Journal of the Serbian Chemical Society
JSCS-info@shd.org.rs • www.shd.org.rs/JSCS
J. Serb. Chem. Soc. 83 (5) 539–548 (2018)
JSCS–5094
UDC 547.424+547.455–124:542.913:
66.095.12:547.455.623'915.5
Original scientific paper

Synthesis of 1,3-divalent glycoconjugates with diverse structures and their functionalization

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(Received 5 September 2017, revised and accepted 14 February 2018)

Abstract: A series of novel 1,3-difunctionalized glycoconjugates were synthesized using a sequence of regioselective functionalization and stereoselective glycosidation of D-glucose and D-GlcNAc. Regioselective C-3 functionalization of sugar molecules was achieved by chemical functionalization of isopropylidene or oxazoline protected sugar derivatives. The structural diversity at the anomeric carbon was explored by stereoselective chemical glycosidation. The oxazoline protected D-GlcNAc derivative gave either pyranose or furanose derivatives on glycosidation depending on the amount of Lewis acid used. The diversely functionalized glycoconjugates with azide or alkyne groups are potentially useful for the synthesis of multifunctionalized complex glycoconjugates *via* click reactions.

Keywords: glycoconjugate; regioselective; stereoselective; chemical synthesis; click reaction, glycolipids.

INTRODUCTION

Chemical synthesis of diversely functionalized biomolecules with targeted medical applications is a rapidly growing area of research in synthetic organic chemistry and chemical biology. Diversity oriented chemical synthesis of hybrid biomolecules not only generates a large number of compounds within a shorter period, but also produces a series of diversely functionalized molecules from the common starting material and by a common methodology. The concepts used regularly in the diversity-oriented synthesis are orthogonal protection and deprotection, functionalization of molecules by regioselective synthesis or cyclization of molecules to generate macrocycles with different scaffold structures.[1–3] Carbohydrates, being the most abundant biomolecule with unparalleled structural

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https://doi.org/10.2298/JSC170905030S

diversity, are regularly used as an instant source of chiral backbone in the area of diversity-oriented synthesis. In natural glycoconjugates, sugars are attached to other biomolecules like protein and lipid with different chemical linkages and with different stereochemistry.[4–6] The glycan part controls the solubility, folding and other physical characteristics of the natural glycoconjugates modulating their biological functions.[7] However, the potential of glycoconjugates in the area of medicinal chemistry are still not explored to the full extent due to their micro-heterogeneity and low bioavailability. Glycoconjugates synthesized in pure form using an easy synthetic methodology are useful in this regard.[8,9] The presence of a multiple number of chiral centres and the different relative orientation of the hydroxyl groups with respect to each other make carbohydrates a source of chiral backbones that can easily be diversely functionalized with the help of selective protection and deprotection methods.[10–13] Carbohydrates are frequently used for the synthesis of various structurally diverse biomolecules, such as multivalent compounds and glycoamino acid mimics. Compared to monofunctionalized glycoconjugates, multifunctionalized glycoconjugates with different functional groups in the same sugar moiety have a better binding affinity with various bacteria, virus or lectins. In the literature, many diversely functionalized glycoconjugates are reported to be synthesized using a click reaction.[14–16] Recently, the synthesis of diversely functionalized "clickable" glycopeptoids[17] and other glycoconjugates,[18,19] such as triazole containing glycolipids, that are potentially useful in the area of chemical biology, were reported. In this present work, a series of novel difunctionalized glycoconjugate in which the sugar molecules were functionalized with azide or alkyne or both groups, which could be used for synthesis of complex glycoconjugates, was synthesized using Cu(I) catalyzed click reactions. The diversity oriented synthesis of these complex glycoconjugates was achieved by selective protection of some of the hydroxyl groups of the sugar molecule followed by functionalization of the other groups. This synthetic methodology following the sequence of selective protection, chemical functionalization and glycosidation prior to selective deprotection resulted in the formation of novel 1,3-difunctionalized glycoconjugates not only with diverse functionalization, but also with different scaffolds with hexopyranose or hexofuranose rings of the sugar.

1,2:5,6-Di-*O*-isopropylidene-α-D-glucofuranose is reported in the literature of carbohydrate synthesis for the chemical modification at the C-3 hydroxyl group of the sugar ring followed by modification of the other hydroxyl groups.[20–23] Similarly, 1,2-oxazoline protected sugar molecules can be used not only for selective functionalization, but also as acceptor in chemical glycosidation reactions.[24–27] Another advantage of 1,2-oxazoline protection is the β-selectivity in the chemical glycosidation reaction due to neighbouring group parti-

cipation of the C-2 acetamido group in addition to the scope for the formation of hexofuranose and hexopyranose rings as products (Fig. 1).

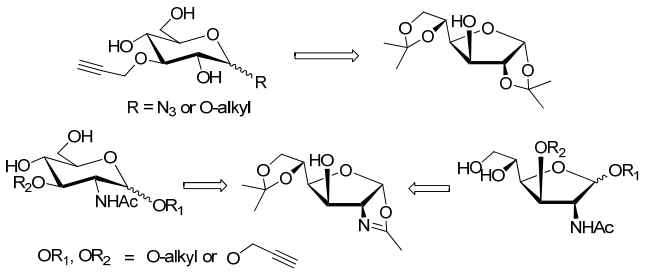


Fig. 1. Synthesis of 1,3-functionalized glycoconjugates.

EXPERIMENTAL

General Information

All the solvents were used after distillation and dry solvents were prepared using standard methods. All reagents purchased from commercial sources were used without any purification. ^{1}H- and ^{13}C-NMR spectra were recorded using 400 and 500 MHz NMR spectrometer. All mass spectra were recorded in Q-TOF electrospray ionization spectrometer. Column chromatography was performed over 100–200 mesh silica with ethyl acetate and hexane as the eluent.

Analytical and spectral data of the synthesized compounds are given in Supplementary material to this paper.

Syntheses

Synthesis of 1,2,4,6-tetra-O-*acetyl-3*-O-*propargyl-D-glucopyranose (**4**)*. A solution of sodium hydride (240 mg, 10 mmol) in dry DMF (10 mL) in a 100-mL round bottom flask was cooled to 0 °C and a solution of diacetone glucose (1.3 g, 5.0 mmol in 10 mL DMF) was added. The reaction was continued at that temperature for 30 min and then propargyl bromide (10 mmol) was added under stirring. The reaction mixture was allowed to come to room temperature and the reaction continued for 24 h at room temperature. After completion of the reaction, as indicated by TLC, ethyl acetate (50 mL) was added followed by water (50 mL) and the two layers were separated. The organic layer was washed with distilled water (3×30 mL) followed by brine solution (30 mL), dried over anhydrous sodium sulphate and concentrated to dryness. The crude product was dissolved in a mixture of THF and water (9:1). To this solution, Dowex H^{+} (30 wt. %) resin was added. The reaction mixture was stirred for 24 h at room temperature. After disappearance of the starting material, confirmed by TLC analysis, the reaction mixture was filtered through filter paper. After filtration of the resin, the filtrate was then concentrated and repeatedly washed with ethyl acetate to give a syrup. Acetylation of the hydroxyl groups of the syrupy product was realised using acetyl chloride along with sodium acetate as base to obtain 1,2,4,6-tetra-*O*-acetyl-3-*O*-propargyl-D-glucopyranose.[28] The crude product was purified by column chromatography to give an overall yield of 80 %.

Synthesis of 2,4,6-tri-O-*acetyl-3*-O-*propargyl*-β-*D-glucopyranosyl azide (**5**)*. 1,2,4,6--Tetra-*O*-acetyl-3-*O*-propargyl-D-glucopyranose (**4**, 386 mg, 1 mmol) was dissolved in dry DCM (10 mL). To this, $TMSN_3$ (1.5 mmol) was added followed by a 1.0 M solution of $SnCl_4$

in dry DCM (0.5 mL, 0.5 mmol). The reaction was continued at room temperature until the starting material was consumed. The reaction mixture was diluted with DCM (50 mL) and washed with distilled water (3×30 mL) followed by brine solution (30 mL). The crude product obtained after concentrating the organic layer was purified by column chromatography using a mixture of ethyl acetate and hexane (1:3) to afford 2,4,6-tri-*O*-acetyl-3-*O*-propargyl-*β*-D--glucopyranosyl azide (**5**) in 90 % yield.

*Synthesis of 1,3-difunctionalized glycolipid **6***. 1,2,4,6-Tetra-*O*-acetyl-3-*O*-propargyl-D--glucopyranose (**4**, 386 mg, 1.0 mmol) was dissolved in dry DCM. To this, *n*-dodecanol (1.5 mmol) was added followed by a 1 M solution of $SnCl_4$ in dry DCM (0.5 mL, 0.5 mmol). The reaction was continued until the disappearance of compound **4**. The reaction mixture was then diluted with DCM (50 mL) and washed with distilled water (3×30 mL). The organic layer was dried over anhydrous sodium sulphate and concentrated to dryness. The crude product was purified by column chromatography using a mixture of ethyl acetate and hexane (1:2) to give the corresponding *n*-dodecyl glucoside (**6**) in 80 % yield.

Synthesis of methyl 2,4,6-tri-O-*acetyl-3*-O-*propargyl*-α-*D-glucopyranoside (7)*. 3-*O*-Propargyl-D-glucopyranose (**3**, 1 mmol) was dissolved in dry methanol. To this, IR 120 H^+ resin (0.5 g) was added and the reaction mixture was stirred at room temperature. After completion of the reaction, as indicated by TLC, the crude product was filtered and concentrated to dryness to give a syrup. The syrupy product was per-*O*-acetylated using acetyl chloride along with sodium acetate as base in acetonitrile at 60 °C to give the methyl 2,4,6-tri-*O*-acetyl-3-*O*--propargyl-*α*-D-glucopyranoside in 90 % yield after column purification using a mixture of ethyl acetate and hexane (1:2) as eluent.

*Synthesis of 1,3-difunctionalized GlcNAc derivatives **10** and **11***. 2-Acetamido-2-deoxy--D-glucopyranose (5 mmol) was converted to the corresponding oxazoline derivative **8** following a literature procedure using dry acetone and ferric chloride.[22]

Sodium hydride (96 mg, 4.0 mmol) dissolved in dry DMF (5 mL) was cooled to 0 °C. To this, oxazoline **8** (2 mmol) dissolved in DMF (5 mL) was added dropwise under stirring. After 30 min, propargyl bromide (2 mmol) was added to the reaction mixture and the reaction allowed to come to room temperature and continued until the starting material had been consumed. The reaction mixture was diluted with ethyl acetate (50 mL) and the organic layer was repeatedly washed with water, dried over sodium sulphate and concentrated to dryness to obtain the crude product **9**, which was used for further reactions without any purification. The crude product **9** (1 mmol) obtained in the previous step was dissolved in anhydrous propargyl alcohol (1 mL). To this, *p*-TSA (0.5 equiv.) was added under nitrogen. The reaction was continued until disappearance of the starting material. The reaction mixture was dried under vacuum. Acetylation of hydroxyl groups was realised using acetic anhydride and pyridine (1:1, 2 mL). The crude product was purified by column chromatography using a mixture of ethyl acetate and hexane (1:1) to afford compound **10**.

Compound **11** was prepared from **9** using the same methodology as that for **10** except *n*-decanol (1 mL for 1 mmol) was used in place of propargyl alcohol.

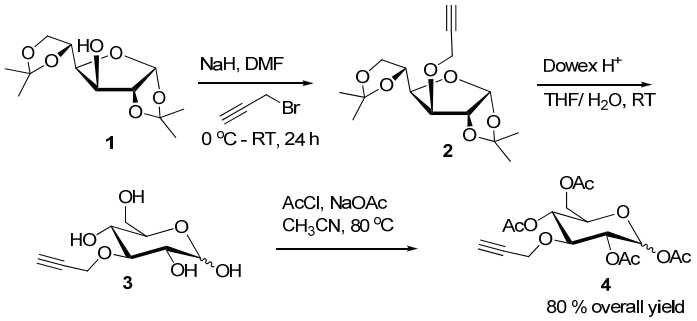
*Synthesis of 1,3-difunctionalized GlcNAc derivatives **13** and **14***. A solution of oxazoline **8** (2 mmol) in dry DMF (5 mL) was added dropwise to a mixture of sodium hydride (96 mg, 4 mmol) in dry DMF (5 mL) under stirring at 0 °C. After 30 min, *n*-decyl bromide (2 mmol) was added to the reaction mixture and stirring was continued at room temperature until the starting material had disappeared. The reaction mixture was diluted with ethyl acetate (50 mL) and the organic layer was repeatedly washed with water, dried over sodium sulphate and concentrated to dryness to obtain the crude product **12**.

Crude product **12** (1 mmol) was dissolved in anhydrous *n*-decanol (1 mL) and *p*-TSA (0.2 equiv.) was added under nitrogen. The reaction mixture was dried under vacuum after disappearance of the starting material. Purification of the product using column chromatography with ethyl acetate and hexane (1:1) as the eluent resulted in compound **13**.

Compound **14** was prepared from **12** using the similar methodology to that used for **13** except 1 equiv. of *p*-TSA (in place of 0.2 equiv. used in synthesis of compound **13**) and propargyl alcohol (1 mL for 1 mmol) in place of *n*-decanol, followed by overnight reaction with a mixture of acetic anhydride and pyridine (1:1, 2 mL).

RESULTS AND DISCUSSION

The synthesis of 1,3-difunctionalized glycoconjugates derived from D-glucose was initiated by the alkylation of the C-3 hydroxyl group of 1,2:5,6-di-*O*--isopropylidene-*α*-D-glucofuranose (**1**) with propargyl bromide using sodium hydride as the base in dry DMF to furnish the corresponding C-3 *O*-propargylated derivative **2**. The two acetonide protecting groups were removed under acidic condition using Dowex H^+ resin in aqueous THF to obtain C-3 *O*-propargylated glucopyranose **3**. Per-*O*-acetylation of compound **3** was realised using acetyl chloride and sodium acetate in acetonitrile. The crude product was purified by column chromatography using a mixture of ethyl acetate and hexane as eluent to furnish 1,2,4,6-tetra-*O*-acetyl-3-*O*-propargyl-D-glucopyranose (**4**) in 80 % overall yield over three steps (Scheme 1).[27]



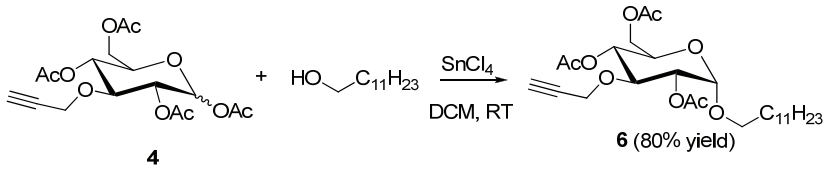
Scheme 1. Synthesis of 1,2,4,6-tetra-*O*-acetyl-3-*O*-propargyl-D-glucopyranose (**4**).

Since compound **4** is suitably functionalised at the C-3 position and the anomeric acetate group is a good glycosyl donor, it was chosen as a versatile intermediate for the synthesis of various novel 1,3-difunctionalised glycoconjugates. 1,2,4,6-Tetra-*O*-acetyl-3-*O*-propargyl-D-glucopyranose (**4**) was converted to the corresponding 2,4,6-tri-*O*-acetyl-3-*O*-propargyl-*β*-D-glucopyranosyl azide (**5**) in 90 % yield by reaction with $TMSN_3$ and $SnCl_4$ as catalyst (Scheme 2).

In the ^{1}H-NMR (500 MHz, $CDCl_3$) spectrum of **5**, the anomeric proton appeared as a doublet at 4.52 ppm with a coupling constant of 9.0 Hz, confirming the *β*-linkage. The formation of the compound was further confirmed by ^{1}H–^{1}H COSY, ^{13}C-NMR and ESI-MS HRMS spectral data.

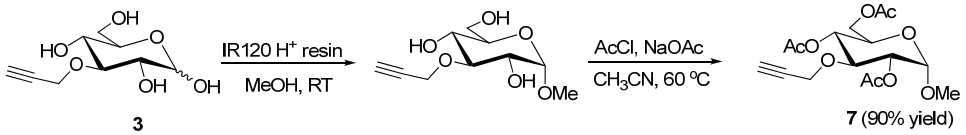
Scheme 2. Synthesis of 2,4,6-tri-*O*-acetyl-3-*O*-propargyl-*β*-D-glucopyranosyl azide **5**.

The methodology of synthesising 1,3-difunctionalized glycoconjugates was further extended to the preparation of other glycoconjugates, such as the *α*-linked C-3 *O*-propargylated glycolipid. For the synthesis of selectively functionalized glycolipids, 1,2,4,6-tetra-*O*-acetyl-3-*O*-propargyl-D-glucopyranose (**4**) was chosen as the glycosyl donor. Glycosidation was realised by taking *n*-dodecanol and $SnCl_4$ in dry DCM as catalyst to furnish the 3-*O*-propargylated glycolipid **6** as the *α*-isomer (Scheme 3). The formation of the *α*-isomer was confirmed by ^{1}H-NMR where the anomeric proton appeared as a doublet at 5.06 ppm with a coupling constant of 3.6 Hz. The formation of the compound was further confirmed by ^{1}H–^{1}H COSY, ^{13}C-NMR and the presence of the molecular ion peak in the ESI-MS HRMS spectroscopic data.



Scheme 3. Synthesis of C-3 propargylated glycolipid **6**.

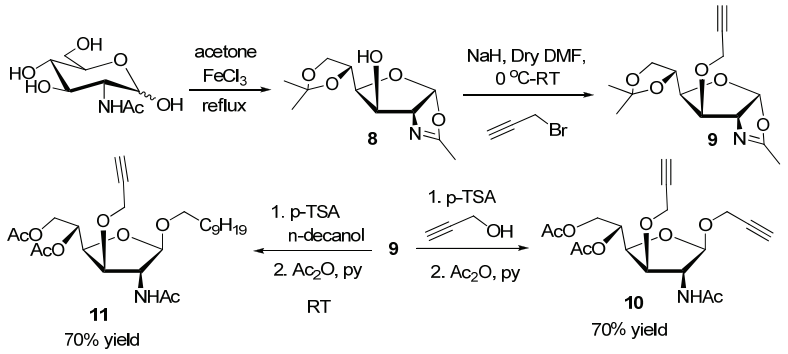
In addition to the C-3 propargylated per-*O*-acetylated derivative **4**, the 3-*O*--propargylated free sugar derivative **3** was also used in the glycosidation reaction under acidic conditions. The reaction of compound **3** with methanol in the presence of a catalytic amount of IR120 H^+ resin followed by per-*O*-acetylation of the hydroxyl groups using acetyl chloride in presence of sodium acetate resulted in the formation of the 3-*O*-propargylated per-*O*-acetylated methyl glycoside **7** (Scheme 4). The anomeric proton had a coupling constant of 2.8 Hz with the H-2 proton in the ^{1}H-NMR spectrum, which suggested the formation of the isomer as the only product. Formation of the compound was further confirmed by other spectroscopic techniques, *i.e.*, ^{1}H–^{1}H COSY, ^{13}C-NMR and presence of the molecular ion peak in the ESI-MS HRMS spectroscopic data.



Scheme 4. Synthesis of C-3 functionalized methyl glycoside **7**.

After synthesizing different 1,3-difunctionalized glycoconjugates derived from D-glucose, several 1,3-difuctionalized glycoconjugates were synthesized from 2-acetamido-2-deoxy-D-glucopyranose (D-GlcNAc). For the synthesis of D-GlcNAc derivatives, a novel oxazoline intermediate **8** was synthesized following a literature procedure, by reacting 2-acetamido-2-deoxy-D-glucopyranose with acetone catalyzed by ferric chloride. The 1,2-oxazoline ring of sugars has advantages over 1,2-isopropylidene protections, not only for its facile opening but also for selective formation of a *β*-glycosidic bond.[22]

Oxazoline **8** was reacted with propargyl bromide using sodium hydride as base to synthesize the 3-*O*-propargylated oxazoline derivative **9**. Compound **9** was used for glycosidation using different alcohols, *i.e.*, propargyl alcohol and *n*-decanol, using *p*-TSA (0.5 mol %) as catalyst followed by per-*O*-acetylation using acetic anhydride and pyridine to furnish the 1,3-dipropargylated GlcNAc derivative **10** and 3-*O*-propargylated *n*-decyl glucoside **11**, respectively (Scheme 5). Formation of both the compounds was confirmed by NMR and ESI-MS HRMS spectroscopic data.

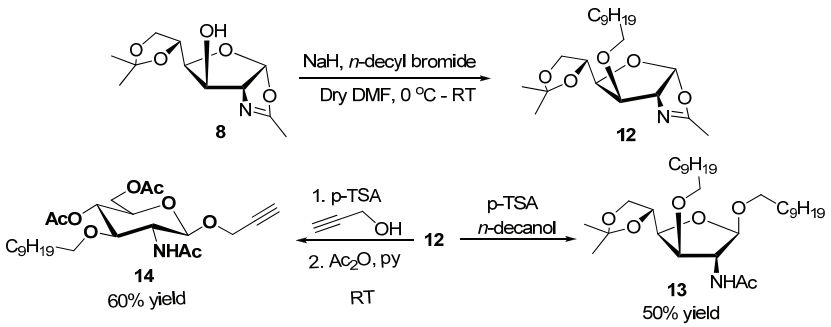


Scheme 5. Synthesis of C-3 propargyl functionalized GlcNAc derivatives.

The ^{1}H-NMR spectrum of compound **10** revealed the formation of furanose glycoside where the anomeric proton appeared as a multiplet in the range 5.09––5.03 ppm along with the H-4 proton. The exocyclic H-5 proton appeared as a multiplet in the 3.95–3.91 ppm range. Two alkyne protons appeared as multiplets in the 2.51–2.49 ppm range. In case of compound **11**, the anomeric proton appeared as a doublet at 4.85 ppm with a coupling constant of 2.4 Hz, confirming the formation of the furanose ring. The Lewis acid (0.5 mol % *p*-TSA) used in these reactions for glycosidation also catalyzed the deprotection of the 5,6-isopropylidene group.

After synthesizing the 3-*O*-propargylated glycosides, attempts were made towards the synthesis of the corresponding C-3 decyl glycosides. For the synthesis of these derivatives, oxazoline **8** was used as the synthon and was reacted

with *n*-decyl bromide using sodium hydride as the base to obtain the C-3 *O*-decyl derivative **12**, which was used for the glycosidation reaction (Scheme 6). Compound **12** was reacted with two different alcohols in presence of *p*-TSA in different amounts. When it was reacted with *n*-decanol using 0.2 mol % of *p*-TSA, the resultant product, compound **13**, was found to be a furanose glycoside without affecting the acetonide protection. In the ^{1}H-NMR spectrum of compound **13**, the anomeric proton appeared as a singlet at 4.88 ppm. Two singlets appeared at 1.43 and 1.35 ppm, indicating the presence of acetonide protection. The formation of the compound was further confirmed by ESI-MS HRMS. When compound **12** was reacted with propargyl alcohol with 1 mol % of *p*-TSA followed by per-*O*-acetylation using acetic anhydride and pyridine, the resulting glycoconjugate **14** was found to be in the hexopyranose form, for which the anomeric proton was found to be a doublet at 4.85 ppm with a coupling constant of 8.0 Hz. This experiment showed the scope of the reaction for the synthesis of glycosides with different conformations (hexopyranose or hexofuranose) using different amounts of the Lewis acid.



Scheme 6. Synthesis of C-3 decyl functionalized GlcNAc derivatives.

CONCLUSIONS

In summary, seven 1,3-difunctionalized glycoconjugates were synthesized from oxazoline or isopropylidene protected carbohydrate derivatives that yielded either pyranose or furanose derivatives depending on the amount of Lewis acid used in glycosidation. This is a unique example of substrate specific regio and stereoselectivity synthesis of furanose and pyranose ring containing glycolipids with one or two long chain alkyl groups or even propargyl groups. The propargyl functionalized glycolipids are useful synthetic biomolecules that can be utilized as clickable chemical ligating agent for the synthesis of hybrid glycolipids by a Cu(I)-catalyzed click reaction with azide functionalized biomolecules. 2,4,6-Tri-*O*-acetyl-3-*O*-propargyl-*β*-D-glucopyranosyl azide could be used for the synthesis of complex glycoconjugates or glycopolymers by a [3+2] cycloaddition reaction. The concept of selective protection and deprotection of the hydroxyl groups

is potentially useful for the functionalization of the carbohydrate derivatives at different positions leading to biologically important glycoconjugates. This methodology for formation of hexopyranose or hexofuranose ring containing glycosides derived from D-glucose or D-GlcNAc could be explored for the synthesis of other diversely functionalized glycoconjugates.

SUPPLEMENTARY MATERIAL

Analytical and spectral data of the synthesized compounds are available electronically at the pages of the journal website: http://www.shd.org.rs/JSCS/, or from the corresponding author on request.

ИЗВОД

СИНТЕЗА 1,3-ДИВАЛЕНТНИХ ГЛИКОКОНЈУГАТА РАЗНОВРСНЕ СТРУКТУРЕ И ФУНКЦИОНАЛИЗАЦИЈЕ

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Синтетисана је серија нових 1,3-дифункционализованих гликоконјугата, секвенцијама региоселективне функционализације и стереоселективне гликозидације D-глукозе и D-GlcNAc. Региоселективна C-3 функционализација молекула шећера постигнута је на изопропилиден- или оксазолин-заштићеним дериватима шећера. Структурна разноврсност аномерних деривата је испитана стереоселективном гликозидацијом. Оксазолин-заштићени дериват као производ реакције даје пиранозни или фуранозни дериват у зависности од количине примењене Луисове киселине као катализатора. Гликоконјугати са азидним или алкинским групама могу имати примену у синтези мултифункционализованих сложених гликоконјугата применом клик („*click*“) реакције.

(Примљено 5. септембра 2017, ревидирано и прихваћено 14. фебруара 2018)

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