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Synthesis of epoxide 10 from *S*-(+)-carvone. A solution of 4 N NaOH (48 mL, 192.0 mmol, 0.3 equiv) was slowly added to a solution of *S*-(+)-carvone (100.0 g, 665 mmol, 1.0 equiv) in MeOH (1000 mL) at 0 °C, followed by the dropwise addition of 35% hydrogen peroxide solution (70.0 mL, 792.6 mmol, 1.2 equiv) over 3 h. After the reaction was complete as established by TLC analysis, it was quenched by the slow addition of saturated Na₂SO₃ solution (200 mL) and extracted with CH₂Cl₂ (3 x 300 mL). The organic extracts were dried over Na₂SO₄ and concentrated to afford the carvone epoxide product which was used without further purification. A solution of this epoxide (101.8 g, 612.4 mmol, 1.0 equiv) and PtO₂ (0.72 g, 3.18 mmol, 0.095 equiv) in EtOH (500 mL) was stirred under a hydrogen atmosphere (1 atm) at 25 °C for 12 h. The reaction mixture was then filtered through a celite pad eluting with Et₂O and concentrated. The crude product was purified by flash chromatography (silica gel, 5% EtOAc in hexane) to afford epoxide **10** (97.8 g, 87%, two steps) as a colorless oil. *R*_f = 0.40 (silica gel, EtOAc-hexane, 1:10); FT-IR (neat) ν_{max} 2959, 2873, 1708, 1466, 1438, 1369, 1111, 884, 814 cm⁻¹; ¹H NMR²⁶ (400 MHz, CDCl₃) δ 3.36 (d, *J* = 3.2 Hz, 1 H, C-12), 2.45 (ddd, *J* = 17.0, 4.0, 1.6 Hz, 1 H, C-1), 2.25 (ddd, *J* = 14.4, 6.0, 3.1 Hz, 1 H, C-1), 1.83 (m, 1 H, C-14), 1.77 (dd, *J* = 14.9, 11.2 Hz, 1 H, C-13), 1.62 (dd, *J* = 14.8, 10.6 Hz, 1 H, C-13), 1.41 (sept, *J* = 6.6 Hz, 1 H, C-18), 1.36 (s, 3 H, C-17), 0.84 (d, *J* = 6.8 Hz, 3 H, C-19 or C-20), 0.82 (d, *J* = 6.8 Hz, 3 H C-19 or C-20); ¹³C NMR (100.6 MHz, CDCl₃) δ 206.5, 61.4, 58.8, 40.6, 33.7, 31.7, 27.1, 19.6, 19.5, 15.2.

Synthesis of 11 through a formaldehyde aldol reaction. To a solution of diisopropylamine (14.06 mL, 107.26 mmol, 1.2 equiv) in THF (400 mL) at -78 °C was added a solution of 1.6 M *n*-BuLi in hexanes (67.1 mL, 107.3 mmol, 1.2 equiv). The reaction was then allowed to warm-up to 0 °C and stirred for 30 min after which a solution of ketone **10** (15.0 g, 89.2 mmol, 1.0 equiv) in THF (100 mL) was added dropwise via cannula at -78 °C over 1.5 h and stirring continued for 30 min thereafter. A solution of formaldehyde, prepared by cracking paraformaldehyde (33.0 g, 1.10 mol, 12.2 equiv) at 140 °C and bubbling the resulting gas through THF (500 mL) at -78 °C for 45 min, was added to the enolate solution via cannula over 1 h at -78 °C. The reaction mixture was then allowed to warm to 0 °C, quenched by addition of saturated NH₄Cl solution (100 mL), and extracted with ether (3 x 300 mL). The combined organic extracts were dried over Na₂SO₄ and concentrated. The crude product was filtered through a short pad of silica and eluted with 10% EtOAc in hexane to afford the corresponding alcohol (*ca.* 10.9 g, *ca.* 63%). To a solution of this alcohol (10.9 g, 55.0 mmol, 1.0 equiv), triethylamine (46 mL, 330 mmol, 6.0 equiv), and 4-DMAP (328 mg, 2.68 mmol, 0.05 equiv) in CH₂Cl₂ (200 mL) at 0 °C was added TBSCl (9.9 g, 66.0 mmol, 1.2 equiv). The reaction mixture was stirred at 25 °C for 12 h and, after the end of the reaction was established by TLC analysis, quenched via addition of MeOH (10 mL) and water (100 mL). The organic layer was separated, dried over Na₂SO₄ and concentrated. The crude product was purified by flash chromatography (silica gel, 3% EtOAc in hexane) to afford silyl ether **11** (8.21 g, 53%, two steps). *R*_f = 0.70 (silica gel, EtOAc-hexane, 1:10); FT-IR (neat) ν_{max} 2958, 2931, 2856, 1705, 1471, 1254, 1109, 882, 835, 777 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 3.95 (dd, *J* = 9.9, 4.4 Hz, 1 H, C-2), 3.74 (dd, *J* = 9.9, 5.1 Hz, 1 H, C-2), 3.37 (d, *J* = 3.5 Hz, 1 H, C-12), 2.19-2.07 (m, 2 H), 2.01-1.96 (m, 1 H), 1.80-1.77 (m, 1 H), 1.61 (dd, *J* = 14.3, 11.8 Hz, 1 H), 1.36 (s, 3 H, C-17), 0.91 (d, *J* = 6.9 Hz, 3 H, C-19 or C-20), 0.83 (s, 9 H, TBS), 0.73 (d, *J* = 6.9 Hz, 3 H, C-19 or C-20), -0.01 (s, 3 H, TBS), -0.03 (s, 3 H, TBS); ¹³C NMR (100.6 MHz, CDCl₃) δ 208.5, 62.0, 61.9, 59.8, 53.3, 35.2,

28.5, 25.7, 22.5, 20.9, 18.1, 16.5, 15.5, -5.6; HRMS (FAB) calcd for $C_{17}H_{33}O_3Si$
($M+H^+$): 313.2199, found 313.2210.

Synthesis of 12 through enantioselective reduction of ketone 11. To a solution of ketone **11** (19.2 g, 61.4 mmol) in THF (300 mL) at -78 °C was added 1.0 M L-Selectride in THF (73.7 mL, 73.7 mmol, 1.2 equiv) via cannula over 1.5 h. The reaction mixture was stirred at the same temperature for an additional 30 min and, after the complete consumption of the starting ketone was established by TLC, quenched by addition of saturated NH₄Cl solution (100 mL) and allowed to warm to 0 °C. Excess 35% hydrogen peroxide (8.0 mL, 79.8 mmol, 1.3 equiv) solution was then added and the mixture was stirred at 0 °C for 1 h. The reaction mixture was extracted with EtOAc (3 x 200 mL) and the organic extracts were dried over Na₂SO₄ and concentrated. The crude product was purified by flash chromatography (silica gel, 5% EtOAc in hexane) to afford the secondary alcohol **12** (18.0 g, 93%) as a light yellow colored oil. *R_f* = 0.32 (silica gel, EtOAc-hexane, 1:10); FT-IR (neat) 3553, 3506, 2955, 2882, 1471, 1436, 1388, 1266, 1255, 1092, 1068, 1006, 960, 905, 836, 776 cm⁻¹; ¹H NMR (400 MHz, CDCl₃) δ 4.09 (dd, *J* = 8.6, 3.8 Hz, 1 H, C-10), 3.62 (m, 2 H, C-2), 3.20 (m, 1 H, C-12), 2.43 (d, *J* = 8.6 Hz, 1 H, OH), 2.02 (m, 1 H), 1.66 (m, 1 H), 1.48-1.30 (m, 3 H), 1.43 (s, 3 H, C-17), 0.88 (s, 9 H, TBS), 0.86 (d, *J* = 6.8 Hz, 3 H, C-19 or C-20), 0.74 (d, *J* = 6.8 Hz, 3 H, C-19 or C-20), 0.04 (s, 6 H); ¹³C NMR (100.6 MHz, CDCl₃) δ 68.6, 62.2, 61.6, 60.2, 43.6, 30.3, 25.9, 25.8, 24.1, 22.1, 20.9, 18.2, 15.4, -5.5; HRMS (FAB) calcd for C₁₇H₃₄O₃Si (M+H⁺): 315.2355, found 315.2349.

Synthesis of allylic alcohol 13 via the corresponding mesylate. To a solution of alcohol **12** (29.0 g, 92.2 mmol, 1.0 equiv) and triethylamine (33.8 mL, 243.0 mmol, 2.6 equiv) in CH_2Cl_2 (250 mL) at 0 °C was added methanesulfonyl chloride (8.2 mL, 106.3 mmol, 1.15 equiv) dropwise over 1 h. The reaction mixture was stirred at 0 °C for 2 h (the progress of the reaction was monitored by TLC), quenched by addition of brine, and extracted with EtOAc (3 x 300 mL). The combined organic extracts were dried over Na_2SO_4 and concentrated. The product was filtered through a short pad of silica gel eluting with ether to afford the expected mesylate which was immediately used for the next step without further purification. To a solution of $\text{NaC}_{10}\text{H}_8$, prepared by the addition of Na-metal (12.3 g, 535.6 mmol, 5.8 equiv) to naphthalene (80.3 g, 627.1 mmol, 6.8 equiv) in THF (1800 mL) and allowing the mixture to stir for 2 h, was added a solution of the mesylate in THF (300 mL) dropwise via cannula at 0 °C. The reaction mixture was stirred for 30 min (TLC monitoring), quenched by addition of saturated NH_4Cl solution (200 mL), treated with brine and extracted with EtOAc (3 x 300 mL). The organic extracts were dried over Na_2SO_4 and concentrated. The crude product was purified by flash chromatography (silica gel, 10% EtO₂ in hexane followed by 10% EtOAc in hexane) to afford allylic alcohol **13** (24.2 g, 85%, two steps) as a colorless oil. R_f = 0.53 (silica gel, EtOAc-hexane, 1:3); FT-IR (neat) ν_{max} 3351, 2956, 2931, 2857, 1468, 1254, 1095, 1058, 837, 776 cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 5.45-5.43 (m, 1 H, C-10), 3.93 (t, J = 3.6 Hz, 1 H, C-12), 3.63 (dd, J = 9.7, 4.6 Hz, 1 H, C-2), 3.43 (dd, J = 9.7, 6.0 Hz, 1 H, C-2), 2.03 (br-s, 1 H, OH), 1.85-1.78 (m, 1 H), 1.77 (t, J = 1.7 Hz, 3 H), 1.75-1.63 (m, 2 H), 1.53-1.40 (m, 2 H), 0.91 (d, J = 6.8 Hz, 3 H, C-19 or C-20), 0.86 (s, 9 H, TBS), 0.79 (d, J = 6.8 Hz, 3 H, C-19 or C-20), 0.02 (s, 3 H, TBS), 0.01 (s, 3 H, TBS); ^{13}C NMR (100.6 MHz, CDCl_3) δ 136.4, 127.2, 68.0, 65.4, 41.1, 35.1, 30.5, 27.9, 25.9, 21.4, 20.8, 18.3, 17.4, -5.3, -5.4; HRMS (FAB) calcd for $\text{C}_{17}\text{H}_{34}\text{NaO}_2\text{Si}$ ($\text{M}+\text{Na}^+$): 321.2226, found 321.2219; $[\alpha]_{\text{D}}^{25}$ +32.6 (c 1.1, CHCl_3).