Supplemental Information

"A Convenient, *in situ* Generation of Anhydrous Hydrogen Iodide for the Preparation of α-Glycosyl Iodides and Vicinal Iodohydrins, and for the Catalysis of Ferrier Glycosylation"

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2,3,4,6-Tetra-*O*-acetyl-α-D-glucopyranosyl Iodide (10). (1) From the β-Per-*O*-acetate Anomer 8: To a flame-dried, 50-mL, round-bottom flask equipped with a stir bar, reflux condenser, and N_2 inlet, were added per-*O*-acetyl-β-D-glucose (0.83 g, 2.13 mmol), CH_2Cl_2 (22 mL), I_2 (0.294 g, 1.16 mmol), and thiolacetic acid (0.17 mL, 2.39 mmol). The solution was heated at reflux for 30 min. The reaction mixture was cooled to room temperature and washed first with 10% aqueous $Na_2S_2O_3$ (1 x 10 mL) and then with water (1 x 10 mL). The organic layer was dried (Na_2SO_4) and concentrated *in vacuo*. Purification of the crude yellow oil by silica gel flash column chromatography (hexanes/ethyl acetate = 3:1) gave 0.75 g (77%) of the α-glucopyranosyl iodide **10** as a white amorphous solid.

From α-anomer 9: Following the procedure described above, per-*O*-acetyl-α-D-glucose (0.928 g, 2.38 mmol), CH_2Cl_2 (25 mL), I_2 (0.331 g, 1.30 mmol), and thiolacetic acid (0.19 mL, 2.65 mmol) were dissolved in 25 mL of CH_2Cl_2. After purification by silica gel chromatography (hexanes/ethyl acetate 2:1), 0.642 g (59%) of the glucosyl iodide was isolated as a white amorphous solid. Identification of the product compound was ascertained by correlation of the ^{1}H NMR spectrum to literature reports.[1]

2,3,4,6-Tetra-*O*-acetyl-α-D-mannopyranosyl Iodide (12). Following the procedure described for the synthesis of **10**, per-*O*-acetyl-α-D-mannose (**11**) (0.454 g, 1.16 mmol), I_2 (0.162 g, 0.64 mmol), and thiolacetic acid (0.09 mL, 1.28 mmol) were dissolved in 12 mL of CH_2Cl_2. After purification by silica gel flash column chromatography (hexanes/ethyl acetate 2:1), 0.399 g (76%) of the mannosyl iodide **12** was isolated as a white amorphous solid. Identification of the product compound was ascertained by correlation of the ^{1}H NMR spectrum to literature reports.[1]

2,3,6,2′,3′,4′,6′-Hepta-*O*-acetyl-α-lactosyl Iodide (1b). To a flame-dried, 500-mL, round-bottom flask equipped with a stir bar, reflux condenser, and N_2 inlet, were added per-*O*-acetyl-α-D-lactose (**13**) (12.84 g, 18.9 mmol), CH_2Cl_2 (300 mL), I_2 (4.80 g, 18.9 mmol), and thiolacetic acid (2.7 mL, 37.7 mmol). The solution was heated at reflux for 20 min. The reaction mixture was cooled to room temperature and washed first with 10% aqueous $Na_2S_2O_3$ (1 x 200 mL) and then with water (1 x 100 mL). The organic layer was dried (Na_2SO_4, K_2CO_3) and concentrated *in vacuo*. Purification of the crude yellow oil by silica gel flash column chromatography (hexane/ethyl acetate = 2:1) gave 9.03 g (64%) of the lactosyl iodide **1b** as a white amorphous solid. Identification of the product compound was ascertained by correlation of the ^1H NMR spectrum to literature reports.[1]

2,3,6,2′,3′,4′,6′-Hepta-*O*-acetyl-α-D-maltosyl Iodide (16). From the Per-*O*-acetyl-maltose β-Anomer (14): Following the procedure describd for the synthesis of **10**, per-*O*-acetyl-β-D-maltose (**14**) (0.305 g, 0.448 mmol), CH_2Cl_2 (8 mL), I_2 (0.063 g, 0.246 mmol), and thiolacetic acid (35 μL, 0.489 mmol) were dissolved in 8 mL of CH_2Cl_2. After purification of the prude product by silica gel flash column chromatography (hexanes/ethyl acetate = 1:1), 0.237 g (71%) of the maltosyl iodide **16** was obtained as a white amorphous solid.

From α-Anomer 15: To a flame-dried, 5-mL, round-bottom flask equipped with a stir bar, reflux condenser, and N_2 inlet, were added, per-*O*-acetyl-α-D-maltose (0.075 g, 0.11 mmol), CH_2Cl_2 (2 mL), and an HI solution (1.17 mL of 0.105 M HI, prepared by dissolving 0.133 g of I_2 and 75 μL of thiolacetic acid to the mark with CH_2Cl_2 in a 10.00-mL volumetric flask). The solution was heated at reflux for 30 min. The reaction mixture was cooled to room temperature and washed first with 10% aqueous $Na_2S_2O_3$ (1 x 0.5 mL) and then with water (1 x 0.5 mL). The organic layer was dried (Na_2SO_4) and concentrated *in vacuo*. After purification of the crude reaction product by silica gel flash column chromatography (hexanes/ethyl acetate 2:1), 44.5 mg (54%) of the maltosyl iodide **16** was obtained as a white amorphous solid. ^1H NMR (400 MHz, $CDCl_3$) δ 6.90 (d, 1H, H-1, $J_{1,2}$ = 4.4 Hz), 5.52 (dd, 1H, H-3, $J_{3,2}$ = 8.8 Hz, $J_{3,4}$ = 9.5 Hz), 5.42 (d, 1H, H-1′, $J_{1',2'}$ = 3.6 Hz), 5.38 (dd, 1H, H-3′, $J_{3',4'}$ = 9.8

Hz, $J_{3',2'}$ = 10.0 Hz), 5.08 (dd, 1H, H-4′, $J_{4',3'}$ = 9.8 Hz, $J_{4',5'}$ = 9.8 Hz), 4.88 (dd, 1H, H-2′, $J_{2',1'}$ = 3.6 Hz, $J_{2',3'}$ = 10.6 Hz), 4.28 and 4.51 (ABq, 2H, H-6 and 7, J_{AB} = 12.5 Hz; 4.28 and 4.51 peaks are further split by 2.3 Hz and 3.7 Hz, respectively), 4.11 (dd, 1H, H-2, $J_{2,1}$ = 4.4 Hz, $J_{2,3}$ = 8.8 Hz), 4.09 (dd, 1H, H-4, $J_{4,3}$ = 9.5 Hz, $J_{4,5}$ = 9.9 Hz), 4.06 and 4.25 (ABq, 2H, H-6′and 7′ J_{AB} = 12.4 Hz; 4.06 both 4.25 and 4.06 peaks are further split by 3.6 Hz), 4.00-4.04 (m, 1H, H-5), 3.96 (ddd, 1H, H-5′, $J_{5',4'}$ = 9.8 Hz, $J_{5',6'}$ =2.6 Hz, $J_{5',7'}$ = 2.6 Hz), 2.15 (s, 3H,OAc), 2.10 (s, 3H,OAc), 2.09 (s, 3H,OAc), 2.07 (s, 3H, OAc), 2.04 (s, 6H, 2 x OAc), 2.02 (s, 3H,OAc). ^{1}H NMR (400 MHz, benzene-d$_6$) δ 6.64 (d, 1H, H-1, $J_{1,2}$ = 4.4 Hz), 5.82 (dd, 1H, H-3′, $J_{3',4'}$ = 9.5 Hz, $J_{3',2'}$ = 9.9 Hz), 5.76 (dd, 1H, H-3, $J_{3,4}$ = 9.2 Hz, $J_{3,2}$ = 9.5 Hz), 5.55 (d, 1H, H-1′, $J_{1',2'}$ = 4.0), 5.40 (dd, 1H, H-4′, $J_{4',3'}$ = 9.5 Hz, $J_{4',5'}$ = 9.9 Hz), 5.07 (dd, 1H, H-2′, $J_{2',1'}$ = 4.0 Hz, $J_{2',3'}$ = 9.9 Hz), 4.34 and 4.40 (ABq, 2H, H-6′, H-7′, J_{AB} = 12.4 Hz; 4.34 and 4.40 peaks are further split by 2.6 Hz and 3.3 Hz, respectively), 4.25 and 3.95 (ABq, 2H, H-6, H-7, J_{AB} = 12.5 Hz; 4.25 and 3.95 peaks are further split by 2.6 Hz and ~3 Hz, respectively), 4.09 (ddd, 1H, H-5′, $J_{5',4'}$ = 9.9 Hz, $J_{5',6'}$ = 3.3 Hz, $J_{5',7''}$ = 2.6 Hz), 3.99 (dd, 1H, H-2, $J_{2,1}$ = 4.4 Hz, $J_{2,3}$ = 9.5 Hz), 3.97 (dd, 1H, H-4, $J_{4,3}$ = 9.2 Hz, $J_{4,5}$ = 9.8 Hz), 3.87 (ddd, 1H, H-5, $J_{5,6}$ = 2.5 Hz, $J_{5,7}$ = ~3.0, $J_{5,4}$ = 9.8 Hz), 1.86 (s, 3H, OAc), 1.78 (s, 3H, OAc), 1.76 (s, 3H, OAc), 1.71 (s, 3H, OAc), 1.68 (s, 3H, OAc), 1.67 (s, 3H, OAc), 1.58 (s, 3H, OAc). ^{13}C NMR (100.58 MHz, CDCl$_3$) δ 170.69, 170.49, 170.27, 169.87, 169.66, 169.49, 169.43, 95.85 (C-1′), 75.18 (C-5), 73.85 (C-3), 72.82 (C-1), 71.41 (C-4), 70.73 (C-2), 70.04 (C-2′), 69.29 (C-3′), 68.68 (C-5′), 67.97 (C-4′), 61.77 (C-6), 61.39 (C-6′), 22.66, 20.86, 20.77, 20.77, 20.68, 20.65, 20.59. ^{13}C NMR (100.58 MHz, benzene-d$_6$) δ 170.57, 170.00, 169.54, 169.37, 169.20, 169.00, 169.00, 96.24 (C-1′), 75.64 (C-5), 74.44 (C-3), 72.92 (C-1), 71.56 (C-4), 70.93 (C-2), 70.62 (C-2′), 69.90 (C-3′), 69.24 (C-5′), 68.77 (C-4′), 61.86

(C-6), 61.64 (C-6′), 20.59, 20.38, 20.26, 20.22, 20.16, 20.14, 20.08. HRMS. Calcd for $C_{26}H_{39}NO_{17}I$ ($[M+ NH_4]^+$): m/z 764.1263. Found: m/z 764.1233.

General Method for the Preparation of β-Iodohydrins from Epoxides: To a flame-dried, 25-mL, round-bottom flask equipped with a stir bar, rubber septum, and N_2 inlet were added CH_2Cl_2 (15 mL), I_2 (1.04 mmol), and thiolacetic acid (2.07 mmol). The epoxide group-containing compound (2.06 mmol) was added to the stirred solution. The resulting solution was stirred at room temperature for 20 min and then washed successively with 10% aqueous $NaHCO_3$ (1 x 5 mL) and water (1 x 10 mL). The organic layer was dried ($MgSO_4$) and evaporated *in vacuo*. The crude oil thus obtained was purified by silica gel flash column chromatography (hexanes/CH_2Cl_2 1:1).

General Method for the Glycosylation of Thiols and Alcohols: To a flame-dried, 25 mL, round-bottom flask equipped with a stir bar, reflux condenser, and N_2 inlet is added tri-*O*-acetyl-D-glucal (0.375 mmol), CH_2Cl_2 (8 mL), the thiol or alcohol compound (0.44 mmol), and a 5 mol% HI solution (75 μL of a 0.24 M solution of HI, prepared by dissolving 0.158 g of I_2 and 90 μL of thiolacetic acid in CH_2Cl_2 to the mark with in a 10.00 mL-volumetric flask). The solution is heated at reflux for 30 min. The reaction mixture is cooled to room temperature and washed successively with aqueous $NaHCO_3$ (1 x 4 mL) and with water (1 x 4 mL). The organic layer is dried ($MgSO_4$), and concentrated *in vacuo*. The resulting crude oil is purified by silica gel flash column chromatography (CH_2Cl_2/acetone 20:1).

Methyl-α-D-[2,3,4-Tri-*O*-acetyl-6-*O*-(4′,6′-di-*O*-acetyl-2′,3′-dideoxy-α-D-hex-2′-enopyranosyl)]glucopyranoside (37). To a flame-dried, 25-mL, round-bottom flask equipped with a stir bar, reflux condenser, and N_2 inlet were added tri-*O*-acetyl-D-glucal (0.102 g, 0.375 mmol), CH_2Cl_2 (8 mL), methyl-α-D-(2,3,4-tri-*O*-acetyl)glucoside (**36**) (0.141 g, 0.44 mmol), and 5 mol% HI solution (75 μL of 0.24 M solution of HI, prepared by dissolving 0.158 g of I_2 and 0.125 mL of 1,3-propanedithiol to the mark with CH_2Cl_2 in a 10.00-mL volumetric flask). The solution was heated at reflux for 1 hour, then cooled to room temperature. The reaction mixture was washed successively with $NaHCO_3$ (1 x 4 mL) and with water (1 x 4 mL). The organic layer was dried ($MgSO_4$) and concentrated *in vacuo*. Purification of the resulting crude product by silica gel flash column chromatography (CH_2Cl_2/acetone 20:1) afforded 0.16 g (80%) of **37** as a white amorphous solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (ddd, 1H, H-2′, $J_{2',3'} = 10.6$ Hz, $J_{2',1'} = 1.1$ Hz, $J_{2',4'} = 1.0$ Hz), 5.84 (ddd, 1H, H-3′, $J_{3',2'} = 10.6$ Hz, $J_{3',1'} = 2.5$ Hz, $J_{3',4'} = 1.8$ Hz), 5.48 (dd, 1H, H-3, $J_{3,2} = 10.3$ Hz, $J_{3,4} = 9.3$ Hz), 5.31-5.36 (m, 1H, H-4′), 5.17 (1H, H-4, $J_{4,5} = 10.1$ Hz, $J_{4,3} = 9.3$ Hz), 5.05 (ddd, 1H, H-1′, $J_{1',3'} = 2.5$ Hz, $J_{1',2'} = 1.1$, $J_{1',4'} \approx 1$), 4.95 (d, 1H, H-1, $J_{1,2} = 3.5$ Hz), 4.89 (dd, 1H, H-2, $J_{2,3} = 10.3$ Hz, $J_{2,1} = 3.5$ Hz), 4.28 and 4.09 (ABq, 2H, H-6′ and 7′, $J_{AB} = 12.4$ Hz; 4.28 and 4.09 peaks are further split by 4.7 and 2.2 Hz, respectively), 4.09 (ddd, 1H, H-5′, $J_{5',4'} = 9.5$ Hz, $J_{5',6'} = 4.7$ Hz, $J_{5',7'} = 2.2$ Hz), 3.93 (ddd, 1H, H-5, $J_{5,4} = 10.1$ Hz, $J_{5,6} = 3.8$ Hz, $J_{5,7} = 2.7$ Hz), 3.84 and 3.63 (ABq, 2H, H-6 and 7, $J_{AB} = 10.3$ Hz; 3.84 and 3.63 peaks are further split by 3.8 and 2.7 Hz, respectively), 3.41 (s, 3H, OCH_3), 2.10 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.05 (s, 3H, OAc), 2.01 (s, 3H, OAc). ^{13}C NMR (100.58 MHz, $CDCl_3$) δ 170.74, 170.33, 170.17, 170.16, 169.64, 129.56 (C-2′), 127.19 (C-3′), 96.73 (C-1), 94.55 (C-1′), 70.81 (C-2), 70.39 (C-3), 69.02 (C-4), 67.94 (C-5), 66.94 (C-5′), 66.27 (C-6), 65.05 (C-4′), 62.68 (C-6′), 55.45 ($-OCH_3$), 20.99, 20.82, 20.75, 20.74, 20.70. $[\alpha]_D^{22}$ +116.1° (*c* = 4.42, $CHCl_3$). Anal. Calcd for $C_{23}H_{32}O_{14} \cdot 0.5\ H_2O$: C, 51.02; H, 6.14. Found: C, 51.12; H, 5.97. HRMS. Calcd for $C_{23}H_{36}NO_{14}$ ($[M + NH_4]^+$): m/z 550.2136. Found: m/z 550.2116.

[1] Thiem, J.; Meyer, B. *Chem.Ber.* **1980**, *113*, 3075-3085.