

# **Efficient Synthesis of the C<sub>7</sub>-C<sub>20</sub> Subunit of Amphidinolides C and F**

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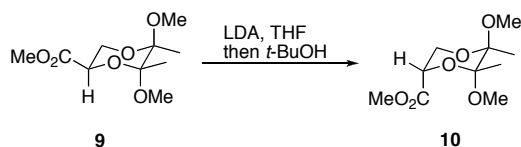
**Electronic Supplementary Information: Experimental**

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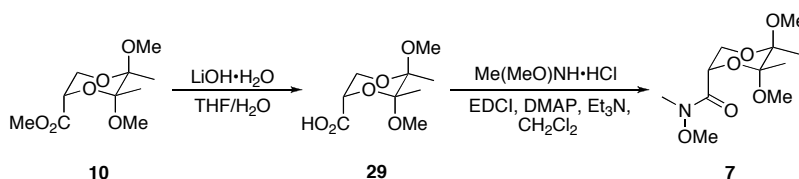
**General.** Infrared spectra were recorded neat unless otherwise indicated and are reported in  $\text{cm}^{-1}$ .  $^1\text{H}$  NMR spectra were recorded in deuterated solvents and are reported in ppm relative to tetramethylsilane and referenced internally to the residually protonated solvent.  $^{13}\text{C}$  NMR spectra were recorded in deuterated solvents and are reported in ppm relative to tetramethylsilane and referenced internally to the residually protonated solvent.

Routine monitoring of reactions was performed using EM Science DC-Alufolien silica gel, aluminum-backed TLC plates. Flash chromatography was performed with the indicated eluents on EM Science Gedurian 230-400 mesh silica gel.

Air and/or moisture sensitive reactions were performed under usual inert atmosphere conditions. Reactions requiring anhydrous conditions were performed under a blanket of argon, in glassware dried in an oven at  $120^\circ\text{C}$  or by a bunsen flame, then cooled under argon. Solvents and commercial reagents were purified in accord with literature procedures or used without further purification.

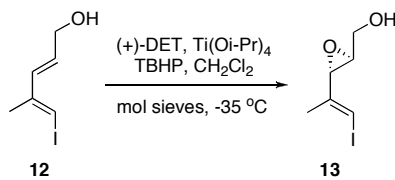


**Axial Ester 10:** To a stirred solution of diisopropylamine (517 mg, 0.72 mL, 5.17 mmol) in THF (2.6 mL) at  $-78^\circ\text{C}$  was added *n*-BuLi (2.0 mL, 5.00 mmol, 2.5 M in hexanes). After 15 min at  $-78^\circ\text{C}$ , the reaction was warmed to  $0^\circ\text{C}$  and stirred for 10 min. This LDA solution was then cannulated to a stirred solution of equatorial ester **9**<sup>1</sup> (1.01 g, 4.31 mmol) in THF (16 mL) at  $-78^\circ\text{C}$ . After 30 min, *t*-BuOH (861 mg, 1.10 mL, 11.6 mmol) was slowly added to the yellow reaction mixture with the evolution of gas. After 30 min, the reaction was quenched with sat. aq.  $\text{NH}_4\text{Cl}$  (10 mL) and the aqueous layer was extracted with  $\text{Et}_2\text{O}$  (3 X 50 mL). The combined organic layer was washed with brine (30 mL) and the dried ( $\text{MgSO}_4$ ) extract was concentrated *in vacuo*. The residue was passed through a small plug of silica gel, eluting with 50%  $\text{Et}_2\text{O}$  / hexanes (100 mL). The solvent was removed *in vacuo* and the yellow solid was purified by recrystallization from hexane to give known axial ester **10**<sup>1</sup> (444 mg, 1.89 mmol, 44%) as white solid:  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.12-4.17 (m, 2H), 3.97-4.02 (m, 1H), 3.81 (s, 3H), 3.32 (s, 3H), 3.31 (s, 3H), 1.37 (s, 3H), 1.32 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  171.1, 99.6, 98.7, 68.1, 57.6, 52.0, 50.1, 48.2, 18.0, 17.7.

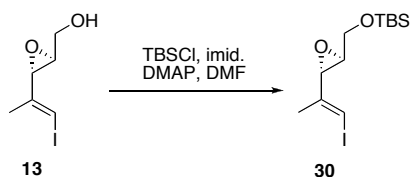


**Weinreb Amide 7:** To a stirred solution of known ester **10**<sup>1</sup> (1.01 g, 4.32 mmol) in THF /  $\text{H}_2\text{O}$  (1:1, 22 mL) was added  $\text{LiOH}\cdot\text{H}_2\text{O}$  (201 mg, 4.79 mmol) at rt. After 4 h, the solution was adjusted to pH 4 with aq.  $\text{HCl}$  (4 mL, 1M) and the aqueous layer was extracted with  $\text{EtOAc}$  (6 X 30 mL). The combined organic layer was washed with brine (30 mL) and the dried ( $\text{MgSO}_4$ ) extract was concentrated *in vacuo* to give crude acid **29**.

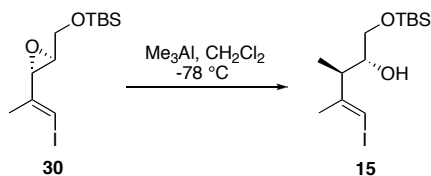
The crude acid **29** was redissolved in  $\text{CH}_2\text{Cl}_2$  (21 mL) and  $\text{Me}(\text{OMe})\text{NH}\cdot\text{HCl}$  (500 mg, 5.10 mmol),  $\text{Et}_3\text{N}$  (511 mg, 0.71 mL, 5.10 mmol), EDCI (978 mg, 5.10 mmol) and DMAP (103 mg, 0.851 mmol) were added sequentially at rt. After 24 h, the reaction mixture was concentrated *in vacuo* and the residue was dissolved in  $\text{EtOAc}$  / water (2:1, 90 mL). The aqueous layer was extracted with  $\text{EtOAc}$  (3 X 50 mL) and combined organic layer was washed with sat. aq.  $\text{NaHCO}_3$ , water and brine (25 mL each). The dried ( $\text{MgSO}_4$ ) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 40-50%  $\text{EtOAc}$  / hexanes, to give Weinreb amide **7** (897 mg, 3.41 mmol, 79%) as white solid: Mp.  $49-50^\circ\text{C}$ ;  $[\alpha]_{\text{D}}^{23} = -87.7$  ( $c = 1.02$ ,  $\text{CHCl}_3$ ); IR: (neat) 3586, 3515, 2986, 2943, 2829, 1668, 1467, 1369  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.78 (s br, 1H), 4.11-4.15 (m, 1H), 3.90 (dd,  $J = 11.2, 4.4$  Hz, 1H), 3.78 (s, 3H), 3.38 (s, 3H), 3.35 (s, 3H), 3.22 (s br, 3H), 1.39 (s, 3H), 1.37 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  170.8, 100.1, 99.2, 67.2, 61.4, 59.5, 48.9, 48.2, 32.1, 18.1, 17.9; HRMS (CI+) calcd. for  $\text{C}_{11}\text{H}_{22}\text{NO}_6$  (M+H) 264.1447, found 264.1448.



**Epoxide 13:** To a stirred suspension of 4 Å mol sieves (2.50 g) in dry  $\text{CH}_2\text{Cl}_2$  (30 mL) at  $-35\text{ }^\circ\text{C}$  was added  $\text{Ti}(\text{O}i\text{-Pr})_4$  (563 mg, 0.59 mL, 1.97 mmol) followed by (+)-DET (605 mg, 0.50 mL, 2.96 mmol). The resulting mixture was stirred for 1 h and then TBHP (5.40 mL, 29.6 mmol, 5.5 M in decane) was added. After 1 h, a solution of allylic alcohol **12**<sup>2</sup> (2.21 g, 9.86 mmol) in  $\text{CH}_2\text{Cl}_2$  (30 mL) was added dropwise over 45 min. After 16 h at  $-35\text{ }^\circ\text{C}$ , the reaction was quenched with sat. aq.  $\text{NaHCO}_3$  (20 mL) and diluted with  $\text{Et}_2\text{O}$  (50 mL). The resulting solution was passed through a celite pad and the aqueous layer was extracted with  $\text{Et}_2\text{O}$  (3 X 60 mL) and the combined organic layer was washed with  $\text{H}_2\text{O}$  and brine (50 mL each). The dried ( $\text{MgSO}_4$ ) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 15-20%  $\text{EtOAc}$  / hexanes, to give epoxide **13** (2.06 g, 8.58 mmol, 87%) as white solid. Enantiomeric excess was determined by chiral HPLC [4.6 X 250 mm, Daicel AD column, 96:4 hexanes / *i*-PrOH, 0.5 mL  $\text{min}^{-1}$ , retention times 33.2 min (major) and 36.2 (minor)] to be 95% ee: Mp. 47-48  $^\circ\text{C}$ ;  $[\alpha]_{\text{D}}^{23} = -20.3$  ( $c = 1.61$ ,  $\text{CHCl}_3$ ); IR: (neat) 3390, 3046, 2981, 2921, 2867, 1603, 1434, 1380, 1293, 1233, 1151, 1069, 1031, 999, 879, 786  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.45 (s, 1H), 3.96 (d,  $J = 12.6$  Hz, 1H), 3.67-3.73 (m, 1H), 3.55 (d,  $J = 2.0$  Hz, 1H), 3.16 (dt  $J = 3.9, 2.9$  Hz, 1H), 2.14 (s br, 1H), 1.75 (d,  $J = 0.88$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.4, 80.1, 61.0, 58.2, 57.1, 19.0; HRMS (EI+) calcd. for  $\text{C}_6\text{H}_9\text{O}_2\text{I}$  (M<sup>+</sup>) 239.9648, found 239.9639.

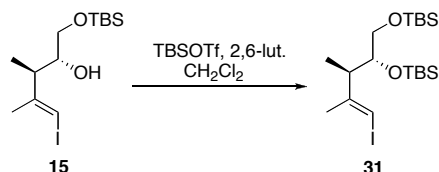


**TBS Ether 30:** To a stirred solution of alcohol **13** (1.95 g, 8.12 mmol) in DMF (12 mL) at  $0\text{ }^\circ\text{C}$  were added imidazole (967 mg, 14.2 mmol), TBS chloride (1.59 g, 10.5 mmol) and DMAP (245 mg, 2.03 mmol) sequentially. After 1 h, the reaction was quenched with sat. aq.  $\text{NH}_4\text{Cl}$  (20 mL) and diluted with  $\text{Et}_2\text{O}$  (50 mL). The aqueous layer was extracted with  $\text{Et}_2\text{O}$  (2 X 50 mL) and the dried ( $\text{MgSO}_4$ ) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 4-8%  $\text{EtOAc}$  / hexanes, to give **30** (2.85 g, 8.04 mmol, 99%) as colorless oil:  $[\alpha]_{\text{D}}^{23} = -11.1$  ( $c = 1.07$ ,  $\text{CHCl}_3$ ); IR: (neat) 2954, 2921, 2888, 2856, 1472, 1456, 1374, 1353, 1255, 1151, 1102, 1059, 1004, 960, 879, 824, 775, 666  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.42 (s, 1H), 3.87 (dd,  $J = 12.0, 3.1$  Hz, 1H), 3.74 (dd,  $J = 12.0, 4.2$  Hz, 1H), 3.44 (d,  $J = 1.8$ , 1H), 3.07-3.09 (m, 1H), 1.76 (d,  $J = 1.0$  Hz, 3H), 0.92 (s, 9H), 0.10 (s, 3H), 0.09 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.9, 79.4, 62.6, 58.5, 57.4, 25.8, 19.1, 18.3, -5.3; HRMS (CI+) calcd. for  $\text{C}_{12}\text{H}_{24}\text{OSiI}$  (M+H) 355.05906, found 355.05960.

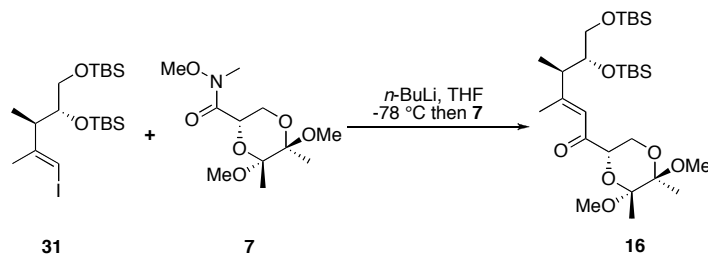


**Alcohol 15:** To a stirred solution of epoxide **30** (167 mg, 0.471 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was added a solution of  $\text{Me}_3\text{Al}$  (102 mg, 136  $\mu\text{L}$ , 1.41 mmol) in  $\text{CH}_2\text{Cl}_2$  (2 mL) at  $-78\text{ }^\circ\text{C}$ . After 1 h at  $-78\text{ }^\circ\text{C}$ , the reaction mixture was quenched with sat. aq. Rochelle's salt (5 mL) and diluted with  $\text{Et}_2\text{O}$  (20 mL). The resulting mixture was stirred vigorously at rt for 15 min to get two clear layers. The aqueous layer was extracted with  $\text{Et}_2\text{O}$  (4 X 20 mL) and the combined organic layer was washed with brine (20 mL). The dried ( $\text{MgSO}_4$ ) extract was concentrated *in*

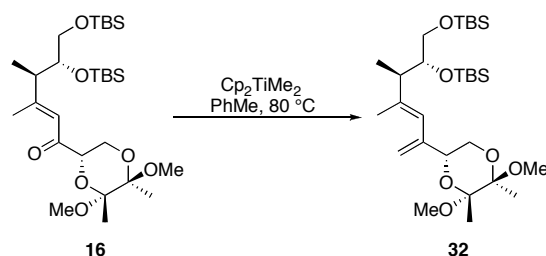
*vacuo* and purified by flash chromatography over silica gel, eluting with 5-10% EtOAc / hexanes, to give alcohol **15** (167 mg, 0.451 mmol, 95%) as colorless oil:  $[\alpha]_D^{23} = +9.4$  ( $c = 1.00$ ,  $\text{CHCl}_3$ ); IR: (neat) 3564, 3466, 2954, 2927, 2856, 1472, 1456, 1255, 1113, 1091, 879, 835, 775, 672  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (300 MHz,  $\text{CDCl}_3$ )  $\delta$  6.03 (s, 1H), 3.71 (dd,  $J = 9.5, 2.8$  Hz, 1H), 3.53-3.60 (m, 1H), 3.48 (dd,  $J = 9.5, 6.5$  Hz, 1H), 2.57 (dq,  $J = 7.3, 7.0$  Hz, 1H), 2.36 (d,  $J = 3.9$  Hz, 1H), 1.86 (d,  $J = 0.9$  Hz, 3H), 1.03 (d,  $J = 7.0$  Hz, 3H), 0.92 (s, 9H), 0.09 (s, 6H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  149.7, 76.6, 73.2, 65.0, 45.9, 25.8, 20.8, 18.2, 15.6, -5.3, -5.4; HRMS (CI+) calcd. for  $\text{C}_{13}\text{H}_{28}\text{O}_2\text{ISi}$  (M+H) 371.0904, found 371.0887.



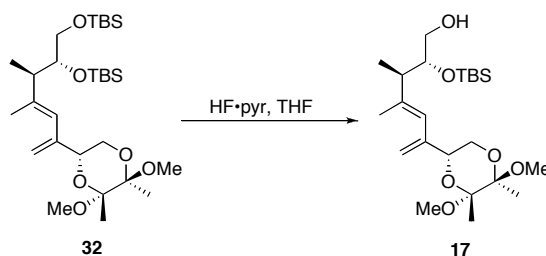
**Bis TBS Ether 31:** To a stirred solution of **15** (644 mg, 1.73 mmol) in  $\text{CH}_2\text{Cl}_2$  (11 mL) were added 2,6-lutidine (406 mg, 0.44 mL, 3.80 mmol) followed after 5 min by TBSOTf (921 mg, 0.80 mL, 3.47 mmol) at 0 °C. The reaction was allowed to warm up to rt. After 2 h, the reaction was quenched with sat. aq.  $\text{NaHCO}_3$  (10 mL) and diluted with  $\text{Et}_2\text{O}$  (30 mL). The aqueous layer was extracted with  $\text{Et}_2\text{O}$  (2 X 30 mL) and the combined organic layer was washed with  $\text{H}_2\text{O}$  and brine (20 mL each). The dried ( $\text{MgSO}_4$ ) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 1% EtOAc / hexanes, to give bis TBS ether **31** (822 mg, 1.69 mmol, 98%) as colorless oil:  $[\alpha]_D^{23} = +14.5$  ( $c = 1.05$ ,  $\text{CHCl}_3$ ); IR: (neat) 2954, 2921, 2883, 2850, 1472, 1396, 1358, 1244, 1102, 1059, 950, 933, 841, 770, 666  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.98 (s, 1H), 3.58 (dt,  $J = 6.8, 4.7$  Hz, 1H), 3.48 (dd,  $J = 9.9, 4.8$  Hz, 1H), 3.39 (dd,  $J = 9.9, 7.0$  Hz, 1H), 2.74 (qd,  $J = 7.1, 4.5$  Hz, 1H), 1.83 (s, 3H), 1.09 (d,  $J = 7.1$  Hz, 3H), 0.91 (s, 9H), 0.90 (s, 9H), 0.07 (s, 6H), 0.05 (s, 6H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  148.9, 77.6, 75.8, 65.4, 45.5, 25.9, 25.8, 22.2, 18.2, 18.0, 15.8, -4.3, -4.9, -5.4, -5.6; HRMS (CI+) calcd. for  $\text{C}_{19}\text{H}_{42}\text{O}_2\text{ISi}_2$  (M+H) 485.1768, found 485.1777.



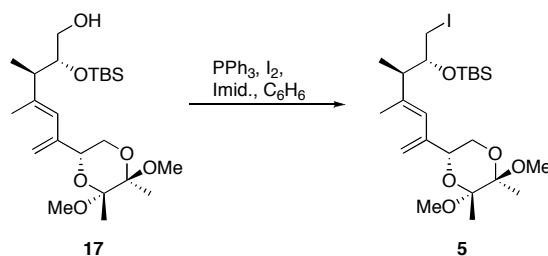
**Enone 16:** To a stirred solution of vinyl iodide **31** (400 mg, 0.826 mmol) in THF (6.5 mL) at -78 °C was added *n*-BuLi (0.30 mL, 0.757 mmol, 2.5 M in hexanes) dropwise. After 2 h at -78 °C, a solution of Weinreb amide **7** (181 mg, 0.688 mmol) in THF (6.5 mL) was added dropwise over 15 min. After another 1.5 h, the reaction was quenched with sat. aq.  $\text{NH}_4\text{Cl}$  (10 mL) and the aqueous layer was extracted with  $\text{Et}_2\text{O}$  (3 X 30 mL). The dried ( $\text{MgSO}_4$ ) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 5-8% EtOAc / hexanes, to give enone **16** (362 mg, 0.646 mmol, 94%) as colorless oil:  $[\alpha]_D^{23} = -37.0$  ( $c = 1.01$ ,  $\text{CHCl}_3$ ); IR: (neat) 2954, 2927, 2856, 1685, 1609, 1472, 1374, 1249, 1146, 1113, 1037, 835, 775  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  6.55 (s, 1H), 4.23 (dd,  $J = 6.1, 4.4$  Hz, 1H), 4.10 (dd,  $J = 11.2, 6.1$  Hz, 1H), 3.90 (dd,  $J = 11.2, 4.4$  Hz, 1H), 3.69-3.73 (m, 1H), 3.50 (dd,  $J = 10.2, 5.1$  Hz, 1H), 3.44 (dd,  $J = 10.2, 6.3$  Hz, 1H), 3.34 (s, 3H), 3.30 (s, 3H), 2.58 (qd,  $J = 7.1, 4.6$  Hz, 1H), 2.23 (d,  $J = 0.96$ , 3H), 1.39 (s, 3H), 1.33 (s, 3H), 1.14 (d,  $J = 7.1$ , 3H), 0.90 (s, 9H), 0.89 (s, 9H), 0.074 (s, 3H), 0.070 (s, 3H), 0.045 (s, 3H), 0.042 (s, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  197.2, 163.3, 121.1, 100.1, 99.2, 76.2, 75.1, 65.2, 58.9, 49.7, 48.3, 46.4, 25.9, 25.8, 19.4, 18.2, 18.0, 17.99, 17.93, 16.0, -4.2, -4.9, -5.34, -5.38; HRMS (ES+) calcd. for  $\text{C}_{28}\text{H}_{56}\text{O}_7\text{Si}_2\text{Na}$  (M+Na) 583.3462, found 581.3470.



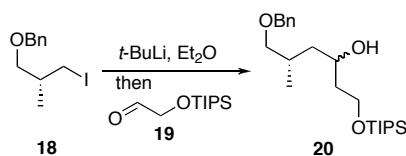
**Diene 32:** To a stirred solution of enone **16** (225 mg, 0.401 mmol) in toluene (3 mL) in a sealed tube was added Petasis reagent<sup>3</sup> (0.92 mL, 1.20 mmol, 1.3 M in toluene) and heated at 80 °C for 4 h in dark. The reaction was cooled down to rt and diluted with pentane (5 mL) and the precipitated solid was filtered off (rinse with 3 X 5 mL pentane). The solvent was evaporated *in vacuo* and the residue was directly purified by flash chromatography over silica gel, eluting 3-4% EtOAc / hexanes, to give diene **32** (199 mg, 0.356 mmol, 89%) as colorless oil:  $[\alpha]_{\text{D}}^{23} = -2.0$  ( $c = 1.00$ ,  $\text{CHCl}_3$ ); IR: (neat) 2948, 2927, 2850, 1472, 1374, 1249, 1151, 1113, 1042, 830, 781  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.67 (s, 1H), 5.46 (s, 1H), 4.99 (s, 1H), 4.59 (dd,  $J = 11.3, 3.5$  Hz, 1H), 3.81 (t,  $J = 11.1$  Hz, 1H), 3.65-3.70 (m, 2H), 3.46 (d,  $J = 5.8$  Hz, 2H), 3.41 (s, 3H), 3.36 (s, 3H), 2.46 (qd,  $J = 7.1, 4.2$  Hz, 1H), 1.77 (d,  $J = 1.1$ , 3H), 1.44 (s, 3H), 1.39 (s, 3H), 1.08 (d,  $J = 7.1$ , 3H), 0.90 (s, 18H), 0.08 (s, 6H), 0.04 (s, 6H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  143.0, 142.1, 123.6, 114.3, 100.9, 100.1, 76.4, 73.7, 65.9, 65.5, 48.6, 48.3, 45.3, 25.99, 25.92, 18.3, 18.1, 17.9, 16.8, 16.0, -4.1, -4.8, -5.35, -5.39; HRMS (ES<sup>+</sup>) calcd. for  $\text{C}_{29}\text{H}_{58}\text{O}_6\text{Si}_2\text{Na}$  ( $\text{M}+\text{Na}$ ) 581.3670, found 581.3646.



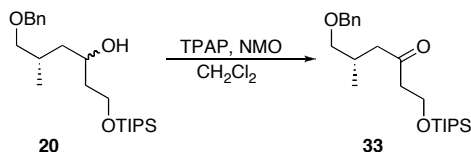
**Alcohol 17:** To a stirred solution of bis TBS ether **32** (156 mg, 0.279 mmol) in THF (3 mL) in a plastic bottle at 0 °C was added HF·pyr stock solution<sup>4</sup> (1.2 mL). After 30 min, the reaction was warmed to rt. After 6 h, the reaction was recooled to 0 °C and another portion of HF·pyr (0.60 mL) was added. After 20 min, the reaction was warmed to rt. After additional 2 h, the reaction was quenched with sat. aq.  $\text{NaHCO}_3$  (5 mL) and the aqueous layer was extracted with EtOAc (3 X 30 mL). The dried ( $\text{MgSO}_4$ ) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 20-25% EtOAc / hexanes, to give alcohol **17** (113 mg, 0.254 mmol, 91%) as colorless oil:  $[\alpha]_{\text{D}}^{23} = -26.0$  ( $c = 1.01$ ,  $\text{CHCl}_3$ ); IR: (neat) 3490, 2953, 2929, 2883, 2855, 2832, 1470, 1462, 1372, 1252, 1147, 1116, 1042, 874, 835, 777  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.74 (s, 1H), 5.44 (s, 1H), 5.01 (s, 1H), 4.59 (dd,  $J = 10.9, 3.7$  Hz, 1H), 3.77-3.84 (m, 2H), 3.69 (dd,  $J = 10.8, 3.8$  Hz, 1H), 3.50-3.59 (m, 2H), 3.40 (s, 3H), 3.36 (s, 3H), 2.49 (dq,  $J = 6.8, 6.7$  Hz, 1H), 1.80 (t,  $J = 6.3$ , 1H), 1.78 (d,  $J = 1.2$  Hz, 3H), 1.43 (s, 3H), 1.39 (s, 3H), 1.08 (d,  $J = 7.0$ , 3H), 0.92 (s, 9H), 0.11 (s, 3H), 0.09 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.8, 141.9, 123.4, 115.2, 100.8, 100.0, 75.0, 73.8, 65.5, 64.2, 48.6, 48.3, 46.0, 25.8, 18.2, 18.1, 17.8, 16.6, 14.8, -4.4, -4.6; HRMS (ES<sup>+</sup>) calcd. for  $\text{C}_{23}\text{H}_{44}\text{O}_6\text{SiNa}$  ( $\text{M}+\text{Na}$ ) 467.2805, found 467.2802.



**Iodide 5:** To a stirred solution of alcohol **17** (85 mg, 0.191 mmol) in benzene (3 mL) at 0 °C were added imidazole (39 mg, 0.574 mmol), PPh<sub>3</sub> (126 mg, 0.478 mmol) and I<sub>2</sub> (97 mg, 0.382 mmol) sequentially. After 10 min, the reaction was warmed to rt. After 1 h, the reaction was quenched with sat. aq. Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> (5 mL) and diluted with EtOAc (20 mL). The aqueous layer was extracted with EtOAc (3 X 20 mL) and the dried (MgSO<sub>4</sub>) extract was concentrated *in vacuo*. The residue was purified by flash chromatography over silica gel, eluting with 10-15% EtOAc / hexanes, to give iodide **5** (91 mg, 0.164 mmol, 86%) as colorless oil:  $[\alpha]_D^{23} = +4.0$  ( $c = 1.02$ , CHCl<sub>3</sub>); IR: (neat) 2949, 2929, 2883, 2859, 2824, 1458, 1372, 1252, 1147, 1116, 1042, 835, 773 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  5.79 (s, 1H), 5.48 (s, 1H), 5.03 (s, 1H), 4.61 (dd,  $J = 11.3, 3.4$  Hz, 1H), 3.84 (dd,  $J = 11.2, 11.0$  Hz, 1H), 3.70 (dd,  $J = 10.8, 3.7$  Hz, 1H), 3.63 (dt,  $J = 6.5, 4.5$  Hz, 1H), 3.42 (s, 3H), 3.37 (s, 3H), 3.18 (dd,  $J = 10.0, 4.2$  Hz, 1H), 3.14 (dd,  $J = 10.0, 6.6$  Hz, 1H), 2.59-2.66 (m, 1H), 1.79 (d,  $J = 1.1$  Hz, 3H), 1.44 (s, 3H), 1.40 (s, 3H), 1.05 (d,  $J = 7.0, 3H$ ), 0.92 (s, 9H), 0.12 (s, 3H), 0.08 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  142.7, 140.9, 124.3, 114.9, 100.9, 100.1, 74.6, 73.8, 65.8, 48.7, 48.3, 46.9, 25.8, 18.2, 18.0, 17.9, 16.5, 15.3, 11.4, -4.2, -4.7; HRMS (ES+) calcd. for C<sub>23</sub>H<sub>43</sub>O<sub>5</sub>ISiNa (M+Na) 577.1822, found 577.1810.

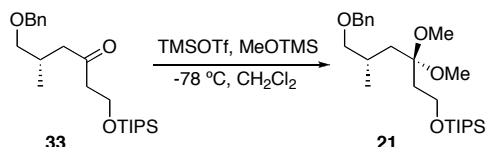


**Alcohol 20:** To a stirred solution of known iodide **18**<sup>5</sup> (1.20 g, 4.13 mmol) in Et<sub>2</sub>O (50 mL) at -78 °C suspended with 4 Å mol. sieves (2.50 g) was added *t*-BuLi (5.8 mL, 9.30 mmol, 1.6 M in pentane). After 15 min, the reaction was warmed to rt for 30 min and recooled to -78 °C. The known aldehyde **19**<sup>6</sup> (1.15 g, 4.96 mmol) in Et<sub>2</sub>O (20 mL) was cannulated to it and stirred at same temperature for 45 min. The reaction was warmed to rt for 45 min and then quenched with sat. aq. NH<sub>4</sub>Cl (30 mL). The mol. sieves was filtered off and the aqueous layer was extracted with EtOAc / Et<sub>2</sub>O (1:1, 3 X 70 mL). The combined organic layer was washed with brine (50 mL). The dried (MgSO<sub>4</sub>) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 8-15% EtOAc / hexanes, to give alcohol **20** (1.17 g, 2.96 mmol, 72%) as colorless oil:  $[\alpha]_D^{23} = -2.7$  ( $c = 1.00$ , CHCl<sub>3</sub>); IR: (neat) 3466, 2941, 2886, 2867, 1454, 1092, 1069, 878, 734, 676 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, two diastereomers)  $\delta$  7.29-7.36 (m, 5H), 4.538 (s, 2H (major isomer)), 4.531 (s, 2H (minor isomer)), 3.89-4.01 (m, 3H), 3.72 (d,  $J = 2.8$  Hz, 1H, major isomer), 3.66 (d,  $J = 2.6$  Hz, 1H, minor isomer), 3.32-3.40 (m, 2H), 2.01-2.08 (m, 1H), 1.59-1.74 (m, 3H), 1.46-1.55 (m, 1H), 1.27-1.33 (m, 1H), 1.07-1.18 (m, 21H), 1.00 (d,  $J = 6.8$  Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  138.6, 128.3, 127.5, 127.4, 76.5, 75.6, 73.0, 72.9, 69.7, 69.5, 63.0, 42.3, 42.1, 39.4, 38.8, 30.4, 30.2, 18.0, 17.9, 17.3, 11.8; HRMS (ES+) calcd. for C<sub>23</sub>H<sub>42</sub>O<sub>3</sub>SiNa (M+Na) 417.2801, found 417.2805.

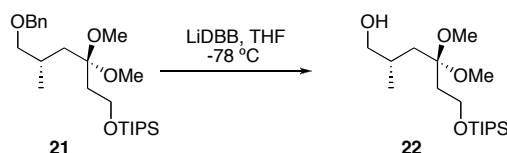


**Ketone 33:** To a stirred solution of alcohol **20** (940 mg, 2.38 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (40 mL) at 0 °C were sequentially added 4 Å mol. sieves (2.50 g), NMO (558 mg, 4.76 mmol) and TPAP (42 mg, 0.119 mmol). After 5 min, the reaction was warmed to rt. After 3 h, the solid was filtered off (rinsed with EtOAc / hexanes (30 mL, 1:1)) and the solvent was removed *in vacuo*. The residue was purified by flash chromatography over silica gel, eluting

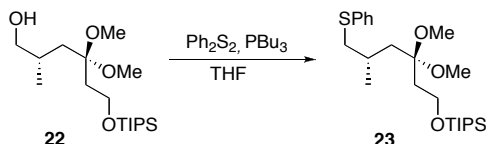
with 8-12% EtOAc / hexanes, to give ketone **33** (910 mg, 2.31 mmol, 97%) as colorless oil:  $[\alpha]_D^{23} = +0.45$  ( $c = 1.32$ ,  $\text{CHCl}_3$ ); IR: (neat) 2959, 2943, 2867, 1718, 1456, 1364, 1108, 884, 743, 683  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.29-7.38 (m, 5H), 4.50 (s, 2H), 3.97 (t,  $J = 6.3$  Hz, 2H), 3.37 (dd,  $J = 9.1, 5.4$  Hz, 1H), 3.29 (dd,  $J = 9.1, 6.7$  Hz, 1H), 2.66 (dd,  $J = 16.0, 5.2$  Hz, 1H), 2.63 (t,  $J = 6.3$  Hz, 2H), 2.36-2.44 (m, 1H), 2.33 (dd,  $J = 16.0, 7.6$  Hz, 1H), 1.04-1.12 (m, 21H), 0.96 (d,  $J = 6.5$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  209.5, 138.5, 128.3, 127.5, 127.4, 75.0, 72.9, 59.2, 48.0, 46.2, 29.5, 17.9, 17.1, 11.9; HRMS (CI+) calcd. for  $\text{C}_{23}\text{H}_{41}\text{O}_3\text{Si}$  (M+H) 393.2825, found 393.2834.



**Ketal 21:** To a stirred solution of ketone **33** (380 mg, 0.967 mmol) in  $\text{CH}_2\text{Cl}_2$  (0.55 mL) at  $-78$  °C was added MeOTMS (408 mg, 0.54 mL, 3.87 mmol) followed by TMSOTf (21.5 mg, 17.5  $\mu\text{L}$ , 96.7  $\mu\text{mol}$ ). After 36 h at  $-78$  °C, the reaction was quenched with pyridine (0.30 mL) and the resulting mixture was poured into sat. aq.  $\text{NaHCO}_3$  (10 mL). The aqueous layer was extracted with  $\text{CH}_2\text{Cl}_2$  (3 X 50 mL) and the dried ( $\text{MgSO}_4$ ) extract was concentrated *in vacuo*. The residue was purified by flash chromatography over silica gel, eluting with 6-10% of EtOAc / hexanes, to give ketal **21** (352 mg, 0.802 mmol, 83%) as colorless oil:  $[\alpha]_D^{23} = +3.9$  ( $c = 1.24$ ,  $\text{CHCl}_3$ ); IR: (neat) 2937, 2894, 2867, 1462, 1151, 1086, 1059, 884, 732, 688  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.26-7.37 (m, 5H), 4.52 (s, 2H), 3.68-3.79 (m, 2H), 3.37 (dd,  $J = 8.9, 5.9$  Hz, 1H), 3.29 (dd,  $J = 8.9, 6.4$  Hz, 1H), 3.178 (s, 3H), 3.172 (s, 3H), 1.93-2.06 (m, 3H), 1.75 (dd,  $J = 14.8, 4.8$  Hz, 1H), 1.42 (dd,  $J = 14.8, 7.5$  Hz, 1H), 1.07-1.13 (m, 21H), 1.05 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  138.8, 128.2, 127.4, 127.3, 102.2, 75.9, 72.9, 59.2, 47.7, 47.6, 36.4, 29.8, 18.1, 18.0, 11.9; HRMS (ES+) calcd. for  $\text{C}_{25}\text{H}_{46}\text{O}_4\text{SiNa}$  (M+Na) 461.3063, found 461.3047.

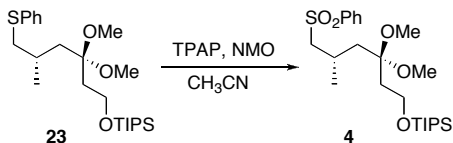


**Alcohol 22:** To a stirred solution of benzyl ether **21** (264 mg, 0.601 mmol) in THF (6 mL) at  $-78$  °C was added freshly prepared LiDBB solution<sup>7</sup> (10.5 mL, 4.20 mmol, 0.4 M in THF) in one portion. After 5 min, the reaction was quenched with sat. aq.  $\text{NH}_4\text{Cl}$  (7 mL). The resulting mixture was diluted with EtOAc (50 mL) and  $\text{H}_2\text{O}$  (7 mL) and the aqueous layer was extracted with EtOAc (3 X 30 mL). The dried extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 10-15% of EtOAc / hexanes, to give alcohol **22** (189 mg, 0.542 mmol, 90%) as colorless oil:  $[\alpha]_D^{23} = -9.5$  ( $c = 1.01$ ,  $\text{CHCl}_3$ ); IR: (neat) 3444, 2943, 2888, 2861, 1151, 1086, 1059, 884, 638  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ )  $\delta$  3.72-3.78 (m, 2H), 3.56 (ddd,  $J = 11.0, 7.7, 4.2$  Hz, 1H), 3.40 (ddd,  $J = 11.0, 6.6, 4.8$  Hz, 1H), 3.22 (s, 3H), 3.19 (s, 3H), 3.08 (dd,  $J = 7.7, 4.8$  Hz, 1H), 2.01-2.06 (m, 2H), 1.88-1.99 (m, 1H), 1.79 (dd,  $J = 14.6, 8.5$  Hz, 1H), 1.49 (dd,  $J = 14.6, 4.1$  Hz, 1H), 1.06-1.15 (m, 21H), 0.95 (d,  $J = 6.8$  Hz, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  102.2, 68.6, 59.4, 47.9, 39.0, 36.5, 32.1, 18.9, 18.0, 11.9; HRMS (ES+) calcd. for  $\text{C}_{18}\text{H}_{40}\text{O}_4\text{SiNa}$  (M+Na) 371.2594, found 371.2599.

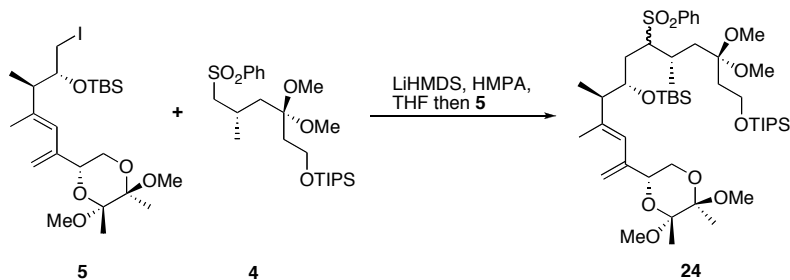


**Sulfide 23:** To a stirred solution of alcohol **22** (184 mg, 0.527 mmol) in THF (1.2 mL) at  $0$  °C were added  $\text{Ph}_2\text{S}_2$  (231 mg, 1.05 mmol) followed by  $\text{PBU}_3$  (243 mg, 0.30 mL, 1.21 mmol). After 10 min, the reaction was warmed to rt. After 5 h, the solvent was removed *in vacuo* and the residue was directly loaded onto silica gel and purified by flash chromatography, eluting with 2-5% EtOAc / hexanes, to give sulfide **23** (230 mg, 0.521 mmol, 99%) as colorless oil:  $[\alpha]_D^{23} = +2.0$  ( $c = 1.05$ ,  $\text{CHCl}_3$ ); IR: (neat) 2941, 2890, 2863, 1454, 1092, 1061, 882, 734,

688  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.35 (d,  $J = 7.5$  Hz, 2H), 7.26-7.30 (m, 2H), 7.16 (t,  $J = 7.2$  Hz, 1H), 3.65-3.75 (m, 2H), 3.178 (s, 3H), 3.171 (s, 3H), 3.14 (dd,  $J = 12.7, 5.4$  Hz, 1H), 2.75 (dd,  $J = 12.7, 7.6$  Hz, 1H), 1.92-1.99 (m, 3H), 1.78 (dd,  $J = 14.7, 5.7$  Hz, 1H), 1.53 (dd,  $J = 14.7, 7.0$  Hz, 1H), 1.13 (d,  $J = 6.6$  Hz, 3H), 1.05-1.11 (m, 21H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  137.3, 128.8, 128.7, 125.5, 102.0, 59.2, 47.7, 41.4, 39.1, 36.4, 29.6, 20.4, 18.0, 11.9; HRMS (CI<sup>+</sup>) calcd. for  $\text{C}_{24}\text{H}_{44}\text{O}_3\text{SiS}$  (M<sup>+</sup>) 440.2781, found 440.2772.



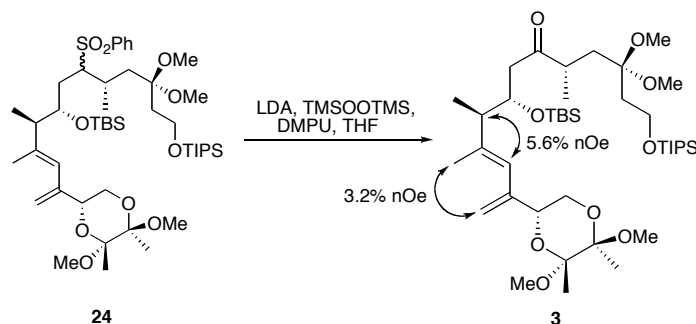
**Sulfone 4:** To a stirred solution of sulfide **23** (205 mg, 0.465 mmol) in  $\text{CH}_3\text{CN}$  (2.5 mL) were sequentially added 4 Å mol. sieves (300 mg), NMO (164 mg, 1.39 mmol) and TPAP (17 mg, 46.5  $\mu\text{mol}$ ) at rt. After 6 h, another portion of TPAP (8.5 mg, 23.3  $\mu\text{mol}$ ) was added. After additional 12 h, the reaction was diluted with EtOAc / hexanes (5 mL, 1:1) and passed through a small plug of silica gel (rinsed with EtOAc / hexanes (50 mL, 1:1)). Solvent was removed *in vacuo* pressure and the residue was purified by flash chromatography over silica gel, eluting with 15-20% EtOAc / hexanes, to give sulfone **4** (204 mg, 0.432 mmol, 93%) as a colorless oil:  $[\alpha]_{\text{D}}^{23} = +0.55$  ( $c = 1.09$ ,  $\text{CHCl}_3$ ); IR: (neat) 2941, 2890, 2859, 1462, 1443, 1318, 1306, 1147, 1084, 1046, 882, 750, 688  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.92-7.94 (m, 2H), 7.63-7.67 (m, 1H), 7.55-7.59 (m, 2H), 3.73 (dd,  $J = 14.3, 2.5$  Hz, 1H), 3.56-3.67 (m, 2H), 3.08 (s, 3H), 3.04 (s, 3H), 2.84 (dd,  $J = 14.3, 9.5$  Hz, 1H), 2.15-2.20 (m, 1H), 1.75-1.82 (m, 1H), 1.70 (dd,  $J = 14.6, 9.0$  Hz, 1H), 1.42-1.52 (m, 2H), 1.18 (d,  $J = 6.6$  Hz, 3H), 1.04-1.08 (m, 21H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{CDCl}_3$ )  $\delta$  139.9, 133.4, 129.1, 128.0, 101.7, 61.4, 59.1, 47.6 (2 carbons), 39.9, 36.1, 25.3, 21.5, 18.0, 11.9; HRMS (ES<sup>+</sup>) calcd. for  $\text{C}_{24}\text{H}_{44}\text{O}_5\text{SiSNa}$  (M<sup>+</sup>Na) 495.2576, found 495.2560.



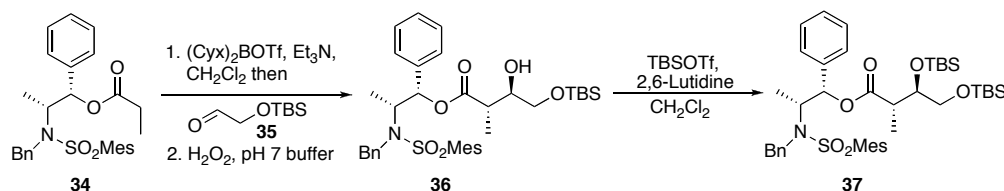
**Coupled Sulfone 24:** To a stirred solution of sulfone **4** (54.5 mg, 0.115 mmol) in THF (0.40 mL) at  $-78$  °C was added LiHMDS (104  $\mu\text{L}$ , 104  $\mu\text{mol}$ , 1M in THF). After 30 min, the reaction was warmed to  $0$  °C and treated with HMPA (100  $\mu\text{L}$ ) followed by a solution of iodide **5** (32.0 mg, 57.7  $\mu\text{mol}$ ) in THF (0.40 mL). After 1 h, the reaction was warmed to rt. After 6 h, the reaction was quenched with sat. aq.  $\text{NH}_4\text{Cl}$  (5 mL) at  $0$  °C and diluted with EtOAc (20 mL). The aqueous layer was extracted with EtOAc (3 X 20 mL) and the dried ( $\text{MgSO}_4$ ) extract was concentrated *in vacuo*. The residue was purified by flash chromatography over silica gel, eluting with 10-25% EtOAc / hexanes, to sequentially give coupled sulfone **24** (44.5 mg, 49.4  $\mu\text{mol}$ , 86%, dr (2:1)) as colorless oil followed by recovered sulfone **4** (25.7 mg, 54.3  $\mu\text{mol}$ ):  $[\alpha]_{\text{D}}^{23} = -21.5$  ( $c = 1.00$ ,  $\text{CHCl}_3$ ); IR: (neat) 2945, 2890, 2863, 2832, 1462, 1439, 1372, 1299, 1252, 1143, 1112, 1084, 1042, 878, 835, 773, 734, 688  $\text{cm}^{-1}$ ;  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.87-7.91 (m, 2H), 7.61-7.66 (m, 1H), 7.52-7.59 (m, 2H), 5.76 (s, 1H (minor isomer)), 5.61 (s, 1H (major isomer)), 5.46 (s, 1H), 5.00 (s, 1H (major isomer)), 4.98 (s, 1H (minor isomer)), 4.55-4.61 (m, 1H), 4.21 (td,  $J = 6.6, 2.9$  Hz, 1H (minor isomer)), 4.08 (td,  $J = 8.8, 3.4$  Hz, 1H (major isomer)), 3.87-3.94 (m, 1H (major isomer)), 3.78-3.84 (m, 1H), 3.63-3.75 (m, 2H), 3.52-3.56 (m, 1H (major isomer)), 3.43 (s, 3H (major isomer)), 3.40-3.42 (m, 1H, (minor isomer)), 3.41 (s, 3H, (minor isomer)), 3.37 (s, 3H, (major isomer)), 3.36 (s, 3H, (minor isomer)), 3.19-3.21 (m, 1H (major isomer)), 3.19 (s, 3H (major isomer)), 3.16 (s, 3H (major isomer)), 3.04 (s, 3H (minor isomer)), 2.98 (s, 3H (major isomer)), 2.55 (q,  $J = 7.1$  Hz, 1H (minor isomer)), 2.41 (qd,  $J = 7.0, 2.8$  Hz, 1H (minor isomer)), 2.33 (qd,  $J = 6.9, 2.9$  Hz, 1H (major isomer)), 2.14-2.21 (m, 2H), 1.97-2.07 (m, 1H), 1.09-1.19 (m, 1H), 1.82 (s, 3H (minor isomer)), 1.76 (s, 3H (major isomer)), 1.58-1.74 (m, 2H), 1.41-1.47 (m, 1H), 1.46 (s, 3H (major isomer)),



1.43 (s, 3H (minor isomer)), 1.40 (s, 3H (major isomer)), 1.39 (s, 3H (minor isomer)), 1.30-1.37 (m, 1H), 1.26 (d,  $J = 12.8$  Hz, 3H (major isomer)), 1.05-1.16 (m, 27 H), 0.90 (s, 9H (major isomer)), 0.89 (s, 9H (minor isomer)), 0.16 (s, 3H (minor isomer)), 0.12 (s, 3H (minor isomer)), 0.098 (s, 3H (major isomer)), 0.090 (s, 3H (major isomer));  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  142.8, 142.6, 141.7, 141.0, 139.9, 139.2, 133.3, 129.1, 129.0, 128.57, 128.51, 124.2, 123.3, 116.0, 115.2, 102.0, 101.8, 100.9, 100.1 (2 peaks), 73.9, 73.6, 72.2, 72.1, 65.8, 65.7, 65.4, 65.0, 59.3, 59.2, 48.7 (2 peaks), 48.34, 48.31, 47.96, 47.94, 47.8, 47.7, 47.6, 46.9, 46.2, 38.9, 36.9, 36.5, 34.0, 29.7, 29.4, 29.3, 28.3, 28.1, 27.4, 25.9, 25.8, 18.46, 18.43, 18.3, 18.1, 18.06, 18.04, 17.95, 17.91, 17.8, 16.4, 14.5, 12.0, 11.9, -4.1, -4.30, -4.38, -4.4; HRMS (ES<sup>+</sup>) calcd. for  $\text{C}_{47}\text{H}_{86}\text{O}_{10}\text{Si}_2\text{SNa}$  (M+Na) 921.5378, found 921.5389.



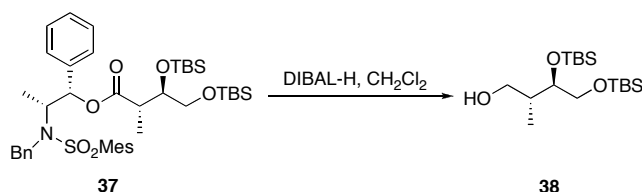
**Ketone 3:** To a stirred solution of diisopropylamine (7.0  $\mu\text{L}$ , 47.8  $\mu\text{mol}$ ) in THF (0.30 mL) at  $-78$   $^\circ\text{C}$  was added *n*-BuLi (20.0  $\mu\text{L}$ , 47.8  $\mu\text{mol}$ , 2.5 M in hexanes). After 15 min, the reaction was warmed to  $0$   $^\circ\text{C}$  and stirred for 10 min. The reaction was recooled to  $-20$   $^\circ\text{C}$  and treated with DMPU (106 mg, 0.10 mL, 0.827 mmol). A solution of sulfone **24** (21.5 mg, 23.9  $\mu\text{mol}$ ) in THF (0.30 mL) was added via cannula. After 15 min, neat TMSOOTMS (26  $\mu\text{L}$ , 0.119 mmol) was added to the reaction in one portion. After additional 30 min, the reaction was slowly warmed to rt over 1 h and another portion of TMSOOTMS (13  $\mu\text{L}$ , 59.7  $\mu\text{mol}$ ) was added. After 1 h, the reaction was quenched with sat. aq.  $\text{NH}_4\text{Cl}$  (2 mL) and diluted with EtOAc (10 mL). The aqueous layer was extracted with EtOAc (3 X 10 mL) and the dried ( $\text{MgSO}_4$ ) extract was concentrated *in vacuo*. The residue was purified by flash chromatography over silica gel, eluting with 5-25% EtOAc / hexanes with 2%  $\text{Et}_3\text{N}$ , to sequentially give ketone **3** (9.4 mg, 12.2  $\mu\text{mol}$ , 51% (87% BORSM)) as colorless oil followed by recovered sulfone **24** (8.9 mg, 9.9  $\mu\text{mol}$ , 41%):  $[\alpha]_{\text{D}}^{23} = -5.0$  ( $c = 0.61$ ,  $\text{CHCl}_3$ ); IR: (neat) 2949, 2890, 2863, 2828, 1715, 1462, 1372, 1252, 1147, 1116, 1046, 878, 835, 777, 676  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  5.57 (s, 1H), 5.46 (s, 1H), 4.98 (s, 1H), 4.58 (dd,  $J = 11.4, 3.4$  Hz, 1H), 4.27-4.30 (m, 1H), 3.80 (dd,  $J = 11.3, 10.9$  Hz, 1H), 3.71 (td,  $J = 7.3, 3.0$  Hz, 2H), 3.64 (dd,  $J = 10.8, 3.7$  Hz, 1H), 3.41 (s, 3H), 3.35 (s, 3H), 3.14 (s, 3H), 3.08 (s, 3H), 2.58-2.69 (m, 3H), 2.43 (qd,  $J = 7.0, 3.5$  Hz, 1H), 2.23 (dd,  $J = 14.5, 8.8$  Hz, 1H), 1.92 (t,  $J = 7.4$  Hz, 2H), 1.78 (d,  $J = 0.9$  Hz, 3H), 1.40-1.45 (m, 1H), 1.43 (s, 3H), 1.38 (s, 3H), 1.06-1.14 (m, 24H), 1.01 (d,  $J = 7.0, 3\text{H}$ ), 0.90 (s, 9H), 0.11 (s, 3H), 0.06 (s, 3H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ )  $\delta$  212.1, 142.8, 142.4, 123.8, 114.8, 101.5, 100.9, 100.1, 73.6, 70.1, 65.7, 59.3, 48.6, 48.3, 48.0, 47.9, 47.4, 46.7, 41.9, 36.7 (2 carbons), 25.8, 18.3, 18.2, 18.0 (2 carbons), 17.1, 14.7, 11.9, -4.5, -4.9; HRMS (ES<sup>+</sup>) calcd. for  $\text{C}_{41}\text{H}_{80}\text{O}_9\text{Si}_2\text{Na}$  (M+Na) 795.5239, found 795.5221.



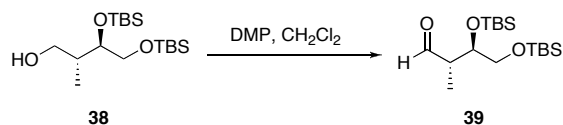
**Aldol product 37:** To a stirred solution of **34**<sup>8</sup> (1.20 g, 2.50 mmol) in  $\text{CH}_2\text{Cl}_2$  (13 mL) was added  $\text{Et}_3\text{N}$  (705 mg, 0.98 mL, 7.00 mmol) dropwise at rt and then cooled it down to  $-78$   $^\circ\text{C}$ . A solution of  $(\text{Cyx})_2\text{BOTf}$  (6.5 mL, 6.5 mmol, 1M in hexane) was added dropwise over 30 min. After 3 h, the aldehyde **35**<sup>9</sup> (871 mg, 5.00 mmol) in  $\text{CH}_2\text{Cl}_2$  (5 mL) was added dropwise to it. After an additional 1 h at  $-78$   $^\circ\text{C}$ , the reaction was warmed to  $0$   $^\circ\text{C}$ . After another 2.5 h, pH 7 buffer solution (22 mL) and 30%  $\text{H}_2\text{O}_2$  (6 mL) were added to the solution. After vigorous

stirring for 12 h at rt, the reaction mixture was concentrated *in vacuo* and partitioned between H<sub>2</sub>O (25 mL) and CH<sub>2</sub>Cl<sub>2</sub> (50 mL). The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (3 X 30 mL) and the combined organic layer was washed with H<sub>2</sub>O (30 mL). The dried (MgSO<sub>4</sub>) extract was concentrated *in vacuo* and then high vacuum was applied for 2 h. The crude was passed through a small plug of silica gel (50 g), eluting with 100% EtOAc (150 mL) to get impure **36**.

The crude **36** was redissolved in CH<sub>2</sub>Cl<sub>2</sub> (6.5 mL) and were added 2,6-lutidine (738 mg, 0.80 mL, 5.00 mmol) followed by TBSOTf (1.26 g, 1.1 mL, 5.00 mmol) at 0 °C. After 3 h, the reaction mixture was quenched with sat. aq. NaHCO<sub>3</sub> (10 mL) and diluted with CH<sub>2</sub>Cl<sub>2</sub> (50 mL) and H<sub>2</sub>O (20 mL). The aqueous layer was extracted with CH<sub>2</sub>Cl<sub>2</sub> (4 X 50 mL) and the combined organic layer was washed with H<sub>2</sub>O and brine (25 mL each). The dried (MgSO<sub>4</sub>) extract was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with 3-8 % EtOAc / hexanes, to give bis TBS ether **37** (1.40 g, 1.82 mmol, 73%, dr (10:1)) as dense colorless oil: [ $\alpha$ ]<sub>D</sub><sup>23</sup> = -19.7 (*c* = 1.01, CHCl<sub>3</sub>); IR: (neat) 2954, 2927, 2883, 2856, 1745, 1598, 1472, 1456, 1331, 1255, 1157, 1097, 1009, 852, 781, 732, 699, 661 cm<sup>-1</sup>; <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>)  $\delta$  7.36-7.39 (m, 2H), 7.17-7.30 (m, 4H), 7.09-7.14 (m, 2H), 6.88 (s, 2H), 6.80 (d, *J* = 7.0 Hz, 2H), 5.73 (d, *J* = 5.5 Hz, 1H), 4.84 (d, *J* = 16.3 Hz, 1H), 4.48 (d, *J* = 16.3 Hz, 1H), 4.04-4.12 (m, 1H), 3.90 (q, *J* = 5.1 Hz, 1H), 3.48-3.57 (m, 2H), 2.62-2.71 (m, 1H), 2.44 (s, 6H), 2.31 (s, 3H), 1.19 (d, *J* = 6.9 Hz, 3H), 1.08 (d, *J* = 7.2 Hz, 3H), 0.87 (s, 18H), 0.07 (s, 3H), 0.06 (s, 3H), 0.006 (s, 3H), 0.001 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  172.3, 142.4, 140.4, 138.5, 138.3, 133.1, 132.1, 128.3, 128.2, 128.0, 127.7, 127.2, 126.4, 77.8, 74.7, 65.1, 56.7, 48.1, 43.7, 25.9, 25.8, 22.9, 20.9, 18.3, 18.1, 14.5, 12.5, -4.3, -4.8, -5.4, -5.5; HRMS (ES<sup>+</sup>) calcd. for C<sub>42</sub>H<sub>65</sub>O<sub>6</sub>Si<sub>2</sub>Na (M+Na) 790.3969, found 790.3943.

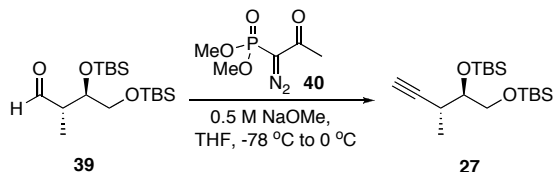


**Alcohol 38:** To a stirred solution of **37** (1.74 g, 2.27 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (22 mL) at -78 °C was added DIBAL-H (5.23 mL, 5.23 mmol, 1M in CH<sub>2</sub>Cl<sub>2</sub>). After 3 h, the reaction diluted with Et<sub>2</sub>O (60 mL) and quenched with aq. Rochelle's salt (0.5 M, 30 mL) and stirred vigorously for 45 min to get two clear layers. The aq. layer was extracted with Et<sub>2</sub>O (3 X 50 mL) and the dried (MgSO<sub>4</sub>) extract was concentrated *in vacuo* and purified by chromatography over silica gel, eluting with 10-15 % Et<sub>2</sub>O / pentane, to give alcohol **38** (657 mg, 1.89 mmol, 83%) as colorless oil. [ $\alpha$ ]<sub>D</sub><sup>23</sup> = +5.9 (*c* = 0.81, CHCl<sub>3</sub>); IR: (neat) 3417, 2954, 2927, 2883, 2850, 1472, 1462, 1255, 1097, 1031, 835, 775 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.72-3.80 (m, 2H), 3.55-3.67 (m, 3H), 2.97 (dd, *J* = 7.1, 4.5 Hz, 1H), 1.90-1.99 (m, 1H), 1.05 (d, *J* = 7.1 Hz, 3H), 0.916 (s, 9H), 0.914 (s, 9H), 0.11 (s, 3H), 0.10 (s, 3H), 0.09 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  77.3, 65.1, 64.6, 37.1, 25.9, 25.8, 18.2, 18.0, 14.0, -4.3, -4.9, -5.43, -5.47; HRMS (CI<sup>+</sup>) calcd. for C<sub>17</sub>H<sub>40</sub>O<sub>3</sub>Si<sub>2</sub> (M<sup>+</sup>) 349.2594, found 349.2593.

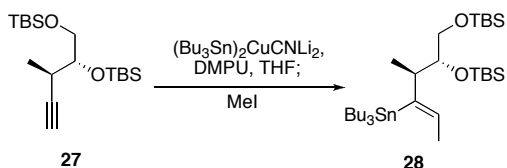


**Aldehyde 39:** To a stirred solution of alcohol **38** (420 mg, 1.20 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) at 0 °C was added DMP (1.01 g, 2.40 mmol) in one portion. After 5 min, the reaction was warmed to rt. After another 1.5 h, the reaction mixture was quenched with sat. aq. NaHCO<sub>3</sub> (10 mL) and diluted with Et<sub>2</sub>O (30 mL). The aqueous layer was extracted with Et<sub>2</sub>O (2 X 30 mL). The dried (MgSO<sub>4</sub>) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting 2-3 % Et<sub>2</sub>O / pentane, to give aldehyde **39** (399 mg, 1.15 mmol, 96 %) as colorless oil: [ $\alpha$ ]<sub>D</sub><sup>23</sup> = +29.4 (*c* = 1.00, CHCl<sub>3</sub>); IR: (neat) 2948, 2921, 2888, 2856, 1723, 1472, 1260, 1108, 835, 775 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  9.76 (d, *J* = 1.6 Hz, 1H), 4.05 (td, *J* = 6.1, 3.7 Hz, 1H), 3.60 (d, *J* = 6.1 Hz, 2H), 2.59 (qdd, *J* = 7.0, 3.8, 1.6 Hz, 1H), 1.13 (d, *J* = 7.0 Hz, 3H), 0.90 (s, 18H), 0.10 (s, 6H), 0.06 (s, 6H); <sup>13</sup>C

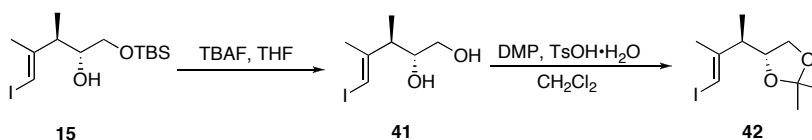
NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  203.6, 74.0, 64.6, 49.8, 25.8, 25.7, 18.2, 18.0, 9.4, -4.3, -5.0, -5.5; HRMS (ES<sup>+</sup>) calcd. for C<sub>17</sub>H<sub>39</sub>O<sub>3</sub>Si<sub>2</sub> (M+H) 347.2438, found 347.2425.



**Alkyne 27:** To a stirred solution of Ohira-Bestmann reagent **40**<sup>10</sup> (693 mg, 3.60 mmol) in THF (20 mL) at  $-78$  °C was added NaOMe solution (7.2 mL, 3.60 mmol, 0.5M in THF) dropwise over 30 min. A solution of aldehyde **39** (359 mg, 1.03 mmol) in THF (7 mL) was added dropwise to the solution and slowly warmed to 0 °C over 2 h. The reaction was quenched with sat. aq. NH<sub>4</sub>Cl (10 mL) and diluted with Et<sub>2</sub>O (25 mL) and the aqueous layer was extracted with Et<sub>2</sub>O (3 X 50 mL). The dried (MgSO<sub>4</sub>) extract was purified by chromatography over silica gel, eluting with 1-2% Et<sub>2</sub>O / pentane, to give alkyne **27** (341 mg, 0.995 mmol, 96%) as colorless oil:  $[\alpha]_D^{23} = +4.2$  ( $c = 1.63$ , CHCl<sub>3</sub>); IR: (neat) 3308, 2954, 2927, 2888, 2856, 1472, 1456, 1358, 1255, 1129, 1086, 1026, 1004, 955, 835, 781, 666, 634 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  3.73 (dd,  $J = 9.3, 5.9$  Hz, 1H), 3.61-3.65 (m, 1H), 3.57 (dd,  $J = 9.3, 5.4$  Hz, 1H), 2.73-2.80 (m, 1H), 2.03 (d,  $J = 2.5$  Hz, 1H), 1.21 (d,  $J = 7.2$  Hz, 3H), 0.92 (s, 18H), 0.09 (s, 9H), 0.08 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  85.7, 75.2, 69.5, 65.2, 29.6, 25.9, 25.8, 18.3, 18.1, 16.9, -4.1, -4.8, -5.3; HRMS (CI<sup>+</sup>) calcd. for C<sub>18</sub>H<sub>39</sub>O<sub>2</sub>Si<sub>2</sub> (M+H) 343.2489, found 343.2486.

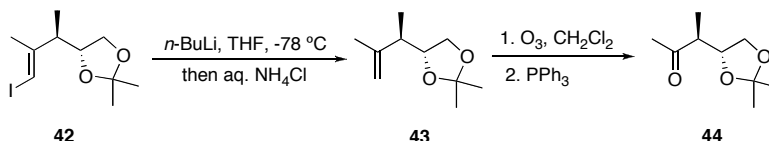


**Vinyl Stannane 28:** To a stirred suspension of CuCN (52 mg, 0.584 mmol) in THF (4 mL) at  $-78$  °C was added *n*-BuLi (0.48 mL, 1.18 mmol, 2.5 M in hexanes). The mixture was slowly warmed to  $-40$  °C for 15 min, then re-cooled to  $-78$  °C and Bu<sub>3</sub>SnH (340 mg, 0.31 mL, 1.16 mmol) was added. After 15 min, a solution of alkyne **27** (50 mg, 0.146 mmol) in THF (4 mL) was added to the reaction. After another 30 min, DMPU (413 mg, 0.39 mL, 3.22 mmol) was added. After additional 30 min, MeI (414 mg, 0.18 mL, 2.92 mmol) was added and allowed to warm to rt. After 14 h, the reaction was quenched with sat. aq. NH<sub>4</sub>Cl (4 mL) and diluted with Et<sub>2</sub>O (15 mL). The aqueous layer was extracted with Et<sub>2</sub>O (3 X 15 mL) and the dried (MgSO<sub>4</sub>) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with pentane (100 mL), to give vinyl stannane **28** (78 mg, 0.121 mmol, 83%) as colorless oil:  $[\alpha]_D^{23} = -7.4$  ( $c = 1.02$ , CHCl<sub>3</sub>); IR: (neat) 2954, 2921, 2856, 1462, 1255, 1118, 1086, 1004, 830, 775 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>)  $\delta$  6.26 (q,  $J = 6.5$  Hz, 1H), 3.59-3.65 (m, 2H), 3.45 (dd,  $J = 9.6, 5.8$  Hz, 1H), 2.48-2.55 (m, 1H), 1.73 (d,  $J = 6.5$  Hz, 3H), 1.46-1.54 (m, 6H), 1.29-1.38 (m, 6H), 1.01 (d,  $J = 7.1$  Hz, 3H), 0.89-1.02 (m, 15H), 0.91 (s, 18H), 0.09 (s, 3H), 0.08 (s, 3H), 0.04 (s, 6H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>)  $\delta$  146.2, 134.7, 77.2, 65.4, 45.5, 29.2, 27.5, 26.06, 26.03, 20.2, 18.4, 18.2, 16.2, 13.6, 10.6, -3.9, -4.6, -5.33, -5.35; HRMS (CI<sup>+</sup>) calcd. for C<sub>31</sub>H<sub>69</sub>O<sub>2</sub>Si<sub>2</sub>Sn (M+H) 649.3858, found 649.3827.



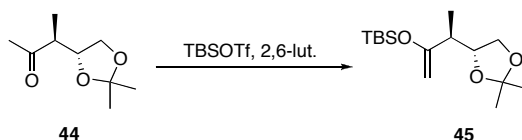
**Acetone 42:** To a stirred solution of alcohol **15** (996 mg, 2.69 mmol) in THF (30 mL) was added TBAF (5.4 mL, 5.4 mmol, 1 M in THF) at rt. After 1 h, the reaction was quenched with H<sub>2</sub>O (15 mL) and diluted with EtOAc (20 mL). The aqueous layer was extracted with EtOAc (4 X 50 mL) and the combined organic layer was washed with H<sub>2</sub>O and brine (20 mL each). The dried (MgSO<sub>4</sub>) extract was concentrated *in vacuo* to give crude diol **41**.

The crude diol **41** was redissolved in CH<sub>2</sub>Cl<sub>2</sub> (24 mL) and dimethoxy propane (1.40 g, 1.65 mL, 13.4 mmol) followed by TsOH•H<sub>2</sub>O (52 mg, 0.269 mmol) was added to it at rt. After 12 h, the reaction was quenched with sat. aq. NaHCO<sub>3</sub> (15 mL) and the aqueous layer was extracted with Et<sub>2</sub>O (3 X 50 mL). The dried (MgSO<sub>4</sub>) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 5-10% EtOAc / hexanes, to give acetone **42** (685 mg, 2.31 mmol, 86%) as colorless oil: [α]<sub>D</sub><sup>23</sup> = +7.8 (*c* = 1.00, CHCl<sub>3</sub>); IR: (neat) 2981, 2932, 2878, 1451, 1380, 1364, 1260, 1211, 1157, 1059, 862 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 6.04 (s, 1H), 4.00-4.07 (m, 2H), 3.60-3.65 (m, 1H), 2.53-2.60 (m, 1H), 1.87 (s, 3H), 1.40 (s, 3H), 1.35 (s, 3H), 1.01 (d, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 148.9, 109.2, 77.8, 76.9, 67.7, 46.6, 26.7, 25.5, 21.6, 15.3; HRMS (EI+) calcd. for C<sub>10</sub>H<sub>17</sub>O<sub>2</sub>I (M<sup>+</sup>) 296.02736, found 296.02680.

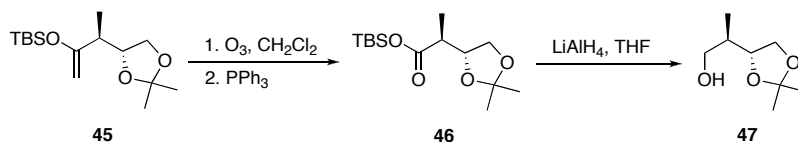


**Methyl Ketone 44:** To a stirred solution of vinyl iodide **42** (764 mg, 2.58 mmol) in THF (16 mL) at -78 °C was added *n*-BuLi (1.2 mL, 3.00 mmol, 2.5 M in hexanes) dropwise. After 2 h, the reaction was quenched with sat. aq. NH<sub>4</sub>Cl (10 mL) and the aqueous layer was extracted with Et<sub>2</sub>O (3 X 50 mL). The combined organic layer was dried over MgSO<sub>4</sub> and concentrated *in vacuo* to give crude alkene **43**.

To a stirred solution of crude alkene **43** in CH<sub>2</sub>Cl<sub>2</sub> (20 mL) at -78 °C was bubbled ozone gas until a pale blue color persisted. Argon gas was bubbled until the solution became colorless and PPh<sub>3</sub> (2.03 g, 7.74 mmol) was added to it and the cooling bath was removed. After 3 h at rt, the solvent was evaporated *in vacuo* and the crude mixture was loaded directly onto silica gel and was purified by flash chromatography, eluting with 20-25% Et<sub>2</sub>O / pentane, to give ketone **44** (302 mg, 1.75 mmol, 68%) as colorless oil: [α]<sub>D</sub><sup>23</sup> = +5.6 (*c* = 1.10, CHCl<sub>3</sub>); IR: (neat) 2986, 2932, 1712, 1456, 1369, 1249, 1211, 1151, 1053, 852 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.21 (dt, *J* = 8.3, 6.5 Hz, 1H), 4.08 (dd, *J* = 8.3, 6.2 Hz, 1H), 3.65 (dd, *J* = 8.3, 6.8 Hz, 1H), 2.76 (dq, *J* = 7.6, 7.0 Hz, 1H), 2.23 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H), 1.05 (d, *J* = 7.0 Hz, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 210.6, 109.2, 76.9, 67.4, 50.3, 29.7, 26.6, 25.3, 12.3; HRMS (CI+) calcd. for C<sub>9</sub>H<sub>17</sub>O<sub>3</sub> (M+H) 173.1178, found 173.1162.



**TBS Enol Ether 45:** To a stirred solution of ketone **44** (200 mg, 1.16 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (7 mL) at 0 °C were added 2,6-lutidine (498 mg, 0.54 mL, 4.64 mmol) followed by TBSOTf (614 mg, 0.53 mL, 2.32 mmol). After 1.5 h, the reaction was quenched with sat. aq. NaHCO<sub>3</sub> (5 mL) and diluted with Et<sub>2</sub>O (20 mL) and H<sub>2</sub>O (5 mL). The aqueous layer was extracted with Et<sub>2</sub>O (2 X 30 mL) and the dried (MgSO<sub>4</sub>) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 3-5% EtOAc / hexanes, to give TBS enol ether **45** (315 mg, 1.10 mmol, 95%) as colorless oil: [α]<sub>D</sub><sup>23</sup> = -12.8 (*c* = 1.03, CHCl<sub>3</sub>); IR: (neat) 2986, 2959, 2932, 2850, 1630, 1478, 1363, 1255, 1064, 999, 841, 781 cm<sup>-1</sup>; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ 4.21 (dd, *J* = 13.6, 7.2 Hz, 1H), 4.11 (d, *J* = 0.8 Hz, 1H), 4.07 (s, 1H), 3.97 (dd, *J* = 8.0, 6.2 Hz, 1H), 3.66 (t, *J* = 8.0 Hz, 1H), 2.41 (dq, *J* = 7.2, 6.9 Hz, 1H), 1.43 (s, 3H), 1.36 (s, 3H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.95 (s, 9H), 0.21 (s, 3H), 0.19 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ 160.1, 108.6, 89.5, 77.1, 66.8, 43.4, 26.6, 25.7, 25.5, 18.1, 13.2, -4.6, -4.7; HRMS (CI+) calcd. for C<sub>15</sub>H<sub>31</sub>O<sub>3</sub>Si (M+H) 287.2043, found 287.2044.



**Acetonide Alcohol 47:** To a stirred solution of **45** (141 mg, 0.492 mmol) in  $\text{CH}_2\text{Cl}_2$  (10 ml) at  $-78\text{ }^\circ\text{C}$  was bubbled ozone gas until a pale blue color persisted. Argon gas was bubbled until the solution became colorless and  $\text{PPh}_3$  (386 mg, 1.47 mmol) was added to it and the cooling bath was removed. After 3 h at rt, the solvent was evaporated *in vacuo* to give crude **46**.

The crude **46** was redissolved in dry THF (2 mL). This solution was added dropwise to a mixture of  $\text{LiAlH}_4$  (112 mg, 2.95 mmol) in dry THF (2 mL) at  $0\text{ }^\circ\text{C}$  over 15 min and stirred at that temperature for 3 h. The reaction was quenched with minimal amount of methanol (15 drops) and diluted with EtOAc (20 mL) and water (5 mL) and the aqueous layer was extracted with EtOAc (3 X 15 mL). The dried ( $\text{MgSO}_4$ ) extract was concentrated *in vacuo* and purified by flash chromatography over silica gel, eluting with 30-35% EtOAc / hexanes, to give known acetonide alcohol **47**<sup>11</sup> (42 mg, 0.262 mmol, 53%) as colorless oil:  $[\alpha]_{\text{D}}^{23} = -10.9$  ( $c = 1.04$ ,  $\text{C}_6\text{H}_6$ ),  $-18.7$  ( $c = 0.90$ ,  $\text{CHCl}_3$ );  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ )  $\delta$  4.11 (dd,  $J = 8.0, 6.0$  Hz, 1H), 3.96 (q,  $J = 7.6$  Hz, 1H), 3.60-3.70 (m, 3H), 2.77 (dd,  $J = 8.0, 2.8$  Hz, 1H), 1.87 (m, 1H), 1.44 (s, 3H), 1.39 (s, 3H), 0.85 (d,  $J = 6.9$  Hz, 3H);  $^{13}\text{C NMR}$  (100 MHz,  $\text{C}_6\text{D}_6$ )  $\delta$  108.9, 79.9, 68.4, 66.5, 39.3, 26.5, 25.6, 12.7.

## References

1. S. V. Ley and P. Michel, *Synthesis*, 2004, 147-150.
2. (a) I. Hanisch and R. Bruckner, *Synlett*, 2000, 374-378. (b) N. Yin, G. Wang, M. Quin and E. Negishi, *Angew. Chem. Int. Ed.*, 2006, **45**, 2916-2920.
3. J. F. Payack, D. L. Hughs, D. Cai, I. F. Cottrell and T. R. Verhoeven, *Org. Synth.*, 2003, 19-26.
4. The stock solution was prepared by mixing  $\text{HF}\cdot\text{pyr}$  (1 mL, 70% HF in pyridine), pyridine (2 mL) and 5 THF (5 mL).
5. (a) J. W. White and M. Kawaski, *J. Org. Chem.*, 1992, **57**, 5292-5300. (b) B. G. Vong, S. Abraham, A. X. Xiang and E. A. Theodorakis, *Org. Lett.*, 2003, **5**, 1617-1620.
6. Kopecky, D. J.; Rychnovsky, S. D. *J. Am. Chem. Soc.*, **2001**, *123*, 8420-8421.
7. (a) To a stirred solution of DBB (1.85 g, 6.8 mmol) in THF (17 mL) at  $0\text{ }^\circ\text{C}$  was added lithium wire (0.65 g,  $\sim 34$  mmol). The reaction was sonicated for 10 min and then stirred for additional 2 h. (b) P. K. Freeman and L. L. Hutchinson, *J. Org. Chem.*, 1980, **45**, 1924-1930.
8. (a) A. Abiko, J.-F. Liu, and S. Masamune, *J. Am. Chem. Soc.*, 1997, **119**, 2586-2587. (b) T. Inoue, J.-F. Liu, D. C. Buske, and A. Abiko, *J. Org. Chem.*, 2002, **67**, 5250-5256.
9. J. A. Lafontaine, D. P. Provencal, C. Gardelli and J. W. Leahy, *J. Org. Chem.*, 2004, **68**, 4215-4234.
10. (a) S. Ohira, *Synth. Commun.*, 1989, **19**, 561-564. (b) S. Müller, B. Liepold, G. Roth and H. J. Bestmann, *Synlett*, 1996, 521-522.
11. (a) K. C. Nicolaou, D. P. Papahatjis, D. A. Claremon, R. L. Magolda and R. E. Dolle, *J. Org. Chem.*, 1985, **50**, 1440-1456. (b) I. Shiina, M. Hashizume, Y. Yama, H. Oshiumi, T. Shimazaki, Y. Takarauma and R. Ibuka, *Eur. J. Chem.*, 2005, **11**, 6601-6608. (c) M. Larcheveque and S. Henrot, *Tetrahedron*, **1987**, *43*, 2303-2310.