Concerning the Origin of the Highly β -Selective Glycosidation Reactions of 2-Deoxy-2-iodo-glucopyranosyl Trichloroacetimidates (Supporting Information)

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General Methods: All reaction solvents were purified before use. Tetrahydrofuran, dichloromethane, acetonitrile, toluene, and benzene were purified by passing through a solvent column¹ composed of activated A-1 alumina. Unless indicated, all chemicals were used as purchased without further purification. Crushed 4 Å molecular sieves were activated by thorough flame-drying under high vacuum immediately prior to use.

Physical Properties and Spectroscopic Measurements: Proton nuclear magnetic resonance (¹H NMR) spectra and carbon-13 (¹³C) NMR spectra were recorded on a Varian VXR-400 spectrometer at 400 MHz and 100 MHz respectively or on a Varian Inova-500 spectrometer at 500 MHz and 126 MHz respectively. The proton signal of residual, non-deuterated solvent (δ 7.26 ppm for CHCl₃) was used as an internal reference for ¹H spectra measured in these solvents. For ¹³C spectra, chemical shifts are reported relative to the δ 77.23 ppm resonance of CDCl₃. Coupling constants are reported in Hz. Infrared (IR) spectra were recorded as thin films on a Perkin-Elmer Spectrum 1000 FTIR. Optical rotations were measured on a Rudolph Autopol III polarimeter using a quartz cell with 1 mL capacity and a 10 cm path length. Mass spectra were recorded on a VG 70-250-S spectrometer manufactured by Micromass Corp. (Manchester UK).

Analytical thin layer chromatography (TLC) was performed on Kieselgel 60 F₂₅₄ glass plates precoated with a 0.25 mm thickness of silica gel. The TLC plates were visualized with UV light and/or by staining with Hanessian solution (a mixture of ceric sulfate and ammonium molybdate in aqueous sulfuric acid). Column chromatography was generally performed using Kieselgel 60 (230-400 mesh) silica gel. Unless noted otherwise, all compounds isolated by chromatography were sufficiently pure by ¹H NMR analysis for use in subsequent reactions. The amount of silica gel used for purification was 50-100 : 1 weight ratio of silica : crude product.

HPLC purifications were performed by using a HPLC system composed of two Rainin HPLC pumps connected to various Dynamax[®] axial compression columns packed with Rainin 60 Å irregular silica gel. Samples were loaded into the system with a 2 mL Rheodyne 7125 injector and were detected using either a Rainin Dynamax[®] UV-C detector or a Rainin Dynamax[®] RI-1 detector. Integration of the various signals was performed using the reprocessing program within the Dynamax[®] HPLC Method Manager.

Experimental

3,4,6-Tri-*O*-*tert*-butyldiphenylsilyl-glycol (10). A solution of tri-*O*-acetyl glycol **9** (2.01 g, 7.4 mmol) in methanol (15 mL) was treated with methanolic NaOMe. The mixture was allowed to stir for 15 min at 23 °C and neutralized with solid CO₂. The solvent was evaporated under reduced pressure to afford the tetraol as a syrup, which was used without further purification. The tetraol was dissolved in a mixture of 20 mL THF and 10 mL DMF. To this was added imidazole (2.5 g, 36.7 mmol) followed by TBDPSCI (7.2 mL, 27.7 mmol) and the solution was heated at 70 °C for 12h. The reaction mixture was then diluted with EtOAc (50 mL) and hexanes (10 mL), and washed with water (3x50 mL). The organic layer was dried

(Na₂SO₄), filtered, concentrated under reduced pressure and the residue was purified by chromatography (5% EtOAc in hexanes) to afford **10** as a clear syrup (6.38 g, >99%), the spectral data of which was consistent with that reported in the literature.²

2-Deoxy-2-iodo-3,4,6-tri-*O*-tert-butylphenyldiphenylsilyl- β -D-glucopyranosyl acetate (11**).** To a solution of glycal **10** (2.12 g, 2.5 mmol) in 15 mL toluene was added HOAc (0.9 mL, 15.7 mmol) and NIS (1.17 g, 5.2 mmol). The reaction mixture was stirred vigorously at 100 °C for 10 min. Upon cooling, 1M aqueous Na₂S₂O₃ was added until the solution was colorless. Saturated aqueous NaHCO₃ was added until the pH was neutral and the solution was then extracted with EtOAc (2x100 mL). The organic layer was dried (MgSO₄), filtered, concentrated under reduced pressure and the residue was purified by chromatography (5% EtOAc in hexanes) to afford the β -gluco isomer **11** (2.33 g, 90%) and the α -manno isomer (0.16 g, 6%) as white solids. Data for **11**: $[\alpha]_D^{24.0^\circ\text{C}} = +7.4$ ($c = 18.3$, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.61-7.15(m, 30H), 6.55 (d, 1H, $J = 6.7$ Hz), 4.47 (d, 1H, $J = 3.2$ Hz), 4.23 (dd, 1H, $J = 8.6, 4.9$ Hz), 3.89 (d, 1H, $J = 6.7$ Hz), 3.84 (dd, 1H, $J = 10.7, 8.6$ Hz), 3.71 (d, 1H, $J = 3.1$ Hz), 3.18 (dd, 1H, $J = 10.7, 4.9$ Hz), 2.09 (s, 3H), 1.04 (s, 9H), 0.96 (s, 9H), 0.82 (s, 9H); ¹³C NMR (100 MHz, CDCl₃) δ 169.27, 136.20, 136.11, 136.07, 135.88, 135.77, 135.74, 133.82, 133.68, 133.03, 132.74, 132.73, 132.43, 130.15, 130.06, 130.04, 129.93, 129.64, 129.59, 128.02, 127.96, 127.88, 127.79, 127.68, 94.45, 82.86, 77.16, 70.79, 65.61, 27.20, 26.98, 26.95, 24.92, 21.18, 19.33, 19.20, 18.99; IR (thin film) 2959.2, 2931.4, 2892.6, 2858.2, 1769.1, 1589.7, 1471.9, 1427.7, 1391.6, 1362.0, 1211.4, 1112.3, 1052.7, 1006.4, 909.1, 822.8, 777.4, 737.9, 700.9 cm⁻¹; HRMS (ES) calcd for C₅₆H₆₇IO₆Si₃Na (M+Na)⁺ 1069.3188, found 1069.3187.

2-Deoxy-2-iodo-4,6-*O*-benzylidene- β -D-glucopyranosyl acetate (12**).** To a stirred solution of iodoacetate **11** (2.4 g, 2.3 mmol) in 25 mL CH₃CN, was added HF•Et₃N (1.4g, 11.6 mmol). The reaction mixture was then heated at 65 °C for 18h. Saturated aqueous NaHCO₃ (25 mL) was then added, and the solution was extracted with EtOAc (6x50 mL). The organic phase was dried (MgSO₄), filtered, and evaporated under reduced pressure to afford the triol as a pale yellow solid, which was used without further purification. To a solution of the triol in 50 mL THF was added benzaldehyde dimethyl acetal (2.8 mL, 18.6 mmol) followed by catalytic TsOH•H₂O. The solution was stirred at 23 °C for 12h. Et₃N (0.5 mL, 3.6 mmol) was then added, and the reaction mixture was concentrated under reduced pressure, and the residue was purified by chromatography (3:1 hexanes:EtOAc) to afford benzylidene acetal **12** as a white solid (803 mg, 82%): $[\alpha]_D^{24.3^\circ\text{C}} = +20.8$ ($c = 9.8$, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 7.50-7.46 (m, 2H), 7.40-7.37 (m, 3H), 6.00 (d, 1H, $J = 9.6$ Hz), 5.57 (s, 1H), 4.38 (dd, 1H, $J = 10.4, 5.0$ Hz), 4.04 (ddd, 1H, $J = 10.3, 8.9, 2.8$), 3.94 (app t, 1H, $J = 9.9$), 3.77 (app t, 1H, $J = 10.2$), 3.65 (app td, 1H, $J = 9.6, 4.9$ Hz), 3.55 (app t, 1H, $J = 9.2$ Hz), 2.81 (d, 1H, $J = 2.8$ Hz), 2.18 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.9, 136.7, 129.7, 128.6, 126.5, 102.1, 94.4, 80.9, 74.7, 68.2, 67.3, 31.6, 20.8; IR (thin film) 2921.9, 1760.6, 1450.4, 1373.1, 1312.1, 1219.3, 1089.5, 1029.7, 989.7, 890.8, 739.3, 695.6 cm⁻¹; HRMS (ES) calcd for C₁₆H₂₁IO₇Na (M+MeOH+Na)⁺ 475.0230, found 475.0234.

2-Deoxy-2-iodo-3-*O*-*tert*-butyldimethylsilyl-4,6-*O*-benzylidene-D-glucopyranoside (13) A solution of **12** (581 mg, 1.4 mmol), TBDMS-Cl (730 mg, 4.8 mmol), and imidazole (500 mg, 7.3 mmol) in DMF (30 mL) was heated at 65 °C for 12h. The reaction mixture was then diluted with water (30 mL), EtOAc (50 mL), and hexanes (10 mL), and then shaken. The organic layer was washed with water, dried (Na₂SO₄), filtered and concentrated under reduced pressure. The crude iodoacetate was passed through a short pad of silica gel and eluted with 10% EtOAc in hexanes to provide a clear syrup, which was then stirred in MeOH (14 mL). To this was added 300 μ L of 11.0 M NH₂NH₂ (3.3 mmol). After being stirred for 45 min at 23 °C, the reaction mixture was diluted with saturated aqueous NaHCO₃ (30mL) and EtOAc (30 mL), and then shaken. The aqueous layer was extracted with EtOAc (30 mL). The organic layers were combined, dried (Na₂SO₄), filtered, concentrated under reduced pressure, and the residue was purified by chromatography (3:1 hexanes:EtOAc) to provide hemiacetal **13** as a white foam (588 mg, 86%) as a 1:1 ratio of α : β isomers: $[\alpha]_D^{24.2^\circ C} = +37.5$ ($c = 10.4$, CHCl₃); ¹H NMR (500 MHz, CDCl₃) α anomer: δ 7.50-7.45 (m, 2H), 7.40-7.36 (m, 3H), 5.51 (s, 1H), 5.39 (t, 1H, $J = 3.5$ Hz), 4.27 (dd, 1H, $J = 10.0, 5.0$ Hz), 4.23 (dd, 1H, $J = 9.9, 8.6$ Hz), 4.21 (app td, 1H, $J = 9.8, 5.0$ Hz), 3.99 (m, 1H), 3.72 (app t, 1H, $J = 10.1$ Hz), 3.47 (m, 1H, OH), 3.46 (m, 1H), 0.88 (s, 9H), 0.17 (s, 3H), -0.03 (s, 3H); β anomer: δ 7.50-7.45 (m, 2H), 7.40-7.36 (m, 3H), 5.50 (s, 1H), 5.01 (dd, 1H, $J = 9.0, 5.9$ Hz), 4.35 (dd, 1H, $J = 10.5, 4.8$ Hz), 3.99 (m, 1H), 3.98 (m, 1H, OH), 3.82 (app t, 1H, $J = 9.7$ Hz), 3.78 (app t, 1H, $J = 10.4$ Hz), 3.51 (app td, 1H, $J = 9.6, 4.8$ Hz), 3.44 (m, 1H), 0.89 (s, 9H), 0.17 (s, 3H), -0.03 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 137.08, 136.91, 129.48, 129.42, 128.41, 128.40, 126.69, 126.63, 102.62, 102.47, 98.24, 95.13, 83.44, 82.31, 76.47, 72.16, 69.06, 68.62, 66.79, 63.28, 38.22, 34.57, 26.35, 26.32, 18.66, -3.47, -4.00, -4.09; IR (thin film) 2953.2, 2928.8, 2883.6, 2856.5, 1459.5, 1379.4, 1250.0, 1215.0, 1157.1, 1114.0, 1093.2, 1028.3, 980.2, 912.6, 837.9, 779.8, 764.3, 696.7 cm⁻¹; HRMS (ES) calcd for C₁₉H₂₉IO₅SiNa (M+Na)⁺ 515.0727, found 515.0718.

2-Deoxy-2-iodo-3-*O*-*tert*-butyldimethylsilyl-4,6-*O*-benzylidene-D-glucopyranosyl trichloroacetimidates (8a, 8b). To a solution of hemiacetal **13** (344 mg, 0.70 mmol) in trichloroacetonitrile (2 mL, 19.9 mmol) at 0 °C was added DBU (40 μ L, 0.27 mmol). The reaction mixture was stirred for 1h at 0 °C, then concentrated and the crude product was purified by chromatography (8:1 hexanes:EtOAc) to provide the β -imidate **8b** (223 mg, 50%) and the α -imidate **8a** (60 mg, 13%) as white foams, as well as a trace amount of imidate **14**.

2-Deoxy-2-iodo-3-*O*-*tert*-butyldimethylsilyl-4,6-*O*-benzylidene- α -D-glucopyranosyl trichloroacetimidate (8a). $[\alpha]_D^{24.5^\circ C} = +103.7$ ($c = 32.7$, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 8.74 (s, 1H), 7.51-7.47 (m, 2H), 7.39-7.36 (m, 3H), 6.50 (d, 1H, $J = 3.3$ Hz), 5.53 (s, 1H), 4.29 (dd, 1H, $J = 10.5, 4.9$ Hz), 4.25 (dd, 1H, $J = 10.1, 8.8$ Hz), 4.15 (dd, 1H, $J = 10.2, 3.4$ Hz), 4.11 (app td, 1H, $J = 10.0, 4.9$ Hz), 3.75 (app t, 1H, $J = 10.4$ Hz), 3.56 (app t, 1H, $J = 9.2$ Hz), 0.89 (s, 9H), 0.19 (s, 3H), 0.00 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 160.82, 136.88, 129.46, 128.38, 126.62, 102.56, 97.01, 96.98, 82.81, 72.56, 68.71, 65.72, 30.04, 26.30, 18.66, -3.43, -4.03; IR (thin film) 3343.5, 2954.6, 2928.8, 2885.0, 2856.6, 1673.5, 1471.6, 1376.1, 1281.7, 1250.8, 1156.2, 1122.0, 1072.7, 1011.3, 975.4, 853.7, 795.8, 780.7 cm⁻¹; HRMS (ES) calcd for C₂₂H₃₃Cl₃INO₆SiNa (M+MeOH+Na)⁺ 690.0085, found 690.0100.

2-Deoxy-2-iodo-3-*O*-*tert*-butyldimethylsilyl-4,6-*O*-benzylidene- β -D-glucopyranosyl trichloroacetimidate (8b). $[\alpha]_D^{24.2^\circ C} = -5.3$ ($c = 12.0$, CHCl₃); ¹H NMR (500 MHz, CDCl₃) δ 8.73 (s, 1H), 7.48-7.45 (m, 2H), 7.39-7.35 (m, 3H), 6.16 (ABXY, 1H, $\nu_A = \nu_B = 2035.3$ Hz, $\nu_X = 3081.6$ Hz, $\nu_Y = 1764.8$ Hz, $J_{AX} = 9.4$ Hz, $J_{AB} = 9.4$ Hz, $J_{BY} = 9.3$ Hz), 5.50 (s, 1H), 4.39 (dd, 1H, $J = 10.5, 5.0$ Hz), 4.07 (ABXY, 1H, as above), 3.80 (app t, 1H, 10.3 Hz), 3.66 (app td, 1H, $J = 9.7, 5.1$ Hz), 3.47 (ABXYd, 1H, as above with $J_{H4H5} = 9.3$ Hz), 0.87 (s, 9H), 0.16 (s, 3H), -0.04 (s, 3H); ¹³C NMR (126 MHz, CDCl₃) δ 160.74, 136.93, 129.51, 128.42, 126.64, 102.50, 98.38, 82.12, 76.59, 68.58, 67.25, 32.83, 26.31, 18.64, -3.47, -4.13; IR (thin film) 3343.0, 2928.9, 2857.1, 1677.2, 1471.5, 1377.9, 1286.9, 1249.9, 1156.6, 1136.2, 1075.7,

993.5, 834.2, 797.0, 779.8, 696.2, 646.8 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{22}\text{H}_{33}\text{Cl}_3\text{INO}_6\text{SiNa}$ ($\text{M}+\text{MeOH}+\text{Na}$)⁺ 690.0085, found 690.0113.

2-Deoxy-2-iodo-3-*O*-*tert*-butyldimethylsilyl-4,6-*O*-benzylidene- α -D-mannoopyranosyl

trichloroacetimidate (14). $[\alpha]_{\text{D}}^{25.2^\circ\text{C}} = -6.4$ ($c = 11.0$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 8.66 (s, 1H), 7.52-7.48 (m, 2H), 7.39-7.33 (m, 3H), 6.59 (s, 1H), 5.63 (s, 1H), 4.54 (dd, 1H, $J = 4.8, 1.2$ Hz), 4.31 (dd, 1H, $J = 10.3, 4.8$ Hz), 4.12 (app td, 1H, $J = 9.9, 4.8$ Hz), 4.05 (app t, 1H, $J = 9.3$ Hz), 3.87 (app t, 1H, $J = 10.1$ Hz), 3.39 (dd, 1H, $J = 9.1, 4.4$ Hz), 0.92 (s, 9H), 0.09 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 160.13, 137.35, 129.15, 128.33, 126.26, 101.98, 100.48, 80.88, 68.53, 67.79, 66.94, 35.40, 25.94, 18.45, -4.14, -4.77; IR (thin film) 3343.7, 1953.4, 2929.1, 2884.3, 2857.2, 1673.4, 1471.5, 1378.6, 1338.9, 1293.6, 1266.9, 1214.4, 1191.9, 1131.7, 1108.1, 1060.3, 1011.0, 967.1, 935.3, 903.2, 859.5, 837.7, 795.4, 780.6, 746.3, 697.2, 642.5 cm^{-1} .

Representative procedure for glycosidation using imidates 8a and 8b:

To a solution of acceptor **15** (21 mg, 0.052 mmol), imidate **8a** (47 mg, 0.074 mmol), and 4 Å MS in CH_2Cl_2 (7 mL) at -78°C was added TBDMS-OTf (4 μL , 0.017 mmol). The mixture was stirred at -78°C for 1h, then Et_3N (20 μL) was added. The reaction was allowed to warm to room temperature, and washed with saturated aqueous NaHCO_3 . The aqueous layer was extracted with CHCl_3 and the organic layers were dried (Na_2SO_4), filtered, concentrated under reduced pressure. The crude product was then chromatographed (4:1 hexanes:EtOAc) to afford disaccharides **18a** and **18b** as white foams (37 mg, 89%).

Methyl 2,3,4-Tri-*O*-benzoyl-6-*O*-(2-deoxy-2-iodo-3-*O*-*tert*-butyldimethylsilyl-4,6-*O*-benzylidene-D-glucopyranosyl)-(1→6)- β -D-glucopyranoside (18b). $[\alpha]_{\text{D}}^{24.1^\circ\text{C}} = +27.4$ ($c = 11.6$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 8.00-7.95 (m, 4H), 7.87 (m, 2H), 7.52 (m, 2H), 7.46-7.34 (m, 10H), 7.29 (m, 2H), 6.15 (app tt, 1H, $J = 9.6, 2.0$ Hz), 5.54 (app t, 1H, $J = 9.9$ Hz), 5.45 (s, 1H), 5.29-5.25 (m, 2H), 4.76 (d, 1H, $J = 9.2$ Hz), 4.32 (m, 1H), 4.29 (dd, 1H, $J = 10.5, 5.0$ Hz), 4.02 (dd, 1H, $J = 11.1, 2.4$ Hz), 3.94 (dd, 1H, $J = 9.8, 8.5$ Hz), 3.83 (dd, 1H, $J = 11.2, 6.4$ Hz), 3.76 (app t, 1H, $J = 9.5$ Hz), 3.70 (app t, 1H, $J = 10.2$ Hz), 3.53 (s, 3H), 3.43 (app td, 1H, $J = 9.6, 4.8$ Hz), 3.35 (app t, 1H, $J = 9.0$ Hz), 0.85 (s, 9H), 0.13 (s, 3H), -0.08 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.02, 165.52, 137.06, 133.62, 133.55, 133.25, 130.14, 130.10, 129.90, 129.47, 129.44, 129.33, 129.29, 128.64, 128.61, 128.47, 128.40, 126.63, 104.05, 102.40, 97.06, 82.49, 76.66, 72.27, 70.76, 69.93, 69.22, 68.89, 68.71, 66.58, 56.18, 35.51, 26.34, 18.67, -3.43, -4.14; IR (thin film) 2930.2, 2884.0, 2856.7, 1731.6, 1602.2, 1584.6, 1492.3, 1452.1, 1380.1, 1333.4, 1315.3, 1280.5, 1177.4, 1095.1, 1069.9, 1028.0, 980.3, 915.7, 838.5, 758.5, 709.2 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{47}\text{H}_{53}\text{IO}_{13}\text{SiNa}$ ($\text{M}+\text{Na}$)⁺ 1003.2198, found 1003.2191.

Methyl 2,3,4-Tri-*O*-benzoyl-6-*O*-(2-deoxy-2-iodo-3-*O*-*tert*-butyldimethylsilyl-4,6-*O*-benzylidene-D-glucopyranosyl)-(1→6)- α -D-glucopyranoside (18a). $[\alpha]_D^{24.2^\circ\text{C}} = +82.1$ ($c = 2.8$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 7.98 (m, 4H), 7.87 (m, 2H), 7.51 (m, 2H), 7.47-7.34 (m, 10H), 7.29 (m, 2H), 6.18 (app t, 1H, $J = 9.8$ Hz), 5.60 (app t, 1H, $J = 9.9$ Hz), 5.47 (s, 1H), 5.31 (dd, 1H, $J = 10.2, 3.6$ Hz), 5.27 (d, 1H, $J = 3.6$ Hz), 5.00 (d, 1H, $J = 3.2$ Hz), 4.35 (ddd, 1H, $J = 10.3, 6.9, 1.9$ Hz), 4.19 (dd, 1H, $J = 10.3, 4.9$ Hz), 4.18 (dd, 1H, $J = 10.1, 8.6$ Hz), 4.03 (app td, 1H, $J = 10.0, 4.9$ Hz), 3.95 (dd, 1H, $J = 10.3, 3.3$ Hz), 3.88 (dd, 1H, $J = 11.4, 6.8$ Hz), 3.68 (app t, 1H, $J = 10.3$ Hz), 3.67 (dd, 1H, $J = 11.4, 1.9$ Hz), 3.54 (s, 3H), 3.41 (dd, 1H, $J = 9.5, 8.8$ Hz), 0.86 (s, 9H), 0.14 (s, 3H), -0.05 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.05, 165.57, 137.33, 133.65, 133.55, 133.27, 130.17, 130.13, 129.90, 129.49, 129.35, 129.18, 128.67, 128.63, 128.49, 128.34, 126.72, 102.59, 100.73, 97.12, 83.40, 72.48, 72.35, 70.78, 69.75, 69.05, 67.26, 63.36, 55.91, 33.03, 26.38, 18.72, -3.46, -4.02; IR (thin film) 2928.9, 2855.6, 1731.8, 1602.0, 1451.8, 1376.3, 1315.1, 1279.1, 1261.3, 1157.1, 1132.7, 1093.1, 1069.7, 1027.2, 980.9, 853.1, 838.2, 780.0, 762.1, 708.6 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{47}\text{H}_{53}\text{IO}_{13}\text{SiNa}$ ($\text{M}+\text{Na}$) $^+$ 1003.2198, found 1003.2206.

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Methyl 2-*O*-Benzoyl-4,6-*O*-benzylidene-3-*O*-(2-deoxy-2-iodo-3-*O*-*tert*-butyldimethylsilyl-4,6-*O*-benzylidene-D-glucopyranosyl)-(1→3)- β -D-glucopyranoside (19). $[\alpha]_D^{24.1^\circ\text{C}} = +32.9$ ($c = 12.6$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 8.14 (m, 2H), 7.61 (m, 1H), 7.54-7.47 (m, 4H), 7.44-7.34 (m, 8H), 5.58 (s, 1H), 5.42 (s, 1H), 5.20 (dd, 1H, $J = 9.6, 3.9$ Hz), 5.08 (d, 1H, $J = 3.9$ Hz), 4.99 (d, 1H, $J = 9.0$ Hz), 4.50 (app t, 1H, $J = 9.4$ Hz), 4.32 (dd, 1H, $J = 10.1, 4.7$ Hz), 4.20 (dd, 1H, $J = 10.4, 4.9$ Hz), 3.94 (app td, 1H, $J = 9.9, 4.7$ Hz), 3.84 (dd, 1H, $J = 9.7, 8.3$ Hz), 3.83 (app t, 1H, $J = 10.3$ Hz), 3.75 (app t, 1H, $J = 9.4$ Hz), 3.73 (app t, 1H, $J = 9.4$ Hz), 3.67 (app t, 1H, $J = 10.1$ Hz), 3.39 (s, 3H), 3.38 (m, 1H), 3.32 (app td, 1H, $J = 9.6, 4.8$ Hz), 0.79 (s, 9H), 0.03 (s, 3H), -0.12 (s, 3H); ^{13}C NMR (126 MHz, CDCl_3) δ 166.10, 137.49, 137.08, 133.49, 130.33, 130.06, 129.39, 129.31, 128.61, 128.40, 128.36, 126.60, 126.29, 103.28, 102.29, 101.52, 97.78, 82.41, 80.09, 76.80, 75.75, 73.67, 69.14, 68.82, 66.39, 62.48, 55.65, 35.88, 26.26, 18.57, -3.52, -4.15; IR (thin film) 2953.0, 2930.1, 2880.9, 1857.4, 1722.6, 1602.4, 1470.5, 1452.5, 1378.0, 1333.0, 1314.3, 1271.3, 1217.1, 1178.3, 1094.9, 1070.7, 1052.4, 1028.8, 999.7, 915.1, 838.4, 779.5, 758.8, 711.1, 698.3, 650.6, 666.3 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{40}\text{H}_{49}\text{IO}_{11}\text{SiNa}$ ($\text{M}+\text{Na}$) $^+$ 883.1987, found 883.1992.

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Methyl 2,3,6-Tri-*O*-benzoyl-4-*O*-(2-deoxy-2-iodo-3-*O*-*tert*-butyldimethylsilyl-4,6-*O*-benzylidene-D-glucopyranosyl)-(1→4)- β -D-glucopyranoside (20). $[\alpha]_D^{24.1^\circ\text{C}} = +86.9$ ($c = 10.5$, CHCl_3); ^1H NMR (500 MHz, CDCl_3) δ 8.13 (m, 2H), 8.03 (m, 2H), 8.00 (m, 2H), 7.63 (m, 1H), 7.56-7.49 (m, 4H), 7.43 (app t, 2H, $J = 7.8$ Hz), 7.38 (app t, 2H, $J = 7.8$ Hz), 7.33-7.30 (m, 5H), 5.99 (dd, 1H, $J = 10.3, 8.8$ Hz), 5.23 (dd, 1H, $J = 10.3, 3.7$ Hz), 5.14 (s, 1H), 5.13 (d, 1H, $J = 3.7$ Hz), 4.96-4.91 (m, 2H), 4.81 (d, 1H, $J = 8.8$ Hz), 4.26 (app dt, 1H, $J = 10.3, 3.0$ Hz), 4.20 (app t, 1H, $J = 9.3$ Hz), 3.84-3.79 (m, 2H), 3.72 (app t, 1H, $J = 9.4$ Hz), 3.46 (s, 3H), 3.09-3.02 (m, 2H), 2.81 (m, 1H), 0.82 (s, 9H), 0.07 (s, 3H), -0.15 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.29, 166.17, 165.41, 136.86, 133.54, 133.52, 133.39, 130.37, 130.14, 129.86, 129.42, 129.28, 128.78, 128.63, 128.60, 128.32, 126.56, 102.85, 102.16, 97.03, 82.11, 76.46, 75.87, 72.01, 71.22, 68.52, 68.13, 66.33, 63.77, 55.74, 36.17, 26.31, 18.62, -3.49, -4.21; IR (thin film) 3066.9, 3034.5, 2955.3, 2929.5, 2883.6, 2856.6, 1727.5, 1602.2, 1584.6, 1492.4, 1452.1, 1379.4, 1333.7, 1314.3, 1273.2, 1176.9, 1110.7, 1094.7, 1069.9, 1028.2, 983.7, 915.9, 838.3, 759.8, 710.3 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{47}\text{H}_{53}\text{IO}_{13}\text{SiNa}$ ($\text{M}+\text{Na}$) $^+$ 1003.2198, found 1003.2206.

It is worth noting that we previously reported exclusive α -glycosidation using 2-deoxy-2-iodo- α -mannopyranosyl acetates.³ In view of the TMS-OTf-promoted β -selective glycosidations using 2-*O*-benzyl-4,6-*O*-benzylidene mannopyranosyl trichloroacetimidates reported by Schmidt,⁴ we reasoned that we should also observe β -selectivity with donor **14** if the iodine substituent is non-participating in the mechanistic pathway. The β -selectivity was attributed to the torsional effect of the benzylidene acetal. We observed that the 2-iodo substituent, the glycosidation of acceptor **15** with imidate **14** proceeded with exclusive formation of the α -mannoside **26**, lending support to the participatory effect of the iodine substituent.

Methyl 2,3,4-Tri-*O*-benzoyl-6-*O*-(2-deoxy-2-iodo-3-*O*-tert-butyldimethylsilyl-4,6-*O*-benzylidene-D-mannopyranosyl)-(1→6)- α -D-glucopyranoside (26**).** ¹H NMR (500 MHz, CDCl₃) δ 7.99 (m, 2H), 7.95 (m, 2H), 7.87 (m, 2H), 7.54-7.27 (m, 10H), 6.16 (app t, 1H, *J* = 9.9 Hz), 5.58 (app t, 1H, *J* = 9.9 Hz), 5.56 (s, 1H), 5.29-5.24 (m, 3H), 4.28 (dd, 1H, *J* = 4.5, 0.9 Hz), 4.23 (ddd, 1H, *J* = 10.2, 5.3, 3.0 Hz), 4.10 (dd, 1H, *J* = 9.8, 4.0 Hz), 3.90-3.82 (m, 3H), 3.77 (app t, 1H, *J* = 9.9 Hz), 3.64 (dd, 1H, *J* = 11.0, 3.0 Hz), 3.49 (s, 3H), 3.38 (dd, 1H, *J* = 8.6, 4.5 Hz), 0.90 (s, 9H), 0.08 (s, 3H), 0.04 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.03, 166.01, 165.45, 137.72, 133.65, 133.59, 133.30, 130.13, 130.04, 129.86, 129.38, 129.21, 129.01, 128.96, 128.69, 128.62, 128.48, 128.21, 126.34, 103.15, 101.84, 97.21, 81.29, 72.26, 70.56, 69.83, 68.65, 68.38, 66.79, 66.68, 64.96, 55.77, 38.34, 25.98, 18.41, -4.13, -4.83; IR (thin film) 2951.3, 2929.0, 2855.7, 1732.0, 1602.0, 1451.8, 1377.1, 1315.5, 1278.6, 1264.6, 1214.5, 1177.9, 1159.0, 1106.0, 1068.9, 1026.7, 918.4, 860.9, 838.1, 780.1, 751.1, 708.8 cm⁻¹; HRMS (ES) calcd for C₄₇H₅₃IO₁₃SiNa (M+Na)⁺ 1003.2198, found 1003.2188.

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⁴ Weingart, R.; Schmidt, R. R. *Tetrahedron Lett.* **2000**, *41*, 8753.