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Synthesis of 2,3-Unsaturated Alkynyl *O*-Glucosides from Tri-*O*-acetyl-D-glucal by Using Montmorillonite K-10/Iron(III) Chloride Hexahydrate with Subsequent Copper(I)-Catalyzed 1,3-Dipolar Cycloaddition

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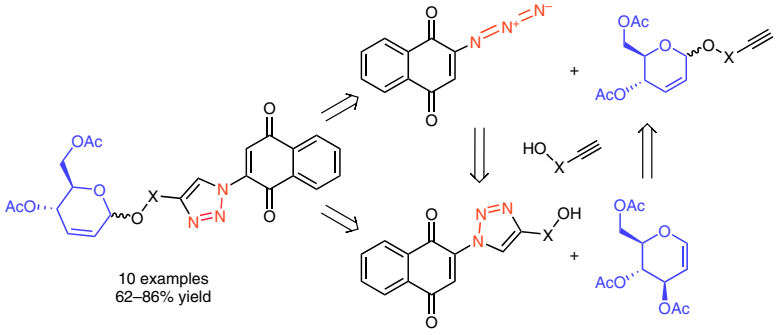

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Abstract Two strategies were considered for the synthesis of 2,3-unsaturated *O*-glucosyl-1,2,3-triazoles. The first, involving reaction between tri-*O*-acetyl-D-glucal and triazole alcohols gave no stereoselectivity. A second strategy provided 2,3-unsaturated *O*-glycosides from glycals and alkynols through a Ferrier rearrangement; this method, employing montmorillonite K-10 doped with iron(III) chloride hexahydrate in dichloromethane afforded new glycosides in good to excellent yields within short times and with high α-stereoselectivities. Subsequently, the glucosides were coupled with 2-azido-1,4-naphthoquinone to produce a new series of 1,2,3-1*H*-triazolyl *O*-glucoside derivatives through a click reaction.

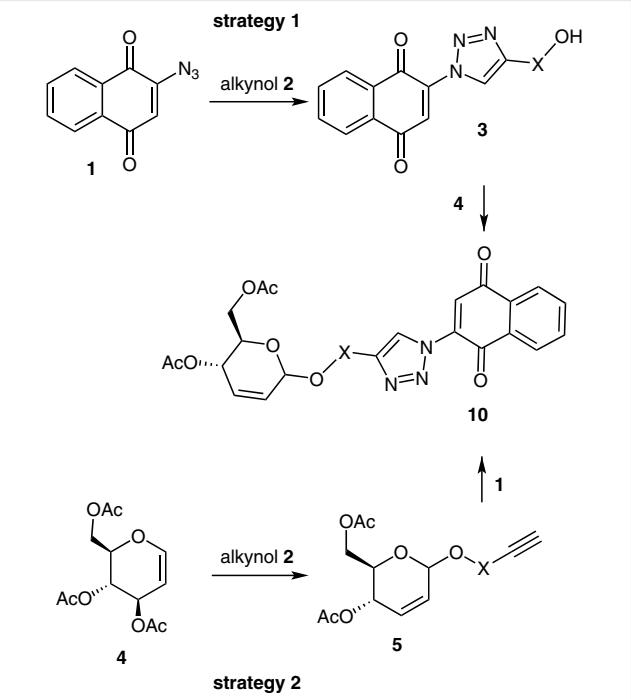
Key words rearrangements, triazoles, glycosides, alkynes, copper, click reactions

Carbohydrate chemistry has grown rapidly as a result of its importance in glycoscience, biochemistry, and biology. A diversity of strategies have been described for the synthesis of building blocks of neoglycoconjugates.[1,2] With regard to new approaches for synthesizing natural scaffolds, glycals have been used as versatile chiral synthetic intermediates in total syntheses such as those of (+)-apicularen A,[3] (+)-blasticidin S,[4] and cryptopyranmoscatone A1.[5]

The glycosylation reaction is a protocol that permits the linking of a donor (a sugar moiety) with an anomeric activated leaving group and a nucleophilic acceptor (e.g., an alcohol or glycosyl compound).[6] The Type I Ferrier reaction is a well-known protocol for the preparation of 2,3-unsaturated *O*-glycosides from glycals.[7,8] To promote this reaction, various procedures have been used. The main modifications in these methodologies have been related to the various Lewis acids used. Gómez and co-workers[8] have reviewed a wide range of conditions for the reaction and they have presented comparative studies of various acceptor and donor substrates, catalysts, solvents, temperatures, reaction times, yields, selectivities, and workups. Among the conditions and Lewis acids used for *O*-glycoside syntheses through allylic rearrangement are catalysis by palladium,[1] iodine monobromide,[9] copper(II) triflate,[10] zinc(II) bromide,[11] titanium trichloride monotriflate,[12] bromodimethylsulfonium bromide,[13] tellurium(IV) chloride,[14] gold(III) chloride,[15] indium(III) chloride,[16] or niobium(V) chloride,[17] as well as microwave irradiation,[18,19] the use of ionic liquids,[20] or the use of montmorillonite K-10[21] or montmorillonite K-10-supported bismuth(III) triflate.[22]

Iron is one of the most abundant metals on earth; consequently, it is inexpensive, ecofriendly, and has been widely investigated in organic synthesis.[23] In the last decade, iron salts have been used as Lewis acids in Ferrier reactions. Examples include iron(III) chloride,[24] iron(III) chloride combined with an ionic liquid,[25] iron(III) nitrate,[26] iron(III) sulfate under microwave irradiation,[27] iron(III) triflate,[28] and iron(III) chloride hexahydrate/chloroform.[29] While we were preparing this manuscript, Zhou and co-workers described the use of iron(III) chloride hexahydrate as a catalyst.[30]

Copper(I)-catalyzed azide–alkyne cycloaddition[31] has been employed to give 1,4-disubstituted 1,2,3-triazoles through the concept of click chemistry. Some examples of this reaction are based on carbohydrate frameworks.[2b,32] The synthesis of 1,2,3-triazolyl glycoside derivatives from glycals has been recently reported;[33–35] molecular iodine[33] and boron trifluoride etherate[34] have been used as Lewis acids in the glycosylation steps. Yadav and co-workers[35] de-



Scheme 1 Two strategies for the synthesis of 1,2,3-1*H*-triazol-4-yl glucosides

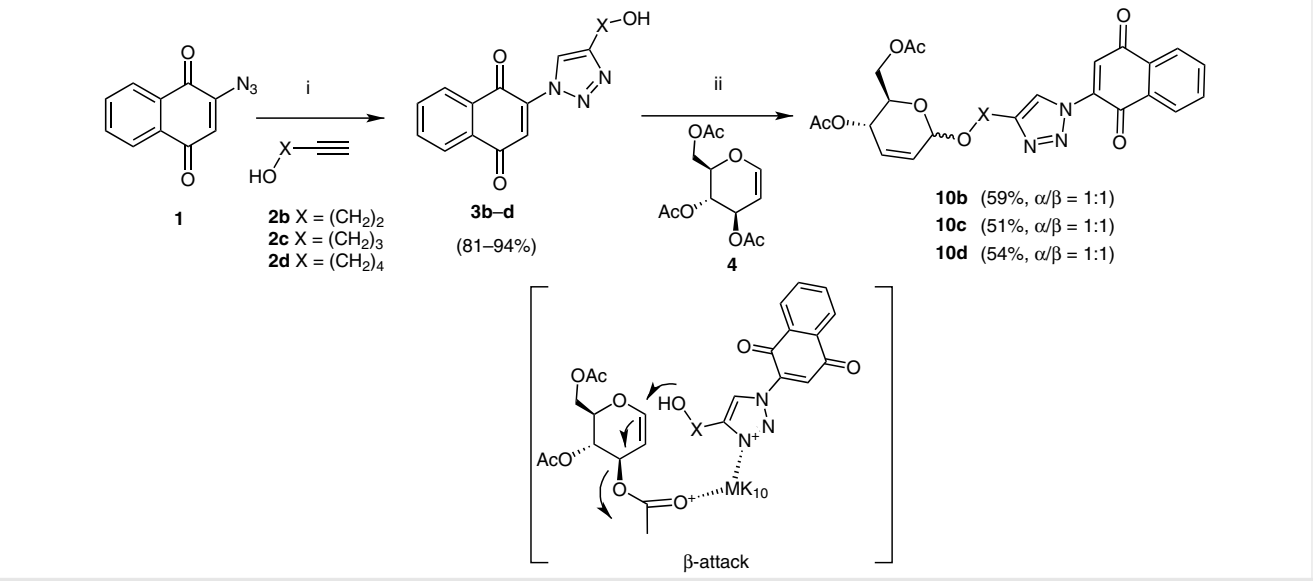
scribed a tandem Ferrier/click reaction that uses a copper(II)triflate/trimethylsilyl azide/copper system to obtain triazole glycoconjugates.

1,4-Naphthoquinone has a well-established chemistry and it has been identified with many biological activities, such as antitumor,[36a] anti-*Trypanosoma cruzi*,[36b] antifungal, and antiviral activities.[36c] Lin and co-workers described one example of a β-*C*-glucopyranosyl-1,4-naphthoquinone linked to a triazole nucleus that showed activity as an inhibitor of phosphotyrosine phosphatase 1B.[36d] As part of our interest in the synthesis of 1,2,3-triazolyl glucosides conjugated with 1,4-naphthoquinone, we reported some time ago a single example of a 1*H*-1,2,3-triazol-4-yl glucoside;[37] on that occasion, we used montmorillonite K-10 as a catalyst to promote the allylic rearrangement, but no detailed study was performed.

In attempts to prepare 1*H*-1,2,3-triazol-4-yl glucosides, we investigated two strategies (Scheme 1) with respect to the effects of the workup and reaction time on the yield and stereoselectivity.

First, we examined strategy 1 for the synthesis of 1*H*-1,2,3-triazol-4-yl glucosides (Scheme 1). The 1,3-dipolar cycloaddition conditions that we previously developed[37] were used to promote the reaction of 2-azido-1,4-naphthoquinone **1** with the alkynols **2b**–**d** (Scheme 2). The corresponding products **3b**–**d** were obtained in 81–94% yield.

Next, we used Toshima's protocol (montmorillonite K-10 in refluxing dichloromethane)[21] for the synthesis of *O*-glucosides **10b**–**d** with yields of 59, 51, and 54%, respectively. However, these reactions provided no stereoselectivity (α/β = 1:1). The α/β ratio was determined from the ^{1}H NMR spectra. The signals of the anomeric hydrogen appeared as a broad singlet at various chemical shifts ($\delta_{\alpha H\text{-}1}$ ≈ 5.05 ppm and $\delta_{\beta H\text{-}1}$ ≈ 5.15 ppm), with identical integrations (1 H) for each signal.



Scheme 2 Synthesis of 2-(1*H*-1,2,3-triazol-4-yl)-1,4-naphthoquinones by strategy 1. *Reagents and conditions*: (i) CuI, MeCN, 12 h; (ii) MK10, CH_2Cl_2, reflux, 3 h.

In *O*-glycosylation reactions of glycals, the α-isomer is usually predominant, due to an anomeric effect.[38] The formation of the β-anomer in the same ratio as the α-anomer can be explained by an intramolecular S_N2' mechanism. The use of an intramolecular S_N2' reaction to explain stereoselectivity in glycosylation reactions has been reported in the literature.[17,39] We believe that montmorillonite K-10 (MK10) can coordinate with the nitrogen sites of the triazole ring, because of their basicity. The carbonyl group at the C-3 position can also interact to favor β-attack.[40,41]

We then turned our attention to strategy 2, beginning with the preparation of the *O*-glucosyl alkynes by using montmorillonite K-10 (30 wt% with respect to triacetate **4**).[21] This gave *O*-glucosyl alkyne **5a** in 81% yield after three hours (Table 1, entry 1). Similar conditions gave compound **5c** in a moderate yield of 44% (entry 3), but failed to give **5e** from 2-methylbut-3-yn-2-ol (**2e**) (entry 7). Actually, only few methods have been successfully used with tertiary alcohols in the Ferrier reaction.[12,14,42–43] To optimize the reaction with tertiary alcohols, we decided to dope the montmorillonite K-10 (MK10) with 5 mass% of iron(III) chloride hexahydrate. Experiments with 10% (w/w of **4**) of the iron(III)-doped clay produced satisfactory results only for primary alcohols (not shown). On the other hand, with 20% (w/w of **4**) of the iron(III)-doped clay, we obtained compound **5e** with a yield of 80% after 10 minutes (entry 8). Under these optimized conditions, glucosides **5a** and **5c** were obtained in 93% and 81% yield, respectively (entries 2 and 4). This procedure was not suitable for reactions with the more-hindered nucleophile 1,1-diphenylprop-2-yn-1-ol.

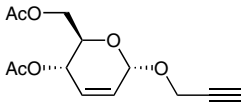
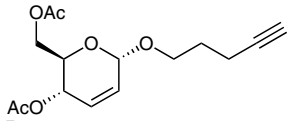
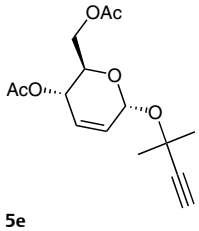
We also attempted to use iron(III) chloride hexahydrate as the sole catalyst; however, even after three hours at the reflux, the reaction remained incomplete (entry 5). Tan and co-workers obtained similar results, but their reaction was completed when the solvent dichloromethane was replaced with chloroform, and anhydrous iron(III) chloride was used as the catalyst.[29] With our catalyst [MK10-(5% $FeCl_3·6H_2O$)] at room temperature, the products **5c** and **5e** were obtained in yields of 55 and 48%, respectively; moreover, substrate **4** was also recovered (entries 6 and 9).

As shown in Table 1, a synergistic effect of MK10 and iron(III) chloride hexahydrate was observed in the Ferrier reaction in refluxing dichloromethane, as the number of Lewis acid sites increased when only 1 mol% of iron(III) chloride was used.

The 2,3-unsaturated alkynyl *O*-glucosides **5a**–**j** were synthesized under our established optimal reaction conditions [20% MK10-$FeCl_3·6H_2O$, CH_2Cl_2, reflux, 10 min (see Table 1, entries 2, 4, and 8)]. Glucosides **5a**–**j** were obtained in good to excellent yields of 80–98% (Table 2).

As expected,[7–30] the conformation of compounds **5a**–**j** was established as $^0H_5$ from the large $^3J_{4,5}$ coupling constant (8.6–10.1 Hz). The shift of the anomeric protons ($\delta_{\alpha H\text{-}1}$) for compounds **5a**–**d** ranged from 5.02 to 5.24 ppm; for **5e**–**h** and **5j**, it ranged from 5.37 to 5.73 ppm, due to an anisotropic effect on H-1 resulting from its proximity to the alkyne

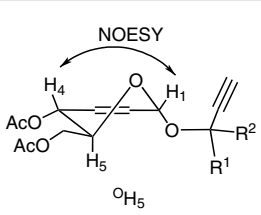
Table 1 Optimization of Conditions for the Ferrier Reaction[a]

Entry	Catalyst	Yield[b] (%)	Time	Product
1	MK10	81	3 h	 **5a**
2	MK10/$FeCl_3·6H_2O$	93	10 min	
3	MK10	44	3 h	 **5c**
4	MK10/$FeCl_3·6H_2O$	81	10 min	
5	$FeCl_3·6H_2O$	–[c]	3 h	
6	MK10/$FeCl_3·6H_2O$[d]	55	3 h	
7	MK10	trace	3 h	 **5e**
8	MK10/$FeCl_3·6H_2O$	80	10 min	
9	MK10/$FeCl_3·6H_2O$[d]	48	3 h	

[a] Reaction conditions: CH_2Cl_2, reflux.
[b] Yield after chromatographic separation.
[c] Incomplete reaction.
[d] At r.t. (30 °C). The starting material was recovered.

group (Figure 1). Furthermore, the anomeric configurations of **5a** and **5e** were determined by NOESY experiments, which confirmed that H_1 and H_4 were on the same side. The ^{1}H NMR spectra of the compounds **5a**–**j** showed that the α-anomer was the major product, with α/β ratios of 3:1 to 10:1.

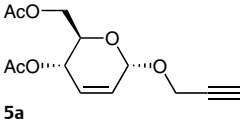
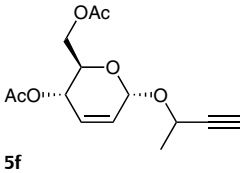
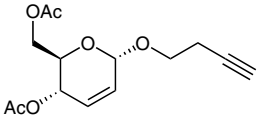
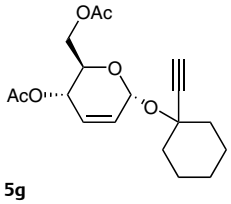
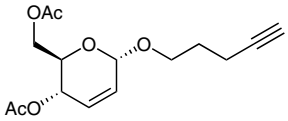
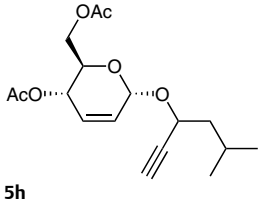
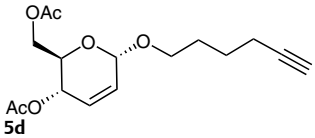
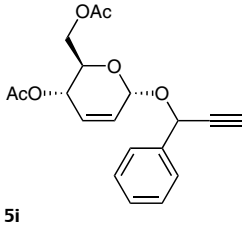
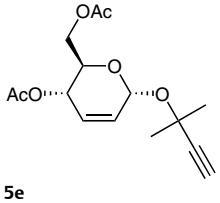
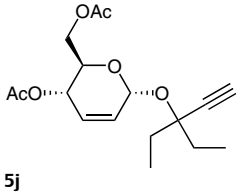
We propose the following mechanistic pathway. First, complexation of the Lewis acid (xM^{n+}) with the C_3 acetyl group results in complex **A**, with a synergistic effect when the MK10 is doped with iron(III) chloride (Scheme 3). Subsequently, elimination of the acetyl group produces an allylic oxocarbenium ion (intermediate **B**), the conversion of which into intermediate **C** is helped by the neighboring ace-



	R^1	R^2	δ(H-1) (ppm)
5a	H	H	5.24
5f	H	Me	5.37
5e	Me	Me	5.65
5j	Et	Et	5.65
5g	–(CH$_2$)$_5$–		5.73

Figure 1 Anisotropic effects on $\delta_{H\text{-}1}$ in the *O*-glucosides

Table 2 Synthesis of 2,3-Unsaturated Alkynyl *O*-Glucosides

Major product	Yield[a] (%) (α/β ratio)[b]	Ref.	Major product	Yield (%) (α/β ratio)[b]	Ref.
 **5a**	93 (5:1)	15,29	 **5f**	95 (–)[c]	15
 **5b**	92 (3:1)	14	 **5g**	86 (5:1)	
 **5c**	81 (5:1)	44	 **5h**	90 (–)[c]	
 **5d**	98 (10:1)		 **5i**	97 (–)[c]	
 **5e**	80 (6:1)	14	 **5j**	90 (3:1)	

[a] Isolated yield.
[b] Determined by ^{1}H NMR.
[c] Not determined (complex diastereoisomeric mixture).

tyl group on C-4. Anchimeric assistance by a bulky protecting groups at the C-5 position to explain the formation of an α-anomer has already been described in the literature.[7,45] The transition-states **D/D′** have their β-face sterically blocked by anchimeric assistance from the acetoxymethyl group. Finally, nucleophilic α-attack on **D/D′** leads to the protonated species **E** and, subsequently, the major products **5a**–**j**.

In addition, when **5a** (α/β = 5:1) was treated with 20% MK10-(5% $FeCl_3·6H_2O$) in refluxing dichloromethane for 30 minutes, the anomeric ratio remained unchanged, i.e. no anomerization occurred.

Attempts to recycle the catalyst were moderately effective. Unlike an aza-Michael reaction, where preheating of the MK10-$FeCl_3$ at 120 °C was required,[46] we used a catalyst that was not pretreated at high temperature, making the catalyst more ecofriendly; moreover, the low catalyst loading makes the current protocol economical.

Continuing on, we applied our new procedure as strategy 1, with the aim of finding an effective approach to the reaction of 1,2,3-triazole alcohols and tri-*O*-acetyl-D-glucal. Surprisingly, no reaction occurred, even after three hours. It is known that 1,2,3-triazoles are potentially versatile ligands for metal coordination.[47] It is therefore likely that the strong basicity of the 1,2,3-triazole alcohol quenched the acidity of the $FeCl_3$-doped MK10 clay (Figure 2). This could be indicative of a Lewis-acid property over the catalyst, but is inconclusive regarding any redox effect.

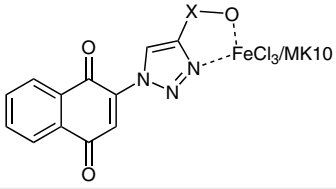
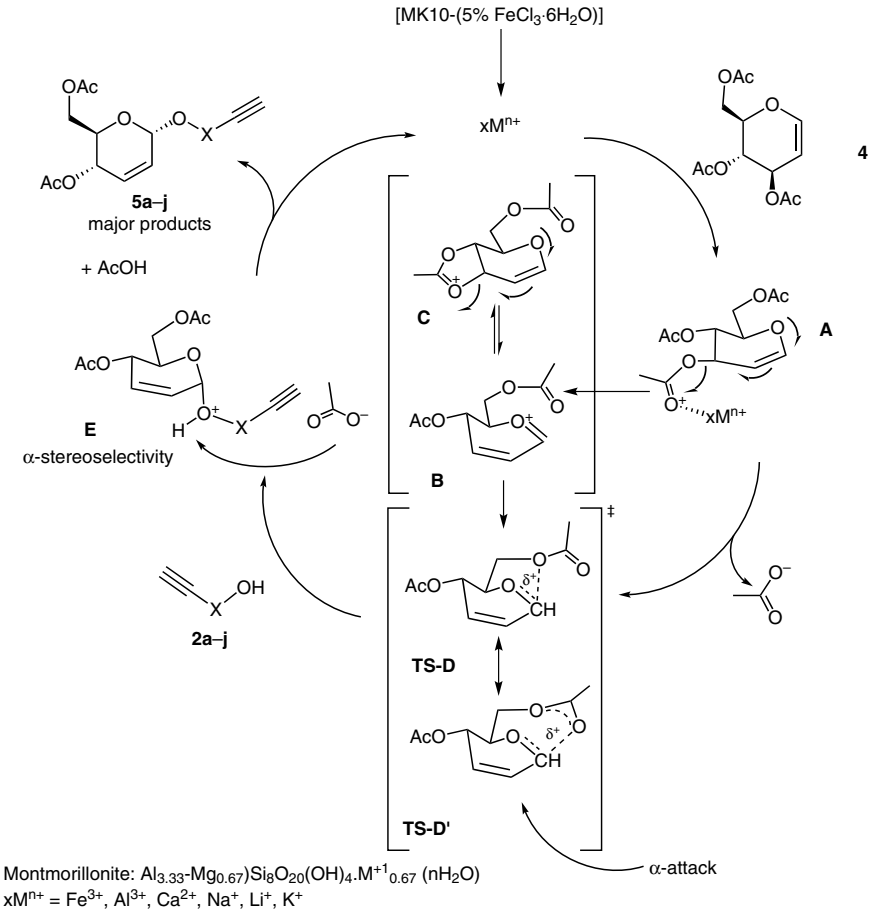


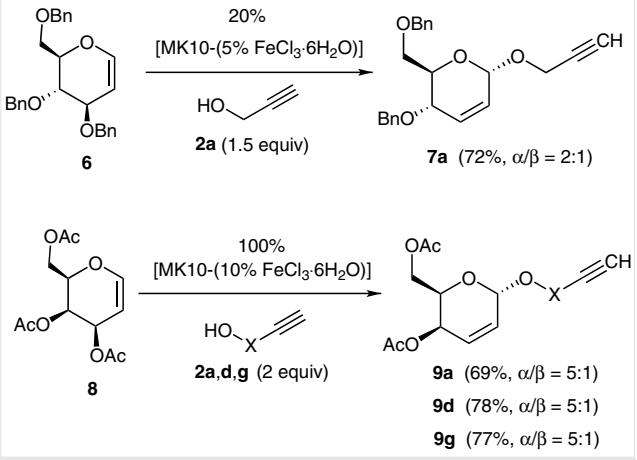
Figure 2 Hypothesis for quenching of 1,2,3-triazole alcohols in Lewis acid catalysis

To evaluate the efficiency and generality of the catalyst system, we used two other glycals: 3,4,6-tri-*O*-benzyl-D-glucal (**6**) and 3,4,6-tri-*O*-acetyl-D-galactal (**8**) (Scheme 4). When glucal **6** was treated under the conditions shown in Table 2, the reaction with propargyl alcohol (**2a**) afforded glycoside **7a** in 72% yield with an α/β ratio of 2:1 (Scheme



Scheme 3 Proposed mechanistic pathway to alkynyl *O*-glucosides with MK10/$FeCl_3·6H_2O$

4). From glucal **6**, α-selectivity was also possible via a transition state such as **TS-D** (see Scheme 3). When galactal **8** was treated with propargyl alcohol (**2a**) under the same conditions, the reaction was incomplete, even after three hours (Scheme 4). Several factors might have influenced the reactivity of **8**; for instance, in the absence of the intermediate **C** (see Scheme 3), the reaction would have needed more time and/or a stronger Lewis acid to remove the acetyl group from the 3-position.[30,48] Consequently, the yields were enhanced by using 100% (w/w of **8**) of the 10% $FeCl_3$-loaded catalyst [MK10-(10% $FeCl_3$·$6H_2O$)]. Two equivalents of alcohol **2a**, **2d**, or **2g** were found to be optimal to obtain **9a**, **9d**, and **9g** in 69% (α/β = 5:1), 78% (α/β = 5:1), and 77% (α/β = 5:1) yield, respectively. The α-selectivity from tri-*O*-acetyl-D-galactal (**8**) might indicate that the presence of an axial acetyl group in the 4-position (the position closest to the C-1 atom) causes a bulk effect that helps to form a transition state such as **D/D′**.



Scheme 4 Synthesis of *O*-glycosides from glycals by using MK10/$FeCl_3$·$6H_2O$

With the 2,3-unsaturated alkynyl *O*-glucosides **5a**–**j** in hand, we focused on the synthesis of new 1*H*-1,2,3-triazol-4-yl glucoside derivatives.

Attempts to promote a one-pot reaction, led to no appreciable amounts of product (Table 3, entries 1–3). Initially, we attempted to perform the copper(I)-catalyzed azide–alkyne cycloaddition immediately removal of the heterogeneous catalyst by filtration, even though acetic acid and iron(III) chloride remained in the solution. When we subsequently added copper(I) iodide, no reaction was apparent on TLC, even after prolonged reaction times (entry 1). In a further attempt, we evaporated the dichloromethane after the filtration step and then added copper(I) iodide and acetonitrile, but only traces of the product were formed (entry 2). When triethylamine was used, a complex mixture was obtained (entry 3).

Table 3 Attempts to Prepare Triazolyl Glucoside **10e**

Entry	Conditions	Yield (%)
1	CuI, CH_2Cl_2, 24 h (AcOH/$FeCl_3$)[a]	–[b]
2	CuI, MeCN, 20 h (AcOH/$FeCl_3$)[a]	–[c]
3	CuI, Et_3N, MeCN, 20 min (AcOH/$FeCl_3$)[a]	–[d]
4	CuI, MeCN	44[e]
5	CuI, Et_3N, MeCN. 0.5 h	54[f,g]
6	CuI, MeCN, 12 h	78 (12.0)[g,h]

[a] In the presence of residual AcOH/$FeCl_3$ from the glycosylation step.
[b] No reaction.
[c] Traces (20 h).
[d] Complex mixture (20 min).
[e] Yields for two steps. First step: glycosylation (10 min) followed by a leaching procedure; second step: cycloaddition (12 h).
[f] 2-Amino-1,4-naphthoquinone was formed and substrate **5** was recovered.
[g] Isolated yield.
[h] **5e** (1.0 mmol) + **1** (0.75 mmol).

We then tried a leaching procedure using a saturated solution of sodium bicarbonate. After extraction, the solvent was evaporated, and the residue was dissolved in acetonitrile and treated with 2-azido-1,4-naphthoquinone in the presence of 10 mol% of copper(I) iodide (Table 3, entry 4). The mixture was purified by column chromatography to give glucoside **10e** in 44% yield. For this reaction, with purification of **5e**, the global yield was 62% after two steps.

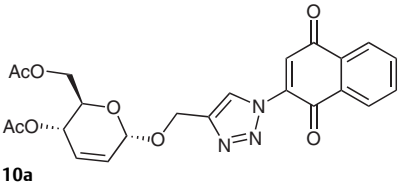
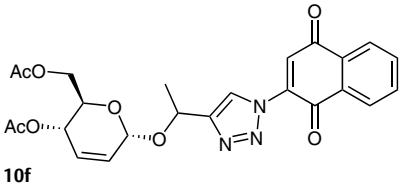
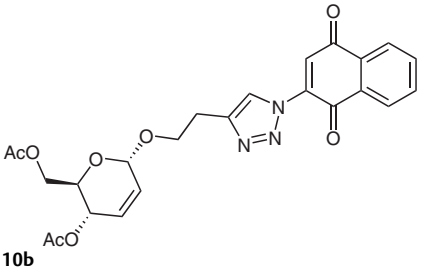
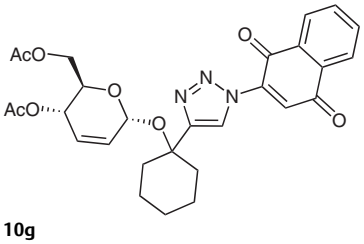
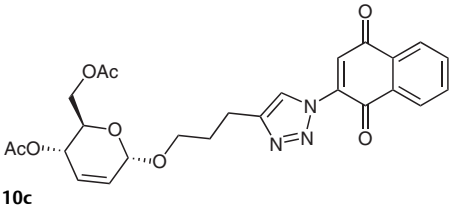
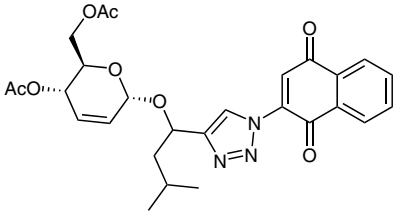
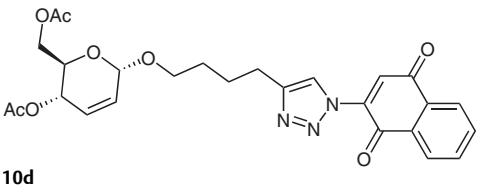
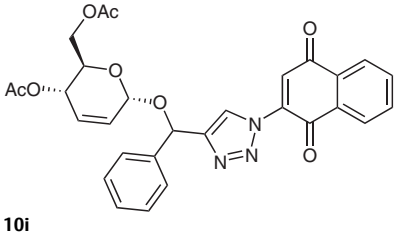
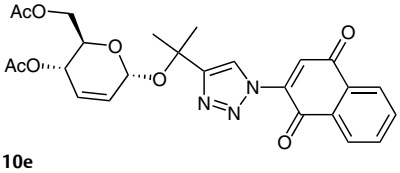
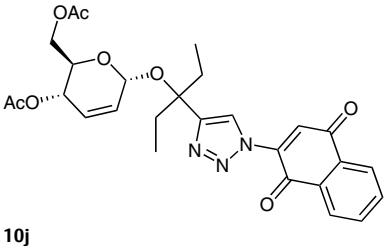
Once the glycosylation step was complete, the cycloaddition reaction was fast; treatment with copper(I) iodide and triethylamine in acetonitrile at room temperature for 30 minutes gave 1*H*-1,2,3-triazol-4-yl glucoside **10e** in 54% yield (Table 3, entry 5). In the absence of triethylamine, **10e** in was obtained in 78% after 12 hours (entry 6). This is in accord with our previous results.[37] Furthermore, a mixture of 1 mmol of glucoside **5e** and 0.75 mmol of 2-azido-1,4-naphthoquinone (**1**) showed better behavior than that achieved with an excess of **1**. On the basis of the good results that we obtained (entry 6), we synthesized 1*H*-1,2,3-triazol-4-yl glucosides **10a**–**j** by using copper(I) iodide in acetonitrile at room temperature (Table 4). The reactions were completed in 12 hours, giving **10a**–**j** in yields of 62–88%.

Scheme 5 shows our proposed mechanism. 2-Azido-1,4-naphthoquinone (**1**) is an electron-deficient azide and, consequently, more reactive, so the reaction can proceed without base catalysis. On the other hand, this chemical property also favors a copper-assisted decomposition via a nitrene intermediate **E** after loss of a nitrogen molecule (**D** → **E**).[47] Copper-assisted reduction might explain the formation of 2-amino-1,4-naphthoquinone via these intermediates. Apparently, in the presence of triethylamine, the reduction was faster than cycloaddition, resulting in the observed increase in formation of the amino derivative under basic conditions, and low yields of the cycloadduct. The re-

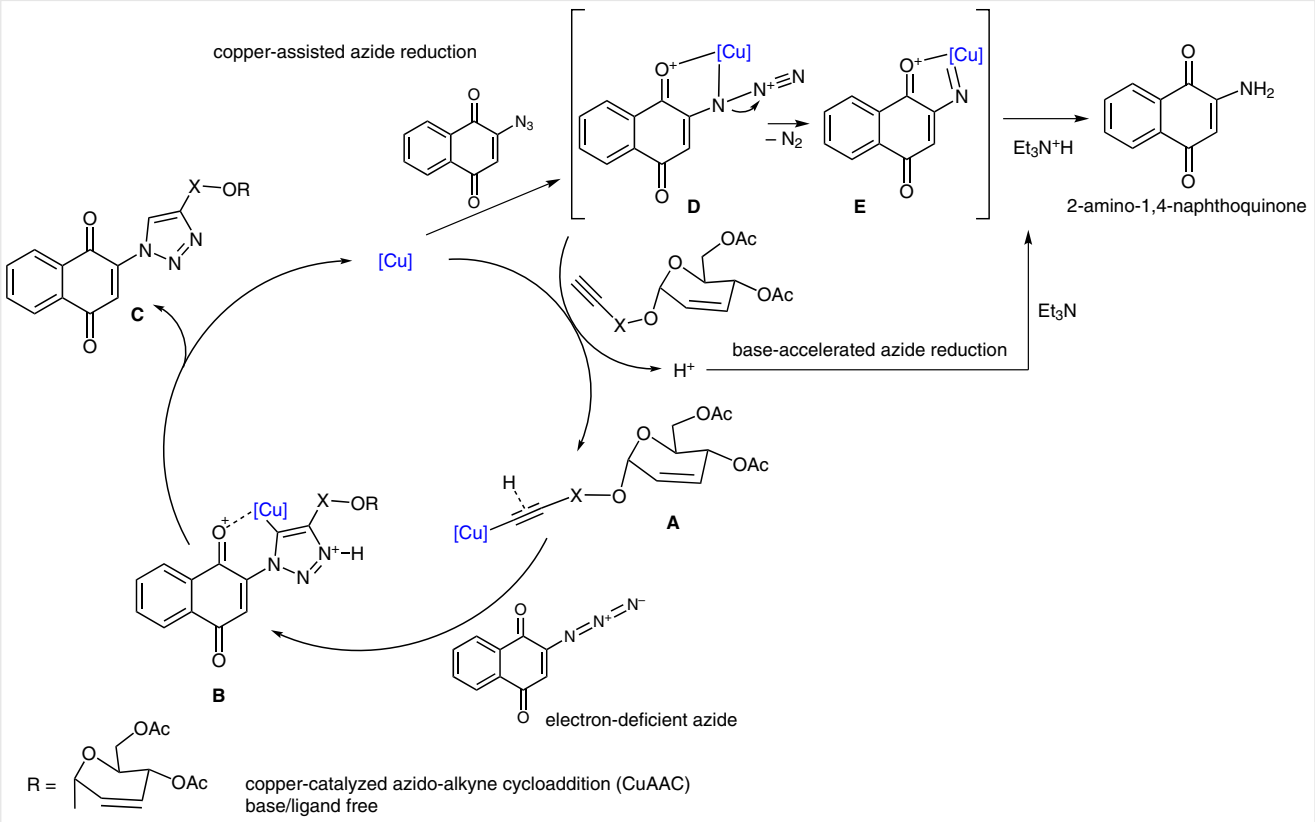
action can proceed without a base via intermediates **A** and **B**. The formation of 2-amino-1,4-naphthoquinone was also observed, but in minor proportions.

We have described a simple and efficient method for the synthesis of 2,3-unsaturated alkynyl *O*-glycosides by using inexpensive and ecofriendly montmorillonite K-10 doped with iron(III) chloride hexahydrate as the catalyst. This protocol provides glucosides **5a**–**j** in good to excellent yields (80–98%) and high α-anomeric stereoselectivity. Other glycals such tri-*O*-benzyl-D-glucal or tri-*O*-acetyl-D-galactal can be used as substrates for preparing *O*-glycosides. Subsequently, we prepared the 1,2,3-1*H*-triazol-4-yl

Table 4 Synthesis of 1*H*-1,2,3-Triazol-4-yl Glucoside Derivatives **10a**–**j**

Major product	Yield[a] (%) (α/β)[b]	Major product	Yield[a] (%) (α/β)[b]
 **10a**	73 (α only)	 **10f**	84 (–)[c]
 **10b**	82 (3:1)	 **10g**	83 (10:1)
 **10c**	62 (5:1)	 **10h**	78 (–)[c]
 **10d**	86 (10:1)	 **10i**	62 (–)[c]
 **10e**	78 (9:1)	 **10j**	83 (5:1)

[a] Isolated yield.
[b] Determined by ^{1}H NMR.
[c] Not determined (complex diastereoisomeric mixture).



Scheme 5 Proposed mechanistic pathway for the formation of 1*H*-1,2,3-triazol-4-yl glucoside derivatives

glucoside derivatives **10a–j** by means of a copper(I)-catalyzed 1,3-dipolar cycloaddition. Despite our attempts, it was not possible to develop a procedure for a one-pot synthesis of the 1,2,3-triazoles; however, by leaching the reaction mixture, a one-pot two-step procedure was performed, with a global yield of 44%. Furthermore, we defined a better strategy for preparing these target molecules for future explorations of their biological profiles.

All organic solvents were of analytical grade. Melting points were determined in a capillary tube in a PFM II BioSan apparatus. Elemental analyses were carried out by using an EA1110 CHNS-O analyzer. IR spectra were recorded on an IFS66 Bruker spectrophotometer by using KBr discs. NMR spectra were obtained with a Varian Unity Plus-300 spectrometer with $CDCl_3$ as solvent, and were calibrated for the solvent signal. Optical rotations were measured by using an Anton-Paar model MCP200 polarimeter. Air- and moisture-sensitive reactions were performed under an inert atmosphere of argon. The purification was performed by column chromatography on Merck silica gel 60 (70–230 mesh). All reactions were monitored by TLC (GF-254). Montmorillonite K-10 was purchased from Sigma-Aldrich. 2-Azido-1,4-naphthoquinone (**1**),[37] 3,4,6-tri-*O*-acetyl-D-glucal (**4**), 3,4,6-tri-*O*-acetyl-D-galactal (**8**),[49] and 3,4,6-tri-*O*-benzyl-D-glucal (**6**)[50] were prepared by the reported procedures.

K-10/Iron(III) Chloride Catalyst [MK10/(5%$FeCl_3$·6H_2O)]

$FeCl_3$·6 H_2O (50 mg) was mixed with montmorillonite K-10 (1 g) and acetone (2 mL) in a round-bottomed flask. The mixture was homogenized and the solvent was evaporated under reduced pressure.

Hydroxyalkyl-1,2,3-Triazoles (3b–d); General Procedure

The general procedure was adapted from that described in the literature.[37] 2-Azido-1,4-naphthoquinone (**1**; 1 mmol) and the appropriate alkynol **2b–d** (1.5 mmol) were mixed at 0 °C under argon in MeCN (2 mL). The mixture was then stirred at r.t. (25–30 °C) in the absence of light for 12 h. The product was purified by flash column chromatography [silica gel, hexane–EtOAc (6:4)].

2-[4-(2-Hydroxyethyl)-1*H*-1,2,3-triazol-1-yl]-1,4-naphthoquinone (3b)

Green solid; yield: 253 mg (94%); mp 119–121 °C; R_f = 0.1.

IR (KBr): 3277 (OH), 3184, 2927, 1677, 1655, 1615, 1593, 1294, 1224, 1051, 1017, 776, 716 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.10 (br s, 1 H, OH), 3.08 (t, *J* = 6.3 Hz, 2 H, CH_2), 4.03 (t, *J* = 6.2 Hz, 2 H, CH_2), 7.72 (s, 1 H, H_{naphth}), 7.82–7.87 (m, 2 H, H-Ar), 8.14–8.21 (m, 2 H, H-Ar), 8.52 (s, 1 H, H_{triaz}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 28.7, 61.4, 123.9, 126.4, 126.5, 127.2, 131.0, 131.4, 134.4, 135.0, 139.4, 146.5, 179.4, 183.8.

Anal. Calcd for $C_{14}H_{11}N_3O_3$ (269.25): C, 62.45; H, 4.12. Found: C, 62.41; H, 3.94.

2-[4-(3-Hydroxypropyl)-1*H*-1,2,3-triazol-1-yl]-1,4-naphthoquinone (3c)

Yellow solid; yield: 230 mg (81%); mp 118–120 °C; R_f = 0.1.

IR (KBr): 3410 (OH), 3183, 2961, 2935, 1678, 1654, 1623, 1586, 1298, 1262, 1055, 790, 718 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.81 (br s, 1 H, OH), 2.03 (q, *J* = 6.6 Hz, 2 H, CH_2), 2.95 (t, *J* = 7.2 Hz, 2 H, CH_2), 3.76 (t, *J* = 6.3 Hz, 2 H, CH_2), 7.74 (s, 1 H, H_{naphth}), 7.83–7.87 (m, 2 H, H-Ar), 8.14–8.22 (m, 2 H, H-Ar), 8.44 (s, 1 H, H_{triaz}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 21.9, 31.8, 61.8, 123.2, 126.3, 126.6, 127.2, 131.1, 131.5, 134.4, 135.0, 139.4, 148.6, 179.5, 183.9.

Anal. Calcd for $C_{15}H_{13}N_3O_3$ (283.28): C, 63.60; H, 4.63. Found: C, 63.66; H, 4.24.

2-[4-(3-Hydroxybutyl)-1*H*-1,2,3-triazol-1-yl]-1,4-naphthoquinone (3d)

Green solid; yield: 244 mg (82%); mp 99–101 °C; R_f = 0.2.

IR (KBr): 3351 (OH), 3165, 2926, 2852, 1678, 1653, 1614, 1590, 1298, 1331, 1295, 1051, 717 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.69 (q, *J* = 6.6 Hz, 2 H, CH_2), 1.86 (q, *J* = 7.8 Hz, 2 H, CH_2), 1.95 (br s, 1 H, OH), 2.86 (t, *J* = 7.8 Hz, 2 H, CH_2), 3.71 (t, *J* = 6.2 Hz, 2 H, CH_2), 7.72 (s, 1 H, H_{naphth}), 7.80–7.86 (m, 2 H, H-Ar), 8.13–8.20 (m, 2 H, H-Ar), 8.41 (s, 1 H, H_{triaz}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 25.2, 25.3, 32.0, 62.4, 123.0, 126.1, 126.5, 127.2, 131.1, 131.4, 134.3, 134.9, 139.4, 149.1, 179.4, 183.9.

Anal. Calcd for $C_{16}H_{15}N_3O_3$ (297.30): C, 64.64; H, 5.09. Found: C, 64.90; H, 5.33.

2,3-Unsaturated Alkynyl *O*-Glycosides 5a–j, 7a, 9a, 9d, and 9g; General Procedures

Method A. To a solution of tri-*O*-acetyl-D-glucal (**4**; 1 mmol) in CH_2Cl_2 (2 mL; dried with $CaCl_2$) at 0 °C was added MK10-(5% $FeCl_3$·6 H_2O) (20 wt% w.r.t. **4**; 54.4 mg or 0.01 mmol $FeCl_3$). The appropriate alcohol (1.5 mmol) was then added.

Method B. To a solution of tri-*O*-benzyl-D-glucal **6** (83 mg, 0.2 mmol) in CH_2Cl_2 (2 mL; dried with $CaCl_2$) at 0 °C was added MK10-(5% $FeCl_3$·6 H_2O) (20 wt% w.r.t. **6**; 17 mg or 0.003 mmol $FeCl_3$). The appropriate alcohol (0.3 mmol, 1.5 equiv) was then added

Method C. To a solution of tri-*O*-acetyl-D-galactal **8** (100 mg, 0.37 mmol) in CH_2Cl_2 (2 mL; dried with $CaCl_2$) at 0 °C was added MK10-(10% $FeCl_3$·6 H_2O) (100 wt% w.r.t. **8**; 100 mg or 0.02 mmol $FeCl_3$). The appropriate alcohol (0.74 mmol, 2 equiv) was then added.

Workup. The mixture was refluxed for 10 min. Removal of the catalyst by filtration and evaporation of the solvent under vacuum gave a residue that was purified by flash column chromatography [silica gel, hexane–EtOAc (7:3; 50 mL)].

Prop-2-yn-1-yl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (5a)

[CAS Reg. No. 121237–62–5][14,15,29]

White solid; yield: 249 mg (93%); mp 55–57 °C (Lit.[15] 56–58 °C); R_f = 0.3; $[\alpha]_D^{25}$ +170 (*c* 0.1, CH_2Cl_2) [Lit.[29] +156.4 (*c* 1.0, CH_3Cl)].

IR (KBr): 3279, 2904, 2110 (C≡C), 1739 (C=O), 1377, 1237, 1042 cm^{-1}.

But-3-yn-1-yl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (5b)

[CAS Reg. No. 135195–22–1][14]

Colorless oil; yield: 260 mg (92%); R_f = 0.3; $[\alpha]_D^{25}$ +130 (*c* 0.1, CH_2Cl_2) [Lit.[14] +91.3 (*c* 1.0, MeOH)].

Pent-4-yn-1-yl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (5c)

[CAS Reg. No. 1173831–41–8][44]

Colorless oil; yield: 240 mg (81%); R_f = 0.6; $[\alpha]_D^{25}$ +160 (*c* 0.1, CH_2Cl_2).

IR (KBr): 3283, 2934, 2092 (C≡C), 1743 (C=O), 1435, 1371, 1231, 1033 c m^{-1}.

Hex-5-yn-1-yl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (5d)

Colorless oil; yield: 304 mg (98%); R_f = 0.4; $[\alpha]_D^{25}$ +140 (*c* 0.1, CH_2Cl_2).

IR (KBr): 3288, 2942, 2092 (C≡C), 1745 (C=O), 1371, 1239, 1041 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.59–1.65 (m, 2 H, CH_2), 1.72–1.75 (m, 2 H, CH_2), 1.96 (t, *J* = 2.7 Hz, 1 H, CH), 2.09 (s, 3 H, CH_3CO), 2.11 (s, 3 H, CH_3CO), 2.24 (td, *J* = 7.0, 2.7 Hz, 2 H, CH_2), 3.55 (dt, *J* = 9.8, 5.8 Hz, 1 H, CH_2), 3.81 (dt, *J* = 9.8, 6.2 Hz, 1 H, CH_2), 4.10 (ddd, *J* = 9.8, 5.5, 2.4 Hz, 1 H, H-5), 4.19 (dd, *J* = 12.1, 2.7 Hz, 1 H, H-6), 4.25 (dd, *J* = 12.1, 5.4 Hz, 1 H, H-6′), 5.03 (br s, 1 H, H-1), 5.31 (ddd, *J* = 9.8, 2.7, 1.5 Hz, 1 H, H-4), 5.83 (ddd, *J* = 10.2, 2.3, 1.5 Hz, 1 H, H-2), 5.89 (dd, *J* = 10.6, 1.2 Hz, 1 H, H-3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.1, 20.8, 21.0, 25.2, 28.7, 63.1, 65.3, 66.9, 68.2, 68.6, 84.1, 94.4, 127.8, 129.0, 170.3, 170.8.

Anal. Calcd for $C_{16}H_{22}O_6$ (310.34): C, 61.92; H, 7.15. Found: C, 62.26; H, 7.49.

1,1-Dimethylprop-2-yn-1-yl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (5e)

[CAS Reg. No. 1400767–35–2][14]

Colorless oil; yield: 237 mg (80%); R_f = 0.4; $[\alpha]_D^{25}$ +170 (*c* 0.1, CH_2Cl_2) [Lit.[14] +51.7 (*c* 0.5, MeOH)].

IR (KBr): 3276, 2922, 2074 (C≡C), 1740 (C=O), 1438, 1368, 1228, 1026 cm^{-1}.

(*R,S*)-1-Methylprop-2-yn-1-yl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (5f)

[CAS Reg. No. 1192736–23–4][15]

Colorless oil; yield: 268 mg (95%), (Lit.[15] 72%); R_f = 0.3 (hexane–EtOAc, 8:2); $[\alpha]_D^{25}$ +90 (*c* 0.1, CH_2Cl_2).

IR (KBr): 3270, 2933, 2110 (C≡C), 1740 (C=O), 1439, 1371, 1229, 1034 cm^{-1}.

The ^1H and ^{13}C NMR data are for a mixture rich in one diastereomer (2:1) after a second slow column chromatographic purification.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.47 (d, *J* = 7.0 Hz, 3 H, CH_3), 2.07 (s, 3 H, CH_3CO), 2.08 (s, 3 H, CH_3CO), 2.44 (d, *J* = 2.4 Hz, 1 H, CH), 4.06 (ddd, *J* = 9.8, 5.9, 2.7 Hz, 1 H, H5), 4.17–4.22 (m, 2 H, H-6 and H-6′), 4.55 (dq, *J* = 6.9, 2.0 Hz, 1 H, CHO), 5.31 (ddd, *J* = 9.8, 3.1, 1.6 Hz, 1 H, H-4), 5.37 (br s, 1 H, H-1), 5.83 (ddd, *J* = 10.4, 1.5, 1.5 Hz, 1 H, H-2), 5.90 (br d, *J* = 10.2 Hz, 1 H, H-3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 20.9, 22.0, 62.0, 63.0, 65.3, 67.2, 73.5, 82.8, 91.7, 127.7, 129.4, 170.2, 170.7.

1-Ethynylcyclohexyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (5g)

Colorless oil; yield: 289 mg (86%); R_f = 0.5; $[\alpha]_D^{25}$ +140 (*c* 0.1, CH_2Cl_2).

IR (KBr): 3272, 2937, 2860, 2060 (C≡C), 1745 (C=O), 1450, 1371, 1236, 1031 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 1.24–1.90 (m, 10 H, $5CH_2$), 2.08 (s, 6 H, $2CH_3CO$), 2.57 (s, 1 H, CH), 4.14–4.25 (m, 3 H, H-5, H-6, and H-6′), 5.28 (d, *J* = 8.6 Hz, 1 H, H-4), 5.73 (br s, 1 H, H-1), 5.80 (br d, *J* = 10.6 Hz, 1 H, H-2), 5.87 (br d, *J* = 10.5 Hz, 1 H, H-3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8, 22.9, 25.2, 38.6, 63.2, 65.2, 67.2, 75.1, 84.4, 90.7, 128.4, 129.1, 170.3, 170.8.

Anal. Calcd for $C_{18}H_{24}O_6$ (336.38): C, 64.27; H, 7.19. Found: C, 64.65; H, 7.50.

(*R*,*S*)-1-Isobutylprop-2-yn-1-yl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (5h)

Colorless oil; yield: 292 mg (90%); R_f = 0.6; $[\alpha]_D^{25}$ +180 (*c* 0.1, CH_2Cl_2).

IR (KBr): 3274, 2958, 2936, 2093 (C≡C), 1745 (C=O), 1370, 1236, 1028 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.90–0.95 (m, 12 H, $4CH_3$, *R*/*S*), 1.52–1.62 (m, 2 H, CH, *R*/*S*), 1.67–1.76 (m, 2 H, CH_2, *R*/*S*), 1.80–1.90 (m, 2 H, CH_2, *R* or *S*), 2.06–2.08 (m, 12 H, $4CH_3CO$, *R*/*S*), 2.42 (d, *J* = 2.0 Hz, 1 H, CH, *R* or *S*), 2.44 (d, *J*= 2.0 Hz, 1 H, CH, *R* or *S*), 4.04 (ddd, *J* = 9.4, 5.5, 2.4 Hz, 2 H, H-5, *R*/*S*), 4.15–4.25 (m, 4 H, H-6 and H-6′, *R*/*S*), 4.31–4.36 (m, 1 H, CHO, *R* or *S*), 4.49–4.53 (m, 1 H, CHO, *R* or *S*), 5.16 (br s, 1 H, H-1, *R* or *S*), 5.27–5.30 (m, 2 H, H-4, *R*/*S*), 5.40 (br s, 1 H, H-1, *R* or *S*), 5.77–5.83 (m, 2 H, H-2, *R*/*S*), 5.89 (br d, *J* = 10.1 Hz, 2 H, H-3, *R*/*S*).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 20.9, 21.9, 22.5, 22.7, 24.4, 44.4, 44.8, 62.4, 63.1, 64.5, 64.9, 65.2, 67.2, 72.9, 73.9, 82.4, 91.3, 94.6, 127.3, 127.7, 129.1, 129.5, 170.1, 170.2, 170.7, 170.8.

Anal. Calcd for $C_{17}H_{24}O_6$ (324.37): C, 62.95; H, 7.46. Found: C, 63.32; H, 7.22.

(*R*,*S*)-1-Phenylprop-2-yn-1-yl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (5i)

[CAS Reg. No. 957636–17–8] (No data).

Yellow oil; yield: 334 mg (97%); R_f = 0.6; $[\alpha]_D^{25}$ +80 (*c* 0.1, CH_2Cl_2).

IR (KBr): 3289, 2923, 2129 (C≡C), 1739 (C=O), 1454, 1372, 1239, 1022, 947, 738, 699, 645 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 2.01–2.14 (m, 12 H, 2 × CH_3CO, *R*/*S*), 2.65 (d, *J* = 2.3 Hz, 1 H, CH, *R* or *S*), 2.68 (d, *J* = 1.9 Hz, 1 H, CH, *R* or *S*), 4.11–4.31 (m, 6 H, H-5, H-6 and H-6′, *R*/*S*), 5.08 (d, *J* = 2.0 Hz, 1 H, H-1, *R* or *S*), 5.33–5.39 [m, 2 H (H-4, *R* or *S*; H-1, *R* or *S*)], 5.47 (dd, *J* = 10.1, 2.0 Hz, 1 H, H-4, *R* or *S*), 5.57 (br s, 2 H, CHO, *R*/*S*), 5.71–5.94 (m, 4 H, H-2 and H-3, *R*/*S*), 7.35–7.42 (m, 6 H, H_{Ar}), 7.50–7.57 (m, 4 H, *ortho*-H_{Ar}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8 (2 C), 20.9 (2 C), 62.6, 63.1, 65.1, 65.3, 67.3, 67.4, 68.3, 69.0, 74.8, 75.1, 76.2, 80.7, 82.1, 91.9, 92.4, 126.6, 127.3, 127.5 (2 C), 127.6, 127.8, 128.5, 128.6, 128.7 (3 C), 128.9, 129.6, 129.8, 137.6, 137.7, 170.2, 170.3, 170.7, 170.8.

Anal. Calcd for $C_{19}H_{20}O_6$ (344.36): C, 66.27; H, 5.85. Found: C, 66.58; H, 5.47.

1,1-Diethylprop-2-yn-1-yl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (5j)

Colorless oil; yield: 291 mg (90%); R_f = 0.7; $[\alpha]_D^{25}$ +100 (*c* 0.1, CH_2Cl_2).

IR (KBr): 3277, 2975, 2941, 2074 (C≡C), 1746 (C=O), 1372, 1238, 1028 cm^{-1}.

^1H NMR (300 MHz, $CDCl_3$): δ = 0.96 (t, *J* = 7.1 Hz, 3 H, CH_3), 0.97 (t, *J* = 7.6 Hz, 3 H, CH_3), 1.65–1.73 (m, 2 H, CH_2), 1.80–1.94 (m, 2 H, CH_2), 2.07 (s, 6 H, 2 × CH_3CO), 2.56 (s, 1 H, CH), 4.10–4.16 (m, 2 H, H-5 and H-6), 4.23 (dd, *J* = 12.5, 5.9 Hz, 1 H, H-6′), 5.27 (ddd, *J* = 9.4, 2.9, 1.8 Hz, 1 H, H-4), 5.65 (br s, 1 H, H-1), 5.78 (ddd, *J* = 10.0, 2.9, 1.8 Hz, 1 H, H-2), 5.86 (br d, *J* = 10.6 Hz, 1 H, H-3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 8.3, 8.4, 20.7, 20.8, 31.7, 32.4, 34.2, 62.9, 63.2, 65.2, 67.2, 83.4, 90.9, 128.3, 128.9, 170.3, 170.9.

Anal. Calcd for $C_{17}H_{24}O_6$ (324.37): C, 62.95; H, 7.46. Found: C, 62.98; H, 7.77.

Prop-2-yn-1-yl 4,6-Di-*O*-benzyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (7a)

[CAS Reg. No. 251914–74–6][51,52]

Colorless oil; yield: 54 mg (72%, α/β = 2:1); (Lit.[51] 74% α/β = 8:1); R_f = 0.5 (hexane–EtOAc, 8:2); $[\alpha]_D^{25}$ +69.8 (*c* 0.3, CH_2Cl_2) [Lit.[52] +158 (*c* 2.7, CH_3Cl)].

Prop-2-yn-1-yl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (9a)

[CAS Reg. No. 158053–95–3][15,51]

Colorless oil; yield: 68 mg (69%, α/β = 5:1) (Lit.[51] 75%, α/β = 19:1); $[\alpha]_D^{25}$ –101.4 (*c* 0.7, CH_2Cl_2) [Lit.[15] –107.9 (*c* 0.5, $CHCl_3$)].

Hex-5-yn-1-yl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (9d)

Colorless oil; yield: 89 mg (78%, α/β = 5:1); R_f = 0.6; $[\alpha]_D^{25}$ –79.6 (*c* 0.2, CH_2Cl_2).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.59–1.65 (m, 2 H, CH_2), 1.70–1.79 (m, 2 H, CH_2), 1.96 (t, *J* = 3.0 Hz, 1 H, C≡CH), 2.08 (br s, 6 H, 2 × CH_3CO), 2.24 (td, *J* = 7.0, 2.9 Hz, 2 H, CH_2), 3.54 (dt, *J* = 9.4, 6.5 Hz, 1 H, CH_2), 3.82 (dt, *J* = 9.9, 6.5 Hz, 1 H, CH_2), 4.21–4.24 (m, 2 H, H-6 and H-6′), 4.35 (ddd, *J* = 7.6, 5.8, 2.9 Hz, 1 H, H-5), 5.02 (dd, *J* = 5.2, 2.4 Hz, 1 H, H-4), 5.07 (d, *J* = 2.9 Hz, 1 H, H-1), 6.03 (dd, *J* = 10.0, 3.0 Hz, 1 H, H-2), 6.12 (dd, *J* = 10.0, 4.7 Hz, 1 H, H-3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 18.1, 20.8 (2 C), 25.2, 28.6, 62.8, 62.9, 66.8, 67.8, 68.6, 84.1, 93.8, 125.1, 130.6, 170.4, 170.6.

Anal. Calcd for $C_{16}H_{22}O_6$ (310.34): C, 61.92; H, 7.15. Found: C, 62.35; H, 7.47.

1-Ethynylcyclohexyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*threo*-hex-2-enopyranoside (9g)

Yellow oil; yield: 95 mg (77%, α/β = 5:1); R_f = 0.6; $[\alpha]_D^{25}$ –38.1 (*c* 0.4, CH_2Cl_2).

^1H NMR (300 MHz, $CDCl_3$): δ = 1.53–1.71 (m, 10 H, $5CH_2$), 2.05 (s, 3 H, $2CH_3CO$), 2.07 (s, 3 H, $2CH_3CO$), 2.48 (s, 1 H, CH), 4.20–4.22 (m, 2 H, H-6 and H-6′), 4.42 (ddd, *J* = 6.5, 6.5, 2.4 Hz, 1 H, H-5), 5.03 (dd, *J* = 5.9, 3.0 Hz, 1 H, H-4), 5.79 (br d, *J* = 2.9 Hz, 1 H, H-1), 5.99 (dd, *J* = 10.0, 3.5 Hz, 1 H, H-2), 6.12 (dd, *J* = 9.9, 2.9 Hz, 1 H, H-3).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 23.0, 25.1, 25.2, 38.7, 62.8 (2 C), 67.0, 72.1, 75.4, 84.3, 90.3, 124.6, 131.8, 170.4, 170.6.

Anal. Calcd for $C_{18}H_{24}O_6$ (336.38): C, 64.27; H, 7.19. Found: C, 64.01; H, 7.34.

1*H*-1,2,3-Triazol-1-yl Glucoside Derivatives 10a–j; General Procedure

2-Azido-1,4-naphthoquinone (**1**; 0.75 mmol) was added to a solution of the appropriate 2,3-unsaturated alkynyl *O*-glucoside **5a**–**j** (1 mmol) and CuI (10 mol%, 0.1 mmol) in MeCN (2 mL) at 0 °C, and the mixture was stirred at r.t. (25–30 °C) for 12 h. Because of their proximity to 2-amino-1,4-naphthoquinone on TLC, the products was purified by two-step column chromatography [silica gel, hexane–EtOAc (6:4, 100 mL) then CH_2Cl_2–EtOAc (9:1, 100 mL)].

[1-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-1*H*-1,2,3-triazol-4-yl]methyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (10a)

[CAS Reg. No. 1353244-67-3][37]

Yellow solid; yield: 341 mg (73%); mp 115 °C (Lit.[37] 108–110 °C); $[\alpha]_D^{25}$ +70 (*c* 0.1, CH_2Cl_2) [Lit.[31] +56 (*c* 0.4, CH_3Cl)].

IR (KBr): 3165, 3073, 2944, 1745, 1677, 1655, 1372, 1233, 1032, 972 cm^{-1}.

[1-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-1*H*-1,2,3-triazol-4-yl]ethyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (10b)

Green solid; yield: 394 mg (82%); mp 76–78 °C; R_f = 0.23 (hexane–EtOAc, 7:3); $[\alpha]_D^{25}$ +100 (*c* 0.1, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.08 (s, 3 H, CH_3CO), 2.10 (s, 3 H, CH_3CO), 3.17 (t, *J* = 6.5 Hz, 2 H, CH_2), 3.88 (dt, *J* = 13.1, 6.4 Hz, 2 H, CH_2O), 4.10–4.26 (m, 3 H, H-5, H-6, H-6′), 5.10 (br s, 1 H, H-1), 5.33 (d, *J* = 9.9 Hz, 1 H, H-4), 5.86 (dd, *J* = 9.8, 2.0 Hz, 1 H, H-2), 5.91 (br d, *J* = 10.5 Hz, 1 H, H-3), 7.76 (s, 1 H, H_{naphth}), 7.81–7.89 (m, 2 H, H_{naphth}), 8.15–8.18 (m, 1 H, H_{naphth}), 8.20–8.23 (m, 1 H, H_{naphth}), 8.51 (s, 1 H, H_{triaz}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8, 21.0, 26.5, 63.0, 65.3, 67.1, 67.3, 94.6, 123.9, 126.3, 126.6, 127.2, 127.5, 129.3, 131.1, 131.5, 134.3, 135.0, 139.4, 146.1, 170.2, 170.8, 179.4, 183.8.

Anal. Calcd for $C_{24}H_{23}N_3O_8$ (481.45): C, 59.87; H, 4.82. Found: C, 60.20; H, 4.90.

[1-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-1*H*-1,2,3-triazol-4-yl]propyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (10c)

Yellow solid; yield: 307 mg (62%); mp 50–52 °C; R_f = 0.1 (hexane–EtOAc, 7:3); $[\alpha]_D^{25}$ +120 (*c* 0.1, CH_2Cl_2).

IR (KBr): 3165, 3076, 2949, 1738, 1678, 1655, 1374, 1228, 1018, 976 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.07 (s, 3 H, CH_3CO), 2.08 (s, 3 H, CH_3CO), 2.11–2.07 (m, 2 H, CH_2) 2.93 (td, *J* = 7.6, 2.3 Hz, 2 H, CH_2), 3.60 (dt, *J* = 11.7, 5.8 Hz, 1 H, CH_2O), 3.88 (dt, *J* = 12.9, 6.4 Hz, 1 H, CH_2O), 4.12 (ddd, *J* = 12.3, 5.3, 2.3 Hz, 1 H, H-5), 4.17 (dd, *J* = 11.2, 2.3 Hz, 1 H, H-6), 4.25 (dd, *J*= 11.8, 5.8 Hz, 1 H, H-6′), 5.05 (br s, 1 H, H-1), 5.31 (d, *J* = 11.8 Hz, 1 H, H-4), 5.87–5.96 (m, 2 H, H-2 and H-3), 7.73 (s, 1 H, H_{naphth}), 7.81–7.85 (m, 2 H, H_{naphth}), 8.13–8.16 (m, 1 H, H_{naphth}), 8.18–8.21 (m, 1 H, H_{naphth}), 8.43 (s, 1 H, H_{triaz}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 20.9, 22.3, 29.1, 63.0, 65.2, 66.9, 67.8, 94.4, 123.0, 126.1, 126.5 (2 C), 127.2, 127.7, 129.1, 131.1, 134.3, 135.0, 139.3, 148.5, 170.2, 170.7, 179.5, 183.8.

Anal. Calcd for $C_{25}H_{25}N_3O_8$ (495.48): C, 60.60; H, 5.09. Found: C, 60.49; H, 5.26.

[1-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-1H-1,2,3-triazol-4-yl]butyl 4,6-Di-O-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (10d)

Green solid; yield: 438 mg (86%); mp 74–75 °C; R_f = 0.3 (hexane–EtOAc, 7:3); $[\alpha]_D^{25}$ +70 (*c* 0.1, CH_2Cl_2).

IR (KBr): 3162, 3071, 2926, 2866, 1732, 1677, 1654, 1373, 1238, 1017, 985 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.74 (m, 2 H, CH_2), 1.87 (m, 2 H, CH_2), 2.08 (s, 3 H, CH_3CO), 2.10 (s, 3 H, CH_3CO), 2.87 (t, *J* = 7.5 Hz, 2 H, CH_2), 3.57 (dt, *J* = 9.8, 6.2 Hz, 1 H, CH_2O), 3.85 (dt, *J* = 9.8, 6.3 Hz, 1 H, CH_2O), 4.11 (ddd, *J* = 9.4, 5.5, 2.4 Hz, 1 H, H-5), 4.18 (dd, *J* = 11.7, 2.3 Hz, 1 H, H-6), 4.25 (dd, *J* = 12.1, 5.5 Hz, 1 H, H-6′), 5.04 (br s, 1 H, H-1), 5.32 (ddd, *J* = 9.8, 2.7, 1.6 Hz, 1 H, H-4), 5.84 (ddd, *J* = 10.2, 2.4, 1.6 Hz, 1 H, H-2), 5.89 (dd, *J* = 10.5, 1.2 Hz, 1 H, H-3), 7.75 (s, 1 H, H_{naphth}), 7.83–7.86 (m, 2 H, H_{naphth}), 8.15–8.18 (m, 1 H, H_{naphth}), 8.20–8.22 (m, 1 H, H_{naphth}), 8.42 (s, 1 H, H_{triaz}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8, 21.0, 25.3, 25.9, 29.2, 63.0, 65.3, 66.9, 68.4, 94.4, 123.0, 126.1, 126.5, 127.2, 127.8, 129.0, 131.1, 131.5, 134.3, 135.0, 139.4, 149.0, 170.3, 170.8, 179.5, 183.9.

Anal. Calcd for $C_{26}H_{27}N_3O_8$ (509.51): C, 61.29; H, 5.34. Found: C, 61.38; H, 5.45.

[1-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-1*H*-1,2,3-triazol-4-yl]-1-methylethyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (10e)

Yellow oil; yield: 387 mg (78%); R_f = 0.3 (hexane–EtOAc, 6:4); $[\alpha]_D^{25}$ +130 (*c* 0.1, CH_2Cl_2).

IR (KBr): 2981, 2930, 1742, 1682, 1664, 1370, 1297, 1240, 1026 cm^{-1}.

^{1}H NMR (300MHz, $CDCl_3$): δ = 1.77 (s, 3 H, CH_3), 1.82 (s, 3 H, CH_3), 2.08 (s, 3 H, CH_3CO), 2.09 (s, 3 H, CH_3CO), 4.10–4.13 (m, 1 H, H-5), 4.16–4.23 (m, 2 H, H-6 and H-6′), 5.23 (br s, 1 H, H-1), 5.27 (br d, *J* = 9.4 Hz, 1 H, H-4), 5.77 (ddd, *J* = 10.2, 1.9, 1.9 Hz, 1 H, H-2), 5.88 (br d, *J* = 10.2 Hz, 1 H, H-3), 7.78 (s, 1 H, H_{naphth}), 7.85–7.87 (m, 2 H, H_{naphth}), 8.17–8.19 (m, 1 H, H_{naphth}), 8.21–8.23 (m, 1 H, H_{naphth}), 8.60 (s, 1 H, H_{triaz}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8, 21.0, 27.2, 28.9, 63.0, 65.2, 67.0, 74.1, 89.9, 123.2, 126.6 (2 C), 127.2, 128.7, 128.8, 131.5, 134.4, 135.0, 139.3, 153.8, 170.3, 170.8, 179.4, 183.8.

Anal. Calcd for $C_{25}H_{25}N_3O_8$ (495.48): C, 60.60; H, 5.09. Found: C, 60.27; H, 5.55.

(*R*,*S*)-1-[1-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-1*H*-1,2,3-triazol-4-yl]ethyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (10f)

Green solid; yield 404 mg (84%); mp 94–96 °C; R_f = 0.5 (hexane–EtOAc, 6:4); $[\alpha]_D^{25}$ +90 (*c* 0.1, CH_2Cl_2).

IR (KBr): 3155, 2944, 1737, 1681, 1622, 1372, 1241, 1017 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.67 (d, *J* = 6.6 Hz, 3 H, CH_3, *R* or *S*), 1.71 (d, *J* = 6.7 Hz, 3 H, CH_3, *R* or *S*), 2.04 (s, CH_3CO, *R* or *S*) 2.07 (s, 3 H, CH_3CO, *R* or *S*), 2.10 (s, 3 H, CH_3CO, *R* or *S*), 2.14 (s, 3 H, CH_3CO, *R* or *S*), 4.03 (dd, *J* = 12.1, 2.3 Hz, 1 H, H-6, *R* or *S*), 4.07–4.14 (m, 2 H, H-5, *R*/*S*), 4.17–4.32 [m, 5 H (H-6, *R* or *S*; H-6′, *R*/*S*; CHO, *R*/*S*)], 5.22 (br s, 1 H, H-1, *R* or *S*), 5.23 (br s, 1 H, H-1, *R* or *S*), 5.33–5.36 (m, 2 H, H-4, *R*/*S*), 5.81–5.94 (m, 4 H, H-2 and H-3, *R*/*S*), 7.76 and 7.77 (2 × s, 2 H, H_{naphth}, *R*/*S*), 7.84–7.87 (m, 4 H, H_{naphth}, *R*/*S*), 8.16–8.23 (m, 4 H, H_{naphth}, *R*/*S*), 8.61 (s, 2 H, H_{triaz}, *R*/*S*).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.0, 20.8, 21.0, 21.8, 62.6, 63.1, 65.2, 65.4, 67.0, 67.2, 68.1, 92.7, 93.0, 110.0, 123.2, 123.4, 126.6, 127.2, 127.6, 127.7, 129.3, 129.6, 131.0, 131.4, 134.4, 135.0, 135.1, 139.2, 150.7, 170.2, 170.8, 179.3, 183.7.

Anal. Calcd for $C_{24}H_{23}N_3O_8$ (481.45): C, 59.87; H, 4.82. Found: C, 60.01; H, 4.73.

1-[1-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-1*H*-1,2,3-triazol-4-yl]cyclohexyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (10g)

Yellow oil; yield: 445 mg (83%); R_f = 0.3 (hexane–EtOAc, 7:3); $[\alpha]_D^{25}$ +100 (*c* 0.1, CH_2Cl_2).

^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.42–1.87 (m, 10 H, H-cyclohexyl), 2.06 (s, 3 H, CH_3CO), 2.08 (s, 3 H, CH_3CO), 4.07 (dd, *J* = 11.8, 1.6 Hz, 1 H, H-6), 4.13–4.23 (m, 2 H, H-5 and H-6′), 5.10 (br s, 1 H, H-1), 5.24 (br d, *J* = 9.4 Hz, 1 H, H-4), 5.70 (ddd, *J* = 10.2, 1.9, 1.9 Hz, 1 H, H-2), 5.84 (br d, *J* = 10.2 Hz, 1 H, H-3), 7.78 (s, 1 H, H_{naphth}), 7.85–7.87 (m, 2 H, H_{naphth}), 8.16–8.22 (m, 2 H, H_{naphth}), 8.63 (s, 1 H, H_{triaz}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.8, 21.0, 21.9, 22.3, 25.4, 35.4, 36.7, 37.9, 62.9, 65.1, 67.2, 75.5, 89.8, 124.1, 126.5, 126.6, 127.2, 128.3, 128.9, 131.1, 131.5, 134.4, 135.0, 139.3, 170.3, 170.7, 179.4, 183.8.

Anal. Calcd for $C_{28}H_{29}N_3O_8$ (535.55): C, 62.80; H, 5.46. Found: C, 62.74; H, 5.45.

(*R*,*S*)-[1-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-1*H*-1,2,3-triazol-4-yl]-3-methylbutyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (10h)

Brown oil; yield: 408 mg (78%); R_f = 0.6 (hexane–EtOAc, 6:4); $[\alpha]_D^{25}$ +110 (*c* 0.1, CH_2Cl_2).

IR (KBr): 2969, 2925, 1742, 1682, 1664, 1370, 1239, 1016 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.82–0.90 (m, 12 H, 4 × CH_3, *R*/*S*), 2.07 (s, 6 H, 2 × CH_3CO, *R*/*S*), 2.10 (s, 6 H, CH_3CO, *R*/*S*), 2.12–2.25 (m, 8 H, CH_2, CH, CHO, *R*/*S*), 4.10–4.15 (m, 2 H, H-6, *R*/*S*), 4.18–4.23 (m, 4 H, H-5 and H-6′, *R*/*S*), 5.20 (br s, 2 H, H-1, *R*/*S*), 5.27 (d, *J* = 8.6 Hz, 2 H, H-4, *R*/*S*), 5.78 (ddd, *J* = 10.2, 2.0, 2.0 Hz, 2 H, H-2, *R*/*S*), 5.88 (br d, *J* = 10.2 Hz, 2 H, H-3, *R*/*S*), 7.78 (s, 2 H, H_{naphth}, *R*/*S*), 7.83–7.88 (m, 4 H, H_{naphth}, *R*/*S*), 8.16–8.22 (m, 4 H, H_{naphth}, *R*/*S*), 8.61 (s, 2 H, H_{triaz}, *R*/*S*).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 7.7, 7.8, 20.8, 21.0, 28.3, 29.8, 62.9, 65.0, 67.4, 80.5, 89.4, 110.0, 124.6, 126.4, 126.6, 127.2, 128.5, 128.8, 131.1, 131.5, 134.4, 135.0, 139.3, 152.0, 170.3, 170.8, 179.4, 183.8.

Anal. Calcd for $C_{27}H_{29}N_3O_8$ (523.53): C, 61.94; H, 5.58. Found: C, 61.55; H, 5.53.

(*R*,*S*)-[1-(1,4-dioxo-1,4-dihydronaphthalen-2-yl)-1*H*-1,2,3-triazol-4-yl](phenyl)methyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (10i)

Green solid; yield: 337 mg (62%); mp 58–60 °C; R_f = 0.5 (hexane–EtOAc, 6:4); $[\alpha]_D^{25}$ +50 (*c* 0.1, CH_2Cl_2).

IR (KBr): 3065, 2926, 2856, 1742, 1663, 1623, 1371, 1236, 1017, 734 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 2.02 (s, 3 H, CH_3CO, *R* or *S*), 2.08 (s, 3 H, CH_3CO, *R* or *S*), 2.10 (s, 3 H, CH_3CO, *R* or *S*), 2.14 (s, 3 H, CH_3CO, *R* or *S*), 3.79 (dd, *J* = 12.1, 2.0 Hz, 1 H, H-6, *R* or *S*), 4.03 (ddd, *J* = 9.4, 4.7, 2.0 Hz, 1 H, H-5, *R* or *S*), 4.11 (dd, *J* = 12.1, 5.1 Hz, 1 H, H-6′, *R* or *S*), 4.28–4.36 (m, 3 H, H-5, H-6 and H-6′, *R* or *S*), 5.12 (d, *J* = 2.8 Hz, 1 H, H-1, *R* or *S*), 5.33–5.38 (m, 2 H, H-4, *R*/*S*), 5.45 (br s, 1 H, H-1, *R* or *S*), 5.86 (ddd, *J* = 10.1, 2.7, 2.7 Hz, 1 H, H-2, *R* or *S*), 5.91–5.96 [m, 3 H (H-2, *R* or *S*; H-3, *R*/*S*)], 6.15, 6.17 (2 × s, 2 H, CHO, *R*/*S*), 7.32–7.45 (m, 6 H, H_{Ar}, *R*/*S*), 7.53 (d, *J* = 7.1 Hz, 4 H, *ortho*-H_{Ar}, *R*/*S*), 7.74 (s, 1 H, H_{naphth}, *R* or *S*), 7.76 (s, 1 H, H_{naphth}, *R* or *S*), 7.81–7.88 (m, 4 H, H_{naphth}, *R* or *S*), 8.15–8.20 (m, 4 H, H_{naphth}, *R* or *S*), 8.44 (s, 1 H, H_{triaz}, *R* or *S*), 8.48 (s, 1 H, H_{triaz}, *R* or *S*).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 20.7, 20.9, 21.0 (2 C), 62.5, 62.9, 65.2, 65.3, 67.3, 73.0, 74.0, 91.8, 93.8, 110.0, 124.1, 124.3, 126.5, 126.6, 126.7, 126.9, 127.1, 127.2, 127.4, 127.5, 128.2, 128.3, 128.6, 128.8, 128.9, 129.8, 131.0, 131.4, 134.4 (2 C), 135.0, 135.1, 140.1, 170.2, 170.4, 179.2, 183.7.

Anal. Calcd for $C_{29}H_{25}N_3O_8$ (543.52): C, 64.08; H, 4.64. Found: C, 63.71; H, 4.76.

1-[1-(1,4-Dioxo-1,4-dihydronaphthalen-2-yl)-1*H*-1,2,3-triazol-4-yl]-1-ethylpropyl 4,6-Di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (10j)

Yellow oil; yield: 435 mg (83%); R_f = 0.4 (hexane–EtOAc, 6:4); $[\alpha]_D^{25}$ +70 (*c* 0.1, CH_2Cl_2).

IR (KBr): 2968, 2930, 1742, 1663, 1593, 1457, 1370, 1237, 1007 cm^{-1}.

^{1}H NMR (300 MHz, $CDCl_3$): δ = 0.81–0.93 (m, 6 H, CH_3), 2.07 (s, 3 H, CH_3CO), 2.10 (s, 3 H, CH_3CO), 2.11–2.23 (m, 4 H, CH_2), 4.13 (dd, *J* = 13.7, 4.5 Hz, 1 H, H-6), 4.18–4.28 (m, 2 H, H-5 and H-6′), 5.20 (br s, 1 H, H-1), 5.27 (br d, *J* = 11.5 Hz, 1 H, H-4), 5.77 (ddd, *J* = 10.2, 2.1, 2.1 Hz, 1 H, H-2), 5.88 (br d, *J* = 10.5 Hz, 1 H, H-3), 7.79 (s, 1 H, H_{naphth}), 7.83–7.89 (m, 2 H, H_{naphth}), 8.16–8.22 (m, 2 H, H_{naphth}), 8.61 (s, 1 H, H_{triaz}).

^{13}C NMR (75 MHz, $CDCl_3$): δ = 7.7, 7.9, 20.8, 21.0, 28.3, 29.8, 62.9, 65.0, 67.4, 80.5, 89.4, 124.6, 126.4, 126.6, 127.2, 128.5, 128.8, 131.1, 131.5, 134.4, 135.0, 139.3, 152.0, 170.3, 170.7, 179.5, 183.8.

Anal. Calcd for $C_{27}H_{29}N_3O_8$ (523.53): C, 61.94; H, 5.58. Found: C, 62.15; H, 5.66.

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Supporting Information

Supporting information for this article is available online at http://dx.doi.org/10.1055/s-0034-1378829.

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