

Alcohol 11 : To a stirred solution of alkene **10** (2.44 g, 8.53 mmol in dry THF (54 mL) cooled at 0 °C was added a 0.5 M solution of 9-BBN in THF (68 mL, 34 mmol). The reaction mixture was stirred at 0 °C for 1 h and at room temperature for 15 h. After the solution was re-cooled to 0 °C, 10 mL of ethanol, 34 mL of a saturated aqueous sodium acetate and 11 mL of 30% hydrogen peroxide were added in that order. The mixture was stirred at 0 °C for 1 h and at room temperature for 5 h, then the solution was diluted with 300 mL of ether, washed with 2 × 150 mL of water, 150 mL of saturated aqueous sodium bicarbonate, and 150 mL of saturated aqueous ammonium chloride, dried (Na₂SO₄) and then concentrated. The residual oil was purified by column chromatography on silica gel (200 g, CHCl₃-EtOAc, 32:1→16:1→8:1→4:1→0:1) and by column chromatography on silica gel (100 g, hexane-CHCl₃-EtOAc, 20:1:1→20:2:1→0:0:1) to give **11** (2.57 g, 99%) as a colorless oil: IR (CHCl₃) 3600-3280 (br), 1258, 1080, 838 cm⁻¹; ¹H-NMR (270 MHz, CDCl₃) [noted only the signal of major diastereomer] δ 3.93-3.87 (m, 2 H), 3.74 (d, *J* = 4.0 Hz, 2 H), 3.96-3.64 (m, 2 H), 2.82 (dd, *J* = 6.6, 5.0 Hz, 1 H), 1.94 (m, 1 H), 1.42 (s, 3 H), 1.38 (s, 3 H), 0.94 (d, *J* = 6.9 Hz, 3 H), 0.90 (s, 9 H), 0.08 (s, 6 H); ¹³C-NMR (67.8 MHz, CDCl₃) [noted only the signal of major diastereomer] δ 108.8, 82.7, 80.5, 66.9, 64.3, 38.5, 27.4, 27.1 (2C), 25.9 (3C), 18.4, 13.3, -5.4, -5.5; MS (FAB) *m/z* 327 (M+Na)⁺. HRMS (FAB) calcd for C₁₅H₃₂O₄SiNa [(M+Na)⁺] 327.1968, found 327.1951.

Acetylene 15 : To a solution of alcohol **6** (15.4 mg, 45.5 μmol) and 2,6-di-*tert*-butyl-4-methylpyridine (40.6 mg, 198 μmol) in dry CH₂Cl₂ (0.70 mL) cooled to -30 °C was added trifluoromethanesulfonic anhydride (0.020 mL, 118 μmol). The reaction mixture was warmed to -10 °C and stirred at -10 °C for 40 min, and then the mixture was concentrated *in vacuo* to give the clear oil of the desired triflate.

To a solution of 4-*t*-butyldimethylsilyloxy-1-butyne (103 mg, 559 μmol) in dry THF (3.5 mL) cooled at -78 °C were added HMPA (0.0080 mL, 1.04 mmol) and a 1.56 M solution of *n*-BuLi (0.30 mL, 468 μmol) in hexane. The mixture was stirred at -78 °C for 30 min, warmed to -35 °C, and kept at this temperature for 10 min. In the meantime, the triflate described above was dissolved in dry THF (0.8 mL), and the resulting solution was added dropwise to the acetylide solution at -35 °C. This solution was allowed to warm to room temperature over 5 h. The reaction was quenched with 1:1 saturated aqueous ammonium chloride / water (3.0 mL) and extracted with EtOAc (3 × 5 mL). The combined extracts were washed with water (5 mL) and brine (5 mL), dried (Na₂SO₄), concentrated. The residual oil was purified by column chromatography on silica gel (14 g, hexane-EtOAc, 12:1→8:1→1:1→0:1) to give **15** (18.8 mg, 82%) as a colorless oil; [α]_D²⁸ +14 (c 0.21, CHCl₃); IR (CHCl₃) 1610, 1515, 1250, 1090, 840, 730 cm⁻¹; ¹H-NMR (270 MHz, CDCl₃) δ 7.26 (br d, *J* = 8.6 Hz, 2 H), 6.87 (br d, *J* = 8.6 Hz, 2 H), 4.43 (s, 2 H), 3.88 (dt, *J* = 6.6, 5.3 Hz, 1 H), 3.80 (s, 3 H), 3.69 (t, *J* = 6.6 Hz, 1 H), 3.69 (t, *J* = 7.3 Hz, 2 H), 3.44 (t, *J* = 6.6 Hz, 2 H), 2.58-2.33 (m, 4 H), 1.80-1.46 (m, 4 H), 1.40 (s, 3 H), 1.38 (s, 3 H), 1.20 (m, 1 H), 0.94 (d, *J* = 6.6 Hz, 3 H), 0.89 (s, 9 H), 0.06 (s, 6 H); ¹³C-NMR (67.8 MHz, CDCl₃) δ 159.1, 130.7, 129.2 (2C), 113.8 (2C), 108.4, 84.3, 79.2, 77.1, 72.6, 70.3, 62.2, 55.3, 35.7, 28.9, 27.5, 27.4, 27.3, 25.9 (3C), 24.4, 23.2, 18.3, 15.8, -5.3 (2C); MS (FAB) *m/z* 527 (M+Na)⁺; HRMS(FAB) calcd for C₂₉H₄₈O₅SiNa [(M+Na)⁺] 527.3169, found 527.3170.

Attenol A (1) and Attenol B (2) : To a stirred solution of ketone **3** (10.7 mg, 18.0 μmol) in MeOH (0.5 mL) was added pyridium *p*-toluenesulfonate (10.1 mg, 40.2 μmol) and stirred at room temperature for 84 h. The reaction mixture was diluted with triethylamine (0.8 mL) and concentrated. The residual oil was purified by column chromatography on silica gel (2 g, Benzene-Acetone, 8:1→6:1→3:1→2:1→0:1) to give Attenol A (**1**) (4.5 mg, 65%) and Attenol B

(2) (1.1 mg, 17%) as a colorless oil; **1**: $[\alpha]_D^{28}$ -9.7 ° (c 0.35, CHCl₃); IR (CHCl₃) 3460, 1460, 1440 cm⁻¹; ¹H-NMR (800 MHz, CDCl₃) δ 5.81 (ddt, *J* = 17.0, 10.2, 6.0 Hz, 1 H), 5.69 (m, 1 H), 5.54 (m, 1 H), 5.01 (br. d, *J* = 17.0 Hz, 1 H), 4.96 (br. d, *J* = 10.2 Hz, 1 H), 4.32 (m, 1 H), 3.83 (m, 1 H), 3.72 (br. s, 1 H, OH), 3.72-3.68 (m, 2 H), 3.65 (m, 1H), 3.32 (dd, *J* = 10.1, 1.5 Hz, 1 H), 2.58 (br. s, 1 H, OH), 2.52 (br. dt, *J* = 14.3, 8.8 Hz, 1 H), 2.42 (m, 1 H), 2.29 (m, 1 H), 2.14-2.08 (m, 3 H), 2.04-1.99 (m, 2 H), 1.84 (m, 1 H), 1.77-1.70 (m, 5 H), 1.66-1.64 (m, 2 H), 1.60-1.42 (m, 6 H), 0.88 (d, *J* = 6.2 Hz, 3 H); ¹³C-NMR (201 MHz, CDCl₃) δ 138.7, 129.6, 128.0, 114.6, 106.4, 78.04, 77.98, 70.1, 69.6, 62.0, 43.6, 38.5, 36.6, 33.9, 33.7, 33.0, 30.9, 30.8, 30.4, 29.0, 25.1, 17.3; MS (FAB) *m/z* 405 (M+Na)⁺; HRMS (FAB) calcd for C₂₂H₃₈O₅Na [(M+Na)⁺] 405.2617, found 405.2635. **2**: $[\alpha]_D^{29}$ +34 ° (c 0.073, CHCl₃); IR (CHCl₃) 3400, 1460, 1440 cm⁻¹; ¹H-NMR (600 MHz, CDCl₃) δ 5.81 (ddt, *J* = 17.2, 10.2, 6.8 Hz, 1 H), 5.56-5.49 (m, 2 H), 5.02 (br. d, *J* = 17.2 Hz, 1 H), 4.95 (br. d, *J* = 10.2 Hz, 1 H), 4.09 (t, *J* = 6.8 Hz, 1 H), 4.04 (br. s, 1 H, OH), 4.00-3.83 (m, 2 H), 3.93 (s, 1 H), 3.63-3.59 (m, 2H), 3.39 (br. s, 1 H, OH), 2.62 (br. s, 1 H, OH), 2.44-2.35 (m, 2 H), 2.35-2.24 (m, 2 H), 2.10-2.04 (m, 2 H), 2.02 (m, 1 H), 1.94-1.75 (m, 3 H), 1.75-1.48 (m, 8 H), 1.48-1.40 (m, 2 H), 1.34 (dd, *J* = 15.2, 5.7 Hz, 1 H), 1.11 (d, *J* = 7.1 Hz, 3 H); ¹³C-NMR (201 MHz, CDCl₃) δ 138.8, 128.5, 127.8, 114.5, 109.6, 83.1, 80.1, 70.2, 69.2, 61.9, 42.5, 36.9, 34.5, 33.74, 33.69, 31.3, 31.2, 30.3 (2C), 25.0, 23.1, 16.9; MS (FAB) *m/z* 405 (M+Na)⁺; HRMS(FAB) calcd for C₂₂H₃₈O₅Na [(M+Na)⁺] 405.2617, found 405.2636.

¹H NMR data for all new compounds

silyl ether : ¹H-NMR (270 MHz, CDCl₃) δ 3.98 (dt, *J* = 7.9, 4.6 Hz, 1 H), 3.91-3.84 (m, 2 H), 3.80-3.63 (m, 3 H), 2.36 (dd, *J* = 7.9, 4.6 Hz, 1 H), 1.41 (s, 3 H), 1.40 (s, 3 H), 0.90 (s, 9 H), 0.08 (s, 6 H).

8 : ¹H-NMR (270 MHz, CDCl₃) δ 9.77 (d, *J* = 1.7 Hz, 1 H), 4.33 (dd, *J* = 7.3, 1.7 Hz, 1 H), 4.12 (dt, *J* = 7.3, 4.3 Hz, 1 H), 3.80 (d, *J* = 4.3 Hz, 2 H), 1.47 (s, 3 H), 1.39 (s, 3 H), 0.90 (s, 9 H), 0.08 (s, 6 H).

9 : ¹H-NMR (270 MHz, CDCl₃) δ 4.31 (d, *J* = 7.6 Hz, 1 H), 4.05 (ddd, *J* = 8.1, 7.6, 7.3 Hz, 1 H), 3.87 (dd, *J* = 11.3, 8.1 Hz, 1 H), 3.75 (dd, *J* = 11.3, 7.3 Hz, 1 H), 2.28 (s, 3 H), 1.45 (s, 3 H), 1.42 (s, 3 H), 0.90 (s, 9 H), 0.08 (s, 6 H).

10 : ¹H-NMR (270 MHz, CDCl₃) δ 5.05 (br s, 1 H), 4.95 (br s, 1 H), 4.36 (d, *J* = 8.3 Hz, 1 H), 3.85-3.66 (m, 3 H), 1.78 (s, 3 H), 1.44 (s, 3 H), 1.42 (s, 3 H), 0.90 (s, 9 H), 0.07 (s, 6 H).

aldehyde : ¹H-NMR (270 MHz, CDCl₃) δ 9.78 (d, *J* = 2.3 Hz, 0.89 H), 9.74 (d, *J* = 1.3 Hz, 0.11 H), 4.14 (dd, *J* = 7.3, 6.3 Hz, 1 H), 4.00-3.68 (m, 3 H), 2.62 (m, 1 H), 1.39 (s, 6 H), 1.16 (d, *J* = 6.9 Hz, 3 H), 0.90 (s, 9 H), 0.07 (s, 6 H).

12 : ¹H-NMR (270 MHz, CDCl₃) δ 7.01 (dd, *J* = 15.8, 7.9 Hz, 0.87 H), 6.91 (dd, *J* = 15.8, 7.9 Hz, 0.13 H), 5.87 (dd, *J* = 15.8, 1.0 Hz, 0.13 H), 5.84 (d, *J* = 15.8, 1.0 Hz, 0.87 H), 4.19 (q, *J* = 6.9 Hz, 2 H), 3.94-3.62 (m, 4 H), 2.61 (m, 1 H), 1.379 (s, 3 H), 1.377 (s, 3 H), 1.29 (t, *J* = 6.9 Hz, 3 H), 1.15 (d, *J* = 6.9 Hz, 3 H), 0.90 (s, 9 H), 0.07 (s, 6 H).

13 : ¹H-NMR (270 MHz, CDCl₃) δ 4.12 (q, *J* = 6.9 Hz, 2 H), 3.86 (dt, *J* = 6.9, 4.0 Hz, 1 H), 3.76 (t, *J* = 6.9 Hz, 1 H), 3.73 (dd, *J* = 10.9, 4.0 Hz, 1 H), 3.67 (dd, *J* = 10.9, 4.0 Hz, 1 H), 2.43-2.28 (m, 2 H), 1.96 (m, 1 H), 1.72 (m, 1 H), 1.48 (m, 1 H), 1.39 (s, 3 H), 1.37 (s, 3 H), 1.25 (t, *J* = 6.9 Hz, 3 H), 0.93 (d, *J* = 6.9 Hz, 3 H), 0.90 (s, 9 H), 0.07 (s, 6 H).

14 : $^1\text{H-NMR}$ (270 MHz, CDCl_3) δ 3.85 (dt, $J = 6.9, 4.3$ Hz, 1 H), 3.78-3.68 (m, 5 H), 1.78-1.64 (m, 2 H), 1.63-1.48 (m, 2 H), 1.39 (s, 3 H), 1.37 (s, 3 H), 1.24 (m, 1 H), 0.94 (d, $J = 6.9$ Hz, 3 H), 0.90 (s, 9 H), 0.07 (s, 6 H).

p-methoxybenzyl ether : $^1\text{H-NMR}$ (270 MHz, CDCl_3) δ 7.26 (br d, $J = 8.6$ Hz, 2 H), 6.87 (br d, $J = 8.6$ Hz, 2 H), 4.43 (s, 2 H), 3.80 (s, 3 H), 3.85-3.41 (m, 6 H), 1.80-1.51 (m, 4 H), 1.38 (s, 3 H), 1.37 (s, 3 H), 1.21 (m, 1 H), 0.92 (d, $J = 6.9$ Hz, 3 H), 0.89 (s, 9 H), 0.08 (s, 6 H).

6 : $^1\text{H-NMR}$ (270 MHz, CDCl_3) δ 7.26 (br d, $J = 8.6$ Hz, 2 H), 6.87 (br d, $J = 8.6$ Hz, 2 H), 4.43 (s, 2 H), 3.90 (ddd, $J = 7.6, 5.3, 3.0$ Hz, 1 H), 3.80 (s, 3 H), 3.78 (ddd, $J = 11.9, 6.3, 3.0$ Hz, 1 H), 3.68 (t, $J = 7.6$ Hz, 1 H), 3.58 (ddd, $J = 11.9, 6.3, 5.3$ Hz, 1 H), 3.44 (t, $J = 6.3$ Hz, 2 H), 1.92 (t, $J = 6.3$ Hz, 1 H), 1.78-1.51 (m, 4 H), 1.40 (s, 6 H), 1.22 (m, 1 H), 0.91 (d, $J = 6.9$ Hz, 3 H).

16 : $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 7.26 (br d, $J = 8.3$ Hz, 2 H), 6.87 (br d, $J = 8.3$ Hz, 2 H), 5.57 (m, 1 H), 5.51 (m, 1 H), 4.43 (s, 2 H), 3.83 (td, $J = 7.1, 4.2$ Hz, 1 H), 3.80 (s, 3 H), 3.61 (t, $J = 7.1$ Hz, 2 H), 3.51 (t, $J = 7.1$ Hz, 1 H), 3.44 (t, $J = 6.6$ Hz, 2 H), 2.42-2.22 (m, 4 H), 1.78-1.42 (m, 4 H), 1.38 (s, 3 H), 1.36 (s, 3 H), 1.22 (m, 1 H), 0.92 (d, $J = 6.8$ Hz, 3 H), 0.89 (s, 9 H), 0.05 (s, 6 H).

17 : $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 5.61-5.49 (m, 2 H), 3.84 (dt, $J = 4.2, 7.3$ Hz, 1 H), 3.64-3.50 (m, 2 H), 3.62 (t, $J = 7.1$ Hz, 1 H), 3.52 (t, $J = 7.1$ Hz, 1 H), 2.42-2.22 (m, 4 H), 1.76-1.49 (m, 4 H), 1.46 (br s, 1 H), 1.38 (s, 3 H), 1.37 (s, 3 H), 1.22 (m, 1 H), 0.93 (d, $J = 6.9$ Hz, 3 H), 0.90 (s, 9 H), 0.05 (s, 6 H).

5 : $^1\text{H-NMR}$ (270 MHz, CDCl_3) δ 9.78 (t, $J = 2.0$ Hz, 1 H), 5.63-5.47 (m, 2 H), 3.85 (dt, $J = 4.6, 7.3$ Hz, 1 H), 3.62 (t, $J = 7.3$ Hz, 2 H), 3.49 (t, $J = 7.3$ Hz, 1 H), 2.62-2.24 (m, 4 H), 2.05-1.83 (m, 2 H), 1.72-1.48 (m, 2 H), 1.40 (s, 3 H), 1.38 (s, 3 H), 1.26 (m, 1 H), 0.92 (d, $J = 6.6$ Hz, 3 H), 0.89 (s, 9 H), 0.05 (s, 6 H).

19 : $^1\text{H-NMR}$ (270 MHz, CDCl_3) δ 5.79 (ddt, $J = 16.8, 11.2, 6.6$ Hz, 1 H), 5.02 (br d, $J = 16.8$ Hz, 1 H), 4.95 (br d, $J = 11.2$ Hz, 1 H), 4.05 (t, $J = 6.9$ Hz, 1 H), 2.94-2.78 (m, 4 H), 2.17-2.04 (m, 3 H), 1.94-1.71 (m, 3 H), 1.68-1.58 (m, 2 H).

alcohol : $^1\text{H-NMR}$ (270 MHz, CDCl_3) δ 7.38-7.26 (m, 5 H), 5.79 (ddt, $J = 16.8, 11.2, 6.6$ Hz, 1 H), 5.02 (br d, $J = 16.8$ Hz, 1 H), 4.97 (br d, $J = 11.2$ Hz, 1 H), 4.58 (s, 2 H), 4.15 (m, 1 H), 3.45 (d, $J = 5.6$ Hz, 1 H), 3.17 (d, $J = 2.6$ Hz, 1 H), 3.01-2.72 (m, 4 H), 2.25 (dd, $J = 15.2, 8.3$ Hz, 1 H), 2.15-1.84 (m, 7 H), 1.72-1.48 (m, 2 H).

20 : $^1\text{H-NMR}$ (270 MHz, CDCl_3) δ 7.39-7.26 (m, 5 H), 5.75 (ddt, $J = 16.8, 11.2, 6.6$ Hz, 1 H), 5.05-4.95 (m, 2 H), 4.55 (s, 2 H), 4.26 (m, 1 H), 3.49 (dd, $J = 9.6, 4.6$ Hz, 1 H), 3.44 (dd, $J = 9.6, 5.9$ Hz, 1 H), 2.99 (d, $J = 4.3$ Hz, 1 H), 2.66 (dd, $J = 16.8, 6.9$ Hz, 1 H), 2.58 (dd, $J = 16.8, 5.0$ Hz, 1 H), 2.45 (t, $J = 7.3$ Hz, 2 H), 2.05 (br q, $J = 6.6$ Hz, 2 H), 1.73-1.62 (m, 6 H).

21 : $^1\text{H-NMR}$ (270 MHz, CDCl_3) δ 7.39-7.26 (m, 5 H), 5.80 (ddt, $J = 13.5, 10.2, 6.6$ Hz, 1 H), 5.00 (br d, $J = 13.5$ Hz, 1 H), 4.95 (br d, $J = 10.2$ Hz, 1 H), 4.56 (s, 2 H), 4.30 (m, 1 H), 3.90 (m, 1 H), 3.50 (dd, $J = 9.2, 3.6$ Hz, 1 H), 3.43 (dd, $J = 9.2, 7.6$ Hz, 1 H), 2.73 (d, $J = 4.0$ Hz, 1 H),

2.43 (d, $J = 4.6$ Hz, 1 H), 2.07 (br q, $J = 6.6$ Hz, 2 H), 1.70-1.37 (m, 6 H).

acetone : $^1\text{H-NMR}$ (270 MHz, CDCl_3) δ 7.35-7.26 (m, 5 H), 5.80 (ddt, $J = 13.5, 10.2, 6.6$ Hz, 1 H), 5.02 (br d, $J = 13.5$ Hz, 1 H), 4.94 (br d, $J = 10.2$ Hz, 1 H), 4.62 (d, $J = 12.2$, 1 H), 4.55 (d, $J = 12.2$, 1 H), 3.77 (m, 1 H), 3.50 (dd, $J = 10.6, 4.3$ Hz, 1 H), 3.43 (dd, $J = 10.6, 6.6$ Hz, 1 H), 2.06 (br q, $J = 6.6$ Hz, 2 H), 1.71-1.34 (m, 6 H), 1.38 (s, 3 H), 1.37 (s, 3 H).

22 : $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 5.80 (ddt, $J = 17.1, 10.5, 6.6$ Hz, 1 H), 5.00 (br d, $J = 17.1$, 1 H), 4.95 (br d, $J = 10.5$, 1 H), 3.95 (m, 1 H), 3.76 (m, 1 H), 3.62 (ddd, $J = 11.6, 7.8, 3.6$ Hz, 1 H), 3.51 (ddd, $J = 11.6, 7.8, 3.8$ Hz, 1 H), 2.06 (br q, $J = 2$ H), 1.95 (br s, 1 H), 1.65 (ddd, $J = 12.3, 9.3, 5.6$ Hz, 1 H), 1.56-1.40 (m, 4 H), 1.38 (s, 3 H), 1.36 (s, 3 H).

4 : $^1\text{H-NMR}$ (270 MHz, CDCl_3) δ 7.94-7.90 (m, 2 H), 7.70-7.54 (m, 3 H), 5.79 (ddt, $J = 17.2, 10.2, 6.6$ Hz, 1 H), 4.99 (m, 1 H), 4.94 (m, 1 H), 4.14-3.69 (m, 2 H), 3.31 (ddd, $J = 14.2, 10.6, 5.3$ Hz, 1 H), 3.09 (ddd, $J = 14.2, 10.2, 5.3$ Hz, 1 H), 2.10-2.00 (m, 2 H), 2.00-1.79 (m, 2 H), 1.64-1.22 (m, 6 H), 1.28 (s, 3 H), 1.27 (s, 3 H).

3 : $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ 5.80 (ddt, $J = 17.1, 10.3, 6.8$ Hz, 1 H), 5.59-5.49 (m, 2 H), 5.00 (br d, $J = 17.1$ Hz, 1 H), 4.94 (br d, $J = 10.3$ Hz, 1 H), 3.84 (dt, $J = 4.2, 7.3$ Hz, 1 H), 3.79-3.69 (m, 2 H), 3.61 (t, $J = 7.1$ Hz, 2 H), 3.48 (t, $J = 7.1$ Hz, 1 H), 2.59-2.25 (m, 8 H), 2.05 (br. q, $J = 6.8$ Hz, 2 H), 1.92-1.25 (m, 11 H), 1.37 (s, 3 H), 1.36 (s, 3 H), 1.32 (s, 3 H), 1.31 (s, 3 H), 0.90 (d, $J = 4.9$ Hz, 3 H), 0.89 (s, 9 H), 0.05 (s, 6 H).