SUPPORTING INFORMATION

Total Synthesis of Solandelactones E and F, Homoeicosanoids from the Hydroid
Solanderia secunda.

James D. White*, William H. C. Martin, Christopher M. Lincoln, and Jongtae Yang

Department of Chemistry, Oregon State University, Corvallis, Oregon 97331

Email: james.white@oregonstate.edu
(1R,2S)-1-(Trityloxymethyl)-2-vinylcyclopropane. Triflic anhydride (246 µL, 1.46 mmol) was added dropwise via syringe to a stirred solution of (2R,4Z)-6-(tri-n-butylstannyl)-1-trityloxy-hex-4-en-2-ol (1, 630 mg, 0.973 mmol) and collidine (192 µL, 1.46 mmol) in CH₂Cl₂ (10 mL) at -78 ºC under argon, and the mixture was stirred for 1 h. Et₃N (443 µL, 3.42 mmol) was added dropwise via syringe, and the mixture was stirred for an additional 19 h at -78 ºC. The mixture was allowed to warm to ambient temperature and concentrated under reduced pressure. The residue was purified by column chromatography (2-4% EtOAc in hexane, containing 1% Et₃N) to yield 302 mg (91%) of (1R,2S)-1-(trityloxymethyl)-2-vinylcyclopropane (2) as a >36:1 mixture of trans and cis vinylcyclopropanes (Chiral OD, 0.85 mL/min, 100% hexanes): [α]D̂₂³ -45.3 (c 1.0, CHCl₃); IR (neat) 3083, 3059, 3021, 2993, 2955, 2915, 2868, 1635, 1597, 1491, 1448, 1402, 1317, 1218, 1182, 1153 cm⁻¹; ¹H NMR (300 MHz, CDCl₃) δ 0.66 (t, J = 6.9 Hz, 2H), 1.07-1.23 (m, 1H), 1.24-1.34 (m, 1H), 2.94 (dd, J = 6.5, 9.6 Hz, 1H), 3.07 (dd, J = 6.1, 9.6 Hz, 1H), 4.88 (dd, J = 1.7, 10.3 Hz, 1H), 5.06 (ddd, J = 0.5, 1.7, 17.1 Hz, 1H), 5.45 (ddt, J = 8.5, 10.2, 17.1 Hz, 2H), 7.20-7.34 (m, 9H), 7.44-7.49 (m, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 11.9, 20.4, 20.6, 66.7, 86.2, 111.9, 126.9, 127.7, 128.7, 141.2, 144.3; MS (CI) m/z 340 (M)⁺, 263, 243, 228, 183, 165, 143, 105, 91; HRMS (CI) m/z 340.1827 (calcd for C₂₅H₂₄O: 340.1827).
(1R,2R)-1-(Trityloxymethyl)-2-[1-(R)-tert-butyldimethylsiloxy-4-hydroxypropyl]cyclopropane. K$_2$OsO$_4$•2H$_2$O (49.4 mg, 5 mol%) and NaIO$_4$ (341 mg, 1.60 mmol) were added to a stirred solution of (1R,2S)-1-(trityloxymethyl)-2-vinylcyclopropane (545 mg, 1.60 mmol) in THF (17 mL) and H$_2$O (14 mL). After 1 h, an additional quantity of NaIO$_4$ was added (1.02 g, 4.80 mmol) and the reaction was stirred for 17 h. Saturated aqueous Na$_2$S$_2$O$_3$ (8.8 mL) was added and, after 30 min, the mixture was extracted with 75% EtOAc in hexane (3 x 50 mL). The combined extracts were dried (Na$_2$SO$_4$), filtered, and concentrated under reduced pressure to give aldehyde 3 as an unstable oil.

TiCl$_4$ (3.20 mL, 1.0 M in CH$_2$Cl$_2$, 2 eq) was added slowly to a stirred solution of 1-((S)-4-isopropyl-5,5-diphenyl-2-thioxooxazolidin-3-yl)ethanone (4, 1.09 g, 3.20 mmol, 2 eq) in CH$_2$Cl$_2$ (7.75 mL) at 0 ºC under argon. After 10 min, (-)-sparteine (739 µL, 3.20 mmol, 2 eq) and N-methylpyrrolidone (309 µL, 3.20 mmol, 2 eq) were added and the mixture was stirred an additional 30 min at 0 ºC. The solution was cooled to -78 ºC and a solution of the aldehyde obtained above in CH$_2$Cl$_2$ (3.5 mL) was added dropwise over 10 min under argon. After 49 h at -78 ºC, the reaction was quenched with saturated aqueous NH$_4$Cl (15 mL) and extracted with CH$_2$Cl$_2$ (3 x 40 mL). The combined organic extracts were dried (Na$_2$SO$_4$), filtered, and concentrated under reduced pressure to give unstable alcohol 5.

TBSOTf (1.13 mL, 98%, 4.80 mmol) and collidine (632 µL, 4.80 mmol) were added sequentially to a stirred solution of the aldol product obtained above in CH$_2$Cl$_2$ (28 mL) at -78 ºC under argon. After 16 h at -78 ºC, the reaction mixture was quenched with saturated aqueous NH$_4$Cl (10 mL) and extracted with CH$_2$Cl$_2$ (2 x 20 mL). The
combined organic extracts were dried (Na$_2$SO$_4$), filtered, concentrated under reduced pressure and dried in vacuo to give 6.

A suspension of LiCl (813 mg, 19.2 mmol) and NaBH$_4$ (365 mg, 9.6 mmol) in THF (17 mL) was stirred at ambient temperature under argon for 1 h, and a solution of 6 obtained above in THF (10 mL) was added slowly. After 18 h, the reaction mixture was added to a separatory funnel containing saturated aqueous NaHCO$_3$ (25 mL) and was extracted with CH$_2$Cl$_2$ (4 x 25 mL). The combined organic extracts were dried (Na$_2$SO$_4$), filtered, and concentrated under reduced pressure. The residue was purified on a column of silica gel (2-50% EtOAc in cyclohexane) to afford 186 mg (23%, 4 steps) of (1R,2R)-1-(trityloxy)methyl)-2-[1-(R)-tert-butyldimethylsiloxy-4-hydroxy-propyl]cyclopropane (7): [α]$_D^{23}$ -23.2 (c 1.0, CHCl$_3$); IR (neat) 3440, 3085, 3060, 3023, 3000, 2954, 2928, 2884, 2856, 1491, 1471, 1449, 1377, 1360, 1255, 1217, 1173, 1154 cm$^{-1}$; $^1$H NMR (300 MHz, acetone-d$_6$) δ 0.09 (s, 3H), 0.11 (s, 3H), 0.36 (td, $J$ = 4.8, 8.4 Hz, 1H), 0.54 (td, $J$ = 4.9, 8.6 Hz, 1H), 0.73-0.88 (m, 1H), 0.91 (s, 9H), 0.96-1.12 (m, 1H), 1.81 (dd, $J$ = 6.3Hz, 13.4 Hz, 1H), 1.93 (ddd, $J$ = 5.1, 6.8, 13.4 Hz, 1H), 2.80 (dd, $J$ = 7.4, 9.6 Hz, 1H), 3.11 (dd, $J$ = 5.8, 9.6 Hz, 1H), 3.45 (ddd, $J$ = 5.0, 7.9, 13.6 Hz, 2H), 3.69-3.80 (m, 2H), 7.20-7.27 (m, 3H), 7.28-7.35 (m, 6H), 7.44-7.50 (m, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) δ -4.7, -3.9, 9.7, 16.2, 18.0, 23.3, 25.8, 39.3, 60.3, 67.0, 75.3, 86.3, 126.9, 127.7, 128.6, 144.3; MS (Cl) $m/z$ 501 (M-H)$^+$, 484, 457, 352, 293, 243, 165; HRMS (CI) $m/z$ 501.2823 (calcd for C$_{32}$H$_{41}$O$_3$Si: 501.2823).
(3R)-6-(tert-Butyldiphenylsilanyloxy)-3-hydroxy-1-(4S-isopropyl-2-thioxothiazolidin-3-yl)hex-4-en-1-one. To a solution of 1-(4-isopropyl-2-thioxothiazolidin-3-yl)ethanone (9, 0.645g, 3.42 mmol) in CH$_2$Cl$_2$ (25 mL) at 0 °C was added titanium tetrachloride (416 µL, 3.80 mmol). After 5 min, the solution was cooled to -78 °C and diisopropylethylamine (662 µL, 3.80 mmol) was added dropwise over 5 min. The solution was stirred at -78 °C for 2 h and 4-(tert-butyldiphenylsilanyloxy)but-2-enal (8, 740mg, 2.28 mmol) in CH$_2$Cl$_2$ (7 mL) was added via cannula over 5 min. The dark solution was stirred at -78 °C for a further 6 h, then was quenched with a saturated solution of ammonium chloride (10 mL) and extracted with CH$_2$Cl$_2$ (3 x 20 mL). The organic phase was dried over sodium sulfate and the solvent was removed. Column chromatography (10% to 25% EtOAc in pentane) gave 10 (1.154g, 94%) as a yellow oil: [α]$_{D}^{23}$ +172.5 (c 1.8; CHCl$_3$); IR (neat): 3462 (br), 3067, 2959, 2852, 1695, 1471, 1247, 1105 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 7.73-7.69 (4H, m), 7.49-7.40 (6H, m), 5.90 (1H, dd, $J$ = 15.7, 3.2 Hz), 5.85 (1H, dd, $J$ = 15.7, 3.9 Hz), 5.18 (1H, ddd, $J$ = 7.9, 6.4, 0.9 Hz), 4.73 (1H, m), 4.27 (2H, s), 3.66 (1H, dd, $J$ = 17.7, 3.0 Hz), 3.54 (1H, dd, $J$ = 11.4, 7.9 Hz), 3.36 (1H, ddd, $J$ = 17.7, 8.8, 0.8 Hz), 3.06 (1H, dd, $J$ = 11.4, 0.9 Hz), 2.83 (1H, brs), 2.41 (1H, oct, $J$ = 6.4 Hz), 1.13-1.08 (12H, m), 1.03 (3H, d, $J$ = 6.7 Hz); $^{13}$C NMR (CDCl$_3$) δ 203.0, 172.5, 135.6 (x4), 133.6, 130.3, 130.2, 129.7, 127.7 (x4), 71.4, 68.3, 63.8, 45.3, 36.4, 30.9, 30.7, 26.9 (x3), 19.3, 19.1, 17.9; MS (Cl) m/z 550 (M$^+$ + Na), 510 (M$^+$ - OH); HRMS m/z 550.1849 (calcd for C$_{28}$H$_{37}$NO$_3$NaSiS$_2$ 550.1882).

(3R)-6-(tert-Butyldiphenylsilanyloxy)-3-hydroxyhex-4-enoic Acid Methoxymethylamide. To a solution of 6-(tert-butyldiphenylsilanyloxy)-3-hydroxy-1-
(4-isopropyl-2-thioxothiazolidin-3-yl)hex-4-en-1-one (10, 220 mg, 0.41 mmol) in CH$_2$Cl$_2$ (5 mL) at room temperature were added imidazole (300 mg, 4.40 mmol) and HN(OCH$_3$)CH$_2$HCl (215 mg, 2.21 mmol, azeotroped from benzene three times). The heterogeneous solution was stirred at room temperature for 16 h, then was quenched with a saturated solution of ammonium chloride (10 mL) and extracted with CH$_2$Cl$_2$ (3 x 20 mL). The organic phase was dried over sodium sulfate and the solvent was removed. Column chromatography (25% EtOAc in pentane) gave 11 (0.126g, 71%) as a pale yellow oil: [α]$^D_{23} +19.1$ (c 2.2 CHCl$_3$); IR (neat): 3437 (br), 2925, 2856, 1652, 1475, 1424, 1110 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 7.70-7.67 (4H, m), 7.43-7.36 (6H, m), 5.89 (1H, ddd, $J = 15.5, 3.3, 0.9$ Hz), 5.82 (1H, m), 4.61 (1H, m), 4.24 (2H, m), 3.89 (1H, s), 3.69 (3H, s), 3.20 (3H, s), 2.70 (1H, dd, $J = 16.7, 2.2$ Hz), 2.60 (1H, dd, $J = 16.7, 9.1$ Hz), 1.07 (9H, s); $^{13}$C NMR (CDCl$_3$) δ 173.3, 135.6 (x4), 133.7, 130.6, 129.6, 129.7 (x2), 127.7 (x4), 68.3, 63.8, 61.3, 38.4, 31.9, 26.9 (x3), 19.3; MS (CI) m/z 450 (M$^+$ + Na), 410 (M$^+$ - OH); HRMS m/z 450.2057 (calcd for C$_{24}$H$_{33}$NO$_4$NaSi 450.2077).

(3R)-3-[15,2R-(tert-Butyldiphenylsilanyloxy)methyl)cyclopropyl]-3-hydroxy-N-methoxy-N-methylpropionamide. To a solution of 6-(tert-butyldiphenylsilanyloxy)-3-hydroxyhex-4-enoic acid methoxymethylamide (11, 0.427 g, 1.16 mmol) in CH$_2$Cl$_2$ (12 mL) at -15 ºC was added diethyl-zinc (5.8 mL, 5.8 mmol, 1M in hexanes) followed by diidomethane (0.467 mL, 5.80 mmol). The solution was allowed to warm to room temperature over 1 h and was stirred for a further 2 h. The reaction was quenched with a saturated solution of ammonium chloride (10 mL) and the mixture was extracted with CH$_2$Cl$_2$ (3 x 20mL). The organic phase was dried over sodium sulfate and the solvent was removed to give pure 12, (0.427g, 97%) as a colorless oil: [α]$^D_{23} +13.4$ (c 0.65 CHCl$_3$); IR (neat) 3458 (br), 2933, 2851, 1647, 1428, 1114 cm$^{-1}$; $^1$H NMR (CDCl$_3$) δ 7.73-7.66 (4H, m), 7.47-7.37 (6H, m), 4.33 (1H, brs), 3.82 (1H, dd, $J = 10.6, 5.2$ Hz), 3.67 (3H, s), 3.46 (1H, dt, $J = 9.2, 2.2$ Hz), 3.32 (1H, dd, $J = 10.6, 7.3$ Hz), 3.23 (3H, s), 2.97 (1H, brd, $J = 16.6$ Hz), 2.75 (1H, dd, $J = 16.6, 9.8$ Hz), 1.08 (9H, s), 1.07-0.87 (2H,
m), 0.68 (1H, ddd, J = 8.3, 8.3, 5.1 Hz), 0.52 (1H, ddd, J = 8.3, 8.3, 5.1 Hz) 

\(^{13}\text{C NMR (CDCl}_3\) \(\delta\) 173.9, 135.6 (x4), 133.8, 129.7 (x3), 127.7 (x4), 72.3, 66.6, 61.4, 38.1, 32.1, 26.9 (x3), 22.7, 19.3, 18.7, 8.7; MS (CI) \(m/z\) 441 (M\(^+\)), 408, 398, 384; HRMS \(m/z\) 441.2335 (calcd for C\(_{25}\)H\(_{35}\)NO\(_4\)Si 450.2077).

![Chemical structure](image)

(3R)-3-[1S,2R-(tert-Butyldiphenylsilanyloxy)methyl]cyclopropyl]-N-methoxy-N-methyl-3-triethylsilanyloxypropionamide. To a solution of 3-[2-(tert-butyldiphenylsilanyloxy)methyl]cyclopropyl]-3-hydroxy-N-methoxy-N-methylpropionamide (12, 0.408 g, 0.91 mmol) in CH\(_2\)Cl\(_2\) (6 mL) at 0 °C were added 2,6-lutidine (0.20 mL, 1.82 mmol) and TESOTf (0.308 mL, 1.37 mmol). The solution was stirred at 0 °C for 45 min, the reaction was quenched with a saturated solution of sodium hydrogen carbonate (10 mL) and the mixture was extracted with CH\(_2\)Cl\(_2\) (3 x 20 mL). The organic phase was washed with brine, dried over sodium sulfate, and the solvent was removed. Column chromatography (10% EtOAc in pentane) gave 13 (0.500 g, 98%) as a pale yellow oil: \([\alpha]^{23}_D\) -2.3 (c 2.0 CHCl\(_3\)); IR (neat): 2958, 2879, 1671, 1472, 1429, 1111, 1075 \(\text{cm}^{-1}\); \(^1\text{H NMR (CDCl}_3\) \(\delta\) 7.73-7.67 (4H, m), 7.45-7.37 (6H, m), 3.81 (1H, ddd, J = 8.1, 8.1, 4.5 Hz), 3.70 (1H, dd, J = 10.6, 5.6 Hz), 3.69 (3H, s), 3.48 (1H, dd, J = 14.4, 8.3 Hz), 2.60 (1H, dd, J = 14.4, 4.4 Hz), 1.09 (9H, s), 1.00-0.93 (2H, m), 0.99 (9H, t, J = 8.1Hz), 0.64 (6H, q, J = 8.1 Hz), 0.62 (1H, m), 0.49 (1H, ddd, J = 9.4, 4.5, 4.4 Hz);

\(^{13}\text{C NMR (CDCl}_3\) \(\delta\) 173.3, 135.6 (x4), 133.9, 129.6 (x3), 127.7 (x4), 72.2, 66.5, 61.2, 40.7, 32.0, 26.9 (x3), 23.7, 19.2, 18.4, 9.0, 6.9 (x3), 6.5 (x3); MS (CI) \(m/z\) 578 (M\(^+\) + Na), 346 (M\(^+\) - OTES); HRMS \(m/z\) 578.3074 (calcd for C\(_{31}\)H\(_{49}\)NO\(_4\)NaSi\(_2\) 578.3098).

![Chemical structure](image)

(3R)-3-[1S,2R-(tert-Butyldiphenylsilanyloxy)methyl]cyclopropyl]-3-triethylsilanyloxypropionaldehyde. To a solution of 3-[2-(tert-
butyldiphenylsilanyloxymethyl)cyclopropyl\-N-methoxy\-N-methyl-3-triethylsilanyloxypropionamide (13, 0.120 g, 0.220 mmol) in THF (2 mL) at -78 °C was added DIBAL-H (0.26 mL, 1M solution in THF) over a period of 5 min. After 10 min, the reaction was quenched with a saturated solution of Rochelle’s salt (8 mL), and the mixture was allowed to warm to room temperature and extracted with CH₂Cl₂ (3 x 20 mL). The organic phase was dried over sodium sulfate and the solvent was removed to give 14 as a colorless oil that was used in the next step without further purification: [α]$_{23}^D$ -7.8 (c 1.2 CHCl₃); IR (neat): 2950, 2872, 1722, 1469, 1112 cm$^{-1}$; $^1$H NMR (CDCl₃) δ 9.87 (1H, t, J = 2.5 Hz), 7.71-7.67 (4H, m), 7.46-7.39 (6H, m), 3.74-3.64 (2H, m), 3.40 (1H, dd, J = 10.4, 6.3 Hz), 2.70 (1H, ddd, J = 15.5, 6.5, 2.5 Hz), 2.64 (1H, ddd, J = 15.5, 5.2, 2.5 Hz), 1.07 (9H, s), 1.00-0.89 (11H, m), 0.66-0.56 (7H, m), 0.50 (1H, ddd, J = 9.4, 4.5, 4.4 Hz); $^{13}$C NMR (CDCl₃) δ 201.9, 135.6 (x4), 133.8, 129.7 (x3), 127.7 (x4), 71.3, 66.3, 52.1, 26.9 (x3), 23.6, 19.2, 18.5, 9.2, 6.9 (x3), 5.3 (x3); MS (CI) m/z 519 (M$^+$ + Na); HRMS m/z 519.2761 (calcd for C$_{29}$H$_{44}$O$_3$NaSi$_2$ 519.2727).

(5R)-5-[1S,2R-(tert-Butyldiphenylsilanyloxymethyl)cyclopropyl]-5-triethylsilanyloxypent-1-en-3-ol.

To a solution of 3-[2-(tert-butyldiphenylsilanyloxymethyl)cyclopropyl]-3-triethylsilanyloxypropionaldehyde (14, 0.116 g, 0.220 mmol) in THF (3 mL) at -78 °C was added vinylmagnesium bromide (0.44 mL, 1M solution in THF). After 40 min, some starting material was still apparent by tlc analysis and an additional quantity of vinylmagnesium bromide (0.22 mL) was added. After a further 10 min, the reaction was quenched with a saturated solution of ammonium chloride, and the mixture was allowed to warm to room temperature and extracted with CH₂Cl₂ (3 x 20 mL). The organic phase was dried over sodium sulfate and the solvent was removed. Column chromatography (10% EtOAc in pentane) gave 15 (0.074 g, 85%, 1:1 mixture of diastereomers) as a pale yellow oil: IR (neat): 3459 (br s), 2960, 2870, 1652, 1424, 1110 cm$^{-1}$; $^1$H NMR (CDCl₃) δ 7.73-7.67 (8H, m), 7.49-7.39 (12H, m), 5.89 (2H, ddd, J = 17.2, 10.9, 5.2 Hz), 5.30 (2H, m), 5.11 (2H, m), 4.56 (1H,
(5R)-5-[15,2R-(tert-Butyldiphenylsilyl oxyxymethyl)cyclopropyl]-5-hydroxypent-1-en-3-ol. To 5-[2-(tert-butyldiphenylsilyloxymethyl)cyclopropyl]-5-triethylsilyloxypent-1-en-3-ol (15, 18 mg, 0.034 mmol) was added a mixture of acetic acid, THF and water (6:2:1, 2.0 mL). The solution was stirred for 1 h at room temperature and the reaction was quenched with NaHCO₃. The mixture was extracted with CH₂Cl₂ (3 x 20 mL) and the organic phase was dried over sodium sulfate to give 16 as a colorless oil that was carried forward to the next reaction without further purification: IR (neat): 3367 (br s), 2927, 2853, 1733, 1472, 1428, 1263, 1115, 1076, 823 cm⁻¹; ¹H NMR (CDCl₃) δ 7.72-7.67 (8H, m), 7.49-7.39 (12H, m), 5.92 (2H, m), 5.33 (1H, d, J = 17.2 Hz), 5.29 (1H, d, J = 17.2 Hz), 5.17 (1H, d, J = 10.6 Hz), 5.14 (1H, d, J = 10.6 Hz), 4.53 (1H, m), 4.40 (1H, m), 3.76 (2H, m), 3.40 (2H, ddd, J = 10.9, 7.3 Hz), 3.27 (2H, dq, J = 8.6, 3.6 Hz), 1.97-1.76 (4H, m), 1.08 (18H, s), 1.03-0.86 (4H, m), 0.56 (2H, ddd, J = 9.6, 4.6, 4.6 Hz), 0.48 (2H, m); ¹³C NMR (CDCl₃) δ 140.7, 135.6, 133.8, 129.7, 127.7, 114.3, 76.3, 73.4, 73.2, 70.4, 66.4, 43.1, 42.2, 29.7, 26.9, 24.0, 23.6, 19.2, 18.7, 18.7, 8.1, 8.0, 1.1; MS (Cl) m/z 433 (M⁺ + Na); HRMS m/z 433.2166  (calcd for C₂₅H₄₄O₃NaSi 433.2175).
(4R)-4-[1S,2R-(tert-Butyldiphenylsilanyloxymethyl)cyclopropyl]-6-vinyl-[1,3]-dioxan-2-one. To 5-[2-(tert-butyldiphenylsilanyloxymethyl)cyclopropyl]-5-hydroxypent-1-en-3-ol (16, 0.105 g, 0.26 mmol) in CH$_2$Cl$_2$ (2 mL) at -78 °C were added 4Å molecular sieves, Et$_3$N (0.154 mL, 1.52 mmol), pyridine (0.120 g, 1.52 mmol) and triphosgene (0.386 g, 1.30 mmol). The solution was stirred for 30 min, the reaction was quenched with an aqueous solution of NH$_4$Cl (2 mL), and the organic phase was washed with an aqueous solution of CuSO$_4$, water and brine. The organic phase was dried over sodium sulfate and the solvent was removed to give 17 (113 mg, quant) as a colorless oil that was carried forward to the next reaction without further purification: IR (neat): 2963, 2912, 2843, 1742, 1424, 1260, 1105 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.67-7.61 (8H, m), 7.45-7.35 (12H, m), 5.92-5.78 (2H, m), 5.07 (1H, m), 4.81 (1H, m), 3.87-3.76 (4H, m), 3.42-3.29 (2H, m), 2.24-2.13 (2H, m), 1.89-1.76 (2H, m), 1.12-0.90 (22H, m), 0.74-0.58 (4H, m); $^{13}$C NMR (CDCl$_3$) $\delta$ 149.0, 148.8, 135.6, 134.4, 134.3, 133.6, 133.5, 129.8, 127.8, 118.3, 118.2, 82.1, 79.7, 78.6, 77.4, 77.1, 76.8, 76.2, 65.7, 65.6, 33.5, 31.5, 26.9, 26.6, 20.6, 20.4, 19.3, 18.5, 18.3, 8.6, 8.2; MS (Cl) m/z 459 (M$^+$ + Na); HRMS m/z 459.1978 (calcd for C$_{26}$H$_{32}$O$_4$NaSi 459.1968).

(8R)-8-[1S,2R-(tert-Butyldiphenylsilanyloxymethyl)cyclopropyl]-3,4,7,8-tetrahydrooxocin-2-one. To 4-[2-(tert-butyldiphenylsilanyloxymethyl)cyclopropyl]-6-vinyl-[1,3]-dioxan-2-one (17, 0.025 g, 0.06 mmol) in toluene (2 mL) was added dicyclopentadienyldimethyltitanium (0.044 g of a 33% by wt solution in toluene). The solution was stirred in the absence of light at 100 °C for 2 h. The reaction vessel was cooled to room temperature and the solvent was removed. Column chromatography (10% EtOAc in pentane) gave 18 (0.011 g, 43%, 63% brsm) as a colorless oil: $[\alpha]^{23}_D$ -173.3 (c 0.45 CHCl$_3$); IR (neat): 2958, 2929, 2855, 1746, 1478, 1425, 1110, 1074 cm$^{-1}$; $^1$H NMR (CDCl$_3$) $\delta$ 7.68-7.64 (4H, m), 7.45-7.36 (6H, m), 5.83-5.72 (2H, m), 3.94 (1H, dt, $J = 10.4, 1.3$ Hz), 3.75 (1H, dd, $J = 10.6, 4.9$ Hz), 3.40 (1H, dd, $J = 10.6, 6.9$ Hz), 2.86 (9H, m), 2.73 (1H, ddd, $J = 13.5, 6.1, 3.4$ Hz), 2.60 (1H, ddd, $J = 13.5, 10.6, 5.7$ Hz),

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2.34-2.23 (2H, m), 2.12 (1H, m), 1.05 (9H, s), 0.97 (1H, m), 0.88 (1H, m), 0.64 (1H, ddd, J = 8.8, 4.9, 4.9 Hz), 0.50 (1H, ddd, J = 8.8, 5.2, 5.2 Hz); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 177.0, 135.6 (x4), 133.8 (x2), 132.7, 129.7 (x2), 128.4, 127.7 (x4), 81.8, 66.1, 37.8, 26.9 (x3), 24.5, 20.4, 19.6, 19.2, 8.6; MS (Cl) \(m/z\) 457 (M\(^+\) + Na); HRMS \(m/z\) 452.2604 (calcd for C\(_{27}\)H\(_{38}\)NO\(_3\)Si 452.2621).

\(8R\)-8-[1S,2R-(tert-Butyldiphenylsilanyloxymethyl)cyclopropyl]-3,4,7,8-tetrahydrooxocin-2-one. To 8-[2-(tert-butyldiphenylsilanyloxymethyl)cyclopropyl]-3,4,7,8-tetrahydrooxocin-2-one (18, 0.012 g, 0.027 mmol) in THF (1.5 mL) was added TBAF (0.068 mL, 1M in THF) at room temperature. After 1 h, the reaction was quenched with an aqueous solution of NH\(_4\)Cl (0.5 mL and was extracted with CH\(_2\)Cl\(_2\) (4 x 10 mL). The combined organic fractions were dried over sodium sulfate and the solvent was removed. Column chromatography (50\% EtOAc in pentane) gave 19 (0.004 g, 74\%) as a colorless oil: \([\alpha]^{23}\)\(_D\) +5.8 (c 0.4 CHCl\(_3\)); IR (neat): 3435, 2923, 2850, 1742, 1433, 1330, 1212, 1013 cm\(^{-1}\); \(^1\)H NMR (CDCl\(_3\)) \(\delta\) 5.79 (1H, m), 5.73 (1H, m), 4.04 (1H, dt, J = 8.5, 1.9 Hz), 3.55 (1H, dd, J = 11.2, 6.7 Hz), 3.46 (1H, dd, J = 11.2, 7.3 Hz), 2.85 (1H, m), 2.73 (1H, ddd, J = 13.5, 6.0, 2.9 Hz), 2.62 (1H, ddd, 13.5, 10.3, 6.5 Hz), 2.31 (1H, ddd, J = 13.2, 7.6, 1.6 Hz), 2.11 (1H, m), 1.11 (1H, m), 1.00 (1H, ddd, J = 13.0, 8.6, 4.7 Hz), 0.75 (1H, dt, J = 10.5, 5.2 Hz), 0.55 (1H, dt, J = 10.5, 5.2 Hz); \(^{13}\)C NMR (CDCl\(_3\)) \(\delta\) 177.0, 132.8, 128.1, 80.9, 66.0, 37.7, 34.3, 24.5, 20.7, 19.7, 8.7; MS.

(S)-3-(tert-Butyldimethylsilanyloxy)-4-(trityloxy)butan-1-ol. To a solution of (S)-methyl 3-(tert-butyldimethylsilyloxy)-4-(trityloxy)butanoate (22, 257 mg, 0.524 mmol) in CH\(_2\)Cl\(_2\) (5 mL) at 0 °C was added DIBAL-H (205 \(\mu\)L, 1.152 mmol), and the mixture was stirred for 30 min. The reaction was quenched with saturated sodium
potassium tartrate (2.5 mL), and the mixture was stirred for 3 h. After the aqueous phase
was extracted with CH$_2$Cl$_2$ (3 x 3 mL), the combined organic layer was dried over
magnesium sulfate, filtered, and concentrated under reduced pressure. Column
chromatography (silica gel, 20% EtOAc in hexanes) gave 23 (208 mg, 86%): $[\alpha]_D^{23}$ -16.3
c (1.4, CHCl$_3$); IR (CDCl$_3$) 3432 cm$^{-1}$; $^1$H NMR (400 MHz, CDCl$_3$): $\delta$ 7.44-7.47 (m, 6H),
7.21-7.34 (m, 9H), 4.025 (m, 1H), 3.67-3.79 (m, 2H), 3.16 (dd, $J = 4.8, 9.3, 1H$), 3.08
(dd, $J = 7.1, 9.2, 1H$), 2.35 (t, $J = 5.3, 1H$), 1.97-2.06 (m, 1H), 1.80-1.88 (m, 1H), 0.85 (s, 
9H), 0.04 (s, 3H), -0.05 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ 144.2, 128.9, 128.0,
127.2, 86.9, 71.0, 67.0, 60.2, 36.9, 26.0, 18.2, -4.4, -4.8; HRMS (CI) m/z 385.2192 (calcd
for C$_{23}$H$_{33}$O$_3$Si: 385.2199).

(\(S,Z\))-tert-Butyldimethyl-[1-(trityloxy)decc-4-en-2-yl]oxy|silane. To a solution
of (\(S\))-3-(tert-butyldimethylsilyloxy)-4-(trityloxy)butan-1-ol (23, 136 mg, 0.294 mmol)
and 4-methylmorpholine-N-oxide (51.6 mg, 0.44 mmol) in CH$_2$Cl$_2$ (6 mL) was added 4Å
molecular sieves (326 mg, powdered). After 10 min, TPAP (20.7 mg, 58.8 µmol) was
added to the mixture and stirring was continued for 1 h. The mixture was diluted with
pentane (12 mL), filtered through a short column of silica gel (20% EtOAc in pentane),
and concentrated under reduced pressure to give an aldehyde (126.4 mg). The aldehyde
was used for the next step without further purifications.

To a solution of \(n\)-hexyltriphenylphosphonium bromide (314 mg, 0.735 mmol) in
THF (3 mL) was added sodium hexamethyldisilazane (0.735 mL, 0.735 mmol 1.0 M in
THF) and the resulting orange solution was stirred for 15 min. The mixture was cooled
to -78 °C and a solution of the aldehyde obtained above in THF (3 mL) was added
dropwise. After stirring for 2 h at -78 °C, the mixture was allowed to warm to room
temperature, and was stirred for 6 h. To this solution was added brine (12 mL) and the
mixture was extracted with ether (3 x 10 mL). The combined extracts were dried over
magnesium sulfate, filtered, and concentrated under reduced pressure. Column
chromatography (silica gel, 2% EtOAc in petroleum ether) gave 24 (128.6 mg, 83%):
[α]_D^{23} = -1.5 (c 1.0, CHCl₃); IR (neat) 2955, 2928, 2853, 1490, 1471, 1449, 1255, 1074, 1000, 834, 775, 704 cm⁻¹; ^1H NMR (400 MHz, CDCl₃): δ 7.46-7.48 (m, 6H), 7.21-7.31 (m, 9H), 5.28 - 5.41 (m, 2H), 3.81 (quin, J = 5.6 Hz, 1H), 3.07 (dd, J = 5.4, 9.2 Hz, 1H), 2.99 (dd, J = 5.5, 9.3 Hz, 1H), 2.41 (m, 1H), 2.23 (m, 1H), 1.97 (quin, J = 6.8 Hz, 2H), 1.28 (m, 6H), 0.88 (t, J = 6.8 Hz, 3H) 0.87 (s, 9H), 0.04 (s, 3H), 0.01 (s, 3H); ^13C NMR (100 MHz, CDCl₃): δ 144.5, 132.0, 129.0, 127.9, 127.1, 125.6, 86.7, 72.2, 67.6, 33.1, 31.8, 29.6, 27.6, 26.1, 22.8, 18.3, 14.3, -4.2, -4.5; HRMS (CI) m/z 551.3325 (calcd for C₃₅H₄₈O₂SiNa (M⁺ + Na): 551.3321).

(S,Z)-2-(tert-Butyldimethylsilanyloxy)dec-4-en-1-ol. A solution of (S,Z)-tert-butylidimethyl[1-(tritylloxy)dec-4-en-2-yloxy]silane (24, 41 mg, 0.078 mmol) in formic acid and acetonitrile (1:3; 5.2 mL) was stirred for 35 min. The solution was diluted with ether (30 mL), and washed with brine and saturated NaHCO₃ until neutral. The organic layer was dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Column chromatography (silica gel, 2% EtOAc in petroleum ether) gave 25 (9.6 mg, 48%): [α]_D^{23} +18.7 (c 1.0, CHCl₃); IR (neat) 3400, 2956, 2928, 2857, 1462, 1361, 1254, 1104, 1043, 836, 776 cm⁻¹; ^1H NMR (400 MHz, CDCl₃): δ 5.30 – 5.50 (m, 2H), 3.74 (m, 1H), 3.55 (dd, J = 3.6, 11.0 Hz, 1H), 3.44 (dd, J = 5.5, 11.0 Hz, 1H), 2.25 (m, 2H), 2.02 (q, J = 7.0 Hz, 2H), 1.81 (s, 1H), 0.90 (s, 9H), 0.89 (t, J = 7.0 Hz, 3H), 0.10 (s, 3H), 0.09 (s, 3H); ^13C NMR (100 MHz, CDCl₃): δ 132.8, 124.8, 73.1, 66.2, 32.3, 31.8, 29.5, 27.6, 26.1, 22.8, 18.3, 14.3, -4.2, -4.5; HRMS (CI) m/z 287.2396 (calcd for C₂₅H₅₀O₂Si: 287.2406).
**tert-Butyl[(S,1E,5Z)-1-iodoundeca-1,5-dien-3-yloxy]dimethylsilane.** To a solution of (S,Z)-2-(tert-butyldimethylsilyloxy)dec-4-en-1-ol (25, 23 mg, 80.3 µmol) and 4-methylmorpholine-\(N\)-oxide (14.0 mg, 120 µmol) in \(\text{CH}_2\text{Cl}_2\) (3.5 mL) was added 4Å molecular sieves (93 mg, powdered). After 10 min, TPAP (5.6 mg, 16.1 µmol) was added to the mixture and stirring was continued for 1 h. The mixture was diluted with pentane (7 mL), filtered through a short column of silica gel (20% EtOAc in pentane), and concentrated under reduced pressure to give an aldehyde (19.6 mg) which was used for the next step without further purification.

\(\text{CrCl}_2\) was added to a flask which contained the aldehyde obtained above and CHI\(_3\) (63.2 mg, 0.161 mmol). THF (1 mL) was added to the flask under Ar at 0 °C and the mixture was stirred for 16 h at 0 °C. The reaction was quenched with saturate NaCl and the mixture was extracted with ether (3 x 6 mL). The combined organic extracts were dried over magnesium sulfate, filtered, and concentrated under reduced pressure. Column chromatography (petroleum ether) gave 26 (12.1 mg, 37%): \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta\) 6.53 (dd, \(J = 5.7, 14.4\) Hz, 1H), 6.21 (dd, \(J = 0.9, 14.4\) Hz, 1H), 5.29-5.50 (m, 2H), 4.09 (q, \(J = 6.0\) Hz, 1H), 2.23 (m, 1H), 2.00 (q, \(J = 7.1\) Hz, 2H), 1.25-1.36 (m, 6H), 0.89 (t, \(J = 7.0\) Hz, 3H), 0.89 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H); \(^1\)C NMR (100 MHz, CDCl\(_3\)): \(\delta\) 149.0, 132.9, 124.3, 75.9, 75.3, 35.9, 31.8, 29.5, 27.7, 26.0, 22.8, 18.4, 14.3, -4.4, -4.6.

![Structure](image)

\((3S,1E,5Z)-3\)-Hydroxy-1-iodoundeca-1,5-diene. To a solution of \(\)tert-butyl[(S,1E,5Z)-1-iodoundeca-1,5-dien-3-yloxy]dimethylsilane (26, 11.5 mg, 28 µmol) in THF (0.2 mL) at room temperature was added TBAF (56 µL, 1M THF, 56 µmol). After 30 min, the reaction was quenched with saturated \(\text{NH}_4\text{Cl}\) solution and the mixture was extracted with \(\text{CH}_2\text{Cl}_2\) (5 x 6 mL). The combined organic extracts were dried over sodium sulfate, filtered, and concentrated under reduced pressure. Column chromatography (12% ethyl acetate/pentane) gave 27 (8.0 mg, 97%) as a colorless oil whose data were in agreement with those previously reported.\(^{5b}\)
Solandelactones E and F. To 8-(2-hydroxymethylcyclopropyl)-3,4,7,8-tetrahydrooxocin-2-one (19, 0.004 g, 0.020 mmol) in \( \text{CH}_2\text{Cl}_2 \) (1 mL) was added 4Å molecular sieves (0.024 g) and \( N \)-methylmorpholine \( N \)-oxide (0.0036 g, 0.030 mmol). Tetrapropylammonium perruthenate (0.0016 g, 0.0046 mmol) was added and after 20 min at room temperature the solution was passed through a short plug of silica gel. Removal of the solvent gave unstable aldehyde 20 (0.004 g, quant) as a colorless oil which was carried forward without further purification: \( ^1\text{H} \) NMR (CDCl\(_3\)) \( \delta \) 9.21 (1H, d, \( J = 4.6\text{Hz} \)), 5.81 (1H, dddd, \( J = 11.0, 9.6, 6.9, 1.6 \text{Hz} \)), 5.74 (1H, m), 4.28 (1H, ddd, \( J = 10.6, 6.7, 1.9 \text{Hz} \)), 2.84 (1H, m), 2.74 (1H, ddd, \( J = 13.4, 5.9, 3.0 \text{Hz} \)), 2.60 (1H, dddd, \( J = 14.1, 10.3, 7.2, 1.4 \text{Hz} \)), 2.32 (1H, ddd, \( J = 14.1, 8.1, 1.3 \text{Hz} \)), 2.13 (1H, dddd, \( J = 12.3, 6.6, 5.0, 3.0 \text{Hz} \)), 1.94 (1H, ddd, \( J = 8.8, 8.8, 4.0 \text{Hz} \)), 1.79 (1H, dddd, \( J = 10.6, 6.6, 6.6, 4.0 \text{Hz} \)), 1.33 (1H, dt, \( J = 9.5, 4.7 \text{Hz} \)), 1.28 (1H, m); \( ^{13}\text{C} \) NMR (CDCl\(_3\)) \( \delta \) 199.9, 176.5, 133.2, 127.6, 77.8, 37.7, 34.0, 27.5, 25.0, 24.4, 12.5.

A mixture of 20 and 27 was thoroughly dried by azeotropic removal of benzene (twice). To the mixture was added degassed dimethyl sulfoxide (0.5 mL), chromium(II) chloride (6.6 mg, 0.054 mmol) and nickel(II) chloride (0.05 mg) and the green solution was stirred at room temperature for 18 h. The reaction was quenched by addition of saturated aqueous ammonium chloride and the mixture was extracted with ethyl acetate (3 x 5 mL). The combined organic extracts were dried over sodium sulfate, after which column chromatography (50% EtOAc in pentane) gave solandelactone E (28, 3.7 mg, 53%) and solandelactone F (29, 1.0 mg, 15%) as colorless oils: 28 [\( \alpha \)]\text{D}^{23} +2.7 (c 0.03 MeOH); IR (neat): 3401, 2921, 2848, 1746, 1455, 1214, 1099, 1057 cm\(^{-1}\); \( ^1\text{H} \) NMR (CDCl\(_3\)) \( \delta \) 5.84-5.72 (4H, m), 5.59 (1H, dt, \( J = 12.0, 6.7 \text{Hz} \)), 5.38 (1H, dt, \( J = 12.0, 6.7 \text{Hz} \)), 4.19 (1H, m), 4.04 (1H, ddd, \( J = 10.5, 8.1, 2.1 \text{Hz} \)), 3.67 (1H, dd, \( J = 7.4, 3.5 \text{Hz} \)), 2.86 (1H, m), 2.73 (1H, ddd, \( J = 13.0, 5.3, 3.2 \text{Hz} \)), 2.63 (1H, ddd, \( J = 14.1, 10.6, 6.0 \text{Hz} \)).
Hz), 2.35-2.22 (4H, m), 2.12 (2H, m), 2.05 (2H, m), 1.38-1.30 (6H, m), 1.14 (1H, ddd, $J$ = 12.6, 8.5, 4.7 Hz), 1.01 (1H, m), 0.89 (3H, t, $J$ = 6.7 Hz), 0.75 (1H, dt, $J$ = 10.0, 5.0 Hz), 0.61 (1H, dt, $J$ = 10.0, 5.0 Hz); $^{13}$C NMR (CDCl$_3$) δ 177.0, 134.1, 133.2, 132.8, 131.7, 128.1, 124.1, 80.9, 74.5, 71.5, 37.8, 35.3, 34.3, 31.5, 29.3, 27.5, 24.5, 23.4, 22.6, 20.7, 14.1, 8.1; MS (CI) m/z 385 (M$^+$ + Na), 345 (M$^+$ - OH; HRMS m/z 385.2371 (calcd for C$_{22}$H$_{34}$O$_4$Na 385.2355).

Both solandelactones E and F undergo mutarotation in MeOH due to methanolysis of the lactone.

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