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Anomeric α-azido acid (2-azido-2-deoxy-hept-2-ulopyranosonic acid) derivatives en route to peptides incorporating sugar amino acids

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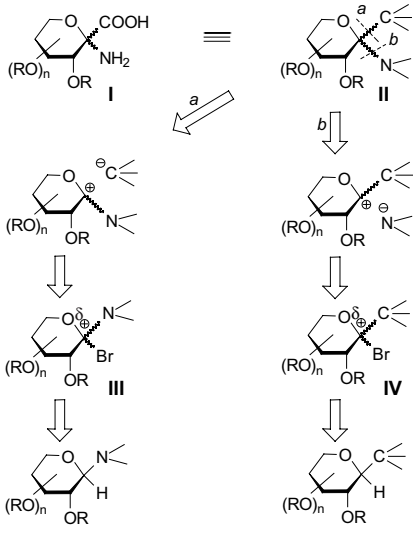
Abstract—Per-*O*-acylated 2,6-anhydro-aldoheptonic acids of D-*glycero*-D-*gulo* and D-*glycero*-L-*manno* configuration obtained by nitrosation of the corresponding aldonamides were transformed into methyl-, *tert*-butyl-, 2,2,2-trichloroethyl-, and pentachlorophenyl esters, acid chlorides and glycinamides by standard procedures. Radical-mediated bromination either by bromine in boiling $CHCl_3$ under illumination, or NBS in refluxing CCl_4 in the presence of Bz_2O_2 or AIBN, or $Na_2S_2O_4$–$KBrO_3$ in CH_2Cl_2–water biphasic solvent mixture at rt gave *axial* anomers of the 2-bromides of the above esters and acid chlorides (2-bromo-2-deoxy-α-D-hept-2-ulopyranosonic acid derivatives), while a glycinamide was split along the $–H_2C–NH–$ bond. Anomeric bromides of the glycinamides were obtained by *N*-acylation of a glycine ester with the pentachlorophenyl 2-bromo-2-deoxy-ulosonates. In this reaction the *axial* anomeric bromide proved stable. Sodium azide in DMSO or DMF was used for the substitution of the anomeric bromides. These reactions proceeded with inversion in the case of each ester and glycinamide to produce *equatorial* azides (2-azido-2-deoxy-β-D-hept-2-ulopyranosonic acid derivatives). The azide substitution in 2-bromo-2-deoxy-α-D-*galacto*-hept-2-ulopyranosonic acid chloride gave 2-azido-2-deoxy-α-D-*galacto*-hept-2-ulopyranosonic acid azide with retention of the anomeric configuration. This acid azide was coupled with a glycine ester to give an *axial* anomeric azide. These transformations represent highly stereoselective routes to both anomers of dipeptides incorporating anomeric α-azido acids.

1. Introduction

Hybrids of sugars and amino acids have received considerable attention over the past decade because, in the form of *O*- and *N*-glycosides of amino acid side chains, such compounds are crucial elements of glycoproteins.[1,2] In order to obtain hydrolytically stable counterparts of the above linking moieties a plethora of synthetic methods for *C*-glycosyl amino acids have been elaborated.[3] Amino acids on various carbohydrate scaffolds have been widely investigated in drug design, and in building up artificial glycopeptides as well as unnatural biopolymers.[4–6] A unique combination of an α-amino acid and a sugar arises in the anomeric α-amino acid type compounds, also called fused sugar glycines,[3] where the anomeric carbon of the sugar is the asymmetric centre of the amino acid (**I**, Scheme 1). Preparative methods to obtain various derivatives of anomeric α-amino acids (from the point of view of carbohydrate chemistry *N*-glycosides of 2-ulosonic acid derivatives) have been reviewed recently.[3,5]



Scheme 1.

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Stepwise introduction of the carbon and nitrogen functionalities to the anomeric carbon can among other ways be designed along disconnections *a* and *b* in the generalised formula **II** in Scheme 1. In such reaction sequences the formation of substrates **III** and **IV** for the last nucleophilic substitution is of prime importance. While compounds of type **III** could not be prepared in radical-mediated halogenations of *N*-glycosyl derivatives,[7] various bromides of type **IV** have been described in the literature. The main preparative procedures involve radical-mediated bromination[8] of acyl-,[9–12] isopropylidene-,[13–16] or silyl[13,14,16,17] protected 2,5-[14–17] or 2,6-[9–13] anhydro-aldonic acid esters,[12–15]-amides,[10–12] and -nitriles,[9,11,12] and ionic bromination of a benzylated 2,6-anhydro-aldonic ester.[18] In a specific oxidation of dichloro exoglycals furanoid 2-chloro-2-deoxy-ulosonic esters analogous to **IV** were obtained.[19] A pyranoid 2-bromo-2-deoxy-ulosonic ester was prepared by conventional HBr–AcOH treatment of the parent anomeric *O*-acetate.[20]

Several of these products were subjected to azide substitution reactions to yield the corresponding furanoid[14–17,19] and pyranoid[13,18,21–23] 2-azido-ulosonic esters,[13–19,23] amides[21,22] and nitriles.[21] Both furanoid and pyranoid 2-azido-ulosonic esters were prepared from thiazolyl ketol acetate precursors.[24] Oxidative transformations of ulosyl azides were also applied to obtain furanoid[25,26] and pyranoid[26] 2-azido-ulosonic acid derivatives.

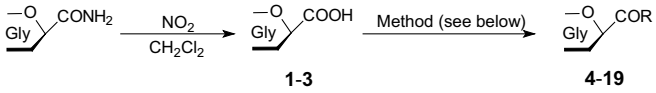
Herein the aim is to investigate the feasibility of radical-mediated brominations and subsequent azide substitutions to obtain 2-bromo- and 2-azido-2-deoxy-ulosonic acid derivatives (**IV** and **II**, respectively), which can be suitable for further manipulations to incorporate them into peptides.

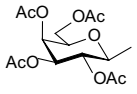
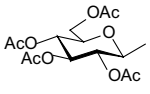
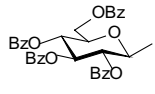
2. Results and discussion

The starting 2,6-anhydro-heptonic acids **1**–**3** were prepared by nitrosation of the corresponding heptonamides according to a literature protocol.[27] Standard procedures were used for the transformations of these acids, and the prepared derivatives are collected in Table 1. Formation of methyl esters **4** and **5** was straightforward using diazomethane. For the preparation of *tert*-butyl esters **6**–**8** several known methods were tried, however, only acid catalysed transesterification with *t*BuOAc proved satisfactory. The trichloroethyl esters **9**–**11** were obtained by a DCC-DMAP mediated coupling of trichloroethanol with the corresponding acid. Pentachlorophenol in the presence of DCC yielded active esters **12**–**14**. Acylated glycines **15**–**17** were prepared from **12**–**14**, respectively, because direct DCC coupling of acids **1**–**3** with glycine methyl ester gave large amounts of by-products. Acid chlorides **18** and **19** were made with PCl_5 as described.[28]

For brominations of the prepared acid derivatives (Table 2) three methods were investigated: bromine in $CHCl_3$ in the presence K_2CO_3 (method ***G***[11]); NBS in CCl_4 in the presence of Bz_2O_2 or AIBN (method ***H***[8]); $Na_2S_2O_4$–$KBrO_3$ in CH_2Cl_2–water biphasic solvent mixture (method ***I***[12]). Each of these methods resulted in

Table 1. Preparation of 2,6-anhydro-aldonic acids and their derivatives

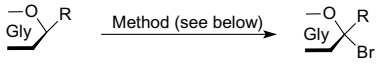


	Gly (***Method***: yield [%])		
			
Starting acid	**1** (82; lit.[27] 87)	**2** (72; lit.[27] 86)	**3** (76)
R			
–OMe	**4**[a] (***A***: 99)		**5** (***A***: 99)
–O*t*Bu	**6** (***B***: 77)	**7** (***B***: 42)	**8** (***B***: 73)
$-OCH_2CCl_3$	**9** (***C***: 78)	**10** (***C***: 70)	**11** (***C***: 76)
$-OC_6Cl_5$	**12** (***D***: 75)	**13** (***D***: 71)	**14** (***D***: 89)
$-NHCH_2COOMe$	**15** (***E***: 76)	**16** (***E***: 57)	**17** (***E***: 72)
–Cl	**18** (***F***: 75; lit.[28] 80)		**19** (***F***: 75)

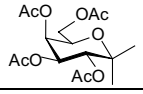
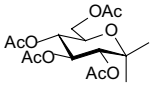
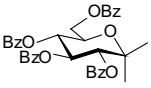
Method ***A***: CH_2N_2, Et_2O, acetone, rt, 5 min
B: *t*BuOAc, 60% aq $HClO_4$, rt, 3 d
C: CCl_3CH_2OH, DCC, DMAP, CH_2Cl_2, rt, 2–4 h
D: C_6Cl_5OH, DCC, CH_2Cl_2, rt, 4–6 h
E: Gly-$COOC_6Cl_5$ (**12**–**14**), $MeOOCCH_2NH_2{\cdot}HCl$, Et_3N, abs. 1,4-dioxane, rt
F: PCl_5, Et_2O, reflux, 3 h

[a] This compound was prepared earlier by transformation of acetylated *C*-glucopyranosyl nitromethane[29] or glucopyranosyl cyanide derivatives.[30]

Table 2. Bromination reactions of 2,6-anhydro-aldonic acid derivatives



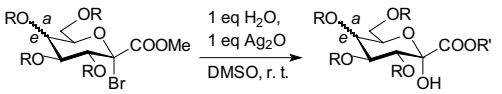
20-30

R	Gly (***Method***: yield [%])		
			
–COOH	Decomposition with methods ***G***, ***H*** and ***I***	Not investigated	
–COOMe	**20** (***G***: 75[a]) (***I***: 77[b])		**21** (***G***: 80) (***H***: 68) (***I***: 54 + 21 **32**)
–COO*t*Bu	**22** (***G***: decomposition) (***H***: clean reaction) (***I***: 85[b])		**23** (***G***: decomposition) (***H***: 83[b]) (***I***: 72[b])
$-COOCH_2CCl_3$	**24**[c] (***I***)	**25** (***I***)	**26**[d] (***I***)
$-COOC_6Cl_5$	**27** (***G***: 99) (***I***: 91)	**28** (***G***: 99)	**29** (***G***: 89)
–CONHCH$_2$COOMe	See text and Scheme 3	Not investigated	
–COCl	**30** (***H***: not isolated) See also Scheme 4		Decomposition

Method ***G***: Br_2, abs. $CHCl_3$, K_2CO_3, reflux
H: NBS, Bz_2O_2, or AIBN, abs. CCl_4, reflux
I: $Na_2S_2O_4$, $KBrO_3$, CH_2Cl_2, H_2O, rt

[a] Traces of **35** were separated by column chromatography.
[b] Crude product sufficiently pure for further transformation.
[c] Formed together with an unidentified bromine containing by-product and not isolated in a pure state (see text also).
[d] Formed together with **33** which was isolated after the azide substitution reaction.

multicomponent product mixtures when tried with acid **1**. Methyl esters **4** and **5** gave brominated products **20** and **21**, respectively, under each condition in 70–80% yields, except method ***I*** with **5** when ulosonic ester **32** was formed in significant proportion. Formation of **31** was not observed during transformation of **4** by method ***I***. Ulosonic esters **31** and **32** were also obtained by silver oxide promoted hydrolysis of bromides **20** and **21** in separate experiments (Scheme 2).



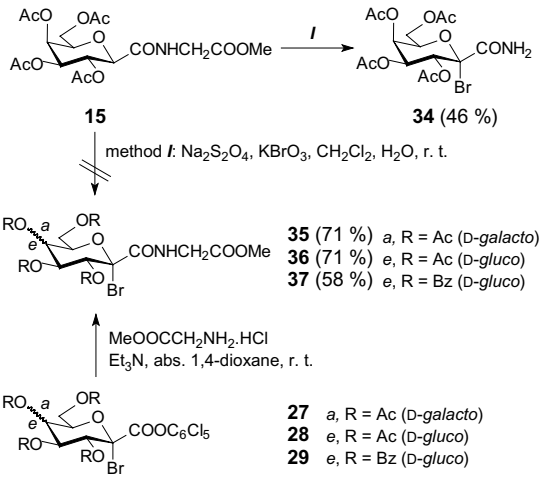
20 *a*, R = Ac (D-*galacto*) **31** (74 %) R' = Me
21 *e*, R = Bz (D-*gluco*) **32** (52 %) R' = Me
e, R = Bz (D-*gluco*) **33** R' = CH_2CCl_3

Scheme 2.

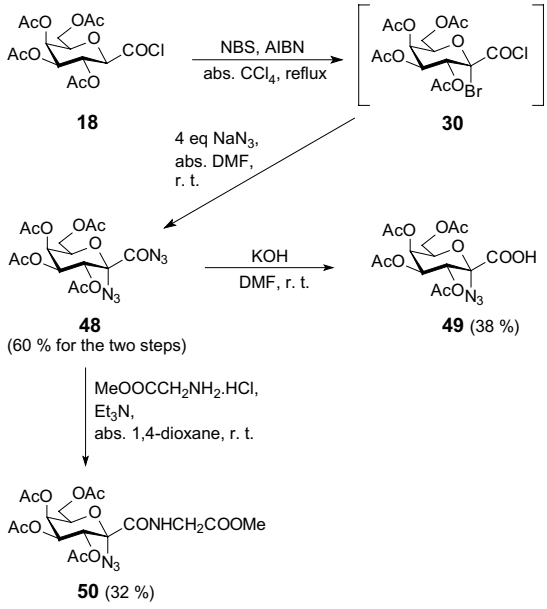
tert-Butyl esters **6** and **8** decomposed when brominated with method ***G***, but were transformed via clean reactions into bromides **22** and **23**, respectively, by methods ***H*** and ***I***. By method ***I*** trichloroethyl esters **9** and **10** each gave two bromine containing products, which were not separated, but immediately subjected to azide substitution. NMR spectra showed a ~10:1 ratio for the two compounds, and evidenced that the main products were **24** and **25**. We speculated that the minor products could be 1-bromo-2,2,2-trichloroethyl esters of the corresponding ulosonic acids (or those of the anomeric bromides **24** and **25**), which might arise from bromination of the methylene group (–COOCH_2CCl_3) with a captodative substitution pattern.[8] Bromination of **11** gave **26**, and the by-product isolated after the azide substitution reaction proved to be ulosonic ester **33**. Active esters **12**–**14** were brominated by methods ***G*** or ***I*** to give high yields of **27**–**29**, respectively. A modified Hell–Vollhard–Zelinsky reaction of acid chloride **18** under conditions ***H*** resulted in bromide **30**. Unfortunately, several attempts at brominating **19** proved unsuccessful, only formation of complex reaction mixtures was observed. Similarly, bromination of **15** under conditions of each method ***G***, ***H*** and ***I*** failed to give the expected bromide **35**, only 2-bromo-ulosonamide **34**[10] could be isolated from the multicomponent mixture (Scheme 3). Therefore, the targeted bromides **35**–**37** were prepared by substitution with glycine methyl ester in the brominated active esters **27**–**29**, respectively, whereby the anomeric bromides remained untouched.

Azide substitutions in the bromo derivatives were performed with NaN_3 in DMSO or DMF solutions as described previously.[21] With the exception of bromides of active esters **27** and **29**, which decomposed under these conditions, the transformations gave azides **38**–**47** in good yields without difficulties (Table 3).

Reaction of **30** with excess NaN_3 produced 2-azido-ulosonic azide **48** with retained anomeric configuration



Scheme 3.



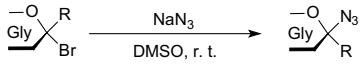
Scheme 4.

(Scheme 4). Although mechanistic features were not studied in detail this unexpected result can be explained in two plausible ways. First, chloride ions liberated by azide from the acid chloride moiety (which must be more reactive than the anomeric bromide in this particular compound) invert configuration of the anomeric carbon which, in a second inversion during the azide substitution, gives the retention product. A similar process could be elicited by external chloride in the case of 2-bromo-2-deoxy-ulosononitriles.[21] Second, substitutions by azide ions may have some radical nucleophilic character (S_{RN} or SET reactions) that was demonstrated with 2-bromo-ulosononitriles, as well.[21] This would imply the appearance of glycosyl radicals on the reaction pathway, which are known to exhibit axial selectivity in their reactions.[31] As the azide substitution of **30** performed in the presence of radical traps (1,4-dinitrobenzene, galvinoxyl) resulted in mixtures of unidentified products, among which **48** could not be detected, the understanding of the stereoselectivity of this reaction in this way can also be relevant. Acylation of glycine methyl ester with **48** gave **50**, which is the epimer of **45**.

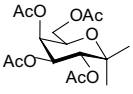
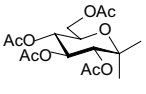
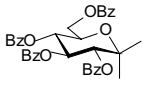
2-Azido-ulosonic azide **48** was also transformed into anomeric α-azido acid **49** by KOH in DMF (Scheme 4). In order to obtain the epimer of **49** the hydrolysis of *tert*-butyl ester **40** was investigated first, however, several established methods brought about no change at all or resulted in decomposition. Deprotection of trichloroethyl ester **42** (Scheme 5) under the usual Zn/AcOH conditions gave anomeric α-amino acid **52**, while Zn dust in the presence of 1-methylimidazole (NMI) left the azido group unchanged to yield **51**.[32]

Structural elucidation of the new compounds was straightforward by established NMR methods. The configuration of the anomeric carbons lacking hydrogens was deduced from the three bond coupling between H-2 (parent carbohydrate numbering) and the carbon attached to the anomeric centre as described earlier.[9,21] The presence of the azide group was shown by the IR spectra as expected (see Experimental).

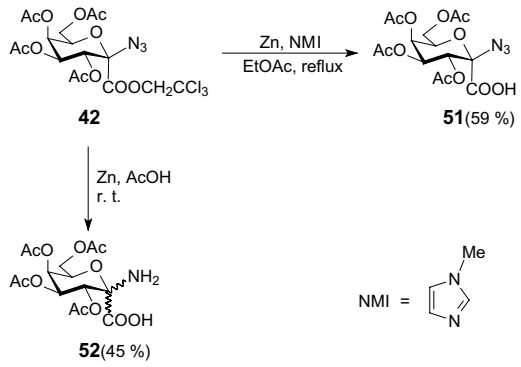
Table 3. Azide substitutions in the brominated 2,6-anhydro-aldonic acid derivatives



38-47

R	Gly (Yield [%])		
			
–COOMe	**38** (84)		**39** (75)
–COO*t*Bu	**40** (69)		**41** (56)
–$COOCH_2CCl_3$	**42** (59[a])	**43** (60[a])	**44** (59[a])
–$COOC_6Cl_5$	Decomposition		Decomposition
–$CONHCH_2COOMe$	**45** (65)	**46** (69)	**47** (66)

[a] Yield refers to two steps: bromination and azide substitution.



Scheme 5.

3. Conclusion

Investigation of the radical-mediated bromination of several derivatives of per-*O*-acylated *C*-(β-D-glycopyranosyl)formic acids (2,6-anhydro-D-hept-2-ulopyranosonic acids) revealed that bromine can be introduced in an *axial* position at the anomeric carbon of methyl-, *tert*-butyl-, 2,2,2-trichloroethyl-, and pentachlorophenyl esters and acid chlorides. Similar bromination of glycinamides gave only *C*-(1-bromo-1-deoxy-β-D-glycopyranosyl)formamides. This cleavage showed similar reactivity of the amino acid moiety and the anomeric centre. Bromo derivatives of glycinamides could be obtained by acylation of glycine esters by the bromide of pentachlorophenyl esters. In this reaction the anomeric bromide was not substituted.

Replacement of the anomeric bromide with azide ion took place with inversion in the esters and the glycinamides to yield *equatorial* azides. On the other hand, retention at the anomeric centre and formation of an acid azide was observed in the reaction of the acid chloride derivative. Acylation of glycine methyl ester by this latter acid azide opened up a route to a glycinamide with an *axial* azide group. In this way highly selective synthetic sequences have been found for both anomers of dipeptides containing anomeric α-azido acids.

4. Experimental

4.1. General methods

Melting points were measured in open capillary tubes or on a Kofler hot stage and are uncorrected. Optical rotations were determined on a Perkin–Elmer 241 polarimeter at room temperature. IR spectra were taken with a Perkin–Elmer 16 PC FT-IR spectrometer. NMR spectra were recorded with Bruker WP 360 SY (360/90 MHz for $^{1}H/^{13}C$) and Varian UNITYINOVA 400 WB (400/100 MHz for $^{1}H/^{13}C$) spectrometers. Chemical shifts are referenced to internal Me_4Si (^{1}H) or the residual solvent signal (^{13}C). TLC was performed on DC Alurolle Kieselgel 60 F_{254} (Merck), the plates were visualised by gentle heating. For column chromatography Kieselgel 60 (Merck, particle size 0.063–0.200 mm) was used. Distilled solvents (CH_2Cl_2, $CHCl_3$, 1,4-dioxane, DMSO) were dried by storage over 4 Å molecular sieves. Organic solutions were dried over anhydrous $MgSO_4$ and concentrated in vacuo at 40–50 °C (water bath).

4.2. General procedure I

*For the preparation of per-*O*-acylated* C-*(β-*D*-glycopyranosyl)formic acids (2,6-anhydro aldonic acids)* **1**–**3** (adapted from Ref. 27): A per-*O*-acylated 2,6-anhydro aldonamide (5.5 g) was dissolved in abs. CH_2Cl_2 (50 mL) and a solution of NO_2 (obtained by heating $PbNO_3$) in abs. CH_2Cl_2 (10 mL, saturated at −20 °C) was added dropwise. The reaction mixture was stirred at room temperature and monitored by TLC (eluent: toluene–acetone 1:1). After completion of the transformation the solvent was evaporated, and the crude product purified by crystallisation from Et_2O.

4.2.1. *C*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-formic acid (3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-D-*glycero*-L-*manno*-heptonic acid) 1. Prepared from 3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-D-*glycero*-L-*manno*-heptonamide[27] according to general procedure I. Yield: 82% (lit.[27] 86%) white crystalline product; mp: 132–134 °C; (lit.[27] 132–134 °C). The NMR data were identical with the published ones.

4.2.2. *C*-(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)formic acid (3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-D-*glycero*-D-*gulo*-heptonic acid) 2. Prepared from 3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-D-*glycero*-D-*gulo*-heptonamide[27] according to general procedure I. Yield: 72% (lit.[27] 85%) white crystalline product; mp: 129–131 °C (lit.[27] 138–140 °C). The NMR data were identical with the published ones.

4.2.3. *C*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-formic acid (2,6-anhydro-3,4,5,7-tetra-*O*-benzoyl-D-*glycero*-D-*gulo*-heptonic acid) 3. Prepared from 2,6-anhydro-3,4,5,7-tetra-*O*-benzoyl-D-*glycero*-D-*gulo*-heptonamide[11] according to general procedure I. Yield: 4.18 g (76%) white crystalline product; mp 181–184 °C; $[\alpha]_D = +14$ (*c* 0.41, $CHCl_3$); ν_{max} (KBr): 3328–2840, 1732, 1490, 1270, 1070, 708; ^{1}H NMR ($CDCl_3$) δ (ppm): 8.01–7.81 (20H, m, Ph), 5.94 (1H, s, COOH), 5. 94 (1H, pseudo t, $J = 9.4$, 9.0 Hz, H-2), 5.75–5.67 (2H, m, H-3, H-4), 4.64 (1H, dd, $J = 12.0$, 4.2 Hz, H-6), 4.5 (1H, dd, $J = 12.0$, 2.1 Hz, H-6′), 4.35 (1H, d, $J = 9.0$ Hz, H-1), 4.22 (1H, ddd, $J = 12.0$, 4.2, 2.1 Hz, H-5); ^{13}C NMR ($CDCl_3$) δ (ppm): 165.7 (COOH),165.4, 165.1 (3) (CO), 133.4–128.3 (aromatics), 76.3 (C-1), 76.3, 73.7, 69.9, 69.1 (C-3 to C-5), 63.2 (C-6). Anal. Calcd for $C_{35}H_{28}O_{11}$ (624.61): C, 67.30; H, 4.52. Found: C, 67.35; H, 4.49.

4.3. Method *A*: preparation of per-*O*-acylated methyl C-(β-D-glycopyranosyl)formates (methyl 2,6-anhydro-aldonates) 4 and 5

A per-*O*-acylated 2,6-anhydro-aldonic acid (**1** or **3**, 3 g) was dissolved in acetone (50 mL) and diazomethane in Et_2O solution was added. After disappearance of the

starting material (TLC, ethyl acetate–hexane 1:1) the solvent was removed in vacuo, and the residue was crystallised from Et_2O.

4.3.1. Methyl *C*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)formate (methyl 3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-D-*glycero*-L-*manno*-heptonate) 4. Prepared from **1** according to Method ***A***. Yield: 3.09 g (99%) white crystalline product; mp: 146–148 °C; $[\alpha]_D = +17$ (*c* 1.17, $CHCl_3$); ν_{max} (KBr): 3904, 1760, 1376, 1240, 1070; ^1H NMR ($CDCl_3$) δ (ppm): 5.45 (1H, dd, $J = 3.7$, 1.2 Hz, H-4), 5.37 (1H, t, $J = 9.9$, 9.8 Hz, H-2), 5.11 (1H, dd, $J = 9.9$, 3.7 Hz, H-3), 4.17–4.12 (2H, m, H-6, H-6′), 3.99 (1H, d, $J = 9.8$ Hz, H-1), 3.95 (1H, ddd, $J = 6.7$, 6.7, 1.2 Hz, H-5), 3.76 (3H, s, OCH_3), 2.23, 2.11, 2.10, 2.06 (12H, 4 × s, OAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.2, 170.1, 169.8, 169.4 (CO), 167.4 (*C*OOCH$_3$), 76.8 (C-1), 74.6, 71.3, 67.1, 66.6 (C-2 to C-5), 61.5 (C-6), 52.8 (OCH_3), 20.5, 20.4 (CH_3). Anal. Calcd for $C_{16}H_{22}O_{11}$ (390.35): C, 49.23; H, 5.68. Found: C, 48.90; H, 5.88.

4.3.2. Methyl *C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formate (methyl 2,6-anhydro-3,4,5,7-tetra-*O*-benzoyl-D-*glycero*-D-*gulo*-heptonate) 5. Prepared from **3** according to Method ***A***. Yield: 3.03 g (99%) white crystalline product; mp: 149–150 °C; $[\alpha]_D = +14$ (*c* 1.22, $CHCl_3$); ν_{max} (KBr): 3850, 3066, 1732, 1490, 1270, 1070, 708; ^1H NMR ($CDCl_3$) δ (ppm): 8.02–7.25 (20H, m, Ph), 5.96 (1H, t, $J = 10.0$, 9.8 Hz, H-3), 5.69 (1H, t, $J = 9.8$, 9.8 Hz, H-4), 5.71 (1H, t, $J = 10.0$, 9.9 Hz, H-2), 4.64 (1H, dd, $J = 11.7$, 4.9 Hz, H-6), 4.52 (1H, dd, $J = 11.7$, 3.1 Hz, H-6′), 4.36 (1H, d, $J = 9.9$ Hz, H-1), 4.18 (1H, ddd, $J = 9.8$, 4.9, 3.1 Hz, H-5), 3.68 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$) δ (ppm): 167.2 (*C*OOCH$_3$), 165.9, 165.6, 165.0, 164.9 (CO), 133.3–128.1 (aromatics), 76.7 (C-1), 76.2, 73.4, 70.2, 69.1 (C-2 to C-5), 63.1 (C-6), 52.7 (OCH_3). Anal. Calcd for $C_{36}H_{30}O_{11}$ (638.63): C, 67.71; H, 4.73; O, 27.56. Found: C, 67.68; H, 4.74; O, 27.60.

4.4. Method *B*: preparation of per-*O*-acylated *tert*-butyl *C*-(β-D-glycopyranosyl)formates (*tert*-butyl 2,6-anhydro aldonates) 6–8

A per-*O*-acylated 2,6-anhydro-aldonic acid **1** or **2** or **3** was dissolved in *tert*-butyl acetate (6 mL/mmol) and 60% $HClO_4$ (0.1 equiv) was added to the solution. The reaction mixture was stirred at room temperature for 3 days. After completion of the reaction (TLC, ethyl acetate–hexane 1:1) the solution was diluted with CH_2Cl_2 (10 mL) 4× and washed with water (10 mL), satd. aqueous $NaHCO_3$ (2×10 mL) and water (10 mL). After drying the solvent was evaporated in vacuo, and the crude product crystallised during standing at 4 °C or was purified by column chromatography in the case of **8**.

4.4.1. *tert*-Butyl *C*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)formate (*tert*-butyl 3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-D-*glycero*-D-*manno*-heptonate) 6. Prepared from **1** (0.30 g, 0.70 mmol) according to Method ***B***. Yield: 0.26 g (77%) white crystalline product; mp: 74–77 °C; $[\alpha]_D = +12$ (*c* 1.1, $CHCl_3$); ν_{max} (KBr): 2976, 1750, 1372, 1214, 1020; ^1H NMR ($CDCl_3$) δ (ppm): 5.43 (1H, dd, $J = 3.7$, <1 Hz, H-4), 5.38 (1H, dd, $J = 10.8$, 9.6 Hz, H-2), 5.07 (1H, dd, $J = 9.6$, 3.7 Hz, H-3), 4.18–4.15 (2H, m, H-6, H-6′), 3.95 (1H, ddd, $J = 7.5$, 7.5, <1 Hz, H-5), 3.90 (1H, d, $J = 10.8$ Hz, H-1), 2.18, 20.5, 2.04, 1.98 (12H, 4 × s, OAc), 1.45 (9H, s, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.3, 170.0, 169.0 (CO), 166.0 (*C*OOC(CH$_3$)$_3$), 82.9 (COO*C*(CH$_3$)$_3$), 77.1 (C-1), 74.2, 71.7, 67.0, 66.4 (C-2 to C-5), 61.4 (C-6), 27.7 (COOC(*C*H$_3$)$_3$), 20.6, 20.5 (CH_3). Anal. Calcd for $C_{19}H_{28}O_{11}$ (432.42): C, 52.77; H, 6.53. Found: C, 52.69; H, 6.61.

4.4.2. *tert*-Butyl *C*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)formate (*tert*-butyl 3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-D-*glycero*-D-*gulo*-heptonate) 7. Prepared from **2** (0.20 g, 0.53 mmol) according to Method ***B***. Yield: 0.09 g (42%) white crystalline product; mp: 101–103 °C; $[\alpha]_D = -5$ (*c* 1.02, $CHCl_3$); ν_{max} (KBr): 2972, 1760, 1376, 1220, 1026; ^1H NMR ($CDCl_3$) δ (ppm): 5.26–5.18 (2H, m, H-2, H-3), 5.10 (1H, dd, $J = 9.4$, 9.2 Hz, H-4), 4.26 (1H, dd, $J = 12.5$, 4.6 Hz, H-6), 4.15 (1H, dd, $J = 12.5$, 2.0 Hz, H-6′), 3.91 (1H, d, $J = 9.8$ Hz, H-1), 3.70 (1H, ddd, $J = 12.5$, 4.6, 2.0 Hz, H-5), 2.09, 2.03, 2.01 (12H, 4 × s, OAc), 1.45 (9H, s, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.5, 170.1, 169.2, 168.8 (CO), 165.7 (*C*OOC(CH$_3$)$_3$), 82.9 (COO*C*(CH$_3$)$_3$), 77.0 (C-1), 75.7, 73.7, 69.2, 67.9 (C-2 to C-5), 61.9 (C-6), 27.7 (COOC(*C*H$_3$)$_3$), 20.6, 20.5 (CH_3). Anal. Calcd for $C_{19}H_{28}O_{11}$ (432.42): C, 52.77; H, 6.53. Found: C, 52.61; H, 6.41.

4.4.3. *tert*-Butyl *C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formate (*tert*-butyl 2,6-anhydro-3,4,5,7-tetra-*O*-benzoyl-D-*glycero*-D-*gulo*-heptonate) 8. Prepared from **3** (0.30 g, 0.69 mmol) according to Method ***B***. Purified by column chromatography (eluent: ethyl acetate–hexane 1:2), conversion 95%. Yield: 0.229 g (73%) white crystalline product; mp: 119–121 °C; $[\alpha]_D = +29$ (*c* 1.05, $CHCl_3$); ν_{max} (KBr): 3062, 2978, 1740, 1492, 1096, 708; ^1H NMR ($CDCl_3$) δ (ppm): 8.18–7.22 (20H, m, Ph), 5.94 (1H, dd, $J = 9.8$, 9.2 Hz, H-2), 5.76 (1H, t, $J = 10.5$, 10.5 Hz, H-4), 5.72 (1H, dd, $J = 10.5$, 9.8 Hz, H-3), 4.64 (1H, dd, $J = 12.5$, 3.3 Hz, H-6), 4.54 (1H, dd, $J = 12.5$, 5.2 Hz, H-6′), 4.48 (1H, d, $J = 9.8$ Hz, H-1), 4.18 (1H, ddd, $J = 12.5$, 5.2, 3.3 Hz, H-5), 2.05 (9H, s, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ (ppm): 166.1, 165.7, 165.1 (CO), 164.8 (*C*OOC(CH$_3$)$_3$), 133.3–128.2 (aromatics), 83.0 (COO*C*(CH$_3$)$_3$), 76.0 (C-1), 73.9, 69.9, 69.3, 63.2 (C-2 to C-5), 27.5 (COOC(*C*H$_3$)$_3$). Anal. Calcd for $C_{39}H_{36}O_{11}$ (680.11): C, 68.81; H, 5.33. Found: C, 68.96; H, 5.43.

4.5. Method *C*: preparation of per-*O*-acylated 2,2,2-trichloroethyl *C*-(β-D-glycopyranosyl)formates (2,2,2-trichloroethyl 2,6-anhydro-aldonates) 9–11

A per-*O*-acylated 2,6-anhydro-aldonic acid **1** or **2** or **3** was dissolved in abs. CH_2Cl_2 (10 mL/mmol), and 3 equiv 2,2,2-trichloroethanol, 1 equiv DCC, and 0.1 equiv DMAP were added. The reaction mixture was stirred at room temperature until TLC (ethyl acetate–hexane 1:1) showed complete transformation

(~4 h). After filtration the solvent was removed in vacuo, and the residue purified by column chromatography (eluent: ethyl acetate–hexane 1:1).

4.5.1. 2,2,2-Trichloroethyl *C*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)formate (2,2,2-trichloroethyl 3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-D-*glycero*-L-*manno*-heptonate) 9. Prepared from **1** (0.30 g, 0.80 mmol) according to Method ***C***. Yield: 0.30 g (75%) colourless oil (R_f = 0.39, ethyl acetate–hexane 1:1); $[\alpha]_D = -6$ (*c* 0.20, $CHCl_3$); ν_{max} ($CHCl_3$): 2968, 1756, 1370, 1236, 1070, 700; ^{1}H NMR ($CDCl_3$) δ (ppm): 5.47 (1H, dd, *J* = 2.9, <1 Hz, H-4), 5.41 (1H, dd, *J* = 10.3, 9.6 Hz, H-2), 5.15 (1H, dd, *J* = 9.6, 2.9 Hz, H-3), 4.90 (1H, d, *J* = 11.8 Hz, CH_2), 4.66 (1H, d, *J* = 11.8 Hz, CH_2), 4.20 (1H, d, *J* = 9.6 Hz, H-1), 4.19–4.17 (2H, m, H-6, H-6′), 4.02 (1H, ddd, *J* = 5.9, 6.0, <1 Hz, H-5), 2.18, 2.06, 2.05, 2.04 (12H, 4 × s, OAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.3, 170.2, 169.8, 169.5 (CO), 165.6 (*C*OOCH$_2$CCl$_3$), 94.1 (COOCH$_2$*C*Cl$_3$), 76.1 (C-1), 74.8 (COO*C*H$_2$CCl$_3$), 74.4, 71.3, 66.9, 66.5 (C-2 to C-5), 61.3 (C-6), 20.7, 20.5, 20.4 (CH_3). Anal. Calcd for $C_{17}H_{21}Cl_3O_{11}$ (507.71): C, 40.22; H, 4.17; Cl, 20.95. Found: C, 40.02; H, 3.98; Cl, 20.80.

4.5.2. 2,2,2-Trichloroethyl *C*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)formate (2,2,2-trichloroethyl 3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-D-*glycero*-D-*gulo*-heptonate) 10. Prepared from **2** (0.40 g, 1.06 mmol) according to Method ***C***: Yield: 0.38 g (70%) white crystalline product from Et_2O; mp: 115–117 °C; $[\alpha]_D = -2$ (*c* 0.21, $CHCl_3$); ν_{max} (KBr): 2980, 1738, 1270, 1090, 640; ^{1}H NMR ($CDCl_3$) δ (ppm): 5.29 (1H, t, *J* = 9.4, 9.2 Hz, H-2), 5.25 (1H, t, *J* = 9.2, 9.2 Hz, H-3), 5.14 (1H, t, *J* = 9.2, 9.2 Hz, H-4), 4.85 (1H, d, *J* = 11.9 Hz, CH_2), 4.69 (1H, d, *J* = 12.0 Hz, CH_2), 4.27 (1H, dd, *J* = 11.8, 5.2 Hz, H-6), 4.22 (1H, d, *J* = 9.4 Hz, H-1), 4.11 (1H, dd, *J* = 11.8, 6.2 Hz, H-6′), 3.77 (1H, ddd, *J* = 11.8, 6.2, 5.6Hz, H-5), 2.10, 2.05, 2.03 (12H, 4 × s, OAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.7, 170.2, 169.4, 169.3 (CO), 165.5 (*C*OOCH$_2$CCl$_3$), 93.9 (COOCH$_2$*C*Cl$_3$), 76.0 (C-1), 74.8 (COO*C*H$_2$CCl$_3$), 75.9, 73.4, 69.4, 67.7 (C-2 to C-5), 61.8 (C-6). Anal. Calcd for $C_{17}H_{21}Cl_3O_{11}$ (507.71): C, 40.22; H, 4.17; Cl, 20.95. Found: C, 39.96; H, 4.29; Cl, 20.85.

4.5.3. 2,2,2-Trichloroethyl *C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formate (2,2,2-trichloroethyl 2,6-anhydro-3,4,5,7-tetra-*O*-benzoyl-D-*glycero*-D-*gulo*-heptonate) 11. Prepared from **3** (0.30 g, 0.48 mmol) according to Method ***C***. Yield: 0.28 g (76%) white crystalline product from ethyl acetate–hexane; mp 163–164 °C; $[\alpha]_D = +15$ (*c* 0.42, $CHCl_3$); ν_{max} (KBr): 3060, 2980, 1732, 1270, 1090, 708, 640; ^{1}H NMR ($CDCl_3$) δ (ppm): 8.08–7.22 (20H, m, Ph), 6.00 (1H, t, *J* = 9.6, 9.6 Hz, H-2), 5.80–5.70 (2H, m, H-3, H-4), 4.85 (1H, d, *J* = 11.8 Hz, CH_2), 4.68 (1H, dd, *J* = 12.5, 2.2 Hz, H-6), 4.58 (1H, d, *J* = 11.8 Hz, CH_2), 4.54 (1H, d, *J* = 9.6 Hz, H-1), 4.52 (1H, dd, *J* = 12.5, 5.1 Hz, H-6′), 4.23 (1H, ddd, *J* = 12.5, 5.1, 2.2 Hz, H-5); ^{13}C NMR ($CDCl_3$) δ (ppm): 166.0 (*C*OOCH$_2$CCl$_3$), 165.7, 165.5, 165.2, 165.1 (CO), 133.5–128.3 (aromatics), 93.5 (COOCH$_2$*C*Cl$_3$), 76 4 (C-1), 74.9 (COO*C*H$_2$CCl$_3$), 76.4, 73.5, 70.2, 69.0 (C-2 to C-5), 62.9 (C-6). Anal. Calcd for $C_{37}H_{29}Cl_3O_{11}$ (756.00): C, 58.79; H, 3.87; Cl, 14.07. Found: C, 58.60; H, 3.71; Cl, 13.88.

4.6. Method *D*: preparation of per-*O*-acylated pentachlorophenyl *C*-(β-D-glycopyranosyl)formates (pentachlorophenyl 2,6-anhydro-aldonates) 12–14

A per-*O*-acylated 2,6-anhydro-aldonic acid **1** or **2** or **3** was dissolved in abs. CH_2Cl_2 (15 mL/mmol), and 3 equiv pentachlorophenol and 1 equiv DCC were added. The reaction mixture was stirred at rt and monitored by TLC (ethyl acetate–hexane 1:1). When the reaction was completed, the solvent was evaporated in vacuo, and the crude product purified by column chromatography (eluent: ethyl acetate–hexane 1:1).

4.6.1. Pentachlorophenyl *C*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)formate (pentachlorophenyl 3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-D-*glycero*-L-*manno*-heptonate) 12. Prepared from **1** (0.5 g, 1.33 mmol) according to Method ***D***. Yield: 0.62 g (75%) white crystalline product from Et_2O; mp: 130–132 °C; $[\alpha] = +21$ (*c* 1.02, $CHCl_3$); ν_{max} (KBr): 3436, 1754, 1364, 1226, 1096, 600; ^{1}H NMR ($CDCl_3$) δ (ppm): 5.66 (1H, t, *J* = 9.8, 9.8 Hz, H-2), 5.49 (1H, dd, *J* = 3.3, <1 Hz, H-4), 5.16 (1H, dd, *J* = 9.8, 3.3 Hz, H-3), 4.44 (1H, d, *J* = 9.8 Hz, H-1), 4.26 (1H, dd, *J* = 11.2, 6.6 Hz, H-6), 4.19 (1H, dd, *J* = 11.2, 6.6 Hz, H-6′), 4.10 (1H, ddd, *J* = 6.6, 6,6, <1 Hz, H-5), 2.21, 2.07, 2.04, 2.02 (12H, 4 × s, OAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.3, 170.2, 170.0, 168.8 (CO), 162.8 (*C*OOC$_6$Cl$_5$), 143.2–127.3 (aromatics), 76.3 (C-1), 75.0, 71.8, 66.9, 65.9 (C-2 to C-5), 61.1 (C-6), 20.6, 20.5 (CH_3). Anal. Calcd for $C_{21}H_{19}Cl_5O_{11}$ (624.64): C, 40.38; H, 3.07; Cl, 28.38. Found: C, 40.18; H, 2.92; Cl, 28.20.

4.6.2. Pentachlorophenyl *C*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)formate (pentachlorophenyl 3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-D-*glycero*-D-*gulo*-heptonate) 13. Prepared from (0.2 g 0.53 mmol) **2** according to Method ***D***. Yield: 0.23 g (71%) white crystalline product from Et_2O; mp: 148–150 °C; $[\alpha]_D = -15$ (*c* 1.03, $CHCl_3$); ν_{max} (KBr): 3420, 1752, 1370, 1220, 1056, 600; ^{1}H NMR ($CDCl_3$) δ (ppm): 5.48 (1H, pseudo t, *J* = 10.5, 9.8 Hz, H-2), 5.30 (1H, pseudo t, *J* = 9.8, 9.2 Hz, H-4), 5.22 (1H, pseudo t, *J* = 9.8, 9.2 Hz, H-3), 4.46 (1H, d, *J* = 10.5 Hz, H-1), 4.34 (1H, dd, *J* = 12.5, 4.6 Hz, H-6), 4.22 (1H, dd, *J* = 12.5, 2.0 Hz, H-6′), 3.86 (1H, ddd, *J* = 12.5, 4.6, 2.0 Hz, H-5), 2.10, 2.05, 2.00, 1.95 (12H, 4 × s, OAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.5, 170.2, 169.2, 168.8 (CO), 162.7 (*C*OOC$_6$Cl$_5$), 143.1–127.2 (aromatics), 76.3 (C-1), 75.9, 73.8, 68.9, 67.6 (C-2 to C-5), 61.7 (C-6), 20.6, 20.5 (CH_3). Anal. Calcd for $C_{21}H_{19}Cl_5O_{11}$ (624.64): C, 40.38; H, 3.07; Cl, 28.38. Found: C, 40.09; H, 3.17; Cl, 28.12.

4.6.3. Pentachlorophenyl *C*-(2,3,4,6-tetra-*O*-benzoyl-β-D-glucopyranosyl)formate (pentachlorophenyl 2,6-anhydro-3,4,5,7-tetra-*O*-benzoyl-D-*glycero*-D-*gulo*-heptonate) 14. Prepared from **3** (0.50 g, 0.80 mmol) according to

Method ***D***. Yield: 0.63 g (89%) white crystalline product from Et_2O; mp: 171–173 °C; $[\alpha]_D$ = +24 (*c* 1.01, $CHCl_3$); ν_{max} (KBr): 3904, 1742, 1584, 1492, 1270, 1070, 708, 620; ^1H NMR ($CDCl_3$) δ (ppm): 8.18–7.25 (20H, m, Ph), 6.04 (1H, dd, *J* = 9.8, 9.2 Hz, H-2), 5.96 (1H, pseudo t, *J* = 9.8, 9.2 Hz, H-3), 5.78 (1H, pseudo t, *J* = 9.8, 9.2 Hz, H-4), 4.82 (1H, d, *J* = 9.8 Hz, H-1), 4.72 (1H, dd, *J* = 12.5, 3.3 Hz, H-6), 4.55 (1H, dd, *J* = 12.5, 5.9 Hz, H-6′), 4.31 (1H, ddd, *J* = 12.5, 5.9, 3.3 Hz, H-5); ^{13}C NMR ($CDCl_3$) δ (ppm): 165.9, 165.7, 165.1, 164.6 (CO), 162.7 (*C*OOC_6Cl_5), 143.1–127.3 (aromatics), 76.8 (C-1), 76.6, 73.9, 69.4, 69.1 (C-2 to C-5), 62.8 (C-6). Anal. Calcd for $C_{41}H_{27}Cl_5O_{11}$ (872.92): C, 56.41; H, 3.12; Cl, 20.31. Found: C, 56.10; H, 2.95; Cl, 20.20.

4.7. Method *E*: preparation of *N*-(per-*O*-acyl-2,6-anhydro-aldonoyl)glycine methylesters 15–17, and *N*-(per-*O*-acyl-2-substituted-2-deoxy-hept-2-ulopyranosonoyl)-glycine methylesters 35–37 and 50

An acid derivative **12**–**14**, or **27**–**29**, or **48** was dissolved in abs. 1,4-dioxane (3 mL/mmol), and MeO_2CCH_2-NH_2·HCl (2 equiv) followed by Et_3N (2 equiv) were added. The mixture was stirred at rt and monitored by TLC (ethyl acetate–hexane 1:1) until the starting material disappeared. The solvent was then evaporated in vacuo, and the residue purified by column chromatography (eluent: ethyl acetate–hexane 1:1). The product crystallised during standing at rt.

4.7.1. *N*-[(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-carbonyl]glycine methylester (*N*-(3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-D-*glycero*-L-*manno*-heptonoyl)glycine methylester) 15. Prepared from **12** (0.25 g 0.40 mmol) according to Method ***E***. Yield: 0.14 g (76%) white crystalline product; mp: 114–117 °C; $[\alpha]_D$ = +27 (c 0.98, $CHCl_3$); ν_{max} (KBr): 3370, 2950, 1752, 1370, 1230, 1070, 720; ^1H NMR ($CDCl_3$) δ (ppm): 7.20 (1H, t, *J* = 5.3, 5.3 Hz, NH), 5.48 (1H, dd, *J* = 3.7, 1.0 Hz, H-4), 5.34 (1H, t, *J* = 10.0, 10.0, H-2), 5.12 (1H, dd, *J* = 10.0, 3.7 Hz, H-3), 4.24 (1H, dd, *J* = 11.0, 6.8 Hz, H-6),4.15 (1H, dd, *J* = 18.4, 5.3 Hz, CH_2), 4.12 (1H, dd, *J* = 11.0, 3.2 Hz, H-6′), 4.06 (1H, ddd, *J* = 6.8, 6.8, 1.0 Hz, H-5), 3.98 (1H, d, *J* = 10.0 Hz, H-1), 3.94 (1H, dd, *J* = 18.4, 5.3 Hz, CH_2), 3.78 (3H, s, OCH_3), 2.18, 2.08, 1.98 (12H, 4 × s, OAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.2 (*C*OOCH_3), 169.9, 169.8, 169.7, 169.6 (CO), 167.0 (*C*ONH), 76.0 (C-1), 74.3, 71.2, 67.0, 66.3 (C-2 to C-5), 61.3 (C-6), 52.2 (COO*C*H_3), 40.6 (CH_2), 20.6, 20.5, 20.4 (CH_3). Anal. Calcd for $C_{18}H_{25}NO_{12}$ (447.40): C, 48.32; H, 5.63; N, 3.13. Found: C, 48.01; H, 5.70; N, 3.36.

4.7.2. *N*-[(2,3,4,6-Tetra-*O*-acetyl-β-D-glucopyranosyl)-carbonyl]glycine methylester (*N*-(3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-D-*glycero*-D-*gulo*-heptonoyl)glycine methylester) 16. Prepared from **13** (0.15 g, 0.24 mmol) according to Method ***E***. Yield: 0.06 g (57%) white crystalline product; mp: 111–113 °C; $[\alpha]_D$ = +10 (*c* 0.97, $CHCl_3$); ν_{max} (KBr): 3368, 2972, 1760, 1370, 1230, 1070, 720; ^1H NMR ($CDCl_3$) δ (ppm): 6.92 (1H, t, *J* = 5.3, 5.3 Hz, NH), 5.27 (1H, t, *J* = 9.5, 9.5 Hz, H-2), 5.15 (1H, dd, *J* = 10.0, 9.5, H-3), 5.09 (1H, dd, *J* = 10.0, 9.5 Hz, H-4), 4.29 (1H, dd, *J* = 12.6, 5.3 Hz, H-6), 4.21 (1H, dd, *J* = 12.6, 2.1 Hz, H-6′), 4.17 (1H, dd, *J* = 18.4, 5.3 Hz, CH_2), 3.97 (1H, d, *J* = 9.5 Hz, H-1), 3.95 (1H, dd, *J* = 18.4, 5.3 Hz, CH_2), 3.78 (1H, ddd, *J* = 12.6, 5.3, 2.1, Hz, H-5), 3.76 (3H, s, OCH_3), 2.12, 2.05, 2.03, 1.99 (12H, 4 × s, OAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.5 (*C*OOCH_3), 169.9, 169.6, 169.3, 169.2 (CO), 166.8 (*C*ONH), 75.7 (C-1), 75.7, 73.3, 69.2, 68.0 (C-2 to C-5), 61.7 (C-6), 52.3 (COO*C*H_3), 40.7 (*C*H_2), 20.6, 20.5 (CH_3). Anal. Calcd for $C_{18}H_{25}N_1O_{12}$ (447.70): C, 48.32; H; 5.63; N, 3.13. Found: C, 48.42; H, 5.46; N, 3.26.

4.7.3. *N*-[(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-carbonyl]glycine methylester (*N*-(2,6-anhydro-3,4,5,7-tetra-*O*-benzoyl-D-*glycero*-D-*gulo*-heptonoyl)glycine methylester) 17. Prepared from **14** (0.20 g, 0.23 mmol) according to Method ***E***. Yield: 0.11 g (72%) colourless oil (R_f = 0.33, ethyl acetate–hexane 1:1); $[\alpha]_D$ = +10 (*c* 0.96, $CHCl_3$); ν_{max} ($CHCl_3$): 3648, 2950, 1736, 1522, 1492, 1268, 1070, 708; ^1H NMR ($CDCl_3$) δ (ppm): 8.12–7.22 (20H, m, Ph), 7.07 (1H, t, *J* = 5.3, 5.3 Hz, NH), 5.95 (1H, t, *J* = 9.2, 9.2 Hz, H-2), 5.71 (1H, dd, *J* = 9.8, 9.2, H-3), 5.69 (1H, dd, *J* = 9.8, 9.2 Hz, H-4), 4.73 (1H, dd, *J* = 12.5, 2.6 Hz, H-6), 4.53 (1H, dd, *J* = 12.5, 4.6 Hz, H-6′), 4.34 (1H, d, *J* = 9.2 Hz, H-1), 4.23 (1H, ddd, *J* = 9.2, 4.6, 2.6 Hz, H-5), 4.09 (1H, dd, *J* = 18.4, 5.3 Hz, CH_2), 3.96 (1H, dd, *J* = 18.4, 5.3 Hz, CH_2), 3.71 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$) δ (ppm): 166.8 (*C*OOCH_3), 166.8, 166.1, 165.6, 165.2 (CO), 165.1 (*C*ONH), 133.5–128.2 (aromatics), 76.2 (C-1), 76.2, 73.6, 69.9, 69.0 (C-2 to C-5), 62.7 (C-6), 52.2 (COO*C*H_3), 40.8 (*C*H_2). Anal. Calcd for $C_{38}H_{33}NO_{12}$ (695.68): C, 65.61; H, 4.78; N, 2.01. Found: C, 65.41; H, 4.56; N, 2.26.

4.8. Method *F*: preparation of per-*O*-acylated *C*-(β-D-glycopyranosyl)formyl chlorides (2,6-anhydro-aldonoyl chlorides) 18 and 19

(Adapted from Ref. 28): A per-*O*-acylated 2,6-anhydro-aldonic acid **1** or **3** was suspended in abs. Et_2O (10 mL/mmol), and treated with PCl_5 (1.1 equiv). The mixture was boiled under reflux until a clear solution was obtained (~3 h). After cooling hexane (15 mL/mmol) was added to the mixture to induce crystallisation at −20 °C in the case of **18**, or the volatiles were removed to yield a pure crude product.

4.8.1. *C*-(2,3,4,6-Tetra-*O*-acetyl-β-D-galactopyranosyl)-formyl chloride (3,4,5,7-tetra-*O*-acetyl-2,6-anhydro-D-*glycero*-L-*manno*-heptonoyl chloride) 18. Prepared from **1** (0.20 g, 0.53 mmol) according to Method ***F***. Yield: 0.20 g (75%, lit.[28] 80%) colourless crystalline product from hexane; mp: 105–106 °C (lit.[28] 100 °C).

4.8.2. *C*-(2,3,4,6-Tetra-*O*-benzoyl-β-D-glucopyranosyl)-formyl chloride (2,6-anhydro-3,4,5,7-tetra-*O*-benzoyl-D-*glycero*-D-*gulo*-heptonoyl chloride) 19. Prepared from **3** (0.50 g, 0.80 mmol) according to Method ***F***. Yield: 0.50 g (99%), yellowish oil (R_f = 0.10, ethyl acetate–hexane 3:1); $[\alpha]_D$ = +10 (*c* 0.42, $CHCl_3$); ν_{max} ($CHCl_3$):

3672, 1754, 1552, 1492, 1380, 1270, 1094, 708; ^{1}H NMR ($CDCl_3$) δ (ppm): 8.06–7.22 (20H, m, Ph), 5. 97 (1H, t, J = 9.6, 9.6 Hz, H-2), 5.78–5.66 (2H, m, H-3, H-4), 4.65 (1H, dd, J = 12.5, <1 Hz, H-6), 4.52 (1H, dd, J = 12.5, 4.4 Hz, H-6′), 4.40 (1H, d, J = 9 6 Hz, H-1), 4.22 (1H, ddd, J = 12.5, 4.4, <1 Hz, H-5); ^{13}C NMR ($CDCl_3$) δ (ppm): 169.8 (*C*OCl), 166.3, 165.7, 165.3, 165.1 (CO), 133.5–128.3 (aromatics), 76.2 (C-1), 76.0, 73.5, 69.8, 69.0 (C-2 to C-5), 63.1 (C-6). Anal. Calcd for $C_{35}H_{27}ClO_{11}$ (643.05): C, 65.37; H, 4.23; Cl, 5.51. Found: C, 65.15; H, 4.49; Cl, 5.35.

4.9. Brominations

4.9.1. Method *G*. A per-*O*-acylated 2,6-anhydro-aldonic acid ester was dissolved in abs. $CHCl_3$ (15 mL/mmol), and bromine (3.5 equiv) and some K_2CO_3 (acid scavenger) were added. The mixture was placed in an Erlenmeyer flask above a heat lamp (375 W, distance from the lamp ~2–3 cm, height of the solution 1–2 cm), and refluxed. If the mixture decolourised bromine (0.5 equiv) was added again. When TLC (ethyl acetate–hexane, 1:1) showed complete transformation $CHCl_3$ (10 mL/mmol) was added, and the mixture washed with 1 M aq $Na_2S_2O_3$ satd. aq $NaHCO_3$ (2×) and water. After drying the solvent was removed in vacuo, and the residue purified by crystallisation or column chromatography if necessary.

4.9.2. Method *H*. A per-*O*-acylated 2,6-anhydro-aldonic acid ester was dissolved in abs. CCl_4 or abs. $CHCl_3$ (10 mL/mmol), NBS (1 equiv), and AIBN or Bz_2O_2 (0.1 equiv) were added. The mixture was refluxed until the starting material disappeared (TLC, ethyl acetate–hexane 1:1). It was then diluted with $CHCl_3$ (15 mL/mmol) and washed with 1 M aq $Na_2S_2O_3$, satd. aq $NaHCO_3$ (2×), and water, then dried. After filtration and removal of the solvent in vacuo the residue was purified by crystallisation or column chromatography if necessary.

4.9.3. Method *I*. A per-*O*-acylated-2,6-anhydro-aldonic acid ester was dissolved in CH_2Cl_2 (3 mL/mmol), and $KBrO_3$ (6 equiv) and $Na_2S_2O_4$ (6 equiv) in aqueous solutions (3 mL of each) were added in one portion (in case of larger scale reactions the $Na_2S_2O_4$ solution was added dropwise to the other components). The mixture was stirred at rt until disappearance of the starting material (TLC), then diluted with CH_2Cl_2 (6 mL/mmol). Aq $Na_2S_2O_3$ (1 M) was added, shaken well, and then separated. The organic phase was further washed with satd. aq $NaHCO_3$ (2×), and water, then dried. After filtration and removal of the solvent in vacuo the residue was purified by crystallisation or column chromatography if necessary.

4.9.4. Methyl *C*-(2,3,4,6-tetra-*O*-acetyl-1-bromo-1-deoxy-β-D-galactopyranosyl)formate (methyl 3,4,5,7-tetra-*O*-acetyl-2-bromo-2-deoxy-α-D-*galacto*-hept-2-ulopyranosonate) 20. Prepared from **4** (1.50 g, 3.83 mmol) according to Method ***G***, purified by column chromatography (eluent: ethyl acetate–hexane 1:1). Yield: 1.16 g (65%) colourless oil (R_f = 0.57, ethyl acetate–hexane 1:1); $[\alpha]_D$ = +150 (c 1.02, $CHCl_3$); ν_{max} ($CHCl_3$): 3904, 1764, 1378, 1270, 1080; ^{1}H NMR ($CDCl_3$) δ (ppm): 5.52 (1H, dd, J = 3.6, 1.6 Hz, H-4), 5.46 (1H, d, J = 10.5 Hz, H-2), 5.34 (1H, dd, J = 10.5, 3.6 Hz, H-3), 4.53 (1H, ddd, J = 6.8, 6.3, 1.6 Hz, H-5), 4.26 (1H, dd, J = 11.6, 6.8 Hz, H-6), 4.19 (1H, dd, J = 11.6, 6.3 Hz, H-6′), 3.85 (3H, s, OCH_3), 2.16, 2.10, 2.07, 1.99 (12H, 4 × s, OAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.2, 169.8, 169.7, 169.1 (CO), 164.7 (*C*$OOCH_3$, $^3J_{COOMe,H\text{-}2}$ = 2.4 Hz), 94.4 (C-1), 72.8, 69.8, 66.7, 66.3 (C-2 to C-5), 60.4 (C-6), 53.8 (OCH_3), 20.7, 20.5, 20.4 (CH_3). Anal. Calcd for $C_{16}H_{21}BrO_{11}$ (469.16): C, 40.96; H, 4.52; Br, 17.03. Found: C, 41.24; H, 4.48; Br, 17.25.

Compound **20** was obtained by Method ***I*** in 77% yield.

4.9.5. Methyl *C*-(2,3,4,6-tetra-*O*-benzoyl-1-bromo-1-deoxy-β-D-glucopyranosyl)formate (methyl 3,4,5,7-tetra-*O*-benzoyl-2-bromo-2-deoxy-α-D-*gluco*-hept-2-ulopyranosonate) 21. Prepared from **5** (1.50 g, 2.35 mmol) according to Method ***G***. Yield: 1.35 g (80%) white crystalline product; mp: 188–190 °C; $[\alpha]_D$ = +129 (c 1.19, $CHCl_3$); ν_{max} (KBr): 3854, 3650, 1742, 1492, 1378, 1270, 1096, 708; ^{1}H NMR ($CDCl_3$) δ (ppm): 8.09–7.26 (20H, m, Ph), 6.17 (1H, dd, J = 10.0, 9.5 Hz, H-3), 5.85 (1H, dd, J = 10.5, 10.0 Hz, H-4), 5.84 (1H, d, J = 9.5 Hz, H-2), 4.77 (1H, ddd, J = 10.5, 4.2, 2.6 Hz, H-5), 4.69 (1H, dd, J = 12.6, 4.2 Hz, H-6), 4.58 (1H, dd, J = 12.6, 2.6 Hz, H-6′), 3.77 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$) δ (ppm): 165.9 (*C*$OOCH_3$, $^3J_{COOMe,\ H\text{-}2}$ = 2.4 Hz), 165.4, 164.9, 164.6 (2) (CO), 133.5–128.3 (aromatics), 94.0 (C-1), 74.3, 72.1, 70.6, 67.8 (C-2 to C-5), 61.9 (C-6), 53.9 (OCH_3). Anal. Calcd for $C_{36}H_{29}BrO_{11}$ (717.53): C, 60.26; H, 4.07; Br, 11.14. Found: C, 59.98; H, 4.10; Br, 11.35.

By using Method ***I*** the crude mixture contained compound **36** as a by-product. Column chromatography (eluent: ethyl acetate–hexane, 1:2) gave **21** in 54% yield.

By Method ***H*** **21** was obtained in 68% yield.

4.9.6. *tert*-Butyl *C*-(2,3,4,6-tetra-*O*-acetyl-1-bromo-1-deoxy-β-D-galactopyranosyl)formate (*tert*-butyl 3,4,5,7-tetra-*O*-acetyl-2-bromo-2-deoxy-α-D-*galacto*-hept-2-ulopyranosonate) 22. Prepared from **6** (0.1 g, 0.23 mmol) according to Method ***I***. Yield: 0.1 g (85%) yellowish crude syrup (R_f = 0.5, ethyl acetate–hexane 1:1) sufficiently pure for the next transformation. Spectroscopic characterisation could not be carried out because of easy decomposition of the compound.

4.9.7. *tert*-Butyl *C*-(2,3,4,6-tetra-*O*-benzoyl-1-bromo-1-deoxy-β-D-glucopyranosyl)formate (*tert*-butyl 3,4,5,7-tetra-*O*-benzoyl-2-bromo-2-deoxy-α-D-*gluco*-hept-2-ulopyranosonate) 23. Prepared from **8** (0.1 g, 0.14 mmol) according to Method ***H***. Yield: 0.092 g (83%) yellowish crude syrup (R_f = 0.46, ethyl acetate–hexane 1:1) sufficiently pure for the next transformation. Spectroscopic characterisation could not be carried out because of easy decomposition of the compound. By using Method ***I*** the yield was 72%.

4.9.8. 2,2,2-Trichloroethyl *C*-(2,3,4,6-tetra-*O*-acetyl-1-bromo-1-deoxy-β-D-galactopyranosyl)formate (2,2,2-trichloroethyl 3,4,5,7-tetra-*O*-acetyl-2-bromo-2-deoxy-α-D-*galacto*-hept-2-ulopyranosonate) 24. Prepared from **9** (0.96 g, 1.89 mmol) according to Method ***I***. Yield: 0.88 g colourless oil ($R_f = 0.41$, ethyl acetate–hexane 1:1) (crude product contaminated with an unidentified bromine containing by-product, $R_f = 0.45$, ethyl acetate–hexane 1:1). This was used for the azide substitution to give **42**. ^{1}H NMR ($CDCl_3$) δ (ppm): 5.54 (1H, dd, $J = 2.9$, 1.5 Hz, H-4), 5.50 (1H, d, $J = 10.3$ Hz, H-2), 5.37 (1H, dd, $J = 10.3$, 2.9 Hz, H-3), 4.89 (1H, d, $J = 11.8$ Hz, CH_2), 4.79 (1H, d, $J = 11.8$ Hz, CH_2), 4.55 (1H, ddd, $J = 5.9$, 5.1, 1.5 Hz, H-5), 4.26–4.21 (2H, m, H-6, H-6′), 2.17, 2.11, 2.06, 2.00 (12H, 4 × s, OAc).

4.9.9. 2,2,2-Trichloroethyl *C*-(2,3,4,6-tetra-*O*-acetyl-1-bromo-1-deoxy-β-D-glucopyranosyl)formate (2,2,2-trichloroethyl 3,4,5,7-tetra-*O*-acetyl-2-bromo-2-deoxy-α-D-*gluco*-hept-2-ulopyranosonate) 25. Prepared from **10** (0.20 g, 0.39 mmol) according to Method ***I***. Yield: 0.23 g colourless oil ($R_f = 0.43$, ethyl acetate–hexane 1:1) (crude product contaminated with an unidentified by-product ($R_f = 0.28$, ethyl acetate–hexane 1:1) in 5:1 ratio). This was used for the azide substitution to give **43**. ^{1}H NMR ($CDCl_3$) δ (ppm): 5.52 (1H, t, $J = 9.2$, 9.2 Hz, H-3), 5.34 (1H, d, $J = 9.2$ Hz, H-2), 5.26 (1H, t, $J = 10.6$, 9.2 Hz, H-4), 4.89 (1H, d, $J = 11.9$ Hz, CH_2), 4.79 (1H, d, $J = 11.9$ Hz, CH_2), 4.39 (1H, dd, $J = 13.2$, 4.0 Hz, H-6), 4.34 (1H, ddd, $J = 13.2$, 4.0, 2.6 Hz, H-5), 4.19 (1H, dd, $J = 13.2$, 2.6 Hz, H-6′), 2.11 (2), 2.05, 2.01.

4.9.10. 2,2,2-Trichloroethyl *C*-(2,3,4,6-tetra-*O*-benzoyl-1-bromo-1-deoxy-β-D-glucopyranosyl)formate (2,2,2-trichloroethyl 3,4,5,7-tetra-*O*-benzoyl-2-bromo-2-deoxy-α-D-*gluco*-hept-2-ulopyranosonate) 26. Prepared from **11** (0.30 g, 0.40 mmol) according to Method ***I***. Yield: 0.30 g yellowish oil ($R_f = 0.41$, ethyl acetate–hexane 1:2), which contained the corresponding hydroxy derivative **33** in 5:1 ratio; ^{1}H NMR ($CDCl_3$) δ (ppm): 8.08–7.24 (20H, m, Ph), 6.20 (1H, dd, $J = 9.6$, 9.2 Hz, H-3), 5.88 (1H, d, $J = 9.2$ Hz, H-2), 5.84 (1H, dd, $J = 9.6$, 9.2 Hz, H-4), 4.85 (1H, d, $J = 11.9$ Hz, CH_2), 4.79 (1H, ddd, $J = 11.9$, 3.9, 2.6 Hz, H-5), 4.73 (1H, d, $J = 11.9$ Hz, CH_2), 4.72 (1H, dd, $J = 11.9$, 2.6 Hz, H-6), 4.57 (1H, dd, $J = 11.9$, 3.9 Hz, H-6′).

4.9.11. Pentachlorophenyl *C*-(2,3,4,6-tetra-*O*-acetyl-1-bromo-1-deoxy-β-D-galactopyranosyl)formate (pentachlorophenyl 3,4,5,7-tetra-*O*-acetyl-2-bromo-2-deoxy-α-D-*galacto*-hept-2-ulopyranosonate) 27. Prepared from **12** (0.30 g, 0.48 mmol) according to Method ***G***. Yield: 0.33 g (99%) yellowish oil ($R_f = 0.58$, ethyl acetate–hexane 1:1); $[\alpha]_D = +57$ (c 1.02, $CHCl_3$); ν_{max} ($CHCl_3$): 3430, 1760, 1370, 1230, 1026, 600; ^{1}H NMR ($CDCl_3$) δ (ppm): 5.64 (1H, d, $J = 10.5$ Hz, H-2), 5.58 (1H, dd, $J = 3.3$, 1.3 Hz, H-4), 5.41 (1H, dd, $J = 10.5$, 3.3 Hz, H-3), 4.63 (1H, ddd, $J = 6.6$, 6.6, 1.3 Hz, H-5), 4.31 (1H, dd, $J = 11.2$, 6.6 Hz, H-6), 4.27 (1H, dd, $J = 11.2$, 6.6 Hz, H-6′), 2.20, 2.08, 2.00 (12H, 3 × s, OAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.1, 169.8, 169.7, 168.5 (CO), 160.2 ($COOC_6Cl_5$, $^3J_{COOC6Cl5,H\text{-}2} = <1$ Hz), 142.7–127.3 (aromatics), 93.1 (C-1), 73.1, 69.8, 66.5, 66.2 (C-2 to C-5), 60.2 (C-6), 20.6, 20.5, 20.3 (CH_3). Anal. Calcd for $C_{21}H_{18}BrCl_5O_{11}$ (703.54): C, 35.85; H, 2.58; Br, 11.30; Cl, 25.20. Found: C, 35.62; H, 2.28; Br, 11.25; Cl, 24.96.

By using Method ***I*** **27** was obtained in 91% yield.

4.9.12. Pentachlorophenyl *C*-(2,3,4,6-tetra-*O*-acetyl-1-bromo-1-deoxy-β-D-glucopyranosyl)formate (pentachlorophenyl 3,4,5,7-tetra-*O*-acetyl-2-bromo-2-deoxy-α-D-*gluco*-hept-2-ulopyranosonate) 28. Prepared from **13** according to Method ***G***. Yield: 0.11 g (97%) colourless oil ($R_f = 0.52$, ethyl acetate–hexane 1:1); $[\alpha]_D = +49$ (c 1.11, $CHCl_3$); ν_{max} ($CHCl_3$): 3438, 1756, 1368, 1230, 1056, 600; ^{1}H NMR ($CDCl_3$) δ (ppm): 5.55 (1H, t, $J = 9.5$, 9.5 Hz, H-3), 5.48 (1H, d, $J = 9.5$ Hz, H-2), 5.34 (1H, dd, $J = 9.5$, 8.9 Hz, H-4), 4.47–4.37 (2H, m, H-5, H-6), 4.28 (1H, dd, $J = 13.7$, 3.7 Hz, H-6′), 2.11, 2.08, 2.07, 2.02 (12H, 4 × s, OAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.3, 169.8, 169.1, 168.6 (CO), 160.2 ($COOC_6Cl_5$, $^3J_{COOC6Cl5,H\text{-}2} = 2.2$ Hz), 142.7–132.3 (aromatics), 91.8 (C-1), 74.0, 71.8, 69.6, 66.4 (C-2 to C-5), 60.5 (C-6), 20.5, 20.4 (CH_3). Anal. Calcd for $C_{21}H_{18}BrCl_5O_{11}$ (703.54): C, 35.85; H, 2.58; Br, 11.30; Cl, 25.20. Found: C, 35.71; H, 2.40; Br, 11.18; Cl, 25.26.

4.9.13. Pentachlorophenyl *C*-(2,3,4,6-tetra-*O*-benzoyl-1-bromo-1-deoxy-β-D-glucopyranosyl)formate (pentachlorophenyl 3,4,5,7-tetra-*O*-benzoyl-2-bromo-2-deoxy-α-D-*gluco*-hept-2-ulopyranosonate) 29. Prepared from **14** according to Method ***G***. Yield: 0.19 g (89%) yellowish oil ($R_f = 0.52$, ethyl acetate–hexane 1:2); $[\alpha]_D = +39$ (c 1.03, $CHCl_3$); ν_{max} ($CHCl_3$): 3650, 2962, 1736, 1522, 1490, 1378, 1264, 1090, 708, 610; ^{1}H NMR ($CDCl_3$) δ (ppm): 8.08–7.25 (20H, m, Ph), 6.24 (1H, t, $J = 9.5$, 9.5 Hz, H-3), 6.04 (1H, d, $J = 9.5$ Hz, H-2), 5.95 (1H, dd, $J = 10.5$, 9.5 Hz, H-4), 4.90–4.80 (2H, m, H-5, H-6), 4.60 (1H, dd, $J = 12.6$, 3.7 Hz, H-6′); ^{13}C NMR ($CDCl_3$) δ (ppm): 165.7, 165.5, 164.9, 164.3 (CO), 160.2 ($COOC_6Cl_5$, $^3J_{COOC6Cl5,H\text{-}2} = 3.2$ Hz), 142.7–126.1 (aromatics), 92.6 (C-1), 74.6, 72.0, 70.4, 67.6 (C-2 to C-5), 61.4 (C-6). Anal. Calcd for $C_{41}H_{26}BrCl_5O_{11}$ (951.83): C, 51.74; H, 2.75; Br, 8.39; Cl, 18.62. Found: C, 51.71; H, 2.60; Br, 8.18; Cl, 18.36.

4.10. General procedure II

For the preparation of per-O-*acylated methyl* C-*(1-hydroxy*-β-D-*glycopyranosyl)formates (methyl hept-2-ulopyranosonates)* **31** and **32**: A methyl per-*O*-acyl-2-bromo-2-deoxy-α-D-*glyco*-hept-2-ulopyranosonate **20** or **21** was suspended in DMSO (5 mL/mmol), Ag_2O (1 equiv) and water (1 equiv) were added. The reaction mixture was stirred at rt in the dark and monitored by TLC (ethyl acetate–hexane 5:4). After disappearance of the starting bromide it was filtered on Celite, the filtrate was diluted with water (25 mL/mmol), washed with Et_2O (5×). After drying the solvent was removed in vacuo to give a clean product.

4.10.1. Methyl *C*-(2,3,4,6-tetra-*O*-acetyl-1-hydroxy-β-D-galactopyranosyl)formate (methyl 3,4,5,7-tetra-*O*-acetyl-α-D-*galacto*-hept-2-ulopyranosonate) 31. Prepared from **20** (0.25 g, 0.53 mmol) according to general procedure II. Yield: 0.15 g (74%) colourless oil (R_f = 0.53, ethyl acetate–hexane 5:4); $[\alpha]_D$ = +55 (*c* 1.26, $CHCl_3$); ν_{max} ($CHCl_3$):3658, 3440, 1758, 1362, 1232, 1050; ^1H NMR ($CDCl_3$) δ (ppm): 5.59 (1H, d, *J* = 10.6 Hz, H-2), 5.49 (1H, dd, *J* = 3.2, 1.3 Hz, H-4), 5.35 (1H, dd, *J* = 10.6, 3.2 Hz, H-3), 4.56 (1H, s, OH), 4.48 (1H, ddd, *J* = 6.9, 6.9, 1.3 Hz, H-5), 4.16 (1H, dd, *J* = 11.5, 6.9 Hz, H-6), 4.06 (1H, dd, *J* = 11.5, 6.9 Hz, H-6′), 3.86 (3H, s, OCH_3), 2.18, 2.03, 2.02, 1.97 (12H, 4 × s, OAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.4, 170.3, 170.0, 169.5 (CO), 168.6 (*C*OOCH$_3$, $^3J_{COOCH3,H\text{-}2}$ = 2.2 Hz), 94.6 (C-1), 68.7, 68.6, 67.9, 67.7 (C-2 to C-5), 61.4 (C-6), 54.1 (COO*C*H$_3$), 20.7, 20.6 (CH_3). Anal. Calcd for $C_{16}H_{22}O_{12}$ (406.26): C, 47.30; H, 5.47. Found: C, 47.54; H, 5.65.

4.10.2. Methyl *C*-(2,3,4,6-tetra-*O*-benzoyl-1-hydroxy-β-D-glucopyranosyl)formate (methyl 3,4,5,7-tetra-*O*-benzoyl-α-D-*gluco*-hept-2-ulopyranosonate) 32. Prepared from **21** (0.35 g, 0.49 mmol) according to general procedure II. Yield: 0.17 g (52%), white crystalline product from diethylether; mp: 147–151 °C; $[\alpha]_D$ = +52 (*c* 1.14, $CHCl_3$); ν_{max} (KBr): 3652, 3648, 2962, 1736, 1520, 1496, 1372, 1264, 1088, 708, 610; ^1H NMR ($CDCl_3$) δ (ppm): 8.07–7.24 (20H, m, Ph), 6.20 (1H, dd, *J* = 10.2, 9.8 Hz, H-3), 5.90 (1H, d, *J* = 10.2 Hz, H-2), 5.83 (1H, t, *J* = 9.9, 9.8 Hz, H-4), 4.72 (1H, ddd, *J* = 9.9, 4.7, 3.0 Hz, H-5), 4.71 (1H, s, OH), 4.61 (1H, dd, *J* = 12.4, 4.7 Hz, H-6), 4.49 (1H, dd, *J* = 12.4, 3.0 Hz, H-6′), 3.86 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$) δ (ppm): 168.7 (*C*OOCH$_3$, $^3J_{COOCH3,H\text{-}2}$ = 2.1 Hz), 166.2, 165.7, 165.2, 165.1 (CO), 133.6–128.3 (aromatics), 94.4 (C-1), 71.4, 71.4, 70.0, 69.4 (C-2 to C-5), 61.4 (C-6), 54.1 (COO*C*H$_3$). Anal. Calcd for $C_{36}H_{30}O_{12}$ (654.54): C, 66.06; H, 4.63. Found: C, 65.74; H, 4.68.

4.10.3. 2,2,2-Trichloroethyl *C*-(2,3,4,6-tetra-*O*-benzoyl-1-hydroxy-β-D-glucopyranosyl)formate (2,2,2-trichloroethyl 3,4,5,7-tetra-*O*-benzoyl-α-D-*gluco*-hept-2-ulopyranosonate) 33. Isolated by column chromatography as a by-product from the preparation of **44**. Yield: 0.03 g (14% for two steps from **11**) colourless oil (R_f = 0.26, ethyl acetate–hexane 1:2); $[\alpha]_D$ = +45 (*c* 0.40, $CHCl_3$); ^1H NMR ($CDCl_3$) δ (ppm): 8.06–7.26 (20H, m, Ph), 6.18 (1H, t, *J* = 9.2, 8.8 Hz, H-3), 5.92 (1H, d, *J* = 9.2 Hz, H-2), 5.87 (1H, t, *J* = 9.8, 8.8 Hz, H-4), 4.87 (1H, d, *J* = 12.0 Hz, CH_2), 4.83 (1H, d, *J* = 12.0 Hz, CH_2), 4.72–4.61 (3H, m, H-5, H-6, OH), 4.46 (1H, dd, *J* = 11.8, 2.2 Hz, H-6′); ^{13}C NMR ($CDCl_3$) δ (ppm): 166.8, 166.0, 165.7, 165.1 (CO), 164.9 (*C*OOCH$_2$CCl$_3$, $^3J_{COOCH2CCl3,H\text{-}2}$ = <1 Hz.), 133.5–128.2 (aromatics), 93.5 (C-1), 84.6 (COOCH$_2$*C*Cl$_3$), 75.7 (COO*C*H$_2$CCl$_3$), 71.2, 71.1, 70.1, 68.9 (C-2 to C-5), 62.2 (C-6). Anal. Calcd for $C_{37}H_{29}Cl_3O_{12}$ (772.00): C, 57.57; H, 3.79; Cl, 13.78. Found: C, 57.17; H, 3.60; Cl, 13.50.

4.10.4. *N*-[(2,3,4,6-Tetra-*O*-acetyl-1-bromo-1-deoxy-β-D-galactopyranosyl)carbonyl]glycine methylester (*N*-(3,4,5,7-tetra-*O*-acetyl-2-bromo-2-deoxy-α-D-*galacto*-hept-2-ulopyranosonoyl)glycine methylester) 35. Prepared from **27** (0.30 g, 0.43 mmol) according to Method ***E***. Yield: 0.18 g (71%) colourless oil (R_f = 0.22, ethyl acetate–hexane 1:1); $[\alpha]_D$ = +96 (*c* 0.79, $CHCl_3$); ν_{max} ($CHCl_3$): 3378, 2960, 1754, 1680, 1370, 1260, 1070; ^1H NMR ($CDCl_3$) δ (ppm): 7.02 (1H, t, *J* = 5.3, 5.3 Hz, NH), 5.55 (1H, dd, *J* = 3.2, 1.0 Hz, H-4), 5.43 (1H, d, *J* = 10.5 Hz, H-2), 5.33 (1H, dd, *J* = 10.5, 3.2 Hz, H-3), 4.56 (1H, ddd, *J* = 6.8, 6.6, 1.0 Hz, H-5), 4.31 (1H, dd, *J* = 12.1, 6.8 Hz, H-6), 4.22 (1H, dd, *J* = 12.1, 6.3 Hz, H-6′), 4.12 (1H, dd, *J* = 18.4, 5.3 Hz, CH_2), 4.03 (1H, dd, *J* = 18.4, 5.3 Hz, CH_2), 3.79 (3H, s, OCH_3), 2.17, 2.13, 2.10, 1.99 (12H, 4 × s, OAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.4 (*C*OOCH$_3$), 169.8, 169.3 (CO), 164.9 (*C*ONH, $^3J_{CONH,H\text{-}2}$ = 2.2 Hz), 94.0 (C-1), 73.5, 69.7, 66.5, 66.5 (C-2 to C-5), 60.7 (C-6), 52.5 (COO*C*H$_3$), 41.1 (*C*H$_2$), 20.8, 20.5, 20.4 (CH_3). Anal. Calcd for $C_{18}H_{24}N_1BrO_{12}$ (526.30): C, 41.08; H, 4.60; N, 2.66; Br, 15.18. Found: C, 41.20; H, 4.58; N, 2.56; Br, 15.08.

4.10.5. *N*-[(2,3,4,6-Tetra-*O*-acetyl-1-bromo-1-deoxy-β-D-glucopyranosyl)carbonyl]glycine methylester (*N*-(3,4,5,7-tetra-*O*-acetyl-2-bromo-2-deoxy-α-D-*gluco*-hept-2-ulopyranosonoyl)glycine methylester) 36. Prepared from **28** (0.56 g, 0.80 mmol) according to Method ***E***. Yield: 0.30 g (71%), colourless oil (R_f = 0.16, ethyl acetate–hexane 1:1); $[\alpha]_D$ = +76 (*c* 1.12, $CHCl_3$); ν_{max} ($CHCl_3$): 3376, 2954, 1758, 1670, 1354, 1252, 1040; ^1H NMR ($CDCl_3$) δ (ppm): 7.06 (1H, t, *J* = 5.3, 5.3 Hz, NH), 5.50 (1H, t, *J* = 10.0, 9.5 Hz, H-3), 5.24 (1H, d, *J* = 10.0 Hz, H-2), 5.22 (1H, t, *J* = 10.0, 9.5 Hz, H-4), 4.38–4.32 (3H, m, H-5, H-6, H-6′), 4.09 (1H, dd, *J* = 18.4, 3.1 Hz, CH_2), 4.02 (1H, dd, *J* = 18.4, 3.1 Hz, CH_2) 3.78 (3H, s, OCH_3), 2.14, 2.12, 2.07, 2.01 (12H, 4 × s, OAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.8 (*C*OOCH$_3$), 169.8, 169.3, 169.2 (CO), 164.8 (*C*ONH, $^3J_{CONH,H\text{-}2}$ = <1 Hz), 92.5 (C-1), 74.2, 71.6, 69.6, 66.5 (C-2 to C-5), 60.5 (C-6), 52.5 (COO*C*H$_3$), 41.1 (*C*H$_2$), 20.6, 20.4 (CH_3). Anal. Calcd for $C_{18}H_{24}NBrO_{12}$ (526.30): C, 41.08; H, 4.60; N, 2.66; Br, 15.18. Found: C, 41.10; H, 4.62; N, 2.60; Br, 15.06.

4.10.6. *N*-[(2,3,4,6-Tetra-*O*-benzoyl-1-bromo-1-deoxy-β-D-glucopyranosyl)carbonyl]glycine methylester (*N*-(3,4,5,7-tetra-*O*-benzoyl-2-bromo-2-deoxy-α-D-*gluco*-hept-2-ulopyranosonoyl)glycine methylester) 37. Prepared from **29** (0.11 g, 0.11 mmol) according to Method ***E***. Yield: 0.05 g (53%) yellowish oil (R_f = 0.34, ethyl acetate–hexane 1:1); $[\alpha]_D$ = +79 (*c* 0.77, $CHCl_3$); ν_{max} ($CHCl_3$): 3650, 2654, 1736, 1600, 1270, 1092, 708; ^1H NMR ($CDCl_3$) δ (ppm): 8.18–7.24 (20H, m, Ph), 7.20 (1H, t, *J* = 5.3, 5.3 Hz, NH), 6.15 (1H, t, *J* = 9.5, 9.5 Hz, H-3), 5.82 (1H, t, *J* = 10.0, 9.5 Hz, H-4), 5.78 (1H, d, *J* = 9.5 Hz, H-2), 4.84 (1H, dd, *J* = 12.6, 2.1 Hz, H-6), 4.78 (1H, ddd, *J* = 12.6, 4.2, 2.1 Hz, H-5), 4.56 (1H, dd, *J* = 12.6, 4.2 Hz, H-6′), 4.07 (1H, dd, *J* = 17.9, 5.3 Hz, CH_2), 4.02 (1H, dd, *J* = 17.9, 5.3 Hz,

CH_2), 3.72 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$) δ (ppm): 169.2 ($COOCH_3$), 165.5 ($CONH$, $^3J_{CONH,\ H\text{-}2}$ = 4.4 Hz), 165.0, 164.5 (CO), 133.8–128.3 (aromatics), 93.0 (C-1), 74.8, 71.9, 70.3, 67.7 (C-2 to C-5), 61.5 (C-6), 52.4 ($COOCH_3$), 41.2 (CH_2). Anal. Calcd for $C_{38}H_{32}NBrO_{12}$ (774.58): C, 58.93; H, 4.16; N, 1.81; Br, 10.32. Found: C, 58.63; H, 4.32; N, 1.85; Br, 10.06.

4.11. Azide substitutions

General procedure III for the preparation of derivatives of per-*O*-acylated *C*-(1-azido-1-deoxy-α-D-glycopyranosyl)-formic acids (2-azido-2-deoxy-β-D-*glyco*-hept-2-ulopyranosonic acids) 38–47: A per-*O*-acylated 2-bromo-2-deoxy-α-D-*glyco*-hept-2-ulopyranosonic acid derivative was dissolved in abs. DMSO (2 mL/mmol) unless stated otherwise, and NaN_3 (2 equiv) was added. The mixture was stirred at room temperature. When the starting material disappeared (TLC, ethyl acetate–hexane 1:1), water (10 mL/mmol) was added and the aqueous phase washed with Et_2O (5×). The organic phase was washed with water, dried, and the solvent evaporated in vacuo. The crude product was purified by crystallisation or by column chromatography if necessary.

4.11.1. Methyl *C*-(2,3,4,6-tetra-*O*-acetyl-1-azido-1-deoxy-α-D-galactopyranosyl)formate (methyl 3,4,5,7-tetra-*O*-acetyl-2-azido-2-deoxy-β-D-*galacto*-hept-2-ulopyranosonate) 38. Prepared from **20** (0.50 g, 1.06 mmol) according to general procedure III. Yield: 0.45 g (84%) white crystalline product from diethylether; mp: 95–97 °C; $[\alpha]_D$ = +55 (*c* 1.61, $CHCl_3$); ν_{max} (KBr): 3904, 2122, 1762, 1378, 1240, 1216, 1076; ^1H NMR ($CDCl_3$) δ (ppm): 5.58 (1H, dd, *J* = 11.1, 3.6 Hz, H-3), 5.49 (1H, d, *J* = 11.1 Hz, H-2), 5.35 (1H, dd, *J* = 3.6, <1 Hz, H-4), 4.53 (1H, ddd, *J* = 6.6, 6.6, <1 Hz, H-5), 4.18 (1H, dd, *J* = 12.5, 6.6 Hz, H-6), 4.16 (1H, dd, *J* = 12.5, 6.6 Hz, H-6′), 3.90 (3H, s, OCH_3), 2.18, 2.06, 2.04, 1.97 (12H, 4 × s, OAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.0, 169.8, 169.5, 168.8 (CO), 165.8 ($COOCH_3$, $^3J_{COOMe,H\text{-}2}$ = 4.1 Hz), 90.6 (C-1), 72.0, 68.7, 68.3, 66.7 (C-2 to C-5), 61.0 (C-6), 53.2 (OCH_3), 20.4, 20.3, 20.2 (CH_3). Anal. Calcd for $C_{16}H_{21}N_3O_{11}$ (431.36): C, 44.55; H, 4.91; N, 9.74. Found: C, 44.10; H, 5.06; N, 9.56.

4.11.2. Methyl *C*-(1-azido-2,3,4,6-tetra-*O*-benzoyl-1-deoxy-α-D-glucopyranosyl)formate (methyl 2-azido-3,4,5,7-tetra-*O*-benzoyl-2-deoxy-β-D-*gluco*-hept-2-ulopyranosonate) 39. Prepared from **21** (1.20 g, 1.67 mmol) according to general procedure III. Yield: 0.90 g (80%) colourless oil, which crystallised from methanol (57%); mp: 121–123 °C; $[\alpha]_D$ = +41 (*c* 1.22, $CHCl_3$); ν_{max} (KBr): 3854, 3064, 2128, 1736, 1492, 1452, 1270, 1094, 708; ^1H NMR ($CDCl_3$) δ (ppm): 8.01–7.20 (20H, m, Ph), 6.36 (1H, dd, *J* = 10.5, 9.5 Hz, H-3), 5.81 (1H, dd, *J* = 9.5, 9.4 Hz, H-4), 5.70 (1H, d, *J* = 10.5 Hz, H-2), 4.70–4.60 (2H, m, H-6, H-6′) 4.51 (1H, ddd, *J* = 11.6, 5.2, 2.3 Hz, H-5), 3.90 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$) δ (ppm): 165.3, 164.9, 164.5 (CO), 165.9 ($COOCH_3$, $^3J_{COOMe,H\text{-}2}$ = 4.1 Hz), 133.5–128.2 (aromatics), 90.1 (C-1), 73.3, 71.9, 71.0, 68.8 (C-2 to C-5), 62.5 (C-6), 53.4 (OCH_3). Anal. Calcd for $C_{36}H_{29}N_3O_{11}$ (679.54): C, 63.63; H, 4.31; N, 6.18. Found: C, 63.54; H, 4.36; N, 6.00.

4.11.3. *tert*-Butyl *C*-(2,3,4,6-tetra-*O*-acetyl-1-azido-1-deoxy-α-D-galactopyranosyl)formate (*tert*-butyl 3,4,5,7-tetra-*O*-acetyl-2-azido-2-deoxy-β-D-*galacto*-hept-2-ulopyranosonate) 40. Prepared from **22** (0.12 g, 0.23 mmol crude product) according to general procedure III. Purified by column chromatography (eluent: ethyl acetate–hexane, 1:1): Yield: 0.09 g (69%) colourless oil (R_f = 0.37, ethyl acetate–hexane 1:1); $[\alpha]_D$ = +65 (*c* 0.77, $CHCl_3$); ν_{max} ($CHCl_3$): 2978, 2128, 1754, 1372, 1214, 1024; ^1H NMR ($CDCl_3$) δ (ppm): 5.67 (1H, dd, *J* = 10.5, 3.7 Hz, H-3), 5.49 (1H, dd, *J* = 3.7, 1.6 Hz, H-4), 5.31 (1H, d, *J* = 10.5 Hz, H-2), 4.53 (1H, ddd, *J* = 6.3, 6.3, 1.6 Hz, H-5), 4.18–4.13 (2H, m, H-6, H-6′), 2.18, 2.06, 2.05, 1.97 (12H, 4 × s, OAc), 1.58 (9H, s, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.2, 170.0, 169.8, 168.9 (CO), 164.0 ($COOC(CH_3)_3$, $^3J_{COOtBu,\ H\text{-}2}$ = 6.6 Hz), 90.6 (C-1), 85.4 ($COOC(CH_3)_3$), 72.0, 68.9, 68.7, 66.8 (C-2 to C-5), 61.4 (C-6), 27.8 ($C(CH3)_3$), 20.5 (CH_3). Anal. Calcd for $C_{19}H_{27}N_3O_{11}$ (473.44): C, 48.20; H, 5.75; N, 8.88. Found: C, 48.10; H, 5.66; N, 8.56.

4.11.4. *tert*-Butyl *C*-(1-azido-2,3,4,6-tetra-*O*-benzoyl-1-deoxy-α-D-glucopyranosyl)formate (*tert*-butyl 2-azido-3,4,5,7-tetra-*O*-benzoyl-2-deoxy-α-D-*gluco*-hept-2-ulopyranosonate) 41. Prepared from **23** (0.09, 0.12 mmol crude product) according to general procedure III. Purified by column chromatography (eluent: ethyl acetate–hexane,1:2): Yield: 0.05 g (46%) colourless oil (R_f = 0.46, ethyl acetate–hexane 1:1); $[\alpha]_D$ = +37 (*c* 1.18, $CHCl_3$); ν_{max} ($CHCl_3$): 3064, 2978, 2130, 1736, 1268, 1092, 708; ^1H NMR ($CDCl_3$) δ (ppm): 8.10–7.22 (20H, m, Ph), 6.44 (1H, dd, *J* = 9.8, 9.2 Hz, H-3), 5.73 (1H, t, *J* = 9.8, 9.2 Hz, H-4), 5.62 (1H, d, *J* = 9.8 Hz, H-2), 4.72–4.62 (2H, m, H-5, H-6), 4.50 (1H, dd, *J* = 12.6, 6.3 Hz, H-6′), 1.60 (9H, s, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ (ppm): 166.0, 165.5, 165.1, 164.7 (CO), 164.0 ($COOC(CH_3)_3$, $^3J_{COOtBu,H\text{-}2}$ = 4.4 Hz), 133.5–128.2 (aromatics), 90.3 (C-1), 85.6 ($COOC(CH_3)_3$), 73.2, 72.0, 71.2, 69.0 (C-2 to C-5), 62.8 (C-6), 27.9 ($C(CH_3)_3$). Anal. Calcd for $C_{39}H_{35}N_3O_{11}$ (721.73): C, 64.90; H, 4.89; N, 5.82. Found: C, 64.64; H, 4.76; N, 5.80.

4.11.5. 2,2,2-Trichloroethyl *C*-(2,3,4,6-tetra-*O*-acetyl-1-azido-1-deoxy-α-D-galactopyranosyl)formate (2,2,2-trichloroethyl 3,4,5,7-tetra-*O*-acetyl-2-azido-2-deoxy-β-D-*galacto*-hept-2-ulopyranosonate) 42. Prepared from **24** (1.35 g, 2.30 mmol crude product) according to general procedure III. Purified by column chromatography (eluent, ethyl acetate–hexane, 1:1): Yield: 1.01 g (75% for two steps from **9**) colourless oil (R_f = 0.53, ethyl acetate–hexane 1:2); $[\alpha]_D$ = +51 (*c* 0.24, $CHCl_3$); ν_{max} ($CHCl_3$): 2968, 2128, 1754, 1370, 1230, 1068, 722; ^1H NMR ($CDCl_3$) δ (ppm): 5.67 (1H, dd, *J* = 10.3, 3.7 Hz, H-3), 5.53 (1H, dd, *J* = 3.7, 2.2 Hz, H-4), 5.43 (1H, d, *J* = 10.3 Hz, H-2), 5.01 (1H, d, *J* = 11.8 Hz, CH_2), 4.92 (1H, d, *J* = 11.8 Hz, CH_2), 4.55 (1H, ddd, *J* = 6.6, 5.9, 2.2 Hz, H-5), 4.19–4.15 (2H, m, H-6, H-6′), 2.20, 2.07, 2.04, 1.98 (12H, 4 × s, OAc); ^{13}C NMR

($CDCl_3$) δ (ppm): 170.2, 169.9, 169.6, 168.9 (CO), 163.9 ($COOCH_2CCl_3$, $^3J_{COOCH2CCl3,H\text{-}2}$ = 8.3 Hz), 93.6 ($COOCH_2CCl_3$), 90.7 (C-1), 75.1 ($COOCH_2CCl_3$), 72.5, 68.7, 68.3, 66.7 (C-2 to C-5), 61.2 (C-6), 20.6, 20.5, 20.4 (CH_3). Anal. Calcd for $C_{17}H_{20}Cl_3N_3O_{11}$ (548.72): C, 37.21; H, 3.67; Cl, 19.38; N, 7.66. Found: C, 37.10; H, 3.60; Cl, 19.30; N, 7.56.

4.11.6. 2,2,2-Trichloroethyl *C*-(2,3,4,6-tetra-*O*-acetyl-1-azido-1-deoxy-α-D-glucopyranosyl)formate (2,2,2-trichloroethyl 3,4,5,7-tetra-*O*-acetyl-2-azido-2-deoxy-β-D-*gluco*-hept-2-ulopyranosonate) 43. Prepared from **25** (0.20 g, 0.34 mmol crude product) according to general procedure III. Purified by column chromatography (eluent, ethyl acetate–hexane, 1:1): Yield: 0.09 g (60% for two steps from **10**) yellowish oil (R_f = 0.50, ethyl acetate–hexane 1:1); $[\alpha]_D$ = +36 (*c* 0.20, $CHCl_3$); ν_{max} ($CHCl_3$): 2968, 2128, 1754, 1370, 1230, 1068, 722; ^{1}H NMR ($CDCl_3$) δ (ppm): 5.74 (1H, dd, *J* = 10.6, 9.2 Hz, H-3), 5.23 (1H, dd, *J* = 10.6, 9.2 Hz, H-4), 5.21 (1H, d, *J* = 9.2 Hz, H-2), 5.02 (1H, d, *J* = 11.9 Hz, CH_2), 4.93 (1H, d, *J* = 11.9 Hz, CH_2), 4.31–4.24 (2H, m, H-5, H-6), 4.16 (1H, dd, *J* = 10.6, <1 Hz, H-6′) 2.10, 2.06, 2.04, 1.99 (12H, 4 × s, OAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.5, 169.7, 169.3, 168.8 (CO), 163.8 ($COOCH_2CCl_3$, $^3J_{COOCH2CCl3,H\text{-}2}$ = 6.0 Hz), 93.5 ($COOCH_2CCl_3$), 89.1 (C-1), 75.1 ($COOCH_2CCl_3$), 73.0, 71.3, 70.9, 67.5 (C-2 to C-5), 61.4 (C-6), 20.6, 20.5 (CH_3). Anal. Calcd for $C_{17}H_{20}Cl_3N_3O_{11}$ (548.72): C, 37.21; H, 3.67; Cl, 19.38; N, 7.66. Found: C, 37.15; H, 3.65; Cl, 19.28; N, 7.49.

4.11.7. 2,2,2-Trichloroethyl *C*-(1-azido-2,3,4,6-tetra-*O*-benzoyl-1-deoxy-α-D-glucopyranosyl)formate (2,2,2-trichloroethyl 2-azido-3,4,5,7-tetra-*O*-benzoyl-2-deoxy-β-D-*gluco*-hept-2-ulopyranosonate) 44. Prepared from **26** (0.23 g, 0.27 mmol crude product) according to general procedure III. Purified by column chromatography (eluent, ethyl acetate–hexane: 1:3): Yield: 0.10 g (59% for two steps from **11**) white crystalline product from methanol; mp: 177–179 °C; $[\alpha]_D$ = +45 (*c* 0.41, $CHCl_3$); ν_{max} (KBr): 3904, 3066, 2132, 1740, 1584, 1570, 1490, 1374, 1270, 1070, 708; ^{1}H NMR ($CDCl_3$) δ (ppm): 8.05–7.25 (20H, m, Ph), 6.46 (1H, dd, *J* = 10.4, 9.6 Hz, H-3), 5.82 (1H, dd, *J* = 10.4, 9.6 Hz, H-4), 5.77 (1H, d, *J* = 10.4 Hz, H-2), 5.05 (1H, d, *J* = 12.0 Hz, CH_2), 5.00 (1H, d, *J* = 12.0 Hz, CH_2), 4.71–4.68 (2H, m, H-5, H-6), 4.52 (1H, dd, *J* = 12.2, 5.3 Hz, H-6′); ^{13}C NMR ($CDCl_3$) δ (ppm): 165.9, 165.3, 165.0, 164.5 (CO), 163.9 ($COOCH_2CCl_3$, $^3J_{COOCH2CCl3,H\text{-}2}$ = 4.0 Hz), 133.7–128.3 (aromatics), 93.5 ($COOCH_2CCl_3$), 90.3 (C-1), 75.3 ($COOCH_2CCl_3$), 73.6, 71.8, 70.9, 68.8 (C-2 to C-5), 62.5 (C-6). Anal. Calcd for $C_{37}H_{28}Cl_3N_3O_{11}$ (797.01): C, 55.76; H, 3.54; Cl, 13.34; N, 5.27. Found: C, 55.66; H, 3.60; Cl, 13.30; N, 5.26.

4.11.8. *N*-[(2,3,4,6-Tetra-*O*-acetyl-1-azido-1-deoxy-α-D-galactopyranosyl)carbonyl]glycine methylester (*N*-(3,4,5,7-tetra-*O*-acetyl-2-azido-2-deoxy-β-D-*galacto*-hept-2-ulopyranosonoyl)glycine methylester) 45. Prepared from **35** (0.18 g, 0.34 mmol) according to general procedure III. Yield: 0.11 g (65%) white crystalline product from diethylether; mp: 135–136 °C; $[\alpha]_D$ = +1 (*c* 0.93, $CHCl_3$); ν_{max} (KBr): 3370, 2958, 2134, 1744, 1680, 1370, 1252, 1068; ^{1}H NMR ($CDCl_3$) δ (ppm): 7.08 (1H, t, *J* = 5.9, 5.9 Hz, NH), 5.84 (1H, dd, *J* = 10.5, 3.3 Hz, H-3), 5.55 (1H, dd, *J* = 3.3, 1.3 Hz, H-4), 5.51 (1H, d, *J* = 10.5 Hz, H-2), 4.87 (1H, ddd, *J* = 6.6, 2.6, 1.3 Hz, H-5,), 4.16 (1H, dd, *J* = 12.5, 2.6 Hz, H-6), 4.15 (1H, dd, *J* = 18.4, 5.9 Hz, CH_2), 4.10 (1H, dd, *J* = 12.5, 6.6 Hz, H-6′), 3.95 (1H, dd, *J* = 18.4, 4.6 Hz, CH_2), 3.78 (3H, s, OCH_3), 2.17, 2.10, 2.04, 1.97 (12H, 4 × s, OAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.3 ($COOCH_3$), 169.8, 169.7, 169.5, 169.2 (CO), 165.3 (*C*ONH, $^3J_{CONH,H\text{-}2}$ = 6.5 Hz), 89.3 (C-1), 72.4, 69.1, 68.0, 67.3 (C-2 to C-5), 61.3 (C-6), 52.5 ($COOCH_3$), 40.8 (CH_2), 20.6, 20.5 (CO). Anal. Calcd for $C_{18}H_{24}N_4O_{12}$ (488.41): C, 44.27; H, 4.95; N, 11.47. Found: C, 44.15; H, 4.76; N, 11.50.

4.11.9. *N*-[(2,3,4,6-Tetra-*O*-acetyl-1-azido-1-deoxy-α-D-glucopyranosyl)carbonyl]glycine methylester (*N*-(3,4,5,7-tetra-*O*-acetyl-2-azido-2-deoxy-β-D-*gluco*-hept-2-ulopyranosonoyl)glycine methylester) 46. Prepared from **36** (0.14 g, 0.26 mmol) according to general procedure III. Yield: 0.09 g (69%) oil, which crystallised on standing at 4 °C to give white crystals; mp: 97–99 °C; $[\alpha]_D$ = −5 (*c* 1.04, $CHCl_3$); ν_{max} (KBr): 3372, 2954, 2136, 1752, 1684, 1350, 1242, 1068; ^{1}H NMR ($CDCl_3$) δ (ppm): 7.20 (1H, t, *J* = 5.3, 5.3 Hz, NH), 5.87 (1H, t, *J* = 8.8, 8.8 Hz, H-3), 5.30–5.24 (2H, m, H-2, H-4), 4.64 (1H, ddd, *J* = 10.0, 3.7, 2.2 Hz, H-5,), 4.26 (1H, dd, *J* = 12.1, 2.2 Hz, H-6), 4.18 (1H, dd, *J* = 12.5, 3.7 Hz, H-6′) 4.13 (1H, dd, *J* = 18.4, 5.3 Hz, CH_2), 4.02 (1H, dd, *J* = 18.4, 5.3 Hz, CH_2), 3.78 (3H, s, OCH_3), 2.10, 2.05, 2.01 (12H, 3 × s, OAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.5 ($COOCH_3$), 169.6, 169.5, 169.1 (CO), 164.9 (*C*ONH, $^3J_{CONH,H\text{-}2}$ = 4.1 Hz), 88.6 (C-1), 72.6, 71.1, 70.8, 67.5 (C-2 to C-5), 61.3 (C-6), 52.4 ($COOCH_3$), 40.8 (CH_2), 20.4, 20.3 (CO). Anal. Calcd for $C_{18}H_{24}N_4O_{12}$ (488.41): C, 44.27; H, 4.95; N, 11.47. Found: C, 44.35; H, 4.56; N, 11.26.

4.11.10. *N*-[(1-Azido-2,3,4,6-tetra-*O*-benzoyl-1-deoxy-α-D-glucopyranosyl)carbonyl]glycine methylester (*N*-(2-azido-3,4,5,7-tetra-*O*-benzoyl-2-deoxy-β-D-*gluco*-hept-2-ulopyranosonoyl)glycine methylester) 47. Prepared from **37** (0.07 g, 0.09 mmol) according to general procedure III. Yield: 0.04g (66%) colourless oil (R_f = 0.44, ethyl acetate–hexane 1:1); $[\alpha]_D$ = −13 (*c* 0.77, $CHCl_3$); ν_{max} ($CHCl_3$): 3648, 2954, 2128, 1732, 1600, 1522, 1264, 1092, 708; ^{1}H NMR ($CDCl_3$) δ (ppm): 8.20–7.24 (20H, m, Ph), 7.20 (1H, t, *J* = 5.3, 5.3 Hz, NH), 6.64 (1H, t, *J* = 9.5, 9.5 Hz, H-3), 5.86 (1H, dd, *J* = 10.0, 9.5 Hz, H-4), 5.78 (1H, d, *J* = 9.5 Hz, H-2), 5.10 (1H, ddd, *J* = 12.6, 3.7, 2.6 Hz, H-5,), 4.71 (1H, dd, *J* = 12.6, 2.6 Hz, H-6), 4.45 (1H, dd, *J* = 12.6, 3.7 Hz, H-6′) 4.14 (1H, dd, *J* = 17.9, 5.3 Hz, CH_2), 4.0 (1H, dd, *J* = 17.9, 5.3 Hz, CH_2), 3.54 (3H, s, OCH_3); ^{13}C NMR ($CDCl_3$) δ (ppm): 168.9 ($COOCH_3$), 166.0 (*C*ONH, $^3J_{CONH,H\text{-}2}$ = 6.5 Hz), 165.2, 165.1, 164.9 (CO), 133.6–128.2 (aromatics), 89.1 (C-1), 73.4, 71.6, 71.1, 68.6 (C-2 to C-5), 62.2 (C-6), 52.4 ($COOCH_3$), 41.1 (CH_2). Anal. Calcd for $C_{38}H_{32}N_4O_{12}$ (736.70): C, 69.96; H, 4.38; N, 7.61. Found: C, 69.85; H, 4.45; N, 7.36.

4.11.11. *C*-(2,3,4,6-Tetra-*O*-acetyl-1-azido-1-deoxy-β-D-galactopyranosyl)formic acid azide (3,4,5,7-tetra-*O*-acetyl-2-azido-2-deoxy-α-D-*galacto*-hept-2-ulopyranosonoyl azide) 48. Prepared from **30** according to general procedure III with 4 equiv NaN_3 in dry DMF. Purified by column chromatography (eluent: ethyl acetate–hexane 1:1): Yield: 0.07 g (60% for two steps from **18**) colourless oil (R_f = 0.58, ethyl acetate–hexane 2:1); $[\alpha]_D$ = +110 (*c* 0.20, $CHCl_3$); ν_{max} ($CHCl_3$): 2948, 2152, 1754, 1370, 1220, 1084; ^{1}H NMR ($CDCl_3$) δ (ppm): 5.53 (1H, dd, *J* = 3.7, <1 Hz, H-4), 5.49 (1H, d, *J* = 10.3 Hz, H-2), 5.32 (1H, dd, *J* = 10.3, 3.7 Hz, H-3), 4.51 (1H, ddd, *J* = 6.6, 6.6, <1 Hz, H-5), 4.24 (1H, dd, *J* = 11.8, 6.6 Hz, H-6), 4.19 (1H, dd, *J* = 11.8, 6.6 Hz, H-6′), 2.18, 2.12, 2.07, 1.99 (12H, 4 × s, OAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 171.4 (*C*ON$_3$, $^3J_{CON3,H-2}$ = <1 Hz), 170.1, 169.8, 169.7, 168.9, (CO), 95.0 (C-1), 73.2, 69.8, 66.4, 66.2 (C-2 to C-5), 60.3 (C-6), 20.7, 20.5, 20.4 (CH_3). Anal. Calcd for $C_{15}H_{18}N_6O_{10}$ (442.34): C, 40.73; H, 4.10; N, 19.00. Found: C, 40.70; H, 4.16; N, 19.25.

4.11.12. *C*-(2,3,4,6-Tetra-*O*-acetyl-1-azido-1-deoxy-β-D-galactopyranosyl)formic acid (3,4,5,7-tetra-*O*-acetyl-2-azido-2-deoxy-α-D-*galacto*-hept-2-ulopyranosonic acid) 49. Compound **48** (0.05 g, 0.11 mmol) and KOH (0.01 g, 0.18 mmol) were stirred in abs. DMF at rt for 21 h. The mixture was then diluted with water (10 mL), acidified to pH ~1 with 2 M HCl, and extracted with Et_2O (5 × 4 mL). After drying and removal of the solvent the residue was purified by column chromatography (eluent: $CHCl_3$–MeOH 7:3) to give 18 mg (38%) white crystals. Mp 155–158 °C; $[\alpha]_D$ = +33 (*c* 0.24, MeOH); ν_{max} ($CHCl_3$): 3904, 3420–2900 2130, 1752, 1230, 724; ^{1}H NMR (MeOD) δ (ppm): 5.96 (1H, dd, *J* = 10.6, 4.0 Hz, H-3), 5.46 (1H, dd, *J* = 4.0, <1 Hz, H-4), 5.24 (1H, d, *J* = 10.6 Hz, H-2), 4.89 (1H, ddd, *J* = 6.6, 6.6, <1 Hz, H-5), 4.59 (1H, s, COOH), 4.18 (1H, dd, *J* = 11.9, 6.6 Hz, H-6), 4.10 (1H, dd, *J* = 11.9, 6.6 Hz, H-6′), 2.16, 2.02, 2.01, 1.92 (12H, 4 × s, OAc); ^{13}C NMR (MeOD) δ (ppm): 172.1 (*C*OOH, $^3J_{COOH,H-2}$ = <1 Hz), 172.0 (2), 171.7, 171.4 (CO), 93.7 (C-1), 72.8, 71.4, 70.5, 69.1 (C-2 to C-5), 62.9 (C-6), 20.7, 20.6 (2), 20.5 (CH_3). Anal. Calcd for $C_{15}H_{19}N_6O_{11}$ (417.33): C, 43.17; H, 4.59; N, 10.07. Found: C, 42.96; H, 4.16; N, 9.80.

4.11.13. *N*-[(2,3,4,6-Tetra-*O*-acetyl-1-azido-1-deoxy-β-D-galactopyranosyl)carbonyl]glycine methylester (*N*-(3,4,5,7-tetra-*O*-acetyl-2-azido-2-deoxy-α-D-*galacto*-hept-2-ulopyranosonoyl)glycine methylester) 50. Prepared from **48** (0.09 g, 0.20 mmol) according to Method ***E***. Purified by column chromatography (eluent: ethyl acetate–hexane 1:1): Yield: 0.03 g (32%) colourless oil (R_f = 0.33, ethyl acetate–hexane 3:1); $[\alpha]_D$ = +42 (*c* 0.38, $CHCl_3$); ν_{max} ($CHCl_3$): 3398, 2956, 2135, 1754, 1698, 1372, 1220, 1084; ^{1}H NMR ($CDCl_3$) δ (ppm): 7.02 (1H, t, *J* = 5.1, 5.1 Hz, NH), 5.55 (1H, dd, *J* = 2.9, 1.5 Hz, H-4), 5.43 (1H, d, *J* = 9.5 Hz, H-2), 5.33 (1H, dd, *J* = 9.5, 2.9 Hz, H-3), 4.57 (1H, ddd, *J* = 6.6, 6.7, 1.5 Hz, H-5), 4.31 (1H, dd, *J* = 11.8, 6.6 Hz, H-6), 4.21 (1H, dd, *J* = 11.8, 5.9 Hz, H-6′), 4.13 (1H, dd, *J* = 18.9, 5.1 Hz, CH_2), 4.03 (1H, dd, *J* = 18.9, 5.1 Hz, CH_2), 3.79 (3H, s, OCH_3), 2.18, 2.13, 2.10, 1.99 (12H, 4 × s, OAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.4 (*C*OOCH$_3$), 169.8, 169.3 (CO), 165.0 (*C*ONH, $^3J_{CONH,H-2}$ = 2.8 Hz), 94.0 (C-1), 73.6, 73.4, 69.7, 66.5 (C-2 to C-5), 60.7 (C-6), 52.5 (COO*C*H$_3$), 41.1 (*C*H$_2$), 20.9, 20.8, 20.7, 20.6 (CO). Anal. Calcd for $C_{18}H_{24}N_4O_{12}$ (488.41): C, 44.27; H, 4.95; N, 11.47. Found: C, 44.19; H, 4.78; N, 11.55.

4.11.14. *C*-(2,3,4,6-Tetra-*O*-acetyl-1-azido-1-deoxy-α-D-galactopyranosyl)formic acid (3,4,5,7-tetra-*O*-acetyl-2-azido-2-deoxy-β-D-*galacto*-hept-2-ulopyranosonic acid) 51. Trichloroethyl ester **42** (0.05 g, 0.09 mmol) was suspended in abs. ethyl acetate (5 mL) and Zn dust (0.023 g, 3.3 equiv, activated by washing with 2 M HCl (2×), water (2×), acetone (2×) and diethylether (2×), then air dried on a glass filter) and 1-methylimidazole (NMI, 0.021 mL, 3 equiv) were added. The reaction mixture was stirred and refluxed till TLC (ethyl acetate–hexane 1:1) showed complete disappearance of the starting material. After filtration on a Celite bed EtOAc (5 mL) was added, and the filtrate washed by satd. aqueous $NaHCO_3$ (2×5 mL). The aqueous phase was acidified with 2 M HCl to pH ~2–3 and extracted with Et_2O (5 × 5 mL). After drying and removal of the solvent 0.03 g (59%) chromatographically uniform yellowish oil (R_f = 0.70, $CHCl_3$–MeOH 1:1) was obtained; $[\alpha]_D$ = +17 (*c* 0.20, $CHCl_3$); ν_{max} ($CHCl_3$): 3200–2800, 2130, 1746, 1372, 1222, 1064, 954, 714; ^{1}H NMR ($CDCl_3$) δ (ppm): 5.66 (1H, dd, *J* = 10.3, 2.9 Hz, H-3), 5.53 (1H, dd, *J* = 2.9, <1 Hz, H-4), 5.40 (1H, d, *J* = 10.3 Hz, H-2), 5.19 (1H, s, COOH), 4.62 (1H, ddd, *J* = 6.9, 6.6, <1 Hz, H-5), 4.20 (1H, dd, *J* = 11.8, 6.6 Hz, H-6), 4.16 (1H, dd, *J* = 11.8, 6.9 Hz, H-6′), 2.20, 2.10, 2.07, 1.99 (12H, 4 × s, OAc); ^{13}C NMR ($CDCl_3$) δ (ppm): 170.8 (*C*OOH, $^3J_{COOH,H-2}$ = 5.5 Hz), 170.2, 169.3, 167.1 (CO), 90.5 (C-1), 72.0, 69.0, 68.2, 66.9 (C-2 to C-5), 61.3 (C-6), 20.7, 20.6 (CO). Anal. Calcd for $C_{15}H_{19}N_3O_{11}$ (417.33): C, 43.17; H, 4.59; N, 10.07. Found: C, 43.22; H, 4.57; N, 10.00.

4.11.15. *C*-(2,3,4,6-Tetra-*O*-acetyl-1-amino-1-deoxy-D-galactopyranosyl)formic acid (3,4,5,7-tetra-*O*-acetyl-2-amino-2-deoxy-D-*galacto*-hept-2-ulopyranosonic acid) 52. Trichloroethyl ester **42** (0.18 g, 0.33 mmol) was suspended in glacial acetic acid (1 mL) and Zn dust (0.18 g, 10 equiv) was added. The mixture was stirred at rt until disappearance of the starting material, then diluted with water and filtered on a Celite bed. The filtrate was acidified with 2 M HCl to pH ~ 3 and extracted with Et_2O (5 × 5 mL). The organic phase was dried, the solvent removed to give 0.06 g (45%) yellowish oil; $[\alpha]_D$ = +31 (*c* 0.21, $CHCl_3$); R_f = 0.59 ($CHCl_3$–MeOH 1:1); ν_{max} ($CHCl_3$): 3200–2800, 1746, 1372, 1222, 1064, 954, 714; ^{1}H NMR ($CDCl_3$): δ (ppm): 7.10 (3H, very broad s, COOH, NH_2), 5.67 (1H, d, *J* = 10.6 Hz, H-2), 5.51 (1H, dd, *J* = 1.3, <1 Hz, H-4), 5.38 (1H, dd, *J* = 10.6, 4.0 Hz, H-3), 4.52 (1H, ddd, *J* = 6.6, 6.6, <1 Hz, H-5), 4.21–4.08 (2H, m, H-6, H-6′) 2.20, 2.06 (2), 1.99 (12H, 3 × s, OAc); ^{13}C NMR ($CDCl_3$): δ (ppm): 170.9 (*C*OOH), 170.6, 170.3, 170.2, 169.3 (CO), 94.4 (C-1), 68.8, 68.5, 67.9, 67.6 (C-2 to C-5), 61.4 (C-6), 20.6, 20.5 (CH_3). Anal. Calcd for

$C_{15}H_{21}NO_{11}$ (391.33): C, 46.04; H, 5.41; N, 3.58. Found: C, 46.22; H, 5.57; N, 3.36.

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