Total Synthesis of Brevenal

Hiroyoshi Takamura, Shigetoshi Kikuchi, Yuichi Nakamura, Yuji Yamagami,
Takayuki Kishi, Isao Kadota*, and Yoshinori Yamamoto

General. Reagents and starting materials were obtained from commercial suppliers and used without further purification unless otherwise noted. All other solvents were used as purchased. Reactions requiring anhydrous conditions were performed under an argon atmosphere. The NMR spectra were recorded on JEOL JNM-AL400 (^1H , ^{13}C NMR). Chemical shifts were reported in delta units (δ) relative to chloroform (7.24), benzene (7.15). IR spectra were recorded on a JASCO FT/IR-460 plus. Optical rotations were measured by a JASCO DIP-1000. Mass spectra were measured by Micromass LCT (ESI TOF-MS). Thin layer chromatography (TLC) was performed on Merck silica gel 60F-254 plates. Column chromatography was performed with Kanto Chemical silica gel 60N (40-100 mesh, spherical, neutral) or Fuji Silysia silica gel BW-300 (200-400 mesh).

Bis-benzyl Ether 8. To a solution of **7** (11.3 g, 40.8 mmol) in DMF (200 mL) at room temperature were added imidazole (5.56 g, 81.6 mmol) and TBSCl (9.24 g, 61.2 mmol). After stirring for 2 hours at 50 °C, the reaction mixture was quenched with MeOH. The mixture was diluted with EtOAc and washed with water and brine, and concentrated. The residue was passed through a short silica gel column (hexane/EtOAc, 10:1) to give the crude silyl ether, which was used for the next reaction directly.

To a solution of the crude silyl ether in CH_2Cl_2 (180 mL) at -78 °C was added DIBAL-H (168 mL, 163.3 mmol, 0.97 M solution in hexane). The resultant mixture was allowed to warm to room temperature over 5.5 hours before the reaction was quenched with MeOH. The mixture was filtered through a Celite pad, and the filtrate was concentrated. The residue was purified by chromatography (hexane/EtOAc, 25:1 to 10:1 to 6:1 to 2:1) to give the corresponding primary alcohol (11.6 g, 72% for the 2 steps, 90% based on recovery) and

unreacted starting material (3.22 g, 20% recovery): colorless oil; $R_f = 0.38$ (hexane/EtOAc, 4:1); $[\alpha]_D^{28} -32.4$ (c 1.00, CHCl₃); IR (neat) 3466, 3033, 1072 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.26 (m, 5 H), 5.78 (ddd, $J = 17.1, 10.5, 6.0$ Hz, 1 H), 5.29 (ddd, $J = 17.1, 1.6, 1.6$ Hz, 1 H), 5.17 (ddd, $J = 10.5, 1.6, 1.0$ Hz, 1 H), 4.58 (d, $J = 11.7$ Hz, 1 H), 4.51 (d, $J = 11.7$ Hz, 1 H), 3.78 (dd, $J = 9.0, 6.0$ Hz, 1 H), 3.68 (dd, $J = 12.0, 4.4$ Hz, 1 H), 3.62-3.48 (m, 2 H), 3.25 (ddd, $J = 11.2, 9.3, 4.9$ Hz, 1 H), 2.17 (ddd, $J = 9.3, 4.6, 4.6$ Hz, 1 H), 2.02 (dd, $J = 9.5, 3.7$ Hz, 1 H), 1.62 (q, $J = 12.0$ Hz, 1 H), 1.17 (s, 3 H), 0.85 (s, 9 H), 0.02 (s, 3 H), 0.00 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 138.4, 136.4, 128.3, 127.6, 127.5, 116.9, 76.5, 75.7, 73.2, 71.5, 70.8, 67.7, 34.8, 25.8, 18.1, 13.7, -4.1, -4.4; HRMS (ESI TOF) calcd for C₂₂H₃₆O₄SiNa (M+Na)⁺ 415.2281, found 415.2275.

To the stirred suspension of KH (5.81 g, 72.4 mmol, 50%, prewashed with hexane) in THF (100 mL) at 0 °C were added the solution of the alcohol (19.0 g, 48.3 mmol) in THF (100 mL) and BnBr (8.6 mL, 72.4 mmol). After stirring for 1 hour at room temperature, the reaction mixture was quenched with MeOH. The mixture was diluted with EtOAc, washed with water and brine. Concentration and chromatography (hexane/EtOAc, 100:1 to 50:1) gave **8** (23.1 g, 99%): light yellow oil; $R_f = 0.53$ (hexane/EtOAc, 10:1); $[\alpha]_D^{23} -29.6$ (c 1.00, CHCl₃); IR (neat) 3030, 1093 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.23 (m, 10 H), 5.85 (ddd, $J = 17.1, 10.5, 6.1$ Hz, 1 H), 5.31 (ddd, $J = 17.1, 2.0, 2.0$ Hz, 1 H), 5.16 (ddd, $J = 10.5, 2.0, 1.0$ Hz, 1 H), 4.64 (d, $J = 12.6$ Hz, 1 H), 4.54 (d, $J = 12.6$ Hz, 1 H), 4.53 (d, $J = 11.8$ Hz, 1 H), 4.43 (d, $J = 11.8$ Hz, 1 H), 3.77 (dd, $J = 9.0, 6.1$ Hz, 1 H), 3.72 (dd, $J = 12.2, 4.6$ Hz, 1 H), 3.55 (d, $J = 10.6$ Hz, 1 H), 3.44 (d, $J = 10.6$ Hz, 1 H), 3.30 (ddd, $J = 11.0, 9.2, 4.6$ Hz, 1 H), 2.15 (ddd, $J = 12.0, 4.9, 4.9$ Hz, 1 H), 1.62 (q, $J = 12.0$ Hz, 1 H), 1.17 (s, 3 H), 0.85 (s, 9 H), 0.01 (s, 3 H), -0.01 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 138.7, 138.6, 136.8, 128.2, 127.6, 127.5, 127.4, 127.3, 116.8, 76.0, 74.7, 73.6, 73.5, 71.4, 70.7, 34.9, 25.9, 18.1, 13.7, -4.1, -4.4; HRMS (ESI TOF) calcd for C₂₂H₃₆O₄SiNa (M+Na)⁺ 505.2750, found 505.2739.

Homoallylic Alcohol 9. Ozone was passed through a solution of **8** (2.88 g, 5.96 mmol) in MeOH/CH₂Cl₂ (6.0 mL/4.5 mL) at -78 °C until the solution turned blue. After removal of excess ozone with an oxygen stream, the mixture was treated with Me₂S (1.32 mL, 17.9 mmol) and allowed to warm to room temperature with stirring. Concentration gave the corresponding crude aldehyde, which was used for the next reaction directly.

To a solution of (-)-Ipc₂BOMe (3.77 g, 11.9 mmol) in Et₂O (15 mL) at 0 °C was added allylMgBr (11.9 mL, 11.9 mmol, 1.0 M solution in Et₂O). After stirring for 70 min at room

temperature, the mixture was cooled to -78 °C. To this mixture was added a solution of crude aldehyde in Et₂O (15 mL). After stirring for 1 hour at -78 °C, the reaction mixture was allowed to warm to room temperature over a period of 1.5 hours with stirring before the mixture was treated with MeOH at 0 °C. To the mixture were added 3 N NaOH (7.0 mL) and 30% H₂O₂ (7.0 mL) at the same temperature and the reaction mixture was stirred for 40 min at 30 °C. The reaction mixture was quenched with satd Na₂SO₃ at 0 °C and then stirred for 20 min at room temperature. The mixture was diluted with EtOAc, and washed with water and brine. Concentration and chromatography (hexane/EtOAc, 5:1) gave **9** (2.99 g, 95% for the 2 steps) as a single stereoisomer: colorless oil; *R_f* = 0.30 (hexane/EtOAc, 4:1); [α]_D²³ -36.2 (c 1.00, CHCl₃); IR (neat) 3492, 2980, 1087 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.32-7.25 (m, 10 H), 5.92 (dddd, *J* = 17.1, 9.8, 7.1, 7.1 Hz, 1 H), 5.10 (dd, *J* = 17.1, 1.5 Hz, 1 H), 5.06 (ddd, *J* = 9.8, 1.5, 1.0 Hz, 1 H), 4.59 (d, *J* = 12.4 Hz, 1 H), 4.54 (d, *J* = 12.4 Hz, 1 H), 4.52 (d, *J* = 11.7 Hz, 1 H), 4.47 (d, *J* = 11.7 Hz, 1 H), 3.82 (m, 1 H), 3.68 (dd, *J* = 12.0, 4.6 Hz, 1 H), 3.58-3.52 (m, 1 H), 3.53 (d, *J* = 10.5 Hz, 1 H), 3.40 (d, *J* = 10.5 Hz, 1 H), 3.36 (dd, *J* = 9.0, 5.4 Hz, 1 H), 2.41-2.32 (m, 1 H), 2.30-2.22 (m, 1 H), 2.12 (ddd, *J* = 12.0, 4.6, 4.6 Hz, 1 H), 1.59 (q, *J* = 12.0 Hz, 1 H), 1.13 (s, 3 H), 0.86 (s, 9 H), 0.06 (s, 3 H), 0.05 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 138.6, 138.5, 135.3, 128.2, 127.5, 127.4, 116.8, 77.2, 75.6, 74.6, 73.5, 73.4, 72.2, 71.7, 70.5, 36.6, 35.2, 25.8, 17.9, 13.6, -3.6, -4.6; HRMS (ESI TOF) calcd for C₃₁H₄₆O₅SiNa (M+Na)⁺ 549.3012, found 549.2993.

Lactone 6. To the solution of **9** (7.23 g, 13.7 mmol) in CH₂Cl₂ (60 mL) at room temperature were added DIPEA (14.1 mL, 82.3 mmol) and MOMCl (4.1 mL, 54.9 mmol). After stirring for 1 hour, the reaction mixture was quenched with MeOH. The mixture was diluted with EtOAc, washed with satd NH₄Cl, satd NaHCO₃ and brine. Concentration and chromatography (hexane/EtOAc, 20:1 to 10:1 to 5:1) gave the corresponding MOM ether (7.43 g, 95%): colorless oil; *R_f* = 0.60 (hexane/EtOAc, 4:1); [α]_D²⁴ -46.9 (c 1.00, CHCl₃); IR (neat) 3030, 2929, 1641 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.31-7.23 (m, 10 H), 5.93 (dddd, *J* = 17.1, 10.0, 7.1, 7.1 Hz, 1 H), 5.07 (dd, *J* = 17.1, 2.0 Hz, 1 H), 5.01 (dd, *J* = 10.0, 2.0 Hz, 1 H), 4.71 (d, *J* = 6.9 Hz, 1 H), 4.63 (d, *J* = 12.0 Hz, 1 H), 4.61 (d, *J* = 6.9 Hz, 1 H), 4.55 (d, *J* = 11.5 Hz, 1 H), 4.52 (d, *J* = 12.0 Hz, 1 H), 4.49 (d, *J* = 11.5 Hz, 1 H), 3.87 (ddd, *J* = 9.5, 3.7, 1.0 Hz, 1 H), 3.72 (dd, *J* = 12.0, 4.4 Hz, 1 H), 3.60-3.56 (m, 1 H), 3.58 (d, *J* = 10.5 Hz, 1 H), 3.47 (d, *J* = 10.5 Hz, 1 H), 3.43 (ddd, *J* = 9.0, 4.8, 4.8 Hz, 1 H), 3.35 (s, 3 H), 2.49-2.40 (m, 1 H), 2.29-2.20 (m, 1 H), 2.12 (ddd, *J* = 12.0, 4.6, 4.6 Hz, 1 H), 1.57 (q, *J* = 12.0 Hz, 1 H), 1.14 (s,

3 H), 0.86 (s, 9 H), 0.04 (s, 3 H), 0.03 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.9, 138.7, 136.3, 128.2, 128.1, 127.5, 127.4, 127.3, 127.2, 116.4, 95.9, 77.2, 76.5, 74.7, 73.6, 73.3, 71.6, 67.3, 55.6, 35.1, 33.9, 25.8, 17.9, 13.3, -3.7, -4.6; HRMS (ESI TOF) calcd for $\text{C}_{33}\text{H}_{50}\text{O}_6\text{SiNa}$ ($\text{M}+\text{Na}$) $^+$ 593.3275, found 593.3295.

To a solution of 2-methyl-2-butene (0.5 mL, 4.55 mmol) in THF (2 mL) at 0 °C was added $\text{BH}_3\cdot\text{SMe}_2$ (0.2 mL, 2.28 mmol) and stirred for 15 min at the same temperature. To the mixture was added a solution of the MOM ether (260 mg, 0.455 mmol) in THF (2.5 mL) and stirred for 1 hour at room temperature. To the mixture were added 3 N NaOH and 30% H_2O_2 at 0 °C and the reaction mixture was stirred for 10 min at room temperature. The reaction mixture was quenched with satd Na_2SO_3 at 0 °C and stirred for 20 min at room temperature. The mixture was diluted with EtOAc, washed with water and brine. Concentration gave the crude alcohol, which was used for the next reaction directly.

To a solution of the crude alcohol in CH_2Cl_2 (2 mL) and DMSO (0.5 mL) at 0 °C were added Et_3N (0.3 mL, 2.28 mmol) and $\text{SO}_3\cdot\text{pyr}$. (217 mg, 1.37 mmol), and stirred for 1 hour at room temperature. The mixture was diluted with EtOAc, washed with satd NH_4Cl , water and brine. Concentration gave the crude aldehyde, which was used for the next reaction directly.

To a solution of the crude aldehyde in *t*-BuOH (1.5 mL) and 2-methyl-2-butene (1.5 mL) at 0 °C were added 5% NaH_2PO_4 (3.0 mL) and NaClO_2 (412 mg, 4.55 mmol), and the mixture was stirred vigorously for 3 hours at the same temperature. The mixture was diluted with Et_2O , washed with water and brine. Concentration gave the crude carboxylic acid **10**, which was used for the next reaction directly.

To a solution of the crude carboxylic acid **10** was added TBAF (2.3 mL, 2.30 mmol, 1.0 M solution in THF), and stirred for 7 hours at 50 °C. The mixture was diluted with Et_2O , washed with satd NH_4Cl , water and brine. Concentration gave the crude hydroxy carboxylic acid, which was used for the next reaction directly.

To a solution of the crude hydroxy carboxylic acid in THF (3.0 mL) were added Et_3N (0.13 mL, 0.910 mmol) and 2,4,6-trichlorobenzoyl chloride (0.11 mL, 0.675 mmol). After stirring for 1.5 hours at room temperature, the reaction mixture was concentrated under reduced pressure and diluted with toluene (10 mL). To the mixture was added DMAP (111 mg, 0.910 mmol) in toluene (7 mL), and stirred for 40 min at room temperature. The mixture was diluted with EtOAc and filtered through a Celite pad. The filtrate was concentrated and the residue was purified by chromatography (hexane/EtOAc, 5:1 to 2.5:1) to give **6** (144 mg, 67% for the 5 steps): yellow oil; R_f = 0.53 (hexane/EtOAc, 1:1); $[\alpha]_D^{22}$ +3.2 (c 1.00, CHCl_3); IR (neat)

3031, 1739, 1038 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.32-7.22 (m, 10 H), 4.84 (d, J = 6.6 Hz, 1 H), 4.62-4.55 (m, 1 H), 4.61 (d, J = 6.6 Hz, 1 H), 4.57 (d, J = 12.0 Hz, 1 H), 4.53 (d, J = 12.0 Hz, 1 H), 4.45 (d, J = 12.0 Hz, 1 H), 4.44 (d, J = 12.0 Hz, 1 H), 4.03-3.98 (m, 1 H), 3.72 (dd, J = 12.0, 4.4 Hz, 1 H), 3.57-3.52 (m, 1 H), 3.52 (d, J = 10.5 Hz, 1 H), 3.40 (d, J = 10.5 Hz, 1 H), 3.32 (s, 3 H), 3.03 (t, J = 13.0 Hz, 1 H), 2.45-2.35 (m, 2 H), 2.11-2.02 (m, 1 H), 1.90-1.76 (m, 2 H), 1.15 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 174.6, 138.3, 138.2, 128.3, 128.2, 127.6, 127.5, 127.4, 97.2, 77.2, 74.6, 74.0, 73.4, 73.2, 72.4, 71.5, 70.0, 55.6, 30.3, 27.6, 27.1, 13.1; HRMS (ESI TOF) calcd for $\text{C}_{27}\text{H}_{34}\text{O}_7\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 493.2202, found 493.2216.

Enol Ether 12. To a solution of **6** (699 mg, 1.48 mmol), DMPU (0.98 mL, 3.70 mmol) and $(\text{PhO})_2\text{POCl}$ (0.55 mL, 2.67 mmol) in THF (10 mL) was added KHMDS (5.9 mL, 2.95 mmol, 0.5 M solution in toluene) at $-78\text{ }^\circ\text{C}$. After stirring for 25 min at $-78\text{ }^\circ\text{C}$, the reaction mixture was quenched with NaHCO_3 aq./MeOH and the resultant mixture was allowed to warm to room temperature. The mixture was diluted with Et_2O , washed with water and brine and concentrated. The insoluble material of the resultant mixture was filtered off through a filter paper, and the filtrate was concentrated. The residue was passed through a short pad of silica gel column (hexane/EtOAc, 2:1) to give the crude enol phosphate **11**, which was used for the next reaction without further purification.

To a solution of **5** (1.63 g, 2.64 mmol) in Et_2O (15 mL) at $-78\text{ }^\circ\text{C}$ was added $t\text{-BuLi}$ (4.4 mL, 5.28 mmol, 1.2 M solution in pentane) rapidly, and the mixture was stirred for 3 min at $-78\text{ }^\circ\text{C}$. To the mixture were added 9-BBN-OMe (6.6 mL, 6.60 mmol, 1.0 M solution in hexane) and THF (12 mL) at $-78\text{ }^\circ\text{C}$, and the mixture was allowed to warm to room temperature over 1.5 hours. To the mixture were added 3M K_3PO_4 aq. (2.2 mL, 6.60 mmol) and a solution of the crude enol phosphate **11** and $\text{PdCl}_2(\text{dppf})$ (122 mg, 0.149 mmol) in DMF/THF (15/3 mL), and then stirred for 40 min at room temperature. To the reaction mixture were added 3N NaOH and 30% H_2O_2 at $0\text{ }^\circ\text{C}$, and then stirred for 20 min at room temperature. The mixture was quenched with satd Na_2SO_3 at $0\text{ }^\circ\text{C}$ and stirred for 30 min at room temperature. The resultant mixture was diluted with EtOAc, washed with water and brine. Concentration and chromatography (hexane/EtOAc, 10:1 to 8:1 containing 0.5% Et_3N) gave **12** (1.13 g, 81% for the 2 steps): yellow oil; R_f = 0.34 (hexane/EtOAc, 4:1); $[\alpha]_D^{25} +17.5$ (c 1.00, CHCl_3); IR (neat) 3028, 2933, 1109 cm^{-1} ; ^1H NMR (400 MHz, C_6D_6) δ 7.82-7.76 (m, 4 H), 7.34-7.03 (m, 18 H), 6.81 (d, J = 8.8 Hz, 2 H), 4.94 (d, J = 6.4 Hz, 1 H), 4.73 (dd, J = 8.3, 3.4 Hz, 1 H), 4.71 (d, J = 6.4 Hz, 1 H), 4.52 (d, J = 12.0 Hz, 1 H), 4.49-4.37 (m, 4 H), 4.27 (d, J = 12.0 Hz, 1 H),

4.02-3.93 (m, 2 H), 3.83 (dd, $J = 12.0, 4.6$ Hz, 1 H), 3.76-3.66 (m, 2 H), 3.57 (d, $J = 10.5$ Hz, 1 H), 3.53 (dd, $J = 9.5, 2.2$ Hz, 1 H), 3.42 (d, $J = 10.5$ Hz, 1 H), 3.35-3.25 (m, 1 H), 3.31 (s, 3 H), 3.30 (s, 3 H), 2.56 (dd, $J = 12.0, 2.7$ Hz, 1 H), 2.52 (ddd, $J = 11.7, 5.0, 5.0$ Hz, 1 H), 2.33-2.12 (m, 3 H), 1.99-1.61 (m, 6 H), 1.18 (s, 9 H), 1.18 (s, 3 H), 1.13 (d, $J = 6.8$ Hz, 3 H); ^{13}C NMR (100 MHz, C_6D_6) δ 159.5, 158.2, 139.4, 139.3, 136.0, 134.4, 131.9, 129.9, 129.4, 128.5, 128.4, 127.9, 127.6, 114.0, 105.2, 96.7, 82.2, 78.3, 77.4, 75.2, 74.1, 73.8, 73.4, 71.8, 71.6, 71.5, 64.5, 55.3, 54.9, 39.8, 33.6, 32.5, 29.6, 28.2, 27.3, 27.2, 19.6, 15.4, 13.4; HRMS (ESI TOF) calcd for $\text{C}_{58}\text{H}_{74}\text{O}_9\text{SiNa}$ ($\text{M}+\text{Na}$) $^+$ 965.0000, found 965.0001.

Hydroxy Ketone 15. To a solution of **12** (332 mg, 0.352 mmol) in THF (1.5 mL) at 0 °C was added $\text{BH}_3 \cdot \text{THF}$ (3.5 mL, 3.50 mmol, 1.0 M solution in THF) and stirred for 40 min at the same temperature. After the slowly addition of MeOH at 0 °C until the bubbling was stopped, 3N NaOH (2 mL) and 30% H_2O_2 (2 mL) were added to the mixture, and the resultant mixture was stirred for 20 min at the same temperature. The mixture was quenched with satd Na_2SO_3 at 0 °C and stirred for 30 min at room temperature. The resultant mixture was diluted with EtOAc, washed with water and brine. Concentration gave the crude alcohol **13**, which was used for the next reaction directly.

To a stirred solution of the crude alcohol **13** and MS4A in CH_2Cl_2 (3 mL) at 0 °C were added TPAP (14.1 mg, 40.1 μmol) and NMO (82.5 mg, 0.704 mmol). After stirring for 1.5 hours at room temperature, the mixture was filtered through a short silica gel column (hexane/EtOAc, 2:1) to give the crude ketone, which was used for the next reaction directly.

To a solution of the crude ketone in toluene (3 mL) was added DBU (0.11 mL, 0.704 mmol). After stirring for 3 hours at 110 °C, the mixture was cooled to room temperature and filtered through a short silica gel column (hexane/EtOAc, 2:1) to give ketone **14**, which was used for the next reaction without further purification.

To a solution of the ketone **14** in CH_2Cl_2 (7.5 mL) and NaHCO_3 aq. (1.5 mL) was added DDQ (160 mg, 0.704 mmol) and stirred for 30 min at room temperature, and then the reaction mixture was diluted with CH_2Cl_2 and water. The mixture was extracted with CH_2Cl_2 , and the organic layer was washed with water and brine. Concentration and chromatography (hexane/EtOAc, 7:1 to 4:1 to 2:1) gave **15** (263 mg, 89% for the 4 steps): light yellow oil; $R_f = 0.33$ (hexane/EtOAc, 2:1); $[\alpha]_D^{26} -32.8$ (c 0.97, CHCl_3); IR (neat) 3686-3243, 2940, 1715 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.67-7.63 (m, 4 H), 7.40-7.20 (m, 16 H), 4.74 (d, $J = 6.8$ Hz, 1H), 4.57 (d, $J = 11.5$ Hz, 1 H), 4.57 (d, $J = 6.8$ Hz, 1 H), 4.53 (d, $J = 12.0$ Hz, 1 H), 4.45

(d, $J = 12.0$ Hz, 1 H), 4.40 (d, $J = 11.5$ Hz, 1 H), 4.09 (bd, $J = 7.8$ Hz, 1 H), 3.84 (dd, $J = 10.1$, 3.4 Hz, 1 H), 3.72-3.63 (m, 3 H), 3.58 (bd, $J = 3.9$ Hz, 2 H), 3.53-3.46 (m, 1 H), 3.51 (d, $J = 10.3$ Hz, 1 H), 3.41 (d, $J = 10.3$ Hz, 1 H), 3.33 (s, 3 H), 2.99 (d, $J = 12.9$ Hz, 1 H), 2.73 (dd, $J = 12.9$, 7.8 Hz, 1 H) 2.35 (ddd, $J = 11.7$, 3.9, 3.9 Hz, 1 H), 2.22 (bs, 1 H), 1.81-1.40 (m, 8 H), 1.17 (s, 3 H), 1.03 (s, 9 H), 0.90 (d, $J = 6.6$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 212.7, 138.5, 138.4, 135.5, 133.7, 129.5, 128.2, 127.6, 127.50, 127.47, 127.43, 127.38, 96.2, 85.9, 77.5, 77.2, 74.8, 74.7, 74.4, 73.5, 71.6, 71.3, 64.1, 55.6, 43.7, 36.0, 35.5, 31.7, 30.6, 29.5, 26.9, 19.3, 13.6, 13.4; HRMS (ESI TOF) calcd for $\text{C}_{50}\text{H}_{66}\text{O}_9\text{SiNa}$ ($\text{M}+\text{Na}$) $^+$ 861.4374, found 861.4376.

***O,S*-Acetal 16.** To a solution of **15** (182 mg, 0.217 mmol) in THF (2 mL) were added EtSH (0.32 mL, 4.35 mmol) and $\text{Zn}(\text{OTf})_2$ (115 mg, 0.326 mmol) and stirred for 15 min at room temperature. The reaction mixture was quenched with Et_3N and the insoluble material was filtered off through a Celite pad. The filtrate was concentrated and purified by chromatography (hexane/EtOAc, 15:1) to give **16** (171 mg, 89%): colorless oil; $R_f = 0.53$ (hexane/EtOAc, 4:1); $[\alpha]_D^{27} -38.9$ (c 1.00, CHCl_3); IR (neat) 3030, 2931 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.66-7.61 (m, 4 H), 7.42-7.32 (m, 6 H), 7.32-7.20 (m, 10 H), 4.72 (d, $J = 6.6$ Hz, 1 H), 4.65 (d, $J = 6.6$ Hz, 1 H), 4.57 (d, $J = 11.8$ Hz, 1 H), 4.54 (d, $J = 12.2$ Hz, 1 H), 4.48 (d, $J = 12.2$ Hz, 1 H), 4.39 (d, $J = 11.8$ Hz, 1 H), 4.15 (dd, $J = 11.8$, 5.0 Hz, 1 H), 4.00-3.95 (m, 1 H), 3.93 (d, $J = 9.5$ Hz, 1 H), 3.85-3.78 (m, 1 H), 3.75-3.57 (m, 4 H), 3.48 (d, $J = 10.5$ Hz, 1 H), 3.41 (d, $J = 10.5$ Hz, 1 H), 3.33 (s, 3 H), 2.68 (dd, $J = 15.8$, 5.1 Hz, 1 H), 2.41-2.21 (m, 4 H) 2.03 (ddd, $J = 12.4$, 12.4, 4.5 Hz, 1 H), 1.83-1.75 (m, 1 H) 1.72-1.35 (m, 6 H), 1.19 (t, $J = 7.6$ Hz, 3 H), 1.16 (s, 3 H), 1.02 (s, 9 H), 0.90 (d, $J = 7.1$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.7, 138.6, 135.5, 134.0, 129.5, 128.2, 127.5, 127.4, 127.3, 127.2, 96.4, 93.0, 77.2, 75.9, 75.1, 74.4, 73.9, 73.7, 73.4, 72.7, 71.7, 70.9, 63.9, 55.4 46.0, 35.5, 31.9, 31.6, 29.5, 28.7, 26.9, 19.3, 14.4, 13.3, 12.9; HRMS (ESI TOF) calcd for $\text{C}_{52}\text{H}_{70}\text{O}_8\text{SSiNa}$ ($\text{M}+\text{Na}$) $^+$ 905.4459, found 905.4427.

Tricycle 17. To a solution of **16** (171 mg, 0.194 mmol) in CH_2Cl_2 (2 mL) at 0 $^\circ\text{C}$ were added Me_2Zn (1.9 mL, 1.90 mmol, 1.0 M solution in hexane) and $\text{Zn}(\text{OTf})_2$ (2.6 mg, 0.58 mmol), and the reaction mixture was allowed to warm to room temperature over 1 hour with stirring. After quenching with $\text{MeOH}/\text{Et}_3\text{N}$ (1:1), the resultant mixture was diluted with Et_2O and stirring with Celite. The mixture was filtered through a Celite pad, and then the filtrate was

concentrated and purified by chromatography (hexane/EtOAc, 10:1) to give **17** (163 mg, quant.): colorless oil; R_f = 0.50 (hexane/EtOAc, 4:1); $[\alpha]^{24}_D$ -18.7 (c 0.97, CHCl₃); IR (neat) 3030, 2931 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.65 (dd, J = 7.8, 1.4 Hz, 4 H), 7.42-7.32 (m, 6 H), 7.32-7.20 (m, 10 H), 4.73 (d, J = 6.6 Hz, 1 H), 4.70 (d, J = 6.6 Hz, 1 H), 4.58 (d, J = 11.7 Hz, 1 H), 4.56 (d, J = 12.2 Hz, 1 H), 4.49 (d, J = 12.2 Hz, 1 H), 4.41 (d, J = 11.7 Hz, 1 H), 4.17 (dd, J = 11.5, 5.1 Hz, 1 H), 3.98-3.93 (m, 1 H), 3.75-3.57 (m, 4 H), 3.50 (d, J = 10.5 Hz, 1 H), 3.43 (d, J = 10.5 Hz, 1 H), 3.36 (s, 3 H), 3.46-3.31 (m, 2 H), 2.35 (ddd, J = 11.9, 4.6, 4.6 Hz, 1 H), 2.20 (dd, J = 16.1, 3.7 Hz, 1 H), 1.90 (dd, J = 15.9, 3.9 Hz, 1 H), 1.77-1.24 (m, 8 H), 1.18 (s, 3 H), 1.14 (s, 3 H), 1.04 (s, 9 H), 0.90 (d, J = 7.1 Hz, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 138.7, 138.6, 135.5, 134.0, 129.4, 128.2, 128.1, 127.5, 127.4, 127.3, 127.2, 96.0, 77.4, 77.1, 76.5, 76.1, 75.0, 73.9, 73.5, 73.3, 72.9, 71.0, 63.9, 55.3, 46.1, 34.9, 32.7, 31.9, 29.8, 29.2, 29.1, 26.9, 20.5, 19.3, 13.3, 12.4; HRMS (ESI TOF) calcd for C₅₁H₆₈O₈SiNa (M+Na)⁺ 859.4581, found 859.4512.

Alcohol 18. A mixture of **17** (181 mg, 0.216 mmol) and Pd(OH)₂-C (60.0 mg) in THF (2 mL) was stirred under H₂ atmosphere at room temperature. After 4 hours, the catalyst was filtered off, and the filtrate was concentrated to give the crude diol, which was used for the next reaction directly.

To a solution of the crude diol in DMF (1 mL) were added imidazole (148 mg, 2.18 mmol) and TESCl (0.18 mL, 1.09 mmol) and stirred for 30 min at room temperature. The reaction mixture was quenched with MeOH and diluted with Et₂O, and washed with water and brine. Concentration gave the crude bis-silyl ether, which was used for the next reaction directly.

To a solution of the crude bis-silyl ether in MeOH (2 mL) and CH₂Cl₂ (2 mL) at 0 °C was added PPTS (11.0 mg, 43.6 μ mol) and stirred for 1 hour at the same temperature. After the reaction mixture was quenched with Et₃N, the resulting mixture was concentrated and purified by chromatography (hexane/EtOAc, 20:1 to 5:1) to give **18** (148 mg, 89% for the 3 steps): colorless oil; R_f = 0.37 (hexane/EtOAc, 4:1); $[\alpha]^{23}_D$ -13.7 (c 0.97, CHCl₃); IR (neat) 3655-3299, 2953, 1087 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.64 (dd, J = 8.0, 1.6 Hz, 4 H), 7.42-7.31 (m, 6 H), 4.71 (d, J = 6.7 Hz, 1 H), 4.66 (d, J = 6.7 Hz, 1 H), 4.12 (dd, J = 11.1, 5.0 Hz, 1 H), 3.88 (dd, J = 11.8, 4.8 Hz, 1 H), 3.84 (t, J = 3.7 Hz, 1 H), 3.69-3.56 (m, 3 H), 3.50-3.34 (m, 3 H), 3.37 (s, 3 H), 3.28 (d, J = 9.0 Hz, 1 H), 2.56 (dd, J = 9.8, 2.7 Hz, 1 H), 2.18 (dd, J = 15.9, 3.8 Hz, 1 H), 2.08 (ddd, J = 12.0, 4.6, 4.6 Hz, 1 H), 1.91 (dd, J = 15.9, 3.8 Hz, 1 H), 1.79-1.20 (m, 8 H), 1.16 (s, 3 H), 1.03 (s, 3 H), 1.02 (s, 9 H), 0.95-0.90 (m, 12 H),

0.92 (d, $J = 7.8$ Hz, 3 H), 0.58 (q, $J = 7.8$ Hz, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 135.5, 134.0, 129.4, 127.5, 97.3, 79.0, 77.4, 75.7, 73.6, 73.0, 71.0, 67.3, 66.5, 63.9, 55.5, 46.5, 36.0, 34.8, 32.7, 29.2, 29.1, 26.9, 20.5, 19.3, 13.0, 12.4, 6.9, 5.1; HRMS (ESI TOF) calcd for $\text{C}_{43}\text{H}_{70}\text{O}_8\text{Si}_2\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 793.4507, found 793.4514.

Alcohol 20. To a solution of **18** (270 mg, 0.345 mmol) and MS4A (30 mg) in CH_2Cl_2 (3.5 mL) at 0 °C were added TPAP (12.1 mg, 34.5 μmol) and NMO (80.8 mg, 0.690 mmol), and stirred for 30 min at room temperature. The mixture was filtered through a short silica gel column (hexane/EtOAc, 2:1) to give the crude aldehyde, which was used for the next reaction directly.

A mixture of the crude aldehyde and $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Me}$ (346 mg, 1.04 mmol) in benzene (3.5 mL) was refluxed for 4 hours. The mixture was purified by chromatography (hexane/EtOAc, 20:1 to 5:1) to give the corresponding unsaturated ester (141 mg, 96% for the 2 steps): colorless oil; $R_f = 0.48$ (hexane/EtOAc, 4:1); $[\alpha]_D^{22} -21.8$ (c 0.76, CHCl_3); IR (neat) 2952, 1727, 1661 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.64 (dd, $J = 6.3, 1.6$ Hz, 4 H), 7.42-7.32 (m, 6 H), 7.05 (d, $J = 15.6$ Hz, 1 H), 5.98 (d, $J = 15.6$ Hz, 1 H), 4.77 (d, $J = 6.7$ Hz, 1 H), 4.69 (d, $J = 6.7$ Hz, 1 H), 4.16 (dd, $J = 11.6, 5.0$ Hz, 1 H), 3.95 (t, $J = 3.8$ Hz, 1 H), 3.71-3.57 (m, 3 H), 3.71 (s, 3 H), 3.50 (dd, $J = 11.6, 4.8$ Hz, 1 H), 3.45-3.39 (m, 1 H), 3.40 (s, 3 H), 3.32 (d, $J = 8.8$ Hz, 1 H), 2.21 (dd, $J = 16.0, 3.8$ Hz, 1 H), 2.07 (ddd, $J = 12.0, 4.8, 4.8$ Hz, 1 H), 1.89 (dd, $J = 16.0, 3.8$ Hz, 1 H), 1.75-1.21 (m, 8 H), 1.22 (s, 3 H), 1.16 (s, 3 H), 1.02 (s, 9 H), 0.92 (t, $J = 8.1$ Hz, 9 H), 0.91 (d, $J = 7.6$ Hz, 3 H), 0.56 (q, $J = 8.1$ Hz, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.2, 152.2, 135.5, 134.0, 129.4, 127.5, 118.1, 96.3, 77.2, 76.8, 75.9, 73.5, 72.6, 71.5, 71.0, 63.9, 55.5, 51.5, 46.1, 36.2, 34.8, 32.7, 29.2, 29.1, 26.9, 22.7, 20.5, 19.3, 14.8, 12.4, 6.9, 5.0; HRMS (ESI TOF) calcd for $\text{C}_{46}\text{H}_{72}\text{O}_9\text{Si}_2\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 847.4612, found 847.4606.

A mixture of the ester (278 mg, 0.332 mmol) and Pd-C (55.0 mg) in EtOAc (5 mL) was stirred under H_2 atmosphere at room temperature. After 3 hours, the catalyst was filtered off through a short silica gel column (EtOAc) and filtrate was concentrated to give the crude saturated ester, which was used for the next reaction directly.

To a solution of the crude ester in THF (2 mL) and H_2O (2 mL) was added $\text{LiOH}\cdot\text{H}_2\text{O}$ (41.8 mg, 0.996 mmol). After stirring for 10 hours at 75 °C, an additional amount of $\text{LiOH}\cdot\text{H}_2\text{O}$ (41.8 mg, 0.996 mmol) was added to the reaction mixture, and then the reaction mixture was stirred for further 6.5 hours at the same temperature. The reaction mixture was cooled to

0 °C, diluted with Et₂O, and then the mixture was carefully neutralized with 0.5 N HCl. The resultant mixture was diluted with EtOAc, washed with water and brine, and the resultant aqueous layer was extracted with EtOAc (2 times). The organic layer was concentrated to give the crude carboxylic acid **3**, which was used for next reaction directly.

To a solution of the crude carboxylic acid **3** in THF (1.5 mL) were added Et₃N (0.21 mL, 1.49 mmol) and 2,4,6-trichlorobenzoyl chloride (0.13 mL, 0.830 mmol). After stirring for 40 min at room temperature, the mixture was concentrated under reduced pressure and diluted with toluene (5 mL). To the resulting mixture was added a solution of **4** (310.7 mg, 0.644 mmol) and DMAP (142.0 mg, 1.16 mmol) in toluene (5 mL). After stirring for 1.5 hours at room temperature, the mixture was diluted with EtOAc, added Celite, and the resulting mixture was filtered through a Celite pad. The filtrate was concentrated and the residue was passed through a short silica gel column (hexane/EtOAc, 4:1) to give a mixture of ester **19** and unreacted **4**. The mixture was used for the next reaction without further purification.

To a solution of the mixture of **19** and **4** in MeOH (2 mL) and CH₂Cl₂ (2 mL) at 0 °C was added CSA (15.4 mg, 66.4 μmol) and stirred for 70 min at the same temperature before the reaction mixture was quenched with Et₃N. The mixture was concentrated and purified by chromatography (hexane/EtOAc, 20:1 to 4:1 to 2:1) to give **20** (281 mg, 74% for the 4 steps): colorless oil; R_f = 0.41 (hexane/EtOAc, 2:1); $[\alpha]_D^{25}$ -23.7 (c 0.83, CHCl₃); IR (neat) 3637-3243, 2929, 1737 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.64 (dd, J = 7.9, 1.6 Hz, 4 H), 7.42-7.32 (m, 6 H), 7.31 (s, 2 H), 5.81 (dd, J = 17.3, 10.7 Hz, 1 H), 5.16 (dd, J = 17.3, 1.2 Hz, 1 H), 5.08 (dd, J = 10.7, 1.2 Hz, 1 H), 4.82-4.76 (m, 1 H), 4.70 (d, J = 6.6 Hz, 1 H), 4.63 (d, J = 6.6 Hz, 1 H), 4.65 (s, 2 H), 4.11 (dd, J = 11.5, 4.9 Hz, 1 H), 3.88 (t, J = 3.6 Hz, 1 H), 3.69-3.56 (m, 3 H), 3.48 (t, J = 6.1 Hz, 2 H), 3.44-3.32 (m, 2 H), 3.36 (s, 3 H), 3.24 (d, J = 9.3 Hz, 1 H), 2.46 (ddd, J = 17.4, 7.0, 7.0 Hz, 1 H), 2.39 (d, J = 5.4 Hz, 1 H), 2.31 (ddd, J = 17.4, 7.0, 7.0 Hz, 1 H), 2.17 (dd, J = 16.0, 3.5 Hz, 1 H), 2.10 (ddd, J = 11.7, 4.5, 4.5 Hz, 1 H), 1.94-1.84 (m, 3 H), 1.83-1.42 (m, 10 H), 1.39-1.28 (m, 2 H), 1.24 (s, 3 H), 1.15 (s, 3 H), 1.11 (s, 3 H), 1.02 (s, 9 H), 0.89 (d, J = 6.8 Hz, 3 H), 0.84 (s, 9 H), 0.06 (s, 3 H), 0.04 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 174.7, 142.9, 137.2, 135.5, 134.6, 134.0, 132.3, 129.4, 128.2, 127.5, 114.3, 95.9, 78.8, 77.4, 76.9, 76.5, 75.8, 75.6, 73.4, 73.2, 70.9, 70.4, 69.4, 66.5, 63.9, 55.2, 46.0, 34.9, 34.8, 33.9, 32.6, 29.2, 29.1, 27.7, 26.9, 26.4, 25.9, 25.6, 22.3, 20.5, 19.3, 18.3, 15.5, 12.4, -2.0; HRMS (ESI TOF) calcd for C₆₀H₈₉Cl₃O₁₁Si₂Na (M+Na)⁺ 1171.4899, found 1171.4878.

Mixed Acetal 22. To a solution of **20** (214 mg, 0.186 mmol) and **21** (0.18 mL, 0.559 mmol) in CH₂Cl₂ (3 mL) was added CSA (8.6 mg, 0.037 mmol). After stirring for 15 min at room temperature, the reaction mixture was quenched with Et₃N. Concentration and chromatography (hexane/EtOAc, 100:1 to 50:1 to 15:1 to 4:1 containing 0.5% Et₃N) gave **22** (245 mg, 88%, quant. based on recovery) and unreacted **20** (25.1 mg, 12% recovery): colorless oil; *R_f* = 0.54 (hexane/EtOAc, 4:1); IR (neat) 2928, 1737, 1101 cm⁻¹; ¹H NMR (400 MHz, C₆D₆) δ 7.82-7.77 (m, 4 H), 7.27-7.09 (m, 6 H), 6.94-6.91 (m, 2 H), 5.93-5.83 (m, 1 H), 5.21-5.11 (m, 2 H), 5.04-4.97 (m, 1 H), 4.80-4.74 (m, 2 H), 4.50-4.34 (m, 4 H), 4.02-3.94 (m, 1 H), 3.89-3.59 (m, 3 H), 3.48-3.10 (m, 11 H), 2.80-2.55 (m, 2 H), 2.46-2.02 (m, 3 H), 2.00-1.46 (m, 18 H), 1.45-1.33 (m, 6 H), 1.30-1.16 (m, 21 H), 1.04-0.84 (m, 30 H), 0.18-0.11 (m, 6 H).

Allyl Stannane 23. To a solution of **22** (89.3 mg, 59.1 μmol) in CH₂Cl₂ (4 mL) at -15 °C were added HMDS (0.39 mL, 1.77 mmol) and TMSI (84 μL, 0.59 mmol) and stirred for 1.5 hours at the same temperature. The reaction mixture was quenched with satd NaHCO₃, diluted with AcOEt, washed with water and brine, and the resultant aqueous layer was extracted with EtOAc. Concentration and chromatography (hexane/EtOAc, 100:1 to 20:1 to 10:1 to 8:1 containing 2% Et₃N) gave **23** (76.8 mg, 91%): colorless oil; *R_f* = 0.51 (hexane/EtOAc, 4:1); [α]_D²³ -8.6 (c 0.78, C₆D₆); IR (neat) 3668-3280, 2929, 1736 cm⁻¹; ¹H NMR (400 MHz, C₆D₆) δ 7.83-7.77 (m, 4 H), 7.26-7.21 (m, 6 H), 6.93 (s, 2 H), 5.84 (dd, *J* = 17.4, 10.7 Hz, 1 H), 5.17 (dd, *J* = 17.4, 1.2 Hz, 1 H), 5.08 (dd, *J* = 9.9, 2.3 Hz, 1 H), 4.98 (dd, *J* = 10.7, 1.2 Hz, 1 H), 4.68 (ddd, *J* = 9.0, 9.0, 6.0 Hz, 1 H), 4.44 (s, 2 H), 4.14 (dd, *J* = 9.6, 7.2 Hz, 1 H), 3.97 (bs, 1 H), 3.79-3.65 (m, 2 H), 3.60 (ddd, *J* = 10.7, 10.7, 4.4 Hz, 1 H), 3.45-3.25 (m, 5 H), 2.54-2.42 (m, 3 H), 2.37 (dd, *J* = 15.9, 2.9 Hz, 1 H), 2.33-2.21 (m, 2 H), 2.13-1.99 (m, 2 H), 1.97-1.85 (m, 2 H), 1.84-1.48 (m, 20 H), 1.45-1.33 (m, 8 H), 1.29 (s, 3 H), 1.20 (s, 3 H), 1.19 (s, 9 H), 1.01 (s, 9 H), 1.01-0.96 (m, 18 H), 0.16 (s, 3 H), 0.12 (s, 3 H); ¹³C NMR (100 MHz, C₆D₆) δ 173.4, 143.3, 140.6, 137.5, 136.0, 134.6, 134.5, 133.0, 129.9, 128.4, 127.9, 114.3, 107.3, 80.0, 78.9, 77.7, 77.4, 75.7, 75.4, 75.2, 72.5, 71.1, 70.6, 70.5, 66.8, 64.5, 47.9, 35.5, 35.4, 33.7, 33.3, 30.0, 29.8, 29.5, 29.1, 28.0, 27.3, 27.1, 26.5, 26.3, 23.3, 20.2, 19.6, 18.8, 16.2, 14.2, 12.8, 9.9, 6.6, -1.6, -1.7; HRMS (ESI TOF) calcd for C₇₃H₁₁₅Cl₃O₁₀Si₂SnNa (M+Na)⁺ 1455.6014, found 1455.6338.

Silyl Ether 24. To a solution of **23** (170 mg, 0.119 mmol) in CH₂Cl₂ (3 mL) at 0 °C were

added 2,6-lutidine (0.14 mL, 1.19 mmol) and TBSOTf (0.08 mL, 0.348 mmol). After stirring for 30 min at 0 °C, an additional amount of TBSOTf (0.04 mL, 0.174 mmol) was added to the reaction mixture, and then the reaction mixture was further stirred for 30 min at the same temperature. The reaction mixture was quenched with MeOH, diluted with EtOAc, and washed with satd NaHCO₃ and brine. Concentration and chromatography (hexane/EtOAc, 1:0 to 50:1 to 20:1 containing 0.5% Et₃N) gave **24** (175 mg, 95%): colorless oil; *R_f* = 0.56 (hexane/EtOAc, 7:1); [α]_D²³ -1.6 (c 0.75, C₆D₆); IR (neat) 2928, 1738, 1089 cm⁻¹; ¹H NMR (400 MHz, C₆D₆) δ 7.83-7.76 (m, 4 H), 7.28-7.21 (m, 6 H), 6.93 (s, 2 H), 5.88 (dd, *J* = 17.3, 10.7 Hz, 1 H), 5.68 (d, *J* = 5.9 Hz, 1 H), 5.19 (dd, *J* = 17.3, 1.5 Hz, 1 H), 5.14 (dd, *J* = 10.1, 2.1 Hz, 1 H), 5.01 (dd, *J* = 10.7, 1.2 Hz, 1 H), 4.65 (ddd, *J* = 9.0, 9.0, 6.0 Hz, 1 H), 4.44 (s, 2 H), 4.45-4.40 (m, 1 H), 3.99 (bs, 1 H), 3.88-3.79 (m, 1 H), 3.79-3.62 (m, 2 H), 3.49-3.32 (m, 4 H), 3.23 (d, *J* = 9.3 Hz, 1 H), 2.76-2.58 (m, 2 H), 2.42-2.32 (m, 2 H), 2.22 (dd, *J* = 16.0, 3.0 Hz, 1 H), 2.10-2.01 (m, 1 H), 2.01-1.90 (m, 2 H), 1.89-1.49 (m, 19 H), 1.45-1.33 (m, 6 H), 1.31 (s, 3 H), 1.23 (s, 3 H), 1.22 (s, 3 H), 1.19 (s, 9 H), 1.09 (s, 9 H), 1.05 (d, *J* = 7.1 Hz, 3 H), 1.02-0.97 (m, 15 H), 1.01 (s, 9 H), 0.21 (s, 3 H), 0.19 (s, 3 H), 0.18 (s, 3 H), 0.13 (s, 3 H); ¹³C NMR (100 MHz, C₆D₆) δ 172.9, 143.5, 140.8, 137.5, 136.0, 134.6, 134.5, 133.1, 129.9, 128.3, 127.9, 114.3, 107.2, 81.7, 78.4, 78.0, 77.7, 76.4, 75.2, 73.1, 72.6, 71.2, 70.6, 66.8, 64.4, 49.8, 36.1, 35.6, 33.9, 33.3, 30.0, 29.8, 29.6, 29.0, 28.0, 27.3, 27.1, 26.43, 26.37, 26.3, 22.8, 21.2, 19.6, 18.8, 18.6, 15.2, 14.2, 13.0, 9.9, 6.7, -1.6, -1.7, -4.0, -4.3; HRMS (ESI TOF) calcd for C₇₉H₁₂₉Cl₃O₁₀Si₃SnNa (M+Na)⁺ 1569.6881, found 1569.6549.

Diene 25. To a solution of **24** (24.6 mg, 15.9 μ mol) in CH₂Cl₂ (1.5 mL) at -78 °C was added DIBAL-H (32 μ L, 32.6 μ mol, 1.02M solution in hexane). After stirring for 30 sec at -78 °C, a precooled (-40 °C) solution of pyridine (8 μ L, 98.9 μ mol) and DMAP (7.8 mg, 63.6 μ mol) in CH₂Cl₂ (0.3 mL) and (ClCH₂CO)₂O (22 mg, 0.129 mmol) in CH₂Cl₂ (0.7 mL) at were added to the reaction mixture. The reaction mixture was allowed to warm to -10 °C over 1 hour with stirring, and then quenched with H₂O. The resulting mixture was diluted with Et₂O, and then washed with satd NaK tartrate, satd CuSO₄ (2 times), water, satd NaHCO₃ and brine. The resultant aqueous layer was extracted with EtOAc. Concentration of the combined organic layer gave the crude α -chloroacetoxy ether **2**, which was used for the next reaction without further purification.

To the stirring suspension of MgBr₂·OEt₂ (41.1 mg, 0.159 mmol) and MS5A (30 mg) in CH₂Cl₂ (1.5 mL) at -78 °C was added a precooled (-40 °C) solution of **2** in CH₂Cl₂ (1.5 mL),

dried over MS5A. The mixture was allowed to warm to 0 °C over 50 min, and then quenched with Et₃N. The mixture was filtered through a short silica gel column (EtOAc) and concentrated. The residue was purified by chromatography (hexane/EtOAc, 1:0 to 40:1 to 20:1 to 10:1) to give **25** (10.2 mg, 52% for the 2 steps): colorless oil; R_f = 0.42 (hexane/EtOAc, 7:1); $[\alpha]_D^{23}$ -8.6 (c 0.63, CHCl₃); IR (neat) 2929, 1471, 1428, 1081 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.64 (dd, J = 7.4, 1.5 Hz, 4 H), 7.42-7.31 (m, 6 H), 7.31 (s, 2 H), 5.90 (dd, J = 17.6, 10.7 Hz, 1 H), 5.63 (ddd, J = 17.1, 10.7, 5.1 Hz, 1 H), 5.20 (dd, J = 17.1, 1.5 Hz, 1 H), 5.18 (d, J = 17.6 Hz, 1 H), 5.15 (d, J = 10.7 Hz, 1 H), 5.01 (dd, J = 10.7, 1.5 Hz, 1 H), 4.66 (s, 2 H), 4.29 (d, J = 4.6 Hz, 1 H), 4.21 (dd, J = 11.3, 5.0 Hz, 1 H), 3.95 (bs, 1 H), 3.70-3.36 (m, 8 H), 3.17 (d, J = 9.3 Hz, 1 H), 3.07 (dd, J = 7.1, 2.7 Hz, 1 H), 2.05-1.20 (m, 19 H), 1.26 (s, 3 H), 1.15 (s, 3 H), 1.12 (s, 3 H), 1.03 (s, 9 H), 0.92-0.88 (m, 12 H), 0.83 (s, 9 H), 0.06 (s, 3 H), 0.05 (s, 6 H), 0.03 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 145.6, 137.9, 137.2, 135.5, 134.5, 134.1, 132.4, 129.4, 128.2, 127.5, 114.4, 114.1, 87.3, 82.7, 82.2, 77.6, 77.5, 77.2, 76.2, 75.2, 72.7, 72.5, 71.4, 70.8, 66.6, 64.0, 49.5, 35.0, 34.9, 34.4, 32.5, 29.3, 29.1, 28.2, 27.5, 26.9, 26.1, 26.0, 23.3, 20.9, 20.2, 19.3, 18.3, 18.2, 15.5, 12.4, -1.9, -1.9, -3.9, -5.0; HRMS (ESI TOF) calcd for C₆₇H₁₀₃Cl₃O₉Si₃Na (M+Na)⁺ 1265.5868, found 1265.6018.

Pentacycle 27. To a solution of **25** (10.9 mg, 8.77 μ mol) in toluene (2.9 mL) at room temperature were added three portions of the Grubbs catalyst **26** (7.2 $\times$ 3 mg, 8.75 $\times$ 3 μ mol) at 15 min intervals, during which time the reaction mixture was stirred at 100 °C. After stirring for 15 min at 100 °C, an additional amount of 1st generation Grubbs catalyst (3.6 mg, 4.37 μ mol) was added to the reaction mixture at room temperature. After stirring for 15 min at 100 °C, the reaction was quenched with Et₃N at room temperature, diluted with Et₂O/EtOAc, and stirred for additional 30 min at room temperature. The resultant mixture was filtered through a short silica gel column (EtOAc) and concentrated. The residue was purified by 3-times chromatographies (hexane/EtOAc, 40:1 to 20:1, CH₂Cl₂/EtOAc, 1:0 to 100:1 to 50:1, hexane/EtOAc, 40:1 to 30:1 to 20:1) to give **27** (7.4 mg, 69%): colorless oil; R_f = 0.46 (hexane/EtOAc, 7:1); $[\alpha]_D^{24}$ -11.0 (c 0.67, CHCl₃); IR (neat) 2929, 1090 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.67-7.61 (m, 4 H), 7.42-7.31 (m, 6 H), 7.31 (s, 2 H), 5.63 (dd, J = 13.3, 2.3 Hz, 1 H), 5.41 (dd, J = 13.3, 1.5 Hz, 1 H), 4.67 (s, 2 H), 4.16 (dd, J = 11.3, 4.8 Hz, 1 H), 3.95 (bs, 1 H), 3.89 (bd, J = 9.3 Hz, 1H), 3.75-3.46 (m, 5 H), 3.39 (dd, J = 6.1, 6.1 Hz, 1 H), 3.31 (d, J = 10.7 Hz, 1 H), 3.28-3.18 (m, 3 H), 2.06 (ddd, J = 11.5, 4.3, 4.3, 1 H), 2.03-1.95 (m, 1 H), 1.94-1.21 (m, 17 H), 1.17 (s, 3 H), 1.14 (s, 3 H), 1.11 (s, 3 H), 1.02 (s, 9 H), 0.89 (s, 9 H),

0.88 (d, $J = 6.6$ Hz, 3 H), 0.81 (s, 9 H), 0.07 (s, 6 H), 0.04 (s, 3 H), 0.03 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.8, 137.2, 135.5, 134.5, 134.1, 132.4, 129.9, 129.4, 128.2, 127.5, 88.2, 86.3, 83.9, 80.2, 78.3, 77.6, 77.2, 76.0, 75.7, 73.1, 73.0, 72.6, 71.2, 70.8, 66.6, 64.0, 49.5, 38.1, 35.0, 33.7, 32.6, 30.4, 29.3, 29.1, 27.2, 26.9, 26.7, 26.0, 25.8, 21.9, 20.9, 19.3, 18.3, 18.2, 17.7, 12.3, -1.9, -2.1, -4.1, -4.9; HRMS (ESI TOF) calcd for $\text{C}_{65}\text{H}_{99}\text{Cl}_3\text{O}_9\text{Si}_3\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 1237.5554, found 1237.5496.

Benzyl ether 28. A mixture of **27** (5.7 mg, 4.69 μmol) and Pd-C (5.6 mg) and Et_3N (50 μL) in EtOH (1 mL) at room temperature was stirred under H_2 atmosphere. After 1.5 hours, the catalyst was filtered off through a short silica gel column (EtOAc) and the filtrate was concentrated to give the crude benzyl ether, which was used for the next reaction directly.

To a vigorously stirred solution of the crude benzylether, pyridine (85 μL , 1.06 mmol) and $\text{KO}_2\text{CN}=\text{NCO}_2\text{K}$ (68.3 mg, 0.352 mmol) in MeOH (1 mL) at room temperature was added a solution of AcOH (40 μL , 0.704 mmol) in MeOH (0.3 mL) over 75 min. The reaction mixture was quenched with satd NH_4Cl , diluted with Et_2O , and washed with satd CuSO_4 , water, satd NaHCO_3 and brine. The aqueous layer was extracted with Et_2O . After concentration of the combined organic layer, the residue containing starting material was subjected to the above same procedure. The residue containing no starting material was purified by chromatography (hexane/EtOAc, 40:1 to 20:1 to 15:1) to give **28** (4.4 mg, 84% for the 2 steps): colorless oil; $R_f = 0.39$ (hexane/EtOAc, 7:1); $[\alpha]^{24}_{\text{D}} -13.1$ (c 0.21, CHCl_3); IR (neat) 2929, 1090 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.64 (dd, $J = 7.8, 1.5$ Hz, 4 H), 7.41-7.20 (m, 11 H), 4.49 (s, 2 H), 4.17 (dd, $J = 11.5, 5.1$ Hz, 1 H), 3.94 (dd, $J = 3.7, 3.7$ Hz, 1 H), 3.73-3.56 (m, 3 H), 3.51-3.43 (m, 2 H), 3.42-3.36 (m, 1 H), 3.34-3.15 (m, 4 H), 3.10 (dd, $J = 12.2, 3.9$ Hz, 1 H), 2.13-1.20 (m, 23 H), 1.14 (s, 3 H), 1.10 (s, 3 H), 1.06 (s, 3 H), 1.02 (s, 9 H), 0.89 (s, 9 H), 0.88 (d, $J = 6.3$ Hz, 3 H), 0.81 (s, 9 H), 0.05 (s, 3 H), 0.03 (s, 6 H), 0.03 (s, 3 H); (400 MHz, C_6D_6) δ 7.83-7.73 (m, 4 H), 7.33 (d, $J = 7.6$ Hz, 2 H), 7.26-7.06 (m, 9 H), 4.42 (dd, $J = 11.4, 5.7$ Hz, 1 H), 4.36 (s, 2 H), 4.03 (bs, 1 H), 3.92 (ddd, $J = 11.7, 9.3, 4.9$ Hz, 1 H), 3.78-3.60 (m, 2 H), 3.59-3.27 (m, 6 H), 3.23 (ddd, $J = 8.9, 8.9, 3.7$ Hz, 1 H), 3.17 (dd, $J = 12.0, 4.0$ Hz, 1 H), 2.34 (ddd, $J = 12.0, 4.0, 4.0$ Hz, 1 H), 2.25-2.15 (m, 2 H), 2.10-1.65 (m, 13 H), 1.65-1.42 (m, 5 H), 1.40-1.25 (m, 2 H), 1.24 (s, 3 H), 1.19 (s, 9 H), 1.15 (s, 3 H), 1.13 (s, 3 H), 1.09 (s, 9 H), 1.05 (d, $J = 7.1$ Hz, 3 H), 0.94 (s, 9 H), 0.20 (s, 3 H), 0.17 (s, 3 H), 0.07 (s, 3 H), 0.06 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 138.6, 135.5, 134.1, 129.4, 128.2, 127.6, 127.5, 127.4, 88.2, 86.6, 85.0, 82.2, 77.6, 77.2, 76.1, 75.5, 73.1, 72.9, 72.8, 72.6, 70.8, 70.7, 64.0, 49.5, 37.8, 37.7, 35.0,

33.9, 32.6, 29.6, 29.3, 29.1, 28.9, 27.3, 27.0, 26.0, 25.8, 24.0, 20.9, 19.3, 18.3, 18.1, 16.2, 12.4, -2.0, -2.2, -4.2, -4.8; (100 MHz, C₆D₆) δ 139.5, 136.0, 134.5, 129.9, 128.5, 127.9, 127.5, 88.7, 86.6, 85.0, 83.0, 78.1, 77.7, 76.6, 76.2, 73.8, 73.4, 73.3, 73.1, 71.2, 71.0, 64.4, 50.0, 38.1, 35.6, 34.8, 33.3, 30.3, 30.0, 29.63, 29.56, 27.9, 27.3, 26.5, 26.4, 26.2, 24.1, 21.4, 19.6, 18.7, 18.5, 16.1, 13.0, -1.8, -1.9, -3.8, -4.6; HRMS (ESI TOF) calcd for C₆₅H₁₀₄O₉Si₃Na (M+Na)⁺ 1135.6886, found 1135.6899.

Alcohol 29. A mixture of **28** (5.6 mg, 5.03 μ mol) and Pd(OH)₂-C (7.2 mg) in EtOAc (1.2 mL) was stirred under H₂ atmosphere at room temperature. After 45 min, the catalyst was filtered off through a short silica gel column (EtOAc) and the filtrate was concentrated and purified by chromatography (hexane/EtOAc, 10:1 to 7:1 to 4:1) to give **29** (4.6 mg, 89%): colorless oil; R_f = 0.20 (hexane/EtOAc, 4:1); $[\alpha]_D^{22}$ -9.1 (c 0.87, CHCl₃); IR (neat) 3606-3144, 2928, 1731, 1085 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.66-7.61 (m, 4 H), 7.41-7.31 (m, 6 H), 4.17 (dd, J = 11.6, 5.0 Hz, 1 H), 3.94 (dd, J = 3.7, 3.7 Hz, 1 H), 3.73-3.56 (m, 5 H), 3.41-3.22 (m, 3 H), 3.22-3.16 (m, 2 H), 3.10 (dd, J = 12.1, 3.7 Hz, 1 H), 2.17-1.20 (m, 23 H), 1.14 (s, 3 H), 1.12 (s, 3 H), 1.08 (s, 3 H), 1.02 (s, 9 H), 0.89 (s, 9 H), 0.88 (d, J = 6.3 Hz, 3 H), 0.81 (s, 9 H), 0.06 (s, 3 H), 0.04 (s, 3 H), 0.03 (s, 3 H), 0.03 (s, 3 H); ¹³C NMR (100 MHz, CDCl₃) δ 135.5, 134.1, 129.4, 127.5, 88.3, 86.5, 84.8, 82.3, 77.6, 77.2, 76.0, 75.5, 73.1, 72.9, 72.5, 70.8, 64.0, 63.0, 49.5, 37.7, 37.5, 35.0, 33.9, 32.5, 30.3, 29.8, 29.6, 29.3, 29.1, 28.8, 26.9, 26.5, 26.0, 25.8, 24.0, 20.9, 19.3, 18.3, 18.1, 16.1, 12.4, -2.0, -2.2, -4.2, -4.8; HRMS (ESI TOF) calcd for C₅₈H₉₈O₉Si₃Na (M+Na)⁺ 1045.6416, found 1045.6412.

(Z)-Diene 31. To a solution of **29** (4.8 mg, 4.69 μ mol) in CH₂Cl₂ (0.4 mL) and DMSO (0.1 mL) at 0 °C was added Et₃N (65 μ L, 0.469 mmol) and SO₃·pyr. (37.3 mg, 0.235 mmol), and stirred for 1 hour at room temperature. The mixture was diluted with EtOAc, and washed with satd NH₄Cl, water and brine. Concentration gave the crude aldehyde, which was used for the next reaction directly.

To the stirring suspension of **30** (126.7 mg, 0.235 mmol) in THF (0.3 mL) at -30 °C was added NaHMDS (0.19 mL, 0.190 mmol, 1.0 M solution in THF). After stirring for 15 min at the same temperature, the mixture was cooled to -78 °C. To this solution was added a precooled (-78 °C) solution of the crude aldehyde in THF (0.7 mL), and then the reaction mixture was allowed to warm to room temperature over 1 hour with stirring. After stirring for additional 15 min at room temperature, the reaction was quenched with satd NaHCO₃, diluted

with EtOAc, and washed with water and brine. The organic layer was concentrated and the resulting residue was purified by chromatography (hexane/EtOAc, 40:1 to 20:1 to 10:1) to give the phenylselenide with inseparable byproducts containing. This crude phenylselenide was used for the next reaction without further purification.

To a solution of the crude phenylselenide in THF (0.6 mL) at room temperature were added NaHCO_3 (7.9 mg, 93.8 μL) and 30% H_2O_2 (0.2 mL), and stirred for 21 hours at 30 °C. The reaction mixture was quenched with satd Na_2SO_3 at 0 °C, and then the mixture was diluted with EtOAc and washed with water and brine. Concentration and chromatography (hexane/EtOAc, 100:1 to 70:1 to 40:1 to 20:1) gave **31** (4.4 mg, 90% for the 3 steps): colorless oil; R_f = 0.38 (hexane/EtOAc, 10:1); $[\alpha]_D^{24}$ -14.3 (c 0.20, CHCl_3); IR (neat) 2930, 1737, 1643, 1087 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.64 (dd, J = 7.8, 1.5 Hz, 4 H), 7.41-7.31 (m, 6 H), 6.63 (ddd, J = 16.8, 11.1, 10.0 Hz, 1 H), 6.01 (dd, J = 11.1, 10.0 Hz, 1 H), 5.41 (ddd, J = 10.0, 6.6, 6.6 Hz, 1 H), 5.18 (d, J = 16.8 Hz, 1 H), 5.07 (d, J = 10.0 Hz, 1 H), 4.17 (dd, J = 11.6, 5.0 Hz, 1 H), 3.94 (dd, J = 3.7, 3.7 Hz, 1 H), 3.74-3.56 (m, 3 H), 3.39 (dd, J = 6.8, 6.8, 1 H), 3.30-3.15 (m, 4 H), 3.11 (dd, J = 12.1, 3.8 Hz, 1 H), 2.36-2.19 (m, 2 H), 2.19-1.20 (m, 21 H), 1.14 (s, 3 H), 1.10 (s, 3 H), 1.06 (s, 3 H), 1.02 (s, 9 H), 0.89 (s, 9 H), 0.88 (d, J = 6.3 Hz, 3 H), 0.82 (s, 9 H), 0.06 (s, 3 H), 0.05 (s, 3 H), 0.04 (s, 3 H), 0.03 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 135.5, 134.1, 132.7, 132.1, 129.6, 129.4, 127.5, 117.0, 86.9, 86.3, 85.2, 82.1, 77.6, 77.2, 76.1, 75.5, 73.1, 72.9, 72.6, 70.8, 64.0, 49.5, 37.8, 37.7, 35.0, 34.0, 32.6, 30.2, 29.8, 29.7, 29.3, 29.1, 28.8, 27.0, 26.0, 25.9, 25.8, 24.8, 24.1, 20.9, 19.3, 18.3, 18.1, 16.3, 12.4, -2.0, -2.2, -4.2, -4.8; HRMS (ESI TOF) calcd for $\text{C}_{61}\text{H}_{100}\text{O}_8\text{Si}_3\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 1067.6624, found 1067.6631.

Alcohol 32. To a solution of **31** (3.3 mg, 3.16 μmol) in THF (0.1 mL) at room temperature was added a solution of TBAF/AcOH [0.1 mL, the solution was prepared from 0.5 mL of TBAF (1.0 M solution in THF) and 30 μL of AcOH]. After stirring for 11 hours, the mixture was diluted with EtOAc, and washed with satd NaHCO_3 , water and brine. Concentration and chromatography (hexane/EtOAc, 7:1 to 4:1 to 3:1) gave **32** (2.4 mg, 94%): colorless oil; R_f = 0.10 (hexane/EtOAc, 4:1); $[\alpha]_D^{23}$ -22.3 (c 0.12, CHCl_3); IR (neat) 3661-3120, 2928, 1737, 1643, 1089 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.63 (ddd, J = 16.8, 11.0, 9.8 Hz, 1 H), 6.01 (dd, J = 11.0, 10.2 Hz, 1 H), 5.41 (ddd, J = 10.2, 7.1, 7.1 Hz, 1 H), 5.17 (d, J = 16.8 Hz, 1 H), 5.07 (d, J = 9.8 Hz, 1 H), 4.22 (dd, J = 11.6, 5.0 Hz, 1 H), 3.95 (dd, J = 3.7, 3.7 Hz, 1 H), 3.74-3.59 (m, 2 H), 3.59-3.46 (m, 2 H), 3.30-3.14 (m, 4 H), 3.11 (dd, J = 12.2, 3.9 Hz, 1 H),

2.92 (bs, 1 H), 2.38-2.20 (m, 2 H), 2.18-1.95 (m, 3 H), 1.91-1.20 (m, 18 H), 1.23 (s, 3 H), 1.10 (s, 3 H), 1.06 (s, 3 H), 0.93 (d, $J = 6.8$ Hz, 3 H), 0.90 (s, 9 H), 0.82 (s, 9 H), 0.06 (s, 3 H), 0.05 (s, 3 H), 0.04 (s, 3 H), 0.03 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 132.7, 132.1, 129.6, 117.0, 86.9, 86.3, 85.2, 82.0, 78.5, 77.2, 76.2, 75.5, 73.2, 72.5, 72.3, 62.8, 49.3, 37.8, 37.7, 34.9, 33.9, 33.6, 30.6, 30.5, 30.1, 29.8, 28.8, 26.0, 25.8, 24.8, 24.0, 20.7, 18.3, 18.1, 16.3, 12.6, -2.0, -2.2, -4.2, -4.8; HRMS (ESI TOF) calcd for $\text{C}_{45}\text{H}_{82}\text{O}_8\text{Si}_2\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 829.5446, found 829.5440.

Preparation of the Phosphonate 33.

Garner, P.; Ramakanth, S. *J. Org. Chem.* **1987**, 52, 2629-2631.

A mixture of 3-hydroxy-2-butanone (500 mg, 5.68 mmol) and $\text{Ph}_3\text{P}=\text{CHCO}_2\text{Me}$ (2.28 g, 6.82 mmol) in benzene (10 mL) was refluxed for 14.5 hours. The mixture was concentrated and purified by chromatography (hexane/EtOAc, 4:1 to 1.5:1) to give the known ester (810 mg, 99%) as a single stereoisomer.

To a stirred solution of the hydroxyl ester (158 mg, 1.10 mmol) obtained above, imidazole (105 mg, 1.54 mmol) and PPh_3 (433 mg, 1.65 mmol) in CH_2Cl_2 (10 mL) at $0\text{ }^\circ\text{C}$ was added CBr_4 (511 mg, 1.54 mmol). After stirring for 1 hour at room temperature, the reaction was quenched with satd Na_2SO_3 , diluted with Et_2O , and washed with water and brine. Concentration and chromatography (hexane/EtOAc, 1:0 to 20:1 to 10:1 to 5:1) gave the bromide (219 mg, 96%): colorless oil; $R_f = 0.60$ (Hexane/EtOAc, 2:1); IR (neat) 2950, 1720, 1649 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.90 (d, $J = 0.7$ Hz, 1 H), 4.63 (q, $J = 6.8$ Hz, 1 H), 3.70 (s, 3 H), 2.26 (s, 3 H), 1.78 (d, $J = 6.8$ Hz, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.5, 157.0, 116.3, 53.2, 51.3, 23.8, 15.2; HRMS (ESI TOF) calcd for $\text{C}_7\text{H}_{11}\text{BrO}_2\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 228.9840, found 228.9855.

A mixture of the bromide (401 mg, 1.94 mmol) and $\text{P}(\text{OEt})_3$ (0.29 mL, 1.75 mmol) was

heated for 9.5 hours at 140 °C with stirring. After cooling to room temperature, the mixture was directly subjected to a silica gel column chromatography (hexane/EtOAc, 4:1 to 2:1 to 1:1 to 1:3) to give **33** (435 mg, 94%): colorless oil; R_f = 0.25 (Hexane/EtOAc, 1:2); IR (neat) 3475, 2983, 1645 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.79 (d, J = 4.9 Hz, 1 H), 4.12-4.01 (m, 4 H), 3.65 (s, 3 H), 2.67 (dq, J = 23.9, 7.2 Hz, 1 H), 2.26-2.24 (m, 3 H), 1.34 (dd, J = 18.3, 7.3 Hz, 3 H), 1.27 (ddd, J = 7.2, 4.3, 4.3 Hz, 6 H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.5 (d, J = 2.5 Hz), 155.8 (d, J = 8.3 Hz), 118.2 (J = 11.6 Hz), 62.3 (d, J = 6.6 Hz), 62.1 (d, J = 6.6 Hz), 51.0, 42.5 (d, J = 135.2 Hz), 18.4, 16.4, 16.3, 13.8 (d, J = 5.8 Hz); HRMS (ESI TOF) calcd for $\text{C}_{11}\text{H}_{21}\text{O}_5\text{PNa}$ ($\text{M}+\text{Na}$) $^+$ 287.1024, found 287.1010.

Unsaturated Ester 34. To a solution of **32** (2.4 mg, 2.97 μmol) in CH_2Cl_2 (0.3 mL) and DMSO (0.1 mL) at 0 °C was added Et_3N (41 μL , 0.297 mmol) and $\text{SO}_3 \cdot \text{pyr.}$ (23.6 mg, 0.149 mmol), and the reaction mixture was stirred for 45 min at room temperature. The mixture was diluted with EtOAc, washed with satd NH_4Cl , water and brine, and concentrated. The residue was filtered through a short silica gel column (Et_2O) to give the crude aldehyde, which was used for the next reaction directly.

To a solution of phosphate **33** (92.3 mg, 0.349 mmol) in THF (0.2 mL) -78 °C was added $n\text{-BuLi}$ (0.19 mL, 0.297 mmol, 1.59 M solution in hexane), and stirred for 10 min at the same temperature. After stirring for additional 50 min at 0 °C, the mixture was cooled to -78 °C. To this mixture was added a precooled (-78 °C) solution of the crude aldehyde obtained in THF (0.7 mL). The reaction mixture was allowed to warm to room temperature over 1 hour with stirring, and then the mixture was stirred for 26 hours at room temperature. The reaction was quenched with satd NH_4Cl , diluted with EtOAc, and washed with water and brine. Concentration and chromatography (hexane/EtOAc, 100:1 to 70:1 to 40:1 to 20:1) gave **34** (2.4 mg, 88% for the 2 steps): colorless oil; R_f = 0.59 (hexane/EtOAc, 4:1); $[\alpha]_D^{23}$ -22.4 (c 0.12, CHCl_3); IR (neat) 2929, 1719, 1609, 1086 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.63 (ddd, J = 17.1, 10.9, 10.2 Hz, 1 H), 6.01 (dd, J = 10.9, 10.0 Hz, 1 H), 5.93 (t, J = 7.1 Hz, 1 H), 5.82 (s, 1 H), 5.41 (ddd, J = 10.0, 7.3, 7.3 Hz, 1 H), 5.18 (d, J = 17.1 Hz, 1 H), 5.07 (d, J = 10.2 Hz, 1 H), 4.19 (dd, J = 11.5, 5.1 Hz, 1 H), 3.95 (dd, J = 3.4, 3.4 Hz, 1 H), 3.74-3.62 (m, 1 H), 3.69 (s, 3 H), 3.45-3.39 (m, 1 H), 3.30-3.15 (m, 4 H), 3.11 (dd, J = 12.2, 4.1 Hz, 1 H), 2.37-1.20 (m, 23 H), 2.29 (s, 3 H), 1.78 (s, 3 H), 1.17 (s, 3 H), 1.10 (s, 3 H), 1.06 (s, 3 H), 0.91 (d, J = 7.1 Hz, 3 H), 0.90 (s, 9 H), 0.82 (s, 9 H), 0.06 (s, 3 H), 0.05 (s, 3 H), 0.04 (s, 3 H), 0.04 (s, 3 H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.9, 156.7, 135.8, 133.5, 132.7, 132.1, 129.6,

117.0, 113.8, 86.9, 86.3, 85.2, 82.1, 77.7, 77.2, 76.1, 75.5, 73.1, 72.8, 72.6, 70.7, 50.9, 49.5, 37.8, 37.7, 35.0, 34.0, 32.9, 32.5, 30.2, 29.80, 29.76, 28.8, 26.0, 25.9, 25.8, 24.8, 24.0, 20.9, 18.3, 18.1, 16.3, 15.5, 14.1, 12.6, -2.0, -2.2, -4.2, -4.8; HRMS (ESI TOF) calcd for $C_{52}H_{90}O_9Si_2Na$ ($M+Na$)⁺ 937.6021, found 937.6024.

Triol 35. To a solution of **34** (2.4 mg, 2.62 μ mol) in CH_2Cl_2 (0.7 mL) at -78 °C was added DIBAL-H (10 μ L, 10.2 μ mol, 1.02 M solution in hexane). After stirring for 15 min, the reaction was quenched with MeOH and diluted with Et_2O . The mixture was filtered through a short silica gel column (Et_2O to EtOAc), and the filtrate was concentrated to give the crude allyl alcohol, which was used for the next reaction directly.

A mixture of the crude allyl alcohol and TBAF (0.2 mL, 0.2 mmol, 1.0 M solution in THF) was stirred for 32 hours at 75 °C in a sealed tube. The mixture was diluted with EtOAc, and washed with water and brine. Concentration and chromatography (hexane/EtOAc, 1:1 to 1:2 to 0:1) gave **35** (1.7 mg, 98% for the 2 steps): colorless oil; R_f = 0.19 (hexane/EtOAc, 1:1); $[\alpha]_D^{25}$ -22.4 (c 0.08, benzene); IR (neat) 3649-3114, 2929, 1643, 1087 cm^{-1} ; 1H NMR (400 MHz, C_6D_6) δ 6.76 (ddd, J = 16.8, 10.9, 10.5 Hz, 1 H), 6.08 (dd, J = 10.9, 10.5 Hz, 1 H), 5.70 (t, J = 6.3 Hz, 1 H), 5.65 (t, J = 7.3 Hz, 1 H), 5.45 (ddd, J = 10.5, 7.3, 7.3 Hz, 1 H), 5.16 (d, J = 16.8 Hz, 1 H), 5.06 (d, J = 10.5 Hz, 1 H), 4.10-4.05 (m, 3 H), 4.01 (dd, J = 11.4, 5.5 Hz, 1 H), 3.70 (ddd, J = 11.2, 9.7, 5.2 Hz, 1 H), 3.45 (dd, J = 9.6, 2.8 Hz, 1 H), 3.44-3.39 (m, 1 H), 3.34 (ddd, J = 8.4, 8.4, 7.5 Hz, 1 H), 3.20-3.12 (m, 2 H), 2.93 (dd, J = 12.3, 4.0 Hz, 1 H), 2.39-2.07 (m, 9 H), 1.95-1.23 (m, 17 H), 1.81 (s, 3 H), 1.71 (s, 3 H), 1.22 (s, 3 H), 1.12 (s, 3 H), 0.99 (d, J = 7.1 Hz, 3 H), 0.97 (s, 3 H); ^{13}C NMR (100 MHz, C_6D_6) δ 138.2, 136.1, 132.9, 132.6, 130.1, 127.5, 125.5, 117.2, 87.4, 86.2, 84.7, 82.0, 77.2, 76.7, 75.1, 74.1, 73.7, 70.8, 69.9, 60.1, 48.0, 38.6, 37.8, 35.5, 34.6, 33.6, 33.4, 30.8, 30.0, 29.4, 26.1, 25.3, 23.7, 19.4, 16.3, 14.4, 14.3, 13.0; HRMS (ESI TOF) calcd for $C_{39}H_{62}O_8Na$ ($M+Na$)⁺ 681.4343, found 681.4343.

Brevenal (1). To a solution of **35** (1.0 mg, 1.52 μ mol) in CH_2Cl_2 (0.2 mL) at room temperature was added MnO_2 (4.0 mg, 46.0 μ mol). After stirring for 1 hour, the mixture was filtered through a short silica gel column (EtOAc), and the filtrate was concentrated. The residue was purified by chromatography (hexane/EtOAc, 2:1 to 1:1 to 1:2) to give **1** (1.0 mg, quant.): colorless oil; R_f = 0.30 (hexane/EtOAc, 1:1); $[\alpha]_D^{23}$ -27.7 (c 0.05, benzene); IR (neat) 3655-3163, 2935, 1657, 1619, 1087 cm^{-1} ; 1H NMR (400 MHz, C_6D_6) δ 10.08 (d, J = 7.6 Hz, 1

H), 6.76 (ddd, $J = 16.8, 10.2, 10.0$ Hz, 1 H), 6.14 (d, $J = 7.6$ Hz, 1 H), 6.08 (dd, $J = 10.7, 10.2$ Hz, 1 H), 5.81 (t, $J = 7.2$ Hz, 1 H), 5.45 (ddd, $J = 10.7, 7.8, 7.8$ Hz, 1 H), 5.16 (d, $J = 16.8$ Hz, 1 H), 5.06 (d, $J = 10.0$ Hz, 1 H), 4.10-4.04 (m, 3 H), 4.01 (dd, $J = 10.7, 6.3$ Hz, 1 H), 3.71 (ddd, $J = 10.5, 9.5, 5.1$ Hz, 1 H), 3.45 (dd, $J = 9.5, 2.4$ Hz, 1 H), 3.39-3.31 (m, 1 H), 3.28 (ddd, $J = 9.0, 2.9, 2.9$ Hz, 1 H), 3.21-3.13 (m, 2 H), 2.94 (dd, $J = 12.3, 4.0$ Hz, 1 H), 2.38-1.97 (m, 9 H), 1.97-1.38 (m, 14 H), 1.79 (s, 3 H), 1.55 (s, 3 H), 1.18 (s, 3 H), 1.14 (s, 3 H), 1.13-1.06 (m, 1 H), 0.97 (s, 3 H), 0.96 (d, $J = 7.3$ Hz, 3 H); ^{13}C NMR (100 MHz, C_6D_6) δ 190.5, 156.1, 135.9, 134.5, 132.9, 132.6, 130.1, 126.0, 117.2, 87.4, 86.2, 84.8, 82.0, 77.3, 76.8, 76.5, 75.1, 74.0, 73.3, 70.9, 70.0, 47.5, 38.6, 37.8, 35.4, 34.6, 33.6, 32.8, 30.8, 30.0, 29.5, 26.6, 25.3, 23.7, 19.4, 16.3, 14.0, 13.9, 12.9; HRMS (ESI TOF) calcd for $\text{C}_{39}\text{H}_{60}\text{O}_8\text{Na}$ ($\text{M}+\text{Na}$) $^{+}$ 679.4186, found 679.4190.

[illegible]

```

DFILE      WWD82w871x\data\Yyam
COMNT
DATIM      Fri Oct 26 14:00:36
OBNUC      1H
EXMOD      NON
OBFRR      399.65 MHz
OBSET      124.00 KHz
OBFIN      10500.00 Hz
POINT      32768
FREQU      7993.60 Hz
SCANS      23
ACQTM      4.0993 sec
PD         2.9010 sec
PWI        6.40 usec
IRNUC      1H
CTEMP      25.2 c
SLVNT      CDCL3
XREF       7.24 ppm
BF         0.12 Hz
RGAIN      18

```

The ¹³C NMR spectrum of poly(2-vinylpyridine) shows several characteristic peaks. The aromatic region contains peaks at 138, 125, 118, and 77 ppm. The aliphatic region shows peaks at 66, 64, 62, 41, 25, 18, and 14 ppm. The peak at 77 ppm is the solvent peak for CDCl₃.

FILE	W0626571x\data4\Yuv
COMNT	
DATE	Tue Apr 28 13:35:54
ORIG	13G
EXNO	60M
ORFQ	100.40 MHz
OBSE	125.00 kHz
ORFIN	10400.00 Hz
POINT	32768
FREQ	27173.90 Hz
SCANS	361
ACQTM	1.2059 sec
PD	1.7840 sec
PHI	6.60 sec/c
IRFUC	TH
CTEMP	26.9 c
SOLNT	CDCL3
EXREF	77.00 ppm
BF	2.00 Hz
GAIN	24

-PAGER 0 8:

WV082w071x\data\Yanagami\Brevensal\WBC ring\YY-159-data.als

WV082w071x\data\Yanagami\Brevensal\WBC ring\YY-159-C13.als

W4082w871x\data\Yamagami\Brevona\BRC_ring\YY-168-data.xls

```

DF FILE          W082w871xvdatzW4ym
COMNT
DATIM            Tue Nov 06 23:47:50
CONJC            1H
EXMOD            NOM
OBFREQ           399.65 MHz
OBSSET           124.00 kHz
OBF IN           10500.00 Hz
POINT            32768
FREQU            7993.60 Hz
SCANS            16
ACQTM            4.0993 sec
PD               2.9010 sec
PWI              6.40 used
IRNUC            1H
CTEMP            26.0 c
SLVINT           CDCL3
EXREF            7.24 ppm
BF               0.12 Hz
RGAIN            19

```

W4D62w871x\data\Yamagami\Brevenal\WBC ring\YYY-168-C13.als

```

FILE      WDSZwB7Tz\data\FYan
CONT      Wed Nov 07 00:07:45
DATIN     13C
GENUC     BGM
EXNO      100.40 MHz
OBSSET    125.00 KHz
OBSFREQ    10500.00 Hz
POINT      32768
FREQU      27173.90 Hz
SCANS      1024
ACQTIME    1.2059 sec
PULPROG    1.7940 sec
PWT         6.80 usec
IRNUC      1H
CTEMP      27.1 c
SLVNT      CDCL3
EXREF      77.00 ppm
BF          2.00 Hz
RGAIN      24

```

Chemical structure of compound **12** is shown above the spectrum. The structure is a complex polycyclic molecule featuring a TBDPSO group, a Me group, an OMPM group, and an OMOM group. The spectrum displays several peaks with corresponding chemical shifts (ppm) and integrations:

Chemical Shift (ppm)	Integration
4.33	1.91
21.68	0.99, 1.87, 5.12, 1.00, 1.97, 0.69, 2.19, 1.12, 1.05
7.43	1.96, 3.08, 7.24
13.71	3.49

```

DFILE          #WDS2w671xWdataWk1k
CONNT
DATIM          Thu Oct 18 22:48:33
CENUC          1H
EXMOD          NMR
OBFRO          399.65 MHz
OBSCT          124.00 kHz
OBF IN         10500.00 Hz
POINT          32768
FREQU          7993.60 Hz
SCANS          8
ACQTM         4.0993 sec
PD             2.9010 sec
PMT           6.40 usec
IRNUC          1H
CTEMP          25.9 c
SLVNT          CDCl3
EXFRT          7.15 ppm
BF             0.12 Hz
RGAIN          10

```

```

DFILE      WDB82w871xWdataRKik
CONNT
DATIM      Thu Oct 18 23:16:57
OBNJC      13C
EXMOD      BGM
OFFRO      100.40 Mhz
OBSCT      125.00 KHz
OFFIN      10500.00 Hz
POINT      32768
FREQU      27173.90 Hz
SCANS      508
ACQTM      1.2059 sec
PD         1.7940 sec
PMT        6.60 usec
IRNUC      1H
CTEMP      27.7 c
SILVNT     CSD6
EJREF      128.00 ppm
BF         2.00 Hz
RGAIN      18

```


W4082w871x4data\Kikuchi\WABC ring\SK-428.als

DFILE W4082w871x4data\Kik
CONVT Thu Nov 01 17:31:06
DATUM
OBNUC 1H
EXMOD NON
OBPRO 399.65 Mhz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQ 7993.60 Hz
SCANS 8
ACQTM 4.0993 sec
PD 2.9010 sec
PWI 6.40 usec
IRNUC 1H
CTEMP 24.1 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 18

W4082w871x4data\Kikuchi\WABC ring\SK-428-13C.als

DFILE W4082w871x4data\Kik
CONVT Thu Nov 01 18:35:02
DATUM
OBNUC 13C
EXMOD BOW
OBPRO 100.40 Mhz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQ 27173.90 Hz
SCANS 1223
ACQTM 1.2059 sec
PD 1.7940 sec
PWI 6.80 usec
IRNUC 1H
CTEMP 25.7 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 23

W082w871x\data\Wakamura\WNY-140.als

DFILE W082w871x\data\Wak
 COUNT Mon Oct 29 16:45:24
 DATIM 1H
 OBMUC NON
 EXMOD
 OBFRQ 399.65 MHz
 OBSET 124.00 KHz
 OFF IN 10500.00 Hz
 POINT 32768
 FREQ 7993.60 Hz
 SCANS 9
 ACQTM 4.0993 sec
 PD 2.9010 sec
 PW1 6.40 usec
 IRMUC 1H
 CTEMP 24.7 c
 SLVNT CDCL3
 EXREF 7.24 ppm
 BF 0.12 Hz
 RGAIN 12

W082w871x\data\Wakamura\WNY-140 (D13).als

DFILE W082w871x\data\Wak
 COUNT Mon Oct 29 17:54:34
 DATIM 13C
 OBMUC BOM
 EXMOD
 OBFRQ 100.40 MHz
 OBSET 125.00 KHz
 OFF IN 10500.00 Hz
 POINT 32768
 FREQ 27173.90 Hz
 SCANS 512
 ACQTM 1.2059 sec
 PD 1.7940 sec
 PW1 6.80 usec
 IRMUC 1H
 CTEMP 26.9 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 2.00 Hz
 RGAIN 24

WVD82w871x\data\Wkikuchi\ABC ring\SK-563.als

DFILE WVD82w871x\data\Wkik
 COMNT
 DATIM Wed Apr 09 14:31:48
 OBNUC 1H
 EXMOD NON
 OFRQ 399.65 MHz
 OBSE 124.00 KHz
 OFIN 10500.00 Hz
 POINT 32768
 FREQU 7993.60 Hz
 SCANS 8
 ACQTM 4.0993 sec
 PD 2.9010 sec
 PWI 6.40 usec
 IRNUC 1H
 CTMP 8.5 c
 SLVNT CDCL3
 EXREF 7.24 ppm
 BF 0.12 Hz
 RGAIN 18

WVD82w871x\data\Wkikuchi\ABC ring\SK-563-13C.als

DFILE WVD82w871x\data\Wkik
 COMNT
 DATIM Wed Apr 09 15:27:25
 OBNUC 13C
 EXMOD BCM
 OFRQ 100.40 MHz
 OBSE 125.00 KHz
 OFIN 10500.00 Hz
 POINT 32768
 FREQU 27173.90 Hz
 SCANS 818
 ACQTM 1.2059 sec
 PD 1.7940 sec
 PWI 6.80 usec
 IRNUC 1H
 CTMP 6.1 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 3.00 Hz
 RGAIN 24

W082w871x\data\Kikuchi\A-E ring\SK-572(c6d6).als

DFILE W082w871x\data\Kik
COMNT Thu Apr 17 12:03:48
DATIM 1H
OBNUC NON
EXMOD 399.65 MHz
OBFREQ 124.00 KHz
OBSET 10500.00 Hz
OBFIN 32768
POINT 7983.60 Hz
FREQ 8
SCANS 4.0993 sec
ACQTM 2.9010 sec
PD 6.40 usec
PWI 1H
IRNUC 24.5 c
CTEMP C6D6
SLVNT 7.15 ppm
EXREF 0.12 Hz
BF 16
RGAIN

W082w871x\data\Kikuchi\A-E ring\SK-572-13C(c6d6).als

DFILE W082w871x\data\Kik
COMNT Thu Apr 17 13:46:32
DATIM 13C
OBNUC BOM
EXMOD 100.40 MHz
OBFREQ 125.00 KHz
OBSET 10500.00 Hz
OBFIN 32768
POINT 27173.90 Hz
FREQ 1770
SCANS 1.2059 sec
ACQTM 1.7940 sec
PD 6.80 usec
PWI 1H
IRNUC 25.3 c
CTEMP C6D6
SLVNT 128.00 ppm
EXREF 2.00 Hz
BF 16
RGAIN

WV082w871x\data\Kikuchi\A-E ring\SK-584.als

DFILE WV082w871x\data\Kik
COMNT Thu Apr 24 12:41:10
DATIM 1H
OBNUC NON
EXMOD 399.65 MHz
OBFRQ 124.00 KHz
OBSET 10500.00 Hz
OBFIN 32768
POINT 7993.60 Hz
FREQU 8
SCANS 4.0993 sec
ACQTM 2.9010 sec
PD 6.40 usec
PWI 1H
IRNUC 25.2 c
CTEMP CDCL3
SLVNT 7.24 ppm
EXREF 0.12 Hz
BF 12
RGAIN

WV082w871x\data\Kikuchi\A-E ring\SK-584-13C.als

DFILE WV082w871x\data\Kik
COMNT Thu Apr 24 13:52:57
DATIM 13C
OBNUC BCM
EXMOD 100.40 MHz
OBFRQ 125.00 KHz
OBSET 10500.00 Hz
OBFIN 32768
POINT 27173.90 Hz
FREQU 1372
SCANS 1.2059 sec
ACQTM 1.7940 sec
PD 6.80 usec
PWI 1H
IRNUC 25.5 c
CTEMP CDCL3
SLVNT 77.00 ppm
EXREF 2.00 Hz
BF 24
RGAIN

WVD82w871x\data\Kikuchi\A-E ring\SK-586-591.als

DFILE WVD82w871x\data\Kik
 COMNT Sat May 10 16:03:18
 DATIM
 OBNUC 1H
 EXMOD NON
 OBFRQ 399.65 MHz
 OBSET 124.00 KHz
 OBF IN 10500.00 Hz
 POINT 32768
 FREQU 7993.60 Hz
 SCANS 32
 ACQTM 4.0993 sec
 PD 2.9010 sec
 PWI 6.40 usec
 IRNUC 1H
 CTMP 6.8 c
 SLVNT CDCL3
 EXREF 7.24 ppm
 BF 0.12 Hz
 RGAIN 15

WVD82w871x\data\Kikuchi\A-E ring\SK-586-591-13C.als

DFILE WVD82w871x\data\Kik
 COMNT Sat May 10 16:59:16
 DATIM
 OBNUC 13C
 EXMOD BCM
 OBFRQ 100.40 MHz
 OBSET 125.00 KHz
 OBF IN 10500.00 Hz
 POINT 32768
 FREQU 27173.90 Hz
 SCANS 1002
 ACQTM 1.2059 sec
 PD 1.7940 sec
 PWI 6.80 usec
 IRNUC 1H
 CTMP 8.7 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 2.00 Hz
 RGAIN 24

W082w871x\data\Kikuchi\A-E ring\SK-853-2.als

DFILE W082w871x\data\Kik
 COUNT Thu Nov 27 22:43:02
 DATIM 1H
 OBNUC NON
 EXMOD
 OBFRO 399.65 MHz
 OBSET 124.00 KHz
 OBFIN 10500.00 Hz
 POINT 32768
 FREQU 7993.60 Hz
 SCANS 64
 ACQTM 4.0993 sec
 PD 2.9010 sec
 PWI 6.40 usec
 IRNUC 1H
 CTMP 26.1 c
 SLVNT CDCL3
 EXREF 7.24 ppm
 BF 0.12 Hz
 RGAIN 17

W082w871x\data\Kikuchi\A-E ring\SK-853-13C.als

DFILE W082w871x\data\Kik
 COUNT Fri Nov 28 07:12:09
 DATIM 13C
 OBNUC BCM
 EXMOD
 OBFRO 100.40 MHz
 OBSET 125.00 KHz
 OBFIN 10500.00 Hz
 POINT 32768
 FREQU 27173.90 Hz
 SCANS 10000
 ACQTM 1.2059 sec
 PD 1.7940 sec
 PWI 6.80 usec
 IRNUC 1H
 CTMP 25.8 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 2.00 Hz
 RGAIN 24

Y4D82w871x\data\Kikuchi\A-E ring\SK-853 (c6d6).als

DFILE Y4D82w871x\data\Kik
 COMNT Fri Nov 28 12:28:07
 DATIM 1H
 ORNUC NON
 EXMOD 399.65 MHz
 OFRO 124.00 KHz
 OBSET 10500.00 Hz
 OFIN 32768
 POINT 7993.60 Hz
 FREQ 64
 SCANS 4.0993 sec
 ACQTM 2.9010 sec
 PD 6.40 usec
 PWI 1H
 IRNUC 26.2 c
 CTMP C6D6
 SLVNT 7.15 ppm
 EXREF 0.12 Hz
 BF 17
 RGAIN

Y4D82w871x\data\Kikuchi\A-E ring\SK-853 (c6d6)-13C.als

DFILE Y4D82w871x\data\Kik
 COMNT Fri Nov 28 18:46:45
 DATIM 13C
 ORNUC BCM
 EXMOD 100.40 MHz
 OFRO 125.00 KHz
 OBSET 10500.00 Hz
 OFIN 32768
 POINT 27173.90 Hz
 FREQ 7306
 SCANS 1.2058 sec
 ACQTM 1.7940 sec
 PD 6.80 usec
 PWI 1H
 IRNUC 26.8 c
 CTMP C6D6
 SLVNT 128.00 ppm
 EXREF 2.00 Hz
 BF 18
 RGAIN

W082w871x\data\Kikuchi\A-E ring\SK-854.als

DFILE W082w871x\data\Kik
 COMNT Sat Nov 29 16:27:52
 DATIM 1H
 OBNUC NON
 EXMOD
 OBFRQ 399.65 MHz
 OBSET 124.00 KHz
 OBFIN 10500.00 Hz
 POINT 32768
 FREQ 7993.60 Hz
 SCANS 64
 ACQTM 4.0993 sec
 PD 2.9010 sec
 PWI 6.40 usec
 IRNUC 1H
 CTMP 25.7 c
 SLVNT CDCL3
 EXREF 7.24 ppm
 BF 0.12 Hz
 RGAIN 15

W082w871x\data\Kikuchi\A-E ring\SK-854-13C.als

DFILE W082w871x\data\Kik
 COMNT Sun Nov 30 00:51:33
 DATIM 13C
 OBNUC BCM
 EXMOD
 OBFRQ 100.40 MHz
 OBSET 125.00 KHz
 OBFIN 10500.00 Hz
 POINT 32768
 FREQ 27173.90 Hz
 SCANS 10000
 ACQTM 1.2059 sec
 PD 1.7940 sec
 PWI 6.80 usec
 IRNUC 1H
 CTMP 26.7 c
 SLVNT CDCL3
 EXREF 77.00 ppm
 BF 2.00 Hz
 RGAIN 24

YVD82w871x\data\WKikuchi\A-E ring\SK-857+861.als

DFILE YVD82w871x\data\WKik
COMNT
DATIM Fri Dec 05 23:52:33
OBNUC 1H
EXMOD NON
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQ 7993.60 Hz
SCANS 16
AQTM 4.0993 sec
PD 2.9010 sec
PWI 6.40 usec
IRNUC 1H
CTEMP 25.3 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 18

YVD82w871x\data\WKikuchi\A-E ring\SK-857-130.als

DFILE YVD82w871x\data\WKik
COMNT
DATIM Tue Dec 02 07:48:38
OBNUC 13C
EXMOD BCM
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQ 27173.90 Hz
SCANS 13287
AQTM 1.2059 sec
PD 1.7940 sec
PWI 6.80 usec
IRNUC 1H
CTEMP 26.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24

W082w871x\data\Kikuchi\A-E ring\SK-862.als

DFILE W082w871x\data\Kik
COMNT Sat Dec 06 17:32:09
DATIM 1H
OBNUC NON
EXMOD
OBFRQ 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQ 7993.60 Hz
SCANS 32
ACQTM 4.0993 sec
PD 2.9010 sec
PWI 6.40 usec
IRNUC 1H
CTEMP 25.5 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 19

W082w871x\data\Kikuchi\A-E ring\SK-862-13C.als

DFILE W082w871x\data\Kik
COMNT Sun Dec 07 10:17:28
DATIM 13C
OBNUC BCM
EXMOD
OBFRQ 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQ 27173.90 Hz
SCANS 20000
ACQTM 1.2059 sec
PD 1.7940 sec
PWI 6.80 usec
IRNUC 1H
CTEMP 26.5 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 22

\\D82w871x\data\Kikuchi\A-E ring\SK-864.als

DFILE \\D82w871x\data\Kik
COMNT
DATIM Tue Dec 09 03:05:55
OBNUC 1H
EXMOD NON
OBPRO 399.65 MHz
OBSET 124.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQ 7993.60 Hz
SCANS 64
ACQTM 4.0993 sec
PD 2.9010 sec
PWI 6.40 usec
IRNUC 1H
CTEMP 26.1 c
SLVNT CDCL3
EXREF 7.24 ppm
BF 0.12 Hz
RGAIN 18

\\D82w871x\data\Kikuchi\A-E ring\SK-864-13C.als

DFILE \\D82w871x\data\Kik
COMNT
DATIM Tue Dec 09 12:02:51
OBNUC 13C
EXMOD BCM
OBPRO 100.40 MHz
OBSET 125.00 KHz
OBFIN 10500.00 Hz
POINT 32768
FREQ 27173.90 Hz
SCANS 10670
ACQTM 1.2059 sec
PD 1.7940 sec
PWI 6.80 usec
IRNUC 1H
CTEMP 26.8 c
SLVNT CDCL3
EXREF 77.00 ppm
BF 2.00 Hz
RGAIN 24

W082w871x\data\Kikuchi\A-E ring\SK-866 (c6d6).als

DFILE W082w871x\data\Kik
 COMNT Mon Feb 02 01:44:36
 DATIM 1H
 OBNUC NON
 EXMOD 399.65 MHz
 OBFRO 124.00 KHz
 OBSET 10500.00 Hz
 OBFIN 32768
 POINT 7993.60 Hz
 FREQ 64
 SCANS 4.0993 sec
 ACQTM 2.9010 sec
 PD 6.40 usec
 PWT 1H
 TRNUC 26.2 c
 CTMP C6D6
 SLVNT 7.15 ppm
 EXREF 0.12 Hz
 BF 21
 RGAIN

-NMR 0 8:

W082w871x\data\Kikuchi\A-E ring\SK-866-13C (c6d6).als

DFILE W082w871x\data\Kik
 COMNT Mon Feb 02 11:58:01
 DATIM 13C
 OBNUC BCM
 EXMOD 100.40 MHz
 OBFRO 125.00 KHz
 OBSET 10500.00 Hz
 OBFIN 32768
 POINT 27173.90 Hz
 FREQ 12178
 SCANS 1.2059 sec
 ACQTM 1.7940 sec
 PD 6.80 usec
 PWT 1H
 TRNUC 26.5 c
 CTMP C6D6
 SLVNT 128.00 ppm
 EXREF 2.00 Hz
 BF 18
 RGAIN

-NMR 0 8:

Chemical structure of Brevenal (1) is shown above the ¹H NMR spectrum. The structure is a complex polycyclic molecule with multiple stereocenters and functional groups, including a carboxylic acid and several hydroxyl groups.

The ¹H NMR spectrum (400 MHz, CDCl₃) displays the following peaks (ppm) and integrations:

Chemical Shift (ppm)	Integration
10.91	0.91
7.20	1.00
6.20	2.02
5.80	0.98
5.40	0.99
5.10	1.02
4.10	2.13
3.80	1.00
3.50	0.93
3.20	1.86
2.90	1.94
2.60	1.03
2.10	1.02
1.80	8.74
1.50	23.00
1.20	6.11
0.90	6.09

```

FILE          *WD82w871x\data\WK1
CONNT
DATIM         Tue Feb 03 02:29:00
GBNUC         1H
EXMCO         NON
GBSET         399.65 MHz
GBF IN        124.00 KHz
POINT         10500.00 Hz
FREGU         32768
SCANS         7993.60 Hz
ACQTM         128
PD            4.0993 sec
PW1           2.9010 sec
IRNUC         1H
CTEMP         25.5 c
SLVNT         C6D6
EXREF         7.15 ppm
BF            0.12 Hz
RGAIN         23

-NMR 0 8:

```

The ¹³C NMR spectrum of poly(2-vinylpyridine) displays a sharp, intense peak at approximately 123 ppm, corresponding to the pyridine ring carbons. The aliphatic region (25-75 ppm) shows a complex set of peaks for the polymer backbone and side chain, with a small peak at ~18 ppm likely representing the solvent (DMSO-d₆). The x-axis is labeled from 200 to 0 ppm.

```

FILE      14082w871xkdataYan
COMMT
DATE      Tue Feb 03 13:26:22
EPOCH     130
EPOCH     BCD
OBSID     100.40  MHz
OBSSET    125.00  KHz
OBS IN    10500.00 Hz
POINT     32768
FREQ      27173.80  Hz
SIGNALS   13000
ACQTH     1.2059  sec
PD        1.7840  sec
PWI       8.90   usec
PRNUC     TH
CTEMP     26.3  c
SNTYPE    OBSID
EXPRES    126.00  ppm
EXPRES    2.00   Hz
BF         18
RESAIN

```