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

Sharon A. Blair, Jason M. Tenenbaum, K. A. Woerpel*
Department of Chemistry, University of California, Irvine, California 92697
A. Synthesis of Starting Materials
i) Synthesis of Silyl Anion ..... S-2
ii) Synthesis of Enoates
ii) Synthesis of Enoates ..... S-3 ..... 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 $\mathrm{C}-\mathrm{Si}$ 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: ${ }^{1} \mathrm{H}$ NMR and ${ }^{13} \mathrm{C}$ 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 $\delta$ scale, multiplicity $(\mathrm{br}=$ broad, $\mathrm{s}=$ singlet, $\mathrm{d}=$ doublet, $\mathrm{t}=$ triplet, $\mathrm{q}=$ quartet, quint $=$ quintet, and $\mathrm{m}=$ 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 ( $30 \mathrm{~m} \times 0.32 \mathrm{~mm}$ ) wall-coated with DB-1 ( $\mathrm{J} \&$ W Scientific) was used with helium as the carrier gas ( 16 psi column head pressure). GC-MS analyses were conducted on a Finnigan TraceMS from $50^{\circ} \mathrm{C}$ for 1 min then ramped $10^{\circ} \mathrm{C} / \mathrm{min}$ to $270^{\circ} \mathrm{C}$. 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, $\mathrm{CH}_{2} \mathrm{Cl}_{2}, \mathrm{Et}_{2} \mathrm{O}$, and toluene were purified by filtration through activated alumina according to the
method of Grubbs. ${ }^{1}$ Hexane, benzene, trichlorosilane, and $\mathrm{BF}_{3} \cdot \mathrm{Et}_{2} \mathrm{O}$ were purified by distillation from $\mathrm{CaH}_{2} . \mathrm{NaH}$ and $\mathrm{Li}^{\circ}$ were washed with hexanes and dried under reduced pressure prior to use. Ethyl crotonate, crotonaldehyde, and isobutyraldehyde were purified by distillation over $\mathrm{CaCl}_{2}$. All other reagents were used as received.

## A-i. Synthesis of Silyl Anion.



Dimesitylchlorosilane. To a mixture of mesityllithium etherate ${ }^{2}(19.96 \mathrm{~g}, 99.7 \mathrm{mmol})$ in 84 mL of benzene was added a solution of trichlorosilane ( $5.0 \mathrm{~mL}, 50 \mathrm{mmol}$ ) 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 $(4 \times 100 \mathrm{~mL})$. The washes were combined and concentrated in vacuo to afford an orange oil. The oil was purified by bulb-to-bulb distillation $\left(165-170{ }^{\circ} \mathrm{C} / 0.1\right.$ Torr) to give the known compound as a white solid ${ }^{2}(7.79 \mathrm{~g}, 70 \%):{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 6.83(\mathrm{~s}, 4 \mathrm{H}), 6.12(\mathrm{~s}, 1 \mathrm{H}), 2.42(\mathrm{~s}, 12 \mathrm{H}), 2.27(\mathrm{~s}, 6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 125 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 144.3,140.6,129.4,128.0,23.1,21.1 ; \mathrm{IR}(\mathrm{KBr}) 3021,2966,2921,2197,1606,1077,836$ $\mathrm{cm}^{-1}$; HRMS (CI/isobutane) $m / z$ calcd for $\mathrm{C}_{18} \mathrm{H}_{23} \mathrm{ClSi}\left(\mathrm{M}^{+}\right) 302.1258$, found 302.1251. Anal. Calcd for $\mathrm{C}_{18} \mathrm{H}_{23} \mathrm{ClSi}$ : C, 71.37; H, 7.65. Found: C, $71.33 ; \mathrm{H}, 7.79$.

$$
\begin{gathered}
\text { Mes } \\
\text { Mes-Si-H } \\
\substack{\mathrm{Li}^{\prime}}
\end{gathered}
$$

Dimesitylsilyllithium (4). Lithium powder ( $0.58 \mathrm{~g}, 84 \mathrm{mmol}, 30 \%$ dispersion in mineral oil, washed with hexanes) was suspended in 7 mL of THF. To the cooled $\left(0^{\circ} \mathrm{C}\right)$ suspension, a cooled $\left(0^{\circ} \mathrm{C}\right)$ solution of dimesitylchlorosilane $(4.0 \mathrm{~g}, 13 \mathrm{mmol})$ 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 ${ }^{3,4}(2.04 \mathrm{~g}, 50 \%):{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{C}_{6} \mathrm{D}_{6}$ ) $\delta 6.93(\mathrm{~s}, 4 \mathrm{H}), 4.77(\mathrm{~s}, 1 \mathrm{H}), 3.38(\mathrm{br}$ $\mathrm{s}, 12 \mathrm{H}), 2.71$ ( $\mathrm{s}, 12 \mathrm{H}$ ), 2.27 ( $\mathrm{s}, 6 \mathrm{H}$ ), 1.23 (br s, 12H).

## A-ii. Synthesis of Enoates.



Ethyl (2R*, 3R*)-3-benzyloxy-2,4-dimethyl-pentanoate. To a solution of ethyl ( $2 R, 3 R$ )-2,4-dimethyl-3-hydroxypentanoate ${ }^{5}(1.0 \mathrm{~g}, 5.8 \mathrm{mmol})$ in 13 mL of $2: 1 \mathrm{CH}_{2} \mathrm{Cl}_{2} /$ cyclohexane was added benzyl trichloroacetimidate ( $1.3 \mathrm{~mL}, 7.0 \mathrm{mmol}$ ), followed by TfOH ( $0.11 \mathrm{~mL}, 1.2 \mathrm{mmol}$ ). After 3 h at $22^{\circ} \mathrm{C}$, 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 $\mathrm{H}_{2} \mathrm{O}$, 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 $(0.76 \mathrm{~g}, 51 \%)$ : ${ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.32(\mathrm{~m}, 3 \mathrm{H}), 7.26(\mathrm{~m}$, $2 \mathrm{H}), 4.56(\mathrm{~m}, 2 \mathrm{H}), 4.13(\mathrm{q}, J=7.1,2 \mathrm{H}), 3.55(\mathrm{~m}, 1 \mathrm{H}), 2.67(\mathrm{dq}, J=7.0,5.6,1 \mathrm{H}), 1.81(\mathrm{dq}, J=$ $13.4,6.7,1 \mathrm{H}), 1.26(\mathrm{t}, J=7.1,3 \mathrm{H}), 1.23(\mathrm{~d}, J=7.0,3 \mathrm{H}), 1.00(\mathrm{~d}, J=6.7,3 \mathrm{H}), 0.96(\mathrm{~d}, J=6.8$, $3 \mathrm{H}){ }^{13}{ }^{13} \mathrm{CNR}\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 175.6,138.7,128.2,127.5,127.4,85.7,74.7,60.3,42.4,31.6$, 19.7, 18.2, 14.1, 11.7; IR (thin film) 3030, 2963, 1731, 1455, $1065 \mathrm{~cm}^{-1}$; HRMS (CI+/NH3) $\mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{16} \mathrm{H}_{25} \mathrm{O}_{3}(\mathrm{M}+\mathrm{H})^{+}$265.1804, found 265.1801. Anal. Calcd for $\mathrm{C}_{16} \mathrm{H}_{24} \mathrm{O}_{3}: \mathrm{C}, 72.69 ; \mathrm{H}$, 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 ( $-78{ }^{\circ} \mathrm{C}$ ) solution of ethyl ( $2 R^{*}, 3 R^{*}$ )-3-benzyloxy-2,4-dimethyl-pentanoate ( $0.67 \mathrm{~g}, 2.5 \mathrm{mmol}$ ) in 25 mL of $\mathrm{Et}_{2} \mathrm{O}$ was added dropwise over $5 \mathrm{~min} i-\mathrm{Bu}_{2} \mathrm{AlH}(2.5 \mathrm{~mL}, 3.8 \mathrm{mmol}, 1.5 \mathrm{M}$ in toluene). After 10 $\mathrm{min}, 1 \mathrm{~mL}$ of MeOH was added, followed by 2 mL of $\mathrm{H}_{2} \mathrm{O}$. The solution was warmed to $22{ }^{\circ} \mathrm{C}$
over 1 h . 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 $\mathrm{Et}_{2} \mathrm{O}(3 \times 30 \mathrm{~mL})$. The combined organic layers were dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated in vacuo to afford the aldehyde. In a separate flask, triethyl phosphonoacetate ( $0.75 \mathrm{~mL}, 3.8 \mathrm{mmol}$ ) was added to a slurry of $\mathrm{NaH}(0.15 \mathrm{~g}, 3.8 \mathrm{mmol}, 60 \%$ dispersion in oil, washed with hexanes) in 19 mL of THF. The reaction mixture was stirred for 1 h at $22^{\circ} \mathrm{C}$. A solution of the aldehyde in 8 mL of THF was added to the reaction mixture. After 45 min at $22{ }^{\circ} \mathrm{C}, 7 \mathrm{~mL}$ of ammonium chloride (saturated aqueous) was added and the mixture was diluted with 20 mL of $\mathrm{H}_{2} \mathrm{O}$. The organic layer was separated and the aqueous layer was extracted with EtOAc $(2 \times 30 \mathrm{~mL})$. The combined organic layers were washed with brine $(2 \times 50 \mathrm{~mL})$, dried over sodium sulfate, filtered, and concentrated in vacuo to give a $97: 3$ mixture of $\mathrm{E} / \mathrm{Z}$ 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 ${ }^{1} \mathrm{H}$ NMR spectroscopy ( $0.57 \mathrm{~g}, 78 \%$ ): ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.33$ (m, $4 \mathrm{H}), 7.27(\mathrm{~m}, 1 \mathrm{H}), 7.00(\mathrm{dd}, J=15.7,8.1,1 \mathrm{H}), 5.84(\mathrm{dd}, J=15.7,1.2,1 \mathrm{H}), 4.55(\mathrm{~d}, J=1.6,2 \mathrm{H})$, $4.19(\mathrm{q}, J=7.1,2 \mathrm{H}), 3.10(\mathrm{t}, J=5.6,1 \mathrm{H}), 2.63(\mathrm{~m}, 1 \mathrm{H}), 1.83(\mathrm{~m}, 1 \mathrm{H}), 1.29(\mathrm{t}, J=7.1,3 \mathrm{H}), 1.13(\mathrm{~d}$, $J=6.7,3 \mathrm{H}), 0.97(\mathrm{~d}, J=6.9,3 \mathrm{H}), 0.96(\mathrm{~d}, J=6.7,3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 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, $1181 \mathrm{~cm}^{-1}$; HRMS $\left(\mathrm{CI}+/ \mathrm{NH}_{3}\right) \mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{18} \mathrm{H}_{27} \mathrm{O}_{3}$ $(\mathrm{M}+\mathrm{H})^{+}$291.1960, found 291.1963. Anal. Calcd for $\mathrm{C}_{18} \mathrm{H}_{26} \mathrm{O}_{3}: \mathrm{C}, 74.45 ; \mathrm{H}, 9.02$. 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 $(0.98 \mathrm{~g}, 2.3 \mathrm{mmol})$ in 4.3 mL of $10: 1$ pyridine $/ \mathrm{CH}_{2} \mathrm{Cl}_{2}$ was added a solution of $\left(2 R^{*}, 3 R^{*}\right)$-3-(tert-buty-dimethylsiloxy)-2,4-dimethyl-1-pentanol ${ }^{6}$ ( $0.52 \mathrm{~g}, 2.1$ mmol ) in 1 mL of $10: 1$ pyridine $/ \mathrm{CH}_{2} \mathrm{Cl}_{2}$ and the solution was stirred for 45 min . The solution was diluted with 20 mL of $\mathrm{Et}_{2} \mathrm{O}$ and poured into 25 mL of $1: 1 \mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3} / \mathrm{NaHCO}_{3}$ (saturated aqueous).

The organic layer was separated, and the aqueous layer was extracted with $\mathrm{Et}_{2} \mathrm{O}(3 \times 20 \mathrm{~mL})$. The combined organic layers were washed with $\mathrm{NaHCO}_{3}(2 \times 30 \mathrm{~mL})$ and brine $(2 \times 30 \mathrm{~mL})$, dried over $\mathrm{Mg}_{2} \mathrm{SO}_{4}$, filtered, and concentrated in vacuo to give the aldehyde. In a separate flask, triethyl phosphonoacetate ( $0.42 \mathrm{~mL}, 2.1 \mathrm{mmol}$ ) in 4.2 mL of THF was added dropwise to a mixture of $\mathrm{NaH}(0.084 \mathrm{~g}, 2.1 \mathrm{mmol}, 60 \%$ dispersion in mineral oil, washed with hexanes) in 4.2 mL of THF. After 1 h , the aldehyde in 1 mL of THF was added and the mixture was stirred for 1.25 h . To the solution was added 5 mL of $\mathrm{NH}_{4} \mathrm{Cl}$ (saturated aqueous) and the mixture was diluted with 25 mL of $\mathrm{H}_{2} \mathrm{O}$. The organic layer was separated and the aqueous layer was extracted with EtOAc ( $3 \times 30$ mL ). The combined organic layers were dried over $\mathrm{MgSO}_{4}$, 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 ${ }^{1} \mathrm{H}$ NMR spectroscopy ( $0.34 \mathrm{~g}, 52 \%$ ): ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 6.98$ $(\mathrm{dd}, J=15.8,7.8,1 \mathrm{H}), 5.78(\mathrm{dd}, J=15.8,1.3,1 \mathrm{H}), 4.18(\mathrm{dq}, J=7.1,1.6,2 \mathrm{H}), 3.38(\mathrm{t}, J=4.9,1 \mathrm{H})$, $2.51(\mathrm{dd}, J=13.2,6.5,1 \mathrm{H}), 1.72(\mathrm{dtd}, J=13.6,6.8,4.6,1 \mathrm{H}), 1.29(\mathrm{t}, J=7.1,3 \mathrm{H}), 1.05(\mathrm{~d}, J=6.8$, $3 \mathrm{H}), 0.91(\mathrm{~s}, 9 \mathrm{H}), 0.89(\mathrm{~d}, J=6.9,3 \mathrm{H}), 0.85(\mathrm{~d}, J=6.8,3 \mathrm{H}), 0.05(\mathrm{~s}, 3 \mathrm{H}), 0.03(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 166.8,153.0,120.1,80.1,60.1,40.8,32.0,26.2,20.3,18.4,17.6,14.9,14.2$, 3.76, -3.84; IR (thin film) 2958, 1721, 1652, 1464, 1254, $1179 \mathrm{~cm}^{-1} ; \mathrm{HRMS}\left(\mathrm{CI}+/ \mathrm{NH}_{3}\right) \mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{16} \mathrm{H}_{31} \mathrm{O}_{3} \mathrm{Si}\left(\mathrm{M}-\mathrm{CH}_{3}\right)^{+}$299.2042, found 299.2040. Anal. Calcd for $\mathrm{C}_{17} \mathrm{H}_{34} \mathrm{O}_{3} \mathrm{Si}: \mathrm{C}, 64.92 ; \mathrm{H}$, 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 $\left(0^{\circ} \mathrm{C}\right)$ solution of ethyl $(4 R, 5 R)$-E-4,6-dimethyl-5-hydroxy-hept-2-eneoate ${ }^{7}(1.0 \mathrm{~g}, 5.0 \mathrm{mmol})$ in 20 mL of $\mathrm{CH}_{3} \mathrm{CN}$ was added pivalic anhydride ( $1.5 \mathrm{~mL}, 7.5 \mathrm{mmol}$ ), followed by a solution of $\mathrm{Sc}(\mathrm{OTf})_{3}(0.025 \mathrm{~g}, 0.050 \mathrm{mmol})$ in $0.5 \mathrm{~mL} \mathrm{CH}_{3} \mathrm{CN}$. After the solution was warmed to $22{ }^{\circ} \mathrm{C}$ for $2 \mathrm{~h}, 10 \mathrm{~mL}$ of sodium bicarbonate (saturated aqueous) was added. The mixture was diluted with 50 mL of $\mathrm{H}_{2} \mathrm{O}$ and 50 mL of $\mathrm{Et}_{2} \mathrm{O}$. The organic layer was separated, and the aqueous layer was
extracted with $\mathrm{Et}_{2} \mathrm{O}(3 \times 50 \mathrm{~mL})$. The combined organic layers were dried over $\mathrm{MgSO}_{4}$, 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 ( $1.1 \mathrm{~g}, 79 \%$ ): ${ }^{1} \mathrm{H} \mathrm{NMR}$ ( 500 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 6.80(\mathrm{dd}, J=15.7,8.3,1 \mathrm{H}), 5.81(\mathrm{~d}, J=15.7,1 \mathrm{H}), 4.76(\mathrm{dd}, J=7.3,4.9,1 \mathrm{H}), 4.16(\mathrm{q}, J$ $=7.1,2 \mathrm{H}), 2.63(\mathrm{~m}, 1 \mathrm{H}), 1.84(\mathrm{~m}, 1 \mathrm{H}), 1.27(\mathrm{t}, J=7.1,3 \mathrm{H}), 1.19(\mathrm{~s}, 9 \mathrm{H}), 1.01(\mathrm{~d}, J=6.7,3 \mathrm{H}), 0.86$ $(\mathrm{d}, J=6.8,6 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.9,166.3,149.9,121.5,78.7,60.3,38.7,30.0$, 27.29, 27.26, 19.7, 16.3, 14.9, 14.2; IR (thin film) 2973, 1731, 1651, 1281, $1158 \mathrm{~cm}^{-1}$; HRMS $\left(\mathrm{CI}+/ \mathrm{NH}_{3}\right) \mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{14} \mathrm{H}_{23} \mathrm{O}_{3}\left(\mathrm{M}-\mathrm{OC}_{2} \mathrm{H}_{5}\right)^{+}$239.1647, found 239.1644.


D-1,2,5,6-O-(3-pentylidene)-mannitol. To a solution of D-mannitol ( $6.2 \mathrm{~g}, 34 \mathrm{mmol}$ ) in 15 mL of DMF was added camphorsulfonic acid $(0.25 \mathrm{~g}, 1.0 \mathrm{mmol})$. The reaction mixture was heated to $40{ }^{\circ} \mathrm{C}$ and 3,3-dimethoxypentane ( $9.5 \mathrm{~g}, 72 \mathrm{mmol}$ ) was added dropwise over 15 min . Complete dissolution occurred after 45 min . The solution was stirred for another 4 h at $40^{\circ} \mathrm{C}$. The solution was cooled to $25^{\circ} \mathrm{C}$ and a few drops of $\mathrm{Et}_{3} \mathrm{~N}$ were added. The solution was diluted with 100 mL of MTBE and washed with brine $(4 \times 100 \mathrm{~mL})$. The combined organic layers were filtered through sodium sulfate and concentrated in vacuo to give a white solid ${ }^{8}$ ( $9.03 \mathrm{~g}, 83 \%$ ) : ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 4.15(\mathrm{~m} .4 \mathrm{H}), 3.92(\mathrm{~m}, 2 \mathrm{H}), 3.77(\mathrm{t}, J=6.2,2 \mathrm{H}), 2.85(\mathrm{~d}, J=6.8,2 \mathrm{H}), 1.65(\mathrm{~m}, 8 \mathrm{H})$, 0.89 (m, 12H); ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 113.2,76.1,71.5,67.3,29.5,28.9,8.2,8.0$; IR ( KBr ) 3422 , 2975, 2883, 1464, 1086, $916 \mathrm{~cm}^{-1}$; HRMS (FAB+) $m / z$ calcd for $\mathrm{C}_{16} \mathrm{H}_{31} \mathrm{O}_{6}(\mathrm{M}+\mathrm{H})^{+}$ 319.2120, found 319.2117.


Ethyl (R)-E-4,5-O-(3-pentylidene)-4,5-dihydroxy-2-pentenoate (1c). To a mixture of $\mathrm{KHCO}_{3}(0.28 \mathrm{~g}, 2.8 \mathrm{mmol})$ and $\mathrm{KIO}_{4}(7.2 \mathrm{~g}, 31 \mathrm{mmol})$ in 44 mL of $\mathrm{H}_{2} \mathrm{O}$ was added a solution of D-1,2,5,6-O-(3-pentilidene)-mannitol ( $9.0 \mathrm{~g}, 28 \mathrm{mmol}$ ) in 18 mL of THF dropwise over 5 min . The reaction mixture was stirred at $25^{\circ} \mathrm{C}$ for 5 h and then cooled to $5{ }^{\circ} \mathrm{C}$. The mixture was filtered through Celite and the solids were washed with 20 mL of EtOAc. The filtrate was warmed to $25{ }^{\circ} \mathrm{C}$ 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 $(2 \times 20 \mathrm{~mL})$. The combined organic layers were filtered through sodium sulfate and concentrated in vacuo. The resulting oil was purified by bulb-to-bulb distillation ( $50^{\circ} \mathrm{C}, 0.1$ Torr) to yield the aldehyde. In a separate flask, triethylphosphonoacetate ( $6.5 \mathrm{~mL}, 33 \mathrm{mmol}$ ), $i-\mathrm{Pr}_{2} \mathrm{NEt}$ ( $6.5 \mathrm{~mL}, 37 \mathrm{mmol}$ ), and the aldehyde $(4.9 \mathrm{~g}, 31 \mathrm{mmol})$ were added to $\mathrm{LiCl}(1.7 \mathrm{~g}, 37 \mathrm{mmol})$ in 31 mL of $\mathrm{CH}_{3} \mathrm{CN}$. The solution was stirred at $25^{\circ} \mathrm{C}$ for 1.5 h . The mixture was diluted with 60 mL of $\mathrm{H}_{2} \mathrm{O}$ and the organic layer was separated. The aqueous layer was extracted with $\mathrm{Et}_{2} \mathrm{O}(4 \times 50 \mathrm{~mL})$. The combined organic layers were dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated in vacuo to give a colorless oil as a 98:2 mixture of $\mathrm{E} / \mathrm{Z}$ isomers as determined by $\mathrm{GCMS}-\mathrm{CI} / \mathrm{NH}_{4} \mathrm{Cl}$. The oil was purified by flash chromatography (1:99 to 10:90 EtOAc/hexanes) to yield as product a colorless $\operatorname{oil}^{8}(3.8 \mathrm{~g}, 54 \%):{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 6.87(\mathrm{dd}, J=15.6,6.0,1 \mathrm{H}), 6.11(\mathrm{dd}, J=15.6$, $1.2,1 \mathrm{H}), 4.66(\mathrm{~m}, 1 \mathrm{H}), 4.20(\mathrm{q}, J=7.0,2 \mathrm{H}$ and $\mathrm{m}, 1 \mathrm{H}), 3.62(\mathrm{t}, J=8.0,1 \mathrm{H}), 1.68(\mathrm{~m}, 4 \mathrm{H}), 1.30(\mathrm{t}, J$ $=7.0,3 \mathrm{H}), 0.92(\mathrm{q}, J=7.6,6 \mathrm{H}){ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 165.9,144.2,122.4,114.1,75.3$, 69.3, $60.5,53.4,29.7,29.4,14.1,8.0$; IR (thin film): 2977, 1723, 1663, $1465,1175,1079 \mathrm{~cm}^{-1}$; HRMS (LSIMS) $m / z$ calcd for $\mathrm{C}_{12} \mathrm{H}_{21} \mathrm{O}_{2}(\mathrm{M}+\mathrm{H})^{+}$229.1440, found 229.1442. Anal. Calcd for $\mathrm{C}_{12} \mathrm{H}_{20} \mathrm{O}_{2}: \mathrm{C}, 63.14 ; \mathrm{H}, 8.83$. Found: C, 63.04; H, 8.76.

( $\boldsymbol{R}$ )-E-4,5- $\boldsymbol{O}$-isopropylidine-4,5-dihydroxy-2-pentenoate. To a cooled $\left(0^{\circ} \mathrm{C}\right)$ mixture of 1,2,5,6-diisopropylidine-D-mannitol ( $2.5 \mathrm{~g}, 9.7 \mathrm{mmol}$ ) in 25 mL of sodium bicarbonate (saturated aqueous) was added dropwise a solution of $\mathrm{NaIO}_{4}(2.5 \mathrm{~g}, 12 \mathrm{mmol})$ in 20 mL of $\mathrm{H}_{2} \mathrm{O}$. The reaction mixture was warmed to $22{ }^{\circ} \mathrm{C}$ for 1 h . Triethyl phosphonoacetate ( $4.4 \mathrm{~mL}, 20 \mathrm{mmol}$ ) was added, followed by a solution of $\mathrm{K}_{2} \mathrm{CO}_{3}(28 \mathrm{~g}, 200 \mathrm{mmol})$ in 35 mL of $\mathrm{H}_{2} \mathrm{O}$, and the mixture was stirred for 18 h . The reaction mixture was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 75 \mathrm{~mL})$. 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 $\mathrm{E} / \mathrm{Z}$ isomers as a colorless oil by GCMS$\mathrm{CI} / \mathrm{NH}_{4} \mathrm{CI}$. The resulting oil was purified by flash column chromatography (10:90 EtOAc/hexanes) to give the product as a colorless oil ${ }^{9}(2.8 \mathrm{~g}, 72 \%)$ : ${ }^{1} \mathrm{H} \mathrm{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 6.88$ (dd, $J=$ $15.6,5.7,1 \mathrm{H}), 6.10(\mathrm{dd}, J=15.6,1.4,1 \mathrm{H}), 4.67(\mathrm{dq}, J=7.0,1.3,1 \mathrm{H}), 4.20(\mathrm{q}, J=7.1,2 \mathrm{H}$ and dd, $J$ $=8.3,6.8,1 \mathrm{H}), 3.68(\mathrm{dd}, J=8.2,7.2,1 \mathrm{H}), 1.45(\mathrm{~s}, 3 \mathrm{H}), 1.41(\mathrm{~s}, 3 \mathrm{H}), 1.30(\mathrm{t}, J=7.1,3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (125 MHz, $\mathrm{CDCl}_{3}$ ) $\delta 165.7,144.5,122.2,109.9,74.7,68.6,60.3,26.2,25.5,14.0 ;$ HRMS $\left(\mathrm{CI}+/ \mathrm{NH}_{3}\right) m / z$ calcd for $\mathrm{C}_{10} \mathrm{H}_{17} \mathrm{O}_{4}(\mathrm{M}+\mathrm{H})^{+}$201.1127, found 201.1122. [ $\left.\alpha\right]^{25}{ }_{\mathrm{D}} 24.1$ (c 0.220, $\mathrm{CHCl}_{3}$ ).


(S)-4-Benzyl-3-[(2R,3S)-3-hydroxy-2-methyl-3-phenyl-propionyl]-oxazolidin-2-one. To a mixture of (S)-4-benzyl-3-propionyl-oxazolidin-2-one ( $0.98 \mathrm{~g}, 4.3 \mathrm{mmol}$ ) and $\mathrm{MgCl}_{2}(0.046 \mathrm{~g}$, $0.43 \mathrm{mmol})$ in 8.6 mL of EtOAc was added $\mathrm{Et}_{3} \mathrm{~N}(1.2 \mathrm{~mL}, 8.6 \mathrm{mmol})$, benzaldehyde ( $0.48 \mathrm{~mL}, 4.7$ $\mathrm{mmol})$, and $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{SiCl}(0.81 \mathrm{~mL}, 6.4 \mathrm{mmol})$, respectively. The mixture was stirred for 24 h at 22 ${ }^{\circ} \mathrm{C}$. The reaction mixture was filtered through a silica gel column with 200 mL of $\mathrm{Et}_{2} \mathrm{O}$. 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 solid ${ }^{11}$ (1.3 g, 93\%): ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 7.43(\mathrm{~m}, 2 \mathrm{H}), 7.38(\mathrm{~m}, 2 \mathrm{H}), 7.33-7.27(\mathrm{~m}, 4 \mathrm{H}), 7.15(\mathrm{~m}, 2 \mathrm{H}), 4.82(\mathrm{t}, J=7.7,1 \mathrm{H}), 4.69$ $(\mathrm{m}, 1 \mathrm{H}), 4.35(\mathrm{dq}, J=7.0,1 \mathrm{H}), 4.19(\mathrm{~m}, 1 \mathrm{H}), 4.14(\mathrm{dd}, J=9.1,2.8,1 \mathrm{H}), 3.19(\mathrm{dd}, J=13.6,3.4$, $1 \mathrm{H}), 3.12(\mathrm{~d}, J=7.3,1 \mathrm{H}), 2.67(\mathrm{dd}, J=13.6,9.3,1 \mathrm{H}), 1.11(\mathrm{~d}, J=6.9,3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 125 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 176.5,153.4,142.0,133.1,129.3,128.8,128.4,127.9,127.1,126.6,77.2,65.8,55.2$, 44.2, 37.4, 14.7; HRMS $\left(\mathrm{CI}+/ \mathrm{NH}_{3}\right) m / z$ calcd for $\mathrm{C}_{20} \mathrm{H}_{21} \mathrm{NO}_{4}\left(\mathrm{M}^{+}\right)$339.1471, found 339.1464; $[\alpha]_{\mathrm{D}}^{25}-9.43\left(c 0.795, \mathrm{CHCl}_{3}\right)$.

(4S,5S)-5-Methyl-2,4-diphenyl-1,3-dioxane. To a cooled ( $0^{\circ} \mathrm{C}$ ) solution of (S)-4-Benzyl-3-[(2R,3S)-3-hydroxy-2-methyl-3-phenyl-propionyl]-oxazolidin-2-one $(0.54 \mathrm{~g}, 1.6 \mathrm{mmol})$ and $\mathrm{MeOH}(0.065 \mathrm{~mL}, 1.6 \mathrm{mmol})$ in 5.3 mL of THF was added $\mathrm{LiBH}_{4}(0.035 \mathrm{~g}, 1.6 \mathrm{mmol})$. The reaction mixture was stirred at $0{ }^{\circ} \mathrm{C}$ 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and 30 mL of sodium potassium tartrate (saturated aqueous). The organic layer was separated and the aqueous layer was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \times 50 \mathrm{~mL})$. The organic layers were combined and washed with brine $(2 \times 70 \mathrm{~mL})$, 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 $(0.24 \mathrm{~mL}, 1.6 \mathrm{mmol})$ and CSA $(0.015 \mathrm{~g})$, respectively at $22{ }^{\circ} \mathrm{C}$. The reaction mixture was stirred at $22^{\circ} \mathrm{C}$ 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 was washed with $\mathrm{H}_{2} \mathrm{O}$ (4 $\times 50 \mathrm{~mL})$ and brine $(3 \times 50 \mathrm{~mL})$. The organic layer was dried over sodium sulfate, filtered, and concentrated in vacuo to give a pale yellow oil as a 97:3 mixture of diastereomers as determined by ${ }^{1} \mathrm{H}$ 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 ${ }^{1} \mathrm{H}$ NMR spectroscopy ( $0.25 \mathrm{~g}, 63 \%$ ): ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.55(\mathrm{~m}, 2 \mathrm{H}), 7.42(\mathrm{~m}, 2 \mathrm{H})$, $7.34(\mathrm{~m}, 6 \mathrm{H}), 5.68(\mathrm{~s}, 1 \mathrm{H}), 4.38(\mathrm{~d}, J=10.0,1 \mathrm{H}), 4.26(\mathrm{dd}, J=11.4,4.6,1 \mathrm{H}), 3.69(\mathrm{t}, J=11.3$, $1 \mathrm{H}), 2.16(\mathrm{~m}, 1 \mathrm{H}), 0.66(\mathrm{~d}, J=6.7,3 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 139.6,138.4,128.7$, $128.2,128.1,128.0,127.4,126.2,101.5,86.3,73.3,35.8,12.2$; IR (thin film) 3063, 2958, 1454, 1111, $754 \mathrm{~cm}^{-1}$; HRMS $\left(\mathrm{CI}+/ \mathrm{NH}_{3}\right) \mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{17} \mathrm{H}_{19} \mathrm{O}_{2}(\mathrm{M}+\mathrm{H})^{+}$255.1385, found 255.1390. Anal. Calcd for $\mathrm{C}_{17} \mathrm{H}_{18} \mathrm{O}_{2}$ : C, 80.28; H, 7.13. Found: C, 80.41; H 7.15. $[\alpha]^{25}{ }_{\mathrm{D}}-38.7$ (c 0.315, $\mathrm{CHCl}_{3}$ ).

(2S,3S)-3-Benzyloxy-2-methyl-3-phenyl-propan-1-ol: To a cooled $\left(-78{ }^{\circ} \mathrm{C}\right)$ solution of (4S,5S)-5-Methyl-2,4-diphenyl-1,3-dioxane ( $0.25 \mathrm{~g}, 0.98 \mathrm{mmol}$ ) in 5 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ was added dropwise over $5 \mathrm{~min} i-\mathrm{Bu}_{2} \mathrm{AlH}$ ( $3.3 \mathrm{~mL}, 4.9 \mathrm{mmol}, 1.5 \mathrm{M}$ in toluene). The solution was warmed to $22{ }^{\circ} \mathrm{C}$ for 18 h . The reaction mixture was cooled to $0^{\circ} \mathrm{C}$ and 2 mL of MeOH was added. The mixture was diluted with 20 mL of sodium potassium tartrate (saturated aqueous) and stirred for 2 h . The organic layer was separated, and the aqueous layer was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 50$ $\mathrm{mL})$. 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 ${ }^{1} \mathrm{H}$ NMR spectroscopy ( $0.22 \mathrm{~g}, 89 \%$ ): ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.39(\mathrm{~m}, 2 \mathrm{H}), 7.34(\mathrm{~m}, 5 \mathrm{H}), 7.28(\mathrm{~m}, 3 \mathrm{H}), 4.42(\mathrm{~d}, J=11.6,1 \mathrm{H}), 4.21(\mathrm{~d}, J=11.6,1 \mathrm{H}), 4.19(\mathrm{~d}, J$ $=8.8,1 \mathrm{H}), 3.68(\mathrm{~m}, 2 \mathrm{H}), 3.23(\mathrm{~m}, 1 \mathrm{H}), 2.11(\mathrm{~m}, 1 \mathrm{H}), 0.66(\mathrm{~d}, J=7.0,3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( 125 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 140.3,137.7,128.4,128.3,127.9,127.8,127.7,127.4,87.1,70.4,67.4,41.9,13.7$; IR (thin film) $3419,3029,2875,1494,1454,1063 \mathrm{~cm}^{-1}$; HRMS $\left(\mathrm{CI}+/ \mathrm{NH}_{3}\right) \mathrm{m} / z$ calcd for $\mathrm{C}_{17} \mathrm{H}_{21} \mathrm{O}_{2}$ $(\mathrm{M}+\mathrm{H})^{+}$257.1541, found 257.1540. Anal. Calcd for $\mathrm{C}_{17} \mathrm{H}_{20} \mathrm{O}_{2}: \mathrm{C}, 79.65 ; \mathrm{H}, 7.86$. Found: C, 79.67; H 8.05. $[\alpha]_{\mathrm{D}}^{25}-180\left(c 0.120, \mathrm{CHCl}_{3}\right)$.


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

## B. Conjugate Addition Reactions



Ethyl ( $3 R^{*}, 4 S^{*}, 5 R^{*}$ )-5-benzyloxy-3-(dimesitylsilyl)-6,4-dimethyl-heptanoate (2a). To a cooled $\left(-78{ }^{\circ} \mathrm{C}\right)$ solution of $\mathrm{Me}_{2} \mathrm{Zn}(1.8 \mathrm{~mL}, 3.5 \mathrm{mmol}, 2.0 \mathrm{M}$ in toluene) in 23 mL of THF, was added a cooled $\left(0^{\circ} \mathrm{C}\right)$ solution of silyllithium $4(1.5 \mathrm{~g}, 3.5 \mathrm{mmol})$ in 3.5 mL of THF. The solution was warmed to $0^{\circ} \mathrm{C}$ for 5 min and then re-cooled to $-78{ }^{\circ} \mathrm{C}$. To a separate flask, MeLi $(0.30 \mathrm{~mL}$, $0.35 \mathrm{mmol}, 1.2 \mathrm{M}$ in $\left.\mathrm{Et}_{2} \mathrm{O}\right)$ was added to a cooled $\left(-78{ }^{\circ} \mathrm{C}\right)$ slurry of $\mathrm{CuCN}(0.016 \mathrm{~g}, 0.18 \mathrm{mmol})$ in 4.5 mL of THF. The slurry was warmed to $-30^{\circ} \mathrm{C}$, stirred for 5 min , cooled to $-78{ }^{\circ} \mathrm{C}$, and stirred for 5 min . The cuprate solution was added to the zincate solution, and the mixture was stirred at $-78{ }^{\circ} \mathrm{C}$ for 10 min . To the reaction solution was added $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{SiCl}(1.3 \mathrm{~mL}, 10.5 \mathrm{mmol})$ followed by a cooled $\left(-78^{\circ} \mathrm{C}\right)$ solution of enoate $\mathbf{1 a}(1.0 \mathrm{~g}, 3.4 \mathrm{mmol})$ in 2.0 mL of THF. After 5 h at $-78^{\circ} \mathrm{C}, 5 \mathrm{~mL} \mathrm{NH} 4 \mathrm{Cl}$ (saturated aqueous) was added, and the mixture was warmed to $25^{\circ} \mathrm{C}$. 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 $\mathrm{Et}_{2} \mathrm{O}(3 \times 30 \mathrm{~mL})$. The combined organic layers were dried with $\mathrm{MgSO}_{4}$, 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 $1: 99 \mathrm{EtOAc} /$ hexanes) to give the product as a white solid ( $1.5 \mathrm{~g}, 83 \%$ ): mp $125-127{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.26(\mathrm{~m}, 4 \mathrm{H}), 7.20(\mathrm{~m}, 1 \mathrm{H}), 6.78(\mathrm{~s}, 2 \mathrm{H}), 6.73$ $(\mathrm{s}, 2 \mathrm{H}), 5.17(\mathrm{~d}, J=6.8,1 \mathrm{H}), 4.65(\mathrm{~d}, J=11.0,1 \mathrm{H}), 4.60(\mathrm{~d}, J=11.0,1 \mathrm{H}), 3.67(\mathrm{dq}, J=10.7,7.1$, $1 \mathrm{H}), 3.44(\mathrm{dq}, J=10.7,7.2,1 \mathrm{H}), 3.19(\mathrm{dd}, J=6.8,4.2,1 \mathrm{H}), 2.97(\mathrm{dd}, J=17.1,4.6,1 \mathrm{H}), 2.62(\mathrm{~m}$, $1 \mathrm{H}), 2.42(\mathrm{~s}, 6 \mathrm{H}), 2.40(\mathrm{~s}, 6 \mathrm{H}), 2.29(\mathrm{~m}, 1 \mathrm{H}), 2.22(\mathrm{~s}, 3 \mathrm{H}), 2.19(\mathrm{~s}, 3 \mathrm{H}), 2.06(\mathrm{~m}, 1 \mathrm{H}), 1.95(\mathrm{dq}, J=$ $13.5,6.7,1 \mathrm{H}), 1.07(\mathrm{~d}, J=7.0,3 \mathrm{H}), 0.95(\mathrm{t}, J=7.1,3 \mathrm{H}), 0.90(\mathrm{~d}, J=6.7,3 \mathrm{H}), 0.87(\mathrm{~d}, J=6.8$, $3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 173.9,145.1,144.6,139.2,139.0138 .8,129.2,129.1,128.8$, $128.7,128.1,127.2,127.1,92.2,75.1,59.9,34.0,32.3,31.5,24.3,23.8,23.5,20.9,20.2,18.5,13.8$, 10.4; IR (KBr pellet) 3029, 2966, 1721, 1604, 1464, $1109 \mathrm{~cm}^{-1}$; HRMS (TOF MS ES+/Na) $\mathrm{m} / \mathrm{z}$
calcd for $\mathrm{C}_{36} \mathrm{H}_{50} \mathrm{O}_{3} \mathrm{SiNa}(\mathrm{M}+\mathrm{Na})^{+}$581.3427, found 581.3422. Anal. Calcd for $\mathrm{C}_{36} \mathrm{H}_{50} \mathrm{O}_{3} \mathrm{Si}$ : C, 77.37; H, 9.02. Found: C, 77.45; H, 9.10.


Ethyl (3R*,4R*,5R*)-3-(dimesitylsilyl)-5-(2,2-dimethylpropionyloxy)-4,6-dimethylhept-2-eneoate. To a cooled $\left(-78^{\circ} \mathrm{C}\right)$ solution of $\mathrm{Me}_{2} \mathrm{Zn}(0.18 \mathrm{~mL}, 0.35 \mathrm{mmol}, 2.0 \mathrm{M}$ in toluene $)$ in 2.3 mL of THF was added a cooled $\left(0^{\circ} \mathrm{C}\right)$ solution of silyllithium $4(0.15 \mathrm{~g}, 0.35 \mathrm{mmol})$ in 0.4 mL of THF. The solution was warmed to $0{ }^{\circ} \mathrm{C}$ for 5 min and then re-cooled to $-78{ }^{\circ} \mathrm{C}$. In a separate flask, $\mathrm{MeLi}\left(0.029 \mathrm{~mL}, 0.035 \mathrm{mmol}, 1.2 \mathrm{M}\right.$ in $\left.\mathrm{Et}_{2} \mathrm{O}\right)$ was added to a cooled $\left(-78{ }^{\circ} \mathrm{C}\right)$ slurry of $\mathrm{CuCN}(0.0016 \mathrm{~g}, 0.018 \mathrm{mmol})$ in 0.45 mL of THF. The slurry was warmed to $-30^{\circ} \mathrm{C}$, stirred for 5 min, cooled to $-78^{\circ} \mathrm{C}$, and stirred for 5 min . The cuprate solution was added to the zincate solution and the mixture was stirred at $-78{ }^{\circ} \mathrm{C}$ for 10 min . To the reaction solution was added $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{SiCl}$ $(0.13 \mathrm{~mL}, 1.0 \mathrm{mmol})$ followed by a cooled $\left(-78^{\circ} \mathrm{C}\right)$ solution of ethyl $\left(4 R^{*}, 5 R^{*}\right)$-E-5-(2,2-dimethyl-propionyloxy)-4,6-dimethylhept-2-eneoate $(0.097 \mathrm{~g}, 0.34 \mathrm{mmol})$ in 0.2 mL of THF. After 18 h at $-78{ }^{\circ} \mathrm{C}, 5 \mathrm{~mL}$ of $\mathrm{NH}_{4} \mathrm{Cl}$ (saturated aqueous) was added and the mixture was warmed to $25^{\circ} \mathrm{C}$. The mixture was diluted with 50 mL of $\mathrm{H}_{2} \mathrm{O}$. The organic layer was separated, and the aqueous layer was extracted with $\mathrm{Et}_{2} \mathrm{O}(3 \times 30 \mathrm{~mL})$. The combined organic layers were dried with $\mathrm{MgSO}_{4}$, 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 ( $0.12 \mathrm{~g}, 64 \%$ ): mp $128-130{ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( 500 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 6.80(\mathrm{~s}, 2 \mathrm{H}), 6.77(\mathrm{~s}, 2 \mathrm{H}), 5.15(\mathrm{~d}, J=6.7,1 \mathrm{H}), 4.76(\mathrm{dd}, J=7.6,4.1,1 \mathrm{H}), 3.96$ $(\mathrm{dq}, J=14.3,7.1,1 \mathrm{H}), 3.81(\mathrm{dq}, J=14.3,7.1,1 \mathrm{H}), 2.59(\mathrm{dd}, J=16.7,7.5,1 \mathrm{H}), 2.50(\mathrm{~m}, 2 \mathrm{H}), 2.43$ (s, 6H), 2.39 (s, 6H), $2.23(\mathrm{~s}, 3 \mathrm{H}), 2.21(\mathrm{~s}, 3 \mathrm{H}), 2.05(\mathrm{~m}, 2 \mathrm{H}), 1.18(\mathrm{~s}, 9 \mathrm{H}), 1.12(\mathrm{t}, J=7.1,3 \mathrm{H})$, $0.95(\mathrm{~d}, J=7.0,3 \mathrm{H}), 0.76(\mathrm{~d}, J=6.8,3 \mathrm{H}), 0.64(\mathrm{~d}, J=6.7,3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 178.0,173.8,145.1,144.7,139.1,139.0,129.04,128.96,128.86,128.4,80.9,60.4,39.2,34.0$, 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, $1160 \mathrm{~cm}^{-1} ; \operatorname{HRMS}\left(\mathrm{CI}+/ \mathrm{NH}_{3}\right) \mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{34} \mathrm{H}_{51} \mathrm{O}_{4} \mathrm{Si}(\mathrm{M}-\mathrm{H})^{+}$
551.3556, found 551.3553. Anal. Calcd for $\mathrm{C}_{34} \mathrm{H}_{52} \mathrm{O}_{4} \mathrm{Si}: \mathrm{C}, 73.86 ; \mathrm{H}, 9.48$. Found: C, 73.89; H, 9.63.

(3S,4R)-3-(dimesitylsilyl)-4,5-O-(3-pentilidene)-4,5-dihydroxypentanoate 2 c . To a cooled $\left(0^{\circ} \mathrm{C}\right)$ solution of $\mathrm{Me}_{2} \mathrm{Zn}(1.0 \mathrm{~mL}, 2.0 \mathrm{mmol}, 2.0 \mathrm{M}$ in toluene) in 13 mL of THF was added a cooled $\left(0^{\circ} \mathrm{C}\right)$ solution of $\mathbf{1 5}(0.83 \mathrm{~g}, 2.0 \mathrm{mmol})$ in 2.2 mL of THF. The solution was stirred at $0{ }^{\circ} \mathrm{C}$ for 20 min and then cooled to $-78^{\circ} \mathrm{C}$. In a separate flask, $\mathrm{MeLi}(0.075 \mathrm{~mL}, 0.11 \mathrm{mmol}, 1.45 \mathrm{M}$ in $\left.\mathrm{Et}_{2} \mathrm{O}\right)$ was added to a cooled $\left(-7{ }^{\circ} \mathrm{C}\right)$ slurry of $\mathrm{CuCN}(0.005 \mathrm{~g}, 0.06 \mathrm{mmol})$ in 1.5 mL of THF. The slurry was warmed to $-30^{\circ} \mathrm{C}$, stirred for 5 min , cooled to $-78^{\circ} \mathrm{C}$, and stirred for 5 min . The cuprate solution was added to the zincate solution and the mixture was stirred at $-78^{\circ} \mathrm{C}$ for 10 min . To the reaction solution was added a cooled $\left(-78{ }^{\circ} \mathrm{C}\right)$ solution of enoate $\mathbf{1 c}(0.43 \mathrm{~g}, 1.9 \mathrm{mmol})$ in 1.3 mL of THF. After 2.5 h at $-78^{\circ} \mathrm{C}, 3 \mathrm{~mL} \mathrm{NH}_{4} \mathrm{Cl}$ (saturated aqueous) was added, and the mixture was warmed to $25^{\circ} \mathrm{C}$. 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 $\mathrm{Et}_{2} \mathrm{O}(3 \times$ 70 mL ). The combined organic layers were dried with $\mathrm{MgSO}_{4}$, 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 $2: 98 \mathrm{EtOAc} /$ hexanes) to give the product as a viscous yellow oil ( $0.77 \mathrm{~g}, 82 \%$ ): ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 6.79(\mathrm{~s}, 2 \mathrm{H}), 6.77(\mathrm{~s}, 2 \mathrm{H}), 5.08(\mathrm{~d}, \mathrm{~J}=6.0$, $1 \mathrm{H}), 4.12(\mathrm{dt}, J=8.2,6.0,1 \mathrm{H}), 4.05(\mathrm{dq}, J=10.8,7.2,1 \mathrm{H}), 3.95(\mathrm{dq}, J=10.8,7.2,1 \mathrm{H}), 3.44(\mathrm{dd}, J$ $=8.3,5.9,1 \mathrm{H}), 3.27(\mathrm{t}, J=8.4,1 \mathrm{H}), 2.64(\mathrm{~m}, 2 \mathrm{H}), 2.41(\mathrm{~s}, 6 \mathrm{H}$ and $\mathrm{m}, 1 \mathrm{H}), 2.37(\mathrm{~s}, 6 \mathrm{H}), 2.22(\mathrm{~s}$, $6 \mathrm{H}), 1.49(\mathrm{~m}, 4 \mathrm{H}), 1.17(\mathrm{t}, J=7.2,3 \mathrm{H}), 0.84(\mathrm{t}, J=7.4,3 \mathrm{H}), 0.77(\mathrm{t}, J=7.4,3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (125 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 173.8,144.9,144.4,139.4,139.3,129.2,129.0,128.8,127.6,78.4,77.2,69.0,60.3$, 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, $846 \mathrm{~cm}^{-1}$; HRMS (LSI) $m / z$ calcd for $\mathrm{C}_{30} \mathrm{H}_{43} \mathrm{O}_{4} \mathrm{Si}(\mathrm{M}-\mathrm{H})^{+}$495.2930, found 495.2929. Anal. Calcd for $\mathrm{C}_{30} \mathrm{H}_{44} \mathrm{O}_{4} \mathrm{Si}$ : C, 72.54; H, 8.93. Found: C, 72.75; H, 8.97.

( $3 S^{*}, 4 R^{*}$ )-3-(dimesitylsilyl)-4,5-O-isopropylidine-4,5-dihydroxypentanoate. To a cooled $\left(-78^{\circ} \mathrm{C}\right)$ solution of $\mathrm{Me}_{2} \mathrm{Zn}(0.36 \mathrm{~mL}, 0.72 \mathrm{mmol}, 2.0 \mathrm{M}$ in toluene $)$ in 4.8 mL of THF, was added a cooled $\left(0^{\circ} \mathrm{C}\right)$ solution of silyllithium $4(0.30 \mathrm{~g}, 0.72 \mathrm{mmol})$ in 0.7 mL of THF. The solution was stirred at $0{ }^{\circ} \mathrm{C}$ for 5 min and then cooled to $-78{ }^{\circ} \mathrm{C}$. In a separate flask, MeLi $(0.063 \mathrm{~mL}, 0.076$ $\mathrm{mmol}, 1.2 \mathrm{M}$ in $\left.\mathrm{Et}_{2} \mathrm{O}\right)$ was added to a cooled $\left(-78{ }^{\circ} \mathrm{C}\right)$ slurry of $\mathrm{CuCN}(0.003 \mathrm{~g}, 0.036 \mathrm{mmol})$ in 0.9 mL of THF. The slurry was warmed to $-30^{\circ} \mathrm{C}$, stirred for 5 min , cooled to $-78^{\circ} \mathrm{C}$, and stirred for 5 min . The cuprate solution was added to the zincate solution and stirred at $-78{ }^{\circ} \mathrm{C}$ for 10 min . To the reaction solution was added a cooled $\left(-78{ }^{\circ} \mathrm{C}\right)$ solution of $(R)-E-4,5-O$-dimethylacetonide-4,5-dihydroxy-2-pentenoate $(0.14 \mathrm{~g}, 0.70 \mathrm{mmol})$ in 0.4 mL of THF. After 3 h at $-78{ }^{\circ} \mathrm{C}, 3 \mathrm{~mL}$ of $\mathrm{NH}_{4} \mathrm{Cl}$ (saturated aqueous) was added and the mixture was warmed to $25^{\circ} \mathrm{C}$. The organic layer was separated and the aqueous layer was extracted with $\mathrm{Et}_{2} \mathrm{O}(3 \times 50 \mathrm{~mL})$. The combined organic layers were dried with $\mathrm{MgSO}_{4}$, 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 $2: 98 \mathrm{EtOAc} /$ hexanes ) to give the product as a colorless oil $(0.19 \mathrm{~g}$, $59 \%):{ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 6.79(\mathrm{~s}, 2 \mathrm{H}), 6.77(\mathrm{~s}, 2 \mathrm{H}), 5.06(\mathrm{~d}, J=6.1,1 \mathrm{H}), 4.14(\mathrm{q}, J=$ $7.1,1 \mathrm{H}), 4.06(\mathrm{dq}, J=10.8,7.1,1 \mathrm{H}), 3.95(\mathrm{dq}, J=14.3,7.1,1 \mathrm{H}), 3.49(\mathrm{dd}, J=8.5,6.0,1 \mathrm{H}), 3.33$ $(\mathrm{t}, J=8.1,1 \mathrm{H}), 2.63(\mathrm{~m}, 2 \mathrm{H}), 2.41(\mathrm{~m}, 1 \mathrm{H}$ and $\mathrm{s}, 6 \mathrm{H}), 2.37(\mathrm{~s}, 6 \mathrm{H}), 2.23(\mathrm{~s}, 6 \mathrm{H}), 1.32(\mathrm{~s}, 3 \mathrm{H}), 1.21$ $(\mathrm{s}, 3 \mathrm{H}), 1.18(\mathrm{t}, J=7.1,3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 173.9,144.9,144.5,139.4,139.3$, $129.2,129.0,128.7,127.6,108.2,77.9,68.6,60.3,33.0,26.4,25.7,25.5,23.7,23.5,21.0,20.9$, 14.0; IR (thin film) 2983, 1732, 1604, 1453, 1056, $846 \mathrm{~cm}^{-1} ;$ HRMS (CI+/NH3) $\mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{28} \mathrm{H}_{39} \mathrm{O}_{4} \mathrm{Si}(\mathrm{M}-\mathrm{H})^{+} 467.2617$, found 467.2619. Anal. Calcd for $\mathrm{C}_{28} \mathrm{H}_{40} \mathrm{O}_{4} \mathrm{Si}: \mathrm{C}, 71.75 ; \mathrm{H}, 8.60$. Found: C, 71.47; H, 8.56. $[\alpha]^{25}-72.5\left(c 0.120, \mathrm{CHCl}_{3}\right)$.


Ethyl (3S,4R,5S)-5-benzyloxy-3-(dimesitylsilyl)-4-methyl-5-phenyl-pentanoate (2e). To a cooled $\left(-78{ }^{\circ} \mathrm{C}\right)$ solution of $\mathrm{Me}_{2} \mathrm{Zn}(0.48 \mathrm{~mL}, 0.96 \mathrm{mmol}, 2.0 \mathrm{M}$ in toluene) in 6 mL of THF was added a cooled $\left(0^{\circ} \mathrm{C}\right)$ solution of silyllithium $4(0.40 \mathrm{~g}, 0.96 \mathrm{mmol})$ in 1.2 mL of THF. The solution was stirred at $0^{\circ} \mathrm{C}$ for 5 min and then cooled to $-78{ }^{\circ} \mathrm{C}$. In a separate flask, MeLi $(0.080$ $\mathrm{mL}, 0.096 \mathrm{mmol}, 1.2 \mathrm{M}$ in $\left.\mathrm{Et}_{2} \mathrm{O}\right)$ was added to a cooled $\left(-78{ }^{\circ} \mathrm{C}\right)$ slurry of $\mathrm{CuCN}(0.004 \mathrm{~g}, 0.048$ mmol ) in 1.2 mL of THF. The slurry was warmed to $-30^{\circ} \mathrm{C}$, stirred for 5 min , cooled to $-78^{\circ} \mathrm{C}$, and stirred for 5 min . The cuprate solution was added to the zincate solution, and the mixture was stirred at $-78{ }^{\circ} \mathrm{C}$ for 10 min . To the mixture was added $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{SiCl}(0.38 \mathrm{~mL}, 2.9 \mathrm{mmol})$ followed by a cooled $\left(-78^{\circ} \mathrm{C}\right)$ solution of enoate $\mathbf{1 e}(0.30 \mathrm{~g}, 0.92 \mathrm{mmol})$ in 0.7 mL of THF. After 18 h at $-78{ }^{\circ} \mathrm{C}, 5 \mathrm{~mL}$ of $\mathrm{NH}_{4} \mathrm{Cl}$ (saturated aqueous) was added, and the mixture was warmed to $25^{\circ} \mathrm{C}$. The mixture was diluted with 50 mL of water and acidified with 3 mL of 1 N HCl . The aqueous layer was extracted with $\mathrm{Et}_{2} \mathrm{O}(3 \times 30 \mathrm{~mL})$. The combined organic layers were dried with $\mathrm{MgSO}_{4}$, filtered, and concentrated in vacuo to yield a yellow oil as a 93:7 mixture of diastereomers as determined by ${ }^{1} \mathrm{H}$ 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 ( $0.41 \mathrm{~g}, 76 \%$ ): ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.34-7.22(\mathrm{~m}, 10 \mathrm{H}), 6.73(\mathrm{~s}, 2 \mathrm{H}), 6.72(\mathrm{~s}, 2 \mathrm{H}), 5.20(\mathrm{~d}, J=7.0,1 \mathrm{H}), 4.34(\mathrm{~d}$, $J=11.4,1 \mathrm{H}), 4.18(\mathrm{~d}, J=11.5,1 \mathrm{H}), 4.03(\mathrm{~d}, J=9.0,1 \mathrm{H}), 3.76(\mathrm{dq}, J=14.2,7.1,1 \mathrm{H}), 3.51(\mathrm{dq}, J$ $=14.3,7.1,1 \mathrm{H}), 3.42(\mathrm{~m}, 1 \mathrm{H}), 2.41(\mathrm{~s}, 6 \mathrm{H}), 2.39(\mathrm{~s}, 6 \mathrm{H}), 2.27(\mathrm{~d}, J=7.2,2 \mathrm{H}), 2.23(\mathrm{~s}, 3 \mathrm{H}), 2.20(\mathrm{~s}$, $3 \mathrm{H}), 2.19(\mathrm{~m}, 1 \mathrm{H}), 1.02(\mathrm{t}, J=7.1,3 \mathrm{H}), 0.72(\mathrm{~d}, J=7.0,3 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$ $\delta 173.5,145.1,141.4,138.8,129.1,129.0,128.9,128.6,128.2,128.0,127.9,127.7,127.5,127.2$, 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, $840 \mathrm{~cm}^{-1}$; HRMS $\left(\mathrm{CI}+/ \mathrm{NH}_{3}\right) \mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{39} \mathrm{H}_{47} \mathrm{O}_{3} \mathrm{Si}(\mathrm{M}-\mathrm{H})^{+}$591.3295, found 591.3289. Anal. Calcd for $\mathrm{C}_{39} \mathrm{H}_{48} \mathrm{O}_{3} \mathrm{Si}: \mathrm{C}, 79.01$; H, 8.16. Found: C, 78.80; H, 8.37. [ $\left.\alpha\right]^{25}{ }_{\mathrm{D}} 29.9$ (c 0.405, $\mathrm{CHCl}_{3}$ ).

## C. Enolate Alkylation



Ethyl (2R*, 3R*, $4 S^{*}, 5 R^{*}$ )-5-benzyloxy-3-(dimesitylsilyl)-2,4,6-trimethyl-heptanoate (5a).
To a cooled $\left(-78{ }^{\circ} \mathrm{C}\right)$ solution of diisopropylamine $(0.35 \mathrm{~mL}, 2.5 \mathrm{mmol})$ in 1.2 mL of THF was added $n$ - BuLi ( $0.95 \mathrm{~mL}, 2.3 \mathrm{mmol}, 2.4 \mathrm{M}$ in hexanes). The solution was warmed to $0{ }^{\circ} \mathrm{C}$ for 30 min and then re-cooled to $-78^{\circ} \mathrm{C}$. To the solution was added ester $\mathbf{2 a}(1.1 \mathrm{~g}, 2.0 \mathrm{mmol})$ in 2 mL of THF followed by 1.7 mL of HMPA. After 1.5 h at $-78^{\circ} \mathrm{C}$, MeI ( $1.2 \mathrm{~mL}, 20 \mathrm{mmol}$ ) was added. The reaction mixture was warmed to $22{ }^{\circ} \mathrm{C}$ for $18 \mathrm{~h}, 5 \mathrm{~mL}$ of $\mathrm{NH}_{4} \mathrm{Cl}$ (saturated aqueous) was added, and the mixture was diluted with 70 mL of MTBE. The organic layer was washed with $\mathrm{H}_{2} \mathrm{O}(4 \times$ $50 \mathrm{~mL})$ and brine $(4 \times 50 \mathrm{~mL})$. 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 ( $0.96 \mathrm{~g}, 87 \%$ ): ${ }^{1} \mathrm{H}$ NMR ( 500 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.30(\mathrm{~m}, 4 \mathrm{H}), 7.23(\mathrm{~m}, 1 \mathrm{H}), 6.77(\mathrm{~s}, 2 \mathrm{H}), 6.73(\mathrm{~s}, 2 \mathrm{H}), 5.30(\mathrm{~d}, J=6.1,1 \mathrm{H}), 4.52$ $(\mathrm{d}, J=10.9,1 \mathrm{H}), 4.45(\mathrm{~d}, J=11.0,1 \mathrm{H}), 4.10(\mathrm{tdd}, J=10.8,7.1,3.7,2 \mathrm{H}), 3.01(\mathrm{dd}, J=9.0,2.2$, $1 \mathrm{H}), 2.97(\mathrm{~m}, 1 \mathrm{H}), 2.73(\mathrm{~m}, 1 \mathrm{H}), 2.47(\mathrm{br} \mathrm{s}, 6 \mathrm{H}), 2.42(\mathrm{br} \mathrm{s}, 6 \mathrm{H}), 2.22(\mathrm{~s}, 3 \mathrm{H}), 2.19(\mathrm{~s}, 3 \mathrm{H}), 2.06$ $(\mathrm{m}, 1 \mathrm{H}), 1.87(\mathrm{~m}, 1 \mathrm{H}), 1.27(\mathrm{~m}, 6 \mathrm{H}), 1.09(\mathrm{~d}, J=7.0,3 \mathrm{H}), 0.93(\mathrm{~d}, J=6.8,3 \mathrm{H}), 0.64(\mathrm{~d}, J=6.8$, $3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 178.2,144.5,144.2,139.1,138.9,138.6,130.8,129.6,129.4$, $129.0,128.2,127.5,127.3,87.8,75.5,60.5,38.9,37.0,30.0,28.8,24.4,24.0,21.3,21.0,20.9,17.4$, 15.6, 14.1, 13.4; IR (thin film) 3027, 2967, 1727, 1604, 1453, $909 \mathrm{~cm}^{-1}$; HRMS (CI+/NH3) $\mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{40} \mathrm{H}_{51} \mathrm{O}_{3} \mathrm{Si}(\mathrm{M}-\mathrm{H})^{+}$571.3608, found 571.3611. Anal. Calcd for $\mathrm{C}_{40} \mathrm{H}_{52} \mathrm{O}_{3} \mathrm{Si}$ : C, 77.57; H , 9.15. Found: C, 77.64; H, 9.34.

## D. Intramolecular Hydrosilylation Reactions


(3R*)-1-Oxa-3-[( $\left.1 S^{*}, 2 R^{*}\right)$-2-benzyloxy-1,3-dimethylbutyl]-5-ethoxy-2,2-
(dimesityl)silacyclopentane (3a). To a cooled $\left(0^{\circ} \mathrm{C}\right)$ solution of silyl ester 2a ( $0.40 \mathrm{~g}, 0.72$ mmol ) in 5 mL of THF was added $n-\mathrm{Bu}_{4} \mathrm{NF}(0.072 \mathrm{~mL}, 0.072 \mathrm{mmol}, 1.0 \mathrm{M}$ in THF). The solution was stirred for 5 min at $0^{\circ} \mathrm{C}$. To the mixture was added 3 mL of sodium bicarbonate (saturated aqueous) and the mixture was partitioned between 30 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and 30 mL of sodium bicarbonate (saturated aqueous). The organic layer was separated, and the aqueous layer was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 30 \mathrm{~mL})$. 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, $756 \mathrm{~cm}^{-1}$; HRMS (CI+/NH ${ }_{3}$ ) $\mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{36} \mathrm{H}_{49} \mathrm{O}_{3} \mathrm{Si}(\mathrm{M}-\mathrm{H})^{+} 557.3451$, found 557.3441. Anal. Calcd for $\mathrm{C}_{36} \mathrm{H}_{50} \mathrm{O}_{3} \mathrm{Si}$ : C, 77.37; H , 9.02. Found: C, $77.10 ; \mathrm{H}, 9.02$. Major isomer, characteristic peaks: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.31(\mathrm{~m}, 4 \mathrm{H}), 7.23(\mathrm{~m}, 1 \mathrm{H}), 6.77(\mathrm{~s}, 2 \mathrm{H}), 6.71(\mathrm{~s}, 2 \mathrm{H}), 5.07(\mathrm{~m}, 1 \mathrm{H}), 4.61(\mathrm{~d}, J=11.1,1 \mathrm{H}), 4.56$ $(\mathrm{d}, J=11.2,1 \mathrm{H}), 3.93(\mathrm{dq}, J=9.4,7.2,1 \mathrm{H}), 3.51(\mathrm{dq}, J=9.3,7.0,1 \mathrm{H}), 2.98(\mathrm{t}, J=5.3,1 \mathrm{H}), 2.41$ $(\mathrm{s}, 6 \mathrm{H}), 2.39(\mathrm{~s}, 6 \mathrm{H}), 2.23(\mathrm{~s}, 3 \mathrm{H}), 2.21(\mathrm{~s}, 3 \mathrm{H}), 1.92(\mathrm{~m}, 1 \mathrm{H}), 1.22(\mathrm{t}, J=7.1,3 \mathrm{H}), 0.93(\mathrm{~d}, J=6.8$, $3 \mathrm{H}), 0.85(\mathrm{~d}, J=6.8,3 \mathrm{H}), 0.73(\mathrm{~d}, J=6.8,3 \mathrm{H})$; Minor product, characteristic peaks: $\delta 5.30(\mathrm{~m}$, $0.19 \mathrm{H}), 3.34(\mathrm{~m}, 0.21 \mathrm{H}), 0.66(\mathrm{~d}, J=6.9,0.66 \mathrm{H})$; Major product: ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 144.0,139.2,139.1,129.2,128.9,128.2,127.34,127.26,102.0,90.9,75.5,63.6,33.9,33.5,31.5$, 30.5, 23.82, 23.75, 21.0, 20.9, 20.7, 17.8, 15.2, 12.0; Minor product, characteristic peaks: $\delta 143.4$, $138.6,134.0,131.3,128.8,128.2,127.4,127.3,100.8,90.8,75.3,62.4,33.7,33.6,30.6,29.7,39.0$, 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 $\left(-78^{\circ} \mathrm{C}\right)$ solution of $\mathrm{Me}_{2} \mathrm{Zn}(1.2 \mathrm{~mL}, 2.4 \mathrm{mmol}, 2.0 \mathrm{M}$ in toluene) in 16 mL of THF was added a cooled $\left(0^{\circ} \mathrm{C}\right)$ solution of silyllithium $4(1.0 \mathrm{~g}, 2.4 \mathrm{mmol})$ in 3.0 mL of THF. The solution was warmed to $0{ }^{\circ} \mathrm{C}$ for 5 min and then re-cooled to $-78{ }^{\circ} \mathrm{C}$. In a separate flask, MeLi ( $0.20 \mathrm{~mL}, 0.24 \mathrm{mmol}, 1.2 \mathrm{M}$ in $\mathrm{Et}_{2} \mathrm{O}$ ) was added to a cooled $\left(-78{ }^{\circ} \mathrm{C}\right)$ slurry of $\mathrm{CuCN}(0.011 \mathrm{~g}$, 0.12 mmol ) in 3.0 mL of THF. The slurry was warmed to $-30^{\circ} \mathrm{C}$, stirred for 5 min , cooled to -78 ${ }^{\circ} \mathrm{C}$, and stirred for 5 min . The cuprate solution was added to the zincate solution and the mixture was stirred at $-78{ }^{\circ} \mathrm{C}$ for 10 min . To the mixture was added a cooled $\left(-78^{\circ} \mathrm{C}\right)$ solution of ethyl $(R)$-E-4-benzyloxy-5-methyl-hex-2-eneoate ${ }^{12,13}(0.60 \mathrm{~g}, 2.3 \mathrm{mmol})$ in 1.9 mL of THF. After 18 h at $-78^{\circ} \mathrm{C}, 5 \mathrm{~mL}$ of $\mathrm{NH}_{4} \mathrm{Cl}$ (saturated aqueous) was added, and the mixture was warmed to $25^{\circ} \mathrm{C}$ and diluted with 50 mL of water. The organic layer was separated, and the aqueous layer was extracted with $\mathrm{Et}_{2} \mathrm{O}(3 \times 40 \mathrm{~mL})$. The combined organic layers were dried with $\mathrm{MgSO}_{4}$, filtered, and concentrated in vacuo to yield a colorless oil as a 96:4 mixture of diastereomers as determined by ${ }^{1} \mathrm{H}$ NMR spectroscopy. To a cooled $\left(0^{\circ} \mathrm{C}\right)$ solution of the oil in 9.3 mL of THF was added $n$ $\mathrm{Bu}_{4} \mathrm{NF}\left(0.28 \mathrm{~mL}, 0.28 \mathrm{mmol}, 1 \mathrm{M}\right.$ in THF). The solution was stirred for 40 min at $0{ }^{\circ} \mathrm{C}$. To the reaction mixture was added 3 mL of sodium bicarbonate (saturated aqueous) was added, and the mixture was partitioned between 30 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and 30 mL of sodium bicarbonate (saturated aqueous). The organic layer was separated, and the aqueous layer was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times$ 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 ${ }^{1} \mathrm{H}$ 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 ( $0.47 \mathrm{~g}, 63 \%$ ): Mixture: IR (thin film) 3027, 2969, 1605, 1454, $1070 \mathrm{~cm}^{-1} ;$ HRMS $\left(\mathrm{CI}+/ \mathrm{NH}_{3}\right) \mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{31} \mathrm{H}_{39} \mathrm{O}_{3} \mathrm{Si}\left(\mathrm{M}-\mathrm{C}_{3} \mathrm{H}_{7}\right)^{+}$ 487.2668, found 487.2667. Anal. Calcd for $\mathrm{C}_{34} \mathrm{H}_{46} \mathrm{O}_{3} \mathrm{Si}: \mathrm{C}, 76.93$; H, 8.73. Found: C, 76.97; H , 8.79. Major isomer: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.27(\mathrm{~m}, 1 \mathrm{H}), 7.22(\mathrm{~m}, 4 \mathrm{H}), 6.76(\mathrm{~s}, 2 \mathrm{H}), 6.67$
$(\mathrm{s}, 2 \mathrm{H}), 5.16(\mathrm{dd}, J=5.0,3.7,1 \mathrm{H}), 4.37(\mathrm{~d}, J=10.9,1 \mathrm{H}), 4.29(\mathrm{~d}, J=10.9,1 \mathrm{H}), 3.98(\mathrm{dq}, J=14.2$, 7.1, 1H), $3.52(\mathrm{~m}, 2 \mathrm{H}), 2.54(\mathrm{~m}, 1 \mathrm{H}), 2.39(\mathrm{~s}, 6 \mathrm{H}), 2.34(\mathrm{~s}, 6 \mathrm{H}), 2.30(\mathrm{~m}, 1 \mathrm{H}), 2.22(\mathrm{~s}, 3 \mathrm{H}), 2.19(\mathrm{~s}$, $3 \mathrm{H}), 2.15(\mathrm{~m}, 1 \mathrm{H}), 1.58(\mathrm{~m}, 1 \mathrm{H}), 1.24(\mathrm{t}, J=7.1,3 \mathrm{H}), 0.95(\mathrm{~d}, J=6.8,3 \mathrm{H}), 0.72(\mathrm{~d}, J=6.9,3 \mathrm{H})$; Minor isomer, characteristic peaks: $\delta 7.08(\mathrm{~d}, J=7.1,0.58 \mathrm{H}), 6.72(\mathrm{~s}, 0.59 \mathrm{H}), 5.32(\mathrm{t}, J=4.1$, $0.26 \mathrm{H}), 4.15(\mathrm{~d}, J=11.8,0.30 \mathrm{H}), 3.30(\mathrm{dq}, J=14.1,7.1,0.25 \mathrm{H}), 3.21(\mathrm{dd}, J=6.5,3.8,0.28 \mathrm{H})$, $3.14(\mathrm{~d}, J=11.5,0.25 \mathrm{H}), 2.61(\mathrm{~m}, 0.19 \mathrm{H}), 1.98(\mathrm{~m}, 0.61 \mathrm{H}), 0.96(\mathrm{~m}, 3.3 \mathrm{H})$; Major product: ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 144.2,143.3,139.6,139.1,139.0,133.9,130.2,129.12,129.08,127.9$, $127.4,126.9,102.1,82.8,73.6,63.8,33.5,32.8,30.8,23.84,23.79,23.2,21.0,20.8,16.8,15.3$; Minor product, characteristic peaks: $\delta 143.8,139.7,138.7$, 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 $\left(0^{\circ} \mathrm{C}\right)$ solution of activated $4 \AA$ molecular sieves $(0.10 \mathrm{~g})$ and $n-\mathrm{Bu}_{4} \mathrm{NF}\left(0.44 \mathrm{~mL}, 0.44 \mathrm{mmol}, 1 \mathrm{M}\right.$ in THF) in 11 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ was added a solution of silane ester $\mathbf{2 c}(0.66 \mathrm{~g}, 1.3 \mathrm{mmol})$ in 7.4 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. The solution was warmed to 25 ${ }^{\circ} \mathrm{C}$ 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and 90 mL of sodium carbonate (saturated aqueous). The organic layer was separated, and the aqueous layer was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 40 \mathrm{~mL})$. 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/ $\mathrm{NH}_{4} \mathrm{Cl}$. The oil was purified by flash chromatography (hexanes to 3:97 EtOAc:hexanes) to give each diastereomer as a colorless oil ( $0.60 \mathrm{~g}, 91 \%$, combined yield): Mixture: IR (thin film) 3025, 2880, 2246, 1605, 1455, 1075, 980, $734 \mathrm{~cm}^{-1}$; HRMS (LSIMS) $\mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{30} \mathrm{H}_{44} \mathrm{O}_{4} \mathrm{Si}(\mathrm{M}-\mathrm{H})^{+}$495.2931, found 495.2927. Major isomer: ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 6.76(\mathrm{~s}, 2 \mathrm{H}) ; 6.72(\mathrm{~s}, 2 \mathrm{H}) ; 5.22(\mathrm{dd}, J=5.3,1.0,1 \mathrm{H}), 4.32(\mathrm{ddd}, J=10.8,8.8,5.6,1 \mathrm{H})$, $3.90(\mathrm{dq}, J=9.1,7.0,1 \mathrm{H}), 3.49(\mathrm{dq}, J=9.1,7.1,1 \mathrm{H}), 3.11(\mathrm{t}, J=7.8,1 \mathrm{H}), 2.97(\mathrm{dd}, J=7.7,5.6$,
$1 \mathrm{H}), 2.58(\mathrm{~m}, 1 \mathrm{H}), 2.41(\mathrm{~s}, 6 \mathrm{H}), 2.34(\mathrm{~s}, 6 \mathrm{H}), 2.22(\mathrm{~d}, J=5.0,6 \mathrm{H}$ and $\mathrm{m}, 1 \mathrm{H}), 2.08(\mathrm{ddd}, J=10.8$, $6.5,2.2,1 \mathrm{H}), 1.57(\mathrm{~m}, 2 \mathrm{H}), 1.49(\mathrm{~m}, 2 \mathrm{H}), 1.19(\mathrm{t}, J=7.0,3 \mathrm{H}), 0.87(\mathrm{t}, J=7.5,3 \mathrm{H}), 0.83(\mathrm{t}, J=7.5$, $3 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(125 \mathrm{MHz} \mathrm{CDCl}_{3}\right.$ ) $\delta 143.9,143.2,139.6,139.3,132.6,129.5,129.23,129.19$, 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: ${ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 6.76(\mathrm{~s}, 2 \mathrm{H}), 6.70(\mathrm{~s}, 2 \mathrm{H}), 5.37(\mathrm{dd}, J=5.9,4.2,1 \mathrm{H}), 3.89$ $(\mathrm{m}, 1 \mathrm{H}), 3.64(\mathrm{dq}, J=9.6,7.1,1 \mathrm{H}), 3.42(\mathrm{~m}, 3 \mathrm{H}), 2.47(\mathrm{~m}, 1 \mathrm{H}), 2.40(\mathrm{~s}, 6 \mathrm{H}), 2.33(\mathrm{~m}, 1 \mathrm{H}), 2.29(\mathrm{~s}$, $6 \mathrm{H}), 2.21(\mathrm{~d}, J=5.0,6 \mathrm{H}), 2.02(\mathrm{~m}, 1 \mathrm{H}), 1.57(\mathrm{~m}, 2 \mathrm{H}), 1.33(\mathrm{q}, J=7.5,2 \mathrm{H}), 1.03(\mathrm{t}, J=7.0,3 \mathrm{H})$, $0.87(\mathrm{t}, J=7.4,3 \mathrm{H}), 0.59(\mathrm{t}, J=7.4,3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 143.6,143.0,139.2$, $138.9,132.8,130.2,129.0,128.9,111.9,101.3,77.2,76.5,69.2,63.2,34.3,30.4,30.0,29.2,23.6$, 23.3, 23.0, 20.94, 20.93, 14.9, 8.1, 7.8.

(3R*)-1-Oxa-3-[(1S*,2R*)-2-(tert-butyl-dimethylsiloxy)-1,3-dimethylbutyl]-5-ethoxy-2,2(dimesityl)silacyclopentane (3d). To a cooled $\left(-78{ }^{\circ} \mathrm{C}\right)$ solution of $\mathrm{Me}_{2} \mathrm{Zn}(0.50 \mathrm{~mL}, 0.99$ $\mathrm{mmol}, 2.0 \mathrm{M}$ in toluene) in 6.6 mL of THF was added a cooled $\left(0^{\circ} \mathrm{C}\right)$ solution of silyllithium 4 $(0.44 \mathrm{~g}, 1.0 \mathrm{mmol})$ in 1.0 mL of THF. The solution was warmed to $0^{\circ} \mathrm{C}$ for 5 min and then cooled to $-78^{\circ} \mathrm{C}$. In a separate flask, $\mathrm{MeLi}\left(0.085 \mathrm{~mL}, 0.1 \mathrm{mmol}, 1.2 \mathrm{M}\right.$ in $\left.\mathrm{Et}_{2} \mathrm{O}\right)$ was added to a cooled $\left(-78^{\circ} \mathrm{C}\right)$ slurry of $\mathrm{CuCN}(0.006 \mathrm{~g}, 0.05 \mathrm{mmol})$ in 1.3 mL of THF. The slurry was warmed to -30 ${ }^{\circ} \mathrm{C}$, stirred for 5 min , cooled to $-78^{\circ} \mathrm{C}$, and stirred for 5 min . The cuprate solution was added to the zincate solution and the mixture was stirred at $-78^{\circ} \mathrm{C}$ for 10 min . To the reaction solution was added $\left(\mathrm{CH}_{3}\right)_{3} \mathrm{SiCl}(0.40 \mathrm{~mL}, 3.0 \mathrm{mmol})$ followed by a cooled $\left(-78{ }^{\circ} \mathrm{C}\right)$ solution of enoate $\mathbf{1 d}(0.30$ $\mathrm{g}, 0.95 \mathrm{mmol}$ ) in 0.6 mL of THF. After 18 h at $-78{ }^{\circ} \mathrm{C}, 5 \mathrm{~mL}$ of $\mathrm{NH}_{4} \mathrm{Cl}$ (saturated aqueous) was added, and the mixture was warmed to $25^{\circ} \mathrm{C}$ and diluted with 50 mL of water. The aqueous layer was extracted with $\mathrm{Et}_{2} \mathrm{O}(3 \times 30 \mathrm{~mL})$. The combined organic layers were dried with $\mathrm{MgSO}_{4}$, 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 $\left(0^{\circ} \mathrm{C}\right)$ solution of the oil in 3.4 mL of THF was added $n$ $\mathrm{Bu}_{4} \mathrm{NF}\left(0.10 \mathrm{~mL}, 0.10 \mathrm{mmol}, 1 \mathrm{M}\right.$ in THF). The solution was stirred for 40 min at $0{ }^{\circ} \mathrm{C}$. To the
solution was added 3 mL of sodium bicarbonate (saturated aqueous) and the mixture was partitioned between 30 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and 30 mL of sodium bicarbonate (saturated aqueous). The organic layer was separated, and the aqueous layer was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 20 \mathrm{~mL})$. 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 $5: 95 \mathrm{CH}_{2} \mathrm{Cl}_{2}$ :hexanes) to give the product as a pale yellow oil ( $0.19 \mathrm{~g}, 63 \%$ ): ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 6.78(\mathrm{~s}, 2 \mathrm{H}), 6.72(\mathrm{~s}, 2 \mathrm{H}), 5.08(\mathrm{~m}$, $1 \mathrm{H}), 3.96(\mathrm{dq}, J=14.2,7.1,1 \mathrm{H}), 3.53(\mathrm{dq}, J=14.2,7.1,1 \mathrm{H}), 3.33(\mathrm{dd}, J=6.8,2.1,1 \mathrm{H}), 2.44(\mathrm{~m}$, $1 \mathrm{H}), 2.42(\mathrm{~s}, 6 \mathrm{H}), 2.41(\mathrm{~s}, 6 \mathrm{H}), 2.24(\mathrm{~s}, 3 \mathrm{H}), 2.23(\mathrm{~s}, 3 \mathrm{H}), 2.15(\mathrm{dd}, J=10.6,5.2,1 \mathrm{H}), 2.01(\mathrm{~m}, 2 \mathrm{H})$, $1.81(\mathrm{dtd}, J=13.6,6.8,2.1,1 \mathrm{H}), 1.24(\mathrm{t}, J=7.0,3 \mathrm{H}), 0.90(\mathrm{~s}, 9 \mathrm{H}), 0.86(\mathrm{~d}, J=6.9,3 \mathrm{H}), 0.83$ (d, $J$ $=6.7,3 \mathrm{H}), 0.65(\mathrm{~d}, J=6.8,3 \mathrm{H}), 0.04(\mathrm{~s}, 3 \mathrm{H}), 0.01(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $\left.125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 144.0$, $143.4,139.1,139.0,134.0,131.7,129.2,128.9,101.8,81.7,63.6,34.6,33.1,31.6,30.8,26.4,23.9$, $23.8,21.2,21.01,20.95,18.7,16.1,15.2,13.5,-3.2,-3.3$; IR (thin film) $3024,2954,1606,1462$, $1045 \mathrm{~cm}^{-1}$; HRMS $\left(\mathrm{CI}+/ \mathrm{NH}_{3}\right) \mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{35} \mathrm{H}_{57} \mathrm{O}_{3} \mathrm{Si}_{2}(\mathrm{M}-\mathrm{H})^{+}$581.3846, found 581.3850. Anal. Calcd for $\mathrm{C}_{35} \mathrm{H}_{58} \mathrm{O}_{3} \mathrm{Si}_{2}$ : C, $72.10 ; \mathrm{H}, 10.03$. 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 $\left(0^{\circ} \mathrm{C}\right)$ solution of silyl ester $\mathbf{2 e}(0.19 \mathrm{~g}, 0.32$ $\mathrm{mmol})$ in 2 mL of THF was added $n-\mathrm{Bu}_{4} \mathrm{NF}(0.032 \mathrm{~mL}, 0.032 \mathrm{mmol}, 1 \mathrm{M}$ in THF). The solution was stirred for 30 min at $0^{\circ} \mathrm{C}$. To the reaction mixture was added 3 mL of sodium carbonate (saturated aqueous) and the mixture was partitioned between 30 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and 30 mL of sodium bicarbonate (saturated aqueous). The organic layer was separated, and the aqueous layer was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 30 \mathrm{~mL})$. 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 ${ }^{1} \mathrm{H}$ 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 ( $0.15 \mathrm{~g}, 79 \%$ ): Mixture: IR (thin film) 3027, 2972, 1604, 1453, 1064, $908 \mathrm{~cm}^{-1}$; HRMS (TOF MS ES+/Na) $m / z$ calcd for $\mathrm{C}_{39} \mathrm{H}_{48} \mathrm{O}_{3} \mathrm{SiNa}(\mathrm{M}+\mathrm{Na})^{+}$615.3270, found 615.3262. Anal. Calcd for $\mathrm{C}_{39} \mathrm{H}_{48} \mathrm{O}_{3} \mathrm{Si}$ : C, 79.01; H, 8.16. Found: C, 78.82; H, 8.42. Major isomer, characteristic peaks: ${ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.34-7.23(\mathrm{~m}, 10 \mathrm{H}), 6.76(\mathrm{~s}, 2 \mathrm{H}), 6.65(\mathrm{~s}, 2 \mathrm{H})$, $5.07(\mathrm{dd}, J=8.2,4.0,1 \mathrm{H}), 4.41(\mathrm{~d}, J=11.9,1 \mathrm{H}), 4.13(\mathrm{~d}, J=11.9,1 \mathrm{H}), 3.95(\mathrm{~m}, 2 \mathrm{H}), 3.53(\mathrm{~m}$, $1 \mathrm{H}), 2.78(\mathrm{~m}, 1 \mathrm{H}), 2.38(\mathrm{~s}, 6 \mathrm{H}), 2.37(\mathrm{br} \mathrm{s}, 6 \mathrm{H}), 2.22(\mathrm{~s}, 3 \mathrm{H}), 2.15(\mathrm{~s}, 3 \mathrm{H}), 1.22(\mathrm{t}, J=7.1,3 \mathrm{H})$, $0.32(\mathrm{~d}, J=6.9,3 \mathrm{H})$; Minor product, characteristic peaks: $\delta 5.31(\mathrm{~m}, 0.17 \mathrm{H}), 4.15(\mathrm{~d}, J=12.0$, $0.24 \mathrm{H}), 3.33(\mathrm{dq}, J=14.1,7.1,0.17 \mathrm{H}), 3.15(\mathrm{~m}, 0.15 \mathrm{H}), 0.95(\mathrm{t}, J=7.1,0.61 \mathrm{H})$; Major product: ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 144.0,143.9,141.7,139.0,138.9,138.8,133.8,131.7,129.12$, $128.8,128.24,128.19,127.64,127.5,127.3,102.1,85.3,70.6,63.7,38.4,32.8,28.0,23.6,20.9$, 15.3, 13.2; Minor product, characteristic peaks: $\delta 141.8,138.7,138.4,133.5,129.06,128.6,128.15$, $127.67,127.2,101.0,85.7,70.7,62.1,38.7,33.0,29.7,24.6,23.2,15.0,13.5$.

$\left(3 R^{*}, 4 R^{*}\right)$-1-Oxa-3-[( $\left.1 S^{*}, 2 R^{*}\right)$-2-benzyloxy-1,3-dimethylbutyl]-5-ethoxy-4-methyl-2,2-
(dimesityl)silacyclopentane (6a). To a cooled $\left(0^{\circ} \mathrm{C}\right)$ solution of ester $\mathbf{5 a}(0.96 \mathrm{~g}, 1.7 \mathrm{mmol})$ in 11 mL of THF was added $n-\mathrm{Bu}_{4} \mathrm{NF}\left(0.17 \mathrm{~mL}, 0.17 \mathrm{mmol}, 1.0 \mathrm{M}\right.$ in THF). After 45 min at $0{ }^{\circ} \mathrm{C}$, additional $n-\mathrm{Bu}_{4} \mathrm{NF}(0.17 \mathrm{~mL}, 0.17 \mathrm{mmol}, 1.0 \mathrm{M}$ in THF) was added, and the solution was stirred for 1 h at $0^{\circ} \mathrm{C}$. 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and 30 mL of sodium bicarbonate (saturated aqueous). The organic layer was separated, and the aqueous layer was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 30 \mathrm{~mL})$. 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, $977 \mathrm{~cm}^{-1}$; HRMS (TOF MS ES+/Na) m $/ z$ calcd for $\mathrm{C}_{37} \mathrm{H}_{52} \mathrm{O}_{3} \mathrm{SiNa}(\mathrm{M}+\mathrm{Na})^{+}$595.3583, found 595.3580. Major isomer: ${ }^{1} \mathrm{H}$ NMR (500
$\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.29(\mathrm{~m}, 3 \mathrm{H}), 7.21(\mathrm{~m}, 2 \mathrm{H}), 6.73(\mathrm{~s}, 2 \mathrm{H}), 6.71(\mathrm{~s}, 2 \mathrm{H}), 5.01(\mathrm{~d}, J=4.3,1 \mathrm{H}), 4.30$ $(\mathrm{d}, J=11.8,1 \mathrm{H}), 4.07(\mathrm{~m}, 1 \mathrm{H}), 3.89(\mathrm{dq}, J=14.2,7.1,1 \mathrm{H}), 3.50(\mathrm{dq}, J=14.0,7.0,1 \mathrm{H}), 3.08(\mathrm{t}, J=$ 5.1, 1H), $2.41(\mathrm{~s}, 6 \mathrm{H}), 2.31(\mathrm{br} \mathrm{s}, 6 \mathrm{H}$ and m, 1H), $2.22(\mathrm{~s}, 3 \mathrm{H}), 2.21(\mathrm{~s}, 3 \mathrm{H}), 2.11(\mathrm{dd}, J=7.8,5.6$, $1 \mathrm{H}), 1.96(\mathrm{dq}, J=13.5,6.5,1 \mathrm{H}), 1.20(\mathrm{t}, J=7.1,3 \mathrm{H}), 1.13(\mathrm{~d}, J=7.1,3 \mathrm{H}), 1.05(\mathrm{~d}, J=6.9,3 \mathrm{H})$, $0.95(\mathrm{~m}, 1 \mathrm{H}), 0.90(\mathrm{~d}, J=6.7,3 \mathrm{H}), 0.84(\mathrm{~d}, J=6 . .9,3 \mathrm{H})$; minor product, characteristic peaks: $\delta$ $4.59(\mathrm{~m}, 0.29 \mathrm{H}), 4.54(\mathrm{~d}, J=11.2,0.19 \mathrm{H}), 4.51(\mathrm{~d}, J=11.0,0.19 \mathrm{H}), 3.69(\mathrm{dq}, J=14.1,7.0$, $0.16 \mathrm{H}), 3.45(\mathrm{~m}, 0.12 \mathrm{H}), 3.38(\mathrm{dd}, J=8.9,2.1,0.21 \mathrm{H}), 3.18(\mathrm{~m}, 0.10 \mathrm{H})$; major product, characteristic peaks: ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 139.7$, 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: $\delta 106.4,75.7,74.6,63.2,42.1,36.3,32.8,30.1,21.3$, 16.2, 15.7, 12.7.

## E. Lewis acid-mediated Nucleophilic Substitution Reactions


$\left(3 R^{*}, 5 S^{*}\right)$-1-Oxa-3-[(1S*, $2 R^{*}$ )-2-benzyloxy-1,3-dimethylbutyl]-5-(3-propenyl)-2,2-
(dimesityl)silacyclopentane. To a cooled $\left(-78{ }^{\circ} \mathrm{C}\right)$ solution of acetal $\mathbf{3 a}(0.23 \mathrm{~g}, 0.41 \mathrm{mmol})$ in 14 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ was added allyltrimethylsilane ( $0.13 \mathrm{~mL}, 0.82 \mathrm{mmol}$ ) followed by $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}$ $(0.052 \mathrm{~mL}, 0.41 \mathrm{mmol})$. The solution was warmed to $22{ }^{\circ} \mathrm{C}$ for 2 h , and 10 mL of sodium bicarbonate (saturated aqueous) was added. The organic layer was separated and the aqueous layer was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 50 \mathrm{~mL})$. 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 ( $0.21 \mathrm{~g}, 91 \%$ ): ${ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.33(\mathrm{~m}, 5 \mathrm{H}), 6.73(\mathrm{~s}, 2 \mathrm{H}), 6.71(\mathrm{~s}, 2 \mathrm{H}), 5.76(\mathrm{ddt}, J=17.1,10.1,6.9,1 \mathrm{H})$, $4.97(\mathrm{~m}, 2 \mathrm{H}), 4.62(\mathrm{~s}, 2 \mathrm{H}), 4.16(\mathrm{~m}, 1 \mathrm{H}), 2.88(\mathrm{~m}, 1 \mathrm{H}), 2.38(\mathrm{~s}, 6 \mathrm{H}), 2.34(\mathrm{br} \mathrm{s}, 6 \mathrm{H}), 2.29-2.11(\mathrm{~m}$, $4 \mathrm{H}), 2.22(\mathrm{~s}, 3 \mathrm{H}), 2.21(\mathrm{~s}, 3 \mathrm{H}), 1.94(\mathrm{~m}, 1 \mathrm{H}), 1.80(\mathrm{dq}, J=13.2,6.6,1 \mathrm{H}), 1.68(\mathrm{~m}, 1 \mathrm{H}), 0.88(\mathrm{~d}, J=$ $6.6,3 \mathrm{H}), 0.78(\mathrm{~d}, J=6.9,3 \mathrm{H}), 0.62(\mathrm{~d}, J=6.8,3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta$ 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, $1067 \mathrm{~cm}^{-1} ;$ HRMS (TOF MS ES+ +Na ) $m / z$ calcd for $\mathrm{C}_{37} \mathrm{H}_{50} \mathrm{O}_{2} \mathrm{SiNa}(\mathrm{M}+\mathrm{Na})^{+}$577.3478, found 577.3480. Anal. Calcd for $\mathrm{C}_{37} \mathrm{H}_{50} \mathrm{O}_{2} \mathrm{Si}$ : C, 80.09; H, 9.08. Found: C, 79.90; H, 9.25.

$\left(3 R^{*}, 5 S^{*}\right)$-1-Oxa-3-[(1S*,2R*)-2-(tert-butyl-dimethylsiloxy)-1,3-dimethylbutyl]-5-(3-
propenyl)-2,2-(dimesityl)silacyclopentane. To a cooled solution ( $-78{ }^{\circ} \mathrm{C}$ ) of acetal $\mathbf{3 d}(0.15 \mathrm{~g}$, 0.26 mmol ) in 8.7 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ was added allyltrimethylsilane ( $0.083 \mathrm{~mL}, 0.52 \mathrm{mmol}$ ) followed by $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(0.033 \mathrm{~mL}, 0.26 \mathrm{mmol})$. The solution was warmed to $0{ }^{\circ} \mathrm{C}$ 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 30 \mathrm{~mL})$. 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ :hexanes) to give the product, a viscous oil, as a single diastereomer as determined by ${ }^{1} \mathrm{H}$ NMR spectroscopy $(0.13 \mathrm{~g}, 87 \%)$ : ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 6.78(\mathrm{~s}, 2 \mathrm{H})$, $6.76(\mathrm{~s}, 2 \mathrm{H}), 5.82(\mathrm{ddt}, J=17.3,10.2,7.0,1 \mathrm{H}), 5.01(\mathrm{~m}, 2 \mathrm{H}), 4.21(\mathrm{~m}, 1 \mathrm{H}), 3.29(\mathrm{t}, J=3.9,1 \mathrm{H})$, $2.46(\mathrm{~s}, 6 \mathrm{H}), 2.39(\mathrm{br} \mathrm{s}, 6 \mathrm{H}), 2.26(\mathrm{~s}, 3 \mathrm{H}), 2.25(\mathrm{~s}, 3 \mathrm{H}$ and m, 1H), $2.20(\mathrm{~m}, 3 \mathrm{H}), 1.86(\mathrm{~m}, 1 \mathrm{H}), 1.69$ (dt, $J=15.6,7.0,1 \mathrm{H}), 1.49(\mathrm{~m}, 1 \mathrm{H}), 0.94(\mathrm{~s}, 9 \mathrm{H}), 0.77(\mathrm{~d}, J=5.3,3 \mathrm{H}), 0.75(\mathrm{~d}, J=5.1,3 \mathrm{H}), 0.69$ $(\mathrm{d}, J=6.9,3 \mathrm{H}), 0.11(\mathrm{~s}, 3 \mathrm{H}), 0.10(\mathrm{~s}, 3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $\left.125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 143.8,143.3,138.8$, 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, $1048 \mathrm{~cm}^{-}$ ${ }^{1}$; HRMS $\left(\mathrm{CI}+/ \mathrm{NH}_{3}\right) m / z$ calcd for $\mathrm{C}_{33} \mathrm{H}_{51} \mathrm{O}_{2} \mathrm{Si}_{2}\left(\mathrm{M}-\mathrm{C}_{3} \mathrm{H}_{7}\right)^{+}$535.3427, found 535.3427. Anal. Calcd for $\mathrm{C}_{36} \mathrm{H}_{58} \mathrm{O}_{2} \mathrm{Si}_{2}: \mathrm{C}, 74.68 ; \mathrm{H}, 10.10$. Found: C, $74.90 ; \mathrm{H}, 10.23$.

(3S,5R)-1-Oxa-3-[(1R,2S)-2-benzyloxy-1-methyl-2-phenyl-ethyl]-5-(3-propenyl)-2,2-
(dimesityl)silacyclopentane. To a cooled $\left(-78^{\circ} \mathrm{C}\right)$ solution of acetal $\mathbf{3 e}(0.14 \mathrm{~g}, 0.24 \mathrm{mmol})$ in 8 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ was added allyltrimethylsilane $(0.076 \mathrm{~mL}, 0.48 \mathrm{mmol})$ followed by $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(0.030$ $\mathrm{mL}, 0.24 \mathrm{mmol}$ ). After the solution was warmed to $22{ }^{\circ} \mathrm{C}$ for $2 \mathrm{~h}, 5 \mathrm{~mL}$ of sodium bicarbonate (saturated aqueous) was added. The organic layer was separated and the aqueous layer was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 40 \mathrm{~mL})$. 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 ${ }^{1} \mathrm{H}$ 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 ( $0.12 \mathrm{~g}, 86 \%$ ): ${ }^{1} \mathrm{H}$ NMR ( $\left.500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.35-7.24(\mathrm{~m}, 10 \mathrm{H}), 6.71(\mathrm{~s}, 2 \mathrm{H}), 6.66(\mathrm{~s}, 2 \mathrm{H}), 5.75$ (ddt, $J=17.0$, $10.4,7.0,1 \mathrm{H}), 4.95(\mathrm{~m}, 2 \mathrm{H}), 4.42(\mathrm{~d}, J=12.0,1 \mathrm{H}), 4.22(\mathrm{~m}, 1 \mathrm{H}), 4.14(\mathrm{~d}, J=11.9,1 \mathrm{H}), 4.04(\mathrm{~d}, J$ $=7.6,1 \mathrm{H}), 2.84(\mathrm{~m}, 1 \mathrm{H}), 2.34(\mathrm{~s}, 6 \mathrm{H}), 2.28(\mathrm{br} \mathrm{s}, 6 \mathrm{H}), 2.21(\mathrm{~s}, 3 \mathrm{H}$ and $\mathrm{m}, 1 \mathrm{H}), 2.17(\mathrm{~s}, 3 \mathrm{H}), 2.15-$ $2.03(\mathrm{~m}, 3 \mathrm{H}), 1.68(\mathrm{~m}, 1 \mathrm{H}), 0.42(\mathrm{~d}, J=7.0,3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 143.6,141.6$, $138.9,138.6,138.5,135.9,133.8,132.1,128.9,128.8,128.17,128.15,127.51,127.46,127.36$, $127.2,85.8,76.2,70.7,42.7,39.2,31.4,25.3,23.8,22.7,20.99,20.95,13.8$; IR (thin film) 3027, 2927, 1604, 1453, 1065, $909 \mathrm{~cm}^{-1}$; HRMS (TOF MS ES+/Na) $m / z$ calcd for $\mathrm{C}_{40} \mathrm{H}_{48} \mathrm{O}_{2} \mathrm{SiNa}$ $(\mathrm{M}+\mathrm{Na})^{+}$611.3322, found 611.3318. Anal. Calcd for $\mathrm{C}_{40} \mathrm{H}_{48} \mathrm{O}_{2} \mathrm{Si}$ : C, 81.58; H, 8.22. Found: C, 81.31; H, 8.39. $[\alpha]^{25}{ }_{\mathrm{D}}-213.1\left(c 0.130, \mathrm{CHCl}_{3}\right)$.

(3R*, $\left.4 R^{*}, 5 S^{*}\right)$-1-Oxa-3-[(1S $\left.{ }^{*}, 2 R^{*}\right)$-2-benzyloxy-1,3-dimethylbutyl]-4-methyl-5-(3-
propenyl)-2,2-(dimesityl)silacyclopentane. To a cooled $\left(-78{ }^{\circ} \mathrm{C}\right)$ solution of acetal $\mathbf{6 a}(0.86 \mathrm{~g}$, 1.5 mmol ) in 50 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ was added allyltrimethylsilane ( $0.48 \mathrm{~mL}, 3.0 \mathrm{mmol}$ ) followed by $\mathrm{BF}_{3} \cdot \mathrm{OEt}_{2}(0.19 \mathrm{~mL}, 1.5 \mathrm{mmol})$. The solution was warmed to $0^{\circ} \mathrm{C}$ 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 $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 50 \mathrm{~mL})$. 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 ( $0.71 \mathrm{~g}, 84 \%$ ): ${ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.29(\mathrm{~m}, 5 \mathrm{H}), 6.71(\mathrm{~m}, 4 \mathrm{H}), 5.77(\mathrm{ddt}, J=17.0,10.1,6.8,1 \mathrm{H}), 4.93$ $(\mathrm{m}, 2 \mathrm{H}), 4.57(\mathrm{~s}, 2 \mathrm{H}), 3.99(\mathrm{~m}, 1 \mathrm{H}), 3.39(\mathrm{dd}, J=9.1,2.2,1 \mathrm{H}), 2.38(\mathrm{~m}, 12 \mathrm{H}), 2.20(\mathrm{~s}, 3 \mathrm{H}), 2.19(\mathrm{~s}$, $3 \mathrm{H}), 2.15(\mathrm{~m}, 4 \mathrm{H}), 1.92(\mathrm{dt}, J=14.3,7.2,1 \mathrm{H}), 1.85(\mathrm{~m}, 1 \mathrm{H}), 1.25(\mathrm{~d}, J=7.2,3 \mathrm{H}), 1.01(\mathrm{~d}, J=7.2$, $3 \mathrm{H}), 0.99(\mathrm{~d}, J=6.9,3 \mathrm{H}), 0.89(\mathrm{~d}, J=6.9,3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 139.1,138.8$, $138.4,135.9,133.6,130.8,128.2,127.4,127.3,115.8,88.9,81.4,76.0,41.5,40.4,37.2,32.8,30.1$, 22.9, 21.2, 21.0, 20.9, 16.6, 15.5, 15.1; IR (thin film) $3026,2964,1605,1453,758 \mathrm{~cm}^{-1}$; HRMS (TOF MS ES+ +Na ) $m / z$ calcd for $\mathrm{C}_{38} \mathrm{H}_{52} \mathrm{O}_{2} \mathrm{SiNa}(\mathrm{M}+\mathrm{Na})^{+} 591.3634$, found 591.3628.

## F. Oxidation of C-Si Bond


( $3 R^{*}, 4 S^{*}, 5 R^{*}, 7 S^{*}$ )-3-benzyloxy-2,4-dimethyl-dec-9-ene-5,7-diol (7a). To a mixture of $\mathrm{CsOH} \cdot \mathrm{H}_{2} \mathrm{O}(0.76 \mathrm{~g}, 4.7 \mathrm{mmol})$ in 5.2 mL of NMP was added tert-butylhydroperoxide ( 0.53 mL , $3.8 \mathrm{mmol}, 70 \%$ aqueous). A solution of $\left(3 R^{*}, 5 S^{*}\right)$-1-oxa-3-[( $\left.1 S^{*}, 2 R^{*}\right)$-2-benzyloxy-1,3-dimethylbutyl]-5-(3-propenyl)-2,2-(dimesityl)silacyclopentane ( $0.26 \mathrm{~g}, 0.47 \mathrm{mmol}$ ) in 2.9 mL of NMP was added, followed by $\mathrm{CsF}(0.37 \mathrm{~g}, 2.6 \mathrm{mmol})$. After $10 \mathrm{~h}, 15 \mathrm{~mL}$ of $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ (saturated aqueous) was added. The mixture was diluted with 100 mL of MTBE and washed with $\mathrm{H}_{2} \mathrm{O}$ (4
$\times 30 \mathrm{~mL})$ and brine $(3 \times 30 \mathrm{~mL})$. The organic layer was dried over sodium sulfate, filtered, and concentrated in vacuo. The resulting oil was purified by flash column chromatography (10:90 $\mathrm{EtOAc} /$ hexanes $)$ to yield the product as a yellow oil $(0.097 \mathrm{~g}, 69 \%)$ : ${ }^{1} \mathrm{H} \mathrm{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta$ $7.33(\mathrm{~m}, 4 \mathrm{H}), 7.26(\mathrm{~m}, 1 \mathrm{H}), 5.80(\mathrm{ddt}, J=17.4,10.4,7.2,1 \mathrm{H}), 5.10(\mathrm{~m}, 2 \mathrm{H}), 4.63(\mathrm{q}, J=11.4,2 \mathrm{H})$, $3.97(\mathrm{~m}, 1 \mathrm{H}), 3.89(\mathrm{tt}, J=8.0,4.0,1 \mathrm{H}), 3.50(\mathrm{~d}, J=4.2,1 \mathrm{H}), 3.45(\mathrm{dd}, J=7.4,2.5,1 \mathrm{H}), 2.95(\mathrm{~d}, J$ $=3.3,1 \mathrm{H}), 2.25(\mathrm{~m}, 2 \mathrm{H}), 1.94(\mathrm{dq}, J=13.6,6.8,1 \mathrm{H}), 1.87(\mathrm{~m}, 1 \mathrm{H}), 1.65(\mathrm{~m}, 2 \mathrm{H}), 1.05(\mathrm{~d}, J=6.7$, $3 \mathrm{H}), 0.91(\mathrm{~d}, J=6.8,3 \mathrm{H}), 0.85(\mathrm{~d}, J=7.0,3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 138.9,134.7$, $128.3,127.6,127.4,117.7,85.5,73.9,71.3,68.3,42.0,40.0,39.6,30.6,20.2,19.6,11.3$; IR (thin film) 3406, 3030, 2958, 1641, 1454, $1068 \mathrm{~cm}^{-1}$; HRMS $\left(\mathrm{CI}+/ \mathrm{NH}_{3}\right) \mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{19} \mathrm{H}_{31} \mathrm{O}_{3}$ $(\mathrm{M}+\mathrm{H})^{+}$307.2273, found 307.2274. Anal. Calcd for $\mathrm{C}_{19} \mathrm{H}_{30} \mathrm{O}_{3}: \mathrm{C}, 74.47$; H, 9.87. Found: C, 74.88; H, 10.02.

$\left(3 R^{*}, 4 S^{*}, 5 R^{*}, 7 S^{*}\right)$-2,4-dimethyl-dec-9-ene-3,5,7-triol (7d). From 7a: To a cooled ( $-78{ }^{\circ} \mathrm{C}$ ) flask containing $\sim 5 \mathrm{~mL}$ of condensed ammonia was added $\mathrm{Na}^{0}$ metal ( $0.015 \mathrm{~g}, 0.64 \mathrm{mmol}$ ) until the solution retained a blue color. After 10 min at $-78^{\circ} \mathrm{C}$, a solution of diol $7 \mathrm{a}(0.050 \mathrm{~g}, 0.16 \mathrm{mmol})$ in 2 mL of THF was added. If the blue color faded, more $\mathrm{Na}^{0}$ metal $(0.015 \mathrm{~g}, 0.64 \mathrm{mmol})$ was added. After 10 min at $-78^{\circ} \mathrm{C}, 5 \mathrm{~mL}$ of MeOH was added and the mixture was stirred for 30 min at -78 ${ }^{\circ} \mathrm{C}$. The mixture was warmed to $25^{\circ} \mathrm{C}$, stirred for 30 min , and partitioned between 10 mL of $\mathrm{NaH}_{2} \mathrm{PO}_{4}$ (saturated aqueous) and 20 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. The organic layer was separated and the aqueous layer was extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \times 20 \mathrm{~mL})$. 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 ( $0.035 \mathrm{~g},>99 \%$ ): ${ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 5.83$ (ddt, $J=17.4,10.4,7.0,1 \mathrm{H}$ ), $5.15(\mathrm{~m}, 2 \mathrm{H}), 4.00(\mathrm{~m}, 2 \mathrm{H}), 3.83(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 3.57(\mathrm{~d}, J=8.6,1 \mathrm{H}), 3.06(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 2.93(\mathrm{br} \mathrm{s}, 1 \mathrm{H})$, $2.30(\mathrm{t}, J=6.7,2 \mathrm{H}), 1.85(\mathrm{ddd}, J=13.7,9.9,3.0,1 \mathrm{H}), 1.69(\mathrm{~m}, 2 \mathrm{H}), 1.55(\mathrm{ddd}, J=14.3,8.0,2.3$, $1 \mathrm{H}), 1.02(\mathrm{~d}, J=6.5,3 \mathrm{H}), 0.96(\mathrm{~d}, J 7.1,3 \mathrm{H}), 0.81(\mathrm{~d}, J=6.6,3 \mathrm{H}) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)$
$\delta 134.7,118.1,77.0,72.7,68.4,41.8,40.4,39.0,31.2,19.8,18.9,10.2$; IR (thin film) 3362, 2963, 1641, 1462, $1070 \mathrm{~cm}^{-1}$; HRMS $\left(\mathrm{CI}+/ \mathrm{NH}_{3}\right) m / z$ calcd for $\mathrm{C}_{12} \mathrm{H}_{25} \mathrm{O}_{3}(\mathrm{M}+\mathrm{H})^{+}$217.1804, found 217.1800. Anal. Calcd for $\mathrm{C}_{12} \mathrm{H}_{24} \mathrm{O}_{3}$ : C, 66.63; H, 11.18. Found: C, 66.87; H, 11.20. From (3R*,5S*)-1-Oxa-3-[(1S*,2R*)-2-(tert-butyl-dimethylsiloxy)-1,3-dimethylbutyl]-5-(3-propenyl)-2,2-(dimesityl)silacyclopentane: To a mixture of $\mathrm{CsOH} \cdot \mathrm{H}_{2} \mathrm{O}(0.36 \mathrm{~g}, 2.1 \mathrm{mmol})$ in 2.3 mL of NMP was added cumene hydroperoxide ( $0.30 \mathrm{~mL}, 1.7 \mathrm{mmol}, 88 \%$ aqueous). A solution of $\left(3 R^{*}, 5 S^{*}\right)$-1-oxa-3-[(1 $\left.1 S^{*}, 2 R^{*}\right)$-2-(tert-butyl-dimethylsiloxy)-1,3-dimethylbutyl]-5-(3-propenyl)-2,2-(dimesityl)silacyclopentane $(0.12 \mathrm{~g}, 0.21 \mathrm{mmol})$ in 1.5 mL of NMP was added, followed by CsF $(0.19 \mathrm{~g}, 1.2 \mathrm{mmol})$. After 18 h , solid $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}(0.30 \mathrm{~g})$ was added and stirred for 2 h . The mixture was diluted with 20 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, filtered through a fritted glass funnel, and washed with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \times 20 \mathrm{~mL})$. The solution was concentrated in vacuo, and the remaining NMP was removed by bulb-to-bulb distillation $\left(60{ }^{\circ} \mathrm{C} / 0.1\right.$ Torr). The resulting oil was purified by flash column chromatography ( $10: 90$ to $30: 70 \mathrm{EtOAc} / \mathrm{hexanes}$ ) to yield the product as a yellow oil ( $0.036 \mathrm{~g}, 80 \%$ ): ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 5.83$ (ddt, $J=17.5,10.4,7.1,1 \mathrm{H}$ ), 5.14 (m, 2H), 3.99 (br s, 2H), 3.87 (br s, 1H), $3.56(\mathrm{~d}, J=9.2,1 \mathrm{H}), 3.11(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 2.96(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 2.30(\mathrm{t}, J=$ $6.8,2 \mathrm{H}), 1.85(\mathrm{~m}, 1 \mathrm{H}), 1.68(\mathrm{~m}, 2 \mathrm{H}), 1.56(\mathrm{~m}, 1 \mathrm{H}), 1.02(\mathrm{~d}, J=6.5,3 \mathrm{H}), 0.96$ (dd, $J=7.9,1.9,3 \mathrm{H})$, $0.82(\mathrm{~d}, J=6.7,3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 134.7,118.0,77.0,72.6,68.4,41.8,40.4$, 38.9, 31.1, 19.8, 18.9, 10.2; HRMS $\left(\mathrm{CI}+/ \mathrm{NH}_{3}\right) \mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{12} \mathrm{H}_{25} \mathrm{O}_{3}(\mathrm{M}+\mathrm{H})^{+}$217.1804, found 217.1794.

## Proof of Stereochemistry for triol 7d by chemical correlation


$\left(3 R^{*}, 4 S^{*}, 5 R^{*}, 7 S^{*}\right)$-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).

(1S,2S,3S,5R)-1-benzyloxy-2-methyl-1-phenyl-oct-7-ene-3,5-diol (7e). To a mixture of $\mathrm{CsOH} \cdot \mathrm{H}_{2} \mathrm{O}(1.6 \mathrm{~g}, 9.3 \mathrm{mmol})$ in 10 mL of NMP was added cumenehydroperoxide $(1.2 \mathrm{~mL}, 7.4$ mmol, $88 \%$ aqueous). A solution of (3S,5R)-1-Oxa-3-[(1R,2S)-2-benzyloxy-1-methyl-2-phenyl-ethyl]-5-(3-propenyl)-2,2-(dimesityl)silacyclopentane ( $0.55 \mathrm{~g}, 0.93 \mathrm{mmol}$ ) in 4.7 mL of NMP was added, followed by $\operatorname{CsF}$ ( $0.77 \mathrm{~g}, 5.1 \mathrm{mmol}$ ). After $10 \mathrm{~h}, 15 \mathrm{~mL}$ of $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ (saturated aqueous) was added and the mixture was stirred for 1 h . The mixture was diluted with 50 mL of $\mathrm{H}_{2} \mathrm{O}$ and extracted with MTBE ( $3 \times 50 \mathrm{~mL}$ ). The organic layer was washed with $\mathrm{H}_{2} \mathrm{O}(4 \times 30 \mathrm{~mL})$ and brine $(3 \times 30 \mathrm{~mL})$. 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 $(0.17 \mathrm{~g}, 53 \%)$ : ${ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.34(\mathrm{~m}, 10 \mathrm{H}), 5.82$ (ddt, $J=17.2,10.1,7.1,1 \mathrm{H}), 5.07(\mathrm{~m}, 2 \mathrm{H}), 4.99(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 4.37(\mathrm{~d}, J=11.5,1 \mathrm{H}), 4.24(\mathrm{~d}, J=9.3$, $1 \mathrm{H}), 4.20(\mathrm{~d}, J=11.5,1 \mathrm{H}), 4.02(\mathrm{~m}, 2 \mathrm{H}), 3.61(\mathrm{br} \mathrm{s}, 1 \mathrm{H}), 2.31(\mathrm{dt}, J=13.9,7.0,1 \mathrm{H}), 2.22(\mathrm{dt}, J=$ $13.4,6.7,1 \mathrm{H}), 2.11(\mathrm{~m}, 1 \mathrm{H}), 1.67(\mathrm{~m}, 2 \mathrm{H}), 0.52(\mathrm{~d}, J=6.9,3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 139.9,137.2,135.1,128.44,128.42,128.1,127.9,127.8,117.2,87.8,74.0,70.4,68.0,44.1,42.0$, 38.6, 12.9; IR (thin film) $3421,3030,2922,1641,1453,1061 \mathrm{~cm}^{-1}$; HRMS (CI+/NH ${ }_{3}$ ) $\mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{22} \mathrm{H}_{29} \mathrm{O}_{3}(\mathrm{M}+\mathrm{H})^{+}$341.2117, found 341.2109. Anal. Calcd for $\mathrm{C}_{22} \mathrm{H}_{28} \mathrm{O}_{3}: \mathrm{C}, 77.61$; $\mathrm{H}, 8.29$. Submitted. $[\alpha]^{25}{ }_{\mathrm{D}}-69.6\left(c 0.135, \mathrm{CHCl}_{3}\right)$.

( $3 R^{*}, 4 S^{*}, 5 R^{*}, 6 R^{*}, 7 S^{*}$ )-3-benzyloxy-2,4,6-trimethyl-dec-9-ene-5,7-diol (8a). To a mixture of $\mathrm{CsOH} \cdot \mathrm{H}_{2} \mathrm{O}(2.1 \mathrm{~g}, 12 \mathrm{mmol})$ in 14 mL of NMP was added tert-butylhydroperoxide ( 1.4 mL , $9.8 \mathrm{mmol}, 70 \%$ aqueous $)$. A solution of $\left(3 R^{*}, 4 R^{*}, 5 S^{*}\right)$-1-oxa-3-[( $\left.1 S^{*}, 2 R^{*}\right)$-2-benzyloxy-1,3-dimethylbutyl]-4-methyl-5-(3-propenyl)-2,2-(dimesityl)silacyclopentane ( $0.69 \mathrm{~g}, 1.2 \mathrm{mmol}$ ) in 6.2 mL of NMP was added, followed by CsF ( $1.0 \mathrm{~g}, 6.8 \mathrm{mmol}$ ). After 10 h at $70{ }^{\circ} \mathrm{C}, 15 \mathrm{~mL}$ of $\mathrm{Na}_{2} \mathrm{~S}_{2} \mathrm{O}_{3}$ (saturated aqueous) was added. The mixture was diluted with 100 mL of MTBE and
washed with $\mathrm{H}_{2} \mathrm{O}(4 \times 30 \mathrm{~mL})$ and brine $(3 \times 30 \mathrm{~mL})$. 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 , $84 \%):{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.36(\mathrm{~m}, 4 \mathrm{H}), 7.28(\mathrm{~m}, 1 \mathrm{H}), 5.80(\mathrm{~m}, 1 \mathrm{H}), 5.11(\mathrm{~m}, 2 \mathrm{H}), 4.80$ $(\mathrm{d}, J=11.5,1 \mathrm{H}), 4.65(\mathrm{~d}, J=11.6,1 \mathrm{H}), 4.02(\mathrm{~d}, J=10.1,1 \mathrm{H}), 3.68(\mathrm{dq}, J=9.2,4.6,1 \mathrm{H}), 3.45(\mathrm{dd}$, $J=8.1,1.9,1 \mathrm{H}), 3.29(\mathrm{~s}, 1 \mathrm{H}), 2.53(\mathrm{~d}, J=4.2,1 \mathrm{H}), 2.30(\mathrm{~m}, 2 \mathrm{H}), 1.92(\mathrm{~m}, 2 \mathrm{H}), 1.65(\mathrm{~m}, 1 \mathrm{H}), 1.09$ $(\mathrm{d}, J=6.6,3 \mathrm{H}), 1.01(\mathrm{~d}, J=7.1,3 \mathrm{H}), 0.91(\mathrm{~d}, J=6.8,3 \mathrm{H}), 0.77(\mathrm{~d}, J=7.0,3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR $(125$ $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 139.1,135.0,128.3,127.6,127.3,117.6,85.4,75.5,74.5,71.3,40.137 .4,37.0$, 30.7, 20.2, 20.1, 10.2, 10.1; IR (thin film) 3386, 3030, 2971, 1641, 1454, $1068 \mathrm{~cm}^{-1}$; HRMS $\left(\mathrm{CI}+/ \mathrm{NH}_{3}\right) m / z$ calcd for $\mathrm{C}_{17} \mathrm{H}_{27} \mathrm{O}_{3}\left(\mathrm{M}-\mathrm{C}_{3} \mathrm{H}_{5}\right)^{+}$279.1960, found 279.1957. Anal. Calcd for $\mathrm{C}_{20} \mathrm{H}_{32} \mathrm{O}_{3}: \mathrm{C}, 74.96 ; \mathrm{H}, 10.06$. Found: C, $75.94 ; \mathrm{H}, 9.96$.

## G. Reactions of 1,3-Diols


( $4 S^{*}, 6 R^{*}$ )-4-Allyl-6-[( $\left.1 S^{*}, 2 R^{*}\right)$-2-benzyloxy-1,3-dimethyl-butyl]-2,2-dimethyl-1,3-
dioxane. To a solution of diol $7 \mathrm{a}(0.034 \mathrm{~g}, 0.11 \mathrm{mmol})$ and 2,2-dimethoxypropane ( $1.5 \mathrm{~mL}, 12$ $\mathrm{mmol})$ in 1 mL of acetone was added CSA $(<0.005 \mathrm{~g})$. After 5 min , a few drops of $\mathrm{Et}_{3} \mathrm{~N}$ were added. The solution was concentrated in vacuo. The resulting oil was purified by flash column chromatography (hexanes to $0.5: 99.5 \mathrm{EtOAc} / \mathrm{hexanes}$ ) to yield the product as a colorless oil ( 0.034 $\mathrm{g}, 89 \%):{ }^{1} \mathrm{H} \operatorname{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.33(\mathrm{~m}, 4 \mathrm{H}), 7.25(\mathrm{~m}, 1 \mathrm{H}), 5.80(\mathrm{ddt}, J=17.1,10.8,6.8$, $1 \mathrm{H}), 5.07(\mathrm{~m}, 2 \mathrm{H}), 4.62(\mathrm{~s}, 2 \mathrm{H}), 3.84(\mathrm{dq}, J=9.2,6.3,1 \mathrm{H}), 3.77(\mathrm{ddd}, J=9.0,6.2,1 \mathrm{H}), 3.41(\mathrm{dd}, J$ $=8.1,1.9,1 \mathrm{H}), 2.30(\mathrm{dt}, J=13.8,6.9,1 \mathrm{H}), 2.19(\mathrm{dt}, J=13.7,7.0,1 \mathrm{H}), 1.89(\mathrm{dq}, J=13.6,6.8,1 \mathrm{H})$, $1.73(\mathrm{~m}, 1 \mathrm{H}), 1.63(\mathrm{~m}, 2 \mathrm{H}), 1.34(\mathrm{~s}, 3 \mathrm{H}), 1.31(\mathrm{~s}, 3 \mathrm{H}), 1.02(\mathrm{~d}, J=6.7,3 \mathrm{H}), 0.90(\mathrm{~d}, J=6.9,3 \mathrm{H})$, $0.88(\mathrm{~d}, J=7.0,3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR (125 MHz, $\left.\mathrm{CDCl}_{3}\right) \delta 139.7,134.6,128.2,127.1,127.0,116.7$, $100.2,83.6,74.2,68.1,66.3,41.4,40.2,36.9,31.6,25.2,25.1,19.8,19.7,8.9$; IR (thin film) 3067 , 2981, 1642, 1454, 1377, $1224 \mathrm{~cm}^{-1}$; HRMS $\left(\mathrm{CI}+/ \mathrm{NH}_{3}\right) \mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{21} \mathrm{H}_{31} \mathrm{O}_{3}\left(\mathrm{M}-\mathrm{CH}_{3}\right)^{+}$
331.2273, found 331.2273. Anal. Calcd for $\mathrm{C}_{22} \mathrm{H}_{34} \mathrm{O}_{3}$ : C, 76.26; H, 9.89. Found: C, 76.05; H , 9.90 .

## 1,3-Trans Diol Stereochemistry Proven by the Method of Rychnovsky ${ }^{14}$


( $\left.4 S^{*}, 6 R^{*}\right)$-4-Allyl-6-[( $1 S^{*}, 2 R^{*}$ )-2-benzyloxy-1,3-dimethyl-butyl]-2,2-dimethyl-1,3-dioxane.
$\mathrm{C}_{\mathrm{a}}: \quad \delta 25.2$
$\mathrm{C}_{\mathrm{b}}$ : $\quad \delta 25.1$
Note: $\mathrm{C}_{\mathrm{a}}$ and $\mathrm{C}_{\mathrm{b}}$ The chemical shift in the ${ }^{13} \mathrm{C}$ NMR spectrum for $\mathrm{C}_{\mathrm{a}}$ and $\mathrm{C}_{\mathrm{b}}$ were assigned by HMQC. The 1,3-cis diol results in chemical shifts of 19 and 30 ppm for the acetonide methyl groups.

(4S,5R)-4-(dimesitylsilyl)-5-hydroxymethyl-dihydro-furan-2-one. To a solution of (3S,4R)-3-(dimesitylsilyl)-4,5-O-isopropylidine-4,5-dihydroxypentanoate ( $0.24 \mathrm{~g}, 0.51 \mathrm{mmol}$ ) in 2 mL of EtOH was added 0.23 mL of concentrated HCl , and the solution was stirred for 2 h . The EtOH was removed in vacuo, and the resulting oil was diluted with 30 mL of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$. The organic layer was washed with sodium bicarbonate (saturated aqueous, $2 \times 50 \mathrm{~mL}$ ), 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 ( $0.20 \mathrm{~g},>99 \%$ ): mp 62-64 ${ }^{\circ} \mathrm{C} .{ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 6.84(\mathrm{~s}, 2 \mathrm{H}), 6.82(\mathrm{~s}, 2 \mathrm{H}), 5.19(\mathrm{~d}, J=5.2,1 \mathrm{H}), 4.45(\mathrm{ddd}, J=$ $9.2,4.1,2.4,1 \mathrm{H}), 3.63(\mathrm{ddd}, J=12.7,5.7,2.1,1 \mathrm{H}), 3.13(\mathrm{ddd}, J=11.8,7.4,4.4,1 \mathrm{H}), 2.94(\mathrm{dd}, J=$ 16.2, 7.8, 1H), 2.66 (m, 1H), 2.61 (m, 1H), $2.39(\mathrm{~s}, 6 \mathrm{H}), 2.37(\mathrm{~s}, 6 \mathrm{H}), 2.26(\mathrm{~s}, 3 \mathrm{H}), 2.25(\mathrm{~s}, 3 \mathrm{H})$, $1.72(\mathrm{~m}, 1 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.3,144.3,144.0,139.81,139.78,129.2,129.1$, 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, $1450 \mathrm{~cm}^{-1}$; HRMS $\left(\mathrm{CI}+/ \mathrm{NH}_{3}\right) m / z$ calcd for $\mathrm{C}_{23} \mathrm{H}_{34} \mathrm{NO}_{3} \mathrm{Si}\left(\mathrm{M}+\mathrm{NH}_{4}\right)^{+} 400.2308$, found
400.2318. Anal. Calcd for $\mathrm{C}_{23} \mathrm{H}_{30} \mathrm{O}_{3} \mathrm{Si}: \mathrm{C}, 72.21 ; \mathrm{H}, 7.90$. Found: C, 71.96; H, 7.90. $[\alpha]^{25}{ }_{\mathrm{D}}$ -116.8 (c 0.0950, $\mathrm{CHCl}_{3}$ ).

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

(4S,5R)-4-(dimesitylsilyl)-5-hydroxymethyl-dihydro-furan-2-one.
$\mathbf{H}_{\mathrm{a}}$ irradiated: $\mathrm{H}_{\mathrm{b}}$ (1.4\%)
$\mathbf{H}_{\mathrm{c}}$ irradiated: $\mathrm{H}_{\mathrm{d}}(1.0 \%)$
Note: There was no NOE observed between $\mathrm{H}_{\mathrm{a}}$ and $\mathrm{H}_{\mathrm{c}}$ or $\mathrm{H}_{\mathrm{b}}$ and $\mathrm{H}_{\mathrm{d}}$. (Mixing time was 0.5 s .)

(4R,6S)-4-Allyl-6-[(1S,2S)-2-benzyloxy-1-methyl-2-phenyl-ethyl]-2,2-dimethyl-1,3-
dioxane. To a solution of $7 \mathbf{e}(0.035 \mathrm{~g}, 0.10 \mathrm{mmol}), 1.2 \mathrm{~mL}$ of 2,2-dimethoxypropane, and 0.7 mL of acetone was added CSA $(<0.005 \mathrm{~g})$. After 5 min , a few drops of $\mathrm{Et}_{3} \mathrm{~N}$ 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 ( $>99 \%$ ): ${ }^{1} \mathrm{H}$ NMR ( 500 $\left.\mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.31(\mathrm{~m}, 10 \mathrm{H}), 5.77(\mathrm{ddt}, J=17.1,10.2,6.9,1 \mathrm{H}), 5.06(\mathrm{~m}, 2 \mathrm{H}), 4.39(\mathrm{~d}, J=11.8$, $1 \mathrm{H}), 4.30(\mathrm{~d}, J=7.4,1 \mathrm{H}), 4.19(\mathrm{~d}, J=11.8,1 \mathrm{H}), 3.95(\mathrm{dt}, J=9.3,6.4,1 \mathrm{H}), 3.80(\mathrm{dq}, J=9.7,6.3$, $1 \mathrm{H}), 2.26(\mathrm{~m}, 2 \mathrm{H}), 2.15(\mathrm{dt}, J=13.7,6.9,1 \mathrm{H}), 1.69(\mathrm{ddd}, J=12.7,9.4,5.8,1 \mathrm{H}), 1.39(\mathrm{~s}, 3 \mathrm{H}), 1.35$ $(\mathrm{s}, 3 \mathrm{H}$ and $\mathrm{m}, 1 \mathrm{H}), 0.67(\mathrm{~d}, J=7.0,3 \mathrm{H}) ;{ }^{13} \mathrm{C} \operatorname{NMR}\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 139.9,138.6,134.6$, $128.3,128.1,127.8,127.6,127.4,116.7,100.2,81.8,70.3,66.6,66.4,43.7,40.2,33.4,25.1,10.1$; HRMS $\left(\mathrm{CI}+/ \mathrm{NH}_{3}\right) m / z$ calcd for $\mathrm{C}_{24} \mathrm{H}_{29} \mathrm{O}_{3}\left(\mathrm{M}-\mathrm{CH}_{3}\right)^{+}$365.2117, found 365.2111. $[\alpha]^{25}{ }_{\mathrm{D}}-51.1(c$ $0.235, \mathrm{CHCl}_{3}$ ).

1,3-Trans Diol Stereochemistry Proven by the Method of Rychnovsky ${ }^{14}$

(4R,6S)-4-Allyl-6-[(1S,2S)-2-benzyloxy-1-methyl-2-phenyl-ethyl]-2,2-dimethyl-1,3-dioxane.
$\mathrm{C}_{\mathrm{a}}: \quad \delta 25.1$
$\mathrm{C}_{\mathrm{b}}$ : $\quad \delta 25.1$
Note: $\mathrm{C}_{\mathrm{a}}$ and $\mathrm{C}_{\mathrm{b}}$ have the same chemical shift in the ${ }^{13} \mathrm{C}$ 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)-1,3dioxane. A round bottom flask fitted with a Dean-Stark trap and reflux condenser was charged with $7 \mathbf{e}(0.098 \mathrm{~g}, 0.29 \mathrm{mmol})$ and 4-nitrobenzaldehyde $(0.058 \mathrm{~g}, 0.38 \mathrm{mmol})$ in 14 mL of benzene. CSA ( $<0.020 \mathrm{~g}$ ) was added and the solution was heated to reflux for 12 h . The solution was cooled to $22^{\circ} \mathrm{C}$ and a few drops of $\mathrm{Et}_{3} \mathrm{~N}$ 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 $0.5: 99.5 \mathrm{EtOAc} / \mathrm{hexanes)}$ to yield separate samples of both diastereomers as yellow oils ( $0.076 \mathrm{~g}, 54 \%$ ): Major isomer: ${ }^{1} \mathrm{H}$ NMR ( $\left.500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 8.19(\mathrm{~d}$, $J=8.8,2 \mathrm{H}), 7.61(\mathrm{~d}, J=8.7,2 \mathrm{H}), 7.34(\mathrm{~m}, 10 \mathrm{H}), 5.83(\mathrm{~m}, 1 \mathrm{H}$ and s, 1H), $5.12(\mathrm{~m}, 2 \mathrm{H}), 4.45(\mathrm{~d}, J$ $=11.8,1 \mathrm{H}), 4.39(\mathrm{~d}, J=7.5,1 \mathrm{H}), 4.31(\mathrm{dd}, J=14.8,6.6,1 \mathrm{H}), 4.23(\mathrm{~m}, 2 \mathrm{H}), 4.19(\mathrm{~d}, J=11.7,1 \mathrm{H})$, $2.82(\mathrm{dt}, J=15.2,7.6,1 \mathrm{H}), 2.38(\mathrm{dt}, J=13.1,6.5,1 \mathrm{H}), 2.06(\mathrm{dt}, J=13.0,6.0,1 \mathrm{H}), 1.41(\mathrm{~d}, J=$ $12.4,1 \mathrm{H}), 0.76(\mathrm{~d}, J=7.0,3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 148.0,145.8,139.6,138.3,134.4$, $128.3,127.9,127.8,127.7,127.6,127.1,123.4,117.4,92.8,81.1,72.5,72.2,70.4,43.6,35.2,28.1$, 10.2; IR (thin film) 3064, 2930, 1607, 1522, 1454, $1347 \mathrm{~cm}^{-1}$; HRMS (TOF MS ES+/Na) $m / z$
calcd for $\mathrm{C}_{29} \mathrm{H}_{31} \mathrm{NO}_{5} \mathrm{Na}(\mathrm{M}+\mathrm{Na})^{+}$496.2100, found 496.2109. $[\alpha]_{\mathrm{D}}^{25} 1.0\left(c 0.10, \mathrm{CHCl}_{3}\right)$. Minor isomer: ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 8.15(\mathrm{~d}, J=8.8,2 \mathrm{H}), 7.37(\mathrm{~d}, J=8.7,2 \mathrm{H}), 7.34(\mathrm{~m}, 4 \mathrm{H})$, $7.29(\mathrm{~m}, 5 \mathrm{H}), 7.23(\mathrm{~m}, 1 \mathrm{H}), 5.84$ (ddt, $J=17.2,10.2,7.0,1 \mathrm{H}), 5.73(\mathrm{~s}, 1 \mathrm{H}), 5.12(\mathrm{~m}, 2 \mathrm{H}), 4.78(\mathrm{~d}, J$ $=3.8,1 \mathrm{H}), 4.64(\mathrm{~d}, J=12.4,1 \mathrm{H}), 4.25(\mathrm{~d}, J=12.4,1 \mathrm{H}), 4.04(\mathrm{dtd}, J=12.1,6.4,2.3,1 \mathrm{H}), 3.65(\mathrm{dd}$, $J=11.3,5.4,1 \mathrm{H}), 2.94(\mathrm{~m}, 1 \mathrm{H}), 2.41(\mathrm{dt}, J=13.7,6.6,1 \mathrm{H}), 2.26(\mathrm{dt}, J=13.8,6.9,1 \mathrm{H}), 1.78$ (ddd, $J=14.0,11.6,6.1,1 \mathrm{H}), 1.64(\mathrm{~d}, J=13.7,1 \mathrm{H}), 0.81(\mathrm{~d}, J=6.8,3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 147.9,145.5,138.5,137.4,133.5,128.4,128.1,128.0,127.8,127.63,127.55,127.1,123.3,117.7$, 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 $\mathrm{cm}^{-1}$; HRMS (TOF MS ES+/Na) $m / z$ calcd for $\mathrm{C}_{29} \mathrm{H}_{31} \mathrm{NO}_{5} \mathrm{Na}(\mathrm{M}+\mathrm{Na})^{+}$496.2100, found 496.2118. $[\alpha]^{25}{ }_{\mathrm{D}}-0.66\left(c 0.305, \mathrm{CHCl}_{3}\right)$.

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


( $2 R, 4 R^{*}, 6 S^{*}$ )-4-Allyl-6-[(1S*, $\left.2 S^{*}\right)$-2-benzyloxy-1-methyl-2-phenyl-ethyl)-2-(4-nitro-phenyl)-1,3-dioxane
$\mathbf{H}_{\mathrm{b}}$ irradiated:
$\mathrm{H}_{\mathrm{c}}(5.1 \%)$
$\mathrm{H}_{\mathrm{a}}(3.9 \%)$
$\mathbf{H}_{\mathrm{e}}$ irradiated:
$\mathrm{H}_{\mathrm{d}}(6.8 \%)$
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 )

(2S,4R,6S)-4-Allyl-6-[(1S,2S)-2-benzyloxy-1-methyl-2-phenyl-ethyl]-2-(4-nitro-phenyl)-1,3-dioxane. $\mathbf{H}_{\mathrm{a}}$ irradiated:
$\mathbf{H}_{\mathrm{d}}$ irradiated:
$\mathrm{H}_{\mathrm{b}}$ (1.3\%)
$\mathrm{H}_{\mathrm{b}}$, (3.0\%)
$\mathrm{H}_{\mathrm{c}}$ (4.8\%)
$-\quad \mathrm{H}_{\mathrm{f}}(0.9 \%)$
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 $\mathrm{H}_{\mathrm{e}}$ and $\mathrm{H}_{\mathrm{d}}$. If the other 1,3trans 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 .)

$\left(2 R^{*}, 4 S^{*}, 5 R^{*}, 6 R^{*}\right)-4$-Allyl-6-[( $\left.1 S^{*}, 2 R^{*}\right)$-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 $8 \mathrm{a}(0.050 \mathrm{~g}, 0.16 \mathrm{mmol})$ and 4-nitrobenzaldehyde $(0.032 \mathrm{~g}, 0.21$ $\mathrm{mmol})$ in 8 mL of benzene. CSA $(<0.005 \mathrm{~g})$ was added and the solution was heated to reflux for 12 h . After the solution was cooled to $22^{\circ} \mathrm{C}$, a few drops of $\mathrm{Et}_{3} \mathrm{~N}$ 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 ( $0.063 \mathrm{~g}, 86 \%$ ): ${ }^{1} \mathrm{H}$ NMR ( 500 MHz , $\left.\mathrm{CDCl}_{3}\right) \delta 8.21(\mathrm{~d}, J=8.6,2 \mathrm{H}), 7.57(\mathrm{~d}, J=8.8,2 \mathrm{H}), 7.33(\mathrm{~m}, 4 \mathrm{H}), 7.28(\mathrm{~m}, 1 \mathrm{H}), 5.78(\mathrm{ddt}, J=$ $17.1,10.2,6.9,1 \mathrm{H}), 5.30(\mathrm{~s}, 1 \mathrm{H}), 5.08(\mathrm{~m}, 2 \mathrm{H}), 4.82(\mathrm{~d}, J=12.2,1 \mathrm{H}), 4.42(\mathrm{~d}, J=12.2,1 \mathrm{H}), 3.92$ (br t, $J=7.8,1 \mathrm{H}), 3.86(\mathrm{dd}, J=10.1,2.0,1 \mathrm{H}), 3.45(\mathrm{dd}, J=9.2,2.5,1 \mathrm{H}), 2.62(\mathrm{dt}, J=15.1,7.5$, $1 \mathrm{H}), 2.31(\mathrm{dt}, J=14.1,7.0,1 \mathrm{H}), 1.93(\mathrm{~m}, 2 \mathrm{H}), 1.58(\mathrm{~m}, 1 \mathrm{H}), 1.15(\mathrm{~d}, J=7.0,3 \mathrm{H}), 1.10(\mathrm{~d}, J=6.6$,
$3 \mathrm{H}), 0.87(\mathrm{~d}, J=6.3,3 \mathrm{H}), 0.83(\mathrm{~d}, J=6.9,3 \mathrm{H}) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 148.0,145.9$, 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) $3067,2973,1609,1524,1348,1104 \mathrm{~cm}^{-1} ;$ HRMS $\left(\mathrm{CI}+/ \mathrm{NH}_{3}\right) m / z$ calcd for $\mathrm{C}_{27} \mathrm{H}_{34} \mathrm{NO}_{5}(\mathrm{M}-\mathrm{H})^{+}$452.2437, found 452.2442. Anal. Calcd for $\mathrm{C}_{27} \mathrm{H}_{35} \mathrm{NO}_{5}: \mathrm{C}, 71.50 ; \mathrm{H}, 7.78$. Submitted.

Proof of Stereochemistry by Coupling Constant Anaylsis

( $2 R^{*}, 4 S^{*}, 5 R^{*}, 6 R^{*}$ )-4-Allyl-6-[( $\left.1 S^{*}, 2 R^{*}\right)$-2-benzyloxy-1,3-dimethyl-
butyl]-2-(4-nitro-phenyl)-5-methyl-1,3-dioxane.
$\mathbf{H}_{\mathrm{a}}$ : dd, $J=10.1$ (axial, $\mathrm{ax}_{\mathrm{a}}-\mathrm{ax}_{\mathrm{b}}$ ), 2.0 (coupling to H on $\mathrm{C}-2$ )
$\mathbf{H}_{\mathrm{b}}$ : m
$\mathbf{H}_{\mathrm{c}}: \quad$ br $\mathrm{t}, J=7.8\left(\mathrm{eq}_{\mathrm{c}}-\mathrm{ax}_{\mathrm{b}}, \mathrm{eq}_{\mathrm{c}}-\mathrm{CH}_{2} \mathrm{CHCH}_{2}\right)$
Note: If the stereochemistry at C-5 was $S$ configuration, The $\mathrm{J}_{\mathrm{Ha}-\mathrm{Hb}}$ should be small.

## H. One flask Formation of Oxasilacyclopentane Acetal


(3R,4S)-1-Oxa-3,4-dimethyl-5-ethoxy-2,2-di(mesityl)silacyclopentane (6f). To a cooled $\left(-78^{\circ} \mathrm{C}\right)$ solution of $\mathrm{Me}_{2} \mathrm{Zn}(0.12 \mathrm{~mL}, 0.24 \mathrm{mmol}, 2.0 \mathrm{M}$ in toluene) in 1.6 mL of THF was added a cooled $\left(0^{\circ} \mathrm{C}\right)$ solution of silyllithium $4(0.10 \mathrm{~g}, 0.24 \mathrm{mmol})$ in 0.25 mL of THF. The solution was warmed to $0^{\circ} \mathrm{C}$ for 5 min and then re-cooled to $-78^{\circ} \mathrm{C}$. In a separate flask, MeLi $(0.020 \mathrm{~mL}$, $0.024 \mathrm{mmol}, 1.2 \mathrm{M}$ in $\left.\mathrm{Et}_{2} \mathrm{O}\right)$ was added to a cooled $\left(-78{ }^{\circ} \mathrm{C}\right)$ slurry of $\mathrm{CuCN}(0.001 \mathrm{~g}, 0.012$ mmol ) in 0.3 mL of THF. The slurry was warmed to $-30^{\circ} \mathrm{C}$, stirred for 5 min , cooled to $-78{ }^{\circ} \mathrm{C}$, and stirred for 5 min . The resulting solution was added to the reaction solution and stirred at -78 ${ }^{\circ} \mathrm{C}$ for 10 min . To the reaction solution was added a cooled $\left(-78{ }^{\circ} \mathrm{C}\right)$ solution of ethyl transcrotonate $(0.026 \mathrm{~g}, 0.23 \mathrm{mmol})$ in 0.2 mL of THF. After 5 min at $-78{ }^{\circ} \mathrm{C}, \mathrm{CH}_{3} \mathrm{I}(0.088 \mathrm{~mL}, 1.4$ mmol ) was added, and the mixture was warmed to $22^{\circ} \mathrm{C}$ for 12 h . The mixture was cooled to $0{ }^{\circ} \mathrm{C}$,
$n-\mathrm{Bu}_{4} \mathrm{NF}\left(0.24 \mathrm{~mL}, 0.24 \mathrm{mmol}, 1.0 \mathrm{M}\right.$ in THF) was added, and the mixture was warmed to $22{ }^{\circ} \mathrm{C}$ for 1 h . 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 $\mathrm{Et}_{2} \mathrm{O}(3 \times 25 \mathrm{~mL})$. The combined organic layers were dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated in vacuo to give the product as a $70: 30$ mixture of diastereomers as determined by ${ }^{1} \mathrm{H}$ NMR spectroscopy. The resulting oil was purified by flash column chromatography (hexanes to $1: 99 \mathrm{EtOAc} / \mathrm{hexanes}$ ) to give the product as a pale yellow oil ( $0.072 \mathrm{~g}, 79 \%$ ): ${ }^{1} \mathrm{H}$ NMR ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) major isomer $\delta$ $6.79(\mathrm{~s}, 2 \mathrm{H}), 6.73(\mathrm{~s}, 2 \mathrm{H}), 4.64(\mathrm{~d}, J=7.9,1 \mathrm{H}), 3.94(\mathrm{dq}, J=9.7,7.1,1 \mathrm{H}), 3.53(\mathrm{dq}, J=9.7,7.0$, $1 \mathrm{H}), 2.44(\mathrm{~s}, 6 \mathrm{H}), 2.39(\mathrm{~s}, 6 \mathrm{H}), 2.23(\mathrm{~s}, 3 \mathrm{H}), 2.22(\mathrm{~s}, 3 \mathrm{H}), 1.70(\mathrm{~m}, 1 \mathrm{H}), 1.42(\mathrm{~m}, 1 \mathrm{H}), 1.23(\mathrm{t}, J=$ $7.1,3 \mathrm{H}), 1.07(\mathrm{~d}, J=6.8,6 \mathrm{H})$; minor isomer, characteristic peaks: $\delta 5.04(\mathrm{~d}, J=3.2,0.15 \mathrm{H}), 3.44$ $(\mathrm{dq}, J=9.5,7.1,0.16 \mathrm{H}), 3.28(\mathrm{dq}, J=9.7,6.9,0.13 \mathrm{H}), 2.41(\mathrm{~s}, 1.2 \mathrm{H}), 2.30(\mathrm{~s}, 1.1 \mathrm{H}), 1.75(\mathrm{~m}$, $0.36 \mathrm{H}), 0.88(\mathrm{~m}, 1.3 \mathrm{H})$; major product: ${ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 144.6,143.6,139.2,139.0$, 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: $\delta 144.1,143.4,138.7,138.6,133.3,129.3,128.4,102.8,62.0,45.5$, 29.7, 26.3, 23.6, 23.3, 14.9, 13.8, 12.0; HRMS $\left(\mathrm{CI}+/ \mathrm{NH}_{3}\right) \mathrm{m} / \mathrm{z}$ calcd for $\mathrm{C}_{25} \mathrm{H}_{36} \mathrm{O}_{2} \mathrm{Si}$ submitted. Characterization data for material obtained from three separate steps: HRMS (EI-GCMS) $m / z$ calcd for $\mathrm{C}_{25} \mathrm{H}_{35} \mathrm{O}_{2} \mathrm{Si}(\mathrm{M}-\mathrm{H})^{+}$395.2405, major anomer: found 395.2408; minor anomer: found 395.2418. Anal. Calcd for $\mathrm{C}_{25} \mathrm{H}_{36} \mathrm{O}_{2} \mathrm{Si}: \mathrm{C}, 75.70 ; \mathrm{H}, 9.15$. Found: C, 75.53; H, 9.18.

## I. X-Ray Crystallographic Data



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

A colorless crystal of approximate dimensions $0.17 \times 0.26 \times 0.37 \mathrm{~mm}$ was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART ${ }^{1}$ program package was used to determine the unit-cell parameters and for data collection ( $25 \mathrm{sec} / \mathrm{frame}$ scan time for a sphere of diffraction data). The raw frame data was processed using SAINT ${ }^{2}$ and SADABS $^{3}$ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL ${ }^{4}$ program. The diffraction symmetry was $2 / m$ and the systematic absences were consistent with the monoclinic space groups $C 2, C m$ or $C 2 / m$. It was later determined that the noncentrosymmetric space group $C 2$ was correct.

The structure was solved by direct methods and refined on $\mathrm{F}^{2}$ by full-matrix least-squares techniques. The analytical scattering factors ${ }^{5}$ for neutral atoms were used throughout the analysis. Hydrogen atoms were located from a difference-Fourier map and refined ( $\mathrm{x}, \mathrm{y}, \mathrm{z}$ and $\mathrm{U}_{\text {iso }}$ ) 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, $w R 2=0.2052$ and Goof $=1.072$ for 247 variables refined against 4782 data. As a comparison for refinement on $\mathrm{F}, \mathrm{R} 1=0.0629$ for those 4092 data with $\mathrm{I}>2.0 \sigma(\mathrm{I})$. The absolute structure could not be assigned by inversion of the model or by refinement of the Flack parameter ${ }^{6}$.



Table 1. Crystal data and structure refinement for ( $\mathbf{2}^{\prime} \mathbf{R}^{*}, \mathbf{3}^{\prime} \mathbf{S}^{*}, \mathbf{4} S^{*}$ )-4-Benzyl-3-(3'-hydroxy-2'-methyl-3'-phenyl-propionyl)-oxazolidin-2-one.

Identification code
Empirical formula
Formula weight
Temperature
Wavelength
Crystal system
kaw30
$\mathrm{C}_{20} \mathrm{H}_{21} \mathrm{~N} \mathrm{O}_{4} \_\left(\mathrm{C}_{6} \mathrm{H}_{14}\right)$
382.46

173(2) K
$0.71073 \AA$
Monoclinic

Space group
Unit cell dimensions

Volume
Z
Density (calculated)
Absorption coefficient F(000)
Crystal size
Theta range for data collection
Index ranges
Reflections collected
Independent reflections
Completeness to theta $=28.27^{\circ}$
Absorption correction
Max. and min. transmission
Refinement method
Data / restraints / parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices [I > 2sigma(I)]
R indices (all data)
Absolute structure parameter
Extinction coefficient
Largest diff. peak and hole

C2
$\mathrm{a}=25.012(6) \AA \quad \alpha=90^{\circ}$.
$b=5.5115(13) \AA \quad \beta=106.141(4)^{\circ}$.
$\mathrm{c}=15.991(4) \AA$
$\gamma=90^{\circ}$.
2117.5(8) $\AA^{3}$

4
$1.200 \mathrm{Mg} / \mathrm{m}^{3}$
$0.082 \mathrm{~mm}^{-1}$
820
$0.37 \times 0.26 \times 0.17 \mathrm{~mm}^{3}$
1.84 to $28.27^{\circ}$.
$-33 \leq h \leq 32,-7 \leq k \leq 7,-21 \leq l \leq 21$
11335
$4782[\mathrm{R}(\mathrm{int})=0.0286]$
97.2\%

None
0.9863 and 0.9705

Full-matrix least-squares on $\mathrm{F}^{2}$
4782 / 2 / 247
1.072
$\mathrm{R} 1=0.0629, \mathrm{wR} 2=0.1926$
$\mathrm{R} 1=0.0739, \mathrm{wR} 2=0.2052$
-0.2(16)
0.0027 (17)
0.945 and -0.227 e. $\AA^{-3}$

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

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :--- | ---: | ---: | ---: | :--- |
| $\mathrm{N}(1)$ | $3486(1)$ | $8655(4)$ | $5213(1)$ | $27(1)$ |
| $\mathrm{O}(1)$ | $2657(1)$ | $9993(4)$ | $5267(1)$ | $34(1)$ |
| $\mathrm{O}(2)$ | $2765(1)$ | $9353(4)$ | $3941(1)$ | $31(1)$ |
| $\mathrm{O}(3)$ | $4322(1)$ | $6884(5)$ | $5493(1)$ | $41(1)$ |
| $\mathrm{O}(4)$ | $4613(1)$ | $9674(4)$ | $4082(1)$ | $36(1)$ |
| $\mathrm{C}(1)$ | $3565(1)$ | $9117(5)$ | $6142(2)$ | $28(1)$ |
| $\mathrm{C}(2)$ | $2962(1)$ | $9433(6)$ | $61618)$ | $33(1)$ |
| $\mathrm{C}(3)$ | $2950(1)$ | $9324(5)$ | $4718(2)$ | $28(1)$ |
| $\mathrm{C}(4)$ | $3907(1)$ | $7526(6)$ | $4933(2)$ | $30(1)$ |
| $\mathrm{C}(5)$ | $3824(1)$ | $7085(5)$ | $3974(2)$ | $28(1)$ |
| $\mathrm{C}(6)$ | $4391(1)$ | $7333(5)$ | $3780(2)$ | $28(1)$ |
| $\mathrm{C}(7)$ | $4329(1)$ | $7072(5)$ | $2813(2)$ | $30(1)$ |
| $\mathrm{C}(8)$ | $4036(1)$ | $8813(6)$ | $2234(2)$ | $37(1)$ |
| $\mathrm{C}(9)$ | $3982(1)$ | $8605(7)$ | $1346(2)$ | $43(1)$ |
| $\mathrm{C}(10)$ | $4223(1)$ | $6689(7)$ | $1034(2)$ | $45(1)$ |
| $\mathrm{C}(11)$ | $4522(2)$ | $4959(7)$ | $1608(2)$ | $47(1)$ |
| $\mathrm{C}(12)$ | $4573(1)$ | $5147(6)$ | $2499(2)$ | $37(1)$ |
| $\mathrm{C}(13)$ | $3924(1)$ | $11386(6)$ | $6455(2)$ | $38(1)$ |
| $\mathrm{C}(14)$ | $4039(1)$ | $11617(6)$ | $7430(2)$ | $35(1)$ |
| $\mathrm{C}(15)$ | $4393(1)$ | $9980(7)$ | $7975(2)$ | $41(1)$ |
| $\mathrm{C}(16)$ | $4484(1)$ | $10095(7)$ | $8873(2)$ | $46(1)$ |
| $\mathrm{C}(17)$ | $4230(2)$ | $11849(8)$ | $9239(2)$ | $48(1)$ |
| $\mathrm{C}(18)$ | $3875(2)$ | $13488(7)$ | $8702(2)$ | $49(1)$ |
| $\mathrm{C}(19)$ | $3779(2)$ | $13376(6)$ | $7803(2)$ | $44(1)$ |
| $\mathrm{C}(20)$ | $3578(1)$ | $4554(6)$ | $3750(2)$ | $39(1)$ |
| $\mathrm{C}(21)$ | $2672(2)$ | $8690(12)$ | $8254(4)$ | $75(1)$ |
| $\mathrm{C}(22)$ | $2446(2)$ | $8751(13)$ | $9052(4)$ | $79(2)$ |
| $\mathrm{C}(23)$ | $2600(4)$ | $6310(20)$ | $9603(7)$ | $86(3)$ |
| $\mathrm{C}(24)$ | $2607(4)$ | $11189(19)$ | $9562(6)$ | $80(2)$ |
|  |  |  |  |  |

Table 3. Bond lengths $[\AA]$ and angles $\left[{ }^{\circ}\right]$ for $\left(\mathbf{2}^{\prime} \mathbf{R}^{*}, \mathbf{3}^{\prime} S^{*}, \mathbf{4} S^{*}\right)$-4-Benzyl-3-(3'-hydroxy-2'-methyl-3'-phenyl-propionyl)-oxazolidin-2-one.

| $\mathrm{N}(1)-\mathrm{C}(4)$ | $1.399(3)$ |
| :--- | :--- |
| $\mathrm{N}(1)-\mathrm{C}(3)$ | $1.404(3)$ |
| $\mathrm{N}(1)-\mathrm{C}(1)$ | $1.465(3)$ |
| $\mathrm{O}(1)-\mathrm{C}(3)$ | $1.341(3)$ |
| $\mathrm{O}(1)-\mathrm{C}(2)$ | $1.455(3)$ |
| $\mathrm{O}(2)-\mathrm{C}(3)$ | $1.199(3)$ |
| $\mathrm{O}(3)-\mathrm{C}(4)$ | $1.220(3)$ |
| $\mathrm{O}(4)-\mathrm{C}(6)$ | $1.434(4)$ |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | $1.526(3)$ |
| $\mathrm{C}(1)-\mathrm{C}(13)$ | $1.539(4)$ |
| $\mathrm{C}(4)-\mathrm{C}(5)$ | $1.510(3)$ |
| $\mathrm{C}(5)-\mathrm{C}(20)$ | $1.527(4)$ |
| $\mathrm{C}(5)-\mathrm{C}(6)$ | $1.538(3)$ |
| $\mathrm{C}(6)-\mathrm{C}(7)$ | $1.517(3)$ |
| $\mathrm{C}(7)-\mathrm{C}(12)$ | $1.387(4)$ |
| $\mathrm{C}(7)-\mathrm{C}(8)$ | $1.392(4)$ |
| $\mathrm{C}(8)-\mathrm{C}(9)$ | $1.393(4)$ |
| $\mathrm{C}(9)-\mathrm{C}(10)$ | $1.377(5)$ |
| $\mathrm{C}(10)-\mathrm{C}(11)$ | $1.389(5)$ |
| $\mathrm{C}(11)-\mathrm{C}(12)$ | $1.397(4)$ |
| $\mathrm{C}(13)-\mathrm{C}(14)$ | $1.509(3)$ |
| $\mathrm{C}(14)-\mathrm{C}(15)$ | $1.389(5)$ |
| $\mathrm{C}(14)-\mathrm{C}(19)$ | $1.390(5)$ |
| $\mathrm{C}(15)-\mathrm{C}(16)$ | $1.392(4)$ |
| $\mathrm{C}(16)-\mathrm{C}(17)$ | $1.374(5)$ |
| $\mathrm{C}(17)-\mathrm{C}(18)$ | $1.385(6)$ |
| $\mathrm{C}(18)-\mathrm{C}(19)$ | $1.391(4)$ |
| $\mathrm{C}(21)-\mathrm{C}(22)$ | $1.534(8)$ |
| $\mathrm{C}(22)-\mathrm{C}(24)$ | $1.566(12)$ |
| $\mathrm{C}(22)-\mathrm{C}(23)$ | $1.597(13)$ |
| $\mathrm{C}(23)-\mathrm{C}(24) \# 1$ | $1.562(12)$ |
| $\mathrm{C}(24)-\mathrm{C}(23) \# 2$ | $1.562(12)$ |
|  |  |


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

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

Table 4. Anisotropic displacement parameters $\left(\AA^{2} \mathrm{x} 10^{3}\right)$ for ( $\mathbf{2}^{\mathbf{\prime}} \mathbf{R}^{*}, \mathbf{3}^{\prime} \mathbf{S}^{*}, \mathbf{4} \mathbf{S}^{*}$ )-4-Benzyl-3-(3'-hydroxy-2'-methyl-3'-phenyl-propionyl)-oxazolidin-2-one. The anisotropic displacement factor exponent takes the form: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathrm{~N}(1)$ | $23(1)$ | $36(1)$ | $21(1)$ | $-2(1)$ | $6(1)$ | $-1(1)$ |
| $\mathrm{O}(1)$ | $28(1)$ | $47(1)$ | $28(1)$ | $-4(1)$ | $9(1)$ | $6(1)$ |
| $\mathrm{O}(2)$ | $27(1)$ | $39(1)$ | $25(1)$ | $0(1)$ | $4(1)$ | $4(1)$ |
| $\mathrm{O}(3)$ | $26(1)$ | $72(2)$ | $26(1)$ | $4(1)$ | $6(1)$ | $10(1)$ |
| $\mathrm{O}(4)$ | $31(1)$ | $49(1)$ | $28(1)$ | $-7(1)$ | $7(1)$ | $-7(1)$ |
| $\mathrm{C}(1)$ | $28(1)$ | $35(1)$ | $20(1)$ | $-1(1)$ | $8(1)$ | $-4(1)$ |
| $\mathrm{C}(2)$ | $32(1)$ | $45(2)$ | $23(1)$ | $0(1)$ | $10(1)$ | $1(1)$ |
| $\mathrm{C}(3)$ | $26(1)$ | $32(1)$ | $28(1)$ | $1(1)$ | $10(1)$ | $2(1)$ |
| $\mathrm{C}(4)$ | $23(1)$ | $41(2)$ | $25(1)$ | $-1(1)$ | $7(1)$ | $-1(1)$ |
| $\mathrm{C}(5)$ | $23(1)$ | $40(2)$ | $22(1)$ | $-2(1)$ | $8(1)$ | $2(1)$ |
| $\mathrm{C}(6)$ | $25(1)$ | $38(1)$ | $24(1)$ | $-1(1)$ | $8(1)$ | $0(1)$ |
| $\mathrm{C}(7)$ | $28(1)$ | $38(2)$ | $25(1)$ | $-2(1)$ | $10(1)$ | $-2(1)$ |
| $\mathrm{C}(8)$ | $42(2)$ | $43(2)$ | $29(1)$ | $0(1)$ | $13(1)$ | $5(1)$ |
| $\mathrm{C}(9)$ | $51(2)$ | $47(2)$ | $30(1)$ | $5(1)$ | $9(1)$ | $2(1)$ |
| $\mathrm{C}(10)$ | $57(2)$ | $56(2)$ | $26(1)$ | $-10(1)$ | $15(1)$ | $-9(2)$ |
| $\mathrm{C}(11)$ | $55(2)$ | $50(2)$ | $40(2)$ | $-13(2)$ | $21(1)$ | $2(2)$ |
| $\mathrm{C}(12)$ | $40(2)$ | $39(2)$ | $34(2)$ | $-4(1)$ | $13(1)$ | $3(1)$ |
| $\mathrm{C}(13)$ | $49(2)$ | $42(2)$ | $23(1)$ | $-3(1)$ | $11(1)$ | $-15(1)$ |
| $\mathrm{C}(14)$ | $38(1)$ | $44(2)$ | $24(1)$ | $-6(1)$ | $11(1)$ | $-15(1)$ |
| $\mathrm{C}(15)$ | $35(1)$ | $59(2)$ | $29(1)$ | $-10(1)$ | $8(1)$ | $-4(1)$ |
| $\mathrm{C}(16)$ | $43(2)$ | $64(2)$ | $26(1)$ | $-3(1)$ | $1(1)$ | $-2(2)$ |
| $\mathrm{C}(17)$ | $58(2)$ | $61(2)$ | $24(1)$ | $-6(2)$ | $11(1)$ | $-10(2)$ |
| $\mathrm{C}(18)$ | $68(2)$ | $47(2)$ | $36(2)$ | $-8(2)$ | $21(2)$ | $1(2)$ |
| $\mathrm{C}(19)$ | $59(2)$ | $38(2)$ | $34(2)$ | $-3(1)$ | $10(1)$ | $-4(1)$ |
| $\mathrm{C}(20)$ | $34(1)$ | $45(2)$ | $42(2)$ | $-9(1)$ | $16(1)$ | $-8(1)$ |
|  |  |  |  |  |  |  |

Table 5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for ( $\mathbf{2}^{\prime} \mathbf{R}^{*}, 3^{\prime} S^{*}, 4 S^{*}$ )-4-Benzyl-3-(3'-hydroxy-2'-methyl-3'-phenyl-propionyl)-oxazolidin-2-one.

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

Table 6. Torsion angles [ ${ }^{\circ}$ ] for $\left(\mathbf{2}^{\prime} \mathbf{R}^{*}, \mathbf{3}^{\prime} \mathbf{S}^{*}, \mathbf{4} \mathbf{S}^{*}\right)$-4-Benzyl-3-(3'-hydroxy-2'-methyl-3'-phenyl-propionyl)-oxazolidin-2-one.

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


| C(4)-C(5)-C(6)-O(4) | $-55.3(3)$ |
| :--- | :---: |
| $\mathrm{C}(20)-\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{O}(4)$ | $-174.8(2)$ |
| $\mathrm{C}(4)-\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(7)$ | $-176.3(2)$ |
| $\mathrm{C}(20)-\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(7)$ | $64.2(3)$ |
| $\mathrm{O}(4)-\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(12)$ | $125.1(3)$ |
| $\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(12)$ | $-115.5(3)$ |
| $\mathrm{O}(4)-\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)$ | $-53.2(3)$ |
| $\mathrm{C}(5)-\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)$ | $66.2(3)$ |
| $\mathrm{C}(12)-\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{C}(9)$ | $1.0(4)$ |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{C}(9)$ | $-0.8(3)$ |
| $\mathrm{C}(7)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10)$ | $0.0(5)$ |
| $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)$ | $0.5(5)$ |
| $\mathrm{C}(9)-\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{C}(12)$ | $-0.4(4)$ |
| $\mathrm{C}(8)-\mathrm{C}(7)-\mathrm{C}(12)-\mathrm{C}(11)$ | $-178.7(3)$ |
| $\mathrm{C}(6)-\mathrm{C}(7)-\mathrm{C}(12)-\mathrm{C}(11)$ | $-0.4(5)$ |
| $\mathrm{C}(10)-\mathrm{C}(11)-\mathrm{C}(12)-\mathrm{C}(7)$ | $-174.3(2)$ |
| $\mathrm{N}(1)-\mathrm{C}(1)-\mathrm{C}(13)-\mathrm{C}(14)$ | $73.1(3)$ |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(13)-\mathrm{C}(14)$ | $70.2(3)$ |
| $\mathrm{C}(1)-\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{C}(15)$ | $-106.8(3)$ |
| $\mathrm{C}(1)-\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{C}(19)$ | $0.1(5)$ |
| $\mathrm{C}(19)-\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(16)$ | $-177.0(3)$ |
| $\mathrm{C}(13)-\mathrm{C}(144)-\mathrm{C}(15)-\mathrm{C}(16)$ | $-0.7(5)$ |
| $\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{C}(17)$ | $0.8(5)$ |
| $\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(18)$ | $-0.4(6)$ |
| $\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(19)$ | $0.3(5)$ |
| $\mathrm{C}(15)-\mathrm{C}(14)-\mathrm{C}(19)-\mathrm{C}(18)$ | $177.4(3)$ |
| $\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{C}(19)-\mathrm{C}(18)$ | $-0.1(5)$ |
| $\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(14)$ | $179.4(6)$ |
| $\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{C}(23)-\mathrm{C}(24) \# 1$ | $51.9(10)$ |
| $\mathrm{C}(24)-\mathrm{C}(22)-\mathrm{C}(23)-\mathrm{C}(24) \# 1$ | $-58.3(6)$ |
| $\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{C}(24)-\mathrm{C}(23) \# 2$ | $-50.7(10)$ |
| $\mathrm{C}(23)-\mathrm{C}(22)-\mathrm{C}(24)-\mathrm{C}(23) \# 2$ |  |

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.
2. 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:

$\mathrm{wR} 2=\left[\Sigma\left[\mathrm{w}\left(\mathrm{F}_{\mathrm{o}}{ }^{2}-\mathrm{F}_{\mathrm{o}}{ }^{2}\right)^{2}\right] / \Sigma\left[\mathrm{w}\left(\mathrm{F}_{\mathrm{o}}{ }^{2}\right)^{2}\right]^{1 / 2}\right.$
$\mathrm{R} 1=\Sigma| | \mathrm{F}_{\mathrm{o}}\left|-\left|\mathrm{F}_{\mathrm{c}}\right|\right| / \Sigma\left|\mathrm{F}_{\mathrm{o}}\right|$
Goof $=\mathrm{S}=\left[\Sigma\left[\mathrm{w}\left(\mathrm{F}_{\mathrm{o}}^{2}-\mathrm{F}_{\mathrm{c}}{ }^{2}\right)^{2}\right] /(\mathrm{n}-\mathrm{p})\right]^{1 / 2}$ 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 $0.11 \times 0.28 \times 0.31 \mathrm{~mm}$ was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART ${ }^{1}$ program package was used to determine the unit-cell parameters and for data collection ( $25 \mathrm{sec} / \mathrm{frame}$ scan time for a sphere of diffraction data). The raw frame data was processed using SAINT ${ }^{2}$ and SADABS $^{3}$ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL ${ }^{4}$ program. The diffraction symmetry was $2 / m$ and the systematic absences were consistent with the centrosymmetric monoclinic space group $P 2_{1} / n$ which was later determined to be correct.

The structure was solved by direct methods and refined on $\mathrm{F}^{2}$ by full-matrix least-squares techniques. The analytical scattering factors ${ }^{5}$ for neutral atoms were used throughout the analysis. Hydrogen atoms were either located from a difference-Fourier map and refined ( $\mathrm{x}, \mathrm{y}, \mathrm{z}$ and $\mathrm{U}_{\mathrm{iso}}$ ) or were included using a riding model. At convergence, $\mathrm{wR} 2=0.1367$ and GOF $=1.022$ for 366 variables refined against 8020 data. As a comparison for refinement on $\mathrm{F}, \mathrm{R} 1=0.0486$ for those 5683 data with $\mathrm{I}>2.0 \sigma(\mathrm{I})$.



Table 1. Crystal data and structure refinement for ester 2a.

Identification code
Empirical formula
kaw26 (Jason Tenenbaum)
$\mathrm{C}_{36} \mathrm{H}_{50} \mathrm{O}_{3} \mathrm{Si}$

| Formula weight | 558.85 |
| :---: | :---: |
| Temperature | 173(2) K |
| Wavelength | 0.71073 Å |
| Crystal system | Monoclinic |
| Space group | $P 2{ }_{1} / n$ |
| Unit cell dimensions | $\begin{array}{ll} \mathrm{a}=12.6902(5) \AA & \alpha=90^{\circ} . \\ \mathrm{b}=12.2857(5) \AA & \beta=96.2520(10)^{\circ} . \\ \mathrm{c}=21.1888(8) \AA & \gamma=90^{\circ} . \end{array}$ |
| Volume | 3283.9(2) $\AA^{3}$ |
| Z | 4 |
| Density (calculated) | $1.130 \mathrm{Mg} / \mathrm{m}^{3}$ |
| Absorption coefficient | $0.104 \mathrm{~mm}^{-1}$ |
| F(000) | 1216 |
| Crystal size | $0.31 \times 0.28 \times 0.11 \mathrm{~mm}^{3}$ |
| Theta range for data collection | 1.79 to $28.31^{\circ}$. |
| Index ranges | $-16 \leq h \leq 16,-15 \leq k \leq 16,-28 \leq l \leq 28$ |
| Reflections collected | 34702 |
| Independent reflections | $8020[\mathrm{R}(\mathrm{int})=0.0478]$ |
| Completeness to theta $=28.31^{\circ}$ | 98.0\% |
| Absorption correction | None |
| Max. and min. transmission | 0.9887 and 0.9685 |
| Refinement method | Full-matrix least-squares on $\mathrm{F}^{2}$ |
| Data / restraints / parameters | 8020 / 0 / 366 |
| Goodness-of-fit on $\mathrm{F}^{2}$ | 1.022 |
| Final R indices [ $\mathrm{I}>2$ sigma(I)] | $\mathrm{R} 1=0.0486, \mathrm{wR} 2=0.1170$ |
| R indices (all data) | $\mathrm{R} 1=0.0802, \mathrm{wR} 2=0.1367$ |
| Extinction coefficient | 0.0015(4) |
| Largest diff. peak and hole | 0.389 and -0.352 e. $\mathrm{A}^{-3}{ }^{-3}$ |

Table 2. Atomic coordinates ( $\mathrm{x} 10^{4}$ ) and equivalent isotropic displacement parameters $\left(\AA^{2} \mathrm{x}\right.$ $10^{3}$ ) for Ester 2a. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

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


| C(17) | $3918(2)$ | $7237(2)$ | $4748(1)$ | $57(1)$ |
| :--- | ---: | ---: | ---: | ---: |
| C(18) | $4415(2)$ | $7801(2)$ | $4296(1)$ | $46(1)$ |
| C(19) | $5673(1)$ | $6883(1)$ | $1286(1)$ | $24(1)$ |
| 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 $[\AA]$ and angles $\left[{ }^{\circ}\right]$ for Ester 2a.

| $\mathrm{Si}(1)-\mathrm{C}(19)$ | $1.8979(18)$ |
| :--- | :--- |
| $\mathrm{Si}(1)-\mathrm{C}(28)$ | $1.8993(18)$ |
| $\mathrm{Si}(1)-\mathrm{C}(1)$ | $1.9065(18)$ |
| $\mathrm{O}(1)-\mathrm{C}(12)$ | $1.428(2)$ |
| $\mathrm{O}(1)-\mathrm{C}(3)$ | $1.439(2)$ |
| $\mathrm{O}(2)-\mathrm{C}(9)$ | $1.208(2)$ |
| $\mathrm{O}(3)-\mathrm{C}(9)$ | $1.341(2)$ |
| $\mathrm{O}(3)-\mathrm{C}(10)$ | $1.456(2)$ |
| $\mathrm{C}(1)-\mathrm{C}(8)$ | $1.541(2)$ |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | $1.563(2)$ |
| $\mathrm{C}(2)-\mathrm{C}(7)$ | $1.529(2)$ |
| $\mathrm{C}(2)-\mathrm{C}(3)$ | $1.540(2)$ |
| $\mathrm{C}(3)-\mathrm{C}(4)$ | $1.536(3)$ |
| $\mathrm{C}(4)-\mathrm{C}(6)$ | $1.524(3)$ |
| $\mathrm{C}(4)-\mathrm{C}(5)$ | $1.527(3)$ |
| $\mathrm{C}(8)-\mathrm{C}(9)$ | $1.504(3)$ |
| $\mathrm{C}(10)-\mathrm{C}(11)$ | $1.500(3)$ |
| $\mathrm{C}(12)-\mathrm{C}(13)$ | $1.497(3)$ |
| $\mathrm{C}(13)-\mathrm{C}(18)$ | $1.376(3)$ |
| $\mathrm{C}(13)-\mathrm{C}(14)$ | $1.389(3)$ |
| $\mathrm{C}(14)-\mathrm{C}(15)$ | $1.384(3)$ |
| $\mathrm{C}(15)-\mathrm{C}(16)$ | $1.372(4)$ |
| $\mathrm{C}(16)-\mathrm{C}(17)$ | $1.372(4)$ |
| $\mathrm{C}(17)-\mathrm{C}(18)$ | $1.387(3)$ |
| $\mathrm{C}(19)-\mathrm{C}(20)$ | $1.414(3)$ |
| $\mathrm{C}(19)-\mathrm{C}(24)$ | $1.417(2)$ |
| $\mathrm{C}(20)-\mathrm{C}(21)$ | $1.396(3)$ |
| $\mathrm{C}(20)-\mathrm{C}(25)$ | $1.515(3)$ |
| $\mathrm{C}(21)-\mathrm{C}(22)$ | $1.379(3)$ |
| $\mathrm{C}(22)-\mathrm{C}(23)$ | $1.385(3)$ |


| $\mathrm{C}(22)-\mathrm{C}(26)$ | 1.508(3) |
| :---: | :---: |
| C(23)-C(24) | 1.394(3) |
| C(24)-C(27) | $1.506(3)$ |
| C(28)-C(29) | 1.413(2) |
| C(28)-C(33) | 1.421(2) |
| C(29)-C(30) | $1.394(2)$ |
| C(29)-C(34) | $1.506(2)$ |
| $\mathrm{C}(30)-\mathrm{C}(31)$ | $1.388(2)$ |
| $\mathrm{C}(31)-\mathrm{C}(32)$ | 1.387 (3) |
| $\mathrm{C}(31)-\mathrm{C}(35)$ | $1.506(3)$ |
| C(32)-C(33) | 1.393 (3) |
| $\mathrm{C}(33)-\mathrm{C}(36)$ | $1.509(2)$ |
| $\mathrm{C}(19)-\mathrm{Si}(1)-\mathrm{C}(28)$ | 111.16(8) |
| $\mathrm{C}(19)-\mathrm{Si}(1)-\mathrm{C}(1)$ | 110.45(8) |
| $\mathrm{C}(28)-\mathrm{Si}(1)-\mathrm{C}(1)$ | 118.40(8) |
| $\mathrm{C}(12)-\mathrm{O}(1)-\mathrm{C}(3)$ | 115.02(14) |
| $\mathrm{C}(9)-\mathrm{O}(3)-\mathrm{C}(10)$ | 116.35(16) |
| $\mathrm{C}(8)-\mathrm{C}(1)-\mathrm{C}(2)$ | 112.88(14) |
| $\mathrm{C}(8)-\mathrm{C}(1)-\mathrm{Si}(1)$ | 108.99(12) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{Si}(1)$ | 110.61(11) |
| $\mathrm{C}(7)-\mathrm{C}(2)-\mathrm{C}(3)$ | 110.83(14) |
| $\mathrm{C}(7)-\mathrm{C}(2)-\mathrm{C}(1)$ | 112.93(14) |
| $\mathrm{C}(3)-\mathrm{C}(2)-\mathrm{C}(1)$ | 112.08(14) |
| $\mathrm{O}(1)-\mathrm{C}(3)-\mathrm{C}(4)$ | 108.04(14) |
| $\mathrm{O}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | 109.13(14) |
| $\mathrm{C}(4)-\mathrm{C}(3)-\mathrm{C}(2)$ | 114.66(15) |
| $\mathrm{C}(6)-\mathrm{C}(4)-\mathrm{C}(5)$ | 110.58(18) |
| $\mathrm{C}(6)-\mathrm{C}(4)-\mathrm{C}(3)$ | 112.46(16) |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{C}(3)$ | 110.00(17) |
| $\mathrm{C}(9)-\mathrm{C}(8)-\mathrm{C}(1)$ | 113.35(15) |
| $\mathrm{O}(2)-\mathrm{C}(9)-\mathrm{O}(3)$ | 123.79(17) |
| $\mathrm{O}(2)-\mathrm{C}(9)-\mathrm{C}(8)$ | 124.83(16) |
| $\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(8)$ | 111.32(16) |
| $\mathrm{O}(3)-\mathrm{C}(10)-\mathrm{C}(11)$ | 111.07(18) |
| $\mathrm{O}(1)-\mathrm{C}(12)-\mathrm{C}(13)$ | 107.50(15) |
| $\mathrm{C}(18)-\mathrm{C}(13)-\mathrm{C}(14)$ | 118.4(2) |
| $\mathrm{C}(18)-\mathrm{C}(13)-\mathrm{C}(12)$ | 121.26(19) |
| $\mathrm{C}(14)-\mathrm{C}(13)-\mathrm{C}(12)$ | 120.35(19) |
| $\mathrm{C}(15)-\mathrm{C}(14)-\mathrm{C}(13)$ | 120.2(2) |
| $\mathrm{C}(16)-\mathrm{C}(15)-\mathrm{C}(14)$ | 120.8(2) |
| $\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{C}(17)$ | 119.4(2) |
| $\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(18)$ | 120.0(2) |
| $\mathrm{C}(13)-\mathrm{C}(18)-\mathrm{C}(17)$ | 121.2(2) |
| $\mathrm{C}(20)-\mathrm{C}(19)-\mathrm{C}(24)$ | 117.82(16) |
| $\mathrm{C}(20)-\mathrm{C}(19)-\mathrm{Si}(1)$ | 121.88(14) |
| $\mathrm{C}(24)-\mathrm{C}(19)-\mathrm{Si}(1)$ | 120.30(13) |
| $\mathrm{C}(21)-\mathrm{C}(20)-\mathrm{C}(19)$ | 119.88(18) |
| $\mathrm{C}(21)-\mathrm{C}(20)-\mathrm{C}(25)$ | 116.85(17) |
| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(25)$ | 123.27(17) |
| $\mathrm{C}(22)-\mathrm{C}(21)-\mathrm{C}(20)$ | 122.50(19) |
| $\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{C}(23)$ | 117.55(18) |
| $\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{C}(26)$ | 121.3(2) |
| $\mathrm{C}(23)-\mathrm{C}(22)-\mathrm{C}(26)$ | 121.1(2) |
| $\mathrm{C}(22)-\mathrm{C}(23)-\mathrm{C}(24)$ | 122.38(18) |


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

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

|  | $\mathrm{U}^{11}$ | $\mathrm{U}^{22}$ | $\mathrm{U}^{33}$ | $\mathrm{U}^{23}$ | $\mathrm{U}^{13}$ | $\mathrm{U}^{12}$ |
| :--- | :--- | :--- | :--- | :--- | :--- | :--- |
| $\mathrm{Si}(1)$ | $22(1)$ | $20(1)$ | $21(1)$ | $-1(1)$ | $1(1)$ | $1(1)$ |
| $\mathrm{O}(1)$ | $24(1)$ | $34(1)$ | $24(1)$ | $2(1)$ | $4(1)$ | $0(1)$ |
| $\mathrm{O}(2)$ | $27(1)$ | $29(1)$ | $31(1)$ | $4(1)$ | $2(1)$ | $-1(1)$ |
| $\mathrm{O}(3)$ | $37(1)$ | $24(1)$ | $43(1)$ | $6(1)$ | $2(1)$ | $-5(1)$ |
| $\mathrm{C}(1)$ | $21(1)$ | $22(1)$ | $24(1)$ | $1(1)$ | $3(1)$ | $0(1)$ |
| $\mathrm{C}(2)$ | $23(1)$ | $23(1)$ | $24(1)$ | $1(1)$ | $4(1)$ | $2(1)$ |
| $\mathrm{C}(3)$ | $23(1)$ | $26(1)$ | $27(1)$ | $-1(1)$ | $6(1)$ | $0(1)$ |
| $\mathrm{C}(4)$ | $34(1)$ | $30(1)$ | $35(1)$ | $-3(1)$ | $8(1)$ | $6(1)$ |
| $\mathrm{C}(5)$ | $53(1)$ | $34(1)$ | $44(1)$ | $-10(1)$ | $9(1)$ | $10(1)$ |
| $\mathrm{C}(6)$ | $61(2)$ | $27(1)$ | $46(1)$ | $2(1)$ | $13(1)$ | $11(1)$ |
| $\mathrm{C}(7)$ | $25(1)$ | $33(1)$ | $31(1)$ | $-1(1)$ | $2(1)$ | $2(1)$ |
| $\mathrm{C}(8)$ | $23(1)$ | $25(1)$ | $29(1)$ | $3(1)$ | $2(1)$ | $-2(1)$ |
| $\mathrm{C}(9)$ | $30(1)$ | $24(1)$ | $24(1)$ | $2(1)$ | $8(1)$ | $-4(1)$ |
| $\mathrm{C}(10)$ | $44(1)$ | $23(1)$ | $58(1)$ | $6(1)$ | $4(1)$ | $0(1)$ |
| $\mathrm{C}(11)$ | $37(1)$ | $40(1)$ | $58(2)$ | $16(1)$ | $-2(1)$ | $-5(1)$ |
| $\mathrm{C}(12)$ | $27(1)$ | $42(1)$ | $26(1)$ | $3(1)$ | $2(1)$ | $1(1)$ |
| $\mathrm{C}(13)$ | $28(1)$ | $42(1)$ | $23(1)$ | $0(1)$ | $2(1)$ | $0(1)$ |
| $\mathrm{C}(14)$ | $55(1)$ | $50(1)$ | $38(1)$ | $2(1)$ | $18(1)$ | $11(1)$ |
| $\mathrm{C}(15)$ | $52(2)$ | $76(2)$ | $37(1)$ | $3(1)$ | $21(1)$ | $11(1)$ |
| $\mathrm{C}(16)$ | $44(1)$ | $72(2)$ | $33(1)$ | $10(1)$ | $10(1)$ | $-10(1)$ |
| $\mathrm{C}(17)$ | $71(2)$ | $49(2)$ | $55(2)$ | $12(1)$ | $22(1)$ | $1(1)$ |
| $\mathrm{C}(18)$ | $56(1)$ | $46(1)$ | $39(1)$ | $4(1)$ | $20(1)$ | $7(1)$ |
| $\mathrm{C}(19)$ | $27(1)$ | $23(1)$ | $22(1)$ | $-1(1)$ | $4(1)$ | $1(1)$ |
| $\mathrm{C}(20)$ | $32(1)$ | $28(1)$ | $32(1)$ | $-3(1)$ | $1(1)$ | $-1(1)$ |
| $\mathrm{C}(21)$ | $44(1)$ | $23(1)$ | $37(1)$ | $-5(1)$ | $2(1)$ | $-2(1)$ |
| $\mathrm{C}(22)$ | $47(1)$ | $26(1)$ | $28(1)$ | $0(1)$ | $5(1)$ | $9(1)$ |
| $\mathrm{C}(23)$ | $33(1)$ | $31(1)$ | $23(1)$ | $3(1)$ | $5(1)$ | $9(1)$ |
| $\mathrm{C}(24)$ | $28(1)$ | $27(1)$ | $17(1)$ | $2(1)$ | $6(1)$ | $3(1)$ |
| $\mathrm{C}(25)$ | $35(1)$ | $30(1)$ | $61(2)$ | $-11(1)$ | $-7(1)$ | $-4(1)$ |
| $\mathrm{C}(26)$ | $72(2)$ | $27(1)$ | $51(1)$ | $-4(1)$ | $-1(1)$ | $16(1)$ |
|  |  |  |  |  |  |  |


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

Table 5. Hydrogen coordinates ( $\mathrm{x} 10^{4}$ ) and isotropic displacement parameters $\left(\AA^{2} \times 10^{3}\right)$ for Ester 2a.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :--- | ---: | ---: | ---: | :--- |
|  |  |  |  |  |
| H(1A) | 5486 | 8845 | 2401 | 26 |
| H(2A) | 4400 | 10248 | 1755 | 28 |
| H(3A) | 5087 | 10574 | 2814 | 30 |
| H(4A) | 2939 | 11353 | 2664 | 39 |
| H(5A) | 3606 | 12801 | 3331 | 65 |
| H(5B) | 4754 | 12247 | 3404 | 65 |
| H(5C) | 3785 | 11656 | 3687 | 65 |
| H(6A) | 3544 | 12918 | 2169 | 66 |
| H(6B) | 3726 | 11859 | 1754 | 66 |
| H(6C) | 4702 | 12397 | 2185 | 66 |
| H(7A) | 2580 | 10273 | 1887 | 44 |
| H(7B) | 2682 | 9092 | 2207 | 44 |
| H(7C) | 2865 | 9241 | 1477 | 44 |
| H(8A) | 3805 | 8006 | 2717 | 31 |
| H(8B) | 3762 | 7403 | 2046 | 31 |
| H(10A) | 5946 | 5127 | 2857 | 50 |
| H(10B) | 4975 | 4309 | 2686 | 50 |
| H(11A) | 5510 | 4270 | 3780 | 68 |
| H(11B) | 4323 | 4723 | 3655 | 68 |
| H(11C) | 5288 | 5548 | 3825 | 68 |
| H(12A) | 5134 | 10185 | 3897 | 38 |
| H(12B) | 5341 | 9053 | 3551 | 38 |
| H(14A) | 3569 | 10220 | 4575 | 56 |
| H(15A) | 2703 | 9263 | 5313 | 65 |
| H(16A) | 2937 | 7398 | 5435 | 59 |
| H(17A) | 4018 | 6474 | 4795 | 69 |
| H(18A) | 4850 | 7416 | 4035 | 55 |
| H(21A) | 4982 | 4400 | 843 | 42 |
| H(23A) | 7796 | 5403 | 1686 | 35 |
| H(25A) | 3583 | 5478 | 601 | 64 |
| H(25B) | 3852 | 6690 | 394 | 64 |
| H(25C) | 3469 | 6470 | 1078 | 64 |
| H(26A) | 6316 | 3090 | 10444 | 76 |
| H(26B) | 7105 | 3322 | 1672 | 76 |
| H(26C) | 7478 | 3558 | 987 | 76 |
| H(27A) | 8157 | 7142 | 1980 | 41 |
|  |  |  |  |  |


| 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 [ ${ }^{\circ}$ ] for Ester 2a.

| $\mathrm{C}(19)-\mathrm{Si}(1)-\mathrm{C}(1)-\mathrm{C}(8)$ | $-40.78(14)$ |
| :--- | :---: |
| $\mathrm{C}(98)-\mathrm{Si}(1)-\mathrm{C}(1)-\mathrm{C}(8)$ | $-170.55(11)$ |
| $\mathrm{C}(19)-\mathrm{Si}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | $-165.45(11)$ |
| $\mathrm{C}(28)-\mathrm{Si}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | $64.79(14)$ |
| $\mathrm{C}(8)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(7)$ | $-38.7(2)$ |
| $\mathrm{Si}(1)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(7)$ | $83.68(16)$ |
| $\mathrm{C}(8)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | $87.31(18)$ |
| $\mathrm{Si}(1)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | $-150.28(12)$ |
| $\mathrm{C}(12)-\mathrm{O}(1)-\mathrm{C}(3)-\mathrm{C}(4)$ | $-116.78(17)$ |
| $\mathrm{C}(12)-\mathrm{O}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | $117.95(16)$ |
| $\mathrm{C}(7)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{O}(1)$ | $65.48(18)$ |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{O}(1)$ | $-61.69(18)$ |
| $\mathrm{C}(7)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{C}(4)$ | $-55.8(2)$ |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{C}(4)$ | $176.98(15)$ |
| $\mathrm{O}(1)-\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(6)$ | $-175.20(17)$ |
| $\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(6)$ | $-53.3(2)$ |
| $\mathrm{O}(1)-\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(5)$ | $61.1(2)$ |
| $\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(5)$ | $-177.00(17)$ |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(8)-\mathrm{C}(9)$ | $-154.89(15)$ |
| $\mathrm{Si}(1)-\mathrm{C}(1)-\mathrm{C}(8)-\mathrm{C}(9)$ | $81.79(16)$ |
| $\mathrm{C}(10)-\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{O}(2)$ | $-1.3(3)$ |
| $\mathrm{C}(10)-\mathrm{O}(3)-\mathrm{C}(9)-\mathrm{C}(8)$ | $-178.56(16)$ |
| $\mathrm{C}(1)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{O}(2)$ | $33.1(3)$ |
| $\mathrm{C}(1)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{O}(3)$ | $-149.70(15)$ |
| $\mathrm{C}(9)-\mathrm{O}(3)-\mathrm{C}(10)-\mathrm{C}(11)$ | $85.5(2)$ |
| $\mathrm{C}(3)-\mathrm{O}(1)-\mathrm{C}(12)-\mathrm{C}(13)$ | $175.79(15)$ |
| $\mathrm{O}(1)-\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(18)$ | $105.5(2)$ |
| $\mathrm{O}(1)-\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(14)$ | $-73.0(2)$ |
| $\mathrm{C}(18)-\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{C}(15)$ | $-1.5(3)$ |
| $\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{C}(15)$ | $177.0(2)$ |
| $\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(16)$ | $1.6(4)$ |
| $\mathrm{C}(14)-\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{C}(17)$ | $-0.7(4)$ |
| $\mathrm{C}(15)-\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(18)$ | $-0.3(4)$ |
| $\mathrm{C}(14)-\mathrm{C}(13)-\mathrm{C}(18)-\mathrm{C}(17)$ | $0.6(4)$ |
| $\mathrm{C}(12)-\mathrm{C}(13)-\mathrm{C}(18)-\mathrm{C}(17)$ | $-177.9(2)$ |
|  |  |


| $\mathrm{C}(16)-\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(13)$ | $0.3(4)$ |
| :--- | :---: |
| $\mathrm{C}(28)-\mathrm{Si}(1)-\mathrm{C}(19)-\mathrm{C}(20)$ | $-124.87(15)$ |
| $\mathrm{C}(1)-\mathrm{Si}(1)-\mathrm{C}(19)-\mathrm{C}(20)$ | $101.61(16)$ |
| $\mathrm{C}(28)-\mathrm{Si}(1)-\mathrm{C}(19)-\mathrm{C}(24)$ | $54.57(16)$ |
| $\mathrm{C}(1)-\mathrm{Si}(1)-\mathrm{C}(19)-\mathrm{C}(24)$ | $-78.95(15)$ |
| $\mathrm{C}(24)-\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)$ | $-0.6(3)$ |
| $\mathrm{Si}(1)-\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)$ | $178.84(15)$ |
| $\mathrm{C}(24)-\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(25)$ | $179.39(19)$ |
| $\mathrm{Si}(1)-\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(25)$ | $-1.2(3)$ |
| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(22)$ | $0.4(3)$ |
| $\mathrm{C}(25)-\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(22)$ | $-179.6(2)$ |
| $\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{C}(23)$ | $-0.1(3)$ |
| $\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{C}(26)$ | $-179.2(2)$ |
| $\mathrm{C}(11)-\mathrm{C}(22)-\mathrm{C}(23)-\mathrm{C}(24)$ | $0.0(3)$ |
| $\mathrm{C}(26)-\mathrm{C}(22)-\mathrm{C}(23)-\mathrm{C}(24)$ | $179.10(19)$ |
| $\mathrm{C}(22)-\mathrm{C}(23)-\mathrm{C}(24)-\mathrm{C}(19)$ | $-0.2(3)$ |
| $\mathrm{C}(22)-\mathrm{C}(23)-\mathrm{C}(24)-\mathrm{C}(27)$ | $178.57(17)$ |
| $\mathrm{C}(20)-\mathrm{C}(19)-\mathrm{C}(24)-\mathrm{C}(23)$ | $0.5(3)$ |
| $\mathrm{Si}(1)-\mathrm{C}(19)-\mathrm{C}(24)-\mathrm{C}(23)$ | $-178.93(13)$ |
| $\mathrm{C}(20)-\mathrm{C}(19)-\mathrm{C}(24)-\mathrm{C}(27)$ | $-178.21(17)$ |
| $\mathrm{Si}(1)-\mathrm{C}(19)-\mathrm{C}(24)-\mathrm{C}(27)$ | $2.3(2)$ |
| $\mathrm{C}(19)-\mathrm{Si}(1)-\mathrm{C}(28)-\mathrm{C}(29)$ | $-113.76(15)$ |
| $\mathrm{C}(1)-\mathrm{Si}(1)-\mathrm{C}(28)-\mathrm{C}(29)$ | $15.68(18)$ |
| $\mathrm{C}(19)-\mathrm{Si}(1)-\mathrm{C}(28)-\mathrm{C}(33)$ | $65.25(15)$ |
| $\mathrm{C}(1)-\mathrm{Si}(1)-\mathrm{C}(28)-\mathrm{C}(33)$ | $-165.31(12)$ |
| $\mathrm{C}(33)-\mathrm{C}(28)-\mathrm{C}(29)-\mathrm{C}(30)$ | $-0.4(2)$ |
| $\mathrm{Si}(1)-\mathrm{C}(28)-\mathrm{C}(29)-\mathrm{C}(30)$ | $178.56(13)$ |
| $\mathrm{C}(33)-\mathrm{C}(28)-\mathrm{C}(29)-\mathrm{C}(34)$ | $-179.91(16)$ |
| $\mathrm{Si}(1)-\mathrm{C}(28)-\mathrm{C}(29)-\mathrm{C}(34)$ | $-0.9(3)$ |
| $\mathrm{C}(28)-\mathrm{C}(29)-\mathrm{C}(30)-\mathrm{C}(31)$ | $-0.2(3)$ |
| $\mathrm{C}(34)-\mathrm{C}(29)-\mathrm{C}(30)-\mathrm{C}(31)$ | $179.33(16)$ |
| $\mathrm{C}(29)-\mathrm{C}(30)-\mathrm{C}(31)-\mathrm{C}(32)$ | $0.4(3)$ |
| $\mathrm{C}(29)-\mathrm{C}(30)-\mathrm{C}(31)-\mathrm{C}(35)$ | $-179.24(18)$ |
| $\mathrm{C}(30)-\mathrm{C}(31)-\mathrm{C}(32)-\mathrm{C}(33)$ | $0.1(3)$ |
| $\mathrm{C}(35)-\mathrm{C}(31)-\mathrm{C}(32)-\mathrm{C}(33)$ | $179.68(18)$ |
| $\mathrm{C}(31)-\mathrm{C}(32)-\mathrm{C}(33)-\mathrm{C}(28)$ | $-0.7(3)$ |
| $\mathrm{C} 31)-\mathrm{C}(32)-\mathrm{C}(33)-\mathrm{C}(36)$ | $179.82(17)$ |
| $\mathrm{C}(29)-\mathrm{C}(28)-\mathrm{C}(33)-\mathrm{C}(32)$ | $0.9(2)$ |
| $\mathrm{Si}(1)-\mathrm{C}(28)-\mathrm{C}(33)-\mathrm{C}(32)$ | $-178.24(13)$ |
| $\mathrm{C}(29)-\mathrm{C}(28)-\mathrm{C}(33)-\mathrm{C}(36)$ | $-179.68(16)$ |
| $\mathrm{Si}(1)-\mathrm{C}(28)-\mathrm{C}(33)-\mathrm{C}(36)$ | $1.2(2)$ |
|  |  |

## References

7. SMART Software Users Guide, Version 5.1, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
8. SAINT Software Users Guide, Version 6.0, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
9. Sheldrick, G. M. SADABS, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
10. Sheldrick, G. M. SHELXTL Version 5.10, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
11. International Tables for X-Ray Crystallography 1992, Vol. C., Dordrecht: Kluwer AcademicPublishers.

## Definitions:

$\mathrm{wR} 2=\left[\Sigma\left[\mathrm{w}\left(\mathrm{F}_{\mathrm{o}}{ }^{2}-\mathrm{F}_{\mathrm{o}}{ }^{2}\right)^{2}\right] / \Sigma\left[\mathrm{w}\left(\mathrm{F}_{\mathrm{o}}{ }^{2}\right)^{2}\right]^{1 / 2}\right.$
$\mathrm{R} 1=\Sigma| | \mathrm{F}_{\mathrm{o}}\left|-\left|\mathrm{F}_{\mathrm{c}}\right|\right| / \Sigma\left|\mathrm{F}_{\mathrm{o}}\right|$
GOF $=\mathrm{S}=\left[\Sigma\left[\mathrm{w}\left(\mathrm{F}_{\mathrm{o}}^{2}-\mathrm{F}_{\mathrm{c}}^{2}\right)^{2}\right] /(\mathrm{n}-\mathrm{p})\right]^{1 / 2}$ 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 $0.28 \times 0.30 \times 0.37 \mathrm{~mm}$ was mounted on a glass fiber and transferred to a Bruker CCD platform diffractometer. The SMART ${ }^{1}$ program package was used to determine the unit-cell parameters and for data collection ( $25 \mathrm{sec} / \mathrm{frame}$ scan time for a sphere of diffraction data). The raw frame data was processed using SAINT ${ }^{2}$ and SADABS $^{3}$ to yield the reflection data file. Subsequent calculations were carried out using the SHELXTL ${ }^{4}$ program. The diffraction symmetry was $2 / m$ and the systematic absences were consistent with the centrosymmetric monoclinic space group $P 2_{1} / n$ which was later determined to be correct.

The structure was solved by direct methods and refined on $\mathrm{F}^{2}$ by full-matrix least-squares techniques. The analytical scattering factors ${ }^{5}$ for neutral atoms were used throughout the analysis. Hydrogen atoms were either located from a difference-Fourier map and refined ( $\mathrm{x}, \mathrm{y}, \mathrm{z}$ and $\mathrm{U}_{\mathrm{is} 0}$ ) or were included using a riding model. Carbon atoms $\mathrm{C}(10), \mathrm{C}(11)$ and $\mathrm{C}(12)$ 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 $\mathrm{F}, \mathrm{R} 1=0.0568$ for those 6075 data with $\mathrm{I}>2.0 \sigma(\mathrm{I})$.



Table 1. Crystal data and structure refinement for Ethyl ( $3 R, 4 R, 5 R$ )-3-(dimesitylsilyl)-5-(2,2-dimethyl-propionyloxy)-4,6-dimethyl-hept-2-eneoate.

Identification code
Empirical formula
Formula weight
Temperature
Wavelength
Crystal system
Space group
Unit cell dimensions

Volume
Z
Density (calculated)
Absorption coefficient
F(000)
Crystal size
Theta range for data collection
Index ranges
Reflections collected
Independent reflections
Completeness to theta $=28.30^{\circ}$
Absorption correction
Max. and min. transmission
Refinement method
Data / restraints / parameters
Goodness-of-fit on $\mathrm{F}^{2}$
Final R indices [ $\mathrm{I}>2 \operatorname{sigma}(\mathrm{I})$ ]
R indices (all data)
Extinction coefficient
Largest diff. peak and hole
kaw33 (Jason Tenenbaum)
$\mathrm{C}_{34} \mathrm{H}_{52} \mathrm{O}_{4} \mathrm{Si}$
552.85

173(2) K
$0.71073 \AA$
Monoclinic
$P 2_{1} / n$
$\mathrm{a}=12.7614(5) \AA \quad \alpha=90^{\circ}$.
$b=12.5893(5) \AA \quad \beta=92.4460(10)^{\circ}$.
$\mathrm{c}=20.3324(8) \AA \quad \gamma=90^{\circ}$.
3263.6(2) $\AA^{3}$

4
$1.125 \mathrm{Mg} / \mathrm{m}^{3}$
$0.106 \mathrm{~mm}^{-1}$
1208
$0.37 \times 0.30 \times 0.28 \mathrm{~mm}^{3}$
1.85 to $28.30^{\circ}$.
$-17 \leq h \leq 16,-16 \leq k \leq 15,-27 \leq l \leq 26$
34367
$7948[\mathrm{R}(\mathrm{int})=0.0347]$
98.1\%

None
0.9710 and 0.9619

Full-matrix least-squares on $\mathrm{F}^{2}$
7948 / 0 / 357
1.030
$\mathrm{R} 1=0.0568, \mathrm{wR} 2=0.1482$
$\mathrm{R} 1=0.0777, \mathrm{wR} 2=0.1660$
0.0008(5)
0.668 and -0.458 e. $\AA^{-3}$

Table 2. Atomic coordinates ( $\mathrm{x} 10^{4}$ ) and equivalent isotropic displacement parameters ( $\AA^{2} \mathrm{x}$ $10^{3}$ ) for Ethyl ( $3 R, 4 R, 5 R$ )-3-(dimesitylsilyl)-5-(2,2-dimethyl-propionyloxy)-4,6-dimethyl-hept-2eneoate. $\mathrm{U}(\mathrm{eq})$ is defined as one third of the trace of the orthogonalized Uij tensor.

|  | x | y | z | U(eq) |
| :---: | :---: | :---: | :---: | :---: |
| $\overline{\mathrm{Si}}$ (1) | 5213(1) | 8088(1) | 1303(1) | 22(1) |
| $\mathrm{O}(1)$ | 3786(1) | 9218(1) | 3371(1) | 33(1) |
| O(2) | 5324(1) | 9133(2) | 3936(1) | 63(1) |
| $\mathrm{O}(3)$ | 5839(1) | 6618(1) | 2901(1) | 37(1) |
| $\mathrm{O}(4)$ | 4540(1) | 5501(1) | 2570(1) | 45(1) |
| $\mathrm{C}(1)$ | 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) |
| $\mathrm{C}(7)$ | 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) | 6792(2) | 6440(2) | 1417(1) | 26(1) |
| C(23) | 3971(2) | 5999(2) | 728(1) | 42(1) |
| C(24) | 6948(3) | 3454(2) | 1109(2) | 60(1) |
| C (25) | 7528(2) | 7265(2) | 1711(1) | 33(1) |
| C(26) | 6077(1) | 9115(1) | 915(1) | 23(1) |
| C(27) | 6099(2) | 9082(2) | 216(1) | 25(1) |
| C(28) | 6742(2) | 9784(2) | -113(1) | 30(1) |
| C(29) | 7364(2) | 10530(2) | 217(1) | 31(1) |
| C(30) | 7334(2) | 10572(2) | 900(1) | 27(1) |
| C(31) | 6705(1) | 9884(2) | 1250(1) | 24(1) |
| C(32) | 5435(2) | 8317(2) | -196(1) | 31(1) |
| C(33) | 8060(2) | 11281(2) | -144(1) | 48(1) |
| C(34) | 6750(2) | 10022(2) | 1988(1) | 30(1) |

Table 3. Bond lengths $\left[\AA\right.$ ] and angles [ ${ }^{\circ}$ ] for Ethyl ( $3 R, 4 R, 5 R$ )-3-(dimesitylsilyl)-5-(2,2-dimethyl-propionyloxy)-4,6-dimethyl-hept-2-eneoate.

| Si(1)-C(26) | 1.8938(19) |
| :---: | :---: |
| $\mathrm{Si}(1)-\mathrm{C}(17)$ | $1.8978(19)$ |
| $\mathrm{Si}(1)-\mathrm{C}(1)$ | $1.9080(18)$ |
| $\mathrm{O}(1)-\mathrm{C}(8)$ | 1.340(3) |
| $\mathrm{O}(1)-\mathrm{C}(3)$ | 1.463 (2) |
| $\mathrm{O}(2)-\mathrm{C}(8)$ | $1.197(3)$ |
| $\mathrm{O}(3)-\mathrm{C}(14)$ | $1.205(3)$ |
| $\mathrm{O}(4)-\mathrm{C}(14)$ | $1.350(3)$ |
| $\mathrm{O}(4)-\mathrm{C}(15)$ | 1.464 (3) |
| $\mathrm{C}(1)-\mathrm{C}(13)$ | $1.543(3)$ |
| $\mathrm{C}(1)-\mathrm{C}(2)$ | 1.562(2) |
| $\mathrm{C}(2)-\mathrm{C}(7)$ | $1.533(3)$ |
| $\mathrm{C}(2)-\mathrm{C}(3)$ | $1.535(3)$ |
| $\mathrm{C}(3)-\mathrm{C}(4)$ | 1.534(3) |
| $\mathrm{C}(4)-\mathrm{C}(5)$ | 1.522(4) |
| C(4)-C(6) | 1.527(4) |
| $\mathrm{C}(8)-\mathrm{C}(9)$ | 1.537(3) |
| $\mathrm{C}(9)-\mathrm{C}(12 \mathrm{~B})$ | 1.341 (8) |
| $\mathrm{C}(9)-\mathrm{C}(10)$ | $1.454(7)$ |
| $\mathrm{C}(9)-\mathrm{C}(10 \mathrm{~B})$ | 1.525 (7) |
| $\mathrm{C}(9)-\mathrm{C}(11)$ | $1.549(5)$ |
| $\mathrm{C}(9)-\mathrm{C}(11 \mathrm{~B})$ | $1.632(7)$ |
| $\mathrm{C}(9)-\mathrm{C}(12)$ | $1.655(6)$ |
| $\mathrm{C}(13)-\mathrm{C}(14)$ | $1.505(3)$ |
| $\mathrm{C}(15)-\mathrm{C}(16)$ | $1.489(5)$ |
| $\mathrm{C}(17)-\mathrm{C}(18)$ | $1.412(3)$ |
| $\mathrm{C}(17)-\mathrm{C}(22)$ | 1.420 (3) |
| $\mathrm{C}(18)-\mathrm{C}(19)$ | $1.401(3)$ |
| $\mathrm{C}(18)-\mathrm{C}(23)$ | $1.514(3)$ |
| $\mathrm{C}(19)$-C(20) | $1.384(3)$ |
| $\mathrm{C}(20)-\mathrm{C}(21)$ | 1.383(3) |
| $\mathrm{C}(20)-\mathrm{C}(24)$ | 1.517(3) |
| $\mathrm{C}(21)-\mathrm{C}(22)$ | 1.393 (3) |
| $\mathrm{C}(22)$ - $\mathrm{C}(25)$ | $1.506(3)$ |
| $\mathrm{C}(26)-\mathrm{C}(31)$ | $1.413(3)$ |
| C(26)-C(27) | 1.423 (2) |
| C(27)-C(28) | $1.395(3)$ |
| $\mathrm{C}(27)-\mathrm{C}(32)$ | $1.512(3)$ |
| C(28)-C(29) | $1.385(3)$ |
| C(29)-C(30) | $1.391(3)$ |
| C(29)-C(33) | $1.509(3)$ |
| $\mathrm{C}(30)-\mathrm{C}(31)$ | $1.395(3)$ |
| $\mathrm{C}(31)-\mathrm{C}(34)$ | 1.511(3) |
| $\mathrm{C}(26)-\mathrm{Si}(1)-\mathrm{C}(17)$ | 112.30(8) |
| $\mathrm{C}(26)-\mathrm{Si}(1)-\mathrm{C}(1)$ | 118.13(8) |
| $\mathrm{C}(17)-\mathrm{Si}(1)-\mathrm{C}(1)$ | 110.60(8) |
| $\mathrm{C}(8)-\mathrm{O}(1)-\mathrm{C}(3)$ | 118.62(16) |
| $\mathrm{C}(14)-\mathrm{O}(4)-\mathrm{C}(15)$ | 116.31(19) |
| $\mathrm{C}(13)-\mathrm{C}(1)-\mathrm{C}(2)$ | 113.28(15) |
| $\mathrm{C}(13)-\mathrm{C}(1)-\mathrm{Si}(1)$ | 107.92(12) |


|  |  |
| :--- | :---: |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{Si}(1)$ | $109.94(12)$ |
| $\mathrm{C}(7)-\mathrm{C}(2)-\mathrm{C}(3)$ | $11.49(16)$ |
| $\mathrm{C}(7)-\mathrm{C}(2)-\mathrm{C}(1)$ | $113.42(16)$ |
| $\mathrm{C}(3)-\mathrm{C}(2)-\mathrm{C}(1)$ | $112.01(15)$ |
| $\mathrm{O}(1)-\mathrm{C}(3)-\mathrm{C}(4)$ | $107.15(16)$ |
| $\mathrm{O}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | $108.29(16)$ |
| $\mathrm{C}(4)-\mathrm{C}(3)-\mathrm{C}(2)$ | $114.96(18)$ |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{C}(6)$ | $110.5(2)$ |
| $\mathrm{C}(5)-\mathrm{C}(4)-\mathrm{C}(3)$ | $110.2(2)$ |
| $\mathrm{C}(6)-\mathrm{C}(4)-\mathrm{C}(3)$ | $11.18(19)$ |
| $\mathrm{O}(2)-\mathrm{C}(8)-\mathrm{O}(1)$ | $123.3(2)$ |
| $\mathrm{O}(2)-\mathrm{C}(8)-\mathrm{C}(9)$ | $124.1(2)$ |
| $\mathrm{O}(1)-\mathrm{C}(8)-\mathrm{C}(9)$ | $112.61(18)$ |
| $\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(9)-\mathrm{C}(10)$ | $135.5(5)$ |
| $\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(9)-\mathrm{C}(10 \mathrm{~B})$ | $124.7(5)$ |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(10 \mathrm{~B})$ | $37.3(3)$ |
| $\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(9)-\mathrm{C}(8)$ | $107.6(4)$ |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(8)$ | $116.9(3)$ |
| $\mathrm{C}(10 \mathrm{~B})-\mathrm{C}(9)-\mathrm{C}(8)$ | $110.5(3)$ |
| $\mathrm{C}(110)-\mathrm{C}(9)-\mathrm{C}(11)$ | $51.6(4)$ |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(11)$ | $109.3(4)$ |
| $\mathrm{C}(10 \mathrm{~B})-\mathrm{C}(9)-\mathrm{C}(11)$ | $136.8(4)$ |
| $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(11)$ | $110.6(2)$ |
| $\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(9)-\mathrm{C}(11 \mathrm{~B})$ | $111.8(5)$ |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(11 \mathrm{~B})$ | $62.3(4)$ |
| $\mathrm{C}(10 \mathrm{~B})-\mathrm{C}(9)-\mathrm{C}(11 \mathrm{~B})$ | $99.5(4)$ |
| $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(11 \mathrm{~B})$ | $99.9(3)$ |
| $\mathrm{C}(11)-\mathrm{C}(9)-\mathrm{C}(11 \mathrm{~B})$ | $60.5(3)$ |
| $\mathrm{C}(12 \mathrm{~B})-\mathrm{C}(9)-\mathrm{C}(12)$ | $50.6(4)$ |
| $\mathrm{C}(10)-\mathrm{C}(9)-\mathrm{C}(12)$ | $110.9(4)$ |
| $\mathrm{C}(10 \mathrm{~B})-\mathrm{C}(9)-\mathrm{C}(12)$ | $79.9(4)$ |
| $\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(12)$ | $108.2(3)$ |
| $\mathrm{C}(1)-\mathrm{C}(9)-\mathrm{C}(12)$ | $99.6(3)$ |
| $\mathrm{C}(11 \mathrm{~B})-\mathrm{C}(9)-\mathrm{C}(12)$ | $150.3(4)$ |
| $\mathrm{C}(14)-\mathrm{C}(13)-\mathrm{C}(1)$ | $112.84(16)$ |
| $\mathrm{O}(3)-\mathrm{C}(14)-\mathrm{O}(4)$ | $123.86(19)$ |
| $\mathrm{O}(3)-\mathrm{C}(14)-\mathrm{C}(13)$ | $125.54(19)$ |
| $\mathrm{O}(4)-\mathrm{C}(14)-\mathrm{C}(13)$ | $110.59(18)$ |
| $\mathrm{O}(4)-\mathrm{C}(15)-\mathrm{C}(16)$ | $110.4(2)$ |
| $\mathrm{C}(18)-\mathrm{C}(17)-\mathrm{C}(22)$ | $117.59(17)$ |
| $\mathrm{C}(18)-\mathrm{C}(17)-\mathrm{Si}(1)$ | $121.66(14)$ |
| $\mathrm{C}(22)-\mathrm{C}(17)-\mathrm{Si}(1)$ | $120.73(14)$ |
| $\mathrm{C}(19)-\mathrm{C}(18)-\mathrm{C}(17)$ | $119.93(19)$ |
| $\mathrm{C}(19)-\mathrm{C}(18)-\mathrm{C}(23)$ | $116.65(19)$ |
| $\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(23)$ | $123.42(18)$ |
| $\mathrm{C}(20)-\mathrm{C}(19)-\mathrm{C}(18)$ | $122.3(2)$ |
| $\mathrm{C}(21)-\mathrm{C}(20)-\mathrm{C}(19)$ | $117.8(2)$ |
| $\mathrm{C}(21)-\mathrm{C}(20)-\mathrm{C}(24)$ | $120.8(2)$ |
| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(24)$ | $121.4(2)$ |
| $\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(22)$ | $122.0(2)$ |
| $\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{C}(17)$ | $120.31(18)$ |
| $\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{C}(25)$ | $117.74(18)$ |
| $\mathrm{C}(17)-\mathrm{C}(22)-\mathrm{C}(25)$ | $121.92(17)$ |
| $\mathrm{C}(31)-\mathrm{C}(26)-\mathrm{C}(27)$ | $117.78(17)$ |
|  |  |


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

Table 4. Anisotropic displacement parameters ( $\AA^{2} \times 10^{3}$ ) 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: $-2 \pi^{2}\left[h^{2} a^{* 2} U^{11}+\ldots+2 h k a^{*} b^{*} U^{12}\right]$

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

Table 5. Hydrogen coordinates ( $\times 10^{4}$ ) and isotropic displacement parameters ( $\AA^{2} \times 10^{3}$ ) for Ethyl ( $3 R, 4 R, 5 R$ )-3-(dimesitylsilyl)-5-(2,2-dimethyl-propionyloxy)-4,6-dimethyl-hept-2eneoate.

|  | x | y | z | $\mathrm{U}(\mathrm{eq})$ |
| :--- | ---: | ---: | ---: | ---: |
|  |  |  |  |  |
| H(1A) | 5439 | 8441 | 2470 | 27 |
| H(2A) | 4383 | 9856 | 1873 | 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(10A) | 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) | 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) | $4279(17)$ | $8123(17)$ | $944(10)$ | $26(5)$ |

Table 6. Torsion angles [ ${ }^{\circ}$ ] for Ethyl ( $3 R, 4 R, 5 R$ )-3-(dimesitylsilyl)-5-(2,2-dimethyl-propionyloxy)-4,6-dimethyl-hept-2-eneoate.

| C(26)-Si(1)-C(1)-C(13) | -172.64(12) |
| :---: | :---: |
| $\mathrm{C}(17)-\mathrm{Si}(1)-\mathrm{C}(1)-\mathrm{C}(13)$ | -41.30(14) |
| $\mathrm{C}(26)-\mathrm{Si}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | 63.36(15) |
| $\mathrm{C}(17)-\mathrm{Si}(1)-\mathrm{C}(1)-\mathrm{C}(2)$ | -165.30(12) |
| $\mathrm{C}(13)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(7)$ | -38.2(2) |
| $\mathrm{Si}(1)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(7)$ | 82.58(17) |
| $\mathrm{C}(13)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | 89.05(19) |
| $\mathrm{Si}(1)-\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)$ | -150.13(13) |
| $\mathrm{C}(8)-\mathrm{O}(1)-\mathrm{C}(3)-\mathrm{C}(4)$ | -113.6(2) |
| $\mathrm{C}(8)-\mathrm{O}(1)-\mathrm{C}(3)-\mathrm{C}(2)$ | 121.90(19) |
| $\mathrm{C}(7)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{O}(1)$ | 62.5(2) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{O}(1)$ | -65.77(19) |
| $\mathrm{C}(7)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{C}(4)$ | -57.2(2) |
| $\mathrm{C}(1)-\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{C}(4)$ | 174.46(17) |
| $\mathrm{O}(1)-\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(5)$ | 63.0(2) |
| $\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(5)$ | -176.6(2) |
| $\mathrm{O}(1)-\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(6)$ | -174.2(2) |
| $\mathrm{C}(2)-\mathrm{C}(3)-\mathrm{C}(4)-\mathrm{C}(6)$ | -53.8(3) |
| $\mathrm{C}(3)-\mathrm{O}(1)-\mathrm{C}(8)-\mathrm{O}(2)$ | -5.0(3) |
| $\mathrm{C}(3)-\mathrm{O}(1)-\mathrm{C}(8)-\mathrm{C}(9)$ | 175.32(18) |
| $\mathrm{O}(2)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(12 \mathrm{~B})$ | -32.9(5) |
| $\mathrm{O}(1)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(12 \mathrm{~B})$ | 146.8(4) |
| $\mathrm{O}(2)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10)$ | 147.7(4) |
| $\mathrm{O}(1)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10)$ | -32.6(5) |
| $\mathrm{O}(2)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10 \mathrm{~B})$ | -172.0(4) |
| $\mathrm{O}(1)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(10 \mathrm{~B})$ | 7.7(4) |
| $\mathrm{O}(2)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(11)$ | 21.8(4) |
| $\mathrm{O}(1)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(11)$ | -158.5(3) |
| $\mathrm{O}(2)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(11 \mathrm{~B})$ | 83.9(4) |
| $\mathrm{O}(1)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(11 \mathrm{~B})$ | -96.4(3) |
| $\mathrm{O}(2)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(12)$ | -86.3(4) |
| $\mathrm{O}(1)-\mathrm{C}(8)-\mathrm{C}(9)-\mathrm{C}(12)$ | 93.4(3) |
| $\mathrm{C}(2)-\mathrm{C}(1)-\mathrm{C}(13)-\mathrm{C}(14)$ | -156.30(16) |
| $\mathrm{Si}(1)-\mathrm{C}(1)-\mathrm{C}(13)-\mathrm{C}(14)$ | 81.75(17) |
| $\mathrm{C}(15)-\mathrm{O}(4)-\mathrm{C}(14)-\mathrm{O}(3)$ | -2.7(3) |
| $\mathrm{C}(15)-\mathrm{O}(4)-\mathrm{C}(14)-\mathrm{C}(13)$ | 178.2(2) |
| $\mathrm{C}(1)-\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{O}(3)$ | 28.8(3) |
| $\mathrm{C}(1)-\mathrm{C}(13)-\mathrm{C}(14)-\mathrm{O}(4)$ | -152.21(17) |
| $\mathrm{C}(14)-\mathrm{O}(4)-\mathrm{C}(15)-\mathrm{C}(16)$ | 86.2(3) |
| $\mathrm{C}(26)-\mathrm{Si}(1)-\mathrm{C}(17)-\mathrm{C}(18)$ | -128.98(16) |
| $\mathrm{C}(1)-\mathrm{Si}(1)-\mathrm{C}(17)-\mathrm{C}(18)$ | 96.71(17) |
| $\mathrm{C}(26)-\mathrm{Si}(1)-\mathrm{C}(17)-\mathrm{C}(22)$ | 52.68(17) |
| $\mathrm{C}(1)-\mathrm{Si}(1)-\mathrm{C}(17)-\mathrm{C}(22)$ | -81.63(16) |
| $\mathrm{C}(22)-\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(19)$ | $1.2(3)$ |
| $\mathrm{Si}(1)-\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(19)$ | -177.17(16) |
| $\mathrm{C}(22)-\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(23)$ | -179.86(19) |
| $\mathrm{Si}(1)-\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(23)$ | $1.7(3)$ |
| $\mathrm{C}(17)-\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)$ | -0.9(3) |
| $\mathrm{C}(23)-\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)$ | -179.9(2) |
| $\mathrm{C}(18)-\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)$ | -0.6(4) |
| C(18)-C(19)-C(20)-C(24) | 178.8(2) |


| $\mathrm{C}(19)-\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(22)$ | $1.9(3)$ |
| :--- | :---: |
| $\mathrm{C}(24)-\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(22)$ | $-177.5(2)$ |
| $\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{C}(17)$ | $-1.5(3)$ |
| $\mathrm{C}(20)-\mathrm{C}(21)-\mathrm{C}(22)-\mathrm{C}(25)$ | $176.6(2)$ |
| $\mathrm{C}(18)-\mathrm{C}(17)-\mathrm{C}(22)-\mathrm{C}(21)$ | $-0.1(3)$ |
| $\mathrm{Si}(1)-\mathrm{C}(17)-\mathrm{C}(22)-\mathrm{C}(21)$ | $178.35(15)$ |
| $\mathrm{C}(18)-\mathrm{C}(17)-\mathrm{C}(22)-\mathrm{C}(25)$ | $-178.11(18)$ |
| $\mathrm{Si}(1)-\mathrm{C}(17)-\mathrm{C}(22)-\mathrm{C}(25)$ | $0.3(2)$ |
| $\mathrm{C}(7)-\mathrm{Si}(1)-\mathrm{C}(26)-\mathrm{C}(31)$ | $-110.44(17)$ |
| $\mathrm{C}(1)-\mathrm{Si}(1)-\mathrm{C}(26)-\mathrm{C}(31)$ | $20.1(2)$ |
| $\mathrm{C}(17)-\mathrm{Si}(1)-\mathrm{C}(26)-\mathrm{C}(27)$ | $68.23(16)$ |
| $\mathrm{C}(1)-\mathrm{Si}(1)-\mathrm{C}(26)-\mathrm{C}(27)$ | $-161.19(13)$ |
| $\mathrm{C}(31)-\mathrm{C}(26)-\mathrm{C}(27)-\mathrm{C}(28)$ | $1.0(3)$ |
| $\mathrm{Si}(1)-\mathrm{C}(26)-\mathrm{C}(27)-\mathrm{C}(28)$ | $-177.78(14)$ |
| $\mathrm{C}(31)-\mathrm{C}(26)-\mathrm{C}(27)-\mathrm{C}(32)$ | $-178.03(17)$ |
| $\mathrm{Si}(1)-\mathrm{C}(26)-\mathrm{C}(27)-\mathrm{C}(32)$ | $3.2(2)$ |
| $\mathrm{C}(26)-\mathrm{C}(27)-\mathrm{C}(28)-\mathrm{C}(29)$ | $-0.4(3)$ |
| $\mathrm{C}(32)-\mathrm{C}(27)-\mathrm{C}(28)-\mathrm{C}(29)$ | $178.68(19)$ |
| $\mathrm{C}(27)-\mathrm{C}(28)-\mathrm{C}(29)-\mathrm{C}(30)$ | $-0.3(3)$ |
| $\mathrm{C}(27)-\mathrm{C}(28)-\mathrm{C}(39)-\mathrm{C}(33)$ | $179.7(2)$ |
| $\mathrm{C}(28)-\mathrm{C}(29)-\mathrm{C}(30)-\mathrm{C}(1)$ | $0.4(3)$ |
| $\mathrm{C}(33)-\mathrm{C}(29)-\mathrm{C}(30)-\mathrm{C}(31)$ | $-179.6(2)$ |
| $\mathrm{C}(29)-\mathrm{C}(30)-\mathrm{C}(31)-\mathrm{C}(26)$ | $0.2(3)$ |
| $\mathrm{C}(29)-\mathrm{C}(30)-\mathrm{C}(31)-\mathrm{C}(34)$ | $-179.93(18)$ |
| $\mathrm{C}(27)-\mathrm{C}(26)-\mathrm{C}(31)-\mathrm{C}(30)$ | $-0.9(3)$ |
| $\mathrm{Si}(1)-\mathrm{C}(26)-\mathrm{C}(31)-\mathrm{C}(30)$ | $177.74(14)$ |
| $\mathrm{C}(27)-\mathrm{C}(26)-\mathrm{C}(31)-\mathrm{C}(34)$ | $179.22(17)$ |
| $\mathrm{Si}(1)-\mathrm{C}(26)-\mathrm{C}(31)-\mathrm{C}(34)$ | $-2.1(3)$ |

## References.

12. SMART Software Users Guide, Version 5.1, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
13. SAINT Software Users Guide, Version 6.0, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
14. Sheldrick, G. M. SADABS, Version 2.03, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 2000.
15. Sheldrick, G. M. SHELXTL Version 5.10, Bruker Analytical X-Ray Systems, Inc.; Madison, WI 1999.
16. International Tables for X-Ray Crystallography 1992, Vol. C., Dordrecht: Kluwer AcademicPublishers.

## Definitions:

$\mathrm{wR} 2=\left[\Sigma\left[\mathrm{w}\left(\mathrm{F}_{\mathrm{o}}{ }^{2}-\mathrm{F}_{\mathrm{c}}{ }^{2}\right)^{2}\right] / \Sigma\left[\mathrm{w}\left(\mathrm{F}_{\mathrm{o}}{ }^{2}\right)^{2}\right]^{1 / 2}\right.$
$\mathrm{R} 1=\Sigma| | \mathrm{F}_{\mathrm{o}}\left|-\left|\mathrm{F}_{\mathrm{c}}\right|\right| / \Sigma\left|\mathrm{F}_{\mathrm{o}}\right|$
Goof $=\mathrm{S}=\left[\Sigma\left[\mathrm{w}\left(\mathrm{F}_{\mathrm{o}}^{2}-\mathrm{F}_{\mathrm{c}}^{2}\right)^{2}\right] /(\mathrm{n}-\mathrm{p})\right]^{1 / 2}$ 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.

## References:

(1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K. Organometallics 1996, 15, 1518.
(2) Zigler, S. S.; Johnson, L. M.; West, R. J. Organomet. Chem. 1988, 341, 187-198.
(3) Roddick, D. M.; Heyn, R. H.; Tilley, T. D. Organometallics 1989, 8, 324-330.
(4) The anion readily quenched in the NMR solvent, so it is difficult to gauge its purity.
(5) Abiko, A.; Liu, J.-F.; Masamune, S. J. Org. Chem. 1996, 61, 2590-2591.
(6) Crimmins, M. T.; King, B. W.; Tabet, E. A.; Chaudhary, K. J. Org. Chem. 2001, 66, 894902.
(7) Fleming, I.; Jones, G. R.; Kindon, N. D.; Landais, Y.; Leslie, C. P.; Morgan, I. T.; Peukert, S.; Sarkar, A. K. J. Chem. Soc. Perkin Trans. I 1996, 1171-1196.
(8) Schmid, C. R.; Bradley, D. A. Synthesis 1992, 587-590.
(9) Takano, S.; Kurotaki, A.; Takahashi, M.; Ogasawara, K. Synthesis 1986, 403-406.
(10) The diastereoselectivity was determined from the silylated product, prior to addition of TFA, because the hydrolized product decomposes on the GC.
(11) Evans, D. A.; Tedrow, J. S.; Shaw, J. T.; Downey, C. W. J. Am. Chem. Soc. 2002, 124, 393393.
(12) Gung, B. W.; Melnick, J. P.; Wolf, M. A.; King, A. J. Org. Chem. 1995, 60, 1947-1951.
(13) Gung, B. W.; Melnick, J. P.; Wolf, M. A.; Marshall, J. A.; Beaudoin, S. J. Org. Chem. 1994, 59, 5609-5613.
(14) Rychnovsky, S. D.; Rogers, B.; Yang, G. J. Org. Chem. 1993, 58, 3511-3515.

