An Efficient Synthesis of *N*-Allylglycosylamides from Unprotected Carbohydrates

Wayne Spevak,[†] Falguni Dasgupta,[‡] Christopher J. Hobbs,[†] and Jon O. Nagy*[,†]

Center for Advanced Materials, Lawrence Berkeley National Laboratory, Berkeley, California 94720, and Glycomed, Inc., Atlantic Avenue, Alameda, California 94501

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Synthetic, multivalent, carbohydrate assemblies are important tools in studying the avidity of many naturally occuring lectins for their ligands. This report details a simple, high-yielding three-step procedure to convert unprotected carbohydrates into *N*-allylglycosides. This method compliments the reductive amination procedure but allows the reducing-end pyranose ring to remain intact. No carbohydrate protecting groups are needed, and the resulting *N*-allylglycosylamide can be easily linked to other molecules. Two examples of analogs of silyl Lewis^x and sulfo Lewis^x have been derivatized by this process.

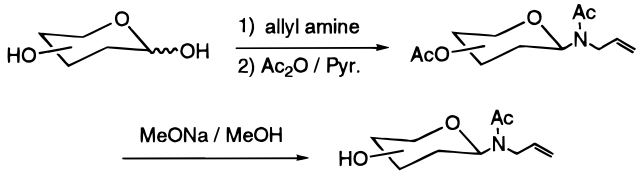
Introduction

Carbohydrate−lectin interactions play a key role in biological processes such as cell recognition during pathogenic infection,[1−3] control of differentiation,[4] clearance of tumor cells,[5] and inflammation.[6] Recently, lectin-mediated carbohydrate binding has been shown to stimulate signal transduction.[7,8] In general, however, the binding strength of lectins for carbohydrates is low compared to other biological recognition events.[9] Nature quite often employs a strategy to improve binding by expressing many copies of a carbohydrate on a single scaffold. In this manner, multivalent forms of the carbohydrate bind through avidity, orders of magnitude higher. To study these important biological interactions, synthetic particles that incorporate known amounts of specific oligosaccharides must be prepared. Because the desired carbohydrate may be extremely expensive or available in only limited supply, the linking chemistry must be simple and efficient. In this paper, we present a nonreductive method that compliments the reductive amination reaction for introducing a linking handle on the glycosidic position of a carbohydrate.

Results and Discussion

Inspired by the facile method of Lockhoff[10] for the formation of long chain glycosylamide glycolipids, we explored extending this work to amines containing functionality. We have developed a general three-step strategy to introduce an *N*-acetylallylamine group onto oligosaccharides (Scheme 1).

Scheme 1



In this method, unprotected oligosaccharides are dissolved in neat allylamine. In most cases the carbohydrate is readily soluble in this solvent at ambient temperature. However, if after several hours the starting material is incompletely dissolved, some water may be added. This tends to lengthen the reaction time but has no adverse effect on yield.

The initial step in this transformation is the attack of allylamine on the anomeric hydroxyl group. Due to the weak anomeric effect of the nitrogen atom, only the β-glucopyranosylamine is obtained.[11] However, heating the solution leads to the formation of mixtures of α and β anomers and other side products. The excess of amine inhibits the formation of *N*,*N*-diglycosylamines. A number of examples of *N*-allyl glycosides have been reported in the literature.[12−15] In one report, the *N*-allyl glycoside is directly isolated;[15] in all other cases, the amine is immediately converted to a urea prior to isolation and characterization. In our hands, we have found that the carbohydrate aminals easily hydrolyze back to the parent sugar, lowering the isolated yields. However, immediate acylation gives a stable product. The following table shows representative examples of carbohydrates that have been converted into the peracetylated *N*-allylglycosylamides (**1**−**8**). The *N*-acetate group in nearly all cases displays restricted rotation, giving rise to multiplic-

* To whom correspondence should be addressed. Tel.: (510) 486-4964. E-mail: jonagy@lbl.gov.
[†] Center for Advanced Materials.
[‡] Glycomed, Inc.
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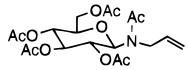
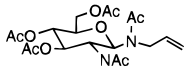
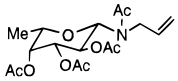
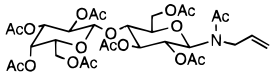
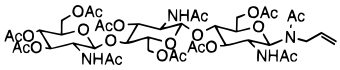
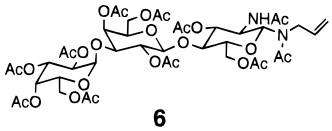
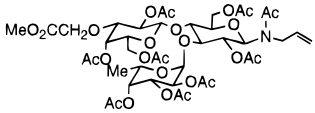
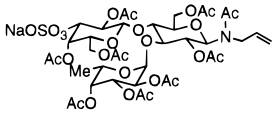
Table 1. Selected Examples of Carbohydrates Converted to *N*-Allylglycosamides

STARTING SUGAR	PER ACETYLATED N-GLYCOSIDES	N-ALLYL GLYCOSYLAMIDES
Glucose	 **1**	Glc β-N(Ac)CH_2CH=CH **9**
NAc-Glucosamine	 **2**	GlcNAc β-N(Ac)CH_2CH=CH **10**
Fucose	 **3**	Fuc β-N(Ac)CH_2CH=CH **11**
Lactose	 **4**	Lac β-N(Ac)CH_2CH=CH **12**
Tri-NAc-Chitotriose	 **5**	Tri-NAc-Chitotriose β-N(Ac)CH_2CH=CH **13**
Gal α-1,3 Gal β-1,4 GlcNAc	 **6**	Gal α-1,3 Gal β-1,4 GlcNAc β-N(Ac)CH_2CH=CH **14**
3'-Acetic acid- Gal β–1,4 [Fuc α-1,3] Glc (Sialyl Lewis ^{X} analog)	 **7**	3'-(Methyl 2-Acetate)- Gal β –1,4 [Fuc α-1,3] Glc β-N(Ac)CH_2CH=CH **15**
3'-Sulfo- Gal β–1,4 [Fuc α-1,3] Glc (Sulfo Lewis ^{X} analog)	 **8**	3'-Sulfo- Gal β–1,4 [Fuc α-1,3] Glc β-N(Ac)CH_2CH=CH **16**

ity of signals in the carbon and proton NMR spectra. Heating of the material to at least 85 °C in DMSO shows peak coalescence. This phenomenon was also observed for the long chain and aryl glycosyl amides.[10,16]

The reaction of 3′-acetic acid-Gal-*β*-1,4-[Fuc α-1,3]Glc in this procedure followed by methanol treatment gives a mixture of the methyl ester (**7**) and various lactones.[17] Compound **7** can be purified from the mix in 55% yield; however, directly treating the crude mixture with sodium methoxide[18] (Zemplén conditions) converts the ester and lactones directly to compound **15** in 76% overall yield. The other peracetylated glycosides are likewise treated to give deprotected *N*-allyl glycosylamides (Table 1).

An allylic group at the glycosyl position is an extremely versatile functionality serving to both protect the anomeric position, allowing modifications to other parts of the oligosaccharide, and act as a ready handle for specific linking reactions.[19−23]

There are many ways to introduce functionality to the reducing end of oligosaccharides. In typical carbohydrate synthesis the standard method for glycosyl functionalization involves protection of the hydroxyl groups and activation of the glycosyl position. This is usually accomplished with concomitant generation of strong acids (e.g., glycosyl halides)[24] or by the use of strong bases (as

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in acetamide formation, the Schmidt reaction).[25] Extremely sensitive carbohydrate linkages, as in fucosyloligosaccharides, can be intolerant of these conditions. For large oligosaccharides or natural product samples available only in minute quanitities the use of complicated protection/deprotection chemistry is problematic or inefficient. Further complications can occur when *N*-acetyl groups are present in the 2-position. The formation of oxazolines as byproducts is common.[26]

Alternatively, and in a more direct manner, there are several ways to introduce linking groups to an unprotected oligosaccharide's glycosidic position. This can be accomplished by reductive amination if the pyranose or furanose ring of the reducing end carbohydrate is not important. However, when the integrity of this ring is necessary for biological activity, strategies employing the formation of an amine glycoside are used. Owing to the greater nucleophilicity of the nitrogen atom in unsubstituted glycosylamines, this group can be selectivly derivatized.[27] Glycosylamines can be prepared by treatment of the carbohydrate with aqueous ammonium carbonate[28] (the Kochetkov reaction) or, alternatively, anhydrous,[27] methanolic,[29] or aqueous[30] ammonia. A recent report of a large nunber of mono- and oligosaccharides subjected to the Kochetkov reaction has appeared.[31]

There are various drawbacks with these methods. Glycosylamines are not stable compounds.[30,31] Hydrolysis in neutral or slightly acidic aqueous solution is facile. The Kochetkov method is also complicated by the difficulty involved in removal of the ammonium carbonate.[31] The vigorus and prolonged (>3 days) lyophilization that is needed to adaquately purify the samples leads to reduction in yields. In addition, a major side product, resulting from a single molecule of ammonia glycosylating two carbohydrate molecules (*N*,*N*-diglycosylamines), can be seen in each of these methods.

The method we have described is a nonreductive technique for efficiently derivatizing oligosaccharides with allylamide groups at the glycosidic position. The one-pot, two step reaction gives a stable, crude product, readily purifiable. The product is obtained exclusivly in the β-form. No carbohydrate protecting groups are needed, although the hydroxyl groups become acylated during the amine acylation step. Since the solvent/reactant (allylamine) is volatile, simple evaporation followed by the per-acetylation step gives a product that is easy to purify by silica gel chromatography, in high yield. The *O*-acetyl groups are also readily removed by methoxide in high yield. The products are stable in air in both the *O*-acetylated and-deacetylated form. This method is perfectly suitable for sensitive carbohydrates (e.g., fucosylated derivatives) and can be easily carried out on very small scales (<5 mg) or large scales (>20 g). No byproducts resulting from formation of *N*,*N*-diglycosylamines or oxazolidines (in the case of 2-NAc carbohydrates, e.g., compounds **2**, **5**, and **6**) were observed.

This methodology has enabled us to take oligosaccharides from synthetic and natural sources and prepare them for multimerization. Compounds **15** and **16** are prepared from 3′-(acetic acid)- and 3′-sulfo-Lewis X analogs which are implicated as antagonists toward selectins in the inflammation response.[32] Multivalent particles containing these linked analogs show extremely potent P-selectin inhibition[33] and will be the subject of future reports with L- and E-selectin.

Experimental Section

General Procedures. Materials were obtained from commercial suppliers: D-glucose (Sigma), D-lactose (Malinckrodt), *N*-acetyl-D-glycosamine (U.S. Biochemicals), L-fucose (Aldrich), and Galα-1,3-Galβ-1,4-GlcNAc (Dextra Labs Ltd.). 3′-Acetic acid- and 3′-sulfo-Galβ-1,4 (Fucα-1,3)Glu were gifts from Glycomed Inc. (Alameda). Tri-*N*-acetyl-chitotriose was obtained from hydrolysis and acelyation of crude chitosan[34] and was used without further purification. Allylamine was obtained from Aldrich and is classified as a highly toxic material. Due to it's high volatility, evaporation and all other handling should be carried out in an efficient fume hood. Deionized water was used in all manipulations. The silica gel used in column chromatography was Kieselgel 60 (Merck, 230−400). Thin layer chromatography (TLC) was performed using Analtech silica gel GHLF coated on glass plates. TLC plates were visualized using molybdate stain (72 g of ammonium molybdate, 3 g of ceric sulfate, 50 mL of concentrated sulfuric acid, and 250 mL of water). Melting points were determined in capillaries and are uncorrected. ^{1}H NMR spectra were determined at either 400, 500, or 200 MHz as indicated. Chemical shifts are reported as parts per million (δ), positive values indicating shifts downfield of tetramethylsilane. ^{1}H NMR spectra determined in D_2O and DMSO-d_6 are reported relative to 4.61 and 2.49 ppm, respectively. The ^{1}H NMR spectra determined in $CDCl_3$ are reported relative to 7.25 ppm. The ^{1}H NMR spectra determined in CD_3OD are reported relative to the HOD signal at 4.63 ppm. ^{1}H NMR data are tabulated in order: multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad), number of protons, and coupling constant(s) in Hz. ^{13}C NMR spectra were proton decoupled and measured at either 100 or 125 MHz. Chemical shifts are reported relative to the central peak of $CDCl_3$ at 77.0 ppm, the central peak of CD_3OD at 49.0 ppm, or the central peak of DMSO-d_6 at 39.5 ppm. All high-temperature NMR experiments were performed on a 400 MHz instrument. Fast atom bombardment (FAB^+) mass spectra and electron ionization (EI^+) mass spectra were recorded at the UC Berkeley Mass Spectral Laboratory. Elemental analyses were performed by the microanalytical laboratory operated by the College of Chemistry at the University of California, Berkeley.

General Procedure for the Preparation of Peracetylated β-NAc-allyl Glycosides from Free Sugars. Neat allylamine was added to the carbohydrate containing a free reducing end to give a 0.5−0.1 M solution. The reaction was stoppered and stirred at ambient temperature for not less than 48 h. Small quantities of water can be added if the entire amount of carbohydrate does not dissolve after 6 h of stirring. Heating of the reaction is not recommended, since this leads to production of significant quantities of impurities. The initial allylamine glycoside product was unstable to thin-layer silica gel chromatography; therefore, this technique cannot be used to measure the progress of the reaction. Typically, a small aliquot was removed from the reaction, peracetylated (as described below), and compared to a sample of the starting sugar that has been peracetylated. The peracetylated glycosylamide product was always seen as a slightly more polar

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product on TLC than the peracetylated oligosaccharide. Upon complete conversion of starting material into amino glycoside product, the solvent was removed by evaporation and the crude solid was treated with toluene and evaporated several times. The flask was then chilled in an ice bath, and a solution of 60% pyridine, 40% acetic anhydride was added to give a solution containing 500 mol % excess of acetic anhydride. The reaction was protected from moisture, stirred, and allowed to warm to ambient temperature overnight. The solvent was removed by evaporation, and the residue was dissolved in toluene and evaporated several times. The crude product was purified by flash chromatography. Nearly all the purifed peracetylated *N*-allylglycosylamides displayed multiplicity of signals in the proton and carbon NMR spectra. This was especially evident for the allyl, *N*-acetyl, and anomeric carbon and proton signals. Heating these compounds to 85 °C in DMSO-d_6 showed peak coalessence.

***N*-(2,3,4,6-Tetra-*O*-acetyl-*β*-D-glucopyranosyl)-3-acetamido-1-propene (1):** amination reaction time, 72 h (neat allylamine); chromatographed with ethyl acetate−hexane 1/2; white solid (89%); mp 125 °C; $[\alpha]^{25}_D = +2.3$ (c = l, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.95 (s, 3H), 1.97 (s, 3H), 2.00 (s, 3H), 2.02 (s, 3H), 2.04 (s, 3H), 3.73−3.82 (m, 2H), 3.85−3.93 (m, 1H),4.09 (dd, 1H, J = 2.0, 12.4 Hz), 4.15 (dd, 1H, J = 4.8, 12.2 Hz), 5.00 (t, 2H, J = 9.6 Hz), 5.12 (bd 2H, J = 16.0 Hz), 5.30 (t, 1H, J = 9.7 Hz), 5.67−5.77 (m, 1H), 5.92 (d, 1H, J = 9.4 Hz); ^{13}C NMR (500 MHz, $CDCl_3$) δ 20.47 (3C), 20.59, 22.08, 46.38, 61.86, 68.28, 68.74, 73.25, 74.00, 80.12, 117.01, 134.76, 169.46, 169.81, 170.40 (2C), 172.31; HRMS FAB m/z for $C_{19}H_{28}NO_{10}$ calcd 430.1705 (MH^+), found 430.1713.

***N*-(2-*N*-Acetyl-3,4,6-tri-*O*-acetyl-*β*-D-glucopyranosyl)-3-acetamido-1-propene (2):** amination reaction time, 72 h (neat allylamine); chromatographed with ethyl acetate; white solid (60%); mp 132−134 °C; $[\alpha]^{25}_D = -2.1$ (c = 1, $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.83 (s, 3H), 1.99 (s, 3H), 2.00 (s, 3H), 2.04 (s, 3H), 2.05 (s, 3H), 3.74 (m,1H), 3.88 (m, 2H), 4.13 (m, 2H), 4.25 (ddd, 1H, J = 9.7, 9.7, 9.8 Hz), 5.08 (dd, 1H, J = 9.7, 9.7 Hz), 5.09 (m, 2H), 5.17 (dd, 1H, J = 9.7, 9.7 Hz), 5.76 (m, 1H), 5.79 (d, 1H, J = 9.7 Hz), 6.64 (d, 1H, J = 9.8 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 20.54, 20.59, 20.64, 22.03, 22.98, 46.65, 51.24, 62.03, 68.26, 73.36, 74.29, 81.06, 117.11, 134.90, 169.30, 170.28, 170.51, 170.85, 172.80; mass spectrum (FAB^+) 429 (MH^+). Anal. Calcd for $C_{19}H_{28}N_2O_9$: C, 53.26; H, 6.59; N, 6.54. Found: C, 52.93; H, 6.61; N, 6.39.

***N*-(2,3,4-Tri-*O*-acetyl-*β*-L-fucopyranosyl)-3-acetamido-1-propene (3):** amination reaction time, 72 h (neat allylamine); chromatographed with ethyl acetate−hexane 1/2; viscous oil (98%); ^{1}H NMR (200 MHz, $CDCl_3$) δ 1.09 (d, 3H, J = 6.4 Hz), 1.91 (s, 3H), 1.92 (s, 3H), 1.99 (s, 3H), 2.11 (s, 3H), 3.82 (m, 2H), 3.90 (m, 1H), 5.15 (m, 5H), 5.77 (m, 1H), 5.81 (d, 1H, J = 9.0 Hz); ^{13}C NMR (50 MHz, $CDCl_3$) δ 16.07, 20.46, 20.52 (2C), 22.08, 46.54, 66.56 (0.5C), 66.81 (0.5C), 70.25, 71.03 (0.5C), 71.33 (0.5C), 71.64 (0.5C), 71.92 (0.5C), 80.29, 116.59 (0.5C), 116.72 (0.5C), 135.38, 169.71, 170.17, 170.24, 172.11; HRMS FAB m/z for $C_{17}H_{26}NO_8$ calcd 372.1658 (MH^+), found 372.1657.

***N*-[4-*O*-*β*-(2,3,4,6-Tetra-*O*-acetyl-D-galactopyranosyl)-(2,3,6-tri-*O*-acetyl)-*β*-D-glucopyranosyl]-3-acetamido-1-propene (4):** amination reaction time, 72 h (neat allylamine); chromatographed with chloroform−methanol 200/1; white solid (98%); mp 85−90 °C (scinters); $[\alpha]^{25}_D = -2.0$ (c = 1, $CHCl_3$); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ 1.88 (s, 1.5H), 1.89 (s, 1.5H), 1.92 (s, 3H), 1.96(s, 3H), 1.99 (s, 3H), 2.00 (s, 3H), 2.04 (s, 3H), 2.07 (s, 3H), 2.09 (s, 3H), 3.65 (m, 0.5H), 3.81−3.91 (m, 2.5H), 3.95−4.01 (m, 4H), 4.22 (t, 1H, J = 6.6 Hz), 4.34 (t, 1H, J = 10.3 Hz), 4.77 (t, 1H, J = 8.4 Hz), 4.85 (dd, 1H, J = 8.0, 10.0 Hz), 4.91−5.00 (m, 2H), 5.04-5.11 (m, 1H), 5.16−5.23 (m, 2.5H), 5.29 (m, 0.5H), 5.45 (d, 0.5H, J = 8.9 Hz), 5.63−5.75 (m, 1H), 5.83 (d, 0.5H, J = 8.9 Hz); ^{1}H NMR (400 MHz, DMSO-d_6, 105 °C) δ 1.89 (s, 3H), 1.91 (s, 3H), 1.97 (s, 3H), 1.98 (s, 3H), 2.00 (s, 3H), 2.03 (s, 3H), 2.04 (s, 3H), 2.08 (s, 3H), 3.76 (m, 1H), 3.86 (app q, 2H, J = 10.0, 18.2 Hz), 3.91 (m, 1H), 4.05 (m, 3H), 4.18 (dt, 1H, J = 1.1, 6.4 Hz), 4.39 (dd, 1H, J = 2.0, 12.0 Hz), 4.75 (d, 1H, J = 7.9 Hz), 4.87 (dd, 1H, J = 7.9, 16.2 Hz), 5.00 (app t, 2H), 5.10 (dd, 1H, J = 1.5, 16.0 Hz), 5.14 (dd, 1H, J = 3.6, 10.3 Hz), 5.23 (t, 1H, J = 9.1 Hz), 5.26 (dd, 1H, J = 1.2, 3.5 Hz), 5.53 (br, 1H), 5.69 (m, 1H); ^{13}C NMR (100 MHz, DMSO-d_6, 25 °C) δ 20.22, 20.28 (2C), 20.38, 20.50, 21.72 (2C), 21.92, 60.79, 62.05, 67.04, 68.70 (0.5C), 68.90 (0.5C), 69.62, 70.23, 72.78, 72.97, 73.50 (0.5C), 73.68 (0.5C), 75.90, 79.10, 83.54, 99.91, 115.81 (0.5C), 116.42 (0.5C), 134.79 (0.5C), 135.52 (0.5C), 168.97, 169.22, 169.36, 169.43, 169.81 (0.5C), 169.82 (0.5C), 170.11, 170.18, 171.28; ^{13}C NMR (100 MHz, DMSO-d_6, 105 °C) δ 19.56, 19.61 (2C), 19.64, 19.73, 19.81, 19.84, 21.20, 60.55, 61.65, 66.95, 68.79, 68.95, 69.63, 70.12, 72.79, 73.65, 75.23, 99.37, 115.42, 134.76, 168.30, 168.45, 16863, 168.69, 169.13, 169.15, 169.35, 170.09; mass spectrum (FAB^+) 718 (MH^+). Anal. Calcd for $C_{31}H_{43}NO_{18}$: C, 51.88; H, 6.04; N, 1.95. Found: C, 51.49; H, 6.03; N, 1.87.

***N*-[(2-Acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-*β*-D-glucopyranosyl)-(1→4)-*O*-(2-acetamido-3,6-di-*O*-acetyl-2-deoxy-*β*-D-glucopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-acetyl-2-deoxy-*β*-D-glucopyranosyl]-3-acetamido-1-propene (5):** amination reaction time, 90 h (allylamine plus small amount of H_2O); chromatographed with cloroform−methanol 20/1; white solid (84%); mp 280−282 °C dec; $[\alpha]^{25}_D = -17.2$ (c = 2, $CHCl_3$/MeOH, 50/50); ^{1}H NMR (500 MHz, $CDCl_3/CD_3OD$: 1/1, ref CD_3OD to 3.30 ppm) δ 1.82 (s, 3H), 1.87 (s, 3H), 1.96 (s, 3H), 1.97 (s, 3H), 1.98 (s, 3H), 1.99 (s, 3H), 2.00 (s, 3H), 2.03 (s, 3H), 2.04 (s, 3H), 2.06 (s, 3H), 2.11 (s, 3H), 3.57-3.75 (m, 7H), 3.79 (dd, 1H, J = 6.7, 17.6 Hz), 3.89 (bd, 1H, J = 13.3 Hz), 3.99 (dd, 1H, J = 1.9, 12.5 Hz), 4.06 (m, 2H), 4.10 (t, 1H, J = 10.2 Hz), 4.35 (t, 1H, J = 12.5 Hz), 4.36 (t, 1H, J = 11.1 Hz), 4.46 (bd, 1H, J = 11.5 Hz), 4.57 (m, 1H), 4.67 (d, 1H, J = 8.4 Hz), 4.95 (t, 1H, J = 9.7 Hz), 5.10 (m, 4H), 5.25 (t, 1H, J = 9.8 Hz), 5.66 (bd, 1H, J = 9.8 Hz), 5.67−5.74 (m, 1H). ^{13}C NMR (100 MHz, $CDCl_3/CD_3OD$: 1/1, ref CD_3OD to 49.00 ppm) 20.62 (2C), 20.69, 20.77, 20.88, 20.96 (2C), 22.30, 22.65, 22.85 (2C), 49.0 (2C buried under solvent), 51.60, 55.31, 55.59, 56.39, 62.47, 62.92, 63.40, 69.21, 72.15, 72.91, 73.24, 73.53, 74.36, 75.75, 76.52, 81.41, 101.14, 117.39, 135.45, 170.61, 171.22, 171.32 (2C), 171.35 (2C), 171.64, 171.80, 171.92, 172.59, 172.68; HRMS FAB m/z for $C_{43}H_{63}N_4O_{23}$ calcd 1003.3883 (MH^+), found 1003.3900.

***N*-[(2,3,4,6-Tetra-*O*-acetyl-α-D-galactopyranosyl)(1→3)-(2,4,6-tri-*O*-acetyl-*β*-D-galactopyranosyl)-(1→4)-2-acetamido-3,6-di-*O*-acetyl-2-deoxy-*β*-D-glucopyranosyl]-3-acetamido-1-propene (6):** amination reaction time 96 h (neat allylamine); chromatographed with chloroform−methanol 20/1; white solid (93%); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.85 (s, 3H), 1.92 (s, 3H), 2.03 (s, 3H), 2.04 (s, 3H), 2.05 (s, 3H), 2.06 (s, 6H), 2.08 (s, 3H), 2.13 (s, 6H), 2.16 (s, 3H), 3.65−3.70 (m, 1H), 3.74 (t, 1H, J = 9.3 Hz), 3.78 (t, 1H, J = 7.0 Hz), 3.82 (dd, 2H, J = 2.9, 10.5 Hz), 3.84−3.91 (m, 2H), 4.00−4.20 (m, 7H), 4.44 (bt, 2H, J = 8.0Hz), 5.06−5.20 (m, 5H), 5.21−5.26 (m, 1H), 5.31 (d, 1H, J = 2.6 Hz), 5.43 (d, 1H, J = 2.0 Hz), 5.67−5.84 (m, 1H), 5.72 (d, 1H, J = 9.8 Hz), 5.85 (d, 1H, J = 9.7 Hz); HRMS FAB m/z for $C_{43}H_{61}N_2O_{25}$ calcd 1005.3570 (MH^+), found 1005.3563.

***N*-[3-((Methoxycarbonyl)methyl)-2,4,6-tri-*O*-acetyl-*β*-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-*O*-2,6-di-*O*-acetyl-*β*-D-glucopyranosyl]-3-acetamido-1-propene (7):** amination reaction time 72 h (neat allylamine); treated crude product with methanol for three hours at ambient temperature; chromatographed with chloroform−methanol 30/1; white solid (55%); mp 108−111 °C; $[\alpha]^{25}_D = -35.9$ (c = 3, $CHCl_3$); ^{1}H NMR (500 MHz, $CDCl_3$) δ 1.06 (d, 3H, J = 6.5 Hz), 1.89 (s, 3H), 1.91 (s, 3H), 1.94 (s, 3H), 1.95 (s, 3H), 2.00 (s, 3H), 2.02 (s, 3H), 2.07 (s, 3H), 2.09 (bs, 6H), 3.31 (dd, 1H, J = 3.5, 9.4 Hz), 3.46 (bt, 1H, J = 8.7 Hz), 3.58−3.72 (m, 4H), 3.72 (s, 3H), 3.80 (m, 2H), 4.04−4.07 (m, 1H), 4.11 (q, 2H, J = 18.8 Hz), 4.21 (dd, 1H, J = 8.5, 11.2 Hz), 4.30 (d, 1H, J = 7.7 Hz),4.30−4.33 (m, 1H), 4.46 (q, 1H, J = 5.7 Hz), 4.65 (dd, 1H, J = 1.7, 12.1 Hz), 4.92−4.96 (m, 3H), 5.06 (bd, 2H, J = 16.4 Hz), 5.14 (bdd, 1H, J = 3.1, 10.8 Hz), 5.27 (bd, 2H, J = 19.7 Hz), 5.61−5.73 (m, 1H), 5.72 (d, 1H, J = 9.2 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.70, 20.44, 20.56 (5C), 20.70 (3C), 21.94, 46.66, 52.33, 60.94, 63.85, 64.82, 66.06, 67.81, 68.15, 70.24, 70.62, 71.27, 72.05, 74.20, 74.75, 75.46, 80.05, 81.33, 95.39, 102.90, 116.75, 135.17, 169.56, 170.04, 170.33 (2C), 170.42, 170.50, 170.58, 170.72, 171.99,

172.26; HRMS FAB *m/z* for $C_{40}H_{58}NO_{24}$ calcd 936.3349 ($MH^+ - COCH_2$), found 936.3341.

***N*-[(3-Sulfo-2,4,6-tri-*O*-acetyl-β-D-galactopyranosyl)-(1→4)-*O*-[(2,3,4-tri-*O*-acetyl-α-L-fucopyranosyl)-(1→3)]-*O*-2,6-di-*O*-acetyl-β-D-glucopyranosyl]-3-acetamido-1-propene (8):** amination reaction time 72 h (neat allylamine); chromatographed with chloroform−methanol 10/1; white solid (90%); mp 173−175 °C dec; $[\alpha]^{25}_D = -44.3$ (*c* = 1.2, CH_3OH); ^{1}H NMR (500 MHz, CD_3OD) δ 0.98 (d, 3H, *J* = 6.6 Hz), 1.71 (s, 3H), 173 (s, 3H), 1.77 (s, 3H), 1.79 (s, 3H), 1.85 (s, 1.5H), 1.86 (s, 1.5H), 1.86 (s, 3H), 1.87 (s, 3H), 1.92 (s, 3H), 1.94 (s, 3H), 3.50−3.58 (m, 1H), 3.63 (t, 1H, *J* = 9.6 Hz), 3.73 (bd, 1H, *J* = 16.9 Hz), 3.82−3.88 (m, 1H), 3.93 (dt, 1H, *J* = 5.2 Hz), 4.08 (dd, 1H, *J* = 6.3, 11.7 Hz), 4.10−4.18 (m, 1H), 4.39 (bdd, 1H, *J* = 10.0 Hz), 4.49 (dd, 2H, *J* = 8.2, 15.3 Hz), 4.67−4.70 (m, 2H), 4.80−5.02 (m, 7H), 5.09 (dd, 2H, *J* = 3.8, 12.9 Hz), 5.19 (bs, 1H), 5.44 (d, 1H, *J* = 3.4 Hz), 5.44−5.61 (m, 1H); ^{13}C NMR (100 MHz, CD_3OD) δ 16.36, 20.43, 20.63, 20.75 (3C), 20.81, 20.91 (2C), 21.22, 22.30, (2C buried under solvent signal), 62.86, 63.08, 65.53, 69.55, 69.67, 70.04, 71.22, 72.84 (2C), 75.54, 76.04, 76.62, 76.81, 96.89, 101.90, 117.46, 136.57, 171.46 (2C), 171.52, 171.99, 172.10, 172.32 (2C), 172.38, 174.69; HRMS FAB *m/z* for $C_{39}H_{54}NO_{26}SNa_2$ calcd 1030.2440 ($M+2Na^+$), found 1030.2450.

General Procedure for the Preparation of βNAc-allyl Glycosides. The peracetylated β-NAc allyl glycoside is dissolved in anhydrous methanol to give a 0.1−0.01 M solution. A catalytic amount (several drops) of 1 N NaOMe in MeOH was added (pH ∼ 10), and the reaction was stirred at ambient temperature for 3 h. Just enough Dowex 50 resin (H^+ form) was added to neutralize the base, and then the solution was filtered and evaporated to dryness. The products are usually pure enough to require no further pruification; however they can be recrystalized as in some cases below.

***N*-(β-D-glucopyranosyl)-3-acetamido-1-propene (9):** isolated as a white solid (98%); mp 137−139 °C; $[\alpha]^{25}_D = -4.2$ (*c* = 1, H_2O); ^{1}H NMR (500 MHz, CD_3OD) δ 1.95 (s, 1H), 2.03 (s, 2H), 3.09 (q, 1H, *J* = 9.4 Hz), 3.16−3.29 (m, 2.4H), 3.33 (t, 0.6H, *J* = 8.8 Hz), 3.46 (dq, 1H, *J* = 2.8, 5.3,6.0 Hz), 3.66 (dt, 1H, *J* = 2.0, 12.9 Hz), 3.81 (dd, 1H, *J* = 5.1,15.3 Hz), 3.88 (dd, 1H, *J* = 6.1, 16.6 Hz), 4.67 (d, 0.6H, *J* = 8.9 Hz), 4.87 (dd, 0.4H, *J* = 1.2, 10.3 Hz), 5.02 (m, 1H, *J* = 1.4, 11.9, 17.3 Hz), 5.13 (d, 0.4H, *J* = 17.3 Hz), 5.37 (dd, 0.6H, *J* = 8.9 Hz), 5.65−5.73 (m, 0.6H, *J* = 0.8, 5.9, 10.5 Hz), 5.73−5.84 (m, 0.4H, *J* = 5.5, 10.7 Hz); ^{13}C NMR (100 MHz, CD_3OD) δ 22.07 (0.6C), 22.49 (0.4C), 44.86 (0.4C), 47.35 (0.6C), 62.79, 71.17 (0.6C), 71.26 (0.4C), 71.94, 79.07 (0.4C), 80.17 (0.6C), 83.71, 88.78, 116.55 (0.6C), 117.27 (0.4C), 136.44 (0.6C), 136.58 (0.4C), 174.35 (0.6C), 175.39 (0.4C); HRMS FAB *m/z* for $C_{11}H_{20}NO_6$ calcd 262.1291 (MH^+), found 262.1288. Anal. Calcd for $C_{11}H_{19}NO_6$: C, 50.57; H, 7.33; N, 5.36. Found: C, 50.52; H, 7.52; N, 5.34.

***N*-(2-*N*-Acetyl-β-D-glucopyranosyl)-3-acetamido-1-propene (10):** isolated as a white solid (99%); mp 96−98 °C (scinters); $[\alpha]^{25}_D = +17.3$ (*c* = 1, H_2O); ^{1}H NMR (200 MHz, CD_3OD) δ 1.94 (s, 1.83H), 1.98 (s, 1.17H), 2.09 (s, 1.83H), 2.24 (s, 1.17H), 3.38 (m, 2H), 3.61 (m, 1H), 3.83 (m, 1H), 3.91 (m, 1H), 3.95 (m, 1H), 5.16 (m, 4H), 5.66 (d, 1H, *J* = 9.7 Hz), 5.91 (m, 1H), 7.97 (d, 0.61H, *J* = 9.5 Hz), 8.07 (d, 0.39H, *J* = 8.8 Hz); ^{13}C NMR (50 MHz, CD_3OD) δ 22.41, 22.81 (0.5C), 22.91 (0.5C), 48.01, 54.01 (0.5C), 54.89 (0.5C), 62.89, 71.83, 76.36, 80.48, 82.60 (0.5C), 87.30 (0.5C), 116.66 (0.5C), 117.24 (0.5C), 136.14 (0.5C), 137.13 (0.5C), 173.54 (0.5C), 173.62 (0.5C), 174.13 (0.5C), 174.91 (0.5C); HRMS FAB *m/z* for $C_{13}H_{23}N_2O_6$ calcd 303.1556 (MH^+), found 303.1551.

***N*-(β-L-Fucopyranosyl)-3 acetamido-1-propene (11):** recrystallized from ethylacetate isolated as a white solid (60%); mp 133−134 °C; ^{1}H NMR (200 MHz, $CDCl_3/CD_3OD$) δ 1.14 (t, 3H, *J* = 6.1 Hz), 1.99 (s, 1.68H), 2.06 (s, 1.32H), 3.54 (m, 4H), 3.70 (m, 1H), 4.21 (d, 0.17H, *J* = 4.2 Hz), 4.35 (d, 0.1H, *J* = 4.3 Hz), 4.54 (d, 0.53H, *J* = 8.7 Hz), 4.67 (d, 0.2H, *J* = 4.9 Hz), 5.04 (m, 2.4H), 5.32 (d, 0.6H, *J* = 8.6 Hz), 5.76 (m, 1H); ^{13}C NMR (50 MHz, $CDCl_3/CD_3OD$) δ 16.03, 21.52 (0.6C), 21.83 (0.4 C), 43.78 (0.6C), 46.01 (0.4C), 67.68, 71.11 (0.6C), 71.38 (0.4C), 72.53, 74.48 (0.6C), 74.68 (0.4C), 82.31 (0.6C), 87.71 (0.4C), 115.85 (0.6C), 116.39 (0.4C), 134.72, 172.18 (0.6C), 173.64 (0.4C); mass spectrum (FAB^+) 246 (MH^+). Anal. Calcd for $C_{11}H_{19}NO_5$: C, 53.87; H, 7.81; N, 5.71. Found: C, 54.03; H, 7.75; N, 5.64.

***N*-(4-*O*-β-D-Galactopyranosyl-β-D-glucopyranosyl)-3-acetamido-1-propene (12):** recrystallized from $MeOH/CH_2Cl_2$ isolated as a white solid (79%); mp 195−196 °C; $[\alpha]^{25}_D = +12.2$ (*c* = 1, H_2O); ^{1}H NMR (400 MHz, DMSO-d_6, 25 °C) δ 1.99 (s, 1.17H), 2.07 (s, 1.83H), 3.42 (m, 5H), 3.72 (m, 1H), 3.89 (m, 2H), 4.08 (app. q, 1H, *J* = 5.2, 10.5 Hz), 4.20 (m, 1H), 4.50 (m, 2H), 4.62 (t, 1H, *J* = 4.5 Hz), 4.76 (m, 2H), 4.95 (d, 0.63H, *J* = 10.3 Hz), 5.10 (m, 2H), 5.25 (d, 0.37H, *J* = 17.2 Hz), 5.32 (d, 0.63H, *J* = 5.7 Hz), 5.40 (d, 0.37H, *J* = 9.4 Hz), 5.75 (m, 0.63H), 5.87 (m, 0.37H); ^{1}H NMR (400 MHz, DMSO-d_6, 85 °C) δ 2.06 (s, 3H), 3.35 (m, 2H), 3.48 (m, 1H), 3.58 (m, 2H), 3.68 (t, 1H, *J* = 3.8 Hz), 3.75 (m, 1H), 3.86 (dd, 1H, *J* = 4.9, 16.3 Hz), 3.99 (dd, 1H, *J* = 5.4, 17.4 Hz), 4.15 (m, 2H), 4.26 (d, 1H, *J* = 7.4 Hz), 4.32 (t, 1H, *J* = 5.3 Hz), 4.36 (d, 1H, *J* = 5.4 Hz), 4.61 (s, 1H), 4.74 (d, 1H, *J* = 4.1 Hz), 5.01 (br s, 1H), 5.17 (br s, 1H), 5.84 (br s, 1H); ^{13}C NMR (50 MHz, DMSO-d_6, 25 °C) δ 21.94 (0.4C), 22.25 (0.6C), 42.84 (0.4C), 45.45 (0.6C), 60.45, 68.19, 69.78, 70.35 (0.4C), 70.58 (0.6C), 73.29, 75.59, 76.93, 77.12, 80.20, 81.41, 86.64, 103.81, 115.43 (0.4C), 116.33 (0.6C), 136.25, 170.76 (0.4C), 171.41 (0.6C); HRMS FAB *m/z* for $C_{17}H_{30}NO_{11}$ calcd 424.1819 (MH^+), found 424.1818. Anal. Calcd for $C_{17}H_{29}NO_{11}$: C, 48.22; H, 6.90; N, 3.31. Found: C, 47.56; H, 7.19; N, 3.36.

***N*-[(2-Acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-*O*-(2-acetamido-2-deoxy-β-D-glucopyranosyl)-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl]-3-acetamido-1-propene (13):** white solid (88%); mp 182−183 °C dec; $[\alpha]^{25}_D = -6.2$ (*c* = 1, H_2O); ^{1}H NMR (500 MHz, CD_3OD) δ 1.68 (s, 2H), 1.71 (s, 1H), 1.78 (s, 3H), 1.81 (s, 3H), 1.84 (s, 2H), 1.97 (bs, 1H), 3.09 (dt, 2H, *J* = 1.7, 3.2, 4.8 Hz), 3.14 (dd, 0.6H, *J* = 2.2, 6.5 Hz), 3.16 (dd, 0.4H, *J* = 2.2, 6.5 Hz), 3.17 (m, 2H, *J* = 2.0, 5.4, 7.4 Hz), 3.23 (dd, 1H, *J* = 8.6, 10.3 Hz), 3.37−3.44 (m, 4H), 3.50 (dd, 2H, *J* = 8.5, 10.3 Hz), 3.54−3.63 (m, 4H, *J* = 1.6, 10.0, 19.0 Hz), 3.69 (dd, 1H, *J* = 2.1, 11.9 Hz), 3.70−3.93 (m, 3H), 4.29 (t, 2H, *J* = 8.7 Hz), 4.81 (d, 0.6H, *J* = 10.1 Hz), 4.97 (m, 1.8H, *J* = 17.5 Hz), 5.40 (bs, 0.6H), 5.54−5.63 (m, 0.4H, *J* = 4.7, 10.5, 16.9 Hz), 5.68−5.77 (m, 0.6H, *J* = 4.6, 7.2, 10.5, 14.8 Hz); ^{13}C NMR (100 MHz, CD_3OD) δ 22.39, 22.73, 23.01, 23.07, 53.55, 54.22, 56.64, 57.38, 61.65, 61.80, 62.58, 72.00, 74.09, 74.65, 74.78, 75.74, 76.52, 78.15, 79.04, 80.83, 81.54, 103.01, 103.21, 116.68 (0.2C), 117.22 (0.8C), 137.16, 173.53, 173.70, 173.81, 175.01; HRMS FAB *m/z* for $C_{29}H_{49}N_4O_{16}$ calcd 709.3144 (MH^+), found 709.3147.

***N*-[(α-D-galactopyranosyl)-(1→3)-(β-D-galactopyranosyl)-(1→4)-2-acetamido-2-deoxy-β-D-glucopyranosyl]-3-acetamido-1-propene (14):** white solid (96%); ^{1}H NMR (500 MHz, CD_3OD) δ 1.73 (s, 2H), 1.76 (s, 1H), 1.83 (s, 1H), 1.88 (s, 2H), 3.34 (bdd, 1H, *J* = 6.2, 10.8 Hz), 3.42 (dd, 1H, *J* = 4.6, 6.9 Hz), 3.46 (d, 1H, *J* = 9.8 Hz), 3.50 (bs, 2H), 3.52−3.56(m, 4H), 3.60 (m, 2H, *J* = 7.6, 9.2, 11.5 Hz), 3.67 (bs, 3H), 3.67 (bd, 1H, *J* = 4.2 Hz), 3.72 (bs, 1H), 3.74 (d, 2H, *J* = 0.8Hz), 3.87 (bs, 1H), 4.04 (bt, 1H, *J* = 6.0 Hz), 4.27 (bd, 1H, *J* = 5.8 Hz), 4.86 (bs, 1H), 4.91−5.05 (m, 2.6H, *J* = 9.9, 10.6, 18.0 Hz), 5.47 (bs, 0.4H), 5.61−5.66 (m, 0.4H, *J* = 5.5, 6.4 Hz), 5.67−5.78 (m, 0.6H, *J* = 2.6, 3.5, 4.5, 6.7 Hz); ^{13}C NMR (100 MHz, CD_3OD) δ 22.63, 22.71, 53.58, 62.21, 62.46, 62.79, 66.69, 70.19, 71.05, 71.18, 71.39, 72.30, 74.70, 76.72, 79.15, 80.01, 80.25, 81.12, 97.79, 105.15, 107.09, 116.69(0.2C), 117.20 (0.8C), 137.17, 174.10, 175.05; HRMS FAB *m/z* for $C_{25}H_{43}N_2O_{16}$ calcd 627.2613 (MH^+), found 627.2615.

***N*-[O-(3-*O*-((Methoxycarbonyl)methyl)-β-D-galactopyranosyl)-(1→4)-*O*-[(α-L-fucopyranosyl)-(1→3)]-*O*-(β-D-glucopyranosyl]-3-acetamido-1-propene (15):** purified by silica gel column chromatography eluting with 3:2:1 ethyl acetate: 2-propanol:H_2O; white solid (76%); mp 190 °C dec; $[\alpha]^{25}_D = -43.9$ (*c* = 1.5, H_2O); ^{1}H NMR (200 MHz, D_2O) δ 1.02 (d, 3H, *J* = 6.4 Hz), 2.02 (s, 1.3H), 2.08 (s, 1.7H), 3.29 (app dd, 1H, *J* = 2.6, 9.8 Hz), 3.41 (t, 3H, *J* = 7.1 Hz), 3.52−3.84 (m, 14H), 3.89 (s, 3H), 4.31 (d, 1H, *J* = 7.3 Hz), 4.64 (m, 2H, obscured by HOD signal), 5.04 (m, 2.5H), 5.26 (d, 1H, *J* = 3.7 Hz), 5.36 (d, 0.5H, *J* = 8.2 Hz), 5.62−5.76 (m 1H); ^{13}C NMR (100 MHz, D_2O) δ 16.25, 22.18 (0.4C), 22.68 (0.6C), 44.78 (0.4C), 47.50 (0.6C), 60.58, 62.64, 66.08, 67.53, 69.01 (0.4C), 69.21 (0.6C), 70.23,

71.00, 72.00, 72.47 (0.4C), 72.94 (0.6C), 73.16, 75.81, 78.23, 78.42, 78.70, 79.01, 82.75, 83.54, 88.04, 99.39 (0.4C), 102.66 (0.6C), 117.56 (0.6C), 118.30 (0.4C), 134.78 (0.4C), 134.89 (0.6C), 176.18 (0.4C), 177.63 (0.6C), 179.43; HRMS FAB *m/z* for $C_{26}H_{43}NO_{17}$ calcd 664.2427 ($M + Na^+$), found 664.2429.

***N*-[(3-Sulfo-*β*-D-glactopyranosyl)-(1→4)-*O*-[(α-L-fucopyranosyl)-(1→3)]-*O*-*β*-D-glucopyranosyl]-3-acetamido-1-propene (16):** yellow solid (71%); mp 200 °C dec; $[\alpha]^{25}_D = -40.3$ ($c = 1.5$, H_2O); ^{1}H NMR (500 MHz, CD_3OD) δ 0.93 (d, 3H, J = 6.6 Hz), 1.88 (s, 1.1H), 1.96 (s, 1.9H), 3.21−3.33 (m, 2H), 3.40-3.47 (m, 2H, J = 4.8, 5.8, 6.4, 9.5 Hz), 3.49 (bs, 2H), 3.54 (m, 3H, J = 3.5, 4.0 Hz), 3.60 (bt, 1H, J = 9.5 Hz), 3.58−3.65 (m, 1H), 3.69 (bdt, 2H, J = 2.8, 9.7 Hz), 3.77 (dd, 1H, J = 5.5, 14.4 Hz), 3.77−3.83 (m, 1H), 3.96 (bdd, 2H, J = 2.2, 14.0 Hz), 4.28 (dd, 1H, J = 3.2, 7.6 Hz), 4.56 (q, 1H, J = 6.6 Hz), 4.80 (d, 1H, J = 9.9 Hz), 4.96 (m, 1H, J = 16.6 Hz), 5.05 (d, 0.6H, J = 17.2 Hz), 5.16 (d, 0.4H, J = 3.9 Hz), 5.17 (d, 0.6H, J = 3.8 Hz), 5.27 (d, 0.4H, J = 9.0 Hz), 5.59−5.66 (m, 0.6H, J = 4.9, 5.6, 6.3 Hz), 5.66−5.74 (m, 0.4H, J = 4.8, 5.3, 6.4 Hz); ^{13}C NMR (100 MHz, D_2O) δ 16.59, 22.11 (0.5C), 22.53 (0.5C), 47.61, 61.43, 62.79, 67.53, 68.36, 70.35, 71.19, 72.98, 73.36, 73.74, 74.48, 76.36, 79.58, 80.42, 82.04, 84.09, 88.92, 100.37 (0.6C), 103.62 (0.4C), 116.62 (0.6C), 117.27 (0.4C), 136.44 (0.6C), 136.62 (0.4C), 174.38 (0.6C), 175.52 (0.4C); HRMS FAB *m/z* for $C_{23}H_{39}NO_{18}SNa$ calcd 672.1786 (MH^+), found 672.1792.

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Supporting Information Available: ^{1}H NMR spectra for compounds **1**, **3**, **5**, **7**, **8**, **10**, **13**, **15**, and **16** (9 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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