Approach to the Synthesis of
the C\textsuperscript{1}-C\textsuperscript{11} and C\textsuperscript{14}-C\textsuperscript{18} portion of Leucascandrolide A\textsuperscript{a}

T. J. Hunter,\textsuperscript{b} J. Zheng\textsuperscript{c} and G. A. O’Doherty\textsuperscript{c,*}

\textsuperscript{a} This manuscript is dedicated to Barry M. Trost on the occasion of this 75th birthday.

\textsuperscript{b} MilliporeSigma, 645 Science Drive, Madison, Wisconsin 53711, United States.

\textsuperscript{c} Department of Chemistry and Chemical Biology, Northeastern University, Boston, Massachusetts 02115, United States.

Corresponding author e-mail: g.odoherty@neu.edu

Supporting Information

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Section A: General Information

Melting points are uncorrected. $^1$H and $^{13}$C NMR spectra were recorded on Varian VXR-300 (300 MHz) or Varian VXR-500 (500 MHz) spectrometers. Chemical shifts are reported relative to internal tetramethylsilane (δ 0.00 ppm) or residual solvent signal. Infrared (IR) spectra were obtained on a Prospect MIDAC FT-IR spectrometer. Optical rotations were measured with a Jasco DIP-370 digital polarimeter in the solvent specified. Flash column chromatography was performed on ICN reagent 60 (60-200 mesh) silica gel. Analytical thin-layer chromatography was performed with precoated glass-backed plates (Whatman K6F 60Å, F$_{254}$) and visualized by quenching of fluorescence and by charring after treatment with $p$-anisaldehyde or potassium permanganate stain. R$_f$ values are obtained by elution in the stated solvent ratios (v/v). Ether and THF were distilled from benzophenone and sodium metal. Methylene chloride and triethylamine were distilled from calcium hydride. Unless otherwise noted, solvents were reagent grade and were used without purification. Commercial reagents were used without purification unless otherwise noted.
Section B: Experimental Procedures

Ethyl (2E,4E)-6-((2S,4S,6R)-6-(2-((tert-butyldimethylsilyl)oxy)ethyl)-2-phenyl-1,3-dioxan-4-yl)hexa-2,4-dienoate (11): To phosphonate 10 (74 mg, 0.33 mmol) in 2 mL of THF was added 14 mg (0.33 mmol) LiOH·H₂O and 320 mg of 4 Å molecular sieves. This mixture was heated at reflux for 30 min. before 108 mg (0.30 mmol) of aldehyde 9 dissolved in 1 mL of THF was added. This mixture was heated at reflux for 6 h and then filtered through a plug of celite. The solvent was removed under reduced pressure and the crude product was purified by silica gel chromatography to produce dienoate 11 (92 mg) in 68% yield as a clear oil: [α]₀ 1.5° (c 1.3, CH₂Cl₂) IR (neat) 3035, 2954, 2857, 1644, 1620, 1470, 1462, 1452, 1428, 1402, 1391, 1367, 1345, 1303, 1256, 1221, 1176, 1133, 1097, 1028 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 7.50 (m, 2H), 7.36 (m, 3H), 7.27 (dd, J = 15.5, 10.5 Hz, 1H), 6.27 (dd, J = 15,10 Hz, 1H), 6.20 (ddd, J = 15, 6.5, 6.5 Hz, 1H), 5.82 (d, J = 15.5 Hz, 1H), 5.53 (s, 1H), 4.21 (q, J = 7 Hz, 2H), 4.02 (ddddd, J = 11, 8, 4, 2.5 Hz, 1H), 3.94 (ddddd, J = 11.5, 6.5, 6.5, 2.5 Hz, 1H), 3.83 (ddddd, J = 10, 8.5, 5 Hz, 1H), 3.73 (ddddd, J = 10.5, 5.5, 5.5 Hz, 1H), 2.56 (ddddd, J = 14.5, 7, 7 Hz, 1H), 2.44 (ddddd, J = 13, 6.5, 6.5 Hz, 1H), 1.84 (ddddd, J = 13, 8.5, 5, 5 Hz, 1H), 1.75 (ddddd, J = 14, 10, 5.5, 5 Hz, 1H), 1.63 (ddddd, J = 13, 2, 2 Hz, 1H), 1.46 (ddddd, J = 13, 11, 11 Hz, 1H), 1.30 (t, J = 7 Hz, 3H), 0.90 (s, 9H), 0.06 (s, 6H); ¹³C NMR (CDCl₃, 75 MHz) δ 196.0, 167.0, 144.3, 138.9, 138.6, 130.6, 128.5, 128.0, 125.9, 120.0, 100.4, 75.8, 73.3, 60.1, 58.7, 39.3, 38.8, 36.6, 25.9, 14.2, -5.4; HRMS (FAB) calcd for [C₂₆H₄₀O₅Si + H]⁺: 461.2723 Found: 461.2726; Anal. Calcd for C, 67.79; H, 8.75; Found: C, 67.81; H, 9.01.
Ethyl (4S,5S,E)-6-((2R,4S,6R)-6-((tert-butyldimethylsilyl)oxy)ethyl)-2-phenyl-1,3-dioxan-4-yl)-4,5-dihydroxyhex-2-enoate (12): Into a 25 mL round bottom flask containing 74 mg (0.16 mmol) of dienoate 11 was added 2 mL of t-BuOH, 2 mL of water, K$_3$Fe(CN)$_6$ (159 mg, 0.482 mmol), K$_2$CO$_3$ (67 mg, 0.482 mmol), MeSO$_2$NH$_2$ (15 mg, 0.16 mmol) and (DHQ)$_2$-PHAL (8 mg, 10 μmol). The mixture was stirred at room temperature for 15 minutes and then cooled to 0°C. To this solution was added OsO$_4$ (2 mg, 8 μmol) and the reaction was stirred vigorously at 0°C overnight. The reaction was quenched with saturated aqueous sodium sulfite (4 mL) at room temperature. Ethyl acetate (5 mL) was added to the reaction mixture, and after separation of the layers, the aqueous phase was further extracted with the organic solvent (2 x 10 mL). The combined organic layers were washed with 2N KOH (10 mL) to remove the methanesulfonamide, and brine, and then dried over anhydrous sodium sulfate. After removal of the solvents in vacuo, flash chromatography on silica gel afforded 56 mg (71% yield) of 12 as a clear oil: R$_f$ = 0.3 (3:2 hexanes:EtOAc); [α]$_D$ 1.8º (c 1.14, CH$_2$Cl$_2$); IR (neat) 3435, 3068, 3037, 2955, 2856, 1722, 1714, 1660, 1548, 1512, 1495, 1470, 1454, 1392, 1369, 1344, 1252, 1176, 1100, 1027 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.46 (m, 2H), 7.36 (m, 3H), 6.94 (dd, $J$ = 15.5, 5 Hz, 1H), 6.14 (dd, $J$ = 15.5, 1.5 Hz, 1H), 5.53 (s, 1H), 4.20 (q, $J$ = 7 Hz, 2H), 4.19 (m, 2H), 4.06 (m, 1H), 3.98 (ddd, $J$ = 9, 4.5, 3 Hz, 1H), 3.83 (ddd, $J$ = 10, 8.5, 5 Hz, 1H), 3.73 (ddd, $J$ = 10.5, 5.5, 5.5 Hz, 1H), 1.80-1.93 (m, 3H), 1.72-1.79 (m, 1H), 1.60 (m, 2H), 1.29 (t, $J$ = 7.5 Hz, 3H), 0.90 (s, 9H), 0.06 (s, 6H); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 166.2, 146.4, 138.4, 128.8, 128.3,
Ethyl (E)-3-((4S,5S)-5-(((2R,4R,6R)-6-(2-((tert-butyldimethylsilyl)oxy)ethyl)-2-phenyl-1,3-dioxan-4-yl)methyl)-2-oxo-1,3-dioxolan-4-yl)acrylate (13): Into a 10 mL volumetric flask containing 55 mg (0.11 mmol) of diol 12 and 35 μL pyridine was placed 1 mL of CH$_2$Cl$_2$. This mixture was cooled to 0 °C and 17 mg of triphosgene (0.316 mmol) dissolved in 1 mL of CH$_2$Cl$_2$ was added slowly using an addition funnel. The reaction was stirred for 2 h and quenched with saturated aqueous NH$_4$Cl (5 mL). The layers were separated and the aqueous layer was extracted with CH$_2$Cl$_2$ (3 x 10 mL). The combined organic layers were washed with saturated aqueous sodium bicarbonate (10 mL), brine (10 mL), and dried over anhydrous sodium sulfate. After removal of the solvents in vacuo, flash chromatography on silica gel afforded 13 as a clear, colorless oil (45 mg, 79%): R$_f$ = 0.26 (4:1 hexanes:EtOAc); [α]$_D$ –26.1° (c 1.8, CH$_2$Cl$_2$); IR (neat) 2930, 2858, 1816, 1725, 1561, 1546, 1472, 1369, 1344, 1308, 1257, 1170, 1101, 1027 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.46 (m, 2H), 7.36 (m, 3H), 6.78 (dd, $J$ = 15.9, 5.4 Hz, 1H), 6.06 (dd, $J$ = 15.6, 1.2 Hz, 1H), 5.52 (s, 1H), 4.91 (ddd, $J$ = 6.6, 5.4, 1.2 Hz, 1H), 4.67 (ddd, $J$ = 12.9, 6.3, 6.3 Hz, 1H), 4.20 (q, $J$ = 7.2 Hz, 2H), 4.00-4.12 (m, 2H), 3.81 (ddd, $J$ = 10.2, 8.4, 4.8 Hz, 1H), 3.72 (ddd, $J$ = 10.5, 5.4, 5.4 Hz, 1H), 2.03 (d, $J$ = 6 Hz, 1H), 2.01 (d, $J$ = 6.9 Hz, 1H), 1.72-1.90 (m, 2H), 1.68 (ddd, $J$ = 13.2, 2.4, 2.4 Hz, 1H), 1.48 (ddd, $J$ = 12.9, 11.1, 11.1 Hz, 1H), 1.28 (t, $J$ = 7.2 Hz, 3H), 0.89 (s, 9H), 0.05 (s, 6H); $^{13}$C NMR (CDCl$_3$, 75 MHz): 164.8,
153.4, 139.0, 138.0, 128.8, 128.2, 126.0, 124.7, 100.8, 80.0, 78.2, 73.2, 72.6, 61.0, 58.5, 39.8, 38.7, 37.1, 25.9, 18.2, 14.1, -5.39, -5.44; HRMS (FAB) calcd for [C$_{27}$H$_{40}$O$_8$Si + H]$^+$: 521.2571 Found: 521.2608.

Ethyl (R,E)-6-((2R,4S,6R)-6-(2-(tert-butyldimethylsilyl)oxy)ethyl)-2-phenyl-1,3-dioxan-4-yl)-5-hydroxyhex-2-enoate (anti-14a): Into a 10 mL, round bottomed flask fitted with a condenser and maintained under nitrogen was placed 37 mg (0.071 mmol) of carbonate 13, 0.7 mg (0.7 μmol) of Pd$_2$(dba)$_3$·CHCl$_3$, 0.5 mg (0.035 μmol) of PPh$_3$, and 1 mL of THF. Triethylamine (50 μL, 0.36 mmol) and formic acid (13 μL, 0.36 mmol) were added and the mixture was allowed to reflux for three hours. The reaction was cooled to room temperature, quenched with saturated aqueous sodium bicarbonate (2 mL), and diluted with ether (4 mL). The aqueous layer was extracted with ether (3 x 10 mL). The organic layer was washed with brine (10 mL) and dried with anhydrous sodium sulfate. After removal of the solvents in vacuo, flash chromatography on silica gel afforded anti-14a as a yellow oil (26 mg, 79%): $R_f = 0.16$ (4:1 hexanes:EtOAc); $[\alpha]_D$ 8.1° (c 1.25, CH$_2$Cl$_2$); IR (neat) 3490, 3036, 2929, 2858, 1786, 1722, 1657, 1630, 1586, 1493, 1462, 1452, 1408, 1390, 1370, 1344, 1255, 1211, 1099, 1028 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) δ 7.47 (m, 2H), 7.35 (m, 3H), 6.98 (ddd, $J = 15.6, 7.2, 7.2$ Hz, 1H), 5.91 (ddd, $J = 15.6, 1.2, 1.2$ Hz, 1H), 5.53 (s, 1H), 4.18 (q, $J = 7.2$ Hz, 2H), 4.18 (m, 2H), 4.05 (m, 1H), 3.82 (ddd, $J = 10.2, 8.4, 4.8$ Hz, 1H), 3.73 (ddd, $J = 10.5, 5.4, 5.4$ Hz, 1H), 2.40 (m, 2H), 1.70-1.90 (m, 2H), 1.57 (m, 2H), 1.28 (t, $J = 7.2$ Hz, 3H), 0.90 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) δ 166.2, 144.8, 138.4, 128.6, 128.1, 125.8, 123.8, 100.6, 74.0, 61.0, 42.2, 37.7, 33.4, 28.3, 22.4, 12.5, 10.0, 9.4; MS (ESI) m/z calcd for C$_{27}$H$_{40}$O$_8$Si: 521.2571 Found: 521.2608.
73.4, 66.8, 60.2, 58.7, 41.9, 40.3, 38.8, 36.6, 25.9, 18.3, 14.2, -5.4, -5.4; HRMS (FAB) calcd for 
\([C_{26}H_{42}O_{6}Si + H]^+\): 479.2829  Found: 479.2817.

(S)-1-((2R,4S,6R)-6-(2-((tert-butyldimethylsilyl)oxy)ethyl)-2-phenyl-1,3-dioxan-4-yl)pent-4-
en-2-ol (syn-16a) and (R)-1-((2R,4S,6R)-6-(2-((tert-butyldimethylsilyl)oxy)ethyl)-2-phenyl-
1,3-dioxan-4-yl)pent-4-en-2-ol (anti-16a): To a solution of aldehyde 9 in 3 mL of THF at 
–78 °C was added 0.62 mL of allylmagnesium chloride (2 M solution in THF). The reaction was 
allowed to warm to room temperature and stirred for 3 h, after which 1 mL of methanol, 10 mL 
of a saturated sodium bicarbonate solution, and 10 mL of ether were added. The aqueous layer 
was extracted with ether (3 x 10 mL). The organic layers were combined and washed with brine 
and dried over anhydrous sodium sulfate. Removal of the solvents in vacuo followed by silica 
gel chromatography yielded the alcohol (249 mg, 89%) as a clear oil and a mixture of 
diastereomers. Spectroscopic data for the syn diastereomer syn-16a: \([\alpha]_D\) 11.7° (c 1.25,
CH2Cl2); IR (neat) 3462, 3072, 3036, 2930, 2859, 2737,1868,1830, 1772, 1734, 1684, 1654,
1541, 1508, 1472, 1404, 1344, 1256, 1018 cm\(^{-1}\); \(^1\)H NMR (CDCl3, 300 MHz) \(\delta\) 7.47 (m, 2H),
7.35 (m, 3H), 5.85 (dddd, \(J = 17.1, 10.2, 6.9, 6.9\) Hz, 1H), 5.57 (s, 1H), 5.13 (m, 2H), 4.03-4.19
(m, 2H), 3.99 (dddd, \(J = 9, 6.5, 6.5, 3\) Hz, 1H), 3.83 (ddd, \(J = 10.2, 8.4, 4.8\) Hz, 1H), 3.73 (ddd, \(J =
10.5, 5.4, 5.4\) Hz, 1H), 2.27 (m, 2H), 1.70-1.91 (m, 4H), 1.65 (ddd, \(J = 13.2, 2.7, 2.7\) Hz, 1H),
1.52 (ddd, \(J = 13.2, 10.8, 10.8\) Hz, 1H), 0.91 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); \(^13\)C NMR
(CDCl3, 75 MHz) \(\delta\) 138.2, 134.6, 128.7, 128.2, 125.8, 117.5, 100.5, 77.4, 73.4, 70.4, 58.6, 41.9,
Spectroscopic data for the anti diastereomer \textit{anti-16a}: $[\alpha]_D$ 4.4° (c 1.22, CH$_2$Cl$_2$); IR (neat) 3446, 3072, 3072, 2951, 2928, 2857, 1472, 1463, 1405, 1387, 1344, 1255, 1215, 1177, 1148, 1102, 1064, 1028 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.48 (m, 2H), 7.34 (m, 3H), 5.84 (dddd, $J$ = 17.7, 9.3, 7.2, 7.2 Hz, 1H), 5.54 (s, 1H), 5.12 (m, 2H), 4.19 (m, 1H), 4.04 (m, 2H), 3.83 (ddd, $J$ = 10.2, 8.4, 4.8 Hz, 1H), 3.73 (ddd, $J$ = 10.5, 5.4, 5.4 Hz, 1H), 2.26 (m, 2H), 1.69-1.90 (m, 4H), 1.57 (m, 2H), 0.90 (s, 9H), 0.06 (s, 3H), 0.05 (s, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 138.6, 134.6, 128.5, 128.1, 125.9, 117.9, 100.5, 74.1, 73.4, 66.9, 58.7, 42.2, 42.0, 38.8, 36.9, 25.9, 18.3, -5.4, -5.4; HRMS (FAB) calcd for [C$_{23}$H$_{38}$O$_4$Si + Na]$^+$: 429.2437 Found: 429.2425.

\begin{center}
\includegraphics{17.png}
\end{center}

\textbf{1-((2R,4R,6R)-6-((tert-butyldimethylsilyl)oxy)ethyl)-2-phenyl-1,3-dioxan-4-yl)pent-4-en-2-one (17):} Into a 10 mL round bottomed flask was placed 25 mg (0.062 mmol) of alcohol in 1 mL of CH$_2$Cl$_2$. To this solution was added 39 mg (0.092 mmol) of Dess-Martin periodane. The reaction was stirred for 2 h. Ether was added to the reaction and the solution was filtered through a pad of silica gel, followed by removal of the solvents under reduced pressure. The crude product was purified by silica gel chromatography to produce 80 mg (88% yield) of ketone 17 as a clear oil: $[\alpha]_D$ 22.3° (c 2.6, CH$_2$Cl$_2$); IR (neat) 2952, 2928, 2857, 1720, 1641, 1470, 1453, 1389, 1345, 1253, 1215, 1100, 1025 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.47 (m, 2H), 7.34 (m, 3H), 5.93 (dddd, $J$ = 17.4, 10.5, 7.2, 7.2 Hz, 1H), 5.50 (s, 1H), 5.18 (m, 2H), 4.36 (m, 1H), 4.05 (m, 1H), 3.83 (ddd, $J$ = 10.5, 8.4, 5.1 Hz, 1H), 3.73 (ddd, $J$ = 10.5, 5.4, 5.4 Hz, 1H),
3.25 (m, 2H), 2.91 (dd, \( J = 16.5, 7.2 \text{ Hz}, 1\H \)), 2.58 (dd, \( J = 16.2, 5.4 \text{ Hz}, 1\H \)), 1.75-1.90 (m, 2H), 1.72 (ddd, \( J = 12.9, 2.4, 2.4 \text{ Hz}, 1\H \)), 1.45 (ddd, \( J = 12.6, 11.1, 11.1 \text{ Hz}, 1\H \)), 0.90 (s, 9H), 0.06 (s, 6H); \( ^{13} \text{C NMR (CDCl}_3, 75 \text{ MHz}) \delta 206.3, 138.4, 130.0, 128.4, 128.0, 125.8, 119.0, 100.3, 73.2, 72.9, 58.6, 48.7, 48.0, 38.7, 36.8; 25.8, 18.2, -5.4, -5.5; \) HRMS (ESI) calcd for \([\text{C}_{23}\text{H}_{36}\text{O}_4\text{Si} + \text{Na}]^+\): 427.2281 Found: 427.2270.

**((S)-1-((2R,4S,6R)-6-((tert-butyldimethylsilyl)oxy)ethyl)-2-phenyl-1,3-dioxan-4-yl)pent-4-en-2-ol (**syn-16a**)):** To a solution of ketone (263 mg, 0.65 mmol) in THF (6 mL) at -90 °C was added a 1.0 M solution of L-selectride in THF (1.3 mL, 1.3 mmol). After stirring for 3 h a solution of 30% \( \text{H}_2\text{O}_2 \) and 1 M \( \text{NaOH} \) was added and the reaction was allowed to warm to room temperature and diluted with \( \text{Et}_2\text{O} \). The organic layer was separated, washed with a saturated solution of sodium thiosulfate, brine, and then dried (\( \text{Na}_2\text{SO}_4 \)), filtered, and concentrated. The crude material was purified by flash chromatography to provide 227 mg (86%) of alcohol **syn-16a** as a mixture (4:1) of diastereomers.

**Tert-butyl(((S)-1-((2R,4R,6R)-6-((tert-butyldimethylsilyl)oxy)ethyl)-2-phenyl-1,3-dioxan-4-yl)pent-4-en-2-yl)oxy)diphenylsilane (**syn-18a**):** To a solution of alcohol **syn-16a** (86 mg, 0.211 mmol) and imidazole (43 mg, 0.56 mmol) in DMF (1 mL) was added TBDPSCI
(116 mg, 0.42 mmol). The reaction stirred for 18 h and then quenched with saturated aqueous sodium bicarbonate (5 mL) and diluted with ether (10 mL). The layers were separated and the aqueous layer was extracted with ether (2 x 10 mL). The combined organic layers were washed with brine (10 mL), and dried over anhydrous sodium sulfate. After removal of the solvents in vacuo, flash chromatography on silica gel afforded *syn*-18a as a clear, colorless oil (113 mg, 83%): \([\alpha]_D 12.6^\circ (c 1.2, \text{CH}_2\text{Cl}_2)\); IR (neat) 3072, 3049, 2930, 2856, 1960, 1898, 1826, 1776, 1736, 1590, 1567, 1546, 1472, 1463, 1428, 1390, 1252, 1109, 1027 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta 7.69 (m, 5H), 7.34 (m, 10H), 5.78 (ddddd, \(J = 17, 10, 7, 7\) Hz, 1H), 5.51 (s, 1H), 4.98 (m, 2H), 3.94 (m, 2H), 3.79 (m, 2H), 3.69 (dd, \(J = 10, 5, 5\) Hz, 1H), 2.36 (d, \(J = 13.5, 7, 7\) Hz, 1H), 2.26 (m, 1H), 1.93 (dd, \(J = 13.5, 6.5, 6.5\) Hz, 1H), 1.72 (dddd, \(J = 13.5, 9, 4.5, 4.5\) Hz, 1H), 1.63 (m, 2H), 1.27 (m, 1H), 1.16 (m, 1H), 1.08 (s, 9H), 0.92 (s, 9H), 0.07 (s, 6H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \(\delta 138.8, 135.9, 135.8, 135.4, 134.5, 134.1, 134.0, 129.5, 128.2, 127.9, 127.5, 127.4, 125.9, 117.2, 100.2, 73.7, 73.1, 69.4, 58.7, 42.1, 41.4, 38.8, 36.9, 27.0, 26.8, 25.9, 19.3, -5.3, -5.4; HRMS (FAB) calcd for \([\text{C}_{39}\text{H}_{56}\text{O}_{4}\text{Si}_2 + \text{H}]^+\): 645.3795  Found: 645.3756.

![TBDPSO](image)

**Tert-butyl(((R)-1-((2R,4R,6R)-6-((tert-butyldimethylsilyl)oxy)ethyl)-2-phenyl-1,3-dioxan-4-yl)pent-4-en-2-yl)oxy)diphenylsilane (anti-18a):** Following the procedure above, the TBDPS-protected alcohol *anti*-18a was produced (76 mg) in 78% yield from alcohol *anti*-16a as a clear, colorless oil: \([\alpha]_D -0.4^\circ (c 1.2, \text{CH}_2\text{Cl}_2)\); IR (neat) 3072, 2953, 2857, 1961, 1898, 1832, 1656, 1590, 1546, 1472, 1428, 1406, 1390, 1344, 1311, 1255, 1106, 1028 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\), 500 MHz) \(\delta 7.67 (m, 5H), 7.37 (m, 3H), 7.30 (m, 7H), 5.72 (ddddd, \(J = 17, 10, 7, 7\) Hz,
1H), 5.12 (s, 1H), 4.96 (m, 1H), 4.91 (m, 1H), 4.19 (m, 1H), 3.95 (m, 1H), 3.84 (m, 1H), 3.79 (ddd, \( J = 10, 8.5, 5 \) Hz, 1H), 3.70 (ddd, \( J = 11, 6, 6 \) Hz, 1H), 2.20 (m, 2H), 1.65-1.81 (m, 3H), 1.60 (ddd, \( J = 14, 9, 2.5 \) Hz, 1H), 1.28 (m, 2H), 1.07 (s, 9H), 0.92 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \( \delta \) 138.8, 135.9, 135.8, 135.4, 134.3, 134.1, 129.5, 129.4, 128.2, 127.9, 127.3, 127.3, 126.0, 117.0, 100.0, 73.2, 73.0, 68.9, 58.8, 42.9, 42.4, 38.8, 37.4, 27.0, 26.8, 25.9, 19.4, -5.3, -5.4; HRMS (FAB) calcd for \([\text{C}_{39}\text{H}_{56}\text{O}_4\text{Si}_2 + \text{H}]^+\): 645.3795 Found: 645.3756.

(2-((2R,4R,6S)-6-((S)-2-(benzyloxy)pent-4-en-1-yl)-2-phenyl-1,3-dioxan-4-yl)ethoxy)(tert-butyldimethylsilane (syn-18b): To a solution of alcohol syn-16a (382 mg, 0.94 mmol) in methylene chloride (2 mL) was added benzyl trichloroacetimidate (283 mg, 1.13 mmol). The mixture was stirred at room temperature for 24 h and then quenched with saturated aqueous sodium bicarbonate (2 mL). The layers were separated and the aqueous layer was extracted with CH\(_2\)Cl\(_2\) (2 x 5 mL). The organic layers were combined, washed with brine (5 mL), dried (Na\(_2\)SO\(_4\)), filtered, and concentrated. Purification on a silica gel column gave 224 mg of benzyl ether syn-18b (48%): \( R_f = 0.16 \) (4:1 hexanes:EtOAc); [\( \alpha \)]\(_D\) \( 25.9^\circ \) (c 1.05, CH\(_2\)Cl\(_2\)); IR (neat) 3066, 3033, 2952, 2856, 1640, 1496, 1472, 1454, 1388, 1342, 1253, 1214, 1106, 1028 cm\(^{-1}\); \(^{1}\)H NMR (CDCl\(_3\), 300 MHz) \( \delta \) 7.48 (m, 2H), 7.34 (m, 8H), 5.88 (dddd, \( J = 17.1, 10.2, 6.9, 6.9 \) Hz, 1H), 5.50 (s, 1H), 5.56 (m, 2H), 4.62 (d, \( J = 11.7 \) Hz, 1H), 4.68 (d, \( J = 11.7 \) Hz, 1H), 3.99 (m, 2H), 3.83 (ddd, \( J = 10.5, 8.7, 5.4 \) Hz, 1H), 3.71 (m, 1H), 2.42 (m, 2H), 2.05 (ddd, \( J = 14.1, 6.9, 6.9 \) Hz, 1H), 1.65-1.85 (m, 4H), 1.44 (m, 2H), 0.91 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); \(^{13}\)C NMR (CDCl\(_3\), 75 MHz) \( \delta \) 138.7, 138.4, 134.4, 128.3, 128.2, 127.9, 127.8, 127.5, 125.9, 117.2, 100.3,
(2R,4S,6R)-4-((S)-2-(benzyloxy)pent-4-en-1-yl)-6-((4-methoxybenzyl)oxy)ethyl)-2-phenyl-1,3-dioxane (syn-18c): To a solution of alcohol (111 mg, 0.27 mmol) in THF (2.5 mL) was added benzyl bromide (92 mg, 0.54 mmol), 31 mg (0.8 mmol) of 60% NaH in mineral oil, followed by tetrabutylammonium iodide (10 mg, 0.027 mmol). The reaction was stirred for 24 h and then quenched with saturated aqueous sodium bicarbonate (5 mL). The layers were separated and the aqueous layer was extracted with ether (3 x 5 mL). The combined organic layers were washed with brine (10 mL) and dried over anhydrous sodium sulfate. After removal of the solvents in vacuo, flash chromatography on silica gel afforded syn-18c as a clear, colorless oil (67 mg, 49%): Rf = 0.54 (4:1 hexanes:EtOAc); $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.46 (m, 2H), 7.32 (m, 8H), 7.26 (d, $J = 8.5$ Hz, 2H), 6.86 (d, $J = 8.5$ Hz, 2H), 5.87 (dddd, $J = 17.5$, 10.5, 7, 7 Hz, 1H), 5.49 (s, 1H), 5.10 (m, 2H), 4.60 (d, $J = 11.5$ Hz, 1H), 4.48 (d, $J = 12$ Hz, 1H), 4.47 (d, $J = 11.5$ Hz, 1H), 4.43 (d, $J = 12$ Hz, 1H), 3.96 (m, 3H), 3.79 (s, 3H), 3.66 (m, 1H), 3.57 (m, 1H), 2.42 (m, 2H), 2.04 (ddd, $J = 14$, 7, 7 Hz, 1H), 1.90 (m, 2H), 1.69 (m, 1H), 1.48 (dddd, $J = 13.5$, 13.5, 2.5, 2.5 Hz, 1H), 1.37 (dddd, $J = 13$, 13, 11, 2 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 159.2, 138.9, 138.7, 134.6, 130.6, 129.3, 128.4, 128.1, 128.1, 127.6, 126.1, 117.4, 113.8, 113.8, 100.4, 76.3, 73.9, 73.8, 72.7, 70.7, 65.8, 55.3, 40.0, 38.3, 36.6, 34.5; HRMS (ESI) calcd for [C$_{32}$H$_{38}$O$_5$ + Na]$^+$: 525.2617 Found: 525.2623.
(2R,4S,6R)-4-((R)-2-(benzyl oxy)pent-4-en-1-yl)-6-((4-methoxybenzyl)oxy)ethyl)-2-phenyl-1,3-dioxane (anti-18c): Following the procedure above, the benzyl-protected alcohol anti-18c was produced (71 mg) in 52% yield from alcohol anti-16b as a clear, colorless oil: Rf = 0.54 (4:1 hexanes:EtOAc), [α]D 23.8° (c 1.08, CH2Cl2); IR (neat) 3066, 3034, 3006, 2917, 2860, 1698, 1641, 1614, 1586, 1514, 1496, 1455, 1345, 1303, 1247, 1174, 1100, 1030 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 7.40 (m, 2H), 7.33 (m, 8H), 7.26 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 5.86 (dddd, J = 17, 10, 7, 7 Hz, 1H), 5.42 (s, 1H), 5.10 (m, 2H), 4.68 (d, J = 11.5 Hz, 1H), 4.48 (d, J = 11.5 Hz, 1H), 4.47 (d, J = 12 Hz, 1H), 4.43 (d, J = 11.5 Hz, 1H), 4.05 (m, 1H), 4.00 (dddd, J = 11, 8.5, 4.5, 2.5 Hz, 1H), 3.88 (m, 1H), 3.79 (s, 3H), 3.66 (ddd, J = 9.5, 8, 5.5 Hz, 1H), 3.56 (ddd, J = 9, 5.5, 5.5 Hz, 1H), 2.37 (m, 2H), 1.91 (dddd, J = 14, 8, 5.5, 5.5 Hz, 1H), 1.82 (dddd, J = 14, 8, 6, 4.5 Hz, 1H), 1.74 (dddd, J = 14.5, 9.5, 3 Hz, 1H), 1.66 (dddd, J = 14, 10, 2.5 Hz, 1H), 1.55 (dddd, J = 13, 2.5, 2.5 Hz, 1H), 1.41 (dddd, J = 13, 11.5, 11.5 Hz, 1H); ¹³C NMR (CDCl₃, 125 MHz) δ 159.2, 139.0, 138.8, 134.5, 130.6, 129.3, 128.4, 128.1, 128.0, 127.7, 126.0, 117.4, 113.8, 112.4, 100.1, 74.1, 73.8, 73.3, 72.7, 71.7, 65.7, 55.3, 41.3, 38.8, 37.5, 36.1; HRMS (ESI) calcd for [C₃₂H₃₈O₅ + Na]⁺: 525.2617 Found: 525.2623.

(2R,4R,6S)-4-((S)-2-(methoxymethoxy)pent-4-en-1-yl)-6-((4-methoxybenzyl)oxy)ethyl)-2-phenyl-1,3-dioxane (syn-18d): A solution of alcohol (800 mg, 1.94 mmol) and
diisopropylethylamine (2 mL) in CH₂Cl₂ (10 mL) was cooled to 0 ºC. To this solution was added DMAP (71 mg, 0.582 mmol), followed by MOMCl (0.59 mL, 7.76 mmol). The reaction was warmed up to room temperature, stirred for 4 h and quenched with saturated aqueous NH₄Cl (10 mL). The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (3 x 10 mL). The combined organic layers were washed with saturated aqueous sodium bicarbonate (10 mL), brine (10 mL), and dried over anhydrous sodium sulfate. After removal of the solvents in vacuo, flash chromatography on silica gel afforded syn-18d as a clear, colorless oil (769 mg, 87%): R_f = 0.38 (4:1 hexanes:EtOAc); [α]D 33.6° (c 1.1, CH₂Cl₂); IR (neat) 2924, 1640, 1614, 1586, 1514, 1456, 1344, 1303, 1248, 1213, 1098, 1032 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.46 (m, 2H), 7.35 (m, 3H), 7.27 (d, J = 9 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 5.85 (dddd, J = 17.1, 10.2, 7.2, 7.2 Hz, 1H), 5.52 (s, 1H), 5.11 (m, 2H), 4.69 (d, J = 6.9 Hz, 1H), 4.65 (d, J = 6.9 Hz, 1H), 4.49 (d, J = 11.7 Hz, 1H), 4.43 (d, J = 11.7 Hz, 1H), 4.02 (m, 2H), 3.86 (dddd, J = 12, 5.7, 5.7, Hz, 1H), 3.79 (s, 3H), 3.68 (dddd, J = 9.3, 8.1, 5.4 Hz, 1H), 3.58 (dddd, J = 9.3, 5.4, 5.4 Hz, 1H), 3.38 (s, 3H), 2.39 (m, 2H), 1.99 (dddd, J = 14, 6.9, 6.9 Hz, 1H), 1.88 (dddd, J = 13.8, 8.1, 5.7, 5.7 Hz, 1H), 1.85 (m, 1H), 1.72 (dddd, J = 14.5, 6, 6 Hz, 1H), 1.67 (dddd, J = 13.2, 2.1, 2.1 Hz, 1H), 1.43 (dddd, J = 12.9, 11.1, 11.1 Hz, 1H); ¹³C NMR (CDCl₃, 75 MHz) δ 159.0, 138.7, 134.4, 130.4, 129.1, 128.3, 128.0, 125.9, 117.4, 113.6, 100.3, 95.3, 73.7, 73.6, 73.4, 72.5, 65.5, 55.5, 55.1, 40.2, 38.8, 36.9, 36.0; HRMS (ESI) calcd for [C₂₇H₃₆O₆ + Na]⁺: 479.2410  Found: 479.2406.

(2R,4R,6S)-4-(2-((4-methoxybenzyl)oxy)ethyl)-6-((R)-2-(methoxymethoxy)pent-4-en-1-yl)-2-phenyl-1,3-dioxane (anti-18d): Following the procedure above, the MOM-protected alcohol...
*anti*-18d was produced (195 mg) in 85% yield from alcohol *anti*-16b as a clear, colorless oil: $R_f = 0.38$ (4:1 hexanes:EtOAc); $[\alpha]_D -2.7^\circ$ (c 1.0, CH$_2$Cl$_2$); IR (neat) 3071, 3035, 2950, 2920, 1641, 1614, 1586, 1515, 1455, 1404, 1344, 1303, 1248, 1102, 1040 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.47 (m, 2H), 7.35 (m, 3H), 7.28 (d, $J = 8.7$ Hz, 2H), 6.87 (d, $J = 8.7$ Hz, 2H), 5.83 (dddd, $J = 17.7, 10.8, 7.2, 7.2$ Hz, 1H), 5.52 (s, 1H), 5.09 (m, 2H), 4.76 (d, $J = 6.6$ Hz, 1H), 4.69 (d, $J = 6.6$ Hz, 1H), 4.49 (d, $J = 11.4$ Hz, 1H), 4.44 (d, $J = 11.4$ Hz, 1H), 4.05 (m, 3H), 3.79 (s, 3H), 3.69 (ddd, $J = 9.6, 8.1, 5.4$ Hz, 1H), 3.58 (ddd, $J = 9.3, 5.4, 5.4$ Hz, 1H), 3.40 (s, 3H), 2.35 (m, 2H), 1.83-1.97 (m, 2H), 1.65-1.81 (m, 2H), 1.59 (ddd, $J = 13.2, 2.7, 2.7$ Hz, 1H), 1.44 (ddd, $J = 12.6$, 10.8, 10.8 Hz, 1H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 159.0, 138.8, 134.2, 130.4, 129.2, 128.3, 128.0, 125.8, 118.4, 113.6, 100.0, 95.8, 73.6, 73.9, 73.0, 72.6, 72.6, 65.5, 55.5, 55.0, 41.1, 39.5, 37.4, 36.0; HRMS (ESI) calcd for [C$_{27}$H$_{36}$O$_6$ + Na]$^+$: 479.2410 Found: 479.2423.

Ethyl (S,E)-5-(benzyloxy)-6-((2R,4S,6R)-6-(2-((tert-butyldimethylsilyl)oxy)ethyl)-2-phenyl-1,3-dioxan-4-yl)hex-2-enoate (syn-15b): To a solution of alkene syn-18b (225 mg, 0.453 mmol) in 2 mL of CH$_2$Cl$_2$ was added ethyl acrylate (113 mg, 1.13 mmol) and Grubbs’s second-generation catalyst (6 mg, 6.8 μmol). This mixture was heated at reflux for 4 h. The reaction was cooled to room temperature and the solvent was removed under reduced pressure. The crude product was purified using column chromatography on silica gel to afford enoate syn-15b (221 mg, 96%) as a clear oil: $R_f = 0.29$ (9:1 hexanes:EtOAc); $[\alpha]_D 11.5^\circ$ (c 1.05, CH$_2$Cl$_2$); IR (neat) 3034, 2953, 2857, 1722, 1657, 1496, 1454, 1368, 1343, 1321, 1258, 1212, 1167, 1100, 1028 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.47 (m, 2H), 7.33 (m, 8H), 7.00 (ddd, $J = 15.6, 7.5,$
7.5 Hz, 1H), 5.90 (d, $J = 15.6$ Hz, 1H), 5.49 (s, 1H), 4.58 (d, $J = 11.7$ Hz, 1H), 4.49 (d, $J = 11.7$ Hz, 1H), 4.19 (q, $J = 7.2$ Hz, 2H), 3.97 (m, 2H), 3.77 (m, 3H), 2.54 (m, 2H), 2.06 (ddd, $J = 14.7$, 6.9, 6.9 Hz, 1H), 1.80 (m, 1H), 1.70 (m, 2H), 1.43 (m, 2H), 1.29 (q, $J = 7.2$ Hz, 3H), 0.91 (s, 9H), 0.07 (s, 6H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 166.1, 144.8, 138.6, 138.0, 128.3, 128.2, 128.0, 127.8, 127.6, 125.8, 123.7, 100.3, 73.6, 73.5, 73.2, 70.7, 60.1, 58.7, 39.9, 38.8, 36.9, 36.6, 25.9, 18.2, 14.2, -5.4, -5.4; HRMS (ESI) calcd for [C$_{33}$H$_{48}$O$_6$Si + Na]$^+$: 591.3118 Found: 591.3112.

**Ethyl (S,E)-5-(benzyloxy)-6-((2R,4S,6R)-6-(2-((4-methoxybenzyl)oxy)ethyl)-2-phenyl-1,3-dioxan-4-yl)hex-2-enoate (syn-15c):** To a solution of alkene syn-18c (166 mg, 0.33 mmol) in 2 mL of CH$_2$Cl$_2$ was added ethyl acrylate (83 mg, 0.83 mmol) and Grubbs’s second-generation catalyst (4 mg, 5 μmol). This mixture was heated at reflux for 4 h. The reaction was cooled to room temperature and the solvent was removed under reduced pressure. The crude product was purified using column chromatography on silica gel to afford enoate syn-15c (172 mg, 91%) as a clear oil: $[\alpha]_D$ 12.3° (c 1.0, CH$_2$Cl$_2$); IR (neat) 2922, 1715, 1652, 1614, 1514, 1455, 1248, 1172, 1099, 1028 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) $\delta$ 7.43 (m, 2H), 7.33 (m, 8H), 7.27 (d, $J = 9$ Hz, 2H), 7.00 (ddd, $J = 15$, 7.5, 7.5 Hz, 1H), 6.87 (d, $J = 8.5$ Hz, 1H), 5.89 (d, $J = 16$ Hz, 1H), 5.49 (s, 1H), 4.57 (d, $J = 11.5$ Hz, 1H), 4.49 (d, $J = 11.5$ Hz, 1H), 4.48 (d, $J = 11.5$ Hz, 1H), 4.43 (d, $J = 11.5$ Hz, 1H), 4.19 (q, $J = 7$ Hz, 2H), 3.79 (s, 3H), 3.79 (m, 1H), 3.65 (ddd, $J = 9.5$, 8.5, 5.5 Hz, 1H), 3.56 (ddd, $J = 9.5$, 6, 6 Hz, 1H), 2.54 (m, 2H), 2.05 (ddd, $J = 14$, 7, 7 Hz, 1H), 1.89 (ddd, $J = 14.5$, 9, 6, 6 Hz, 1H), 1.79 (ddddd, $J = 14.5$, 8.5, 6, 4.5 Hz, 1H), 1.68 (dd, $J = 14.5$, 6, 6 Hz, 1H), 1.46 (ddd, $J = 13$, 3, 3 Hz, 1H), 1.39 (ddd, $J = 12.5$, 10.5, 10.5 Hz, 1H), 1.29 (q, $J =$
7.5 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz) $\delta$ 166.4, 159.2, 145.0, 138.7, 138.2, 130.6, 129.3, 128.6, 128.4, 128.2, 128.0, 127.8, 126.0, 123.8, 113.8, 100.4, 73.9, 73.8, 73.7, 72.7, 70.9, 65.7, 60.3, 55.3, 40.0, 37.0, 36.8, 36.1, 14.3; HRMS (ESI) calcd for [C$_{35}$H$_{42}$O$_7$ + Na]$^+$: 597.2828.  
Found: 597.2844.

Ethyl (5S,7R,9R,E)-5-(benzyl oxy)-7,9-dihydroxy-11-((4-methoxybenzyl)oxy)undec-2-enoate (syn-19c): To a flask containing 172 mg (0.30 mmol) of benzylidene syn-15c was added 1.5 mL of 80% acetic acid. This mixture was heated at 60 °C for 4 h and then concentrated under reduced pressure to yield 105 mg (72%) of diol syn-19c: [α]$_D$ 17.1° (c 0.9, CH$_2$Cl$_2$); IR (neat) 3466, 2937, 1716, 1652, 1614, 1586, 1516, 1456, 1245, 1092 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 300 MHz) $\delta$ 7.33 (m, 5H), 7.25 (d, $J$ = 8.7 Hz, 2H), 6.97 (ddd, $J$ = 15, 7.2, 7.2 Hz, 1H), 6.88 (d, $J$ = 8.4 Hz, 2H), 5.90 (d, $J$ = 15.6 Hz, 1H), 4.64 (d, $J$ = 11.7 Hz, 1H), 4.48 (d, $J$ = 11.7 Hz, 1H), 4.45 (s, 2H), 4.20 (q, $J$ = 7.2 Hz, 2H), 4.01 (m, 2H), 3.82 (m, 1H), 3.81 (s, 3H), 3.64 (m, 2H), 2.53 (m, 2H), 1.66-1.85 (m, 3H), 1.51-1.60 (m, 2H), 1.45 (ddd, $J$ = 14.1, 2.7, 2.7 Hz, 1H), 1.30 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 75 MHz) $\delta$ 166.0, 159.1, 144.1, 137.6, 129.9, 129.2, 128.4, 127.8, 127.8, 123.9, 113.7, 76.8, 72.8, 71.2, 70.8, 70.7, 68.0, 60.1, 55.1, 43.3, 41.5, 36.9, 36.2, 14.1; HRMS (ESI) calcd for [C$_{28}$H$_{38}$O$_7$ + Na]$^+$: 509.2515  Found: 509.2540.
Ethyl (S,E)-6-((2R,4S,6R)-6-(2-((4-methoxybenzyl)oxy)ethyl)-2-phenyl-1,3-dioxan-4-yl)-5-(methoxymethoxy)hex-2-enoate (syn-19d): To a solution of alkene syn-15d (185 mg, 0.405 mmol) in 2.5 mL of CH₂Cl₂ was added ethylacrylate (100 mg, 1.0 mmol) and Grubbs’s second-generation catalyst (5.2 mg, 6.1 μmol). This mixture was heated at reflux for 4 h. The reaction was cooled to room temperature and the solvent was removed under reduced pressure. The crude product was purified using column chromatography on silica gel to afford enoate syn-19d (192 mg, 90%) as a clear oil: Rₜ = 0.28 (4:1 hexanes:EtOAc); [α]ₐ 16.2° (c 1.0, CH₂Cl₂); IR (neat) 2943, 1717, 1684, 1653, 1616, 1586, 1559, 1540, 1507, 1457 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.45 (m, 2H), 7.35 (m, 3H), 7.27 (d, J = 9 Hz, 2H), 7.00 (ddd, J = 15.6, 7.5, 7.5 Hz, 1H), 6.87 (d, J = 9 Hz, 2H), 5.90 (ddd, J = 15.6, 1.2, 1.2 Hz, 1H), 5.51 (s, 1H), 4.67 (d, J = 6.9 Hz, 1H), 4.64 (d, J = 6.9 Hz, 1H), 4.49 (d, J = 11.4 Hz, 1H), 4.44 (d, J = 11.4 Hz, 1H), 4.19 (q, J = 7.2 Hz, 2H), 4.00 (m, 3H), 3.80 (s, 3H), 3.68 (ddd, J = 9.3, 7.8, 5.1 Hz, 1H), 3.58 (ddd, J = 9.6, 5.4, 5.4 Hz, 1H), 3.38 (s, 3H), 2.54 (m, 2H), 2.00 (ddd, J = 13.8, 7.2, 6 Hz, 1H), 1.80-1.94 (m, 2H), 1.71 (ddd, J = 14.4, 5.4, 5.4 Hz, 1H), 1.65 (ddd, J = 12.9, 2.7, 2.7 Hz, 1H), 1.45 (ddd, J = 12.9, 11.1, 11.1 Hz, 1H), 1.29 (q, J = 6.9 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 166.0, 159.0, 144.8, 138.6, 130.4, 129.1, 128.4, 128.0, 125.9, 123.7, 113.6, 100.3, 95.4, 73.6, 73.4, 72.8, 72.5, 65.4, 60.1, 55.6, 55.1, 40.3, 37.2, 36.9, 36.0, 14.2; HRMS (ESI) calcd for [C₃₀H₄₀O₈ + Na]⁺: 551.2621 Found: 551.2611.

Ethyl (R,E)-6-((2R,4S,6R)-6-(2-((4-methoxybenzyl)oxy)ethyl)-2-phenyl-1,3-dioxan-4-yl)-5-(methoxymethoxy)hex-2-enoate (anti-15d): Following the procedure above, the enoate anti-
15d was produced (208 mg) in 92% yield from alkene anti-18d as a clear, colorless oil: $R_f = 0.28$ (4:1 hexanes:EtOAc); $[\alpha]_D^{2.6^\circ} (c 1.5, \text{CH}_2\text{Cl}_2)$; IR (neat) 2944, 1715, 1694, 1682, 1667, 1651, 1614, 1586, 1556, 1514, 1454, 1367, 1344, 1303, 1247, 1210, 1174, 1153, 1100, 1035 cm$^{-1}$; $^1\text{H NMR}$ (CDCl$_3$, 300 MHz) $\delta$ 7.45 (m, 2H), 7.35 (m, 3H), 7.28 (d, $J = 8.4$ Hz, 2H), 6.98 (ddd, $J = 15.3$, 7.5, 7.5 Hz, 1H), 6.87 (d, $J = 8.4$ Hz, 2H), 5.88 (d, $J = 15.6$ Hz, 1H), 5.50 (s, 1H), 4.72 (d, $J = 6.9$ Hz, 1H), 4.69 (d, $J = 6.9$ Hz, 1H), 4.48 (d, $J = 11.7$ Hz, 1H), 4.43 (d, $J = 11.7$ Hz, 1H), 4.18 (q, $J = 6.9$ Hz, 2H), 4.00-4.18 (m, 3H), 3.78 (s, 3H), 3.68 (ddd, $J = 9.3$, 8.1, 5.4 Hz, 1H), 3.57 (ddd, $J = 9.3$, 5.4, 5.4 Hz, 1H), 3.39 (s, 3H), 2.38-2.60 (m, 2H), 1.80-1.96 (m, 2H), 1.70 (m, 2H), 1.57 (ddd, $J = 13.2$, 2.4, 2.4 Hz, 1H), 1.43 (ddd, $J = 12.9$, 11.4, 11.4 Hz, 1H), 1.29 (t, $J = 7.2$ Hz, 3H); $^{13}\text{C NMR}$ (CDCl$_3$, 75 MHz) $\delta$ 166.3, 159.2, 144.6, 138.7, 130.5, 129.3, 128.5, 128.2, 125.9, 124.0, 113.8, 100.2, 96.1, 73.7, 73.0, 72.7, 72.3, 65.6, 60.3, 55.8, 55.3, 41.4, 38.0, 37.4, 36.1, 14.3; HRMS (ESI) calcd for $[\text{C}_{30}\text{H}_{40}\text{O}_8 + \text{Na}]^+$: 551.2621 Found: 551.2611.

Ethyl (5S,7R,9R,E)-7,9-dihydroxy-11-((4-methoxybenzyl)oxy)-5-(methoxymethoxy)undec-2-enoate (syn-19d): To a flask containing 50 mg I$_2$ in 250 mL MeOH was added 773 mg (1.46 mmol) of enoate syn-15d. This mixture was heated at reflux for 5 h. The majority of the methanol was then removed under reduced pressure, and the product was dissolved in ethyl acetate (50 mL). The organic layer was washed with aqueous sodium thiosulfate (20 mL), brine (20 mL), and dried over anhydrous sodium sulfate. After removal of the solvents in vacuo, flash chromatography on silica gel afforded syn-19d as a clear, colorless oil (512 mg, 80%): $R_f = 0.1$ (3:2 hexanes:EtOAc); $[\alpha]_D^{3.3^\circ} (c 0.9, \text{CH}_2\text{Cl}_2)$; IR (neat) 3460, 2942, 1715, 1652, 1614, 1586,
1515, 1446, 1370, 1245 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.27 (d, J = 8.7 Hz, 2H), 6.95 (ddd, 
J = 15.6, 7.8, 7.8 Hz, 1H), 6.88 (d, J = 8.7 Hz, 2H), 5.90 (ddd, J = 15.6, 1.5, 1.5 Hz, 1H), 4.70 (d, 
J = 7.2 Hz, 1H), 4.67 (d, J = 7.2 Hz, 1H), 4.46 (s, 2H), 4.19 (q, J = 7.2 Hz, 2H), 3.95-4.10 (m, 
3H), 3.81 (s, 3H), 3.65 (m, 2H), 3.39 (s, 3H), 2.51 (m, 2H), 1.68-1.88 (m, 3H), 1.50-1.60 (m, 
3H), 1.29 (t, J = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 166.1, 159.1, 144.3, 129.2, 123.8, 
113.7, 113.7, 95.3, 74.8, 72.8, 71.7, 70.3, 68.1, 60.1, 55.7, 55.1, 43.2, 41.7, 37.0, 36.8, 14.2; 

![Ethyl (5R,7R,9R,E)-7,9-dihydroxy-11-((4-methoxybenzyl)oxy)-5-(methoxymethoxy)undec-2-enoate (anti-19g)](image)

Ethyl (5R,7R,9R,E)-7,9-dihydroxy-11-((4-methoxybenzyl)oxy)-5-(methoxymethoxy)undec-2-enoate (anti-19g): Following the procedure above, the diol anti-19d was produced (225 mg) in 71% yield from enoate anti-15d as a clear, colorless oil: Rₓ = 0.1 (3:2 hexanes:EtOAc); [α]D – 33.7° (c 1.0, CH₂Cl₂); IR (neat) 3454, 2938, 1715, 1652, 1586, 1556, 1515, 1445, 1369, 1250, 
1174, 1100, 1036 cm⁻¹; ¹H NMR (CDCl₃, 300 MHz) δ 7.25 (d, J = 8.7 Hz, 2H), 6.96 (ddd, J = 
15.6, 7.5, 7.5 Hz, 1H), 6.88 (d, J = 8.7 Hz, 2H), 5.88 (ddd, J = 15.6, 1.2, 1.2 Hz, 1H), 4.72 (d, J = 
6.6 Hz, 1H), 4.68 (d, J = 6.6 Hz, 1H), 4.46 (s, 2H), 4.19 (q, J = 7.2 Hz, 2H), 4.10 (m, 1H), 3.96 
(m, 2H), 3.82 (s, 3H), 3.66 (m, 2H), 3.42 (s, 3H), 2.47 (m, 2H), 1.70-1.85 (m, 2H), 1.53-1.63 (m, 
3H), 1.49 (ddd, J = 14.1, 2.4, 2.4 Hz, 1H), 1.29 (t, J = 7.2 Hz, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 
166.0, 159.1, 144.4, 129.8, 129.2, 123.8, 113.7, 96.4, 73.7, 72.9, 72.0, 68.3, 68.2, 60.1, 55.7, 
55.1, 43.2, 42.5, 38.0, 36.8, 14.1; HRMS (ESI) calcd for [C₂₃H₃₆O₈ + Na]⁺: 463.2308 Found: 
463.2322.
Ethyl (R,E)-6-((2R,4R,6R)-6-((tert-butyldimethylsilyl)oxy)ethyl)-2-phenyl-1,3-dioxan-4-yl)-5-((tert-butyldiphenylsilyl)oxy)hex-2-enoate (**anti-15a**): To a solution of alkene **anti-18a** (95 mg, 0.15 mmol) in 2 mL of CH$_2$Cl$_2$ was added ethyl acrylate (37 mg, 0.37 mmol) and Grubbs’s second-generation catalyst (6.4 mg, 7.5 μmol). This mixture was heated at reflux for 4 h. The reaction was cooled to room temperature and the solvent was removed under reduced pressure. The crude product was purified using column chromatography on silica gel to afford enoate **anti-15a** (95 mg, 88%) as a clear oil: [α]$_D$ –0.8° (c 1.0, CH$_2$Cl$_2$); IR (neat) 3072, 3049, 2934, 2857, 1724, 1656, 1590, 1561, 1546, 1472, 1428, 1390, 1368, 1298, 1258, 1104 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) δ 7.66 (m, 5H), 7.38 (m, 3H), 7.30 (m, 7H), 6.88 (ddd, $J$ = 15.5, 7.5, 7.5 Hz, 1H), 5.69 (ddd, $J$ = 16, 1.5, 1.5 Hz, 1H), 5.11 (s, 1H), 4.16 (q, $J$ = 7 Hz, 2H), 4.16 (m, 1H), 3.93 (m, 1H), 3.83 (m, 1H), 3.79 (ddd, $J$ = 10.5, 8.5, 5 Hz, 1H), 3.69 (ddd, $J$ = 10.5, 5.5, 5.5 Hz, 1H), 2.31 (m, 2H), 1.76 (ddd, $J$ = 13.5, 8.5, 5.5 Hz, 1H), 1.66 (m, 4H), 1.41 (ddd, $J$ = 13, 2.5, 2.5 Hz, 1H), 1.28 (t, $J$ = 7 Hz, 3H), 1.07 (s, 9H), 0.92 (s, 9H), 0.07 (s, 3H), 0.06 (s, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 166.3, 144.9, 138.8, 136.0, 136.0, 135.6, 134.0, 133.8, 129.7, 128.4, 128.0, 127.6, 127.6, 126.2, 123.8, 100.2, 73.3, 73.0, 68.6, 60.2, 58.8, 43.4, 40.8, 38.9, 37.4, 27.1, 26.9, 26.0, 19.4, 14.3, -5.2, -5.3; HRMS (FAB) calcd for [C$_{42}$H$_{60}$O$_6$ + H]$^+$: 717.4007 Found: 717.3975.
Ethyl 2-((2R,4R,6R)-4-(benzyloxy)-6-((R)-2-hydroxy-4-((4-methoxybenzyl)oxy)butyl)-
tetrahydro-2H-pyran-2-yl)acetate (syn-20c): To diol syn-19c (30 mg, 0.062 mmol) in 1 mL
THF cooled to –40 ºC was added potassium tert-butoxide (0.7 mg, 0.062 mmol). This reaction
was allowed to warm up to room temperature and stirred for 4 h, when it was quenched with
saturated aqueous ammonium chloride (2 mL) and diluted with ether (5 mL). The aqueous layer
was extracted with ether (2 x 5 mL). The combined organic layers were washed with brine,
dried over anhydrous sodium sulfate, filtered, and concentrated. The crude product was purified
by silica gel chromatography to produce syn-20c (21 mg) in 70% yield as a clear oil: [α]D 14.5°
(c 0.95, CH2Cl2); IR (neat) 3515, 2944, 1732, 1613, 1514, 1455, 1248, 1173, 1098 cm⁻¹; ¹H
NMR (CDCl₃, 500 MHz) δ 7.35 (m, 5H), 7.25 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 4.55
(d, J = 12 Hz, 1H), 4.51 (d, J = 11.5 Hz, 1H), 4.45 (d, J = 11.5 Hz, 1H), 4.41 (d, J = 11.5 Hz,
1H), 4.28 (dddd, J = 11.5, 9, 4, 1.5 Hz, 1H), 4.15 (q, J = 7 Hz, 2H), 4.12 (m, 1H), 4.01 (dddd, J =
12, 7, 4.5, 2.5 Hz, 1H), 3.85 (m, 1H), 3.80 (s, 3H), 3.59 (m, 2H), 2.48 (dd, J = 15, 8.5 Hz, 1H),
2.39 (dd, J = 15.5, 4.5 Hz, 1H), 1.91 (m, 1H), 1.66-1.83 (m, 3H), 1.59 (dddd, J = 14.5, 9.5, 9.5 Hz,
1H), 1.51 (dddd, J = 14.5, 2.5, 2.5 Hz, 1H), 1.43 (m, 2H), 1.26 (q, J = 7 Hz, 3H); ¹³C NMR
(CDCl₃, 75 MHz) δ 170.9, 158.9, 138.4, 130.5, 129.1, 128.2, 127.4, 127.2, 113.6, 73.5, 72.5,
70.7, 70.0, 69.5, 68.9, 67.2, 60.5, 55.1, 42.6, 41.0, 37.2, 35.8, 34.8, 14.0; HRMS (ESI) calcd for
Ethyl 2-((2R,4R,6R)-4-(benzyloxy)-6-((R)-2-methoxy-4-((4-methoxybenzyl)oxy)butyl)tetrahydro-2H-pyran-2-yl)acetate (syn-21c): To a solution of alcohol syn-20c (19 mg, 0.04 mmol) in CH₂Cl₂ (2 mL) was added Proton Sponge (51 mg, 0.24 mmol), 4 Å molecular sieves (72 mg), and trimethyloxonium tetrafluoroborate (30 mg, 0.2 mmol). After about 1.5 h, the reaction was filtered through a fritted funnel, washing with ethyl acetate (5 x 10 mL). The filtrate was washed with water (1 x 20 mL) and 1M CuSO₄ (2 x 20 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The crude product was purified by silica gel chromatography to produce methyl ether syn-21c (15 mg) in 75% yield as a clear oil: Rₜ = 0.16 (4:1 hexanes:EtOAc); [α]_D^20 20.4° (c 0.7, CH₂Cl₂); IR (neat) 2924, 1732, 1694, 1682, 1652, 1614, 1557, 1538, 1514, 1455, 1372, 1247, 1170, 1092 cm⁻¹;¹H NMR (CDCl₃, 500 MHz) δ 7.35 (m, 4H), 7.28 (m, 1H), 7.26 (d, J = 9 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 4.54 (d, J = 12 Hz, 1H), 4.51 (d, J = 12 Hz, 1H), 4.44 (d, J = 11.5 Hz, 1H), 4.41 (d, J = 11.5 Hz, 1H), 4.22 (dddd, J = 13, 7.5, 5, 1.5 Hz, 1H), 4.12 (q, J = 7 Hz, 2H), 3.93 (dddd, J = 11, 8.6, 5, 2 Hz, 1H), 3.85 (m, 1H), 3.80 (s, 3H), 3.54 (m, 2H), 3.47 (m, 1H), 3.29 (s, 3H), 2.48 (dd, J = 15, 8 Hz, 1H), 2.37 (dd, J = 14.5, 5 Hz, 1H), 1.93 (m, 1H), 1.74-88 (m, 4H), 1.47 (dddd, J = 14, 7, 4.5 Hz, 1H), 1.38 (m, 2H), 1.24 (t, J = 7 Hz, 3H);¹³C NMR (CDCl₃, 125 MHz) δ 171.2, 159.1, 138.8, 130.8, 129.3, 128.4, 127.5, 127.4, 113.7, 75.3, 72.6, 71.1, 70.1, 69.3, 69.1, 66.8, 60.4, 56.6, 55.3, 41.7, 40.0, 35.8, 35.2, 33.9, 14.3; HRMS (ESI) calcd for [C₂₉H₄₀O₇ + Na]⁺: 523.2672 Found: 523.2671.
Ethyl 2-((2R,4R,6R)-4-(methoxymethoxy)-6-((R)-2-hydroxy-4-(4-methoxybenzyl)-oxy)butyl)-tetrahydro-2H-pyran-2-yl)acetate (syn-20d): To diol syn-19d (46 mg, 0.104 mmol) in 1 mL THF cooled to –40 ºC was added potassium tert-butoxide (12 mg, 0.104 mmol). This reaction was allowed to warm up to room temperature and stirred for 7 h, when it was quenched with saturated aqueous ammonium chloride (2 mL) and diluted with ether (5 mL). The aqueous layer was extracted with ether (2 x 5 mL). The combined organic layers were washed with brine, dried over anhydrous sodium sulfate, filtered, and concentrated. The crude product was purified by silica gel chromatography to produce pyran syn-20d (28 mg) in 61% yield as a clear oil: [α]D 11.7° (c 1.2, CH2Cl2); IR (neat) 3522, 2924, 1732, 1615, 1515, 1456, 1248, 1034 cm⁻¹; 1H NMR (CDCl3, 500 MHz) δ 7.26 (d, J = 8.5 Hz, 2H), 6.87 (d, J = 8.5 Hz, 2H), 4.68 (s, 2H), 4.45 (d, J = 11.5 Hz, 1H), 4.42 (d, J = 11.5 Hz, 1H), 4.23 (dddd, J = 11.5, 9, 4.5, 2 Hz, 1H), 4.14 (q, J = 7 Hz, 2H), 4.14 (m, 1H), 4.03 (m, 2H), 3.81 (s, 3H), 3.59 (m, 2H), 3.38 (s, 3H), 2.48 (dd, J = 15.5, 9 Hz, 1H), 2.38 (dd, J = 15, 4 Hz, 1H), 1.84-1.68 (m, 4H), 1.60 (ddd, J = 14.5, 9.5, 9.5 Hz, 1H), 1.51 (ddd, J = 14.5, 2.5, 2.5 Hz, 1H), 1.48-1.41 (m, 2H), 1.26 (t, J = 7 Hz, 3H); 13C NMR (CDCl3, 75 MHz) δ 171.0, 158.9, 130.4, 129.1, 113.5, 94.8, 73.5, 72.5, 69.5, 69.1, 69.0, 67.2, 60.6, 55.3, 55.1, 42.6, 41.0, 37.1, 36.3, 35.5, 14.0 ; HRMS (ESI) calcd for [C23H36O8⁺ + Na]⁺: 463.2308 Found: 463.2329.
Ethyl 2-((2R,4R,6R)-6-((R)-2-methoxy-4-((4-methoxybenzyl)oxy)butyl)-4-(methoxymethoxy)tetrahydro-2H-pyran-2-yl)acetate (syn-21d): To a solution of alcohol syn-20d (36 mg, 0.082 mmol) in CH$_2$Cl$_2$ (4 mL) was added Proton Sponge (105 mg, 0.492 mmol), 4 Å molecular sieves (148 mg), and trimethyloxonium tetrafluoroborate (61 mg, 0.41 mmol). After about 1.5 h, the reaction was filtered through a fritted funnel, washing with ethyl acetate (5 x 10 mL). The filtrate was washed with water (1 x 20 mL) and 1M CuSO$_4$ (2 x 20 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The crude product was purified by silica gel chromatography to produce methyl ether syn-21d (36 mg) in 97% yield as a clear oil: 

R$_f = 0.17$ (4:1 hexanes:EtOAc); [α]$_D$ 16.6° (c 1.0, CH$_2$Cl$_2$); IR (neat) 2934, 1738, 1614, 1586, 1514, 1464, 1368, 1302, 1248, 1151, 1099, 1038 cm$^{-1}$; $^1$H NMR (CDCl$_3$, 500 MHz) δ 7.26 (d, $J$ = 8.5 Hz, 2H), 6.87 (d, $J$ = 8.5 Hz, 2H), 4.68 (d, $J$ = 7 Hz, 1H), 4.66 (d, $J$ = 7 Hz, 1H), 4.44 (d, $J$ = 11.5 Hz, 1H), 4.41 (d, $J$ = 11.5 Hz, 1H), 4.17 (dddd, $J$ = 14, 8, 5.5, 2 Hz, 1H), 4.11 (q, $J$ = 7 Hz, 2H), 4.02 (m, 1H), 3.87 (dddd, $J$ = 11.5, 8.5, 4.5, 2 Hz, 1H), 3.81 (s, 3H), 3.53 (m, 2H), 3.46 (m, 1H), 3.37 (s, 3H), 3.29 (s, 3H), 2.48 (dd, $J$ = 15, 8.5 Hz, 1H), 2.35 (dd, $J$ = 15, 5 Hz, 1H), 1.73-1.88 (m, 5H), 1.35-1.49 (m, 3H), 1.23 (t, $J$ = 7 Hz, 3H); $^{13}$C NMR (CDCl$_3$, 125 MHz) δ 171.1, 159.1, 130.8, 129.2, 113.7, 94.9, 75.3, 72.6, 69.7, 69.3, 69.2, 66.8, 60.4, 56.5, 55.4, 55.3, 41.7, 39.9, 36.5, 35.9, 33.9, 14.3; HRMS (ESI) calcd for [C$_{24}$H$_{38}$O$_8$ + Na]$^+$: 477.2464 Found: 477.2463.

(R)-4-((tert-butyldimethylsilyl)oxy)-3-hydroxybutanal (23): To a solution of alcohol 22 (1.50 g, 5.2 mmol) in CH$_2$Cl$_2$ (20 mL) was added NMO (2.44 g of a 50% solution in H$_2$O, 10.4 mmol).
This solution was cooled down to 0°C and OsO₄ (13 mg, 0.05 mmol) was added and the reaction was stirred overnight. The reaction was quenched with saturated aqueous sodium sulfite (10 mL). The layers were separated and the aqueous layer was extracted with EtOAc (2 x 20 mL). The combined organic layers were washed with saturated aqueous ammonium chloride (20 mL), brine (15 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The crude triol was then dissolved in methanol (20 mL) and H₂O (20 mL) and NaIO₄ (1.64 g, 7.65 mmol) was added. The reaction was stirred for 4 h when saturated aqueous sodium bicarbonate (30 mL) and EtOAc (150 mL) were added. The layers were separated and the aqueous layer was extracted with EtOAc (2 x 50 mL). The combined organic layers were washed with brine (25 mL), dried over anhydrous sodium sulfate, filtered, and concentrated to give crude aldehyde 23 (772 mg, 68%) as a clear oil: Rᵣ = 0.64 (3:2 hexanes:EtOAc); [α]D –0.6° (c 1.0, CH₂Cl₂); IR (neat) 3439, 2930, 2858, 2739, 1728, 1472, 1464, 1390, 1362, 1255, 1110, 1007 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 9.86 (dd, J = 1.5, 1.5 Hz, 1H), 4.21 (m, 1H), 3.67 (dd, J = 9.9, 4.2 Hz, 1H), 3.54 (dd, J = 9.9, 6.3 Hz, 1H), 2.62 (m, 2H), 0.91 (s, 9H), 0.07 (s, 3H), 0.07 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 201.4, 67.2, 66.2, 46.9, 25.7, 18.1, -5.6, -5.6; HRMS (ESI) calcd for [C₁₀H₂₂O₃ Si+ Na]+: 241.1236  Found: 241.1246.

(R)-6-((tert-butyldimethylsilyl)oxy)-5-hydroxyhex-1-en-3-one (24): To a solution of aldehyde 23 (300 mg, 1.37 mmol) in THF (10 mL) cooled to -78 °C was added vinylMgBr (4.4 mL of a 1M solution in THF). The reaction was stirred for 3 h and then warmed to room temperature. The reaction was quenched with saturated aqueous sodium bicarbonate (10 mL) and diluted with
ether. The layers were separated and the aqueous layer was extracted with ether (3 x 10 mL). The organic layers were combined, washed with brine (15 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The crude diol was dissolved in CH₂Cl₂ (10 mL) and MnO₂ (1.08 g, 12.5 mmol) was added. The reaction was stirred overnight and then filtered through a pad of celite. The solvent was removed under reduced pressure and the crude product was purified with silica gel chromatography to give 284 mg (85% yield) of enone 24: \( R_f = 0.38 \) (4:1 hexanes:EtOAc); \([\alpha]_D = 11.1^\circ \) (c 1.0, CH₂Cl₂); IR (neat) 3472, 2955, 2930, 2858, 1682, 1614, 1472, 1403, 1362, 1256, 1120, 1006 cm⁻¹; \(^1\)H NMR (CDCl₃, 500 MHz) \( \delta \) 6.38 (dd, \( J = 18, 10.5 \) Hz, 1H), 6.26 (dd, \( J = 18, 1 \) Hz, 1H), 5.90 (dd, \( J = 10.5, 1 \) Hz, 1H), 4.16 (m, 1H), 3.65 (dd, \( J = 10, 5 \) Hz, 1H), 3.59 (dd, \( J = 10, 5.5 \) Hz, 1H), 2.93 (d, \( J = 4.5 \) Hz, 1H), 2.81 (d, \( J = 6 \) Hz, 1H), 0.90 (s, 9H), 0.08 (s, 3H), 0.08 (s, 3H); \(^1^3\)C NMR (CDCl₃, 125 MHz) \( \delta \) 200.1, 136.8, 129.0, 68.3, 66.3, 42.3, 25.9, 18.3, -5.4, -5.4; HRMS (ESI) calcd for \([C_{12}H_{24}O_3 Si+ Na]^+\) : 267.1392 Found: 267.1400.

![Structure of 25](image)

\( \text{2-}((2R,4R,6R)-6-((R)-2\text{-methoxy-4-((4-methoxybenzyl)oxy)butyl})-4-\text{(methoxymethoxy)-tetrahydro-2H-pyran-2-yl)acetic acid (25):} \) To a solution of ester \( \text{syn-21d} \) (60 mg, 0.132 mmol) in THF (1 mL) and H₂O (1 mL) was added LiOH (4.5 mg, 0.185 mmol). This solution was allowed to stir for 5 h. The reaction was acidified to pH 4 with 1 M HCl and diluted with ethyl acetate. The layers were separated and the organic layer was washed with brine and dried over anhydrous sodium sulfate, filtered, and concentrated. The crude product was purified by silica gel chromatography to produce carboxylic acid 25 (52 mg) in 92% yield as a clear oil:
[α]D −2.2° (c 1.0, CH2Cl2); IR (neat) 2936, 1732, 1714, 1586, 1514, 1464, 1442, 1360, 1302, 1248, 1172, 1150, 1101, 1037 cm−1; 1H NMR (CDCl3, 500 MHz) δ 7.27 (d, J = 9 Hz, 2H), 6.87 (d, J = 9 Hz, 2H), 4.67 (s, 2H), 4.44 (s, 2H), 4.16 (ddd, J = 13.5, 7.5, 5.5, 2 Hz, 1H), 4.03 (m, 1H), 3.94 (ddd, J = 10.5, 8.5, 3.5, 2 Hz, 1H), 3.80 (s, 3H), 3.47-3.57 (m, 3H), 3.37 (s, 3H), 3.28 (s, 3H), 2.47 (m, 2H), 1.74-1.87 (m, 5H), 1.48 (ddd, J = 14.5, 6, 4 Hz, 1H), 1.40-1.47 (m, 2H); 13C NMR (CDCl3, 125 MHz) δ 173.3, 159.2, 130.4, 129.4, 113.8, 95.0, 76.1, 72.7, 70.7, 69.4, 69.0, 66.5, 56.5, 55.5, 55.3, 40.9, 39.8, 36.5, 35.8, 33.5; HRMS (ESI) calcd for [C22H34O8 + Na]+: 449.2151  Found: 449.2154.

(R)-1-((tert-butyldimethylsilyl)oxy)-4-oxohex-5-en-2-yl 2-((2R,4R,6R)-6-((R)-2-methoxy-4-((4-methoxybenzyl)oxy)butyl)-4-(methoxymethoxy)tetrahydro-2H-pyran-2-yl)acetate (26):

To a solution of alcohol 24 (15.5 mg, 0.063 mmol) and acid 25 in CH2Cl2 (1 mL) was added DCC (26 mg, 0.126 mmol) and 5 mg (0.042 mmol) of DMAP. The reaction was stirred at room temperature and after 4 h, diluted with ether (3 mL), filtered through a glass wool plug, and washed successively with aqueous NaHSO4, saturated aqueous NaHCO3, and brine. The organic layer was dried (NaSO4) and evaporated to yield crude ester. The product was purified with flash chromatography to yield ester 26 as a clear oil (18 mg, 64%): [α]D 17.6° (c 1.3, CH2Cl2); IR (neat) 2927, 1739, 1685, 1614, 1514, 1464, 1362, 1248, 1100, 1040 cm−1; 1H NMR (CDCl3,
300 MHz) δ 7.25 (d, J = 8.7 Hz, 2H), 6.87 (d, J = 8.7 Hz, 2H), 6.35 (dd, J = 17.7, 10.2 Hz, 1H), 6.23 (dd, J = 17.7, 1.5 Hz, 1H), 5.86 (dd, J = 9.9, 1.5 Hz, 1H), 5.29 (m, 1H), 4.67 (d, J = 2.1 Hz, 1H), 4.65 (d, J = 2.1 Hz, 1H), 4.42 (s, 2H), 4.13 (m, 2H), 4.01 (m, 1H), 3.87 (m, 1H), 3.80 (s, 3H), 3.75 (dd, J = 10.8, 4.5 Hz, 1H), 3.66 (dd, J = 10.8, 4.8 Hz, 1H), 3.53 (m, 2H), 3.45 (m, 1H), 3.36 (s, 3H), 3.28 (s, 3H), 2.98 (dd, J = 16.5, 6.3, Hz, 1H), 2.88 (dd, J = 16.5, 6.9 Hz, 1H), 2.48 (dd, J = 15.3, 7.5 Hz, 1H), 2.33 (dd, J = 15, 5.7 Hz, 1H), 1.79 (m, 5H), 1.31-1.50 (m, 3H), 0.87 (s, 9H), 0.04 (s, 3H), 0.03 (s, 3H); ¹³C NMR (CDCl₃, 75 MHz) δ 197.3, 170.0, 158.9, 136.4, 130.5, 129.0, 128.6, 113.6, 94.7, 75.0, 72.4, 70.6, 69.4, 69.2, 68.7, 66.5, 63.4, 56.3, 55.2, 55.1, 41.3, 39.9, 39.9, 36.2, 35.6, 33.8, 25.7, 18.1, -5.5; HRMS (ESI) calcd for [C₃₄H₅₆O₁₀Si + Na]⁺: 675.3540 Found: 675.3534.

(R)-1-((tert-butyldimethylsilyl)oxy)-4-oxohex-5-en-2-yl 2-((2R,4R,6R)-6-((R)-4-hydroxy-2-methoxybutyl)-4-(methoxymethoxy)tetrahydro-2H-pyran-2-yl)acetate (27): To a solution of PMB ether 26 (30 mg, 0.046 mmol) in 1 mL of CH₂Cl₂ was added 5 μL of H₂O and 16 mg (0.69 mmol) of DDQ. This reaction was stirred for 2 h when saturated aqueous sodium bicarbonate (1 mL) was added to the reaction along with more CH₂Cl₂ (5 mL). The layers were separated and the aqueous layer was extracted with CH₂Cl₂ (2 x 5 mL). The organic layers were combined and washed with brine (5 mL), dried over anhydrous sodium sulfate, filtered, and concentrated. The crude product was purified with silica gel chromatography to yield 19 mg (78%) of alcohol 27:
R_f = 0.12 (3:2 hexanes:EtOAc); [α]_D 26.2° (c 1.0, CH₂Cl₂); IR (neat) 3493, 2932, 1738, 1688, 1613, 1546, 1464, 1404, 1360, 1253, 1150, 1101, 1040 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 6.36 (dd, J = 17.5, 10.5 Hz, 1H), 6.24 (dd, J = 18, 1 Hz, 1H), 5.88 (dd, J = 10.5, 1 Hz, 1H), 5.29 (m, 1H), 4.68 (d, J = 7 Hz, 1H), 4.66 (d, J = 7 Hz, 1H), 4.13 (m, 1H), 4.02 (m, 1H), 3.88 (dddd, J = 11.5, 9.5, 4, 2 Hz, 1H), 3.77 (dd, J = 11, 4.5 Hz, 1H), 3.75 (m, 2H), 3.68 (dd, J = 10.5, 4.5 Hz, 1H), 3.59 (m, 1H), 3.36 (s, 3H), 3.33 (s, 3H), 2.98 (dd, J = 16.5, 5.5 Hz, 1H), 2.91 (dd, J = 16.5, 7.5 Hz, 1H), 2.45 (dd, J = 15.5, 8 Hz, 1H), 2.34 (dd, J = 15.5, 5 Hz, 1H), 1.77-1.91 (m, 3H), 1.64-1.76 (m, 3H), 1.36-1.50 (m, 2H), 0.88 (s, 9H), 0.05 (s, 3H), 0.05 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 197.6, 170.3, 136.6, 128.8, 94.9, 77.9, 70.8, 69.6, 69.2, 68.9, 65.9, 63.5, 56.4, 55.4, 41.3, 40.1, 39.2, 36.7, 35.7, 35.6, 25.8, 18.3, -5.4; HRMS (ESI) calcd for [C₂₆H₄₈O₉Si + Na]⁺: 555.2965 Found: 555.2969.

(R)-1-((tert-butyldimethylsilyl)oxy)-4-oxohex-5-en-2-yl 2-((2R,4R,6R)-6-((S)-2-methoxy-4-oxobutyl)-4-(methoxymethoxy)tetrahydro-2H-pyran-2-yl)acetate (3): To a solution of alcohol 27 (10 mg, 0.19 mmol) in 0.5 mL of CH₂Cl₂ was added 12 mg (0.029 mmol) of Dess-Martin periodane. The reaction was stirred for 2 h. Ether was added to the reaction and the solution was filtered through a pad of silica gel, followed by removal of the solvents under reduced pressure. The crude product was purified by silica gel chromatography to produce 7 mg (70% yield) of aldehyde 3 as a clear oil: R_f = 0.26 (3:2 hexanes:EtOAc); [α]_D 16.1° (c 0.7,
CH₂Cl₂); IR (neat) 2930, 2858, 1732, 1682, 1403, 1360, 1253, 1189, 1150, 1104, 1040 cm⁻¹; ¹H NMR (CDCl₃, 500 MHz) δ 9.77 (dd, J = 2.5, 1.5 Hz, 1H), 6.35 (dd, J = 17.5, 10.5 Hz, 1H), 6.24 (dd, J = 18, 1 Hz, 1H), 5.87 (dd, J = 10.5, 1 Hz, 1H), 5.29 (m, 1H), 4.68 (d, J = 7 Hz, 1H), 4.66 (d, J = 7 Hz, 1H), 4.13 (m, 1H), 4.02 (m, 1H), 3.82-3.96 (m, 2H), 3.76 (dd, J = 11, 4.5 Hz, 1H), 3.68 (dd, J = 11, 5 Hz, 1H), 3.37 (s, 3H), 3.32 (s, 3H), 2.98 (dd, J = 17, 6 Hz, 1H), 2.90 (dd, J = 16.5, 7 Hz, 1H), 2.69 (ddd, J = 16.5, 4.5, 1.5 Hz, 1H), 2.58 (ddd, J = 16.5, 7.5, 3 Hz, 1H), 2.45 (dd, J = 15, 7.5 Hz, 1H), 2.33 (dd, J = 15.5, 5 Hz, 1H), 1.86 (ddd, J = 14, 9, 4.5 Hz, 1H), 1.81 (m, 1H), 1.73 (m, 3H), 1.54 (ddd, J = 14.5, 7.5, 4 Hz, 1H), 1.26 (m, 1H), 0.88 (s, 9H), 0.05 (s, 3H), 0.05 (s, 3H); ¹³C NMR (CDCl₃, 125 MHz) δ 201.9, 197.5, 170.2, 136.6, 128.8, 94.9, 73.4, 70.8, 69.5, 68.8, 63.5, 56.6, 55.4, 47.7, 41.3, 40.1, 39.2, 36.5, 35.6, 31.6, 25.8, 18.3, -5.4; HRMS (ESI) calcd for [C₂₆H₄₆O₉Si + CH₃OH + Na]⁺: 585.3071 Found: 585.3057.
Section C: $^1$H and $^{13}$C NMR Spectra

$^1$H NMR(500MHz, CDCl$_3$)
$^{13}$C NMR (75 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{1}$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (75 MHz, CDCl$_3$)
$^1$H NMR(300MHz, CDCl$_3$)
$^{13}$C NMR (75MHz, CDCl$_3$)
$^1$H NMR(300MHz, CDCl$_3$)
$^{13}$C NMR (75 MHz, CDCl$_3$)
$^1$H NMR (300 MHz, CDCl$_3$)
$^{13}$C NMR (100MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (75 MHz, CDCl$_3$)
\[ ^1H \text{ NMR}(500\text{MHz, CDCl}_3) \]
$\text{TBDPSO O O O OTBS}$

$^{13}\text{C NMR (75MHz, CDCl}_3)$
$^1$H NMR (300MHz, CDCl$_3$)
$^{13}$C NMR(75MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR(125MHz, CDCl$_3$)
^1H NMR (500 MHz, CDCl₃)
$^{13}$C NMR (75 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
$^1\text{H NMR}(500\text{MHz, CDCl}_3)$
$^{13}$C NMR (125 MHz, CDCl$_3$)
\[ ^1\text{H NMR}(300\text{MHz, CDCl}_3) \]
$^{13}$C NMR (75 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (125MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{1}H$ NMR(500MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (125MHz, CDCl$_3$)
$^{13}$C NMR (75MHz, CDCl$_3$)
$^1$H NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR(75MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^{1}H$ NMR (500 MHz, CDCl$_3$)
$^{13}$C NMR (125 MHz, CDCl$_3$)
$^1$H NMR(300MHz, CDCl$_3$)
$^{13}$C NMR (75 MHz, CDCl$_3$)
$^{1}H\text{ NMR}(500\text{MHz, CDCl}_3)$
$^{13}\text{C NMR}(125\text{MHz, CDCl}_3)$
^1H NMR(500MHz, CDCl$_3$)
$\text{^13C NMR(125MHz, CDCl}_3\text{)}$