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## ACS Publications

# Enantioselective Synthesis of the Elaiophylin Aglycone 

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## Supporting Information

General Information: Melting points are uncorrected. Optical rotations were measured on a Jasco DIP-0181 digital polarimeter with a mercury lamp and reported as follows: $[\alpha]^{\circ} \mathrm{C} \lambda(c \mathrm{~g} / 100 \mathrm{ml}$, solvent). Infrared spectra were recorded on a Perkin Elmer model 1600 FT-IR spectrometer. ${ }^{1} \mathrm{H}$ NMR spectra were recorded on Bruker AM-500 ( 500 MHz ) or AM- 400 ( 400 MHz ) spectrometers. Chemical shifts are reported in ppm from tetramethylsilane with the solvent resonance as the internal standard (deuterochloroform: $\delta 7.26 \mathrm{ppm}$, benzene: $\delta 7.15 \mathrm{ppm}$ ). Data are reported as follows: chemical shift, multiplicity ( $\mathrm{s}=$ singlet, $\mathrm{d}=$ doublet, $t=$ triplet, $q=$ quartet, $b r=$ broad, $m=m u l t i p l e t$, coupling constants ( Hz ), integration, and assignment. Elaiophylin numbering ${ }^{1}$ is used for proton assignments of all intermediates. ${ }^{13} \mathrm{C}$ NMR spectra were recorded on Bruker AM- $500(125 \mathrm{MHz})$ or AM-400 ( 100 MHz ) spectrometers with complete proton decoupling. Chemical shifts are reported in ppm from tetramethylsilane with the solvent as the internal standard (deuterochloroform: $\delta 77.07 \mathrm{ppm}$, benzene: $\delta 128.0 \mathrm{ppm}$ ). Mass spectra were obtained on a JEOL AX-505 or SX-102 high resolution magnetic sector mass spectrometer by the Harvard University Mass Spectrometry Laboratory. Combustion analyses were performed by Atlantic Microlab (Norcross, GA). Analytical thin layer chromatography was performed on EM Reagent 0.25 mm silica gel 60-F plates. Flash chromatography was performed using EM silica gel 60 ( $230-240$ mesh). Solvents for extraction and chromatography were HPLC grade. Unless otherwise noted, all reactions were conducted in oven ( $80^{\circ} \mathrm{C}$ ) or flamedried glassware with magnetic stirring under an inert atmosphere of dry nitrogen. When necessary, solvents and reagents were dried prior to use. Deuterochloroform was stored over $4 \AA$ molecular sieves. Tetrahydrofuran (THF) and diethyl ether were distilled from potassium metal/benzophenone ketyl. Methanol was distilled from magnesium methoxide. Dichloromethane $\left(\mathrm{CH}_{2} \mathrm{Cl}_{2}\right), 2,6-\mathrm{lutidine}$, $N, N$-diisopropylethylamine, triethylamine, diisopropylamine, and 1,1,1,3,3,3-hexamethyldisilazane were distilled from calcium hydricle. Dimethylsulfoxide (DMSO) was distilled under reduced pressure from calcium hydride and stored over $4 \AA$ molecular sieves. Dichlorophenylborane, methacrolein, and oxalyl chloride were distilled prior to use. All other commercially obtained reagents were used as received.


Methyl (2R,3R)-2-ethyl-3-hydroxybutanoate. The ethylation of methyl ( $R$ )-3-hydroxybutanoate ${ }^{2}$ was performed according to the method of Seebach and co-workers. ${ }^{3}$ Purification via flash chromatography ( $30 \%$ EtOAc/hexanes) afforded an $82 \%$ yield of methyl ( $2 R, 3 R$ )-2-ethyl-3-hydroxybutanoate as a clear, colorless oil. TLC $R_{f}=0.62$ ( $50 \%$ EtOAc/hexanes); $[\alpha]_{365-14.2}{ }^{23}$ (c $1.0, \mathrm{CH}_{2} \mathrm{Cl}_{2}$ ); IR (neat) $3453,2968,2937,2879,1737,1460,1435,1379,1274$, $1240,1197,1171,1119,1093,1063,995,919,799 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 3.92\left(\mathrm{dq}, 1 \mathrm{H}, J=6.8,6.5 \mathrm{~Hz}, \mathrm{C}_{15}-\mathrm{H}\right), 3.72$ $\left(\mathrm{s}, 3 \mathrm{H}, \mathrm{OCH}_{3}\right), 2.47(\mathrm{~d}, J=7.3 \mathrm{~Hz}, 1 \mathrm{H}, \mathrm{OH}), 2.32\left(\mathrm{dt}, 1 \mathrm{H}, J=8.5,6.0 \mathrm{~Hz}, \mathrm{C}_{14}-\mathrm{H}\right), 1.68\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right), 1.21(\mathrm{~d}, 3 \mathrm{H}, J=6.5$ $\left.\mathrm{Hz}, \mathrm{C}_{15}-\mathrm{CH}_{3}\right), 0.92\left(\mathrm{t}, 3 \mathrm{H}, J=7.4 \mathrm{~Hz}, \mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 176.0,68.1,54.3,51.6,22.7,21.6,11.7$; Exact mass calcd. for $\mathrm{C}_{7} \mathrm{H}_{15} \mathrm{O}_{3}\left[(\mathrm{M}+\mathrm{H})^{+}\right]$: 147.1021 ; found: 147.1017 (EI).


Methyl (2R,3R)-2-ethyl-3-tert-butyldimethylsilyloxybutanoate. To a solution of methyl ( $2 R, 3 R$ )-2-ethyl-3hydroxybutanoate ( $458 \mathrm{mg}, 3.13 \mathrm{mmol}$ ) in 6 ml of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at $0{ }^{\circ} \mathrm{C}$ was added tert-butyldimethylsilyl trifluoromethanesulfonate ( $755 \mu \mathrm{l}, 3.29 \mathrm{mmol}$ ), followed by 2,6 -lutidine ( $438 \mu 1,3.76 \mathrm{mmol}$ ). After stirring for 1 h at $0{ }^{\circ} \mathrm{C}$, the reaction was quenched by the addition of $0.5 \mathrm{~N} \mathrm{HCl}(10 \mathrm{ml})$ and extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(3 \times 10 \mathrm{ml})$. The combined organic layers were washed with brine ( 10 ml ), dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated in vacuo. Purification via flash chromatography ( $5 \% \mathrm{EtOAc}$ /hexanes) afforded $800 \mathrm{mg}(98 \%)$ of methyl ( $2 R, 3 R$ )-2-ethyl-3-tert-butyldimethylsilyloxybutanoate as a clear, colorless oil. TLC $R_{f}=0.71\left(10 \%\right.$ EtOAc/hexanes); $[\alpha]_{365}^{23}-82.6^{\circ}\left(c 1.0, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; $\operatorname{IR}$ (neat) 2954, 2931, 2884, 2857, $1740,1473,1463,1446,1434,1378,1256,1195,1172,1118,1079,1001,977,832,776 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 3.96$ (dq, $\left.1 \mathrm{H}, J=7.8,6.2 \mathrm{~Hz}, \mathrm{C}_{15}-H\right), 3.66(\mathrm{~s}, 3 \mathrm{H}, \mathrm{OCH} 3), 2.31(\mathrm{ddd}, 1 \mathrm{H}, J=10.0,7.9,4.9 \mathrm{~Hz}, \mathrm{C} 14-H), 1.52\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right), 1.14$ (d, $\left.3 \mathrm{H}, J=6.2 \mathrm{~Hz}, \mathrm{C}_{15}-\mathrm{CH}_{3}\right), 0.87\left(\mathrm{t}, 3 \mathrm{H}, J=7.4 \mathrm{~Hz}, \mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH} 3\right), 0.85(\mathrm{~s}, 9 \mathrm{H}, \mathrm{SiC}(\mathrm{CH} 3) 3), 0.04\left(\mathrm{~s}, 3 \mathrm{H}\right.$, one of $\left.\mathrm{Si}\left(\mathrm{CH}_{3}\right) 2\right), 0.01$ (s, 3H, one of $\mathrm{Si}\left(\mathrm{CH}_{3}\right) 2$ ); ${ }^{13} \mathrm{C}$ NMR $\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 175.1,69.9,56.6,51.2,25.7,21.5,21.4,17.9,12.1,-4.2,-5.1$; Exact mass calcd. for $\mathrm{C}_{13} \mathrm{H}_{29} \mathrm{O}_{3} \mathrm{Si}\left[(\mathrm{M}+\mathrm{H})^{+}\right]$: 261.1886 ; found: $261.1888(\mathrm{CI})$.

(2S,3R)-2-ethyl-3-tert-butyldimethylsilyloxy-1-butanol. To a solution of methyl ( $2 R, 3 R$ )-2-ethyl-3-tertbutyldimethylsilyloxybutanoate ( $1.7 \mathrm{~g}, 6.53 \mathrm{mmol}$ ) in 10 ml of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at $-78{ }^{\circ} \mathrm{C}$ was added DIBAl- $\mathrm{H}(18.9 \mathrm{ml}, 1 \mathrm{M}$ in $\mathrm{CH}_{2} \mathrm{Cl}_{2}, 18.9 \mathrm{mmol}$ ) dropwise via syringe. After stirring for 1 h at $-78^{\circ} \mathrm{C}$, the reaction was warmed to $-40^{\circ} \mathrm{C}$ and stirred for an additional 0.5 h . The solution was then recooled to $-78^{\circ} \mathrm{C}$ and transferred via cannula to a solution of 1:1 $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ /saturated $\mathrm{Na} / \mathrm{K}$ tartrate $(50 \mathrm{ml})$ at $0{ }^{\circ} \mathrm{C}$. The mixture was warmed to ambient temperature and stirred for 0.5 h . Separation of the layers was followed by extraction with $\mathrm{Et}_{2} \mathrm{O}(2 \times 10 \mathrm{ml})$ The combined organic layers were dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated in vacuo. Purification via flash chromatography ( $20 \% \mathrm{EtOAc} / \mathrm{hexanes}$ ) afforded 1.51 g (quant.) of ( $2 \mathrm{~S}, 3 R$ )-2-ethyl-3-tert-butyldimethylsilyloxy-1-butanol as a clear, colorless oil. TLC $R_{f}=0.37$ ( $10 \% \mathrm{EtOAc} / \mathrm{hexanes}$ ); [ $\left.\alpha\right]_{365}^{23}-47.2^{\circ}\left(c 1.0, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; IR (neat) $3443,2957,2930,2884,2858,1472,1463,1376,1361,1255,1154,1108,1079,1032,1005,962,938,836,775,665 \mathrm{~cm}^{-1}$; ${ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 3.98\left(\mathrm{dd}, 1 \mathrm{H}, J=8.6,5.9 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C}_{13}-\mathrm{H}_{2}\right), 3.95\left(\mathrm{dd}, 1 \mathrm{H}, J=5.9,3.1 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C}_{13}-\mathrm{H}_{2}\right), 3.60(\mathrm{dq}$, $\left.1 \mathrm{H}, J=6.3,4.7 \mathrm{~Hz}, \mathrm{C}_{15}-H\right), 3.09$ (br. s, $\left.1 \mathrm{H}, \mathrm{OH}\right), 1.56\left(\mathrm{dq}, 1 \mathrm{H}, J=20.7,7.6 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH} 3\right), 1.43(\mathrm{dq}, 1 \mathrm{H}, J=20.7,7.6$ Hz , one of $\left.\mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right), 1.25\left(\mathrm{~d}, 3 \mathrm{H}, J=6.3 \mathrm{~Hz}, \mathrm{C}_{15}-\mathrm{CH}_{3}\right), 1.21\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{C}_{14}-\mathrm{H}\right), 0.95\left(\mathrm{t}, 3 \mathrm{H}, J=7.6 \mathrm{~Hz}, \mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right), 0.89(\mathrm{~s}$, $\left.9 \mathrm{H}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right)_{3}\right), 0.09\left(\mathrm{~s}, 6 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 72.9,62.4,48.0,25.8,22.5,22.0,17.9,12.0,-4.2,-5.0$; Exact mass calcd. for $\mathrm{C}_{12} \mathrm{H}_{29} \mathrm{O}_{2} \mathrm{Si}\left[(\mathrm{M}+\mathrm{H})^{+}\right]: 233.1937$; found: 233.1933 (FAB).

( $2 R, 3 R$ )-2-ethyl-3-tert-butyldimethylsilyloxy-1-butanal (5). To a solution of oxalyl chloride ( $30 \mu \mathrm{l}, 0.34 \mathrm{mmol}$ ) in 3 ml of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at $-78{ }^{\circ} \mathrm{C}$ was added dimethyl sulfoxide ( $50 \mu \mathrm{l}, 0.71 \mathrm{mmol}$ ) dropwise via syringe. After stirring for 10 $\min$ at $-78{ }^{\circ} \mathrm{C}$, a solution of ( $2 S, 3 R$ )-2-ethyl-3-tert-butyldimethylsilyloxy-1-butanol ( $50 \mathrm{mg}, 0.21 \mathrm{mmol}$ ) in 2 ml of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ was added dropwise via cannula. The solution was then stirred for 20 min at $-78{ }^{\circ} \mathrm{C}$, followed by the addition of triethylamine ( $200 \mu \mathrm{l}, 1.44 \mathrm{mmol}$ ). After stirring for 1 h at $-78^{\circ} \mathrm{C}$, the reaction mixture was poured into a solution of sat. $\mathrm{NH}_{4} \mathrm{Cl}$ $(10 \mathrm{ml})$ and stirred for 10 min at ambient temperature. The layers were separated and extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \times 5 \mathrm{ml})$. The combined organic layers were washed with brine, dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated in vacuo. Purification via flash chromatography ( $10 \% \mathrm{EtOAc} / \mathrm{hexanes}$ ) afforded 49.5 mg (quant.) of 5 as a clear, colorless oil. TLC $R_{f}=0.61$ ( $10 \%$ EtOAc/hexanes); $[\alpha]_{365}^{23}-63.8^{\circ}\left(c 1.0, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; IR (neat) $2958,2930,2884,2857,1710,1472,1463,1377,1256,1120,986,835,775 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H} \mathrm{NMR}$ $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 9.68\left(\mathrm{~d}, 1 \mathrm{H}, J=3.9 \mathrm{~Hz}, \mathrm{C}_{13}-H\right), 4.06\left(\mathrm{dq}, 1 \mathrm{H}, J=6.3,4.8 \mathrm{~Hz}, \mathrm{C}_{15}-H\right), 2.08\left(\mathrm{dt}, 1 \mathrm{H}, J=13.2,4.8 \mathrm{~Hz}, \mathrm{C}_{14}-\mathrm{H}\right)$, $1.72\left(\mathrm{ddq}, 1 \mathrm{H}, J=13.2,7.5,5.0 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right), 1.53\left(\mathrm{ddq}, 1 \mathrm{H}, J=13.2,7.5,5.0 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right), 1.20(\mathrm{~d}, 3 \mathrm{H}, J$ $\left.=6.3 \mathrm{~Hz}, \mathrm{C}_{15}-\mathrm{CH}_{3}\right), 0.90\left(\mathrm{t}, 3 \mathrm{H}, J=7.5 \mathrm{~Hz}, \mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right), 0.86\left(\mathrm{~s}, 9 \mathrm{H}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right) 3\right), 0.06\left(\mathrm{~s}, 3 \mathrm{H}\right.$, one of $\left.\mathrm{Si}\left(\mathrm{CH}_{3}\right) 2\right), 0.05(\mathrm{~s}, 3 \mathrm{H}$, one of $\left.\mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 205.7,68.9,61.1,25.8,22.3,19.6,18.0,11.9,-4.1,-5.0$.

( $4 R, 5 S, 6 R$ )-2,5-diethyl-4-hydroxy-6-tert-butyldimethylsilyloxyheptene (7). Aldehyde 5 ( $175 \mathrm{mg}, 0.76$ mmol ) and ethallylstannane $6(682 \mathrm{mg}, 1.9 \mathrm{mmol})$ were combined in 10 ml of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and cooled to $-78{ }^{\circ} \mathrm{C}$. Boron trifluoride diethyl etherate ( $96 \mu \mathrm{l}, 0.84 \mathrm{mmol}$ ) was added dropwise via syringe, and the mixture was stirred for 45 min at $-78{ }^{\circ} \mathrm{C}$. The reaction was quenched by the addition of sat. $\mathrm{NaHCO}_{3}(10 \mathrm{ml})$ and extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \times 10 \mathrm{ml})$. The combined organic layers were dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated in vacuo. GLC analysis of the unpurified reaction mixture (DB-1701 column, $50-130^{\circ} \mathrm{C} @ 1.5^{\circ} \mathrm{C} / \mathrm{min}, 15 \mathrm{psi}$ ) revealed a $92: 8$ ratio of the desired Felkin isomer ( $\mathrm{t}_{\mathrm{r}}=62.42 \mathrm{~min}$ ) to anti-Felkin isomer ( $\mathrm{t}_{\mathrm{r}}=60.53 \mathrm{~min}$ ). Purification via flash chromatography ( $1 \% \mathrm{EtOAc} / \mathrm{hexanes}$ ) afforded $203 \mathrm{mg}(89 \%)$ of the major diastereomer as a clear, colorless oil. TLC $R_{f}=0.75$ ( $10 \% \mathrm{EtOAc} / \mathrm{hexanes}$ ); $[\alpha]_{365}^{23}-22.0^{\circ}$ ( $c 0.8$, $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ); IR (neat) $3521,3076,2959,2932,2885,2858,1645,1463,1377,1362,1254,1107,1035,964,899,835,776 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 4.80\left(\mathrm{~s}, 1 \mathrm{H}\right.$, one of $\left.\mathrm{C}_{11}-\mathrm{CH}_{2}\right), 4.79\left(\mathrm{~s}, 1 \mathrm{H}\right.$, one of $\left.\mathrm{C}_{11}-\mathrm{CH}_{2}\right), 4.32\left(\mathrm{t}, 1 \mathrm{H}, \mathrm{J}=7.0 \mathrm{~Hz}, \mathrm{C}_{13}-\mathrm{H}\right), 4.18(\mathrm{dq}$, $\left.1 \mathrm{H}, J=6.4,2.0 \mathrm{~Hz}, \mathrm{C}_{15}-H\right), 3.65(\mathrm{~s}, 1 \mathrm{H}, \mathrm{OH}), 2.34\left(\mathrm{dd}, 1 \mathrm{H}, J=13.9,7.2 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C}_{12}-\mathrm{H}_{2}\right), 2.13(\mathrm{dd}, 1 \mathrm{H}, J=13.9,6.9 \mathrm{~Hz}$, one of $\left.\mathrm{C}_{12}-\mathrm{H}_{2}\right), 2.05\left(\mathrm{q}, 2 \mathrm{H}, J=7.4 \mathrm{~Hz}, \mathrm{C}_{10}-\mathrm{H}_{2}\right), 1.61-1.42\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH} 3\right), 1.25\left(\mathrm{~d}, 3 \mathrm{H}, J=6.4 \mathrm{~Hz}, \mathrm{C}_{15}-\mathrm{CH} 3\right), 1.04(\mathrm{t}, 3 \mathrm{H}, J=$ $\left.7.4 \mathrm{~Hz}, \mathrm{C}_{10}-\mathrm{CH}_{3}\right), 0.93\left(\mathrm{t}, 3 \mathrm{H}, J=7.5 \mathrm{~Hz}, \mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right), 0.88\left(\mathrm{~s}, 10 \mathrm{H}, \mathrm{SiC}\left(\mathrm{CH}_{3}\right) 3\right.$ and $\left.\mathrm{C}_{14}-\mathrm{H}\right), 0.10(\mathrm{~s}, 3 \mathrm{H}$, one of $\mathrm{Si}(\mathrm{CH} 3) 2), 0.09$ (s, 3H, one of $\left.\mathrm{Si}\left(\mathrm{CH}_{3}\right)_{2}\right)$; ${ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 148.7,110.2,70.1,68.4,49.0,41.3,28.9,25.9,22.3,17.9,16.9,12.6,12.4$, $-4.1,-5.1$; Exact mass calcd. for $\mathrm{C}_{17} \mathrm{H}_{37} \mathrm{O}_{2} \mathrm{Si}\left[(\mathrm{M}+\mathrm{H})^{+}\right]: 301.2563$; found: 301.2565 (CI).

( $4 R, 5 R, 6 R$ )-2,5-diethyl-4,6-dihydroxyheptene. To a solution of $7(72.5 \mathrm{mg}, 0.24 \mathrm{mmol})$ in 1 ml of THF at Me ambient temperature was added tetrabutylammonium fluoride ( $480 \mu \mathrm{l}, 1 \mathrm{M}$ solution in THF, 0.48 mmol ). After stirring for 10 min , the reaction mixture was diluted with 10 ml of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and quenched with 1 N HCl ( 10 ml ). Separation of the layers was followed by extraction with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \times 10 \mathrm{ml})$. The combined organic layers were dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated in vacuo. Purification via flash chromatography ( $50 \% \mathrm{EtOAc} / \mathrm{hexanes}$ ) afforded $43 \mathrm{mg}(96 \%)$ of ( $4 R, 5 R, 6 R$ )-2,5-diethyl-4,6-dihydroxyheptene as a clear, colorless oil. TLC $R_{f}=0.61$ ( $50 \%$ EtOAc/hexanes); $[\alpha] 365-8.36^{\circ}\left(c 1.0, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right.$ ); IR (neat) $3346,3077,2968,2932,2873,1646,1458,1428,1370,1326,1246,1101$, $1065,1021,890 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H} \operatorname{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 4.86\left(\mathrm{q}, 1 \mathrm{H}, J=1.5 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C}_{11}-\mathrm{CH}_{2}\right), 4.82\left(\mathrm{~d}, 1 \mathrm{H}, J=0.6 \mathrm{~Hz}\right.$, one of $\mathrm{C}_{11}-$ $\mathrm{CH}_{2}$ ) , 4.14 (ddd, $\left.1 \mathrm{H}, J=9.4,4.1,2.0 \mathrm{~Hz}, \mathrm{C}_{13}-H\right), 3.98(\mathrm{dq}, 1 \mathrm{H}, J=6.4,5.4 \mathrm{~Hz}, \mathrm{C} 15-H), 3.13(\mathrm{br} . \mathrm{s}, 2 \mathrm{H}$, both $\mathrm{O} H), 2.29(\mathrm{dd}, 1 \mathrm{H}, J=$
$13.8,9.4 \mathrm{~Hz}$, one of $\left.\mathrm{C}_{12}-\mathrm{H}_{2}\right), 2.16\left(\mathrm{dd}, 1 \mathrm{H}, \mathrm{J}=13.8,4.1 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C}_{12}-\mathrm{H}_{2}\right), 2.11-1.98\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{C}_{10}-\mathrm{H}_{2}\right), 1.54-1.42\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{C}_{14}-\mathrm{H}\right)$, $1.38-1.29\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right), 1.22\left(\mathrm{~d}, 3 \mathrm{H}, J=6.4 \mathrm{~Hz}, \mathrm{C}_{15}-\mathrm{CH}_{3}\right), 1.02\left(\mathrm{t}, 3 \mathrm{H}, J=7.4 \mathrm{~Hz}, \mathrm{C}_{10}-\mathrm{CH} 3\right), 0.94(\mathrm{t}, 3 \mathrm{H}, J=7.3 \mathrm{~Hz}$, $\left.\left.\mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right) ;{ }^{13} \mathrm{C} \mathrm{NMR} \mathrm{(100} \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 148.3,111.0,69.4,68.8,49.3,40.3,28.6,22.2,18.7,12.6,12.3$; Exact mass calcd. for $\mathrm{C}_{11} \mathrm{H}_{23} \mathrm{O}_{2}\left[(\mathrm{M}+\mathrm{H})^{+}\right]: 187.1698$; found: 187.1698 ( EI ).

( $4 R, 5 R, 6 R$ )-2,2-di-tert-butyl-5-ethyl-6-(2-ethylallyl)-4-methyl-1,3-dioxa-2-silacyclohexane. To a solution of ( $4 R, 5 R, 6 R$ )-2,5-diethyl-4,6-dihydroxyheptene ( $600 \mathrm{mg}, 3.22 \mathrm{mmol}$ ) in 30 ml of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at $0{ }^{\circ} \mathrm{C}$ was added 2,6-lutidine ( $1.1 \mathrm{ml}, 9.66 \mathrm{mmol}$ ). After stirring for 2 min , di-tert-butylsilyl bis(trifluoromethanesulfonate) ( 1.5 $\mathrm{ml}, 4.19 \mathrm{mmol}$ ) was added dropwise via syringe. The mixture was stirred for 1 h at $0^{\circ} \mathrm{C}$, followed by quenching with sat. $\mathrm{NaHCO}_{3}(20 \mathrm{ml})$. Separation of the layers was followed by extraction with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \mathrm{x}$ 20 ml ). The combined organic layers were dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated in vacuo. Purification via flash chromatography ( $5 \%$ EtOAc/hexanes) afforded $957 \mathrm{mg}(91 \%$ ) of ( $4 R, 5 R, 6 R$ )-2,2-di-tert-butyl-5-ethyl-6-(2-ethylallyl)-4-methyl-1,3-dioxa-2-silacyclohexane as a clear, colorless oil. TLC $R_{f}=0.89(5 \% \mathrm{EtOAc} /$ hexanes $) ;[\alpha]_{365}^{23}+193.0^{\circ}\left(c 1.0, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; IR (neat) $3083,2967,2934,2890,2859,1646,1475,1461,1376,1363,1211,1138,1120,1077,1052,984,961,888,825,781,735,646 \mathrm{~cm}^{-1}$; ${ }^{1} \mathrm{H} \mathrm{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 4.87\left(\mathrm{~s}, 1 \mathrm{H}\right.$, one of $\left.\mathrm{C}_{11}-\mathrm{CH}_{2}\right), 4.83\left(\mathrm{~s}, 1 \mathrm{H}\right.$, one of $\left.\mathrm{C}_{11}-\mathrm{CH}_{2}\right), 4.34$ (ddd, $1 \mathrm{H}, J=10.2,4.6,3.0 \mathrm{~Hz}$, $\left.\mathrm{C}_{13}-H\right), 4.08\left(\mathrm{dq}, 1 \mathrm{H}, J=8.1,6.2 \mathrm{~Hz}, \mathrm{C}_{15}-H\right), 2.28\left(\mathrm{dd}, 1 \mathrm{H}, J=14.8,10.2 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C}_{12}-H_{2}\right), 2.17(\mathrm{dd}, 1 \mathrm{H}, J=14.8,3.0 \mathrm{~Hz}$, one of $\left.\mathrm{C}_{12}-\mathrm{H}_{2}\right), 2.11\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{C}_{10}-\mathrm{H}_{2}\right), 1.75\left(\mathrm{~m}, 1 \mathrm{H}\right.$, one of $\left.\mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH} 3\right), 1.47\left(\mathrm{~m}, 1 \mathrm{H}\right.$, one of $\left.\mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right), 1.21(\mathrm{~d}, 3 \mathrm{H}, J=6.2 \mathrm{~Hz}$, $\left.\mathrm{C}_{15}-\mathrm{CH} 3\right), 1.13\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{C}_{14}-\mathrm{H}\right), 1.06\left(\mathrm{t}, 3 \mathrm{H}, J=7.4 \mathrm{~Hz}, \mathrm{C}_{10}-\mathrm{CH}_{3}\right), 1.00(\mathrm{~s}, 9 \mathrm{H}$, one of $\mathrm{SiC}(\mathrm{CH} 3) 3), 0.99(\mathrm{~s}, 9 \mathrm{H}$, one of $\mathrm{SiC}(\mathrm{CH} 3) 3)$, $0.91\left(t, 3 H, J=7.4 \mathrm{~Hz}, \mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 149.0,109.9,72.3,70.0,50.0,37.9,28.8,27.9,27.4,23.3$, 21.3, 21.1, 20.8, 12.5, 12.3; Exact mass calcd. for $\mathrm{C}_{19} \mathrm{H}_{38} \mathrm{O}_{2} \mathrm{Si}$ : 326.2641 ; found: 326.2633 (EI).


1-[(4R, 5R, 6R)-2,2-di-tert-butyl-5-ethyl-4-methyl-1,3-dioxa-2-silacyclohex-6-yl]-2-butanone (8). To a solution of ( $4 R, 5 R, 6 R$ )-2,2-di-tert-butyl-5-ethyl-6-(2-ethylallyl)-4-methyl-1,3-dioxa-2-silacyclohexane (110 $\mathrm{mg}, 0.337 \mathrm{mmol}$ ) in 3.5 ml of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ and 1.5 ml of methanol at $-78^{\circ} \mathrm{C}$ was added a drop of pyridine and 5 mg Sudan III. Ozone was bubbled through the reaction mixture for 5 min turning the indicator from red to yellow. The flask was then purged with nitrogen and dimethyl sulfide ( $250 \mu 1,3.37 \mathrm{mmol}$ ) was added. The mixture was warmed to ambient temperature and stirred for 3 h , followed by concentration in vacuo. Purification via flash chromatography ( $5 \%$ EtOAc/hexanes) afforded $99.8 \mathrm{mg}(90 \%)$ of 8 as a clear, colorless oil. TLC $R_{f}=0.58$ ( $10 \%$ EtOAc/hexanes); $[\alpha]_{365}^{23}+180.1{ }^{\circ}\left(c 1.0, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; IR (neat) $2969,2935,2891,2859,1717,1475,1461,1377,1364,1218,1137,1076,1039,980,825$, $786,646 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 4.72$ (ddd, $\left.1 \mathrm{H}, J=10.9,4.9,2.6 \mathrm{~Hz}, \mathrm{C}_{13}-H\right), 4.01\left(\mathrm{dq}, 1 \mathrm{H}, J=8.5,6.2 \mathrm{~Hz}, \mathrm{C}_{15}-\mathrm{H}\right)$, $2.73\left(\mathrm{dd}, 1 \mathrm{H}, J=14.8,10.9 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C}_{12}-\mathrm{H}_{2}\right), 2.58\left(\mathrm{dq}, 1 \mathrm{H}, J=17.9,7.3 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C}_{10}-\mathrm{H}_{2}\right), 2.53(\mathrm{dq}, 1 \mathrm{H}, J=17.9$, 7.3 Hz , one of $\left.\mathrm{C}_{10}-\mathrm{H}_{2}\right), 2.33\left(\mathrm{dd}, 1 \mathrm{H}, J=14.8,2.6 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C}_{12}-\mathrm{H}_{2}\right), 1.79\left(\mathrm{~m}, 1 \mathrm{H}\right.$, one of $\left.\mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right), 1.47\left(\mathrm{~m}, 1 \mathrm{H}\right.$, one of $\left.\mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right)$, $1.21\left(\mathrm{~d}, 3 \mathrm{H}, J=6.2 \mathrm{~Hz}, \mathrm{C}_{15}-\mathrm{CH}_{3}\right), 1.07\left(\mathrm{t}, 3 \mathrm{H}, J=7.3 \mathrm{~Hz}, \mathrm{C}_{10}-\mathrm{CH}_{3}\right), 1.02\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{C}_{14}-H\right), 0.98\left(\mathrm{~s}, 9 \mathrm{H}\right.$, one of $\left.\mathrm{SiC}\left(\mathrm{CH}_{3}\right) 3\right), 0.97(\mathrm{~s}$, 9 H , one of $\left.\mathrm{SiC}\left(\mathrm{CH}_{3}\right) 3\right), 0.92\left(\mathrm{t}, 3 \mathrm{H}, J=7.1 \mathrm{~Hz}, \mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 210.4,71.3,69.8,49.5,45.0,36.2$, 27.7, 27.4, 23.1, 21.3, 21.2, 20.7, 12.1, 7.7; Exact mass calcd. for $\mathrm{C}_{18} \mathrm{H}_{37} \mathrm{O}_{3} \mathrm{Si}\left[(\mathrm{M}+\mathrm{H})^{+}\right]: 329.2512$; found: 329.2526 (CI).


Bn
(4R)-4-benzyl-3-[( $2 R, 3 S$ )-3-hydroxy-2,4-dimethyl-4-pentenoyl]-2-oxazolidinone. To a solution of imide $9^{4}$ $\left(16 \mathrm{~g}, 68.6 \mathrm{mmol}\right.$ ) in 150 ml of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at $0{ }^{\circ} \mathrm{C}$ was added di- $n$-butylboron triflate ${ }^{5}(20.5 \mathrm{ml}, 82.3 \mathrm{mmol})$ dropwise via syringe followed by $N, N$-diisopropylethylamine ( $15.5 \mathrm{ml}, 89.2 \mathrm{mmol}$ ). The reaction mixture was cooled to $-78{ }^{\circ} \mathrm{C}$, and methacrolein ( $12.8 \mathrm{ml}, 154.7 \mathrm{mmol}$ ) was added dropwise from an addition funnel. The solution was stirred at $-78^{\circ} \mathrm{C}$ for 20 min followed by warming to $0{ }^{\circ} \mathrm{C}$ and stirring for 1 h . The reaction was quenched by the addition of 100 ml of pH 7 phosphate buffer followed by 150 ml of methanol. After $5 \mathrm{~min}, 100 \mathrm{ml}$ of $30 \%$ aqueous hydrogen peroxide in 200 ml of methanol was added dropwise in order to maintain a temperature $<10{ }^{\circ} \mathrm{C}$ (caution: initial reaction is highly exothermic). After stirring for 1 h at $0^{\circ} \mathrm{C}$, the reaction mixture was concentrated in vacuo. The resulting mixture was extracted with $\mathrm{Et}_{2} \mathrm{O}$ ( $3 \times 200 \mathrm{ml}$ ). The combined organic layers were washed with brine, dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated in vacuo. Purification via flash chromatography ( $20 \% \mathrm{EtOAc} /$ hexanes) afforded $17.98 \mathrm{~g}(86 \%)$ of ( $4 R$ )-4-benzyl-3-[(2R 23 , 3S)-3-hydroxy-2,4-dimethyl-4-pentenoyl]-2-oxazolidinone as a clear, colorless oil. TLC $R_{f}=0.23$ (30\% EtOAc/hexanes); [ $\left.\alpha\right]$ ] ${ }_{365}^{23}$ $-214.4{ }^{\circ}$ ( c $1.0, \mathrm{CH}_{2} \mathrm{Cl}_{2}$ ); IR (neat) $3513,3028,2977,2938,1779,1698,1453,1385,1209,1108,986,904,762,746,702 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.36-7.20\left(\mathrm{~m}, 5 \mathrm{H}, \mathrm{Ph} \mathrm{H}_{5}\right), 5.13\left(\mathrm{~d}, 1 \mathrm{H}, J=0.8 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C}_{6}-\mathrm{CH} 2\right), 4.98(\mathrm{dd}, 1 \mathrm{H}, J=3.0,1.5 \mathrm{~Hz}$, one of $\mathrm{C}_{6}-\mathrm{CH}_{2}$ ), 4.71 (dddd, $1 \mathrm{H}, J=16.6,9.5,3.3,3.1 \mathrm{~Hz}, \mathrm{CHN}$ ), 4.42 (br. $\left.\mathrm{s}, 1 \mathrm{H}, \mathrm{C} 7-\mathrm{H}\right), 4.22\left(\mathrm{dd}, 1 \mathrm{H}, J=16.6,9.1 \mathrm{~Hz}\right.$, one of $\left.\mathrm{CH}_{2} \mathrm{O}\right), 4.19$ (dd, $1 \mathrm{H}, J=9.1,3.1 \mathrm{~Hz}$, one of $\mathrm{CH}_{2} \mathrm{O}$ ), $3.97\left(\mathrm{dq}, 1 \mathrm{H}, J=7.0,3.1 \mathrm{~Hz}, \mathrm{C}_{8}-H\right), 3.27(\mathrm{dd}, 1 \mathrm{H}, J=13.4,3.3 \mathrm{~Hz}$, one of PhCH ), $2.94(\mathrm{~d}$, $1 \mathrm{H}, J=3.2 \mathrm{~Hz}, \mathrm{OH}), 2.80\left(\mathrm{dd}, 1 \mathrm{H}, J=13.4,9.5 \mathrm{~Hz}\right.$, one of $\left.\mathrm{PhCH}_{2}\right), 1.73\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}_{6}-\mathrm{CH} 3\right), 1.19\left(\mathrm{~d}, 3 \mathrm{H}, J=7.0 \mathrm{~Hz}, \mathrm{C}_{8}-\mathrm{CH} 3\right) ;{ }^{13} \mathrm{C}$ NMR ( $100 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 177.1,153.0,143.7,135.1,129.5,129.0,127.5,111.9,73.9,66.3,55.3,40.1,37.8,19.5,10.0$; Exact mass calcd. for $\mathrm{C}_{17} \mathrm{H}_{21} \mathrm{NO}_{4}$ : 303.1471 ; found: 303.1457 (EI).

(4R)-4-benzyl-3-[(2R,3S)-2,4-dimethyl-3-(triethylsilyloxy)-4-pentenoyl]-2-oxazolidinone. To a solution of (4R)-4-benzyl-3-[( $2 R, 3 S$ )-3-hydroxy-2,4-dimethyl-4-pentenoyl]-2-oxazolidinone ( $17.88 \mathrm{~g}, 58.9 \mathrm{mmol}$ ) in 150 ml of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at $0^{\circ} \mathrm{C}$ was added 2,6-lutidine ( $8.2 \mathrm{ml}, 70.7 \mathrm{mmol}$ ) followed by triethylsilyl trifluoromethanesulfonate ( $14 \mathrm{ml}, 61.9 \mathrm{mmol}$ ). The reaction mixture was stirred for 0.5 h at $0{ }^{\circ} \mathrm{C}$ and then quenched by the addition of 30 ml of methanol. The solution was concentrated in vacuo and then taken up in $\mathrm{Et}_{2} \mathrm{O}$ ( 200 ml ). The resulting mixture was washed with sat. $\mathrm{NH}_{4} \mathrm{Cl}$, which was then extracted with additional $\mathrm{Et}_{2} \mathrm{O}(2 \times 100 \mathrm{ml})$. The combined organic layers were dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated in vacuo. Purification via flash chromatography ( $10 \%$ EtOAc/hexanes) afforded $22.65 \mathrm{~g}(92 \%)$ of (4R)-4-benzyl-3-[(2R,3S)-2,4-dimethyl-3-(triethylsilyloxy)-4-pentenoyl]-2-oxazolidinone as a clear, colorless oil. TLC $R_{f}=0.66\left(20 \%\right.$ EtOAc/hexanes); [ $\alpha{ }^{23} 35-182.8^{\circ}\left(c 1.0, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right.$ ); IR (neat) 2955, 2912, 2877, 1782, $1701,1454,1380,1209,1105,1088,1011,975,902,856,835,743,726 ., 702 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H} \mathrm{NMR}(500 \mathrm{MHz}, \mathrm{CDCl} 3) 87.35-7.21(\mathrm{~m}, 5 \mathrm{H}$, $\mathrm{Ph} \mathrm{H}_{5}$ ) $4.94\left(\mathrm{~d}, 1 \mathrm{H}, J=0.8 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C}_{6}-\mathrm{CH}_{2}\right), 4.83\left(\mathrm{~s}, 1 \mathrm{H}\right.$, one of $\left.\mathrm{C}_{6}-\mathrm{CH}_{2}\right), 4.58$ (dddd, $1 \mathrm{H}, J=16.3,9.7,3.2,2.5 \mathrm{~Hz}, \mathrm{CHN}$ ), 4.38 $(\mathrm{d}, 1 \mathrm{H}, J=6.8 \mathrm{~Hz}, \mathrm{C} 7-H), 4.16\left(\mathrm{dd}, 1 \mathrm{H}, J=9.0,2.5 \mathrm{~Hz}\right.$, one of $\left.\mathrm{CH}_{2} \mathrm{O}\right), 4.13(\mathrm{dd}, 1 \mathrm{H}, J=16.3,9.0 \mathrm{~Hz}$, one of CH 2 O$), 4.04(\mathrm{dq}, 1 \mathrm{H}, J$ $\left.=6.8,6.8 \mathrm{~Hz}, \mathrm{C}_{8}-\mathrm{H}\right), 3.28\left(\mathrm{dd}, 1 \mathrm{H}, J=13.3,3.2 \mathrm{~Hz}\right.$, one of $\left.\mathrm{PhCH}_{2}\right), 2.76(\mathrm{dd}, 1 \mathrm{H}, J=13.3,9.7 \mathrm{~Hz}$, one of PhCH 2$), 1.72(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C} 6-$ $\left.\mathrm{CH}_{3}\right), 1.23\left(\mathrm{~d}, 3 \mathrm{H}, J=6.8 \mathrm{~Hz}, \mathrm{C} 8-\mathrm{CH}_{3}\right), 0.95\left(\mathrm{t}, 9 \mathrm{H}, J=8.0 \mathrm{~Hz}, \mathrm{Si}\left(\mathrm{CH}_{2} \mathrm{CH}_{3}\right) 3\right), 0.58\left(\mathrm{~m}, 6 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{2} \mathrm{CH} 3\right) 3\right) ;{ }^{13} \mathrm{C} \mathrm{NMR}(100 \mathrm{MHz}$, $\mathrm{CDCl}_{3}$ ) $\delta 175.0,153.1,146.0,135.4,129.5,129.0,127.4,112.5,77.2,66.1,55.7,42.5,37.8,17.7,12.7,6.9,4.8$; Exact mass calcd. for $\mathrm{C}_{23} \mathrm{H}_{36} \mathrm{NO}_{4} \mathrm{Si}\left[(\mathrm{M}+\mathrm{H})^{+}\right]: 418.2414$; found: $418.2400(\mathrm{CI})$.

(2S, 3R)-2,4-dimethyl-3-(triethylsilyloxy)-4-penten-1-ol. To a solution of (4R)-4-benzyl-3-[(2R,3S)-2,4-dimethyl-3-(triethylsilyloxy)-4-pentenoyl]-2-oxazolidinone ( $22.0 \mathrm{~g}, 52.68 \mathrm{mmol}$ ) in 250 ml of Et 2 O and 1.04 ml of water ( 57.7 mmol ) at ambient temperature was added lithium borohydride ( $29.0 \mathrm{ml}, 2 \mathrm{M}$ in THF, 58 mmol ) via syringe (gas evolution). After stirring for 3 h , the cloudy, white solution was quenched by the addition of saturated $\mathrm{Na} / \mathrm{K}^{+}$tartrate solution ( 150 ml ). The mixture was then stirred for 20 min before the layers were separated and extracted with $\mathrm{Et}_{2} \mathrm{O}$ ( $2 \times 100 \mathrm{ml}$ ). The combined organic layers were dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated in vacuo. Purification via flash chromatography ( $30 \% \mathrm{Et}_{2} \mathrm{O}$ /pentane) afforded $11.2 \mathrm{~g}(87 \%)$ of $(2 S, 3 R)$-2,4-dimethyl-3-(triethylsilyloxy)-4-penten-1-ol as a clear, colorless oil, along with $8.1 \mathrm{~g}(87 \%)$ recovered oxazolidinone. TLC $R_{f}=0.65\left(30 \% \mathrm{Et}_{2} \mathrm{O} /\right.$ pentane $)$; $[\alpha]_{365}^{23}+52.6^{\circ}\left(c 1.0, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)$; IR (neat) $3350,2955,2913,2877,1652,1457,1414,1379,1239,1117,1078,1027,1010,973,900,831,740,725 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 4.93\left(\mathrm{~d}, 1 \mathrm{H}, J=1.1 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C}_{6}-\mathrm{CH}_{2}\right), 4.88\left(\mathrm{~d}, 1 \mathrm{H}, J=1.1 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C}_{6}-\mathrm{CH}_{2}\right), 4.08\left(\mathrm{~d}, 1 \mathrm{H}, J=4.3 \mathrm{~Hz}, \mathrm{C}_{7}-\right.$ $H), 3.58\left(\mathrm{ddd}, 1 \mathrm{H}, J=9.0,5.4,4.4 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C} 9-\mathrm{H}_{2}\right), 3.48\left(\mathrm{ddd}, 1 \mathrm{H}, J=9.0,8.3,4.4 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C} 9-\mathrm{H}_{2}\right), 2.05(\mathrm{t}, 1 \mathrm{H}, J=4.4 \mathrm{~Hz}$, OH ), 1.86 (dddq, $1 \mathrm{H}, J=8.3,5.7,5.4,4.3 \mathrm{~Hz}, \mathrm{C} 8-H), 1.72\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}_{6}-\mathrm{CH}_{3}\right), 0.95\left(\mathrm{t}, 9 \mathrm{H}, J=6.3 \mathrm{~Hz}, \mathrm{Si}\left(\mathrm{CH}_{2} \mathrm{CH} 3\right) 3\right), 0.87(\mathrm{~d}, 3 \mathrm{H}, J=$ $\left.5.7 \mathrm{~Hz}, \mathrm{C}_{8}-\mathrm{CH}_{3}\right), 0.60\left(\mathrm{q}, 6 \mathrm{H}, J=6.3 \mathrm{~Hz}, \mathrm{Si}\left(\mathrm{CH}_{2} \mathrm{CH}_{3}\right) 3\right) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 146.5,112.0,78.6,66.1,39.4,18.7,12.1$, 6.9, 4.9; Exact mass calcd. for $\mathrm{C}_{13} \mathrm{H}_{28} \mathrm{O}_{2} \mathrm{Si}$ : 244.1859 ; found: 244.1862 (EI).

(3R, 4S)-2,4-dimethyl-3-(triethylsilyloxy)-5-(triphenylmethoxy)-pentene (10). To a solution of (2S, 3R)-2,4-dimethyl-3-(triethylsilyloxy)-4-penten-1-ol ( $1.2 \mathrm{~g}, 4.91 \mathrm{mmol}$ ) in 7 ml of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at ambient temperature was added triethylamine ( $1.23 \mathrm{ml}, 8.84 \mathrm{mmol}$ ) followed by triphenylmethyl chloride ( $1.64 \mathrm{~g}, 5.89 \mathrm{mmol}$ ) and 4dimethylaminopyridine ( $30 \mathrm{mg}, 0.25 \mathrm{mmol}$ ). After stirring for 6 h , the solution was diluted with hexanes ( 25 ml ), filtered through a plug of celite, and concentrated in vacuo. Purification via flash chromatography ( $2 \% \mathrm{EtOAc} / \mathrm{hexanes}$ ) afforded 2.2 g ( $92 \%$ ) of 10 as a clear, colorless oil. TLC $R_{f}=0.90$ ( $4 \%$ EtOAc/hexanes); [ $\left.\alpha\right]_{365}^{23}+19.4^{\circ}$ (c $1.0, \mathrm{CH}_{2} \mathrm{Cl}_{2}$ ); IR (neat) 3086,3059 , $3022,2955,2935,2912,2875,1650,1597,1490,1448,1413,1373,1238,1125,1059,1004,898,831,743,704,632 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H} \operatorname{NMR}$ $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.49-7.23\left(\mathrm{~m}, 15 \mathrm{H},\left(\mathrm{Ph} \mathrm{H}_{5}\right) 3\right), 4.83\left(\mathrm{~s}, 1 \mathrm{H}\right.$, one of $\left.\mathrm{C}_{6}-\mathrm{CH}_{2}\right), 4.74\left(\mathrm{~s}, 1 \mathrm{H}\right.$, one of $\left.\mathrm{C}_{6}-\mathrm{CH}_{2}\right), 4.09(\mathrm{~d}, 1 \mathrm{H}, \mathrm{J}=5.5$ $\left.\mathrm{Hz}, \mathrm{C}_{7}-\mathrm{H}\right), 3.08\left(\mathrm{dd}, 1 \mathrm{H}, J=9.0,5.7 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C} 9-\mathrm{H}_{2}\right), 2.94\left(\mathrm{dd}, 1 \mathrm{H}, J=9.0,6.8 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C} 9-\mathrm{H}_{2}\right), 1.87(\mathrm{dq}, 1 \mathrm{H}, J=6.8,5.7 \mathrm{~Hz}$, $\left.\mathrm{C}_{8}-\mathrm{H}\right), 1.62\left(\mathrm{~s}, 3 \mathrm{H}, \mathrm{C}_{6}-\mathrm{CH}_{3}\right), 0.99\left(\mathrm{~d}, 3 \mathrm{H}, J=6.8 \mathrm{~Hz}, \mathrm{C}_{8}-\mathrm{CH}_{3}\right), 0.91\left(\mathrm{t}, 9 \mathrm{H}, J=7.9 \mathrm{~Hz}, \mathrm{Si}\left(\mathrm{CH}_{2} \mathrm{CH} 3\right) 3\right), 0.60-0.45(\mathrm{~m}, 6 \mathrm{H}$, $\mathrm{Si}\left(\mathrm{CH}_{2} \mathrm{CH}_{3}\right) 3$ ); ${ }^{13} \mathrm{C} \mathrm{NMR}^{\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right)}$ § $146.4,144.6,128.8,127.7,126.8,111.5,86.4,77.2,66.2,37.9,18.2,12.3,7.0,4.9$; Exact mass calcd. for $\mathrm{C}_{32} \mathrm{H}_{42} \mathrm{O}_{2} \mathrm{Si}$ : 486.2954 ; found: 486.2966 (EI).

( $2 S, 3 S, 4 S$ )-2,4-dimethyl-3-(triethylsilyloxy)--5-(triphenylmethoxy)-pentanol. To a solution of 10 (113 mg, 0.23 mmol ) in 3 ml of THF at $0^{\circ} \mathrm{C}^{\circ}$ was added a solution of $9-\mathrm{BBN}$ dimer ( $91 \mathrm{mg}, 0.37 \mathrm{mmol}$ ) in 1 ml THF via cannula. After stirring for 3 h at $0{ }^{\circ} \mathrm{C}$, the reaction was quenched by the addition of 0.5 ml of ethanol and 0.5 ml pH 7 phosphate buffer. 0.5 ml of $30 \%$ aqueous hydrogen peroxide solution was added slowly, and the mixture was stirred for 4 h , allowing the bath to warm from $0^{\circ} \mathrm{C}$ to ambient temperature. Saturated aqueous sodium sulfite solution ( 10 ml ) was added. The layers were separated and extracted with $\mathrm{Et}_{2} \mathrm{O}(3 \times 10 \mathrm{ml})$. The combined organic layers were dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated in vacuo. ${ }^{1} \mathrm{H}$ NMR analysis of the unpurified reaction mixture ( 400 MHz ) revealed only one detectable diastereomer. Purification via flash chromatography ( $5 \% \mathrm{EtOAc} / \mathrm{hexanes}$ ) afforded 104 mg ( $89 \%$ ) of ( $2 S, 3 S, 4 S$ )-2,4-dimethyl-3-
(triethylsilyloxy)--5-(triphenylmethoxy)-pentanol as a clear, colorless oil. TLC $R_{f}=0.52$ ( $20 \%$ EtOAc/hexanes); [ $\alpha$ ] ${ }_{365}^{23}-35.6^{\circ}$ (c 1.0 , $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ ); IR (neat) $3442,3086,3058,3022,2956,2934,2911,2875,1597,1490,1448,1414,1380,1239,1222,1088,1064,1033$, $1007,763,743,706,632 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR ( $400 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 7.45-7.22(\mathrm{~m}, 15 \mathrm{H},(\mathrm{Ph} H 5) 3), 3.78(\mathrm{dd}, 1 \mathrm{H}, J=6.3,3.3 \mathrm{~Hz}, \mathrm{C} 7-\mathrm{H})$, $3.56\left(\mathrm{t}, 2 \mathrm{H}, J=5.0 \mathrm{~Hz}, \mathrm{C} 5-\mathrm{H}_{2}\right), 3.03\left(\mathrm{dd}, 1 \mathrm{H}, J=9.0,6.6 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C} 9-\mathrm{H}_{2}\right), 2.99\left(\mathrm{dd}, 1 \mathrm{H}, J=9.0,6.7 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C} 9-\mathrm{H}_{2}\right), 2.51(\mathrm{t}$, $1 \mathrm{H}, J=5.0 \mathrm{~Hz}, \mathrm{OH}), 1.98(\mathrm{dq}, 1 \mathrm{H}, J=6.8,3.3 \mathrm{~Hz}, \mathrm{C} 8-H), 1.73\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{C}_{6}-H\right), 0.96\left(\mathrm{~d}, 3 \mathrm{H}, J=6.9 \mathrm{~Hz}, \mathrm{C}_{8}-\mathrm{CH}_{3}\right), 0.95(\mathrm{~d}, 3 \mathrm{H}, J=7.0$ $\left.\mathrm{Hz}, \mathrm{C}_{6}-\mathrm{CH}_{3}\right), 0.87\left(\mathrm{t}, 9 \mathrm{H}, \mathrm{J}=7.8 \mathrm{~Hz}, \mathrm{Si}\left(\mathrm{CH}_{2} \mathrm{CH}_{3}\right) 3\right), 0.54-0.38\left(\mathrm{~m}, 6 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{2} \mathrm{CH}_{3}\right) 3\right) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 144.3$, $128.8,127.8,127.0,86.6,78.1,66.4,66.2,38.7,38.2,15.5,12.2,7.0,5.2$; Exact mass calcd. for $\mathrm{C}_{32} \mathrm{H}_{44} \mathrm{O}_{3} \mathrm{SiNa}\left[(\mathrm{M}+\mathrm{Na})^{+}\right]$: 527.2957; found: 527.2962 (FAB, m-nitrobenzyl alcohol, added NaI ).

( $2 S, 3 S, 4 S$ )-2,4-dimethyl-3-(triethylsilyloxy)--5-(triphenylmethoxy)-pentanal (11). To a solution of oxalyl chloride ( $2.25 \mathrm{ml}, 25.65 \mathrm{mmol}$ ) in 100 ml of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at $-78{ }^{\circ} \mathrm{C}$ was added dimethyl sulfoxide ( $3.75 \mathrm{ml}, 52.9$ mmol ) dropwise via syringe. After stirring for 10 min at $-78{ }^{\circ} \mathrm{C}$, a solution of $(2 S, 3 S, 4 S)$-2,4-dimethyl-3-(triethylsilyloxy)--5-(triphenylmethoxy)-pentanol ( $8.09 \mathrm{~g}, 16.0 \mathrm{mmol}$ ) in 25 ml of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ was added dropwise via cannula. The solution was then stirred for 20 min at $-78^{\circ} \mathrm{C}$, followed by the addition of triethylamine ( $15.0 \mathrm{ml}, 107.4 \mathrm{mmol}$ ). After stirring for 1 h at $-78{ }^{\circ} \mathrm{C}$, the reaction mixture was poured into a solution of sat. $\mathrm{NH}_{4} \mathrm{Cl}(100 \mathrm{ml})$ and stirred for 10 min at ambient temperature. The layers were separated and extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \times 50 \mathrm{ml})$. The combined organic layers were washed with brine, dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated in vacuo. Purification via flash chromatography (5\% EtOAc/hexanes) afforded $7.9 \mathrm{~g}(98 \%)$ of 11 as a clear, colorless oil. TLC $R_{f}=0.75(10 \% \mathrm{EtOAc} /$ hexanes $) ;\left[\alpha_{b 65}^{23}-136.6^{8}\left(c 1.0, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)\right.$; IR (neat) $3086,3058,3023,2956,2935,2911,2876,2730,2707,1727,1597,1490,1456,1448,1152,1115,1087,1067,1036,1009,763,744$, $707,632 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 9.66(\mathrm{~d}, 1 \mathrm{H}, J=2.3 \mathrm{~Hz}, \mathrm{C} 5-H), 7.41-7.18\left(\mathrm{~m}, 15 \mathrm{H},\left(\mathrm{Ph} \mathrm{H}_{5}\right) 3\right), 4.01(\mathrm{dd}, 1 \mathrm{H}, J=6.3$, $\left.3.1 \mathrm{~Hz}, \mathrm{C}_{7}-\mathrm{H}\right), 3.03\left(\mathrm{dd}, 1 \mathrm{H}, J=9.1,6.7 \mathrm{~Hz}\right.$, one of $\mathrm{C}_{9}-\mathrm{H}_{2}$ ), $3.00\left(\mathrm{dd}, 1 \mathrm{H}, J=9.1,6.9 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C}_{9}-\mathrm{H}_{2}\right), 2.46(\mathrm{ddq}, 1 \mathrm{H}, J=7.0,3.1$, $\left.2.3 \mathrm{~Hz}, \mathrm{C}_{6}-H\right), 1.91(\mathrm{dq}, 1 \mathrm{H}, J=6.8,3.3 \mathrm{~Hz}, \mathrm{C} 8-H), 1.00\left(\mathrm{~d}, 3 \mathrm{H}, J=7.0 \mathrm{~Hz}, \mathrm{C}_{6}-\mathrm{CH}_{3}\right), 0.91\left(\mathrm{~d}, 3 \mathrm{H}, J=6.8 \mathrm{~Hz}, \mathrm{C}_{8}-\mathrm{CH} 3\right), 0.80(\mathrm{t}, 9 \mathrm{H}$, $\left.J=8.0 \mathrm{~Hz}, \mathrm{Si}\left(\mathrm{CH}_{2} \mathrm{CH} 3\right) 3\right), 0.45-0.33\left(\mathrm{~m}, 6 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{2} \mathrm{CH}_{3}\right) 3\right) ;{ }^{3}{ }^{3} \mathrm{C} \mathrm{NMR}\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 204.9,144.2,128.8,127.8,127.0$, 86.7, $74.8,66.2,50.5,38.0,11.8,6.9,5.2$; Anal. calcd. for $\mathrm{C}_{32} \mathrm{H}_{42} \mathrm{O}_{3} \mathrm{Si}: \mathrm{C}, 76.45 ; \mathrm{H}, 8.42$; found: $\mathrm{C}, 76.40 ; \mathrm{H}, 8.47$.


Ethyl (2E, 4E, 6S , 7S, 8S )-6,8-dimethyl-7-(triethylsilyloxy)-9-(triphenylmethoxy)-2,4nonadienoate. To a solution of $1,1,1,3,3,3$-hexamethyldisilazane ( $3.33 \mathrm{ml}, 15.8 \mathrm{mmol}$ ) in 75 ml of THF at $-78^{\circ} \mathrm{C}$ was added $n$-butyllithium ( $6.3 \mathrm{ml}, 2.5 \mathrm{M}$ in hexanes, 15.75 mmol ) dropwise via syringe. After stirring for 15 min at $-78{ }^{\circ} \mathrm{C}$, triethyl 4 -phosphonocrotonate ( $3.5 \mathrm{ml}, 15.8 \mathrm{mmol}$ ) was added dropwise via syringe. The reaction mixture was then stirred for 20 min at $-78^{\circ} \mathrm{C}$, followed by the dropwise cannula addition of a solution of $11(7.8 \mathrm{~g}, 15.5 \mathrm{mmol})$ in 50 ml of THF. The reaction mixture was stirred for 11 h allowing the bath to warm from $-78^{\circ} \mathrm{C}$ to ambient temperature. The reaction was quenched by the addition of sat. $\mathrm{NH}_{4} \mathrm{Cl}(100 \mathrm{ml})$ and extracted with $\mathrm{Et}_{2} \mathrm{O}(2 \times 50 \mathrm{ml})$. The combined organic layers were washed with brine, dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated in vacuo. ${ }^{1} \mathrm{H}$ NMR analysis of the unpurified reaction mixture ( $500 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) revealed a $92: 8$ ratio of $E, E: Z, E$ isomers. Purification via flash chromatography ( $5 \%$ ${ }_{23} \mathrm{EtOAc} / \mathrm{hexanes}$ ) afforded $7.875 \mathrm{~g}(85 \%)$ of the major diastereomer as a clear, colorless oil. TLC $R_{f}=0.72(20 \% \mathrm{EtOAc} / \mathrm{hexanes}) ;[\alpha]$
 1239, 1224, 1140, 1095, 1062, 1034, 1002, 744, 707, 632 $\mathrm{cm}^{-1}$; ${ }^{1} \mathrm{H} \mathrm{NMR}\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.43-7.22\left(\mathrm{~m}, 15 \mathrm{H},\left(\mathrm{Ph} \mathrm{H}_{5}\right) 3\right.$ ), 7.20 (dd, $\left.1 \mathrm{H}, J=15.3,10.9 \mathrm{~Hz}, \mathrm{C}_{3}-H\right), 6.06\left(\mathrm{dd}, 1 \mathrm{H}, J=15.3,8.4 \mathrm{~Hz}, \mathrm{C}_{5}-H\right), 5.93\left(\mathrm{dd}, 1 \mathrm{H}, J=15.3,10.9 \mathrm{~Hz}, \mathrm{C}_{4}-H\right), 5.72(\mathrm{~d}, 1 \mathrm{H}, J=15.3$ $\left.\mathrm{Hz}, \mathrm{C}_{2}-H\right), 4.21\left(\mathrm{q}, 2 \mathrm{H}, J=7.1 \mathrm{~Hz}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 3.67\left(\mathrm{t}, 1 \mathrm{H}, J=4.5 \mathrm{~Hz}, \mathrm{C}_{7}-H\right), 3.01\left(\mathrm{dd}, 1 \mathrm{H}, J=8.9,5.8 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C} 9-\mathrm{H}_{2}\right), 2.91$ (dd, $1 \mathrm{H}, J=8.9,6.7 \mathrm{~Hz}$, one of $\mathrm{C} 9-\mathrm{H}_{2}$ ), $2.27(\mathrm{~m}, 1 \mathrm{H}, \mathrm{C} 6-H), 1.86(\mathrm{~m}, 1 \mathrm{H}, \mathrm{C} 8-H), 1.30\left(\mathrm{t}, 3 \mathrm{H}, J=7.1 \mathrm{~Hz}, \mathrm{OCH}_{2} \mathrm{CH}_{3}\right), 0.99(\mathrm{~d}, 3 \mathrm{H}, J$ $\left.=6.9 \mathrm{~Hz}, \mathrm{C}_{6}-\mathrm{CH}_{3}\right), 0.97\left(\mathrm{~d}, 3 \mathrm{H}, J=6.9 \mathrm{~Hz}, \mathrm{C}_{8}-\mathrm{CH}_{3}\right), 0.86\left(\mathrm{t}, 9 \mathrm{H}, J=8.0 \mathrm{~Hz}, \mathrm{Si}\left(\mathrm{CH}_{2} \mathrm{CH}_{3}\right) 3\right), 0.49-0.40\left(\mathrm{~m}, 6 \mathrm{H}, \mathrm{Si}\left(\mathrm{CH}_{2} \mathrm{CH}_{3}\right) 3\right) ;{ }^{13} \mathrm{C}$ NMR ( $125 \mathrm{MHz}, \mathrm{CDCl}_{3}$ ) $\delta 167.3,147.2,145.2,144.4,128.8,128.0,127.7,126.9,119.4,86.4,77.2,66.3,60.2,41.8,38.2,17.8,14.4$, 13.0, 7.1, 5.4; Exact mass calcd. for $\mathrm{C}_{38} \mathrm{H}_{50} \mathrm{O}_{4} \mathrm{SiNa}\left[(\mathrm{M}+\mathrm{Na})^{+}\right]$: 621.3376 ; found: 621.3360 ( FAB , $m$-nitrobenzyl alcohol, added $\mathrm{NaI})$.


Ethyl ( $2 E, 4 E, 6 S, 7 S, 8 S$ )-7-hydroxy-6,8-dimethyl-9-(triphenylmethoxy)-2,4-nonadienoate (12). $\mathrm{CO}_{2}$ Et To a solution of Ethyl ( $2 E, 4 E, 6 S, 7 S, 8 S$ )-6,8-dimethyl-7-(triethylsilyloxy)-9-(triphenylmethoxy)-2,4-nonadienoate ( $950 \mathrm{mg}, 1.59 \mathrm{mmol}$ ) in 20 ml of THF at $0{ }^{\circ} \mathrm{C}$ in a Nalgene tube was added 3.0 ml of pyridinium hydrofluoride. After stirring for 4 h at $0^{\circ} \mathrm{C}$, the reaction was quenched by the addition of sat. $\mathrm{NaHCO}_{3}(30 \mathrm{ml})$ and extracted with $\mathrm{Et}_{2} \mathrm{O}(2 \times 20 \mathrm{ml})$. The combined organic layers were washed with brine, dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated in vacuo. Purification via flash chromatography ( $10 \% \mathrm{EtOAc} / \mathrm{hexanes}$ ) afforded 715 mg ( $93 \%$ ) of $\mathbf{1 2}$ as a white foam. TLC $R_{f}=0.36(20 \%$ EtOAc/hexanes $) ;\left[\alpha{ }_{165-146.9}{ }^{\circ}\left(c 1.0, \mathrm{CH}_{2} \mathrm{Cl}_{2}\right)\right.$; IR (neat) $3504,3086,3056,3022,2973,2929$, $2873,1710,1639,1616,1490,1448,1367,1302,1261,1223,1140,1033,1002,764,746,706,648,632 \mathrm{~cm}^{-1} ;{ }^{1} \mathrm{H} \mathrm{NMR}(400 \mathrm{MHz}$, $\left.\mathrm{CDCl}_{3}\right) \delta 7.39-7.16\left(\mathrm{~m}, 16 \mathrm{H},\left(\mathrm{Ph}_{5}\right) 3\right.$ and $\left.\mathrm{C}_{3}-H\right), 6.06\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{C} 5-H\right.$ and $\left.\mathrm{C}_{4}-H\right), 5.72\left(\mathrm{~d}, 1 \mathrm{H}, J=15.3 \mathrm{~Hz}, \mathrm{C}_{2}-H\right), 4.13(\mathrm{q}, 2 \mathrm{H}, J=$
$7.1 \mathrm{~Hz}, \mathrm{OCH}_{2} \mathrm{CH}_{3}$ ), 3.48 (ddd, $\left.1 \mathrm{H}, J=6.2,4.7,3.0 \mathrm{~Hz}, \mathrm{C} 7-H\right), 3.21\left(\mathrm{dd}, 1 \mathrm{H}, J=9.1,5.3 \mathrm{~Hz}\right.$, one of $\mathrm{C} 9-\mathrm{H}_{2}$ ), $3.05(\mathrm{dd}, 1 \mathrm{H}, J=9.1$, 4.3 Hz , one of $\left.\mathrm{C}_{9}-\mathrm{H}_{2}\right), 2.34(\mathrm{~d}, 1 \mathrm{H}, J=3.0 \mathrm{~Hz}, \mathrm{OH}), 2.27\left(\mathrm{~m}, 1 \mathrm{H}, \mathrm{C}_{6}-H\right), 1.79(\mathrm{~m}, 1 \mathrm{H}, \mathrm{C} 8-H), 1.23\left(\mathrm{t}, 3 \mathrm{H}, J=7.1 \mathrm{~Hz}, \mathrm{OCH}_{2} \mathrm{CH} 3\right)$, $1.00\left(\mathrm{~d}, 3 \mathrm{H}, J=7.0 \mathrm{~Hz}, \mathrm{C}_{6}-\mathrm{CH}_{3}\right), 0.90\left(\mathrm{~d}, 3 \mathrm{H}, J=6.8 \mathrm{~Hz}, \mathrm{C}_{8}-\mathrm{CH}_{3}\right) ;{ }^{13}{ }^{3} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 167.2,146.8,144.9,143.9$, $128.7,128.6,127.9,127.1,119.9,86.9,76.9,67.4,60.2,40.7,35.8,16.9,14.4,10.8$; Exact mass calcd. for $\mathrm{C}_{32} \mathrm{H}_{36} \mathrm{O}_{4} \mathrm{Na}\left[(\mathrm{M}+\mathrm{Na})^{+}\right]$: 507.2.511; found: 507.2505 (FAB, m-nitrobenzyl alcohol, added NaI).

( $2 E, 4 E, 6 S, 7 S, 8 S$ )-7-hydroxy-6,8-dimethyl-9-(triphenylmethoxy)-2,4-nonadienoic acid (13). ${ }^{H}$ The hydrolysis of ester 12 was performed according to the method of Seebach and co-workers. ${ }^{6}$ Purification via flash chromatography ( $50 \%$ EtOAc/hexanes) afforded a $98 \%$ yield of 13 as a white foam. TLC $R_{f}=0.30$ ( $60 \%$ EtOAc/hexanes); The following spectral data are consistent with previously reported values: ${ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.44-7.21\left(\mathrm{~m}, 16 \mathrm{H},\left(\mathrm{Ph} \mathrm{H}_{5}\right) 3\right.$ and $\left.\mathrm{C}_{3}-\mathrm{H}\right), 6.16\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{C}_{5}-\mathrm{H}\right.$ and $\left.\mathrm{C}_{4}-\mathrm{H}\right)$, $5.77\left(\mathrm{~d}, 1 \mathrm{H}, J=15.3 \mathrm{~Hz}, \mathrm{C}_{2}-H\right), 3.55\left(\mathrm{dd}, 1 \mathrm{H}, J=7.8,3.2 \mathrm{~Hz}, \mathrm{C}_{7}-H\right), 3.27\left(\mathrm{dd}, 1 \mathrm{H}, J=9.1,5.2 \mathrm{~Hz}\right.$, one of $\left.\mathrm{C} 9-\mathrm{H}_{2}\right), 3.12(\mathrm{dd}, 1 \mathrm{H}, J=$ $9.1,4.2 \mathrm{~Hz}$, one of $\left.\mathrm{C} 9-\mathrm{H}_{2}\right), 2.34\left(\mathrm{dq}, 1 \mathrm{H}, J=7.4,7.0 \mathrm{~Hz}, \mathrm{C}_{6}-\mathrm{H}\right), 2.05\left(\mathrm{~s}, 1 \mathrm{H}, \mathrm{C}_{7}-\mathrm{OH}\right), 1.85(\mathrm{~m}, 1 \mathrm{H}, \mathrm{C} 8-H), 1.06(\mathrm{~d}, 3 \mathrm{H}, J=7.0 \mathrm{~Hz}$, $\left.\mathrm{C}_{6}-\mathrm{CH}_{3}\right), 0.97\left(\mathrm{~d}, 3 \mathrm{H}, J=6.8 \mathrm{~Hz}, \mathrm{C}_{8}-\mathrm{CH}_{3}\right) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 171.9,148.3,147.3,143.9,128.7,128.4,128.0,127.1$, $118.9,86.9,77.3,67.4,40.8,35.8,16.9,10.8$; Exact mass calcd. for $\mathrm{C}_{30} \mathrm{H}_{32} \mathrm{O}_{4} \mathrm{Na}\left[(\mathrm{M}+\mathrm{Na})^{+}\right]$: 479.2198 ; found: 479.2189 (FAB, $m$ nitrobenzyl alcohol, added NaI ).

(3E, 5E, 7S , 8S, $11 E, 13 E, 15 S, 16 S$, )-8,16-bis[(1S)-1-triphenylmethoxymethylethyl]-7,15-dimethyl-1,9-dioxacyclohexadeca-3,5,11,13-tetraene-2,10-dione (14). To a solution of 13 ( $995 \mathrm{mg}, 2.18 \mathrm{mmol}$ ) in 50 ml of toluene at ambient temperature was added triethylamine ( 910 $\mu \mathrm{l}, 6.54 \mathrm{mmol})$. After stirring for $2 \mathrm{~min}, ~ 2,4,6$-trichlorobenzoyl chloride ( $360 \mu \mathrm{l}, 2.29 \mathrm{mmol}$ ) was added dropwise via syringe. The solution was stirred for 1 h at ambient temperature, followed by the addition of 4-dimethylaminopyridine ( $27 \mathrm{mg}, 0.22 \mathrm{mmol}$ ). After stirring for 45 min , the reaction was quenched by the addition of 1 M sodium bisulfate solution ( 50 ml ) and extracted with $\mathrm{Et}_{2} \mathrm{O}$ ( $3 \times 50 \mathrm{ml}$ ). The combined organic layers were washed with sat. $\mathrm{NaHCO}_{3}$, dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated in vacuo. Purification via flash chromatography ( $10 \%$ EtOAc/hexanes) afforded 595 mg ( $62 \%$ ) of 14 as a white, crystalline solid. TLC $R_{f}=0.63(20 \% \mathrm{EtOAc} / \mathrm{hexanes})$; The following spectral data are consistent with previously reported values: ${ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 7.46-7.20\left(\mathrm{~m}, 30 \mathrm{H},\left(\mathrm{Ph} H_{5}\right) 3\right), 6.91\left(\mathrm{dd}, 2 \mathrm{H}, J=15.3,11.2 \mathrm{~Hz}, \mathrm{C}_{3}-H\right), 5.95(\mathrm{dd}, 2 \mathrm{H}, J=15.0,11.2 \mathrm{~Hz}$, $\left.\mathrm{C}_{4}-H\right), 5.64(\mathrm{dd}, 2 \mathrm{H}, J=15.0,9.9 \mathrm{~Hz}, \mathrm{C} 5-H), 5.49\left(\mathrm{~d}, 2 \mathrm{H}, J=15.3 \mathrm{~Hz}, \mathrm{C}_{2}-H\right), 5.01(\mathrm{dd}, 2 \mathrm{H}, J=10.3,1.4 \mathrm{~Hz}, \mathrm{C} 7-H), 3.08(\mathrm{dd}, 2 \mathrm{H}, J$ $=9.2,7.7 \mathrm{~Hz}$, one of each $\left.\mathrm{C} 9-\mathrm{H}_{2}\right), 3.00\left(\mathrm{dd}, 2 \mathrm{H}, J=9.2,6.5 \mathrm{~Hz}\right.$, one of each $\left.\mathrm{C} 9-\mathrm{H}_{2}\right), 2.41(\mathrm{~m}, 2 \mathrm{H}, \mathrm{C} 6-\mathrm{H}), 1.98(\mathrm{br} . \mathrm{q}, 2 \mathrm{H}, J=6.6 \mathrm{~Hz}$, $\left.\mathrm{C}_{8}-H\right), 1.02\left(\mathrm{~d}, 6 \mathrm{H}, J=6.6 \mathrm{~Hz}, \mathrm{C}_{6}-\mathrm{CH}_{3}\right), 0.89\left(\mathrm{~d}, 6 \mathrm{H}, J=6.9 \mathrm{~Hz}, \mathrm{C}_{8}-\mathrm{CH}_{3}\right) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 167.4,145.2,144.5$, $144.3,128.9,128.0,127.8,126.9,121.4,86.6,76.4,66.0,41.9,34.0,15.8,10.3$; Exact mass calcd. for $\mathrm{C}_{60} \mathrm{H}_{60} \mathrm{O}_{6} \mathrm{Na}\left[(\mathrm{M}+\mathrm{Na})^{+}\right]$: 899.4288; found: 899.4281 (FAB, m-nitrobenzyl alcohol, added NaI ).

( $3 E, 5 E, 7 S, 8 S, 11 E, 13 E, 15 S, 16 S$,)-8,16-bis[(1S)-1-hydroxymethylethyl]-7,15-dimethylOH 1,9-dioxacyclohexadeca-3,5,11,13-tetraene-2,10-dione (15). The tritlyl deprotection of 14 was performed according to the method of Seebach and co-workers. ${ }^{6}$ Purification via flash chromatography ( $50 \% \mathrm{EtOAc} /$ hexanes) afforded a $65 \%$ yield of 15 as a white, crystalline solid. TLC $R_{f}=0.27$ ( $60 \% \mathrm{EtOAc} /$ hexanes); The following spectral data are consistent with previously reported values: ${ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 6.96\left(\mathrm{dd}, 2 \mathrm{H}, J=15.3,11.2 \mathrm{~Hz}, \mathrm{C}_{3}-H\right), 6.10$ (dd, $\left.2 \mathrm{H}, J=15.0,11.2 \mathrm{~Hz}, \mathrm{C}_{4}-H\right), 5.67\left(\mathrm{~d}, 2 \mathrm{H}, J=15.3 \mathrm{~Hz}, \mathrm{C}_{2}-H\right.$ ), 5.63 (dd, $2 \mathrm{H}, J=15.0,9.7$ $\left.\mathrm{Hz}, \mathrm{C}_{5}-\mathrm{H}\right), 4.80\left(\mathrm{dd}, 2 \mathrm{H}, J=10.3,2.0 \mathrm{~Hz}, \mathrm{C}_{7}-\mathrm{H}\right.$ ) , 3.47 (br. s, 2 H , one of each $\mathrm{C}_{9}-\mathrm{H}_{2}$ ), $3.34\left(\mathrm{t}, 2 \mathrm{H}, J=10.9 \mathrm{~Hz}\right.$, one of each $\mathrm{C} 9-\mathrm{H}_{2}$ ), 2.78 (br. s, 2H, OH), 2.52 (ddq, $\left.2 \mathrm{H}, J=10.3,9.7,6.7 \mathrm{~Hz}, \mathrm{C}_{6}-H\right), 2.13(\mathrm{ddq}, 2 \mathrm{H}, J=7.3,6.9,2.0 \mathrm{~Hz}, \mathrm{C} 8-H), 1.04(\mathrm{~d}, 6 \mathrm{H}, J=6.7 \mathrm{~Hz}$, $\left.\mathrm{C}_{6}-\mathrm{CH}_{3}\right), 0.85\left(\mathrm{~d}, 6 \mathrm{H}, \mathrm{J}=6.9 \mathrm{~Hz}, \mathrm{C}_{8}-\mathrm{CH}_{3}\right) ;{ }^{13} \mathrm{C}$ NMR $\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 169.1,144.9,144.3,131.8,121.3,76.8,64.7,41.0,35.5$, 15.2, 9.1; Exact mass calcd. for $\mathrm{C}_{22} \mathrm{H}_{32} \mathrm{O}_{6} \mathrm{Na}\left[(\mathrm{M}+\mathrm{Na})^{+}\right]: 415.2097$; found: 415.2091 ( $\mathrm{FAB}, m$-nitrobenzyl alcohol, added NaI ).

(3E, $5 E, 7 S, 8 S, \quad 11 E, 13 E, 15 S, 16 S,)-8,16$-bis[(1R)-1-formylethyl]-7,15-dimethyl-1,9-dioxacyclohexadeca-3,5,11,13-tetraene-2,10-dione (16). The Swern oxidation of diol 15 was performed according to the method of Seebach and co-workers. ${ }^{3}$ Purification via flash chromatography ( $40 \%$ EtOAc/hexanes) afforded a $96 \%$ yield of 16 as a white, crystalline solid. TLC $R_{f}=0.33$ ( $40 \%$ EtOAc/hexanes); The following spectral data are consistent with previously reported values: ${ }^{1} \mathrm{H}$ NMR $\left(500 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 9.67(\mathrm{~s}, 2 \mathrm{H}, \mathrm{C} 9-H), 6.96$ (dd, $2 \mathrm{H}, J=15.4,11.2$ $\left.\mathrm{Hz}, \mathrm{C}_{3}-H\right), 6.05\left(\mathrm{dd}, 2 \mathrm{H}, J=15.0,11.2 \mathrm{~Hz}, \mathrm{C}_{4}-H\right), 5.65(\mathrm{dd}, 2 \mathrm{H}, J=15.0,9.9 \mathrm{~Hz}, \mathrm{C} 5-H), 5.57(\mathrm{~d}$,
$\left.2 \mathrm{H}, J=15.4 \mathrm{~Hz}, \mathrm{C}_{2}-H\right), 5.40\left(\mathrm{dd}, 2 \mathrm{H}, J=10.3,2.3 \mathrm{~Hz}, \mathrm{C}_{7}-H\right), 2.72\left(\mathrm{dq}, 2 \mathrm{H}, J=7.0,2.3 \mathrm{~Hz}, \mathrm{C}_{8}-H\right), 2.52(\mathrm{ddq}, 2 \mathrm{H}, J=10.3,9.9,6.7$ $\left.\mathrm{Hz}, \mathrm{C}_{6}-H\right), 1.19\left(\mathrm{~d}, 6 \mathrm{H}, J=7.0 \mathrm{~Hz}, \mathrm{C}_{8}-\mathrm{CH}_{3}\right), 1.10\left(\mathrm{~d}, 6 \mathrm{H}, J=6.7 \mathrm{~Hz}, \mathrm{C}_{6}-\mathrm{CH}_{3}\right) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(125 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 202.0,167.1,145.5$, $143.2,131.9,121.2,74.2,46.9,41.8,15.5,6.7$; Exact mass calcd. for $\mathrm{C}_{22} \mathrm{H}_{28} \mathrm{O}_{6} \mathrm{Na}\left[(\mathrm{M}+\mathrm{Na})^{+}\right]: 411.1784$; found: 411.1791 ( $\mathrm{FAB}, m$ nitrobenzyl alcohol, added NaI ).

(3E, $5 E, 7 S, 8 S, 11 E, 13 E, 15 S, 16 S,)-8,16-b i s[(1 S, 2 R, 3 S)-5 \cdots$ [(4R,5R,6R)-2,2-di-tert-butyl-5-ethyl-6-methyl-1,3-dioxa-2-silacyclohex-4-yl]-2-hydroxy-1,3-dimethyl-4-oxopentyl]-7,15-dimethyl-1,9-dioxacyclohexadeca-3,5,11,13-tetraene-2,10dione (17). To a solution of ketone $8(228 \mathrm{mg}, 0.69 \mathrm{mmol})$ in 3 ml of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ at $-78{ }^{\circ} \mathrm{C}$ was added a solution of dichlorophenylborane ( $195 \mu \mathrm{l}, 1.5 \mathrm{mmol}$ ) in 1.5 ml of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ dropwise via cannula. After stirring for 20 min at $-78^{\circ} \mathrm{C}, N, N$-diisopropylethylamine ( $343 \mu \mathrm{l}, 1.97 \mathrm{mmol}$ ) was added dropwise via syringe. The reaction mixture was stirred at $-78{ }^{\circ} \mathrm{C}$ for 0.5 h , followed by warming to $0{ }^{\circ} \mathrm{C}$ and stirring for 0.5 h . The solution was recooled to $-78{ }^{\circ} \mathrm{C}$ and dialdehyde 16 ( $90 \mathrm{mg}, 0.23 \mathrm{mmol}$ ) was added as a solution in 1.5 ml of $\mathrm{CH}_{2} \mathrm{Cl}_{2}$ dropwise via cannula. After stirring for 1 h at $-78^{\circ} \mathrm{C}$, the reaction was quenched by the addition of $1: 1$ methanol $/ \mathrm{pH} 7$ phosphate buffer ( 10 ml ) and warmed to 0 ${ }^{\circ} \mathrm{C}$. After 5 min , a solution of $1: 1$ methanol $/ 30 \%$ aqueous hydrogen peroxide ( 15 ml ) was added dropwise. After stirring for 0.5 h at 0 ${ }^{\circ} \mathrm{C}$, the reaction mixture was diluted $\mathrm{CH}_{2} \mathrm{Cl}_{2}$, washed with sat. $\mathrm{NaHCO}_{3}(20 \mathrm{ml})$, and extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \times 20 \mathrm{ml})$. The combined organic layers were dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated in vacuo. ${ }^{1} \mathrm{H}$ NMR analysis of the unpurified reaction mixture ( 500 MHz ) revealed only one detectable aldol diastereomer. Purification via flash chromatography ( $20 \% \mathrm{EtOAc} / \mathrm{hexanes} \mathrm{)}$ afforded $160 \mathrm{mg}(66 \%)$ of 17 as a white, crystalline solid. TLC $R_{f}=0.46(40 \% \mathrm{EtOAc} / \mathrm{hexanes}) ; \mathrm{m} . \mathrm{p} .176-177{ }^{\circ} \mathrm{C} ;[\alpha]_{365}^{23}+454.1^{\circ}$ ( $c$ $1.0, \mathrm{CH}_{2} \mathrm{Cl}_{2}$ ); $\mathrm{IR}\left(\mathrm{CDCl}_{3}\right) 3488,3154,2974,2935,2901,2860,2253,1816,1793,1710,1639,1473,1381,1095,1000,964,914$, $738,651 \mathrm{~cm}^{-1},{ }^{1} \mathrm{H} \mathrm{NMR}\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 6.96\left(\mathrm{dd}, 2 \mathrm{H}, J=15.3,11.2 \mathrm{~Hz}, \mathrm{C}_{3}-H\right), 6.05(\mathrm{dd}, 2 \mathrm{H}, J=15.0,11.2 \mathrm{~Hz}, \mathrm{C} 4-H), 5.66$ (dd, $2 \mathrm{H}, J=15.0,9.7 \mathrm{~Hz}, \mathrm{C} 5-H), 5.60\left(\mathrm{~d}, 2 \mathrm{H}, J=15.3 \mathrm{~Hz}, \mathrm{C}_{2}-H\right), 5.10\left(\mathrm{dd}, 2 \mathrm{H}, J=10.3,1.5 \mathrm{~Hz}, \mathrm{C}_{7}-H\right), 4.75(\mathrm{ddd}, 2 \mathrm{H}, J=10.7,7.3$, $\left.2.6 \mathrm{~Hz}, \mathrm{C}_{13}-H\right), 4.02\left(\mathrm{dq}, 2 \mathrm{H}, J=7.4,6.3 \mathrm{~Hz}, \mathrm{C}_{15}-H\right), 3.76(\mathrm{ddd}, 2 \mathrm{H}, J=8.9,3.3,1.9 \mathrm{~Hz}, \mathrm{C} 9-H), 3.39(\mathrm{~d}, 2 \mathrm{H}, J=3.3 \mathrm{~Hz}, \mathrm{OH}), 2.85$ (dq, $\left.2 \mathrm{H}, J=7.1,1.9 \mathrm{~Hz}, \mathrm{C}_{10}-H\right), 2.80\left(\mathrm{dd}, 2 \mathrm{H}, J=15.0,10.7 \mathrm{~Hz}\right.$, one of each $\left.\mathrm{C}_{12}-\mathrm{H}_{2}\right), 2.49\left(\mathrm{ddq}, 2 \mathrm{H}, J=10.3,9.7,6.7 \mathrm{~Hz}, \mathrm{C}_{6}-\mathrm{H}\right)$, 2.37 (dd, $2 \mathrm{H}, J=15.0,2.6 \mathrm{~Hz}$, one of each $\mathrm{C}_{12}-\mathrm{H}_{2}$ ) $1.92(\mathrm{ddq}, 2 \mathrm{H}, J=8.9,7.0,1.5 \mathrm{~Hz}, \mathrm{C} 8-\mathrm{H}), 1.73\left(\mathrm{~m}, 2 \mathrm{H}\right.$, one of each $\mathrm{C}_{14}-$ $\mathrm{CH}_{2} \mathrm{CH}_{3}$ ), $1.48\left(\mathrm{~m}, 2 \mathrm{H}\right.$, one of each $\left.\mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right), 1.22\left(\mathrm{~d}, 6 \mathrm{H}, J=6.3 \mathrm{~Hz}, \mathrm{C}_{15}-\mathrm{CH}_{3}\right), 1.14\left(\mathrm{~d}, 6 \mathrm{H}, J=7.1 \mathrm{~Hz}, \mathrm{C}_{10}-\mathrm{CH}_{3}\right), 1.04(\mathrm{~d}$, $\left.6 \mathrm{H}, J=6.7 \mathrm{~Hz}, \mathrm{C}_{6}-\mathrm{CH}_{3}\right), 1.08-1.03\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{C}_{14}-\mathrm{H}\right), 0.96(\mathrm{~s}, 18 \mathrm{H}$, one of each $\mathrm{SiC}(\mathrm{CH} 3) 3), 0.94(\mathrm{~s}, 18 \mathrm{H}$, one of each $\mathrm{SiC}(\mathrm{CH} 3) 3)$, $0.93\left(\mathrm{t}, 6 \mathrm{H}, J=7.5 \mathrm{~Hz}, \mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right), 0.88\left(\mathrm{~d}, 6 \mathrm{H}, J=7.0 \mathrm{~Hz}, \mathrm{C}_{8}-\mathrm{CH}_{3}\right) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 213.5,168.4,145.2$, $144.6,131.4,121.2,76.5,71.5,70.8,69.9,49.5,47.3,43.5,41.6,35.9,27.7,27.3,23.2,21.3,21.0,20.8,15.2,12.3,9.2,8.1$; Unit mass calcd. for $\mathrm{C}_{58} \mathrm{H}_{100} \mathrm{O}_{12} \mathrm{SiNa}\left[(\mathrm{M}+\mathrm{Na})^{+}\right]$: 1067 ; found: 1067 ( FAB , m-nitrobenzyl alcohol, added Nal ).

(3E, $5 E, 7 S, 8 S, 11 E, 13 E, 15 S, 16 S,)-8,16-b i s[(1 S, 2 R, 3 S)-3-$ [( $2 R, 4 R, 5 S, 6 R)$-5-ethyl-3,4,5,6-tetrahydro-2,4-dihydroxy-6-methyl-2H-pyran-2-yl]-2-hydroxy-1-methylbutyl]-7,15-dimethyl-1,9-
dioxacyclohexadeca-3,5,11,13-tetraene-2,10-dione (2). To a solution of 17 ( $90 \mathrm{mg}, 0.086 \mathrm{mmol}$ ) in 5 ml of THF at ambient temperature in a Nalgene tube was added 0.5 ml of a buffered solution of pyridinium hydrofluoride (stock solution prepared from 1 g of Aldrich pyridinium hydrofluoride, 1.5 ml of pyridine, and 6.5 ml of THF) and 1 drop of water. After stirring for 3 h , the reaction was diluted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(15 \mathrm{ml})$, quenched by the addition of sat. $\mathrm{NaHCO}_{3}(20 \mathrm{ml})$, and extracted with $\mathrm{CH}_{2} \mathrm{Cl}_{2}(2 \times 15 \mathrm{ml})$. The combined organic layers were washed with brine, dried over $\mathrm{MgSO}_{4}$, filtered, and concentrated in vacuo. Purification via flash chromatography ( $60 \%$ ${ }_{23} \mathrm{EtOAc} / \mathrm{hexanes}$ ) afforded $60 \mathrm{mg}(91 \%)$ of 2 as a white, crystalline solid. TLC $R_{f}=0.33$ ( $80 \% \mathrm{EtOAc} /$ hexanes); m.p. 170-171 C ; [ $\alpha$ ] ${ }_{\mathrm{D}}^{23}+27.8^{\circ}\left(c_{0} 0.3, \mathrm{CHCl}_{3}\right)$; IR (neat) $3487,2970,2939,2881,1700,1639,1615,1463,1383,1348,1306,1282,1223,1182,1147$, $1080,1065,999,876 \mathrm{~cm}^{-1},{ }^{1} \mathrm{H}$ NMR $\left(400 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 6.97\left(\mathrm{dd}, 2 \mathrm{H}, J=15.4,11.1 \mathrm{~Hz}, \mathrm{C}_{3}-H\right), 6.12(\mathrm{dd}, 2 \mathrm{H}, J=15.0,11.1 \mathrm{~Hz}$, $\left.\mathrm{C}_{4}-H\right), 5.68\left(\mathrm{~d}, 2 \mathrm{H}, J=15.4 \mathrm{~Hz}, \mathrm{C}_{2}-H\right), 5.62\left(\mathrm{dd}, 2 \mathrm{H}, J=15.0,9.5 \mathrm{~Hz}, \mathrm{C}_{5}-H\right), 5.32\left(\mathrm{~d}, 2 \mathrm{H}, J=1.8 \mathrm{~Hz}, \mathrm{C}_{11}-\mathrm{OH}\right), 4.72(\mathrm{dd}, 2 \mathrm{H}, J=$ $\left.10.1,1.4 \mathrm{~Hz}, \mathrm{C}_{7}-H\right), 4.16(\mathrm{~d}, 2 \mathrm{H}, J=3.6 \mathrm{~Hz}, \mathrm{C} 9-\mathrm{OH}), 4.10(\mathrm{ddd}, 2 \mathrm{H}, J=10.0,3.6,1.5 \mathrm{~Hz}, \mathrm{C}-H), 3.94\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{C}_{13}-\mathrm{H}\right), 3.86(\mathrm{dq}, 2 \mathrm{H}$, $\left.J=10.2,6.2 \mathrm{~Hz}, \mathrm{C}_{15}-H\right), 2.54\left(\mathrm{ddq}, 2 \mathrm{H}, J=10.1,9.5,6.8 \mathrm{~Hz}, \mathrm{C}_{6}-H\right), 2.28\left(\mathrm{dd}, 2 \mathrm{H}, J=11.9,4.7 \mathrm{~Hz}, \mathrm{C}_{12}-\mathrm{H}_{\mathrm{eq}}\right), 1.95(\mathrm{ddq}, 2 \mathrm{H}, J=$ $\left.10.0,6.9,1.4 \mathrm{~Hz}, \mathrm{C}_{8}-H\right), 1.71\left(\mathrm{q}, 2 \mathrm{H}, J=7.1 \mathrm{~Hz}, \mathrm{C}_{10}-\mathrm{H}\right), 1.66\left(\mathrm{~s}, 2 \mathrm{H}, \mathrm{C}_{13}-\mathrm{OH}\right), 1.62\left(\mathrm{~m}, 2 \mathrm{H}\right.$, one of each $\left.\mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right), 1.49(\mathrm{~m}$, 2 H , one of each $\left.\mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH}_{3}\right), 1.16\left(\mathrm{dt}, 2 \mathrm{H}, J=11.7,2.0 \mathrm{~Hz}, \mathrm{C}_{12}-\mathrm{Hax}_{\mathrm{ax}}\right), 1.10\left(\mathrm{~d}, 6 \mathrm{H}, J=6.2 \mathrm{~Hz}, \mathrm{C}_{15}-\mathrm{CH} 3\right), 1.07\left(\mathrm{~m}, 2 \mathrm{H}, \mathrm{C}_{14}-\mathrm{H}\right)$, $1.03\left(\mathrm{~d}, 6 \mathrm{H}, J=6.8 \mathrm{~Hz}, \mathrm{C}_{6}-\mathrm{CH}_{3}\right), 0.99\left(\mathrm{~d}, 6 \mathrm{H}, J=7.1 \mathrm{~Hz}, \mathrm{C}_{10}-\mathrm{CH} 3\right), 0.89\left(\mathrm{t}, 6 \mathrm{H}, J=7.6 \mathrm{~Hz}, \mathrm{C}_{14}-\mathrm{CH}_{2} \mathrm{CH} 3\right), 0.80(\mathrm{~d}, 6 \mathrm{H}, J=6.9 \mathrm{~Hz}$, $\left.\mathrm{C}_{8}-\mathrm{CH}_{3}\right) ;{ }^{13} \mathrm{C} \mathrm{NMR}\left(100 \mathrm{MHz}, \mathrm{CDCl}_{3}\right) \delta 170.1,145.1,144.4,132.1,121.0,99.2,77.9,70.6,67.0,66.9,50.9,43.5,41.5,40.8,35.9$, $19.4,19.3,15.0,9.8,8.8,7.0$; Exact mass calcd. for $\mathrm{C}_{42} \mathrm{H}_{68} \mathrm{O}_{12} \mathrm{Na}\left[(\mathrm{M}+\mathrm{Na})^{+}\right]$: 787.4608 ; found: 787.4592 (FAB, $m$-nitrobenzyl alcohol, added NaI ).

## Footnotes and References:

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$12$


$13$


$14$


$15$



16


$17$



Elaiolide (2)


