Supplementary Information for

Total Synthesis of (±)-Pallambins C and D

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General Information

Unless stated otherwise, all reactions were carried out under an argon atmosphere under anhydrous conditions and all reagents were purchased from commercial suppliers without further purification. Solvent drying by standard methods were employed when necessary. The plates used for thin-layer chromatography (TLC) were E. Merck silica gel 60F254 (0.24 nm thickness) precoat ed on aluminum plates, and then visualized under UV light (365 nm and 254 nm) or through staining with a 5% of dodecamolybdophosphoric acid in ethanol and subsequent heating. Column chromatography was performed using E. Merck silica gel (230-400 mesh). Melting points were measured on an Electrothermal 9100 apparatus without correction. NMR spectra were recorded on a Bruker Advance III 400 spectrometer (400.00 MHz for 1H and 100 MHz for 13C) and a Bruker 400 MHz NMR AV400Q (400.00 MHz for 1H and 100 MHz for 13C) at room temperature. Solvent signal was used as reference for 1H, 13C NMR (CDCl3, 7.26, 77.16 ppm; C6D6, 7.16, 128.06 ppm). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, dd = double doublet, td = triple doublet, dt = double triplet, dq = double quartet, m = multiplet. Mass spectra (ESI, EI and FAB) were obtained with a ThermoFinnigan MAT 95 XL spectrometer and determined at an ionized voltage of 70 eV unless otherwise mentioned. Elemental analyses were performed at Shanghai Institute of Organic Chemistry, The Chinese Academy of Sciences, China. Infrared spectra (IR) were recorded on a Perkin Elmer (Spectrum One) FT-IR spectrometer.
Experimental details and characteristic data for compounds

From Wieland-Miescher ketone to 11

Synthesis of compound 6

To a stirred solution of (±)-Wieland-Miescher ketone (12.0 g, 67.4 mmol) and CeCl₃•7H₂O (37.6 g, 101 mmol) in MeOH (250 mL) at -78 °C was added NaBH₄ (5.1 g, 13.5 mmol) in one portion. The reaction was stirred for 20 min at -78 °C and warmed up to rt, filtered through Celite. The filtered cake was washed with MeOH (200 mL x 2). After evaporation, the residue was partitioned between EA (500 mL) and saturated NH₄Cl (500 mL), and the aqueous phase was extracted with EA (300 mL x 3). The combined organic phase was dried over Na₂SO₄, and evaporated to give a residue, which was purified by a flash column (silical gel, Hex/EA = 2:1) to afford 6 (10.6 g, 86%) as a white solid. mp 151.0-152.0 °C. ¹H NMR (400 MHz, CDCl₃) δ = 5.41 (s, 1H), 4.18 (brs, 1H), 3.29-3.24 (m, 1H), 2.18-2.10 (m, 1H), 2.01-1.93 (m, 2H), 1.86-1.75 (m, 3H), 1.61-1.54 (m, 1H), 1.48-1.43 (m, 4H), 1.34-1.23 (m, 1H), 1.07 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 144.92, 126.06, 79.22, 67.79, 40.76, 33.64, 31.46, 30.85, 29.00, 24.71, 16.92 ppm; IR (neat) 2934, 2860, 1658, 1445, 1050, 931 cm⁻¹; HRMS (EI) m/z Calcd for C₁₁H₁₈O₂ [M]⁺: 182.1301, found 182.1306.

Synthesis of compound 6a

To a stirred solution of compound 6 (14.2 g, 78 mmol) in DMF (160 mL) at was
added NaH (~60%, 12.5 g, 312 mmol) in portions 0 °C. The formed mixture was stirred for 30 min at the same temperature, and then BnBr (28 mL, 234 mmol) was added dropwise during 15 min. The reaction was allowed to warm to rt and stirred for 20 h. The reaction mixture was pre-cooled in ice bath and quenched with water (500 mL), extracted with EA (300 mL x 2), washed with brine (300 mL), dried over Na2SO4, concentrated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 100:1-50:1) to afford 6a (26.8 g, 95%) as a colorless oil.  

1H NMR (400 MHz, CDCl3) δ = 7.38-7.27 (m, 10H), 5.49 (s, 1H), 4.66 (d, J = 11.9 Hz, 1H), 4.62 (d, J = 11.9 Hz, 1H), 4.56 (d, J = 12.0 Hz, 1H), 4.43 (d, J = 11.9 Hz, 1H), 3.97-3.94 (m, 1H), 2.98 (dd, J = 4.2, 11.6 Hz, 1H), 2.21-2.15 (m, 1H), 2.04-1.96 (m, 4H), 1.82-1.79 (m, 1H), 1.60-1.54 (m, 2H), 1.38-1.31 (m, 1H), 1.26-1.17 (m, 1H), 1.15 (s, 3H); 13C NMR (100 MHz, CDCl3) δ = 145.59, 139.40, 139.14, 128.45, 128.35, 127.81, 127.56, 127.54, 127.45, 123.39, 86.46, 74.48, 71.44, 70.05, 41.13, 34.07, 31.78, 26.74, 25.35, 24.63, 17.99 ppm; IR (neat) 2937, 2860, 1658, 1453, 1358, 1094, 1070, 734, 696 cm⁻¹; HRMS (EI) m/z Calcd for C25H30O2 [M]+: 362.2240, found 362.2254.

Synthesis of compound 7

To a well stirred suspension of compound 6a (19.7 g, 54.4 mmol) and NaHCO3 (20 g, 238.1 mmol) in DCM (500 mL) was added mCPBA (~70%, 20 g, 81.4 mmol). The reaction was stirred for 3 h at rt, and then was partitioned with water (500 mL). The aqueous phase was extracted with DCM (300 mL), and the combined organic phase was washed with saturated NaHCO3 (300 mL) and brine (300 mL), dried over Na2SO4, evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 40:1-20:1) to afford 7 (17.7 g, 86%) as a colorless oil. 1H NMR (400 MHz, CDCl3) δ = 7.38-7.27 (m, 10H), 4.65 (d, J = 11.1 Hz, 1H), 4.63 (s, 2H), 4.44 (d, J = 11.8 Hz, 1H), 3.72 (dd, J = 7.8, 8.1 Hz, 1H), 3.37-3.33 (m, 1H), 3.04 (s, 1H), 2.04-1.98 (m, 2H), 1.94-1.89 (m, 1H), 1.76-1.73 (m, 1H), 1.65-1.56 (m, 3H), 1.53-1.43 (m, 1H), 1.32-1.24 (m, 1H), 1.19 (s, 3H), 0.96 (d, J = 14.4 Hz, 1H) ppm; 13C NMR (100 MHz, CDCl3) δ = 139.31, 138.33, 128.58, 128.35, 127.86, 127.53, 127.46, 83.69, 72.70, 71.68, 71.32, 66.62, 61.53, 38.88, 29.14, 27.56, 26.48, 24.07, 20.74, 16.25 ppm; IR (neat) 2948, 2868, 1605, 1497, 1454, 1360, 1093, 1073, 738, 702 cm⁻¹; HRMS (ESI) m/z Calcd for C25H30O3Na [M+Na]+: 401.2087, found 401.2100; Anal. Calcd for C25H30O3: C, 79.33; H, 7.99; found C, 79.28; H, 8.15.

Synthesis of compound 8
To a stirred solution of MeMgI in minimized amount of Et₂O [prepared from Mg turnings (5.5 g, 230 mmol) and MeI (13.7 mL, 220 mmol), and distilled off most of the solvent Et₂O] was added a solution of the epoxide above (16.8 g, 44.4 mmol) in benzene (300 mL), and the reaction was stirred under reflux for 12 h. After being cooled to 0 °C, the reaction was quenched with 5% HCl (500 mL), extracted with EA (300 mL x 2). The combined organic phase was washed with saturated NaHCO₃ (300 mL) and brine (300 mL), dried over Na₂SO₄, evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 20:1-10:1) to afford 8 (15.6 g, 89%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ = 7.37-7.27 (m, 10H), 4.61 (d, J = 11.8 Hz, 1H), 4.55 (d, J = 11.9 Hz, 1H), 4.49 (d, J = 11.9 Hz, 1H), 4.44 (d, J = 11.8 Hz, 1H), 4.09-4.04 (m, 1H), 3.56 (dd, J = 4.5, 11.5 Hz, 1H), 2.12-1.96 (m, 2H), 1.89-1.60 (m, 8H), 1.09 (s, 3H), 1.05 (d, J = 7.6 Hz, 3H), 0.74 (s, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 139.72, 139.32, 128.45, 128.31, 127.55, 127.47, 127.45, 127.32, 82.12, 78.91, 76.60, 71.89, 69.96, 45.71, 42.42, 32.81, 30.35, 26.26, 23.52, 19.05, 15.26, 10.33 ppm; IR (neat) 2939, 2867, 1496, 1453, 1386, 1364, 1095, 1071, 953, 735, 698 cm⁻¹; HRMS (ESI) m/z Calcd for C₂₆H₃₄O₃Na [M+Na]⁺: 417.2400, found 417.2390; Anal. Calcd for C₂₆H₃₄O₃: C, 79.15; H, 8.69; found C, 78.96; H, 8.92.

Synthesis of compound 9

To a stirred solution of compound 8 (18.3 g, 46.4 mmol) and pyridine (100 mL) in DCM (250 mL) at 0 °C was added a solution of SOCl₂ (10 mL, 138 mmol) in DCM (50 mL) dropwise during 10 min. The reaction was stirred for 30 min at the same temperature and quenched with ice water (500 mL). The aqueous phase was extracted with DCM (300 mL), and the combined organic phase was washed with 5% HCl (300 mL) and brine (300 mL), dried over Na₂SO₄, evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 100:1-50:1) to afford 9 (16.1 g, 92%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ = 7.42-7.32 (m, 10H), 5.42 (brs, 1H), 4.75 (d, J = 11.9 Hz, 1H), 4.65 (d, J = 11.9 Hz, 1H), 4.54 (d, J = 12.1 Hz, 1H), 4.50 (d, J = 12.0 Hz, 1H), 3.50-3.45 (m, 1H), 3.19 (dd, J = 3.1, 12.2 Hz, 1H), 2.91-2.84 (m, 1H), 2.25-2.10 (m, 3H), 2.00-1.68 (m, 4H), 1.28 (s, 3H), 1.26 (d, J = 7.5 Hz, 3H), 1.15 (dt, J = 3.9, 13.5 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 145.67, 139.42, 139.19, 128.39, 128.28, 127.47, 127.40, 127.34, 122.34, 85.61, 79.91, 71.20, 69.66, 41.55, 39.29, 36.53, 25.17, 23.19, 22.72, 20.64, 16.55 ppm; IR (neat) 2940, 2870, 1605, 1496, 1454, 1363, 1099, 1074, 1028, 734, 696 cm⁻¹; HRMS (ESI) m/z Calcd for C₂₆H₃₂O₃Na [M+Na]⁺: 399.2295, found 399.2286.

Synthesis of compound 9a
To a stirred solution of compound 9 (14.7 g, 39.1 mmol) in Et₂O (400 mL) was added BH₃•Me₂S (neat, 8 mL, 80 mmol) dropwise during 10 min. The reaction was stirred for 20 h at rt, and then was added water/THF (1:1,100 mL) slowly at -10 °C. NaOH (3M, 100 mL) and 30% H₂O₂ (50 mL) were added successively, and the formed mixture was stirred for 10 h at rt. Cooled to 0 °C, saturated Na₂S₂O₃ was added dropwise during 30 min, and the stirring continued for 30 min. The aqueous phase was extracted with Et₂O (300 mL), and the combined organic phase was washed with saturated NH₄Cl (300 mL) and brine (300 mL), dried over Na₂SO₄, evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EtO = 5:1) to afford 9a (12.6 g, 82%) as a colorless oil. ¹H NMR (400 MHz, CDCl₃) δ = 7.38-7.28 (m, 10H), 4.63 (d, J = 11.8 Hz, 1H), 4.61 (d, J = 11.8 Hz, 1H), 4.48 (d, J = 11.9 Hz, 1H), 4.41 (d, J = 11.8 Hz, 1H), 3.82 (dt, J = 4.1, 10.4 Hz, 1H), 3.42-3.37 (m, 1H), 2.89 (dd, J = 4.0, 11.4 Hz, 1H), 2.69-2.65 (m, 1H), 2.13-2.09 (m, 1H), 2.04-2.00 (m, 1H), 1.95-1.91 (m, 1H), 1.74-1.68 (m, 2H), 1.57-1.47 (m, 2H), 1.33-1.23 (m, 1H), 1.07-1.04 (m, 2H), 1.03 (d, J = 7.4 Hz, 3H), 1.01 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 139.25, 139.17, 128.44, 128.33, 127.58, 127.46, 86.88, 80.59, 71.49, 69.61, 66.96, 51.45, 39.43, 37.01, 34.23, 30.28, 24.97, 23.27, 14.72, 9.14 ppm; IR (neat) 2936, 2856, 1637, 1453, 1384, 1363, 1073, 1027, 735, 697 cm⁻¹; HRMS (ESI) m/z Calcd for C₂₆H₃₄O₃Na [M + Na]⁺: 417.2400, found 417.2391; Anal. Calcd for C₂₆H₃₄O₃: C, 79.15; H, 8.69; found C, 78.61; H, 9.07.

Synthesis of compound 9b

To a stirred solution of compound 9a (12.6 g, 32 mmol), pyridine (3.5 mL) and DMAP (0.5 g) in DCM (50 mL) was added Ac₂O (3.6 mL, 35 mmol) dropwise during 5 min at 0 °C. The reaction was stirred for 1 h at rt, and then was quenched with ice water (100 mL). The aqueous phase was extracted with DCM (100 mL), and the combined organic phase was washed with 5% HCl (100 mL x 2) and brine (100 mL x 2), dried over Na₂SO₄, evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EtO = 10:1) to afford 9b (13.8 g, 99%) as a white solid. mp 80.5-81.8 °C. ¹H NMR (400 MHz, CDCl₃) δ = 7.36-7.27 (m, 10H), 5.01 (dt, J = 4.8, 11.1 Hz, 1H), 4.61 (d, J = 12.2 Hz, 1H), 4.58 (d, J = 13.0 Hz, 1H), 4.51 (d, J = 11.9 Hz, 1H), 4.41 (d, J = 11.8 Hz, 1H), 3.41-3.36 (m, 1H), 2.90 (dd, J = 4.0, 11.5 Hz, 1H), 2.44-2.40 (m, 1H), 2.21-2.16 (m, 1H), 2.08-2.03 (m, 1H), 2.05 (s, 3H), 1.95-1.91 (m, 1H), 1.76-1.66 (m, 2H), 1.62-1.51 (m, 1H), 1.35-1.21 (m, 2H), 1.09-1.01 (m, 1H), 1.04 (s, 3H), 0.91 (d, J = 7.4 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ = 170.70,
139.21, 139.15, 128.45, 128.36, 127.54, 127.50, 86.46, 80.59, 71.49, 70.10, 69.86, 48.88, 39.75, 36.90, 30.84, 30.31, 24.69, 22.97, 21.35, 14.59, 9.13 ppm; \textbf{IR} (neat) 2940, 2861, 1735, 1454, 1365, 1244, 1098, 1075, 1027, 735, 698 cm$^{-1}$; \textbf{HRMS} (ESI) m/z Calcd for C$_{28}$H$_{36}$O$_{4}$Na [M + Na]$^+$ 459.2506, found 459.2496; \textbf{Anal.} Calcd for C$_{28}$H$_{36}$O$_{4}$: C, 77.03; H, 8.31; found C, 76.72; H, 8.14.

\textbf{Synthesis of compound 10}

To a solution of compound 9b (18.5 g, 42.4 mmol) in EtOH (500 mL) was added Pd/C (10%, 2 g), and the reaction was stirred for 20 h at rt under an atmosphere of H$_2$. The reaction mixture was filtered through Celite and washed with MeOH (500 mL), then concentrated and purified by a flash column (silica gel, Hex/EA = 2:1) to afford 10 (10.3 g, 95%) as a white solid. mp 168.7-170.1 °C. The structure of 10 was confirmed by X-ray crystallographic results. $^1$H NMR (400 MHz, CDCl$_3$) \(\delta = 4.97 \text{ (dt, } J = 4.8 \text{ Hz, 11.2 Hz, 1H)}, 3.71-3.66 \text{ (m, 1H)}), 3.21 \text{ (dd, } J = 3.6 \text{, 11.3 Hz, 1H}), 2.29-2.25 \text{ (m, 1H)}, 2.15-2.11 \text{ (m, 1H)}, 2.02 \text{ (s, 3H)}, 1.83 \text{ (td, } J = 3.2 \text{, 13.2 Hz, 1H)}, 1.74-1.70 \text{ (m, 1H)}, 1.66-1.63 \text{ (m, 2H)}, 1.45-1.28 \text{ (m, 4H)}, 1.18-1.10 \text{ (m, 1H)}, 0.94 \text{ (s, 3H)} \text{ ppm}; ^{13}$C NMR (100MHz, CDCl$_3$) \(\delta = 170.75, 79.26, 73.69, 69.79, 48.57, 38.93, 36.53, 33.64, 30.32, 28.62, 25.69, 21.28, 13.45, 8.59 \text{ ppm}; \textbf{IR} (neat) 2931, 2869, 1735, 1712, 1639, 1242, 1057, 1015 cm$^{-1}$; \textbf{HRMS} (ESI) m/z Calcd for C$_{14}$H$_{24}$O$_{4}$Na [M + Na]$^+$ 279.1567, found 279.1569; \textbf{Anal.} Calcd for C$_{14}$H$_{24}$O$_{4}$: C, 65.60; H, 9.44; found C, 65.39; H, 9.30.

\textbf{Synthesis of compound 10a}

To a stirred solution of compound 10 (9.6 g, 37.5 mmol) in acetone (400 mL) at 0 °C was added Jones’ reagent dropwise [prepared from CrO$_3$ (27 g) and conc. H$_2$SO$_4$ (23 mL), and diluted to 100 mL with water] until TLC indicated the starting material was consumed completely. The reaction was quenched with iPrOH (10 mL) and filtered through Celite. The filtered cake was washed with acetone (400 mL). After concentration, the residue was partitioned between DCM (500 mL) and water (300 mL). The aqueous phase was extracted with DCM (200 mL x 2). The combined organic phase was washed with saturated NaHCO$_3$ (200 mL ) and brine (200 mL), dried over Na$_2$SO$_4$, evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 6:1-3:1) to afford 10a (8.7 g, 92%) as a colorless oil, and revealed by $^1$H NMR a mixture of the C-4 methyl diastereomers with a $\alpha/\beta$ ratio of 7:3. mp 61.4-65.2 °C. $^1$H NMR (400 MHz, CDCl$_3$) \(\delta = 5.36 \text{ (dt, } J = 4.5, 11.0 \text{ Hz,}\)}
0.7H), 5.18 (td, J = 5.6, 9.4 Hz, 0.3H), 2.83-2.33 (m, 6H), 2.19-1.74 (m, 6H), 1.65-1.58 (m, 1H), 1.40 (s, 1.93 H), 1.31 (s, 0.85H), 1.16 (d, J = 7.8 Hz, 1.93 H), 1.09 (d, J = 6.8 Hz, 0.85 H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) = 213.16, 211.24, 170.60, 71.80, 67.99, 50.68, 46.61, 46.28, 45.02, 44.28, 36.02, 35.18, 34.52, 34.05, 32.49, 30.79, 29.39, 21.57, 21.12, 19.20, 17.84, 14.07 ppm; IR (neat) 2954, 1736, 1711, 1458, 1429, 1379, 1241, 1062, 1030 cm \(^{-1}\); HRMS (EI) \(m/z\) Calcd for C\(_{14}\)H\(_{20}\)O\(_4\) [M]+ 252.1356, found 252.1345; Anal. Calcd for C\(_{14}\)H\(_{20}\)O\(_4\): C, 66.65; H, 7.99; found C, 66.23; H, 7.81.

**Synthesis of compound 11**

![Diagram](image.png)

To a stirred solution of compound 10a (7.8 g, 31 mmol) in EtOH (150 mL) was added CH(OEt)\(_3\) (3.5 mL, 21 mmol) and pTsOH•H\(_2\)O (150 mg, 0.8 mmol). The reaction was stirred for 30 min at rt, and then quenched with saturated NaHCO\(_3\) (150 mL), extracted with DCM (300 mL x 2). The combined organic phase was washed with brine (200 mL x 2), dried over Na\(_2\)SO\(_4\), and evaporated to give a residue, which was purified by flash column (silica gel, Hex/EA = 10:1-5:1) to afford 11 (6.2 g, 61%, 90% brsm) as a white solid, and recovered dione (2.5 g, 32%). mp 83.5-85.0 °C. \(^{1}\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) = 5.27 (dt, J = 4.7, 11.1 Hz, 1H), 3.44-3.32 (m, 4H), 2.67 (dt, J = 6.7, 14.6, 1H), 2.35-2.19 (m, 3H), 2.08 (dd, J = 4.5, 11.9, 1H), 2.04 (s, 3H), 1.86-1.42 (m, 5H), 1.17 (s, 3H), 1.12 (t, J = 6.6 Hz, 6H), 0.92 (d, J = 7.5 Hz, 3H) ppm; \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) = 212.79, 170.71, 101.82, 68.76, 54.92, 54.70, 47.04, 45.75, 35.35, 35.25, 30.93, 29.53, 23.91, 21.23, 19.68, 15.39, 15.29, 11.48 ppm; IR (neat) 2974, 1738, 1714, 1639, 1378, 1238, 1097, 1048, 1033 cm \(^{-1}\); HRMS (EI) \(m/z\) Calcd for C\(_{18}\)H\(_{30}\)O\(_5\) [M]+ 326.2088, found 326.2090; Anal. Calcd for C\(_{18}\)H\(_{30}\)O\(_5\): C, 66.23; H, 9.26; found C, 66.29; H, 9.39.

**Synthesis of compound 12**

![Diagram](image.png)

To a solution of compound 11 (7.9 g, 24.2 mmol) in MeOH (200 mL) was added K\(_2\)CO\(_3\) (2 g), and the formed mixture was stirred for 4 h at rt. The reaction was quenched with saturated NH\(_4\)Cl (100 mL), and extracted with DCM (250 mL x 3). The combined organic phase was washed with brine (100 mL), dried over Na\(_2\)SO\(_4\), and evaporated under vacuum to give 11a as white solid, which was dissolved in EtOH (30 mL), and then was added dropwise to a stirred solution of hydrazine monohydrate (20 mL) and Et\(_3\)N (20 mL) in EtOH (10 mL). The solution was stirred under reflux for 3 h. After evaporation, the residue was partitioned between EA (200
mL) and water (50 mL), and the aqueous phase was extracted with EA (100 mL x 3). The combined organic phase was washed with brine (50 mL), dried over Na₂SO₄, evaporated and dried under vacuum to give the hydrazone as a white solid, which was then used directly for the next process.

To a stirred solution of I₂ (19 g, 75 mmol) in THF (80 mL) was added a solution of TMG (1,1,3,3-tetramethylguanidine) (20 mL, 160 mmol) in THF (80 mL) dropwise during 30 min at rt, and then a solution of the above hydrazone in THF (80 mL) was added dropwise during 10 min. The reaction was stirred at rt for 10 min, cooled and quenched with saturated Na₂S₂O₃ (100 mL), partitioned between EA (300 mL) and water (100 mL). The aqueous phase was extracted with EA (200 mL), and the combined organic phase was washed with brine (100 mL x 2), dried over Na₂SO₄, evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA/Et₃N = 20:1:0.01) to afford 12 (8.0 g, 84%) as a pale yellow syrup. ¹H NMR (400 MHz, C₆D₆) δ = 5.89 (dd, J = 2.8, 5.1 Hz, 1H), 3.58 (brs, 1H), 3.43-3.35 (m, 3H), 3.21-3.17 (m, 1H), 2.57-2.54 (m, 1H), 2.19 (dd, J = 4.4, 11.6, 1H), 2.01-1.93 (m, 1H), 1.74-1.71 (m, 1H), 1.63-1.55 (m, 3H), 1.51-1.47 (m, 1H), 1.11 (t, J = 7.1 Hz, 3H), 1.05 (t, J = 7.0 Hz, 3H), 0.94-0.92 (m, 6H) ppm; ¹³C NMR (100 MHz, C₆D₆) δ = 134.71, 117.85, 102.88, 64.39, 55.05, 54.95, 48.15, 42.99, 40.98, 39.90, 34.68, 25.66, 20.80, 15.57, 15.52, 11.52 ppm; IR (neat) 2971, 2926, 1645, 1634, 1449, 1385, 1086, 1049 cm⁻¹; HRMS (EI) m/z Calcd for C₁₆H₂₇IO₃ [M]+ 394.0999, found 394.0986.

**Synthesis of compound 12a**

To a stirred solution of compound 12 (4 g, 10 mmol) in DMF (40 mL) at 0 °C was added NaH (~60%, 2 g, 50 mmol) in portions. After stirring for 30 min, BnBr (3.5 mL, 29 mmol) was added dropwise during 5 min. The reaction was warmed up to rt and stirred for 20 h. Cooled to 0 °C, the reaction was quenched with water (40 mL), extracted with EA (100 mL x 2), washed with saturated NH₄Cl (100 mL) and brine (100 mL), dried over Na₂SO₄, evaporated and dried under vacuum to give a residue, which was used directly for the next process.

The residue above was dissolved in benzene (100 mL), followed by addition of ethylene glycol (4 mL) and pTSOH·H₂O (400 mg, 2.1 mmol). The reaction was stirred under reflux for 20 h with the Dean-Stark apparatus to remove water formed, and then cooled to rt, partitioned between EA (100 mL) and water (100 mL). The organic phase was washed with saturated NaHCO₃ (100 mL) and brine (100 mL), dried over Na₂SO₄, evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA/EA = 50:1-30:1) to afford 12a (4.1 g, 89%) as a pale yellow semi-solid. ¹H NMR (400 MHz, CDCl₃) δ = 7.37-7.27 (m, 5H), 6.17 (dd, J = 2.8, 5.2 Hz, 1H), 4.64 (d, J = 11.4 Hz, 1H), 4.42 (d, J = 11.4 Hz, 1H), 3.97-3.88 (m, 4H), 3.77-3.70 (m, 1H), 2.66 (td, J = 5.6, 17.2 Hz, 1H), 2.32-2.26 (m, 2H), 2.12 (dq, J = 2.8, 8.8 Hz, 1H), 1.89-1.81 (m, 1H), 1.65-1.61 (m, 1H), 1.57-1.49 (m, 2H), 1.03 (s,
3H), 0.97 (d, J = 7.3 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 138.54, 134.05, 128.49, 127.86, 127.77, 117.25, 111.57, 71.36, 71.02, 64.48, 64.23, 47.58, 42.34, 40.20, 37.40, 36.15, 27.62, 20.72, 12.01 ppm; IR (neat) 2945, 2881, 1453, 1373, 1355, 1099, 736, 698 cm$^{-1}$; HRMS (ESI) m/z Calcd for C$_{21}$H$_{28}$IO$_3$ [M+H]$^+$ 455.1078, found 455.1085.

**Synthesis of compound 13**

A suspension of compound 12a (4.5 g, 10 mmol), Pd(OAc)$_2$ (225 mg, 1 mmol) and Et$_3$N (5.5 mL, 40 mmol) in MeOH/DMF (64 mL, 7/1) was degassed and charged with CO (balloon), stirred at 55 °C for 24 h. The reaction mixture was cooled to rt, diluted with EA (100 mL) and filtered through Cellite. The filtrate was washed with water (50 mL), saturated NH$_4$Cl (50 mL) and brine (50 mL). The organic phase was collected, dried over Na$_2$SO$_4$, and evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 50:1-20:1) to afford 13 (3.1 g, 81%) as a white solid. mp 99.5-100.2 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.35-7.27 (m, 5H), 6.59 (dd, J = 3.1, 4.6 Hz, 1H), 4.67 (d, J = 11.4 Hz, 1H), 4.45 (d, J = 11.4 Hz, 1H), 3.96-3.87 (m, 4H), 3.68 (s, 3H), 2.85 (dd, J = 3.1, 5.2 Hz, 1H), 2.34-2.29 (m, 1H), 2.34-2.29 (m, 1H), 2.19 (d, J = 4.6, 11.5 Hz, 1H), 1.93 (m, J = 3.1, 4.1, 5.2 Hz, 1H), 1.52-1.44 (m, 2H), 1.27 (s, 3H), 1.02 (d, J = 7.5 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 167.28, 140.62, 138.67, 135.19, 128.50, 127.86, 127.75, 111.37, 71.41, 71.04, 64.39, 64.17, 51.38, 47.56, 38.05, 36.09, 33.89, 33.09, 27.05, 21.20, 12.18 ppm; IR (neat) 2981, 2950, 2882, 1714, 1435, 1359, 1239, 1101, 1077, 737, 699 cm$^{-1}$; HRMS (ESI) m/z Calcd for C$_{23}$H$_{31}$O$_5$ [M+H]$^+$ 387.2166, found 387.2163. Anal. Calcd for C$_{23}$H$_{30}$O$_5$: C, 71.48; H, 7.82; found C, 71.49; H, 7.84.

**Synthesis of compound 13a**

To a solution of compound 13 (3 g, 7.8 mmol) in DCM (30 mL) at -78 °C was added DIBAL-H solution (15 mL, 1 M in toluene) dropwise during 5 min, and the reaction was stirred at the same temperature for 20 min. The reaction was quenched with saturated NH$_4$Cl (20 mL), diluted with DCM (50 mL) and water (50 mL). The organic phase was washed with brine (50 mL x 2), dried over Na$_2$SO$_4$, and evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 2:1) to afford 13a (2.7 g, 97%) as a white solid. mp 109.7-110.7 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.35-7.27 (m, 5H), 5.54-5.52 (m, 1H), 4.67 (d, J = 11.4 Hz, 1H), 4.43 (d, J = 11.4 Hz, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 167.28, 140.62, 138.67, 135.19, 128.50, 127.86, 127.75, 111.37, 71.41, 71.04, 64.39, 64.17, 51.38, 47.56, 38.05, 36.09, 33.89, 33.09, 27.05, 21.20, 12.18 ppm; IR (neat) 2981, 2950, 2882, 1714, 1435, 1359, 1239, 1101, 1077, 737, 699 cm$^{-1}$; HRMS (ESI) m/z Calcd for C$_{23}$H$_{30}$O$_5$ [M+H]$^+$ 387.2166, found 387.2163. Anal. Calcd for C$_{23}$H$_{30}$O$_5$: C, 71.48; H, 7.82; found C, 71.49; H, 7.84.
Hz, 1H), 4.13-4.06 (m, 2H), 3.97-3.88 (m, 4H), 3.81-3.74 (m, 1H), 2.81-2.74 (m, 1H), 2.40-2.33 (m, 1H), 2.13-2.05 (m, 2H), 1.92 (dt, J = 5.0, 13.3 Hz, 1H), 1.73-1.66 (m, 2H), 1.55-1.49 (m, 1H), 1.22 (brs, 1H), 1.13 (s, 3H), 1.01 (d, J = 7.5 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 146.33, 138.87, 128.45, 127.86, 127.64, 119.91, 111.49, 72.17, 70.75, 64.36, 64.18, 62.72, 47.19, 37.98, 36.15, 33.46, 33.25, 26.98, 21.93, 12.14 ppm; IR (neat) 2929, 2883, 1454, 1383, 1355, 1092, 988 cm$^{-1}$; HRMS (ESI) m/z Calcd for C$_{22}$H$_{31}$O$_4$ [M+H]$^+$ 359.2217, found 359.2245. Anal. Calcd for C$_{22}$H$_{30}$O$_4$: C, 73.71; H, 8.44; found C, 73.36; H, 8.96.

Synthesis of compound 14

To a stirred solution of compound 13a (2.7 g, 7.5 mmol), DIPEA (6 mL, 36 mmol) and DMAP (10 mg) in toluene (50 mL) was added MOMCl (2.3 mL, 30 mmol) dropwise during 5 min at rt. The reaction was stirred at 70 °C for 20 h and then allowed to rt. The reaction was quenched with water (50 mL), extracted with EA (100 mL x 2), washed with saturated NaHCO$_3$ (50 mL) and brine (50 mL), dried over Na$_2$SO$_4$, and evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 20:1-10:1) to afford 14 (2.9 g, 96%) as a pale yellow oil.

$^1$H NMR (400 MHz, CDCl$_3$) δ = 7.35-7.28 (m, 5H), 5.55 (brs, 1H), 4.67 (d, J = 11.4 Hz, 1H), 4.61 (s, 2H), 4.42 (d, J = 11.4 Hz, 1H), 4.03 (d, J = 12.3 Hz, 1H), 3.96-3.88 (m, 5H), 3.81-3.75 (m, 1H), 3.36 (s, 3H), 2.77 (td, J = 5.5, 17.5 Hz, 1H), 2.39-2.33 (m, 1H), 2.12-2.05 (m, 2H), 1.92 (dt, J = 5.2, 13.0 Hz, 1H), 1.71-1.65 (m, 2H), 1.52 (d, J = 1.7, 13.5 Hz, 1H), 1.10 (s, 3H), 1.01 (d, J = 7.5 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ = 142.70, 138.89, 128.43, 127.87, 127.62, 122.09, 111.51, 95.65, 72.11, 70.71, 67.20, 64.35, 64.18, 55.50, 47.15, 37.95, 36.13, 33.47, 33.36, 27.00, 21.69, 12.15 ppm; IR (neat) 2923, 2883, 1725, 1454, 1382, 1358, 1098, 698 cm$^{-1}$; HRMS (ESI) m/z Calcd for C$_{24}$H$_{34}$O$_5$Na [M+Na]$^+$ 425.2298, found 425.2294.

Synthesis of compound 14a

To a stirred solution of compound 14 (2.6 g, 6.5 mmol) in Et$_2$O (60 mL) was added BH$_3$•Me$_2$S (neat, 1.3 mL, 13 mmol) dropwise during 10 min. The reaction was stirred for 20 h at rt, and then was added water/THF (1:1, 20 mL) slowly at -10 °C. NaOH (3M, 20 mL) and 30% H$_2$O$_2$ (10 mL) were added successively, and the resultant mixture was stirred for 10 h at rt. Cooled to 0 °C, saturated Na$_2$S$_2$O$_3$ was added dropwise during 30 min, and the stirring continued for additional 30 min. The aqueous phase was extracted with Et$_2$O (100 mL), and the combined organic phase
was washed with saturated NH₄Cl (100 mL) and brine (100 mL), dried over Na₂SO₄,
and evaporated to give a residue, which was purified by a flash column (silica gel,
Hex/EtO = 10:1-2:1) to afford 14a (2.1 g, 77%) as a colorless oil. ¹H NMR (400 MHz,
C₆D₆) δ = 7.32-7.30 (m, 2H), 7.18-7.15 (m, 2H), 7.10-7.06 (m, 1H), 4.53 (d, J = 11.4 Hz,
1H), 4.29 (s, 2H), 4.16 (d, J = 11.5 Hz, 1H), 3.87-3.80 (m, 1H), 3.70 (dd, J = 3.2, 9.9 Hz,
1H), 3.57-3.36 (m, 6H), 3.34 (d, J = 2.7 Hz, 1H), 3.09 (s, 3H), 2.77 (td, J = 4.6, 11.8 Hz,
1H), 2.68-2.61 (m, 1H), 2.05 (dd, J = 4.8, 11.2 Hz, 1H), 1.89 (dd, J = 4.6, 4.1, 3.6 Hz,
1H), 1.65-1.46 (m, 4H), 1.39-1.34 (m, 1H), 1.12 (d, J = 7.6 Hz, 3H), 0.67 (s, 3H) ppm;
¹³C NMR (100 MHz, C₆D₆) δ = 139.63, 128.54, 128.00, 127.59, 111.39, 96.65, 73.08,
70.53, 69.80, 67.78, 64.25, 64.08, 56.00, 51.18, 50.77, 41.60, 36.72, 36.39, 36.22, 27.14,
16.65, 12.55 ppm; IR (neat) 2934, 2884, 1453, 1386, 1148, 1101, 1030, 924, 698 cm⁻¹;
HRMS (ESI) m/z Calcd for C₂₄H₃₆O₆Na [M+Na]⁺ 443.2404, found 443.2424.

Synthesis of compound 15

To a stirred solution of compound 14a (2 g, 4.8 mmol), pyridine (1 mL) and DMAP
(100 mg) in DCM (20 mL) was added Ac₂O (0.7 mL, 7.1 mmol) at 0 °C. The reaction
was warmed up to rt and stirred for 2 h, and then quenched with water (20 mL). The
aqueous phase was extracted with DCM (50 mL), and the combined organic phase
was washed with 5% HCl (50 mL) and brine (50 mL), dried over Na₂SO₄, and
evaporated to give a residue, which was purified by a flash column (silica gel,
Hex/EtO = 7:1-5:1) to afford 15 (2.1 g, 95%) as a white solid. mp 92.7-94.0 °C. ¹H NMR
(400 MHz, C₆D₆) δ = 7.30-7.28 (m, 2H), 7.18-7.14 (m, 2H), 7.09-7.06 (m, 1H),
5.27 (dt, J = 5.0, 11.5 Hz, 1H), 4.45-4.39 (m, 3H), 4.05 (d, J = 11.5 Hz, 1H), 3.58 (d,
J = 3.5 Hz, 2H), 3.52-3.39 (m, 5H), 3.17 (s, 3H), 2.83 (td, J = 4.8, 11.3 Hz, 1H),
2.64-2.58 (m, 1H), 2.03 (dd, J = 4.8, 11.2 Hz, 1H), 1.95 (dt, J = 5.8, 12.6 Hz, 1H),
1.80 (s, 3H), 1.70-1.66 (m, 2H), 1.55-1.38 (m, 3H), 1.10 (d, J = 7.6 Hz, 3H), 0.90 (s,
3H) ppm; ¹³C NMR (100 MHz, C₆D₆) δ = 169.94, 138.53, 128.55, 127.59, 111.41,
96.81, 73.07, 70.80, 69.61, 64.49, 64.24, 64.08, 55.03, 54.43, 50.74, 38.20, 36.78,
36.62, 36.52, 27.10, 20.94, 16.83, 12.36 ppm; IR (neat) 2946, 2885, 1733, 1369, 1245,
1148, 1101, 1030, 924, 698 cm⁻¹; HRMS (ESI) m/z Calcd for C₂₆H₃₈O₇Na [M+Na]⁺
485.2510, found 485.2517.

Synthesis of compound 15b

To a solution of compound 15 (2 g, 4.3 mmol) in EtOH (50 mL) was added Pd/C (200
mg, 10%). The reaction was degassed and charged with H₂ (balloon), stirred at 50 °C for 4 h. Cooled to rt, the reaction mixture was diluted with EA (200 mL), filtered through Celite. The filtrate was concentrated and the residue was dried under vacuum to give 15a as a colorless oil, which was used directly for the next process.

To a stirred solution of compound 15a and Et₃N (3 mL) in DCM (40 mL) was added MsCl (0.6 mL, 7.5 mmol) dropwise during 10 min at -78 °C. The reaction was stirred at the same temperature for 40 min, and then quenched with water (20 mL), extracted with DCM (30 mL x 2). The combined organic phase was washed with brine (40 mL x 2), dried over Na₂SO₄, and evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 7:1-5:1) to afford 15b (1.8 g, 92%) as a white solid. mp. 109.5-110.7 °C.

**1H NMR** (400 MHz, C₆D₆) δ = 5.15 (dt, J = 5.0, 11.5 Hz, 1H), 5.15 (dt, J = 5.1, 11.3 Hz, 1H), 4.37 (d, J = 6.4 Hz, 1H), 4.33 (d, J = 6.5 Hz, 1H), 3.50-3.44 (m, 6H), 3.12 (s, 3H), 2.99-2.94 (m, 1H), 2.32-2.30 (m, 1H), 2.27 (s, 3H), 2.01 (dd, J = 4.6, 11.6 Hz, 1H), 1.85-1.77 (m, 1H), 1.75 (s, 3H), 1.66-1.53 (m, 3H), 1.43-1.29 (m, 2H), 1.20 (d, J = 7.6 Hz, 3H), 0.65 (s, 3H) ppm; **13C NMR** (100 MHz, C₆D₆) δ = 169.69, 110.93, 96.68, 76.88, 68.60, 64.29, 64.17, 55.03, 53.99, 49.58, 39.50, 38.87, 36.87, 36.71, 36.38, 26.59, 20.76, 16.10, 12.06 ppm; **IR** (neat) 2944, 2879, 1735, 1451, 1342, 1244, 1174, 1150, 1100, 1032, 931, 903 cm⁻¹; **HRMS** (ESI) m/z Calcd for C₂₀H₃₄O₉SNa [M+Na]⁺ 473.1816, found 473.1810.

**Synthesis of compound 16**

A solution of compound 15b (1.7 g, 3.8 mmol) and PPTS (100 mg, 0.4 mmol) in acetone/water (30 mL, 9/1) was stirred under reflux for 24 h. Cooled to rt, the reaction mixture was partitioned between EA (100 mL) and water (50 mL), washed with saturated NaHCO₃ (50 mL) and brine (50 mL), dried over Na₂SO₄, and evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 3:2) to afford 16 (1.3 g, 85%) as a white solid. mp. 118.5-121.2 °C. **1H NMR** (400 MHz, C₆D₆) δ = 5.07 (dt, J = 5.0, 11.5 Hz, 1H), 4.80 (dt, J = 5.1, 11.2 Hz, 1H), 4.34 (d, J = 6.4 Hz, 1H), 4.30 (d, J = 6.5 Hz, 1H), 3.38-3.31 (m, 2H), 3.11 (s, 3H), 3.05-2.99 (m, 1H), 2.76-2.69 (m, 1H), 2.20-2.11 (m, 1H), 2.15 (s, 3H), 2.03-1.99 (m, 1H), 1.72 (s, 3H), 1.60-1.53 (m, 2H), 1.34 (dd, J = 5.8, 11.4 Hz, 1H), 1.06 (d, J = 7.7 Hz, 3H), 1.03-0.95 (m, 2H), 0.50 (s, 3H) ppm; **13C NMR** (100 MHz, C₆D₆) δ = 210.87, 169.47, 96.72, 74.97, 68.07, 64.10, 55.11, 53.31, 50.75, 43.70, 38.32, 38.62, 37.96, 36.54, 33.80, 20.66, 15.50, 13.44 ppm; **IR** (neat) 2936, 2891, 1732, 1709, 1336, 1242, 1172, 1151, 1045, 931, 905 cm⁻¹; **HRMS** (ESI) m/z Calcd for C₁₈H₃₀O₈SNa [M+Na]⁺ 429.1554, found 429.1541; **Anal.** Calcd for C₁₈H₃₀O₈S: C, 53.19; H, 7.44; found C, 53.55; H, 7.20.

**Synthesis of compound 16a**
To a stirred solution of compound 16 (1.3 g, 3.2 mmol) in EA (35 mL) at 0 °C was added PhSeCl (0.6 g, 4.8 mmol) and pTsOH•H₂O (67 mg, 0.35 mmol). The reaction was stirred at the same temperature for 2.5 h, and then diluted with DCM (35 mL), followed by addition of pyridine (1.5 mL) and H₂O₂ (30%, 1.5 mL). The stirring continued at 0 °C for 45 min, and aqueous CuSO₄ (10%, 15 mL) was added. The resultant mixture was stirred for additional 10 min, diluted with water (50 mL), extracted with DCM (50 mL x 2). The combined organic phase was washed with saturated Na₂S₂O₃ (50 mL), 5% HCl (50 mL) and brine (50 mL), dried over Na₂SO₄, and evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 3:2) to afford 16a (0.92 g, 71%) as a white solid. mp 93.8-95.4 °C.

**NMR**

**1H NMR** (400 MHz, C₆D₆) δ = 6.77 (d, J = 10.4 Hz, 1H), 5.86 (d, J = 10.4 Hz, 1H), 4.97 (dt, J = 5.2, 11.4 Hz, 1H), 4.33 (d, J = 6.5 Hz, 1H), 4.28 (d, J = 4.2 Hz, 2H), 3.41 (d, J = 3.9 Hz, 2H), 3.09 (s, 3H), 3.03-2.97 (m, 1H), 2.82-2.74 (m, 1H), 2.20 (s, 3H), 1.76-1.72 (m, 1H), 1.69 (s, 3H), 1.54-1.46 (m, 1H), 1.40-1.35 (m, 1H), 1.21 (d, J = 7.8 Hz, 3H), 0.57 (s, 3H) ppm; **13C NMR** (100 MHz, C₆D₆) δ = 199.81, 169.49, 154.48, 126.65, 96.60, 74.15, 67.79, 63.93, 55.20, 49.75, 48.92, 39.76, 39.19, 39.12, 38.47, 20.59, 17.64, 13.83 ppm; **IR** (neat) 2938, 2890, 1736, 1676, 1338, 1240, 1176, 1031, 936 cm⁻¹; **HRMS** (ESI) m/z Calcd for C₁₈H₂₉O₈S [M+H]⁺ 405.1578, found 405.1611; **Anal.** Calcd for C₁₈H₂₈O₈S: C, 53.45; H, 6.98; found C, 53.74; H, 6.88.

**Synthesis of compound 4**

To a solution of compound 16a (800 mg, 2 mmol) in MeOH (20 mL) was added K₂CO₃ (200 mg). The reaction was stirred for 3 h at rt, and then partitioned between EA (50 mL) and water (20 mL), extracted with EA (20 mL x 2). The combined organic phase was washed with brine (20 mL), dried over Na₂SO₄, evaporated and dried under vacuum to give 5 as a white solid (700 mg, 98%), which was used directly for the next process.

To a stirred solution of compound 5 in tBuOH (20 mL) was added tBuOK (2.4 g, 21 mmol) rapidly. The reaction was stirred at 70 °C for 15 min, and then cooled at an ice bath, quenched with saturated NH₄Cl (20 mL), partitioned between EA (50 mL) and water (20 mL). The aqueous phase was extracted with EA (50 mL), and the combined organic phase was washed with brine (20 mL x 2), dried over Na₂SO₄, evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 3:1-2:1) to afford 4 (0.32 g, 61%) as a white semi-solid. **1H NMR** (400 MHz, C₆D₆) δ = 6.33 (dd,
$J = 1.8, 9.6 \text{ Hz, 1H}$, 6.04 (d, $J = 9.6 \text{ Hz, 1H}$), 5.58 (td, $J = 10.2, 16.7 \text{ Hz, 1H}$), 4.98-4.92 (m, 2H), 4.43 (s, 2H), 4.06 (brs, 1H), 3.58 (dd, $J = 5.4, 10.0 \text{ Hz, 1H}$), 3.48-3.44 (m, 2H), 3.16 (s, 3H), 2.37 (d, $J = 9.6 \text{ Hz, 1H}$), 2.06 (dd, $J = 5.0, 9.1 \text{ Hz, 1H}$), 1.88 (s, 3H), 0.88 (s, 3H) ppm; $^{13}\text{C NMR}$ (100 MHz, $\text{C}_6\text{D}_6$) $\delta = 200.78, 158.44, 134.07, 128.34, 120.16, 96.93, 81.94, 67.80, 64.26, 60.89, 55.36, 54.86, 46.09, 18.67, 18.45 ppm; IR (neat) 2964, 2930, 1668, 1455, 1382, 1150, 1110, 1061, 919 cm$^{-1}$; HRMS (ESI) m/z Calcd for $\text{C}_{15}\text{H}_{22}\text{O}_4\text{Na} [\text{M+Na}]^+$ 289.1410, found 289.1429.

**Synthesis of compound 17**

To a solution of compound 4 (300 mg, 1.1 mmol) in DCM (15 mL) was added DMP (700 mg, 1.7 mmol). The reaction was stirred at rt for 40 min, and then was quenched with saturated $\text{Na}_2\text{S}_2\text{O}_3$ (10 mL), extracted with DCM (20 mL x 2). The combined organic phase was washed with saturated $\text{NaHCO}_3$ (20 mL) and brine (20 mL), dried over $\text{Na}_2\text{SO}_4$, and evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 4:1) to afford 17 (268 mg, 90%) as a colorless oil. $^{1}\text{H NMR}$ (400 MHz, $\text{C}_6\text{D}_6$) $\delta = 6.03$ (d, $J = 2.2, 9.6 \text{ Hz, 1H}$), 5.72-5.62 (m, 2H), 5.05-4.99 (m, 2H), 4.21 (s, 2H), 3.80 (dd, $J = 4.1, 10.1 \text{ Hz, 1H}$), 3.31 (dd, $J = 2.4, 10.2 \text{ Hz, 1H}$), 3.11 (dd, $J = 2.0, 9.4 \text{ Hz, 1H}$), 3.04 (s, 3H), 1.92 (dd, $J = 2.4, 4.0 \text{ Hz, 1H}$), 1.45 (s, 3H), 0.94 (s, 3H) ppm; $^{13}\text{C NMR}$ (100 MHz, $\text{C}_6\text{D}_6$) $\delta = 210.67, 192.45, 157.85, 132.70, 127.06, 121.43, 96.51, 69.47, 65.25, 64.52, 55.28, 54.97, 44.01, 17.85, 13.79 ppm; IR (neat) 2932, 2884, 1747, 1681, 1450, 1373, 1132, 1151, 1112, 1033, 920 cm$^{-1}$; HRMS (ESI) m/z Calcd for $\text{C}_{15}\text{H}_{20}\text{O}_4\text{Na} [\text{M+Na}]^+$ 287.1254, found 287.1254.

**Synthesis of compound 17a**

To a stirred solution of compound 17 (400 mg, 1.5 mmol) and CeCl$_3$•7H$_2$O (840 mg, 2.3 mmol) in MeOH (15 mL) at -78 °C was added NaBH$_4$ (60 mg, 1.5 mmol) in portions during 15 min, and the stirring continued for 5 min at the same temperature. The reaction was quenched with saturated NH$_4$Cl (10 mL), extracted with EA (30mL x 2). The combined organic phase was washed with brine (20 mL x 2), dried over Na$_2$SO$_4$, and evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 4:1-1:1) to afford 17a (181 mg, 45%) as a colorless oil. Other generated isomers were mixed and oxidized to the starting material diketone, which was used again for this reduction. After three recycles, the desired alcohol 17a (314 mg, total 78%) was obtained. $^{1}\text{H NMR}$ (400 MHz, $\text{C}_6\text{D}_6$) $\delta = 6.17$ (td, $J = 9.9, 17.1 \text{ Hz, 1H}$), 5.58 (dd, $J = 3.7, 9.6 \text{ Hz, 1H}$), 5.46 (d, $J = 9.5 \text{ Hz, 1H}$), 5.13 (dd, $J = 2.2,$}
17.1 Hz, 1H), 5.06 (dd, J = 2.4, 10.2 Hz, 1H), 4.25 (s, 2H), 3.74 (dd, J = 4.6, 10.0 Hz, 1H), 3.66-3.64 (m, 1H), 3.34 (dd, J = 2.5, 10.0 Hz, 1H), 3.08 (s, 3H), 2.82 (d, J = 9.7 Hz, 1H), 2.01 (dd, J = 2.5, 4.6 Hz, 1H), 1.41 (d, J = 7.2 Hz, 1H), 1.29 (s, 3H), 1.04 (s, 3H) ppm; $^{13}$C NMR (100 MHz, C$_6$D$_6$) δ = 219.71, 140.82, 135.90, 127.82, 118.55, 96.49, 70.63, 65.68, 58.94, 57.10, 56.24, 55.18, 42.72, 18.37, 16.46 ppm; IR (neat) 2962, 2929, 2874, 1738, 1451, 1373, 1150, 1106, 1049, 1013, 917 cm$^{-1}$; HRMS (ESI) m/z Calcd for C$_{15}$H$_{22}$O$_4$Na [M+Na]$^+$ 289.1410, found 289.1405.

**Synthesis of compound 18**

To a stirred solution of compound 17a (330 mg, 1.2 mmol) and Et$_3$N (0.7 mL, 5.0 mmol) in DCM (10 mL) at ice-salt bath was added TBSOTf (0.8 mL, 3.5 mmol) dropwise during 5 min. The reaction was allowed to warm to 0 °C and stirred under argon atmosphere for 3 h, and then quenched with saturated NaHCO$_3$ (5 mL). The aqueous phase was extracted with DCM (20 mL), and the combined organic phase was washed with brine (20 mL), dried over Na$_2$SO$_4$, and evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 40:1) to afford 18 (424 mg, 90%) as a colorless oil. $^1$H NMR (400 MHz, C$_6$D$_6$) δ = 6.40 (td, J = 10.3, 16.6 Hz, 1H), 5.51 (s, 2H), 5.15 (dd, J = 2.3, 8.5 Hz, 1H), 5.12 (s, 1H), 4.28 (s, 2H), 3.83 (s, 1H), 3.78 (dd, J = 4.8, 10.0 Hz, 1H), 3.42 (dd, J = 2.4, 10.0 Hz, 1H), 3.11 (s, 3H), 2.85 (d, J = 10.0 Hz, 1H), 2.10 (dd, J = 2.4, 4.7 Hz, 1H), 1.34 (s, 3H), 1.11 (s, 3H), 0.94 (s, 9H), -0.01(s, 3H), -0.04 (s, 3H) ppm; $^{13}$C NMR (100 MHz, C$_6$D$_6$) δ = 219.83, 140.49, 136.89, 127.82, 117.06, 96.56, 70.80, 65.75, 59.29, 57.18, 55.20, 42.87, 25.92, 18.48, 18.23, 17.34, 1.41, -4.35, -5.00 ppm; IR (neat) 2957, 2930, 2885, 2858, 1742, 1691, 1473, 1463, 1253, 1151, 1066, 883, 777 cm$^{-1}$; HRMS (ESI) m/z Calcd for C$_{21}$H$_{36}$O$_4$SiNa [M+Na]$^+$ 403.2275, found 403.2297.

**Synthesis of compound 19**

To a stirred mixture of Mg (192 mg, 8 mmol) and TiCl$_4$ (0.21 mL, 2 mmol) in DCM (4 mL) at 0 °C was added a solution of compound 18 (380 mg, 1 mmol) in DCM/THF (3 mL/2 mL) dropwise during 2 min. The reaction was stirred for 45 min at 0 °C under argon atmosphere, and the resulting green-black mixture was stirred for additional 25 min at rt. The reaction mixture was re-cooled to 0 °C, and then quenched with saturated K$_2$CO$_3$ (2 mL), diluted with EA (50 mL), filtered through Celite. The filtrate was washed with saturated NaHCO$_3$ (20 mL) and brine (20 mL), dried over Na$_2$SO$_4$, evaporated to give a residue, which was purified by a flash
column (silica gel, Hex/EA = 40:1-20:1) to afford 19 (291 mg, 77%) as a colorless oil.

**1H NMR** (400 MHz, C6D6) δ = 6.37 (td, J = 10.1, 17.0 Hz, 1H), 5.58 (s, 2H), 5.16-5.06 (m, 4H), 4.45 (s, 2H), 3.70 (s, 1H), 3.58 (dd, J = 6.8, 10.0 Hz, 1H), 3.43 (dd, J = 4.7, 10.2 Hz, 1H), 3.18 (s, 3H), 2.61-2.59 (m, 1H), 2.29 (d, J = 10.0 Hz, 1H), 1.29 (s, 3H), 1.14 (s, 3H), 0.99 (s, 9H), 0.06(s, 3H), 0.03 (s, 3H) ppm; **13C NMR** (100 MHz, C6D6) δ = 159.58, 139.47, 138.20, 127.82, 116.19, 110.00, 96.81, 75.73, 70.10, 58.28, 55.15, 54.76, 51.11, 44.54, 26.03, 21.40, 19.48, 18.29, -4.07, -4.88 ppm; **IR** (neat) 2956, 2929, 2858, 1635, 1251, 1151, 1112, 1064, 1042, 886, 836, 774 cm\(^{-1}\); **HRMS** (ESI) m/z Calcd for C22H38O3SiNa [M+Na]+ 401.2482, found 401.2501.

**Synthesis of compound 20**

To a solution of compound 19 (240 mg, 0.63 mmol) in butanone/water (5mL/0.5 mL) was added NaI (286 mg, 1.9 mmol) and PPTS (240 mg, 0.95 mmol). The reaction was stirred under reflux for 20 h, and then cooled to rt, partitioned between EA (20 mL) and water (20 mL), extracted with EA (10 mL x 2). The combined organic phase was washed with saturated NaHCO₃ (10 mL) and brine (10 mL), dried over Na₂SO₄, and evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA =20:1-10:1) to afford 20 (119 mg, 56%) as a colorless oil.

**1H NMR** (400 MHz, C6D6) δ = 6.33 (td, J = 10.1, 17.0 Hz, 1H), 5.57-5.50 (m, 2H), 5.13-5.01 (m, 4H), 3.66 (d, J = 3.1 Hz, 1H), 3.51-3.45 (m, 1H), 3.33-3.28 (m, 1H), 2.35-2.32 (m, 1H), 2.21 (d, J = 10.0 Hz, 1H), 1.23 (s, 3H), 1.03 (s, 3H), 0.99 (s, 9H), 0.05(s, 3H), 0.02 (s, 3H) ppm; **13C NMR** (100 MHz, C6D6) δ = 159.48, 139.45, 138.04, 127.63, 116.23, 109.83, 75.78, 63.92, 58.26, 51.21, 44.45, 26.01, 21.26, 19.14, 18.28, -4.08, -4.90 ppm; **IR** (neat) 2957, 2929, 2857, 1635, 1251, 1112, 1064, 1042, 886, 836, 774 cm\(^{-1}\); **HRMS** (EI) m/z Calcd for C20H34O2Si [M]+ 334.2323, found 334.2324.

**Synthesis of compound 21**

To a stirred solution of compound 20 (100 mg, 0.3 mmol) and VO(acac)₂ (1.6 mg, 0.006 mmol) in benzene (3 mL) was added TBHP (5.5 M in octane, 66 μL, 0.36 mmol) at rt. The reaction was stirred for 4 h, and then diluted with EA (20 mL). The solution was washed with saturated NaHCO₃ (10 mL) and brine (10 mL), dried over Na₂SO₄, and evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA =15:1) to afford 21 (90 mg, 86%) as a colorless oil.

**1H NMR** (400 MHz, C6D6) δ = 6.20 (td, J = 10.1, 17.0 Hz, 1H), 5.50-5.43 (m, 2H), 5.08-5.00 (m, 2H), 3.71-3.65 (m, 1H), 3.53 (d, J = 3.4 Hz, 1H), 3.50-3.44 (m, 1H), 2.46 (dd, J = 5.6,
8.3 Hz, 1H), 2.41 (d, J = 10.0 Hz, 1H), 2.33 (d, J = 4.5 Hz, 1H), 2.28 (d, J = 4.5 Hz, 1H), 1.82 (dd, J = 3.9, 7.5 Hz, 1H), 0.95 (s, 9H), 0.94 (s, 3H), 0.93 (s, 3H), 0.01 (s, 3H), -0.02 (s, 3H) ppm; 13C NMR (100 MHz, C6D6) δ = 139.59, 137.32, 126.69, 116.77, 72.84, 69.17, 61.46, 58.10, 53.26, 48.67, 48.52, 44.15, 25.95, 19.09, 18.24, 16.09, -4.03, -4.97 ppm; IR (neat) 2958, 2929, 1635, 1256, 1063, 837, 774 cm⁻¹; HRMS (ESI) m/z Calcd for C20H34O3SiNa [M+Na]⁺ 373.2169, found 373.2170.

Synthesis of compound 22

To a stirred solution of compound 21 (80 mg, 0.23 mmol) in Et2O (8 mL) was added LAH (43 mg, 1.1 mmol) at rt. The reaction was stirred under reflux for 7 h. After being cooled to 0 °C, the reaction was quenched with Na2SO4•10 H2O (5 g) in portions and stirred for additional 2 h at rt, filtered. The filtered cake was washed with EA (10 mL x 3), and the combined filtrate was evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 10:1-5:1) to afford 22 (72 mg, 90%) as a white solid. mp 91.0-92.0 °C. 1H NMR (400 MHz, C6D6) δ = 6.27 (td, J = 10.2, 16.9 Hz, 1H), 5.50 (dd, J = 3.6, 9.4 Hz, 1H), 5.45 (dd, J = 1.2, 9.6 Hz, 1H), 5.10-5.04 (m, 2H), 3.79 (d, J = 3.5 Hz, 1H), 3.64-3.58 (m, 1H), 3.55-3.50 (m, 1H), 2.48 (d, J = 10.1 Hz, 1H), 2.12 (s, 1H), 1.88 (t, J = 5.3 Hz, 1H), 1.62 (dd, J = 4.3, 9.0 Hz, 1H), 1.14 (s, 3H), 1.07 (s, 3H), 1.00 (s, 9H), 0.89 (s, 3H), 0.07 (s, 3H), 0.06 (s, 3H) ppm; 13C NMR (100 MHz, C6D6) δ = 140.63, 138.50, 126.06, 115.91, 81.76, 70.47, 61.84, 59.31, 57.59, 53.59, 43.76, 42.48, 26.05, 19.27, 18.31, 16.14, -3.97, -4.88 ppm; IR (neat) 2958, 2929, 2857, 2886, 1462, 1374, 1253, 1048, 1022, 836, 774 cm⁻¹; HRMS (ESI) m/z Calcd for C20H36O3SiNa [M+Na]⁺ 375.2326, found 375.2337.

Synthesis of compound 23

To a solution of compound 22 (60 mg, 0.17 mmol) in DCM (9 mL) was added DMP (144 mg, 0.34 mmol) and NaHCO3 (71 mg, 0.85 mmol). The reaction was stirred at rt for 3 h, and then quenched with saturated NaHCO3 (10 mL), extracted with DCM (20 mL x 2). The combined organic phase was washed with NaHCO3 (20 mL) and brine (20 mL), dried over Na2SO4, and evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 10:1) to afford 23 (53 mg, 88%) as a white solid. mp 108.5-109.7 °C. 1H NMR (400 MHz, C6D6) δ = 9.70 (d, J = 5.3 Hz, 1H), 6.18 (td, J = 10.1, 17.0 Hz, 1H), 5.39 (dd, J = 3.9, 9.4 Hz, 1H), 5.25 (d, J = 9.4 Hz, 1H), 5.06 (dd, J = 2.4, 10.2 Hz, 1H), 5.02 (dd, J = 2.4, 17.1 Hz, 1H), 3.63 (d, J = 3.8 Hz, 1H), 2.69 (d, J = 10.0 Hz, 1H), 2.25 (d, J = 5.3 Hz, 1H), 1.07 (s, 1H), 0.96 (s, 12H), 0.89 (s,
3H), 0.86 (s, 3H), 0.01 (s, 3H), 0.00 (s, 3H) ppm; $^{13}$C NMR (100 MHz, C$_6$D$_6$) $\delta$ = 201.08, 138.66, 137.20, 127.87, 116.59, 82.76, 70.05, 69.84, 58.40, 53.80, 44.50, 26.38, 25.97, 18.69, 18.24, 15.91, -4.06, -4.99 ppm; IR (neat) 2958, 2929, 2855, 1710, 1374, 1251, 1055, 881, 772 cm$^{-1}$; HRMS (ESI) $m/z$ Calcd for C$_{20}$H$_{34}$O$_3$SiNa [M+Na]$^+$ 373.2169, found 373.2193.

**Synthesis of compound 24**

![Diagram](image)

To a stirred solution of compound 23 (25 mg, 0.071 mmol) in THF (5 mL) at 0 °C was added vinyl magnesium bromide (0.18 mL, 1M; freshly prepared following typical method) dropwise during 5 min. The reaction was stirred for 3 h at 0 °C under argon atmosphere, and then quenched with saturated NH$_4$Cl (5 mL), extracted with EA (10 mL x 2). The combined organic phase was washed with saturated NaHCO$_3$ (10 mL) and brine (10 mL), dried over Na$_2$SO$_4$, and evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 10:1) to afford 24 (13 mg, 48%) as a white semi-solid.

$^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ = 6.31 (td, $J$ = 10.1, 17.0 Hz, 1H), 6.14-6.05 (m, 1H), 5.50 (s, 2H), 5.20-5.11 (m, 3H), 5.00 (td, $J$ = 1.5, 10.4 Hz, 1H), 4.27-4.23 (m, 1H), 3.80 (d, $J$ = 1.8 Hz, 1H), 2.96 (d, $J$ = 8.2 Hz, 1H), 2.75 (d, $J$ = 10.1 Hz, 1H), 2.22 (s, 1H), 1.62 (d, $J$ = 3.3 Hz, 1H), 1.23 (s, 3H), 1.13 (s, 3H), 1.07 (s, 3H), 1.00 (s, 6H) ppm; $^{13}$C NMR (100 MHz, C$_6$D$_6$) $\delta$ = 143.20, 141.50, 139.74, 125.95, 84.35, 74.19, 70.44, 62.27, 58.11, 53.90, 44.91, 30.09, 27.20, 26.05, 25.98, 20.25, 18.31, 16.28, -3.96, -4.86 ppm; IR (neat) 2956, 2929, 2857, 1636, 1462, 1256, 1050, 836, 773 cm$^{-1}$; HRMS (ESI) $m/z$ Calcd for C$_{22}$H$_{38}$O$_3$SiNa [M+Na]$^+$ 401.2482, found 401.2492.

**Synthesis of compound 25**

![Diagram](image)

To a stirred mixture of Pd(OAc)$_2$ (1 mg, 0.005 mmol) and CuCl$_2$ (17 mg, 0.13 mmol) in THF (0.5 mL) was added 1,1,3,3-tetramethylthiourea (TMTU) (0.7 mg, 0.005 mmol) at rt, and the formed mixture was stirred for 30 min under argon atmosphere. To this solution was added propene oxide (PO) (0.018 mL, 0.25 mmol) and NH$_4$OAc (4 mg, 0.005 mmol), and the mixture was purged with CO, followed by dropwise addition of enediol 24 (19 mg, 0.05 mmol) in THF (0.1 mL) during 2 min, and the reaction was stirred at 50 °C under CO atmosphere for 12 h. After being cooled to rt, the reaction mixture was diluted with EA (20 mL), filtered through Celite. The filtrate was washed with saturated NH$_4$Cl (10 mL) and brine (10 mL), dried over Na$_2$SO$_4$,
and evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EtOAc = 10:1-5:1) to afford 25 (16 mg, 78%) as a white semi-solid. $^1$H NMR (400 MHz, C$_6$D$_6$) $\delta$ = 6.22 (td, $J$ = 10.0, 17.1 Hz, 1H), 5.53 (dd, $J$ = 4.0, 9.5 Hz, 1H), 5.40 (d, $J$ = 9.5 Hz, 1H), 5.22 (dd, $J$ = 2.2, 17.1 Hz, 1H), 5.08 (dd, $J$ = 2.4, 10.0 Hz, 1H), 3.90 (dd, $J$ = 3.0, 6.6 Hz, 1H), 3.78 (d, $J$ = 3.9 Hz, 1H), 3.65 (dd, $J$ = 3.2, 4.4 Hz, 1H), 2.62 (d, $J$ = 10.1 Hz, 1H), 2.28 (d, $J$ = 17.6 Hz, 1H), 1.74 (dd, $J$ = 4.5, 17.6 Hz, 1H), 1.59 (d, $J$ = 6.6 Hz, 1H), 1.30 (s, 3H), 1.26 (s, 3H), 0.97 (s, 9H), 0.87 (s, 3H), 0.05 (s, 3H), 0.04 (s, 3H) ppm; $^{13}$C NMR (100 MHz, C$_6$D$_6$) $\delta$ = 173.87, 139.66, 137.14, 126.86, 116.86, 94.71, 85.29, 78.10, 70.09, 62.78, 57.78, 51.87, 44.98, 34.51, 25.98, 20.64, 19.89, 18.29, 16.16, -3.98, -4.93 ppm; IR (neat) 2957, 2928, 2857, 1783, 1635, 1258, 1059, 774 cm$^{-1}$; HRMS (ESI) m/z Calcd for C$_{23}$H$_{36}$O$_4$SiNa [M+Na]$^+$ 427.2275, found 427.2271.

**Synthesis of compound 26 and 27**

To a solution of compound 25 (10 mg, 0.025 mmol) in THF (5 mL) was added LDA (0.15 mL, 1 M in THF, 0.15 mmol, freshly prepared following typical method) at -78 $^\circ$C. The resultant mixture was stirred at the same temperature for 20 min, and acetaldehyde (10 $\mu$L, 0.17 mmol) was added. The reaction was stirred at -78 $^\circ$C for 3 h, and then quenched with saturated NH$_4$Cl (5 mL), extracted with EA (10 mL x 2). The combined organic phase was washed with saturated NaHCO$_3$ (10 mL) and brine (10 mL), dried over Na$_2$SO$_4$, and evaporated to give a residue, which was subjected to the next process without further purification.

**Procedure A:**
To a solution of the above crude product in DCM (5 mL) was added Et$_3$N (60 $\mu$L, 0.43 mmol), DMAP (1 mg) and MsCl (10 $\mu$L, 0.12 mmol). The resultant mixture was stirred at 35 $^\circ$C for 40 h, and then quenched with saturated NH$_4$Cl (5 mL), extracted with DCM (10 mL x 2). The combined organic phase was washed with saturated NaHCO$_3$ (5 mL) and brine (5 mL), dried over Na$_2$SO$_4$, and evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EtOAc = 8:1) to afford 26 (2.7 mg, 25% two steps) and 27 (6.5 mg, 61% two steps), both as a white semi-solid.

**Procedure B:**
To a solution of the above crude product in DCM (0.5 mL) was added Et$_3$N (60 $\mu$L, 0.43 mmol), DMAP (1 mg) and MsCl (10 $\mu$L, 0.12 mmol). The resultant mixture was stirred at rt for 20 h, and then quenched with saturated NH$_4$Cl (5 mL), extracted with DCM (10 mL x 2). The combined organic phase was washed with saturated NaHCO$_3$ (5 mL) and brine (5 mL), dried over Na$_2$SO$_4$, and evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EtOAc = 8:1) to afford 26 (5.5 mg, 52% two steps) and 27 (3.2 mg, 30% two steps).
Compound 26. \( ^1H \text{NMR} \) (400 MHz, C\(_6\)D\(_6\)) \( \delta = 6.23 \) (td, \( J = 10.1, 17.1 \) Hz, 1H), 5.96 (q, \( J = 7.2 \) Hz, 1H), 5.54 (dd, \( J = 3.9, 9.5 \) Hz, 1H), 5.42 (d, \( J = 9.5 \) Hz, 1H), 5.19 (dd, \( J = 2.1, 17.0 \) Hz, 1H), 5.06 (dd, \( J = 2.3, 10.1 \) Hz, 1H), 4.14 (d, \( J = 3.2 \) Hz, 1H), 4.06 (dd, \( J = 3.4, 6.8 \) Hz, 1H), 3.80 (d, \( J = 3.8 \) Hz, 1H), 2.71 (d, \( J = 10.1 \) Hz, 1H), 1.97 (d, \( J = 7.3 \) Hz, 3H), 1.71 (d, \( J = 6.8 \) Hz, 1H), 1.30 (s, 3H), 1.28 (s, 3H), 0.97 (s, 3H), 0.95 (s, 9H), 0.05 (s, 3H), 0.02 (s, 3H) ppm; \( ^{13}C \text{NMR} \) (100 MHz, C\(_6\)D\(_6\)) \( \delta = 167.84, 142.69, 139.78, 137.17, 127.16, 126.78, 116.80, 95.33, 83.55, 81.26, 70.14, 62.91, 57.84, 52.01, 45.16, 25.98, 21.09, 20.09, 18.28, 16.25, 14.14, -3.99, -4.93 ppm; IR (neat) 2957, 2929, 2857, 1761, 1686, 1258, 1130, 1117, 1053, 869, 837 cm\(^{-1}\); HRMS (ESI) m/z Calcd for C\(_{25}\)H\(_{38}\)O\(_4\)SiNa [M+Na]\(^+\) 453.2432, found 453.2430.

Compound 27. \( ^1H \text{NMR} \) (400 MHz, C\(_6\)D\(_6\)) \( \delta = 6.72 \) (dq, \( J = 0.9, 7.2 \) Hz, 1H), 6.22 (td, \( J = 10.0, 17.1 \) Hz, 1H), 5.54 (dd, \( J = 4.0, 9.5 \) Hz, 1H), 5.43 (d, \( J = 9.4 \) Hz, 1H), 5.16 (dd, \( J = 2.2, 17.0 \) Hz, 1H), 5.05 (dd, \( J = 2.4, 10.0 \) Hz, 1H), 4.39 (d, \( J = 3.0 \) Hz, 1H), 4.08 (dd, \( J = 3.7, 7.1 \) Hz, 1H), 3.79 (d, \( J = 3.9 \) Hz, 1H), 2.64 (d, \( J = 10.2 \) Hz, 1H), 1.75 (d, \( J = 7.1 \) Hz, 1H), 1.41 (d, \( J = 7.2 \) Hz, 3H), 1.38 (s, 3H), 1.26 (s, 3H), 0.96 (s, 3H), 0.95 (s, 9H), 0.05 (s, 3H), 0.02 (s, 3H) ppm; \( ^{13}C \text{NMR} \) (100 MHz, C\(_6\)D\(_6\)) \( \delta = 168.66, 139.78, 139.74, 137.09, 128.71, 126.77, 116.83, 95.79, 84.02, 76.69, 70.08, 62.75, 57.90, 51.95, 45.18, 25.97, 21.23, 20.18, 18.27, 16.29, 15.39, -4.01, -4.95 ppm; IR (neat) 2957, 2929, 2857, 1766, 1693, 1056, 773 cm\(^{-1}\); HRMS (ESI) m/z Calcd for C\(_{25}\)H\(_{38}\)O\(_4\)SiNa [M+Na]\(^+\) 453.2432, found 453.2430.

Synthesis of compound 26a

To a solution of compound 26 (5 mg, 0.012 mmol) in CH\(_3\)CN (1 mL) was added aqueous HF (aq. 40%, 0.2 mL). The reaction was stirred at rt for 20 h, and then quenched with saturated NaHCO\(_3\) (2 mL), extracted with EA (5 mL x 2). The combined organic phase was washed with brine (5 mL x 2), dried over Na\(_2\)SO\(_4\), and evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 3:1) to afford 26a (3.3 mg, 90%) as a white semi-solid. \( ^1H \text{NMR} \) (400 MHz, C\(_6\)D\(_6\)) \( \delta = 5.97-5.82 \) (m, 2H), 5.59 (dd, \( J = 4.0, 9.5 \) Hz, 1H), 5.35 (d, \( J = 9.4 \) Hz, 1H), 5.12 (dd, \( J = 1.4, 17.1 \) Hz, 1H), 4.96 (dd, \( J = 2.0, 10.3 \) Hz, 1H), 4.07 (d, \( J = 3.3 \) Hz, 1H), 4.00 (dd, \( J = 3.4, 6.8 \) Hz, 1H), 3.58-3.55 (m, 1H), 2.66 (d, \( J = 9.5 \) Hz, 1H), 1.98 (d, \( J = 7.3 \) Hz, 3H), 1.64 (d, \( J = 6.7 \) Hz, 1H), 1.28 (s, 3H), 1.26 (s, 3H), 1.15 (d, \( J = 8.3 \) Hz, 1H), 0.84 (s, 3H) ppm; \( ^{13}C \text{NMR} \) (100 MHz, C\(_6\)D\(_6\)) \( \delta = 167.82, 142.68, 139.74, 135.62, 127.37, 127.14, 119.13, 95.30, 83.53, 81.15, 69.90, 62.74, 56.30, 51.96, 45.01, 20.85, 19.98, 15.43, 14.13 ppm; IR (neat) 2961, 2925, 1755, 1684, 1374, 1215, 1131, 1031, 1011, 965 cm\(^{-1}\); HRMS (ESI) m/z Calcd for C\(_{15}\)H\(_2\)O\(_4\)Na [M+Na]\(^+\) 339.1567, found 339.1568.
Synthesis of pallambin C (1)

To a solution of compound 26a (3 mg, 0.0095 mmol) in DCM (0.5 mL) was added DMP (8 mg, 0.019 mmol) and NaHCO₃ (4 mg, 0.048 mmol). The reaction was stirred at rt for 1 h, and then quenched with saturated Na₂S₂O₃ (2 mL), extracted with DCM (5 mL x 2). The combined organic phase was washed with aqueous NaHCO₃ (5 mL) and brine (5 mL), dried over Na₂SO₄, and evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 3:1) to afford 1 (2.8 mg, 95%) as a colorless oil.

1H NMR (400 MHz, CDCl₃) δ = 6.71-6.66 (m, 2H), 5.89 (d, J = 9.6 Hz, 1H), 5.54 (td, J = 9.8, 16.9 Hz, 1H), 5.22-5.15 (m, 2H), 4.88 (dd, J = 3.2, 6.7 Hz, 1H), 4.84 (d, J = 3.2 Hz, 1H), 2.83 (dd, J = 1.6, 9.5 Hz, 1H), 2.53 (d, J = 6.7 Hz, 1H), 2.25 (d, J = 7.3 Hz, 1H), 1.42 (s, 3H), 1.14 (s, 3H), 1.04 (s, 3H) ppm; 13C NMR (100 MHz, CDCl₃) δ = 201.56, 168.38, 157.11, 144.82, 132.39, 127.01, 126.10, 121.78, 94.17, 83.13, 82.34, 63.98, 62.79, 60.83, 47.02, 22.43, 19.68, 14.60, 12.88 ppm; IR (neat) 2967, 2929, 1759, 1681, 1375, 1118, 916 cm⁻¹; HRMS (ESI) m/z Calcd for C₁₉H₂₃O₄ [M+H]⁺ 315.1591, found 315.1606.

Synthesis of compound 27a

To a solution of compound 27 (5 mg, 0.012 mmol) in CH₃CN (1 mL) was added aqueous HF (aq. 40%, 0.2 mL). The reaction was stirred at rt for 20 h, and then quenched with saturated NaHCO₃ (2 mL), extracted with EA (5 mL x 2). The combined organic phase was washed with brine (5 mL x 2), dried over Na₂SO₄, and evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 3:1) to afford 27a (3.3 mg, 90%) as a white semi-solid.

1H NMR (400 MHz, C₆D₆) δ = 6.72 (q, J = 7.2 Hz, 1H), 5.86 (td, J = 9.9, 17.2 Hz, 1H), 5.59 (dd, J = 4.0, 9.4 Hz, 1H), 5.35 (d, J = 9.4 Hz, 1H), 5.09 (dd, J = 1.4, 17.2 Hz, 1H), 4.95 (dd, J = 1.9, 10.2 Hz, 1H), 4.32 (d, J = 3.1 Hz, 1H), 4.02 (dd, J = 3.6, 7.0 Hz, 1H), 3.55-3.52 (m, 1H), 2.61 (d, J = 9.4 Hz, 1H), 1.67 (d, J = 7.0 Hz, 1H), 1.39 (d, J = 7.2 Hz, 3H), 1.31 (s, 3H), 1.23 (s, 3H), 1.15 (d, J = 8.3 Hz, 1H), 0.83 (s, 3H) ppm; 13C NMR (100 MHz, C₆D₆) δ = 168.64, 139.75, 135.56, 128.68, 127.33, 119.11, 95.78, 84.00, 76.58, 69.84, 62.57, 56.37, 51.94, 45.02, 20.97, 20.07, 15.48, 15.40 ppm; IR (neat) 2956, 2927, 1756, 1693, 1375, 1217, 1143, 1074, 1031, 738 cm⁻¹; HRMS (ESI) m/z Calcd
for C\textsubscript{19}H\textsubscript{24}O\textsubscript{4}Na [M+Na]\textsuperscript{+} 339.1567, found 339.1568.

**Synthesis of pallambin D (2)**

To a solution of compound 27a (3 mg, 0.0095 mmol) in DCM (0.5 mL) was added DMP (8 mg, 0.019 mmol) and (4 mg, 0.048 mmol). The reaction was stirred at rt for 2 h, and then quenched with saturated Na\textsubscript{2}S\textsubscript{2}O\textsubscript{3} (2 mL), extracted with DCM (5 mL x 2). The combined organic phase was washed with aqueous NaHCO\textsubscript{3} (5 mL) and brine (5 mL), dried over Na\textsubscript{2}SO\textsubscript{4}, and evaporated to give a residue, which was purified by a flash column (silica gel, Hex/EA = 3:1) to afford 2 (2.6 mg, 89%) as a white solid. mp 184.5-185.7 °C (lit.\textsuperscript{[1]} mp 191 °C).\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ = 7.00 (q, J = 7.3 Hz, 1H), 6.69 (dd, J = 1.9, 9.5 Hz, 1H), 5.89 (d, J = 9.6 Hz, 1H), 5.53 (td, J = 9.8, 16.9 Hz, 1H), 5.20-5.15 (m, 2H), 5.09 (d, J = 3.2 Hz, 1H), 4.90 (dd, J = 3.6, 7.0 Hz, 1H), 2.76 (dd, J = 1.8, 9.4 Hz, 1H), 2.56 (d, J = 7.0 Hz, 1H), 2.03 (d, J = 7.2 Hz, 3H), 1.42 (s, 3H), 1.16 (s, 3H), 1.01 (s, 3H) ppm; \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) δ = 201.61, 169.53, 157.12, 141.89, 132.37, 127.68, 126.97, 121.73, 94.51, 83.80, 77.76, 64.03, 62.79, 60.62, 47.03, 22.50, 19.78, 16.18, 12.84 ppm; IR (neat) 2967, 2931, 1764, 1682, 1376, 1209, 1121, 1072, 973 cm\textsuperscript{-1}; HRMS (ESI) m/z Calcd for C\textsubscript{19}H\textsubscript{23}O\textsubscript{4} [M+H]\textsuperscript{+} 315.1591, found 315.1594.

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Spectral comparison between natural and synthetic Pallambin C (1):

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Basic crystal data for compounds 2, 10, 11, 16 and 22

CCDC 879025 (2), CCDC 879026 (10), CCDC 879027 (11), CCDC 879028 (16) and CCDC 879029 (22) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Chem. Commun.
Deposition Number(s) 879025 879026 879027 879028 879029
CIF files for 5 structures are attached to this message.

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ORTEP diagram of compound 2. Thermal ellipsoids were plotted at 30 % probability level. Hydrogen atoms are omitted for clarity.
ORTEP diagram of compound 10. Thermal ellipsoids were plotted at 30 % probability level. Hydrogen atoms are omitted for clarity.

ORTEP diagram of compound 11. Thermal ellipsoids were plotted at 30 % probability level. Hydrogen atoms are omitted for clarity.
ORTEP diagram of compound 16. Thermal ellipsoids were plotted at 30% probability level. Hydrogen atoms are omitted for clarity.

ORTEP diagram of compound 22. Thermal ellipsoids were plotted at 30% probability level. Hydrogen atoms are omitted for clarity.
$^1$H NMR spectroscopic comparison (0.5-7.0 ppm)

natural
600 MHz in CDCl$_3$

synthetic
400 MHz in CDCl$_3$

pallamin C (t)
\(^{13}\text{C} \text{NMR spectroscopic comparison} \ (0-210 \text{ ppm})\)

natural
150MHz in CDCl\(_3\)

synthetic
100 MHz in CDCl\(_3\)

pallamin C (1)
\[^1\text{H} \text{NMR spectroscopic comparison (0.5-7.2 ppm)}\]

natural
600 MHz in CDCl\textsubscript{3}

synthetic
400 MHz in CDCl\textsubscript{3}
\(^{13}\text{C} \text{ NMR spectroscopic comparison (5-210 ppm)}\)

natural
150 MHz in CDCl\(_3\)

synthetic
100 MHz in CDCl\(_3\)
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 ppm

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PROCNO                1
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RG                  101
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DE                 6.50 usec
TE                298.9 K
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TD0                   1
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SF          400.1900141 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

NAME          XS-1-7-A1
EXPNO                 2
PROCNO                1
Date          20110919
Time              18.57
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 176
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  203
DW               20.800 usec
DE                 6.50 usec
TE                299.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
======== CHANNEL f1 ========
NUC1                13C
P1                 9.90 usec
PL1               -2.00 dB
PL1W        55.33689499 W
SFO1        100.6379183 MHz
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2               -1.00 dB
PL12              15.16 dB
PL13              18.62 dB
PL2W        13.56617069 W
PL12W        0.32844096 W
PL13W        0.14806664 W
SFO2        400.1916008 MHz
SI                32768
SF          100.6278427 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40

Bruker Advance III 400
NAME          XS-1-7-A1
EXPNO                 2
PROCNO                1
Date          20110919
Time              18.57
INSTRUM           spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT           CDCl3
NS                 176
DS                    4
SWH           24038.461 Hz
FIDRES         0.366798 Hz
AQ            1.3631988 sec
RG                  203
DW               20.800 usec
DE                 6.50 usec
TE                299.3 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
======== CHANNEL f1 ========
NUC1                13C
P1                 9.90 usec
PL1               -2.00 dB
PL1W        55.33689499 W
SFO1        100.6379183 MHz
======== CHANNEL f2 ========
CPDPRG2         waltz16
NUC2                 1H
PCPD2             90.00 usec
PL2               -1.00 dB
PL12              15.16 dB
PL13              18.62 dB
PL2W        13.56617069 W
PL12W        0.32844096 W
PL13W        0.14806664 W
SFO2        400.1916008 MHz
SI                32768
SF          100.6278427 MHz
WDW                  EM
SSB                   0
LB                 1.00 Hz
GB                    0
PC                 1.40
### Table 1: NMR Spectroscopy Data

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### Figure 1: NMR Spectrum of Compound 1

- Chemical Formula: C$_3$H$_5$O$_2$
- Exact Mass: 394.26
- Elemental Analysis: C: 75.15, H: 8.65, O: 12.17

### Figure 2: NMR Spectrum of Compound 2

- Chemical Formula: C$_5$H$_5$O$_2$
- Exact Mass: 524.35
- Elemental Analysis: C: 79.15, H: 6.80, O: 12.17

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**Bruker Advance III 400**

The NMR spectra were recorded on a Bruker Advance III 400 spectrometer. The experimental conditions and parameters are detailed in the supplementary material.
Chemical Formula: C₅H₈O₃
Exact Mass: 256.17
Elemental Analysis: C, 85.60; H, 9.44; O, 24.97
Electronic Supplementary Material (ESI) for Chemical Communications
This journal is © The Royal Society of Chemistry 2012
NAME       XS-1-38-A1
EXPNO       1
PROCNO      1
Date_        20101006
Time         11.02
INSTRUM      spect
PROBHD      5 mm PABBO BB-
PULPROG       zg30
TD            65536
SOLVENT     CDCl3
NS             8
DS             2
SWH       8223.685 Hz
FIDRES     0.125483 Hz
AQ            3.9846387 sec
RG              80.6
DW            60.800 usec
DE             6.50 usec
TE           297.9 K
D1        1.00000000 sec
TD0                   1
======== CHANNEL f1 ========
NUC1                 1H
P1                14.00 usec
PL1               -1.00 dB
PL1W       13.56617069 W
SFO1        400.1924713 MHz
SI                32768
SF          400.1900144 MHz
WDW                  EM
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm

NAME       XS-1-38-A1
EXPNO       2
PROCNO      1
Date_        20101006
Time         11.09
INSTRUM      spect
PROBHD   5 mm PABBO BB-
PULPROG          zgpg30
TD                65536
SOLVENT     CDCl3
NS            500
DS             4
SWH           24038.461 Hz
FIDRES     0.366798 Hz
AQ            1.3631988 sec
RG              228
DW            20.800 usec
DE             6.50 usec
TE           298.4 K
D1           2.00000000 sec
D11          0.03000000 sec
TD0                   1
======== CHANNEL f1 ========
NUC1                13C
P1                 9.90 usec
PL1               -2.00 dB
PL1W       55.33689499 W
SFO1        100.6379183 MHz

210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm
Bruker Advance III 400
NAME: EX-1-91-A1
EXPNO: 1
PROCNO: 1
Date: 20110409
Time: 10.48
INSTRUM: spect
PROBHD: 5 mm PADUL 13C
PULPROG: zg30
TD: 65536
SOLVENT: C6D6
NS: 8
DS: 2
SWH: 8223.685 Hz
FIDRES: 0.125483 Hz
AQ: 3.9846387 sec
RG: 80.6
DW: 60.800 usec
DE: 6.50 usec
TE: 294.1 K
D1: 1.00000000 sec
TD0: 1
======== CHANNEL f1 ========
NUC1: 1H
P1: 14.83 usec
PL1: 0.00 dB
PL1W: 8.31434441 W
SFO1: 400.1324710 MHz
SI: 32768
SF: 400.1300438 MHz
WDW: EM
SSB: 0
LB: 0.30 Hz
GB: 0
PC: 1.00

Bruker Advance III 400
NAME: EX-1-91-A1
EXPNO: 2
PROCNO: 1
Date: 20110409
Time: 10.56
INSTRUM: spect
PROBHD: 5 mm PADUL 13C
PULPROG: zgpg30
TD: 65536
SOLVENT: C6D6
NS: 202
DS: 4
SWH: 24038.461 Hz
FIDRES: 0.366798 Hz
AQ: 1.3631988 sec
RG: 203
DW: 20.800 usec
DE: 6.50 usec
TE: 294.6 K
D1: 2.00000000 sec
D11: 0.03000000 sec
TD0: 1
======== CHANNEL f1 ========
NUC1: 13C
P1: 9.68 usec
PL1: -0.60 dB
PL1W: 41.24164963 W
SFO1: 100.6228298 MHz

======== CHANNEL f2 ========
CPDPRG2: waltz16
NUC2: 1H
PCPD2: 90.00 usec
PL2: 0.00 dB
PL12: 15.66 dB
PL13: 15.92 dB
PL2W: 8.31434441 W
PL12W: 0.22585411 W
PL13W: 0.21272963 W
SFO2: 400.1316005 MHz
SI: 32768
SF: 100.6127444 MHz
WDW: EM
SSB: 0
LB: 1.00 Hz
GB: 0
PC: 1.40

Electronic Supplementary Material (ESI) for Chemical Communications
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pallamin D (2)
Chemical Formula: C_{14}H_{12}O_{2}
Exact Mass: 314.15

Elemental Analysis: C, 72.59; H, 7.05; O, 20.36

pallamin D (2)
Chemical Formula: C_{14}H_{12}O_{2}
Exact Mass: 314.15

Elemental Analysis: C, 72.59; H, 7.05; O, 20.36