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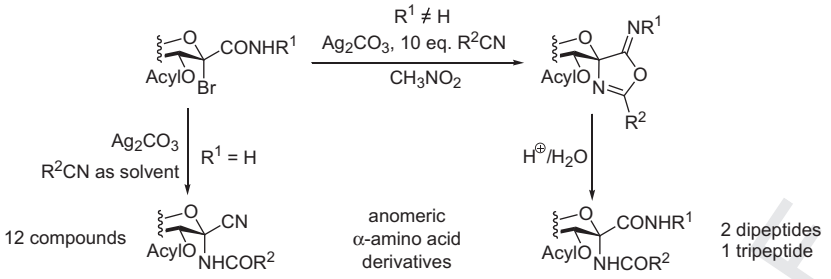
Graphical abstract

Ritter-type reaction of *C*-(1-bromo-1-deoxy-D-glycopyranosyl)formamides and its application for the synthesis of oligopeptides incorporating anomeric α-amino acids pp xxx–xxx

Katalin Czifrák, Viktor Gyóllai, Katalin E. Kövér, László Somsák *



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Ritter-type reaction of *C*-(1-bromo-1-deoxy-D-glycopyranosyl)formamides and its application for the synthesis of oligopeptides incorporating anomeric α-amino acids

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Oligopeptide

ABSTRACT

O-Peracetylated or -perbenzoylated *C*-(1-bromo-1-deoxy-D-glycopyranosyl)formamides of D-*gluco*, D-*galacto*, and D-*arabino* configuration were reacted with Ag(I)-salts or HgO in nitrile solvents to give *N*-acyl-1-cyano-D-glycopyranosylamines with an axial C–N bond at the anomeric centre. In the presence of $HgBr_2$, $Hg(CN)_2$, or $InCl_3$ the anomer of the above glycosylamine with an equatorial C–N bond was also isolated or detected. In CH_3NO_2 solutions as few as 5–10 equiv of the nitrile were sufficient to get acceptable yields for the products. Under similar conditions N-substituted *C*-(2,3,4,6-tetra-*O*-acetyl-1-bromo-1-deoxy-β-D-galactopyranosyl)formamides gave anomeric spiro-oxazoline derivatives which, upon mild acidic hydrolysis, opened up to di- and tripeptides of anomeric α-amino acids. Q1

1. Introduction

Ritter-type reactions involve combination of a carbocation (carbenium ion) with a nitrile (generally applied in high excess or as the solvent) to give a nitrilium ion which, after ensuing transformations by nucleophiles, may furnish carboxamides as well as heterocycles.[1,2] Glycosyl-nitrilium ions (**II** formed from glycosylium ions **I** and nitriles, Scheme 1) are known to play important roles in directing the stereoselectivity of glycosylation reactions towards the formation of equatorial glycosides.[3] On the other hand, attack of various external or internal nucleophiles onto glycosyl-nitrilium ions lead to several types of products rendering these transformations highly valuable in the carbohydrate field as well. Protecting groups in the sugar moieties can have a bearing on the configuration of glycosyl-nitrilium ions which tend to be axial (**II**) in the presence of non-participating protective groups demonstrated by NMR and computational methods[4] as well as by the structure of the end-products (vide infra). However, participating protection of the substituent in position 2 may force the formation of equatorial glycosyl-nitrilium ions (**III**). In these cases high equatorial selectivity can be observed in the products but, interestingly, exclusive axial selectivities were also reported in some transformations.

Thus, in the presence of non-participating 2-substituents, axial *N*-glycopyranosylamides were obtained from type **II** intermediates on the action of water,[5] and *N*,*N*-bis-acylamide products were formed with several aromatic carboxylic acids[6–8] and amino acids[9–11] as external nucleophiles. Carboxylic acids were also used as internal nucleophiles for the synthesis of several anomeric β-amino acid and peptide derivatives.[12–15] Further internal O-nucleophiles, such as a 2-*O*-Zn salt obtained from a 1,2-epoxide[16] and a 2-*O*-benzyl group[17] gave 1,2-annelated oxazolines, while the CH_2OH appendage of heptulopyranose[18] or fructopyranose[19] derivatives furnished spiro-oxazolines, each with an axial C–N bond at the anomeric carbon. 2-*N*-Substituents were also observed to attack the axial glycosyl-nitrilium ion and furnished 1,2-annelated imidazolines.[20,21]

With participating substituents next to the anomeric carbon, the outcome of the reactions is less predictable. With amino acids as well as aromatic carboxylic acids as external nucleophiles 2-deoxy-2-phthalimido[22] and 2-deoxy-2-tetrachlorophthalimido[11] D-glucopyranosyl derivatives gave equatorial *N*,*N*-bis-acylamide type products. Starting from *O*-perbenzoylated D-glucose, the equatorial amide was formed in low yield accompanied by several by-products in the presence of water as the nucleophile.[23] Under similar conditions *O*-peracetylated D-glucose, D-galactose, and D-mannose each gave mixtures of axial and equatorial amides with a large excess of the latter. To explain this for the D-mannose case, equilibration of the amides was invoked.[24] The internal

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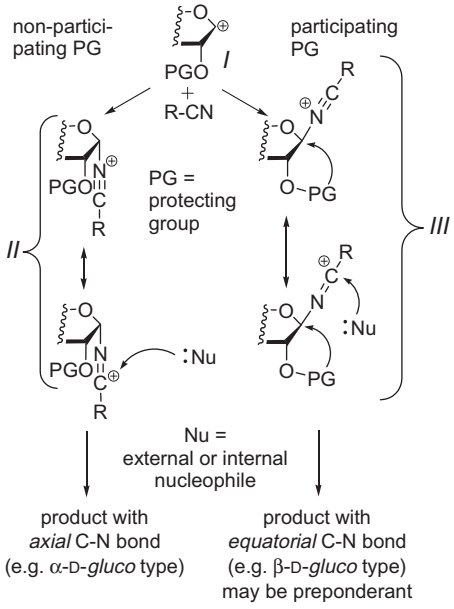


Scheme 1.

nucleophile CH_2OH group of a 3-*O*-benzoyl D-fructopyranose derivative gave only one spiro-oxazoline with an axial C–N bond.[19]

Unprotected sugars were reported to give 1,2-*cis* configured *N*-glycosylamides in liquid HF with both furanoid and pyranoid rings depending on the sugar configuration.[25] D-Glucose was converted to *N*-β-D-glucopyranosylamides with several nitriles in the presence of TMSOTf–$AgClO_4$ under mechanochemical conditions.[26]

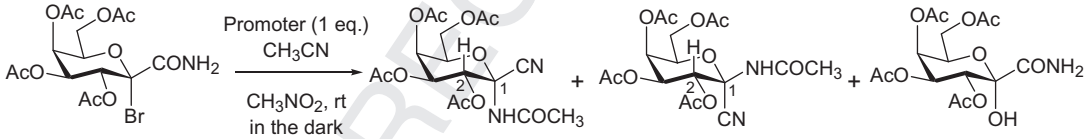
Some years ago we reported on the facile transformation of *C*-(1-bromo-1-deoxy-D-glycopyranosyl)formamides into *N*-acyl-1-cyano-D-glycopyranosylamines in the presence of Ag_2CO_3 in nitriles as solvents.[27] In this paper, a detailed investigation of this reaction and its extension to the synthesis of some oligopeptide derivatives with an anomeric α-amino acid moiety are presented.

2. Results and discussion

A Ritter-type reaction of *C*-(2,3,4,6-tetra-*O*-acetyl-1-bromo-1-deoxy-β-D-galactopyranosyl)formamide[28] (**1**, Table 1, entry 1) was first observed during an attempted exchange of the bromine to fluorine by AgF in dry CH_3CN. Under such conditions, widely applied for the synthesis of glycosyl fluoride derivatives (see Refs. 29–31 and references cited therein), an unexpected product, actually compound **2** was isolated in 70% yield instead of the expected *C*-(2,3,4,6-tetra-*O*-acetyl-1-deoxy-1-fluoro-α-D-galactopyranosyl)-formamide. In the presence of Ag_2CO_3 **1** was transformed to **2** in a very clean reaction (entry 2), while AgOTf gave the same result under significantly shorter reaction time (entry 6). The new product crystallized out during removal of the solvent after the usual work-up, did not exhibit characteristic fluoride couplings, had one exchangeable proton, and five methyl resonances in its ^1H NMR spectrum, and showed a CN signal in the ^{13}C NMR spectrum. Vicinal proton–proton couplings indicated that the sugar ring adopted a $^4C_1$ conformation. The CN resonance appeared as a pseudo triplet in the proton coupled carbon spectrum with ~3 Hz splittings due to couplings with H-2 and the NH protons. This allowed us to deduce the equatorial orientation for the CN group based on the $^3J_{H\text{-}2,CN}$ coupling in the $^4C_1$ conformation.[32–34]

Some other promoters[3] were also tried to perform this transformation. HgO (entry 7) gave similar results to those obtained with silver salts, but in the presence of $HgBr_2$, HgO–$HgBr_2$, $Hg(CN)_2$ and $InCl_3$ (entries 8, 12, 13, and 17, respectively) a second product identified as **3**, the anomer of **2**, was also detected and isolated from the mixtures. Appearance of **4**[35] in the reaction conducted

Table 1
Reaction of *C*-(2,3,4,6-tetra-*O*-acetyl-1-bromo-1-deoxy-β-D-galactopyranosyl)formamide (**1**) with CH_3CN under various conditions



1 **2** **3** **4**

Entry	Promoter	CH_3CN (equiv)	Reaction time	Product ratio (%) by ^1H NMR		
				2	**3**	**4**
1	AgF	As solvent	3 d	70[a,b]	—	—
2	Ag_2CO_3	As solvent	3 d	100	—	—
3		10	5 d	77	—	23
4		5	7 d	68	—	32
5		1.5	12 d	30		55[c]
6	AgOTf	As solvent	1 min	100	—	—
7	HgO	As solvent	8 h	100	—	—
8	$HgBr_2$	As solvent	1 d	72	28	—
9		10	1 d	41	33	26
10		5	1 d	30	25	36[c]
11		1.5	1 d	24	17	46[c]
12	HgO–$HgBr_2$	As solvent	16 h	91	9	—
13	$Hg(CN)_2$	As solvent	1 d	84	8	8
14		10	1 d	63	13	13[c]
15		5	1 d	53	16	21[c]
16		1.5	1 d	52	10	23[c]
17	$InCl_3$	As solvent	1 d	83	17	—
18		10	1 d	59	29	12
19		5	1 d	71	14	15
20		1.5	1 d	35	24	27[c]

[a] Isolated yield.
[b] *C*-(2,3,4,6-Tetra-*O*-acetyl-1-fluoro-α-D-galactopyranosyl)formamide was isolated in ~3% yield from the mother liquor.
[c] Together with an unidentified product in ~10–15% ratio.

with $Hg(CN)_2$ (entry 13) must be due to traces of water in the solvent. The structure of **3** was proven by NMR spectra showing characteristics similar to those of **2**, except for the appearance of the CN resonance as a pseudo triplet type with ~6 Hz coupling constants. Thus, the $^3J_{H\text{-}2,CN}$ couplings for **2** and **3** support the gauche and the antiperiplanar arrangements, respectively, of the nuclei involved in the $^4C_1$ conformation, and provide thereby unequivocal evidence for the anomeric configuration of these compounds.[32–34]

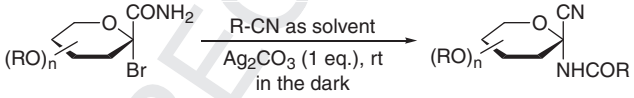
Having in mind the extension of this reaction to nitriles not applicable as solvents, several co-solvents were tried. In the presence of 5 equiv of CH_3CN the transformation of **1** was either incomplete or gave complex product mixtures in CH_2Cl_2, 1,4-dioxane, HMPT, and benzene (in the light of their reactivity alcohols, esters, ketones,[36] and sulfoxides[36] were not considered as solvents). However, in CH_3NO_2 rather clean reactions were observed: with the mercury(II) salts and $InCl_3$ (entries 9–11, 14–16, and 18–20, respectively) **2** and **3** were detected and, due to traces of water in the solvent CH_3NO_2, **4** also appeared in increasing ratios as the amount of CH_3CN decreased. A conceivable anomerization of **2** to **3** was excluded by experiments conducted with pure **2** or **3** in CH_3NO_2 in the presence of 2 equiv of $HgBr_2$ or $Hg(CN)_2$ showing no change of these compounds even at elevated temperatures such as 100 °C. On the other hand, with Ag_2CO_3 only **4** was observed as a by-product (entries 3–5). Thus, CH_3NO_2 and silver salts facilitate the use of nitriles in smaller excess maintaining the axial selectivity of the reaction.

Next the extension of the reaction to other nitriles applied as solvents and to starting *C*-(1-bromo-1-deoxy-D-glycopyranosyl)formamides **5**,[37] **6**,[38] and **7**[35] besides **1** was investigated (Table 2). In these experiments Ag_2CO_3 was used because of the cost, stability, and easy handling of the reagent. The results show that under these conditions several *O*-acyl protected 1-acylamino-1-deoxy-D-glycopyranosyl cyanides **8**–**18** can be obtained in acceptable to good yields. In each compound the cyano group occupies an equatorial position as shown by the $^3J_{H\text{-}2,CN}$ couplings in the range of 2.2–3.2 Hz indicating the incorporation of the nitrile reagent in an axial direction.

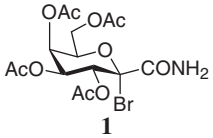
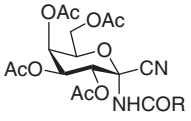
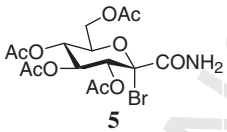
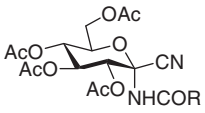
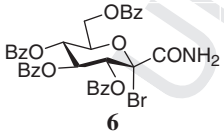
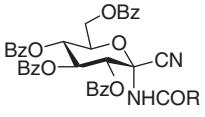
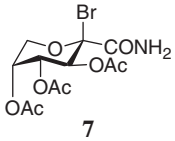
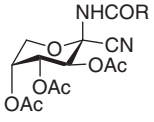
This Ritter-type reaction was also investigated with *N*-substituted *C*-(2,3,4,6-tetra-*O*-acetyl-1-bromo-1-deoxy-β-D-galactopyranosyl)formamides **19**[32] and **20** (Scheme 2). Compound **20** was prepared from pentachlorophenyl *C*-(2,3,4,6-tetra-*O*-acetyl-1-bromo-1-deoxy-β-D-galactopyranosyl)formate and L-alanine methyl-ester according to the procedure described for **19**.[32] Bromides **19** and **20** were each reacted with 1 equiv of Ag_2CO_3 in CH_3CN as the solvent to give the spiro-oxazoline derivatives **21** and **23** in good and modest yield, respectively. The reaction of **19** with 10 equiv of the solid benzyloxycarbonylamino-acetonitrile was performed in CH_3NO_2 in the presence of 1 equiv of Ag_2CO_3 to give the spiro compound **22**.

The structure of compounds **21**–**23** was established by NMR methods. The absence of exchangeable protons as well as resonances characteristic for imidate type carbons (155.8–158.2 ppm) were in accordance with the spirocyclic structures. Spectra for **22** exhibited two series of resonances indicating the presence of *E*/*Z* isomers along the C-5 = N bond, while for **21** and **23** only one isomer was present. This configurational issue was not investigated further. The $^4C_1$ conformation of the sugar rings was unequivocally assigned with the use of vicinal proton–proton coupling constants (see Section 3). The configuration of the anomeric carbon was established on the basis of three-bond heteronuclear couplings between H-2 and the exocyclic imine type carbon C-5 attached to C-1 of the sugar part (parent monosaccharide numbering). These couplings were measured using a sensitivity enhanced gradient long-range ^{13}C–^1H correlation experiment (G-HSQMBC),[39] and values around 3 Hz indicated *gauche* arrangement of the relevant atoms in the $^4C_1$ conformation.

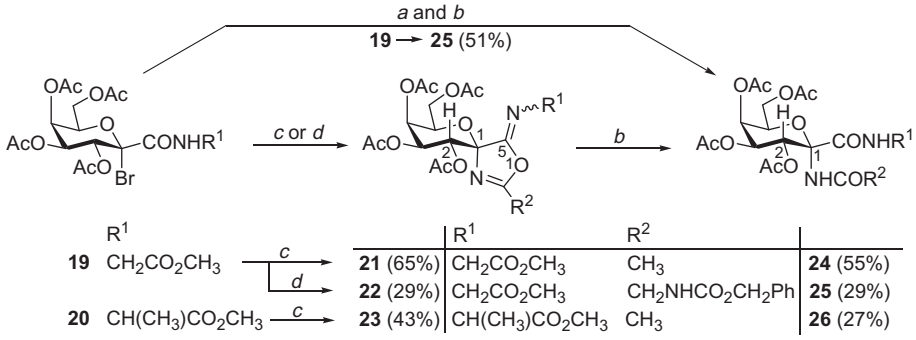
Table 2
Preparation of *O*-peracylated *N*-acyl-1-cyano-D-glycopyranosylamines



1, 5-7 **2, 8-18**

Starting compound	R	Yield (%)	Product
 **1**	CH_3– CH_3CH_2– CH_2=CH– CH_2=CH–CH_2– CH_3OCH_2–	**2** (76) **8** (74) **9** (57) **10** (62) **11** (24)	
 **5**	CH_3– CH_3CH_2–	**12** (36)[a] **13** (53)	
 **6**	CH_3– CH_3CH_2– $(CH_3)_3C$–	**14** (78)[33] **15** (57) **16** (27)	
 **7**	CH_3– CH_2=CH–	**17** (41) **18** (43)	

[a] With 2 equiv AgF.



Scheme 2. Reagents and conditions: (a) 1 equiv AgOTf, 10 equiv $PhCH_2OCONHCH_2CN$, CH_3NO_2, in the dark, rt; (b) 1 equiv CF_3CO_2H or CH_3CO_2H, 2 equiv H_2O, CH_2Cl_2, rt; (c) 1 equiv Ag_2CO_3, CH_3CN, in the dark, rt; (d) 1 equiv Ag_2CO_3, 10 equiv $PhCH_2OCONHCH_2CN$, CH_3NO_2, in the dark, rt.

Spiro-oxazolines **21**–**23** were opened up by mild acidic hydrolysis to peptide derivatives **24**–**26**, respectively. Carrying out the Ritter-reaction of **19** with benzyloxycarbonylamino-acetonitrile and the hydrolysis of the intermediate spiro-derivative in a continuous operation improved the overall yield of **25** to 51% for the two steps.

For **24**–**26** the NMR structural elucidation showed the presence of amide carbonyls (166.1–167.3 ppm) instead of imidate type carbons. The $^3J_{H\text{-}2,CONHR1}$ couplings were obtained from experiments as above, and the 2.4–2.9 Hz values were indicative of the equatorial position of the $CONHR^1$ moiety. To corroborate this configurational assignment dipeptide **29**, the anomeric pair of **24**, was also synthesised (Scheme 3). Azide **27**[32] was reduced by Raney-Ni to glycosylamine **28**. In this reaction the formation of anomers or anomerisation of the formed glycosylamine cannot be excluded, however, the product **28** isolated from the crude mixture by crystallization existed in the β-D-anomeric configuration as revealed by the $^3J_{H\text{-}2,CONHR1}$ of 5.8 Hz coupling. Conventional acetylation of **28** by AcCl in pyridine gave a mixture of **24** and **29** (possibly due to anomerisation of **28** under the reaction conditions) which could be separated by column chromatography. For **29** the $^3J_{H\text{-}2,CONHR1}$ coupling was 5.3 Hz, and thus these heteronuclear three-bond coupling values for the anomeric pairs **24** and **29** proved the configuration of the anomeric carbon in both compounds.

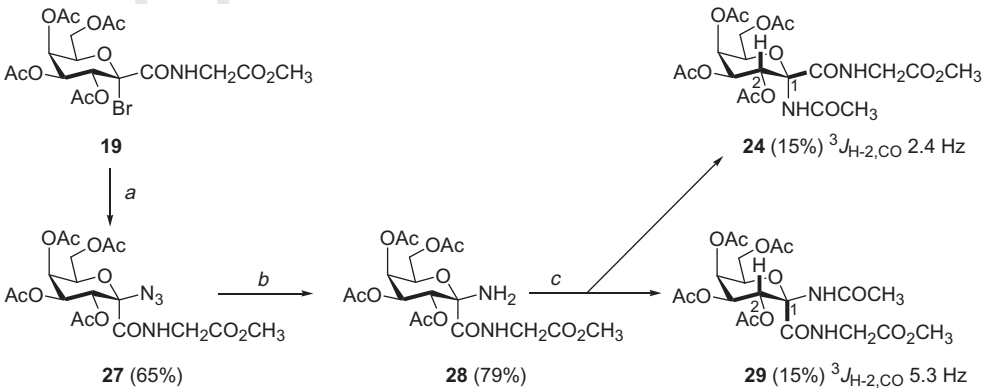
The formation of the new compounds by nitrile incorporation can be explained following the mechanistic proposal shown in Scheme 4. A promoter facilitates removal of a bromide ion from the substrates (**1**, **5**–**7**, **19**, **20**) to give glycosylium ion **B**. Axial attack of a nitrile may give glycosyl-nitrilium ion represented by resonance forms **F** and **G**. Intramolecular nucleophilic attack by the amide carbonyl oxygen may lead to spirocyclic intermediate **H** which, on losing a proton, gives spiro-oxazolines **21**–**23** as well as **D**. Tautomeric ring opening of the oxazoline in **D** and a subsequent tautomerization of **C** result in the end-products **2**, and **8**–**18**. In the presence of promoters other than silver salts formation of **3** was also observed. Since the anomeric interconversion of **2** and **3** was excluded, this can be accounted for by neighbouring group participation of the acyl protecting groups of O-2 as illustrated by **E** resulting in an equatorial attack of the nitrile. Glycosyl-nitrilium ion **A** may then follow similar transformations as those starting with **G**, and end up with **3** as the isolable product. We have no explanation for the finding that with silver salts no compounds of type **3** were formed.

In conclusion, a Ritter-type reaction of a series of *O*-peracylated *C*-(1-bromo-1-deoxy-D-glycopyranosyl)formamides and nitriles promoted by silver salts gave access to *N*-acyl-1-cyano-D-glycopyranosylamines which can be regarded as anomeric α-amino acid derivatives[40–43] and new derivatives of artificial ketoses.[44] The reaction was extended to *N*-substituted *C*-(1-bromo-1-deoxy-β-D-galactopyranosyl)formamides which gave anomeric spiro-oxazoline derivatives. In each of these compounds the newly formed C–N bond at the anomeric carbon was axially oriented in spite of the participating protecting groups at the equatorial O-2. Mild acidic hydrolysis of the spiro-oxazolines led to di- and tripeptides incorporating anomeric α-amino acids, thereby complementing reported synthetic methods for this class of sugar–peptide derivatives.[45–50]

3. Experimental

3.1. General methods

Melting points were measured in open capillary tubes or on a Kofler hot-stage and are uncorrected. Optical rotations were determined with a Perkin–Elmer 241 polarimeter at room temperature.



Scheme 3. Reagents and conditions: (a) 2 equiv NaN_3, DMSO, rt; (b) ~2 equiv Raney-Ni, H_2, EtOAc, 70 °C; (c) 2 equiv CH_3COCl, pyridine, rt.

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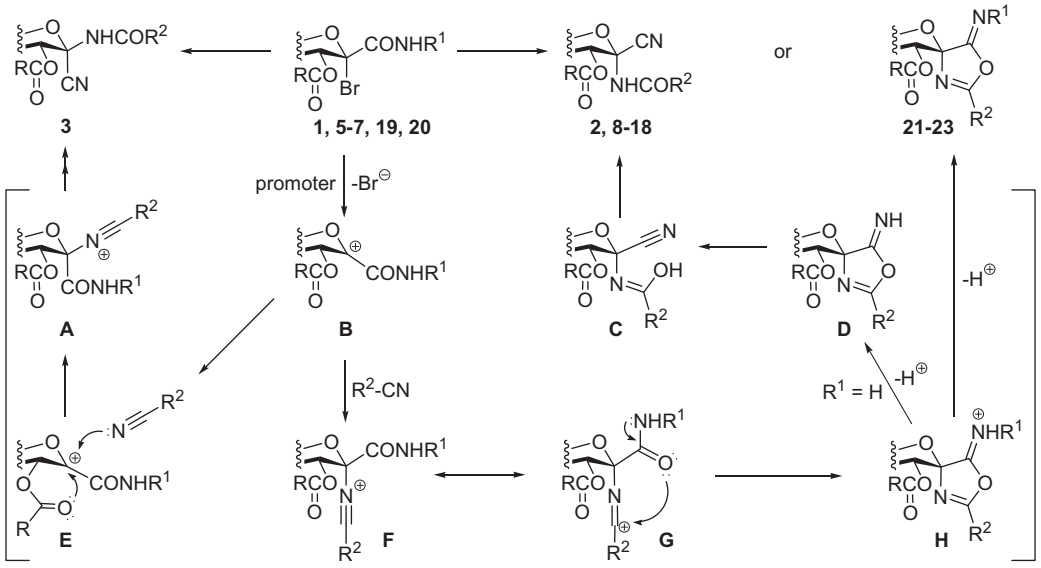

Scheme 4.

NMR spectra were recorded with Bruker 200 (200/50 MHz for $^{1}H/^{13}C$), Bruker 360 (360/90 MHz for $^{1}H/^{13}C$) or Avance DRX 500 (500/125 MHz for $^{1}H/^{13}C$) spectrometers. Chemical shifts are referenced to Me4Si (^{1}H), or to the residual solvent signals (^{13}C). TLC was performed on DC-Alurolle Kieselgel 60 F_{254} (Merck), and the plates were visualised under UV light and by gentle heating. For column chromatography Kieselgel 60 (Merck, particle size 0.063–0.200 mm) was used. Organic solutions were dried over anhydrous $MgSO_4$ and concentrated under diminished pressure at 40–50 °C (water bath). CH_3CN, CH_3NO_2 were distilled from P_2O_5, other nitriles, AgOTf, and AgF were purchased from Sigma-Aldrich and used without further purification. Ag_2CO_3 was prepared from $AgNO_3$ and K_2CO_3, and dried over P_2O_5.

3.2. General procedure for the preparation of *O*-peracylated *N*-acyl-1-cyano-D-glycopyranosylamines) (2-acylamino-2-deoxy-hept(hex)-2-ulopyranosononitriles) (2, 8–18)

An *O*-peracylated *C*-(1-bromo-1-deoxy-D-glycopyranosyl)formamide (**1**,[28] **5**,[37] **6**,[38] or **7**,[35] 0.25 mmol) was dissolved in a nitrile (1 mL), and silver carbonate (0.07 g, 0.25 mmol) or silver fluoride (0.063 g, 0.50 mmol) was added in one portion. The mixture was stirred at rt in the dark until complete disappearance of the starting material (2–3 days, TLC 3:1 EtOAc–hexane). It was then diluted with acetone (9 mL), filtered through a Celite pad, the filter cake was washed with acetone (3 mL), and the filtrate was concentrated. The residue was purified by column chromatography or crystallisation to give pure products.

3.2.1. *N*-Acetyl-2,3,4,6-tetra-*O*-acetyl-1-cyano-α-D-galactopyranosylamine (2-acetamido-3,4,5,7-tetra-*O*-acetyl-2-deoxy-α-D-*galacto*-hept-2-ulopyranosononitrile) (2)

Prepared from **1** (0.51 g, 1.12 mmol) in CH_3CN according to Section 3.2. Reaction time 2 d, purification by column chromatography (1:3 EtOAc–$CHCl_3$), yield 0.35 g (76%) white crystals. Mp: 155–156 °C; $[\alpha]_D$ +49 (*c* 1.15, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm) 7.90 (s, 1H, NH), 5.75 (d, 1H, $J_{2,3}$ 10.7 Hz, H-2), 5.30 (dd, 1H $J_{2,3}$ 10.7 Hz, $J_{3,4}$ 3.4 Hz, H-3), 5.27 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{4,5}$ 1.1 Hz, H-4), 4.26 (t, 1H, $J_{5,6}$ 6.0 Hz, $J_{5,6'}$ 6.0 Hz, H-5), 4.10–4.08 (m, 2H, H-6, H-6′), 2.20, 2.19 (2), 2.03, 1.99 (4s, 15H, $OCOCH_3$, $NHCOCH_3$); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 171.2 ($NHCOCH_3$), 170.3, 170.0, 169.7 168.2 (*C*O), 114.7 (*C*N, $^{3}J_{H\text{-}2,CN}$ = ~3.0), 77.7 (C-1), 67.7, 67.5, 67.3, 66.7 (C-2–C-5), 60.6 (C-6), 22.9 ($NHCOCH_3$), 20.3 (2), 20.5 (2) (CH_3); Anal. Calcd for $C_{17}H_{22}N_2O_{10}$ (414.36): C, 49.28; H, 5.35; N, 6.76. Found: C, 48.27; H, 5.43; N, 6.35.

3.2.2. *N*-Acetyl-2,3,4,6-tetra-*O*-acetyl-1-cyano-β-D-galactopyranosylamine (2-acetamido-3,4,5,7-tetra-*O*-acetyl-2-deoxy-β-D-*galacto*-hept-2-ulopyranosononitrile) (3)

Compound **1** (0.50 g, 1.10 mmol) was dissolved in a mixture of dry CH_3NO_2 (5 mL), CH_3CN (10 equiv) was added, and the solution was stirred with freshly activated molecular sieves overnight. $HgBr_2$ (0.50 g, 1.39 mmol) was added in one portion. The mixture was stirred at rt until complete disappearance of the starting material (TLC, 3:1 EtOAc–hexane) (2–3 days). It was then diluted with $CHCl_3$, filtered through a Celite pad, and the filtrate was concentrated under diminished pressure. The residue was dissolved in $CHCl_3$ and washed several times with 1 M KBr solution in order to remove mercury salts. The crude oil was purified by column chromatography (1:1→3:1 EtOAc–hexane) to give pure products: **2** (0.08 g, 20%) and **3** (0.15 g, 33%), **4** (0.07 g, 15%).

Compound **3** was obtained as white crystals. Mp 161–163 °C; $[\alpha]_D$ +262 (*c* 0.17, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm) 7.21 (s, 1H, NH), 5.53 (dd, 1H, $J_{3,4}$ 3.1 Hz, $J_{4,5}$ 1.3 Hz, H-4), 5.41 (dd, 1H, $J_{2,3}$ 10.5 Hz, $J_{3,4}$ 3.1 Hz, H-3), 5.22 (d, 1H, $J_{2,3}$ 10.5 Hz, H-2), 4.44 (t, 1H, $J_{5,6}$ 6.8 Hz, $J_{5,6'}$ 6.8 Hz, H-5), 4.21–4.16 (m, 2H, H-6, H-6′), 2.21, 2.16, 2.06 (2), 2.01 (4s, 15H, $OCOCH_3$, $NHCOCH_3$); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 171.7 ($NHCOCH_3$), 170.1, 169.6, 169.3 169.1 (*C*O), 111.9 (*C*N, $^{3}J_{H\text{-}2,CN}$ = ~5.8 Hz), 79.9 (C-1), 71.2, 68.5 (2), 66.1 (C-2–C-5), 60.2 (C-6), 23.1 ($NHCOCH_3$), 20.5, 20.4, 20.3, 20.2 (CH_3); Anal. Calcd for $C_{17}H_{22}N_2O_{10}$ (414.36): C, 49.28; H, 5.35; N, 6.76. Found: C, 48.77; H, 5.23; N, 6.00.

3.2.3. *N*-Propanoyl-2,3,4,6-tetra-*O*-acetyl-1-cyano-α-D-galactopyranosylamine (3,4,5,7-tetra-*O*-acetyl-2-deoxy-2-propanamido-α-D-*galacto*-hept-2-ulopyranosononitrile) (8)

Prepared from **1** (0.05 g, 0.11 mmol) in CH_3CH_2CN according to Section 3.2. Reaction time 2 d, purification by column chromatography (1:3 EtOAc–$CHCl_3$), yield 0.035 g (74%) white crystals. Mp: 186–187 °C; $[\alpha]_D$ +55 (*c* 0.91, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm) 7.68 (s, 1H, NH), 5.76 (d, 1H, $J_{2,3}$ 10.6 Hz, H-2), 5.30 (dd, 1H, $J_{2,3}$ 10.6 Hz, $J_{3,4}$ 3.4 Hz, H-3), 5.38 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{4,5}$ 1.0 Hz, H-4), 4.26 (t, 1H, $J_{5,6}$ 6.6 Hz, $J_{5,6'}$ 6.6 Hz, H-5), 4.10 (m, 2H,

H-6, H-6′), 2.42 (q, 2H, *J* 7.3 Hz, *J* 7.3 Hz, CH_2), 2.20, 2.17, 2.02, 1.98 (4s, 12H, $OCOCH_3$), 1.21 (t, 3H, *J* 7.3 Hz, *J* 7.3 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 174.5 ($NHCOCH_2CH_3$), 170.3, 170.0, 169.7 168.1 (*C*O), 114.8 (*C*N, $^3J_{H\text{-}2,CN}$ = ~3.0), 77.6 (C-1), 67.6 (2), 67.4, 67.3, 66.7 (C-2–C-5), 60.6 (C-6), 28.9 ($NHCOCH_2CH_3$), 20.3 (2), 20.5 (2) (CH_3), 8.9 ($NHCOCH_2CH_3$); Anal. Calcd for $C_{18}H_{24}N_2O_{10}$ (428.39): C, 50.47; H, 5.65; N, 6.54. Found: C, 50.41; H, 5.93; N, 6.67.

3.2.4. *N*-Propenoyl-2,3,4,6-tetra-*O*-acetyl-1-cyano-α-D-galacto-pyranosylamine (3,4,5,7-tetra-*O*-acetyl-2-deoxy-2-propen-amido-α-D-*galacto*-hept-2-ulopyranosononitrile) (9)

Prepared from **1** (0.05 g, 0.11 mmol) in CH_2CHCN according to Section 3.2. Reaction time 2 d, purification by column chromatography (1:3 EtOAc–$CHCl_3$), yield 0.03 g (57%) white crystals. Mp: 158–160 °C; $[\alpha]_D$ +61 (*c* 0.80, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 7.20 (s, 1H, NH), 6.51 (d, 1H, *J* 7.3 Hz, CH_2), 6.29 (dd, 1H, *J* 7.3 Hz, *J* 6.9 Hz, CH), 5.86 (d, 1H, *J* 6.9 Hz, CH_2), 5.78 (d, 1H, $J_{2,3}$ 10.6 Hz, H-2), 5.25 (dd, 1H, $J_{2,3}$ 10.6 Hz, $J_{3,4}$ 2.8 Hz, H-3), 5.39 (dd, 1H, $J_{3,4}$ 2.8 Hz, $J_{4,5}$ 1.1 Hz, H-4), 4.23 (t, 1H, $J_{5,6}$ 6.6 Hz, $J_{5,6'}$ 6.6 Hz, H-5), 4.18 (dd, 1H, $J_{6,6'}$ 10.7 Hz, $J_{5,6}$ 6.6 Hz, H-6), 4.09 (dd, 1H, $J_{6,6'}$ 10.7 Hz, $J_{5,6}$ 6.6 Hz, H-6), 2.20, 2.16, 2.02, 1.99 (4s, 12H, $OCOCH_3$); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 170.3 ($NHCOCH{=}CH_2$), 170.1, 170.0, 169.7, 168.1 (*C*O), 130.2 (*C*H=CH_2), 128.8 (CH=CH_2), 114.5 (*C*N, $^3J_{H\text{-}2,CN}$ = ~3.2), 78.2 (C-1), 68.1, 67.7, 67.6, 66.7 (C-2–C-5), 60.6 (C-6), 20.5 (2), 20.4 (2) (CH_3); Anal. Calcd for $C_{18}H_{22}N_2O_{10}$ (426.37): C, 50.70; H, 5.20; N, 6.57. Found: C, 49.93; H, 5.12; N, 6.39.

3.2.5. *N*-(But-3-enoyl)-2,3,4,6-tetra-*O*-acetyl-1-cyano-α-D-galac-topyranosylamine (3,4,5,7-tetra-*O*-acetyl-2-(but-3-enamido)-2-deoxy-α-D-*galacto*-hept-2-ulopyranosononitrile) (10)

Prepared from **1** (0.10 g, 0.22 mmol) in CH_2CHCH_2CN according to Section 3.2. Reaction time 2 d, purification by column chromatography (1:3 EtOAc–$CHCl_3$), yield 0.06 g (62%) white crystals. Mp: 149–150 °C; $[\alpha]_D$ +57 (*c* 0.88, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 6.85 (s, 1H, NH), 5.99 (m, 1H, CH), 5.38 (d, 1H, $J_{2,3}$ 10.7 Hz, H-2), 5.40–5.35 (m, 2H, H-3, H-4), 5.14 (m, 2H, CH_2), 4.20 (m, 3H, H-5, H-6, H-6′), 3.19 (d, 2H, *J* 7.3 Hz, CH_2), 2.20, 2.16, 2.03, 2.00 (4s, 12H, $OCOCH_3$); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 170.3 ($NHCOCH_2CH{=}CH_2$), 170.0, 169.9 167.8, 167.7 (*C*O), 129.9 ($NHCOCH_2CH{=}CH_2$), 120.5 ($NHCOCH_2CH{=}CH_2$), 114.4 (*C*N, $^3J_{H\text{-}2,CN}$ = ~3.1 Hz), 78.0 (C-1), 68.0, 67.7, 67.6, 66.6 (C-2–C-5), 60.7 (C-6), 41.0 ($NHCOCH_2CH{=}CH_2$) 20.5 (2), 20.4, 20.3 (CH_3); Anal. Calcd for $C_{19}H_{24}N_2O_{10}$ (440.40): C, 51.82; H, 5.49; N, 6.36. Found: C, 51.34; H, 5.43; N, 6.55.

3.2.6. *N*-Methoxyacetyl-2,3,4,6-tetra-*O*-acetyl-1-cyano-α-D-galac-topyranosylamine (3,4,5,7-tetra-*O*-acetyl-2-deoxy-2-methoxy-acetamido-α-D-*galacto*-hept-2-ulopyranosononitrile) (11)

Prepared from **1** (0.10 g, 0.22 mmol) in CH_3OCH_2CN according to Section 3.2. Reaction time 2 d, purification by column chromatography (1:3 EtOAc–$CHCl_3$), yield 0.02 g (24%) white crystals. Mp: 149–151 °C; $[\alpha]_D$ +29 (*c* 1.22, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 7.34 (s, 1H, NH), 5.78 (d, 1H, $J_{2,3}$ 10.9 Hz, H-2), 5.41 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{4,5}$ 1.1 Hz, H-4), 5.11 (dd, 1H, $J_{2,3}$ 10.9 Hz, $J_{3,4}$ 3.2 Hz, H-3), 4.22–4.05 (m, 3H, H-5, H-6, H-6′), 4.04 (d, 1H, *J* 6.9 Hz, CH_2), 3.97 (d, 1H, *J* 6.9 Hz, CH_2), 3.49 (s, 3H, OCH_3), 2.21, 2.17, 2.03, 2.01 (4s, 12H, $OCOCH_3$); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 170.4 ($NHCOCH_2OCH_3$), 170.1, 169.9 169.3, 167.7 (*C*O), 114.1 (*C*N, $^3J_{H\text{-}2,CN}$ = ~3.0), 77.8 (C-1), 71.6 ($NHCO\text{-}CH_2OCH_3$), 68.1, 67.8, 67.5, 66.4 (C-2–C-5), 60.5 (C-6), 59.3 ($NHC\text{-}OCH_2OCH_3$), 20.6 (2), 20.4, 20.3 (CH_3); Anal. Calcd for $C_{18}H_{24}N_2O_{11}$ (444.39): C, 48.65; H, 5.44; N, 6.30. Found: C, 50.00; H, 5.70; N, 6.47.

3.2.7. *N*-Acetyl-2,3,4,6-tetra-*O*-acetyl-1-cyano-α-D-glucopyrano-sylamine (2-acetamido-3,4,5,7-tetra-*O*-acetyl-2-deoxy-α-D-*gluco*-hept-2-ulopyranosononitrile) (12)

Prepared from **5** (0.60 g, 1.32 mmol) in CH_3CN with AgF according to Section 3.2. Reaction time 1 d, purification by column chromatography (1:1→3:1 EtOAc–hexane), yield 0.20 g (36%) white crystals. Mp 179–181 °C; $[\alpha]_D$ +57 (*c* 1.01, acetone).

^1H NMR ($(CD_3)_2CO$, 200 MHz): δ (ppm) 8.72 (s, 1H, NH), 5.52 (d, 1H, $J_{2,3}$ 10.0 Hz, H-2), 5.42 (dd, 1H, $J_{3,4}$ 4.5 Hz, $J_{4,5}$ 2.4 Hz, H-4), 5.16 (dd, 1H, $J_{2,3}$ 9.8 Hz, $J_{3,4}$ 4.5 Hz, H-3), 4.31 (dd, 1H, $J_{6,6'}$ 12.3 Hz, $J_{5,6}$ 6.0 Hz, H-6), 4.02 (dd, 1H, $J_{6,6'}$ 12.3 Hz, $J_{5,6}$ 6.0 Hz, H-6′), 2.11, 2.10, 2.02, 1.99, 1.96 (5s, 15H, $NHCOCH_3$,$OCOCH_3$); ^{13}C NMR ($(CD_3)_2CO$, 50 MHz): δ (ppm) 170.7 ($NHCOCH_3$), 170.4, 170.2, 169.8, 168.9 (*C*O), 115.9 (*C*N, $^3J_{H\text{-}2,CN}$ = ~3.0 Hz), 78.1 (C-1), 71.5, 71.1, 69.2, 68.5 (C-2–C-5), 61.8 (C-6), 22.9 ($NHCOCH_3$), 20.5, 20.4 (2), 20.3(CH_3); Anal. Calcd for $C_{17}H_{22}N_2O_{10}$ (414.364): C, 49.28; H, 5.35; N, 6.76. Found: C, 48.52; H, 5.60; N, 6.70.

3.2.8. *N*-Propanoyl-2,3,4,6-tetra-*O*-acetyl-1-cyano-α-D-gluco-pyranosylamine (3,4,5,7-tetra-*O*-acetyl-2-deoxy-2-propan-amido-α-D-*gluco*-hept-2-ulopyranosononitrile) (13)

Prepared from **5** (0.31 g, 0.69 mmol) in CH_3CH_2CN according to Section 3.2. Reaction time 3 d, purification by column chromatography (1:3 EtOAc–$CHCl_3$), yield 0.16 g (53%) white crystals from EtOAc. Mp: 187–189 °C; $[\alpha]_D$ +25 (*c* 0.61, $CHCl_3$); ^1H NMR ($CDCl_3$, 200 MHz): δ (ppm) 6.97 (s, 1H, NH), 5.57 (d, 1H, $J_{2,3}$ 9.8 Hz, H-2), 5.31 (dd, 1H, $J_{3,4}$ 4.4 Hz, $J_{4,5}$ 1.1 Hz, H-4), 5.16 (dd, 1H, $J_{2,3}$ 9.8 Hz, $J_{3,4}$ 4.4 Hz, H-3), 4.29 (dd, 1H, $J_{6,6'}$ 12.5 Hz, $J_{5,6}$ 6.0 Hz, H-6), 4.00 (dd, 1H, $J_{6,6'}$ 12.5 Hz, $J_{5,6}$ 6.0 Hz, H-6), 3.96 (t, 1H, $J_{5,6}$ 6.0 Hz, $J_{5,6'}$ 6.0 Hz, H-5), 2.42 (q, 2H, *J* 7.3 Hz, *J* 7.2 Hz, CH_2CH_3), 2.16, 2.11, 2.03 (2) (3s, 12H, $OCOCH_3$), 1.21 (t, 3H, *J* 7.3 Hz, *J* 7.2 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$, 50 MHz): δ (ppm) 173.4 ($NHCOCH_2CH_3$), 170.3, 169.8, 168.7, 167.6 (*C*O), 114.1 (*C*N, $^3J_{H\text{-}2,CN}$ = ~3.0 Hz), 76.0 (C-1), 70.1, 69.8, 68.2, 66.9 (C-2–C-5), 60.6 (C-6), 28.7 (CH_2CH_3), 20.2, 20.1, 20.0, 19.9 (CH_3), 8.4 (CH_2CH_3); Anal. Calcd for $C_{18}H_{24}N_2O_{10}$ (428.391): C, 50.47; H, 5.65; N, 6.54. Found: C, 50.03; H, 5.52; N, 6.23.

3.2.9. *N*-Propanoyl-2,3,4,6-tetra-*O*-benzoyl-1-cyano-α-D-gluco-pyranosylamine (3,4,5,7-tetra-*O*-benzoyl-2-deoxy-2-propan-amido-α-D-*gluco*-hept-2-ulopyranosononitrile) (15)

Prepared from **6** (0.30 g, 0.43 mmol) in CH_3CH_2CN according to Section 3.2. Reaction time 2 d, purification by column chromatography (1:3 EtOAc–CH_2Cl_2), yield 0.17 g (57%) white crystals. Mp: 239–241 °C; $[\alpha]_D$ +62.0 (*c* 1.03, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm): 8.00–7.08 (m, 20H, ArH), 7.71 (s, 1H, NH), 6.88 (pseudo t, 1H, *J* 9.8 Hz, *J* 9.2 Hz, H-3 or H-4), 6.36 (d, 1H, $J_{2,3}$ 9.8 Hz, H-2), 5.82 (pseudo t, 1H, *J* 9.8 Hz, *J* 9.2 Hz, H-3 or H-4), 4.46–4.40 (m, 3H, H-5, H-6, H-6′), 2.40 (pseudo q, 2H, *J* 7.2 Hz, *J* 5.2 Hz, CH_2), 1.10 (pseudo t, 3H, *J* 7.2 Hz, *J* 5.2 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm): 166.1 ($NHCOCH_2CH_3$), 166.1, 165.8, 164.8, 164.7 (*C*O), 134.0–127.4 (benzoyl ArC), 114.8 (CN, $^3J_{H\text{-}2,CN,}$ = ~2.2 Hz), 77.8 (C-1), 71.4, 70.8, 69.2, 68.5 (C-2–C-5), 62.0 (C-6), 29.0 ($NHCOCH_2CH_3$), 8.10 ($NHCOCH_2CH_3$); Anal. Calcd for $C_{38}H_{32}N_2O_{10}$ (676.69): C, 67.45; H, 4.77; N, 4.14. Found: C, 67.10; H, 4.36; N, 4.01.

3.2.10. *N*-Pivaloyl-2,3,4,6-tetra-*O*-benzoyl-1-cyano-α-D-gluco-pyranosylamine (3,4,5,7-tetra-*O*-benzoyl-2-deoxy-2-pival-amido-α-D-*gluco*-hept-2-ulopyranosononitrile) (16)

Prepared from **6** (0.20 g, 0.28 mmol) in $(CH_3)_3CCN$ according to Section 3.2. Reaction time 2 d, purification by column chromatography (1:2 EtOAc–Hexane), yield 0.06 g (27%) white crystals and compound **4** (0.05 g, 27%). Mp: 226–229 °C; $[\alpha]_D$ +37 (*c* 0.98, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm): 8.10–7.24 (m, 20H, ArH), 6.85 (s, 1H, NH), 6.13 (d, 1H, $J_{2,3}$ 9.8 Hz, H-2), 5.70 (pseudo

t, 2H, *J* 9.8 Hz, *J* 9.2 Hz in each, H-3, H-4), 4.62 (dd, 1H, $J_{6,6'}$ 12.5 Hz, $J_{5,6}$ 2.6 Hz, H-6), 4.46 (dd, 1H, $J_{6,6'}$ 12.6 Hz, $J_{5,6'}$ 5.9 Hz, H-6′), 4.34 (ddd, 1H, $J_{4,5}$ 9.8 Hz, $J_{5,6}$ 5.9 Hz, $J_{5,6'}$ 2.6 Hz, H-5), 1.33 (s, 9H, C_4H_9); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm): 177.6 ($NHCOC(CH_3)_3$), 166.0, 165.9, 164.9, 163.5 (CO), 133.5–127.6 (benzoyl ArC), 114.4 (CN, $^3J_{H\text{-}2,CN}$ = ~2.6 Hz), 77.8 (C-1), 71.6, 70.6, 69.6, 68.5 (C-2–C-5), 67.0 ($NHCOC(CH_3)_3$), 62.2 (C-6), 27.2 ($NHCOC(CH_3)_3$) Anal. Calcd for $C_{40}H_{36}N_2O_{10}$ (704.74): C, 68.17; H, 5.15; N, 3.97. Found: C, 68.00; H, 4.86; N, 4.11.

3.2.11. *N*-Acetyl-2,3,4-tri-*O*-acetyl-1-cyano-β-D-arabinopyranosylamine (2-acetamido-3,4,5-tri-*O*-acetyl-2-deoxy-β-D-*arabino*-hex-2-ulopyranosononitrile) (17)

Prepared from **7** (0.14 g, 0.36 mmol) in CH_3CN according to Section 3.2. Reaction time 2 d, purification by column chromatography (1:1→3:1 EtOAc–Hexane), yield 0.05 g (41%) white crystals from CH_2Cl_2–Et_2O. Mp: 170–172 °C; $[\alpha]_D$ −29 (*c* 1.07, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm) 8.53 (s, 1H, NH), 5.69 (d, 1H, $J_{2,3}$ 9.6 Hz, H-2), 5.34 (dd, 1H, $J_{2,3}$ 9.6 Hz, $J_{3,4}$ 5.0 Hz, H-3), 5.30 (ddd, 1H, $J_{3,4}$ 5.0 Hz, $J_{4,5}$ 2.5 Hz, $J_{4,5'}$ 1.6 Hz, H-4), 4.06 (dd, 1H, $J_{6,6'}$ 13.5 Hz, $J_{5,6}$ 2.5 Hz, H-5), 3.80 (dd, 1H, $J_{6,6'}$ 13.5 Hz, $J_{5,6}$ 1.6 Hz, H-5′), 2.13 (2), 2.08, 1.96 (3s, 12H, $OCOCH_3$, CH_3); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 170.9 ($NHCOCH_3$), 170.1, 169.8, 168.2 (*C*O), 114.7 (*C*N, $^3J_{H\text{-}2,CN}$ = ~3.1 Hz), 78.0 (C-1), 67.9, 66.9, 66.8 (C-2–C-4), 61.6 (C-5), 23.0 (CH_3), 20.7, 20.5, 20.4 (CH_3); Anal. Calcd for $C_{14}H_{18}N_2O_8$ (342.30): C, 49.12; H, 5.30; N, 8.18. Found: C, 50.10; H, 5.57; N, 8.33.

3.2.12. *N*-Propenoyl-2,3,4-tri-*O*-acetyl-1-cyano-β-D-arabinopyranosylamine (3,4,5-tri-*O*-acetyl-2-deoxy-2-propenamido-β-D-*arabino*-hex-2-ulopyranosononitrile) (18)

Prepared from **7** (0.31 g, 0.81 mmol) in CH_2CHCN according to Section 3.2. Reaction time 2 d, purification by column chromatography (1:1→3:1 EtOAc–hexane), yield 0.12 g (43%) as a colourless syrup. R_f = 0.28 (1:1 EtOAc–hexane); $[\alpha]_D$ −28 (*c* 1.06, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 200 MHz): δ (ppm) 6.90 (s, 1H, NH), 6.51 (d, 1H, *J* 7.5 Hz, CH_2), 6.29 (dd, 1H, *J* 7.5 Hz, *J* 6.9 Hz, CH), 5.86 (d, 1H, *J* 7.5 Hz, CH_2), 5.77 (d, 1H, $J_{2,3}$ 8.8 Hz, H-2), 5.28 (dd, 1H, $J_{2,3}$ 8.8 Hz, $J_{3,4}$ 3.5 Hz, H-3), 5.24 (ddd, 1H, $J_{3,4}$ 3.5 Hz, $J_{4,5}$ 2.6 Hz, $J_{4,5'}$ 1.2 Hz, H-4), 4.05–3.94 (m, 2H, H-5, H-5′), 2.18, 2.17, 2.06 (3s, 9H, $OCOCH_3$); ^{13}C NMR ($CDCl_3$, 50 MHz): δ (ppm) 170.0 ($NHCOCH{=}CH_2$), 169.6, 168.3, 165.6 (*C*O), 129.7 ($CH_2{=}CH$), 128.9 ($CH_2{=}CH$), 114.5 (*C*N, $^3J_{H\text{-}2,CN}$ = ~3.1 Hz), 78.1 (C-1), 67.7, 66.9, 66.7 (C-2–C-4), 61.6 (C-5), 23.0 (CH_3), 20.7, 20.5, 20.4 (CH_3); Anal. Calcd for $C_{15}H_{18}N_2O_8$ (354.31): C, 50.85; H, 5.12; N, 7.91. Found: C, 50.30; H, 5.37; N, 8.13.

3.3. *N*-(2,3,4,6-Tetra-*O*-acetyl-1-bromo-1-deoxy-β-D-galactopyranosylcarbonyl)]-L-alanine methylester (*N*-(3,4,5,7-tetra-*O*-acetyl-2-bromo-2-deoxy-α-D-*galacto*-hept-2-ulopyranosonoyl)-L-alanine methylester) (20)

Pentachlorophenyl *C*-(2,3,4,6-tetra-*O*-acetyl-1-bromo-1-deoxy-β-D-galactopyranosyl)formate[32] (0.30 g, 0.43 mmol) was dissolved in dry 1,4-dioxane (3 mL) and methyl L-alaninate·HCl (2 equiv), and Et_3N (2 equiv) were added. The reaction mixture was stirred at rt and monitored by TLC (1:1 EtOAc–hexane). After completion of the reaction the solvent was removed. The obtained crude product was purified by column chromatography (1:1 EtOAc–hexane) to give 0.18 g (73%) **20** as colourless oil. R_f = 0.24 (1:1 EtOAc–hexane); $[\alpha]_D$ +83 (*c* 0.73, $CHCl_3$); IR ν_{max} ($CHCl_3$): 3380, 2958, 1758, 1678, 1374, 1262, 1070 cm^{-1}; ^{1}H NMR ($CDCl_3$, 360 MHz) δ (ppm): 7.15 (t, 1H, *J* = 6.8, 6.8 Hz, NH), 5.54 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{4,5}$ 1.6 Hz, H-4), 5.42 (d, 1H, $J_{2,3}$ 10.0 Hz, H-2), 5.32 (dd, 1H, $J_{2,3}$ 10.0 Hz, $J_{3,4}$ 3.2 Hz, H-3), 4.60–4.48 (m, 4H, H-5, H-6, H-6′, CH), 3.79 (s, 3H, OCH_3), 2.18, 2.12, 2.09, 1.98 (4s, 12H, $OCOCH_3$), 1.45 (d, 3H, *J* 6.8 Hz, $CH(CH_3)$); ^{13}C NMR ($CDCl_3$, 125 MHz) δ (ppm): 172.5 ($COOCH_3$), 170.2, 169.8, 169.7, 169.1 (CO), 164.2 (CONH, $^3J_{H\text{-}2,CONHCH2CO2Me}$ = 2.2 Hz), 94.3 (C-1), 73.3, 69.7, 66.4, 66.4 (C-2–C-5), 60.5 (C-6), 52.5 ($COOCH_3$), 48.0 (*C*H), 20.8, 20.7, 20.5, 20.4 (CH_3), 17.6 ($CH(CH_3)$. Anal. Calcd for $C_{19}H_{26}N_1Br_1O_{12}$ (540.32): C, 42.24; H, 4.85; N, 2.59; Br, 14.79. Found: C, 41.80; H, 4.68; N, 2.44; Br, 15.10.

3.4. *N*-[(1*R*)-2,3,4,6-Tetra-*O*-acetyl-1,5-anhydro-D-galactitol-spiro[1.4]-2-methyl-2-oxazolin-5-ylidene]glycine methylester (21)

Compound **19**[32] (0.20 g, 0.38 mmol) was dissolved in dry CH_3CN (2 mL) and Ag_2CO_3 (1.1 equiv) was added. The solution was stirred at rt in the dark until complete transformation of the starting material (4 d, TLC 3:1 EtOAc–hexane). The mixture was filtrated on a Celite pad and the solvent was removed from the filtrate. The obtained crude product was purified by column chromatography (3:1 EtOAc–hexane) to give **21** (0.09 g, 65%) as a colourless oil, R_f = 0.39 (3:1 EtOAc–hexane), $[\alpha]_D$ +0.1 (*c* 0.44, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm): 5.70 (d, 1H, $J_{2,3}$ 10.6 Hz, H-2), 5.56 (dd, 1H, $J_{3,4}$ 4.0 Hz, $J_{4,5}$ <1 Hz, H-4), 5.46 (dd, 1H, $J_{2,3}$ 10.6 Hz, $J_{3,4}$ 4.0 Hz, H-3), 4.62 (ddd, 1H, $J_{5,6}$ 6.6 Hz, $J_{5,6'}$ 6.6 Hz, $J_{4,5}$ <1 Hz, H-5), 4.25 (s, 2H, CH_2), 4.19 (dd, 1H, $J_{6,6'}$ 11.9 Hz, $J_{5,6}$ 6.6 Hz, H-6), 4.10 (dd, 1H, $J_{6,6'}$ 11.9 Hz, $J_{5,6'}$ 6.6 Hz, H-6′), 3.77 (s, 3H, OCH_3), 2.25 (s, 3H, CH_3), 2.19, 2.03, 2.01, 1.97 (4s, 12H, $OCOCH_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 170.4, 170.2, 170.0, 168.7 (*C*O), 165.3 (*C*=N), 158.2 (*C*=N, $^3J_{H\text{-}2,C=NCH2COOCH3}$ = ~3.1 Hz), 95.7 (C-1), 70.8, 69.5, 68.3, 67.9 (C-2–C-5), 61.4 (C-6), 52.1 (OCH_3), 50.3 (CH_2), 20.7, 20.5, 20.5, 20.4 ($OCOCH_3$), 14.9 (CH_3); Anal. Calcd for $C_{20}H_{26}N_2O_{12}$ (486.44): C, 49.38; H, 5.39; N, 5.76. Found: C, 49.55; H, 5.56; N, 5.80.

3.5. *N*-[(1*R*)-2,3,4,6-Tetra-*O*-acetyl-1,5-anhydro-D-galactitol-spiro[1.4]-2-benzyloxycarbonylaminomethyl-2-oxazolin-5-ylidene]glycine methylester (22)

Compound **19** (0.17 g, 0.33 mmol) was dissolved in dry CH_3NO_2 (3 mL), $NCCH_2NHCOOCH_2Ph$ (10 equiv) and Ag_2CO_3 (1.1 equiv) were added. The mixture was stirred in the dark at rt for 6 d. After completion of the reaction (TLC, 3:1 EtOAc–hexane) the mixture was filtered on a Celite pad and the solvent was removed. The crude oil was purified by column chromatography (3:1 EtOAc–hexane) to give 0.04 g (29%) of **22** (1:1 mixture of two isomers) as a colourless oil. R_f = 0.29 (EtOAc); ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm): 7.44–7.32 (m, 5H, Ph), 7.01 (s, 1H, NH), 5.71 (d, 1H, $J_{2,3}$10.6 Hz, H-2), 5.58–5.52 (m, 2H, H-4, H-4′), 5.48-5.30 (m, 3H, H-2′, H-3, H-3′), 5.20-5.14 (m, 2H, CH_2), 4.60–4.62 (m, 2H, H-5, H-5′), 4.32–4.04 (m, 10H, H-6a, H-6a′, H-6b, H-6b′, CH_2a, CH_2b, CH_2Ph), 3.79 (s, 3H, OCH_3), 2.19, 2.17, 2.13, 2.11, 2.03, 2.01, 1.99, 1.97 (8s, 24H, $OCOCH_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 170.5, 170.3, 170.1 (2), 169.9, 169.4, 168.8 (2) (CO), 168.2 (CO_2CH_3), 165.1 (C=N), 157.1, 157.0 (CO_2CH_2Ph), 135.9–128.2 (aromatics), 95.3 (C-1), 94.1 (C-1′), 73.6, 71.0, 69.8, 69.5, 68.3, 67.9, 67.5, 66.6 (C-2–C-5 and C-2′–C-5′), 71.0 (CH_2), 60.7 (C-6), 60.4 (C-6′), 52.6 (OCH_3), 52.2 (OCH_3'), 41.2 (2) (CH_2, CH_2'), 20.9 (6), 20.5 (CH_3)

3.6. *N*-[(1*R*)-2,3,4,6-Tetra-*O*-acetyl-1,5-anhydro-D-galactitol-spiro[1.4]-2-methyl-2-oxazolin-5-ylidene]-L-alanine methylester (23)

Compound **20** (0.60 g, 1.10 mmol) was dissolved in dry CH_3CN (10 mL) and Ag_2CO_3 (1.1 equiv) was added. After stirring for 4 d in the dark the mixture was filtered on a Celite pad and the solvent was removed. The obtained crude product was purified by column chromatography (3:1 EtOAc–hexane) to give 0.24 g (43%) **23** as a

colourless oil. R_f = 0.19 (1:1 EtOAc–hexane), $[\alpha]_D$ +1 (*c* 0.41, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm): 5.65 (d, 1H, $J_{2,3}$10.6 Hz, H-2), 5.54 (dd, 1H, $J_{3,4}$ 4.0 Hz, $J_{4,5}$ <1 Hz, H-4), 5.42 (dd, 1H, $J_{2,3}$ 10.6 Hz, $J_{3,4}$ 4.0 Hz, H-3), 4.58 (ddd, 1H, $J_{5,6}$ 6.6 Hz, $J_{5,6'}$ 6.6 Hz, $J_{4,5}$ <1 Hz, H-5), 4.42 (q, 1H, *J* 6.9 Hz, *J* 6.4 Hz, CH), 4.18 (dd, 1H, $J_{6,6'}$ 11.9 Hz, $J_{5,6}$ 6.6 Hz, H-6), 4.11 (1H, $J_{6,6'}$ 11.9 Hz, $J_{5,6'}$ 6.6 Hz, H-6′), 3.70 (s, 3H, OCH_3), 2.24 (s, 3H, CH_3), 2.20, 2.03, 2.01, 1.99 (4s, 12H, $OCOCH_3$), 1.48 (d, 3H, *J* 6.4 Hz, $CH(CH_3)$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 171.3, 170.4, 170.2, 169.9 (*C*O), 165.2 (*C*=N), 155.8 (*C*=N, $^3J_{H\text{-}2,C=NCH\text{-}}$ = ~3.3 Hz), 95.5 (C-1), 70.6, 69.5, 68.4, 67.9 (C-2–C-5), 61.3 (C-6), 56.6 (*C*H), 52.0 (O*C*H$_3$), 20.6, 20.5, 20.4, 20.3 (OCO*C*H$_3$), 18.2 (CH(*C*H$_3$), 14.9 (*C*H$_3$); Anal. Calcd for $C_{21}H_{28}N_2O_{12}$ (500.44): C, 51.12; H, 5.70; N, 6.26. Found: C, 50.85; H, 5.52; N, 5.96.

3.7. General procedure for the hydrolysis of spiro-oxazolines 21–23 to oligopeptides 24–26

Compounds **21–23** each was dissolved in CH_2Cl_2 (1 mL/0.1 mmol), CF_3COOH or AcOH (1 equiv) and water (2 equiv) were added. The mixture was stirred at rt until disappearance of the starting material (TLC, 3:1 EtOAc–hexane). It was then diluted with CH_2Cl_2 and washed with satd aq $NaHCO_3$ solution (2 × 5 mL), water (5 mL), dried, and the solvent removed. The obtained syrup was purified by column chromatography.

3.7.1. *N*-(2,3,4,6-Tetra-*O*-acetyl-1-acetamido-1-deoxy-β-D-galactopyranosylcarbonyl)glycine methylester (*N*-(2-acetamido-3,4,5,7-tetra-*O*-acetyl-2-deoxy-α-D-*galacto*-hept-2-ulopyranosonoyl)glycine methylester) (24)

Prepared from **21** (0.05 g, 0.10 mmol) according to General procedure **3.7.** Purified by column chromatography (9:1 EtOAc–MeOH), yield (0.02 g, 55%) of **24** as a colourless syrup. R_f = 0.42 (9:1 EtOAc–hexane); $[\alpha]_D$ +69 (*c* 0.38, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm): 7.28 (t, 1H, *J* 5.8 Hz, *J* 5.8 Hz, NH), 6.37 (s, 1H, NH), 5.45 (d, 1H, $J_{2,3}$ 10.6 Hz, H-2), 5.56 (dd, 1H, $J_{3,4}$ 3.3 Hz, $J_{4,5}$ 1.1 Hz, H-4), 5.22 (dd, 1H, $J_{2,3}$ 10.6 Hz, $J_{3,4}$ 3.3 Hz, H-3), 4.33–3.98 (m, 5H, H-5, H-6, H-6′, CH_2), 3.78 (s, 3H, OCH_3), 2.20, 2.09, 2.06, 1.99 (4s, 12H, $OCOCH_3$), 2.09 (s, 3H, $NHCOCH_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 170.9, 170.5, 170.1, 169.5 (*C*O), 170.1 (*C*O$_2$CH$_3$), 168.6 (NH*C*OCH$_3$), 167.3 (*C*ONHCH$_2$, $^3J_{H\text{-}2,CONHCH2COOCH3}$ = ~2.4 Hz), 83.7 (C-1), 68.7, 68.4, 67.0 (2) (C-2–C-5), 60.8 (C-6), 52.3 (O*C*H$_3$), 41.3 (*C*H$_2$), 23.5 (NHCO*C*H$_3$), 20.6 (3), 20.5 (CH$_3$); Anal. Calcd for $C_{20}H_{28}N_2O_{13}$ (504.45): C, 47.62; H, 5.59; N, 5.55. Found: C, 47.44; H, 5.36; N, 5.65.

3.7.2. *N*-(2,3,4,6-Tetra-*O*-acetyl-1-*Z*-glycylamido-1-deoxy-β-D-galactopyranosylcarbonyl)glycine methylester (*N*-(3,4,5,7-tetra-*O*-acetyl-2-deoxy-2-*Z*-glycylamido-α-D-*galacto*-hept-2-ulopyranosonoyl)glycine methylester) (25)

Prepared from **22** (0.04 g, 0.06 mmol) according to Section 3.7. Purified by column chromatography (9:1 EtOAc–MeOH), yield 0.01 g (27%) of **24** as a colourless oil. R_f = 0.13 (5:1 EtOAc–hexane); $[\alpha]_D$ +58 (*c* 0.160, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm): 7.38–7.32 (m, 5H, ArH), 7.30 (s, 1H, NH), 7.18 (s, 1H, NH), 5.51 (s, 1H, NH), 5.46 (d, 1H, $J_{2,3}$ 10.6 Hz, H-2), 5.44 (dd, 1H, $J_{3,4}$ 3.4 Hz, $J_{4,5}$ 1.1 Hz, H-4), 5.19 (dd, 1H, $J_{2,3}$ 10.6 Hz, $J_{3,4}$ 3.4 Hz, H-3), 5.12–5.08 (m, 2H, CH_2), 4.29–3.86 (m, 5H, H-5, H-6, H-6′, CH_2), 3.77 (s, 3H, OCH_3), 2.20, 2.06, 2.05, 1.95 (4s, 12H, $OCOCH_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 170.6, 170.2, 170, 169.9 (2), 169.5, 168.8, 168.7 (*C*O$_2$CH$_3$, NH*C*OCH$_2$, NH*C*O$_2$, *C*O), 166.7 (*C*ONCH$_2$, $^3J_{H\text{-}2,CONHCH2COOCH3}$ = ~2.9 Hz); 156.8 (–*C*O$_2$CH$_2$Ph), 133.0–128.6 (aromatics), 83.8 (C-1), 69.2, 68.5, 67.1 (2) (C-2–C-5), 67.1 (*C*H$_2$), 65.6 (*C*H$_2$), 60.8 (C-6), 52.4 (OCH$_3$), 41.4 (2) (*C*H$_2$), 20.6 (6), 20.5 (2) (CH$_3$); Anal. Calcd for $C_{28}H_{35}N_3O_{15}$ (653.60): C, 51.46; H, 5.40; N, 6.43. Found: C, 51.65; H, 5.56; N, 6.72.

3.7.3. *N*-(2,3,4,6-Tetra-*O*-acetyl-1-acetamido-1-deoxy-β-D-galactopyranosylcarbonyl)-L-alanine methylester (*N*-(2-acetamido-3,4,5,7-tetra-*O*-acetyl-2-deoxy-α-D-*galacto*-hept-2-ulopyranosonoyl)-L-alanine methylester) (26)

Prepared from **23** (0.05 g, 0.10 mmol) according to Section 3.7. Purified by column chromatography (3:1 EtOAc–hexane), yield 0.015 g (29%) of **26** as colourless oil. R_f = 0.15 (EtOAc); $[\alpha]_D$ +69.0 (*c* 0.40, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm): 7.28 (t, 1H, *J* 5.8 Hz, *J* 5.8 Hz, NH), 6.27 (s, 1H, NH), 5.46–5.42 (m, 2H, H-2, H-4), 5.19 (dd, 1H, $J_{2,3}$ 10.6 Hz, $J_{3,4}$ 3.3 Hz, H-3), 4.52 (q, 1H, *J* 6.8 Hz, *J* 6.4 Hz, CH), 4.35 (dd, 1H, $J_{6,6'}$ 11.9 Hz, $J_{5,6}$ 6.6 Hz, H-6), 4.25 (ddd, 1H, $J_{5,6}$ 6.6 Hz, $J_{5,6'}$ 6.6 Hz, $J_{4,5}$ 0.9 Hz, H-5), 4.14 (1H, dd, $J_{6,6'}$ 11.9 Hz, $J_{5,6'}$ 6.6 Hz, H-6′), 3.79 (s, 3H, OCH_3), 2.23 (s, 3H, NHC-OCH_3); 2.10, 2.07, 2.06, 2.00 (4s, 12H, $OCOCH_3$), 1.46 (d, 3H, *J* 6.4 Hz, $CH(CH_3)$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 173.1, 171.3, 171.0, 170.7 (*C*O), 170.5 (*C*O$_2$CH$_3$), 168.9 (NH*C*OCH$_3$), 166.7 (*C*ONHCH$_2$, $^3J_{H\text{-}2,CONHCH2COOCH3}$ = ~2.4 Hz), 83.9 (C-1), 69.2, 68.9, 67.4 (2) (C-2–C-5), 60.8 (C-6), 52.8 (O*C*H$_3$), 48.9 (*C*H), 24.0 (NHCO*C*H$_3$), 20.9, 20.6, (2), 20.5 (CH$_3$), 18.4 (CH(*C*H$_3$)); Anal. Calcd for $C_{21}H_{30}N_2O_{13}$ (518.45): C, 49.90; H, 5.72; N, 5.60. Found: C, 49.63; H, 5.56; N, 5.44.

3.8. *N*-(2,3,4,6-Tetra-*O*-acetyl-1-amino-1-deoxy-α-D-galactopyranosylcarbonyl)glycine methylester (*N*-(3,4,5,7-tetra-*O*-acetyl-2-amino-2-deoxy-β-D-*galacto*-hept-2-ulopyranosonoyl)glycine methylester) (28)

Azide **27**[32] (0.10 g, 0.20 mmol) was dissolved in dry EtOAc (5 mL) and Raney-Ni (~0.2 g, 2 equiv) was added to the solution. The mixture was stirred at 70 °C and monitored by TLC (3:1 EtOAc–hexane). After completion of the reaction the mixture was filtered on a Celite pad and the solvent was removed. The obtained syrup was crystallised from EtOH to give 0.07 g (79%) of **28** as a white crystalline product. Mp: 123–126 °C; $[\alpha]_D$ +77 (*c* 1.06, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm): 7.53 (t, 1H, *J* 5.3 Hz, *J* 5.3 Hz, NH), 5.62 (dd, 1H, $J_{2,3}$ 11.0 Hz, $J_{3,4}$ 3.2 Hz, H-3), 5.50 (dd, 1H, $J_{3,4}$ 3.2 Hz, $J_{4,5}$ <1 Hz, H-4), 5.24 (d, 1H, $J_{2,3}$ 11.0 Hz, H-2), 5.13 (ddd, 1H, $J_{5,6}$ 6.3 Hz, $J_{5,6'}$ 6.3, $J_{4,5}$ <1 Hz, H-5), 4.18 (dd, 1H, *J* 18.4 Hz, *J* 5.3 Hz, CH_2), 4.10 (dd, 1H, $J_{6,6'}$ 11.5 Hz, $J_{5,6}$ 6.3 Hz, H-6), 4.02 (dd, 1H, $J_{6,6'}$ 11.0 Hz, $J_{5,6'}$ 6.3 Hz, H-6′), 3.95 (dd, 1H, *J* 18.4 Hz, *J* 5.3 Hz, CH_2), 3.78 (s, 3H, OCH_3); 2.29 (s, 2H, NH_2), 2.16, 2.12, 2.04, 1.95 (4s, 12H, $OCOCH_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 170.4 (*C*O$_2$CH$_3$), 170.3, 170.1, 169.8, 169.6 (CO), 169.5 (*C*ONH, $^3J_{H\text{-}2,CONHCH2COOCH3}$ = ~5.8 Hz), 86.5 (C-1), 71.3, 70.4, 68.9, 68.0 (C-2–C-5), 62.0 (C-6), 52.3 (*C*OOCH$_3$), 40.7 (*C*H$_2$), 20.6 (2), 20.5 (2) (CO); Anal. Calcd for $C_{18}H_{26}N_2O_{12}$ (462.41): C, 46.75; H, 5.67; N, 6.06. Found: C, 46.45; H, 5.76; N, 5.90.

3.9. *N*-(2,3,4,6-Tetra-*O*-acetyl-1-acetamido-1-deoxy-α-D-galactopyranosylcarbonyl)glycine methylester (*N*-(3,4,5,7-tetra-*O*-acetyl-2-acetamido-2-deoxy-β-D-*galacto*-hept-2-ulopyranosonoyl)glycine methylester) (29)

Compound **28** (0.26 g, 0.56 mmol) was dissolved in dry pyridine (5 mL) and AcCl (0.08 mL, 1.12 mmol) was added. The mixture was stirred at rt overnight and monitored by TLC (99:1 EtOAc–MeOH). The volatiles were then removed, followed by co-evaporations with $PhCH_3$ (2x5 mL). The residue was dissolved in EtOAc (10 mL) and washed with water. The water phase was washed with EtOAc (5 × 10 mL). The combined organic phase was dried, the solvent removed, and the residue purified by column chromatography (99:1 EtOAc–MeOH) to give 0.045 g, (15%) of compound **29** as a colourless oil in the first fraction (R_f = 0.23, 99:1 EtOAc–MeOH) and 0.045 g (15%) of compound **24** as the second fraction (R_f = 0.31, 99:1 EtOAc–MeOH).

Characterisation data for **29**: $[\alpha]_D$ +153 (*c* 0.078, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm): 7.86 (t, 1H, *J* 5.8 Hz, *J* 5.8 Hz, NH), 7.06 (s, 1H, NH), 5.63 (dd, 1H, $J_{2,3}$ 10.5 Hz, $J_{3,4}$ 3.3 Hz, H-3), 5.47 (dd, 1H, $J_{3,4}$ 3.3 Hz, $J_{4,5}$ 1.0 Hz, H-4), 5.23 (d, 1H, $J_{2,3}$ 10.5 Hz, H-2), 4.60 (pseudo t, 1H, $J_{5,6}$ 6.7 Hz, $J_{5,6'}$ 6.4 Hz, H-5), 4.14–3.05 (m, 4H, H-6, H-6′, CH_2), 3.74 (s, 3H, OCH_3), 2.15, 2.14, 2.02, 1.96 (4s, 12H, $OCOCH_3$), 2.01 (s, 3H, $NHCOCH_3$); ^{13}C NMR ($CDCl_3$, 125 MHz): δ (ppm): 172.7, 170.2 (3), 169.6 (*C*O, *C*$OOCH_3$), 169.3 ($NHCOCH_3$), 166.3 ($CONHCH_2$, $^3J_{H\text{-}2,CONHCH2COOCH3}$ = ~5.3 Hz), 85.8 (C-1), 71.1, 70.1, 68.1, 67.2 (C-2–C-5), 61.2 (C-6), 52.4 (OCH_3), 41.1 (CH_2), 24.1 ($NHCOCH_3$), 20.9, 20.6 20.5 (2) (CH_3); Anal. Calcd for $C_{20}H_{28}N_2O_{13}$ (504.45): C, 47.62; H, 5.59; N, 5.55. Found: C, 47.14; H, 5.31; N, 5.25.

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