Supporting Information:

Total Synthesis of Callipeltoside A

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General Information: ^1H - and ^{13}C -NMR were taken in CDCl_3 at 400 MHz and 75.0 MHz respectively unless specified otherwise. Chemical shifts are reported in parts per million using the solvent resonance internal standard (chloroform, 7.24 and 77.0 ppm, unless specified otherwise). Data are reported as follows: chemical shift, multiplicity (app = apparent, par obsc = partially obscured, ovrlp = overlapping, s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad, abq = ab quartet), coupling constant, and integration. Ratios of diastereomers (dr) were determined by ^1H -NMR (400 MHz) operating at a signal/noise ratio of >200:1. Infrared Resonance spectra were recorded on a Nicolet Impact 400 FT-IR spectrometer. Optical rotations were recorded on an AUTOPOL III digital polarimeter at 589 nm, and are reported as $[\alpha]_D$ (concentration in grams/100 mL solvent). High resolution mass spectra (HRMS) were obtained on a Figan MAT-90 spectrometer on the Boston University Mass Spectrometry Laboratory. Tetrahydrofuran (THF), ethyl ether (Et_2O), methylene chloride (CH_2Cl_2), benzene, methanol and acetonitrile were purified by passage through a column of activated alumina under positive pressure of argon. All other reagents were used as supplied. All reactions were carried out in oven-dried glassware under an argon atmosphere unless otherwise noted. Analytical thin layer chromatography was performed on Whatman Reagent silica gel 60 Å plates. Flash chromatography was performed on E. Merck silica gel 230-400 mesh.

(2R, 3S, 4R, 5S)-[5-Benzyloxy methyl-3-(dimethyl-phenyl-silanyl)-4-methyl-tetrahydro-furan-2-yl]-acetic acid methyl ester 10. To a solution of aldehyde (4.2 g, 28.1 mmol) in CH_2Cl_2 (0.4 M, 70 mL) at -78°C , was added 3.3 mL of SnCl_4 (28.1 mmol). After stirring for 10 min., a solution of (*S*)-crotylsilane **9** in CH_2Cl_2 (5 mL) was added dropwise to the resulting mixture. After stirring at -78°C for 12 h, the reaction was quenched by the addition of water (50 mL). The organic layer was separated and the aqueous layer was extracted with dichloromethane (3 x 50 mL). The organic layer was dried over MgSO_4 , filtered and concentrated *in vacuo*. Chromatography on silica gel (10%, EtOAc /hexane eluant) gave 10 g of furan as a colorless oil. $[\alpha]_D^{20} +2.46^\circ$ (c 0.90, CHCl_3). IR (neat) 2954, 2871, 1740, 1251, 1112, 838, 736, 700 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.48-7.46 (m, 2H), 7.33-7.23 (m, 3H), 4.36 (dt, $J = 3.30, 8.57$ Hz, 1H), 3.60 (ovrlp s, 3H), 3.58 (ovrlp m, 1H), 3.48-3.40 (m, 2H), 2.36 (dd, $J = 8.2, 15.0$ Hz, 1H),

2.21 (dd, $J = 3.30, 15.2$ Hz, 1H), 2.00-1.92 (m, 1H), 1.03 (t, $J = 9.6$ Hz, 1H), 0.90 (d, $J = 6.26$ Hz, 3H), 0.34 (s, 3H), 0.33 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 171.7, 138.7, 137.4, 133.9, 129.5, 128.4, 128.1, 127.8, 127.6, 85.0, 78.0, 73.5, 71.4, 51.7, 41.9, 40.5, 40.0, 18.4, -3.6, -4.1; HRMS (CI/ NH_3) m/z calcd for $\text{C}_{24}\text{H}_{33}\text{O}_4\text{Si}$ 413.2148, found 413.2109.

Observed NOE:

(5S, 6S)-7-Benzyloxy-6-hydroxy-5-methyl-hept-3-enoic acid methyl ester. A solution of furan **10** (4.67 g, 11.33 mmol) in 220 mL of CH_2Cl_2 (0.05 M) at -78°C was treated with a solution of SbCl_5 in CH_2Cl_2 (1 M, 12.5 mL, 12.47 mmol). The resulting light yellow reaction solution was warmed to -50°C and stirred for 12h. The reaction was diluted by the addition of 100 mL of distilled water. The resulting white precipitate suspension was filtered through a short plug of Celite and washed with CH_2Cl_2 . The filtrate was collected and the organic layer was separated. The aqueous layer was extracted with CH_2Cl_2 (3 x 100 mL). The organic layer was dried over MgSO_4 , filtered and concentrated *in vacuo*. Chromatography on silica gel (20%, EtOAc/hexane eluant) gave 2.8 g of alcohol as a colorless oil. $[\alpha]_D^{20} -12.2^\circ$ (c 0.65, CHCl_3). IR (neat) 3470, 2954, 2871, 1739, 1454, 1168, 1104, 974, 754, 699 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.34-7.27 (m, 5H), 5.58-5.55 (m, 2H), 4.53 (s, 2H), 3.66 (s, 3H), 3.65-3.62 (m, 1H), 3.51 (dd, $J = 3.3, 9.6$ Hz, 1H), 3.39 (dd, $J = 7.6, 9.6$ Hz, 1H), 3.05 (app d, $J = 5.6$ Hz, 2H), 2.36 (m, 1H), 2.26 (d, $J = 3.3$ Hz, 1H), 1.02 (d, $J = 6.92$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 172.2, 138.0, 135.8, 128.3, 127.6, 122.8, 73.6, 73.3, 72.5, 51.7, 39.6, 37.8, 16.5; HRMS (CI/ NH_3) m/z calcd for $\text{C}_{16}\text{H}_{23}\text{O}_4$ 279.1596, found 279.1637.

(5S, 6S)-7-Benzyloxy-6-methoxy-5-methyl-hept-3-enoic acid methyl ester A solution of alcohol (2.8 g, 10.14 mmol) in 250 mL of CH_2Cl_2 was treated with Proton Sponge[®] (13.0 g, 60.84 mmol) and 19.5 g of 4Å molecular sieve. To the resulting white suspension was then added Me_3OBF_4 (7.45 g, 50.68 mmol). The reaction mixture was allowed to stir for 6h before it was filtrated through a short plug of Celite. The filtrate was concentrated *in vacuo*. The resulting mixture was filtrate through another short plug of Celite and washed with EtOAc (100 mL). The filtrate was then washed with 5% HCl (100 mL). The organic layer was separated, dried over MgSO_4 , filtered and concentrated

in vacuo. Chromatography on silica gel (20%, EtOAc/hexane eluant) gave 2.8 g of the methyl ether as a colorless oil (95% yield). $[\alpha]_D^{20}$ -19.7° (c 1.8, CHCl₃). IR (neat) 2952, 2900, 1740, 1454, 1168, 1102, 973, 738, 698 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.29 (m, 3H), 7.28-7.24 (m, 2H), 5.53-5.50 (m, 2H), 4.51 (Abq, *J* = 12.2 Hz, 2H), 3.65 (s, 3H), 3.46 (dd, *J* = 1.98, 4.29 Hz, 1H), 3.42 (dd, *J* = 4.29, 10.2 Hz, 1H), 3.01 (d, *J* = 5.60 Hz, 2H), 2.51-2.48 (m, 1H), 1.01 (d, *J* = 6.92, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 172.2, 138.3, 135.7, 128.2, 127.5, 122.1, 83.8, 73.3, 70.7, 58.7, 51.6, 38.4, 37.8, 16.2; HRMS (CI/NH₃) *m/z* calcd for C₁₇H₂₅O₄ 293.1961, found 293.1995.

(2R, 3S)-4-Benzyloxy-3-methoxy-2-methyl-but-3-enal 11. Into a stirred solution of olefin (5 g, 17.12 mmol) in 245 mL of MeOH/CH₂Cl₂ (v/v, 3 : 1) at -78 °C, was bubbled ozone gas until starting material disappeared as evidenced by monitoring TLC. Methyl sulfide (10 mL, 137 mmol) was then added to the reaction mixture. After it was allowed to slowly warm to room temperature over 12h, the reaction mixture was concentrated *in vacuo*. The residue was dissolved in 100 mL of Et₂O and washed with H₂O (50 mL), Saturated NaHCO₃ (50 mL), and brine (50 mL) subsequently. The organic layer was dried over MgSO₄, filtered and concentrated *in vacuo*. This material was used directly without further purification. $[\alpha]_D^{20}$ -43.8° (c 0.71, CHCl₃). IR (neat) 2934, 1725, 1454, 1106 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 9.72 (d, *J* = 1.7 Hz, 1H), 7.33-7.28 (m, 5H), 4.52 (Abq, *J* = 12.2 Hz, 2H), 3.62-3.50 (m, 3H), 3.40 (s, 3H), 2.75-2.68 (m, 1H), 1.05 (d, *J* = 7.25 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 203.4, 137.9, 128.4, 127.7, 81.0, 73.6, 68.9, 58.1, 48.0, 9.9; HRMS (CI/NH₃) *m/z* calcd for C₁₃H₁₈O₃ 222.1256, found 222.1261.

(2R, 5R, 6R)-6-[(1R, 2S)-3-Benzyloxy-2-methoxy-1-methyl-propyl]-5-methyl-5,6-dihydro-2H-pyran-2-carboxylic acid methyl ester 6. To a solution of aldehyde (2.56 g, 12.08 mmol) and crotylsilane (4.23 g, 12.08 mmol) in CH₂Cl₂ (0.05 M, 240 mL) at -70 °C, was added 1.07 mL of TfOH (12.08 mmol). The resulting solution was allowed to stir at -70 °C for 24h. After which time, the reaction was quenched by the addition of saturated aqueous NaHCO₃ (100 mL). The organic layer was separated, and the aqueous layer was extracted with CH₂Cl₂ (3 x 100 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. Chromatography on silica gel (10%, EtOAc/hexane eluant) gave 3.6 g of dihydropyran **6** as a colorless oil (85% yield). $[\alpha]_D^{20}$ +6.47° (c 0.51, CHCl₃). IR (neat) 3031, 2933, 1753, 1455, 1267, 1195, 1153, 1098, 782, 752, 699 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.23 (m, 5H), 5.83 (ddd, *J* = 2.0, 3.3, 9.7 Hz, 1H), 5.76 (ddd, *J* = 1.98, 1.98, 9.8 Hz, 1H), 4.69-4.67 (m, 1H), 4.57 (abq, *J* = 12.5 Hz, 2H), 3.83 (dd, *J* = 2.3, 10.5 Hz, 1H), 3.73-3.70 (ovrlp m, 1H), 3.71 (s, 3H), 3.51-3.42 (ovrlp m, 2H), 3.47 (s, 3H), 2.29-2.22 (m, 1H), 2.07-1.99 (m, 1H), 0.90 (d, *J* = 7.25 Hz, 3H), 0.83 (d, *J* = 7.25 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ

171.9, 138.9, 134.7, 128.6, 128.1, 127.8, 122.6, 81.4, 76.6, 76.3, 73.8, 72.7, 68.8, 57.7, 52.2, 57.7, 52.2, 36.3, 30.4, 17.3, 9.0; HRMS (CI/NH₃) *m/z* calcd for C₂₀H₂₈O₅ 348.1937, found 348.1962.

(5*R*, 6*R*)-6-[(1*R*, 2*S*)-3-Benzyloxy-2-methoxy-1-methyl-propyl]-5-methyl-4-oxo-5,6-dihydro-2*H*-pyran-2-carboxylic acid methyl ester 14. To a solution of dihydropyran (3.96 g, 11.19 mmol) in CH₂Cl₂ (0.2 M, 56 mL), was added *m*-CPBA (3.54 g, 12.31 mmol) in one portion at room temperature. After stirring at room temperature for 12 hours, the reaction was quenched by the addition of saturated Na₂S₂O₃, followed by the addition of saturated NaHCO₃. The aqueous layer was extracted with dichloromethane (3 × 80 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. Chromatography on silica gel (20%, EtOAc/hexane eluant) gave 3.25 g of diastereomeric epoxide mixture as a colorless oil (80% yield). The epoxides (3.25 g, 8.92 mmol) were then dissolved in 45 mL of methanol (0.2 M), followed by the addition of K₂CO₃ (1.23 g, 8.92 mmol). The suspension was stirred at room temperature for 2 h. After which time, the reaction mixture was diluted with H₂O (50 mL), the aqueous layer was extracted with EtOAc (3 × 80 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The obtained alcohol (2.88 g, 7.91 mmol) was then dissolved in 40 mL of CH₂Cl₂, to which was added 3.96 g of 4Å molecular sieves (500 mg/mmol) followed by the addition of PDC (5.95 g, 15.82 mmol). The dark brown suspension was allowed to stir for 2 h at room temperature before it was filtered through a short plug of Celite. The filtrate was concentrated *in vacuo*. Chromatography on silica gel (10%, EtOAc/hexane eluant) gave 2.1 g of enone as a colorless oil (65% yield). [α]_D²⁰ -94.9° (c 0.37, CHCl₃). IR (neat) 2976, 2937, 2886, 1745, 1684, 1613, 1259, 1107, 736 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.30 (m, 3H), 7.29-7.25 (m, 2H), 6.17 (s, 1H), 4.62 (d, *J* = 12.2 Hz, 1H), 4.55 (par obsc dd, *J* = 2.0, 13.2 Hz, 1H), 4.52 (d, *J* = 12.2 Hz, 1H), 3.83 (s, 3H), 3.79 (dd, *J* = 2.0, 10.7 Hz, 1H), 3.49-3.42 (overlp m, 2H), 3.38 (s, 3H), 2.58-2.49 (m, 1H), 2.19-2.11 (m, 1H), 1.06 (d, *J* = 6.92 Hz, 3H), 0.91 (d, *J* = 6.92 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 196.5, 162.3, 158.2, 138.1, 127.7, 108.3, 83.7, 80.1, 73.5, 68.2, 58.0, 52.9, 41.0, 35.6, 8.9, 8.8; HRMS (CI/NH₃) *m/z* calcd for C₂₀H₂₇O₆ 363.1808, found 363.1842.

(4*R*, 5*R*, 6*R*)-6-[(1*R*, 2*S*)-3-Benzyloxy-2-methoxy-1-methyl-propyl]- 4- hydroxy-5-methyl -5,6-dihydro-2*H*-pyran-2-carboxylic acid methyl ester. The enone (1.75 g, 4.83 mmol) and CeCl₃•7H₂O were dissolved in 24 mL of methanol at room temperature, the resulting mixture was then cooled to -78 °C, to which was added NaBH₄ in one

portion. The reaction mixture was allowed to stir for 1 h at -78 °C before it was diluted by the addition of 5% HCl. The aqueous layer was extracted with Et₂O (3 × 50 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. Chromatography on silica gel (35%, EtOAc/hexane eluant) gave 1.6 g of the pure alcohol as a colorless oil (93% yield). [α]_D²⁰ -46.0° (c 0.70, CHCl₃). IR (neat) 3447, 2974, 2933, 1733, 1651, 1454, 1440, 1260, 1106, 755, 700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.30 (m, 3H), 7.29-7.24 (m, 2H), 5.90 (d, *J* = 2.3 Hz, 1H), 4.55 (Abq, *J* = 12.2 Hz, 2H), 4.08 (dd, *J* = 2.3, 10.7 Hz, 1H), 4.04 (par obsc dt, *J* = 2.3, 8.7 Hz, 1H), 3.78-3.74 (overlp, 4H), 3.48-3.38 (m, 2H), 3.38 (s, 3H), 2.10-2.03 (m, 1H), 1.71-1.65 (m, 1H), 1.47 (d, *J* = 7.6 Hz, 1H), 1.01 (d, *J* = 6.6 Hz, 1H), 0.83 (d, *J* = 6.92 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 163.2, 144.5, 138.2, 128.2, 127.6, 127.5, 113.1, 80.5, 79.2, 73.3, 69.9, 68.7, 58.1, 52.0, 36.6, 34.9, 34.9, 13.2, 8.42; HRMS (CI/NH₃) *m/z* calcd for C₂₀H₂₈O₆ 365.1965, found 365.1948.

(4*R*, 5*R*, 6*R*)-6-[(1*R*, 2*S*)-3-Benzoyloxy-2-methoxy-1-methyl-propyl]-4-(*tert*-butyl-dimethyl-silyloxy)-5-methyl-5,6-dihydro-2*H*-pyran-2-carboxylic acid methyl ester **15.** To a solution of alcohol (1.75 g, 4.83 mmol) and 2,6-lutidine (0.84 mL, 7.25 mmol) in 12 mL of CH₂Cl₂ at -78 °C, was added 1.34 mL of TBSOTf (5.79 mmol). The reaction mixture was allowed to stir for 3 h before it was quenched by the addition of 10 mL of H₂O. The organic phase was separated and the aqueous layer was extracted with dichloromethane (3 x 15 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. Chromatography on silica gel (10%, EtOAc/hexane eluant) gave 2.2 g of TBS ether **15** (97% yield). [α]_D²⁰ +5.29° (c 0.51, CHCl₃). IR (neat) 2954, 2931, 2857, 1737, 1651, 1463, 1359, 1257, 1095, 836, 757 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.24 (m, 5H), 5.78 (d, *J* = 2.0 Hz, 1H), 4.56 (ABq, *J* = 12.2 Hz, 2H), 4.09-4.05 (overlp, 2H), 3.75 (par obsc dd, *J* = 1.7, 14.5 Hz, 1H), 3.73 (s, 3H), 3.47-3.38 (overlp, 3H), 3.38 (s, 3H), 2.08-2.03 (m, 1H), 1.78-1.72 (m, 1H), 0.93 (d, *J* = 6.92 Hz, 3H), 0.90 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 163.3, 144.0, 138.3, 128.3, 127.6, 127.5, 113.5, 80.6, 79.0, 73.4, 70.7, 68.9, 58.2, 51.9, 36.4, 35.2, 25.8, 25.6, 18.0, 13.3, 8.48, -4.1, -4.7; HRMS (CI/NH₃) *m/z* calcd for C₂₆H₄₂O₆Si 478.2751, found 478.2753.

(4*R*, 5*R*, 6*R*)-1-{6-[(1*R*, 2*S*)-3-Benzoyloxy-2-methoxy-1-methyl-propyl]-4-(*tert*-butyl-dimethyl-silyloxy)-5-methyl-5,6-dihydro-4*H*-pyran-2-yl}-2-diazo-ethanone. To a solution of methyl ester (1.85 g, 3.81 mmol) in 15 mL of THF/MeOH/H₂O (v/v, 3:1:1), was added 320 mg of LiOH (7.63 mmol) at room temperature. After stirring for 3 h, the

reaction was quenched by the addition 5% HCl till pH was 4-5. The organic phase was separated and the aqueous layer was extracted with Et₂O (3 x 20 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. The unpurified carboxylic acid was then dissolved in 19 mL of CH₂Cl₂, to which was added freshly distilled (ClCO)₂ (4.57 mmol, 0.4 mL) followed by the addition of 29 μ L of DMF (0.38 mmol). After stirring for 15 min. at room temperature, the reaction mixture was concentrated *in vacuo*, and the resulting residue was dissolved in dry ether. To an ethereal solution of CH₂N₂ (ca. 20 equiv.) was added a solution of the foregoing acid chloride dropwise at 0 °C. The cloudy yellow mixture was stirred for 30 min before it was quenched by the addition of 50 mL of H₂O. The resulting mixture was stirred until gas evolution stopped. The organic phase was separated and the aqueous layer was extracted with Et₂O (3 x 50 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. Chromatography on silica gel (10%, EtOAc/hexane eluant) gave 1.3 g of diazoketone as yellow oil (70% yield). [α]_D²⁰ -24.8° (c 0.32, CHCl₃). IR (neat) 3132, 3031, 2930, 2886, 2857, 2247, 2105, 1619, 1471, 1463, 1358, 1338, 1292, 1198, 1093, 880, 836, 735 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.24 (m, 5H), 5.71 (d, *J* = 2.0 Hz, 1H), 5.63 (br s, 1H), 4.57 (ABq, *J* = 12.0 Hz, 2H), 4.13-4.04 (overlp, 2H), 3.74 (dd, *J* = 2.6, 10.9 Hz, 1H), 3.47 (dd, *J* = 4.3, 10.5 Hz, 1H), 3.48 (s, 3H), 3.28-3.21 (m, 1H), 2.09-2.03 (m, 1H), 1.79-1.70 (m, 1H), 0.92 (d, *J* = 6.92, 3H), 0.89 (s, 9H), 0.83 (d, *J* = 6.92 Hz, 3H), 0.11 (s, 3H), 0.08 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 182.3, 149.0, 138.2, 128.4, 127.7, 108.5, 81.0, 79.1, 73.5, 70.6, 69.2, 58.4, 53.5, 36.4, 35.2, 25.7, 17.9, 13.2, 8.5, -4.3, -4.9; HRMS (CI/NH₃) *m/z* calcd for C₂₆H₄₁N₂O₅Si 489.2785, found 489.2819.

(4R, 5R, 6R)-{6-[(1R, 2S)-3-Benzyloxy-2-methoxy-1-methyl-propyl]-4-(tert-butyl-dimethyl-silanyloxy)-5-methyl-5,6-dihydro-4H-pyran-2-yl}-acetic acid methyl ester 16. To a suspension of silver benzoate (409 mg, 1.78 mmol) in methanol (0.3 M, 6 mL), was added a solution of diazoketone (870 mg, 1.78 mmol) in 2.9 mL of pyridine. The resulting reaction mixture was stirred at room temperature for 24 h before it was quenched by the addition of saturated aqueous NaHCO₃ (10 mL). The organic phase was separated and the aqueous layer was extracted with Et₂O (3 x 15 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. Chromatography on silica gel (10%, EtOAc/hexane eluant) gave 0.7 g of the methyl ester (80% yield). [α]_D²⁰ -38.5° (c 0.34, CHCl₃). IR (neat) 2930, 2857, 1747, 1683, 1456, 1361, 1257, 1188, 1093, 1046, 960, 836, 756 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.34-7.24 (m, 5H), 4.57 (ABq, *J* = 12.0 Hz, 2H), 4.56 (br s, 1H), 4.03 (dt, *J* = 2.0, 10.9 Hz, 1H), 3.71 (dd, *J* = 2.3, 10.5 Hz, 1H), 3.41 (dd, *J* = 4.0, 10.7 Hz, 1H), 3.36 (s, 3H), 3.27-3.23 (m, 1H), 3.0 (ABq, *J* = 15.5 Hz, 1H), 2.03-1.96 (m, 1H), 1.74-1.64 (m, 1H), 0.89 (overlp, 12H), 0.76 (d, *J* = 6.92, 3H), 0.07 (s, 3H), 0.06 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 170.6, 148.4, 138.4, 128.4, 127.7, 127.6, 104.3, 80.6, 78.2, 73.4, 71.1, 69.1, 58.2, 51.8, 39.7, 36.7, 35.3, 25.8, 17.9, 13.1, 8.2, -4.2, -4.7; HRMS (CI/NH₃) *m/z* calcd for C₂₇H₄₅O₆Si 493.2985, found 493.2985.

(2S, 4R, 5R, 6R)-{6-[(1R, 2S)-3-Benzoyloxy-2-methoxy-1-methyl-propyl]-4-(tert-butyl-dimethyl-silanyloxy)-2-methoxy-5-methyl-5,6-tetrahydro-pyran-2-yl}-acetic acid methyl ester. To a solution of enol ether (193 mg, 0.39 mmol) in CH₂Cl₂ (0.05 M, 7.8 mL), was added 0.39 mL of methanol followed by the addition of 9.1 mg of CSA (0.04 mmol). The mixture was stirred for 2 h at room temperature before it was quenched by the addition of saturated aqueous NaHCO₃. The organic phase was separated and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. Chromatography on silica gel (10%, EtOAc/hexane eluant) gave 198 mg of the methyl lactol ether (97% yield). $[\alpha]_D^{20}$ -37.0° (c 1.15, CHCl₃). IR (neat) 2930, 2857, 1744, 1456, 1376, 1252, 1093, 837 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.33-7.24 (m, 5H), 4.54 (s, 2H), 3.76 (dd, *J* = 1.98, 10.7 Hz, 1H), 3.67-3.59 (ovrlp m, 2H), 3.63 (s, 1H), 3.39 (dd, *J* = 3.96, 10.9 Hz, 1H), 3.34-3.29 (ovrlp m, 1H), 3.33 (s, 3H), 2.54 (ABq, *J* = 13.5 Hz, 2H), 2.08 (ovrlp dd, *J* = 4.6, 12.9, 1H), 2.02 (m, 1H), 1.64 (dd, *J* = 10.9, 12.9 Hz, 1H), 1.45-1.37 (m, 1H), 0.87 (s, 9H), 0.84 (d, *J* = 6.59 Hz, 3H), 0.74 (d, *J* = 7.25 Hz, 3H), 0.04 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 170.0, 138.4, 128.4, 127.9, 127.7, 98.8, 81.1, 73.4, 72.9, 70.5, 68.2, 56.4, 51.5, 47.8, 43.0, 41.8, 39.7, 34.9, 25.8, 17.9, 12.5, 8.2, -4.2, -4.9; HRMS (CI/NH₃) *m/z* calcd for C₂₈H₄₉O₇Si 525.3248, found 525.3286.

(2S, 4R, 5R, 6R)-{6-[(1R, 2S)-3-hydroxy-2-methoxy-1-methyl-propyl]-4-(tert-butyl-dimethyl-silanyloxy)-2-methoxy-5-methyl-5,6-tetrahydro-pyran-2-yl}-acetic acid methyl ester. To a solution of benzyl ether (204 mg, 0.39 mmol) in 1.3 mL of EtOAc, was added Pd/C (20 mg). The resulting suspension was charged with a hydrogen balloon. After stirring for 5 h at room temperature, the mixture was filtrated through a short plug of Celite. The filtrate was concentrated *in vacuo* afforded the crude material. Chromatography on silica gel (50%, EtOAc/hexane eluant) gave 157 mg of the pure primary alcohol as a colorless oil (93% yield). $[\alpha]_D^{20}$ -29.1° (c 0.55, CHCl₃). IR (neat) 3462, 2931, 2857, 1743, 1463, 1438, 1377, 1318, 1251, 1087, 873, 837, 777 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.94 (ddd, *J* = 3.3, 3.96, 8.2 Hz, 1H), 3.65 (s, 3H), 3.65-3.61 (ovrlp m, 1H), 3.59-3.50 (ovrlp m, 2H), 3.33 (s, 3H), 3.27-3.24 (m, 1H), 3.20 (s, 3H), 2.62 (ABq, *J* = 13.5 Hz, 2H), 2.09 (dd, *J* = 4.6, 12.9, 1H), 2.04 (m, 1H), 1.82 (dd, *J* = 4.3, 8.1 Hz, 1H), 1.67 (dd, *J* = 10.9, 12.7 Hz, 1H), 1.47-1.39 (m, 1H), 0.87 (s, 9H), 0.85 (d, *J* = 6.9 Hz, 3H), 0.80 (d, *J* = 6.9 Hz, 3H), 0.05 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 169.9, 99.0, 82.4, 73.3, 70.4, 59.5, 56.2, 51.6, 47.9, 42.9, 41.8, 39.8, 34.0, 25.8, 17.9,

12.5, 8.0, -4.2, -4.9; HRMS (CI/NH₃) *m/z* calcd for C₂₁H₄₃O₇Si 435.2778, found 435.2698.

(2*S*, 4*R*, 5*R*, 6*R*)-{4-(*tert*-butyl-dimethyl-silanyloxy)-2-methoxy-6-[(1*R*, 2*S*)-2-methoxy-1-methyl-3-oxo-propyl]-5-methyl-5,6-tetrahydro-pyran-2-yl}-acetic acid methyl ester 4. To a solution of alcohol (204 mg, 0.39 mmol) in 7.8 mL of CH₂Cl₂, was added 195 mg of 4 Å molecular sieve (500 mg/mmol) followed by the addition of PDC (734 mg, 1.95 mmol). The dark brown suspension was allowed to stir for 12 h at room temperature before it was filtrated through a short plug of Celite. The filtrate was concentrated *in vacuo*. Chromatography on silica gel (10%, EtOAc/hexane eluant) gave 157mg of aldehyde (93% yield). [α]_D²⁰ -30.9° (c 0.45, CHCl₃). IR (neat) 2932, 2858, 1736, 1464, 1252, 1128, 1089, 1035, 838, 776 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 9.55 (d, *J* = 4.6 Hz, 1H), 3.69-3.62 (ovrlp m, 1H), 3.66 (s, 3H), 3.60 (dd, *J* = 1.6, 10.1 Hz, 1H), 3.31 (s, 3H), 3.18 (s, 3H), 2.6 (app s, 2H), 2.11 (dd, *J* = 4.6, 12.9, 1H), 2.09 (m, 1H), 1.66 (dd, *J* = 10.9, 12.7 Hz, 1H), 1.48-1.38 (m, 1H), 0.87 (s, 9H), 0.85 (d, *J* = 6.9 Hz, 3H), 0.81 (d, *J* = 7.3 Hz, 3H), 0.05 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 203.2, 169.8, 99.1, 86.5, 72.0, 70.2, 57.7, 51.6, 47.9, 42.9, 41.6, 39.4, 34.7, 25.7, 17.9, 12.3, 7.4, -4.2, -4.9; HRMS (CI/NH₃) *m/z* calcd for C₂₁H₄₀O₇Si 432.2543, found 432.2525.

[(1*S*, 2*R*)-2-Chloro-cyclopropyl]-methanol 19. To a mixture of dioxaborolane (1 g, 3.7 mmol), allylic alcohol (311 mg, 3.4 mmol) and 4 Å molecular sieves in CH₂Cl₂ (0.2 M, 17 mL) at -15 °C, was added freshly prepared solution of Zn(CH₂I)₂·DME complex in CH₂Cl₂ (1M, 17 mL) at a rate to keep the internal temperature below -10 °C. The resulting mixture was allowed to warm to room temperature and stirred for 24 h. A saturated aqueous NH₄Cl was added, and the layers were separated. The aqueous layer was extracted three times with ether (3 × 30 mL). The organic layer was dried over MgSO₄, filtered and concentrated *in vacuo*. The crude mixture was then dissolved in 3.4 mL of ether. The resulting mixture was then stirred for 12 h with 0.12 mL of aqueous KOH (5 M), and the layers were separated. The aqueous layer was washed three times with ether. The organic layer was dried over MgSO₄, filtered and concentrated *in vacuo*. Chromatography on silica gel (20%, EtOAc/hexane eluant) gave 296 mg of the cyclopropane as a colorless oil (82% yield). [α]_D²⁰ - 54.5° (c 0.56, CHCl₃). IR (neat) 3334, 2929, 2876, 1712, 1442, 1272, 1030, 682 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.57 (dd, *J* = 6.26, 11.5 Hz, 1H), 3.45 (dd, *J* = 6.92, 11.5 Hz, 1H), 2.90 (m, 1H), 1.49 (m, 1H), 1.43 (brs, 1H), 1.00 (m, 1H), 0.89 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 63.7, 30.7, 24.3, 13.4; HRMS (CI/NH₃) *m/z* calcd for C₄H₈OCl 107.0262, found 107.0268.

(1R, 2S)-1-Chloro-2-(2,2-dibromo-vinyl)-cyclopropane 20. To a solution of alcohol (526 mg, 4.96 mmol) in CH_2Cl_2 (16 mL) was added 2.46 g of 4 Å molecular sieves (500 mg/mmol) and PDC (3.75 g, 9.92 mmol). The resulting dark brown solution was allowed to stir for 4 h at ambient temperature. The reaction mixture was then filtrated through a short plug of silica gel and washed with CH_2Cl_2 . The filtrate was concentrated *in vacuo* at 0 °C. The crude aldehyde was used directly without further purification. In a separate flask, PPh_3 (2.6 g, 9.92 mmol) was added to a solution of CBr_4 (1.64 g, 4.96 mmol) in CH_2Cl_2 (8.2 mL) at 0 °C. The resulting bright red solution was stirred for 20 min at the same temperature. The above prepared crude aldehyde was then added via cannula, and the resulting red solution was stirred for 2 h at 0 °C to room temperature. The solution was poured into 100 mL ice-cold pentane, and filtered through a silica plug with 200 mL of pentane. Removal of the solvent and chromatography on silica gel (pentane eluant) gave 781 mg of dibromide as a colorless oil (61% yield). $[\alpha]_{\text{D}}^{20}$ -70.9° (c 0.65, CHCl_3). IR (neat) 3048, 3006, 2955, 2923, 1432, 1360, 1279, 936, 781, 684 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.81 (d, J = 8.9 Hz, 1H), 3.04 (m, 1H), 2.01 (m, 1H), 1.34 (m, 1H), 1.13 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 137.1, 89.6, 33.0, 26.0, 17.5; HRMS (CI/ NH_3) m/z calcd for $\text{C}_5\text{H}_5\text{Br}_2\text{Cl}$ 257.8446, found 257.8435.

(E)-5-((1S, 2R)-2-Chloro-cyclopropyl)-pent-2-en-4-yn-ol 22. A solution of dibromide (600 mg, 2.33 mmol), vinylstanne (890 mg, 2.56 mmol), Pd_2dba_3 (53 mg, 0.06 mmol), tris(4-methoxyphenyl)phosphine (123 mg, 0.35 mmol) and *N,N*-diisopropylethylamine (0.6 mL, 3.50 mmol) in DMF (12 mL) was flushed with argon and heated at 80 °C for 12 h. The reaction mixture was diluted with ether (50 mL), washed with water (3×30 mL). The organic layer was separated and dried over MgSO_4 , filtered and concentrated *in vacuo*. Chromatography on silica gel (20%, EtOAc/hexane eluant) gave 247 mg of the pure enyne as a yellow oil (68% yield). $[\alpha]_{\text{D}}^{20}$ -232.2° (c 0.49, CHCl_3). IR (neat) 3331, 3029, 2921, 2860, 2221, 1431, 1257, 1094, 998, 953, 688 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.16 (dt, J = 5.27, 15.8 1H), 5.66 (dt, J = 1.65, 15.8 1H), 4.16 (brs, 2H), 3.16 (m, 1H), 1.76 (m, 1H), 1.46 (brs, 1H), 1.25 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 141.6, 110.1, 89.5, 76.3, 62.7, 34.0, 19.0, 11.7; HRMS (CI/ NH_3) m/z calcd for $\text{C}_8\text{H}_9\text{ClO}$ 156.0342, found 156.0358.

(1S, 2R)-1-((E)-5-Bromo-pent-3-en-1-ynyl)-2-chloro-cyclopropane. To a solution of alcohol (120 mg, 0.77 mmol) and PPh_3 (202 mg, 0.77 mmol) in CH_2Cl_2 (2 mL) at -40 °C, was added a solution of CBr_4 (255 mg, 0.77 mmol) in CH_2Cl_2 (2 mL). The mixture was stirred at this temperature for 1h. A saturated aqueous solution of NaHCO_3 was then added and the mixture was warmed to room temperature. The organic layer was extracted with CH_2Cl_2 (3×5 mL). The combined organic layers were dried over MgSO_4 , filtered

and concentrated *in vacuo*. Chromatography on silica gel (hexane eluant) gave 165 mg of the pure bromide as a colorless oil (98% yield). $[\alpha]_D^{20}$ -192.2° (c 0.99, CHCl₃). IR (neat) 3010, 2962, 2220, 1624, 1431, 1257, 1202, 950, 688 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.17 (dt, *J* = 7.9, 15.5 Hz, 1H), 5.66 (d, *J* = 15.5 Hz, 1H), 3.94 (d, *J* = 7.58 Hz, 2H), 3.18-3.14 (m, 1H), 1.79-1.75 (m, 1H), 1.30-1.26 (m, 1H); ¹³C NMR (75 MHz, CDCl₃) δ 137.9, 114.2, 91.6, 75.7, 34.1, 31.6, 19.1, 11.7; HRMS (CI/NH₃) *m/z* calcd for C₈H₉BrCl 218.9574, found 218.9557.

[(*E*)-5-((1*S*, 2*R*)-2-Chloro-cyclopropyl)-pent-2-en-4-ynyl]-phosphonic acid diethyl ester 23. A solution of bromide (145 mg, 0.66 mmol) in freshly distilled triethyl phosphite (0.7 mL, 1M) was heated to 100 °C for 4h. The triethyl phosphite was then removed under vacuum at 90 °C. The residue was purified by chromatography on silica gel (50%, EtOAc/hexane eluant) gave 180 mg of title compound as a clear oil (99% yield). $[\alpha]_D^{20}$ -134.9° (c 0.8, CHCl₃). IR (neat) 3420, 2984, 2427, 2113, 1255, 1026, 961cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 5.95 (dt, *J* = 7.6, 15.2 Hz, 1H), 5.52 (dd, *J* = 4.3, 15.6 Hz, 1H), 4.09 (m, 4H), 3.14 (m, 1H), 2.59 (dd, *J* = 7.6, 22.6 Hz, 2H), 1.73 (m, 1H), 1.29 (m, 8H); ¹³C NMR (75 MHz, CDCl₃) δ 132.3 (d, *J* = 12.6 Hz), 114.1 (d, *J* = 15.7 Hz), 88.9, 76.3 (d, *J* = 5.4 Hz), 62.7 (d, *J* = 6.6 Hz), 33.9, 31.8, 18.9, 16.2 (d, *J* = 6.0 Hz), 11.6; HRMS (CI/NH₃) *m/z* calcd for C₁₂H₁₈ClO₃P 276.0682, found 276.0646.

***tert*-Butyl-[(4*E*, 6*E*)-(1*S*, 3*R*)-9-((1*S*, 2*R*)-2-chloro-cyclopropyl)-1-methyl-3-trityloxy-nona-4,6-dien-8-ynyloxy]-diphenyl-silane 25.** To a solution of phosphonate (140 mg, 0.5 mmol) in THF (1.7 mL, 0.3 M) at -78 °C, was added 0.56 mL of LHMDS (1M in THF, 0.56 mmol) dropwise. The solution was stirred at -78 °C for 30 minutes. After which time, a solution of aldehyde (303 mg, 0.5 mmol) in THF was added in one portion to the above solution. The solution was stirred at -78 °C for 4 h before it was warmed to room temperature. After additional 12 h, the reaction was quenched by the addition of water. The organic phase was separated and the aqueous layer was extracted with ether (3 x 10 mL). The combined organic layers were dried over MgSO₄, filtered and concentrated *in vacuo*. Chromatography on silica gel (5%, EtOAc/hexane eluant) gave 325 mg of title compound (89% yield). $[\alpha]_D^{20}$ -1.33° (c 0.53, CHCl₃). IR (neat) 3069, 3025, 2962, 2930, 2857, 1448, 1428, 1111, 983, 909, 737, 705cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 7.56-7.54 (m, 4H), 7.42-7.32 (m, 6H), 7.30-7.14 (m, 15H), 5.95 (dd, *J* = 10.5, 15.5 Hz, 1H), 5.30 (dd, *J* = 10.5, 15.2 Hz, 1H), 5.13 (d, *J* = 15.8 Hz, 1H), 5.04 (dd, *J* = 7.25, 15.5 Hz, 1H), 3.73-3.68 (m, 1H), 3.55-3.50 (m, 1H), 3.18-3.15 (m, 1H), 1.81-1.72 (m, 1H), 1.70-1.66 (m, 1H), 1.58-1.48 (m, 1H), 1.29-1.24 (m, 2H), 0.96 (s, 9H), 0.81 (d, *J* = 5.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ; HRMS (CI/NH₃) *m/z* calcd for C₄₈H₅₀O₂SiCl 721.3269, found 721.3234.

(5E, 7E)-(2S, 4R)- 10-((1S, 2R)-2-Chloro-cyclopropyl)-4-trityloxy-deca-5,7-dien-9-yn-2-ol. To a solution of TBDPS ether (830 mg, 1.15 mmol) in THF (3.8 mL, 0.3 M), was added 2.3 mL of TBAF in 1M THF solution. The reaction mixture was stirred for 12 hours at room temperature. The reaction was quenched by the addition of 5 mL of water. The organic phase was separated and the aqueous layer was extracted with dichloromethane (3 x 10 mL). The combined organic layers were dried over MgSO_4 , filtered and concentrated *in vacuo*. Chromatography on silica gel (10%, EtOAc/hexane eluant) gave 506 mg of alcohol (91% yield). $[\alpha]_D^{20} + 50.3^\circ$ (c 0.35, CHCl_3). IR (neat) 3425, 3058, 3022, 2964, 2927, 1490, 1448, 1063, 1036, 985, 704 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.49-7.45 (m, 6H), 7.30-7.21 (m, 9H), 6.24 (dd, $J = 10.4, 15.6$ Hz, 1H), 5.81 (dd, $J = 10.4, 15.2$ Hz, 1H), 5.60 (dd, $J = 6.7, 15.2$ Hz, 1H), 5.35 (d, $J = 15.2$ Hz, 1H), 4.29-4.25 (m, 1H), 4.0-3.80 (m, 1H), 3.18-3.13 (m, 1H), 3.11 (br s, 1H), 1.81-1.77 (m, 1H), 1.39-1.32 (m, 2H), 1.29-1.24 (m, 2H), 0.96 (d, $J = 6.1$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 144.0, 140.8, 136.7, 128.9, 128.7, 127.8, 127.3, 110.4, 91.3, 88.3, 77.7, 73.9, 64.5, 43.9, 34.2, 23.4, 19.2, 12.0; HRMS (CI/ NH_3) m/z calcd for $\text{C}_{32}\text{H}_{33}\text{O}_2\text{Cl}$ 484.2169, found 484.2254.

5-[(4E, 6E)-(1S, 3R)- 9-((1S, 2R)-2-Chloro-cyclopropyl)-1-methyl-3-trityloxy-nona-4,6-dien-8-ynylsulfanyl]-1-phenyl-1H-tetrazole. To a solution of alcohol (506 mg, 1.05 mmol), 1-phenyl-1H-tetrazole-5-thiol (561 mg, 3.15 mmol) and triphenylphosphine (413 mg, 1.58 mmol) in 5 mL of THF (0.2 M), was added 0.31 mL of diisopropyl azodicarboxylate (1.58 mmol) dropwise at 0 $^\circ\text{C}$. The resulting reaction mixture was stirred for 12 hours at room temperature before it was concentrated *in vacuo*. Chromatography on silica gel (10%, EtOAc/hexane eluant) gave 541 mg of desired sulfide as a colorless oil (80 % yield) $[\alpha]_D^{20} -65.4^\circ$ (c 0.25, CHCl_3). IR (neat) 3059, 3021, 2926, 2869, 1735, 1597, 1499, 1448, 1387, 1218, 1045, 985, 760 707 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.56-7.43 (m, 11H), 7.24-7.15 (m, 9H), 6.19 (dd, $J = 10.4, 15.6$ Hz, 1H), 5.67 (dd, $J = 10.4, 15.6$ Hz, 1H), 5.49 (dd, $J = 7.3, 15.6$ Hz, 1H), 5.29 (dd, $J = 1.2, 15.6$ Hz, 1H), 4.08-4.05 (m, 1H), 3.82-3.73 (m, 1H), 3.17-3.13 (m, 1H), 3.11 (br s, 1H), 1.90-1.83 (m, 1H), 1.80-1.75 (m, 1H), 1.63-1.52 (m, 1H), 1.34 (d, $J = 6.70$ Hz, 3H), 1.28-1.24 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 153.4, 144.5, 140.7, 136.3, 133.7, 130.0, 129.6, 129.5, 128.9, 127.7, 127.1, 123.9, 110.7, 94.5, 91.4, 87.5, 77.7, 72.7, 42.5, 41.1, 34.3, 31.5, 22.4, 19.2, 12.0; HRMS (CI/ NH_3) m/z calcd for $\text{C}_{39}\text{H}_{35}\text{Cl N}_4\text{OS}$ 642.2220, found 642.2191.

MgSO₄ and concentrated *in vacuo*. Chromatography on silica gel (50%, EtOAc/hexane eluant) gave 1.1 mg of callipeltoside A aglycon.

In a separate operation, the TBS ether-methyl glycoside (5 mg, 7.7 μ mol) was dissolved in 0.1 mL of THF, to which was added 15 μ L of TBAF solution in THF (1M, 15 μ mol). After stirring at room temperature for 6h, additional 15 μ L of TBAF solution was added to the reaction mixture. One more portion of 15 μ L of TBAF solution was added 12h later. After stirring for additional 6h, the reaction was quenched by the addition of saturated aqueous NH₄Cl solution. The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 $\times$ 5 mL). The combined organic extracts were dried over MgSO₄ and concentrated *in vacuo*. Chromatography on silica gel (50%, EtOAc/hexane eluant) gave 3 mg of secondary alcohol. The foregoing material was immediately dissolved in 0.12 mL of wet CH₃CN (H₂O/CH₃CN, v/v, 1:3), to which was added 90 μ L of PPTS solution in CH₃CN (9 mM). The resulting reaction mixture was allowed to stir for 24h, before the reaction was quenched by the addition of saturated aqueous NaHCO₃. The layers were separated, and the aqueous layer was extracted with CH₂Cl₂ (3 $\times$ 5 mL). The combined organic extracts were dried over MgSO₄ and concentrated *in vacuo*. Chromatography on silica gel (30%, EtOAc/CH₂Cl₂ eluant) gave 2.6 mg of the aglycon. $[\alpha]_D^{20}$ -20.6° (c 0.16, CHCl₃). IR (neat) 3443, 2925, 2360, 1700 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 6.49 (dd, *J* = 10.5, 15.2 Hz, 1H), 6.28 (dd, *J* = 11.2, 15.2 Hz, 1H), 5.85-5.78 (m, 1H), 5.76 (dd, *J* = 6.6, 14.8 Hz, 1H), 5.57 (d, *J* = 15.2 Hz, 1H), 5.30 (d, *J* = 9.2 Hz, 1H), 5.02 (d, *J* = 2.5 Hz, 1H), 3.79 (dd, *J* = 2.5, 9.2 Hz, 1H), 3.79-3.74 (m, 1H), 3.60 (d, *J* = 2.6, 9.2 Hz, 1H), 3.21 (s, 3H), 3.18 (m, 1H), 2.54 and 2.44 (Abq, *J* = 12.8 Hz, 2H), 2.31-2.26 (m, 2H), 2.24-2.19 (m, 1H), 2.10 (dd, *J* = 4.6, 11.9 Hz, 1H), 1.81-1.78 (m, 1H), 1.71 (s, 3H), 1.42-1.36 (m, 1H); 1.31-1.28 (m, 3H), 0.97 (d, *J* = 6.6 Hz, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 171.9, 140.2, 132.7, 132.4, 131.0, 127.9, 112.5, 95.4, 92.3, 79.8, 77.2, 74.9, 71.5, 69.5, 55.2, 46.9, 44.7, 43.7, 40.0, 36.7, 34.2, 19.2, 16.0, 11.9, 6.4; HRMS (CI/NH₃) *m/z* calcd C₂₆H₃₅O₆Cl 478.2122, found 478.2167.

(3aR, 4S, 7R, 7aR)-6-(1S, 5R, 9R, 10R, 11R, 12R)- (E)-5-[(1E, 3E)-6-((1R, 2S)-2-chloro-cyclopropyl)-hexa-1,3-dien-5-ynyl]-1-hydroxy-9-methoxy-7,10,12-trimethyl 3-oxo-4,15-dioxabicyclo [9.3.1] pentadec-7-en-13-yloxy]-7-methoxy-4,7a-dimethyl- tetrahydropyrano-[3,4-d]oxazol-2-one 1.

A mixture of alcohol (2 mg, 4.2 μ mol) and trichloroacetimidate (2.6 mg, 5.5 μ mol) were dried by benzene azeotrope, diluted with CH_2Cl_2 (0.2 mL), and transferred via cannula into a flask containing freshly flame dried molecular sieves 4 $\text{\AA}$ (20 mg). This mixture was stirred for 10 min. at room temperature and then cooled to -30 $^\circ\text{C}$. TMSOTf (0.56 μ mol, 20 μ L of stock solution made from 50 μ L of TMSOTf in 10 mL of CH_2Cl_2) was then added dropwise, and the mixture was stirred for 15 min. Triethylamine (0.5 mL) was then added, and the mixture was warmed to room temperature. A saturated solution of sodium bicarbonate (0.5 mL) was added, and the mixture was extracted three times with CH_2Cl_2 (3 $\times$ 3 mL). The combined organic phases were washed with brine, dried over magnesium sulfate and concentrated *in vacuo*. Chromatography on silica gel (30%, EtOAc/ CH_2Cl_2 eluant) gave 3.0 mg of glycosilated product.

This product was diluted with THF (0.1 mL) and buffered TBAF (5 μ L of stock solution made from 1 mL of a 1M solution of TBAF in THF and 0.1 mL of acetic acid) was added at room temperature. After 5 min, the reaction mixture was diluted with saturated sodium bicarbonate (0.5 mL). The mixture was extracted three times with CH_2Cl_2 (3 $\times$ 3 mL). The combined organic phases were washed with brine, dried over magnesium sulfate and concentrated *in vacuo*. Chromatography on silica gel (70%, EtOAc/ CH_2Cl_2 eluant) gave 2.0 mg of callipeltoside A. $[\alpha]_{\text{D}}^{20}$ -18.3 $^\circ$ (c 0.10, CHCl_3). IR (neat) 3444, 2926, 1703, 1152 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 6.53 (dd, J = 10.7, 15.6 Hz, 1H), 6.37 (dd, J = 10.7, 14.3 Hz, 1H), 5.87 (m, 1H), 5.83 (m, 1H), 5.67 (dd, J = 2.1, 15.4 Hz, 1H), 5.28 (d, J = 9.8 Hz, 1H), 4.72 (d, J = 6.1 Hz, 1H), 3.99 (dq, J = 1.5, 6.4 Hz, 1H), 3.90 (dd, J = 2.4, 9.5 Hz, 1H), 3.76 (ddd, J = 4.6, 5.9, 11.7 Hz, 1H), 3.67 (dd, J = 2.4, 10.4 Hz, 1H), 3.60 (s, 3H), 3.43 (d, J = 6.1 Hz, 1H), 3.46 (d, J = 1.7 Hz, 1H), 3.27 (m, 1H), 3.22 (s, 3H), 2.55 and 2.48 (Abq, J = 12.8 Hz, 2H), 2.36 (m, 1H), 2.30 (m, 1H), 2.26 (m, 1H), 1.84 (m, 1H), 1.75 (s, 3H), 1.58 (m, 1H), 1.51 (s, 3H), 1.43 (t, J = 11.7, 1H), 1.31 (m, 1H), 1.10 (d, J = 6.4 Hz, 3H), 1.01 (d, J = 6.7 Hz, 3H), 0.97 (d, J = 6.8 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 172.9, 161.2, 141.7, 134.4, 132.1, 128.5, 113.6, 103.8, 96.7, 92.9, 83.6, 83.2, 81.6, 78.9, 76.6, 72.9, 65.5, 62.9, 62.1, 55.4, 47.8, 46.2, 44.7, 40.0, 38.3, 35.2, 23.2, 19.9, 16.4, 16.1 12.9, 6.9; HRMS (CI/ NH_3) m/z calcd $\text{C}_{35}\text{H}_{48}\text{O}_{10}\text{ClN}$ 677.2967, found 677.2966.

¹H NMR comparison for callipeltoside A (CD₃OD)

	natural callipeltoside A ¹	synthetic callipeltoside A
Atom	δ in ppm (500 MHz)	δ in ppm (400 MHz)
1		
2	2.56 (d, 12.7); 2.50 (d, 12.7)	2.55 (d, 12.8); 2.48 (12.8)
3		
4	2.25 (m); 1.43 (t, 11.7)	2.26 (m); 1.43 (t, 11.7)
5	3.76 (ddd, 11.7, 5.9, 4.9)	3.76 (ddd, 11.7, 5.9, 4.6)
6	1.58 (m)	1.58 (m)
7	3.68 (dd, 10.5, 2.4)	3.67 (dd, 10.4, 2.4)
8	2.27 (m)	2.26 (m)
9	3.91 (dd, 9.5, 2.2)	3.90 (dd, 9.5, 2.4)
10	5.30 (br dd, 9.5)	5.28 (d, 9.8)
11		
12	2.37 (m); 2.31 (m)	2.36 (m), 2.30(m)
13	5.86 (m)	5.83 (m)
14	5.87 (m)	5.87 (m)
15	6.37 (dd, 14.2, 10.5)	6.37 (14.3, 10.7)
16	6.53 (dd, 15.3, 10.5)	6.53 (15.6, 10.7)
17	5.68 (dd, 15.3, 1.7)	5.67 (15.4, 2.1)
18		
19		
20	1.85 (m)	1.84 (m)
21	3.28 (m)	3.27 (m)
22	1.31 (m)	1.31 (m)
23(C11-Me)	1.78 (s)	1.75 (s)
24(C8-Me)	0.99 (d, 6.9)	0.97 (d, 6.8)
25(C6-Me)	1.03 (d, 6.4)	1.01 (d, 6.7)
OMe (C9)	3.25 (s)	3.22 (s)
OH		
1'	4.74 (d, 6.1)	4.72 (d, 6.1)
2'	3.42 (d, 6.1)	3.43 (d, 6.1)
3'		
4'	3.48 (d, 1.7)	3.46 (d, 1.7)
5'	3.99 (dq, 6.5, 1.7)	3.99 (dq, 6.4, 1.5)
6'(C5'-Me)	1.12 (d, 6.5)	1.10 (d, 6.4)
7'		
8'(C3'-Me)	1.54 (s)	1.51 (s)
OMe(C2')	3.63 (s)	3.60 (s)
NH		

¹³C NMR comparison for callipeltoside A (CD₃OD)

	natural callipeltoside A ¹	synthetic callipeltoside A
Atom	δ in ppm (125 MHz)	δ in ppm (75 MHz)
1	172.4	172.9
2	46.0	46.2
3	97.0	96.7
4	44.5	44.7
5	78.7	78.9
6	39.8	40.0
7	76.4	76.6
8	38.2	38.3
9	81.4	81.6
10	128.3	128.5
11	134.1	134.4
12	47.8	47.8
13	72.7	72.9
14	134.2	134.4
15	132.0	132.1
16	141.5	141.7
17	113.4	113.6
18	78.3	78.9
19	92.4	92.9
20	12.0 ²	12.9
21	34.7 ²	35.2
22	19.3	19.9
23(C11-Me)	16.3	16.4
24(C8-Me)	6.8	6.9
25(C6-Me)	12.8	12.9
OMe (C9)	55.4	55.4
OH		
1'	103.6	103.8
2'	83.2	83.2
3'	83.8	83.6
4'	62.7	62.9
5'	65.3	65.5
6'(C5'-Me)	15.9	16.1

¹ Zampella, A.; D'Auria, M.V.; Minale, L.; Debitus, C.; Roussakis, C. *J. Am. Chem. Soc.* **1996**, *118*, 11085-11088.

² For the reassignment of C-20 and C-21, see Paterson, I; Davies, R. D. M.; Marquez, R. *Angew. Chem. Int. Ed.* **2001**, *40*, 603-607.

7'	161.2	161.2
8'(C3'-Me)	23.0	23.2
OMe(C2')	62.0	62.1
NH

¹H NMR (400 MHz, CDCl₃)

^{13}C NMR (75 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

¹³C NMR (75 MHz, CDCl₃)

¹H NMR (400 MHz, CDCl₃)

S31

^{13}C NMR (75 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

^{13}C NMR (75 MHz, CDCl_3)

^1H NMR (400 MHz, CDCl_3)

¹³C NMR (75 MHz, CDCl₃)