2-Deoxy-2-Iodo-α-Manno- and Talopyranosyl Acetates: Highly Stereoselective Glycosyl Donors for the Synthesis of 2-Deoxy-α-Glycosides

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SUPPORTING INFORMATION

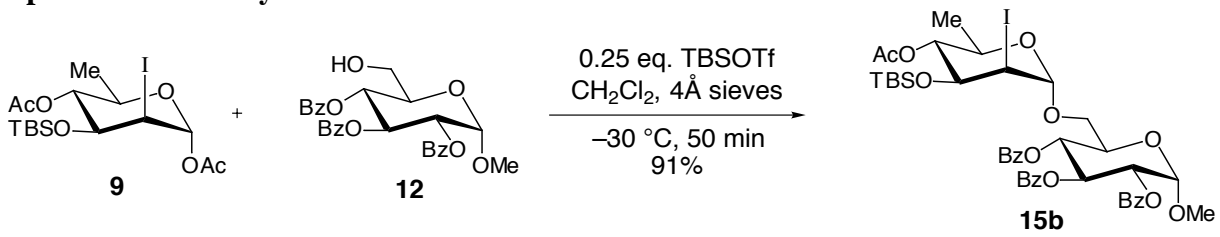
Representative experimental procedures for the glycosidation reactions and Bu_3SnH reductions of the 2-deoxy-2-iodo glycosides, and tabulated spectroscopic data for **15a**-**c**, **16a,b**, **17a-c**, **18c**, **19**, **20** and **23**-**25** (11 pages). See any current masthead page for ordering information.

General Procedures

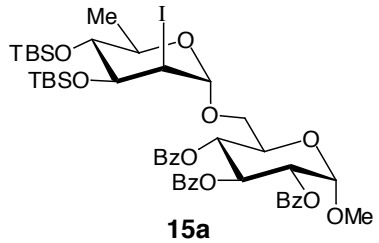
All glycosidation reactions were conducted in flame-dried or oven-dried glassware under an atmosphere of dry nitrogen using methylene chloride distilled over CaH_2. ^1H and ^{13}C NMR spectra were measured at 500 and 100 MHz respectively on commercial NMR instruments. Chemical shifts are reported in δ with coupling constants reported in Hz. Residual chloroform was used as internal reference (δ 7.26 for ^1H and δ 77.0 for ^{13}C). High resolution mass spectra were measured at 70 eV on a Micromass Corp. VG 70-250-S spectrometer at the University of Michigan Mass Spectrometry Laboratory. Fast atom bombardment (FAB) mass spectra were obtained using 3–nitrobenzyl alcohol as the matrix. Chemical ionization (CI) mass spectra were obtained using NH_3 and/or CH_4 as the reagent gas. Optical rotations were measured on a Rudolph Autopol III polarimeter using a quartz cell with 1 mL capacity and a 10 cm path length. Melting points are uncorrected. Elemental analyses were performed by the University of Michigan Combustion Analysis Laboratory.

Analytical thin layer chromatography (TLC) was performed using plates coated with a 0.25 mm thickness of silica gel containing PF254 indicator (Analtech), and compounds were visualized with UV light, potassium iodide/iodine stain, p-anisaldehyde stain or ceric ammonium molybdate stain. Flash chromatography was performed using Kieselgel 60 (230-400 mesh). High performance liquid chromatography (HPLC) was performed on a system utilizing a Rainin SD-200 pump and a Rainin HPXL pump with a gradient solvent system of hexanes and ethyl acetate, a Rheodyne 7125 injector, and a Rainin UV-C UV detector at 254 nm. Depending on sample size, HPLC purifications were carried out with Rainin Dynamax-60A Si 83-111-C 10 mm, Dynamax-60A Si 83-121-C 21 mm, or Microsorb Si 80-140-C8 41 mm columns.

Representative Glycosidation Procedure

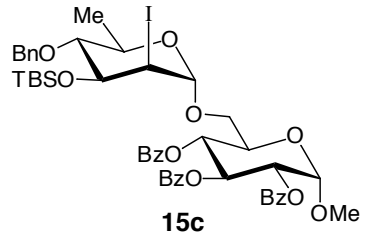


To a solution of donor **9** (48 mg, 0.10 mmol) and acceptor **12** (65 mg, 0.13 mmol) in 0.4 mL of CH_2Cl_2 was added flame dried 4Å molecular sieves (12 mg). The suspension was stirred at room temperature for 10 min, then was cooled to –30 °C and *t*–butyldimethylsilyl triflate (6 μL, 0.026 mmol) was added. After 50 min, the reaction was quenched by the addition of 0.1 mL of Et_3N. The cold bath was removed and sat $NaHCO_3$ solution added. The mixture was extracted with CH_2Cl_2 and the combined extracts were dried (anhyd. Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by silica gel chromatography using 30% EtOAc in hexanes as the eluent to afford the disaccharide **15b** as the sole product (85.4 mg, 91%): mp 148-150 °C; [α] +60.5° (c 0.62, CH_2Cl_2); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 4 H), 7.88 – 7.86 (m, 2 H), 7.54 – 7.51 (m, 2 H), 7.45 – 7.37 (m, 5 H), 7.31 – 7.28 (m, 2 H), 6.13 (apparent t, *J* = 9.8 Hz, 1 H), 5.60 (apparent t, *J* = 10.0 Hz, 1 H), 5.27 – 5.25 (m, 2 H), 5.16 (s, 1 H), 4.93 (apparent t, *J* = 9.3 Hz, 1 H), 4.26 – 4.22 (m, 2 H), 3.84 (dd, *J* = 11.2, 5.1 Hz, 1 H), 3.65 – 3.59 (m, 2 H), 3.48 (s, 3 H), 3.35 (dd, *J* = 8.8, 4.2 Hz, 1 H), 2.06 (s, 3 H), 1.00 (d, *J* = 6.3 Hz, 3 H), 0.90 (s, 9 H), 0.11 (s, 3 H), 0.09 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 165.9, 165.8, 165.0, 133.4, 133.1, 129.9, 129.8, 129.7, 129.2, 129.0, 128.9, 128.4, 128.2, 101.6, 97.0, 75.5, 72.1, 70.5, 69.2, 68.2, 67.3, 66.0, 55.4, 37.0, 31.8, 29.7, 29.3, 25.8, 25.6, 22.7, 21.1, 17.9, 17.3, –4.7, –4.8; IR (thin film) 2946, 2927, 2855, 1732, 1602, 1584, 1492, 1451, 1388, 1372, 1331, 1316, 1280, 1259, 1230, 1194, 1178, 1147, 1105, 1069, 1044, 1027, 947, 922, 865, 839, 778, 709, 686, 668 cm^{-1}; high resolution FAB MS calcd for $C_{42}H_{51}IO_{13}Si$ ($M+Na^+$) 941.2041, found 941.2030. *Anal.* Calcd for $C_{42}H_{51}IO_{13}Si$: C, 54.90; H, 5.59. Found: C, 55.19; H, 5.84.



15a

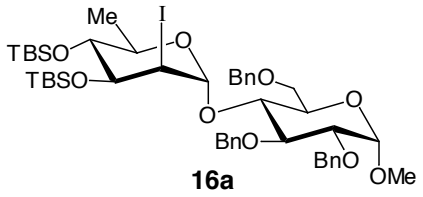
Data for **15a**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.86 (m, 6 H), 7.53 – 7.49 (m, 2 H), 7.44 – 7.36 (m, 5 H), 7.31 – 7.28 (m, 2 H), 6.13 (apparent t, *J* = 9.8 Hz, 1 H), 5.59 (apparent t, *J* = 9.9 Hz, 1 H), 5.24 – 5.21 (m, 2 H), 5.11 (s, 1 H), 4.30 (s, 1 H), 4.20 (ddd, *J* = 10.3, 5.4, 2.4 Hz, 1 H), 3.83 (dd, *J* = 11.2, 5.4 Hz, 1 H), 3.67 – 3.55 (m, 3 H), 3.47 (s, 3 H), 3.20 (br s, 1 H), 1.13 (d, *J* = 6.3 Hz, 3 H), 0.98 (s, 9 H), 0.90 (s, 9 H), 0.15 (s, 3 H), 0.13 (s, 3 H), 0.12 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.0, 133.3, 133.0, 129.9, 129.8, 129.7, 129.2, 129.0, 128.4, 128.2, 96.9, 76.3, 72.2, 70.5, 69.3, 68.5, 55.4, 29.7, 26.5, 26.1, 18.4, 18.3, 18.1, –4.5; IR (thin film) 2955, 2930, 2857, 1733, 1602, 1585, 1472, 1463, 1452, 1388, 1361, 1316, 1280, 1260, 1178, 1106, 1069, 1028, 983, 938, 918, 880, 863, 839, 801, 777, 709, 686 cm^{-1}; high resolution MS (CI, CH_4+NH_3) calcd for $C_{46}H_{63}IO_{12}Si_2$ ($M–H^+$) 989.2824, found 989.2778.



15c

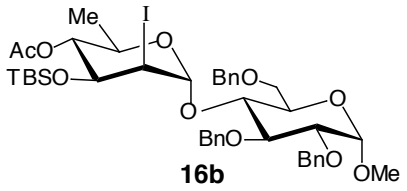
Data for **15c**: ^{1}H NMR (500 MHz, $CDCl_3$) d 7.99 – 7.85 (m, 6 H), 7.53 – 7.25 (m, 14 H), 6.13 (apparent t, *J* = 9.8 Hz, 1 H), 5.55 (apparent t, *J* = 9.9 Hz, 1 H), 5.25 – 5.21 (m, 2 H), 5.11 (s, 1 H), 4.87, 4.54 (AB system, *J* = 11.2 Hz, 2 H), 4.22 – 4.17 (m, 2 H), 3.81 (dd, *J* = 11.2, 5.4 Hz, 1 H), 3.68 – 3.63 (m, 1 H), 3.58 (dd, *J* = 11.2, 2.7 Hz, 1 H), 3.46 (s, 3 H), 3.32 (d, *J* = 5.6 Hz, 1 H), 1.12 (d, *J* = 6.3 Hz, 3 H), 0.95 (s, 9 H), 0.10 (s, 3 H), 0.08 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 165.1, 138.4, 133.3, 133.0, 129.9, 129.8, 129.7, 129.2, 129.0, 128.4, 127.8, 127.5, 101.6, 96.9, 82.9, 75.3, 72.1, 70.5, 69.8, 69.5, 68.8, 68.3, 66.1, 55.4, 39.0, 29.7, 25.9, 18.0, 17.7, –0.6, –4.5, –4.7; IR (thin film) 2951, 2928, 2855, 1732, 1602, 1584, 1492, 1471, 1462, 1451, 1382, 1361, 1335, 1315, 1280, 1261, 1195, 1178, 1106, 1069, 1027, 984, 912,

866, 839, 800, 778, 734, 709, 686, 648, 617 cm^{-1}; high resolution FAB MS calcd for $C_{47}H_{55}IO_{12}Si$ ($M+Na^+$) 989.2405, found 989.2399.



16a

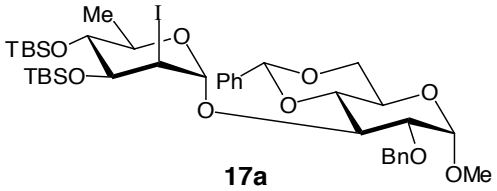
Data for **16a**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 15 H), 5.49 (d, *J* = 2.7 Hz, 1 H), 5.10 (d, *J* = 11.0 Hz, 2 H), 4.71, 4.58 (AB system, *J* = 12.0 Hz, 2 H), 4.65, 4.51 (AB system, *J* = 12.0 Hz, 2 H), 4.61 (d, *J* = 3.4 Hz, 1 H), 4.24 (s, 1 H), 3.90 (br s, 1 H), 3.80 (dd, *J* = 10.0, 3.9 Hz, 1 H), 3.76 – 3.68 (m, 3 H), 3.62 (dd, *J* = 10.7, 5.4 Hz, 2 H), 3.55 (dd, *J* = 9.8, 3.4 Hz, 1 H), 3.41 (s, 3 H), 3.01 (br s, 1 H), 1.18 (d, *J* = 6.1 Hz, 3 H), 0.91 (s, 9 H), 0.90 (s, 9 H), 0.11 (s, 3 H), 0.09 (s, 6 H), 0.06 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 137.8. 128.4, 128.3, 128.1, 127.9, 127.5, 127.4, 97.6, 81.5, 80.4, 76.3, 75.2, 73.5, 73.1, 69.5, 69.4, 55.3, 29.7, 26.6, 26.3, 26.1, 26.0, 18.3, 18.2, 18.0, –3.3, –4.1, –4.4; IR (thin film) 3085, 3063, 3030, 2952, 2928, 2896, 2857, 1497, 1472, 1462, 1453, 1388, 1360, 1290, 1258, 1137, 1116, 1098, 1051, 1028, 1005, 938, 913, 879, 863, 838, 802, 776, 734, 696, 668 cm^{-1}; high resolution MS (CI, NH_3+CH_4) calcd for $C_{46}H_{69}IO_9Si_2$ ($M+NH_4^+$) 966.3869, found 966.3837.



16b

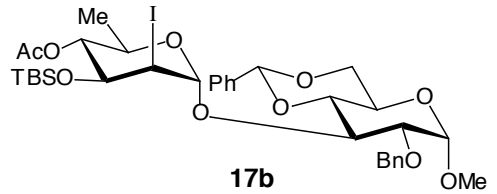
Data for **16b**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.28 (m, 15 H), 5.52 (s, 1 H), 5.10, 4.66 (AB system, *J* = 11.1 Hz, 2 H), 4.96 (apparent t, *J* = 9.3 Hz, 1 H), 4.71, 4.58 (AB system, *J* = 12.0 Hz, 2 H), 4.64, 4.50 (AB system, *J* = 12.1 Hz, 2 H), 4.16 (dd, *J* = 4.2, 1.5 Hz, 1 H), 3.89 (apparent t, *J* = 9.1 Hz, 1 H), 3.81 – 3.76 (m, 2 H), 3.73 – 3.65 (m, 3 H), 3.62 (dd, *J* = 10.7, 5.1 Hz, 1 H), 3.55 (dd, *J* = 9.6, 3.5 Hz, 1 H), 3.41 (s, 3 H), 3.20 (dd, *J* = 8.0, 4.2 Hz, 1 H), 2.05 (s, 3 H), 1.06 (d, *J* = 6.3 Hz, 3 H), 0.85 (s, 9 H), 0.02 (s, 3 H), –0.01 (s, 3 H); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 169.5, 138.0, 137.8, 128.5, 128.3, 128.1, 128.0, 127.6, 127.5, 127.4, 103.8, 97.6, 94.4, 81.3, 80.2, 77.9, 75.8, 75.3, 73.5, 73.1, 69.5, 69.3, 67.9, 67.4, 65.8, 55.4, 37.8, 29.7, 25.5, 21.1, 17.8, 17.5, 15.2, –4.7; IR (thin film) 2952, 2928, 2896, 2856, 1751, 1496, 1472, 1453, 1388, 1369, 1294, 1249, 1230, 1147, 1103, 1047, 1029, 987, 946, 865, 838, 777, 736, 697, 668 cm^{-1}; high resolution FAB MS calcd for $C_{42}H_{57}IO_{10}Si$ ($M+Na^+$) 899.2663, found 899.2624.



17a

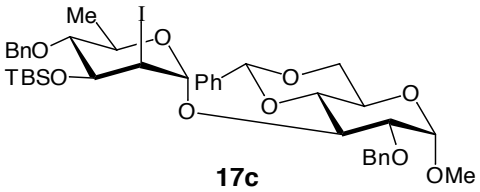
Data for **17a**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.33 (m, 10 H), 5.66 (br s, 1H), 5.33 (s, 1 H), 4.86, 4.63 (AB system, *J* = 11.0 Hz, 2 H), 4.58 (d, *J* = 2.4 Hz, 1 H), 4.39 (s, 1 H), 4.26 (dd, *J* = 10.0, 4.7 Hz, 2 H), 4.03 (br s, 1 H), 3.80 (dt, *J* = 10.0, 4.9 Hz, 1 H), 3.70 (apparent t, *J* = 10.3 Hz, 1 H), 3.62 – 3.55 (br m, 2 H), 3.47 (dd, *J* = 5.9, 3.6 Hz, 1 H), 3.39 (s, 3 H), 3.19 (br s, 1 H), 1.24 (d, *J* = 6.3 Hz, 3 H), 0.96 (s, 9 H), 0.89 (s, 9 H), 0.13 (s, 3 H), 0.11 (s, 3 H), 0.10 (s, 3 H), 0.09 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 128.9, 128.5, 128.2, 128.1, 94.4, 82.8, 77.6, 76.5, 73.7, 70.8, 69.0, 29.7, 26.5, 26.1, 18.7, 18.3, 18.0, 0.5, –4.3; IR (thin film) 3065, 3034, 2953, 2929, 2857, 1496, 1472, 1463, 1452, 1387, 1372, 1291, 1258, 1212, 1178, 1111, 1090, 1055, 1045, 1001, 973, 938, 919, 879, 864, 839, 803, 776, 747, 733, 697, 668, 655 cm^{-1}; high resolution MS (CI, CH_4) calcd for $C_{39}H_{61}IO_9Si_2$ ($M+H^+$) 857.2977, found 857.2981.



17b

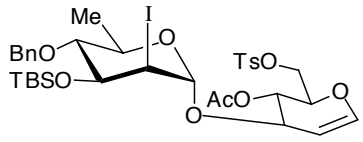
Data for **17b**: ^1H NMR (500 MHz, $CDCl_3$) δ 7.47 – 7.32 (m, 10 H), 5.73 (s, 1 H), 5.54 (s, 1 H), 4.96 (apparent t, *J* = 9.4 Hz, 1 H), 4.79, 4.63 (AB system, *J* = 11.8 Hz, 2 H), 4.63 (d, *J* = 3.7 Hz, 1 H), 4.34 (dd, *J* = 4.4, 1.2 Hz, 1 H), 4.28 – 4.24 (m, 2 H), 4.15 – 4.09 (m, 1 H), 3.78 (dt, *J* = 10.2, 4.4 Hz, 1 H), 3.70 (apparent t, *J* = 10.2 Hz, 1 H), 3.58 (apparent t, *J* = 9.4 Hz, 1 H),

3.50 (dd, J = 9.5, 3.7 Hz, 1 H), 3.39 (s, 3 H), 3.35 (dd, J = 8.9, 4.3 Hz, 1 H), 2.02 (s, 3 H), 1.10 (d, J = 6.3 Hz, 3 H), 0.89 (s, 9 H), 0.09 (s, 3 H), 0.06 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 137.7, 136.8, 128.9, 128.5, 128.2, 128.1, 125.8, 101.6, 101.0, 98.8, 82.6, 77.8, 75.9, 74.0, 73.5, 68.9, 67.5, 67.2, 61.8, 55.3, 37.1, 31.9, 29.7, 25.6, 21.1, 17.9, 17.7, –4.5, –4.7; IR (thin film) 2946, 2928, 2856, 1749, 1497, 1472, 1463, 1453, 1373, 1341, 1295, 1270, 1249, 1232, 1177, 1147, 1104, 1090, 1040, 997, 978, 947, 926, 890, 865, 838, 796, 778, 748, 697, 677, 656 cm^{-1}; high resolution FAB MS calcd for $C_{35}H_{49}IO_{10}Si$ (M+Na$^+$) 807.2037, found 807.2036.



17c

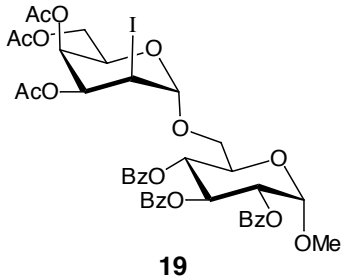
Data for **17c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.26 (m, 15 H), 5.66 (s, 1 H), 5.52 (s, 1 H), 4.87 (A of AB system, J = 11.2 Hz, 1 H), 4.82 (A of AB system, J = 11.7 Hz, 1 H), 4.60 – 4.57 (m, 3 H), 4.37 (d, J = 3.4 Hz, 1 H), 4.27 – 4.21 (m, 2 H), 4.14 – 4.09 (m, 2 H), 3.79 (dt, J = 9.9, 4.7 Hz, 1 H), 3.74 (s, 1 H), 3.69 (apparent t, J = 10.4 Hz, 1 H), 3.54 (apparent t, J = 9.3 Hz, 1 H), 3.46 (dd, J = 9.5, 3.9 Hz, 1 H), 3.37 (s, 3 H), 1.20 (d, J = 6.1 Hz, 3 H), 0.93 (s, 9 H), 0.07 (s, 3 H), 0.06 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.6, 137.7, 136.9, 128.9, 128.5, 128.3, 128.2, 128.0, 127.5, 127.4, 125.9, 101.9, 101.1, 99.0, 83.3, 82.7, 78.0, 75.1, 74.7, 73.9, 70.0, 69.0, 68.8, 61.8, 55.3, 39.3, 31.9, 29.7, 25.9, 22.7, 18.1, 18.0, –4.4, –4.6; IR (thin film) 3064, 3032, 2951, 2927, 2855, 1497, 1470, 1460, 1453, 1373, 1339, 1291, 1265, 1212, 1176, 1116, 1089, 1060, 1042, 1029, 998, 973, 930, 866, 838, 802, 777, 748, 697, 677, 655 cm^{-1}; high resolution FAB MS calcd for $C_{40}H_{53}IO_9Si$ (M+Na$^+$) 855.2401, found 855.2419.



18c

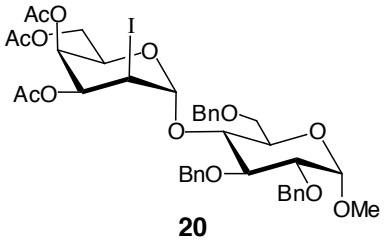
Data for **18c**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78 (apparent d, J = 8.3 Hz, 2 H), 7.35 – 7.26 (m, 7 H), 6.17 (d, J = 6.4 Hz, 1 H), 5.22 (s, 1 H), 5.01 (apparent t, J = 4.5 Hz, 1 H), 4.90, 4.58

(AB system, J = 11.2 Hz, 2 H), 4.79 (dd, J = 5.8, 4.2 Hz, 1 H), 4.29 – 4.25 (m, 2 H), 4.19 (dd, J = 3.9, 1.5 Hz, 1 H), 4.14 (dd, J = 9.5, 1.7 Hz, 1 H), 4.00 (dd, J = 3.9, 3.2 Hz, 1 H), 3.79 – 3.73 (m, 1 H), 3.38 (apparent t, J = 8.9 Hz, 1 H), 3.21 (dd, J = 8.3, 3.9 Hz, 1 H), 2.42 (s, 3 H), 2.07 (s, 3 H), 1.23 (d, J = 6.4 Hz, 3 H), 0.97 (s, 9 H), 0.12 (s, 3 H), 0.11 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.5, 144.9, 143.8, 138.1, 132.5, 129.9, 128.4, 128.1, 128.0, 127.7, 101.9, 100.2, 82.9, 75.5, 73.0, 69.9, 69.7, 69.2, 67.9, 66.4, 38.5, 33.2, 31.9, 30.1, 29.7, 29.4, 26.7, 25.9, 22.7, 21.6, 20.8, 18.0, 17.8; IR (thin film) 2956, 2926, 2854, 1748, 1648, 1598, 1497, 1454, 1370, 1292, 1233, 1190, 1178, 1119, 1104, 1044, 1006, 980, 864, 838, 815, 778, 745, 698, 670 cm^{-1}; high resolution FAB MS calcd for $C_{34}H_{47}IO_{10}SSi$ (M+Na$^+$) 825.1602, found 885.1616.



19

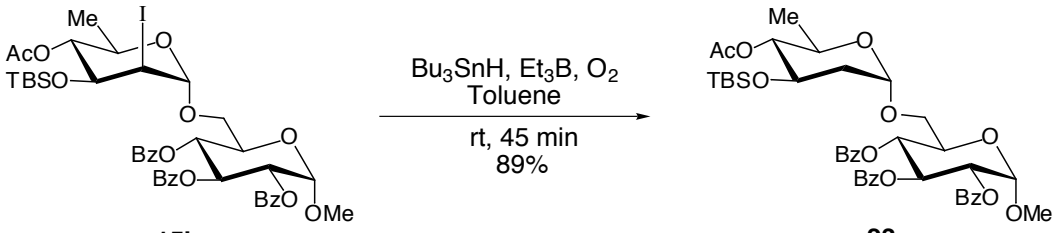
Data for **19**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 – 7.94 (m, 4 H), 7.87 – 7.85 (m, 2 H), 7.52 – 7.27 (m, 9 H), 6.15 (apparent t, J = 9.7 Hz, 1 H), 5.61 (apparent t, J = 9.7 Hz, 1 H), 5.38 – 5.37 (m, 2 H), 5.37 – 5.24 (m, 2 H), 4.92 (dd, J = 4.9, 3.7 Hz, 1 H), 4.30 – 4.26 (m, 2 H) 4.23 (ddd, J = 10.3, 4.9, 2.7 Hz, 1 H), 4.06 – 4.01 (m, 2 H), 3.89 (dd, J = 11.0, 4.9 Hz, 1 H), 3.66 (dd, J = 11.0, 2.4 Hz, 1 H), 3.48 (s, 3 H), 2.17 (s, 3 H), 2.07 (s, 3 H), 1.86 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 170.0, 169.3, 165.7, 165.3, 133.5, 133.3, 133.1, 129.9, 129.8, 129.6, 129.1, 129.0, 128.8, 128.5, 128.4, 128.2, 102.7, 97.0, 72.0, 70.3, 69.2, 68.1, 66.7, 66.3, 65.4, 65.1, 62.4, 55.7, 21.0, 20.9, 20.7, 20.4; IR (thin film) 3065, 2934, 2850, 1731, 1602, 1584, 1492, 1452, 1372, 1316, 1263, 1230, 1177, 1108, 1096, 1069, 1055, 1028, 978, 916, 856, 803, 711, 687 cm^{-1}; high resolution FAB MS calcd for $C_{40}H_{41}IO_{16}$ (M+Na$^+$) 927.1337, found 927.1333.



20

Data for **20**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.34 – 7.26 (m, 15 H), 5.68 (s, 1 H), 5.27 (apparent t, *J* = 2.6 Hz, 1 H), 5.07, 4.70 (AB system, *J* = 11.2 Hz, 2 H), 4.84 (apparent t, *J* = 4.0 Hz, 1 H), 4.70, 4.61 (AB system, *J* = 12.2 Hz, 2 H), 4.60 (s, 1 H), 4.58, 4.53 (AB system, *J* = 11.0 Hz, 2 H), 4.28 (dt, *J* = 6.7 Hz, 2.1 Hz, 1 H), 4.16 (dd, *J* = 4.6, 0.7 Hz, 1 H), 4.09 – 4.02 (m, 2 H), 3.93 – 3.90 (m, 1 H), 3.77 – 3.68 (m, 4 H), 3.53 (dd, *J* = 9.5, 3.4 Hz, 1 H), 3.39 (s, 3 H), 2.13 (s, 3 H), 1.98 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 170.0, 169.4, 138.3, 137.9, 137.7, 128.5, 128.4, 128.1, 128.0, 127.7, 127.6, 127.4, 104.1, 97.7, 80.8, 80.1, 77.4, 75.2, 73.4, 73.2, 69.5, 68.8, 67.5, 65.2, 65.0, 61.8, 55.3, 21.7, 21.0, 20.8, 20.7; IR (thin film) 3064, 3031, 2928, 1749, 1497, 1454, 1371, 1322, 1230, 1158, 1095, 1049, 978, 910, 874, 738, 699, 668 cm^{-1}; high resolution FAB MS calcd for $C_{40}H_{47}IO_{13}$ (M+Na$^+$) 885.1959, found 885.1939.

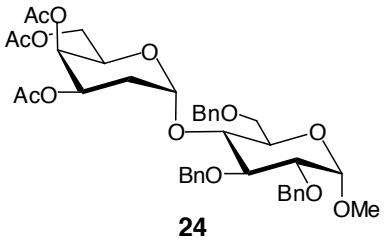
Representative C(2)-Iodo Reduction Procedure



15b **23**

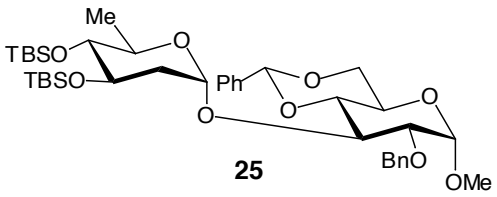
A solution of the disaccharide **15b** (31 mg, 0.034 mmol), Bu_3SnH (23 μL, 0.084 mmol) and Et_3B (8 μL, 1M in hexanes, 0.008 mmol) in 0.4 mL of toluene was stirred at room temperature. An aliquot of the reaction mixture was taken after 30 min and analyzed by ^{1}H NMR spectroscopy, showed that the reduction was complete. The reaction mixture was diluted with EtOAc (5 mL) and washed with $NaHCO_3$. The combined organic extracts were dried (anhyd. Na_2SO_4) and concentrated under reduced pressure. The crude product was purified by flash column chromatography using 30% EtOAc in hexanes as the eluent to afford the product **23** (24 mg, 89%): ^{1}H NMR (500 MHz, $CDCl_3$)

δ 8.00 – 7.95 (m, 4 H), 7.89 – 7.87 (m, 2 H), 7.53 – 7.50 (m, 2 H), 7.43 – 7.36 (m, 5 H), 7.31 – 7.28 (m, 2 H), 6.13 (apparent t, J = 9.7 Hz, 1 H), 5.60 (apparent t, J = 9.9 Hz, 1 H), 5.28 – 5.25 (m, 2 H), 4.85 (d, 3.2 Hz, 1 H), 4.57 (apparent t, J = 9.4 Hz, 1 H), 4.25 (ddd, J = 10.0, 5.4, 2.4 Hz, 1 H), 4.08 – 4.03 (m, 1 H), 3.82 (dd, J = 11.2, 5.4 Hz, 1 H), 3.61 – 3.54 (m, 2 H), 3.48 (s, 3 H), 2.05 (dd, J = 12.6, 5.1 Hz, 1 H), 2.06 (s, 3 H), 1.71 (dt, J = 12.5, 3.7 Hz, 1 H), 0.94 (d, J = 6.3 Hz, 3 H), 0.85 (s, 9 H), 0.05 (s, 6 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 165.9, 165.8, 165.0, 133.4, 133.3, 133.0, 129.9, 129.8, 129.7, 129.3, 129.1, 128.4, 128.2, 97.3, 96.9, 77.6, 72.2, 70.7, 69.4, 68.4, 67.2, 66.0, 65.6, 55.3, 38.9, 29.7, 25.6, 21.2, 17.8, 17.3, –4.6, –4.9; IR (thin film) 2951, 2927, 2854, 1733, 1602, 1585, 1491, 1460, 1452, 1388, 1374, 1315, 1280, 1260, 1248, 1194, 1176, 1163, 1129, 1105, 1070, 1052, 1027, 983, 931, 922, 862, 838, 777, 709, 686, 668 cm^{-1}; high resolution FAB MS calcd for $C_{42}H_{52}O_{13}Si$ (M+Na$^+$) 815.3075, found 815.3038.



24

Data for **24**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.35 – 7.27 (m, 15 H), 5.47 (d, J = 3.2 Hz, 1 H), 5.20 (s, 1 H), 5.19 – 5.15 (m, 1 H), 5.05 (A of AB system, J = 11.0 Hz, 1 H), 4.73 (A of AB system, J = 12.2 Hz, 1 H), 4.67 – 4.61 (m, 4 H), 4.54 (B of AB system, J = 12.2 Hz, 1 H), 3.99 (apparent t, J = 6.3 Hz, 1 H), 3.94 – 3.87 (m, 3 H), 3.77 (ddd, J = 10.0, 4.8, 2.3 Hz, 1 H), 3.70 – 3.64 (m, 3 H), 3.53 (dd, J = 9.6, 3.5 Hz, 1 H), 3.42 (s, 3 H), 2.09 (s, 3 H), 1.98 (s, 3 H), 1.97 (s, 3 H), 1.91 (dt, J = 12.7, 3.9, 1 H), 1.71 (dd, J = 12.7, 5.1 Hz, 1 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.3, 170.0, 138.5, 138.1, 137.9, 128.5, 128.4, 128.1, 128.0, 127.6, 127.5, 127.4, 99.2, 97.7, 94.4, 81.8, 80.1, 76.2, 75.4, 73.2, 73.1, 69.6, 69.1, 67.3, 66.4, 65.8, 62.3, 55.3, 30.4, 29.7, 20.9, 20.7; IR (thin film) 2918, 2849, 1747, 1497, 1453, 1368, 1236, 1164, 1096, 1080, 1048, 1026, 738, 698 cm^{-1}.



25

Data for **25**: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.45 – 7.31 (m, 10 H), 5.50 (s, 1 H), 5.33 (d, *J* = 2.2 Hz, 1 H), 4.88, 4.64 (AB system, *J* = 12.2 Hz, 2 H), 4.53 (d, *J* = 3.7 Hz, 1 H), 4.28 (apparent t, *J* = 9.3 Hz, 1 H), 4.23 (dd, *J* = 10.3, 4.9 Hz, 1 H), 4.01 (ddd, *J* = 11.0, 8.3, 4.7 Hz, 1 H), 3.97 – 3.92 (m, 1 H), 3.80 (dt, *J* = 10.0, 4.6 Hz, 1 H), 3.68 (apparent t, *J* = 10.3 Hz, 1 H), 3.54 (apparent t, *J* = 9.5 Hz, 1 H), 3.43 (dd, *J* = 9.5, 3.7 Hz, 1 H), 3.38 (s, 3 H), 3.15 (apparent t, *J* = 8.3 Hz, 1 H), 2.09 (ddd, *J* = 13.2, 4.6, 1.5 Hz, 1 H), 1.62 (dt, *J* = 13.2, 3.7 Hz, 1 H), 1.20 (d, *J* = 6.4 Hz, 3 H), 0.91 (s, 9 H), 0.87 (s, 9 H), 0.10 (s, 6 H), 0.09 (s, 3 H), 0.07 (s, 3 H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.1, 137.3, 128.9, 128.5, 128.3, 128.2, 128.0, 126.0, 101.4, 99.2, 97.0, 83.3, 78.5, 77.6, 74.0, 72.6, 70.7, 69.1, 69.0, 61.8, 55.2, 39.4, 26.3, 26.1, 19.0, 18.4, 18.0, –2.7, –3.0, –4.0, –4.2; IR (thin film) 2951, 2929, 2856, 1472, 1460, 1452, 1388, 1372, 1359, 1251, 1207, 1173, 1091, 1061, 1042, 1000, 982, 922, 895, 858, 835, 776, 748, 697 cm^{-1}.