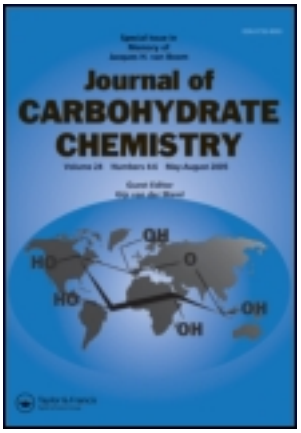


Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lcar20

Synthesis of β-Glycosyl Amides from N-Glycosyl Dinitrobenzenesulfonamides

Vishwanath Gaitonde [a] & Steven J. Sucheck [a]
[a] Department of Chemistry and School for Green Chemistry and Engineering, The University of Toledo, Toledo, OH, 43606, USA
Version of record first published: 02 Jul 2012.

To cite this article: Vishwanath Gaitonde & Steven J. Sucheck (2012): Synthesis of β-Glycosyl Amides from N-Glycosyl Dinitrobenzenesulfonamides, Journal of Carbohydrate Chemistry, 31:4-6, 353-370

To link to this article: http://dx.doi.org/10.1080/07328303.2012.663431

Journal of Carbohydrate Chemistry, 31:353–370, 2012

ISSN: 0732-8303 print / 1532-2327 online
DOI: 10.1080/07328303.2012.663431

Synthesis of β-Glycosyl Amides from *N*-Glycosyl Dinitrobenzenesulfonamides

Vishwanath Gaitonde and Steven J. Sucheck

Department of Chemistry and School for Green Chemistry and Engineering, The University of Toledo, Toledo, OH 43606, USA

The *N*-glycosyl-2,4-dinitrobenzenesulfonamides were accessed via benzoyl-protected β-glycosyl azides. The azides were reduced with Adams' catalyst to the corresponding amines. The glycosylamines were sulfonated with 2,4-dinitrobenzenesulfonyl chloride to form *N*-glycosyl-2,4-dinitrobenzenesulfonamides in moderate yields. β-Glycosyl amides were then prepared in 67% to 81% yields by treatment of the sulfonamides with thioacetic acid and cesium carbonate. The conversion of the glycosylsulfonamide to the glycosyl amide proceeded with high stereoselectivity.

Keywords β-Glycosyl amides; 2,4-Dinitrobenzenesulfonamides; Thioacids; Meisenheimer complex

INTRODUCTION

Glycosyl amide linkages are found in a variety of natural products. It is also notable that the glycosyl amide can be activated and used as a glycosyl donor.[1] A popular strategy for accessing the β-glycosyl amide linkage found in *N*-linked glycopeptides is the Lansbury aspartylation, which involves the direct coupling of a glycosylamine to an activated aspartic acid on a protected peptide.[2] The intermediate glycosylamines are frequently accessed by the Kochetkov reaction[3] or by deprotection of a sugar anomeric azide to access the amine.[4] Aspartylations have also been performed using less active esters under microwave-mediated conditions.[5] A limitation of the method is that the starting glycosylamines are relatively unstable[6] and the hemiaminal is prone to mutarotation to give a mixture of anomers, thus making

Received December 21, 2011; accepted January 31, 2012.
Address correspondence to Steven J. Sucheck, Department of Chemistry and School for Green Chemistry and Engineering, The University of Toledo, 2801 W. Bancroft Street, Toledo, Ohio 43606, USA. E-mail: steve.sucheck@utoledo.edu

stereocontrol difficult.[7] Further, diglycosylamines have also been observed as by-products of glycosylamine-forming reactions.[8,9] Thus, methods for forming the β-glycosyl amide linkage that do not involve an anomeric amine can be considered advantageous. Several methods for improving this basic transformation have been explored; however, most are overly complex and have noted limitations.[10,11] Alternative strategies to access the β-glycosyl amide include the use of the Staudinger reduction–acylation process,[10,11] starting from β-glycosyl azides. However, anomerization remains a significant problem, and mixtures of anomers are often obtained.[12,13] These same azides have also been used in traceless Staudinger ligations using 2-diphenylphosphanylphenyl alkanoates. The diastereoselectivity of these reactions appears dependent on the sugar-protecting group.[14] Glycosyl azides have also been reported to react with thioacids to yield the amide,[15] while per-acylated sugars in the presence of methanesulfonic acid and nitrile form glycosyl amides via a Ritter-type reaction.[16] Further, β-glycosyl isonitriles and carboxylic acids under the influence of microwaves react to afford formylated β-glycosyl amides.[17] Thus, there have been sustained efforts to identify more stereoselective routes to generate β-glycosyl amides.

2,4-Dinitrobenzenesulfonyl chloride (dNBS-Cl) has been used to protect primary amines. The resulting 2,4-dinitrobenzenesulfonamides (dNBS) have in turn been used to synthesize secondary amines and diamines by Fukuyama et al.[18,19] 2,4-Dintrobenzenesulfonamides were later exploited to generate amides, thioamides, ureas, and thioureas proceeding through the *ipso* attack of various S and O nucleophiles on the sulfonamide to produce the Meisenheimer complex.[20,21] In the case of a reaction between thioacids and dNBSs, the sulfonamide nitrogen ultimately attacks a thioester on the disintegration of the Meisenheimer complex (Fig. 1). Only recently has this chemistry been taken up as a possible chemoselective approach to form peptide linkages[22–24] and neoglycoconjugates.[25] Our lab has reported that a β-glycosyl amide can be formed from the reaction between 2,4-dinitrobenzenesulfonyl β-N-glycosides and thioacids.[26] During the course of the study, we found it notable that the reaction was fast and no α-anomer was isolated. Herein we explore the scope of that reaction by examining several additional sugar congeners.

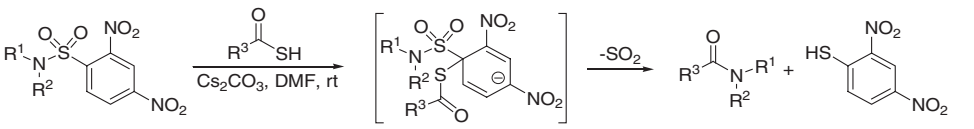
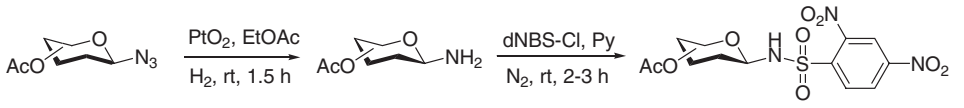


Figure 1: Mechanism of amide formation.

RESULTS AND DISCUSSION

We chose four monosaccharides, D-glucose, D-galactose, D-mannose, and D-arabinose, and a disaccharide, D-maltose, as a representative set of saccharides to explore the scope of the reaction between 2,4-dinitrobenzenesulfonyl β-N-glycosides and thioacids. Initially we began by selecting D-glucose and D-galactose and converted each into the corresponding β-glycosyl azides **1** and **2**, respectively.[27] Reduction of glycosyl azides was accomplished using Adams' catalyst to generate the respective glycosylamines. As free glycosylamines are prone to anomerization, the reduced glycosylamine was immediately subjected to sulfonation with dNBS-Cl in pyridine. The resulting per-*O*-acetylated-β-glycosyl-2,4-dinitrobenezenesulfonamides **3** and **4** were formed in 24% to 30% yield (Table 1). Disappointed by the low yields, we attempted to modify the conditions to improve the yield (Table 2). Pd/C-H_2 in methanol and PtO_2-H_2 in either ethanol or ethyl acetate were used for the initial reduction steps. Solvents were kept anhydrous, and there appeared to be no difference in the quality or dryness of the intermediate glycosylamine. The concentration of base pyridine was varied between neat solvent and 2.0 and 4.0 equivalents, because we were concerned that high concentrations of base would lead to a competing deprotection reaction. The dNBS-Cl reagent was also varied between 1.5 and 2.5 equivalents, and the use of catalytic DMAP was explored. No noticeable

Table 1: Preparation of *N*-2,4-dinitrobenzenesulfonamide from glycosyl azides via glycosylamines



Per-*O*-acetylated glycosyl azide | Per-*O*-acetylated glycosylamine | Per-*O*-acetylated *N*-dNBS glycoside

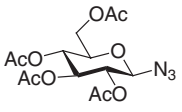
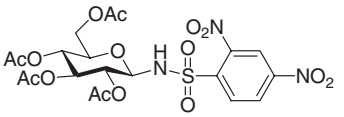
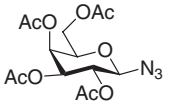
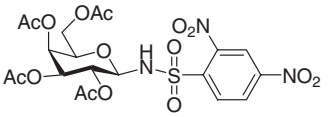
Azides	*N*-dNBS glycosides	Yield
 **1**	 **3**	24%
 **2**	 **4**	27–30%

Table 2: Conditions for reduction/sulfonation of per-*O*-acetylated glycosyl azide **1** and **2**

Entry	Compound	Reagents	Solvent	Temperature	Time	Yield[a]
a	**1**	Pd/C, H_2	MeOH	rt	40 min	24%
		dNBS-Cl, (1.5 eq.), N_2	Pyridine	rt	3.0 h	
b	**1**	PtO_2, H_2	EtOH	rt	2 h	25%
		dNBS-Cl (1.5 eq.), N_2	Pyridine	0°C–rt	3.5 h	
c	**1**	PtO_2, H_2	EtOH	rt	1.5 h	27%
		dNBS-Cl (1.5 eq.), N_2 DMAP (cat.)	Pyridine (2.0 eq.), CH_2Cl	0°C–rt	2.5 h	
d	**1**	PtO_2, H_2	EtOAc	rt	1.5	24%
		dNBS-Cl (2.5 eq.), N_2	Pyridine (4.0 eq.), CH_2Cl	0°C–rt	3.0 h	
e	**2**	Pd/C, H_2	MeOH	rt	30 min	24%
		dNBS-Cl (1.5 eq.), N_2	Pyridine	rt	3.5 h	
f	**2**	PtO_2, H_2	EtOH	rt	1.5 h	30%
		dNBS-Cl (1.5 eq.), N_2	Pyridine	0°C–rt	3.5 h	
g	**2**	PtO_2, H_2	EtOH	rt	1.5 h	26%
		dNBS-Cl (1.5 eq.), N_2 DMAP (cat.)	Pyridine (4.0 eq.), CH_2Cl	0°C–rt	3.0 h	
h	**2**	PtO_2, H_2	EtOAc	rt	1.5 h	28%
		dNBS-Cl (2.5 eq.), N_2	Pyridine	0°C–rt	2.5 h	

[a]Combined yields over two-step reaction.

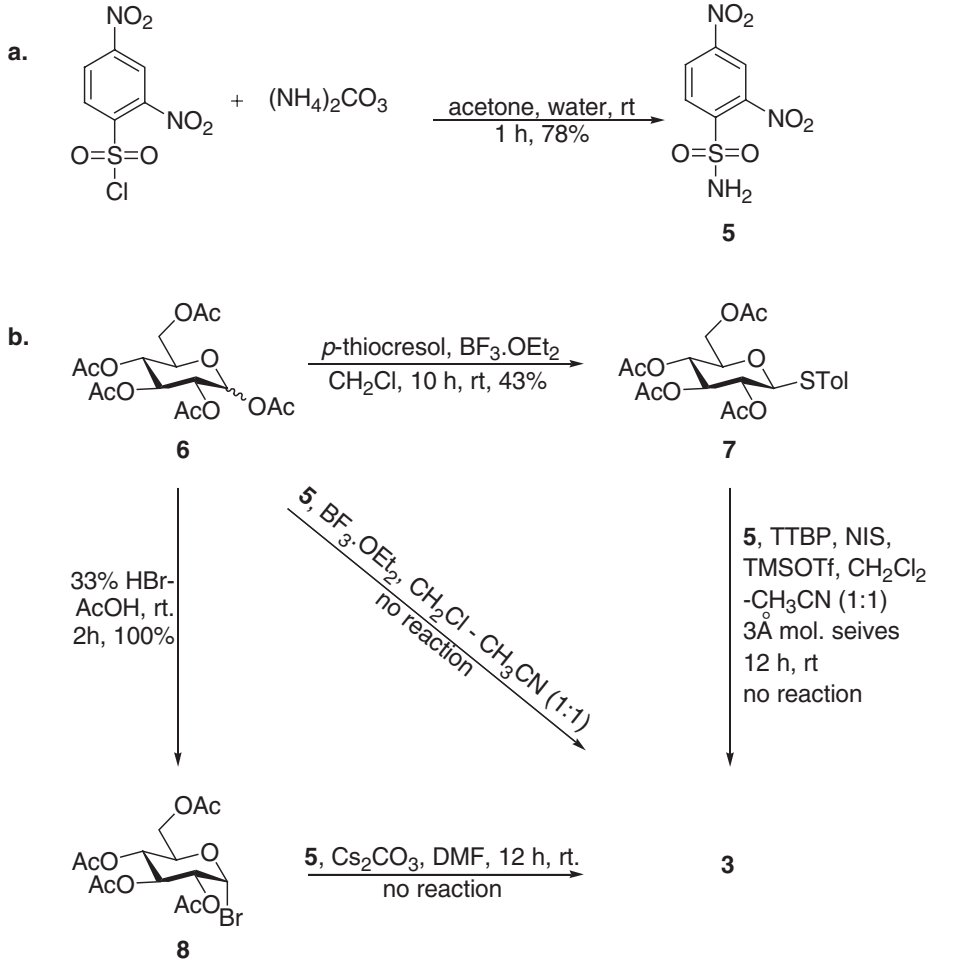
improvement in yield was achieved. Mass spectral analysis of the glycosylsulfonamide reaction mixtures suggested liability of acetyl groups under reaction conditions. ESI-MS showed $m/z = 600.08$, 558, 516, 474, and 423 M+Na, indicating a progressive loss of acetyl groups with intermediates appearing as sodium adducts. The apparent sensitivity of the acetyl group led us to examine other potential routes to access the glycosyl sulfonamides.

Various strategies to access the glycosylsulfonamides **3** and **4** were explored. Initially the dNBS-Cl was converted to 2,4-dinitrobenzenesulfonamide (**5**) in 78% yield by reacting with ammonium carbonate in a mixture of acetone/water (1:1) (Scheme 1). We prepared the 4-methylphenyl 2,3,4,6-tetra-*O*-acetyl-β-D-thioglucopyranoside (**7**) from α/β-D-glucose pentaacetate (**6**) and *p*-thiocresol in the presence of $BF_3.OEt_2$.[28,29] Then, we explored the glycosylation of sulfonamide **5** with thioglycoside **7** in the presence of 2,4,6-tri-*tert*-butylpyridine (TTBP), *N*-iodosuccinimide (NIS), and trimethylsilyl trifluoromethanesulfonate (TMSOTf).[30] To our surprise, this reaction failed. We attribute the lack of reactivity to the electron-deficient sulfonamide **5,**

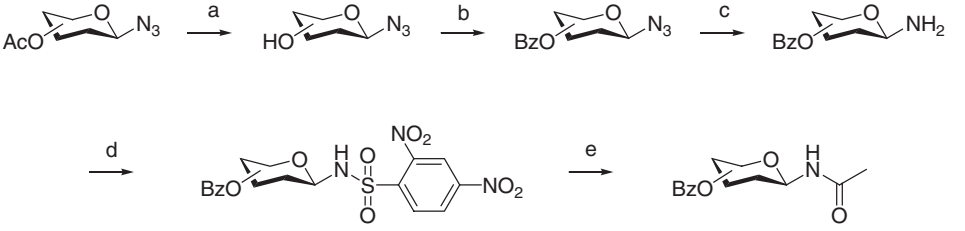
which is possibly a very poor nucleophile. In an alternative approach, pentaacetate **6** was converted to 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl bromide (**8**), followed by reacting **8** with **5** in the presence of Cs_2CO_3 to produce compound **3**. Cs_2CO_3 was deemed a sufficiently strong base, because the pK_a of the acidic sulfonamide NH was estimated to be 8.2 using Chemaxon software. Again, no desired product was obtained. Peracetate **6** was directly reacted with **5** in the presence of $BF_3.OEt_2$. In this case trace product was obtained according to mass spectral analysis of the crude reaction mixture; however, the yield was not synthetically useful. The various attempts are summarized in Scheme 1. We also accessed the known glucosylamine and treated it with the dNBS-Cl to access the sulfonamide free of protecting groups. The polar compound was difficult to handle and purify. Acetylation of this intermediate with acetic anhydride in pyridine resulted in an isolable pentaacetate, which contained an N-acetyl group on the sulfonamide nitrogen (data not shown). It is possible that acylation using less basic conditions could yield a more direct route to our desired target.

At this point a less direct approach to access the glycosyl sulfonamides was considered. Benzoate-protecting groups are reported to be less readily hydrolyzed in comparison to acetates, and the tendency for benzoate migration, in contrast to acetates, is not nearly as strong. Therefore, the β-glycosyl azides **1** and **2** were converted to their benzoyl-protected congeners **12** and **13**, respectively (Table 3). These compounds were further subjected to reduction to the free amine using Adams' catalyst to produce intermediate glycosylamines followed by sulfonation with dNBS-Cl. The desired β-glycosylsulfonamides **17** and **18** were obtained in 44% and 48% yields, respectively. While these yields are still modest, they represented a significant improvement over the yields obtained from the acetate-protected sugars. We had also considered that the improved yield may be a result of increased nucleophilicity of the anomeric amine when benzoates are present. However, the benzoyl group should be more withdrawing owing to the sp^2 centers of the phenyl ring. Supporting this notion is experimental evidence in the form of relative reactivity data comparing per-acetyl and per-benzoyl thioglucosides in model glycosylation reactions.[31] The data reveal per-benzoyl as slightly more deactivating that per-acetyl. In addition, pK_a studies comparing per-acetylated and per-benzoylated 1-deoxynojirimycin derivatives show the benzoyl congener (pK_a 3.4) to be slightly more electron withdrawing than the acetate (pK_a 3.5).[32] With this data in hand the 2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranosyl azide (**9**), 2,3,4-tetra-*O*-acetyl-β-D-arabinopyranosyl azide (**10**), and 2,3,6,2′,3′,4′,6′-hepta-*O*-acetyl-β-maltosyl azide (**11**) were prepared using known procedures and converted to the corresponding benzoyl-protected glycosyl azides **14**, **15**, and **16** in very good yields (Table 3).

With a representative series of β-glycosyl azides, we envisioned converting each to the corresponding β-glycosyl sulfonamide. These sulfonamides would

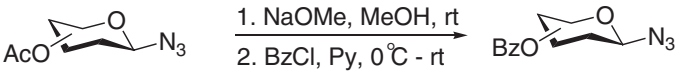


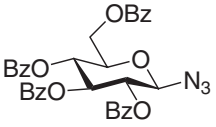
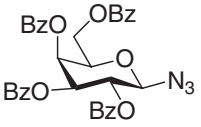
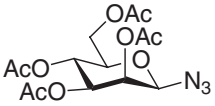
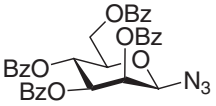
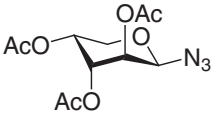
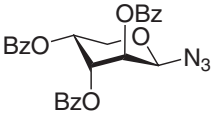
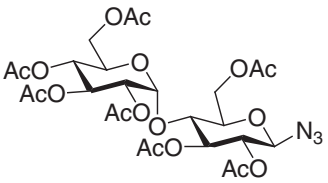
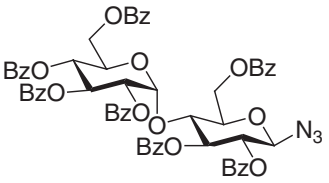
Scheme 1: (a) Synthesis of 2,4-dinitrobenzenesulfonamide (**5**). (b) Alternative route explored to access glycosyl sulfonamide **3**.



Scheme 2: Synthetic route to access β-glycosyl amides from per-*O*-acetylated β-D- glucosyl, -galactosyl, -arabinosyl, -mannosyl, and -maltosyl azide. Reagents and conditions: (a) NaOMe, 1 h, rt. (b) BzCl, pyridine, 12–14 h, 0°C–rt, (87–93% over two steps). (c) PtO_2, H_2, EtOAc, 1.5 h, rt. (d) dNBS-Cl, pyridine, DMAP (cat.), 30–60 min, rt, (43–48% over two steps). (e) Thioacetic acid, Cs_2CO_3, DMF, 20–30 min, rt, (67–81%).

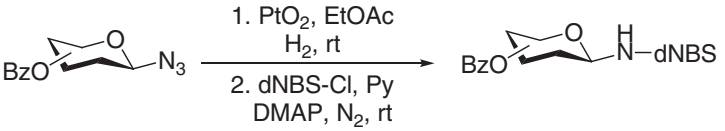
Table 3: Synthesis of per-*O*-benzoylated glycosyl azides from per-*O*-acetylated glycosyl azides

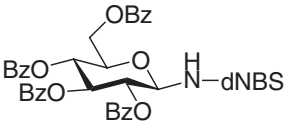
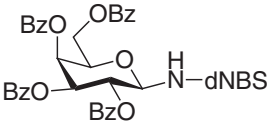
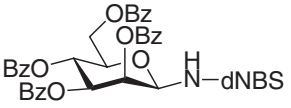
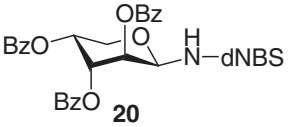
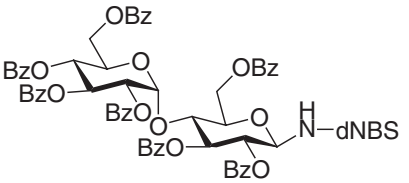


Peracetate	Perbenzoate	Time in h (Step)	Yield
1	 **12**	(1) 1.5 (2) 14.5	(1) 98% (2) 93%
2	 **13**	(1) 1.5 (2) 14.0	(1) 98% (2) 92%
 **9**	 **14**	(1) 1.0 (2) 15.0	(1) 100% (2) 89%
 **10**	 **15**	(1) 1.0 (2) 14.0	(1) 100% (2) 92%
 **11**	 **16**	(1) 1.5 (2) 14.5	(1) 98% (2) 87%

then be combined with a thioacid and the yield, reaction time, and propensity for anomerization determined. The overall reaction sequence is shown in Scheme 2. Thus, β-glycosyl azides **14**, **15**, and **16** were treated with PtO_2-H_2 to form the corresponding glycosylamines followed by treatment with dNBS-Cl in pyridine with catalytic DMAP to form the sulfonamides **19**, **20**, and **21**,

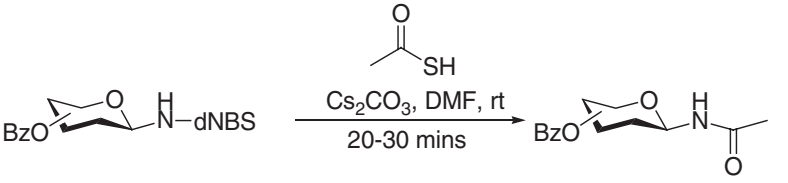
Table 4: Formation of *N*-dNBS glycoside from per-*O*-benzoylated glycosyl azide

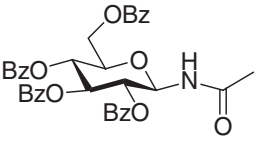
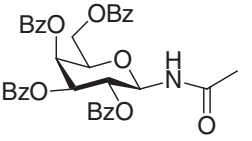
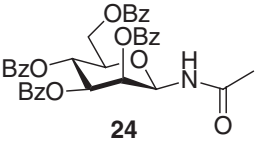
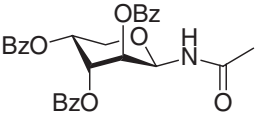
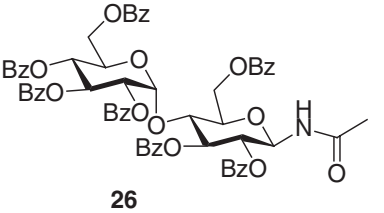


Perbenzoate	*N*-dNBS glycoside	Time in h (Step)	Yield
12	 **17**	(1) 1.5 (2) 1.0	(1) 98% (2) 44%
13	 **18**	(1) 1.5 (2) 1.0	(1) 98% (2) 48%
14	 **19**	(1) 2.0 (2) 0.75	(1) 100% (2) 45%
15	 **20**	(1) 1.0 (2) 0.5	(1) 97% (2) 45%
16	 **21**	(1) 1.5 (2) 1.5	(1) 98% (2) 43%

respectively, in 43% to 45% yields (Table 4). β-Glycosyl sulfonamides **17–21** reacted smoothly with thioacetic acid in the presence of Cs_2CO_3 to generate β-glucosyl amides **22–26**, respectively, in 67% to 81% yields. Reactions were complete in 20 to 30 min (Table 5), and the β-anomers appeared to be the exclusive products. Coupling constants for the $^3J_{\text{H-1,H-2}}$ and $^3J_{\text{H-1,NH}}$ for **23–26**

Table 5: Formation of per-*O*-benzoylated glycosylamides from per-*O*-benzoylated glycosyl sulfonamide



N-dNBS glycoside	*N*-glycosylamide	Yield
17	 **22**	67%
18	 **23**	68%
19	 **24**	81%
20	 **25**	73%
21	 **26**	67%

were in the range of 9.0 to 9.6 Hz, with the H-1 signals all appearing as apparent triplets. The coupling constants for $^3J_{\text{H-1,H-2}}$ and $^3J_{\text{H-1,NH}}$ in the known β-glycosyl amides, such as 1-acetamido-1-deoxy-2,3,4,6-tetraacetyl-β-D-glucose, are also in the range of 9.0 Hz, with H-1 appearing as an apparent triplet.[33] On the other hand, the coupling pattern of H-1 in α-glycosyl amides usually appears as a doublet of doublets in compounds with H-2 in the axial position.[34]

In conclusion, we have shown that a variety of β-glycosyl-2,4-dinitrobenzenesulfonamides can be accessed in moderate yields from the benzoyl-protected β-glycosyl azides. Some mutarotation of the glycosylamine during the conversion from per-*O*-acetylated glycosyl azide compounds to glycosyl-2,4-dinitrobenzenesulfonamides ($\sim$5–10%) was usually observed. While considerable effort was required to manipulate the starting sugars into the β-glycosyl-sulfonamides, it is likely that more direct routes to these intermediates can be developed, which would improve the utility of the strategy. The electron-deficient sulfonamides reacted with thioacetic acid, rapidly, in good yield, and in high stereoselectively. Furthermore, it is likely that the β-glycosyl-2,4-dinitrobenzenesulfonamides behave similarly to *N*-alkyl 2,4-dinitrobenzenesulfonamides, which suggests they could be used to access secondary glycosylamides, thioamides, ureas, thioureas, and potentially even guanidinium derivatives. Examples of these reactions would further expand the usefulness of glycosyl-2,4-dinitrobenzenesulfonamides.

EXPERIMENTAL

General Methods

The starting sugars D-glucose, D-galactose, D-mannose, D-arabinose, and D-maltose and other fine chemicals were purchased from Acros Organics. Boron trifluoride diethyl etherate was from Sigma-Aldrich. The chemicals were used without further purification. All solvents were obtained from Fisher Scientific Co. Dichloromethane was dried and distilled following the standard procedures, while pyridine, dimethyl, sulfoxide, and dimethylformamide were stored over 4 Å molecular sieves. Silica (230–400 mesh) for flash column chromatography was obtained from Sorbent Technologies; precoated plates for thin-layer chromatography (TLC) were from E. Merck. TLCs (Silica Gel 60, F_{254}) were visualized under UV light by charring (5% H_2SO_4–MeOH) or by use of a ninhydrin solution. Flash column chromatography was performed on 230–400 mesh silica gel using solvents as received. ^{1}H NMR spectra were recorded either on a Varian VXRS 400 MHz or an INOVA 600 MHz spectrometer in $CDCl_3$ using residual $CHCl_3$ as an internal reference. ^{13}C NMR spectra were recorded at 100 or 150 MHz in $CDCl_3$ using the triplet centered at δ 77.0. ^{1}H-^{1}H gCOSY

was performed on a 600 MHz spectrometer. High-resolution mass spectrometry (HRMS) was performed on an ESI-TOF mass spectrometer for $m/z < 1000$; for $m/z > 1000$ MALDI-TOF data was obtained.

General Procedures

*Synthesis of 2,3,4,6-tetra-*O*-benzoyl-β-*D*-glucopyranosyl azide (12), 2,3,4, 6-tetra-*O*-benzoyl-β-*D*-galactopyranosyl azide (13), 2,3,4,6-tetra-*O*-benzoyl-β-*D*-mannopyranosyl azide (14), 2,3,4-tri-*O*-benzoyl-β-*D*-arabinopyranosyl azide (15), and 2,3,6,2′,3′,4′,6′-hepta-*O*-benzoyl-β-maltosyl azide (16)*

The starting materials 2,3,4,6-tetra-*O*-acetyl-β-D-glucosyl azide,[27] 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl azide,[27] 2,3,4-tri-*O*-acetyl-β-D-arabinopyranosyl azide,[27] and 2,3,6,2′,3′,4′,6′-hepta-*O*-acetyl-β-maltosyl azide[27] were all prepared from a known literature procedure. The 2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranosyl azide could not be prepared in our hands using reference 27; however, we could access the known compound starting from the glycosyl chloride followed by displacement with tetrabutylammonium azide.[35] Once in hand, 2.0 g of the respective per-*O*-acetylated-β-glycosyl azides was dissolved in 15 mL anhydrous methanol in a round-bottom flask and stirred until complete dissolution under nitrogen atmosphere. A catalytic amount of sodium metal (ca. 25 mg) was added to the flask and the solution was allowed to stir for about 1 h. The completion of the reaction was monitored using TLC. On completion the solution was neutralized with Amberlite IR 120 H resin. The resin was filtered and rinsed with additional methanol followed by concentration of the filtrate to dryness on a rotary evaporator under reduced pressure. The products were dried under high vacuum and used in the next step without further purification. The polyols were dissolved in 10 mL of anhydrous pyridine under N_2 atmosphere and cooled to 0°C. Benzoyl chloride (1.5 equiv. per −OH) was added dropwise to the stirred solution. After addition of benzoyl chloride was complete, the reaction mixtures were brought to rt and stirred for a time respective to each compound (Table 3). Completion of the reactions was monitored by TLC. After completion, 2 to 3 mL methanol was added to quench residual benzoyl chloride. The solutions were diluted with toluene, evaporated to dryness, and purified by flash column chromatography on silica gel using 20% ethyl acetate in toluene as an eluent. The 2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl azide (**12**),[36,37] 2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl azide (**13**),[38] and 2,3,4,6-tetra-*O*-benzoyl-β-D-mannopyranosyl azide (**14**)[37] are reported.

Synthesis of N-*(2,3,4,6-tetra*-O-*benzoyl-β*-D-*glucopyranosyl)-2,4-dinitrobenzenesulfonamide (17),* N-*(2,3,4,6-tetra*-O-*benzoyl-β*-D-*galactopyranosyl)-2,4-dinitrobenzenesulfonamide (18),* N-*(2,3,4,6-tetra*-O-*benzoyl-β*-D-*mannopyranosyl)-2,4-dinitrobenzenesulfonamide (19),* N-*(2,3,4-tri*-O-*benzoyl-β*-D-*arabinopyranosyl)-2,4-dinitrobenzenesulfonamide (20), and* N-*(2,3,6,2′,3′,4′,6′-hepta*-O-*benzyl-β-maltosyl)-2,4-dinitrobenzenesulfonamide (21)*

Per-*O*-benzoylated-*β*-glycosyl azide, 1.5 g, was dissolved in 10 mL of anhydrous ethyl acetate and transferred to a reaction flask containing platinum oxide (0.17 equiv.). The solution was placed under 1 atm of H_2 atmosphere and allowed to stir according to the respective times shown in Table 4. Completion of the reaction was monitored by TLC. The reaction was worked up by filtering through a bed of Celite 545 in a sintered glass funnel. The filtrate was concentrated by rotatory evaporation under reduced pressure. The concentrated glycosyl amines were used in the sulfonation without further purification. Crude per-*O*-benzoylated-*β*-glycosylamine was dissolved in 15 mL of anhydrous pyridine with a catalytic amount of DMAP under an N_2 atmosphere. 2,4-Dinitrobenzenesulfonyl chloride (1.5 equiv.) was added to the solution and the reaction was allowed to stir for the respective time as shown in Table 4. Completion of the reaction was monitored with TLC. The reaction was worked up by diluting with 50 mL of ice-cold water and followed by extraction with 3×50 mL portions of ethyl acetate. The organic layers were combined and washed successively with saturated $NaHCO_3$ and brine. It was dried over anhydrous Na_2SO_4. The solution was concentrated by rotatory evaporation under reduced pressure. The products were purified by flash column chromatography using silica gel using 25% acetone in hexanes as an eluent.

Synthesis of N-*(2,3,4,6-tetra*-O-*benzoyl-β*-D-*glucopyranosyl) acetamide (22),* N-*(2,3,4,6-tetra*-O-*benzoyl-β*-D-*galactopyranosyl) acetamide (23),* N-*(2,3,4,6-tetra*-O-*benzoyl-β*-D-*mannopyranosyl) acetamide (24),* N-*(2,3,4-tri*-O-*benzoyl-β*-D-*arabinopyranosyl) acetamide (25), and* N-*(2,3,6,2′,3′,4′,6′-hepta*-O-*benzoyl-β-maltosyl) acetamide (26)*

To a suspension of cesium carbonate (2 equiv.) in 10 mL of anhydrous DMF was added thioacetic acid (2 equiv.). The mixture was stirred for 10 min at rt under N_2 atmosphere before addition of 300 mg of *N*-glycosyl 2,4-dinitrobenzenesulfonamide. The resulting solution was further stirred for the time given in Table 5. Completion of the reaction was monitored by TLC. After completion, the reaction was worked up by diluting with EtOAc and washing the organic layer with saturated aqueous NH_4Cl followed by brine. The organic layer was dried over anhydrous Na_2SO_4 and concentrated under

reduced pressure by rotatory evaporator. The product was purified by flash column chromatography on silica gel using 30% acetone in hexanes as an eluent. The physical data for *N*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl) acetamide (**22**) matches the previously reported data.[15]

Spectral Data

^{1}H NMR and ^{13}C NMR spectra for known compounds matched the data reported in the cited references. Data for new compounds are reported below.

2,3,4-Tri-O-*benzoyl-β*-D-*arabinopyranosyl azide (15)*

Colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14–7.27 (m, 15H, aromatic), 5.74 (m, 1H, H-4), 5.72 (s, 1H, H-3), 5.64 (dd, 1H, J = 3.6 Hz, 9.6 Hz, H-2), 4.97 (d, 1H, J = 6.0 Hz, H-1), 4.42 (dd, 1H, J = 3.0 Hz, 13.2 Hz, H-5), 4.03 (d, 1H, J = 13.2 Hz, H-5′). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.7–165.38 (3C, carbonyl), 133.9–128.61 (18C, aromatic), 88.28 (1C, C-1), 70.9–65.59 (4C, ring carbon). HRMS: m/z $[M+Na]^+$ calcd for $C_{26}H_{21}N_3O_7Na$ is 510.1277, found 510.1290.

2,3,6,2′,3′,4′,6′-Hepta-O-*benzoyl-β-maltosyl azide (16)*

Colorless solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.11–7.16 (m, 35H, aromatic), 6.08 (t, 1H, J = 9.9 Hz, H-3′), 5.78 (t, 1H, J = 9.3 Hz, H-3), 5.75 (d, 1H, J = 4.2 Hz, H-1'), 5.66 (t, 1H, J = 9.9 Hz, H-4′), 5.27 (dd, 1H, J = 8.7 Hz, 9.3 Hz, H-2), 5.24 (dd, 1H, J = 3.9Hz, 10.5 Hz, H-2′), 4.94 (dd, 1H, J = 2.1 Hz, 12.3 Hz, H-6_b), 4.91 (d, 1H, J = 8.4 Hz, H-1), 4.77 (dd, 1H, J = 3.9 Hz, 12.3 Hz, H-6_a), 4.51 (t, 1H, J = 9.3 Hz, H-4), 4.45 (m, 1H, H-5′), 4.40 (dd, 1H, J = 3.0 Hz, 12.0 Hz, H-$6'_a$), 4.27 (dd, 1H, J = 3.6 Hz, 12.0 Hz, H-$6'_b$), 4.18 (m, 1H, H-5). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.31–165.09 (7C, carbonyl), 133.75–125.48 (42C, aromatic), 96.67 (1C, C-1'), 88.06 (1C, C-1), 75.15–62.65 (10C, ring carbon). MALDI: m/z $[M+Na]^+$ calcd for $C_{61}H_{49}N_3O_{17}$ is 1095.31, found 1118.341.

N-*(2,3,4,6-Tetra*-O-*benzoyl-β*-D-*glucopyranosyl)-2,4-dinitrobenzenesulfonamide (17)*

Yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.40–7.23 (m, 23H, aromatic), 6.02 (t, 1H, J = 9.6 Hz, H-3), 5.64 (t, 1H, J = 9.9 Hz, H-4), 5.46 (t, 1H, J = 9.3 Hz, H-2), 5.29 (d, 1H, J = 9.0 Hz, H-1), 4.48 (d, 1H, J = 9.6 Hz, H-6′), 4.23–4.19 (m, 2H, H-5, H-6). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.23–165.21 (4C, carbonyl), 149.76–120.81 (30C, aromatic), 83.81 (1C, C-1), 74.24–62.10 (5C, ring carbon). HRMS: m/z $[M+Na]^+$ calcd for $C_{40}H_{31}N_3O_{15}SNa$ is 848.1374, found 848.1343.

N-*(2,3,4,6-Tetra*-O-*benzoyl-β*-D-*galactopyranosyl)-2,4-dinitrobenzenesulfonamide (18)*

Yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.38–7.21 (m, 23H, aromatic), 6.89 (d, 1H, J = 9.6 Hz, NH), 6.00 (d, 1H, J = 3.6 Hz, H-4), 5.79 (dd, 1H, J = 3.0 Hz, 10.2 Hz, H-3), 5.72 (t, 1H, J = 9.6 Hz, H-2), 5.27 (d, 1H, J = 9.0 Hz, H-1), 4.46 (m, 1H, H-5), 4.28 (dd, 1H, J = 2.7 Hz, 9.3 Hz, H-6), 4.12 (dd, 1H, J = 7.2 Hz, 14.4 Hz, H-6′). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.22–165.48 (4C, carbonyl), 149.60–120.77 (30C, aromatic), 84.03 (1C, C-1), 73.63–60.62 (5C, ring carbon). HRMS: m/z $[M+Na]^+$ calcd for $C_{40}H_{31}N_3O_{15}SNa$ is 848.1374, found 848.1349.

N-*(2,3,4,6-Tetra*-O-*benzoyl-β*-D-*mannopyranosyl)-2,4-dinitrobenzenesulfonamide (19)*

Yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.57–7.27 (m, 23H, aromatic), 6.85 (d, 1H, J = 9.6 Hz, NH), 5.98 (s, 1H, H-2), 5.94 (t, 1H, J = 10.2 Hz, H-4), 5.67 (t, 1H, J = 10.2 Hz, H-3), 5.53 (d, 1H, J = 10.2 Hz, H-1), 4.43 (d, 1H, J = 12.0 Hz, H-6), 4.08 (d, 1H, J = 8.4 Hz, H-5), 3.99 (d, 1H, J = 11.4 Hz, H-6′). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.57–165.31 (4C, carbonyl), 150.13–121.28 (30C, aromatic), 81.46 (1C, C-1), 74.10–61.21 (5C, ring carbon). HRMS: m/z $[M+Na]^+$ calcd for $C_{40}H_{31}N_3O_{15}SNa$ is 848.1374, found 848.1364.

N-*(2,3,4-Tri*-O-*benzoyl-β*-D-*arabinopyranosyl)-2,4-dinitrobenzenesulfonamide (20)*

Pale yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.40–7.25 (m, 18H, aromatic), 6.98 (s, 1H, NH), 5.72 (s, 1H, H-3), 5.71 (s, 1H, H-2), 5.68 (s, 1H, H-4), 5.10 (d, 1H, J = 6.6 Hz, H-1), 4.18 (d, 1H, J = 13.8 Hz, H-5), 3.95 (d, 1H, J = 13.8 Hz, H-5′). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.9–165.54 (3C, carbonyl), 149.7–120.85 (24C, aromatic), 84.34 (1C, C-1), 71.02–66.34 (4C, ring carbon). HRMS: m/z $[M+Na]^+$ calcd for $C_{32}H_{25}N_3O_{13}SNa$ is 714.1006, found 714.1006.

N-*(2,3,6,2′,3′,4′,6′-Hepta*-O-*benzoyl-β-maltosyl)-2,4-dinitrobenzenesulfonamide (21)*

Yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.37–7.17 (m, 38H, aromatic), 6.85 (s, 1H, NH), 6.06 (t, 1H, J = 10.2 Hz, H-3′), 5.86 (t, 1H, J = 9.3 Hz, H-3), 5.76 (d, 1H, J = 3.6 Hz, H-1'), 5.65 (t, 1H, J = 9.9 Hz, H-4′), 5.24 (d, 1H, J = 3.6 Hz, H-2′), 5.23 (d, 1H, J = 4.2 Hz, H-2), 5.19 (d, 1H, J = 6.6 Hz, H-1), 4.71 (d, 1H, J = 10.8 Hz, H-6_a), 4.49 (dd, 1H, J = 3.3 Hz, 12.3 Hz, H-6_b), 4.45 (dd, 1H, J = 3.0 Hz, 12.0 Hz, H-6′$_b$), 4.39 (m, 2H, H-5′, H-4), 4.27 (dd, 1H, J = 3.6 Hz, 12.0 Hz, H-6′$_a$), 4.07 (m, 1H, H-5). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.29–164.97 (7C, carbonyl), 149.77–120.82 (48C, aromatic), 96.76 (1C, C-1'), 83.43 (1C, C-1), 74.89–62.34 (10C, ring carbons). MALDI: m/z $[M+Na]^+$ calcd for $C_{67}H_{53}N_3O_{23}SNa$ is 1322.269, found 1322.237.

N-*(2,3,4,6-Tetra*-O-*benzoyl-β*-D-*galactopyranosyl) acetamide (23)*

Pale yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.08–7.23 (m, 20H, aromatic), 6.65 (d, 1H, $J = 8.4$ Hz, NH), 6.05 (m, 1H, H-4), 5.81 (dd, 1H, $J = 3.3$ Hz, 9.9 Hz, H-3), 5.65 (t, 1H, $J = 9.9$ Hz, H-2), 5.60 (t, 1H, $J = 9.0$ Hz, H-1), 4.63 (dd, 1H, $J = 6.6$ Hz, 10.8 Hz, H-6), 4.48 (t, 1H, $J = 13.2$ Hz, H-5), 4.39 (dd, 1H, $J =$ 6.9 Hz, 11.1 Hz, H-6′), 1.99 (s, 1H, -CH_3). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.59 (1C, amide carbonyl), 167.26–165.54 (4C, carbonyl), 134.10–128.50 (m, 24C, aromatic), 79.09 (1C, C-1), 73.12–62.07 (5C, ring carbon), 23.64 (1C, -CH_3). HRMS: m/z $[M+Na]^+$ calcd for $C_{36}H_{31}NO_{10}Na$ is 660.1846, found 660.1862.

N-*(2,3,4,6-Tetra*-O-*benzoyl-β*-D-*mannopyranosyl) acetamide (24)*

Pale yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.14–7.24 (m, 20H, aromatic), 6.42 (d, 1H, $J = 9.6$ Hz, NH), 6.08 (t, 1H, $J = 10.2$ Hz, H-4), 5.86 (d, 1H, $J = 9.6$ Hz, H-1), 5.85 (d, 1H, $J = 2.4$ Hz, H-2), 5.68 (dd, 1H, $J =$ 3.0 Hz, 10.2 Hz, H-3), 4.72 (dd, 1H, $J = 2.1$ Hz, 12.3 Hz, H-6′), 4.47 (dd, 1H, $J = 3.9$ Hz, 12.3 Hz, H-6), 4.26 (m, 1H, H-5), 1.99 (s, 1H, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.59 (1C, amide carbonyl), 166.27–165.46 (4C, carbonyl), 134.11–128.49 (m, 24C, aromatic), 76.59 (1C, C-1), 74.28–62.86 (5C, ring carbon), 23.54 (1C, $-CH_3$). HRMS: m/z $[M+Na]^+$ calcd for $C_{36}H_{31}NO_{10}Na$ is 660.1846, found 660.1829.

N-*(2,3,4-Tri*-O-*benzoyl-β*-D-*arabinopyranosyl) acetamide (25)*

Pale yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.09–7.26 (m, 15H, aromatic), 6.75 (d, 1H, $J = 9.6$ Hz, NH), 5.77 (d, 1H, $J = 3.6$ Hz, H-3), 5.75 (s, 1H, H-4), 5.68 (t, 1H, $J = 9.3$ Hz, H-2), 5.47 (t, 1H, $J = 9.0$ Hz, H-1), 4.27 (d, 1H, $J = 13.2$ Hz, H-$5_{equatorial}$), 4.05 (d, 1H, $J = 13.8$ Hz, H-5_{axial}), 1.98 (s, 1H, $-CH_3$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.76 (1C, amide carbonyl), 167.2–165.5 (3C, carbonyl), 134.01–128.51 (18C, aromatic), 79.38 (1C, C-1), 71.5–66.4 (4C, ring carbon), 23.7 (1C, -CH_3). HRMS: m/z $[M+Na]^+$ calcd for $C_{28}H_{25}NO_8Na$ is 526.1478, found 526.1495.

N-*(2,3,6,2′,3′,4′,6′-Hepta*-O-*benzoyl-β-maltosyl) acetamide (26)*

Yellow solid. ^{1}H NMR (600 MHz, $CDCl_3$): δ 8.10–7.18 (m, 35H, aromatic), 6.49 (d, 1H, $J = 9.0$ Hz, NH), 6.07 (t, 1H, $J = 10.2$ Hz, H-3′), 5.91 (t, 1H, $J =$ 9.3 Hz, H-3), 5.75 (d, 1H, $J = 3.0$ Hz, H-1'), 5.66 (t, 1H, $J = 9.6$ Hz, H-4′), 5.52 (t, 1H, $J = 9.3$ Hz, H-1), 5.25 (dd, 1H, $J = 3.0$ Hz, 10.2 Hz, H-2′), 5.18 (t, 1H, $J = 9.6$ Hz, H-2), 4.88 (d, 1H, $J = 12.0$ Hz, H-6_a), 4.75 (d, 1H, $J =$ 9.6 Hz, H-6_b), 4.50 (t, 1H, $J = 9.3$ Hz, H-4), 4.38 (m, 2H, H-5′, H-6′$_b$), 4.20 (m, 2H, H-5, H-6′$_a$). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.54–164.95 (7C, carbonyl), 133.96–128.23 (42C, aromatic), 96.51 (1C, C-1'), 78.48 (1C, C-1), 75.09–62.53 (10C, ring carbon). MALDI: m/z $[M+Na]^+$ calcd for $C_{63}H_{53}NO_{18}$ is 1111.33, found 1134.305.

ACKNOWLEDGMENTS

This work was supported in part by a grant to SJS by the National Institutes of Health (GM094734).

REFERENCES

1. (a) Pleuss, N.; Kunz, H. N-glycosyl amides: Removal of the anomeric protecting group and conversion into glycosyl donors. *Angew. Chem. Int. Ed.* **2003**, *42*, 3174–3176. (b) Pleuss, N.; Kunz, H. N-glycosyl amides as glycosyl donors in stereoselective glycosylation reactions. *Synthesis* **2005**, 122–130.

2. Cohen-Anisfeld, S.T.; Lansbury, P.T. A practical, convergent method for glycopeptide synthesis. *J. Am. Chem. Soc.* **1993**, *115*, 10531–10537.

3. Likhosherstov, L.; Novikova, O.; Derevitskaya, V.A.; Kochetkov, N.K. A new simple synthesis of amino sugar β-D-glycosylamines. *Carbohydr. Res.* **1986**, *146*, C1–C5.

4. Wen, S.; Guo, Z. Unprotected oligosaccharides as phase tags: Solution-phase synthesis of glycopeptides with solid-phase workups. *Org. Lett.* **2001**, *3*, 3773–3776.

5. Real-Fernández, F.; Nuti, F.; Bonache, M.A.; Boccalini, M.; Chimichi, S.; Chelli, M.; Papini, A.M. Microwave-assisted reaction of glycosylamine with aspartic acid. *Amino Acids* **2010**, *39*, 599–604.

6. Danishefsky, S.J.; Hu, S.; Cirillo, P.F.; Eckhardt, M.; Seeberger, P.H. A highly convergent total synthetic route to glycopeptides carrying a high-mannose core pentasaccharide domain N-linked to a natural peptide motif. *Chem. Eur. J.* **1997**, *3*, 1617–1628.

7. Amadori, M. Products of condensation between glucose and *p*-phenetidine. I. *Atti Accad. Nazl. Lincei* **1925**, *2*, 337–342.

8. Bejugam, M.; Flitsch, S.L. An efficient synthetic route to glycoamino acid building blocks for glycopeptide synthesis. *Org. Lett.* **2004**, *6*, 4001–4004.

9. Vetter, D.; Gallop, M.A. Strategies for the synthesis and screening of glycoconjugates. 1. A library of glycosylamines. *Bioconjugate Chem.* **1995**, *6*, 316–318.

10. He, Y.; Hinklin, R.J.; Chang, J.; Kiessling, L.L. Stereoselective N-Glycosylation by Staudinger Ligation. *Org. Lett.* **2004**, *6*, 4479–4482.

11. (a) Inazu, T.; Kobayashi, K. A new simple method for the synthesis of N^{α}-Fmoc-N^{β}-glycosylated-L-asparagine derivatives. *Synlett*, **1993**, 869–870. (b) Bianchi, A.; Russo, A.; Bernardi, A. Neo-glycoconjugates: stereoselective synthesis of α-glycosyl amides via Staudinger Ligation reactions. *Tetrahedron Asymm.* **2005**, *16*, 381–386. (c) Saxon, E.; Armstrong, J.I.; Bertozzi, C.R. A "Traceless" Staudinger Ligation for the chemoselective synthesis of amide bonds. *Org. Lett.*, **2000**, *2*, 2141–2143. (d) Saxon, E.; Bertozzi, C.R. Cell surface engineering by a modified Staudinger reaction. *Science*, **2000**, *287*, 2007–2010.

12. Kovács, L.; Ösz, E.; Domokos, V.; Holzer, W.; Györgydeák, Z. An easy access to anomeric glycosyl amides and imines (Schiff bases) via transformation of glycopyranosyl trimethylphosphinimides. *Tetrahedron*, **2001**, *57*, 4609–4621.

13. Schierholt, A.; Shaikh, H.A.; Schmidt-Lassen, J.; Lindhorst, T.K. Utilizing Staudinger Ligation for the synthesis of glycoamino acid building blocks and other glycomimetics. *Eur. J. Org. Chem.* **2009**, 3783–3789.

14. (a) Nisic, F.; Bernardi, A. Stereoselective synthesis of N-galactofuranosyl amides. *Carbohydr. Res.* **2011**, *346*, 465–471. (b) Bianchi, A.; Bernardi, A. Traceless Staudinger

Ligation of glycosyl azides with triaryl phosphines: Stereoselective synthesis of glycosyl amides. *J. Org. Chem.* **2006**, *71*, 4565–4577.

15. Shangguan, N.; Katukojvala, S.; Greenberg, R.; Williams, L.J. The reaction of thio acids with azides: A new mechanism and new synthetic applications. *J. Am. Chem. Soc.* **2003**, *125*, 7754–7755.

16. Song, X.; Hollingsworth, R.I. A stereoselective synthesis of N-β-D-glycosyl amides by a Ritter-type reaction. *Synlett* **2006**, 3451–3454.

17. Li, X.; Danishefsky, S.J. New chemistry with old functional Groups: On the reaction of isonitriles with carboxylic acids - A route to various amide types. *J. Am. Chem. Soc.* **2008**, *130*, 5446–5448.

18. Fukuyama, T.; Jow, C.K.; Cheung, M. 2- and 4-nitrobenzenesulfonamides: Exceptionally versatile means for preparation of secondary amines and protection of amines. *Tetrahedron Lett.* **1995**, *36*, 6373–6376.

19. Fukuyama, T.; Cheung, M.; Jow, C.K.; Hidai, Y.; Kan, T. 2,4-Dinitrobenzenesulfonamides: A simple and practical method for the preparation of a variety of secondary amines and diamines. *Tetrahedron Lett*. **1997**, *38*, 5831–5834.

20. Messeri, T.; Sternbach, D.D.; Tomkinson, N.C.O. A novel deprotection/functionalization sequence using 2,4-dinitrobenzenesulfonamide: Part 1. *Tetrahedron Lett*. **1998**, *39*, 1669–1672.

21. Messeri, T.; Sternbach, D.D.; Tomkinson, N.C.O. A novel deprotection/functionalization sequence using 2,4-dinitrobenzenesulfonamide. Part 2. *Tetrahedron Lett*. **1998**, *39*, 1673–1676.

22. Crich, D.; Sana, K.; Guo, S. Amino acid and peptide synthesis and functionalization by the reaction of thioacids with 2,4-dinitrobenzenesulfonamides. *Org. Lett.* **2007**, *9*, 4423–4426.

23. Crich, D.; Sharma, I. Triblock peptide and peptide thioester synthesis with reactivity-differentiated sulfonamides and peptidyl thioacids. *Angew. Chem. Int. Ed.* **2009**, *48*, 7591–7594.

24. Karmakar, P.; Talan, R.S.; Sucheck, S.-J. Mixed-phase synthesis of glycopeptides using a *N*-peptidyl-2,4-dinitrobenzenesulfonamide-thioacid ligation strategy. *Org. Lett.* **2011**, *13*, 5298–5301.

25. Crich, D.; Bowers, A.A. Cyclic thioanhydrides: linchpins for multicomponent coupling reactions based on the reaction of thioacids with electron-deficient sulfonamides and azides. *Org. Lett.* **2007**, *9*, 5323–5325.

26. Talan, R.S.; Sanki, A.K.; Sucheck, S.J. Facile synthesis of *N*-glycosyl amides using a *N*-glycosyl-2,4-dinitrobenzenesulfonamide and thioacids. *Carbohydr. Res.* **2009**, *344*, 2048–2050.

27. Kumar, R.; Maulik, P.R.; Misra, A.K. Significant rate accelerated synthesis of glycosyl azides and glycosyl 1,2,3-triazole conjugates. *Glycoconjugate J.* **2008**, *25*, 595–602.

28. Garegg, P.J. Thioglycosides as glycosyl donors in oligosaccharide synthesis. *Adv. Carbohydr. Chem. Biochem.*, **1997**, *52*, 179–205.

29. Hansen, S.G.; Skrydstrup, T. Studies directed to the synthesis of oligochitosans - preparation of building blocks and their evaluation in glycosylation studies. *Eur. J. Org. Chem.* **2007**, 3392–3401.

30. (a) Crich, D.; Smith, M. 1-Benzenesulfinyl piperidine/trifluoromethanesulfonic anhydride: a potent combination of shelf-stable reagents for the low-temperature conversion of thioglycosides to glycosyl triflates and for the formation of diverse glycosidic

linkages. *J. Am. Chem. Soc.* **2001**, *123*, 9015–9020. (b) Ren, C.T.; Tsai, Y.H.; Yang, Y.L.; Zou, W.; Wu, S.H. Synthesis of a tetrasaccharide glycosyl glycerol precursor to glycolipids of *Meiothermus taiwanensis* ATCC BAA-400. *J. Org. Chem.* **2007**, *72*, 5427–5430.

31. Zhang, Z.; Ollmann, I.R.; Ye, X.-S.; Wischnat, R.; Wong, C.-H. Programmable one-pot oligosaccharide synthesis. *J. Am. Chem. Soc.* **1999**, *121*, 734–753.

32. Heuckendorff, M.; Pedersen, C.M.; Bols, M. Quantifying electronic effects of common carbohydrate protecting groups in a piperidine model system. *Chem. Eur. J.* **2010**, *16*, 13982–13994.

33. Fazio, F.; Wong, C.-H. $RuCl_3$-promoted amide formation from azides and thioacids. *Tetrahedron Lett.* **2003**, *44*, 9083–9085.

34. Isac-García, J.; Calvo-Flores, F.G.; Hernández-Mateo, F.; Santoyo-González, F. Synthesis of glycosylamines from glycosyl isothiocyanates and bis(tributyltin) oxide. *Eur. J. Org. Chem.* **2001**, 383–390.

35. (a) Wang, Q.; Fu, J.; Zhang, J. A facile preparation of peracylated α-aldopyranosyl chlorides with thionyl chloride and tin tetrachloride. *Carbohydr. Res.* **2008**, *343*, 2989–2991. (b) Slamova, K.; Marhol, P.; Bezouska, K.; Lindkvist, L.; Hansen, S.G.; Kren, V.; Jensen, H.H. Synthesis and biological activity of glycosyl-1*H*-1,2,3-triazoles. *Bioorg. Med. Chem. Lett.* **2010**, *20*, 4263–4265.

36. Li, C.; Arasappan, A.; Fuchs, P.L. Tetramethylguanidinium azide as a new reagent for the stereoselective synthesis of glycosyl azides. *Tetrahedron Lett.* **1993**, *34*, 3535–3538.

37. Watt, J.A.; Gannon, C.T.; Loft, K.J.; Dinev, Z.; Williams, S.J. 'Click' preparation of carbohydrate 1-benzotriazoles, 1,4-disubstituted, and 1,4,5-trisubstituted triazoles and their utility as glycosyl donors. *Aust. J. Chem.* **2008**, *61*, 837–846.

38. Sureshbabu, V.V.; Venkataramanarao, R.; Hemantha, H. A facile synthesis of C-terminal neoglycopeptides: incorporation of urea moiety between sugars and peptides employing Curtius rearrangement. *Int. J. Pept. Res. Ther.* **2008**, *14*, 34–40.