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One-pot synthesis of *O*-glycosyl triazoles by O-glycosylation–click reaction

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ABSTRACT

2,3-Unsaturated-glycosyl triazoles were synthesized in a simple one-pot process under mild condition via tandem O-glycosylation using iodine promoter and a mild CuAAC reaction. Thirty examples of a variety of *O*-glycosyl triazoles were obtained in good to excellent yields and α-anomeric selectivity.

1. Introduction

1,2,3-Triazole moiety has proven to be an important structural scaffold in biomaterials[1] for drug discovery that show a broad range of biological activities such as anti-bacterial, anti-viral, anti-fungal, anti-parasitic, anti-HIV, anti-tumor, and anti-tuberculosis. In addition, triazoles are advantageously employed in the fields of materials science and polymer chemistry.[2] Consequently, interest in the development of efficient methods for the synthesis of triazoles, bearing multiple and diverse substitution patterns, has continued. The most prominent method to synthesize 1,2,3-triazole is the Cu(I)-catalyzed Huisgen 1,3-dipolar cycloaddition of azide and alkyne (CuAAC), the most widely used click reaction.[3]

In the field of carbohydrate research, several attempts have been made to utilize click chemistry for the synthesis of bioactive triazole-glycosides and consequently screening for their biological data.[4] 1,2,3-Triazole-glycosides have been reported to posses galactin-3 inhibitory effect[4b] in which galectin-3 has been demonstrated to be involved in cancer and inflammation. Triazole-glycosides can be generally prepared from the reaction of propargyl glycosides and azides or azido glycosides and alkynes.[5] For example, Miller et al.[6a] synthesized analogues of neoglycopeptide using microwave-assisted CuAAC reaction of a propargylated glycoside with an azido-functionalized amino acid. Alternatively, Salunke et al.[6b] reported the synthesis of 1,2,3-benzotriazole-linked glycoconjugates via CuAAC reactions of azido glycosides with various terminal alkynes.

Recently, one-pot synthetic strategies have become a very attractive alternative to traditional sequential approaches for preparing triazole compounds. Muller reported the one-pot three component Sonogashira coupling–TMS–deprotection–CuAAC sequence for the rapid synthesis of triazolyl NH-heterocycle.[7] Yadav et al.,[8] reported the tandem synthesis of 2,3-unsaturated-*N*-glycosyl triazoles which was started with glycosylation of glucal with azide followed by click reaction of the resulting azidoglycoside to obtain the product. However, Yadav's method provided only one type of target with a certain triazole ring bearing directly to the glycoside. To search the new methods for the synthesis of diverse triazole glycosides, alternative ways that could lead to more targets with convenient procedures are desired. In this work, we report herein a concise synthetic approach to new analogues of 2,3-unsaturated-*O*-glycosyl triazoles (**2**) using one pot reaction involving an iodine catalyzed glycosylation followed by click reaction (Scheme 1). 2,3-Unsaturated-*O*-glycosyl triazoles have been reported to posses α-glucosidase, glycogen phosphorylase, and glucose-6-phosphatase inhibitory activities which is important in development of new anti-diabetic agents.[9]

In our previous reports, we demonstrated a practical approach to 2,3-unsaturated *O*-glycosides via Ferrier reaction[10] from glycal by iodine catalyst. Several *O*-glycosides could be obtained in high yield and high stereoselective, for example *O*-propargyl, butynyl, and pentynyl glycosides could be obtained in 94–99% yields in the presence of iodine as a promoter.[11] We envisioned that molecular iodine catalyst in the glycosidation step could be combined with Meldal's copper catalyzed [3+2] cycloaddition of azides and alkynes to produce glycosyl triazoles in one pot.

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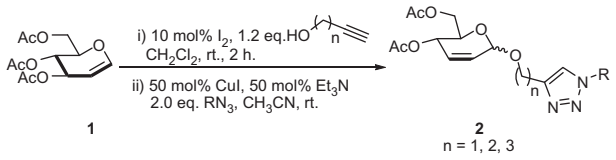
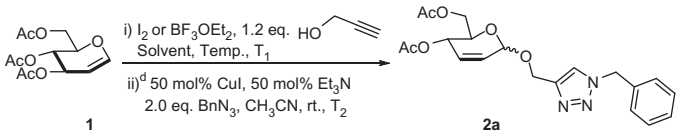


Scheme 1. Synthesis of 2,3-unsaturated-*O*-glycosyl triazoles.

Table 1
Optimization of tandem O-glycosidation–Click reactions[a]



Entry	Lewis acid (equiv)	Solvent[b]	Temp. (°C)	T_1/T_2 (h)	Yield[c] (%)
1	I_2 (0.5)	CH_3CN	rt	2/3	27
2	I_2 (0.1)	CH_3CN	rt	2/3	45
3	I_2 (0.1)	CH_3CN/CH_2Cl_2 (1:1)	rt	2/3	82
4	I_2 (0.1)	CH_2Cl_2	rt	2/3	86
5	BF_3OEt_2 (0.2)	CH_3CN	0	0.5/24	94

[a] All reactions were carried out with 0.146 mmol of D-glucal (**1**), concentration 0.146 M.
[b] Solvent used for step 1.
[c] Isolated yield.
[d] The reaction was completed in longer time when using CuI less than 50 mol %.

2. Results and discussion

We desired the synthesis involving glycosylation of D-glucal (**1**) with different alkynyl alcohols subsequently followed by click reaction with various azides to obtain the target *O*-glycosyl triazoles. The click reaction in the second step was carried out using copper iodide as the Cu(I) source and triethylamine and acetonitrile as the solvent.

First, tandem glycosylation of D-glucal (**1**) with propargyl alcohol followed by CuACC reaction with benzyl triazole in acetonitrile was studied as a model reaction as shown in Table 1. Iodine was used as catalyst in glycosylation step and to study the ability to allow tandem glycosylation–click reaction. When using 0.5 equiv of iodine in acetonitrile, product **2a** was obtained in low yield (entry 1). Using iodine 0.1 equiv, triazole glycoside **2a** was obtained in moderate yield (entry 2). Among the reactions using iodine, the use of dichloromethane as solvent was found to provide triazole glycoside in the highest yields (entries 3 and 4). $BF_3{\cdot}OEt_2$ was used as catalyst to compare the activity with iodine both in the first step and the ability to allow tandem click reaction in the second step. It was observed that *O*-glycoside formation was completed in 30 min on TLC, however finishing the second step of click reaction was observed after 24 h (entry 5).

In order to determine the scope of this one pot reaction, the reaction sequence involved glycosylation of D-glucal with propargyl, butynyl, or pentynyl alcohols followed by CuACC reaction using various benzyl and long-chain aliphatic azides which were studied under the optimized reaction conditions (Table 1, entry 4). As shown in Table 2, the tandem glycosylation–click reactions of benzylazide with butynyl and pentynyl-glycosides were performed smoothly as propargyl-glycoside to give products **2b** and **2c** in good yields (entries 2 and 3). Changing to electron deficient nitro-benzyl azides and electron rich methoxy-and di-methoxy benzyl azides did not show significant differences in terms of the reactivity and reaction yields. The reaction went smoothly with *m*-nitrobenzylazide to complete conversion in the second step in 1 h, producing **4a**–**4c** in 83–96% yields (entries 7–9). For the synthesis of triazole-glycosides with different substituents on the N-1 atom of triazole moiety, the click reaction was extended using aliphatic azides. The reaction of phenyl ethyl azide works well under this one pot condition to obtain high yield of product in shorter time (entries 19–21). Long chain aliphatic azides such as lauryl, omega-undecylenyl, and oleyl azides can be proceeded smoothly to obtain the product with comparable yield as shown in entries 22–30 (Table 2). However, the reactions of long carbon chain oleyl azide (entries 28–30) were carried out in longer time to complete the reaction.

3. Conclusion

In conclusion, we have developed an efficient and convenient method for the synthesis of 2,3-unsaturated-glycosyl triazoles. This method used inexpensive iodine reagent to promote the glycosylation and allows for subsequent copper catalyzed click reaction to proceed in one pot which limiting the experimental, work-up and purification step. Thirty examples of new triazole-glycosides were obtained in high yields, with α-anomeric selectivity.

4. Experimental

4.1. General methods

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

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

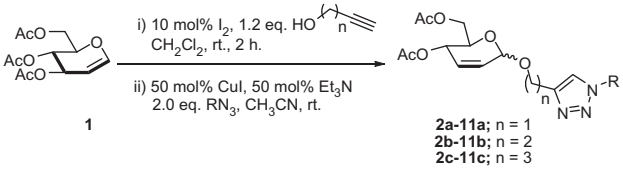
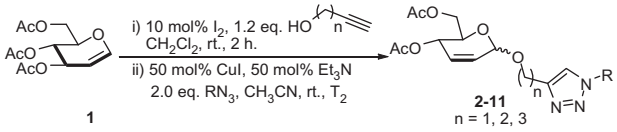
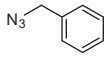
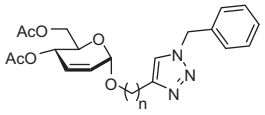
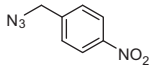
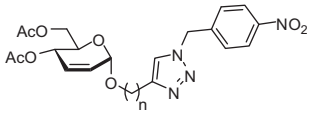
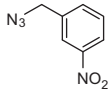
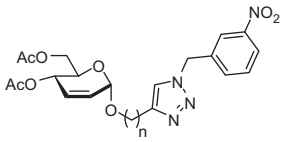
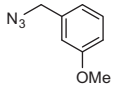
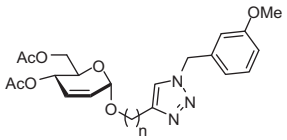
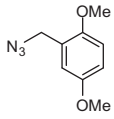
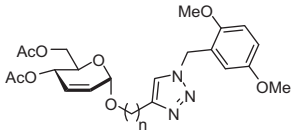
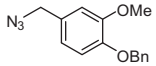
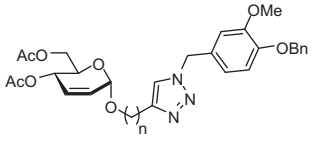
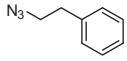
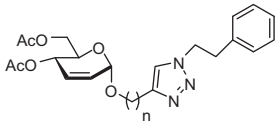
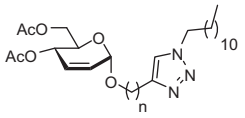
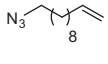
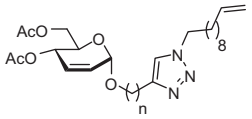
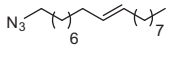
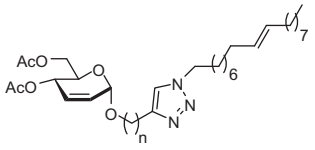


Table 2
O-Glycosidation–Click reactions

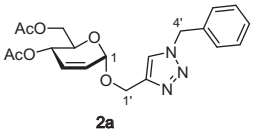


Entry	Azide[a]	Major product	Yield[b,c] (%)	Time[d] (T_2)/h
1			**2a**, n = 1,86	3
2			**2b**, n = 2, 73	5
3			**2c**, n = 3, 79	5
4			**3a**, n = 1,71	5
5			**3b**, n = 2, 84	2
6			**3c**, n = 3, 71	2
7			**4a**, n = 1,96	1
8			**4b**, n = 2, 84	1
9			**4c**, n = 3, 83	1
10			**5a**, n = 1,78	3
11			**5b**, n = 2, 91	3
12			**5c**, n = 3, 74	2
13			**6a**, n = 1,70	3
14			**6b**, n = 2, 89	2
15			**6c**, n = 3, 91	5
16			**7a**, n = 1,79	2
17			**7b**, n = 2, 73	2
18			**7c**, n = 3, 73	2
19			**8a**, n = 1,98	1
20			**8b**, n = 2, 79	1
21			**8c**, n = 3, 75	1
22			**9a**, n = 1,85	2
23			**9b**, n = 2, >99	2
24			**9c**, n = 3, 90	2
25			**10a**, n = 1,86	2
26			**10b**, n = 2, 82	2
27			**10c**, n = 3, 73	2
28			**11a**, n = 1,76	4
29			**11b**, n = 2, 75	4
30			**11c**, n = 3, 71	4

[a] Azides were freshly prepared.
[b] Yields are given for isolated compound.
[c] Mixture of isomers, α:β = 9:1 for n = 1, α:β = 10:1 for n = 2, α:β = 12:1 for n = 3 (determined by ^{1}H NMR of the crude reaction mixture).
[d] T_2 = Reaction time of the second step.

To a stirred solution of 3,4,6-tri-*O*-acetyl-D-glucal **1** (40.0 mg, 0.146 mmol) in dried CH_2Cl_2 (1.0 mL) were added alkynyl alcohol (0.176 mmol) and iodine powder (3.7 mg, 0.015 mmol) under gas-nitrogen at room temperature. Stirring was continued at room temperature for 2 h. After TLC showed the completed conversion, the volatiles were removed to obtain the residue which was dissolved with CH_3CN (1.0 mL), followed by the addition of CuI (13.9 mg, 0.073 mmol), Et_3N (10.2 μL, 0.073 mmol), and alkyl azide (0.292 mmol) respectively. The reaction mixture was stirred at room temperature for 1–5 h. After TLC showed the completed 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 (EtOAc/*n*-hexane) to give the 2,3-unsaturated *O*-glycosyl triazole products **2–11** in good to excellent yields.

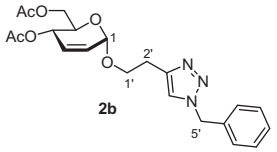
4.3. Spectral data of 2,3-unsaturated *O*-glycosyl triazole derivatives



2a

4.3.1. 1-Benzyl-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxymethyl)-1,2,3-1*H*-triazole (2a)

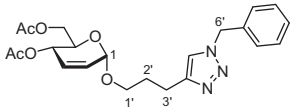
Pale yellow solid; α-anomer R_f = 0.43 (50% EtOAc/*n*-hexane); mp 52–54 °C; $[\alpha]_D^{24}$ +54.3 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$): 2923, 2848, 1741, 1657, 1632, 1494, 1450, 1428, 1370, 1228, 1038, 964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.49 (s, 1H, triazolyl-H), 7.41–7.36 (m, 3H, Ph), 7.32–7.27 (m, 2H, Ph), 5.90 (br d, 1H, *J* = 10.0 Hz, H-2), 5.82 (ddd, 1H, *J* = 10.0, 2.5, 1.5 Hz, H-3), 5.54 (s, 2H, C*H*$_2$Ph), 5.34 (ddd, 1H, *J* = 10.0, 2.5, 1.0 Hz, H-4), 5.17 (br s, 1H, H-1), 4.90 (d, 1H, *J* = 12.0 Hz, H-1′a), 4.71 (d, 1H, *J* = 12.0 Hz, H-1′b), 4.25 (dd, 1H, *J* = 12.0, 5.0 Hz, H-6a), 4.16 (dd, 1H, *J* = 12.0, 2.5 Hz, H-6b), 4.13 (ddd, 1H, *J* = 10.0, 5.0, 2.5 Hz, H-5), 2.01 (s, 3H, OAc), 2.00 (s, 3H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.78 (C═O), 170.23 (C═O), 144.92 (C-2′), 134.51 (Ph), 129.52 (C-2), 129.15 (2 × Ph), 128.82 (Ph), 128.19 (2 × Ph), 127.44 (C-3), 122.51 (C-3′), 93.87 (C-1), 67.07 (C-5), 65.25 (C-4), 62.82 (C-6), 61.64 (C-1′), 54.20 (C-4′), 20.93 (CH_3), 20.79 (CH_3); HRMS (ESI) *m/z* calcd for $C_{20}H_{23}N_3O_6Na$ $[M+Na]^+$ 424.1485, found 424.1484.



2b

4.3.2. 1-Benzyl-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (2b)

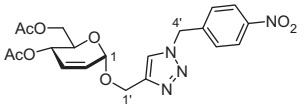
Pale orange oil; α-anomer R_f = 0.39 (50% EtOAc/*n*-hexane); $[\alpha]_D^{23}$ +57.1 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$): 2923, 2848, 1740, 1657, 1633, 1465, 1454, 1421, 1370, 1275, 1260, 1225, 1038, 971 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.42–7.24 (m, 5H, Ph), 7.32 (br s, 1H, triazolyl-H), 5.88 (br d, 1H, *J* = 10.0 Hz, H-2), 5.76 (dm, 1H, *J* = 10.0 Hz, H-3), 5.52 (s, 2H, C*H*$_2$Ph), 5.29 (d, 1H, *J* = 10.0 Hz, H-4), 5.03 (br s, 1H, H-1), 4.21 (dd, 1H, *J* = 12.0, 5.5 Hz, H-6a), 4.12 (dd, 1H, *J* = 12.0, 2.0 Hz, H-6b), 4.08–3.97 (m, 2H, H-5, H-1′a), 3.84–3.75 (m, 1H, H-1′b), 3.05 (t, 2H, *J* = 6.0 Hz, H-2′), 2.01 (s, 3H, OAc), 1.97 (s, 3H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.80 (C═O), 170.22 (C═O), 145.33 (C-3′), 134.83 (Ph), 129.24 (C-2), 129.08 (2 × Ph), 128.69 (Ph), 128.00 (2 × Ph), 127.60 (C-3), 121.60 (C-4′), 94.52 (C-1), 67.63 (C-1′), 67.00 (C-5), 65.31 (C-4), 62.91 (C-6), 54.11 (C-5′), 26.58 (C-2′), 20.97 (CH_3), 20.76 (CH_3); HRMS (ESI) *m/z* calcd for $C_{21}H_{25}N_3O_6Na$ $[M+Na]^+$ 438.1641, found: 438.1599.



2c

4.3.3. 1-Benzyl-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxypropyl)-1,2,3-1*H*-triazole (2c)

Pale yellow oil; α-anomer R_f = 0.42 (50% EtOAc/*n*-hexane); $[\alpha]_D^{24}$ +66.4 (*c* 1.02, $CHCl_3$); IR ($CHCl_3$): 2928, 2870, 1740, 1550, 1497, 1456, 1435, 1370, 1230, 1039, 978 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.39 (br s, 1H, triazolyl-H), 7.39–7.35 (m, 2H, Ph), 7.30–7.22 (m, 3H, Ph), 5.89 (br d, 1H, *J* = 10.0 Hz, H-2), 5.82 (ddd, 1H, *J* = 10.0, 3.0, 2.0 Hz, H-3), 5.51 (s, 2H, C*H*$_2$Ph), 5.32 (ddd, 1H, *J* = 10.0, 3.0, 2.0 Hz, H-4), 5.02 (br s, 1H, H-1), 4.24 (dd, 1H, *J* = 12.0, 5.0 Hz, H-6a), 4.17 (dd, 1H, *J* = 12.0, 2.5 Hz, H-6b), 4.10 (ddd, 1H, *J* = 10.0, 5.0, 2.5 Hz, H-5), 3.82 (dt, 1H, *J* = 10.0, 6.0 Hz, H-1′a), 3.56 (dt, 1H, *J* = 10.0, 6.0 Hz, H-1′b), 2.85–2.76 (m, 2H, H-3′), 2.10 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.04–1.95 (m, 2H, H-2′); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.79 (C═O), 170.28 (C═O), 147.94 (C-4′), 134.89 (Ph), 129.08 (2 × Ph), 129.06 (C-2), 128.68 (Ph), 128.01 (2 × Ph), 127.82 (C-3), 120.63 (C-5′), 94.43 (C-1), 67.94 (C-1′), 66.94 (C-5), 65.32 (C-4), 63.00 (C-6), 54.04 (C-6′), 29.38 (C-2′), 22.49 (C-3′), 20.97 (CH_3), 20.77 (CH_3); HRMS (ESI) *m/z* calcd for $C_{22}H_{27}N_3O_6Na$ $[M+Na]^+$ 452.1798, found: 452.1793.

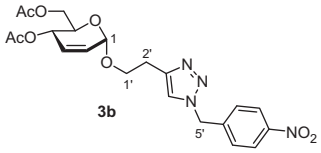


3a

4.3.4. 1-(4-Nitrobenzyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxymethyl)-1,2,3-1*H*-triazole (3a)

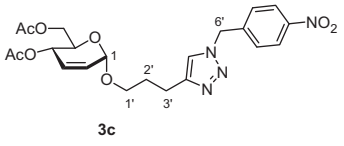
Orange solid; α-anomer R_f = 0.24 (50% EtOAc/*n*-hexane); mp 78–80 °C; $[\alpha]_D^{23}$ +31.2 (*c* 1.02, $CHCl_3$); IR ($CHCl_3$): 2922, 2852, 1741, 1657, 1632, 1524, 1465, 1421, 1260, 1229, 1038, 967 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, 2H, *J* = 8.0 Hz, Ph), 7.61 (br s, 1H, triazolyl-H), 7.44 (d, 2H, *J* = 8.0 Hz, Ph), 5.91 (d, 1H, *J* = 10.0 Hz, H-2), 5.83 (d, 1H, *J* = 10.0 Hz, H-3), 5.66 (s, 2H, C*H*$_2$Ph), 5.34 (d, 1H, *J* = 10.0 Hz, H-4), 5.19 (br s, 1H, H-1), 4.92 (d, 1H, *J* = 12.0 Hz, H-1′a), 4.74 (d, 1H, *J* = 12.0 Hz, H-1′b), 4.23 (dd, 1H, *J* = 12.0, 5.0 Hz, H-6a), 4.17 (dd, 1H, *J* = 12.0, 2.0 Hz, H-6b), 4.15–4.08 (m, 1H, H-5), 2.03 (s, 3H, OAc), 2.01 (s, 3H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.80 (C═O), 170.23 (C═O), 148.13 (Ph), 145.50 (C-2′), 141.51 (Ph), 129.68 (C-2), 128.72 (2 × Ph), 127.28 (C-3), 124.32 (2 × Ph), 122.97 (C-3′), 94.03 (C-1), 67.07 (C-5),

65.26 (C-4), 62.77 (C-6), 61.61 (C-1′), 53.16 (C-4′), 20.93 (CH_3), 20.81(CH_3); HRMS (ESI) *m/z* calcd for $C_{20}H_{22}N_4O_8Na$ $[M+Na]^+$ 469.1335, found: 469.1282.



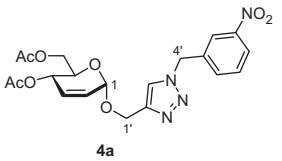
4.3.5. 1-(4-Nitrobenzyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (3b)

Pale yellow oil; α-anomer R_f = 0.24 (50% EtOAc/*n*-hexane); $[\alpha]_D^{26}$ +70.9 (*c* 0.26, $CHCl_3$); IR ($CHCl_3$): 2922, 2852, 1739, 1659, 1633, 1521, 1468, 1421, 1421, 1346, 1273, 1260, 1225, 1036, 971 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.25 (d, 2H, *J* = 9.0 Hz, Ph), 7.44 (br s, 1H, triazolyl-H), 7.41 (d, 2H, *J* = 9.0 Hz, Ph), 5.89 (br d, 1H, *J* = 10.0 Hz, H-2), 5.79 (dt, 1H, *J* = 10.0, 2.0 Hz, H-3), 5.66 (s, 2H, C*H*$_2$Ph), 5.31 (dm, 1H, *J* = 10.0 Hz, H-4), 5.06 (br s, 1H, H-1), 4.22 (dd, 1H, *J* = 12.0, 5.0 Hz, H-6a), 4.17 (dd, 1H, *J* = 12.0, 2.5 Hz, H-6b), 4.12–4.04 (m, 1H, H-1′a), 4.10 (ddd, 1H, *J* = 10.0, 5.0, 2.5 Hz, H-5), 3.87–3.78 (m, 1H, H-1′b), 3.09 (t, 2H, *J* = 6.0 Hz, H-2′), 2.10 (s, 3H, OAc), 2.08 (s, 3H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.84 (C═O), 170.24 (C═O), 148.03 (Ph), 145.95 (C-3′), 141.94 (Ph), 129.40 (C-2), 128.49 (2 × Ph), 127.49 (C-3), 124.27 (2 × Ph), 121.89 (C-4′), 94.54 (C-1), 67.49 (C-1′), 65.00 (C-5), 65.34 (C-4), 62.90 (C-6), 53.00 (C-5′), 26.57 (C-2′), 20.97 (CH_3), 20.79 (CH_3); HRMS (ESI) *m/z* calcd for $C_{21}H_{24}N_4O_8Na$ $[M+Na]^+$ 483.1492, found: 483.1435.



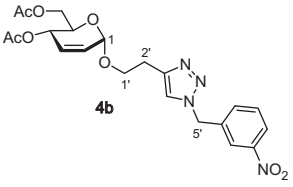
4.3.6. 1-(4-Nitrobenzyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxypropyl)-1,2,3-1*H*-triazole (3c)

Pale yellow oil; α-anomer R_f = 0.28 (50% EtOAc/*n*-hexane); $[\alpha]_D^{26}$ +32.7 (*c* 0.25, $CHCl_3$); IR ($CHCl_3$): 2922, 2848, 1738, 1657, 1627, 1522, 1465, 1421, 1346, 1275, 1260, 1229, 1039, 975 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, 2H, *J* = 8.5 Hz, Ph), 7.41 (d, 2H, *J* = 8.5 Hz, Ph), 7.34 (br s, 1H, triazolyl-H), 5.90 (br d, 1H, *J* = 10.0 Hz, H-2), 5.83 (dt, 1H, *J* = 10.0, 3.0 Hz, H-3), 5.63 (s, 2H, C*H*$_2$Ph), 5.33 (ddd, 1H, *J* = 10.0, 3.0, 2.0 Hz, H-4), 5.03 (br s, 1H, H-1), 4.24 (dd, 1H, *J* = 12.0, 5.0 Hz, H-6a), 4.17 (dd, 1H, *J* = 12.0, 2.5 Hz, H-6b), 4.10 (ddd, 1H, *J* = 10.0, 5.0, 2.5 Hz, H-5), 3.84 (dt, 1H, *J* = 10.0, 6.0 Hz, H-1′a), 3.58 (dt, 1H, *J* = 10.0, 6.0 Hz, H-1′b), 2.89–2.80 (m, 2H, H-3′), 2.10 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.06–1.97 (m, 2H, H-2′); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.84 (C═O), 170.30 (C═O), 148.49 (C-4′), 148.03 (Ph), 141.96 (Ph), 129.18 (C-2), 128.51 (2 × Ph), 127.72 (C-3), 124.30 (2 × Ph), 120.96 (C-5′), 94.45 (C-1), 67.85 (C-1′), 66.91 (C-5), 65.27 (C-4), 62.93 (C-6), 52.99 (C-6′), 29.33 (C-2′), 22.46 (C-3′), 21.00 (CH_3), 20.82 (CH_3); HRMS (ESI) *m/z* calcd for $C_{22}H_{26}N_4O_8Na$ $[M+Na]^+$ 497.1648, found: 497.1613.



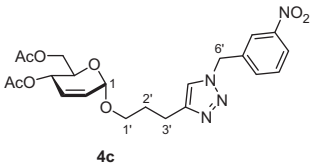
4.3.7. 1-(3-Nitrobenzyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxymethyl)-1,2,3-1*H*-triazole (4a)

Pale yellow solid; α-anomer R_f = 0.32 (50% EtOAc/*n*-hexane); mp: 96–98 °C; $[\alpha]_D^{25}$ +36.8 (*c* 0.5, $CHCl_3$); IR ($CHCl_3$): 2922, 2851, 1740, 1659, 1633, 1533, 1468, 1421, 1351, 1230, 1039, 964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.24 (d, 1H, *J* = 8.0 Hz, Ph), 8.19 (br s, 1H, Ph), 7.69 (br s, 1H, triazolyl-H), 7.64 (d, 1H, *J* = 8.0 Hz, Ph), 7.59 (t, 1H, *J* = 8.0 Hz, Ph), 5.91 (d, 1H, *J* = 10.0 Hz, H-2), 5.83 (d, 1H, *J* = 10.0 Hz, H-3), 5.67 (s, 2H, C*H*$_2$Ph), 5.34 (d, 1H, *J* = 10.0 Hz, H-4), 5.19 (br s, 1H, H-1), 4.92 (d, 1H, *J* = 10.0 Hz, H-1′a), 4.74 (d, 1H, *J* = 10.0 Hz, H-1′b), 4.24 (dd, 1H, *J* = 12.0, 5.0 Hz, H-6a), 4.17 (dd, 1H, *J* = 12.0, 2.0 Hz, H-6b), 4.12 (ddd, 1H, *J* = 10.0, 5.0, 2.0 Hz, H-5), 2.02 (s, 3H, OAc), 2.00 (s, 3H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.82 (C═O), 170.24 (C═O), 148.57 (Ph), 146.00 (C-2′), 136.63 (Ph), 134.03 (Ph), 130.33 (Ph), 129.65 (C-2), 127.31 (C-3), 123.76 (Ph), 122.95 (Ph, C-3′), 94.02 (C-1), 67.06 (C-5), 65.27 (C-4), 62.78 (C-6), 61.34 (C-1′), 53.17 (C-4′), 20.93 (CH_3), 20.81 (CH_3); HRMS (ESI) *m/z* calcd for $C_{20}H_{22}N_4O_8Na$ $[M+Na]^+$ 469.1335, found: 469.1273.



4.3.8. 1-(3-Nitrobenzyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (4b)

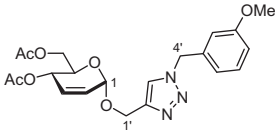
Pale yellow oil; α-anomer R_f = 0.35 (50% EtOAc/*n*-hexane); $[\alpha]_D^{25}$ +39.2 (*c* 0.5, $CHCl_3$); IR ($CHCl_3$): 2923, 2852, 1740, 1659, 1632, 1531, 1468, 1421, 1350, 1229, 1038, 971 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.26–8.21 (m, 1H, Ph), 8.16 (br s, 1H, Ph), 7.63–7.55 (m, 2H, Ph), 7.43 (br s, 1H, triazolyl-H), 5.89 (br d, 1H, *J* = 10.0 Hz, H-2), 5.79 (ddd, 1H, *J* = 10.0, 3.0, 2.0 Hz, H-3), 5.65 (s, 2H, C*H*$_2$Ph), 5.30 (ddd, 1H, *J* = 10.0, 3.0, 2.0 Hz, H-4), 5.06 (br s, 1H, H-1), 4.22 (dd, 1H, *J* = 12.5, 5.0 Hz, H-6a), 4.16 (dd, 1H, *J* = 12.5, 2.0 Hz, H-6b), 4.12–4.06 (m, 1H, H-1′a), 4.03 (ddd, 1H, *J* = 10.0, 5.0, 2.0 Hz, H-5), 3.82 (ddd, 1H, *J* = 10.0, 6.0, 3.0 Hz, H-1′b), 3.08 (t, 2H, *J* = 6.0 Hz, H-2′), 2.10 (s, 3H, OAc), 2.08 (s, 3H, OAc); [v] (100 MHz, $CDCl_3$): δ 170.82 (C═O), 170.24 (C═O), 148.58 (Ph), 145.97 (C-3′), 136.98 (Ph), 133.98 (Ph), 130.26 (Ph), 129.38 (C-2), 127.51 (C-3), 123.69 (Ph), 122.75 (Ph), 121.76 (C-4′), 94.57 (C-1), 67.52 (C-1′), 67.01 (C-5), 65.36 (C-4), 62.94 (C-6), 53.02 (C-5′), 26.59 (C-2′), 20.97 (CH_3), 20.77 (CH_3); HRMS (ESI) *m/z* calcd for $C_{21}H_{24}N_4O_8Na$ $[M+Na]^+$ 483.1492, found: 483.1448.



4c

4.3.9. 1-(3-Nitrobenzyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxypropyl)-1,2,3-1*H*-triazole (4c)

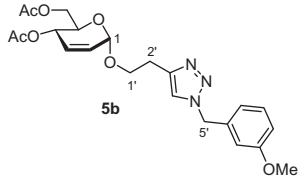
Pale orange oil; α-anomer R_f = 0.25 (50% EtOAc/*n*-hexane); $[\alpha]_D^{24}$ +43.1 (*c* 0.5, $CHCl_3$); IR ($CHCl_3$): 2922, 2848, 1734, 1528, 1454, 1365, 1349, 1273, 1260, 1222, 1035, 975 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 8.25–8.20 (m, 1H, Ph), 8.15 (br s, 1H, Ph), 7.61–7.55 (m, 3H, triazolyl-H, Ph), 5.89 (br d, 1H, *J* = 10.0 Hz, H-2), 5.83 (dm, 1H, *J* = 10.0 Hz, H-3), 5.65 (s, 2H, C*H*$_2$Ph), 5.32 (d, 1H, *J* = 10.0 Hz, H-4), 5.03 (br s, 1H, H-1), 4.24 (dd, 1H, *J* = 12.0, 5.0 Hz, H-6a), 4.18 (dd, 1H, *J* = 12.0, 2.0 Hz, H-6b), 4.15–4.07 (m, 1H, H-5), 3.91–3.79 (m, 1H, H-1′a), 3.66–3.54 (m, 1H, H-1′b), 2.93–2.75 (m, 2H, H-3′), 2.10 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.11–2.07 (m, 2H, H-2′); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.82 (C=O), 170.28 (C=O), 148.50 (Ph), 148.48 (C-4′), 137.04 (Ph), 133.81 (Ph), 130.26 (Ph), 129.14 (C-2), 127.75 (C-3), 123.67 (Ph), 122.75 (Ph), 120.88 (C-5′), 94.46 (C-1), 67.85 (C-1′), 67.23 (C-5), 65.33 (C-4), 62.97 (C-6), 52.98 (C-6′), 29.32 (C-2′), 22.45 (C-3′), 20.97 (CH_3), 20.78 (CH_3); HRMS (ESI) *m/z* calcd for $C_{22}H_{26}N_4O_8H$ $[M+H]^+$ 475.1857, found: 475.1784.



5a

4.3.10. 1-(3-Methoxybenzyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxymethyl)-1,2,3-1*H*-triazole (5a)

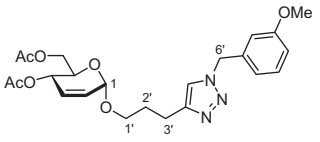
Pale yellow solid; α-anomer R_f = 0.27 (50% EtOAc/*n*-hexane); mp: 74–76 °C; $[\alpha]_D^{24}$ +50.0 (*c* 1.02, $CHCl_3$); IR ($CHCl_3$): 2922, 2848, 1735, 1649, 1598, 1487, 1457, 1432, 1365, 1260, 1233, 1038, 967 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.49 (s, 1H, triazolyl-H), 7.29 (t, 1H, *J* = 8.0 Hz, Ph), 6.91–6.83 (m, 2H, Ph), 6.81 (br s, 1H, Ph), 5.89 (br d, 1H, *J* = 10.0 Hz, H-2), 5.82 (dt, 1H, *J* = 10.0, 2.5 Hz, H-3), 5.44 (s, 2H, C*H*$_2$Ph), 5.32 (ddd, 1H, *J* = 10.0, 2.5, 1.0 Hz, H-4), 5.16 (br s, 1H, H-1), 4.89 (d, 1H, *J* = 12.0 Hz, H-1′a), 4.70 (d, 1H, *J* = 12.0 Hz, H-1′b), 4.24 (dd, 1H, *J* = 12.0, 5.0 Hz, H-6a), 4.15 (dd, 1H, *J* = 12.0, 2.0 Hz, H-6b), 4.15–4.08 (m, 1H, H-5), 3.80 (s, 3H, OMe), 2.08 (s, 3H, OAc), 2.07 (s, 3H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.80 (C=O), 170.25 (C=O), 160.13 (Ph), 144.89 (C-2′), 135.91 (Ph), 130.22 (Ph), 129.50 (C-2), 127.44 (C-3), 122.57 (C-3′), 120.37 (Ph), 114.20 (Ph), 113.88 (Ph), 93.86 (C-1), 67.06 (C-5), 65.25 (C-4), 62.82 (C-6), 61.61 (C-1′), 55.31 (C-4′), 54.13 (OMe), 20.93 (CH_3), 20.79 (CH_3); HRMS (ESI) *m/z* calcd for $C_{21}H_{25}N_3O_7Na$ $[M+Na]^+$ 454.1590, found: 454.1547.



5b

4.3.11. 1-(3-Methoxybenzyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (5b)

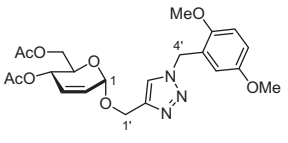
Pale yellow oil; α-anomer R_f = 0.46 (50% EtOAc/*n*-hexane); $[\alpha]_D^{26}$ +80.7 (*c* 0.51, $CHCl_3$); IR ($CHCl_3$): 2923, 2848, 1723, 1659, 1627, 1601, 1587, 1410, 1369, 1321, 1273, 1260, 1225, 1041, 975 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.33 (br s, 1H, triazolyl-H), 7.29 (t, 1H, *J* = 8.0 Hz, Ph), 6.89 (dd, 1H, *J* = 8.0, 2.5 Hz, Ph), 6.85 (d, 1H, *J* = 8.0 Hz, Ph), 6.79 (br s, 1H, Ph), 5.88 (br d, 1H, *J* = 10.0 Hz, H-2), 5.77 (dt, 1H, *J* = 10.0, 2.5 Hz, H-3), 5.48 (s, 2H, C*H*$_2$Ph), 5.29 (ddd, 1H, *J* = 10.0, 2.5, 1.0 Hz, H-4), 5.03 (br s, 1H, H-1), 4.21 (dd, 1H, *J* = 12.0, 5.5 Hz, H-6a), 4.12 (dd, 1H, *J* = 12.0, 2.0 Hz, H-6b), 4.08–3.98 (m, 1H, H-1′a), 4.01 (ddd, 1H, *J* = 10.0, 5.5, 2.0 Hz, H-5), 3.83–3.73 (m, 1H, H-1′b), 3.80 (s, 3H, OMe), 3.04 (t, 2H, *J* = 6.0 Hz, H-2′), 2.10 (s, 3H, OAc), 2.06 (s, 3H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.82 (C=O), 170.26 (C=O), 160.10 (Ph), 145.36 (C-3′), 136.38 (Ph), 130.15 (Ph), 129.23 (C-2), 127.61 (C-3), 121.54 (C-4′), 120.17 (Ph), 114.00 (Ph), 113.73 (Ph), 94.53 (C-1), 67.66 (C-1′), 67.00 (C-5), 65.29 (C-4), 62.91 (C-6), 55.30 (OMe), 54.00 (C-5′), 26.53 (C-2′), 20.97 (CH_3), 20.76 (CH_3); HRMS (ESI) *m/z* calcd for $C_{22}H_{27}N_3O_7Na$ $[M+Na]^+$ 468.1747, found: 468.1706.



5c

4.3.12. 1-(3-Methoxybenzyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxypropyl)-1,2,3-1*H*-triazole (5c)

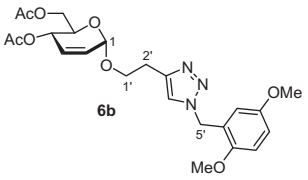
Pale yellow oil; α-anomer R_f = 0.29 (50% EtOAc/*n*-hexane); $[\alpha]_D^{24}$ +70.2 (*c* 0.51, $CHCl_3$); IR ($CHCl_3$): 2922, 2848, 1736, 1657, 1631, 1598, 1587, 1465, 1432, 1368, 1273, 1260, 1225, 1038, 978 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.33–7.23 (m, 2H, triazolyl-H, Ph), 6.92–6.79 (m, 3H, Ph), 5.89 (br d, 1H, *J* = 10.0 Hz, H-2), 5.82 (dt, 1H, *J* = 10.0, 3.0 Hz, H-3), 5.47 (s, 2H, C*H*$_2$Ph), 5.32 (ddd, 1H, *J* = 10.0, 3.0, 2.0 Hz, H-4), 5.03 (br s, 1H, H-1), 4.25 (dd, 1H, *J* = 12.0, 5.0 Hz, H-6a), 4.16 (dd, 1H, *J* = 12.0, 2.0 Hz, H-6b), 4.11 (ddd, 1H, *J* = 10.0, 5.0, 2.0 Hz, H-5), 3.84 (dt, 1H, *J* = 10.0, 6.0 Hz, H-1′a), 3.81 (s, 3H, OMe), 3.57 (dt, 1H, *J* = 10.0, 6.0 Hz, H-1′b), 2.85–2.76 (m, 2H, H-3′), 2.10 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.04–1.96 (m, 2H, H-2′); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.75 (C=O), 170.25 (C=O), 160.08 (Ph), 147.88 (C-4′), 136.35 (Ph), 130.11 (Ph), 129.01 (C-2), 127.82 (C-3), 120.70 (C-5′), 120.16 (Ph), 114.02 (Ph), 113.67 (Ph), 94.39 (C-1), 67.90 (C-1′), 66.92 (C-5), 65.31 (C-4), 62.99 (C-6), 55.26 (OMe), 53.92 (C-6′), 29.35 (C-2′), 22.46 (C-3′), 20.93 (CH_3), 20.73 (CH_3); HRMS (ESI) *m/z* calcd for $C_{23}H_{29}N_3O_7Na$ $[M+Na]^+$ 482.1903, found: 482.1890.



6a

4.3.13. 1-(2,5-Dimethoxybenzyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxymethyl)-1,2,3-1*H*-triazole (6a)

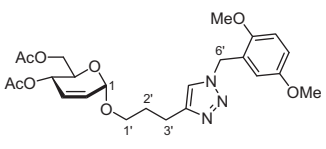
Pale orange solid; α-anomer R_f = 0.35 (50% EtOAc/*n*-hexane); mp: 90–92 °C; $[\alpha]_D^{24}$ +57.5 (*c* 1.02, $CHCl_3$); IR ($CHCl_3$): 2923, 2852, 1742, 1657, 1632, 1505, 1466, 1428, 1227, 1042, 964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.58 (br s, 1H, triazolyl-H), 6.89–6.86 (m, 2H, Ph), 6.81 (br s, 1H, Ph), 5.90 (br d, 1H, *J* = 10.0 Hz, H-2), 5.84 (br d, 1H, *J* = 10.0 Hz, H-3), 5.52 (s, 2H, C*H*$_2$Ph), 5.35 (d, 1H, *J* = 10.0 Hz, H-4), 5.19 (br s, 1H, H-1), 4.90 (d, 1H, *J* = 12.0 Hz, H-1′a), 4.70 (d, 1H, *J* = 12.0 Hz, H-1′b), 4.27 (dd, 1H, *J* = 12.0, 5.0 Hz, H-6a), 4.17 (dd, 1H, *J* = 12.0, 2.0 Hz, H-6b), 4.17–4.11 (m, 1H, H-5), 3.85 (s, 3H, OMe), 3.76 (s, 3H, OMe), 2.02 (s, 3H, OAc), 2.00 (s, 3H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.86 (C═O), 170.28 (C═O), 153.65 (Ph), 151.28 (Ph), 144.32 (C-2′), 129.91 (C-2), 127.49 (C-3), 123.61 (Ph), 122.91 (C-3′), 116.28 (Ph), 114.92 (Ph), 111.88 (Ph), 93.75 (C-1), 67.05 (C-5), 65.25 (C-4), 62.83 (C-6), 61.52 (C-1′), 55.99 (OMe), 55.75 (OMe), 49.07 (C-4′), 20.93 (CH_3), 20.77 (CH_3); HRMS (ESI) *m/z* calcd for $C_{22}H_{27}N_3O_8Na$ $[M+Na]^+$ 484.1696, found: 484.1640.



6b

4.3.14. 1-(2,5-Dimethoxybenzyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (6b)

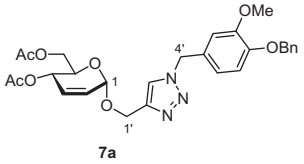
Pale orange oil; α-anomer R_f = 0.39 (50% EtOAc/*n*-hexane); $[\alpha]_D^{24}$ -0.53 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$): 2924, 2852, 1742, 1660, 1633, 1505, 1466, 1430, 1371, 1227, 1044, 975 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38 (br s, 1H, triazolyl-H), 6.88–6.85 (m, 2H, Ph), 6.75 (br s, 1H, Ph), 5.88 (br d, 1H, *J* = 10.0 Hz, H-2), 5.78 (dt, 1H, *J* = 10.0, 2.0 Hz, H-3), 5.50 (s, 2H, C*H*$_2$Ph), 5.31 (dm, 1H, *J* = 10.0 Hz, H-4), 5.04 (br s, 1H, H-1), 4.23 (dd, 1H, *J* = 12.0, 5.5 Hz, H-6a), 4.13 (dd, 1H, *J* = 12.0, 2.0 Hz, H-6b), 4.08–3.99 (m, 2H, H-5, H-1′a), 3.87–3.73 (m, 1H, H-1′b), 3.85 (s, 3H, OMe), 3.75 (s, 3H, OMe), 3.04 (t, 2H, *J* = 6.0 Hz, H-2′), 2.10 (s, 3H, OAc), 2.07 (s, 3H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.84 (C═O), 170.27 (C═O), 153.71 (Ph), 151.18 (Ph), 144.80 (C-3′), 129.22 (C-2), 127.66 (C-3), 124.06 (Ph), 121.79 (C-4′), 116.03 (Ph), 114.63 (Ph), 111.78 (Ph), 94.59 (C-1), 67.82 (C-1′), 66.99 (C-5), 65.26 (C-4), 62.90 (C-6), 56.01 (OMe), 55.76 (OMe), 48.95 (C-5′), 26.63 (C-2′), 20.84 (CH_3), 20.79 (CH_3); HRMS (ESI) *m/z* calcd for $C_{23}H_{29}N_3O_8Na$ $[M+Na]^+$ 498.1852, found: 498.1801.



6c

4.3.15. 1-(2,5-Dimethoxybenzyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxypropyl)-1,2,3-1*H*-triazole (6c)

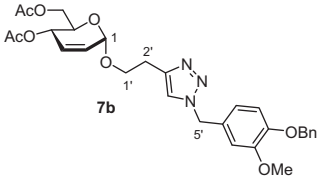
Pale yellow oil; α-anomer R_f = 0.30 (50% EtOAc/*n*-hexane); $[\alpha]_D^{24}$ +71.6 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$): 2923, 2848, 1740, 1657, 1632, 1504, 1467, 1428, 1369, 1273, 1260, 1225, 1043, 978 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.31 (br s, 1H, triazolyl-H), 6.88–6.81 (m, 2H, Ph), 6.76 (br s, 1H, Ph), 5.89 (br d, 1H, *J* = 10.0 Hz, H-2), 5.83 (dm, 1H, *J* = 10.0 Hz, H-3), 5.49 (s, 2H, C*H*$_2$Ph), 5.31 (dm, 1H, *J* = 10.0 Hz, H-4), 5.02 (br s, 1H, H-1), 4.25 (dd, 1H, *J* = 12.0, 5.0 Hz, H-6a), 4.16 (dd, 1H, *J* = 12.0, 2.0 Hz, H-6b), 4.08–4.07 (m, 1H, H-5), 3.85 (s, 3H, OMe), 3.76–3.68 (m, 1H, H-1′a), 3.75 (s, 3H, OMe), 3.60–3.58 (dt, 1H, *J* = 10.0, 6.0 Hz, H-1′b), 2.85–2.75 (m, 2H, H-3′), 2.10 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.02–1.94 (m, 2H, H-2′); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.84 (C═O), 170.32 (C═O), 153.68 (2 × Ph), 147.40 (C-4′), 129.05 (C-2), 127.83 (C-3), 123.93 (Ph), 121.05 (C-5′), 116.04 (Ph), 114.52 (Ph), 111.45 (Ph), 94.42 (C-1), 68.01 (C-1′), 66.92 (C-5), 65.29 (C-4), 63.01 (C-6), 55.95 (OMe), 55.71 (OMe), 49.09 (C-6′), 31.24 (C-2′), 22.82 (C-3′), 21.00 (CH_3), 20.79 (CH_3); HRMS (ESI) *m/z* calcd for $C_{24}H_{31}N_3O_8Na$ $[M+Na]^+$ 512.2009, found: 512.1985.



7a

4.3.16. 1-(4-Benzyloxy-3-methoxybenzyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxymethyl)-1,2,3-1*H*-triazole (7a)

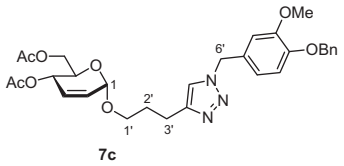
White solid; α-anomer R_f = 0.27 (50% EtOAc/*n*-hexane); mp: 64–66 °C; $[\alpha]_D^{26}$ +13.9 (*c* 1.02, $CHCl_3$); IR ($CHCl_3$): 2923, 2848, 1741, 1657, 1633, 1515, 1465, 1417, 1369, 1261, 1229, 1037, 964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.42 (br s, 1H, triazolyl-H), 7.48–7.29 (m, 5H, Ph), 6.87 (d, 1H, *J* = 8.5 Hz, Ph), 6.84 (br s, 1H, Ph), 6.81 (dd, 1H, *J* = 8.5, 2.0 Hz, Ph), 5.90 (br d, 1H, *J* = 10.0 Hz, H-2), 5.82 (dt, 1H, *J* = 10.0, 2.0 Hz, H-3), 5.44 (s, 2H, C*H*$_2$Ph), 5.34 (dm, 1H, *J* = 10.0 Hz, H-4), 5.16 (br s, 3H, H-1, C*H*$_2$Ph), 4.89 (d, 1H, *J* = 12.0 Hz, H-1′a), 4.70 (d, 1H, *J* = 12.0 Hz, H-1′b), 4.25 (dd, 1H, *J* = 12.0, 5.0 Hz, H-6a), 4.17 (dd, 1H, *J* = 12.0, 2.5 Hz, H-6b), 4.12 (ddd, 1H, *J* = 10.0, 5.0, 2.5 Hz, H-5), 3.88 (s, 3H, OMe), 2.00 (s, 3H, OAc), 1.99 (s, 3H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.78 (C═O), 170.24 (C═O), 150.13 (Ph), 148.64 (Ph), 144.82 (C-2′), 136.75 (Ph), 129.53 (C-2), 127.34 (Ph), 128.60 (2 × Ph), 127.97 (Ph), 127.42 (C-3), 127.22 (2xPh), 122.41 (C-3′), 120.86 (Ph), 113.98 (Ph), 111.88 (Ph), 93.86 (C-1), 71.00 (C*H*$_2$Ph), 67.05 (C-5), 65.24 (C-4), 62.80 (C-6), 61.31 (C-1′), 56.09 (OMe), 54.09 (C-4′), 20.94 (CH_3), 20.80 (CH_3); HRMS (ESI) *m/z* calcd for $C_{28}H_{31}N_3O_8Na$ $[M+Na]^+$ 560.2009, found: 560.2008.



7b

4.3.17. 1-(4-Benzyloxy-3-methoxybenzyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (7b)

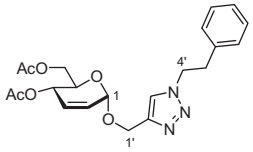
Pale yellow oil; α-anomer R_f = 0.36 (50% EtOAc/*n*-hexane); $[\alpha]_D^{26}$ +67.9 (*c* 0.51, $CHCl_3$); IR ($CHCl_3$): 2923, 2848, 1734, 1605, 1590, 1508, 1455, 1417, 1366, 1260, 1273, 1222, 1031, 967 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.45–7.30 (m, 6H, triazolyl-H, Ph), 6.88–6.75 (m, 3H, Ph), 5.87 (br d, 1H, *J* = 10.0 Hz, H-2), 5.76 (dt, 1H, *J* = 10.0, 2.5 Hz, H-3), 5.42 (s, 2H, CH_2Ph), 5.30 (ddd, 1H, *J* = 10.0, 2.5, 1.0 Hz, H-4), 5.16 (s, 2H, CH_2Ph), 5.03 (br s, 1H, H-1), 4.22 (dd, 1H, *J* = 12.0, 5.5 Hz, H-6a), 4.14 (dd, 1H, *J* = 12.0, 2.0 Hz, H-6b), 4.04 (dt, 1H, *J* = 9.5, 7.0 Hz, H-1′a), 4.02 (ddd, 1H, *J* = 10.0, 5.5, 2.0 Hz, H-5), 3.85 (s, 3H, OMe), 3.79 (dt, 1H, *J* = 9.5, 7.0 Hz, H-1′b), 3.06–2.98 (m, 2H, H-2′), 2.08 (s, 3H, OAc), 2.05 (s, 3H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.80 (C═O), 170.26 (C═O), 150.07 (Ph), 148.52 (Ph), 145.00 (C-3′), 136.77 (Ph), 129.28 (C-2), 128.60 (2 × Ph), 127.97 (Ph), 127.69 (Ph), 127.59 (C-3), 127.22 (2 × Ph), 121.32 (C-4′), 120.60 (Ph), 113.88 (Ph), 111.69 (Ph), 94.53 (C-1), 70.98 (CH_2Ph), 67.66 (C-1′), 66.99 (C-5), 65.25 (C-4), 62.88 (C-6), 56.07 (OMe), 53.94 (C-5′), 26.61 (C-2′), 20.96 (CH_3), 20.77 (CH_3); HRMS (ESI) *m/z* calcd for $C_{29}H_{33}N_3O_8Na$ $[M+Na]^+$ 574.2165, found: 574.2091.



7c

4.3.18. 1-(4-Benzyloxy-3-methoxybenzyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxypropyl)-1,2,3-1*H*-triazole (7c)

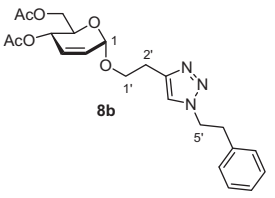
Pale yellow oil; α-anomer R_f = 0.35 (50% EtOAc/*n*-hexane); $[\alpha]_D^{26}$ +42.1 (*c* 0.51, $CHCl_3$); IR ($CHCl_3$): 2923, 2848, 1738, 1657, 1632, 1517, 1465, 1421, 1365, 1275, 1260, 1034, 971 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.46–7.30 (m, 6H, triazolyl-H, Ph), 6.89–6.77 (m, 3H, Ph), 5.89 (br d, 1H, *J* = 10.0 Hz, H-2), 5.82 (dt, 1H, *J* = 10.0, 3.0 Hz, H-3), 5.42 (s, 2H, CH_2Ph), 5.32 (ddd, 1H, *J* = 10.0, 3.0, 2.0 Hz, H-4), 5.17 (s, 2H, CH_2Ph), 5.03 (br s, 1H, H-1), 4.25 (dd, 1H, *J* = 12.0, 5.0 Hz, H-6a), 4.17 (dd, 1H, *J* = 12.0, 2.0 Hz, H-6b), 4.14–4.07 (m, 1H, H-5), 3.90–3.79 (m, 1H, H-1′a), 3.86 (s, 3H, OMe), 3.56 (dt, 1H, *J* = 10.0, 6.0 Hz, H-1′b), 2.84–2.75 (m, 2H, H-3′), 2.10 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.02–1.94 (m, 2H, H-2′); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.84 (C═O), 170.33 (C═O), 150.08 (Ph), 148.52 (Ph), 148.00 (C-4′), 136.78 (Ph), 129.09 (C-2), 128.62 (2xPh), 127.98 (Ph), 127.80 (C-3), 127.71 (Ph), 127.24 (2 × Ph), 120.65 (Ph), 120.50 (C-5′), 113.88 (Ph), 111.68 (Ph), 94.42 (C-1), 71.00 (CH_2Ph), 67.93 (C-1′), 66.92 (C-5), 65.29 (C-4), 62.99 (C-6), 56.08 (OMe), 53.96 (C-6′), 29.39 (C-2′), 22.50 (C-3′), 21.00 (CH_3), 20.80 (CH_3); HRMS (ESI) *m/z* calcd for $C_{30}H_{35}N_3O_8Na$ $[M+Na]^+$ 588.2322, found: 588.2291.



8a

4.3.19. 1-(2-Phenylethyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxymethyl)-1,2,3-1*H*-triazole (8a)

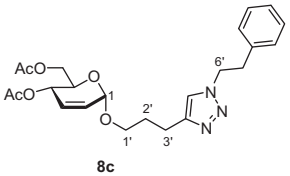
Pale yellow oil; α-anomer R_f = 0.33 (50% EtOAc/*n*-hexane); $[\alpha]_D^{24}$ +58.9 (*c* 1.02, $CHCl_3$); IR ($CHCl_3$): 2923, 2851, 1740, 1454, 1435, 1368, 1228, 1038, 1020, 965 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 8.03 (br s, 1H, triazolyl-H), 7.32 (t, 2H, *J* = 7.0 Hz, Ph), 7.24 (t, 2H, *J* = 7.0 Hz, Ph), 7.23 (d, 1H, *J* = 7.0 Hz, Ph), 5.89 (m, 2H, H-2, H-3), 5.24 (d, 1H, *J* = 10.0 Hz, H-4), 5.16 (s, 1H, H-1), 4.74 (d, 1H, *J* = 12.0 Hz, H-1′a), 4.64 (t, 2H, *J* = 7.0 Hz, H-4′), 4.62 (d, 1H, *J* = 12.0 Hz, H-1′b), 4.18 (dd, 1H, *J* = 12.0, 5.0 Hz, H-6a), 4.14 (dd, 1H, *J* = 12.0, 3.0 Hz, H-6b), 4.00 (ddd, 1H, *J* = 10.0, 5.0, 2.0 Hz, H-5), 3.19 (t, 2H, *J* = 7.0 Hz, H-5′), 2.09 (s, 3H, OAc), 2.07 (s, 3H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.85 (C═O), 170.30 (C═O), 144.90 (C-2′), 136.96 (Ph), 129.48 (C-2), 128.83 (2 × Ph), 128.63 (2 × Ph), 127.48 (Ph), 127.13 (C-3), 123.05 (C-3′), 93.53 (C-1), 67.19 (C-5), 65.28 (C-4), 62.86 (C-6), 61.33 (C-1′), 54.64 (C-4′), 37.03 (C-5′), 20.98 (CH_3), 20.85 (CH_3); HRMS (ESI) *m/z* calcd for $C_{21}H_{25}N_3O_6H$ $[M+H]^+$ 416.1822, found: 416.1822.



8b

4.3.20. 1-(2-Phenylethyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (8b)

Pale yellow oil; α-anomer R_f = 0.26 (50% EtOAc/*n*-hexane); $[\alpha]_D^{26}$ +94.2 (*c* 0.52, $CHCl_3$); IR ($CHCl_3$): 2924, 2851, 1741, 1454, 1435, 1370, 1256, 1228, 1068, 971 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 7.84 (br s, 1H, triazolyl-H), 7.31 (t, 2H, *J* = 7.0 Hz, Ph), 7.25 (d, 1H, *J* = 7.0 Hz, Ph), 7.23 (t, 2H, *J* = 7.0 Hz, Ph), 5.88 (m, 2H, H-2, H-3), 5.20 (d, 1H, *J* = 10.0 Hz, H-4), 5.11 (s, 1H, H-1), 4.60 (t, 2H, *J* = 7.0 Hz, H-5′), 4.14 (d, 2H, *J* = 4.0 Hz, H-6), 3.95–3.87 (m, 2H, H-5, H-1′a), 3.77–3.70 (m, 1H, H-1′b), 3.17 (t, 2H, *J* = 7.0 Hz, H-6′), 2.92 (t, 2H, *J* = 7.0 Hz, H-2′), 2.07 (s, 3H, OAc), 2.03 (s, 3H, OAc); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.78 (C═O), 170.67 (C═O), 144.59 (C-3′), 137.15 (Ph), 129.19 (C-2), 128.77 (2 × Ph), 128.66 (2 × Ph), 127.68 (Ph), 127.05 (C-3), 121.88 (C-4′), 94.50 (C-1), 67.78 (C-1′), 66.99 (C-5), 65.33 (C-4), 62.93 (C-6), 51.47 (C-5′), 36.76 (C-6′), 26.54 (C-2′), 20.94 (CH_3), 20.77 (CH_3); HRMS (ESI) *m/z* calcd for $C_{22}H_{27}N_3O_6H$ $[M+H]^+$ 430.1978, found: 430.1975.

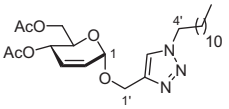


8c

4.3.21. 1-(2-Phenylethyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxypropyl)-1,2,3-1*H*-triazole (8c)

Yellow oil; α-anomer R_f = 0.23 (50% EtOAc/*n*-hexane); $[\alpha]_D^{26}$ +45.5 (*c* 0.50, $CHCl_3$); IR ($CHCl_3$): 2924, 2874, 1741, 1454, 1435,

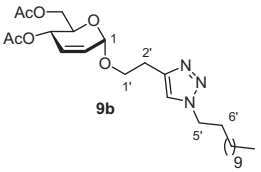
1370, 1253, 1230, 1040, 979 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6): δ 7.83 (br s, 1H, triazolyl-H), 7.31 (t, 2H, J = 7.0 Hz, Ph), 7.25 (d, 1H, J = 7.0 Hz, Ph), 7.22 (t, 2H, J = 7.0 Hz, Ph), 5.93 (dt,1H, J = 10.0, 1.0 Hz, H-2), 5.88 (d, 1H, J = 10.0 Hz, H-3), 5.20 (d, 1H, J = 10.0 Hz, H-4), 5.06 (s, 1H, H-1), 4.58 (t, 2H, J = 7 Hz, H-6′), 4.17 (dd, 1H, J = 12.0, 5.0 Hz, H-6a), 4.12 (dd, 1H, J = 12.0, 3.0 Hz, H-6b), 4.00 (ddd, 1H, J = 10.0, 5.0, 2.0 Hz, H-5), 3.70 (dt, 1H, J = 10.0, 7.0 Hz, H-1′a), 3.60 (dt, 1H, J = 10.0, 7.0 Hz, H-1′b), 3.17 (t, 2H, J = 7 Hz, H-7′), 2.67 (t, 2H, J = 7.0 Hz, H-3′), 2.09 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.87 (p, 2H, J = 7.0 Hz, H-2′); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.79 (C═O), 170.28 (C═O), 147.08 (C-4′), 137.18 (Ph), 129.36 (C-2), 128.84 (2 × Ph), 128.67 (2 × Ph), 127.83 (Ph), 127.03 (C-3), 121.13 (C-5′), 94.43 (C-1), 67.90 (C-1′), 66.94 (C-5), 65.33 (C-4), 63.00 (C-6), 51.48 (C-6′), 36.78 (C-7′), 29.46 (C-2′), 22.34 (C-3′), 20.95 (CH_3), 20.77 (CH_3); HRMS (ESI) m/z calcd for $C_{23}H_{29}N_3O_6H$ $[M+H]^+$ 444.2135, found: 444.2129.



9a

4.3.22. 1-(Dodecyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxymethyl)-1,2,3-1*H*-triazole (9a)

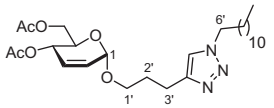
Pale yellow oil; α-anomer R_f = 0.55 (50% EtOAc/*n*-hexane); $[\alpha]_D^{27}$ +53.1 (*c* 0.50, $CHCl_3$); IR ($CHCl_3$): 2925, 2851, 1745, 1460, 1437, 1370, 1228, 1039, 1018, 965 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.48 (s, 1H, triazolyl-H), 5.84 (d, 1H, J = 10.0 Hz, H-2), 5.77 (d, 1H, J = 10.0 Hz, H-3), 5.27 (d, 1H, J = 10.0 Hz, H-4), 5.12 (s, 1H, H-1), 4.85 (dd, 1H, J = 12.0, 1.2 Hz, H-1′a), 4.65 (dd, 1H, J = 12.0, 1.2 Hz, H-1′b), 4.27 (t, 2H, J = 7.6 Hz, H-4′), 4.20 (dd, 1H, J = 12.0, 5.0 Hz, H-6a), 4.13 (dd, 1H, J = 12.0, 2.0 Hz, H-6b), 4.13–4.05 (m, 1H, H-5), 2.05 (s, 3H, OAc), 2.01 (s, 3H, OAc), 1.90–1.77 (m, 2H, H-5′), 1.33–1.10 (m, 18H, CH_2), 0.81 (dd, 3H, J = 7.0, 5.2 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.81 (C═O), 170.25 (C═O), 144.35 (C-2′), 129.51 (C-2), 127.49 (C-3), 122.40 (C-3′), 93.77 (C-1), 67.32 (C-5), 65.30 (C-4), 62.88 (C-6), 61.59 (C-1′), 50.41 (C-4′), 31.88 (CH_2), 30.29 (CH_2), 29.57 (2 × CH_2), 29.43 (CH_2), 29.36 (CH_2), 29.30 (CH_2), 28.99 (CH_2), 26.51 (CH_2), 22.66 (CH_2), 20.94 (CH_3), 20.80 (CH_3), 14.09 (CH_3); HRMS (ESI) m/z calcd for $C_{25}H_{41}N_3O_6H$ $[M+H]^+$ 480.3074, found: 480.3068.



9b

4.3.23. 1-(Dodecyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (9b)

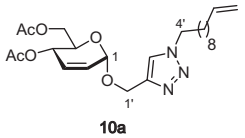
Pale yellow oil; α-anomer R_f = 0.44 (50% EtOAc/*n*-hexane); $[\alpha]_D^{25}$ +81.7 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$): 2925, 2851, 1744, 1460, 1435, 1368, 1256, 1227, 1040, 971 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.36 (s, 1H, triazolyl-H), 5.89 (d, 1H, J = 10.0 Hz, H-2), 5.81 (d, 1H, J = 10.0 Hz, H-3), 5.31 (d, 1H, J = 10.0 Hz, H-4), 5.07 (s, 1H, H-1), 4.33 (t, 2H, J = 7.6 Hz, H-5′), 4.23 (dd, 1H, J = 12.0, 5.6 Hz, H-6a), 4.15 (dd, 1H, J = 12.0, 2.4 Hz, H-6b), 4.10–4.00 (m, 2H, H-5, H-1′a), 3.80 (dt, 1H, J = 10.0, 3.2 Hz, H-1′b), 3.05 (dt, 2H, J = 6.8, 5.2 Hz, H-2′), 2.09 (s, 3H, OAc), 2.08 (s, 3H, OAc), 1.96–1.83 (m, 2H, H-6′), 1.43–1.18 (m, 18H, CH_2), 0.88 (t, 3H, J = 6.8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.81 (C═O), 170.23 (C═O), 144.75 (C-3′), 129.26 (C-2), 127.67 (C-3), 121.33 (C-4′), 94.53 (C-1), 67.77 (C-1′), 67.03 (C-5), 65.33 (C-4), 62.93 (C-6), 50.24 (C-5′), 31.89 (CH_2), 30.33 (CH_2), 29.59 (2 × CH_2), 29.51 (CH_2), 29.39 (CH_2), 29.31 (CH_2), 29.01 (CH_2), 26.60 (C-2′), 26.52 (CH_2), 22.66 (CH_2), 20.96 (CH_3), 20.77 (CH_3), 14.09 (CH_3); HRMS (ESI) m/z calcd for $C_{26}H_{43}N_3O_6H$ $[M+H]^+$ 494.3230, found: 494.3225.



9c

4.3.24. 1-(Dodecyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxypropyl)-1,2,3-1*H*-triazole (9c)

Pale yellow oil; α-anomer R_f = 0.45 (50% EtOAc/*n*-hexane); $[\alpha]_D^{23}$ +62.7 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$): 2925, 2851, 1744, 1460, 1435, 1371, 1229, 1041, 1018, 979 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.30 (s, 1H, triazolyl-H), 5.89 (d, 1H, J = 10.0 Hz, H-2), 5.84 (ddd, 1H, J = 10.0, 2.4, 1.6 Hz, H-3), 5.31 (ddd, 1H, J = 10.0, 2.4, 1.2 Hz, H-4), 5.05 (s, 1H, H-1), 4.30 (t, 2H, J = 7.6 Hz, H-6′), 4.25 (dd, 1H, J = 12.0, 5.2 Hz, H-6a), 4.17 (dd, 1H, J = 12.0, 2.4 Hz, H-6b), 4.08–4.15 (m, 1H, H-5), 3.84 (dt, 1H, J = 10.0, 6.0 Hz, H-1′a), 3.58 (dt, 1H, J = 10.0, 6.0 Hz, H-1′b), 2.81 (m, 2H, H-3′), 2.09 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.07–1.95 (m, 2H, H-2′), 1.93–1.82 (m, 2H, H-7′), 1.38–1.18 (m, 18H, CH_2), 0.88 (t, 3H, J = 6.4 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.81 (C═O), 170.30 (C═O), 147.37 (C-4′), 129.08 (C-2), 127.84 (C-3), 120.49 (C-5′), 94.46 (C-1), 68.01 (C-1′), 66.95 (C-5), 65.33 (C-4), 63.02 (C-6), 50.24 (C-6′), 31.89 (CH_2), 30.34 (CH_2), 29.59 (2 × CH_2), 29.50 (C-2′, CH_2), 29.38 (CH_2), 29.31 (CH_2), 29.00 (CH_2), 26.52 (CH_2), 22.67 (CH_2), 22.47 (C-3′), 20.96 (CH_3), 20.77 (CH_3), 14.10 (CH_3); HRMS (ESI) m/z calcd for $C_{27}H_{45}N_3O_6H$ $[M+H]^+$ 508.3387, found: 508.3389.

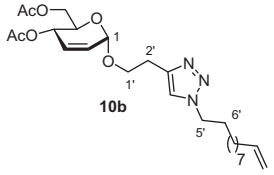


10a

4.3.25. 1-(Undecylenyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxymethyl)-1,2,3-1*H*-triazole (10a)

Pale yellow oil; α-anomer R_f = 0.26 (40% EtOAc/*n*-hexane); $[\alpha]_D^{26}$ +66.5 (*c* 0.25, $CHCl_3$); IR ($CHCl_3$): 2927, 2851, 1744, 1457, 1438, 1368, 1256, 1228, 1039, 1015, 962 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.55 (s, 1H, triazolyl-H), 5.91 (d, 1H, J = 10.0 Hz, H-2), 5.89–5.73 (m, 2H, H-3, C*H*═CH_2), 5.35 (d, 1H, J = 10.0 Hz, H-4), 5.19 (s, 1H, H-1), 5.05–4.87 (m, 2H, CH═C*H*$_2$), 4.92 (d, 1H, J = 12.0 Hz, H-1′a), 4.72 (d, 1H, J = 12.0 Hz, H-1′b), 4.34 (t, 2H, J = 6.8 Hz, H-4′), 4.27 (dd, 1H, J = 12.0, 5.2 Hz, H-6a), 4.24–4.11 (m, 2H, H-6b, H-5), 2.19–1.99 (m, 2H, C*H*$_2$CH═CH_2), 2.09 (s, 3H,

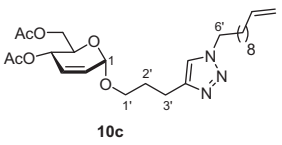
OAc), 2.08 (s, 3H, OAc), 1.97–1.84 (m, 2H, H-5′), 1.45–1.20 (m, 12H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.87 (C═O), 170.80 (C═O), 144.34 (C-2′), 139.14 (HC═CH_2), 129.53 (C-2), 127.48 (C-3), 122.46 (C-3′), 114.19 (HC═CH_2), 93.78 (C-1), 67.06 (C-5), 65.27 (C-4), 62.87 (C-6), 61.59 (C-1′), 50.40 (C-4′), 33.77 (CH_2), 30.31 (CH_2), 29.32 (2 × CH_2), 29.03 (CH_2), 28.97 (CH_2), 28.87 (CH_2), 26.50 (CH_2), 20.98 (CH_3), 20.85 (CH_3); HRMS (ESI) *m/z* calcd for $C_{24}H_{37}N_3O_6H$ $[M+H]^+$ 464.2761, found: 464.2755.



10b

4.3.26. 1-(Undecylenyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (10b)

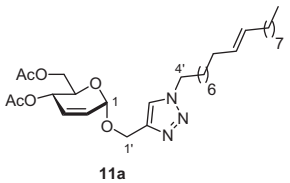
Yellow oil; α-anomer R_f = 0.37 (50% EtOAc/*n*-hexane); $[\alpha]_D^{25}$ +58.3 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$): 2926, 2851, 1744, 1460, 1438, 1368, 1227, 1039, 973 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (s, 1H, triazolyl-H), 5.90 (d, 1H, *J* = 10.0 Hz, H-2), 5.87–5.74 (m, 2H, H-3, C*H*═CH_2), 5.31 (dd, 1H, *J* = 9.6, 1.6 Hz, H-4), 5.07 (s, 1H, H-1), 5.04–4.90 (m, 2H, CH═CH_2), 4.32 (t, 2H, *J* = 7.2 Hz, H-5′), 4.24 (dd, 1H, *J* = 12.0, 5.2 Hz, H-6a), 4.16 (dd, 1H, *J* = 12.0, 2.4 Hz, H-6b), 4.10–4.00 (m, 2H, H-5, H-1′a), 3.90–3.70 (m, 1H, H-1′b), 3.06 (t, 2H, *J* = 6.4 Hz, H-2′), 2.17–1.98 (m, 2H, CH_2CH═CH_2), 2.09 (s, 3H, OAc), 2.08 (s, 3H, OAc), 1.96–1.77 (m, 2H, H-6′), 1.45–1.20 (m, 12H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.81 (C═O), 170.23 (C═O), 144.76 (C-3′), 139.11 (H*C*═CH_2), 129.25 (C-2), 127.66 (C-3), 121.33 (C-4′), 114.17 (HC═*C*H_2), 94.52 (C-1), 67.76 (C-1′), 67.02 (C-5), 65.32 (C-4), 62.92 (C-6), 50.23 (C-5′), 33.75 (CH_2), 30.32 (CH_2), 29.32 (2 × CH_2), 29.02 (CH_2), 28.97 (CH_2), 28.86 (CH_2), 26.60 (C-2′), 26.50 (CH_2), 20.96 (CH_3), 20.77 (CH_3); HRMS (ESI) *m/z* calcd for $C_{25}H_{39}N_3O_6H$ $[M+H]^+$ 478.2917, found: 478.2919.



10c

4.3.27. 1-(Undecylenyl)-4-(4,6-di-*O*-acetyl-2,3-dideox-α-D-*erythro*-hex-2-enopyranos-1-yloxypropyl)-1,2,3-1*H*-triazole (10c)

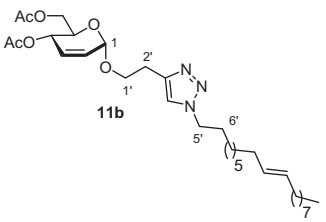
Pale yellow oil; α-anomer R_f = 0.40 (50% EtOAc/*n*-hexane); $[\alpha]_D^{26}$ +49.8 (*c* 0.50, $CHCl_3$); IR ($CHCl_3$): 2927, 2851, 1743, 1454, 1435, 1368, 1275, 1260, 1228, 1040, 1018, 979 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.30 (s, 1H, triazolyl-H), 5.89 (d, 1H, *J* = 10.0 Hz, H-2), 5.87–5.75 (m, 2H, H-3, C*H*═CH_2), 5.31 (d, 1H, *J* = 9.6, 1.2 Hz, H-4), 5.04 (s, 1H, H-1), 4.99–4.89 (m, 2H, CH═CH_2), 4.30 (t, 2H, *J* = 7.6 Hz, H-6′), 4.25 (dd, 1H, *J* = 12.0, 5.2 Hz, H-6a), 4.17 (dd, 1H, *J* = 12.0, 2.4 Hz, H-6b), 4.14–4.08 (m, 1H, H-5), 3.84 (dt, 1H, *J* = 9.6, 6.0 Hz, H-1′a), 3.58 (dt, 1H, *J* = 9.6, 6.0 Hz, H-1′b), 2.91–2.73 (m, 2H, H-3′), 2.10–1.95 (m, 4H, H-2′, CH_2CH═CH_2), 2.09 (s, 3H, OAc), 2.08 (s, 3H, OAc), 1.95–1.80 (m, 2H, H-7′), 1.45–1.20 (m, 12H, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.78 (C═O), 170.28 (C═O), 147.36 (C-4′), 139.12 (HC═CH_2), 129.07 (C-2), 127.84 (C-3), 120.47 (C-5′), 114.16 (HC═*C*H_2), 94.45 (C-1), 68.00 (C-1′), 66.95 (C-5), 65.33 (C-4), 63.01 (C-6), 50.19 (C-6′), 33.74 (CH_2), 30.32 (2 × CH_2), 29.30 (C-2′, CH_2), 29.02 (CH_2), 28.96 (CH_2), 28.86 (CH_2), 26.49 (CH_2), 22.47 (C-3′), 20.95 (CH_3), 20.77 (CH_3); HRMS (ESI) *m/z* calcd for $C_{26}H_{41}N_3O_6H$ $[M+H]^+$ 492.3074, found: 492.3078.



11a

4.3.28. 1-(Oleyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxymethyl)-1,2,3-1*H*-triazole (11a)

Pale yellow oil; α-anomer R_f = 0.28 (30% EtOAc/*n*-hexane); $[\alpha]_D^{24}$ +52.9 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$): 2928, 2851, 1744, 1457, 1438, 1371, 1230, 1040, 1018, 971 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (s, 1H, triazolyl-H), 5.92 (d, 1H, *J* = 10.0 Hz, H-2), 5.85 (ddd, 1H, *J* = 10.0, 2.8, 2.0 Hz, H-3), 5.42–5.29 (m, 3H, H-4, C*H*═C*H*), 5.19 (s, 1H, H-1), 4.93 (d, 1H, *J* = 12.0 Hz, H-1′a), 4.73 (d, 1H, *J* = 12.0 Hz, H-1′b), 4.35 (t, 2H, *J* = 7.2 Hz, H-4′), 4.28 (dd, 1H, *J* = 12.0, 5.2 Hz, H-6a), 4.21 (dd, 1H, *J* = 12.0, 2.4 Hz, H-6b), 4.20–4.13 (m, 1H, H-5), 2.13 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.07–1.97 (m, 4H, CH_2CH═CHCH_2), 1.96–1.86 (m, 2H, H-5′), 1.42–1.21 (m, 22H, CH_2), 0.89 (t, 3H, *J* = 6.8 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.84 (C═O), 170.27 (C═O), 144.36 (C-2′), 130.05 (HC═CH), 129.68 (HC═CH), 129.52 (C-2), 127.49 (C-3), 122.40 (C-3′), 93.78 (C-1), 67.08 (C-5), 65.30 (C-4), 62.88 (C-6), 61.60 (C-1′), 50.40 (C-4′), 31.90 (CH_2), 30.30 (CH_2), 29.75 (CH_2), 29.68 (2 × CH_2), 29.51 (CH_2), 29.31 (2 × CH_2), 29.15 (CH_2), 28.98 (CH_2), 27.21 (CH_2), 27.15 (CH_2), 26.52 (CH_2), 22.67 (CH_2), 20.95 (CH_3), 20.82 (CH_3), 14.10 (CH_3); HRMS (ESI) *m/z* calcd for $C_{31}H_{51}N_3O_6H$ $[M+H]^+$ 562.3856, found: 562.3856.

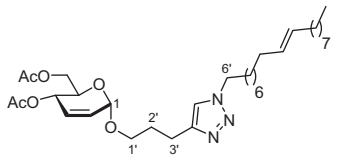


11b

4.3.29. 1-(Oleyl)-4-(4,6-di-*O*-acetyl-2,3-dideox-α-D-*erythro*-hex-2-enopyranos-1-yloxyethyl)-1,2,3-1*H*-triazole (11b)

Pale yellow oil; α-anomer R_f = 0.20 (30% EtOAc/*n*-hexane); $[\alpha]_D^{24}$ +66.8 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$): 2927, 2851, 1745, 1460, 1438, 1371, 1228, 1040, 1015, 971 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.36 (s, 1H, triazolyl-H), 5.90 (d, 1H, *J* = 10.0 Hz, H-2), 5.82 (d, 1H, *J* = 10.0 Hz, H-3), 5.42–5.27 (m, 3H, H-4, C*H*═C*H*), 5.07 (s, 1H, H-1), 4.32 (t, 2H, *J* = 7.2 Hz, H-5′), 4.24 (dd, 1H, *J* = 12.0, 5.6 Hz, H-6a), 4.16 (dd, 1H, *J* = 12.0, 2.4 Hz, H-6b), 4.10–4.00 (m, 2H, H-5, H-1′a), 3.81 (dt, 1H, *J* = 9.6, 6.8 Hz, H-1′b), 3.06 (t, 2H, *J* = 6.4 Hz, H-2′), 2.09 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.07–1.94 (m, 4H,

$CH_2CH{=}CHCH_2$), 1.94–1.80 (m, 2H, H-6′), 1.50–1.19 (m, 22H, CH_2), 0.88 (t, 3H, J = 6.4 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.82 (C=O), 170.24 (C=O), 144.76 (C-3′), 130.04 (HC=CH), 129.68 (HC=CH), 129.26 (C-2), 127.66 (C-3), 121.32 (C-4′), 94.52 (C-1), 67.77 (C-1′), 67.02 (C-5), 65.32 (C-4), 62.92 (C-6), 50.22 (C-5′), 31.89 (CH_2), 30.34 (CH_2), 29.75 (CH_2), 29.69 ($2 \times CH_2$), 29.51 (CH_2), 29.31 ($2 \times CH_2$), 29.16 (CH_2), 28.99 (CH_2), 27.21 (CH_2), 27.15 (CH_2), 26.60 (C-2′), 26.52 (CH_2), 22.67 (CH_2), 20.96 (CH_3), 20.77 (CH_3), 14.10 (CH_3); HRMS (ESI) m/z calcd for $C_{32}H_{53}N_3O_6Na$ $[M+Na]^+$ 598.3832, found: 598.3829.



11c

4.3.30. 1-(Oleyl)-4-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranos-1-yloxypropyl)-1,2,3-1*H*-triazole (11c)

Pale yellow oil; α-anomer R_f = 0.26 (40% EtOAc/*n*-hexane); $[\alpha]_D^{24}$ +62.3 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$): 2927, 2851, 1743, 1457, 1435, 1370, 1275, 1260, 1228, 1041, 1015, 976 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.20 (s, 1H, triazolyl-H), 5.82 (d, 1H, J = 10.0 Hz, H-2), 5.77 (d, 1H, J = 10.0 Hz, H-3), 5.35–5.20 (m, 3H, H-4, C*H*=C*H*), 4.97 (s, 1H, H-1), 4.23 (t, 2H, J = 7.6, H-6′), 4.18 (dd, 1H, J = 12.0, 5.6 Hz, H-6a), 4.14–4.01 (m, 1H, H-5), 4.10 (dd, 1H, J = 12.0, 2.4 Hz, H-6b), 3.77 (dt, 1H, J = 9.6, 3.6 Hz, H-1′a), 3.50 (dt, 1H, J = 9.6, 6.0 Hz, H-1′b), 2.85–2.67 (m, 2H, H-3′), 2.11–1.75 (m, 6H, H-2′, $CH_2CH{=}CHCH_2$), 2.02 (s, 3H, OAc), 2.01 (s, 3H, OAc), 2.00–1.75 (m, 2H, H-7′), 1.37–1.05 (m, 22H, CH_2), 0.80 (t, 3H, J = 6.4 Hz, CH_3); ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.81 (C=O), 170.29 (C=O), 147.38 (C-4′), 130.04 (HC=CH), 129.70 (HC=CH), 129.09 (C-2), 127.84 (C-3), 120.47 (C-5′), 94.46 (C-1), 68.02 (C-1′), 66.96 (C-5), 65.34 (C-4), 63.02 (C-6), 50.22 (C-6′), 32.21 (CH_2), 30.35 (CH_2), 29.76 (CH_2), 29.69 ($3 \times CH_2$), 29.51 (CH_2), 29.31 ($2 \times CH_2$), 29.16 (CH_2), 29.00 (CH_2), 27.22 (CH_2), 27.16 (CH_2), 26.40 (CH_2), 22.68 (CH_2), 22.49 (C-3′), 20.97 (CH_3), 20.79 (CH_3), 14.11 (CH_3); HRMS (ESI) m/z calcd for $C_{33}H_{55}N_3O_6Na$ $[M+Na]^+$ 612.3989, found: 612.3986.

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