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Straightforward Route for Anchoring a Glucosyl Moiety onto Nucleophilic Species: Reaction of Amines and Alcohols with Carboxymethyl 3,4,6-Tri-*O*-acetyl-α-D-glucopyranoside 2-*O*-Lactone

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The base-catalyzed reaction of carboxymethyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside 2-*O*-lactone (prepared from isomaltulose) with amino acids and fatty amines under basic catalysis gave a series of new pseudoglucopeptides, nonionic amphiphiles, and polymerizable derivatives. The same reaction applied to alcohols provided the corresponding 2-(α-D-glucopyranosyloxy)acetyl esters with either basic or acidic catalysts.

Introduction

The opening of carbohydrate lactones is an efficient method for anchoring a carbohydrate moiety onto an organic molecule, which is an alternative to glycosylation. Such ring-opening reactions have played a key role in providing access to a variety of conjugates such as amphiphilic derivatives,[1−7] carbohydrate terminated dendrimers,[8,9] and hybrid polymers.[10] During the course of our studies aimed at employing readily available sugars as starting materials for chemical synthesis,[11] we have found that a new bicyclic glucose-based lactone (**5**) can be conveniently obtained from either isomaltulose or trehalulose.[12] Isomaltulose is derived from sucrose by bioconversion and is also a cheap and adaptable organic raw material obtained from renewable resources.[13] The lactone ring is distinct from the pyranose ring, since its opening by nucleophilic species can provide new conjugates in which the cyclic structure of a carbohydrate is preserved whereas acyclic derivatives are obtained from classical sugar lactones. Only uronic acid lactones or more complex bicyclic structures based on carbohydrates have been used in similar strategies, with the purpose of preparing either surfactants or pseudoglycopeptides.[14,15]

We now report a study of the scope of nucleophilic openings of the lactone **5** with respect to the nature of amines and alcohols, the feasibility of deprotecting products, and the type of catalysis. We thereby describe the synthesis of a series of new glucose-containing derivatives which can be categorized as pseudoglycopeptides, surfactants, and polymerizable compounds.

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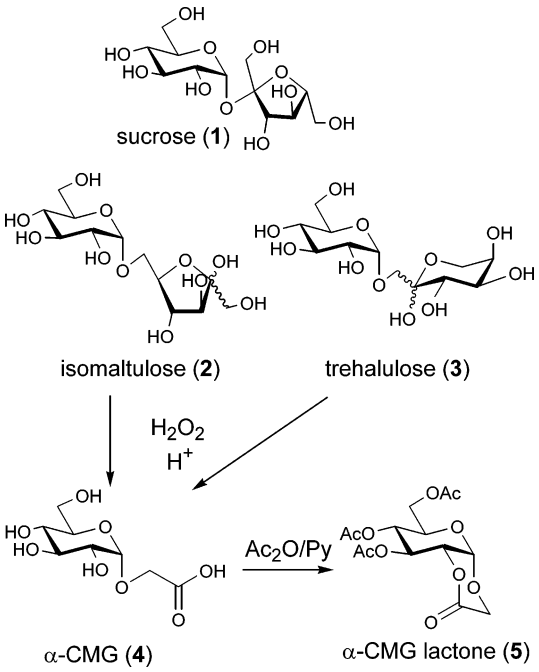
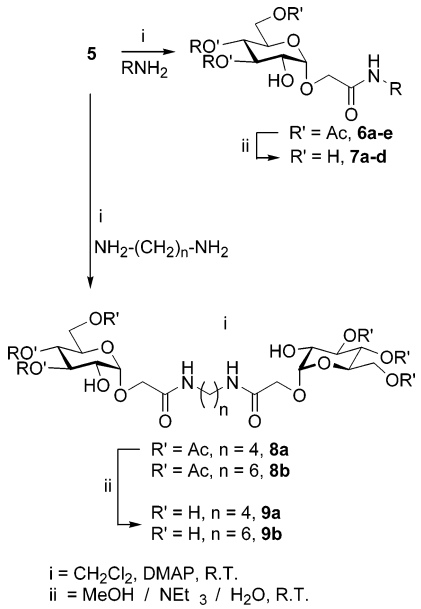
SCHEME 1



SCHEME 2



Results and Discussion

Oxidation of isomaltulose (**2**), trehalulose (**3**), 6-α-D-glucopyranosyl-D-fructofuranose, and 1-α-D-glucopyranosyl-D-fructopyranose, respectively, with hydrogen peroxide (Scheme 1) provided carboxymethyl α-D-glucopyranoside (α-CMG, **4**).[12] As in other oxidation reactions of isomaltulose,[16,17] oxidation starts at the reducing end of the fructose moiety, via sequential cleavage of either one- or two-carbon atom units. The precise outcome of this sequence was not established, but it was observed that the pH played an important role, because of its influence on many factors of the reaction, namely the (i) possible further oxidation of α-CMG (**4**), (ii) acid-catalyzed hydrolysis of the glycosidic bond of **4**, (iii) acid-catalyzed transformation of isomaltulose into glucosyl hydroxymethyl furfural and its subsequent oxidation, and (iv) direct degradation of hydrogen peroxide. Under basic conditions, very slow formation of α-CMG (**4**) was observed although isomaltulose was totally consumed. Under acidic conditions (pH 2), α-CMG (**4**) was obtained in 35% yield (not isolated, determined by ion-exchange chromatography). Increasing the pH led to slower reactions and lower yields, except in the presence of sodium tungstate[18] (38% yield at pH 4). The same procedures applied to trehalulose (**3**) gave α-CMG (**4**) in slower rates (47−59% based on starting material recovery).[12] Direct treatment of the crude reaction mixture containing α-CMG (**4**) under acetylating conditions (acetic anhydride, pyridine) gave the triacetylated bicyclic lactone **5** (carboxymethyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside 2-*O*-lactone) which was isolated in 20−30% overall yield starting from isomaltulose (**2**). During acylation, an intermediate mixed anhydride is formed (by attack of the carboxylate ion) which gives the *δ*-lactone by intramolecular reaction with OH-2, leaving the three remaining hydroxyl groups to be simply acylated. Although relatively low yields were obtained, the preparation of **4** and **5** is advantageous over the alternative of glycosylation which is multistep, necessitating protection−deprotection steps and the use of more expensive reagents. Furthermore, hydrogen peroxide is cheap, readily available, and does not generate byproducts.[19]

During the characterization of the lactone **5**, it was observed that a new compound was formed in low yield in the presence of ethanol, which was identified as the ethyl ester **11a**. This compound resulted from the opening of the lactone, thus providing a free OH-2 and three acetyl groups at OH-3, -4, and -6 (vide infra). We tried to take advantage of the relative fragility of this lactone linkage versus the acetyl groups to form glycosyloxy-acetylated derivatives from various nucleophilic species. With surfactants and polymerizable compounds being the typical targets for new carbohydrate-derived products, the ring-opening reaction was first applied to a series of aliphatic primary amines (C_{12}, C_{14}, C_{16}), propargylamine, and 2-(methacryloyloxy)ethylamine (Scheme 2 and Table 1). The new glucose-derived acetamides (**6a**−**e**) were formed in good yield under basic catalysis (DMAP) in dichloromethane at room temperature. The amides **6a**−**d** were readily deacetylated (MeOH−NEt_3−H_2O) to provide the free-sugar-based amides **7a**−**d**. The amide **6e** was obtained in a lower yield compared to the others in the series because of its high polymerizability. This also prevented **7e** being obtained in satisfactory yield. We previously experienced such difficulties in the case of related sucrose methacrylates.[20] Similar reaction of the diamines 4-aminobutylamine and 6-aminobutylamine

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TABLE 1. Opening of Triacetyl Lactone 5 by Amines and Diamines[a]

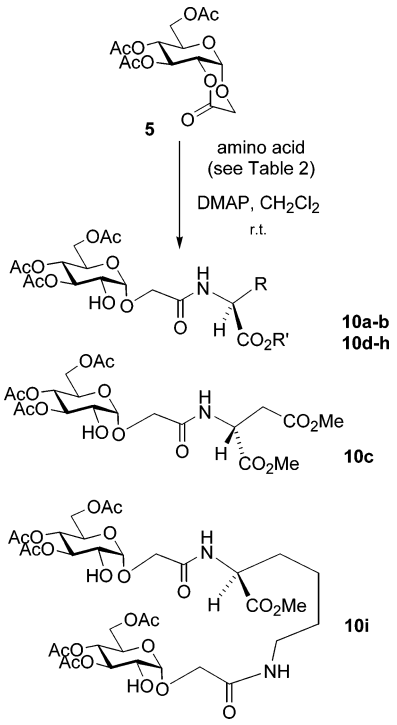
R	time (h)	product	yield (%)
$-C_{12}H_{25}$	12	**6a**	84
$-C_{14}H_{29}$	12	**6b**	78
$-C_{16}H_{33}$	20	**6c**	76
$-CH_2C{\equiv}CH$	48	**6d**	71
$-CH_2CH_2OC(O)C(CH_3){=}CH_2$	48	**6e**	55
$-C_4H_8-$	12	**8a**	72
$-C_6H_{12}-$	12	**8b**	73

[a] At room temperature.

gave the *N*,*N*′-bis(glycosyloxy)diacetamides **8a**,**b**, which were deacetylated to give the bolaamphiphilic derivatives **9a**,**b**, respectively. Carbohydrate-based surfactants of this type have recently received special interest due to their physicochemical properties, including the possibility to be incorporated into lipidic membranes. Such structures have been also prepared by reaction of a furanurono-6,3-lactone with diamines or by acylation of 2-deoxy-2-amino sugars.[14]

In view of the widespread occurrence of glycopeptides in biological processes, various strategies have been established for the synthesis of analogues and mimetics such as conjugates.[21] Also, highly functionalized species can be constructed onto carbohydrate scaffolds in other domains such as peptidomimetics.[22] This prompted us to examine the opening of α-CMG lactone (**5**) by variously protected amino acids to form new pseudoglycopeptides. We first studied the simplest amino acid glycine, protected as an ethyl ester. Thus, reaction with the lactone **5** gave the corresponding amide **10a** in 60% yield. In the case of a substituted amino acid such as aspartic acid dimethyl ester, no racemization was observed despite the basic conditions used. The glycosyloxyacetamides **10b** and **10c** were obtained regioselectively starting from either L- or the D-amino acids (and not a mixture of two epimers). In the case of lysine methyl ester having an unprotected terminal amino group on the side chain, thus bearing two available reactive amino groups, the *N*,*N*′-bis(glycosyl) diacetamide **10i** was obtained in 55% yield. It is interesting to note that in this case, a monomide at the side chain amino group leaving the α-aminoester function still available for protection incorporation into a peptide sequence was obtained as a side product (5%). The alternative lysine monoamide derivative **10h**, possessing a carbohydrate moiety at the α-aminoester end was obtained starting from benzyloxycarbonyl N-protected lysine methyl ester (Scheme 3 and Table 2). Although these compounds have not yet been deacetylated, some methods for the removal of acetyl groups without racemization of chiral α-amino acid centers have been reported. Notably, hydrazine in either methanol or methanol-dichloromethane has been used in the final carbohydrate deacetylation step of the synthesis of glycopeptides, e.g., for the preparation of a polymeric glucosyl-L-serine and an helical periodic glycopeptide.[23,24] It was also used for the deprotection of an acylated hydroxylamine in amino acid based approaches to (+)-FR900482 and an *N*-acylated amino acid.[25,26] Alternatively, catalytic sodium methoxide in methanol was used for *O*-acyl group deprotection in the final step to a disaccharidic hexapeptide.[27] In addition, some neutral organotin catalysts were shown to function with several different functional groups.[28]

SCHEME 3



Alcohols were also found to react regioselectively with the lactone **5** to give the corresponding partially acetylated esters **11a**−**f**. The reaction could be conducted in the presence of base, acid, or lanthanide salts, using either an excess of alcohol as a solvent (or mixed with CH_2Cl_2) or in a controlled amount with CH_2Cl_2 (Scheme 4 and Table 3). In contrast, reaction of methanol, with **5**, under basic conditions, gave the fully deactetylated methyl ester **13a** in 68% yield. However, since there is no efficient regioselective means by which such com-

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TABLE 2. Opening of Triacetyl Lactone 5 by Amino Acids

AA	R	R′	AA/**5**[a]	DMAP/**5**[a]	time (days)	product	yield[b] (%)
GLY	H	Et	3	3	3	**10a**	60
L-ASP	$-CH_2CO_2Me$	Me	3	3	4	**10b**	76
D-ASP	$-CH_2CO_2Me$	Me	3	4	7	**10c**	71
GLU	$-CH_2CH_2CO_2Me$	Me	3	4	3	**10d**	65
PHE	$-CH_2C_6H_5$	Me	2	3	3	**10e**	92
TYR	$-CH_2C_6H_4O^tBu$	^{t}Bu	0.5	1	4	**10f**	66[a]
ASN	$-H_2CONH_2$	^{t}Bu	2	3	7	**10g**	84
LYS	$-(CH_2)_4NHCbz$[c]	Me	3	4	4	**10h**	87
LYS	$-(CH_2)_4NH_2$	Et	0.5	1	6	**10i**	55[d]

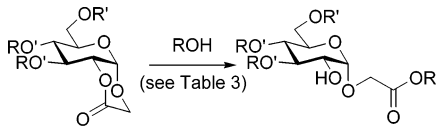
[a] Based on AA. [b] Based on **5**. [c] Cbz: benzyloxycarbonyl. [d] Molar ratio.

TABLE 3. Opening of Lactones 5 and 12 by Alcohols

R	lactone	method[a]	catalyst (equiv[b])	time (days)	R′	product	yield (%)
Et	**5**	A		7	Ac	**11a**	26
Et	**5**	A	NEt_3 (1) or DMAP (2)	1.5−2	Ac	**11a**	40−50
Me	**5**	A	DMAP (2)	2	H	**13a**	68
$-CH(CH_3)_2$	**5**	A	DMAP (2)	7	Ac	**11c**	54
$-CH_2CH_2CH_3$	**5**	B (5)	DMAP (0.6)	7[c]	Ac	**11b**	83
$-CH_2CH=CH_2$	**5**	B (9)	DMAP (0.6)	5	Ac	**11d**	88
$-CH_2C\equiv CH$	**5**	B (3)	DMAP (3)	3[c]	Ac	**11e**	39
$-(CH_2)_2OC(O)C(Me)=CH_2$	**5**	B (3)	DMAP (3)	10	Ac	**11f**	31
Et	**5**	A	APTS or $AlCl_3$ (0.1)	1−1.5	Ac	**11a**	50−42
Et	**5**	A	$Ln(CF_3SO_3)_3$ (0.1)[d]	1−1.5	Ac	**11a**	46−54
Et	**12**	A	DMAP (2)	12[e]	H	**13b**	59
$-CH_2CH_2CH_3$	**12**	A	DMAP (5)	5[e]	H	**13c**	40
$-CH_2CH=CH_2$	**12**	A	DMAP (5)	3[e]	H	**13d**	57

[a] A = alcohol as solvent; B = dichloromethane as solvent (equivalents of alcohol in brackets). [b] Based on lactone. [c] At reflux of CH_2Cl_2. [d] Ln = La, Sc, or Yb. [e] In hours.

SCHEME 4



R' = Ac, **5**
R' = AcCl, **12**

R' = Ac, **11a-f**
R' = H, **13a-d**

pounds may be deacetylated without also cleaving the aglycon ester, such routes are of diminished interest in comparison with those using the amines described above. An alternative route to esters having an unprotected carbohydrate group was to start from the chloroacetylated lactone **12**, thus enabling the chloroacetyl groups to be removed concomitantly in the presence of excess alcohol and base, leading to give the fully deprotected glucosyloxyacetylated compounds **13b**−**d**.

In conclusion, we have shown that the readily available carboxymethyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside 2-*O*-lactone (**5**) was a useful synthon for anchoring a carbohydrate moiety onto the nitrogen atom of amines via the selective opening of the lactone ring. The reaction of this lactone with amino acids gave rise to a new type of pseudoglycopeptides. New amphiphilic and polymerizable compounds were also prepared from aliphatic and unsaturated amines. In the case of alcohols, glycosyloxyacetylated derivatives were obtained from the same lactone and its choroacetylated analogue.

Experimental Section

General Methods. Merck 60H (40−63 μm) silica gel was used for column chromatography. Analytical TLC was performed on Merck 60 F_{254} silica gel aluminum plates. A solution of 10% H_2SO_4 in EtOH was used to develop the plates. Isomaltulose was obtained from TCI. Mixtures of solvents are given in volume.

Triacetyl Lactone (5) and Tris(2-chloroacetyl) Lactone (12). A mixture of isomaltulose (**2**) (34.2 g, 100.0 mmol), sodium tungstate dihydrate (7.9 g, 24.0 mmol), 30% (w/w) aqueous hydrogen peroxide (200 mL, 1960 mmol), and 85% phosphoric acid (1.38 g, 12 mmol) was adjusted to pH 4 by addition of a solution of ammonia in water (32%). The mixture was stirred at 90 °C for 1−2 days while maintaining pH 4 by addition of aqueous ammonia. Alternatively, the reaction could be achieved at pH 2 without tungstate ions.[12] Excess oxidant, if present (KI/I_2 colorimetric test), was quenched with aqueous sodium sulfite, and the medium was adjusted to pH 9 with ammonia. Water (500 mL) was added, and the resulting solution was freeze-dried. The crude solid containing carboxymethyl α-D-glucopyranoside (**4**) was taken up with anhydrous pyridine (180 mL). Acetic anhydride (110 mL) and DMAP (0.2 g) were added at 0 °C, and the mixture was allowed to warm to room temperature. After the mixture was stirred for 48 h, solvents were removed under reduced pressure using co-distillation with toluene. The residue was taken up with water (200 mL), extracted with CH_2Cl_2 (3 × 300 mL) and the combined organic layers were dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The crude product was purified by silica gel chromatography. Elution with hexane/AcOEt (1/1), R_f = 0.38, gave the desired product as a white solid (10.3 g, 29%), which was recrystallized from Et_2O. **5**: mp 125−127 °C; $[\alpha]^{20}_D$ +141 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.98−2.07 (3s, 9H), 4.05−4.12 (m, 1H), 4.19−4.30 (m, 2H), 4.40 (dd, 1H, *J* = 3.0, 9.4 Hz), 4.48 (d, 1H, *J* = 17.7 Hz), 4.66 (d, 1H, *J* = 17.7 Hz), 5.04 (t, 1H, *J* = 9.8 Hz), 5.32 (d, 1H, *J* = 3.0 Hz), 5.53 (t, 1H, *J* = 9.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.91, 21.06, 61.71, 64.89, 67.31, 70.47, 71.91, 76.35, 91.51, 163.76, 169.81, 170.41, 170.91; MS (FAB) *m*/*z* = 331,1 $[M - Me]^+$. Anal. Calcd for $C_{14}H_{18}O_{10}$: C, 48.55; H, 5.24. Found: C, 48.32; H, 4.97.

Alternatively, the crude solid (35 g) containing carboxymethyl α-D-glucopyranoside (**4**, see above) was dissolved in a

mixture of CH_2Cl_2 (150 mL) and pyridine (30 mL, 0.37 mol), and a solution of chloroacetyl chloride (30 mL, 0.38 mol) in CH_2Cl_2 (150 mL) was introduced over 8 h. The solution was stirred at room temperature for 15 h. The same workup as described for **5** gave the desired product as a white solid (3.2 g, 22%), $R_f = 0.31$ (hexane/AcOEt 1/1). **12**: $[\alpha]^{20}_D$ +123 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 3.95−4.15 (3s, 6H), 4.25−4.40 (m, 3H), 4.47 (dd, 1H, $J = 3.0, 9.6$ Hz), 4.50 (d, 1H, $J = 17.9$ Hz), 4.70 (d, 1H, $J = 17.9$ Hz), 5.15 (t, 1H, $J = 9.6$ Hz), 5.35 (d, 1H, $J = 3.0$ Hz), 5.64 (t, 1H, $J = 9.6$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 40.57, 40.74, 40.94, 62.98, 65.02, 68.59, 69.89, 73.45, 75.99, 91.45, 163.24, 166.68, 167.18, 167.34; HRMS (FAB) calcd for $[M + Li]^+$ 454.9890, found 454.9910. Anal. Calcd for $C_{14}H_{15}Cl_3O_{10}$: C, 37.39; H, 3.36; Cl, 23.65. Found: C, 37.42; H, 3.11; Cl, 23.40.

General Procedure for the Opening of Triacetyl Lactone (5) by Amines and Diamines. To a solution of **5** (typical range 50−200 mg, ca.20 mg/mL, ca.0.06 M) in anhydrous CH_2Cl_2 (10 mL) were added DMAP (2 equiv for **6b** and **6c**, 3 equiv for **6a** and **6d**, 4 equiv for **6e**, 0.1 equiv for **8a** and **8b**) and either the amine or diamine (2 equiv for **6b**, **6c**, 3 equiv for **6a**, **6e, 6d**, 0.5 equiv for **8a** and **8b**). The mixture was stirred at room temperature for 20 h except for **8a** and **8b** (12 h). The solvent was removed under reduced pressure, and the residue was purified by chromatography, eluting with hexane/AcOEt (1/4) for **6d**, **6a**, **6e** or (2/3) for **6b**, **6c**, AcOEt/EtOH (9/1) for **8a** and **8b**, to afford the desired amides or diamides.

General Procedure for the Basic Hydrolysis of Acetyl Groups of 2-(Tri-*O*-acetyl-α-D-glucopyranosyloxy)acetamides (6a−d) and *N*,*N*′-Bis-acetamides (8a,b). The compound was dissolved in a mixture of MeOH/NEt_3/H_2O 8/1/1 (10 mL for 250 mg of product). After complete reaction (2−4 days), the solvents were removed and the residue was purified by silica gel chromatography to afford the deprotected amides **7a**−**d** and diamides **9a**,**b**.

(*N*-Dodecylcarbamoyl)methyl 3,4,6-Tri-*O*-acetyl-α-D-glucopyranoside (6a) and (*N*-Dodecylcarbamoyl)methyl α-D-Glucopyranoside (7a). 6a: yield 84% (66 mg, white solid); $R_f = 0.42$ (hexane/AcOEt 1/4); $[\alpha]^{20}_D$ +88 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 0.84 (t, 3H, $J = 7.0$ Hz), 1.12−1.33 (m, 18H), 1.39−1.55 (m, 2H), 1.96−2.15 (3s, 9H), 3.09 (s, 1OH), 3.12−3.29 (m, 2H), 3.78 (dd, 1H, $J = 4.0, 9.9$ Hz), 3.94−4.10 (m, 2H), 4.04 (d, 1H, $J = 15.8$ Hz), 4.17 (d, 1H, $J = 15.8$ Hz), 4.25 (dd, 1H, $J = 4.8, 12.5$ Hz), 4.87 (d, 1H, $J = 3.7$ Hz), 4.99 (t, 1H, $J = 9.9$ Hz), 5.23 (t, 1H, $J = 9.9$ Hz), 7.20 (t, 1NH, $J = 5.7$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.03, 20.55, 20.63, 20.80, 22.60, 26.88, 29.25, 29.55, 31.82, 39.15, 61.75, 67.21, 67.84, 67.95, 70.32, 73.44, 99.03, 168.81, 169.53, 170.59, 171.37; HRMS (FAB) calcd for $[M + Li]^+$ 538.3203, found 538.3210. **7a:** elution AcOEt/EtOH (4/1); $R_f = 0.37$; yield 98%; white solid; $[\alpha]^{20}_D$ +91 (*c* 0.5, MeOH); ^{1}H NMR (300 MHz, CD_3OD) δ 0.94 (t, 3H, $J = 7.0$ Hz), 1.21−1.45 (m, 18H), 1.49−1.65 (m, 2H), 3.23−3.39 (m, 3H), 3.52 (dd, 1H, $J = 3.7, 9.6$ Hz), 3.56−3.64 (m, 1H), 3.66−3.75 (m, 2H), 3.80−3.90 (m, 1H), 4.06 (d, 1H, $J = 15.8$ Hz), 4.22 (d, 1H, $J = 15.8$ Hz), 4.85 (d, 1H, $J = 3.7$ Hz); ^{13}C NMR (75 MHz, CD_3OD) δ 14.37, 23.72, 28.03, 30.37, 30.52, 30.69, 30.81, 33.09, 40.14, 62.48, 67.83, 71.55, 73.19, 74.38, 74.92, 101.06, 171.89; HRMS (FAB) calcd for $[M + Li]^+$ 412.2886, found 412.2890. Anal. Calcd for $C_{20}H_{40.2}NO_{7.6}$ (**7a**·0.6H_2O): C, 57.69; H, 9.73; N, 3.36. Found: C, 57.55; H, 9.89; N, 3.58.

(*N*-Propargylcarbamoyl)methyl 3,4,6-Tri-*O*-acetyl-α-D-glucopyranoside (6d) and (*N*-Propargylcarbamoyl)-methyl α-D-Glucopyranoside (7d). 6d: yield 71% (164 mg, white solid); $R_f = 0.23$ (hexane/AcOEt 1/4); $[\alpha]^{20}_D$ +115 (*c* 0.4, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00−2.09 (2s, 9H), 2.24 (t, 1H, $J = 2.6$ Hz), 3.75−3.84 (m, 1H), 3.89 (d, 1OH, $J = 7.7$ Hz), 3.96−4.12 (m, 5H), 4.23 (d, 1H, $J = 4.8$ Hz), 4.27 (d, 1H, $J = 3.3$ Hz), 4.93 (d, 1H, $J = 3.7$ Hz), 5.00 (t, 1H, $J = 9.6$ Hz), 5.25 (t, 1H, $J = 9.6$ Hz), 7.71 (t, 1NH, $J = 5.1$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 21.02, 21.12, 21.31, 29.06, 62.22, 67.73, 68.26, 68.50, 70.84, 72.03, 73.79, 79.62, 99.51, 169.28, 170.00, 171.11, 171.97; HRMS (FAB) calcd for $[M + Li]^+$ 408.1482, found 408.1516. Anal. Calcd for $C_{17}H_{23}NO_{10}$: C, 50.87; H, 5.78; N, 3.49. Found: C, 50.74; H, 5.98; N, 3.51. **7d:** elution CH_2Cl_2/Me_2CO/MeOH/H_2O (56/20/20/4); $R_f = 0.29$; yield 98%; white solid; $[\alpha]^{20}_D$ +128 (*c* 0.4, MeOH); ^{1}H NMR (300 MHz, CD_3OD) δ 2.55 (t, 1H, $J = 2.5$ Hz), 3.25 (t, 3H, $J = 9.6$ Hz), 3.40 (dd, 1H, $J = 3.8, 9.6$ Hz), 3.45−3.53 (m, 1H), 3.57−3.66 (m, 2H), 3.75 (dd, 1H, $J = 2.3, 11.9$ Hz), 3.94 (dd, 1H, $J = 17.5, 2.6$), 3.97 (d, 1H, $J = 15.7$ Hz), 4.02 (dd, 1H, $J = 17.5, 2.6$ Hz), 4.17 (d, 1H, $J = 15.7$ Hz), 4.77 (d, 1H, $J = 3.8$ Hz); ^{13}C NMR (75 MHz, CD_3OD) δ 29.31, 62.79, 68.09, 71.82, 72.63, 73.54, 74.63, 75.18, 80.56, 101.25, 172.07; HRMS (FAB) calcd for $[M + Li]^+$ 282.1165, found 282.1160. Anal. Calcd for $C_{11}H_{17.8}NO_{7.4}$ (**7d**·0.4H_2O): C, 46.61; H, 6.33; N, 5.29. Found: C, 46.63; H, 6.45; N, 5.31.

[*N*-[2-(Methacryloyloxy)ethyl]carbamoyl]methyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (6e): yield 55% (76 mg, colorless oil); $R_f = 0.16$ (hexane/AcOEt 1/4); $[\alpha]^{20}_D$ +108 (*c* 0.6, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.91 (s, 1H), 2.00−2.09 (3s, 9H), 3.46−3.57 (m, 1H), 3.60−3.71 (m, 1H), 3.77 (dd, 1H, $J = 3.7, 9.9$ Hz), 3.94−4.40 (m, 7H+1OH), 4.89 (d, 1H, $J = 3.3$ Hz), 5.00 (t, 1H, $J = 9.6$ Hz), 5.28 (t, 1H, $J = 9.9$ Hz), 5.60 (s, 1H), 6.13 (s, 1H), 7.65 (s, 1NH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 18.71, 21.11, 21.21, 21.33, 39.22, 60.96, 62.42, 63.66, 68.59, 70.89, 73.74, 99.75, 127.21, 136.31, 168.58, 170.14, 171.20, 171.60, 171.85; HRMS (FAB) calcd for $[M + Na]^+$ 482.1850, found 482.1862. Anal. Calcd for $C_{20}H_{29}NO_{12}$: C, 50.52; H, 6.15; N, 2.95. Found: C, 50.39; H, 6.28; N, 2.79.

***N*,*N*′-(1,6-Butamethylene)bis[2-(3,4,6-tri-*O*-acetyl-α-D-glucopyranosyloxy)acetamide] (8a) and *N*,*N*′-(1,6-Butamethylene)bis[2-(α-D-glucopyranosyloxy)acetamide] (9a). 8a:** yield 72% (202 mg, white solid); $[\alpha]^{20}_D$ +129 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.49−1.65 (m, 4H), 1.96−2.10 (3s, 18H), 2.8−3.2 (m, 2H, 1OH), 3.12−3.23 (m, 2H), 3.31−3.43 (m, 2H), 3.49 (s, 2H), 3.76 (dd, 2H, $J = 3.7, 9.6$ Hz), 3.93−4.29 (m, 10H), 4.85 (d, 2H, $J = 3.7$ Hz), 4.98 (t, 2H, $J = 9.9$ Hz), 5.25 (t, 2H, $J = 9.6$ Hz), 7.88 (t, 2NH, $J = 5.5$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.61, 20.69, 20.93, 25.99, 38.66, 61.78, 67.28, 68.00, 70.20, 73.17, 99.41, 169.57, 169.93, 170.66, 171.27; HRMS (FAB) calcd for $[M + Li]^+$ 787.2960, found 787.2979. Anal. Calcd for $C_{32}H_{50.6}N_2O_{21.3}$ (**8a**·1.3H_2O): C, 47.79; H, 6.34; N, 3.48. Found: C, 47.78; H, 6.24; N, 3.40. **9a**: elution AcOEt/MeOH/H_2O (6/3/1); $R_f = 0.23$; yield 94%; white solid; $[\alpha]^{20}_D$ +126 (*c* 0.5, H_2O); ^{1}H NMR (300 MHz, D_2O) δ 1.49−1.66 (m, 4H), 3.25−3.33 (m, 4H), 3.43 (t, 2H, $J = 9.9$ Hz), 3.61 (dd, 2H, $J = 3.7, 9.6$ Hz), 3.64−3.70 (m, 2H), 3.72−3.81 (m, 4H), 3.85 (dd, 2H, $J = 2.5, 12.2$ Hz), 4.10 (d, 2H, $J = 15.6$ Hz), 4.24 (d, 2H, $J = 15.6$ Hz), 4.96 (d, 2H, $J = 3.7$ Hz); ^{13}C NMR (75 MHz, D_2O) δ 26.13, 39.05, 60.81, 66.73, 69.78, 71.54, 72.68, 73.24, 99.21, 172.12; HRMS (FAB) calcd for $[M + Li]^+$ 535.2326, found 535.2354. Anal. Calcd for $C_{20}H_{39.8}N_2O_{15.9}$ (**9a**·1.9H_2O): C, 42.68; H, 7.12; N, 4.97. Found: C, 42.63; H, 7.22; N, 4.95.

General Procedure for Opening of Triacetyl Lactone (5) by Partially Protected Amino Acids. To a solution of **5** in anhydrous CH_2Cl_2 were added DMAP and a protected amino acid (in molar equivalents according to Table 2). After complete reaction (3−7 days, room temperature), the solvent was removed and the residue was submitted to silica gel chromatography to give the glycosylated amino acid derivatives **10a**−**i**. Typical reactions were run with 150−500 mg of the starting lactone **5** in 10 mL of CH_2Cl_2.

***N*-[2-(3,4,6-Tri-*O*-acetyl-α-D-glucopyranosyloxy)acetyl]-glycine ethyl ester (10a):** elution CH_3CN; $R_f = 0.70$; yield 60% (384 mg); white solid; $[\alpha]^{20}_D$ +115 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.27 (t, 3H, $J = 7.2$ Hz), 1.92−2.15 (3s, 9H), 2.99 (s, 1 OH), 3.83 (dd, 1H, $J = 3.7, 9.9$ Hz), 3.93 (dd, 2H, $J = 4.8, 18.4$ Hz), 3.99−4.33 (m, 7H), 4.96 (d, 1H, $J = 3.7$ Hz), 5.02 (t, 1H, $J = 9.9$ Hz), 5.28 (t, 1H, $J = 9.6$ Hz), 7.62 (t, 1 NH, $J = 5.3$ Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.07, 20.58, 20.67, 20.82, 40.73, 61.69, 61.80, 67.21, 67.81, 68.15, 70.49, 73.11, 99.06, 169.27, 169.54, 170.04, 170.60, 171.41; HRMS

(FAB) calcd for $[M + Li]^+$ 456.1693, found 456.1701. Anal. Calcd for $C_{18}H_{27}NO_{12}$: C, 48.10; H, 6.05; N, 3.11. Found: C, 48.35; H, 6.15; N, 3.36.

***N*-[2-(3,4,6-Tri-*O*-acetyl-α-D-glucopyranosyloxy)acetyl]-L-aspartic acid dimethyl ester (10b):** elution AcOEt; R_f = 0.44; yield 76% (277 mg); white solid; $[\alpha]^{20}_D$ +110 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.83−2.16 (3s, 9H), 2.85 (dd, 1H, *J* = 4.8, 16.9 Hz), 2.93 (dd, 1H, *J* = 4.8, 16.9 Hz), 3.24 (s, 1 OH), 3.65 (s, 3H), 3.74 (s, 3H), 3.76 (dd, 1H, *J* = 3.7, 9.9 Hz), 3.95−4.06 (m, 2H), 4.09 (d, 1H, *J* = 15.8 Hz), 4.12−4.29 (m, 2H), 4.77−4.88 (m, 2H), 4.98 (t, 1H, *J* = 9.9 Hz), 5.25 (t, 1H, *J* = 9.6 Hz), 7.87 (d, 1 NH, *J* = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.59, 20.68, 20.83, 35.92, 48.28, 52.25, 52.91, 61.75, 67.05, 67.73, 68.18, 70.50, 73.08, 99.15, 168.71, 169.56, 170.53, 171.35, 171.49; HRMS (FAB) calcd for $[M + Li]^+$ 514.1748, found 514.1757. Anal. Calcd for $C_{20}H_{29}NO_{14}$: C, 46.75; H, 5.82; N, 2.72. Found: C, 46.70; H, 5.81; N, 2.97.

***N*-[2-(3,4,6-Tri-*O*-acetyl-α-D-glucopyranosyloxy)acetyl]-D-aspartic acid dimethyl ester (10c):** elution AcOEt (1/4); R_f = 0.21; yield 71% (156 mg); oil; $[\alpha]^{20}_D$ +69 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00−2.07 (3s, 9H), 2.81 (dd, 1H, *J* = 4.8, 17.3 Hz), 3.03 (dd, 1H, *J* = 4.8, 17.3 Hz), 3.68 (s, 3H), 3.70−3.75 (m, 4H), 3.81 (s, 1 OH), 3.97−4.08 (m, 2H), 4.13 (d, 1H, *J* = 15.8 Hz), 4.19−4.28 (m, 2H), 4.86−4.95 (m, 1H), 4.98 (d, 1H, *J* = 3.7 Hz), 5.00 (t, 1H, *J* = 9.9 Hz), 5.27 (t, 1H, *J* = 9.6 Hz), 7.97 (d, 1 NH, *J* = 8.8 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.42, 20.52, 20.68, 35.77, 47.77, 52.03, 52.61, 61.57, 66.84, 67.62, 68.03, 70.22, 72.58, 98.91, 168.75, 169.38, 170.54, 171.16, 171.24; HRMS (FAB) calcd for $[M + Li]^+$ 514.1748, found 514.1730. Anal. Calcd for $C_{20}H_{29.6}NO_{14.3}$ (**10c**·$0.3H_2O$): C, 46.84; H, 5.81; N, 2.73. Found: C, 46.52; H, 5.90; N, 3.35.

***N*-[2-(3,4,6-Tri-*O*-acetyl-α-D-glucopyranosyloxy)acetyl]-L-glutamic acid dimethyl ester (10d):** elution hexane/AcOEt (1/4); yield 65% (243 mg); white solid; R_f = 0.46 (CH_3CN); $[\alpha]^{20}_D$ +90 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.97−2.18 (m, 11H), 2.38−2.50 (m, 2H), 2.99 (s, 1 OH), 3.64 (s, 3H), 3.72 (s, 3H), 3.76 (dd, 1H, *J* = 3.7, 9.9 Hz), 3.95−4.08 (m, 3H), 4.20−4.31 (m, 2H), 4.49−4.58 (m, 1H), 4.91 (d, 1H, *J* = 3.7 Hz), 5.00 (t, 1H, *J* = 9.9 Hz), 5.30 (t, 1H, *J* = 9.6 Hz), 8.05 (d, 1 NH, *J* = 7.3 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.59, 20.68, 20.81, 26.01, 30.43, 51.85, 52.39, 52.53, 61.76, 67.24, 67.87, 68.02, 70.63, 73.29, 99.18, 168.73, 169.56, 170.58, 171.13, 171.52, 174.78; HRMS (FAB) calcd for $[M + Li]^+$ 528.1904, found 528.1923. Anal. Calcd for $C_{21}H_{31.6}NO_{14.3}$ (**10d**·$0.3H_2O$): C, 47.87; H, 6.04; N, 2.65. Found: C, 47.81; H, 6.07; N, 2.87.

***N*-[2-(3,4,6-Tri-*O*-acetyl-α-D-glucopyranosyloxy)acetyl]-L-phenylalanine methyl ester (10e):** elution hexane/AcOEt (1/4); R_f = 0.40; yield 92% (210 mg); white solid; $[\alpha]^{20}_D$ +118 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.98−2.10 (3s, 9H), 2.25 (s, 1 OH), 3.06 (dd, 1H, *J* = 5.8, 13.9 Hz), 3.21 (dd, 1H, *J* = 5.8, 13.9 Hz), 3.66 (dd, 1H, *J* = 3.7, 9.8 Hz), 3.74 (s, 3H), 3.92−4.08 (m, 3H), 4.18 (d, 1H, *J* = 16.2 Hz), 4.25 (dd, 1H, *J* = 4.6, 12.3 Hz), 3.66 (d, 1H, *J* = 3.7 Hz), 4.82−4.95 (m, 1H), 4.99 (t, 1H, *J* = 9.8 Hz), 5.19 (t, 1H, *J* = 9.6 Hz), 7.09−7.33 (m, 5H), 7.36 (d, 1 NH, *J* = 7.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.59, 20.68, 20.84, 37.63, 52.47, 52.80, 61.71, 66.90, 67.60, 68.09, 70.48, 73.32, 98.81, 127.15, 128.55, 129.23, 136.00, 168.51, 169.54, 170.58, 171.48, 171.69; MS (FAB) *m*/*z* = 532.3 $[M + Li]^+$. Anal. Calcd for $C_{24}H_{31}NO_{12}$: C, 54.85; H, 5.94; N, 2.66. Found: C, 55.07; H, 6.03; N, 2.82.

***N*-[2-(3,4,6-Tri-*O*-acetyl-α-D-glucopyranosyloxy)acetyl]-*O*-*tert*-butyl-L-tyrosine *tert*-butyl ester (10f):** elution hexane/AcOEt (2/3); yield 66% (123 mg); white solid; R_f = 0.56 (hexane/AcOEt 1/4); $[\alpha]^{20}_D$ +105 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.18−1.42 (3s, 18H), 1.93−2.10 (3s, 9H), 2.47 (s, 1 OH), 2.93−3.10 (m, 2H), 3.67 (dd, 1H, *J* = 3.7, 9.9 Hz), 3.91−4.08 (m, 3H), 4.19 (d, 1H, *J* = 16.2 Hz), 4.23 (dd, 1H, *J* = 4.8, 12.5 Hz), 3.69 (d, 1H, *J* = 3.7 Hz), 4.71−4.82 (m, 1H), 4.99 (t, 1H, *J* = 9.9 Hz), 5.20 (t, 1H, *J* = 9.6 Hz), 6.88 (d, 2H, *J* = 8.5 Hz), 7.04 (d, 2H, *J* = 8.5 Hz), 7.30 (d, 1 NH, *J* = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.59, 20.69, 20.84, 27.89, 28.76, 37.44, 53.29, 61.75, 66.94, 67.67, 68.08, 70.48, 73.32, 78.45, 82.49, 98.92, 124.02, 129.89, 131.04, 154.33, 168.26, 169.57, 170.48, 170.60, 171.40; HRMS (FAB) calcd for $[M + Li]^+$ 646.3050, found 646.3069. Anal. Calcd for $C_{31}H_{45}NO_{13}$: C, 58.20; H, 7.09; N, 2.19. Found: C, 57.99; H, 7.05; N, 2.20.

***N*α-[2-(3,4,6-Tri-*O*-acetyl-α-D-glucopyranosyloxy)acetyl]-L-asparagine *tert*-butyl ester (10g):** elution CH_3CN; R_f = 0.44; yield 84% (325 mg); white solid; $[\alpha]^{20}_D$ +100 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.35−1.50 (s, 9H), 1.94−2.08 (3s, 9H), 2.78 (d, 2H, *J* = 5.1 Hz), 3.76 (dd, 1H, *J* = 3.7, 9.9 Hz), 3.93−4.12 (m, 3H), 4.14−4.29 (m, 2H), 4.62−4.73 (m, 1H), 3.84 (d, 1H, *J* = 3.7 Hz), 4.97 (t, 1H, *J* = 9.9 Hz), 5.29 (t, 1H, *J* = 9.6 Hz), 6.04 (s, 1 NH), 6.27 (s, 1 NH), 8.11 (d, 1 NH, *J* = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.59, 20.69, 20.89, 27.80, 37.07, 49.46, 61.82, 67.02, 68.02, 69.99, 72.71, 82.83, 99.24, 169.02, 169.40, 169.62, 170.63, 171.03, 172.95; HRMS (FAB) calcd for $[M + Li]^+$ 541.2220, found 541.2249. Anal. Calcd for $C_{22}H_{34}N_2O_{13}$: C, 49.43; H, 6.41; N, 5.24. Found: C, 49.42; H, 6.51; N, 5.88.

***N*α-[2-(3,4,6-Tri-*O*-acetyl-α-D-glucopyranosyloxy)acetyl]-*N*ε-(benzyloxycarbonyl)-L-lysine methyl ester (10h):** elution CH_2Cl_2/AcOEt (1/1); yield 87% (402 mg); white solid; R_f = 0.50 (AcOEt); $[\alpha]^{20}_D$ +77 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.20−1.54 (m, 4H), 1.63−1.87 (m, 2H), 1.93−2.10 (3s, 9H), 3.0−3.3 (m, 2H + 1 OH), 2.25 (s, 1H), 3.69 (s, 3H), 3.78 (dd, 1H, *J* = 3.7, 9.6 Hz), 3.97−4.12 (m, 3H), 4.17−4.30 (m, 2H), 4.48−4.61 (m, 1H), 4.83 (d, 1H, *J* = 3.7 Hz), 4.98 (t, 1H, *J* = 9.9 Hz), 5.05 (s, 2H), 5.29 (t, 1H, *J* = 9.6 Hz), 7.25−7.35 (m, 6H), 7.67 (d, 1 NH, *J* = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 20.60, 20.67, 20.82, 22.44, 29.53, 31.17, 40.60, 51.69, 52.39, 61.82, 66.78, 67.18, 67.88, 68.11, 70.12, 73.30, 98.37, 127.94, 128.21, 128.55, 136.22, 156.97, 169.12, 169.62, 170.61, 171.29, 172.18; MS (FAB) *m*/*z* = 647.3 $[M + Li]^+$. Anal. Calcd for $C_{29}H_{40}N_2O_{14}$: C, 54.37; H, 6.29; N, 4.37. Found: C, 54.69; H, 6.44; N, 4.63.

***N*α,*N*ε-Bis[2-(3,4,6-tri-*O*-acetyl-α-D-glucopyranosyloxy)-acetyl]-L-lysine ethyl ester (10i):** elution AcOEt/EtOH (9/1); R_f = 0.41; yield 55% (156 mg); white solid; $[\alpha]^{20}_D$ +118 (*c* 0.5, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.26 (t, 3H, *J* = 7.0 Hz), 1.32−1.57 (m, 4H), 1.63−1.87 (m, 2H), 1.94−2.10 (6s, 18H), 3.05 (s, 2 OH), 3.20−3.33 (m, 2H), 3.72−3.84 (m, 2H), 3.93−4.30 (m, 12H), 4.45−4.58 (m, 1H), 4.85 (d, 1H, *J* = 3.7 Hz), 4.88 (d, 1H, *J* = 3.7 Hz), 4.98 (t, 1H, *J* = 9.9 Hz), 5.00 (t, 1H, *J* = 9.9 Hz), 5.25 (t, 1H, *J* = 9.6 Hz), 5.28 (t, 1H, *J* = 9.6 Hz), 7.51 (t, 1 NH, *J* = 5.7 Hz), 7.70 (d, 1 NH, *J* = 8.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ 13.99, 20.50, 20.59, 20.77, 22.71, 28.55, 31.48, 38.31, 51.85, 53.67, 61.51, 61.71, 67.05, 67.34, 67.91, 69.51, 69.99, 73.01, 73.10, 98.27, 169.41, 169.51, 170.55, 170.99, 171.74; HRMS (FAB) calcd for $[M + Li]^+$ 873.3328, found 873.3349. Anal. Calcd for $C_{36}H_{56.6}N_2O_{23.3}$ (**10i**·$1.3H_2O$): C, 48.57; H, 6.40; N, 3.14. Found: C, 48.58; H, 6.31; N, 3.12.

General Procedure for the Opening of Triacetyl Lactone (5) and Tris(2-chloroacetyl) lactone (12) by Alcohols. Procedure A. The lactone (typically 50−200 mg, **5** or **12)** was solubilized in alcohol (methanol, ethanol, propanol, 2-propanol, allylic alcohol), and CH_2Cl_2 was added if needed to ensure complete solubilization (with propanol, allylic alcohol, and for experiments with lactone **12**). Typically, 50 mg of **5** or **12** was solubilized in 1−5 mL of alcohol and 0.5−2 mL of CH_2Cl_2 if needed. Catalyst was added (DMAP for the typical procedure, or $Yb(CF_3SO_3)_3$, $La(CF_3SO_3)_3$, $Sc(CF_3SO_3)_3$, NEt_3, $AlCl_3$, or APTS in proportions as given in Table 3), and the mixture was allowed to react at room temperature for 0.5−7 days for lactone **5** or 3−12 h for lactone **12**.

Procedure B. Lactone **5** or **12** was solubilized in dichloromethane (typically: 50 mg of **5** in 1 mL of CH_2Cl_2), and alcohol (propanol, allylic alcohol, or propargylic alcohol) and DMAP were added in proportions as given in Table 3. With ethane-1,2-diol, pyridine was used as solvent instead of dichloromethane.

After completion of the reaction, the solvent was removed under reduced pressure and the residue was purified by silica

gel chromatography to afford the esters **11a**−**f**, and **13a** from **5** and esters **13b**−**d** from **12**.

(Ethoxycarbonyl)methyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (11a): elution hexane/AcOEt (2/3); yield 50% (28 mg); colorless oil; R_f = 0.56 (hexane/AcOEt 1/4); $[\alpha]^{20}_D$ +154 (*c* 1.0, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.25 (t, 3H, *J* = 7.0 Hz), 1.98−2.07 (3s, 9H), 2.96 (d, 1 OH, *J* = 10.3 Hz), 3.68 (td, 1H, *J* = 3.7, 9.9 Hz), 4.01−4.28 (m, 7H), 4.93 (d, 1H, *J* = 3.7 Hz), 4.97 (t, 1H, *J* = 9.9 Hz), 5.26 (t, 1H, *J* = 9.9 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ, 14.05, 20.54, 20.63, 20.79, 61.51, 61.81, 65.45, 67.91, 68.36, 70.51, 73.05, 99.57, 169.53, 169.76, 170.56, 170.80; HRMS (FAB) calcd for $[M + Li]^+$ 399.1478, found 399.1507. Anal. Calcd for $C_{16}H_{24}O_{11}$: C, 48.98; H, 6.16. Found: C, 48.67; H, 6.16.

(Propargyloxycarbonyl)methyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (11e): elution hexane/AcOEt (1/1); R_f = 0.65; yield 39% (135 mg); white solid; $[\alpha]^{20}_D$ +146 (*c* 1.3, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.00−2.08 (3s, 9H), 2.52 (t, 1H, *J* = 2.6 Hz), 2.80 (d, 1 OH, *J* = 10.7 Hz), 3.72 (td, 1H, *J* = 3.7, 9.9 Hz), 4.05 (dd, 1H, *J* = 2.2, 12.1 Hz), 4.09−4.17 (m, 1H), 4.25 (dd, 1H, *J* = 4.4, 12.1 Hz), 4.32 (d, 2H, *J* = 2.2 Hz), 4.77 (d, 1H, *J* = 2.6 Hz), 4.98 (d, 1H, *J* = 3.7 Hz), 5.01 (t, 1H, *J* = 9.6 Hz), 5.28 (t, 1H, *J* = 9.6 Hz); ^{13}C NMR (75 MHz, $CDCl_3$) δ, 21.29, 21.38, 21.53, 53.43, 62.45, 65.98, 68.45, 69.12, 71.22, 73.66, 76.50, 77.32, 100.31, 169.66, 170.25, 171.30, 171.56; HRMS (FAB) calcd for $[M + Na]^+$ 409.1322, found 409.1324. Anal. Calcd for $C_{17}H_{22}O_{11}$: C, 50.75; H, 5.51. Found: C, 50.53; H, 5.61.

[[2-(Methacryloyloxy)ethoxy]carbonyl]methyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside (11f): elution hexane/AcOEt (1/1); R_f = 0.46; yield 31% (42 mg); white solid; $[\alpha]^{20}_D$ +130 (*c* 0.6, CH_2Cl_2); ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.92 (t, 3H, *J* = 1.5 Hz), 1.99−2.08 (3s, 9H), 2.92 (s, 1 OH), 3.65−3.75 (m, 1H), 4.04 (dd, 1H, *J* = 2.2, 12.1 Hz), 4.10 (ddd, 1H, *J* = 2.2, 4.0, 9.9 Hz), 4.24 (dd, 1H, *J* = 4.0, 12.1 Hz), 4.28 (s, 2H), 4.33−4.45 (m, 4H), 4.96 (d, 1H, *J* = 3.7 Hz), 5.00 (t, 1H, *J* = 9.9 Hz), 5.27 (t, 1H, *J* = 9.6 Hz), 5.56−5.63 (m, 1H), 6.08−6.14 (m, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ, 18.64, 21.01, 21.10, 21.25, 62.20, 62.38, 63.55, 65.64, 68.27, 68.81, 70.91, 73.41, 99.91, 126.72, 136.14, 167.41, 169.99, 170.02, 171.01, 171.23; HRMS (FAB) calcd for $[M + Na]^+$ 483.1690, found 483.1696. Anal. Calcd for $C_{20}H_{28}O_{13}$: C, 50.42; H, 5.92. Found: C, 50.06; H, 6.09.

(Methoxycarbonyl)methyl α-D-glucopyranoside (13a): elution AcOEt/MeOH/H_2O (6/3/1); R_f = 0.63; yield 68% (16 mg); white solid; $[\alpha]^{20}_D$ +146 (*c* 1.0, MeOH); ^{1}H NMR (300 MHz, D_2O) δ 3.43 (t, 1H, *J* = 9.8 Hz), 3.57 (dd, 1H, *J* = 3.8, 9.8 Hz), 3.78 (s, 3H), 3.70−3.90 (m, 4H), 4.31 (d, 1H, *J* = 16.6 Hz), 4.35 (d, 1H, *J* = 16.6 Hz), 4.98 (d, 1H, *J* = 3.8 Hz); ^{13}C NMR (75 MHz, D_2O) δ, 52.91, 60.80, 65.03, 69.80, 71.63, 72.65, 73.23, 99.03, 172.97; HRMS (FAB) calcd for $[M + Li]^+$ 259.1005, found 259.1003. Anal. Calcd for $C_9H_{17.4}O_{8.7}$ (**13a**·0.7H_2O): C, 40.81; H, 6.62. Found: C, 40.82; H, 6.63.

[(Allyloxy)carbonyl]methyl α-D-glucopyranoside (13d): elution CH_3CN/EtOH (4/1); R_f = 0.41; yield 57% (35 mg); colorless oil; $[\alpha]^{20}_D$ +128 (*c* 1.0, MeOH); ^{1}H NMR (300 MHz, D_2O) δ 3.43 (t, 1H, *J* = 9.6 Hz), 3.58 (dd, 1H, *J* = 3.7, 9.6 Hz), 3.69−3.87 (m, 4H), 4.38 (s, 2H), 4.68−4.74 (m, 2H), 5.00 (d, 1H, *J* = 3.7 Hz), 5.32 (dd, 1H, *J* = 1.5, 10.5 Hz), 5.39 (dd, 1H, *J* = 1.5, 17.2 Hz), 5.91−6.07 (m, 1H); ^{13}C NMR (75 MHz, D_2O) δ 60.79, 65.19, 66.77, 69.79, 71.64, 72.66, 73.23, 99.13, 119.36, 131.84, 172.16; HRMS (FAB) calcd for $[M + Li]^+$ 285.1161, found 285.1180. Anal. Calcd for $C_{11}H_{18.8}O_{8.4}$ (**13d**·0.4H_2O): C, 46.28; H, 6.63. Found: C, 46.15; H, 6.48.

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Supporting Information Available: NMR spectra (^{1}H and ^{13}C) for all compounds and data for compounds **6b**,**c**, **7b**,**c**, **8b**, **9b**, **11b**−**d**, and **13b**,**c**. This material is available free of charge via the Internet at http://pubs.acs.org.

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