Stereoselective Synthesis of 2-Deoxy- β -Galactosides via 2-Deoxy-2-bromo- and 2-Deoxy-2-iodo-galactopyranosyl Donors

Supporting Information

Timothy B. Durham and William R. Roush*

General Methods: All reaction solvents were purified before use. Tetrahydrofuran, dichloromethane, and toluene were purified by passage through a solvent column¹ composed of activated A-1 alumina. Unless indicated, all commercial reagents were used as received without further purification.

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 125 MHz respectively. The proton signal of residual, non-deuterated solvent (δ 7.26 ppm for CHCl₃, δ 7.16 ppm for C₆D₅H) or tetramethylsilane (δ 0 ppm, CDCl₃) was used as an internal reference for ¹H spectra. For ¹³C spectra, chemical shifts are reported relative to the δ 77.23 ppm resonance of CDCl₃ or the δ 128.39 ppm resonance of C₆D₆. 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 stain (a mixture of ceric sulfate and ammonium molybdate in aqueous sulfuric acid), KMnO₄, or *p*-anisaldehyde solutions. 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.

HPLC purifications were performed by using a HPLC system composed of two Rainin HPXL 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 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

4-Acetyl-6-bromo-3-(tert-Butyldimethylsilyl)-D-galactal (SI-1): Galactal derivative **4**² (2.34 g, 5.13 mmol), Bu₄NBr (16.9 g, 52.3 mmol), and activated 3 Å MS (~5 g) were suspended in dry toluene under a nitrogen atmosphere. The suspension was stirred vigorously and slowly warmed to 95 °C. After 2 days, the reaction was cooled to 23 °C and then further cooled with an ice-bath to induce precipitation of the salt residues. The solid precipitates were removed by vacuum filtration and the filtrate was concentrated on a rotary evaporator to give an oil. The oil was purified by flash chromatography (10:1 hexanes/EtOAc) to provide the title compound as a yellow oil (1.54 g, 82%): [α]_D^{25°C} = -43.5° (c = 1.3, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 6.36 (dd, *J* = 6.00, 1.00 Hz, 1H), 5.31 (dd, *J* = 3.50, 2.50 Hz, 1H), 4.72 (ddd, *J* = 6.12, 3.12, 0.87, 1H), 4.49 (td, *J* = 4.33, 1.62 Hz, 1H), 4.29 (m, 1H), 3.66 (dd, *J* = 11.00, 8.50 Hz, 1H), 3.48 (dd, *J* = 11.00, 4.50, 1H), 2.14 (s, 3H), 0.88 (s, 9H), 0.10 (s, 3H), 0.06 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.40, 143.41, 103.61, 75.67, 68.12, 63.01, 30.08, 25.87, 21.12, 18.27, -

4.72, -4.89; IR (thin film) 1749 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{14}\text{H}_{25}\text{BrO}_4\text{SiNa}$ ($\text{M}+\text{Na}$) $^{+}$ 524.9920, found 524.9925 m/z .

Representative Procedure for the Haloacetoxylation of Galactals: Galactal derivative **SI-1** (318 mg, 0.870 mmol) was dissolved in dry CH_2Cl_2 (15 mL) under nitrogen in a foil-covered round-bottom flask. To the resulting solution, at 23 $^{\circ}\text{C}$, was added AcOH (100 μL , 1.75 mmol) followed by *N*-iodosuccinimide (324 mg, 1.44 mmol). After 40 min, the starting galactal was consumed and the reaction was quenched by the addition of 10 % $\text{Na}_2\text{S}_2\text{O}_3$ (20 mL) and the resulting mixture was stirred vigorously for 5 min. The mixture was diluted with EtOAc (100 mL), transferred to a separatory funnel, and the aqueous layer was discarded. The organic phase was washed with 10 % $\text{Na}_2\text{S}_2\text{O}_3$ (10 mL), saturated NaCl solution, dried over Na_2SO_4 , filtered, and concentrated. The residue was purified by chromatography (10:1 hexanes/EtOAc) to provide acetates **5** (164 mg, 34%) and **6** (237 mg, 50%) as yellow oils. The anomers of **6** were separable by HPLC, under the same isocratic solvent conditions, providing samples for analytical purposes. The 2-bromo-galactosyl acetate derivatives **SI-6**, **SI-7**, and **17** were prepared using the same general protocol by substituting NBS for NIS as the halogen source.

Acetyl 4-*O*-acetyl-6-bromo-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-2-iodo- α -D-talopyranoside (5**):** partial data: $[\alpha]_{\text{D}}^{25^{\circ}\text{C}} = +32.7^{\circ}$ ($c = 0.9$, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 5.44 (d, $J = 2.00$ Hz, 1H), 4.27 (td, $J = 6.75$, 2.00, 1H), 4.12 (d, $J = 5.50$ Hz, 1H), 3.60 (app t, $J = 4.25$ Hz, 1H), 3.42 (dd, $J = 10.50$, 7.00, 1H), 3.36 (dd, $J = 10.75$, 6.75, 1H), 2.18 (s, 3H), 2.15 (s, 3H), 0.92 (s, 9H), 0.13 (s, 3H), 0.13 (s, 3H); IR (thin film) 1748 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{16}\text{H}_{28}\text{BrIO}_6\text{SiNa}$ ($\text{M}+\text{Na}$) $^{+}$ 572.9781, found 572.9795 m/z .

Acetyl 4-*O*-acetyl-6-bromo-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-2-iodo- α -D-galactopyranoside (α -6**):** $[\alpha]_{\text{D}}^{27^{\circ}\text{C}} = +91.7^{\circ}$ ($c = 0.6$, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 6.38 (d, $J = 3.50$, 1H), 5.39 (app d, $J = 2.00$, 1H), 4.36 (dd, $J = 10.75$, 3.25, 1H), 4.23 (dd, $J = 7.50$, 6.50, 1H), 4.13 (dd, $J = 11.00$, 3.00, 1H), 3.26 (app d, $J = 6.50$, 1H), 2.19 (s, 3H), 2.14 (s, 3H), 0.91 (s, 9H), 0.26 (s, 3H), 0.16 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.97, 168.98, 93.15, 72.42, 70.77, 70.14, 29.02, 28.72, 25.92, 20.95, 20.92, 18.09, -3.94, -4.05; IR (thin film) 1755 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{16}\text{H}_{28}\text{BrIO}_6\text{SiNa}$ ($\text{M}+\text{Na}$) $^{+}$ 572.9781, found 572.9783 m/z .

Acetyl 4-*O*-acetyl-6-bromo-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-2-iodo- β -D-galactopyranoside (β -6**):** $[\alpha]_{\text{D}}^{27^{\circ}\text{C}} = +15.0^{\circ}$ ($c = 1.5$, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 5.90 (d, $J = 9.50$ Hz, 1H), 5.29 (dd, $J = 3.25$, 0.75 Hz, 1H), 4.13 (dd, $J = 10.50$, 9.50 Hz, 1H), 3.96 (td, $J = 6.00$, 1.00, 1H), 3.93 (dd, $J = 10.50$, 3.50, 1H), 3.34 (dd, $J = 11.00$, 7.00, 1H), 3.30 (dd, $J = 10.75$, 6.25 Hz, 1H), 2.18 (s, 3H), 2.15 (s, 3H), 0.91 (s, 3H), 0.25 (s, 3H), 0.15 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.97, 168.91, 94.58, 75.24, 74.45, 70.11, 31.81, 28.14, 25.92, 20.99, 20.91, 18.11, -3.97, -4.01; IR (thin film) 1773, 1749 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{16}\text{H}_{28}\text{BrIO}_6\text{SiNa}$ ($\text{M}+\text{Na}$) $^{+}$ 572.9781, found 572.9782 m/z .

Representative Procedure for the Conversion of Anomeric Acetates to Trichloroacetimidates. A mixture of anomeric galactosides **6** (33 mg, 0.0599 mmol) was dissolved in 4 : 1 MeOH : Et₂O (1 mL). To this solution was added aqueous 35 % wt hydrazine solution (7 μL , 0.221 mmol). The resulting solution was stirred for 16 h and then diluted with EtOAc (10 mL). The organic solution was washed with water (10 mL). The aqueous wash was then extracted with EtOAc (4 x 10mL). All of the organic phases were combined, washed with saturated NaCl solution, dried over Na_2SO_4 , filtered, and concentrated. The residue was purified by flash chromatography (4:1 hexanes/EtOAc) to provide the hemiacetal (23 mg) as a white solid. This material was used directly in the next reaction.

The hemiacetal (23 mg, 0.045 mmol) was dissolved in dry CH₂Cl₂ under nitrogen and cooled to 0 °C. Cl₃CCN (0.3 mL) was added and the solution allowed to cool for 5 min. DBU (2 µL, 0.013 mmol) was then added and the solution became yellow. The solution was stirred for 1 h and then concentrated on the rotary evaporator. The residue was *quickly* chromatographed on a short column of silica gel (10:1 hexanes/EtOAc) to give imidates **2** as an inseparable 25 : 75 β/α mixture of anomers (determined by ¹H NMR). This material was dried under vacuum and then used directly in the next reaction.

General Procedure for Glycosidation Reactions. The donor (2 equiv) and acceptor (1 equiv) were dissolved in dry CH₂Cl₂ (concentration of the acceptor was 0.15 – 0.22 mmol) under nitrogen and cooled to the indicated temperature (–78 °C, –23 °C, or 0 °C). To the cooled solution was then added the promotor (TMSOTf or TBSOTf, 0.1 to 0.5 equiv). The reaction was monitored by TLC analysis. When all of the acceptor was consumed, the reaction was quenched with Et₃N and warmed to 23 °C. The resulting mixture was diluted with EtOAc and washed with saturated sodium bicarbonate solution, saturated NaCl solution, dried over Na₂SO₄, filtered, and concentrated on a rotary evaporator. The diastereoselectivity of the reaction was then determined by ¹H NMR analysis, after which the crude mixture was purified by flash chromatography. In some cases, additional preparative HPLC purification was required to provide materials for analytical purposes.

Methyl 4,6-benzylidene-2-*O*-benzoyl-3-*O*-(4-*O*-acetyl-6-bromo-3-*O*-(*tert*-butyldimethylsilyl)-2-deoxy-2-iodo-β-*D*-galactopyranosyl)-(1→3)-α-*D*-glucopyranoside (β-8). Purification by flash chromatography (10 : 1 hexanes/ EtOAc) provided the title compound as a yellow oil: [α]_D^{25°C} = +36.6° (c = 1.3, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 8.16 (m, 2H), 7.37-7.61 (m, 8H), 5.61 (s, 1H), 5.21 (dd, *J* = 9.75, 3.75, 1H), 5.15 (d, *J* = 3.00, 1H), 5.08 (d, *J* = 4.00 Hz, 1H), 4.89 (d, *J* = 9.50 Hz, 1H), 4.52 (app t, *J* = 9.25 Hz, 1H), 4.31 (dd, *J* = 10.00, 5.00 Hz, 1H), 3.95 (m, 2H), 3.84 (m, 2H) 3.67 (dd, *J* = 10.75, 3.25 Hz, 1H), 3.54 (app t, *J* = 6.50 Hz, 1H) 3.39 (s, 3H), 3.20 (dd, *J* = 10.50, 7.50 Hz, 1H), 3.15 (dd, *J* = 10.50, 6.00 Hz, 1H) 2.04 (s, 3H), 0.82 (s, 9H), 0.11 (s, 3H), 0.05 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 170.06, 166.08, 137.50, 133.46, 1340.45, 130.04, 129.40, 128.54, 126.46, 102.98, 101.81, 97.77, 80.64, 76.26, 74.57, 74.21, 73.40, 70.04, 69.20, 62.31, 55.69, 34.77, 29.92, 28.46, 25.88, 20.89, 18.03, –3.98, –4.04; IR (thin film) 1752, 1725 cm^{–1}; HRMS (ES) calcd for C₃₅H₄₆BrIO₁₁SiNa (M+Na)⁺ 899.0935, found 899.0948 *m/z*.

3,4-Bis-(*O*-benzyl)-6-tosyloxy-*D*-galactal (SI-3). Galactal **SI-2**³ (790 mg, 2.42 mmol), TsCl (516 mg, 2.71 mmol), and DMAP (303 mg, 2.48 mmol) were dissolved in dry CH₂Cl₂ (25 mL) under a nitrogen atmosphere. The use of ≥ 1 equiv of DMAP was necessary in order for the reaction to go to completion. To the resulting solution was then added Et₃N (340 µL, 2.44 mmol), and the reaction mixture was stirred for 3 h. The reaction was then filtered through a pad of silica (4:1 hexanes/EtOAc) to provide the title compound as a yellow oil (1.11 g, 95%): [α]_D^{26°C} = –11.2° (c = 0.6, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 7.73 (m, 2H), 7.22-7.35 (m, 12H), 6.17 (dd, *J* = 6.50, 1.00 Hz, 1H), 4.85 (dd, *J* = 6.50, 4.50 Hz, 1H), 4.71 (A of AB, *J* = 12.00 Hz, 1H), 4.62 (A of AB, *J* = 11.50 Hz, 1H), 4.57 (B of AB, *J* = 11.50 Hz, 1H), 4.52 (B of AB, *J* = 12.00 Hz, 1H), 4.30 (m, 2H), 4.02 (app t, *J* = 4.00 Hz, 1H), 3.88 (app t, *J* = 4.00 Hz, 1H), 2.40 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 144.76, 143.59, 138.37, 137.72, 132.87, 129.84, 128.50, 128.45, 128.05, 127.95, 127.87, 127.67, 127.54, 99.69, 73.68, 72.53, 72.29, 71.22, 68.32, 68.10, 21.80; IR (thin film) 1644, 1362 cm^{–1}; HRMS (ES) calcd for C₂₇H₂₈O₆SN_a (M+Na)⁺ 503.1504, found 503.1501 *m/z*.

Acetyl 3,4-bis-(*O*-benzyl)-2-deoxy-2-iodo-6-tosyloxy- α,β -D-galactopyranoside (α,β -SI-5). Title compounds were isolated by flash chromatography (4 : 1 $\rightarrow$ 3 : 1 hexanes/EtOAc) as a clear oil (57%). Characterized as a ~1 : 1 mixture of anomers: ^1H NMR (500 MHz, CDCl_3) δ 7.15-7.74 (28H), 6.27 (d, J = 3.50 Hz, 1H), 5.78 (d, J = 9.50 Hz, 1H), 4.85 (m, 2H), 4.67-4.78 (m, 4H), 4.58 (dd, J = 11.50, 3.00 Hz, 1H), 4.48 (d, J = 11.00 Hz, 1H), 4.43 (d, J = 11.00 Hz, 1H), 4.31 (dd, J = 11.00, 9.50 Hz, 1H), 4.16 (app t, J = 6.25 Hz, 1H), 3.80-4.08 (m, 8H), 3.60 (dd, J = 11.50, 2.50 Hz, 1H), 2.42, (s, 6H), 2.14 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 168.95, 168.88, 145.39, 137.75, 137.70, 137.25, 136.94, 132.37, 130.13, 130.12, 128.71, 128.51, 128.49, 128.44, 128.41, 128.36, 128.30, 129.24, 128.16, 128.14, 94.73, 92.87, 82.94, 78.95, 75.12, 74.96, 73.32, 73.21, 73.09, 72.06, 70.86, 67.63, 66.97, 29.66, 27.04, 21.82, 20.91; IR (thin film) 1759 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{29}\text{H}_{31}\text{IO}_8\text{SNa}$ ($\text{M}+\text{Na}$) $^+$ 689.0682, found 689.0696 m/z .

α,β -3,4-Bis-(*O*-benzyl)-2-deoxy-2-iodo-6-tosyloxy-D-galactosyl Trichloroacetimidate (α,β -10). The title compounds were isolated by flash chromatography (4 : 1 hexanes/EtOAc) as a clear oil. Characterized as a 55 : 45 β/α mixture of anomers. Characteristic peaks used for the determination of the ratio of anomers: ^1H NMR (500 MHz, CDCl_3) δ 8.69 (s, 1H, α), 8.67 (s, 1H, β), 6.44 (d, J = 3.00 Hz, 1H, α), 5.95 (d, J = 9.00 Hz, 1H, β).

Acetyl 3,4-bis-(*O*-benzyl)-2-deoxy-2-bromo-6-tosyloxy- α,β -D-galactopyranoside (α,β -SI-7). The title compounds were isolated by flash chromatography (4 : 1 $\rightarrow$ 3 : 1 hexanes/EtOAc) as a clear oil (52%). Characterized as a ~1 : 1 mixture of anomers: ^1H NMR (400 MHz, CDCl_3) δ 7.73 (d, J = 8.00 Hz, 4H), 7.17-7.45 (m, 24H), 6.26 (d, J = 3.20 Hz, 1H), 5.70 (d, J = 9.20 Hz, 1H), 4.70-4.90 (m, 6H), 4.44-4.52 (m, 4H), 3.60-4.25 (m, 10H), 2.42 (s, 6H), 2.14 (s, 3H), 2.09 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.94, 145.39, 137.74, 137.69, 137.47, 137.12, 132.39, 130.14, 130.11, 128.73, 128.71, 128.52, 128.49, 128.40, 128.31, 128.28, 128.16, 128.13, 128.10, 128.08, 93.85, 91.67, 82.25, 78.56, 75.21, 75.05, 74.013, 73.56, 73.52, 73.13, 72.64, 70.87, 67.60, 66.97, 50.25, 48.30, 21.81, 20.89, 20.83; IR (thin film) 1760 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{29}\text{H}_{31}\text{BrO}_8\text{SNa}$ ($\text{M}+\text{Na}$) $^+$ 641.0821, found 648.0820 m/z .

α,β -3,4-Bis-(*O*-benzyl)-2-deoxy-2-bromo-6-tosyloxy-D-galactosyl Trichloroacetimidate (α,β -10). The title compounds were isolated by flash chromatography (4 : 1 $\rightarrow$ 3 : 1 hexanes/EtOAc) as a white foam. Characterized as a 67 : 33 β/α mixture of anomers: ^1H NMR (300 MHz, CDCl_3) δ 8.67 (bs, 2H), 7.71 (m, 4H), 7.18-7.44 (m, 24H), 6.45 (d, J = 3.30 Hz, 1H, α), 5.90 (d, J = 8.70 Hz, 1H, β), 4.72-4.91 (m, 5H), 4.57 (dd, J = 2.85 Hz, 10.95 Hz, 1H), 4.48 (ad, J = 10.8 Hz, 2H), 4.37 (dd, J = 9.15, 10.35 Hz, 1H), 4.26 (at, J = 6.60 Hz, 1H), 3.99-4.11 (m, 6H), 3.87-3.93 (m, 3H), 3.68 (dd, J = 2.55, 10.65 Hz, 1H), 2.40 (s, 6H) m/z .

Methyl 4,6-benzylidene-2-O-benzoyl-3-O-(3,4-bis-(O-benzyl)-2-deoxy-2-iodo-6-tosyloxy-β-D-galactopyranosyl)-(1→3)-α-D-glucopyranoside (β-11). The title compound was isolated by flash chromatography (4 : 1 hexanes/EtOAc) as a clear oil: $[\alpha]_D^{25^\circ} = +46.0^\circ$ (c = 0.8, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 8.13 (m, 2H), 7.68 (d, *J* = 8.00 Hz, 1H), 7.58 (m, 1H), 7.09-7.47 (m, 19H), 5.53 (s, 1H), 5.13 (dd, *J* = 10.00, 4.00 Hz, 1H), 5.06 (d, *J* = 3.50 Hz, 1H), 4.83 (d, *J* = 9.00 Hz, 1H), 4.78 (A of AB, *J* = 11.25 Hz, 1H), 4.65 (A of AB, *J* = 11.00 Hz, 1H), 4.57 (B of AB, *J* = 11.00 Hz, 1H), 4.43 (app t, *J* = 9.25 Hz, 1H), 4.34 (B of AB, *J* = 11.25 Hz, 1H), 4.29 (dd, *J* = 10.00, 4.50 Hz, 1H), 4.16 (dd, *J* = 11.00, 9.00 Hz, 1H), 3.99 (m, 2H), 3.91 (td, *J* = 10.00, 4.50 Hz, 1H), 3.79 (app t, *J* = 10.25 Hz, 1H), 3.71 (m, 2H), 3.51 (app t, *J* = 6.75 Hz, 1H), 3.39 (dd, *J* = 11.50, 3.00 Hz, 1H), 3.37 (s, 3H), 2.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 166.14, 145.37, 138.08, 137.53, 137.22, 130.40, 130.20, 130.03, 129.03, 128.63, 128.54, 128.38, 128.34, 128.24, 128.22, 128.15, 127.96, 127.76, 126.31, 103.09, 101.35, 97.79, 83.58, 80.27, 75.65, 74.69, 73.48, 73.03, 72.31, 69.10, 67.36, 62.43, 55.62, 32.54, 21.89; IR (thin film) 1722 cm⁻¹; HRMS (ES) calcd for C₄₈H₄₉IO₁₃SNa (M+Na)⁺ 1015.1836, found 1018.1832 *m/z*.

Methyl 4,6-benzylidene-2-O-benzoyl-3-O-(3,4-bis-(O-benzyl)-2-deoxy-2-iodo-6-tosyloxy-α-D-galactopyranosyl)-(1→3)-α-D-glucopyranoside (α-11). The title compound was isolated by flash chromatography (4 : 1 hexanes/EtOAc) as a clear oil. An analytical sample was obtained by preparative HPLC purification (75% hexanes/EtOAc): $[\alpha]_D^{25^\circ} = +182.0^\circ$ (c = 0.6, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 8.14 (m, 2H), 7.74 (d, *J* = 8.00 Hz, 1H), 7.66 (m, 1H), 7.20-7.60 (m, 18H), 7.00 (m, 2H), 5.63 (s, 1H), 5.58 (d, *J* = 3.20 Hz, 1H), 5.20 (dd, *J* = 9.75, 3.75 Hz, 1H), 5.00 (d, 3.50 Hz, 1H), 4.67 (A of AB, *J* = 11.00 Hz, 1H), 4.63 (A' of A'B', *J* = 11.00 Hz, 1H), 4.53 (B' of A'B', *J* = 11.00 Hz, 1H), 4.36 (m, 2H), 4.30 (m, 1H), 4.13 (B of AB, *J* = 11.00 Hz, 1H), 4.10 (dd, *J* = 9.50, 7.50 Hz, 1H), 4.01 (m, 1H), 4.96 (app d, *J* = 9.00 Hz, 1H), 3.90 (td, *J* = 9.50, 4.50 Hz, 1H), 3.84 (app t, *J* = 10.00 Hz, 1H), 3.77 (dd, *J* = 9.50, 6.00 Hz, 1H), 3.62 (dd, *J* = 11.50, 2.50 Hz, 1H), 3.42 (s, 3H), 3.41 (m, 1H), 2.32 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 166.14, 145.18, 137.84, 137.53, 137.20, 134.01, 132.68, 130.08, 130.04, 129.21, 128.64, 128.45, 128.28, 128.12, 127.95, 126.27, 101.31, 98.44, 97.83, 82.75, 78.24, 74.79, 73.96, 73.15, 72.22, 71.00, 69.19, 68.76, 68.64, 62.00, 55.73, 29.29, 21.83; IR (thin film) 1723 cm⁻¹; HRMS (ES) calcd for C₄₈H₄₉IO₁₃SNa (M+Na)⁺ 1015.1836, found 1018.1836 *m/z*.

Methyl 4,6-benzylidene-2-O-benzoyl-3-O-(3,4-bis-(O-benzyl)-2-deoxy-2-bromo-6-tosyloxy-α-D-galactopyranosyl)-(1→3)-α-D-glucopyranoside (α-12). The title compound was isolated as a clear oil by flash chromatography (4 : 1 hexanes/EtOAc) followed by preparative HPLC purification (80% hexanes/EtOAc): $[\alpha]_D^{25^\circ} = +85.0^\circ$ (c = 2.3, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 8.13 (m, 2H), 7.21-7.74 (m, 20H), 7.02 (m, 2H), 5.60 (s, 1H), 5.56 (d, *J* = 3.50 Hz, 1H), 5.20 (dd, *J* = 9.75, 3.75 Hz, 1H), 5.00 (d, *J* = 4.00 Hz, 1H), 4.70 (A of AB, *J* = 10.75 Hz, 1H), 4.68 (A of AB, *J* = 11.50 Hz, 1H), 4.55 (B of AB, *J* = 11.50 Hz, 1H), 4.32 (m, 4H), 4.15 (B of AB, *J* = 10.75 Hz, 1H), 4.08 (dd, *J* = 9.50, 6.50 Hz, 1H), 4.00 (app t, *J* = 6.25 Hz, 1H), 3.90 (m, 2H), 3.84 (m, 1H), 3.77 (dd, *J* = 9.75, 7.75 Hz, 1H), 3.68 (dd, *J* = 11.00, 3.00 Hz, 1H), 3.43 (m, 1H), 3.41 (s, 3H), 2.32 (s, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 166.09, 145.15, 137.82, 137.74, 137.20, 133.98, 132.71, 130.04, 130.01, 129.17, 129.14, 128.63, 128.43, 128.41, 128.26, 128.16, 128.12, 128.09, 127.94, 126.16, 101.31, 97.85, 97.69, 82.92, 77.94, 74.86, 74.67, 73.63, 72.17, 71.17, 69.15, 68.64, 68.57, 62.04, 55.71, 49.97, 21.80; IR (thin film) 1723 cm⁻¹; HRMS (ES) calcd for C₄₈H₄₉BrO₁₃SNa (M+Na)⁺ 967.1975, found 967.1982 *m/z*.

Methyl 4,6-benzylidene-2-O-benzoyl-3-O-(3,4-bis-(O-benzyl)-2-deoxy-2-bromo-6-tosyloxy-β-D-galactopyranosyl)-(1→3)-α-D-glucopyranoside (β-12). The title compound was isolated as a clear oil by flash chromatography (4 : 1 hexanes/EtOAc) followed by preparative HPLC purification (80% hexanes/EtOAc): $[\alpha]_D^{25^\circ} = +53.6^\circ$ (c = 0.7, CH₂Cl₂); ¹H NMR (500 MHz, CDCl₃) δ 8.10 (m, 2H), 7.09-7.68 (m, 22H), 5.53 (s, 1H), 5.13 (dd, *J* = 9.50, 4.00 Hz, 1H), 5.06 (d, *J* = 4.00 Hz, 1H), 4.79 (A of AB, *J* = 11.00 Hz, 1H), 4.74 (d, *J* = 8.50 Hz, 1H), 4.65 (A of AB, *J* = 11.00 Hz, 1H), 4.60 (B of AB, *J* = 11.00 Hz, 1H), 4.43 (app t, *J* = 9.25 Hz, 1H), 4.34 (B of AB, *J* = 11.00 Hz, 1H), 4.29 (dd, *J* = 10.00, 4.50 Hz, 1H), 4.06 (dd, *J* = 10.50, 8.50 Hz, 1H), 4.47 (m, 2H), 3.88 (m, 1H), 3.79 (m, 2H), 3.80 (app t, *J* = 9.50 Hz, 1H), 3.50 (app t, *J* = 6.75 Hz, 1H), 3.40 (dd, *J* = 9.75, 1.75 Hz, 1H), 3.37 (s,

3H), 2.41 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.13, 145.37, 138.04, 137.50, 137.37, 133.39, 132.47, 130.30, 130.19, 129.89, 129.09, 128.66, 128.54, 128.37, 128.21, 128.15, 128.14, 128.03, 127.79, 126.29, 102.68, 101.43, 97.85, 82.75, 80.47, 76.12, 74.79, 73.32, 72.77, 72.11, 69.10, 67.26, 62.42, 55.63, 52.71, 29.92, 21.88; IR (thin film) 1722 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{48}\text{H}_{49}\text{BrO}_{13}\text{SNa}$ ($\text{M}+\text{Na}$) $^+$ 967.1975, found 967.1988 m/z .

Methyl 4,3,2-*O*-tribenzoyl-6-*O*-(3,4-bis-(*O*-benzyl)-2-deoxy-2-iodo-6-tosyloxy- β -D-galactopyranosyl)-(1 $\rightarrow$ 6)- α -D-glucopyranoside (β -14). The title compound was isolated as a clear oil by flash chromatography (4 : 1 hexanes/EtOAc) followed by preparative HPLC purification (80% hexanes/EtOAc): $[\alpha]_{\text{D}}^{27^\circ\text{C}} = +42.3^\circ$ ($c = 0.9$, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 7.85-7.98 (m, 6H), 7.71 (m, 2H), 7.11-7.52 (m, 21H), 6.13 (app t, $J = 9.50$ Hz, 1H), 5.45 (app t, $J = 9.75$ Hz, 1H), 5.26 (d, $J = 3.50$ Hz, 1H), 5.23 (dd, $J = 6.75, 3.75$ Hz, 1H), 4.80 (A of AB, $J = 11.50$ Hz, 1H), 4.73 (A of AB, $J = 11.00$ Hz, 1H), 4.69 (B of AB, $J = 11.00$ Hz, 1H), 4.61 (d, $J = 9.00$ Hz, 1H), 4.39 (B of AB, $J = 11.50$ Hz, 1H), 4.78 (ddd, $J = 10.00, 7.00, 2.00$ Hz, 1H), 4.21 (dd, $J = 11.25, 9.25$ Hz, 1H), 3.97 (app d, $J = 6.50$ Hz, 1H), 3.94 (dd, $J = 11.00, 2.00$ Hz, 1H), 3.73 (m, 2H), 3.68 (app t, $J = 6.25$ Hz, 1H), 3.53 (dd, $J = 11.00, 2.50$ Hz, 1H), 3.47 (s, 3H), 2.40 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.00, 165.63, 145.37, 137.91, 137.20, 133.59, 133.52, 133.24, 132.48, 130.21, 130.13, 130.09, 129.88, 129.50, 129.33, 129.18, 128.74, 128.65, 128.61, 128.46, 128.37, 128.29, 128.15, 127.98, 104.07, 96.90, 83.40, 74.79, 73.31, 72.70, 72.51, 72.31, 70.79, 69.97, 69.04, 68.91, 67.63, 56.10, 31.43, 21.86; IR (thin film) 1731 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{55}\text{H}_{53}\text{IO}_{15}\text{SNa}$ ($\text{M}+\text{Na}$) $^+$ 524.9920, found 524.9925 m/z .

Methyl 4,3,2-*O*-tribenzoyl-6-*O*-(3,4-bis-(*O*-benzyl)-2-deoxy-2-iodo-6-tosyloxy- β -D-galactopyranosyl)-(1 $\rightarrow$ 6)- α -D-glucopyranoside (α -14). The title compound was isolated as a clear oil by flash chromatography (4 : 1 hexanes/EtOAc) followed by preparative HPLC purification (80% hexanes/EtOAc): $[\alpha]_{\text{D}}^{27^\circ\text{C}} = +71.0^\circ$ ($c = 0.9$, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 7.86-8.00 (m, 5H), 7.69 (d, $J = 8.40$ Hz, 2H), 7.14-7.53 (m, 22 H), 6.15 (app t, $J = 10.00$ Hz, 1H), 5.67 (app t, $J = 10.00$ Hz, 1H), 5.30 (dd, $J = 10.20, 3.40$ Hz, 1H), 5.22 (d, $J = 3.60$ Hz, 1H), 4.98 (d, $J = 2.80$ Hz, 1H), 4.84 (A of AB, $J = 10.80$ Hz, 1H), 4.76 (app s, 2H), 4.46 (dd, $J = 11.20, 3.20$ Hz, 1H), 4.39 (B of AB, $J = 11.20$ Hz, 1H), 4.24 (dd, $J = 10.40, 3.60$ Hz, 1H), 4.04 (app t, $J = 6.40$ Hz, 1H), 3.93 (m, 2H), 3.84 (dd, $J = 9.60$ Hz, 6.40 Hz, 1H), 3.80 (m, 1H), 3.75 (dd, $J = 11.40, 5.40$ Hz, 1H), 3.60 (app d, $J = 11.20$ Hz, 1H), 3.46 (s, 3H), 2.42 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.03, 165.55, 145.16, 138.01, 137.60, 133.68, 133.55, 133.26, 132.79, 130.16, 130.09, 130.07, 129.89, 129.52, 129.34, 129.18, 128.75, 128.70, 128.62, 128.56, 128.54, 128.48, 128.41, 128.26, 128.18, 128.05, 100.34, 97.12, 78.82, 74.99, 73.87, 73.19, 72.28, 70.84, 69.49, 68.92, 68.47, 66.86, 55.84, 28.71, 21.86; IR (thin film) 1732 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{55}\text{H}_{53}\text{IO}_{15}\text{SNa}$ ($\text{M}+\text{Na}$) $^+$ 1135.2048, found 1135.2056 m/z .

Methyl 4,3,2-*O*-tribenzoyl-6-*O*-(3,4-bis-(*O*-benzyl)-2-deoxy-2-bromo-6-tosyloxy- β -D-galactopyranosyl)-(1 $\rightarrow$ 6)- α -D-glucopyranoside (β -15). The title compound was isolated as a clear oil by flash chromatography (4 : 1 hexanes/EtOAc) followed by preparative HPLC purification (78% hexanes/EtOAc): $[\alpha]_{\text{D}}^{25^\circ\text{C}} = +43.2^\circ$ ($c = 2.2$, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 7.70-7.98 (m, 8H), 7.50 (m, 2H), 7.12-7.44 (m, 19H), 6.12 (app t, $J = 9.75$ Hz, 1H), 5.44 (app t, $J = 10.25, 9.25$ Hz, 1H), 5.25 (d, $J = 3.50$ Hz, 1H), 5.22 (dd, $J = 7.25, 3.75$ Hz, 1H), 4.83 (A of AB, $J = 11.50$ Hz, 1H), 4.73 (app s, 2H), 4.55 (d, $J = 8.50$ Hz, 1H), 4.41 (B of AB, $J = 11.00$ Hz, 1H), 4.28 (m, 1H), 4.12 (dd, $J = 11.00, 8.50$ Hz, 1H), 3.98 (m, 2H), 3.94 (dd, $J = 11.25, 1.75$ Hz, 1H), 3.80 (app d, $J = 1.50$ Hz, 1H), 3.75 (dd, $J = 11.50, 7.00$ Hz, 1H), 3.68 (dd, $J = 7.00, 6.00$ Hz, 1H), 3.54 (dd, $J = 11.00, 3.00$ Hz, 1H), 3.46 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.00, 165.60, 145.38, 137.91, 137.40, 133.59, 133.52, 133.24, 132.50, 133.24, 132.50, 130.21, 130.13, 130.06, 129.88, 129.50, 129.33, 129.18, 128.74, 128.64, 128.60, 128.46, 128.33, 128.31, 128.16, 127.99, 103.37, 96.93, 82.66, 74.86, 73.65, 73.03, 72.47, 72.31, 70.79, 69.88, 69.19, 68.72, 67.65, 55.91, 51.78, 21.85; IR (thin film) 1730 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{55}\text{H}_{53}\text{BrO}_{15}\text{SNa}$ ($\text{M}+\text{Na}$) $^+$ 1087.2180, found 1087.2186 m/z .

Methyl 4,3,2-*O*-tribenzoyl-6-*O*-(3,4-bis-(*O*-benzyl)-2-deoxy-2-bromo-6-tosyloxy- β -D-galactopyranosyl)-(1 $\rightarrow$ 6)- α -D-glucopyranoside (α -15). The title compound was isolated by flash chromatography (4 : 1 hexanes/EtOAc) followed by preparative HPLC purification (78% hexanes/EtOAc). Partial data extracted from mixed fractions: ^1H NMR (400 MHz, CDCl_3) δ 7.93-8.00 (m, 4H), 7.87 (m, 2H), 7.69 (m, 2H), 7.16-7.52 (m, 21H), 6.14 (at, J = 10.00 Hz, 1H), 5.61 (at, J = 10.00 Hz, 1H), 5.27 (dd, J = 3.20, 10.20 Hz, 1H), 5.21 (d, J = 3.60 Hz, 1H), 4.95 (d, J = 3.20 Hz, 1H), 4.87 (A of AB, J = 11.20 Hz, 1H), 4.80 (A' of A'B', J = 11.60 Hz, 1H), 4.75 (B of AB, J = 10.80 Hz, 1H), 4.38-4.43 (m, 2H), 4.23 (m, 1H), 4.05 (m, 1H), 3.75-3.97 (m, 5H), 3.62 (B' of A'B', J = 11.60 Hz, 1H), 3.43 (s, 3H), 2.42 (s, 3H).

3,4,6-tri-(*O*-benzyl)-D-galactal (SI-8). Galactal derivative SI-8 was prepared according to the previously published procedure.⁵

Acetyl 3,4,6-tri-(*O*-benzyl)-2-deoxy-2-iodo- β -D-talopyranoside (SI-9). The title compound was isolated as a yellow oil by flash chromatography (7 : 1 $\rightarrow$ 3 : 1 hexanes/EtOAc): Spectroscopic data obtained for this compound was consistent with that which has been previously reported.⁴

Acetyl 3,4,6-tri-(*O*-benzyl)-2-deoxy-2-iodo- β -D-galactopyranoside (β -16). The title compound was isolated as a yellow oil (1 : 1 β/α) by flash chromatography (7 : 1 $\rightarrow$ 3 : 1 hexanes/EtOAc). The anomers were separated by preparative HPLC (85% hexanes/EtOAc): $[\alpha]_{\text{D}}^{25^\circ\text{C}} = +57.1^\circ$ (c = 0.7, CH_2Cl_2). Spectroscopic data obtained for this compound was consistent with that which has been previously reported.⁴

Acetyl 3,4,6-tri-(*O*-benzyl)-2-deoxy-2-iodo- α -D-galactopyranoside (α -16). The title compound was isolated as a yellow oil (1 : 1 β/α) by flash chromatography (7 : 1 $\rightarrow$ 3 : 1 hexanes/EtOAc). The anomers were separated by preparative HPLC (85% hexanes/EtOAc): $[\alpha]_{\text{D}}^{25^\circ\text{C}} = +95.2^\circ$ (c = 1.1, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 7.21-7.45 (m, 15 H), 6.34 (d, J = 3.50 Hz, 1H), 4.85 (A of AB, J = 11.25 Hz, 1H), 4.71 (A of AB, J = 11.25 Hz, 1H), 4.68 (B of AB, J = 11.25 Hz, 1H), 4.65 (dd, J = 11.25, 3.25 Hz, 1H), 4.51 (B of AB, J = 11.25 Hz, 1H), 4.42 (A of AB, J = 11.75 Hz, 1H), 4.36 (B of AB, J = 11.75 Hz, 1H), 4.08 (app t, J = 7.00 Hz, 1H), 3.99 (app s, 1H), 3.87 (dd, J = 11.25, 2.25 Hz, 1H), 3.59 (app t, J = 8.25 Hz, 1H), 3.49 (dd, J = 9.00, 5.50 Hz, 1H), 2.09 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 168.91, 138.16, 137.67, 137.39, 128.47, 128.46, 128.31, 128.07, 127.99, 127.89, 127.75, 93.04, 79.10, 74.97, 73.90, 73.56, 72.62, 71.93, 68.07, 28.05, 20.81; IR (thin film) 1755 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{29}\text{H}_{31}\text{IO}_6\text{Na}$ ($\text{M}+\text{Na}$)⁺ 625.1063, found 625.1061 m/z .

Acetyl 3,4,6-tri-(*O*-benzyl)-2-deoxy-2-bromo- β -D-galactopyranoside (β -17). The title compound was isolated as a yellow oil (1 : 1 β/α) by flash chromatography (10 : 1 $\rightarrow$ 1 : 1 hexanes/EtOAc). The anomers were separated by preparative HPLC (85% hexanes/EtOAc): $[\alpha]_{\text{D}}^{25^\circ\text{C}} = +36.0^\circ$ (c = 0.5, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 7.25-7.41 (m, 15H), 5.74 (d, J = 9.00 Hz, 1H), 4.86 (A of AB, J = 11.50 Hz, 1H), 4.71 (A' of A'B', J = 11.50 Hz, 1H), 4.67 (B' of A'B', J = 11.50 Hz, 1H), 4.56 (B of AB, J = 11.50 Hz, 1H), 4.44 (A'' of A'''B'', J = 11.50 Hz, 1H), 4.39 (B'' of A'B'', J = 12.00 Hz), 4.29 (dd, J = 10.50, 9.50 Hz, 1H), 3.93 (app d, J = 2.50 Hz, 1H), 3.74 (app t, J = 6.50 Hz, 1H), 3.58 (m, 3H), 2.10 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.19, 138.20, 137.73, 137.35, 128.64, 128.60, 128.41, 128.40, 128.26, 128.23, 128.11, 128.05, 127.90, 94.09, 82.62, 74.97, 74.55, 73.66, 73.25, 73.21, 67.77, 50.96, 20.93; IR (thin film) 1766 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{29}\text{H}_{31}\text{BrO}_6\text{Na}$ ($\text{M}+\text{Na}$)⁺ 577.1202, found 577.1204 m/z .

Acetyl 3,4,6-tri-(*O*-benzyl)-2-deoxy-2-bromo- α -D-galactopyranoside (α -17). The title compound was isolated as a yellow oil (1 : 1 β/α) by flash chromatography (10 : 1 $\rightarrow$ 1 : 1 hexanes/EtOAc). The anomers were separated by preparative HPLC (85% hexanes/EtOAc): $[\alpha]_D^{25.0^\circ} = +102.6^\circ$ ($c = 0.7$, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 7.19-7.41 (15H), 6.34 (d, $J = 3.50$ Hz, 1H), 4.86 (A of AB, $J = 11.25$ Hz, 1H), 4.69 (m, 2H), 4.58 (dd, $J = 11.00$, 3.50 Hz, 1H), 4.51 (B of AB, $J = 11.25$ Hz, 1H), 4.41 (A of AB, $J = 11.75$ Hz, 1H), 4.35 (B of AB, $J = 11.75$ Hz, 1H), 4.08 (app t, $J = 7.00$ Hz, 1H), 4.03 (m, 1H), 3.90 (dd, $J = 8.50$, 5.00 Hz, 1H), 3.59 (dd, $J = 9.00$, 7.50 Hz, 1H), 3.49 (dd, $J = 9.50$, 5.50 Hz, 1H), 2.05 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 168.81, 138.09, 137.61, 137.54, 128.39, 128.36, 128.22, 128.02, 127.86, 127.82, 127.79, 127.66, 91.76, 78.61, 74.97, 74.46, 73.44, 72.88, 71.85, 67.96, 48.97, 20.64, ; IR (thin film) 1756 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{29}\text{H}_{31}\text{BrO}_6\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 577.1202, found 577.1200 m/z .

Methyl 4,6-benzylidene-2-*O*-benzoyl-3-*O*-(3,4,6-tri-(*O*-benzyl)-2-deoxy-2-iodo- β -D-galactopyranosyl)-(1 $\rightarrow$ 3)- α -D-glucopyranoside (β -18). The title compound was isolated as a clear glass by flash chromatography (7 : 1 $\rightarrow$ 4 : 1 hexanes/EtOAc) followed by preparative HPLC purification (78% hexanes/EtOAc): $[\alpha]_D^{25^\circ} = +37.6^\circ$ ($c = 1.0$, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 8.15 (m, 2H), 7.57 (m, 1H), 7.49 (d, $J = 7.00$ Hz, 2H), 7.44 (app t, $J = 8.00$ Hz, 2H), 7.19-7.37 (m, 18 H), 5.54 (s, 1H), 5.17 (dd, $J = 9.50$, 4.00 Hz, 1H), 5.07 (d, $J = 4.00$ Hz, 1H), 4.85 (d, $J = 9.00$ Hz, 1H), 4.79 (A of AB, $J = 12.00$ Hz, 1H), 4.61 (A of AB, $J = 11.25$ Hz, 1H), 4.53 (B of AB, $J = 11.25$ Hz, 1H), 4.48 (B of AB, $J = 11.50$ Hz, 1H), 4.48 (app t, $J = 9.25$ Hz, 1H), 4.30 (A of AB, $J = 12.25$ Hz, 1H), 4.29 (m, 1H), 4.23 (B of AB, $J = 12.25$ Hz, 1H), 3.91 (td, $J = 10.00$, 4.50 Hz, 1H), 3.79 (dd, $J = 9.50$, 4.50 Hz, 1H), 3.76 (m, 2H), 3.61 (app t, $J = 8.00$ Hz, 1H), 3.40 (m, 3H), 3.37 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.15, 138.62, 137.98, 137.64, 137.51, 133.34, 130.46, 130.08, 129.09, 128.62, 128.55, 128.47, 128.35, 128.31, 128.21, 128.15, 128.11, 128.05, 127.68, 126.37, 103.31, 101.42, 97.81, 83.99, 80.63, 75.81, 74.67, 73.77, 73.44, 72.98, 72.74, 69.17, 68.42, 62.39, 55.61, 33.80; IR (thin film) 1723 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{48}\text{H}_{49}\text{IO}_{11}\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 951.2217, found 951.2207 m/z .

Methyl 4,6-benzylidene-2-*O*-benzoyl-3-*O*-(3,4,6-tri-(*O*-benzyl)-2-deoxy-2-iodo- α -D-galactopyranosyl)-(1 $\rightarrow$ 3)- α -D-glucopyranoside (α -18). The title compound coeluted with the unreacted donor. Partial data extracted from mixed fractions: ^1H NMR (500 MHz, CDCl_3) δ 8.12 (m, 2H), 7.12-7.51 (m, 23H), 5.71 (d, $J = 3.20$ Hz, 1H), 5.66 (s, 1H), 5.23 (dd, $J = 3.60$, 9.60 Hz, 1H), 5.02 (d, $J = 3.60$ Hz, 1H), 4.73 (A of AB, $J = 11.60$ Hz, 1H), 4.62 (A' of A'B', $J = 10.80$ Hz, 1H), 4.50-4.55 (m, 3H), 4.32-4.43 (m, 3H), 4.24 (B'' of A'B'', $J = 12.00$ Hz, 1H), 3.82-4.05 (m, 3H), 3.85 (at, $J = 9.60$ Hz, 1H), 3.69 (dd, $J = 2.80$, 11.40 Hz, 1H), 3.60 (bs, 2H), 3.48 (m, 2H), 3.38 (s, 3H).

Methyl 4,6-benzylidene-2-*O*-benzoyl-3-*O*-(3,4,6-tri-(*O*-benzyl)-2-deoxy-2-bromo- β -D-galactopyranosyl)-(1 $\rightarrow$ 3)- α -D-glucopyranoside (β -19). The title compound was isolated as a clear oil by flash chromatography (7 : 1 $\rightarrow$ 4 : 1 hexanes/EtOAc): $[\alpha]_D^{27^\circ} = +25.7^\circ$ ($c = 0.7$, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 8.12 (m, 2H), 7.56 (m, 1H), 7.18-7.49 (m, 22H), 5.54 (s, 1H), 5.16 (dd, $J = 9.75$, 3.75 Hz, 1H), 5.06 (d, $J = 4.00$ Hz, 1H), 4.79 (A of AB, $J = 11.50$ Hz, 1H), 4.74 (d, $J = 9.00$ Hz, 1H), 4.60 (A' of A'B', $J = 11.50$ Hz, 1H), 4.55 (B' of A'B', 11.50 Hz, 1H), 4.48 (B of AB, $J = 11.50$ Hz, 1H), 4.46 (app t, $J = 9.25$ Hz, 1H), 4.29 (dd, $J = 10.00$, 5.00 Hz, 1H), 4.27 (A of AB, $J = 11.75$ Hz, 1H), 4.21 (B of AB, $J = 11.75$ Hz, 1H), 4.11 (dd, 10.75, 8.75 Hz, 1H), 3.90 (td, $J = 10.00$, 4.50 Hz, 1H), 3.78 (m, 3H), 3.58 (app t, $J = 8.50$ Hz, 1H), 3.39 (m, 2H), 3.37 (s, 3H), 3.32 (dd, $J = 8.75$, 5.25 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.17, 138.58, 137.96, 137.66, 137.64, 133.32, 130.36, 129.95, 129.14, 128.63, 128.57, 128.49, 128.36, 128.34, 128.19, 128.14, 128.11, 128.05, 127.71, 126.37, 102.99, 101.51, 97.88, 83.15, 80.86, 76.34, 74.78, 73.74, 73.55, 73.35, 73.26, 72.99, 69.19, 68.29, 62.39, 55.63, 53.60; IR (thin film) 1724 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{48}\text{H}_{49}\text{BrO}_{11}\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 903.2356, found 903.2345 m/z .

Methyl 4,6-benzylidene-2-*O*-benzoyl-3-*O*-(3,4,6-tri-(*O*-benzyl)-2-deoxy-2-bromo- α -D-galactopyranosyl)-(1 $\rightarrow$ 3)- α -D-glucopyranoside (α -19). Partial data extracted from mixed fractions: ^1H NMR (400 MHz, CDCl_3) δ 8.12 (m, 2H), 7.13-7.51 (m, 23H), 5.68 (d, J = 3.60 Hz, 1H), 5.63 (s, 1H), 5.24 (dd, J = 3.60, 9.50 Hz, 1H), 5.02 (d, J = 3.60 Hz, 1H), 4.89 (A of AB, J = 11.60 Hz, 1H), 4.20-4.75 (m, 8H), 4.02-4.08 (m, 2H), 3.73-3.96 (m, 3H), 3.46-3.67 (m, 2H), 3.38 (s, 3H).

Methyl 4,3,2-*O*-tribenzoyl-6-*O*-(3,4,6-tri-(*O*-benzyl)-2-deoxy-2-iodo- α -D-galactopyranosyl)-(1 $\rightarrow$ 6)- α -D-glucopyranoside (α -20). The title compound was isolated as a clear oil by flash chromatography (10 : 1 $\rightarrow$ 4 : 1 hexanes/EtOAc): $[\alpha]_{\text{D}}^{27^\circ\text{C}}$ = +98.6° (c = 0.9, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 7.85-8.03 (m, 6H), 7.20-7.50 (m, 24 H), 6.15 (app t, J = 9.75 Hz, 1H), 5.66 (app t, J = 9.75 Hz, 1H), 5.29 (dd, J = 10.25, 3.75 Hz, 1H), 5.21 (d, J = 3.50 Hz, 1H), 5.03 (d, J = 3.00 Hz, 1H), 4.85 (A of AB, J = 11.50 Hz, 1H), 4.72 (app s, 2H), 4.54 (dd, J = 11.50, 3.00 Hz, 1H), 4.49 (B of AB, J = 11.50 Hz, 1H), 4.38 (A of AB, J = 11.75 Hz, 1H), 4.30 (B of AB, J = 11.75 Hz, 1H), 4.28 (m, 1H), 4.00 (app t, J = 6.75 Hz, 1H), 3.93 (dd, J = 11.25, 2.75 Hz, 1H), 3.87 (m, 1H), 3.84 (app t, J = 5.75 Hz, 1H), 3.65 (dd, J = 11.50, 1.50 Hz, 1H), 3.45 (s, 3H), 3.43 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.05, 165.51, 138.53, 138.14, 137.84, 133.57, 133.26, 130.14, 130.05, 129.88, 129.50, 129.32, 129.15, 128.62, 128.58, 128.52, 128.45, 128.41, 128.10, 127.89, 100.33, 97.07, 79.14, 75.05, 74.61, 73.51, 72.88, 72.31, 70.87, 69.93, 69.55, 68.86, 68.79, 66.79, 55.84, 29.81; IR (thin film) 1731 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{55}\text{H}_{53}\text{IO}_{13}\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 524.9920, found 524.9925 m/z .

Methyl 4,3,2-*O*-tribenzoyl-6-*O*-(3,4,6-tri-(*O*-benzyl)-2-deoxy-2-iodo- β -D-galactopyranosyl)-(1 $\rightarrow$ 6)- α -D-glucopyranoside (β -20). The title compound was isolated as a clear oil by flash chromatography (10 : 1 $\rightarrow$ 4 : 1 hexanes/EtOAc): $[\alpha]_{\text{D}}^{27^\circ\text{C}}$ = +79.1° (c = 1.3, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 7.84-7.99 (m, 6H), 7.20-7.51 (m, 24 H), 6.14 (app t, J = 9.75 Hz, 1H), 5.45 (app t, J = 10.00 Hz, 1H), 5.26 (dd, J = 9.75, 3.75 Hz, 1H), 5.23 (d, J = 3.50 Hz, 1H), 4.81 (A of AB, J = 11.50 Hz, 1H), 4.70 (A of AB, J = 11.00 Hz, 1H), 4.65 (B of AB, J = 11.00 Hz, 1H), 4.64 (d, J = 9.00 Hz, 1H), 4.50 (B of AB, J = 11.50 Hz, 1H), 4.40 (A of AB, J = 11.75 Hz, 1H), 4.35 (B of AB, J = 11.75 Hz, 1H), 4.33 (m, 1H), 4.28 (dd, J = 11.00, 9.00 Hz, 1H), 4.00 (dd, J = 11.00, 2.00 Hz, 1H), 3.80 (app d, J = 2.50 Hz, 1H), 3.76 (dd, J = 10.25, 6.25 Hz, 1H), 3.54 (m, 4H), 3.51 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.02, 165.97, 165.65, 138.45, 137.98, 137.48, 133.52, 133.49, 133.20, 130.13, 130.06, 129.86, 129.53, 129.36, 129.21, 128.65, 128.58, 128.42, 128.38, 128.20, 128.07, 127.82, 104.07, 96.87, 83.81, 74.76, 74.17, 73.73, 73.16, 73.04, 72.34, 70.85, 70.03, 69.14, 68.76, 68.43, 56.11, 32.57; IR (thin film) 1731 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{55}\text{H}_{53}\text{IO}_{13}\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 1071.2429, found 1071.2439 m/z .

Methyl 4,3,2-*O*-tribenzoyl-6-*O*-(3,4,6-tri-(*O*-benzyl)-2-deoxy-2-bromo- α -D-galactopyranosyl)-(1 $\rightarrow$ 6)- α -D-glucopyranoside (α -21). The title compound was isolated as a clear oil by flash chromatography (10 : 1 $\rightarrow$ 7 : 1 hexanes/EtOAc): $[\alpha]_{\text{D}}^{27^\circ\text{C}}$ = +82.1° (c = 1.3, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 7.99 (m, 2H), 7.93 (m, 2H), 7.87 (m, 2H), 7.51-7.21 (m, 24H), 6.14 (app t, J = 10.00 Hz, 1H), 5.61 (app t, J = 10.00 Hz, 1H), 5.27 (dd, J = 10.00, 3.50 Hz, 1H), 5.20 (d, J = 3.50, 1H), 5.01 (d, J = 3.00 Hz, 1H), 4.87 (A of AB, J = 11.50 Hz, 1H), 4.76 (A' of A'B', J = 11.50, 1H), 4.72 (B' of A'B', J = 11.50 Hz, 1H), 4.50 (B of AB, J = 11.50 Hz, 1H), 4.47 (dd, J = 10.50, 3.00 Hz, 1H), 4.38 (A of AB, J = 12.00 Hz, 1H), 4.31 (B of AB, J = 12.00 Hz, 1H), 4.28 (m, 1H), 4.01 (app t, J = 6.50 Hz, 1H), 3.96 (dd, J = 11.00, 2.50 Hz, 1H), 3.91 (m, 1H), 3.87 (dd, J = 11.50, 6.00 Hz, 1H), 3.67 (dd, J = 11.50, 2.00, 1H), 3.43-3.42 (m, 1H), 3.43 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.04 (b), 165.53, 138.53, 138.14, 138.04, 133.57, 133.26, 130.14, 130.05, 129.87, 129.50, 129.33, 129.23, 128.62, 128.46, 128.37, 128.06, 127.89, 99.31, 97.10, 78.66, 75.30, 75.14, 73.53, 73.26, 72.31, 70.86, 69.90, 69.61, 68.78, 66.80, 55.74, 50.41, 29.91; IR (thin film) cm^{-1} ; HRMS (ES) calcd for $\text{C}_{55}\text{H}_{53}\text{BrO}_{13}\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 1023.2567, found 1023.2561 m/z .

Methyl 4,3,2-*O*-tribenzoyl-6-*O*-(3,4,6-tri-(*O*-benzyl)-2-deoxy-2-bromo- β -D-galactopyranosyl)-(1 $\rightarrow$ 6)- α -D-glucopyranoside (β -21). The title compound was isolated as a clear oil by flash chromatography (10 : 1 $\rightarrow$ 7 : 1 hexanes/EtOAc): $[\alpha]_{\text{D}}^{27^\circ\text{C}}$ = +52.7° (c = 0.3, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 6.13 (app t, J = 9.75 Hz, 1H), 5.44, (app t, J = 10.00 Hz, 1H), 5.25 (dd, J = 10.00, 3.50, 1H), 5.22 (d, J = 3.50 Hz, 1H), 4.83 (A of AB, J = 11.50

Hz, 1H), 4.69 (app d, $J = 2.50$, 1H), 4.58 (d, $J = 8.50$ Hz, 1H), 4.51 (B of AB, $J = 11.50$ Hz, 1H), 4.41 (A of AB, $J = 11.75$ Hz, 1H), 4.35 (B of AB, $J = 11.75$ Hz, 1H), 4.33 (m, 1H), 4.18 (dd, $J = 10.50$, 8.50 Hz, 1H), 3.99 (dd, $J = 11.25$, 1.75, 1H), 3.86 (app d, $J = 2.50$ Hz, 1H), 3.79 (dd, $J = 11.50$, 7.50 Hz, 1H), 3.50-3.59 (m, 4 H), 3.49 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.01, 165.97, 165.61, 138.44, 137.95, 137.66, 133.52, 133.20, 130.13, 130.05, 129.86, 129.52, 129.35, 129.20, 128.66, 128.58, 128.43, 128.38, 128.29, 128.16, 128.07, 127.82, 103.40, 96.90, 83.07, 74.85, 73.88, 73.73, 73.57, 73.33, 72.34, 70.84, 69.93, 69.29, 68.54, 68.38, 55.92, 55.89, 52.56; IR (thin film) 1731 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{55}\text{H}_{53}\text{BrO}_{13}\text{Na}$ ($\text{M}+\text{Na}$) $^{+}$ 1023.2567, found 1023.2565 m/z .

3,4-Di-O-benzyl-6-deoxy-D-galactal (SI-10). Galactal derivative SI-10 was prepared from 6-deoxy galactal **35**⁶ according to the procedure for the preparation of *ent*-SI-10:⁷ $[\alpha]_{\text{D}}^{26^\circ\text{C}} = -39.1^\circ$ ($c = 2.0$, CH_2Cl_2).

Acetyl 3,4-di-O-benzyl-2,6-dideoxy-2-iodo- β -D-galactopyranoside (β -24). The title compound was isolated as a yellow oil (33 : 67 β/α) by flash chromatography (7 : 1 hexanes/EtOAc). The anomers were separated by preparative HPLC (85% hexanes/EtOAc): $[\alpha]_{\text{D}}^{27^\circ\text{C}} = +125.6^\circ$ ($c = 0.2$, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 7.25-7.48 (m, 10 H), 5.81 (d, $J = 9.50$ Hz, 1H), 4.91 (A of AB, $J = 11.50$ Hz, 1H), 4.75 (A of AB, $J = 11.25$ Hz, 1H), 4.70 (B of AB, $J = 11.25$ Hz, 1H), 4.62 (B of AB, $J = 11.50$ Hz, 1H), 4.37 (dd, $J = 11.00$ 9.50 Hz, 1H), 3.66 (dd, $J = 12.75$, 6.25 Hz, 1H), 3.60 (dd, $J = 11.25$, 2.75 Hz, 1H), 3.51 (m, 1H), 2.12 (s, 3H), 1.20 (s, 3H), 1.19 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.34, 138.09, 137.22, 128.72, 128.61, 128.49, 128.45, 128.37, 128.00, 94.96, 83.89, 75.43, 74.91, 73.19, 72.23, 30.81, 21.04, 16.89; IR (thin film) 1770 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{22}\text{H}_{25}\text{IO}_5\text{Na}$ ($\text{M}+\text{Na}$) $^{+}$ 519.0644, found 519.0646 m/z .

Acetyl 3,4-di-O-acetyl-2,6-dideoxy-2-iodo- α -D-galactopyranoside (α -24). The title compound was isolated as a yellow oil (33 : 67 β/α) by flash chromatography (7 : 1 hexanes/EtOAc). The anomers were separated by preparative HPLC (85% hexanes/EtOAc): $[\alpha]_{\text{D}}^{27^\circ\text{C}} = +190.0^\circ$ ($c = 0.1$, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 7.24-7.48 (m, 10H), 6.34 (d, $J = 3.60$, 1H), 4.90 (A of AB, $J = 11.40$ Hz, 1H), 4.74 (app s, 2H), 4.65 (dd, $J = 11.20$, 3.20, 1H), 4.58 (B of AB, $J = 11.40$ Hz, 1H), 4.03 (dd, $J = 13.20$, 6.40 Hz, 1H), 3.89 (dd, $J = 11.60$, 2.80 Hz, 1H), 3.65 (app d, $J = 1.20$ Hz, 1H), 1.14, (d, $J = 6.40$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 169.10, 138.05, 137.44, 128.57, 128.35, 128.32, 128.15, 128.10, 127.86, 93.25, 79.67, 76.74, 75.06, 72.85, 69.37, 28.19, 20.90, 16.93; IR (thin film) 1754 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{22}\text{H}_{25}\text{IO}_5\text{Na}$ ($\text{M}+\text{Na}$) $^{+}$ 519.0644, found 519.0665 m/z .

Methyl 4,6-benzylidene-2-O-benzoyl-3-O-(3,4-di-O-acetyl-2,6-dideoxy-2-iodo- α -D-galactopyranosyl)-(1 $\rightarrow$ 3)- α -D-glucopyranoside (α -25). The title compound was isolated as a clear oil by flash chromatography (10 : 1 $\rightarrow$ 7 : 1 hexanes/EtOAc): $[\alpha]_{\text{D}}^{27.6^\circ\text{C}} = +178.0^\circ$ ($c = 0.1$, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 8.08 (m, 2H), 7.61 (m, 1H), 7.19-7.52 (m, 17H), 5.65 (m, 2H), 5.22 (dd, $J = 9.50$, 4.00 Hz, 1H), 5.02 (d, $J = 4.00$ Hz, 1H), 4.78 (A of AB, $J = 11.50$ Hz, 1H), 4.67 (A of AB, $J = 11.00$ Hz, 1H), 4.57 (B of AB, $J = 11.00$ Hz, 1H), 4.50 (dd, $J = 11.50$, 3.50 Hz, 1H), 4.48 (app t, $J = 9.25$ Hz, 1H), 4.40 (B of AB, $J = 11.50$ Hz, 1H), 4.34 (dd, $J = 10.00$, 4.50 Hz, 1H), 4.00 (app t, $J = 9.25$ Hz, 1H), 3.94 (ddd, $J = 14.00$, 9.50, 4.00 Hz, 1H), 3.85 (app t, $J = 10.00$ Hz, 1H), 3.83 (app d, $J = 13.00$ Hz, 1H), 3.68 (dd, $J = 11.50$, 2.50 Hz, 1H), 3.39 (s, 3H), 3.19 (app d, $J = 1.50$ Hz, 1H), 0.93 (d, $J = 6.50$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.87, 138.44, 137.94, 137.25, 133.72, 130.05, 129.67, 129.12, 128.70, 128.61, 128.47, 128.39, 128.37, 128.31, 128.02, 127.83, 126.34, 101.27, 98.92, 97.82, 82.56, 79.32, 75.123, 73.04, 72.33, 71.72, 69.19, 66.91, 61.94, 55.59, 30.51, 16.94; IR (thin film) 1724 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{41}\text{H}_{43}\text{IO}_{10}\text{Na}$ ($\text{M}+\text{Na}$) $^{+}$ 845.1799, found 845.1799 m/z .

Methyl 4,3,2-*O*-tribenzoyl-6-*O*-(3,4-di-*O*-acetyl-2,6-dideoxy-2-iodo- α -D-galactopyranosyl)-(1 $\rightarrow$ 6)- α -D-glucopyranoside (α -26). The title compound was isolated as a clear oil by flash chromatography (10 : 1 $\rightarrow$ 4 : 1 hexanes/EtOAc): $[\alpha]_D^{27.8^\circ} = +63.7^\circ$ ($c = 3.2$, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 7.87-8.00 (m, 6H), 7.26-7.53 (m, 19 H), 6.14 (app t, $J = 10.00$ Hz, 1H), 5.65 (app t, $J = 10.00$ Hz, 1H), 5.30 (dd, $J = 10.25$, 3.75 Hz, 1H), 5.23 (d, $J = 3.50$ Hz, 1H), 4.98 (d, $J = 3.00$ Hz, 1H), 4.90 (A of AB, $J = 11.50$ Hz, 1H), 4.77 (A of AB, $J = 11.25$ Hz, 1H), 4.74 (B of AB, $J = 11.25$ Hz, 1H), 4.55 (B of AB, $J = 11.50$ Hz, 1H), 4.53 (dd, $J = 11.50$, 3.00 Hz, 1H), 4.29 (ddd, $J = 10.12$, 5.62, 1.87 Hz, 1H), 3.92 (dd, $J = 11.25$, 2.25 Hz, 1H), 3.85 (dd, $J = 12.00$, 5.50 Hz, 1H), 3.82 (dd, $J = 11.50$, 5.50 Hz, 1H), 3.63 (dd, $J = 11.25$, 1.75 Hz, 1H), 3.53 (app d, $J = 1.50$ Hz, 1H), 3.47 (s, 3H), 0.95 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.07, 166.06, 165.49, 138.43, 137.89, 133.66, 133.57, 133.27, 130.15, 129.99, 129.88, 129.49, 129.29, 129.20, 128.69, 128.66, 128.62, 128.61, 128.56, 128.48, 128.45, 128.14, 127.91, 100.28, 97.09, 79.63, 77.18, 75.09, 73.00, 72.33, 70.89, 69.50, 68.70, 67.04, 66.68, 55.82, 29.78, 16.79; IR (thin film) 1732 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{48}\text{H}_{47}\text{IO}_{12}\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 965.2010, found 965.2015 m/z .

6-*O*-Benzoyl-3,4-di-*O*-isopropylidene-D-galactal (33). Galactal derivative **33** was prepared according to the previously published procedure.⁸

Acetyl 6-*O*-benzoyl-3,4-di-*O*-isopropylidene-2-deoxy-2-iodo- β -D-galactoside (β -34). The title compound was isolated as a yellow oil (78 : 22 β/α) by flash chromatography (7 : 1 hexanes/EtOAc). The anomers were partially separated by preparative HPLC (87% hexanes/EtOAc): $[\alpha]_D^{27.6^\circ} = +30.5^\circ$ ($c = 0.2$, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 8.04 (m, 2H), 7.57 (m, 1H), 7.45 (app t, $J = 8.00$ Hz, 2H), 5.78 (d, $J = 10.00$ Hz, 1H), 4.62 (dd, $J = 5.00$, 3.00 Hz, 1H), 4.60 (app t, $J = 5.75$ Hz, 1H), 4.54 (dd, $J = 11.75$, 7.25 Hz, 1H), 4.39 (ddd, $J = 7.00$, 4.50, 2.00 Hz, 1H), 4.10 (dd, 5.00, 2.00 Hz, 1H), 3.91 (app t, $J = 9.25$ Hz, 1H), 2.16 (s, 3H), 1.56 (s, 3H), 1.38 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 168.91, 166.46, 133.41, 129.92, 129.85, 128.62, 110.93, 93.47, 81.70, 73.55, 72.47, 63.67, 29.93, 28.39, 26.21, 20.97; IR (thin film) 1766, 1723 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{18}\text{H}_{21}\text{IO}_7\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 499.0230, found 499.0236 m/z .

Methyl 4,6-benzylidene-2-*O*-benzoyl-3-*O*-(6-*O*-benzoyl-3,4-di-*O*-isopropylidene-2-deoxy-2-bromo- β -D-galactopyranosyl)-(1 $\rightarrow$ 3)- α -D-glucopyranoside (β -41) The title compound was isolated as a glass by flash chromatography (7 : 1 hexanes/EtOAc). $[\alpha]_D^{26^\circ} = +38.8^\circ$ ($c = 1.4$, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 8.12 (m, 2H), 8.00 (m, 2H), 7.38-7.60 (m, 8H), 7.24-7.30 (m, 3H), 5.58 (s, 1H), 5.20 (dd, $J = 10.00$, 4.00 Hz, 1H), 5.08 (d, $J = 4.00$ Hz, 1H), 4.74 (d, $J = 9.50$ Hz, 1H), 4.61 (dd, $J = 11.25$, 6.25 Hz, 1H), 4.43 (m, 2H), 4.38 (dd, $J = 9.00$, 5.00 Hz, 1H), 4.30 (dd, $J = 10.00$, 4.50 Hz, 1H), 4.01 (dt, $J = 9.16$, 3.25 Hz, 1H), 3.97 (dd, $J = 5.00$, 2.50 Hz, 1H), 3.88 (dd, $J = 9.75$, 4.25 Hz, 1H), 3.80 (m, 3H), 3.33 (s, 3H), 1.45 (s, 3H), 1.30 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.37, 165.97, 137.29, 133.46, 133.31, 130.27, 130.12, 129.96, 129.89, 129.51, 129.14, 128.62, 128.55, 128.28, 126.49, 126.28, 110.47, 101.97, 101.49, 97.72, 82.21, 80.04, 76.16, 73.66, 73.46, 71.34, 69.12, 63.43, 62.57, 55.66, 32.58, 28.36, 26.25; IR (thin film) 1724 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{37}\text{H}_{39}\text{IO}_{12}\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 825.1384, found 825.1401 m/z .

Methyl 2,3,4-*O*-tribenzoyl-6-*O*-(6-*O*-benzoyl-3,4-di-*O*-isopropylidene-2-deoxy-2-iodo- β -D-galactopyranosyl)-(1 $\rightarrow$ 6)- α -D-glucopyranoside (β -42). The title compound was isolated as a yellow oil by flash chromatography (10 : 1 $\rightarrow$ 7 : 1 hexanes/EtOAc): $[\alpha]_{\text{D}}^{27.6^\circ\text{C}} = +20.3^\circ$ ($c = 3.2$, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 8.05 (m, 2H), 7.98 (m, 2H), 7.86 (m, 4H), 7.62-7.27 (m, 12H), 6.15 (M, 1H), 5.48 (app t, $J = 9.75$ Hz, 1H), 5.25 (app s, 1H), 5.24 (dd, $J = 10.25$, 4.75, 1H), 4.65 (dd, $J = 11.75$, 4.75, 1H), 4.58 (d, $J = 9.00$ Hz, 1H), 4.56 (dd, $J = 9.00$, 5.00 Hz, 1H), 4.51 (dd, $J = 12.00$, 7.50 Hz, 1H), 4.34 (ddd, $J = 9.50$, 6.50, 2.00 Hz, 1H), 4.19 (ddd, $J = 7.00$, 4.50, 2.00 Hz, 1H), 3.80 (m, 2H), 3.54 (s, 3H), 1.51 (s, 3H), 1.36 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.50, 166.02, 165.96, 165.57, 133.58, 133.54, 133.51, 133.26, 130.14, 130.03, 129.95, 129.86, 129.48, 129.30, 129.13, 128.79, 128.61, 128.47, 110.76, 102.66, 97.04, 82.15, 73.72, 72.26, 71.68, 70.71, 69.95, 69.05, 63.73, 56.24, 31.89, 29.91, 28.39, 26.29; IR (thin film) 1728 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{44}\text{H}_{43}\text{IO}_{14}\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 945.1595, found 945.1601 m/z .

3,4-Di-*O*-(carbonyl)-6-dideoxy-D-galactal (36). Galactal **35**⁶ (1.29g, 6.02 mmol) was dissolved in MeOH (50 mL) and the resulting solution cooled to 0 °C. Ammonia was bubbled through the solution until it was saturated. The mixture was then allowed to slowly warm to 23 °C and stirred for 12 h. The reaction mixture was concentrated on a rotary evaporator. The resulting residue was taken up in EtOAc and then concentrated (x 3) to drive off residual MeOH and then further dried under vacuum for 2 h. The residual material was then taken up in dry THF (49 mL) under nitrogen. To the resulting solution was added CDI (1.65g, 10.2 mmol) followed by a few crystals of imidazole. The reaction mixture was stirred for 6 h and then concentrated on the rotary evaporator and the residue was purified by flash chromatography (4:1 hexanes/EtOAc) to provide the title compound as a yellow oil (580 mg, 62%): $[\alpha]_{\text{D}}^{27^\circ\text{C}} = -32.7^\circ$ ($c = 0.6$, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 6.68 (d, $J = 6.50$ Hz, 1H), 5.22 (dd, $J = 7.75$, 3.25 Hz, 1H), 4.93 (ddd, $J = 6.50$, 3.50, 1.50 Hz, 1H), 4.78 (app d, $J = 8.00$ Hz, 1H), 4.06 (ddd, $J = 13.50$, 6.50, 1.00 Hz, 1H), 1.46 (d, $J = 7.00$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 154.32, 149.81, 97.64, 76.46, 70.16, 69.60, 16.81; IR (thin film) 1790 cm^{-1} ; HRMS (ES) calcd for $\text{C}_7\text{H}_8\text{O}_4\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 156.0423, found 156.0425 m/z .

3,4-Di-*O*-(carbonyl)-2,6-dideoxy-2-bromo- α -D-galactopyranosyl trichloroacetimidate(39). To a solution of carbonate **36** (264 mg, 1.69 mmol) in THF (18 mL) in a foil covered flask was added H_2O (670 μL) followed by *N*-bromosuccinimide (622 mg, 3.49 mmol). After being stirred vigorously stirring for 80 min, the solution was diluted with EtOAc (100 mL) and washed with 10 wt% $\text{Na}_2\text{S}_2\text{O}_3$ solution (2 x 30 mL) followed by saturated NaCl solution. The organic extracts were dried over anhydrous Na_2SO_4 , filtered, and concentrated. The residue was purified by flash chromatography (2:1 hexanes/EtOAc) to give the 2-bromo sugar as a mixture of anomers (358 mg, 84%). ^1H NMR analysis of the mixture did not show any of the *talo* diastereomer. This material was used without further purification in the next step.

The 2-bromo sugar (358 mg, 1.41 mmol) was dissolved in dry CH_2Cl_2 (7 mL) under nitrogen and cooled to 0 °C with an icebath. To the solution was then added Cl_3CCN (7 mL). This mixture was stirred at 0 °C for 10 min, DBU (60 μL , 0.401 mmol) was added and the reaction stirred at 0 °C for 1.5 h. The crude mixture was concentrated on the rotary evaporator and the residual oil purified by flash chromatography (4:1 hexanes/EtOAc) on DavisilTM silica

gel (grade 643, 200-425 mesh, 150A, pH = 7.0 in water) to give imidate **39** (420 mg, 75%) as a yellow oil which solidified upon standing. Imidate **39** was found to be a stable solid which could be stored for several weeks frozen in dry benzene. Partial data: ^1H NMR (400 MHz, C_6D_6) δ 8.60 (s, 1H), 6.20 (d, J = 3.60 Hz, 1H), 4.45 (dd, J = 8.00, 6.80 Hz, 1H), 3.99 (dq, J = 6.60, 2.60 Hz, 1H), 3.50 (dd, J = 6.60, 2.60 Hz, 1H), 3.45 (dd, J = 8.20, 3.80 Hz, 1H), 1.06 (d, J = 6.80 Hz, 1H); ^{13}C NMR (100 MHz, C_6D_6) δ 160.22, 153.21, 94.49, 91.31, 77.26, 76.93, 65.01, 44.76, 15.98.

6-*O*-Benzyl-3,4-di-*O*-(carbonyl)-D-galactal (38**).** Galactal derivative **38** was prepared according to the previously published procedure.⁹

6-*O*-Benzyl-3,4-di-*O*-(carbonyl)-2-deoxy-2-bromo- α -D-galactopyranosyl trichloroacetimidate (40**).** Imidate **40** was prepared according to the same procedure as imidate **39**: ^1H NMR (500 MHz, C_6D_6) δ 8.52 (s, 1H), 7.08-7.19 (m, 5 H), 6.18 (d, J = 3.50 Hz, 1H), 4.31 (app t, J = 9.25 Hz, 1H), 4.25 (td, J = 6.50, 2.50 Hz, 1H), 4.21 (app s, 2H), 3.80 (dd, J = 6.50, 2.50 Hz, 1H), 3.52 (dd, J = 9.75, 7.25 Hz, 1H), 3.49 (dd, J = 6.25, 9.75 Hz, 1H), 3.34 (dd, J = 3.75, 8.50 Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 160.22, 153.01, 138.34, 129.01, 128.92, 128.48, 128.43, 94.09, 76.90, 74.45, 74.02, 68.24, 68.14, 44.59.

Methyl 4,6-benzylidene-2-*O*-benzoyl-3-*O*-(6-*O*-benzyl-3,4-di-*O*-(carbonyl)-2-deoxy-2-iodo- β -D-galactopyranosyl)-(1 $\rightarrow$ 3)- α -D-glucopyranoside (**β -43).** The title compound was isolated as a clear oil by flash chromatography (4 : 1 hexanes/EtOAc): $[\alpha]_{\text{D}}^{28^\circ\text{C}}$ = +21.4° (c = 0.5, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 8.04-8.06 (m, 2H), 7.59-7.62 (m, 3H), 7.46-7.49 (m, 2H), 7.21-7.38 (m, 6H), 7.21 (m, 2H), 5.63 (s, 1H), 5.26 (d, J = 4.00 Hz, 1H), 5.07 (m, 2H), 4.89 (dd, J = 8.62, 2.87 Hz, 1H), 4.79 (dd, J = 8.75, 2.25 Hz, 1H), 4.42 (m, 1H), 4.30 (dd, J = 4.75, 10.25 Hz, 1H), 4.15 (ddd, J = 8.00, 6.00, 2.50 Hz, 1H), 4.12 (A of AB, J = 12.00 Hz, 1H), 4.02 (B of AB, J = 12.00 Hz, 1H), 3.92 (dd, J = 8.00, 4.50 Hz, 1H), 3.91 (m, 1H), 3.80 (app t, J = 10.25 Hz, 1H), 3.70 (app t, J = 9.50 Hz, 1H), 3.41 (dd, J = 9.50, 6.00 Hz, 1H), 3.29 (dd, J = 9.25, 7.75 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.87, 153.57, 137.96, 137.81, 133.82, 130.01, 129.36, 129.30, 128.86, 128.61, 128.35, 128.00, 127.91, 127.11, 102.42, 99.31, 97.85, 79.70, 75.33, 75.13, 74.70, 73.44, 72.48, 69.15, 68.76, 68.44, 62.95, 55.62, 43.08; IR (thin film) 1815, 1724 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{35}\text{H}_{35}\text{BrO}_{12}\text{Na}$ ($\text{M}+\text{Na}$)⁺ 748.1210, found 748.1214 m/z .

Methyl 4,6-benzylidene-2-*O*-benzoyl-3-*O*-(6-*O*-benzyl-3,4-di-*O*-(carbonyl)-2-deoxy-2-iodo- α -D-galactopyranosyl)-(1 $\rightarrow$ 3)- α -D-glucopyranoside (**α -43).** The title compound was isolated by flash chromatography (4 : 1 hexanes/EtOAc) followed by purification by preparative HPLC (80% hexanes/EtOAc) to give mixed fractions from which partial data was extracted: ^1H NMR (500 MHz, CDCl_3) δ 8.08 (m, 2H), 7.22-7.49 (m, 13H), 5.65 (d, J = 3.50 Hz, 1H), 5.22 (dd, J = 3.50, 9.50 Hz, 1H), 5.05-5.11 (m, 1H), 5.01 (d, J = 4.00 Hz, 1H), 4.84 (dd, J = 6.50, 9.00 Hz, 1H), 4.76 (m, 1H), 4.51 (m, 1H), 4.45 (A of AB, J = 11.25 Hz, 1H), 4.42 (B of AB, J = 11.25 Hz, 1H), 4.34-4.39 (m, 1H), 4.24-4.27 (m, 2H), 3.95 (m, 1H), 3.82-3.88 (m, 2H), 3.60 (dd, J = 6.50, 9.50 Hz, 1H), 3.51 (dd, J = 7.00, 9.50 Hz, 1H), 3.42 (s, 3H).

Methyl 2,3,4-*O*-tribenzoyl-6-*O*-(6-*O*-benzyl-3,4-di-*O*-(carbonyl)-2-deoxy-2-bromo- β -D-galactopyranosyl)-(1 $\rightarrow$ 6)- α -D-glucopyranoside (**β -44).** The title compound was isolated as a clear oil by flash chromatography (4 : 1

→ 2 : 1 hexanes/EtOAc): $[\alpha]_D^{28^\circ} = +11.8^\circ$ ($c = 0.5$, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 7.97 (m, 4H), 7.86 (m, 2H), 7.26-7.54 (m, 14H), 6.15 (app t, $J = 9.80$ Hz, 1H), 5.26 (app t, $J = 9.80$ Hz, 1H), 5.26 (dd, $J = 10.00$, 3.60 Hz, 1H), 5.22 (d, $J = 3.60$ Hz, 1H), 5.02 (dd, $J = 7.80$, 4.60 Hz, 1H), 4.91 (d, $J = 5.20$ Hz, 1H), 4.83 (dd, $J = 7.80$, 2.20 Hz, 1H), 4.29 (m, 1H), 4.21 (m, 1H), 4.00 (m, 2H), 3.65 (m, 3H), 3.49 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.03, 265.94, 165.66, 153.21, 137.53, 133.73, 133.56, 133.28, 130.14, 130.13, 129.88, 129.43, 129.27, 129.08, 128.73, 128.70, 128.62, 128.48, 128.23, 128.04, 100.45, 97.06, 73.95, 73.32, 72.22, 70.54, 69.77, 69.72, 68.93, 68.35, 68.27, 55.96, 44.78, 29.92; IR (thin film) 1818, 1729 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{42}\text{H}_{39}\text{BrO}_{14}\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 869.1421, found 869.1428 m/z .

Methyl 2,3,4-*O*-tribenzoyl-6-*O*-(6-*O*-benzyl-3,4-di-*O*-(carbonyl)-2-deoxy-2-bromo- β -D-galactopyranosyl)-(1→6)- α -D-glucopyranoside (α -44). The title compound was isolated as a clear oil by flash chromatography (4 : 1 → 2 : 1 hexanes/EtOAc): $[\alpha]_D^{28^\circ} = +20.0^\circ$ ($c = 0.3$, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ 7.85-7.99 (m, 5H), 7.22-7.54 (m, 15H), 6.15 (app t, $J = 9.80$ Hz, 1H), 4.01 (app t, $J = 10.00$ Hz, 1H), 5.25 (m, 2H), 5.12 (dd, $J = 8.80$, 6.40 Hz, 1H), 5.08 (d, $J = 3.60$ Hz, 1H), 4.74 (dd, $J = 6.60$, 2.60 Hz, 1H), 4.44 (s, 3H), 4.26 (m, 1H), 4.20 (td, $J = 2.67$, 6.50 Hz, 1H), 3.96 (dd, $J = 8.80$, 3.20 Hz, 1H), 3.91 (dd, $J = 11.80$, 4.60 Hz, 1H), 3.73 (m, 1H), 3.59 (m, 2H), 3.47 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.01, 165.59, 153.59, 137.64, 133.84, 133.65, 133.37, 130.15, 130.03, 129.88, 129.33, 129.19, 128.96, 128.77, 128.66, 128.52, 128.17, 128.08, 127.88, 97.81, 97.30, 77.88, 75.57, 73.78, 72.22, 70.61, 69.05, 68.68, 68.14, 66.92, 65.61, 55.94, 45.91, 29.93; IR (thin film) 1819, 1729 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{42}\text{H}_{39}\text{BrO}_{14}\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 869.1421, found 869.1382 m/z .

Acetyl 3,4-di-*O*-(carbonyl)-2,6-dideoxy-2-iodo- β -D-galactopyranoside (37). The title compound was isolated as a clear oil by flash chromatography (4 : 1 → 2 : 1 hexanes/EtOAc): $[\alpha]_D^{25^\circ} = +23.5^\circ$ ($c = 0.2$, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 6.02 (d, $J = 7.00$ Hz, 1H), 5.24 (dd, $J = 7.50$, 6.00 Hz, 1H), 4.61 (dd, $J = 7.50$, 2.00 Hz, 1H), 4.37 (ddd, $J = 13.00$, 7.00, 2.00 Hz, 1H), 4.08 (dd, $J = 6.50$, 6.00 Hz, 1H), 2.14 (s, 3H), 1.45 (d, $J = 6.50$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.00, 153.15, 93.03, 79.55, 76.13, 68.15, 20.88, 20.02, 16.85; IR (thin film) 1806, 1769 cm^{-1} ; HRMS (ES) calcd for $\text{C}_9\text{H}_{11}\text{IO}_6\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 364.9498, found 364.9493 m/z .

Methyl 4,6-benzylidene-2-*O*-benzoyl-3-*O*-(3,4-di-*O*-(carbonyl)-2,6-dideoxy-2-iodo- β -D-galactopyranosyl)-(1→3)- α -D-glucopyranoside (β -45). The title compound was isolated as a clear oil by flash chromatography (7 : 1 → 4 : 1 hexanes/EtOAc) followed by preparative HPLC purification (100 → 67% hexanes/EtOAc): $[\alpha]_D^{27^\circ} = +54.9^\circ$ ($c = 1.2$, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 8.09-8.11 (m, 2H), 7.55-7.62 (m, 3H), 7.46-7.49 (m, 2H), 7.38-7.35 (m, 3H), 5.61 (s, 1H), 5.14 (dd, $J = 9.50$, 3.50 Hz, 1H), 5.06 (d, $J = 3.50$ Hz, 1H), 5.00 (d, $J = 6.50$ Hz, 1H), 4.96 (dd, 7.50, 6.00 Hz, 1H), 4.42 (app t, $J = 9.50$ Hz, 1H), 4.31 (m, 2H), 3.81-3.96 (m, 4H), 3.75 (app t, $J = 9.25$ Hz, 1H), 3.39 (s, 3H), 1.16 (d, $J = 6.50$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.91, 153.29, 137.47, 133.67, 130.21, 129.70, 129.31, 128.73, 128.31, 126.66, 102.05, 101.17, 97.86, 80.07, 76.24, 75.95, 73.90, 69.16, 67.50, 62.70, 55.66, 22.68, 16.78; IR (thin film) 1806, 1722 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{28}\text{H}_{29}\text{IO}_{11}\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 691.0652, found 691.0630 m/z .

Methyl 2,3,4-*O*-tribenzoyl-6-*O*-(3,4-di-*O*-(carbamoyl)-2,6-dideoxy-2-iodo- β -D-galactopyranosyl)-(1 $\rightarrow$ 6)- α -D-glucopyranoside (β -46). The title compound was isolated as a clear oil by flash chromatography (4 : 1 $\rightarrow$ 2 : 1 hexanes/EtOAc): $[\alpha]_D^{28^\circ} = +43.7^\circ$ ($c = 0.3$, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 7.87-7.91 (m, 3H), 7.77-7.79 (m, 2H), 7.42-7.47 (m, 2H), 7.30-7.36 (m, 5H), 7.19-7.23, 6.08 (app t, $J = 9.50$ Hz, 1H), 5.42 (app t, $J = 9.75$ Hz, 1H), 5.19 (dd, $J = 10.25$, 3.25 Hz, 1H), 5.16 (d, $J = 7.00$ Hz, 1H), 4.72 (d, $J = 7.00$ Hz, 1H), 4.33 (dd, $J = 7.00$, 2.50 Hz, 1H), 4.29 (ddd, $J = 9.50$, 7.00, 2.50 Hz, 1H), 3.99 (ddd, $J = 13.00$, 6.00, 2.00 Hz, 1H), 3.94 (dd, $J = 11.25$, 2.25 Hz, 1H), 3.83 (app t, $J = 7.00$ Hz, 1H), 3.66 (dd, $J = 11.50$, 7.00 Hz, 1H), 3.45 (s, 3H), 1.29 (d, $J = 6.50$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.01, 165.94, 165.66, 153.15, 133.71, 133.56, 133.27, 130.09, 130.05, 129.83, 129.39, 129.21, 129.06, 128.65, 128.60, 128.45, 101.54, 97.03, 81.00, 76.61, 72.19, 70.56, 69.88, 68.96, 68.43, 68.08, 56.11, 23.13, 16.60; IR (thin film) 1809, 1731 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{35}\text{H}_{33}\text{IO}_{13}\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 811.0864, found 811.0867 m/z .

Methyl 4,6-benzylidene-2-*O*-benzoyl-3-*O*-(3,4-di-*O*-(carbamoyl)-2,6-dideoxy-2-bromo- β -D-galactopyranosyl)-(1 $\rightarrow$ 3)- α -D-glucopyranoside (β -47). The title compound was isolated as a clear oil by flash chromatography (2 : 1 hexanes/EtOAc): $[\alpha]_D^{27^\circ} = +65.0^\circ$ ($c = 0.2$, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 8.08 (m, 2H), 7.58 (m, 3H), 7.47 (m, 2H), 7.36 (m, 3H), 5.61 (s, 1H), 5.13 (dd, $J = 9.50$, 4.00 Hz, 1H), 5.06 (d, $J = 4.00$ Hz, 1H), 4.96 (d, $J = 6.00$ Hz, 1H), 4.84 (dd, $J = 7.75$, 5.25 Hz, 1H), 4.48 (app t, $J = 9.25$ Hz, 1H), 4.40 (dd, $J = 7.25$, 2.25 Hz, 1H), 4.31 (dd, 10.00, 5.00 Hz, 1H), 3.93 (td, $J = 10.00$, 4.50 Hz, 1H), 3.85 (qd, $J = 7.00$, 2.00 Hz, 1H), 3.80 (m, 1H), 4.08 (app t, $J = 9.25$ Hz, 1H), 3.90 (s, 3H), 1.13 (d, $J = 6.50$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.91, 153.537, 137.44, 133.66, 130.10, 129.55, 129.31, 128.70, 128.29, 126.64, 102.05, 100.48, 97.85, 80.10, 78.32, 76.37, 76.29, 73.76, 69.12, 67.29, 62.68, 55.63, 45.89, 16.65; IR (thin film) 1818, 1724 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{28}\text{H}_{29}\text{BrO}_{11}\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 643.0791, found 643.0807 m/z .

Methyl 2,3,4-*O*-tribenzoyl-6-*O*-(3,4-di-*O*-(carbamoyl)-2,6-dideoxy-2-bromo- β -D-galactopyranosyl)-(1 $\rightarrow$ 3)- α -D-glucopyranoside (β -48). The title compound was isolated as a clear oil by flash chromatography (2 : 1 hexanes/EtOAc): $[\alpha]_D^{28^\circ} = +37.0^\circ$ ($c = 0.2$, CH_2Cl_2); ^1H NMR (400 MHz, CDCl_3) δ ; ^{13}C NMR (500 MHz, CDCl_3) δ 7.85-7.99 (m, 5H), 7.26-7.54 (m, 10H), 6.16 (app t, $J = 9.75$ z, 1H), 5.48 (app t, $J = 10.00$ Hz, 1H), 5.26 (dd, $J = 10.00$, 3.50 Hz, 1H), 5.23 (d, $J = 3.50$ Hz, 1H), 5.00 (dd, $J = 7.50$, 6.00 Hz, 1H), 4.80 (d, $J = 6.00$ Hz, 1H), 4.53 (dd, $J = 7.50$, 2.00 Hz, 1H), 4.31 (ddd, $J = 9.50$, 7.00, 2.00 Hz, 1H), 4.06 (qd, $J = 6.37$, 2.12 Hz, 1H), 4.01 (dd, $J = 11.25$, 2.25 Hz, 1H), 3.90 (app t, $J = 6.00$ Hz, 1H), 3.75 (dd, $J = 11.25$, 6.75 Hz, 1H), 3.51 (s, 3H), 1.36 (d, $J = 6.50$ Hz, 1H); IR (thin film) 1819, 1728 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{55}\text{H}_{53}\text{BrO}_{13}\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 763.1002, found 763.0980 m/z .

Methyl 2,3,6-*O*-tribenzoyl-4-*O*-(3,4-di-*O*-(carbonyl)-2,6-dideoxy-2-bromo- β -D-galactopyranosyl)-(1 $\rightarrow$ 6)- α -D-glucopyranoside (β -50). The title compound was isolated as a crystalline solid by flash chromatography (2 : 1 hexanes/EtOAc): $[\alpha]_D^{28} = +75.3^\circ$ ($c = 0.3$, CH_2Cl_2); ^1H NMR (500 MHz, CDCl_3) δ 8.10 (m, 2H), 7.98 (m, 4H), 7.63 (m, 1H), 7.51 (m, 4H), 7.37 (m, 4H), 6.01 (dd, $J = 10.25, 9.25$ Hz, 1H), 5.21 (dd, $J = 10.25, 3.75$ Hz, 1H), 5.13 (d, $J = 3.50$ Hz, 1H), 4.89 (app t, $J = 7.25$ Hz, 1H), 4.81 (dd, $J = 12.00, 4.00$ Hz, 1H), 4.73 (dd, $J = 12.50, 2.00$ Hz, 1H), 4.67 (d, $J = 7.50$ Hz, 1H), 4.28 (dd, $J = 7.00, 2.00$ Hz, 1H), 4.25 (dd, $J = 3.75, 1.75$ Hz, 1H), 4.14 (app t, $J = 5.00$ Hz, 1H), 3.77 (app t, $J = 7.25$ Hz, 1H), 3.63 (dq, $J = 6.58, 2.12$ Hz, 1H), 3.46 (s, 3H), 0.90 (d, $J = 7.00$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3) δ 166.31, 166.18, 165.54, 153.03, 133.61, 133.25, 130.15, 130.12, 129.90, 129.85, 129.13, 128.79, 128.62, 128.48, 100.63, 97.05, 79.95, 76.81, 76.32, 72.00, 70.91, 68.43, 68.33, 63.17, 55.77, 47.85, 15.68; IR (thin film) 1819, 1723 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{35}\text{H}_{33}\text{BrO}_{13}\text{Na}$ ($\text{M}+\text{Na}$) $^+$ 763.1002, found 763.0967 m/z .

References

- (1) Pangborn, A. B.; Giardello, M. A.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics* **1996**, *15*, 1518.
- (2) Roush, W. R.; Lin, X.-F. *J. Am. Chem. Soc.* **1995**, *117*, 2236-2250.
- (3) Jacquinet, J.-C. *Carbohydr. Res.* **1990**, *199*, 153-181.
- (4) Kirschning, A.; Plumeier, C.; Rose, L. *Chem. Commun.* **1998**, 33-34.
- (5) Czernecki, S.; Ayadi, E.; Randriamandimby, D. *J. Org. Chem.* **1994**, *1994*, 8256-8260.
- (6) Tulshian, D. B.; Fraser-Reid, B. *J. Am. Chem. Soc.* **1981**, *103*, 474-475.
- (7) Hanessian, S.; Rogel, O. *J. Org. Chem.* **2000**, *65*, 2667-2674.
- (8) Zhang, Z.; Magnusson, G. *J. Org. Chem.* **1995**, *60*, 7304-7315.
- (9) Desphande, P. P.; Kim, H. M.; Zatorski, A.; Park, T.-K.; Ragupathi, G.; Livingston, P. O.; Live, D.; Danishefsky, S. J. *J. Am. Chem. Soc.* **1998**, *120*, 1600-1614.