EurJOC
European Journal of Organic Chemistry

A Journal of ChemPubSoc Europe

Accepted Article

Title: Investigation of Glycosyl Nitrates as Building Blocks for Chemical Glycosylation

Authors: Tinghua Wang, Yashapal Singh, Keith Stine, and Alexei V. Demchenko

To be cited as: *Eur. J. Org. Chem.* 10.1002/ejoc.201801272

Link to VoR: http://dx.doi.org/10.1002/ejoc.201801272

Supported by
ACES Asian Chemical Editorial Society

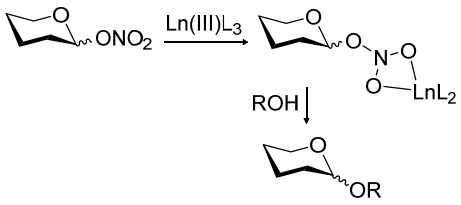
WILEY-VCH

Investigation of Glycosyl Nitrates as Building Blocks for Chemical Glycosylation

Tinghua Wang, Yashapal Singh, Keith J. Stine, and Alexei V. Demchenko*

Abstract

Glycosyl nitrates are important synthetic intermediates in the synthesis of 2-aminosugars, 1,2-orthoesters or, more recently, 2-OH glucose. However, glycosyl nitrates have never been glycosidated. Presented herein is our first attempt to use glycosyl nitrates as glycosyl donors for O-glycosylation. Lanthanide triflates showed good affinity to activate the nitrate leaving group.



Keywords: glycosylation, leaving group, nitrate, oligosaccharides, activation

Key Topic: Glycosylation or Carbohydrates

Address: Tinghua Wang, Dr. Yashapal Singh, Prof. Keith J. Stine, and Prof. Alexei V. Demchenko*

Department of Chemistry and Biochemistry, University of Missouri – St. Louis

One University Boulevard, St. Louis, Missouri 63121, USA

e-mail: demchenkoa@umsl.edu

www: http://www.umsl.edu/chemistry/Faculty/demchenko.html

Introduction

With recent advances in the area of glycomics,[1-9] we now know that half of the proteins in the human body are glycosylated[10] and cells present a multitude of glycostructures.[11] Glycan and glycoconjugate biomarkers are present in all body fluids, able to transmit a plethora of biological information, and hence offer fantastic opportunities for diagnostics. Changes in the level and distribution of glycans as well as changes in glycosylation and branching patterns can indicate presence and progression of a disease.[12-19] With improved understanding of the functions of carbohydrates the demand for the development of new glycosylation reactions that will offer new capabilities for obtaining complex glycan biomarkers has increased.

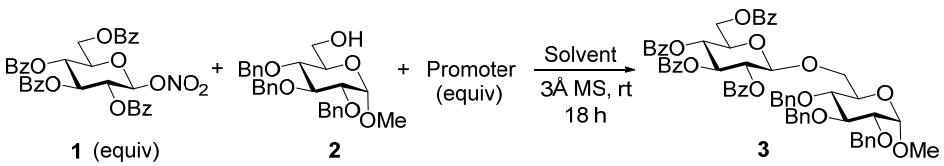
Recently we reported the synthesis of 1,3,4,6-tetra-*O*-acetyl-α-D-glucopyranose (2-OH glucose) wherein glycosyl nitrates were found to be the key intermediates.[20] Glycosyl nitrates have been known for years, but their application was limited to their use as precursors for other leaving groups after azidonitration reaction of glycals.[21-22] Another, less known application, is the synthesis of 1,2-orthoesters.[23] However, glycosyl nitrates have never been glycosidated beyond the synthesis of aliphatic glycosides of aminosugars with charged nucleophiles[24-25] or under microwave irradiation conditions.[22] The ability to form 2-OH glucose from glycosyl nitrates without additional reagents implies that the anomeric nitro group can act as a suitable leaving group in glycosylation. Reported herein is our first attempt to study glycosyl nitrates as glycosyl donors in chemical glycosylation reactions with a variety of sugar alcohols as glycosyl acceptors.

Results and Discussion

A preliminary series of experiments involved reactions promoted with different Lewis acids, common in many glycosylation reactions with reactive donors. However, reactions in the presence of $FeCl_3$, $ZrCl_4$, $SnCl_4$ or TMSOTf were sluggish, and some resulted in the preferential formation of the corresponding 1,2-orthoester side product albeit in moderate yields. See the supporting information (SI) for further details on preliminary screening of promoters. A preliminary set of experiments with heavy metal triflates was far more successful. Whereas AgOTf and $Cu(OTf)_2$ still led to the formation of substantial amounts of the 1,2-orthoester along with some glycoside, $Bi(OTf)_3$ and $Ba(OTf)_2$ provided the highest conversion rates and yields of the desired *O*-glycoside product. Thus, when benzoylated glucosyl nitrate **1**[20] and primary acceptor **2**[26] were coupled in the presence of sub-stoichiometric $Bi(OTf)_3$ (0.5 equiv) in acetonitrile, disaccharide **3** was obtained in 32% yield, albeit without any detectable 1,2-orthoester by-product formation (entry 1, Table 1). When excess $Bi(OTf)_3$ (1.1 or 1.5 equiv) was used, the yield of disaccharide **3** increased to 38% and 45% (entries 2 and 3, respectively). However, the formation of the product was accompanied by the formation of the nitrate-transfer by-product, methyl 2,3,4-tri-*O*-benzyl-6-*O*-nitro-α-D-glucopyranoside (see the SI for details). In reactions between donor **1** and acceptor **2** in presence of $Ba(OTf)_2$ (1.1 or 1.5 equiv) in CH_3CN disaccharide **3** was obtained in 65% and 63% yield (entries 4 and 5). However, the corresponding 1,2-orthoester was also formed as the side product (see the SI for details). We have also investigated 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl nitrate[20] as glycosyl donor. These glycosylations, however, were much less efficient due to a number of side reactions leading to the predominance of the donor-acceptor acetyl transfer products (no data shown).

10.1002/ejoc.201801272

Table 1. The establishment and optimization of reaction conditions for the glycosidation of per-benzoylated glucosyl donor **1** with glycosyl acceptor **2**

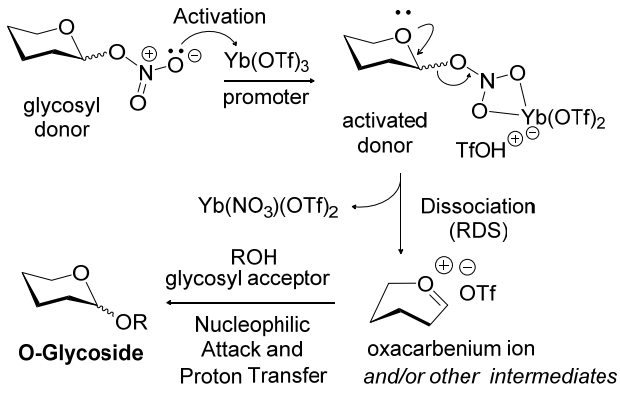


Entry	Equiv of 1	Promoter (equiv)	Solvent	Yield of 3
1	1.1	$Bi(OTf)_3$ (0.5)	CH_3CN	32%
2	1.1	$Bi(OTf)_3$ (1.1)	CH_3CN	38%[a]
3	1.1	$Bi(OTf)_3$ (1.5)	CH_3CN	45%[a]
4	1.1	$Ba(OTf)_2$ (1.1)	CH_3CN	65%[b]
5	1.1	$Ba(OTf)_2$ (1.5)	CH_3CN	63%[b]
6	1.1	$Yb(OTf)_3$ (1.1)	CH_3CN	57%
7	1.1	$Yb(OTf)_3$ (1.5)	CH_3CN	62%
8	1.1	$Yb(OTf)_3$ (1.1)	Et_2O	74%
9	1.1	$Yb(OTf)_3$ (1.5)	Et_2O	78%
10	1.2	$Yb(OTf)_3$ (1.5)	Et_2O	85%
11	1.2	$Yb(OTf)_3$ (1.5)	CH_3CN	63%
12	1.2	$Yb(OTf)_3$ (1.5)	CH_2Cl_2	55%
13	1.2	$Yb(OTf)_3$ (1.5)	1,2-DCE	53%
14	1.5	$Yb(OTf)_3$ (1.5)	Et_2O	91%
15	1.2	$Yb(OTf)_3$ (1.5)	Et_2O/CH_2Cl_2, 4/1, v/v	76%
16	1.2	$Yb(OTf)_3$ (1.5)	Et_2O/CH_2Cl_2, 1/1, v/v	83%
17	1.2	$Yb(OTf)_3$ (1.5)	Et_2O/CH_2Cl_2, 1/4, v/v	75%
18	1.2	$Yb(OTf)_3$ (1.5)	Et_2O/1,2-DCE, 5/1, v/v	78%
19	1.2	$Yb(OTf)_3$ (1.5)	Et_2O/1,2-DCE, 1/1, v/v	88%
20	1.2	$Yb(OTf)_3$ (1.5)	Et_2O/1,2-DCE, 1/5, v/v	79%
21	1.2	$Er(OTf)_3$ (1.5)	Et_2O/1,2-DCE, 1/1, v/v	77%
22	1.2	$Gd(OTf)_3$ (1.5)	Et_2O/1,2-DCE, 1/1, v/v	76%
23	1.2	$Sm(OTf)_3$ (1.5)	Et_2O/1,2-DCE, 1/1, v/v	61%
24	1.2	$Ce(OTf)_3$ (1.5)	Et_2O/1,2-DCE, 1/1, v/v	60%

[a] Methyl 2,3,4-tri-*O*-benzyl-6-*O*-nitro-α-D-glucopyranoside by-product was also formed.
[b] The corresponding 1,2-orthoester byproduct was also formed.

Having established that glycosyl nitrates can indeed serve as potential glycosyl donors for *O*-glycosylation, we were still somewhat disappointed by the conversion yields and the formation of a number of by-products. In order to address these issues, we turned the attention to investigating lanthanide(III) triflates that are known to act as nitrate capture reagents.[27-28] We assumed that the application of lanthanides would be beneficial for our reaction in order to prevent the nitrate-transfer products observed in some preliminary experiments. The glycosylation reaction typically begins by the formation of the activated donor-promoter complex as a result of the interaction of the leaving group and the promoter. In the presence of the lanthanide ions the nitrate leaving group will be activated via the formation of a stable bi-dentate complex as shown in Scheme 1.[29] This anticipated pathway differentiates the glycosyl nitrate leaving group from other leaving groups wherein the activation takes place in a monodentate manner.[30]

Scheme 1. Proposed mechanism of the nitrate activation with lanthanides



Upon the subsequent dissociation of the glycosyl donor, and expulsion of the activated leaving group in the rate-determining step (RDS), oxacarbenium ion is typically formed. Other intermediates may also form at this stage with or without a counter-anion or the reaction solvent involvement. As a consequence of the sp^2-hybridization of the anomeric carbon the subsequent

glycosyl acceptor (ROH) is possible either from the bottom or the top face of the ring leading to the formation of a mixture of diastereomers. Reactions with glycosyl donors equipped with the neighboring participating acyl groups are typically 1,2-*trans*-selective due to the intermediacy of the acyloxonium ion. Once the proton transfer occurs, the formation of the glycosidic bond is irreversible (the termination step).[31]

Lanthanide ions with higher charge-to-size ratio, such as Yb(III), are expected to bind the nitrate group more strongly than those with smaller ratios. Hence, we selected $Yb(OTf)_3$ as the promoter for the subsequent study. To our delight, a clean reaction between nitrate donor **1** and acceptor **2** in presence of $Yb(OTf)_3$ (1.1 or 1.5 equiv) was observed, and no side products were detected. However, the reaction was still fairly sluggish and disaccharide **3** was obtained in 57% and 62% yield in 18 h (entry 6 and 7, respectively). Nevertheless, we felt that this result was sufficient to begin further investigations in order to refine the reaction conditions. The next step to improve the reaction rate and enhance the yield of the glycosylation reaction was to investigate different solvents in $Yb(OTf)_3$-promoted reactions. The yield of disaccharide **3** was increased to 74% when glycosylation reaction between donor **1** and acceptor **2** was performed in the presence of $Yb(OTf)_3$ (1.1 equiv) in diethyl ether as the solvent (entry 8). Increasing the amount of the promoter to 1.5 equiv led to a further increase in the yield of disaccharide **3** (78%, entry 9).

At this stage we switched to investigating the amount of the glycosyl donor on the outcome of this reaction. The use of donor **1** in a higher excess, 1.2 equiv vs. previously used 1.1 equiv, led to an increase in the yield of disaccharide **3** to a very respectable 85% (entry 10). The solvent effect should be particularly noted in these reactions because reactions performed in CH_3CN, CH_2Cl_2 or $ClCH_2CH_2Cl$ (1,2-DCE) afforded disaccharide **3** in much lower yields of

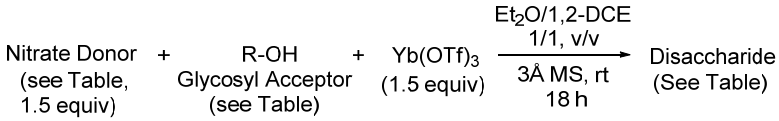
63%, 55% or 53%, respectively (entries 11-13). When the amount of donor **1** was further increased to 1.5 equiv, the reaction in the presence of $Yb(OTf)_3$ (1.5 equiv) afforded disaccharide **3** in an excellent yield of 91% (entry 13). However, we felt that this increase was not sufficiently substantial to justify the use of such a large excess of the donor.

Although the best result was achieved in Et_2O as the reaction solvent, the use of ethereal solvents in general is not ideal for glycosylation reactions due to moderate solubility of many sugar building blocks. Considering the excellent solubility of protected carbohydrates in halogenated hydrocarbons, and the fact that the yields of **3** in neat CH_2Cl_2 or 1,2-DCE were only moderate (53-55%) vs. the reaction in neat ether (85%, entry 10) we next endeavored studying Et_2O in combination with CH_2Cl_2 or 1,2-DCE as reaction solvents. Using Et_2O/CH_2Cl_2 as the reaction solvent in different ratios (entries 15-17) brought us to the realization that the best yield of disaccharide **3** (83%, entry 16) can be achieved in Et_2O/CH_2Cl_2, 1/1, v/v). Similarly, using Et_2O/1,2-DCE as the reaction solvent in different ratios (entries 18-20) allowed us to achieve the best yield of disaccharide **3** (88%, entry 19) in Et_2O/1,2-DCE, 1/1, v/v). A series of other lanthanide (III) triflates were screened and while $Er(OTf)_3$ and $Gd(OTf)_3$ were found to have comparable activity to that of $Yb(OTf)_3$, $Sm(OTf)_3$ and $Ce(OTf)_3$ were found to be somewhat less reactive (entries 21-24).

In a further attempt to enhance the yield of glycosylation reactions, we performed the reaction using a large excess of donor **1** (1.5 equiv.) using the optimized solvent Et_2O/1,2-DCE (1/1, v/v). As a result, disaccharide **3** was obtained in 80% yield (Table 2, entry 1). A very similar outcome (18 h, 81%) was achieved when the electronically deactivated methyl 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside was used as the glycosyl acceptor. Although the use of donor excess was unnecessary for glycosylation of primary acceptor **2**, in further experiments with the

secondary acceptors and other less reactive series of glycosyl nitrates (*vide infra*) the donor excess (1.5 equiv) was found beneficial for obtaining practical yields. With the optimized reaction conditions, per-benzoylated glycosyl donors of the D-gluco, D-manno and D-galacto series were then investigated with both primary and secondary glycosyl acceptors. The glycosylation reaction between donor **1** and secondary 2-OH acceptor **4**[26] produced disaccharide **5** in 88% yield (entry 2). When 3-OH acceptor **6**[26] was glycosylated with donor **1**, disaccharide **7** was obtained in 94% yield (entry 3). 4-OH acceptor **8**[26] is less reactive than other secondary acceptors tested herein, and this was reflected in a lower yield of disaccharide **9** (67%, entry 4).

Table 2. Glycosidation of per-benzoylated glycosyl donors of the D-gluco, D-manno and D-galacto series with various glycosyl acceptors



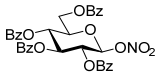
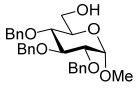
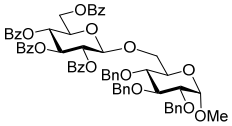
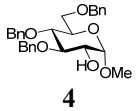
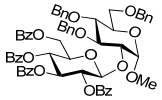
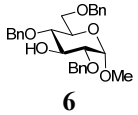
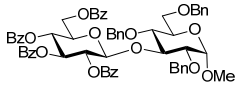
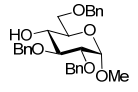
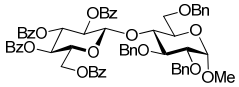
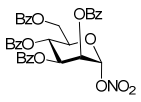
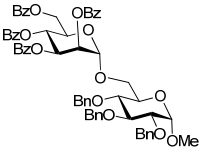
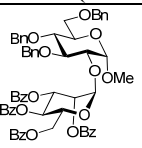
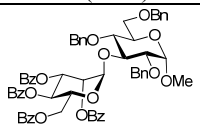
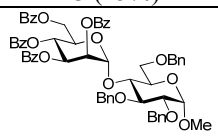
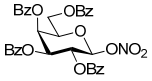
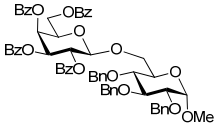
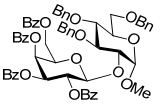
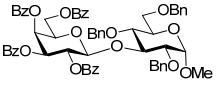
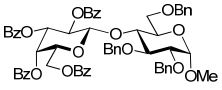
Entry	Donor	Acceptor	Product (Yield)
1	 **1**	 **2**	 **3** (80%)
2	**1**	 **4**	 **5** (88%)
3	**1**	 **6**	 **7** (94%)
4	**1**	 **8**	 **9** (67%)
5	 **10**	**2**	 **11** (71%)

Table 2 (contd). Glycosidation of per-benzoylated glycosyl donors of the D-gluco, D-manno and D-galacto series with various glycosyl acceptors

Entry	Donor	Acceptor	Product (Yield)
6	**10**	**4**	 **12** (43%)
7	**10**	**6**	 **13** (25%)
8	**10**	**8**	 **14** (12%)
9	 **15**	**2**	 **16** (79%)
10	**15**	**4**	 **17** (79%)
11	**15**	**6**	 **18** (72%)
12	**15**	**8**	 **19** (71%)

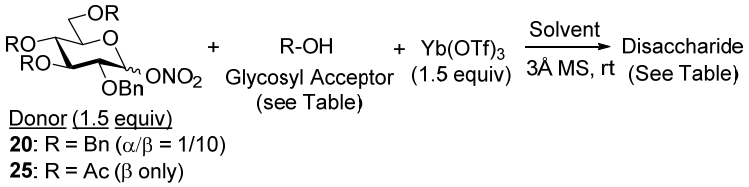
We then turned our attention to studying per-benzoylated mannosyl nitrate **10** that was found to be fairly unreactive. Although a good yield for disaccharide **11** was achieved for the reaction of donor **10** with the primary 6-OH acceptor **2** (71%, entry 5), reactions with the secondary acceptors gave yields that were below a practical value. Thus, disaccharides **12**-**14** were obtained in modest yields of 12-43% that were in line with the relative reactivity of glycosyl acceptors (entries 6-8). In contrast, per-benzoylated galactosyl nitrate **15** was sufficently reactive, similar to that of glucosyl nitrate **1**. This was translated to good yields (71-79%) of

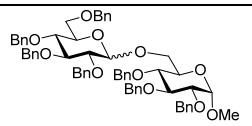
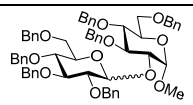
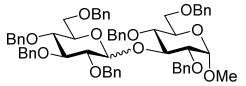
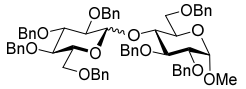
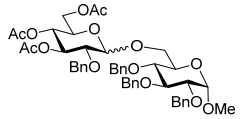
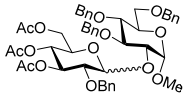
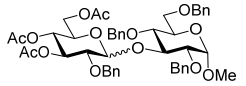
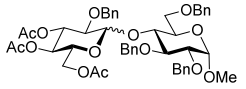
disaccharides **16-19** irrespectively of the nature of the glycosyl acceptor used (entries 9-12).

Based on successful attempts with per-benzoylated glycosyl nitrate donors we endeavored to investigate glycosyl donors with a non-participating benzyl group at C-2. Glycosidations of per-benzylated (armed) glucosyl nitrate **20** proceeded much more rapidly than those with per-benzoylated (disarmed) nitrate **1**. Thus, glycosylation reaction between donor **20** and 6-OH acceptor **2** in acetonitrile smoothly produced disaccaride **21** in 96% yield within 1 h (Table 3, entry 1). The use of acetonitrile as the solvent favored the formation of the β-isomer of **21** (α/β = 1/3.7). When diethyl ether was used as the solvent instead, a nearly quantitave yield (99% yield, entry 2) was acheived in 3 h. The stereoselectivity was inverted toward the preferential formation of the α-linked disaccharide **21** (α/β = 1.6/1). Also glycosylation in Et_2O/1,2-DCE (1/1, v/v) was slightly α-selective (85%, α/β = 1.3/1, entry 3). These results follow the general trend of known solvent effects on the stereoselectivity of glycosylation reactions.[32]

Although glycosidation of donor **20** with secondary acceptors **4**, **6** and **8** requred longer reaction time (18 h), disaccharides **22-24** were produced in excellent yields of 90-96% albeit with low selectivity (entries 4-6). We also investigated glycosidation of nitrate **25** equipped with the superdisarming, 3,4,6-tri-*O*-acetyl-2-*O*-benzyl protecting group pattern.[33] All reactions with this donor were slower, which was also reflected in a higher stereocontrol albeit lower yields ranging from 68% (α/β = 2.3/1) for reactive primary acceptor **2** to 36% (α/β > 20/1) for the least reactive 4-OH acceptor **8**. The results of these reactions, the synthesis of disaccharides **26-29** are summarized in entries 7-11. We note that the yield of these glycosylations can be improved by performing the reactions at elevated temperatures (see the footnote for Table 3).

Table 3. Glycosidation of donors **20** and **25** with a non-participating benzyl group at C-2 with various glycosyl acceptors in different solvents



Entry	Donor	Acceptor	Solvent (time)	Product (yield, ratio α/β)
1	**20**	**2**	CH_3CN (1 h)	 **21** (96%, α/β = 1/3.7)
2	**20**	**2**	Et_2O (3 h)	**21** (99%, α/β = 1.6/1)
3	**20**	**2**	Et_2O/1,2-DCE, 1/1, v/v (4 h)	**21** (85%, α/β = 1.3/1)
4	**20**	**4**	Et_2O/1,2-DCE, 1/1, v/v (18 h)	 **22** (96%, α/β = 1.1/1)
5	**20**	**6**	Et_2O/1,2-DCE, 1/1, v/v (18 h)	 **23** (94%, α/β = 1.1/1)
6	**20**	**8**	Et_2O/1,2-DCE, 1/1, v/v (18 h)	 **24** (90%, α/β = 1.3/1)
7	**25**	**2**	CH_3CN (18 h)[a]	 **26** (44%, α/β = 1/3.1)
8	**25**	**2**	Et_2O/1,2-DCE, 1/1, v/v (18 h)	**26** (68%, α/β = 2.3/1)
9	**25**	**4**	Et_2O/1,2-DCE, 1/1, v/v (18 h)	 **27** (37%, α/β = 5.6/1)
10	**25**	**6**	Et_2O/1,2-DCE, 1/1, v/v (18 h)	 **28** (40%, α/β = 4.3/1)
11	**25**	**8**	Et_2O/1,2-DCE, 1/1, v/v (18 h)	 **29** (36%, α/β > 20/1)

[a] The yield was increased to 60% when the reaction was performed at 50 °C.

Conclusions

Presented herein is our first attempt to employ glycosyl nitrates as donors in *O*-glycosylation reactions. Lanthanide ions with higher charge-to-size ratios showed good affinity to bind the nitrate leaving group. High reaction yields were achieved with per-benzylated and per-benzoylated donors of the D-glucose and D-galactose series with both primary and secondary glycosyl acceptors in various solvents. On the other hand, 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-protected glucosyl nitrate and per-benzoylated D-mannosyl nitrate were found to be much less reactive, which resulted in fair yields in reactions with secondary acceptors. The latter results imply that further investigations of more reactive promoters maybe of interest.

Experimental

General. The reactions were performed using commercial reagents and the ACS grade solvents used for reactions were purified and dried in accordance with standard procedures. Column chromatography was performed on silica gel 60 (70-230 mesh), reactions were monitored by TLC on Kieselgel 60 F_{254}. The compounds were detected by examination under UV light and by charring with 10% sulfuric acid in methanol. Solvents were removed under reduced pressure at <40 °C. CH_2Cl_2 and 1,2-dichloromethane (1,2-DCE) were distilled from CaH_2, and Et_2O was distilled from Na directly prior to application. Molecular sieves (3 Å), used for reactions, were crushed and activated in vacuo at 390 °C for 8 h in the first instance and then for 2-3 h at 390 °C directly prior to application. Optical rotations were measured using a 'Jasco P-1020' polarimeter. ^{1}H NMR spectra were recorded at 300 MHz, ^{13}C NMR spectra were recorded at 75 MHz. The ^{1}H NMR chemical shifts are referenced to tetramethylsilane (TMS, δ_H = 0 ppm) for ^{1}H NMR spectra for solutions in $CDCl_3$. The ^{13}C NMR chemical shifts are referenced to the central signal

of $CDCl_3$ (δ_C = 77.16 ppm) for solutions in $CDCl_3$. Mass analysis was performed using an Agilent 6230 ESI TOF LC/MS mass spectrometer.

Synthesis of glycosyl nitrate donors

2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl nitrate (1) was obtained from 2,3,4,6-tetra-*O*-benzoyl-α-D-glucopyranosyl bromide[34] as described previously.[20]

2,3,4,6-Tetra-*O*-benzoyl-α-D-mannopyranosyl nitrate (10). $AgNO_3$ was added to a solution of 2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl bromide[35] (5.85 g, 8.87 mmol) in dry acetonitrile (15 mL) and the resulting mixture was stirred for 5 min at rt. After that, the solids were filtered off through a pad of Celite and the filtrate was concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (~500 mL) and washed with water (100 mL), 1% aq. NaOH (100 mL), and water (3 × 100 mL). The organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo*. The residue was purified by column chromatography on silica gel (ethyl acetate–hexane gradient elution) to afford the title compound (4.05 g, 71% yield) as a white amorphous solid. Analytical data for **10**: R_f = 0.48 (ethyl acetate/hexanes, 3/7, v/v); $[\alpha]_D^{22}$ -31.8 (c = 1, $CHCl_3$); ^{1}H-n.m.r. (300 MHz): δ, 4.50 (dd, 1H, $J_{6a,6b}$ = 12.3 Hz, H-6a), 4.60 (dt, 1H, $J_{5,6a}$ = 3.8 Hz, $J_{5,6b}$ = 2.5 Hz, H-5), 4.72 (d, 1H, H-6b), 5.78 (dd, 1H, $J_{3,4}$ = 10.0, H-3), 5.84 (dd, 1H, $J_{2,3}$ = 3.4 Hz, H-2), 6.24 (dd, 1H, $J_{4,5}$ = 12.7 Hz, H-4), 6.49 (d, 1H, $J_{1,2}$ = 1.9 Hz, H-1), 7.22-7.69 (m, 12H, aromatic), 7.85 (d, J = 7.1 Hz, 2H, aromatic), 7.96 (d, J = 7.1 Hz, 2H, aromatic), 8.07 (t, J = 7.9 Hz, 4H, aromatic) ppm; ^{13}C-n.m.r. (75 MHz): δ, 62.1, 65.7, 67.8, 69.6, 71.5, 96.5, 128.5 (×2), 128.6 (×7), 128.8 (×2), 129.8, 129.8 (×2), 129.9 (×2), 129.9 (×2), 130.0 (×2), 133.3, 133.6, 133.8, 134.0, 165.1, 165.3, 165.4, 166.0 ppm; HR-ESI MS $[M+Na]^+$ calcd for $C_{34}H_{27}NO_{12}Na$

calcd: 664.1431, found 664.1424.

2,3,4,6-Tetra-*O*-benzoyl-β-D-galactopyranosyl nitrate (15). $AgNO_3$ was added to a solution of 2,3,4,6-tetra-*O*-benzoyl-α-D-galactopyranosyl bromide[36] (2.79 g, 4.23 mmol) in dry acetonitrile (15 mL) and the resulting mixture was stirred for 5 min at rt. After that, the solids were filtered off through a pad of Celite and the filtrate was concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (~250 mL) and washed with water (50 mL), 1% aq. NaOH (50 mL), and water (3 × 50 mL). The organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo* to afford the title compound (2.58 g, 95% yield) as a white amorphous solid. Analytical data for **10**: R_f = 0.74 (ethyl acetate/hexanes, 3/7, v/v); $[\alpha]_D^{22}$ +105.8 (c = 1, $CHCl_3$); ^{1}H-n.m.r. (300 MHz): δ, 4.46 (dd, 1H, $J_{6a,6b}$ = 10.6 Hz, $J_{5,6a}$ = 5.7 Hz, H-6a), 4.59-4.51 (m, 1H, H-5), 4.65 (dd, 1H, $J_{5,6b}$ = 6.4 Hz, H-6b), 5.74 (dd, 1H, $J_{3,4}$ = 3.3 Hz, H-3), 5.91 (dd, 1H, $J_{2,3}$ = 10.1 Hz, H-2), 6.05 (dd, 1H, $J_{4,5}$ = 1.2 Hz, H-4), 6.14 (d, 1H, $J_{1,2}$ = 8.4 Hz, H-1), 7.22-7.70 (m, 12H, aromatic), 7.83-7.74 (m, 2H, aromatic), 8.05-7.92 (m, 4H, aromatic), 8.13-8.05 (m, 2H, aromatic). ^{13}C-n.m.r. (75 MHz): δ, 61.8, 66.3, 67.6, 71.7, 72.7, 97.8, 128.4, 128.5 (×2), 128.7 (×5), 128.7, 128.9 (×2), 129.2, 129.9 (×4), 130.0 (×2), 130.1 (×2), 133.5, 133.7, 133.9, 134.0, 164.9, 165.4, 165.5, 166.1 ppm; HR-ESI MS $[M+Na]^+$ calcd for $C_{34}H_{27}NO_{12}Na$ calcd: 664.1431, found 664.1419.

2,3,4,6-Tetra-*O*-benzyl-D-glucopyranosyl nitrate (20). $AgNO_3$ was added to a solution of 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl chloride[37-38] (0.45 g, 0.80 mmol) in dry acetonitrile (5.0 mL) and the resulting mixture was stirred for 5 min at rt. After that, the solids were filtered off through a pad of Celite and the filtrate was concentrated under reduced pressure. The residue

was dissolved in CH_2Cl_2 (~100 mL) and washed with water (20 mL), 1% aq. NaOH (20 mL), and water (3 × 20 mL). The organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo* to afford the title compound (α/β = 1/10, 451.3 mg, 96% yield) as a clear syrup. Analytical data for β-**20**: R_f = 0.70 (ethyl acetate/hexanes, 3/7,v/v): ^{1}H-n.m.r. (300 MHz): δ, 3.50-3.64 (m, 2H, H-2, 4), 3.80-3.65 (m, 4H, H-3, 5, 6a, 6b), 5.00-4.41 (m, 8H, 4 × C*H*$_2$Ph), 5.76 (d, 1H, $J_{1,2}$ = 8.2 Hz, H-1), 7.13 (dd, 3H, *J* = 2.9, 6.6 Hz, aromatic), 7.43-7.22 (m, 17H, aromatic) ppm; ^{13}C-n.m.r. (75 MHz): δ, 68.0, 73.7, 75.2, 75.4, 75.8, 76.0, 76.9, 78.9, 84.8, 100.2, 127.9 (×2), 128.0 (×6), 128.1, 128.2, 128.3 (×2), 128.6 (×6), 128.7 (×2), 137.4, 137.8, 137.9, 138.2; HR-ESI MS $[M+Na]^+$ calcd for $C_{34}H_{35}NO_8Na$ calcd: 608.2260, found 608.2252.

3,4,6-Tri-*O*-acetyl-2-*O*-benzyl-D-glucopyranosyl nitrate (25). $AgNO_3$ was added to a solution of 3,4,6-tri-*O*-acetyl-2-*O*-benzyl-α-D-glucopyranosyl bromide[39] (653.4 mg, 1.42 mmol) in dry acetonitrile (6.0 mL) and the resulting mixture was stirred for 5 min at rt. After that, the solids were filtered off through a pad of Celite and the filtrate was concentrated under reduced pressure. The residue was dissolved in CH_2Cl_2 (~100 mL) and washed with water (20 mL), 1% aq. NaOH (20 mL), and water (3 × 20 mL). The organic layer was separated, dried over $MgSO_4$, and concentrated *in vacuo* to afford the title compound (501.3 mg, 86% yield, α/β = 1/25) as a clear syrup. Analytical data for β-**25**: R_f = 0.73 (ethyl acetate/hexanes, 1/1, v/v); ^{1}H-n.m.r. (300 MHz): δ, 1.92, 2.02, 2.07 (3 s, 9H, 3 x $COCH_3$), 3.61 (dd, 1H, $J_{2,3}$ = 9.2 Hz, H-2), 3.86 (ddd, 1H, $J_{5,6a}$ = 2.2 Hz, $J_{5,6b}$ = 4.6 Hz, H-5), 4.10 (dd, 1H, $J_{6a,6b}$ = 12.5 Hz, H-6a), 4.30 (dd, 1H, H-6b), 4.67 (dd, 2H, ^2J = 11.7 Hz, C*H*$_2$Ph), 5.01 (dd, 1H, $J_{4,5}$ = 10.0 Hz, H-4), 5.27 (dd, 1H, $J_{3,4}$ = 9.4 Hz, H-3), 5.74 (d, 1H, $J_{1,2}$ = 8.3 Hz, H-1), 7.46-7.03 (m, 5H, aromatic); ^{13}C n.m.r. (75 MHz): δ, 20.7, 20.8

(×2), 61.4, 67.7, 72.7, 73.8, 75.0, 75.6, 99.6, 128.2 (×2), 128.4, 128.7 (×2), 136.9, 169.7, 170.0, 170.7 ppm; HR-ESI MS $[M+Na]^+$ calcd for $C_{19}H_{23}NO_{11}Na$ calcd: 464.1169, found 464.1164.

Synthesis of disaccharides

A typical glycosylation procedure. A mixture of glycosyl donor (0.0675 mmol or as indicated in tables), glycosyl acceptor (0.045 mmol), and freshly activated molecular sieves (3 Å, 150 mg) in acetonitirle (1.0 mL, or other solvents as indicated in tables) was stirred under argon for 1 h at rt. Promoter (0.05–0.0675 mmol) was added, and the resulting mixture was stirred at rt for the time indicated in tables. The solids were filtered off through a pad of Celite and rinsed successively with CH_2Cl_2. The combined filtrate (~40 mL) was washed with water (10 mL), sat. aq. Na_2CO_3 (10 mL) and water (2 × 10 mL). The organic phase was separated, dried with $MgSO_4$, and concentrated in vacuo. The residue was purified by column chromatography on silica gel (ethyl acetate–hexane gradient elution) to afford a disaccharide in yields listed below and in tables.

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (3) was obtained from donor **1**[20] and acceptor **2**[26] as a clear syrup in yields listed in tables. Analytical data for **3** was in accordance with that reported previously.[40]

Methyl 2-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (5) was obtained from donor **1**[20] and acceptor **4**[26] as a clear syrup in 88% yield. Analytical data for **5** was in accordance with that reported previously.[41]

Methyl 3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (7) was obtained from donor **1**[20] and acceptor **6**[26] as a clear syrup in 94% yield. Analytical data for **7** was in accordance with that reported previously.[26]

Methyl 4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (9) was obtained from donor **1**[20] and acceptor **8**[26] as a clear syrup in 67% yield. Analytical data for **9** was in accordance with that reported previously.[40]

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (11) was obtained from donor **10** and acceptor **2**[26] as a clear syrup in 71% yield. Analytical data for **11** was in accordance with that reported previously.[41]

Methyl 2-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (12) was obtained from donor **10** and acceptor **4**[26] as a clear syrup in 43% yield. Analytical data for **12** was in accordance with that reported previously.[42]

Methyl 3-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (13) was obtained from donor **10** and acceptor **6**[26] as a clear syrup in 25% yield. Analytical data for **13**: R_f = 0.50 (ethyl acetate/toluene, 15/85, v/v); $[\alpha]_D^{22}$ -0.97 (c = 1, $CHCl_3$); ^{1}H-n.m.r. (300 MHz): δ, 3.39 (s, 3H, OCH_3), 3.62-3.79 (m, 4H, H-2, 5, 6a, 6b), 3.83 (dd, 1H, $J_{4,5}$ = 9.6 Hz, H-4), 3.98 (dd, 1H, $J_{5',6a'}$ = 3.7 Hz, $J_{6a',6b'}$ = 12.4 Hz, H-6a'), 4.31 (dd, 1H, $J_{3,4}$ = 9.2 Hz, H-3), 4.45 (dd, 1H, $J_{5',6b'}$ = 2.0 Hz, H-6b'), 4.52 (dd, 2H, ^2J = 12.0 Hz, CH_2Ph), 4.62-4.80 (m, 4H, 2 × CH_2Ph), 4.81-4.92 (m, 2H, H-1, 5'), 5.57 (d, 1H, $J_{1',2'}$ = 1.3 Hz, H-1'), 5.82 (dd,

1H, $J_{2',3'}$ = 3.1 Hz, H-2'), 5.94 (dd, 1H, $J_{3',4'}$ = 10.2 Hz, H-3'), 6.05 (dd, 1H, $J_{4',5'}$ = 10.1 Hz, H-4'), 6.96-8.18 (m, 35H, aromatic); ^{13}C-n.m.r. (75 MHz): δ, 55.1, 62.5, 66.4, 68.1, 68.4, 69.7, 70.3, 70.4, 72.3, 73.5, 74.6, 76.2, 77.8, 79.1, 97.2, 97.7, 127.4, 127.6 (×3), 127.8, 128.0 (×2), 128.1 (×3), 128.3 (×7), 128.4 (×3), 128.5 (×2), 129.1 (×2), 129.3, 129.6 (×2), 129.7 (×2), 129.8 (×5), 130.1, 132.7, 133.1, 133.2 (×2), 137.5 (×3), 165.1, 165.2, 165.7, 166.2 ppm; HR-ESI MS $[M+Na]^+$ calcd for $C_{62}H_{58}NO_{15}Na$ calcd: 1065.3673, found 1065.3662.

Methyl 4-*O*-(2,3,4,6-tetra-*O*-benzoyl-α-D-mannopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (14) was obtained from donor **10** and acceptor **8**[26] as a clear syrup in 12% yield. Analytical data for **14** was in accordance with that reported previously.[43]

Methyl 6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (16) was obtained from donor **15** and acceptor **2**[26] as a clear syrup in 79% yield. Analytical data for **16** was in accordance with that reported previously.[44]

Methyl 2-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (17) was obtained from donor **15** and acceptor **4**[26] as a clear syrup in 79% yield. Analytical data for **17** was in accordance with that reported previously.[45]

Methyl 3-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (18) was obtained from donor **15** and acceptor **6**[26] as a clear syrup in 72% yield. Analytical data for **18** was in accordance with that reported previously.[45]

Methyl 4-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-galactopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (19) was obtained from donor **15** and acceptor **8**[26] as a clear syrup in 71% yield. Analytical data for **19** was in accordance with that reported previously.[41]

Methyl 2,3,4-tri-*O*-benzyl-6-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-α-D-glucopyranoside (21) was obtained from donor **20** and acceptor **2**[26] as a clear syrup in yields and α/β ratios listed in tables. Analytical data for **21** was in accordance with that reported previously.[40]

Methyl 3,4,6-tri-*O*-benzyl-2-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-α-D-glucopyranoside (22) was obtained from donor **20** and acceptor **4**[26] as a clear syrup in 96% yield with α/β = 1.1/1. Analytical data for **22** was in accordance with that reported previously.[41]

Methyl 2,4,6-tri-*O*-benzyl-3-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-α-D-glucopyranoside (23) was obtained from donor **20** and acceptor **6**[26] as a clear syrup in 94% yield with α/β = 1.1/1. Analytical data for **23** was in accordance with that reported previously.[46]

Methyl 2,3,6-tri-*O*-benzyl-4-*O*-(2,3,4,6-tetra-*O*-benzyl-D-glucopyranosyl)-α-D-glucopyranoside (24) was obtained from donor **20** and acceptor **8**[26] as a clear syrup in 90% yield with α/β = 1.3/1. Analytical data for **24** was in accordance with that reported previously.[40]

Methyl 6-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-D-glucopyranosyl)-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (26) was obtained from donor **25** and acceptor **2**[26] as a clear syrup in yields

and α/β ratios listed in tables. Analytical data for **26** was in accordance with that reported previously.[47]

Methyl 2-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-D-glucopyranosyl)-3,4,6-tri-*O*-benzyl-α-D-glucopyranoside (27) was obtained from donor **25** and acceptor **4**[26] as a clear syrup in 37% yield (α/β = 5.6/1). Analytical data for **27** was in accordance with that reported previously.[41]

Methyl 3-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-D-glucopyranosyl)-2,4,6-tri-*O*-benzyl-α-D-glucopyranoside (28) was obtained from donor **25** and acceptor **6**[26] earlier as a clear syrup in 40% yield (α/β = 4.3/1). Analytical data for **28** was in accordance with that reported previously.[48]

Methyl 4-*O*-(3,4,6-tri-*O*-acetyl-2-*O*-benzyl-D-glucopyranosyl)-2,3,6-tri-*O*-benzyl-α-D-glucopyranoside (29) was obtained from donor **25** and acceptor **8**[26] as a clear syrup in 90% yield (α/β > 20/1). Analytical data for **29** was in accordance with that reported previously.[41]

Methyl 2,3,4-tri-*O*-benzoyl-6-*O*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)-α-D-glucopyranoside (31) was obtained from donor **1** and methyl 2,3,4-tri-*O*-benzoyl-α-D-glucopyranoside (**30**)[49] as a clear syrup in 81% yield. Analytical data for **31** was in accordance with that reported previously.[50]

ASSOCIATED CONTENT

Supporting Information. Additional experimental details, ^{1}H and ^{13}C NMR spectra for all new and selected known compounds have been supplied as the Supporting Information. This material is available free of charge via the Internet.

AUTHOR INFORMATION

Corresponding Author

* Alexei V. Demchenko. E-mail: demchenkoa@umsl.edu

Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

Funding Sources

This work was supported by grants from the National Institute of General Medical Sciences (GM120673) and the National Science Foundation (CHE-1800350) .

References:

[1] M. Janković, *J. Med. Biochem.* **2011**, *30*, 213-223.
[2] P. M. Drake, W. Cho, B. Li, A. Prakobphol, E. Johansen, N. L. Anderson, F. E. Regnier, B. W. Gibson, S. J. Fisher, *Clin. Chem.* **2010**, *56*, 223-236.
[3] N. Leymarie, J. Zaia, *Anal. Chem.* **2012**, *84*, 3040-3048.
[4] O. Blixt, S. Han, L. Liao, Y. Zeng, J. Hoffmann, S. Futakawa, J. C. Paulson, *J. Am. Chem. Soc.* **2008**, *130*, 6680-6681.
[5] X. Song, J. Heimburg-Molinaro, D. F. Smith, R. D. Cummings, *Methods Mol. Biol.* **2012**, *800*, 163-171.
[6] D. F. Smith, R. D. Cummings, *Curr. Opin. Virol.* **2014**, *7*, 79-87.
[7] L. Wang, R. D. Cummings, D. F. Smith, M. Huflejt, C. T. Campbell, J. C. Gildersleeve, J.

Q. Gerlach, M. Kilcoyne, L. Joshi, S. Serna, N. C. Reichardt, N. Parera Pera, R. J. Pieters, W. Eng, L. K. Mahal, *Glycobiology* **2014**, *24*, 507-517.
[8] J. Katrlík, J. Švitel, P. Gemeiner, T. Kožár, J. Tkac, *Med. Res. Rev.* **2010**, *30*, 394–418.
[9] N. Fujitani, J.-i. Furukawa, K. Araki, T. Fujioka, Y. Takegawa, J. Piao, T. Nishioka, T. Tamura, T. Nikaido, M. Ito, Y. Nakamura, Y. Shinohara, *Proc. Nat. Acad. Sci.* **2013**, *110*, 2105-2110.
[10] A. Varki, R. D. Cummings, J. D. Esko, H. H. Freeze, C. R. Bertozzi, P. Stanley, G. W. Hart, M. E. Etzler, *Essentials of glycobiology*, Second ed., CSH Laboratory Press, New York, **2009**.
[11] D. S. Alonzi, D. C. A. Neville, R. H. Lachmann, R. A. Dwek, T. D. Butters, *Biochem. J.* **2008**, *409*, 571-580.
[12] H. O. Celso A. Reis, Luisa Silva, Catarina Gomes, Leonor David, *J. Clin. Pathol.* **2010**, *63*, 322-329.
[13] B. Adamczyk, T. Tharmalingam, P. M. Rudd, *Biochim. Biophys. Acta* **2012**, *1280*, 1347-1353.
[14] Z. Yin, X. Huang, *J. Carbohydr. Chem.* **2012**, *31*, 143-186.
[15] L. R. Ruhaak, S. Miyamoto, C. B. Lebrilla, *Molec. Cell. Proteomics* **2013**, *12*, 846-855.
[16] Y. L. Huang, J. T. Hung, S. K. Cheung, H. Y. Lee, K. C. Chu, S. T. Li, Y. C. Lin, C. T. Ren, T. J. Cheng, T. L. Hsu, A. L. Yu, C. Y. Wu, C. H. Wong, *Proc. Nat. Acad. Sci.* **2013**, *110*, 2517-2522.
[17] S. R. Stowell, T. Ju, R. D. Cummings, *Annu. Rev. Pathol.* **2015**, *10*, 473-510.
[18] C. B. Lebrilla, H. J. An, *Molec. Biosystems* **2009**, *5*, 17-20.
[19] D. L. Meany, Z. Zhang, L. J. Sokoll, H. Zhang, D. W. Chan, *J. Proteome Res.* **2009**, *8*, 613-619.
[20] T. Wang, S. S. Nigudkar, J. P. Yasomanee, N. P. Rath, K. J. Stine, A. V. Demchenko, *Org. Biomol. Chem.* **2018**, *6*, 3596-3604.
[21] A. F. G. Bongat, A. V. Demchenko, *Carbohydr. Res.* **2007**, *342*, 374-406.
[22] D. J. Keith, S. D. Townsend, *Carbohydr. Res.* **2017**, *442*, 20-24.
[23] S. E. Zurabyan, M. M. Tikhomirov, V. A. Nesmeyanov, A. Y. Khorlin, *Carbohydr. Res.* **1973**, *26*, 117-123.
[24] H. Paulsen, U. Von Deesen, H. Tietz, *Carbohydr. Res.* **1985**, *137*, 63-77.
[25] S. A. Svarovsky, J. J. Barchi, *Carbohydr. Res.* **2003**, *338*, 1925-1935.
[26] S. C. Ranade, S. Kaeothip, A. V. Demchenko, *Org. Lett.* **2010**, *12*, 5628-5631.
[27] F. J. Waller, A. G. M. Barrett, D. C. Braddock, D. Rampsrasad, *Chem. Commun.* **1997**, 613-614.
[28] F. J. Waller, A. G. M. Barrett, D. C. Braddock, R. M. McKinnell, D. Ramprasad, *J. Chem. Soc., Perkin Trans. 1* **1999**, 867-872.
[29] D. Hannachi, N. Ouddai, H. Chermette, *Dalton transactions* **2010**, *39*, 3673-3680.
[30] S. C. Ranade, A. V. Demchenko, *J. Carbohydr. Chem.* **2013**, *32*, 1-43.
[31] D. M. Whitfield, *Adv. Carbohydr. Chem. Biochem.* **2009**, *62*, 83-159.
[32] S. S. Nigudkar, A. V. Demchenko, *Chem. Sci.* **2015**, *6*, 2687–2704.
[33] M. N. Kamat, A. V. Demchenko, *Org. Lett.* **2005**, *7*, 3215-3218.
[34] R. U. Lemieux, in *Methods in Carbohydrate Chemistry, Vol. 2* (Eds.: R. L. Whistler, M. L. Wolform), Academic Press Inc., New York and London, **1963**, pp. 226-228.
[35] M. Dowlut, D. G. Hall, O. Hindsgaul, *J. Org. Chem.* **2005**, *70*, 9809-9813.
[36] K. P. R. Kartha, H. J. Jennings, *J. Carbohydr. Chem.* **1990**, *9*, 777-781.

[37] V. D. Grob, T. G. Squires, J. R. Vercellotti, *Carbohydr. Res.* **1969**, *10*, 595-597.
[38] M. B. Tatina, D. T. Khong, Z. M. A. Judeh, *Eur. J. Org. Chem.* **2018**, *2018*, 2208-2213.
[39] S. Brennan, P. A. Finan, *J. Chem. Soc., C* **1970**, 1742-1744.
[40] B. A. Garcia, D. Y. Gin, *J. Am. Chem. Soc.* **2000**, *122*, 4269-4279.
[41] P. Pornsuriyasak, A. V. Demchenko, *Chem. Eur. J.* **2006**, *12*, 6630-6646.
[42] Y. Singh, T. Wang, S. A. Geringer, K. J. Stine, A. V. Demchenko, *J. Org. Chem.* **2018**, *83*, 374-381.
[43] K. S. Kim, D. B. Fulse, J. Y. Baek, B. Y. Lee, H. B. Jeon, *J. Am. Chem. Soc.* **2008**, *130*, 8537-8547.
[44] J. Tatai, P. Fugedi, *Org. Lett.* **2007**, *9*, 4647-4650.
[45] S. J. Hasty, M. A. Kleine, A. V. Demchenko, *Angew. Chem. Int. Ed.* **2011**, *50*, 4197-4201.
[46] H. Chiba, S. Funasaka, T. Mukaiyama, *Bull. Chem. Soc. Jpn.* **2003**, *76*, 1629-1644.
[47] S. S. Nigudkar, T. Wang, S. G. Pistorio, J. P. Yasomanee, K. J. Stine, A. V. Demchenko, *Org. Biomol. Chem.* **2017**, *15*, 348-359.
[48] S. Kaeothip, S. J. Akins, A. V. Demchenko, *Carbohydr. Res.* **2010**, *345*, 2146-2150.
[49] F. Zhang, W. Zhang, Y. Zhang, D. P. Curran, G. Liu, *J. Org. Chem.* **2009**, *74*, 2594-2597.
[50] S. Yamago, K. Kokubo, O. Hara, S. Masuda, J. Yoshida, *J. Org. Chem.* **2002**, *67*, 8584-8592.