Supplementary Material (ESI) for Organic and Biomolecular Chemistry

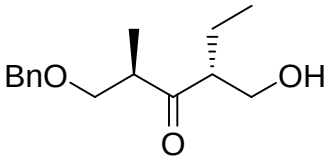
Supporting Information:

General:

All reactions were carried out in dried glassware under an atmosphere of argon. Solvents were destilled or dried using standard methods prior to use where appropriate. All chemicals were purchased from commercial suppliers and used without further purification. Flash chromatography was performed using silica gel 60 (230–400 mesh provided by Macherey-Nagel). TLC was performed using precoated aluminium foil sheets silica gel 60 F_{254} provided by Merck. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AM 400 or DRX 500, using the residual signals of the solvent as standard. Multiplicities are described as: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad. Coupling constants *J* are reported in Hz. Numbers of attached protons in the ^{13}C spectra were elucidated using DEPT90 and 135 and are given in the form: p = primary (RCH_3), s = secondary (R_2CH_2), t = tertiary (R_3CH), q = quartenary (R_4C). Mass spectrometry (MS) as well as high resultion MS (HRMS) was performed on a Finnigan MAT 90 using electron impact (EI) at 70 eV. Ion mass/charge ratios (*m*/*z*) are reported as values in atomic mass units followed by the intensities relative to the base peak in parathenses. Infrared spectra (IR) were obtained on a Bruker IFS 88 as film on KBr and are reported as values in cm^{-1} using the following abbreviations for absorption strength: s = strong, m = medium, w = weak. Elemental analysis was performed on a Heraeus CHN-O-Rapid and are given as percentage values with the abbreviation calc. = calculated.

Experimental procedures:

1-Benzyloxy-4-hydroxymethyl-2-methyl-hexan-3-one (**2**):

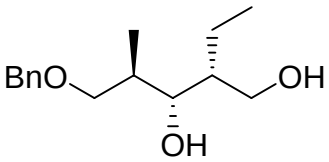


Chlorodicyclohexylborane (1.71 mL, 1.71 mmole, 1.5 equiv., 1 M in hexanes) was dissolved in Et_2O (3 mL) and cooled to –78 °C. Triethylamine (0.29 mL, 0.21 g, 2.05 mmole, 1.8 equiv.) and 1-benzyloxy-2-methyl-hexan-3-one (**4**, 251 mg, 1.14 mmole) in Et_2O (5 mL) were slowly added. The mixture was warmed to 0°C and stirred for 2 h. After recooling to –78 °C, gaseous formaldehyde (produced from dried *para*-formaldehyde by heating, 137 mg, 4.56 mmole, 4.0 equiv.) was transferred into the reaction vessel. Stirring was continued for 2 h at –78 °C and for 14 h at –26 °C. The reaction mixture was then warmed to 0 °C, quenched by addition of MeOH/pH7 buffer (10 mL, 1:1) and H_2O_2 (5 mL, 30%) and stirred for 1 h. After adding H_2O (60 mL) the phases were separated and the aqueous phase was

extracted with CH_2Cl_2 (3 × 60 mL). The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel, hexanes/Et_2O 3:1) yielding the *anti* diastereomer as a pale yellow oil (243 mg, 0.97 mmole, 85%). The diastereomeric ratio was determined from the ^1H NMR spectrum of the crude product (dr = 19:1).

$[\alpha]_D^{20}$ = +11.9° ($CHCl_3$, 1.34 g/100 mL). – ^1H NMR ($CDCl_3$, 500 MHz): δ = 0.89 (t, *J* = 7.5 Hz, 3 H, CH_2CH_3), 1.04 (d, *J* = 7.0 Hz, 3 H, $CHCH_3$), 1.44–1.53 (m, 1 H, $CH_AH_BCH_3$), 1.61–1.69 (m, 1H, $CH_AH_BCH_3$), 2.41 (br. s, 1 H, OH), 2.69–2.74 (m, 1 H, $C(O)CHCH_2CH_3$), 3.05–3.12 (m, 1 H, $CHCH_3$), 3.42 (dd, *J* = 8.9 Hz, *J* = 5.0 Hz, 1 H, $BnOCH_AH_B$), 3.64–3.72 (m, 2 H, CH_AH_BOH und $BnOCH_AH_B$), 3.81 (dd, *J* = 11.4 Hz, *J* = 7.9 Hz, 1 H, CH_AH_BOH), 4.43 (d, J = 11.9 Hz, 1 H, Ar-CH_AH_B), 4.48 (d, J = 1.9 Hz, 1 H, Ar-CH_aH_b), 7.24–7.35 (m, 5 H, Ar-H). – ^{13}C NMR ($CDCl_3$, 125 MHz): δ = 11.9 (p), 13.8 (p), 20.7 (s), 44.7 (t), 55.7 (t), 62.5 (s), 72.3 (s), 73.4 (s), 127.6 (t, C-Ar), 127.7 (2×, t, C-Ar), 128.4 (2×, t, C-Ar), 138.6 (q, C-Ar), 217.0 (q, C=O). – IR (film on KBr): 3447 (s), 3088 (w), 3063 (m), 3031 (m), 2967 (s), 2934 (s), 2876 (s), 1707 (s), 1496 (m), 1455 (s), 1375 (m), 1249 (m), 1206 (m), 1159 (m), 1101 (s), 1101 (s), 1029 (s), 990 (m), 909 (w), 738 (m), 698 (m). – MS (EI, 70 eV): *m/z* (%): 255 ($[M^+]$, 0.6), 144 (30), 108 (12), 91 (100), 71 (12), 55 (22). – HRMS ($C_{15}H_{22}O_3$): calcd. 250.1569, found 250.1566. – EA ($C_{15}H_{22}O_3$): calcd. C 71.97, H 8.86, found C 71.94, H 8.69.

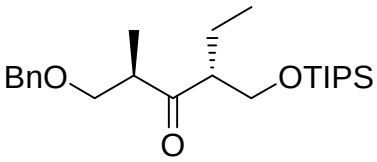
2-Benzyloxymethyl-4-hydroxymethyl-hexan-3-ol (**5**):



Sodium triacetoxyborohydride (5.65 g, 26.7 mmole, 4.0 equiv.) was dissolved in THF (75 mL) and cooled to 0 °C. 1-Benzyloxy-4-hydroxymethyl-2-methyl-hexan-3-one (**2**, 1.67 g, 6.67 mmole) in THF (35 mL) and acetic acid (5 mL) were added. The reaction mixture was stirred at 0 °C for 30 min. and 16 h at rt. The reaction was quenched by addition of sat. aqueous Rochelle's salt solution (100 mL) and stirred for 10 h. Sat. aqueous $NaHCO_3$ solution (100 mL) and CH_2Cl_2 (100 mL) were added, phases separated and the aqueous phase extracted with CH_2Cl_2 (3 × 75 mL). The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel, hexanes/ethyl acetate 3:1) yielding the monoprotected triol as a colorless oil (1.51 g, 6.00 mmole, 90%). The diastereomeric ratio was determined from the ^1H NMR spectrum of the crude product (dr = 9:1).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.77 (d, *J* = 6.9 Hz, 3 H, CHC*H*$_3$), 0.97 (t, *J* = 7.3 Hz, 3 H, CH_2CH_3), 1.33–1.47 (m, 2 H, CHC*H*$_A$H$_B$CH$_3$, C*H*CH$_3$), 1.55–1.72 (m, 1 H, CHCH$_A$*H*$_B$CH$_3$), 1.98–2.13 (m, 1 H, C*H*CH$_2$CH$_3$), 3.44 (br. s, O*H*), 3.39–3.53 (m, 2 H, C*H*$_2$OH), 3.60–3.65 (m, 1 H, C*H*OH), 3.81–3.95 (m, 2 H, BnOC*H*$_2$), 4.53 (br. s, 2 H, PhC*H*$_2$O), 7.27–7.40 (m, 5 H, Ar-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ =12.1 (p), 13.3 (p), 18.4 (s), 36.8 (t), 41.0 (t), 64.7 (s), 70.1 (s), 73.3 (s), 75.2 (s), 127.3 (2×, t, C-Ar), 127.6 (t, C-Ar), 128.3 (2x, t, C-Ar), 138.3 (q, C-Ar). – EA ($C_{25}H_{42}SiO_3$): calcd. C 71.39, H 9.59, found C 71.20, H 9.43.

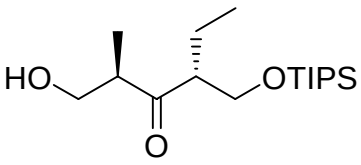
1-Benzyloxy-2-methyl-4-triisopropylsilanyloxymethyl-hexan-3-one (**6**):



Imidazole (4.68 g, 68.7 mmole, 2.0 equiv.) was dissolved in DMF (85 mL). 1-Benzyloxy-4-hydroxymethyl-2-methyl-hexan-3-one (**2**, 8.60 g, 34.4 mmole) and TIPSCl (7.92 g, 41.2 mmole, 1.2 equiv.) were added and was stirred for 50 h at rt. The reaction was quenched by addition of H_2O (250 mL) and the mixture was extracted with Et_2O (4 × 125 mL). The combined organic phases were dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel, hexanes/ethyl acetate 9:1) yielding the diprotected compound as a pale yellow oil (13.8 g, 33.9 mmole, 99%).

$[\alpha]_D^{20}$ = – 31.8 ° ($CHCl_3$, 0.78 g/100 mL). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.86 (t, *J* = 7.5 Hz, 3 H, CH_2CH_3), 1.00–1.06 (m, 21 H, TIPS), 1.08 (d, *J* = 7.0 Hz, 3 H, CHC*H*$_3$), 1.32–1.45 (m, 1 H, C*H*$_A$H$_B$CH$_3$), 1.57–1.68 (m, 1 H, CH$_A$*H*$_B$CH$_3$), 2.82–2.90 (m, 1 H, C*H*CH$_2$CH$_3$), 2.99–3.07 (m, 1 H, C*H*CH$_3$), 3.42 (dd, *J* = 9.1 Hz, *J* = 5.7 Hz, 1 H, BnOC*H*$_A$H$_B$), 3.67 (dd, *J* = 9.1 Hz, *J* = 7.3 Hz, 1 H, BnOCH$_A$*H*$_B$), 3.71 (dd, *J* = 9.5 Hz, *J* = 5.0Hz, 1 H, TIPSOC*H*$_A$H$_B$),3.85 (dd, *J* = 9.5 Hz, *J* = 8.4 Hz, 1 H, TIPSOCH$_A$*H*$_B$), 4.46 (d, *J* = 12.0 Hz, 1 H, Ar-C*H*$_a$H$_b$), 4.51 (d, *J* = 12.0 Hz, 1 H, Ar- CH$_a$*H*$_b$), 7.24–7.35 (m, 5 H, Ar-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.0 (3×, t, TIPS), 12.1 (p), 13.0 (p), 18.0 (6×, p, TIPS), 21.3 (s), 47.3 (t), 55.6 (t), 64.7 (s), 72.1 (s), 73.3 (s), 127.5 (2×, t, C-Ar), 127.6 (t, C-Ar), 128.3 (2×, t, C-Ar), 138.3 (q, C-Ar), 215.6 (q, C=O). – IR (film on KBr): 3030 (w), 2942 (s), 2865 (s), 1713 (m), 1462 (m), 1382 (m), 1250 (w), 1101 (s), 1069 (m), 1029 (m), 996 (m), 883 (m), 790 (m), 734 (m), 682 (m), 659 (m). – MS (EI, 70 eV): *m/z* (%): 406 ([M$^+$], 0.04), 363 (50), 257 (36), 255 (17), 91 (100). – HRMS ($C_{25}H_{42}SiO_3$): calcd. 406.2903, found 406.2906. – EA ($C_{25}H_{42}SiO_3$): calcd. C 70.88, H 10.41, found C 70.92, H 9.96.

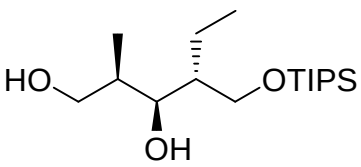
1-Hydroxy-2-methyl-4-triisopropylsilanyloxymethyl-hexan-3-one (**7**):



1-Benzyloxy-2-methyl-4-triisopropylsilanyloxymethyl-hexan-3-one (**6**, 5.00 g, 12.3 mmole) was dissolved in MeOH (60 mL) and Palladium on charcoal (10%, 150 mg) was added. The reaction vessel was purged with H_2 several times and then stirred for 4 h under H_2 atmosphere. The reaction mixture was filtered over Celite®, washing with Et_2O (100 mL). The organic phase was concentrated, taken up in Et_2O (100 mL) and filtered to remove traces of palladium. The deprotected product was received as a pale yellow oil (3.86 g, 12.2 mmole, 99%).

$[\alpha]_D^{20}$ = – 10.7 ° ($CHCl_3$, 0.98 g/100 mL). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ =0.91 (t, *J* = 7.5 Hz, 3 H, CH_2CH_3), 0.99–1.10 (m, 21 H, TIPS), 1.13 (d, *J* = 7.2 Hz, 3 H, $CHCH_3$), 1.37–1.46 (m, 1 H, $CH_AH_BCH_3$), 1.52–1.61 (m, 1 H, $CH_AH_BCH_3$), 2.39 (br. s, 1 H, OH), 2.82–2.87 (m, 1 H, $CHCH_3$), 2.87–2.92 (m, 1 H, $CHCH_2CH_3$), 3.64–3.71 (m, 2 H, $HOCH_AH_B$ and $TIPSOCH_AH_B$), 3.78 (dd, *J* = 11.3 Hz, *J* = 7.4 Hz, 1 H, $HOCH_AH_B$), 3.89–3.93 (m, 1 H, $TIPSOCH_AH_B$). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.0 (3×, t, TIPS), 12.1 (p), 12.7 (p), 18.1 (6×, p, TIPS), 22.2 (s), 49.0 (t), 54.9 (t), 64.5 (s), 64.6 (s), 216.2 (q). – IR (film on KBr): 3448 (w), 2942 (s), 2867 (s), 1709 (m), 1463 (m), 1383 (m), 1254 (w), 1101 (m), 1068 (m), 1016 (m), 997 (m), 883 (m), 790 (m), 682 (m), 659 (m). – MS (EI, 70 eV): *m/z* (%): 317 ($[M^+$+H], 0.1), 273 (100), 243 (54), 131 (55), 119 (36), 103 (35), 95 (28), 75 (34), 43 (47). – HRMS ($C_{17}H_{36}SiO_3$+H): calcd. 317.2512, found 317.2507. – EA ($C_{17}H_{36}SiO_3$): calcd. C 64.50, H 11.46, found C 64.73, H 10.95.

2-Methyl-4-triisopropylsilanyloxymethyl-hexane-1,3-diol (**8**):

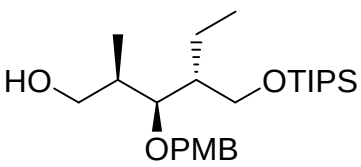


Sodium triacetoxyborohydride (1.59 g, 7.50 mmole, 3.0 equiv.) was dissolved in THF (30 mL) and cooled to 0 °C. 1-Hydroxy-2-methyl-4-triisopropylsilanyloxymethyl-hexan-3-one (**7**, 791 mg, 2.50 mmole) in THF (30 mL) and acetic acid (2 mL) were added. The reaction mixture was stirred at 0 °C for 30 min and 16 h at rt. The reaction was quenched by addition of sat. aqueous Rochelle's salt solution (25 mL) and stirred for 10 h. Sat. aqueous $NaHCO_3$ solution (25 mL) and CH_2Cl_2 (50 mL) were added, phases separated and the aqueous phase extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel, hexanes/ethyl acetate 3:1) yielding the monoprotected triol as a

colorless oil (573 mg, 1.80 mmole, 90%). The diastereomeric ratio was determined from the ^{1}H NMR spectrum of the crude product (dr = 9:1).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.87 (t, *J* = 7.4 Hz, 3 H, CH_2CH_3), 0.99 (d, *J* = 7.0 Hz, 3 H, $CHCH_3$), 1.00–1.06 (m, 21 H, TIPS), 1.25–1.46 (m, 2 H, $CHCH_AH_BCH_3$, $CHCH_2CH_3$), 1.55–1.70 (m, 1 H, $CHCH_AH_BCH_3$), 1.70–1.84 (m, 1 H, $CHCH_3$), 3.27 (br. s, OH), 3.58–3.81 (m, 3 H, CH_2OH, CHOH), 3.85 (dd, *J* = 9.5 Hz, *J* = 5.0 Hz, 1 H, $TIPSOCH_AH_B$), 3.99 (dd, *J* = 9.5 Hz, *J* = 8.4 Hz, 1 H, $TIPSOCH_AH_B$). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.0 (3×, t, TIPS), 12.1 (p), 13.0 (p), 18.0 (6×, p, TIPS), 21.3 (s), 38.3 (t), 42.9 (t), 64.7 (s), 69.1 (s), 73.3 (t). – EA ($C_{17}H_{38}SiO_3$): calcd. C 64.09, H 12.02, found C 64.26, H 12.11.

3-(4-Methoxy-benzyloxy)-2-methyl-4-triisopropylsilanyloxymethyl-hexan-1-ol (**9**):



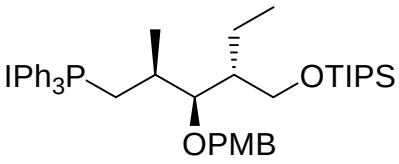
2-Methyl-4-triisopropylsilanyloxymethyl-hexane-1,3-diol (**8**, 1.36 g, 4.30 mmole) was dissolved in $CHCl_3$ (50 mL) containing 4 Å molecular sieves. *P*-Anisaldehyde dimethyl acetal (3.92 g, 21.5 mmole, 5.0 equiv.) and *p*-toluenesulfonic acid monohydrate (80 mg) were added and the mixture was stirred for 5 h at rt. The reaction was quenched with sat. aqueous $NaHCO_3$ solution (35 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 75 mL). The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel, hexanes/ethyl acetate 9:1) yielding the acetal as a pale yellow oil (1.78 g, 4.08 mmole, 95%) which was used without further purification.

The above acetal (574 mg, 1.55 mmole) was dissolved in CH_2Cl_2 and cooled to 0 °C. DIBAL (7.75 mL, 7.75 mmole, 5.2 equiv., 1 M in toluene) was added dropwise and the mixture stirred for 4 h at 0 °C. The reaction was quenched by careful addition of MeOH (2.5 mL) and was diluted with sat. aqueous Rochelle's salt solution (100 mL) and ethyl acetate (50 mL). The phases were separated and the aqueous phase was extracted with ethyl acetate (2 × 50 mL). The combined organic phases were dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel, hexanes/ethyl acetate 3:1) yielding the diprotected alcohol as a pale yellow oil (391 g, 1.05 mmole, 68%) along with some completely deprotected compound (40 mg, 0.15 mmole, 10%).

^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.88–0.95 (m, 6 H, CH_2CH_3, $CHCH_3$) , 1.00–1.08 (m, 21 H, TIPS), 1.13–1.24 (m, 1 H, $CHCH_AH_BCH_3$), 1.32–1.39 (m, 1 H, $CHCH_3$), 1.52–1.64 (m, 1 H, $CHCH_AH_BCH_3$), 1.93–2.05 (m, 1 H, $CHCH_2CH_3$), 2.20 (br. s, 1 H, OH), 3.53–3.73 (m, 4 H,

C*H*OPMB, TIPSOC*H*$_A$H$_B$, HOC*H*$_2$), 3.80 (br. s, 3 H, OC*H*$_3$), 3.81–3.88 (m, 1 H, TIPSOCH$_A$*H*$_B$), 4.43–4.67 (m, 2 H, OC*H*$_2$Ar), 6.87 (d, 2 H, *J* = 8.6 Hz, Ar-H), 7.20–7.28 (m, 2 H, Ar-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = 12.0 (p), 15.1 (s), 18.0 (t), 18.8 (s), 20.5 (s), 37.5 (t), 45.0 (t), 55.2 (p), 62.3 (s), 66.8 (s), 73.4 (p), 80.1 (t), 113.7 (t, C-Ar), 129.1 (t, C-Ar), 131.1 (q, C-Ar), 159.1 (q, C-Ar). – IR (film on KBr): 2960 (m), 2941 (m), 2866 (m), 1514 (m), 1463 (w), 1248 (m), 1094 (m), 1038 (m), 684 (w). – MS (EI, 70 eV): *m/z* (%): 439 ([M$^+$], 1.1), 341 (8), 302 (46), 257 (11), 128 (28), 121 (100), 97 (32). – HRMS ($C_{25}H_{46}SiO_4$): calcd. 439.3244, found 439.3249. – EA ($C_{25}H_{46}SiO_4$): calcd. C 68.44, H 10.57, found C 68.40, H 10.20.

[3-(4-Methoxy-benzyloxy)-2-methyl-4-triisopropylsilanyloxymethyl-hexyl]-triphenyl-phosphonium iodide (**10**):



Imidazole (180mg, 2.64 mmole, 2.2 equiv.), triphenylphosphine (629 mg, 2.40 mmole, 2.0 equiv.) and 3-(4-Methoxy-benzyloxy)-2-methyl-4-tri-*iso*-propylsilanyloxy-methyl-hexan-1-ol (526 mg, 1.20 mmol) were dissolved in CH_2Cl_2. Iodine (609 mg, 2.40 mmol, 2.0 equiv.) was added in one portion. The mixture was stirred at rt for 1 h before being quenched by addition of sat. aqueous $Na_2S_2O_3$ solution (2.5 mL). After addition of CH_2Cl_2 (15 mL), the phases were separated, the aqueous phase was washed with H_2O (10 mL) and brine (10 mL), dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel, hexanes/ethyl acetate 9:1) to yield the corresponding iodide as a pale yellow oil (658 mg, 100%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ = 0.81–0.91 (m, 3 H, CH$_2$C*H*$_3$), 0.95–1.05 (m, 24 H, TIPS, CHC*H*$_3$), 1.13–1.24 (m, 1 H, CHC*H*$_A$H$_B$CH$_3$), 1.32–1.39 (m, 1 H, C*H*CH$_3$1.52–1.64(m, 1 H, CHC*H*$_A$H$_B$CH$_3$), 1.85–1.98 (m, 1 H, C*H*CH$_2$CH$_3$), 3.11–3.26 (m, 1 H, C*H*OPMB), 3.53 (dd, 1 H, *J* = 6.7 Hz, *J* = 4.0 Hz, IC*H*$_A$H$_B$), 3.55–3.63 (m, 1 H, ICH$_A$*H*$_B$), 3.80 (dd, 1 H, *J* = 9.9 Hz, *J* = 4.7 Hz, TIPSOCH$_A$*H*$_B$), 3.73 (s, 3 H, OC*H*$_3$), 3.80 (dd, 1 H, *J* = 9.9 Hz, *J* = 4.7 Hz, TIPSOC*H*$_A$H$_B$), 4.47 (d, 1 H, *J* = 11.0 Hz, OC*H*$_A$H$_B$Ar), 4.53 (d, 1 H, *J* = 11.0 Hz, OCH$_A$*H*$_B$Ar), 6.79 (d, 2 H, *J* = 8.3 Hz, Ar-H), 7.20 (d, 2 H, *J* = 8.3 Hz, Ar-H).^{13}C NMR ($CDCl_3$, 125 MHz): δ = 12.1 (6×, p, TIPS), 14.9 (s), 15.5 (p), 18.1 (3×, t, TIPS), 18.5 (s), 20.5 (s), 38.4 (t), 45.5 (t), 55.3 (p), 62.0 (s), 74.5 (s), 81.4 (t), 113.7 (2×, t, C-Ar), 128.9 (2×, t, C-Ar), 131.2 (q, C-Ar), 159.0 (q, C-Ar). – IR (film on KBr): 2959 (m), 2941 (m), 2865 (m), 1613 (w), 1514 (m), 1462 (m), 1382 (w), 1301 (w), 1248 (m), 1172 (m), 1097 (m), 1066 (m),

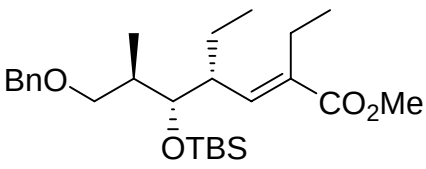
1040 (m), 995 (w), 882 (w), 821 (w), 681 (w). – MS (EI, 70 eV): *m/z* (%): 548 ([M^+], 0.42), 237 (12), 174 (18), 121 (100), 75 (11), 58 (63). – HRMS ($C_{25}H_{45}IO_3Si$): calcd. 548.2183, found 548.2176. – EA ($C_{25}H_{45}IO_3Si$): calcd. C 54.73, H 8.27, found C 54.66, H 8.39.

A mixture of the above iodide (373 mg, 0.68 mmole) and triphenylphosphine (1.78 g, 6.80 mmole, 10.0 equiv.) was heated to 95 °C upon melting of the phosphine and was kept at this temperature for 20 h. After cooling, toluene (1 mL) was added and the mixture was directly subjected to column chromatography (silica gel, CH_2Cl_2 → CH_2Cl_2/MeOH 19:1 → 9:1) providing the product as a yellowish foam (461 mg, 0.57 mmole, 84%).

– No NMR data obtained due to low solubility in common NMR solvents –

IR (film on KBr): 2944 (w), 2887 (w), 1612 (w), 1513 (w), 1463 (w), 1438 (w), 1390 (w), 1250 (w), 1177 (w), 1111 (w), 1066 (w), 996 (w), 919 (w), 882 (w), 747 (w), 721 (w), 690 (w). – MS (EI, 70 eV): *m/z* (%): 810 ([M^+], 0.33), 485 (71), 347 (73), 262 (100), 183 (83), 121 (72), 108 (34). – HRMS ($C_{43}H_{60}IO_3PSi$): calcd. 810.3095, found 810.3091. – EA ($C_{43}H_{60}IO_3PSi$): calcd. C 63.69, H 7.46, found C 63.56, H 7.14.

7-Benzyloxy-5-(tert-butyl-dimethyl-silanyloxy)-2,4-diethyl-6-methyl-hept-2-enoic acid methyl ester (**13**):



2-Benzyloxymethyl-4-hydroxymethyl-hexan-3-ol (**5**, 781 mg, 3.12 mmole) was dissolved in CH_2Cl_2 (5 mL). Iodobenzene diacetate (1.21 g, 3.74 mmole, 1.2 equiv.) and TEMPO (98 mg, 0.62 mmole, 0.2 equiv.) were added and the mixture was stirred for 7 h at rt. The reaction was quenched by addition of sat. aqueous NH_4Cl solution (10 mL) and sat. aqueous $Na_2S_2O_3$ solution (10 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were dried over $MgSO_4$ and dried *in vacuo*. The crude product was used in the following reaction without further purification.

2-(Triphenyl-λ^5-phosphanylidene)-butyric acid methyl ester (1.36 g, 3.74 mmole, 1.2 equiv.) was suspended in benzene (10 mL) and the crude aldehyde (781 mg, 3.12 mmol) in benzene (5 mL) was added. The mixture was heated to reflux for 18 h. After cooling to rt, the reaction was quenched by addition of H_2O (20 mL). The phases were separated and the aqueous phase was extracted with ethyl acetate (3 × 25 mL). The combined organic phases were dried over Na_2SO_4 and concentrated *in vacuo*. The crude product was purified by column

chromatography (silica gel, hexanes/ethyl acetate 3:1) yielding the olefin alcohol as colorless yellow oil (836 mg, 2.50 mmole, 80% over 2 steps).

The olefin (759 mg, 2.27 mmole) was dissolved in CH_2Cl_2 and cooled to 0°C. 2,6-Lutidine (486 mg, 4.54 mmole, 2.0 equiv.) and *tert*-butyldimethylsilyl trifluoromethanesulfonate (665 mg, 2.5 mmole, 1.1 equiv.) were added and the mixture was stirred for 1 h at 0 °C and 20 h at rt. The reaction was quenched by addition of sat. aqueous $NaHCO_3$ solution (10 mL). The phases were separated and the aqueous phase was extracted with CH_2Cl_2 (3 × 20 mL). The combined organic phases were dried over $MgSO_4$ and concentrated *in vacuo*. The crude product was purified by column chromatography (silica gel, hexanes/ethyl acetate 9:1) yielding the protected olefin as colorless oil (815 mg, 1.82 mmole, 80%).

$[\alpha]_D^{20}$ = +7.1° ($CHCl_3$, 1.94 g/100 mL). – ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 0.02 (s, 3 H, SiC*H*$_3$), 0.07 (s, 3 H, SiC*H*$_3$), 0.78 (t, 3 H, *J* =7.5 Hz, C=CCH$_2$C*H*$_3$), 0.86–0.91 (m, 12 H, 3 × SiCC*H*$_3$, CHC*H*$_3$), 0.99 (t, 3 H, *J* = 7.5 Hz, CHCH$_2$C*H*$_3$), 1.21–1.32 (m, 1 H, CHC*H*$_A$H$_B$CH$_3$), 1.68–1.78 (m, 1 H, CHCH$_A$*H*$_B$CH$_3$), 1.94–2.05 (m, 1 H, BnOCH$_2$C*H*), 2.29 (q, 2 H, *J* = 7.5 Hz, C=CC*H*$_2$CH$_3$), 2.47–2.57 (m, 1 H, C*H*CH$_2$CH$_3$), 3.21–3.29 (m, 1 H, BnOC*H*$_A$H$_B$), 3.46–3.57 (m, 2 H, BnOCH$_A$*H*$_B$ and C*H*OTBS), 3.72 (s, 3 H, OC*H*$_3$), 4.46 (d, 2 H, *J* = 2.0 Hz, C*H*$_2$ benzylic), 6.54 (d, 1 H, *J* = 10.9 Hz, C=C*H*), 7.28–7.35 (m, 5 H, Ar-H). – ^{13}C NMR ($CDCl_3$, 100 MHz): δ = –4.1 (p), –4.0 (p), 12.0 (p), 13.7 (p), 15.0 (p), 18.4 (q), 20.5 (s), 22.8 (s), 25.7 (q), 26.1 (3×, p, TBS), 38.6 (t), 44.0 (t), 51.5 (t), 72.5 (s), 73.0 (s), 127.4 (t, C-Ar), 127.5 (2 ×, t, C-Ar), 128.3 (2 ×, t, C-Ar), 133.9 (), 138.7 (q, C-Ar), 144.6 (t), 168.2 (q). – IR (film on KBr): 3030 (w), 2957 (s), 2932 (m), 2877 (m), 2857 (m), 1716 (s), 1643 (w), 1496 (w), 1462 (m), 1435 (w), 1361 (w), 1303 (m), 1253 (m), 1225 (m), 1189 (w), 1092 (m), 1052 (m), 1006 (m), 939 (w), 886 (w), 862 (m), 837 (m), 810 (w), 775 (m), 735 (w), 698 (w). – MS (EI, 70 eV): *m/z* (%):448 ([M$^+$], 0.06), 293 (43), 187 (42), 145 (22), 91 (100). – HRMS ($C_{26}H_{45}O_4Si$): calcd. 449.3087, found 449.3090. – EA ($C_{26}H_{44}O_4Si$): calcd. C 69.45, H 9.88, found C 69.47, H 9.69.