Tetrahedron: *Asymmetry* 19 (2008) 1919–1933

Contents lists available at ScienceDirect

Tetrahedron: *Asymmetry*

journal homepage: www.elsevier.com/locate/tetasy

# Synthesis of new mono- and disaccharidic carboxymethylglycoside lactones (CMGLs) and their use toward 1,2-bisfunctionalized carbohydrate synthons

Rouba Cheaib [a,b], Arkadiusz Listkowski [a,b,†], Stéphane Chambert [a,b], Alain Doutheau [a,b], Yves Queneau [a,b,*]

[a] *INSA Lyon, Laboratoire de Chimie Organique, Bâtiment J. Verne, 20 av A. Einstein, F-69621 Villeurbanne, France*
[b] *CNRS, UMR 5246, Institut de Chimie et Biochimie Moléculaires et Supramoléculaires, Université Lyon 1; INSA-Lyon; CPE-Lyon; Bâtiment CPE, 43 bd du 11 novembre 1918, F-69622 Villeurbanne, France*

ARTICLE INFO

*Article history:*
Received 17 June 2008
Accepted 11 July 2008
Available online 20 August 2008

ABSTRACT

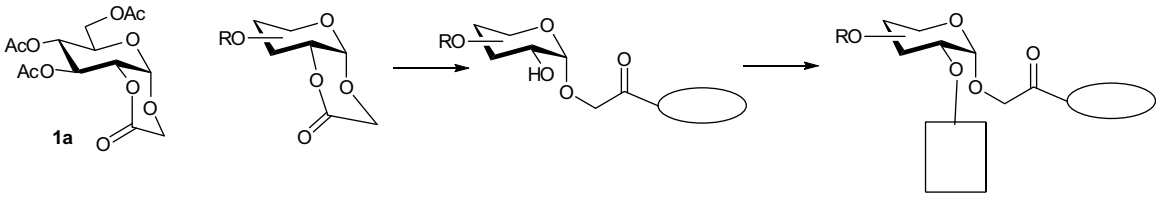
A general and convenient access to mono- and disaccharidic carboxymethyl glycoside lactones (CMGLs) is described. By taking advantage of the free OH at the 2-position, obtained after the opening of CMGLs by amines, the synthesis of a series of new 1,2-bisfunctionalized carbohydrate synthons is reported.



## 1. Introduction

In the recent years, carbohydrates have emerged as attractive systems for serving as the skeleton of molecular scaffolds, due to their multifunctionality and high structural diversity, able to display a number of substituents in a sterically defined manner,[1] for example, in the field of sugar amino acids.[2] The carboxylic acid function arising from carboxymethyl ethers is often employed as a connecting linkage; for example, in the synthesis of glycodendrimers,[3] such as those used for the study of biologically relevant protein–carbohydrate interactions.[3d] Carboxymethyl glycosides have also been recently grafted onto cyclopeptide scaffolds.[4] It has also been reported that carboxymethyl disaccharides can be used for the synthesis of single-tailed glycolipids, which are practical tools for probing carbohydrate–carbohydrate interactions.[5]

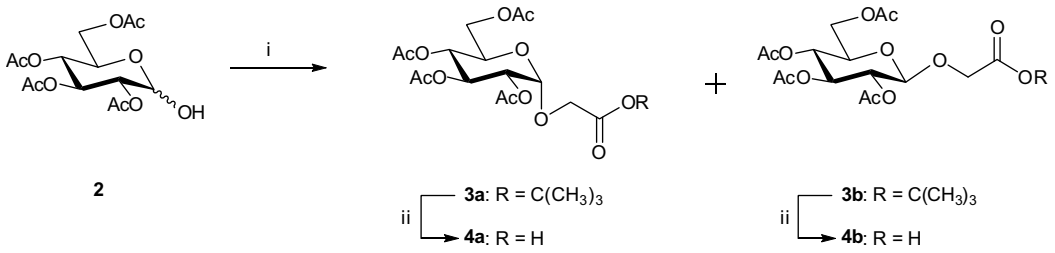
In our group, particular interest has been devoted toward the synthesis and use of a bicyclolactonic derivative from glucose, 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside 2-*O*-lactone[6] (α-CMGlcL, **1a**, Scheme 1). Lactone **1a** readily reacts with nucleophilic species leading efficiently to pseudoglucoconjugates (carbohydrate amino-acid hybrids, pseudodisaccharides, pseudoglycolipids).[6–11] Our first reported synthesis of this lactone involved a readily available disaccharide, isomaltulose, as the starting material, in a two-step oxidation–acetylation sequence.[6] However, only conjugates possessing an α-glucopyranosyl residue can be targeted by this approach. Recently, we reported an alternative preparation of carboxymethyl glycoside lactones (CMGLs) via the oxidation of allyl glycosides. Glucose or galactose-based CMGLs with either an α or β configuration at the anomeric center were thus obtained.[11] We have developed an even shorter approach based on anomeric alkylation with *tert*-butyl bromoacetate, which is reported herein. Also, the full synthetic potential of the CMGL synthons by stepwise lactone opening and functionalization at the 2-position is revealed, leading to 1,2-bisfunctionalized carbohydrates (Scheme 1). This offers an alternative to other methods, most of them being glycosylation reactions[12] using intermediates such as 1,2-isopropylidene acetals,[13] 1,2-orthoester,[14] 1,2-*O*-stannylene acetals,[15] glycals, and 1,2-anhydrosugars,[16] or strategies involving selective de-*O*-benzylation at the 2-position with TIBAL, DIBAL-H,[17] or Lewis acid catalysts,[18] or the recent one-pot access to 3-*O*-benzyl-4,6-*O*-benzylidene glucosides by tandem catalysis.[19] Since the CMGL approach is not a glycosylation process, the advantage relies




**Scheme 1.** CMGL approach toward 1,2-bisfunctionalized carbohydrate derivatives.

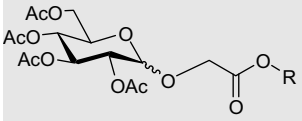
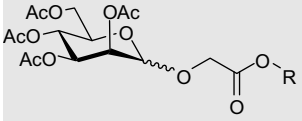
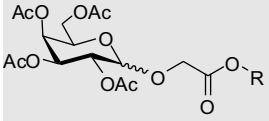
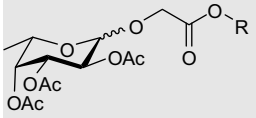
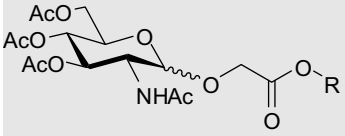
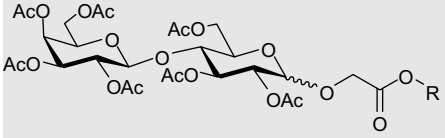
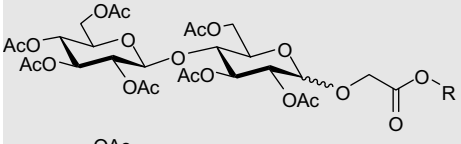
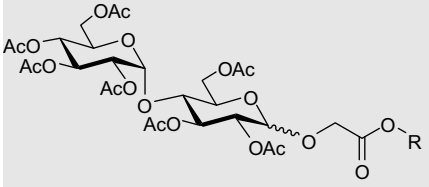
* Corresponding author.
*E-mail address:* yves.queneau@insa-lyon.fr (Y. Queneau).
† Current address: Institute of Physical Chemistry, Polish Academy of Sciences ul. Kasprzaka 44/52 01-224 Warsaw, Poland.

0957-4166/$ - see front matter © 2008 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetasy.2008.07.016




**Scheme 2.** Reagents and conditions: (i) DMF, $K_2CO_3$ (2.5–5 equiv), *tert*-butyl bromoacetate (2 equiv), rt, 48 h, 88% (α/β = 6.1:1); (ii) $CH_2Cl_2$, TFA, quant.

**Table 1**
Alkylation of the free 1-OH of peracetylated sugars by *tert*-butyl bromoacetate[a]

| Structure | R = C(CH3)3 | | | R = H |
|---|---|---|---|---|
| | Compound | Yield (%) | α:β | Compound |
|  | α = **3a**<br>β = **3b** | 88 | 6.1:1 | α = **4a**<br>β = **4b** |
|  | α = **5a**<br>β = **5b** | 91 | 32.3:1 | α = **12a**<br>β = **12b** |
|  | α = **6a**<br>β = **6b** | 94 | 8.1:1 | α = **13a**<br>β = **13b** |
|  | α = **7a**<br>β = **7b** | 74 | 4.8:1 | α = **14a**<br>β = **14b** |
|  | α = **8a**<br>β = **8b** | 85 | 6.7:1[b] | α = **15a** |
|  | α = **9a**<br>β = **9b** | 68 | 3.35:1 | α = **16a**<br>β = **16b** |
|  | α = **10a**<br>β = **10b** | 85 | 3.35:1[b] | α = **17a** |
|  | α = **11a**<br>β = **11b** | 88 | 4.9:1 | α = **18a**<br>β = **18b** |

[a] The α:β ratio was determined using $^1$H NMR (300 MHz, $CDCl_3$) by integrating the anomeric protons on the mixtures of anomers, and the chemical shifts of the H-1 were confirmed on the pure compounds, for example, $\delta$ 5.21 ppm, $J$ = 3.6 Hz for **6a** and $\delta$ 4.59 ppm, $J$ = 7.9 Hz for **6b**.

[b] In the case of *N*-AcGlc **8ab** and cellobiose **10ab**, only the α-anomer could be isolated as pure material after chromatography and transformed further to the acid.

notably in the fixation of the anomeric configuration at the level of the synthon, instead of being related to selectivity control.

## 2. Results and discussion

### 2.1. Preparation of carboxymethyl glycosides (*tert*-butyl esters and acids)

Direct anomeric functionalization by *tert*-butyl bromoacetate appeared as an attractive alternative to the aforementioned methods, using the well-known base-catalyzed O-alkylation of anomeric hydroxyl groups with aliphatic reagents. This route has been extensively studied by Schmidt et al.,[20] with the main alkylating agents used being dialkyl sulfates, benzyl bromide, allyl bromide,[21] or various *O*-triflates, all allowing the synthesis of disaccharides.[22] The stereochemical outcome of anomeric alkylation is known to depend on many parameters, such as the base, the solvent, and its effect on solubility and concentration, the temperature, chelation effects, the presence of additives, and on the nature of the electrophilic species.[20–25]

We first studied the reaction with *tert*-butyl bromoacetate on acetylated sugars having only the anomeric hemiacetal as the available hydroxyl group, which is easily obtained from the peracetylated derivatives by selective anomeric deprotection of the readily available corresponding peracetylated sugars,[26] such as compound **2** obtained from peracetylated glucose (Scheme 2).

The alkylation of hemiacetal **2** with *tert*-butyl bromoacetate occurred under very mild conditions (room temperature, DMF, $K_2CO_3$), leading to the two separable anomers **3a** and **3b** in 88% yield and a 6.1:1 ratio in favor of the α-anomer. Applied to various mono- and disaccharides (Table 1), *tert*-butyl esters **5**–**11** were also obtained, with significant selectivity for the α-anomers in all cases. While these products were prepared as intermediates for CMGLs synthesis, their corresponding free carboxylic acids (CMGs) are also interesting synthons. For this purpose, selective deprotection of the *tert*-butyl ester in the presence of acetyl groups in acidic conditions leading to the corresponding acids **4ab**, **12ab**–**18ab** was obtained using TFA in quantitative yields in pure anomeric forms.

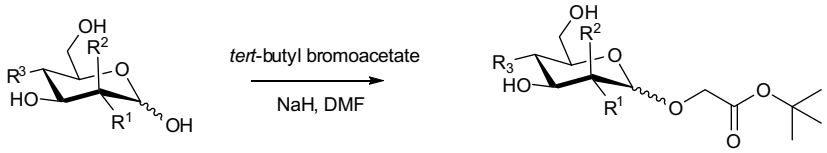
We then studied the reaction of unprotected sugars. Whereas in the presence of $K_2CO_3$ the reaction proved to be sluggish and not selective for the anomeric position, the use of sodium hydride permitted us to obtain fair yields of the desired monoalkylation at the anomeric position. Thus, glucose, mannose, *N*-acetyl glucosamine, maltose, and lactose **19**–**23** were treated in DMF with 1 equiv of sodium hydride and 1 equiv of *tert*-butyl bromoacetate for 15 h at room temperature (Table 2). Galactose led to a more complex mixture in which the α-furanoside was the major product.[21] The corresponding glycosides **24ab**–**28ab** were isolated as α:β mixtures after chromatography on silica gel, and the α:β ratios were determined by proton NMR spectroscopy. Under these conditions, a higher β-anomer proportion in the mixture (α:β ratio ranging from 1:1 to 1:2) was observed except for *N*-acetyl glucosamine, which exhibited an α orientation, which is consistent with the reported observations for the case of allyl bromide.[20,21,27]

With the final goal being to access CMGLs from as many sugar types as possible, it was thus interesting to obtain both anomers in most cases, with moderate to significant orientation toward one or the other depending on the choice of the conditions (partially acetylated sugars, $K_2CO_3$, or unprotected sugars, NaH). Separation of the anomers proved to be easier at the level of the acetylated *tert*-butyl esters than of the free glycosides.

### 2.2. Synthesis of acetylated carboxymethylglycoside lactones

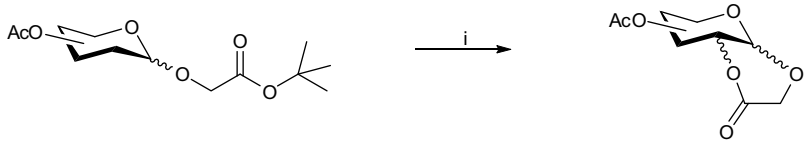
Deacetylation of esters **3ab** and **5ab**–**11ab** or acids **4ab** and **12ab**–**18ab**, each of them in pure anomeric form, with 1 M aq NaOH in MeOH with eventual intermediate TFA *tert*-butyl esters cleavage led to the fully deprotected carboxymethyl glycosides. Closing the lactonic ring was achieved by treatment of the latter acids with acetic anhydride in pyridine (Scheme 3, Table 3). The β-lactones derived from mannose **30** and maltose **33b** were obtained from the mixtures **25ab** and **27ab**, respectively, from which the pure β-anomer was isolated after acetylation.

**Table 2**
Alkylation of unprotected carbohydrates by *tert*-butyl bromoacetate[a,b]




| | Substrate | Yield (%) | Product (αβ mixtures) | α:β |
|---|---|---|---|---|
| $R^1$ = OH, $R^2$ = H, $R^3$ = OH | **19** | 50 | **24ab** | 1:2.8 |
| $R^1$ = H, $R^2$ = OH, $R^3$ = OH | **20** | 55 | **25ab** | 1:1 |
| $R^1$ = NHAc, $R^2$ = H, $R^3$ = OH | **21** | 77 | **26ab** | 2.8:1 |
| $R^1$ = OH, $R^2$ = H, $R^3$ = α-Glc | **22** | 49 | **27ab** | 1:1.8 |
| $R^1$ = OH, $R^2$ = H, $R^3$ = β-Gal | **23** | 57 | **28ab** | 1:2 |

[a] $^1$H NMR (300 MHz, DMSO-$d_6$) of the mixture **26** exhibited typical patterns for H-1 signals: H-1(α):$\delta$ 4.75 ppm, $J$ = 3.6 Hz; H-1(β):$\delta$ 4.34 ppm, $J$ = 8.5 Hz, which were confirmed by 2D HSQC correlation experiments, and allowed to determine the α:β ratio by intergration.
[b] Galactose led mainly to the α-furanosidic glycoside.




**Scheme 3.** Reagents and conditions: (i) (1) TFA, $CH_2Cl_2$; 3 h; NaOH, MeOH, rt, 1 h; $Ac_2O$, pyridine, rt, 12 h, 60–87% (see Table 3).

### 2.3. Carboxymethylglycoside lactone opening and access to 1,2-bisfunctionalized systems

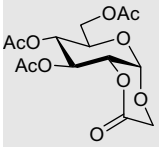
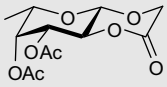
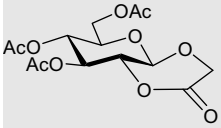
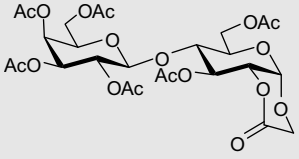
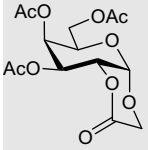
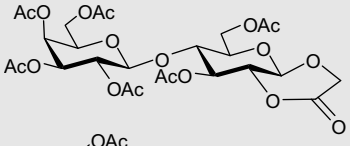
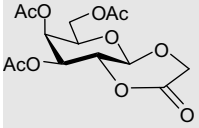
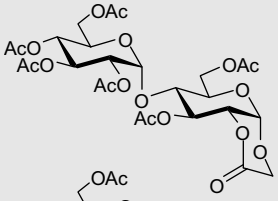
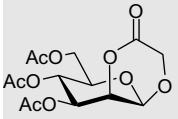
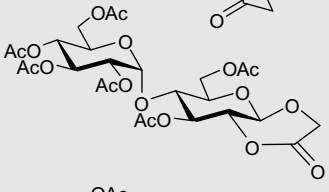
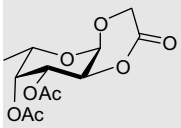
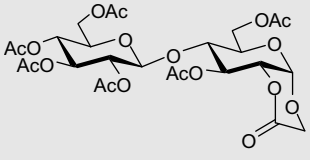
With the availability of CMGLs being ensured, their potential usefulness toward 1,2-bisfunctionalized platforms was investigated, taking one monosaccharidic (α-gluco, **1a**) and one disaccharidic (α-malto, **33a**) lactone as examples for different functionalizations at the C-2 OH. The opening of the lactone ring was performed using allylamine or propargylamine, these two functional groups offering a wide range of subsequent conjugation opportunities by means of metathesis or Cu(I)-mediated Huisgen cycloaddition ('click' chemistry).[28] The formation of the amides occurred by the simple addition of the amine on the lactone, at room temperature, leading to compounds **35**, **36**, and **44** in 85–96% yields (Scheme 4).

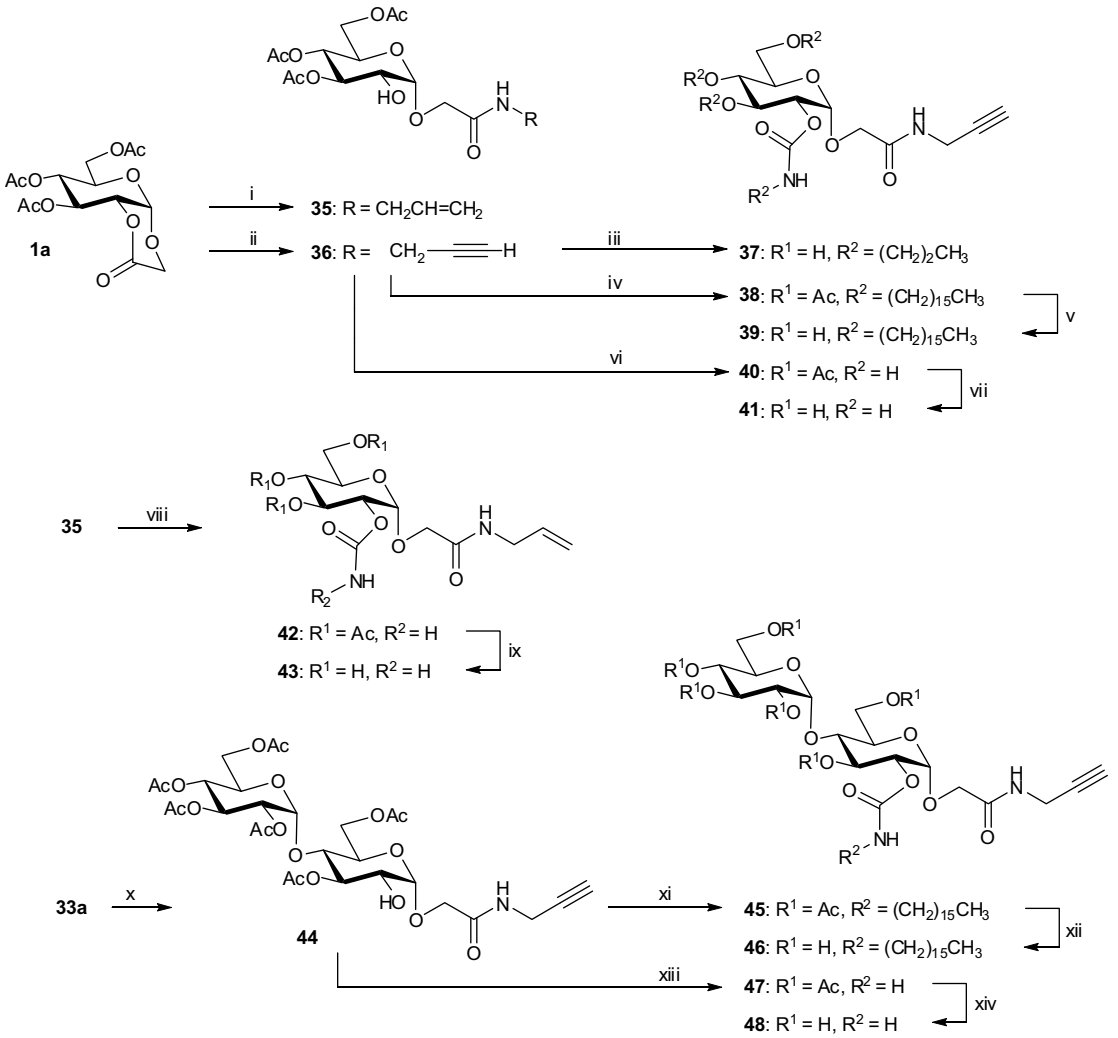
As a first example of second functionalization, amides **35**, **36**, and **44** were transformed to 2-*O*-alkylcarbamate derivatives. The reactions were performed with propyl or hexadecyl isocyanate under anhydrous conditions using catalytic amounts of triethylamine. For example, the reaction of amide **36** with propylisocyanate was completed within 12 h, as indicated by TLC. In this case, the corresponding acetylated intermediate was contaminated by dipropyl urea even after chromatography, and was thus directly deacetylated in a $Et_3N/MeOH/H_2O$ mixture to afford carbamate **37** in 72% overall yield. Hexadecylcarbamates **38** and **45** obtained in 74% and 94% yields from amides **36** and **44**, respectively, could be purified more easily by filtration of dihexadecyl urea, which precipitated in the reaction mixture prior to chromatography. Deacetylation ($NEt_3/MeOH/H_2O$) furnished **39** and **46** in 77% and 73% yields, respectively. Such compounds bearing a long hydrophobic chain might be intermediates toward new carbohydrate-based amphiphilic systems.[29,30]

A functional group transformation of C-2 OH to $OCONH_2$ was then achieved according to a procedure used in the synthesis of moenomycin-type inhibitors[31] by first reacting alcohols **35**, **36**, and **44** with trichloroacetylisocyanate, followed by a short silica gel chromatography and direct treatment of the intermediate trichloroacetyl carbamate with zinc in methanol to afford the corresponding carbamates **42**, **40**, and **47** in 88%, 91%, and 95% yields, respectively. Deprotection using $NEt_3/H_2O/MeOH$ led to **43**, **41**, and **48** in excellent yields. The full potential of synthons **41** and **48** is illustrated by their transformation by Cu(I)-mediated Huisgen cycloadditions with 5′-azido-5′-deoxyuridine,[32] in 84% and 81% yields, to compounds **49** and **50**, which might be considered as glycosyltransferase substrate analogues (Scheme 5).

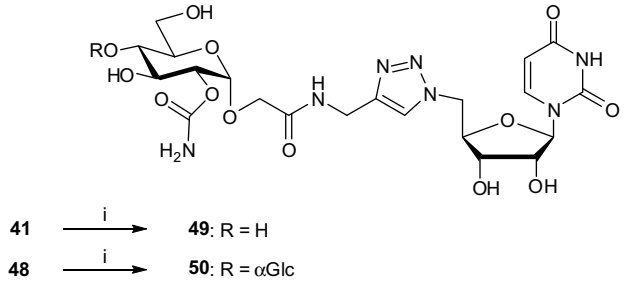
In a second set of experiments, etherification at O-2 was studied. The introduction of a protected carboxylic acid moiety, suitable, for example, for subsequent peptidic coupling reactions or to be able to bring an ionized function, was achieved by reaction in DMF with *tert*-butyl bromoacetate in the presence of $K_2CO_3$ leading, in 72% yield, to compound **51**, which was deprotected to the free acid **52** in quantitative yield. A propargyl ether linkage

**Table 3**
Structure of the obtained CMGLs

| Product | | Yield (%) | Product | | Yield (%) |
|---|---|---|---|---|---|
|  | **1a** | 83 |  | **31b** | 60 |
|  | **1b** | 71 |  | **32a** | 70 |
|  | **29a** | 87 |  | **32b** | 60 |
|  | **29b** | 64 |  | **33a** | 80 |
|  | **30** | 74 |  | **33b** | 64 |
|  | **31a** | 84 |  | **34** | 73 |




**Scheme 4.** Reagents and conditions: (i) allylamine (1.5 equiv), $CH_2Cl_2$, rt, 12 h, 92%; (ii) propargylamine (1.5 equiv), $CH_2Cl_2$, rt, 12 h, 96%; (iii) propylisocyanate (1.5 equiv), $CH_2Cl_2$, $Et_3N$, rt, 24 h, then $CH_3OH/H_2O/Et_3N$, rt, 12 h, 72%; (iv) hexadecylisocyanate (2 equiv), $CH_2Cl_2$, $Et_3N$, rt, 14 h, 74%; (v) $CH_3OH/H_2O/Et_3N$, rt, 3 h, 77%; (vi) trichloroacetylisocyanate (1.6 equiv), $CH_2Cl_2$, −15 °C, 1 h, then Zn, $CH_3OH$, rt, 30 min, 91%; (vii) $CH_3OH/H_2O/Et_3N$, rt, 12 h, 97%; (viii) trichloroacetylisocyanate (1.6 equiv), $CH_2Cl_2$, −15 °C, 1 h, then Zn, $CH_3OH$, rt, 30 min, 88%; (ix) $CH_3OH/H_2O/Et_3N$, rt, 12 h, 94%; (x) propargylamine (1.5 equiv), $CH_2Cl_2$, rt, 12 h, 85%; (xi) hexadecylisocyanate (2 equiv), $CH_2Cl_2$, $Et_3N$, rt, 48 h, 90%; (xii) $CH_3OH/H_2O/Et_3N$, rt, 16 h, 73%; (xiii) trichloroacetylisocyanate (1.6 equiv), $CH_2Cl_2$, −15 °C, 2 h then Zn, $CH_3OH$, rt, 30 min, 93%; (xiv) $CH_3OH/H_2O/Et_3N$, rt, 12 h, 91%.



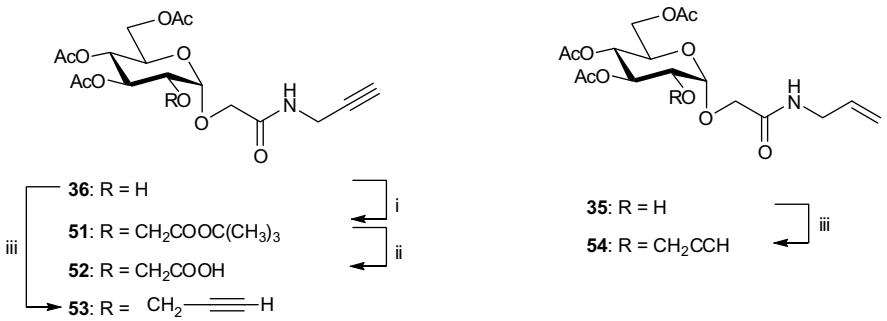

**Scheme 5.** Reagents and conditions: (i) 5′-azido-5′-deoxyuridine (1.2 equiv), $CuSO_4$ (0.01 equiv), sodium ascorbate (0.1 equiv), *tert*-butanol/$H_2O$, rt, 12 h, 84% from **41**, 81% from **48**.

could also be obtained by reaction with propargyl bromide, using 1.2 equiv of NaH to give access to compounds **53** and **54** in 55% and 56% yields, respectively (Scheme 6).

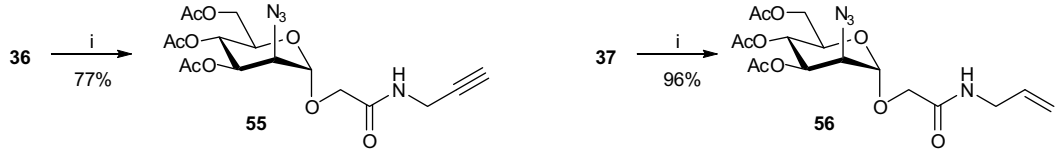
Finally, azido-alkenes or alkynes were targeted as versatile bifunctional systems: the 2-deoxy-2-azido *manno* derivatives **55** and **56** were prepared by substitution of the triflates obtained from the propargyl amide **35** and the allyl amide **36** using $NaN_3$, in 77% and 96% yields, respectively (Scheme 7).

## 3. Conclusion

In conclusion, a new access toward carboxymethyl glycoside lactones by using *tert*-butyl bromoacetate as an electrophilic reagent in anomeric alkylation reactions is described, alternative to the isomaltulose and the allyl glycoside approaches previously reported. A toolbox of new acetylated mono- and disaccharidic lactones was prepared, most of them in their α and β configuration. The synthetic potential of these lactones toward 1,2-bisfunctionalized carbohydrates synthons was illustrated by the preparation of compounds having either a *N*-allyl or *N*-propargyl carbamoylmethyl group at the anomeric position, and carbamate, ether or azido functions at position 2. Studies on the properties of some of these compounds as biologically active molecules or for the preparation of new materials are currently in progress, as well as the access to more complex multi-dimensional platforms via the CMGL strategy.




**Scheme 6.** Reagents and conditions: (i) *tert*-butylbromoacetate (1.2 equiv), $K_2CO_3$ (2.5 equiv), DMF, rt, 16 h, 72%; (ii) TFA, $CH_2Cl_2$, rt, 2 h, 90%; (iii) NaH, propargyl bromide (2.5 equiv), rt, 30 min, 55%.




**Scheme 7.** Reagents and conditions: (i) $Tf_2O$ (1.5 equiv), pyridine (2 equiv), $CH_2Cl_2$, −17 °C, 1 h, then $NaN_3$ (20 equiv), $Bu_4NI$, DMF, 60 °C, 15 h, 77%.

## 4. Experimental

### 4.1. General

All chemicals were purchased from Aldrich. Organic solutions were dried over anhydrous sodium sulfate. The reactions were monitored by thin-layer chromatography on Silica Gel 60 F254 (Merck); detection was carried out by charring with a 5% $H_2SO_4$ solution in ethanol. Silica gel (Kieselgel 60, 70–230 mesh ASTM, Merck) was used for flash chromatography. NMR spectra were recorded with a Bruker ALS300, DRX300, or DRX500 spectrometer. Chemical shift ($\delta$) and coupling constants ($J$) are reported in ppm and Hertz, respectively. Optical rotations were measured with a Perkin–Elmer 241 polarimeter at room temperature. Elemental analyses were performed by 'Service Central de Microanalyses du CNRS' 69360 Solaize (France).

### 4.2. General procedure for preparation of peracetylated (*tert*-butyloxycarbonyl)methyl glycosides 3, 5–11 from partially acetylated carbohydrates

To a 75 mM solution of partially acetylated carbohydrates, having a free hydroxyl group at the reducing end in anhydrous DMF, was added $K_2CO_3$ (2.5–5 equiv) followed by 2 equiv of *tert*-butyl bromoacetate. The reaction mixture was stirred under nitrogen for 2 days, after which salts were filtered and rinsed with $CH_2Cl_2$. Solvents were removed under reduced pressure, and the obtained oily residue was taken in $CH_2Cl_2$, and washed twice with water. Combined organic fractions were dried over $Na_2SO_4$, filtered, and the solvent was evaporated. The oily residue was subjected to a short silica gel column chromatography to give the corresponding (*tert*-butyloxycarbonyl)methyl glycosides **3**, **5**–**11** carboxymethyl D-glycopyranoside-*tert*-butyl esters as a mixture of anomers (see Scheme 1 and Table 1). When possible, separation of each pure anomer was then realized over silica gel.

### 4.3. (*tert*-Butyloxycarbonyl)methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranoside 3a

72%, white solid. $[\alpha]_D$ = +129 ($c$ 1.0, $CH_2Cl_2$); mp: 88 °C; (LRMS-ESI) $m/z$ for $C_{20}H_{30}O_{12}Na$ $(M+Na)^+$ = 485.0; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.46 (s, 9H), 2.02 (s, 3H), 2.03 (s, 3H), 2.10 (s, 3H), 2.13 (s, 3H), 4.07–4.22 (m, 2H, H-5, H-6b), 4.10 (AB system, $\delta_a$ 4.05, $\delta_b$ 4.15, 2H, $J$ = 16.4 Hz, H-7), 4.27 (dd, 1H, $J$ = 4.0 Hz, $J$ = 12.1 Hz, H-6a), 4.92 (dd, 1H, $J$ = 3.9 Hz, $J$ = 9.8 Hz, H-2), 5.09 (d, 1H, $J$ = 9.8 Hz, H-4), 5.17 (d, 1H, $J$ = 3.8 Hz, H-1), 5.54 (t, 1H, $J$ = 9.8 Hz, H-3); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.6, 20.6, 20.7, 20.7 ($4CH_3$), 28.0 ($CH_3$, *t*-Bu), 61.7 (C-6), 64.7 (C-7), 67.8 (C-5), 68.4 (C-4), 69.7 (C-3), 70.4 (C-2), 82.0 (Cq), 95.7 (C-1), 168.2, 169.6, 169.9, 170.3, 170.6 (5CO). Anal. Calcd for $C_{20}H_{30}O_{12}$: C, 51.94; H, 6.54. Found: C, 51.82; H, 6.45.

### 4.4. (*tert*-Butyloxycarbonyl)methyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranoside 3b

8%, white crystals. $[\alpha]_D$ = −29 ($c$ 1.0, $CH_2Cl_2$); mp: 102 °C (neat); LRMS (ESI) $m/z$ for $C_{20}H_{30}O_{12}Na$ $(M+Na)^+$ = 485.0; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.47 (s, 9H), 2.01 (s, 3H), 2.02 (s, 3H), 2.09 (s, 3H), 2.10 (s, 3H), 3.72 (ddd, 1H, $J$ = 2.2 Hz, $J$ = 4.5 Hz, $J$ = 9.6 Hz, H-5), 4.11–4.16 (m, 3H, H-7, H-6a), 4.27 (dd, 1H, $J$ = 4.5 Hz, $J$ = 12.4 Hz, H-6b), 4.68 (d, 1H, $J$ = 7.8 Hz, H-1), 5.04 (dd, 1H, $J$ = 7.8 Hz, $J$ = 9.6 Hz, H-2), 5.10 (t, 1H, $J$ = 9.6 Hz, H-4), 5.25 (t, 1H, $J$ = 9.6 Hz, H-3); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.6, 20.6, 20.7, 20.7 ($4CH_3$), 28.0 ($CH_3$, *t*-Bu), 61.8 (C-6), 65.4 (C-7), 68.3 (C-4), 71.0 (C-2), 71.8 (C-5), 72.6 (C-3), 81.9 (Cq), 100.1 (C-1), 168.1, 169.4, 169.6, 170.1, 170.6 (5CO). Anal. Calcd for $C_{20}H_{30}O_{12}$: C, 51.94; H, 6.54. Found: C, 51.88, H, 6.55.

### 4.5. (*tert*-Butyloxycarbonyl)methyl 2,3,4,6-tetra-*O*-acetyl-α-D-mannopyranoside 5a

83%, white crystals. $[\alpha]_D$ = +57 ($c$ 1.0, $CH_2Cl_2$); mp: +85 °C (neat). LRMS (ESI) $m/z$ for $C_{20}H_{30}O_{12}Na$ $(M+Na)^+$ = 485.0; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.48 (s, 9H), 1.99 (s, 3H), 2.05 (s, 3H), 2.11 (s, 3H), 2.16 (s, 3H), 4.09 (dd, 1H, $J$ = 2.25 Hz, $J$ = 12.1 Hz, H-6a), 4.11 (AB system AB, $\delta_a$ 4.05, $\delta_b$ 4.17, 2H, $J$ = 16.3 Hz, H-7), 4.18 (m, 1H, H-5), 4.30 (dd, 1H, $J$ = 4.7 Hz, $J$ = 12.1 Hz, H-6b), 4.96 (d, 1H, $J$ = 0.6 Hz, H-1), 4.31–4.37 (m, 3H, H-2, H-3, H-4); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.7, 20.8, 20.8, 20.9 ($4CH_3$), 28.0 ($CH_3$, *t*-Bu), 62.5 (C-6), 65.0 (C-7), 66.1 (C-4), 69.1, 69.3 (C-2, C-3), 69.5 (C-5), 82.3 (Cq), 97.9 (C-1), 168.4, 169.8, 169.8, 169.8,

170.6 (5CO). Anal. Calcd for $C_{20}H_{30}O_{12}$: C, 51.94; H, 6.54. Found: C, 52.08; H, 6.56.

### 4.6. (*tert*-Butyloxycarbonyl)methyl 2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranoside 5b

Isolated from reaction of mannose **20** with *tert*-butyl bromoacetate followed by acetylation in 11% yield (see Section 4.26), pale yellow oil. $[\alpha]_D = +46$ (*c* 1, $CHCl_3$); HRMS (ESI) *m*/*z* calculated for $C_{20}H_{30}O_{12}Na$ $(M+Na)^+ = 485.1635$, found 485.1636; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.44 (s, 9H), 1.95 (s, 3H), 2.00 (s, 3H), 2.06 (s, 3H), 2.15 (s, 3H), 3.64 (m, 1H, H-5), 4.11 (dd, 1H, *J* = 2.6 Hz, *J* = 12.2 Hz, H-6b), 4.21–4.07 (m, 2H, H-7), 4.27 (dd, 1H, *J* = 5.3 Hz, *J* = 12.2 Hz, H-6a), 4.84 (d, 1H, *J* = 1.0 Hz, H-1), 5.05 (dd, 1H, *J* = 3.2 Hz, *J* = 10.0 Hz, H-3), 5.23 (dd, 1H, *J* = 9.9 Hz, *J* = 10.0 Hz, H-4), 5.55 (dd, 1H, *J* = 1.0 Hz, *J* = 3.2 Hz, H-2); $^{13}C$ NMR ($CDCl_3$, 75 MHz): $\delta$ (ppm) 20.4, 20.6, 20.6, 20.7 ($4CH_3$), 28.0 ($CH_3$, *t*-Bu), 62.3 (C-7), 65.4 (C-6), 65.9 (C-4), 68.6 (C-2), 80.8 (C-3), 72.4 (C-5), 82.1 (Cq), 97.5 (C-1), 169.3, 169.5, 169.8, 170.1, 170.6 (5CO). Anal. Calcd for $C_{20}H_{30}O_{12}$: C, 51.94; H, 6.54. Found: C, 51.53; H, 6.37.

### 4.7. (*tert*-Butyloxycarbonyl)methyl 2,3,4,6-tetra-*O*-acetyl-α-D-galactopyranoside 6a

65%, white crystals. $[\alpha]_D = +110$ (*c* 1.5, $CH_2Cl_2$); mp: 102 °C (neat); LRMS-(ESI) *m*/*z* for $C_{20}H_{30}O_{12}Na$ $(M+Na)^+ = 485.0$; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.46 (s, 9H), 1.99 (s, 3H), 2.05 (s, 3H), 2.14 (s, 6H), 4.10 (AB system, $\delta_a$ 4.06, $\delta_b$ 4.14, *J* = 16.6 Hz, H-7), 4.04–4.16 (m, 2H, H-5, H-6b), 4.36 (pseudo-t, 1H, *J* = 6.6 Hz, H-6a), 5.17 (dd, 1H, *J* = 3.6 Hz, *J* = 10.4 Hz, H-2), 5.21 (d, 1H, *J* = 3.6 Hz, H-1), 5.42 (dd, 1H, *J* = 3.6 Hz, *J* = 10.4 Hz, H-3), 5.48 (pseudo-d, 1H, *J* = 3.6 Hz, H-4); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.6, 20.6, 20.7, 20.9 ($4CH_3$), 28.1 ($CH_3$, *t*-Bu), 61.6 (C-7), 64.5 (C-6), 66.8 (C-5), 67.2 (C-3), 67.6 (C-2), 68.0 (C-4), 82.1 (Cq), 96.1 (C-1), 168.3, 169.8, 170.2, 170.4, 170.6 (5CO). Anal. Calcd for $C_{20}H_{30}O_{12}$: C, 51.94; H, 6.54. Found: C, 51.86; H, 6.64.

### 4.8. (*tert*-Butyloxycarbonyl)methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranoside 6b

9%, white crystals. $[\alpha]_D = -16$ (*c* 1.0, $CH_2Cl_2$); mp: 98 °C (neat); LRMS (ESI) *m*/*z* for $C_{20}H_{30}O_{12}Na$ $(M+Na)^+ = 484.99$; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.42 (s, 9H), 1.93 (s, 3H), 2.00 (s, 3H), 2.06 (s, 3H), 2.10 (s, 3H), 3.86 (ddd, 1H, *J* = 1.0 Hz, *J* = 6.8 Hz, *J* = 13.4 Hz, H-5), 4.08–4.13 (m, 2H, H-6), 4.11 (s, 2H, H-7), 4.59 (d, 1H, *J* = 7.9 Hz, H-1), 5.00 (dd, 1H, *J* = 3.4 Hz, *J* = 10.5 Hz, H-3), 5.19 (dd, 1H, *J* = 7.9 Hz, *J* = 10.5 Hz, H-2), 5.33 (dd, 1H, *J* = 1.0 Hz, *J* = 3.4 Hz, H-4); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.6, 20.6, 20.7, 20.9 ($4CH_3$), 28.1 ($CH_3$, *t*-Bu), 61.2 (C-6), 61.2 ( C-6), 65.2 (C-4), 66.9 (C-2), 68.5 (C-5), 70.7 (C-3), 81.9 (Cq), 100.5 (C-1), 168.2, 169.9, 170.1, 170.2, 170.4 (5CO). Anal. Calcd for $C_{20}H_{30}O_{12}$: C, 51.94; H, 6.54. Found: C, 51.49; H, 6.57.

### 4.9. (*tert*-Butyloxycarbonyl)methyl 2,3,4,6-tetra-*O*-acetyl-α-L-fucopyranoside 7a

45%, white solid. $[\alpha]_D = -103$ (*c* 3.0, $CH_2Cl_2$); mp: 120 °C; LRMS (ESI) *m*/*z* for $C_{18}H_{28}O_{10}$ $(M+Na)^+ = 426.9$; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.03 (d, 3H, *J* = 6.5 Hz, H-6), 1.36 (s, 9H), 1.88 (s, 3H), 2.04 (s, 3H), 2.07 (s, 3H), 3.98 (AB system: $\delta_a$ 3.94, $\delta_b$ 4.04, *J* = 16.5 Hz, H-7), 4.19 (dq, 1H, *J* = 1.0 Hz, *J* = 6.5 Hz, H-5), 5.11 (d, 1H, *J* = 3.7 Hz, H-1), 5.24 (dd, 1H, *J* = 1.0 Hz, *J* = 3.0 Hz, H-4), 5.34 (dd, 1H, *J* = 3.0 Hz, *J* = 10.2 Hz, H-3), 5.35 (dd, 1H, *J* = 3.7 Hz, *J* = 10.2 Hz; H-2); $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ (ppm) 15.6 (C-6), 20.5, 20.6, 20.6, 20.8 ($CH_3$), 28.0 ($CH_3$, *t*-Bu), 64.6 (C-7), 64.9 (C-5), 67.6 (C-4), 67.6 (C-3), 71.0 (C-2), 81.7 (Cq), 96.1 (C-1), 168.4, 169.8, 170.4, 170.5 (4CO). Anal. Calcd for $C_{18}H_{28}O_{10}$: C, 53.46; H, 6.98. Found: C, 53.47; H, 6.96.

### 4.10. (*tert*-Butyloxycarbonyl)methyl 2,3,4,6-tetra-*O*-acetyl-β-L-fucopyranoside 7b

12%, white crystals. $[\alpha]_D = +10$ (*c* 2.0, $CH_2Cl_2$); mp: 114 °C (neat); HRMS (ESI) *m*/*z* calculated for $C_{18}H_{28}O_{10}$ $(M+Na)^+ = 427.1580$, found 427.1577; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) 1.20 (d, 3H, *J* = 6.4 Hz, H-6), 1.44 (s, 9H), 1.97 (s, 3H), 2.09 (s, 3H), 2.15 (s, 3H), 3.78 (dq, 1H, *J* = 0.8 Hz, *J* = 6.4 Hz, H-5), 4.15 (s, 2H, H-7), 4.58 (d, 1H, *J* = 7.9 Hz, H-1), 5.03 (dd, 1H, *J* = 3.4 Hz, *J* = 10.5 Hz, H-3), 5.25 (dd, 1H, *J* = 7.9 Hz, *J* = 10.5 Hz, H-2), 5.26 (dd, 1H, *J* = 0.8 Hz, *J* = 3.4 Hz, H-4); $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ (ppm) 16.0 (C-6), 20.5, 20.6, 20.8 ($CH_3$, *t*-Bu), 28.0 ($3CH_3$), 65.0 (C-7), 68.5 (C-2), 69.2 (C-5), 70.1 (C-4), 71.1 (C-3), 81.6 (Cq), 100.2 (C-1), 168.3, 169.9, 170.0, 170.1 (4CO). Anal. Calcd for $C_{18}H_{28}O_{10}$: C, 53.46; H, 6.98 found: C, 53.19; H, 6.73.

### 4.11. (*tert*-Butyloxycarbonyl)methyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-Glucopyranoside 8a

65%, white solid. $[\alpha]_D = +73$ (*c* 1.0, $CH_2Cl_2$); mp: 140 °C; LRMS (ESI) *m*/*z* for $C_{20}H_{31}NO_{11}$ $(M+Na)^+ = 484.0$; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.48 (s, 9H), 2.00 (s, 3H), 2.02 (s, 3H), 2.03 (s, 3H), 2.10 (s, 3H), 4.07–4.11 (m, 4H, H-5, H-6b, H-7), 4.18 (dd, 1H, *J* = 4.7 Hz, *J* = 13.0 Hz; H-6a), 4.37 (dd, 1H, *J* = 6.6 Hz, *J* = 13.0 Hz, H-6a), 4.37 (td, 1H, *J* = 3.6 Hz, *J* = 10.3 Hz, H-2), 4.85 (d, 1H, *J* = 3.6 Hz, H-1), 5.15 (t, 1H, *J* = 10.3 Hz, H-4), 5.48 (t, 1H, *J* = 10.3 Hz, H-3), 6.47 (d, 1H, *J* = 9.2 Hz, N*H*); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.4, 20.4, 20.5, 23.0 ($4CH_3$), 27.9 ($CH_3$, *t*-Bu), 51.4 (C-2), 61.6 (C-6), 65.1 (C-7), 67.8 (C-4), 68.3 (C-5), 71.0 (C-3), 82.4 (Cq), 98.2 (C-1), 168.6, 169.1, 170.3, 170.5, 170.9 (5CO). Anal. Calcd for $C_{20}H_{31}NO_{11}$: C, 52.06; H, 6.74; N, 3.04. Found: C, 51.90; H, 6.69; N, 3.01.

### 4.12. (*tert*-Butyloxycarbonyl)methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranoside 9a

40%, white solid. $[\alpha]_D = +30$ (*c* 1.0, $CH_2Cl_2$); mp: 92–97 °C; HRMS (ESI) *m*/*z* calculated for $C_{32}H_{46}O_{20}$ $(M+Na)^+ = 773.2480$, found 773.2481; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) 1.43 (s, 9H), 1.96 (s, 3H), 2.05 (s, 6H), 2.06 (s, 3H), 2.11 (s, 3H), 2.13 (s, 3H), 2.16 (s, 3H), 3.76 (t, 1H, *J* = 10.1 Hz, H-4), 3.86 (t, 1H, *J* = 6.4 Hz, H-5′), 4.03–4.13 (m, 6H, H-7, H-5, H-6′, H-6b), 4.47 (dd, 1H, *J* = 1.9 Hz, *J* = 12.3 Hz, H-6a), 4.47 (d, 1H, *J* = 8.0 Hz, H-1′); 4.82 (dd, 1H, *J* = 3.8 Hz, *J* = 10.1 Hz, H-2), 4.94 (dd, 1H, *J* = 3.5 Hz, *J* = 10.4 Hz, H-3′), 5.09 (d, 1H, *J* = 3.8 Hz, H-1), 5.10 (dd, 1H, *J* = 8.0 Hz, *J* = 10.4 Hz, H-2′), 5.33 (d, *J* = 3.5 Hz, H-4′), 5.52 (t, 1H, *J* = 10.1 Hz, H-3); $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ (ppm) 20.9, 21.0, 21.1, 21.2, 21.3, 21.3, 21.3 ($7CH_3$), 28.4 ($CH_3$, *t*-Bu), 61.2 (C-6′), 62.2 (C-6), 64.8 (C-7), 67.0 (C-4′), 67.0 (C-5), 69.2 (C-2′), 69.6 (C-3), 69.8 (C-2), 71.0 (C-5′), 71.4 (C-3′), 76.7 (C-4), 82.4 (Cq), 95.8 (C-1), 101.4 (C-1′), 168.5, 169.4, 169.8, 170.5, 170.6, 170.7, 170.8, 171.0 (8CO). Anal. Calcd for $C_{32}H_{46}O_{20}$: C, 51.20; H, 6.18. Found: C, 50.82; H, 6.07.

### 4.13. (*tert*-Butyloxycarbonyl)methyl 2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside 9b

2%, white solid. $[\alpha]_D = +5$ (*c* 1.0, $CH_2Cl_2$); mp: 93 °C; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.48 (s, 9H), 1.98 (s, 3H), 2.05 (s, 3H),

2.07 (s, 3H), 2.08 (s, 3H), 2.10 (s, 3H), 2.14 (s, 3H), 2.17 (s, 3H), 3.59 (m, 1H, H-5), 3.83 (t, 1H, $J$ = 9.2 Hz, H-4), 3.88 (t, 1H, $J$ = 6.8 Hz, H-5′), 4.03–4.12 (m, 3H, H-6′, H-6a), 4.12 (s, 2H, H-7), 4.48 (d, 1H, $J$ = 8.0 Hz, H-1′), 4.49 (dd, 1H, $J$ = 11.0 Hz, H-6b), 4.62 (d, 1H, $J$ = 7.7 Hz, H-1), 4.92–4.98 (m, 2H, H-1, H-3′), 5.11 (dd, 1H, $J$ = 7.7 Hz, $J$ = 10.2 Hz, H-2′), 5.23 (t, 1H, $J$ = 9.2 Hz, H-3), 5.35 (d, 1H, $J$ = 3.1 Hz, H-4′); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ (ppm) 20.9, 21.0, 21.0, 21.0, 21.2, 21.2, 21.3 ($7CH_3$), 28.4 ($CH_3$, *t*-Bu), 61.2 (C-6′), 62.3 (C-6), 65.9 (C-7), 67.0 (C-4′), 69.5 (C-2′), 71.1 (C-5′), 71.4–71.8 (C-2, C-3′), 71.8 (C-3), 72.9 (C-5), 76.5 (C-4), 82.3 (Cq), 100.2 (C-1), 101.4 (C-1′), 168.5, 169.4, 170.1, 170.3, 170.5, 170.55, 170.7, 170.7 (8CO). Anal. Calcd for $C_{32}H_{46}O_{20}$: C, 51.20; H, 6.18. Found: C, 51.05; H, 6.25.

### 4.14. (*tert*-Butyloxycarbonyl)methyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranoside 10a

72%, white solid. $[\alpha]_D$ = +43 (*c* 1.0, $CH_2Cl_2$); mp: 160–162 °C; HRMS (ESI) *m*/*z* calculated for $C_{32}H_{46}O_{20}$ $(M+Na)^+$ = 773.2480, found 773.2478; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.43 (s, 9H), 1.97 (s, 3H), 2.00 (s, 3H), 2.01 (s, 3H), 2.03 (s, 3H), 2.08 (s, 3H), 2.10 (s, 3H), 2.13 (s, 3H), 3.64–3.69 (m, 1H, H-5′), 3.75 (t, 1H, $J$ = 9.9 Hz, H-4), 3.99–4.17 (m, 5H, H-5, H-6′b, H-6b, H-7), 4.37 (dd, 1H, $J$ = 4.3 Hz, $J$ = 12.4 Hz, H-6′a), 4.49 (dd, 1H, $J$ = 1.7 Hz, $J$ = 11.9 Hz, H-6a), 4.53 (d, 1H, $J$ = 7.9 Hz, H-1′), 4.84 (dd, 1H, $J$ = 3.7 Hz, $J$ = 9.9 Hz, H-2), 4.93 (t, 1H, $J$ = 8.6 Hz, H-4′), 5.04–5.18 (m, 2H, H-2′, H-3′), 5.10 (d, $J$ = 3.7 Hz, H-1), 5.50 (t, 1H, $J$ = 9.9 Hz, H-3); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.5, 20.5, 20.6, 20.6, 20.7, 20.8, 20.9 ($7CH_3$), 28.4 ($CH_3$, *t*-Bu), 61.7–61.8 (C-6′, C-6), 64.4 (C-7), 67.7 (C-2′), 68.8 (C-5), 69.1 (C-3), 70.5–71.7 (C-2 or C-5′), 71.9 (C-4′), 73.0 (C-3′), 76.5 (C-4), 82.4 (Cq), 95.4 (C-1), 100.7 (C-1′), 169.3, 169.5, 170.0, 170.5, 170.7, 170.8, 170.8, 178.3 (8CO). Anal. Calcd for $C_{32}H_{46}O_{20}$: C, 51.20; H, 6.18. Found: C, 50.81; H, 6.24.

### 4.15. (*tert*-Butyloxycarbonyl)methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranoside 11a

70%, white foam. $[\alpha]_D$ = +69 (*c* 0.5, $CH_2Cl_2$); HRMS (ESI) *m*/*z* calculated for $C_{32}H_{46}O_{20}$ $(M+Na)^+$ = 773.2480, found 773.2481; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.48 (s, 9H), 2.02 (s, 3H), 2.03 (s, 3H), 2.04 (s, 3H), 2.08 (s, 3H), 2.11 (s, 3H), 2.12 (s, 3H), 2.16 (s, 3H), 3.94 (m, 1H, H-5′), 4.05 (t, 1H, $J$ = 9.2 Hz, H-4), 4.08 (dd, 1H, $J$ = 1.5 Hz, $J$ = 8.3 Hz, H-6′a), 4.15 (AB system $\delta_a$ 4.08, $\delta_b$ 4.17, 2H, $J$ = 16.5 Hz, H-7), 4.16–4.30 (m, 3H, H-5, H-6a, H-6′b), 4.48 (dd, 1H, $J$ = 2.5 Hz, $J$ = 12.4 Hz, H-6a), 4.80 (dd, 1H, $J$ = 3.6 Hz, $J$ = 9.8 Hz, H-2), 4.88 (dd, 1H, $J$ = 3.9 Hz, $J$ = 10.3 Hz, H-2′), 5.09 (t, 1H, $J$ = 9.6 Hz, H-4′), 5.12 (d, 1H, $J$ = 3.6 Hz, H-1), 5.38 (t, 1H, $J$ = 9.8 Hz, H-3′), 5.45 (d, 1H, $J$ = 3.9 Hz, H-1′), 5.60 (t, 1H, $J$ = 9.8 Hz, H-3); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.6, 20.6, 20.7, 20.7, 20.7, 20.8, 20.9 ($7CH_3$), 28.1 ($CH_3$, *t*-Bu), 61.4 (C-6′), 62.6 (C-6), 64.5 (C-7), 68.0 (C-4′), 68.3 (C-5′), 68.4 (C-5), 69.3 (C-3′), 70.0 (C-2′), 71.0 (C-2), 72.2 (C-3), 72.3 (C-4), 82.1 (Cq), 95.4 (C-1′), 95.5 (C-1), 168.2, 169.5, 169.7, 169.9, 170.5, 170.5, 170.5, 170.7 (8CO). Anal. Calcd for $C_{32}H_{46}O_{20}$: C, 51.20; H, 6.18. Found: C, 51.17; H, 6.21.

### 4.16. (*tert*-Butyloxycarbonyl)methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside 11b

Isolated from reaction of maltose **22** with *tert*-butyl bromoacetate followed by acetylation in 11% yield (see Section 4.26), colorless oil. $[\alpha]_D$ = +59 (*c* 0.3, $CH_2Cl_2$); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) 1.40 (s, 9H), 1.93 (s, 3H), 1.94 (s, 3H), 1.95 (s, 3H), 1.97 (s, 3H), 2.00 (s, 3H), 2.03 (s, 3H), 2.08 (s, 3H), 3.61 (m, 1H, H-5), 3.88 (ddd, 1H, $J$ = 2.4 Hz, $J$ = 5.1 Hz, $J$ = 10.2 Hz, H-5′), 3.96 (t, 1H, $J$ = 9.1 Hz, H-4), 3.97 (dd, 1H, $J$ = 2.4 Hz, $J$ = 12.9 Hz, H-6′a), 4.06 (s, 2H, H-7), 4.15 (dd, 1H, $J$ = 5.1 Hz, $J$ = 12.9 Hz, H-6′b), 4.18 (dd, 1H, $J$ = 4.1 Hz, $J$ = 12.6 Hz, H-6a), 4.42 (dd, 1H, $J$ = 2.5 Hz, $J$ = 12.6 Hz, H-6b), 4.61 (d, 1H, $J$ = 7.6 Hz, H-1), 4.79 (dd, 1H, $J$ = 4.0 Hz, $J$ = 10.2 Hz, H-2′), 4.81 (dd, 1H, $J$ = 7.9 Hz, $J$ = 9.1 Hz, H-2), 4.98 (t, 1H, $J$ = 10.2 Hz, H-4′), 5.21 (t, 1H, $J$ = 9.1 Hz, H-3), 5.29 (t, 1H, $J$ = 10.2 Hz, H-3′), 5.33 (d, 1H, $J$ = 4.0 Hz, H-1′); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ (ppm) 20.7, 20.7, 20.8, 20.9, 20.9, 21.0, 21.0 ($7CH_3$), 28.2 ($CH_3$, *t*-Bu), 61.1 (C-6′), 62.8 (C-6), 65.6 (C-7), 68.1 (C-4′), 68.6 (C-5′), 69.4 (C-3′), 70.1 (C-2′), 72.0 (C-2), 72.3 (C-5), 72.7 (C-4), 75.2 (C-3), 82.0 (Cq), 95.6 (C-1′), 99.7 (C-1), 168.2, 169.5, 170.0, 170.0, 170.2, 170.6; 170.6; 170.7 (8CO). Anal. Calcd for $C_{32}H_{46}O_{20}$: C, 51.20; H, 6.18. Found C, 51.15; H, 6.26.

### 4.17. General procedure for the preparation of peracetylated carboxymethyl glycosides 4, 12–18

Carboxymethyl glycoside *tert*-butyl esters **3**, **5**–**11** were dissolved in a 50 vol % TFA (20 equiv) solution in $CH_2Cl_2$. The reaction mixture was stirred at rt for 3 h, coevaporated twice with toluene and concentrated. The residue was chromatographed through a silica gel plug using a pentane/ethyl acetate gradient to give the corresponding acids **4**, **12**–**18** in quantitative yields. Full characterization of the following compounds have already been published in the literature: **4a**,[33] **4b**,[34] **12a**,[35] **13a**,[35] **13b**,[36] **14b**.[37]

### 4.18. Carboxymethyl 2,3,4,6-tetra-*O*-acetyl-β-D-mannopyranoside 12b

Pale yellow oil. $[\alpha]_D$ = −47 (*c* 2.0, $CH_2Cl_2$); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.94 (s, 3H), 1.99 (s, 3H), 2.05 (s, 3H), 2.13 (s, 3H), 3.67 (m, 1H, H-5), 4.11 (dd, 1H, $J$ = 12.6 Hz, $J$ = 2.6 Hz, H-6b), 4.25 (dd, 1H, $J$ = 4.7 Hz, $J$ = 12.6 Hz, H-6a), 4.30 (s, 2H, H-7), 4.85 (ls, 1H, H-1), 5.05 (dd, 1H, $J$ = 1.9 Hz, $J$ = 9.8 Hz, H-3), 5.19 (t, 1H, $J$ = 9.8 Hz, H-4), 5.50 (d, 1H, $J$ = 1.9 Hz; H-2); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.6, 20.6, 20.7, 20.8 ($4CH_3$), 62.5 (C-6), 65.0 (C-7), 65.9 (C-4), 68.7 (C-2), 71.0 (C-3), 72.4 (C-5), 97.8 (C-1), 170.1, 170.5, 171.1, 171.6, 171.6 (5CO). Anal. Calcd for $C_{16}H_{22}O_{12}$: C, 45.29; H, 5.70. Found: C, 45.61; H, 5.58.

### 4.19. Carboxymethyl 2,3,4,6-tetra-*O*-acetyl-α-L-fucopyranoside 14a

Pale yellow oil. $[\alpha]_D$ = −135 (*c* 1.0, $CH_2Cl_2$); LRMS (ESI) *m*/*z* for $C_{14}H_{20}O_{10}$ $(M+Na)^+$ = 371.0; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.05 (d, 3H, $J$ = 6.0 Hz, H-6), 1.91 (s, 3H), 2.02 (s, 3H), 2.08 (s 3H), 4.07–4.26 (m, 3H, H-5, H-7), 5.13 (dd, 1H, $J$ = 3.3 Hz, $J$ = 10.7 Hz, H-2), 5.19 (d, 1H, $J$ = 3.3 Hz, H-1), 5.33 (ls, 1H, H-4), 5.41 (dd, 1H, $J$ = 3.3 Hz, $J$ = 10.7 Hz, H-3); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 15.6 (C-6), 20.4, 20.5, 20.5 ($3CH_3$), 63.7 (C-7), 65.0 (C-5), 67.6–67.8 (C-2, C-3), 71.0 (C-4), 96.0 (C-1), 125.2, 128.1, 128.1, 128.9 (4CO). Anal. Calcd for $C_{14}H_{20}O_{10}.H_2O$: C, 45.90; H, 6.05. Found: C, 45.50; H, 5.70.

### 4.20. Carboxymethyl 2-acetamido-3,4,6-tri-*O*-acetyl-2-deoxy-α-D-glucopyranoside 15a

White solid. $[\alpha]_D$ = +81 (*c* 0.5, $CH_2Cl_2$); mp: 96 °C; HRMS(ESI) *m*/*z* calculated for $C_{16}H_{23}O_{11}N$ $(M+Na)^+$ = 428.1169, found 428.1167; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 2.02 (s, 3H), 2.03 (s, 6H), 2.10 (s, 3H), 4.03–4.13 (m, 2H, H-6b, H-5), 4.19–4.40 (m, 4H, H-2,

H-7, H-6a), 4.90 (d, 1H, $J$ = 3.6 Hz, H-1), 5.14 (t, 1H, $J$ = 10.3 Hz, H-4), 5.27 (t, 1H, $J$ = 9.8 Hz, H-3), 6.59 (d, 1H, $J$ = 9.2 Hz, N*H*); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.5, 20.7, 20.7, 22.7 ($4CH_3$), 51.7 (C-2), 61.8 (C-6), 64.6 (C-7), 67.8 (C-4), 68.4 (C-5), 70.9 (C-3), 97.9 (C-1), 169.4, 170.8, 171.2, 171.8, 172.2 (5CO). Anal. Calcd for $C_{16}H_{23}O_{11}N{\cdot}0.5H_2O$: C, 46.38; H, 5.84; N, 3.38. Found: C, 46.39; H, 5.61; N, 3.30.

### 4.21. Carboxymethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galacto-pyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranoside 16a

Pale yellow oil. $[\alpha]_D$ = +57 ($c$ 1.0, $CH_2Cl_2$); HRMS (ESI) $m/z$ calculated for $C_{28}H_{38}O_{20}$ $(M+Na)^+$ = 717.1854, found 717.1858; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.97 (s, 3H), 2.05 (s, 3H), 2.07 (s, 6H), 2.09 (s, 3H), 2.14 (s, 3H), 2.17 (s, 3H), 3.78 (t, 1H, $J$ = 9.9 Hz, H-4), 3.89 (t, 1H, $J$ = 7.0 Hz, H-5′), 4.02–4.20 (m, 4H, H-5, H-6′, H-6b), 4.26 (s, 2H, H-7), 4.46 (dd, 1H, $J$ = 1.7 Hz, $J$ = 11.5 Hz, H-6a), 4.50 (d, 1H, $J$ = 7.9 Hz, H-1′), 4.82 (dd, 1H, $J$ = 3.7 Hz, $J$ = 9.9 Hz, H-2), 4.97 (dd, 1H, $J$ = 3.4 Hz, $J$ = 10.4 Hz, H-3′), 5.11 (dd, 1H, $J$ = 7.9 Hz, $J$ = 10.4 Hz, H-2′), 5.12 (d, 1H, $J$ = 3.7 Hz, H-1), 5.36 (dd, 1H, $J$ = 0.9 Hz, $J$ = 3.4 Hz, H-4′), 5.51 (t, 1H, $J$ = 9.9 Hz, H-3); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ (ppm) 20.9, 21.0, 21.0, 21.0, 21.2, 21.3, 21.8 ($7CH_3$), 61.3 (C-6′), 62.2 (C-6), 64.3 (C-7), 67.1 (C-4′), 69.3 (C-5), 69.6 (C-2′), 69.8 (C-3), 71.0 (C-5′), 71.1 (C-2), 71.4 (C-3′), 76.4 (C-4), 96.1 (C-1), 101.2 (C-1′), 169.8, 170.5, 170.8, 170.9, 171.1, 171.1, 171.3, 173.6 (8CO). Anal. Calcd for $C_{28}H_{38}O_{20}{\cdot}H_2O$: C, 47.19; H, 5.66. Found: C, 47.47; H, 5.55.

### 4.22. Carboxymethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galacto-pyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside 16b

Colorless oil. $[\alpha]_D$ = −6 ($c$ 1.0, $CH_2Cl_2$). HRMS (ESI) $m/z$ calculated for $C_{28}H_{38}O_{20}$ $(M+Na)^+$ = 717.1854, found 717.1853; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.90 (s, 3H), 1.97 (s, 3H), 1.99 (s, 9H), 2.06 (s, 3H), 2.08 (s, 3H), 3.59 (m, 1H, H-5), 3.76 (t, 1H, $J$ = 9.3 Hz, H-4), 3.84 (t, 1H, $J$ = 6.7 Hz, H-5′), 3.98–4.07 (m, 3H, H-6′, H-6a), 4.22 (s, 2H, H-7), 4.41–4.45 (m, 2H, H-1′, H-6b), 4.56 (d, 1H, $J$ = 7.7 Hz, H-1), 4.86–4.93 (m, 2H, H-2, H-3′), 5.02 (dd, 1H, $J$ = 7.8 Hz, $J$ = 10.1 Hz, H-2′), 5.16 (t,1H, $J$ = 9.2 Hz, H-3), 5.28 (d, 1H, $J$ = 2.8 Hz, H-4′); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.5, 20.6, 20.6, 20.6, 20.7, 20.8, 20.8 ($7CH_3$), 60.9 (C-6′), 61.8 (C-6), 65.3 (C-7), 66.7 (C-4′), 69.2 (C-5), 70.7 (C-5′), 71.0–71.3 (C-2, C-3′), 72.4 (C-3), 72.9 (C-5), 76.0 (C-4), 100.1 (C-1), 101.0 (C-1′), 169.3, 169.8, 170.0, 170.1, 170.2, 170.3, 170.6, 170.7 (8CO). Anal. Calcd for $C_{28}H_{38}O_{20}{\cdot}H_2O$: C, 47.19; H, 5.66. Found: C, 47.52; H, 5.55.

### 4.23. Carboxymethyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranoside 17a

White solid. $[\alpha]_D$ = +50 ($c$ 0.5, $CH_2Cl_2$); mp: 165–167 °C; HRMS(ESI) $m/z$ calculated for $C_{28}H_{38}O_{20}$ $(M+Na)^+$ = 717.1854, found 717.1850; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.92 (s, 3H), 1.94 (s, 3H), 1.96 (s, 6H), 2.02 (s, 3H), 2.02 (s, 3H), 2.07 (s, 3H), 3.61 (m, 1H, H-5′), 3.68 (t, 1H, $J$ = 9.6 Hz, H-4), 3.97–4.01 (m, 2H, H-5, H-6′a), 4.06 (dd, 1H, $J$ = 4.5 Hz, $J$ = 12.3 Hz, H-6b), 4.18 (s, 2H, H-7), 4.42–4.49 (m, 2H, H-1′, H-6a), 4.74 (dd, 1H, $J$ = 3.7 Hz, $J$ = 10.3 Hz, H-2), 4.86 (t, 1H, $J$ = 8.5 Hz, H-4′), 4.97–5.11 (m, 3H, H-1, H-2′, H-3′), 5.42 (t, 1H, $J$ = 9.8 Hz, H-3); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.5, 20.5, 20.5, 20.6, 20.6, 20.8, 21.4 ($7CH_3$), 61.6–61.6 (C-6, C-6′), 64.3 (C-7), 67.8 (C-2′), 68.9 (C-5), 69.1 (C-3), 70.6 (C-2), 71.7 (C-5′), 71.9 (C-4′), 73.0 (C-3′), 76.4 (C-4), 95.6 (C-1), 100.6 (C-1′), 169.3, 169.5, 170.0, 170.5, 170.7, 170.8, 170.8, 178.3 (8CO). Anal. Calcd for $C_{28}H_{38}O_{20}{\cdot}1.5H_2O$: C, 46.60; H, 5.73. Found: C, 46.68; H, 5.51.

### 4.24. Carboxymethyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-α-D-glucopyranoside 18a

Pale yellow oil. $[\alpha]_D$ = +91 ($c$ 0.5, $CH_2Cl_2$); HRMS (ESI) $m/z$ calculated for $C_{28}H_{38}O_{20}$ $(M+Na)^+$ = 717.1854, found 717.1858; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.94 (s, 3H), 1.96 (s, 3H), 1.96 (s, 3H), 1.97 (s, 3H), 1.99 (s, 3H), 2.03 (s, 3H), 2.08 (s, 3H), 3.88 (m, 1H, H-5′), 3.93 (t, 1H, $J$ = 9.7 Hz, H-4), 3.98 (dd, 1H, $J$ = 1.9 Hz, $J$ = 12.3 Hz, H-6′a), 4.00–4.10 (m, 1H, H-5), 4.15–4.22 (m, 5H, H-5, H-6b, H-6′b, H-7), 4.39 (dd, 1H, $J$ = 2.2 Hz, $J$ = 12.3 Hz, H-6a), 4.70 (dd, 1H, $J$ = 3.8 Hz, $J$ = 9.7 Hz, H-2), 4.79 (dd, 1H, $J$ = 3.8 Hz, $J$ = 10.1 Hz, H-2′), 5.00 (t, 1H, $J$ = 10.1 Hz, H-4′), 5.03 (d, 1H, $J$ = 3.8 Hz, H-1), 5.30 (t, 1H, $J$ = 10.4 Hz, H-3′), 5.36 (d, 1H, $J$ = 3.8 Hz, H-1′), 5.51 (t, 1H, $J$ = 9.7 Hz, H-3); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.6, 20.6, 20.6, 20.7, 20.7, 20.8, 20.9 ($7CH_3$), 67.2 (C-6′), 68.0 (C-6), 68.0 (C-7), 68.4 (C-4′), 69.4 (C-5), 70.0 (C-5′), 70.0 (C-3′), 70.9 (C-2′), 72.0 (C-2), 72.4 (C-3), 74.0 (C-4), 93.8 (C-1′), 95.7 (C-1), 169.6, 170.0, 170.1, 170.6, 170.8, 170.8, 170.8, 173.1 (8CO). Anal. Calcd for $C_{28}H_{38}O_{20}$: C, 48.42; H, 5.51. Found: C, 48.37; H, 5.85.

### 4.25. Carboxymethyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-2,3,6-tri-*O*-acetyl-β-D-glucopyranoside 18b

Pale yellow oil. $[\alpha]_D$ = +61 ($c$ 0.3, $CH_2Cl_2$); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) 1.93 (s, 3H), 1.95 (s, 3H), 1.96 (s, 3H), 1.98 (s, 3H), 2.03 (s, 3H), 2.03 (s, 3H), 2.08 (s, 3H), 3.65 (m, 1H, H-5), 3.88 (br d, 1H, $J$ = 9.8 Hz, H-5′), 3.93–3.99 (m, 2H, H-6′a, H-4), 4.16 (dd, 1H, $J$ = 4.1 Hz, $J$ = 12.0 Hz, H-6a), 4.18 (dd, 1H, $J$ = 3.4 Hz, $J$ = 12.9 Hz, H-6′b), 4.24 (s, 2H, H-7), 4.44 (br d, 1H, $J$ = 12.0 Hz, H-6b), 4.62 (d, 1H, $J$ = 7.6 Hz, H-1), 4.78 (dd, 1H, $J$ = 3.6 Hz, $J$ = 9.8 Hz, H-2′), 4.81 (dd, 1H, $J$ = 7.4 Hz, $J$ = 9.6 Hz, H-2), 4.98 (t, 1H, $J$ = 9.8 Hz, H-4′), 5.22 (t, 1H, $J$ = 9.6 Hz, H-3), 5.28 (t, 1H, $J$ = 9.8 Hz, H-3′), 5.33 (d, 1H, $J$ = 3.6 Hz, H-1′); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ (ppm) 20.7, 20.7, 20.7, 20.8, 20.9, 21.0, 21.0 ($7CH_3$), 53.8 (C-6′), 61.6 (C-6), 62.6 (C-7), 68.1 (C-4), 68.7 (C-5′), 69.4 (C-3′), 70.1 (C-2′), 71.9 (C-2), 72.5 (C-5), 72.6 (C-4), 75.0 (C-3), 95.7 (C-1′), 99.9 (C-1), 169.6, 170.0, 170.1, 170.3, 170.7, 170.7, 170.7, 170.7 (8CO). Anal. Calcd for $C_{28}H_{38}O_{20}$: C, 48.42; H, 5.51. Found: C, 48.73; H, 5.87.

### 4.26. General procedure for the preparation of (*tert*-butyl-oxycarbonyl)methyl glycosides 24–28 from glycosides 19–23

To a 220 mM solution of the carbohydrate in anhydrous DMF was added NaH (1 equiv), followed by 1 equiv of *tert*-butyl bromoacetate. The reaction mixture was stirred under a nitrogen atmosphere for 3 days. Then DMF was removed under reduced pressure, and the oily residue was purified by column chromatography ($CH_2Cl_2/CH_3OH$ 9/1), to give the corresponding carboxymethyl glycoside *tert*-butyl ester as a mixture of anomers. Compounds **5b** and **11b** were purified by silica gel chromatography after being subjected to conventional peracetylation conditions (pyridine, $Ac_2O$).

### 4.27. General procedure for preparation of carboxymethyl glycoside lactones 1, 29–34

To a 0.1 M solution of carboxymethyl glycoside in methanol, NaOH (1M, 10 equiv) was added. The mixture was stirred at rt for 30 min and the solvents were removed under reduced pressure. The residue was then reacted overnight in a 50 vol % acetic anhydride in pyridine. After evaporation, the yellow oil was dissolved in $CH_2Cl_2$ and washed with an aqueous $NH_4Cl$ solution (10%). The organic phase was dried over $Na_2SO_4$, filtered, and the solvent was removed by evaporation to give, after purification over silica

gel, the pure corresponding carboxymethyl glycoside lactone. Full characterization of the following compounds have already been published in the literature: **1a**,[6] **1b**,[11] **29a**,[11] **29b**[11] (yields are given in the text).

### 4.28. Carboxymethyl-3,4,6-tri-*O*-acetyl-β-D-mannopyranoside-2-*O*-lactone 30

74%, white foam. $[\alpha]_D = -55$ (*c* 1.0, $CH_2Cl_2$); LRMS (ESI) *m*/*z* for $C_{14}H_{18}O_{10}$ $(M+H)^+ = 346.88$; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.99 (s, 3H), 2.01 (s, 3H), 2.05 (s, 3H), 3.73 (m, 1H, H-5), 4.14 (m, 2H, H-6), 4.38 (AB system, $\delta_a$ 4.29, $\delta_b$ 4.46, 2H, *J* = 17.5 Hz, H-7), 4.85 (dd, 1H, *J* = 1.1 Hz, *J* = 3.0 Hz, H-2), 5.03 (dd, 1H, *J* = 3.0 Hz, *J* = 10.1 Hz, H-3), 5.03 (d, 1H, *J* = 1.1 Hz, H-1), 5.27 (t, 1H, *J* = 10.1 Hz, H-4); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.6, 20.6, 20.7 ($3CH_3$), 60.3 (C-7), 61.9 (C-6), 64.7 (C-4), 70.7 (C-3), 73.0 (C-5), 75.0 (C-2), 90.4 (C-1), 165.0, 169.3, 170.4, 170.7 (4CO). Anal. Calcd for $C_{14}H_{18}O_{10}\cdot 0.2H_2O$: C, 48.06; H, 5.30. Found: C, 48.03; H, 5.03.

### 4.29. Carboxymethyl-3,4-di-*O*-acetyl-α-L-fucopyranoside-2-*O*-lactone 31a

84%, white solid. $[\alpha]_D = -124$ (*c* 1.0, $CH_2Cl_2$); mp: 156–158 °C; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) 1.12 (d, 3H, *J* = 6.6 Hz, H-6), 2.00 (s, 3H), 2.11 (s, 3H), 4.32 (br q, 1H, *J* = 6.6 Hz, H-5), 4.50 (AB system $\delta_a$ 4.43, $\delta_b$ 4.58, 2H, *J* = 17.8 Hz, H-7), 4.55 (dd, 1H, *J* = 3.1 Hz, *J* = 8.5 Hz, H-2), 5.25 (d, 1H, *J* = 3.1 Hz, H-1), 5.27 (dd, 1H, *J* = 3.1 Hz, *J* = 10.2 Hz, H-4), 5.38 (dd, 1H, *J* = 3.1 Hz, *J* = 10.2 Hz, H-3); $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ (ppm) 15.9 (C-6), 20.7, 20.8 ($2CH_3$), 64.8 (C-7), 67.6 (C-5), 70.0 (C-3), 70.7 (C-4), 73.6 (C-2), 92.0 (C-1), 164.2, 170.2, 170.3 (3CO). Anal. Calcd for $C_{12}H_{16}O_8$: C, 50.0; H, 5.59. Found: C, 49.81; H, 5.40.

### 4.30. Carboxymethyl-3,4,6-tri-*O*-acetyl-β-L-fucopyranoside-2-*O*-lactone 31b

60%, white solid. $[\alpha]_D = -88$ (*c* 1.0, $CH_2Cl_2$); mp: 95–96 °C; HRMS (ESI) *m*/*z* calculated for $C_{12}H_{16}O_8$ $(M+Na)^+ = 311.0743$, found 311.0745; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.22 (d, 3H, *J* = 6.5 Hz, H-6), 1.99 (s, 3H), 3.98 (s, 3H), 3.98 (dq, 1H, *J* = 1.2 Hz, *J* = 6.5 Hz, H-5), 4.44 (dd, 1H, *J* = 7.7 Hz, *J* = 10.7 Hz, H-2), 4.55 (AB system: $\delta_a$ 4.47, $\delta_b$ 4.63, 2H, *J* = 17.5 Hz, H-7), 4.73 (d, 1H, *J* = 7.7 Hz, H-1), 5.10 (dd, 1H, *J* = 3.6 Hz, *J* = 10.6 Hz, H-3), 5.23 (dd, 1H, *J* = 1.2 Hz, *J* = 3.6 Hz, H-4); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 15.7 (C-6), 20.4, 20.5 ($2CH_3$), 64.5 (C-7), 69.8–69.9 (C-4, C-3), 71.3 (C-5), 74.8 (C-2), 95.2 (C-1), 165.6, 169.8, 170.1 (3CO). Anal. Calcd for $C_{12}H_{16}O_8\cdot 1.7H_2O$: C, 45.16; H, 6.14. Found: C, 45.21; H, 6.00.

### 4.31. Carboxymethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galacto-pyranosyl-(1→4)-3,6-di-*O*-acetyl-α-D-glucopyranoside-2-*O*-lactone 32a

64% white solid. $[\alpha]_D = +68$ (*c* 1.0, $CH_2Cl_2$); mp: 106–114 °C; HRMS (ESI) *m*/*z* calculated for $C_{26}H_{34}O_{18}$ $(M+Na)^+ = 657.1643$, found 657.1645; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.97 (s, 3H), 2.04 (s, 3H), 2.07 (s, 3H), 2.13 (s, 3H), 2.14 (s, 3H), 2.17 (s, 3H), 3.77 (t, 1H, *J* = 9.6 Hz, H-4), 3.89 (t, 1H, *J* = 6.2 Hz, H-5′), 4.04–4.22 (m, 4H, H-5, H-6′, H-6b), 4.35 (d, 1H, *J* = 3.4 Hz, *J* = 9.6 Hz, H-2), 4.47–4.52 (m, 2H, H-1′, H-6a), 4.52 (AB system, $\delta_a$ 4.69, $\delta_b$ 4.49, *J* = 17.8 Hz, H-7), 4.96 (dd, 1H, *J* = 3.4 Hz, *J* = 10.3 Hz, H-3′), 5.12 (dd, 1H, *J* = 7.8 Hz, *J* = 10.3 Hz, H-2′), 5.29 (d, 1H, *J* = 3.4 Hz, H-1), 5.36 (dd, 1H, *J* = 1.1 Hz, *J* = 3.4 Hz, H-4′), 5.56 (t, 1H, *J* = 9.6 Hz, H-3);$^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ (ppm) 20.5, 20.6, 20.7, 20.7, 20.8, 20.9 ($6CH_3$), 60.8 (C-6′), 61.5 (C-6), 64.4 (C-7), 66.6 (C-4′), 69.2 (C-2′), 70.7 (C-5′), 70.8 (C-5), 70.9 (C-3′), 71.2 (C-3), 74.8 (C-4), 74.8 (C-2), 90.9 (C-1), 100.9 (C-1′), 162.9, 163.7, 169.0, 169.7, 170.1, 170.2, 170.4 (7CO). Anal. Calcd for $C_{26}H_{34}O_{18}H_2O$: C, 48.75; H, 5.46. Found: C, 48.77; H, 5.47.

### 4.32. Carboxymethyl 2,3,4,6-tetra-*O*-acetyl-β-D-galacto-pyranosyl-(1→4)-3,6-di-*O*-acetyl-β-D-glucopyranoside-2-*O*-lactone 32b

60% white foam. $[\alpha]_D = +5$ (*c* 1.0, $CH_2Cl_2$); LRMS (ESI) *m*/*z* for $C_{26}H_{34}O_{18}$ $(M+Na)^+ = 675.1$; $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) 1.90 (s, 3H), 1.98 (s, 3H), 2.00 (s, 3H), 2.06 (s, 6H), 2.09 (s, 3H), 3.75–3.76 (m, 2H, H-4, H-5), 3.82 (t, 1H, *J* = 7.2 Hz, H-5′), 4.01 (dd, 1H, *J* = 7.2 Hz, *J* = 11.0 Hz, H-6′a), 4.08–4.11 (m, 2H, H-6a, H-6′b), 4.12 (dd, 1H, *J* = 7.7 Hz, *J* = 10.4 Hz, H-2), 4.41–4.45 (m, 2H, H-1′, H-6b), 4.51 (AB system, $\delta_a$ 4.49, $\delta_b$ 4.58, 2H, *J* = 17.5 Hz, H-7), 4.72 (d, 1H, *J* = 7.7 Hz, H-1), 4.90 (dd, 1H, *J* = 3.5 Hz, *J* = 10.4 Hz, H-3′), 5.03 (dd, 1H, *J* = 7.9 Hz, *J* = 10.4 Hz, H-2′), 5.27–5.29 (m, 2H, H-3, H-4′); $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ (ppm) 20.6, 20.7, 20.7, 20.7, 20.9, 20.9 ($6CH_3$), 60.9 (C-6′), 61.7 (C-6), 64.4 (C-7), 66.6 (C-3 or C-4′), 69.1 (C-2′), 70.7 (C-3 or C-4′), 70.9 (C-3′), 71.0 (C-5′), 74.8 (C-4), 76.0 (C-5), 76.9 (C-2), 94.8 (C-1), 101.1 (C-1′), 164.9, 169.1, 169.3, 170.1, 170.2, 170.3, 170.4 (7CO). Anal. Calcd for $C_{26}H_{34}O_{18}$: C, 49.21; H, 5.40. Found: C, 48.92; H, 5.48.

### 4.33. Carboxymethyl 2,3,4,6-tetra-*O*-acetyl-a-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-α-D-glucopyranoside-2-*O*-lactone 33a

80% white foam. $[\alpha]_D = +109$ (*c* 1.0, $CH_2Cl_2$); HRMS (ESI) *m*/*z* calculated for $C_{26}H_{34}O_{18}$ $(M+Na)^+ = 657.1643$, found 657.1640; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 2.01 (s, 3H), 2.03 (s, 3H), 2.06 (s, 3H), 2.10 (s, 3H), 2.12 (s, 3H), 2.15 (s, 3H), 3.94 (m, 1H, H-5), 3.99 (t, 1H, *J* = 9.2 Hz, H-4), 4.07 (dd, 1H, *J* = 2.3 Hz, *J* = 12.4 Hz, H-6′a), 4.20–4.28 (m, 4H, H-6′b, H-6a,H-5, H-2), 4.48–4.74 (m, 3H, H-6b and AB system $\delta_a$ 4.51, $\delta_b$ 4.71, 2H, *J* = 17.9 Hz, H-7), 4.85 (dd, 1H, *J* = 3.9 Hz, *J* = 10.3 Hz, H-2′), 5.08 (t, 1H, *J* = 9.9 Hz, H-4′), 5.30 (d, 1H, *J* = 2.8 Hz, H-1), 5.36 (t, 1H, *J* = 10.1 Hz, H-3′), 5.48 (d, 1H, *J* = 3.9 Hz, H-1′), 5.64 (t, 1H, *J* = 9.4 Hz, H-3); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.6, 20.6, 20.7, 20.7, 20.9, 21.0 ($6CH_3$), 61.4 (C-6′), 62.2 (C-6), 64.3 (C-7), 67.9 (C-4′), 68.7 (C-5′), 69.3 (C-3′), 70.1 (C-2′), 70.6 (C-2), 71.2 (C-4), 73.4 (C-3), 76.4 (C-5), 90.8 (C-1), 95.7 (C-1′), 163.4, 169.5, 170.0, 170.0, 170.4, 170.6, 170.7 (7CO). Anal. Calcd for $C_{26}H_{34}O_{18}$: C, 49.21; H, 5.40. Found: C, 49.40; H, 5.43.

### 4.34. Carboxymethyl 2,3,4,6-tetra-*O*-acetyl-a-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-β-D-glucopyranoside-2-*O*-lactone 33b

64% colorless oil. $[\alpha]_D = +54$ (*c* 0.3, $CH_2Cl_2$); $^1H$ NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) 1.94 (s, 3H), 1.96 (s, 3H), 2.00 (s, 3H), 2.03 (s, 3H), 2.04 (s, 3H), 2.08 (s, 3H), 3.84 (m, 1H, H-5), 3.88 (ddd, 1H, *J* = 2.5 Hz, *J* = 6.0 Hz, *J* = 10.4 Hz, H-5′), 3.98 (t, 1H, *J* = 9.0 Hz, H-4), 4.00 (dd, 1H, *J* = 2.5 Hz, *J* = 12.3 Hz, H-6′a), 4.05 (dd, 1H, *J* = 7.9 Hz, *J* = 10.4 Hz, H-2), 4.16 (dd, 1H, *J* = 3.6 Hz, *J* = 12.3 Hz, H-6a), 4.17 (dd, 1H, *J* = 6.0 Hz, *J* = 12.3 Hz, H-6′b), 4.44 (dd, 1H, *J* = 2.2 Hz, *J* = 12.3 Hz, H-6b), 4.49 (AB system, $\delta_a$ 4.42, $\delta_b$ 4.57, 2H, *J* = 17.5 Hz, H-7), 4.75 (d, 1H, *J* = 7.9 Hz, H-1), 4.81 (dd, 1H, *J* = 4.2 Hz, *J* = 10.3 Hz, H-2′), 5.00 (t, 1H, *J* = 10.3 Hz, H-4′), 5.29 (t, 1H, *J* = 10.3 Hz, H-3′), 5.35 (d, 1H, *J* = 4.2 Hz, H-1′), 5.36 (dd, 1H, *J* = 9.0 Hz, *J* = 10.4 Hz, H-3); $^{13}C$ NMR (125 MHz, $CDCl_3$): $\delta$ (ppm) 20.7, 20.7, 20.7, 20.8, 20.9, 21.0 ($6CH_3$), 61.5 (C-6′), 62.6 (C-6), 64.4 (C-7), 68.0 (C-4′), 68.9 (C-5′), 69.3 (C-3′), 69.4 (C-2′), 69.9 (C-4), 72.5 (C-3), 73.3 (C-5), 74.4 (C-2), 94.6 (C-1), 95.9 (C-1′), 169.5, 169.5, 169.6, 170.0, 170.5, 170.6, 170.7 (7CO). Anal. Calcd for $C_{26}H_{34}O_{18}\cdot 0.5H_2O$: C, 48.52; H, 5.48. Found C, 48.38; H, 5.19.

### 4.35. Carboxymethyl 2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-α-D-glucopyranoside-2-*O*-lactone 34

73%, white solid. $[\alpha]_D$ = +44 (*c* 1.0, $CH_2Cl_2$); mp: 188 °C; LRMS (ESI) *m*/*z* for $C_{26}H_{34}O_{18}$ $(M+Na)^+$ = 657.1; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.92 (s, 3H), 1.94 (s, 3H), 1.96 (s, 3H), 2.02 (s, 3H), 2.04 (s, 3H), 2.07 (s, 3H), 3.62 (m, 1H, H-5′), 3.67 (t, 1H, *J* = 9.6 Hz, H-4), 4.00 (dd, 1H, *J* = 1.9 Hz, *J* = 12.4 Hz, H-6′a), 4.01–4.12 (m, 2H, H-5, H-6a), 4.28 (dd, 1H, *J* = 3.0 Hz, *J* = 9.6 Hz, H-2), 4.32 (dd, 1H, *J* = 4.1 Hz, *J* = 12.6 Hz, H-6′b), 4.39–4.47 (m, 2H, H-1′, H-6b), 4.53 (AB system $\delta_a$ 4.42, $\delta_b$ 4.62, 2H, *J* = 17.8 Hz, H-7), 4.87 (t, 1H, *J* = 8.8 Hz, H-2′), 5.01 (t, 1H, *J* = 8.8 Hz, H-4′), 5.07 (t, 1H, *J* = 8.8 Hz, H-3′), 5.23 (d, 1H, *J* = 3.0 Hz, H-1), 5.47 (t, 1H, *J* = 9.6 Hz, H-3); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.6, 20.6, 20.6, 20.7, 20.7, 20.9 ($6CH_3$), 61.4–61.6 (C-6, C-6′), 64.5 (C-7), 67.8 (C-4′), 70.9 (C-5), 71.1 (C-3), 71.5 (C-5′), 72.0 (C-2), 72.8 (C-3′), 75.2 (C-4), 76.2 (C-2), 91.0 (C-1), 100.7 (C-1′), 163.6, 169.0, 169.3, 169.7, 170.3, 170.3, 170.5 (7CO). Anal. Calcd for $C_{26}H_{34}O_{18}\cdot 0.5H_2O$: C, 48.52; H, 5.48. Found: C, 48.53; H, 5.38.

### 4.36. (*N*-Allylcarbamoyl)methyl 3,4,6-tri-*O*-acetyl-α-D-glucopyranoside 35

To a solution of lactone **1a** (4 g, 11.5 mmol) in anhydrous $CH_2Cl_2$ (8 mL), allylamine (1.30 mL, 17 mmol, 1.5 equiv) was added, and the reaction mixture was stirred for 12 h at room temperature under nitrogen. After evaporation of the solvent under reduced pressure, the residue was purified over silica gel ($CH_2Cl_2$/$CH_3OH$: 35/1) to give the amide **35** (4.29 g, 92%) as a colorless oil. $[\alpha]_D$ = +118 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.99 (s, 3H), 2.02 (s, 3H), 2.03 (s, 3H) (3OAc), 3.78 (dd, 1H, *J* = 3.7 Hz, *J* = 10.1 Hz, H-2), 3.91 (s, 2H, NHC*H*$_2$), 4.00–4.25 (m, 5H, H-5, H-6, H-7), 4.90 (d, 1H, *J* = 3.7 Hz, H-1), 4.97 (t, 1H, *J* = 9.8 Hz, H-4), 5.07–5.11 (m, 2H, CH=C*H*$_2$), 5.23 (t, 1H, *J* = 9.6 Hz, H-3), 5.72–5.85 (m, 1H, *CH*=CH$_2$), 7.55 (t, 1H, *J* = 5.6 Hz, NH); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.7, 20.8, 21.0 ($3CH_3$), 41.5 (NH*C*H$_2$), 61.9 (C-6), 67.4 (C-7), 68.0 (C-5), 68.1 (C-4), 70.3 (C-2), 73.3 (C-3), 99.3 (C-1), 116.4 (CH=*C*H$_2$), 133.7 (*C*H=CH$_2$), 169.2, 169.4, 169.4, 170.7 (4CO). Anal. Calcd for $C_{17}H_{25}NO_{10}$: C, 50.62; H, 6.52; N, 3.47. Found: C, 50.28; H, 6.31; N, 3.37.

### 4.37. (*N*-Propargylcarbamoyl)methyl 2-*O*-propylcarbamoyl-α-D-glucopyranoside 37

To a solution of compound **36** (200 mg, 0.498 mmol) in anhydrous $CH_2Cl_2$ (3 mL), propyl isocyanate (0.070 mL, 0.747 mmol, 1.5 equiv) and a catalytic amount of triethylamine were added. The reaction mixture was stirred at room temperature for 24 h, before being quenched with $CH_3OH$ (0.1 mL), the solution was diluted with $CH_2Cl_2$ (10 mL) and washed twice with 5 mL of an aqueous solution of $NH_4Cl$ (10%). The organic layer was dried over $Na_2SO_4$, and the solvents were evaporated. The residue was dissolved in $CH_3OH$/$H_2O$/$NEt_3$ (8/1/1, 2 mL) and stirred at room temperature for 12 h. After evaporation, the residue was purified over silica gel ($CH_2Cl_2$/acetone/$CH_3OH$/$H_2O$: 78/10/10/2) to give the desired carbamate **37** (130 mg, 72%) as a white solid. $[\alpha]_D$ = +11 (*c* 0.3, $CH_3OH$); mp: 120 °C; $^1$H NMR (300 MHz, $CD_3OD$): $\delta$ (ppm) 0.94 (t, 3H, *J* = 7.0 Hz, $CH_2CH_2CH_3$), 1.54 (q, 2H, *J* = 7.0 Hz, $CH_2CH_2CH_3$), 2.65 (ls, 1H, CCH), 3.10 (dt, 2H, *J* = 2.8 Hz, *J* = 7.0 Hz, $CH_2CH_2CH_3$), 3.42 (t, 1H, *J* = 9.6 Hz, H-4), 3.89 (t, 1H, *J* = 9.6 Hz, H-3), 4.60–4.73 (m, 2H, H-5, H-6a), 3.84 (dd, 1H, *J* = 1.9 Hz, *J* = 11.7 Hz, H-6b), 4.02–4.07 (m, 3H, H-7a, NHC*H*$_2$), 4.23 (d, 1H, *J* = 15.4 Hz, H-7b), 4.56 (dd, 1H, *J* = 3.6 Hz, *J* = 9.6 Hz, H-2), 5.01 (d, 1H, *J* = 3.6 Hz, H-1); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 11.6 ($CH_3$), 24.0 ($CH_2CH_2CH_3$), 29.1 (NHCH$_2$), 43.6 ($CH_2CH_2CH_3$), 62.3 (C-6), 67.6 (C-7), 71.5 (C-4), 72.3 (*C*CH), 72.3 (C-3), 74.3 (C-5), 74.7 (C-2), 80.4 (–CC*H*), 98.5 (C-1), 158.1, 171.4 (2CO). Anal. Calcd for $C_{15}H_{24}N_2O_8\cdot 0.25H_2O$: C, 49.38; H, 6.77; N, 7.68. Found: C, 49.54; H, 6.87; N, 7.69.

### 4.38. (*N*-Propargylcarbamoyl)methyl 3,4,6-tri-*O*-acetyl-2-*O*-hexadecylcarbamoyl-α-D-glucopyranoside 38

To a solution of compound **36** (0.210 g, 0.523 mmol) in anhydrous $CH_2Cl_2$ (1 mL), hexadecyl isocyanate (0.32 mL, 1.04 mmol, 2 equiv) and triethylamine were added. The reaction mixture was stirred for 14 h at room temperature before being quenched with $CH_3OH$ (0.5 mL). The undesired urea was filtered, rinsed with $CH_2Cl_2$ (10 mL), and the resulting solution was washed twice with 5 mL of an aqueous $NH_4Cl$ solution (10%). The organic phase was then dried over $Na_2SO_4$, and the solvents were evaporated. The residue obtained was purified over silica gel ($CH_2Cl_2$/$CH_3OH$: 30/1) to give carbamate **38** (258 mg, 74%) as a colorless oil. $[\alpha]_D$ = +78 (*c* 1.0, $CH_2Cl_2$); $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) 0.88 (t, 3H, *J* = 6.7 Hz, $CH_3$), 1.25 (m, 26H, $13CH_2$), 1.49 (t, 2H, *J* = 6.6 Hz, $CH_2$), 2.04 (s, 6H), 2.10 (s, 3H) (3OAc), 2.27 (t, 1H, *J* = 1.5 Hz, CC*H*), 3.09 (m, 2H, NHC*H*$_2$CH$_2$), 4.00–4.27 (m, 4H, H-5, H-6a, NHC*H*$_2$), 4.14 (AB system, 2H, $\delta_a$ 4.04, $\delta_b$ 4.23, *J* = 15.7 Hz, H-7), 4.25 (dd, 1H, *J* = 4.7 Hz, H-6b), 4.92 (dd, 1H, *J* = 3.6 Hz, *J* = 10.1 Hz, H-2), 4.99 (t, 1H, *J* = 5.7 Hz, NH), 5.04 (d, 1H, *J* = 3.6 Hz, H-1), 5.09 (t, 1H, *J* = 10.1 Hz, H-4), 5.45 (t, 1H, *J* = 10.1 Hz, H-3), 6.87 (ls, 1H, NH); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ (ppm) 14.2 ($CH_3$), 20.7, 20.8, 20.9 ($3CH_3$), 29.4–32.0 ($15CH_2$), 41.4 (NH*C*H$_2$), 61.8 (C-6), 67.5 (C-7), 68.2 (C-4), 68.2 (C-5), 70.3 (C-3), 70.8 (C-2), 70.3 (*C*CH), 79.5 (C*C*H), 97.5 (C-1), 154.9, 168.2, 169.5, 170.7, 170.7 (5CO). Anal. Calcd for $C_{34}H_{56}N_2O_{11}$: C, 61.06; H, 8.44; N, 4.19. Found: C, 60.91; H, 8.41; N, 4.22.

### 4.39. (*N*-Propargylcarbamoyl)methyl 2-*O*-hexadecylcarbamoyl-α-D-glucopyranoside 39

The acetyated compound **38** (0.185 g, 0.277 mmol) was dissolved in 5 mL of $CH_3OH$/$H_2O$/$NEt_3$ (8/1/1). After 3 h, the solvents were evaporated, co-evaporated with water, and the product was purified over a silica gel ($CH_2Cl_2$/acetone/$CH_3OH$/$H_2O$: 78/10/10/2) to give the carbamate **39** (125 mg, 77%) as white crystals. $[\alpha]_D$ = +43 (*c* 1.0, $CH_3OH$); mp: 128 °C (neat); $^1$H NMR (500 MHz, $CD_3OD$): $\delta$ (ppm) 0.89 (t, 3H, *J* = 6.9 Hz, $CH_2CH_2CH_3$), 1.28–1.32 (m, 26H, $13CH_2$), 1.50 (m, 2H, NHCH$_2$C*H*$_2$), 2.60 (t, 1H, *J* = 2.5 Hz, CC*H*), 3.10 (m, 2H, NHC*H*$_2$CH$_2$), 3.39 (t, 1H, *J* = 9.4 Hz, H-4), 3.58–3.61 (m, 1H, H-5), 3.70 (dd, 1H, *J* = 5.6 Hz, *J* = 12.0 Hz, H-6b), 3.85 (dd, 1H, *J* = 1.9 Hz, *J* = 12.0 Hz, H-6a), 3.86 (t, 1H, *J* = 9.4 Hz, H-3), 4.03–4.10 (m, 3H, H-7b, NHC*H*$_2$), 4.23 (d, 1H, *J* = 15.4 Hz, H-7b), 4.56 (dd, 1H, *J* = 3.8 Hz, *J* = 9.4 Hz, H-2), 5.01 (d, 1H, *J* = 3.8 Hz, H-1); $^{13}$C NMR (125 MHz, $CD_3OD$): $\delta$ (ppm) 14.4 ($CH_3$), 23.7–33.0 ($15CH_2$), 41.9 (NHCH$_2$), 62.4 (C-6), 67.7 (C-7), 71.6 (C-4), 72.3 (*C*CH), 72.4 (C-3), 74.4 (C-5), 74.7 (C-2), 80.4 (–CC*H*), 98.6 (C-1), 158.1, 171.4 (2CO). Anal. Calcd for $C_{28}H_{50}N_2O_8H_2O$: C, 57.51; H, 9.42; N, 4.79. Found: C, 57.59; H, 9.15; N, 4.72.

### 4.40. (*N*-Propargylcarbamoyl)methyl 3,4,6-tri-*O*-acetyl-2-*O*-carbamoyl-α-D-glucopyranoside 40

To a solution of compound **36** (130 mg, 0.32 mmol) in anhydrous $CH_2Cl_2$ (2 mL), trichloroacetyl isocyanate (0.06 mL, 0.52 mmol, 1.6 equiv) was added at −15 °C. The reaction was allowed warm to room temperature over 1 h and then quenched with $CH_3OH$ (2 mL). Solvents were evaporated, and the product was shortly chromatographed over silica gel using $CH_2Cl_2$/$CH_3OH$ (35/1). The product was then dissolved in $CH_3OH$ (3 mL) and zinc powder (4.85 mmol, 318 mg, 15 equiv) was added. The reaction mixture was stirred for 30 min and then filtered. After evaporation, the residue was purified over silica gel to give the carbamate **40**

(131 mg, 91%) as a colorless oil. $[\alpha]_D$ = +98 (*c* 1.0, $CH_2Cl_2$); $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.97 (s, 3H), 1.98 (s, 3H), 2.03 (s, 3H), 2.24 (t, 1H, *J* = 2.4 Hz, CC*H*), 3.93–4.06 (m, 4H, NHC$H_2$, H-5, H-6a), 4.09 (AB system, 2H, $\delta_a$ 4.00, $\delta_b$ 4.18, *J* = 15.6 Hz, H-7), 4.19 (dd, 1H, *J* = 4.5 Hz, *J* = 12.4 Hz, H-6b), 4.84 (dd, 1H, *J* = 3.8 Hz, *J* = 9.8 Hz, H-2), 5.00 (d, 1H, *J* = 3.8 Hz, H-1), 5.02 (t, 1H, *J* = 9.8 Hz, H-4), 5.16 (br s, 2H, CON$H_2$), 5.41 (t, 1H, *J* = 9.8 Hz, H-3), 6.83 (t, 1H, *J* = 5.3 Hz, NH); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.6, 20.8, 20.8 (3OAc), 28.8 (NH$CH_2$), 61.7 (C-6), 67.4 (C-7), 68.2 (C-5), 68.2 (C-4), 70.0 (C-3), 71.1 (C-2), 72.1 (*C*CH), 79.5 (C*C*H), 97.1 (C-1), 155.2, 168.3, 169.5, 170.6, 170.7 (5CO). Anal. Calcd for $C_{18}H_{24}N_2O_{11}\cdot H_2O$: C, 46.75; H, 5.67; N, 6.06. Found: C, 46.71; H, 5.38; N, 6.10.

### 4.41. (*N*-Propargylcarbamoyl)methyl 2-*O*-carbamoyl-α-D-glucopyranoside 41

Compound **40** (131 mg, 0.29 mmol) was stirred in $CH_3OH/H_2O/NEt_3$ (8/1/1, 5 mL) at room temperature for 12 h. After evaporation of the solvents under reduced pressure, the residue was chromatographed over silica gel ($CH_2Cl_2/CH_3OH$: 4/1) to give the carbamate **41** (90 mg, 97%) as white crystals. $[\alpha]_D$ = +32 (*c* 0.5, $CH_3OH$); mp 154 °C (neat); HRMS-ESI calculated for $C_{12}H_{18}N_2O_8\cdot Na^+$ ($MNa^+$) 341.0961, found 341.0963; $^1H$ NMR (500 MHz, $CD_3OD$): $\delta$ (ppm) 2.62 (t, 1H, *J* = 2.2 Hz, CC*H*), 3.42 (t, 1H, *J* = 9.8 Hz, H-4), 3.64 (ddd, 1H, *J* = 2.2 Hz, *J* = 5.6 Hz, *J* = 9.8 Hz, H-5), 3.72 (dd, 1H, *J* = 5.6 Hz, *J* = 12.0 Hz, H-6a), 3.85 (dd, 1H, *J* = 2.2 Hz, *J* = 12.0 Hz, H-6b), 3.91 (t, 1H, *J* = 9.8 Hz, H-3), 4.07 (d, 2H, *J* = 2.2 Hz, NHC$H_2$), 4.15 (AB system, 2H, $\delta_a$ 4.07, $\delta_b$ 4.23, *J* = 15.3 Hz, H-7), 4.54 (dd, 1H, *J* = 3.8 Hz, *J* = 9.6 Hz, H-2), 5.02 (d, 1H, *J* = 3.8 Hz, H-1); $^{13}C$ NMR (125 MHz, $CD_3OD$): $\delta$ (ppm) 29.1 (NH$CH_2$), 62.4 (C-6), 67.7 (C-7), 71.6 (C-4), 72.3 (*C*CH), 72.3 (C-3), 74.3 (C-5), 74.7 (CC*H*), 74.8 (C-2), 98.5 (C-1), 159.0, 171.4 (2CO).

### 4.42. (*N*-Allylcarbamoyl)methyl 3,4,6-tri-*O*-acetyl-2-*O*-carbamoyl-α-D-glucopyranoside 42

To a solution of compound **35** (200 mg, 0.49 mmol) in anhydrous $CH_2Cl_2$ (3 mL), trichloroacetyl isocyanate (0.09 mL, 0.79 mmol, 1.6 equiv) was added at −15 °C. The reaction was allowed to warm to room temperature over 1 h, after which the reaction was then quenched with $CH_3OH$ (2 mL). Solvents were evaporated, and the residue was shortly chromatographed over silica gel ($CH_2Cl_2/CH_3OH$: 35/1). The residue was then dissolved in $CH_3OH$ (2 mL), and zinc powder was added (7.35 mmol, 480 mg, 15 equiv). The mixture was stirred for 1 h and filtered. Solvents were evaporated, and the residue was purified over silica gel to give the carbamate **42** (195 mg, 88%) as white crystals. $[\alpha]_D$ = +107 (*c* 1.0, $CH_2Cl_2$); mp: 116 °C (neat); $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.98 (s, 6H), 2.03 (s, 3H), (3OAc), 3.88 (ls, 2H, NHC$H_2$), 3.94–4.22 (m, 5H, H-5, H-6, H-7), 4.81 (dd, 1H, *J* = 3.8 Hz, *J* = 10.2 Hz, H-2), 5.02 (t, 1H, *J* = 10.2 Hz, H-4), 5.03 (d, 1H, *J* = 3.8 Hz, H-1), 5.09–5.13 (m, 2H, CH=C$H_2$), 5.19 (ls, 2H, CON$H_2$), 5.40 (t, 1H, *J* = 10.2 Hz, H-3), 5.72–5.85 (m, 1H, *CH*=$CH_2$), 6.72 (t, 1H, *J* = 5.6 Hz, NH); $^{13}C$ NMR (75 MHz, $CD_3OD$): $\delta$ (ppm) 20.5, 20.7, 20.7 ($3CH_3$), 41.4 (NH$CH_2$), 61.7 (C-6), 67.2 (C-7), 68.0 (C-5), 68.2 (C-4), 70.0 (C-3), 71.0 (C-2), 96.9 (C-1), 116.6 (CH=$CH_2$), 133.9 (*C*H=$CH_2$), 155.2, 168.3, 169.4, 170.4, 170.6 (5CO). Anal. Calcd for $C_{18}H_{26}N_2O_{11}$: C, 48.43; H, 5.87; N, 6.28. Found: C, 48.27; H, 5.38; N, 6.10.

### 4.43. (*N*-Allylcarbamoyl)methyl 2-*O*-carbamoyl-α-D-glucopyranoside 43

A solution of compound **42** (95 mg, 0.21 mmol) in $CH_3OH/H_2O/NEt_3$ (8/1/1, 1 mL) was stirred at room temperature for 12 h. Solvents were evaporated under reduced pressure, and the obtained residue was chromatographed over silica gel ($CH_2Cl_2/CH_3OH$: 4/1) to give the product **43** (63 mg, 94%) as white crystals. $[\alpha]_D$ = +51 (*c* 0.5, $CH_3OH$); mp: 164 °C (neat); $^1H$ NMR (300 MHz, $CD_3OD$): $\delta$ (ppm) 3.42 (t, 1H, *J* = 9.6 Hz, H-4), 3.48–3.90 (m, 6H, H-3, H-6, H-5, NHC$H_2$), 4.10 (AB system, 2H, $\delta_a$ 4.06, $\delta_b$ 4.23, *J* = 15.8 Hz, H-7), 4.53 (dd, 1H, *J* = 3.6 Hz, *J* = 10.0 Hz, H-2), 5.03 (d, 1H, *J* = 3.6 Hz, H-1), 5.11–5.27 (m, 2H, CH=C$H_2$), 5.81–5.94 (m, 1H, C*H*=$CH_2$); $^{13}C$ NMR (75 MHz, $CD_3OD$): $\delta$ (ppm) 42.3 (NH$CH_2$), 62.4 (C-6), 67.7 (C-7), 71.4 (C-4), 71.5 (C-3), 72.3 (C-5), 73.2 (C-2), 100.9 (C-1), 116.5 (CH=$CH_2$), 135.1 (*C*H=$CH_2$), 159.0, 172.0 (2CO). Anal. Calcd for $C_{12}H_{20}N_2O_8\cdot H_2O$: C, 44.17; H, 6.38; N, 8.59. Found: C, 44.29; H, 6.72; N, 8.33.

### 4.44. (*N*-Propargylcarbamoyl)methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-α-D-glucopyranoside 44

To a solution of compound **33a** (500 mg, 0.78 mmol) in anhydrous $CH_2Cl_2$ (3 mL), propargylamine (1.18 mmol, 0.08 mL, 1.5 equiv) was added. The solution was stirred at rt for 8 h, and the solvents were evaporated. The residue was chromatographed over silica gel ($CH_2Cl_2/CH_3OH$: 30/1) to give compound **44** (462 mg, 85%) as a white foam. $[\alpha]_D$ = +107 (*c* 0.3, $CH_2Cl_2$); $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.94 (s, 3H), 1.96 (s, 3H), 1.98 (s, 3H), 2.04 (s, 3H), 2.05 (s, 3H), 2.07 (s, 3H) (6OAc), 2.22 (t, 1H, *J* = 2.4 Hz, CC*H*), 3.53 (m, 2H, H-5, H-4), 3.80–4.20 (m, 9H, H-7, H-2, H-5′, H-6b, H-6′, NHC$H_2$), 4.35 (dd, 1H, *J* = 2.2 Hz, *J* = 12.0 Hz, H-6a), 4.80 (dd, 1H, *J* = 4.0 Hz, *J* = 10.2 Hz, H-2′), 4.81 (d, 1H, *J* = 3.4 Hz, H-1), 5.00 (t, 1H, *J* = 10.2 Hz, H-4′), 5.24 (t, 1H, *J* = 10.2 Hz, H-3′), 5.29 (t, 1H, *J* = 9.6 Hz, H-3), 5.41 (d, 1H, *J* = 4.0 Hz, H-1′), 7.59 (t, 1H, *J* = 5.2 Hz, NH); $^{13}C$ NMR (75 MHz $CDCl_3$): $\delta$ (ppm) 20.6, 20.6, 20.6, 20.7, 20.9, 21.3 (6OAc), 28.7 (NH$CH_2$), 61.5 (C-6′), 62.8 (C-6), 67.2 (C-7), 68.0 (C-4′), 68.6 (C-5′or C-2), 69.4 (C-3), 70.2 (C-2′), 71.3 (C-5′ or C-2), 71.7 (CC*H*), 72.4 (C-4), 76.1 (C-3′), 76.1 (*C*CH), 95.6 (C-1), 98.8 (C-1′), 168.9, 169.5, 170.0, 170.6, 170.7, 170.7, 170.7, 172.0 (8CO). Anal. Calcd for $C_{29}H_{39}NO_{18}$: C, 50.51; H, 5.70; N, 2.03. Found: C, 50.61; H, 5.72; N, 2.03.

### 4.45. (*N*-Propargylcarbamoyl)methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-*O*-hexadecylcarbamoyl-α-D-glucopyranoside 45

To a solution of compound **44** (100 mg, 0.145 mmol) in anhydrous $CH_2Cl_2$ (2 mL), hexadecyl isocyanate (0.09 mL, 0.29 mmol, 2 equiv) and a catalytic amount of triethylamine were added. The mixture was stirred for 48 h at room rt before being quenched with methanol (0.5 mL). The mixture was filtered, evaporated, and the obtained residue was purified over silica gel ($CH_2Cl_2/CH_3OH$: 30/1) to give carbamate **45** (125 mg, 90% yield) as a colorless oil. $[\alpha]_D$ = +77 (*c* 0.5, $CH_2Cl_2$); $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 0.81 (t, 3H, *J* = 6.0 Hz, $CH_3$), 1.20 (m, 26H, $13CH_2$), 1.40 (m, 2H, $CH_2$), 1.94 (s, 3H), 1.96 (s, 3H), 1.96 (s, 3H), 1.99 (s, 3H), 2.03 (s, 3H), 2.07 (s, 3H) (6OAc), 2.22 (t, 1H, *J* = 2.4 Hz, CC*H*), 3.06 (m, 2H, $CH_2$), 3.88–4.20 (m, 8H, H-4, H-5, H-5′, H-6b, H-6′, NHC$H_2$), 4.05 (AB system, 2H, $\delta_a$ 3.90, $\delta_b$ 4.18, *J* = 15.8 Hz, H-7), 4.38 (dd, 1H, *J* = 2.2 Hz, *J* = 12.2 Hz, H-6a), 4.74 (dd, 1H, *J* = 3.6 Hz, *J* = 9.5 Hz, H-2), 4.79 (dd, 1H, *J* = 3.8 Hz, *J* = 10.0 Hz, H-2′), 4.86 (d, 1H, *J* = 3.6 Hz, H-1), 4.99 (t, 1H, *J* = 10.0 Hz, H-4′), 5.06 (t, 1H, *J* = 6.6 Hz, NH), 5.29 (t, 1H, *J* = 10.0 Hz, H-3′), 5.36 (d, 1H, *J* = 3.8 Hz, H-1′), 5.41 (t, 1H, *J* = 9.5 Hz, H-3), 6.90 (t, 1H, *J* = 5.0 Hz, NH); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 14.2 ($CH_3$), 20.7, 20.7, 20.7, 20.8, 20.8, 20.9 (6OAc), 21.1–32.0 ($15CH_2$), 41.4 (NH$CH_2$), 61.5 (C-6′), 62.7 (C-6), 67.4 (C-7), 68.0 (C-5 or C-5′or C-4), 68.6 (C-5 or C-5′or C-4), 68.7 (C-4′), 69.4 (C-3′), 70.2 (C-2′), 71.1 (C-2), 71.9 (C-3), 72.7 (CCH), 72.8 (C-5 or C-5′or C-4), 79.0 (*C*CH), 95.8

(C-1), 97.3 (C-1′), 169.8, 170.3, 170.7, 170.8, 170.8, 170.9, 170.9, 170.3 (8CO). Anal. Calcd for $C_{46}H_{72}N_2O_{19}$: C, 57.73; H, 7.58; N, 2.93. Found: C, 57.37, H, 7.78, N, 2.86.

### 4.46. (*N*-Propargylcarbamoyl)methyl α-D-glucopyranosyl-(1→4)-2-*O*-hexadecylcarbamoyl-α-D-glucopyranoside 46

A solution of compound **45** (76 mg, 0.079 mmol) in $CH_3OH$/$H_2O$/$NEt_3$ (8/1/1, 2 mL) was stirred at room temperature for 16 h. Solvents were evaporated, and the residue was chromatographed over silica gel ($CH_2Cl_2$/$CH_3OH$: 1/1) to give the carbamate **46** (41 mg, 73%) as a white solid. $[\alpha]_D$ = +57 (c 0.5, $CH_3OH$); mp: 118–120 °C; $^1H$ NMR (300 MHz, $CD_3OD$): $\delta$ (ppm) 0.97 (t, 3H, $J$ = 6.6 Hz, $CH_3$), 1.35 (m, 28H, 14$CH_2$), 1.59 (t, 1H, $J$ = 6.0 Hz, CC*H*), 3.19 (dt, 2H, $J$ = 1.5 Hz, $J$ = 7.0 Hz, NHC$H_2$CH$_2$), 3.67–3.93 (m, 12H, H-2′, H-3′, H-4′, H-5′, H-6′, H-6, H-4, H-5, NHC$H_2$), 4.10 (m, 2H, H-7a, H-3), 4.24–4.26 (m, 3H, H-7b, NHC$H_2$), 4.68 (dd, 1H, $J$ = 3.7 Hz, $J$ = 10.3 Hz, H-2), 5.08 (d, 1H, $J$ = 3.7 Hz, H-1), 5.27 (d, 1H, $J$ = 3.9 Hz, H-1′); $^{13}C$ NMR (75 MHz, $CD_3OD$): $\delta$ (ppm) 14.4 ($CH_3$), 23.4–41.8 (15$CH_2$), 48.4 (NH*C*H$_2$), 61.4 (C-6), 62.5 (C-6′), 67.6 (C-7), 71.2, 71.9, 72.1, 72.5, 73.7, 73.9, 74.4, 74.7 (C-2, C-3, C-4, C-5, C-2′, C-3′, C-4′, C-5′), 80.0 (C*C*H), 80.7 (*C*CH), 98.3 (C-1), 102.6 (C-1′), 157.6, 170.9 (2CO). Anal. Calcd for $C_{34}H_{60}N_2O_{13}\cdot H_2O$: C, 56.49; H, 8.65; N, 3.88. Found: C, 56.18; H, 8.56; N, 3.58.

### 4.47. (*N*-Propargylcarbamoyl)methyl 2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl-(1→4)-3,6-di-*O*-acetyl-2-*O*-carbamoyl-α-D-glucopyranoside 47

To a solution of compound **44** (87 mg, 0.13 mmol) in anhydrous $CH_2Cl_2$ (1 mL), trichloroacetyl isocyanate (0.024 mL, 0.20 mmol, 1.6 equiv) was added at −15 °C. The reaction was stirred for 2 h before being quenched with $CH_3OH$ (1 mL). Solvents were evaporated, and the residue was shortly chromatographed over silica gel ($CH_2Cl_2$/$CH_3OH$: 35/1). After evaporation, the residue obtained was dissolved in $CH_3OH$ (2 mL), and zinc powder (124 mg, 1.89 mmol, 15 equiv) was added. The mixture was stirred for 30 min, filtered and evaporated. Silica gel column chromatography ($CH_2Cl_2$/$CH_3OH$: 35/1) afforded the carbamate **47** (86 mg, 93%) as a white foam. $[\alpha]_D$ = +61 (*c* 1.0, $CH_2Cl_2$); HRMS-ESI calculated for $C_{30}H_{40}N_2O_{19}\cdot Na^+$ ($MNa^+$) 755.2123, found 755.2123; $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.94 (s, 3H), 1.96 (s, 3H), 1.99 (s, 6H), 2.04 (s, 3H), 2.08 (s, 3H), (6$CH_3$), 2.22 (t, $J$ = 2.5 Hz, CC*H*), 3.89–4.22 (m, 10H, H-4, H-5, H-6a, H-4′, H-5′, H-6′, H-7, NHC$H_2$), 4.03 (dd, 1H, $J$ = 2.0 Hz, $J$ = 12.1 Hz, H-6a), 4.72 (dd, 1H, $J$ = 3.8 Hz, $J$ = 10.1 Hz, H-2), 4.79 (dd, 1H, $J$ = 3.9 Hz, $J$ = 10.2 Hz, H-2′), 4.90 (d, 1H, $J$ = 3.8 Hz, H-1), 5.00 (t, 1H, $J$ = 3.9 Hz, $J$ = 10.2 Hz, H-4′), 5.29 (dd, 1H, $J$ = 9.6 Hz, $J$ = 10.2 Hz, H-3′), 5.36 (d, 1H, $J$ = 4.0 Hz, H-1′), 5.45 (dd, 1H, $J$ = 8.3 Hz, $J$ = 10.1 Hz, H-3), 6.87 (t, 1H, $J$ = 4.90 Hz, NH); $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.7, 20.7, 20.7, 20.8, 20.9, 21.1 (6$CH_3$), 28.9 (NH*C*H$_2$), 61.6 (C-6′), 62.7 (C-6), 67.4 (C-7), 68.0 (C-4′), 68.7 (C-5 or C-4 or C-5′), 68.7 (C-5 or C-4 or C-5′), 69.4 (C-3′), 70.2 (C-2′), 71.5 (C-2), 72.1 (*C*CH), 72.5 (C-3), 72.8 (C-5′ or C-5 or C-4), 79.5 (*C*CH), 95.1 (C-1), 97.0 (C-1′), 155.2, 163.8, 168.4, 169.6, 170.1, 170.6, 170.7, 170.7 (8CO) Anal. Calcd for $C_{30}H_{40}N_2O_{19}$: C, 49.18; H, 5.50; N, 3.82. Found: C, 49.48; H, 5.74, N, 3.81.

### 4.48. (*N*-Propargylcarbamoyl)methyl α-D-glucopyranosyl-(1→4)-2-*O*-carbamoyl-α-D-glucopyranoside 48

Compound **47** (390 mg, 0.53 mmol) was stirred in $CH_3OH$/$NEt_3$/$H_2O$ (8/1/1, 2 mL) for 12 h at rt. Solvents were evaporated, and the residue was chromatographed over silica gel, affording the carbamate **48** (233 mg, 91%) as a colorless oil. $[\alpha]_D$ = +11 (*c* 0.3, $CH_3OH$); HRMS-ESI calculated for $C_{18}H_{28}N_2O_{13}\cdot Na^+$ ($MNa^+$) 503.1489, found 503.1493; $^1H$ NMR (500 MHz, $CD_3OD$): $\delta$ (ppm) 2.5 (t, $J$ = 2.2 Hz, CC*H*) 3.58–3.84 (m, 10H, H-4, H-5, H-6, H-2′, H-3′, H-4′, H-5′, H-6′), 4.04 (s, 2H, NHC$H_2$), 4.11 (AB system, 2H, $\delta_a$ 4.03, $\delta_b$ 4.19, $J$ = 15.3 Hz, H-7), 4.18 (t, 1H, $J$ = 10.1 Hz, H-3), 4.56 (dd, 1H, $J$ = 3.7 Hz, $J$ = 10.1 Hz, H-2), 5.00 (d, 1H, $J$ = 3.7 Hz, H-1), 5.21 (d, 1H, $J$ = 3.7 Hz, H-1′); $^{13}C$ NMR (125 MHz, $CD_3OD$): $\delta$ (ppm) 29.1 (NH*C*H$_2$), 61.8 (C-6), 62.7 (C-6′), 67.4 (C-7), 71.5, 72.2, 72.2, 72.8, 74.1, 74.3, 74.7, 75.0, 79.5 (C-2, C-3, C-4, C-5, C-2′, C-3′, C-4′, C-5′, C*C*H), 80.8 (*C*CH), 98.4 (C-1), 102.7 (C-1′), 158.8, 171.3 (2CO).

### 4.49. *N*-Methyl[-4-[1-(5′-deoxyuridine)-1,2,3-triazole]]-carboxymethyl-2-*O*-carbamoyl-α-D-glucopyranoside 49

A solution of compound **41** (25 mg, 0.078 mmol), 5′-azido-5′-deoxyuridine (16 mg, 0.094 mmol, 1.2 equiv), sodium ascorbate (1M, 7.8 μL, 7.8 μmol, 0.1 equiv), and $CuSO_4$ (0.3 M, 2.6 μL, 0.78 μmol, 0.01 equiv) in *tert*-butanol/$H_2O$ (2/1, 1.5 mL) was stirred at room temperature for 12 h. To the reaction mixture DOWEX-$Na^+$ 50X8 resin (50 mg) was then added. The solution was filtered and rinsed with water. After evaporation, the obtained residue was chromatographed over silica gel (AcOEt/EtOH/$H_2O$: 6/3/1) to give adduct **49** (39 mg, 84%) as a colorless oil. $[\alpha]_D$ = +50 (*c* 0.3, $H_2O$); HRMS (ESI) *m*/*z* calculated for $C_{21}H_{29}N_7O_{13}Na$ $(M+Na)^+$ = 610.1721, found 610.1715; $^1H$ NMR (500 MHz, $CD_3OD$) $\delta$ (ppm) 3.40 (t, 1H, $J$ = 9.6 Hz, H-4), 3.61 (m, 1H, H-5), 3.70 (dd, 1H, $J$ = 5.3 Hz, $J$ = 11.8 Hz, H-6a), 3.83 (dd, 1H, $J$ = 1.6 Hz, $J$ = 11.8 Hz, H-6b), 3.87 (t, 1H, $J$ = 9.6 Hz, H-3), 4.01 (t, 1H, $J$ = 5.7 Hz, H-3′), 4.15 (AB system, 2H, $\delta_a$ 4.09, $\delta_b$ 4.22, $J$ = 15.4 Hz, H-7), 4.19–4.28 (m, 2H, H-2′, H-4′), 4.53–4.55 (m, 3H, H-2, CON$H_2$), 4.59 (br s, 2H, NHC$H_2$), 4.70 (dd, 1H, $J$ = 6.9 Hz, $J$ = 14.8 Hz, H-5′a), 4.81 (dd, 1H, $J$ = 3.1 Hz, $J$ = 14.8 Hz, H-5′b), 5.00 (d, 1H, $J$ = 3.7 Hz, H-1), 5.72–5.74 (m, 2H, CHC*H*CO, H-1′), 7.40 (d, 1H, $J$ = 8.2 Hz, C*H*CHCO), 7.90 (s, 1H, CC*H*N); $^{13}C$ NMR (125 MHz $CD_3OD$): $\delta$ (ppm) 35.2 (NH*C*H$_2$), 52.5 (C-5′), 62.4 (C-6), 67.7 (C-7), 71.6 (C-4), 71.9 (C-3′), 72.4 (C-3), 74.1 (C-2′), 74.4 (C-5), 74.7 (C-2), 82.9 (C-4′), 93.1 (C-1′), 98.6 (C-1), 103.1 (CH*C*HCO), 125.5 (*C*CHN), 143.3 (*C*HCHCO), 146.0 (*C*CHN), 152.1, 158.9, 166.1, 171.9 (4CO). Anal. Calcd for $C_{21}H_{29}N_7O_{13}\cdot 1.1H_2O$: C, 41.53, H, 5.18, N, 16.14. found: C, 41.16; H, 4.77, N, 16.58.

### 4.50. *N*-Methyl[-4-[1-(5′-deoxyuridine)-1,2,3-triazole]]-carboxymethyl α-D-glucopyranosyl-(1→4)-2-*O*-carbamoyl-α-D-glucopyranoside 50

To a solution of compound **48** (39 mg, 0.081 mmol) in a *tert*-butanol/$H_2O$ solution (1/1, 1 mL), 5′-azido-5′-deoxyuridine (16.5 mg, 0.097 mmol, 1.2 equiv), sodium ascorbate (1M, 8.1 μL, 8.12 μmol, 0.1 equiv), and $CuSO_4$ (0.3 M, 2.7 μL, 0.81 μmol, 0.01equiv) were added. The mixture was stirred at room temperature for 12 h. Solvents were evaporated, and the residue was chromatographed over silica gel (AcOEt/EtOH/$H_2O$ 6/4/1) to give compound **50** (49 mg, 81%) as a colorless oil. $[\alpha]_D$ = +105 (*c* 0.3, $H_2O$); HRMS-(ESI) calculated for $C_{27}H_{39}N_7O_{18}Na$ $(M+Na)^+$ = 772.2249, found 772.2256; $^1H$ NMR (500 MHz, $D_2O$): $\delta$ (ppm) 3.41 (t, $J$ = 9.6 Hz, H-4′), 3.57 (dd, $J$ = 3.0 Hz, $J$ = 9.6 Hz, H-2′), 3.66–3.86 (m, 9H, H-3′, H-5′, H-5, H-2′, H-6, H-6′, H-4), 4.10–4.29 (m, 5H, H-2″, H-3″, 3.70 (AB system, 2H, $\delta_a$ 4.13, $\delta_b$ 4.27, $J$ = 15.5 Hz, H-7), 4.21 (t, 1H, $J$ = 9.45 Hz, H-3)), 4.37 (m, 1H, H-4″), 4.48–4.95 (m, 5H, H-2, H-5″a, H-5″b, CON$H_2$), 5.07 (d, 1H, $J$ = 2.5 Hz, H-1), 5.42 (d, 1H, $J$ = 3.0 Hz, H-1′), 5.76 (ls, 1H, H-1″), 5.81 (d, 1H, $J$ = 7.1 Hz, CHC*H*CO), 7.28 (d, 1H, $J$ = 7.1 Hz, C*H*CHCO), 7.95 (s, 1H, CC*H*N); $^{13}C$ NMR (125 MHz, $D_2O$): $\delta$ (ppm) 34.4 (NH*C*H$_2$), 51.1 (C-5″), 60.6 (C-6′ or C-6), 60.8 (C-6′ or C-6), 66.6 (C-7), 69.6 (C-4′), 70.2 (C-3″), 71.1 (C-4), 71.4 (C-3), 72.0 (C-2′), 72.9 (C-2″), 73.1 (C-2), 73.2 (C-5′ or C-3′), 73.2 (C-5′ or C-3′), 76.5 (C-5), 81.0 (C-4″), 91.6 (C-1″), 96.8 (C-1), 100.0 (C-1′), 102.6

(CHCHCO), 125.4 (CCHN), 142.6 (*C*HCHCO), 144.9 (*C*CHN), 151.9, 158.3, 166.7, 172.0 (4CO).

### 4.51. (*N*-Propargylcarbamoyl)methyl 3,4,6-tri-*O*-acetyl-2-*O*-[(*tert*-butyloxycarbonyl)methyl]-α-D-glucopyranoside 51

To a solution of compound **36** (260 mg, 0.648 mmol) in anhydrous DMF (3 mL), $K_2CO_3$ (223 mg, 1.62 mmol, 2.5 equiv) was added as well as *tert*-butyl bromoacetate (0.11 mL, 0.78 mmol, 1.2 equiv). The mixture was stirred at room temperature for 16 h before being filtered. Solvents were evaporated under reduced pressure, and the residue was taken in $CH_2Cl_2$ (10 mL), washed twice with 30 mL of an aqueous 10% $NH_4Cl$ solution. The organic layer was then dried over $Na_2SO_4$. After evaporation and purification over silica gel (AcOEt/pentane: 2/1), compound **51** was obtained as a white foam (238 mg, 72%). $[\alpha]_D = +75$ (*c* 0.5, $CH_2Cl_2$); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.41 (s, 9H), 1.95 (s, 3H), 2.0 (s, 3H), 2.02 (s, 3H) (3OAc), 2.12 (t, 1H, *J* = 2.5 Hz, CC*H*), 3.54 (dd, 1H, *J* = 3.7 Hz, *J* = 9.9 Hz, H-2), 3.96–4.26 (m, 7H, H-5, H-6, H-7′, NHC$H_2$), 4.10 (AB system, 2H, $\delta_a$ 3.99, $\delta_b$ 4.22, *J* = 16.8 Hz, H-7), 4.91 (t, 1H, *J* = 9.9 Hz, H-4), 5.20 (d, 1H, *J* = 3.7 Hz, H-1), 5.38 (t, 1H, *J* = 9.8 Hz, H-3), 7.63 (t, 1H, *J* = 5.1 Hz, N*H*); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.6, 20.7, 20.8 (3 Ac), 28.1 ($CH_3$, *t*-Bu), 28.8 (NHC$H_2$), 61.7 (C-6), 67.2 (C-7′), 67.8 (C-5), 68.2 (C-4), 69.8 (C-7), 71.3 (CCH), 72.6 (C-3), 78.4 (C-2), 79.4 (–CCH), 82.5 (Cq), 98.5 (C-1), 168.9, 169.1, 169.8, 170.1, 170.5 (5CO). Anal. Calcd for $C_{23}H_{33}NO_2{\cdot}0.67H_2O$: C, 52.37; H, 6.57; N, 2.66. Found: C, 52.02; H, 6.40; N, 2.53.

### 4.52. (*N*-Propargylcarbamoyl)methyl 3,4,6-tri-*O*-acetyl-2-*O*-[(carboxy)methyl]-α-D-glucopyranoside 52

To a solution of compound **51** (153 mg, 0.297 mmol) in anhydrous $CH_2Cl_2$ (1 mL), TFA (0.7 mL, 30 equiv) was added. The mixture was stirred for 3 h at room temperature before being coevaporated twice with toluene (10 mL). The residue was shortly chromatographed over silica gel (AcOEt/pentane: 3/1) to give product **52** (123 mg, 90%) as a pale yellow oil. $[\alpha]_D = +58$ (*c* 0.3, $CH_2Cl_2$); HRMS-ESI calculated for $C_{19}H_{25}NO_{12}{\cdot}Na^+$ ($MNa^+$) 482.1274, found 482.1273; $^1$H NMR (500 MHz, $CDCl_3$): $\delta$ (ppm) 2.02 (s, 3H), 2.09 (s, 3H), 2.10 (s, 3H) (3OAc), 2.25 (t, 1H, *J* = 2.2 Hz, CC*H*), 3.65 (dd, 1H, *J* = 3.4 Hz, *J* = 9.8 Hz, H-2), 3.96–4.26 (m, 8H, H-5, H-6, H-7a, H-7′, NHC$H_2$), 4.40 (d, 1H, *J* = 16.8 Hz, H-7b), 4.99 (t, 1H, *J* = 9.8 Hz, H-4), 5.30 (d, 1H, *J* = 3.4 Hz, H-1), 5.46 (t, 1H, *J* = 9.8 Hz, H-3), 7.85 (t, 1H, *J* = 4.1 Hz, NH); $^{13}$C NMR (125 MHz, $CDCl_3$): $\delta$ (ppm) 20.7, 20.8, 21.0 (3 Ac), 29.2 (NHC$H_2$), 61.8 (C-6), 67.6 (C-7′), 68.1 (C-5), 68.4 (C-4), 69.3 (C-7), 72.0 (CCH), 72.0 (C-3), 78.8 (C-2), 78.9 (CC*H*), 98.8 (C-1), 170.2, 170.6, 170.6, 171.1, 172.9 (5CO). Anal. Calcd for $C_{19}H_{25}NO_{12}{\cdot}0.6H_2O$: C, 48.53; H, 5.62; N, 2.98. Found: C, 48.55; H, 5.47; N, 3.52.

### 4.53. (*N*-Propargylcarbamoyl)methyl 3,4,6-tri-*O*-acetyl-2-*O*-(propargyl)-α-D-glucopyranoside 53

To a solution of compound **36** (100 mg, 0.25 mmol) in anhydrous DMF (2 mL), 4 Å molecular sieves were added as well as NaH (12 mg, 0.3 mmol, 1.2 equiv) and propargyl bromide (0.03 mL, 0.62 mmol, 2.5 equiv). The reaction was stirred for 30 min before being quenched with acetic anhydride (1 mL). The mixture was filtered and evaporated. The residue was taken in $CH_2Cl_2$ (10 mL) and washed twice with water (20 mL). The organic layer was dried over $Na_2SO_4$, and the solvents were evaporated. The residue was chromatographed over silica gel (AcOEt/pentane: 2/1) to give the product **53** (62 mg, 56%) as a colorless oil. $[\alpha]_D = +36$ (*c* 0.3, $CH_2Cl_2$); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 2.02 (s, 3H), 2.07 (s, 3H), 2.09 (s, 3H) (3OAc), 2.24 (t, 1H, *J* = 2.5 Hz, CC*H*), 2.51 (t, 1H, *J* = 2.2 Hz, CC*H*), 3.81 (dd, 1H, *J* = 3.7 Hz, *J* = 9.7 Hz, H-2), 4.00–4.42 (m, 9H, H-5, H-6, H-7, NHC$H_2$, OC$H_2$), 4.98–5.04 (m, 2H, H-1, H-4), 5.42 (t, 1H, *J* = 9.7 Hz, H-3), 7.45 (t, 1H, *J* = 5.5 Hz, N*H*); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.7, 20.8, 21.0 ($3CH_3$), 28.8 (NHC$H_2$), 59.6 (OC$H_2$), 61.8 (C-6), 67.6 (C-7), 68.2 (C-4), 68.8 (C-5), 71.8 (C-3), 76.3 (CCH), 76.6 (C-2), 77.4 (CCH), 78.9 (CCH), 79.3 (CCH), 98.3 (C-1), 168.9, 169.9, 170.3, 170.7 (4CO). Anal. Calcd for $C_{20}H_{25}NO_{10}{\cdot}0.43H_2O$: C, 53.79; H, 6.22; N, 3.14. Found: C, 53.47; H, 5.90; N, 3.00. 71.8,

### 4.54. (*N*-Allylcarbamoyl)methyl 3,4,6-tri-*O*-acetyl-2-*O*-(propargyl)-α-D-glucopyranoside 54

To a solution of compound **35** (52 mg, 0.129 mmol) in anhydrous DMF (1 mL), 4 Å molecular sieves were added as well as NaH (7.4 mg, 0.155 mmol, 1.2 equiv) and propargyl bromide (0.019 mL, 0.258 mmol, 2 equiv). The solution was stirred at room temperature for 30 min before being quenched with acetic anhydride (0.5 mL). After filtration, the residue was dissolved in $CH_2Cl_2$ (5 mL) and was washed twice with water (10 mL), and the organic layer was dried over $Na_2SO_4$. The solvents were then evaporated under reduced pressure, and the residue was purified over silica (AcOEt/pentane: 2/1) to give the product **54** (32 mg, 55%) as a colorless oil. $[\alpha]_D = +36$ (*c* 0.3, $CH_2Cl_2$); $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 2.02 (s, 3H), 2.07 (s, 3H), 2.07 (s, 3H) (3OAc), 2.60 (t, 1H, *J* = 2.35 Hz, –CC*H*), 3.80 (dd, 1H, *J* = 3.6 Hz, *J* = 9.9 Hz, H-2), 3.93–4.11 (m, 5H, H-5, NHC$H_2$, C$H_2$CCH), 4.17–4.35 (m, 4H, H-6, H-7), 5.04 (d, 1H, *J* = 3,6 Hz, H-1), 5.08 (t, 1H, *J* = 9.5 Hz, H-4), 5.14–5.31 (m, 2H, CH=C$H_2$), 5.46 (t, 1H, *J* = 9.5 Hz, H-3), 5.81–5.94 (m, 1H, C*H*=CH$_2$), 7.55 (t, 1H, *J* = 5.8 Hz, N*H*); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.7, 20.8, 21.0 ($3CH_3$), 41.6 (NHC$H_2$), 59.5 (OC$H_2$), 61.8 (C-6), 67.7 (C-7), 68.1, 68.4 (C-4, C-5), 71.9 (C-3), 75.9 (CCH), 76.6 (C-2), 78.9 (CCH), 98.3 (C-1), 116.9 (CH=C$H_2$), 133.8 (C*H*=CH$_2$), 168.8, 168.8, 170.2, 170.7 (4CO). Anal. Calcd for $C_{20}H_{27}NO_{10}{\cdot}H_2O$: C, 52.28; H, 6.36; N, 3.05. Found: C, 51.93; H, 6.07; N, 2.95.

### 4.55. (*N*-Propargylcarbamoyl)methyl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-mannopyranoside 55

To a solution of compound **36** (94 mg, 0.23 mmol) in anhydrous $CH_2Cl_2$ (2 mL), pyridine (38 μL, 0.47 mmol, 2 equiv) and 4 Å molecular sieves were added. To this mixture, a solution of triflic anhydride (88 μL, 0.35 mmol, 1.5 equiv) in $CH_2Cl_2$ (200 μL) was added dropwise at −17 °C. The reaction mixture was warmed to room temperature over 1 h. The mixture was then filtered, rinsed with $CH_2Cl_2$, and washed twice with a $NaHCO_3$ solution (10%, 10 mL) and dried over $Na_2SO_4$. Solvents were evaporated, and the residue was dissolved in anhydrous DMF (2 mL). To this solution, 4 Å molecular sieves, $NaN_3$ (304 mg, 4.68 mmol, 20 equiv), and a catalytic amount of tetrabutylammonium iodide were added. The reaction was stirred at 60 °C overnight before being filtered. After evaporation, the residue was purified over silica gel (toluene/AcOEt: 2/1) to give the desired azide **55** (70 mg, 77%) as a pale yellow oil. $[\alpha]_D = +27$ (*c* 1.0, $CH_2Cl_2$); HRMS-ESI calculated for $C_{17}H_{22}N_4O_9{\cdot}Na^+$ ($MNa^+$) 449.1284, found 449.1291; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.99 (s, 3H), 2.03 (s, 3H), 2.05 (s, 3H) (3OAc), 2.22 (t, 1H, *J* = 2.5 Hz, CC*H*), 3.85 (m, 1H, H-5), 4.03–4.09 (m, 4H, H-2, H-6a, NHC$H_2$), 4.09 (AB system, 2H, $\delta_a$ 4.00, $\delta_b$ 4.17, *J* = 15.0 Hz, H-7), 4.18 (dd, 1H, *J* = 5.2 Hz, *J* = 12.2 Hz, H-6b), 4.84 (ls, 1H, H-1), 5.21–5.33 (m, 2H, H-3, H-4), 6.60 (t, 1H, *J* = 5.5 Hz, N*H*); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.6, 20.7, 20.8 ($3CH_3$), 28.8 (NHC$H_2$), 61.0 (C-2), 62.0 (C-6), 65.7 (C-4), 67.0 (C-7), 69.4 (C-5), 70.9 (C-3), 72.0 (CCH), 79.1 (CCH), 98.4 (C-1), 167.6, 169.5, 170.3, 170.7 (4CO).

### 4.56. (*N*-Allylcarbamoyl)methyl 3,4,6-tri-*O*-acetyl-2-azido-2-deoxy-α-D-mannopyranoside 56

The procedure described for obtaining compound **55** (see Section 4.55) was performed on compound **35** (520 mg, 1.29 mmol) to give azide **56** (527 mg, 96%) as a pale yellow oil. $[\alpha]_D$ = +69 (*c* 0.5, $CH_2Cl_2$); HRMS-ESI calculated for $C_{17}H_{24}N_4O_9{\cdot}Na^+$ ($MNa^+$) 451.1441, found 451.1442; $^1$H NMR (300 MHz, $CDCl_3$): $\delta$ (ppm) 1.99 (s, 3H), 2.03 (s, 3H), 2.05 (s, 3H) (3OAc), 3.82–3.91 (m, 3H, H-5, NHC*H*$_2$), 4.03 (dd, 1H, *J* = 2.2 Hz, *J* = 12.3 Hz, H-6a), 4.05 (AB system, 2H, $\delta_a$ 3.97, $\delta_b$ 4.14, *J* = 15.3 Hz, H-7), 4.09 (dd, 1H, *J* = 1.7 Hz, *J* = 3.2 Hz, H-2), 4.18 (dd, 1H, *J* = 5.3 Hz, *J* = 12.3 Hz, H-6b), 4.85 (d, 1H, *J* = 1.7 Hz, H-1), 5.09–5.21 (m, 2H, CH=C*H*$_2$), 5.22–5.28 (m, 2H, H-3, H-4), 5.70–5.90 (m, 1H, C*H*=CH$_2$), 6.47 (t, 1H, *J* = 5.3 Hz, N*H*); $^{13}$C NMR (75 MHz, $CDCl_3$): $\delta$ (ppm) 20.4, 20.5, 20.6 (3OAc), 41.3 (NH*C*H$_2$), 60.9 (C-2), 61.9 (C-6), 65.5 (C-4), 66.7 (C-7), 69.1 (C-5), 70.7 (C-3), 98.0 (C-1), 116.5 (CH=*C*H$_2$), 133.6 (*C*H=CH$_2$), 167.6, 169.3, 170.0, 170.5 (4CO).

## Acknowledgments

Financial support from MESR, CNRS, and the 'Cluster de recherche Chimie de la Région Rhône-Alpes' are gratefully acknowledged.

## References

1. For recent reviews, see: (a) Meutermans, W.; Le, G. T.; Becker, B. *ChemMedChem* **2006**, *1*, 1164–1194; (b) Murphy, P. V. *Eur. J. Org. Chem.* **2007**, 4177–4187.
2. (a) Wessel, H. P. In *Carbohydrates in Chemistry and Biology*; Ernst, B., Hart, G. W., Sinaÿ, P., Eds.; Wiley-CCH: Weinheim, Germany, 2000; Vol. 1, pp 565–585; (b) Wessel, H. P. In *GlycoScience: Chemistry and Chemical Biology, Part II*; Fraser-Reid, B. O., Tatsuta, K., Thiem, J., Eds.; Springer: Heidelberg, Germany, 2001; pp 2725–2752; (c) Gruner, S. A. W.; Locardi, E.; Lohof, E.; Kessler, H. *Chem. Rev.* **2002**, *102*, 491–514; (d) Schweizer, F. *Angew. Chem., Int. Ed.* **2002**, *41*, 230–253.
3. (a) Dean, B.; Oguchi, H.; Cai, S.; Otsuji, E.; Tashiro, K.; Hakomori, S.-I.; Toyokuni, T. *Carbohydr. Res.* **1993**, *245*, 175–192; (b) Binder, W. H.; Schmidt, W. *Monatsh. Chem.* **1995**, *126*, 923–931; (c) Choudhury, A. K.; Kitaoka, M.; Hayashi, K. *Eur. J. Org. Chem.* **2003**, 2462–2470; (d) Autar, R.; Khan, A. S.; Schad, M.; Hacker, J.; Liskamp, R. M. J.; Pieters, R. J. *ChemBioChem* **2003**, *4*, 1317–1325; (e) Li, Y.; Zhang, X.; Chu, S.; Yu, K.; Guan, H. *Carbohydr. Res.* **2004**, *339*, 873–879; (f) Autar, R.; Liskamp, R. M. J.; Pieters, R. J. *Carbohydr. Res.* **2005**, *340*, 2436–2442.
4. Virta, P.; Karskela, M.; Lönnberg, H. *J. Org. Chem.* **2006**, *71*, 1989–1999.
5. Santacroce, P. V.; Basu, A. *Angew. Chem., Int. Ed.* **2003**, *42*, 95–97.
6. Trombotto, S.; Bouchu, A.; Descotes, G.; Queneau, Y. *Tetrahedron Lett.* **2000**, *41*, 8273–8277.
7. Trombotto, S.; Danel, M.; Fitremann, J.; Bouchu, A.; Queneau, Y. *J. Org. Chem.* **2003**, *68*, 6672–6678.
8. Le Chevalier, A.; Pierre, R.; Kanso, R.; Chambert, S.; Doutheau, A.; Queneau, Y. *Tetrahedron Lett.* **2006**, *47*, 2431–2434.
9. Chambert, S.; Cowling, S. J.; MacKenzie, G.; Goodby, J. W.; Doutheau, A.; Queneau, Y. *J. Carbohydr. Chem.* **2007**, *26*, 27–39.
10. Sol, V.; Charmot, A.; Trombotto, S.; Queneau, Y.; Krausz, P. *J. Carbohydr. Chem.* **2006**, *25*, 345–360.
11. Listkowski, A.; Ing, P.; Cheaib, R.; Chambert, S.; Doutheau, A.; Queneau, Y. *Tetrahedron: Asymmetry* **2007**, *18*, 2201–2210.
12. Garegg, P. J. *Adv. Carbohydr. Chem. Biochem.* **2004**, *59*, 69–134; Toshima, K.; Tatsuta, K. *Chem. Rev.* **1993**, *93*, 1503–1531.
13. Close, D. M. *Chem. Rev.* **1979**, *79*, 491–513.
14. (a) Lemieux, R. U.; Morgan, A. R. *Can. J. Chem.* **1965**, *43*, 2199–2201; (b) Nitz, M.; Purse, B. W.; Bundle, D. R. *Org. Lett.* **2000**, *2*, 2939–2942.
15. David, S.; Hanessian, S. *Tetrahedron* **1985**, *41*, 643–663.
16. (a) Lemieux, R. U.; Ratcliffe, R. M. *Can. J. Chem.* **1979**, *2*, 1244–1251; (b) Danishefsky, S. J.; Bilodeau, M. T. *Angew. Chem., Int. Ed.* **1996**, *35*, 1380–1419; (c) Seeberger, P. H.; Danishefsky, S. J. *Acc. Chem. Res.* **1998**, *31*, 685–695; For a recent reference, see: (d) Li, Y.; Tang, P.; Chen, Y.; Yu, B. *J. Org. Chem.* **2008**, *73*, 4323–4325.
17. Lecourt, T.; Herault, A.; Pearce, A. J.; Sollogoub, M.; Sinaÿ, P. *Chem. Eur. J.* **2004**, *10*, 2960–2971.
18. Martin, O. R.; Kurz, K. G.; Rao, S. P. *J. Org. Chem.* **1987**, *52*, 2922–2925.
19. Français, A.; Urban, D.; Beau, J. M. *Angew. Chem., Int. Ed.* **2007**, *46*, 8662–8665.
20. Schmidt, R. R. In *Modern Methods in Carbohydrate Synthesis*; Kahn, S. H., O'Neill, R. A., Eds.; Hardwood Academic Publishers, 1996; pp 20–54.
21. Klotz, W.; Schmidt, R. R. *Liebigs Ann. Chem.* **1993**, 683–690.
22. Schmidt, R. R. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 212–235.
23. Klotz, W.; Schmidt, R. R. *J. Carbohydr. Chem.* **1994**, 1093–1101.
24. Lubineau, A.; Escher, S.; Alais, J.; Bonnaffé, D. *Tetrahedron Lett.* **1997**, *38*, 4087–4090.
25. Vauzeilles, B.; Dausse, B.; Palmier, S.; Beau, J.-M. *Tetrahedron Lett.* **2001**, *42*, 7567–7570.
26. Excoffier, G.; Gagnaire, D.; Utille, J.-P. *Carbohydr. Res.* **1975**, *39*, 368–373.
27. Differing results reported in Refs. 21 and 25 concerning the reaction of *N*-acyl glucosamines with allyl bromide suggest that concentration and solubility play important roles in the selectivity outcome of this reaction.
28. For a recent review on carbohydrate-based substrates used in Huisgen cycloadditions, see: Dedola, S.; Nepogodiev, S. A.; Field, R. A. *Org. Biomol. Chem.* **2007**, *5*, 1006–1017.
29. Queneau, Y.; Chambert, S.; Besset, C.; Cheaib, R. *Carbohydr. Res.* **2008**, in press, doi.org/10.1016/j.carres.2008.02.008.
30. Goodby, J. W.; Görtz, V.; Cowling, S. J.; MacKenzie, G.; Martin, P.; Plusquellec, D.; Benvegnu, T.; Boullanger, P.; Lafont, D.; Queneau, Y.; Chambert, S.; Fitremann, J. *J. Chem. Soc. Rev.* **2007**, *36*, 1971–2032.
31. (a) Möller, U.; Hobert, K.; Donnerstag, A.; Wagner, P.; Müller, D.; Fehlhaber, H.-W.; Markus, A.; Welzel, P. *Tetrahedron* **1993**, *49*, 1635–1648; (b) Luning, J.; Möller, U.; Müller, D.; Welzel, P.; Markus, A.; van Heijenoort, Y.; van Heijenoort, J. *Tetrahedron* **1993**, *49*, 10587–10596.
32. Eager, A. R.; Finney, N. S. *J. Org. Chem.* **2004**, *69*, 613–618.
33. Pierre, R.; Chambert, S.; Alirachedi, F.; Danel, M.; Trombotto, S.; Doutheau, A.; Queneau, Y. *C.R. Chim.* **2008**, *11*, 61–66.
34. Binder, W. H.; Schmid, W. *Monatsh. Chem.* **1995**, *126*, 923–931.
35. Grandjean, C.; Santraine, V.; Fardel, N.; Polidori, A.; Pucci, B.; Gras-Masse, H.; Bonnet, D. *Tetrahedron Lett.* **2004**, *45*, 3451–3454.
36. Sasaki, A.; Naoichi, M. JP Patent 06271597.
37. Filippov, D. V.; van den Elst, H.; Tromp, C. M.; van der Marel, G. A.; van Boeckel, C. A. A.; Overkleeft, H. S.; van Boom, J. H. *Synlett* **2004**, 773–778.