

Supporting Information

A Convergent Stereocontrolled Total Synthesis of (–)-Terpestacin

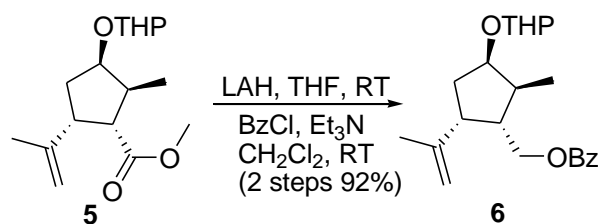
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General experimental details

^1H and ^{13}C NMR spectra were recorded on either at 400 MHz (^1H) and 100 MHz (^{13}C) or at 500 MHz (^1H) and 125 MHz (^{13}C), and were internally referenced to residual proton solvent signals (note: CDCl_3 referenced at $\delta 7.26$ and 77.0 ppm, respectively). Data for ^1H NMR were reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet), integration, coupling constant (Hz) and assignment. Data for ^{13}C NMR were reported in terms of chemical shifts and no special nomenclature was used for equivalent carbons. High-resolution mass spectra (HRMS) were obtained using electrospray ionization (ESI) or electron ionization (EI). Optical Rotations were measured at 589 nm.



Compound 6: LiAlH₄ (4.9 g, 0.129 mol, 1 eq) was added over 20 min at RT to a stirred solution of **5** (36.39 g, 0.129 mol) in THF (360 mL). The reaction mixture was kept at RT for 3 h before it was quenched with H₂O (4.9 mL), followed by sequential addition of NaOH (2 M, 10 mL) and H₂O (15 mL). The resulting mixture was filtered on a Büchner funnel, and the solid was washed with ethyl acetate (5×60 mL). The combined organic extracts were concentrated under vacuum to give a crude oil (31.4 g) which was dissolved in CH₂Cl₂ (300 mL). Et₃N (20.6 mL) and BzCl (14.52 mL) were sequentially added to the reaction mixture at RT. The reaction mixture was kept at RT for 10 h before it was quenched with saturated NaHCO₃ (30 mL). The mixture was washed with water (100 mL). The organic layer was separated and the aqueous layer was back extracted with CH₂Cl₂ (3 × 50 mL). The combined organic extracts were

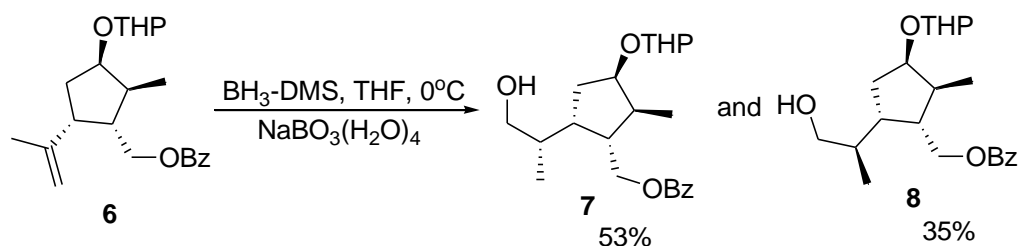
dried over MgSO₄, filtered and evaporated under reduced pressure to afford compound **6**, which was purified via silica gel flash column chromatography to give a pale yellow oil (42.5 g, 92%, over two steps). R_f: 0.2 (petroleum ether/ethyl acetate = 30/1).

¹H NMR (CDCl₃, 400 MHz): δ 8.02 (m, 4H), 7.55 (m, 2H), 7.43 (m, 4H), 4.83 (m, 2H), 4.73 (s, 2H), 4.71 (t, J = 3.4 Hz, 1H), 4.60 (dd, J = 4.6, 3.0 Hz, 1H), 4.26-4.20 (m, 3H), 4.12-4.04 (m, 3H), 3.92-3.86 (m, 2H), 3.53-3.48 (m, 2H), 3.08 (ddd, J = 9.5, 9.5, 8.1 Hz, 1H), 2.99 (ddd, J = 10.3, 10.3, 6.7 Hz, 1H), 2.28 (m, 2H), 2.09 (m, 2H), 2.02-1.66 (m, 8H), 1.80 (s, 6H), 1.62-1.45 (m, 8H), 1.21 (d, J = 7.0 Hz, 3H), 1.09 (d, J = 7.0 Hz, 3H).

¹³C NMR (CDCl₃, 125 MHz): δ 166.7, 144.75, 144.71, 132.8, 130.5, 129.5, 128.3, 111.04, 110.95, 100.4, 94.9, 81.0, 76.3, 66.6, 66.5, 62.8, 61.8, 45.1, 44.98, 44.96, 44.9, 42.6, 42.5, 37.6, 34.8, 31.1, 30.8, 25.6, 25.5, 23.70, 23.66, 19.9, 19.3, 14.8, 14.7.

HRMS (ESI-TOF): calc'd for C₂₂H₃₀O₄Na[M + Na]⁺: 381.2042, found: 381.2033.

[α]_D²⁰: -14.7 (C = 3.00, CH₂Cl₂).



Compound 7 and compound 8: To a solution of **6** (18.6 g, 0.052 mol, 1 eq) in THF (100 mL) at 0 °C was added BH₃•DMS (2 M in THF, 26 mL, 1 eq). After the reaction mixture was kept at 0 °C for 3 h, water (45 mL) was slowly added followed by the addition of sodium perborate (24 g, 3 eq). The mixture was maintained at room temperature (water bath) for 2 h with vigorous stirring. The two phases were separated, and the aqueous phase was extracted with ether (3 × 50 mL). The combined organic phase was washed with saturated NaCl solution (50 mL), dried over MgSO₄, filtered and evaporated under reduced pressure. The crude residue was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to provide compound **7** (10.2 g, 53%, R_f: 0.25: petroleum ether/ethyl acetate = 3/1) and compound **8** (6.8 g, 35%, R_f: 0.2: petroleum ether/ethyl acetate = 3/1). Both are pale yellow oil.

Compound 7: ¹H NMR (CDCl₃, 400 MHz): δ 8.03 (m, 4H), 7.56 (m, 2H), 7.45 (m, 4H), 4.68 (t, J = 3.4 Hz, 1H), 4.56 (dd, J = 4.6, 2.8 Hz, 1H), 4.46 (dd, J = 5.6, 5.6 Hz, 1H), 4.43 (dd, J = 5.5, 5.5 Hz, 1H), 4.24-4.14 (m, 4H), 3.89 (m, 2H), 3.71 (m, 2H), 3.50 (m, 2H), 3.42 (m, 2H), 2.37-2.11 (m, 6H), 1.99 (ddd, J = 13.4, 7.3, 1.9 Hz, 1H), 1.89-1.48 (m, 17H), 1.16 (d, J = 6.8 Hz, 3H), 1.05 (d, J = 6.8 Hz, 3H), 0.97 (d, J = 4.8 Hz, 3H), 0.96 (d, J = 4.8 Hz, 3H).

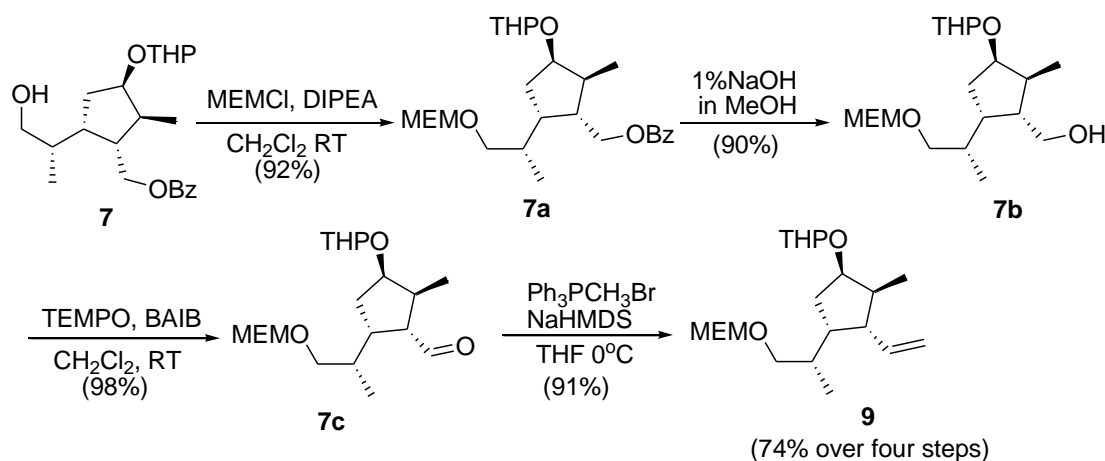
¹³C NMR (CDCl₃, 125 MHz): δ 166.8, 132.9, 130.3, 129.5, 128.4, 100.1, 95.4, 79.8, 75.8, 67.8, 67.7, 66.0, 65.9, 62.9, 62.0, 45.4, 45.3, 42.3, 42.1, 40.1, 39.9, 36.7, 35.8, 35.6, 34.2, 31.2, 30.8, 25.6, 25.5, 20.0, 19.4, 16.1, 16.0, 14.9, 14.8.

HRMS (ESI-TOF): calc'd for $C_{22}H_{32}O_5Na$ $[M + Na]^+$: 399.2147, found: 399.2150.
 $[\alpha]_D^{20}$: -18.0 (C = 1.65, CH_2Cl_2).

Compound **8**: 1H NMR ($CDCl_3$, 400 MHz): δ 8.03 (m, 4H), 7.56 (m, 2H), 7.45 (m, 4H), 4.66 (t, J = 3.3 Hz, 1H), 4.54 (dd, J = 5.1, 2.6 Hz, 1H), 4.45 (dd, J = 6.7, 4.6 Hz, 1H), 4.43 (dd, J = 6.6, 4.5 Hz, 1H), 4.26 (m, 1H), 4.21-4.11 (m, 3H), 3.89 (m, 2H), 3.65 (m, 2H), 3.52-3.42 (m, 4H), 2.33-2.12 (m, 6H), 2.01 (ddd, J = 13.0, 6.8, 1.5 Hz, 1H), 1.91-1.49 (m, 17H), 1.16 (d, J = 7.1 Hz, 3H), 1.10 (d, J = 6.5 Hz, 3H), 1.09 (d, J = 6.5 Hz, 3H), 1.06 (d, J = 7.1 Hz, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 166.8, 132.9, 130.3, 129.5, 128.4, 100.0, 95.7, 80.0, 76.1, 67.5, 67.4, 65.9, 65.8, 63.2, 62.1, 45.33, 45.30, 41.5, 41.33, 41.27, 37.0, 35.8, 35.7, 34.8, 31.2, 30.9, 25.6, 25.5, 20.1, 19.5, 16.9, 16.8, 15.05, 15.01.

HRMS (ESI-TOF): calc'd for $C_{22}H_{32}O_5Na$ $[M + Na]^+$: 399.2147, found: 399.2145.
 $[\alpha]_D^{20}$: -18.6 (C = 1.23, CH_2Cl_2).



Compound 9: To a solution of **7** (10.2 g, 0.027 mol, 1 eq) in CH_2Cl_2 (100 mL) was sequentially added diisopropylethylamine (5.20 mL, 1.1 eq) and MEMCl (3.13 mL, 1.01 eq) at RT. The reaction mixture was kept at RT for 3 h before it was quenched with saturated $NaHCO_3$ (30 mL). The mixture was washed with water (50 mL). The organic layer was separated and the aqueous layer was back extracted with CH_2Cl_2 (3×40 mL). The combined organic extracts were dried over $MgSO_4$, filtered on silica gel, and evaporated under reduced pressure to afford crude compound **7a** (11.6 g, 92%) as a yellow oil, which was used without further purification.

To a solution of **7a** in MeOH (100 mL) was added NaOH (0.9962 g). After 10 h, the reaction mixture was concentrated to about 50 mL, diluted with ether (150 mL) and washed with water (100 mL). The organic layer was separated and the aqueous layer was back extracted with ether (3×50 mL). The combined organic extracts were dried over $MgSO_4$, filtered and evaporated under reduced pressure to afford compound **7b**, which was purified via silica gel flash column chromatography (petroleum ether/ethyl acetate = 2/1) to give a pale yellow oil (**7b**, 8.1 g, 90%, R_f : 0.25: petroleum ether/ethyl acetate = 2/1).

To a solution of **7b** (8.1 g, 0.0225 mol) in CH₂Cl₂ (100 mL) was added TEMPO (0.1756 g, 0.05 eq) and diacetoxyiodobenzene (7.9 g, 1.1 eq) at RT. The reaction mixture was kept at RT for 3 h before it was quenched with saturated NaHCO₃ (20 mL). The mixture was washed with water (50 mL). The aqueous layer was back extracted with CH₂Cl₂ (3 × 40 mL). The combined organic extracts were dried over MgSO₄, filtered and evaporated under reduced pressure to afford compound **7c**, which was purified via silica gel flash column chromatography (petroleum ether/ethyl acetate = 3/1) to give a pale yellow oil (**7c**, 7.9 g, 98%, R_f: 0.33: petroleum ether/ethyl acetate = 3/1).

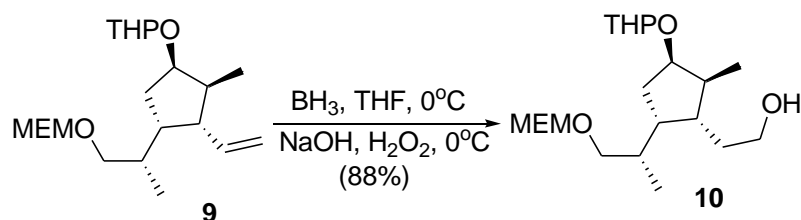
In a flame dried, argon purged round bottom flask, methyltriphenylphosphonium bromide (7.9 g, 1 eq) and THF (60 mL) was added. The flask was cooled to -20 °C, and then NaHMDS (1 M in THF, 22.1 mL, 1eq) was added dropwise. The reaction mixture was kept at -20 °C for 2 h before **7c** (7.9 g, 0.0221 mol, 1 eq) in THF (20 mL) was added dropwise. The reaction mixture was kept at -20 °C for 1 h, warmed to 0 °C and stirred for 1 h. The reaction solution was poured into a mixture of ether (300 mL) and water (200 mL). The two phases were separated, and the aqueous layer was back extracted with ether (3 × 50 mL). The combined organic extracts were dried over MgSO₄, filtered and evaporated under reduced pressure to afford compound **9**, which was purified via silica gel flash column chromatography (petroleum ether/ethyl acetate = 10/1) to give a pale yellow oil (**9**, 7.1 g, 91% , R_f: 0.25: petroleum ether/ethyl acetate = 10/1).

Compound **9**: ¹H NMR (CDCl₃, 400 MHz): δ 5.73 (m, 2H), 4.99 (m, 4H), 4.69-4.66 (5H, including Single at 4.68), 4.55 (dd, J = 4.6, 2.8 Hz, 1H), 4.14 (ddd, J = 4.8, 4.8, 1.0 Hz, 1H), 4.10 (ddd, J = 5.6, 5.6, 2.0 Hz, 1H), 3.88 (m, 2H), 3.66 (m, 4H), 3.59-3.54 (m, 6H), 3.49 (m, 2H), 3.39 (s, 6H), 3.20 (dd, J = 7.7, 1.9 Hz, 1H), 3.17 (dd, J = 7.8, 1.8 Hz, 1H), 2.32 (m, 2H), 2.18 (m, 2H), 1.94 (ddd, J = 13.4, 7.6, 2.1 Hz, 1H), 1.88-1.39 (m, 19H), 1.03 (d, J = 7.0Hz, 3H), 0.924 (d, J = 7.4Hz, 3H), 0.918 (d, J = 6.6 Hz, 3H), 0.91 (d, J = 6.9 Hz, 3H).

¹³C NMR (CDCl₃, 125 MHz): δ 139.9, 139.7, 115.13, 115.05, 99.8, 95.6, 95.2, 80.3, 76.5, 72.2, 72.1, 71.8, 66.6, 66.5, 62.8, 61.8, 59.0, 52.3, 52.1, 45.3, 45.1, 41.3, 41.1, 36.4, 34.2, 34.0, 33.8, 31.2, 30.8, 25.65, 25.55, 19.9, 19.3, 16.2, 16.1, 13.5, 13.3.

HRMS (ESI-TOF): calc'd for C₂₀H₃₆O₅Na [M + Na]⁺: 379.2460, found: 379.2467.

[α]_D²⁰: -23.6 (C = 2.21, CH₂Cl₂).



Compound 10: To a solution of **9** (7.0 g, 0.0196 mol, 1 eq) in THF (100 mL) at 0 °C was added BH₃•THF (1 M in THF, 23.6 mL, 1.2 eq). After the reaction mixture was kept at 0 °C for 5 h, NaOH (3 M, 23.6 mL, 3.6 eq) was slowly added followed by the

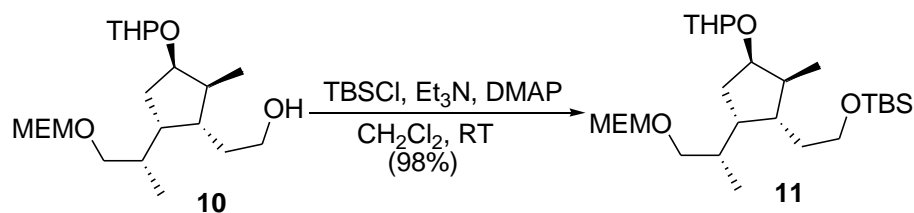
addition of H₂O₂ (34% in water, 8 mL, 3.6 eq) and the mixture was maintained at the same temperature for 2 h with vigorous stirring. The mixture was diluted with ether (200 mL), washed with water (100 mL) and saturated NH₄Cl (100 mL). The aqueous layer was back extracted with ether (3 × 80 mL). The combined organic phase was washed with saturated NaCl solution (100 mL) and dried over MgSO₄, filtered and evaporated under reduced pressure to afford compound **10**, which was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 2/1) to give a pale yellow oil (**10**, 6.5 g, 88%, R_f: 0.25: petroleum ether/ethyl acetate = 3/2).

¹H NMR (CDCl₃, 400 MHz): δ 4.69 (m, 4H), 4.62 (t, J = 3.3 Hz, 1H), 4.50 (m, 1H), 4.17 (m, 2H), 3.87 (m, 2H), 3.73-3.54 (m, 14H), 3.47 (m, 2H), 3.34 (s, 6H), 3.18 (d, J = 8.7 Hz, 1H), 3.16 (d, J = 8.6 Hz, 1H), 2.14-1.43 (m, 28H, including -OH), 1.28 (m, 2H), 1.03 (d, J = 7.1 Hz, 3H), 0.94 (d, J = 6.5 Hz, 3H), 0.92 (d, J = 6.8 Hz, 6H).

¹³C NMR (CDCl₃, 125 MHz): δ 99.3, 96.0, 95.36, 95.34, 78.8, 75.9, 72.0, 71.9, 66.74, 66.73, 62.8, 62.1, 61.7, 61.6, 59.0, 43.4, 43.0, 42.8, 42.3, 40.9, 40.8, 35.7, 33.7, 33.5, 32.8, 32.4, 31.2, 30.8, 25.6, 25.5, 19.9, 19.5, 16.7, 16.5, 15.07, 15.05.

HRMS (ESI-TOF): calc'd for C₂₀H₃₈O₆Na [M + Na]⁺: 397.2566, found: 397.2562.

[α]_D²⁰: -14.7 (C = 3.38, CH₂Cl₂).



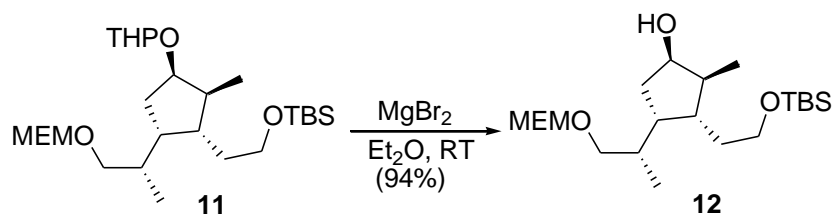
Compound 11: To a solution of **10** (6.3 g, 0.0168 mol, 1 eq) in CH₂Cl₂ (100 mL) at RT was added Et₃N (3 mL, 1.3 eq), TBSCl (2.78 g, 1.1 eq) and DMAP (0.1 g, 0.05 eq). After being kept at RT for 8 h, the reaction mixture was washed with water (50 mL). The aqueous layer was back extracted with CH₂Cl₂ (3 × 50 mL). The combined organic phase was washed with saturated NaCl solution (50 mL) and dried over MgSO₄, filtered and evaporated under reduced pressure to afford compound **11**, which was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 5/1) to give a pale yellow oil (**11**, 8.1 g, 98%, R_f: 0.5: petroleum ether/ethyl acetate = 5/1).

¹H NMR (CDCl₃, 400 MHz): δ 4.69 (s, 4H), 4.62 (t, J = 3.3 Hz, 1H), 4.51 (dd, J = 4.6, 2.5 Hz, 1H), 4.17 (m, 2H), 3.88 (m, 2H), 3.72-3.54 (m, 12H), 3.48 (m, 4H), 3.39 (s, 6H), 3.24 (d, J = 6.8 Hz, 1H), 3.21 (d, J = 8.2 Hz, 1H), 2.15-1.45 (m, 26H), 1.23 (m, 2H), 1.02 (d, J = 7.1 Hz, 3H), 0.93 (d, J = 6.1 Hz, 3H), 0.92 (d, J = 6.2 Hz, 3H), 0.91 (d, J = 7.2 Hz, 3H), 0.89 (s, 18H), 0.042 (s, 6H), 0.041 (s, 6H).

¹³C NMR (CDCl₃, 125 MHz): δ 99.3, 96.0, 95.7, 78.8, 76.0, 72.3, 72.2, 71.8, 66.7, 66.6, 62.8, 62.13, 62.06, 59.0, 43.17, 43.14, 42.9, 42.0, 40.8, 40.6, 35.6, 33.7, 33.5, 32.4, 32.0, 31.2, 30.8, 26.0, 25.64, 25.55, 19.9, 19.5, 18.3, 16.5, 16.3, 15.01, 14.97, -5.3.

HRMS (ESI-TOF): calc'd for C₂₆H₅₂O₆SiNa [M + Na]⁺: 511.3431, found: 511.3424.

$[\alpha]_D^{20}$: -2.89 (C = 2.04, CH₂Cl₂).



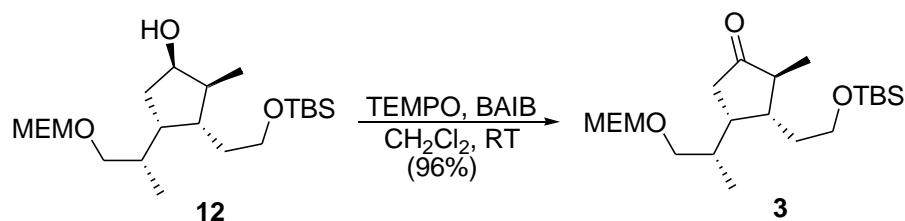
Compound 12: To a solution of **11** (8.0 g, 0.0164 mol, 1 eq) in ether (100 mL) at RT was added the solution of MgBr₂ (5 eq) in ether (100 mL) (prepared from the reaction of Mg and 1,2-dibromoethane). The reaction mixture was kept at RT for 16 h before it was quenched with saturated NaHCO₃ (100 mL). The mixture was washed with water (100 mL). The aqueous layer was back extracted with ether (3 × 80 mL). The combined organic phase was dried over MgSO₄, filtered and evaporated under reduced pressure to afford compound **12**, which was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 4/1) to give a pale yellow oil (**12**, 6.2 g, 94% , R_f: 0.3: petroleum ether/ethyl acetate = 3/1).

¹H NMR (CDCl₃, 400 MHz): δ 4.69 (s, 2H), 4.18 (m, 1H), 3.69-3.54 (m, 6H), 3.47 (dd, J = 9.4, 4.6 Hz, 1H), 3.39 (s, 3H), 3.24 (dd, J = 9.3, 7.6 Hz 1H), 2.18 (m, 1H), 1.87 (m, 1H), 1.80 (m, 1H), 1.75-1.64 (m, 4H), 1.30 (br, 1H), 1.26 (m, 1H), 0.99 (d, J = 6.6 Hz, 3H), 0.92 (d, J = 6.6 Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H).

¹³C NMR (CDCl₃, 125 MHz): δ 95.6, 74.0, 72.4, 71.8, 66.7, 62.1, 59.0, 44.2, 42.7, 40.6, 37.3, 33.2, 32.7, 25.9, 18.3, 16.1, 14.4, -5.3.

HRMS (ESI-TOF): calc'd for C₂₁H₄₄O₅SiNa [M + Na]⁺: 427.2856, found: 427.2874.

$[\alpha]_D^{20}$: +8.0 (C = 1.63, CH₂Cl₂).



Compound 3: To a solution of **12** (6.0 g, 0.0148 mol) in CH₂Cl₂ (100 mL) was added TEMPO (0.116 g, 0.05 eq) and diacetoxyiodobenzene (5.3 g, 1.1 eq) at RT. The reaction mixture was kept at RT for 3 h, before quenched with saturated NaHCO₃ (20 mL). The mixture was wash with water (50 mL). The aqueous layer was back extracted with CH₂Cl₂ (3 × 50 mL). The combined organic extracts were dried over MgSO₄, filtered and evaporated under reduced pressure to afford compound **3**, which was purified via silica gel flash column chromatography (petroleum ether/ethyl acetate = 7/1) to give a pale yellow oil (**3**, 5.7 g, 96%, R_f: 0.2: petroleum ether/ethyl acetate = 7/1).

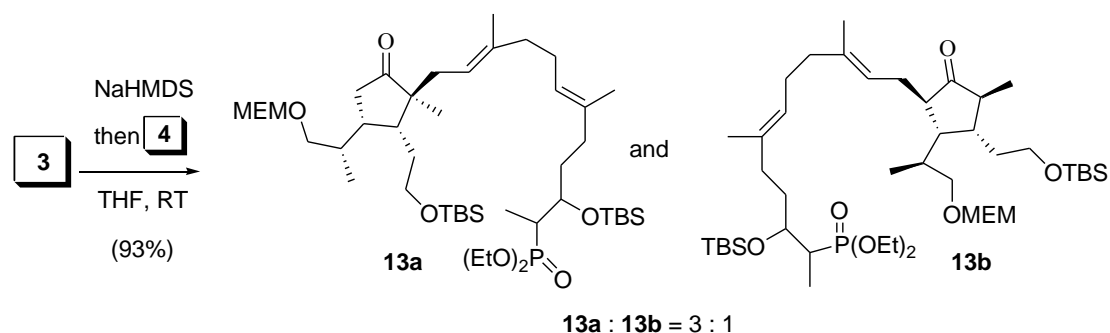
¹H NMR (CDCl₃, 400 MHz): δ 4.71 (s, 2H), 3.72-3.55 (m, 6H), 3.50 (dd, J = 9.4, 4.8

Hz, 1H), 3.39 (s, 3H), 3.37 (dd, $J = 9.5, 6.8$ Hz 1H), 2.36-2.26 (m, 2H), 2.17 (m, 1H), 2.12-2.02 (m, 2H), 1.95 (m, 1H), 1.78 (m, 1H), 1.36 (m, 1H), 1.09 (d, $J = 7.5$ Hz, 3H), 0.93 (d, $J = 6.7$ Hz, 3H), 0.89 (s, 9H), 0.04 (s, 6H).

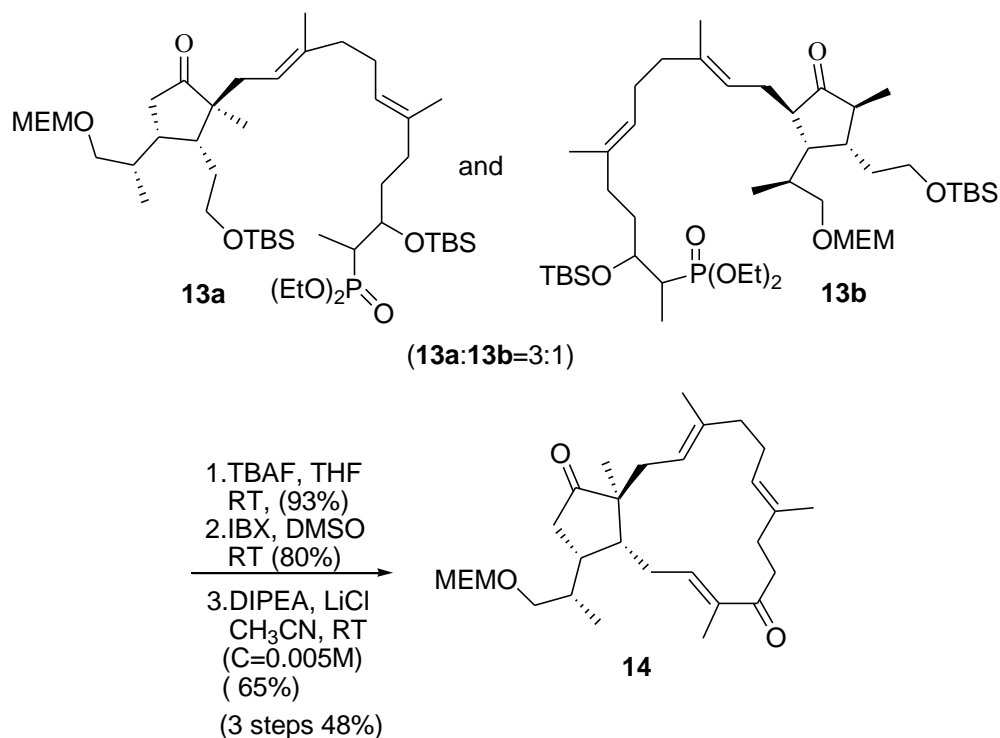
^{13}C NMR (CDCl_3 , 125 MHz): δ 221.8, 95.7, 71.8, 71.1, 66.8, 61.2, 59.0, 48.6, 42.0, 40.2, 38.6, 33.4, 31.3, 25.9, 18.3, 16.1, 15.9, -5.37, -5.40.

HRMS (ESI-TOF): calc'd for $\text{C}_{21}\text{H}_{42}\text{O}_5\text{SiNa}$ [$\text{M} + \text{Na}$] $^+$: 425.2699, found: 425.2716.

$[\alpha]_{\text{D}}^{20}$: -24.6 ($C = 1.95$, CH_2Cl_2).



Compound (13a, 13b): To a solution of **3** (0.750 g, 0.00186 mol, 1 eq) in THF (7 mL) at RT was slowly added NaHMDS (2 M in THF, 0.88 mL, 0.95 eq) during 1h, the solution was stirred at RT for additional hour. Allylic bromide **4** (1.00 g, 1 eq) in THF (7 mL) was added. The reaction mixture was kept at RT for 30 min. The reaction mixture was diluted with ether (50 mL) and then quenched with saturated NH_4Cl (7 mL) and water (20 mL). The organic layer was separated and the aqueous layer was back extracted with ether (3×30 mL). The combined organic phase was washed with saturated NaCl solution (50 mL), dried over MgSO_4 , filtered and evaporated under reduced pressure. The crude residue was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 2/1) to give a mixture of isomers as a pale yellow oil (**13a** and **13b**, 1.48g, 93%, R_f : 0.25: petroleum ether/ethyl acetate = 2/1) (**13a/13b** = 3:1).



Compound 14: To a solution of the mixture of **13a** and **13b** (**13a:13b** = 3:1) (1.40 g) in THF (20 mL) was added $n\text{Bu}_4\text{NF}$ (1 M in THF, 3.42 mL, 2.1 eq). The reaction mixture was kept at RT for 7 h, before it was quenched with saturated NH_4Cl (20 mL). The mixture was diluted with ether (50 mL) and water (30 mL) was added. The organic layer was separated and the aqueous layer was extracted with ether (3 \times 30 mL). The combined organic phase was dried over MgSO_4 , filtered and evaporated under reduced pressure. The crude residue was purified by using flash chromatography on silica gel ($\text{CH}_2\text{Cl}_2/\text{MeOH}$ = 30:1) to give a pale yellow oil mixture of diol isomers (0.96 g, 93%, R_f : 0.2: $\text{CH}_2\text{Cl}_2/\text{MeOH}$ = 30:1).

To the above diol isomers (0.96 g, 1.52 mmol) in DMSO (5 mL) was added IBX (0.93 g, 2.2 eq). The reaction mixture was kept at RT for 5 h. The reaction mixture was diluted with ether (50 mL) and water (50 mL) was added. The organic layer was separated and the aqueous layer was back extracted with ether (3 \times 50 mL). The combined organic phase was washed with saturated NaCl solution (30 mL), dried over MgSO_4 , filtered and evaporated under reduced pressure. The crude residue was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 1/5) to give a pale yellow oil mixture of ketoaldehyde isomers (0.76 g, 80%, R_f : 0.33: petroleum ether/ethyl acetate = 1/5).

To the above ketoaldehyde isomers (0.76 g, 1.21 mmol) in CH_3CN (240 mL) was added LiCl (0.51 g, 10 eq) and DIPEA (2.1 mL, 10 eq). The reaction mixture was kept at RT for 6 days. The mixture was concentrated under reduced pressure, dissolved in CH_2Cl_2 (50 mL) and water (50 mL) was added. The organic layer was separated and the aqueous layer was extracted with ether (3 \times 30 mL). The combined organic phase was dried over MgSO_4 , filtered and evaporated under reduced pressure to afford compound **14**, which was purified by using flash chromatography on silica

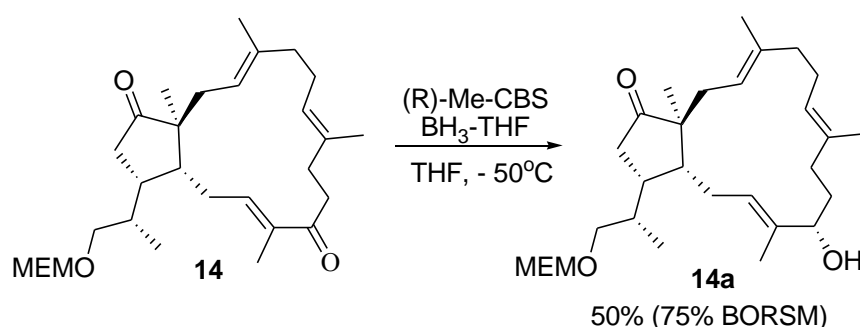
gel (petroleum ether/ethyl acetate = 4/1) to give a pale yellow oil (**14**, 0.373 g, 65%, Rf: 0.2: petroleum ether/ethyl acetate = 4/1).

¹H NMR (CDCl₃, 400 MHz): δ 6.50 (t, 4.8 Hz, 1H), 5.13 (m, 2H), 4.71 (s, 2H), 3.67 (dd, J = 5.7, 3.6 Hz, 2H), 3.57 (dd, J = 9.5, 4.1 Hz, 1H), 3.53 (dd, J = 5.7, 3.5 Hz, 2H), 3.40 (dd, J = 9.5, 6.6 Hz, 1H), 3.37 (s, 3H), 2.77 (ddd, J = 14.7, 9.3, 5.5 Hz, 1H), 2.56 (m, 1H), 2.52-2.41 (m, 3H), 2.30-1.89 (m, 12H), 1.71 (s, 3H), 1.62 (s, 6H), 1.06 (d, J = 6.6 Hz, 3H), 0.95 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz): δ 221.7, 202.4, 144.8, 138.5, 135.7, 134.9, 123.3, 120.1, 95.8, 71.7, 71.2, 66.9, 59.1, 56.1, 44.0, 40.5, 40.2, 39.7, 36.8, 36.5, 34.6, 34.4, 24.9, 23.8, 17.9, 17.3, 16.0, 15.7, 11.4.

HRMS (ESI-TOF): calc'd for C₂₉H₄₆O₅Na [M + Na]⁺: 497.3243, found: 497.3242.

[α]_D²⁰: +1.9 (C = 0.94, CH₂Cl₂).

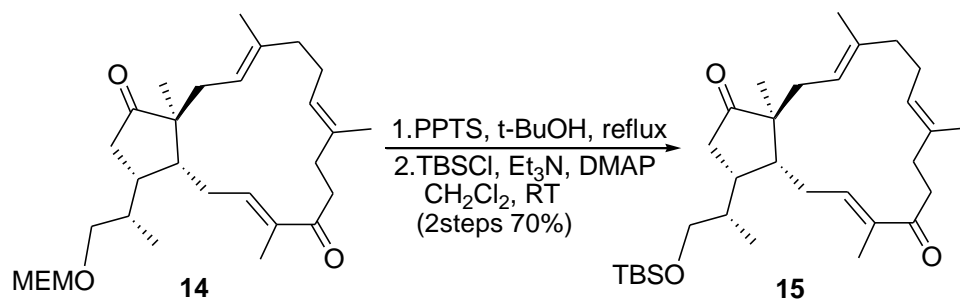


Compound 14a: A solution of **14** (0.136 g, 0.29 mmol) in THF (4 mL) was cooled to -50 °C. To this solution was slowly added BH₃ (1.7 eq, 1 M in THF), then slowly added R-(Me)-CBS (1 eq, 1 M in toluene) in 1 h. The reaction mixture was kept at this temperature for 1 h and then quenched with MeOH (1 mL) then saturated NH₄Cl (3 mL). The mixture was allowed to warm to RT, diluted with ether (10 mL), washed with water (10 mL). The aqueous layer was back extracted with ether (3 × 10 mL). The combined organic phase was washed with saturated NaCl solution (10 mL), dried over MgSO₄, filtered and evaporated under reduced pressure to afford compound **14a**, which was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 2/1) to give the starting material (**14**, 0.045 g) and a colorless oil [**14a**, 0.068 g, 50% (75% BORSM), Rf: 0.25: petroleum ether/ethyl acetate = 2/1].

¹H NMR (CDCl₃, 400 MHz): δ 5.17 (m, 3H), 4.71 (s, 2H), 3.94 (m, 1H), 3.68 (d, J = 5.5 Hz, 1H), 3.67 (d, J = 5.7 Hz, 1H), 3.61 (dd, J = 9.4, 3.5 Hz, 1H), 3.56 (d, J = 5.7 Hz, 1H), 3.55 (d, J = 5.3 Hz, 1H), 3.39 (s, 3H), 3.30 (dd, J = 9.2, 7.2 Hz, 1H), 2.40 (dd, J = 17.4, 5.5 Hz, 1H), 2.26-1.79 (m, 14H), 1.68-1.62 (m, 2H), 1.62 (s, 6H), 1.56 (s, 3H), 1.05 (d, J = 6.5 Hz, 3H), 1.01 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz) δ 222.9, 137.5, 135.3, 133.1, 130.6, 124.4, 121.7, 95.6, 76.8, 71.7, 70.7, 66.6, 58.9, 55.6, 44.5, 41.1, 40.1, 39.7, 35.1, 34.9, 34.7, 29.8, 23.8, 22.8, 17.8, 17.3, 15.9, 15.4, 10.8.

HRMS (EI-TOF): calc'd for C₂₉H₄₈O₅ [M]⁺: 476.3502, found: 476.3510.



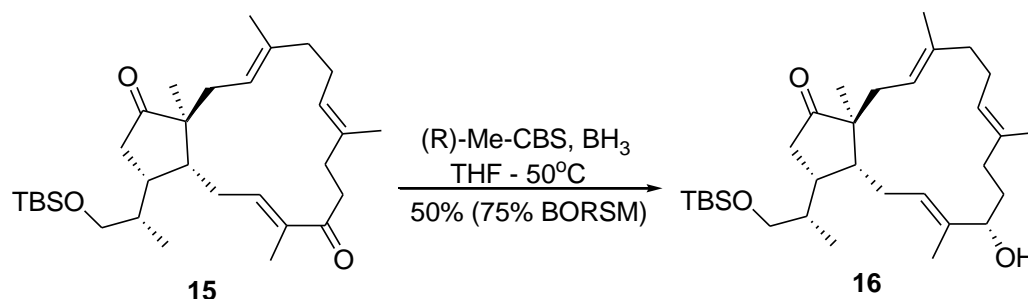
Compound 15: To a solution of **14** (0.35 g, 0.74 mmol) in *t*-BuOH (5 mL) was added PPTS (2 eq). The reaction mixture was refluxed for 8 h, diluted with ether (30 mL) and water (30 mL) was added. The organic layer was separated and the aqueous layer was extracted with ether (3 × 50 mL). The combined organic phase was washed with saturated NaCl solution (30 mL), dried over MgSO₄, filtered and evaporated under reduced pressure. The crude residue was dissolved in CH₂Cl₂ (10 mL) and added TBSCl (1.5 eq), DMAP (0.05 eq) and Et₃N (2 eq). The reaction mixture was kept at RT for 10 h. The mixture was wash with water (30 mL). The aqueous layer was back extracted with CH₂Cl₂ (3 × 30 mL). The combined organic phase was washed with saturated NaCl solution (30 mL), dried over MgSO₄, filtered and evaporated under reduced pressure to afford compound **15**, which was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1) to give a colorless oil (**15**, 0.258 g, 70%, R_f: 0.2: petroleum ether/ethyl acetate = 10/1).

¹H NMR (CDCl₃, 400 MHz): δ 6.51 (t, J = 5.3 Hz, 1H), 5.15 (m, 2H), 3.60 (dd, J = 9.9, 4.0 Hz, 1H), 3.50 (dd, J = 9.9, 5.6 Hz, 1H), 2.76 (ddd, J = 14.8, 9.3, 5.5 Hz, 1H), 2.57 (m, 1H), 2.48-2.42 (m, 3H), 2.38 -1.90 (m, 11H), 1.81 (m, 1H), 1.71 (s, 3H), 1.63 (s, 3H), 1.62 (s, 3H), 1.00 (d, J = 6.6 Hz, 3H), 0.94 (s, 3H), 0.90 (s, 9H), 0.05 (s, 6H).

¹³C NMR (CDCl₃, 125 MHz): δ 220.0, 202.4, 145.0, 138.4, 135.7, 134.9, 123.3, 120.2, 66.3, 56.1, 44.0, 40.5, 40.2, 39.2, 36.8, 36.5, 36.4, 34.4, 25.9, 25.0, 23.9, 18.4, 18.0, 16.9, 16.0, 15.7, 11.4, -5.4.

HRMS (ESI-TOF): calc'd for C₃₁H₅₃O₃Si [M + H]⁺: 501.3764, found: 501.3759.

[α]_D²⁰: +18.9 (C = 0.95, CH₂Cl₂).



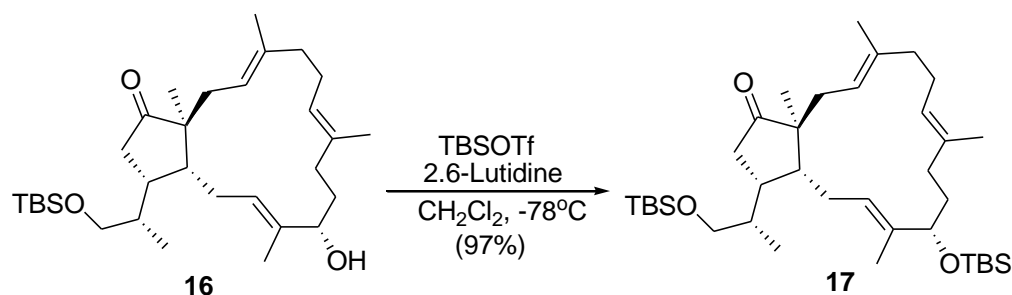
Compound 16: A solution of **15** (0.32 g, 0.64 mmol) in THF (8 mL) was cooled to -50 °C. To this solution was slowly added BH₃ (1.7 eq, 1 M in THF), then slowly added R-(Me)-CBS (1 eq, 1 M in toluene) in 1 h. The reaction mixture was kept at

this temperature for 1 h and then quenched with MeOH (2 mL) then saturated NH₄Cl (7 mL). The mixture was allowed to warm to RT, diluted with ether (20 mL), washed with water (20 mL). The aqueous layer was back extracted with ether (3 × 30 mL). The combined organic phase was washed with saturated NaCl solution (10 mL), dried over MgSO₄, filtered and evaporated under reduced pressure to afford compound **16**, which was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 10/1 to 5/1) to give the starting material (**15**, 0.106 g) and a colorless oil [**16**, 0.161 g, 50% (75% BORSM), R_f: 0.25: petroleum ether/ethyl acetate = 6/1].

¹H NMR (CDCl₃, 400 MHz): δ 5.17 (m, 3H), 3.97 (dd, J = 9.1, 3.7 Hz, 1H), 3.60 (dd, J = 9.8, 3.6 Hz, 1H), 3.43 (dd, J = 9.8, 6.1 Hz, 1H), 2.36 (ddd, J = 17.4, 6.5, 1.3 Hz, 1H), 2.27-1.66 (m, 16 H), 1.64 (s, 3H), 1.63 (s, 3H), 1.57 (s, 3H), 0.99 (d, J = 6.2 Hz, 3H), 1.00 (s, 3H), 0.89 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz) δ 223.1, 137.4, 135.2, 133.3, 130.4, 124.3, 121.7, 76.95, 65.8, 55.5, 44.4, 41.0, 39.7, 39.4, 36.5, 34.9, 30.1, 25.9, 23.8, 23.0, 18.4, 17.9, 16.8, 15.9, 15.5, 11.1, -5.37, -5.39.

HRMS (ESI-TOF): calc'd for C₃₁H₅₅O₃Si [M + H]⁺: 503.3920, found: 503.3919.

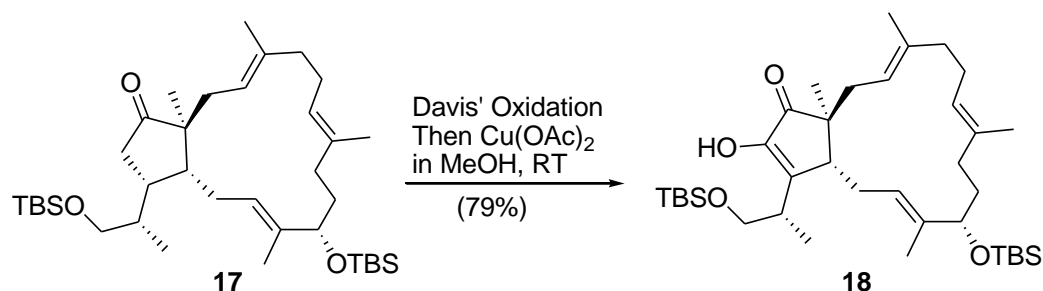


Compound 17: A solution of **16** (0.15 g, 0.30 mmol) and 2.6 lutidine (0.07 mL, 2 eq) in CH₂Cl₂ (8 mL) was cooled to -78 °C. To this solution was slowly added TBSOTf (0.07 mL, 1.05 eq). The reaction mixture was kept at this temperature for 1 h, and then quenched with MeOH (1 mL). The mixture was allowed to warm to RT, washed with water (20 mL). The aqueous layer was back extracted with CH₂Cl₂ (3 × 20 mL). The combined organic phase was washed with saturated NaCl solution (10 mL), dried over MgSO₄, filtered and evaporated under reduced pressure to afford compound **17**, which was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 30/1) to give a colorless oil (**17**, 0.178 g, 97%, R_f: 0.25: petroleum ether/ethyl acetate = 30/1).

¹H NMR (CDCl₃, 400 MHz): δ 5.18 (t, 8.0 Hz, 1H), 5.13 (m, 1H), 5.00 (m, 1H), 3.92 (dd, J = 8.2, 5.3 Hz, 1H), 3.63 (dd, J = 9.8, 3.3 Hz, 1H), 3.40 (dd, J = 9.8, 6.7 Hz, 1H), 2.36 (dd, J = 17.1, 6.1 Hz, 1H), 2.26-1.66 (m, 16H), 1.63 (s, 3H), 1.61 (s, 3H), 1.50 (s, 3H), 1.00 (d, J = 6.6 Hz, 3H), 0.97 (s, 3H), 0.90 (s, 9H), 0.85 (s, 9H), 0.05 (s, 3H), 0.04 (s, 3H), 0.00 (s, 6H).

¹³C NMR (CDCl₃, 125 MHz) δ 223.3, 137.5, 136.3, 133.0, 128.7, 123.5, 121.8, 77.5, 65.7, 55.4, 44.5, 41.1, 39.9, 39.4, 36.5, 35.1, 34.7, 31.6, 25.94, 25.86, 23.8, 22.8, 18.4, 18.1, 18.0, 16.8, 15.9, 10.8, -4.6, -4.8, -5.3, -5.4.

HRMS (EI-TOF): calc'd for $C_{37}H_{68}O_3Si_2$ $[M]^+$: 616.4707, found: 616.4714
 $[\alpha]_D^{20}$: -31.8 (C = 0.44, CH_2Cl_2).

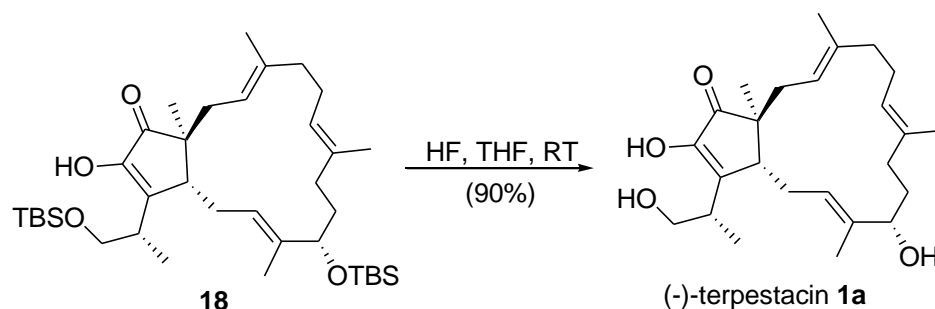


Compound 18: A solution of **17** (0.16 g, 0.26 mmol) in THF (5 mL) was cooled to $-45\text{ }^\circ\text{C}$. To this solution was slowly added NaHMDS (1.5 eq, 2 M in THF). The reaction mixture was kept at this temperature for 1 h, and then cooled to $-78\text{ }^\circ\text{C}$. To this solution was slowly added N-Sulfonyloxaziridines (1.5 eq) in THF (1 mL). The reaction mixture was kept at $-78\text{ }^\circ\text{C}$ for 1 h, then quenched with saturated NH_4Cl (2 mL). The mixture was stirred at $-78\text{ }^\circ\text{C}$ for 1 h, and then allowed to warm to RT. The mixture was diluted with ether (20 mL) and washed with water (20 mL). The aqueous layer was back extracted with ether ($3 \times 30\text{ mL}$). The combined organic phase was washed with saturated NaCl solution (10 mL), dried over $MgSO_4$, filtered and evaporated under reduced pressure. The crude residue was dissolved in MeOH (5 mL). To this solution was added $Cu(OAc)_2$ (50 eq). The reaction mixture was kept at RT for 10 h, and then diluted with ether (20 mL), washed with water (20 mL). The aqueous layer was back extracted with ether ($3 \times 30\text{ mL}$). The combined organic phase was dried over $MgSO_4$, filtered and evaporated under reduced pressure to afford compound **18**, which was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 20/1) to give a colorless oil (**18**, 0.129 g, 79%, Rf: 0.2: petroleum ether/ethyl acetate = 20/1).

1H NMR ($CDCl_3$, 400 MHz): δ 6.45 (brs, 1H), 5.25 (m, 2H), 5.13 (m, 1H), 4.03 (dd, J = 8.2, 5.4 Hz, 1H), 3.84 (dd, J = 9.6, 6.5 Hz, 1H), 3.80 (dd, J = 9.6, 4.9 Hz, 1H), 2.66 (dd, J = 11.3, 2.3 Hz, 1H), 2.61 (m, 1H), 2.45-2.26 (m, 4H), 2.16-1.94 (m, 3H), 1.82 (m, 2H), 1.75- 1.59 (m, 3H), 1.65 (s, 3H), 1.62 (s, 3H), 1.51 (s, 3H), 1.25 (dd, J = 7.1 Hz, 3H), 0.98 (s, 3H), 0.90 (s, 9H), 0.87 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H), 0.01 (s, 3 H), -0.02 (s, 3H).

^{13}C NMR ($CDCl_3$, 125 MHz) δ 207.8, 149.1, 146.8, 138.0, 137.3, 132.9, 126.7, 123.8, 121.7, 76.7, 66.8, 49.6, 48.9, 40.5, 39.0, 37.0, 34.5, 31.5, 28.3, 25.90, 25.89, 23.9, 18.3, 18.2, 16.5, 16.0, 15.4, 14.5 10.4, -4.6 , -4.8 , -5.46 , -5.50 .

HRMS (ESI-TOF): calc'd for $C_{37}H_{67}O_4Si_2$ $[M + H]^+$: 631.4578, found: 631.4575.
 $[\alpha]_D^{20}$: +3.0 (C = 0.37, CH_2Cl_2).



(-)-Terpestacin 1a: To a solution of **18** (0.100 g 0.158 mmol) in THF (3 mL) was added aqueous HF (46%, 0.3 mL). The reaction mixture was kept at RT for 3 h. The mixture was diluted with ether (20 mL) and washed with water (20 mL). The aqueous layer was back extracted with ether (3 × 20 mL). The combined organic phase was washed with saturated NaHCO₃ (30 mL), dried over MgSO₄, filtered and evaporated under reduced pressure to afford (-)-terpestacin **1a**, which was purified by using flash chromatography on silica gel (petroleum ether/ethyl acetate = 1/1) to give a white solid (**1a**, 0.057 g, 90%, R_f: 0.33: petroleum ether/ethyl acetate = 1/1).

¹H NMR (CDCl₃, 400 MHz): δ = 5.94 (brs, 1H), 5.39 (m, 1H), 5.23 (dd, J = 10.3, 5.2 Hz, 1H), 5.12 (m, 1H), 4.05 (dd, J = 9.8, 3.5 Hz, 1H), 3.88 (dd, J = 10.4, 7.0 Hz, 1H), 3.81 (dd, J = 10.4, 5.4 Hz, 1H), 2.70 (dd, J = 11.4, 2.1 Hz, 1H), 2.67 (m, 1H), 2.43 (d, J = 17.2 Hz, 1H), 2.37 (dd, J = 13.7, 10.6 Hz, 1H), 2.29- 2.23 (m, 2H), 2.12-2.07 (m, 2H), 2.04- 1.88 (m, 2H), 1.81- 1.65 (m, 4H), 1.63 (s, 3H), 1.62 (s, 3H), 1.56 (s, 3H), 1.29 (d, J = 7.1 Hz, 3H), 0.98 (s, 3H).

¹³C NMR (CDCl₃, 125 MHz) δ 208.1, 149.3, 146.8, 138.0, 136.4, 132.9, 129.0, 124.3, 121.6, 76.5, 66.0, 49.6, 49.0, 40.3, 39.3, 37.1, 34.9, 29.8, 28.8, 23.8, 16.2, 15.5, 15.3, 14.3, 10.4.

HRMS (ESI-TOF): calc'd for C₂₅H₃₈O₄Na [M + Na]⁺: 425.2668, found: 425.2657.

[α]_D²⁰: -27.5 (C = 1.54, CHCl₃); [α]_D²⁰: -21.1 (C = 1.07, MeOH).

