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Selective Deprotection Method of *N*-Phenylcarbamoyl Group

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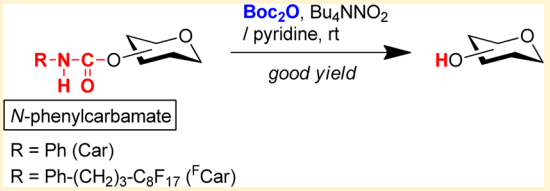
Supporting Information

ABSTRACT: We report an improved method for the selective deprotection of the *N*-phenylcarbamoyl group, which yields the corresponding alcohol without affecting other protecting groups. Deprotection was performed using di-*tert*-butyl dicarbonate and tetra-*n*-butylammonium nitrite (Boc_2O and Bu_4NNO_2) in pyridine at room temperature. This method is also effective for deprotecting the fluorous *N*-phenylcarbamoyl group.



Protecting groups are essential tools in organic chemistry. Introduction and removal of protecting groups are often key steps in the synthesis of oligosaccharides and polyfunctional natural products.[1−3] Consequently, demand continues for more varied, robust, economical, and/or chemically differentiable protecting groups.[4]

One such protecting group, the *N*-phenylcarbamoyl (Car) group, is sometimes used to protect hydroxy groups in carbohydrates due to its stability over a wide pH range and its ability to direct stereochemistry during glycosylation (i.e., the neighboring group participating effect) similar to an ester group. Therefore, it would be advantageous if the deprotection conditions for removing ester and carbamate type protecting groups were orthogonal.

The *N*-phenylcarbamoyl group is easily introduced with phenyl isocyanate/pyridine.[5] However, the traditional cleaving method requires reflux conditions such as (i) NaOMe/MeOH,[6] (ii) $LiAlH_4$/THF or dioxane,[7] (iii) Cl_3SiH, Et_3N, or CH_2Cl_2 at 25−80 °C,[8] or (iv) strong acid. Accordingly, other functional and protecting groups are often affected as well, except in the case of condition (iii). We previously reported a mild and selective method for deprotection of the *N*-phenylcarbamoyl group using Ac_2O and Bu_4NNO_2 in pyridine[9] (Figure 1) and its

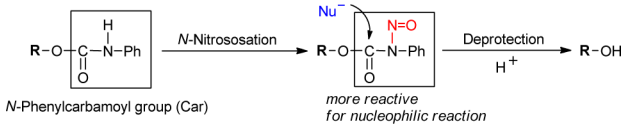


Figure 1. Deprotection procedure of the *N*-phenylcarbamoyl group (Car).

application to the synthesis of partially acylated trisaccharide esters, telephiose A, and oligosaccharides.[10] The deprotection reaction proceeds via *N*-nitrosation, i.e., activation of the carbonyl group attached to nitrogen. Deprotection is performed by nucleophilic attack on the carbonyl group, whereas nucleophilic attack at the *N*-nitroso nitrogen atom leads to the starting compound (no deprotection). However, this method has disadvantages such as the need for repeated addition of acetic anhydride and subsequent warming to 40 °C. In some cases, the reaction takes a long time and gives low yields due to formation of acetylated or migrated (migration of Car) side products. Moreover, the fluorous *N*-phenylcarbamoyl group [^{F}Car ($CONHC_6H_4(CH_2)_3C_8F_{17}$)], developed by Takeuchi's group,[11] was not deprotected by this method. Thus, an alternate deprotection method is still desired. We report herein an improved method for selective deprotection of hydroxy groups with the *N*-phenylcarbamoyl group, using di-*tert*-butyl dicarbonate and tetra-*n*-butylammonium nitrite (Boc_2O and Bu_4NNO_2) in pyridine at room temperature (rt). This method also deprotects the fluorous *N*-phenylcarbamyl group without affecting other protecting groups.

A major objective in devising a new deprotection method is to prevent the formation of undesired acylated or migrated side products. Thus, we examined the reaction with various acid anhydrides under the previous deprotection conditions using 1,2:5,6-di-*O*-isopropylidene-3-*O*-(*N*-phenylcarbamoyl)-α-D-glucofuranose (**1a**) as a substrate to compare with the original method using Ac_2O.[9] Entry 1 in Table 1 is cited as the reference using the previous conditions.[9] First, strong acid anhydrides, such as trifluoroacetic anhydride, methanesulfonic anhydride, and trifluoromethanesulfonic anhydride, were examined (Table 1, entries 2−4), which gave unsuccessful results. Next, the steric effect of the anhydride was examined by using Piv_2O (pivalic anhydride (trimethylacetic anhydride)) (entry 5), which gave the corresponding deprotected product **1c**[12] in 75% yield. Boc_2O (di-*tert*-butyl dicarbonate) (entry 6) promoted the reaction to give the corresponding product in better yield than the other reagents. Upon consideration of the above results, we examined the reaction with Boc_2O in more detail. The results with Boc_2O under convenient and mild conditions are shown in entries 7 and 8. Under these conditions, the Car group was deprotected within 2 h to give the deprotected product in better yield. Furthermore, we

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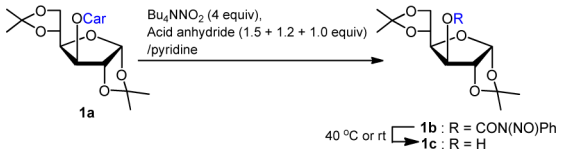
Table 1. Deprotection of *N*-Phenylcarbamoyl Group of 1a Using Various Acid Anhydrides and Bu_4NNO_2



entry	acid anhydride (first + second + third equiv)	temp (°C)	time (h)	yield (%) 1b[9]	yield (%) 1c[12]
1[9]	Ac_2O (1.5, 1.2, 1.0)	0 → 40	7	100	76
2	$(CF_3CO)_2O$ (1.5, 1.2, 1.0)	0 → 40	7	20	trace
3	Ms_2O (1.5, 1.2, 1.0)	0 → 40	7	no reaction	no deprotection
4	Tf_2O (1.5, 1.2, 1.0)	0 → 40	7	no reaction	no deprotection
5	Piv_2O (1.5, 1.2, 1.0)	0 → 40	2	100	75
6	Boc_2O (1.5, 1.2, 1.0)	0 → 40	5	100	77
7	Boc_2O (3.7)[a]	rt[b]	2	100	86
8	Boc_2O (2.0)	rt	2	100	83

[a]3.0 equiv of Bu_4NNO_2 was used. [b]Room temperature. [c]On TLC after first portion of acid anhydride. [d]Isolated.

examined the deprotection of fluorous phenyl (^{F}Car) of **1d**,[11] which was not deprotected under the previous conditions (Figure 2). The deprotected product of **1c** was obtained in 96% yield albeit over a longer reaction time. These conditions will be useful for syntheses of natural products using this fluorous protecting group.

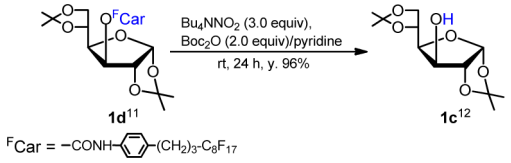


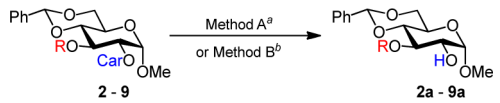
Figure 2. Deprotection of ^{F}Car group using Boc_2O and Bu_4NNO_2.

Next, the effect on other protecting groups was examined under these conditions using other substrates containing acetyl (Ac), benzoyl (Bz), pivaloyl (Piv), *tert*-butyldimethylsilyl (TBDMS), methoxymethyl (MOM), and allyloxycarbonyl (Alloc) groups (Table 2, entries 1−6). The reactions proceeded over shorter reaction times (ca. one-sixth to one-third) to give the corresponding deprotected products (**2a**,[13] **3a**,[14] **4a**,[8] **5a**,[15] **6a**,[16] **7a**[13c,17]) in similar yields without affecting the other protecting groups (entries 1−6). Additionally, methanesulfonyl (Ms) and *p*-tolylsulfonyl (Ts) groups were examined (entries 7 and 8). These groups were not affected at all under the reaction conditions, providing **8a**[18] and **9a**[19] in excellent yields.

The effect on the triphenylmethyl (Tr) group was also examined using substrate **10** (Figure 3). The reaction was complete in 2 h at room temperature (rt) to give the corresponding deprotected product **10a**[9] in 98% yield without affecting other protecting groups.

The deprotection procedure is also compatible with some common donors like sulfide **11**, **12**,[10c] and glycal **13** as shown in Figure 4.

Table 2. Selective Deprotection of Car Group Using Boc_2O and Bu_4NNO_2 in the Presence of Various Protecting Groups



Entry	Substrate	Method	Time (h)	Product	Yield (%)[c]
1	**2**: R = Ac	A (Ac_2O)	6	**2a**[13]	93
		B (Boc_2O)	1		90
2	**3**: R = Bz	A (Ac_2O)	8	**3a**[14]	93
		B (Boc_2O)	2.5		92
3	**4**: R = Piv	A (Ac_2O)	8	**4a**[9]	83
		B (Boc_2O)	3		96
4	**5**: R = TBDMS	A (Ac_2O)	12	**5a**[15]	quant.
		B (Boc_2O)	3.5		79
5	**6**: R = MOM	A (Ac_2O)	10	**6a**[16]	79
		B (Boc_2O)	4		92
6	**7**: R = Alloc	B (Boc_2O)	1	**7a**[13c,17]	87
7	**8**: R = Ms	B (Boc_2O)	1	**8a**[18]	89
8	**9**: R = Ts	B (Boc_2O)	1	**9a**[19]	87

[a]Method A: Bu_4NNO_2 (4.0 equiv), Ac_2O (1.5 + 1.2 + 1.0 equiv)/Py, 0 → 40 °C. [b]Method B: BU_4NNO_2 (3.0 equiv), Boc_2O (2.0 equiv)/Py, rt. [c]Isolated yield.

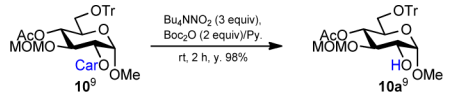


Figure 3. Selective deprotection of Car group.

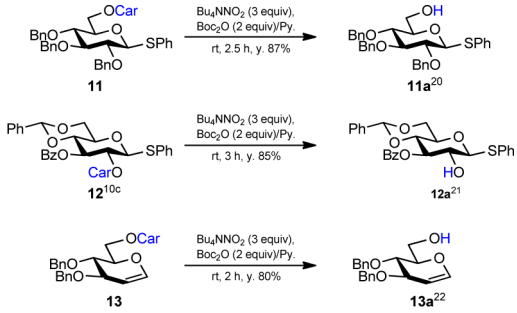


Figure 4. Deprotection of Car group in some glycosyl donors **11**−**13**.

In general, it is known that an acyl migration of a 1,2-*cis*-diol occurs more easily than that of a 1,2-*trans*-diol. Therefore, these improved deprotection conditions (using Boc_2O) were also applied to compounds **14** and **15** containing 1,2-*cis*-diols (Table 3). The deprotection reactions of the axially orientated *O*-Car group in **14** and **15** with Boc_2O required an excess amount of reagent (5.0 equiv) and a longer reaction time (6 h). However, the expected 2-OH derivatives (**14a**,[13d,23] **15a**[13a,25]) were obtained in moderate yields with small amounts of 3-OH derivatives (acyl migration products; **14b**,[24,25] **15b**[25b,26]). In contrast, the previous method using Ac_2O did not work well.

Finaly, the effect on the phthalimide group as one of well used *N*-protecting group in oligosaccharide synthesis was also examined using substrate **16** (Figure 5). The reaction was complete in 4 h at rt but to give 4-OH derivative **16b**[27] in 70% yield not the desired deprotected product (6-OH) **16a**.[28] The deprotection procedure is also compatible with the phthalimide group but did not prevent acyl migration (**16a** is immediately migrated into **16b** under the deprotecting conditions).

The proposed deprotection mechanism is shown in Scheme 1. Initially, *t*-BuOCOO$^-$$^+$N=O (**A**), generated from Boc_2O and

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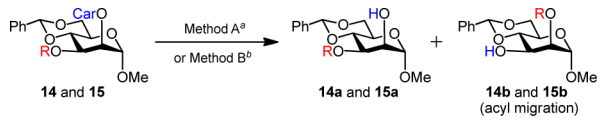
Table 3. Selective Deprotection of Car Group Containing 1,2-*cis*-Diol Moiety



Entry	Substrate	Method	Time (h)	Yield (%)[c] 2-OH deriv.	3-OH deriv. (acyl migration)	Recovered SM[d]
1	**14**: R = Ac	A (Ac_2O)	6	14	*trace*	65
		B (Boc_2O)	6	74	5	5
2	**15**: R = Bz	A (Ac_2O)	6	*trace*	ND[d]	98
		B (Boc_2O)	6	70	3	9

[a]Method A: Bu_4NNO_2 (8.0 equiv), Ac_2O (3.0 + 2.4 + 2.0 equiv)Py, 0 → 40 °C. [b]Method B: Bu_4NNO_2 (8.0 equiv), Boc_2O (5.0 equiv)Py, rt. [c]Isolated yield. [d]Starting material. [e]Not determined.

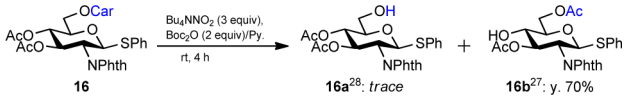
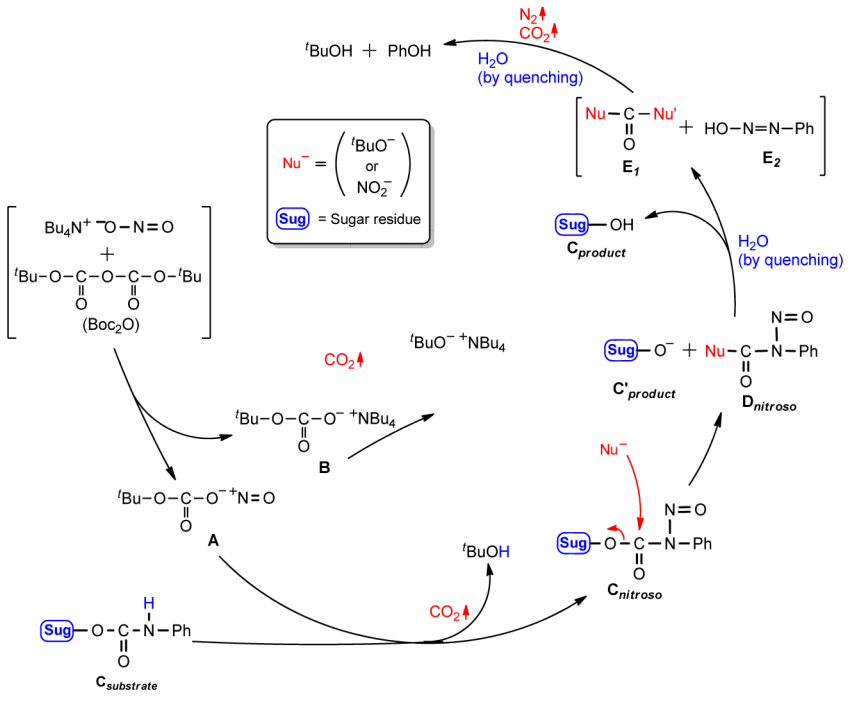


Figure 5. Deprotection of Car group in 2-deoxy-2-phthalimide glycosyl sulfide **16**.

Bu_4NNO_2, reacts with the sugar substrate ($\mathbf{C}_{substrate}$) to yield the *N*-nitroso compound ($\mathbf{C}_{nitroso}$) quantitatively. Next, nucleophilic attack on the carbonyl of $\mathbf{C}_{nitroso}$ by *t*-BuOCOO$^-$ and/or *t*-BuO$^-$ leads to the deprotected product ($\mathbf{C}_{product}$) and the *trans*-reacted *N*-nitroso compound ($\mathbf{D}_{nitroso}$). The resulting *N*-nitroso compound $\mathbf{D}_{nitroso}$ gradually degrades to carbon dioxide ($CO_2\uparrow$), nitrogen gas ($N_2\uparrow$), and some ionic species via carbonate ($\mathbf{E}_1$) and phenyldiazo hydroxide ($\mathbf{E}_2$). Part of the generated $^+N{=}O$ rapidly oxidizes to nitrogen dioxide by dissolved O_2 in pyridine, and the color of the reaction mixture immediately turns from clear yellow to brownish yellow. The formation of *tert*-BuOCOO$^-$ $^+NBu_4$ (**B**) was confirmed by ^1H NMR spectroscopy measured in pyridine-d_5. The above results may indicate that the shortened reaction time at room temperature (rt) may result in the higher nucleophilicity of *t*-BuOCOO$^-$ and/or *t*-BuO$^-$ generated in situ than that of CH_3COO^-. Under these mild conditions, the selectivity of the nucleophilic attack between the carbonyl and *N*-nitroso functionalities may increase to give preferable results. Therefore, the sulfonate anion ($ROSO_3^-$) generated in situ does not work well because of its lower nucleophilicity than that of CH_3COO^- (Table 1, entries 3 and 4).

It is commonly assumed that the resulting *tert*-butyl carbonate anion (*t*-BuOCOO$^-$) may gradually decompose into *tert*-butoxide anion and carbon dioxide. Although the various organic carbonates have been synthesized and studied by Rossi[29] and Mayr,[30] the *tert*-butyl carbonate anion may be unstable enough to exist in situ under these reaction conditions. This proposed deprotection mechanism is further supported by mechanistic studies on nitrosation−deaminocyclization of monocarbamoylated vicinal amino alcohols and diols.[31] Because nucleophilic attack on the nitrogen atom of the *N*-nitroso function leads to starting material, this deprotection procedure requires an excess amount of reagents relative to the substrates (determined on a case-by-case basis). The proposed mechanism via *N*-nitroso intermediate $\mathbf{C}_{nitroso}$ is suggested by careful monitoring of the existence of the intermediate on TLC. The intermediate $\mathbf{C}_{nitroso}$ remains until the deprotection reaction is completed, as confirmed by ^1H, ^{13}C, and ^{15}N NMR spectroscopy measurements[9] in DMSO-d_6 in the deprotection reaction of **1a**. Finally, the proposed deprotection mechanism could give sugar alcohol and some small molecules such as *tert*-butanol, phenol, CO_2, N_2, and diazo compound (azo coupling product), but such compounds were not well detected after the usual work up. These results raise the possibility that this deprotection mechanism may be distinct from the original one. More critical evidence in support of the deprotection mechanism is now under investigation.

Scheme 1. Proposed Deprotection Mechanism



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In summary, we have developed a practical method for selective deprotection of the *N*-phenylcarbamoyl group using Bu_4NNO_2 (4.0−3.0 equiv) and Boc_2O (3.0−2.0 equiv) in pyridine at room temperature. The method is also effective for deprotecting the fluorous *N*-phenylcarbamyl group in an orthogonal manner. We believe that this new method will find wide application in natural product and oligosaccharide syntheses.

EXPERIMENTAL SECTION

Original Deprotecting Procedure Using Ac_2O. To a stirred solution of *N*-phenylcarbamoyl derivative and tetra-*n*-butylammonium nitrite (4.0 molar equiv) in pyridine (substrate/Py = 100 mg/2 mL) was added acetic anhydride (1.5 molar equiv) at 0 °C under Ar and kept until the disappearance of starting compound on TLC. After confirmation of the corresponding *N*-nitroso derivative, the reaction mixture was warmed to 40 °C and kept at that temperature for 2 h. The resulting mixture was cooled to 0 °C again, and acetic anhydride (1.2 molar equiv) was added, warmed to 40 °C again, and kept at 40 °C for 2 h. This procedure was repeated once more using acetic anhydride (1.0 molar equiv). The resulting reaction mixture was diluted with EtOAc (30 mL), washed with saturated aq $NaHCO_3$ solution and brine, dried over anhydr $MgSO_4$, and concentrated in vacuo to give the corresponding alcohol, which was purified by silica gel column chromatography with hexane−ethyl acetate.

Improved Deprotecting Procedure Using Boc_2O. To a solution of *N*-phenylcarbamoyl derivative and tetra-*n*-butylammonium nitrite (4.0 molar equiv) in pyridine (substrate/Py = 100 mg/2 mL) was added di-*tert*-butyl dicarbonate (2.0 molar equiv) at 0 °C under Ar and the mixture stirred at room temperature. While the deprotecting reaction was proceeding, 3 mol of gas for each 1 mol of starting compound was generated. After the disappearance of starting compound on TLC, the resulting reaction mixture was poured into saturated aq NH_4Cl solution, extracted with EtOAc (30 mL), washed with brine and water, dried over anhydr $MgSO_4$, and concentrated in vacuo to give the corresponding alcohol, which was purified by silica gel column chromatography with hexane−ethyl acetate.

*1,2:5,6-Di-O-isopropylidene-3-O-(N-phenylcarbamoyl)-α-D-glucofuranose (**1a**).*[9] Yield 6.7 g (92%) as colorless amorphous powder from **1c** (5.0 g): $[\alpha]_D^{25}$ −43.3 (*c* 0.98, $CHCl_3$); IR (KBr neat) ν 3323 cm^{-1} (NH), 1733 cm^{-1} (C═O); ^1H NMR (600 MHz, $CDCl_3$) δ 7.37−7.07 (5H, m), 6.85 (1H, s), 5.89 (1H, d, *J* = 3.6 Hz), 5.26 (1H, d, *J* = 2.9 Hz), 4.65 (1H, d, *J* = 3.6 Hz), 4.29 (1H, ddd, *J* = 8.2 Hz, *J* = 6.0 Hz, *J* = 4.6 Hz), 4.23 (1H, dd, *J* = 2.9 Hz, *J* = 8.2 Hz), 4.10 (1H, dd, *J* = 6.0 Hz, *J* = 8.4 Hz), 4.04 (1H, dd, *J* = 8.4 Hz, *J* = 4.6 Hz), 1.54, 1.43, 1.33, 1.31 (3H × 4, each s); ^{13}C NMR (150 MHz) δ 129.1, 112.3, 109.5, 104.9, 83.4, 79.7, 72.3, 67.2, 26.9, 26.7, 26.1, 25.3; ^{15}N NMR (50.6 MHz, DMSO-d_6, CH_3NO_2, −5.00 ppm) δ −270.5. Anal. Calcd for $C_{19}H_{25}NO_7$: C,60.14; H, 6.64; N, 3.69. Found: C, 60.36; H, 6.79; N, 3.49.

*1,2:5,6-Di-O-isopropylidene-3-O-((p-4,4,5,5,6,6,7,7,8,8,9,9,10,10,-11,11,11-heptadecafluoroundecyl)-N-phenylcarbamoyl)-α-D-glucofuranose (**1d**).*[11] Yield 707 mg (80%) as colorless amorphous powder from **1c** (400 mg): $[\alpha]_D^{25}$ −22.5 (*c* 1.37, $CHCl_3$); IR (KBr neat) ν 3328 cm^{-1} (NH), 1735 cm^{-1} (C═O); ^1H NMR (600 MHz, $CDCl_3$) δ 7.37−7.07 (5H, m), 6.85 (1H, br s), 5.89 (1H, d, *J* = 3.6 Hz), 5.26 (1H, d, *J* = 2.9 Hz), 4.65 (1H, d, *J* = 3.6 Hz), 4.29 (1H, ddd, *J* = 8.2 Hz, *J* = 6.0 Hz, *J* = 4.6 Hz), 4.23 (1H, dd, *J* = 2.9 Hz, *J* = 8.2 Hz,), 4.10 (1H, dd, H-6, *J* = 6.0 Hz, *J* = 8.4 Hz), 4.04 (1H, dd, *J* = 4.6 Hz, *J* = 8.4 Hz), 2.67 (2H, dd, *J* = 7.6 Hz), 2.06 (2H, m), 1.92 (2H, m), 1.54, 1.43, 1.33, 1.31 (3H × 4, each s, $C(CH_3)_2$); ^{13}C NMR (150 MHz) δ 129.0, 112.3, 109.5, 105.0, 83.4, 79.7, 72.4, 67.3, 34.3, 26.9, 26.7, 26.2, 25.3; HRMS (ESI-TOF) calcd for $C_{30}H_{30}F_{17}NO_7$ *m*/*z* $[M + Na]^+$ 862.1649, found 862.1689.

*Methyl 3-O-Acetyl-4,6-O-benzylidene-2-O-(N-phenylcarbamoyl)-α-D-glucopyranoside (**2**).* Yield 910 mg (83%) as colorless needles from methyl 4,6-*O*-benzylidene-2-*O*-(*N*-phenylcarbamoyl)-D-glucopyranoside (1.00 g): $[\alpha]_D^{25}$ +109.5 (*c* 0.89, $CHCl_3$); mp 199−202 °C (hexane−EtOH); IR (KBr disk) ν 3432 cm^{-1} (NH), 1707 cm^{-1} (C═O); ^1H NMR (600 MHz, $CDCl_3$) δ 7.46−7.10 (10H, m), 6.82 (1H, s), 5.69 (1H, dd, *J* = 9.7 Hz, *J* = 9.7 Hz), 5.52 (1H, s), 5.02 (1H, d, *J* = 3.6 Hz), 4.91 (1H, dd, *J* = 3.6 Hz, *J* = 9.7 Hz,), 4.32 (1H, dd, *J* = 4.2 Hz, *J* = 9.8 Hz), 3.94 (1H, ddd, *J* = 9.5 Hz, *J* = 10.0 Hz, *J* = 4.2 Hz), 3.79 (1H, dd, *J* = 10.0 Hz, *J* = 9.8 Hz), 3.69 (1H, dd, *J* = 9.5 Hz, *J* = 9.7 Hz), 3.43 (3H, s), 2.05 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.5, 170.2, 137.3, 136.9, 129.2, 129.1, 129.1, 128.2, 128.2, 126.2, 126.2, 126.2, 123.8, 118.5, 101.6, 98.0, 79.1, 72.2, 69.0, 68.9, 62.3, 55.4, 20.9. Anal. Calcd for $C_{23}H_{25}NO_8$ (466.4): C, 62.29; H, 5.68; N, 3.16. Found: C, 61.89; H, 5.73; N, 3.21.

*Methyl 3-O-Benzoyl-4,6-O-benzylidene-2-O-(N-phenylcarbamoyl)-α-D-glucopyranoside (**3**).* Yield 1.15 g (91%) as colorless needles from methyl 4,6-*O*-benzylidene-2-*O*-(*N*-phenylcarbamoyl)-α-D-glucopyranoside (1.00 g): $[\alpha]_D^{25}$ +32.2 (*c* 0.90, $CHCl_3$); mp 219−222 °C (hexane−EtOH); IR (KBr disk) ν 3344 cm^{-1} (NH), 1725 cm^{-1} (C═O); ^1H NMR (600 MHz, $CDCl_3$) δ 8.04−7.22 (15H, m), 6.84 (1H, s), 5.89 (1H, dd, *J* = 9.5 Hz, *J* = 9.5 Hz), 5.54 (1H, s), 5.11 (1H, dd, *J* = 3.9 Hz, *J* = 9.5 Hz), 5.10 (1H, d, *J* = 3.9 Hz), 4.35 (1H, dd, *J* = 4.9 Hz, *J* = 10.4 Hz), 4.04 (1H, ddd, *J* = 10.3 Hz, *J* = 10.3 Hz, *J* = 4.9 Hz,), 3.86 (1H, dd, *J* = 10.3 Hz, *J* = 10.4 Hz), 3.85 (1H, dd, *J* = 10.3 Hz, *J* = 9.5 Hz), 3.48 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 165.7, 137.2, 136.9, 133.1, 129.8, 129.6, 129.0, 129.0, 129.0, 129.0, 128.4, 128.2, 128.2, 128.2,126.2, 126.1, 126.1, 123.8, 118.7, 118.7, 101.6, 98.1, 79.4, 72.2, 69.7, 68.9, 62.5, 55.5. Anal. Calcd for $C_{28}H_{27}NO_8$ (528.5): C, 66.52; H, 5.38; N, 2.77. Found: C, 66.26; H, 5.36; N, 2.39.

*Methyl 4,6-O-Benzylidene-2-O-(N-phenylcarbamoyl)-3-O-pivaloyl-α-D-glucopyranoside (**4**).* Yield 778 mg (91%) as colorless prisms from methyl 4,6-*O*-benzylidene-2-*O*-(*N*-phenylcarbamoyl)-α-D-glucopyranoside (710 mg): $[\alpha]_D^{25}$ +85.6 (*c* 0.50, $CHCl_3$); mp 204−208 °C (hexane−EtOH); IR (KBr disk) ν 3325 cm^{-1} (NH), 1723 cm^{-1} (C═O); ^1H NMR (600 MHz, $CDCl_3$) δ 7.44−7.26 (10H, m), 6.95 (1H, s), 5.61 (1H, dd, *J* = 9.6 Hz, *J* = 9.6 Hz), 5.54 (1H, s), 5.01 (1H, dd, *J* = 9.6 Hz, *J* = 3.8 Hz), 4.99 (1H, d, *J* = 3.8 Hz), 4.34 (1H, dd, *J* = 4.8 Hz, *J* = 10.3 Hz), 3.95 (1H, ddd, *J* = 9.6 Hz, *J* = 10.3 Hz, *J* = 4.8 Hz), 3.80 (1H, dd, *J* = 10.3 Hz, *J* = 10.3 Hz), 3.73 (1H, dd, *J* = 9.6 Hz, *J* = 9.6 Hz), 3.44 (3H, s), 1.15 (9H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 177.5, 137.3, 137.0, 129.1, 129.1, 129.1, 128.9, 128.2, 128.2, 128.2, 125.9, 125.9, 125.9, 123.8, 118.6, 101.2, 98.2, 79.3, 68.9, 68.8, 62.4, 55.4, 38.9, 27.0, 27.0, 27.0. Anal. Calcd for $C_{26}H_{31}NO_8$ (508.5): C, 64.31; H, 6.44; N, 2.89. Found: C, 64.51; H, 6.53; N, 2.89.

*Methyl 4,6-O-Benzylidene-2-O-(N-phenylcarbamoyl)-3-O-tert-butyldimethylsilyl-α-D-glucopyranoside (**5**).* Yield 1.55 g (80%) as colorless needles from methyl 4,6-*O*-benzylidene-2-*O*-(*N*-phenylcarbamoyl)-α-D-glucopyranoside (1.50 g): $[\alpha]_D^{22}$ +44.1 (*c* 1.03, $CHCl_3$); mp 153−155 °C (hexane−EtOH); IR (KBr disk) ν 3337 cm^{-1} (NH), 1736 cm^{-1} (C═O); ^1H NMR (600 MHz, $CDCl_3$) δ 7.50−7.07 (10H, m), 6.71 (1H, s), 5.54 (1H, s), 4.95 (1H, d, *J* = 3.8 Hz), 4.86 (1H, dd, *J* = 9.3 Hz, *J* = 3.8 Hz), 4.29 (1H, dd, *J* = 4.6 Hz, *J* = 10.0 Hz), 4.15 (1H, dd, *J* = 9.1 Hz, *J* = 9.3 Hz), 3.84 (1H, ddd, *J* = 9.3 Hz, *J* = 10.1 Hz, *J* = 4.6 Hz), 3.77 (1H, dd, *J* = 10.1 Hz, *J* = 10.0 Hz), 3.55 (1H, dd, *J* = 9.3 Hz, *J* = 9.1 Hz), 3.42 (3H, s), 0.80 (9H, s), 0.00 (6H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.4, 137.2, 129.1, 129.0, 128.1, 126.2, 123.8, 101.8, 98.3, 82.2, 69.7, 69.0, 62.3, 55.3, 25.6, 25.6, 25.6, 18.1, −0.0, −4.2. Anal. Calcd for $C_{27}H_{37}NO_7Si$ (515.67): C, 62.89; H, 7.23; N, 2.72. Found: C, 62.81; H, 7.38; N, 2.77.

*Methyl 4,6-O-Benzylidene-3-O-methoxymethyl-2-O-(N-phenylcarbamoyl)-α-D-glucopyranoside (**6**).* Yield 2.93 g (88%) as colorless needles from methyl 4,6-*O*-benzylidene-2-*O*-(*N*-phenylcarbamoyl)-α-D-glucopyranoside (3.00 g): $[\alpha]_D^{22}$ +84.0 (*c* 1.16, $CHCl_3$); mp 171−173 °C (hexane−EtOH); IR (KBr disk) ν 3303 cm^{-1} (NH), 1701 cm^{-1} (C═O); ^1H NMR (600 MHz, $CDCl_3$) δ 7.49−7.26 (10H, m), 6.86 (1H, s), 5.57 (1H, s), 4.98 (1H, d, *J* = 3.6 Hz), 4.93 (1H, dd, *J* = 9.6 Hz, *J* = 3.6 Hz), 4.86, 4.73 (2H, each d, *J* = 6.7 Hz), 4.31 (1H, dd, *J* = 4.8 Hz, *J* = 10.1 Hz), 4.20 (1H, dd, *J* = 9.5 Hz, *J* = 9.6 Hz), 3.88 (1H, ddd, *J* = 9.5 Hz, *J* = 10.1 Hz, *J* = 4.8 Hz,), 3.80 (1H, dd, *J* = 10.1 Hz, *J* = 10.1 Hz), 3.68 (1H, dd, *J* = 9.5 Hz, *J* = 9.5 Hz), 3.43 (3H, s), 3.32 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 137.4, 137.2, 129.2, 129.0, 128.2, 126.1, 123.8, 118.6, 101.6, 98.1, 97.2, 81.4, 73.1, 68.9, 62.3, 55.7, 55.3. Anal. Calcd for $C_{23}H_{27}NO_8$ (445.45): C, 62.01; H, 6.11; N, 3.14. Found: C, 61.62; H, 6.24; N, 2.85.

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*Methyl 3-O-Allyloxycarbonyl-4,6-O-benzylidene-2-O-(N-phenylcarbamoyl)-α-D-glucopyranoside (**7**).* Yield 630 mg (80%) as colorless needles from methyl 4,6-*O*-benzylidene-2-*O*-(*N*-phenylcarbamoyl)-α-D-glucopyranoside (650 mg): $[\alpha]_D^{23}$ +61.6 (*c* 0.98, $CHCl_3$); mp 169−172 °C (hexane−EtOH); IR (KBr disk) ν 3340 cm^{-1} (NH), 1716 cm^{-1} (C═O); ^1H NMR (600 MHz, $CDCl_3$) δ 7.47−7.07 (10H, m), 6.83 (1H, s), 5.84 (1H, m), 5.53 (1H, s), 5.41 (1H, dd, *J* = 9.8 Hz, *J* = 9.8 Hz), 5.27, 5.13 (2H, each m), 5.07 (1H, d, *J* = 3.8 Hz), 4.93 (1H, dd, *J* = 3.8 Hz, *J* = 9.8 Hz), 4.60 (2H, m), 4.33 (1H, dd, *J* = 4.8 Hz, *J* = 10.3 Hz), 3.95 (1H, ddd, *J* = 4.8 Hz, *J* = 9.6 Hz, *J* = 10.3 Hz), 3.80 (1H, dd, *J* = 10.3 Hz, *J* = 10.3 Hz), 3.74 (1H, dd, *J* = 9.6 Hz, *J* = 9.8 Hz), 3.43 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.4, 137.3, 136.8, 131.2, 129.1, 129.1, 129.1, 128.2, 128.2, 128.2, 126.2, 126.2, 123.8, 118.9, 118.6, 101.6, 97.9, 79.0, 73.3, 72.1, 68.8, 68.7, 62.3, 55.5, 55.5. Anal. Calcd for $C_{25}H_{27}NO_9$ (485.48): C, 61.85; H, 5.60; N, 2.89. Found: C, 61.82; H, 5.64; N, 2.62.

*Methyl 4,6-O-Benzylidene-3-O-methanesulfonyl-2-O-(N-phenylcarbamoyl)-α-D-glucopyranoside (**8**).* Yield 940 mg (78%) as colorless needles from methyl 4,6-*O*-benzylidene-2-*O*-(*N*-phenylcarbamoyl)-α-D-glucopyranoside (1.00 g): $[\alpha]_D^{23}$ +75.5° (*c* 1.02, $CHCl_3$); mp 192−194 °C (hexane−EtOH); IR (KBr disk) ν 3356 cm^{-1} (NH), 1711 cm^{-1} (C═O), 1539 cm^{-1} (C═C), 1361, 1168 cm^{-1} (SO_2); ^1H NMR (600 MHz, $CDCl_3$) δ 7.46−7.26 (10H, m), 7.01 (1H, s), 5.58 (1H, s), 5.12 (1H, d, *J* = 3.8 Hz), 5.11 (1H, dd, *J* = 9.6 Hz, *J* = 9.6 Hz), 4.91 (1H, dd, *J* = 9.6 Hz, *J* = 3.8 Hz), 4.35 (1H, dd, *J* = 4.8 Hz, *J* = 10.3 Hz), 3.94 (1H, ddd, *J* = 9.6 Hz, *J* = 10.5 Hz, *J* = 4.8 Hz), 3.82 (1H, dd, *J* = 10.3 Hz, *J* = 10.5 Hz), 3.78 (1H, dd, *J* = 9.6 Hz, *J* = 9.6 Hz), 3.45 (3H, s), 2.96 (3H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 136.5, 129.4, 129.1, 128.4, 126.0, 126.0, 101.9, 98.3, 79.0, 77.6, 77.2, 68.8, 62.4, 55.6, 38.8. Anal. Calcd for $C_{22}H_{25}NO_9S$ (479.50): C, 55.11; H, 5.26; N, 2.92. Found: C, 55.42; H, 5.30; N, 2.61.

*Methyl 4,6-O-Benzylidene-2-O-(N-phenylcarbamoyl)-3-O-tolylsulfonyl-α-D-glucopyranoside (**9**).* Yield 610 mg (68%) as colorless needles from methyl 4,6-*O*-benzylidene-2-*O*-(*N*-phenylcarbamoyl)-α-D-glucopyranoside (650 mg): $[\alpha]_D^{25}$ +57.3 (*c* 1.05, $CHCl_3$); mp 179−182 °C (hexane−EtOH); IR (KBr disk) ν 3365 cm^{-1} (NH), 1712 cm^{-1} (C═O), 1365, 1173 cm^{-1} (SO_2); ^1H NMR (600 MHz, $CDCl_3$) δ 7.70−6.96 (14H, m), 6.73 (1H, s), 5.42 (1H, s), 5.20 (1H, dd, *J* = 9.6 Hz, *J* = 9.6 Hz), 5.06 (1H, d, *J* = 3.8 Hz), 4.89 (1H, dd, *J* = 3.8 Hz, *J* = 9.6 Hz), 4.31 (1H, dd, *J* = 4.8 Hz, *J* = 10.3 Hz), 3.90 (1H, ddd, *J* = 4.8 Hz, *J* = 9.6 Hz, *J* = 10.4 Hz), 3.76 (1H, dd, *J* = 10.4 Hz, *J* = 10.3 Hz), 3.68 (1H, dd, *J* = 9.6 Hz, *J* = 9.6 Hz), 3.43 (3H, s), 2.20 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 152.0, 144.3, 137.3, 136.7, 134.4, 129.3, 129.1, 128.1, 127.9, 126.3, 123.8, 118.8, 101.7, 98.3, 78.8, 77.3, 71.8, 68.7, 62.5, 55.5, 21.5. Anal. Calcd for $C_{28}H_{29}NO_9S$ (555.60): C, 60.53; H, 5.26; N, 2.52. Found: C, 60.69; H, 5.58; N, 2.19.

*Methyl 4-O-Acetyl-3-O-methoxymethyl-2-O-(N-phenylcarbamoyl)-6-O-triphenylmethyl-α-D-glucopyranoside (**10**).* Yield 411 mg (3 steps, 74%) as colorless amorphous from **6** by hydrolysis, tritylation and acetylation (510 mg): $[\alpha]_D^{25}$ +63.8 (*c* 0.99, $CHCl_3$); IR (KBr neat) ν 3323 cm^{-1} (CONH), 1740 cm^{-1} (C═O); ^1H NMR (600 MHz, $CDCl_3$) δ 7.47−7.27 (20H, m), 6.87 (1H, s), 5.04 (1H, d, *J* = 3.4 Hz), 5.00 (1H, dd, *J* = 10.3 Hz, *J* = 10.3 Hz), 4.92 (1H, dd, *J* = 3.4 Hz, *J* = 10.3 Hz), 4.68, 4.61 (2H, each d, *J* = 6.9 Hz), 4.01 (1H, dd, *J* = 10.3 Hz, *J* = 10.3 Hz), 3.88 (1H, ddd, *J* = 6.2 Hz, *J* = 1.4 Hz, *J* = 10.3 Hz), 3.50 (3H, s), 3.25 (3H, s), 3.18 (1H, dd, *J* = 10.3 Hz, *J* = 6.2 Hz), 3.10 (1H, dd, *J* = 1.4 Hz, *J* = 10.3 Hz), 1.78 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.2, 143.7, 143.7, 143.7, 137.9, 137.4, 129.1, 129.1, 129.0, 129.0, 129.0, 128.7, 128.7, 128.7, 128.2, 128.2, 127.8, 127.8, 127.7, 127.7, 127.7, 126.9, 125.2, 123.7, 97.7, 97.0, 86.6, 76.5, 73.2, 70.3, 69.0, 62.7, 55.8, 55.0, 21.4, 20.6, 20.6. Anal. Calcd for $C_{37}H_{39}NO_9$ (664.7): C, 69.25; H, 6.13; N, 2.18. Found: C, 68.89; H, 6.15; N, 1.82.

*Phenyl 2,3,4-Tri-O-benzyl-6-O-(N-phenylcarbamoyl)-1-thio-β-D-glucopyranoside (**11**).* To a solution of **11a**[20] (501 mg, 0.924 mmol) in pyridine (20 mL) was added phenyl isocyanate (121 μL, 1.1 mmol) at 0 °C and the mixture stirred for 1 h. After the disappearance of the starting compound on TLC with hexane−EtOAc (2:1 v/v), the mixture was evaporated in vacuo. The resulting crude crystal was purified by recrystallization with hexane-EtOH to give **11** (501 mg, 82% yield): $[\alpha]_D^{25}$ +8.9 (*c* 1.51, $CHCl_3$); mp 131−132 °C (hexane−EtOH, colorless needles); IR (KBr disk) ν 3369 cm^{-1} (NH), 1703 cm^{-1} (C═O); ^1H NMR (600 MHz, $CDCl_3$) δ 7.55−7.06 (25H, m), 6.55 (1H, br s), 4.94, 4.87 (2H, each d, *J* = 10.8 Hz), 4.93, 4.75 (2H, each d, *J* = 10.2 Hz), 4.85, 4.62 (2H, each d, *J* = 10.2 Hz), 4.67 (1H, d, *J* = 10.2 Hz), 4.44 (1H, d, *J* = 12.0 Hz), 4.34 (1H, m), 3.74 (1H, dd, *J* = 9.0 Hz, *J* = 9.0 Hz), 3.57−3.53 (2H, m), 3.50 (1H, dd, *J* = 10.2 Hz, *J* = 9.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 138.2, 137.8, 137.5, 133.3, 132.4, 129.1, 128.8, 128.5, 128.5, 128.5, 128.4, 128.3, 128.2, 127.8, 123.5, 118.5, 87.6, 86.7, 81.0, 77.2, 77.1, 75.8, 75.5, 75.0; HRMS (ESI-TOF) calcd for $C_{40}H_{39}NO_6S$ *m*/*z* $[M + Na]^+$ 684.2396, found 684.2376. Anal. Calcd for $C_{40}H_{39}NO_6S$ (661.81): C, 72.59; H, 5.94; N, 2.12. Found: C, 72.21; H, 5.60; N, 1.99.

*Phenyl 3-O-Benzoyl-4,6-O-benzylidene-2-O-(N-phenylcarbamoyl)-1-thio-β-D-glucopyranoside (**12**[10c]).* To a solution of **12a**[21] (50 mg, 0.11 mmol) in pyridine (2 mL) were added phenyl isocyanate (13 μL, 0.12 mmol) and 4-dimethylaminopyridine (5 mg, 41 μmol) at 0 °C and the mixture stirred at room temperature for 30 min. After disappearance of the starting compound on TLC with toluene−acetone (16:1 v/v), the mixture was evaporated in vacuo. The resulting crude crystal was purified by recrystallization with hexane−EtOAc to give **12** (57.5 mg, 92% yield): $[\alpha]_D^{25}$ +14.2 (*c* 1.0, $CHCl_3$); mp 192−193 °C (hexane−EtOH, colorless prisms); IR (KBr, disk) ν 3295 cm^{-1} (NH), ν 1722 cm^{-1} (C═O); ^1H NMR (600 MHz, $CDCl_3$) δ 8.05−7.23 (15H, m), 6.70 (1H, br s), 5.67 (1H, dd, *J* = 9.6 Hz, *J* = 9.6 Hz), 5.51 (1H, s), 5.19 (1H, dd, *J* = 10.2 Hz, *J* = 9.6 Hz), 4.91 (1H, d, *J* = 10.2 Hz), 4.42 (1H, dd, *J* = 4.9 Hz, *J* = 10.6 Hz), 3.86 (1H, dd, *J* = 9.6 Hz, *J* = 9.6 Hz), 3.85 (1H, dd, *J* = 10.6 Hz, *J* = 9.6 Hz), 3.68 (1H, ddd, *J* = 9.6 Hz, *J* = 4.9 Hz, *J* = 9.6 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.9, 136.7, 133.3, 132.9, 132.0, 129.9, 129.1, 129.1, 129.0, 128.4, 128.3, 128.2, 126.1, 120.6, 101.5, 86.9, 78.4, 73.4, 70.9, 68.5. Anal. Calcd for $C_{33}H_{29}NO_7S$ (583.65): C, 67.91; H, 5.01; N, 2.40. Found: C, 68.18; H, 5.11; N, 2.05.

*3,4-Di-O-benzyl-6-O-(N-phenylcarbamoyl)-D-glucal (**13**).* To a solution of **13a**[22] (622 mg, 1.91 mmol) in dry pyridine (10 mL) was added phenyl isocyanate (227 μL, 2.1 mmol) at 0 °C and the mixture stirred at rt for 8 h. After the reaction was complete, the mixture was evaporated in vacuo. The remaining residue was purified by recrystallization with hexane−acetone to give **13** (680 mg, yield 80%): $[\alpha]_D^{25}$ +41 (*c* 0.3, $CHCl_3$); mp 133−134 °C (hexane−acetone, colorless needles); IR (KBr disk) ν 3337 cm^{-1} (NH), 1701 cm^{-1} (C═O), 1646, 1598, 1531 cm^{-1} (C═C); ^1H NMR (600 MHz, $CDCl_3$) δ 7.37−7.06 (15H, m), 6.57 (1H, br s), 6.41 (1H, d, *J* = 6.0 Hz), 4.93 (1H, dd, *J* = 3.0 Hz, *J* = 6.0 Hz), 4.85, 4.71 (2H, each d, *J* = 11.4 Hz), 4.67, 4.57 (2H, each d, *J* = 12.0 Hz), 4.50 (1H, dd, *J* = 2.4 Hz, *J* = 12.0 Hz), 4.45 (1H, dd, *J* = 4.8 Hz, *J* = 11.4 Hz), 4.24 (1H, ddd, *J* = 6.0 Hz, *J* = 3.0 Hz, *J* = 2.4 Hz), 3.98 (1H, ddd, *J* = 8.4 Hz, *J* = 2.4 Hz, *J* = 2.4 Hz), 3.79 (1H, dd, *J* = 8.4 Hz, *J* = 6.0 Hz); ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.3, 138.1, 137.7, 129.1, 128.5, 128.5, 128.3, 127.9, 127.8, 123.5, 100.1, 75.4, 75.2, 73.5, 70.5, 63.3; HRMS (ESI-TOF) calcd for $C_{27}H_{27}NO_5Na$ *m*/*z* $[M + Na]^+$ 468.1787, found 468.1795. Anal. Calcd for $C_{27}H_{27}NO_5$ (445.19): C, 72.79; H, 6.11; N, 3.14. Found: C, 72.41; H, 5.88; N, 3.18.

*Methyl 3-O-Acetyl-4,6-O-benzylidene-2-O-(N-phenylcarbamoyl)-α-D-mannopyranoside (**14**).* Yield 106 mg (88%) as colorless amorphous from **14a**: $[\alpha]_D^{25}$ −29.9 (*c* 0.95, $CHCl_3$); IR (KBr disk) ν 3332 cm^{-1} (NH), 1743 cm^{-1} (C═O); ^1H NMR (600 MHz, $CDCl_3$) δ 7.47−7.09 (10H, m), 6.86 (1H, br s), 5.59 (1H, s), 5.43 (1H, dd, *J* = 3.5 Hz, *J* = 10.3 Hz), 5.36 (1H, dd, *J* = 1.4 Hz, *J* = 3.5 Hz), 4.80 (1H, d, *J* = 1.4 Hz), 4.33 (1H, dd, *J* = 4.8 Hz, *J* = 10.3 Hz), 4.10 (1H, dd, *J* = 10.3 Hz, *J* = 10.3 Hz), 4.00 (1H, ddd, *J* = 10.3 Hz, *J* = 10.3 Hz, *J* = 4.8 Hz), 3.87 (1H, dd, *J* = 10.3 Hz, *J* = 10.3 Hz), 3.44 (3H, s), 2.03 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.9, 137.4, 137.0, 129.2, 128.3, 126.2, 102.1, 99.9, 76.2, 68.8, 68.5, 63.7, 55.3, 20.9; HRMS (ESI-TOF) calcd for $C_{23}H_{25}NO_8Na$ *m*/*z* $[M + Na]^+$ 466.1480, found 466.1495.

*Methyl 3-O-Benzoyl-4,6-O-benzylidene-2-O-(N-phenylcarbamoyl)-α-D-mannopyranoside (**15**).* Yield 211 mg (86%) as colorless amorphous from **15a**: $[\alpha]_D^{28}$ −68.6 (*c* 0.23, $CHCl_3$); IR (KBr disk) ν 3386 cm^{-1} (NH), 1729, 1710 cm^{-1} (C═O); ^1H NMR (600 MHz, $CDCl_3$) δ 7.99−7.07 (10H, m), 6.84 (1H, br s), 5.73 (1H, dd, *J* = 3.6

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Hz, J = 10.3 Hz), 5.62 (1H, s), 5.48 (1H, dd, J = 1.6 Hz, J = 3.6 Hz), 4.86 (1H, d, J = 1.6 Hz), 4.36 (1H, dd, J = 4.8 Hz, J = 10.3 Hz), 4.23 (1H, dd, J = 10.3 Hz, J = 10.3 Hz), 4.07 (1H, ddd, J = 10.3 Hz, J = 10.3 Hz, J = 4.8 Hz), 3.91 (1H, dd, J = 10.3 Hz, J = 10.3 Hz), 3.47 (3H, s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 165.4, 137.2, 137.0, 133.0, 129.8, 129.8, 129.1, 129.0, 128.2, 128.2, 126.1, 101.9, 99.9, 76.6, 68.9, 68.8, 63.7, 55.4; HRMS (ESI-TOF) calcd for $C_{28}H_{27}O_8NNa$ m/z [M + Na]$^+$ 528.1634, found 528.1657.

Phenyl 3,4-di-O-Acetyl-2-deoxy-2-phthalimido-6-O-(N-phenylcarbamoyl)-1-thio-β-D-glucopyranoside (16). To a solution of **16a**[28] (476 mg, 0.98 mmol) in dry pyridine (5 mL) was added phenyl isocyanate (130 μL, 1.2 mmol) at 0 °C and the mixture stirred at rt for 3 h. After the reaction was complete, the mixture was evaporated in vacuo. The resulting residue was purified by silica gel column chromatography with hexane−EtOAc (2:1) to give **16** (563 mg, yield 95%): $[\alpha]_D^{26}$ +51.8 (c 1.0, $CHCl_3$); colorless amorphous; IR (KBr neat) ν 1742 cm^{-1} (NH), 1720 cm^{-1} (C═O), 1601, 1546, 1536 cm^{-1} (C═C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.88−7.08 (14H, m), 6.75 (1H, br s), 5.81 (1H, dd, J = 9.6 Hz, J = 9.6 Hz), 5.73 (1H, d, J = 10.8 Hz), 5.18 (1H, dd, J = 9.6 Hz, J = 9.6 Hz), 4.42 (1H, dd, J = 1.8 Hz, J = 12.0 Hz), 4.35 (1H, dd, J = 10.8 Hz, J = 9.6 Hz), 4.29 (1H, dd, J = 12.0 Hz, J = 4.8 Hz), 3.96 (1H, ddd, J = 1.8 Hz, J = 4.8 Hz, J = 9.6 Hz), 2.05, 1.84 (3H × 2, each s); ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.1, 169.6, 137.6, 134.5, 134.3, 133.7, 130.6, 129.1, 128.9, 128.5, 123.7, 82.9, 76.1, 71.7, 68.6, 53.6, 20.7, 20.4; HRMS (ESI-TOF) calcd for $C_{31}H_{28}N_2O_9SNa$ m/z [M + Na]$^+$ 627.1413, found 627.1386.

N-Nitroso Intermediate ***1b***.[9] This compound was unstable.

1,2:5,6-Di-O-isopropylidene-α-D-glucofuranose (1c).[12] Yield 35.6 mg (86%) as colorless needles from **1a** (60 mg).

Methyl 3-O-Acetyl-4,6-O-benzylidene-α-D-glucopyranoside (2a).[13] Yield 32.9 mg (90%) as colorless needles from **2** (50 mg).

Methyl 4,6-O-Benzylidene-3-O-benzoyl-α-D-glucopyranoside (3a).[14] Yield 35.2 mg (92%) as colorless needles from **3** (50 mg).

Methyl 4,6-O-Benzylidene-3-O-pivaloyl-α-D-glucopyranoside (4a).[9] Yield 72.2 mg (96%) as colorless needles from **4** (100 mg).

Methyl 4,6-O-Benzylidene-3-O-tert-butyldimethylsilyl-α-D-glucopyranoside (5a).[15] Yield 60.4 mg (79%) as colorless amorphous from **5** (100 mg)

Methyl 4,6-O-Benzylidene-3-O-methoxymethyl-α-D-glucopyranoside (6a).[16] Yield 67.6 mg (92%) as colorless needles from **6** (100 mg).

Methyl 3-O-Allyloxycabonyl-4,6-O-benzylidene-α-D-glucopyranoside (7a).[1317] Yield 65.8 mg (87%) as colorless amorphous from **7** (100 mg).

Methyl 4,6-O-Benzylidene-3-O-methanesulfonyl-α-D-glucopyranoside (8a).[18] Yield 66.6 mg (89%) as colorless needles from **8** (100 mg)

Methyl 4,6-O-Benzylidene-3-O-(p-tolylsulfonyl)-α-D-glucopyranoside (9a).[19] Yield 68.2 mg (87%) as coloeless needles from **9** (100 mg).

Methyl 4-O-Acetyl-3-O-methoxymethyl-6-O-triphenylmethyl-α-D-glucopyranoside (10a).[9] Yield 80.0 mg (98%) as colorless needles from **10** (100 mg).

Phenyl 2,3,4-Tri-O-benzyl-1-thio-β-D-glucopyranoside (11a).[20] Yield 37 mg (87%) as colorless needles from **11** (52 mg).

Phenyl 3-O-Benzoyl-4,6-O-benzylidene-1-thio-β-D-glucopyranoside (12a).[10c,21] Yield 42 mg (80%) as colorless needles from **12** (62 mg).

3,4-Di-O-benzyl-D-glucal (13a).[22] Yield 30 mg (80%) as a colorless syrup from **13** (51 mg).

Methyl 3-O-Acetyl-4,6-O-benzylidene-α-D-mannopyranoside (14a).[13d,23] Yield 54 mg (74%) as a colorless syrup from **14** (100 mg).

Methyl 2-O-Acetyl-4,6-O-benzylidene-α-D-mannopyranoside (14b).[23b,24] Yield 3.7 mg (5%) as a colorless amorphous from **14** (100 mg).

Methyl 3-O-Benzoyl-4,6-O-benzylidene-α-D-mannopyranoside (15a).[13a,25] Yield 53.5 mg (70%) as a colorless syrup from **15** (100 mg).

Methyl 2-O-Benzoyl-4,6-O-benzylidene-α-D-mannopyranoside (15b).[25b,26] Yield 2.3 mg (3%) as a colorless amorphous from **15** (100 mg).

Phenyl 4,6-Di-O-acetyl-2-deoxy-2-phthalimido-1-thio-β-D-glucopyranoside (16b).[27] Yield 24 mg (70%) as a colorless amorphous from **16** (42 mg).

Methyl 4,6-O-Benzylidene-2-O-(N-phenylcarbamoyl)-α-D-glucopyranoside. Commercially available methyl 4,6-*O*-benzylidene-α-D-glucopyranoside (11.1 g, 39.2 mmol) was reacted with phenyl isocyanate (5.1 mL, 47.0 mmol) in pyridine (100 mL). The crude product was was purified by recrystallization with hexane−EtOAc to give methyl 4,6-*O*-benzylidene-2-*O*-(*N*-phenylcarbamoyl)-α-D-glucopyranoside (11.30 g, 72% yield): $[\alpha]_D^{25}$ +68.7 (c 1.01, $CHCl_3$); mp 202−206 °C (hexane−EtOH, colorless needles); IR (KBr disk) ν 3449 cm^{-1} (OH), 1639 cm^{-1} (C═O); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.51−7.05 (10H, m), 7.05 (1H, br s), 5.56 (1H, s), 5.03 (1H, d, J = 3.8 Hz), 4.83 (1H, dd, J = 3.8 Hz, J = 9.6 Hz), 4.30 (1H, dd, J = 4.8 Hz, J = 10.3 Hz), 4.23 (1H, ddd, J = 9.5 Hz, J = 3.1 Hz, J = 9.6 Hz), 3.86 (1H, ddd, J = 9.5 Hz, J = 10.3 Hz, J = 4.8 Hz), 3.78 (1H, dd, J = 10.3 Hz, J = 10.3 Hz), 3.58 (1H, dd, J = 9.5 Hz, J = 9.5 Hz), 3.43 (3H, s), 2.72 (1H, d, J = 3.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.4, 136.9, 129.3, 129.0, 128.3, 126.3, 123.7, 118.6, 102.0, 98.0, 81.3, 74.0, 68.8, 68.8, 62.0, 55.4. Anal. Calcd for $C_{21}H_{23}NO_7$ (401.41): C, 62.83; H, 5.78; N, 3.49. Found: C, 63.12; H, 5.71; N, 3.50.

Methyl 3-O-Methoxymethyl-2-O-(N-phenylcarbamoyl)-6-O-triphenylmethyl-α-D-glucopyranoside. Compound **6** (0.66 g, 1.48 mmol) was hydrolyzed with 70% aqueous acetic acid (50 mL), and then the obtained crude 4,6-diol was reacted with triphenylmethyl chloride (0.39 g, 1.11 mmol) and 4-dimethylaminopyridine (10 mg) in pyridine (5 mL). The resulting crude product was purified on a column of silica gel with hexane−-EtOAc (3:1 v/v) to give 6-*O*-trityl derivative (0.53 g, 75% yield over two steps): $[\alpha]_D^{25}$ +29.7 (c 0.45, $CHCl_3$); colorless amorphous; IR (KBr neat) ν 3058 cm^{-1} (NH), 1716 cm^{-1} (C═O), 1540 cm^{-1} (C═C); ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.49−7.22 (20H, m), 6.79 (1H, s), 4.99 (1H, d, J = 3.8 Hz), 4.89 (1H, dd, J = 9.9 Hz, J = 3.8 Hz), 4.76, 4.69 (2H, each d, J = 6.7 Hz), 3.80 (1H, s), 3.79 (1H, ddd, J = 8.8 Hz, J = 2.7 Hz, J = 6.7 Hz), 3.75 (1H, dd, J = 8.8 Hz, J = 9.9 Hz), 3.53 (1H, dd, J = 8.8 Hz, J = 8.8 Hz), 3.48 (3H, s), 3.45 (1H, dd, J = 10.1 Hz, J = 2.7 Hz,), 3.39 (3H, s), 3.33 (1H, dd, J = 6.7 Hz, J = 10.1 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ 143.9, 137.5, 129.1, 128.7, 127.8, 127.0, 123.7, 118.5, 98.2, 97.1, 86.7, 82.2, 77.20, 70.5, 70.4, 63.6, 56.0, 55.0; HRMS (ESI-TOF) calcd for $C_{35}H_{37}NO_8Na$ m/z [M + Na]$^+$ 622.2417, found 622.2407. Anal. Calcd for $C_{35}H_{37}NO_8$ (599.67): C, 70.10; H, 6.22; N, 2.34. Found: C, 70.23; H, 6.60; N, 2.61.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Copies of ^{1}H, ^{13}C, and ^{15}N NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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