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Convenient one-pot synthesis of triazolylethyl-2,3-unsaturated-*O*-glycoside derivatives

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ABSTRACT

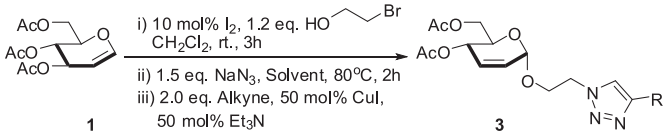
An efficient and convenient synthesis of new derivatives of triazolylethyl-2,3-unsaturated-*O*-glycoside has been developed using sequential one-pot glycosylation-azidation-CuAAc reactions procedure. Various substituted alkynes have been employed for the click reaction to obtain a variety of *O*-glycosylethyl triazole adducts in good to excellent yields with good α-anomeric selectivity.

1. Introduction

The Huisgen 1,3-dipolar cycloaddition of azides and alkynes catalyzed by Cu(I) (CuAAC) to afford triazoles is one of the most powerful reactions in click chemistry to connect two distinct molecules, used in various fields of organic and medicinal chemistry.[1] In the field of carbohydrate chemistry, the application of CuAAc reaction has gained increasing interested for the synthesis of triazole-glycoside substrates for drug discovery.[2] Glycosides with a 1,2,3-triazole ring possess a variety of biological activities such as α-glucosidase inhibitory,[3] anti-oxidant,[4] anti-tuberculosis,[5] anti-proliferative,[6] anti-microbial,[7] SGLT2 inhibitors,[8] anti-inflammatory,[9] cytotoxicity,[10] anti-cancer,[11] anti-parasite[12] and galactin-3 inhibitory effects.[13] Since 1,2,3-triazole glycosides have become increasingly useful and important, the development of a simple and efficient method for their synthesis in a one-pot operation, thus avoiding isolation, handling and chromatography, would be desirable to provide the desired products in good yield and in the most efficient way.[14]

Triazole-glycosides can be prepared from the coupling of propargyl glycosides and azides, or azido glycosides and alkynes. The azide and alkyne functionalities can be introduced at the desired position but generally at the C-1 position of the glycoside. Although a large number of triazole-glycosides derivatives have been synthesized so far, the development of the unique structure of triazolyl-2,3-unsaturated-*O*-glycosides has been limited.[15]

In our previous reports, we demonstrated a convenient one-pot approach to 2,3-unsaturated-glycosyl triazoles via tandem O-glycosylation using an iodine promoter and a mild CuAAC reaction.[16] In this work, we report herein the convenient and efficient procedure for synthesizing new analogs of triazolylethyl-2,3-unsaturated-*O*-glycosides from D-glucal by using a sequential one-pot glycosylation-azidation-CuAAc procedure, without any purification of the intermediates generated at each stage (Scheme 1).



Scheme 1. Synthesis of triazolylethyl-2,3-unsaturated-*O*-glycosides.

2. Results and discussion

In our initial investigations, the synthesis of azidoethyl glycoside was studied and was found to be easily prepared by iodine catalyzed glycosylation of D-glucal with bromoethanol, for in situ generation of *O*-glycosyl ethyl bromide, followed by subsequent

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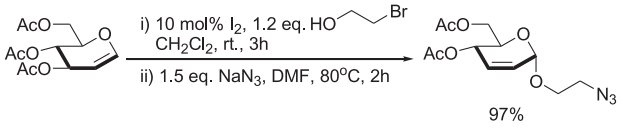
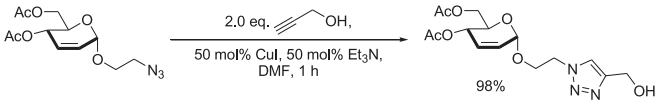
0040-4020/

nucleophilic substitution in the presence of sodium azide to obtain azidoethylglycoside in excellent yield in one pot (Scheme 2).



Scheme 2. Synthesis of azidoethyl glycosides.

The presence of the 2-azidoethyl aglycon would enable click reaction approaches with a variety of alkynes. The click reaction of the resulting isolated azidoethylglycoside with propargyl alcohol was performed smoothly using CuI as catalyst to afford triazolylethyl-2,3-unsaturated-*O*-glycosides in excellent yield (Scheme 3). Based on the good results of two reactions process, we chose to combine and examine the sequential addition of reagents and other reactants in one-pot. We first performed the glycosylation for in situ generation of *O*-glycosyl ethyl bromide, followed by addition of sodium azide to obtain azidoethyl glycoside, which underwent the Huisgen CuACC reaction with a variety of alkynes to furnish a series of *O*-glycosyl ethyl triazole derivatives.



Scheme 3. Synthesis of triazolylethyl-2,3-unsaturated-*O*-glycosides.

As shown in Table 1, our initial investigations focused on glycosylation via Ferrier rearrangement of D-glucal with bromoethanol using 10 mol % iodine to promote the reaction at room temperature. It was observed on TLC that *O*-glycoside formation was completed to obtain *O*-glycosylethylbromide in 3 h. Next, to the reaction was added 1.5 equiv of sodium azide to generate in situ glycosyl azide, followed by the click reaction with 2.0 equiv of propargyl alcohol in the presence of 50 mol % CuI. The use of DMF as solvent in the second step was found to be necessary to promote the azidation reaction to furnish the product in 5 h at RT (Table 1, entry 2). When using acetonitrile, we were unable to obtain the desired product (entry 1).

To shorten the reaction time in the azidation step, the reaction temperature was raised to 80 °C. Under these conditions, azidation could be complete to afford product in 2 h, however the click reaction step took as long as 5 h to afford a quantitative yield of product (entry 3). The use of Et_3N as a base was found to promote the click reaction to completion in 1 h affording the desired product in 91% yield with α-anomeric selectivity (Table 1, entry 4). The one pot reaction progress can be conveniently monitored at each step by TLC, and the reactions clearly proceed without noticeable amount of by product.

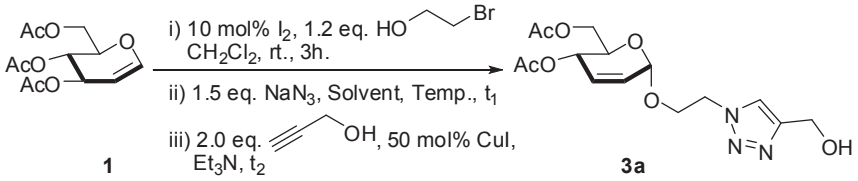
Using the optimal conditions shown in Table 1, entry 4, the scope and limitations of this one pot methodology have been examined. Various substituted alkynes have been employed to furnish a series of *O*-glycosylethyl triazole adducts and the results are summarized in Table 2.

The propargyl alcohol **2a** reacted smoothly to afford **3a** in 91% yield, and the longer chain butynyl and pentynyl alcohols afforded products **3b** and **3c** in >99% and 82% yield, respectively (Table 2, entries 1–3). The use of more hindered alkynes **2d** and **2e** still afforded the desired product in good yield, providing the triazole glycosides **3d** and **3e** in 77% and 72% yield (entries 4–5). Alkyne-bearing cyclobutanol was found to readily undergo cycloaddition and is well tolerated. We next examined both electron-rich and electron-deficient phenyl alkynes **2f**–**2h**, which were carried out at 40 °C and reacted smoothly to give the products **3f**–**3h** in good yields (entries 6–8). The yields were found to excellent with the propargyl ether derivatives **2i**-**2l** (entries 9–12) and **2o**-**2q** (entries 15–17) providing the product in quantitative yield. The benzaldehyde group-bearing propargyl ether in **2l** and **2m** were well tolerated in this one-pot reaction (entries 12–13). Alkyne **2n** containing a coumarin substituent was employed to synthesize triazole glycosides in high yield with this one pot method (entry 14).

3. Conclusion

We have successfully demonstrated the efficient synthesis of new class of triazolylethyl 2,3-unsaturated *O*-glycoside derivatives with good α-anomeric selectivity in a one-pot manner using sequential O-glycosylation-azidation-cycloaddition procedure, thus avoiding the isolation and handling of potentially explosive organic azides. This method can be applied to various alkyne substrates and should be of general utility for the synthesis of this unique scaffold in an efficient way.

Table 1
One-pot glycosylation azidation click reaction of D-glucal **1** under various conditions



Entry	Solvent[b]	Temp (°C)	Et_3N (equiv)	t_1(h)	t_2(h)	Yield[a,c] (%)
1	CH_3CN	RT	—	20	—	—[d]
2	DMF	RT	—	5	5	94
3	DMF	80	—	2	5	>99
4	DMF	80	0.5	2	1	91

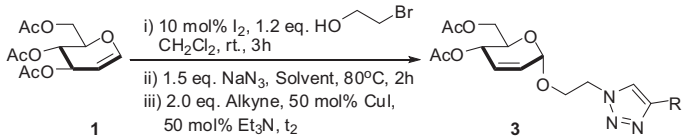
[a] All reactions were carried out with 0.073 mmol of D-glucal (**1**).
[b] Solvent used for step 2.
[c] Yields are given for isolated compound. The ratio α:β=9:1 was determined on the basis of ^1H NMR integration of the crude reaction mixture.
[d] Trace product of 2-azidoethyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-erythrohex-2-enopyranoside.

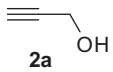
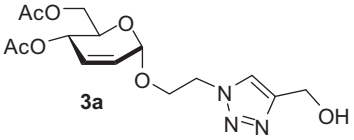
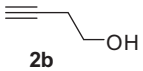
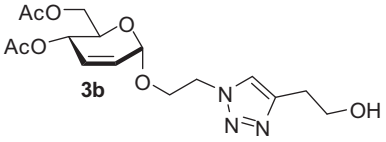
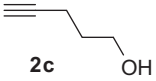
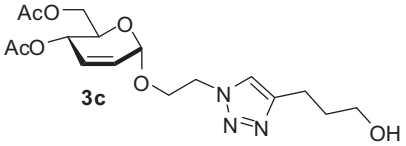
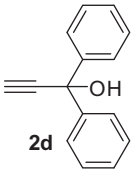
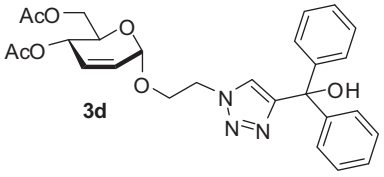
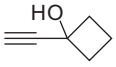
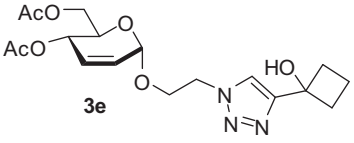
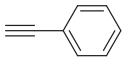
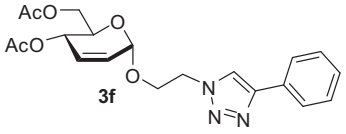
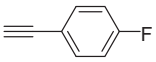
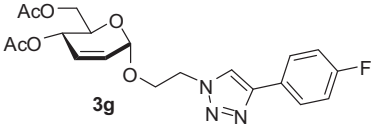
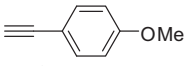
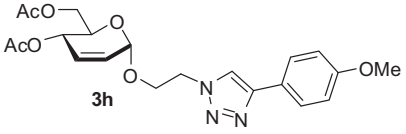
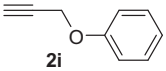
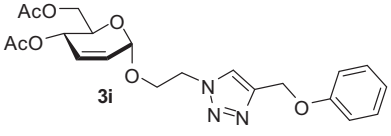
4. Experimental

4.1. General methods

All chemicals were purchased from commercial sources and used without further purification. Proton NMR spectra were

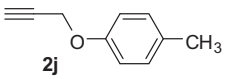
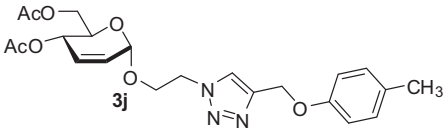
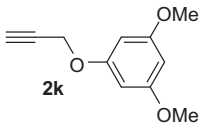
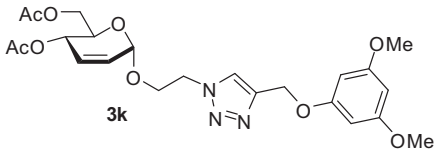
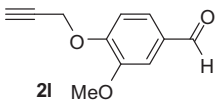
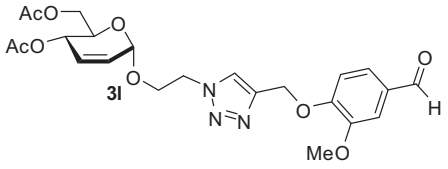
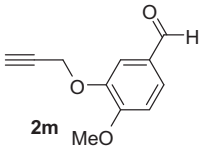
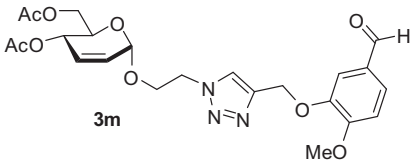
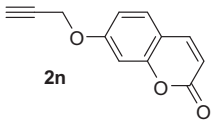
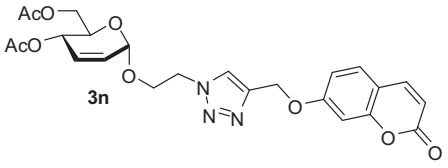
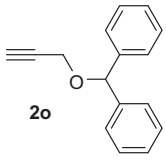
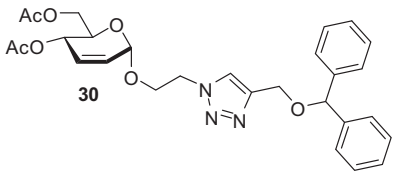
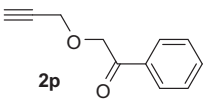
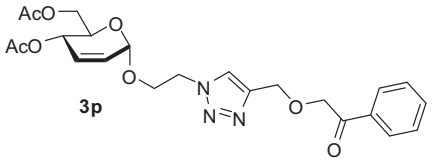
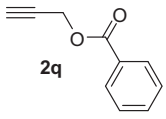
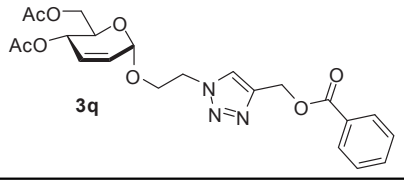
Table 2
Synthesis of 2,3-unsaturated-*O*-glycosyl triazoles **3** via one-pot glycosylation azidation click reaction



Entry	Alkyne	t_2 (h)	Product	Yield[a,b] (%)
1	 **2a**	1	 **3a**	91
2	 **2b**	1.5	 **3b**	>99
3	 **2c**	2	 **3c**	82
4	 **2d**	2	 **3d**	77
5	 **2e**	1	 **3e**	72
6	 **2f**	2	 **3f**	79[c]
7	 **2g**	7	 **3g**	78[c]
8	 **2h**	24	 **3h**	88[c]
9	 **2i**	2	 **3i**	96

(*continued on next page*)

Table 2 (*continued*)

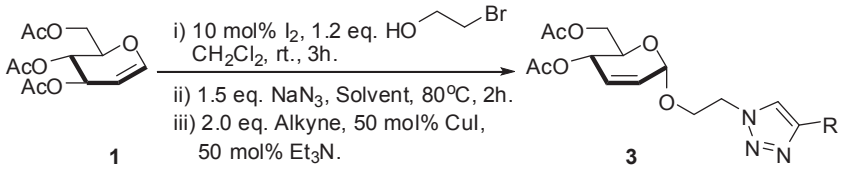
Entry	Alkyne	t_2 (h)	Product	Yield[a,b] (%)
10	 **2j**	4	 **3j**	>99
11	 **2k**	1	 **3k**	>99
12	 **2l**	4	 **3l**	>99
13	 **2m**	5	 **3m**	89
14	 **2n**	3	 **3n**	83
15	 **2o**	1	 **30**	>99
16	 **2p**	1.5	 **3p**	>99
17	 **2q**	4	 **3q**	>99

[a] All reactions were carried out with 0.073 mmol of D-glucal (**1**).
[b] Yields are given for isolated compound. The ratio α:β=9:1 was determined on the basis of ^{1}H NMR integration of the crude reaction mixture.
[c] The reactions were carried out at 40 °C.

recorded on a Bruker Avance (400 MHz). All spectra were measured in $CDCl_3$ solvent and chemical shifts are reported as δ values in parts per million (ppm) relative to tetramethylsilane (δ 0.00) or $CDCl_3$ (δ 7.26) as internal standard. Data are reported as follows; chemical shift (multiplicity, integrate intensity or assignment, coupling constants in Hertz, assignment). Carbon NMR spectra were recorded on a BRUKER AVANC (100 MHz). All spectra were measured in $CDCl_3$ solvent and chemical shifts are reported as δ values in parts per million (ppm) relative to $CDCl_3$ (δ 77.0) as internal standard. High-resolution mass spectra (HRMS) data were obtained with a Finnigan MAT 95. Infrared spectra were determined on a PERKIN ELMER FT/IR-2000S spectrophotometer and are reported in wave number (cm^{-1}). Analytical thin-layer chromatography (TLC) was conducted on precoated TLC plates; silica gel 60F-254 [E. Merck,

Darmstadt, Germany]. Silica gel columns for open-column chromatography utilized silica gel 60 (0.040–0.063 mm) [E. Merck, Darmstadt, Germany]. Melting points were measured using a Melting point apparatus (Griffin) and are uncorrected. Yields are given for isolated compound after purification. The ratio of isomer α:β was determined on the basis of 1H NMR integration of the crude reaction mixture. The spectroscopic data for major isomer (α) outlined as followed.

4.2. General procedure for synthesis of 2,3-unsaturated *O*-glycosyl triazole derivatives



For the first step, a stirred solution of 3,4,6-tri-*O*-acetyl-D-glucal **1** (20.0 mg, 0.073 mmol) in dried CH_2Cl_2 (1.0 mL) was added 2-bromoethanol (0.088 mmol) and I_2 catalyst (10 mol%) under nitrogen at room temperature. The stirring was continued at room temperature for 3.0 h. After TLC showed complete conversion, the volatiles were removed using a rotary evaporator. The obtained residue was redissolved in DMF (1.0 mL), followed by addition of sodium azide (7.1 mg, 0.109 mmol). The reaction mixture was stirred at 80 °C for 2.0 h. After TLC showed complete conversion, the following reagents were added in the order: CuI (6.6 mg, 0.037 mmol), Et_3N (3.7 mg, 0.037 mmol) and alkyne (0.146 mmol), respectively. The reaction mixture was stirred at room temperature for 1–24 h. After TLC showed complete conversion, the reaction mixture was diluted with EtOAc (20 mL), washed with satd aq NH_4Cl (20 mL), and extracted with EtOAc (3×20 mL). The combined organic layer was washed with brine (20 mL), dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure. The residues were purified by silica gel column chromatography to give the 2,3-unsaturated-*O*-glycosyl triazole products **3**.

5. Spectroscopic data of 2,3-unsaturated *O*-glycosyl triazole derivatives

5.1. 4-(1-Hydroxymethyl)-1-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (3a)

91% yield (23.6 mg) as a mixture (α:β=9:1); isolated α-form was obtained as a pale yellow oil; R_f (80% EtOAc/*n*-hexane) 0.23; $[\alpha]_D^{20}$ +35.98 (*c* 1.02, $CHCl_3$); ν_{max} ($CHCl_3$): 3468, 2952, 2924, 2851, 1740, 1454, 1435, 1371, 1047, 1015, 982 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.67 (1H, s), 5.89 (1H, d, *J*=10.0 Hz), 5.77 (1H, dt, *J*=10.0, 2.0 Hz), 5.25 (1H, ddd, *J*=10.0, 4.0, 2.0 Hz), 4.99 (1H, s), 4.78 (2H, s), 4.62–4.56 (2H, m), 4.18–4.05 (3H, m), 3.94–3.84 (1H, m), 3.84 (1H, ddd, *J*=10.0, 5.0, 2.0 Hz), 2.09 (3H, s), 2.04 (3H, s); δ_C (100 MHz, $CDCl_3$) 170.9, 170.3, 147.9, 129.8, 126.9, 122.1, 94.5, 67.2, 66.8, 65.2, 62.9, 50.4, 20.9, 20.8; HRMS (ESI): found: 378.1272; $C_{15}H_{21}N_3O_7Na$ $(M+Na)^+$ requires 378.1277.

5.2. 4-(2-Hydroxyethyl)-1-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (3b)

>99% yield (27.1 mg) as a configuration mixture (α:β=9:1); isolated α-form was obtained as a pale yellow oil; R_f (80% EtOAc/*n*-hexane) 0.23; $[\alpha]_D^{20}$ +74.30 (*c* 1.01, $CHCl_3$); ν_{max} ($CHCl_3$): 3468, 2952, 2924, 2851, 1741, 1454, 1432, 1371, 1275, 1259, 1236, 1048, 1021, 982 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.55 (1H, br s), 5.87 (1H, d, *J*=10.0 Hz), 5.76 (1H, dt, *J*=10.0, 2.0 Hz), 5.25 (1H, d, *J*=10.0 Hz), 4.98 (1H, s), 4.56 (2H, t, *J*=5.0 Hz), 4.18–4.07 (5H, m), 4.05–3.85 (1H, m), 3.86–3.78 (1H, m), 2.99–2.87 (2H, m), 2.08 (3H, s), 2.05 (3H, s); δ_C (100 MHz, $CDCl_3$) 170.8, 170.2, 145.6, 129.7, 126.9, 122.7, 94.5, 67.2, 66.8, 65.1, 62.8, 61.8, 50.2, 28.7, 20.9, 20.7; HRMS (ESI): found 392.1434; $C_{16}H_{23}N_3O_7Na$ $(M+Na)^+$ requires 392.1434.

5.3. 4-(3-Hydroxypropyl)-1-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (3c)

82% yield (23.0 mg) as a configuration mixture (α:β=9:1); isolated α-form was obtained as a pale yellow oil; R_f (100% EtOAc) 0.31; $[\alpha]_D^{20}$ +55.36 (*c* 0.50, $CHCl_3$); ν_{max} ($CHCl_3$): 3468, 2947, 2924, 2851, 1743, 1454, 1438, 1368, 1273, 1256, 1231, 1046, 1018, 973 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.42 (1H, s), 5.89 (1H, d, *J*=10.0 Hz), 5.77 (1H, dt, *J*=10.0, 2.0 Hz), 5.26 (1H, d, *J*=10.0 Hz), 4.99 (1H, s), 4.55 (2H, t, *J*=5.0 Hz), 4.20–4.10 (2H, m), 4.10 (1H, dd, *J*=12.0, 2.0 Hz), 3.89 (1H, dt, *J*=11.0, 5.0 Hz), 3.84 (1H, ddd, *J*=10.0, 5.0, 2.0 Hz), 3.69 (2H, t, *J*=7.0 Hz), 2.83 (2H, t, *J*=7.0 Hz), 2.08 (3H, s), 2.06 (3H, s), 1.97–1.88 (2H, m); δ_C (100 MHz, $CDCl_3$) 170.8, 170.2, 147.5, 129.8, 126.9, 121.9, 94.5, 67.3, 66.9, 65.1, 62.8, 61.8, 50.2, 31.9, 22.0, 20.9, 20.7; HRMS (ESI): found 406.1590; $C_{17}H_{25}N_3O_7Na$ $(M+Na)^+$ requires 406.1590.

5.4. 4-(1,1-Diphenyl-1-hydroxymethyl)-1-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (3d)

77% yield (28.5 mg) as a configuration mixture (α:β=9:1); isolated α-form was obtained as a pale yellow oil; R_f (50% EtOAc/*n*-hexane) 0.45; $[\alpha]_D^{20}$ +40.83 (*c* 1.01, $CHCl_3$); ν_{max} ($CHCl_3$): 3468, 2941, 2924, 2846, 1742, 1491, 1449, 1371, 1234, 1046, 1015, 973 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.40–7.24 (10H, m), 7.23 (1H, s), 5.88 (1H, d, *J*=10.0 Hz), 5.66 (1H, d, *J*=10.0 Hz), 5.25 (1H, d, *J*=10.0 Hz), 4.96 (1H, s), 4.63–4.49 (2H, m), 4.22–4.10 (2H, m), 4.08 (1H, dd, *J*=12.0, 2.0 Hz), 3.90–3.76 (2H, m), 2.05 (6H, s); δ_C (100 MHz, $CDCl_3$) 170.8, 170.2, 154.0, 145.9, 145.7, 129.8, 128.0, 127.5, 127.2, 127.2, 126.8, 123.9, 94.4, 77.2, 67.2, 66.6, 65.2, 62.9, 50.2, 20.9, 20.7; HRMS (ESI): found 530.1903; $C_{27}H_{29}N_3O_7Na$ $(M+Na)^+$ requires 530.1903.

5.5. 4-(1-Hydroxycyclobutyl)-1-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (3e)

72% yield (20.8 mg) as a configuration mixture (α:β=9:1); isolated α-form was obtained as a pale yellow oil; R_f (60% EtOAc/*n*-hexane) 0.19; $[\alpha]_D^{20}$ +50.58 (*c* 0.50, $CHCl_3$); ν_{max} ($CHCl_3$): 3445, 2926, 2851, 1743, 1463, 1449, 1432, 1371, 1230, 1046, 1015, 971 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.56 (1H, s), 5.89 (1H, d, *J*=10.0 Hz), 5.78 (1H, d, *J*=10.0 Hz), 5.24 (1H, ddd, *J*=10.0, 4.0, 2.0 Hz), 4.99 (1H, s),

4.65–4.50 (2H, m), 4.18–4.08 (3H, m), 3.93–3.84 (1H, m), 3.83–3.75 (1H, m), 2.08 (3H, s), 2.05 (3H, s), 2.02–1.92 (2H, m) 1.92–1.82 (2H, m), 1.82–1.69 (2H, m); δ_C (100 MHz, $CDCl_3$): δ 170.9, 170.2, 155.6, 129.7, 126.9, 120.7, 94.3, 69.4, 67.2, 66.7, 65.2, 62.8, 50.2, 38.2, 22.0, 20.9, 20.8; HRMS (ESI): found 418.1825; $C_{18}H_{25}N_3NaO_7$ $(M+Na)^+$ requires 418.1590.

5.6. 4-(Phenyl)-1-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (3f)

79% yield (23.1 mg) as a configuration mixture (α:β=9:1); isolated α-form was obtained as a orange s oil; R_f (50% EtOAc/*n*-hexane) 0.44; $[\alpha]_D^{20}$ +0.27 (*c* 1.00, $CHCl_3$); ν_{max} ($CHCl_3$): 2952, 2925, 1741, 1483, 1466, 1441, 1412, 1370, 1229, 1071, 1042, 968 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.88 (1H, s), 7.83 (2H, d, *J*=7.0 Hz), 7.43 (2H, t, *J*=7.0 Hz), 7.34 (1H, t, *J*=7.0 Hz), 5.90 (1H, d, *J*=10.0 Hz), 5.79 (1H, dt, *J*=10.0, 2.0 Hz), 5.26 (1H, d, *J*=10.0 Hz), 5.02 (1H, s), 4.65 (2H, t, *J*=5.0 Hz), 4.20 (1H, dt, *J*=11.0, 5.0 Hz), 4.14 (1H, dd, *J*=12.0, 5.0 Hz), 4.07 (1H, dd, *J*=12.0, 2.0 Hz), 3.95 (1H, dt, *J*=11.0, 5.0 Hz), 3.86 (1H, ddd, *J*=10.0, 5.0, 2.0 Hz), 2.06 (3H, s), 2.03 (3H, s); δ_C (100 MHz, $CDCl_3$) 170.7, 170.2, 147.7, 130.6, 129.7, 128.8, 128.3, 126.9, 125.7, 120.7, 94.5, 67.2, 66.8, 65.0, 62.8, 50.3, 20.8, 20.7; HRMS (ESI): found 424.1481; $C_{20}H_{23}N_3O_6Na$ $(M+Na)^+$ requires 424.1485.

5.7. 4-(4-Fluorophenyl)-1-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (3g)

78% yield (23.9 mg) as a configuration mixture (α:β=9:1); isolated α-form was obtained as an orange oil; R_f (80% EtOAc/*n*-hexane) 0.84; $[\alpha]_D^{20}$ +97.49 (*c* 1.00, $CHCl_3$); ν_{max} ($CHCl_3$): 2952, 2924, 2851, 1741, 1608, 1558, 1497, 1454, 1435, 1407, 1370, 1227, 1155, 1041, 973 cm^{-1}; δ_H (400 MHz, $CDCl_3$): δ 7.83 (1H, s), 7.83–7.76 (2H, m), 7.20–7.08 (2H, m), 5.91 (1H, d, *J*=10.0 Hz), 5.80 (1H, dt, *J*=10.0, 2.0 Hz), 5.27 (1H, d, *J*=10.0 Hz), 5.02 (1H, s), 4.65 (2H, t, *J*=5.0 Hz), 4.27–4.16 (1H, m), 4.14 (1H, dd, *J*=12.0, 5.0 Hz), 4.08 (1H, dd, *J*=12.0, 2.0 Hz), 4.00–3.90 (1H, m), 3.90–3.82 (1H, m), 2.06 (3H, s), 2.04 (3H, s); δ_C (100 MHz, $CDCl_3$) 170.7, 170.1, 163.9, 146.9, 135.2, 129.8, 127.5, 127.4, 126.9, 120.4, 115.9, 115.7, 94.5, 67.3, 66.8, 65.1, 62.8, 50.4, 20.9, 20.7; HRMS (ESI): found 442.1390; $C_{20}H_{22}FN_3NaO_6$ $(M+Na)^+$ requires 442.1390.

5.8. 4-(4-Methoxyphenyl)-1-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (3h)

88% yield (27.7 mg) as a configuration mixture (α:β=9:1); isolated α-form was obtained as an orange oil; R_f (80% EtOAc/*n*-hexane) 0.81; $[\alpha]_D^{20}$ +0.68 (*c* 1.00, $CHCl_3$); ν_{max} ($CHCl_3$): 2947, 2923, 2853, 1741, 1617, 1558, 1499, 1456, 1440, 1371, 1247, 1225, 1074, 1040, 973 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.79 (1H, s), 7.75 (2H, d, *J*=9.0 Hz), 6.95 (2H, d, *J*=9.0 Hz), 5.89 (1H, d, *J*=10.0 Hz), 5.78 (1H, dt, *J*=10.0, 2.0 Hz), 5.26 (1H, d, *J*=10.0 Hz), 5.02 (1H, s), 4.63 (2H, t, *J*=5.0 Hz), 4.20 (1H, dt, *J*=11.0, 5.0 Hz), 4.14 (1H, dd, *J*=12.0, 5.0 Hz), 4.08 (1H, dd, *J*=12.0, 2.0 Hz), 3.95 (1H, dt, *J*=11.0, 5.0 Hz), 3.91–3.82 (1H, m), 3.84 (3H, s), 2.06 (3H, s), 2.04 (3H, s); δ_C (100 MHz, $CDCl_3$) 170.7, 170.2, 159.6, 147.7, 135.2, 129.8, 127.0, 126.9, 119.8, 114.3, 94.5, 67.3, 66.9, 65.1, 62.8, 55.3, 50.3, 20.9, 20.7; HRMS (ESI): found 454.1597; $C_{21}H_{25}N_3O_7Na$ $(M+Na)^+$ requires 454.1590.

5.9. 4-(Phenoxymethyl)-1-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (3i)

96% yield (30.2 mg) as a configuration mixture (α:β=9:1); isolated α-form was obtained as a orange oil; R_f (50% EtOAc/*n*-hexane) 0.39; $[\alpha]_D^{20}$ +25.70 (*c* 1.00, $CHCl_3$); ν_{max} ($CHCl_3$): 2952, 2923, 2851, 1741, 1597, 1586, 1491, 1454, 1429, 1371, 1239, 1045, 1029, 1010, 987 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.73 (1H, s), 7.29 (1H, t, *J*=8.0 Hz), 7.28 (1H, t, *J*=8.0 Hz), 6.99 (2H, d, *J*=8.0 Hz), 6.97 (1H, t, *J*=8.0 Hz), 5.90 (1H, d, *J*=10.0 Hz), 5.72 (1H, dt, *J*=10.0, 2.0 Hz), 5.27 (1H, d, *J*=10.0 Hz), 5.23 (2H, s), 4.98 (1H, s), 4.66–4.57 (2H, m), 4.23–4.13 (2H, m), 4.09 (1H, dd, *J*=12.0, 2.0 Hz), 3.96–3.84 (2H, m), 2.06 (6H, s); δ_C (100 MHz, $CDCl_3$) 170.7, 170.2, 158.2, 144.3, 129.8, 129.5, 126.9, 123.6, 121.3, 114.8, 94.6, 67.3, 66.9, 65.1, 62.8, 61.9, 50.3, 20.9, 20.7; HRMS (ESI): found 454.1593; $C_{21}H_{25}N_3O_7Na$ $(M+Na)^+$ requires 454.1590.

5.10. 4-(4-Methylphenoxymethyl)-1-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (3j)

>99% yield (32.8 mg) as a configuration mixture (α:β=9:1); isolated α-form was obtained as an orange oil; R_f (50% EtOAc/*n*-hexane) 0.29; $[\alpha]_D^{20}$ +22.57 (*c* 1.02, $CHCl_3$); ν_{max} ($CHCl_3$): 2952, 2922, 2851, 1741, 1611, 1583, 1510, 1460, 1435, 1370, 1230, 1045, 1013, 976 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.71 (1H, s), 7.08 (2H, d, *J*=8.0 Hz), 6.87 (2H, d, *J*=8.0 Hz), 5.88 (1H, d, *J*=10.0 Hz), 5.71 (1H, dt, *J*=10.0, 2.0 Hz), 5.27 (1H, d, *J*=10.0 Hz), 5.19 (2H, s), 4.97 (1H, s), 4.60 (2H, dt, *J*=6.0, 4.0 Hz), 4.24–4.12 (2H, m), 4.09 (1H, dd, *J*=12.0, 2.0 Hz), 3.96–3.84 (2H, m), 2.28 (3H, s), 2.07 (3H, s), 2.06 (3H, s); δ_C (100 MHz, $CDCl_3$) 170.7, 170.2, 156.1, 144.5, 130.5, 129.9, 129.8, 126.9, 123.6, 114.6, 94.7, 67.3, 66.9, 65.1, 62.8, 62.1, 50.3, 20.9, 20.7, 20.5; HRMS (ESI): found 468.1731; $C_{22}H_{27}N_3O_7Na$ $(M+Na)^+$ requires 468.1747.

5.11. 4-(3,5-Dimethoxyphenoxymethyl)-1-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (3k)

>99% yield (35.9 mg) as a configuration mixture (α:β=9:1); isolated α-form was obtained as a pale yellow oil; R_f (50% EtOAc/*n*-hexane) 0.20; $[\alpha]_D^{20}$ +34.82 (*c* 1.02, $CHCl_3$); ν_{max} ($CHCl_3$): 2952, 2925, 2851, 1740, 1597, 1471, 1459, 1429, 1368, 1229, 1203, 1192, 1152, 1046, 976 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.73 (1H, s), 6.17 (2H, s), 6.16 (1H, s), 5.88 (1H, d, *J*=10.0 Hz), 5.73 (1H, dt, *J*=10.0, 2.0 Hz), 5.26 (1H, d, *J*=10.0 Hz), 5.16 (2H, s), 4.97 (1H, s), 4.66–4.54 (2H, m), 4.22–4.13 (2H, m), 4.10 (1H, dd, *J*=12.0, 2.0 Hz), 3.96–3.84 (2H, m), 3.75 (6H, s), 2.06 (6H, s); δ_C (100 MHz, $CDCl_3$) 170.7, 170.2, 161.5, 160.1, 144.0, 129.8, 126.9, 123.6, 94.7, 93.7, 93.4, 67.8, 66.9, 65.1, 62.8, 62.0, 55.4, 50.3, 20.9, 20.8; HRMS (ESI): found 514.1806; $C_{23}H_{29}N_3O_9Na$ $(M+Na)^+$ requires 514.1801.

5.12. 4-Vanillinyloxymethyl-1-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (3l)

>99% yield (35.9 mg) as a configuration mixture (α:β=9:1); isolated α-form was obtained as an orange oil; R_f (70% EtOAc/*n*-hexane) 0.32; $[\alpha]_D^{20}$ +16.65 (*c* 1.00, $CHCl_3$); ν_{max} ($CHCl_3$): 2952, 2924, 2851, 1740, 1678, 1594, 1583, 1510, 1488, 1452, 1427, 1371, 1260, 1233, 1074, 1045, 982 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 9.85 (1H, s), 7.81 (1H, s), 7.44 (1H, d, *J*=8.0 Hz), 7.42 (1H, s), 7.25 (1H, d, *J*=8.0 Hz), 5.89 (1H, d, *J*=10.0 Hz), 5.73 (1H, dt, *J*=10.0, 2.0 Hz), 5.40 (2H, s), 5.28 (1H, d, *J*=10.0 Hz), 4.98 (1H, s), 4.68–4.53 (2H, m), 4.24–4.12 (2H, m), 4.12 (1H, dd, *J*=12.0, 2.0 Hz), 3.97–3.84 (2H, m), 3.93 (3H, s), 2.09 (3H, s), 2.07 (3H, s); δ_C (100 MHz, $CDCl_3$) 190.9, 170.7, 170.2, 153.0, 149.9, 143.5, 130.6, 129.8, 126.9, 126.9, 123.8, 114.5, 114.0, 94.7, 67.3, 66.8, 65.1, 62.8, 56.9, 50.3, 20.9, 20.7; HRMS (ESI): found 512.1644: $C_{23}H_{27}N_3O_9Na$ $(M+Na)^+$ requires 512.1645.

5.13. 4-(Isovanillinyloxymethyl)-1-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (3m)

89% yield (31.8 mg) as a configuration mixture (α:β=9:1); isolated α-form was obtained as a yellow oil; R_f (70% EtOAc/*n*-hexane) 0.42; $[\alpha]_D^{20}$ +24.65 (*c* 1.00, $CHCl_3$); ν_{max} ($CHCl_3$): 2963, 2925, 2846, 1740, 1684, 1594, 1585, 1510, 1460, 1435, 1370, 1266, 1236, 1134, 1134, 1046, 1010, 973 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 9.85 (1H, s), 7.78 (1H, s), 7.57 (1H, s), 7.51 (1H, d, *J*=8.0 Hz), 7.00 (1H, d, *J*=8.0 Hz), 5.89 (1H, d, *J*=10.0 Hz), 5.74 (1H, dt, *J*=10.0, 2.0 Hz), 5.32 (2H, s), 5.27 (1H, d, *J*=10.0 Hz), 4.99 (1H, br s), 4.68–4.53 (2H, m), 4.24–4.12 (1H, m), 4.20 (1H, dd, *J*=12.0, 5.0 Hz), 4.12 (1H, dd, *J*=12.0, 2.0 Hz), 3.97–3.86 (2H, m), 3.94 (3H, s), 2.07 (3H, s), 2.06 (3H, s); δ_C (100 MHz, $CDCl_3$) 190.7, 170.8, 170.2, 154.9, 148.2, 143.4, 130.0, 129.8, 126.9, 126.8, 124.0, 112.1, 111.0, 94.7, 67.3, 66.9, 65.1, 62.9, 62.8, 56.2, 50.4, 20.9, 20.7; HRMS (ESI): found 512.1646; $C_{23}H_{27}N_3O_9Na$ $(M+Na)^+$ requires 512.1645.

5.14. 4-(Coumarinyloxymethyl)-1-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (3n)

83% yield (30.3 mg) as a configuration mixture (α:β=9:1); isolated α-form was obtained as a orange oil; R_f (50% EtOAc/*n*-hexane) 0.12; $[\alpha]_D^{20}$ +26.43 (*c* 1.00, $CHCl_3$); ν_{max} ($CHCl_3$): 2947, 2924, 2851, 1734, 1612, 1552, 1505, 1460, 1426, 1401, 1373, 1275, 1230, 1124, 1046, 1004, 985 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.78 (1H, s), 7.63 (1H, d, *J*=9.0 Hz), 7.39 (1H, d, *J*=9.0 Hz), 6.97–6.91 (2H, m), 6.27 (1H, d, *J*=9.0 Hz), 5.89 (1H, d, *J*=10.0 Hz), 5.73 (1H, dt, *J*=10.0, 2.0 Hz), 5.28 (1H, d, *J*=10.0 Hz), 5.26 (2H, s), 4.99 (1H, s), 4.70–4.55 (2H, m), 4.25–4.14 (1H, m), 4.18 (1H, dd, *J*=12.0, 5.0 Hz), 4.10 (1H, dd, *J*=12.0, 2.0 Hz), 3.97–3.84 (2H, m), 2.07 (3H, s), 2.06 (3H, s); δ_C (100 MHz, $CDCl_3$) 170.7, 170.1, 160.3, 160.9, 155.7, 143.3, 142.9, 129.9, 128.9, 127.8, 123.9, 113.5, 112.8, 102.1, 94.6, 67.3, 66.8, 65.1, 62.8, 62.3, 50.4, 20.9, 20.7; HRMS (ESI): found 522.1487; $C_{24}H_{25}N_3O_9Na$ $(M+Na)^+$ requires 522.1488.

5.15. 4-(Benzhydryloxymethyl)-1-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (3o)

>99% yield (38.2 mg) as a configuration mixture (α:β=9:1); isolated α-form was obtained as an orange oil; R_f (50% EtOAc/*n*-hexane) 0.43; $[\alpha]_D^{20}$ +21.17 (*c* 1.00, $CHCl_3$); ν_{max} ($CHCl_3$): 2952, 2924, 2851, 1742, 1488, 1454, 1367, 1275, 1256, 1228, 1088, 1049, 1029, 973 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.59 (1H, s), 7.34–7.15 (10H, m), 5.82 (1H, d, *J*=10.0 Hz), 5.67 (1H, dt, *J*=10.0, 2.0 Hz), 5.45 (1H, s), 5.20 (1H, d, *J*=10.0 Hz), 4.92 (1H, s), 4.60 (2H, s), 4.57–4.47 (2H, m), 4.18–4.06 (2H, m), 4.04 (1H, dd, *J*=12.0, 2.0 Hz), 3.90–3.79 (2H, m), 1.99 (3H, s), 1.96 (3H, s); δ_C (100 MHz, $CDCl_3$) 170.7, 170.2, 145.5, 141.7, 129.8, 128.4, 127.6, 123.1, 126.9, 123.5, 94.7, 82.9, 67.3, 66.9, 65.1, 62.8, 62.4, 50.2, 20.9, 20.7; HRMS (ESI): found 544.2061; $C_{28}H_{31}N_3O_7Na$ $(M+Na)^+$ requires 544.2060.

5.16. 4-(Phenacyloxymethyl)-1-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (3p)

>99% yield (34.8 mg) as a configuration mixture (α:β=9:1); isolated α-form was obtained as a pale yellow oil; R_f (50% EtOAc/*n*-hexane) 0.48; $[\alpha]_D^{20}$ +16.18 (*c* 0.50, $CHCl_3$); ν_{max} ($CHCl_3$): 2952, 2925, 2851, 1741, 1629, 1600, 1510, 1463, 1438, 1382, 1370, 1256, 1228, 1046, 1029, 1007, 962 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.80–7.70 (4H, m), 7.43 (1H, t, *J*=7.0 Hz), 7.34 (1H, t, *J*=7.0 Hz), 7.29–7.14 (2H, m), 5.85 (1H, d, *J*=10.0 Hz), 5.66 (1H, dt, *J*=10.0, 2.0 Hz), 5.33 (2H, s), 5.25 (1H, d, *J*=10.0 Hz), 4.95 (1H, s), 4.65–4.54 (2H, m), 4.22–4.11 (2H, m), 4.09 (1H, dd, *J*=12.0, 2.0 Hz), 3.96–3.84 (2H, m), 2.05 (3H, s), 2.04 (3H, s); δ_C (100 MHz, $CDCl_3$) 170.7, 170.2, 156.1, 144.1, 134.4, 129.8, 129.6, 127.6, 126.9, 126.9, 126.5, 123.9, 123.7, 118.8, 94.6, 67.3, 66.8, 65.1, 62.7, 62.0, 50.4, 20.9, 20.7; HRMS (ESI): found 496.1675; $C_{23}H_{27}N_3NaO_8$ $(M+Na)^+$ requires 496.1696.

5.17. 4-(Benzoyloxymethyl)-1-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (3q)

>99% yield (33.5 mg) as a configuration mixture (α:β=9:1); isolated α-form was obtained as a pale orange oil; R_f (50% EtOAc/*n*-hexane) 0.27; $[\alpha]_D^{20}$ +45.61 (*c* 0.52, $CHCl_3$); ν_{max} ($CHCl_3$): 2952, 2924, 2851, 1741, 1717, 1600, 1583, 1452, 1371, 1272, 1237, 1108, 1068, 1046, 1024, 971 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.03 (2H, d, *J*=8.0 Hz), 7.81 (1H, s), 7.55 (1H, t, *J*=8.0 Hz), 7.42 (2H, t, *J*=8.0 Hz), 5.88 (1H, d, *J*=10.0 Hz), 5.73 (1H, dt, *J*=10.0, 2.0 Hz), 5.47 (2H, s), 5.26 (1H, d, *J*=10.0 Hz), 4.97 (1H, s), 4.67–4.54 (2H, m), 4.22–4.13 (2H, m), 4.09 (1H, dd, *J*=12.0, 2.0 Hz), 3.95–3.84 (2H, m), 2.06 (6H, s); δ_C (100 MHz, $CDCl_3$) 170.7, 170.2, 166.5, 142.9, 133.3, 129.8, 129.7, 128.4, 126.8, 124.4, 94.7, 67.3, 66.8, 65.1, 62.8, 58.1, 50.3, 20.9, 20.8; HRMS (ESI): found 482.1539; $C_{22}H_{25}N_3O_8Na$ $(M+Na)^+$ requires 482.1539.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.09.026.

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