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Stereoselective diversity-oriented syntheses of functionalized saccharides from bicyclic carbohydrate 1,2-lactones

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ABSTRACT

Bicyclic carbohydrate 1,2-lactones have been synthesized in only two steps and high yields by saponification and subsequent cyclization from known malonate addition products to glycals. The *gluco*-configured lactone serves as an important precursor for diversity-oriented syntheses. Thus, stereoselective opening of the lactone ring was realized with various nucleophiles in the presence of $Sc(OTf)_3$. This enabled the introduction of different substituents at the anomeric position, to afford a broad variety of 1-functionalized carbohydrates. On the other hand, stereoselective α-substitution of the *gluco*-configured lactone with different electrophiles and subsequent ring opening gives a collection of 2-functionalized saccharides. More than 30 products have been isolated in analytically pure form, and their configurations were unequivocally established by various NMR methods. Thus, carbohydrate 1,2-lactones are attractive precursors for the stereoselective synthesis of diverse saccharides.

1. Introduction

Access to synthetic carbohydrates is an urgent need for the development of carbohydrate-based drugs, vaccines, adjuvants as well as novel drug delivery systems.[1] Compared to nucleic acids and peptides, carbohydrates remain relatively underexplored,[2] which is due in part to the difficulty associated with the synthesis of diverse carbohydrates and related analogs.[3] It is this complexity; however, that makes carbohydrates a rich source of molecular diversity with numerous biological applications. Since the early reports by Schreiber et al.,[4] diversity-oriented synthesis (DOS) has become a new paradigm for developing structurally diverse small molecules as probes to investigate biological pathways and also to provide the chemical space in drug discovery issues.[5]

Lactones, especially γ-lactones, as industrial intermediates and enzyme inhibitors,[6] represent an important class of organic compounds and can be synthesized by various methods.[7] Very recently, Trabocchi et al. reported the generation of molecular diversity of morpholine analogs by employing a bicyclic morpholine 2,3-lactone,[8] which suggests that lactones can serve as an important precursor for diverse synthesis. However, only few carbohydrate-based lactones were reported although such structures should increase the water solubility and related bioavailability. D-Glucono-1,5-lactone, representing a cheap chiral building block, is easily prepared by oxidation of the anomeric position of D-glucose.[9] Carbohydrate-fused 1,7-lactones[10] are available from uronic acids and allow stereoselective glycosylations by nucleophilic opening at the anomeric position.[11]

Carbohydrate-fused γ-lactones found less attention with some examples for 2,3-lactones **1**, which were synthesized over many steps.[12] Besides two papers on functionalized 1,2-lactones **2** (Fig. 1, R=I or NHAr),[13] our group published the first entry to unsubstituted carbohydrate 1,2-lactones **3** (Fig. 1, R=H) in two communications very recently.[14] Herein, we describe in full detail the scope of this new method, various synthetic transformations, mechanistic rationalizations of the stereoselectivities, and structural elucidation of all products. Thus, bicyclic carbohydrate 1,2-lactones **3** are ideal substrates for the stereoselective diversity-oriented syntheses of 1- and 2-functionalized saccharides.

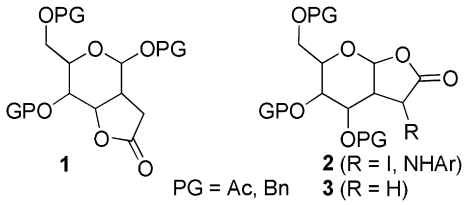

Fig. 1. Carbohydrate-fused γ-lactones.

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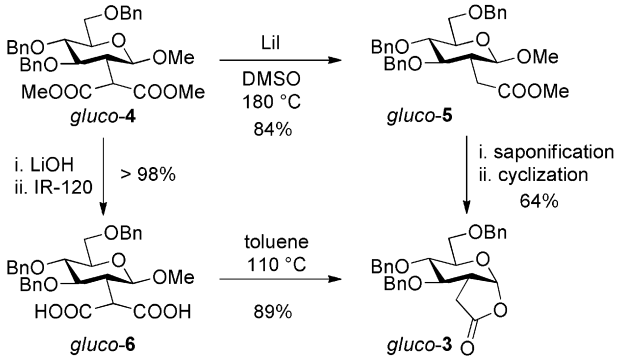
2. Results and discussion

2.1. Synthesis of bicyclic carbohydrate 1,2-lactones

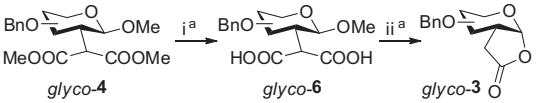
Toward our studies on transition-metal-mediated radical reactions,[15] we developed a one-step entry to 2-*C*-branched carbohydrates **4** by addition of dimethyl malonate to glycals in high yields and stereoselectivities.[16] Since we already succeeded in the cleavage to the ester *gluco*-**5** under drastic reaction conditions (Scheme 1),[17] our initial synthetic effort on *gluco*-**3** started with decarboxylation product *gluco*-**5**. However, the desired lactone *gluco*-**3** was obtained in only moderate yield (Scheme 1). Therefore, we looked for a milder and more convenient method. In the first step, saponification with LiOH afforded the malonic acid *gluco*-**6** quantitatively. Surprisingly, the lactone *gluco*-**3** was formed by simple heating to 110 °C in high yield (Scheme 1). This cyclization is forced by the elimination of carbon dioxide and methanol entropically, and is superior to the synthesis via ester *gluco*-**5**.



Scheme 1. Synthesis of carbohydrate 1,2-lactone *gluco*-**3**.

To optimize the synthesis and develop a general entry to carbohydrate 1,2-lactones *glyco*-**3**, different 2-*C*-branched saccharides *glyco*-**4** were investigated.[17b] The corresponding free dicarboxylic acids *glyco*-**6** were used without purification, and cyclized under acidic conditions at 110 °C (Table 1). The method is suitable for hexoses (entries 1 and 2), pentoses (entries 3 and 4), and disaccharides (entries 5 and 6), and provides the hitherto unknown carbohydrate 1,2-lactones *glyco*-**3** in only two steps and high yields from malonate addition products **4**.[14a]

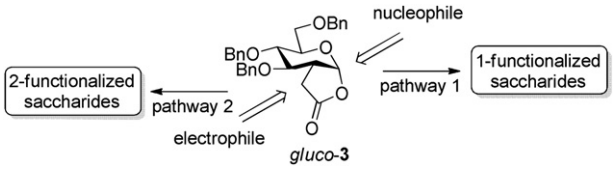
Table 1
Synthesis of carbohydrate 1,2-lactones **3**



Entry	Malonate	Product	Yield[b] [%]
1	*gluco*-**4**	*gluco*-**3**	92
2	*galacto*-**4**	*galacto*-**3**	91
3	*xylo*-**4**	*xylo*-**3**	88
4	*arabino*-**4**	*arabino*-**3**	88
5	*malto*-**4**	*malto*-**3**	87
6	*lacto*-**4**	*lacto*-**3**	84

[a] (i) LiOH, MeOH/H_2O, reflux, IR-120. (ii) HOAc, toluene, reflux.
[b] Yields of analytically pure products, isolated by column chromatography.

Since lactone *gluco*-**3** provides the most common configuration in nature, we became interested in its selective functionalization by two different methods (Scheme 2). One idea was the reaction with nucleophiles at the anomeric center (pathway 1), which would offer an easy entry to 1-functionalized saccharides. On the other hand, 2-functionalized saccharides would be available by α-substitution of the γ-lactone with different electrophiles and subsequent ring opening (pathway 2).

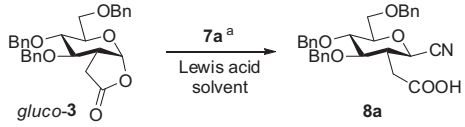


Scheme 2. Diversity-oriented syntheses from lactone *gluco*-**3**.

2.2. Synthesis of 1-functionalized saccharides

First of all, we investigated the synthesis of 1-functionalized saccharides with commercially available trimethylsilyl cyanide (TMSCN) **7a** as nucleophile (Table 2). Lewis acids like TMSOTf[11a,b] or $SnCl_4$[11c,e] have been proven to be suitable catalysts for openings of 1,7-lactones at the anomeric center.[18] However, lactone *gluco*-**3** gave no conversion (TMSOTf, entry 1) or cleavage of the *O*-benzyl protecting groups ($SnCl_4$, entries 2 and 3) in either CH_2Cl_2 or CH_3CN. In addition, only decomposition products were formed when $TiCl_4$ (entries 4 and 5) or $BF_3{\cdot}OEt_2$ (entry 6) were used as catalysts. Finally, the best condition was found with $Sc(OTf)_3$[18] in CH_2Cl_2, which was previously applied for the opening of substituted lactones **2** in CH_3CN.[13a] In our experiments, three solvents led to different results (Table 2, entries 7–9) indicating a remarkable solvent effect.[19] The combination of Sc(OTf)$_3$ and CH_2Cl_2 proceeded smoothly and the ring-opened product **8a** was isolated in 90% yield (entry 9). Thus, a nitrile group was easily introduced at the anomeric center, and we could investigate the applicability of a broad variety of other nucleophiles **7**.

Table 2
Opening of carbohydrate 1,2-lactone *gluco*-**3** with TMSCN

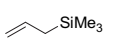
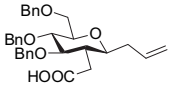
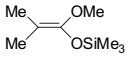
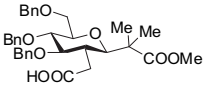
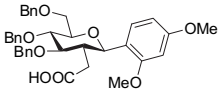
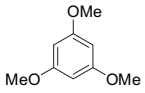
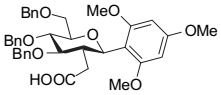


Entry	Lewis acid	Solvent	Results[b]
1	TMSOTf	CH_2Cl_2	A
2	$SnCl_4$	CH_2Cl_2	B
3	$SnCl_4$	CH3CN	B
4	$TiCl_4$	CH_2Cl_2	C
5	$TiCl_4$	CH3CN	C
6	$BF_3{\cdot}OEt_2$	CH_2Cl_2	C
7	$Sc(OTf)_3$	THF	B
8	$Sc(OTf)_3$	CH_3CN	A
9	$Sc(OTf)_3$	CH_2Cl_2	90%[c]

[a] **7a** is TMSCN.
[b] A: no conversion; B: cleavage of *O*-benzyl protecting group; C: decomposition of *gluco*-**3**.
[c] Yields of analytically pure products, isolated by column chromatography.

C-Glycosides are of current interest in chemistry, biology, and medicine.[20] They possess a rich source of chirality and have been used as building blocks in natural product synthesis.[21] Therefore, we investigated the reaction of lactone *gluco*-**3** with various *C*-nucleophiles **7b**–**e** in the presence of $Sc(OTf)_3$ (Table 3). Indeed, we could isolate 1,2-bis-*C*-branched glucose derivatives **8b**,**c** in high yields (entries 1 and 2). Additionally, electron rich arenes enabled the simple synthesis of *C*-aryl glycosides **8d**,**e** (entries 3 and 4), but the transformation failed with electron poor anisole.[22] The opening proceeded for all reactions stereoselectively to β-anomers, and subsequent epimerization was not observed.

Table 3
Opening of lactone *gluco*-**3** with *C*-nucleophiles **7b**–**e**[a]

Entry	*C*-Nucleophile **7**		Product **8**[b] (%)	
1		**7b**		**8b** (83)
2		**7c**		**8c** (85)
3		**7d**		**8d** (67)
4		**7e**		**8e** (77)

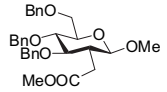
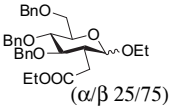
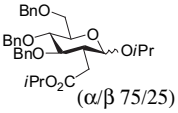
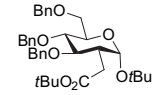
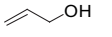
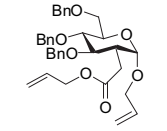
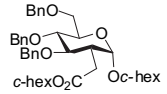
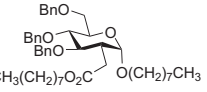
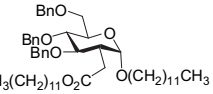
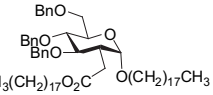
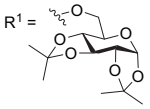
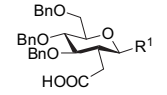
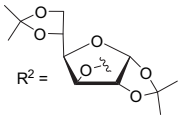
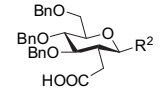
[a] In the presence of $Sc(OTf)_3$, procedure and conditions see Experimental.
[b] Yields of analytically pure products, isolated by column chromatography.

Next, the lactone opening was investigated with various alcohols (Table 4, entries 1–9) to provide biologically important *O*-glycosides,[9c,23] where the free carboxylic acid was directly esterified under the reaction conditions after ring opening. Surprisingly, α/β selectivities strongly depend on the different *O*-nucleophiles and the reaction times. Methanol (**7f**) afforded the β-methyl glucoside **8f** (entry 1) after 30 min in excellent yield, whereas an epimerization to the α-anomer, which was not separable from the β anomer, occurred after several hours. On the other hand, ethanol (**7g**) and 2-propanol (**7h**) furnished anomeric mixtures (entries 2 and 3), which were separated by column chromatography and isolated in analytically pure form (see Experimental). Other alcohols **7i**–**n**, even sterically hindered *tert*-butyl alcohol (**7i**) and cyclohexanol(**7j**), also reacted as nucleophiles under such conditions (Table 4, entries 4–9). Interestingly, α-glucosides **8i**–**n** were isolated selectively after longer reaction times. Such an anomerization is important for further transformations of the products. Glycosides **8l**–**n**, which contain two long alkyl chains and represent mimics of carbohydrate-based phospholipids,[24] were obtained with octanol (entry 7), dodecanol (entry 8), and even octadecanol (entry 9). Unfortunately, the reaction of lactone *gluco*-**3** with protected carbohydrates **7o**,**p** gave only low conversion in dichloromethane. Thus, different solvents were investigated, and the best result was found with 1,2-dichloroethane. Finally, disaccharides **8o**,**p** were isolated in moderate yields after 80 min (Table 4, entries 10 and 11). The liability of the glycosidic bond in the presence of $Sc(OTf)_3$ required short reaction times, which explains the selective formation of β-anomers and the absence of esterification of the carboxylic acid group.

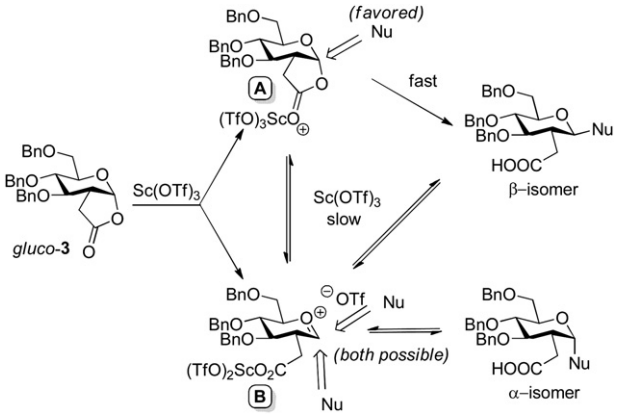
Our mechanistic rationale of α/β anomerization during *O*-glycosylation is based on two possible intermediates **A** and **B**, with the $Sc(OTf)_3$ activated lactone **A** formed in the first step (Scheme 3). Fast reactions with nucleophiles like methanol afford β-anomers, due to the selective attack from the opposite face. On the other hand, after longer reaction times, the intermediate **A** might open to the anomeric cation **B**, which can be trapped by the nucleophile from both sides. Under thermodynamic control, an equilibrium via intermediate **B** is possible, with the preferred formation of α-anomers. For such long reaction times, a subsequent esterification in the presence of the Lewis acid takes place (Table 4, entries 2–9). The isolation of products **8o**,**p** is in accordance to this hypothesis, since the liability of the disaccharide requires short reaction times, resulting in β-anomers with free acid groups (entries 10 and 11). Herein we describe the mechanism of such reactions with $Sc(OTf)_3$ for the first time, but similar α/β anomerizations have been previously reported in the presence of $SnCl_4$.[11e]

Not only *C*- and *O*-glycosides, but also *N*- and *S*-glycosides are very important compounds in current glycochemistry and glycobiology.[9c,23] Thus, the third topic of our studies was the reaction of lactone *gluco*-**3** with various *hetero*-nucleophiles **7q**–**u** in the presence of $Sc(OTf)_3$ (Table 5, entries 1–5). The reaction with aqueous ammonia is especially attractive, since it opens simple access to bicyclic lactam **8q** (entry 1) in excellent yield. Glucosyl azide **8r** was formed with trimethylsilyl azide (**7r**) as nucleophile,

Table 4
Opening of lactone *gluco*-**3** with *O*-nucleophiles **7f**–**p**[a]

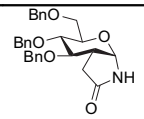
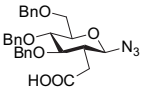
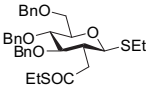
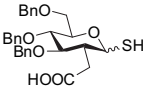
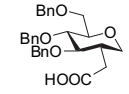
Entry	*O*-Nucleophile **7**		Product **8**[b] (%)	
1	MeOH	**7f**		**8f**[c] (92)
2	EtOH	**7g**	 (α/β 25/75)	**8g** (86)
3	*i*-PrOH	**7h**	 (α/β 75/25)	**8h** (78)
4	*t*-BuOH	**7i**		**8i** (65)
5		**7j**		**8j** (78)
6	Cyclohexanol	**7k**		**8k** (55)
7	$CH_3(CH_2)_7OH$	**7l**		**8l** (60)
8	$CH_3(CH_2)_{11}OH$	**7m**		**8m** (56)
9	$CH_3(CH_2)_{17}OH$	**7n**		**8n** (52)
10		**7o**		**8o** (53)
11		**7p**		**8p** (30)

[a] In the presence of $Sc(OTf)_3$, procedure and conditions see Experimental.
[b] Yields of analytically pure products, isolated by column chromatography.
[c] Compound **8f** is identical with compound **5**.



Scheme 3. Proposed mechanism for α/β anomerization.

Table 5
Opening of lactone *gluco*-**3** with *hetero*-nucleophiles **7q**–**u**[a]

Entry	*hetero*-Nucleophile **7**		Product **8**[b] (%)	
1	25% NH_3/H_2O	**7q**		**8q** (95)
2	$TMSN_3$	**7r**		**8r** (75)
3	EtSH	**7s**		**8s** (82)
4	$(TMS)_2S$	**7t**		**8t** (85)
5	Et_3SiH	**7u**		**8u** (78)

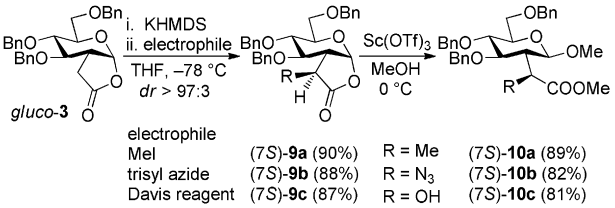
[a] In the presence of $Sc(OTf)_3$, procedure and conditions see Experimental.
[b] Yields of analytically pure products, isolated by column chromatography.

which can be applied in 'click chemistry'[25] or as precursor for preparation of dendrimers.[26] During this reaction, the intermediary silyl ester was hydrolyzed during work-up (entry 2). Ethanethiol (**7s**) afforded ethyl thioglucoside **8s** (entry 3) as a potential glycosyl donor[27] in good yield. All reactions proceeded with excellent stereoselectivities under exclusive formation of β-anomers, of course the hemithioacetal **8t** is in equilibrium with its α form (entry 4). This glycosyl thiol is a very useful building block for the synthesis of certain glycoconjugates that may be considered as analogs of glycopeptides and glycoproteins.[28] Finally, 1-deoxy derivate **8u** was synthesized in 78% yield by hydride opening (entry 5).

In summary, the opening of lactone *gluco*-**3**, which is easily available from D-glucal, with different nucleophiles proceeded smoothly with high stereoselectivities in moderate to good yields. Five *C*-glycosides (Tables 2 and 3), eleven *O*-glycosides (Table 4), and five hetero-glycosides (Table 5) were isolated in analytically pure form. Thus, a diverse set of more than 20 different 1-functionalized saccharides was synthesized from the same precursor in only few steps.

2.3. Synthesis of 2-functionalized saccharides

In the next part of our diversity-oriented synthesis we became interested in further functionalizations of the 2-position. The α-alkylation of lactone *gluco*-**3** seemed to be very attractive, since carbohydrate 2,3-lactones exhibit very good stereoselectivities.[12c,29] Indeed, in our previous studies we established potassium hexamethyldisilazide (KHMDS) as a suitable base for the α-deprotonation of lactone *gluco*-**3** at low temperatures.[14b] Thus, methylated product (7*S*)-**9a** was isolated in high yield as a sole diastereomer (Scheme 4).



Scheme 4. Stereoselective synthesis of 2-functionalized glucosides (7*S*)-**10**.

To extend the potential of our method and to determine the structure of all products, we examined the assembly of heteroatoms at the 7-position of the glucose backbone. Thus, reaction with trisyl azide[30] afforded azide (7*S*)-**9b** in 88% yield. Unfortunately, MoO_5[31] as oxidant gave no conversion of lactone *gluco*-**3**, but with Davis reagent[32] the α-hydroxy ester (7*S*)-**9c** was obtained in 87% yield in only one step (Scheme 4). Both reactions proceeded again with excellent stereoselectivities, and the products were isolated in analytically pure form. Next, the lactone ring was smoothly re-opened with methanol in the presence of Sc $(OTf)_3$. Under such conditions, the methyl esters (7*S*)-**10** were isolated in good yields without epimerization (Scheme 4). Therefore, we developed a convenient method to prepare 2-functionalized saccharides from the lactone *gluco*-**3** in only few steps.

The exclusive formation of one diastereomer for all reactions can be explained by steric interactions of the attacking electrophile with the sugar backbone, as already postulated in our previous communication.[14b] Herein we present detailed structural and conformational elucidations by NMR methods. Due to the fixed bicyclic structure of the lactone, coupling constants and NOE effects are very distinctive. Thus, both lactones *gluco*-**3** and (7*S*)-**9a** show an unusually large coupling constant of $J_{1,2}$=5.0 Hz, being mid-way between the normal values for axial–equatorial and axial–axial interactions (Fig. 2).

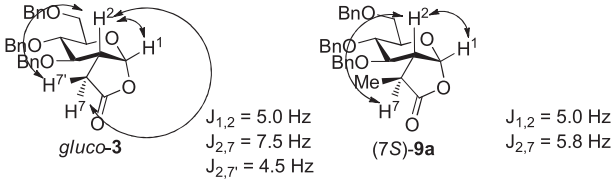


Fig. 2. Structural comparison of lactones *gluco*-**3** and (7*S*)-**9a**.

This indicates that the conformation of the pyranoside ring is distorted by the lactone from a chair to something approaching a half-chair.[12c] Additionally, lactone *gluco*-**3** has two coupling constants $J_{2,7}$=7.5 Hz and $J_{2,7'}$=4.5 Hz, whereas lactone (7*S*)-**9a** shows only $J_{2,7}$=5.8 Hz (Fig. 2). Since this value is in between 4.5 and 7.5 Hz, again the conformation of the bicyclic ring system must have been distorted, and a clear determination of the configuration at the 7-position was not possible by coupling constants. Therefore, we performed detailed NOE studies with lactone **9a**. Distinctive

cross-peaks of the methyl group with 2-H and even 1-H unequivocally established the *S*-configuration at the 7-position (Fig. 3).

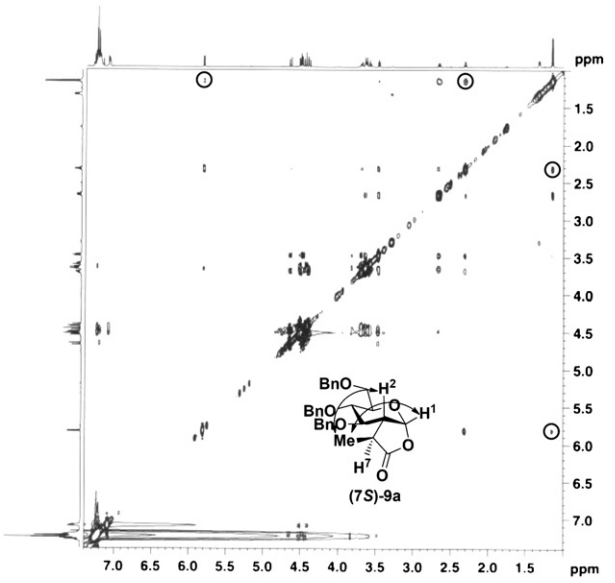
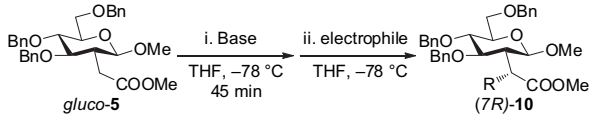


Fig. 3. NOE measurements (600 MHz) of (7*S*)-**9a**.

To open a selective entry to the 7*R*-isomers, we became interested in the direct α-alkylation of ester *gluco*-**5**, which is easily available from D-glucal in only few steps.[17] Now the methylene group is not fixed within a bicyclic structure and the attack of the electrophile can occur from different faces. Additionally, a suitable base had to be found for deprotonation at low temperature (Table 6).

Table 6
Deprotonation and trapping of ester *gluco*-**5**



Entry	Base	R[a]	Conv.[b] (%)	7*R*:7*S*[b]	7*R*-**10**[c] (%)
1	LDA	Me	50	88:12	7*R*-**10a** (30)
2	LDA/DMPU	Me	55	89:11	7*R*-**10a** (25)
3	LDA/HMPA	Me	50	91:9	7*R*-**10a** (32)
4	LDA/HMPT	Me	60	90:10	7*R*-**10a** (42)
5	LiHMDS	Me	90	92:8	7*R*-**10a** (71)
6	NaHMDS	Me	95	95:5	7*R*-**10a** (79)
7	KHMDS	Me	>97	>97:3	7*R*-**10a** (90)
8	KHMDS	N_3	>97	>97:3	7*R*-**10b** (82)
9	KHMDS	OH	>97	>97:3	7*R*-**10c** (85)

[a] Electrophiles: iodomethane, 2-sulfonyloxaziridine or trisyl azide.
[b] Determined by NMR spectra of the crude products.
[c] Yields of analytically pure products, isolated by column chromatography.

Indeed, the reaction with lithium diisopropylamide (LDA) and subsequent methylation already afforded the product **10a** in a ratio of 7*R*/7*S*=88:12 (entry 1). However, the pure epimer (7*R*)-**10a** was isolated in only 30% yield due to the low conversion of 50%. The conversions and yields could not be improved by addition of 1,3-dimethyl-3,4,5,6-tetrahydro-2(1*H*)-pyrimidinone (DMPU) (entry 2), hexamethylphosphoramide (HMPA) (entry 3) or hexamethylphosphorous triamide (HMPT) (entry 4). More efficient deprotonations were realized with stronger hexamethyldisilazides (HMDS) (entries 5–7), and already the lithium salt provided remarkably higher conversions and stereoselectivities. Finally, the best condition was found with the potassium salt, since the NMR spectra indicated full conversion and the highly selective formation of a sole product. Thus, the glycoside (7*R*)-**10a** was isolated in 90% yield in analytically pure form (entry 7). To extend the scope of our method, the assembly of heteroatoms at the 7-position of the glucose backbone was investigated. Thus, electrophiles like trisyl azide or the Davis reagent afforded the substituted methyl esters (7*R*)-**10b**,**c** in 82% and 85% yield with excellent stereoselectivities, respectively (Table 6, entries 8 and 9). All products were isolated in analytically pure form.

The determination of the configurations of esters **10** was more challenging than for lactones **9**, since NOE measurements were not possible, due to the free rotation around the C-2–7 bond. However, very similar coupling constants for all *S*-isomers ($J_{2,7}$=5.8–6.6 Hz), and *R*-isomers ($J_{2,7}$=1.8–2.1 Hz) clearly indicate that the configurations of the newly formed stereogenic centers of all main products **10** are identical (Fig. 4).

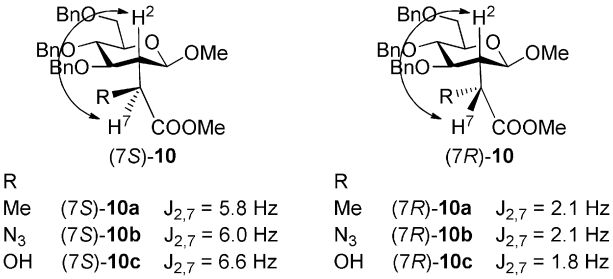


Fig. 4. Structural comparison of esters (7*S*)-**10** and (7*R*)-**10**.

Furthermore, a direct comparison of the ^{1}H NMR spectra of the two isomers (7*S*)-**10a**, obtained from the lactone opening of **9a** (Scheme 4), and (7*R*)-**10a** exhibit remarkable differences (Fig. 5). Thus, the chemical shifts of the methyl and CO_2Me group differ by more than 0.1 ppm. Therefore, both epimers can be easily distinguished by their ^{1}H NMR spectra. Since ester (7*S*)-**10a** was obtained from the known *S*-configured lactone **9a**; all products from the α-alkylation (Table 6) have exactly the opposite *R*-configuration. Thus, the synthesis of both epimers from the same precursor has been realized in only few steps.

The excellent stereoselectivities for all reactions can be rationalized by the formation of two different intermediates **A** or **B** (Scheme 5). Chelation of the metal ion by the ester enolate and an adjacent oxygen atom of the sugar backbone stabilizes the whole system. Two possibilities to the anomeric center (**A**) and to the 3-position (**B**) exist. From our studies with lactone *gluco*-**3** we know, that electrophiles attack the carbohydrate ring only from the top face (Scheme 4). Thus, intermediate **B** must be clearly favored, since it affords the *R*-configured products **10**, which is indeed the case (Table 6). The chelation proceeds most efficiently with potassium as counterion, explaining the best selectivities with KHMDS (entries 7–9). This interpretation is in accordance to a recent study, where the fixation of a potassium enolate to the 3-position and not to the anomeric center was discussed as well.[33] Overall, we developed a new concept of chelation-control in carbohydrate chemistry and realized a stereodivergent synthesis at the glucose backbone from easily available precursors.

2.4. Synthesis of other functionalized saccharides

To obtain more diverse structures of functionalized saccharides, we investigated some more transformations (Scheme 6). Thus, nitrile **8a** was smoothly converted into the diester **11** in 86% yield.

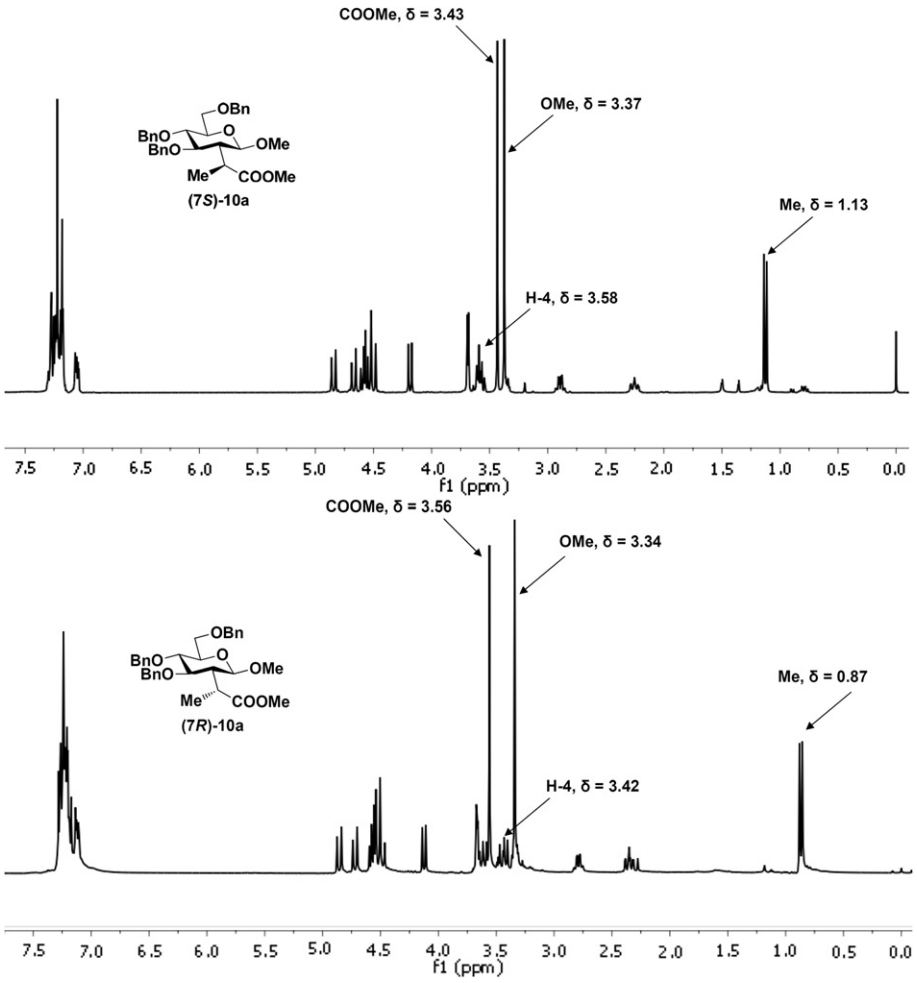
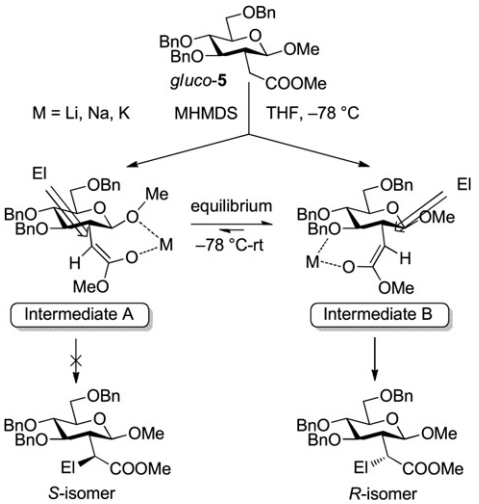
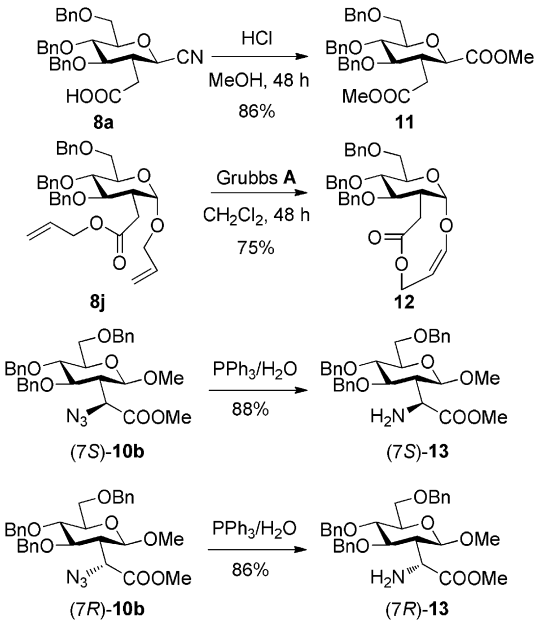


Fig. 5. Comparison of ^{1}H NMR spectra of (7*S*)-**10a** and (7*R*)-**10a**.

Such 1,2-bis-*C*-branched glucose derivates with methyl ester groups at the 1-positon are suitable intermediates in total synthesis.[34] Interestingly, allyl ester **8j** is predestined for ring-closing metathesis,[35] since due to the selective α/β anomerization during the lactone opening, both double bonds occupy the same side of the carbohydrate. Successfully, we synthesized macrolide **12**, which,



Scheme 5. Proposed mechanism for the selective α-substitution of ester *gluco*-**5**.



Scheme 6. Transformations of carbohydrate analogs **8a**, **8j**, and **10b**.

flanked by the saccharide, should possess interesting biological properties.[36] Finally, azides **10b** were transformed into 2-*C*-branched glyco-amino esters **13** by the convenient Staudinger reduction (Scheme 6).[37] Such interesting compounds, which have been synthesized by completely different reaction pathways previously,[38] led to an additional structural proof for the configurations at the 7-position.

3. Conclusion

In conclusion, we have developed a convenient and general entry to bicyclic carbohydrate 1,2-lactones in only two steps from malonates, which are easily available by radical additions to glycals. Stereoselective diversity-oriented syntheses (DOS) of functionalized saccharides have been realized by using such γ-lactones as important precursors. A broad variety of carbohydrate 1-analogs have been obtained by ring opening with different nucleophiles at the anomeric center. This pathway offers an opportunity to synthesize biologically important *C*-, *O*-, and *hetero*-glycosides, which can be used for attractive future applications. On the other hand, various 2-functionalized saccharides have been synthesized by α-deprotonation of lactones or esters and subsequent trapping with electrophiles. All products were isolated in good to high yields in analytically pure form. The stereoselectivities are remarkably high and can be controlled by the reaction pathway via lactone or ester. Thus, *R* or *S* isomers are selectively available; their absolute configurations were unequivocally determined by detailed NMR studies. Overall more than 30 carbohydrate analogs have been synthesized from one precursor, demonstrating the potential of diversity-oriented syntheses in carbohydrate chemistry.

4. Experimental

4.1. General

All reactions were carried out under argon by using standard Schlenk techniques. Solvents and commercially available chemicals were purified by standard methods or used as purchased. Excess of malonate was removed by a Kugelrohrofen (GKR-50, Büchi). TLC was performed on aluminum sheets silica gel 60 F_{254} (Merck, Darmstadt). Silica gel (63–200 μm, Woelm, Erlangen) was used for column chromatography. Optical rotations were measured on a JASCO P-1020 polarimeter, melting points on a Büchi SMP 20 apparatus (uncorrected). IR spectra were recorded on a Perkin–Elmer 1600 FT-IR spectrometer. NMR spectra were recorded either on a Bruker AC 300, AC 400 or AC 500 with $CDCl_3$ as the solvent and internal standard. Elemental analyses were performed on an ELEMENTAR vario EL analysator. High resolution mass spectroscopy (HRMS) was recorded on a Thermo Finnigan MAT 95 sectorfield spectrometer.

4.2. General procedure for the lactonization

A solution of addition product **4** (2.0 mmol) and $LiOH \cdot H_2O$ (210 mg, 5.0 mmol) in MeOH/H_2O (4:1, 20 mL) was heated under reflux for 1 h. After cooling to room temperature, the solvent was removed under vacuum. Then the crude product was dissolved in toluene and the pH value was adjusted to 3–4 with acetic acid. The solution was heated under reflux for 1 h. After evaporating the solvent the crude product was purified by flash chromatography (cyclohexane/ethyl acetate 7:1) to afford the lactone **3** in analytically pure form.

*4.2.1. (3aR,4R,5S,6R,7aR)-4,5-Dibenzyloxy-6-benzyloxymethyl-2-oxo-hexahydro-furo[2,3-b]pyran (gluco-**3**).* A white solid; mp 87–89 °C; $[\alpha]_D^{20}$ +21.8 (*c* 0.99, $CHCl_3$); R_f=0.33 (*c*-hexane/ethyl acetate 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.40 (dd, *J*=15.5, 7.5 Hz, 1H, 7′-H), 2.53 (dd, *J*=15.5, 4.5 Hz, 1H, 7-H), 2.58 (dddd, *J*=10.5, 7.5, 5.0, 4.5 Hz, 1H, 2-H), 3.41 (ddd, *J*=9.0, 4.5, 3.0 Hz, 1H, 5-H), 3.62 (dd, *J*=10.5, 2.0 Hz, 1H, 3-H), 3.72 (dd, *J*=10.5, 3.0 Hz, 1H, 6′-H), 3.73 (dd, *J*=10.5, 4.5 Hz, 1H, 6-H), 3.72 (dd, *J*=9.0, 2.0 Hz, 1H, 4-H), 4.46 (d, *J*=12.0 Hz, 1H, *CH*$_2$—Ph), 4.51 (d, *J*=11.0 Hz, 1H, *CH*$_2$—Ph), 4.52 (d, *J*=11.5 Hz, 1H, *CH*$_2$—Ph), 4.55 (d, *J*=12.0 Hz, 1H, *CH*$_2$—Ph), 4.64 (d, *J*=11.0 Hz, 1H, *CH*$_2$—Ph), 4.76 (d, *J*=11.5 Hz, 1H, *CH*$_2$—Ph), 5.76 (d, *J*=5.0 Hz, 1H, 1-H), 7.10–7.29 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=34.2 (t, C-7), 40.7 (d, C-2), 68.3 (t, C-6), 73.6, 74.1, 74.4 (3t, *C*H$_2$—Ph), 72.9, 76.5, 79.2 (3d, C-3, C-4, C-5), 101.4 (d, C-1), 127.7, 127.9, 128.1, 128.4, 128.5, 128.6 (6d, arom, C—H), 137.6, 137.7, 137.8 (3s, arom, *C*—CH$_2$O), 172.6 (s, *C*OOR); IR (film): ν=3088, 3064, 3029, 2915, 2868, 1771, 1498, 1278 cm^{-1}; elemental analysis (%) calcd for $C_{29}H_{30}O_6$: C 73.40, H 6.37; found: C 73.25, H 6.42.

*4.2.2. (3aR,4R,5R,6R,7aR)-4,5-Dibenzyloxy-6-benzyloxymethyl-2-oxo-hexahydro-furo[2,3-b]pyran (galacto-**3**).* A white solid; mp 81–83 °C; $[\alpha]_D^{20}$ +35.0 (*c* 1.00, $CHCl_3$); R_f=0.35 (*c*-hexane/ethyl acetate 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.48 (dd, *J*=17.5, 6.5 Hz, 1H, 7′-H), 2.60 (dd, *J*=17.5, 7.0 Hz, 1H, 7-H), 2.76 (dddd, *J*=10.5, 7.0, 6.5, 4.5 Hz, 1H, 2-H), 3.24 (dd, *J*=10.5, 2.0 Hz, 1H, 3-H), 3.55 (dd, *J*=9.0, 5.5 Hz, 1H, 6′-H), 3.60 (dd, *J*=9.0, 1.0 Hz, 1H, 6-H), 3.91 (dd, *J*=7.5, 2.0 Hz, 1H, 4-H), 4.00 (ddd, *J*=7.5, 5.5, 1.0 Hz, 1H, 5-H), 4.32 (d, *J*=11.5 Hz, 1H, *CH*$_2$—Ph), 4.40 (d, *J*=12.0 Hz, 1H, *CH*$_2$—Ph), 4.46 (d, *J*=12.0 Hz, 1H, *CH*$_2$—Ph), 4.55 (d, *J*=11.5 Hz, 1H, *CH*$_2$—Ph), 4.64 (d, *J*=11.5 Hz, 1H, *CH*$_2$—Ph), 4.78 (d, *J*=11.5 Hz, 1H, *CH*$_2$—Ph), 5.76 (d, *J*=4.5 Hz, 1H, 1-H), 7.18–7.32 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=34.8 (t, C-7), 37.2 (d, C-2), 68.1 (t, C-6), 71.5, 73.5, 74.3 (3t, *C*H$_2$—Ph), 69.4, 72.4, 78.2 (3d, C-3, C-4, C-5), 102.2 (d, C-1), 127.8, 127.9, 128.0, 128.3, 128.4, 128.7 (6d, arom, C—H), 137.0, 137.7, 138.1 (3s, arom, *C*—CH$_2$O), 173.0 (s, *C*OOR); IR (film): ν=3545, 3028, 2915, 1771, 1607, 1455, 1259 cm^{-1}; elemental analysis (%) calcd for $C_{29}H_{30}O_6$: C 73.40, H 6.37; found: C 73.29, H 6.40.

*4.2.3. (3aR,4R,5R,7aR)-4,5-Dibenzyloxy-2-oxo-hexahydro-furo[2,3-b]pyran (xylo-**3**).* A colorless syrup; $[\alpha]_D^{20}$ +26.7 (*c* 0.92, $CHCl_3$); R_f=0.37 (*c*-hexane/ethyl acetate 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.43 (dd, *J*=16.0, 8.0 Hz, 1H, 6′-H), 2.47 (dddd, *J*=9.5, 8.0, 5.0, 4.0 Hz, 1H, 2-H), 2.73 (dd, *J*=16.0, 5.0 Hz, 1H, 6-H), 3.49–3.53 (m, 2H, 5-H, 5′-H), 3.71 (ddd, *J*=6.5, 3.0, 2.0 Hz, 1H, 4-H), 3.83 (dd, *J*=9.5, 3.0 Hz, 1H, 3-H), 4.49 (d, *J*=12.0 Hz, 1H, *CH*$_2$—Ph), 4.52 (d, *J*=11.5 Hz, 1H, *CH*$_2$—Ph), 4.58 (d, *J*=12.0 Hz, 1H, *CH*$_2$—Ph), 4.69 (d, *J*=11.5 Hz, 1H, *CH*$_2$—Ph), 5.59 (d, *J*=4.0 Hz, 1H, 1-H), 7.18–7.30 (m, 10H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=32.1 (t, C-6), 40.4 (d, C-2), 61.9 (t, C-5), 71.9, 73.6 (2t, *C*H$_2$—Ph), 74.7, 76.3 (2d, C-3, C-4), 100.1 (d, C-1), 127.7, 127.8, 128.0, 128.1, 128.6 (5d, arom, C—H), 137.5, 137.6 (2s, arom, *C*—CH$_2$O), 174.1 (s, *C*OOR); IR (film): ν=3068, 2931, 1955, 1788, 1450, 1235 cm^{-1}; elemental analysis (%) calcd for $C_{21}H_{22}O_5$: C 71.17, H 6.26; found: C 71.32, H 6.16.

*4.2.4. (3aS,4S,5R,7aS)-4,5-Dibenzyloxy-2-oxo-hexahydro-furo[2,3-b]pyran (arabino-**3**).* A colorless syrup; $[\alpha]_D^{20}$ +32.9 (*c* 0.96, $CHCl_3$); R_f=0.39 (*c*-hexane/ethyl acetate 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.50 (dd, *J*=17.5, 1.5 Hz, 1H, 6′-H), 2.60 (dd, *J*=17.5, 7.5 Hz, 1H, 6-H), 2.76 (dddd, *J*=9.5, 7.5, 4.5, 1.5 Hz, 1H, 2-H), 3.64 (dd, *J*=12.5, 6.5 Hz, 1H, 5′-H), 3.74 (ddd, *J*=6.5, 3.0, 2.5 Hz, 1H, 4-H), 3.83 (dd, *J*=9.5, 2.5 Hz, 1H, 3-H), 4.00 (dd, *J*=12.5, 3.0 Hz, 1H, 5-H), 4.29 (d, *J*=11.5 Hz, 1H, *CH*$_2$—Ph), 4.54 (d, *J*=11.5 Hz, 1H, *CH*$_2$—Ph), 4.56 (d, *J*=12.0 Hz, 1H, *CH*$_2$—Ph), 4.68 (d, *J*=12.0 Hz, 1H, *CH*$_2$—Ph), 5.77 (d, *J*=4.5 Hz, 1H, 1-H), 7.18–7.32 (m, 10H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=34.5 (t, C-6), 37.5 (d, C-2), 62.4 (t, C-5), 71.0, 71.3 (2t, *C*H$_2$—Ph), 68.9, 76.1 (2d, C-3, C-4), 102.0 (d, C-1), 127.8, 127.9, 128.2, 128.5, 128.6 (5d, arom, C—H), 137.2, 137.7 (2s, arom, *C*—CH$_2$O), 173.4 (s, *C*OOR); IR (film): ν=3062, 2930, 1780, 1454,

1204 cm^{-1}; elemental analysis (%) calcd for $C_{21}H_{22}O_5$: C 71.17, H 6.26; found: C 71.03, H 6.33.

*4.2.5. (3aR,4R,5S,6R,7aR)-4-Benzyloxy-5-[2,3,4,6-tetra-O-benzyl-2-deoxy-α-D-glucopyranosyl]-6-benzyloxymethyl-2-oxo-hexahydro-furo[2,3-b] pyran (malto-**3**).* A colorless syrup; $[\alpha]_D^{20}$ +58.5 (*c* 1.01, $CHCl_3$); R_f=0.42 (*c*-hexane/ethyl acetate 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.18 (dd, *J*=17.5, 9.5 Hz, 1H, 13′-H), 2.79 (dddd, *J*=10.5, 9.5, 8.0, 6.5 Hz, 1H, 2-H), 2.85 (dd, *J*=17.5, 8.0 Hz, 1H, 13-H), 3.31 (dd, *J*=9.5, 2.0 Hz, 1H, 12′-H), 3.43 (dd, *J*=9.5, 3.5 Hz, 1H, 12-H), 3.49 (dd, *J*=10.5, 7.5 Hz, 1H, 3-H), 3.50 (dd, *J*=10.5, 7.5 Hz, 1H, 10-H), 3.59 (dd, *J*=9.5, 7.5 Hz, 1H, 4-H), 3.60 (ddd, *J*=9.5, 6.5, 4.0 Hz, 1H, 5-H), 3.61 (ddd, *J*=10.5, 3.5, 2.0 Hz, 1H, 11-H), 3.67 (dd, *J*=12.5, 8.0 Hz, 1H, 6′-H), 3.71 (dd, *J*=12.5, 4.5 Hz, 1H, 6-H), 3.76 (dd, *J*=10.0, 7.5 Hz, 1H, 9-H), 3.98 (dd, *J*=10.0, 3.5 Hz, 1H, 8-H), 4.29 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.30 (d, *J*=11.5 Hz, 1H, CH_2–Ph), 4.35 (d, *J*=3.5 Hz, 1H, 7-H), 4.37 (d, *J*=11.5 Hz, 1H, CH_2–Ph), 4.46 (d, *J*=1.5 Hz, 2H, CH_2–Ph), 4.47 (d, *J*=12.5 Hz, 1H, CH_2–Ph), 4.54 (d, *J*=12.5 Hz, 1H, CH_2–Ph), 4.59 (d, *J*=11.0 Hz, 1H, CH_2–Ph), 4.78 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.79 (d, *J*=11.0 Hz, 1H, CH_2–Ph), 4.81 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.83 (d, *J*=11.5 Hz, 1H, CH_2–Ph), 5.89 (d, *J*=6.5 Hz, 1H, 1-H), 7.00–7.25 (m, 30H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=30.2 (t, C-13), 36.1 (d, C-2), 68.1, 70.0 (2t, C-6, C-12), 71.0, 73.4, 73.5, 73.8, 75.0, 75.6 (6t, CH_2–Ph), 71.1, 71.4, 72.2, 74.2, 77.4, 79.6, 81.7 (7d, C-3, C-4, C-5, C-8, C-9, C-10, C-11), 96.6, 99.6 (2d, C-1, C-7), 127.5, 127.6, 127.7, 127.8, 127.9, 128.0, 128.3, 128.4, 128.7 (9d, arom, C–H), 137.5, 137.8, 137.9, 138.0, 138.2, 138.5 (6s, arom, *C*–CH_2O), 174.8 (s, COOR); IR (film): ν=3029, 2860, 1717, 1451, 1040 cm^{-1}; elemental analysis (%) calcd for $C_{56}H_{58}O_{11}$: C 74.15, H 6.45; found: C 74.36, H 6.28.

*4.2.6. (3aR,4R,5S,6R,7aR)-4-Benzyloxy-5-[2,3,4,6-tetra-O-benzyl-2-deoxy-β-D-galactopyranosyl]-6-benzyloxymethyl-2-oxo-hexahydro-furo[2,3-b] pyran (lacto-**3**).* A colorless syrup; $[\alpha]_D^{20}$ +66.1 (*c* 1.01, $CHCl_3$); R_f=0.40 (*c*-hexane/ethyl acetate 3:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.56 (dddd, *J*=10.5, 8.5, 6.0, 4.5 Hz, 1H, 2-H), 2.57 (s, 2H, 13-H, 13′-H), 3.32 (ddd, *J*=10.5, 6.5, 3.0 Hz, 1H, 11-H), 3.38 (dd, *J*=8.5, 3.0 Hz, 2H, 12-H, 12′-H), 3.44 (dd, *J*=12.0, 7.5 Hz, 1H, 6-H), 3.48 (dd, *J*=10.5, 6.5 Hz, 1H, 10-H), 3.50 (dd, *J*=10.5, 7.5 Hz, 1H, 3-H), 3.57 (ddd, *J*=10.0, 7.5, 3.5 Hz, 1H, 5-H), 3.67 (dd, *J*=10.0, 7.5 Hz, 1H, 4-H), 3.72 (d, *J*=7.5 Hz, 1H, 7-H), 3.73 (dd, *J*=12.0, 3.5 Hz, 1H, 6′-H), 3.81 (d, *J*=3.0, 1H, 9-H), 3.98 (dd, *J*=9.5, 6.5 Hz, 1H, 8-H), 4.24 (d, *J*=11.5 Hz, 1H, CH_2–Ph), 4.27 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.31 (d, *J*=11.5 Hz, 1H, CH_2–Ph), 4.40 (d, *J*=11.0 Hz, 1H, CH_2–Ph), 4.47 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.48 (d, *J*=11.5 Hz, 1H, CH_2–Ph), 4.64 (d, *J*=11.0 Hz, 1H, CH_2–Ph), 4.65 (s, 2H, CH_2–Ph), 4.73 (d, *J*=11.0 Hz, 1H, CH_2–Ph), 4.88 (d, *J*=11.5 Hz, 1H, CH_2–Ph), 4.90 (d, *J*=11.5 Hz, 1H, CH_2–Ph), 5.74 (d, *J*=4.5 Hz, 1H, 1-H), 7.11–7.29 (m, 30H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=33.6 (t, C-13), 39.8 (d, C-2), 67.9, 68.5 (2t, C-6, C-12), 72.8, 73.2, 73.5, 73.9, 74.6, 75.4 (6t, CH_2–Ph), 72.6, 73.4, 73.6, 75.1, 78.2, 79.5, 82.4 (7d, C-3, C-4, C-5, C-8, C-9, C-10, C-11), 101.0, 103.7 (2d, C-1, C-7), 127.4, 127.6, 127.7, 127.8, 127.9, 128.0, 128.2, 128.3, 128.4 (9d, arom, C–H), 137.9, 138.3, 138.4, 138.5, 138.7, 138.8 (6s, arom, *C*–CH_2O), 173.7 (s, COOR); IR (film): ν=3088, 2911, 1780, 1498, 1071 cm^{-1}; elemental analysis (%) calcd for $C_{56}H_{58}O_{11}$: C 74.15, H 6.45; found: C 74.42, H 6.50.

4.3. General procedure for the opening of lactone

A solution of *gluco*-**3** (1.0 mmol), $Sc(OTf)_3$ (738 mg, 1.5 mmol, 1.5 equiv), and Drierite® (20–40 mesh) (1.36 g, 10.0 mmol, 10.0 equiv) in absolute dry dichloromethane (20 mL) was stirred at 0 °C with argon protection. After 30 min the nucleophile **7** (5.0 equiv) was added to the solution. Then the solution was stirred at room temperature until TLC showed complete conversion of the starting material. The reaction was quenched with saturated $NaHCO_3$ solution and the mixture was extracted with dichloromethane (3×20 mL), the combined organic extracts were dried (Na_2SO_4) and concentrated. The crude product was purified by flash chromatography. Compounds **8g** and **8h** are separable by column.

*4.3.1. [3,4,6-Tri-O-benzyl-2-deoxy-2-C-(acetic acid)-β-D-glucopyranosyl] carbonitrile (**8a**).* A colorless syrup; $[\alpha]_D^{20}$ +34.1 (*c* 0.89, $CHCl_3$); R_f=0.38 (*c*-hexane/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.23 (dddd, *J*=10.4, 9.6, 4.8, 4.0 Hz, 1H, 2-H), 2.49 (dd, *J*=17.6, 4.8 Hz, 1H, 7′-H), 2.74 (dd, *J*=17.6, 4.0 Hz, 1H, 7-H), 3.40 (ddd, *J*=9.2, 6.0, 2.8 Hz, 1H, 5-H), 3.56 (dd, *J*=11.6, 6.0 Hz, 1H, 6′-H), 3.58 (dd, *J*=9.2, 3.0 Hz, 1H, 4-H), 3.59 (dd, *J*=11.6, 2.8 Hz, 1H, 6-H), 3.64 (dd, *J*=10.4, 3.0 Hz, 1H, 3-H), 4.39 (d, *J*=10.4 Hz, 1H, CH_2–Ph), 4.43 (d, *J*=9.6 Hz, 1H, 1-H), 4.46 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.51 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.55 (d, *J*=10.4 Hz, 1H, CH_2–Ph), 4.69 (d, *J*=10.4 Hz, 1H, CH_2–Ph), 4.82 (d, *J*=10.4 Hz, 1H, CH_2–Ph), 7.07–7.27 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=31.0 (t, C-7), 42.6 (d, C-2), 67.5 (d, C-1), 68.3 (t, C-6), 73.7, 74.9, 75.2 (3t, CH_2–Ph), 79.0, 80.3, 81.0 (3d, C-3, C-4, C-5), 116.1 (s, C≡N), 127.8, 127.9, 128.4, 128.5, 128.6 (5d, arom, C–H), 137.6, 137.7, 137.8 (3s, arom, *C*–CH_2O), 175.9 (s, COOH); IR (film): ν=3030, 2949, 2235, 1731, 1456, 1259 cm^{-1}; elemental analysis (%) calcd for $C_{30}H_{31}NO_6$: C 71.84, H 6.23, N 2.79; found: C 71.55, H 6.06, N 2.84.

*4.3.2. 3-[3,4,6-Tri-O-benzyl-2-deoxy-2-C-(formic acid)-β-D-glucopyranosyl]-1-propene (**8b**).* A colorless syrup; $[\alpha]_D^{20}$ +35.7 (*c* 0.94, $CHCl_3$); R_f=0.39 (*c*-hexane/ethyl acetate 1:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.04–2.08 (m, 1H, CH_2CH=CH_2), 2.06 (dd, *J*=16.0, 7.5 Hz, 1H, 7′-H), 2.32–2.39 (m, 1H, CH_2CH=CH_2), 2.44 (dddd, *J*=10.0, 7.5, 7.0, 4.5 Hz, 1H, 2-H), 2.57 (dd, *J*=16.0, 7.0 Hz, 1H, 7-H), 3.49 (dd, *J*=9.5, 3.5 Hz, 1H, 4-H), 3.56 (dd, *J*=14.0, 2.5 Hz, 1H, 6′-H), 3.61 (dd, *J*=14.0, 6.5 Hz, 1H, 6-H), 3.63 (ddd, *J*=9.5, 6.5, 2.5 Hz, 1H, 5-H), 3.69 (dd, *J*=10.0, 3.5 Hz, 1H, 3-H), 4.04 (dt, *J*=10.5, 4.5 Hz, 1H, 1-H), 4.42 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.44 (d, *J*=11.0 Hz, 1H, CH_2–Ph), 4.53 (d, *J*=11.5 Hz, 1H, CH_2–Ph), 4.57 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.63 (d, *J*=11.0 Hz, 1H, CH_2–Ph), 4.78 (d, *J*=11.5 Hz, 1H, CH_2–Ph), 5.00 (dt, *J*=16.0, 9.5 Hz, 2H, CH_2CH=CH_2), 5.71 (dddd, *J*=17.0, 10.0, 7.0, 3.5 Hz, 1H, CH_2CH=CH_2), 7.06–7.27 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=31.6 (t, CH_2=$CHCH_2$), 32.6 (t, C-7), 40.5 (d, C-2), 68.9 (t, C-6), 73.4, 74.2, 74.3 (3t, CH_2–Ph), 72.5, 73.0, 79.0 (3d, C-3, C-4, C-5), 79.9 (d, C-1), 116.9 (t, CH_2=$CHCH_2$), 127.6, 127.7, 127.8, 128.3, 128.4 (5d, arom, C–H), 134.3 (d, CH_2=$CHCH_2$), 138.0, 138.1, 138.2 (3s, arom, *C*–CH_2O), 177.8 (s, COOH); IR (film): ν=3031, 2968, 1737, 1453, 1267 cm^{-1}; elemental analysis (%) calcd for $C_{32}H_{36}O_6$: C 74.39, H 7.02; found: C 74.45, H 7.16.

*4.3.3. Methyl 2-[3,4,6-tri-O-benzyl-2-deoxy-2-C-(formic acid)-β-D-glucopyranosyl]-2-methylpropionate (**8c**).* A colorless syrup; $[\alpha]_D^{20}$ +21.8 (*c* 0.92, $CHCl_3$); R_f=0.36 (*c*-hexane/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.13, 1.20 (2s, 3H, each, CH_3), 2.04 (dddd, *J*=10.4, 8.4, 6.8, 3.0 Hz, 1H, 2-H), 2.12 (dd, *J*=17.2, 6.8 Hz, 1H, 7′-H), 2.46 (dd, *J*=17.2, 3.0 Hz, 1H, 7-H), 3.39 (ddd, *J*=9.6, 4.2, 2.0 Hz, 1H, 5-H), 3.50 (d, *J*=8.4 Hz, 1H, 1-H), 3.55 (s, 3H, COO*Me*), 3.59 (dd, *J*=14.4, 2.0 Hz, 1H, 6′-H), 3.66 (dd, *J*=14.4, 4.2 Hz, 1H, 6-H), 3.72 (dd, *J*=9.6, 3.0 Hz, 1H, 4-H), 3.75 (dd, *J*=10.4, 3.0 Hz, 1H, 3-H), 4.47 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.51 (d, *J*=11.2 Hz, 1H, CH_2–Ph), 4.53 (d, *J*=11.2 Hz, 1H, CH_2–Ph), 4.55 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.66 (d, *J*=11.2 Hz, 1H, CH_2–Ph), 4.85 (d, *J*=11.2 Hz, 1H, CH_2–Ph), 7.11–7.26 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=18.9, 24.2 (2q, CH_3), 31.4 (t, C-7), 41.0 (d, C-2), 46.1 (s, $(CH_3)_2C$COOMe), 52.0 (q, COO*Me*), 69.3 (t, C-6), 73.3, 74.5, 74.7 (3t, CH_2–Ph), 79.3, 80.2, 80.7 (3d, C-3, C-4, C-5), 83.3 (d, C-1), 127.4, 127.7, 127.8, 128.3, 128.4 (5d, arom, C–H), 138.2, 138.3, 138.5 (3s, arom, *C*–CH_2O), 177.2, 177.4 (2s, COOH, COOMe); IR (film): ν=3031, 2952, 1787, 1453, 1266 cm^{-1};

elemental analysis (%) calcd for $C_{34}H_{40}O_8$: C 70.81, H 6.99; found: C 70.93, H 7.06.

*4.3.4. 2-[3,4,6-Tri-O-benzyl-2-deoxy-2-C-(formic acid)-β-D-glucopyranosyl]-1,5-dimethoxybenzene (**8d**).* A colorless syrup; $[\alpha]_D^{20}$ +47.8 (*c* 0.88, $CHCl_3$); R_f=0.37 (*c*-hexane/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.49 (dddd, *J*=10.2, 8.4, 5.7, 3.0 Hz, 1H, 2-H), 2.54 (dd, *J*=17.4, 3.0 Hz, 1H, 7′-H), 2.86 (dd, *J*=17.4, 5.7 Hz, 1H, 7-H), 3.19 (ddd, *J*=9.9, 5.1, 3.6 Hz, 1H, 5-H), 3.58 (dd, *J*=14.1, 3.6 Hz, 1H, 6′-H), 3.59 (dd, *J*=9.9, 3.0 Hz, 1H, 4-H), 3.65 (s, 3H, OMe), 3.67 (dd, *J*=14.1, 5.1 Hz, 1H, 6-H), 3.71 (dd, *J*=10.2, 3.0 Hz, 1H, 3-H), 3.73 (s, 3H, OMe), 4.31 (d, *J*=11.1 Hz, 1H, *CH*$_2$—Ph), 4.33 (d, *J*=12.0 Hz, 1H, *CH*$_2$—Ph), 4.43 (d, *J*=11.1 Hz, 1H, *CH*$_2$—Ph), 4.57 (d, *J*=12.0 Hz, 1H, *CH*$_2$—Ph), 4.58 (d, *J*=11.1 Hz, 1H, *CH*$_2$—Ph), 4.74 (d, *J*=11.1 Hz, 1H, *CH*$_2$—Ph), 4.40 (d, *J*=8.4 Hz, 1H, 1-H), 7.11–7.30 (m, 18H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=30.9 (t, C-7), 43.0 (d, C-2), 55.3, 55.8 (2q, OMe), 69.5, 69.7 (3d, arom, C—H), 71.2 (t, C-6), 73.2, 73.8, 74.2 (3t, CH_2—Ph), 76.0, 77.9, 78.5 (3d, C-3, C-4, C-5), 92.3 (d, C-1), 106.8 (s, *C*(MeOCCH)), 127.6, 127.7, 127.8, 128.0, 128.2, 128.3, 128.5 (7d, arom, C—H), 137.3, 137.5, 138.1 (3s, arom, *C*—CH_2O), 159.6, 160.9 (2s, arom, *C*—OMe), 176.8 (s, COOH); IR (film): ν=3030, 2868, 1789, 1737, 1453, 1268, 1204 cm^{-1}; elemental analysis (%) calcd for $C_{37}H_{40}O_8$: C 72.53, H 6.58; found: C 72.40, H 6.76.

*4.3.5. 2-[3,4,6-Tri-O-benzyl-2-deoxy-2-C-(formic acid)-β-D-glucopyranosyl]-1,3,5-dimethoxybenzene (**8e**).* A colorless syrup; $[\alpha]_D^{20}$ +41.6 (*c* 0.97, $CHCl_3$); R_f=0.37 (*c*-hexane/ethyl acetate 1:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.51 (dddd, *J*=10.8, 8.1, 6.3, 2.7 Hz, 1H, 2-H), 2.57 (dd, *J*=17.4, 2.7 Hz, 1H, 7′-H), 2.85 (dd, *J*=17.4, 6.3 Hz, 1H, 7-H), 3.26 (ddd, *J*=9.6, 5.1, 4.2 Hz, 1H, 5-H), 3.58 (dd, *J*=14.7, 4.2 Hz, 1H, 6′-H), 3.59 (dd, *J*=9.6, 3.3 Hz, 1H, 4-H), 3.65 (s, 3H, OMe), 3.66 (s, 3H, OMe), 3.67 (dd, *J*=14.7, 5.1 Hz, 1H, 6-H), 3.71 (dd, *J*=10.8, 3.3 Hz, 1H, 3-H), 3.73 (s, 3H, OMe), 4.33 (d, *J*=1.2 Hz, 2H, *CH*$_2$—Ph), 4.43 (d, *J*=11.1 Hz, 1H, *CH*$_2$—Ph), 4.57 (d, *J*=11.1 Hz, 1H, *CH*$_2$—Ph), 4.58 (d, *J*=11.1 Hz, 1H, *CH*$_2$—Ph), 4.74 (d, *J*=11.1 Hz, 1H, *CH*$_2$—Ph), 4.43 (d, *J*=8.1 Hz, 1H, 1-H), 7.11–7.30 (m, 17H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=31.0 (t, C-7), 42.0 (d, C-2), 55.3, 55.5, 55.8 (3q, OMe), 69.6 (2d, C(MeOC*C*H)$_2$), 71.1 (t, C-6), 73.4, 74.1, 74.6 (3t, *C*H$_2$—Ph), 75.9, 78.4, 78.8 (3d, C-3, C-4, C-5), 91.1 (d, C-1), 106.8 (s, *C*(MeOCCH)$_2$), 127.7, 127.8, 127.9, 128.0, 128.1, 128.4, 128.5 (7d, arom, C—H), 137.6, 137.8, 138.0 (3s, arom, *C*—CH_2O), 159.6, 159.8, 161.9 (3s, arom, *C*—OMe), 177.7 (s, *C*OOH); IR (film): ν=3031, 2952, 1737, 1729, 1453, 1271 cm^{-1}; elemental analysis (%) calcd for $C_{38}H_{42}O_9$: C 71.01, H 6.59; found: C 71.41, H 6.78.

*4.3.6. Methyl 3,4,6-tri-O-benzyl-2-deoxy-2-C-[(methoxy-carbonyl)-methyl]-β-D-glucopyranoside (β-**8f**).* A colorless syrup; $[\alpha]_D^{20}$ +14.2 (*c* 0.97, $CHCl_3$); R_f=0.42 (*c*-hexane/ethyl acetate 4:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.09 (dddd, *J*=10.8, 8.7, 5.7, 5.4 Hz, 1H, 2-H), 2.39 (dd, *J*=15.3, 5.7 Hz, 1H, 7-H), 2.47 (dd, *J*=15.3, 5.4 Hz, 1H, 7′-H), 3.41 (s, 3H, OMe), 3.43 (ddd, *J*=9.9, 5.4, 3.9 Hz, 1H, 5-H), 3.45 (dd, *J*=10.8, 9.0 Hz, 1H, 3-H), 3.49 (s, 3H, COO*Me*), 3.56 (dd, *J*=9.9, 9.0 Hz, 1H, 4-H), 3.67–3.70 (m, 2H, 6-H, 6′-H), 4.22 (d, *J*=8.7 Hz, 1H, 1-H), 4.50 (d, *J*=12.0 Hz, 1H, *CH*$_2$—Ph), 4.51 (d, *J*=11.7 Hz, 1H, *CH*$_2$—Ph), 4.54 (d, *J*=11.7 Hz, 1H, *CH*$_2$—Ph), 4.59 (d, *J*=12.0 Hz, 1H, *CH*$_2$—Ph), 4.71 (d, *J*=11.1 Hz, 1H, *CH*$_2$—Ph), 4.84 (d, *J*=11.1 Hz, 1H, *CH*$_2$—Ph), 7.09–7.30 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=31.9 (t, C-7), 44.8 (d, C-2), 51.4 (q, COO*Me*), 56.9 (q, OMe), 69.0 (t, C-6), 73.5, 74.7, 74.8 (3t, *C*H$_2$—Ph), 75.2, 79.9, 82.1 (3d, C-3, C-4, C-5), 103.4 (d, C-1), 127.6, 127.7, 127.8, 128.3, 128.4 (5d, arom, C—H), 138.0, 138.2, 138.3 (3s, arom, *C*—CH_2O), 172.6 (s, *C*OOMe); IR (film): ν=3030, 2949, 1736, 1452, 1260 cm^{-1}; elemental analysis (%) calcd for $C_{31}H_{36}O_7$: C 71.52, H 6.97; found: C 71.45, H 7.16.

*4.3.7. Methyl 3,4,6-tri-O-benzyl-2-deoxy-2-C-[(methoxy-carbonyl)-methyl]-α-D-glucopyranoside (α-**8f**).* A colorless syrup; R_f=0.42 (*c*-hexane/ethyl acetate 4:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.27 (dd, *J*=15.9, 9.0 Hz, 1H, 7-H), 2.61 (dd, *J*=15.9, 5.1 Hz, 1H, 7′-H), 2.80 (dddd, *J*=10.8, 9.0, 5.1, 3.3 Hz, 1H, 2-H), 3.23 (s, 3H, OMe), 3.51 (s, 3H, COO*Me*), 3.54 (ddd, *J*=9.9, 6.0, 3.6 Hz, 1H, 5-H), 3.55 (dd, *J*=10.8, 9.0 Hz, 1H, 3-H), 3.58 (dd, *J*=9.9, 9.0 Hz, 1H, 4-H), 3.82 (dd, *J*=13.2, 3.6 Hz, 1H, 6-H), 3.85 (dd, *J*=13.2, 6.0 Hz, 1H, 6′-H), 4.37 (d, *J*=11.7 Hz, 1H, *CH*$_2$—Ph), 4.41 (d, *J*=11.7 Hz, 1H, *CH*$_2$—Ph), 4.45 (d, *J*=11.4 Hz, 1H, *CH*$_2$—Ph), 4.48 (d, *J*=11.4 Hz, 1H, *CH*$_2$—Ph), 4.63 (d, *J*=11.4 Hz, 1H, *CH*$_2$—Ph), 4.74 (d, *J*=3.3 Hz, 1H, 1-H), 4.81 (d, *J*=11.4 Hz, 1H, *CH*$_2$—Ph), 7.16–7.30 (m, 20H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=32.3 (t, C-7), 37.6 (d, C-2), 51.3 (q, COO*Me*), 55.2 (q, OMe), 69.6 (t, C-6), 71.5, 73.5, 74.4 (3t, *C*H$_2$—Ph), 69.6, 71.9, 78.3 (3d, C-3, C-4, C-5), 100.3 (d, C-1), 127.5, 127.7, 127.8, 128.0, 128.2, 128.4 (6d, arom, C—H), 138.0, 138.1, 138.2 (3s, arom, *C*—CH_2O), 173.1 (s, *C*OOMe).

*4.3.8. Ethyl 3,4,6-tri-O-benzyl-2-deoxy-2-C-[(ethoxycarbonyl)-methyl]-β-D-glucopyranoside (β-**8g**).* A colorless syrup; $[\alpha]_D^{20}$ +18.8 (*c* 0.91, $CHCl_3$); R_f=0.43 (*c*-hexane/ethyl acetate 4:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.10 (t, *J*=3.0 Hz, $COOCH_2CH_3$), 1.13 (t, *J*=3.9 Hz, OCH_2CH_3), 2.09 (dddd, *J*=10.5, 8.7, 6.3, 4.8 Hz, 1H, 2-H), 2.34 (dd, *J*=15.3, 6.3 Hz, 1H, 7′-H), 2.50 (dd, *J*=15.3, 4.8 Hz, 1H, 7-H), 3.36–3.48 (m, 4H, $COOCH_2CH_3$, OCH_2CH_3), 3.51 (dd, *J*=14.1, 5.4 Hz, 1H, 6′-H), 3.59 (ddd, *J*=9.3, 7.2, 5.4 Hz, 1H, 5-H), 3.65 (dd, *J*=10.5, 6.9 Hz, 1H, 3-H), 3.85 (dd, *J*=9.3, 6.9 Hz, 1H, 4-H), 3.95 (dd, *J*=14.1, 7.2 Hz, 1H, 6-H), 4.31 (d, *J*=8.7 Hz, 1H, 1-H), 4.48 (d, *J*=12.0 Hz, 1H, *CH*$_2$—Ph), 4.50 (d, *J*=10.8 Hz, 1H, *CH*$_2$—Ph), 4.54 (d, *J*=11.1 Hz, 1H, *CH*$_2$—Ph), 4.56 (d, *J*=12.0 Hz, 1H, *CH*$_2$—Ph), 4.70 (d, *J*=10.8 Hz, 1H, *CH*$_2$—Ph), 4.82 (d, *J*=11.1 Hz, 1H, *CH*$_2$—Ph), 7.08–7.28 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.1, 14.9 (2q, $COOCH_2CH_3$, OCH_2CH_3), 32.0 (t, C-7), 44.8 (d, C-2), 60.2, 65.1 (2t, $COOCH_2CH_3$, OCH_2CH_3), 69.1 (t, C-6), 73.5, 74.6, 74.8 (3t, *C*H$_2$—Ph), 75.1, 79.9, 82.0 (3d, C-3, C-4, C-5), 102.3 (d, C-1), 127.5, 127.6, 127.7, 127.8, 128.3, 128.4 (6d, arom, C—H), 138.1, 138.2, 138.3 (3s, arom, *C*—CH_2O), 172.2 (s, *C*$OOCH_2CH_3$); IR (film): ν=3031, 2952, 1738, 1731, 1497, 1435, 1268 cm^{-1}; elemental analysis (%) calcd for $C_{33}H_{40}O_7$: C 72.24, H 7.35; found: C 72.65, H 7.11.

*4.3.9. Ethyl 3,4,6-tri-O-benzyl-2-deoxy-2-C-[(ethoxycarbonyl)-methyl]-α-D-glucopyranoside (α-**8g**).* A colorless syrup; $[\alpha]_D^{20}$ +24.2 (*c* 0.96, $CHCl_3$); R_f=0.43 (*c*-hexane/ethyl acetate 4:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.07 (t, *J*=7.2 Hz, $COOCH_2CH_3$), 1.13 (t, *J*=7.2 Hz, OCH_2CH_3), 2.31 (dddd, *J*=10.2, 9.0, 5.1, 3.0 Hz, 1H, 2-H), 2.32 (dd, *J*=19.8, 5.1 Hz, 1H, 7′-H), 2.54 (dd, *J*=19.8, 9.0 Hz, 1H, 7-H), 3.34 (ddd, *J*=9.6, 7.2, 3.3 Hz, 1H, 5-H), 3.56–3.67 (m, 4H, $COOCH_2CH_3$, OCH_2CH_3), 3.63 (dd, *J*=9.6, 6.6 Hz, 1H, 4-H), 3.69 (dd, *J*=10.2, 6.6 Hz, 1H, 3-H), 3.93 (dd, *J*=14.4, 3.3 Hz, 1H, 6′-H), 3.99 (dd, *J*=14.4, 7.2 Hz, 1H, 6-H), 4.44 (d, *J*=11.1 Hz, 1H, *CH*$_2$—Ph), 4.45 (d, *J*=12.0 Hz, 1H, *CH*$_2$—Ph), 4.55 (d, *J*=11.1 Hz, 1H, *CH*$_2$—Ph), 4.59 (d, *J*=11.7 Hz, 1H, *CH*$_2$—Ph), 4.70 (d, *J*=11.1 Hz, 1H, *CH*$_2$—Ph), 4.83 (d, *J*=3.0 Hz, 1H, 1-H), 4.84 (d, *J*=11.1 Hz, 1H, *CH*$_2$—Ph), 7.04–7.30 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.1, 14.9 (2q, $COOCH_2CH_3$, OCH_2CH_3), 32.7 (t, C-7), 42.9 (d, C-2), 60.2, 63.5 (2t, $COOCH_2CH_3$, OCH_2CH_3), 68.8 (t, C-6), 73.5, 74.7, 75.0 (3t, *C*H$_2$—Ph), 71.0, 79.8, 80.7 (3d, C-3, C-4, C-5), 98.4 (d, C-1), 127.5, 127.6, 127.7, 127.8, 128.3, 128.4 (6d, arom, C—H), 138.1, 138.2, 138.5 (3s, arom, *C*—CH_2O), 172.4 (s, *C*$OOCH_2CH_3$); IR (film): ν=3030, 2948, 1739, 1728, 1473, 1435, 1260 cm^{-1}; elemental analysis (%) calcd for $C_{33}H_{40}O_7$: C 72.24, H 7.35; found: C 72.25, H 7.30.

*4.3.10. iso-Propyl 3,4,6-tri-O-benzyl-2-deoxy-2-C-[(iso-propoxy-carbonyl)-methyl]-β-D-glucopyranoside (β-**8h**).* A colorless syrup; $[\alpha]_D^{20}$ +22.5 (*c* 1.05, $CHCl_3$); R_f=0.44 (*c*-hexane/ethyl acetate 4:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.08 (t, *J*=6.0 Hz, $COOCH(CH_3)_2$), 1.13 (t, *J*=6.3 Hz, $OCH(CH_3)_2$), 2.02 (dddd, *J*=10.5, 8.7, 5.4, 4.5 Hz, 1H, 2-H), 2.38 (dd, *J*=15.6, 5.4 Hz, 1H, 7′-H), 2.48 (dd, *J*=15.6, 4.5 Hz, 1H, 7-H), 3.39 (ddd, *J*=9.0, 6.0, 2.7 Hz, 1H, 5-H), 3.47–3.60 (m, 2H, $COOCH(CH_3)_2$, $OCH(CH_3)_2$), 3.52 (dd, *J*=10.5, 4.8 Hz, 1H, 3-H), 3.63 (dd,

J=9.0, 4.8 Hz, 1H, 4-H), 3.67 (dd, J=12.3, 2.7 Hz, 1H, 6′-H), 3.87 (dd, J=12.3, 6.0 Hz, 1H, 6-H), 4.46 (d, J=8.7 Hz, 1H, 1-H), 4.49 (d, J=12.0 Hz, 1H, CH_2—Ph), 4.51 (d, J=11.1 Hz, 1H, CH_2—Ph), 4.53 (d, J=12.0 Hz, 1H, CH_2—Ph), 4.56 (d, J=11.1 Hz, 1H, CH_2—Ph), 4.71 (d, J=10.8 Hz, 1H, CH_2—Ph), 4.82 (d, J=10.8 Hz, 1H, CH_2—Ph), 7.10–7.29 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.7, 21.8, 21.9, 23.5 (4q, $COOCH(CH_3)_2$, $OCH(CH_3)_2$), 31.7 (t, C-7), 44.8 (d, C-2), 69.1 (t, C-6), 67.6, 71.5 (2d, $COOCH(CH_3)_2$, $OCH(CH_3)_2$), 73.4, 74.6, 74.7 (3t, CH_2—Ph), 75.1, 80.1, 81.8 (3d, C-3, C-4, C-5), 100.8 (d, C-1), 127.5, 127.6, 127.7, 127.8, 128.3, 128.4 (6d, arom, C—H), 138.1, 138.3, 138.4 (3s, arom, C—CH_2O), 171.7 (s, $COOCH(CH_3)_2$); IR (film): ν=3031, 2952, 1792, 1729, 1453, 1437, 1272 cm^{-1}; elemental analysis (%) calcd for $C_{35}H_{44}O_7$: C 72.89, H 7.69; found: C 73.03, H 7.42.

*4.3.11. iso-Propyl 3,4,6-tri-O-benzyl-2-deoxy-2-C-[(iso-propoxycarbonyl)-methyl]-α-D-glucopyranoside (α-**8h**).* A colorless syrup; $[\alpha]_D^{20}$ +31.7 (c 1.02, $CHCl_3$); R_f=0.44 (c-hexane/ethyl acetate 4:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.00 (t, J=6.0 Hz, $COOCH(CH_3)_2$), 1.11 (t, J=6.3 Hz, $OCH(CH_3)_2$), 2.25 (dd, J=16.2, 6.9 Hz, 1H, 7′-H), 2.31 (dddd, J=10.5, 8.4, 6.9, 2.7 Hz, 1H, 2-H), 2.56 (dd, J=16.2, 8.4 Hz, 1H, 7-H), 3.55 (ddd, J=9.0, 6.0, 3.6 Hz, 1H, 5-H), 3.59–3.65 (m, 2H, $COOCH(CH_3)_2$, $OCH(CH_3)_2$), 3.66 (dd, J=12.0, 3.6 Hz, 1H, 6′-H), 3.73 (dd, J=10.5, 3.6 Hz, 1H, 3-H), 3.76 (dd, J=9.0, 3.6 Hz, 1H, 4-H), 3.78 (dd, J=12.0, 6.0 Hz, 1H, 6-H), 4.44 (d, J=11.7 Hz, 1H, CH_2—Ph), 4.53 (d, J=11.7 Hz, 1H, CH_2—Ph), 4.59 (d, J=12.3 Hz, 1H, CH_2—Ph), 4.69 (d, J=10.8 Hz, 1H, CH_2—Ph), 4.84 (d, J=10.8 Hz, 1H, CH_2—Ph), 4.88 (d, J=12.3 Hz, 1H, CH_2—Ph), 4.96 (d, J=2.7 Hz, 1H, 1-H), 7.4–7.30 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=21.4, 21.7, 21.8, 23.3 (4q, $COOCH(CH_3)_2$, $OCH(CH_3)_2$), 32.9 (t, C-7), 42.8 (d, C-2), 68.9 (t, C-6), 67.6, 69.4 (2d, $COOCH(CH_3)_2$, $OCH(CH_3)_2$), 73.5, 74.8, 75.0 (3t, CH_2—Ph), 70.9, 79.8, 80.7 (3d, C-3, C-4, C-5), 96.8 (d, C-1), 127.4, 127.5, 127.6, 127.8, 128.3, 128.4 (6d, arom, C—H), 138.1, 138.2, 138.6 (3s, arom, C—CH_2O), 171.9 (s, $COOCH(CH_3)_2$); IR (film): ν=3030, 2948, 1800, 1729, 1453, 1437, 1272 cm^{-1}; elemental analysis (%) calcd for $C_{35}H_{44}O_7$: C 72.89, H 7.69; found: C 72.67, H 7.55.

*4.3.12. tert-Butyl 3,4,6-tri-O-benzyl-2-deoxy-2-C-[(tert-butoxycarbonyl)-methyl]-α-D-glucopyranoside (**8i**).* A colorless syrup; $[\alpha]_D^{20}$ +20.6 (c 0.90, $CHCl_3$); R_f=0.44 (c-hexane/ethyl acetate 4:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.14, 1.33 (s, 9H, each, $OC(CH_3)_3$), 2.12 (dd, J=15.6, 5.1 Hz, 1H, 7′-H), 2.24 (dddd, J=10.5, 5.1, 3.3, 3.0 Hz, 1H, 2-H), 2.52 (dd, J=15.6, 3.0 Hz, 1H, 7-H), 3.50–3.60 (m, 2H, 6-H, 6′-H), 3.63 (dd, J=9.6, 3.9 Hz, 1H, 4-H), 3.74 (dd, J=10.5, 3.9 Hz, 1H, 3-H), 3.90 (ddd, J=9.6, 3.3, 1.8 Hz, 1H, 5-H), 4.43 (d, J=12.0 Hz, 1H, CH_2—Ph), 4.45 (d, J=10.8 Hz, 1H, CH_2—Ph), 4.53 (d, J=11.1 Hz, 1H, CH_2—Ph), 4.61 (d, J=12.0 Hz, 1H, CH_2—Ph), 4.70 (d, J=10.8 Hz, 1H, CH_2—Ph), 4.84 (d, J=11.1 Hz, 1H, CH_2—Ph), 5.18 (d, J=3.3 Hz, 1H, 1-H), 7.04–7.30 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=28.1, 28.6 (6q, CH_3), 33.7 (t, C-7), 43.4 (d, C-2), 69.0 (t, C-6), 74.6 (s, $OC(CH_3)_3$), 73.5, 74.8, 75.1 (3t, CH_2—Ph), 80.2 (s, $COOC(CH_3)_3$), 70.5, 80.0, 80.6 (3d, C-3, C-4, C-5), 93.0 (d, C-1), 127.5, 127.6, 127.8, 127.9, 128.3, 128.4 (6d, arom, C—H), 138.2, 138.3, 138.6 (3s, arom, C—CH_2O), 171.8 (s, $COOC(CH_3)_3$); IR (film): ν=3027, 2922, 1631, 1496, 1452, 1361, 1257 cm^{-1}; elemental analysis (%) calcd for $C_{37}H_{48}O_7$: C 73.48, H 8.00; found: C 73.84, H 7.87.

*4.3.13. Allyl 3,4,6-tri-O-benzyl-2-deoxy-2-C-[(allyloxycarbonyl)-methyl]-α-D-glucopyranoside (**8j**).* A colorless syrup; $[\alpha]_D^{20}$ +9.5 (c 0.93, $CHCl_3$); R_f=0.43 (c-hexane/ethyl acetate 4:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.33 (dddd, J=11.5, 8.0, 6.5, 2.5 Hz, 1H, 2-H), 2.35 (dd, J=19.0, 6.5 Hz, 1H, 7′-H), 2.58 (dd, J=19.0, 8.0 Hz, 1H, 7-H), 3.59–3.66 (m, 4H, $COOCH_2CH{=}CH_2$, $OCH_2CH{=}CH_2$), 3.72 (dd, J=10.5, 5.5 Hz, 1H, 4-H), 3.84 (ddd, J=10.5, 5.5, 2.0 Hz, 1H, 5-H), 4.07 (dd, J=13.0, 2.0 Hz, 1H, 6′-H), 4.35 (dd, J=13.0, 5.5 Hz, 1H, 6-H), 4.42 (dd, J=11.5, 5.5 Hz, 1H, 3-H), 4.45 (d, J=11.5 Hz, 1H, CH_2—Ph), 4.46 (d, J=11.5 Hz, 1H, CH_2—Ph), 4.55 (d, J=11.5 Hz, 1H, CH_2—Ph), 4.59 (d, J=11.5 Hz, 1H, CH_2—Ph), 4.70 (d, J=11.5 Hz, 1H, CH_2—Ph), 4.85 (d, J=11.0 Hz, 1H, CH_2—Ph), 4.89 (d, J=2.5 Hz, 1H, 1-H), 5.08 (dd, J=10.5, 1.0 Hz, 1H, $OCH_2CH{=}CH_2'$), 5.12 (dd, J=10.5, 1.0 Hz, 1H, $OCH_2CH{=}CH_2$), 5.16 (dd, J=3.5, 1.5 Hz, 1H, $COOCH_2CH{=}CH_2'$), 5.19 (dd, J=3.5, 1.5 Hz, 1H, $COOCH_2CH{=}CH_2$), 5.73–5.82 (m, 2H, $COOCH_2CH{=}CH_2$, $OCH_2CH{=}CH_2$), 7.05–7.29 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=32.5 (t, C-7), 42.8 (d, C-2), 65.0, 68.0 (2t, $COOCH_2CH{=}CH_2$, $OCH_2CH{=}CH_2$), 68.7 (t, C-6), 73.4, 74.7, 75.0 (3t, CH_2—Ph), 71.1, 79.7, 80.5 (3d, C-3, C-4, C-5), 97.9 (d, C-1), 117.0, 118.1 (2t, $COOCH_2CH{=}CH_2$, $OCH_2CH{=}CH_2$), 127.5, 127.6, 127.7, 127.8, 128.3 (5d, arom, C—H), 132.2, 134.0 (2d, $COOCH_2CH{=}CH_2$, $OCH_2CH{=}CH_2$), 138.0, 138.1, 138.4 (3s, arom, C—CH_2O), 171.9 (s, $COOCH_2CH{=}CH_2$); IR (film): ν=3031, 2959, 1732, 1678, 1455, 1268 cm^{-1}; elemental analysis (%) calcd for $C_{35}H_{40}O_7$: C 73.40, H 7.04; found: C 73.48, H 6.99.

*4.3.14. cyclo-Hexyl 3,4,6-tri-O-benzyl-2-deoxy-2-C-[(cyclo-hexyloxycarbonyl)-methyl]-α-D-glucopyranoside (**8k**).* A colorless syrup; $[\alpha]_D^{20}$ −15.8 (c 0.90, $CHCl_3$); R_f=0.40 (c-hexane/ethyl acetate 6:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.16–1.74 (m, 20H, COO*c-hex*, O*c-hex*), 2.29 (dd, J=17.7, 8.7 Hz, 1H, 7′-H), 2.47 (dddd, J=10.5, 9.3, 8.7, 2.4 Hz, 1H, 2-H), 2.58 (dd, J=17.7, 9.3 Hz, 1H, 7-H), 2.77 (dt, J=8.4, 2.1 Hz, 1H, O*CH*), 3.47 (ddd, J=8.7, 4.5, 3.3 Hz, 1H, 5-H), 3.54–3.66 (m, 2H, 6-H, 6′-H), 3.60 (dd, J=8.7, 3.6 Hz, 1H, 4-H), 3.73 (dd, J=10.5, 3.6 Hz, 1H, 3-H), 3.83 (dt, J=9.3, 1.5 Hz, 1H, COO*CH*), 4.44 (d, J=12.0 Hz, 1H, CH_2—Ph), 4.49 (d, J=10.8 Hz, 1H, CH_2—Ph), 4.54 (d, J=11.1 Hz, 1H, CH_2—Ph), 4.60 (d, J=12.0 Hz, 1H, CH_2—Ph), 4.70 (d, J=10.8 Hz, 1H, CH_2—Ph), 4.85 (d, J=11.1 Hz, 1H, CH_2—Ph), 5.01 (d, J=2.4 Hz, 1H, 1-H), 7.04–7.33 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=23.7, 23.9, 25.4, 25.7, 26.9, 31.2, 31.7, 33.1 (10t, COO*c-hex*, O*c-hex*), 33.4 (t, C-7), 43.0 (d, C-2), 69.0 (t, C-6), 71.0, 72.7 (2d, COO*C*H, O*C*H), 73.5, 74.8, 75.1 (3t, CH_2—Ph), 74.8, 79.9, 80.8 (3d, C-3, C-4, C-5), 96.7 (d, C-1), 127.5, 127.6, 127.8, 127.9, 128.3, 128.4 (15d, arom, C—H), 138.1, 138.2, 138.6 (3s, arom, C—CH_2O), 171.9 (s, *C*OO*c*-hex); IR (film): ν=3031, 2948, 1737, 1453, 1437, 1260 cm^{-1}; ESI-HRMS ($C_{41}H_{52}O_7$): calcd for [M+Na] 679.3611; found 679.3636.

*4.3.15. Octyl 3,4,6-tri-O-benzyl-2-deoxy-2-C-[(octyloxycarbonyl)-methyl]-α-D-glucopyranoside (**8l**).* A colorless syrup; $[\alpha]_D^{20}$ +54.2 (c 0.98, $CHCl_3$); R_f=0.37 (c-hexane/ethyl acetate 6:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ=0.79 (t, J=6.5 Hz, $COOCH_2(CH_2)_6CH_3$), 0.82 (t, J=7.0 Hz, $OCH_2(CH_2)_6CH_3$), 1.12–1.28 (m, 24H, $COOCH_2(CH_2)_6CH_3$, $OCH_2(CH_2)_6CH_3$), 1.42–1.56 (m, 4H, $COOCH_2(CH_2)_6CH_3$, $OCH_2(CH_2)_6CH_3$), 2.29 (dd, J=16.0, 9.0 Hz, 1H, 7′-H), 2.60 (dd, J=16.0, 5.5 Hz, 1H, 7-H), 2.79 (dddd, J=11.0, 9.0, 5.5, 3.5 Hz, 1H, 2-H), 3.23 (ddd, J=9.0, 6.5, 3.5 Hz, 1H, 5-H), 3.49 (dd, J=12.5, 3.5 Hz, 1H, 6′-H), 3.56 (dd, J=9.0, 3.5 Hz, 1H, 4-H), 3.86 (dd, J=12.5, 6.5 Hz, 1H, 6-H), 3.92 (dd, J=11.0, 3.5 Hz, 1H, 3-H), 4.36 (d, J=12.0 Hz, 1H, CH_2—Ph), 4.38 (d, J=11.5 Hz, 1H, CH_2—Ph), 4.44 (d, J=12.0 Hz, 1H, CH_2—Ph), 4.48 (d, J=11.5 Hz, 1H, CH_2—Ph), 4.63 (d, J=11.5 Hz, 1H, CH_2—Ph), 4.81 (d, J=11.5 Hz, 1H, CH_2—Ph), 4.85 (d, J=3.5 Hz, 1H, 1-H), 7.15–7.28 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.0, 14.1 (2q, CH_3), 22.6, 22.7, 25.9, 26.2, 26.9, 28.6, 29.1, 29.2, 29.3, 29.4, 29.5, 31.8, 31.9 (12t, $COOCH_2(CH_2)_6CH_3$, $OCH_2(CH_2)_6CH_3$), 32.8 (t, C-7), 37.6 (d, C-2), 64.4, 67.9 (2t, $COOCH_2(CH_2)_6CH_3$, $OCH_2(CH_2)_6CH_3$), 69.5 (t, C-6), 71.5, 73.5, 74.3 (3t, CH_2—Ph), 69.6, 71.9, 78.6 (3d, C-3, C-4, C-5), 99.0 (d, C-1), 127.4, 127.6, 127.8, 128.0, 128.2, 128.4 (6d, arom, C—H), 138.1, 138.3, 138.9 (3s, arom, C—CH_2O), 171.9 (s, $COOCH_2(CH_2)_6CH_3$); IR (film): ν=3031, 2952, 1737, 1729, 1453, 1437, 1272, 1206 cm^{-1}; elemental analysis (%) calcd for $C_{45}H_{64}O_7$: C 75.38, H 9.00; found: C 75.35, H 9.09.

*4.3.16. Dodecyl 3,4,6-tri-O-benzyl-2-deoxy-2-C-[(dodecyloxycarbonyl)-methyl]-α-D-glucopyranoside (**8m**).* A colorless syrup; $[\alpha]_D^{20}$ +50.1 (c 0.88, $CHCl_3$); R_f=0.39 (c-hexane/ethyl acetate 6:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.80 (t, J=6.9 Hz, $COOCH_2(CH_2)_{10}CH_3$), 0.81 (t, J=6.0 Hz, $OCH_2(CH_2)_{10}CH_3$), 1.12–1.28 (m, 40H, $COOCH_2(CH_2)_{10}CH_3$,

$OCH_2(CH_2)_{10}CH_3$), 1.42–1.56 (m, 4H, $COOCH_2(CH_2)_{10}CH_3$, $OCH_2(CH_2)_{10}CH_3$), 2.29 (dd, *J*=16.0, 9.0 Hz, 1H, 7′-H), 2.60 (dd, *J*=16.0, 5.5 Hz, 1H, 7-H), 2.79 (dddd, *J*=11.0, 9.0, 5.5, 3.5 Hz, 1H, 2-H), 3.23 (ddd, *J*=9.0, 6.5, 3.5 Hz, 1H, 5-H), 3.49 (dd, *J*=12.5, 3.5 Hz, 1H, 6′-H), 3.56 (dd, *J*=9.0, 3.5 Hz, 1H, 4-H), 3.86 (dd, *J*=12.5, 6.5 Hz, 1H, 6-H), 3.92 (dd, *J*=11.0, 3.5 Hz, 1H, 3-H), 4.33 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.39 (d, *J*=11.5 Hz, 1H, CH_2–Ph), 4.45 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.47 (d, *J*=11.5 Hz, 1H, CH_2–Ph), 4.66 (d, *J*=11.5 Hz, 1H, CH_2–Ph), 4.80 (d, *J*=11.5 Hz, 1H, CH_2–Ph), 4.84 (d, *J*=4.0 Hz, 1H, 1-H), 7.04–7.30 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.2, 14.3 (2q, CH_3), 22.5, 22.8, 25.7, 26.2, 26.9, 28.6, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (12t, $COOCH_2(CH_2)_{10}CH_3$, $OCH_2(CH_2)_{10}CH_3$), 32.7 (t, C-7), 43.0 (d, C-2), 64.6, 67.8 (2t, $COOCH_2(CH_2)_{10}CH_3$, $OCH_2(CH_2)_{10}CH_3$), 68.9 (t, C-6), 73.5, 74.8, 75.0 (3t, CH_2–Ph), 71.0, 79.8, 80.8 (3d, C-3, C-4, C-5), 98.6 (d, C-1), 127.5, 127.6, 127.8, 128.3, 128.4 (5d, arom, C–H), 138.1, 138.2, 138.6 (3s, arom, *C*–CH_2O), 172.5 (s, $COOCH_2(CH_2)_{10}CH_3$); IR (film): ν=3030, 2950, 1736, 1452, 1436, 1206 cm^{-1}; elemental analysis (%) calcd for $C_{53}H_{80}O_7$: C 76.77, H 9.72; found: C 76.15, H 9.12.

*4.3.17. Octadecyl 3,4,6-tri-O-benzyl-2-deoxy-2-C-[(octadecyloxycarbonyl)-methyl]-α-D-glucopyranoside (**8n**).* A colorless syrup; $[\alpha]_D^{20}$ +37.9 (*c* 0.96, $CHCl_3$); R_f=0.42 (*c*-hexane/ethyl acetate 6:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.80 (t, *J*=6.9 Hz, $COOCH_2(CH_2)_{16}CH_3$), 0.82 (t, *J*=6.6 Hz, $OCH_2(CH_2)_{16}CH_3$), 1.12–1.28 (m, 64H, $COOCH_2(CH_2)_{16}CH_3$, $OCH_2(CH_2)_{16}CH_3$), 1.43–1.50 (m, 4H, $COOCH_2(CH_2)_{16}CH_3$, $OCH_2(CH_2)_{16}CH_3$), 2.31 (dd, *J*=19.5, 5.7 Hz, 1H, 7′-H), 2.54 (dd, *J*=19.5, 8.7 Hz, 1H, 7-H), 3.24 (dddd, *J*=10.5, 8.7, 5.7, 3.6 Hz, 1H, 2-H), 3.55 (dd, *J*=12.9, 6.3 Hz, 1H, 6′-H), 3.57 (ddd, *J*=9.3, 6.3, 4.8 Hz, 1H, 5-H), 3.59 (dd, *J*=10.5, 3.3 Hz, 1H, 3-H), 3.60 (dd, *J*=12.9, 4.8 Hz, 1H, 6-H), 3.71 (dd, *J*=9.3, 3.3 Hz, 1H, 4-H), 3.92 (d, *J*=10.8 Hz, 1H, CH_2–Ph), 3.93 (d, *J*=3.6 Hz, 1H, 1-H), 4.45 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.55 (d, *J*=11.1 Hz, 1H, CH_2–Ph), 4.59 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.69 (d, *J*=10.8 Hz, 1H, CH_2–Ph), 4.85 (d, *J*=11.1 Hz, 1H, CH_2–Ph), 7.04–7.30 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.1, 14.2 (2q, CH_3), 22.4, 22.7, 25.7, 25.9, 26.2, 26.9, 28.6, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 (12t, $COOCH_2(CH_2)_{16}CH_3$, $OCH_2(CH_2)_{16}CH_3$), 32.7 (t, C-7), 43.0 (d, C-2), 64.6, 67.8 (2t, $COOCH_2(CH_2)_{16}CH_3$, $OCH_2(CH_2)_{16}CH_3$), 68.9 (t, C-6), 73.5, 74.8, 75.0 (3t, CH_2–Ph), 71.0, 79.8, 80.8 (3d, C-3, C-4, C-5), 98.7 (d, C-1), 127.5, 127.6, 127.7, 127.8, 127.9, 128.3, 128.4 (15d, arom, C–H), 138.1, 138.2, 138.6 (3s, arom, *C*–CH_2O), 172.5 (s, $COOCH_2(CH_2)_{16}CH_3$); IR (film): ν=3030, 2952, 1799, 1454, 1432, 1206 cm^{-1}; ESI-HRMS ($C_{65}H_{104}O_7$): calcd for [M+H] 997.7860; found 997.7811.

*4.3.18. 3,4,6-Tri-O-benzyl-2-deoxy-2-C-(formic acid)-β-D-glucopyranosyl-(1→6)-(1,2:3,4-di-O-isopropylidene)-α-D-galactopyranoside (**8o**).* A colorless syrup; $[\alpha]_D^{20}$ +48.9 (*c* 0.98, $CHCl_3$); R_f=0.42 (*c*-hexane/ethyl acetate 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ=1.23, 1.25, 1.36, 1.49 (4s, each, 3H, $O_2C(CH_3)_2$), 2.18 (dddd, *J*=10.5, 8.5, 7.5, 4.5 Hz, 1H, 8-H), 2.34 (dd, *J*=15.0, 7.5 Hz, 1H, 13′-H), 2.52 (dd, *J*=15.0, 4.5 Hz, 1H, 13-H), 3.39 (ddd, *J*=8.0, 7.0, 2.5 Hz, 1H, 5-H), 3.42 (dd, *J*=10.5, 3.5 Hz, 1H, 9-H), 3.54–3.65 (m, 2H, 12-H, 12′-H), 3.62 (dd, *J*=9.0, 3.5 Hz, 1H, 10-H), 3.68 (dd, *J*=11.0, 7.0 Hz, 1H, 6′-H), 3.90 (dd, *J*=7.5, 1.5 Hz, 1H, 11-H), 4.01 (dd, *J*=11.0, 2.5 Hz, 1H, 6-H), 4.12 (dd, *J*=8.0, 2.0 Hz, 1H, 4-H), 4.23 (dd, *J*=5.0, 2.0 Hz, 1H, 3-H), 4.26 (dd, *J*=5.0, 2.0 Hz, 1H, 2-H), 4.34 (d, *J*=8.5 Hz, 1H, 7-H), 4.46 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.50 (d, *J*=11.0 Hz, 1H, CH_2–Ph), 4.56 (d, *J*=11.5 Hz, 1H, CH_2–Ph), 4.57 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.70 (d, *J*=11.0 Hz, 1H, CH_2–Ph), 4.82 (d, *J*=11.5 Hz, 1H, CH_2–Ph), 5.42 (d, *J*=5.0 Hz, 1H, 1-H), 7.09–7.290 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=24.2, 24.3, 24.9, 25.9 (4q, CH_3), 32.0 (t, C-13), 45.0 (d, C-8), 68.8, 69.3 (2t, C-6, C-12), 73.5, 74.6, 74.8 (3t, CH_2–Ph), 68.0, 70.3, 70.7, 71.4, 75.1, 79.5, 82.0 (7d, C-2, C-3, C-4, C-5, C-9, C-10, C-11), 96.4, 103.2 (2d, C-1, C-7), 109.0, 109.4 (2s, $(CH_3)_2COO$), 127.5, 127.7, 127.8, 128.3, 128.4 (5d, arom, C–H), 138.0, 138.1, 138.2 (3s, arom, *C*–CH_2O), 174.9 (s, *C*OOH); IR (film): ν=3031, 2949, 1729, 1452, 1437, 1271, 1207 cm^{-1}; elemental analysis (%) calcd for $C_{41}H_{50}O_{12}$: C 67.01, H 6.86; found: C 66.74, H 7.08.

*4.3.19. 3,4,6-Tri-O-benzyl-2-deoxy-2-C-(formic acid)-β-D-glucopyranosyl-(1→3)-(1,2:5,6-di-O-isopropylidene)-α-D-glucopyranoside (**8p**).* A colorless syrup; $[\alpha]_D^{20}$ +34.7 (*c* 0.96, $CHCl_3$); R_f=0.43 (*c*-hexane/ethyl acetate 2:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.24, 1.29, 1.37, 1.42 (4s, each, 3H, $O_2C(CH_3)_2$), 2.38–2.46 (m, 1H, 13′-H), 2.45 (ddt, *J*=10.8, 7.6, 7.2 Hz, 1H, 8-H), 2.54 (dd, *J*=16.0, 7.2 Hz, 1H, 13-H), 3.41 (ddd, *J*=8.0, 6.0, 2.8 Hz, 1H, 5-H), 3.61–3.73 (m, 2H, 12-H, 12′-H), 3.62 (d *J*=10.4 Hz, 1H, 11-H), 3.71 (dd, *J*=9.6, 2.4 Hz, 1H, 10-H), 3.72 (dd, *J*=8.4, 1.6 Hz, 1H, 3-H), 3.91 (dd, *J*=10.8, 5.2 Hz, 1H, 9-H), 4.00 (dd, *J*=8.0, 1.6 Hz, 1H, 4-H), 4.09 (dd, *J*=8.4, 2.0 Hz, 1H, 2-H), 4.25 (dd, *J*=13.6, 2.8 Hz, 1H, 6′-H), 4.27 (dd, *J*=13.6, 6.0 Hz, 1H, 6-H), 4.46 (d, *J*=7.6 Hz, 1H, 7-H), 4.49 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.51 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.52 (d, *J*=11.2 Hz, 1H, CH_2–Ph), 4.55 (d, *J*=11.6 Hz, 1H, CH_2–Ph), 4.64 (d, *J*=11.2 Hz, 1H, CH_2–Ph), 4.76 (d, *J*=11.6 Hz, 1H, CH_2–Ph), 5.77 (d, *J*=4.8 Hz, 1H, 1-H), 7.10–7.26 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=25.8, 26.4, 27.2, 27.4 (4q, CH_3), 33.5 (t, C-13), 46.5 (d, C-8), 70.3, 70.8 (2t, C-6, C-12), 75.0, 76.1, 76.3 (3t, CH_2–Ph), 69.5, 71.8, 72.2, 72.9, 76.6, 81.0, 83.5 (7d, C-2, C-3, C-4, C-5, C-9, C-10, C-11), 97.9, 104.7 (2d, C-1, C-7), 110.5, 110.9 (2s, $(CH_3)_2COO$), 129.0, 129.2, 129.3, 129.8, 129.9 (5d, arom, C–H), 139.5, 139.6, 139.7 (3s, arom, *C*–CH_2O), 176.4 (s, *C*OOH); IR (film): ν=3030, 2951, 1729, 1437, 1271, 1207 cm^{-1}; elemental analysis (%) calcd for $C_{41}H_{50}O_{12}$: C 67.01, H 6.86; found: C 67.32, H 6.97.

*4.3.20. (2R,3S,4R,4aR,7aR)-2-Benzyoxymethyl-3,4-dibenzyoxy-6-oxo-hexahydro-pyrano[2,3-b] pyrrole (**8q**).* A white solid; mp 159–161 °C; $[\alpha]_D^{20}$ +7.4 (*c* 1.00, DMSO); R_f=0.36 (dichloromethane/methanol 10:1); ^{1}H NMR (500 MHz, DMSO-d_6): δ=2.14 (dddd, *J*=10.0, 5.0, 4.0, 3.0 Hz, 1H, 2-H), 2.15 (dd, *J*=14.5, 5.0 Hz, 1H, 7′-H), 2.88 (dd, *J*=14.5, 3.0 Hz, 1H, 7-H), 3.41 (ddd, *J*=9.5, 4.5, 1.5 Hz, 1H, 5-H), 3.54 (dd, *J*=9.5, 3.5 Hz, 1H, 4-H), 3.59 (dd, *J*=10.5, 1.5 Hz, 1H, 6′-H), 3.66 (dd, *J*=10.5, 4.5 Hz, 1H, 6-H), 3.89 (dd, *J*=10.0, 3.5 Hz, 1H, 3-H), 4.47 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.53 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.54 (d, *J*=11.0 Hz, 1H, CH_2–Ph), 4.57 (d, *J*=11.0 Hz, 1H, CH_2–Ph), 4.71 (d, *J*=11.0 Hz, 1H, CH_2–Ph), 4.77 (d, *J*=11.0 Hz, 1H, CH_2–Ph), 6.45 (d, *J*=4.0 Hz, 1H, 1-H), 6.77 (s, 1H, NH), 7.20–7.34 (m, 15H, arom, H); ^{13}C NMR (75 MHz, DMSO-d_6): δ=32.9 (t, C-7), 42.7 (d, C-2), 69.1 (t, C-6), 72.2, 73.7, 73.9 (3t, CH_2–Ph), 70.0, 79.8, 79.9 (3d, C-3, C-4, C-5), 91.7 (d, C-1), 127.3, 127.4, 127.5, 128.1, 128.2, 128.3 (6d, arom, C–H), 138.2, 138.3, 138.5 (3s, arom, *C*–CH_2O), 173.1 (s, *C*ONHR); IR (film): ν=3030, 2949, 1736, 1452, 1260 cm^{-1}; elemental analysis (%) calcd for $C_{29}H_{31}NO_5$: C 73.55, H 6.60, N 2.96; found: C 73.50, H 6.88, N 3.06.

*4.3.21. Azido 3,4,6-tri-O-benzyl-2-deoxy-2-C-(formic acid)-β-D-glucopyranoside (**8r**).* A colorless syrup; $[\alpha]_D^{20}$ +19.9 (*c* 0.87, $CHCl_3$); R_f=0.41 (*c*-hexane/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.00 (dddd, *J*=10.8, 9.6, 5.2, 4.8 Hz, 1H, 2-H), 2.42 (dd, *J*=16.8, 4.8 Hz, 1H, 7′-H), 2.50 (dd, *J*=16.8, 5.2 Hz, 1H, 7-H), 3.50 (ddd, *J*=9.2, 6.4, 2.1 Hz, 1H, 5-H), 3.52 (dd, *J*=15.6, 2.1 Hz, 1H, 6′-H), 3.58 (dd, *J*=15.6, 6.4 Hz, 1H, 6-H), 3.63 (dd, *J*=9.2, 2.0 Hz, 1H, 4-H), 3.69 (dd, *J*=10.8, 2.0 Hz, 1H, 3-H), 4.51 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.53 (d, *J*=11.2 Hz, 1H, CH_2–Ph), 4.56 (d, *J*=11.2 Hz, 1H, CH_2–Ph), 4.59 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.63 (d, *J*=9.6 Hz, 1H, 1-H), 4.71 (d, *J*=11.2 Hz, 1H, CH_2–Ph), 4.84 (d, *J*=11.2 Hz, 1H, CH_2–Ph), 7.10–7.30 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=31.2 (t, C-7), 44.2 (d, C-2), 68.5 (t, C-6), 73.6, 74.8, 75.0 (3t, CH_2–Ph), 77.3, 79.3, 81.3 (3d, C-3, C-4, C-5), 89.2 (d, C-1), 127.7, 127.8, 128.0, 128.4, 128.5 (5d, arom, C–H), 137.8, 137.9, 138.0 (3s, arom, *C*–CH_2O), 176.7 (s, *C*OOH); IR (film): ν=3030, 2952, 1800, 1738, 1453, 1268 cm^{-1};

elemental analysis (%) calcd for $C_{29}H_{31}N_3O_6$: C 67.30, H 6.04, N 8.12; found: C 67.05, H 6.06, N 8.64.

*4.3.22. Ethylthio 3,4,6-tri-O-benzyl-2-deoxy-2-C-[(ethylthioxycarbonyl)-methyl]-β-D-glucopyranoside (**8s**).* A colorless syrup; $[\alpha]_D^{20}$ +11.4 (*c* 0.98, $CHCl_3$); R_f=0.49 (*c*-hexane/ethyl acetate 1:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=1.11 (t, *J*=7.2 Hz, 3H, SCH_2CH_3), 1.15 (t, *J*=7.2 Hz, 3H, SCH_2CH_3), 2.28–2.38 (m, 4H, SCH_2CH_3), 2.43 (dd, *J*=16.4, 7.6 Hz, 1H, 7′-H), 2.45 (dddd, *J*=10.8, 8.0, 7.6, 4.4 Hz, 1H, 2-H), 2.57 (dd, *J*=16.4, 4.4 Hz, 1H, 7-H), 2.64 (ddd, *J*=9.6, 5.2, 3.6 Hz, 1H, 5-H), 3.57 (dd, *J*=10.0, 5.2 Hz, 1H, 6′-H), 3.65 (dd, *J*=9.6, 4.0 Hz, 1H, 4-H), 3.68 (dd, *J*=10.0, 3.6 Hz, 1H, 6-H), 3.96 (dd, *J*=10.8, 4.0 Hz, 1H, 3-H), 4.44 (d, *J*=12.4 Hz, 1H, CH_2–Ph), 4.47 (d, *J*=12.4 Hz, 1H, CH_2–Ph), 4.50 (d, *J*=11.6 Hz, 1H, CH_2–Ph), 4.51 (d, *J*=11.6 Hz, 1H, CH_2–Ph), 4.54 (d, *J*=11.6 Hz, 1H, CH_2–Ph), 4.63 (d, *J*=11.6 Hz, 1H, CH_2–Ph), 4.86 (d, *J*=8.0 Hz, 1H, 1-H), 7.16–7.28 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=14.2, 14.3 (2q, SCH_2CH_3), 24.4, 25.0 (2t, SCH_2CH_3), 33.5 (t, C-7), 41.8 (d, C-2), 70.4 (t, C-6), 73.5, 73.6, 73.9 (3t, CH_2–Ph), 55.0, 70.5, 79.8 (3d, C-3, C-4, C-5), 82.2 (d, C-1), 127.9, 128.0, 128.1, 128.5, 128.6, 128.7 (6d, arom, C–H), 137.3, 137.4, 137.6 (3s, arom, *C*–CH_2O), 186.1 (s, COSR); IR (film): ν=3031, 2952, 1800, 1738, 1731, 1453, 1268, 1215 cm^{-1}; elemental analysis (%) calcd for $C_{33}H_{40}O_5S_2$: C 68.24, H 6.94, S 11.04; found: C 68.05, H 6.66, S 10.78.

*4.3.23. Thio 3,4,6-tri-O-benzyl-2-deoxy-2-C-(formic acid)-β-D-glucopyranoside (**8t**).* A colorless syrup (mixed isomers); $[\alpha]_D^{20}$ +11.4 (*c* 0.98, $CHCl_3$); R_f=0.38 (*c*-hexane/ethyl acetate 1:1); β-isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.08 (dddd, *J*=11.1, 8.1, 6.0, 4.8 Hz, 1H, 2-H), 2.10 (dd, *J*=15.6, 4.8 Hz, 1H, 7′-H), 2.23 (dd, *J*=15.6, 6.0 Hz, 1H, 7-H), 2.64 (ddd, *J*=9.9, 6.6, 4.2 Hz, 1H, 5-H), 3.50 (dd, *J*=11.1, 8.7 Hz, 1H, 3-H), 3.60 (dd, *J*=12.3, 6.6 Hz, 1H, 6′-H), 3.67 (dd, *J*=12.3, 4.2 Hz, 1H, 6-H), 4.11 (dd, *J*=9.9, 8.7 Hz, 1H, 4-H), 4.49 (d, *J*=11.4 Hz, 1H, CH_2–Ph), 4.52 (d, *J*=3.3 Hz, 2H, CH_2–Ph), 4.53 (d, *J*=11.4 Hz, 1H, CH_2–Ph), 4.54 (d, *J*=8.1 Hz, 1H, 1-H), 4.69 (d, *J*=10.8 Hz, 1H, CH_2–Ph), 4.71 (d, *J*=10.8 Hz, 1H, CH_2–Ph), 7.06–7.29 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=33.9 (t, C-7), 48.0 (d, C-2), 68.8 (t, C-6), 73.5, 74.7, 74.9 (3t, CH_2–Ph), 79.5, 79.6, 79.8 (3d, C-3, C-4, C-5), 82.7 (d, C-1), 127.6, 127.7, 127.8, 127.9, 128.4 (5d, arom, C–H), 137.8, 137.9, 138.0 (3s, arom, *C*–CH_2O), 177.3 (s, COOH); α-isomer: ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.20 (dd, *J*=16.5, 7.5 Hz, 1H, 7′-H), 2.21 (dddd, *J*=10.8, 7.5, 5.1, 2.7 Hz, 1H, 2-H), 2.52 (dd, *J*=16.5, 5.1 Hz, 1H, 7-H), 2.68 (ddd, *J*=9.3, 7.5, 4.5 Hz, 1H, 5-H), 3.43 (dd, *J*=11.1, 7.2 Hz, 1H, 3-H), 3.66 (d, *J*=3.6 Hz, 2H, 6-H, 6′-H), 4.05 (dd, *J*=9.3, 7.2 Hz, 1H, 4-H), 4.45 (d, *J*=12.3 Hz, 1H, CH_2–Ph), 4.51 (d, *J*=3.3 Hz, 2H, CH_2–Ph), 4.57 (d, *J*=12.3 Hz, 1H, CH_2–Ph), 4.59 (d, *J*=2.7 Hz, 1H, 1-H), 4.85 (d, *J*=11.1 Hz, 1H, CH_2–Ph), 4.85 (d, *J*=11.1 Hz, 1H, CH_2–Ph), 7.06–7.29 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=33.3 (t, C-7), 43.1 (d, C-2), 68.5 (t, C-6), 73.5, 74.7, 75.3 (3t, CH_2–Ph), 72.1, 79.4, 79.8 (3d, C-3, C-4, C-5), 79.9 (d, C-1), 127.6, 127.7, 127.8, 127.9, 128.4 (5d, arom, C–H), 137.8, 137.9, 138.0 (3s, arom, *C*–CH_2O), 177.0 (s, COOH); IR (film): ν=2953, 1796, 1734, 1726, 1452, 1268, 1207 cm^{-1}; ESI-HRMS ($C_{29}H_{32}O_6S$): calcd for [M+H] 509.1998; found 509.1994.

*4.3.24. 3,4,6-Tri-O-benzyl-1-deoxy-2-deoxy-2-C-(formic acid)-β-D-glucopyranoside (**8u**).* A colorless syrup; $[\alpha]_D^{20}$ +26.9 (*c* 0.93, $CHCl_3$); R_f=0.45 (dichloromethane/methanol 8:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.02 (dd, *J*=15.6, 8.1 Hz, 1H, 7′-H), 2.23 (dddt, *J*=11.1, 8.7, 7.8, 4.5 Hz, 1H, 2-H), 2.47 (dd, *J*=15.6, 4.5 Hz, 1H, 7-H), 3.10 (dd, *J*=11.4, 4.2 Hz, 1H, 1′-H), 3.33 (dd, *J*=14.4, 6.3 Hz, 1H, 6′-H), 3.55 (dd, *J*=11.4, 9.3 Hz, 1H, 1-H), 3.61 (dd, *J*=14.4, 3.3 Hz, 1H, 6-H), 3.87 (ddd, *J*=9.6, 6.3, 3.3 Hz, 1H, 5-H), 3.95 (dd, *J*=9.6, 4.8 Hz, 1H, 4-H), 4.00 (dd, *J*=11.1, 4.8 Hz, 1H, 3-H), 4.46 (d, *J*=12.3 Hz, 1H, CH_2–Ph), 4.47 (d, *J*=11.1 Hz, 1H, CH_2–Ph), 4.55 (d, *J*=12.3 Hz, 1H, CH_2–Ph), 4.56 (d, *J*=11.4 Hz, 1H, CH_2–Ph), 4.70 (d, *J*=11.1 Hz, 1H, CH_2–Ph), 4.86 (d, *J*=11.4 Hz, 1H, CH_2–Ph), 6.98–7.27 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=32.6 (t, C-7), 39.3 (d, C-2), 69.0, 69.8 (2t, C-1, C-6), 73.6, 74.8, 74.9 (3t, CH_2–Ph), 79.8, 79.9, 84.0 (3d, C-3, C-4, C-5), 127.7, 127.8, 127.9, 128.0, 128.4, 128.6, 128.8 (7d, arom, C–H), 137.9, 138.0, 138.1 (3s, arom, *C*–CH_2O), 177.1 (s, COOH); IR (film): ν=3030, 2946, 1738, 1451, 1258 cm^{-1}; elemental analysis (%) calcd for $C_{29}H_{32}O_6$: C 73.09, H 6.77; found: C 73.00, H 6.89.

4.4. General procedure for the deprotonation of lactone 3 and ester 5, subsequent trapping with electrophiles

A solution of lactone **3** (235 mg, 0.5 mmol) or ester **5** (258 mg, 0.5 mmol) in dry tetrahydrofuran (10 mL) was cooled to −78 °C under an argon atmosphere. At this temperature potassium hexamethyldisilazide (1.5 mL, 0.75 mmol) was added slowly. After 45 min, iodomethane (0.16 mL, 2.5 mmol), 2-phenylsulfonyl-3-phenyloxaziridine (Davis reagent, 265 mg, 1.0 mmol) or trisyl azide (310 mg, 1.0 mmol) was added dropwise within 10 min. The solution was stirred until TLC showed complete conversion of the starting material. A saturated solution of ammonium chloride (10 mL) was added, and the mixture was extracted with dichloromethane (3×10 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated. The crude products **9** and **10** were analyzed by NMR spectroscopy and purified by flash chromatography (*c*-hexane/ethyl acetate 7:1).

*4.4.1. (3S,3aS,4R,5S,6R,7aR)-4,5-Dibenzyloxy-6-benzyloxymethyl-3-methyl-2-oxo-hexahydro-furo[2,3-b]pyran (7S-**9a**).* A colorless syrup; $[\alpha]_D^{20}$ −2.4 (*c* 0.63, $CHCl_3$); R_f=0.36 (*c*-hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.16 (d, *J*=7.5 Hz, 3H, CH_3), 2.33 (dt, *J*=11.7, 5.7 Hz, 1H, 2-H), 2.68 (qd, *J*=7.5, 5.7 Hz, 1H, 7-H), 3.48 (ddd, *J*=10.5, 4.8, 3.0 Hz, 1H, 5-H), 3.60–3.70 (m, 2H, 3-H, 4-H), 3.69 (dd, *J*=12.9, 4.8 Hz, 1H, 6′-H), 3.72 (dd, *J*=12.9, 3.0 Hz, 1H, 6-H), 4.42 (d, *J*=11.4 Hz, 1H, CH_2–Ph), 4.44 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.48 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.53 (d, *J*=11.4 Hz, 1H, CH_2–Ph), 4.54 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.67 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 5.76 (d, *J*=5.7 Hz, 1H, 1-H), 7.08–7.31 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=15.4 (q, CH_3), 38.9 (d, C-7), 46.6 (d, C-2), 68.7 (t, C-6), 73.2, 73.3, 73.5 (3t, CH_2–Ph), 72.3, 75.8, 77.5 (3d, C-3, C-4, C-5), 99.3 (d, C-1), 127.7, 127.8, 128.0, 128.4, 128.5, 128.6 (6d, arom, C–H), 137.6, 137.7, 137.8 (3s, arom, *C*–CH_2O), 177.1 (s, COOR); IR (film): ν=3452, 3032, 1963, 1771, 1710, 1624, 1490, 1447, 1345, 1094 cm^{-1}; elemental analysis calcd (%) for $C_{30}H_{32}O_6$ (488.57): C 73.75, H 6.60; found: C 74.05, H 6.76.

*4.4.2. (3S,3aS,4R,5S,6R,7aR)-3-Azido-4,5-dibenzyloxy-6-benzyloxymethyl-2-oxo-hexahydro-furo[2,3-b] pyran (7S-**9b**).* A colorless syrup; $[\alpha]_D^{20}$ −2.6 (*c* 0.89, $CHCl_3$); R_f=0.38 (*c*-hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.44 (ddd, *J*=11.7, 5.4, 4.8 Hz, 1H, 2-H), 3.48 (ddd, *J*=10.5, 4.5, 2.4 Hz, 1H, 5-H), 3.60 (dd, *J*=12.9, 4.5 Hz, 1H, 6′-H), 3.64 (dd, *J*=11.7, 8.1 Hz, 1H, 3-H), 3.68 (dd, *J*=10.5, 8.1 Hz, 1H, 4-H), 3.72 (dd, *J*=12.9, 2.4 Hz, 1H, 6-H), 3.98 (d, *J*=4.8 Hz, 1H, 7-H), 4.43 (d, *J*=11.4 Hz, 1H, CH_2–Ph), 4.46 (d, *J*=11.7 Hz, 1H, CH_2–Ph), 4.47 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.51 (d, *J*=12.0 Hz, 1H, CH_2–Ph), 4.54 (d, *J*=11.4 Hz, 1H, CH_2–Ph), 4.65 (d, *J*=11.7 Hz, 1H, CH_2–Ph), 5.83 (d, *J*=5.4 Hz, 1H, 1-H), 7.09–7.33 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=45.2 (d, C-2), 60.3 (d, C-7), 68.3 (t, C-6), 73.3, 73.4, 73.5 (3 t, CH_2–Ph), 72.8, 75.2, 75.3 (3d, C-3, C-4, C-5), 99.8 (d, C-1), 127.8, 127.9, 128.0, 128.1, 128.3, 128.4, 128.5, 128.7 (8d, arom, C–H), 137.2, 137.3, 137.7 (3s, arom, *C*–CH_2O), 170.4 (s, COOR); IR (film): ν=3424, 3058, 3032, 2952, 1738, 1456, 1438, 1149, 1087, 1021 cm^{-1}; HRMS(ES) ($C_{29}H_{29}N_3O_6$): calcd for [M+Na] 538.1954; found 538.1945.

*4.4.3. (3S,3aS,4R,5S,6R,7aR)-4,5-Dibenzyloxy-6-benzyloxymethyl-3-hydroxy-2-oxo-hexahydro-furo[2,3-b]pyran (7S-**9c**).* A colorless syrup; $[\alpha]_D^{20}$ −0.6 (*c* 0.86, $CHCl_3$); R_f=0.25 (*c*-hexane/ethyl acetate

2:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.71 (ddd, J=11.1, 6.9, 5.7 Hz, 1H, 2-H), 3.57 (dd, J=9.3, 9.0 Hz, 1H, 4-H), 3.56–3.66 (m, 2H, 6-H, 6′-H), 3.61 (ddd, J=9.3, 5.7, 2.7 Hz, 1H, 5-H), 3.63 (dd, J=11.1, 9.0 Hz, 1H, 3-H), 3.73 (d, J=6.9 Hz, 1H, 7-H), 4.37 (d, J=12.0 Hz, 1H, CH_2–Ph), 4.40 (d, J=11.4 Hz, 1H, CH_2–Ph), 4.44 (d, J=12.0 Hz, 1H, CH_2–Ph), 4.51 (d, J=11.4 Hz, 1H, CH_2–Ph), 4.52 (d, J=12.0 Hz, 1H, CH_2–Ph), 4.61 (d, J=12.0 Hz, 1H, CH_2–Ph), 5.94 (d, J=5.7 Hz, 1H, 1-H), 7.08–7.32 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=46.1 (d, C-2), 68.8 (t, C-6), 70.1 (d, C-7), 72.7, 73.0, 73.5 (3t, CH_2–Ph), 72.7, 74.9, 75.3 (3d, C-3, C-4, C-5), 99.6 (d, C-1), 127.8, 127.9, 128.1, 128.4, 128.6, 128.6 (6d, arom, C–H), 137.3, 137.5, 137.8 (3s, arom, C–CH_2O), 174.5 (s, COOR); IR (film): ν=3029, 2863, 1748, 1496, 1453, 1361, 1208, 1027 cm^{-1}; ESI-HRMS ($C_{29}H_{30}O_7$): calcd for [M+Na] 513.1889; found 513.1874.

4.5. General procedure for the opening of lactones 9

A mixture of lactone **9** (0.5 mmol) and Drierite® (20–40 mesh) (680 mg) in dry methanol (10 mL) was stirred at 0 °C under argon atmosphere. At this temperature $Sc(OTf)_3$ (370 mg, 0.75 mmol, 1.5 equiv) was added and after 30 min TLC showed complete conversion. The reaction was quenched with saturated sodium hydrogen carbonate solution (10 mL) and the mixture was extracted with dichloromethane (3×20 mL). The combined organic extracts were dried (Na_2SO_4) and concentrated and the crude products **10** were purified by flash chromatography (*c*-hexane/ethyl acetate 7:1).

*4.5.1. Methyl (7S)-3,4,6-tri-O-benzyl-2-deoxy-2-C-[(methoxy-carbonyl)-ethyl]-β-D-glucopyranoside (7S-**10a**).* A colorless syrup; $[\alpha]_D^{20}$ −3.5 (*c* 0.88, $CHCl_3$); R_f=0.37 (*c*-hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=1.13 (d, J=7.2 Hz, 3H, CH_3), 2.25 (ddd, J=11.1, 8.7, 5.8 Hz, 1H, 2-H), 2.89 (qd, J=7.2, 5.8 Hz, 1H, 7-H), 3.35 (dt, J=9.3, 3.3 Hz, 1H, 5-H), 3.37 (s, 3H, OMe), 3.43 (s, 3H, COOMe), 3.58 (dd, J=9.3, 8.7 Hz, 1H, 4-H), 3.60 (dd, J=11.1, 8.7 Hz, 1H, 3-H), 3.69 (d, J=3.3 Hz, 2H, 6-H), 4.18 (d, J=8.7 Hz, 1H, 1-H), 4.50 (d, J=12.0 Hz, 1H, CH_2–Ph), 4.52 (d, J=10.8 Hz, 1H, CH_2–Ph), 4.57 (d, J=10.8 Hz, 1H, CH_2–Ph), 4.59 (d, J=12.0 Hz, 1H, CH_2–Ph), 4.67 (d, J=10.8 Hz, 1H, CH_2–Ph), 4.84 (d, J=10.8 Hz, 1H, CH_2–Ph), 7.04–7.31 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=12.3 (q, CH_3), 35.6 (d, C-7), 49.5 (d, C-2), 51.4 (q, COO*Me*), 56.7 (q, OMe), 69.0 (t, C-6), 73.5, 74.5, 74.6 (3t, CH_2–Ph), 75.1, 79.5, 80.6 (3d, C-3, C-4, C-5), 102.5 (d, C-1), 127.4, 127.6, 127.7, 127.8, 128.2, 128.3, 128.4 (7d, arom, C–H), 138.0, 138.2, 138.4 (3s, arom, C–CH_2O), 175.3 (s, COOMe); IR (film): ν=3463, 3024, 2926, 2949, 1738, 1456, 1362, 1217, 1054 cm^{-1}; elemental analysis calcd (%) for $C_{32}H_{38}O_7$ (534.64): C 71.89, H 7.16; found: C 71.77, H 6.96.

*4.5.2. Methyl (7S)-3,4,6-tri-O-benzyl-2-deoxy-2-C-[(azido)-(methoxy-carbonyl)-methyl]-β-D-glucopyranoside (7S-**10b**).* A colorless syrup; $[\alpha]_D^{20}$ +4.9 (*c* 1.09, $CHCl_3$); R_f=0.37 (*c*-hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.35 (ddd, J=11.4, 8.7, 6.0 Hz, 1H, 2-H), 3.29 (s, 3H, OMe), 3.36 (ddd, J=9.9, 5.7, 2.7 Hz, 1H, 5-H), 3.47 (s, 3H, COOMe), 3.58 (dd, J=9.9, 8.1 Hz, 1H, 4-H), 3.58 (dd, J=12.6, 5.7 Hz, 1H, 6′-H), 3.66 (dd, J=12.6, 2.7 Hz, 1H, 6-H), 4.05 (dd, J=11.4, 8.1 Hz, 1H, 3-H), 4.44 (d, J=11.4 Hz, 1H, CH_2–Ph), 4.50 (d, J=12.0 Hz, 1H, CH_2–Ph), 4.51 (d, J=6.0 Hz, 1H, 7-H), 4.59 (d, J=12.0 Hz, 1H, CH_2–Ph), 4.63 (d, J=8.7 Hz, 1H, 1-H), 4.65 (d, J=11.4 Hz, 1H, CH_2–Ph), 4.80 (d, J=11.1 Hz, 1H, CH_2–Ph), 4.84 (d, J=11.1 Hz, 1H, CH_2–Ph), 7.00–7.26 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=45.9 (d, C-2), 52.3 (q, COO*Me*), 57.1 (d, C-7), 60.4 (q, OMe), 69.1 (t, C-6), 71.1, 73.4, 73.5 (3t, CH_2–Ph), 72.1, 74.3, 78.0 (3d, C-3, C-4, C-5), 100.9 (d, C-1), 127.4, 127.7, 127.8, 127.9, 128.0, 128.1, 128.2, 128.4 (8d, arom, C–H), 137.8, 137.9, 138.6 (3s, arom, C–CH_2O), 176.3 (s, COOMe); IR (film): ν=3435, 3079, 3053, 2924, 2849, 1737, 1631, 1494, 1452, 1204, 1065 cm^{-1}; HRMS(ES) ($C_{31}H_{35}N_3O_7$): calcd for [M+Na] 584.2373; found 584.2349.

*4.5.3. Methyl (7S)-3,4,6-tri-O-benzyl-2-deoxy-2-C-[(hydroxy)-(methoxy-carbonyl)-methyl]-β-D-glucopyranoside (7S-**10c**).* A colorless syrup; $[\alpha]_D^{20}$ −3.1 (*c* 0.79, $CHCl_3$); R_f=0.28 (*c*-hexane/ethyl acetate 2:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.21 (ddd, J=11.1, 8.7, 6.6 Hz, 1H, 2-H), 3.35 (s, 3H, OMe), 3.36 (ddd, J=10.5, 5.1, 3.6 Hz, 1H, 5-H), 3.49 (s, 3H, COOMe), 3.64 (dd, J=10.5, 9.0 Hz, 1H, 4-H), 3.68–3.72 (m, 2H, 6-H), 3.80 (dd, J=11.1, 9.0 Hz, 1H, 3-H), 4.32 (d, J=8.7 Hz, 1H, 1-H), 4.42 (d, J=10.8 Hz, 1H, CH_2–Ph), 4.50 (d, J=12.3 Hz, 1H, CH_2–Ph), 4.51 (d, J=6.6 Hz, 1H, 7-H), 4.52 (d, J=10.8 Hz, 1H, CH_2–Ph), 4.60 (d, J=12.3 Hz, 1H, CH_2–Ph), 4.68 (d, J=10.8 Hz, 1H, CH_2–Ph), 4.85 (d, J=10.8 Hz, 1H, CH_2–Ph), 7.03–7.30 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=50.8 (d, C-2), 52.4 (q, COO*Me*), 57.0 (q, OMe), 66.6 (d, C-7), 68.8 (t, C-6), 73.5, 74.7, 74.9 (3t, CH_2–Ph), 74.3, 74.8, 80.4 (3d, C-3, C-4, C-5), 101.6 (d, C-1), 127.4, 127.6, 127.7, 127.8, 128.1, 128.3, 128.4 (7d, arom, C–H), 137.9, 138.2, 138.3 (3s, arom, C–CH_2O), 175.3 (s, COOMe); IR (film): ν=3441, 3030, 2869, 1723, 1605, 1496, 1453, 1361, 1261, 1207, 1055 cm^{-1}; ESI-HRMS ($C_{31}H_{36}O_8$): calcd for [M+H] 537.2488; found 537.2478.

*4.5.4. Methyl (7R)-3,4,6-tri-O-benzyl-2-deoxy-2-C-[(methoxy-carbonyl)-ethyl]-β-D-glucopyranoside (7R-**10a**).* A colorless syrup; $[\alpha]_D^{20}$ −8.7 (*c* 1.11, $CHCl_3$); R_f=0.37 (*c*-hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=0.87 (d, J=7.2 Hz, 3H, CH_3), 2.35 (ddd, J=11.4, 8.7, 2.1 Hz, 1H, 2-H), 2.79 (qd, J=7.2, 2.1 Hz, 1H, 7-H), 3.33 (ddd, J=9.0, 6.3, 3.6 Hz, 1H, 5-H), 3.34 (s, 3H, OMe), 3.42 (dd, J=9.0, 9.3 Hz, 1H, 4-H), 3.48 (dd, J=12.6, 3.6 Hz, 1H, 6′-H), 3.56 (s, 3H, COOMe), 3.61 (dd, J=12.6, 6.3 Hz, 1H, 6-H), 3.67 (dd, J=11.4, 9.3 Hz, 1H, 3-H), 4.12 (d, J=8.7 Hz, 1H, 1-H), 4.48 (d, J=12.0 Hz, 1H, CH_2–Ph), 4.52 (d, J=10.8 Hz, 1H, CH_2–Ph), 4.56 (d, J=11.1 Hz, 1H, CH_2–Ph), 4.58 (d, J=12.0 Hz, 1H, CH_2–Ph), 4.72 (d, J=10.8 Hz, 1H, CH_2–Ph), 4.86 (d, J=11.1 Hz, 1H, CH_2–Ph), 7.11–7.29 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=10.0 (q, CH_3), 35.3 (d, C-7), 48.7 (d, C-2), 51.5 (q, COO*Me*), 57.0 (q, OMe), 69.1 (t, C-6), 73.5, 74.3, 74.7 (3t, CH_2–Ph), 75.1, 79.5, 80.2 (3d, C-3, C-4, C-5), 102.0 (d, C-1), 127.6, 127.8, 127.9, 128.0, 128.3, 128.4, 128.5 (7d, arom, C–H), 138.0, 138.1, 138.2 (3s, arom, C–CH_2O), 175.7 (s, COOMe); IR (film): ν=3456, 3024, 2922, 2858, 1801, 1738, 1490, 1453, 1358, 1270, 1064 cm^{-1}; elemental analysis calcd (%) for $C_{32}H_{38}O_7$ (534.64): C 71.89, H 7.16; found: C 72.05, H 7.23.

*4.5.5. Methyl (7R)-3,4,6-tri-O-benzyl-2-deoxy-2-C-[(azido)-(methoxy-carbonyl)-methyl]-β-D-glucopyranoside (7R-**10b**).* A colorless syrup; $[\alpha]_D^{20}$ +12.0 (*c* 0.81, $CHCl_3$); R_f=0.37 (*c*-hexane/ethyl acetate 3:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.25 (ddd, J=11.1, 8.4, 2.1 Hz, 1H, 2-H), 3.32 (dd, J=12.0, 3.0 Hz, 1H, 6′-H), 3.33 (s, 3H, OMe), 3.56 (ddd, J=9.3, 6.3, 3.0 Hz, 1H, 5-H), 3.58 (dd, J=9.3, 7.5 Hz, 1H, 4-H), 3.64 (s, 3H, COOMe), 3.65 (dd, J=12.0, 6.3 Hz, 1H, 6-H), 4.20 (dd, J=11.1, 7.5 Hz, 1H, 3-H), 4.21 (d, J=10.8 Hz, 1H, CH_2–Ph), 4.47 (d, J=12.0 Hz, 1H, CH_2–Ph), 4.53 (d, J=2.1 Hz, 1H, 7-H), 4.56 (d, J=11.4 Hz, 1H, CH_2–Ph), 4.56 (d, J=8.4 Hz, 1H, 1-H), 4.57 (d, J=12.0 Hz, 1H, CH_2–Ph), 4.73 (d, J=10.8 Hz, 1H, CH_2–Ph), 4.88 (d, J=11.4 Hz, 1H, CH_2–Ph), 7.09–7.32 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=49.2 (d, C-2), 52.3 (q, COO*Me*), 57.3 (d, C-7), 58.5 (q, OMe), 68.8 (t, C-6), 73.6, 74.7, 75.1 (3t, CH_2–Ph), 74.9, 78.8, 79.9 (3d, C-3, C-4, C-5), 101.0 (d, C-1), 127.6, 127.8, 128.0, 128.1, 128.3, 128.4, 128.6 (7d, arom, C–H), 137.9, 138.0, 138.1 (3s, arom, C–CH_2O), 170.4 (s, COOMe); IR (film): ν=3437, 3058, 3028, 2951, 1801, 1738, 1494, 1454, 1439, 1264, 1213 cm^{-1}; ESI-HRMS ($C_{31}H_{35}N_3O_7$): calcd for [M+Na] 584.2373; found 584.2336.

*4.5.6. Methyl (7R)-3,4,6-tri-O-benzyl-2-deoxy-2-C-[(hydroxy)-(methoxy-carbonyl)-methyl]-β-D-glucopyranoside (7R-**10c**).* A colorless syrup; $[\alpha]_D^{20}$ −6.8 (*c* 1.11, $CHCl_3$); R_f=0.28 (*c*-hexane/ethyl acetate 2:1); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.14 (ddd, J=11.1, 8.7, 1.8 Hz, 1H,

2-H), 3.32 (s, 3H, OMe), 3.38 (ddd, *J*=9.6, 6.3, 2.4 Hz, 1H, 5-H), 3.58 (dd, *J*=9.6, 8.7 Hz, 1H, 4-H), 3.65 (dd, *J*=12.3, 6.3 Hz, 1H, 6′-H), 3.66 (s, 3H, COOMe), 3.68 (dd, *J*=12.3, 2.4 Hz, 1H, 6-H), 3.76 (dd, *J*=11.1, 8.7 Hz, 1H, 3-H), 4.33 (d, *J*=8.7 Hz, 1H, 1-H), 4.39 (d, *J*=1.8 Hz, 1H, 7-H), 4.47 (d, *J*=12.0 Hz, 1H, C*H*$_2$—Ph), 4.52 (d, *J*=11.1 Hz, 1H, C*H*$_2$—Ph), 4.56 (d, *J*=12.0 Hz, 1H, C*H*$_2$—Ph), 4.65 (d, *J*=11.1 Hz, 1H, C*H*$_2$—Ph), 4.75 (d, *J*=11.1 Hz, 1H, C*H*$_2$—Ph), 4.87 (d, *J*=11.1 Hz, 1H, C*H*$_2$—Ph), 7.10–7.28 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=50.6 (d, C-2), 52.4 (q, COO*Me*), 57.3 (q, OMe), 66.3 (d, C-7), 69.0 (t, C-6), 73.5, 74.7, 75.4 (3t, *C*H$_2$—Ph), 75.0, 79.6, 79.7 (3d, C-3, C-4, C-5), 100.8 (d, C-1), 127.5, 127.7, 127.8, 128.3, 128.4 (5d, arom, C—H), 138.1, 138.2, 138.3 (3s, arom, *C*—CH$_2$O), 175.7 (s, *C*OOMe); IR (film): ν=3028, 2921, 2853, 1735, 1497, 1453, 1358, 1294, 1250, 1213, 1183 cm^{-1}; ESI-HRMS ($C_{31}H_{36}O_8$): calcd for [M+H] 537.2488; found 537.2477.

4.6. Pinner reaction

A solution of **8a** (501 mg, 1.0 mmol) in an HCl–MeOH mixture [prepared by slow addition of AcCl (1.0 mL) to anhydrous MeOH (20 mL) at 0 °C] was heated to 65 °C until TLC showed complete conversion of starting material. After cooling to room temperature, the solvent was evaporated. The crude product was purified by flash chromatography (*c*-hexane/ethyl acetate 8:1).

*4.6.1. Methyl 2,6-anhydro-4,5,7-tri-O-benzyl-2-deoxy-2-C-(methoxy-carbonyl methyl)-D-gluco-D-glycero-hepturonate (**11**).* A colorless syrup; $[\alpha]_D^{20}$ +19.1 (*c* 1.02, $CHCl_3$); R_f=0.29 (*c*-hexane/ethyl acetate 4:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=2.29 (dddd, *J*=10.0, 8.4, 5.6, 4.8 Hz, 1H, 2-H), 2.37 (dd, *J*=16.8, 4.8 Hz, 1H, 7′-H), 2.45 (dd, *J*=16.8, 5.6 Hz, 1H, 7-H), 3.45 (ddd, *J*=9.6, 6.0, 5.6 Hz, 1H, 5-H), 3.47 (s, 3H, CO_2Me), 3.53 (dd, *J*=10.0, 6.4 Hz, 1H, 3-H), 3.57 (dd, *J*=9.6, 6.4 Hz, 1H, 4-H), 3.59–3.66 (m, 2H, 6-H, 6′-H), 3.64 (s, 3H, CO_2Me), 3.94 (d, *J*=11.4 Hz, 1H, *CH*$_2$—Ph), 4.49 (d, *J*=10.6 Hz, 1H, *CH*$_2$—Ph), 4.52 (d, *J*=8.4 Hz, 1H, 1-H), 4.54 (d, *J*=11.6 Hz, 1H, *CH*$_2$—Ph), 4.55 (d, *J*=11.6 Hz, 1H, *CH*$_2$—Ph), 4.69 (d, *J*=10.6 Hz, 1H, *CH*$_2$—Ph), 4.85 (d, *J*=11.4 Hz, 1H, *CH*$_2$—Ph), 7.06–7.28 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=31.2 (t, C-7), 41.4 (d, C-2), 51.5, 52.1 (2q, COO*Me*), 68.8 (t, C-6), 73.4, 74.7, 74.9 (3t, *C*H$_2$—Ph), 78.5, 79.5, 79.6 (3d, C-3, C-4, C-5), 82.6 (d, C-1), 127.5, 127.6, 127.7, 127.8, 127.9, 128.3, 128.4 (7d, arom, C—H), 137.8, 138.0, 138.1 (3s, arom, *C*—CH$_2$O), 169.5, 171.8 (2s, *C*OOMe); IR (film): ν=3031, 2952, 1800, 1738, 1731, 1453, 1268 cm^{-1}; elemental analysis (%) calcd for $C_{32}H_{36}O_8$: C 70.06, H 6.61; found: C 70.12, H 6.68.

4.7. Ring-closing metathesis

A solution of **8j** (572 mg, 1.0 mmol) and Grubbs' catalyst (A) (83 mg, 0.1 mmol) in dry and degassed CH_2Cl_2 (20 mL) was stirred at room temperature for 48 h. The solvent was removed under reduced pressure. The crude product was purified by flash chromatography (*c*-hexane/ethyl acetate 6:1).

*4.7.1. (8aR,9R,10S,11R,12aS,Z)-9,10-Bis(benzyloxy)-11-(benzyloxymethyl)-8a,9,10,11-tetra-hydro-2H-pyrano[2,3-b][1,6]dioxecin-7(5H, 8H, 12aH)-one (**12**).* A colorless syrup; $[\alpha]_D^{20}$ −39.6 (*c* 1.00, $CHCl_3$); R_f=0.35 (*c*-hexane/ethyl acetate 2:1); ^{1}H NMR (500 MHz, $CDCl_3$): δ=2.36 (dddd, *J*=10.5, 6.0, 4.0, 3.5 Hz, 1H, 2-H), 2.47 (dd, *J*=15.5, 6.0 Hz, 1H, 7′-H), 2.73 (dd, *J*=15.5, 4.0 Hz, 1H, 7-H), 3.68 (ddd, *J*=10.0, 6.0, 2.5 Hz, 1H, 5-H), 3.70 (dd, *J*=10.0, 6.0 Hz, 1H, 4-H), 3.71 (dd, *J*=13.5, 6.0 Hz, 1H, 6′-H), 3.78 (dd, *J*=13.5, 2.5 Hz, 1H, 6-H), 3.79 (dd, *J*=10.5, 6.0 Hz, 1H, 3-H), 3.83 (dd, *J*=12.0, 1.5 Hz, 1H, O*CH*$_2$CH=CHCH$_2$O), 4.19 (d, *J*=13.0 Hz, 1H, O*CH*$_2$CH=CHCH$_2$O), 4.43 (d, *J*=13.0 Hz, 1H, OCH$_2$CH=CH*CH*$_2$O), 4.52 (d, *J*=11.5 Hz, 1H, *CH*$_2$—Ph), 4.54 (d, *J*=11.0 Hz, 1H, *CH*$_2$—Ph), 4.63 (d, *J*=11.5 Hz, 1H, *CH*$_2$—Ph), 4.66 (d, *J*=12.5 Hz, 1H, *CH*$_2$—Ph), 4.71 (d, *J*=12.0 Hz, 1H, OCH$_2$CH=CH*CH*$_2$O), 4.79 (d, *J*=11.0 Hz, 1H, *CH*$_2$—Ph), 4.91 (d, *J*=12.5 Hz, 1H, *CH*$_2$—Ph), 4.93 (d, *J*=3.5 Hz, 1H, 1-H), 5.72 (dt, *J*=12.0, 2.5 Hz, 2H, OCH$_2$*CH*=*CH*CH$_2$O), 7.15–7.36 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=32.4 (t, C-7), 42.9 (d, C-2), 63.5, 67.0 (2t, O*C*H$_2$CH=*C*HCH$_2$O), 68.7 (t, C-6), 73.5, 74.7, 75.2 (3t, *C*H$_2$—Ph), 71.1, 79.6, 80.4 (3d, C-3, C-4, C-5), 97.5 (d, C-1), 127.4, 128.1 (2d, OCH$_2$*C*H=*C*HCH$_2$O), 127.6, 127.7, 127.9, 128.3, 128.4 (5d, arom, C—H), 138.0, 138.2, 138.4 (3s, arom, *C*—CH$_2$O), 171.9 (s, *C*OOR); IR (film): ν=3031, 2952, 1799, 1737, 1729, 1453, 1271, 1207 cm^{-1}; elemental analysis (%) calcd for $C_{33}H_{36}O_7$: C 72.77, H 6.66; found: C 72.68, H 6.80.

4.8. Reduction of azides (7*R*)- or (7*S*)-10b

To a solution of azido-sugars (7*R*)-**10b** or (7*S*)-**10b** (280 mg, 0.5 mmol) in freshly distilled tetrahydrofuran (10 mL) were added water (0.11 mL, 6 mmol) and triphenylphosphine (395 mg, 1.5 mmol) under argon atmosphere. The mixture was stirred at room temperature until TLC showed complete conversion of the starting material. The solvent was removed, and the residue was purified by flash chromatography (*c*-hexane/ethyl acetate 1:1) to afford the corresponding protected amino acids **13**.

*4.8.1. Methyl (7S)-3,4,6-tri-O-benzyl-2-deoxy-2-C-[(amino)-(methoxy-carbonyl)-methyl]-β-D-glucopyranoside (7S-**13**).* A colorless syrup; $[\alpha]_D^{20}$ −19.2 (*c* 0.92, $CHCl_3$); R_f=0.22 (*c*-hexane/ethyl acetate 1:2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.35 (ddd, *J*=11.4, 8.7, 6.0 Hz, 1H, 2-H), 3.29 (s, 3H, OMe), 3.36 (ddd, *J*=9.9, 5.7, 2.7 Hz, 1H, 5-H), 3.47 (s, 3H, COOMe), 3.58 (dd, *J*=9.9, 8.1 Hz, 1H, 4-H), 3.58 (dd, *J*=12.6, 5.7 Hz, 1H, 6′-H), 3.66 (dd, *J*=12.6, 2.7 Hz, 1H, 6-H), 4.05 (dd, *J*=11.4, 8.1 Hz, 1H, 3-H), 4.44 (d, *J*=11.4 Hz, 1H, C*H*$_2$—Ph), 4.50 (d, *J*=12.0 Hz, 1H, C*H*$_2$—Ph), 4.51 (d, *J*=6.0 Hz, 1H, 7-H), 4.59 (d, *J*=12.0 Hz, 1H, C*H*$_2$—Ph), 4.63 (d, *J*=8.7 Hz, 1H, 1-H), 4.65 (d, *J*=11.4 Hz, 1H, C*H*$_2$—Ph), 4.80 (d, *J*=11.1 Hz, 1H, C*H*$_2$—Ph), 4.84 (d, *J*=11.1 Hz, 1H, C*H*$_2$—Ph), 7.00–7.26 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=44.7, 44.8 (2d, C-2, C-7), 51.4 (q, COO*Me*), 56.9 (q, OMe), 69.0 (t, C-6), 73.5, 74.7, 74.8 (3t, *C*H$_2$—Ph), 75.2, 79.9, 82.0 (3d, C-3, C-4, C-5), 103.4 (d, C-1), 127.5, 127.6, 127.7, 127.8, 128.3, 128.4 (6d, arom, C—H), 138.0, 138.1, 138.2 (3s, arom, *C*—CH$_2$O), 176.6 (s, *C*OOMe); IR (film): ν=3471, 3088, 3062, 3028, 2952, 1738, 1494, 1453, 1435, 1358, 1213, 1153 cm^{-1}; ESI-HRMS ($C_{31}H_{37}NO_7$): calcd for [M+H] 536.2648; found 536.2633.

*4.8.2. Methyl (7R)-3,4,6-tri-O-benzyl-2-deoxy-2-C-[(amino)-(methoxy-carbonyl)-methyl]-β-D-glucopyranoside (7R-**13**).* A colorless syrup; $[\alpha]_D^{20}$ −12.5 (*c* 1.04, $CHCl_3$); R_f=0.21 (*c*-hexane/ethyl acetate 1:2); ^{1}H NMR (300 MHz, $CDCl_3$): δ=2.17 (ddd, *J*=10.8, 8.7, 2.1 Hz, 1H, 2-H), 3.31 (s, 3H, OMe), 3.36 (ddd, *J*=9.3, 6.6, 3.6 Hz, 1H, 5-H), 3.58 (s, 3H, COOMe), 3.59 (dd, *J*=9.3, 9.0 Hz, 1H, 4-H), 3.60 (d, *J*=2.1 Hz, 1H, 7-H), 3.61–3.68 (m, 2H, 6-H), 3.73 (dd, *J*=10.8, 9.0 Hz, 1H, 3-H), 4.26 (d, *J*=8.7 Hz, 1H, 1-H), 4.47 (d, *J*=12.0 Hz, 1H, C*H*$_2$—Ph), 4.53 (d, *J*=10.8 Hz, 1H, C*H*$_2$—Ph), 4.57 (d, *J*=12.0 Hz, 1H, C*H*$_2$—Ph), 4.63 (d, *J*=11.7 Hz, 1H, C*H*$_2$—Ph), 4.75 (d, *J*=10.8 Hz, 1H, C*H*$_2$—Ph), 4.86 (d, *J*=11.7 Hz, 1H, C*H*$_2$—Ph), 7.12–7.29 (m, 15H, arom, H); ^{13}C NMR (75 MHz, $CDCl_3$): δ=50.1, 50.4 (2d, C-2, C-7), 51.9 (q, COO*Me*), 57.0 (q, OMe), 69.0 (t, C-6), 73.4, 73.5, 73.6 (3t, *C*H$_2$—Ph), 74.9, 78.5, 80.2 (3d, C-3, C-4, C-5), 101.2 (d, C-1), 127.5, 127.7, 127.8, 128.3, 128.4, 128.5 (6d, arom, C—H), 138.1, 138.2, 138.3 (3s, arom, *C*—CH$_2$O), 176.1 (s, *C*OOMe); IR (film): ν=3434, 3083, 3062, 3027, 2922, 1728, 1709, 1496, 1453, 1362, 1102, 1028 cm^{-1}; ESI-HRMS ($C_{31}H_{37}NO_7$): calcd for [M+H] 536.2648; found 536.2653.

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