SUPPORTING INFORMATION

Concise Synthesis of (S,S)-(+)-Dehydrohomoancepsenolide

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General. All reactions were carried out under Ar in pre-dried glassware using Schlenk techniques. The solvents were dried by distillation over the drying agents indicated and were stored and transferred under Ar: CH_2Cl_2 (P_4O_{10}), toluene (Na/K), Et_2O, THF (magnesium/anthracene), EtOH (Mg). Flash chromatography: Merck silica gel (230-400 mesh). Mp: Gallenkamp apparatus (uncorrected). NMR: Spectra were recorded on a Bruker DPX 300 spectrometer in the solvent indicated. Chemical shifts (δ) are given in ppm relative to TMS, coupling constants (*J*) in Hz. The multiplicity in the ^{13}C NMR spectra refers to the geminal protons (DEPT). IR: Nicolet FT-7199, wavenumbers in cm^{-1}. MS: Finnigan MAT 8200 (70 eV); HRMS: Finnigan MAT SSQ 7000 (70 eV). Elemental analyses: Dornis & Kolbe, Mülheim. Commercially available reagents (Aldrich, Fluka) were used as received.

2-(Bromomethyl)acrylic acid (*S*)-1-methylallylester (*S*-6). A solution of PPh_3 (1.78 g, 6.6 mmol) and (*R*)-1-buten-3-ol (*R*)-**4** (0.86 mL, 10 mmol, er ≥ 97:3) in Et_2O (10 mL) was slowly added to a solution of diethyl azodicarboxylate (DEAD, 0.95 mL, 6.6 mmol) and 2-(bromomethyl)acrylic acid **5** (1.10 g, 6.6 mmol) in Et_2O (10 mL) at 0 °C

After stirring for 16 hours at ambient temperature, the precipitated solids were filtered off through a pad of silica and the filtrate was evaporated. Flash chromatography (hexane/EtOAc, 10:1) of the crude product afforded ester (*S*)-**6** as a colorless liquid (1.00 g, 71%); $[\alpha]_D^{20}$ = + 5.5° (c = 0.5; $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.32 (s, 1H), 5.93 (s, 1H), 5.85 (ddd, 1H, *J* = 16.8, 10.0, 6.5 Hz), 5.45 (quin, 1H, *J* = 6,5 Hz), 5.27 (d, 1H, *J* = 16.8 Hz), 5.15 (d, 1H, *J* = 10.0 Hz), 4.17 (s, 1H), 1.36 (d, 3H, *J* = 6.5 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 163.9 (C), 137.7 (C), 137.2 (CH), 128.9 (CH_2), 116.0 (CH_2), 72.0 (CH), 29.3 (CH_2), 19.8 (CH_3); IR (neat): 3089, 2983, 1724, 1632, 1350, 1307, 1223, 1187, 990, 931 cm^{-1}; MS (EI) *m/z* (rel. intensity): 220 ([M^+], < 1), 149 (72), 147 (74), 139 (23), 121 (17), 119 (18), 111 (11), 93 (28), 71 (11), 55 (100), 54 (27), 53 (12), 42 (14), 40 (26), 39 (61), 29 (22), 27 (24); $C_8H_{11}O_2Br$ (218.90) *calcd*: C, 43.86; H, 5.06; *found*: C, 43.70; H, 5.20.

2-Methylene-undec-9-ynoic acid (*S*)-1-methylallylester (9). A stirred suspension of zinc dust (1.63 g, 25.0 mmol) and 1,2-dibromoethane (107 μL, 5 mol%) in THF (25 mL) was heated to 60 °C for 1 min. The mixture was allowed to cool to ambient temperature prior to addition of TMSCl (77 μl, 3 mol%) and stirring for another 15 min. A solution of 1,5-diiodopentane **7** (930 μL, 6.3 mmol) in THF (5 mL) was then slowly introduced to the suspension of the activated zinc and the mixture was stirred at 40°C for 24 h. Remaining solids were allowed to settle at room temperature and the supernatant liquid was transferred via cannula into a cooled (–60°C) solution of CuCN (0.535 g, 6.2 mmol) and LiCl (0.529 g, 12.5 mmol) in THF (20 mL). The resulting yellow-green mixture turned blue while stirring for another 15 min at 0°C. The reaction mixture was again cooled to –78 °C and 1-iodo-1-propyne (0.35 g, 2.1 mmol) dissolved in THF (3 mL) was introduced. After stirring for 15 h at – 35 °C, a solution of ester **(*S*)-6** (2.00 g, 9.4 mmol) in THF (3 mL) was added at – 78°C and the mixture was kept for 1h at ambient temperature. For work-up, the resulting blue suspension was diluted with ether (100 mL) and washed with sat. aq. NH_4Cl (100 mL). The aqueous phase was extracted with ether (3 x 50 mL), the combined organic layers were

dried (Na_2SO_4), filtered and evaporated. Flash chromatography (hexane/EtOAc, 50:1) of the crude material afforded compound **9** as a colorless liquid (754 mg, 70%). $[\alpha]_D^{20}$ = + 14.2° (c = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.11 (d, 1H, *J* = 1.4 Hz), 5.85 (ddd, 1H, *J* = 17.1, 10.5, 5.8 Hz), 5.48 (t, 1H, *J* = 1.4 Hz), 5.38 (tquin., 1H, *J* = 5.8, 1.4 Hz), 5.23 (dt, 1H, *J* = 17.1, 1.4 Hz), 5.11 (dt, 1H, *J* = 10.5, 1.4 Hz), 2.27 (t, 2H, *J* = 7.0 Hz), 2.09 (tq, 2H, *J* = 6.8, 2.5 Hz), 1.75 (t, 3H, *J* = 2.5 Hz), 1.58 – 1,34 (m, 8H), 1.32 (d, 3H, *J* = 6.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5 (C), 141.2 (C), 137.7 (CH), 124.3 (CH_2), 115.6 (CH_2), 79.3 (C), 75.4 (C), 71.1 (CH), 31.8 (CH_2), 28.9 (CH_2), 28.7 (CH_2), 28.6 (CH_2), 28.3 (CH_2), 19.9 (CH_3), 18.7 (CH_2), 3.4 (CH_3); IR (neat): 3089, 2980, 2932, 1717, 1631, 1449, 1373, 1274, 1170, 1140, 1048, 990, 937 cm^{-1}; MS (EI) *m/z* (rel. intensity): 248 ([M^+], < 1), 147 (14), 121 (18), 109 (13), 108 (14), 107 (31), 105 (16), 95 (21), 93 (42), 91 (18), 81 (32), 79 (31), 69 (14), 68 (24), 67 (35), 55 (100), 53 (26), 43 (14), 41 (31), 39 (19), 29 (19), 27 (14). HR-MS *calcd*: 248.17763; *found*: 248.17780.

5-(*S*)-(Methyl)-3-(non-7-ynyl)-(5*H*)-furan-2-one (11). Solutions of substrate **9** (450 mg, 1.89 mmol) and the ruthenium complex $(PCy_3)_2Cl_2Ru$=CHPh **10** (265 mg, 16 mol%) in CH_2Cl_2 (50 mL each) were added over a period of ca. 8 h via two dropping funnels to refluxing CH_2Cl_2 (900 mL). After 24 hours reaction time, the solvent was evaporated and the residue was purified by flash chromatography (pentane/Et_2O, 10:1) affording product **11** as a pale yellow liquid (291 mg, 70 %). $[\alpha]_D^{20}$ = + 18.5° (c = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.95 (q, 1H, *J* = 1.5 Hz), 4.95 (qq, 1H, *J* = 6.7, 1.7 Hz), 2.22 (t, 2H, *J* = 7.5 Hz), 2.08 (qt, 2H, *J* = 6.7, 2.5 Hz), 1.72 (t, 3H, *J* = 2.5 Hz), 1.54 – 1.20 (m, 11H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.8 (C), 149.0 (CH), 134.1 (C), 79.1 (C), 77.4 (CH), 75.4 (C), 28.8 (CH_2), 28.6 (CH_2), 28.4 (CH_2), 27.2 (CH_2), 25.0 (CH_2), 19.1 (CH_3), 18.6 (CH_2), 3.4 (CH_3); IR (neat): 3078, 2979, 2932, 1755, 1653, 1449, 1319, 1119, 1101, 1084, 1066, 1026 cm^{-1}; MS (EI) *m/z* (rel. intensity): 220 ([M^+], 3), 191 (15), 175 (19), 165 (11), 153 (44), 147 (14), 133 (18), 121 (15), 119 (24), 112 (41), 111 (16), 109 (55), 108 (30), 107 (39), 105 (26), 95 (35),

94 (16), 91 (33), 81 (46), 80 (18), 79 (75), 77 (25), 68 (62), 67 (100), 66 (17), 65 (17), 55 (52), 54 (20), 53 (55), 43 (71), 41 (76), 39 (45), 29 (22), 27 (35). HR-MS *calcd*: 220.14633; *found*: 220.14626.

1,14-Bis-[5-(*S*)-methyl-(5*H*)-furan-2-on-3-yl]-tetradec-7-yne (13). A solution of (tBuO)$_3$W≡CCMe$_3$ **12** (46 mg, 10 mol%) in toluene (10 mL) was added to a solution of compound **11** (204 mg, 0.977 mmol) in toluene (80 mL). The resulting mixture was heated at 100 °C for 21 h. The solvent was removed *in vacuo* and the residue was purified by flash chromatography (hexane/EtOAc, 4:1) delivering product **13** as a colorless syrup (146 mg, 75 %). $[\alpha]_D^{20}$ = + 37.5° (c = 1.0, $CHCl_3$); ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.97 (q, 2H, J = 1.7 Hz), 4.97 (qq, 2H, J = 6.8, 1.7 Hz), 2.24 (tt, 4H, J = 7.3, 1.5 Hz), 2.11 (t, 4H, J = 6.8 Hz), 1.60 – 1.31 (m, 22H); ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.8 (C), 149.0 (CH), 134.1 (C), 80.1 (C), 77.4 (CH), 28.9 (CH_2), 28.7 (CH_2), 28.4 (CH_2), 27.3 (CH_2), 25.1 (CH_2), 19.2 (CH_3), 18.7 (CH_2); IR (neat): 3081, 2980, 2932, 1753, 1653, 1454, 1373, 1319, 1101, 1084, 1026 cm^{-1}; MS (EI) m/z (rel. intensity): 386 ([M^+], 29), 368 (35), 340 (11), 275 (16), 234 (13), 220 (27), 205 (12), 201 (21), 191 (19), 187 (26), 177 (20), 175 (21), 173 (27), 167 (29), 161 (20), 159 (26), 153 (23), 147 (32), 145 (24), 139 (16), 135 (21), 133 (34), 123 (24), 121 (39), 119 (32), 112 (32), 111 (20), 109 (42), 108 (24), 107 (49), 105 (35), 95 (65), 94 (25), 93 (68), 91 (48), 81 (78), 90 (24), 79 (83), 77 (28), 67 (100), 55 (60), 53 (25), 43 (82), 41 (61); HR-MS *calcd*: 386.24570; *found*: 386.24543.

(1,14-Bis-[5-(*S*)-methyl-(5*H*)-furan-2-on-3-yl]-tetradec-7-ene (3). Quinoline (95 µL of a stock solution [40 µL quinoline in 20 mL hexane]) and alkyne **13** (25 mg, 0.064 mmol) were dissolved in hexane/EtOH (5 mL, 1:1). Commercially available Lindlar catalyst (13 mg, 10 mol%) was added and the resulting suspension was stirred for 10 min under an atmosphere of H_2 (1 atm). The catalyst was filtered off through a pad of Celite, the solvent was evaporated and the residue was purified by flash chromatography (hexane/EtOAc, 2:1) to afford dehydrohomoancepsenolide (**3**) as a

colorless solid (24 mg, 94%). Mp = 99-100°C; $[\alpha]_D^{20}$ = + 27.2° (c = 1.0; $CHCl_3$) [ref.[7]: $[\alpha]_D^{25}$ = + 29.7° (c = 2.1, $CHCl_3$)]; ^{1}H NMR (300 MHz, CD_2Cl_2): δ 6.96 (q, 2H, *J* = 1.4 Hz), 5.33 (m, 2H), 4.97 (dq, 2H, *J* = 6.7, 1.2 Hz), 2.24 (t, 4H, *J* = 7.8), 1.97 (m, 4H), 1.52 (m, 4H), 1.37 (d, 6H, *J* = 6.8 Hz), 1.30 (m, 12H); ^{13}C NMR (75 MHz, CD_2Cl_2): δ 173.9 (C), 148.9 (CH), 134.3 (C), 129.8 (CH), 77.2 (CH), 29.6 (CH_2), 29.1 (CH_2), 28.9 (CH_2), 27.4 (CH_2), 27.1 (CH_2), 25.2 (CH_2), 19.2 (CH_3); IR (KBr): 3076, 2978, 2920, 2851, 1747, 1652, 1463, 1374, 1321, 1120, 1085, 1028, 759 cm^{-1}; MS (EI) *m/z* (rel. intensity): 388 ([M^+], 100), 370 (56), 345 (13), 342 (14), 277 (10), 195 (10), 189 (27), 175 (41), 161 (31), 149 (22), 147 (25), 139 (17), 137 (16), 136 (22), 135 (32), 133 (22), 123 (25), 122 (22), 121 (35), 112 (30), 109 (37), 107 (32), 95 (56), 93 (43), 81 (70), 79 (44), 69 (38), 67 (95), 55 (79), 43 (91), 41 (67); $C_{24}H_{36}O_4$ (388.22) *calcd*: C, 74.19; H, 9.34; *found*: C, 74.28; H, 9.26.