Insights into Conversion of Propargylic Tosylates into Bromoallenes

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Table of Contents

General Information ............................................................................................................. S 2
Synthetic route to 10b (Scheme S1) .................................................................................. S 2
Synthetic route to 10e (Scheme S2) .................................................................................. S 2
Synthesis of 7a, 7b, 7c ........................................................................................................ S 3
Synthesis of 7d and 7a' ...................................................................................................... S 4
Synthesis of 10a, 17 and 18 ............................................................................................. S 5
Synthesis of 19, 20 ........................................................................................................... S 6
Synthesis of 21, (±)-22 ..................................................................................................... S 7
Synthesis of (R)-22, 10b .................................................................................................. S 8
Synthesis of 23, 10c, 10d ................................................................................................ S 9
Synthesis of 25, 26 .......................................................................................................... S 10
Synthesis of 27, 28, 29 .................................................................................................... S 11
Synthesis of 10e, data for 8 and 9 .................................................................................. S 12
Cleaving TBS in 8 giving 8' .............................................................................................. S 13
Data for 11a, 11b, 12a ..................................................................................................... S 13
Conversion of 11b to 11b' ............................................................................................... S 14
Data for 11c, 11d, 12c, 12a ............................................................................................. S 14
Data for 11e .................................................................................................................... S 15
Conversion of 11e to 11e' ............................................................................................. S 15
References for Supporting Information .......................................................................... S 15
NMR for 7a, 7a', 7b, 7c, 7d ............................................................................................. S 16
NMR for 8, 8', 9, 10b, 10c ............................................................................................. S 26
NMR for 10d, 10e, ........................................................................................................ S 36
NMR for 11b, 11b', 11c, 11d ........................................................................................ S 40
NMR for 11e, 11e', 12a, 12c ........................................................................................ S 48
NMR for 12a, 17, 18 ...................................................................................................... S 56
NMR for (Z)-19, (E)-19 ................................................................................................. S 62
NMR for 20, 21 ............................................................................................................ S 66
NMR for (±)-22, 23 ....................................................................................................... S 70
NMR for 25, 26 ............................................................................................................. S 74
NMR for 27, 28, 29 ...................................................................................................... S 78
**General Information.** Dry solvents were obtained as follows: THF was distilled over Na/Ph$_2$CO under argon prior to use. CH$_3$CN, DMF, DMSO, and CH$_2$Cl$_2$ were distilled over CaH$_2$ prior to use. Dry Et$_2$O for the bromoalleneation was “anhydrous” diethyl ether of reagent grade (with H$_2$O content < 0.3%) from commercial sources and used as such without any further purification. All other reagents were commercially available and were used as received. PE (chromatography solvent) refers to petroleum ether (b.p. 60-90 °C). TBS and TIPS (protecting groups) refer to dimethyl-$t$-butylsilyl and trisopropylsilyl group, respectively. PCC stands for pyridinium chlorochromate. DDQ refers to 2,3-dichloro-5,6-dicyano-1,4-benzoquinone.

Scheme S1. Synthesis of 10b.

Scheme S2. Synthesis of 10e.
Synthesis of 7a. A solution of the known starting alcohol\(^1\) (4.071 g, 20.32 mmol), Et\(_3\)N (4.3 mL, 30.45 mmol), \(p\)-TsCl (4.643 g, 24.36 mmol), DMAP (122 mg, 1.00 mmol) in CH\(_2\)Cl\(_2\) (100 mL) was stirred at ambient temperature for 5 h. The reaction mixture was diluted with EtOAc, washed with aq. sat. NH\(_4\)Cl, H\(_2\)O, and brine before being dried over anhydrous Na\(_2\)SO\(_4\). Removal of the solvent by rotary evaporation and column chromatography (50:1 PE/EtOAc) on silica gel gave tosylate 7a as a colorless oil (6.100 g, 17.23 mmol, 85%): \([\alpha]_D^{26} +44.25 (c 1.50, \text{CHCl}_3); 97.9\%\) e.e. as determined by HPLC on a CHFT-IRALPAK IC column (0.46 cm × 25 cm) eluting with 98:2 hexane/i-PrOH at a rate of 1.0 mL/min with UV detector set to 220 nm (\(t_R(\text{Major}) = 24.58\) min, \(t_R(\text{Minor}) = 26.93\) min). \(^1\)H NMR (300 MHz, CDCl\(_3\) \(\delta\) 7.82 (ddd, \(J = 2.0, 4.0, 8.5\) Hz, 2H), 7.35-7.30 (m, 2H), 5.05 (ddd, \(J = 2.1, 5.2, 6.6\) Hz, 1H), 3.84 (dd, \(J = 6.7, 11.2\) Hz, 1H), 3.80 (dd, \(J = 5.0, 11.2\) Hz, 1H), 2.44 (s, 3H), 2.43 (d, \(J = 2.0\) Hz, 1H), 0.86 (s, 9H), 0.043 (s, 3H), 0.041 (s, 3H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\) \(\delta\) 144.8, 133.8, 129.6, 128.1, 76.8 (2'C), 71.4, 65.0, 25.7, 21.6, 18.2, −5.4, −5.3; FT-IR (film) 3283, 2954, 2930, 2885, 2858, 2858, 2127, 1598, 1472, 1464, 1371, 1256, 1191, 1097, 1020, 910, 836, 779, 665 cm\(^{-1}\). ESI-MS \(\text{m/z} 377.1 ([\text{M}+\text{Na}]^+)\), 409.2 ([\text{M}+\text{MeOH}+\text{Na}]^+); ESI-HRMS calcd for C\(_{17}\)H\(_{28}\)O\(_4\)SiNaS ([\text{M}+\text{Na}]^+) 377.1213, found 377.1218.

Synthesis of 7b. A solution of the known starting alcohol\(^1\) (200 mg, 1.00 mmol), Et\(_3\)N (0.21 mL, 1.50 mmol), and MsCl (0.093 mL, 1.20 mmol) in CH\(_2\)Cl\(_2\) (5 mL) was stirred at 0 °C for 30 min. The reaction mixture was diluted with EtOAc, washed with aq. sat. NH\(_4\)Cl, H\(_2\)O, and brine before being dried over anhydrous Na\(_2\)SO\(_4\). Removal of the solvent by rotary evaporation and column chromatography (20:1 PE/EtOAc) on silica gel afforded mesylate 7b as a colorless oil (240 mg, 0.86 mmol, 86%): \([\alpha]_D^{25} +54.35 (c 1.20, \text{CHCl}_3). \(^1\)H NMR (300 MHz, CDCl\(_3\) \(\delta\) 5.15 (dt, \(J = 2.3, 6.0\) Hz, 1H), 3.87 (d, \(J = 5.6\) Hz, 2H), 3.10 (s, 3H), 2.69 (d, \(J = 2.4\) Hz, 1H), 0.89 (s, 9H), 0.08 (s, 6H); \(^{13}\)C NMR (75 MHz, CDCl\(_3\) \(\delta\) 77.5, 76.9, 72.0, 65.0, 39.0, 25.7, 18.2, −5.4, −5.5; FT-IR (film) 3284, 3031, 2887, 2859, 2127, 1473, 1370, 1257, 1180, 1135, 1086 cm\(^{-1}\). ESI-MS \(\text{m/z} 301.2 ([\text{M}+\text{Na}]^+)\), 333.2 ([\text{M}+\text{MeOH}+\text{Na}]^+); ESI-HRMS calcd for C\(_{11}\)H\(_{22}\)O\(_4\)SiNaS ([\text{M}+\text{Na}]^+) 301.09003, found 301.09108.

Synthesis of 7c. A solution of the known starting alcohol\(^1\) (200 mg, 1.00 mmol), Et\(_3\)N (0.21 mL, 1.50 mmol), \(p\)-CF\(_3\)C\(_6\)H\(_4\)SO\(_2\)Cl (294 mg, 1.2 mmol) and DMAP (1 mg) in CH\(_2\)Cl\(_2\) (5 mL) was stirred at ambient temperature over night. The reaction mixture was diluted with EtOAc, washed with aq. sat. NH\(_4\)Cl, H\(_2\)O, and brine before being dried over anhydrous Na\(_2\)SO\(_4\). Removal of the solvent by rotary evaporation and column chromatography (45:1 PE/EtOAc) on silica gel afforded
7c as a colorless oil (333 mg, 0.82 mmol, 82%): $[\alpha]_D^{25} +42.79$ (c 1.48, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 8.09 (d, $J = 8.1$ Hz, 2H), 7.81 (d, $J = 7.7$ Hz, 2H), 5.14 (t, $J = 5.0$ Hz, 1H), 3.85 (d, $J = 5.8$ Hz, 2H), 2.46 (s, 1H), 0.85 (s, 9H), 0.04 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 140.5, 135.6 and 135.1 (two middle lines of a quartet, $^3J_{C-F} = 33$ Hz, with two outer lines buried in the noise), 128.6, 126.2 (q, $^3J_{C-F} = 3.4$ Hz), 124.9 and 121.2 (two middle lines of a quartet, $^1J_{C-F} = 272$ Hz, with two outer lines buried in the noise), 77.6, 76.2, 72.6, 65.0, 18.2, −5.5, −5.6; FT-IR (film) 3310, 3106, 2956, 2931, 2887, 2859, 2130, 1610, 1473, 1407, 1380, 1325, 1194, 1064, 913, 843, 780 cm$^{-1}$. ESI-MS $m/z$ 431.1 ([M+Na]$^+$), 463.2 ([M+MeOH+Na]$^+$); ESI-HRMS calcd for C$_{17}$H$_{23}$O$_4$F$_3$SSiNa ([M+Na]$^+$) 431.0931, found 431.0950.

Synthesis of 7d. A solution of the known starting alcohol$^1$ (200 mg, 1.00 mmol), Et$_3$N (0.21 mL, 1.50 mmol), 2,4,6-tri-isopropyl-benzenesulfonyl chloride (363 mg, 1.2 mmol) and DMAP (183 mg, 1.50 mmol) in CH$_2$Cl$_2$ (5mL) was stirred at ambient temperature over night. The reaction mixture was diluted with EtOAc, washed with aq. sat. NH$_4$Cl, H$_2$O, and brine before being dried over anhydrous Na$_2$SO$_4$. Removal of the solvent by rotary evaporation and column chromatography (50:1 PE/EtOAc) on silica gel afforded 7d as a colorless oil (462 mg, 1.00 mmol, 100%): $[\alpha]_D^{25} +7.77$ (c 1.30, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.17 (s, 2H), 5.16 (dt, $J = 2.2$, 2.6 Hz, 1H), 4.17 (heptet, $J = 6.8$ Hz, 2H), 3.91-3.80 (m, 2H), 2.91 (heptet, $J = 6.9$ Hz, 1H), 2.28 (d, $J = 1.7$ Hz, 1H), 1.31-1.23 (m, 18H), 0.88 (s, 9H), 0.072 (s, 3H), 0.066 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 153.6, 150.5, 130.8, 123.5, 77.1, 76.5, 70.5, 65.1, 34.2, 29.6, 25.7, 24.7, 24.6, 23.6, 18.2, −5.4, −5.5; FT-IR (film) 3312, 2958, 2930, 2869, 2127, 1600, 1463, 1381, 1351, 1180, 897, 839, 779 cm$^{-1}$. ESI-MS $m/z$ 489.3 ([M+Na]$^+$); MALDI-HRMS calcd for C$_{25}$H$_{42}$O$_4$SSiNa ([M+Na]$^+$) 489.2465, found 489.2471.

Removal of TBS in 7a (7a'). DDQ (35 mg, 0.15 mmol) was added to a solution of 7a (354 mg, 1.00 mmol) in CH$_3$CN-H$_2$O (9:1 v/v, 10 mL) stirred at ambient temperature. The stirring was continued at the same temperature over night. The reaction mixture was diluted with EtOAc, washed with aq. sat. NaHSO$_3$, aq. sat.NH$_4$Cl, H$_2$O, and brine before being dried over anhydrous Na$_2$SO$_4$. Removal of the solvent by rotary evaporation and column chromatography (3:1 PE/EtOAc) on silica gel afforded 7a' as a colorless oil (240 mg, 1.00 mmol, 100%): $[\alpha]_D^{23} +71.90$ (c 0.65, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.84 (d, $J = 8.1$ Hz, 2H), 7.35 (d, $J = 8.1$ Hz, 2H), 5.13 (dt, $J = 2.3$, 5.5 Hz, 1H), 3.83 (t, $J = 5.5$ Hz, 2H), 2.50 (br s, OH, 1H), 2.47 (d, $J = 2.4$ Hz, 1H), 2.45 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 145.2, 133.3, 129.8, 128.1, 77.6, 76.2, 71.7, 64.6, 21.7; FT-IR (film) 3546, 3285, 2928, 2127, 1597, 1363, 1191, 1176, 1096, 900, 814, 668, cm$^{-1}$. ESI-MS $m/z$ 263.1 ([M+Na]$^+$); ESI-HRMS Calcd for C$_{11}$H$_{12}$O$_4$SNa ([M+Na]$^+$) 263.03485, found 263.03486.
Synthesis of 10a. Cf. our previous work. 

![Chemical Structure](image)

Synthesis of 17. The known bromide 13 (3.437 g, 15 mmol) was dissolved in dry THF (10 mL), 2 mL of this solution was added via a syringe to a suspension of freshly prepared Mg turnings (437 mg, 18 mmol) and a small grain of solid I2 in dry THF (5 mL) stirred at ambient temperature under argon. The stirring was continued until the color of iodine faded. The remaining solution of 13 was then introduced slowly to keep the mixture gently boiling (ca. over 1 h). After completion of the addition, the mixture was heated to reflux for another hour before being cooled down to ambient temperature for following described reaction with aldehyde 16.

A solution of the known alcohol 15 (3.066 g, 15 mmol), PCC (6.480 g, 30 mmol), and NaOAc (6.480 g, 81 mmol) in dry CH2Cl2 (75 mL) was stirred at ambient temperature for 6 h. The solvent was removed by rotary evaporation. The residue was chromatographed (eluting with PE) on silica gel to give aldehyde 16.

A portion of the above prepared 16 (910 mg, 3.18 mmol) was dissolved in dry THF (50 mL). The solution was stirred at -78°C under argon when the above prepared Grinard reagent (14, prepared from 13) was introduced via a syringe. After completion of the addition, the cooling bath was allowed to warm naturally to ambient temperature. The reaction mixture was diluted with EtOAc, washed with aq. NH4Cl, H2O, and brine before being dried over anhydrous Na2SO4. Removal of the solvent by rotary evaporation and column chromatography (6:1 PE/ EtOAc) on silica gel afforded alcohol 17 as a colorless oil (2.043 g, 5.79 mmol, 39% from 15): 1H NMR (300 MHz, CDCl3) δ 7.41-7.22 (m, 5H), 4.52 (s, 2H), 3.71-3.56 (m, 3H), 3.51 (t, J = 6.3 Hz, 2H), 3.13 (br s, OH, 1H), 1.90-1.35 (m, 8H), 0.90 (s, 9H), 0.07 (s, 6H); 13C NMR (75 MHz, CDCl3) δ 138.3, 128.3, 127.6, 127.5, 72.9, 71.1, 70.5, 63.5, 34.6, 34.4, 29.2, 26.2, 25.9, 18.3, -5.4; FT-IR (film) 3427, 3088, 3064, 3030, 2929, 2857, 1496, 1471, 1454, 1388, 1361, 1255, 1099, 835, 776, 735, 697 cm-1. ESI-MS m/z 353.1 ([M+H]+), 375.1 ([M+Na]+); ESI-HRMS calcd. for C20H37O3Si ([M+H]+) 353.25065, found 353.25113.

Synthesis of 18. A solution of alcohol 17 (1.983 g, 5.62 mmol), PCC (2.428 g, 11.24 mmol), and NaOAc (2.428 g, 29.61 mmol) in dry CH2Cl2 (75 mL) was stirred at ambient temperature for 6 h. The solvent was removed by rotary evaporation. The residue was chromatographed (6:1 PE/EtOAc) on silica gel to give keton 18 as a colorless oil (1.544 g, 4.40 mmol, 78%): 1H NMR (300 MHz, CDCl3) δ 7.41-7.22 (m, 5H), 4.49 (s, 2H), 3.61 (t, J = 6.2 Hz, 2H), 3.49 (t, J = 6.0 Hz, 2H), 2.61-2.41 (m, 4H), 1.98-1.69 (m, 4H), 0.89 (s, 9H), 0.04 (s, 6H); 13C NMR (75 MHz, CDCl3) δ 210.6, 138.4, 128.3, 127.6, 127.5, 72.8, 69.3, 62.2, 39.4, 39.1, 26.8, 25.9, 23.8, 18.3, -5.4; FT-IR
The synthesis of compounds 19 and 20 is described in detail below.

**Synthesis of 19.** A solution of (EtO)2(PO)CH2CO2Et (2.2 mL, 10.9 mmol) in dry THF (7 mL) was added dropwise to a mixture of NaH (438 mg, 10.9 mmol) in dry THF (5 mL) stirred at 0 °C under argon. The mixture was stirred for another 2 h at the same temperature. A solution of ketone 18 (1.544 g, 4.38 mmol) in dry THF (8 mL) was then introduced. The mixture was heated to reflux overnight before being cooled down to ambient temperature, diluted with EtOAc, washed with aq. sat. NH4Cl, H2O and brine, and dried over anhydrous Na2SO4. Removal of the solvent by rotary evaporation and column chromatography (15:1 PE/EtOAc) on silica gel afforded (Z)-19 (less polar, 610 mg, 1.45 mmol, 33.1%) and (E)-19 (more polar, 690 mg, 1.64 mmol, 37.4) as colorless oils.

(Total yield: 71%)

Data for (Z)-19: 1H NMR (500 MHz, CDCl3) δ 7.44-7.22 (m, 5H), 5.60 (s, 1H), 4.45 (s, 2H), 4.09 (q, J = 7.1 Hz, 2H), 3.60 (t, J = 6.5 Hz, 2H), 3.43 (t, J = 6.3 Hz, 2H), 2.59 (t, J = 8.0 Hz, 2H), 2.22 (t, J = 7.6 Hz, 2H), 1.74 (quintet, J = 7.6 Hz, 2H), 1.63 (quintet, J = 7.9 Hz, 2H), 1.22 (t, J = 7.1 Hz, 3H), 0.85 (s, 9H), 0.05 (s, 6H); 13C NMR (125 MHz, CDCl3) δ 166.4, 163.5, 138.5, 128.4, 127.62, 127.55, 115.7, 72.9, 69.5, 63.2, 59.5, 35.0, 31.8, 28.6, 27.7, 25.9, 18.3, 14.3, –5.3; FT-IR (film) 3031, 2953, 2929, 2857, 1716, 1642, 1471, 1454, 1255, 1178, 1144, 1103, 1040, 836, 775, 735, 697 cm–1. ESI-MS m/z 421.1 ([M+H]+), 443.1 ([M+Na]+); ESI-HRMS calcd. for C24H41O4Si ([M+H]+) 421.27686, found 421.27744.

Data for (E)-19: 1H NMR (500 MHz, CDCl3) δ 7.37-7.24 (m, 5H), 5.62 (s, 1H), 4.46 (s, 2H), 4.09 (q, J = 7.2 Hz, 2H), 3.60 (t, J = 6.2 Hz, 2H), 3.48 (t, J = 6.6 Hz, 2H), 2.69-2.59 (m, 2H), 2.24-2.13 (m, 2H), 1.83-1.56 (m, 4H), 1.23 (t, J = 7.1 Hz, 3H), 0.85 (s, 9H), 0.05 (s, 6H); 13C NMR (125 MHz, CDCl3) δ 166.4, 163.6, 138.6, 128.3, 127.6, 115.7, 72.9, 69.5, 63.2, 59.5, 34.7, 30.8, 29.0, 28.7, 25.9, 18.3, 14.3, –5.3; FT-IR (film) 3031, 2953, 2929, 2857, 1716, 1642, 1471, 1454, 1255, 1178, 1144, 1103, 1040, 836, 775, 736, 697 cm–1. ESI-MS m/z 421.1 ([M+H]+), 443.1 ([M+Na]+); ESI-HRMS calcd. for C24H40NaO4Si ([M+Na]+) 443.25881, found 443.25947.

**Synthesis of 20.** A mixture of 19 (Z/E mixture, 1.300 g, 3.09 mmol) and 10% Pd-C (240 mg) in EtOAc (15 mL) was stirred at ambient temperature under H2 (1 atm) for 8 h. The solids were filtered off. The filtrate was concentrated on a rotary evaporator. The residue was chromatographed (4:1 PE/EtOAc) on silica gel to give 20 as a colorless oil (854 mg, 2.57 mmol, 83%); 1H NMR (300 MHz, CDCl3) δ 4.13 (q, J = 7.0 Hz, 2H), 3.65 (t, J = 6.4 Hz, 2H), 3.59 (t, J = 6.3 Hz, 2H), 2.35-2.18 (m, 2H), 1.98-1.87 (m, 1H), 1.65-1.30 (m, 9H), 1.26 (t, J = 7.1 Hz, 3H), 0.89 (s, 9H), 0.05 (s, 6H); 13C NMR (75 MHz, CDCl3) δ 173.5, 63.2, 62.9, 60.2, 39.1, 34.3, 29.8.
29.7, 29.5, 25.9, 18.3, 14.2, –5.3; FT-IR (film) 3447, 2931, 2858, 1736, 1472, 1255, 1098, 836, 775 cm⁻¹. ESI-MS m/z 355.0 ([M+Na⁺]); ESI-HRMS calcd. for C₁₇H₃₆NaO₄Si ([M+Na⁺]) 335.22751, found 355.22658.

**Synthesis of 21.** A solution of alcohol 20 (834 mg, 2.51 mmol), TBSCI (451 mg, 3.01 mmol), and imidazole (256 mg, 3.77 mmol) in DMF (3 mL) was stirred at ambient temperature over night. The mixture was then diluted with EtOAc, washed with aq. sat. NH₄Cl, H₂O and brine, and dried over anhydrous Na₂SO₄. Removal of the solvent by rotary evaporation and column chromatography (40:1 PE/EtOAc) on silica gel afforded 21 as a colorless oil (1.040 g, 2.33 mmol, 93%): ¹H NMR (300 MHz, CDCl₃) δ 4.12 (q, J = 7.2 Hz, 2H), 3.58 (t, J = 6.4 Hz, 4H), 2.24 (d, J = 6.8 Hz, 2H), 1.96-1.82 (m, 1H), 1.57-1.29 (m, 8H), 1.25 (t, J = 7.2 Hz, 3H), 0.88 (s, 18H), 0.04 (s, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 173.4, 63.3, 60.1, 39.1, 34.6, 29.84, 29.75, 26.0, 18.3, 14.2, -5.3; FT-IR (film) 2930, 2858, 1738, 1472, 1463, 1255, 1159, 1100, 1036, 836, 775 cm⁻¹. ESI-MS m/z 469.2 ([M+Na⁺]); ESI-HRMS calcd. for C₂₃H₅₀NaO₄Si₂ ([M+Na⁺]) 469.31398, found 469.31335.

**Synthesis of (±)-22.** DIBAL-H (1 M in cyclohexane, 2.33 mL, 2.33 mmol) was added to a solution of ester 21 (1.040 g, 2.33 mmol) in dry toluene (12 mL) stirred at –78 °C under argon. After completion of the addition, the mixture was stirred at the same temperature for 1 h before excess hydride was destroyed by addition of MeOH (2 mL). The mixture was diluted with EtOAc, washed with aq. sat. NH₄Cl, H₂O and brine, and dried over anhydrous Na₂SO₄. Removal of the solvent by rotary evaporation and column chromatography (30:1 PE/EtOAc) on silica gel afforded the intermediate aldehyde as a colorless oil, which was immediately dissolved in dry THF (10 mL) and stirred under argon. With cooling (–78 °C), HC≡CMgCl (5 mL, 2.5 mmol, 0.5 M in THF) was introduced. The stirring was continued while the bath was allowed to warm naturally to ambient temperature. The stirring was then diluted with EtOAc, washed with aq. sat. NH₄Cl, H₂O and brine, and dried over anhydrous Na₂SO₄. Removal of the solvent by rotary evaporation and column chromatography (8:1 PE/EtOAc) on silica gel afforded (±)-22 as a colorless oil (860 mg, 2.01 mmol, 86%): ¹H NMR (300 MHz, CDCl₃) δ 4.43 (t, J = 5.7 Hz, 1H), 3.60 (t, J = 6.4 Hz, 2H), 3.59 (t, J = 6.5 Hz, 2H), 2.46 (d, J = 2.1 Hz, 1H), 2.06 (br s, OH, 1H), 1.77-1.59 (m, 3H), 1.57-1.45 (m, 4H), 1.39-1.27 (m, 4H), 0.90 (s, 9H), 0.89 (s, 9H), 0.051 (s, 6H), 0.047 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 85.2, 72.8, 63.41, 63.38, 60.7, 42.1, 33.4, 29.49, 29.46, 29.41, 29.2, 26.0, 18.34, 18.33, –5.3; FT-IR (film) 3422, 3312, 2930, 2938, 2107, 1472, 1255, 1098 cm⁻¹. ESI-MS m/z 429.1 ([M+H⁺]), 451.2 ([M+Na⁺]); MALDI-HRMS Calcd. for C₂₃H₆₈O₃Si₂Na ([M+Na⁺]) 451.30342, found 451.3038.
Synthesis of (R)-22. A solution of Dess-Martin periodinane (1.152 g, 2.71 mmol) and (±)-22 (776 mg, 1.81 mmol) in dry CH2Cl2 (10 mL) was stirred at ambient temperature for 6 h. Aq. sat. NaHCO3 (10 mL) was added, followed by aq. sat. Na2S2O3 (10 mL). The cloudy mixture was stirred until it became clear. The phases were separated. The organic layer was washed with H2O and brine before being dried over anhydrous Na2SO4. Removal of the solvent by rotary evaporation and column chromatography (50:1 PE/EtOAc) on silica gel afforded the intermediate ketone as a colorless oil (518 mg, 1.22 mmol), which was immediately dissolved in dry THF (12 mL) and treated (dropwise) with (R)-2-Me-CBS-oxazaborolidin (1.0 M in toluene, 2.44 mL, 2.44 mmol) at –40 °C under argon. After stirring at the same temperature for 10 min, BH3·Me2S (2.0 M in THF, 1.0 mL, 2.0 mmol) was introduced dropwise. The mixture was stirred for another 1 h at –40 °C before EtOH (5 mL) was added to destroy the excess hydride. The mixture was stirred at ambient temperature for 15 min before being partitioned between H2O and Et2O. The phases were separated. The organic layer was washed with H2O and brine, and dried over anhydrous Na2SO4. Removal of the solvent by rotary evaporation and column chromatography (8:1 PE/EtOAc) on silica gel afforded (R)-22 as a colorless oil (479 mg, 1.12 mmol, 92% overall): [α]D25 +2.23 (c 1.08, CHCl3). For other spectral data, cf (±)-22.

Synthesis of 10b. A solution of (R)-22 (459 mg, 1.07 mmol), Et3N (0.22 mL, 1.61 mmol), TsCl (265 mg, 1.39 mmol), and DMAP (12 mg, 0.10 mmol) was stirred at ambient temperature over night. The mixture was then diluted with EtOAc, washed with aq. sat. NH4Cl, H2O and brine, and dried over anhydrous Na2SO4. Removal of the solvent by rotary evaporation and column chromatography (100:1 PE/EtOAc) on silica gel afforded 10b as a colorless oil (500 mg, 0.86 mmol, 80%): [α]D23 +16.48 (c 0.79, CHCl3). 1H NMR (300 MHz, CDCl3) δ 7.84-7.80 (m, 2H), 7.33 (dd, J = 0.7, 9.3 Hz, 2H), 5.09 (dt, J = 2.1, 7.2 Hz, 1H), 3.56 (t, J = 6.4 Hz, 4H), 2.45 (s, 3H), 2.40 (d, J = 2.2 Hz, 1H), 1.87-1.69 (m, 2 H), 1.58 (quinet, J = 6.2 Hz, 1H), 1.50-1.21 (m, 8H), 0.90 (s, 18H), 0.05 (s, 12H); 13C NMR (75 MHz, CDCl3) δ 144.8, 133.9, 129.6, 128.1, 79.3, 76.2, 69.9, 63.25, 63.17, 33.2, 29.29, 29.27, 29.1, 28.9, 25.9, 21.6, 18.3, –5.3; FT-IR (film) 3311, 2952, 2886, 2857, 2125, 1598, 1472, 1463, 1372, 1255, 1190, 1177, 1097, 836, 813, 776, 667 cm–1. ESI-MS m/z 605.1 ([M+Na]+), 583.2 ([M+H]+); ESI-HRMS calcd. for C30H55O5SSi2 ([M+H]+) 583.33033, found 583.3296. Because the polarity of 10b is too small, determination of the e.e. value was performed on its derivative 23.
Synthesis of 23. DDQ (3 mg, 0.01 mmol) was added to a solution of 10b (17 mg, 0.040 mmol) in CH$_3$CN-H$_2$O (9:1 v/v, 1 mL) stirred at ambient temperature. The stirring was continued at the same temperature over night. The reaction mixture was diluted with EtOAc, washed with aq. sat. NaHSO$_3$, aq. sat. NH$_4$Cl, H$_2$O, and brine before being dried over anhydrous Na$_2$SO$_4$. Removal of the solvent by rotary evaporation and column chromatography (1:2 PE/EtOAc) on silica gel afforded 23 as a colorless oil (14 mg, 0.040 mmol, 100%): $[\alpha]_D^{25} +21.19$ (c 0.60, CHCl$_3$), 77.2% e.e. as determined by HPLC on a CHFT-IRALPAK OJ$^{-}$H column (0.46 cm $\times$ 25 cm) eluting with 80:20 n-hexane/i-PrOH at a flow rate of 0.7 mL/min with the UV detector set to 214 nm $(t_{R(Major)} = 24.95$ min, $t_{R(Minor)} = 18.99$ min). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.82 (dt, $J = 8.4$, 1.9 Hz, 2 H), 7.33 (d, $J = 8.0$ Hz, 2 H), 5.09 (ddd, $J = 2.1$, 6.2, 8.2 Hz, 1 H), 3.61 (t, $J = 6.3$ Hz, 2 H), 3.60 (t, $J = 6.3$ Hz, 2 H), 2.51 (br s, OH, 2 H), 2.45 (s, 3 H), 2.42 (d, $J = 2.1$ Hz, 1 H), 1.92-1.69 (m, 2 H), 1.64 (quinet, $J = 6.2$ Hz, 1 H), 1.60-1.26 (m, 8 H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 145.0, 133.6, 129.7, 129.6, 128.0, 79.0, 76.4, 69.8, 62.7, 62.6, 39.9, 32.9, 29.0, 28.9, 28.7, 21.6; FT-IR (film): 3552, 3388, 3291, 2934, 2867, 2122, 1597, 1454, 1365, 1189, 1176 cm$^{-1}$. ESI-MS m/z 377.0 ([M+Na$^+$]); MALDI-HRMS calcd for C$_{18}$H$_{26}$O$_5$SNa ([M+Na$^+$]) 377.13932, found 377.1392.

Synthesis of 10c. A solution of alcohol 7a$'$ (150 mg, 0.62 mmol), DMAP (8 mg, 0.06 mmol) in Ac$_2$O (0.18 mL, 1.87 mmol) was stirred at ambient temperature over night. The reaction mixture was diluted with EtOAc, washed with H$_2$O and brine before being dried over anhydrous Na$_2$SO$_4$. Removal of the solvent by rotary evaporation and column chromatography (4:1 PE/EtOAc) on silica gel afforded 10c as a white solid (175 mg, 0.62 mmol, 100%): M.p. 139-140 °C. $[\alpha]_D^{23} +58.32$ (c 1.00, CHCl$_3$). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.82 (d, $J = 8.5$ Hz, 2H), 7.35 (d, $J = 7.8$ Hz, 2H), 5.26 (ddd, $J = 3.0$, 7.8, 7.8 Hz, 1H), 4.31 (dd, $J = 3.6$, 12.5 Hz, 1H), 4.21 (dd, $J = 8.1$, 12.2 Hz, 1H), 2.50 (d, $J = 1.8$ Hz, 1H), 2.46 (s, 3H), 2.01 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 170.2, 145.2, 133.3, 129.7, 128.1, 77.7, 75.3, 68.1, 64.3, 21.6, 20.5; FT-IR (film): 3280, 2957, 2923, 2852, 2129, 1751, 1597, 1366, 1224, 1176, 1190, 1176, 1095, 1050, 1018, 904, 814, 771 cm$^{-1}$. ESI-MS 304.9 ([M+Na$^+$]); MALDI-HRMS calcd for C$_{13}$H$_{14}$O$_5$SNa ([M+Na$^+$]) 305.04542, found 305.0452.

Synthesis of 10d. A solution of t-BuOK (840 mg, 7.5 mmol) in t-BuOH (15 mL) and anhydrous Et$_2$O (15 mL) was added to a solution of CCl$_3$CN (7.5 mL, 75 mmol) in anhydrous Et$_2$O (15 mL) stirred at 0 °C over 15 min. After completion of the addition, the mixture was stirred at ambient temperature for 1 h and heated to reflux for another 1 h. The volatiles were removed on a rotary
evaporator. The residue was diluted with *n*-pentante. The solids were filtered off. The filtrate was concentrated on a rotary evaporator to dryness to give Cl₃C(C=N)O-t-Bu as a yellow solid, which was used immediately in the preparation of 10d.

A solution of alcohol 7a (181 mg, 0.75 mmol), BF₃·Et₂O (10 µL) and the above prepared Cl₃C(C=N)O-t-Bu (165 mg, 0.75 mmol) was stirred at ambient temperature for 5 h. The reaction mixture was diluted with EtOAc, washed with aq. sat. NaHCO₃, H₂O, and brine before being dried over anhydrous Na₂SO₄. Removal of the solvent by rotary evaporation and column chromatography (15:1 PE/EtOAc) on silica gel afforded 10d as a colorless oil (125 mg, 0.42 mmol, 56%): [α]D23 +64.47 (c 0.90, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 7.83 (dt, J = 2.0, 8.3 Hz, 2H), 7.33 (d, J = 8.3 Hz, 2H), 5.07 (ddd, J = 2.3, 4.7, 7.0 Hz, 1H), 3.61 (dd, J = 7.4, 10.6 Hz, 1H), 3.55 (dd, J = 4.7, 10.3 Hz, 1H), 2.48 (d, J = 2.0 Hz, 1H), 2.44 (s, 3H), 1.11 (s, 9H); ¹³C NMR (75 MHz, CDCl₃) δ 144.7, 133.7, 129.5, 128.2, 77.3, 76.6, 74.0, 70.6, 64.0, 27.2, 21.6; FT-IR (film) 3278, 2975, 2931, 2127, 1598, 1366, 1177, 910, 813, 779 cm⁻¹. EI-MS m/z (%) 281 (M+–CH₃, 2), 223 (11), 155 (41), 139 (66), 91 (51), 57 (100); EI-HRMS calcd. for C₁₄H₁₇O₄S ([M–CH₃]+) 281.0848, found 281.0849.

**Synthesis of 25.** A solution of the known 5 alcohol 24 (256 mg, 1.47 mmol), TIPSCl (0.37 mL, 1.76 mmol), and imidazole (150 mg, 2.21 mmol) in DMF (1.5 mL) was stirred at ambient temperature over night. The reaction mixture was diluted with EtOAc, washed with aq. sat. NH₄Cl, H₂O, and brine before being dried over anhydrous Na₂SO₄. Removal of the solvent by rotary evaporation and column chromatography (50:1 PE/EtOAc) on silica gel afforded 25 as a colorless oil (486 mg, 2.21 mmol, 100%): [α]D25 −3.03 (c 0.98, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 4.17- 4.03 (m, 2H), 3.66 (t, J = 6.4 Hz, 2H), 2.04 (s, 3H), 1.75-1.14 (m, 7H), 1.07 (s, 18H), 1.06 (s, 3H), 0.92 (d, J = 6.5 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 171.1, 63.5, 63.0, 35.4, 32.9, 30.3, 29.6, 21.0, 19.4, 18.0, 12.0; FT-IR (film) 2942, 2867, 1463, 1383, 1366, 1237, 1103, 1061, 882, 680 cm⁻¹. ESI-MS m/z 331.2 ([M+H]+), 353.1 ([M+Na]+); ESI-HRMS calcd. for C₁₈H₃₉O₃Si ([M+H]+) 331.26630, found 331.26682.

**Synthesis of 26.** A mixture of 25 (486 mg, 1.47 mmol) and K₂CO₃ (406 mg, 2.94 mmol) in MeOH (7.5 mL) was stirred at ambient temperature for 2 h. The reaction mixture was diluted with EtOAc, washed with aq. sat. NH₄Cl, H₂O, and brine before being dried over anhydrous Na₂SO₄. Removal of the solvent by rotary evaporation and column chromatography (10:1 PE/EtOAc) on silica gel afforded 26 as a colorless oil (370 mg, 1.28 mmol, 87%): [α]D24 −2.79 (c 1.03, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 3.67 (t, J = 6.4 Hz, 4H), 1.69-1.14 (m, 8H), 1.07 (s, 18H), 0.91(d, J = 6.5 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 63.6, 61.1, 39.8, 33.0, 30.3, 29.3, 19.6, 18.0, 11.9; FT-IR (film) 3346, 2942, 2867, 1463, 1383, 1366, 1237, 1103, 1061, 882, 680 cm⁻¹. EI-MS m/z (%) 245 (M⁺−CH₃, 5.7) (5.68), 131 (28), 119 (29), 103 (23), 97 (75), 75 (25), 69 (25), 55 (100); EI-HRMS calcd. for C₁₆H₃₆O₂Si (M⁺) 288.2485, found 288.2481.
Synthesis of 27. Dess-Martin periodinane (2.502 g, 6 mmol) was added to a solution of alcohol 26 (946 mg, 3.28 mmol) in dry CH₂Cl₂ (17 mL) stirred at ambient temperature. The mixture was stirred at the same temperature for 6 h before aq. sat. NaHCO₃ and aq. sat. Na₂S₂O₃ were added. The cloudy mixture was stirred until it became clear. The phases were separated. The organic layer was washed with H₂O and brine, and dried over anhydrous Na₂SO₄. Removal of the solvent by rotary evaporation and column chromatography (15:1 PE/EtOAc) on silica gel afforded the intermediate aldehyde as a colorless oil (910 mg, 3.18 mmol, 97%), which was directly dissolved in dry THF (15 mL) and treated with HC≡CMgCl (0.5 M in THF, 8.0 mL, 4.0 mmol) at -78 °C. After completion of the addition, the stirring was continued while the cooling bath was allowed to warm to ambient temperature naturally. The mixture was diluted with EtOAc, washed with aq. sat. NH₄Cl, H₂O, and brine before being dried over anhydrous Na₂SO₄. Removal of the solvent by rotary evaporation and column chromatography (10:1 PE/EtOAc) on silica gel afforded 27 as a colorless oil (a 1:1 diastereomeric mixture, 840 mg, 2.69 mmol, 82% from 26): ¹H NMR (300 MHz, CDCl₃) δ 4.45 (dd, J = 6.5, 12.2 Hz, 1H), 3.73-3.59 (m, 2H), 2.49-2.44 (m, 1H), 1.94-1.13 (m, 18H), 1.10-1.00 (m, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 85.4, 85.0, 72.9, 72.6, 63.6, 63.5, 60.9, 60.4, 45.1, 44.8, 32.9, 32.8, 30.2, 30.1, 29.3, 29.0, 19.6, 19.3, 18.0, 17.7, 12.0; FT-IR (film) 3400 (br), 3312, 2942, 2867, 2111, 1463, 1382, 1248, 1101, 1068, 882, 680 cm⁻¹.

Synthesis of 28. A mixture of 27 (839 mg, 2.69 mmol), vinyl acetate (1.3 mL, 14.09 mmol) and Novozym 435 (157 mg) in n-hexane (14 mL) was stirred at ambient temperature for 27 h. Solids were filtered off. The filtrate was concentrated on a rotary evaporator. The residue was chromatographed (20:1 PE/EtOAc) on silica gel to give acetate 28 as a colorless oil (405 mg, 1.15 mmol, 43%): [α]D^23 -40.97 (c 0.94, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 5.38 (dt, J = 2.1, 7.3 Hz, 1H), 3.65 (t, J = 6.4 Hz, 2H), 2.44 (d, J = 2.1 Hz, 1H), 2.07 (s, 3H), 1.87-1.15 (m, 7H), 1.04 (s, 18H), 1.03 (s, 3H), 0.93 (d, J = 5.9 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 169.9, 81.3, 73.5, 63.5, 62.7, 41.4, 33.0, 30.1, 29.3, 21.0, 19.3, 18.0, 11.9; FT-IR (film) 3313, 2941, 2866, 2119, 1746, 1463, 1371, 1232, 1102, 1020, 882, 679 cm⁻¹. ESI-MS m/z 377.2 ([M+Na]^+); ESI-HRMS calcd. for C₂₀H₃₈O₃SiNa ([M+Na]^+) 377.2482, found 377.2490.

Synthesis of 29. A mixture of 28 (405 mg, 1.14 mmol) and K₂CO₃ (315 mg, 2.28 mmol) in MeOH (5 mL) was stirred at ambient temperature for 2 h before being diluted with EtOAc, washed with aq. sat. NH₄Cl, H₂O, and brine before being dried over anhydrous Na₂SO₄. Removal of the solvent by rotary evaporation and column chromatography (10:1 PE/EtOAc) on silica gel afforded 29 as a
colorless oil (356 mg, 1.14 mmol, 100%); $[\alpha]_D^{25} -9.24 (c 0.95, CHCl_3)$.

$^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.43 (t, $J = 6.3$ Hz, 1 H), 3.66 (t, $J = 6.4$ Hz, 2 H), 2.46 (d, $J = 2.0$ Hz, 1 H), 2.04 (broad, 1 H, OH), 1.83-1.13 (m, 7 H), 1.05 (s, 18 H), 1.04 (s, 3 H), 0.92 (d, $J = 6.0$ Hz, 3 H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 85.0, 72.9, 63.5, 60.9, 44.8, 32.8, 30.1, 29.3, 19.6, 18.0, 12.0; FT-IR (film) 3400 (br), 3312, 2942, 2867, 2111, 1463, 1382, 1248, 1101, 1068, 882, 680 cm$^{-1}$. EI-MS: $m/z$ 269 ($M^+–C_3H_7$, 3.50), 149 (10), 131 (56), 119 (36), 103 (47), 93 (80), 79 (100), 75 (53), 55 (41); EI-HRMS calcd. for C$_{18}$H$_{36}$O$_2$Si ($M^+$) 312.2845, found 312.2845.

Synthesis of 10e. A solution of 29 (356 mg, 1.15 mmol), Et$_3$N (0.24 mL, 1.73 mmol), TsCl (286 mg, 1.50 mmol), and DMAP (12 mg, 0.10 mmol) was stirred at ambient temperature over night. The mixture was then diluted with EtOAc, washed with aq. sat. NH$_4$Cl, H$_2$O and brine, and dried over anhydrous Na$_2$SO$_4$. Removal of the solvent by rotary evaporation and column chromatography (30:1 PE/EtOAc) on silica gel afforded 10e as a colorless oil (400 mg, 0.86 mmol, 75%): $[\alpha]_D^{24} -29.60 (c 0.84, CHCl_3), 97.4%$ d.e. as determined by HPLC on a CHF-IRALPAK IC column (0.46 cm × 25 cm) eluting with 100:1 n-Hexane/i-ProOH at a flow rate of 0.7 mL/min with the UV detector set to 214 nm ($t_R$(Major) = 37.89 min, $t_R$(Minor) = 40.99 min). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.81 (d, $J = 8.2$ Hz, 2 H), 7.33 (d, $J = 8.2$ Hz, 2 H), 5.10 (dt, $J = 1.8, 7.0$ Hz, 1H), 3.63 (t, $J = 6.4$ Hz, 2H), 2.44 (s, 3H), 2.40 (d, $J = 2.2$ Hz, 1H), 1.88-1.10 (m, 7H), 1.05 (s, 18H), 1.03 (s, 3H), 0.88 (d, $J = 5.6$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 144.8, 133.9, 129.6, 128.1, 79.1, 76.3, 70.1, 63.4, 42.5, 32.6, 30.0, 29.0, 21.7, 19.3, 18.0, 11.9; FT-IR (film) 3310, 2942, 2866, 2124, 1598, 1463, 1371, 1190, 1178, 1098, 884, 669 cm$^{-1}$. ESI-MS $m/z$ 467.1 ($[M+H]^+$), 489.2 ($[M+Na]^+$); ESI-HRMS calcd for C$_{25}$H$_{43}$O$_4$SSi ($[M+H]^+$) 467.26458, found 467.26464.

Data for 8: $[\alpha]_D^{25} +157.55 (c 2.86, CHCl_3)$, 85% e.e. as determined on its desilylated derivative 8’ (cf. below). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 6.05 (dt, $J = 2.5, 5.5$ Hz, 1H), 5.46 (q, $J = 5.7$ Hz, 1H), 4.31 (dd, $J = 2.4, 5.7$ Hz, 2H), 0.91 (s, 9H), 0.097 (s, 3H), 0.096 (s, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 201.2, 101.1, 73.7, 59.9, 25.8, 18.3, −5.25, −5.31; FT-IR (film) 3060, 2955, 2929, 2885, 2857, 1961, 1472, 1390, 1256, 1091, 835 cm$^{-1}$. EI-MS $m/z$ (%) 249 ($M^+ (^{81}Br)$–CH$_3$, 0.27), 247 ($M^+ (^{81}Br)$–CH$_3$, 0.23), 207 (18), 205 (17), 139 (100), 137 (99); EI-HRMS calcd for C$_{10}$H$_{19}$OBrSi ($M^+$) 262.0389, found 262.0397.

Data for 9: $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.43 (dt, $J = 2.3, 6.6$ Hz, 1H), 3.93 (dd, $J = 6.5, 10.7$ Hz, 1H), 3.87 (dd, $J = 7.3, 10.7$ Hz, 1H), 2.62 (d, $J = 2.0$ Hz, 1H), 0.92 (s, 9H), 0.12 (s, 6H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 80.5, 75.5, 67.4, 36.5, 25.7, 18.3, −5.3; FT-IR (film) 3311, 2955, 2930, 2886, 2858, 2120, 1472, 1464, 1257, 1127, 838 cm$^{-1}$. EI-MS $m/z$ (%) 207 ($M^+ (^{81}Br)$–C$_4$H$_9$, 14.61), 205 ($M^+ (^{79}Br)$–C$_4$H$_9$, 14.19), 139 (98), 137 (100); EI-HRMS calcd for C$_{10}$H$_{19}$OBrSi ($M^+$) 262.0389, found 262.0391.
Cleaving the TBS group in 8 leading to 8'. n-Bu₄NF (1 M solution in THF, 0.25 mL, 0.25 mmol) was added to a solution of 8 (57 mg, 0.22 mmol) in THF (1 mL). The mixture was stirred at ambient temperature for 1h before being diluted with Et₂O, washed with H₂O and brine, and dried over anhydrous Na₂SO₄. Removal of the solvent by rotary evaporation and column chromatography (2:1 PE/Et₂O) on silica gel gave alcohol 8' as a colorless oil (30 mg, 0.20 mmol, 92%): [α]D²² +209.74 (c 1.15, CHCl₃), 94.8% e.e. as determined by HPLC on a CHF-T-IRALPAK IC column (0.46 cm × 25 cm) eluting with 95:5 n-Hexane/i-PrOH at a flow rate of 0.8 mL/min with the UV detector set to214 nm (tR(Major) = 12.19 min, tR(Minor) = 11.49 min). ¹H NMR (300 MHz, CDCl₃) δ 6.13 (dt, J = 5.7, 2.3 Hz, 1H), 5.56 (q, J = 5.6 Hz, 1H), 4.36-4.21 (br s, 2H), 2.16 (br s, 1H, OH); ¹³C NMR (75 MHz, CDCl₃) δ 201.0, 100.8, 74.6, 59.2; FT-IR (film) 3349, 3058, 2925, 2871, 1959, 1714, 1455, 1387, 1190, 1120, 1047, 1018, 833, 657 cm –¹. EI-MS m/z (%) 150 (M⁺ (81Br), 9.56), 148 (M + (79Br), 10.13), 120 (48), 118 (46), 69 (100); EI-HRMS calcd. For C₄H₅OBr (M+) 147.9524, found147.9519.

Data for 11a: cf ref 2

Data for 12a: [α]D²⁷ +2.91 (c 0.65, CHCl₃). ¹H NMR (300 MHz, CDCl₃) δ 5.22 (s, 2H), 4.46 (dt, J = 2.3, 6.9 Hz, 1H), 3.47 (s, 3H), 2.65 (d, J = 2.3 Hz, 1H), 2.36 (d, J = 7.5 Hz, 2H), 2.05-1.95 (m, 2H), 1.74-1.46 (m, 4H), 1.41-1.19 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 173.3, 90.2, 82.5, 74.9, 57.6, 39.3, 35.9, 34.2, 29.0, 28.9, 28.4, 27.1, 24.7; FT-IR (film) 3291, 2930, 2856, 2117, 1742, 1464, 1150, 1087, 932 cm⁻¹. ESI-MS m/z 327.0 ([M (79Br)+Na]+); ESI-HRMS calcd for C₁₃H₂₁O₃BrNa ([M+Na]+) 327.0566; found 327.0559.

Data for 11b: [α]D²⁰ +68.07 (c 0.95, CHCl₃), 75.8% e.e. as determined on its diacetate derivative 11b' (cf below). ¹H NMR (300 MHz, CDCl₃) δ 5.95-5.88 (m, 1H), 5.39-5.29 (m, 1H), 3.60 (t, J = 6.4 Hz, 4 H), 2.15 (t, J = 6.7 Hz, 2H), 1.61-1.13 (m, 9H), 0.90 (s, 18H), 0.05 (s, 12H); ¹³C NMR (75 MHz, CDCl₃) δ 202.6, 99.1, 71.8, 63.4, 37.1, 32.6, 29.9, 29.8, 29.4, 29.3, 26.0, 18.3, -5.3; FT-IR (film) 3060, 2953, 2929, 2896, 2857, 1955, 1471, 1462, 1255, 1059 cm⁻¹. ESI-MS m/z (%) 435 (M⁺ (81Br)–C₄H₉, 3.84), 433[M⁺ (79Br)–C₄H₉, 3.62], 147 (86), 105 (100); EI-HRMS calcd. for C₁₉H₂₆O₂BrSi₂ (M⁺ (81Br) –C₄H₉) 433.1417, found 433.1422.
Conversion of 11b into 11b'. n-Bu4NF (1 M solution in THF, 0.3 mL, 0.3 mmol) was added to a solution of 11b (28 mg, 0.057 mmol) in THF (1 mL). The mixture was stirred at ambient temperature for 1 h before being diluted with Et2O, washed with H2O and brine, and dried over anhydrous Na2SO4. Removal of the solvent left a crude oil, which was directly dissolved in CH2Cl2 (1 mL) and treated with Ac2O (32 µL, 0.29 mmol) and DMAP (1 mg) at ambient temperature. The mixture was then stirred overnight before being diluted with EtOAc, washed with aq. sat. NH4Cl, H2O and brine, and dried over anhydrous Na2SO4. Removal of the solvent by rotary evaporation and column chromatography (5:1 PE/EtOAc) on silica gel afforded diacetate 11b' as a colorless oil (17 mg, 0.050 mmol, 88%): [α]D27 +81.21 (c 0.60, CHCl3), 75.7 % e.e. as determined by HPLC on a CHFT-IRALPAK AS−H column (0.46 cm × 25 cm) eluting with 95:5 n-Hexane/i-PrOH at a flow rate of 0.7 mL/min with the UV detector set to 214 nm (tR(Major) = 15.52 min, tR(Minor) = 19.22 min). 1H NMR (300 MHz, CDCl3) δ 5.98-5.92 (m, 1 H), 5.33 (q, J = 6.8 Hz, 1 H), 4.06 (t, J = 6.9 Hz, 4 H), 2.16 (t, J = 6.9 Hz, 2 H), 2.06 (s, 6 H), 1.71-1.51 (m, 5 H), 1.44-1.30 (m, 4 H); 13C NMR (75 MHz, CDCl3) δ 202.7, 171.2, 98.4, 72.1, 64.62, 64.59, 64.5, 36.8, 32.2, 29.44, 29.37, 25.8, 25.7, 21.0; FT-IR (film) 3061, 2934, 2858, 1953, 1738, 1239 cm –1. ESI-MS m/z 369.0 ([M+Na]+); ESI-HRMS calcd for C15H23BrO4Na ([M+Na]+) 369.06719, found 369.06695.

Data for 11c: [α]D27 +184.78 (c 0.98, CHCl3), 92.4% e.e. as determined on its deacetyl derivative 8' under the same conditions as described above. 1H NMR (300 MHz, CDCl3) δ 6.14-6.08 (m, 1H), 5.49 (q, J = 6.1 Hz, 1H), 4.69 (dd, J = 2.1, 6.1 Hz, 2H), 2.10 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 202.6, 170.3, 95.7, 74.1, 60.1, 20.7; FT-IR (film) 3069, 2935, 1954, 1370, 1228, 1030 cm –1. EI-MS m/z (%) 150 (M+ (81Br)-CH2CO, 25), 148 (25), 111 (34), 43 (100); EI-HRMS calcd for C4H5OBr (M+ (81Br)-CH2CO) 147.9524, found 147.9526.

Data for 12c: [α]D25 +21.19 (c 0.60, CHCl3). 1H NMR (300 MHz, CDCl3) δ 4.63 (dt, J = 2.3, 6.8 Hz, 1H), 4.39 (d, J = 6.9 Hz, 2H), 2.67 (d, J = 2.5 Hz, 1H), 2.14 (s, 3H); 13C NMR (75 MHz, CDCl3) δ 170.2, 79.0, 76.3, 66.5, 29.7, 20.6; FT-IR (film) 3299, 2924, 2854, 2148, 1736, 1461, 1377 cm –1. EI-MS m/z (%) 192 (M+ (81Br), 0.2), 190 (M+ (81Br), 0.2), 111 (13), 73 (53), 43 (100); EI-HRMS calcd. for C6H7O2Br (M+) 189.9629, found 189.9631.

Data for 11d: [α]D27 +135.36 (c 0.47, CHCl3), 96.2% e.e. as determined on its derivative 8' under the same conditions as described above. 1H NMR (300 MHz, CDCl3) δ 6.03 (dt, J = 5.8, 2.0 Hz, 1H), 5.46 (q, J = 6.1 Hz, 1H), 4.14-3.99 (m, 2H), 1.23 (s, 9H); 13C NMR (75 MHz, CDCl3) δ 201.7, 99.7, 74.1, 73.1, 59.1, 27.6; FT-IR (film) 3059, 2924, 2853, 1961, 1726, 1600, 1460, 1365, 1261, 1191, 1076 cm –1. EI-MS m/z (%) 206 (M+ (81Br), 0.2), 204 (0.2), 133 (9), 131 (9), 57 (100); EI-HRMS calcd. for C8H13OBr (M+) 206.0129, found 206.0137.
Data for 11e: $[\alpha]_D^{23} = -125.18$ (c 0.83, CHCl$_3$), 94.3 % d.e. as determined on its desilyl derivative 11e’ (cf below). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.92 (dt, $J = 5.7$, 2.1 Hz, 1H), 5.37 (ddd, $J = 5.7$, 7.4, 7.4 Hz, 1H), 3.68 (t, $J = 6.5$ Hz, 2H), 2.23-2.14 (m, 1H), 2.06-1.96 (m, 1H), 1.69-1.37 (m, 3H), 1.30-1.17 (m, 2H), 1.07 (s, 18H), 1.06 (s, 3H), 0.95 (d, $J = 6.6$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 202.6, 99.3, 71.8, 63.6, 35.8, 32.6, 32.5, 30.4, 19.5, 18.0, 12.0; FT-IR (film) 3061, 2941, 2866, 1955, 1735, 1462, 1382, 1260, 1197, 1105, 882, 681, 655 cm$^{-1}$. EI-MS m/z (%) 333 (M$^+$ (81Br)–C$_3$H$_7$, 4), 331 (M$^+$ (79Br)–C$_3$H$_7$, 4.08), 209 (8), 183 (26), 181 (28), 167 (19), 165 (18), 121 (53), 93 (100), 79 (100), 69 (70); EI-HRMS calcd. for C$_{18}$H$_{35}$OBrSi (M$^+$) 374.1641, found 374.1646.

Data for Compound 12e (a mixture of diastereoisomers): $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 4.58-4.47 (m, 1H), 3.67 (t, $J = 6.6$ Hz, 2H), 2.66-2.62 (m, 1H), 2.17-1.97 (m, 1H), 1.91-1.79 (m, 2H), 1.70-1.16 (m, 4H), 1.06 (s, 18H), 1.05 (s, 3H), 0.93 (d, $J = 6.6$ Hz, 3H).

Conversion of 11e into 11e’. n-Bu$_4$NF (1 M solution in THF, 0.1 mL, 0.1 mmol) was added to a solution of 11b (18 mg, 0.048 mmol) in THF (1 mL). The mixture was stirred at ambient temperature for 1h before being diluted with EtOAc, washed with aq. sat. NH$_4$Cl, H$_2$O and brine, and dried over anhydrous Na$_2$SO$_4$. Removal of the solvent by rotary evaporation and column chromatography (6:1 PE/EtOAc) on silica gel afforded diacetate 11b’ as a colorless oil (9 mg, 0.040 mmol, 83%): $[\alpha]_D^{24} = -205.02$ (c 0.83, CHCl$_3$), 93.9 % e.e. as determined by HPLC on a CHFT-IRALPAK OJ–H column (0.46 cm × 25 cm) eluting with 100:1 n-Hexane/i-PrOH at a flow rate of 0.7 mL/min with the UV detector set to 214 nm ($t_R$(Major) = 41.77 min, $t_R$(Minor) = 45.27 min). $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 5.93 (dt, $J = 5.7$, 2.1 Hz, 1H), 5.36 (ddd, $J = 5.7$, 7.7, 7.7 Hz, 1H), 3.65 (t, $J = 6.6$ Hz, 2H), 2.22-2.13 (m, 1H), 2.07-1.98 (m, 1H), 1.71-1.36 (m, 5 H), 1.30-1.18 (m, 1H), 0.95 (d, $J = 6.6$ Hz, 3H); $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 202.6, 99.3, 71.9, 63.2, 35.7, 32.6, 32.2, 30.1, 19.4; FT-IR (film) 3348, 3059, 2928, 2871, 1954, 1723, 1459, 1196 cm$^{-1}$. EI-MS m/z (%) 205 (M$^+$–CH$_3$, 1.8), 203 (1.4), 134 (95), 132 (99), 41 (100); EI-HRMS calcd. for C$_9$H$_{15}$OBr (M$^+$) 218.0306, found 218.0302.

References for the Supporting Information part

S 30

300 MHz, CDCl3
S 39

75 MHz, CDCl3
S 40

300 MHz, CDCl3
S 42

300 MHz, CDCl₃
Chemical Formula: C₉H₇BrO₂
Exact Mass: 189.96294
Molecular Weight: 191.02258
S 58

300 MHz, CDCl3
S 64

500 MHz, CDCl₃
75 MHz, CDCl3