JOC Article

Selective Reduction of Anomeric Azides to Amines with Tetrathiomolybdate: Synthesis of β-D-Glycosylamines

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A number of β-D-glycosyl azide derivatives undergo reduction on treatment with tetrathiomolybdate to produce the corresponding β-D-glycosylamines exclusively without anomerization under very mild and neutral reaction conditions. Acetyl, allyl, benzoyl, and benzyl protective groups are left untouched under the reaction conditions. An exclusive selectivity in the reduction of anomeric azides is observed, while the C-2 and C-6 azides are left untouched.

The glycopeptides are central to the chemistry and biology of glycoproteins, which have gained considerable prominence in recent years due to their biological and pharmacological significance.[1] In particular, the investigations directed toward understanding the role of oligosaccharides in glycopeptides continue to attract considerable attention because of their significant role in affecting the structure and function of *O*-glycoproteins and *N*-glycoproteins.[2] In this context, a user-friendly procedure is highly desirable in order to synthesize glycosylamines with the desired stereochemistry, which has far reaching relevance in the synthesis of *N*-glycopeptides. Of the various procedures available for the synthesis of the amines, the reduction of azides is the most attractive because of their easy accessibility.[3] The most prominent reagents employed for such conversions are LAH[4] and metal-catalyzed hydrogenations,[5] which are generally nonselective. However, there are serious impediments associated with the reduction of sugar azides to the corresponding amines. For example, the reduction should be carried out without affecting the protective groups[6] and in the case of anomeric azides, the anomerization of the reduced product is the major limitaion.[7] Although a number of methods have been developed for stereoselective and chemoselective reduction of anomeric azides,[8] an efficient strategy for producing anomeric amines with stereochemical integrity is still a challenging problem.[1d] Herein we report a facile synthetic strategy for the selective reduction of anomeric azides to β-pyranosylamines utilizing benzyltriethylammonium tetrathiomolybdate **1**[9] under mild and neutral reaction conditions. In addition, a regioselective reaction to produce 2-azido-β-pyranosylamine in high yields is also described.

In our research program to explore the utility of benzyltriethylammonium tetrathiomolybdate ($[BnNEt_3]_2MoS_4$), **1**, in organic synthesis,[10] we have reported earlier the synthesis of disulfides[11] and diselenides.[12] While aryl azides on treatment with **1** led to the formation of arylamines, alkyl azides gave imines as a product of the reaction (Scheme 1).[13]

The sugar azides **2**,[14] **4**,[15] **6**,[16] **8**,[17] **10**,[18] **12**,[19] **14**,[19] **16**,[20] **17**,[21] **18**,[20] **20**,[22] and **22**[14] were synthesized using standard protocols. The diazide **20** was synthesized from the corresponding triacetyl galactal. The azide **17** was synthesized from the corresponding glucosamine utilizing diazotransfer methodology.

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† Honorary Professor, Jawaharlal Nehru Center for Advanced Scientific Research, Bangalore. Dedicated to Professor Goverdhan Mehta on the occasion of his 60th birthday.

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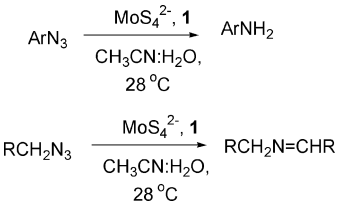
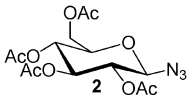
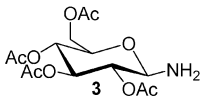
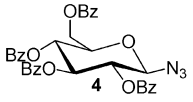
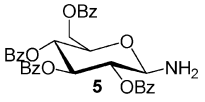
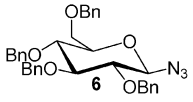
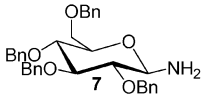
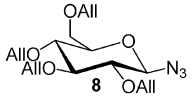
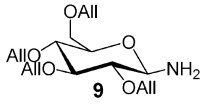
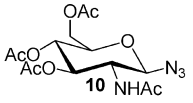
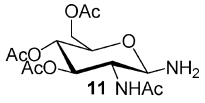
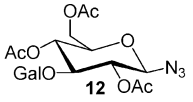
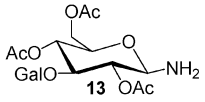
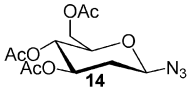
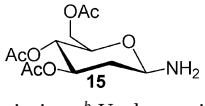
SCHEME 1



In the initial experiments, treatment of glycopyronasyl azide **2** with tetrathiomolybdate **1** (1 equiv) at room temperature (CH_3CN/EtOH (1:1), 28 °C, stirring, 8 h) produced an excellent yield of the reduced product, tetra-*O*-acetyl-β-glycosylamine, **3**[23] (96%). Interestingly, the reaction of the anomeric azide **2** with **1** is analogous to the reaction of aryl azides rather than the alkyl azides. It is important to recognize that the reduction is completely selective and only the β-anomer is formed exclusively in near quantitative yield. Further, the reaction of benzyl-, benzoyl-, and allyl-protected β-glycosyl azides **4**, **6**, and **8** produced the corresponding β-glycosylamines **5**,[15] **7**,[16] and **9** in very good yields, indicating the versatility of the reaction (entries 3−5; Table 1). Unlike the LAH reduction or metal-catalyzed reductions, the other protective groups were not affected under the reaction conditions. Treatment of the *N*-acetylglucosaminyl-β-azide **10** with tetrathiomolybdate **1** gave the corresponding 2-acetamido-3,4,6-tri-*O*-acetyl-glucopyranosylamine **11**[18] in excellent yield. This amine **11** is an important starting material for the synthesis of N-linked glycopeptides.[8b,24] The methodology was also applied in the case of disaccharide-derived azide **12**, which on treatment with **1** gave the corresponding anomeric amine **13** in very good yield. To check the effect of the neighboring group at C-2 in these reactions, the 2-deoxy derivative **14** was subjected to reaction with **1**, and in this case also the amine **15** was isolated as the only product.

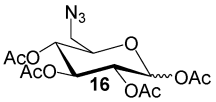
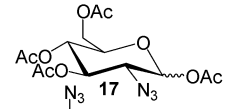
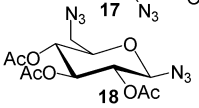
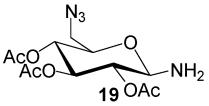
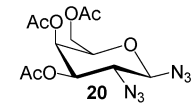
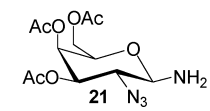
After optimizing the conditions for the reduction of anomeric azides, the methodology was applied for the reduction of C-2 and C-6 azides. Surprisingly, reaction of C-6 and C-2 azides (**16**[20] and **17**,[21] respectively; entries 1 and 2, Table 2) with tetrathiomolybdate **1** did not produce any reduction products even after an extended reaction time (72 h). The unreactivity of C-2 and C-6 azides toward tetrathiomolybdate **1** presents a unique opportunity to explore the reactivity of anomeric azides in the presence of other sugar azides with tetrathiomolybdate **1**. Thus diazides **18** and **20** on treatment with tetrathiomolybdate **1** (excess) produced 6-azido-β-glycosylamine **19** and 2-azido-β-glycosylamine **21**, respectively, as the only products in excellent yield (entries 3 and 4, Table 2). It is interesting to note that the C-6 and C-2 azides are inert under the reaction conditions, whereas the anomeric azides are selectively reduced to the cor-

TABLE 1. Reduction of Anomeric Azides with Tetrathiomolybdate 1

Entry	Substrate	Time (h)	Product[c]	Yield (%)[d]
1		8[a]		96
2	**2**	2[b]	**3**	96
3		7[a] 1.5[b]		96
4		8[a] 2[b]		92
5		6[a] 3[b]		90
6		8[a] 4[b]		92
7		6[a] 1[b]		96
8		8[a] 2[b]		94

[a] Reactions carried out under stirring. [b] Under sonication. [c] All compounds exhibited expected spectral and analytical data. [d] Isolated yields.

TABLE 2. Selective Reduction of Anomeric Azides with Tetrathiomolybdate 1

Entry	Substrate	Time (h)	Product[c]	Yield (%)[d]
1		72[a or b]	No Reaction	
2		72[a or b]	No Reaction	
3		6[a] 2[b]		90
4		6[a] 2[b]		90

[a] Reactions carried out under stirring. [b] Under sonication. [c] All compounds exhibited expected spectral and analytical data. [d] Isolated yields.

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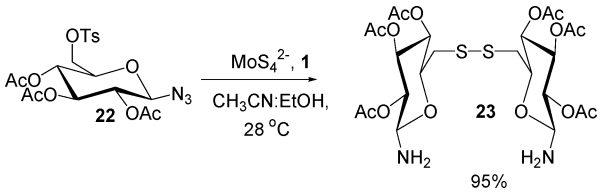
SCHEME 2. Sulfur Transfer and Reduction of Azides Assisted by Tetrathiomolybdate 1



responding β-glycosylamines, **19** and **21**, in very good yields. To the best of our knowledge, this type of regioselective reduction of anomeric azides is very rare.

Additionally, this methodology presents an opportunity to synthesize an interesting diaminodisulfide analogue **23** in one pot. Accordingly, treatment of 6-tosyl-2,3,4-tri-*O*-acetyl-β-D-glucopyranosyl azide **22**[14] with tetrathiomolybdate **1** (2 equiv) produced the corresponding β-glycosylamine disulfide **23** as the only product in excellent yield (Scheme 2). Interestingly, this transformation involves two processes mediated by tetrathiomolybdate **1**: sulfur transfer to form the disulfide and at the same time the reduction of the anomeric azide. It turned out that when the reaction of **2** with **1** was carried out under sonochemical conditions (CH_3CN/EtOH, ultrasonic cleaning bath, 25 kHz, 28 °C), it was completed in 2 h giving rise to the β-glycosylamine **3** in 96% yield. Therefore, all the subsequent experiments on reduction of azido sugars were also carried out under sonochemical conditions.

A plausible mechanism based on the reactivity of tetrathiomolybdate is presented in Scheme 3. There are two possible modes of attack of the sulfur nucleophile of **1** on organic azide. In pathway A, MoS_4^{2-} attacks the α-nitrogen of the azide to give a *N*-sulfenylamine **24** following nitrogen extrusion, which subsequently gives rise to the amine and the mononuclear persulfido molybdenum(IV) species **25**. The intermediate **25** gets converted to the Mo(V) dimmer, $Mo_2S_8^{2-}$, **26**. It is also possible to visualize a pathway B where the MoS_4^{2-}, **1** attacks the γ-nitrogen of the azide resulting in intermediate **27**, which decomposes to give the amine, N_2, and mononuclear molybdenum species **25**. Irrespective of which pathway is followed, the expected byproduct is Mo(V) dimer, **26**. This Mo(V) dimer, **26**, has been synthesized by other routes.[25] In the reaction of anomeric azides with **1**, the molybdenum byproduct has been isolated and characterized as **26**.[26] The observed selectivity of **1** at the anomeric azide may be due to increased electrophilicity at this center.

In summary, we have developed a mild and neutral method to synthesize β-glycosylamines in excellent yield under mild and neutral conditions using tetrathiomolybdate **1** as the key reagent. The striking feature of this methodology is that it tolerates a number of other functional groups. More importantly, the stereoselective reaction produces exclusively the β-anomer, presents a rare regioselectivity in the reduction of anomeric azides in the presence of C-2 and C-6 azides, and may find useful applications in carbohydrate chemistry.

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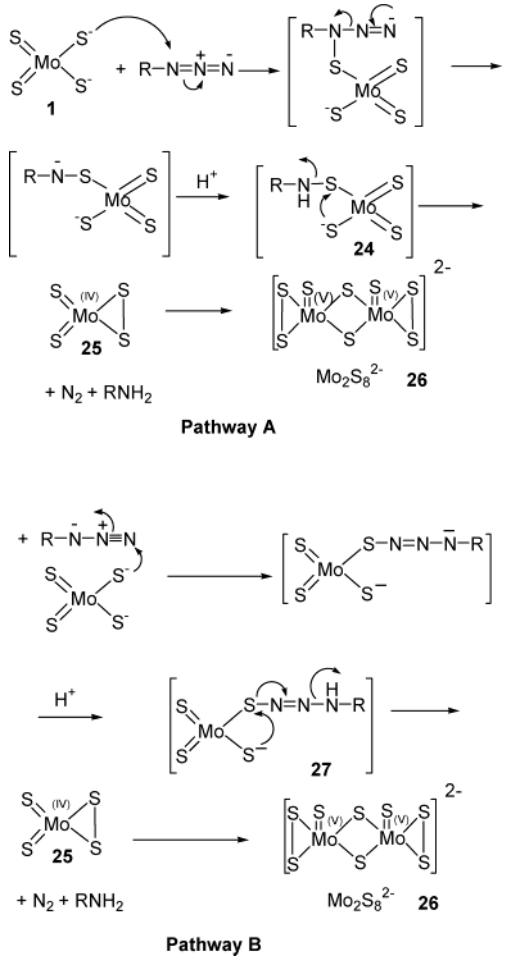
(26) IR spectrum (KBr) of the molybdenum byproduct shows a strong absorption at 520 cm^{-1} assignable to a persulfido molybdenum species.

SCHEME 3



Experimental Section

General Methods. All reactions were performed in an oven-dried apparatus. Reaction mixtures were stirred magnetically unless otherwise stated. The products were characterized by NMR, FTIR, and GCMS. Commercial-grade solvents were distilled prior to use. Chloroform, dichloromethane, and acetonitrile were initially dried over phosphorus pentoxide and stored over 4 Å molecular sieves. ^1H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively. Coupling constants are reported in hertz. Infrared (IR) spectra were measured as $CHCl_3$ solution or as thin film.

Data for 2,3,4,6-Tetra-*O*-allyl-β-D-glucopyranosyl Azide (8).[17] IR (neat): 3080, 3016, 2114, 1646 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.99−5.85 (m, 4H), 3.32−5.14 (m, 8H), 4.50 (d, 1H, J = 9 Hz), 4.22−4.31 (m, 4H), 4.15−4.02 (m, 4H), 3.67 (q, 2H, J = 11 Hz), 3.40 (bs, 3H), 3.13 (t, 1H, J = 7.5 Hz). ^{13}C NMR (75 MHz, $CDCl_3$): δ 134.9. 134.5, 134.4, 134.4, 117.4, 117.1, 116.9, 116.7, 89.9, 84.2, 80.8, 76.9, 76.8, 74.3, 73.8, 73.7, 72.5, 68.3. EIMS m/*z*: 337 (M^+ − 28).

Data for 2-Acetamido-2-deoxy-3,4,6-tri-*O*-acetyl-β-D-glucopyranosyl Azide (10).[18] IR (neat): 3332 (NH), 2104 (N_3), 1748 and 1660 (CO) cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 5.27 (dd, 1H, J = 9.9 Hz), 5.10 (dd, 1H, J = 9.6 Hz), 4.81 (d, 1H, J = 9.3 Hz), 4.28 (dd, 1H, J = 4.5 Hz, J = 12.3 Hz), 4.16 (dd, 1H, J = 2.1 Hz, J = 12.3 Hz), 3.93 (m, 1H), 3.78−3. 84 (m,1H), 2.11 (s, 3H), 2.04 (s, 3H), 2. 03 (s,3H), 1.98 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 170.8, 170.6, 170.5, 169.2, 88.3, 73.8, 72.1, 68.0, 61.8, 53.9, 23.1, 20.6, 20.5, 20.5. EIMS *m*/*z*: 373 (MH^+).

Hepta-*O*-acetyl-β-D-lactopyranosyl Azide (12).[19] IR (neat): 2942, 2120, 1755 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ

5.35 (d, 1H, $J = 3.3$ Hz), 5.21 (t, 1H, $J = 9.0$ Hz), 5.11 (dd, 1H, $J = 8.1$ Hz, $J = 10.2$ Hz), 4.96 (dd, 1H, $J = 3.3$ Hz, $J = 10.2$ Hz), 4.86 (t, 1H, $J = 9.0$ Hz), 4.64 (d, 1H, $J = 8.7$ Hz), 4.48−4.53 (m, 2H), 4.05−4.16 (m, 3H), 3.88, (t, 1H, $J = 6.9$ Hz), 3.82 (t, 1h, $J = 9.9$ Hz), 3.71 (ddd, 1H, $J = 1.5$ Hz, $J = 4.8$ Hz, $J = 9.9$ Hz), 2.15 (s, 3H), 2.14 (s, 3H), 2.08 (s, 3H), 2.07 (s, 3H), 2.05 (bs, 6H), 1.97 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.3, 170.1, 170.0, 169.6, 169.5, 169.0, 101.1, 87.7, 75.7, 74.7, 72.5, 70.9, 70.9, 70.7, 69.0, 66.5, 61.7, 60.8, 20.8, 20.7, 20.6, 20.6, 20.6, 20.6, 20.5.

Data for 2,3,4-Tri-*O*-acetyl-6-azido-6-deoxy-β-D-glucopyranosyl Azide (18).[20] IR (neat): 2942, 2119, 1756 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.22 (t, $J = 9.3$ Hz, 1H), 5.05 (t, $J = 9.9$ Hz, 1H), 4.96 (t, $J = 9.0$ Hz, 1H), 4.67 (d, $J = 9.0$ Hz, 1H), 3.75−3.81 (m, 1H), 3.37−3.43 (m, 2H), 2.08 (s, 3H), 2.04 (s, 3H), 2.02 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 169.3, 87.7, 75.7, 72.4, 70.5, 68.9, 50.9, 20.6, 20.5; EIMS *m*/*z*: 314 ($M^+ - 42$). Anal. Calcd for $C_{12}H_{16}N_6O_7$: C, 40.45; H, 4.53. Found: C, 40.37; H, 4.69.

Data for 3,4,6-Tri-*O*-acetyl-2-azido-2-deoxy-β-D-glucopyranosyl Azide (20).[22] IR (neat): 2115, 1750 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.37 (d, $J = 1.5$ Hz, 1H), 4.84 (dd, $J = 2.7$, 10.5 Hz, 1H), 4.62 (d, $J = 8.7$ Hz, 1H), 4.10−4.21 (m, 2H), 3.96 (t, $J = 6.6$ Hz, 1H), 3.59 (dd, $J = 9.3$, 10.2 Hz, 1H) 2.17 (s, 3H), 2.06 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.3, 169.9, 169.6, 89.3, 72.6, 71.4, 66.0, 61.1, 60.4, 20.6, 20.54, 20.52.

General Procedure for the Reduction of β-D-Glycosyl Azides. (a) The azides **2**, **4**, **6**, **8**, **10**, **12**, or **14** (1 mmol) and tetrathiomolybdate **1** (1 mmol) were stirred at room temperature (28 °C) in acetonitrile/ethanol (1:1, 3 mL) for the time indicated in the table. After completion of the reaction (TLC), the solvent was evaporated under reduced pressure. The black residue was extracted with CH_2Cl_2/ether (1:10, 4 × 5 mL) and filtered through a pad of Celite, and the solvent was evaporated. The residue was purified on silica gel column ($CHCl_3$/MeOH, 9:1) to furnish amines **3**, **5**, **7**, **9**, **11**, **13**, or **15**, respectively. (b) Similar experiments under sonication (CH_3CN/EtOH, ultrasonic cleaning bath, 25 kHz) furnished products **3**, **5**, **7**, **9**, **11**, **13**, or **15**, respectively, in a shorter period of time (Table 1).

Data for 2,3,4,6-Tetra-*O*-allyl-β-D-glucopyranosylamine (9). IR (neat): 3431, 1747, 1624 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.03−5.85 (m, 4H), 5.312−5.14 (m, 8H), 4.41−4.21 (m, 5H), 4.13−3.98 (m, 4H), 3.69−3.55(m, 2H), 3.40−3.33 (m, 3H), 2.97 (t, 1H, $J = 7.5$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 135.2, 135.0, 134.8, 134.5, 117.4, 117.1, 116.8, 116.5, 85.9, 85.2, 82.7, 77.65, 75.5, 74.3, 73.7, 73.6, 72.5, 69.0; EIMS: m/*z*: 340-(M^++1). Analysis:calcd for $C_{18}H_{29}NO_5$: C, 63.69; H, 8.61. Found: C, 63.09; H, 8.33.

Data for 2-Acetamido-2-deoxy-3,4,6-trio-O-acetyl-β-D-glucopyranosylamine (11).[18] IR (neat): 3330(NH), 2105 (N_3) cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.84 (d, 1H, $J = 9.3$ Hz), 5.03−5.17 (m, 2H), 4.22 (dd, 1H, $J = 4.8$ Hz, $J = 12.3$ Hz), 4.02−4.15 (m, 2H), 3.98 (d, 1H, $J = 9$ Hz), 3.62−3.68 (m, 1H), 2.10 (s, 3H), 2.05 (s, 3H), 2.03 (s 3H), 1.98 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.5, 170.8, 170.7, 169.3, 86.3, 73.3, 72.7, 68.4, 62.3, 54.8, 23.2, 20.7, 20.6, 20.5. EIMS *m*/*z*: 369 (M^+ + 23). HRMS: calcd for $C_{14}H_{22}N_2O_8$, 369.1274; found, 369.1288.

Data for Hepta-*O*-acetyl-β-D-lactopyranosylamine (13). IR (neat): 3410, 2943, 1746 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.35 (d, 1H, $J = 2.7$ Hz), 5.23 (t, 1H, $J = 9.3$ Hz), 5.11 (dd, 1H, $J = 7.8$ Hz, $J = 10.2$ Hz), 4.95 (dd, 1H, $J = 3.3$ Hz, $J = 10.2$ Hz), 4.73 (t, 1H, $J = 9.3$ Hz), 4.47 (d, 1H, $J = 8.1$ Hz), 4.46 (m, 1H), 4.04−4.17 (m, 4H), 3.87 (t, 1H, $J = 6.9$ Hz), 3.73 (t, 1H, $J = 9.6$ Hz), 3.59 (m, 1H), 2.16 (s, 3H), 2.13 (s, 3H), 2.07 (s, 6H), 2.05 (bs, 6H), 1.96 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.5, 170.4, 170.3, 170.1, 170.1, 169.6, 169.0, 101.0, 84.6, 73.6, 72.9, 72.4, 70.9, 70.6, 69.0, 66.5, 62.3, 60.7, 20.9, 20.8, 20.8, 20.6, 20.6, 20.6, 20.6, 20.4. EIMS *m*/*z*: 658 (M^+ + 23). HRMS: calcd for $C_{26}H_{37}NO_{17}$ + Na, 658.1959; found, 658.1944.

Data for compound 2,3,4-Tri-*O*-acetyl-6-azido-6-deoxy-β-D-glucopyranosylamine (19). IR (neat): 3410, 2104, 1751 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.24 (t, $J = 9.9$ Hz, 1H), 4.97 (t, $J = 9.9$ Hz, 1H), 4.82 (t, $J = 9.3$ Hz, 1H), 4.21 (d, $J = 8.7$ Hz, 1H), 3.63−3.69 (m, 1H), 3.31−3.32 (m, 2H), 2.07 (s, 3H), 2.04 (s, 3H), 2.01 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.22, 170.19, 169.6, 84.9, 73.8, 73.0, 71.9, 69.9, 51.4, 20.8, 20.6. EIMS *m*/*z*: 331(M^+ + 1). Anal. Calcd for $C_{12}H_{18}N_4O_7$: C, 43.64; H, 5.49. Found: C, 43.57; H, 5.46.

Data for 2-Deoxy-2-azido-3,4,6-Tri-*O*-acetyl-β-D-glycopyranosylamine (21). IR (neat): 3343, 2114, 1747 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.34 (d, $J = 2.7$ Hz, 1H), 4.84 (dd, $J = 1.8$, 10.8 Hz, 1H), 4.07−4.10 (m, 3H), 3.86 (t, $J = 6.6$ Hz, 1H), 3.45 (dd, $J = 10.2$, 9.6 Hz, 1H), 2.16 (s, 3H), 2.05 (s, 6H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.4, 17.0, 169.8, 85.6, 72.2, 71.5, 66.8, 62.2, 61.7, 20.7, 20.67, 20.63. CIMS m/*z*: 331 (M^+ + 1). Anal. Calcd for $C_{12}H_{18}N_4O_7$: C, 43.64; H, 5.49. Found: C, 43.77; H, 5.76.

Data for Compound 23. IR (neat): 3370, 1747 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.08 (bs, 1H), 4.83 (bs, 1H), 4.57 (bs, 3H), 3.18 (m, 2H), 2.17 (s, 3H), 2.15 (s, 3H), 2.12 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 170.06, 169.85, 169.15, 87.35, 73.55, 71.50, 71.25, 69.91, 45.72, 21.05, 21.03, 20.96. EIMS m/*z*: 642 (M^+ + 2). Anal. Calcd for $C_{24}H_{36}N_2O_{14}S_2$: C, 44.99; H, 5.66. Found: C, 44.66; H, 5.52.

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Supporting Information Available: ^{1}H and ^{13}C NMR spectra for compounds **8**−**13**, **18**−**21**, and **23**. This material is available free of charge via the Internet at http://pubs.acs.org.

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