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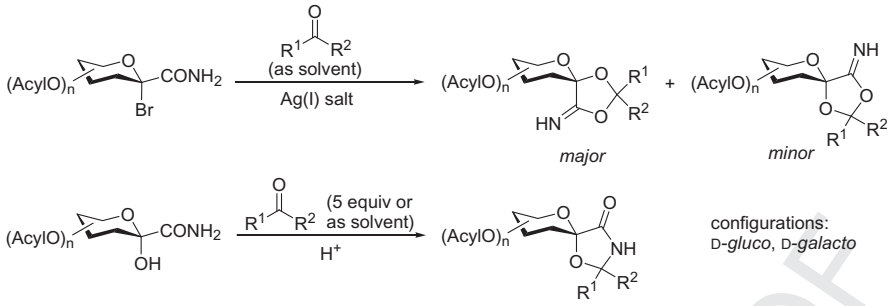
Graphical abstract

Anomeric spirocycles by solvent incorporation: reactions of *O*-peracylated (glyculopyranose and glyculopyranosyl bromide)onamide derivatives with ketones pp xxx–xxx

András Páhi, Katalin Czifrák, Katalin E. Kövér, László Somsák *



Highlights

• Ketone incorporation reactions. • Preparation of glycopyranosylidene-spiro-(4-imino-1,3-dioxolanes). • Preparation of glycopyranosylidene-spiro-(oxazolidin-4-ones).

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Anomeric spirocycles by solvent incorporation: reactions of *O*-peracylated (glyculopyranose and glyculopyranosyl bromide) onamide derivatives with ketones

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ABSTRACT

Reactions of *O*-peracetylated (α-D-*galacto*-heptulopyranosyl bromide)onamide and *O*-perbenzoylated (α-D-*gluco*-heptulopyranosyl bromide)onamide with ketones in the presence of silver(I) salt promoters gave the corresponding *O*-peracylated 1′,5′-anhydro-D-glycitol-spiro-[1′,5]-4-imino-2,2-disubstituted-1,3-dioxolanes. The D-*galacto* configured starting compounds furnished both spiro epimers, while the D-*gluco* counterparts yielded only configurationally inverted products. Under acidic conditions, *O*-perbenzoylated α-D-*gluco*-heptulopyranosonamide and ketones yielded the protected 1′,5′-anhydro-D-glucitol-spiro-[1′,5]-2,2-disubstituted-oxazolidin-4-ones, which were *O*-debenzoylated by the Zemplén protocol. These compounds had no inhibition against rabbit muscle glycogen phosphorylase *b*.

1. Introduction

Spirocyclic motifs are widespread among natural products and synthetic compounds, and often exhibit interesting and useful biological activities.[1–3] Spirocycles involving the anomeric carbon of monosaccharide derivatives are also well known, and have been, among others, shown to possess antiparasitic,[4] antibacterial, antifungal,[5] antidiabetic,[6] herbicide,[7] glycosidase[8–10] and glycogen phosphorylase[11] inhibitory activities.

Synthetic strategies to obtain spirocycles were amply reviewed,[1–3] and ring closure of geminally disubstituted cyclic compounds were highlighted as one of several generally applied approaches towards various spiro derivatives. Following this principle for the preparation of anomeric spirocycles the necessary starting compounds can be selected from monosaccharides homo- or heterobifunctionalized at the anomeric centre.[1] The latter type precursors are represented among others by derivatives of ulose type sugars utilized, for example, for the syntheses of many sorts of spironucleosides.[12] In this line we reported the transformations of (glyculopyranosyl bromide)onic acid derivatives[13] to glycopyranosylidene-spiro-(thio)hydantoins,[14,15] -thiazolidinones,[16] and -oxazolines,[17] as well as that of (glyculopyranosyl thiocyanate)ononitriles to glycopyranosylidene-spiro-thiazolines.[18]

Some years ago we observed that on generation of the corresponding glycosylium ion from (glyculopyranosyl bromide)onamides (e.g., **1**) by Ag_2CO_3 in acetone spiro-imino-dioxolanes **2a** and **3a** (Table 1) were formed by incorporation of the solvent.[19] This reaction can be regarded as a direct *O*-glycosylation of a ketone which is a very rare transformation: formation of acetal glycosides in the presence of ketones was described from *O*-peracetylated *N*-(2,4-dinitrophenyl)-α-D-glucosaminyl bromide (but not from acetobromoglucose),[20] TMS-glycosides[21,22] and *O*-perbenzylated 1-thioglycosides.[23] Formal glycosylation of ketones by a special intramolecular aglycon delivery was recently reported.[24]

In this paper full experimental details are reported for the extension of the above ketone incorporation in reactions of (glyculopyranosyl bromide)onamides. Furthermore, studies on the reactions of (glyculopyranose)onamides and ketones as well as detailed structural elucidation of the compounds are also described.

2. Results and discussion

Following the first observation[19] on incorporation of acetone into the products in the reaction of **1** (Table 1, entry 1) in the presence of Ag_2CO_3, the applicability of other ketones and promoters

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[1] Strictly speaking these compounds might no more have a 'real' anomeric, that is, an acetal type carbon in many cases, however, for the sake of simplicity this term will be used here.

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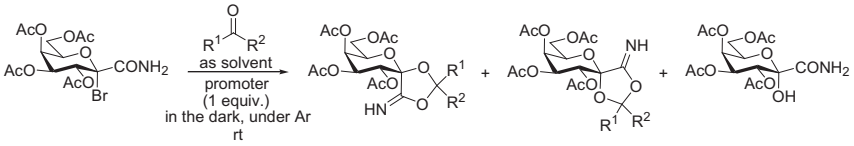
Table 1
Reaction of *O*-peracetylated (α-D-*galacto*-heptulopyranosyl bromide)onamide (**1**) with ketones



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

Entry		R^1	R^2	Promoter	R. time (d)	Yield (%)		
1	**a**[a]	Me	Me	Ag_2CO_3	1	71	4	5
2	**b**	Me	Et	Ag_2CO_3	6	49[b]	[c]	[c]
3				AgOTf	6	43[b]	19*	38
4	**c**	Et	Et	AgOTf	3	32	14	27
5	**d**	$-(CH_2)_4-$		AgOTf	6	48	Traces	26
6	**e**	$-(CH_2)_5-$		AgOTf	2	44	8	25

[a] From Ref. 19.
[b] Two diastereomers.
[c] Observed but not isolated.

were investigated. With butanone both Ag_2CO_3 and AgOTf gave similar results (entries 2 and 3) expectedly furnishing the spiro-dioxolanes **2b** and **3b** as inseparable diastereomeric mixtures. Symmetrical ketones (entries 4–6) also gave the spiro-epimers **2c–e** as the main products whereby **3c–e** could be isolated in much lower yields. From each reaction mixture the hydrolytic product **4** could be isolated in 25–38% yields.

Similar reactions of the D-*gluco* configured **5** are collected in Table 2. Comparisons of entries 1, 3 and 5 with entries 2, 4 and 6, respectively, show that the use of AgOTf is superior to that of Ag_2CO_3 in terms of reaction times, although the higher efficiency of the former is not always reflected in the yields. In these reactions of **5** only spiro-epimer **6** was observed in the reaction mixtures (besides the hydrolyis product **7**).

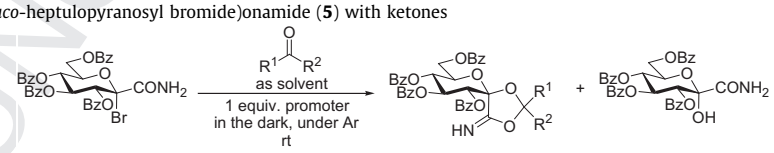
Attempts to reduce the amount of the ketones to 5–10 equiv in nitromethane as the solvent proved unsuccesful, and the only products to be observed were **4** and **7**. Trials to use aldehydes as the carbonyl reagents resulted in multicomponent mixtures from which no discrete products could be isolated.

Reactions of (D-*gluco*-hept-2-ulopyranose)onamide **7** with ketones were investigated next (Table 3). As in similar cyclizations of non-carbohydrate α-hydroxy-carboxamides *p*-toluenesulfonic acid (*p*TSA) was frequently applied to promote the transformation[25] this acid was tried first. However, no reaction of **7** could be observed with acetone as the solvent in the presence of either catalytic or stoichiometric amounts of *p*TSA. On the other hand, catalytic triflic acid (TfOH) elicited the reaction (entry 1), and raising its amount to one equivalent significantly increased the yield of **8a** (entry 2). Under the same conditions butanone gave an inseparable diastereomeric mixture of **8b** (entry 3). The amount of the ketone could be diminished to 5 equiv, and both THF and toluene proved suitable solvents to prepare **8c–f** in good yields (entries 4–7). In these reactions formation of one compound was observed in each case (disregarding diasteromers **8b**). Reactions with aldehydes gave only decomposition products.

Spiro-oxazolidinones **8** were *O*-debenzoylated by the Zempén protocol to give compounds **9** in very good yields. These derivatives were tested as possible inhibitors of rabbit muscle glycogen phosphorylase *b*, however, showed no inhibition up to 625 μM concentration.

Structural elucidation of the products (following the mass spectrometric determination of the molecular masses) was carried out by NMR methods as illustrated for the compounds depicted in Figure 1 (see also Table 4 for selected NMR data of the compounds). Proton spectra showed splitted resonances for a pyranoid ring in the $^4C_1$ conformation as well as the expected signals of the aliphatic parts and the presence of an exchangable proton assigned as an NH for each compound (see details in Section 3). The carbon spectra contained (besides the expected resonances for the sugar ring, the acyl protecting groups and the aliphatic moieties) signals for three carbons with no attached hydrogens. Those in the range of 99.9–100.7 ppm were assigned as the C-[1′,5] spiro centres. Resonances of 112.5–122.2 and 158.2–160.9 ppm (clearly distinct from the C=O resonances of the protective groups) were indicative of acetal and imidate type carbons, respectively, in compounds **2**, **3** and **6**. On the contrary, the spectra of compounds **8** exhibited

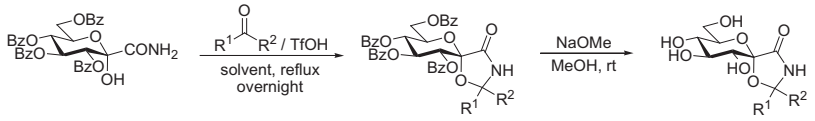
Table 2
Reaction of *O*-perbenzoylated (α-D-*gluco*-heptulopyranosyl bromide)onamide (**5**) with ketones



5 **6** **7**

Entry		R^1	R^2	Promoter	R. time (d)	Yield (%)	
1	**a**	Me	Me	Ag_2CO_3	11	17	41
2				AgOTf	1	37	46
3	**c**	Et	Et	Ag_2CO_3	20	5	34
4				AgOTf	1	46	35
5	**d**	$-(CH_2)_4-$		Ag_2CO_3	13	56	18
6	**e**	$-(CH_2)_5-$		AgOTf	1	28	35

Table 3
Reaction of 3,4,5,7-tetra-*O*-benzoyl-α-D-*gluco*-heptulopyranosonamide (**5**) with ketones



7 **8** **9**

Entry		R^1	R^2	Ketone (equiv.)	Solvent	Acid (equiv.)	Yield (%)	
1	**a**	Me	Me	As solvent	—	0.1	58	94
2				As solvent	—	1.0	89	
3	**b**	Me	Et	As solvent	—	1.0	92[a]	96
4	**c**	Et	Et	5	THF	1.0	69	91
5	**d**	$-(CH_2)_4-$		5	THF	1.0	86	91
6	**e**	$-(CH_2)_5-$		5	Toluene	1.0	69	96
7	**f**	$-(CH_2)_6-$		5	Toluene	1.0	71	77

[a] Two diastereomers.

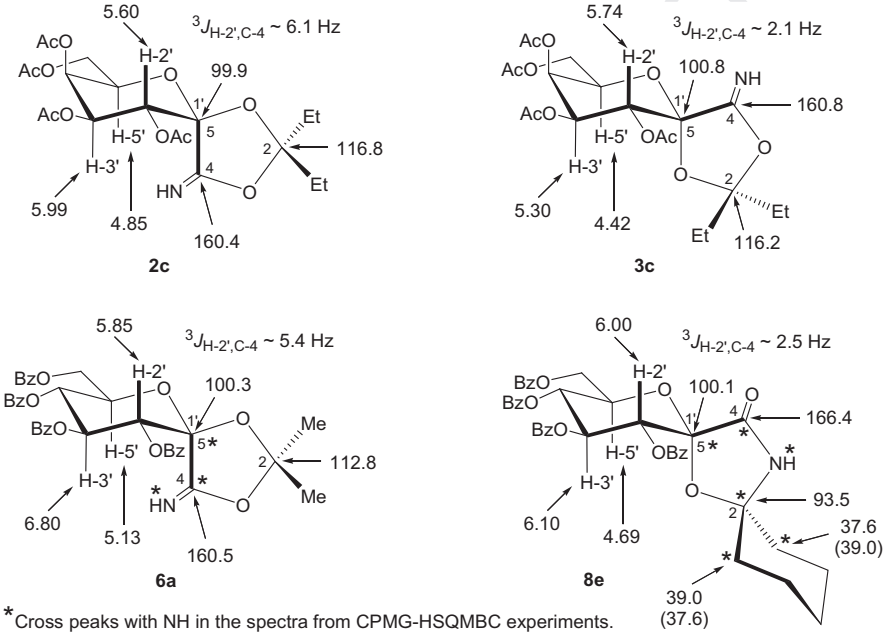
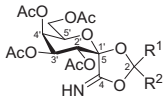


Figure 1. Representative NMR data for the structural elucidation of the new compounds.

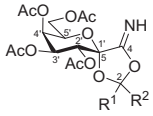
an additional signal in the range of the benzoyl carbonyls (162.4–166.6 ppm) and from these that of the highest chemical shift was (tentatively) assigned to amide C-4. A resonance in the range of 92.4–100.1 ppm could be attributed to an aminal type carbon and this corroborated that the nitrogen was in an endocyclic position in **8**. To confirm the difference in the constitution of the heterocyclic parts of the spirocycles, CMPG-HSQMBC experiments[26–28] were carried out with **6a** and **8e**. In these spectra cross peaks (indicated by asterisks in the formulae of the respective compounds in Fig. 1) between NH and C-4 and C-5, but not with C-2, were observed for **6a** to further prove the imino-dioxolane structure. On the other hand, cross peaks between NH and C-2, C-4 and C-5, as well as with carbons of the aliphatic substituent were present for **8e** to verify the oxazolidinone ring. For **8e** this measurement also corroborated the chemical shift assignment of amide C-4. The configuration of the spiro carbons C-[1′,5] was established as *R* for **2** and **6**, and *S* for **3** and **8** based on the three bond heteronuclear coupling constants between H-2 and C-4 shown in Figure 1 indicating the *trans* diaxial versus *gauche* relationships between the respective nuclei in the $^4C_1$ conformation of the sugar ring. Although these couplings could not be measured for each compound due to insufficient sample quantities, no doubt was left about the spiro configuration of the other members of the series. Namely, the proton resonances had characteristic shifts depending on the C-[1′,5] configuration (cf. Fig. 1 and Table 4): H-2′ had a downfield shift of ~0.1–0.2 ppm if the C=NH/C=O was on the same side of the pyranoid ring; similarly, downfield shifts were observed for H-3′ (~0.7 ppm) and H-5′ (~0.4 ppm) when they were in the same situation. Analogous ^{1}H chemical shift patterns were observed earlier for other glycopyranosylidene-spiro-heterocycles.[14,15]

Formation of spirocycles **2**, **3** and **6** can be understood by following the mechanistic proposal in Scheme 1. The silver salt promoter facilitates the generation of the corresponding glycosyliumion **B1** from **1** or **5**. Nucleophilic attack of a ketone with anchimeric assistance of the 2-*O*-acyl group (**D1**) may lead to carbocation **A1** while without neighbouring group participation the epimeric cation, represented by resonance forms **E1** and **F1**, can be formed. Intramolecular attack of the amide oxygen (illustrated in details for **F1** only), the harder part of this functional group,

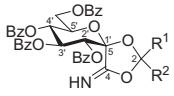
Table 4
Selected NMR data for the *O*-peracylated compounds[a] **2**, **3**, **6** and **8** (δ [ppm], J [Hz])



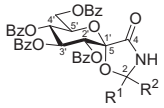
	2a[b]	**2b**	**2c**	**2d**	**2e**
H-2′	5.58	5.54/5.59	5.60	5.57	5.57
H-3′	6.00	6.05/5.89	5.99	5.98	6.01
H-5′	4.88	4.75/4.85	4.85	4.84	4.85
C-[1′,5]	100.4	100.2/100.3	99.9	100.1	100.1
C-2	112.6	114.7/114.1	116.8	116.2	113.2
C-4	160.9	160.4/160.2	160.4	158.8	158.2
$^3J_{H\text{-}2',C\text{-}4}$	5.6	4.1	6.1	6.1	5.3



	3a[b]	**3b**	**3c**	**3e**
H-2′	5.74	5.74/5.69	5.74	5.75
H-3′	5.25	5.35/5.20	5.30	5.26
H-5′	4.41	4.43/4.39	4.42	4.41
C-[1′,5]	100.3	100.9/100.9	100.8	100.8
C-2	112.5	114.8/113.8	116.2	113.1
C-4	161.2	160.2/160.2	160.8	160.3
$^3J_{H\text{-}2',C\text{-}4}$	n.m.[c]	n.m.[c]	2.1	n.m.[c]



	6a	**6c**	**6d**	**6e**
H-2′	5.85	5.92	5.87	5.87
H-3′	6.80	6.82	6.82	6.82
H-5′	5.13	5.13	5.12	5.14
C-[1′,5]	100.3	99.9	99.9	99.8
C-2	112.8	116.6	122.2	113.5
C-4	160.5	160.6	160.3	160.4
$^3J_{H\text{-}2',C\text{-}4}$	5.4	4.9	4.9	5.0



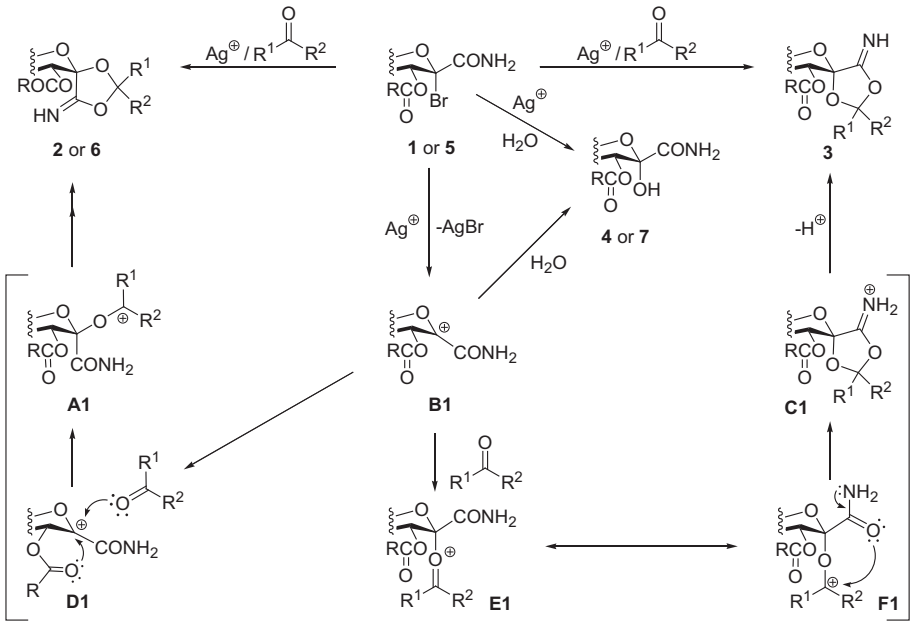
	8a	**8b**	**8c**	**8d**	**8e**	**8f**
H-2′	5.96	5.99/5.97	6.00	5.97	6.00	5.98
H-3′	6.09	6.10/6.09	6.10	6.08	6.10	6.08
H-5′	4.66	4.63/4.63	4.64	4.63	4.69	4.66
H-4′	5.73	5.72/5.71	5.70	5.73	5.71	5.70
C-[1′,5]	100.5	100.3/100.35	100.2	100.7	100.1	100.1
C-2	92.4	94.9, 94.5	97.1	100.1	93.5	97.2
C-4	166.0	166.4/166.1	166.6	166.1	166.4	166.1
$^3J_{H\text{-}2',C\text{-}4}$	n.m.[c]	n.m.[c]	n.m.[c]	n.m.[c]	2.5	n.m.[c]

[a] For substituents R^1 and R^2 see the respective tables (Table 1 for **2** and **3**, Table 2 for **6**, and Table 3 for **8**).
[b] Data taken from Ref. 19.
[c] Not measured because of insufficient sample quantity.

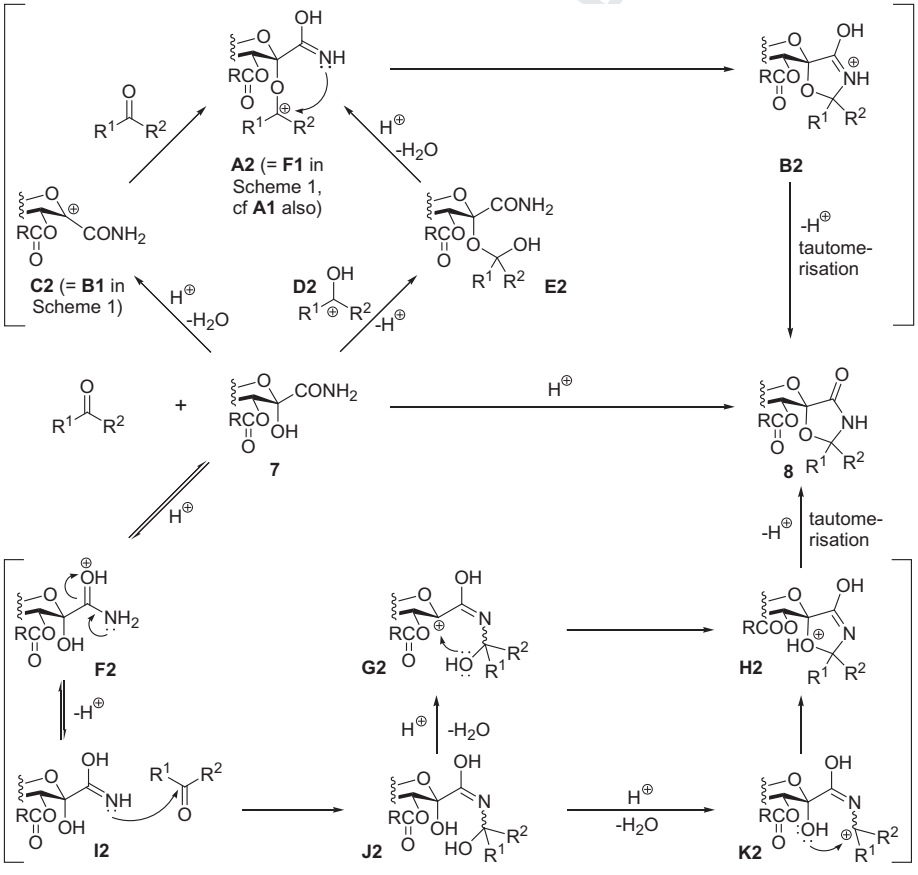
may give the cyclized iminium ion **C1**. Deprotonation of this intermediate and that of the analogous one (not shown) derived from **A1** give then the isolated products of retained (**3**) and inverted configuration (**2**), respectively. Formation of the by-products **4** and **7** are to be explained by the water content of the solvents attacking on glycosyliumion **B1**. The finding that from the D-*gluco* configured **5** only the formation of **6** was observed,[2] while **1** of the D-*galacto* configuration gave both epimers **2** and **3**, may be indicative of a remote participation[29] of the axial 4-*O*-acetyl group of **1** facilitating the formation of **3**.

A mechanistic proposal for the formation of spirocycles **8** (Scheme 2) can be more complex since, due to the presence of several functional groups whose protonation may start the reaction, alternative pathways may occur simultaneously. The first (most tempting) possibility is the protonation of the glycosidic OH in **7** followed by loss of water to give glycosyliumion **C2** which is the same intermediate as **B1** in Scheme 1. Attack of a ketone on **C2** would give **A2** (equal to intermediate **F1** in Scheme 1), however, the formation of the epimeric intermediate **A1** (shown in Scheme 1) must also be taken into account. This possibility renders this pathway less probable since only the configurationally retained epimer **8** was observed in the reactions. Formation of **A2** (without epimerization) should also be possible via protonation and subsequent dehydration of a mixed hemiketal **E2** which can develop from **7** by nucleophilic addition of the glycosidic OH to the ketone or its protonated form **D2**. Ring closure of **A2** (=**F1**) occurred by the nucleophilic attack of the amide oxygen under conditions of Scheme 1 (cf. **F1**→**C1**) to give the imino-dioxolanes **3**, however, these compounds were not present in the reactions of **7** (Scheme 2). Considering the different reaction conditions this may raise two possibilities: (i) imino-dioxolanes may be formed as primary

[2] It is to be noted that from the acetylated counterpart of **5** formation of a very minor amount (6%) of the inverted product was reported.[19]



Scheme 1. Proposed mechanism for the formation of 1′,5′-anhydro-D-glycitol-spiro-[1′,5]-4-imino-1,3-dioxolanes **2**, **3**, and **6**.



Scheme 2. Possible mechanistic pathways for the formation of 1′,5′-anhydro-D-glucitol-spiro-[1′,5]-oxazolidin-4-ones **8**.

products which then give oxazolidinones **8** in a proton catalysed equilibration; (ii) ring closure takes place by a N-nucleophilic attack of the hydroximide tautomer of the amide moiety. The first possibility was ruled out by an experiment in which an imino-dioxolane **6** was subjected to the conditions of the formation of **8**. Thus, **6a** was boiled in acetone in the presence of TfOH (1 equiv) for 24 h, however, no change could be detected by TLC. The second possibility can be reasonable since tautomerization of amides under acidic conditions (cf. **7**→**F2**→**I2**) is a known phenomenon.[30] Thus, **A2** may ring-close to protonated hydroxy-oxazoline **B2** which, after deprotonation and tautomerization can give the isolated **8**.

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Since α-hydroxy-carboxamides and carbonyl compounds are known to furnish oxazoles under acidic conditions, the generally accepted mechanism of the Fischer oxazole synthesis[25] should also be considered in the present transformation. Protonation of the amide oxygen of **7** as shown in **F2** may result in a tautomerization[30] to give at least a minor proportion of **I2** which can attack the ketone (or its protonated form **D2**) as a N-nucleophile to give intermediate **J2**. Protonation of a hydroxyl group in **J2** may lead to elimination of water to produce either carbocation **G2** or **K2**, both of which can ring close to **H2** by the nucleophilic attack of the remaining OH on the positively charged carbon. Due to the presence of three electron releasing substituents, carbocation **K2** might be more stable than glycosyliumion **G2**, therefore, formation of **H2** via **K2** might be preferred. This is also made likely by the formation of a single isomer of **8** that would probably not be the case in route **J2**→**G2**→**H2**. Final deprotonation and tautomerization of **H2** may then yield the isolable product **8**.

In conclusion, the reactions of (glyculopyranose and glyculopyranosyl bromide)onamides with ketones gave access to the preparation of new anomeric spirocycles, namely, 1′,5′-anhydro-D-glycitol-spiro-[1′,5]-4-imino-2,2-disubstituted-dioxolanes and 1′,5′-anhydro-D-glycitol-spiro-[1′,5]-2,2-disubstituted-oxazolidin-4-ones. The structures were unambiguously assigned by NMR methods. Detailed mechanisms were proposed to explain the formation of both constitutional isomers as well as the stereoselectivities of the ring forming reactions. The spiro-oxazolidinones were tested against rabbit muscle glycogen phosphorlyase *b*, however, had no inhibitory effect.

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. NMR spectra were recorded with Bruker 200 (200:50 MHz for $^{1}H/^{13}C$), Bruker DRX 360 (360:90 MHz for $^{1}H/^{13}C$) or Avance II 500 (500:125 MHz for $^{1}H/^{13}C$) spectrometers. Chemical shifts are referenced to Me_4Si (^{1}H), or to the solvent signals or DSS in D_2O (^{13}C). Mass spectra were recorded by a Bruker micrOTOF-Q instrument. TLC was performed on DC-Alurolle Kieselgel 60 F_{254} (Merck), and the plates were visualized under UV light and by gentle heating. For column chromatography Kieselgel 60 (Merck, particle size 0.063–0.200 mm) was used. Dichloromethane was distilled from P_4O_{10} and acetone from $CaSO_4$) and stored over 4 Å molecular sieves. Organic solutions were dried over anhydrous $MgSO_4$ and concentrated under diminished pressure at 40–50 °C (water bath).

3.2. General procedure I for the preparation of *O*-peracylated 1′,5′-anhydro-D-glycitol-spiro-[1′,5]-4-imino-2,2-disubstituted-1,3-dioxolanes 2, 3 and 6

To a solution of an *O*-peracylated (glyculopyranosyl bromide)onamide **1**[31] or **5**[32] (0.50 g) in a dry ketone (5 mL) containing molecular sieves (3 Å) Ag_2CO_3 (1 equiv) or AgOTf/Et_3N (1 equiv) was added. The mixture was stirred at rt in the dark under Ar atmosphere until TLC (1:1 or 1:2 EtOAc–hexane) showed complete transformation of the starting material. Then the mixture was filtered on a Celite pad and the solvent removed under diminished pressure. The crude product was purified by column chromatography.

3.2.1. (1′*R*,2*RS*)- and (1′*S*,2*RS*)-2′,3′,4′,6′-tetra-*O*-acetyl-1′,5′-anhydro-D-galactitol-spiro-[1′,5]-2-ethyl-4-imino-2-methyl-1,3-dioxolanes (2b and 3b)

Prepared from **1** (0.50 g, 1.10 mmol) and butanone in the presence of AgOTf according to General procedure I (Section 3.2). Column chromatography (1:1 EtOAc–hexane) gave three fractions.

Fraction I: 0.21 g (43%) of an inseparable diastereomeric mixture of **2b** as a colourless oil; R_f = 0.71 (1:1 EtOAc–hexane).

Characterization of diastereomer A: ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm) 7.40 (s, 1H, NH), 6.05 (dd, 1H, $J_{2',3'}$ 11.1 Hz, $J_{3',4'}$ 3.2 Hz, H-3′), 5.54 (d, 1H, $J_{2',3'}$ 11.1 Hz, H-2′), 5.51 (dd, 1H, $J_{3',4'}$ 3.2 Hz, $J_{4',5'}$ 1.0 Hz, H-4′), 4.75 (ddd, 1H, $J_{5',6'a}$ 6.8 Hz, $J_{5',6'b}$ 6.3 Hz, $J_{4',5'}$ 1.0 Hz, H-5′), 4.20–4.02 (m, 2H, H-6′a, H-6′b), 2.15, 2.05, 1.95, 1.93 (4s, 12H, $OCOCH_3$), 1.70 (q, 2H, *J* 7.3 Hz, CH_2CH_3), 1.35 (s, 3H, CH_3), 0.88 (t, 3H, *J* 7.3 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 170.3, 170.0, 169.6, 169.3 (*CO*), 160.4 (C-4, $^{3}J_{H-2',C-4}$ = ~4.1 Hz), 114.7 (C-2), 100.2 (C-1′), 69.8, 68.8, 67.5, 66.9 (C-2′–C-5′), 61.3 (C-6′), 33.4 (CH_2CH_3), 25.6 (CH_3), 20.7, 20.5, 20.3, 20.2 ($COCH_3$); 6.9 (CH_2CH_3).

Characterization of diastereomer B: ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm) 7.40 (s, 1H, NH), 5.89 (dd, 1H, $J_{2',3'}$ 11.1 Hz, $J_{3',4'}$ 3.2 Hz, H-3′), 5.59 (1H, d, $J_{2',3'}$ 11.1 Hz, H-2′), 5.48 (dd, 1H, $J_{3',4'}$ 3.2 Hz, $J_{4',5'}$ 1.0 Hz, H-4′), 4.85 (ddd, 1H, $J_{5',6'a}$ 6.8 Hz, $J_{5',6'b}$ 6.3 Hz, $J_{4',5'}$ 1.0 Hz, H-5′), 4.20–4.02 (m, 2H, H-6′a, H-6′b), 2.16, 2.04, 1.98, 1.94 (4s, 12H, $OCOCH_3$), 1.85 (q, 2H, *J* 7.3 Hz, CH_2CH_3), 1.55 (s, 3H, CH_3), 0.96 (t, 3H, *J* 7.3 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 170.2, 170.0, 169.8, 169.1 (*CO*), 160.2 (C-4), 114.1 (C-2), 100.3 (C-1′), 69.9, 68.8, 67.2 (2) (C-2′–C-5′), 61.3 (C-6′), 32.4 (CH_2CH_3), 25.6 (CH_3), 20.8, 20.5, 20.3, 20.1 ($OCOCH_3$), 6.9 (CH_2CH_3). Calcd for $C_{19}H_{27}NO_{11}$ (Mol. Wt.: 445.42, Ex. Mass.: 445.16); ESI-MS (positive mode) *m*/*z*: 468.148 $[M+Na]^+$, 913.305 $[2M+Na]^+$.

Fraction II: 0.10 g (19%) of an inseparable diastereomeric mixture of **3b** as a yellowish oil; R_f = 0.36 (1:1 EtOAc–hexane).

Characterization of diastereomer C: ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm) 7.48 (s, 1H, NH), 5.74 (d, 1H, $J_{2',3'}$ 11.1 Hz, H-2′), 5.51 (dd, 1H, $J_{3',4'}$ 3.2 Hz, $J_{4',5'}$ 1.0 Hz, H-4′), 5.35 (dd, 1H, $J_{2',3'}$ 11.1 Hz, $J_{3',4'}$ 3.2 Hz, H-3′), 4.43 (ddd, 1H, $J_{5',6'a}$ 6.8, $J_{5',6'b}$ 6.3 Hz, $J_{4',5'}$ 1.0 Hz, H-5′), 4.20–4.03 (m, 2H, H-6′a, H-6′b), 2.10, 2.08, 2.01, 1.98 (4s, 12H, $OCOCH_3$), 1.88 (q, 2H, *J* 7.3 Hz, CH_2CH_3), 1.54 (s, 3H, CH_3), 1.00 (t, 3H, *J* 7.3 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 170.4, 170.2, 169.8, 169.1 (*CO*), 160.2 (C-4), 114.8 (C-2), 100.9 (C-1′), 69.7, 68.6, 67.7, 66.5 (C-2′–C-5′), 61.7 (C-6′), 32.4 (CH_2CH_3), 25.8 (CH_3), 20.7, 20.5, 20.2, 20.1 ($COCH_3$); 6.8 (CH_2CH_3).

Characterization of diastereomer D: ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm) 7.48 (s, 1H, NH), 5.69 (d, 1H, $J_{2',3'}$ 11.1 Hz, H-2′), 5.49 (dd, 1H, $J_{3',4'}$ 3.2 Hz, $J_{4',5'}$ 1.0 Hz, H-4′), 5.20 (dd, 1H, $J_{2',3'}$ 11.1 Hz, $J_{3',4'}$ 3.2 Hz, H-3′), 4.39 (ddd, 1H, $J_{5',6'a}$ 6.8 Hz, $J_{5',6'b}$ 6.3 Hz, $J_{4',5'}$ 1.0 Hz, H-5′), 4.18–4.02 (m, 2H, H-6′a, H-6′b), 2.11, 2.09, 1.99, 1.97 (4s, 12H, $OCOCH_3$), 1.86 (2H, q, *J* 7.3 Hz, CH_2CH_3), 1.61 (s, 3H, CH_3), 1.26 (t, 3H, *J* 7.3 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$, 90 MHz) δ (ppm): 170.4, 170.0, 169.9, 169.6 (*CO*), 160.2 (C-4), 113.8 (C-2), 100.9 (C-1′), 69.7, 67.6, 66.2 (2) (C-2′–C-5′), 60.3 (C-6′), 33.5 (CH_2CH_3), 24.2 (CH_3), 20.7, 20.6, 20.2, 20.1 ($COCH_3$); 7.9 (CH_2CH_3). Calcd for $C_{19}H_{27}NO_{11}$ (Mol. Wt.: 445.42, Ex. Mass.: 445.16); ESI-MS (positive mode) *m*/*z*: 468.147 $[M+Na]^+$, 913.304 $[2M+Na]^+$.

Fraction III: 0.16 g (38%) of **4**[14] as a white solid.

3.2.2. (1′*R*)- and (1′*S*)-2′,3′,4′,6′-tetra-*O*-acetyl-1′,5′-anhydro-D-galactitol-spiro-[1′,5]-2,2-diethyl-4-imino-1,3-dioxolanes (2c and 3c)

Prepared from **1** (0.50 g, 1.10 mmol) and pentan-3-one with AgOTf according to General procedure I (Section 3.2). Column chromatography (1:1 EtOAc–hexane) gave three fractions.

Fraction I: 0.16 g (32%) of **2c** as white crystals; mp: 100–102 °C; $[\alpha]_D$ +37 (*c* 0.90, $CHCl_3$); ^{1}H NMR ($CDCl_3$, 360 MHz): δ (ppm) 7.45 (s, 1H, NH), 5.99 (dd, 1H, $J_{2',3'}$ 11.1 Hz, $J_{3',4'}$ 3.7 Hz, H-3′), 5.60 (d, 1H, $J_{2',3'}$ 11.1 Hz, H-2′), 5.50 (dd, 1H, $J_{3',4'}$ 3.7 Hz, $J_{4',5'}$ 1.2 Hz, H-4′), 4.85 (ddd, 1H, $J_{5',6'a}$ 6.8 Hz, $J_{5',6'b}$ 6.3 Hz, $J_{4',5'}$ 1.2 Hz, H-5′), 4.17 (dd, 1H, $J_{6'a,6'b}$ 11.6 Hz, $J_{5',6'a}$ 6.8 Hz, H-6′a), 4.09 (dd, 1H, $J_{6'a,6'b}$ 11.6 Hz, $J_{5',6'b}$ 6.3 Hz, H-6′b), 2.17, 2.06, 2.02, 1.96 (4s, 12H, $OCOCH_3$), 1.87 (q, 2H, *J* 7.3 Hz, CH_2CH_3), 1.72 (q, 2H, *J* 7.3 Hz, CH_2-

CH_3), 0.96 (t, 3H, *J* 7.3 Hz, CH_2CH_3), 0.88 (t, 3H, *J* 7.3 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 170.1 (2), 169.6, 169.2 (*C*O), 160.4 (C-4, $^3J_{H\text{-}2',C\text{-}4'}$ = ~6.1 Hz from HSQMBC at 125 MHz), 116.8 (C-2), 99.9 (C-1′), 69.7, 68.9, 67.3 (2) (C-2′–C-5′), 61.3 (C-6′), 31.2, 29.4 (CH_2CH_3), 20.5, 20.4 (2), 20.2 ($COCH_3$); 7.8, 6.7 (CH_2CH_3).

Fraction II: 0.07 g (14%) of **3c** as a white crystals, mp: 61–63 °C; $[\alpha]_D$ +59 (*c* 1.00, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 7.42 (s, 1H, NH), 5.74 (d, 1H, $J_{2',3'}$ 11.1 Hz, H-2′), 5.51 (dd, 1H, $J_{3',4'}$ 3.2 Hz, $J_{4',5'}$ 1.1 Hz, H-4′), 5.30 (dd, 1H, $J_{2',3'}$ 11.1 Hz, $J_{3',4'}$ 3.2 Hz, H-3′), 4.42 (ddd, 1H, $J_{5',6'a}$ 6.8 Hz, $J_{5',6'b}$ 6.3 Hz, $J_{4',5'}$ 1.1 Hz, H-5′), 4.16 (dd, 1H, $J_{6'a,6'b}$ 11.6 Hz, $J_{5',6'a}$ 6.8 Hz, H-6′a), 4.11 (dd, 1H, $J_{6'a,6'b}$ 11.6 Hz, $J_{5',6'b}$ 6.3 Hz, H-6′b), 2.19, 2.03, 2.01, 1.98 (4s, 12H, $OCOCH_3$), 1.88 (q, 2H, *J* 7.3 Hz, CH_2CH_3), 1.84 (q, 2H, *J* 7.3 Hz, CH_2CH_3), 0.99 (t, 3H, *J* 7.3 Hz, CH_2CH_3), 0.95 (t, 3H, *J* 7.3 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 170.3 (2), 170.1, 168.6 (*C*O), 160.8 (C-4, $^3J_{H\text{-}2',C\text{-}4}$ = ~2.1 Hz from HSQMBC at 125 MHz), 116.2 (C-2), 100.8 (C-1′), 69.6, 69.2, 67.7, 66.1 (C-2′–C-5′), 61.8 (C-6′), 31.6, 29.0 (CH_2CH_3), 20.8, 20.5, 20.3 (2) ($COCH_3$); 8.0, 6.6 (CH_2CH_3); Calcd for $C_{20}H_{29}NO_{11}$ (Mol. Wt.: 459.44, Ex. Mass.: 459.17); ESI-MS (positive mode) *m*/*z*: 482.163 $[M+Na]^+$, 941.337 $[2M+Na]^+$.

Fraction III: 0.12 g (27%) of **4**[14] as a white solid.

3.2.3. (1′*R*)- and (1′*S*)-2′,3′,4′,6′-tetra-*O*-acetyl-1′,5′-anhydro-D-galactitol-spiro-[1′,5]-4-imino-1,3-dioxolane-spiro-[2,1″]-cyclopentanes (2d and 3d)

Prepared from **1** (0.20 g, 0.44 mmol) and cyclopentanone with AgOTf according to General procedure I (Section 3.2). Column chromatography (1:1 EtOAc–hexane) gave three fractions.

Fraction I: 0.10 g (48%) of **2d** as white crystals; mp: 148–150 °C; $[\alpha]_D$ +28 (*c* 0.20, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 7.40 (s, 1H, NH), 5.98 (dd, 1H, $J_{2',3'}$ 11.1 Hz, $J_{3',4'}$ 3.6 Hz, H-3′), 5.57 (d, 1H, $J_{2',3'}$ 11.1 Hz, H-2′), 5.50 (dd, 1H, $J_{3',4'}$ 3.6 Hz, $J_{4',5'}$ 1.1 Hz, H-4′), 4.85 (ddd, 1H, $J_{5',6'a}$ 6.8 Hz, $J_{5'6'b}$ 6.3 Hz, $J_{4',5'}$ 1.1 Hz, H-5′), 4.15 (dd, 1H, $J_{6'a,6'b}$ 11.6 Hz, $J_{5',6'a}$ 6.8 Hz, H-6′a) 4.09 (dd, 1H, $J_{6'a,6'b}$ 11.6 Hz, $J_{5',6'b}$ 6.3 Hz, H-6′b), 2.16, 2.05, 2.03, 1.97 (4s, 12H, $OCOCH_3$), 1.92–1.84 (m, 4H, 2× CH_2), 1.82–1.68 (m, 4H, 2× CH_2); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm): 170.0 (2), 169.6, 169.0 (*C*O), 158.8 (C-4, $^3J_{H\text{-}2',C\text{-}4}$ = ~6.1 Hz), 116.2 (C-2), 100.1 (C-1′), 69.9, 68.6, 67.3, 67.2 (C-2′–C-5′), 61.2 (C-6′), 38.2, 36.6, 23.6, 22.6 (4× *C*H$_2$), 20.6, 20.5 (2), 20.4 ($COCH_3$); Calcd for $C_{20}H_{27}NO_{11}$ (Mol. Wt.: 457.43, Ex. Mass.: 457.16); ESI-MS (positive mode) *m*/*z*: 480.149 $[M+Na]^+$, 937.306 $[2M+Na]^+$.

Fraction II: Traces of **3d** insufficient for NMR characterization. Calcd for $C_{20}H_{27}NO_{11}$ (Mol. Wt.: 457.43, Ex. Mass.: 457.16); ESI-MS (positive mode) *m*/*z*: 480.147 $[M+Na]^+$, 937.306 $[2M+Na]^+$.

Fraction III: 0.045 g (26%) of **4**[14] as a white solid.

3.2.4. (1′*R*)- and (1′*S*)-2′,3′,4′,6′-tetra-*O*-acetyl-1′,5′-anhydro-D-galactitol-spiro-[1′,5]-4-imino-1,3-dioxolane-spiro-[2,1]-cyclohexanes (2e and 3e)

Prepared from **1** (0.50 g, 1.10 mmol) and cyclohexane with AgOTf according to General procedure I (Section 3.2). Column chromatography (1:1 EtOAc–hexane) gave three fractions.

Fraction I: 0.23 g (44%) of **2e** as white crystals; mp: 124–126 °C; $[\alpha]_D$ +14 (*c* 0.22, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 7.40 (s, 1H, NH), 6.01 (dd, 1H, $J_{2',3'}$ 10.5 Hz, $J_{3',4'}$ 3.2 Hz, H-3′), 5.57 (d, 1H, $J_{2',3'}$ 10.5 Hz, H-2′), 5.51 (dd, 1H, $J_{3',4'}$ 3.2 Hz, $J_{4',5'}$ 1.0 Hz, H-4′), 4.85 (ddd, 1H, $J_{5',6'a}$ 7.3 Hz, $J_{5',6'b}$ 6.3 Hz, $J_{4',5'}$ 1.0 Hz, H-5′), 4.10–4.08 (m, 2H, H-6′a, H-6′b), 2.18, 2.08, 2.04, 1.97 (4s, 12H, $OCOCH_3$), 1.87–1.81 (m, 2H, CH_2), 1.77–1.56 (m, 4H, 2× CH_2), 1.53–1.33 (m, 2H, CH_2), 1.30–1.23 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 170.8 (2), 169.2, 169.8 (*C*O), 158.2 (C-4, $^3J_{H\text{-}2',C\text{-}4}$ = ~5.3 Hz), 113.2 (C-2), 100.1 (C-1′), 69.9, 68.9, 67.5 (2) (C-2′–C-5′), 61.3 (C-6′), 37.2, 36.4, 24.4, 23.1 (2) (5× CH_2), 20.8, 20.6 (2), 20.3 ($COCH_3$); Calcd for $C_{21}H_{29}NO_{11}$ (Mol. Wt.: 471.46, Ex. Mass.: 471.17); ESI-MS (positive mode) *m*/*z*: 494.164 $[M+Na]^+$, 965.339 $[2M+Na]^+$.

Fraction II: 0.04 g (8%) of **3e** as white crystals; mp: 112–114 °C; $[\alpha]_D$ +23 (*c* 0.20, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 7.40 (s, 1H, NH), 5.75 (d, 1H, $J_{2',3'}$ 10.5 Hz, H-2′), 5.50 (dd, 1H, $J_{3',4'}$ 3.2 Hz, $J_{4',5'}$ 1.0 Hz, H-4′), 5.26 (dd, 1H, $J_{2',3'}$ 10.5 Hz, $J_{3',4'}$ 3.2 Hz, H-3′), 4.41 (ddd, 1H, $J_{5',6'a}$ 7.3 Hz, $J_{5',6'b}$ 6.3 Hz, $J_{4',5'}$ 1.0 Hz, H-5′), 4.16 (dd, 1H, $J_{6'a,6'b}$ 11.6 Hz, $J_{5',6'a}$ 7.3 Hz, H-6′a), 4.07 (dd, 1H, $J_{6'a,6'b}$ 11.6 Hz, $J_{5',6'b}$ 6.3 Hz, H-6′b), 2.20, 2.06, 2.01, 1.95 (4s, 12H, $OCOCH_3$), 1.88–1.81 (m, 2H, CH_2), 1.79–1.60 (m, 6H, 3× CH_2), 1.52–1.41 (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 170.3 (2), 168.9, 168.8 (*C*O), 160.3 (C-4), 113.1 (C-2), 100.8 (C-1′), 69.7, 69.3, 67.7, 66.0 (C-2′–C-5′), 61.8 (C-6′), 37.0, 36.0, 24.3, 23.3 (2) (5× CH_2), 20.6 (2), 20.5 (2) ($COCH_3$); Calcd for $C_{21}H_{29}NO_{11}$ (Mol. Wt.: 471.46, Ex. Mass.: 471.17); ESI-MS (positive mode) *m*/*z*: 494.164 $[M+Na]^+$, 965.336 $[2M+Na]^+$.

Fraction III: 0.11 g (25%) of **4**[14] as a white solid.

3.2.5. (1′*R*)-2′,3′,4′,6′-Tetra-*O*-benzoyl-1′,5′-anhydro-D-glucitol-spiro-[1′,5]-2,2-dimethyl-4-imino-1,3-dioxolane (6a)

Prepared from **5** (0.50 g, 0.71 mmol) and acetone with AgOTf according to General procedure I (Section 3.2). Column chromatography (1:2 EtOAc–hexane than EtOAc) gave two fractions.

Fraction I: 0.18 g (37%) of **6a** as a colourless oil; R_f = 0.51 (1:2 EtOAc–hexane); $[\alpha]_D$ +63 (*c* 0.52, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 8.04–7.24 (m, 20H, ArH), 7.73 (s, 1H, NH), 6.80 (pseudo t, 1H, $J_{2',3'}$ 10.2 Hz, $J_{3',4'}$ 9.7 Hz, H-3′), 5.85 (d, 1H, $J_{2',3'}$ 10.2 Hz, H-2′), 5.76 (pseudo t, 1H, $J_{4',5'}$ 9.9 Hz, $J_{3',4'}$ 9.7 Hz, H-4′), 5.13 (ddd, 1H, $J_{4',5'}$ 9.9 Hz, $J_{5',6'b}$ 4.5 Hz, $J_{5',6'a}$ 1.2 Hz, H-5′), 4.63 (dd, 1H, $J_{6'a,6'b}$ 12.0 Hz, $J_{5',6'a}$ 1.2 Hz, H-6′a), 4.47 (dd, 1H, $J_{6'a,6'b}$ 12.0 Hz, $J_{5',6'b}$ 4.5 Hz, H-6′b), 1.61, 1.29 (2s, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 166.0, 165.4, 165.3, 164.8 (*C*O), 160.5 (C-4, $^3J_{H\text{-}2',C\text{-}4}$ = ~5.4 Hz, from HSQMBC at 125 MHz), 112.8 (C-2), 100.3 (C-1′), 70.8, 70.7, 70.5, 69.4 (C-2′–C-5′), 63.1 (C-6′), 27.6, 26.7 (CH_3); Calcd for $C_{38}H_{33}NO_{11}$ (Mol. Wt.: 679.67, Ex. Mass.: 679.21); ESI-MS (positive mode) *m*/*z*: 702.190 $[M+Na]^+$, 1381.399 $[2M+Na]^+$.

Fraction II: 0.21 g (46%) of **7**[32] as a white solid.

3.2.6. (1′*R*)-2′,3′,4′,6′-Tetra-*O*-benzoyl-1′,5′-anhydro-D-glucitol-spiro-[1′,5]-2,2-diethyl-4-imino-1,3-dioxolane (6c)

Prepared from **5** (0.50 g, 0.71 mmol) and pentan-3-one with AgOTf according to General procedure I (Section 3.2). Column chromatography (1:2 EtOAc–hexane than EtOAc) gave two fractions.

Fraction I: 0.23 g (46%) of **6c** as a white foam; R_f = 0.49 (1:2 EtOAc–hexane); $[\alpha]_D$ +60 (*c* 0.40, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 8.05–7.20 (m, 20H, ArH), 7.71 (s, 1H, NH), 6.82 (pseudo t, 1H, $J_{2',3'}$ 10.2 Hz, $J_{3',4'}$ 9.8 Hz, H-3′), 5.92 (d, 1H, $J_{2',3'}$ 10.2 Hz, H-2′), 5.76 (pseudo t, 1H, $J_{3',4'}$ 9.8 Hz, $J_{4',5'}$ 9.7 Hz, H-4′), 5.13 (ddd, 1H, $J_{4',5'}$ 9.7 Hz, $J_{5',6'b}$ 5.6 Hz, $J_{5',6'a}$ 2.2 Hz, H-5′), 4.64 (dd, 1H, $J_{6'a,6'b}$ 12.0 Hz, $J_{5',6'a}$ 2.2 Hz, H-6′a), 4.50 (dd, 1H, $J_{6'a,6'b}$ 12.0 Hz, $J_{5',6'b}$ 5.6 Hz, H-6′b), 1.87 (q, 2H, *J* 7.2 Hz, CH_2CH_3), 1.57 (q, 2H, *J* 7.4 Hz, CH_2CH_3), 0.90 (t, 3H, *J* 7.4 Hz, CH_2CH_3), 0.63 (t, 3H, *J* 7.4 Hz, CH_2CH_3); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 165.9, 165.4 (2), 164.8 (*C*O), 160.6 (C-4, $^3J_{H\text{-}2',C\text{-}4}$ = ~4.9 Hz), 116.6 (C-2), 99.9 (C-1′), 70.9, 70.7, 70.5, 69.5 (C-2′–C-5′), 63.0 (C-6′), 31.2, 29.1 (CH_2CH_3), 7.8, 6.6 (CH_2CH_3); Calcd for $C_{40}H_{37}NO_{11}$ (Mol. Wt.: 707.72, Ex. Mass.: 707.24); ESI-MS (positive mode) *m*/*z*: 730.223 $[M+Na]^+$, 1437.468 $[2M+Na]^+$.

Fraction II: 0.16 g (35%) of **7**[32] as a white solid.

3.2.7. (1′*R*)-2′,3′,4′,6′-Tetra-*O*-benzoyl-1′,5′-anhydro-D-glucitol-spiro-[1′,5]-4-imino-1,3-dioxolane-spiro-[2,1″]-cyclopentane (6d)

Prepared from **5** (0.50 g, 0.71 mmol) and cyclopentanone with Ag_2CO_3 according to General procedure I (Section 3.2). Column

chromatography (1:2 EtOAc–hexane than EtOAc) gave two fractions.

Fraction I: 0.28 g (56%) of **6d** as a white foam; R_f = 0.55 (1:2 EtOAc–hexane); $[\alpha]_D$ +62 (*c* 0.46, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 8.05–7.22 (m, 20H, ArH), 7.75 (s, 1H, NH), 6.82 (pseudo t, 1H, $J_{2',3'}$ 10.2 Hz, $J_{3',4'}$ 9.8 Hz, H-3′), 5.87 (d, 1H, $J_{2',3'}$ 10.2 Hz, H-2′), 5.79 (pseudo t, 1H, $J_{4',5'}$ 9.9 Hz, $J_{3',4'}$ 9.8 Hz, H-4′), 5.12 (ddd, 1H, $J_{4',5'}$ 9.9 Hz, $J_{5',6'b}$ 4.6 Hz, $J_{5',6'a}$ 2.8 Hz, H-5′), 4.63 (dd, 1H, $J_{6'a,6'b}$ 12.1 Hz, $J_{5',6'a}$ 2.8 Hz, H-6′a), 4.49 (dd, 1H, $J_{6'a,6'b}$ 12.1 Hz, $J_{5',6'b}$ 4.6 Hz, H-6′b), 2.15–2.07 (m, 2H, CH_2), 1.91–1.86 (m, 2H, CH_2), 1.75–1.54 (m, 4H, 2× CH_2); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 165.9, 165.3, 165.2, 164.8 (*C*O), 160.3 (C-4, $^3J_{H\text{-}2',C\text{-}4}$ = ~4.9 Hz), 122.2 (C-2), 99.9 (C-1′), 70.8, 70.6, 70.5, 69.4 (C-2′–C-5′), 62.9 (C-6′), 38.0, 36.3, 23.3, 22.4 (4× CH_2); Calcd for $C_{40}H_{35}NO_{11}$ (Mol. Wt.: 705.71, Ex. Mass.: 705.22); ESI-MS (positive mode) *m*/*z*: 728.207 $[M+Na]^+$, 1433.434 $[2M+Na]^+$.

Fraction II: 0.08 g (18%) of **7**[32] as a white solid.

3.2.8. (1′*R*)-2′,3′,4′,6′-Tetra-*O*-benzoyl-1′,5′-anhydro-D-glucitol-spiro-[1′,5]-4-imino-1,3-dioxolane-spiro-[2,1″]-cyclohexane (6e)

Prepared from **5** (0.50 g, 0.71 mmol) and cyclohexanone with AgOTf according to General procedure I (Section 3.2). Column chromatography (1:2 EtOAc–hexane than EtOAc) gave two fractions.

Fraction I: 0.14 g (28%) of **6e** as a white foam; R_f = 0.61 (1:2 EtOAc–hexane than EtOAc); $[\alpha]_D$ +53 (*c* 0.40, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 8.04–7.24 (m, 20H, ArH), 7.75 (s, 1H, NH), 6.82 (pseudo t, 1H, $J_{2',3'}$ 10.2 Hz, $J_{3',4'}$ 9.9 Hz, H-3′), 5.87 (d, 1H, $J_{2',3'}$ 10.2 Hz, H-2′), 5.77 (pseudo t, 1H, $J_{3',4'}$ 9.9 Hz, $J_{4',5'}$ 9.7 Hz, H-4′), 5.14 (ddd, 1H, $J_{4',5'}$ 9.7 Hz, $J_{5',6'b}$ 5.0 Hz, $J_{5',6'a}$ 2.4 Hz, H-5′), 4.61 (dd, 1H, $J_{6'a,6'b}$ 12.2 Hz, $J_{5',6'a}$ 2.4 Hz, H-6′a), 4.49 (dd, 1H, $J_{6'a,6'b}$ 12.2 Hz, $J_{5',6'b}$ 5.0 Hz, H-6′b), 1.86–1.83 (m, 2H, CH_2), 1.55–1.26 (m, 8H, 4× CH_2); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 165.9, 165.3, 165.2, 164.8 (*C*O), 160.4 (C-4, $^3J_{H\text{-}2',C\text{-}4}$ = ~5.0 Hz), 113.5 (C-2), 99.8 (C-1′), 70.7 (2), 70.5, 69.5 (C-2′–C-5′), 63.0 (C-6′), 37.0, 36.0, 24.1, 22.9, 22.8 (5× CH_2); Calcd for $C_{41}H_{37}NO_{11}$ (Mol. Wt.: 719.73, Ex. Mass.: 719.24); ESI-MS (positive mode) *m*/*z*: 742.224 $[M+Na]^+$, 1461.462 $[2M+Na]^+$.

Fraction II: 0.16 g (35%) of **7**[32] as a white solid.

3.3. General procedure II for the preparation of *O*-perbenzoylated 1′,5′-anhydro-D-glucitol-spiro-[1′,5]-2,2-disubstituted-oxazolidin-4-ones 8

Ulosonamide **7**[32] was dissolved in a ketone or in a mixture of dry THF or toluene and 5 equiv of a ketone, then TfOH (1 equiv) was added. The mixture was stirred at reflux temp until TLC (9:1 $CHCl_3$–acetone) showed complete transformation of the starting material. Then the mixture was diluted with chloroform, washed with satd aq $NaHCO_3$, and with water, dried, and the solvent was evaporated. The remaining syrup was purified by column chromatography (18:1 $CHCl_3$–acetone).

3.3.1. (1′*S*)-2′,3′,4′,6′-Tetra-*O*-benzoyl-1′,5′-anhydro-D-glucitol-spiro-[1′,5]-2,2-dimethyl-oxazolidin-4-one (8a)

Prepared from **7** (0.1 g, 0.15 mmol) and acetone (5 ml) according to General procedure II (Section 3.3) to give 0.09 g (89%) of **8a** as a white solid. Mp.: 104–107 °C; R_f = 0.74 (9:1 $CHCl_3$–acetone); $[\alpha]_D$ +45 (*c* 0.40, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 8.70 (s, 1H, NH), 7.99–7.20 (m, 20H, ArH), 6.09 (t, 1H, $J_{2',3'}$ 9.8 Hz, $J_{3',4'}$ 9.8 Hz, H-3′), 5.96 (d, 1H, $J_{2',3'}$ 9.8 Hz, H-2′), 5.73 (t, 1H, $J_{4',5'}$ 9.8 Hz, $J_{3',4'}$ 9.8 Hz, H-4′), 4.66 (ddd, 1H, $J_{4',5'}$ 9.8 Hz, $J_{5',6'b}$ 5.5 Hz, $J_{5',6'a}$ 2.4 Hz, H-5′), 4.58 (dd, 1H, $J_{6'a,6'b}$ 12.3 Hz, $J_{5',6'a}$ 2.4 Hz, H-6′a), 4.47 (dd, 1H, $J_{6'a,6'b}$ 12.3 Hz, $J_{5',6'b}$ 5.5 Hz, H-6′b), 1.64 (s, 3H, CH_3), 1.57 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 166.0 (C-4), 165.8, 165.7, 165.1, 164.3 (*C*O), 133.4–128.1 (ArC), 100.5 (C-1′), 92.4 (C-2), 71.8, 70.1, 69.4, 68.3 (C-2′–C-5′), 63.2 (C-6′), 29.5 (CH_3), 28.3 (CH_3); Calcd for $C_{38}H_{33}NO_{11}$ (Mol. Wt.: 679.67, Ex. Mass.: 679.21); ESI-MS (positive mode) *m*/*z*: 702.192 $[M+Na]^+$, 1381.402 $[2M+Na]^+$.

3.3.2. (1′*S*,2*RS*)-2′,3′,4′,6′-Tetra-*O*-benzoyl-1′,5′-anhydro-D-glucitol-spiro-[1′,5]-2-ethyl-2-methyl-oxazolidin-4-ones (8b)

Prepared from **7** (0.1 g, 0.15 mmol) and butanone (5 ml) according to General procedure II (Section 3.3) to give 0.1 g (92%) an inseparable mixture of **8b** as a white solid. R_f = 0.58 (9:1 $CHCl_3$–acetone); $[\alpha]_D$ +22 (*c* 0.42, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 8.89 (s, 1H, NH), 8.05–7.24 (m, 20H, ArH), 6.10, 6.09 (t, 1H, $J_{2',3'}$ 10.4 Hz, $J_{3',4'}$ 9.8 Hz, H-3′), 5.99, 5.97 (d, 1H, $J_{2',3'}$ 10.4 Hz, H-2′), 5.72, 5.71 (t, 1H, $J_{4',5'}$ 9.8 Hz, $J_{3',4'}$ 9.8 Hz, H-4′), 4.63 (ddd, 1H, $J_{4',5'}$ 9.8 Hz, $J_{5',6'b}$ 5.5 Hz, $J_{5',6'a}$ 2.4 Hz, H-5′), 4.59 (dd, 1H, $J_{6'a,6'b}$ 12.3 Hz, $J_{5',6'a}$ 2.4 Hz, H-6′a), 4.45 (dd, 1H, $J_{6'a,6'b}$ 12.3 Hz, $J_{5',6'b}$ 5.5 Hz, H-6′b), 1.89, 1.85 (2q, 2H, *J* 7.5 Hz, CH_2), 1.65, 1.56 (2s, 3H, CH_3), 0.98, 0.95 (2t, 3H, *J* 7.5 Hz CH_3); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 166.4, 166.1 (C-4), 165.9, 165.6, 165.1, 164.3 (*C*O), 133.4–128.1 (ArC), 100.3 (C-1′), 94.9, 94.5 (C-2), 71.7, 70.3, 69.9, 69.4, 69.3, 68.6, 68.4 (C-2′–C-5′), 63.2 (C-6′), 34.9, 33.7 (CH_2), 27.3, 26.1 (CH_3), 8.0, 7.5 (CH_3); Calcd for $C_{39}H_{35}NO_{11}$ (Mol. Wt.: 693.70, Ex. Mass.: 693.22); ESI-MS (positive mode) *m*/*z*: 716.209 $[M+Na]^+$, 1409.435 $[2M+Na]^+$.

3.3.3. (1′*S*)-2′,3′,4′,6′-Tetra-*O*-benzoyl-1′,5′-anhydro-D-glucitol-spiro-[1′,5]-2,2-diethyl-oxazolidin-4-one (8c)

Prepared from **7** (0.1 g, 0.15 mmol) and pentan-3-one (82 µl, 0.75 mmol) in dry THF (5 ml) according to General procedure II (Section 3.3) to give 0.07 g (69%) of **8c** as a white solid. Mp.: 101–103 °C; R_f = 0.66 (9:1 $CHCl_3$–acetone); $[\alpha]_D$ +27 (*c* 0.32, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 9.07 (s, 1H, NH), 8.00–7.17 (m, 20H, ArH), 6.10 (t, 1H, $J_{2',3'}$ 9.8 Hz, $J_{3',4'}$ 9.8 Hz, H-3′), 6.00 (d, 1H, $J_{2',3'}$ 9.8 Hz, H-2′), 5.70 (t, 1H, $J_{4',5'}$ 9.8 Hz, $J_{3',4'}$ 9.8 Hz, H-4′), 4.64 (ddd, 1H, $J_{4',5'}$ 9.8 Hz, $J_{5',6'b}$ 6.7 Hz, $J_{5',6'a}$ 2.4 Hz, H-5′), 4.60 (dd, 1H, $J_{6'a,6'b}$ 12.3 Hz, $J_{5',6'a}$ 2.4 Hz, H-6′a), 4.45 (dd, 1H, $J_{6'a,6'b}$ 12.3 Hz, $J_{5',6'b}$ 6.7 Hz, H-6′b), 1.86, 1.75 (2q, 4H, *J* 7.0 Hz, CH_2), 0.89, 0.85 (2t, 6H, *J* 7.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 166.6 (C-4), 165.9, 165.6, 165.1, 164.3 (*C*O), 133.4–128.1 (ArC), 100.2 (C-1′), 97.1 (C-2), 71.6, 70.2, 69.4, 68.6 (C-2′–C-5′), 63.3 (C-6′), 32.2 (CH_2), 30.9 (CH_2), 7.8 (CH_3), 7.3 (CH_3); Calcd for $C_{40}H_{37}NO_{11}$ (Mol. Wt.: 707.72, Ex. Mass.: 707.24); ESI-MS (positive mode) *m*/*z*: 730.225 $[M+Na]^+$, 1437.464 $[2M+Na]^+$.

3.3.4. (1′*S*)-2′,3′,4′,6′-Tetra-*O*-benzoyl-1′,5′-anhydro-D-glucitol-spiro-[1′,5]-4-oxo-oxazolidine-spiro-[2,1″]-cyclopentane (8d)

Prepared from **7** (0.1 g, 0.15 mmol) and cyclopentanone (70 µl, 0.75 mmol) in dry THF (5 ml) according to General procedure II (Section 3.3) to give 0.08 g (78%) of **8d** as a white solid. Mp.: 180–182 °C; R_f = 0.72 (9:1 $CHCl_3$–acetone); $[\alpha]_D$ +49 (*c* 0.62, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 8.84 (s, 1H, NH), 8.04–7.28 (m, 20H, ArH), 6.08 (t, 1H, $J_{2',3'}$ 9.8 Hz, $J_{3',4'}$ 9.8 Hz, H-3′), 5.97 (d, 1H, $J_{2',3'}$ 9.8 Hz, H-2′), 5.73 (t, 1H, $J_{4',5'}$ 9.2 Hz, $J_{3',4'}$ 9.8 Hz, H-4′), 4.63 (ddd, 1H, $J_{4',5'}$ 9.2 Hz, $J_{5',6'b}$ 6.1 Hz, $J_{5',6'a}$ 3.1 Hz, H-5′), 4.58 (dd, 1H, $J_{6'a,6'b}$ 12.3 Hz, $J_{5',6'a}$ 3.1 Hz, H-6′a), 4.47 (dd, 1H, $J_{6'a,6'b}$ 12.3 Hz, $J_{5',6'b}$ 6.1 Hz, H-6′b), 2.08–1.71 (m, 8H, 4× CH_2); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 166.1 (C-4), 165.9, 165.7, 165.1, 164.3 (*C*O), 133.4–128.1 (ArC), 100.7 (C-1′), 100.1 (C-2), 71.8, 70.2, 69.4, 68.3 (C-2′–C-5′), 63.2 (C-6′), 39.9, 37.7, 23.1, 22.6 (CH_2); Calcd for $C_{40}H_{35}NO_{11}$ (Mol. Wt.: 705.71, Ex. Mass.: 705.22); ESI-MS (positive mode) *m*/*z*: 728.210 $[M+Na]^+$, 1433.435 $[2M+Na]^+$.

3.3.5. (1′*S*)-2′,3′,4′,6′-Tetra-*O*-benzoyl-1′,5′-anhydro-D-glucitol-spiro-[1′,5]-4-oxo-oxazolidine-spiro-[2,1″]-cyclohexane (8e)

Prepared from **7** (0.1 g, 0.15 mmol) and cyclohexanone (80 µl, 0.75 mmol) in dry toluene (5 ml) according to General procedure

II (Section 3.3) to give 0.07 g (69%) of **8e** as a white solid. Mp.: 178–181 °C; R_f = 0.78 (9:1 $CHCl_3$–acetone); $[\alpha]_D$ +52 (*c* 0.46, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 9.00 (s, 1H, NH), 8.12–7.30 (m, 20H, ArH), 6.10 (t, 1H, $J_{2',3'}$ 9.8 Hz, $J_{3',4'}$ 9.8 Hz, H-3′), 6.00 (d, 1H, $J_{2',3'}$ 9.8 Hz, H-2′), 5.71 (t, 1H, $J_{4',5'}$ 9.8 Hz, $J_{3',4'}$ 9.8 Hz, H-4′), 4.69 (ddd, 1H, $J_{4',5'}$ 9.8 Hz, $J_{5',6'b}$ 6.7 Hz, $J_{5',6'a}$ 3.1 Hz, H-5′), 4.63 (dd, 1H, $J_{6'a,6'b}$ 12.3 Hz, $J_{5',6'a}$ 3.1 Hz, H-6′a), 4.45 (dd, 1H, $J_{6'a,6'b}$ 12.3 Hz, $J_{5',6'b}$ 6.7 Hz, H-6′b), 1.92–1.32 (m, 10H, 5× CH_2); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 166.4 (C-4, $^3J_{H\text{-}2',C\text{-}4}$ = 2.5 Hz from HSQMBC at 125 MHz), 166.0, 165.7, 165.2, 164.3 (*C*O), 133.4–128.2 (Ar*C*), 100.1 (C-1′), 93.5 (C-2), 71.8, 70.3, 69.4, 68.3 (C-2′–C-5′), 63.3 (C-6′), 39.0, 37.6, 24.3, 22.9, 22.6 (CH_2); Calcd for $C_{41}H_{37}NO_{11}$ (Mol. Wt.: 719.73, Ex. Mass.: 719.24); ESI-MS (positive mode) *m/z*: 742.222 $[M+Na]^+$, 1462.462 $[2M+Na]^+$.

3.3.6. (1′*S*)-2′,3′,4′,6′-Tetra-*O*-benzoyl-1′,5′-anhydro-D-glucitol-spiro-[1′,5]-4-oxo-oxazolidine-spiro-[2,1″]-cycloheptane (8f)

Prepared from **7** (0.1 g, 0.15 mmol) and cycloheptanone (81 µl, 0.75 mmol) in dry toluene (5 ml) according to General procedure II (Section 3.3) to give 0.08 g (71%) of **8f** as a white solid. Mp.: 124–126 °C; R_f = 0.55 (9:1 $CHCl_3$–acetone); $[\alpha]_D$ +59 (*c* 0.36, $CHCl_3$); ^1H NMR ($CDCl_3$, 360 MHz): δ (ppm) 9.31 (s, 1H, NH), 8.00–7.18 (m, 20H, ArH), 6.08 (t, 1H, $J_{2',3'}$ 9.8 Hz, $J_{3',4'}$ 9.8 Hz, H-3′), 5.98 (d, 1H, $J_{2',3'}$ 9.8 Hz, H-2′), 5.70 (t, 1H, $J_{4',5'}$ 9.8 Hz, $J_{3',4'}$ 9.8 Hz, H-4′), 4.66 (ddd, 1H, $J_{4',5'}$ 9.8 Hz, $J_{5',6'b}$ 6.8 Hz, $J_{5',6'a}$ 3.1 Hz, H-5′), 4.61 (dd, 1H, $J_{6'a,6'b}$ 12.3 Hz, $J_{5',6'a}$ 3.1 Hz, H-6′a), 4.44 (dd, 1H, $J_{6'a,6'b}$ 12.3 Hz, $J_{5',6'b}$ 6.8 Hz, H-6′b), 2.12–1.45 (m, 12H, 6× CH_2); ^{13}C NMR ($CDCl_3$, 90 MHz): δ (ppm) 166.1 (C-4), 165.9, 165.6, 165.1, 164.2 (*C*O), 133.3–128.1 (Ar*C*), 100.1 (C-1′), 97.2 (C-2), 71.8, 70.1, 69.4, 68.3 (C-2′–C-5′), 63.2 (C-6′), 42.4, 41.2, 28.2, 28.1, 21.4, 21.1 (CH_2); Calcd for $C_{42}H_{39}NO_{11}$ (Mol. Wt.: 733.76, Ex. Mass.: 733.25); ESI-MS (positive mode) *m/z*: 756.240 $[M+Na]^+$, 1490.498 $[2M+Na]^+$.

3.4. General procedure III for the removal of *O*-acyl protecting groups

An *O*-acylated compound was dissolved in the minimum volume of abs MeOH and a few drops of NaOMe in MeOH (~1 M) were added. The mixture was stirred at rt until TLC (9:1 $CHCl_3$–MeOH) showed complete transformation of the starting material. It was then neutralized with a cation exchange resin Amberlyst 15 (H^+ form). Filtration and solvent removal left a syrup which was purified by column chromatography ($CHCl_3$–MeOH).

3.4.1. (1′*S*)-1′,5′-Anhydro-D-glucitol-spiro-[1′,5]-2,2-dimethyl-oxazolidin-4-one (9a)

Prepared from **8a** (0.14 g, 0.20 mmol) according to General procedure III (Section 3.4) to give 0.05 g (94%) of **9a** as a white solid. Mp.: 97–99 °C; R_f = 0.3 (8:2 $CHCl_3$–MeOH); $[\alpha]_D$ +50 (*c* 0.28, MeOH); ^1H NMR (D_2O 360 MHz): δ (ppm) 3.90–3.67 (m, 5H, H-2′, H-3′ or H-4′, H-5′, H-6′ab), 3.51 (pseudo t, 1H, *J* = 8.7 Hz, 7.7 Hz, H-3′ or H-4′), 1.61 (s, 3H, CH_3), 1.58 (s, 3H, CH_3); ^{13} NMR (D_2O, 90 MHz): δ (ppm) 168.4 (C-4), 102.3 (C-1′), 92.6 (C-2), 74.1, 73.6, 69.7, 69.4 (C-2′–C-5′), 60.6 (C-6′), 28.6 (CH_3), 27.1 (CH_3); Calcd for $C_{10}H_{17}NO_7$ (Mol. Wt.: 263.24, Ex. Mass.: 263.10); ESI-MS (positive mode) *m/z*: 286.088 $[M+Na]^+$, 549.192 $[2M+Na]^+$, 812.290 $[3M+Na]^+$.

3.4.2. (1′*S*,2*RS*)-1′,5′-Anhydro-D-glucitol-spiro-[1′,5]-2-ethyl-2-methyl-oxazolidin-4-ones (9b)

Prepared from **8b** (0.17 g, 0.25 mmol) according to General procedure III (Section 3.4) to give 0.06 g (96%) of **9b** as a white solid. R_f = 0.3 (8:2 $CHCl_3$–MeOH); $[\alpha]_D$ +53 (*c* 0.46, MeOH); ^1H NMR (D_2O 360 MHz): δ (ppm) 3.82–3.44 (m, 6H, H-2′, H-3′, H-4′, H-5′, H-6′ab), 1.79–1.75 (m, 2H, CH_2), 1.51, 1.48 (2s, 3H, CH_3), 0.90, 0.86 (2t, 3H, *J* 7.5 Hz CH_3); ^{13}C NMR (D_2O, 90 MHz): δ (ppm) 168.9, 168.6 (C-4), 102.2, 101.9 (C-1′), 95.2, 94.7 (C-2), 74.3, 73.9, 73.5, 69.8, 69.7, 69.5, 69.3 (C-2′–C-5′), 60.5 (C-6′), 34.1, 33.0 (CH_2), 26.4, 25.3 (CH_3), 7.3, 6.9 (CH_3); Calcd for: $C_{11}H_{19}NO_7$ (Mol. Wt.: 277.27, Ex. Mass.: 277.12); ESI-MS (positive mode) *m/z*: 300.104 $[M+Na]^+$, 577.225 $[2M+Na]^+$, 854.342 $[3M+Na]^+$.

3.4.3. (1′*S*)-1′,5′-Anhydro-D-glucitol-spiro-[1′,5]-2,2-diethyl-oxazolidin-4-one (9c)

Prepared from **8c** (0.14 g, 0.20 mmol) according to General procedure III (Section 3.4) to give 0.05 g (91%) of **9c** as a white solid. Mp.: 70–72 °C; R_f = 0.3 (8:2 $CHCl_3$–MeOH); $[\alpha]_D$ +48 (*c* 0.44, MeOH); ^1H NMR (D_2O 360 MHz): δ (ppm) 3.82–3.61 (m, 5H, H-2′, H-3′ or H-4′, H-5′, H-6′ab), 3.44 (t, 1H, *J* = 7.6 Hz, 7.6 Hz, H-3′ or H-4′) 1.82–1.75 (m, 4H, 2× CH_2), 0.89, 0.87 (2t, 6H, *J* 7.5 Hz, 2× CH_3); ^{13}C NMR (D_2O, 90 MHz): δ (ppm) 168.9 (C-4), 101.9 (C-1′), 97.3 (C-2), 74.1, 73.5, 69.9, 69.4 (C-2′–C-5′), 60.5 (C-6′), 31.4, 30.7 (CH_2), 7.1, 6.9 (CH_3); Calcd for $C_{12}H_{21}NO_7$ (Mol. Wt.: 291.30, Ex. Mass.: 291.13); ESI-MS (positive mode) *m/z*: 314.120 $[M+Na]^+$, 605.255 $[2M+Na]^+$, 896.387 $[3M+Na]^+$.

3.4.4. (1′*S*)-1′,5′-Anhydro-D-glucitol-spiro-[1′,5]-oxazolidin-4-one-spiro-[2,1″]-cyclopentane (9d)

Prepared from **8d** (0.19 g, 0.27 mmol) according to General procedure III (Section 3.4) to give 0.07 g (91%) of **9d** as a white solid. Mp.: 112–115 °C; R_f = 0.3 (8:2 $CHCl_3$–MeOH); $[\alpha]_D$ +46 (*c* 0.43, MeOH); ^1H NMR (D_2O 360 MHz): δ (ppm) 3.82–3.62 (m, 5H, H-2′, H-3′ or H-4′, H-5′, H-6′ab), 3.44 (pseudo t, 1H, *J* = 7.8 Hz, 7.3 Hz, H-3′ or H-4′) 1.94–1.69 (m, 8H, 4× CH_2); ^{13}C NMR (D_2O, 90 MHz): δ (ppm) 168.6 (C-4), 101.9, 101.8 (C-1′, C-2), 74.2, 73.6, 69.6, 69.3 (C-2′–C-5′), 60.5 (C-6′), 39.3, 36.9, 22.8, 22.2 (CH_2); Calcd for $C_{12}H_{19}NO_7$ (Mol. Wt.: 289.28, Ex. Mass.: 289.12); ESI-MS (positive mode) *m/z*: 312.104 $[M+Na]^+$, 601.222 $[2M+Na]^+$, 890.335 $[3M+Na]^+$.

3.4.5. (1′*S*)-1′,5′-Anhydro-D-glucitol-spiro-[1′,5]-oxazolidin-4-one-spiro-[2,1″]-cyclohexane (9e)

Prepared from **8e** (0.18 g, 0.25 mmol) according to General procedure III (Section 3.4) to give 0.07 g (96%) of **9e** as a white solid. Mp.: 123–126 °C; R_f = 0.3 (8:2 $CHCl_3$–MeOH); $[\alpha]_D$ +42 (*c* 0.32, MeOH); ^1H NMR (D_2O 360 MHz): δ (ppm) 3.86–3.62 (m, 5H, H-2′, H-3′ or H-4′, H-5′, H-6′ab), 3.48 (pseudo t, 1H, *J* = 8.9 Hz, 7.9 Hz, H-3′ or H-4′) 1.87–1.37 (m, 10H, 5× CH_2); ^{13}C NMR (D_2O, 90 MHz): δ (ppm) 168.6 (C-4), 101.8 (C-1′), 93.6 (C-2), 74.3, 73.6, 69.7, 69.4 (C-2′–C-5′), 60.6 (C-6′), 38.5, 36.6, 23.9, 22.6, 22.2 (CH_2); Calcd for $C_{13}H_{21}NO_7$ (Mol. Wt.: 303.31, Ex. Mass.: 303.13); ESI-MS (positive mode) *m/z*: 326.120 $[M+Na]^+$, 629.253 $[2M+Na]^+$, 932.384 $[3M+Na]^+$.

3.4.6. (1′*S*)-1′,5′-Anhydro-D-glucitol-spiro-[1′,5]-oxazolidin-4-one-spiro-[2,1″]-cycloheptane (9f)

Prepared from **8f** (0.19 g, 0.26 mmol) according to General procedure III (Section 3.4) to give 0.06 g (77%) of **9f** as a white solid. Mp.: 116–119 °C; R_f = 0.3 (8:2 $CHCl_3$–MeOH); $[\alpha]_D$ +48 (*c* 0.30, MeOH); ^1H NMR (D_2O 360 MHz): δ (ppm) 3.88–3.67 (m, 5H, H-2′, H-3′ or H-4′, H-5′, H-6′ab), 3.50 (pseudo t, 1H, *J* = 7.4 Hz, 7.2 Hz, H-3′ or H-4′) 2.14–1.52 (m, 12H, 6× CH_2); ^{13}C NMR (D_2O, 90 MHz): δ (ppm) 168.4 (C-4), 101.9 (C-1′), 97.4 (C-2), 74.2, 73.6, 69.8, 69.4 (C-2′–C-5′), 60.6 (C-6′), 41.8, 40.6, 28.3, 28.2, 21.1, 21.0 (CH_2); Calcd for $C_{14}H_{23}NO_7$ (Mol. Wt.: 317.33, Ex. Mass.: 317.15); ESI-MS (positive mode) *m/z*: 340.136 $[M+Na]^+$, 657.287 $[2M+Na]^+$, 974.436 $[3M+Na]^+$.

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