SUPPORTING INFORMATION

Total Synthesis of Phorboxazole A. I. Preparation of Four Subunits

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Methyl 2-((2S,4R,6R)-4-(tert-butyldiphenylsilyloxy)-6-(2-(chloromethyl)oxazol-4-yl)-tetrahydro-2H-pyran-2-yl)acetate (7). To a mixture of 6 (112 mg, 0.238 mmol), dichlorobis(acetonitrile)palladium(II) (6.2 mg, 24 µmol, 10 mol%) and sublimed p-benzoquinone (12.9 mg, 0.119 mmol) under carbon monoxide at room temperature were added methanol (6 mL) and acetonitrile (6 mL), and the mixture was stirred at room temperature for 2 h. Over the next 10 h, ten further additions of p-benzoquinone (13 mg, 0.12 mmol, 0.5 equivalent) in MeOH-MeCN (1:1, 2 mL) were made to the reaction mixture at regular intervals. After 11 h the solution was concentrated under reduced pressure and the residue was purified by flash chromatography on silica gel (hexane: EtOAc 12:1) to produce 7 (72 mg, 58%) as a colorless oil: [α]D23 +13.4 (c 2.10, CHCl3); IR (thin film) 2930, 2857, 1740, 1428, 1112, 702 cm⁻¹; ¹H NMR (300 MHz, CDCl3) δ 7.55 (s, 1H), 7.54 (m, 10 H), 4.58 (s, 2H), 4.56 (m, 1H), 4.30 (s, 1H), 3.67 (s, 3H), 2.64 (dd, J = 15, 7 Hz, 1H), 2.37 (dd, J = 16, 6 Hz, 1H), 1.80 (m, 4H), 1.11 (s, 9H); ¹³C NMR (75 MHz, CDCl3) δ 171.7, 159.4, 159.2, 143.0, 141.2, 137.7, 136.9, 136.2, 136.1, 134.3, 134.2, 130.2, 128.1, 69.6, 68.7, 67.7, 66.2, 65.9, 52.0, 41.5, 41.0, 40.4, 38.4, 37.8, 36.8, 36.3, 36.1, 27.3, 19.7, 19.5; MS (CI) m/z 528 (M⁺), 492, 470, 436, 367, 327, 307, 254, 225, 199, 183, 153; HRMS (CI) m/z 528.1977 (caled for C28H35NO5Si35Cl: 528.1973).
(R)-1-(tert-Butyldiphenylsilyloxy)hex-5-en-3-ol. In an argon-flushed 50 mL round bottomed flask fitted with a rubber septum, argon inlet, and magnetic stirring bar, (+)-B-methoxydiisopinocampheylborane (3.212 g, 10.15 mmol) was dissolved in diethyl ether (25 mL) and the solution was cooled to 0 °C. Allylmagnesium bromide (1.0M solution in hexane, 8.6 mL) was added and the mixture was allowed to warm to room temperature.

The solvent was removed under vacuum and the residue was extracted with pentane (10 mL x 4). The resulting suspension was filtered under argon through a Schlenk tube via cannula, and pentane was removed from the filtrate under vacuum. The residue was dissolved in diethyl ether (25 mL), and the solution was cooled to -100° C. To this solution was added a solution of 9 (1.34 g, 4.29 mmol) in Et$_2$O (25 mL) at -78 °C via cannula. The mixture was stirred at -100 °C for 1 h, and the reaction was quenched with methanol (1.0 mL). The mixture was allowed to warm to room temperature, treated with saturated sodium bicarbonate solution (10 mL) and 30% hydrogen peroxide (5 mL), and was stirred for 10 h. The mixture was extracted with ether (25mL x 3), and the extract was washed with brine (20 mL), dried (MgSO$_4$) and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane: EtOAc, 25:1) to yield a homoallylic alcohol (1.522 g, 88%) with enantiomeric ratio >96:4 by Mosher ester analysis of its
\(^{19}\)F NMR spectrum: \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.65 – 7.61 (m, 4H), 7.42 – 7.34 (m, 6H), 5.83 (ddt, \(J = 7, 10, 17\) Hz, 1H), 5.12 – 5.05 (m, 2H), 3.95 – 3.90 (m, 1H), 3.88 – 3.80 (m, 2H), 3.20 (d, \(J = 3\) Hz, 1H), 2.27 – 2.22 (m, 2H), 1.73 – 1.68 (m, 2H), 1.03 (s, 9H).

\((S)-5-(\textit{tert}-\text{Butyldiphenylsilyloxy})-3-(\text{triethylsilyloxy})\text{pentanal (10).}\) A solution of the homoallylic alcohol prepared above (99 mg, 0.28 mmol) in dichloromethane (9 mL) was cooled to 0 °C and treated with 2,6-lutidine (0.097 mL, 0.837 mmol) and triethylsilyl trifluoromethanesulfonate (95 \(\mu\)L, 0.42 mmol). The mixture was stirred at 0 °C for 30 min and at room temperature for 5 h, and then was quenched with saturated sodium bicarbonate solution. After the addition of dichloromethane (10 mL), the pH of the aqueous phase was adjusted to ca. 7.0 with 1M HCl. The aqueous phase was extracted with dichloromethane (10 mL \(\times\) 3), and the combined organic phases were dried (MgSO\(_4\)), filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane: EtOAc, 40:1) to yield a silyl ether (117 mg, 90%) as a colorless oil: \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.65 – 7.61 (m, 4H), 7.42 – 7.34 (m, 6H), 5.78 (ddt, \(J = 17, 10, 7\) Hz, 1H), 5.02 – 4.96 (m, 2H), 3.97 – 3.91 (m, 1H), 3.74 – 3.64 (m, 2H), 2.24 – 2.15 (m, 2H), 1.70 – 1.62 (m, 2H), 1.02 (s, 9H), 0.91 (t, \(J = 8\) Hz, 9H), 0.55 (q, \(J = 8\) Hz, 6H).
Into a precooled (-78 °C) solution of the silyl ether prepared above (50 mg, 0.107 mmol) in dichloromethane (5 mL) was bubbled ozone until a light blue color persisted. The ozonide was quenched by addition of triphenylphosphine (140 mg, 0.534 mmol) and the mixture was warmed to room temperature and stirred for 30 min. The reaction mixture was concentrated and purified via flash chromatography on silica (hexane: EtOAc, 10:1) to yield 10 (40 mg, 80%) as a colorless oil: $^1$H NMR (300 MHz, CDCl$_3$) δ 9.80 (t, $J$ = 2 Hz, 1H), 7.68 – 7.64 (m, 4H), 7.45 – 7.28 (m, 6H), 4.46 (tt, $J$ = 6, 6 Hz, 1H), 3.81 – 3.66 (m, 2H), 2.63 – 2.47 (m, 2H), 1.91 – 1.68 (m, 2H), 1.07 (s, 9H), 0.94 (t, $J$ = 8 Hz, 9H), 0.60 (q, $J$ = 8 Hz, 6H).

(R)-9,9-Diethyl-2,2-dimethyl-3,3-diphenyl-7-(prop-2-ynyl)-4,8-dioxa-3,9-disilaundecane (12). Freshly prepared sodium methoxide (75 mL, 1M solution in methanol) was added to a solution of dimethyl 1-diazo-2-oxopropylphosphonate (11, 178 mg, 0.924 mmol) in THF (10 mL) at -78 °C. After 5 min, 10 (174 mg, 0.370 mmol) was added and the reaction was stirred for 10 min at -78 °C, then warmed to room temperature. After 30 min, the reaction was quenched by adding ammonium chloride solution (5 mL). The aqueous phase was extracted with diethyl ether (10 mL x 3), and the combined organic phases were dried (MgSO$_4$), filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane: EtOAc, 20:1) to yield 12 (154 mg, 90%) as a colorless oil: $^1$H NMR
(300 MHz, CDCl$_3$) δ 7.70 – 7.66 (m, 4H), 7.46 – 7.26 (m, 6H), 4.13 – 4.05 (m, 1H), 3.83 – 3.70 (m, 2H), 2.42 – 2.32 (m, 2H), 2.00 (t, $J$ = 3 Hz, 1H), 1.92 – 1.86 (m, 1H), 1.81 – 1.70 (m, 1H), 1.06 (s, 9H), 0.96 (t, $J$ = 8 Hz, 9H), 0.62 (q, $J$ = 8 Hz, 6H).

(5)-Bromo-1-(tert-butylidiphenylsilyloxy)hex-5-en-3-ol (14). To a stirred solution of 12 (196 mg, 0.42 mmol) in MeOH (5 mL) was added pyridinium $p$-toluenesulfonate (5 mg). The mixture was stirred for 2 h and concentrated under reduced pressure. The resulting oil was purified by flash chromatography on silica gel (hexane:EtOAc, 15:1) to produce an alcohol (148 mg, 99%) as a colorless oil: $^1$H NMR (300 MHz, CDCl$_3$) δ 7.68 – 7.65 (m, 4H), 7.42 – 7.25 (m, 6H), 4.10 – 4.05 (m, 1H), 3.92 – 3.81 (m, 2H), 3.41 (d, $J$ = 3 Hz, 1H), 2.44 – 2.40 (m, 2H), 2.02 (t, $J$ = 3 Hz, 1H), 1.83 – 1.78 (m, 2H), 1.05 (s, 9H).

To a solution of the alcohol prepared above (148 mg, 0.42 mmol) in dichloromethane (5 mL) at 0 °C under argon was added $B$-bromo-9-borabicyclo[3.3.1]nonane (13, 1.0M, 2 mL, 2 mmol). The mixture was allowed to warm to room temperature and stirred overnight, then the mixture was cooled to 0 °C and ethanolamine (0.5 mL) and methanol (2 mL) were added. The mixture was diluted with diethyl ether (10 mL) and washed with a saturated aqueous solution of sodium potassium tartrate (10 mL). The phases were separated and the organic layer was dried (MgSO$_4$), and concentrated under reduced pressure. The crude product was
purified by flash chromatography on silica gel (hexane: EtOAc, 30:1) to yield 14 (153 mg, 84%) as a colorless oil: $^1$H NMR (300 MHz, CDCl$_3$) δ 7.68 – 7.65 (m, 4H), 7.46 – 7.28 (m, 6H), 5.70 (d, $J$ = 1 Hz, 1H), 5.53 (d, $J$ = 1 Hz, 1H), 4.30 – 4.26 (m, 1H), 3.93 – 3.88 (m, 2H), 3.23 (brs, 1H), 2.71 – 2.50 (m, 2H), 1.84 – 1.78 (m, 2H), 1.07 (s, 9H).

**(R)-9,9-Diethyl-2,2-dimethyl-3,3-diphenyl-7-(2-((trimethylsilyl)methyl)allyl)-4,8-dioxa-3,9-disilaundecane (8).** A solution of 14 (153 mg, 0.353 mmol) in dichloromethane (7 mL) was cooled to 0 °C and treated with 2,6-lutidine (0.21 mL, 1.81 mmol) and triethylsilyl trifluoromethanesulfonate (0.21 mL, 0.93 mmol). The mixture was stirred at 0 °C for 30 min and at room temperature for 5 h, and then was quenched with saturated sodium bicarbonate solution. The aqueous phase was extracted with dichloromethane (10 mL x 3), and the combined organic phases were dried (MgSO$_4$), filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane: EtOAc, 40:1) to yield a silyl ether (161 mg, 83%) as a colorless oil: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.68 – 7.65 (m, 4H), 7.33 – 7.25 (m, 6H), 5.57 (s, 1H), 5.41 (d, $J$ = 1 Hz, 1H), 4.26 – 4.20 (m, 1H), 3.76 – 3.65 (m, 2H), 2.58 – 2.48 (m, 2H), 1.95 – 1.71 (m, 1H), 1.69 – 1.59 (m, 1H), 1.03 (s, 9H), 0.91 (t, $J$ = 8 Hz, 9H), 0.58 (q, $J$ = 8 Hz, 6H).

To a solution of (trimethylsilyl)methylmagnesium chloride (1.0M solution in diethyl ether, 0.69 mL, 0.69 mmol) in THF (12 mL) was added a solution of vinyl
bromide (252 mg, 0.46 mmol) in THF (2 mL) followed by [1,3-

bis(diphenylphosphino)propane]nickel(II) chloride (NiDPPPCl₂, 25 mg, 46 µmol).
The mixture was heated at reflux for 12 h then allowed to cool to room temperature.
The reaction was quenched with saturated ammonium chloride solution (15 mL) and
diethyl ether (15 mL) was added. The phases were separated and the organic phase
was dried (MgSO₄) and concentrated under reduced pressure. The crude product was
purified by flash chromatography on silica gel (hexane: EtOAc, 200:1) to yield 8 (220
mg, 86%) as a colorless oil: ¹H NMR (300 MHz, CDCl₃) δ 7.67 – 7.65 (m, 4H), 7.39 –
7.35 (m, 6H), 4.58 (d, J = 10 Hz, 2H), 4.15 – 4.05 (m, 1H), 3.80 – 3.66 (m, 2H), 2.17
(dd, J = 6, 13 Hz, 1H), 2.05 (dd, J = 7, 13 Hz, 1H), 1.85 – 1.70 (m, 1H), 1.62 – 1.55
(m, 1H), 1.52 (s, 2H), 1.04 (s, 9H), 0.92 (t, J = 8 Hz, 9H), 0.57 (q, J = 8 Hz, 6H), 0.01
(s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 144.6, 136.0, 134.5, 134.4, 129.9, 128.0,
110.3, 68.5, 61.2, 47.2, 40.3, 27.5, 27.3, 19.6, 7.4, 5.5, -1.0.

((4R,5R)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl)dimethanol. To a stirred solution of
lithium aluminum hydride (4.16 g, 0.109 mol) in ether (80 mL) was added (4S,5S)-
diethyl 2,2-dimethyl-1,3-dioxolane-4,5-dicarboxylate (15.746 g, 65.24 mmol) in ether
(40 mL) dropwise over 40 min. The resulting mixture was gently refluxed for 24 h
then was cooled to 0–5 °C and cautiously treated with water (4.2 mL), 4N aqueous
sodium hydroxide solution (4.2 mL), and water (12.6 mL). The mixture was stirred at room temperature until the gray color of unquenched lithium aluminum hydride had completely disappeared. The mixture was filtered on a Büchner funnel and the inorganic precipitate was extracted with THF. The combined organic extracts were dried (Na$_2$SO$_4$), and concentrated under reduced pressure. The resulting oil was purified by flash chromatography to afford 7.78 g (73%) of ((4R,5R)-2,2-dimethyl-1,3-dioxolane-4,5-diyl)dimethanol as a colorless oil.

((4R,5R)-5-((tert-Butyldimethylsilyloxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methanol. Sodium hydride (1.36 g, 33.9 mmol) was suspended in THF (50 mL) after being washed with hexane. ((4R,5R)-2,2-Dimethyl-1,3-dioxolane-4,5-diyl)dimethanol (5.50 g, 33.9 mmol) was added to this mixture at room temperature and the mixture was stirred for 45 min, at which time a large amount of an opaque white precipitate had formed. tert-Butyldimethylsilyl chloride was added and vigorous stirring was continued overnight. The mixture was poured into ethyl acetate (250 mL), washed with 10% aqueous potassium carbonate (50 mL), and brine (50 mL), dried (Na$_2$SO$_4$), and concentrated under reduced pressure. The resulting oil was purified by flash chromatography on silica gel to give 7.60 g (81%) of ((4R,5R)-5-((tert-butyldimethylsilyloxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methanol as a
colorless oil: [α]_{D}^{23} -16.3 (c 7.5, CHCl₃); IR (neat) 3471, 2986, 2930, 2858, 1472, 1463, 1370, 1254, 1217, 1167, 1082, 1004, 837, 778, 675 cm⁻¹; ^1H NMR (300 MHz, CDCl₃) δ 4.00 (dd, J = 5, 8 Hz, 1H), 3.92 – 3.89 (m, 2H), 3.82 – 3.64 (m, 3H), 2.38 (dd, J = 5, 8 Hz, 1H), 1.42 (s, 3H), 1.40 (s, 3H), 0.90 (s, 9H), 0.09 (s, 6H); ^13C NMR (75 MHz, CDCl₃) δ 109.5, 80.5, 78.4, 64.1, 63.1, 27.4, 27.3, 26.2, 18.7, -5.1; MS (Cl) m/z 277 (M+H)^+, 261, 245, 220, 219, 187, 161, 143, 131, 117, 89; HRMS (Cl) m/z 277.1833 (calcd for C₁₃H₂₉O₄Si: 277.1835).

((4R,5R)-5-((tert-Butyldimethyisilyloxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methyl 4-methylbenzenesulfonate. A solution of the alcohol prepared above (1.323 g, 4.79 mmol) and p-toluenesulfonyl chloride (1.37 g, 7.17 mmol) in pyridine (5 mL) was stirred for 16 h at 0 °C and then diluted with water and extracted with ethyl acetate (20 mL x 3). The combined organic extracts were washed with aqueous sodium bicarbonate solution (30 mL) and brine (20 mL), then dried (Na₂SO₄). The solvents were removed under reduced pressure and the resulting oil was purified by flash chromatography on silica gel (hexane: EtOAc, 5:1) to yield 1.88 g (91%) of tosylate as a colorless oil: [α]_{D}^{23} +6.6 (c 5, CHCl₃); IR (neat) 2986, 2930, 2857, 1598, 1471, 1462, 1369, 1253, 1178, 1095, 983, 838, 780, 665, 555 cm⁻¹; ^1H NMR (300 MHz, CDCl₃) δ 7.81 (d, J = 8 Hz, 2H), 7.34 (d, J = 8 Hz, 2H), 4.26 – 4.18 (m, 1H),
4.14 – 4.05 (m, 2H), 3.87 – 3.81 (m, 1H), 3.78 (dd, J = 4, 10 Hz, 1H), 3.64 (dd, J = 6, 10 Hz, 1H), 2.45 (s, 3H), 1.35 (s, 3H), 1.33 (s, 3H), 0.86 (s, 9H), 0.04 (s, 6H); \(^{13}\text{C}\) NMR (75 MHz, CDCl\(_3\)) \(\delta\) 145.3, 133.2, 130.2, 128.4, 110.4, 77.6, 76.9, 70.1, 63.7, 27.3, 27.2, 26.2, 22.0, 18.6, -5.1; MS (CI) \(m/z\) 431 (M+H)+, 415, 373, 355, 315, 271, 259, 229, 201, 173, 143; HRMS (CI) \(m/z\) 431.1916 (calcd for C\(_{20}\)H\(_{35}\)O\(_6\)SSi: 431.1924).

tert-Butyl((4R,5S)-5-(iodomethyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methoxy)dimethylsilane. A solution of the tosylate prepared above (8.07 g, 18.7 mmol) and sodium iodide (8.43 g, 56.2 mmol) in acetone (50 mL) was refluxed for 30 h. The solvent was evaporated, water (50 mL) was added, and the resulting solution was extracted with ether (50 mL x 3). The combined organic layer was dried (Na\(_2\)SO\(_4\)) and evaporated under reduced pressure. The resulting oil was purified by flash chromatography on silica gel (hexane: EtOAc, 12:1) to give 7.00 g (96%) of an iodide as a colorless oil: \(\alpha\)\(_{D}^{23}\) +2.8 (c 5.0, CHCl\(_3\)); IR (neat) 2986, 2954, 2929, 2857, 1471, 1370, 1253, 1137, 1091, 1005, 938, 838, 778, 675 cm\(^{-1}\); \(^{1}\text{H}\) NMR (300 MHz, CDCl\(_3\)) \(\delta\) 3.92 – 3.78 (m, 3H), 3.76 – 3.68 (m, 1H), 3.42 (dd, \(J = 5, 10, 1\)H), 3.31 (dd, \(J = 5, 10, 1\)H), 1.56 (s, 3H), 1.47 (s, 3H), 0.91 (s, 9H), 0.08 (s, 6H); \(^{13}\text{C}\) NMR (75 MHz, CDCl\(_3\)) \(\delta\) 109.9, 81.5, 78.3, 64.1, 27.9, 27.7, 26.3, 18.7, 7.3, -5.0; MS (CI) \(m/z\)
387 (M+H)$^+$, 371, 313, 285, 271, 241, 184, 143, 117, 75; HRMS (CI) m/z 387.0855 (calcd for C$_{13}$H$_{28}$IO$_3$Si: 387.0853).

2-((4$R$,5$R$)-5-((tert-Butyldimethylsilyloxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)acetonitrile. A solution of the iodide prepared above (0.118 g, 0.199 mmol) and potassium cyanide (0.032 g, 0.49 mmol) in dimethyl sulfoxide (0.7 mL) was stirred for 3 d at room temperature. Water (15 mL) was added to the reaction mixture and the resulting solution was extracted with ethyl acetate (10 mL x 3), washed with brine (10 mL), dried (Na$_2$SO$_4$), and concentrated under reduced pressure. The resulting oil was purified by flash chromatography on silica gel to afford 0.056 g (99%) of a nitrile as a colorless oil: [α]$_D$$^2$ +7.1 (c 1.1, CHCl$_3$); IR (neat) 2988, 2955, 2930, 2858, 2253, 1472, 1372, 1253, 1143, 1088, 1006, 972, 837, 779, 671 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.09 – 4.03 (m, 1H), 3.91 – 3.84 (m, 2H), 3.65 (dd, $J = 2$, 5, 10 Hz, 1H), 2.81 (dd, $J = 4$, 17 Hz, 1H), 2.64 (dd, $J = 4$, 17 Hz, 1H), 1.44 (s, 3H), 1.38 (s, 3H), 0.88 (s, 9H), 0.06 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 117.1, 110.4, 79.7, 75.0, 63.7, 27.4, 26.2, 22.4, 18.6, -5.1; MS (CI) m/z 286 (M+H)$^+$, 267, 228, 170, 156, 140, 117, 97, 73; HRMS (CI) m/z 286.1835 (calcd for C$_{14}$H$_{28}$NO$_3$Si: 286.1839).
2-((4R,5R)-5-((tert-Butyldimethylsilyloxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)acetaldehyde (16). In an argon-flushed round bottomed flask fitted with a rubber septum, argon inlet, and magnetic stirring bar, the nitrile prepared above (0.287g, 1 mmol) was dissolved in diethyl ether (3 mL) and cooled to -78 °C. Neat diisobutylaluminum hydride (0.197 mL, 1.1 mmol) was added slowly and the mixture was stirred for 2 h. The solution was transferred to a pre-cooled (0 °C) sat’d potassium sodium tartrate solution via a double-tipped needle, the mixture was stirred overnight and the layers were separated. The aqueous layer was extracted with diethyl ether (10 mL x 3) and the combined organic layers were dried (Na₂SO₄) and concentrated under reduced pressure. The resulting oil was purified by flash chromatography on silica gel (hexane: EtOAc, 10:1) to yield 16 (200 mg, 69%) as a colorless oil: [α]_D⁡23 +2.2 (c 5.0, CHCl₃); IR (neat) 2987, 2955, 2930, 2858, 1730, 1472, 1380, 1254, 1086, 837, 778 cm⁻¹; ^1H NMR (300 MHz, CDCl₃) δ 9.80 (dd, J = 2, 2 Hz, 1H), 4.35 (ddd, J = 4, 8, 8 Hz, 1H), 3.83 (dd, J = 4, 10 Hz, 1H), 3.73 (ddd, J = 4, 6, 8 Hz, 1H), 3.66 (dd, J = 6, 10 Hz, 1H), 2.75 (ddd, J = 2, 4, 17 Hz, 1H), 2.66 (ddd, J = 2, 8, 17 Hz, 1H), 1.39 (s, 3H), 1.38 (s, 3H), 0.88 (s, 9H), 0.05 (s, 6H); ^13C NMR (75 MHz, CDCl₃) δ 200.4, 190.7, 80.7, 74.6, 63.8, 47.5, 27.5, 27.2, 26.2, 18.7, -5.1; MS (Cl) m/z 287 (M-H)⁺, 273, 245, 231, 213, 173, 155, 145, 115; HRMS (Cl) m/z 287.1676 (calcd for C₁₄H₂₇O₄Si : 287.1679).
(S)-1-((4R,5R)-5-(tert-Butyldimethylsilyloxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)pent-4-en-2-ol (17).  In an argon-flushed 50 mL round-bottomed flask fitted with a rubber septum, argon inlet, and magnetic stirring bar, (-)-B-methoxydiisopinocampheylborane (1.98 g, 6.26 mmol) was dissolved in diethyl ether (7 mL) and the solution was cooled to 0 °C. Allylmagnesium bromide (1.0M solution in hexane, 5.36 mL) was added and the mixture was allowed to warm to room temperature. After 1 h, the solution was cooled to -100 °C and 16 (0.967 g, 3.35 mmol) dissolved in diethyl ether (10 mL) was added slowly via cannula. The mixture was allowed to warm to -78 °C for 1 h, then to 0 °C. After 1 h, 30% hydrogen peroxide (1.37 mL), and 4N NaOH (0.68 mL) were added to the reaction mixture was stirred overnight. The mixture was diluted with water (10 mL) and extracted with diethyl ether (20 mL x 3), dried (Na₂SO₄) and concentrated. The resulting oil was purified by flash chromatography on silica gel (hexane: EtOAc, 20:1) to produce a mixture of 17 and isopinocampheol (1.53 g) as a colorless oil. This was used in the next step without further purification: IR (neat) 3482, 3073, 2929, 2858, 1469, 1372, 1253, 1216, 1084, 913, 836, 777 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 5.83 (ddd, J = 7, 10, 17 Hz, 1H), 5.17 – 5.07 (m, 2H), 4.15 – 4.01 (m, 1H), 3.98 – 3.87 (m, 1H), 3.87 – 3.64
(m, 3H), 2.36 – 2.20 (m, 2H), 1.94 – 1.77 (m, 2H), 1.41 (s, 3H), 1.38 (s, 3H), 0.89 (s, 9H), 0.06 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 135.1, 118.2, 117.9, 109.0, 81.6, 80.9, 79.7, 77.6, 77.2, 70.9, 68.6, 64.1, 63.9, 42.4, 40.1, 39.5, 27.7, 27.3, 26.3, 18.7, -5.0, -5.1; MS (Cl) $m/z$ 331 (M+H)$^+$, 316, 315, 273, 255, 215, 197, 145, 123, 89, 75; HRMS (Cl) $m/z$ 331.2299 (calcd for C$_{17}$H$_{35}$O$_3$Si : 331.2305).

**tert-Butyl((((4R,5R)-5-((S)-2-methoxypent-4-enyl)-2,2-dimethyl-1,3-dioxolan-4-yl)methoxy)dimethylsilane (18).** To a stirred solution of 17 (32 mg, 0.097 mmol) in THF (1.2 mL) was added sodium hydride (12 mg, 0.30 mmol), and the mixture was refluxed for 1 h. The solution was cooled to room temperature, and methyl iodide was added dropwise. The solution was refluxed for 1.5 h, cooled to 0 °C, diluted with water (1 mL) and extracted with diethyl ether (5 mL x 3). The combined organic layers were washed with brine (5 mL), dried (Na$_2$SO$_4$) and concentrated under reduced pressure. The resulting oil was purified by column chromatography on silica gel to yield 18 (26 mg, 79% from 16) as a colorless oil: [$\alpha$]$_D^{23}$ +2.5 (c 6.6, CHCl$_3$); IR (neat) 3077, 2984, 2930, 2858, 1472, 1378, 1369, 1253, 1216, 1137, 1095, 913, 837, 777 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.82 (ddd, $J$ = 7, 10, 17 Hz, 1H), 5.13 – 5.06 (m, 2H), 4.06 (ddd, $J$ = 3, 8, 9 Hz, 1H), 3.78 – 3.71 (m, 2H), 3.70 – 3.61 (m, 1H), 3.52 –
3.44 (m, 1H), 3.38 (s, 3H), 2.33 – 2.29 (m, 2H), 1.74 (ddd, \( J = 3, 9, 14 \) Hz, 1H), 1.63 (ddd, \( J = 4, 9, 14 \) Hz, 1H), 1.40 (s, 3H), 1.38 (s, 3H), 0.90 (s, 9H), 0.07 (s, 6H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \( \delta \) 134.8, 117.6, 108.9, 82.0, 77.6, 75.9, 63.9, 57.4, 38.9, 38.8, 27.8, 27.4, 26.3, 18.8, -4.9; MS (CI) \( m/z \) 345 (M+H)\(^+\), 331, 289, 257, 231, 199, 171, 169, 125, 113, 75; HRMS (CI) \( m/z \) 345.2459 (calcd for C\(_{18}\)H\(_{37}\)O\(_4\)Si : 345.2461).

4-((4R,5R)-5-((tert-Butyldimethylsilyloxy)methyl)-2,2-dimethyl-1,3-dioxolan-4-yl)-3-methoxybutanal (19). In to a precooled (-78 °C) solution of 18 (0.362 g, 1.05 mmol) in dichloromethane (12 mL) was bubbled ozone until a light blue color persisted in the solution. The ozonide was quenched by addition of triphenylphosphine (1.38 g, 5.26 mmol) and the mixture was warmed to room temperature and stirred for 30 min. The reaction mixture was concentrated and purified via flash chromatography on silica to yield 19 (0.346 g, 95%) as a colorless oil: \( [\alpha]_D^{23} \) +9.0 (c 2.6, CHCl\(_3\)); IR (neat) 2985, 2954, 2930, 2858, 1727, 1472, 1463, 1379, 1253, 1216, 1087, 1005, 837, 778 cm\(^{-1}\); \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta \) 9.80 (dd, \( J = 2, 2 \) Hz, 1H), 4.00 (ddd, \( J = 2, 8, 10 \) Hz, 1H), 3.92 (ddd, \( J = 5, 5, 7, 8 \) Hz, 1H), 3.80 – 3.74 (m, 1H), 3.69 – 3.61 (m, 2H), 3.38 (s, 3H), 2.69 (ddd, \( J = 2, 5, 16 \) Hz, 1H), 2.62 (ddd, \( J = 2, 7, 16 \) Hz, 1H), 1.96 (ddd, \( J = 2, 8, 14 \) Hz, 1H), 1.62 (ddd, \( J = 5, 10, \))
14 Hz, 1H), 1.37 (s, 3H), 1.35 (s, 3H), 0.88 (s, 9H), 0.05 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 201.7, 109.2, 81.5, 76.1, 74.7, 63.8, 57.7, 49.2, 39.1, 27.7, 27.3, 26.3, 18.7, -5.0, -5.1; MS (Cl) m/z 347 (M+H)$^+$, 329, 303, 287, 255, 245, 213, 197, 173, 143, 129, 85, 73; HRMS (Cl) m/z 347.2249 (calcd for C$_{17}$H$_{35}$O$_5$Si : 347.2254).

1-((2$R$,4$R$,6$R$)-4,6-Dimethoxy-tetrahydro-2H-pyran-2-yl)ethane-1,2-diol (20). A solution of 19 (52 mg, 0.15 mmol) and pyridinium $p$-toluenesulfonate (2 mg) in methanol (2 mL) was gently refluxed for 12 h. The reaction mixture was concentrated and the resulting oil was purified by flash chromatography on silica gel (CH$_2$Cl$_2$: MeOH, 95:5) to yield 20 (27 mg, 87%) as a colorless oil: $[\alpha]_D^{23}$ -87.5 (c 1.19, CHCl$_3$); IR (neat) 3420, 2930, 2829, 1456, 1374, 1205, 1121, 1046, 1005, 966, 888 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.90 (d, $J = 3$ Hz, 1H), 3.84 – 3.61 (m, 5H), 3.34 (s, 3H), 3.32 (s, 3H), 2.61 (d, $J = 5$ Hz, 1H), 2.23 – 2.13 (m, 2H), 2.03 – 1.98 (m, 1H), 1.49 – 1.28 (m, 2H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 99.7, 74.2, 72.3, 69.2, 64.2, 55.9, 55.1, 36.3, 33.7; MS (Cl) m/z 207 (M+H)$^+$, 197, 175, 156, 143, 117, 113, 87, 71; HRMS (Cl) m/z 207.1230 (calcd for C$_9$H$_{19}$O$_5$ : 207.1232).
2-(tert-Butyldimethylsilyloxy)-1-((2R,4R,6R)-4,6-dimethoxy-tetrahydro-2H-pyran-2-yl)ethanol (21). Imidazole (18.8 mg, 0.276 mmol), tert-butyldimethylsilyl chloride (41 mg, 0.28 mmol) and 4-N,N-dimethylaminopyridine (2 mg) were added to a solution of 20 (26 mg, 0.13 mmol) in DMF (1 mL). After 12 h, the mixture was poured into saturated aq. sodium bicarbonate (5 mL) and extracted with diethyl ether (5 mL x 3). The combined organic layer was washed with brine (5 mL), dried (Na$_2$SO$_4$) and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane: EtOAc, 5:1) to yield 21 (31 mg, 78%) as a colorless oil: IR (neat) 3473, 2955, 2930, 2858, 2362, 1472, 1362, 1254, 1123, 1053, 1003, 967, 837, 776 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 4.89 (d, $J = 3$ Hz, 1H), 3.82 (ddd, $J = 2$, 4, 12 Hz, 1H), 3.70 – 3.55 (m, 4H), 3.32 (s, 3H), 3.30 (s, 3H), 2.44 (d, $J = 5$ Hz, 1H), 2.13 (ddddd, $J = 2$, 3, 4, 13 Hz, 1H), 2.01 – 1.96 (m, 1H), 1.48 – 1.38 (m, 2H), 0.89 (s, 9H), 0.07 (s, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 99.6, 74.3, 72.7, 67.7, 64.0, 55.8, 55.0, 36.4, 33.7, 26.2, 18.6, -5.0; MS (Cl) m/z 321 (M+H)$^+$, 313, 289.1, 257.1, 239.1, 213, 199, 173, 145, 117, 89, 75; HRMS (Cl) m/z 319.1941 (M$^+$ – H) (calcd for C$_{15}$H$_{31}$O$_2$Si : 319.1941).
5-((2R,4R,6R)-4,6-Dimethoxytetrahydro-2H-pyran-2-yl)-2,2,8,9,9-hexamethyl-3,3-diphenyl-4,7-dioxa-3,8-disiladecane. A solution of 21 (282 mg, 0.879 mmol) in dichloromethane (7.5 mL) was cooled to 0 °C and treated with 2,6-lutidine (0.32 mL, 2.6 mmol) and tert-butyldiphenylsilyl trifluoromethanesulfonate (529 mg, 1.32 mmol). The mixture was stirred at 0 °C for 30 min and at room temperature for 5 h, and then was quenched with saturated sodium bicarbonate solution. After the addition of dichloromethane (25 mL), the pH of the aqueous phase was adjusted to ca. 7.0 with 1M HCl. The aqueous phase was extracted with dichloromethane (20 mL x 3), and the combined organic phases were dried (MgSO₄), filtered, and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane: EtOAc, 15:1) to yield a bis(silyl) ether (471 mg, 96%) as a colorless oil: [α]D²³ -50.0 (c 0.95, CHCl₃); IR (neat) 3069, 3045, 2955, 2930, 2894, 2857, 2826, 1472, 1427, 1389, 1361, 1303, 1256, 1204, 1191, 1123, 1111, 1050, 1006, 972, 939, 927, 898, 836, 776, 739, 702 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.74 – 7.70 (m, 4H), 7.44 – 7.33 (m, 6H), 4.86 (d, J = 3 Hz, 1H), 3.77 – 3.67 (m, 3H), 3.59 – 3.45 (m, 2H), 3.29 (s, 3H), 3.19 (s, 3H), 2.12 – 2.04 (m, 1H), 1.90 – 1.82 (m, 1H), 1.46 – 1.18 (m, 2H), 1.06 (s, 9H), 0.79 (s, 9H), -0.11 (s, 3H), -0.15 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 136.4, 134.6, 134.3, 130.1, 129.9, 128.0, 127.8, 99.3, 76.2, 73.4, 67.7, 63.7,
55.7, 54.8, 36.7, 33.2, 27.5, 26.3, 20.0, 18.6, -1.0, -5.2; MS (CI) m/z 501 (M – t-Bu)⁺, 469, 437, 385, 345, 313, 261, 199, 147, 113, 89; HRMS (CI) m/z 501.2489 (calcd for C₂₇H₄₁O₅Si₂: 501.2493, M – t-Bu).

2-(tert-Butyldiphenylsilyloxy)-2-((2R,4R,6R)-4,6-dimethoxy-tetrahydro-2H-pyran-2-yl)ethanol. The silyl ether prepared above (57 mg, 0.096 mmol) and pyridinium p-toluenesulfonate (1.2 mg, 4.8 µmol) were dissolved in methanol (5 mL) and the solution was heated for 3 h. After the reaction was complete, the mixture was poured into saturated sodium bicarbonate solution and extracted with diethyl ether (5 mL x 3). The combined organic layer was washed with brine (5 mL), dried (Na₂SO₄) and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane: EtOAc, 3:1) to yield a monosilyl ether (34 mg, 75%) as a colorless oil: [α]₂⁰D +36.0 (c 0.75, CHCl₃); IR (neat) 3462, 2930, 2856, 1472, 1427, 1362, 1261, 1112, 1049, 822, 776, 740, 703 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.74 – 7.67 (m, 4H), 7.47 – 7.35 (m, 6H), 4.79 (d, J = 3 Hz, 1H), 3.84 (dt, J = 5, 5 Hz, 1H), 3.72 (ddd, J = 2, 4, 12 Hz, 1H), 3.71 – 3.60 (m, 2H), 3.57 – 3.46 (m, 1H), 3.31 (s, 3H), 3.12 (s, 3H), 2.13 – 2.03 (m, 2H), 1.80 (bs, 1H), 1.45 – 1.25 (m, 2H), 1.09 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 136.4, 136.1, 134.2, 133.7, 130.4, 130.3, 128.2,
99.5, 74.4, 72.9, 69.9, 64.1, 55.8, 55.0, 36.6, 32.3, 27.5, 19.8; MS (CI) m/z 413 (M – OMe)+, 355, 323, 303, 271, 245, 213, 199, 163, 135, 113, 91; HRMS (CI) m/z 413.2138 (calcd for C_{24}H_{33}O_4Si : 413.2148, M – OMe).

2-(tert-Butyldiphenylsilyloxy)-2-((2R,4R,6S)-4-methoxy-6-(phenylthio)-tetrahydro-2H-pyran-2-yl)ethanol (22). To the alcohol prepared above (207 mg, 0.466 mmol) in 1,2-dichloroethane (6 mL) at 0 °C were added zinc iodide (287 mg, 0.899 mmol) and trimethyl(phenylthio)silane (264 µL, 1.39 mmol). The mixture was allowed to warm to room temperature and stirred for 5 h. After the reaction was complete, the mixture was diluted with diethyl ether (20 mL) and washed with 10% HCl (10 mL). The organic layer was washed with brine (5 mL), dried (Na2SO4) and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane: EtOAc, 10:1) to yield 22 (113 mg, 47%) as a colorless oil: [α]D^23 167 (c 0.75, CHCl3); IR (neat) 3470, 3070, 3049, 2956, 2930, 2890, 2856, 1584, 1472, 1427, 1362, 1260, 1111, 1067, 997, 950, 853, 822, 740, 702 cm\(^{-1}\); \(^1\)H NMR (300 MHz, CDCl3) δ 7.74 – 7.67 (m, 5H), 7.47 – 7.35 (m, 10H), 5.73 (d, J = 5 Hz, 1H), 4.28 (ddd, J = 2, 3, 12 Hz, 1H), 3.79 (dt, J = 5, 4 Hz, 1H), 3.67 – 3.46 (m, 3H), 3.34 (s, 3H), 2.37 – 2.31 (m, 1H), 2.07 – 2.01 (m, 1H), 1.84 (ddd, J = 6,
12, 13 Hz, 1H), 1.55 – 1.40 (m, 1H), 1.08 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$
136.4, 136.2, 136.1, 135.3, 134.2, 133.6, 131.6, 130.4, 129.4, 128.2, 127.5,
85.1, 74.6, 73.6, 70.5, 64.0, 55.8, 37.5, 33.0, 27.6, 19.9; MS (CI) $m/z$ 413 (M – SPh)$^+$
381, 323, 303, 257, 225, 179, 111, 79; HRMS (CI) $m/z$ 413.2135 (calcd for
C$_{24}$H$_{33}$O$_4$Si : 413.21481, M – SPh).

![Chemical Structure](image)

2-(tert-Butyldiphenylsilyloxy)-2-((2R,4R,6S)-4-methoxy-6-(phenylthio)-
tetrahydro-2H-pyran-2-yl)acetaldehyde. A solution of dimethyl sulfoxide (92 µL,
1.3 mmol) and dichloromethane (5 mL) at -78 °C was treated with oxalyl chloride (57
µL, 0.65 mmol) and after 15 min, a solution of 22 (113 mg, 0.216 mmol) in
dichloromethane (4 mL) was added. After 15 min, triethylamine (181 µL, 1.30 mmol)
was added and the mixture was warmed to -10 °C slowly for 1 h, then to room
temperature for 0.5 h. The solution was poured into a mixture of diethyl ether (10
mL) and saturated ammonium chloride solution (10 mL) and the aqueous layer was
extracted with diethyl ether (10 mL x 2). The combined organic layer was washed
with saturated sodium bicarbonate solution (5 mL), dried (Na$_2$SO$_4$) and concentrated
under reduced pressure. The crude product was purified by flash chromatography on
silica gel (hexane: EtOAc, 15:1) to yield an aldehyde (110 mg, 99%) as a colorless oil:
[α]D$^2_23$ -165.0 (c 0.93, CHCl$_3$); IR (neat) 3071, 3048, 2956, 2930, 2890, 2857, 2824, 1736, 1585, 1472, 1427, 1375, 1233, 1113, 1063, 1006, 923, 851, 741, 702 cm$^{-1}$; $^1$H NMR (300 MHz, CDCl$_3$) δ 9.47 (d, $J = 1$ Hz, 1H), 7.66 – 7.61 (m, 5H), 7.41 – 7.21 (m, 10H), 5.68 (d, $J = 5$ Hz, 1H), 4.50 (dt, $J = 12$, 3 Hz, 1H), 4.09 (dd, $J = 1$, 3 Hz, 1H), 3.62 – 3.52 (m, 1H), 3.30 (s, 3H), 2.37 – 2.31 (m, 1H), 1.91 – 1.78 (m, 2H), 1.15 – 1.05 (m, 1H), 1.12 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ 202.5, 136.3, 134.9, 133.2, 133.1, 132.1, 130.5, 129.3, 128.2, 128.2, 127.6, 85.6, 79.8, 77.6, 73.0, 70.8, 55.8, 37.4, 33.5, 27.4, 19.9; MS (Cl) m/z 411 (M-SPh)$^+$ 379, 351, 301, 257, 199, 179, 111, 79; HRMS (Cl) m/z 411.1988 (calcd for C$_{24}$H$_{31}$O$_4$Si : 411.1992, M-SPh).

(E)-Methyl 4-(tert-Butyldiphenylsilyloxy)-4-((2R,4R,6S)-4-methoxy-6-(phenylthio)-tetrahydro-2H-pyran-2-yl)-2-methylbut-2-enoate (24). To a stirred solution of the aldehyde prepared above (110 mg, 0.211 mmol) in toluene (11 mL) was added (carbomethoxyethylidene)triphenylphosphorane (23, 226 mg, 0.649 mmol). The solution was heated to 100 °C for 12 h under an argon atmosphere. The solution was concentrated under reduced pressure and the crude product was purified by flash chromatography on silica gel (hexane: EtOAc, 12:1) to yield 24 (117 mg, 92%) as a colorless oil: [α]D$^2_23$ -151.0 (c 0.98, CHCl$_3$); IR (neat) 3070, 3045, 2950, 2930, 2886,
2857, 1717, 1653, 1472, 1428, 1361, 1240, 1192, 1112, 1057, 998, 949, 909, 822, 741, 702 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.66 – 7.58 (m, 5H), 7.40 – 7.28 (m, 10H), 6.64 (dd, J = 1, 9 Hz, 1H), 5.66 (d, J = 5 Hz, 1H), 4.47 (dd, J = 5, 9 Hz, 1H), 4.28 (ddd, J = 2, 5, 12 Hz, 1H), 3.67 (s, 3H), 3.64 – 3.54 (m, 1H), 3.36 (s, 3H), 2.38 – 2.30 (m, 1H), 2.16 – 2.08 (m, 1H), 1.84 (ddd, J = 6, 12, 13 Hz, 1H), 1.31 (d, J = 1 Hz, 3H), 1.39 – 1.22 (m, 1H), 1.05 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 168.4, 140.4, 136.4, 136.3, 135.5, 133.9, 131.8, 130.2, 130.1, 129.2, 129.1, 128.0, 127.8, 127.3, 85.3, 77.6, 73.5, 72.2, 72.0, 55.9, 52.6, 52.1, 37.5, 33.0, 27.4, 19.7, 16.0, 13.1; MS (CI) m/z 591 (M + H)⁺ 481, 449, 411, 371, 335, 303, 239, 199, 179, 111, 79; HRMS (CI) m/z 591.2603 (calcd for C₃₄H₄₃O₅SiS : 591.2600, M⁺ + H).

![Image](image_url)

(E)-4-(tert-Butyldiphenylsilyloxy)-4-((2R,4R,6S)-4-methoxy-6-(phenylthio)-tetrahydro-2H-pyran-2-yl)-2-methylbut-2-en-1-ol. Ester 24 (37 mg, 63 µmol) was dissolved in toluene (2 mL) and the solution was cooled to -78 °C. Diisobutylaluminum hydride (45 µL, 0.25 mmol) was added and the solution was stirred for 1 h at -78 °C. Saturated Rochelle salt solution (5 mL) and ethyl acetate (10 mL) were added, and the mixture was allowed to warm to room temperature and stirred for 2 h. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (5 mL x 3). The combined organic layer was washed with brine (5
mL), dried (Na₂SO₄) and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane: EtOAc, 5:1) to yield an alcohol (32 mg, 91%) as a colorless oil: [α]D²³ -156.0 (c 1.66, CHCl₃); IR (neat) 3441, 3070, 3049, 2953, 2929, 2890, 2856, 2821, 1472, 1427, 1361, 1158, 1111, 1056, 949, 822, 740, 702 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.67 – 7.58 (m, 5H), 7.40 – 7.28 (m, 10H), 5.76 (d, J = 5 Hz, 1H), 5.31 (dd, J = 1, 9 Hz, 1H), 4.49 (dd, J = 5, 9 Hz, 1H), 4.28 – 4.22 (m, 1H), 3.67 – 3.57 (m, 3H), 3.36 (s, 3H), 2.41 – 2.34 (m, 1H), 2.11 – 2.05 (m, 1H), 1.84 (ddd, J = 6, 12, 13 Hz, 1H), 1.09 (d, J = 1 Hz, 3H), 1.39 – 1.15 (m, 1H), 1.05 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 137.7, 136.5, 136.3, 135.6, 135.1, 134.4, 131.4, 130.0, 129.9, 129.1, 127.9, 127.7, 127.1, 125.2, 85.2, 73.7, 72.7, 72.1, 68.5, 55.9, 37.5, 33.5, 30.1, 27.4, 19.8, 14.2; MS (Cl) m/z 453 (M - SPh)⁺ 421, 375, 343, 275, 239, 199, 179, 111, 79; HRMS (Cl) m/z 453.2454 (calcd for C₂₇H₅₇O₄Si : 453.2461, M⁺ - SPh).

(R,E)-4-(tert-Butyldiphenylsilyloxy)-4-((2R,4R,6S)-4-methoxy-6-(phenylthio)-tetrahydro-2H-pyran-2-yl)-2-methylbut-2-enal (25). A solution of dimethyl sulfoxide (25 µL, 0.35 mmol) and dichloromethane (2 mL) at -78 °C was treated with oxalyl chloride (15 µL, 0.17 mmol). After 15 min, a solution of the alcohol prepared
above (32 mg, 57 µmol) in dichloromethane (2 mL) was added. After 15 min, triethylamine (49 µL, 0.35 mmol) was added. The reaction was warmed to -10 °C slowly for 1 h, then warmed to rt for 0.5 h. The reaction was poured into a mixture of diethyl ether (5 mL) and saturated ammonium chloride solution (5 mL). The aqueous layer was extracted with diethyl ether (5 mL x 3). The combined organic layer was washed with saturated sodium bicarbonate solution (5 mL), dried (Na₂SO₄) and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane : EtOAc = 10 : 1) to yield 25 (27.8 mg, 87%) as a colorless oil: [α]D⁰ -134 (c 0.22, CHCl₃); IR (neat) 3073, 2958, 2928, 2856, 1695, 1470, 1387, 1112, 1005, 949, 908, 822, 804, 741, 702 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 9.07 (s, 1H), 7.65 – 7.57 (m, 4H), 7.40 – 7.29 (m, 11H), 6.25 (dd, J = 1, 9 Hz, 1H), 5.70 (d, J = 5 Hz, 1H), 4.62 (dd, J = 4, 9 Hz, 1H), 4.30 (ddd, J = 2, 4, 12 Hz, 1H), 3.69 – 3.58 (m, 1H), 3.36 (s, 3H), 2.39 – 2.33 (m, 1H), 2.16 – 2.08 (m, 1H), 1.82 (ddd, J = 6, 11, 17 Hz, 1H), 1.46 (d, J = 12 Hz, 0.5H), 1.39 (d, J = 12 Hz, 0.5H), 1.23 (d, J = 1 Hz, 3H), 1.06 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 195.1, 151.7, 139.4, 136.3, 135.1, 133.8, 133.5, 131.9, 130.5, 129.2, 128.2, 128.1, 127.6, 84.9, 73.4, 72.1, 71.9, 55.9, 37.2, 33.3, 27.5, 19.8, 9.8; MS (CI) m/z 561 (M + H)⁺ 529, 451, 419, 373, 341, 305, 273, 239, 195, 163, 111, 75; HRMS (CI) m/z 561.2502 (caled for C₃₃H₄₁O₄SiS : 561.2495, M⁺ + H).
(2E,4E)-Ethyl 6-(tert-Butyldiphenylsilyloxy)-6-((2R,4R,6S)-4-methoxy-6-(phenylthio)-tetrahydro-2H-pyran-2-yl)-4-methylhexa-2,4-dienoate (27). To a slurry of sodium hydride (6.8 mg, 0.17 mmol) in THF (1.5 mL) at 0 °C was added triethyl phosphonoacetate (26, 34 µL, 0.17 mmol). The mixture was stirred for 0.5 h. Aldehyde 25 (31.8 mg, 57 µmol) diluted in THF (2 mL) was added. The reaction was allowed to warm to room temperature and stirred for 1 h. The reaction was quenched by adding water (1 mL) and the mixture was extracted with diethyl ether (5 mL x 3). The combined organic layer was washed with brine (5 mL), dried (Na₂SO₄) and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane : EtOAc = 9 : 1) to yield 27 (29.7 mg, 83%) as a colorless oil: [α]D²³ -161 (c 0.28 , CHCl₃); IR (neat) 3071, 3048, 2953, 2928, 2856, 2824, 1716, 1623, 1472, 1363, 1306, 1270, 1203, 1173, 1111, 1055, 823, 740, 702 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.70 – 7.67 (m, 4H), 7.43 – 7.30 (m, 11H), 7.15 (d, J = 16 Hz, 1H), 5.85 (d, J = 9 Hz, 1H), 5.71 (d, J = 16 Hz, 1H), 5.70 (d, J = 6 Hz, 1H), 4.54 (dd, J = 5, 9 Hz, 1H), 4.32 – 4.22 (m, 3H), 3.68 – 3.58 (m, 1H), 3.38 (s, 3H), 2.41 – 2.35 (m, 1H), 2.14 – 2.08 (m, 1H), 1.84 (ddd, J = 6, 12, 18 Hz, 1H), 1.35 (t, J = 7 Hz, 3H), 1.40 – 1.20 (m, 1H), 1.25 (d, J = 1 Hz, 3H), 1.08 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 167.5, 149.1, 139.8, 136.4, 136.3, 135.4, 134.4, 134.0, 132.2, 130.2, 129.2,
128.0, 127.9, 127.5, 118.0, 85.5, 73.5, 72.5, 72.1, 60.7, 55.8, 37.5, 33.3, 27.5, 19.8, 14.8, 12.9; MS (Cl) m/z 630 (M+), 553, 521, 489, 443, 411, 375, 343, 297, 265, 233, 179, 139, 111, 75; HRMS (Cl) m/z 630.2823 (calcd for C_{37}H_{46}O_{5}SiS : 630.2835, M+).

(2E,4E)-6-(tert-Butyldiphenylsilyloxy)-6-((2R,4R,6S)-4-methoxy-6-(phenylthio)-tetrahydro-2H-pyran-2-yl)-4-methylhexa-2,4-dien-1-ol. Ester 27 (29.7 mg, 0.0947 mmol) was dissolved in toluene (2 mL) and cooled to -78 °C. Diisobutylaluminum hydride (0.07 mL, 0.393 mmol) was added. After the addition was completed, the reaction was stirred for 1 h at -78 °C. Saturated Rochelle salt solution (1 mL) and ethyl acetate (2 mL) were successively added, and the mixture was allowed to warm to room temperature and stirred for 2 h. The organic layer was separated and the aqueous layer was extracted with ethyl acetate (5 mL x 3). The combined organic layer was washed with brine (5 mL), dried (Na_{2}SO_{4}) and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane : EtOAc = 4 : 1) to yield an alcohol (27 mg, 99%) as a colorless oil: \(^1\)H NMR (300 MHz, CDCl_{3}) \(\delta\) 7.70 – 7.60 (m, 4H), 7.40 – 7.15 (m, 11H), 6.09 (d, \(J = 16\) Hz, 1H), 5.68 – 5.58 (m, 2H), 5.48 (d, \(J = 9\) Hz, 1H), 4.51 (dd, \(J = 5, 9\) Hz, 1H), 4.28 – 4.14 (m, 3H), 3.65 – 3.53 (m, 1H), 3.35 (s, 3H), 2.39 – 2.31 (m, 1H), 2.12 – 2.06 (m, 1H), 1.80 (ddd, \(J = 6, 11, 17\) Hz, 1H), 1.40 – 1.20 (m, 1H), 1.21 (d, \(J = 1\) Hz, 3H),
1.04 (s, 9H), 0.90 (d, \( J = 7 \text{ Hz}, 1\text{H})\); \(^{13}\text{C NMR (75 MHz, CDCl}_3\)) \( \delta 136.4, 136.3, 136.1, 135.7, 135.2, 134.4, 132.0, 131.8, 130.0, 129.9, 129.2, 127.9, 127.8, 127.3, 85.6, 73.7, 72.7, 72.2, 64.1, 55.8, 37.6, 33.2, 27.5, 19.8, 13.2; MS (ES) \( m/z \) 606 (M + NH\(_4\))\(^+\) 520, 476, 432, 388, 344, 300, 239, 195; HRMS (ES) \( m/z \) 606.3052 (calcd for C\(_{35}\)H\(_{48}\)NO\(_4\)SiS : 606.3073, M + NH\(_4\))\(^+\)).

(2\text{E,4\text{E}})-6-(\text{tert-Butyldiphenylsilyloxy})-6-((2\text{R,4\text{R},6\text{S}})-4\text{-methoxy}-6-(\text{phenylthio})\text{-tetrahydro-2H-pyran-2-yl})-4\text{-methylhexa-2,4-dienal} (28). A solution of dimethyl sulfoxide (20 \( \mu \text{L}, 0.29 \text{ mmol}) and dichloromethane (2 mL) at -78 °C was treated with oxalyl chloride (13 \( \mu \text{L}, 0.14 \text{ mmol). After 15 min, a solution of the alcohol prepared above (27 mg, 46 \( \mu \text{mol}) in dichloromethane (2 mL) was added. After 15 min, triethylamine (40 \( \mu \text{L}, 0.29 \text{ mmol}) was added. The reaction was warmed to -10 °C slowly for 1 h, then warmed to room temperature for 0.5 h. The reaction was poured into a mixture of diethyl ether (5 mL) and saturated ammonium chloride solution (5 mL). The aqueous layer was extracted with diethyl ether (5 mL x 3). The combined organic layer was washed with saturated sodium bicarbonate solution (5 mL), dried (Na\(_2\)SO\(_4\)) and concentrated under reduced pressure. The crude product was purified by flash chromatography on silica gel (hexane : EtOAc = 10 : 1) to yield 28 (24.7 mg,
90%) as a colorless oil: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 9.51 (d, $J$ = 8 Hz, 1H), 7.70 – 7.60 (m, 4H), 7.40 – 7.15 (m, 11H), 6.83 (d, $J$ = 16 Hz, 1H), 5.94 (dd, $J$ = 8, 16 Hz, 1H), 5.87 (d, $J$ = 9 Hz, 1H), 5.69 (d, $J$ = 6 Hz, 1H), 4.53 (dd, $J$ = 5, 9 Hz, 1H), 4.34 – 4.22 (m, 1H), 3.67 – 3.56 (m, 1H), 3.36 (s, 3H), 2.39 – 2.32 (m, 1H), 2.16 – 2.08 (m, 1H), 1.81 (ddd, $J$ = 6, 11, 17 Hz, 1H), 1.40 – 1.20 (m, 1H), 1.24 (d, $J$ = 1 Hz, 3H), 1.05 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 194.3, 157.2, 141.9, 136.3, 136.3, 135.4, 134.7, 134.0, 133.8, 131.8, 130.3, 130.2, 129.2, 128.6, 128.1, 127.9, 127.4, 85.1, 73.5, 72.4, 71.9, 55.9, 37.3, 33.2, 27.4, 19.8, 13.0; MS (Cl) $m/z$ 587 (M+H)$^+$ 477, 445, 367, 331, 239, 179, 139, 111, 79; HRMS (Cl) $m/z$ 587.2636 (calcd for C$_{35}$H$_{43}$O$_4$SSi : 587.2651, M+H).

(4R,5E,7E,9R)-9-((tert-Butyldiphenylsilyloxy)-9-((2R,4R,6S)-4-methoxy-6-(phenylthio)-tetrahydro-2H-pyran-2-yl)-7-methylnona-1,5,7-trien-4-ol (29). In an argon-flushed round-bottomed flask fitted with a rubber septum, argon inlet, and magnetic stirring bar, (+)-B-methoxydiisopinocampheylborane (65 mg, 0.205 mmol) was dissolved in diethyl ether (1.5 mL) and cooled to 0 °C. Allylmagnesium bromide (0.175 mL, 0.175 mmol, 1.0M solution in diethyl ether) was added via syringe and the mixture was allowed to warm to room temperature. After 1 h, the reaction was cooled to –78 °C and aldehyde 28 (24.7 mg, 42 µmol) dissolved in diethyl ether (1 mL) was
added slowly. After 3 h, 30% hydrogen peroxide (0.4 mL) and saturated sodium bicarbonate (0.8 mL) were added. The reaction was stirred overnight. The mixture was diluted with water (1 mL) and extracted with diethyl ether (5 mL x 3), dried (Na$_2$SO$_4$) and concentrated under reduced pressure. The resulting oil was purified by flash chromatography on silica gel (hexane: EtOAc = 9:1) to produce 29 (21 mg, 79%) as a colorless oil: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.70 – 7.60 (m, 4H), 7.40 – 7.15 (m, 11H), 6.03 (d, $J = 16$ Hz, 1H), 5.88 – 5.74 (m, 1H), 5.68 (d, $J = 5$ Hz, 1H), 5.50 – 5.43 (m, 2H), 5.21 – 5.12 (m, 2H), 4.51 (dd, $J = 5, 9$ Hz, 1H), 4.30 – 4.15 (m, 2H), 3.66 – 3.53 (m, 1H), 3.35 (s, 3H), 2.40 – 2.23 (m, 3H), 2.13 – 2.04 (m, 1H), 1.81 (ddd, $J = 6, 12, 17$ Hz, 1H), 1.40 – 1.20 (m, 1H), 1.18 (d, $J = 1$ Hz, 3H), 1.04 (s, 9H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 136.5, 136.4, 135.8, 135.4, 135.2, 134.7, 134.4, 134.3, 132.0, 131.8, 130.8, 130.0, 129.8, 129.2, 127.9, 127.7, 127.2, 118.6, 85.6, 73.7, 72.7, 72.3, 72.2, 55.9, 42.5, 37.6, 33.3, 27.5, 19.8, 13.2; MS (Cl) m/z 519 (M – SPh)$^+$ 469, 445, 409, 239, 179, 111; HRMS (Cl) m/z 519.2920 (calcd for C$_{32}$H$_{43}$O$_4$Si: 519.2931, M – SPh).

tert-Butyl-((1$R,2E,4E,6R$)-6-methoxy-1-((2$R,4R,6S$)-4-methoxy-6-(phenylthio)-tetrahydro-2H-pyran-2-yl)-3-methylnona-2,4,8-trienyloxy)diphenylsilane (30).

To a stirred solution of alcohol 29 (21 mg, 33 µmol) in THF (2.5 mL) was added
sodium hydride (13 mg, 0.33 mmol) and the mixture was refluxed for 1 h. The solution was cooled to room temperature, and methyl iodide (21 µL, 0.33 mmol) was added. The solution was refluxed for 1.5 h, cooled to 0 °C, diluted with water (1 mL) and extracted with diethyl ether (5 mL x 3). The combined organic layer was washed with brine (5 mL), dried (Na₂SO₄) and concentrated under reduced pressure. The resulting oil was purified by flash chromatography on silica gel (hexane: EtOAc = 19:1) to produce 30 (21.4 mg, 89%) as a colorless oil: [α]ᵩ̂D –174.1 (c 2.2, CHCl₃); IR (neat) 3071, 2956, 2924, 2854, 1463, 1428, 1361, 1260, 1111, 966, 911, 821, 804, 740, 702 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.70 – 7.60 (m, 4H), 7.40 – 7.15 (m, 11H), 5.99 (d, J = 16 Hz, 1H), 5.85 – 5.72 (m, 1H), 5.70 (d, J = 5 Hz, 1H), 5.45 (d, J = 9 Hz, 1H), 5.29 (dd, J = 8, 16 Hz, 1H), 5.14 – 5.05 (m, 2H), 4.51 (dd, J = 5, 9 Hz, 1H), 4.27 (ddd, J = 2, 5, 12 Hz, 1H), 3.66 – 3.55 (m, 2H), 3.36 (s, 3H), 3.22 (s, 3H), 2.42 – 2.21 (m, 3H), 2.14 – 2.05 (m, 1H), 1.82 (ddd, J = 6, 12, 17 Hz, 1H), 1.40 – 1.20 (m, 1H), 1.18 (d, J = 1 Hz, 3H), 1.04 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 137.3, 136.4, 136.4, 135.8, 135.3, 135.0, 134.5, 134.3, 131.9, 131.6, 130.0, 129.8, 129.1, 128.9, 127.9, 127.7, 127.3, 117.3, 85.6, 82.4, 73.6, 72.7, 72.2, 56.6, 55.9, 40.7, 37.6, 33.4, 27.5, 19.8, 13.2; MS (Cl) m/z 643 (M + H)⁺, 611, 579, 533, 501, 469, 419, 355, 323, 277, 245, 199, 179, 111, 75; HRMS (Cl) m/z 643.3280 (calcd for C₃₉H₅₁O₄SiS : 643.3277, M + H).
(4R,6R)-6-((1R,2E,4E,6R)-1-(tert-Butyldiphenylsilyloxy)-6-methoxy-3-methylnona-2,4,8-trienyl)-4-methoxy-tetrahydropyran-2-one (31). To a stirred solution of alcohol 30 (42.5 mg, 66 µmol) in THF-H₂O (5:1, 6 mL) was added silver nitrate (231 mg, 1.36 mmol) and 2,6-lutidine (268 µL, 0.230 mmol), and the mixture was stirred for 3 h at room temperature. The solution was diluted with water (5 mL) and extracted with ethyl acetate (5 mL x 3). The combined organic layer was washed with brine (5 mL), dried (Na₂SO₄) and concentrated under reduced pressure. The resulting oil was purified by flash chromatography on silica gel (hexane: EtOAc = 4:1) to produce a hemiacetal as a colorless oil.

To a stirred solution of the hemiacetal in dichloromethane (5 mL) was added tetrapropylammonium perruthenate (TPAP, 3.8 mg, 11 µmol), 4-methylmorpholine N-oxide (NMO, 45 mg, 0.38 mmol) and 4Å molecular sieves, and the mixture was stirred for 3 h at room temperature. The solution was purified by flash chromatography on silica gel (hexane: EtOAc = 4:1) to produce 31 (30.4 mg, 84%) as a colorless oil: [α]D²³ -55.0 (c 0.55, CHCl₃); IR (neat) 3071, 2928, 2855, 2814, 1748, 1472, 1427, 1360, 1234, 1110, 998, 967, 914, 822, 741, 702 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 7.74 – 7.60 (m, 4H), 7.43 – 7.26 (m, 6H), 6.02 (d, J = 16 Hz, 1H), 5.77 (ddt, J = 17, 11, 7 Hz, 1H), 5.45 (d, J = 9 Hz, 1H), 5.36 (dd, J = 8, 16 Hz, 1H), 5.12 – 5.05
(m, 2H), 4.62 (dd, J = 5, 9 Hz, 1H), 4.20 – 4.14 (m, 1H), 3.72 – 3.57 (m, 2H), 3.34 (s, 3H), 3.23 (s, 3H), 2.87 (ddd, J = 1, 5, 17 Hz, 1H), 2.41 (dd, J = 8, 17 Hz, 1H), 2.34 – 2.21 (m, 3H), 1.60 – 1.50 (m, 1H), 1.28 (d, J = 1 Hz, 3H), 1.06 (s, 9H); 13C NMR (75 MHz, CDCl3) δ 170.1, 136.8, 136.7, 136.3, 134.9, 133.9, 133.7, 130.3, 130.0, 129.9, 129.4, 128.1, 117.3, 82.2, 80.1, 72.8, 71.2, 56.7, 56.4, 40.6, 37.2, 30.3, 30.1, 27.4, 19.8, 15.7, 13.4; MS (Cl) m/z 549 (M + H)⁺ 517, 485, 459, 419, 363, 321, 289, 239, 199, 179, 137, 79; HRMS (Cl) m/z 549.3019 (calcd for C33H45O5Si : 549.3036, M + H).

(3R,4E,6E,8R)-8-(tert-Butyldiphenylsilyloxy)-3-methoxy-8-((4R)-4-methoxy-6-oxo-tetrahydro-2H-pyran-2-yl)-6-methylomega-4,6-dienal. To a stirred solution of 31 (24.1 mg, 44 µmol) in THF-water (1:1, 4.39 mL, 0.01M) was added osmium tetroxide (0.001M in t-BuOH, 176 µL, 0.4 mol %) and sodium periodate (28.2 mg, 132 µmol), and the mixture was stirred at room temperature for 20 h under an argon atmosphere. The reaction was diluted with water (5 mL) and extracted with diethyl ether (5 mL x 3). The combined organic layer was washed with brine (5 mL), dried (Na2SO4) and concentrated under reduced pressure. The resulting oil was purified by flash chromatography on silica gel (hexane: EtOAc = 5:1) to produce an aldehyde (13.7 mg, 57%) as a colorless oil: IR (neat) 3069, 2925, 2854, 1734, 1463, 1427, 1361,
1235, 1156, 1110, 998, 969, 822, 800, 741, 703 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 9.76 (t, J = 2 Hz, 1H), 7.74 – 7.60 (m, 4H), 7.43 – 7.26 (m, 6H), 6.09 (d, J = 16 Hz, 1H), 5.49 (d, J = 8 Hz, 1H), 5.37 (dd, J = 8, 16 Hz, 1H), 4.64 (dd, J = 5, 9 Hz, 1H), 4.21 – 4.09 (m, 2H), 3.72 – 3.63 (m, 1H), 3.35 (s, 3H), 3.25 (s, 3H), 2.88 (dd, J = 5, 17 Hz, 1H), 2.53 (dd, J = 2, 5 Hz, 1H), 2.50 – 2.28 (m, 4H), 1.60 – 1.50 (m, 1H), 1.28 (d, J = 1 Hz, 3H), 1.05 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ; MS (ES) m/z 568 (M⁺ + NH₄⁺); HRMS (ES) m/z 568.3049 (calcd for C₃₂H₄₆NO₆Si: 568.3094, M + NH₄⁺).

(4R,6R)-6-((1R,2E,4E,6R,8E)-9-Bromo-1-(tert-butyldiphenylsilyloxy)-6-methoxy-3-methylnona-2,4,8-trienyl)-4-methoxy-tetrahydropyran-2-one (15).

Chromium(III) bromide monohydrate was flame-dried under vacuum and placed in a preheated oil bath (130 °C) for 24 h. During this period, the color of the chromium(III) bromide changed from black to dark green. THF (7 mL) was added to the anhydrous chromium(III) bromide (467 mg, 1.60 mmol) and the flask was cooled to 0 °C. During this period, the color of the chromium(III) bromide changed from green to dark brown. Lithium aluminium hydride (0.80 mL, 0.8 mmol, 1M solution in THF) was added to the reaction dropwise. During this period, the color of the solution changed from brown to bright green. The aldehyde prepared above (57 mg, 93 µmol) and bromoform (70 µL, 0.801 mmol) were added. The mixture was allowed to warm
to 50 °C and stirred for 12 h at 50 °C. The mixture was diluted with water (10 mL) and extracted with diethyl ether (10 mL x 3). The combined organic layer was washed with brine (5 mL), dried and concentrated under reduced pressure. The resulting oil was purified by flash chromatography on silica gel (hexane: EtOAc = 8:1) to give 15 (23.4 mg, 40%) as an unstable colorless oil. This material was used immediately for coupling reactions with C19-C32 fragment 2.