583(2)	65(1)	
C(6)	3957(2)	11729(2)	2364(2)	61(1)	
C(7)	2950(2)	9159(2)	1999(1)	32(1)	
C(8)	4410(2)	8918(2)	3884(1)	39(1)	
C(9)	3826(2)	8265(2)	4392(1)	47(1)	
C(10)	2729(5)	8525(6)	4472(4)	60(2)	
C(11)	4421(4)	8301(4)	5072(2)	45(1)	
C(12)	3967(4)	6991(4)	4216(3)	67(2)	
C(10B)	2718(5)	8005(6)	4130(4)	70(2)	
C(11B)	3558(6)	9202(6)	4913(3)	59(2)	
C(12B)	4505(6)	7555(6)	4656(4)	57(2)	
C(13)	4229(2)	7324(2)	2413(1)	27(1)	
C(14)	4976(2)	6470(2)	2655(1)	31(1)	
C(15)	5196(2)	4592(2)	2767(2)	57(1)	
C(16)	5101(2)	4365(3)	3481(2)	67(1)	
C(17)	5741(2)	6688(2)	1215(1)	24(1)	
C(18)	5104(2)	5852(2)	963(1)	30(1)	
C(19)	5509(2)	4821(2)	933(1)	39(1)	
C(20)	6532(2)	4582(2)	1134(1)	39(1)	
C(21)	7164(2)	5405(2)	1365(1)	33(1)	
C(22)	6/92(2)	6440(2)	$\frac{141}{(1)}$	26(1)	
C(23)	$\frac{39}{1(2)}$	5999(2)	/28(1)	42(1)	
C(24)	6948(3) 7528(2)	3454(2)	1109(2)	60(1)	
C(25)	/528(2)	7205(2)	1/11(1) 015(1)	33(1)	
C(20)	$\frac{007}{(1)}$	9113(1)	913(1) 216(1)	23(1) 25(1)	
C(27)	0099(2)	9082(2)	210(1) 112(1)	23(1) 20(1)	
C(28)	0/42(2) 7264(2)	9/84(2) 10520(2)	-113(1) -217(1)	30(1) 31(1)	
C(29)	7304(2) 7334(2)	10550(2) 10572(2)	21/(1) 000(1)	31(1) 27(1)	
C(30)	7334(2) 6705(1)	10372(2) 0884(2)	1250(1)	$\frac{2}{(1)}$	
C(31)	5/03(1)	8317(2)	-106(1)	$\frac{24(1)}{31(1)}$	
C(32)	2433(2) 8060(2)	11281(2)	-170(1)	$\frac{31(1)}{48(1)}$	
C(33)	6750(2)	10022(2)	-1++(1) 1088(1)	$\frac{1}{30(1)}$	
C(34)	0730(2)	10022(2)	1900(1)	30(1)	

Table 2. Atomic coordinates (x 10⁴) and equivalent isotropic displacement parameters (Å²x 10³) for Ethyl (3*R*,4*R*,5*R*)-3-(dimesitylsilyl)-5-(2,2-dimethyl-propionyloxy)-4,6-dimethyl-hept-2-eneoate. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

Si(1)-C(26)	1.8938(19)
Si(1)-C(17)	1 8978(19)
$S_{i}(1)-C(1)$	1.9080(18)
O(1) C(8)	1.3000(10)
O(1) - C(3)	1.540(5)
O(1) - C(3)	1.463(2)
O(2)-C(8)	1.197(3)
O(3)-C(14)	1.205(3)
O(4) - C(14)	1.350(3)
O(4)- $C(15)$	1.464(3)
C(1)-C(13)	1 543(3)
C(1) C(13)	1.5+5(5) 1.5(2(2))
C(1)-C(2)	1.502(2)
C(2)-C(7)	1.533(3)
C(2)-C(3)	1.535(3)
C(3)-C(4)	1.534(3)
C(4)-C(5)	1.522(4)
C(4)- $C(6)$	1.527(4)
C(8) - C(9)	1.537(3)
C(0) C(12P)	1.337(3) 1.241(8)
C(9) - C(12B)	1.341(8)
C(9)-C(10)	1.454(7)
C(9)-C(10B)	1.525(7)
C(9)-C(11)	1.549(5)
C(9)-C(11B)	1.632(7)
C(9)-C(12)	1.655(6)
C(13)-C(14)	1 505(3)
C(15) C(16)	1.505(5) 1.480(5)
C(17) - C(10)	1.409(3)
C(17) - C(18)	1.412(3)
C(17)-C(22)	1.420(3)
C(18)-C(19)	1.401(3)
C(18)-C(23)	1.514(3)
C(19)-C(20)	1.384(3)
C(20) - C(21)	1 383(3)
C(20) - C(24)	1517(3)
C(20) C(24)	1.317(3) 1.202(2)
C(21) - C(22)	1.595(5)
C(22)-C(25)	1.506(3)
C(26)-C(31)	1.413(3)
C(26)-C(27)	1.423(2)
C(27)-C(28)	1.395(3)
C(27)-C(32)	1.512(3)
C(28) - C(29)	1 385(3)
C(29) - C(30)	1.302(3) 1.301(3)
C(29) - C(30)	1.591(5) 1.500(2)
C(29)-C(33)	1.309(3)
C(30)-C(31)	1.395(3)
C(31)-C(34)	1.511(3)
C(26)-Si(1)-C(17)	112.30(8)
C(26)-Si(1)-C(1)	118.13(8)
C(17) - Si(1) - C(1)	110 60(8)
C(8) - O(1) - C(3)	118 62(16)
C(14) O(4) C(15)	116.02(10) 116.21(10)
C(14) - O(4) - C(15)	110.31(19)
C(13)-C(1)-C(2)	113.28(15)
C(13)-C(1)-Si(1)	107.92(12)

Table 3. Bond lengths [Å] and angles [°] for Ethyl (3R,4R,5R)-3-(dimesitylsilyl)-5-(2,2-dimethyl-propionyloxy)-4,6-dimethyl-hept-2-eneoate.

C(2)-C(1)-Si(1)	109.94(12)
C(7)-C(2)-C(3)	111.49(16)
C(7)-C(2)-C(1)	113.42(16)
C(3)-C(2)-C(1)	112.01(15)
O(1) - C(3) - C(4)	107.15(16)
O(1) C(2) C(2)	107.13(10) 109.20(16)
O(1) - C(3) - C(2)	108.29(10)
C(4)-C(3)-C(2)	114.96(18)
C(5)-C(4)-C(6)	110.5(2)
C(5)-C(4)-C(3)	110.2(2)
C(6)-C(4)-C(3)	111.18(19)
O(2)-C(8)-O(1)	123.3(2)
O(2) - C(8) - C(9)	124.1(2)
O(1) - C(8) - C(9)	112.61(18)
C(12B)-C(9)-C(10)	135 5(5)
C(12B) - C(9) - C(10B)	124.7(5)
C(12D) - C(1) - C(10D)	127.7(3)
C(10)-C(9)-C(10B)	37.3(3)
C(12B)-C(9)-C(8)	10/.6(4)
C(10)-C(9)-C(8)	116.9(3)
C(10B)-C(9)-C(8)	110.5(3)
C(12B)-C(9)-C(11)	51.6(4)
C(10)-C(9)-C(11)	109.3(4)
C(10B)-C(9)-C(11)	136 8(4)
C(8)-C(9)-C(11)	110.6(2)
C(12B)-C(0)-C(11B)	110.0(2) 111 8(5)
C(10) C(0) C(11B)	62.3(4)
C(10P) C(0) C(11P)	02.3(4)
C(10D) - C(9) - C(11D)	99.3(4)
C(3)-C(9)-C(11B)	99.9(3)
C(11)-C(9)-C(11B)	60.5(3)
C(12B)-C(9)-C(12)	50.6(4)
C(10)-C(9)-C(12)	110.9(4)
C(10B)-C(9)-C(12)	79.9(4)
C(8)-C(9)-C(12)	108.2(3)
C(11)-C(9)-C(12)	99.6(3)
C(11B)-C(9)-C(12)	150.3(4)
C(14)-C(13)-C(1)	112.84(16)
O(3) - C(14) - O(4)	123.86(19)
O(3) - C(14) - C(13)	125.54(19)
O(4)-C(14)-C(13)	110 59(18)
O(4)-C(15)-C(16)	110.4(2)
C(18)-C(17)-C(22)	117.59(17)
C(18) C(17) S(1)	121.66(14)
C(10) - C(17) - SI(1)	121.00(14) 120.72(14)
C(22)-C(17)-SI(1)	120.73(14)
C(19) - C(18) - C(17)	119.95(19)
C(19)-C(18)-C(23)	116.65(19)
C(17)-C(18)-C(23)	123.42(18)
C(20)-C(19)-C(18)	122.3(2)
C(21)-C(20)-C(19)	117.8(2)
C(21)-C(20)-C(24)	120.8(2)
C(19)-C(20)-C(24)	121.4(2)
C(20)-C(21)-C(22)	122.0(2)
C(21)-C(22)-C(17)	120.31(18)
C(21)-C(22)-C(25)	117.74(18)
C(17)-C(22)-C(25)	121.92(17)
C(31)-C(26)-C(27)	117.78(17)
	· · · ·

$\begin{array}{l} C(31)-C(26)-Si(1)\\ C(27)-C(26)-Si(1)\\ C(28)-C(27)-C(26)\\ C(28)-C(27)-C(32)\\ C(26)-C(27)-C(32)\\ C(29)-C(28)-C(27)\\ C(28)-C(29)-C(30)\\ C(28)-C(29)-C(30)\\ C(30)-C(29)-C(33)\\ C(30)-C(29)-C(31)\\ C(30)-C(31)-C(26)\\ C(30)-C(31)-C(34)\\ C(26)-C(31)-C(34)\\ \end{array}$	$126.52(14) \\115.68(14) \\119.78(18) \\117.73(17) \\122.48(17) \\122.32(18) \\117.96(18) \\121.76(19) \\120.3(2) \\121.73(18) \\120.41(17) \\115.91(17) \\123.68(16)$
	120:00(10)

Table 4. Anisotropic displacement parameters (Å²x 10³) for Ethyl (3*R*,4*R*,5*R*)-3-(dimesitylsilyl)-5-(2,2-dimethyl-propionyloxy)-4,6-dimethyl-hept-2-eneoate. The anisotropic displacement factor exponent takes the form: $-2\pi^2$ [h² a^{*2}U¹¹ + ... + 2 h k a^{*} b^{*} U¹²]

	U11	U ²²	U ³³	U ²³	U ¹³	U ¹²	
$\overline{\text{Si}(1)}$	23(1)	21(1)	22(1)	-2(1)	2(1)	-1(1)	
O(1)	26(1)	47(1)	28(1)	-7(1)	6(1)	-5(1)	
O(2)	30(1)	114(2)	44(1)	11(1)	-2(1)	-20(1)	
O(3)	34(1)	35(1)	41(1)	11(1)	1(1)	$1(1)^{-1}$	
O(4)	45(1)	27(1)	63(1)	9(1)	5(1)	-3(1)	
C(1)	22(1)	22(1)	24(1)	1(1)	2(1)	1(1)	
C(2)	25(1)	24(1)	26(1)	-1(1)	3(1)	3(1)	
C(3)	26(1)	32(1)	33(1)	-8(1)	8(1)	-2(1)	
C(4)	38(1)	35(1)	62(2)	-18(1)	12(1)	5(1)	
C(5)	57(2)	56(2)	83(2)	-44(2)	16(2)	1(1)	
C(6)	63(2)	27(1)	92(2)	-4(1)	19(2)	11(1)	
C(7)	26(1)	35(1)	34(1)	-1(1)	-1(1)	4(1)	
C(8)	30(1)	58(2)	29(1)	-9(1)	4(1)	-6(1)	
C(9)	37(1)	75(2)	30(1)	-3(1)	6(1)	-11(1)	
C(13)	27(1)	26(1)	30(1)	2(1)	4(1)	-2(1)	
C(14)	32(1)	28(1)	33(1)	6(1)	7(1)	-1(1)	
C(15)	53(2)	31(1)	89(2)	14(1)	16(2)	2(1)	
C(16)	46(2)	55(2)	99(2)	35(2)	9(2)	4(1)	
C(17)	27(1)	24(1)	23(1)	-2(1)	4(1)	0(1)	
C(18)	32(1)	27(1)	32(1)	-6(1)	2(1)	-1(1)	
C(19)	47(1)	25(1)	43(1)	-11(1)	-2(1)	-3(1)	
C(20)	51(1)	27(1)	37(1)	-6(1)	-1(1)	9(1)	
C(21)	36(1)	32(1)	30(1)	-1(1)	1(1)	9(1)	
C(22)	30(1)	27(1)	23(1)	1(1)	4(1)	2(1)	
C(23)	34(1)	36(1)	55(1)	-17(1)	-4(1)	-5(1)	
C(24)	78(2)	30(1)	69(2)	-14(1)	-17(2)	16(1)	
C(25)	28(1)	30(1)	39(1)	3(1)	-4(1)	0(1)	
C(26)	25(1)	22(1)	23(1)	0(1)	3(1)	2(1)	
C(27)	25(1)	27(1)	24(1)	-1(1)	1(1)	5(1)	
C(28)	29(1)	39(1)	22(1)	4(1)	3(1)	4(1)	
C(29)	28(1)	36(1)	30(1)	8(1)	4(1)	-1(1)	
C(30)	25(1)	26(1)	30(1)	2(1)	1(1)	-1(1)	
C(31)	24(1)	22(1)	25(1)	0(1)	2(1)	2(1)	
C(32)	34(1)	35(1)	23(1)	-4(1)	1(1)	2(1)	
C(33)	45(1)	63(2)	38(1)	13(1)	6(1)	-18(1)	
C(34)	35(1)	29(1)	25(1)	-5(1)	4(1)	-9(1)	

Table 5. Hydrogen coordinates (x 10⁴) and isotropic displacement parameters (Å²x 10³) for Ethyl (3R,4R,5R)-3-(dimesitylsilyl)-5-(2,2-dimethyl-propionyloxy)-4,6-dimethyl-hept-2-eneoate.

	X	У	Z	U(eq)	
H(1A)	5439	8441	2470	27	
H(2A)	4383	9856	1873	$\frac{1}{30}$	
H(3A)	4979	10031	2985	36	
H(4A)	2871	10845	2859	54	
H(5A)	3656	11003	3929	97	
H(5B)	3462	12153	3611	97	
H(5C)	4614	11648	3640	97	
H(6A)	3575	12401	2398	91	
H(6B)	3784	11401	1936	91	
H(6C)	4713	11865	2405	91	
H(7A)	2560	9828	2024	48	
H(7B)	2652	8637	2296	48	
H(7C)	2900	8889	1547	48	
H(10Å)	2665	9281	4578	91	
H(10B)	2457	8099	4830	91	
H(10C)	2325	8371	4062	91	
H(11A)	4407	9026	5246	67	
H(11B)	5149	8079	5024	67	
H(11C)	4082	7819	5376	67	
H(12A)	4172	6917	3759	101	
H(12B)	3302	6621	4272	101	
H(12C)	4511	6682	4512	101	
H(10D)	2280	8643	4147	105	
H(10E)	2421	7446	4401	105	
H(10F)	2741	7759	3674	105	
H(11D)	3619	9896	4700	89	
H(11E)	4052	9164	5295	89	
H(11F)	2841	9109	5058	89	
H(12D)	4946	7898	5000	86	
H(12E)	4947	7279	4312	86	
H(12F)	4116	6968	4848	86	
H(13A)	3764	7518	2771	33	
H(13B)	3783	7040	2043	33	
H(15A)	5937	4748	2678	69	
H(15B)	4977	3960	2506	69	
H(16A)	5546	3757	3606	100	
H(16B)	4369	4198	3567	100	
H(16C)	5324	4988	3739	100	
H(19A)	5067	4265	768	46	
H(21A)	7874	5259	1493	39	
H(23A)	3683	5316	575	63	
H(23B)	3933	6513	366	63	
H(23C)	3563	6262	1092	63	
H(24A)	7683	3444	1270	90	
H(24B)	6898	3195	654	90	
H(24C)	6533	2995	1388	90	
H(25A)	8211	6938	1817	49	

H(25B)	7239	7550	2113	49	
H(25C)	7612	7841	1393	49	
H(28A)	6752	9749	-579	36	
H(30A)	7752	11082	1134	33	
H(32A)	5567	8425	-663	46	
H(32B)	4692	8445	-122	46	
H(32C)	5616	7586	-70	46	
H(33A)	7985	11143	-618	72	
H(33B)	8792	11172	6	72	
H(33C)	7854	12015	-55	72	
H(34A)	7236	10599	2110	44	
H(34B)	6994	9361	2198	44	
H(34C)	6049	10196	2136	44	
H(1)	4279(17)	8123(17)	944(10)	26(5)	
~ /		× ,	~ /		

$\overline{C(26)-Si(1)-C(1)-C(13)}$	-172.64(12)
C(17)-S $i(1)$ - $C(1)$ - $C(13)$	-41.30(14)
C(26)-Si(1)-C(1)-C(2)	63 36(15)
C(17) Si(1) $C(1)$ $C(2)$	165,30(12)
C(17) - S(1) - C(1) - C(2)	-105.50(12)
C(13)-C(1)-C(2)-C(7)	-36.2(2)
$S_1(1) - C_1(1) - C_2(2) - C_1(7)$	82.58(17)
C(13)-C(1)-C(2)-C(3)	89.05(19)
Si(1)-C(1)-C(2)-C(3)	-150.13(13)
C(8)-O(1)-C(3)-C(4)	-113.6(2)
C(8)-O(1)-C(3)-C(2)	121.90(19)
C(7)-C(2)-C(3)-O(1)	62.5(2)
C(1)-C(2)-C(3)-O(1)	-65.77(19)
C(7)-C(2)-C(3)-C(4)	-57.2(2)
C(1)-C(2)-C(3)-C(4)	174.46(17)
O(1)-C(3)-C(4)-C(5)	63.0(2)
C(2)-C(3)-C(4)-C(5)	-176 6(2)
O(1)-C(3)-C(4)-C(6)	-1742(2)
C(2) - C(3) - C(4) - C(6)	-53 8(3)
C(2) - C(3) - C(4) - C(0)	5 0(3)
C(3) - O(1) - C(3) - O(2)	-5.0(5) 175 22(18)
C(3) - C(1) - C(0) - C(1)	1/5.52(16)
O(2)-C(8)-C(9)-C(12B)	-32.9(3)
O(1)-C(8)-C(9)-C(12B)	146.8(4)
O(2)-C(8)-C(9)-C(10)	147.7(4)
O(1)-C(8)-C(9)-C(10)	-32.6(5)
O(2)-C(8)-C(9)-C(10B)	-172.0(4)
O(1)-C(8)-C(9)-C(10B)	7.7(4)
O(2)-C(8)-C(9)-C(11)	21.8(4)
O(1)-C(8)-C(9)-C(11)	-158.5(3)
O(2)-C(8)-C(9)-C(11B)	83.9(4)
O(1)-C(8)-C(9)-C(11B)	-96.4(3)
O(2)-C(8)-C(9)-C(12)	-86.3(4)
O(1)-C(8)-C(9)-C(12)	93.4(3)
C(2)-C(1)-C(13)-C(14)	-156 30(16)
Si(1)-C(1)-C(13)-C(14)	81 75(17)
C(15) - O(4) - C(14) - O(3)	-27(3)
C(15) - O(4) - C(14) - C(13)	1782(2)
C(1)-C(13)-C(14)-O(3)	288(3)
C(1) - C(13) - C(14) - O(3)	152 21(17)
C(14) - C(15) - C(14) - C(14)	-132.21(17) 86 2(2)
C(14)-O(4)-C(13)-C(10)	60.2(5)
C(20)-SI(1)-C(17)-C(18)	-128.98(10)
C(1)-S(1)-C(17)-C(18)	96./1(1/)
C(26)-Si(1)-C(1/)-C(22)	52.68(17)
$C(1)-S_1(1)-C(17)-C(22)$	-81.63(16)
C(22)-C(17)-C(18)-C(19)	1.2(3)
Si(1)-C(17)-C(18)-C(19)	-177.17(16)
C(22)-C(17)-C(18)-C(23)	-179.86(19)
Si(1)-C(17)-C(18)-C(23)	1.7(3)
C(17)-C(18)-C(19)-C(20)	-0.9(3)
C(23)-C(18)-C(19)-C(20)	-179.9(2)
C(18)-C(19)-C(20)-C(21)	-0.6(4)
C(18)-C(19)-C(20)-C(24)	178.8(Ź)
	× /

Table 6. Torsion angles [°] for Ethyl (3R,4R,5R)-3-(dimesitylsilyl)-5-(2,2-dimethyl-propionyloxy)-4,6-dimethyl-hept-2-eneoate.

C(19)-C(20)-C(21)-C(22)	1.9(3)
C(24)-C(20)-C(21)-C(22)	-177.5(2)
C(20)-C(21)-C(22)-C(17)	-1.5(3)
C(20)-C(21)-C(22)-C(25)	$176.\hat{6}(2)$
C(18)-C(17)-C(22)-C(21)	-0.1(3)
Si(1)-C(17)-C(22)-C(21)	178.35(15)
C(18)-C(17)-C(22)-C(25)	-178.11(18)
Si(1)-C(17)-C(22)-C(25)	0.3(2)
C(17)-Si(1)-C(26)-C(31)	-110.44(17)
C(1)-Si(1)-C(26)-C(31)	20.1(2)
C(17)-Si(1)-C(26)-C(27)	68.23(16)
C(1)-Si(1)-C(26)-C(27)	-161.19(13)
C(31)-C(26)-C(27)-C(28)	1.0(3)
Si(1)-C(26)-C(27)-C(28)	-177.78(14)
C(31)-C(26)-C(27)-C(32)	-178.03(17)
Si(1)-C(26)-C(27)-C(32)	3.2(2)
C(26)-C(27)-C(28)-C(29)	-0.4(3)
C(32)-C(27)-C(28)-C(29)	178.68(19)
C(27)-C(28)-C(29)-C(30)	-0.3(3)
C(27)-C(28)-C(29)-C(33)	179.7(2)
C(28)-C(29)-C(30)-C(31)	0.4(3)
C(33)-C(29)-C(30)-C(31)	-179.6(2)
C(29)-C(30)-C(31)-C(26)	0.2(3)
C(29)-C(30)-C(31)-C(34)	-179.93(18)
C(27)-C(26)-C(31)-C(30)	-0.9(3)
Si(1)-C(26)-C(31)-C(30)	177.74(14)
C(27)-C(26)-C(31)-C(34)	179.22(17)
Si(1)-C(26)-C(31)-C(34)	-2.1(3)

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Definitions:

$$wR2 = \left[\Sigma[w(F_0^2 - F_c^2)^2] / \Sigma[w(F_0^2)^2]^{1/2}\right]$$

 $R1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$

Goof = S = $[\Sigma[w(F_o^2-F_c^2)^2] / (n-p)]^{1/2}$ where n is the number of reflections and p is the total number of parameters refined.

The thermal ellipsoid plot is shown at the 50% probability level.

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