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Supporting Information

Total Synthesis of Discodermolide: Optimization of the Effective Tactic

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(2*S*)-3-(4-Methoxybenzyloxy)-2-methyl propanal (15): *p*-Methoxybenzylalcohol (20.0 g, 144.7 mmol, 1.0 equiv) was added to a suspension of NaH (60 % in mineral oil, 0.58 g, 14.5 mmol, 0.1 equiv) in anhydrous diethyl ether (45 mL) over 30 min at 20 °C. The mixture was stirred for 1 h and cooled to 0 °C. Trichloroacetonitrile (23.0 g, 16 mL, 159.2 mmol, 1.1 equiv) was then introduced over 10 min. After 1.5 h the solution was concentrated *in vacuum*. The crude residue was treated with a mixture of pentane (150 mL) and methanol (0.6 mL), stirred at 20 °C for 30 min, and filtered through a pad of celite. Concentration gave the trichloroimidate (40.2 g, 98 % yield) as yellow oil which was used without further purification. A solution of commercial methyl (*S*)-(+)-3-hydroxy-2-methylpropionate **14** (13.9 g, 118 mmol, 1.0 equiv) and pyridinium *p*-toluene sulfonate (PPTS, 1.48 g, 5.9 mmol, 0.05 equiv) in an anhydrous mixture of CH_2Cl_2 (50 mL)/cyclohexane (100 mL) was cooled to 0 °C and treated with crude trichloroimidate (40.2 g, 142 mmol, 1.2 equiv) over 10 min. After 3 h, the mixture was warmed to 20 °C and stirred for 24 h. The solution was filtered through a pad of celite and the solvents were removed under reduced pressure. The crude (2*R*)-3-(4-methoxybenzyloxy)-2-methyl propionate was directly used in the next step without further purification. RN: 132969-71-2; $[\alpha]_D^{20}$ = + 8.3 (*c* = 1.57, $CHCl_3$); ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 7.26 (d, *J* = 8.7 Hz, 2H), 6.88 (d, *J* = 8.7 Hz, 2H), 4.50 (s, 2H), 3.80 (s, 3H), 3.70 (s, 3H), 3.65 (dd, *J* = 8.9, 7.3 Hz, 1H), 3.48 (dd, *J* = 8.9, 5.9 Hz, 1H), 2.79 (dqd, *J* = 7.3, 7.3, 5.9 Hz, 1H), 1.19 (d, *J* = 7.3 Hz, 3H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$) δ = 174.9 (C), 158.9 (C), 129.9 (2CH), 128.9 (C), 113.4 (2CH), 72.4 (CH_2), 71.3 (CH_2), 54.8 (CH_3), 51.3 (CH_3), 39.8 (CH), 13.6 (CH_3); MS: (GC, CI, CH_4): *m/z*: 267 (M^+ + 29), 237, 223, 207, 187, 161, 149, 137, 121, 101, 87; IR (Film) ν = 2939, 2858, 1741, 1729, 1612, 1513, 1462, 1364, 1302, 1248, 1200, 1175, 1089, 1034, 820 cm^{-1}.

A solution of the above ester compound (28.1 g, 118 mmol, 1.0 equiv) in anhydrous THF (50 mL) was added to a suspension of $LiAlH_4$ (5.0 g, 130 mmol, 1.1 equiv) in THF (110 mL) at 0 °C. The reaction mixture was stirred for 3 h at 20 °C then cooled to 0 °C and quenched by successive addition of water (5 mL), 15 % NaOH (5 mL), and then water (15 mL). The resulting mixture was filtered through a pad of celite then treated with $MgSO_4$, filtered, and the solvent was removed under reduced pressure. The residue was then purified by chromatography on silica gel (cyclohexane/ethyl acetate 80:20 to 50:50) to give 20.0 g (81 % yield over 2 steps) of (2*R*)-3-(4-methoxybenzyloxy) 2-methyl propanol. RN: 136320-64-4; $[\alpha]_D^{20}$ = + 14.6 (*c* = 0.87, $CHCl_3$); ^{1}H NMR (400.0 MHz, $CDCl_3$) δ = 7.26 (d, *J* = 8.6 Hz, 2H), 6.90 (d, *J* = 8.6 Hz, 2H), 4.47 (s, 2H), 3.82 (s, 3H), 3.62 (bd, *J* = 5.9 Hz, 2H), 3.54 (dd, *J* = 9.2, 5.0 Hz, 1H), 3.41 (dd, *J* = 9.2, 7.7 Hz, 1H), 2.64 (bs, 1H, OH), 2.07 (dqdd, *J* = 7.7, 6.9, 5.9, 5.0 Hz, 1H), 0.87 (d, *J* = 6.9 Hz, 3H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 159.2 (C), 130.0 (C), 129.2 (2CH), 113.8 (2CH), 75.3 (CH_2), 73.0 (CH_2), 68.0 (CH_2), 55.2 (CH_3), 35.5 (CH), 13.4 (CH_3); MS (GC, CI, CH_4): *m/z* 239: (M^+ + 29), 210, 201, 161, 149, 137, 121, 103, 91, 73, 55; IR (Film) ν = 3301, 2952, 2859, 1612, 1513, 1462, 1363, 1302, 1246, 1173, 1090, 1034, 819 cm^{-1}.

To a vigorously stirred solution of (2*R*)-3-(4-methoxybenzyloxy) 2-methyl propanol (6.0 g, 28.5 mmol, 1.0 equiv), $NaHCO_3$ (7.2 g, 86 mmol, 3 equiv), KBr (3.4 g, 28.5 mmol, 1.0 equiv) and TEMPO (90 mg, 0.57 mmol, 0.2 equiv) in CH_2Cl_2 (60 mL) / H_2O (30 mL) at 0 °C was added dropwise a solution of NaOCl 9.6 % (33 mL, 57 mmol, 1.9 equiv). The mixture was stirred for 10 min and then quenched with a solution of $Na_2S_2O_3$ 1M and extracted with diethyl ether. The organic layer was washed with water and brine, dried over $MgSO_4$ and the solvent removed under reduced pressure to give the title compound **15** as an orange oil (5.8 g, 98 % yield) which was used directly without further purification. **(15):** RN: 132969-60-9; ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 9.72 (d, *J* = 1.7 Hz, 1H), 7.25 (d, *J* = 8.6 Hz, 2H), 6.89 (d, *J* = 8.6 Hz, 2H), 4.47 (s, 2H), 3.82 (s, 3H), 3.65 (dd, *J* = 9.2, 6.4 Hz, 1H), 3.62 (dd, *J* = 9.2, 5.3 Hz, 1H), 2.66 (qddd, *J* = 7.3, 6.4, 5.3, 1.7 Hz, 1H), 1.13 (d, *J* = 7.3 Hz, 3H, CH_3).

(1*Z*,3*R*,4*R*,5S)-1-((*N*,*N*-Diisopropyl)carbamoyloxy)-3,5-dimethyl-4-hydroxy-6-(4-methoxybenzyloxy) hex-1-ene (16): To a quick stirred solution of (*E*)-crotyldiisopropylcarbamate (749 mg, 3.74 mmol, 2.0 equiv) and (-)-sparteine (885 mg, 3.74 mmol, 2.0 equiv) in pentane (5.0 mL) and cyclohexane (830 µL) at -78 °C, was added a solution of *n*BuLi (1.6 *M* in hexanes, 2.3 mL, 3.74 mmol, 2.0 equiv) and after 10 min white crystals appeared. After 3 h of crystallisation at -78 °C, a precooled (-40 °C) solution of titane tetraisopropoxide ($Ti(O^iPr)_4$, 3.4 mL, 11.2 mmol, 6.0 equiv) in pentane (2.0 mL) was quickly added via cannula to the reaction mixture of lithiocarbamate which became limpid and turn orange. After 1 h at -78 °C aldehyde **15** (390 mg, 1.87 mmol, 1.0 equiv) in pentane (1.5 mL) was slowly added to the orange solution. The reaction mixture was stirred for 3 h at -78 °C and quenched by addition of methanol (7.0 mL). The solution was poured into a mixture of diethyl ether-aqueous hydrochloric acid solution (0.5 N). After extraction with diethyl ether, the organic layer was washed with brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was purified by chromatography on silica gel (cyclohexane/diethyl ether 90:10 to 50:60) to give the desired compound **16** (598 mg) and its ***3,4-bis-epi diastereomer*** (19 mg) (85 % yield, selectivity 97:3). **(16):** ^{1}H NMR (270.0 MHz, $CDCl_3$): δ = 7.18 (d, *J* = 8.9 Hz, 2H), 7.05 (d, *J* = 6.6 Hz, 1H), 6.79 (d, *J* = 8.9 Hz, 2H), 4.63 (dd, *J* = 9.9, 6.6 Hz, 1H), 4.37 (s, 2H), 4.08 (bs, 1H), 3.73 (s, 3H, CH_3), 3.68 (bs, 1H), 3.54 (dd, *J* = 8.9, 6.2 Hz, 1H), 3.49 (dd, *J* = 9.2, 2.7 Hz, 1H), 3.45 (dd, *J* = 8.9, 5.7 Hz, 1H), 2.87 (ddq, *J* = 9.9, 9.2, 6.9 Hz, 1H), 2.28 (bs, 1H, OH), 2.00 (qddd, *J* = 6.9, 6.2, 5.7, 2.7 Hz, 1H), 1.30-1.10 (m, 12H, $4CH_3$), 0.90 (d, *J* = 6.9 Hz, 3H, CH_3), 0.87 (d, *J* = 6.9 Hz, 3H, CH_3); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 158.9 (C), 152.8 (C), 135.9 (CH), 130.3 (C), 129.0 (2CH), 113.6 (3CH), 75.7 (CH), 74.0 (CH_2), 72.7 (CH_2), 55.0 (CH_3), 46.8 (CH), 45.4 (CH), 35.1 (CH), 33.8 (CH), 21.4 ($2CH_3$), 20.2 ($2CH_3$), 17.2 (CH_3), 9.8 (CH_3); MS (GC, CI, CH_4): *m/z*: 407, 348, 319, 262, 199, 174, 137, 121. **(*3,4-bis-epi diastereomer of 16*):** ^{1}H NMR (270.0 MHz, $CDCl_3$) : δ = 7.20 (d, *J* = 8.9 Hz, 2H), 7.08 (d, *J* = 6.6 Hz, 1H), 6.79 (d, *J* = 8.9 Hz, 2H), 4.89 (dd, *J* = 9.5, 6.2 Hz, 1H), 4.39 (s, 2H), 4.10 (bs, 1H), 3.75 (s, 3H, CH_3), 3.73 (bs, 1H), 3.54 (m, 1H), 3.49 (m, 1H), 3.43 (dd, *J* = 8.9, 5.7 Hz, 1H), 2.90 (m, 1H), 2.25 (m, 1H), 2.21 (bs, 1H, OH), 1.21 (m, 12H, $4CH_3$), 1.10 (d, *J* = 6.9 Hz, 3H, CH_3), 0.80 (d, *J* = 6.9 Hz, 3H, CH_3).

(3*R*,4*R*,5*S*)-3,5-Dimethyl-6-(4-methoxybenzyloxy)-4-(triethylsilyloxy)-1-(trimethylsilyl) hex-1-yne (17): To a solution of carbamate **16** (3.0 g, 7.43 mmol, 1.0 equiv) in dried CH_2Cl_2 (65 mL) at 0 °C were added 2,6-lutidine (2.6 mL, 22.3 mmol, 3.0 equiv) and TESOTf (2.4 mL, 11.1 mmol, 1.5 equiv). After stirring for 2 h at 20 °C, the reaction was partitioned between diethyl ether and a saturated aqueous NH_4Cl solution and extracted with diethyl ether. The organic layer was washed with brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was purified by chromatography on silica gel (cyclohexane/diethyl ether 100:0 to 85:15) to give the **(**1*Z*,3*R*,4*R*,5*S*)-1-((*N*,*N*-diisopropyl)carbamoyloxy)-3,5-dimethyl-4-(triethylsilyloxy)-6-(4-methoxybenzyloxy) hex-1-ene (3.77 g, 97 % yield) as a yellow oil. ^{1}H NMR (270.0 MHz, $CDCl_3$): δ = 7.16 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 6.6 Hz, 1H), 6.79 (d, *J* = 8.6 Hz, 2H), 4.71 (dd, *J* = 9.9, 6.6 Hz, 1H), 4.32 (s, 2H), 4.01 (bs, 1H), 3.72 (s, 3H, CH_3), 3.68 (bs, 1H), 3.58 (dd, *J* = 4.8, 3.8 Hz, 1H), 3.33 (dd, *J* = 8.9, 6.3 Hz, 1H), 3.15 (dd, *J* = 8.9, 6.9 Hz, 1H), 2.78 (m, 1H), 1.86 (m, 1H), 1.25-1.10 (m, 12H, $4CH_3$), 0.91 (d, *J* = 7.9 Hz, 3H, CH_3), 0.86 (t, *J* = 7.6 Hz, 9H, $3CH_3$), 0.83 (d, *J* = 6.9 Hz, 3H, CH_3), 0.51 (q, *J* = 7.6 Hz, 6H, $3CH_2$); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 158.9 (C), 152.7 (C), 134.4 (CH), 130.5 (C), 128.9 (2CH), 113.5 (CH), 113.4 (2CH), 76.3 (CH), 72.8 (CH_2), 72.4 (CH_2), 54.9 (CH_3), 46.4 (CH), 45.4 (CH), 37.7 (CH), 34.2 (CH), 21.2 ($2CH_3$), 20.1 ($2CH_3$), 18.6 (CH_3), 11.8 (CH_3), 6.9 ($3CH_3$), 5.3 ($3CH_2$); MS (GC, CI, CH_4): *m/z*: 420, 313, 251, 193, 161, 128, 115; elemental analysis calcd (%) for $C_{29}H_{51}NO_5Si$: C 66.75, H 9.85, N 2.68; found: C 66.28, H 9.91, N 2.42.

To a solution of the preceding carbamate (3.77 g, 7.23 mmol, 1.0 equiv) in diethyl ether (80 mL) at -30 °C was added dropwise *t*BuLi (1.5 *M* in pentane, 9.5 mL, 14.3 mmol, 1.98 equiv). The resulting solution was stirred for 45 min between -25/-20 °C and then quenched by addition of a saturated aqueous NH_4Cl solution and extracted with diethyl ether. The organic layer was washed with brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was purified by chromatography on silica gel (cyclohexane/diethyl ether 90:10) to give the (3*R*,4*R*,5*S*)-3,5-dimethyl-6-(4-methoxybenzyloxy)-4-(triethylsilyloxy) hex-1-yne (2.3 g, 84 % yield) as a yellow oil. ^{1}H NMR (270.0 MHz, $CDCl_3$): δ = 7.17 (d, *J* = 8.2 Hz, 2H), 6.77 (d, *J* = 8.2 Hz, 2H), 4.33 (s, 2H), 3.70 (s, 3H, CH_3), 3.70-3.67 (m, 1H), 3.33 (dd, *J* = 8.9, 6.3 Hz, 1H), 3.20 (dd, *J* = 8.9, 6.3 Hz, 1H), 2.54-2.50 (m, 1H), 1.97-1.91 (m, 2H), 1.08 (d, *J* = 6.9 Hz, 3H, CH_3), 0.88 (t, *J* = 7.5 Hz, 9H, $3CH_3$), 0.81 (d, *J* = 6.9 Hz, 3H, CH_3), 0.57 (q, *J* = 7.5 Hz, 6H, $3CH_2$); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 159.0 (C), 130.6 (C), 129.2 (2CH), 113.6 (2CH), 87.5 (C), 75.0 (CH), 73.0 (CH_2), 72.5 (CH_2), 69.6 (CH), 55.1 (CH_3), 36.5 (CH), 31.4 (CH), 17.4 (CH_3), 11.3 (CH_3), 7.0 ($3CH_3$), 5.4 ($3CH_2$); MS (GC, CI, CH_4): *m/z*: 347 (M+29), 323, 227, 187, 173, 137, 121.

To a solution of the preceding alkyne (2.3 g, 6.11 mmol, 1.0 equiv) in THF at -78 °C was added *n*BuLi (1.6 *M* in hexane, 4.0 mL, 6.42 mmol, 1.05 equiv). After 10 min the bath was removed and the reaction mixture was stirred for 1 h at 0 °C. The solution was cooled to -78 °C and freshly distilled TMSCl was added (2.1

mL, 24.4 mmol, 4.0 equiv). The solution was warmed to 20 °C overnight. After addition of Et_3N (6.0 equiv) the mixture was partitioned between diethyl ether and a saturated aqueous NH_4Cl solution and extracted with diethyl ether. The organic layer was washed with brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was purified by chromatography on silica gel (cyclohexane/diethyl ether 100:0 to 90:10) to give protected alkyne **17** (2.54 g, 92 % yield). **(17):** ^{1}H NMR (270.0 MHz, $CDCl_3$): δ = 7.12 (d, *J* = 8.6 Hz, 2H), 6.74 (d, *J* = 8.6 Hz, 2H), 4.29 (2d, *J* = 11.5 Hz, 2H), 3.67 (s, 3H, CH_3), 3.63 (dd, *J* = 6.6, 3.0 Hz, 1H), 3.30 (dd, *J* = 9.2, 7.3 Hz, 1H), 3.12 (dd, *J* = 9.2, 6.6 Hz, 1H), 2.45 (quint, *J* = 6.6 Hz, 1H), 1.87 (ddd, *J* = 7.3, 7.2, 6.6 Hz, 1H), 0.99 (d, *J* = 7.2 Hz, 3H, CH_3), 0.83 (t, *J* = 7.2 Hz, 9H, $3CH_3$), 0.73 (d, *J* = 6.6 Hz, 3H, CH_3), 0.52 (q, *J* = 7.2 Hz, 6H, $3CH_2$), 0.00 (s, 9H, $3CH_3$); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 159.0 (C), 130.6 (C), 129.2 (2CH), 113.6 (2CH), 110.8 (C), 85.2 (C), 75.0 (CH), 73.0 (CH_2), 72.4 (CH_2), 55.1 (CH_3), 36.4 (CH), 32.5 (CH), 17.6 (CH_3), 10.9 (CH_3), 7.0 ($3CH_3$), 5.4 ($3CH_2$), 0.00 ($3CH_3$); MS (GC, EI): *m/z*: 449, 433, 341, 323, 269, 227, 187, 173, 137, 121.

(1*E*/*Z*,3*S*,4R,5*S*)-3,5-Dimethyl-1-methoxy-4-(triethylsilyloxy)-7-(trimethylsilyl) hept-6-yn-1-ene (18): At 0 °C, a solution of protected alcohol **17** (2.08 g, 4.64 mmol, 1.0 equiv) in CH_2Cl_2 (48 mL) was treated with water (2.4 mL) and DDQ (1.27 g, 5.57 mmol, 1.2 equiv). The mixture was stirred for 10 min at 0 °C, warmed to 20 °C and stirred an additional 30 min. The mixture was quenched with a saturated aqueous $NaHCO_3$ solution, diluted with CH_2Cl_2, washed with water and brine. The combined organic layers were dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was purified by chromatography on silica gel (cyclohexane/ethyl acetate 80:20) to give the **(**2*S*,3*R*,4*R*)-2,4-dimethyl-3-(triethylsilyloxy)-1-(trimethylsilyl) hex-5-yn-1-ol (1.31 g, 86 % yield). ^{1}H NMR (270.0 MHz, $CDCl_3$): δ = 3.58-3.49 (m, 3H), 2.53-2.48 (m, 1H), 1.90 (bs, 1H, OH), 1.79-1.70 (m, 1H), 1.03 (d, *J* = 7.3 Hz, 3H, CH_3), 0.83 (t, *J* = 7.6 Hz, 9H, $3CH_3$), 0.74 (d, *J* = 6.9 Hz, 3H, CH_3), 0.50 (q, *J* = 7.6 Hz, 6H, $3CH_2$), 0.00 (s, 9H, $3CH_3$); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 110.0 (C), 86.0 (C), 76.5 (CH), 65.3 (CH_2), 39.4 (CH), 31.5 (CH), 17.6 (CH_3), 12.4 (CH_3), 7.0 ($3CH_3$), 5.3 ($3CH_2$), 0.0 ($3CH_3$); MS (GC, EI): *m/z*: 327, 299, 269, 225, 203.

To a solution of IBX (2.72 g, 9.72 mmol, 2.2 equiv) in DMSO (35 mL) at 20 °C was added the preceding alcohol (1.45 g, 4.42 mmol, 1.0 equiv) in DMSO (10 mL). The mixture was stirred for 3 h, and then cooled to 0 °C. H_2O was added and the solution was filtered through a pad of celite and then extracted with diethyl ether (3X). The organic layer was washed with water, brine, dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude (2*S*,3*S*,4*S*)-2,4-dimethyl-3-(triethylsilyloxy)-6-(trimethylsilyl) hex-5-yn-1-al was used without further purification (1.31 g, 90 % yield). ^{1}H NMR (270.0 MHz, $CDCl_3$): δ = 9.71 (s, 1H), 3.96 (t, *J* = 5.0 Hz, 1H), 2.54 (qd, *J* = 6.9, 5.0 Hz, 1H), 2.43 (qd, *J* = 7.3, 5.0 Hz, 1H), 1.05 (d, *J* = 7.3 Hz, 3H, CH_3), 0.98 (d, *J* = 6.9 Hz, 3H, CH_3), 0.83 (t, *J* = 7.6 Hz, 9H, $3CH_3$), 0.50 (q, *J* = 7.6 Hz, 6H, $3CH_2$), 0.00 (s, 9H, $3CH_3$).

To a cooled (-10 °C) stirred suspension of (methoxymethyl)triphenylphosphonium chloride (3.14 g, 9.15 mmol, 2.3 equiv) in 30 mL of anhydrous THF was added 7.96 mL of lithium bis(trimethylsilyl)amide (1.0 *M* in THF, 7.96 mmol, 2.0 equiv) which became deep red. After 5 min aldehyde prepared before (1.31 g, 3.98 mmol, 1.0 equiv) in THF (5 mL, 5 mL rinse) was added via cannula. The resulting solution was kept at -10 °C for 1 h and then diluted with a saturated aqueous $NaHCO_3$ solution. After extraction with Et_2O and concentration of the organic layer, the residue was rapidly filtered through a pad of silice (cyclohexane/ethyl acetate 90:10) to remove most of the phosphine by-product and concentrated again. Olefin **18** was used without further purification in the lactonisation step (selectivity *Z*/*E* 4:6). **(18):** *Trans isomer*: ^{1}H NMR (270.0 MHz, $CDCl_3$): δ = 6.18 (d, *J* = 12.9 Hz, 1H), 4.53 (dd, *J* =12.9, 9.2 Hz, 1H), 3.43 (s, 3H, CH_3), 3.24 (dd, *J* = 5.9, 5.0 Hz, 1H), 2.50 (m, 1H), 2.20 (m, 1H), 1.02 (d, *J* = 6.9 Hz, 3H, CH_3), 0.85 (t, *J* = 7.9 Hz, 9H, $3CH_3$), 0.80 (d, *J* = 6.9 Hz, 3H, CH_3), 0.51 (q, *J* = 7.9 Hz, 6H, $3CH_2$), 0.00 (s, 9H, $3CH_3$). *Cis isomer*: ^{1}H NMR (270.0 MHz, $CDCl_3$): δ = 5.67 (d, *J* = 6.3 Hz, 1H), 4.20 (dd, *J* = 9.6, 6.3 Hz, 1H), 3.37 (s, 3H, CH_3), 3.36 (dd, *J* = 5.9, 5.3 Hz, 1H), 2.50 (m, 1H), 2.20 (m, 1H), 1.01 (d, *J* = 6.9 Hz, 3H, CH_3), 0.84 (t, *J* = 7.9 Hz, 9H, $3CH_3$), 0.80 (d, *J* = 6.9 Hz, 3H, CH_3), 0.51 (q, *J* = 7.9 Hz, 6H, $3CH_2$), 0.00 (s, 9H, $3CH_3$); MS (GC, EI): *m/z*: 354, 337, 309, 269, 229, 199, 175, 155, 139.

(2*R*/*S*,4*S*,5*R*(1*S*))-4-Methyl-5-(1-methyl-3-(trimethylsilyl)-prop-2-yn-1-yl) tetrahydrofuran-2-ol (19): Compound **18** was dissolved in acetone/water (9:1, 40 mL) and concentrated HCl (140 µL) was added. Then the solution was heated at 65 °C for 1 h, and the reaction was quenched by addition of a saturated aqueous $NaHCO_3$ solution and extracted with Et_2O. The organic layer was washed with water, brine, dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel (cyclohexane/Et_2O 80:20) to give 553 mg of lactol **19** (61 % yield from alcohol **17**). **(19):** ^{1}H NMR (270.0 MHz, $CDCl_3$): δ = 5.50 (d, *J* = 5.0 Hz, 1H), 3.89 (dd, *J* = 6.9, 4.6 Hz, 1H), 3.23 (bs, 1H, OH), 2.41 (m, 1H), 2.22 (m, 1H), 1.97 (m, 1H), 1.75 (m, 1H), 1.08 (d, *J* = 6.9 Hz, 3H, CH), 0.95 (d, *J* = 6.9 Hz, 3H, CH_3), 0.00 (s, 9H, $3CH_3$); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 109.4 (C), 98.3 (CH), 85.2 (C), 84.4 (CH), 41.2 (CH_2), 33.9 (CH), 28.6 (CH), 18.7 (CH_3), 13.5 (CH_3), 0.00 ($3CH_3$); MS (GC, EI): *m/z*: 208, 193, 173, 126, 117, 109, 87.

(2*R*/*S*,4*S*,5*R*(1*S*))-4-Methyl-5-(1-methyl-3-(trimethylsilyl)-prop-2-ynyl)-2-phenylsulfanyl tetrahydrofuran (20): To an ice-cold solution of lactol **19 (**553 mg, 2.44 mmol, 1.0 equiv) and thiophenol (290 µL, 2.78 mmol, 1.14 equiv) in anhydrous Et_2O (25 mL) containing activated 4Å molecular sieves, was added dropwise *via* syringe $BF_3.OEt_2$ (460 µL, 3.78 mmol, 1.55 equiv). After 1 h the reaction was quenched by the addition of a 4*N* NaOH solution and extracted with Et_2O. The organic layer was washed with water, brine, dried over $MgSO_4$ and concentrated. The residue was purified by chromatography on silica gel (cyclohexane/Et_2O 95:5) to give 622 mg of thio-product **20** (80 % yield). **(20):** ^{1}H NMR (270.0 MHz, $CDCl_3$): δ = 7.45 (dd, *J* = 7.9, 1.7 Hz, 2H), 7.13 (d, *J* = 1.7 Hz, 2H), 7.09 (d, *J* = 7.9 Hz, 1H), 5.51 (dd, *J* = 6.9, 5.0 Hz, 1H), 3.84 (dd, *J* = 7.6, 5.2 Hz, 1H), 2.46 (m, 1H), 2.18 (m, 2H), 2.02 (m, 1H), 1.05 (d, *J* = 7.3 Hz, 3H, CH_3), 0.81 (d, *J* = 6.9 Hz, 3H, CH_3), 0.00 (s, 9H, $3CH_3$); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 135.4 (C), 132.0 (2CH), 128.5 (2CH), 127.0 (CH), 109.0 (C), 86.2 (CH), 85.2 (C), 83.3 (CH), 40.8 (CH_2), 34.1 (CH), 27.7 (CH), 17.8 (CH_3), 13.6 (CH_3), 0.00 ($3CH_3$); MS (GC, EI): *m/z*: 318, 209, 193, 167, 151, 137, 121.

(4*R*,5*S*(1*S*))-4-Methyl-5-(1-methyl-3-(trimethylsilyl)-prop-2-ynyl)-2,3-dihydrofuran (21): a) To a solution of the thio-ether **20** (300 mg, 0.9 mmol) and DBU (160 µl, 1.05 mmol, 1.1 equiv) was rapidly heated (40 min) at 200 °C in a short distillation apparatus (Kugelrorh), then the mixture was distilled under vacuum (15 mmHg) at 200-240°C to furnish the title compound **21** (60 mg, 30% yield). b)To a solution of the thio-ether **20** (335 mg, 1.05 mmol, 1.0 equiv) in dry benzene (30 mL) containing $NaHCO_3$ (88 mg, 3.16 mmol, 3.0 equiv) was added at 0 °C *m*-CPBA (70-75 % purity, 310 mg, 1.26 mmol, 1.2 equiv) in benzene. After 1 h Et_3N (440 µL, 3.16 mmol, 3.0 equiv) the resulting sulfoxyde was added and the mixture was heated at reflux for 1 h then cooled to 20 °C. The solution was partitioned between a saturated aqueous $NaHCO_3$ solution and Et_2O. After extraction the organic layer was washed with water in order to remove most of the benzene, dried over $MgSO_4$ and concentrated carefully. The residue was distilled in a Kugelrohr apparatus (80-90 °C, 7.10^{-2} Torr) to give dihydrofuran **21 (**42 mg, 19 % yield). **(21):** ^{1}H NMR (270.0 MHz, $CDCl_3$): δ = 6.26 (dd, *J* = 2.6, 1.6 Hz, 1H), 4.91 (t, *J* = 2.6 Hz, 1H), 4.09 (t, *J* = 8.3 Hz, 1H), 2.78 (m, 2H), 1.19 (d, *J* = 7.3 Hz, 3H, CH_3), 0.92 (d, *J* = 6.6 Hz, 3H, CH_3), 0.00 (s, 9H, $3CH_3$); ^{13}C NMR (67.5 MHz, $CDCl_3$): δ = 144.8 (CH), 108.5 (C), 107.5 (CH), 86.4 (CH), 83.3 (C), 37.6 (CH), 27.5 (CH), 18.7 (CH_3), 14.0 (CH_3), 0.00 ($3CH_3$); MS (GC, EI): *m/z*: 208, 193, 126, 119, 109, 97, 83.

(3*S*,4*R*,5*S*,6*Z*)-3,5-Dimethyl-4-hydroxy-7-(tributylstannyl)-1-trimethylsilyl-oct-6-en-1-yne (22): To a suspension of CuCN (12 mg, 0.12 mmol, 2.0 equiv) in dry Et_2O (3 mL) at -30 °C was added MeLi (1.6 *M* solution in diethyl ether, 1.9 mL, 3.0 mmol, 5.0 equiv). The solution was stirred at -30 °C for 5 min and allowed to warm up to 0 °C for 20 min (pale yellow colour). To a solution of 2,3-dihydrofurane **21** (125 mg, 0.6 mmol, 1.0 equiv) in dry THF (3 mL) at -60 °C was added *t*BuLi (1.5 *M* solution in pentane, 0.45 mL, 0.7 mmol, 1.2 equiv). The mixture was stirred at 0 °C for 50 min. Then the solution of the lithio-dihydrofurane, prepared above, was diluted with 4 mL of THF and added via cannula to the cyanocuprate and the reaction mixture was heated to 35 °C for 3 h. The mixture was cooled at -30 °C and tri-*n*-butyltin chloride (0.85 mL, 3.0 mmol, 5.0 equiv) was added. The reaction mixture was allowed to warm up to 20 °C over 12 h. Finally the reaction mixture was poured into a mixture of a saturated aqueous NH_4Cl solution and concentrated ammonia (4:1) at 0 °C and stirred for 1 h at 20 °C before extraction with diethyl ether. The organic layer was washed with water, brine, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude residue was purified by chromatography on silica gel (cyclohexane/diethyl ether 100:0 to 50:50) to give the title compound **22** (48 mg, 20 % yield). **(22):** ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 5.87 (dq, *J* = 9.6, 1.8 Hz, $J_{^1H-^{117}Sn} = J_{^1H-^{119}Sn}$ = 135.0 Hz, 1H), 3.17 (ddd, *J* = 9.0, 7.5, 3.2 Hz, 1H), 2.73 (m, 1H), 2.32 (m, 1H), 1.90 (d, *J* = 2.0 Hz, $J_{^1H-^{117}Sn} = J_{^1H-^{119}Sn}$ = 41.0 Hz, 3H, CH_3), 1.74 (d, *J* = 9.0 Hz, 1H, OH), 1.53-1.42 (m, 6H, $3CH_2$), 1.34 (sext, *J* = 7.5 Hz, 6H,

$3CH_2$), 1.26 (d, J = 7.0 Hz, 3H, CH_3), 1.08 (d, J = 7.0 Hz, 3H, CH_3), 1.0-0.90 (m, 6H, $3CH_2$), 0.87 (t, J = 7.5 Hz, 9H, $3CH_3$), 0.00 (s, 9H, $3CH_3$); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 142.9 (CH, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 28.8 Hz), 138.1 (C), 109.0 (C), 85.0 (C), 78.0 (CH), 43.5 (CH, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 33.6 Hz), 30.2 (CH), 29.0 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 19.2 Hz), 27.1 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 58.7 Hz), 27.0 (CH_3, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 44.0 Hz), 18.4 (CH_3), 17.0 (CH_3), 13.4 ($3CH_3$), 9.7 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn}$ = 314.4 Hz, $J_{^{13}C\text{-}^{119}Sn}$ = 328.8 Hz), 0.00 ($3CH_3$).

(3*Z*)-4-(Tributylstannyl) pent-3-en-1-ol (12): To a suspension of CuCN (10.5 g, 120 mmol, 2.0 equiv) of in dry Et_2O (60 mL) at -30 °C was added MeLi (1.6 *M* solution in diethyl ether, 188 mL, 300 mmol, 5.0 equiv). The solution was stirred at -30 °C for 5 min and allowed to warm up to 0 °C for 20 min (pale yellow colour). To a solution of commercial 2,3-dihydrofurane **8** (4.6 g, 60 mmol, 1.0 equiv) in dry THF (60 mL) at -60 °C was added *t*BuLi (1.5 *M* solution in pentane, 48 mL, 72 mmol, 1.2 equiv). The mixture was stirred at 0 °C for 50 min. Then the solution of the lithio-dihydrofurane, prepared above, was diluted with 80 mL of THF and added via cannula to the cyanocuprate and the reaction mixture was heated to 35 °C for 3 h. The mixture was cooled at -30 °C and tri-*n*-butyltin chloride (49.1 mL, 181.2 mmol, 5.0 equiv) was added. The reaction mixture was allowed to warm up to 20 °C over 12 h. Finally the reaction mixture was poured into a mixture of a saturated aqueous NH_4Cl solution and concentrated ammonia (4:1) at 0 °C and stirred for 1 h at 20 °C before extraction with diethyl ether. The organic layer was washed with water, brine, dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude residue was purified by chromatography on silica gel (cyclohexane/diethyl ether 100:0 to 50:50) to give the title compound **12** (11.0 g, 49 % yield). **(12):** ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 6.05 (tq, J = 6.4, 1.4 Hz, $J_{^1H\text{-}^{117}Sn} = J_{^1H\text{-}^{119}Sn}$ = 128.7 Hz, 1H), 3.63 (q, J = 7.3 Hz, 2H), 2.25 (td, J = 7.3, 6.4 Hz, 2H), 1.92 (d, J = 1.4 Hz, $J_{^1H\text{-}^{117}Sn} = J_{^1H\text{-}^{119}Sn}$ = 41.7 Hz, 3H, CH_3), 1.50-1.42 (m, 7H, OH, $3CH_2$), 1.31 (sext, J = 7.3 Hz, 6H, $3CH_2$), 0.95-0.91 (m, 6H, $3CH_2$), 0.90 (t, J = 7.3 Hz, 9H, $3CH_3$); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 142.0 (C, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 377.6 Hz), 136.1 (CH, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 26.7 Hz), 62.3 (CH_2), 38.0 (CH_2, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 33.4 Hz), 29.3 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 19.3 Hz), 27.5 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 57.1 Hz), 27.0 (CH_3, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 46.0 Hz), 13.5 ($3CH_3$), 10.0 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn}$ = 314.4 Hz, $J_{^{13}C\text{-}^{119}Sn}$ = 328.0 Hz); MS (GC, CI, CH_4): *m/z*: 319 (M^+-57), 289, 261, 245, 233, 207, 177, 137, 121.

(*R*)-mandelic ester of 29:

(*R*)-mandelic ester of 31: *a) from pure carbamate **29**:* To a solution of compounds **29** (150 mg, 0.24 mmol, 1.0 equiv), obtained from optically pure aldehyde **28**, in CH_2Cl_2 (5 mL) at 20 °C were successively added (*R*)-(-)-methoxyphenylacetic acid (80 mg, 0.48 mmol, 2.0 equiv), DCC (100 mg, 0.48 mmol, 2.0 equiv) and DMAP (10 mg, 0.09 mmol, 0.4 equiv). The resulting mixture was stirred for 4 h at 20 °C then quenched with a saturated aqueous $NaHCO_3$ solution and extracted with Et_2O. The organic layers were washed with water and brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was purified by chromatography on silica gel (cyclohexane/$Et_2$0 85:15) to give 154 mg (84 % yield) of the title **(*R*)-mandelic ester of 29** compound. *b) from a mixture of carbamates **29** and **31:*** To a solution of compounds **29** and **31** (125 mg, 0.21 mmol, 1.0 equiv), obtained from racemic aldehyde **(+/-)-28**, in CH_2Cl_2 (5 mL) at 20 °C were successively added (*R*)-(-)-methoxyphenylacetic acid (71 mg, 0.43 mmol, 2.0 equiv), DCC (88 mg, 0.43 mmol, 2.0 equiv) and DMAP (5 mg, 0.08 mmol, 0.4 equiv). The resulting mixture was stirred for 4 h at 20 °C then quenched with a saturated aqueous $NaHCO_3$ solution and extracted with Et_2O. The organic layers were washed with water and brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was purified by chromatography on silica gel (cyclohexane/$Et_2$0 85:15) to give 85 mg (54 % yield) of the **(*R*)-mandelic ester of 29** and 14 mg of its 3,4-*bis epi* diastereomer (**(*R*)-mandelic ester of 31,** 9 % yield). **((*R*)-mandelic ester of 29):** $[\alpha]_D^{20}$ = + 42.1 (*c* = 1.4, $CHCl_3$); ^{1}H NMR (400.0 MHz, $CDCl_3$); δ = 7.46-7.42 (m, 2H), 7.38-7.22 (m, 3H), 6.82 (d, J = 6.4 Hz, 1H), 5.68 (dq, J = 9.6, 1.8 Hz, $J_{^1H\text{-}^{117}Sn} = J_{^1H\text{-}^{119}Sn}$ = 131.2 Hz, 1H), 4.83 (t, J = 6.0 Hz, 1H), 4.77 (s, 1H), 4.46 (dd, J = 9.6, 6.4 Hz, 1H), 4.17-4.03 (bs, 1H), 3.67-3.53 (bs, 1H), 3.43 (s, 3H, CH_3), 2.90 (dqd, J = 9.6, 6.9, 6.0 Hz, 1H), 2.23 (dqd, J = 9.6, 6.9, 6.0 Hz, 1H), 1.77 (d, J = 1.8 Hz, $J_{^1H\text{-}^{117}Sn} = J_{^1H\text{-}^{119}Sn}$ = 41.7 Hz, 3H, CH_3), 1.52-1.42 (m, 6H, $3CH_2$), 1.31 (sext, J = 7.3 Hz, 6H, $3CH_2$), 1.25-1.18 (m, 12H, $4CH_3$), 0.93-0.87 (m, 18H, $4CH_3$ + $3CH_2$), 0.71 (d, J = 6.9 Hz, 3H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 170.6 (C), 152.7 (C), 142.0 (CH, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 29.7 Hz), 139.1 (C, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 384.4 Hz), 136.7 (C), 135.6 (CH), 128.8 (2CH), 128.6 (2CH), 127.4 (CH), 110.8 (CH), 83.0 (CH), 80.6 (CH), 57.5 (CH_3), 47.1 (CH), 45.5 (CH), 40.8 (CH, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 30.7 Hz), 32.9 (CH), 29.3 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 20.1 Hz), 27.6 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 57.5 Hz), 27.2 (CH_3, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 42.2 Hz), 21.7 ($2CH_3$), 20.4 ($2CH_3$), 17.9 (CH_3), 17.0 (CH_3), 13.8 ($3CH_3$), 10.0 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn}$ = 314.4 Hz, $J_{^{13}C\text{-}^{119}Sn}$ = 328.8 Hz); IR (Film) ν = 2960, 2928, 2872, 2851, 1751, 1710, 1453, 1439, 1374, 1308, 1288, 1210, 1174, 1152, 1135, 1120, 1056, 1000 cm^{-1}; elemental analysis calcd (%) for $C_{38}H_{65}NO_5Sn$: C 62.13, H 8.92, N 1.91; found: C 62.20, H 9.05, N 1.85. **((*R*)-mandelic ester of 31):** $[\alpha]_D^{20}$ = - 36.7 (*c* = 0.9, $CHCl_3$); ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 7.47-7.41 (m, 2H), 7.40-7.30 (m, 3H), 7.05 (d, J = 6.4 Hz, 1H), 5.12 (dq, J = 9.6, 1.8 Hz, $J_{^1H\text{-}^{117}Sn} = J_{^1H\text{-}^{119}Sn}$ = 131.7 Hz, 1H), 4.77 (dd, J = 7.8, 4.6 Hz, 1H), 4.69 (s, 1H), 4.67 (dd, J = 9.6, 6.4 Hz, 1H), 4.29-4.12 (bs, 1H), 3.85-3.71 (bs, 1H), 3.43 (s, 3H, CH_3), 3.00 (dqd, J = 9.6, 6.9, 7.8 Hz, 1H), 2.13 (dqd, J = 9.6, 6.4, 4.6 Hz, 1H), 1.58 (d, J = 1.8 Hz, $J_{^1H\text{-}^{117}Sn} = J_{^1H\text{-}^{119}Sn}$ = 42.1 Hz, 3H, CH_3), 1.50-1.39 (m, 6H, $3CH_2$), 1.38-1.19 (m, 18H, $3CH_2$ + $4CH_3$), 0.98 (d, J = 6.9 Hz, 3H, CH_3), 0.93-0.87 (m, 15H, $3CH_2$ + $3CH_3$), 0.69 (d, J = 6.4 Hz, 3H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 170.2 (C), 153.0 (C), 142.1 (CH, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 27.8 Hz), 138.6 (C), 136.9 (C), 135.8 (CH), 128.8 (2CH), 128.7 (2CH), 127.5 (CH), 112.4 (CH), 82.6 (CH), 80.4 (CH), 57.6 (CH_3), 47.2 (CH), 45.6 (CH), 40.2 (CH, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 32.6 Hz), 32.9 (CH), 29.3 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 20.1 Hz), 27.5 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 58.5 Hz), 27.0 (CH_3, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 45.1 Hz), 21.8 ($2CH_3$), 20.5 ($2CH_3$), 17.6 (CH_3), 15.0 (CH_3), 13.8 ($3CH_3$), 9.7 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 328.8 Hz); IR (Film) ν = 2959, 2928, 2873, 2851, 1752, 1710, 1455, 1439, 1373, 1310, 1285, 1210, 1172, 1154, 1118, 1063, 1005 cm^{-1}.

(*S*)- mandelic ester of 29:

(*S*)- mandelic ester of 31: : *a) from pure carbamate **29**:* To a solution of compound **29** (150 mg, 0.24 mmol, 1.0 equiv), obtained from optically pure aldehyde **28**, in CH_2Cl_2 (5 mL) at 20 °C were successively added (*S*)-(-)-methoxyphenylacetic acid (80 mg, 0.48 mmol, 2.0 equiv), DCC (100 mg, 0.48 mmol, 2.0 equiv) and DMAP (10 mg, 0.09 mmol, 0.4 equiv). The resulting mixture was stirred for 4 h at 20 °C then quenched with a saturated aqueous $NaHCO_3$ solution and extracted with Et_2O. The organic layers were washed with water and brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was purified by chromatography on silica gel (cyclohexane/$Et_2$0 85:15) to give 160 mg (87 % yield) of the (***S*)-mandelic ester of 29** compound. b) *) from a mixture of carbamates **29** and **31:*** To a solution of compounds **29** and **31** (97 mg, 0.165 mmol, 1.0 equiv), obtained from racemic aldehyde **(+/-)-28**, in CH_2Cl_2 (5 mL) at 20 °C were successively added (*S*)-(-)-methoxyphenylacetic acid (55 mg, 0.33 mmol, 2.0 equiv), DCC (68 mg, 0.33 mmol, 2.0 equiv) and DMAP (4 mg, 0.07 mmol, 0.4 equiv). The resulting mixture was stirred for 4 h at 20 °C then quenched with a saturated aqueous $NaHCO_3$ solution and extracted with Et_2O. The organic layers were washed with water and brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was purified by chromatography on silica gel (cyclohexane/$Et_2$0 85:15) to give 82 mg (68 % yield) of (***S*)-mandelic ester of 29** and 24 mg of (***S*)-mandelic ester of 31** (20 % yield). **((*S*)- mandelic ester of 29):** $[\alpha]_D^{20}$ = + 58.6 (*c* = 1.1, $CHCl_3$); ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 7.49-7.41 (m, 2H), 7.40-7.30 (m, 3H), 7.04 (d, J = 6.4 Hz, 1H), 5.13 (dq, J = 9.4, 1.6 Hz, $J_{^1H\text{-}^{117}Sn} = J_{^1H\text{-}^{119}Sn}$ = 131.9 Hz, 1H), 4.77 (dd, J = 7.8, 4.6 Hz, 1H), 4.69 (s, 1H), 4.67 (dd, J = 9.9, 6.4 Hz, 1H), 4.28-4.11 (bs, 1H), 3.88-3.71 (bs, 1H), 3.43 (s, 3H, CH_3), 3.0 (ddq, J = 9.9, 7.8, 6.9 Hz, 1H), 2.13 (dqd, J = 9.4, 6.9, 4.6 Hz, 1H), 1.58 (d, J = 1.6 Hz, $J_{^1H\text{-}^{117}Sn} = J_{^1H\text{-}^{119}Sn}$ = 41.7 Hz, 3H, CH_3), 1.49-1.38 (m, 6H, $3CH_2$), 1.37-1.19 (m, 18H, $3CH_2$ + $4CH_3$), 0.98 (d, J = 6.9 Hz, 3H, CH_3), 0.93-0.83 (m, 15H, $3CH_2$, + $3CH_3$), 0.69 (d, J = 6.9 Hz, 3H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 170.2 (C), 153.0 (C), 142.1 (CH, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 30.7 Hz), 138.6 (C, $J_{^{13}C\text{-}^{117}Sn}$ = 368.1 Hz, $J_{^{13}C\text{-}^{119}Sn}$ = 396.8 Hz), 136.9 (C), 135.8 (CH), 128.8 (2CH), 128.7 (2CH), 127.5 (CH), 112.4 (CH), 82.6 (CH), 80.4 (CH), 57.6 (CH_3), 47.2 (CH), 45.6 (CH), 40.3 (CH, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 33.6 Hz), 32.9 (CH), 29.3 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 19.2 Hz), 27.5 ($3CH_2$ $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 57.5 Hz), 27.0 (CH_3, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 45.1 Hz), 21.8 ($2CH_3$), 20.5 ($2CH_3$), 17.6 (CH_3), 15.4 (CH_3), 13.8 ($3CH_3$), 9.7 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 327.8 Hz); IR (Film) ν = 2960, 2928, 2873, 2852, 1753, 1710, 1454, 1440, 1373, 1309, 1288, 1210, 1175, 1152, 1133, 1118, 1060, 1005 cm^{-1}; elemental analysis calcd (%) for $C_{38}H_{65}NO_5Sn$: C 62.13, H 8.92, N 1.91; found: C 62.220, H 9.04, N 1.96. **((*S*)- mandelic ester of 31):** $[\alpha]_D^{20}$ = - 37.2 (*c* = 1.2, $CHCl_3$); ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 7.47-7.41 (m, 2H), 7.40-7.29 (m, 3H), 6.82 (d, J = 6.4 Hz, 1H), 5.68 (dq, J = 9.6, 1.4 Hz, $J_{^1H\text{-}^{117}Sn} = J_{^1H\text{-}^{119}Sn}$ = 130.7 Hz, 1H), 4.83 (t, J = 6.0 Hz, 1H), 4.77 (s, 1H), 4.45 (dd, J = 9.6, 6.4 Hz, 1H), 4.29-4.08 (bs, 1H), 3.73-3.61 (bs, 1H), 3.43 (s, 3H, CH_3), 2.90 (dqd, J = 9.6, 6.9, 6.0 Hz, 1H), 2.23 (dmd, J = 9.6, 6.0 Hz, 1H), 1.77 (d, J = 1.4 Hz, $J_{^1H\text{-}^{117}Sn} = J_{^1H\text{-}^{119}Sn}$ = 41.2 Hz, 3H, CH_3), 1.50-1.39 (m, 6H, $3CH_2$), 1.36-1.18 (m, 18H, $3CH_2$ + $4CH_3$), 0.95-0.81 (m, 18H, $4CH_3$ + $3CH_2$), 0.70 (d, J = 6.9 Hz, 3H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 170.6 (C), 152.7 (C), 142.0 (CH, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 26.8 Hz), 139.1 (C), 136.9 (C), 135.5 (CH), 128.8 (2CH),

128.7 (2CH), 127.5 (CH), 110.7 (CH), 83.0 (CH), 80.6 (CH), 57.5 (CH_3), 47.0 (CH), 45.4 (CH), 40.8 (CH, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 33.6 Hz), 32.9 (CH), 29.3 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 21.1 Hz), 27.6 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 57.5 Hz), 27.2 (CH_3, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 44.1 Hz), 21.7 ($2CH_3$), 20.5 ($2CH_3$), 17.9 (CH_3), 17.0 (CH_3), 13.8 ($3CH_3$), 10.0 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn}$ = 317.3 Hz, $J_{^{13}C\text{-}^{119}Sn}$ = 329.7 Hz); IR (Film) ν = 2960, 2927, 2870, 2849, 1752, 1710, 1454, 1439, 1375, 1309, 1288, 1210, 1174, 1152, 112, 1056, 1007 cm^{-1}.

***S*)-3-Benzyloxy-2-methyl-propanal (44):** Benzyl alcohol (20.0 g, 184.9 mmol, 1.0 equiv) was added to a suspension of NaH (60 % in mineral oil, 0.740 g, 18.5 mmol, 0.1 equiv) in anhydrous ether (45 mL) over 30 min at 20 °C The mixture was stirred for 1 h and cooled to 0 °C. Trichloroacetonitrile (distilled) (20.5 mL, 204.5 mmol, 1.09 equiv.) was then introduced over 10 min. After 1.5 h the solution was concentrated with the water-bath temperature maintained below 40 °C. The residue was treated with a mixture of pentane (150 mL) and methanol (0.6 mL), stirred at 20 °C for 30 min, and filtered through a pad of celite. Concentration gave the trichloroimidate (44.0 g) as yellow oil, which was used without further purification.

A solution of methyl (*S*)-(+)-3-hydroxy-2-methylpropionate **14** (10 mL, 90.2 mmol, 1.0 equiv) in an anhydrous mixture of CH_2Cl_2/cyclohexane (1:2, 120 mL) was cooled to 0 °C and treated with crude trichloroimidate (27.3 g, 108.1 mmol, 1.2 equiv) and triflic acid (800 µL, 9.0 mmol, 0.1 equiv) over 10 min. After 3 h, the mixture was warmed to 20 °C and stirred for 40 h. The solution was filtered through a pad of celite and concentrated. The residue was purified by chromatography on silica gel (cyclohexane/ethyl acetate 90:10) to give 15.8 g (84 %yield) of (*S*)-3-benzyloxy-2-methyl-propionic acid methyl ester as a yellow oil. RN: 74924-27-9; ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 7.37-7.27 (m, 5H), 4.52 (s, 2H), 3.69 (s, 3H), 3.65 (dd, *J* = 9.3, 1.7 Hz, 1H), 3.49 (dd, *J* = 9.3, 4.9 Hz, 1H), 2.79 (qdd, *J* = 7.1, 4.9, 1.7 Hz, 1H), 1.18 (d, *J* = 7.1 Hz, 3H); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 175.3 (C), 138.1 (C), 128.3 (2CH), 127.6 (2CH), 127.5 (CH), 73.0 (CH_2), 71.9 (CH_2), 51.7 (CH_3), 40.1 (CH), 13.9 (CH_3); MS (GC, EI, CH_4): *m/z*: 208, 176, 148, 121, 107, 102, 91, 85, 79, 65, 51.

A solution of the above compound (15.8 g, 75.8 mmol, 1.0 equiv) in anhydrous THF (50 mL) was cooled to 0 °C and slowly added to a solution of $LiAlH_4$ (1 *M* in THF, 68 mL, 68.2 mmol, 0.9 equiv) over 10 min, warmed gradually to 20 °C, and stirred for 3 h. The reaction mixture was cooled to 0 °C and quenched by addition of water (11 mL), 15 % NaOH (9 mL), and water (11 mL). The resultant mixture was treated with $MgSO_4$, filtered, and the solvent removed under reduced pressure. The residue was then purified by chromatography on silica gel (cyclohexane/ethyl acetate 90:10 to 80:20) to give 12.9 g (94 % yield) of (*S*)-3-benzyloxy-2-methylpropan-1-ol as an orange oil. RN: 63930-49-4; ^{1}H NMR (400. 0MHz, $CDCl_3$): δ = 7.38-7.27 (m, 5H), 4.52 (s, 2H), 3.64-3.53 (m, 3H), 3.42 (dd, *J* = 9.1, 8.2 Hz, 1H), 2.57 (dd, *J* = 6.7, 4.7 Hz, 1H, OH), 2.13-2.00 (m, 1H), 0.88 (d, *J* = 7.0 Hz, 3H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 137.9 (C), 128.4 (CH), 127.7 (2CH), 127.6 (2CH), 75.4 (CH_2), 73.3 (CH_2), 67.8 (CH_2), 35.5 (CH), 13.4 (CH_3); MS (GC, EI, CH_4): *m/z*: 180, 161, 120, 107, 91, 79, 65, 51.

To a solution of IBX (36.2 g, 129.4 mmol, 2.2 equiv) in DMSO (400 mL) at 20 °C was added the preceding alcohol (10.6 g, 58.8 mmol, 1.0 equiv) in DMSO (50 mL). The mixture was stirred for 3 h, and then cooled to 0 °C. H_2O was added and the solution was filtered through a pad of celite and then diluted with diethyl ether. The organic layer was washed with water (5X), brine (2X), dried over $MgSO_4$ and the solvent removed under reduced pressure. The crude (*S*)-3-benzyloxy-2-methyl-propanal **44** was used without further purification (10.1 g, 96 % yield). **(44):** RN: 79027-28-4; ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 9.65 (d, *J* = 1.7 Hz, 1H), 7.31-7.19 (m, 5H), 4.45 (s, 2H), 3.62-3.55 (m, 2H), 2.63-2.55 (m, 1H), 1.05 (d, *J* = 6.9 Hz, 3H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 203.9 (C), 137.9 (C), 128.4 (2CH), 127.8 (2CH), 127.7 (CH), 73.5 (CH_2), 70.0 (CH_2), 46.7 (CH), 10.6 (CH_3); MS (GC, EI, CH_4): *m/z*: 209, 108, 91, 79, 63, 51.

(2*S*,3*S*,4*S*)-1-Benzyloxy-2,4-dimethyl-hex-5-en-3-ol (45): To a solution of freshly sublimed potassium *tert*-butoxide (9.77 g, 87.1 mmol, 1.55 equiv) in THF (130 mL) at -78 °C was slowly added to a solution of *trans*-2-butene (26 mL) in THF (25 mL); *n*BuLi (1.6 M in hexane, 55 mL, 87.8 mmol, 1.55 equiv) was then added and the yellow mixture was stirred at -78 °C for 5 min and at -45 °C for 20 min. The resulting orange solution was cooled to -78 °C, and a solution of (-)-*B*-diisopinocamphenylmethoxyborane (25.1 g, 79.3 mmol, 1.4 equiv) in 46 mL of diethyl ether was added over ca. 15 min. The resulting white solution was stirred at -78 °C for 40 min. Boron trifluoride etherate (12.6 mL, 102.0 mmol, 1.8 equiv) was added followed after 5 min by addition of a solution of aldehyde **44** (10.1 g, 56.7 mmol, 1.0 equiv) in THF (25 mL). The resulting solution was stirred at -78 °C for 5 h. The reaction was then quenched by addition of aqueous NaOH (2.5 *N*, 66 mL) followed by aqueous H_2O_2 (30 %, 20 mL). The acetone-dry ice bath was then removed, and the mixture was heated at 45 °C for 45 min. The cloudy solution was cooled to 20 °C, diluted with diethyl ether (45 mL), washed with brine, dried over $MgSO_4$, filtered and the solvent was removed under reduced pressure. The crude residue was purified by chromatography (cyclohexane/ethyl acetate 100:0 to 90:10) to give 11.0 g (83 % yield) of **45** and 1.27 g (9 % yield) of its **3,4-*bis epi*** diastereomer (92 % overall yield, *ee* 100 %, *de* 90:10). **(45):** $[\alpha]_D^{20}$ = +12.1 (*c* = 5.5, $CHCl_3$); RN: 106357-28-2; ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 7.27-7.22 (m, 5H), 5.72 (ddd, *J* = 18.8, 10.6, 8.6 Hz, 1H), 5.07-5.01 (m, 2H), 4.44 (s, 2H), 3.50 (dd, *J* = 8.9, 5.9 Hz, 2H), 3.55-3.42 (m, 2H), 2.48-2.40 (m, 1H + OH), 1.92-1.87 (m, 1H), 0.90 (d, *J* = 7.3 Hz, 3H, CH_3), 0.88 (d, *J* = 7.3 Hz, 3H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 141.8 (CH), 138.2 (C), 128.3 (2CH), 127.5 (3CH), 115.6 (CH_2), 75.5 (CH), 74.7 (CH_2), 73.4 (CH_2), 41.9 (CH), 34.9 (CH), 15.1 (CH_3), 9.8 (CH_3); MS (GC, EI): *m/z*: 234, 215, 187, 107, 91, 79; IR (Film) ν = 2868, 1074, 1110, 997 cm^{-1}. **(3,4-*bis epi* isomer of 45):** RN: 106357-29-3; ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 7.31-7.18 (m, 5H), 5.83 (ddd, *J* = 18.1, 9.6, 8.6 Hz, 1H), 4.97 (m, 2H), 4.44 (s, 2H), 3.54-3.44 (m, 2H), 3.32-3.30 (m, 1H), 2.40-2.21 (m, 1H), 1.91-1.81 (m, 1H), 1.54 (bs, 1H, OH), 1.03 (d, *J* = 6.9 Hz, 3H, CH_3), 0.82 (d, *J* = 6.9 Hz, 3H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 139.7 (CH), 137.7 (C), 128.4 (2CH), 127.7 (2CH), 127.6 (C), 115.2 (CH_2), 79.7 (CH), 75.4 (CH_2), 73.4 (CH_2), 41.0 (CH), 36.2 (CH), 17.7 (CH_3), 13.8 (CH_3).

(2*S*,3*R*,4*R*,5*S*)-1-Benzyloxy-2,4-dimethyl-5,6-epoxy-hexan-3-ol (46)

(2*S*,3*R*,4*R*,5*R*)-1-Benzyloxy-2,4-dimethyl-5,6-epoxy-hexan-3-ol (47): To a solution of $VO(acac)_2$ (12 mg, 0.042 mmol, 2 mol %) in CH_2Cl_2 (6 mL) at 0 °C were added olefin **45** (500 mg, 2.13 mmol, 1.0 equiv) in CH_2Cl_2 (15 mL) and *t*-BHP (solution 5 M in decane, 640 µL, 3.20 mmol, 1.5 equiv). The temperature was maintained for 20 min and the reaction mixture was stirred overnight at 20 °C. The reaction mixture was partitioned between diethyl ether and a saturated aqueous solution of ammonium chloride and extracted with diethyl ether. The organic layer was washed with brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was purified by chromatography on silica gel (cyclohexane/ethyl acetate 90:10) to give 374 mg (70 % yield) of **46**, 42 mg (8 % yield) of its C5 isomer **47** (78 % overall yield, selectivity 9:1) and 110 mg of starting material **45** (22 % recovered yield). **(46):** $[\alpha]_D^{20}$ = + 0.82 (*c* = 0.7, $CHCl_3$); ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 7.25-7.16 (m, 5H), 4.48 (s, 2H), 3.72-3.69 (m, 1H), 3.50 (dd, *J* = 8.9, 6.3 Hz, 1H), 3.41 (dd, *J* = 8.9, 5.3 Hz, 1H), 2.92-2.87 (m, 1H), 2.84 (bs, 1H, OH), 2.64 (t, *J* = 4.6 Hz, 1H), 2.39 (dd, *J* = 4.6, 3.0 Hz, 1H), 1.94-1.83 (m, 1H), 1.43-1.29 (m, 1H), 0.84 (d, *J* = 6.9 Hz, 3H, CH_3), 0.80 (d, *J* = 6.9 Hz, 3H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ =138.2 (C), 128.2 (2CH), 127.4 (3CH), 76.1 (CH), 74.2 (CH_2), 73.2 (CH_2), 55.5 (CH), 44.8 (CH_2), 39.0 (CH), 35.2 (CH), 12.4 (CH_3), 9.4 (CH_3); IR (Film) ν?= 3471, 2968, 2862, 1653, 1559, 1541, 1496, 1461, 1453, 1410, 1365, 1310, 1258, 1205, 1103, 987, 886 cm^{-1}; MS (GC, EI): *m/z*: 250 ($M^{+\bullet}$), 248, 232, 217, 201, 187, 177, 160, 148, 141, 123, 115, 107, 91, 79, 65, 55; elemental analysis calcd (%) for $C_{15}H_{22}O_3$: C 71.97, H 8.86; found: C 71.78, H 9.06. **(47):** ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 7.37-7.19 (m, 5H), 4.44 (s, 2H), 3.67-3.63 (m, 1H), 3.50 (d, *J* = 5.3 Hz, 2H), 2.89 (ddd, *J* = 6.9, 3.9, 2.9 Hz, 1H), 2.77 (dd, *J* = 4.3, 3.9 Hz, 1H), 2.64 (dd, *J* = 4.3, 2.9 Hz, 1H), 1.86-1.84 (m, 1H), 1.51-1.43 (m, 1H), 0.87 (d, *J* = 6.9 Hz, 3H, CH_3), 0.86 (d, *J* = 6.9 Hz, 3H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 137.9 (C), 128.4 (2CH), 127.7 (2CH), 127.5 (CH), 75.3 (CH_2), 73.4 (CH_2), 55.9 (CH), 47.6 (CH_2), 38.9 (CH), 34.7 (CH), 13.1 (CH_3), 9.3 (CH_3); MS (GC, EI): *m/z*: 250 ($M^{+\bullet}$), 209, 189, 177, 160, 142, 123, 108, 91, 79, 65, 55.

(2*S*,3*R*,4*S*,5*S*)-1-Benzyloxy-2,4-dimethyl-oct-7-en-3,5-diol (48): To a solution of vinyl bromide (1 mL, 13.8 mmol, 4.8 equiv) in diethyl ether (20 mL) at – 78 °C was slowly added *t*BuLi (1.7 M, 16.3 mL, 27.7 mmol, 9.6 equiv). The temperature was maintained for 10 min and then the mixture was stirred for 2 h at 20 °C. In a second flask CuCN (620 mg, 6.9 mmol, 2.4 equiv) was introduced and purged (3 times). THF (10 mL) was added and the resulting suspension was cooled to –78 °C. The freshly prepared solution of vinyl lithium was then slowly added, and the resulting yellow solution was stirred at –20 °C for 25 min. The solution was cooled to –78 °C and the epoxide **46** (722 mg, 2.88 mmol, 1.0 equiv) in THF (10 mL) was added. The resulting mixture was stirred at 0 °C

overnight. A 25 % aqueous ammonia solution was added and the resulting biphasic solution was stirred vigorously until the aqueous layer turned night blue The organic layer was washed with brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was purified by chromatography on silica gel (cyclohexane/ethyl acetate 70:30) to give **48 (**692 mg, 86 % yield). **(48):** ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 7.28-7.16 (m, 5H), 5.82 (tdd, *J* = 14.4, 10.5, 7.9 Hz, 1H), 5.24-5.18 (m, 2H), 4.60 (s, 2H), 4.15 (bs, 1H, OH), 4.05 (bs, 1H, OH), 3.70-3.66 (m, 1H), 3.61 (dt, *J* = 7.6, 3.0 Hz, 1H), 3.50-3.44 (m, 2H), 2.3-2.26 (m, 1H), 2.06 (dt, *J* = 15.0, 7.5 Hz, 1H), 1.93-1.81 (m, 1H), 1.66-1.52 (m, 1H), 1.05 (d, *J* = 6.9 Hz, 3H, CH_3), 0.85 (d, *J* = 6.9 Hz, 3H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 137.8 (C), 134.9 (CH), 128.2 (2CH), 127.5 (2CH), 127.4 (CH), 117.1 (CH_2), 78.1 (CH), 75.1 (CH_2), 75.0 (CH), 73.2 (CH_2), 40.0 (CH), 38.8 (CH_2), 34.9 (CH), 12.4 (CH_3), 9.1 (CH_3); IR (Film) ν = 3371, 2957, 2886, 1653, 1636, 1559, 1454, 1206, 1097, 1028, 983, 911 cm^{-1}; MS (GC, EI): *m/z*: 253, 219, 190, 179, 160, 145, 129, 118, 107, 91, 80, 69, 57, 55; elemental analysis calcd (%) for $C_{17}H_{26}O_3$: C 73.34, H 9.41; found: C 72.69, H 9.15.

(4*S*,5*S*,6*R*,7*S*)-4,6,8-Tris-(*tert*-butyldimethylsilyloxy)-5,7-dimethyl-oct-1-ene (49): To a night blue solution of lithium metal (124 mg, 17.9 mmol, 1.0 equiv) in liquid ammonia and anhydrous THF (10 mL) at –78 °C was added the benzyl product **48** (500 mg, 1.79 mmol, 1.0 equiv) in dry THF (10 mL). The reaction mixture was stirred at –78 °C for 1 h. Then the solution was quenched by addition of solid NH_4Cl (10 g) and the ammonia was allowed to evaporate by permitting the reaction to warm to 20 °C. A saturated aqueous solution of NH_4Cl was then added and the aqueous layer was extracted with ethyl acetate. The organic layer was washed with brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude (2*S*,3*R*,4*S*,5*S*)-2,4-dimethyl-oct-7-ene-1,3,5-triol compound was used without further purification in the next step (300 mg)**.:** ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 5.69 (ddt, *J* = 14.2, 8.2, 5.9 Hz, 1H), 5.10-5.06 (m, 2H), 4.75 (bs, 1H, OH), 4.08 (bs, 1H, OH), 3.79-3.75 (m, 1H), 3.68-3.55 (m, 3H), 2.29-2.23 (m, 1H), 2.08 (quint, *J* = 7.6 Hz, 1H), 1.81-1.76 (m, 1H), 1.65-1.54 (m, 1H), 0.86 (d, *J* = 7.3 Hz, 3H, CH_3), 0.70 (d, *J* = 7.3 Hz, 3H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 134.5 (CH), 118.1 (CH_2), 78.5 (CH), 75.8 (CH), 67.3 (CH_2), 40.2 (CH), 39.4 (CH_2), 36.0 (CH), 12.5 (CH_3), 8.6 (CH_3); MS (GC, EI): *m/z*: 188, 171, 161, 142.

To a solution of the preceding triol (200 mg, 1.06 mmol, 1.0 equiv) in dry CH_2Cl_2 (10 mL) at 0 °C were added 2,6-lutidine (1.1 mL, 9.56 mmol, 9.0 equiv) and TBSOTf (1.1 mL, 4.78 mmol, 4.5 equiv). The reaction mixture was stirred at 20 °C for 3 h, then quenched by addition of a saturated aqueous solution of NH_4Cl and extracted with CH_2Cl_2. The organic layer was washed with brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was purified by chromatography on silica gel (cyclohexane/ethyl acetate 98:2) to give the title compound **49** (560 mg, 99 % yield). **(49):** $[\alpha]_D^{20}$ = - 2.70 (*c* = 1.2, $CHCl_3$); ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 5.79 (dd, *J* = 17.5, 10.1, 7.1 Hz, 1H), 5.04-4.97 (m, 2H), 3.89 (dt, *J* = 8.2, 4.0 Hz, 1H), 3.77 (d, *J* = 7.9 Hz,1H), 3.44 (t, *J* = 9.2 Hz, 1H), 3.32 (dd, *J* = 9.2, 7.3 Hz, 1H), 2.23-2.02 (m, 2H), 1.90-1.74 (m, 2H), 0.86 (s, 9H, $3CH_3$), 0.85 (s, 9H, $3CH_3$), 0.84 (d, *J* = 7.9 Hz, 3H, CH_3), 0.83 (s, 9H, $3CH_3$), 0.80 (d, *J* = 7.9 Hz, 3H, CH_3), 0.00 (s, 6H, $2CH_3$), -0.02 (s, 6H, $2CH_3$), -0.05 (s, 6H, $2CH_3$); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 136.2 (CH), 116.4 (CH_2), 72.1 (CH), 72.0 (CH), 66.1 (CH_2), 43.7 (CH), 38.7 (CH), 36.6 (CH_2), 26.3 ($3CH_3$), 25.9 ($3CH_3$), 25.3 ($3CH_3$), 18.3 (C), 18.2, (C), 18.1 (C), 10.6 (CH_3), 10.0 (CH_3), -2.9 ($2CH_3$), -3.4 (CH_3), -4.1 (CH_3), -4.2 (CH_3), -4.3 (CH_3); IR (Film) ν = 2955, 2930, 2886, 2858, 1645, 1472, 1388, 1361, 1254, 1069, 1044, 1005, 912, 833 cm^{-1}; MS (GC, EI): *m/z*: 474 ($M^{+\bullet}$ - *t*-Bu), 433, 391, 357, 341, 317, 259, 243, 225, 185, 169, 147, 131, 115, 89, 73, 55; elemental analysis calcd (%) for $C_{28}H_{62}O_3Si_3$: C 63.33, H 11.77; found: C 63.12, H 11.98.

(2*S*)-3-(*tert*-Butyldimethylsilyloxy)-2-methyl-propanal (50): To a solution of commercial methyl-(S)-(+)3-hydroxy-2-methylpropionate **14** (3.70 g, 31.3 mmol, 1.0 equiv) in dry DMF (30 mL) were added imidazole (6.70 g, 98.4 mmol, 3.0 equiv) and tert-butyldimethylsilyl chloride (7.06 g, 47 mmol, 1.5 equiv). After 3 h at 20 °C the mixture was quenched with a saturated aqueous NH_4Cl solution and diluted with diethyl ether. The organic layer was washed with water and brine, dried over $MgSO_4$, filtered, and the solvent removed under reduced pressure. The crude residue was purified by chromatography on silica gel (cyclohexane/diethyl ether 100:0 to 90:10) to give 6.80 g (94 % yield) of (2*S*)-methyl-3-(*tert*-butyldimethylsilyloxy)-2-methyl propanoate as a colourless oil. RN: 93454-85-4; ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 3.78 (dd, *J* = 9.6, 6.9 Hz, 1H), 3.68 (s, 3H, CH_3), 3.66 (dd, *J* = 9.6, 6.0 Hz, 1H), 2.66 (qdd, *J* = 6.9, 6.9, 6.0 Hz, 1H), 1.14 (d, *J* = 6.9 Hz, 3H, CH_3), 0.88 (s, 9H, $3CH_3$), 0.04 (s, 6H, $2CH_3$); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 175.4 (C), 65.3 (CH_2), 51.3 (CH_3), 42.6 (CH), 25.8 ($3CH_3$), 18.3 (C), 13.5 (CH_3), -5.5 ($2CH_3$); IR (Film) ν = 2930, 2885, 2858, 1744, 1472, 1436, 1389, 1362, 1257, 1199, 1176, 1098, 837, 777, 668 cm^{-1}; MS (GC, CI, NH_3): *m/z*: 250 ($MH^+ + NH_3$), 233 (MH^+), 201, 175, 132, 106, 91.

To a solution of (*S*)-3-(*tert*-butyldimethylsilyloxy)-2-methyl-propionic acid methyl ester (5.50 g, 23.7 mmol, 1.0 equiv) in CH_2Cl_2 (25 mL) at -35 °C was added diisobutylaluminium hydride (1 *M* solution in CH_2Cl_2, 50.0 mL, 50.0 mmol, 2.1 equiv). The solution was stirred 30 min at -20 °C. Then the mixture was quenched by addition of 10 % aqueous NaOH solution (55 mL of water, 5.50 g of NaOH, 137.5 mmol, 5.8 equiv). The mixture was allowed to warm to 20 °C and then diluted with diethyl ether. The organic layer was washed with water and brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude residue was purified by chromatography on silica gel (cyclohexane /diethyl ether 80:20 to 50:50) to give 4.46 g (92 % yield) of (2*S*)-3-(*tert*-butyldimethylsilyloxy)-2-methyl-propan-1-ol as a colourless oil. RN: 112057-64-4; ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 3.76 (dd, *J* = 9.6, 4.3 Hz, 1H), 3.66 (ddd, *J* = 11.2, 7.0, 4.6 Hz, 1H), 3.60 (ddd, *J* = 11.2, 7.8, 3.9 Hz, 1H), 3.55 (dd, *J* = 9.6, 8.2 Hz, 1H), 2.93 (dd, *J* = 7.0, 3.9 Hz, 1H, OH), 1.95 (ddqdd, *J* = 8.2, 7.8, 6.9, 4.6, 4.3 Hz, 1H), 0.91 (s, 9H, $3CH_3$), 0.83 (d, *J* = 6.9 Hz, 3H, CH_3), 0.08 (s, 6H, $2CH_3$); ^{13}C RMN (100.5 MHz, $CDCl_3$): δ = 68.9 (CH_2), 68.5 (CH_2), 36.9 (CH, C-2), 25.8 ($3CH_3$), 18.1 (C), 13.0 (CH_3), -5.6 ($2CH_3$); IR (Film) ν = 3354, 2955, 2857, 1472, 1389, 1361, 1258, 1090, 1040, 939, 836, 775, 667 cm^{-1}; MS (GC, CI, NH_3): *m/z*: 222 ($MH^+ + NH_3$), 205 (MH^+), 132, 92, 76, 74.

To a solution of oxalyl chloride (1.8 mL, 21.4 mmol, 1.2 equiv) in CH_2Cl_2 (60 mL) at -55 °C was added DMSO (3.1 mL, 42.9 mmol, 2.4 equiv). This was followed 5 min later with the addition via cannula of a solution of the preceding alcohol **(**3.65 g, 17.9 mmol, 1.0 equiv) in CH_2Cl_2 (20 mL). The resulting slurry was stirred for 1 h at -55 °C. Then triethylamine (12.5 mL, 89.3 mmol, 5.0 equiv) was added. The solution was warmed to 20 °C 5 min later and stirred for an additional hour at 20 °C. The solution was diluted with CH_2Cl_2 (80 mL) and washed with 90 mL of ice-cold 1*M* HCl and 90 mL of water. These phases were extracted with CH_2Cl_2 (180 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The crude (*S*)-3-(*tert*-butyldimethylsilyloxy)-2-methyl-propanal **50** was used without further purification (3.40 g, 94 % yield). **(50):** RN: 104701-87-3; ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 8.86 (d, *J* = 1.5 Hz, 1H), 3.78 (dd, *J* = 9.6, 6.9 Hz, 1H), 3.66 (dd, *J* = 9.6, 6.0 Hz, 1H), 2.66 (qddd, *J* = 6.9, 6.9, 6.0, 1.5 Hz, 1H), 1.14 (d, *J* = 6.9 Hz, 3H, CH_3), 0.88 (s, 9H, $3CH_3$,), 0.04 (s, 6H, $2CH_3$); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 204.7 (C), 63.4 (CH_2), 48.8 (CH), 25.8 ($3CH_3$), 18.2 (C), 10.3 (CH_3), -5.5 ($2CH_3$); IR (Film) ν = 2956, 2930, 2885, 2858, 1737, 1472, 1389, 1362, 1256, 1100, 1033, 838, 771, 668 cm^{-1}; MS (GC, CI, NH_3): *m/z*: 220 ($MH^+ + NH_3$), 203 (MH^+), 145, 132, 115, 106, 91, 76, 74.

(*R*)-Mandelate ester of 56: To a solution of compound **56** (40 mg, 0.045 mmol, 1.0 equiv) in CH_2Cl_2 (1 mL) at 20 °C were successively added (*R*)-(-)-methoxyphenylacetic acid (15 mg, 0.091 mmol, 2.0 equiv), DCC (9.5 mg, 0.091 mmol, 2.0 equiv) and DMAP (2 mg, 0.022 mmol, 0.4 equiv). The resulting mixture was stirred for 12 h at 20 °C then quenched with a saturated aqueous $NaHCO_3$ solution and extracted with Et_2O. The organic layers were washed with water and brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was purified by chromatography on silica gel (cyclohexane/AcOEt 95:5 to 70:30) to give 29 mg (63 % yield) of the title compound. **((*R*)-Mandelate ester of 56)**: $[\alpha]_D^{20}$ = - 29.5 (*c* = 0.52, $CHCl_3$); ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 7.50-7.47 (m, 4H), 7.36-7.30 (m, 6H), 6.01 (dq, *J* = 9.6, 1.4 Hz, $J_{^1H\text{-}^{117}Sn} = J_{^1H\text{-}^{119}Sn}$ = 131.2 Hz, 1H), 5.83 (dt, *J* = 11.5, 1.8 Hz, 1H), 4.79 (d, *J* = 6.9 Hz, 1H), 4.78 (s, 1H), 4.74 (s, 1H), 4.68 (d, *J* = 6.9 Hz, 1H), 3.65 (t, *J* = 9.2 Hz, 1H), 3.46 (dd, *J* = 9.2, 5.5 Hz, 1H), 3.45 (s, 3H, CH_3), 3.44 (s, 3H, CH_3), 3.25 (t, *J* = 5.5 Hz, 1H), 3.24 (d, *J* = 10.9 Hz, 1H), 2.75 (qdd, *J* = 6.9, 5,5, 1.8 Hz, 1H), 2.48 (td, *J* = 9.6, 1.8 Hz, 1H), 2.18 (dqd, *J* = 9.6, 6.9, 5.5 Hz, 1H), 2.11 (ddd, *J* = 11.9, 11.5, 1.8 Hz, 1H), 1.90 (d, *J* = 1.4 Hz, $J_{^1H\text{-}^{117}Sn} = J_{^1H\text{-}^{119}Sn}$ = 42.1 Hz, 3H, CH_3), 1.87 (dqd, *J* = 9.2, 6.9, 5.5 Hz, 1H), 1.73 (ddd, *J* = 11.9, 9.6, 1.8 Hz, 1H), 1.53-1.44 (m, 6H, $3CH_2$), 1.45-1.42 (m, 1H), 1.32 (sext, *J* = 7.8 Hz, 6H, $3CH_2$), 1.16 (d, *J* = 6.9 Hz, 3H, CH_3), 0.98 (d, *J* = 6.9 Hz, 3H, CH_3), 0.94 (s, 9H, $3CH_3$), 0.95-0.90 (m, 6H, $3CH_2$), 0.90 (m, 9H, $3CH_3$), 0.81 (d, *J* = 6.9 Hz, 3H, CH_3), 0.52 (d, *J* = 6.4 Hz, 3H, CH_3), 0.07 (s, 3H, CH_3), 0.06 (s, 3H, CH_3); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 169.4 (C), 144.2 (CH), 138.8 (C), 137.7 (C, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 384.0 Hz), 137.0 (C), 129.0 (CH), 128.9 (2CH),

128.3 (CH), 128.0 (2CH), 127.6 (2CH), 125.9 (2CH), 99.0 (CH), 98.3 (CH_2), 88.3 (C), 85.2 (CH), 82.3 (CH), (C), 79.6 (CH), 76.7 (CH), 65.1 (CH_2), 60.1 (CH), 57.3 (CH_3), 56.3 (CH_3), 42.0 (CH), 39.5 (CH_2), 36.7 (CH), 34.8 (CH), 30.3 (CH), 29.4 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 19.2 Hz), 27.5 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 57.5 Hz), 27.4 (CH_3, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 42.6 Hz), 26.1 ($3CH_3$), 18.5 (C), 18.2 (CH_3), 16.3 (CH_3), 13.9 ($3CH_3$), 11.5 (CH_3), 10.1 ($3CH_2$), 9.8 (CH_3), -5.3 (CH_3), -5.2 (CH_3); IR (Film) ν = 2956, 2871, 2855, 1759, 1454, 1462, 1166, 1152, 1114, 1102, 1031 cm^{-1}; elemental analysis calcd (%) for $C_{55}H_{90}O_8SiSn$: C 64.38, H 8.84; found: C 64.15, H 9.02.

(*S*)-Mandelate ester of 56: To a solution of compound **56** (40 mg, 0.045 mmol, 1.0 equiv) in CH_2Cl_2 (1 mL) at 20 °C were successively added (*S*)-(+)-methoxyphenylacetic acid (15 mg, 0.091 mmol, 2.0 equiv), DCC (9.5 mg, 0.091 mmol, 2.0 equiv) and DMAP (2 mg, 0.022 mmol, 0.4 equiv). The resulting mixture was stirred for 12 h at 20 °C then quenched with a saturated aqueous $NaHCO_3$ solution and extracted with Et_2O. The organic layers were washed with water and brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was purified by chromatography on silica gel (cyclohexane/AcOEt 95:5 to 70:30) to give 25 mg (62 % yield) of the title compound. (**(*S*)-Mandelate ester of 56):** $[\alpha]_D^{20}$ = - 1.40 (*c* = 0.60, $CHCl_3$); ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 7.51-7.47 (m, 4H), 7.37-7.27 (m, 6H), 6.00 (dq, *J* = 9.6, 1.8 Hz, $J_{^1H\text{-}^{117}Sn} = J_{^1H\text{-}^{119}Sn}$ = 134.6 Hz, 1H), 5.82 (ddd, *J* = 11.0, 2.3, 1.8 Hz, 1H), 5.00 (s, 1H), 4.84 (s, 1H), 4.72 (d, *J* = 6.9 Hz, 1H), 4.60 (d, *J* = 6.9 Hz, 1H), 3.67 (dd, *J* = 9.6, 9.2 Hz, 1H), 3.49 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.49-3.46 (m, 1H), 3.46 (s, 3H, CH_3), 3.40 (s, 3H, CH_3), 3.19 (t, *J* = 5.5 Hz, 1H), 3.10 (ddd, *J* = 11.9, 10.5, 1.8 Hz, 1H), 2.66 (qdd, *J* = 7.3, 5,5, 1.8 Hz, 1H), 2.31 (ddd, *J* = 11.9, 11.5, 2.3 Hz, 1H), 2.13 (dqd, *J* = 9.6, 6.9, 5.5 Hz, 1H), 1.96 (mdqd, *J* = 9.2, 6.9, 6.0 Hz, 1H), 1.88 (d, *J* = 1.4 Hz, $J_{^1H\text{-}^{117}Sn} = J_{^1H\text{-}^{119}Sn}$ = 42.1 Hz, 3H, CH_3), 1.84 (ddd, *J* = 11.5, 11.0, 1.8 Hz, 1H), 1.61-1.60 (m, 1H), 1.56-1.43 (m, 6H, $3CH_2$), 1.31 (sext, *J* = 7.8 Hz, 6H, $3CH_2$), 1.10 (d, *J* = 7.3 Hz, 3H, CH_3), 0.93 (d, *J* = 6.9 Hz, 3H, CH_3), 0.94 (s, 9H, $3CH_3$), 0.93-0.89 (m, 6H, $3CH_2$), 0.89 (t, 9H, *J* = 7.3 Hz, $3CH_3$), 0.84 (d, *J* = 6.9 Hz, 3H, CH_3), 0.72 (d, *J* = 6.9 Hz, 3H, CH_3), 0.05 (s, 6H, $2CH_3$); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 169.8 (C), 144.2 (CH, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 28.8 Hz), 138.8 (C), 137.7 (C), 136.4 (C), 128.8 (CH), 128.7 (2CH), 128.3 (CH), 128.0 (2CH), 126.9 (2CH), 125.9 (2CH), 99.4 (CH), 98.2 (CH_2), 88.4 (C), 85.2 (CH), 83.1 (CH), 83.0 (C), 80.0 (CH), 79.0 (CH), 65.1 (CH_2), 61.3 (CH), 57.5 (CH_3), 56.2 (CH_3), 42.0 (CH), 39.1 (CH_2), 36.7 (CH), 35.1 (CH), 30.3 (CH), 29.3 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 18.2 Hz), 27.6 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 57.5 Hz), 27.6 (CH_3), 26.1 ($3CH_3$), 18.5 (C), 18.3 (CH_3), 16.2 (CH_3), 13.9 ($3CH_3$), 11.7 (CH_3), 10.0 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn}$ = 325.9, $J_{^{13}C\text{-}^{119}Sn}$ = 312.5 Hz), 9.8 (CH_3), -5.3 (CH_3), -5.2 (CH_3); IR (Film) ν = 2955, 2855, 1755, 1456, 1464, 1155, 1098, 1074, 1031 cm^{-1}; elemental analysis calcd (%) for $C_{55}H_{90}O_8SiSn$: C 64.38, H 8.84; found: C 64.70, H 9.26.

(*R*)-Mandelate ester of 57: To a solution of compound **57** (100 mg, 0.11 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) at 20 °C were successively added (*R*)-(-)-methoxyphenylacetic acid (38 mg, 0.23 mmol, 2.0 equiv), DCC (47 mg, 0.23 mmol, 2.0 equiv) and DMAP (3 mg, 0.022 mmol, 0.2 equiv). The resulting mixture was stirred for 12 h at 20 °C then quenched with a saturated aqueous $NaHCO_3$ solution and extracted with Et_2O. The organic layers were washed with water and brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was purified by chromatography on silica gel (cyclohexane/AcOEt 95:5 to 70:30) to give 89 mg (79 % yield) of the title compound. (**(*R*)-Mandelate ester of 57):** $[\alpha]_D^{20}$ = + 1.76 (*c* = 1.44, $CHCl_3$); ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 7.50-7.47 (m, 4H), 7.39-7.30 (m, 6H), 6.00 (dq, *J* = 9.6, 1.4 Hz, $J_{^1H\text{-}^{117}Sn} = J_{^1H\text{-}^{119}Sn}$ = 132.8 Hz, 1H), 5.71 (ddd, *J* = 9.6, 5.0, 1.4 Hz, 1H), 5.48 (s, 1H), 4.72 (s, 1H), 4.70 (d, *J* = 6.9 Hz, 1H), 4.57 (d, *J* = 6.9 Hz, 1H), 3.74-3.65 (m, 2H), 3.50 (dd, *J* = 9.6, 6.0 Hz, 1H), 3.45-3.39 (m, 1H, H-5), 3.35 (s, 3H, CH_3), 3.29 (s, 3H, CH_3), 3.19 (t, *J* = 5.5 Hz, 1H), 2.64 (qdd, *J* = 6.9, 5.0, 1.4 Hz, 1H), 2.22-2.08 (m, 3H), 2.05-1.97 (m, 1H), 1.89 (d, *J* = 1.4 Hz, $J_{^1H\text{-}^{117}Sn} = J_{^1H\text{-}^{119}Sn}$ = 41.9 Hz, 3H, CH_3), 1.73-1.67 (m, 1H), 1.52-1.46 (m, 6H, $3CH_2$), 1.32 (sext, *J* = 7.3 Hz, 6H, $3CH_2$), 1.10 (d, *J* = 7.3 Hz, 3H, CH_3), 0.97-0.87 (m, 15H, $3CH_2$ + $3CH_3$), 0.94 (d, *J* = not calculated, 3H, CH_3), 0.90 (s, 9H, $3CH_3$), 0.86 (d, *J* = not calculated, 3H, CH_3), 0.81 (d, *J* = 6.9 Hz, 3H, CH_3), 0.05 (s, 6H, $2CH_3$); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 169.3 (C), 144.2 (CH, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 30.6 Hz), 138.8 (C), 137.5 (C, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 371.8 Hz), 135.9 (C), 128.6 (CH), 128.5 (2CH), 128.4 (CH), 128.0 (2CH), 127.4 (2CH), 125.9 (2CH), 99.8 (CH), 98.0 (CH_2), 89.3 (C), 84.9 (CH), 82.5 (CH), 80.2 (C), 79.2 (CH), 78.3 (CH), 64.9 (CH_2), 63.4 (CH), 57.3 (CH_3), 56.1 (CH_3), 42.3 (CH, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 32.6 Hz), 38.4 (CH_2), 36.6 (CH), 34.8 (CH), 30.3 (CH), 29.2 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 19.2 Hz), 27.4 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 57.4 Hz), 27.3 (CH_3, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 46.0 Hz), 25.9 ($3CH_3$), 18.4 (C), 18.3 (CH_3), 15.8 (CH_3), 13.7 ($3CH_3$), 11.5 (CH_3), 9.9 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn}$ = 313.4 Hz, $J_{^{13}C\text{-}^{119}Sn}$ = 327.8 Hz), 9.7 (CH_3), -5.5 (CH_3), -5.4 (CH_3); IR (Film) ν = 2955, 2871, 2855, 1758, 1462, 1455, 1250, 1149, 1102, 1031, 1002, 837, 698 cm^{-1}; elemental analysis calcd (%) for $C_{55}H_{90}O_8SiSn$: C 64.38, H 8.84; found: C 64.22, H 9.12.

(*S*)-Mandelate ester of 57: To a solution of compound **57** (100 mg, 0.11 mmol, 1.0 equiv) in CH_2Cl_2 (2 mL) at 20 °C were successively added (*S*)-(-)-methoxyphenylacetic acid (38 mg, 0.23 mmol, 2.0 equiv), DCC (47 mg, 0.23 mmol, 2.0 equiv) and DMAP (3 mg, 0.022 mmol, 0.2 equiv). The resulting mixture was stirred for 12 h at 20 °C then quenched with a saturated aqueous $NaHCO_3$ solution and extracted with Et_2O. The organic layers were washed with water and brine, dried over $MgSO_4$, filtered and the solvent removed under reduced pressure. The residue was purified by chromatography on silica gel (cyclohexane/AcOEt 95:5 to 70:30) to give 81 mg (72 % yield) of the title compound. (**(*S*)-Mandelate ester of 57):** $[\alpha]_D^{20}$ = + 22.0 (*c* = 1.38, $CHCl_3$); ^{1}H NMR (400.0 MHz, $CDCl_3$): δ = 7.46-7.40 (m, 4H), 7.36-7.29 (m, 6H), 6.00 (dq, *J* = 9.6, 1.8 Hz, $J_{^1H\text{-}^{117}Sn} = J_{^1H\text{-}^{119}Sn}$ = 133.2 Hz, 1H), 5.71 (ddd, *J* = 10.0, 4.6, 1.4 Hz, 1H), 5.43 (s, 1H), 4.76 (d, *J* = 6.9 Hz, 1H,), 4.73 (s, 1H), 4.66 (d, *J* = 6.9 Hz, 1H), 3.72-3.61 (m, 3H), 3.49 (dd, *J* = 9.6, 5.0 Hz, 1H), 3.40 (s, 3H, CH_3), 3.38 (s, 3H, CH_3), 3.24 (dd, *J* = 5.5, 5.0 Hz, 1H), 2.73 (qdd, *J* = 6.9, 5.0, 1.4 Hz, 1H), 2.19 (qdd, *J* = 9.6, 6.9, 5.5 Hz, 1H), 2.06 (td, *J* = 10.0, 2.3 Hz, 1H), 2.00-1.93 (m, 1H), 1.90 (d, *J* = 1.8 Hz, $J_{^1H\text{-}^{117}Sn} = J_{^1H\text{-}^{119}Sn}$ = 42.6 Hz, 3H, CH_3), 1.81 (ddd, *J* = 13.7, 10,0, 4.6 Hz, 1H), 1.65-1.64 (m, 1H), 1.53-1.46 (m, 6H, $3CH_2$), 1.33 (sext, *J* = 7.3 Hz, 6H, $3CH_2$), 1.19 (d, *J* = 6.9 Hz, 3H, CH_3), 1.00 (d, *J* = 6.9 Hz, 3H, CH_3), 0.97-0.86 (m, 15H, $3CH_2$, + $3CH_3$), 0.90 (s, $3CH_3$), 0.84 (d, *J* = 6.9 Hz, 3H, CH_3), 0.74 (d, *J* = 6.4 Hz, 3H, CH_3), 0.04 (s, 6H, $2CH_3$); ^{13}C NMR (100.5 MHz, $CDCl_3$): δ = 169.2 (C), 144.1 (CH, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 27.8 Hz), 138.7 (C), 137.7 (C), 135.9 (C), 128.6 (CH), 128.5 (2CH), 128.3 (CH), 127.9 (2CH), 127.2 (2CH), 125.9 (2CH), 99.7 (CH), 98.0 (CH_2), 89.2 (C), 85.1 (CH), 82.3 (CH), 80.1 (C), 78.9 (CH), 78.5 (CH), 65.8 (CH_2), 65.1 (CH), 57.3 (CH_3), 56.1 (CH_3), 42.3 (CH, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 31.6 Hz), 38.2 (CH_2), 36.5 (CH), 34.6 (CH), 30.3 (CH), 29.2 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 19.2 Hz), 27.7 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 57.4 H), 27.4 (CH_3, $J_{^{13}C\text{-}^{117}Sn} = J_{^{13}C\text{-}^{119}Sn}$ = 40.2 Hz), 25.9 ($3CH_3$), 18.6 (CH_3), 18.2 (C), 16.1 (CH_3), 13.7 ($3CH_3$), 11.6 (CH_3, CH_3-4), 9.9 ($3CH_2$, $J_{^{13}C\text{-}^{117}Sn}$ = 314.4 Hz, $J_{^{13}C\text{-}^{119}Sn}$ = 331.6 Hz), 9.6 (CH_3), -5.5 ($2CH_3$); IR (Film) ν = 2955, 2928, 2871, 2855, 1757, 1454, 1250, 1165, 1148, 1102, 1073, 1031, 1003, 837, 698 cm^{-1}; elemental analysis calcd (%) for $C_{55}H_{90}O_8SiSn$: C 64.38, H 8.84; found: C 64.61, H 8.99.