**Evolution of a Total Synthesis of (–)-Kendomycin Exploiting a
Petasis-Ferrier Rearrangement/Ring-Closing Olefin Metathesis
Strategy**

SUPPORTING INFORMATION

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Reactions were carried out in oven- or flame-dried glassware under an argon atmosphere, unless otherwise noted. All solvents were reagent grade. Diethyl ether (Et₂O) and tetrahydrofuran (THF) were freshly distilled from sodium / benzophenone under argon. Reactions were magnetically stirred and monitored by thin layer chromatography (TLC) with 0.25 mm E. Merck pre-coated silica gel plates. Flash chromatography was performed with silica gel 60 (particle size 0.040 – 0.062 mm) supplied by Silicycle and Sorbent Technologies. Yields refer to chromatographically and spectroscopically pure compounds, unless otherwise stated. All melting points were obtained on a Thomas-Hoover apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Model 283B spectrophotometer or a Jasco Model FT/IR-480 Plus spectrometer. Proton and carbon-13 NMR spectra were recorded on a Bruker AMX-500 spectrometer. Chemical shifts are reported relative to chloroform (δ 7.26), acetone (δ 2.04), or benzene (δ 7.15) for ¹H NMR and chloroform (δ 77.0), acetone (δ 29.8), or benzene (δ 128.0) for ¹³C NMR. Optical rotations were measured on a Perkin-Elmer model 241 polarimeter. High-resolution mass spectra were measured at the University of Pennsylvania Mass Spectrometry Service Center on either a VG Micromass 70/70 H or VG ZAB-E spectrometer. X-ray intensity data were collected at the University of Pennsylvania on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo-K_α radiation (λ =0.71069 Å) at a temperature of 143K. The X-ray crystallographic information files (CIF) for compounds (+)-**30** and (–)-**2** are provided.

Aldehyde 6: A solution of 3,5-dimethoxy-2-hydroxy-4-methyl-benzaldehyde¹ (6.0 g, 30.5 mmol) in dichloromethane (60 mL) was treated with anhydrous potassium carbonate (6.9 g, 50 mmol) and then cooled to –10 °C. Bromine (3.5 mL, 67.3 mmol) was added dropwise via addition funnel, then the reaction mixture was warmed to 0 °C and stirred for 1 h at this temperature. The reaction was quenched with a 1:1 (v/v) mixture of 10% Na₂S₂O₃ and 10% NaHCO₃ aqueous solutions (60

¹ Kitahara, Y.; Nakahara, S.; Numata, R.; Kubo, A. *Chem. Pharm. Bull.* **1985**, 33, 2122.

mL), warmed to room temperature, and then the aqueous phase was extracted with dichloromethane (2 x 50 mL). The combined organic layers were washed with brine (60 mL), dried over Na₂SO₄, and then concentrated *in vacuo*. Flash chromatography purification (5% ethyl acetate in hexanes) afforded the corresponding bromide (8.2 g, 97% yield) as a yellow solid: m.p. 95 - 96 °C; IR (CHCl₃) 2998 (w), 2940 (w), 2844 (w), 1631 (s), 1443 (m), 1401 (m), 1299 (s), 1268 (m), 1105 (m), 998 (m), 956 (w), 760 (m) cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 12.07 (s, 1 H), 10.29 (s, 1 H), 3.87 (s, 3 H), 3.77 (s, 3 H), 2.31 (s, 3 H); ¹³C NMR (125 MHz, CDCl₃) δ 177.8, 154.2, 148.4, 146.3, 136.3, 115.9, 115.2, 60.5, 60.2, 11.0; high resolution mass spectrum (CI+) *m/z* 273.9834 [M⁺; calcd for C₁₀H₁₁O₄Br: 273.9840].

A solution of the above bromide (8.1 g, 29.0 mmol) in dimethylformamide (23 mL) was treated with diisopropylethylamine (9.7 mL, 58.8 mmol) and TBSCl (8.9 g, 58.8 mmol) at room temperature. The reaction mixture was stirred for 1.5 h, then quenched with water (50 mL). The aqueous phase was extracted with Et₂O (3 x 300 mL), and the combined organic layers were washed with brine, dried over Na₂SO₄, and then concentrated *in vacuo*. Flash chromatography purification (2% ethyl acetate in hexanes) afforded **6** (10.8 g, 94% yield) as a yellow waxy solid: m.p. 34-36 °C, IR (CHCl₃) 2933 (s), 2858 (s), 1699 (s), 1448 (s), 1389 (s), 1250 (m), 1099 (m) cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 10.42 (s, 1 H), 3.39 (s, 3 H), 3.32 (s, 3 H), 2.07 (s, 3 H), 1.02 (s, 9 H), 0.14 (s, 6 H); ¹³C NMR (125 MHz, CDCl₃) δ 189.5, 151.2, 150.5, 147.9, 132.6, 126.3, 114.1, 59.9, 59.7, 26.1, 18.7, 10.7, -4.2; high resolution mass spectrum (CI+) *m/z* 389.0783 [M⁺; calcd for C₁₆H₂₅O₄BrSi: 389.0800].

β-Hydroxyacid (+)-7: Trifluoromethanesulfonic acid (1.0 mL, 11.8 mmol) was added to a 1M solution of triethylborane (11.6 mL, 11.6 mmol) in hexanes at 0 °C. The reaction mixture was

warmed to 40 °C for 30 min and then cooled back to 0 °C. A pre-cooled (0 °C) solution of oxazolidinone (+)-**17**² (2.6 g, 11.2 mmol) in dichloromethane (30 mL) was added dropwise, followed by diisopropylethylamine (2.1 mL, 12.0 mmol), and after 30 min at 0 °C, the reaction mixture was cooled to –78 °C. Known aldehyde (+)-**16**³ (1.23 g, 11.0 mmol) in dichloromethane (20 mL) was added dropwise to the reaction mixture, which was stirred at –78 °C for 1 h, and then at 0 °C for an additional 2 h. The reaction was quenched at 0 °C with pH 7 buffer (18 mL). After 10 min, a 1:2 (v/v) mixture of 30% H₂O₂ and methanol was added, and the mixture was stirred for 1 h at 0 °C. Most of the solvent was evaporated *in vacuo*, and then the residue was extracted with EtOAc (3 x 150 mL). The combined organic extracts were washed with 5% aqueous NaHCO₃ and brine (200 mL each), dried over Na₂SO₄, and then concentrated *in vacuo*. Flash chromatography purification with ethyl acetate in hexanes (1:20 → 1:4) as eluent afforded the corresponding aldol adduct (3.2 g, 85% yield) as a colorless oil: $[\alpha]_D^{23} +61.1$ (c 0.825, CHCl₃); IR (CHCl₃) 3526 (br), 3065 (w), 2953 (s), 2865 (m), 1780 (s), 1684 (s), 1456 (w), 1387 (s), 1209 (s), 1110 (m) cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.33 (dd, *J* = 6.1, 8.2 Hz, 2 H), 7.28 (dd, *J* = 1.1, 8.2 Hz, 1 H), 7.22 (dd, *J* = 1.1, 6.1 Hz, 2 H), 5.76 (ddd, *J* = 7.6, 10.2, 17.5 Hz, 1 H), 4.96 (ddd, *J* = 1.2, 1.8, 17.5 Hz, 1 H), 4.92 (ddd, *J* = 0.8, 1.8, 10.2 Hz, 1 H), 4.69 (m, 1 H), 4.23-4.18 (m, 2 H), 3.94 (m, 1 H), 3.75 (dq, *J* = 2.6, 7.1 Hz, 1 H), 3.24 (dd, *J* = 3.3, 13.3 Hz, 1 H), 2.87 (d, *J* = 3.0 Hz, 1 H), 2.78 (dd, *J* = 9.4, 13.4 Hz, 1 H), 2.13 (m, 1 H), 1.60-1.45 (m, 2 H), 1.42-1.28 (m, 2 H), 1.25 (d, *J* = 7.1 Hz, 3 H), 1.00 (d, *J* = 6.7 Hz, 3 H); ¹³C NMR (125 MHz, CDCl₃) δ 177.5, 152.9, 144.2, 134.9, 129.4, 128.9, 127.5, 113.5, 71.4, 66.1, 55.1, 42.0, 37.7, 37.6, 32.7, 31.4, 20.2, 10.3; high resolution mass spectrum (ES+) *m/z* 368.1822 [(M+Na)⁺; calcd for C₂₀H₂₇O₄NNa: 368.1837].

A solution of the above adduct (3.0 g, 8.7 mmol) in a 5:1 (v/v) mixture of THF and water (20 mL) was treated with 30% H₂O₂ (5.2 mL) and LiOH (0.8 g, 19.1 mmol) at 0 °C. After stirring the reaction mixture for 1 h, a saturated aqueous Na₂SO₃ solution (17 mL) was slowly added, and the reaction was allowed to reach room temperature. The mixture was extracted with

² Evans, D. A.; Bartoli, J.; Shih, T. L. *J. Am. Chem. Soc.* **1981**, *103*, 2127.

³ Ireland, R. E.; Anderson, R. C.; Badoud, R.; Fitzsimmons, B. J.; McGarvey, G. J.; Thaisrivongs, S.; Wilcox, C. S. *J. Am. Chem. Soc.* **1983**, *105*, 1988. Barrett, A. G. M.; Carr, R. A. E.; Attwood, S. V.; Richardson, G.; Walshe, N. D. A. *J. Org. Chem.* **1986**, *51*, 4840.

dichloromethane (3 x 60 mL). The aqueous residue was diluted with water (40 mL), cooled to 0 °C, neutralized with 3N aqueous HCl to pH 2-3, and then extracted with EtOAc (3 x 100 mL). The combined organic extracts were washed with brine (200 mL), dried over Na₂SO₄, and then concentrated *in vacuo*. Flash chromatography purification with ethyl acetate in hexanes (1:1 → 100%) as eluent afforded acid (+)-**7** (1.5 g, 92% yield) as a colorless oil: $[\alpha]_{\text{D}}^{23} +10.5$ (c 1.425, C₆H₆); IR (CHCl₃) 2958 (br), 1716 (s), 1456 (w), 1253 (s), 1199 (m), 845 (s) cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 5.66 (ddd, *J* = 7.6, 10.2, 17.4 Hz, 1 H), 4.96 (apparent td, *J* = 1.0, 17.5 Hz, 1 H), 4.93 (apparent td, *J* = 1.0, 10.2 Hz, 1 H), 3.93 (m, 1 H), 2.58 (dq, *J* = 3.4, 7.1 Hz, 1 H), 2.14 (apparent septet, *J* = 6.7 Hz, 1 H), 1.58-1.23 (m, 4 H), 1.20 (d, *J* = 7.2 Hz, 3 H), 1.00 (d, *J* = 6.7 Hz, 3 H); ¹³C NMR (125 MHz, CDCl₃) δ 181.2, 144.1, 113.1, 71.6, 44.1, 37.6, 32.7, 31.2, 20.3, 10.3; high resolution mass spectrum (CI+) *m/z* 187.1329 [(M+H)⁺; calcd for C₁₀H₁₉O₃: 187.1328].

Alcohol (+)-19:⁴ *n*-BuLi (2.5M in hexanes, 38 mL, 95.4 mmol) was added to diisopropylamine (13.4 mL, 95.4 mmol) in THF (100 mL) at –78 °C, and the mixture was stirred for 1 h at the same temperature. A solution of the Evans oxazolidinone (+)-**17** (20.8 g, 89.2 mmol) in THF (40 mL) was then added dropwise *via* cannula at –78 °C, and the mixture was stirred for 30 min. Methallyliodide (34 g, 180 mmol) was added slowly, and the reaction mixture was stirred for 1 h at –78 °C, 2 h at –40 °C, and finally was allowed to warm to –15 °C. The mixture was quenched by addition of saturated aqueous NH₄Cl, and the organic solvent was removed *in vacuo*. The residue was diluted with water and extracted with dichloromethane (4 x 100 mL). The combined organic layers were dried over MgSO₄ and concentrated *in vacuo*. Flash chromatography with 15 % ethyl acetate in hexanes provided the corresponding alkylation product (21.1 g, 82% yield) as a yellow oil: $[\alpha]_{\text{D}}^{23} +60.2$ (c 1.65, CH₂Cl₂); IR (film) 3338 (w), 3074 (w), 2974 (w), 2935 (w), 1780 (s), 1696 (m), 1455 (w), 1387 (m), 1349 (m), 1237 (m), 1208 (m); ¹H NMR (500 MHz, CDCl₃) δ 7.33 (t, *J* = 7.2 Hz, 2 H), 7.27 (t, *J* = 7.2 Hz, 1 H), 7.21 (d, *J* = 6.9 Hz, 2 H), 4.81 (br s, 1 H), 4.76 (br s,

⁴ Lit. value for the known enantiomer: $[\alpha]_{\text{D}}^{23} -3.9$ (c 4.1, CH₂Cl₂). See: Organ, M. G.; Bilokin, Y. V.; Bratovanov, S. *J. Org. Chem.* **2002**, 67, 5176.

1 H), 4.68 (m, 1 H), 4.21-4.14 (m, 2 H), 4.03 (m, 1 H); 3.28 (dd, $J = 3.3, 13.4$ Hz, 1 H), 2.71 (dd, $J = 9.7, 13.4$ Hz, 1 H), 2.56 (dd, $J = 7.0, 13.8$ Hz, 1 H), 2.10 (dd, $J = 7.5, 13.8$ Hz, 1 H), 1.78 (s, 3 H), 1.16 (d, $J = 6.8$ Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3) δ 177.0, 153.1, 142.9, 135.4, 129.4, 128.9, 127.3, 112.5, 66.0, 55.4, 41.8, 38.0, 35.6, 22.3, 16.7; high resolution mass spectrum (CI+) m/z 287.1515 [M^+ ; calcd for $\text{C}_{17}\text{H}_{21}\text{NO}_3$: 287.1521].

MeOH (3.25 mL, 80.1 mmol) was added to a solution of the above material (20.0 g, 69.7 mmol) in Et_2O (300 mL) at 0 °C, followed by LiBH_4 (1.838 g, 80.1 mmol) in two portions. The reaction mixture was maintained at 0 °C for 45 min and at room temperature for 90 min. An aqueous solution of NaOH (11.2 g in 125 mL H_2O) was added, and the mixture was stirred until both phases were clear. The aqueous phase was further extracted with Et_2O (3 x 100 mL) and the combined organic layers were washed with brine and dried over MgSO_4 . Flash chromatography (pentane/ Et_2O 2:1) provided (+)-**19** (7.32 g, 92% yield) as a colorless liquid: $[\alpha]_{\text{D}}^{23} +5.5$ (c 0.86, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 4.77 (m, 1 H), 4.71 (m, 1 H), 3.54-3.43 (m, 2 H), 2.14-2.12 (m, 1 H), 1.84-1.89 (m, 2 H), 1.73 (s, 3 H), 1.39 (m, 1 H), 0.90 (d, $J = 6.5$ Hz, 3 H).

Alkylation product (–)-21: To a solution of alcohol (+)-**19** (2.9 g, 25 mmol) in $\text{Et}_2\text{O}/\text{CH}_3\text{CN}$ (150 mL, 1:4) at 0 °C was added PPh_3 (9.6 g, 36.8 mmol), imidazole (4.5 g, 71.1 mmol), and I_2 (9.0 g, 35.5 mmol) portionwise. The reaction mixture was stirred for 3 h at room temperature and then treated with pentane (300 mL). The mixture was filtered, the precipitate washed with pentane, and the filtrate concentrated *in vacuo* (0 °C). Flash chromatography (pentane) provided the corresponding iodide (4.7 g, 85% yield) as a colorless liquid: $[\alpha]_{\text{D}}^{23} -10.7$ (c 1.060, CHCl_3); IR (film) 3073 (m), 2962 (s), 2924 (s), 1648 (m), 1452 (m), 1375 (m), 1194 (m), 892 (s); ^1H NMR (500 MHz, CDCl_3) δ 4.80 (br s, 1 H), 4.74 (br s, 1 H), 3.25 (dd, $J = 6.1, 9.6$ Hz, 1 H), 3.12 (dd, $J = 6.1, 9.6$ Hz, 1 H), 2.10 (dd, $J = 7.1, 13.7$ Hz, 1 H), 1.89 (dd, $J = 7.1, 13.7$ Hz, 1 H), 1.70 (s, 3 H), 1.66 (m, 1 H), 0.98 (d, $J = 6.5$ Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3) δ 143.2, 112.5, 44.9, 32.5,

27.2, 22.6, 17.2; high resolution mass spectrum (CI+) m/z 224.0052 [M^+ ; calcd for $C_7H_{13}I$: 224.0826].

n-BuLi (2.5M in hexanes, 32 mL, 80 mmol) was added to a suspension of LiCl (10.7 g, 254.0 mmol, dried for 18 h at 130 °C under high vacuum) and diisopropylamine (12.0 mL, 86.0 mmol) in THF (55 mL) at –78 °C. The resulting suspension was warmed to 0 °C for 10 min. An ice-cooled solution of (*R,R*)-pseudoephedrine propionamide⁵ **20** (9.3 g, 42.0 mmol) in THF (120 mL) was added at –78 °C and the mixture was stirred for 1 h at –78 °C, 15 min at 0 °C, and 5 min at room temperature. To this solution was added the iodide described above (4.5 g, 20.0 mmol) at 0 °C, and the reaction mixture was stirred at room temperature for 14 h. The yellow reaction mixture was treated with half-saturated aqueous NH_4Cl (100 mL) and extracted with EtOAc (4 x 100 mL). The combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Flash chromatography (hexanes/EtOAc 3:2) yielded (–)-**21** (6.2 g, 98% yield) as a yellow oil: $[\alpha]_D^{23}$ –81.6 (*c* 1.000, C_6H_6); IR (film) 3384 (s), 3069 (w), 3029 (w), 2965 (m), 2929 (m), 1619 (s), 1453 (m), 1409 (m), 1375 (m); 1H NMR (4:1 rotamer ratio, the asterisk denotes the signals of the minor rotamer, 500 MHz, C_6D_6) δ 7.34 (d, J = 7.7 Hz, 2 H), 7.24* (d, J = 7.3 Hz, 2 H), 6.98-7.19 (m, 3 H); 4.92 (br s, 1 H), 4.86* (br s, 1 H), 4.83* (br s, 1 H), 4.80 (br s, 1 H), 4.73 (br s, 1 H), 4.56 (apparent t, J = 6.7 Hz, 1 H), 4.36 (br s, 1 H), 4.23* (m, 1 H), 3.98* (m, 1 H), 3.01* (m, 1 H), 2.99* (s, 3 H), 2.44 (m, 1 H), 2.36 (s, 3 H), 1.99* (m, 1 H), 1.92-1.80 (m, 1 H), 1.70 (m, 1 H), 1.57 (s, 3 H), 1.54 (m, 1 H), 1.27 (m, 1 H), 1.08* (d, J = 6.7 Hz, 3 H), 1.00 (d, J = 6.7 Hz, 3 H), 0.99 (d, J = 7.0 Hz, 3 H), 0.78 (d, J = 6.0 Hz, 3 H), 0.68* (d, J = 6.6 Hz, 3 H); ^{13}C NMR (the asterisk denotes the signals of the minor rotamer, 125 MHz, C_6D_6) δ 178.3, 171.1*, 144.7*, 143.7, 142.7*, 128.7*, 128.3, 127.4, 127.3*, 126.8, 112.1, 112.0*, 76.4, 75.3*, 59.0, 58.2, 46.5*, 46.4, 41.5, 34.4, 33.5*, 32.8*, 28.8, 26.9*, 22.4*, 22.2, 19.7, 18.1*, 17.4, 15.5*, 14.3 (two overlapped signals); high resolution mass spectrum (CI+) m/z 318.2444 [$(M+H)^+$; calcd for $C_{20}H_{32}NO_2$: 318.2433].

⁵ Myers, A. G.; Yang, B. H.; Chen, H.; McKinstry, L.; Kopecky, D. J.; Gleason, J. L. *J. Am. Chem. Soc.* **1997**, *119*, 6496.

Aldehyde (+)-11. Method A: To a slurry of LiAlH_4 (0.7 g, 18.1 mmol) in hexanes (42 mL, freshly distilled from CaH_2) at 0 °C was added *via* syringe pump EtOAc (2.6 mL, freshly distilled from CaH_2) over 1 h. The mixture was stirred at 0 °C for 45 min and then (–)-**21** (2.5 g, 7.9 mmol) in THF (27 mL) was added *via* cannula at –78 °C. The reaction mixture was stirred at 0 °C for 1.25 h and then transferred *via* pipette to ice-cold TFA (6 mL) in 1M HCl (100 mL). The mixture was stirred for 5 min at room temperature and then extracted with pentane- Et_2O (9:1, 3 x 100 mL). The organic layers were basified with saturated aqueous NaHCO_3 (50 mL), and the separated aqueous phase was extracted with pentane- Et_2O (9:1, 3 x 50 mL). The combined organic extracts were concentrated to one third of the volume *in vacuo* and filtered through a SiO_2 pad (pentane/ Et_2O 9:1). The solvent was removed *in vacuo* and flash chromatography (1.5% Et_2O in pentane as eluent) provided (+)-**11** (960 mg, 77% yield) as a colorless liquid.

Method B: *n*-BuLi (2.5M in hexanes, 65 mmol) was added to diisopropylamine (9.8 ml, 70 mmol) in THF (70 mL) at –78 °C. After stirring the mixture at –78 °C for 10 min and at 0 °C for 10 min, $\text{BH}_3\text{-NH}_3$ (2.3 g, 66.8 mmol) was added in one portion. After stirring the mixture at 0 °C for 15 min and then at room temperature for 15 min, (–)-**21** (5.3 g, 16.7 mmol) in THF (45 mL) was added *via* cannula at 0 °C and the mixture was stirred at room temperature for 3 h. The reaction was quenched by slow addition of aqueous HCl (3N, 150 mL) at 0 °C (gas evolution!). The aqueous phase was extracted with Et_2O (4 x 50 mL), and the combined organic layers were washed with aqueous HCl (3N, 25 mL), aqueous NaOH (2N, 25 mL), and brine (25 mL), and dried over Na_2SO_4 . After concentration *in vacuo*, purification by flash chromatography (pentane/ Et_2O 95:5 → 80:20) provided the C(19) alcohol (2.5 g, 97% yield) as a colorless liquid: $[\alpha]_{\text{D}}^{23}$ –31.8 (*c* 0.880, CHCl_3); IR (film) 3334 (s), 2959 (s), 2918 (s), 2873 (s), 1649 (w), 1457 (m), 1377 (m), 1073 (m), 807 (m); ^1H NMR (500 MHz, CDCl_3) δ 4.74 (br s, 1 H), 4.66 (br s, 1 H), 3.44 (m, 2 H), 1.97 (dd, J = 6.8, 13.6 Hz, 1 H), 1.87 (dd, J = 7.7, 13.6, Hz, 1 H), 1.73 (m, 1 H), 1.69 (s, 3 H), 1.50 (br s, 1 H), 1.34 (m, 1 H), 1.11 (m, 2 H), 0.90 (d, J = 6.7 Hz, 3 H), 0.84 (d, J = 6.5 Hz, 3

H); ^{13}C NMR (125 MHz, CDCl_3) δ 144.6, 111.5, 69.1, 52.1, 40.3, 33.3, 27.7, 22.2, 19.3, 16.2; high resolution mass spectrum (CI+) m/z 156.1513 [(M+H) $^+$; calcd for $\text{C}_{10}\text{H}_{21}\text{O}$: 156.1514].

To a solution of the above alcohol (1.6 g, 10.2 mmol) in $\text{CH}_2\text{Cl}_2/\text{DMSO}$ (1.5:1, 65 mL) was added Et_3N (14.2 mL, 100 mmol) and $\text{SO}_3\cdot\text{Py}$ (6.5 g, 40.9 mmol) at 0 °C. The reaction mixture was stirred at 0 °C for 1 h and quenched with saturated aqueous NaHCO_3 (50 mL). After extraction of the aqueous phase with Et_2O (3 x 50 mL), the combined organic layers were washed with aqueous NaHSO_4 (1M, 2 x 50 mL), saturated aqueous NaHCO_3 (1 x 100 mL), brine (2 x 100 mL), dried over Na_2SO_4 , and concentrated *in vacuo*. Flash chromatography provided aldehyde (+)-**11** (1.4 g, 89%) as a colorless liquid: $[\alpha]_{\text{D}}^{23} +6.3$ (c 1.240, CHCl_3); IR (film) 3074 (w), 2967 (s), 2929 (s), 1707 (s), 1649 (w), 1458 (m), 1377 (m), 888 (m); ^1H NMR (500 MHz, CDCl_3) δ 9.61 (d, J = 1.9 Hz, 1 H), 4.76 (br s, 1 H), 4.66 (br s, 1 H), 2.43 (m, 1 H), 2.00 (dd, J = 6.6, 13.5 Hz, 1 H) 1.90 (dd, J = 6.6, 13.5 Hz, 1 H), 1.70 (m, 1 H), 1.67 (s, 3 H), 1.48 (m, 1 H), 1.30 (m, 1 H), 1.08 (d, J = 7.0 Hz, 3 H), 0.87 (d, J = 6.6 Hz, 3 H); ^{13}C NMR (125 MHz, CDCl_3) δ 205.2, 144.0, 112.0, 46.3, 44.3, 37.3, 28.1, 22.1, 19.2, 13.3; high resolution mass spectrum (CI+) m/z 153.1272 [(M-H) $^+$; calcd for $\text{C}_{10}\text{H}_{17}\text{O}$: 153.1280].

Epoxides 5. Method A: To a solution of aldehyde (+)-**11** (100 mg, 0.65 mmol) and CH_2Br_2 (0.06 mL, 0.85 mmol) in THF (2 mL) was added dropwise 1.6M *n*-BuLi in hexanes (0.49 mL, 0.78 mmol) at -78 °C. The reaction mixture was then stirred for 18 h at room temperature and quenched by addition of saturated aqueous NH_4Cl (2 mL). The aqueous phase was extracted with CH_2Cl_2 (3 x 25 mL), and the combined organic layers were dried over Na_2SO_4 , and then concentrated *in vacuo*. Flash chromatography (hexanes/EtOAc 98:2) provided **5** (69 mg, 63% yield, 1.8:1 mixture of diastereomers) as a colorless liquid: IR (film) 3073 (w), 3047 (w), 2965 (s), 2819 (s), 1649 (m), 1458 (m), 1376 (m), 887 (m); ^1H NMR (The asterisk denotes the minor diastereomer, 500 MHz, CDCl_3) 4.74 (br s, 1 H), 4.65 (br s, 1 H), 2.66-2.75 (m, 2 H), 2.53 (dd, J = 2.8, 4.9 Hz, 1 H), 2.49* (dd, J = 2.9, 4.8 Hz, 1 H), 1.73-2.04 (m, 3 H), 1.73* (s, 3 H), 1.72 (s, 3

H), 1.12-1.44 (m, 3 H), 1.01 (d, $J = 6.6$ Hz, 3 H), 0.91* (d, $J = 6.9$ Hz, 3 H), 0.83* (d, $J = 6.5$ Hz, 3 H), 0.82 (d, $J = 6.5$ Hz, 3 H); ^{13}C NMR (The asterisk denotes the minor diastereomer, 125 MHz, CDCl_3) δ 144.7*, 144.5, 111.8, 111.7*, 57.6, 57.5*, 47.0, 46.7*, 46.6, 46.0*, 41.6*, 40.4, 33.9, 33.7*, 27.7, 22.3, 19.5, 19.4*, 15.4, 14.2*; high resolution mass spectrum (CI+) m/z 169.1583 [(M+H) $^+$; calcd for $\text{C}_{11}\text{H}_{21}\text{O}$: 169.1592].

Method B: To NaH (19.4 g, 0.49 mmol, 60% dispersion in mineral oil, washed twice with anhydrous hexane) was added DMSO (0.8 mL) at room temperature, and the mixture was stirred for 1 h. To the resulting suspension was added (*R*)-(dimethylamino)methylphenyloxosulfoxonium fluoroborate (133 mg, 0.49 mmol) in one portion (gas evolution!). The solution was stirred for 45 min at room temperature. A solution of (+)-**11** (50 mg, 0.32 mmol) in DMSO (1.3 mL) was added *via* cannula at room temperature and the reaction mixture was stirred for 12 h. After addition of water (1 mL), the aqueous phase was extracted with Et_2O (4 x 10 mL). The combined organic layers were washed with brine (2 x 15 mL), dried over Na_2SO_4 and concentrated *in vacuo*. The crude mixture was dissolved in EtOH (5 mL), treated with NaBH_4 (9.8 mg) at 0 °C for 30 min and then at room temperature for 15 min and subjected to the same work-up as described in method A. Preparative thin-layer chromatography (pentane/ Et_2O 9:1) provided epoxide **5** (34 mg, 62% yield) in a diastereomeric ratio of 3.7:1.

Alkyne (+)-10: To a stirred solution of KO^tBu (102 mg, 0.74 mmol) in THF (2 mL) was added dropwise dimethyl-diazomethylphosphonate⁶ (111 mg, 0.74 mmol) in THF (2 mL) at -78 °C. After stirring the reaction mixture at -78 °C for 15 min, aldehyde (+)-**11** (100 mg, 0.65 mmol) in THF (3 mL) was added *via* cannula over 15 min (gas evolution!). After 1 h at -78 °C, the reaction was quenched by addition of saturated aqueous NH_4Cl (2 mL), and the aqueous layer was extracted with pentane (3 x 15 mL). The combined organic layers were dried over Na_2SO_4 and

⁶ (a) Seyferth, D.; Marmor, R. S.; Hilbert, P. *J. Org. Chem.* **1971**, *36*, 1379. (b) Okada, N.; Nishimura, S. *J. Biol. Chem.* **1979**, *254*, 3061. (c) Gilbert, J. C.; Weerasooriya, U. *J. Org. Chem.* **1982**, *47*, 1837. (d) Ohira, S. *Synth. Comm.* **1989**, *19*, 561.

concentrated *in vacuo* (0 °C). Flash chromatography (pentane) provided (+)-**10** (75 mg, 77% yield) as a colorless liquid: $[\alpha]_{\text{D}}^{23} +17.8$ (c 1.100, CHCl₃); IR (film) 3311 (s), 2969 (s), 2922 (s), 1652 (m), 1456 (m), 1376 (m); ¹H NMR (500 MHz, CDCl₃) δ 4.74 (br s, 1 H), 4.66 (br s, 1 H), 2.53 (m, 1 H), 2.00 (dd, *J* = 5.2, 13.1 Hz, 1H), 2.03 (d, *J* = 2.5, 6.6 Hz, 1H), 1.84 (m, 1 H), 1.75 (dd, *J* = 9.0, 13.1 Hz, 1H), 1.70 (s, 3 H), 1.35 (m, 2 H), 1.17 (d, *J* = 6.9 Hz, 3 H), 0.86 (d, *J* = 6.5 Hz, 3 H); ¹³C NMR (125 MHz, CDCl₃) δ 144.6, 111.6, 89.4, 68.0, 45.4, 44.2, 28.6, 23.4, 22.1, 20.9, 19.8; high resolution mass spectrum (CI+) *m/z* 135.1157 [(M–Me)⁺; calcd for C₁₀H₁₅: 135.1174].

Dioxanone (+)-23: To a solution of aldehyde **6** (2.5 g, 6.4 mmol) and acid (+)-**7** (1.0 g, 5.4 mmol) in dichloromethane (55 mL) was added *i*-PrOTMS (3.8 mL, 21.5 mmol)⁷ and TMSOTf (0.4 mL, 2.1 mmol) at –78 °C, and the reaction mixture was stirred overnight at the same temperature. The reaction was quenched at –78 °C with pyridine (5 mL), and then concentrated *in vacuo*. Flash chromatography through silylated silica gel, with ethyl acetate in hexanes (1:19 → 1:1) as eluent, afforded dioxanone (+)-**23** (2.3 g, 77% yield) as a pale yellow oil: $[\alpha]_{\text{D}}^{23} +4.5$ (c 0.600, C₆H₆); IR (CHCl₃) 2932 (s), 1751 (s), 1456 (s), 1399 (s), 1332 (w), 1245 (s), 999 (m), 840 (s) cm^{–1}; ¹H NMR (500 MHz, C₆D₆) δ 6.99 (s, 1 H), 5.50 (ddd, *J* = 7.7, 10.5, 17.0 Hz, 1 H), 4.89 (ddd, *J* = 1.2, 1.8, 17.0 Hz, 1 H), 4.88 (ddd, *J* = 0.7, 1.0, 10.5 Hz, 1 H), 3.84 (td, *J* = 4.6, 9.2 Hz, 1 H), 3.40 (s, 3 H), 3.21 (s, 3 H), 2.56 (m, 1 H), 2.07 (s, 3 H), 1.91 (apparent septet, *J* = 7.1 Hz, 1 H), 1.62 (m, 1 H), 1.36 (d, *J* = 7.4 Hz, 3 H), 1.36 (m, 1 H), 1.23 (m, 1 H), 1.10 (m, 1 H), 1.03 (s, 9 H), 0.86 (d, *J* = 6.7 Hz, 3 H), 0.20 (s, 3 H), 0.16 (s, 3 H); ¹³C NMR (125 MHz, C₆D₆) δ 170.8, 151.9, 149.6, 145.2, 144.1, 129.1, 125.0, 113.4, 113.2, 97.9, 78.8, 59.8, 59.7, 39.7, 37.9, 32.2, 29.8, 26.2, 20.2, 18.7,

⁷ Kurihara, M.; Hakamata, W. *J. Org. Chem.* **2003**, 68, 3413.

12.1, 10.4, -4.3, -4.5; high resolution mass spectrum (ES+) m/z 579.1731 $[(M+Na)^+]$; calcd for $C_{26}H_{41}O_6BrSiNa$: 579.1753].

Enol-acetal **24:** Freshly prepared Cp_2TiMe_2 (3.3 g, 16.0 mmol) in THF (32 mL) was added to a solution of (+)-**23** (3.6 g, 6.4 mmol) in THF (13 mL), and then the reaction mixture was stirred at 60-63 °C (external temperature) for 24 h, *in the dark*. After cooling to room temperature, the reaction mixture was diluted with hexanes (250 mL) and the resulting slurry was filtered through Celite to remove the titanium salts. The filtrate was concentrated *in vacuo* and purified by flash chromatography through silylated silica gel, with 5% ethyl acetate in hexanes as eluent to afford enol-acetal **24** (3.0 g, 85% yield) as a pale yellow oil, which was immediately used in the next reaction: 1H NMR (500 MHz, C_6D_6) δ 6.53 (s, 1 H), 5.55 (ddd, J = 7.5, 10.2, 17.3 Hz, 1 H), 4.92 (ddd, J = 1.3, 1.7, 17.3 Hz, 1 H), 4.89 (ddd, J = 0.97, 1.7, 10.2 Hz, 1 H), 4.63 (s, 1 H), 4.24 (s, 1 H), 3.91 (m, 1 H), 3.45 (s, 3 H), 3.21 (s, 3 H), 2.16 (dq, J = 2.9, 7.0 Hz, 1 H), 2.10 (s, 3 H), 1.94 (apparent septet, J = 7.2 Hz, 1 H), 1.76 (m, 1 H), 1.50 (d, J = 7.0 Hz, 3 H), 1.45-1.25 (m, 2 H), 1.20 (m, 1 H), 1.08 (s, 9 H), 0.89 (d, J = 6.7 Hz, 3 H), 0.24 (s, 3 H), 0.21 (s, 3 H).

Pyranone (+)-25**:** To a solution of **24** (1.6 g, 2.9 mmol) in dichloromethane (36 mL) was added a 1M solution of Me_2AlCl (3.6 mL, 3.6 mmol) in dichloromethane, at -78 °C. The reaction mixture was stirred for 10 min, then was quenched at -78 °C with Et_3N (1.5 mL), followed by saturated

aqueous NaHCO₃ (20 mL). The reaction mixture was then diluted with dichloromethane (100 mL), allowed to warm to 0-5 °C, and neutralized with 1N aqueous HCl to pH 2. The aqueous phase was extracted with dichloromethane (3 x 100 mL), and the combined organic extracts were dried over Na₂SO₄, and then concentrated *in vacuo*. Flash chromatography purification with 5% ethyl acetate in hexanes as eluent afforded pyranone (+)-**25** (1.4 g, 85% yield) as a colorless oil: [α]_D²³ +30.8 (c 0.250, CHCl₃); IR (CHCl₃) 2931 (s), 1716 (s), 1457 (m), 1387 (m), 1259 (m), 1096 (m), 840 (s) cm⁻¹; ¹H NMR (500 MHz, C₆D₆) δ 5.56 (dd, *J* = 3.0, 12.3 Hz, 1 H), 5.53 (ddd, *J* = 7.5, 9.8, 17.2 Hz, 1 H), 4.89 (ddd, *J* = 1.1, 1.8, 17.2 Hz, 1 H), 4.88 (ddd, *J* = 0.7, 1.7, 9.8 Hz, 1 H), 3.78 (dd, *J* = 12.4, 14.4 Hz, 1 H), 3.69 (m, 1 H), 3.43 (s, 3 H), 3.25 (s, 3 H), 2.45 (m, 1 H), 2.35 (ddd, *J* = 1.2, 3.0, 14.4 Hz, 1 H), 2.10 (s, 3 H), 1.95 (apparent septet, *J* = 7.5 Hz, 1 H), 1.79 (m, 1 H), 1.40 (m, 1 H), 1.28 (m, 1 H), 1.23 (d, *J* = 7.2 Hz, 3 H), 1.15 (m, 1 H), 1.01 (s, 9 H), 0.87 (d, *J* = 6.7 Hz, 3 H), 0.19 (s, 3 H), 0.16 (s, 3 H); ¹³C NMR (125 MHz, C₆D₆) δ 208.8, 151.7, 149.7, 144.3, 144.0, 128.9, 126.6, 113.7, 112.9, 80.6, 74.0, 59.8, 59.6, 49.7, 42.0, 38.0, 32.9, 30.1, 26.2, 20.2, 18.7, 10.8, 10.4, -3.8, -4.4; high resolution mass spectrum (ES+) *m/z* 577.1989 [(M+Na)⁺; calcd for C₂₇H₄₃O₅BrSiNa: 577.1960].

α,α' -Dimethylketone (+)-26: A pre-cooled (−78 °C) solution of (+)-**25** (2.1 g, 3.8 mmol) in THF (20 mL) was added to a 1M solution of LHMDS (4.9 mL, 4.9 mmol) in hexanes at −78 °C. The reaction mixture was stirred for 30 min and then for an additional 1 h at −10 °C. A pre-cooled (−10 °C) solution of MeI (0.7 mL, 11.3 mmol) in THF (11 mL) was next added, and the reaction mixture was stirred for 3 h at −20 – 0 °C. The reaction was quenched with saturated aqueous NH₄Cl (2 mL), allowed to reach room temperature, and extracted with Et₂O (3 x 100 mL). The combined organic extracts were dried over Na₂SO₄, and then concentrated *in vacuo*. Flash chromatography

purification with 4% ethyl acetate in hexanes as eluent afforded (+)-**26** (1.5 g, 70% yield) as a colorless oil: $[\alpha]_{\text{D}}^{23} +41.0$ (c 1.585, CHCl_3); IR (CHCl_3) 2955 (s), 2932 (s), 2858 (m), 1712 (s), 1448 (s), 1387 (m), 1238 (m), 1086 (m), 840 (s) cm^{-1} ; ^1H NMR (500 MHz, C_6D_6) δ 5.55 (ddd, $J = 7.5, 10.3, 17.4$ Hz, 1 H), 5.15 (d, $J = 11.1$ Hz, 1 H), 4.91 (ddd, $J = 1.1, 1.7, 17.1$ Hz, 1 H), 4.89 (ddd, $J = 0.8, 1.7, 10.3$ Hz, 1 H), 3.82 (dq, $J = 6.6, 11.0$ Hz, 1 H), 3.71 (m, 1 H), 3.41 (s, 3 H), 3.28 (s, 3 H), 2.53 (dq, $J = 2.5, 7.2$ Hz, 1 H), 2.30 (s, 3 H), 1.98 (apparent septet, $J = 7.3$ Hz, 1 H), 1.80 (m, 1 H), 1.45 (m, 1 H), 1.29 (m, 1 H), 1.28 (d, $J = 7.2$ Hz, 3 H), 1.10 (m, 1 H), 1.01 (d, $J = 6.6$ Hz, 3 H), 1.00 (s, 9 H), 0.91 (d, $J = 6.6$ Hz, 3 H), 0.23 (s, 3 H), 0.11 (s, 3 H); ^{13}C NMR (125 MHz, C_6D_6) δ 211.5, 151.8, 149.8, 144.7, 144.3, 129.0, 126.6, 113.2, 112.9, 80.7, 79.4, 59.8, 59.5, 50.0, 43.5, 38.0, 33.0, 30.1, 26.2, 20.2, 18.6, 11.1, 10.4, 9.4, -3.7, -4.7; high resolution mass spectrum (ES+) m/z 591.2108 $[(\text{M}+\text{Na})^+]$; calcd for $\text{C}_{28}\text{H}_{45}\text{O}_5\text{BrSiNa}$: 591.2117].

Protected alcohol (+)-4: To a solution of (+)-**26** (1.5 g, 2.6 mmol) in ethanol (26 mL) at -78°C was slowly added NaBH_4 (0.2 g, 3.3 mmol), and then the reaction mixture was stirred for 2.5 h at the same temperature. The reaction mixture was quenched with saturated aqueous NH_4Cl (15 mL), allowed to reach room temperature, and extracted with chloroform (3 x 100 mL). The combined organic extracts were dried over Na_2SO_4 , and then concentrated *in vacuo* to give a crude mixture of the corresponding alcohols (5:1 dr). Flash chromatography separation with ethyl acetate-hexanes (1:49 $\rightarrow$ 1:9) as eluent afforded the pure C(7) alcohol (1.2 g, 81% yield) as a colorless oil: $[\alpha]_{\text{D}}^{23} +28.1$ (c 2.140, CHCl_3); IR (CHCl_3) 3329 (br), 2956 (s), 2930 (s), 2857 (m), 1446 (s), 1405 (s), 1384 (m), 1237 (m), 1106 (s), 1024 (m), 839 (s) cm^{-1} ; ^1H NMR (500 MHz, C_6D_6) δ 5.63 (ddd, $J = 7.5, 10.3, 17.4$ Hz, 1 H), 4.95 (apparent td, $J = 1.5, 17.3$ Hz, 1 H), 4.92

(apparent td, $J = 0.8, 10.3$ Hz, 1 H), 4.85 (d, $J = 10.6$ Hz, 1 H), 3.48 (m, 1 H), 3.41 (s, 3 H), 3.39 (m, 1 H), 3.33 (s, 3 H), 2.70 (m, 1 H), 2.15 (s, 3 H), 2.06 (apparent septet, $J = 7.3$ Hz, 1 H), 1.85 (m, 1 H), 1.77 (m, 1 H), 1.52 (m, 1 H), 1.43 (m, 1 H), 1.25 (d, $J = 6.9$ Hz, 3 H), 1.23 (m, 1 H), 1.08 (s, 9 H), 0.96 (dd, $J = 5.8, 10.1$ Hz, 1 H), 0.95 (d, $J = 6.7$ Hz, 3 H), 0.85 (d, $J = 6.5$ Hz, 3 H), 0.28 (s, 3 H), 0.17 (s, 3 H); ^{13}C NMR (125 MHz, C_6D_6) δ 151.7, 149.6, 144.7, 144.5, 129.7, 125.9, 113.6, 112.7, 80.2, 78.4, 78.0, 59.7, 59.5, 39.7, 38.1, 35.1, 33.4, 31.1, 26.3, 20.2, 18.7, 13.2, 10.4, 7.1, -3.6, -4.7; high resolution mass spectrum (ES+) m/z 593.2295 $[(\text{M}+\text{Na})^+]$; calcd for $\text{C}_{28}\text{H}_{47}\text{O}_5\text{BrSiNa}$: 593.2273].

To a solution of the above alcohol (1.2 g, 2.1 mmol) in dichloromethane (7 mL) at -10 °C was added dropwise a mixture of TBSOTf (0.73 mL, 3.2 mmol) and 2,6-lutidine (0.5 mL, 4.2 mmol) in dichloromethane (14 mL). The reaction mixture was stirred for 1 h at -10 °C, and then quenched with saturated aqueous NaHCO_3 (29 mL), allowed to reach room temperature, and extracted with Et_2O (3 x 100 mL). The combined organic extracts were dried over Na_2SO_4 , and then concentrated *in vacuo*. Flash chromatography purification with 3% ethyl acetate in hexanes as eluent afforded (+)-**4** (1.38 g, 95% yield) as a colorless oil: $[\alpha]_{\text{D}}^{23} +35.4$ (c 1.090, CHCl_3); IR (CHCl_3) 2956 (s), 2930 (s), 2857 (m), 1447 (m), 1404 (m), 1387 (m), 1251 (m), 1107 (s), 1075 (s), 1026 (m), 836 (s) cm^{-1} ; ^1H NMR (500 MHz, C_6D_6) δ 5.64 (ddd, $J = 7.5, 10.3, 17.5$ Hz, 1 H), 4.97 (apparent td, $J = 1.4, 17.5$ Hz, 1 H), 4.95 (d, $J = 10.6$ Hz, 1 H), 4.92 (ddd, $J = 0.7, 1.1, 10.3$ Hz, 1 H), 3.70 (dd, $J = 4.6, 9.9$ Hz, 1 H), 3.64 (ddd, $J = 2.0, 4.3, 8.5$ Hz, 1 H), 3.41 (s, 3 H), 3.35 (s, 3 H), 2.95 (qdd, $J = 6.6, 9.9, 10.6$ Hz, 1 H), 2.15 (s, 3 H), 2.09 (apparent septet, $J = 6.9$ Hz, 1 H), 1.98 (ddq, $J = 2.0, 4.6, 6.7$ Hz, 1 H), 1.91 (m, 1 H), 1.65 (m, 1 H), 1.46 (m, 1 H), 1.45 (d, $J = 6.9$ Hz, 3 H), 1.32 (m, 1 H), 1.10 (s, 9 H), 1.02 (s, 9 H), 0.97 (d, $J = 6.7$ Hz, 3 H), 0.91 (d, $J = 6.6$ Hz, 3 H), 0.30 (s, 3 H), 0.19 (s, 3 H), 0.15 (s, 6 H); ^{13}C NMR (125 MHz, C_6D_6) δ 151.8, 149.6, 144.7, 144.4, 129.8, 125.9, 113.6, 112.7, 80.3, 79.4, 78.4, 59.7, 59.4, 41.0, 38.1, 35.3, 33.6, 31.3, 26.3, 26.0, 20.2, 18.7, 18.4, 13.7, 10.4, 7.5, -3.6, -4.0, -4.6, -4.7; high resolution mass spectrum (ES+) m/z 707.3110 $[(\text{M}+\text{Na})^+]$; calcd for $\text{C}_{34}\text{H}_{61}\text{O}_5\text{BrSiNa}$: 707.3138].

Alcohols 27: To a solution of (+)-**4** (77 mg, 0.11 mmol) in THF (0.6 mL) was added *t*-BuLi (1.7M in pentane, 0.13 mL, 0.23 mmol) at $-78\text{ }^{\circ}\text{C}$, and then the reaction mixture was stirred for 5 min at the same temperature. A solution of **5** (38 mg, 0.23 mmol) in THF (0.2 mL) was then added, followed by $\text{BF}_3\cdot\text{OEt}_2$ (17 μL , 0.14 mmol), and the reaction mixture was stirred at $-78\text{ }^{\circ}\text{C}$ for an additional 3 h. The reaction mixture was quenched with MeOH (0.4 mL), then saturated aqueous NH_4Cl (0.4 mL), allowed to reach room temperature, and extracted with Et_2O (3 x 50 mL). The combined organic extracts were dried over Na_2SO_4 , and then concentrated *in vacuo*. Preparative thin-layer chromatography purification with 5% ethyl acetate in hexanes as eluent afforded the alcohols **27** (53 mg, 60% yield, 2:1 dr) as a colorless oil: IR (CHCl_3) 3481 (br), 2956 (s), 2930 (s), 2857 (s), 1454 (s), 1410 (m), 1386 (s), 1333 (m), 1253 (s), 1110 (s), 1071 (s), 1005 (m), 885 (m), 837 (s), 778 (m) cm^{-1} ; ^1H NMR (The asterisk denotes the minor diastereomer, 500 MHz, C_6D_6) δ 5.83* (ddd, $J = 7.7, 10.4, 17.6\text{ Hz}$, 1 H), 5.71 (ddd, $J = 7.6, 10.4, 17.8\text{ Hz}$, 1 H), 5.06* (apparent td, $J = 1.2, 17.6\text{ Hz}$, 1 H), 5.02 (apparent td, $J = 1.3, 17.3\text{ Hz}$, 1 H), 4.99* (br d, $J = 10.3\text{ Hz}$, 1 H), 4.97* (d, $J = 9.5\text{ Hz}$, 1 H), 4.96 (br d, $J = 10.4\text{ Hz}$, 1 H), 4.92 (d, $J = 10.8\text{ Hz}$, 1 H), 4.82* (br s, 1 H), 4.81 (apparent s, 2 H), 4.81* (overlapped, 1 H), 4.19 (d, $J = 5.6\text{ Hz}$, 1 H), 4.07 (m, 1 H), 4.07* (overlapped, 1 H), 3.93* (m, 1 H), 3.66 (dd, $J = 4.9, 10.0\text{ Hz}$, 1 H), 3.63* (dd, $J = 5.1, 10.3\text{ Hz}$, 1 H), 3.60* (apparent td, $J = 2.5, 9.2\text{ Hz}$, 1 H), 3.53 (ddd, $J = 1.8, 4.0, 8.9\text{ Hz}$, 1 H), 3.44* (s, 3 H), 3.40 (s, 3 H), 3.38* (s, 3 H), 3.27 (m, 1 H), 3.25 (s, 3 H), 3.20* (m, 1 H), 3.17 (dd, $J = 2.3, 13.4\text{ Hz}$, 1 H), 3.06* (dd, $J = 10.5, 13.3\text{ Hz}$, 1 H), 2.96 (dd, $J = 10.1, 13.5\text{ Hz}$, 1 H), 2.93* (br d, $J = 13.4\text{ Hz}$, 1 H), 2.26 (m, 1 H), 2.26* (overlapped, 1 H), 2.16* (s, 3 H), 2.13 (m, 1 H), 2.13* (overlapped, 1 H), 2.07 (s, 3 H), 2.03 (m, 1 H), 2.01-1.72 (m, 3 H), 1.71-1.47* (m, 4 H), 1.62* (s, 3 H), 1.60 (s, 3 H), 1.43-1.19 (m, 2 H), 1.24* (d, $J = 7.0\text{ Hz}$, 3 H), 1.21 (d, $J = 7.0\text{ Hz}$, 3 H), 1.14 (m, 1 H), 1.12

(d, $J = 6.7$ Hz, 3 H), 1.09* (d, $J = 6.8$ Hz, 3 H), 1.03 (s, 9 H), 1.01* (s, 9 H), 0.96 (d, $J = 6.4$ Hz, 3 H), 0.94 (d, $J = 7.0$ Hz, 3 H), 0.93 (s, 9 H), 0.92* (s, 9 H), 0.91* (d, $J = 6.7$ Hz, 3 H), 0.82 (d, $J = 6.7$ Hz, 3 H), 0.80* (d, $J = 6.6$ Hz, 3 H), 0.20 (s, 3 H), 0.20 (s, 3 H), 0.17* (s, 3 H), 0.05 (s, 3 H), 0.04 (s, 6 H), 0.04* (overlapped s, 3 H), 0.03* (s, 3 H), 0.02* (s, 3 H); ^{13}C NMR (125 MHz, C_6D_6) δ 153.7*, 152.9, 148.8*, 148.6, 144.9*, 144.8, 144.7, 144.6*, 143.8, 143.0*, 129.7, 129.3*, 129.2*, 129.1, 125.1*, 124.2, 113.0*, 112.9, 111.9, 81.3*, 80.7, 79.3, 78.9, 78.6*, 77.6, 76.7*, 59.7*, 59.6, 59.4, 59.3*, 47.7*, 47.6, 42.1, 40.9*, 40.8, 39.7*, 39.0*, 38.5*, 38.4*, 38.3, 38.2, 37.4, 34.0, 33.8, 33.6*, 32.1*, 31.3, 31.1*, 28.4*, 28.3, 26.4, 26.1, 26.0*, 22.4, 22.3*, 20.4*, 20.3, 19.5*, 19.1, 18.8, 18.7*, 18.4, 18.3*, 15.5*, 13.7, 13.5*, 12.6, 10.2*, 9.9, 7.6*, 7.5, -3.6, -3.8*, -4.0, -4.6, -4.7*, -4.8, -4.9*; high resolution mass spectrum (ES+) m/z 797.5520 $[(\text{M}+\text{Na})^+]$; calcd for $\text{C}_{45}\text{H}_{82}\text{O}_6\text{Si}_2\text{Na}$: 797.5547].

Ketone (+)-29: A solution of **27** (14.6 mg, 0.019 mmol), and pyridine (3 μL , 0.038 mmol) in dichloromethane (0.75 mL) was treated with Dess-Martin periodinane (32.2 mg, 0.076 mmol) at 0 $^{\circ}\text{C}$, and then the reaction mixture was stirred for 2 h at room temperature. The reaction mixture was quenched with a 1:1 (v/v) mixture of saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ and saturated aqueous NaHCO_3 (1 mL) and extracted with Et_2O (3 x 5 mL). The combined organic extracts were washed with water and brine (5 mL each), dried over Na_2SO_4 , and then concentrated *in vacuo*. Preparative thin-layer chromatography purification with 5% ethyl acetate in hexanes as eluent afforded (+)-**29** (12.8 mg, 88% yield) as a colorless oil: $[\alpha]_{\text{D}}^{23} +23.2$ (c 0.190, CHCl_3); IR (CHCl_3) 2928 (s), 2856 (m), 1709 (m), 1461 (m), 1410 (m), 1384 (m), 1253 (m), 1069 (s), 1005 (m), 889 (m), 836 (s), 775 (m) cm^{-1} ; ^1H NMR (500 MHz, C_6D_6) δ 5.69 (ddd, $J = 7.5, 10.3, 17.5$ Hz, 1 H),

5.00 (apparent td, $J = 1.4, 17.5$ Hz, 1 H), 4.96 (d, $J = 10.8$ Hz, 1 H), 4.95 (apparent td, $J = 1.1, 10.3$ Hz, 1 H), 4.81 (br s, 1 H), 4.76 (br s, 1 H), 4.41 (d, $J = 17.2$ Hz, 1 H), 4.28 (d, $J = 17.2$ Hz, 1 H), 3.70 (dd, $J = 4.7, 9.9$ Hz, 1 H), 3.60 (m, 1 H), 3.43 (s, 3 H), 3.34 (s, 3 H), 2.82 (m, 1 H), 2.19 (s, 3 H), 2.11 (apparent septet, $J = 6.7$ Hz, 1 H), 2.09 (m, 1 H), 2.04 (m, 1 H), 1.95 (m, 1 H), 1.82-1.65 (m, 5 H), 1.62 (s, 3 H), 1.50-1.25 (m, 6 H), 1.26 (d, $J = 6.9$ Hz, 3 H), 1.20 (d, $J = 6.8$ Hz, 3 H), 1.12 (s, 9 H), 1.00 (d, $J = 6.7$ Hz, 3 H), 0.99 (s, 9 H), 0.82 (d, $J = 6.2$ Hz, 3 H), 0.32 (s, 3 H), 0.19 (s, 3 H), 0.13 (s, 3 H), 0.12 (s, 3 H); ^{13}C NMR (125 MHz, C_6D_6) δ 203.5, 153.8, 149.9, 145.3, 145.1, 143.9, 129.5, 125.6, 124.8, 113.2, 112.4, 80.8, 79.2, 78.8, 59.6, 59.3, 46.7, 42.5, 41.5, 40.7, 40.5, 38.3, 38.1, 33.5, 31.3, 29.5, 28.2, 26.3, 25.9, 20.0, 19.0, 18.0, 17.6, 16.2, 13.4, 9.9, 7.2, -3.8, -5.4, -5.0 (2 overlapped signals); high resolution mass spectrum (ES+) m/z 795.5405 $[(\text{M}+\text{Na})^+]$; calcd for $\text{C}_{45}\text{H}_{80}\text{O}_6\text{Si}_2\text{Na}$: 795.5391].

Z Olefin (+)-30: A solution of **27** (0.6 g, 0.775 mmol) and second generation Grubbs' catalyst (66 mg, 0.08 mmol) in dichloromethane was stirred at 50-55 °C (external temperature) for 2 d. After cooling to room temperature, the reaction mixture was concentrated *in vacuo* and purified by flash chromatography with 3% ethyl acetate in hexanes as eluent to afford (+)-**30** (0.33 g, 57% yield) as a white solid: m.p. 187-188 °C; $[\alpha]_{\text{D}}^{23} +44.9$ (c 0.550, CHCl_3); IR (CHCl_3) 3508 (br), 2955 (s), 2929 (s), 2856 (m), 1461 (s), 1410 (m), 1387 (m), 1252 (s), 1074 (s), 1004 (m), 886 (m), 836 (s), 774 (m) cm^{-1} ; ^1H NMR (500 MHz, C_6D_6) δ 5.22 (d, $J = 9.7$ Hz, 1 H), 4.91 (d, $J = 10.5$ Hz, 1 H), 4.24 (s, 1 H), 4.06 (d, $J = 8.6$ Hz, 1 H), 3.67 (dd, $J = 4.8, 9.9$ Hz, 1 H), 3.57 (apparent td, $J = 2.2, 10.5$ Hz, 1 H), 3.52 (d, $J = 13.1$ Hz, 1 H), 3.44 (s, 3 H), 3.28 (s, 3 H), 2.83 (dd, $J = 8.8, 13.2$ Hz, 1 H), 2.60 (d, $J = 11.2$ Hz, 1 H), 2.33 (m, 1 H), 2.10 (s, 3 H), 2.06 (m, 1 H), 1.99-1.90 (m, 4 H), 1.82

(m, 1 H), 1.72 (br s, 3 H), 1.81 (m, 1 H), 1.58-1.52 (m, 2 H), 1.34 (m, 1 H), 1.32 (d, $J = 6.0$ Hz, 3 H), 1.30 (d, $J = 6.7$ Hz, 3 H), 1.21 (m, 1 H), 1.15 (d, $J = 6.5$ Hz, 3 H), 1.08 (s, 9 H), 1.07 (d, $J = 6.5$ Hz, 3 H), 1.02 (s, 9 H), 0.82 (d, $J = 6.6$ Hz, 3 H), 0.20 (s, 3 H), 0.14 (s, 3 H), 0.13 (s, 3 H), 0.10 (s, 3 H); ^{13}C NMR (125 MHz, C_6D_6) δ 152.4, 148.6, 143.6, 135.9, 133.0, 130.6, 129.4, 124.3, 80.1, 79.0, 78.1, 74.7, 60.1, 59.4, 43.6, 42.8, 41.3, 39.7, 39.3, 35.0, 34.9, 34.5, 34.4, 33.6, 26.4, 26.3, 26.0, 23.2, 20.6, 18.7, 18.4, 14.4, 13.4, 9.8, 7.4, -3.8, -3.9, -4.7, -4.9; high resolution mass spectrum (ES+) m/z 769.5228 [(M+Na) $^+$; calcd for $\text{C}_{43}\text{H}_{78}\text{O}_6\text{Si}_2\text{Na}$: 769.5234].

Alkyne (+)-31: To an argon purged (3 times) flask containing $\text{PdCl}_2(\text{PPh}_3)_2$ (4.5 mg, 5 mol%), CuI (0.73 mg, 3 mol%), and aldehyde **6** (50 mg, 0.128 mmol) was added degassed diisopropylamine (freeze-thawed 3 times) *via* cannula. Degassed alkyne (+)-**10** (37 μL , 0.192 mmol) was added quickly, and the reaction mixture was heated at 60 $^\circ\text{C}$ for 6.5 h. The solvent was removed *in vacuo* and the product was purified by flash chromatography (hexanes/EtOAc 97:3) to provide (+)-**31** (50 mg, 85% yield) as a yellow oil: $[\alpha]_{\text{D}}^{23} +23.6$ (c 1.500, C_6H_6); IR (film) 2965 (s), 2930 (s), 2858 (m), 1698 (s), 1647 (w), 1567 (w), 1458 (s), 1393 (s), 1284 (s), 1254 (s), 1101 (s); ^1H NMR (500 MHz, CDCl_3) δ 10.45 (s, 1 H), 4.84 (br s, 1 H), 4.80 (br s, 1 H), 3.85 (s, 3 H), 3.69 (s, 3 H), 2.85 (m, 1 H), 2.22 (s, 3 H), 2.14 (dd, $J = 5.5, 13.3$ Hz, 1 H), 1.92 (m, 1 H), 1.79 (dd, $J = 8.8, 13.3$ Hz, 1 H), 1.70 (s, 3 H), 1.54-1.44 (m, 2 H), 1.29 (d, $J = 6.9$ Hz, 3 H), 1.00 (s, 9 H), 0.90 (d, $J = 6.5$ Hz, 3 H), 0.16 (s, 6 H); ^{13}C NMR (125 MHz, CDCl_3) δ 185.2, 155.1, 150.4, 146.5, 144.5, 132.5, 127.1, 114.9, 111.6, 104.9, 73.6, 60.4, 60.1, 45.4, 44.3, 28.6, 25.8, 24.8, 22.2, 20.7, 19.7, 18.6, 10.2, -4.4 (two overlapped signals); high resolution mass spectrum (ES+) m/z 481.2735 [(M+Na) $^+$; calcd for $\text{C}_{27}\text{H}_{42}\text{NaO}_4\text{Si}$: 481.2750].

Dioxanone (+)-32: To a solution of hydroxyacid (+)-7 (20.5 mg, 0.11 mmol), (+)-31 (39 mg, 0.085 mmol), and isopropoxytrimethylsilane (60 μ L, 0.34 mmol) was added TMSOTf (0.15 μ L, 0.85 μ mol) at -78 $^{\circ}$ C and the reaction mixture was stirred next at -20 $^{\circ}$ C for 12 h. After addition of a few drops of Et_3N , the solvent was removed *in vacuo*. The product was purified by flash chromatography (silylated SiO_2 , 0.5% EtOAc in hexanes) to provide (+)-32 (14 mg, 26% yield) as a yellow oil: $[\alpha]_{\text{D}}^{23} +34.6$ (c 1.85, C_6D_6); IR (film) 2956 (s), 2930 (s), 2858 (m), 2360 (w), 1746 (s), 1464 (s), 1398 (s), 1374 (m), 1279 (m), 1250 (s), 1073 (s), 1003 (s); ^1H NMR (500 MHz, C_6D_6) δ 7.02 (s, 1 H), 5.61 (m, 1 H), 5.02 (m, 2 H), 4.91 (br s, 1 H), 4.88 (br s, 1 H), 3.97 (m, 1 H), 3.74 (s, 3 H), 3.33 (s, 3 H), 2.91 (m, 1 H), 2.71 (m, 1 H), 2.22 (s, 3 H), 2.21 (m, 1 H), 2.16-2.02 (m, 2 H), 1.87-1.65 (m, 3 H), 1.75 (s, 3 H), 1.53 (d, $J = 7.3$ Hz, 3 H); 1.42 (d, $J = 6.8$ Hz, 3 H), 1.55-1.33 (m, 3 H), 1.28 (m, 1 H), 1.15 (s, 9 H), 1.03 (d, $J = 6.5$ Hz, 3 H), 0.98 (d, $J = 6.7$ Hz, 3 H), 0.30 (s, 6 H); ^{13}C NMR (125 MHz, C_6D_6) δ 171.3, 157.4, 150.2, 145.1, 144.6, 144.2, 128.7, 127.1, 114.6, 113.6, 112.4, 104.0, 98.0, 78.8, 76.3, 60.3, 60.2, 46.3, 45.3, 40.2, 38.2, 32.7, 29.7, 29.3, 26.7, 25.9, 22.7, 21.5, 20.7, 20.4, 19.2, 12.4, 10.3, -3.8, -3.9; high resolution mass spectrum (ES+) m/z 649.3918 $[(\text{M}+\text{Na})^+]$; calcd for $\text{C}_{37}\text{H}_{58}\text{NaO}_6\text{Si}$: 649.3900].

Enol-acetal (+)-33: To a solution of (+)-**32** (53 mg, 0.085 mmol) in THF (1 mL) was added Cp_2TiMe_2 (0.5M in hexanes, 0.254 mmol) and the mixture was heated at 60 °C for 12 h. The reaction mixture was concentrated *in vacuo* and the product was purified by flash chromatography (silylated SiO_2 , hexanes/EtOAc 4:1) to yield (+)-**33** (46 mg, 87% yield) as a yellow oil: $[\alpha]_{\text{D}}^{23} +57.9$ (c 0.72, C_6H_6); IR (film) 2958 (s), 2930 (s), 2858 (m), 1651 (m), 1576 (w), 1460 (s), 1395 (s), 1258 (s), 1078 (m), 999 (s), 840 (s); ^1H NMR (500 MHz, C_6D_6) δ 6.49 (s, 1 H), 5.59 (ddd, $J = 2.7, 9.2, 17.3$ Hz, 1 H), 4.95 (m, 2 H), 4.83 (br s, 1 H), 4.80 (br s, 1 H), 4.66 (s, 1 H), 4.28 (s, 1 H), 3.94 (m, 1 H), 3.68 (s, 3 H), 3.26 (s, 3 H), 2.86 (m, 1 H), 2.19 (m, 2 H), 2.17 (s, 3 H), 2.04 (m, 2 H), 1.78 (m, 2 H), 1.75 (s, 3 H), 1.63 (m, 1 H), 1.59 (d, $J = 7.0$ Hz, 3 H), 1.48-1.35 (m, 3 H), 1.29 (d, $J = 6.8$ Hz, 3 H), 1.21 (m, 1 H), 1.11 (s, 9 H), 0.94 (d, $J = 6.6$ Hz, 3 H), 0.93 (d, $J = 6.7$ Hz, 3 H), 0.28 (s, 3 H), 0.25 (s, 3 H); ^{13}C NMR (125 MHz, C_6D_6) δ 164.2, 156.9, 149.8, 144.8, 144.5, 143.6, 128.6, 126.9, 114.2, 113.0, 112.0, 102.0, 98.8, 92.6, 87.8, 76.6, 59.9, 59.7, 46.0, 44.8, 38.1, 37.6, 32.5, 30.3, 28.9, 26.5, 25.6, 22.3, 21.0, 20.2, 20.0, 18.9, 14.6, 10.0, -4.1, -4.2; high resolution mass spectrum (ES+) m/z 647.4122 $[(\text{M}+\text{Na})^+]$; calcd for $\text{C}_{38}\text{H}_{60}\text{NaO}_5\text{Si}$: 647.4107].

Pyranone (+)-34: A solution of (+)-**33** (17 mg, 0.027 mmol) in CH_2Cl_2 (0.5 mL) was treated with Me_2AlCl (1M in hexanes, 0.033 mmol) at -78 °C and then stirred for 20 min at -78 °C. The reaction mixture was quenched by addition of Et_3N (0.15 mL) at -78 °C, followed by saturated aqueous NaHCO_3 solution (2 mL). The mixture was extracted with CH_2Cl_2 (3 x 10 mL) and the combined organic layers were dried over Na_2SO_4 and concentrated *in vacuo*. Preparative thin-

layer chromatography (hexanes/EtOAc 4:1) yielded (+)-**34** (10.5 mg, 62% yield) as a yellow oil: $[\alpha]_{\text{D}}^{23} +40.9$ (*c* 0.52, C₆H₆); IR (film) 2958 (s), 2929 (s), 2858 (m), 1714 (s), 1457 (s), 1368 (m), 1259 (m), 1073 (m), 1004 (m), 838 (s); ¹H NMR (500 MHz, C₆D₆) δ 5.57 (ddd, *J* = 2.9, 9.0, 17.1 Hz, 1 H), 5.51 (dd, *J* = 2.7, 12.1 Hz, 1 H), 4.92 (m, 2 H), 4.84 (br s, 1 H), 4.80 (br s, 1 H), 4.09 (dd, *J* = 12.3, 14.2 Hz, 1 H), 3.76 (m, 1 H), 3.65 (s, 3 H), 3.30 (s, 3 H), 2.76 (m, 1 H), 2.50-2.46 (m, 2 H), 2.16 (s, 3 H), 2.1 (dd, *J* = 6.7, 13.2 Hz, 1 H), 1.97 (m, 2 H), 1.79 (m, 2 H), 1.67 (s, 3 H), 1.62-1.40 (m, 2 H), 1.39 (d, *J* = 7.0 Hz, 3 H), 1.48-1.35 (m, 2 H), 1.29 (d, *J* = 6.8 Hz, 3 H), 1.21 (m, 1 H), 1.07 (s, 9 H), 0.91 (d, *J* = 6.6 Hz, 3 H), 0.90 (d, *J* = 6.7 Hz, 3 H), 0.21 (s, 3 H), 0.20 (s, 3 H); ¹³C NMR (125 MHz, C₆D₆) δ 209.5, 157.1, 150.2, 144.5, 144.4, 142.8, 130.9, 128.7, 125.8, 113.7, 113.0, 112.1, 103.6, 80.7, 76.8, 73.8, 59.9, 59.7, 49.7, 46.0, 44.7, 43.1, 38.1, 30.5, 28.9, 26.3, 25.5, 22.3, 20.8, 20.2, 19.6, 18.8, 11.0, 9.9, -3.9, -4.3; high resolution mass spectrum (ES+) *m/z* 647.4079 [(*M*+Na)⁺; calcd for C₃₈H₆₀NaO₅Si: 647.4108].

Z Olefin (+)-36: To a solution of (+)-**32** (30 mg, 0.048 mmol) in CH₂Cl₂ (15 mL) was added Grubbs' second generation catalyst (12 mg, 30 mol%) and the reaction mixture was heated at reflux for 45 h. Two additional portions of catalyst (2 x 8 mg, 20 mol% each) were added during the reaction. The solvent was removed *in vacuo* and the product was purified twice by flash chromatography (silylated SiO₂, hexanes/EtOAc 24:1) to provide (+)-**36** (10 mg, 35% yield) as a yellow oil: $[\alpha]_{\text{D}}^{23} +43.7$ (*c* 0.400, CH₂Cl₂); IR (film) 2957 (s), 2929 (s), 2857 (m), 1763 (s), 1728 (m), 1462 (s), 1392 (s), 1279 (m), 1251 (m), 1206 (m), 1068 (m), 1002 (m), 837 (s); ¹H NMR (500 MHz, C₆D₆) δ 7.32 (s, 1 H), 5.06 (d, *J* = 10.0 Hz, 1 H), 4.10 (m, 1 H), 3.63 (s, 3 H), 3.30 (s, 3 H), 3.11 (m, 1 H), 2.73 (m, 1 H), 2.48 (d, *J* = 13.2 Hz, 1 H), 2.37 (m, 1 H), 2.15 (s, 3 H), 2.08 (m, 1 H),

1.88 (m, 1 H), 1.72 (s, 3 H), 1.49-1.30 (m, 5 H), 1.29 (d, $J = 6.8$ Hz, 3 H), 1.10 (d, $J = 6.8$ Hz, 3 H), 1.03 (s, 9 H), 0.98 (d, $J = 6.5$ Hz, 3 H), 0.95 (d, $J = 6.5$ Hz, 3 H), 0.93 (m, 1 H), 0.19 (s, 6 H); ^{13}C NMR (125 MHz, C_6D_6) δ 171.9, 157.2, 150.1, 143.9, 133.8, 133.6, 128.7, 126.6, 115.2, 104.0, 93.7, 77.0, 76.7, 60.3, 46.7, 39.6, 38.6, 34.2, 33.4, 33.1, 32.6, 30.6, 26.6, 26.3, 25.7, 23.5, 22.0, 20.9, 19.2, 11.2, 10.3, -3.9, -4.1; high resolution mass spectrum (ES+) m/z 621.3576 [(M+Na) $^+$]; calcd for $\text{C}_{35}\text{H}_{54}\text{NaO}_6\text{Si}$: 621.3587].

C(19)-TES ether (–)-39: To a solution of (+)-**30** (43 mg, 0.058 mmol) in pyridine (0.5 mL) at 0 °C was added DMAP (14 mg, 0.116 mmol), TESOTf (65 μL , 0.288 mmol), and 2,6-lutidine (67 μL , 0.576 mmol), then the reaction mixture was allowed to reach room temperature and stirred for 1 h. The reaction was quenched with saturated aqueous NaHCO_3 (0.5 mL), and extracted with Et_2O (3 x 10 mL). The combined organic extracts were dried over Na_2SO_4 , and then concentrated *in vacuo*. Preparative thin-layer chromatography purification with 3% ethyl acetate in hexanes as eluent afforded (–)-**39** (44 mg, 89% yield) as a colorless oil: $[\alpha]_{\text{D}}^{23}$ -20.3 (c 0.630, CHCl_3); IR (CHCl_3) 2950 (s), 1457 (s), 1407 (m), 1376 (s), 1253 (s), 1106 (s), 1068 (s), 1006 (s), 883 (m), 837 (s), 775 (m) cm^{-1} ; ^1H NMR (500 MHz, C_6D_6) δ 5.20 (d, $J = 8.9$ Hz, 1 H), 5.06 (d, $J = 10.4$ Hz, 1 H), 4.66 (dd, $J = 2.1, 7.5$ Hz, 1 H), 3.99 (dd, $J = 9.4, 14.7$ Hz, 1 H), 3.87 (d, $J = 8.5$ Hz, 1 H), 3.72 (dd, $J = 4.6, 10.1$ Hz, 1 H), 3.47 (s, 3 H), 3.14 (s, 3 H), 2.70 (d, $J = 14.3$ Hz, 1 H), 2.62 (s, 1 H), 2.55 (m, 1 H), 2.39 (apparent t, $J = 4.8$ Hz, 1 H), 2.24 (s, 3 H), 2.19 (m, 1 H), 2.08 (m, 1 H), 1.91 (d, $J = 10.7$ Hz, 1 H), 1.87 (m, 1 H), 1.80 (m, 1 H), 1.76 (s, 3 H), 1.67 (apparent t, $J = 13.0$ Hz, 1 H), 1.55 (apparent t, $J = 13.0$ Hz, 1 H), 1.46 (d, $J = 7.0$ Hz, 3 H), 1.40-1.31 (m, 3 H), 1.12 (s, 9 H), 1.07 (s, 9 H), 1.06 (d, $J = 7.2$ Hz, 3 H), 0.99 (d, $J = 7.5$ Hz, 3 H), 0.98 (apparent t, $J = 7.9$

Hz, 9 H), 0.97 (d, $J = 6.5$ Hz, 3 H), 0.96 (d, $J = 7.6$ Hz, 3 H), 0.71-0.53 (m, 6 H), 0.33 (s, 3 H), 0.20 (s, 3 H), 0.19 (s, 3 H), 0.02 (s, 3 H); ^{13}C NMR (125 MHz, C_6D_6) δ 154.1, 148.5, 143.0, 135.1, 132.3, 130.7, 129.7, 123.7, 79.4, 79.3, 77.5, 77.2, 59.3, 58.8, 43.2, 41.6, 38.3, 37.9, 36.8, 32.8, 31.1, 30.6, 30.5, 27.9, 26.4, 26.1, 23.6, 21.3, 19.7, 18.8, 18.4, 17.2, 14.3, 9.9, 8.4, 7.2, 5.2, -3.7, -3.9, -4.5, -4.9; high resolution mass spectrum (ES+) m/z 883.6021 $[(\text{M}+\text{Na})^+]$; calcd for $\text{C}_{49}\text{H}_{92}\text{O}_6\text{Si}_3\text{Na}$: 883.6098].

Monomesylate (+)-40: A solution of (–)-**39** (84 mg, 0.098 mmol) and pyridine (0.3 mL) in THF (2 mL) was treated with OsO_4 (28 mg, 0.11 mmol) at 0 °C, and then the reaction mixture was stirred for 5 h at the same temperature. The reaction mixture was quenched with a 1:1 (v/v) mixture of saturated aqueous NaHSO_3 and saturated aqueous NaHCO_3 (1 mL), and MeOH (0.5 mL), allowed to reach room temperature, stirred for an additional 1 h, and then extracted with Et_2O (3 x 25 mL). The combined organic extracts were washed with saturated aqueous NaHCO_3 and brine (15 mL each), dried over Na_2SO_4 , and then concentrated *in vacuo*. Preparative thin-layer chromatography purification with ethyl acetate-hexanes (1:4) as eluent afforded the C(13,14) diol (69 mg, 78% yield) as a colorless oil: $[\alpha]_{\text{D}}^{23} +35.3$ (c 1.780, C_6H_6); IR (CHCl_3) 3386 (br), 2950 (s), 1458 (s), 1380 (s), 1253 (s), 1068 (s), 1006 (s), 883 (m), 840 (s), 779 (m) cm^{-1} ; ^1H NMR (500 MHz, C_6D_6) δ 4.92 (d, $J = 10.5$ Hz, 1 H), 4.47 (apparent quintet, $J = 3.5$ Hz, 1 H), 3.65-3.54 (m, 3 H), 3.43 (s, 3 H), 3.42 (s, 3 H), 3.14 (apparent t, $J = 5.7$ Hz, 1 H), 2.98 (dd, $J = 3.8, 13.2$ Hz, 1 H), 2.22 (apparent d, $J = 4.4$ Hz, 1 H), 2.17 (s, 3 H), 2.15 (m, 1 H), 1.99 (m, 1 H), 1.90-1.83 (m, 2 H), 1.80 (dd, $J = 2.1, 14.5$ Hz, 1 H), 1.78-1.67 (m, 3 H), 1.59 (m, 1 H), 1.54-1.46 (m, 2 H), 1.35 (m, 1

H), 2.55 (d, $J = 6.9$ Hz, 3 H), 1.24 (s, 3 H), 2.32 (d, $J = 6.5$ Hz, 3 H), 1.12 (s, 9 H), 1.11 (apparent t, $J = 7.9$ Hz, 9 H), 1.05 (d, $J = 6.8$ Hz, 3 H), 0.98 (s, 9 H), 0.96 (d, $J = 6.4$ Hz, 3 H), 0.78 (apparent q, $J = 7.9$ Hz, 6 H), 0.71 (d, $J = 6.6$ Hz, 3 H), 0.31 (s, 3 H), 0.21 (s, 3 H), 0.10 (s, 3 H), 0.09 (s, 3 H); ^{13}C NMR (125 MHz, C_6D_6) δ 154.6, 148.9, 143.5, 129.6, 129.5, 124.4, 82.6, 81.1, 79.3, 79.2, 78.8, 75.5, 59.8, 59.4, 42.7, 42.6, 41.8, 39.1, 37.5, 36.9, 35.4, 32.9, 32.0, 28.5, 26.9, 26.5, 26.0, 22.4, 18.7, 18.3, 17.6, 16.9, 13.6, 10.0, 7.7, 7.6, 5.9, -3.8, -4.0, -4.4, -4.7; high resolution mass spectrum (ES+) m/z 917.6132 [(M+Na) $^+$; calcd for $\text{C}_{49}\text{H}_{94}\text{O}_8\text{Si}_3\text{Na}$: 917.6154].

To a solution of the above diol (56 mg, 0.063 mmol) and pyridine (0.5 mL) in dichloromethane (1.5 mL) at 0 °C was added MsCl (98 μL , 1.26 mmol), and then the reaction mixture was stirred at 0 °C for 2 h. The reaction was quenched with saturated aqueous NaHCO_3 (0.5 mL) and extracted with Et_2O (3 x 25 mL). The combined organic extracts were washed with brine (15 mL), dried over Na_2SO_4 , and then concentrated *in vacuo*. Preparative thin-layer chromatography purification with 30% ethyl acetate in hexanes as eluent afforded (+)-**40** (58 mg, 95% yield) as a colorless oil: $[\alpha]_{\text{D}}^{23} +21.1$ (c 1.880, C_6H_6); IR (CHCl_3) 3532 (br), 2950 (s), 2275 (w), 1735 (w), 1457 (s), 1338 (s), 1253 (s), 1172 (m), 1068 (s), 1006 (s), 921 (m), 840 (s), 779 (m) cm^{-1} ; ^1H NMR (500 MHz, C_6D_6) δ 4.97 (d, $J = 10.4$ Hz, 1 H), 4.68 (d, $J = 2.9$ Hz, 1 H), 4.67 (m, 1 H), 3.63-3.55 (m, 3 H), 3.45 (s, 3 H), 3.41 (s, 3 H), 3.18 (dd, $J = 4.3, 13.5$ Hz, 1 H), 2.29 (s, 3 H), 2.26 (m, 1 H), 2.20 (s, 3 H), 2.21-2.06 (m, 2 H), 1.94 (m, 1 H), 1.90 (dd, $J = 2.5, 14.4$ Hz, 1 H), 1.83 (m, 1 H), 1.70-1.40 (m, 6 H), 1.31 (d, $J = 7.0$ Hz, 3 H), 1.28 (m, 1 H), 1.24 (s, 3 H), 2.21 (d, $J = 6.7$ Hz, 3 H), 1.14 (s, 9 H), 1.09 (apparent t, $J = 7.9$ Hz, 9 H), 1.02 (m, 1 H), 1.00 (s, 9 H), 0.99 (d, $J = 6.8$ Hz, 3 H), 0.87 (d, $J = 6.2$ Hz, 3 H), 0.78 (d, $J = 6.5$ Hz, 3 H), 0.74 (m, 6 H), 0.32 (s, 3 H), 0.28 (s, 3 H), 0.13 (s, 6 H); ^{13}C NMR (125 MHz, C_6D_6) δ 154.4, 148.9, 143.5, 129.7, 129.4, 124.3, 91.4, 79.9, 79.3, 79.1, 77.5, 75.9, 59.8, 59.3, 47.4, 41.9, 40.3, 38.8, 38.0, 37.9, 34.6, 34.2, 33.0, 32.2, 27.9, 26.6, 26.4, 26.0, 22.1, 18.7, 18.4, 16.5, 16.4, 13.6, 9.9, 7.7, 7.4, 5.7, -3.7, -4.0, -4.5, -4.7; high resolution mass spectrum (ES+) m/z 995.5943 [(M+Na) $^+$; calcd for $\text{C}_{50}\text{H}_{96}\text{O}_{10}\text{Si}_3\text{Na}$: 995.5929].

Trans epoxide (+)-41: To a solution of (+)-**40** (69 mg, 0.071 mmol) in THF (2 mL) was added 40 % BnNMe₃OH in MeOH (63 μ L, 0.142 mmol) at 0 °C, and then the reaction mixture was stirred at 0 °C for 1 h. The reaction mixture was then concentrated and directly purified by preparative thin-layer chromatography with ethyl acetate-hexanes (1:4) as eluent, to afford (+)-**41** (45 mg, 84% yield) as a colorless oil: $[\alpha]_D^{23}$ +65.8 (c 0.975, C₆H₆); IR (CHCl₃) 3340 (br), 2931 (s), 1697 (w), 1458 (s), 1376 (m), 1253 (m), 1079 (s), 841 (s), 736 (w) cm⁻¹; ¹H NMR (500 MHz, C₆D₆) δ 8.28 (s, 1 H), 4.69 (d, *J* = 10.5 Hz, 1 H), 3.99 (m, 1 H), 3.93 (s, 3 H), 3.69 (m, 1 H), 3.67 (dd, *J* = 4.5, 10.3 Hz, 1 H), 3.32 (m, 1 H), 3.31 (s, 3 H), 2.79 (dd, *J* = 4.3, 13.2 Hz, 1 H), 2.70 (d, *J* = 6.1 Hz, 1 H), 2.47 (m, 1 H), 2.28 (s, 3 H), 1.82 (m, 1 H), 1.75-1.53 (m, 5 H), 1.47 (m, 1 H), 1.37 (m, 1 H), 1.26 (d, *J* = 6.6 Hz, 3 H), 1.15 (s, 3 H), 1.14 (apparent t, *J* = 8.0 Hz, 9 H), 1.13 (d, *J* = 6.3 Hz, 3 H), 0.98 (s, 9 H), 0.92 (d, *J* = 6.7 Hz, 3 H), 0.90 (d, *J* = 7.1 Hz, 3 H), 0.80 (m, 6 H), 0.77 (d, *J* = 6.7 Hz, 3 H), 0.72 (m, 1 H), 0.13 (s, 6 H), 0.09 (s, 3 H); ¹³C NMR (125 MHz, C₆D₆) δ 151.0, 147.5, 146.9, 124.9, 123.7, 123.0, 83.2, 82.7, 78.3, 74.3, 65.8, 60.2, 59.9, 59.3, 45.2, 42.3, 42.0, 37.1, 34.9, 34.7, 33.9, 33.8, 31.7, 31.5, 28.5, 25.9, 21.5, 19.7, 18.3, 15.3, 14.4, 10.1, 7.4, 6.7, 6.1, -4.1, -4.8; high resolution mass spectrum (ES+) *m/z* 785.5213 [(M+Na)⁺; calcd for C₄₃H₇₈O₇Si₂Na: 785.5138].

***E* Olefin (–)-42:** *n*-BuLi (2.5M in hexanes, 0.4 mL, 1.0 mmol) was added to a solution of WCl_6 (198 mg, 0.5 mmol) in THF (5 mL), at $-78\text{ }^\circ\text{C}$, and then the reaction mixture was allowed to warm to room temperature and stirred for 20 min. A solution of (+)-41 (44 mg, 0.058 mmol) in THF (0.6 mL) was treated next with the $[\text{W}^{4+}]$ solution described above (1.25 mL), at $0\text{ }^\circ\text{C}$, and then the reaction mixture was allowed to warm to room temperature and stirred for an additional 40 min. The reaction was quenched at $0\text{ }^\circ\text{C}$ with saturated aqueous NaHCO_3 (1 mL), and the mixture was extracted with Et_2O (3 x 25 mL). The combined organic layers were dried over Na_2SO_4 , and then concentrated *in vacuo*. Preparative thin-layer chromatography with 15% ethyl acetate in hexanes as eluent afforded (–)-42 (31 mg, 71% yield) as a colorless oil, contaminated with 10-12% of an unidentified isomer. (–)-42: $[\alpha]_{\text{D}}^{23} -310.4$ (*c* 0.710, C_6H_6); IR (CHCl_3) 2953 (s), 2360 (w), 1739 (w), 1458 (m), 1378 (m), 1254 (m), 1109 (s), 1074 (s), 1010 (s), 839 (m); ^1H NMR⁸ (500 MHz, C_6D_6) δ 4.94 (d, *J* = 9.5 Hz, 1 H), 4.60 (d, *J* = 10.5 Hz, 1 H), 4.17 (dd, *J* = 5.0, 10.8 Hz, 1 H), 3.73 (dd, *J* = 4.6, 10.0 Hz, 1 H), 3.62 (m, 1 H), 3.58 (s, 3 H), 3.50 (m, 1 H), 3.35 (s, 3 H), 2.85 (m, 1 H), 2.83 (dd, *J* = 5.1, 13.7 Hz, 1 H), 2.29 (m, 1 H), 2.21 (s, 3 H), 2.00 (m, 1 H), 1.89 (m, 1 H), 1.86 (br d, *J* = 14.7 Hz, 1 H), 1.72-1.49 (m, 5 H), 1.47 (s, 3 H), 1.37-1.26 (m, 2 H), 1.28 (d, *J* = 7.0 Hz, 3 H), 1.26 (d, *J* = 6.5 Hz, 3 H), 1.17 (apparent t, *J* = 7.9 Hz, 9 H), 1.09 (m, 1 H), 1.01 (s, 9 H), 0.97 (d, *J* = 6.4 Hz, 3 H), 0.96 (d, *J* = 6.6 Hz, 3 H), 0.84 (apparent q, *J* = 7.9 Hz, 6 H), 0.77 (d, *J* = 6.6 Hz, 3 H), 0.15 (s, 3 H), 0.14 (s, 3 H); ^{13}C NMR (125 MHz, C_6D_6) δ 151.1, 146.4, 146.3, 132.7, 132.0, 125.5, 124.6, 123.1, 83.6, 82.5, 79.3, 76.2, 60.4, 59.8, 44.4, 41.5, 40.2, 36.2, 35.9, 34.3, 33.4, 31.8, 31.0, 30.1, 28.6, 26.0, 22.1, 19.9, 19.4, 18.3, 14.5, 10.2, 7.7, 6.8, 6.2, -4.0, -4.7; high resolution mass spectrum (ES+) *m/z* 769.5246 $[(\text{M}+\text{Na})^+]$; calcd for $\text{C}_{43}\text{H}_{78}\text{O}_6\text{Si}_2\text{Na}$: 769.5234].

⁸ A signal for the C(4) phenol was not observed in the ^1H NMR spectrum recorded in C_6D_6 .

Alcohol (–)-43: A solution of (–)-42 (15 mg, 0.020 mmol) and pyridinium *p*-toluenesulfonate (1 mg, 0.004 mmol) in MeOH (1.5 mL) was stirred for 6 h at 0 °C. The reaction mixture was quenched with saturated aqueous NaHCO₃ (0.5 mL) and extracted with Et₂O (3 x 25 mL). The combined organic extracts were washed with brine (15 mL), dried over Na₂SO₄, and then concentrated *in vacuo*. Preparative thin-layer chromatography purification with ethyl acetate-hexanes (1:9) as eluent afforded (–)-43 (12 mg, 95% yield) as a colorless oil: $[\alpha]_{\text{D}}^{23}$ –6.6 (*c* 0.500, C₆H₆); IR (CHCl₃) 2930 (s), 2857 (s), 1737 (w), 1458 (s), 1383 (m), 1255 (m), 1104 (s), 999 (m), 883 (w), 837 (m); ¹H NMR⁹ (500 MHz, C₆D₆) δ 5.50 (s, 1 H), 5.12 (d, *J* = 10.8 Hz, 1 H), 4.95 (d, *J* = 9.7 Hz, 1 H), 4.30 (m, 1 H), 3.62 (dd, *J* = 5.0, 9.8 Hz, 1 H), 3.61 (m, 1 H), 3.40 (br d, *J* = 10.9 Hz, 1 H), 3.23 (s, 3 H), 3.12 (dd, *J* = 2.4, 13.2 Hz, 1 H), 3.02 (s, 3 H), 2.83 (dd, *J* = 5.1, 13.1 Hz, 1 H), 2.32 (m, 1 H), 2.24 (m, 1 H), 2.14 (br d, *J* = 14.4 Hz, 1 H), 1.97 (s, 3 H), 1.91 (m, 1 H), 1.89 (m, 1 H), 1.83–1.75 (m, 2 H), 1.74 (dd, *J* = 8.7, 14.3 Hz, 1 H), 1.65 (s, 3 H), 1.62 (m, 1 H), 1.49 (m, 1 H), 1.29 (d, *J* = 6.4 Hz, 3 H), 1.24 (m, 1 H), 1.18 (d, *J* = 6.9 Hz, 3 H), 1.17 (d, *J* = 6.7 Hz, 3 H), 1.02 (s, 9 H), 1.01 (d, *J* = 6.6 Hz, 3 H), 0.95 (m, 1 H), 0.89 (d, *J* = 6.6 Hz, 3 H), 0.12 (s, 3 H), 0.11 (s, 3 H); ¹³C NMR (125 MHz, C₆D₆) δ 151.3, 144.5, 143.8, 133.0, 132.4, 129.4, 124.5, 122.7, 80.9, 79.0, 78.3, 76.8, 59.9, 59.6, 46.9, 41.8, 41.5, 38.2, 38.1, 36.7, 34.9, 33.5, 33.2, 29.9, 26.1, 22.1, 21.9, 20.5, 18.3, 14.3, 13.3, 9.8, 7.4, –4.0, –4.6; high resolution mass spectrum (ES+) *m/z* 655.4402 [(M+Na)⁺; calcd for C₃₇H₆₄O₆SiNa: 655.4369].

⁹ A signal for the C(4) phenol was not observed in the ¹H NMR spectrum recorded in C₆D₆.

o-Quinone (–)-2: A solution of (–)-**43** (12 mg, 0.019 mmol) and pyridine (6 μ L, 0.072 mmol) in dichloromethane (0.7 mL) was treated with Dess-Martin periodinane (32.2 mg, 0.076 mmol) at 0 $^{\circ}$ C, and then the reaction mixture was allowed to warm to room temperature and stirred for an additional 45 min, in the dark. The reaction mixture was quenched with a 1:1 (v/v) mixture of saturated aqueous $\text{Na}_2\text{S}_2\text{O}_3$ and saturated aqueous NaHCO_3 (0.5 mL), and extracted with Et_2O (3 x 5 mL). The combined organic extracts were washed with brine (2 mL), dried over Na_2SO_4 , and then concentrated *in vacuo*. Preparative thin-layer chromatography purification with ethyl acetate-hexanes (1:4) as eluent afforded (–)-**2** (8 mg, 69% yield) as a deep purple solid: m.p. 193–196 $^{\circ}$ C; $[\alpha]_{\text{D}}^{23}$ -38.4 (c 0.320, MeCN); IR (CHCl_3) 2924 (s), 2358 (w), 1717 (m), 1656 (m), 1584 (m), 1516 (m), 1456 (m), 1378 (m), 1328 (m), 1254 (m), 1083 (s), 835 (m); ^1H NMR (500 MHz, C_6D_6) δ 4.79 (d, J = 9.9 Hz, 1 H), 4.68 (d, J = 10.6 Hz, 1 H), 4.24 (d, J = 17.2 Hz, 1 H), 3.32 (dd, J = 4.9, 9.9 Hz, 1 H), 3.26 (s, 3 H), 3.20 (br d, J = 17.6 Hz, 1 H), 3.11 (d, J = 10.5 Hz, 1 H), 2.42 (m, 1 H), 2.12 (m, 1 H), 2.10 (dd, J = 4.0, 13.4 Hz, 1 H), 1.96 (dd, J = 4.1, 13.4 Hz, 1 H), 1.82 (m, 1 H), 1.69 (s, 3 H), 1.68–1.53 (m, 4 H), 1.59 (s, 3 H), 1.40 (ddd, J = 3.5, 11.5, 13.8 Hz, 1 H), 1.37–1.16 (m, 2 H), 1.12 (m, 1 H), 1.01 (d, J = 7.5 Hz, 3 H), 1.00 (s, 9 H), 0.99 (d, J = 6.9 Hz, 3 H), 0.90 (d, J = 6.5 Hz, 3 H), 0.88 (d, J = 6.9 Hz, 3 H), 0.76 (d, J = 6.5 Hz, 3 H), 0.06 (s, 3 H), 0.05 (s, 3 H); ^{13}C NMR (125 MHz, C_6D_6) δ 180.1, 179.2, 166.1, 161.1, 147.2, 136.8, 135.7, 129.8, 120.6, 80.4, 77.6, 76.5, 61.6, 46.4, 42.6, 42.1, 41.3, 39.3, 38.9, 35.8, 33.8, 33.3, 28.7, 26.0, 22.0, 20.5, 18.7, 18.2, 15.2, 14.2, 9.9, 7.5, -4.1 , -4.7 ; high resolution mass spectrum (ES+) m/z 637.3886 [(M+Na) $^{+}$; calcd for $\text{C}_{36}\text{H}_{58}\text{O}_6\text{SiNa}$: 637.3900].

Synthetic (-)-Kendomycin (1): A solution of (-)-**2** (3.5 mg, 5.7 μ mol) in acetonitrile (1 mL) was treated with 48% aqueous HF (50 μ L) at 0 $^{\circ}$ C, in a plastic vial, and then the reaction mixture was allowed to warm to room temperature and stirred for an additional 20 min, in the dark. A color change was observed from orange to yellow. The reaction mixture was quenched with saturated aqueous NaHCO_3 (0.5 mL), and extracted with EtOAc (3 x 5 mL). The combined organic extracts were washed with saturated aqueous NaHCO_3 and brine (3 mL each), dried over Na_2SO_4 , and then concentrated *in vacuo*. Flash chromatography purification with ethyl acetate-hexanes (1:4 $\rightarrow$ 1:1) as eluent afforded (-)-**1** (1.1 mg, 40% yield) as a yellow solid: m.p. 235-238 $^{\circ}$ C; $[\alpha]_{\text{D}}^{23} -79.3$ (c 0.135, MeOH);¹⁰ IR (CHCl_3) 3336 (br), 2922 (s), 1667 (w), 1612 (s), 1574 (s), 1457 (m), 1378 (m), 1329 (s), 1252 (w), 1097 (s); ^1H NMR (500 MHz, Acetone- d_6) δ 8.05 (br s, 1 H), 7.19 (s, 1 H), 6.46 (br s, 1 H), 4.64 (d, J = 10.0 Hz, 1 H), 4.35 (d, J = 10.4 Hz, 1 H), 3.86 (d, J = 4.6 Hz, 1 H), 3.56 (td, J = 4.6, 10.3 Hz, 1 H), 3.53 (ddd, J = 1.2, 2.4, 11.0 Hz, 1 H), 2.41 (m, 1 H), 2.36 (m, 1 H), 2.12 (br d, J = 17.0 Hz, 1 H), 1.96 (m, 1 H), 1.88 (m, 1 H), 1.84 (s, 3 H), 1.71 (m, 1 H), 1.67 (m, 1 H), 1.63 (m, 1 H), 1.61 (s, 3 H), 1.57 (m, 2 H), 1.45 (ddd, J = 3.1, 11.1, 13.3 Hz, 1 H), 1.33 (m, 1 H), 1.25 (m, 1 H), 0.95 (d, J = 7.0 Hz, 3 H), 0.94 (d, J = 6.5 Hz, 3 H), 0.89 (d, J = 6.6 Hz, 3 H), 0.87 (d, J = 6.6 Hz, 3 H), 0.71 (d, J = 6.8 Hz, 3 H); ^{13}C NMR (125 MHz, Acetone- d_6) δ 182.1, 168.6, 146.8, 141.4, 132.1, 130.2, 129.9, 119.1, 111.0, 104.2, 78.7, 77.7, 76.3, 46.1, 41.5, 40.8, 39.7, 38.1, 35.8, 33.6, 33.4, 26.5, 22.7, 19.9, 19.7, 13.3, 12.6, 7.6, 7.2; high resolution mass spectrum (ES+) m/z 487.3042 [(M+H) $^+$; calcd for $\text{C}_{29}\text{H}_{43}\text{O}_6\text{Si}$: 487.3059].

¹⁰ Lit. values: m.p. 258 $^{\circ}$ C; $[\alpha]_{\text{D}}^{20} -80.0$ (c 2.710, MeOH): Bode, H. B.; Zeeck, A. *J. Chem. Soc., Perkin Trans. 1* **2000**, 323.