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Synthesis of Glycosyl Amides Using Selenocarboxylates as Traceless Reagents for Amide Bond Formation

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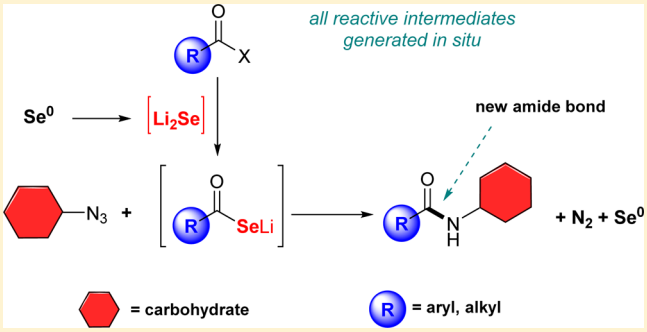
Supporting Information

ABSTRACT: Carbohydrate-derived amides were successfully prepared in good yields from a broad range of substrates, including furanosyl and pyranosyl derivatives. The methodology successfully relied on the in situ generation of lithium selenocarboxylates from Se/$LiEt_3BH$ and acyl chlorides or carboxylic acids and their reaction with sugar azides. A key aspect of the present protocol is that we start from elemental selenium; isolation and handling of all reactive and sensitive selenium-containing intermediates is avoided, therefore providing the selenocarboxylate the status of a traceless reagent.



INTRODUCTION

The amide functional group is one of the most important chemical linkages and is the key connection between amino acids in peptides and proteins. Beyond this well-known role, amides are also present in some of the most important synthetic polymers and in a number of pharmaceutical active ingredients.[1] The glycosyl amide linkage is an important connection found in nature because it is one of the ways in which a sugar unit can be found attached to other biomolecules and natural products such as *N*-glycosides,[2] *N*-glycopeptides,[3] lipopolysaccharides,[4] and ceramides.[5] *N*-glycosyl amides and glycopeptides are known for possessing a wide range of bioactivities, mainly because these classes of carbohydrate derivatives can bind efficiently to specific sites of proteins[6] and are important scaffolds in glycobiology studies.[7]

In the context of amide bond formation, several methods have been described.[8] Although most of them involve the activation of a carboxylic acid with coupling reagents followed by the reaction with an amine, alternative methods have appeared in the literature.[9] Recent systems include the coupling of amines with carboxylic acids promoted by boron compounds,[10] α-ketoacid-hydroxylamine reactions,[11] and Ru-catalyzed oxidative coupling of alcohols and amines.[12] More specifically as it relates to carbohydrate chemistry, a common method is the Staudinger reaction[13] in which a glycosyl azide reacts with diphenylphospanyl-phenyl esters,[14] whose main advantage is to avoid anomeric equilibration in contrast to catalytic hydrogenation of the glycosyl azide, followed by acylation procedures that are limited to β-glycosyl amides.[15]

In connection with our current interest in the development of new strategies using selenium chemistry for the functionalization of carbohydrate derivatives, we sought to develop an efficient synthesis of glycosyl amides. To reduce our plan to practice, we planned to use a reaction between a selenocarboxylate and a carbohydrate-derived azide. The reaction of selenocarboxylates with azides is a more reactive variation of the thioacid-azide ligation (Scheme 1, A).[16]

Precedents can be found in the literature for the reaction of potassium selenobenzoate with electron-deficient azides such as aryl azides bearing electron-withdrawing groups and sulfonyl azides (Scheme 2, B).[17,18] More electron-rich azides, particularly alkyl derivatives, have only resulted in significantly decreased yields or recovery of unreacted starting material. One major drawback that hampers further use of potassium selenobenzoate for amidations is the need for isolation of the selenium salt. An improvement of this protocol was introduced by Hu (Scheme 1, C)[19] through the in situ generation of the reactive selenocarboxylate by the reaction of acyl chlorides with LiAlHSeH (Ishihara reagent[20]). Our initial attempt to use this protocol for the amidation of D-xylose-derived azide **2**, did not furnish desired product **3**, instead leading to decomposition and partial recovery of unreacted azide **2** (Scheme 1, D).

Therefore, we have decided to reinvestigate this reaction and develop a more efficient one-pot protocol in which we could avoid the isolation and manipulation of reactive compounds containing selenium. Our plan was to start with the reduction of elemental selenium to generate a nucleophilic Se^{2-} species that would react with an activated carboxylic acid derivative (e.g., acyl chloride), generating in situ the desired selenocarboxylate. Introduction of the appropriate sugar-based azide in the reaction mixture would trigger a cycloaddition-type reaction leading to a selenotriazoline intermediate whose decomposition would generate the desired glycosyl amide along with harmless

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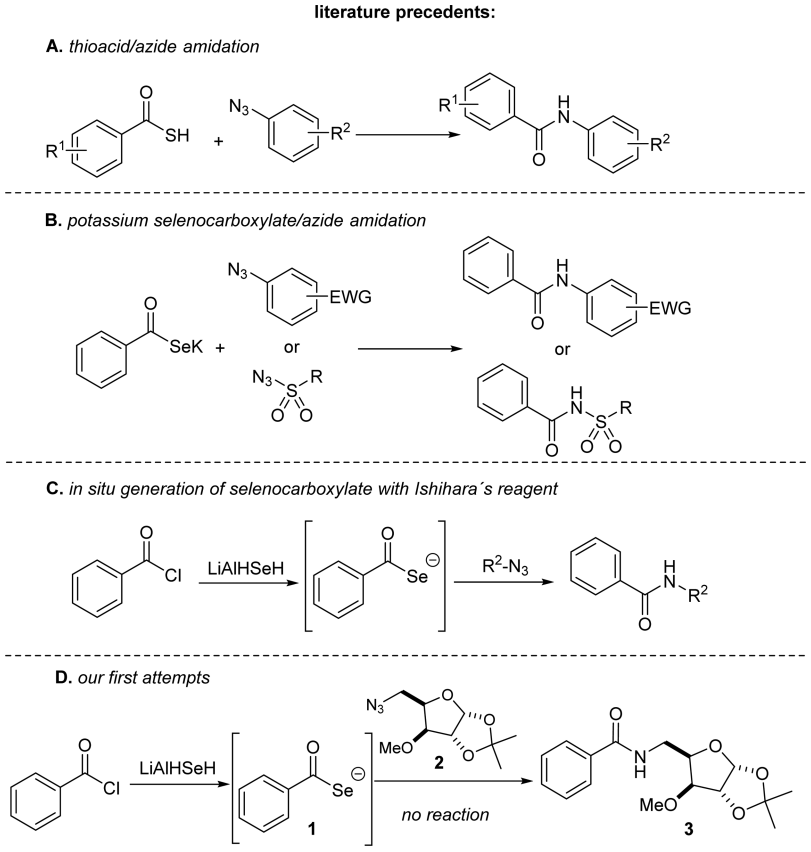
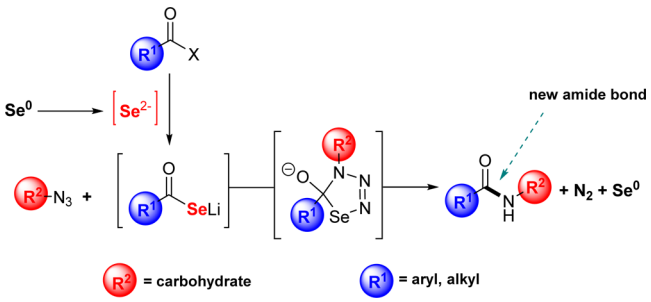
Scheme 1



Scheme 2



gaseous nitrogen and elemental selenium as byproducts (Scheme 2). The overall transformation should not require the manipulation of any selenium intermediates, and the selenocarboxylate might therefore be considered a traceless reagent promoting the amide bond formation.

RESULTS AND DISCUSSION

We started our studies focusing on the in situ generation of the reactive selenocarboxylate. To evaluate the efficiency of our system, we elected 4-nitrophenyl azide as the starting material because it is well-known to be an efficient reaction partner for amidation reactions in previous works.[19] The first reducing agent employed for reduction of elemental selenium was lithium aluminum hydride (Table 1, entry 1). Therefore, formation of LiAlHSeH and reaction with benzoyl chloride, followed by introduction of the azide in the reaction mixture, resulted only in decomposition, and no product was detected in the crude mixture. Our second attempt was changing the reducing agent to $NaBH_4$ for the formation of NaHSe.[21] In this reaction, the desired amide product was formed, however, in low yield (entry 2). We then decided to test our methodology for the amidation reaction using lithium triethylborohydride to reduce elemental selenium to the desired lithium selenide (entry 3). This reaction was first developed by Gladysz et al.[22] and has been used for the rapid and efficient synthesis of selenides and diselenides by our group[23] and by others.[24] However, it has never been used for the synthesis of selenocarbonyl compounds. Therefore, we first reacted the in situ generated Li_2Se with benzoyl chloride to generate the corresponding lithium benzoylselenocarboxylate, which was immediately reacted with 4-nitrophenyl azide, delivering desired amide **4** in 75% isolated yield. Increasing the number of equivalents of the selenocarboxylate led us to obtain amide **4** in essentially quantitative yield when the reaction was performed at 50 °C (entry 4). Lowering the temperature resulted in decreased isolated yield of the desired product (entry 5). We briefly explored the scope of the reaction using aryl azides, and we have found that the reaction is tolerant to sensitive functional groups at the azide. The amidation can be performed in the presence of ester, cyano, and trifluoromethyl functional groups, and products **5**–**7** were isolated in excellent yields (entries 6–8). Furthermore, heterocyclic azides have also proven to be compatible with the amidation conditions. An amide bearing a tetrahydroacridine moiety, **8**, was prepared in 70% yield (entry 9). This heterocyclic compound is derived from the acetylcholinesterase inhibitor tacrine, which was the first FDA-approved drug for treatment of Alzheimer's disease and still serves as a model for the development of new therapeutic agents for Alzheimers.[25] Moreover, benzoxazole-

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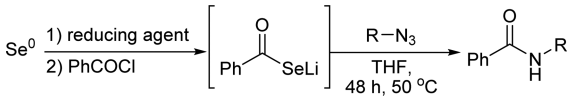
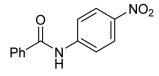
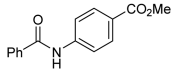
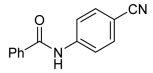
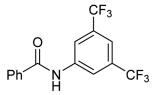
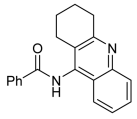
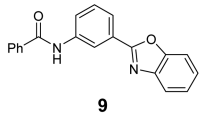
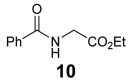
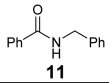
Table 1. Optimization Studies and Scope with Aryl Azides



Entry	Reducing agent	Equiv of selenocarboxylate	Product	Yield (%)[a]
1	$LiAlH_4$	1	 **4**	NR
2	$NaBH_4$	1	**4**	20
3	$LiEt_3BH$	1	**4**	75
4	$LiEt_3BH$	4	**4**	95
5	$LiEt_3BH$	4	**4**	85[b]
6	$LiEt_3BH$	4	 **5**	96
7	$LiEt_3BH$	4	 **6**	87
8	$LiEt_3BH$	4	 **7**	95
9	$LiEt_3BH$	4	 **8**	70
10	$LiEt_3BH$	4	 **9**	40
11	$LiEt_3BH$	4	 **10**	NR
12	$LiEt_3BH$	4	 **11**	20

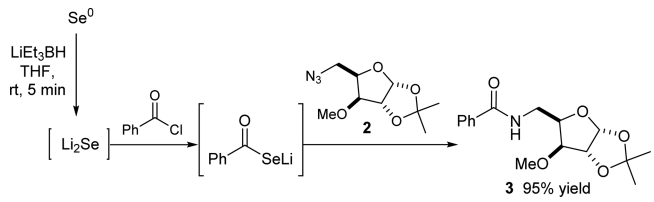
[a]Isolated yields. [b]Reaction performed at rt.

derived amide **9** was also obtained (entry 10). This heterocyclic compound is a fluorescent molecule and belongs to a class of compounds commonly used as fluorophores with potential applications as fluorescent probes and optical sensors.[26] Alkyl azides were also tested under our conditions, and we have found them to be less reactive substrates. Under our conditions, we were not able to obtain product **10** (entry 11), but product **11** was isolated in 20% yield (entry 12). Despite the modest yield with benzyl azide, this reveals the promising reactivity of our system, because previous reports from the literature[19] indicate that aliphatic azides do not react at all with sodium or aluminum selenocarboxylates.

Having validated this new protocol with aryl azides, we moved on to testing the reaction using sugar-derived azide **2**, and gratifyingly, we observed an excellent yield of glucosyl amide **3** when a xylose-derived azide was used as the reaction partner (Scheme 3). The best results were achieved using 4 equiv of the selenocarboxylate, 1 equiv of the azide, and heating at 50 °C for 48 h.

With this promising result in hand, we further investigated the amidation reaction with a broader range of sugar-derived

Scheme 3



azides. We first evaluated the reactivity of azides with a furanosyl backbone in combination with a number of different acyl chlorides. The results of these studies are summarized in Table 2. The reaction of aroyl chlorides as the starting material, in combination with a xylose-derived azide, resulted in the corresponding amides **3** and **12** in very good yields. The use of acyl chlorides possessing alkyl side chains was also possible, and the corresponding amides **13**−**17** were obtained in moderate to excellent yields, varying from 35 to 95%. When a different xylofuranosyl azide with a free OH group was used, the yields dropped dramatically, and the corresponding products **18** and **19** were isolated in 10 and 12%, respectively. Different

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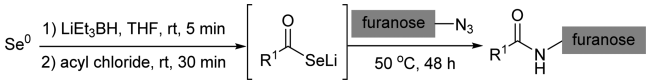
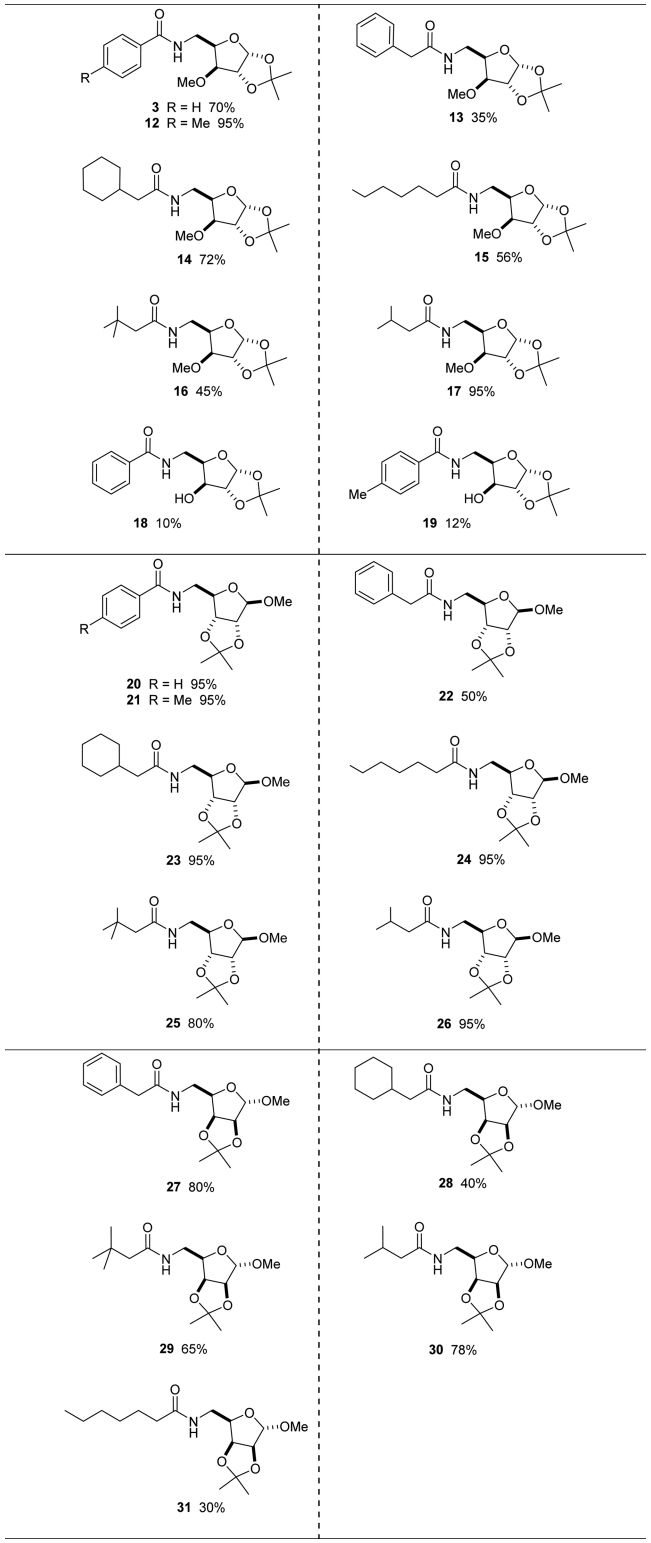
Table 2. Scope of the Reaction Using Furanosyl Azides[a]





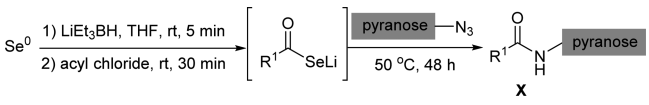
[a]Isolated yields. Reactions performed using 0.25 mmol of the furanosyl azide. The selenocarboxylate (1.0 mmol) was generated in situ by reacting the acyl chloride (1.0 mmol) with Li_2Se [1.0 mmol, formed in situ by the reaction of $LiEt_3BH$ (2.0 mmol, 1 M THF solution) and Se^0 (1.0 mmol)].

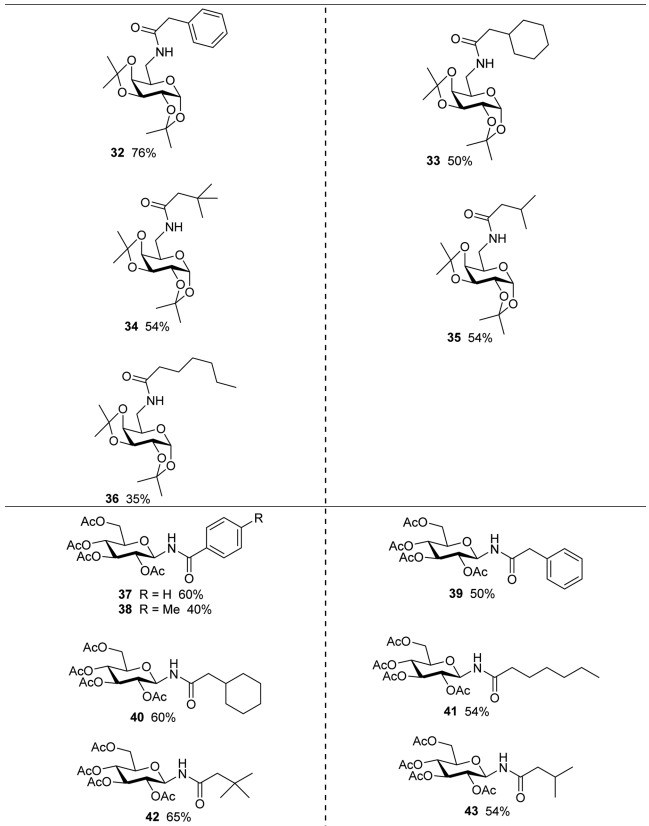
furanosyl azides have also been evaluated, and derivatives from D-ribose (products **20**–**26**) and D-mannose (products **27**–**31**) have been successfully employed in the amidation reaction. Particularly notable are the results achieved for the synthesis of ribofuranosyl amides because the reaction proved to be very efficient across a range of different acyl chlorides used as the selenocarboxylate precursors.

Next, the scope was further investigated using azides possessing a pyranosyl scaffold (Table 3). Amides derived from two different sugars have been studied, and five different galactosyl (products **32**–**36**) and seven glucosyl amides (products **37**–**43**) were prepared. Worth noting is that all glucose derivatives possess the amide linkage at the β-position on the anomeric center of the sugar. In all examples studied, the configuration at this carbon was retained, which is a clear advantage of the present method over a more traditional approach (reduction of the azide to the amine, followed by amide formation) because it is known that anomeric glucosyl amines are relatively unstable and prone to mutarotation, resulting in a mixture of anomers.[27]

The reaction is not limited to the use of acyl chlorides as the precursors for the selenocarboxylates, and we have also successfully used a simple carboxylic acid as the source of the

Table 3. Scope of the Reaction Using Pyranosyl Azides[a]





[a]Isolated yields. Reactions performed using 0.25 mmol of the pyranosyl azide. The selenocarboxylate (1.0 mmol) was generated in situ by reacting the acyl chloride (1.0 mmol) with Li_2Se [1.0 mmol, formed in situ by the reaction of $LiEt_3BH$ (2.0 mmol, 1 M THF solution) and Se^0 (1.0 mmol)].

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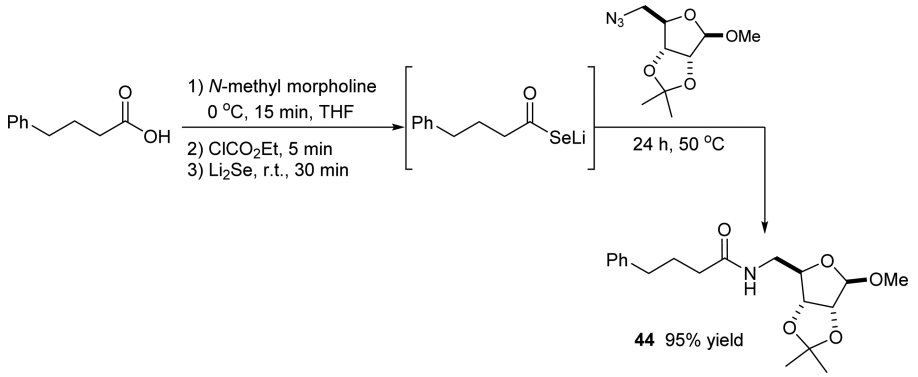
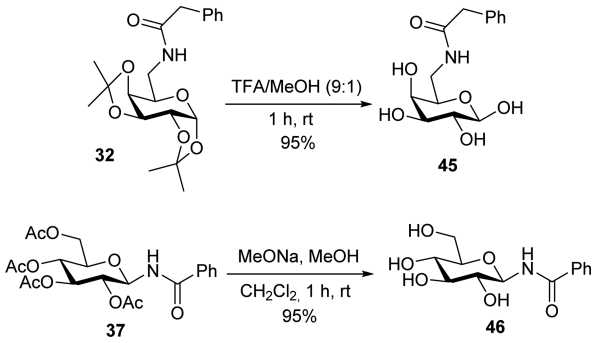
Scheme 4. Carboxylic Acid as the Precursor of Selenocarboxylate



amidation reagent. For example, 4-phenylbutyric acid was activated by reaction with ethyl chloroformate and *N*-methylmorpholine,[28] followed by reaction with Li_2Se for 30 min to generate the corresponding selenocarboxylate (Scheme 4). Introduction of the sugar azide to the reaction mixture and heating at 50 °C for 24 h resulted in evolution on N_2 and precipitation of elemental selenium, indicating completion of the reaction. Desired product **44** was isolated in 95% yield after column chromatography. Notably, the 4-step sequence occurs without isolation of any intermediates, and only stable, easy-to-handle materials have been manipulated. All reactive intermediates are generated in situ, and their handling is avoided. In addition, the byproducts that are formed, Se and N_2, are harmless and removed by simple filtration.

Finally, deprotection of the sugar moieties of selected compounds was performed (Scheme 5). Thus, compound **32**,

Scheme 5



in which the hydroxy groups were masked as acetonides, was treated with trifluoroacetic acid and methanol, furnishing the free sugar moiety in 95% yield. In addition, tetraacetylated glucose derivative **37** was deprotected by the classic Zemplén methodology[29] under very mild conditions using sodium methoxide in methanol to deliver the corresponding tetraol in nearly quantitative yield. Worth pointing out is that the amide moiety remained untouched under these deprotection conditions.

CONCLUSIONS

In summary, a wide range of sugar-derived amides were successfully prepared in good yields for a broad range of substrates, including substituted aryl, furanosyl, and pyranosyl azides. Our new methodology successfully relied on the in situ generation of lithium selenocarboxylates from Se/$LiEt_3BH$ and acyl chlorides or carboxylic acids. A key aspect of the present protocol is that we start from elemental selenium, and the isolation and handling of all reactive and sensitive selenium-containing intermediates is avoided, therefore providing the selenocarboxylate the status of a traceless reagent. Further applications of the present protocol are underway and will be reported in due course.

EXPERIMENTAL SECTION

General Information. NMR spectra were recorded on a 300, 400, or 500 MHz spectrometer (for ^1H NMR) at room temperature using a 5 mm internal diameter probe in chloroform ($CDCl_3$), methanol (CD_3OD), or deuterium oxide (D_2O) and are reported in parts per million (ppm). ESI-QTOF-MS measurements were performed in positive ion mode (m/z 50−2000 range). IR spectra were obtained on an FTIR-ATR instrument. Melting points were measured on an optical microscope apparatus and are uncorrected. Optical rotations were obtained in a polarimeter at 20 °C unless otherwise noted. Flash column chromatography was performed using Silica Gel (230−400 mesh) following the methods described by Still.[30] Thin layer chromatography (TLC) was performed using supported silica gel GF254 with 0.25 mm thickness. For visualization, TLC plates were either placed under ultraviolet light or stained with iodine vapor or acidic vanillin or phosphomolybdic acid. Lithium triethylborohydride was used as a 1 M THF solution. Elemental selenium (100 mesh) was dried in an oven (80 °C) overnight prior to use. Aryl and sugar azides are known compounds and were prepared according to literature procedures.[31,32]

General Procedure for the Preparation of *N*-Glycosyl Amides. Under an argon atmosphere, lithium triethylborohydride (2.0 mmol, 4 equiv) was added over selenium powder (1.0 mmol, 2 equiv), forming Li_2Se as a white solution. THF (2 mL) was added to the mixture, and after 5 min of stirring, the acyl chloride (1.0 mmol, 4 equiv) was then added dropwise; the orange/yellow clear solution that formed was stirred at room temperature for 30 min. After this time, a solution of the glycosyl azide (0.25 mmol in 2 mL of THF, 1 equiv) was added. The reaction was allowed to stir at room temperature for 48 h. After consumption of the starting azide, as shown by TLC, selenium powder precipitated and was removed by filtration prior to quenching the reaction mixture with aqueous saturated $NaHCO_3$ (10 mL) and extraction with CH_2Cl_2 (3 × 15 mL). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography eluting with a mixture of hexane/ethyl acetate (90:10). ***Caution!*** Although the toxicity of elemental selenium is significantly lower than other forms, care should be taken in its handling and disposal.

*N-(5-Deoxy-3-O-methyl-1,2-O-isopropylidene-α-D-xylofurano-side)-5-benzamide (**3**).* Yellow oil; yield of 0.107 g (70%). $[\alpha]_D^{20}$ −13.9 (*c* 0.188, CH_2Cl_2). R_f = 0.4 (10% ethyl acetate/*n*-hexane). ^1H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 7.2 Hz, 2H), 7.56−7.34 (m, 3H), 6.67−6.63 (m, 1H), 5.93 (d, J = 3.8 Hz, 1H), 4.61 (d, J = 3.8 Hz,

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1H), 4.41−4.34 (m, 1H), 4.10 (ddd, J = 14.3, 7.8, 3.7 Hz, 1H), 3.78 (d, J = 3.3 Hz, 1H), 3.52−3.46 (m, 1H), 3.45 (s, 3H), 1.48 (s, 3H), 1.33 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.8, 134.5, 131.6, 128.7, 127.1, 111.9, 105.1, 85.1, 81.9, 78.9, 58.1, 39.2, 26.8, 26.3. IR (ν_{max}, cm^{-1}): 3348, 3064, 2987, 2931, 2825, 1727, 1646, 1539, 1370, 1214, 1072, 1011. HRMS (ESI) m/z: calcd for $C_{16}H_{22}NO_5$ [M + H]$^+$ 308.1498, found 308.1501.

*Methyl Ester-4-(benzoylamino)benzoic Acid (**5**).* Orange solid; yield of 0.123 g (96%). Mp: 66−68 °C. R_f = 0.2 (10% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.14 (br, 1H), 8.07−8.01 (m, 2H), 7.91−7.84 (m, 2H), 7.78−7.72 (m, 2H), 7.60−7.44 (m, 3H), 3.90 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.5, 165.8, 142.1, 134.5, 132.1, 130.8, 128.8, 127.0, 125.8, 119.2, 52.0. IR (ν_{max}, cm^{-1}): 3372, 3219, 2947, 1708, 1666, 1599, 1523, 1273. HRMS (ESI) m/z: calcd for $C_{15}H_{14}NO_3$ [M + H]$^+$ 256.0974, found 256.0978.

*N-(4-Cyanophenyl)benzamide (**6**).* White solid; yield of 0.097 g (87%). Mp: 166−168 °C. R_f = 0.1 (10% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 8.15 (br, 1H), 7.91−7.77 (m, 4H), 7.68−7.46 (m, 5H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 165.9, 142.0, 134.0, 133.3, 132.4, 128.9, 127.1, 119.9, 118.8, 107.3. IR (ν_{max}, cm^{-1}): 3351, 2925, 2225, 1659, 1519, 1408. HRMS (ESI) m/z: calcd for $C_{14}H_{11}N_2O$ [M + H]$^+$ 223.0871, found 223.0851.

*N-[3,5-Bis(trifluoromethyl)phenyl]benzamide (**7**).* Pale yellow solid; yield of 0.170 g (95%). Mp: 112−114 °C. R_f = 0.5 (10% ethyl acetate/*n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): 8.20 (s, 2H), 8.12 (br, 1H), 7.90 (d, J = 10.0 Hz, 2H), 7.66 (s, 1H), 7.62 (t, J = 7.5 Hz, 1H), 7.53 (t, J = 7.5 Hz, 2H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 166.0, 139.4, 132.7, 132.2 (q, J = 33 Hz), 129.1, 127.1, 125.8 (q, J = 273 Hz), 119.8 (m), 117.8 (m). IR (ν_{max}, cm^{-1}): 3264, 2925, 1651, 1559, 1270. HRMS (ESI) m/z: calcd for $C_{15}H_{10}F_6NO$ [M + H]$^+$ 334.0667, found 334.0683.

*N-(1,2,3,4-Tetrahydro-9-acridinyl)benzamide (**8**).* Yellow solid; yield of 0.100 g (70%). Mp: 148−150 °C. R_f = 0.2 (50% ethyl acetate/*n*-hexane). Mp: 148−150 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ 8.50 (br, 1H), 7.82 (d, J = 8.0 Hz, 1H), 7.71 (d, J = 8,0 Hz, 2H), 7.55 (d, J = 8.0 Hz, 1H), 7.47−7.38 (m, 2H), 7.24−7.15 (m, 3H), 2.92 (t, J = 6.5 Hz, 2H), 2.55 (t, J = 6.5 Hz, 2H), 1.73−1.67 (m, 2H), 1.61−1.54 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 166.1, 159.6, 146.6, 138.5, 133.3, 132.0, 128.6, 128.5, 128.4, 127.7, 127.4, 125.6, 123.9, 122.1, 33.7, 25.2, 22.4, 22.1. IR (ν_{max}, cm^{-1}): 2926, 2861, 1647. HRMS (ESI) m/z: calcd for $C_{20}H_{19}N_2O$ [M + H]$^+$ 303.1497, found 303.1509.

*N-[3-(2-Benzoxazolyl)phenyl]benzamide (**9**).* White solid; yield of 0.070 g (40%). Mp: 191−193 °C. R_f = 0.6 (10% ethyl acetate/*n*-hexane). ^{1}H NMR (500 MHz, DMSO-d_6): δ 10.53 (s, 1H), 8.81 (s, 1H), 8.03 (d, J = 7.0 Hz, 3H), 7.94 (d, J = 7.9 Hz, 1H), 7.82 (t, J = 8.8 Hz, 2H), 7.65−7.52 (m, 4H), 7.48−7.38 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6): δ 165.7, 162.2, 150.2, 141.4, 140.0, 134.5, 131.7, 129.6, 128.4 127.7, 126.7, 125.5, 124.8, 123.3, 122.3, 119.8, 118.7, 110.9. IR (ν_{max}, cm^{-1}): 3281, 3060, 1649, 1521, 1419, 1245. HRMS (ESI) m/z: calcd for $C_{20}H_{15}N_2O_2$ [M + H]$^+$ 315.1133, found 315.1137.

*4-Methyl-N-(5-deoxy-3-O-methyl-1,2-O-isopropylidene-α-D-xylofuranoside)-5-benzamide (**12**).* Yellow oil; yield of 0.152 g (95%). $[\alpha]_D^{20}$ −22.4 (c 0.224, CH_2Cl_2). R_f = 0.4 (10% ethyl acetate/*n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.67 (d, J = 8.0 Hz, 2H), 7.22 (d, J = 8.0 Hz, 2H), 6.62 (br, 1H), 5.93 (d, J = 3.8 Hz, 1H), 4.60 (d, J = 3.8 Hz, 1H), 4.43−4.31 (m, 1H), 4.09 (ddd, J = 14.1, 7.8, 3.6 Hz, 1H), 3.78 (d, J = 3.2 Hz, 1H), 3.50−3.45 (m, 1H), 3.44 (s, 3H), 2.39 (s, 3H), 1.48 (s, 3H), 1.32 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.7, 142.0, 131.7, 129.3, 127.1, 111.9, 105.1, 85.1, 81.9, 79.0, 58.1, 39.1, 26.8, 26.3, 21.6. IR (ν_{max}, cm^{-1}): 3355, 3224, 2926, 2360, 1722, 1640, 1537, 1504, 1374, 1259, 1205, 1074, 1020. HRMS (ESI) m/z: calcd for $C_{17}H_{24}NO_5$ [M + H]$^+$ 322.1654, found 322.1655.

*N-(5-Deoxy-3-O-methyl-1,2-O-isopropylidene-α-D-xylofuranoside)-5-benzeneacetamide (**13**).* Yellow oil; yield of 0.052 g (35%). $[\alpha]_D^{20}$ −10.9 (c 0.464, CH_2Cl_2). R_f = 0.3 (10% ethyl acetate/*n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37−7.31 (m, 2H), 7.30−7.24 (m, 3H), 5.94 (br, 1H), 5.83 (d, J = 3.9 Hz, 1H), 4.51 (d, J = 3.9 Hz, 1H), 4.24 (ddd, J = 7.5, 4.7, 3.5 Hz, 1H), 3.74 (ddd, J = 14.1, 7.5, 4.7 Hz, 1H), 3.60 (d, J = 3.5 Hz, 1H), 3.57 (s, 2H), 3.32 (ddd, J = 14.1, 7.2, 4.4 Hz, 1H), 3.24 (s, 3H), 1.46 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.3, 135.1, 129.5, 129.0, 127.3, 111.8, 105.0, 84.8, 81.5, 78.3, 57.7, 43.8, 38.6, 26.8, 26.3. IR (ν_{max}, cm^{-1}): 3291, 3065, 3030, 2986, 2933, 2830, 2102, 1645, 1541, 1377, 1214, 1168, 1076, 1011. HRMS (ESI) m/z: calcd for $C_{17}H_{24}NO_5$ [M + H]$^+$ 322.1654, found 322.1672.

*N-(5-Deoxy-3-O-methyl-1,2-O-isopropylidene-α-D-xylofuranoside)-5-cyclohexaneacetamide (**14**).* Orange solid; yield of 0.056 g (72%). $[\alpha]_D^{20}$ −3.5 (c 0.433, CH_2Cl_2). Mp: 67−69 °C. R_f = 0.3 (10% ethyl acetate/*n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.95−5.89 (m, 1H), 5.87 (d, J = 3.8 Hz, 1H), 4.56 (d, J = 3.8 Hz, 1H), 4.26−4.20 (m, 1H), 3.87 (ddd, J = 14.0, 8.0, 3.6 Hz, 1H), 3.69 (d, J = 3.2 Hz, 1H), 3.39 (s, 3H), 3.21 (ddd, J = 14.0, 8.3, 3.5 Hz, 1H), 2.03 (d, J = 7.1 Hz, 2H), 1.80−1.58 (m, 6H), 1.45 (s, 3H), 1.30 (s, 3H), 1.28−1.18 (m, 2H), 1.16−1.08 (m, 1H), 0.99−0.85 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.8, 111.9, 105.0, 84.8, 81.9, 79.1, 58.0, 44.9, 38.5, 35.5, 33.2, 33.2, 26.8, 26.4, 26.3, 26.2. IR (ν_{max}, cm^{-1}): 3331, 2988, 2924, 2847, 1721, 1641, 1544, 1076, 1019. HRMS (ESI) m/z: calcd for $C_{17}H_{30}NO_5$ [M + H]$^+$ 328.2124, found 328.2134.

*N-(5-Deoxy-3-O-methyl-1,2-O-isopropylidene-α-D-xylofuranoside)-5-heptanamide (**15**).* Yellow oil; yield of 0.044 g (56%). $[\alpha]_D^{20}$ −3.2 (c 0.291, CH_2Cl_2). R_f = 0.4 (10% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.92−5.83 (m, J = 4.7 Hz, 1H), 5.81 (d, J = 3.8 Hz, 1H), 4.49 (d, J = 3.8 Hz, 1H), 4.22−4.11 (m, 1H), 3.80 (ddd, J = 14.2, 8.0, 3.5 Hz, 1H), 3.62 (d, J = 3.3 Hz, 1H), 3.32 (s, 3H), 3.15 (ddd, J = 14.2, 8.4, 3.5 Hz, 1H), 2.09 (t, J = 7.6 Hz, 2H), 1.64−1.44 (m, 2H), 1.39 (s, 3H), 1.23 (s, 3H), 1.22−1.05 (m, 6H), 0.89−0.66 (m, 3H).^{13}C NMR (75 MHz, $CDCl_3$): δ 173.6, 111.8, 105.0, 84.8, 81.8, 79.1, 58.0, 38.5, 36.9, 31.6, 29.0, 26.8, 26.3, 25.8, 22.6, 14.2. IR (ν_{max}, cm^{-1}): 3297, 2928, 2859, 2360, 2103, 1646, 1541, 1378, 1216, 1082, 1013. HRMS (ESI) m/z: calcd for $C_{16}H_{30}NO_5$ [M + H]$^+$ 316.2124, found 316.2123.

*3,3-Dimethyl-N-(5-deoxy-3-O-methyl-1,2-O-isopropylidene-α-D-xylofuranoside)-5-butanamide (**16**).* Orange oil; yield of 0.032 g (45%). $[\alpha]_D^{20}$ −5.3 (c 0.189, $CHCl_3$). R_f = 0.4 (10% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.90 (d, J = 3.8 Hz, 1H), 5.87−5.79 (m, 1H), 4.58 (d, J = 3.8 Hz, 1H), 4.26 (dt, J = 8.2, 3.4 Hz, 1H), 3.90 (ddd, J = 14.2, 8.2, 3.6 Hz, 1H), 3.71 (d, J = 3.4 Hz, 1H), 3.41 (s, 3H), 3.22 (ddd, J = 14.2, 8.2, 3.5 Hz, 1H), 2.06 (s, 2H), 1.47 (s, 3H), 1.32 (s, 3H), 1.03 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.0, 111.9, 105.0, 84.9, 81.9, 79.0, 58.1, 50.8, 38.5, 31.0, 29.9, 26.9, 26.4. IR (ν_{max}, cm^{-1}): 3297, 2955, 2929, 1727, 1639, 1545, 1375, 1217, 1088, 1018. HRMS (ESI) m/z: calcd for $C_{15}H_{28}NO_5$ [M + H]$^+$ 302.1967, found 302.1971.

*3-Methyl-N-(5-deoxy-3-O-methyl-1,2-O-isopropylidene-α-D-xylofuranoside)-5-butanamide (**17**).* Yellow oil; yield of 0.074 g (>95%). $[\alpha]_D^{20}$ −6.8 (c 0.232, CH_2Cl_2). R_f = 0.3 (10% ethyl acetate/*n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.90 (d, J = 3.8 Hz, 1H), 5.88−5.82 (m, 1H), 4.58 (d, J = 3.8 Hz, 1H), 4.31−4.21 (m, 1H), 3.90 (ddd, J = 14.1, 8.0, 3.6 Hz, 1H), 3.71 (d, J = 3.2 Hz, 1H), 3.41 (s, 3H), 3.24 (ddd, J = 14.1, 8.2, 3.5 Hz, 1H), 2.17−2.01 (m, 3H), 1.48 (s, 3H), 1.32 (s, 3H), 0.96 (d, J = 1.6 Hz, 3H), 0.94 (d, J = 1.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.9, 111.9, 105.0, 84.8, 81.9, 79.1, 58.0, 46.2, 38.5, 29.8, 26.8, 26.4, 26.3, 22.6. IR (ν_{max}, cm^{-1}): 3295, 2959, 2929, 1641, 1544, 1373, 1218, 1081, 1013. HRMS (ESI) m/z: calcd for $C_{14}H_{26}NO_5$ [M + H]$^+$ 288.1811, found 288.1808.

*N-(1-Methyl-5-deoxy-2,3-O-isopropylidene-β-D-ribofuranoside)-5-benzamide (**20**).* Yellow oil; yield of 0.105 g (>95%). $[\alpha]_D^{20}$ −65.0 (c 0.620, CH_2Cl_2). R_f = 0.7 (30% ethyl acetate/*n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.82 (d, J = 7.2 Hz, 1H), 7.55−7.34 (m, 3H), 7.16 (br, 1H), 5.04 (s, 1H), 4.68 (d, J = 6.0 Hz, 1H), 4.61 (d, J = 6.0 Hz, 1H), 4.53 (t, J = 4.5 Hz, 1H), 3.95−3.83 (m, 1H), 3.51−3.46 (m, 1H), 3.46 (s, 3H), 1.49 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 167.5, 134.2, 131.7, 128.7, 127.1, 112.6, 110.5, 86.4, 85.8, 82.2, 55.6, 42.6, 26.6, 25.0. IR (ν_{max}, cm^{-1}): 3334, 2986, 2935, 2833, 1737, 1641, 1532, 1371, 1207, 1089, 1043. HRMS (ESI) m/z: calcd for $C_{15}H_{18}NO_4$ [M − OMe]$^+$ 276.1230, found 276.1213; calcd for $C_{16}H_{22}NO_5$ [M + H]$^+$ 308.1498, found 308.1483.

*4-Methyl-N-(1-methyl-5-deoxy-2,3-O-isopropylidene-β-D-ribofuranoside)-5-benzamide (**21**).* Yellow solid; yield of 0.105 g (>95%).

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$[\alpha]_D^{20}$ −63.8 (*c* 0.779, CH_2Cl_2). Mp: 122−125 °C. R_f = 0.7 (30% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.77−7.66 (m, 2H), 7.31−7.17 (m, 3H), 7.16 (br, 1H), 5.03 (s, 1H), 4.68 (d, *J* = 6.0 Hz, 1H), 4.59 (d, *J* = 6.0 Hz, 1H), 4.51 (t, *J* = 4.7 Hz, 1H), 3.86 (ddd, *J* = 14.2, 7.3, 4.7 Hz, 1H), 3.50−3.40 (m, 1H), 3.44 (s, 3H), 2.39 (s, 3H), 1.48 (s, 3H), 1.28 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 167.4, 142.0, 131.3, 129.3, 127.0, 112.5, 110.3, 86.3, 85.7, 82.2, 55.5, 42.5, 26.5, 24.9, 21.5. IR (ν_{max}, cm^{-1}): 3306, 2982, 2928, 2360, 2336, 1718, 1630, 1554, 1372, 1274, 1208, 1088, 1054. HRMS (ESI) *m*/*z*: calcd for $C_{16}H_{20}NO_4$ $[M - OMe]^+$ 290.1392, found 290.1371; calcd for $C_{17}H_{24}NO_5$ $[M + H]^+$ 322.1654, found 322.1639.

*N-(1-Methyl-5-deoxy-2,3-O-isopropylidene-β-D-ribofuranoside)-5-benzeneacetamide (**22**).* Yellow oil; yield of 0.052 g (50%). $[\alpha]_D^{20}$ −54.2 (*c* 0.750, CH_2Cl_2). R_f = 0.6 (30% ethyl acetate/*n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.23 (m, 5H), 6.16 (br, 1H), 4.84 (s, 1H), 4.47 (d, *J* = 6.0 Hz, 1H), 4.32 (d, *J* = 6.0 Hz, 1H), 4.31−4.27 (m, 1H), 3.58 (d, *J* = 3.4 Hz, 2H), 3.56−3.47 (m, 1H), 3.33−3.25 (m, 1H), 3.13 (s, 3H), 1.43 (s, 3H), 1.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.4, 134.9, 129.6, 129.1, 127.5, 112.4, 110.1, 85.8, 85.6, 82.0, 55.2, 44.1, 42.4, 26.4, 24.8. IR (ν_{max}, cm^{-1}): 3304, 3061, 3026, 2985, 2933, 2360, 2339, 1650, 1550, 1520, 1497, 1368, 1213, 1197, 1096, 1071, 1046. HRMS (ESI) *m*/*z*: calcd for $C_{16}H_{20}NO_4$ $[M-OMe]^+$ 290.1392, found 290.1371; calcd for $C_{17}H_{24}NO_5$ $[M + H]^+$ 322.1654, found 322.1643.

*N-(1-Methyl-5-deoxy-2,3-O-isopropylidene-β-D-ribofuranoside)-5-cyclohexaneacetamide (**23**).* Yellow solid; yield of 0.089 g (>95%). $[\alpha]_D^{20}$ −52.9 (*c* 0.750, CH_2Cl_2). Mp: 93−95 °C. R_f = 0.6 (30% ethyl acetate/*n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.25 (br, 1H), 4.97 (s, 1H), 4.58 (d, *J* = 6.0 Hz, 1H), 4.55 (d, *J* = 6.0 Hz, 1H), 4.34 (t, *J* = 5.3 Hz, 1H), 3.58−3.48 (m, 1H), 3.39 (s, 3H), 3.37−3.31 (m, 1H), 2.04 (d, *J* = 4.0 Hz, 1H), 2.03 (d, *J* = 4.0 Hz, 1H),1.75−1.60 (m, 6H), 1.46 (s, 3H), 1.28 (s, 3H), 1.33−1.19 (m, 2H), 1.18−1.07 (m, 1H), 1.00−0.84 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.7, 112.5, 110.2, 86.2, 85.7, 82.2, 55.5, 45.1, 42.2, 35.4, 33.3, 33.3, 26.5, 26.3, 26.2, 26.2, 24.9. IR (ν_{max}, cm^{-1}): 3313, 2989, 2922, 2849, 1730, 1641, 1535, 1376, 1212, 1190, 1161, 1087, 1043. HRMS (ESI) *m*/*z*: calcd for $C_{16}H_{26}NO_4$ $[M - OMe]^+$ 296.1862, found 296.1833; calcd for $C_{17}H_{30}NO_5$ $[M + H]^+$ 328.2124, found 328.2135.

*N-(1-Methyl-5-deoxy-2,3-O-isopropylidene-β-D-ribofuranoside)-5-heptanamide (**24**).* Yellow oil; yield of 0.087 g (>95%). $[\alpha]_D^{20}$ −48.3 (*c* 0.515, CH_2Cl_2). R_f = 0.5 (30% ethyl acetate/*n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.24 (br, 1H), 4.98 (s, 1H), 4.59 (d, *J* = 6.0 Hz, 1H), 4.56 (d, *J* = 6.0 Hz, 1H), 4.35 (t, *J* = 5.3 Hz, 1H), 3.59−3.48 (m, 1H), 3.40 (s, 3H), 3.38−3.31 (m, 1H), 2.18 (t, *J* = 7.6 Hz, 2H), 1.71−1.55 (m, 2H), 1.47 (s, 3H), 1.30 (s, 9H), 0.88 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 173.5, 112.5, 110.2, 86.3, 85.7, 82.2, 55.5, 42.2, 36.9, 31.6, 29.1, 26.5, 25.7, 25.0, 22.6, 14.1. IR (ν_{max}, cm^{-1}): 3296, 2929, 2854, 2361, 1643, 1544, 1373, 1206, 1160, 1092, 1060, 1045, 867, 489. HRMS (ESI) *m*/*z*: calcd for $C_{15}H_{26}NO_4$ $[M - OMe]^+$ 284.1862, found 284.1870; calcd for $C_{16}H_{30}NO_5$ $[M + H]^+$ 316.2124, found 316.2109.

*3,3-Dimethyl-N-(1-methyl-5-deoxy-2,3-O-isopropylidene-β-D-ribofuranoside)-5-butanamide (**25**).* Orange oil; yield of 0.072 g (80%). $[\alpha]_D^{20}$ −63.7 (*c* 0.465, CH_2Cl_2). R_f = 0.4 (30% ethyl acetate/*n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 6.20 (br, 1H), 4.98 (s, 1H), 4.60 (d, *J* = 5.9 Hz, 1H), 4.57 (d, *J* = 5.9 Hz, 1H), 4.35 (t, *J* = 5.4 Hz, 1H), 3.52−3.45 (m, 1H), 3.40 (s, 3H), 3.42−3.35 (m, 1H), 2.06 (s, 2H), 1.47 (s, 3H), 1.30 (s, 3H), 1.04 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.0, 112.5, 110.1, 86.2, 85.6, 82.2, 55.5, 50.8, 42.2, 30.9, 29.9, 26.5, 24.9. IR (ν_{max}, cm^{-1}): 3330, 2948, 2359, 2338, 2360, 2337, 1643, 1540, 1369, 1206, 1092, 1061, 1045. HRMS (ESI) *m*/*z*: calcd for $C_{14}H_{24}NO_4$ $[M^+ - OMe]^+$ 270.1705, found 270.1688; calcd for $C_{15}H_{28}NO_5$ $[M + H]^+$ 302.1967, found 302.1957.

*3-Methyl-N-(1-methyl-5-deoxy-2,3-O-isopropylidene-β-D-ribofuranoside)-5-butanamide (**26**).* Orange solid; yield of 0.072 g (>95%). $[\alpha]_D^{20}$ −64.9 (*c* 0.336, CH_2Cl_2). Mp: 66−68 °C. R_f = 0.4 (30% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 6.25 (br, 1H), 4.99 (s, 1H), 4.60 (d, *J* = 6.0 Hz, 1H), 4.57 (d, *J* = 6.0 Hz, 1H), 4.37 (t, *J* = 5.4 Hz, 1H), 3.60−3.46 (m, 1H), 3.41 (s, 3H), 3.39−3.32 (m, 1H), 2.25−1.88 (m, 3H), 1.48 (s, 3H), 1.30 (s, 3H), 0.97 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.7, 112.5, 110.2, 86.2, 85.6, 82.2, 55.5, 46.3, 42.2, 26.5, 26.2, 24.9, 22.6. IR (ν_{max}, cm^{-1}): 3288, 2951, 2865, 2356, 1753, 1631, 1538, 1367, 1207, 1161, 1087, 1058, 1041, 1012. HRMS (ESI) *m*/*z*: calcd for $C_{13}H_{22}NO_4$ $[M - OMe]^+$ 256.1543, found 256.1549; calcd for $C_{14}H_{26}NO_5$ $[M + H]^+$ 288.1811, found 288.1835.

*N-(1-Methyl-5-deoxy-2,3-O-isopropylidene-β-D-mannofuranoside)-5-benzeneacetamide (**27**).* Yellow solid; yield of 0.041 g (80%). $[\alpha]_D^{20}$ +61.4 (*c* 0.181, CH_2Cl_2). Mp: 78−80 °C. R_f = 0.4 (30% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.40−7.22 (m, 5H), 5.83 (br, 1H), 4.82 (s, 1H), 4.57 (dd, *J* = 5.9, 3.6 Hz, 1H), 4.50 (d, *J* = 5.9 Hz, 1H), 4.03−3.94 (m, 1H), 3.75−3.61 (m, 1H), 3.58 (s, 2H), 3.55−3.39 (m, 1H), 3.22 (s, 3H), 1.37 (s, 3H), 1.25 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 171.3, 135.1, 129.5, 129.1, 127.4, 112.7, 107.1, 85.2, 79.9, 77.6, 54.6, 44.0, 38.8, 26.0, 24.7. IR (ν_{max}, cm^{-1}): 3340, 3360, 3330, 2988, 2935, 1733, 1647, 1539, 1454, 1424, 1380, 1370, 1356, 1260, 1203, 1160, 1008. HRMS (ESI) *m*/*z*: calcd for $C_{16}H_{20}NO_4$ $[M - OMe]^+$ 290.1392, found 290.1363; calcd for $C_{17}H_{24}NO_5$ $[M + H]^+$ 322.1654, found 322.1656.

*N-(1-Methyl-5-deoxy-2,3-O-isopropylidene-β-D-mannofuranoside)-5-cyclohexaneacetamide (**28**).* Yellow oil; yield of 0.0252 g (>95%). $[\alpha]_D^{20}$ +62.9 (*c* 0.332, CH_2Cl_2). R_f = 0.5 (30% ethyl acetate/*n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.85 (br, 1H), 4.88 (s, 1H), 4.67 (dd, *J* = 5.9, 3.7 Hz, 1H), 4.56 (d, *J* = 5.9 Hz, 1H), 4.07 (ddd, *J* = 7.1, 5.6, 3.7 Hz, 1H), 3.77−3.64 (m, 1H), 3.61−3.44 (m, 1H), 3.30 (s, 3H), 2.05 (d, *J* = 7.0 Hz, 2H), 1.84−1.59 (m, 5H), 1.47 (s, 3H), 1.31 (s, 3H), 1.30−1.06 (m, 4H), 1.02−0.81 (m, 2H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.5, 112.5, 106.9, 85.0, 79.8, 77.6, 54.5, 44.9, 38.3, 35.4, 33.0, 33.0, 26.1, 26.03, 25.9, 24.6. IR (ν_{max}, cm^{-1}): 3315, 2927, 2852, 1729, 1641, 1543, 1441, 1381, 1274, 1260, 1205, 1188, 1163, 1138, 1016. HRMS (ESI) *m*/*z*: calcd for $C_{16}H_{26}NO_4$ $[M - OMe]^+$ 296.1862, found 296.1843; calcd for $C_{17}H_{30}NO_5$ $[M + H]^+$ 328.2124, found 328.2146.

*3,3-Dimethyl-N-(1-methyl-5-deoxy-2,3-O-isopropylidene-β-D-mannofuranoside)-5-butanamide (**29**).* Yellow oil; yield of 0.098 g (65%). $[\alpha]_D^{20}$ +68.2 (*c* 0.251, CH_2Cl_2). R_f = 0.4 (30% ethyl acetate/*n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.89 (br, 1H), 4.87 (s, 1H), 4.66 (dd, *J* = 5.9, 3.7 Hz, 1H), 4.54 (d, *J* = 5.9 Hz, 1H), 4.12−4.03 (m, 1H), 3.74−3.64 (m, 1H), 3.53−3.43 (m, 1H), 3.29 (s, 3H), 2.06 (s, 2H), 1.45 (s, 3H), 1.30 (s, 3H), 1.03 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.0, 112.7, 107.1, 85.2, 80.0, 77.8, 54.7, 50.7, 38.5, 31.0, 29.9, 26.1, 24.8. IR (ν_{max}, cm^{-1}): 3294, 2994, 1730, 1632, 1551,1463, 1368, 1110, 1091, 1033, 1002. HRMS (ESI) *m*/*z*: calcd for $C_{14}H_{24}NO_4$ $[M - OMe]^+$ 270.1705, found 270.1713; calcd for $C_{15}H_{28}NO_5$ $[M + H]^+$ 302.1967, found 302.1992.

*3-Methyl-N-(1-methyl-5-deoxy-2,3-O-isopropylidene-β-D-mannofuranoside)-5-butanamide (**30**).* Yellow solid; yield of 0.113 g (78%). $[\alpha]_D^{20}$ +75.6 (*c* 0.415, CH_2Cl_2). Mp: 74−76 °C. R_f = 0.4 (30% ethyl acetate/*n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.00 (br, 1H), 4.88 (s, 1H), 4.68 (dd, *J* = 5.9, 3.7 Hz, 1H), 4.56 (d, *J* = 5.9 Hz, 1H), 4.08 (ddd, *J* = 7.0, 5.5, 3.7 Hz, 1H), 3.71 (ddd, *J* = 13.9, 6.8, 5.5 Hz, 1H), 3.51 (ddd, *J* = 13.9, 7.0, 5.3 Hz, 1H), 3.30 (s, 3H), 2.19−2.03 (m, 3H, α-CH_2), 1.46 (s, 3H), 1.31 (s, 3H), 0.97 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.8, 112.7, 107.0, 85.1, 80.0, 77.7, 54.6, 46.2, 38.4, 26.3, 26.1, 24.7, 22.5, 22.5. IR (ν_{max}, cm^{-1}): 3335, 2955, 2926, 1729, 1639, 1546, 1369, 1270, 1205, 1191, 1164, 1107, 1094, 1073, 1010. HRMS (ESI) *m*/*z*: calcd for $C_{13}H_{22}NO_4$ $[M - OMe]^+$ 256.1549, found 256.1541; calcd for $C_{14}H_{26}NO_5$ $[M + H]^+$ 288.1811, found 288.1803.

*N-(1-Methyl-5-deoxy-2,3-O-isopropylidene-β-D-mannofuranoside)-5-heptanamide (**31**).* Yellow oil; yield of 0.046 g (30%). $[\alpha]_D^{20}$ +66.2 (*c* 0.244, CH_2Cl_2). R_f = 0.4 (30% ethyl acetate/*n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.88 (br, 1H), 4.89 (s, 1H), 4.68 (dd, *J* = 5.9, 3.7 Hz, 1H), 4.56 (d, *J* = 5.9 Hz, 1H), 4.10−4.04 (m, 1H), 3.74−3.66 (m, 1H), 3.53 (ddd, *J* = 13.9, 7.0, 5.2 Hz, 1H), 3.31 (s, 3H), 2.19 (t, *J* = 7.8 Hz, 2H), 1.69−1.58 (m, 2H), 1.47 (s, 3H),1.31 (s, 3H), 1.38−1.23 (m, 6H), 0.88 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.6, 112.7, 107.1, 85.2, 80.1, 77.6, 54.7, 38.5, 36.9, 31.7, 29.0, 26.1, 25.8, 24.8, 22.6, 14.2. IR (ν_{max}, cm^{-1}): 3330, 2923, 2851, 1734, 1639, 1542, 1377, 1267, 1203, 1095, 1080, 1052, 1010. HRMS

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(ESI) m/z: calcd for $C_{15}H_{26}NO_4$ $[M - OMe]^+$ 284.1862, found 284.1874; calcd for $C_{16}H_{30}NO_5$ $[M + H]^+$ 316.2124, found 316.2125.

*N-(6-Deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose)-5-benzeneacetamide (**32**).* White solid; yield of 0.073 g (76%). $[\alpha]_D^{20}$ −21.1 (c 0.416, CH_2Cl_2). Mp: 92−94 °C. R_f = 0.4 (30% ethyl acetate/n-hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.37−7.30 (m, 3H), 7.29−7.23 (m, 2H), 6.01−5.91 (m, 1H), 5.45 (d, J = 4.9 Hz, 1H), 4.56 (dd, J = 7.9, 2.4 Hz, 1H), 4.27 (dd, J = 4.9, 2.4 Hz, 1H), 4.14 (dd, J = 7.9, 1.8 Hz, 1H), 3.86 (ddd, J = 9.0, 3.6, 1.8 Hz, 1H), 3.70 (ddd, J = 13.7, 7.8, 3.6 Hz, 1H), 3.56 (s, 2H), 3.15 (ddd, J = 13.7, 9.0, 4.0 Hz, 1H), 1.44 (s, 3H), 1.39 (s, 3H), 1.31 (s, 3H), 1.30 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 171.5, 135.0, 129.5, 129.0, 127.3, 109.5, 108.9, 96.3, 71.7, 70.9, 70.7, 66.5, 43.9, 40.3, 26.1, 26.0, 25.1, 24.3. IR (ν_{max}, cm^{-1}): 3307, 2922, 2849, 2360, 1728, 1639, 1547, 1448, 1371, 1252, 1205, 1165, 1066, 1002, 892. HRMS (ESI) m/z: calcd for $C_{20}H_{28}NO_6$ $[M + H]^+$ 378.1916, found 378.1938.

*N-(6-Deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose)-5-cyclohexaneacetamide (**33**).* Yellow solid; yield of 0.044 g (50%). $[\alpha]_D^{20}$ −11.8 (c 0.284, CH_2Cl_2). Mp: 76−78 °C. R_f = 0.3 (30% ethyl acetate/n-hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 5.97−5.89 (m,1H), 5.51 (d, J = 5.0 Hz, 1H), 4.59 (dd, J = 8.0, 2.3 Hz, 1H), 4.30 (dd, J = 5.0, 2.3 Hz, 1H), 4.20 (dd, J = 8.0, 1.1 Hz, 1H), 3.91−3.85 (m, 1H), 3.79 (ddd, J = 13.2, 8.1, 3.2 Hz, 1H), 3.13 (ddd, J = 13.2, 9.2, 2.8 Hz, 1H), 2.08 (dd, J = 13.7, 6.5 Hz, 1H), 2.00 (dd, J = 13.7, 7.2 Hz, 1H), 1.82−1.61 (m, 6H), 1.47 (s, 3H), 1.45 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H), 1.29−1.20 (m, 2H), 1.20−1.08 (m, 1H), 1.00−0.86 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.6, 109.3, 108.7, 96.2, 71.6, 70.7, 70.5, 66.69, 44.9, 39.7, 35.3, 33.1, 32.9, 26.1, 26.0, 26.0, 25.9, 25.9, 24.9, 24.2. IR (ν_{max}, cm^{-1}): 3304, 2921, 2847, 1726, 1638, 1547, 1448, 1371, 1254, 1207, 1165, 1065, 1001. HRMS (ESI) m/z: calcd for $C_{20}H_{34}NO_6$ $[M + H]^+$ 384.2386, found 384.2390.

*3,3-Dimethyl-N-(6-deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose)-5-butanamide (**34**).* White solid; yield of 0.048 g (54%). $[\alpha]_D^{20}$ −11.2 (c 0.303, CH_2Cl_2). Mp: 110−112 °C. R_f = 0.5 (30% ethyl acetate/n-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.89−5.81 (m, 1H), 5.51 (d, J = 5.0 Hz, 1H), 4.59 (dd, J = 8.0, 2.3 Hz, 1H), 4.30 (dd, J = 5.0, 2.3 Hz, 1H), 4.23−3.17 (m, 1H), 3.91−3.85 (m, 1H), 3.81 (ddd, J = 13.9, 8.2, 3.2 Hz, 1H), 3.13 (ddd, J = 13.9, 9.5, 3.8 Hz, 1H), 2.09 (d, J = 12.9 Hz, 1H), 2.03 (d, J = 12.9 Hz, 1H), 1.47 (s, 3H), 1.45 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H), 1.04 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 172.0, 109.5, 108.9, 96.4, 71.8, 70.9, 70.7, 66.9, 50.8, 39.9, 30.9, 30.0, 26.2, 26.1, 25.1, 24.4. IR (ν_{max}, cm^{-1}): 3362, 2985, 2949, 2868, 1727, 1660, 1533, 1507, 1368, 1245, 1211, 1170, 1099, 1066. HRMS (ESI) m/z: calcd for $C_{18}H_{32}NO_6$ $[M + H]^+$ 358.2230, found 358.2242.

*3-Methyl-N-(6-deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose)-5-butanamide (**35**).* Yellow solid; yield of 0.046 g (54%). $[\alpha]_D^{20}$ −14.5 (c 0.291, CH_2Cl_2). Mp: 93−95 °C. R_f = 0.3 (30% ethyl acetate/n-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.98−5.86 (m, 1H), 5.51 (d, J = 4.9 Hz, 1H), 4.60 (dd, J = 7.9, 2.3 Hz, 1H), 4.31 (dd, J = 4.9, 2.3 Hz, 1H), 4.21 (dd, J = 7.9, 1.6 Hz, 1H), 3.93−3.85 (m, 1H), 3.79 (ddd, J = 14.0, 8.1, 3.3 Hz, 1H), 3.15 (ddd, J = 14.0, 9.4, 3.8 Hz, 1H), 2.15−1.97 (m, 3H), 1.47 (s, 3H), 1.45 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H), 0.96 (s, 3H), 0.95 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): δ 173.0, 109.5, 108.9, 96.4, 71.8, 70.9, 70.7, 66.8, 46.2, 40.0, 26.3, 26.1, 26.1, 25.1, 24.4, 22.7, 22.5. IR (ν_{max}, cm^{-1}): 3285, 2957, 2930, 1634, 1549, 1370, 1255, 1207, 1167, 1109, 1065, 1001. HRMS (ESI) m/z: calcd for $C_{17}H_{30}NO_6$ $[M + H]^+$ 344.2073, found 344.2054.

*N-(6-Deoxy-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose)-5-heptanamide (**36**).* Yellow oil; yield of 0.032 g (35%). $[\alpha]_D^{20}$ −36.6 (c 0.190, CH_2Cl_2). R_f = 0.5 (30% ethyl acetate/n-hexane). ^{1}H NMR (300 MHz, $CDCl_3$): δ 5.91−5.88 (m, 1H), 5.51 (d, J = 5.0 Hz, 1H), 4.60 (dd, J = 7.9, 2.4 Hz, 1H), 4.31 (dd, J = 5.0, 2.4 Hz, 1H), 4.21 (dd, J = 7.9, 1.9 Hz, 1H), 3.89 (ddd, J = 9.0, 3.4, 1.9 Hz, 1H), 3.77 (ddd, J = 14.0, 8.0, 3.4 Hz, 1H), 3.16 (ddd, J = 14.0, 9.0, 3.7 Hz, 1H), 2.17 (td, J = 7.3, 1.6 Hz, 2H), 1.68−1.55 (m, 2H), 1.48 (s, 3H), 1.45 (s, 3H), 1.34 (s, 3H), 1.32 (s, 3H), 1.31−1.22 (m, 6H), 0.88 (t, J = 6.8 Hz, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.7, 109.5, 108.9, 96.4, 71.8, 70.9, 70.7, 66.7, 40.0, 37.0, 31.7, 29.1, 26.21, 26.1, 25.9, 25.1, 24.4, 22.6, 14.2. IR (ν_{max}, cm^{-1}): 3307, 2982, 2952, 2928, 2859, 1647, 1536, 1374, 1251, 1210, 1169, 1068, 1004. HRMS (ESI) m/z: calcd for $C_{19}H_{34}NO_6$ $[M + H]^+$ 372.2386, found 372.2387.

*N-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)benzamide (**37**).* CAS registry number: 18918-50-8. Orange solid; yield of 0.136 g, (60%). $[\alpha]_D^{20}$ −10.4 (c 0.777, CH_2Cl_2). Mp: 188−190 °C. R_f = 0.5 (30% ethyl acetate/n-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 7.6 Hz, 2H), 7.52 (t, J = 7.6 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.19 (d, J = 9.1 Hz, 1H), 5.45 (t, J = 9.5 Hz, 1H), 5.38 (t, J = 9.5 Hz, 1H), 5.11 (d, J = 9.5 Hz, 1H), 5.06 (d, J = 9.1 Hz, 1H), 4.33 (dd, J = 12.5, 4.3 Hz, 1H), 4.12−4.06 (m, 1H), 3.90 (ddd, J = 9.5, 4.3, 2.1 Hz, 1H), 2.06−2.03 (3s, 12H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.5, 170.7, 170.0, 169.7, 167.3, 132.8, 132.5, 128.8, 127.3, 78.9, 73.6, 72.7, 70.9, 68.3, 61.7, 20.8, 20.7. IR (ν_{max}, cm^{-1}): 3323, 2970, 2944, 2919, 2118, 1742, 1736, 1662, 1527, 1370, 1242, 1219, 1099, 1031. HRMS (ESI) m/z: calcd for $C_{21}H_{26}NO_{10}$ $[M + H]^+$ 452.1551, found 452.1548.

*4-Methyl-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-benzamide (**38**).* CAS registry number: 353264-43-4. White solid; yield of 0.093 g (40%). $[\alpha]_D^{20}$ −25.3 (c 0.396, CH_2Cl_2). Mp: 185−187 °C. R_f = 0.5 (30% ethyl acetate/n-hexane). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.66 (d, J = 8.2 Hz, 2H), 7.25 (d, J = 8.2 Hz, 2H), 7.07 (d, J = 9.1 Hz, 1H), 5.44 (t, J = 9.3 Hz, 1H), 5.39 (t, J = 9.3 Hz, 1H), 5.11 (t, J = 9.2 Hz, 1H), 5.07 (t, J = 9.1 Hz, 1H), 4.34 (dd, J = 12.5, 4.2 Hz, 1H), 4.10 (dd, J = 12.5, 2.1 Hz, 1H), 3.90 (ddd, J = 9.3, 4.2, 2.1 Hz, 1H), 2.40 (s, 3H), 2.08 (s, 3H), 2.05 (2s, 6H), 2.03 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.5, 170.7, 170.0, 169.7, 167.2, 143.1, 130.0, 129.5, 127.4, 79.0, 73.6, 72.7, 70.8, 68.3, 61.7, 21.6, 20.8, 20.85, 20.76, 20.7. IR (ν_{max}, cm^{-1}): 3262, 2920, 2850, 2108, 1744, 1648, 1547, 1370, 1218, 1027, 1054. HRMS (ESI) m/z: calcd for $C_{22}H_{27}NNaO_{10}$ $[M + Na]^+$ 488.1527, found 488.1521.

*N-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)benzeneacetamide (**39**).* CAS registry number: 439595-86-5. Yellow solid; yield of 0.104 g (50%). $[\alpha]_D^{20}$ +0.3 (c 0.946, CH_2Cl_2). Mp: 158−160 °C. R_f = 0.3 (30% ethyl acetate/n-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.39−7.26 (m, 3H), 7.25−7.19 (m, 2H), 6.34 (d, J = 9.6 Hz, 1H), 5.26 (t, J = 9.7 Hz, 1H), 5.21 (t, J = 9,7 Hz, 1H), 5.02 (t, J = 9.6 Hz, 1H), 4.83 (t, J = 9.6 Hz, 1H), 4.30 (dd, J = 12.5, 4.3 Hz, 1H), 4.07 (dd, J = 12.5, 2.1 Hz, 1H), 3.81 (ddd, J = 9.7, 4.3, 2.1 Hz, 1H), 3.58 (d, J = 15.2 Hz, 1H), 3.49 (d, J = 15.2 Hz, 1H), 2.07 (s, 3H), 2.01 (s, 3H), 1.98 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 171.2, 170.5, 170.4, 169.7, 169.4, 133.7, 129.0, 128.9, 127.4, 78.1, 73.4, 72.5, 70.0, 67.9, 61.5, 43.6, 20.6, 20.4, 20.4, 20.2. IR (ν_{max}, cm^{-1}): 3298, 3063, 3032, 2945, 2359, 2107, 1739, 1674, 1539, 1364, 1214, 1028. HRMS (ESI) m/z: calcd for $C_{22}H_{28}NO_{10}$ $[M + H]^+$ 466.1708, found 466.1726.

*N-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-cyclohexaneacetamide (**40**).* Orange solid; yield of 0.138 g (60%). $[\alpha]_D^{20}$ +8.2 (c 1.035, CH_2Cl_2). Mp: 190−192 °C. R_f = 0.5 (30% ethyl acetate/n-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.27 (d, J = 9.6 Hz, 1H), 5.31 (t, J = 9.5 Hz, 1H), 5.27 (t, J = 9.5 Hz, 1H), 5.06 (t, J = 9.5 Hz, 1H), 4.92 (t, J = 9.5 Hz, 1H), 4.33 (dd, J = 12.5, 4.3 Hz, 1H), 4.07 (dd, J = 12.5, 2.1 Hz, 1H), 3.83 (ddd, J = 9.5, 4.3, 2.1 Hz, 1H), 2.08 (s, 3H), 2.03 (s, 6H), 2.02 (s, 3H), 1.80−0.80 (m, 13H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.9, 171.1, 170.8, 170.0, 169.7, 78.1, 73.6, 72.8, 70.6, 68.3, 61.8, 44.9, 35.2, 33.1, 32.9, 26.1, 26.1, 26.0, 20.9, 20.7, 20.7. IR (ν_{max}, cm^{-1}): 3317, 2921, 2850, 1742, 1662, 1526, 1367, 1257, 1212, 1030. HRMS (ESI) m/z: calcd for $C_{22}H_{34}NO_{10}$ $[M + H]^+$ 472.2177, found 472.2187.

*N-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)heptanamide (**41**).* White solid; yield of 0.123 g (54%). $[\alpha]_D^{20}$ +13.3 (c 0.932, CH_2Cl_2). Mp: 90−92 °C. R_f = 0.4 (30% ethyl acetate/n-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.31 (d, J = 9.6 Hz, 1H), 5.31 (t, J = 9.6 Hz, 1H) 5.28 (t, J = 9.6 Hz, 1H), 5.06 (t, J = 9.6 Hz, 1H), 4.92 (t, J = 9.6 Hz, 1H), 4.32 (dd, J = 12.5, 4.4 Hz, 1H), 4.08 (dd, J = 12.5, 2.1 Hz, 1H), 3.83 (ddd, J = 9.6, 4.4, 2.1 Hz, 1H), 2.24−2.11 (m, 2H), 2.08 (s, 3H), 2.04 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.71−1.50 (m, 2H), 1.38−1.19 (m, 6H), 0.93−0.82 (m, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 173.6, 170.8, 170.6, 169.9, 169.6, 78.0, 73.5, 72.8, 70.6, 68.2, 61.7, 36.6, 31.4, 28.8, 25.1, 22.5, 20.7, 20.67, 20.61, 14.0. IR (ν_{max}, cm^{-1}): 3337, 2928, 2855, 2359, 1741, 1669, 1515, 1366, 1213, 1037. HRMS (ESI) m/z: calcd for $C_{21}H_{33}NNaO_{10}$ $[M + Na]^+$ 482.1997, found 482.1971.

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*N-(2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl)-3,3-dimethylbutanamide (**42**).* Yellow solid; yield of 0.121 g (65%). $[\alpha]_D^{20}$ +6.9 (*c* 0.834, CH_2Cl_2). Mp: 88−90 °C. R_f = 0.3 (30% ethyl acetate/*n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.33 (d, *J* = 9.6 Hz, 1H), 5.31 (t, *J* = 9.6 Hz, 1H), 5.27 (t, *J* = 9.6 Hz, 1H), 5.06 (t, *J* = 9.6 Hz, 1H), 4.94 (t, *J* = 9.6 Hz, 1H), 4.32 (dd, *J* = 12.4, 4.4 Hz, 1H), 4.07 (dd, *J* = 12.4, 2.1 Hz, 1H), 3.83 (ddd, *J* = 9.6, 4.4, 2.1 Hz, 1H), 2.07 (s, 3H), 2.03 (s, 3H), 2.03 (s, 3H), 2.02 (s, 3H), 1.26 (s, 2H), 1.00 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.3, 170.9, 170.7, 169.9, 169.7, 77.9, 73.5, 73.0, 70.4, 68.3, 61.8, 50.3, 31.0, 29.6, 20.7, 20.7, 20.6, 20.6. IR (ν_{max}, cm^{-1}):3308, 2954, 2869, 1746, 1673, 1530, 1363, 1210, 1028. HRMS (ESI) *m*/*z*: calcd for $C_{20}H_{32}NO_{10}$ $[M + H]^+$ 446.2021, found 446.2040.

*3-Methyl-N-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranosyl)-butanamide (**43**).* CAS registry number: 756517-45-0. Yellow solid; yield of 0.105 g (54%). $[\alpha]_D^{20}$ +15.0 (*c* 0.490, CH_2Cl_2). Mp: 137−139 °C. R_f = 0.3 (30% ethyl acetate/*n*-hexane). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.31 (d, *J* = 9.6 Hz, 1H), 5.31 (t, *J* = 9.6 Hz, 1H), 5.29 (t, *J* = 9.6 Hz, 1H), 5.06 (t, *J* = 9.6 Hz, 1H), 4.93 (t, *J* = 9.6 Hz, 1H), 4.32 (dd, *J* = 12.5, 4.4 Hz, 1H), 4.08 (dd, *J* = 12.5, 2.1 Hz, 1H), 3.83 (ddd, *J* = 9.6, 4.4, 2.1 Hz, 1H), 2.08 (s, 3H), 2.03 (s, 6H), 2.02 (s, 3H), 1.30−1.20 (m, 2H), 1.02−0.75 (m, 7H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 172.8, 170.9, 170.6, 169.8, 169.5, 77.9, 73.4, 72.6, 70.4, 68.1, 61.6, 45.8, 25.9, 22.3, 22.2, 22.0, 20.6, 20.6, 20.5. IR (ν_{max}, cm^{-1}): 3257, 2959, 2924, 2871, 1742, 1658, 1549, 1367, 1204, 1032. HRMS (ESI) *m*/*z*: calcd for $C_{19}H_{30}NO_{10}$ $[M + H]^+$ 432.1886, found 432.1864.

General Procedure for Amidation Using a Carboxylic Acid. Under an argon atmosphere, to a solution of 4-phenylbutyric acid (1.0 mmol, 0.164 g) in THF (2 mL) was added *N*-methylmorpholine (1.0 mmol, 108 μL). After stirring for 15 min at room temperature, ethyl chloroformate (1.0 mmol, 95 μL) was added, and stirring was prolonged for an additional 5 min. Then, freshly prepared Li_2Se (1 mmol) was slowly added into the obtained mixed anhydride solution using a cannula. After an additional 30 min of stirring, a solution of azide (0.25 mmol in 2 mL of THF) was added over the selenocarboxylate solution using a syringe. The reaction was carried out at 50 °C. When TLC showed the consumption of the starting azide, selenium powder was precipitated, or no further changes of the reaction mixture were observed. The reaction mixture was quenched with aqueous saturated $NaHCO_3$ (10 mL) and extracted with CH_2Cl_2 (3 × 15 mL). The combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by flash column chromatography eluting with a mixture of hexane/ethyl acetate (90:10).

*N-(1-Methyl-5-deoxy-2,3-O-isopropylidene-β-D-ribofuranoside)-5-(4-phenylbutyric) (**44**).* Yellow oil; yield of 0.089 g (95%). $[\alpha]_D^{20}$ −0.3 (*c* 0.631, CH_2Cl_2). R_f = 0.4 (30% ethyl acetate/*n*-hexane). ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.31−7.25 (m, 2H), 7.21−7.16 (m, 3H), 6.16 (br, 1H), 4.97 (s, 1H), 4.58 (d, *J* = 6.0 Hz, 1H), 4.55 (d, *J* = 6.0 Hz, 1H), 4.33 (t, *J* = 5.5 Hz, 1H), 3.53−3.46 (m, 1H), 3.41−3.37 (m, 1H), 3.36 (s, 3H), 2.65 (t, *J* = 7.5 Hz, 2H), 2.19 (t, *J* = 7.5 Hz, 2H), 1.97 (qn, *J* = 7.5 Hz, 2H), 1.47 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$): δ 172.7, 141.3, 128.3, 128.3, 125.8, 112.3, 109.9, 86.0, 85.4, 82.0, 55.2, 42.1, 35.8, 35.0, 26.9, 26.3, 24.8. IR (ν_{max}, cm^{-1}): 3299, 2988, 2934, 2858, 1728, 1640, 1547, 1450, 1374, 1206, 1092, 1058, 1040, 1014. HRMS (ESI) *m*/*z*: calcd for $C_{19}H_{28}NO_5$ $[M + H]^+$ 350.1967, found 350.1969.

General Procedure for *O,O*-Isopropylidene Deprotection. The protected *N*-glucosyl amide (0.3 mmol) was dissolved in a solution of trifluoroacetic acid in methanol (9:1, 5 mL) and stirred for 1 h. Then, the solvents were coevaporated with toluene/chloroform under vacuum, yielding the unprotected *N*-glucosyl amide without further purification.

*N-α-D-Galactopyranose-5-benzeneacetamide (**45**).* White solid; yield of 0.089 g (>95%). $[\alpha]_D^{20}$ +0.3 (*c* 0.437, CH_2Cl_2). Mp: 122−124 °C. R_f = 0.1 (50% ethyl acetate/*n*-hexane). ^{1}H NMR (400 MHz, D_2O): δ 7.58−6.96 (m, 5H), 5.24−5.21 (m, 1H), 4.52 (d, *J* = 7.8 Hz, 1H), 4.17−3.98 (m, 1H), 3.84−3.77 (m, 2H), 3.71−3.64 (m, 1H), 3.62 (s, 4H), 3.54−3.42 (m, 1H), 3.42−3.27 (m, 1H). ^{13}C NMR (101 MHz, D_2O): δ 175.0, 134.8, 129.0, 128.8, 127.2, 96.3, 92.2, 72.6, 71.6, 69.4, 68.8, 68.1, 42.2, 39.8. IR (ν_{max}, cm^{-1}): 3307, 3085, 2980, 2953, 2926, 2857, 2360, 2115, 1729, 1647, 1537, 1455, 1372, 1252, 1207, 1163, 1103, 1065, 1004. HRMS (ESI) *m*/*z*: calcd for $C_{14}H_{20}NO_6$ $[M + H]^+$ 298.1291, found 298.1289.

General Procedure for *O*-Acetyl Deprotection. The protected *N*-glucosyl amide (0.3 mmol) was dissolved in dry MeOH (3 mL), and sodium methoxide (1 M solution in MeOH, 200 μL) was added. The mixture was stirred for 1 h, neutralized with Amberlite IR120 (H), and filtered, and the solvents were coevaporated with toluene to dryness.

*N-β-D-Glucopyranosyl-benzamide (**46**).* CAS registry number: 15354-97-9. White solid; yield of 0.085 g (>95%). $[\alpha]_D^{20}$ +0.4 (*c* 0.010, CH_2Cl_2). Mp: 141−142 °C. R_f = 0.1 (50% ethyl acetate/*n*-hexane). ^{1}H NMR (300 MHz, CD_3OD): δ 7.89−7.82 (m, 2H), 7.55−7.37 (m, 3H), 5.19−5.01 (m, 1H), 3.82 (dd, *J* = 12.0, 2.0 Hz, 1H), 3.65 (dd, *J* = 12.0, 4.8 Hz, 1H), 3.50−3.25 (m, 5H). ^{13}C NMR (75 MHz, CD_3OD): δ 170.9, 135.1, 133.0, 129.4, 128.6, 81.6, 79.7, 78.9, 73.6, 71.3, 62.5. IR (ν_{max}, cm^{-1}): 3300, 2923, 2875, 2361, 2337, 1642, 1522, 1491, 1289, 1071, 1030, 714. HRMS (ESI) *m*/*z*: calcd for $C_{13}H_{18}NO_6$ $[M + H]^+$ 284.1134, found 284.1145.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00832.

NMR spectra for all compounds (PDF)

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Notes

The authors declare no competing financial interest.

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