O-Directed Free Radical Hydrostannations of Propargyl Ethers, Acetals and Alcohols with Ph₃SnH and Et₃B

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**Supporting Information□
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Part 1. Experimental Procedures

Experimental Procedures for the Preparation of the Alkyne Starting Materials

Alkyne 18

$n\text{-BuLi}$ (2.5 M in hexanes, 12.4 mL, 31.0 mmol) was added dropwise over 5 min into a stirred solution of the dibromide **64** (4.0 g, 13.99 mmol) in dry THF (70 mL) at $-78\text{ }^{\circ}\text{C}$ under N_2 . The dark orange solution that formed was stirred at $-78\text{ }^{\circ}\text{C}$ for 1 h and then warmed to rt where it was stirred for further 0.5 h before being recooled to $-78\text{ }^{\circ}\text{C}$. MeI (1.31 mL, 21.04 mmol) was added dropwise over 3 min and the reaction was held at $-78\text{ }^{\circ}\text{C}$ for 20 min before being warmed to rt, where it was stirred for 28 h. H_2O (100 mL) was then added to the reaction mixture which was extracted with Et_2O (3 x 100 mL). The combined organic extracts were dried over MgSO_4 and concentrated *in vacuo*. The crude residue was purified by SiO_2 flash chromatography (gradient elution using 100:1 to 50:1 petrol:EtOAc) to give the target alkyne **18** as a pale yellow liquid (1.12 g, 57%).

Alkyne 21

$n\text{-BuLi}$ (2.5 M in hexanes, 6.18 mL, 15.45 mmol) was added dropwise over 5 min into a solution of dibromide **64** (2.0 g, 6.99 mmol) in dry THF (70 mL) at $-78\text{ }^{\circ}\text{C}$ under N_2 . The resulting dark

orange solution was stirred at -78 °C for 1 h and then allowed to warm to rt where it was stirred for further 0.5 h. EtI (1.23 mL, 15.38 mmol) was added dropwise over 20 sec and stirring was continued at rt for 28 h. H₂O (100 mL) was then added and the reaction mixture was extracted with Et₂O (3 x 100 mL). The combined organic extracts were dried over MgSO₄ and concentrated *in vacuo*. The crude product was purified by SiO₂ flash chromatography (150:1 petrol:EtOAc) to give **21** as a pale yellow liquid (530 mg, 49%).

Data for **21**: [α]_D +42.4 ° (*c* 0.42, CH₂Cl₂); IR (neat) 2986 (s), 2939 (s), 2880 (s), 2241 (w), 1456 (m), 1371 (s), 1321 (m), 1217 (s), 1155 (s), 1063 (s), 1028 (m), 980 (w), 908 (w), 843 (s), 789 (w), 505 (w). ¹H NMR (500 MHz, CDCl₃, 298K) δ 4.65 (m, 1H, (-O)CH₂CH(O-)-), 4.08 (dd, 1H, *J* = 6.2, 7.9 Hz, (-O)CH₂-), 3.79 (dd, 1H, *J* = 7.0, 7.9 Hz, (-O)CH₂-), 2.19 (qd, 2H, *J* = 1.9, 7.5 Hz, CH₃CH₂-), 1.44 (s, 3H, (CH₃)₂C), 1.33 (s, 3H, (CH₃)₂C), 1.10 (t, 3H, *J* = 7.5 Hz, CH₃CH₂-); ¹³C NMR (125 MHz, CDCl₃, 298K) δ 109.8 (CH₃)₂C, 88.2 (CH₃CH₂C-), 76.3 (CH₃CH₂C-), 70.1 ((-O)CH₂-), 65.8 ((-O)CH₂CH(O-)-), 26.3 and 26.0 ((CH₃)₂C), 13.5 (CH₃CH₂-), 12.4 (CH₃CH₂-).

Alkyne 24

n-BuLi (2.5 M in hexanes, 6.18 mL, 15.45 mmol) was added dropwise over 5 min into a solution of the dibromide **64** (2.0 g, 6.99 mmol) in dry THF (70 mL) at -78 °C under N₂. The resulting dark orange solution was stirred at -78 °C for 1 h. It was then allowed to warm up to rt and stirred for further 0.5 h. *n*-PrI (1.5 mL, 15.38 mmol) was injected fast over 30 sec at rt and the reaction mixture was stirred for 72 h. H₂O (100 mL) was added and the reaction mixture was extracted with Et₂O (3 x 200 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude product was purified by SiO₂ flash chromatography (150:1 petrol:EtOAc) to give the slightly impure alkyne **24** as a clear liquid (590 mg, 50%).

Data for **24**: [α]_D +24.8 ° (*c* 1.06, CH₂Cl₂); IR (neat) 2964 (s), 2936 (s), 2876 (s), 2237 (w), 1456 (m), 1433 (w), 1371 (s), 1327 (w), 1217 (s), 1155 (s), 1063 (s), 1030 (m), 995 (w), 934 (w), 843 (s), 791 (w), 505 (w). ¹H NMR (500 MHz, CDCl₃, 298K) δ 4.64 (m, 1H, (-O)CH₂CH(O-)-), 4.07 (dd,

1H, $J = 6.2, 7.9$ Hz, $(-O)CH_2-$), 3.78 (dd, 1H, $J = 6.9, 7.9$ Hz, $(-O)CH_2-$), 2.13 (qd, 2H, $J = 1.9, 7.1$ Hz, $CH_3CH_2CH_2-$), 1.49-1.44 (m, 2H, $CH_3CH_2CH_2-$), 1.42 (s, 3H, $(CH_3)_2C$), 1.32 (s, 3H, $(CH_3)_2C$), 0.92 (t, 3H, $J = 7.4$ Hz, $CH_3CH_2CH_2-$); ^{13}C NMR (125 MHz, $CDCl_3$, 298K) δ 109.8 ($(CH_3)_2C$), 86.7 ($CH_3CH_2CH_2C-$), 77.2 ($CH_3CH_2CH_2C-$), 70.1 ($-OCH_2-$), 65.8 ($-OCH_2CHO-$), 26.2 and 25.9 ($(CH_3)_2C$), 21.8 ($CH_3CH_2CH_2-$), 20.6 ($CH_3CH_2CH_2-$), 13.3 ($CH_3CH_2CH_2-$); FAB (+) HRMS: Calcd. for $C_{10}H_{16}O_2$: (M) $^+$ 168.11502. Found: 168.11473.

Alkyne 27

n -BuLi (2.5 M in hexanes, 12.35 mL, 30.9 mmol) was added dropwise over 5 min to a solution of dibromide **64** (4.0 g, 13.99 mmol) in dry THF (70 mL) at -78 °C under N_2 . The resulting dark orange solution was stirred at -78 °C for 1 h. It was then allowed to warm up to rt and stirred for further 1 h. n -Butyl iodide (2.39 mL, 21.0 mmol) was added over 5 min at rt and the reactants were stirred for a further 34 h. H_2O (30 mL) was added and the reaction mixture was extracted with Et_2O (3 x 50 mL). The combined organic extracts were dried over $MgSO_4$, filtered, and concentrated *in vacuo*. The crude product was purified by SiO_2 flash chromatography (150:1 petrol:EtOAc) to give the desired alkyne **27** as a pale yellow liquid (1.04 g, 41%).

Data for **27**: $[\alpha]_D^{+31.8}$ (c 1.01, CH_2Cl_2); IR (neat) 2986 (s), 2959 (s), 2934 (s), 2873 (s), 1462 (m), 1377 (s), 1242 (s), 1217 (s), 1155 (s), 1064 (s), 1028 (m), 917 (w), 843 (m), 734 (s). 1H NMR (500 MHz, $CDCl_3$, 298K) δ 4.64 (tt, 1H, $J = 1.9$ and 6.4 Hz, $(-O)CH_2CH(O)-$), 4.07 (dd, 1H, $J = 6.2, 7.9$ Hz, $(-O)CH_2-$), 3.77 (dd, 1H, $J = 7.0, 7.8$ Hz, $(-O)CH_2-$), 2.16 (dq, 2H, $J = 1.9, 7.1$ Hz, $CH_3CH_2CH_2CH_2-$), 1.47-1.41 (m, 2H, $CH_3CH_2CH_2CH_2-$), 1.42 (s, 3H, $(CH_3)_2C$), 1.32 (s, 3H, $(CH_3)_2C$), 1.38-1.32 (m, 2H, $CH_3CH_2CH_2CH_2-$), 0.85 (t, 3H, $J = 7.2$ Hz, $CH_3CH_2CH_2CH_2-$); ^{13}C NMR (125 MHz, $CDCl_3$, 298K) δ 109.8 ($(CH_3)_2C$), 86.8 ($CH_3CH_2CH_2CH_2C-$), 77.1 ($CH_3CH_2CH_2CH_2C-$), 70.0 ($-OCH_2-$), 65.8 ($-OCH_2CH(O)-$), 30.4 ($CH_3CH_2CH_2CH_2C-$), 26.2 and 25.9 ($(CH_3)_2C$), 21.8 ($CH_3CH_2CH_2CH_2C-$), 18.3 ($CH_3CH_2CH_2CH_2C-$), 13.5 ($CH_3CH_2CH_2CH_2C-$); CI (+) HRMS: Calcd. for $C_{11}H_{19}O_2$: (M+H) $^+$ 183.13850. Found: 183.13859.

Alkyne 30

n-BuLi (2.5 M in hexanes, 10.8 mL, 27.0 mmol) was added dropwise over 5 min into a solution of the dibromide **66** (4.0 g, 12.27 mmol) in dry THF (61 mL) at -78 °C under N₂. The orange solution that formed was stirred at -78 °C for 1 h. It was then allowed to warm up to rt where it was stirred for further 0.5 h. The reaction flask was cooled to -30 °C and MeI (1.14 mL, 18.31 mmol) was added dropwise over 30 sec. The reactants were stirred at -30 °C for 10 min and then at rt for 14 h. H₂O (100 mL) was added to the reaction mixture and it was extracted with Et₂O (3 x 100 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude residue was purified by SiO₂ flash chromatography with 150:1 petrol:EtOAc; the desired alkyne **30** was isolated as a pale yellow liquid (1.83 g, 83%).

Data for **30**: [α]_D +9.1 ° (*c* 0.73, CH₂Cl₂); IR (neat) 2941 (s), 2863 (s), 2247 (w), 1451 (s), 1367 (s), 1339 (m), 1277 (s), 1249 (w), 1229 (w), 1160 (s), 1109 (s), 1075 (m), 1048 (s), 1020 (m), 992 (w), 924 (s), 846 (m), 823 (w), 779 (w), 655 (w). ¹H NMR (500 MHz, CDCl₃, 298K) δ 4.65 (m, 1H, (-O)CH₂CH(O)-), 4.09 (dd, 1H, *J* = 6.2, 7.9 Hz, (-O)CH₂-), 3.80 (dd, 1H, *J* = 7.1, 7.7 Hz, (-O)CH₂-), 1.83 (d, 3H, *J* = 2.1 Hz, -CH₃), 1.71-1.48 (m, 8H, cyclohexyl), 1.44-1.33 (m, 2H, cyclohexyl); ¹³C NMR (125 MHz, CDCl₃, 298K) δ 110.5 (CH₂)₂C, 82.3 (CH₃CC), 76.3 (CH₃CC), 69.7 ((-O)CH₂-), 65.5 ((-OCH₂CH(O)-), 35.8 and 35.4 (CH₂ cyclohexyl), 25.0, 23.9 and 23.8 (CH₂ cyclohexyl), 3.7 (CH₃); CI+ HRMS: Calcd. for C₁₁H₁₇O₂: (M+H)⁺ 181.12285. Found: 181.12289.

Alkyne 69

To a stirred solution of **68** (964 mg, 6.17 mmol) in dry DMF (31 mL) at rt was added imidazole (923 mg, 13.6 mmol, 2.2 equiv), and the solution cooled to 0 °C. *t*-Butyldiphenylchlorosilane (1.77 mL, 6.81 mmol, 1.1 equiv) was then added dropwise over 2 min. The reactants were stirred at 0 °C for 0.5 h and then at rt for 24 h. Excess solid NaHCO₃ was added to the reaction vessel followed by sat. aq. NaHCO₃ (20 mL) and Et₂O (50 mL). Once the initial effervescence had ceased the reaction mixture was transferred to a separatory funnel, and the organic layer removed. The aqueous layer was then extracted with Et₂O (3 x 50 mL). The combined organic layers were washed with H₂O (100 mL) and dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude residue was then purified by SiO₂ flash chromatography (using 50:1 petrol/EtOAc as eluent) to give **69** as a colorless oil (1.64 g, 67%).

Data for **69**: $[\alpha]_D^{25} -22.6^\circ$ (*c* 0.97, CH₂Cl₂); IR (neat) 3237 (s), 3072 (m), 2990 (m), 2931 (s), 2856 (s), 2125 (w), 1589 (w), 1560 (w), 1473 (m), 1430 (m), 1375 (m), 1362 (w), 1220 (s), 1164 (s), 1115 (s), 1054 (s), 1029 (s), 997 (w), 883 (m), 826 (s), 850 (s), 746 (s), 701 (s), 614 (s), 495 (s); ¹H NMR (500 MHz, CDCl₃) 7.70-7.65 (m, 4H, *t*-BuPh₂Si-), 7.43-7.34 (m, 6H, *t*-BuPh₂Si-), 4.86 (dd, 1H, *J* = 2.1, 5.7 Hz, -HC-C≡CH), 4.24 (m, 1H, *t*-BuPh₂SiOCH₂CH(O)-), 3.97 (dd, 1H, *J* = 7.0, 10.4 Hz, *t*-BuPh₂SiOCH₂-), 3.93 (dd, 1H, *J* = 5.6, 10.4 Hz, *t*-BuPh₂SiOCH₂-), 2.41 (d, 1H, *J* = 2.1 Hz, C≡CH), 1.48 (s, 3H, Me), 1.33 (s, 3H, Me), 1.05 (s, 9H, *t*-Bu-); ¹³C NMR (125 MHz, CDCl₃) 135.7, 135.6, 133.4, 133.3, 129.7, 129.5, 127.7, 127.6, 110.4 (-CMe₂), 79.7 (-(-O)CHCCH), 77.9 (*t*-BuPh₂SiOCH₂CH(O)-), 75.6 (-CCH), 68.2 (*t*-BuPh₂SiOCH₂CH(O)-CH(O)-CCH), 63.4 (*t*-BuPh₂SiOCH₂-), 27.6 (Me-), 26.8 ((CH₃)₃C-), 26.1 (Me), 19.2 ((CH₃)₃C-); HRMS (+ve ion FAB) Calcd. for C₂₄H₃₀NaO₃Si: (M+Na)⁺ 417.18618. Found: 417.18485.

n-BuLi (2.5 M in hexanes, 4.56 mL, 11.4 mmol) was added dropwise over 5 min into a solution of alkyne **69** (3.0 g, 7.6 mmol) in dry THF (38 mL) at -30 °C under N₂. The resulting bright yellow solution was stirred at -30 °C for 40 min. MeI (0.94 mL, 15.1 mmol) was added over 1 min. The reactants were then stirred at -30 °C for 10 min and at rt for 24 h. H₂O (100 mL) was added to the reaction mixture, which was then extracted with Et₂O (3 x 100 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude residue was purified by SiO₂ flash chromatography with 100:1 petrol:EtOAc; alkyne **33a** was obtained as a colorless oil (2.83 g, 91%).

Data for **33a**: $[\alpha]_D^{25} -19.4^\circ$ (*c* 0.91, CH₂Cl₂); IR (neat) 3087 (s), 3042 (s), 2986 (s), 2930 (s), 2863 (s), 2235 (m), 1961 (w), 1894 (w), 1826 (w), 1658 (w), 1585 (m), 1468 (s), 1423 (s), 1373 (s), 1339 (w), 1238 (s), 1092 (s), 1025 (s), 913 (m), 868 (s), 823 (s), 795 (s), 739 (s), 706 (s), 611 (s), 504 (s). ¹H NMR (500 MHz, CDCl₃, 298K) δ 7.72-7.67 (m, 4H, Ph), 7.43-7.7.35 (m, 6H, Ph), 4.87 (m, 1H, -CH(O-)CH(O-)CC-), 4.24 (m, 1H, TBDPSOCH₂CH(O-)-), 3.97 (dd, 1H, *J* = 6.9, 10.2 Hz, TBDPSOCH₂-), 3.88 (dd, 1H, *J* = 5.4, 10.2 Hz, TBDPSOCH₂-), 1.78 (d, 3H, *J* = 2.2 Hz, CH₃C-), 1.48 (s, 3H, (CH₃)₂C-), 1.33 (s, 3H, (CH₃)₂C-), 1.06 (9H, s, (CH₃)₃CSi); ¹³C NMR (125 MHz, CDCl₃, 298K) δ 135.6, 133.5, 133.4, 129.7, 2 x 129.6, 127.65, 127.62 (Ar), 109.7 (CH₃)2C), 83.9 (-(-O)CHCCCCH₃), 78.1 (TBDPSOCH₂CH(O-)-), 74.8 (-(-O)CHCCCCH₃), 68.6 (-(-O)CHCCCH₃), 63.7 (TBDPSOCH₂-), 27.6 and 25.9 ((CH₃)₂C), 26.7 ((CH₃)₃CSi), 19.2 ((CH₃)3CSi), 3.7 (CH₃CC); ESP+ HRMS: Calcd. for C₂₅H₃₂NaO₃Si: (M+Na)⁺ 431.20129. Found: 431.20134.

Alkyne 33b

n-BuLi (2.5 M in hexanes, 0.60 mL, 1.5 mmol) was added dropwise over 2 min into a solution of alkyne **69** (500 mg, 1.27 mmol) in dry THF (12.6 mL) at -30 °C under N₂. The resulting bright yellow solution was stirred at -30 °C for 45 min whereafter EtI (0.15 mL, 1.88 mmol) was added dropwise over 30 sec. The reactants were stirred at -30 °C for 10 min and at rt for 14 h. H₂O (20 mL) was added and the reaction mixture was extracted with Et₂O (3 x 30 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude residue was purified by SiO₂ flash chromatography with 100:1 petrol:EtOAc; alkyne **33b** was isolated as a pale yellow oil (410 mg, 77%).

Data for **33b**: $[\alpha]_D^{25}$ -18.5 ° (c 0.92, CH₂Cl₂); IR (neat) 3049 (w), 2933 (s), 2858 (s), 1470 (m), 1428 (s), 1380 (s), 1231 (s), 1111 (s), 1080 (s), 1030 (m), 824 (m), 740 (m), 705 (m), 612 (m), 508 (m). ¹H NMR (500 MHz, CDCl₃, 298K) δ 7.70-7.65 (m, 4H, Ph), 7.42-7.34 (m, 6H, Ph), 4.86 (td, 1H, *J* = 2.0, 5.8 Hz, -(O)CHCH₂CC₂Et), 4.22 (dd, 1H, *J* = 5.8, 12.3 Hz, TBDPSOCH₂CH(O)-), 3.95 (dd, 1H, *J* = 6.6, 10.3 Hz, TBDPSOCH₂-), 3.87 (dd, 1H, *J* = 5.7 and 10.3 Hz, TBDPSOCH₂-), 2.16-2.11 (dq, 2H, CH₃CH₂-), 1.47 (s, 3H, (CH₃)₂C), 1.33 (s, 3H, (CH₃)₂C), 1.05 (9H, s, (CH₃)₃C-), 1.04 (t, 3H, *J* = 7.5 Hz, CH₃CH₂-); ¹³C NMR (125 MHz, CDCl₃, 298K) δ 135.6 (Ph), 133.6, 133.4 (Ph), 129.6, 127.7 (Ph), 109.8 (CH₃)₂C, 89.7 (-CC₂Et), 78.2 (TBDPSOCH₂CH(O)-), 74.9 (-CC₂Et), 68.5 (TBDPSOCH₂CH(O)-), 63.9 (TBDPSOCH₂-), 27.7 and 26.0 ((CH₃)₂C), 26.8 ((CH₃)₃CSi), 19.2 ((CH₃)₃CSi), 13.5 (CH₃CH₂-), 12.5 (CH₃CH₂-); ESP+ HRMS: Calcd. for C₂₆H₃₄NaO₃Si: (M+Na)⁺ 445.21694. Found: 445.21752.

Alkyne 33c

n-BuLi (2.5 M in hexanes, 1.52 mL, 3.80 mmol) was added dropwise over 2 min into a solution of alkyne **69** (1.0 g, 2.53 mmol) in dry THF (25 mL) at -30 °C under N₂. The bright yellow solution that formed was stirred at -30 °C for 40 min before *n*-PrI (0.37 mL, 3.79 mmol) was added over 1 min. The reactants were then stirred at -30 °C for 10 min and at rt for 1 h before being heated at reflux for 6 h. After cooling to rt, H₂O (50 mL) was added and the reaction mixture was extracted with Et₂O (3 x 100 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude residue was purified by SiO₂ flash chromatography with 100:1 petrol:EtOAc; **33c** was obtained as a colorless oil (760 mg, 69%).

Data for **33c**: $[\alpha]_D^{25}$ -19.9 ° (c 0.80, CH₂Cl₂); IR (neat) 3049 (w), 2961 (s), 2933 (s), 2858 (m), 1469 (m), 1428 (m), 1379 (m), 1230 (m), 1137 (m) 1111 (s), 1079 (s), 1040 (m), 824 (m), 740 (m), 704 (s), 613 (w), 507 (s). ¹H NMR (500 MHz, CDCl₃, 298K) δ 7.69-7.66 (m, 4H, Ph), 7.41-7.33 (m, 6H, Ph), 4.86 (dt, 1H, *J* = 1.9, 5.8 Hz $-\text{(O)CHCHCCPr-}n$), 4.21 (q, 1H, *J* = 6.0 Hz, TBDPSOCH₂CH(O)-), 3.95 (dd, 1H, *J* = 6.4, 10.3 Hz, TBDPSOCH₂-), 3.87 (dd, 1H, *J* = 5.9, 10.3 Hz, TBDPSOCH₂-), 2.10 (td, 2H, *J* = 2.0, 7.1 Hz, CH₃CH₂CH₂C-), 1.47 (s, 3H, (CH₃)₂C), 1.45-1.35 (m, 2H, CH₃CH₂CH₂C-), 1.33 (s, 3H, (CH₃)₂C), 1.04 (s, 9H, (CH₃)₃CSi), 0.87 (t, 3H, *J* = 7.4 Hz, CH₃CH₂CH₂-); ¹³C NMR (125 MHz, CDCl₃, 298K) δ 135.6 (x 2), 133.6, 133.4, 129.7, 129.6 (x 2), 127.6 (x 2), 109.8 (CH₃)₂C, 88.3 ($-\text{CCCH}_2\text{CH}_2\text{CH}_3$), 78.2 (TBDPSOCH₂CH(O)-), 75.7 (CPr-n), 68.5 ($-\text{(O)CHCHCCPr-}n$), 63.9 (TBDPSOCH₂-), 27.7 and 26.1 ((CH₃)₂C), 26.8 ((CH₃)₃CSi), 21.8 (CH₃CH₂CH₂-), 20.8 (CH₃CH₂CH₂C-), 19.2 ((CH₃)₃CSi), 13.5 (CH₃CH₂CH₂-); CI HRMS: Calcd. for C₂₇H₃₆NaO₃Si: (M+Na)⁺ 459.23259. Found: 459.23236.

Iodobenzene (0.74 mL, 6.61 mmol) was added dropwise over 1 min into a stirred solution of alkyne **69** (2.0 g, 5.07 mmol) in dry Et₃N (25 mL) under N₂. CuI (99.999%) (965 mg, 5.07 mmol) was added in one portion followed by Cl₂Pd(PPh₃)₂ (350 mg, 0.50 mmol). The reactants were stirred at rt for 27 h. H₂O (100 mL) was added to the reaction mixture which was then extracted with Et₂O (3x 100 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude residue was purified by SiO₂ flash chromatography with 130:1 petrol:EtOAc as eluent; **33d** was obtained as a colorless oil (1.83 g, 77%).

Data for **33d**: $[\eta]_D$ -8.9 ° (*c* 0.84, CH₂Cl₂); IR (neat) 3070 (w), 2988 (m), 2932 (s), 2857 (s), 1489 (m), 1427 (m), 1379 (m), 1230 (s), 1163 (m), 1110 (s), 1066 (s), 1021 (m), 858 (w), 823 (m), 756 (m), 740 (m), 704 (s), 507 (m). ¹H NMR (500 MHz, CDCl₃, 298K) δ 7.75-7.69 (m, 4H, Ph), 7.48-7.25 (m, 11H, Ph), 5.16 (d, 1H, *J* = 5.7 Hz, -(O)CH₂CCPh), 4.39 (apparent q, 1H, TBDPSOCH₂CH(O)-), 4.10 (dd, 1H, *J* = 7.0, 10.2 Hz, TBDPSOCH₂-), 4.02 (dd, 1H, *J* = 5.6, 10.3 Hz, TBDPSOCH₂-), 1.59 (s, 3H, (CH₃)₂C), 1.43 (s, 3H, (CH₃)₂C), 1.09 (9H, s, (CH₃)₃CSi); ¹³C NMR (125 MHz, CDCl₃, 298K) δ 135.6, 135.57, 133.3, 133.2, 131.7, 129.7, 129.6, 128.4, 128.1, 127.7, 127.6, 122.4 (Ph), 110.3 (CH₃)₂C, 87.5 (PhC₂CH(O)-), 85.0 (PhC₂CH(O)-), 78.3 (TBDPSOCH₂CH(O)-), 69.0 (-(O)CH₂CCPh), 63.7 (TBDPSOCH₂-), 27.7 and 26.2 ((CH₃)₂C), 26.7 ((CH₃)₃CSi), 19.2 ((CH₃)₃CSi); ESP+ HRMS: Calcd. for C₃₀H₃₄NaO₃Si: (M+Na)⁺ 493.21694. Found: 493.21676.

Alkyne 73

Step (i): To a stirred solution of Me₂SO (1.06 mL, 14.94 mmol) in dry CH₂Cl₂ (12.5 mL) under N₂ at -78 °C was added (COCl)₂ (0.66 mL, 7.57 mmol) dropwise over 5 min. Stirring was continued at -78 °C for 40 min whereupon a solution of alcohol **70** (1.0 g, 2.5 mmol) in dry CH₂Cl₂ (12.5 mL) was added dropwise over 5 min. After stirring at -78 °C for 20 min, Et₃N (3.51 mL, 25.2 mmol) was added dropwise over 1 min, and the reactants were allowed to warm to rt. H₂O (10 mL) was then added, the two layers partitioned, and the aqueous layer extracted with CH₂Cl₂ (3 x 20 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated *in vacuo*. The residue was *very rapidly* purified by SiO₂ flash chromatography using 4:1 petrol:EtOAc as eluent; the unstable aldehyde **71** (802 mg, 81%) was obtained as an oil. Aldehyde **71**, which was not characterised any further, was used immediately for the next step as described below.

Step (ii): To a 100 mL round bottomed flask containing the neat aldehyde **71** (802 mg, *ca.* 2 mmol) was added the neat diazophosphonate **72**^{1,2} (576 mg, 3.00 mmol, 1.5 equiv) followed by MeOH (25 mL) and K₂CO₃ (555 mg, 4.00 mmol) in one portion. The resulting suspension was stirred at rt for 16 h, whereafter sat. aq. NH₄Cl (10 mL) was added. The resulting solution was extracted with Et₂O (4 x 20 mL), and the combined ethereal extracts were dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude residue was purified by SiO₂ flash chromatography using 50:1 then 40:1 petrol:EtOAc as eluent to give alkyne **73** as a colorless oil (564 mg, 71%).

Data for **73**: [α]_D -16.1 ° (*c* 1.27, CH₂Cl₂); IR: 3287 (m), 3071 (m), 3050 (w), 2988 (m), 2932 (s), 2858 (s), 1589 (w), 1473 (m), 1429 (s), 1382 (s), 1373 (s), 1214 (s), 1145 (s), 1085 (s), 998 (w), 851 (w), 823 (s), 702 (s), 691 (s), 504 (s); ¹H NMR (500 MHz in CDCl₃) δ 7.80-7.75 (m, 4H, *t*-BuPh₂SiO-), 7.49-7.42 (m, 6H, *t*-BuPh₂SiO-), 4.80 (m, 1H, *J* = 1.1, 7.1 Hz, -(O)CHCCH), 4.25 (dt, 1H, *J* = 3.6, 7.2 Hz, -(O)CH-CH₂OSiPh₂Bu-*t*), 3.89 (d, 2H, *J* = 3.0 Hz, -CH₂OSiPh₂Bu-*t*), 2.55 (s,

^1H , $-\text{C}\equiv\text{CH}$), 1.56 (s, 3H, Me), 1.49 (s, 3H, Me), 1.15 (s, 9H, *t*-Bu); ^{13}C NMR (125 MHz in CDCl_3) δ 135.6; 135.5, 133.0, 132.97, 129.7, 129.69, 127.7, 127.65, 110.5 ($-\text{CMe}_2$), 82.0 ($\text{TBDPSOCH}_2\text{CH}(\text{O}-)$), 81.2 ($-\text{CCH}$), 74.4 ($-\text{CCH}$), 67.0 ($-(\text{O})\text{CHCCH}$), 62.7 (TBDPSOCH_2-), 26.8 (CMe_2), 26.7 ($(\text{CH}_3)_3\text{C}-$), 26.2 (CMe_2), 19.2 ($(\text{CH}_3)_3\text{CSi}$). HRMS: Calcd. for $\text{C}_{24}\text{H}_{30}\text{NaO}_3\text{Si}$: $(\text{M}+\text{Na})^+$ 417.18618. Found: 417.18760.

1. Ohira, S. *Syn. Comm.* **1989**, 19, 561.
2. Muller, S.; Liepold, B.; Roth, G.J.; Bestmann, H. *Synlett* **1996**, 521.

Alkyne **37a**

n-BuLi (2.5 M in hexanes, 0.52 mL, 1.30 mmol) was added dropwise over 5 min into a solution of alkyne **73** (260 mg, 0.66 mmol) in dry THF (38 mL) at $-30\text{ }^\circ\text{C}$ under N_2 . The bright yellow solution that resulted was stirred at $-30\text{ }^\circ\text{C}$ for 45 min whereafter MeI (0.08 mL, 1.30 mmol) was added over 10 sec. The reactants were stirred at $-30\text{ }^\circ\text{C}$ for 10 min, warmed to rt, and then stirred for 16 h. H_2O (20 mL) was added and the reaction mixture was extracted with Et_2O (3 x 20 mL). The combined organic extracts were dried over MgSO_4 , filtered, and concentrated *in vacuo*. The crude residue was purified by SiO_2 flash chromatography with 100:1 petrol:EtOAc as eluent to give the alkyne **37a** as a colorless oil (240 mg, 89%).

Data for **37a**: $[\alpha]_D^{25} -21.5^\circ$ (c 1.09, CH_2Cl_2); IR (neat) 3070 (w), 2987 (m), 2932 (s), 2858 (s), 1470 (m), 1427 (m), 1380 (m), 1241 (m), 1139 (s), 1110 (s), 1026 (s), 824 (m), 741 (m), 704 (s), 610 (w), 506 (s). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.72-7.67 (m, 4H, Ph), 7.46-7.35 (m, 6H, Ph), 4.67 (dq, 1H, $J = 2.1, 7.6\text{ Hz}$, $-\text{CH}(\text{O})\text{CH}(\text{O})\text{CCMe}$), 4.06 (dt, 1H, $J = 4.0, 7.8\text{ Hz}$, $\text{TBDPSOCH}_2\text{CH}(\text{O}-)$), 3.80 (dd, 2H, $J = 4.0, 11.2\text{ Hz}$, TBDPSOCH_2-), 1.84 (d, 3H, $J = 2.1\text{ Hz}$, CH_3C), 1.48 (s, 3H, $(\text{CH}_3)_2\text{C}$), 1.40 (s, 3H, $(\text{CH}_3)_2\text{C}$), 1.06 (9H, s, $(\text{CH}_3)_3\text{CSi}$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 135.6, 133.2, 133.1, 129.7, 129.6, (x 2) 127.7 (Ar), 109.8 ($(\text{CH}_3)_2\text{C}$), 82.9 ($-(\text{O})\text{CHCCH}_3$), 82.0 ($\text{TBDPSOCH}_2\text{CH}(\text{O}-)$), 75.9 ($-(\text{O})\text{CHCCH}_3$), 67.7 ($-(\text{O})\text{CHCCMe}$), 62.7 (TBDPSOCH_2-), 26.8 and 26.5 ($(\text{CH}_3)_2\text{C}$), 26.7 ($(\text{CH}_3)_3\text{CSi}$), 19.3 ($(\text{CH}_3)_3\text{CSi}$), 3.8 (CH_3CC); ESP+ HRMS: Calcd. for $\text{C}_{25}\text{H}_{32}\text{NaO}_3\text{Si}$: $(\text{M}+\text{Na})^+$ 431.20129. Found: 431.20087.

Phenylacetylene **37b**

Iodobenzene (0.11 mL, 0.98 mmol) was added dropwise over 1 min to a stirred solution of alkyne **73** (300 mg, 0.76 mmol) in dry Et_3N (25 mL) under N_2 . CuI (99.999%) (140 mg, 0.74 mmol) was subsequently added in one portion followed by $\text{Cl}_2\text{Pd}(\text{PPh}_3)_2$ (53.3 mg, 0.076 mmol). The reactants were stirred at rt for 2 h 40 min. H_2O (20 mL) was added and the reaction mixture was extracted with EtOAc (3 x 20 mL). The combined organic extracts were dried over MgSO_4 , filtered, and concentrated *in vacuo*. The crude residue was purified by SiO_2 flash chromatography using 130:1 petrol: EtOAc as eluent. The product **37b** was obtained as a yellow oil (310 mg, 87%).

Data for **37b**: $[\alpha]_{\text{D}}^{25} -25.5^{\circ}$ (c 0.93, CH_2Cl_2); IR (neat) 3071 (m), 3051 (m), 2988 (s), 2932 (s), 2858 (s), 2231 (w), 1589 (w), 1489 (s), 1472 (s), 1464 (w), 1445 (w), 1427 (s), 1381 (s), 1371 (s), 1325 (w), 1215 (s), 1142 (s), 1113 (s), 1080 (s), 1009 (m), 949 (w), 914 (w), 858 (w), 824 (s), 756 (s), 741 (s), 702 (s), 691 (s), 613 (m), 505 (s). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.75-7.67 (m, 4H, Ph), 7.46-7.26 (m, 11H, Ph), 4.96 (d, 1H, $J = 7.2$ Hz, $-(\text{O})\text{CHCCPh}$), 4.26 (dt, 1H, $J = 4.2, 7.2$ Hz, $\text{TBDSOCH}_2\text{CH}(\text{O}-)$), 3.88 (d, 2H, $J = 4.2$ Hz, TBDSOCH_2-), 1.55 (s, 3H, $(\text{CH}_3)_2\text{C}$), 1.47 (s, 3H, $(\text{CH}_3)_2\text{C}$), 1.08 (9H, s, $(\text{CH}_3)_3\text{CSi}$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 135.64, 135.6, 133.2, 133.1, 131.8, 129.74, 129.72, 128.5, 128.2, 127.7 (x 2), 122.4 (Ph), 110.4 $(\text{CH}_3)_2\text{C}$, 86.3 $(\text{PhCC}-)$, 86.1 $(\text{PhCC}-)$, 82.1 $(\text{TBDSOCH}_2\text{CH})$, 70.0 $(-(\text{O})\text{CHCCPh})$, 62.9 (TBDSOCH_2-) , 26.9 and 26.4 $((\text{CH}_3)_2\text{C})$, 26.8 $((\text{CH}_3)_3\text{CSi})$, 19.3 $((\text{CH}_3)_3\text{CSi})$; ESP+ HRMS: Calcd. for $\text{C}_{30}\text{H}_{34}\text{NaO}_3\text{Si}$: $(\text{M}+\text{Na})^+$ 493.21694. Found: 493.21714.

Benzyl 2,3-O-Isopropylidene-6-O-Pivaloyl- α -D-Mannopyranoside **75**

To a stirred solution of the diol **74** (10.0 g, 32.2 mmol) in dry CH_2Cl_2 (400 mL) and pyridine (5.2 mL, 3.2 mmol) under N_2 at $-78\text{ }^\circ\text{C}$ was added trimethylacetyl chloride (PvCl) (3.8 mL, 31.0 mmol) over 7 min. The reaction mixture was kept between $-78\text{ }^\circ\text{C}$ and $-40\text{ }^\circ\text{C}$ for 1 h and then at $-40\text{ }^\circ\text{C}$ for 2 h. The mixture was thereafter stored at $-20\text{ }^\circ\text{C}$ for 24 h. After this period, the reaction vessel was cooled to $-30\text{ }^\circ\text{C}$ and a further quantity of PvCl (0.67 mL, 5.44 mmol) was added dropwise over 2 min. The reaction mixture was allowed to warm to rt, and stirred for a further 72 h, whereafter it was re-cooled to $0\text{ }^\circ\text{C}$, and an additional quantity of PvCl (0.67 mL, 5.44 mmol) was introduced over 2 min. The reactants were warmed to rt where they were stirred for 6 h. H_2O (300 mL) was then added, and the two layers were separated. The aqueous extract was then extracted with CH_2Cl_2 (3 x 150 mL), and the organic layers combined, dried over MgSO_4 , filtered, and concentrated *in vacuo*. The crude residue was purified by SiO_2 flash chromatography using 4:1 petrol:EtOAc as eluent. The mono-pivaloate **75** was obtained as a white crystalline solid (9.7 g, 76%).

Data for **75**: m.p. $66\text{--}67\text{ }^\circ\text{C}$; $[\alpha]_{\text{D}}^{20} +17^\circ$ (c 1.22, CHCl_3); IR (neat film) 3427 (br s), 2933 (s), 2894 (s), 1721 (s), 1478 (m), 1455 (m), 1388 (m), 1368 (m), 1329 (w), 1286 (s), 1277 (s), 1172 (s), 1145 (s), 1082 (s), 1051 (s), 1019 (s), 992 (s), 964 (s), 917 (w), 858 (s), 819 (m), 780 (m), 757 (m), 702 (m), 604 (m), 568 (w), 510 (m), 372 (m) cm^{-1} ; ^1H NMR (400 MHz, CDCl_3) δ 7.64 (complex m, 5H), 5.09 (s, 1H), 4.73 (d, $J_{\text{AB}} = 11.6\text{ Hz}$, 1H), 4.53 (d, $J_{\text{AB}} = 11.7\text{ Hz}$, 1H), 4.45 (dd, $J = 5.1$ and 12.1 Hz , 1H), 4.23 (dd, $J = 2.5\text{ Hz}$ and 12.1 Hz , 1H), 4.17 (complex m, 2H), 3.78 (complex m, 1H), 3.49 (complex m, 1H), 3.09 (d, $J = 4.4\text{ Hz}$, 1H), 1.49 (s, 3H), 1.32 (s, 3H), 1.21 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 179.3, 136.7, 128.5, 128.3, 128.2, 109.6, 96.3, 77.9, 75.5, 69.2, 69.0, 63.4, 38.9, 28.0, 27.2, 26.2. Anal. Calcd. For $\text{C}_{21}\text{H}_{30}\text{O}_7$: C, 63.94; H, 7.67. Found: C, 64.10; H, 7.94.

Benzyl 4-Deoxy-2,3-O-Isopropylidene-6-O-Pivaloyl- α -D-Mannopyranoside **77**

Step (i): To a stirred solution of alcohol **75** (22.1 g, 56.1 mol) in dry THF (220 mL) at rt was successively added imidazole (0.22 g, 3.23 mmol) and 80% NaH dispersion in mineral oil (2.44 g, 81.3 mol). The reactants were allowed to stir for 15 min at rt after which CS₂ (19.9 mL, 0.33 mol) was added dropwise over 15 min. After a further 10 min, MeI (22 mL, 0.356 mol) was introduced in one portion and stirring was continued for a further 0.5 h. EtOAc (200 mL) was added to the reaction mixture, followed by H₂O (150 mL, **CAUTIOUSLY!**), and brine (200 mL). The organic layer was separated off and the aqueous extract further extracted with EtOAc (3 x 200 mL). The combined organic layers were washed with H₂O (200 mL), dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude xanthate **76** (28.6 g) was a pale green solid that was used directly for the next reaction without further purification.

Step (ii): To a stirred solution of the crude methyl xanthate **76** (28.6 g) in dry PhMe (440 mL) under N₂ was added AIBN (550 mg, 3.35 mmol) followed by Bu₃SnH (22.4 mL, 83.3 mmol). The reaction mixture was heated at reflux for 40 min, whereupon more AIBN (400 mg, 2.44 mmol) and Bu₃SnH (10.0 mL, 37.2 mmol) were added. After further heating at reflux for 1.5 h, the dark-brown mixture was concentrated *in vacuo* and the residue was purified by SiO₂ flash chromatography with petrol:EtOAc 4:1 as eluent. The title compound **77** was isolated as pale-yellow oil (20.5 g, 97%).

Data for **77**: [α]_D +66.0 ° (c 0.2, CHCl₃); IR (neat film) 2980 (s), 2925 (s), 1732 (s), 1497 (m), 1456 (m), 1381 (s), 1285 (s), 1240 (s), 1221 (s), 1140 (s), 1069 (s), 997 (s), 864 (m), 792 (m), 764 (m), 737 (m), 700 (m) cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.39-7.28 (complex m, 5H), 5.11 (s, 1H), 4.74 (d, *J* = 11.7 Hz, 1H), 4.52 (d, *J* = 11.7 Hz, 1H), 4.37 (complex m, 1H), 4.13 (complex m, 2H), 4.05 (complex m, 2H), 1.88 (complex m, 1H), 1.55 (complex m, 1H), 1.49 (s, 3H), 1.31 (s, 3H), 1.21 (s, 9H); ¹³C NMR (125 MHz, CDCl₃) δ 178.1, 137.0, 128.4, 128.1, 127.9, 126.1, 108.9,

96.4, 72.9, 70.3, 68.7, 66.4, 64.6, 38.7, 30.3, 28.1, 27.2, 26.2. HRMS (FAB, MNOBA matrix)
Calcd. for $C_{21}H_{31}O_7$ (M+H)⁺ 379.21205. Found: 379.21285.

Benzyl 4-Deoxy-2,3-O-Isopropylidene- α -D-Mannopyranoside **78**

To a stirred solution of the 6-*O*-pivaloate **77** (19.1 g, 50.5 mmol) was added a 10% solution of sodium methoxide in MeOH (200 mL). After 2 h at rt, the reaction mixture was neutralized with Amberlyst-15 (H⁺) resin, filtered, and concentrated *in vacuo*. The resulting oil was treated with brine (200 mL) and extracted with EtOAc (4 x 250 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude oily residue crystallized in pure condition from neat petrol (b.p. 60-80 °C) after trituration, yielding **78** as white crystals (12.6 g, 85%). Alternatively, the crude oily residue could be purified by SiO₂ flash chromatography (gradient elution with 10:1-5:1-2:1 hexane:EtOAc) to give the product as a white solid. We have generally found that the trituration isolation procedure is the more convenient.

Data for **78**: m.p. 57.5-58.5 °C; $[\alpha]_D^{25} +103.0^\circ$ (c 0.18, CHCl₃); IR (neat film) 3462 (br s), 2984 (s), 2933 (s), 1497 (m), 1456 (s), 1371 (m), 1244 (s), 1221 (s), 1140 (s), 1070 (s), 995 (s), 864 (s), 891 (m), 739 (s), 700 (s), 515 (m) cm⁻¹; ¹H NMR (500 MHz, CDCl₃, 298K) δ 7.37-7.28 (m, 5H, Ph), 5.10 (s, 1H, H1), 4.73 (d, 1H, *J* = 11.7 Hz, PhCH₂-), 4.52 (d, 1H, *J* = 11.7 Hz, PhCH₂-), 4.39 (m, 1H, H3), 4.01 (d, 1H, *J* = 5.7 Hz, H2), 3.88 (m, 1H, H5), 3.65 (dd, 1H, *J* = 3.4, 11.6 Hz, H6a), 3.60 (dd, *J* = 6.1, 11.6 Hz, H6b), 1.96 (br s, 1H, -OH), 1.89 (ddd, 1H, *J* = 3.7, 6.1, 13.6 Hz, H4a), 1.62 (m, 1H, H4b), 1.49 (s, 3H, (CH₃)₂C), 1.32 (s, 3H, (CH₃)₂C); ¹³C NMR (125 MHz, CDCl₃, 298K) δ 137.1, 128.5, 128.1, 128.0 (Ph), 109.1 (CH₃)₂C, 97.0 (C1), 73.2 (C2), 70.3 (C3), 69.4 (PhCH₂), 67.0 (C5), 65.7 (C6), 29.0 (C4), 27.9 and 26.0 (CH₃)₂C; ESP (+) HRMS: Calcd. for C₁₆H₂₂NaO₅: (M+Na)⁺ 317.13594. Found: 317.13649. Anal. Calcd. for C₁₆H₂₂O₅: C, 65.29; H, 7.53. Found: C, 65.02; H, 7.59.

Alkyne 80

Step i. To a solution of DMSO (0.87 mL, 12.26 mmol) in dry CH_2Cl_2 (10 mL), at $-78\text{ }^\circ\text{C}$ under N_2 was added $(\text{COCl})_2$ (0.54 mL, 6.19 mmol) dropwise over 5 min, and the solution was stirred at that temperature for 40 min. A solution of alcohol **78** (600 mg, 2.04 mmol) in dry CH_2Cl_2 (10 mL) was then added dropwise over 5 min. The white suspension was stirred at $-78\text{ }^\circ\text{C}$ for 15 min, whereafter Et_3N (1.43 mL, 10.26 mmol) was added dropwise over 2 min. The reactants were allowed to warm to rt over 20 min. The reaction was then quenched with H_2O (20 mL) and the organic layer separated off. The aqueous layer was extracted with CH_2Cl_2 (3 x 20 mL). The combined organic extracts were dried over MgSO_4 , filtered, and concentrated *in vacuo*. The crude residue was rapidly purified by SiO_2 flash chromatography using 3:1 hexane:EtOAc as the eluent to give the unstable aldehyde **79** (570 mg) which was used immediately without characterisation.

Step ii. Into a flask containing aldehyde **79** (570 mg) was weighed the diazophosphonate **72**^{1,2} (570 mg, 2.97 mmol). The two materials were placed under an N_2 atmosphere and anhydrous MeOH (19.7 mL) was added at rt. Anhydrous K_2CO_3 (540 mg, 3.94 mmol) was added in one portion at rt. The reaction was stirred for 16 h, whereafter sat. aq. NH_4Cl (20 mL) was added and the mixture extracted with Et_2O (3 x 20 mL). The combined organic extracts were dried over MgSO_4 and concentrated *in vacuo*. The crude residue was purified by SiO_2 flash chromatography (30:1-25:1 hexane:EtOAc) to give the product **80** as a yellow oil (370 mg, 63%).

Data for **80**: $[\alpha]_D^{+29.9}$ (c 0.97, CH_2Cl_2); IR (neat) 3400 (br w), 3285 (s), 2986 (s), 2937 (s), 2096 (w), 1456 (m), 1373 (s), 1300 (w), 1240 (s), 1221 (s), 1134 (s), 1063 (s), 1024 (s), 982 (s), 876 (s), 860 (s), 700 (s), 513 (w) cm^{-1} . ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.35-7.25 (m, 5H, Ph), 5.11 (d, 1H, $J = 1.7\text{ Hz}$ H1), 4.76 (d, 1H, $J = 11.9\text{ Hz}$, PhCH_2 -), 4.54 (d, 1H, $J = 11.8\text{ Hz}$, PhCH_2 -), 4.51 (m, 1H, H5), 4.30 (m, 1H, H3), 3.94 (dd, 1H, $J = 1.9, 5.5\text{ Hz}$, H2), 2.49 (d, 1H, $J = 2.3\text{ Hz}$, HCC -), 2.11 (ddd, 1H, $J = 3.5, 6.2, 13.7\text{ Hz}$, H4a), 1.92 (m, 1H, H4b), 1.47 (s, 3H, $(\text{CH}_3)_2\text{C}$), 1.30 (s, 3H, $(\text{CH}_3)_2\text{C}$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 136.8, 128.2, 127.9, 127.7 (Ph), 108.9 $(\text{CH}_3)_2\text{C}$,

96.6 (C1), 81.8 (HCC-), 73.2 (HCC-), 72.8 (C2), 70.0 (C3), 69.3 (PhCH₂-), 57.3 (C5), 33.8 (C4), 27.7 and 26.0 (CH₃)₂C); ESP (+) HRMS: Calcd. for C₁₇H₂₀NaO₄: (M+Na)⁺ 311.12538. Found: 311.12551.

Alkyne 41

n-BuLi (2.5 M in hexanes, 0.52 mL, 1.30 mmol) was added dropwise over 2 min to a solution of alkyne **80** (250 mg, 0.87 mmol) in dry THF (8.7 mL) at -30 °C under N₂. The yellow solution was stirred at -30 °C for 40 min before MeI (0.11 mL, 1.77 mmol) was added over 30 sec. The reactants were then stirred at -30 °C for 10 min and at rt for 16 h. The reaction was quenched by the addition of H₂O (20 mL) and extracted with Et₂O (3 x 20 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude residue was purified by SiO₂ flash chromatography (gradient 30:1-20:1 hexane:EtOAc) to give alkyne **41** as a colorless oil (200 mg, 76%).

Data for **41**: [α]_D +5.9 ° (*c* 1.01, CH₂Cl₂); IR (neat) 2984 (m), 2920 (m), 1454 (m), 1371 (s), 1240 (s), 1220 (m), 1125 (m), 1063 (s), 1028 (s), 989 (m), 871 (w), 790 (w), 699 (w). ¹H NMR (500 MHz, CDCl₃, 298K) δ 7.36-7.25 (m, 5H, Ph), 5.12 (d, 1H, *J* = 1.0 Hz, H-1), 4.76 (d, 1H, *J* = 11.8 Hz, PhCH₂), 4.54 (d, 1H, *J* = 11.8 Hz, PhCH₂-), 4.47 (m, 1H, H5), 4.30 (m, 1H, H3), 3.93 (dd, 1H, *J* = 1.6, 5.3 Hz, H2), 2.07 (ddd, 1H, *J* = 3.1, 6.4, 13.6 Hz, H4a), 1.87 (m, 1H, H-4b), 1.83 (d, 3H, *J* = 2.1 Hz, CH₃CC), 1.47 (s, 3H, (CH₃)₂C), 1.30 (s, 3H, (CH₃)₂C); ¹³C NMR (125 MHz, CDCl₃, 298K) δ 137.0, 128.3, 128.1, 127.8, 109.0 (-CMe₂), 96.7 (C-1), 81.3 (-CCMe), 77.3 (-CCMe), 72.9 (C2), 70.4 (C-3), 69.3 (PhCH₂-), 57.8 (C5), 34.8 (C4), 27.9 and 26.2 (-CMe₂), 3.5 (-CCMe); ESP (+) HRMS: Calcd. for C₁₈H₂₂NaO₄: (M+Na)⁺ 325.14103. Found: 325.14053.

Alkynol **44c**

n-BuLi (2.5 M in hexanes, 12.4 mL, 31.0 mmol) was added dropwise over 5 min into a stirred solution of dibromide **64** (4.0 g, 13.99 mmol) in dry THF (70 mL) at -78 °C under N₂. The resulting orange-colored solution was stirred at -78 °C for 1 h and then allowed to warm to rt where it was kept for further 0.5 h. MeI (1.31 mL, 21.04 mmol) was then added dropwise over 30 sec. The reactants were stirred at rt for 3.5 h. H₂O (100 mL) was added to the reaction mixture which was extracted with Et₂O (3 x 100 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude product was dissolved in MeOH (30 mL) and *p*-TsOH (133 mg, 0.7 mmol) was added and the reactants were stirred at rt for 18 h. The solvent was removed *in vacuo* and the crude residue was purified by SiO₂ flash chromatography (gradient elution with 2:1-1:1 hexane:EtOAc as eluent) to give **44c** as an amorphous white solid (806 mg, 58%).

Data for **44c**: $[\alpha]_D^{+25.0}$ (c 1.03, CH₂Cl₂); IR (neat) 3296 (br), 2931 (w), 1435 (m), 1334 (m), 1267 (m), 1227 (w), 1149 (w), 1084 (s), 1059 (s), 1028 (s), 885 (s), 814 (m), 704 (br). ¹H NMR (500 MHz, CDCl₃, 298K) δ 4.38 (m, 1H, HOCH₂CH(OH)-), 3.67 (br dd, 1H, *J* = 3.2, 11.5 Hz, HOCH₂-), 3.58 (dd, 1H, *J* = 7.1 and 11.5 Hz, HOCH₂-), 3.30 (br s, 2H, OH), 1.82 (d, 3H, *J* = 2.1 Hz, CH₃C-); ¹³C NMR (125 MHz, CDCl₃, 298K) δ 82.5 (- (HO)CHCCCH₃), 77.0 (- (HO)CHCCCH₃), 66.7 (HOCH₂-), 63.3 (- (HO)CHCCMe), 3.5 (CH₃C).

Alkyne **44a**

Imidazole (570 mg, 8.37 mmol) was added in one portion into a vigorously stirred solution of diol **44c** (200 mg, 0.20 mmol) in dry DMF (13 mL) at rt under N₂. *tert*-Butyldiphenylchlorosilane (1.14 mL, 4.38 mmol) was added dropwise over 1 min to the reaction mixture at rt. The reactants were stirred at rt for 1 h. Excess solid NaHCO₃ (3 spatula loads) was added prior to the dropwise addition of sat. aq. NaHCO₃ (50 mL) over 10 min. The reaction mixture was extracted with Et₂O (3 x 100 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude residue was purified by SiO₂ flash chromatography (using 70:1 hexane:EtOAc as eluent) to give the product alkyne **44a** as a colorless oil (990 mg, 86%).

Data for **44a**: [α]_D +50.5 ° (c 0.97, CH₂Cl₂); IR (neat) 3053 (w), 2959 (s), 2932 (s), 2857 (s), 1589 (w), 1471 (m), 1427 (s), 1386 (w), 1111(s), 1083 (s), 964 (m), 856 (w), 823 (m), 738 (s), 704 (s), 613 (m), 505 (s). ¹H NMR (500 MHz, CDCl₃, 298K) δ 7.79-7.73 (m, 4H, Ph), 7.70-7.64 (m, 4H, Ph), 7.43-7.31 (m, 12H, Ph), 4.53 (m, 1H, TBDPSOCH₂CH(OTBDPS)-), 3.78 (dd, 1H, *J* = 7.0, 10.1 Hz, TBDPSOCH₂-), 3.67 (dd, 1H, *J* = 4.8, 10.1 Hz, TBDPSOCH₂-), 1.58 (d, 3H, *J* = 2.1 Hz, CH₃CC), 1.10 (s, 9H, C(CH₃)₃), 1.04 (s, 9H, C(CH₃)₃); ¹³C NMR (125 MHz, CDCl₃, 298K) δ 136.2, 135.9, 135.7, 135.64, 135.63, 133.9, 133.7, 133.5, 3 x 129.5, 129.3, 127.6, 127.4, 127.2 (Ar), 81.9 (-CCCH₃), 78.6 (-CCCH₃), 68.6 (TBDPSOCH₂-), 65.4 (-(TBDPSO)CHCCMe), 26.9 and 26.7 (2 x SiC(CH₃)₃), 19.3 and 19.2 (2 x SiC(CH₃)₃), 3.3 (CH₃CC).

Alcohol **44b**

To a well stirred solution of diol **44c** (130 mg, 1.30 mmol), in dry CH₂Cl₂ (13 mL) at 0 °C under N₂ was added imidazole (190 mg, 2.79 mmol) in one portion. *tert*-Butyldiphenylchlorosilane (0.37 mL, 1.42 mmol) was added dropwise over 2 min to the reaction mixture at 0 °C, and the reactants were thereafter stirred at 0 °C for 15 min. Sat. aq. NaHCO₃ (10 mL) was added slowly to the reaction mixture, and the layers partitioned. The aqueous layer was extracted with CH₂Cl₂ (3 x 20 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude product was purified by SiO₂ flash chromatography (100:1-50:1-30:1 hexane:EtOAc) to give the alcohol **44b** as a colorless oil (260 mg, 59%).

Data for **44b**: $[\alpha]_D^{25} -12.1^\circ$ (c 0.52, CH_2Cl_2); IR (neat) 3300 (br), 3080 (w), 3051 (w), 2930 (s), 2856 (m), 2237 (w), 1635 (w), 1472 (m), 1427 (s), 1360 (w), 1329 (w), 1313 (w), 1113 (s), 1069 (m), 1045 (m), 997 (w), 883 (m), 852 (m), 824 (s), 702 (s), 610 (s), 490 (s). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.69-7.65 (m, 4H, Ph), 7.45-7.35 (m, 6H, Ph), 4.43 (m, 1H, $\text{TBDPSOCH}_2\text{CH}(\text{OH})-$), 3.76 (dd, 1H, $J = 3.7, 10.2$ Hz, TBDPSOCH_2-), 3.68 (dd, 1H, $J = 7.4$ and 10.2 Hz, TBDPSOCH_2-), 2.50 (very br s, 1H, OH), 1.79 (d, 3H, $J = 2.2$ Hz, $\text{CH}_3\text{C}-$), 1.06 (s, 9H, $-\text{C}(\text{CH}_3)_3$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 135.6, 135.5, 133.0, 132.9, 129.9, 129.8, 127.8, 128.76 (Ar), 82.0 ($-(\text{HO})\text{CHCCCH}_3$), 77.0 ($-(\text{HO})\text{CHCCCH}_3$), 67.9 (TBDPSOCH_2-), 63.3 ($-(\text{HO})\text{CHCCMe}$), 26.8 $\text{SiC}(\text{CH}_3)_3$, 19.2 ($\text{SiC}(\text{CH}_3)_3$), 3.5 ($\text{CH}_3\text{C}-$); ESP+ HRMS: Calcd. for $\text{C}_{21}\text{H}_{26}\text{NaO}_2\text{Si}$: $(\text{M}+\text{Na})^+$ 361.15943. Found: 361.15991.

Alkyne 82

Step i. $(\text{COCl})_2$ (0.62 mL, 7.05 mmol), was added dropwise over 2 min into a stirred solution of dry DMSO (1.01 mL, 14.23 mmol) in dry CH_2Cl_2 (12 mL) at -78°C under N_2 . Stirring was continued at that temperature for 45 min. A solution of alcohol **81** (600 mg, 2.38 mmol) in dry CH_2Cl_2 (12 mL) was then added dropwise over 5 min, and the reactants were stirred at -78°C for 15 min, before Et_3N (1.67 mL, 11.98 mmol) was added over 2 min. After a further 5 min, the reaction mixture was allowed to warm to rt for 15 min, whereafter it was quenched with H_2O (20 mL) and extracted with CH_2Cl_2 (3 x 30 mL). The combined organic extracts were dried over MgSO_4 filtered, and concentrated *in vacuo*. The crude residue was very rapidly purified by SiO_2 flash chromatography using 2:1 hexane:EtOAc as the eluent. The unstable known aldehyde **82** (560 mg, 94%) (see above references) was used immediately without any further characterisation.

Step ii. Into a flask containing aldehyde **82** (560 mg, 2.24 mmol) was weighed the diazophosphonate **72** (520 mg, 2.70 mmol). The two materials were placed under a N_2

atmosphere and anhydrous MeOH (23 mL) was added at rt followed by anhydrous K₂CO₃ (620 mg, 4.49 mmol) in one portion. The reactants were stirred at rt for 16 h. Sat. aq. NH₄Cl (30 mL) was added and the mixture was extracted with EtOAc (3 x 30 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude residue was purified by SiO₂ flash chromatography (40:1-30:1 hexane:EtOAc); the product alkyne **83** was obtained as a colorless oil (170 mg, 29%).

Data for **83**: $[\alpha]_D^{25}$ -37.0 ° (c 0.46, CH₂Cl₂); IR (neat) 3285 (s), 3065 (w), 3032 (w), 2988 (s), 2874 (m), 1497 (w), 1454 (s), 1375 (s), 1256 (s), 1213 (s), 1074 (s), 849 (s), 741 (s), 698 (s). ¹H NMR (500 MHz, CDCl₃, 298K) δ 7.39-7.25 (m, 5H, Ph), 4.84 (d, 1H, *J* = 12.0 Hz, PhCH₂-), 4.58 (d, 1H, *J* = 12.0 Hz, PhCH₂-), 4.27 (dd, 1H, *J* = 6.6, 12.6 Hz, (-O)CH₂CH(O-)), 4.14 (dd, 1H, *J* = 2.1, 6.7 Hz, -(BnO)CH-), 4.10 (dd, 1H, *J* = 6.6, 8.8 Hz, (-O)CH₂-), 3.96 (dd, 1H, *J* = 5.9, 8.8 Hz, (-O)CH₂-), 2.47 (d, 1H, *J* = 2.1 Hz, HCC-) 1.39 (s, 3H, (CH₃)₂C), 1.34 (s, 3H, (CH₃)₂C); ¹³C NMR 125 MHz, CDCl₃, 298K) δ 137.0 (Ph), 128.3 (Ph), 128.1 (Ph), 127.8 (Ph), 110.2 (CH₃)₂C, 79.3 (-CCH), 76.9 ((-O)CH₂CH(O-)), 75.6 (-CCH), 70.7 (PhCH₂-), 70.0 (-(BnO)CH-), 66.2 ((-O)CH₂-), 26.4 and 25.3 (CH₃)₂C; ESP positive HRMS: Calcd. for C₁₅H₁₈NaO₃: (M+Na)⁺ 269.11482. Found: 269.11508.

Alkyne 48

n-BuLi (2.5 M in hexanes, 0.25 mL, 0.63 mmol) was added dropwise over 1 min to a solution of alkyne **83** (100 mg, 0.41 mmol) in dry THF (4.1 mL) at -30 °C under N₂. The resulting yellow solution was stirred at -30 °C for 40 min whereafter MeI (0.37 mL, 5.94 mmol) was added dropwise over 1 min. The reactants were stirred for 10 min at -30 °C and at rt for 3 h. The reaction was then quenched by the addition of H₂O (10 mL) and thereafter extracted with Et₂O (3 x 10 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude residue was purified by SiO₂ flash chromatography (gradient elution with 40:1-30:1 hexane:EtOAc) to give **48** as a colorless oil (90 mg, 85%).

Data for **48**: $[\alpha]_D^{25} -19.4^\circ$ (c 0.91, CH_2Cl_2); IR (neat) 3032 (w), 2987 (s), 2871 (s), 1498 (w), 1457 (s), 1370 (s), 1257 (s), 1213 (s), 1153 (m), 1074 (s), 1029 (m), 853 (s), 738 (s), 698 (s), 512 (w). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.38-7.23 (m, 5H, Ph), 4.81 (d, 1H, $J = 12.1$ Hz, $-\text{CH}_2\text{Ph}$), 4.57 (d, 1H, $J = 12.1$ Hz, $-\text{CH}_2\text{Ph}$), 4.23 (dd, 1H, $J = 6.6$ and 13.0 Hz, $-\text{CH}(\text{O}-)\text{CH}(\text{OBn})-$), 4.10 (m, 1H, $-\text{CH}(\text{OBn})-$), 4.08 (dd, 1H, $J = 6.6$ and 8.6 Hz, $(-\text{O})\text{CH}_2-$), 3.91 (dd, 1H, $J = 6.1$, 8.6 Hz, $(-\text{O})\text{CH}_2-$), 1.86 (d, 3H, $J = 2.1$ Hz, $\text{CH}_3\text{CC}-$), 1.38 (s, 3H, $(\text{CH}_3)_2\text{C}$), 1.34 (s, 3H, $(\text{CH}_3)_2\text{C}$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 137.6, 128.2, 128.0, 127.6 (Ph), 110.1 ($(\text{CH}_3)_2\text{C}$), 83.7 ($(-\text{BnO})\text{HCCCH}_3$), 77.6 ($-\text{OCH}_2\text{CH}(\text{O})-$), 74.7 ($-\text{CCCH}_3$), 70.5 ($-\text{CH}(\text{OBn})-$), 70.4 (PhCH_2-), 66.5 ($(-\text{O})\text{CH}_2-$), 26.5 and 25.4 ($(\text{CH}_3)_2\text{C}$), 3.6 (CH_3CC); ESP (+) HRMS: Calcd. for $\text{C}_{16}\text{H}_{20}\text{NaO}_3$: $(\text{M}+\text{Na})^+$ 283.13047. Found: 283.13006.

Alkyne 86

Step i. Oxalyl chloride (2.70 mL, 30.73 mmol), was added dropwise over 2 min to a stirred solution of dry DMSO (4.39 mL, 56.75 mmol) in dry CH_2Cl_2 (50 mL), at -78°C under N_2 . After 10 min, a solution of alcohol **84** (4.95 g, 10.34 mmol) in dry CH_2Cl_2 (30 mL) was added dropwise over 5 min. Stirring of the solution was continued at -78°C for 15 min, whereafter Et_3N (21.7 mL, 155.7 mmol) was added dropwise over 5 min. After a further 5 min at -78°C , the reaction mixture was allowed to warm to rt over 15 min. It was then quenched with brine (20 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (3 x 50 mL). The combined organic extracts were dried over MgSO_4 , filtered, and concentrated *in vacuo*. The crude aldehyde was very rapidly purified by SiO_2 flash chromatography using 20:1 hexane:EtOAc as the eluent to give the unstable aldehyde **85** (4.10 g, 83%) which was not characterised further but used directly.

Step ii. Into a flask containing aldehyde **85** (2.0 g, 4.20 mmol) was added the diazophosphonate **72**^{1,2} (1.21 g, 6.30 mmol). The two materials were placed under a N₂ atmosphere and anhydrous MeOH (30 mL) was added at rt followed by anhydrous K₂CO₃ (1.16 g, 8.39 mmol) in one portion. The reactants were stirred at rt for 1.5 h, whereafter sat. aq. NH₄Cl (20 mL) was added. After 10 min, the mixture was extracted with EtOAc (3 x 30 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude residue was purified by SiO₂ flash chromatography (gradient elution with 50:1-20:1 hexane:EtOAc as eluent); the product alkyne **86** was isolated as a colorless oil (1.4 g, 71%).

Alkyne 54

n-BuLi (2.5 M in hexanes, 0.43 mL, 1.08 mmol) was added dropwise over 2 min to a stirred solution of alkyne **86** (340 mg, 0.72 mmol) in dry THF (7.2 mL) at -30 °C under N₂. The yellow mixture was stirred at -30 °C for 40 min, whereafter MeI (0.22 mL, 3.53 mmol) was added over 30 sec. Stirring was continued at -30 °C for 10 min and rt for 16 h before the reaction was quenched with H₂O (30 mL) and mixture extracted with Et₂O (3 x 30 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude product was purified by

SiO₂ flash chromatography (with 150:1-100:1 hexane:EtOAc as eluent); alkyne **54** was obtained as a colorless oil (320 mg, 91%).

Data for **54**: $[\alpha]_D^{+2.4}$ (c 0.59, CH₂Cl₂); IR (neat) 3048 (w), 2958 (s), 2932 (s), 2857 (s), 1613 (m), 1513 (s), 1465 (m), 1427 (m), 1383 (w), 1300 (w), 1248 (s), 1111 (s), 1038 (w), 824 (m), 741 (w), 705 (s), 610 (m). ¹H NMR (500 MHz, CDCl₃, 298K) δ 7.78-7.73 (m, 4H, Ph), 7.48-7.35 (m, 6H, Ph), 7.31 (d, 2H, *J* = 8.7 Hz, -PMP), 6.89 (d, 2H, *J* = 8.7 Hz, -PMP), 4.65 (d, 1H, *J* = 10.7 Hz, PhCH₂-), 4.56 (d, 1H, *J* = 10.7 Hz, PhCH₂-), 3.82 (d, 1H, *J* = 10.4 Hz, TBDPSOCH₂-), 3.81 (s, 3H, OCH₃), 3.74 (d, 1H, *J* = 10.4 Hz, TBDPSOCH₂-), 1.93 (q, 2H, *J* = 7.4 Hz, CH₃CH₂-), 1.90 (s, 3H, CH₃C-), 1.13 (s, 9H, (CH₃)₃CSi), 1.05 (t, 3H, *J* = 7.4 Hz, CH₃CH₂-); ¹³C NMR 125 MHz, CDCl₃, 298K) δ 158.8 (Ph), 135.7 (Ph), 135.68 (Ph), 133.6 (Ph), 133.5 (Ph), 131.7 (Ph), 129.6 (Ph), 129.0 (Ph), 127.6 (Ph), 127.5 (Ph), 113.6 (Ph), 83.1 (-C≡CCH₃), 78.4 (-C≡CCH₃), 77.9 (COPMB), 67.0 (TBDPSOCH₂-), 66.1 (PhCH₂-), 55.2 (OCH₃), 29.5 (CH₃CH₂-), 26.8 (CH₃)₃CSi), 19.4 (CH₃)₃CSi), 8.5 (CH₃CH₂-), 3.5 (CH₃CC); ESP positive HRMS: Calcd. for C₃₁H₃₈NaO₃Si: (M+Na)⁺ 509.24824. Found: 509.24889.

Alkyne 51

To a stirred solution of the tertiary PMB ether **54** (110 mg, 0.23 mmol) in CH₂Cl₂ (2.3 mL) and H₂O (0.22 mL) at 0 °C was added DDQ (77 mg, 0.34 mmol) in one portion. The reactants were stirred at 0 °C for 0.5 h and then allowed to warm to rt. After 3 h 15 min, sat. aq. NaHCO₃ (10 mL) was added and the mixture was extracted with CH₂Cl₂ (3 x 20 mL). The combined organic extracts were dried over MgSO₄, filtered, and concentrated *in vacuo*. The crude residue was purified by SiO₂ flash chromatography (using 50:1 hexane:EtOAc as eluent); the title compound **51** was isolated as a colorless oil (76 mg, 92%).

Data for **51**: $[\alpha]_D^{+24.0}$ (c 0.61, CH₂Cl₂); IR (neat) 3448 (br s), 3070 (w), 2962 (s), 2933 (s), 2857 (s), 1469 (m), 1428 (m), 1385 (m), 1326 (w), 1111 (s), 824 (m), 741 (m), 705 (s), 610 (m), 508 (s).

^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.72-7.65 (m, 4H, Ph), 7.44-7.35 (m, 6H, Ph), 3.69 (d, 1H, J = 9.7 Hz, TBDPSOCH_2 -), 3.56 (d, 1H, J = 9.7 Hz, TBDPSOCH_2 -), 2.77 (br s, 1H, -OH), 1.82 (s, 3H, CH_3CC -), 1.69 (m, 1H, $-\text{CH}_2\text{CH}_3$), 1.62 (m, 1H, $-\text{CH}_2\text{CH}_3$), 1.07 (s, 9H, $(\text{CH}_3)_3\text{CSi}$), 0.99 (t, 3H, J = 7.5 Hz, $-\text{CH}_2\text{CH}_3$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 135.7, 135.6, 133.1, 133.0, 129.8, 129.7, 127.8, 127.7 (Ph), 80.7 (CH_3CC -), 80.1 (CH_3CC -), 72.0 ($\text{C}(\text{OH})\text{CH}_2\text{CH}_3$), 70.2 ($-\text{CH}_2\text{OTBDPS}$), 31.1 ($\text{CH}_3\text{CH}_2\text{C}(\text{OH})$), 26.8 ($(\text{CH}_3)_3\text{CSi}$), 19.3 ($(\text{CH}_3)_3\text{CSi}$), 8.5 (CH_3CH_2 -), 3.5 (CH_3CC); CI (-) HRMS: Calcd. for $\text{C}_{23}\text{H}_{30}\text{O}_2\text{Si}$: (M) $^+$ 365.1936714. Found: 365.1955207.

Alkyne 61

n -BuLi (2.5 M in hexanes, 0.30 mL, 0.75 mmol) was added dropwise over 1 min into a stirred solution of alkyne **87** (160 mg, 0.50 mmol) in dry THF (10 mL) at $-30\text{ }^\circ\text{C}$ under N_2 . After stirring at $-30\text{ }^\circ\text{C}$ for 45 min, solid paraformaldehyde (75 mg, 2.50 mmol) was added in one portion, and the reaction was maintained at $-30\text{ }^\circ\text{C}$ for 10 min before being warmed to rt and stirred for 18 h. The reaction was thereafter quenched with H_2O (10 mL) and extracted with EtOAc (3 x 10 mL). The combined organic extracts were dried over MgSO_4 , filtered, and concentrated *in vacuo*. The crude product was purified by SiO_2 flash chromatography (10:1 hexane:EtOAc) to give the alkynol **61** as a colorless oil (130 mg, 74%).

Data for **61**: IR (neat) 3335 (br), 2932 (s), 2858 (s), 2331 (w), 1464 (m), 1427 (s), 1387 (w), 1113 (s), 1092 (s), 1030 (m), 998 (m), 824 (m), 702 (s), 689 (m), 614 (m); ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.71-7.68 (m, 4H, Ph), 7.45-7.37 (m, 3H, Ph), 4.20 (d, 2H, J = 1.8 Hz, $-\text{CH}_2\text{OH}$), 3.73 (dd, 1H, J = 5.8, 9.6 Hz, $-\text{CH}_2\text{OTBDPS}$), 3.56 (dd, 1H, J = 7.6, 9.6 Hz, $-\text{CH}_2\text{OTBDPS}$), 2.70 (m, 1H, $-(\text{CH}_3)\text{C}(\text{H})\text{CH}_2\text{OTBDPS}$), 1.73 (br s, 1H, OH), 1.23 (d, 3H, J = 6.9 Hz, CH_3), 1.08 (s, 9H, $\text{SiC}(\text{CH}_3)_3$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 135.6, 135.5, 133.6, 133.5, 129.6, 127.6 (Ph), 88.2 ($-\text{CH}(\text{CH}_3)\text{CCCH}_2\text{OH}$), 79.3 ($-\text{CH}(\text{CH}_3)\text{CCCH}_2\text{OH}$), 67.5 ($-\text{CH}_2\text{OTBDPS}$), 51.2 ($-\text{CH}_2\text{OH}$), 29.0 ($-(\text{CH}_3)\text{CHCH}_2\text{OTBDPS}$), 26.8 ($(\text{CH}_3)_2\text{CSi}$), 19.3 ($(\text{CH}_3)_2\text{CSi}$), 17.3 ($-(\text{CH}_3)\text{CH}$ -); FAB (+) HRMS: Calcd. for $\text{C}_{22}\text{H}_{29}\text{O}_2\text{Si}$: ($\text{M}+\text{H}$) $^+$ 353.19313. Found: 353.19275.

The *O*-Directed Hydrostannation of The Disubstituted Acetylenes with Ph₃SnH/Et₃B

General Experimental Procedure for the *O*-Directed Free Radical Hydrostannation of Disubstituted Alkynes with Ph₃SnH and Cat. Et₃B

Into a round-bottomed flask containing the alkyne (1 eq) was weighed Ph₃SnH (Aldrich, 1.5 eq). The flask was immediately purged with N₂ and sufficient dry PhMe was added to produce a 0.1M solution of the starting alkyne. Et₃B (Aldrich, 1 M in hexanes, 0.1 eq) was then added dropwise over 30 sec. Air was then injected into the reaction vessel to initiate the reaction. The reactants were stirred at RT until TLC analysis revealed that all of the starting alkyne had been consumed or that the reaction had progressed no further. H₂O was added and the mixture was extracted with EtOAc (x 3). The combined organic extracts were dried (MgSO₄), filtered, and concentrated *in vacuo*.^{*} The crude product was purified by SiO₂ flash chromatography using 150:1-100:1 hexane:EtOAc as eluent (depending upon the compound) to give the desired products. Using this general procedure, the following vinylstannanes were prepared.

^{*}In the vinylstannane ratio determinations that we report below, the NMR estimations were always performed on the crude residues that were obtained after the combined dried (MgSO₄) organic extracts were concentrated *in vacuo*, *prior* to SiO₂ flash chromatography.

Important Note: All minor isomers that were obtained in these hydrostannation reactions have only had their structures tentatively assigned.

Vinylstannanes 19 and 20

Alkyne **18** (400 mg, 2.85 mmol) was reacted with Ph₃SnH (1.50 g, 4.27 mmol) and Et₃B (1 M solution in hexanes, 2.85 mL, 0.285 mmol) in dry PhMe (29 mL) at rt for 4 h. After extractive work-up and concentration, **19** and **20** were shown to be present in 34:1 ratio according to 500 MHz ¹H NMR spectroscopic analysis of the crude residue in CDCl₃. After SiO₂ flash chromatography of this residue with 150:1 petrol/EtOAc as eluent, **19** and **20** were obtained as a 34:1 mixture of regioisomers in the form of a colorless oil (856 mg, 61%).

Data for the major regioisomer **19**: $[\alpha]_D^{+21.9}$ (c 0.88, CH_2Cl_2); IR (neat) 3068 (m), 2989 (s), 2932 (m), 2864 (m), 1621 (w), 1479 (w), 1423 (m), 1372 (m), 1247 (m), 1156 (m), 1060 (s), 1026 (w), 861 (w), 726 (s), 697 (s). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.64-7.51 (m, 6H, Ph), 7.40 - 7.34 (m, 9H, Ph), 6.81 (qd, 1H, $J = 1.3, 6.8$ Hz, ($^3J^{119}\text{Sn}-^1\text{H} = 154.2$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 147.4$ Hz), $\text{CH}_3\text{CH}=\text{C}(\text{SnPh}_3)-$), 4.74 (m, 1H, ($^3J_{\text{SnH}} = 52$ Hz, $(-\text{O})\text{CH}_2\text{CH}(\text{O}-)$), 3.89 (dd, 1H, $J = 6.0, 7.7$ Hz, $(-\text{O})\text{CH}_2-$), 3.49 (dd, 1H, $J = 7.8, 8.6$ Hz, $(-\text{O})\text{CH}_2-$), 1.72 (dd, 3H, $J = 0.9, 6.8$ Hz, ($^4J_{\text{SnH}} = 19.5$ Hz), $\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 1.28 (s, 3H, $(\text{CH}_3)_2\text{C}$), 0.98 (s, 3H, $(\text{CH}_3)_2\text{C}$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 139.5 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 139.1 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 138.3 (Ar), 137.0 (Ar), 128.9 (Ar), 128.6 (Ar), 109.1 ($(\text{CH}_3)_2\text{C}$), 81.9 ($(-\text{O})\text{CH}_2\text{CH}(\text{O}-)$), 70.3 ($(-\text{O})\text{CH}_2\text{CH}(\text{O}-)$), 25.9 and 25.8 ($(\text{CH}_3)_2\text{C}$), 20.5 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$). ESP+ HRMS: Calcd. for $\text{C}_{26}\text{H}_{28}\text{NaO}_2\text{Sn}$: $(\text{M}+\text{Na})^+$ 515.10035. Found: 515.10054.

Vinylstannanes **22** and **23**

Treatment of alkyne **21** (400 mg, 2.60 mmol) with Ph_3SnH (1.6 g, 4.56 mmol) and Et_3B (1 M solution in hexanes, 0.52 mL, 0.52 mmol) in dry PhMe (26 mL) at rt for 17 h gave the vinylstannanes **22** and **23** in 30:1 ratio after extractive work-up and examination of the crude reaction mixture by 500 MHz ^1H NMR spectroscopy in CDCl_3 . After SiO_2 flash chromatography of the crude concentrated residue (gradient elution with 150:1 to 100:1 petrol/EtOAc as eluent), a 32:1 mixture of **22** and **23** was obtained as a colorless oil (784 mg, 60%).

Data for the major regioisomer **22**: $[\alpha]_D^{+23.2}$ (c 0.59, CH_2Cl_2); IR (neat) 3045 (s), 2984 (s), 2933 (s), 2870 (s), 1620 (m), 1480 (m), 1455 (m), 1428 (s), 1377 (s), 1246 (s), 1215 (s), 1158 (s), 1058 (s), 1022 (w), 857 (s), 729 (s), 670 (s). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.62-7.49 (m, 6H, Ph), 7.40-7.30 (m, 9H, Ph), 6.66 (td, 1H, $J = 1.3, 7.4$ Hz, ($^3J^{119}\text{Sn}-^1\text{H} = 154.7$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 147.9$ Hz), $\text{CH}_3\text{CH}_2\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 4.73 (m, 1H, ($^3J^{119}\text{Sn}-^1\text{H} = 48.9$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 46.7$ Hz), $(-\text{O})\text{CH}_2\text{CH}(\text{O}-)$), 3.88 (dd, 1H, $J = 7.7, 6.0$ Hz, $(-\text{O})\text{CH}_2-$), 3.49 (dd, 1H, $J = 7.8, 8.6$ Hz, $(-\text{O})\text{CH}_2-$), 2.04 (m, 2H, $\text{CH}_3\text{CH}_2\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 1.27 (s, 3H, $(\text{CH}_3)_2\text{C}$), 0.97 (s, 3H, $(\text{CH}_3)_2\text{C}$), 0.79 (t, 3H, $J = 7.4$ Hz, $\text{CH}_3\text{CH}_2\text{CH}$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 146.7 ($\text{CH}_3\text{CH}_2\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$)

139.2 ($\text{CH}_3\text{CH}_2\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 137.0 (Ar), 136.3 (Ar), 128.8 (Ar), 128.5 (Ar), 109.1 ($(\text{CH}_3)_2\text{C}$), 81.8 ($(-\text{O})\text{CH}_2\text{CH}(\text{O}-)$), 70.4 ($(-\text{O})\text{CH}_2-$), 28.4 (CH_3CH_2-), 25.9 and 25.8 ($(\text{CH}_3)_2\text{C}$), 13.7 ($\text{CH}_3\text{CH}_2\text{CH}$); ESP+ HRMS: Calcd. for $\text{C}_{27}\text{H}_{30}\text{NaO}_2\text{Sn}$: $(\text{M}+\text{Na})^+$ 529.11600. Found: 529.11645.

Vinylstannanes **25** and **26**

Vinylstannanes **25** and **26** were prepared according to the general procedure outlined above by reacting alkyne **24** (210 mg, 1.25 mmol) with Ph_3SnH (658 mg, 1.87 mmol) and Et_3B (1 M solution in hexanes, 0.125 ml, 0.125 mmol) in dry PhMe (12.5 ml) at rt for 4.5 h. Vinylstannanes **25** and **26** were obtained in 26:1 ratio after extractive work-up and examination of the crude concentrated organic residue by 500 MHz ^1H NMR spectroscopy in CDCl_3 . After SiO_2 flash chromatography of this crude residue (with 150:1 petrol/ EtOAc as eluent), **25** and **26** were isolated as a 27:1 mixture of regioisomers in the form of a colorless oil (382 mg, 59%).

Data for the major regioisomer **25**: $[\alpha]_D^{+19.7}$ (c 0.93, CH_2Cl_2); IR (neat) 3063 (m), 2997 (s), 2954 (s), 2921 (s), 2856 (s), 1616 (w), 1475 (w), 1458 (w), 1431 (s), 1371 (s), 1246 (s), 1213 (s), 1158 (m), 1060 (s), 853 (s), 728 (s), 695 (s). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.66-7.50 (m, 6H, Ph), 7.40-7.30 (m, 9H, Ph), 6.70 (t, 1H, $J = 7.4$ Hz, ($^3J^{119}\text{Sn}-^1\text{H} = 156.1$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 149.2$ Hz), $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{H})=\text{C}(\text{SnPh}_3)$), 4.75 (apparent t, 1H, $J = 7.1$ Hz, ($^3J^{119}\text{Sn}-^1\text{H} = 48.0$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 45.8$ Hz), $(-\text{O})\text{CH}_2\text{CH}(\text{O}-)$), 3.90 (dd, 1H, $J = 6.1, 7.7$ Hz, $(-\text{O})\text{CH}_2-$), 3.52 (dd, 1H, $J = 7.8, 8.5$ Hz, $(-\text{O})\text{CH}_2-$), 2.00 (q, 2H, $J = 7.4$ Hz, $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{H})=\text{C}(\text{SnPh}_3)$), 1.29 (s, 3H, $(\text{CH}_3)_2\text{C}$), 1.21 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{H})=\text{C}(\text{SnPh}_3)$), 0.99 (s, 3H, $(\text{CH}_3)_2\text{C}$), 0.58 (t, 3H, $J = 7.4$ Hz, $\text{CH}_3\text{CH}_2\text{CH}_2$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 145.1 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$) 139.3 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 137.2 (Ar), 137.0 (Ar), 128.8 (Ar), 128.5 (Ar), 109.0 ($(\text{CH}_3)_2\text{C}$), 81.8 ($(-\text{O})\text{CH}_2\text{CH}(\text{O}-)$), 70.4 ($(-\text{O})\text{CH}_2-$), 36.8 ($\text{CH}_3\text{CH}_2\text{CH}_2-$), 25.9 and 25.8 ($(\text{CH}_3)_2\text{C}$), 22.7 ($\text{CH}_3\text{CH}_2\text{CH}_2-$), 13.5 ($\text{CH}_3\text{CH}_2\text{CH}_2-$). CI HRMS: Calcd. for $\text{C}_{28}\text{H}_{32}\text{O}_2\text{Sn}$: $(\text{M})^+$ 520.14188. Found: 520.14158.

Vinylstannanes **28** and **29**

Vinylstannanes **28** and **29** were prepared according the general procedure outlined above by reacting alkyne **27** (400 mg, 2.19 mmol) with Ph_3SnH (1.16 g, 3.30 mmol) and Et_3B (1 M solution in hexanes, 0.219 ml, 0.219 mmol) in dry PhMe (7.2 ml) at rt for 14 h. Vinylstannanes **28** and **29** were obtained in 41:1 ratio after extractive work-up and examination of the crude cocncentrated organic residue by 500 MHz ^1H NMR spectroscopy in CDCl_3 . After SiO_2 flash chromatography of this residue (gradient elution with 200:1 to 100:1 petrol/ EtOAc as eluent), **28** and **29** were isolated as a 24:1 mixture of regioisomers in the form of a colorless oil (748 mg, 64%).

Data for the major regioisomer **28**: $[\alpha]_D^{+16.2}$ (c 0.99, CH_2Cl_2); IR (neat) 3063 (m), 2932 (m), 2867 (s), 1616 (w), 1480 (w), 1431 (s), 1371 (m), 1245 (m), 1213 (m), 1158 (m), 1060 (s), 859 (w), 728 (s), 695 (s). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.70-7.58 (m, 6H, Ph), 7.42-7.35 (m, 9H, Ph), 6.74 (td, 1H, $J = 1.2, 7.4$ Hz, (3J $^{119}\text{Sn}-^1\text{H} = 156.1$ Hz, 3J $^{117}\text{Sn}-^1\text{H} = 149.2$ Hz), $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 4.80 (apparent t, 1H, $J = 7.6$ and 6.4, (3J $^{119}\text{Sn}-^1\text{H} = 48.8$ Hz, 3J $^{117}\text{Sn}-^1\text{H} = 46.6$ Hz), OCH_2CHO), 3.96 (dd, 1H, $J = 6.0, 7.7$ Hz, $(-\text{O})\text{CH}_2-$), 3.57 (dd, 1H, $J = 7.9, 8.4$ Hz, $(-\text{O})\text{CH}_2-$), 2.06 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$) 1.33 (s, 3H, $(\text{CH}_3)_2\text{C}$), 1.21 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$), 1.03 (s, 3H, $(\text{CH}_3)_2\text{C}$), 1.00 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$), 0.67 (t, 3H, $J = 7.3$ Hz, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 145.3 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$) 139.3 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 137.0 (Ar), 136.96 (Ar), 128.8 (Ar), 128.4 (Ar), 109.0 ($(\text{CH}_3)_2\text{C}$), 81.8 ($(-\text{O})\text{CH}_2\text{CH}(\text{O}-)$), 70.3 ($(-\text{O})\text{CH}_2-$), 34.6 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$), 31.6 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$), 25.8 and 25.7 ($(\text{CH}_3)_2\text{C}$), 22.1 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$), 13.7 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2-$); FAB(+) HRMS: Calcd. for $\text{C}_{29}\text{H}_{34}\text{NaO}_2\text{Sn}$: $(\text{M}+\text{Na})^+$ 557.14784. Found: 557.15028.

Vinylstannanes **31** and **32**

Vinylstannanes **31** and **32** were prepared according to the general procedure outlined above by reacting alkyne **30** (400 mg, 2.21 mmol) with Ph_3SnH (1.17 g, 3.33 mmol) and Et_3B (1M solution in hexanes, 0.22 ml, 0.22 mmol) in dry PhMe (22 mL) at rt for 14 h. Vinylstannanes **31** and **32** were obtained in 31:1 ratio after extractive work-up and examination of the crude concentrated organic residue by 500 MHz ^1H NMR spectroscopy in CDCl_3 . After SiO_2 flash chromatography (gradient elution with 150:1 to 100:1 petrol/EtOAc as eluent), the vinylstannane products **31** and **32** were isolated as an inseparable 30:1 mixture of regioisomers in the form of a colorless oil (916 mg, 78%).

Data for the major regioisomer **31**: $[\alpha]_D^{+14.7} +14.7^\circ$ (c 0.88, CH_2Cl_2); IR (neat) 3045 (m), 2936 (s), 2858 (s), 1714 (w), 1622 (m), 1582 (m), 1481 (m), 1428 (s), 1366 (w), 1276 (m), 1162 (s), 1099 (s), 1073 (s), 930 (s), 848 (m), 730 (s), 699 (s). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.64-7.53 (m, 6H, Ph), 7.38-7.30 (m, 9H, Ph), 6.80 (qd, 1H, $J=1.3$, 6.8 Hz, ($^3J^{119}\text{Sn}-^1\text{H} = 155.8$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 148.8$ Hz), $\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 4.73 (m, 1H, ($^3J^{119}\text{Sn}-^1\text{H} = 46.0$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 44.0$ Hz), $(-\text{O})\text{CH}_2\text{CH}(\text{O})-$), 3.88 (dd, 1H, $J = 6.0$, 7.7 Hz, $(-\text{O})\text{CH}_2-$), 3.50 (dd, 1H, $J = 7.9$, 8.4 Hz, $(-\text{O})\text{CH}_2-$), 1.71 (dd, 3H, $J = 0.8$, 6.7 Hz, ($^4J_{\text{SnH}} = 19$ Hz), $\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 1.59-1.44 (m, 4H, cyclohexyl), 1.40-1.22 (m, 4H, cyclohexyl), 1.19-1.07 (m, 2H, cyclohexyl); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 139.2 ($\text{CH}_3\text{CH}=\text{C}(\text{SnPh}_3)-$), 139.1 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 138.6 (Ar), 137.0 (Ar), 128.8 (Ar), 128.5 (Ar), 109.7 ($(\text{CH}_2)_2\text{C}$), 81.4 ($(-\text{O})\text{CH}_2\text{CH}(\text{O})-$), 69.9 ($-\text{OCH}_2-$), 35.4 and 35.3 (CH_2 cyclohexyl), 25.1, 23.9 and 23.8 (CH_2 cyclohexyl), 20.5 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$); CI^+ HRMS: Calcd. for $\text{C}_{29}\text{H}_{30}\text{O}_2\text{Sn}$: ($\text{M}-2\text{H}$) $^+$ 530.12677. Found: 530.13049.

Vinylstannanes **34a** and **35a**

Vinylstannanes **34a** and **35a** were prepared according to the general procedure outlined above by reacting alkyne **33a** (500 mg, 1.22 mmol) with Ph_3SnH (640 mg, 1.83 mmol) and Et_3B (1 M solution in hexanes, 0.12 mL, 0.12 mmol) in dry PhMe (12.2 mL) at rt for 16 h. After extractive work-up, the two vinylstannanes **34a** and **35a** were obtained in approx. 72:1 ratio according to 500 MHz ^1H NMR analysis of the crude concentrated organic residue in CDCl_3 . After SiO_2 flash chromatography of this residue (gradient elution with 150:1 to 100:1 petrol/ EtOAc as eluent), **34a** and **35a** were obtained as a 199:1 mixture of regioisomers in the form of a colorless oil (830 mg, 88%); the chromatographic purification of this mixture appeared to cause a small amount (ca. 3%) of the protodestannylated (*E*)-disubstituted alkene product to be formed (see the dd at δ 6.28 in the expanded region of **34a** in Part 2 of this paper's SI).

Data for the major regioisomer **34a**: $[\alpha]_D^{+28.8}$ (c 0.89, CH_2Cl_2); IR (neat) 3046 (s), 2932 (s), 2857 (s), 1956 (w), 1890 (w), 1820 (w), 1728 (w), 1620 (m), 1588 (w), 1475 (s), 1428 (s), 1379 (s), 1244 (s), 1214 (s), 1168 (s), 1110 (s), 1074 (s), 893 (s), 855 (m), 824 (s), 793 (m), 730 (s), 706 (s), 613 (s), 509 (s). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.66-7.62 (m, 4H, Ph), 7.51-7.38 (m, 8H, Ph), 7.36-7.25 (m, 13H, Ph), 6.76 (qd, 1H, $J = 1.6, 6.8$ Hz, ($^3J^{119}\text{Sn}-^1\text{H} = 156.0$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 149.2$ Hz), $\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 4.87 (dt, 1H, $J = 1.4, 6.7$ Hz, ($^3J^{119}\text{Sn}-^1\text{H} = 35.8$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 34.2$ Hz), $-(\text{O})\text{CHC}=\text{CH}(\text{Me})$), 3.97 (ddd, 1H, $J = 2.7, 2.7, 9.2$ Hz, $\text{TBDPSOCH}_2\text{CH}(\text{O})-$), 3.76 (dd, 1H, $J = 2.7, 10.8$ Hz, TBDPSOCH_2-), 3.56 (dd, 1H, $J = 9.1, 10.8$ Hz, TBDPSOCH_2-), 1.69 (dd, 3H, $J = 1.2, 6.8$ Hz, $\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 1.29 (s, 3H, $(\text{CH}_3)_2\text{C}$), 1.16 (s, 3H, $(\text{CH}_3)_2\text{C}$), 1.02 (9H, s, $(\text{CH}_3)_3\text{CSi}$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 138.9 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$) 138.6 ($\text{CH}_3\text{CH}=\text{CSnPh}_3$), 136.9, 135.7, 135.6, 135.1, 133.9, 133.6, 129.5, 129.4, 128.8, 128.5, 127.6, 127.5 (Ar), 107.9 ($(\text{CH}_3)_2\text{C}$), 81.3 ($-(\text{O})\text{CH}(\text{Ph}_3\text{Sn})\text{C}=\text{CH}(\text{Me})$), 79.3 ($\text{TBDPSOCH}_2\text{CH}(\text{O})-$), 65.3 (TBDPSOCH_2-), 27.3 and 25.6 ($(\text{CH}_3)_2\text{C}$), 26.8 ($(\text{CH}_3)_3\text{CSi}$), 20.9 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 19.2 ($(\text{CH}_3)_3\text{CSi}$); ESP+ HRMS: Calcd. for $\text{C}_{43}\text{H}_{48}\text{NaO}_3\text{SiSn}$: ($\text{M}+\text{Na}$) $^+$ 783.22869. Found: 783.22867.

Vinylstannanes **34b** and **35b**

Compounds **34b** and **35b** were prepared according to the general procedure outlined above by reacting alkyne **33b** (300 mg, 0.71 mmol) with Ph_3SnH (370 mg, 1.05 mmol) and Et_3B (0.071 mL (71 μL), 0.071 mmol) in dry PhMe (7.1 mL) at rt for 18 h. The two vinylstannanes **34b** and **35b** were present in approx. 26:1 ratio after extractive work-up and examination of the crude concentrated reaction mixture by 500 MHz ^1H NMR spectroscopy in CDCl_3 . After SiO_2 flash chromatography of this residue (gradient elution with 150:1 to 100:1 petrol/ EtOAc as eluent), the two products **34b** and **35b** were obtained as a 26:1 mixture of regioisomers as a colorless oil (410 mg, 75%).

Data for the major regioisomer **34b**; $[\alpha]_D^{+30.7}$ (c 0.62, CH_2Cl_2); IR (neat) 3066 (w), 2961 (w), 2932 (m), 2858 (w), 1428 (m) 1378 (w), 1213 (w) 1111 (s), 1074 (s), 825 (w), 730 (s), 701 (s), 614 (w), 508 (m). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.66-7.58 (m, 4H, Ph), 7.45-7.21 (m, 21H, Ph), 6.58 (td, 1H, $J = 1.3, 7.5$ Hz, ($^3J^{119}\text{Sn}-^1\text{H} = 156.7$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 149.8$ Hz), $\text{CH}_3\text{CH}_2\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 4.83 (d, 1H, $J = 6.5$ Hz, ($^3J^{119}\text{Sn}-^1\text{H} = 34.7$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 33.1$ Hz), -(-O) $\text{CHC}=\text{CHCH}_2\text{CH}_3$), 3.95 (ddd, $J = 2.5, 6.8, 9.3$ Hz, 1H, $\text{TBDPSOCH}_2\text{CH}(\text{O})-$), 3.72 (dd, 1H, $J = 2.5, 10.8$ Hz, TBDPSOCH_2-), 3.51 (dd, 1H, $J = 9.7$ and 10.6 Hz, TBDPSOCH_2-), 1.96 (m, 2H, $\text{CH}_3\text{CH}_2\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 1.26 (s, 3H, $(\text{CH}_3)_2\text{C}$), 1.16 (s, 3H, $(\text{CH}_3)_2\text{C}$), 1.00 (9H, s, $(\text{CH}_3)_3\text{CSi}$), 0.68 (t, 3H, $J = 7.4$ Hz, CH_3CH_2-); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 145.9 ($\text{CH}_3\text{CH}_2\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 138.7 ($\text{CH}_3\text{CH}_2\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 136.9, 135.7, 135.6, 133.9, 133.6, 133.1, 129.5, 129.4, 128.9, 128.5, 127.6, 127.5 (Ar), 108.0 ($(\text{CH}_3)_2\text{C}$), 81.0 ($-(\text{O})\text{CHC}(\text{SnPh}_3)=\text{C}(\text{H})\text{CH}_2\text{CH}_3$), 79.0 ($\text{TBDPSOCH}_2\text{CH}(\text{O})-$), 65.4 (TBDPSOCH_2-), 28.8 (CH_3CH_2-), 27.4 and 25.7 ($(\text{CH}_3)_2\text{C}$), 26.8 ($(\text{CH}_3)_3\text{CSi}$), 19.2 ($(\text{CH}_3)_3\text{CSi}$), 13.6 (CH_3CH_2-); ESP+ HRMS: Calcd. for $\text{C}_{44}\text{H}_{50}\text{NaO}_3\text{SiSn}$: ($\text{M}+\text{Na}$) $^+$ 797.24434. Found: 797.24534.

Vinylstannanes **34c** and **35c**

Compounds **34c** and **35c** were prepared via the general procedure outlined above by reacting alkyne **33c** (67 mg, 0.153 mmol) with Ph_3SnH (80.8 mg, 0.23 mmol) and Et_3B (1 M solution in hexanes, 0.015 ml (15 μL), 0.015 mmol) in dry PhMe (1.5 mL) at rt for 18 h. After aqueous extractive work-up, the concentrated organic residue contained the two vinylstannanes **34c** and **35c** in approx. 41:1 ratio according to 500 MHz ^1H NMR spectroscopic analysis in CDCl_3 . After SiO_2 flash chromatography of this residue (with 150:1 petrol/EtOAc as eluent), the major product **34c** was isolated pure as a colorless oil (103 mg, 86%).

Data for the major regioisomer **34c**: $[\alpha]_D^{25} +26.6^\circ$ (c 1.05, CH_2Cl_2); IR (neat) 3047 (m), 2958 (s), 2931 (s), 2858 (s), 1461 (s), 1428 (s), 1380 (s), 1242 (w), 1213 (s), 1111 (s), 1075 (s), 909 (s), 824 (s), 730 (s), 702 (s), 614 (s), 508 (s). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.66-7.59 (m, 4H, Ph), 7.45-7.23 (m, 21H, Ph), 6.60 (td, 1H, $J = 1.5, 8.2$ Hz, ($^3J^{^{119}\text{Sn}-^1\text{H}} = 158.0$ Hz, $^3J^{^{117}\text{Sn}-^1\text{H}} = 151.0$ Hz), $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{C}(\text{SnPh}_3)-$), 4.84 (d, 1H, $J = 6.2$ Hz, ($^3J^{^{119}\text{Sn}-^1\text{H}} = 33.8$ Hz, $^3J^{^{117}\text{Sn}-^1\text{H}} = 32.4$ Hz), $-(\text{O})\text{CH}(\text{Ph}_3\text{Sn})\text{C}=\text{CH}(\text{Pr}-n)$), 3.97 (ddd, $J = 2.5, 6.7, 9.4$ Hz, 1H, $\text{TBDPSOCH}_2\text{CH}(\text{O}-)$), 3.71 (dd, 1H, $J = 2.5, 10.8$ Hz, TBDPSOCH_2-), 3.51 (dd, 1H, $J = 10.7, 10.7$ Hz, $(\text{TBDPSOCH}_2-$), 1.91 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 1.27 (s, 3H, $(\text{CH}_3)_2\text{C}$), 1.17 (s, 3H, $(\text{CH}_3)_2\text{C}$), 1.04 (m, 2H, $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{C}(\text{SnPh}_3)-$), 1.00 (s, 9H, $(\text{CH}_3)_3\text{CSi}$), 0.48 (t, 3H, $J = 7.4$ Hz, $\text{CH}_3\text{CH}_2\text{CH}_2-$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 144.4 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{C}(\text{SnPh}_3)-$) 138.8 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 136.9, 135.7, 135.6, 133.9, 133.8, 133.6, 129.5, 129.4, 128.8, 128.5, 127.6, 127.5 (Ar), 107.9 ($(\text{CH}_3)_2\text{C}$), 81.0 ($\text{OCHCHC}=\text{CH}$), 79.0 ($\text{TBDPSOCH}_2\text{CH}(\text{O}-)$), 65.5 (TBDPSOCH_2-), 37.2 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}$), 27.4 and 25.7 ($(\text{CH}_3)_2\text{C}$), 26.8 ($(\text{CH}_3)_3\text{CSi}$), 22.7 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}$), 19.2 ($(\text{CH}_3)_3\text{CSi}$), 13.5 ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}$); CI HRMS: Calcd. for $\text{C}_{45}\text{H}_{52}\text{NaO}_3\text{SiSn}$: $(\text{M}+\text{Na})^+ 811.25999$. Found: 811.25950.

Vinylstannanes **34d** and **36**

Vinylstannanes **34d** and **36** were prepared according to the general procedure described above by reacting alkyne **33d** (221 mg, 0.47 mmol) with Ph_3SnH (247 mg, 0.70 mmol) and Et_3B (0.047 ml (47 μL), 0.047 mmol) in dry PhMe (4.7 mL) at rt for 18 h. The two vinylstannanes **34d** and **36** were present in approx. 60:1 ratio according to 500 MHz ^1H NMR spectroscopic analysis of the concentrated crude organic extract in CDCl_3 . After SiO_2 flash chromatography of the crude residue (with 150:1 petrol/EtOAc as eluent), the vinylstannane product **34d** was isolated in essentially pure condition as a colorless oil (282 mg, 73%).

Data for **34d**: $[\alpha]_D^{+65} +65^\circ$ (c 0.88, CH_2Cl_2); IR (neat) 3066 (s), 2958 (s), 2932 (s), 2857 (s), 1803 (w), 1592 (m), 1476 (m), 1428 (s), 1380 (s), 1242 (m), 1214 (s), 1165 (m), 1111(s), 1074 (s), 910 (m), 887 (m), 824 (m), 730 (s), 702 (s), 614 (m), 506 (s). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.80 (s, 1H, (3J $^{119}\text{Sn}-^1\text{H}$ = 156.5 Hz, 3J $^{117}\text{Sn}-^1\text{H}$ = 149.5 Hz), $\text{PhC}(\underline{\text{H}})=\text{C}(\text{SnPh}_3)-$), 7.70-7.62 (m, 4H, Ph), 7.39 (m, 2H, Ph), 7.42-7.18 (m, 20 H, Ar), 6.98-6.87 (m, 4H, Ph), 5.10 (dd, 1H, J = 1.8, 6.6 Hz, (3J $^{119}\text{Sn}-^1\text{H}$ = 23.6 Hz, 3J $^{117}\text{Sn}-^1\text{H}$ = 22.6 Hz), $-(\text{O})\text{CH}(\text{O})\underline{\text{C}}\text{H}\text{C}=\text{CH}(\text{Ph})$), 3.99 (ddd, 1H, J = 2.6, 6.6, 9.1 Hz, $\text{TBDPSOCH}_2\text{CH}(\text{O}-)$), 3.70 (dd, 1H, J = 2.6, 10.9 Hz, TBDPSOCH_2-), 3.55 (dd, 1H, J = 9.2, 10.9 Hz, TBDPSOCH_2-), 1.40 (s, 3H, $(\underline{\text{CH}}_3)_2\text{C}$), 1.33 (s, 3H, $(\underline{\text{CH}}_3)_2\text{C}$), 1.04 (9H, s, $(\underline{\text{CH}}_3)_3\text{CSi}$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 143.0 ($\text{PhC}(\text{H})=\text{C}(\text{SnPh}_3)-$) 139.1 ($\text{PhC}(\text{H})=\underline{\text{C}}(\text{SnPh}_3)-$), 138.8, 138.1, 136.8, 135.8, 135.6, 133.7, 133.5, 129.5 (x2), 128.7, 128.4, 128.2, 128.0, 127.9, 127.6, 127.5, and 127.4 (Ar), 108.0 $(\underline{\text{CH}}_3)_2\text{C}$, 80.9 $(\text{O})\text{CH}\underline{\text{C}}\text{H}(\text{O})$ (Ph_3Sn) $\text{C}=\text{CH}(\text{Ph})$, 78.7 ($\text{TBDPSOCH}_2\text{CH}(\text{O}-)$), 65.9 (TBDPSOCH_2-), 27.7 and 25.7 ($(\underline{\text{CH}}_3)_2\text{C}$), 26.9 ($(\underline{\text{CH}}_3)_3\text{CSi}$), 19.2 ($(\underline{\text{CH}}_3)_3\text{CSi}$); ESP+ HRMS: Calcd. for $\text{C}_{48}\text{H}_{50}\text{NaO}_3\text{SiSn}$: ($\text{M}+\text{Na}$) $^+$ 845.24434. Found: 845.24477.

Vinylstannanes **38a** and **39a**

Vinylstannanes **38a** and **38b** were prepared according to the general procedure outlined above by reacting alkyne **37a** (145 mg, 0.36 mmol) with Ph_3SnH (187 mg, 0.53 mmol) and Et_3B (1 M solution in hexanes, 0.036 mL (36 μL), 0.036 mmol) in dry PhMe (3.6 mL) at rt for 17.5 h. After extractive work-up, 500 MHz ^1H NMR spectroscopic analysis of the crude residue in CDCl_3 indicated that the two vinylstannanes **38a** and **39a** were present in approx. 49:1 ratio. Following SiO_2 flash chromatography of this mixture (gradient elution with 150:1 to 100:1 petrol/ EtOAc as eluent), the vinylstannane products **38a** and **39a** were obtained as a colorless oil in the form of a 48:1 mixture of regioisomers (221 mg, 80%).

Data for the major regioisomer **38a**: $[\alpha]_D^{25} -21.1^\circ$ (c 1.28, CH_2Cl_2); IR (neat) 3048 (m), 2958 (s), 2932 (s), 2859 (s), 1621 (w), 1478 (m), 1428 (s), 1380 (s), 1245 (m), 1217 (s), 1111 (s), 1072 (m), 1021 (m), 963 (w), 909 (m), 842 (w), 823 (m), 761 (s), 731 (s), 702 (s), 507 (m). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.72-7.67 (m, 4H, Ph), 7.62-7.25 (m, 21H, Ph), 6.74 (q, 1H, $J = 6.8$ Hz, ($^3J^{119}\text{Sn}-^1\text{H} = 153.9$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 147.2$ Hz), $\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 4.83 (d, 1H, $J = 8.5$ Hz, ($^3J^{119}\text{Sn}-^1\text{H} = 78.7$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 75.3$ Hz), $-(\text{O})\text{CH}(\text{Ph}_3\text{Sn})\text{C}=\text{CH}(\text{Me})$), 3.86 (dd, 1H, $J = 3.4, 11.3$ Hz, TBDPSOCH_2-), 3.77 (ddd, 1H, $J = 3.2, 3.4, 8.6$ Hz, $\text{TBDPSOCH}_2\text{CH}(\text{O}-)-$), 3.69 (dd, 1H, $J = 3.2, 11.3$ Hz, TBDPSOCH_2-), 1.67 (d, 3H, $J = 6.7$ Hz, ($^3J_{\text{SnH}} = 19$ Hz), $\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 1.31 (s, 3H, $(\text{CH}_3)_2\text{CSi}$), 1.07 (9H, s, $(\text{CH}_3)_3\text{C}$), 0.66 (s, 3H, $(\text{CH}_3)_2\text{C}$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 143.0 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 139.8 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 138.9, 137.1, 135.7, 135.67, 133.3, 133.1, 129.7, 129.6, 128.7, 128.4, and 127.7 (Ar), 108.3 ($(\text{CH}_3)_2\text{C}$), 84.2 ($-(\text{O})\text{CH}(\text{Ph}_3\text{Sn})\text{C}=\text{CH}(\text{Me})$), 81.5 ($\text{TBDPSOCH}_2\text{CH}(\text{O}-)-$), 62.4 (TBDPSOCH_2-), 26.8 ($(\text{CH}_3)_3\text{CSi}$), 26.7 and 25.8 ($(\text{CH}_3)_2\text{C}$), 20.5 ($\text{CH}_3\text{CH}=\text{C}$), 19.3 ($(\text{CH}_3)_3\text{CSi}$); ESP+ HRMS: Calcd. for $\text{C}_{43}\text{H}_{48}\text{NaO}_3\text{SiSn}$: $(\text{M}+\text{Na})^+$ 783.22869. Found: 783.22664.

Vinylstannanes **38b** and **40**

Compounds **38b** and **40** were prepared by the general procedure described above by reacting alkyne **37b** (100 mg, 0.21 mmol) with Ph_3SnH (111 mg, 0.32 mmol) and Et_3B (0.021 mL (21 μL), 0.021 mmol) in dry PhMe (2.1 mL) at rt for 190 min. After extractive work-up, examination of the crude concentrated organic residue by 500 MHz ^1H NMR spectroscopy in CDCl_3 indicated that the two vinylstannanes **38b** and **40** were present in approx. 128:1 ratio. After SiO_2 flash chromatography of this residue (with 150:1 petrol/EtOAc as eluent), the vinylstannane products **38b** and **40** were obtained as a colorless oil as a 128:1 mixture (127 mg, 73%).

Data for major stereoisomer **38b**: $[\alpha]_{\text{D}}^{25} -34.0^\circ$ (c 0.75, CH_2Cl_2); IR (neat) 3047 (s), 2930 (s), 2856 (s), 1589 (w), 1577 (w), 1481 (m), 1472 (m), 1462 (m), 1429 (s), 1379 (s), 1248 (s), 1215 (s), 1113 (s), 1074 (s), 997 (w), 960 (w), 922 (w), 860 (w), 824 (m), 787 (w), 729 (s), 698 (s), 605 (w). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.73 (s, 1H, ($^3J^{119}\text{Sn}-^1\text{H} = 155.1$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 148.2$ Hz), $\text{PhC}(\underline{\text{H}})=\text{C}(\text{SnPh}_3)-$), 7.72-7.69 (m, 4H, Ph), 7.45-7.31 (m, 13H, Ph), 7.26-7.17 (m, 8H, Ph), 7.07-7.03 (m, 2H, Ph), 6.97-6.87 (m, 3H, Ph), 5.00 (dd, 1H, $J = 1.1, 8.4$ Hz, ($^3J^{119}\text{Sn}-^1\text{H} = 57.9$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 55.3$ Hz), $-(\text{-O})\text{C}(\underline{\text{H}})(\text{Ph}_3\text{Sn})\text{C}=\text{CH}(\text{Ph})$), 4.01 (ddd, $J = 3.4, 6.9, 8.3$ Hz, 1H, $\text{TBDPSOCH}_2\text{CH}(\text{O-})-$), 3.94 (dd, 1H, $J = 3.4, 11.5$ Hz, TBDPSOCH_2-), 3.80 (dd, 1H, $J = 3.5, 11.5$ Hz, TBDPSOCH_2-), 1.32 (s, 3H, $(\text{CH}_3)_2\text{C}$), 1.08 (9H, s, $(\text{CH}_3)_3\text{CSi}$), 0.90 (s, 3H, $(\text{CH}_3)_2\text{C}$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 145.8 ($(\text{Ph})\underline{\text{C}}\text{H}=\text{C}(\text{SnPh}_3)-$), 142.4 ($(\text{Ph})\text{CH}=\underline{\text{C}}(\text{SnPh}_3)-$), 140.4, 138.4, 137.4, 136.9, 135.7, 133.2, 133.1, 129.7, 129.66, 128.3, 128.1, 127.8, 127.7 (x2), and 127.6 (Ar), 127.5, 108.3 ($\text{CH}_3)_2\text{C}$), 83.4 $-(\text{-O})\underline{\text{C}}\text{H}(\text{Ph}_3\text{Sn})\text{C}=\text{CH}(\text{Ph})$), 81.3 ($\text{TBDPSOCH}_2\underline{\text{C}}\text{H}(\text{O-})-$), 62.8 (TBDPSOCH_2-), 26.6 and 26.2 ($(\underline{\text{C}}\text{H}_3)_2\text{C}$), 26.9 ($(\underline{\text{C}}\text{H}_3)_3\text{CSi}$), 19.3 ($(\text{CH}_3)_3\text{CSi}$); Cl^+ HRMS: Calcd. for $\text{C}_{48}\text{H}_{50}\text{O}_3\text{SiSn}$: (M) $^+$ 822.25510. Found: 822.25633.

Vinylstannanes **42** and **43**

Compounds **42** and **43** were prepared using the general procedure described above by reacting alkyne **41** (130 mg, 0.430 mmol) with Ph_3SnH (226 mg, 0.644 mmol) and Et_3B (1 M solution in hexanes, 0.043 mL (43 μL), 0.043 mmol) in dry PhMe (4.3 mL) at rt for 17 h. The two vinylstannanes **42** and **43** were present in approx. 53:1 ratio after extractive work-up and examination of the crude concentrated organic extracts by 500 MHz ^1H NMR spectroscopy in CDCl_3 . After SiO_2 flash chromatography of this residue (gradient elution with 100:1 then 50:1 then 20:1 petrol/ EtOAc as eluent), the vinylstannane products **42** and **43** were isolated as a colorless oil in the form of a 60:1 mixture of isomers (245 mg, 87%).

Data for the major regioisomer **42**: $[\alpha]_D^{+16.0}$ (c 0.74, CH_2Cl_2); IR (neat) 3063 (m), 2976 (m), 2921 (m), 1621 (w), 1480 (w), 1447 (w), 1426 (s), 1376 (m), 1300 (w), 1240 (m), 1213 (m), 1169 (w), 1126 (m), 1066 (s), 1028 (m), 984 (m), 908 (w), 859 (m), 733 (s), 695 (s), 548 (w), 510 (w). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.68-7.55 (m, 6H, Ph), 7.38-7.26 (m, 12H, Ph), 7.24-7.18 (m, 2H, Ph), 6.62 (qd, 1H, $J = 1.1, 6.8$ Hz, ($^3J^{119}\text{Sn}-^1\text{H} = 159.5$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 152.5$ Hz), $\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 5.04 (s, 1H, H1), 4.57 (d, 1H, $J = 11.8$ Hz, PhCH_2-), 4.40 (d, 1H, $J = 11.6$ Hz, ($^3J^{119}\text{Sn}-^1\text{H} = 64.0$ Hz, $^4J^{117}\text{Sn}-^1\text{H} = 61.2$ Hz), H5), 4.36 (d, 1H, $J = 11.8$ Hz, PhCH_2-), 4.24 (m, 1H, H3), 3.91 (d, 1H, $J = 5.3$ Hz, H2), 1.85 (m, 1H, H4a), 1.69 (d, 3H, $J = 6.6$ Hz, $\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 1.55 (m, 1H, H4b), 1.23 (s, 3H, $(\text{CH}_3)_2\text{C}$), 1.04 (s, 3H, $(\text{CH}_3)_2\text{C}$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 142.7 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 139.9, 138.2 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 137.3, 137.1, 128.5, 2 x 128.4, 128.3, 127.7 (Ar), 108.5 $(\text{CH}_3)_2\text{C}$, 96.6 (C-1), 73.2 (C5), 72.8 (C2), 71.0 (C3), 68.6 (PhCH_2), 36.6 (C4), 27.8 and 26.2 $(\text{CH}_3)_2\text{C}$, 20.1 ($\text{CH}_3\text{CH}=\text{C}$); ESP (+) HRMS: Calcd. for $\text{C}_{36}\text{H}_{38}\text{NaO}_4\text{Sn}$: ($\text{M}+\text{Na}$) $^+$ 677.16843. Found: 677.16867.

Vinylstannanes **45a** and **47**

Vinylstannanes **45a** and **47** were prepared according to the general procedure described above by reacting alkyne **44a** (295 mg, 0.511 mmol) with Ph_3SnH (258 mg, 0.735 mmol) and Et_3B (1 M solution in hexanes, 0.049 mL (49 μL), 0.049 mmol) in dry PhMe (4.9 mL) at rt for 21 h. The two vinylstannanes **45a** and **47** were present in approx. 25:1 ratio after extractive work-up and examination of the crude concentrated organic extract residue by 500 MHz ^1H NMR spectroscopy in CDCl_3 . After SiO_2 flash chromatography of this residue (with 150:1 petrol/ EtOAc as eluent), the vinylstannane products **45a** and **47** were obtained as a 26:1 mixture of isomers in the form of a colorless oil (363 mg, 78%).

Data for the major stereoisomer **45a**: $[\alpha]_D^{+2.2}$ (c 1.12, CH_2Cl_2); IR (neat) 3047 (m), 2931 (s), 2891 (m), 2857 (s), 1622 (w), 1589 (w), 1471 (w), 1427 (s), 1385 (w), 1110 (s), 1073 (s), 823 (m), 730 (s), 702 (s), 613 (m), 506 (s). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.64-7.18 (m, 35H, Ph), 6.49 (q, 1H, $J = 6.7$ Hz, ($^3J^{^{119}\text{Sn}-^1\text{H}} = 160.7$ Hz, $^3J^{^{117}\text{Sn}-^1\text{H}} = 153.7$ Hz), $\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 4.54 (t, 1H, $J = 6.1$ Hz, ($^3J^{^{119}\text{Sn}-^1\text{H}} = 75.2$ Hz, $^3J^{^{117}\text{Sn}-^1\text{H}} = 71.8$ Hz), $\text{TBDP}\text{SOCH}_2\text{CH}(\text{OTBDP})-$), 3.54 (dd, 1H, $J = 6.7, 10.4$ Hz, $\text{TBDP}\text{SOCH}_2-$), 3.50 (dd, 1H, $J = 5.7, 10.3$ Hz, $\text{TBDP}\text{SOCH}_2-$), 1.67 (d, 3H, $J = 6.7$ Hz, ($^4J_{\text{SnH}} = 20$ Hz), $\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 0.95 (s, 9H, $\text{C}(\text{CH}_3)_3$), 0.94 (s, 9H, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 140.1 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 139.5 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 137.2 (Ar), 136.2 (Ar), 135.9, 135.6, 135.5, 134.0, 133.9, 133.6, 133.5, 129.4, 129.3, 129.3, 129.2, 129.1, 128.6, 128.5, 128.3, 127.5, 127.4, 2 x 127.3 (Ar), 81.5 ($\text{TBDP}\text{SOCH}_2\text{CH}(\text{OTBDP})-$), 67.5 ($\text{TBDP}\text{SOCH}_2-$), 27.1 and 26.8 (2 x $\text{SiC}(\text{CH}_3)_3$), 20.7 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 19.2 and 19.16 (2x $\text{SiC}(\text{CH}_3)_3$); CI HRMS: Calcd. for $\text{C}_{55}\text{H}_{60}\text{O}_2\text{Si}_2\text{Sn}$: (M) $^+$ 928.31483. Found: 928.30803.

For the minor stereoisomer **47**, the olefinic proton resonated as a q at δ 6.05 ($J = 6.7$ Hz, $^3J_{\text{SnH}} = 85$ Hz).

Vinylstannanes **45b** and **46b**

Vinylstannanes **45b** and **46b** were prepared via the general procedure described above by reacting alkyne **44b** (100 mg, 0.295 mmol) with Ph_3SnH (155 mg, 0.442 mmol) and Et_3B (1M solution in hexanes, 0.0295 mL (29.5 μL), 0.0295 mmol) in dry PhMe (2.95 mL) at rt for 3 h. After aqueous extractive work up, the two products **45b**:**46b** were shown to be present in the crude concentrated organic residue in 199:1 ratio according to 500 MHz ^1H NMR spectroscopy in CDCl_3 . Purification of this crude organic residue by SiO_2 flash chromatography (gradient elution with 100:1 then 50:1 then 40:1 petrol;EtOAc as eluent), led to **45b** being isolated as a colorless oil in essentially pure condition (164 mg, 81%).

Data for the major regioisomer **45b**: $[\alpha]_D^{25} -21.6^\circ$ (c 0.66, CH_2Cl_2); IR (neat) 3560 (br m), 3046 (s), 2931 (s), 2857 (s), 1957 (w), 1890 (w), 1821 (w), 1626 (m), 1475 (s), 1427 (s), 1387 (m), 1308 (m), 1111 (br s), 1055 (m), 1001 (m), 886 (m), 824 (s), 730 (s), 707 (s), 617 (s), 523 (s), 505 (s). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.65-7.56 (m, 8H, Ph), 7.49-7.31 (m, 17H, Ph), 6.64 (q, 1H, $J = 6.7$ Hz, ($^3J^{119}\text{Sn}-^1\text{H} = 161.6$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 154.4$ Hz), $\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 4.52 (m, 1H, ($^3J^{119}\text{Sn}-^1\text{H} = 65.4$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 62.6$ Hz), $\text{TBDPSOCH}_2\text{CH}(\text{OH})-$), 3.60 (dd, 1H, $J = 4.2$, 10.1 Hz, TBDPSOCH_2-), 3.54 (dd, 1H, $J = 9.0$, 9.8 Hz, TBDPSOCH_2-), 2.89 (br s, 1H, OH), 1.69 (d, 3H, $J = 6.7$ Hz, ($^3J_{\text{SnH}} = 19$ Hz), $\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 1.02 (s, 9H, $\text{C}(\text{CH}_3)_3$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 141.6 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 139.9 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 139.8 (Ar), 137.1 (Ar), 135.3 (Ar), 133.1, 133.0, 129.7, 129.6, 128.6, 128.4, 2 x 127.7 (Ar), 78.7 ($\text{TBDPSOCH}_2\text{CH}(\text{OH})-$), 67.8 (TBDPSOCH_2-), 26.7 ($\text{SiC}(\text{CH}_3)_3$), 20.2 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 19.2 ($-\text{SiC}(\text{CH}_3)_3$); ESP+ HRMS: Calcd. for $\text{C}_{39}\text{H}_{42}\text{NaO}_2\text{SnSi}$: ($\text{M}+\text{Na}$) $^+$ 713.18683. Found: 713.18784.

Vinylstannanes **45c** and **46c**

Vinylstannanes **45c** and **46c** were prepared according the general procedure described above by reacting alkyne **44c** (150 mg, 1.50 mmol) with Ph_3SnH (789 mg, 2.25 mmol) and Et_3B (1 M solution in hexanes, 0.15 mL, 0.15 mmol) in dry PhMe (15 mL) at rt for 18 h. After aqueous extractive work-up, the two vinylstannanes **45c** and **46c** were shown to present in the crude concentrated organic residue in 73:1 ratio according to 500 MHz ^1H NMR spectroscopic analysis in CDCl_3 . After SiO_2 flash chromatography of this residue (with 150:1 petrol/EtOAc as eluent), the essentially pure vinylstannane **45c** was obtained as a white solid (467 mg, 69%).

Data for the major regioisomer **45c**: mp. 65-68 °C; $[\alpha]_D^{25} +13.0^\circ$ (c 1.07, CH_2Cl_2); IR (neat) 3394 (br s OH), 3063 (s), 2972 (s), 2926 (s), 2855 (s), 1623 (w), 1481 (m), 1428 (s), 1381 (m), 1073 (s), 1022 (m), 873 (w), 841 (w), 731 (s), 701 (s). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.65-7.52 (m, 6H, Ph), 7.39-7.31 (m, 9H, Ph), 6.65 (qd, 1H, $J = 1.1, 6.7$ Hz, $^3J^{119}\text{Sn}-^1\text{H} = 159.5$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 152.5$ Hz), $\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$, 4.38 (br m, 1H, ($^3J^{119}\text{Sn}-^1\text{H} = 64.0$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 61.2$ Hz), $\text{HOCH}_2\text{CH}(\text{OH})-$), 3.53 (br d, 1H, $J = 10.9$ Hz, HOCH_2-), 3.43 (br apparent t, 1H, $J = 8.8, 10.1$ Hz, HOCH_2-), 2.39 (br s, 1H, -OH), 1.91 (br s, 1H, -OH), 1.71 (d, 3H, $J = 6.5$ Hz, ($^4J_{\text{SnH}} = 19$ Hz), $\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 142.2 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 139.5 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 139.5 (Ar), 137.0 (Ar), 128.8 (Ar), 128.5 (Ar), 79.0 ($\text{HOCH}_2\text{CH}(\text{OH})-$), 66.8 (HOCH_2-), 20.4 ($\text{CH}_3\text{CH}=\text{C}(\text{SnPh}_3)-$); ESP+ HRMS: Calcd. for $\text{C}_{23}\text{H}_{24}\text{NaO}_2\text{Sn}$: ($\text{M}+\text{Na}$) $^+$ 475.06905. Found: 475.07008.

Vinylstannanes **49** and **50**

Compounds **49** and **50** were prepared according to the general procedure described above by reacting alkyne **48** (71 mg, 0.273 mmol), Ph_3SnH (143 mg, 0.41 mmol), and Et_3B (1 M solution in hexanes, 0.027 mL (27 μL), 0.027 mmol) in dry PhMe (2.7 mL) at rt for 16 h. After aqueous extractive work-up, the two vinylstannanes **49** and **50** were shown to be present in approx. 44:1 ratio according to 500 MHz ^1H NMR spectroscopic analysis of the resulting crude extracted organic residue in CDCl_3 . After SiO_2 flash chromatography of this residue (gradient elution with 50:1 to 40:1 to 30:1 petrol/EtOAc as eluent), the vinylstannanes **49** and **50** were isolated as a 51:1 mixture in the form of a colorless oil (113 mg, 68%).

Data for the major regioisomer **49**: $[\alpha]_D^{25} -56.9^\circ$ (c 0.58, CH_2Cl_2); IR (neat) 3063 (m), 2983 (m), 2933 (m), 2868 (m), 1619 (w), 1480 (w), 1452 (w), 1428 (m), 1379 (m), 1255 (m), 1212 (m), 1156 (w), 1072 (s), 856 (m), 731 (s), 699 (s). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.58-7.47 (m, 6H, Ph), 7.36-7.30 (m, 9H, Ph), 7.25-7.18 (m, 5H, Ph), 6.62 (q, 1H, $J = 6.7$ Hz, $^3J^{119}\text{Sn}-^1\text{H} = 155.6$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 148.8$ Hz), $\text{CH}_3\text{C}(\text{H})=\text{CC}(\text{SnPh}_3)-$, 4.65 (d, 1H, $J = 12.3$ Hz, $-\text{CH}_2\text{Ph}$), 4.47 (d, 1H, $J = 12.3$ Hz, $-\text{CH}_2\text{Ph}$), 4.10 (dd, 1H, $J = 7.6$ and 14.2 Hz, $-(\text{O})\text{CH}_2\text{CH}(\text{O})-$), 4.01 (d, 1H, $J = 7.7$ Hz ($^3J^{119}\text{Sn}-^1\text{H} = 84.9$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 81.1$ Hz), $-\text{CH}(\text{OBn})-$), 3.82 (dd, 1H, $J = 6.5$ and 8.2 Hz, $-(\text{O})\text{CH}_2-$), 3.63 (dd, 1H, $J = 7.8$, 7.9 Hz, $-(\text{O})\text{CH}_2-$), 1.77 (d, 3H, $J = 6.7$ Hz, ($^4J_{\text{SnH}} = 19$ Hz), $\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 1.23 (s, 3H, $(\text{CH}_3)_2\text{C}$), 1.15 (s, 3H, $(\text{CH}_3)_2\text{C}$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 143.0 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 140.9 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 139.3, 138.0, 137.1, 128.8, 128.5, 128.1, 127.9 and 127.2 (Ar), 109.7 ($(\text{CH}_3)_2\text{C}$), 88.1 ($-\text{CH}(\text{OBn})-$), 78.2 ($-(\text{O})\text{CH}_2\text{CH}(\text{O})-$), 69.9 (PhCH_2-), 66.1 ($-(\text{O})\text{CH}_2-$), 26.4 and 25.4 ($(\text{CH}_3)_2\text{C}$), 20.6 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$); ESP (+) HRMS: Calcd. for $\text{C}_{34}\text{H}_{36}\text{NaO}_3\text{Sn}$: $(\text{M}+\text{Na})^+$ 635.15786. Found: 635.15711.

Vinylstannanes **52** and **53**

Compounds **52** and **53** were prepared according to the general procedure described above by reacting alkyne **51** (83 mg, 0.23 mmol) with Ph_3SnH (240 mg, 0.68 mmol) and Et_3B (1 M solution in hexanes, 0.023 mL (23 μL), 0.023 mmol) in dry PhMe (2.3 mL) at rt for 19 h. The two vinylstannanes **52** and **53** were obtained in approx. 32:1 ratio after aqueous extractive work-up and examination of the crude concentrated organic residue by 500 MHz ^1H NMR spectroscopy in CDCl_3 ; a significant amount of starting alkyne **51** also remained. After SiO_2 flash chromatography of this residue (gradient elution with 150:1 then 100:1 then 50:1 petrol/EtOAc as eluent), the products **52** and **53** were isolated as a 36:1 ratio of regioisomers as a colorless oil (48 mg, 30%).

Data for the major regioisomer **52**: $[\alpha]_D^{+14.8}$ (c 0.89, CH_2Cl_2); IR (neat) 3552 (br m), 3065 (m), 2964 (s), 2938 (s), 2857 (s), 1957 (w), 1883 (w), 1820 (w), 1622 (w), 1576 (w), 1477 (m), 1428 (s), 1382 (m), 1303 (w), 1258 (w), 1111 (s), 1073 (s), 998 (m), 825 (m), 729 (s), 699 (s), 609 (m), 507 (s). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.68–7.14 (m, 25H, Ph), 6.35 (q, 1H, $J = 6.8$ Hz, $(^3J_{^{119}\text{Sn}-^1\text{H}} = 177.3$ Hz, $^3J_{^{117}\text{Sn}-^1\text{H}} = 169.5$ Hz), $\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 3.63 (d, 1H, $J = 9.8$ Hz, $\text{TBDP}\text{SOCH}_2-$), 3.48 (d, 1H, $J = 9.8$ Hz, $\text{TBDP}\text{SOCH}_2-$), 2.95 (br s, 1H, -OH), 1.65 (m, 1H, CH_2CH_3-), 1.63 (d, 3H, $J = 6.8$ Hz ($^4J_{\text{SnH}} = 21$ Hz), $\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 1.53 (m, 1H, $-\text{CH}_2\text{CH}_3$), 1.00 (s, 9H, $(\text{CH}_3)_3\text{CSi}$), 0.82 (t, 3H, $J = 7.4$ Hz, $-\text{CH}_2\text{CH}_3$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 146.4, 141.4, 139.1, 137.4, 137.3, 137.2, 137.1, 136.5, 136.1 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), (2 x) 135.6, 132.9, 130.5, 129.8, 129.7, 129.1, 128.8, 128.7, (2 x) 128.6, 128.4, 128.3, 127.7 (x 2) (Ar), 79.3 ($\text{C}(\text{OH})\text{CH}_2\text{CH}_3$), 69.5 ($-\text{CH}_2\text{OTBDPS}$), 30.3 (CH_3CH_2-), 26.9 ($(\text{CH}_3)_3\text{CSi}$), 20.3 ($\text{CH}_3\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 19.3 ($(\text{CH}_3)_3\text{CSi}$), 8.0 (CH_3CH_2-); ESP (+) HRMS: Calcd. for $\text{C}_{41}\text{H}_{46}\text{NaO}_2\text{SiSn}$: $(\text{M}+\text{Na})^+$ 741.21813. Found: 741.21592.

Vinylstannanes **56** and **57**

Using the general procedure described above 2-pentyn-1-ol **55** (200 mg, 2.38 mmol) was reacted with Ph_3SnH (1.25 g, 3.56 mmol) and Et_3B (1 M solution in hexanes, 0.24 mL, 0.24 mmol) in dry PhMe (2.37 mL) at rt for 17 h. After aqueous extractive work-up and concentration of the dried organic extracts, the two vinylstannanes **56** and **57** were shown to be present in approx. 34:1 ratio in the crude residue according to 500 MHz ^1H NMR spectroscopic analysis in CDCl_3 . After SiO_2 flash chromatography (gradient elution with 50:1 then 30:1 then 20:1 petrol/EtOAc as eluent), the two products **56** and **57** were isolated as a white solid that consisted of a 50:1 mixture of regioisomers (796 mg, 77%).

Data for the major regioisomer **56**: mp 65-67 °C; IR (neat) 3547 (w), 3381 (br s, OH), 3063 (s), 2964 (s), 2932 (m), 2870 (m), 1623 (w), 1480 (m), 1427 (w), 1379 (w), 1302 (w), 1258 (w), 1190 (w), 1074 (s), 997 (s), 867 (w), 729 (s), 699 (s). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.72-7.58 (m, 6H, Ph), 7.44-7.32 (m, 9H, Ph), 6.52 (t, 1H, $J = 7.3$ Hz, ($^3J^{119}\text{Sn}-^1\text{H} = 159.4$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 152.3$ Hz), $\text{CH}_3\text{CH}_2\text{C}(\text{H})=\text{C}(\text{SnPh}_3)-$), 4.32 (s, 2H, ($^3J^{119}\text{Sn}-^1\text{H} = 47.8$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 45.7$ Hz), $-\text{CH}_2\text{OH}$), 2.11 (m, 2H, CH_3CH_2-), 1.51 (br s, 1H, -OH), 0.87 (t, 3H, $J = 7.4$ Hz, CH_3CH_2-); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 146.4 ($\text{CH}_2\text{CH}=\text{CSnPh}_3$), 139.7 ($\text{CH}_3\text{CH}_2\text{CH}=\text{CSnPh}_3$), 139.0, 137.0, 128.9 and 128.5, (Ar), 69.8 (CH_2OH), 28.3 ($\text{CH}_3\text{CH}_2\text{CH}$), 13.8 ($\text{CH}_3\text{CH}_2\text{CH}$); CI(-) HRMS: Calcd. for $\text{C}_{23}\text{H}_{23}\text{OSn}$: (M-H) $^+$ 435.07708. Found: 435.07744.

Vinylstannanes **59** and **60**

Compounds **59** and **60** were prepared according the general procedure described above by reacting alkyne **58** (3.0 g, 30.6 mmol) with Ph_3SnH (16.11 g, 45.9 mmol) and Et_3B (1 M solution in hexanes, 3.1 mL, 3.1 mmol) in dry PhMe (306 mL) at rt for 18 h. The two vinylstannanes **59** and **60** were shown to be present in approx. 30:1 ratio after extractive work-up and examination of the crude concentrated organic residue by 500 MHz ^1H NMR spectroscopy in CDCl_3 . After SiO_2 flash chromatography (with 50:1 then 20:1 then 10:1 petrol/EtOAc as eluent), the vinylstannanes **59** and **60** were isolated as a white solid that consisted of a 28:1 mixture of the two regioisomers (9.82 g, 72%).

Data for the major regioisomer **59**: mp 49-51 °C; IR (neat) 3553 (br), 3140 (br s), 3063 (m), 2958 (s), 2930 (w), 2865 (m), 1622 (w), 1481 (w), 1462 (w), 1428 (m), 1381 (m), 1072 (s), 909 (m), 731 (s), 701 (s). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.71-7.58 (m, 6H, Ph), 7.43-7.35 (m, 9H, Ph), 6.29 (d, 1H, $J = 9.9$ Hz, ($^3J^{119}\text{Sn}-^1\text{H} = 160.0$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 153.0$ Hz), $(\text{CH}_3)_2\text{CHC}(\text{H})=\text{C}(\text{SnPh}_3)-$), 4.31 (s, 2H, ($^3J^{119}\text{Sn}-^1\text{H} = 54.2$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 51.8$ Hz), $-\text{CH}_2\text{OH}$), 2.31 (m, 1H, $(\text{CH}_3)_2\text{C}(\text{H})-$), 1.49 (1H, br s, -OH), 0.85 (d, 6H, $J = 6.5$ Hz, $(\text{CH}_3)_2\text{C}(\text{H})-$); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 151.9 ($-\text{CHC}(\text{H})=\text{C}(\text{SnPh}_3)-$), 139.1 ($(\text{CH}_3)_2\text{CHC}(\text{H})=\text{C}(\text{SnPh}_3)-$), 137.4, 137.0 (Ar), 128.8, 128.5, (Ar), 69.9 ($-\text{CH}_2\text{OH}$), 34.3 $(\text{CH}_3)_2\text{C}(\text{H})-$, 22.6 ($(\text{CH}_3)_2\text{C}(\text{H})-$); CI(-) HRMS: Calcd. for $\text{C}_{24}\text{H}_{25}\text{OSn}$: (M-H) $^+$ 449.09273. Found: 449.093539.

Vinylstannanes **62** and **63**

Compounds **62** and **63** were prepared from the alkyne **61** (100 mg, 0.284 mmol), Ph_3SnH (149 mg, 0.424 mmol) and Et_3B (1 M solution in hexanes, 0.042 mL (42 μL), 0.042 mmol) in dry PhMe (4.3 mL) at rt for 72 h following the general procedure described above. After aqueous extractive work-up, analysis of the crude concentrated organic extract residue by 500 MHz ^1H NMR spectroscopy in CDCl_3 indicated that the two vinylstannanes **62** and **63** were present in approx. 22:1 ratio. Following SiO_2 flash chromatography (gradient elution with 50:1 then 20:1 petrol/EtOAc as eluent), the vinylstannanes **62** and **63** were obtained as a colorless oil that consisted of a 22:1 mixture of regioisomers (179 mg, 90%).

Data for the major regioisomer **62**: IR (neat) 3570 (m), 3432 (br m), 3067 (s), 2930 (s), 2856 (s), 1624 (m), 1588 (m), 1469 (m), 1427 (s), 1385 (m), 1189 (m), 1110 (s), 1024 (s), 824 (s), 730 (s), 706 (s), 613 (m), 506 (m). ^1H NMR (500 MHz, CDCl_3 , 298K) δ 7.73-7.58 (m, 10H, Ph), 7.48-7.34 (m, 15H, Ph), 6.41 (d, 1H, $J = 10.0$ Hz, ($^3J^{119}\text{Sn}-^1\text{H} = 160.5$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 153.4$ Hz), -C(H)=C(SnPh₃)CH₂OH), 4.34 (d, 2H, $J = 5.5$ Hz, ($^3J^{119}\text{Sn}-^1\text{H} = 53.0$ Hz, $^3J^{117}\text{Sn}-^1\text{H} = 50.6$ Hz), CH₂OH), 3.49 (dd, 1H, $J = 5.2, 9.7$ Hz, -CH₂OTBDPS), 3.45 (dd, 1H, $J = 6.0, 9.7$ Hz, -CH₂OTBDPS), 2.51 (m, 1H, -(CH₃)C(H)CH₂OTBDPS), 1.44 (br t, 1H, $J = 5.9$ Hz, -OH), 1.07 (s, 9H, SiC(CH₃)₃), 0.93 (d, 3H, $J = 6.6$, -CH₃); ^{13}C NMR (125 MHz, CDCl_3 , 298K) δ 147.6 (CH₃CHCH=C(SnPh₃)), 140.7 (CH₃CHCH=C(SnPh₃)), 139.0, 137.0, 135.62, 135.59, 133.8, 133.6, 129.5, 128.8 and 128.5 and 127.5 (Ar), 70.0 (-CH₂OH), 68.1 (-CH₂OTBDPS), 41.5 (-CH₃CHCH₂OTBDPS), 26.8 ((CH₃)₂CSi), 19.3 ((CH₃)₂CSi), 17.3 (CH₃CH); ESP (+) HRMS: Calcd. for $\text{C}_{40}\text{H}_{44}\text{NaO}_2\text{SiSn}$: (M+Na)⁺ 727.20248. Found: 727.20157.

O-Directed Free Radical Hydrostannations of Propargyl Ethers, Acetals and Alcohols with Ph₃SnH and Et₃B

Paschalis Dimopoulos, Audrey Athlan, Soraya Manaviazar,
Jonathan George, Marcus Walters, Linos Lazarides,
Abil E. Aliev, and Karl J. Hale*

Supporting Information □ Part 2

Spectra of Starting Alkynes

I-PD-9
in CDCl₃ at 298K

I-PD-9
H-H COSY
in CDCl₃

I-PD-9
in CDCl₃ at 298K

I-PD-9
in CDCl₃ at 298K

I-PD-19
in CDCl₃ at 298K

I-PD-19
in CDCl₃ at 298K

I-PD_19 (PD)

I-PD-19
in CDCl₃ at 298K

01060504: Scan 517 (94.73 min)
Base: 154.00 Int: 5.3e+006 Sample: VG 70-SE Positive Ion FAB

I-PD-16 (PD)
In CDCl₃ 298K

I-PD-16 (PD)
H-H COSY
In CDCl₃ 298K

I-PD-16 (PD)
In CDCl₃ 298K

I-PD-16 (PD)
In CDCl₃ 298K

I-PD-16 (PD)
C-H HMQC
In CDCl₃ 298K

pd16c1 #8-19 RT: 0.17-0.92 AV: 17 NL: 2.81E5
T: +e Cl Full ms [79.50-600.50]

Sample I-PD-16
Theoretical mass 183.13850 (M+H)
Measured mass 183.13859
Error 0.52 ppm

I-PD-23_PD
In CDCl3 298K

I-PD-23_PD
In CDCl3 298K

I-PD-23_PD
In CDCl3 298K

I-PD-23_PD
C-H HMQC
In CDCl3 298K

Sample I-PD-23
 Theoretical mass 181.12285 (M+H)
 Measured mass 181.12289
 Error 0.25 ppm

I-PD-28
in CDCl₃ at 298K

I-PD-28
H-H COSY
in CDCl₃

I-PD-28
in CDCl₃ at 298K

I-PD-28
in CDC13 at 298K

I-PD-28
HMOC
in CDCl₃ at 298K

03131004: Scan Avg 71-74 (16.37 - 17.07 min) - Back
 Base: 279.00 Int: 1.43749e+006 Sample: VG-70SE Positive Ion FAB

Sample: I-PD-28 (FAB+Na)
 Instrument Resolution: 7000
 Theoretical Mass: 417.18618
 Measured Mass: 417.18485
 Error: 3.19 ppm

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I-PD-121_PD
In CDC13 298K
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I-PD-121_PD
H-H COSY
In CDCl3 298K

I-PD-121_PD
In CDCl3 298K

I-PD-121_PD
In CDCl3 298K

I-PD-121_PD
C-H HMQC
In CDCl3 298

Sample I-PD-121	
Theoretical mass	431.20129 (M+Na)
Measured mass	431.20134
Error	0.12 ppm

I-PD-30 (PD)
In CDCL3 298K

I-PD-30 (PD)

H-H-COSY

In CDCL3 298K

I-PD-30 (PD)
In CDCl₃ 298K

I-PD-30 (PD)
In CDC13 298K

Sample I-PD-30	
Theoretical mass	445.21694 (M+Na)
Measured mass	445.21752
Error	1.28 ppm

I-PD-135 (PD)
In CDC13 298K

I-PD-135_PD
H-H COSY
In CDCl3 298K

I-PD-135_PD
In CDCl3 298K

I-PD-135_PD
In CDCl3 298K

I-PD-135_PD
H-C HMQC
In CDCl3 298K

I-PD-120 (PD)
In CD13 298K

Chemical structure of compound **1**: A 5-membered cyclic acetal (1,3-dioxolane) substituted with a gem-dimethyl group, a phenylethynyl group, and a tert-butyldiphenylsilyloxy (TBDPSO) group.

I-PD-120 (PD)
In CDCl₃ 298K

I-PD-120 (PD)
In CDC13 298K

Sample I-PD-120	
Theoretical mass	493.21694 (M+N _a)
Measured mass	493.21676
Error	0.36 ppm

I-PD-62
in CDCl₃ at 298K

I-PD-62
H-H COSY
in CDCl₃ at 298K

I-PD-62
in CDCl₃ at 298K

I-PD-62
in CDCl₃ at 298K

C#CC1OC(C)(C)OC1COBOSi(C)(C)C(C)(C)C(C)C

03121004: Scan 72 (16.60 min)
Base: 257.00 Int: 5.71513e+006 Sample: VG 70-SE Negative Cl-Ammonia

I-PD-64_PD
In CDCl3 298K

I-PD-64_PD
In CDC13 298K

I-PD-64_PD
In CDCl3 298K

I-PD-64_PD
C-H HMQC
In CDCl₃ 298

IV-PD-48
in CDCl₃ at 298K

IV-PD-48
H-H COSY
in CDCl₃ at 298K

IV-PD-48
in CDCl₃ at 298K

IV-PD-48
in CDCl₃ at 298K

IV-PD-48
HMQC
in CDCl₃ at 298K

pd48 #11-18 RT: 0.72-1.17 AV: 8 NL: 1.00E6
T: +CESI Full MS [49.50-800.50]

Sample IV-PD-48
Theoretical mass 493.21694 (M+Na)
Measured mass 493.21714
Error 0.40 ppm

I-SM-90
CDCl₃

02201004: Scan Avg 33-34 (7.50 - 7.73 min) - Back
Base: 154.00 Int: 563013 Sample: VG-70SE Positive Ion FAB

I-PD-57
in CDCl₃ at 298K

I-PD-57
in CDCl₃ at 298K

I-PD-57
in CDCl₃ at 298K

I-PD-57
in CDCl₃ at 298K

I-PD-57
in CDCl₃ at 298K

I-PD-148 (PD)
In CDCl₃ 298K

I-PD-148 (PD)
In CDCl₃ 298K

I-PD-148 (PD)
In CDCl₃ 298K

I-PD-148 (PD)
In CDCl₃ 298K

I-PD-148 (PD)
In CDCl₃ 298K

pd148es #34-48 RT: 1.16-1.63 AV: 15 SB: 13 0.12-0.52 NL: 2.91E6
T: + c ESI-Full.ms [99.50-800.50]

Sample I-PD-148
Theoretical mass 311.12538 (M+Na)
Measured mass 311.12551
Error 0.42 ppm

I-PD-149 (PD)
In CDC13 298K

I-PD-149 (PD)
H-H COSY
In CDCl₃ 298K

I-PD-149 (PD)
In CDCl₃ 298K

I-PD-149 (PD)
In CDCl₃ 298K

I-PD-149 (PD)
C-H HMQC
In CDCl3 298K

I-PD-82_PD
In CDCl3 298K

C#CC[C@H](C(C)(C)Si(C)(C)C(C)(C)C)O[Si](C)(C)C(C)(C)C(C)(C)C

I-PD-82_PD
In CDCL3 298K

C#CC(C)(OC(=O)C1CCCCC1)COc2ccc(O)c(c2)Si(C)(C)C

I-PD-91
in CDCl₃ at 298K

I-PD-91
H-H COSY
in CDCl₃ at 298K

I-PD-91
in CDCl₃ at 298K

CC#CC(O)COTBDPS

pd9ies #33-45 RT: 1.13-1.53 AV: 13 SB: 12 0.09-0.46 NL: 6.81E6
T: +cESIFull.ms[99.50-800.50]

I-PD-75
in CDCl₃ at 298K

I-PD-75
H-HCOSY in CDCl₃ at 298K

I-PD-75
in CDCl₃ at 298K

I-PD-75
in CDCl₃ at 298K

I-PD-75
HMOC in CDCl₃ at 298K

02201004: Scan Avg 68.72 (15.67 - 16.60 min) - Back
Base: 136.00 Int: 75497.8 Sample: VG-70SE Positive Ion FAB

Sample: I-PD-75 (FAB+Na)

III-MW-23 in
CDCl₃ at 298 K

III-MW-23
 COSY in
 CDCl₃ at 298 K

III-MW-23
Carbon 13 in
CDCl3 at 298 K

III-MM-23
DEPT in
CDCl₃ at 298 K

III-MW-23
HMOC in
CDCl₃ at 298 K

I-PD-79
in CDCl₃ at 298K

I-PD-79
H-H COSY
in CDCl₃ at 298K

I-PD-79
in CDCl₃ at 298K

I-PD-79
in CDCl₃ at 298K

I-PD-79
HMOC
in CDCl₃ at 298K

pd79es #37-47 RT: 1.27-1.60 AV: 11 SB: 13 0.17-0.57 NL: 6.80E6
T: +C ESI Full ms (99.50-800.50)

Sample I-PD-79
Theoretical mass 269.11482 (M+Na)
Measured mass 269.11508
Error 0.97 ppm

I-PD-81
in CDCL₃ at 298K

I-PD-81 (PD)
H-H COSY
in CDCl₃ at 298K

I-PD-81
in CDCl₃ at 298K

I-PD-81
in CDCl₃ at 298K

I-PD-81
HMQC
in CDCl₃ at 298K

pd81es #44-59 RT: 1.48-1.98 AV: 16 SB: 13 0.04-0.44 NL: 7.24E6
T: +CESI Full ms [99.50-800.50]

Sample I-PD-81
Theoretical mass 283.13047 (M+Na)
Measured mass 283.13006
Error 1.45 ppm

I-PD-88
in CDCl₃ at 298K

I-PD-88
H-H COSY
in CDCl₃ at 298K

I-PD-88
in CDCl₃ at 298K

I-PD-88

in CDC13 at 298K

I-PD-88
 HMQC
 in CDCl₃ at 298K

02011104: Scan Avg 5-11 (1.04 - 2.37 min)
Base: 121.00 Int: 3.06852e+006 Sample: VG 70-SE Positive Cl-Isobutane

I-PD-92 (PD)
In CDCl₃ 298K

I-PD-92 (PD)

I-PD-92 (PD)
In CDCl₃ 298K

I-PD-92 (PD)
In CDC13 298K

I-PD-92 (PD)

Sample I-PD-92	
Theoretical mass	509.24824 (C ₃ H ₃ Si + Na)
Measured mass	509.24889
Error	1.28 ppm

I-PD-150
In CDCl₃ 298K

The chemical structure shows a central carbon atom bonded to a methyl group (Me) on the left, a vinyl group (CH=CH₂) on the right, and a hydroxyl group (OH) on the right. The hydroxyl group is further substituted with an OTBDPS group, which is represented by a vertical line pointing upwards.

I-PD-150 (PD)
In CDCl₃ 298K

I-PD-150 (PD)
In CDC13 298K

03240304: Scan 54 (11.38 min)
 Base: 255.00 Int: 1.48028e+006 Sample: VG 70-SE Negative Cl-Ammonia

I-PD-150
 Instrument Resolution: 6000
 Theoretical Mass: (C₂₃H₃₀O₂Si)
 365.1936714
 Measured Mass: 365.1955207
 Error: 5ppm

I-PD-89 (PD)
In CDCl₃ 298K

I-PD-89 (PD)
H-H COSY
In CDCl₃ 298K

I-PD-89 (PD)
In CDCl₃ 298K

CC(C#CCO)CO[Si](C)(C)C(F)(F)F

I-PD-89 (PD)
In CDCl₃ 298K

pd89 #8-20 RT: 0.59-1.41 AV: 13 SR: 4.011-0.32 NL: 2.55E6
T: +C FAB Full ms (99.50-609.50)

Sample I-PD-89
Positive ion FAB
Theoretical mass 353.19313 (M+H)
Measured mass 353.19275
Error 1.08 ppm

O-Directed Free Radical Hydrostannations of Propargyl Ethers, Acetals and Alcohols with Ph_3SnH and Et_3B

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Jonathan George, Marcus Walters, Linos Lazarides,
Abil Aliev, and Karl J. Hale*

Supporting Information □ Part 3 Spectra of Vinyl Triphenylstannanes

I-PD-101_PD
In CDCl3 298K

I-PD-101_PD
In CDCl3 298K

I-PD-101_PD
In CDCl3 298K

I-PD-101_PD
In CDC13 298K

I-PD-101_PD
In CDCl3 298K

7-15-19

pd5tes #18-31 RT: 0.97-1.63 AV: 14 SB: 5.015-0.95 NL: 5.88E5
T: +c ESI(Full) ms [99.50-900.50]

Sample I-PD-101
Positive ion electrospray
Theoretical mass 515.10035 (M+Na)
Measured mass 515.10054
Error 0.37 ppm

I-PD-12_PD
H-H COSY
In CDCl3 298K

I-PD-12_PD
In CDCl3 298K

I-PD-12_PD
In CDCl3 298K

I-PD-12_PD
C-H HMQC
In CDCl3 298K

pd126s #22-26 RT: 0.84-0.95 AN: 4 SB: 8 0.11-0.37 NL: 2.00E5
T: +c ESI(Full) ms [99.50-1000.50]

Sample I-PD-12
Positive ion electrospray
Theoretical mass 529.11600 (M+Na)
Measured mass 529.11645
Error 0.85 ppm

I-PD-55_PD
In CDCl3 298K

I-PD-55_PD
H-H COSY
In CDCl3 298K

I-PD-55_PD

I-PD-55_PD
In CDCl3 298K

I-PD-55_PD
C-H HMQC
In CDCl3 298K

pd5561 #24-42 RT: 1.47-2.59 AV: 19 NL: 1.62E8
T: +e Cl Full ms [49.50-850.50]

Sample I-PD-55
Theoretical mass 520.14188
Measured mass 520.14158
Error 0.58 ppm

I-PD-18_PD
In CDCl3 298K

I-PD-18_PD
In CDCl3 298K

I-PD-18_PD
In CDCl3 298K

I-PD-18_PD
In CDCl3 298K

I-PD-18_PD
C-H HMQC
In CDCl3 298K

02020704: Scan Avg 305-312 (55.87 - 57.15 min) - Back
 Base: 197.00 Int: 29682.8 Sample: VG 70-SE Positive Ion FAB

I-PD-24 (PD)
In CDCl₃ 298K

I-PD-24 (PD)
In CDCl₃ 298K

I-PD-24 (PD)
H-H COSY
In CDCl3 298K

I-PD-24 (PD)
In CDCl₃ 298K

I-PD-24 (PD)
In CDCl₃ 298K

I-PD-24 (PD)
C-H HMQC
In CDCl₃ 298K

I-PD-131 (PD)
In CDCl₃ 298K

I-PD-131

I-PD-131 (PD)
H-H COSY
In CDCl₃ 298K

I-PD-131 (PD)
In CDCl₃ 298K

I-PD-131 (PD)
In CDC13 298K

I-PD-131 (PD)
C-H HMQC
In CDCl₃ 298K

Sample I-PD-131
Positive ion electrospray
Theoretical mass 783.22869 (M+Na)
Measured mass 783.22867
Error 0.03 ppm

I-PD-34_PD
In CDC13 298K

CC=C(C(=O)OC(C)(C)OC(=O)C)C(=O)OCCOP(=O)(O)O

I-PD-34_PD
In CDCl3 298K

I-PD-34_PD
In CDCl3 298K

I-PD-34_PD
C-H HMQC
In CDCl3 298K

pd34es #18-20 RT: 0.93-1.03 AV: 3 SB: 7 0.11-0.42 NL: 6.56E5
T: + c ESI Full ms [99.50-900.50]

Sample I-PD-34
Positive ion electrospray
Theoretical mass 797.24434 (M+Na)
Measured mass 797.24534
Error 1.25 ppm

I-PD-139 (PD)
In CDCl₃ 298K

I-PD-139 (PD)
In CDCL3 298K

I-PD-139 (PD)
H-H COSY
In CDCl₃ 298K

I-PD-139 (PD)
Ln CDC13 298K

I-PD-139 (PD)
In CDCl₃ 298K

pd139es #22 RT: 0.84 AV: 1 SB: 9 0.11-0.40 NL: 1.39E6
T: +eSI/Full ms [99.50-1000.50]

Sample I-PD-139
Positive ion electrospray
Theoretical mass 811.25999 (M+Na)
Measured mass 811.25950
Error 0.60 ppm

I-PD-50_PD
In CDCl3 298K

I-PD-50
in CDCl₃ at 298K

Chemical structure of compound 1: A five-membered cyclic acetal with a gem-dimethyl group, a TBDPSO group, a Ph₃Sn group, and a Ph group.

I-PD-50
In CDCl₃ 298K

I-PD-50
In CDCl₃ 298K

I-PD-50
C-H HMQC
In CDCl₃ 298K

Sample I-PD-50
Theoretical mass 845.24434 (M+Na)
Measured mass 845.24477
Error 0.51 ppm

C[C@H]1OC(C)(C)O1C=C(c2ccccc2)C(=C(c3ccccc3)C4=CC=CC=C4)C5=CC=CC=C5C6=CC=CC=C6C7=CC=CC=C7C8=CC=CC=C8C9=CC=CC=C9C10=CC=CC=C10C11=CC=CC=C11C12=CC=CC=C12C13=CC=CC=C13C14=CC=CC=C14C15=CC=CC=C15C16=CC=CC=C16C17=CC=CC=C17C18=CC=CC=C18C19=CC=CC=C19C20=CC=CC=C20C21=CC=CC=C21C22=CC=CC=C22C23=CC=CC=C23C24=CC=CC=C24C25=CC=CC=C25C26=CC=CC=C26C27=CC=CC=C27C28=CC=CC=C28C29=CC=CC=C29C30=CC=CC=C30C31=CC=CC=C31C32=CC=CC=C32C33=CC=CC=C33C34=CC=CC=C34C35=CC=CC=C35C36=CC=CC=C36C37=CC=CC=C37C38=CC=CC=C38C39=CC=CC=C39C40=CC=CC=C40C41=CC=CC=C41C42=CC=CC=C42C43=CC=CC=C43C44=CC=CC=C44C45=CC=CC=C45C46=CC=CC=C46C47=CC=CC=C47C48=CC=CC=C48C49=CC=CC=C49C50=CC=CC=C50C51=CC=CC=C51C52=CC=CC=C52C53=CC=CC=C53C54=CC=CC=C54C55=CC=CC=C55C56=CC=CC=C56C57=CC=CC=C57C58=CC=CC=C58C59=CC=CC=C59C60=CC=CC=C60C61=CC=CC=C61C62=CC=CC=C62C63=CC=CC=C63C64=CC=CC=C64C65=CC=CC=C65C66=CC=CC=C66C67=CC=CC=C67C68=CC=CC=C68C69=CC=CC=C69C70=CC=CC=C70C71=CC=CC=C71C72=CC=CC=C72C73=CC=CC=C73C74=CC=CC=C74C75=CC=CC=C75C76=CC=CC=C76C77=CC=CC=C77C78=CC=CC=C78C79=CC=CC=C79C80=CC=CC=C80C81=CC=CC=C81C82=CC=CC=C82C83=CC=CC=C83C84=CC=CC=C84C85=CC=CC=C85C86=CC=CC=C86C87=CC=CC=C87C88=CC=CC=C88C89=CC=CC=C89C90=CC=CC=C90C91=CC=CC=C91C92=CC=CC=C92C93=CC=CC=C93C94=CC=CC=C94C95=CC=CC=C95C96=CC=CC=C96C97=CC=CC=C97C98=CC=CC=C98C99=CC=CC=C99C100=CC=CC=C100

Sample I-PD-50
Theoretical mass 845.24434 (M+Na)
Measured mass 845.24477
Error 0.51 ppm

I-PD-72 (PD)
In CDCl₃ 298K

I-PD-72 CRUDE

I-PD-72 (PD)
In CDCl₃ 298K

I-PD-72 (PD)
In CDCl₃ 298K

I-PD-72 (PD)
In CDCl₃ 298K

[illegible]

IV-PD-51
in CDCl₃ at 298K

IV-PD-51
in CDCl₃ at 298K

IV-PD-51
in CDCl₃ at 298K

IV-PD-51
in CDCl₃ at 298K

IV-PD-51

in CDC13 at 298K

Sample: IV-PD-51
Theoretical Mass: 822.25510
Measured Mass: 822.25633
Error: 1.5 ppm

I-PD-73_PD
In CDC13 298K

I-PD-73_PD
In CDCL3 298K

I-PD-37_PD
H-H COSY
in CDCl3 298K

I-PD-73_PD
In CDCl₃ 298K

I-PD-73_PD
In CDCl3 298K

I-PD-73_PD
C-H HMQC
In CDCl3 298K

In CDC13 298K

I-PD-84_PD

In CDCL3 298K

CC(=C(C)C(OTBDPS)C(C)OBTBDPS)Sn(C)(C)C

I-PD-84_PD
In CDCl3 298K

I-PD-84_PD
In CDCl3 298K

I-PD-84_PD
H-H COSY
In CDCl3 298K

pd8461436-47 RT: 2.00-2.61 AV: 12 NL: 9.83E6
T: +c Cl Full ms [99.50-1100.50]

I-PD-93_PD
In CDCl3 298K

I-PD-93_PD
In CDCl3 298K

CC(=C(C)C(O)COC(=O)C1=CC=CC=C1)C2=CC=CC=C2

I-PD-93-PD
In CDCl3 298K

pd93aee #19-29 RT: 1.00-1.51 AV: 11 SB: 7.008-0.39 NL: 1.66E5
T: + c ESI/Full ms [99.50-900.50]

Sample I-PD-93a
Positive ion electrospray
Theoretical mass 713.18683 (M+Na)
Measured mass 713.18784
Error 1.46 ppm

I-PD-77 (PD)
In CDCl₃ 298K

I-PD-77 (PD)
In CDCl₃ 298K

I-PD-77 (PD)
H-H COSY
In CDCl₃ 298K

I-PD-77 (PD)
In CDCl₃ 298K

I-PD-77 (PD)
In CDCl₃ 298K

I-PD-77 (PD)
C-H HMQC
In CDCl₃ 298K

pd77as #20 RT: 1.04 AV: 1 SB: 4 0.32-0.47 NL: 7.43E5
T: + c ESI Full ms [99.50-900.50]

I-PD-83

I-PD-83_PD
H-H COSY
In CDCl3 298K

I-PD-83_PD
In CDC13 298K

I-PD-83_PD
In CDCl3 298K

I-PD-83_PD
C-H HMQC
In CDCl3 298K

Sample I-PD-83
Positive ion electrospray
Theoretical mass 635.15786 (M+Na)
Measured mass 635.15711
Error 1.18 ppm

I-PD-97 (PD)
In CDCl₃ 298K

I-PD-97 (PD)
In CDC13 298K

I-PD-97 (PD)
H-H COSY
In CDCl₃ 298K

I-PD-97 (PD)
In CDCl₃ 298K

I-PD-97 (PD)
In CDCl₃ 298K

I-PD-97 (PD)
C-H HMQC
In CDCl₃ 298K

pd97es #20-21 RT: 0.77-0.81 AV: 2 SB: 10 0.08-0.41 NL: 1.89E6
T: + c ESI Full ms [99.50-1000.50]

Sample I-PD-97
Positive ion electrospray
Theoretical mass 741.21813 (M+Na)
Measured mass 741.21592
Error 2.98 ppm

I-PD-130 (PD)
In CDCl₃ 298K

I-PD-130 (PD)
In CDCl₃ 298K

I-PD-130 (PD)
In CDCl₃ 298K

I-PD-130 (PD)
H-H COSY
In CDCl3 298K

I-PD-130 (PD)
In CDCl₃ 298K

I-PD-130 (PD)
In CDCl₃ 298K

I-PD-130 (PD)
C-H HMQC
In CDCl₃ 298K

I-PD-154 (PD)
In CDCl₃ 298K

I-PD-154

I-PD-154 (PD)
H-H COSY
In CDCl₃ 298K

I-PD-154 (PD)
In CDCl₃ 298K

I-PD-154 (PD)
In CDCl₃ 298K

I-PD-154 (PD)
C-H HMQC
In CDCl₃ 298K

03290204: Scan Avg 67-72 (13.93 - 15.02 min)
Base: 665.00 Int: 1.55276e+006 Sample: VG 70-SE Negative Cl-Ammonia

I-PD-90 (PD)
In CDCL3 298K

I-PD-90

I-PD-90 (PD)
H-H COSY
In CDCl₃ 298K

I-PD-90 (PD)
In CDCl₃ 298K

I-PD-90 (PD)
In CDCl₃ 298K

I-PD-90 (PD)
C-H HMQC
In CDCl₃ 298K

pd90es #13-15 RT: 0.70-0.80 AV: 3 SB: 6 0.14-0.39 NL: 9.38E5
T: + c ESI Full ms [99.50-900.50]

Sample I-PD-90
Positive ion electrospray
Theoretical mass 727.20248 (M+Na)
Measured mass 727.20157
Error 1.25 ppm

I-PD-51

CRUDE REACTION MIXTURE

O-Directed Free Radical Hydrostannations of Propargyl Ethers, Acetals and Alcohols with Ph₃SnH and Et₃B

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Supporting Information□ Part 4

Product Analysis of Crude Reaction Mixtures By 500 MHz ¹H NMR Spectroscopy: Ratio Determinations

I-PD-11 CRUDE

I-PD-12

IV-PD-111 CRUDE

CRUDE REACTION MIXTURE

I-PD-55 CRUDE

CRUDE REACTION MIXTURE

CRUDE REACTION MIXTURE

I-PD-131 CRUDE

CRUDE REACTION MIXTURE

IV-PD-130 CRUDE

CRUDE REACTION MIXTURE

I-PD-34 CRUDE

I-PD-35 CRUDE

IV-PD-152 CRUDE

I-PD-50
DC13 at

CRUDE REACTION MIXTURE

I-PD-137 CRUDE

CRUDE REACTION MIXTURE

IV-PD-149 CRUDE

CRUDE REACTION MIXTURE

IV-PD-51 CRUDE

CRUDE REACTION MIXTURE

IV-PD-140 CRUDE

CRUDE REACTION MIXTURE

CRUDE REACTION MIXTURE

I-PD-73 CRUDE

CRUDE REACTION MIXTURE

I-PD-84 CRUDE

CRUDE REACTION MIXTURE

CRUDE REACTION MIXTURE

IV-PD-114 CRUDE

I-PD-83 CRUDE

CRUDE REACTION MIXTURE

IV-PD-162 CRUDE

CRUDE REACTION MIXTURE

I-PD-130 CRUDE

CRUDE REACTION MIXTURE

IV-PD-118Crude

I-PD-154 CRUDE

CRUDE REACTION MIXTURE

III-PD-174Crude

I-PD-90 CRUDE