Synthesis of β-*C*-Glycosides of *N*-Acetylglucosamine via Keck Allylation Directed by Neighboring Phthalimide Groups

Barbara A. Roe, Constantine G. Boojamra, Jennifer L. Griggs, and Carolyn R. Bertozzi*

Department of Chemistry, University of California, Berkeley, California 94720

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Oligosaccharides are the most structurally diverse of nature's biopolymers, and they possess tremendous potential for encoding biological information. Cell surface-associated oligosaccharides, in particular, have attracted significant attention in recent years due to their function as determinants for cell−cell recognition during many pathophysiological processes.[1] New methods for the construction of oligosaccharides and their mimetics are essential for studying the biological functions of glycoconjugates and for the development of therapeutic agents. Carbon-linked glycosides (*C*-glycosides) are hydrolytically stable carbohydrate mimetics that have been widely investigated as synthons for natural product synthesis and as biologically active compounds.[2] Major advances in synthetic methodology for *C*-glycosides during the last decade have led to reports of *C*-linked glycoconjugates of staggering complexity, such as trisaccharides, glycopeptides, and glycolipids.[3] Despite these successes, there are still many naturally occurring carbohydrate structures for which the *C*-linked version is not easily constructed.

2-Amino sugars such as *N*-acetylglucosamine (GlcNAc) and *N*-acetylgalactosamine (GalNAc) are major components of many glycoproteins and are attractive targets for the design of *C*-linked mimetics.[4,5] Unfortunately, *C*-glycosyl derivatives of 2-amino sugars are among the most difficult to prepare due to the incompatibility of neighboring nitrogen-based functional groups (i.e., amides, carbamates, and azides) with common *C*-glycosylation strategies.[6,7] Accordingly, few methods for their synthesis have been reported. The two most commonly used strategies for the synthesis of α-linked 2-amino *C*-glycosides are (1) Wittig-type reactions at the anomeric center, followed by recyclization to form the pyranose or furanose products,[7−9] and (2) Lewis acid-catalyzed addition of allyltrimethylsilanes[10] or alkynylstannanes[6,11] to the anomeric center of 2-azido sugars.

Methods for the synthesis of β-linked 2-amino *C*-glycosides are even more limited. These derivatives have been prepared by the alkylation of a 2-acetamido glycosyl halide with diethyl malonate anion,[12] by reduction of β-linked anomeric cyanides to the corresponding methylamino glycosides,[13] and by the condensation of a free reducing 2-acetamido sugar with nitromethane.[14] While these methods are fairly direct, the yields are low in some cases and the functional group at the *C*-glycosyl linkage (i.e., amine or nitro group) cannot be conveniently elaborated.

One of the mildest and most efficient routes to *C*-glycosyl derivatives is the reaction of anomeric radicals with activated alkenes[15−20] or allylstannanes (i.e., Keck allylation).[21−24] Radical-promoted *C*-glycosylations have been used primarily in the synthesis of α-linked products, reflecting the preferred stereoselectivity of anomeric radical addition to the alkene coupling partner. Anomeric radicals can be generated from simple glycosyl halides, and the reactions can be performed in the presence of a diverse range of functional groups. We predicted that Keck allylation at the anomeric center would be compatible with the 2-acetamido group, and as expected,[25] reaction of 2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-α-D-glucopyranosyl chloride (**1**)[26] with allyltributyltin in the presence of AIBN afforded α-linked *C*-glycoside **2** with good stereoselectivity (1:10 β/α) (Scheme 1).

The utility of this method would be greatly enhanced by its extension to β-linked *C*-glycosides, particularly of 2-amino sugars. Here, we report the synthesis of β-linked 2-amino *C*-glycosides using a Keck allylation directed by phthalimide protecting groups on the neighboring 2-amino substituent. We have applied this method to the multigram synthesis of a versatile β-*C*-glycoside of GlcNAc.

The phthalimide group has found widespread use in the protection of 2-amino substituents during oligosaccharide synthesis.[27] Trans-glycosylation products (β-linked in the case of *gluco* or *galacto* derivatives) are obtained due to its participating nature and steric bulk. We reasoned that the steric demands of the 2-phthal-

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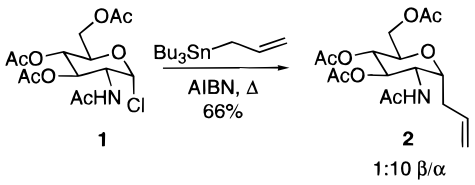
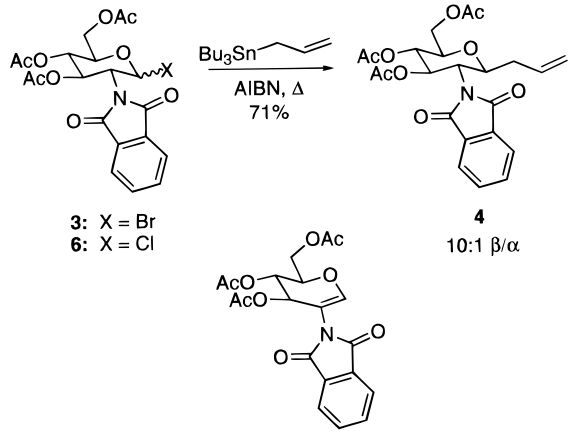
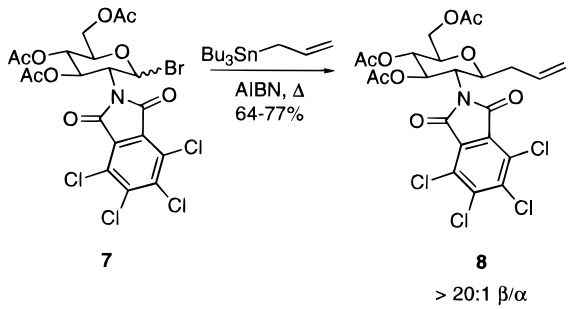
Scheme 1



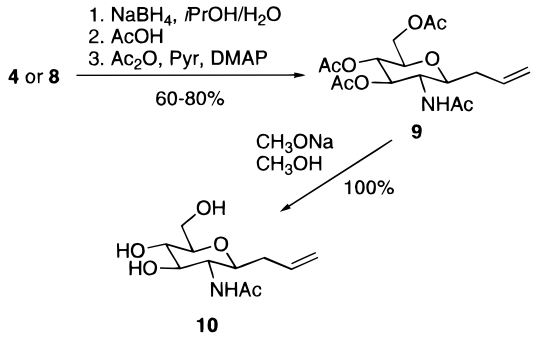
Scheme 2



Scheme 3



Scheme 4



imido group would be sufficient to promote the formation of *trans*-glycosyl, or β-linked, products during radical-promoted *C*-glycosylations of glucosamine. Indeed, treatment of 2-deoxy-2-phthalimido-3,4,6-tri-*O*-acetyl-D-glucopyranosyl bromide (**3**)[27] with allyltributyltin (12 equiv) and AIBN at 80 °C afforded the *C*-allyl derivative **4** in 71% yield with a β/α ratio of 10:1 (Scheme 2).[28] The remarkable stereoselectivity of this reaction appears to be determined by the nature of 2-amino protection, since the α-linked isomer was obtained preferentially when the 2-acetamido derivative **1** was subjected to the same conditions. The change in stereoselectivity observed with the change in protecting group may reflect the increased steric demands of the phthalimido vs the acetamido group.

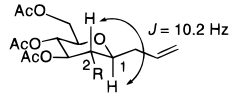
The yield of **4** was dependent on an excess (10−12 equiv) of allyltributyltin. The use of only 3 molar equiv resulted in a 30% yield of compound **4**, with the thermal elimination product **5** accounting for the remainder of the isolable mass. We also examined glycosyl chloride **6** as a substrate for radical-promoted β-*C*-glycosylation.[29] When compound **6** was subjected to the same conditions as compound **3**, no reaction was observed at 80 °C. Increasing the temperature of the reaction to 110 °C resulted in complete conversion to compound **5**.

Although the phthalimide group has been used extensively for amine protection during oligosaccharide synthesis, several groups have reported difficulty in its removal.[30−32] A recently described alternative is the tetrachlorophthalimide (TCP) group, which behaves similarly to the phthalimide during glycosylation reactions but can be removed under very mild conditions, even in the presence of acetate esters.[33,34] We examined the utility of the TCP group in directing β-*C*-glycosylations by subjecting compound **7** to the same conditions used in the synthesis of *C*-glycoside **4** (Scheme 3). Compound **8** was obtained in a yield of 77% with high β-selectivity (>20:1 β/α). A typical yield of 64% was obtained on a large scale (i.e., 15 g).

The phthalimide and TCP groups of compounds **4** and **8**, respectively, were removed by treatment with sodium borohydride followed by acid hydrolysis,[35] and the product was purified as the acetylated derivative **9** (Scheme 4). Other methods for phthalimide deprotection, such as reaction with hydrazine or methylamine, gave less satisfactory yields. Finally, compound **9** was deacetylated to give GlcNAc derivative **10**, which can serve as a precursor to mimics of GlcNAc-based glycoconjugates.

In summary, we have described a new synthesis of β-*C*-glycosides of 2-amino sugars using the phthalimide and TCP protecting groups to control the stereoselectivity of a Keck allylation at the anomeric center. The β-*C*-glycosylation reaction proceeds in high yield with excellent stereoselectivity. The olefinic product can be readily converted to other functionalities, such as aldehydes, amines, alcohols, carboxylic acids, epoxides, etc., and is therefore an excellent synthon for a variety of glycocon-

(28) The stereochemistry of compounds **4** and **8** was assigned on the basis of the coupling constant (*J*) of the anomeric (C-1) proton and the adjacent (C-2) proton (10.2 Hz for both compounds).



R = Phthalimide or TCP

(29) Compound **6** was synthesized in two steps from 2-deoxy-2-phthalimido-1,3,4,6-tetra-*O*-acetyl-D-glucopyranoside (mixture of anomers) using a modification of the procedure described by Lemieux *et al*. (1) 1.1 equiv hydrazine acetate, CH_3CN, rt, 24 h; (2) oxalyl chloride, DMF, 0 °C, 1 h. Lemieux, R. U.; Abbas, S. Z.; Chung, B. Y. *Can. J. Chem.* **1982**, *60*, 58.

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jugate mimetics. In addition, we have extended the utility of the recently described TCP protecting group to *C*-glycosylation chemistry. The novel *C*-glycosyl analogs of GlcNAc described herein will be valuable tools for dissecting the role of oligosaccharides in regulating protein function.

Experimental Section

General Procedures. Materials were obtained from commercial suppliers and were used without further purification unless otherwise noted. The silica gel used in column chromatography was Merck 60 Å, 230−400 mesh. Benzene and acetonitrile were distilled from CaH_2. Anhydrous pyridine was obtained from Aldrich or distilled from CaH_2. ^{1}H NMR spectra were obtained at 400 or 500 MHz. ^{13}C NMR spectra were proton decoupled and acquired at 101 or 126 MHz. Chemical shifts are reported in δ values relative to tetramethylsilane. Coupling constants are reported in hertz. Melting points (Pyrex capillary) are uncorrected. Fast atom bombardment (FAB^+) mass spectra and elemental analyses were obtained at the U. C. Berkeley Mass Spectral Laboratory and Microanalytical Laboratories, respectively.

3-(2-Acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-α-D-glucopyranosyl) propene (2). To a solution of 1.03 g (2.82 mmol) of 2-acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-α-D-glucopyranosyl chloride **1** (prepared according to ref 26) and 9.3 g (28.2 mmol) of allyltributyltin in 7 mL of THF was added 0.14 g (0.85 mmol) of AIBN. The solution was purged with Ar and then heated at reflux for 1 h. The THF was removed *in vacuo*, and the remaining residue was partitioned between 25 mL of CH_3CN and 100 mL of pentane. The CH_3CN layer was extracted with additional pentane (5 × 100 mL) to remove the remaining organotin compounds and then concentrated to dryness. Silica gel chromatography eluting with 2:1 hexanes/EtOAc afforded 0.69 g (66%) of a waxy solid comprising an inseparable mixture of α and β isomers (10:1 α/β as determined by peak integration of the ^{1}H NMR spectrum). Major (α) isomer: IR (thin film) 3290, 3075, 1746, 1658 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.94 (s, 3), 2.04 (s, 3), 2.05 (s, 3), 2.06 (s, 3), 2.24−2.29 (m, 1), 2.35−2.43 (m, 1), 3.84−3.89 (m, 1), 4.08 (dd, 1, J = 3.6, 12.0), 4.18−4.31 (m, 3), 4.92 (app t, 1, J = 6.9), 5.01−5.13 (m, 3), 5.68−5.79 (m, 1), 5.91 (d, 1, J = 8.4); ^{13}C NMR δ 20.7, 20.8, 23.1, 32.0, 50.5, 61.6, 67.8, 70.0, 70.5, 70.9, 117.6, 133.3, 169.0, 169.6, 170.6, 170.9. Anal. Calcd for $C_{17}H_{25}NO_8$: C, 54.98; H, 6.78; N, 3.77. Found: C, 55.09; H, 6.74; N, 3.84. The identity of the minor (β) isomer was confirmed by comparison to the identical compound **9**. *Caution should be exercised at all times during this reaction and workup: Organotin compounds, particularly trialkyltin halides (tributyltin chloride is a product of this reaction), are extremely toxic. Appropriate precautions should be taken to avoid inhalation or contact with organotin compounds.*

3-(2-Deoxy-2-phthalimido-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl) propene (4). A solution of 0.31 g (0.59 mmol) of compound **3** (prepared according to ref 27) and 2.21 mL (7.13 mmol) of allyltributyltin in 3 mL of benzene was purged with Ar for 20 min. The solution was heated to reflux under an atmosphere of Ar, and two 10 mg portions (0.061 mmol) of AIBN were added over the course of 2 h. After 12 h, the solution was cooled to rt and diluted with 3 mL of ether and 15 mL of 10% aqueous KF. The biphasic mixture was stirred vigorously for 24 h. The white solid was filtered, and the filtrate was diluted with 40 mL of ether and washed successively with H_2O (20 mL) and brine (20 mL). The organic layer was then dried over $MgSO_4$ and evaporated. Purification of the crude product by silica gel chromatography eluting with 8:1 $CHCl_3$/hexanes followed by 3:1 hexanes/EtOAc yielded 0.20 g (71% yield) of a white crystalline solid (10:1 β/α as determined by ^{1}H NMR peak integration). The pure β isomer was obtained by recrystallization from hexanes/EtOAc: mp 105−106 °C; IR (KBr) 1756, 1720, 1387 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.82 (s, 3), 2.01 (s, 3), 2.10 (s, 3), 2.25−2.28 (m, 2), 3.80 (ddd, 1, J = 2.3, 4.9, 10.1), 4.12 (dd, 1, J = 2.3, 12.2), 4.23 (app t, 1, J = 10.3), 4.28 (dd, 1, J = 4.9, 12.2), 4.44 (d app t, 1, J = 5.6, 10.4), 4.87−4.94 (m, 2), 5.11 (dd, 1, J = 9.2, 10.1), 5.68−5.76 (m, 1), 5.78 (dd, 1, J = 9.1, 10.3), 7.71−7.75 (m, 2), 7.82−7.84 (m, 2); ^{13}C NMR δ 20.3, 20.5, 20.6, 36.4, 54.2, 62.2, 69.1, 71.5, 74.2, 75.5, 117.5, 123.4, 130.9, 131.4, 132.4, 134.1, 134.3, 167.2, 167.7, 169.4, 170.0, 170.5; HRMS (FAB^+) m/e 460.1605 (MH^+ $C_{23}H_{26}NO_9$ requires 460.1608).

The minor (α) isomer was obtained by HPLC purification (silica gel, 3:1 hexanes/EtOAc): ^{1}H NMR ($CDCl_3$) δ 1.84 (s, 3), 2.03 (s, 3), 2.08 (s, 3), 2.24 (m, 1), 2.82 (m, 1), 3.97 (m, 1), 4.07 (app d, 1, J = 12.1), 4.24 (m, 2), 4.72 (dd, 1, J = 11.4, 5.8), 5.04 (m, 3), 5.66 (m, 1), 6.42 (dd, 1, J = 11.4, 9.1), 7.73 (m, 2), 7.83 (m, 2). *Caution should be exercised at all times during this reaction and workup: Organotin compounds, particularly trialkyltin halides (tributyltin bromide is a product of this reaction), are extremely toxic. Appropriate precautions should be taken to avoid inhalation or contact with organotin compounds.*

2-Deoxy-2-(tetrachlorophthalimido)-3,4,6-tri-*O*-acetyl-D-glucopyranosyl Bromide (7). A solution of 18.1 g (29.4 mmol) of 2-deoxy-2-(tetrachloropthalimido)-1,3,4,6-tetra-*O*-acetyl-D-glucopyranoside[34] in 250 mL of 30% HBr/AcOH at 0 °C was warmed to rt over a 5 h period. The red solution was poured into 250 mL of cold $CHCl_3$ and washed with cold saturated aqueous $NaHCO_3$ (3 × 300 mL). The organic layer was then washed with brine (300 mL) and dried over Na_2SO_4. The solvent was evaporated under reduced pressure to afford 17.2 g (92%) of a colorless foam. Due to its instability, the product (1:1 mixture of anomers) was used in the next step without further purification: IR (thin film) 1746, 1728, 1384, 1369, 1228 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.85 (s, 3), 1.99 (s, 3), 2.02 (s, 3), 2.05 (s, 3), 2.07 (s, 3) 3.88 (m, 1), 4.12 (app t, 2, J = 10.5), 4.27 (dd, 1, J = 12.6, 4.7), 4.37 (m, 2), 4.55 (app t, 1, J = 9.8), 4.62 (dd, 1, J = 11.4, 3.7), 5.10 (app t, 1, J = 9.9), 5.20 (app t, 1, J = 10.2), 5.61 (dd, 1, J = 10.1, 9.2), 6.31 (d, 1, J = 9.6), 6.50 (m, 2); HRMS (FAB^+) m/e 633.8841 (MH^+ $C_{20}H_{17}NO_9Cl_4Br$ requires 633.8837).

3-[2-Deoxy-2-(tetrachlorophthalimido)-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl] propene (8). Small Scale Synthesis. A solution of 1.04 g (1.60 mmol) of **7** and 5.96 mL (19.2 mmol) of allyltributyltin in 6 mL of benzene was purged with Ar for 1 h. The solution was heated at reflux under an Ar atmosphere, and 39 mg (0.24 mmol) of AIBN was added. After 1.5 h, another 39 mg (0.24 mmol) of AIBN was added and the solution was heated at 80 °C overnight. The solution was cooled to room temperature and diluted with 20 mL of ether and 50 mL of 10% aqueous KF, and the biphasic mixture was then stirred vigorously for 24 h. The white precipitate was filtered, and the filtrate was diluted with 200 mL of ether and washed successively with 200 mL of H_2O and 200 mL of brine. The organic layer was dried over $MgSO_4$ and concentrated *in vacuo*. Purification of the crude product by silica gel chromatography eluting with 8:1 $CHCl_3$/hexanes followed by 5:1 hexanes/EtOAc yielded 0.75 g (77%) of a white crystalline solid.

Large Scale Synthesis. A solution of 17.2 g (27.0 mmol) of compound **7** and 100 g (302 mmol) of allyltributyltin in 120 mL of benzene was purged with Ar for 20 min. The solution was heated at reflux under an Ar atmosphere, and 1.33 g (8.12 mmol) of AIBN was added over a period of 2 h. After 9 h, the solution was cooled to rt and subjected to the same purification procedure as described above to yield 10.3 g (64%) of a white crystalline solid. A single isomer (β) was discernible by ^{1}H NMR analysis (i.e., β/α ratio >20:1). While the product was analytically pure (vide infra), it did not have a sharp melting point: IR (thin film) 1748, 1725, 1371, 1352 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.80 (s, 3), 1.96 (s, 3), 2.03 (s, 3), 2.21 (m, 2), 3.71 (ddd, 1, J = 2.3, 4.9, 10.2), 4.05 (dd, 1, J = 2.2, 12.3), 4.15 (app t, 1, J = 10.2), 4.22 (dd, 1, J = 4.9, 12.3), 4.36 (d app t, 1, J = 5.6, 10.6), 4.89 (m, 2), 5.07 (dd, 1, J = 9.2, 10.1), 5.63 (m, 2); ^{13}C NMR δ 20.4, 20.6, 20.7, 36.6, 55.2, 62.2, 68.9, 71.8, 73.9, 75.6, 118.0, 126.7, 127.0, 129.8, 130.0, 132.3, 140.4, 140.7, 162.6, 163.3, 169.4, 170.6, 170.6.; HRMS (FAB^+) m/e 596.0045 (MH^+ $C_{23}H_{22}NO_9Cl_4$ requires 596.0049). Anal. Calcd for $C_{23}H_{21}NO_9Cl_4$: C, 46.26; H, 3.54; N, 2.35. Found: C, 46.55; H, 3.38; N, 2.40. *Caution should be exercised at all times during this reaction and workup: Organotin compounds, particularly trialkyltin halides (tributyltin bromide is a product of this reaction), are extremely toxic. Appropriate precautions should be taken to avoid inhalation or contact with organotin compounds.*

3-(2-Acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl) propene (9). From 4. To a solution of 0.30 g (0.65 mmol) of **4** in 8 mL of 6:1 (v/v) *i*PrOH/H_2O was added 0.18 g (4.64 mmol) of $NaBH_4$ in two portions separated by a 1 h period. The solution was stirred at rt for 7 h, during which time a cloudy

precipitate formed. The mixture was acidified to pH 4 with AcOH, warmed to 80 °C, and stirred under a N_2 atmosphere for 8 h. The solution was concentrated *in vacuo* to a white residue and then coevaporated with 1:1 toluene/MeOH (20 mL) and toluene (2 × 20 mL). The solid was dissolved in 20 mL of anhydrous pyridine and stirred over 4 Å molecular sieves before the addition of 5 mL of Ac_2O and a catalytic amount of 4-(dimethylamino)pyridine (DMAP). The solution was stirred at rt for 18 h under a N_2 atmosphere. The reaction mixture was concentrated, and 20 mL each of H_2O and EtOAc were added. The organic layer was washed with 1 M aqueous HCl (2 × 20 mL), saturated aqueous $NaHCO_3$ (3 × 20 mL), and brine (1 × 20 mL) and then dried ($MgSO_4$) and concentrated. Silica gel chromatography eluting with 1:1 hexanes/EtOAc provided 0.20 g (80%) of a white powder.

From 8. To a stirring solution of 0.32 g (0.54 mmol) of **8** in 6.3 mL of 6:1 (v/v) *i*-PrOH/H_2O was added 0.10 g (2.64 mmol) of $NaBH_4$. After 1 h at rt, another portion (0.10 g, 2.64 mmol) of $NaBH_4$ was added, and the solution was stirred for an additional 7 h during which time a cloudy precipitate formed. The reaction mixture was acidified to pH 4 with AcOH and then heated to 80 °C for 12 h. After being cooled to rt, the solution was concentrated to a residue and coevaporated with 1:1 toluene/MeOH (2 × 10 mL) and toluene (2 × 10 mL). The solid was then dissolved in 10 mL of anhydrous pyridine and stirred over 4 Å molecular sieves for 1 h before the addition of 6 mL of Ac_2O and a catalytic amount of DMAP. The cloudy solution was stirred at rt for 24 h under a N_2 atmosphere. The solution was then concentrated and coevaporated with toluene (3 × 5 mL). The resulting white solid was dissolved in 30 mL of $CHCl_3$, washed with 1 M H_2SO_4 (30 mL), saturated aqueous $NaHCO_3$ (30 mL), and ice water (30 mL), and then dried ($MgSO_4$) and concentrated. Purification by silica gel chromatography eluting with 2:1 hexanes/EtOAc yielded 0.12 g (60%) of an analytically pure white powder. Recrystallization from hexanes/EtOAc gave colorless prisms: mp 181.5−182 °C; IR (thin film) 3310, 1745, 1660, 1544 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.93 (s, 3), 2.01 (s, 3), 2.02 (s, 3), 2.07 (s, 3), 2.27−2.38 (m, 2), 3.30−3.34 (m, 1), 3.57 (ddd, 1, J = 2.4, 5.0, 9.8), 4.02 (app q, 1, J = 10.0), 4.08 (dd, 1, J = 2.4, 12.2), 4.22 (dd, 1, J = 5.1, 12.2), 4.94−5.11 (m, 4), 5.33 (d, 1, J = 9.5), 5.79−5.87 (m, 1); ^{13}C NMR δ 20.6, 20.7, 20.7, 23.2, 36.0, 53.7, 62.5, 68.7, 74.5, 75.6, 79.0, 117.2, 133.8, 169.3, 170.0, 170.7, 171.5; HRMS (FAB$^+$) *m/e* 372.1653 (MH^+ $C_{17}H_{26}NO_8$ requires 372.1658). Anal. Calcd for $C_{17}H_{25}NO_8$: C, 54.98; H, 6.78; N, 3.77. Found: C, 55.23; H, 6.82; N, 3.65.

3-(2-Acetamido-2-deoxy-β-D-glucopyranosyl) propene (10). A solution of 0.26 g (0.86 mmol) of *C*-glycoside **9** in 20 mL of a 100 mM solution of CH_3ONa in MeOH was stirred for approximately 30 min. The solution was neutralized with methanolic HCl to pH 7 and concentrated. Silica gel chromatography eluting with 9:1−5:1 CH_2Cl_2/MeOH yielded 0.21 g (100%) of a white powder: mp 186 °C; IR (KBr) 3282, 1654, 1548, 1458 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 1.80 (s, 3), 1.96−2.04 (m, 1), 2.17−2.23 (m, 1), 2.99−3.03 (m, 2), 3.07−3.12 (m, 1), 3.17−3.21 (m, 1), 3.34−3.41 (m, 2), 3.64 (d, 1, J = 11.8), 4.38 (br s, 1), 4.78 (br s, 1), 4.91−5.01 (m, 3), 5.79−5.90 (m, 1), 7.62 (d, 1, J = 9.1); ^{13}C NMR (CD_3OD) δ 22.9, 37.7, 56.8, 63.1, 72.4, 77.5, 79.6, 81.6, 116.8, 136.2, 173.6; HRMS (FAB$^+$) *m/e* 246.1340 (MH^+ $C_{11}H_{20}NO_5$ requires 246.1341). Anal. Calcd for $C_{11}H_{19}NO_5$: C, 53.87; H, 7.81; N, 5.71. Found: C, 54.05; H, 7.95; N, 5.71.

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Supporting Information Available: ^1H and ^{13}C NMR spectra for compounds **4** and **7** (7 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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