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Synthesis of disaccharide glycosyl donors suitable for introduction of the β-D-Gal*p*-(1 → 3)-α- and -β-D-Gal*p*NAc groups

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Abstract

2-(Trimethylsilyl)ethyl 2-azido-4,6-*O*-benzylidene-2-deoxy-β-D-galactopyranoside (**4**) was glycosylated with phenyl 2,3,4,6-tetra-*O*-acetyl-1-thio-β-D-galactopyranoside to give 2-(trimethylsilyl)ethyl 2-azido-4,6-*O*-benzylidene-2-deoxy-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-galactopyranoside (**6**) in 99% yield. Removal of the benzylidene group and acetylation gave the key intermediate 2-(trimethylsilyl)ethyl 4,6-di-*O*-acetyl-2-azido-2-deoxy-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-β-D-galactopyranoside (**7**), which was transformed into methyl 4,6-di-*O*-acetyl-2-deoxy-2-phthalimido-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-1-thio-β-D-galactopyranoside (**9**) in two steps in an overall yield of 69%. Similarly, **7** was transformed in two steps into 4,6-di-*O*-acetyl-2-azido-2-deoxy-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-galactopyranosyl bromide (**11**) in an over-all yield of 86%. Compounds **9** and **11** are suitable glycosyl donors for introduction of the β-D-Gal*p*-(1 → 3)-β- and -α-D-Gal*p*NAc groups.

Keywords: β-D-Gal*p*-(1 → 3)-D-Gal*p*NAc synthons; 2-(Trimethylsilyl)ethyl glycoside

1. Introduction

The β-D-Gal*p*-(1 → 3)-D-GalNAc disaccharide is present in many biologically important glycolipids and glycoproteins. Several syntheses have been reported [1–7], including methods for the preparation of the disaccharide in a form that makes it suitable as donor for α-glycosylation [4,6–8]. The main problem in synthesizing the disaccharide has been the construction of the glycosidic bond between the Gal and the GalNAc

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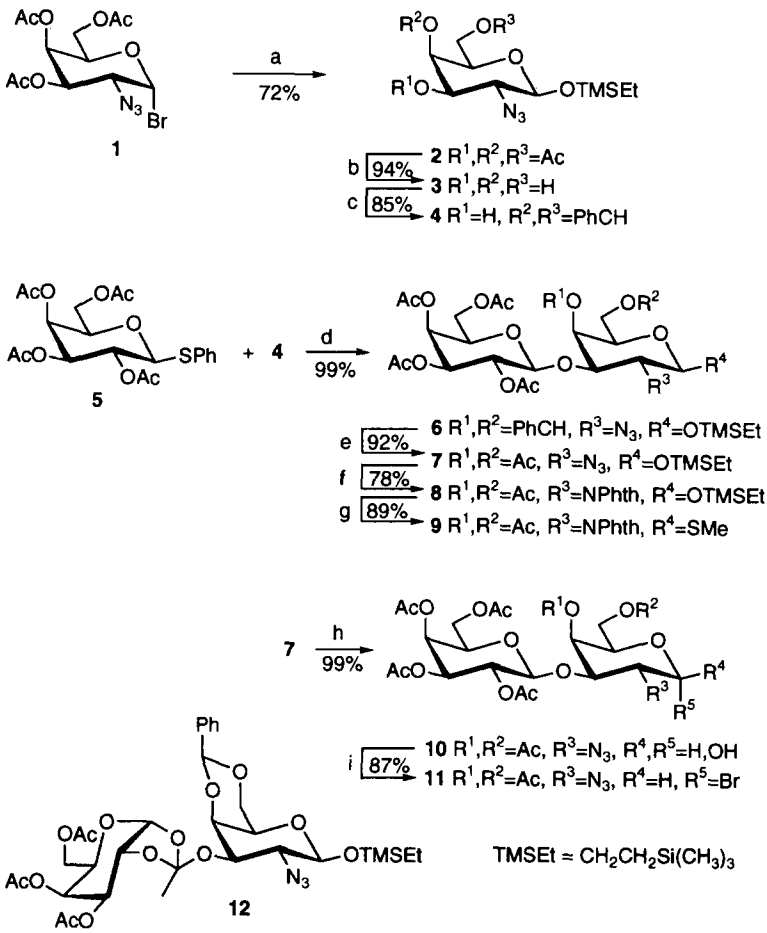

Scheme 1. (a) $Me_3SiCH_2CH_2OH$, Ag–silicate, non-acid-washed molecular sieve 4 Å, room temp., CH_2Cl_2, N_2. (b) MeONa, MeOH, room temp. (c) $PhCH(OMe)_2$, *p*-$MePhSO_3H$, MeCN, room temp. (d) NIS, F_3CSO_3H, acid-washed molecular sieve 4 Å, −45°C, MeCN, CH_2Cl_2, Ar. (e) 80% AcOH, 90°C, then Ac_2O–pyridine, room temp. (f) $NiCl_2 \cdot 6H_2O$, H_3BO_3, $NaBH_4$, 0°C, EtOH, then phthalic anhydride, 22 → 90°C, pyridine. (g) Ac_2O, $BF_3 \cdot Et_2O$, CH_2Cl_2, N_2, then Me_3SiCH_2SH, $F_3CSO_3SiMe_3$, room temp., CH_2Cl_2, N_2. (h) F_3CCO_2H, room temp., CH_2Cl_2, Ar. (i) $(COBr)_2$, room temp., CH_2Cl_2, Ar.

residues [5]. For example, it was recently reported that GalNPhth β-glycosides could be β-galactosylated in the 3-position in only 5% yield [9]. We now report a high-yielding and convenient route to β-D-Gal*p*-(1 → 3)-D-GalNAc precursors as donors suitable for both α- and β-glycosylation. The 2-(trimethylsilyl)ethyl glycoside **7**, carrying a 2-azido functionality, is the key intermediate that was transformed in high yield into both the 2-phthalimido-thioglycoside **9** (useful for β-glycosylation) and the 2-azido glycosyl bromide **11** (useful for α-glycosylation) (Scheme 1).

Glycosylation of 2-(trimethylsilyl)ethanol with the bromo sugar **1** [1,10], using silver silicate [11] as promoter, gave the 2-(trimethylsilyl)ethyl (TMSEt) glycoside **2** (72%, β/α 23:1, determined from the NMR spectrum). Deacetylation of **2** gave **3** (94%, β/α

23:1); a pure β anomer was obtained by recrystallization from an ether/heptane mixture. Benzylidenation of the α/β-mixture of **3** and column chromatography of the crude product gave anomerically pure **4** (85%) which is also a crystalline compound.

Glycosylation of the TMSEt glycoside **4** with the thioglycoside **5** [12] in the presence of *N*-iodosuccinimide [13] (NIS), trifluoromethanesulfonic acid (TfOH), and acid-washed molecular sieve gave the desired crystalline disaccharide **6** in almost quantitative yield (96–99%); no α-glycoside was observed in the crude product mixture. A rather large amount of TfOH (0.4–0.7 equiv) and acid-washed molecular sieve were used in order to avoid formation of the orthoester **12**.

With 0.15 equivalent of TfOH and non-acid-washed molecular sieve, only orthoester **12** (*exo*/*endo* > 4:1) was obtained. Changing to acid-washed sieve but retaining the low amount of TfOH gave orthoester and/or glycoside in an unpredictable and sluggish reaction. Orthoester **12** was transformed into **6** under the successful reaction conditions described above. Initial attempts to glycosylate **4** with various galactosyl halides, using silver triflate as promoter, either failed or gave low yields.

Removal of the benzylidene group in **6**, followed by acetylation of the exposed hydroxyl groups gave the key intermediate glycoside **7** (92%).

The azido group of **7** was reduced with sodium borohydride/nickel chloride/boric acid [14] (''nickel boride'') and the resulting amino group was phthaloylated in a separate reaction to give the TMSEt glycoside **8** (78%). Reduction of the azide group in the presence of phthalic anhydride [15] gave **8** (58%) in a ''one-pot'' procedure.

The TMSEt group of **8** was replaced by an acetyl group by treatment with acetic anhydride/boron trifluoride etherate, a reaction that normally retains the anomeric configuration of the starting TMSEt glycoside [16]. Treatment of the crude disaccharide acetate with trimethylsilylmethanethiol-trimethylsilyl trifluoromethanesulfonate [17] furnished the thioglycoside **9** (89%), suitable as disaccharide β-donor in block synthesis of higher glycosides.

The azido TMSEt glycoside **7** was treated with trifluoroacetic acid in dichloromethane [16] to give the hemiacetal **10** (99%, α/β 4:1). This seems to be the first anomeric deblocking of a TMSEt glycoside carrying an azido group in the 2-position and it was thus quite rewarding to find that it proceeded in as high a yield as in the majority of the numerous examples reported by us and others.

The hemiacetal **10** was transformed into the known [4,7,8] α-bromide **11** (87%) by treatment with oxalyl bromide. Compound **11** is suitable as disaccharide α-donor in block synthesis and therefore complements the β-donor **9**.

2. Experimental

General methods.—Melting points are uncorrected. Optical rotations were measured with a Perkin–Elmer 141 polarimeter. ^{1}H-NMR spectra were recorded with a Varian XL-300 spectrometer. High resolution mass spectra were obtained on a JEOL JMS SX 102 spectrometer. Concentrations were made using rotary evaporation with bath temperature at or below 40°C. TLC was performed on Kieselgel 60 F_{254} plates (Merck). Column chromatography was performed using SiO_2 (Matrex LC-gel; 60 A, 35-70 MY, Grace).

2-(Trimethylsilyl)ethyl 2,4,6-tri-O-acetyl-2-azido-2-deoxy-β-D-galactopyranoside (**2**). —A solution of 2-(trimethylsilyl)ethanol (9.5 g, 80.3 mmol), silver silicate [11] (61 g), and powdered, non-acid-washed molecular sieve (35 g, 4 Å) in dry CH_2Cl_2 (300 mL) was stirred under N_2 for 2 h. 3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-α-D-galactopyranosyl bromide [10] (**1**; 21.1 g, 53.6 mmol), dissolved in dry CH_2Cl_2 (30 mL), was added dropwise. After 20 min, the reaction mixture was filtered (Celite) and concentrated. The residue was chromatographed (3:1 heptane–EtOAc), to give **2** (16.6 g, 72%) as an unseparable 1:23 α/β-mixture; $[\alpha]_D^{25}$ −18° (*c* 0.96, $CHCl_3$). ^{1}H-NMR data ($CDCl_3$): δ 5.33 (dd, 1 H, *J* 1.0, 3.4 Hz, H-4), 4.78 (dd, 1 H, *J* 3.4, 10.9 Hz, H-3), 4.37 (d, 1 H, *J* 8.0 Hz, H-1), 3.84 (ddd, 1 H, *J* 1.1, 7.0, 7.7 Hz, H-5), 3.67 (m, 1 H, OCH_2), 3.66 (dd, 1 H, *J* 7.9, 11.0 Hz, H-2), 2.15–2.05 (3 s, 3 H each, OAc), 1.06 (m, 2 H, CH_2Si), 0.04 (s, 9 H, $SiMe_3$). Mass spectrum: Calcd for $C_{17}H_{29}O_8N_3Si$ (M + NH_4): *m/z* 449.2068; Found: *m/z* 449.2067.

2-(Trimethylsilyl)ethyl 2-azido-2-deoxy-β-D-galactopyranoside (**3**).—Sodium methoxide (2 M, 1.25 mL) was added to a solution of **2** (4.88 g, 11.3 mmol) in dry MeOH (50 mL) and the mixture was stirred for 90 min, then neutralized with Amberlite IR-120 (H^+) resin, filtered, and concentrated to give **3** (3.24 g, 94%, α/β 1:23). A sample was crystallized from ether–heptane to give the pure β-anomer; mp 158–161°C, $[\alpha]_D^{25}$ +9° (*c* 0.79, CH_3OH). ^{1}H-NMR data (CD_3OD): δ 4.28 (m, 1 H, virtual coupling, similar to entry 19 in ref. [18], H-1), 4.05 (m, 1 H, OCH_2), 3.79 (dd, 1 H, *J* 1.1, 2.6 Hz, H-4), 3.73 (m, 2 H, H-2, H-3), 3.65 (m, 1 H, OCH_2), 3.46 (ddd, 1 H, *J* 1.0, 5.5, 6.6 Hz, H-5), 3.42 (m, 2 H, H-6a, H-6b), 1.00 (m, 2 H, CH_2Si), 0.05 (s, 9 H, $SiMe_3$). Mass spectrum: Calcd for $C_{11}H_{23}O_5N_3Si$ (M + NH_4): *m/z* 323.1751; Found: *m/z* 323.1740.

2-(Trimethylsilyl)ethyl 2-azido-4,6-O-benzylidene-2-deoxy-β-D-galactopyranoside (**4**).—A mixture of **3** (1.50 g, 4.91 mmol, α/β 1:23), α,α-dimethoxytoluene (1.2 mL, 7.92 mmol), *p*-toluenesulfonic acid (catalytic amount), and acetonitrile (22 mL) was stirred overnight. Triethylamine (2 mL) was added and the solution was concentrated. Column chromatography (3:1 heptane–EtOAc + 0.1%Et_3N) gave anomerically pure **4** (1.64 g, 85%). An analytical sample was crystallized from heptane; mp 106–107°C, $[\alpha]_D^{25}$ −16° (*c* 0.94, $CHCl_3$). ^{1}H-NMR data ($CDCl_3$): δ 7.52 (m, 2 H, Ph), 7.39 (m, 3 H, Ph), 5.57 (s, 1 H, PhC*H*), 4.36 (dd, 1 H, *J* 1.5, 12.5 Hz, H-6), 4.31 (d, 1 H, *J* 7.6 Hz, H-1), 4.18 (dd, 1 H, *J* 1.1, 3.5 Hz, H-4), 3.45 (m, 1 H, H-5), 1.07 (m, 2 H, CH_2Si), 0.04 (s, 9 H, $SiMe_3$). Mass spectrum: Calcd for $C_{18}H_{27}O_5N_3Si$ (M + NH_4): *m/z* 411.2064; Found: *m/z* 411.2036.

2-(Trimethylsilyl)ethyl 2-azido-4,6-O-benzylidene-2-deoxy-3-O-(2,3,4,6-tetra-O-acetyl-β-D-galactopyranosyl)-β-D-galactopyranoside (**6**).—A mixture of **5** (84 mg, 191 μmol), **4** (50 mg, 127 μmol), powdered, acid-washed molecular sieve (130 mg, AW 300), dry MeCN (1.7 mL), and dry CH_2Cl_2 (0.66 mL) was stirred at room temperature for 1 h under Ar and then cooled to −45°C. To the cooled mixture was added dropwise a solution of *N*-iodosuccinimide (46 mg, 203 μmol) and trifluoromethanesulfonic acid (7.8 μL, 89 μmol) in dry MeCN (0.3 mL). After 1 h 40 min, triethylamine (250 μL) was added and the mixture was filtered (Celite), successively washed with saturated aqueous $Na_2S_2O_3$ and saturated aqueous $NaHCO_3$, dried (Na_2SO_4), and concentrated. Column chromatography (3:2 heptane–EtOAc) gave **6** (91.9 mg, 99%). An analytical

sample was crystallized from heptane–EtOAc; mp 150–152°C, $[\alpha]_D^{25}$ +7° (*c* 0.94, $CHCl_3$). ^{1}H-NMR data ($CDCl_3$): δ 7.54 (m, 2 H, Ph), 7.37 (m, 3 H, Ph), 5.50 (s, 1 H, PhC*H*), 5.39 (d, 1 H, *J* 3.5 Hz, H-4′), 5.26 (dd, 1 H, *J* 7.9, 10.4 Hz, H-2′), 5.26 (dd, 1 H, *J* 3.4, 10.3 Hz, H-3′), 4.81 (d, 1 H, *J* 8.0 Hz, H-1′), 4.30 (d, 1 H, *J* 8.0 Hz, H-1), 3.90 (bt, 1 H, *J* 6.4 Hz, H-5′), 3.79 (dd, 1 H, *J* 7.9, 10.4 Hz, H-2), 3.58 (m, 1 H, OCH_2), 3.46 (dd, 1 H, *J* 3.3, 10.6 Hz, H-3), 3.37 (bs, 1 H, H-5), 2.16–1.99 (4 s, 3 H each, OAc), 1.04 (m, 2 H, CH_2Si), 0.03 (s, 9 H, $SiMe_3$). Mass spectrum: Calcd for $C_{32}H_{45}O_{14}N_3Si$ ($M + NH_4$): *m/z* 741.3015; Found: *m/z* 741.3045.

*2-(Trimethylsilyl)ethyl 4,6-di-*O*-acetyl-2-azido-2-deoxy-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-β-*D*-galactopyranoside* (**7**).—Compound **6** (4.29 g, 5.93 mmol) was dissolved in aq 80% AcOH (130 mL) and kept at 90°C for 2 h. The mixture was concentrated and coevaporated three times with toluene. The residue was acetylated in Ac_2O–pyridine (100 mL, 1:1) overnight. The mixture was concentrated and chromatographed (3:2 heptane–EtOAc), to give **7** (3.91 g, 92%), $[\alpha]_D^{25}$ +10° (*c* 0.95, $CHCl_3$). ^{1}H-NMR data ($CDCl_3$): δ 5.15 (dd, 1 H, *J* 7.8, 10.7 Hz, H-2′), 5.00 (dd, 1 H, *J* 3.4, 10.5 Hz, H-3′), 4.71 (d, 1 H, *J* 7.8 Hz, H-1′), 4.26 (d, 1 H, *J* 7.5 Hz, H-1), 3.89 (m, 1 H, H-5′), 3.73 (m, 1 H, H-5), 3.50 (dd, 1 H, *J* 3.2, 10.3 Hz, H-3), 2.16–1.99 (6 s, 3 H each, OAc), 1.05 (m, 2 H, CH_2Si), 0.04 (s, 9 H, $SiMe_3$). Mass spectrum: Calcd for $C_{29}H_{45}O_{16}N_3Si$ ($M + NH_4$): *m/z* 737.2913; Found: *m/z* 737.2932.

*2-(Trimethylsilyl)ethyl 4,6-di-*O*-acetyl-2-deoxy-2-phthalimido-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-β-*D*-galactopyranoside* (**8**).—To a solution of **7** (614 mg, 853 μmol), nickel(II) chloride hexahydrate (3.86 g, 16.2 mmol), and H_3BO_3 (1.90 g, 30.7 mmol) in EtOH (60 mL) was added dropwise a mixture of $NaBH_4$ (811 mg, 21.4 mmol) in EtOH (25 mL) at 0°C. After 50 min an additional portion of nickel(II) chloride hexahydrate (1.80 g, 7.55 mmol) and $NaBH_4$ (811 mg, 21.4 mmol) in EtOH (25 mL) was added. The mixture was stirred for another 2 h 30 min and then concentrated. The residue was dissolved in CH_2Cl_2 and the solution was successively washed with saturated aq $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated. The residue was dissolved in pyridine (30 mL) and phthalic anhydride (152 mg, 1.02 mmol) was added. The mixture was stirred at room temperature overnight and the temperature was then raised to 90°C. After 2 h 30 min, Ac_2O (25 mL) was added and, after an additional 2 h, the mixture was concentrated. The residue was chromatographed (1:1 heptane–EtOAc) to give **8** (546 mg, 78%), $[\alpha]_D^{25}$ +10° (*c* 0.94, $CHCl_3$). ^{1}H-NMR data ($CDCl_3$): δ 7.87 (m, 2 H, Ph), 7.78 (m, 2 H, Ph), 5.46 (bd, 1 H, *J* 3.2 Hz, H-4), 5.24 (dd, 1 H, *J* 0.8, 3.4 Hz, H-4′), 5.13 (d, 1 H, *J* 8.4 Hz, H-1), 5.02 (dd, 1 H, *J* 7.9, 10.4 Hz, H-2′), 4.78 (dd, 1 H, *J* 3.4, 10.4 Hz, H-3′), 4.70 (dd, 1 H, *J* 3.4, 11.1 Hz, H-3), 4.53 (dd, 1 H, *J* 8.4, 11.1 Hz, H-2), 4.42 (d, 1 H, *J* 7.9 Hz, H-1′), 3.76 (m, 1 H, H-5), 3.49 (m, 1 H, OCH_2), 2.18–1.57 (6 s, 3 H each, OAc). Mass spectrum: Calcd for $C_{37}H_{49}O_{18}NSi$ (M + H): *m/z* 824.2797; Found: *m/z* 824.2792.

*Methyl 4,6-di-*O*-acetyl-2-deoxy-2-phthalimido-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-1-thio-β-*D*-galactopyranoside* (**9**).—To a solution of **8** (140 mg, 170 μmol) in dry CH_2Cl_2 (3.7 mL) was added acetic anhydride (76 μL, 800 μmol) and BF_3 etherate (45 μL, 340 μmol) under N_2. After 1 h 50 min, the mixture was diluted with CH_2Cl_2, washed with saturated aq $NaHCO_3$, dried (Na_2SO_4), concentrated and coevaporated with toluene. The residue was dissolved in dry CH_2Cl_2 (3 mL) and

trimethylsilyl triflate (38 μL, 195 μmol) and trimethylsilylmethanethiol (100 μL, 680 μmol) were added under N_2. After 72 h the mixture was diluted with CH_2Cl_2, washed with saturated aq $NaHCO_3$, dried (Na_2SO_4) and concentrated. Column chromatography (2:3 heptane–EtOAc) gave **9** (121 mg, 89%), $[\alpha]_D^{25}$ +34° (*c* 0.96, $CHCl_3$). ^{1}H-NMR data ($CDCl_3$): δ 7.88 (m, 2 H, Ph), 7.73 (m, 2 H, Ph), 5.51 (bd, 1 H, *J* 3.4 Hz, H-4), 5.25 (dd, 1 H, *J* 1.0, 3.4 Hz, H-4′), 5.14 (d, 1 H, *J* 10.3 Hz, H-1), 5.02 (dd, 1 H, *J* 7.9, 10.3 Hz, H-2′), 4.79 (m, 2 H, H-3, H-3′), 4.63 (t, 1 H, *J* 10.5 Hz, H-2), 3.76 (bt, 1 H, *J* 7.1 Hz, H-5), 2.18–1.57 (7 s, 3 H each, OAc, SMe). Mass spectrum: Calcd for $C_{33}H_{39}O_{17}NS$ (M + H): *m/z* 754.2017; Found: *m/z* 754.2020.

*4,6-Di-*O*-acetyl-2-azido-2-deoxy-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-*D*-galactopyranose* (**10**).—Compound **7** (100 mg, 139 mmol) was dissolved in dry CH_2Cl_2 (1 mL) under argon. Trifluoroacetic acid (2 mL) was added and the mixture was stirred for 80 min. Propyl acetate (3 mL) and toluene (6 mL) were added and the mixture was concentrated. The residue was chromatographed (1:2 heptane–EtOAc) to give **10** (85 mg, 99%, α/β 4:1); $[\alpha]_D^{25}$ +47° (c 1.01 $CHCl_3$). ^{1}H-NMR data for the α-anomer ($CDCl_3$): δ 5.48 (bd, 1 H, *J* 2.5 Hz, H-4), 5.41 (d, 1 H, *J* 3.6 Hz, H-1), 5.01 (dd, 1 H, *J* 3.4, 10.4 Hz, H-3′), 4.72 (d, 1 H, *J* 7.7 Hz, H-1′), 3.74 (dd, 1 H, *J* 3.5, 10.6 Hz, H-3), 2.16–1.97 (6 s, 3 H each, OAc). ^{1}H-NMR data for the β-anomer ($CDCl_3$): δ 5.01 (dd, 1 H, *J* 3.4, 10.4 Hz, H-3′), 4.70 (d, 1 H, *J* 7.8 Hz, H-1′), 4.60 (d, 1 H, *J* 7.8 Hz, H-1), 3.74 (dd, 1 H, *J* 3.5 Hz, H-3), 2.16–1.97 (6 s, 3 H each, OAc). Mass spectrum: Calcd for $C_{24}H_{33}O_{16}N_3$ (M + H): *m/z* 620.1939; Found: *m/z* 620.1942.

*4,6-Di-*O*-acetyl-2-azido-2-deoxy-3-*O*-(2,3,4,6-tetra-*O*-acetyl-β-*D*-galactopyranosyl)-α-*D*-galactopyranosyl bromide* (**11**).—Oxalyl bromide (22.7 μL, 242 μmol) was dissolved in dry CH_2Cl_2 (2 mL) and the mixture was added to a cooled (0°C) solution of **10** (50 mg, 81 μmol) in dry CH_2Cl_2 (2 mL) and dry DMF (17.5 μL, 226 μmol) under Ar. The mixture was stirred for 90 min at 0°C and for 5 h at 22°C, then diluted with CH_2Cl_2, washed with saturated aqueous $NaHCO_3$ and water, dried (Na_2SO_4), and concentrated to give **11** containing < 10% (according to the NMR spectrum) of the starting material **10** (48 mg, 87%). The mixture of **11** and **10** seems to be pure enough for use as glycosyl donor. An analytical sample of **11** was obtained by chromatography (1:2 heptane–EtOAc); $[\alpha]_D^{25}$ +107° (*c* 1.0 $CHCl_3$); lit. [8] +76° (*c* 0.1, $CHCl_3$), lit. [7] +81°). ^{1}H-NMR data were in full accord with those published [8]; ($CDCl_3$) δ 6.48 (d, 1 H, *J* 3.7 Hz, H-1), 5.44 (dd, 1 H, *J* 1.2, 3.4 Hz, H-4′), 5.36 (dd, 1 H, *J* 1.0, 3.4 Hz, H-4), 5.18 (dd, 1 H, *J* 7.7, 10.5 Hz, H-2′), 4.99 (dd, 1 H, *J* 3.4, 10.5 Hz, H-3′), 4.74 (d, 1 H, *J* 7.8 Hz, H-1′), 4.38 (dd, 1 H, *J* 5.1, 7.4 Hz, H-5), 2.15–1.97 (6 s, 3 H each, OAc).

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