

Total synthesis of antillatoxin

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Supporting information:

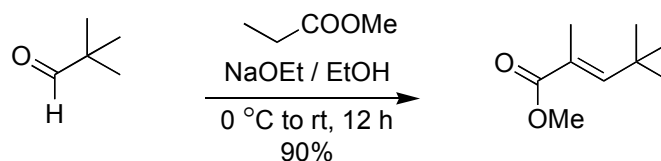
Experimental Section

General:

THF was distilled from sodium/benzophenone. Hexane and dichloromethane were distilled from CaH₂. TLC was carried out with pre-coated Merck 60 F₂₅₄ plates. Silica gel 60 (Merck, 400-630 mesh) was used for column chromatography. Infrared spectra were recorded on a Bio-Rad FTS 165 FTIR spectrometer. Liquid samples were examined as film between NaCl salt plates. ¹H and ¹³C NMR spectra were taken in CDCl₃ on Bruker DPX300 and Bruker AMX500 and referenced to internal tetramethylsilane (SiMe₄). Chemical shifts for ¹H NMR spectra are reported as δ in units of parts per million (ppm) downfield from SiMe₄ (δ 0.0) and relative to the signal of chloroform-d (δ 7.2600, singlet). Multiplicities were given as: s (singlet); brs (broad singlet); d (doublet); t (triplet); q (quartet); dd (doublets of doublet); dt (doublets of triplet); dtq (doublets of triplets of quartet); or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (¹³C NMR) are reported as δ in units of parts per million (ppm) downfield from SiMe₄ (δ 0.0) and relative to the signal of chloroform-d (δ 77, triplet).

Mass spectral analyses were carried out on a VG 7035 micromass mass spectrophotometer at a source temperature of 200 °C and at an ion current of 70 eV. Mass spectral data were reported in units of mass to charge (m/z) and % intensity.

(E)-methyl 2,4,4-trimethylpent-2-enoate



To a mixture of methyl propionate (24.1 mL, 0.25 mol) and sodium sand (1.45 g, 0.063 mol) at 0 °C was added catalytic amount of absolute ethanol (0.4 mL). trimethylacetaldehyde (4.3 g, 5.43 mL, 50 mmol) was added dropwise. The reaction mixture was stirred at 0 °C to room temperature for 12 h. After the reaction was completed, the reaction mixture was poured into saturated NH₄Cl and extracted with ether (x3). The combined organic extracts washed with brine, dried over MgSO₄ and concentrated. The residue was purified by flash chromatography on silica gel, elution with hexane/ethyl acetate, 20:1, to afford the pure product (7.78 g, 90%) as a yellowish oil.

R_f 0.78 (hexane/ethyl acetate, 4:1);

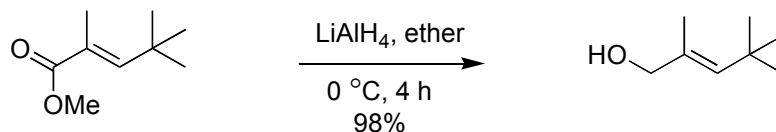
¹H NMR (300 MHz, CDCl₃): δ 1.18 (9H, s, -C(CH₃)₃), 1.95 (3H, d, *J* = 1.4 Hz, -CH₃), 3.72 (3H, s, -OCH₃), 6.80 (1H, q, *J* = 1.4 Hz, -CH=C-) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 13.3 (-CH=C-CH₃), 30.1 (-C(CH₃)₃), 33.0 (-C(CH₃)₃), 51.8 (-OMe), 126.4 (-CH=C-), 151.5 (-CH=C-), 169.8 (-CO₂Me) ppm;

IR (neat, cm⁻¹): 2959, 2870, 1716, 1639, 1466, 1436, 1365, 1284, 1251;

HRMS (EI) m/z (M⁺): obsd 156.1157, calcd 156.1150 for C₉H₁₆O₂.

(E)-2,4,4-trimethylpent-2-en-1-ol



To a mixture of LiAlH₄ (0.4 g, 10.5 mmol) in anhydrous ether (20 mL) at 0 °C was added ester (1.56 g, 10 mmol) in ether (10 mL) dropwise. The reaction mixture was stirred at 0 °C and the reaction progress was monitored by TLC. After completion, the reaction mixture was quenched with saturated Na₂SO₄ at 0 °C until white precipitate was deposited. The mixture was filtered, washed with ether and dried over MgSO₄ and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to afforded product (1.28 g, 98%) as a colorless oil.

R_f 0.47 (hexane/ethyl acetate, 4:1);

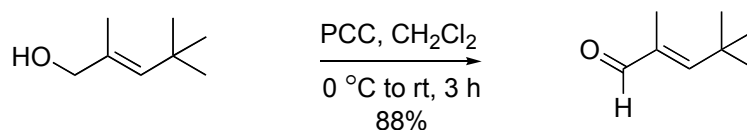
$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 1.12 (9H, s, $-\text{C}(\text{CH}_3)_3$), 1.78 (3H, d, $J = 1.2$ Hz, $-\text{C}-\text{CH}_3$), 3.92 (2H, s, $-\text{CH}_2-\text{OH}$), 5.42 (1H, q, $J = 1.2$ Hz, $-\text{CH}=\text{C}-$) ppm;

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 14.7 ($-\text{CH}=\text{C}-\text{CH}_3$), 30.9 ($-\text{C}(\text{CH}_3)_3$), 32.2 ($-\text{C}(\text{CH}_3)_3$), 70.8 ($-\text{CH}_2\text{OH}$), 133.3 ($-\text{CH}=\text{C}-$), 136.6 ($-\text{CH}=\text{C}-$) ppm;

IR (neat cm^{-1}): 3331, 2957, 2867, 1657, 1465, 1363;

HRMS (EI) m/z (M^+): obsd 128.1196, calcd 128.1201 for $\text{C}_8\text{H}_{13}\text{O}$.

(*E*)-2,4,4-trimethylpent-2-enal



To a mixture of PCC (6.47 g, 30 mmol), 4Å molecular sieve powder (3 g) and silica gel (3 g) in anhydrous CH_2Cl_2 (30 mL) at 0 °C was added alcohol (1.28 g, 10.1 mmol) prediluted in anhydrous CH_2Cl_2 (5 mL). The reaction mixture was stirred for 3 h. After completion (monitored by TLC), the reaction mixture was filtered through silica gel to afford the product (1.1 g, 88%) as a yellowish oil.

R_f 0.75 (hexane/ethyl acetate, 4:1);

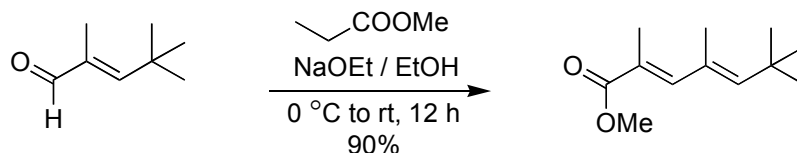
$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 1.24 (9H, s, $-\text{C}(\text{CH}_3)_3$), 1.86 (3H, d, $J = 1.3$ Hz, $-\text{C}-\text{CH}_3$), 6.40 (1H, d, $J = 1.3$ Hz, $-\text{CH}=\text{C}-$), 9.30 (1H, s, $-\text{CHO}$) ppm;

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 9.8 ($-\text{CH}=\text{C}-\text{CH}_3$), 29.7 ($-\text{C}(\text{CH}_3)_3$), 34.2 ($-\text{C}(\text{CH}_3)_3$), 123.8 ($-\text{CH}=\text{C}-$), 138.5 ($-\text{CH}=\text{C}-$), 196.8 ($-\text{CHO}$) ppm;

IR (neat, cm^{-1}): 2961, 2869, 1691, 1643, 1467, 1366, 1231;

HRMS (EI) m/z (M^+): obsd 126.1020, calcd 126.1044 for $\text{C}_8\text{H}_{14}\text{O}$.

(2*E*,4*E*)-methyl 2,4,6,6-tetramethylhepta-2,4-dienoate



To a mixture of methyl propionate (72.3 mL, 0.25 mol) and sodium sand (0.9 g, 39 mmol) at 0 °C was added catalytic amount of absolute ethanol (0.3 mL). Subsequently, aldehyde (3.84 g, 30 mmol) was added dropwise. The reaction mixture was stirred for 12 h. After completion the reaction mixture was poured into sat.

NH₄Cl at 0 °C and extracted with ether. The combined etherates was washed with brine, dried over anhydrous MgSO₄ and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel to afford product (5.3 g, 90%) as a yellowish oil.

R_f 0.78 (hexane/ethyl acetate, 4:1);

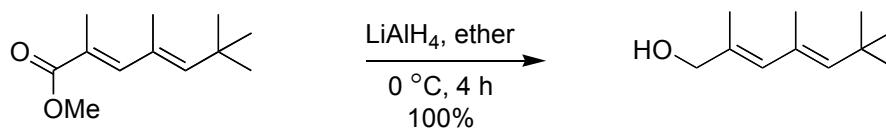
¹H NMR (300 MHz, CDCl₃): δ 1.16 (9H, s, -C(CH₃)₃), 1.91 (3H, d, *J* = 1.3 Hz, -CH=C-CH₃), 1.97 (3H, d, *J* = 1.3 Hz, -CH=C-CH₃), 3.74 (3H, s, -COOCH₃), 5.56 (1H, s, -CH=C-), 7.08 (1H, s, -CH=C-) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 13.9 (-CH=C-CH₃), 17.3 (-CH=C-CH₃), 30.7 (-C(CH₃)₃), 33.0 (-C(CH₃)₃), 51.8 (-OMe), 124.9 (-CH=C-), 130.8 (-CH=C-), 145.3 (-CH=C-), 145.5 (-CH=C-), 169.7 (-CO₂Me) ppm;

IR (neat, cm⁻¹): 2956, 2888, 1713, 1625, 1465, 1435, 1386, 1363;

HRMS (EI) m/z (M⁺): obsd 196.1457, calcd 196.1463 for C₁₂H₂₀O₂.

(2E,4E)-2,4,6,6-tetramethylhepta-2,4-dien-1-ol



To a mixture of LiAlH₄ (0.8 g, 21 mmol) in anhydrous ether (30 mL) at 0 °C was added ester (2.52 g, 12 mmol) in ether (30 mL) dropwise. The reaction mixture was stirred at 0 °C and the reaction progress was monitored by TLC. After completion, the reaction mixture was quenched with saturated Na₂SO₄ at 0 °C until white precipitate was deposited. The mixture was filtered, washed with ether and dried over MgSO₄ and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel, eluting with hexane/ethyl acetate (10:1) to afford the alcohol (2.02 g (100%)) as a colorless oil.

R_f 0.44 (hexane/ethyl acetate, 4:1);

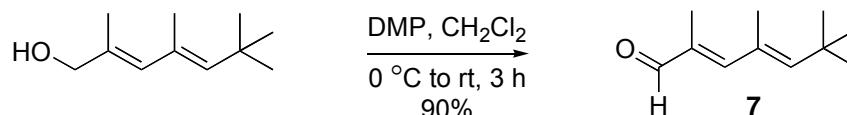
¹H NMR (300 MHz, CDCl₃): δ 1.15 (9H, s, -C(CH₃)₃), 1.79 (3H, d, *J* = 1.35 Hz, -C-CH₃), 1.83 (3H, d, *J* = 1.35 Hz, -C-CH₃), 4.03 (2H, s, -CH₂-OH), 5.33 (1H, brs, -CH=C-), 5.85 (1H, brs, -CH=C-) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 15.2 (-CH=C-CH₃), 17.9 (-CH=C-CH₃), 31.0 (-C(CH₃)₃), 32.6 (-C(CH₃)₃), 69.5 (-CH₂OH), 130.9 (-CH=C-), 131.5 (-CH=C-), 133.8 (-CH=C-), 140.6 (-CH=C-) ppm;

IR (neat cm^{-1}): 3332, 2956, 1645, 1465, 1362;

HRMS (EI) m/z (M^+): obsd 168.1516, calcd 168.1514 for $\text{C}_{11}\text{H}_{20}\text{O}$.

(2E,4E)-2,4,6,6-tetramethylhepta-2,4-dienal (7)



To a solution of Dess-Martin reagent (8.66 g, 20.4 mmol) in anhydrous CH_2Cl_2 (40 mL) was added dropwise alcohol (2.86 g, 17 mmol) prediluted in CH_2Cl_2 (20 mL) at 0 °C. The reaction mixture was stirred under nitrogen at 0 °C for 3 h. After completion, the reaction mixture was diluted with ether and poured slowly into a $\text{Na}_2\text{S}_2\text{O}_3$: NaHCO_3 (1:1) solution and stirred for 10 minutes and extracted with ether. The combine etherate layer was washed with NaHCO_3 , brine and dried over anhydrous MgSO_4 . Solvent was removed by concentration in *vacuo*. The residue was purified by flash chromatography on silica gel to provide aldehyde (2.54 g, 90%) as a yellowish oil.

R_f 0.78 (hexane/ethyl acetate, 4:1);

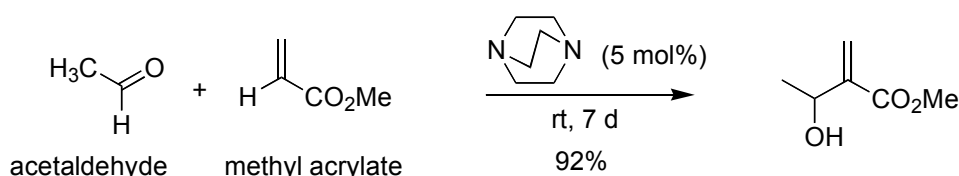
$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 1.20 (9H, s, $-\text{C}(\text{CH}_3)_3$), 1.93 (3H, d, $J = 1.3$ Hz, $-\text{C}-\text{CH}_3$), 2.05 (3H, d, $J = 1.3$ Hz, $-\text{C}-\text{CH}_3$), 5.85 (1H, brs, $-\text{CH}=\text{C}-$), 6.68 (1H, brs, $-\text{CH}=\text{C}-$), 9.37 (1H, s, $-\text{CHO}$) ppm;

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 10.7 ($-\text{CH}=\text{C}-\text{CH}_3$), 17.1 ($-\text{CH}=\text{C}-\text{CH}_3$), 30.6 ($-\text{C}(\text{CH}_3)_3$), 33.3 ($-\text{C}(\text{CH}_3)_3$), 132.0 ($-\text{CH}=\text{C}-$), 135.4 ($-\text{CH}=\text{C}-$), 150.2 ($-\text{CH}=\text{C}-$), 157.3 ($-\text{CH}=\text{C}-$), 196.3 ($-\text{CHO}$) ppm;

IR (neat, cm^{-1}): 2959, 2868, 1727, 1683, 1609, 1466, 1364;

HRMS (EI) m/z (M^+): obsd 166.1368, calcd 166.1358 for $\text{C}_{11}\text{H}_{18}\text{O}$.

Methyl 3-hydroxy-2-methylenebutanoate



To a mixture of methyl acrylate (50 mL, 0.556 mol) and acetaldehyde (47 mL, 0.832 mol) was added 5% mol of DABCO (3.12 g, 0.027 mol). The reaction mixture was stirred at room temperature for 7 d. After completion, CH_2Cl_2 was added and the

mixture was treated with 1M HCl, *sat.* NaHCO₃ solution, brine, dried over anhydrous MgSO₄ and concentrated in *vacuo*. Purification through flash column chromatography with 10 % ethyl acetate in hexane to afford the product (66.6 g, 92%) as a colorless oil.

R_f 0.31 (hexane/ethyl acetate, 4:1);

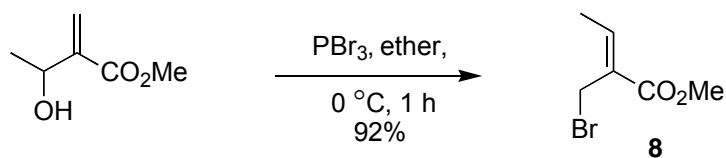
¹H NMR (300 MHz, CDCl₃): δ 1.38 (3H, d, *J* = 6.5 Hz, -CH-CH₃), 2.82 (1H, brs, -OH), 3.79 (3H, s, -COOCH₃), 4.61 (1H, q, *J* = 6.5 Hz, -CH-OH), 5.84 (1H, d, *J* = 0.55 Hz, -C=CH₂), 6.22 (1H, d, *J* = 0.55 Hz, -C=CH₂) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 22.1 (-CH-CH₃), 51.9 (-CO₂Me), 67.1 (-CHOH), 124.2 (-C=CH₂), 143.5 (-C=CH₂), 167.1 (-CO₂Me) ppm;

IR (neat, cm⁻¹): 3426, 2978, 1713, 1630, 1440, 1368;

HRMS (EI) *m/z* (M⁺) : obsd 130.0628, calcd 130.0630 for C₆H₁₀O₃.

(*Z*)-methyl 2-(bromomethyl)but-2-enoate (**8**)



To a solution of alcohol (26 g, 0.2 mol) in anhydrous ether (100 mL) at 0 °C was added phosphorus tribromide (19 mL, 0.2 mol) dropwise. The mixture was stirred at 0 °C for 1 h. After the reaction completed (monitored by TLC), the mixture was poured into ice water. The solution was extracted with ether and the combined etherate was washed with *sat.* NaHCO₃ solution, brine, dried over anhydrous MgSO₄ and concentrated in *vacuo*. The residue was purified by flash chromatography to afford the bromide **8** (35.4 g, 92%) as a colorless oil.

R_f 0.70 (hexane/ethyl acetate, 4:1);

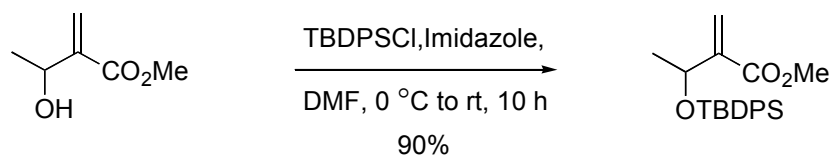
¹H NMR (300 MHz, CDCl₃): δ 1.92 (3H, d, *J* = 7.25 Hz, -CH-CH₃), 3.80 (3H, s, -COOCH₃), 4.24 (2H, s, -CH₂-Br), 7.06 (1H, q, *J* = 7.25 Hz, -CH=C-) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 14.5 (-CH-CH₃), 24.0 (-CH₂Br), 52.1 (-CO₂Me), 130.3 (-C=CH-), 143.4 (-C=CH-), 166.0 (-CO₂Me) ppm;

IR (neat, cm⁻¹): 2991, 2952, 1716, 1645, 1382;

HRMS (EI) *m/z* (M⁺): obsd 191.9814, calcd 191.9786 for C₆H₉⁷⁹BrO₂.

Methyl 3-(*tert*-butyldiphenylsilyloxy)-2-methylenebutanoate



To a stirred solution of alcohol (1.07 g, 8.25 mmol) in anhydrous DMF (20 mL) was added in imidazole (0.9 g, 13 mmol) followed by *tert*-butyldiphenylsilyl chloride (2.5 mL, 9.5 mmol) at 0 °C under nitrogen. The reaction mixture was stirred for 10 h at room temperature. After completion, the reaction mixture was poured into H₂O and extracted with ethyl acetate. The combined organic extracted were washed with brine, dried over anhydrous MgSO₄ and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel, eluting with hexane-ethyl acetate (20:1) to afford product (2.73 g, 90%) as a colorless oil.

R_f 0.69 (hexane/ethyl acetate, 4:1);

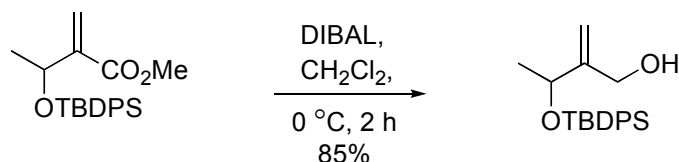
¹H NMR (300 MHz, CDCl₃): δ 1.09 (9H, s, -C(CH₃)₃), 1.18 (3H, d, *J* = 6.24 Hz, -CH-CH₃), 3.70 (3H, s, -CO₂Me), 4.74 (1H, q, *J* = 6.24 Hz, -CH-CH₃), 6.11 (1H, t, *J* = 1.38 Hz, -C=CH₂), 6.24 (1H, t, *J* = 1.05 Hz, -C=CH₂), 7.34-7.43 (6H, m, -Ph-H), 7.59-7.70 (4H, m, -Ph-H) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 19.3 (-C(CH₃)₃), 24.5 (-CHCH₃), 27.0 (-C(CH₃)₃), 51.6 (-OMe), 67.8 (-CH-OTBDPS), 123.9 (-C=CH₂), 127.6, (Ph-C x4), 129.7 (Ph-C x2), 134.1 (Ph-C_q x2), 135.9 (Ph-C x4), 145.1 (-C=CH₂), 166.5 (-CO₂Me) ppm;

IR (neat, cm⁻¹): 3076, 2962, 2941, 1729, 1430;

HRMS (EI) *m/z* [(M-C₄H₉)⁺]: obsd 311.1102, calcd 311.1103 for C₁₈H₁₉O₃Si.

Methyl 3-(*tert*-butyldiphenylsilyloxy)-2-methylenebutanoate



To a solution of ester (9.20 g, 25 mmol) in anhydrous CH₂Cl₂ (150 mL) was added dropwise 1.0 M solution of DIBAL-H (50 mL, 50 mmol) at 0 °C under N₂. The reaction progress was monitored by TLC. After completion, saturated Na₂SO₄ solution was added dropwise until white precipitate was deposited and the mixture was stirred for another 10 minutes at room temperature. The resulting slurry precipitate was filtered and washed with ether. The combined organic layers was

dried over anhydrous MgSO₄, filtered and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel, eluting with hexane-ethyl acetate (10:1) to afford product (7.21 g, 85%) as a colorless oil.

R_f 0.56 (hexane/ethyl acetate, 4:1)

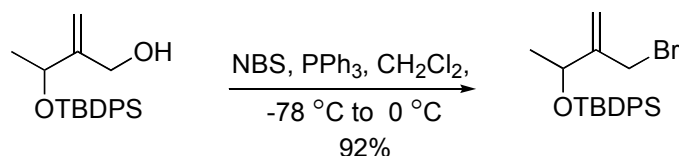
¹H NMR (300 MHz, CDCl₃): δ 1.07 (9H, s, -C(CH₃)₃), 1.19 (3H, d, *J* = 6.6 Hz, -CH-CH₃), 4.11 (1H, dd, *J* = 13.41, 6.96 Hz, -CH₂-OH), 4.29 (1H, dd, *J* = 13.41, 4.53 Hz, -CH₂-OH), 4.43 (1H, q, *J* = 6.6 Hz, -CH-CH₃), 4.99 (2H, dd, *J* = 1.38, 1.05 Hz, -C=CH₂), 7.34-7.44 (6H, m, -Ph-H), 7.64-7.71 (4H, m, -Ph-H) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 19.2 (-C(CH₃)₃), 23.6 (-CHCH₃), 27.0 (-C(CH₃)₃), 63.3 (-CH₂OH), 72.2 (-CH-OTBDPS), 110.5 (-C=CH₂), 127.6 (Ph-C x4), 129.7 (Ph-C x2), 133.5(Ph-C_q), 134.0 (Ph-C_q), 135.9 (Ph-C x4), 151.3 (-C=CH₂) ppm;

IR (neat, cm⁻¹): 3386, 3073, 3052, 2961, 2932, 1473, 1428;

HRMS (EI) m/z [(M-C₄H₉)⁺]: obsd 283.1154, calcd 283.1154 for C₁₇H₁₉O₂Si.

(3-(bromomethyl)but-3-en-2-yloxy)(*tert*-butyl)diphenylsilane



To a solution of alcohol (6.8 g, 20 mmol) in anhydrous CH₂Cl₂ (100 mL) at 0 °C was added PPh₃ (6.4 g, 24 mmol) in one portion. The reaction mixture was stirred at 0 °C for 10 minutes. After all of the PPh₃ has dissolved, NBS (4 g, 22 mmol) was added in one portion at -78 °C. The resulting solution was stirred at -78 °C for 30 minutes then transfer to an ice bath at 0 °C. The reaction progress was monitored by TLC. After completion, ether and H₂O were added subsequently. The mixture was partitioned, and the organic layer was washed with brine, dried over MgSO₄, filtered and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel, eluting with hexane-ethyl acetate (40:1) to afford bromide (7.4 g, 92%) as a colorless oil.

R_f 0.90 (hexane/ethyl acetate, 4:1);

¹H NMR (300 MHz, CDCl₃): δ 1.08 (9H, s, -C(CH₃)₃), 1.21 (3H, d, *J* = 6.42 Hz, -CH-CH₃), 3.98 (2H, s, -CH₂-Br), 4.51 (1H, q, *J* = 6.42 Hz, -CH-CH₃), 5.24 (1H, s, -C=CH₂), 5.32 (1H, s, -C=CH₂), 7.34-7.44 (6H, m, -Ph-H), 7.64-7.71 (4H, m, -Ph-H) ppm;

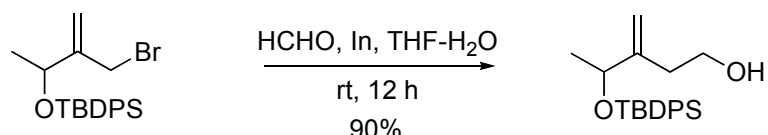
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^{13}C NMR (75 MHz, CDCl_3): δ 19.3 (-C(CH₃)₃), 23.6 (-CHCH₃), 27.0 (-C(CH₃)₃), 32.2 (-CH₂Br), 70.4 (-CH-OTBDPS), 115.2 (-C=CH₂), 127.6 (Ph-C x4), 129.7 (Ph-C x2), 133.6 (Ph-C_q), 134.3 (Ph-C_q), 135.9 (Ph-C x4), 148.9 (-C=CH₂) ppm;

IR (neat, cm^{-1}): 3075, 3052, 2965, 2932, 2859, 1473, 1428;

HRMS (EI) m/z [(M-C₄H₉)⁺]: obsd 345.0308, calcd 345.0310 for C₁₇H₁₈BrOSi.

4-(*tert*-butyldiphenylsilyloxy)-3-methylenepentan-1-ol



To a mixture of bromide (6.0 g, 14.8 mmol) and formaldehyde solution (35%-40% in water) (40 mL) in THF (40 mL) were added indium (3.41 g, 29.6 mmol). The mixture was stirred vigorously at room temperature for 12h, after which the reaction mixture was extracted with ethyl acetate. The organic extracts were washed with H₂O, brine, dried over anhydrous Na₂SO₄ and concentrated in *vacuo*. The crude product was purified by flash chromatography on silica gel, eluting with hexane-ethyl acetate (10:1) to afford product (4.74 g, 90%) as colorless oil.

R_f 0.39 (hexane/ethyl acetate, 4:1);

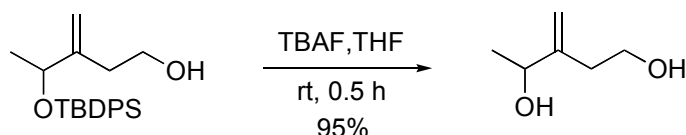
^1H NMR (300 MHz, CDCl_3): δ 1.07 (9H, s, -C(CH₃)₃), 1.15 (3H, d, J = 6.44 Hz, -CH-CH₃), 2.24 (1H, dt, J = 14.81, 5.55 Hz, -CH₂CH₂OH), 2.39 (1H, dt, J = 14.81, 6.63 Hz, -CH₂CH₂OH), 3.58-3.74 (2H, m, -CH₂-OH), 4.27 (1H, q, J = 6.44 Hz, -CH-CH₃), 4.81 (1H, s, C=CH₂), 5.03 (1H, s, -C=CH₂), 7.34-7.45 (6H, m, -Ph-H), 7.64-7.70 (4H, m, -Ph-H) ppm;

^{13}C NMR (75 MHz, CDCl_3): δ 19.2 (-C(CH₃)₃), 23.2 (-CHCH₃), 27.0 (-C(CH₃)₃), 34.8 (-CH₂CH₂OH), 61.5 (-CH₂OH), 73.0 (-CH-OTBDPS), 111.9 (-C=CH₂), 127.6 (Ph-C x4), 129.7 (Ph-C x2), 133.7 (Ph-C_q), 134.1 (Ph-C_q), 135.9 (Ph-C x4), 149.3 (-C=CH₂) ppm;

IR (neat, cm^{-1}): 3441, 3369, 3075, 3052, 2965, 2931, 2858, 1473, 1428;

HRMS (EI) m/z [(M-C₄H₉)⁺]: obsd 297.1316, calcd 297.1311 for C₁₈H₂₁O₂Si.

3-methylenepentane-1,4-diol



To a solution of alcohol (1.0 g, 2.8 mmol) in THF (6 mL) was treated with TBAF (4.2 mL, 1.0 M in THF solution, 4.2 mmol) at room temperature. The mixture was stirred for 30 minutes. After the reaction was completed (monitor by TLC), THF was removed in *vacuo*. The residue was purified by flash chromatography on silica gel, eluting with hexane-ethyl acetate (2:1 to 1:1). The diol was obtained as a colorless oil, (0.30 g, 95%).

R_f 0.12 (hexane/ethyl acetate, 1:1);

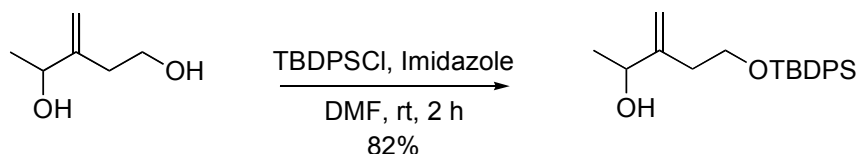
$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 1.30 (3H, d, $J = 6.27$ Hz, $-\text{CH}-\text{CH}_3$), 2.29 (1H, dt, $J = 14.21, 5.22$ Hz, $-\text{CH}_2\text{CH}_2\text{OH}$), 2.42 (1H, dt, $J = 14.21, 6.09$ Hz, $-\text{CH}_2\text{CH}_2\text{OH}$), 3.66-3.82 (2H, m, $-\text{CH}_2-\text{OH}$), 4.30 (1H, q, $J = 6.27$ Hz, $-\text{CH}-\text{CH}_3$), 4.90 (1H, s, $-\text{C}=\text{CH}_2$), 5.10 (1H, s, $-\text{C}=\text{CH}_2$) ppm;

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 22.0 ($-\text{CH}-\text{CH}_3$), 35.0 ($-\text{CH}_2\text{CH}_2\text{OH}$), 62.3 ($-\text{CH}_2\text{OH}$), 70.9 ($-\text{CH}-\text{OH}$), 112.2 ($-\text{C}=\text{CH}_2$), 150.1 ($-\text{C}=\text{CH}_2$) ppm;

IR (neat, cm^{-1}): 3386, 2976, 2936, 2887;

HRMS (EI) m/z [$(\text{M}-\text{H}_2\text{O})^+$]: obsd 98.0733, calcd 98.0732 for $\text{C}_6\text{H}_{10}\text{O}$.

5-(*tert*-butyldiphenylsilyloxy)-3-methylenepentan-2-ol



To a solution of diol (0.60 g, 5 mmol) in anhydrous DMF (30 mL) at 0 °C was added imidazole (0.70 g, 10 mmol) in one portion. After the imidazole has dissolved, *tert*-butyldiphenylsilyl chloride (1.5 mL, 5.75 mmol) was added in. After the reaction was completed (monitor by TLC), the reaction mixture was poured into ice water and extracted with ethyl acetate. The combined organic extract was washed with brine, dried over anhydrous MgSO_4 and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel to afford the product (1.45 g, 82%) as a colorless oil.

R_f 0.66 (hexane/ethyl acetate, 4:1);

$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 1.05 (9H, s, $-\text{C}(\text{CH}_3)_3$), 1.27 (3H, d, $J = 6.45$ Hz, $-\text{CH}-\text{CH}_3$), 2.27 (1H, dt, $J = 14.26, 5.58$ Hz, $-\text{CH}_2\text{CH}_2\text{OTBDPS}$), 2.45 (1H, dt, $J = 14.26, 6.63$ Hz, $-\text{CH}_2\text{CH}_2\text{OTBDPS}$), 3.73-3.83 (2H, m, $-\text{CH}_2\text{OTBDPS}$), 4.27 (1H, q,

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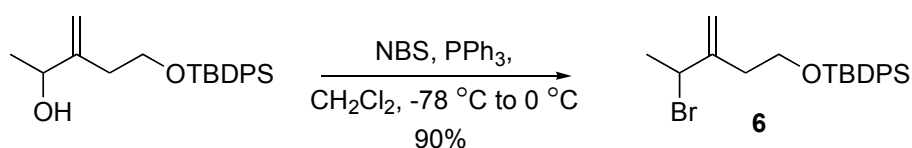
$J = 6.45$ Hz, -CH-OH), 4.83 (1H, s, -C=CH₂), 5.07 (1H, s, -C=CH₂), 7.36-7.46 (6H, m, -Ph-H), 7.66-7.71 (4H, m, -Ph-H) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 19.1 (-C(CH₃)₃), 22.3 (-CHCH₃), 26.8 (-C(CH₃)₃), 34.7 (-CH₂CH₂OTBDPS), 63.1 (-CH₂OTBDPS), 70.8 (-CHOH), 111.2 (-C=CH₂), 127.7 (Ph-C x4), 129.8 (Ph-C x2), 133.4 (Ph-C_q), 134.8 (Ph-C_q), 135.6 (Ph-C x4), 150.6 (-C=CH₂) ppm;

IR (neat, cm⁻¹): 3398, 3072, 3053, 2960, 2931, 2858, 1472, 1458;

HRMS (EI) m/z [(M-C₄H₉)⁺]: obsd 297.1324, calcd 297.1311 for C₁₈H₂₁O₂Si.

(4-bromo-3-methylenepentyloxy)(*tert*-butyl)diphenylsilane (**6**)



To a solution of alcohol (1.05 g, 3 mmol) in anhydrous CH₂Cl₂ (9 mL) at 0 °C was added PPh₃ (0.96 g, 3.6 mmol) in one portion. The reaction mixture was stirred at 0 °C for 10 minutes. After all PPh₃ has dissolved, NBS (0.6 g, 3.3 mmol) was added in one portion at -78 °C. The resulting solution was stirred at -78 °C for 30 minutes then transferred to ice bath at 0 °C. After completion (monitored by TLC), ether and H₂O were added subsequently. The mixture was partitioned, and the organic layer was washed with brine, dried over MgSO₄, filtered and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel, eluting with hexane-ethyl acetate (40:1) to afford **6** (1.12 g, 90%) as a colorless oil.

R_f 0.85 (hexane/ethyl acetate, 4:1);

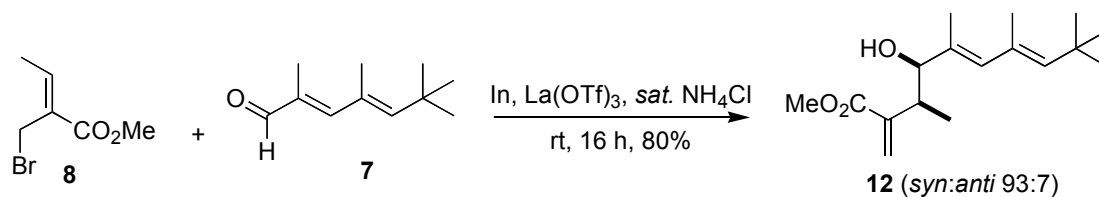
¹H NMR (300 MHz, CDCl₃): δ 1.07 (9H, s, -C(CH₃)₃), 1.77 (3H, d, $J = 6.9$ Hz, -CH-CH₃), 2.40-2.60 (2H, m, -CH₂-C=), 3.84 (2H, t, $J = 6.6$ Hz, -CH₂-O-), 4.69 (1H, q, $J = 6.9$ Hz, -CH-CH₃), 4.95 (1H, s, C=CH₂), 5.21 (1H, s, -C=CH₂), 7.37-7.46 (6H, m, -Ph-H), 7.67-7.70 (4H, m, -Ph-H) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 19.2 (-C(CH₃)₃), 24.2 (-CHCH₃), 26.9 (-C(CH₃)₃), 35.7 (-CH₂CH₂OTBDPS), 52.5 (-CHBr), 63.1 (-CH₂OTBDPS), 113.3 (-C=CH₂), 127.7 (Ph-C x4), 129.7 (Ph-C x2), 133.7 (Ph-C_q), 133.8 (Ph-C_q), 135.6 (Ph-C x4), 147.5 (-C=CH₂) ppm;

IR (neat, cm⁻¹): 3072, 2958, 2931, 2858, 1590, 1428;

HRMS (EI) m/z [(M-C₄H₉)⁺]: obsd 359.0469, calcd 359.0467 for C₁₈H₂₀SiBrO.

Syn-(5E,7E)-methyl 4-hydroxy-3,5,7,9,9-pentamethyl-2-methylenedeca-5,7-dienoate (12)



To a stirred solution of **8** (3.65 mL, 28 mmol) in *sat.* NH₄Cl solution (50 mL) were added indium (2.18 g, 18.9 mmol). After vigorous stirred for 30 minutes at room temperature, La(OTf)₃ (5.5 g, 9 mmol) and **7** (1.57 g, 9.46 mmol) were subsequently added. The mixture was stirred vigorously at room temperature for 16 h. After the reaction was completed (monitored by TLC), the reaction mixture was extracted with ethyl acetate. The organic extracts were combined and washed with *sat.* NaHCO₃ solution, brine, dried over anhydrous Na₂SO₄, and concentrated in *vacuo*. The crude product was purified by flash chromatography on silica gel, eluting with 5% ethyl acetate in hexane gave **12** (2.12 g, 80%) as a colorless oil. The *syn/anti* isomer were obtain in the ratio of 93:7.

R_f 0.47 (hexane/ethyl acetate, 4:1);

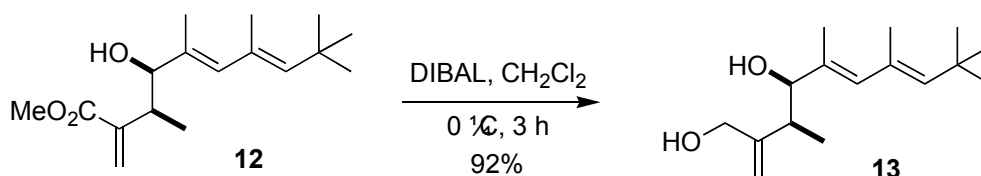
Syn isomer:

¹H NMR (500 MHz, CDCl₃): δ 1.11 (3H, d, *J* = 6.95 Hz, -CH-CH₃), 1.13 (9H, s, -C(CH₃)₃), 1.72 (3H, d, *J* = 1.4 Hz, -C-CH₃), 1.78 (3H, d, *J* = 0.9 Hz, -C-CH₃), 2.99 (1H, ddd, *J* = 6.95, 4.15, 0.95 Hz -CH-CH₃), 3.75 (3H, s, -COOCH₃), 4.08 (1H, d, *J* = 4.15 Hz, -CH-OH), 5.24 (1H, d, *J* = 1.30 Hz, -C=CH₂), 5.64 (1H, d, *J* = 0.95 Hz, -C=CH-), 5.82 (1H, d, *J* = 1.30 Hz, -C=CH₂), 6.24 (1H, d, *J* = 0.95 Hz, -C=CH-) ppm;
¹³C NMR (125 MHz, CDCl₃): δ 13.8 (-CH₃), 13.8 (-CH₃), 17.8 (-CH₃), 30.9 (-C(CH₃)₃), 32.5 (-C(CH₃)₃), 38.9 (-CH-CH₃), 51.7 (-OMe), 78.9 (-CHOH), 125.4 (-C=CH₂), 130.8 (-C=CH-), 131.8 (-C=CH-), 134.5 (-C=CH-), 139.8 (-C=CH-), 143.2 (-C=CH₂), 167.6 (C=O) ppm;

IR (neat, cm⁻¹): 3440, 2954, 1717, 1625, 1437;

HRMS (EI) m/z (M⁺): obsd 280.2032, calcd 280.2039 for C₁₇H₂₈O₃.

Syn-(5E,7E)-3,5,7,9,9-pentamethyl-2-methylenedeca-5,7-diene-1,4-diol (13)



To a mixture of *syn* **12** (0.7 g, 2.5 mmol) in anhydrous CH_2Cl_2 (5 mL), was added DIBAL-H (5 mL, 5 mmol) at 0 °C and stirred for 3h. After reduction was completed (monitored by TLC), *sat.* Na_2SO_4 solution was added until white precipitate was deposited. The mixture was filtered, dried over anhydrous MgSO_4 and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel (hexane ethyl / acetate, 4:1) to afford the pure *syn* **13** (0.58 g, 92%) as a colorless oil.

R_f 0.40 (hexane/ethyl acetate, 2:1);

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ 1.02 (3H, d, $J = 6.96$ Hz, $-\text{CH}-\text{CH}_3$), 1.27 (9H, s, $-\text{C}(\text{CH}_3)_3$), 1.70 (3H, d, $J = 1.05$ Hz, $-\text{C}-\text{CH}_3$), 1.79 (3H, d, $J = 1.05$ Hz, $-\text{C}-\text{CH}_3$), 2.54 (1H, dq, $J = 6.96, 3.84$ Hz, $-\text{CH}-\text{CH}_3$), 2.63 (2H, brs, $-\text{CH}_2\text{OH}$, $-\text{CHOH}$), 4.04 (1H, d, $J = 3.84$ Hz, $-\text{CH}-\text{OH}$), 4.06 (1H, d, $J = 13.23$ Hz, $-\text{CH}_2-\text{OH}$), 4.14 (1H, d, $J = 13.23$ Hz, $-\text{CH}_2-\text{OH}$), 4.99 (1H, brs, $-\text{C}=\text{CH}-$), 5.13 (brs, 1H, $-\text{C}=\text{CH}_2$), 5.25 (1H, d, $J = 1.38$ Hz, $-\text{C}=\text{CH}_2$), 5.87 (1H, brs, $-\text{C}=\text{CH}-$) ppm;

$^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 12.7 ($-\text{CH}-\text{CH}_3$), 14.8 ($-\text{C}-\text{CH}_3$), 18.0 ($-\text{C}-\text{CH}_3$), 30.9 ($-\text{C}(\text{CH}_3)_3$), 32.5 ($-\text{C}(\text{CH}_3)_3$), 41.2 ($-\text{CH}-\text{CH}_3$), 64.7 ($-\text{CH}_2\text{OH}$), 78.8 ($-\text{CHOH}$), 112.7 ($-\text{C}=\text{CH}_2$), 130.9 ($-\text{C}=\text{CH}-$), 131.3 ($-\text{C}=\text{CH}-$), 134.3 ($-\text{C}=\text{CH}-$), 140.0 ($-\text{C}=\text{CH}-$), 151.4 ($-\text{C}=\text{CH}_2$) ppm;

IR (neat, cm^{-1}): 3354, 2958, 1713, 1651, 1644;

HRMS (EI) m/z (M^+): obsd 252.2103, calcd 252.2089 for $\text{C}_{16}\text{H}_{28}\text{O}_2$.

***Syn*-(5*E*,7*E*)-2-((*tert*-butyldiphenylsilyloxy)methyl)-3,5,7,9,9-pentamethyldeca-1,5,7-trien-4-ol (**14**)**



To a solution of *syn* **13** (0.73 g, 2.89 mmol) in anhydrous DMF (9 mL) was added imidazole (0.40 g, 5.78 mmol) and *tert*-butyldiphenylsilyl chloride (0.85 mL, 3.18 mmol) at 0 °C under N_2 . The mixture was stirred at 0 °C to room temperature for 1.5h. After completion, the mixture was poured into water and extracted with ethyl

acetate (x3). The combined organic extract was washed with brine, dried (MgSO₄), concentrated and purified by flash chromatography on silica gel to afford **14** (1.36 g, 96%) as a colorless oil.

R_f 0.46 (hexane/ethyl acetate, 4:1);

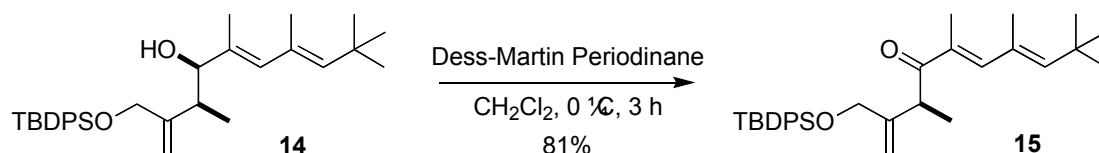
¹H NMR (300 MHz, CDCl₃): δ 1.01 (3H, d, *J* = 6.96 Hz, -CH-CH₃), 1.06 (9H, s, -C(CH₃)₃), 1.14 (9H, s, -C(CH₃)₃), 1.67 (3H, d, *J* = 1.05 Hz, -C-CH₃), 1.79 (3H, d, *J* = 1.38 Hz, -C-CH₃), 2.50 (1H, dq, *J* = 6.96, 4.5 Hz, -CH-CH₃), 3.97 (1H, d, *J* = 4.5 Hz, -CH-OH), 4.12 (1H, d, *J* = 13.6 Hz, -CH₂-O-), 4.19 (1H, d, *J* = 13.6 Hz, -CH₂-O-), 5.00 (1H, s, -C=CH₂), 5.26 (2H, d, *J* = 1.41 Hz, -C=CH-, -C=CH₂), 5.88 (1H, s, -C=CH-), 7.38-7.44 (6H, m, -Ph-H), 7.66-7.70 (4H, m, -Ph-H) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 13.0 (-CH₃), 14.6 (-CH₃), 18.0 (-CH₃), 19.2 (-C(CH₃)₃), 26.8 (-C(CH₃)₃), 29.6 (-C(CH₃)₃), 30.9 (-C(CH₃)₃), 40.1 (-CHCH₃), 65.9 (-CH₂OTBDPS), 77.8 (-CHOH), 111.2 (-C=CH₂), 127.7 (-Ph-C), 129.7 (-Ph-C), 131.0 (-C=CH-), 131.3 (-C=CH-), 133.4 (-Ph-C), 134.1 (-C=CH-), 135.5 (-Ph-C), 139.8 (-C=CH-), 150.5 (-C=CH₂) ppm;

IR (neat, cm⁻¹): 3434, 2929, 1646;

HRMS (EI) *m/z* [(M-C₄H₉)⁺]: obsd 433.2535, calcd 433.2563 for C₂₈H₃₇O₂Si.

(5*E*,7*E*)-2-((*tert*-butyldiphenylsilyloxy)methyl)-3,5,7,9,9-pentamethyldeca-1,5,7-trien-4-one (15)



To a solution of Dess-Martin reagent (1.75 g, 4.12 mmol) in anhydrous CH₂Cl₂ (15 mL) was added dropwise of **14** (1.35 g, 2.75 mmol) prediluted in CH₂Cl₂ (5 mL) at 0 °C. The reaction mixture was stirred under nitrogen at 0 °C for 3h. After completion, the reaction mixture was diluted with ether and poured slowly into a Na₂S₂O₃ : NaHCO₃ (1:1) solution and stirred for 10 minutes and extract with ether. The combine etherate layer was washed with NaHCO₃, brine and dried over anhydrous MgSO₄. Solvent was removed in *vacuo*. The residue was purified by flash chromatography on silica gel to provide **15** (1.09 g, 81%) as a colorless oil.

R_f 0.66 (hexane/ethyl acetate, 4:1);

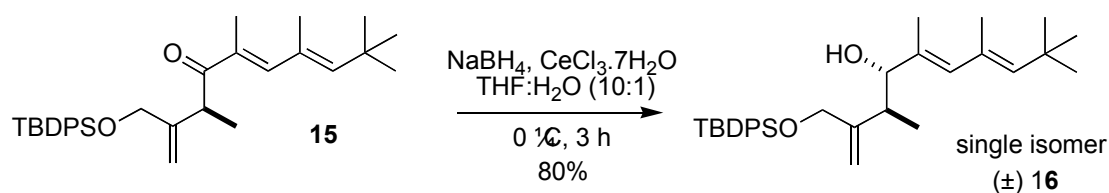
¹H NMR (300 MHz, CDCl₃): δ 1.09 (9H, s, -C(CH₃)₃), 1.17 (9H, s, -C(CH₃)₃), 1.22 (3H, d, *J* = 6.96 Hz, -CH-CH₃), 1.88 (3H, d, *J* = 1.05 Hz, -C-CH₃), 1.91 (3H, d, *J* = 1.05 Hz, -C-CH₃), 4.03 (1H, q, *J* = 6.96 Hz, -CH-CH₃), 4.16 (1H, d, *J* = 13.5 Hz, -CH₂-O-), 4.22 (1H, d, *J* = 13.5 Hz, -CH₂-O-), 4.93 (1H, brs, -C=CH₂), 5.23 (1H, d, *J* = 1.05 Hz, -C=CH₂-), 5.54 (1H, brs, -C=CH-), 6.99 (1H, brs, -C=CH-), 7.36-7.44 (6H, m, -Ph-H), 7.68-7.70 (4H, m, -Ph-H) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 13.4 (-CH₃), 16.9 (-CH₃), 17.4 (-CH₃), 19.2 (-C(CH₃)₃), 26.8 (-C(CH₃)₃), 30.6 (-C(CH₃)₃), 32.9 (-C(CH₃)₃), 42.4 (-CHCH₃), 65.8 (-CH₂OTBDPS), 111.1 (-C=CH₂), 127.7 (-Ph-C x4), 129.7 (-Ph-C x2), 130.9 (Ph-Cq x2), 133.3 (-C=CH), 133.7 (-C=CH), 135.4 (-Ph-C x4), 144.9 (-C=CH-), 145.3 (-C=CH-), 148.4 (-C=CH₂), 203.1 (-C=O) ppm;

IR (neat, cm⁻¹): 2960, 1663, 1648, 1634;

HRMS (EI) m/z (M⁺): obsd 488.3092, calcd 488.3111 for C₃₂H₄₄O₂Si.

***Anti*-(5*E*,7*E*)-2-((*tert*-butyldiphenylsilyloxy)methyl)-3,5,7,9,9-pentamethyldeca-1,5,7-trien-4-ol (**16**)**



To a solution of **15** (490 mg, 1 mmol) in THF:H₂O (10:1) (5 mL) was added CeCl₃·7H₂O (130 mg, 1.5 mmol) at 0 °C. After the mixture was stirred at 0 °C for 15 minutes, NaBH₄ (60 mg, 1.5 mmol) was added and the reaction was stirred for 3h. After the reaction was completed (monitored by TLC), THF was removed under *vacuo*. H₂O was added and the mixture was extracted with ether. The combined etherate layer was washed with brine, dried over MgSO₄, concentrated and purified through flash chromatography on silica gel to afford **16** (396 mg, 80%) as a colorless oil. (*anti:syn* > 99:1)

R_f 0.46 (hexane/ethyl acetate, 4:1);

¹H NMR (300 MHz, CDCl₃): δ 0.87 (3H, d, *J* = 6.96 Hz, -CH-CH₃), 1.07 (9H, s, -C(CH₃)₃), 1.13 (9H, s, -C(CH₃)₃), 1.71 (3H, d, *J* = 1.40 Hz, -C-CH₃), 1.79 (3H, d, *J* = 1.05 Hz, -C-CH₃), 2.39 (1H, dq, *J* = 9.40, 6.96 Hz, -CH-CH₃), 3.80 (1H, dd, *J* = 9.40, 2.45 Hz, -CH-OH), 4.14 (2H, s, -CH₂-O-), 5.09 (1H, s, -C=CH₂), 5.30 (1H, d, *J*

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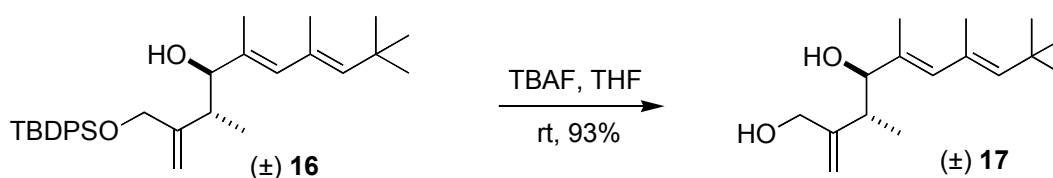
= 1.40 Hz, -C=CH₂-), 5.32 (1H, d, *J* = 1.40 Hz, -C=CH-), 5.80 (1H, s, -C=CH-), 7.36-7.44 (6H, m, -Ph-H), 7.69-7.72 (4H, m, -Ph-H) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 11.9 (-CH₃), 17.5 (-CH₃), 17.9 (-CH₃), 19.1 (-C(CH₃)₃), 26.8 (-C(CH₃)₃), 29.6 (-C(CH₃)₃), 30.9 (-C(CH₃)₃), 41.8 (-CHCH₃), 66.0 (-CH₂OTBDPS), 82.0 (-CHOH), 111.2 (-C=CH₂), 127.7 (-Ph-C x4), 129.8 (-Ph-C x2), 130.6 (-C=CH-), 133.1 (Ph-C_q x2), 134.1 (-C=CH), 134.3 (-C=CH-), 135.6 (-Ph-C x4), 140.2 (-C=CH), 150.3 (-C=CH₂) ppm;

IR (neat, cm⁻¹): 3428, 2957, 2930, 1649, 1558;

HRMS (EI) m/z [(M-C₄H₉)⁺]: obsd 433.2535, calcd 433.2563 for C₂₈H₃₇O₂Si.

***Anti*-(5*E*,7*E*)-3,5,7,9,9-pentamethyl-2-methylenedeca-5,7-diene-1,4-diol (**17**)**



To a solution of **16** (0.5 g, 1.02 mmol) in THF (2 mL) was added TBAF (1.5 mL, 1.0 M in THF, 1.5 mmol). The mixture was stirred for 30 minutes at room temperature. After the reaction was completed (monitored by TLC), the mixture was concentrated *in vacuo* to remove the THF. The residue was purified by flash chromatography on silica gel to afford **17** (0.24 g, 93%) as a colorless oil.

R_f 0.40 (hexane/ethyl acetate, 2:1);

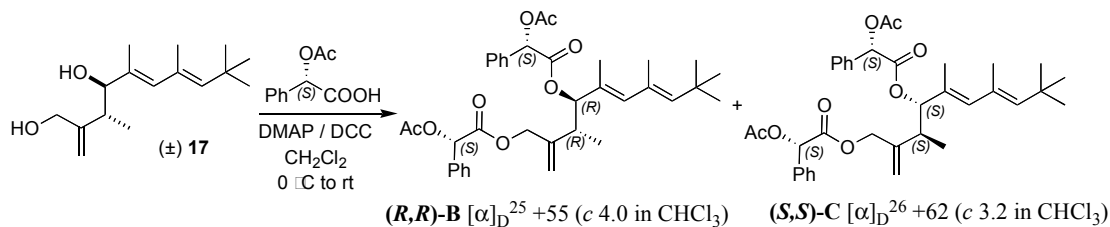
¹H NMR (500 MHz, CDCl₃): δ 0.94 (3H, d, *J* = 6.95 Hz, -CH-CH₃), 1.13 (9H, s, -C(CH₃)₃), 1.73 (3H, d, *J* = 1.4 Hz, -C-CH₃), 1.81 (3H, d, *J* = 0.95 Hz, -C-CH₃), 2.27 (2H, brs, -CH₂OH, -CHOH), 2.48 (1H, dq, *J* = 9.25, 6.95 Hz, -CH-CH₃), 3.82 (1H, d, *J* = 9.25 Hz, -CH-OH), 4.10 (1H, dd, *J* = 12.47, 0.95 Hz, -CH₂-OH), 4.15 (1H, dd, *J* = 12.47, 0.95 Hz, -CH₂-OH), 5.05 (1H, s, -C=CH-), 5.19 (1H, d, *J* = 0.95 Hz, -C=CH₂), 5.31 (1H, d, *J* = 0.95 Hz, -C=CH₂), 5.83 (1H, s, -C=CH-) ppm;

¹³C NMR (125 MHz, CDCl₃): δ 12.1 (-CH-CH₃), 17.6 (-C-CH₃), 17.9 (-C-CH₃), 30.9 (-C(CH₃)₃), 32.6 (-C(CH₃)₃), 41.2 (-CH-CH₃), 65.6 (-CH₂OH), 83.1 (-CHOH), 112.8 (-C=CH₂), 130.7 (-C=CH-), 134.3 (-C=CH-), 134.5 (-C=CH-), 140.6 (-C=CH-), 151.5 (-C=CH₂) ppm;

IR (neat, cm⁻¹): 3353, 2958, 1743, 1643;

HRMS (ESI) m/z (M⁺-1): obsd 251.2011, calcd 252.2011 for C₁₆H₂₇O₂.

(1*S*,1'*S*)-2,2'-((3*R*,4*R*,5*E*,7*E*)-3,5,7,9,9-pentamethyl-2-methylenedeca-5,7-diene-1,4-diyl)bis(oxy)bis(2-oxo-1-phenylethane-2,1-diyl) diacetate (*R,R*)-B and (1*S*,1'*S*)-2,2'-((3*S*,4*S*,5*E*,7*E*)-3,5,7,9,9-pentamethyl-2-methylenedeca-5,7-diene-1,4-diyl)bis(oxy)bis(2-oxo-1-phenylethane-2,1-diyl) diacetate (*S,S*)-C



To a mixture of *anti* (\pm)-**17** (0.24 g, 0.95 mmol), *S*-(+)- α -acetoxyphenylacetic acid (0.56 g, 2.85 mmol) and DMAP (12 mg, 0.095 mmol) in dried CH₂Cl₂ (4 mL) was added DCC (0.39 g, 1.9 mmol) prediluted in 1 mL CH₂Cl₂ dropwise at 0 °C. The reaction mixture was stirred at room temperature for 12 h. After completion, CH₂Cl₂ was removed *via* rotary evaporator and the crude product was directly subjected to column chromatography. Purification by flash chromatography on silica gel (Hex:CH₂Cl₂:EA (3:3:0.2)) afforded two pure enantiomers as colorless oil with 96% overall yield.

(*R,R*)-B

*R*_f 0.36 (hexane/CH₂Cl₂/ethyl acetate, 3:3:0.25);

[α]_D²⁵ +55.4 (*c* 4.0 in CHCl₃);

¹H NMR (500 MHz, CDCl₃): δ 0.72 (3H, d, *J* = 7.4 Hz, -CH-CH₃), 1.12 (9H, s, -C(CH₃)₃), 1.64 (3H, d, *J* = 1.4 Hz, -C-CH₃), 1.76 (3H, d, *J* = 1.35 Hz, -C-CH₃), 2.14 (3H, s, -OAc), 2.19 (3H, s, -OAc), 2.33 (1H, dq, *J* = 9.7, 7.4 Hz, -CH-CH₃), 4.11 (1H, d, *J* = 12.95 Hz, -CH₂-O-), 4.19 (1H, d, *J* = 12.95 Hz, -CH₂-O-), 4.62 (1H, s, -C=CH₂-), 4.68 (1H, s, -C=CH₂), 4.99 (1H, d, *J* = 9.7 Hz, -CH-O-), 5.24 (1H, t, *J* = 1.35 Hz, -C=CH-), 5.85 (1H, s, -C=CH-), 5.87 (1H, s, -CH-OAc), 5.92 (1H, s, -CH-OAc), 7.26-7.27 (3H, m, -Ph-H), 7.33-7.35 (2H, m, -Ph-H), 7.38-7.39 (3H, m, -Ph-H), 7.45-7.47 (2H, m, -Ph-H) ppm;

¹³C NMR (125 MHz, CDCl₃): δ 12.7 (-C-CH₃), 16.9 (OAc), 17.7 (OAc), 20.6 (-C-CH₃), 30.8 (-C(CH₃)₃), 32.5 (-C(CH₃)₃), 38.9 (-CH-CH₃), 67.3 (-CH₂O-), 74.3 (-CH-OAc), 74.4 (-CH-OAc), 84.2 (-CH-O-), 114.5 (-C=CH₂), 127.6 (-Ph-C_m), 127.7 (-Ph-C_m), 128.5 (-Ph-C_o), 128.7 (-Ph-C_o), 129.0 (-Ph-C_p), 129.2 (-Ph-C_p), 129.4 (-HC=C-CH₃), 130.3 (-HC=C-CH₃), 133.7 (-Ph-C_q), 134.0 (-Ph-C_q), 136.3 (-CH=C-

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CH₃), 140.8 (-CH=C-CH₃), 143.9 (-C=CH₂), 167.6 (C=O), 168.3 (C=O), 169.9 (C=O), 170.1 (C=O) ppm;

HRMS (ESI) m/z (M+Na)⁺: obsd. 627.2928, calcd 627.2934 for C₃₆H₄₄NaO₈;

(*S,S*)-**C**

R_f 0.27 (hexane/CH₂Cl₂/ethyl acetate, 3:3:0.25);

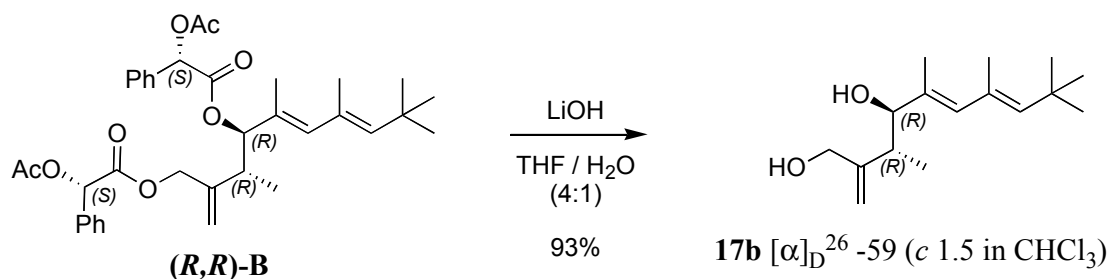
[α]_D²⁶ +62.2 (c 3.2 in CHCl₃);

¹H NMR (500 MHz, CDCl₃): δ 0.82 (3H, d, *J* = 6.95 Hz, -CH-CH₃), 1.09 (9H, s, -C(CH₃)₃), 1.28 (3H, d, *J* = 1.4 Hz, -C-CH₃), 1.64 (3H, d, *J* = 0.95 Hz, -C-CH₃), 2.15 (3H, s, -OAc), 2.20 (3H, s, -OAc), 2.35 (1H, dq, *J* = 9.75, 6.95 Hz, -CH-CH₃), 4.57 (3H, s, -OAc), 4.66 (1H, d, *J* = 12.95 Hz, -CH₂-O-), 4.95 (1H, d, *J* = 9.75 Hz, -CH-O-), 4.98 (1H, s, -C=CH₂-), 5.01 (1H, s, -C=CH₂), 5.06 (1H, t, *J* = 1.4 Hz, -C=CH-), 5.62 (1H, s, -C=CH-), 5.88 (1H, s, -CH-OAc), 5.98 (1H, s, -CH-OAc), 7.32-7.34 (3H, m, -Ph-H), 7.36-7.39 (5H, m, -Ph-H), 7.48-7.50 (2H, m, -Ph-H) ppm;

¹³C NMR (125 MHz, CDCl₃): δ 12.4 (-C-CH₃), 16.7 (OAc), 17.5 (OAc), 20.6 (-C-CH₃), 30.8 (-C(CH₃)₃), 32.5 (-C(CH₃)₃), 38.4 (-CH-CH₃), 67.9 (-CH₂O-), 74.3 (-CH-OAc), 74.5 (-CH-OAc), 84.5 (-CH-O-), 114.5 (-C=CH₂), 127.6 (-Ph-C_m), 127.7 (-Ph-C_m), 128.5 (-Ph-C_o), 128.7 (-Ph-C_o), 129.0 (-Ph-C_p), 129.2 (-Ph-C_p), 129.4, (-HC=C-CH₃), 130.3 (-HC=C-CH₃), 133.7 (-Ph-C_q), 134.0 (-Ph-C_q), 136.3 (-CH=C-CH₃), 140.8 (-CH=C-CH₃), 143.9 (-C=CH₂), 167.6 (C=O), 168.2 (C=O), 169.9 (C=O), 170.1 (C=O) ppm;

HRMS (ESI) m/z (M+Na)⁺: obsd 627.2928, calcd 627.2934 for C₃₆H₄₄NaO₈.

Anti-(*3R,4R,5E,7E*)-3,5,7,9,9-pentamethyl-2-methylenedeca-5,7-diene-1,4-diol (**17b**)



To a solution of (*R,R*)-**B** (40 mg, 0.066 mmol) in THF (1 mL) at 0 °C was added a solution of LiOH (6 mg, 0.14 mmol) in water (1 mL). The resulting mixture was stirred at room temperature for 12 h prior to workup. The mixture was extracted with

ethyl acetate (x5). The combined organic extract was dried over anhydrous Na₂SO₄, filtered and concentrated to afford the desired product **17b** (15.6 mg, 93%) as a white amorphous solid.

R_f 0.40 (hexane/ethyl acetate, 2:1);

$[\alpha]_D^{26}$ -59 (*c* 1.5 in CHCl₃);

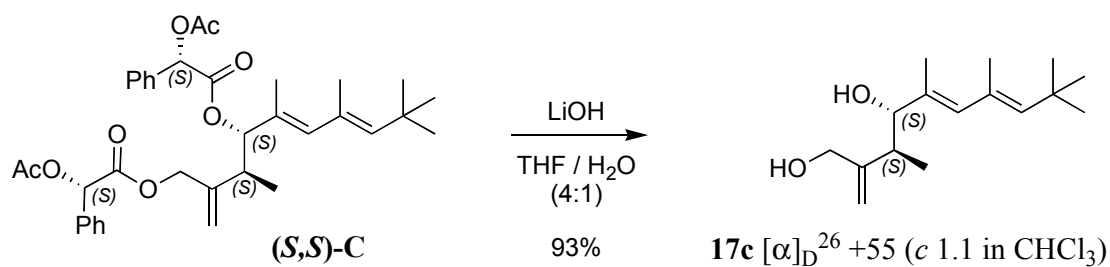
¹H NMR (500 MHz, CDCl₃): δ 0.94 (3H, d, *J* = 6.95 Hz, -CH-CH₃), 1.13 (9H, s, -C(CH₃)₃), 1.73 (3H, d, *J* = 1.4 Hz, -C-CH₃), 1.81 (3H, d, *J* = 0.95 Hz, -C-CH₃), 2.27 (2H, brs, -CH₂OH, -CHOH), 2.48 (1H, dq, *J* = 9.25, 6.95 Hz, -CH-CH₃), 3.82 (1H, d, *J* = 9.25 Hz, -CH-OH), 4.10 (1H, dd, *J* = 12.47, 0.95 Hz, -CH₂-OH), 4.15 (1H, dd, *J* = 12.47, 0.95 Hz, -CH₂-OH), 5.05 (1H, s, -C=CH-), 5.19 (1H, d, *J* = 0.95 Hz, -C=CH₂), 5.31 (1H, d, *J* = 0.95 Hz, -C=CH₂), 5.83 (1H, s, -C=CH-) ppm;

¹³C NMR (125 MHz, CDCl₃): δ 12.1 (-CH-CH₃), 17.6 (-C-CH₃), 17.9 (-C-CH₃), 30.9 (-C(CH₃)₃), 32.6 (-C(CH₃)₃), 41.2 (-CH-CH₃), 65.6 (-CH₂OH), 83.1 (-CHOH), 112.8 (-C=CH₂), 130.7 (-C=CH-), 134.3 (-C=CH-), 134.5 (-C=CH-), 140.6 (-C=CH-), 151.5 (-C=CH₂) ppm;

IR (neat, cm⁻¹): 3353, 2958, 1743, 1643;

HRMS (ESI) m/z (M⁺-1): obsd 251.2011, calcd 251.2011 for C₁₆H₂₇O₂.

***Anti*-(3*S*,4*S*,5*E*,7*E*)-3,5,7,9,9-pentamethyl-2-methylenedeca-5,7-diene-1,4-diol
(17c)**



Follow the same hydrolysis procedure for **17b**, **17c** was obtained as a white amorphous solid in 93% yield.

R_f 0.40 (hexane/ethyl acetate, 2:1);

$[\alpha]_D^{26}$ +55 (*c* 1.1 in CHCl₃);

¹H NMR (500 MHz, CDCl₃): δ 0.94 (3H, d, *J* = 6.95 Hz, -CH-CH₃), 1.13 (9H, s, -C(CH₃)₃), 1.73 (3H, d, *J* = 1.4 Hz, -C-CH₃), 1.81 (3H, d, *J* = 0.95 Hz, -C-CH₃), 2.27 (2H, brs, -CH₂OH, -CHOH), 2.48 (1H, dq, *J* = 9.25, 6.95 Hz, -CH-CH₃), 3.82 (1H, d, *J* = 9.25 Hz, -CH-OH), 4.10 (1H, dd, *J* = 12.47, 0.95 Hz, -CH₂-OH), 4.15 (1H, dd, *J* =

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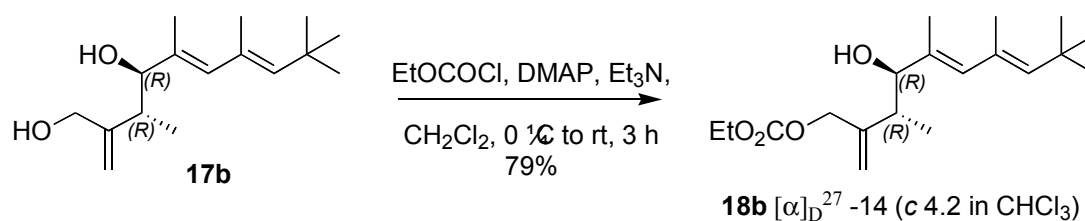
12.47, 0.95 Hz, -CH₂-OH), 5.05 (1H, s, -C=CH-), 5.19 (1H, d, *J* = 0.95 Hz, -C=CH₂),
5.31 (1H, d, *J* = 0.95 Hz, -C=CH₂), 5.83 (1H, s, -C=CH-) ppm;

¹³C NMR (125 MHz, CDCl₃): δ 12.1 (-CH-CH₃), 17.6 (-C-CH₃), 17.9 (-C-CH₃),
30.9 (-C(CH₃)₃), 32.6 (-C(CH₃)₃), 41.2 (-CH-CH₃), 65.6 (-CH₂OH), 83.1 (-CHOH),
112.8 (-C=CH₂), 130.7 (-C=CH-), 134.3 (-C=CH-), 134.5 (-C=CH-), 140.6 (-C=CH-),
151.5 (-C=CH₂) ppm;

IR (neat, cm⁻¹): 3353, 2958, 1743, 1643;

HRMS (ESI) *m/z* (*M*⁺-1): obsd 251.2011, calcd 251.2011 for C₁₆H₂₇O₂.

***Anti*-ethyl (3*R*,4*R*,5*E*,7*E*)-4-hydroxy-3,5,7,9,9-pentamethyl-2-methylenedeca-5,7-dienyl carbonate (18b)**



To a solution of *anti* **17b** (0.31 g, 1.23 mmol), anhydrous triethyl amine (0.51 mL, 3.69 mmol) and DMAP (0.15 g, 1.23 mmol) in CH₂Cl₂ (12 ml) at 0 °C was added ethyl chloroformate (0.117 ml, 1.23 mmol) dropwise. The reaction progress was monitored by TLC. After completion, the reaction mixture was poured into ice water and extracted with ethyl acetate (x3). The combined organic extracts were washed with NaHCO₃, brine, dried (MgSO₄) and concentrated in *vacuo*. Purification by flash chromatography on silica gel afforded **18b** (0.31 g, 79%) as colorless oil.

R_f 0.42 (hexane/ethyl acetate, 4:1);

[α]_D²⁷ -14 (*c* 4.2 in CHCl₃);

¹H NMR (500 MHz, CDCl₃): δ 0.95 (3H, d, *J* = 7.40 Hz, -CH-CH₃), 1.14 (9H, s, -C(CH₃)₃), 1.31 (3H, t, *J* = 6.95 Hz, -OCH₂-CH₃), 1.73 (3H, d, *J* = 1.40 Hz, -C-CH₃), 1.81 (3H, d, *J* = 1.40 Hz, -C-CH₃), 2.45 (1H, dq, *J* = 9.25, 7.4 Hz, -CH-CH₃), 3.85 (1H, d, *J* = 9.25, 1.85 Hz, -CHOH), 4.21 (2H, q, *J* = 6.95 Hz, -CH₂-CH₃-), 4.66 (2H, s, -CH₂-O-), 5.15 (1H, s, -C=CH₂), 5.25 (1H, d, *J* = 0.95 Hz, -C=CH₂), 5.31 (1H, d, *J* = 0.95 Hz, -C=CH-), 5.83 (1H, s, -C=CH-) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 11.9 (-CH₃), 14.2 (-CH₃), 16.9 (-CH₃), 17.8 (-CH₃), 30.9 (-C(CH₃)₃), 32.5 (-C(CH₃)₃), 41.8 (-CHCH₃), 64.1 (-OCH₂CH₃), 68.7 (-

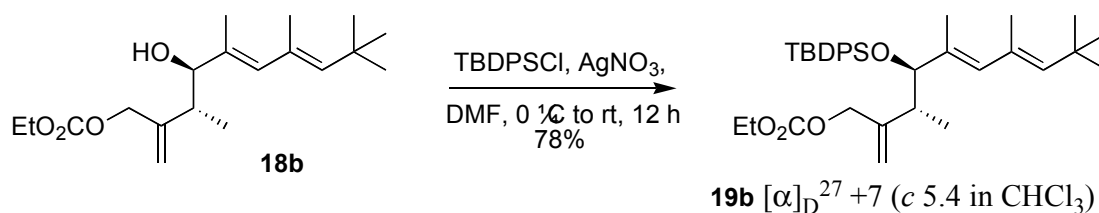
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CH₂OCO₂Et), 81.8 (-CHOH), 113.9 (-C=CH₂), 130.6 (-HC=C-), 133.9 (-HC=C-),
134.4 (-C=CH-), 140.4 (-C=CH-), 145.9 (-C=CH₂), 155.0 (C=O) ppm;

IR (neat, cm⁻¹): 3500, 2959, 1747, 1732, 1651;

HRMS (EI) m/z (M⁺): obsd 324.2295, calcd 324.2310 for C₁₉H₃₂O₄.

***Anti*-(3*R*,4*R*,5*E*,7*E*)-4-(*tert*-butyldiphenylsilyloxy)-3,5,7,9,9-pentamethyl-2-methylenedeca-5,7-dienyl ethyl carbonate (**19b**)**



To a solution of **18b** (0.2 g, 0.6 mmol) in 1 mL DMF was added AgNO₃ (0.2 g, 1.2 mmol) followed by TBDPSCI (0.18 mL, 0.66 mmol). After the reaction was completed (monitored by TLC), the reaction mixture was poured into ice water and extracted with ethyl acetate. The combined organic layer was washed with brine, dried over anhydrous MgSO₄, concentrated in *vacuo* and purified by flash chromatography to afford **19b** (0.263 g, 78%) as a colorless oil.

R_f 0.55 (hexane/ethyl acetate, 4:1);

[α]_D²⁷ +7 (*c* 5.4 in CHCl₃);

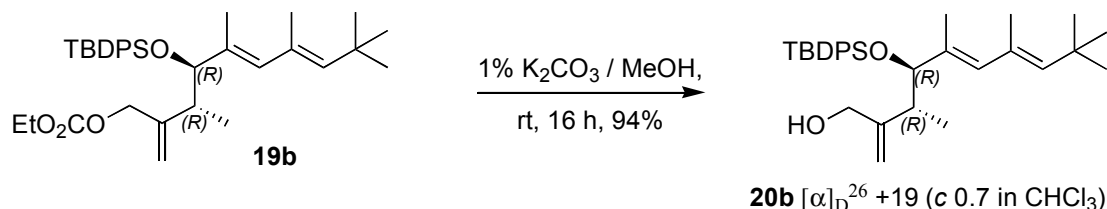
¹H NMR (500 MHz, CDCl₃): δ 0.84 (3H, d, *J* = 7.35 Hz, -CH-CH₃), 1.02 (9H, s, -C(CH₃)₃), 1.08 (9H, s, -C(CH₃)₃), 1.31 (3H, t, *J* = 6.95 Hz, -OCH₂CH₃), 1.55 (3H, s, -C-CH₃), 1.57 (3H, dd, *J* = 4.15, 1.4 Hz, -C-CH₃), 2.42 (1H, dq, *J* = 8.30, 7.35 Hz, -CH-CH₃), 3.94 (1H, d, *J* = 8.30 Hz, -CH-O-), 4.19 (2H, q, *J* = 6.95 Hz, -OCH₂CH₃), 4.43 (1H, d, *J* = 13.45 Hz, -CH₂OCO₂Et), 4.52 (1H, d, *J* = 13.45 Hz, -CH₂OCO₂Et), 4.91 (1H, s, -C=CH₂-), 4.98 (1H, t, *J* = 1.40 Hz, -C=CH-), 5.08 (1H, d, *J* = 0.95 Hz, -C=CH₂-), 5.39 (1H, s, -C=CH-), 7.28-7.41 (6H, m, -Ph-H), 7.58-7.64 (4H, m, -Ph-H) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 13.0 (-CH₃), 14.2 (-CH₃), 16.9 (-CH₃), 17.6 (-CH₃), 19.4 (-C(CH₃)₃), 27.1 (-C(CH₃)₃), 30.9 (-C(CH₃)₃), 32.4 (-C(CH₃)₃), 42.1 (-CHCH₃), 63.7 (-OCH₂-), 69.9 (-CH₂O-), 83.7 (-CHOTBDPS), 113.0 (-C=CH₂), 127.0 (Ph-C x4), 129.3 (Ph-C x2), 130.5 (-CH=C-), 133.7 (Ph-C_q x2), 133.9 (-C=CH-), 134.2 (-C=CH-), 136.2 (Ph-C x4), 139.7 (-CH=C-), 145.8 (-C=CH₂), 154.9 (C=O) ppm;

IR (neat cm⁻¹): 2929, 2859, 1756, 1663;

HRMS (EI) m/z (M⁺): obsd 562.3489, calcd 562.3478 for C₃₅H₅₀O₄Si.

***Anti*-(3*R*,4*R*,5*E*,7*E*)-4-(*tert*-butyldiphenylsilyloxy)-3,5,7,9,9-pentamethyl-2-methylenedeca-5,7-dien-1-ol (20b)**



19b (0.25 g, 0.44 mmol) was dissolved in 1% K₂CO₃ in MeOH solution at room temperature. The solution was stirred at room temperature for 16h. After the reaction was completed (monitored by TLC), the solution was neutralized to pH=7 using 1M HCl. The mixture was extracted with ethyl acetate. The combined organic extracts were washed with brine, dried over anhydrous MgSO₄ and concentrated in *vacuo*. The residue was purified by flash chromatography on silica gel to afford **20b** (0.20 g, 94%) as colorless oil.

R_f 0.22 (hexane/ethyl acetate, 4:1);

[α]_D²⁶ +19 (c 0.7 in CHCl₃);

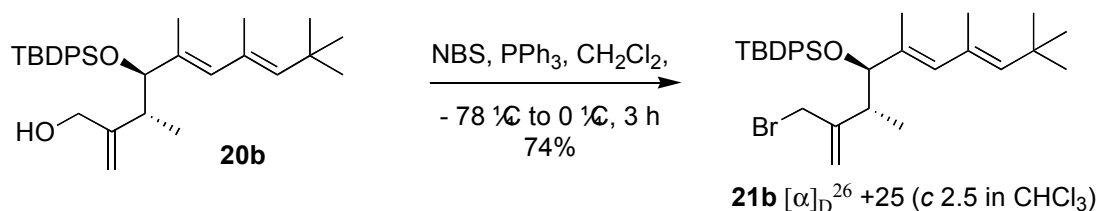
¹H NMR (300 MHz, CDCl₃): δ 0.83 (3H, d, *J* = 6.96 Hz, -CH-CH₃), 1.04 (9H, s, -C(CH₃)₃), 1.10 (9H, s, -C(CH₃)₃), 1.59 (3H, s, -C-CH₃), 1.62 (3H, s, -C-CH₃), 2.46 (1H, dq, *J* = 8.7, 6.96 Hz, -CH-CH₃), 3.90 (1H, d, *J* = 14.28 Hz, -CH₂OH), 3.93 (1H, d, *J* = 8.7 Hz, -CH-O-), 4.03 (1H, d, *J* = 14.28 Hz, -CH₂OH), 4.84 (1H, s, -C=CH₂), 5.01 (2H, d, *J* = 1.38 Hz, -C=CH-, -C=CH₂), 5.38 (1H, s, -C=CH-), 7.29-7.43 (6H, m, -Ph-H), 7.60-7.68 (4H, m, -Ph-H) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 12.3 (-CH₃), 17.2 (-CH₃), 17.6 (-CH₃), 19.4 (-C(CH₃)₃), 27.1 (-C(CH₃)₃), 30.9 (-C(CH₃)₃), 32.4 (-C(CH₃)₃), 41.5 (-CHCH₃), 65.7 (-CH₂OTBDPS), 84.4 (-CHOH), 110.0 (-C=CH₂), 127.1 (Ph-C x2), 127.2 (Ph-C x2), 129.4 (Ph-C x1), 129.5 (Ph-C x1), 130.6 (-C=C-), 133.8 (-C=C-), 133.9 (-C=C-), 134.0 (-C=C-), 134.3 (-C=CH-), 136.3 (Ph-C x2), 136.3 (Ph-C x2), 139.8 (-C=CH-), 151.4 (-C=CH₂) ppm;

IR (neat cm⁻¹): 3354, 2958, 2874, 1654;

HRMS (EI) m/z (M⁺): obsd 490.3288, calcd 490.3267 for C₃₂H₄₆O₂Si.

Anti-((3*R*,4*R*,5*E*,7*E*)-2-(bromomethyl)-3,5,7,9,9-pentamethyldeca-1,5,7-trien-4-yloxy)(*tert*-butyl)diphenylsilane (21b)



To a solution of **20b** (97.6 mg, 0.21 mmol) in anhydrous CH_2Cl_2 (3 mL) at $-78\text{ }^\circ\text{C}$ was added triphenylphosphine (81 mg, 0.31 mmol) in one portion. The mixture was stirred at $-78\text{ }^\circ\text{C}$ for 10 minutes until all the triphenylphosphine dissolved and NBS (47 mg, 0.264 mmol) was added in one portion. The resulting solution was stirred at $-78\text{ }^\circ\text{C}$ for 30 minutes and $0\text{ }^\circ\text{C}$ for 15 minutes. After all the starting material had been consumed (monitored by TLC), ether and H_2O was added in. The mixture was partitioned. The organic layer was washed with brine, dried over anhydrous MgSO_4 and concentrated in *vacuo*. Purification through flash chromatography on silica gel afforded **21b** (88.6 mg, 74%) as a colorless oil.

R_f 0.79 (hexane/ethyl acetate; 4:1);

$[\alpha]_D^{26} +25$ (c 2.5 in CHCl_3);

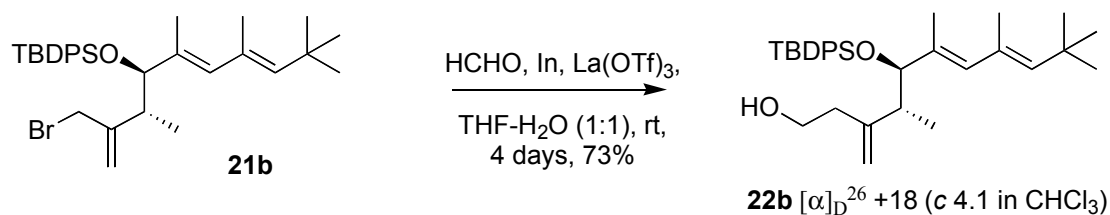
$^1\text{H NMR}$ (500 MHz, CDCl_3): δ 0.93 (3H, d, $J = 6.95$ Hz, $-\text{CH}-\text{CH}_3$), 1.06 (9H, s, $-\text{C}(\text{CH}_3)_3$), 1.12 (9H, s, $-\text{C}(\text{CH}_3)_3$), 1.60 (3H, s, $-\text{C}-\text{CH}_3$), 1.63 (3H, s, $-\text{C}-\text{CH}_3$), 2.62 (1H, dq, $J = 8.3, 6.95$ Hz, $-\text{CH}-\text{CH}_3$), 3.92 (1H, d, $J = 9.75$ Hz, $-\text{CH}_2-\text{Br}$), 3.98 (1H, d, $J = 8.3$ Hz, $-\text{CH}-\text{O}-$), 4.02 (1H, $J = 9.75$ Hz, $-\text{CH}_2-\text{Br}$), 4.94 (1H, s, $-\text{C}=\text{CH}_2-$), 5.02 (1H, s, $-\text{C}=\text{CH}-$), 5.19 (1H, s, $-\text{C}=\text{CH}_2$), 5.43 (1H, s, $-\text{C}=\text{CH}-$), 7.33-7.43 (6H, m, Ph-H), 7.62-7.67 (4H, m, Ph-H) ppm;

$^{13}\text{C NMR}$ (125 MHz, CDCl_3): δ 13.1 ($-\text{CH}_3$), 17.6 ($-\text{CH}_3$), 17.9 ($-\text{CH}_3$), 27.2 ($-\text{C}(\text{CH}_3)_3$), 30.9 ($-\text{C}(\text{CH}_3)_3$), 31.9 ($-\text{C}(\text{CH}_3)_3$), 32.5 ($-\text{C}(\text{CH}_3)_3$), 38.8 ($-\text{CH}_2\text{Br}$), 41.9 ($-\text{CHCH}_3$), 84.9 ($-\text{CHOTBDPS}$), 115.6 ($-\text{C}=\text{CH}_2$), 127.1 (Ph-C x2), 127.2 (Ph-C x2), 129.4 (Ph-C), 129.5 (Ph-C), 130.5 ($-\text{C}=\text{C}-$), 133.8 ($-\text{C}=\text{C}-$), 133.9 ($-\text{C}=\text{C}-$), 134.1 ($-\text{C}=\text{C}-$), 134.4 ($-\text{C}=\text{CH}-$), 136.2 (Ph-C x2), 136.2 (Ph-C x2), 139.9 ($-\text{C}=\text{CH}-$), 148.7 ($-\text{C}=\text{CH}_2$) ppm;

IR (neat cm^{-1}): 2957, 2859, 1636, 1479;

HRMS (EI) m/z [$\text{M}-(\text{C}_4\text{H}_9)^+$]: obsd 497.1723, calcd 497.1750 for $\text{C}_{28}\text{H}_{36}\text{OSi}^{81}\text{Br}$.

Anti-(4*R*,5*R*,6*E*,8*E*)-5-(*tert*-butyldiphenylsilyloxy)-4,6,8,10,10-pentamethyl-3-methyleneundeca-6,8-dien-1-ol (22b)



To a mixture of **21b** (0.4 g, 0.72 mmol) and formaldehyde solution (35-40% in water) (1 ml) in THF (1 mL) were added indium (88 mg, 0.72 mmol) and La(OTf)₃ (0.42 g, 0.72 mmol). The mixture was stirred vigorously at room temperature for 4 days. After the reaction was completed (monitored by TLC), the reaction mixture was extracted with ethyl acetate. The organic extracts were combined and washed with NaHCO₃ solution, brine and dried over anhydrous MgSO₄ and concentrated in *vacuo*. The crude product was purified by flash chromatography on silica gel. Elution with 5% ethyl acetate in hexane resulted **22b** (0.27 g, 73%) as a colorless oil.

R_f 0.31 (hexane/ethyl acetate, 4:1);

$[\alpha]_D^{26} +18$ (c 4.1 in CHCl₃);

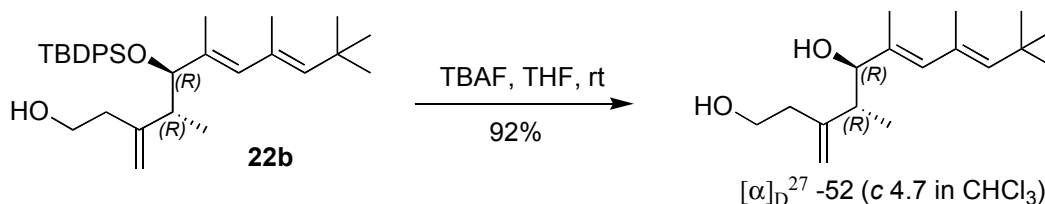
¹H NMR (500 MHz, CDCl₃): δ 0.84 (3H, d, $J = 7.4$ Hz, -CH-CH₃), 1.08 (9H, s, -C(CH₃)₃), 1.14 (9H, s, -C(CH₃)₃), 1.63 (3H, d, $J = 1.4$ Hz, -C-CH₃), 1.65 (3H, d, $J = 0.9$ Hz, -C-CH₃), 2.06 (1H, dt, $J = 14.75, 5.55$ Hz, -CH₂-CH₂-OH), 2.21 (1H, dt, $J = 14.75, 6.95$ Hz, -CH₂-CH₂-OH), 2.43 (1H, dq, $J = 8.3, 7.4$ Hz, -CH-CH₃), 3.61 (2H, td, $J = 7.15, 1.4$ Hz, -CH₂-OH), 4.00 (1H, d, $J = 8.3$ Hz, -CH-OTBDPS), 4.81 (1H, d, $J = 1.4$ Hz, -C=CH₂-), 4.89 (1H, s, -C=CH-), 5.06 (1H, t, $J = 1.4$ Hz, -C=CH₂), 5.46 (1H, s, -C=CH-), 7.32-7.43 (6H, m, -Ph-H), 7.64-7.72 (4H, m, -Ph-H) ppm;

¹³C NMR (125 MHz, CDCl₃): δ 13.3 (-CH₃), 16.8 (-CH₃), 17.6 (-CH₃), 19.4 (-C(CH₃)₃), 27.1 (-C(CH₃)₃), 30.9 (-C(CH₃)₃), 32.4 (-C(CH₃)₃), 38.2 (-CH₂CH₂OH), 44.7 (-CHCH₃), 60.6 (-CH₂OH), 83.2 (-CHOTBDPS), 111.8 (-C=CH₂), 127.0 (-Ph-C x2), 127.2 (-Ph-C x2), 129.2 (-Ph-C), 129.3 (-Ph-C), 130.6 (-C=C-), 133.8 (-C=C-), 134.1 (-C=CH-), 134.2 (-Ph-C_q), 134.2 (-Ph-C_q), 136.2 (-Ph-C x2), 136.3 (-Ph-C x2), 139.7 (-C=CH-), 148.5 (-C=CH₂) ppm;

IR (neat cm⁻¹): 3436, 2935, 2843, 1638, 1457;

HRMS (EI) m/z (M⁺): obsd 504.3408, calcd 504.3424 for C₃₃H₄₈O₂Si.

***Anti*-(4*R*,5*R*,6*E*,8*E*)-4,6,8,10,10-pentamethyl-3-methyleneundeca-6,8-diene-1,5-diol**



Follow the standard desilylation of the TBDPS protecting group with TBAF in THF, diol was obtained as a colourless oil in 92% yield.

R_f 0.39 (hexane/ethyl acetate, 2:1);

[α]_D²⁷ -52 (c 4.7 in CHCl₃);

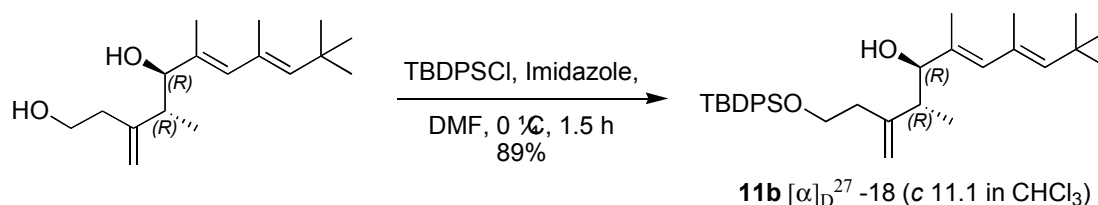
¹H NMR (300 MHz, CDCl₃): δ 0.85 (3H, d, J = 7.32 Hz, -CH-CH₃), 1.12 (9H, s, -C(CH₃)₃), 1.71 (3H, s, -C-CH₃), 1.79 (3H, s, -C-CH₃), 2.22-2.38 (2H, m, -CH₂-CH₂OH), 2.39 (1H, dq, J = 10.08, 7.32 Hz, -CH-CH₃), 2.51 (1H, brs, -OH), 3.00 (1H, brs, -OH), 3.69-3.80 (2H, m, -CH₂-OH), 3.83 (1H, d, J = 10.08 Hz, -CH-OH), 4.99 (1H, s, -C=CH₂-), 5.04 (1H, s, -C=CH₂), 5.29 (1H, s, -C=CH-), 5.81 (1H, s, -C=CH-) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 11.8 (-CH₃), 17.5 (-CH₃), 17.8 (-CH₃), 30.8 (-C(CH₃)₃), 32.5 (-C(CH₃)₃), 37.0 (-CH₂CH₂OH), 43.4 (-CHCH₃), 60.8 (-CH₂OH), 82.0 (-CHOH), 112.9 (-C=CH₂), 130.6 (-C=CH), 134.1 (-C=CH), 134.6 (-C=CH), 140.5 (-C=CH), 149.2 (-C=CH₂) ppm;

IR (neat, cm⁻¹): 3364, 2958, 2863, 2384, 2349, 1641, 1459, 1442;

HRMS (EI) m/z (M⁺): obsd 266.2244, calcd 266.2246 for C₁₇H₃₀O₂.

***Anti*-(4*R*,5*R*,6*E*,8*E*)-1-(*tert*-butyldiphenylsilyloxy)-4,6,8,10,10-pentamethyl-3-methyleneundeca-6,8-dien-5-ol (**11b**)**



Follow the standard procedure for TBDPS protection with TBDPSCl and imidazole in DMF, **11b** was obtained as a colourless oil in 89% yield.

R_f 0.78 (hexane/ethyl acetate, 4:1);

[α]_D²⁷ -18 (c 11.1 in CHCl₃);

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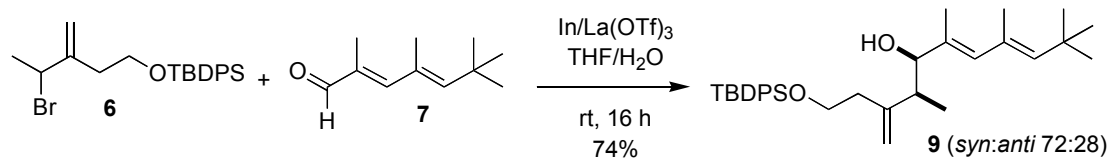
¹H NMR (500 MHz, CDCl₃): δ 0.83 (3H, d, *J* = 6.95 Hz, -CH-CH₃), 1.05 (9H, s, -C(CH₃)₃), 1.15 (9H, s, -C(CH₃)₃), 1.72 (3H, d, *J* = 1.4 Hz, -C-CH₃), 1.82 (3H, d, *J* = 1.4 Hz, -C-CH₃), 2.23-2.30 (2H, m, -CH₂-C-), 2.33 (1H, dq, *J* = 9.70, 6.95 Hz, -CH-CH₃), 3.74 (1H, d, *J* = 9.70 Hz, -CH-OH), 3.77-3.86 (2H, m, -CH₂OTBDPS), 4.94 (1H, s, -C=CH-), 5.01 (1H, s, -C=CH₂), 5.32 (1H, s, -C=CH₂-), 5.81 (1H, s, -C=CH-), 7.37-7.43 (6H, m, -Ph-H), 7.68-7.70 (4H, m, -Ph-H) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 12.0 (-CH₃), 16.9 (-CH₃), 18.0 (-CH₃), 19.2 (-C(CH₃)₃), 26.9 (-C(CH₃)₃), 31.0 (-C(CH₃)₃), 32.6 (-C(CH₃)₃), 36.2 (-CH₂CH₂OTBDPS), 44.9 (-CH-CH₃), 62.9 (-CH₂OTBDPS), 81.0 (-CHOH), 113.3 (-C=CH₂), 127.7 (-Ph-C x4), 129.7 (-Ph-C x2), 130.8 (-C=CH-), 133.8 (-C=CH-), 133.9 (-Ph-C_q x2), 134.5 (-C=CH-), 135.6 (-Ph-C x4), 140.3 (-C=CH-), 148.6 (-C=CH₂) ppm;

IR (neat, cm⁻¹): 3426, 3073, 3051, 2960, 2931, 1639, 1462, 1428;

HRMS (EI) m/z (M⁺): obsd 504.3420, calcd 504.3424 for C₃₃H₄₈SiO₂.

***Syn*-(6*E*,8*E*)-1-(*tert*-butyldiphenylsilyloxy)-4,6,8,10,10-pentamethyl-3-methyleneundeca-6,8-dien-5-ol (**9**)**



To a stirred solution of **6** (1.25 g, 3 mmol) in THF/H₂O (1:1) (10 mL) was added indium (0.52 g, 4.5 mmol). After vigorous stirring for 30 minutes at room temperature, La(OTf)₃ (1.76 g, 3 mmol) and **7** (0.5 g, 3 mmol) were added. The mixture was stirred vigorously at room temperature for 16h. After the reaction was completed (monitored by TLC), the reaction mixture was extracted with ethyl acetate. The organic extracts were combined and washed with *sat.* NaHCO₃ solution, brine, dried over anhydrous Na₂SO₄, and concentrated in *vacuo*. The crude product was purified by flash chromatography on silica gel, eluting with 1% ethyl acetate in hexane resulted **9** (1.12 g, 74%) as a colorless oil, *syn/anti* isomer is in the ratio of 72:28.

R_f 0.75 (hexane/ethyl acetate, 4:1);

¹H NMR (300 MHz, CDCl₃): δ 0.95 (3H, d, *J* = 6.96 Hz, -CH-CH₃), 1.05 (9H, s, -C(CH₃)₃), 1.14 (9H, s, -C(CH₃)₃), 1.65 (3H, d, *J* = 1.05 Hz, -C-CH₃), 1.78 (3H, d, *J* =

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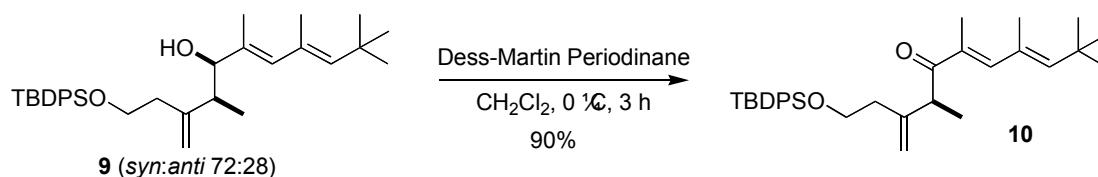
1.05 Hz, -C-CH₃), 2.28-2.42 (3H, m, -CH₂CH₂OTBDPS, -CH-CH₃), 3.78 (2H, t, *J* = 6.96 Hz, -CH₂OTBDPS), 3.94 (1H, d, *J* = 4.89 Hz, -CH-OH), 4.88 (1H, d, *J* = 1.05 Hz, -C=CH₂-), 4.90 (1H, d, *J* = 1.05 Hz, -C=CH₂), 5.25 (1H, t, *J* = 1.05 Hz, -C=CH-), 5.86 (1H, s, -C=CH-), 7.36-7.43 (6H, m, -Ph-H), 7.66-7.69 (4H, m, -Ph-H) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 13.0 (-CH₃), 14.4 (-CH₃), 18.1 (-CH₃), 19.2 (-C(CH₃)₃), 26.9 (-C(CH₃)₃), 31.0 (-C(CH₃)₃), 32.6 (-C(CH₃)₃), 37.8 (-CH₂CH₂OTBDPS), 43.1 (-CH-CH₃), 63.4 (-CH₂OTBDPS), 81.0 (-CHOH), 112.1 (-C=CH₂), 127.7 (-Ph-C x4), 129.6 (-Ph-C x2), 131.1 (-C=CH-), 131.3 (-C=CH-), 133.8 (-C=CH-), 134.1 (-Ph-C_q), 135.6 (-Ph-C x4), 139.8 (-C=CH-), 149.0 (-C=CH₂) ppm;

IR (neat, cm⁻¹): 3466, 3073, 2958, 2860, 1742, 1641, 1469, 1428;

HRMS (EI) *m/z* (M⁺): obsd 504.3408, calcd 504.3424 for C₃₃H₄₈SiO₂.

(6*E*,8*E*)-1-(*tert*-butyldiphenylsilyloxy)-4,6,8,10,10-pentamethyl-3-methyleneundeca-6,8-dien-5-one (10)



To a solution of Dess-Martin reagent (1.39 g, 3.27 mmol) in anhydrous CH₂Cl₂ (10 mL) was added dropwise of **9** (1.1 g, 2.18 mmol) prediluted in CH₂Cl₂ (5 mL) at 0 °C. The reaction mixture was stirred under nitrogen at 0 °C for 3h. After completion, the reaction mixture was diluted with ether and poured slowly into a Na₂S₂O₃ : NaHCO₃ (1:1) solution and stirred for 10 minutes and extract with ether. The combine etherate layer was washed with NaHCO₃, brine and dried over anhydrous MgSO₄. Solvent was removed by concentration in *vacuo*. The residue was purified by flash chromatography on silica gel to provide **10** (0.99 g, (90%)) as a colorless oil.

R_f 0.85 (hexane/ethyl acetate; 4:1);

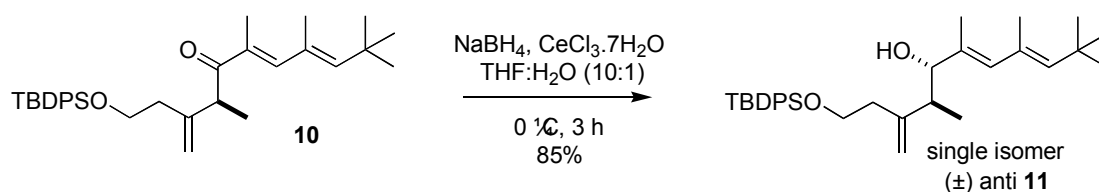
¹H NMR (300 MHz, CDCl₃): δ 1.04 (9H, s, -C(CH₃)₃), 1.16 (9H, s, -C(CH₃)₃), 1.19 (3H, d, *J* = 6.96 Hz, -CH-CH₃), 1.87 (3H, d, *J* = 1.05 Hz, -C-CH₃), 1.88 (3H, d, *J* = 1.41 Hz, -C-CH₃), 2.23 (1H, dt, *J* = 14.64, 6.96 Hz, -CH₂CH₂OTBDPS), 2.34 (1H, dt, *J* = 14.64, 6.96 Hz, -CH₂CH₂OTBDPS), 3.77 (2H, t, *J* = 6.96 Hz, -CH₂OTBDPS), 3.89 (1H, q, *J* = 6.96 Hz, -CH-CH₃), 4.87 (2H, s, -C=CH₂), 5.52 (1H, s, -C=CH-), 6.92 (1H, s, -C=CH-), 7.35-7.45 (6H, m, -Ph-H), 7.65-7.68 (4H, m, -Ph-H) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 13.5 (-CH₃), 17.0 (-CH₃), 17.5 (-CH₃), 19.2 (-C(CH₃)₃), 26.9 (-C(CH₃)₃), 30.7 (-C(CH₃)₃), 33.1 (-C(CH₃)₃), 37.6 (-CH₂CH₂OTBDPS), 46.8 (-CH-CH₃), 63.1 (-CH₂OTBDPS), 112.8 (-C=CH₂), 127.7 (-Ph-C x4), 129.6 (-Ph-C x2), 131.0 (-C=CH-), 133.9 (-Ph-C_q x2), 134.0 (-C=CH-), 135.6 (-Ph-C x4), 144.8 (-C=CH-), 145.3 (-C=CH-), 146.8 (-C=CH₂), 203.5 (-C=O) ppm;

IR (neat, cm⁻¹): 3067, 3051, 2958, 2930, 2858, 1736, 1586, 1429;

HRMS (EI) m/z [M-(C₄H₉)]⁺: obsd 445.2549, calcd 445.2563 for C₂₉H₃₇SiO₂.

***Anti*-(6*E*,8*E*)-1-(*tert*-butyldiphenylsilyloxy)-4,6,8,10,10-pentamethyl-3-methyleneundeca-6,8-dien-5-ol (**11**)**



To a solution of **10** (1.1 g, 2.2 mmol) in THF:H₂O (10:1) (10 mL) was added in CeCl₃·7H₂O (1.64 g, 4.4 mmol) at 0 °C. After the mixture was stirred at 0 °C for 15 minutes, NaBH₄ (0.16 g, 4.4 mmol) was added and the reaction was stirred for 3 h. After the reaction was completed (monitored by TLC), THF was removed under *vacuo*. H₂O was added in and the mixture was extracted with ether. The combined etherate layer was washed with brine, dried over MgSO₄, concentrated and purified through flash chromatography on silica gel to afford *anti* **11** (0.94 g, 85%) as a colorless oil. (*anti:syn* > 99:1)

R_f 0.78 (hexane/ethyl acetate, 4:1);

¹H NMR (500 MHz, CDCl₃): δ 0.83 (3H, d, *J* = 6.95 Hz, -CH-CH₃), 1.05 (9H, s, -C(CH₃)₃), 1.15 (9H, s, -C(CH₃)₃), 1.72 (3H, d, *J* = 1.4 Hz, -C-CH₃), 1.82 (3H, d, *J* = 1.4 Hz, -C-CH₃), 2.23-2.30 (2H, m, -CH₂-C-), 2.33 (1H, dq, *J* = 9.70, 6.95 Hz, -CH-CH₃), 3.74 (1H, d, *J* = 9.70 Hz, -CH-OH), 3.77-3.86 (2H, m, -CH₂OTBDPS), 4.94 (1H, s, -C=CH-), 5.01 (1H, s, -C=CH₂), 5.32 (1H, s, -C=CH₂-), 5.81 (1H, s, -C=CH-), 7.37-7.43 (6H, m, -Ph-H), 7.68-7.70 (4H, m, -Ph-H) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 12.0 (-CH₃), 16.9 (-CH₃), 18.0 (-CH₃), 19.2 (-C(CH₃)₃), 26.9 (-C(CH₃)₃), 31.0 (-C(CH₃)₃), 32.6 (-C(CH₃)₃), 36.2 (-CH₂CH₂OTBDPS), 44.9 (-CH-CH₃), 62.9 (-CH₂OTBDPS), 81.0 (-CHOH), 113.3 (-C=CH₂), 127.7 (-Ph-C x4), 129.7 (-Ph-C x2), 130.8 (-C=CH-), 133.8 (-C=CH-),

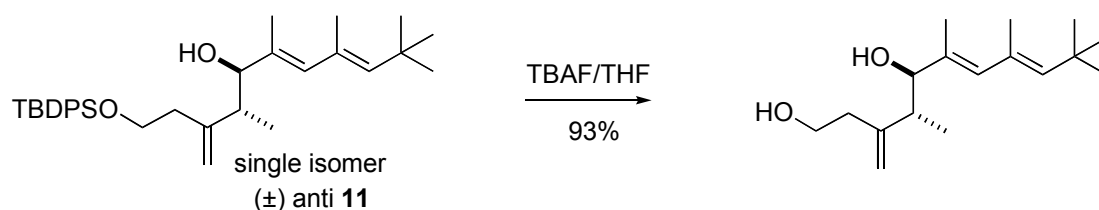
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133.9 (-Ph-Cq x2), 134.5 (-C=CH-), 135.6 (-Ph-C x4), 140.3 (-C=CH-), 148.6 (-C=CH₂) ppm;

IR (neat, cm⁻¹): 3426, 3073, 3051, 2960, 2931, 1639, 1462, 1428;

HRMS (EI) m/z (M⁺): obsd 504.3420, calcd 504.3424 for C₃₃H₄₈SiO₂.

***Anti*-(6*E*,8*E*)-4,6,8,10,10-pentamethyl-3-methyleneundeca-6,8-diene-1,5-diol**



Follow the standard desilylation procedure using TBAF in THF afforded *anti* diol as colourless oil in 93% yield.

R_f 0.39 (hexane/ethyl acetate, 2:1);

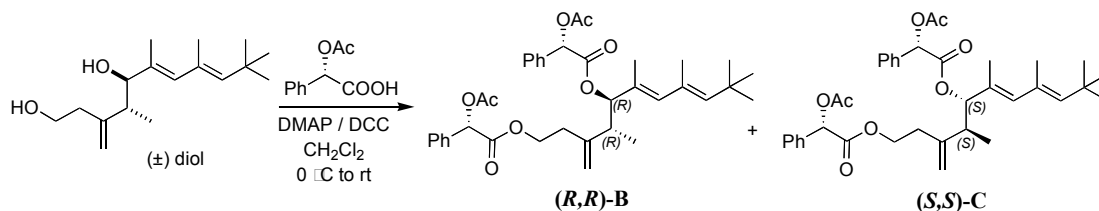
¹H NMR (300 MHz, CDCl₃): δ 0.85 (3H, d, *J* = 7.32 Hz, -CH-CH₃), 1.12 (9H, s, -C(CH₃)₃), 1.71 (3H, s, -C-CH₃), 1.79 (3H, s, -C-CH₃), 2.22-2.38 (2H, m, -CH₂-CH₂OH), 2.39 (1H, dq, *J* = 10.08, 7.32 Hz, -CH-CH₃), 2.51 (1H, brs, -OH), 3.00 (1H, brs, -OH), 3.69-3.80 (2H, m, -CH₂-OH), 3.83 (1H, d, *J* = 10.08 Hz, -CH-OH), 4.99 (1H, s, -C=CH₂-), 5.04 (1H, s, -C=CH₂), 5.29 (1H, s, -C=CH-), 5.81 (1H, s, -C=CH-) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 11.8 (-CH₃), 17.5 (-CH₃), 17.8 (-CH₃), 30.8 (-C(CH₃)₃), 32.5 (-C(CH₃)₃), 37.0 (-CH₂CH₂OH), 43.4 (-CHCH₃), 60.8 (-CH₂OH), 82.0 (-CHOH), 112.9 (-C=CH₂), 130.6 (-C=CH), 134.1 (-C=CH), 134.6 (-C=CH), 140.5 (-C=CH), 149.2 (-C=CH₂) ppm;

IR (neat, cm⁻¹): 3364, 2958, 2863, 2384, 2349, 1641, 1459, 1442;

HRMS (EI) m/z (M⁺): obsd 266.2244, calcd 266.2246 for C₁₇H₃₀O₂.

***Anti*-(1*S*,1'*S*)-2,2'-((4*R*,5*R*,6*E*,8*E*)-4,6,8,10,10-pentamethyl-3-methyleneundeca-6,8-diene-1,5-diyl)bis(oxy)bis(2-oxo-1-phenylethane-2,1-diyl) diacetate (*R,R*)-B and *Anti*-(1*S*,1'*S*)-2,2'-((4*S*,5*S*,6*E*,8*E*)-4,6,8,10,10-pentamethyl-3-methyleneundeca-6,8-diene-1,5-diyl)bis(oxy)bis(2-oxo-1-phenylethane-2,1-diyl) diacetate (*S,S*)-C**



To a mixture of *anti* (±)-diol (0.19 g, 0.71 mmol), *S*-(+)- α -acetoxyphenylacetic acid (0.42 g, 2.13 mmol) and DMAP (9 mg, 0.071 mmol) in dried CH_2Cl_2 (3 mL) was added in DCC (0.37 g, 1.77 mmol) prediluted in 1 mL CH_2Cl_2 dropwise at 0 °C. The reaction mixture was stirred at 0 °C to room temperature for 12h. After completion, CH_2Cl_2 was removed *via* rotary evaporator and the crude product was directly subjected to column chromatography. Purification by flash chromatography on silica gel (Hex: CH_2Cl_2 :EA, 3:3:0.2) afforded two pure enantiomer as colorless oil with 97% overall yield.

(*R,R*)-B

R_f 0.37 (hexane/ CH_2Cl_2 /ethyl acetate, 3:3:0.2);

$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 0.76 (3H, d, $J = 7.29$ Hz, -CH- CH_3), 1.14 (9H, s, -C(CH_3) $_3$), 1.70 (3H, d, $J = 1.05$ Hz, -C- CH_3), 1.78 (3H, d, $J = 1.05$ Hz, -C- CH_3), 2.13 (3H, s, -OAc), 2.19 (3H, s, -OAc), 2.23-2.40 (3H, m, - $\text{CH}_2\text{CH}_2\text{O}$ -, -CH- CH_3), 3.82 (1H, dt, $J = 10.44, 7.65$ Hz, - $\text{CH}_2\text{CH}_2\text{O}$ -), 3.97 (1H, dt, $J = 10.44, 7.32$ Hz, - $\text{CH}_2\text{CH}_2\text{O}$ -), 4.34 (1H, s, -C= CH_2 -), 4.57 (1H, s, -C= CH_2), 4.97 (1H, d, $J = 10.08$ Hz, -CH-O-), 5.27 (1H, s, -C= CH -), 5.85 (1H, s, -CH-OAc), 5.88 (1H, s, -CH-OAc), 5.89 (1H, s, -C= CH -), 7.26-7.28 (3H, m, -Ph-H), 7.35-7.40 (5H, m, -Ph-H), 7.45-7.47 (2H, m, -Ph-H) ppm;

$^{13}\text{C NMR}$ (75 MHz, CDCl_3): δ 12.8 (- CH_3), 16.8 (- CH_3), 17.7 (- CH_3), 20.6 (- CH_3), 30.8 (-C(CH_3) $_3$), 32.1 (- $\text{CH}_2\text{CH}_2\text{O}$ -), 32.5 (-C(CH_3) $_3$), 42.0 (-CH- CH_3), 63.9 (- CH_2O -), 74.4 (-CH-OAc), 74.5 (-CH-OAc), 84.1 (-CH-O-), 111.8 (-C= CH_2), 127.6 (-Ph-C $_m$ x2), 127.8 (-Ph-C $_m$ x2), 128.5 (-Ph-C $_o$ x2), 128.7 (-Ph-C $_o$ x2), 129.0 (-Ph-C $_p$), 129.1 (-Ph-C $_p$), 129.6 (-HC=C- CH_3), 130.4 (-HC=C- CH_3), 133.7 (-Ph-C $_q$), 134.1 (-Ph-C $_q$),

136.4 (-CH=C-CH₃), 140.8 (-CH=C-CH₃), 145.6 (-C=CH₂), 167.6 (C=O), 168.6 (C=O), 169.9 (C=O), 170.2 (C=O) ppm;

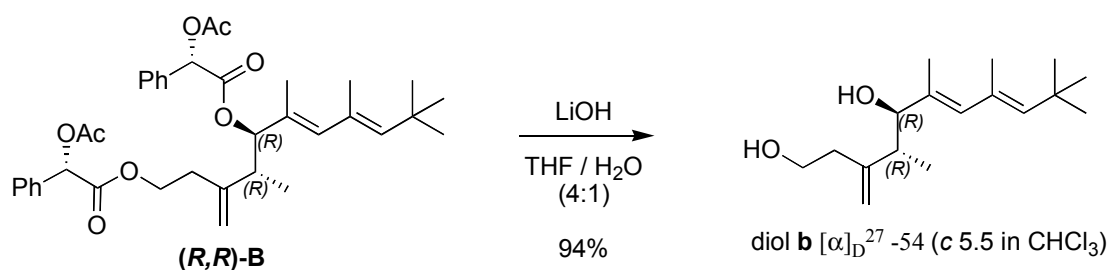
(S,S)-C

R_f 0.26 (hexane/CH₂Cl₂/ethyl acetate, 3:3:0.2);

¹H NMR (300 MHz, CDCl₃): δ 0.85 (3H, d, *J* = 7.32 Hz, -CH-CH₃), 1.12 (9H, s, -C(CH₃)₃), 1.36 (3H, d, *J* = 1.05 Hz, -C-CH₃), 1.68 (3H, d, *J* = 1.05 Hz, -C-CH₃), 2.16 (3H, s, -OAc), 2.20 (3H, s, -OAc), 2.40-2.71 (3H, m, -CH₂CH₂O-, -CH-CH₃), 4.21-4.30 (2H, m, -CH₂-O-), 4.75 (1H, s, -C=CH₂-), 4.88 (1H, s, -C=CH₂-), 5.02 (1H, d, *J* = 10.11 Hz, -CH-O-), 5.11 (1H, s, -C=CH-), 5.73 (1H, s, -C=CH-), 5.89 (1H, s, -CH-OAc), 5.96 (1H, s, -CH-OAc), 7.33-7.41 (6H, m, -Ph-H), 7.49-7.52 (4H, m, -Ph-H) ppm;

¹³C NMR (125 MHz, CDCl₃): δ 12.3 (-CH₃), 16.8 (-CH₃), 17.5 (-CH₃), 20.5 (-CH₃), 30.7 (-C(CH₃)₃), 32.4 (-C(CH₃)₃), 33.3 (-CH₂CH₂O-), 41.3 (-CH-CH₃), 63.9 (-CH₂O-), 74.2 (-CH-OAc), 74.4 (-CH-OAc), 84.3 (-CH-O-), 112.3 (-C=CH₂), 127.5 (-Ph-C_m x2), 127.6 (-Ph-C_m x2), 128.4 (-Ph-C_o x2), 128.6 (-Ph-C_o x2), 128.9 (-Ph-C_p), 129.0 (-Ph-C_p), 129.4, (-HC=C-CH₃), 130.2 (-HC=C-CH₃), 133.8 (-Ph-C_q), 133.9 (-Ph-C_q), 136.2 (-CH=C-CH₃), 140.5 (-CH=C-CH₃), 145.9 (-C=CH₂), 167.6 (C=O), 168.7 (C=O), 169.8 (C=O), 170.1 (C=O) ppm;

Anti-(4R,5R,6E,8E)-4,6,8,10,10-pentamethyl-3-methyleneundeca-6,8-diene-1,5-diol (b)



Follow the standard hydrolysis procedure, diol-**b** was obtained as a colourless oil in 94% yield.

R_f 0.39 (hexane/ethyl acetate, 2:1);

[α]_D²⁷ -54 (c 5.5 in CHCl₃);

¹H NMR (300 MHz, CDCl₃): δ 0.85 (3H, d, *J* = 7.32 Hz, -CH-CH₃), 1.12 (9H, s, -C(CH₃)₃), 1.71 (3H, s, -C-CH₃), 1.79 (3H, s, -C-CH₃), 2.22-2.38 (2H, m, -CH₂-

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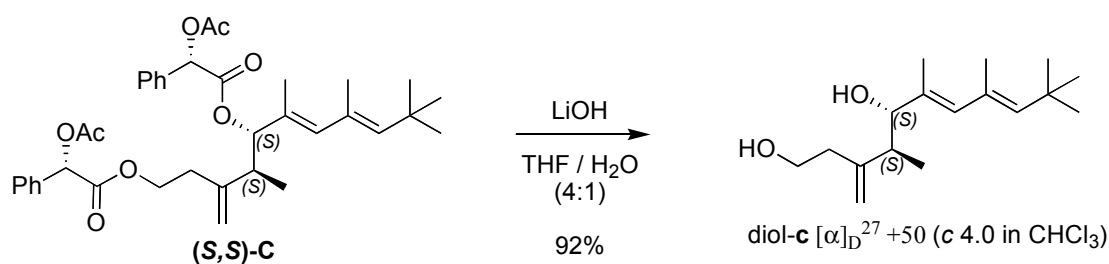
CH₂OH), 2.39 (1H, dq, $J = 10.08, 7.32$ Hz, -CH-CH₃), 2.51 (1H, brs, -OH), 3.00 (1H, brs, -OH), 3.69-3.80 (2H, m, -CH₂-OH), 3.83 (1H, d, $J = 10.08$ Hz, -CH-OH), 4.99 (1H, s, -C=CH₂-), 5.04 (1H, s, -C=CH₂), 5.29 (1H, s, -C=CH-), 5.81 (1H, s, -C=CH-) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 11.8 (-CH₃), 17.5 (-CH₃), 17.8 (-CH₃), 30.8 (-C(CH₃)₃), 32.5 (-C(CH₃)₃), 37.0 (-CH₂CH₂OH), 43.4 (-CHCH₃), 60.8 (-CH₂OH), 82.0 (-CHOH), 112.9 (-C=CH₂), 130.6 (-C=CH), 134.1 (-C=CH), 134.6 (-C=CH), 140.5 (-C=CH), 149.2 (-C=CH₂) ppm;

IR (neat, cm⁻¹): 3364, 2958, 2863, 2384, 2349, 1641, 1459, 1442;

HRMS (EI) m/z (M⁺): obsd 266.2244, calcd 266.2246 for C₁₇H₃₀O₂.

***Anti*-(4*S*,5*S*,6*E*,8*E*)-4,6,8,10,10-pentamethyl-3-methyleneundeca-6,8-diene-1,5-diol (c)**



Follow the standard hydrolysis procedure, diol-c was obtained as a colourless oil in 92% yield.

R_f 0.39 (hexane/ethyl acetate, 2:1);

$[\alpha]_D^{26} +50$ (c 4.0 in CHCl₃);

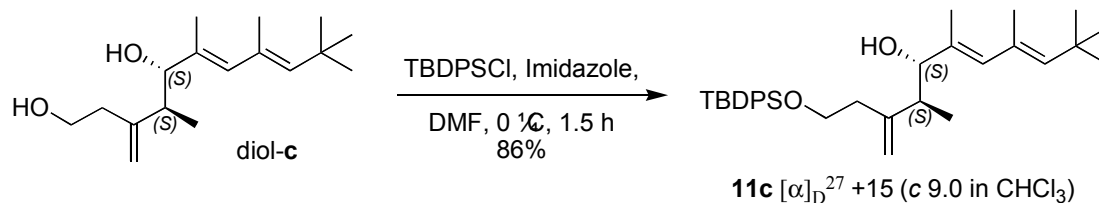
¹H NMR (300 MHz, CDCl₃): δ 0.85 (3H, d, $J = 7.32$ Hz, -CH-CH₃), 1.12 (9H, s, -C(CH₃)₃), 1.71 (3H, s, -C-CH₃), 1.79 (3H, s, -C-CH₃), 2.22-2.38 (2H, m, -CH₂-CH₂OH), 2.39 (1H, dq, $J = 10.08, 7.32$ Hz, -CH-CH₃), 2.51 (1H, brs, -OH), 3.00 (1H, brs, -OH), 3.69-3.80 (2H, m, -CH₂-OH), 3.83 (1H, d, $J = 10.08$ Hz, -CH-OH), 4.99 (1H, s, -C=CH₂-), 5.04 (1H, s, -C=CH₂), 5.29 (1H, s, -C=CH-), 5.81 (1H, s, -C=CH-) ppm;

¹³C NMR (75 MHz, CDCl₃): δ 11.8 (-CH₃), 17.5 (-CH₃), 17.8 (-CH₃), 30.8 (-C(CH₃)₃), 32.5 (-C(CH₃)₃), 37.0 (-CH₂CH₂OH), 43.4 (-CHCH₃), 60.8 (-CH₂OH), 82.0 (-CHOH), 112.9 (-C=CH₂), 130.6 (-C=CH), 134.1 (-C=CH), 134.6 (-C=CH), 140.5 (-C=CH), 149.2 (-C=CH₂) ppm;

IR (neat, cm⁻¹): 3364, 2958, 2863, 2384, 2349, 1641, 1459, 1442;

HRMS (EI) m/z (M^+): obsd 266.2244, calcd 266.2246 for $C_{17}H_{30}O_2$.

***Anti*-(4*S*,5*S*,6*E*,8*E*)-1-(*tert*-butyldiphenylsilyloxy)-4,6,8,10,10-pentamethyl-3-methyleneundeca-6,8-dien-5-ol (11c)**



Follow the standard TBDPS protection using TBDPSCl and imidazole in DMF, **11c** was obtained as a colourless oil in 86% yield.

R_f 0.78 (hexane/ethyl acetate, 4:1);

$[\alpha]_D^{27} +15$ (c 9.0 in $CHCl_3$);

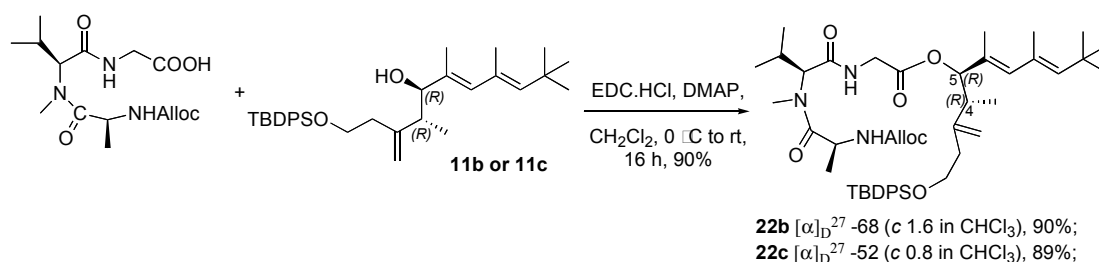
1H NMR (500 MHz, $CDCl_3$): δ 0.83 (3H, d, $J = 6.95$ Hz, -CH- CH_3), 1.05 (9H, s, -C(CH_3) $_3$), 1.15 (9H, s, -C(CH_3) $_3$), 1.72 (3H, d, $J = 1.4$ Hz, -C- CH_3), 1.82 (3H, d, $J = 1.4$ Hz, -C- CH_3), 2.23-2.30 (2H, m, - CH_2 -C-), 2.33 (1H, dq, $J = 9.70, 6.95$ Hz, -CH- CH_3), 3.74 (1H, d, $J = 9.70$ Hz, -CH-OH), 3.77-3.86 (2H, m, - CH_2 OTBDPS), 4.94 (1H, s, -C=CH-), 5.01 (1H, s, -C=CH $_2$), 5.32 (1H, s, -C=CH $_2$ -), 5.81 (1H, s, -C=CH-), 7.37-7.43 (6H, m, -Ph-H), 7.68-7.70 (4H, m, -Ph-H) ppm;

^{13}C NMR (75 MHz, $CDCl_3$): δ 12.0 (- CH_3), 16.9 (- CH_3), 18.0 (- CH_3), 19.2 (-C(CH_3) $_3$), 26.9 (-C(CH_3) $_3$), 31.0 (-C(CH_3) $_3$), 32.6 (-C(CH_3) $_3$), 36.2 (- CH_2CH_2 OTBDPS), 44.9 (-CH- CH_3), 62.9 (- CH_2 OTBDPS), 81.0 (-CHOH), 113.3 (-C=CH $_2$), 127.7 (-Ph-C x4), 129.7 (-Ph-C x2), 130.8 (-C=CH-), 133.8 (-C=CH-), 133.9 (-Ph-C q x2), 134.5 (-C=CH-), 135.6 (-Ph-C x4), 140.3 (-C=CH-), 148.6 (-C=CH $_2$) ppm;

IR (neat, cm^{-1}): 3426, 3073, 3051, 2960, 2931, 1639, 1462, 1428;

HRMS (EI) m/z (M^+): obsd 504.3420, calcd 504.3424 for $C_{33}H_{48}SiO_2$.

(5*S*,8*S*)-((4*R*,5*R*,6*E*,8*E*)-1-(*tert*-butyldiphenylsilyloxy)-4,6,8,10,10-pentamethyl-3-methyleneundeca-6,8-dien-5-yl) 5-isopropyl-6,8-dimethyl-4,7,10-trioxo-11-oxa-3,6,9-triazatetradec-13-en-1-oate (**22b**) and (5*S*,8*S*)-((4*S*,5*S*,6*E*,8*E*)-1-(*tert*-butyldiphenylsilyloxy)-4,6,8,10,10-pentamethyl-3-methyleneundeca-6,8-dien-5-yl) 5-isopropyl-6,8-dimethyl-4,7,10-trioxo-11-oxa-3,6,9-triazatetradec-13-en-1-oate (**22c**)



The *anti* homoallylic alcohol **11b** (0.8 g, 1.58 mmol) and tripeptide acid (1.36 g, 3.96 mmol) were dissolved in CH_2Cl_2 (3 ml), and EDC.HCl (0.76 g, 3.96 mmol) was added followed by the addition of DMAP (0.097 g, 0.79 mmol) at 0 °C. The mixture was stirred for 16 h at room temperature. After completion, monitored by TLC, the reaction mixture was diluted with ether. The combined organic layer was washed with 5% KHSO_4 , water, saturated NaHCO_3 , brine and finally dried over anhydrous MgSO_4 . After filtration, it was concentrated and purified by flash chromatography on silica gel to give **22b** (1.18 g, 90%) as a colorless oil.

22b

R_f 0.15 (hexane/ethyl acetate, 4:1);

$[\alpha]_{\text{D}}^{27}$ -68 (c 1.6 in CHCl_3);

$^1\text{H NMR}$ (500 MHz, CDCl_3): δ 0.82 (6H, dd, $J = 6.95, 0.9$ Hz, $\text{C}_{13}\text{-CH}_3$, Val- CH_3), 0.95 (3H, d, $J = 6.45$ Hz, Val- CH_3), 1.04 (9H, s, $-\text{C}(\text{CH}_3)_3$), 1.13 (9H, s, $-\text{C}(\text{CH}_3)_3$), 1.30 (3H, d, $J = 6.95$ Hz, Ala- CH_3), 1.65 (3H, d, $J = 1.4$ Hz, $\text{C}_{14}\text{-CH}_3$), 1.77 (3H, d, $J = 1.4$ Hz, $-\text{C}_{15}\text{-CH}_3$), 2.24 (1H, d, $J = 6.95$ Hz, $\text{C}_2\text{-H}$), 2.26 (1H, d, $J = 6.95$ Hz, $\text{C}_2\text{-H}$), 2.29 (1H, m, $\text{C}_4\text{-H}$), 2.44 (1H, m, Val- $(\text{CH}_3)_2\text{CH}$), 3.00 (3H, s, N- CH_3), 3.73 (3H, m, Gly- CH_2 , $-\text{CH}_2\text{-O-}$), 3.86 (1H, dd, $J = 18.27, 6.00$ Hz, Gly- CH_2), 4.54 (2H, d, $J = 5.1$ Hz, $\text{CH}_2=\text{CHCH}_2\text{-}$), 4.62 (1H, d, $J = 11.05$ Hz, Val- $\alpha\text{-H}$), 4.66 (1H, dq, $J = 7.85, 6.95$ Hz, Ala- $\alpha\text{-H}$), 4.77 (1H, s, $\text{C}_{12}\text{-H}$), 4.82 (1H, s, $\text{C}_{12}\text{-H}$), 5.02 (1H, d, $J = 10.2$ Hz, $\text{C}_5\text{-H}$), 5.19 (1H, dd, $J = 10.20, 1.35$ Hz, $\text{CH}_2=\text{CHCH}_2\text{-}$), 5.27 (1H, s, $\text{C}_9\text{-H}$), 5.28 (1H, dd, $J = 15.95, 1.40$ Hz, $\text{CH}_2=\text{CHCH}_2\text{-}$), 5.76 (1H, d, $J = 7.85$ Hz, Ala-NH), 5.86

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(1H, s, C₇-H), 5.90 (1H, m, CH₂=CHCH₂-), 6.56 (1H, brs, Gly-NH), 7.38 (6H, m, -Ph-H), 7.67 (4H, m, -Ph-H) ppm;

¹³C NMR (125 MHz, CDCl₃): δ 12.7 (-CH₃), 16.7 (-CH₃), 17.7 (-CH₃), 18.2 (-CH₃), 18.4 (-CH₃), 19.1 (-C(CH₃)₃), 19.5 (-CH₃), 25.4 (-CH-(CH₃)₂), 26.8 (-C(CH₃)₃), 30.3 (-N-CH₃), 30.8 (-C(CH₃)₃), 32.5 (-C(CH₃)₃), 37.5 (-CH₂-), 40.7 (-CH₂-), 42.0 (-CH-), 47.1 (-CH-), 62.5 (-N-CH-), 63.3 (-CH₂-O-), 65.5 (-CH₂-O-), 84.1 (-CH-O-), 111.8 (-C=CH₂), 117.5 (-CH=CH₂), 127.5 (-Ph-C x4), 129.5 (-Ph-C x2), 129.9 (-C=CH-), 130.3 (-C=CH-), 132.7 (-CH=CH₂), 133.8 (-Ph-C_q x2), 135.5 (-Ph-C x4), 136.4 (-CH=C-), 141.0 (-CH=C-), 147.6 (-C=CH₂-), 155.4 (-C=O), 168.2 (-C=O), 169.8 (-C=O), 173.9 (-C=O) ppm;

IR (neat, cm⁻¹): 3313, 3073, 2961, 1726, 1689, 1640, 1529, 1464, 1428;

HRMS (ESI) m/z (M⁺+Na): obsd 852.4972, calcd 852.4959 for C₄₈H₇₁NaN₃O₇Si.

22c

R_f 0.15 (hexane/ethyl acetate, 4:1);

[α]_D²⁷ -52 (c 0.8 in CHCl₃);

¹H NMR (500 MHz, CDCl₃): δ 0.82 (6H, d, J = 6.95 Hz, C₁₃-CH₃, Val-CH₃), 0.94 (3H, d, J = 6.50 Hz, Val-CH₃), 1.04 (9H, s, -C(CH₃)₃), 1.13 (9H, s, -C(CH₃)₃), 1.31 (3H, d, J = 6.95 Hz, Ala-CH₃), 1.65 (3H, d, J = 1.4 Hz, C₁₄-CH₃), 1.77 (3H, d, J = 0.9 Hz, -C₁₅-CH₃), 2.23 (1H, d, J = 6.9 Hz, C₂-H), 2.24 (1H, d, J = 6.95 Hz, C₂-H), 2.28 (1H, m, C₄-H), 2.43 (1H, m, Val-(CH₃)₂CH), 3.00 (3H, s, N-CH₃), 3.66 (1H, dd, J = 18.02, 4.65 Hz, Gly-CH₂), 3.74 (2H, m, -CH₂-O-), 3.94 (1H, dd, J = 18.02, 6.05 Hz, Gly-CH₂), 4.55 (2H, d, J = 5.1 Hz, CH₂=CHCH₂-), 4.61 (1H, d, J = 11.10 Hz, Val-α-H), 4.66 (1H, dq, J = 8.30, 6.95 Hz, Ala-α-H), 4.76 (1H, s, C₁₂-H), 4.81 (1H, s, C₁₂-H), 5.02 (1H, d, J = 10.15 Hz, C₅-H), 5.19 (1H, dd, J = 10.4, 1.4 Hz, CH₂=CHCH₂-), 5.27 (1H, s, C₉-H), 5.29 (1H, dd, J = 18.45, 1.85 Hz, CH₂=CHCH₂-), 5.72 (1H, d, J = 8.30 Hz, Ala-NH), 5.86 (1H, s, C₇-H), 5.90 (1H, m, CH₂=CHCH₂-), 6.46 (1H, brs, Gly-NH), 7.40 (6H, m, -Ph-H), 7.67 (4H, m, -Ph-H) ppm;

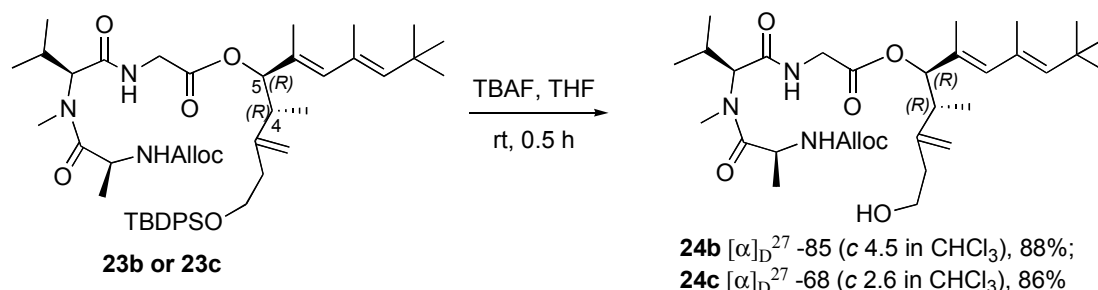
¹³C NMR (125 MHz, CDCl₃): δ 12.7 (-CH₃), 16.8 (-CH₃), 17.7 (-CH₃), 18.3 (-CH₃), 18.4 (-CH₃), 19.1 (-C(CH₃)₃), 19.6 (-CH₃), 25.4 (-CH-(CH₃)₂), 26.8 (-C(CH₃)₃), 30.4 (-N-CH₃), 30.9 (-C(CH₃)₃), 32.6 (-C(CH₃)₃), 37.4 (-CH₂-), 40.8 (-CH₂-), 42.1 (-CH-), 47.1 (-CH-), 62.5 (-N-CH-), 63.3 (-CH₂-O-), 65.6 (-CH₂-O-), 84.2 (-CH-O-), 111.7 (-C=CH₂), 117.5 (-CH=CH₂), 127.6 (-Ph-C x4), 129.6 (-Ph-C x2), 129.9 (-C=CH-),

130.4 (-C=CH-), 132.7 (-CH=CH₂), 133.9 (-Ph-C_q x2), 135.5 (-Ph-C x4), 136.5 (-CH=C-), 141.0 (-CH=C-), 147.8 (-C=CH₂-), 155.4 (-C=O), 168.3 (-C=O), 169.8 (-C=O), 173.9 (-C=O) ppm;

IR (neat, cm⁻¹): 3313, 3073, 2961, 1726, 1689, 1640, 1529, 1464, 1428;

HRMS (ESI) m/z (M⁺+Na): obsd 852.4972, calcd 852.4959 for C₄₈H₇₁NaN₃O₇Si.

(5*S*,8*S*)-((4*R*,5*R*,6*E*,8*E*)-1-hydroxy-4,6,8,10,10-pentamethyl-3-methyleneundeca-6,8-dien-5-yl) 5-isopropyl-6,8-dimethyl-4,7,10-trioxo-11-oxa-3,6,9-triazatetradec-13-en-1-oate (24b) and (5*S*,8*S*)-((4*S*,5*S*,6*E*,8*E*)-1-hydroxy-4,6,8,10,10-pentamethyl-3-methyleneundeca-6,8-dien-5-yl) 5-isopropyl-6,8-dimethyl-4,7,10-trioxo-11-oxa-3,6,9-triazatetradec-13-en-1-oate (24c)



To a solution of **23** (0.092 g, 0.11 mmol) in THF (0.5 mL) was added TBAF (0.22 mL, 1.0 M in THF, 0.22 mmol). The mixture was stirred for 30 minutes at room temperature. After the reaction was completed (monitored by TLC), the mixture was concentrated in *vacuo* to remove the THF. The residue was purified by flash chromatography on silica gel to afford **24** (0.057 g, 88%) as a colorless oil.

24b

R_f 0.20 (hexane/ethyl acetate, 1:1);

[α]_D²⁷ -85 (c 4.5 in CHCl₃);

¹H NMR (500 MHz, CDCl₃): δ 0.80 (3H, d, *J* = 6.50 Hz, Val-CH₃), 0.88 (3H, d, *J* = 6.95 Hz, C₁₃-CH₃), 0.92 (3H, d, *J* = 6.45 Hz, Val-CH₃), 1.10 (9H, s, -C(CH₃)₃), 1.31 (3H, d, *J* = 6.95 Hz, Ala-CH₃), 1.67 (3H, s, C₁₄-CH₃), 1.76 (3H, s, -C₁₅-CH₃), 2.24 (2H, t, *J* = 6.00 Hz, C₂-H), 2.22-2.29 (1H, m, Val-(CH₃)₂CH), 2.49 (1H, dq, *J* = 10.15, 6.95 Hz, C₄-H), 3.00 (3H, s, N-CH₃), 3.69-3.78 (3H, m, Gly-CH₂, -CH₂-OH), 3.98 (1H, dd, *J* = 17.83, 6.00 Hz, Gly-CH₂), 4.52 (2H, d, *J* = 5.10 Hz, CH₂=CHCH₂O-), 4.55 (1H, d, *J* = 11.10 Hz, Val- α -H), 4.65 (1H, dq, *J* = 8.35, 6.95 Hz, Ala- α -H), 4.88 (1H, s, C₁₂-H), 4.90 (1H, s, C₁₂-H), 5.10 (1H, d, *J* = 10.15 Hz, C₅-H), 5.17 (1H, d, *J* = 10.15 Hz, CH₂=CHCH₂O-), 5.26 (1H, s, C₉-H), 5.27 (1H, d, *J* =

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12.00 Hz, CH₂=CHCH₂O-), 5.72 (1H, d, *J* = 8.35 Hz, Ala-NH), 5.88 (1H, s, C₇-H), 5.84-5.92 (1H, m, CH₂=CHCH₂O-), 6.83 (1H, broad t, *J* = 5.05 Hz, Gly-NH) ppm;

¹³C NMR (125 MHz, CDCl₃): δ 12.5 (-CH₃), 16.9 (-CH₃), 17.7 (-CH₃), 18.2 (-CH₃), 18.3 (-CH₃), 19.5 (-CH₃), 25.4 (-CH-(CH₃)₂), 30.4 (-N-CH₃), 30.8 (-C(CH₃)₃), 32.5 (-C(CH₃)₃), 37.0 (-CH₂-CH₂OH), 41.1 (NH-CH₂-), 42.0 (-CH-CH₃), 47.2 (-NH-CH-CH₃), 60.2 (-CH₂-O-), 62.6 (-N-CH-CH(CH₃)₂), 65.6 (-CH₂-O-), 83.9 (-CH-O-), 111.8 (-C=CH₂), 117.6 (-CH=CH₂), 129.7 (-C=CH-), 130.3 (-C=CH-), 132.7 (-CH=CH₂), 136.8 (-CH=C-), 141.1 (-CH=C-), 147.4 (-C=CH₂-), 155.4 (-C=O), 168.3 (-C=O), 170.1 (-C=O), 174.1 (-C=O) ppm;

IR (neat, cm⁻¹): 3320, 3073, 2961, 1727, 1641, 1523, 1464;

HRMS (ESI) m/z (M⁺+Na): obsd 614.3765, calcd 614. 3781 for C₃₂H₅₃NaN₃O₇.

24c

R_f 0.20 (hexane/ethyl acetate, 1:1);

[α]_D²⁷ -68 (*c* 2.6 in CHCl₃);

¹H NMR (500 MHz, CDCl₃): δ 0.81 (3H, d, *J* = 6.50 Hz, Val-CH₃), 0.90 (3H, d, *J* = 6.95 Hz, C₁₃-CH₃), 0.95 (3H, d, *J* = 6.45 Hz, Val-CH₃), 1.12 (9H, s, -C(CH₃)₃), 1.29 (3H, d, *J* = 6.95 Hz, Ala-CH₃), 1.67 (3H, s, C₁₄-CH₃), 1.77 (3H, s, -C₁₅-CH₃), 2.23-2.31 (3H, m, C₂-H, Val-(CH₃)₂CH), 2.50 (1H, dq, *J* = 10.65, 6.95 Hz, C₄-H), 3.02 (3H, s, N-CH₃), 3.71-3.80 (3H, m, Gly-CH₂, -CH₂-OH), 4.04 (1H, dd, *J* = 17.55, 6.45 Hz, Gly-CH₂), 4.53 (2H, d, *J* = 6.90 Hz, CH₂=CHCH₂O-), 4.54 (1H, d, *J* = 10.60 Hz, Val-α-H), 4.64 (1H, dq, *J* = 8.30, 6.95 Hz, Ala-α-H), 4.89 (1H, s, C₁₂-H), 4.91 (1H, s, C₁₂-H), 5.13 (1H, d, *J* = 10.65 Hz, C₅-H), 5.19 (1H, d, *J* = 10.65 Hz, CH₂=CHCH₂O-), 5.27 (1H, s, C₉-H), 5.28 (1H, dd, *J* = 17.25, 1.35 Hz, CH₂=CHCH₂O-), 5.68 (1H, d, *J* = 8.30 Hz, Ala-NH), 5.85-5.90 (1H, m, CH₂=CHCH₂O-), 5.92 (1H, s, C₇-H), 7.14 (1H, broad t, *J* = 5.05 Hz, Gly-NH) ppm;

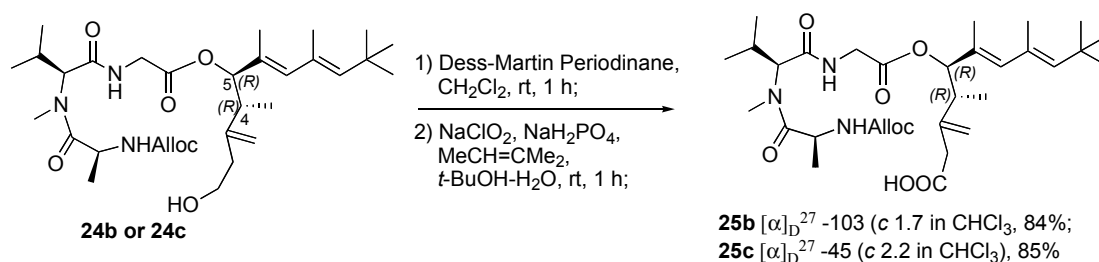
¹³C NMR (125 MHz, CDCl₃): δ 12.5 (-CH₃), 17.3 (-CH₃), 17.7 (-CH₃), 18.3 (-CH₃), 18.4 (-CH₃), 19.5 (-CH₃), 25.6 (-CH-(CH₃)₂), 30.5 (-N-CH₃), 30.8 (-C(CH₃)₃), 32.6 (-C(CH₃)₃), 37.5 (-CH₂-CH₂OH), 41.1 (NH-CH₂-), 41.4 (-CH-CH₃), 47.1 (-NH-CH-CH₃), 59.7 (-CH₂-O-), 62.7 (-N-CH-CH(CH₃)₂), 65.6 (-CH₂-O-), 84.1 (-CH-O-), 111.6 (-C=CH₂), 117.6 (-CH=CH₂), 129.6 (-C=CH-), 130.3 (-C=CH-), 132.7 (-CH=CH₂), 136.9 (-CH=C-), 141.2 (-CH=C-), 147.5 (-C=CH₂-), 155.4 (-C=O), 168.3 (-C=O), 169.6 (-C=O), 174.1 (-C=O) ppm;

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IR (neat, cm^{-1}): 3320, 3073, 2961, 1727, 1641, 1523, 1464;

HRMS (ESI) m/z ($M^+ + \text{Na}$): obsd 614.3765, calcd 614.3781 for $\text{C}_{32}\text{H}_{53}\text{NaN}_3\text{O}_7$.

(7*S*,10*S*,16*R*,17*R*)-10-isopropyl-7,9,17-trimethyl-18-methylene-5,8,11,14-tetraoxo-16-((2*E*,4*E*)-4,6,6-trimethylhepta-2,4-dien-2-yl)-4,15-dioxa-6,9,12-triazaicos-1-en-20-oic acid (**25b**) and (7*S*,10*S*,16*S*,17*S*)-10-isopropyl-7,9,17-trimethyl-18-methylene-5,8,11,14-tetraoxo-16-((2*E*,4*E*)-4,6,6-trimethylhepta-2,4-dien-2-yl)-4,15-dioxa-6,9,12-triazaicos-1-en-20-oic acid (**25c**)



Dess-Martin periodinane oxidation: To a solution of Dess-Martin reagent (48 mg, 0.114 mmol) in anhydrous CH_2Cl_2 (1 mL) was added dropwise of **24b** in CH_2Cl_2 at 0 °C. The reaction mixture was stirred under nitrogen at 0 °C for 2h. After completion, the reaction mixture was diluted with ether and poured slowly into a $\text{Na}_2\text{S}_2\text{O}_3:\text{NaHCO}_3$ (1:1) solution and stirred for 5 minutes and extract with ether. The combine etherate layer was washed with NaHCO_3 , brine and dried over anhydrous MgSO_4 . Concentration in *vacuo* provided the aldehyde and directly used for next step without purification.

The crude aldehyde was dissolved in a mixture of *t*-BuOH and 2-methyl-2-butene (3:1, 9 mL), and pH=4 NaH_2PO_4 water solution (3 mL) was added, followed by NaClO_2 (9.3 mg, 0.084 mmol). The mixture was stirred at room temperature for half an hour, pour into ice-water and extracted with ethyl acetate (3x). The combine organic layer was washed with brine, dried over MgSO_4 and concentrated. Purification through flash column chromatography provided **25b** (38.6 mg, 84%) as a colorless oil.

25b

R_f 0.02 (hexane/ethyl acetate, 1:1);

$[\alpha]_{\text{D}}^{27} -103$ (c 1.7 in CHCl_3);

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¹H NMR (500 MHz, CDCl₃): δ 0.83 (3H, d, *J* = 6.95 Hz, Val-CH₃), 0.93 (3H, d, *J* = 7.4 Hz, C₁₃-CH₃), 0.94 (3H, d, *J* = 6.45 Hz, Val-CH₃), 1.12 (9H, s, -C(CH₃)₃), 1.30 (3H, d, *J* = 6.95 Hz, Ala-CH₃), 1.60 (3H, d, *J* = 1.4 Hz, C₁₄-CH₃), 1.77 (3H, d, *J* = 1.35 Hz, C₁₅-CH₃), 2.27 (1H, m, C₄-H), 2.65 (1H, m, Val-(CH₃)₂CH), 3.13 (3H, s, N-CH₃), 3.61 (1H, dd, *J* = 17.35, 3.70 Hz, Gly-CH₂), 4.32 (1H, dd, *J* = 18.05, 7.85 Hz, Gly-CH₂), 4.54 (2H, d, *J* = 4.65 Hz, CH₂=CHCH₂-), 4.71 (1H, d, *J* = 11.55 Hz, Val-α-H), 4.71 (1H, m, Ala-α-H), 5.03 (1H, s, C₁₂-H), 5.07 (1H, s, C₁₂-H), 5.10 (1H, d, *J* = 11.1 Hz, C₅-H), 5.20 (1H, d, *J* = 10.15 Hz, CH₂=CHCH₂-), 5.27 (1H, d, *J* = 0.95 Hz, C₉-H), 5.30 (1H, dd, *J* = 9, 1.4 Hz, CH₂=CHCH₂-), 5.60 (1H, d, *J* = 7.85 Hz, Ala-NH), 5.88 (1H, m, CH₂=CHCH₂-), 5.93 (1H, s, C₇-H), 7.19 (1H, brs, *J* = 4.65 Hz, Gly-NH) ppm;

¹³C NMR (125 MHz, CDCl₃): δ 12.4 (-CH₃), 17.7 (-CH₃), 18.1 (-CH₃), 18.5 (-CH₃), 19.3 (-CH₃), 26.1 (-CH-(CH₃)₂), 26.3 (-CH₃), 30.8 (-C(CH₃)₃), 30.9 (-CH₃), 32.6 (-C(CH₃)₃), 40.2 (-CH₂-), 41.3 (-CH-), 42.2 (-CH₂-), 47.2 (-CH-), 62.8 (-CH-), 65.7 (-CH₂-O-), 84.2 (-CH-O-), 114.8 (-C=CH₂), 117.8 (-CH=CH₂), 129.3 (-C=CH-), 130.3 (-C=CH-), 132.6 (-CH=CH₂), 137.3 (-CH=C-), 141.3 (-CH=C-), 144.3 (-C=CH₂-), 155.5 (-C=O), 167.9 (-C=O), 169.9 (-C=O), 174.5 (-C=O), 174.6 (-C=O) ppm;

IR (neat, cm⁻¹): 3317, 3086, 2965, 2877, 1722, 1634, 1538, 1455, 1413;

HRMS (ESI) m/z (M⁺+Na): obsd 628.3562, calcd 628.3574 for C₃₂H₅₁NaN₃O₈.

25c

R_f 0.02 (hexane/ethyl acetate, 1:1);

[α]_D²⁷ -45 (*c* 2.2 in CHCl₃);

¹H NMR (500 MHz, CDCl₃): δ 0.83 (3H, d, *J* = 6.9 Hz, Val-CH₃), 0.92 (3H, d, *J* = 6.9 Hz, C₁₃-CH₃), 0.97 (3H, d, *J* = 6 Hz, Val-CH₃), 1.12 (9H, s, -C(CH₃)₃), 1.33 (3H, d, *J* = 6.45 Hz, Ala-CH₃), 1.66 (3H, d, *J* = 1.4 Hz, C₁₄-CH₃), 1.78 (3H, d, *J* = 0.95 Hz, C₁₅-CH₃), 2.29 (1H, m, C₄-H), 2.65 (1H, m, Val-(CH₃)₂CH), 3.07 (3H, s, N-CH₃), 3.78 (1H, dd, *J* = 16.88, 4.6 Hz, Gly-CH₂), 4.11 (1H, dd, *J* = 18.05, 6.45 Hz, Gly-CH₂), 4.55 (2H, d, *J* = 4.65 Hz, CH₂=CHCH₂-), 4.66 (1H, d, *J* = 11.1 Hz, Val-α-H), 4.69 (1H, m, Ala-α-H), 5.04 (1H, s, C₁₂-H), 5.07 (1H, s, C₁₂-H), 5.12 (1H, d, *J* = 10.65 Hz, C₅-H), 5.20 (1H, dd, *J* = 10.63, 1.4 Hz, CH₂=CHCH₂-), 5.28 (1H, d, *J* = 1.35 Hz, C₉-H), 5.28 (1H, m, CH₂=CHCH₂-), 5.61 (1H, d, *J* = 7.4 Hz, Ala-NH), 5.88

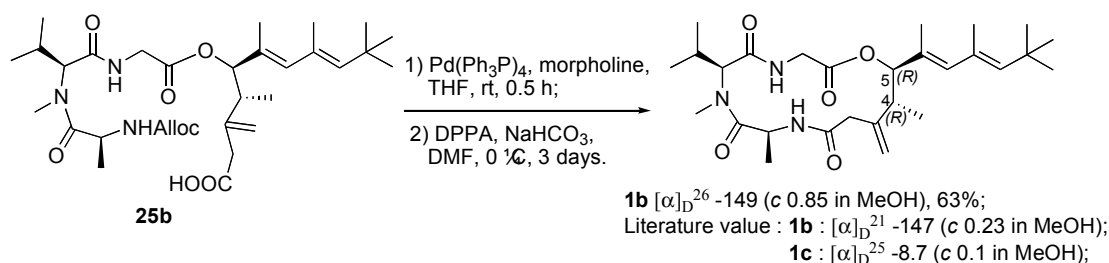
(1H, m, CH₂=CHCH₂-), 5.93 (1H, s, C₇-H), 6.97 (1H, brt, *J* = 5.05 Hz, Gly-NH) ppm;

¹³C NMR (125 MHz, CDCl₃): δ 12.4 (-CH₃), 17.9 (-CH₃), 18.4 (-CH₃), 19.5 (-CH₃), 19.6 (-CH₃), 25.8 (-CH-(CH₃)₂), 25.9 (-CH₃), 30.8 (-C(CH₃)₃), 30.9 (-CH₃), 32.6 (-C(CH₃)₃), 40.8 (-CH₂-), 41.4 (-CH₂-), 41.4 (-CH-), 47.2 (-CH-), 63.0 (-CH-), 65.7 (-CH₂-O-), 83.8 (-CH-O-), 115.1 (-C=CH₂), 117.7 (-CH=CH₂), 129.4 (-C=CH-), 130.4 (-C=CH-), 132.6 (-CH=CH₂), 137.1 (-CH=C-), 141.3 (-CH=C-), 144.0 (-C=CH₂-), 155.5 (-C=O), 167.8 (-C=O), 169.5 (-C=O), 174.1 (-C=O), 174.7 (-C=O) ppm;

IR (neat, cm⁻¹): 3317, 3086, 2965, 2877, 1722, 1634, 1538, 1455, 1413;

HRMS (ESI) *m/z* (M⁺+Na): obsd 628.3562, calcd 628.3574 for C₃₂H₅₁NaN₃O₈.

(4*R*,5*R*)-antillatoxin (1b)



To a solution of the acid **25b** (78 mg, 0.128 mmol) in 1 mL THF was added morpholine (0.11 mL, 1.28 mmol) and Pd(PPh₃)₄ (15 mg, 0.015 mmol). After stirring for 30 min at room temperature, the mixture was diluted with pH=6 buffer solution and extracted with CHCl₃ (x3). The combine organic extract was dried (Na₂SO₄), filtered and concentrated to afford the crude amino acid.

The crude amino acid was dissolved in DMF (50 mL) and cooled to 0 °C. NaHCO₃ (50 mg, 0.706 mmol) and DPPA (72 μL, 0.321 mmol) were added, the mixture solution was stirred at 0 °C for 3 days. The solution was diluted with ethyl acetate, wash with KHSO₄ solution, H₂O, NaHCO₃ and brine. The organic layer was dried (Na₂SO₄), filtered and concentrated. The crude product was purified by flash chromatography on silica gel (Hexane/ethyl acetate, 5:1 to 2:1) to give the desired product **1b** (40.7 mg, 63%) as a colorless oil.

(4*R*, 5*R*)-antillatoxin (1b)

R_f 0.62 (hexane/ethyl acetate, 1:1);

[α]_D²⁶ -149 (c 0.85 in MeOH);

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¹H NMR (500 MHz, CDCl₃): δ 0.85 (3H, d, *J* = 6.95 Hz, Val-CH₃), 0.86 (3H, d, *J* = 7.4 Hz, C₁₃-CH₃), 0.96 (3H, d, *J* = 6.05 Hz, Val-CH₃), 1.11 (9H, s, -C(CH₃)₃), 1.40 (3H, d, *J* = 6.5 Hz, Ala-CH₃), 1.54 (3H, d, *J* = 1.4 Hz, C₁₄-CH₃), 1.77 (3H, d, *J* = 1.4 Hz, C₁₅-CH₃), 2.17 (1H, m, C₄-H), 2.42 (1H, m, Val-(CH₃)₂CH), 2.83 (1H, d, *J* = 13.4 Hz, C₂-H), 2.85 (3H, s, N-CH₃), 2.97 (1H, d, *J* = 12.95 Hz, C₂-H), 3.47 (1H, dd, *J* = 18.28, 1.4 Hz, Gly-CH₂), 4.25 (1H, d, *J* = 11.05 Hz, Val-α-H), 4.67 (1H, dd, *J* = 18.28, 9.92 Hz, Gly-CH₂), 4.99 (1H, s, C₁₂-H), 5.04 (1H, s, C₁₂-H), 5.16 (1H, d, *J* = 11.1 Hz, C₅-H), 5.28 (1H, s, C₉-H), 5.33 (1H, m, Ala-α-H), 5.92 (1H, s, C₇-H), 6.76 (1H, d, *J* = 9.25 Hz, Ala-NH), 7.96 (1H, d, *J* = 9.25 Hz, Gly-NH) ppm;

¹³C NMR (125 MHz, CDCl₃): δ 12.4 (-CH₃), 17.7 (-CH₃), 18.5 (-CH₃), 18.6 (-CH₃), 18.9 (-CH₃), 19.3 (-CH₃), 26.1 (-CH(CH₃)₂), 28.7 (-CH₃), 30.8 (-C(CH₃)₃), 32.6 (-C(CH₃)₃), 38.9 (-CH-), 41.1 (-CH₂-), 43.0 (-CH-), 46.5 (-CH₂-), 67.1 (-CH-), 83.4 (-CH-O-), 113.7 (-C=CH₂), 129.1 (-C=CH-), 130.4 (-C=CH-), 137.2 (-CH=C-), 141.4 (-CH=C-), 144.8 (-C=CH₂-), 167.6 (-C=O), 167.8 (-C=O), 171.0 (-C=O), 173.1 (-C=O) ppm;

IR (neat, cm⁻¹): 3304, 1744, 1682, 1622, 1547;

HRMS (ESI) m/z [(M+Na)⁺]: obsd 526.3258, calcd 526.3257 for C₂₈H₄₅N₃O₅Na.

(4*S*, 5*S*)-antillatoxin (1c)

[α]_D²⁵ -8.7 (*c* 0.1 in MeOH);

¹H NMR (CDCl₃, 500 MHz): δ 0.85 (3H, d, *J* = 7.0 Hz, Val-CH₃), 0.90 (3H, d, *J* = 7.0 Hz, C₁₃-CH₃), 0.95 (3H, m, Val-CH₃), 0.99 (1H, d, *J* = 6.7 Hz, C₄-H), 1.14 (9H, s, -C(CH₃)₃), 1.38 (3H, d, *J* = 6.7 Hz, Ala-CH₃), 1.78 (3H, s, C₁₄-CH₃), 1.88 (3H, s, C₁₅-CH₃), 2.40 (1H, m, Val-(CH₃)₂CH), 2.86 (3H, s, N-CH₃), 3.00 (1H, m, C₂-H), 3.15 (1H, m, C₂-H), 3.94 (1H, dd, *J* = 10.4, 7.3 Hz, Gly-CH₂), 4.03 (1H, dd, *J* = 17.4, 4.6 Hz, Val-α-H), 4.52 (1H, d, *J* = 11.3 Hz, Gly-CH₂), 4.89 (1H, s, C₁₂-H), 4.93 (1H, s, C₉-H), 5.21 (2H, m, C₅-H, C₁₂-H), 5.32 (1H, m, Ala-α-H), 6.01 (1H, s, C₇-H), 6.52 (1H, d, *J* = 10.1 Hz, Ala-NH), 7.54 (1H, br, Gly-NH) ppm.

¹³C NMR (125 MHz, CDCl₃): δ 12.9 (-CH₃), 17.8 (-CH₃), 18.3 (-CH₃), 18.5 (-CH₃), 19.3 (-CH₃), 26.5 (-CH₃), 29.1 (-CH-(CH₃)₂), 29.7 (-CH₃), 30.9 (-C(CH₃)₃), 34.2 (-C(CH₃)₃), 40.6 (-CH-), 42.9 (-CH₂-), 43.2 (-CH-), 43.5 (-CH₂-), 65.9 (-CH-), 83.7 (-CH-O-), 105.3 (-C=CH₂), 129.4 (-C=CH-), 130.4 (-CH=C-), 136.8 (-C=CH-), 141.3

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(-CH=C-), 146.0 (-C=CH₂-), 166.4 (-C=O), 168.2 (-C=O), 171.6 (-C=O), 172.7 (-C=O) ppm.

IR (neat, cm⁻¹): 3304, 1744, 1682, 1622, 1547;

HRMS (ESI) m/z [(M+Na)⁺]: obsd 526.3258, calcd 526.3257 for C₂₈H₄₅N₃O₅Na.