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A practical access to glucose- and allose-based (5+5) 3-spiropseudonucleosides from a common intermediate

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Abstract

A practical access to glucose-based and allose-based spirooxazolidinones is reported. The synthetic sequence consisting of TEMPO-catalyzed oxidation of 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose, Henry reaction and reduction provides amino alcohol with *allo*-configuration on a multigram scale. Alternatively, water elimination from Henry products followed by a rehydration gives an access to diastereomerically pure glucose-based nitro alcohol which upon reduction provides complementary amino alcohol with *gluco*-configuration. The latter amino alcohols are transformed into spirooxazolidinones (3-spiropseudonucleosides) *via* their *N*-Cbz or *N*-phenylcarbamate derivatives. The title compounds easily undergo *N*-derivatization and give highly crystalline materials. Two of the newly obtained (5+5) 3-spiropseudonucleosides are characterized by X-ray crystallography.

Key words: spiropseudonucleosides, spirooxazolidinones, oxidation of diacetone-α-D-glucose, Henry reaction, carbamates, *N*-acyl-oxazolidinones

1. Introduction

Carbohydrate-heterocycle conjugates with spirocyclic junction have raised a particular interest in the last two decades.[1] A crucial moment was the discovery of natural product (+)-hydantocidin (**1**) which possesses herbicidal activity (Figure 1).[2] Since 1990-ties a range of spiro-glycosides has been prepared. From medicinal chemistry viewpoint some of the most prominent examples include glycogen phosphorylase inhibitors.[3] Some spiro-glycosides are known as α-glucosidases inhibitors,[4] others possess moderate cytotoxic activities against tumor cells.[5] On the other hand, glycosidic spiroketals are

valuable building blocks for natural product synthesis,[6] but nitrogen containing spiroglycoheterocycles act as chiral ligands in transition metal catalyzed transformations.[7]

Besides the natural and man-made spironucleosides several spiropseudonucleosides have been obtained as well. The latter term was introduced by Fuentes and co-workers to describe various spiroglycoheterocycles that possess spirocyclic junction at *C*-atoms other than glycosidic position.[8] In this context numbers n+m (e.g.: 5+5) are used to describe the ring size of the carbohydrate moiety and nitrogen containing heterocycle (see, general structure **2**, Figure 1). Thus, carbohydrate-nitrogen heterocycle conjugates with non-glycosidic spiranic junction have been obtained in the series of oxazolidines,[9] hydantoins,[10] piperazinediones,[11] thiazolidines[12] to name but a few. This line of research has brought also other interesting molecular scaffolds that among other applications exhibit glycosidases inhibiting activities.[13] Nevertheless, the number of reported synthesis for sugars with spiroheterocyclic motifs at C(3) is relatively smaller than that at C(1).[13b] In 2009, Fuentes and co-workers reported the synthesis of 3-spirooxazolidinone **3** with *allo*-configuration which represents a class of (5+5) 3-spiropseudonucleosides.[8]

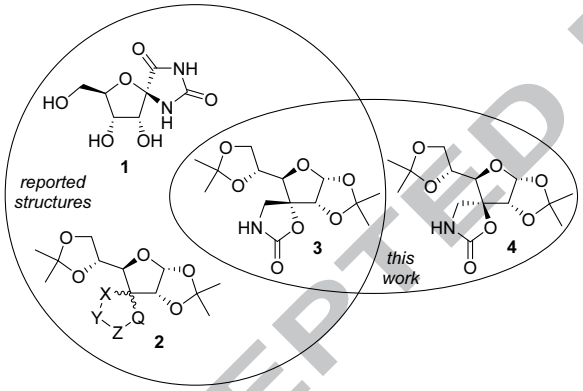


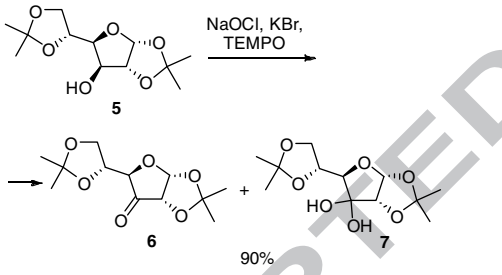
Figure 1. Hydantocidine (**1**) and synthetic spiropseudonucleosides (**2**-**4**).

Here, we would like to report a practical gram-scale approach towards **3**, its diastereoisomer **4** and their *N*-derivatives. The present approach revitalizes the use of the Henry reaction on 1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (diacetone-α-D-glucose) – derived ketone[14] and provides practical preparative procedures towards several useful intermediates in the realm of 3-nitromethyl- and 3-aminomethyl-gluco- and allofuranose derivatives.

2. Results and Discussions

The synthesis starts with oxidation of diacetone-α-D-glucose (**5**). Literature survey shows an extensive use of chromium (VI)-based oxidizing agents to access the corresponding ketone **6** or its hydrate **7**. Thus, the use of pyridinium dichromate[15] pyridinium chlorochromate[16] and Collins' reagent (CrO_3•$2C_6H_5N$)[17] in the academic labs is well documented. Besides their toxicity, these methods lack the possibility for an easy up-scale. For example, oxidation of more than thirty grams of **5** with Collin's reagent brings to difficulties to control the temperature and mass exchange processes. Other oxidation systems for diacetone-D-glucose include Swern type conditions[17,18] which have also found industrial applications,[19] Dess-Martin periodinane[20] and the use of ruthenium catalyzed methods.[21]

On the other hand, TEMPO-catalyzed alcohol oxidations with sodium hypochlorite are well documented and extensively used by synthetic organic chemists.[22] Nevertheless, to the best of our knowledge there are only two reports where TEMPO-catalyzed system is used for oxidation of diacetone-D-glucose.[23] Also in our case TEMPO-catalyzed bleach oxidation with careful temperature and pH adjustment[24] provided an excellent yield of ketone **6** (contains also hydrate **7**) on a 100 g scale.[25] It was discovered that ^{1}H-NMR spectrometry was the most reliable way to control the conversion **5→6+7** (Figure 2).[26]



Scheme 1. TEMPO catalyzed bleach oxidation of diacetone-D-glucose on a hundred gram scale.

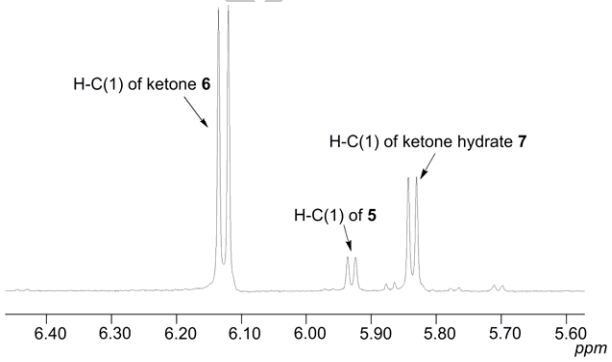
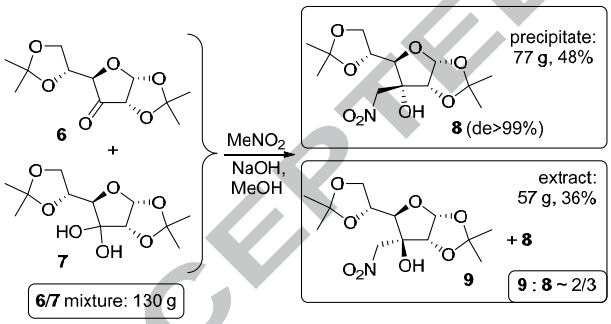


Figure 2. A part of ^{1}H-NMR spectrum (300 MHz, $CDCl_3$) of a crude reaction mixture displaying partial conversion in the reaction **5→6+7**.

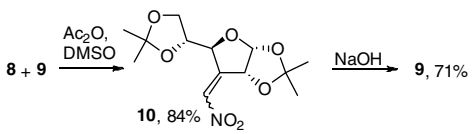
With ketone/ketone hydrate mixture in the hand we turned to the formation of C-C bond at C(3) of the hexofuranose *via* the Henry reaction. It has been known since early 1970ies that Henry reaction on ketone **6** (**6+7→8+9**) occurs with reasonably good diastereoselectivity (Scheme 2).[14,17] In most of cases NaOMe, NaOEt or *t*-BuOK have been used as bases to obtain the corresponding nitromethanate anion.[17,27] Also NaOH is reported as a base in the aforementioned reaction.[28] Despite the fact that the diastereoselectivity of this reaction is mainly substrate-controlled, it is greatly influenced by the choice of base and reaction temperature.[27b] A mechanism of epimerization of the resulting nitro alcohols **8** and **9** under the reaction conditions is also proposed.[27c] In light of the above mentioned facts it is no surprise that nitromethane addition to ketone **6** is scale-dependent. We have developed a practical approach that provides tens of grams of both nitro alcohols with excellent diastereomeric purity. In a typical procedure nitromethane is added to a sodium hydroxide solution in methanol between 0 and + 5 ^{o}C followed by a methanolic solution of ketone/ketone hydrate mixture at the same temperature (Scheme 2). At the end of the reaction the resulting mixture is poured into saturated aqueous solution of ammonium sulfate. It was found that in this way only major diastereoisomer **8** precipitates. Usually the isolated yield of major isomer **8** (de > 99%) reaches almost 50%. The aqueous phase contains diastereomeric mixture of **8** and **9** and the total yield of process exceeds 80%.



Scheme 2. Large scale Henry reaction on ketone **6**.

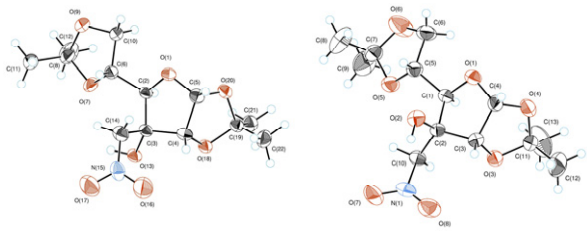
Next, application of Albrecht-Moffatt dehydration-rehydration procedure produced diastereomerically pure **9** in a good yield.[14] The reaction sequence includes treatment of diastereomeric mixture of nitroalcohols **8** and **9** with DMSO/Ac_2O at ambient temperature to yield the nitromethylene intermediate **10** (84%) (Scheme 3).[29] It should be noted that optimization of reaction conditions allowed the use of only 3 equivalents of Ac_2O on a multigram-scale.[28] Treatment of **10** with NaOH in water/THF gave

nitroalcohol **9** in 71% yield. To conclude, according to the present synthetic scheme both diastereomeric nitroalcohols **8** and **9** are available with good isolated yields and excellent de's.



Scheme 3. Transformation of a mixture of diastereomeric nitro alcohols into *gluco*-isomer **9**.

There have been published several reports dealing with elucidation of absolute configuration of products **8** and **9**. Nevertheless, these latter were based on NMR studies at 100 MHz or chemical transformations coupled with CD spectra analysis.[27a] In our hands both nitroalcohols **8** and **9** gave X-ray quality single crystals. These studies provided unambiguous proof of the relative configuration of both isomers after 40 years of their first synthesis (Figure 3).[30,31]



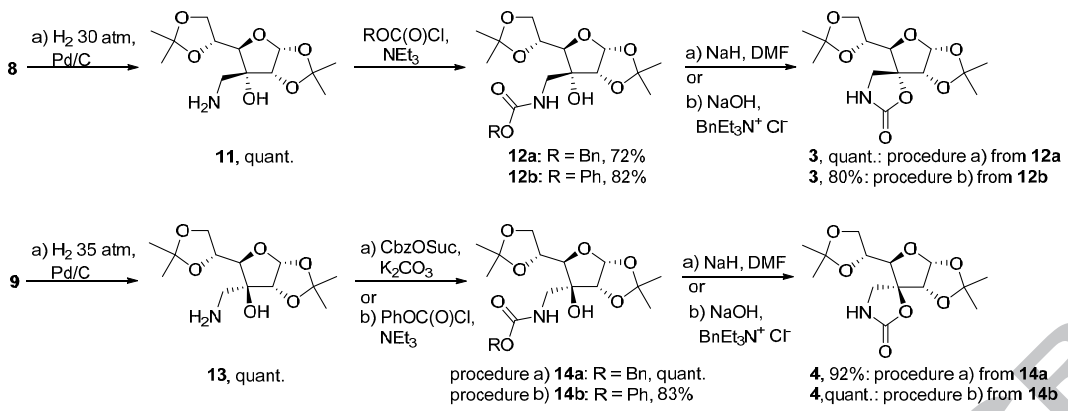
*ORTEP representation of allo-isomer **8***

*ORTEP representation of gluco-isomer **9***

Figure 3. ORTEP representation of nitro alcohols **8** and **9**.

Nitromoieties of **8** and **9** were reduced by H_2 over Pd/C. Reduction occurs already at 10 atm pressure of hydrogen; however, at large scale optimal pressure of hydrogen was around 30 to 40 atm (Scheme 4). Alternatively, reduction can be performed with $LiAlH_4$. Pure aminoalcohols **11** and **13** can be obtained as solids, nevertheless, they can be transformed into corresponding tosylate salts that are highly crystalline materials.

For oxazolidinone ring closure we have chosen carbamate approach.[32] Isomer **11** was transformed into both, benzyl carbamate **12a** and phenyl carbamate **12b**. Cyclisation of both carbamates **12a**,**b** occur well in DMF solution in the presence of NaH.[33] In this way oxazolidinone **3** can be produced quantitatively from Cbz-protected aminoalcohol **12a** in 30 min at ambient temperature.



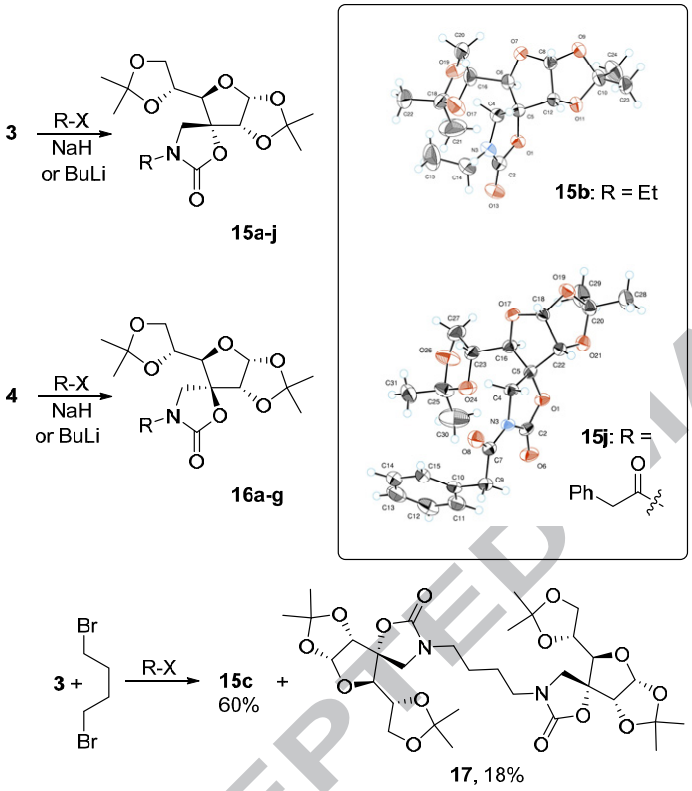
Scheme 4. Synthesis of 3-spiropseudonucleosides from amino alcohols *via* carbamate approach.

For practical reasons solvent can be changed from DMF to THF. This change prolonged reaction time to 4 h and somewhat diminished the isolated yield (90%) of product **3**. On the other hand, phenylcarbamate **12b** underwent cyclisation in biphasic CH_2Cl_2/water system in the presence of NaOH and benzyltriethylammonium chloride. Under the latter reaction conditions isolated yield of target oxazolidinone **3** was 80%. The same approach was used to prepare the corresponding diastereoisomers **14a**,**b**. Thus, reduction of **9**, followed by benzylcarbamate formation produced intermediate **14a** in quantitative yield after 2 steps. When treated with NaH in THF, benzylcarbamate **14a** provided spirooxazolidinone **4** in 92% yield. Experimentally easier phase transfer conditions for cyclization required phenylcarbamate **14b**. The latter was obtained as described above in 83% isolated yield and further cyclized to **4** (quant. yield) in system $NaOH/H_2O/CH_2Cl_2/BnEt_3NCl$.

Next, we elaborated conditions for *N*-derivatization of obtained spiro-oxazolidinones **3** and **4** (Scheme 5, Table 1). Pretreatment of the latter with NaH in DMF solution followed by appropriate alkylating, benzylating, allylating, and propargylating reagents produced the corresponding products **15** and **16** in good isolated yields. Relative configuration of oxazolidinone **15b** as a representative example was unambiguously established by X-ray diffraction analysis.[34] Product **15c** bearing *N*-4-bromobutyl group can in principle undergo further nucleophilic displacements. When oxazolidinone **3** (2 equiv.) was treated with 1,4-dibromobutane (1 equiv.), dimer **17** was isolated in 18% yield along with product **15c** (Scheme 5).

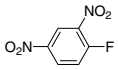
Oxazolidinone **3** underwent also arylation with Sanger reagent (Table 1, entry 7) and acylation with acyl chlorides (Table 1, entries 8-10). The molecular structure of *N*-phenylacetyl derivative **15j** was established by X-ray studies.[35]

X-ray structures of **15b** and **15j** reveal similar features: in both compounds furanose cycle adopts envelope conformations. The spiro atom deviates from the least-square plane by 0.614(5)Å in *N*-ethyl derivative **15b** and by 0.584(3)Å in *N*-phenylacetyl derivative **15j**. In both structures the oxazolidinone plane is almost perpendicular to the tetrahydrofuran plane as dihedral angles between two planes equal to 87.0° and 89.1° in compounds **15b** and **15j**, respectively.



Scheme 5. *N*-Derivatization of 3-spiropseudonucleosides *via* alkylation, arylation and acylation.

Table 1. Synthesis of *N*-derivatized spirooxazolidinones **3→15a-j**, **4→16a-g** (see Scheme 5)

Entry	RX[a]	*allo*-Product **15**, yield	*gluco*-Product **16**, yield
1	MeI	**15a**, 90%	**16a**, 84%
2	EtBr	**15b**, 82%	**16b**, 68%
3	$Br(CH_2)_4Br$	**15c**[b], 82%	-
4	BnBr	**15d**, 91%	**16c**, 83%
5	$H_2C{=}C(CH_3)CH_2Br$	**15e**, 95%	**16d**, 88%
6	$HC{\equiv}CCH_2Br$	**15f**, 89%	**16e**, 92%
7		**15g**, 77%	-
8	AcCl	**15h**, 71%	-
9	*n*-PrC(O)Cl	**15i**, 90%	**16f**, 96%
10	BnC(O)Cl	**15j**, 93%[c]	**16g**, 53%[c]

[a]Reaction conditions if not stated otherwise: NaH, DMF

[b]Product **15c** was isolated as a monomer bearing *N*-4-bromobutyl group when reagents **3** and $Br(CH_2)_4Br$ were used 1:4.

[c]Reaction conditions: BuLi, THF

3. Conclusions

In summary, we have developed a practical access to both diastereomeric forms of oxazolidinone-based (5+5) 3-spiropseudonucleosides and their *N*-alkyl, aryl, and acyl derivatives. Derivatives **15c**, **15e**, **15f**, and **15h** possess appropriate functionalities for further derivatization. This opens possibilities for creation of novel types of spiroglycoconjugates via processes like S_N2, metathesis, and azide-alkyne click reactions. The over-all synthetic scheme uses known reactions, albeit stands out with its practicality, scale-up ability and user friendly approach. Thus, large scale TEMPO catalyzed process was elaborated for oxidation of diacetone-D-glucose. Additionally, efficient and robust conditions for convenient synthesis of either of sugars – 1,2:5,6-di-*O*-isopropylidene-3-*C*-nitromethyl-α-D-*allo*-furanose (**8**) and 1,2:5,6-di-*O*-isopropylidene-3-*C*-nitromethyl-α-D-*gluco*-furanose (**9**) on a multigram scale were developed. Their structures after 40 years were unambiguously assigned by X-ray diffraction analysis. Starting from one common intermediate, nitro alcohol **8**, two 3-*C*-aminomethyl derivatives **11** and **13** with both *allo* and *gluco* configuration can be obtained in an user-friendly manner. In the latter case dehydration-rehydration sequence inverts the configuration at C(3).

Additionally, both diastereoisomeric spirooxazolidinones can serve as chiral auxiliaries in alkylations of enolates arising from the corresponding *N*-acyl derivatives. In this context model compounds **15i**,**j** and **16f**,**g** have shown promising preliminary results that will be reported elsewhere.

4. Experimental section

4.1. General methods

All non-aqueous reactions were carried out under an inert atmosphere of argon in oven-dried glassware unless otherwise noted. Commercial reagents were used without purification. Solvents were distilled prior to use and, if required, dried over standard drying agents (THF from metallic sodium, DMSO, DMF and Et_3N form CaH_2). Analytical thin layer chromatography (TLC) was performed on Merck precoated analytical plates, 0.25 mm thick, silica gel $60F_{254}$. Preparative flash chromatography was performed on silica gel (60 Å, 40-63 μm, ROCC). Melting points were recorded with a *Fisher Digital Melting Point Analyzer Model 355* apparatus and are uncorrected. IR spectra were recorded as thin films on KBr plates or in KBr with *FT-IR Perkin Elmer Spectrum BX*. Optical rotations were measured at 25 °C on a *Anton Paar MCP 500* polarimeter using a sodium lamp as the light source (589 nm). ^1H and ^{13}C NMR spectra were recorded on a *Bruker* 300 MHz and *Varian* 400 MHz spectrometers in $CDCl_3$ or $DMSO_{d6}$. The proton signals for residual non-deuterated solvents (δ 7.26 for $CDCl_3$ and δ 2.50 for $DMSO_{d6}$) and carbon signals (δ 77.1 for $CDCl_3$ and δ 39.5 for $DMSO_{d6}$) were used as an internal references for ^1H-NMR and ^{13}C-NMR spectra, respectively. Chemical shifts (δ) values are reported in ppm and coupling constants *J* in Hz. HRMS spectra (ESI+) were performed using a *Q-TOF Micromass* and elemental analyses on a *Carlo-Erba EA1108* analyzer. Yields refer to chromatographically and spectroscopically homogeneous materials.

4.2. Synthesis of (3*R*)-1,2:5,6-di-*O*-isopropylidene-spiro(3-deoxy-α-D-allofuranose-3,5`-oxazolidin)-2`-one (3)

4.2.1. From benzyloxycarbamate 12a

A solution of **12a** (1.00 g, 2.36 mmol, 1 equiv) in dry DMF (10 mL) was added to a suspension of NaH (60% in mineral oil, 0.200 g, 5.00 mmol, 2.1 equiv) in dry DMF (10 mL) under argon atmosphere at 0 ºC. The resulting mixture was stirred at ambient temperature for 30 min, then ethyl acetate (200 mL) and a saturated aqueous solution of $(NH_4)_2SO_4$ (50 mL) was added. The organic layer was extracted with 15% aqueous solution of NaCl (10 × 50 mL), dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (EtOAc) to afford compound **3** (0.74 g, quant.) as a white solid.

4.2.2. From phenyloxycarbamate 12b

1.02 M solution of NaOH in water (130 mL) and benzyltriethylammonium chloride (0.73 g, 3.2 mmol, 5-mol%) was added to a stirred solution of **12b** (25.80 g, 63.1 mmol, 1 equiv.) in CH_2Cl_2 (100 mL) at 0

ºC. The resulting biphasic reaction mixture was stirred at 0 ºC for 10 min followed by 1 h at ambient temperature. The phases were separated and the aqueous residue was extracted with EtOAc (6 × 50 mL). The CH_2Cl_2 layer was extracted with aq. 2 M NaOH solution (2 × 20 mL) and with brine (5 × 30 mL). The combined EtOAc layer was washed with aq. 2 M NaOH solution (2 × 25 mL) and with brine (5 × 20 mL). Both resulting solutions were dried over Na_2SO_4, filtered and evaporated under reduced pressure to afford the title compound **3** as a white solid (16.00 g, 80%). R_f=0.28 ($CHCl_3$/EtOH 19:1). The analytical data of **3** are consistent with those reported earlier.[8] Mp: 161-162 °C (EtOAc/Hex). $[\alpha]_D^{25}$=51 (*c* 0.8, $CHCl_3$) [lit.[8]: $[\alpha]_D^{25}$=52 (*c* 0.8, CH_2Cl_2)]. ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm) δ: 6.00 (bs, 1H, H-N), 5.71 (d, 1H, ^3J = 3.5 Hz, H-C(1)), 4.48 (d, 1H, ^3J = 3.5 Hz, H-C(2)), 4.19-4.07 (m, 3H, H-C(4), H-C(5), H_a-C(6)), 4.04-3.97 (m, 1H, H_b-C(6)), 3.88 (d, AB syst., 1H, ^2J = 9.0 Hz, H_a-C(4`)), 3.26 (d, AB syst., 1H, $^2J$ = 9.0 Hz, $H_b$-C(4`)), 1.61, 1.44, 1.36, 1.31 (4s, 12H, $(H_3C)_2$C-O-C(1,5)). ^{13}C-NMR (C_6D_6, 75 MHz, ppm) δ: 158.3, 114.3, 110.2, 102.8, 85.4, 83.8, 77.1, 73.7, 68.0, 44.2, 26.7, 26.6, 26.4, 25.2. IR (KBr) ν, cm^{-1}: 3315, 2925, 1770, 1730, 1375, 1265, 1075, 845. Anal. Calcd for $C_{14}H_{21}NO_7$ (315.32): C 53.33, H 6.71, N 4.44. Found C 53.59, H 6.75, N 4.44.

4.3. Synthesis of (3*S*)-1,2:5,6-di-*O*-isopropylidene-spiro(3-deoxy-α-D-glucofuranose-3,5`-oxazolidin)-2`-one (4)

4.3.1. From benzyloxycarbamate 14a

A solution of **14a** (14.65 g, 35.00 mmol, 1 equiv) in dry THF (150 mL) was added to a suspension of NaH (60% in mineral oil, 1.993 g, 83.00 mmol, 2.4 equiv) in dry THF (100 mL) under argon atmosphere at 0 ºC. The resulting mixture was stirred at 0 ºC for 10 min followed by 3 h at ambient temperature. The mixture was poured into a saturated aqueous solution of NH_4Cl (300 mL) and THF was evaporated under reduced pressure. The aqueous residue was extracted with EtOAc (4 × 100 mL). The combined organic layer was dried over Na_2SO_4, filtered and evaporated under reduced pressure. The residue was purified by column chromatography (EtOAc/hexanes 1:5) to afford compound **4** as a white solid (10.07 g; 92%).

4.3.2. From phenyloxycarbamate 14b

1.02 M solution of NaOH (0.42 g, 10.5 mmol, 2.1 equiv) in water (10 mL) and benzyltriethylammonium chloride (0.057 g, 0.249 mmol, 5-mol%) was added to a stirred solution of **14b** (2.04 g, 4.98 mmol, 1 equiv) in CH_2Cl_2 (15 mL) at 0 ºC. The resulting biphasic reaction mixture was stirred at 0 ºC for 10 min followed by 1 h at ambient temperature. The phases were separated and the aqueous residue was extracted with CH_2Cl_2 (9 × 3 mL). The combined organic layer was extracted with solution of 2 M

NaOH (3 × 1.5 mL), with saturated aqueous solution of NaCl (3 × 3 mL) and dried over Na_2SO_4. The resulting solution was filtered and evaporated under reduced pressure to afford the title compound **4** as white solid (1.56 g, quantitative). R_f=0.52 (EtOAc/Hex 3:1); Mp: 89-90 ºC (EtOAc/Hex). $[\alpha]_D^{25}$=26 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm) δ: 5.91 (d, 1H, ^3J = 3.4 Hz, H-C(1)), 5.58 (bs, 1H, H-N-C(3`)), 4.54 (d, 1H, ^3J = 3.4 Hz, H-C(2)), 4.37 (ddd, 1H, ^3J = 8.5, 6.4, 5.1 Hz, H-C(5)), 4.14 (dd, AB syst., 1H, ^2J = 8.9 Hz, ^3J = 6.4 Hz, H_a-C(6)), 4.02 (dd, AB syst., 1H, ^2J = 8.9 Hz, ^3J = 5.1 Hz, H_b-C(6)), 3.89 (d, 1H, ^3J = 8.5 Hz, H-C(4)), 3.83 (d, AB syst., 1H, ^2J = 9.2 Hz, H_a-C(4`)), 3.77 (d, AB syst., 1H, $^2J$ = 9.2 Hz, $H_b$-C(4`)), 1.50, 1.42, 1.34, 1.32 (4s, 12H, $(H_3C)_2$C-O-C(1,5)). ^{13}C-NMR (C_6D_6, 75 MHz, ppm) δ: 157.9, 112.6, 109.8, 105.2, 87.7, 84.3, 81.8, 73.0, 67.7, 41.9, 27.0 (2C), 26.3, 25.2. IR (KBr) ν, cm^{-1}: 3325, 2990, 2938, 2888, 1771, 1376, 1263, 1218, 1165, 1077, 1011, 959. Anal. Calcd for $C_{14}H_{21}NO_7$ (315.32): C 53.33, H 6.71, N 4.44. Found C 53.48, H 6.86, N 4.12.

4.4. Large scale oxidation of diacetone-α-D-glucose (process 5→6+7)

In an open-mouth beaker equipped with mechanical stirrer, a solution of NaBr (4.20 g, 0.04 mol, 0.1 equiv) in water (20 mL) was added to a solution of diacetone-α-D-glucose (**5**) (104 g, 0.4 mol, 1.0 equiv) in CH_2Cl_2 (400 mL), followed by TEMPO (0.300 g, 1.9 mmol, 0.5 mol-%). The resulting mixture was cooled to -5 – -10 ^{o}C (internal temperature) and vigorously stirred, and aqueous solution of NaClO (~1.6 mol/L, pH 9.5, 360 mL, 0.58 mol, 1.45 equiv) was added dropwise in 30 minutes while keeping the internal temperature in the range of -10 - 0 ^{o}C. After addition of the bleach solution, the resulting reaction mixture was stirred for 5 minutes. The organic layer was separated and washed successively with solution of KI (1.60 g, 0.01 mol, 2.5 mol-%) in 0.5 M aqueous hydrochloric acid (100 mL), 10% aqueous solution of $Na_2S_2O_3$ (100 mL), saturated aqueous solution of $NaHCO_3$ (100 mL), and brine (100 mL). After drying (Na_2SO_4), filtration and evaporation under reduced pressure, the crude product (93.0 g, ~90%) contained a mixture of ketone **6** and ketone hydrate **7** in various proportions with the former being the major component. The NMR data and other characteristics of products **6** and **7** fully correspond to those reported earlier (see electronic supporting information)[25,36].

4.5. Synthesis of 3-*C*-nitromethyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (8) and 3-*C*-nitromethyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (9)

Nitromethane (135 mL, 2.5 mol, 5 equiv) was added to a solution of NaOH (40.0 g, 1.00 mol, 2 equiv) in MeOH (500 mL) at 0 °C and stirred for 30 min. The resulting mixture was added to a solution of ketone/ketone hydrate **6/7** (130 g, 0.5 mol, 1 equiv) in MeOH (250 mL) at temperature range 0 - 10 °C

and vigorously stirred. The reaction mixture was stirred at ambient temperature for 2 h and then it was pured into saturated aqueous solution of $(NH_4)_2SO_4$ (1 L). The resulting white precipitate was filtered, washed with water (1 L) and dissolved in ethyl acetate (600 mL). The phases were separated and the organic layer was washed with brine (200 mL), dried over anhydr. Na_2SO_4, filtered and evaporated under reduced pressure to afford the title compound **8** (77 g, 48%, de > 99%) as a white solid. NMR data and other physicochemical data of the product **8** are consistent with those reported earlier (see electronic supporting information).[14,27a]

The first filtrate was extracted with CH_2Cl_2 and the combined organic layer was washed with brine (100 mL), dried over anhydr. Na_2SO_4, filtered and evaporated under reduced pressure to afford dark yellow thick oil (60 g) which consists of epimers **8** (35 g) and **9** (22 g) and a trace amount of unreacted starting materials (**6/7**). The total yield of major isomer **8** is 112 g, 70% and minor isomer **9** – 22.0 g, 14%. The mixture of **8** and **9** is used in the next step without additional purification.

Acetic anhydride (12.7 mL, 0.134 mol, 3 equiv) was added to a stirred solution of a diastereomeric mixture of nitro sugars **8** and **9** (14.3 g, 44.8 mmol, 1 equiv) in dry DMSO (45.45 mL, 0.639 mol, 14 equiv) at ambient temperature. The resulting reaction mixture was stirred at ambient temperature for 68 h and poured under vigorous stirring into a cold acetate buffer solution (24.6 g AcONa in 200 mL H_2O adjusted to pH 7 with AcOH) at 0 °C. The temperature of the mixture during the entire neutralization/workup procedure (5 min) was kept at 0…10 °C. The resulting mixture was further neutralized with saturated aqueous (200 mL) solution of $NaHCO_3$ and solid $NaHCO_3$ (3 g) to pH 6 followed by extraction with 15% EtOAc/Hex (3 × 150 mL). The combined organic layer was washed with brine (6 × 150 mL), dried over anhydr. Na_2SO_4, and evaporated. The purification of the crude product (12.6 g) by column chromatography on silica gel (60 g) (cyclohexane (0.5 L) followed by 10% of EtOAc in cyclohexane) provided 11.3 g (84%). NMR and other physicochemical data of the product **10** are consistent with those reported earlier (see electronic supporting information).[14,29]

To a solution of nitro-ene derivative **10** (22.95 g, 76.2 mmol, 1 equiv) in THF (75 mL) an aqueous (100 ml) solution of NaOH (3.66 g, 91.4 mmol, 1.2 equiv.) was added at 30 °C. The resulting mixture was stirred for 30 min and controlled by TLC. The reaction mixture was neutralized by saturated aqueous (200 mL) solution of $(NH_4)_2SO_4$ (155 g) till pH 6...7. The phases were separated and the aqueous residue was extracted with EtOAc (6 × 100 mL). The organic layers were washed with brine (15 × 100 mL), dried over anhydr. Na_2SO_4, filtered and evaporated under reduced pressure to afford the title compound **9** which was purified by crystallization (EtOAc/Hex). Yield: 17.18 g (71%). NMR and other

physicochemical data of the product **9** are consistent with those reported earlier (see electronic supporting information).[14,27a]

4.6. Synthesis of 3-*C*-aminomethyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (11)

A solution of nitro alcohol **8** (60 g, 0.18 mol, 1 equiv) in MeOH:THF (3:1, 400 mL) was hydrogenated at 30 atm and 40 °C in the presence of 10% Pd/C (5.9 g) for 17 h. The resulting mixture was filtered through celite and washed by MeOH (150 mL). The filtrate was evaporated to dryness under reduced pressure. The crude product **11** (51 g, 99%) is white solid and shows excellent purity and is used in the next step without additional purification. R_f=0.63 (CH_2Cl_2/EtOH 1:4, 1% NH_3). The analytical data of **11** are consistent with those reported earlier.[37] Mp: 122-123 °C (EtOAc/Hex) [lit.[37]: Mp: 122-123 °C]. $[\alpha]_D^{23}$=24 (*c* 1, EtOH) [lit.[37]: $[\alpha]_D^{23}$=25.4 (*c* 0.06, EtOH)]; ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): δ 5.78 (d, 1H, ^3J = 3.8 Hz, H-C(1)), 4.70 (d, 1H, ^3J = 3.8 Hz, H-C(2)), 4.17-4.05 (m, 2H, H-C(5), H_a-C(6)), 3.96-3.88 (m, 1H, H_b-C(6)), 3.85-3.80 (m, 1H, H-C(4)), 3.30-3.23 (m, 2H, H-C(3`)), 2.19-1.45 (bs, 3H, $H_2$N-C(3`), HO-C(3)), 1.60, 1.45, 1.37, 1.36 (4s, 12H, $(H_3C)_2$C-O-C(1,5)). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm) δ: 112.5, 109.8, 103.6, 81.6, 80.5, 79.5, 73.2, 68.0, 42.6, 26.7, 26.5, 25.3. IR (KBr) ν, cm^{-1}: 3500-3400 (bs), 3370, 2990, 1070, 1010.

4.7. Synthesis of 3-*C*-(*N*-Benzyloxycarbonyl)aminomethyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (12a)

Triethylamine (16 mL, 115.1 mmol, 1.5 equiv) was added to a solution of **11** (22.2 g, 76.7 mmol, 1 equiv.) in THF (350 mL). Reaction mixture was cooled to -5 ºC and solution of CbzCl (13.1 mL, 91.8 mmol, 1.2 equiv) was added. The resulting mixture was stirred at ambient temperature for 3 h. Then the excess of THF was evaporated under reduced pressure and dissolve in ethyl acetate (150 mL) and water (300 mL). The aqueous residue was extracted with ethyl acetate (3 × 100 mL). The combined organic layer was washed with saturated aqueous solution of $CuSO_4$ (200 mL), $NaHCO_3$ (200 mL) and NaCl (150 mL), dried over Na_2SO_4, filtered and evaporated under reduced pressure. Purification by crystallization (EtOAc/Hex) yielded **12a** (23.4 g, 72%). R_f=0.55 (EtOAc/Tol 1:2); Mp: 117 °C. $[\alpha]_D^{23}$=36 (*c* 0.38, $CHCl_3$). ^{1}H-NMR ($DMSO_{d6}$, 400 MHz, ppm) δ: 7.39-7.29 (m, 3H, H-C(Ph)), 7.20-7.13 (m, 2H, H-C(Ph)), 5.62 (d, 1H, ^3J = 3.9 Hz, H-C(1)), 5.07 (d, AB syst., 1H, ^2J = 12.5 Hz, H_a-C(a)), 5.04 (d, AB syst., 1H, ^2J = 12.5 Hz, H_b-C(a)), 4.89 (s, 1H, H-N-C(3`)), 4.26 (d, 1H, $^3J$ = 3.9 Hz, H-C(2)), 4.16 (dt, 1H, $^3J$ = 6.2, 6.6 Hz, H-C(5)), 3.96 (dd, 1H, $^2J$ = 7.8 Hz, $^3J$ = 6.6 Hz, $H_a$-C(6)), 3.85 (d, 1H, $^3J$ = 6.2 Hz, H-C(4)), 3.70 (dd, 1H, $^2J$ = 7.8 Hz, $^3J$ = 6.6 Hz, $H_b$-C(6)), 3.15 (m, 2H, H-C(3`)), 1.46, 1.33,

1.26, 1.24 (4s, 12H, $(H_3C)_2C$-O-C(1,5)). ^{13}C-NMR ($DMSO_{d6}$, 100 MHz, ppm) δ: 157.1, 137.2, 128.5, 128.0, 127.9, 111.6, 108.5, 103.1, 80.5, 79.4, 72.8, 66.1, 65.8, 42.6, 42.4, 26.7, 26.5, 26.4, 25.2. IR (KBr) ν, cm^{-1}: 3450, 3345, 2990, 1790, 1730, 1545, 1385, 1245, 1075, 1010, 860. Anal. Calcd for $C_{21}H_{29}NO_8$ (423.46): C 59.56, H 6.90, N 3.31. Found C 59.57, H 6.94, N 3.20.

4.8. Synthesis of 3-*C*-(*N*-Phenyloxycarbonyl)aminomethyl-1,2:5,6-di-*O*-isopropylidene-α-D-allofuranose (12b)

Triethylamine (12.8 mL, 92.0 mmol, 1.2 equiv) was added to a stirred solution of **11** (22.3 g, 77.0 mmol, 1 equiv.) in dry THF (500 mL) under argon atmosphere and the resulting mixture was cooled to 0 ºC. After 10 min phenyl chloroformate (11.0 mL, 85.0 mmol, 1.1 equiv) was added dropwise at 0 ºC. The resulting reaction mixture was stirred at ambient temperature for 1.5 h. Then it was evaporated to dryness under reduced pressure and redissolved in ethyl acetate (500 mL) and saturated aqueous solution of NaCl (500 mL). The phases were separated and the aqueous residue was extracted with EtOAc (4 × 100 mL). Organic layer was washed with brine (8 × 20 mL), dried over Na_2SO_4 and evaporated under reduced pressure. A recrystallisation of crude product from hexane/ethylacetate afforded the title compound **12b** as a white solid (25.8 g, 82%). R_f=0.50 (Tol/EtOAc 1:1); Mp: 125-126 °C (EtOAc/Hex). $[\alpha]_D^{25}$=44 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm) δ: 7.37 (t, 2H, ^3J =8.0 Hz, H-C(Ar)), 7.21 (t, 1H, ^3J = 8.0 Hz, H-C(Ar)), 7.13 (d, 2H, ^3J = 8.0 Hz, H-C(Ar)), 5.80 (d, 1H, ^3J = 4.0 Hz, H-C(1)), 5.65 (dd, 1H, ^3J = 7.8, 4.5 Hz, H-N-C(3`)), 4.42 (d, 1H, $^3J$ = 4.0 Hz, H-C(2)), 4.17-4.10 (m, 2H, H-C(5), $H_a$-C(6)), 3.96-3.89 (m, AB syst., 1H, $H_b$-C(6)), 3.80 (d, 1H, $^3J$ = 7.9 Hz, H-C(4)), 3.61 (dd, AB syst., 2H, $^2J$ = 14.0 Hz, $^3J$ = 7.8 Hz, $H_a$-C(3`)), 3.56 ((dd, AB syst., 2H, ^2J = 14.0 Hz, ^3J = 4.5 Hz, H_b-C(3`)), 2.97 (bs, 1H, HO-C(3)), 1.60, 1.47 (2s, 6H, $(H_3C)_2C$-O-C(1,5)), 1.37 (s, 6H, $(H_3C)_2C$-O-C(1,5)). ^{13}C-NMR ($CDCl_3$, 75.5 MHz, ppm) δ: 156.9, 150.9, 129.4, 125.6, 121.5, 112.7, 109.6, 104.6, 86.2, 82.7, 82.4, 72.3, 67.8, 44.2, 27.1, 26.7, 26.5, 25.1. IR (KBr) ν, cm^{-1}: 3365, 2985, 1720, 1530, 1495, 1485, 1385, 1375, 1215, 1070, 1015, 875, 845. Anal. Calcd for $C_{20}H_{27}NO_8$ (409.17): C 58.67, H 6.65, N 3.42. Found C 58.87, H 6.58, N 3.42.

4.9. Synthesis of 3-(*S*)-3-Aminomethyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (13)

A solution of nitro alcohol **9** (20.72 g, 65.00 mmol, 1 equiv) in ethanol (300 mL) was hydrogenated at 35 atm and 40 °C in the presence of 5% Pd/C (2.10 g) for 14 h. The resulting mixture was filtered through celite and washed by EtOH (100 mL). The filtrate was evaporated to dryness under reduced

pressure. The crude product **13** (18.54 g, 99%) shows excellent purity and is used in the next step without additional purification. R_f=0.64 (CH_2Cl_2/EtOH 1:4, 1% NH_3). The analytical data of **13** are consistent with those reported earlier.[37] Mp: 111 ºC (EtOAc/Hex). $[\alpha]_D^{25}$=19 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm) δ: 5.87 (d, 1H, ^3J = 3.6 Hz, H-C(1)), 4.31 (ddd, 1H, ^3J = 8.1, 6.2, 5.3 Hz, H-C(5)), 4.30 (d, 1H, ^3J = 3.6 Hz, H-C(2)), 4.12 (dd, AB syst., 1H, ^2J = 8.7 Hz, ^3J = 6.2 Hz, H_a-C(6)), 4.02 (dd, AB syst., 1H, ^2J = 8.7 Hz, ^3J = 5.3 Hz, H_b-C(6)), 3.76 (d, 1H, ^3J = 8.1 Hz, H-C(4)), 3.10 (d, AB syst., 1H, ^2J = 13.0 Hz, H_a-C(3`)), 2.93 (d, AB syst., 1H, $^2J$ = 13.0 Hz, $H_b$-C(3`)), 2.21 (bs, 3H, H_2N-C(3`), HO-C(3)), 1.50, 1.41, 1.34, 1.31 (4s, 12H, $(H_3C)_2$C-O-C(1,5)). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm) δ: 112.3, 109.2, 104.7, 86.4, 82.5, 80.0, 72.5, 67.6, 41.9, 27.1, 26.8, 26.5, 25.3. IR (KBr) ν, cm^{-1}: 3332, 3281, 2986, 1617, 1460, 1382, 1165, 1038, 996, 842. Anal. Calcd for $C_{13}H_{23}NO_6$ (289.32): C 53.97, H 8.01, N 4.84. Found C 53.99, H 8.11, N 4.78.

4.10. Synthesis of 3-*C*-(*N*-Benzyloxycarbonyl)aminomethyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (14a)

An ice-cold solution of Na_2CO_3 (4.77 g, 45.00 mmol, 1.3 equiv) in water (200 mL) was added to a solution of **13** (10.00 g, 34.60 mmol, 1 equiv) in THF (150 mL) at 0 ºC. A solution of CbzOSuc (10.35 g, 42.00 mmol, 1.2 equiv) in THF (150 ml) was added dropwise to the previous mixture at 0 ºC. The resulting mixture was stirred at 0 ºC for 10 min followed by 2.5 h at ambient temperature. Then the excess of THF was evaporated under reduced pressure. The aqueous residue was extracted with ethyl acetate (5 × 50 mL). The combined organic layer was washed with saturated aqueous solution of NaCl (6 × 20 mL), dried over Na_2SO_4 and concentrated under reduced pressure. The crude product **14a** (14.65 g, quantitative) is used in the next step without purification. R_f=0.52 (EtOAc/Tol 1:1.2); $[\alpha]_D^{25}$=54 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm) δ: 7.40-7.32 (m, 5H, H-C(Ph)), 5.85 (d, 1H, ^3J = 3.6 Hz, H-C(1)), 5.47 (t, 1H, ^3J = 6.4 Hz, H-N-C(3`)), 5.16 (d, AB syst., 1H, ^2J = 12.3 Hz, H_a-C(a)), 5.12 (d, AB syst., 1H, ^2J = 12.3 Hz, H_b-C(a)), 4.36 (d, 1H, ^3J = 3.6 Hz, H-C(2)), 4.32 (ddd, 1H, ^3J = 8.1, 6.4, 5.3 Hz, H-C(5)), 4.13 (dd, AB syst., 1H, ^2J = 8.9 Hz, ^3J = 6.4 Hz, H_a-C(6)), 3.99 (dd, AB syst., 1H, ^2J = 8.9 Hz, ^3J = 5.3 Hz, H_b-C(6)), 3.80 (dd, AB syst., 1H, ^2J = 14.9 Hz, ^3J = 6.4 Hz, H_a-C(3`)), 3.76 (d, 1H, $^3J$ = 8.1 Hz, H-C(4)), 3.41 (dd, AB syst., 1H, $^2J$ = 14.9 Hz, $^3J$ = 6.4 Hz, $H_b$-C(3`)), 1.49, 1.41, 1.34, 1.30 (4s, 12H, $(H_3C)_2$C-O-C(1,5)). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm) δ: 136.2, 128.8, 128.5, 128.3, 109.7, 104.8, 86.2, 83.0, 82.7, 73.0, 72.6, 67.9, 67.5, 44.3, 27.3, 26.9, 26.6, 25.6, 25.3. IR (KBr) ν, cm^{-1}: 3354, 3033, 2987, 2938, 2890, 1737, 1531, 1455, 1372, 1257, 1165, 1074. HRMS (ESI): m/z Calcd for $C_{21}H_{29}NO_8Na$ ($[M+Na]^+$): 446.1781. Found 446.1791.

4.11. Synthesis of 3-*C*-(*N*-Phenyloxycarbonyl)aminomethyl-1,2:5,6-di-*O*-isopropylidene-α-D-glucofuranose (14b)

Triethylamine (1.45 mL, 10.00 mmol, 1.5 equiv.) was added to a stirred solution of **13** (2.00 g, 6.92 mmol, 1 equiv) in dry THF (14 mL) under argon atmosphere and the resulting mixture was cooled to 0 ºC. After 10 min phenyl chloroformate (1.08 mL, 8.30 mmol, 1.2 equiv) was added dropwise at 0 ºC. The resulting reaction mixture was stirred at 0 ºC for 10 min followed by 1 h at ambient temperature. Then it was evaporated to dryness under reduced pressure and redissolved in ethyl acetate (30 mL). The ethyl acetate layer was washed with saturated aqueous solution of $CuSO_4$ (5 × 15 mL), saturated aqueous solution of $NaHCO_3$ (5 × 20 mL), brine (8 × 20 mL) and dried over Na_2SO_4 and evaporated under reduced pressure. A recrystallisation of crude product from hexane/ethylacetate afforded the title compound **4** as a white solid (2.36 g, 83%). R_f=0.61 (EtOAc/Tol 1:1.5); Mp: 148˚C (EtOAC/Hex). $[\alpha]_D^{25}$= 65 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 7.37 (t, 2H, ^3J =7.5 Hz, H-C(Ar)), 7.22 (t, 1H, ^3J =7.5 Hz, H-C(Ar)), 7.15 (d, 2H, ^3J =7.5 Hz, H-C(Ar)), 5.89 (d, 1H, ^3J =3.6 Hz, H-C(1)), 5.80 (dd, 1H, ^3J = 6.8, 6.0 Hz, H-N-C(3`)), 4.44 (d, 1H, $^3J$ =3.6 Hz, H-C(2)), 4.33 (ddd, 1H, $^3J$ = 6.4, 8.7, 5.3 Hz, H-C(5)), 4.16 (dd, AB syst., 1H, $^2J$ = 8.7 Hz, $^3J$ = 6.4 Hz, $H_a$-C(6)), 4.00 (dd, AB syst., 1H, $^2J$ = 8.7 Hz, $^3J$ = 5.3 Hz, $H_b$-C(6)), 3.84 (dd, AB syst., 1H, $^2J$ = 14.8 Hz, $^3J$ = 6.0 Hz, $H_a$-C(3`)), 3.81 (d, 1H, ^3J = 8.7 Hz, H-C(4)), 3.54 (dd, AB syst., 1H, ^2J = 14.8 Hz, ^3J = 6.8 Hz, H_b-C(3`)), 3.45 (bs, 1H, HO-C(3)), 1.53, 1.45, 1.35, 1.34 (4s, 12H, $(H_3C)_2$C-O-C(1,5)). ^{13}C-NMR ($DMSO_{d6}$), 75 MHz, ppm): 156.9, 150.8, 129.3, 125.6, 121.5, 112.6, 109.6, 104.6, 86.1, 82.6, 82.5, 72.3, 67.8, 44.1, 27.1, 26.7, 26.4, 25.1. IR (KBr) ν, cm^{-1}: 3416, 3364, 3066, 2989, 2926, 2890, 1740, 1552, 1495, 1384, 1373, 1248, 1213, 1168, 1064, 1018. Anal. Calcd for $C_{20}H_{27}NO_8$ (409.43): C 58.67, H 6.65, N 3.42. Found C 58.59, H 6.64, N 3.29.

4.12. General procedure A for the *N*-derivatization of oxazolidinones 3 and 4 with NaH as a base

A solution of compound **3** or **4** in DMF was added to a stirred suspension of NaH (60% suspension in mineral oil) in DMF under argon atmosphere at 0 ºC. The resulting reaction mixture stirred for 15 min and then the corresponding halide was added. The resulting reaction mixture was stirred at 0 ºC for 10 min followed by 1 h at ambient temperature. Then it was treated either with EtOH or MeOH and/or saturated aqueous solution of NH_4Cl. The phases were separated and the aqueous residue was extracted with EtOAc, brine and dried over Na_2SO_4, filtered and evaporated under reduced pressure to afford the

N-derivatized compound **15** or **16**. Purification was done by column chromatography or by crystallization.

4.12.1. (3*R*)-3`-Methyl-1,2:5,6-di-*O*-isopropylidene-spiro(3-deoxy-α-D-allofuranose-3,5`-oxazolidin)-2`-one (15a)

Compound **15a** was prepared by general procedure A. The following amounts of reagents were used: NaH (60% suspension in mineral oil, 0.065 g, 2.69 mmol, 1.7 equiv) suspension in DMF (5.0 mL), compound **3** (0.500 g, 1.59 mmol, 1 equiv) in DMF (5.0 mL), CH_3I (0.15 mL, 2.38 mmol, 1.5 equiv). Reaction was quenched by MeOH (2.0 mL) and neutralized by saturated aqueous solution of NH_4Cl (3.0 mL). Purification by crystalization (EtOAc/Hex) yielded **15a** (0.471 g, 90%). R_f=0.44 ($CHCl_3$/EtOH 19:1); Mp: 117-118 °C (EtOAc/Hex). $[\alpha]_D^{25}$=48 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm) δ: 5.72 (d, 1H, ^3J = 3.6 Hz, H-C(1)), 4.44 (d, 1H, ^3J = 3.6 Hz, H-C(2)), 4.17-4.04 (m, 3H, H-C(4), H-C(5), H_a-C(6)), 3.98 (dd, AB syst., 1H, ^2J = 8.7 Hz, ^3J = 3.6 Hz, H_b-C(6)), 3.76 (d, AB syst., 1H, ^2J = 9.0 Hz, H_a-C(4`)), 3.23 (d, AB syst., 1H, $^2J$ = 9.0 Hz, $H_a$-C(4`)), 2.91 (s, 3H, H-C(a)), 1.60, 1.43, 1.35, 1.31 (4s, 12H, $(H_3C)_2$-C-O-C(1,5)). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm) δ: 156.4, 114.3, 110.2, 102.3, 84.0, 82.2, 77.3, 73.9, 68.1, 50.3, 31.0, 26.7, 26.5, 26.4, 25.3. IR (KBr) ν, cm^{-1}: 2990, 1765, 1755, 1445, 1385, 1375, 1215, 1075, 1010, 870, 845, 755. HRMS (ESI): m/z Calcd for $C_{15}H_{25}NO_7$ ($[M+H]^+$): 330.1553. Found 330.1584.

4.12.2. (3*R*)-3`-Ethyl-1,2:5,6-di-*O*-isopropylidene-spiro(3-deoxy-α-D-allofuranose-3,5`-oxazolidin)-2`-one (15b)

Compound **15b** was prepared by general procedure A. The following amounts of reagents were used: NaH (60% suspension in mineral oil, 0.095 g, 2.39 mmol, 1.5 equiv) suspension in DMF (5.0 mL), compound **3** (0.500 g, 1.56 mmol, 1 equiv) in DMF (5.0 mL), C_2H_5Br (0.13 mL, 1.75 mmol, 1.1 equiv). Reaction was quenched by MeOH (2.0 mL) and neutralized by saturated aqueous solution of NH_4Cl (3.0 mL). Purification by crystallization (EtOAc/Hex) yielded **15b** (0.44 g, 82%). R_f=0.40 ($CHCl_3$/EtOH 19:1); Mp: 151-152 °C (EtOAc/Hex). $[\alpha]_D^{25}$=39 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm) δ: 5.72 (d, 1H, ^3J = 3.6 Hz, H-C(1)), 4.43 (d, 1H, ^3J = 3.6 Hz, H-C(2)), 4.17-4.04 (m, 3H, H-C(4), H-C(5), H_a-C(6)), 3.98 (dd, AB syst., 1H, ^2J = 8.7 Hz, ^3J = 4.0 Hz, H_b-C(6)), 3.78 (d, AB syst., 1H, ^2J = 9.0 Hz, H_a-C(4`)), 3.38 (dq, AB syst., 1H, $^2J$ = 14.0 Hz, $^3J$ = 7.0 Hz, $H_a$-C(a)), 3.29 (dq, AB syst., 1H, $^2J$ = 14.0 Hz, $^3J$ = 7.0 Hz, $H_b$-C(a)), 3.21 (d, AB syst., 1H, $^2J$ = 9.0 Hz, $H_b$-C(4`)), 1.60, 1.43, 1.35, 1.30 (4s, 12H, $(H_3C)_2$-C-O-C(1,5)), 1.17 (t, 3H, ^3J = 7.3 Hz, H-C(b)). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm) δ: 155.8, 114.3, 110.2, 103.0, 84.1, 82.2, 77.6, 73.8, 68.2, 47.4, 38.8, 26.7, 26.5, 26.4, 25.3, 12.2. IR (KBr) ν, cm^{-}

[1]: 2985, 1760, 1750, 1455, 1385, 1215, 1075, 1055, 1010, 875, 845, 755. HRMS (ESI): m/z Calcd for $C_{16}H_{26}NO_7$ ([M+H]$^+$): 343.1709. Found 344.1731.

4.12.3. (3*R*)-3`-(4-Bromobutyl)-1,2:5,6-di-*O*-isopropylidene-spiro(3-deoxy-α-D-allofuranose-3,5`-oxazolidin)-2`-one (15c)

Compound **15c** was prepared by general procedure A. The following amounts of reagents were used: NaH (60% suspension in mineral oil, 0.11 g, 2.7 mmol, 1.7 equiv) suspension in DMF (5.0 mL), compound **3** (0.500 g, 1.6 mmol, 1 equiv) in DMF (5.0 mL), $Br(CH_2)_4Br$ (0.74 mL, 6.4 mmol, 4 equiv). Purification by column chromatography (EtOAc/Hex 45%) yielded **15c** (0.586 g, 82%). R_f=0.31 ($CHCl_3$/EtOH 19:1); Mp: 183-185 °C (EtOAc/Hex). $[\alpha]_D^{25}$=30 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm) δ: 5.72 (d, 1H, ^3J = 3.4 Hz, H-C(1)), 4.45 (d, 1H, ^3J = 3.4 Hz, H-C(2)), 4.17-4.05 (m, 3H, H-C(4), H-C(5), H_a-C(6)), 4.00 (dd, AB syst., 1H, ^2J = 7.7 Hz, ^3J = 3.8 Hz, H_b-C(6)), 3.80 (d, AB syst., 1H, ^2J = 9.0 Hz, H_a-C(4`)), 3.46 (t, 2H, $^3J$ = 6.2 Hz, H-C(d)), 3.38 (dt, AB syst., 1H, $^2J$ = 14.1 Hz, $^3J$ = 7.1 Hz, Hz, $H_a$-C(a)), 3.23 (dt, AB syst., 1H, $^2J$ = 14.1 Hz, $^3J$ = 6.6 Hz, $H_b$-C(a)), 3.20 (d, AB syst., 1H, $^2J$ = 9.0 Hz, $H_b$-C(4`)), 2.02-1.83 (m, 2H, H-C(c)), 1.83-1.67 (m, 2H, H-C(b)), 1.61, 1.43, 1.35, 1.31 (4s, 12H, $(H_3C)_2$-C-O-C(1,5)). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm) δ: 156.2, 114.3, 110.3, 102.9, 84.2, 82.3, 77.5, 73.8, 68.2, 47.9, 43.1, 33.4, 29.0, 26.7, 26.6, 26.4, 25.5, 25.3. IR (KBr) ν, cm^{-1}: 2985, 2355, 1765, 1450, 1385, 1220, 1075, 1040, 1015, 875, 850, 835, 755. Anal. Calcd for $C_{18}H_{28}BrNO_7$ (449.11): C 48.01, H 6.27, N 3.11. Found C 48.12, H 6.26, N 3.07.

4.12.4. (3*R*)-3`-Benzyl-1,2:5,6-di-*O*-isopropylidene-spiro(3-deoxy-α-D-allofuranose-3,5`-oxazolidin)-2`-one (15d)

Compound **15d** was prepared by general procedure A. The following amounts of reagents were used: NaH (60% suspension in mineral oil, 0.02 g, 0.48 mmol, 1.5 equiv) suspension in DMF (1.0 mL), compound **3** (0.10 g, 0.32 mmol, 1 equiv) in DMF (1.0 mL), benzyl bromide (0.11 mL, 1.75 mmol, 5.5 equiv). Reaction was quenched by MeOH (0.2 mL). Additional purification performed by filtration through activated carbon (EtOH:EtOAc 1:4) yielded **15d** (0.12 g, 91%). R_f=0.47 ($CHCl_3$/EtOH 19:1); Mp: 148-151 °C (EtOAc/Hex). $[\alpha]_D^{25}$=20 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 7.39-7.30 (m, 5H, H-C(Ph)), 5.63 (d, 1H, ^3J = 3.4 Hz, H-C(1)), 4.54 (d, AB syst., 1H, ^2J = 15.4 Hz, H_a-C(a)), 4.38 (d, AB syst., 1H, ^2J = 15.4 Hz, H_b-C(a)), 4.36 (d, 1H, ^3J = 3.4 Hz, H-C(2)), 4.20 (d, 1H, ^3J = 8.9 Hz, H-C(4)) 4.08 (dd, AB syst., 1H, ^2J = 8.7 Hz, ^3J = 5.8 Hz, H_a-C(6)), 3.98-3.89 (m, 2H, H-C(5), H_b-C(6)), 3.62 (d, AB syst., 1H, ^2J = 9.0 Hz, H_a-C(4`)), 3.04 (d, AB syst., 1H, $^2J$ = 9.2 Hz, $H_b$-C(4`)), 1.61, 1.46, 1.34, 1.33 (4s, 12H, $(H_3C)_2$-C-O-C(1,5)). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 156.2, 135.4, 128.7, 128.1, 128.0, 114.3, 110.2, 102.9, 84.1, 82.3, 77.4, 73.5, 68.1, 48.4, 47.5, 26.7, 26.5, 26.4, 25.2. IR (KBr) ν,

cm^{-1}: 2990, 2935, 1740, 1455, 1370, 1255, 1215, 1080, 1020, 875, 855, 755, 705. Anal. Calcd for $C_{21}H_{27}NO_7$ (405.44): C 62.21, H 6.71, N 3.45. Found C 62.60, H 7.03, N 3.16.

4.12.5. (3*R*)-3`-(2-Methylallyl)-1,2:5,6-di-*O*-isopropylidene-spiro(3-deoxy-α-D-allofuranose-3,5`-oxazolidin)-2`-one (15e)

Compound **15e** was prepared by general procedure A. The following amounts of reagents were used: NaH (60% suspension in mineral oil, 0.07 g, 1.62 mmol, 1.7 equiv) suspension in DMF (5.0 mL), compound **3** (0.30 g, 0.95 mmol, 1 equiv) in DMF (3.0 mL), 3-chloro-2-methylpropene (0.16 mL, 1.43 mmol, 1.5 equiv). Reaction was quenched by saturated aqueous solution of NH_4Cl (15.0 mL). Purification by filtration through silica gel (EtOAc 40 mL) yielded **15e** (0.340 g, 95%). R_f=0.65 ($CHCl_3$/EtOH 9:1); $[\alpha]_D^{25}$=20 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 5.70 (d, 1H, ^3J = 3.5 Hz, H-C(1)), 4.93 (bs, 2H, H-C(c)), 4.41 (d, 1H, ^3J = 3.5 Hz, H-C(2)), 4.14 (d, 1H, ^2J = 8.7 Hz, H-C(4)), 4.14 (d, AB syst., 1H, ^2J = 8.5 Hz, ^3J = 5.7 Hz, H_a-C(6)), 4.06 (ddd, 1H, ^3J = 8.7, 5.7, 3.4 Hz, H-C(5)), 4.00 (d, AB syst., 1H, ^2J = 8.5 Hz, ^3J = 3.4 Hz, H_b-C(6)), 3.89 (d, AB syst., 1H, ^2J = 14.9 Hz, H_a-C(a)), 3.72 (d, AB syst., 1H, ^3J = 9.4 Hz, H_a-C(4`)), 3.71 (d, AB syst., 1H, $^2J$ = 14.9 Hz, $H_b$-C(a)), 3.08 (d, AB syst., 1H, $^3J$ = 9.4 Hz, $H_b$-C(4`)), 1.74 (s, 3H, H-C(d)), 1.60, 1.43, 1.35, 1.30 (4s, 12H, $(H_3C)_2$-C-O-C(1,5)). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 156.2, 139.8, 114.4, 114.1, 110.3, 103.0, 84.3, 82.3, 77.4, 73.8, 68.3, 50.7, 47.8, 26.8, 26.6, 26.5, 25.2, 19.7. IR (KBr) ν, cm^{-1}: 2985, 1760, 1750, 1450, 1375, 1255, 1075, 1020, 905, 880, 850. Anal. Calcd for $C_{18}H_{27}NO_7$ (369.41): C 58.52, H 7.37, N 3.79. Found C 58.28, H 7.37, N 3.69.

4.12.6. (3*R*)-3`-Propargyl-1,2:5,6-di-*O*-isopropylidene-spiro(3-deoxy-α-D-allofuranose-3,5`-oxazolidin)-2`-one (15f)

Compound **15f** was prepared by general procedure A. The following amounts of reagents were used: NaH (60% suspension in mineral oil, 1.56 g, 65.0 mmol, 1.7 equiv) suspension in DMF (69.0 mL), compound **3** (12.0 g, 38.1 mmol, 1 equiv) in DMF (56.0 mL), propargyl bromide (80% solution in toluene, 6.25 mL, 58.0 mmol 1.5 equiv). Neutralized by saturated aqueous solution of NH_4Cl (8.00 mL). Purification by filtration through silica gel (Tol/EtOAc 13:7) yielded **15f** (12.00 g, 89%). R_f=0.52 (Tol/EtOAc 0.4:1); Mp: 105-108 °C (EtOAc/Hex). $[\alpha]_D^{25}$=27 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 5.73 (d, 1H, ^3J = 3.5 Hz, H-C(1)), 4.46 (d, 1H, ^3J = 3.5 Hz, H-C(2)), 4.17 (dd, AB syst., 1H, ^2J = 17.6 Hz, ^4J = 2.5 Hz, H_a-C(a)), 4.14 (d, 1H, ^3J = 8.3 Hz, H-C(4)), 4.17-4.09 (m, 2H, H-C(5), H_a-C(6)), 4.04 (dd, AB syst., 1H, ^2J = 17.6 Hz, ^4J = 2.5 Hz, H_b-C(a)), 3.97 (dd, AB syst., 1H, ^2J = 8.5 Hz, ^3J = 3.6 Hz, H_b-C(6)), 3.85 (d, AB syst., 1H, ^2J = 9.2 Hz, H_a-C(4`)), 3.34 (d, AB syst., 1H, $^2J$ = 9.2 Hz, $H_b$-C(4`)), 2.31 (t, 1H, ^4J = 2.4 Hz, H-C(c)), 1.61, 1.42, 1.36, 1.30 (4s, 12H, $(H_3C)_2$-C-O-

C(1,5)).^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 155.7, 114.1, 110.4, 103.3, 84.1, 82.6, 77.8, 77.5, 74.0, 73.2, 68.3, 47.1, 34.0, 26.9, 26.8, 26.6, 25.4. IR (KBr) ν, cm^{-1}: 3315, 2995, 1760, 1450, 1385, 1375, 1255, 1220, 1075, 1015, 880, 855. Anal. Calcd for $C_{17}H_{23}NO_7$ (353.37): C 57.78, H 6.56, N 3.96. Found C 57.71, H 6.55, N 3.77.

4.12.7. (3*R*)-3`-(2,4-dinitrophenyl)-1,2:5,6-di-*O*-isopropylidene-spiro(3-deoxy-α-D-allofuranose-3,5`-oxazolidin)-2`-one (15g)

Compound **15g** was prepared by general procedure A. The following amounts of reagents were used: NaH (60% suspension in mineral oil, 0.07 g, 1.62 mmol, 1.7 equiv) suspension in DMF (2.0 mL), compound **3** (0.30 g, 0.95 mmol, 1 equiv) in DMF (2.0 mL), 2,4-dinitrofluorobenzene (0.18 mL, 1.43 mmol, 1.5 equiv). Reaction was quenched by EtOH (2.0 mL) and Neutralized by saturated aqueous solution of NH_4Cl (3.0 mL). Purification by column chromatography (Tol/EtOAc 40%) yielded **15g** (0.350 g, 77%). R_f=0.38 ($CHCl_3$/EtOH 19:1); Mp: 229-231 °C (EtOAc/Hex). $[\alpha]_D^{25}$=-16 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 8.83 (d, 1H, ^4J = 2.6 Hz, H-C(a)), 8.49 (dd, 1H, ^4J = 2.6 Hz, ^3J = 8.9 Hz, H-C(b)), 7.81 (d, 1H, ^3J = 8.9 Hz, H-C(c)), 5.78 (d, 1H, ^3J = 3.6 Hz, H-C(1)), 4.64 (d, 1H, ^3J = 3.6 Hz, H-C(2)), 4.22-4.04 (m, 5H, H-C(4), H-C(5), H-C(6), H_a-C(4`)), 3.85 (d, AB syst., 1H, $^2J$ = 9.0 Hz, $H_b$-C(4`)), 1.65, 1.47, 1.40, 1.31 (4s, 12H, $(H_3C)_2$-C-O-C(1,5)). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 153.1, 145.1, 144.0, 136.7, 127.9, 127.4, 121.6, 114.8, 110.6, 103.0, 83.9, 83.8, 77.2, 73.8, 68.2, 49.5, 26.7, 26.6, 26.5, 25.3. IR (KBr) ν, cm^{-1}: 2985, 2895, 2365, 1755, 1540, 1350, 1090, 1025, 875, 855, 835. Anal. Calcd for $C_{20}H_{23}N_3O_{11}$ (481.13): C 49.90, H 4.82, N 8.73. Found C 49.65, H 4.67, N 8.46. HRMS (ESI): m/z Calcd for $C_{20}H_{24}N_3O_{11}$ ($[M+H]^+$): 482.1411. Found 482.1436.

4.12.8. (3*R*)-3`-Acetyl-1,2:5,6-di-*O*-isopropylidene-spiro(3-deoxy-α-D-allofuranose-3,5`-oxazolidin)-2`-one (15h)

Compound **15h** was prepared by general procedure A. NaH (60% suspension in mineral oil, 0.07 g, 1.62 mmol, 1.7 equiv) suspension in DMF (2.0 mL), compound **3** (0.30 g, 0.95 mmol, 1 equiv) in DMF (2.0 mL), Ac_2O (0.14 mL, 1.43 mmol, 1.5 equiv). Reaction was quenched by saturated aqueous solution of NH_4Cl (3.5 mL). Purification by column chromatography (EtOAc/Tol 35%) yielded **15h** (0.240 g, 71%). R_f=0.45 ($CHCl_3$/EtOH 19:1); $[\alpha]_D^{25}$=13 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 400 MHz, ppm) δ: 5.74 (d, 1H, ^3J = 3.5 Hz, H-C(1)), 4.45 (d, 1H, ^3J = 3.5 Hz, H-C(2)), 4.28 (d, AB syst., 1H, ^2J = 11.5 Hz, H_a-C(4`)), 4.13 (dd, AB syst., 1H, $^2J$ = 8.6 Hz, $^3J$ = 5.1 Hz, $H_a$-C(6)), 4.07 (d, 1H, $^3J$ = 8.9 Hz, H-C(4)), 4.02 (ddd, 1H, $^3J$ = 9.0, 5.1, 3.5 Hz, H-C(5)), 3.97 (dd, AB syst., 1H, $^2J$ = 8.6 Hz, $^3J$ = 3.5 Hz, $H_b$-C(6)), 3.60 (d, AB syst., 1H, $^2J$ = 11.5 Hz, $H_b$-C(4`)), 2.49 (s, 3H, H-C(a)), 1.61, 1.41, 1.36, 1.26 (4s, 12H,

$(H_3C)_2$-C-O-C(1,5)). ^{13}C-NMR ($CDCl_3$, 100.6 MHz, ppm) δ: 170.1, 151.8, 114.6, 110.3, 103.0, 83.7, 82.7, 77.2, 73.4, 68.2, 45.8, 26.7, 26.4, 26.4, 25.1, 23.0. IR (film) ν, cm^{-1}: 2990, 2935, 1790, 1715, 1695, 1485, 1455, 1370, 875, 845, 755. HRMS (ESI): m/z Calcd for $C_{16}H_{23}NO_8Na$ ($[M+Na]^+$): 380.1321. Found 380.1313.

4.12.9. (3*R*)-3`-Butiryl-1,2:5,6-di-*O*-isopropylidene-spiro(3-deoxy-α-D-allofuranose-3,5`-oxazolidin)-2`-one (15i)

Compound **15i** was prepared by general procedure A. The following amounts of reagents were used: NaH (60% suspension in mineral oil, 0.194 g, 0.0081 mmol, 1.7 equiv) suspension in DMF (20.0 mL), compound **3** (1.500 g, 4.76 mmol, 1 equiv) in DMF (15.0 mL), *n*-butyryl chloride (0.768 ml, 7.14 mmol, 1.5 equiv). Purification by column chromatography (EtOAc/Hex 1:4) yielded **15i** (1.658 g, 90%). R_f = 0.58 (EtOAc/Hex 1:1); Mp: 112-113 ºC (EtOAc/Hex). $[\alpha]_D^{25}$=12 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm) δ: 5.74 (d, 1H, ^3J = 3.6 Hz, H-C(1)), 4.45 (d, 1H, ^3J = 3.6 Hz, H-C(2)), 4.28 (d, AB syst., 1H, ^2J = 11.8 Hz, H_a-C(4`)), 4.16-3.96 (m, 4H, H-C(4), H-C(5), H-C(6)), 3.60 (d, AB syst., 1H, $^2J$ = 11.8 Hz, $H_b$-C(4`)), 2.89 (dt, AB syst. 1H, ^2J = 16.5 Hz, ^3J = 7.4 Hz H_a-C(b)), 2.83 (dt, AB syst. 1H, ^2J = 16.5 Hz, ^3J = 7.4 Hz, H_b-C(b)), 1.69 (sextet, 2H, ^3J = 7.4 Hz, H-C(c)), 1.61, 1.41, 1.36, 1.25 (4s, 12H, $(H_3C)_2$C-O-C(1,5)), 0.97 (t, 3H, ^3J = 7.4 Hz, H-C(d)). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm) δ: 173.2, 151.6, 114.7, 110.4, 102.3, 83.8, 82.6, 77.0, 73.4, 68.2, 45.9, 36.9, 26.7, 26.5, 26.4, 25.1, 17.7, 13.7. IR (KBr) ν, cm^{-1}: 2991, 2965, 2936, 2898, 2878, 1790, 1716, 1381, 1321, 1222, 1076, 1039, 1019. Anal. Calcd for $C_{18}H_{27}NO_8$ (385.41): C 56.09, H 7.06, N 3.63. Found C 56.16, H 7.11, N 3.60.

4.13. General procedure B for *N*-acylation of oxazolidinones 3 and 4 with BuLi as a base

2.5 M *n*-BuLi in hexanes was added to a cold solution of compound **3** or **4** in dry THF under argon atmosphere at -78 ºC, stirred for 15 min and then acyl chloride was added. The resulting reaction mixture was stirred for 1 h at -78 ºC followed by 2 h at ambient temperature. The reaction mixture was treated with saturated aqueous solution of NH_4Cl. The phases were separated and the aqueous residue was extracted with EtOAc, brine and dried over Na_2SO_4, filtered and evaporated under reduced pressure to afford compounds **15j** or **16g**. Purification was done by column chromatography.

4.13.1. (3*R*)-3`-Phenylacetyl-1,2:5,6-di-*O*-isopropylidene-spiro(3-deoxy-α-D-allofuranose-3,5`-oxazolidin)-2`-one (15j)

Compound **15j** was prepared by general procedure B. The following amounts of reagents were used: Compound **3** (0.050 g, 0.16 mmol, 1 equiv) in THF (2.0 mL), 2.5 M *n*-BuLi (0.067 ml, 0.17 mmol, 1.05 equiv), phenylacetyl chloride (0.025 ml, 0.19 mmol, 1.2 equiv). Purification by column chromatography

(EtOAc/Hex 1:4) yielded **15j** (0.064 g, 93%). R_f=0.63 (EtOAc/Hex 1:1); Mp: 60 ºC (EtOAc/Hex). $[\alpha]_D^{25}$=12 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm) δ: 7.35-7.28 (m, 5H, H-C(Ph)), 5.74 (d, 1H, ^3J = 3.6 Hz, H-C(1)), 4.44 (d, 1H, ^3J = 3.6 Hz, H-C(2)), 4.30 (d, AB syst., 1H, ^2J = 11.7 Hz, H_a-C(4`)), 4.26 (s, 2H, H-C(b)), 4.15-3.97 (m, 4H, H-C(4), H-C(5), H-C(6)), 3.62 (d, AB syst., 1H, $^2J$ = 11.7 Hz, $H_b$-C(4`)), 1.63, 1.40, 1.36, 1.20 (4s, 12H, $(H_3C)_2$C-O-C(1,5)). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm) δ: 171.0, 151.6, 133.3, 129.7, 128.5, 127.2, 114.7, 110.4, 103.0, 83.8, 82.6, 77.3, 73.5, 68.2, 46.1, 40.9, 26.7, 26.4, 26.3, 25.0. IR (KBr) ν, cm^{-1}: 3065, 3033, 2991, 2939, 2897, 1789, 1686, 1473, 1456, 1382, 1323, 1227, 1127, 1077, 1028. Anal. Calcd for $C_{22}H_{27}NO_8$ (433.45): C 60.96, H 6.28, N 3.23. Found C 60.95, H 6.10 , N 3.06.

4.14. (3*S*)-3`-Methyl-1,2:5,6-di-*O*-isopropylidene-spiro(3-deoxy-α-D-glucofuranose-3,5`-oxazolidin)-2`-one (16a)

Compound **16a** was prepared by general procedure A. The following amounts of reagents were used: NaH (60% suspension in mineral oil, 0.032 g, 0.809 mmol, 1.7 equiv) suspension in DMF (1.5 mL), compound **4** (0.150 g, 0.48 mmol, 1 equiv) in DMF (3.5 mL), CH_3I (0.044 ml, 0.71 mmol, 1.5 equiv). Purification by column chromatography (EtOAc/Hex 1:5) yielded **16a** (0.131 g, 84%).

R_f=0.50 (EtOAc/Hex 1:1); Mp: 112 ºC (EtOAc/Hex). $[\alpha]_D^{25}$= 40 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm) δ: 5.90 (d, 1H, ^3J = 3.6 Hz, H-C(1)), 4.50 (d, 1H, ^3J = 3.6 Hz, H-C(2)), 4.34 (ddd, 1H, ^3J = 8.4, 6.3, 5.1 Hz, H-C(5)), 4.13 (dd, AB syst., 1H, ^2J = 8.9 Hz, ^3J = 6.3 Hz, H_a-C(6)), 4.00 (dd, AB syst., 1H, ^2J = 8.9 Hz, ^3J = 5.1 Hz, H_a-C(6)), 3.87 (d, 1H, ^3J = 8.4 Hz, H-C(4)), 3.80 (d, AB syst., 1H, ^2J = 9.2 Hz, H_a-C(4`)), 3.62 (d, AB syst., 1H, $^2J$ = 9.2 Hz, $H_b$-C(4`)), 2.89 (s, 3H, H-C(a)), 1.50, 1.41, 1.33, 1.31 (4s, 12H, $(H_3C)_2$C-O-C(1,5)). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm) δ: 156.5, 112.9, 109.6, 104.8, 84.4, 84.1, 81.6, 72.4, 67.6, 48.2, 30.9, 26.9, 26.8, 26.4, 24.9. IR (KBr) ν, cm^{-1}: 2989, 2965, 2942, 2886, 1759, 1494, 1432, 1378, 1269, 1246, 1219, 1062, 1042. Anal. Calcd for $C_{15}H_{23}NO_7$ (329.35): C 54.70, H 7.04, N 4.25. Found C 54.64, H 7.07, N 4.17.

4.16. (3*S*)-3`-Ethyl-1,2:5,6-di-*O*-isopropylidene-spiro(3-deoxy-α-D-glucofuranose-3,5`-oxazolidin)-2`-one (16b)

Compound **16b** was prepared by general procedure A. The following amounts of reagents were used: NaH (60% suspension in mineral oil, 0.032 g, 1.35 mmol, 1.7 equiv) suspension in DMF (2.5 mL), compound **4** (0.25 g, 0.79 mmol, 1 equiv) in DMF (2.5 mL), C_2H_5Br (0.09 ml, 1.19 mmol, 1.5 equiv). Purification by column chromatography (EtOAc/Hex 1:4) yielded **16b** (0.184 g, 68%). R_f=0.43 (EtOAc/Hex 1:1); Mp: 122-123 ºC (EtOAc/Hex). $[\alpha]_D^{25}$=46 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz,

ppm) δ: 5.89 (d, 1H, ^3J = 3.6 Hz, H-C(1)), 4.49 (d, 1H, ^3J = 3.6 Hz, H-C(2)), 4.32 (ddd, 1H, ^3J = 8.5, 6.3, 5.2 Hz, H-C(5)), 4.13 (dd, AB syst., 1H, ^2J = 8.9 Hz, ^3J = 6.3 Hz, H_a-C(6)), 4.00 (dd, AB syst., 1H, ^2J = 8.9 Hz, ^3J = 5.2 Hz, H_a-C(6)), 3.86 (d, 1H, ^3J = 8.5 Hz, H-C(4)), 3.76 (d, AB syst., 1H, ^2J = 9.2 Hz, H_a-C(4`)), 3.66 (d, AB syst., 1H, $^2J$ = 9.2 Hz, $H_b$-C(4`)), 3.37 (dq, AB syst., 1H, ^2J = 14.0 Hz, ^3J = 7.0 Hz, H_a-C(a)), 3.26 (dq, AB syst., 1H, ^2J = 14.0 Hz, ^3J = 7.0 Hz, H_b-C(a)), 1.49, 1.40, 1.32, 1.29 (4s, 12H, $(H_3C)_2$C-O-C(1,5)), 1.15 (t, 3H, ^3J = 7.4 Hz, H-C(b)). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm) δ: 156.1, 113.0, 109.7, 104.9, 84.5, 84.3, 82.0, 72.5, 67.8, 45.5, 38.9, 27.0, 26.7, 26.5, 25.1, 12.4. IR (KBr) ν, cm^{-1}: 2982, 2936, 2926, 2889, 2562, 1763, 1712, 1383, 1168, 1039, 1018. Anal. Calcd for $C_{16}H_{25}NO_7$ (343.37): C 55.97, H 7.34, N 4.08. Found C 56.02, H 7.36, N 3.97.

4.17. (3*S*)-3`-Benzyl-1,2:5,6-di-*O*-isopropylidene-spiro(3-deoxy-α-D-glucofuranose-3,5`-oxazolidin)-2`-one (16c)

Compound **16c** was prepared by general procedure A. The following amounts of reagents were used: NaH (60% suspension in mineral oil, 0.011 g, 0.27 mmol, 1.7 equiv) suspension in DMF (0.4 mL), compound **4** (0.050 g, 0.16 mmol, 1 equiv) in DMF (0.5 mL), benzyl bromide (0.028 ml, 0.24 mmol, 1.5 equiv). Purification by crystallization (Hex) yielded **16c** (0.053 g, 83%). R_f=0.64 (EtOAc/Hex 1:1); Mp: 112 ºC (EtOAc/Hex). $[\alpha]_D^{25}$=38 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 7.39-7.27 (m, 5H, H-C(Ph)), 5.90 (d, 1H, ^3J = 3.6 Hz, H-C(1)), 5.66 (d, AB syst., 1H, ^2J = 15.1 Hz, H_a-C(a)), 4.51 (d, 1H, ^3J = 3.6 Hz, H-C(2)), 4.33 (ddd, 1H, ^3J = 8.7, 6.3, 4.9 Hz, H-C(5)), 4.23 (d, AB syst., 1H, ^2J = 15.1 Hz, H_b-C(a)), 4.11 (dd, AB syst., 1H, ^2J = 8.9 Hz, ^3J = 6.3 Hz, H_a-C(6)), 3.96 (dd, AB syst., 1H, ^2J = 8.9 Hz, ^3J = 4.9 Hz, H_b-C(6)), 3.80 (d, 1H, ^3J = 8.7 Hz, H-C(4)), 3.66 (d, AB syst., 1H, ^2J = 9.2 Hz, H_a-C(4`)), 3.57 (d, AB syst., 1H, $^2J$ = 9.2 Hz, $H_b$-C(4`)), 1.46, 1.32, 1.27, 1.16 (4s, 12H, $(H_3C)_2$C-O-C(1,5)). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 156.5, 135.4, 128.8, 128.3, 128.0, 113.0, 109.8, 104.9, 84.7, 84.4, 81.5, 72.5, 67.9, 48.4, 45.7, 27.0, 26.6, 26.5, 25.1. IR (KBr) ν, cm^{-1}: 3034, 2988, 2935, 2886, 1764, 1494, 1448, 1374, 1265, 1231, 1083, 1057, 1015. Anal. Calcd for $C_{21}H_{27}NO_7$ (405.44): C 62.21, H 6.71, N 3.45. Found C 62.20, H 6.70, N 3.41.

4.18. (3*S*)-3`-(2-Methylallyl)-1,2:5,6-di-*O*-isopropylidene-spiro(3-deoxy-α-D-glucofuranose-3,5`-oxazolidin)-2`-one (16d)

Compound **16d** was prepared by general procedure A. The following amounts of reagents were used: NaH (60% suspension in mineral oil, 0.026 g, 1.08 mmol, 1.7 equiv) suspension in DMF (3.00 mL), compound **4** (0.200 g, 0.64 mmol, 1 equiv) in DMF (2.50 mL), 3-chloro-2-methylpropene (0.104 ml,

0.95 mmol, 1.5 equiv). Purification by crystalization (EtOAc/Hex) yielded **16d** (0.207 g, 88%). R_f=0.63 (EtOAc/Hex 1:1.5); Mp: 114-115 ºC (EtOAc/Hex). $[\alpha]_D^{25}$=56 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 5.91 (d, 1H, ^3J = 3.6 Hz, H-C(1)), 4.93 (s, 2H, H-C(c)), 4.51 (d, 1H, ^3J = 3.6 Hz, H-C(2)), 4.38 (ddd, 1H, ^3J = 8.8, 6.2, 5.2 Hz, H-C(5)), 4.15 (dd, AB syst., 1H, ^2J = 8.9 Hz, ^3J = 6.2 Hz, H_a-C(6)), 4.00 (dd, AB syst., 1H, ^2J = 8.9 Hz, ^3J = 5.2 Hz, H_b-C(6)), 3.93 (d, AB syst., 1H, ^2J = 15.1 Hz, H_a-C(4`)), 3.86 (d, 1H, $^3J$ = 8.8 Hz, H-C(4)), 3.67 (d, AB syst., 1H, $^2J$ = 15.1 Hz, $H_b$-C(4`)), 3.66 (s, 2H, H-C(a)), 1.75 (s, 3H, H-C(d)), 1.50, 1.40, 1.34, 1.31 (4s, 12H, $(H_3C)_2$C-O-C(1,5)). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 156.4, 139.5, 113.9, 113.0, 109.8, 104.8, 84.6, 84.3, 81.5, 72.4, 67.7, 50.5, 45.7, 26.9, 26.8, 26.4, 25.0, 19.7. IR (KBr) ν, cm^{-1}: 2991, 2941, 2881, 1760, 1490, 1450, 1374, 1264, 1222, 1078, 1059, 1015, 1001. Anal. Calcd for $C_{18}H_{27}NO_7$ (369.41): C 58.52, H 7.37, N 3.79. Found C 58.59, H 7.38, N 3.76.

4.19. (3*S*)-3`-Propargyl-1,2:5,6-di-*O*-isopropylidene-spiro(3-deoxy-α-D-glucofuranose-3,5`-oxazolidin)-2`-one (16e)

Compound **16e** was prepared by general procedure A. The following amounts of reagents were used: NaH (60% suspension in mineral oil, 0.044 g, 1.11 mmol, 1.7 equiv) suspension in DMF (3.5 mL), compound **4** (0.205 g, 0.65 mmol, 1 equiv) in DMF (3.5 mL), propargyl bromide (80% solution in toluene, 0.11 mL, 0.98 mmol, 1.5 equiv). Purification by column chromatography (EtOAc/Hex 1:3) yielded **16e** (0.210 g, 92%). $R_{f=}$0.50 (EtOAc/Hex 3:1); Mp: 122 ºC (EtOAc/Hex). $[\alpha]_D^{25}$=55 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm): 5.91 (d, 1H, ^3J = 3.6 Hz, H-C(1)), 4.52 (d, 1H, ^3J = 3.6 Hz, H-C(2)), 4.32 (ddd, 1H, ^3J = 8.3, 6.4, 5.1 Hz, H-C(5)), 4.14 (dd, AB syst., 1H, ^2J = 8.9 Hz, ^3J = 6.4 Hz, H_a-C(6)), 4.10 (d, 2H, ^4J = 2.6 Hz, H-C(a)), 4.00 (dd, AB syst., 1H, ^2J = 8.9 Hz, ^3J = 5.1 Hz, H_b-C(6)), 3.90 (d, 1H, ^3J = 8.3 Hz, H-C(4)), 3.89 (d, AB syst., 1H, ^2J = 9.2 Hz, H_a-C(4`)), 3.78 (d, AB syst., 1H, $^2J$ = 9.2 Hz, $H_b$-C(4`)), 2.31 (t, 1H, ^4J = 2.6 Hz, H-C(c)), 1.51, 1.42, 1.34, 1.31 (4s, 12H, $(H_3C)_2$C-O-C(1,5)). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm): 155.7, 113.0, 109.7, 104.8, 85.0, 84.1, 81.6, 76.6, 73.4, 72.4, 67.6, 45.5, 33.9, 26.9, 26.8, 26.4, 25.0. IR (KBr) ν, cm^{-1}: 3300, 2995, 2941, 2889, 2126, 1761, 1443, 1259, 1080, 1016. Anal. Calcd for $C_{17}H_{23}NO_7$ (353.37): C 57.78, H 6.56, N 3.96. Found C 57.61, H 6.53, N 3.86.

4.20. (3*S*)-3`-Butyryl-1,2:5,6-di-*O*-isopropylidene-spiro(3-deoxy-α-D-glucofuranose-3,5`-oxazolidin)-2`-one (16f)

Compound **16f** was prepared by general procedure A. The following amounts of reagents were used: NaH (60% suspension in mineral oil, 0.130 g, 0.003 mmol, 1.7 equiv) suspension in DMF (8.0 mL), compound **4** (0.600 g, 0.002 mmol, 1 equiv) in DMF (12.0 mL), butyryl chloride (0.290 ml, 0.003 mmol, 1.5 equiv). Purification by column chromatography (EtOAc/Hex 1:3) yielded **16f** (0.701 g, 96%). R_f=0.48 (Tol/EtOAc 1:5). $[\alpha]_D^{25}$=50 (*c* 1.0, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm) δ: 5.92 (d, 1H, ^3J = 3.8 Hz, H-C(1)), 4.53 (d, 1H, ^3J = 3.8 Hz, H-C(2)), 4.27 (ddd, 1H, ^3J = 8.9, 6.2, 4.5 Hz, H-C(5)), 4.19 (d, AB syst., 1H, ^2J = 11.8 Hz, H_a-C(4`)), 4.14 (dd, AB sist., 1H, $^2J$ = 8.9 Hz, $^3J$ = 6.2 Hz, $H_a$-C(6)), 4.05 (d, AB syst., 1H, $^2J$ = 11.8 Hz, $H_b$-C(4`)), 3.99 (dd, AB syst., 1H, ^2J = 8.9 Hz, ^3J = 4.5 Hz, H_b-C(6)), 3.87 (d, 1H, ^3J = 8.9 Hz, H-C(4)), 2.92 (dt, AB syst. 1H, ^2J = 16.6 Hz, ^3J = 7.3 Hz, H_a-C(b)), 2.81 (dt, AB syst. 1H, ^2J = 16.6 Hz, ^3J = 7.3 Hz, H_b-C(b)), 1.69 (sextet, 2H, ^3J = 7.3 Hz, H-C(c)), 1.50, 1.35, 1.33, 1.27 (4s, 12H, $(H_3C)_2$C-O-C(1,5)), 0.98 (t, 3H, ^3J = 7.3 Hz, H-C(d)). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm) δ: 172.9, 152.1, 113.2, 109.9, 104.7, 85.0, 84.1, 82.0, 72.5, 67.7, 44.8, 37.0, 26.8, 26.7, 26.3, 24.9, 17.7, 13.7. IR (KBr) ν, cm^{-1}: 2986, 2937, 2879, 1790, 1704, 1374, 1258, 1216, 1140, 1060, 1013. HRMS (ESI): m/z Calcd for $C_{18}H_{28}NO_8$ ($[M+H]^+$): 386.1802. Found 386.1815.

4.21. (3*S*)-3`-Phenylacetyl-1,2:5,6-di-*O*-isopropylidene-spiro(3-deoxy-α-D-glucofuranose-3,5`-oxazolidin)-2`-one (16g)

Compound **16g** was prepared by general procedure B. The following amounts of reagents were used: compound **4** (0.100 g, 0.32 mmol, 1 equiv) in THF (3 mL), 2.5 M *n*-BuLi (0.133 ml, 0.33 mmol, 1.05 equiv), phenylacetyl chloride (0.084 ml, 0.63 mmol, 2 equiv). Purification by column chromatography (EtOAc/Hex 1:10) yielded **16g** (0.073 g, 53%). R_f=0.74 (EtOAc/Hex 1:1); $[\alpha]_D^{25}$=28 (*c* 0.8, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm) δ: 7.34-7.27 (m, 5H, H-C(Ph)), 5.94 (d, 1H, ^3J = 3.6 Hz, H-C(1)), 4.54 (d, 1H, ^3J = 3.6 Hz, H-C(2)), 4.34 (d, AB syst., 1H, ^2J = 15.4 Hz, H_a-C(b)), 4.26 (ddd, 1H, ^3J = 8.9, 6.2, 4.3 Hz, H-C(5)), 4.22 (d, AB syst., 1H, ^2J = 11.8 Hz, H_a-C(4`)), 4.20 (d, AB syst., 1H, $^2J$ = 15.4 Hz, $H_b$-C(b)), 4.14 (dd, 1H, $^2J$ = 8.9 Hz, $^3J$ = 6.2 Hz, $H_a$-C(6)), 4.07 (d, AB syst., 1H, $^2J$ = 11.8 Hz, $H_b$-C(4`)), 3.99 (dd, 1H, ^2J = 8.9 Hz, ^3J = 4.3 Hz, H_b-C(6)), 3.88 (d, 1H, ^3J = 8.9 Hz, H-C(4)), 1.51, 1.33, 1.27, 1.20 (4s, 12H, $(H_3C)_2$C-O-C(1,5)). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm) δ: 170.8, 152.1, 133.5, 129.7, 128.5, 127.2, 113.2, 109.9, 104.8, 85.1, 84.1, 82.2, 75.6, 67.7, 45.1, 41.0, 26.8, 26.5, 26.3, 24.7. IR (KBr) ν, cm^{-1}: 2989, 2937, 2888, 1797, 1789, 1705, 1372, 1360, 1261, 1165, 1134, 1077, 1017. HRMS (ESI): m/z Calcd for $C_{22}H_{28}NO_8$ ($[M+H]^+$): 434.1824. Found 434.1815.

14.22. A mixture of (3a*R*,5*R*,5'*R*,6a*R*)-5-(2,2-Dimethyl-1,3-dioxolan-4-yl)-3'-(4-((3a*R*,5*R*,5'*R*,6a*R*)-5-(2,2-dimethyl-1,3-dioxolan-4-yl)-2,2-dimethyl-2'-oxodihydro-3a*H*-spiro[furo[2,3-*d*][1,3]dioxole-6,5'-oxazolidine]-3'-yl)butyl)-2,2-dimethyldihydro-3a*H*-spiro[furo[2,3-*d*][1,3]dioxole-6,5'-oxazolidin]-2'-one (17) and (3*R*)-3`-(4-Bromobutyl)-1,2:5,6-di-*O*-isopropylidene-spiro(3-deoxy-α-D-allofuranose-3,5`-oxazolidin)-2`-one (15c)

Compound **17** was prepared by general procedure A. The following amounts of reagents were used: NaH (60% suspension in mineral oil, 0.07 g, 1.62 mmol, 1.7 equiv) suspension in DMF (2.0 mL), compound **3** (0.30 g, 0.95 mmol, 1 equiv) in DMF (3.0 mL), $Br(CH_2)_4Br$ (0.06 mL, 1.62 mmol, 0.5 equiv). Reaction was quenched by saturated aqueous solution of NH_4Cl (2.00 mL). Purification by column chromatography (EtOAc/Tol 1:0.3) yielded **17** (0.075 g, 18%) and **15c** (0.252 g, 60%)**.** Data for **17**: R_f=0.25 ($CHCl_3$/EtOH 19:1); Mp: 183-185 °C (EtOAc/Hex). $[\alpha]_D^{25}$=38 (*c* 0.7, $CHCl_3$). ^{1}H-NMR ($CDCl_3$, 300 MHz, ppm) δ: 5.72 (d, 1H, ^3J = 3.4 Hz, H-C(1)), 4.45 (d, 1H, ^3J = 3.4 Hz, H-C(2)), 4.15 (dd, 1H, ^2J = 8.7 Hz, ^3J = 5.5 Hz, H_a-C(6)), 4.14 (d, 1H, ^3J = 8.7 Hz, H-C(4)), 4.07 (ddd, 1H, ^3J = 8.7, 5.5, 3.4 Hz, H-C(5)), 4.01 (dd, 1H, ^2J = 8.7 Hz, ^3J = 3.4 Hz, H_b-C(6)), 3.74 (d, AB syst., 1H, ^2J = 9.2 Hz, H_a-C(4`)), 3.44 (m, 2H, H-C(a)), 3.27 (d, AB syst., 1H, $^2J$ = 9.2 Hz, $H_b$-C(4`)), 1.64-1.59 (m, 2H, H-C(b)), 1.62, 1.44, 1.37, 1.31 (4s, 12H, H_3C-C-O-C(1,5)). ^{13}C-NMR ($CDCl_3$, 75 MHz, ppm) δ: 156.3, 114.2, 110.1, 102.9, 84.1, 82.4, 77.4, 73.8, 68.2, 48.1, 43.6, 26.7, 26.5, 26.4, 25.3, 24.1. IR (KBr) ν, cm^{-1}: 2990, 2940, 2365, 2345, 1755, 1740, 1450, 1375, 1220, 1075, 1015, 875, 850, 755. Anal. Calcd for [$C_{32}H_{48}N_2O_{14}$·0.5 H_2O] (684.31): C 56.13, H 7.07, N 4.09. Found C 55.68, H 7.05, N 4.01.

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Supplementary Material

Supplementary data associated with this article can be found in the online version.

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26. If necessary, the progress of the reaction can be monitored by ^{1}H-NMR, as TLC does not appear to be reliable due to ketone–ketone hydrate equilibrium on the TLC plate. Thus anomeric protons of all three species (**5-7**) are well separated (300 MHz, $CDCl_3$): 6.14 ppm (d, J = 4.5 Hz, H-C(1) of **6**), 5.95 ppm (d, J = 3.6 Hz, H-C(1) of **5**), 5.85 ppm (d, J = 3.6 Hz, H-C(1) of **7**).

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A practical access to glucose- and allose-based (5+5) 3-spiropseudonucleosides from a common intermediate

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Highlights

- Multigram syntheses of carbohydrate-based spirooxazolidinones are developed
- Novel 3-spiropseudonucleosides are characterized by X-ray diffraction analysis
- User-friendly diacetone-α-D-glucose oxidation is elaborated and validated