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Stereoselective synthesis of pseudoglycosides catalyzed by $TeCl_4$ under mild conditions

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ABSTRACT

Catalytic amounts of tellurium(IV) tetrachloride were used to promote the O-glycosylation of 3,4,6-tri-*O*-acetyl-D-glucal to give the corresponding 2,3-unsaturated-O-glycosides. With simple alcohols, the desired compounds were obtained in good yields and excellent anomeric selectivity in a short reaction time using only 2 mol % of the catalyst. The application of the method in the synthesis of a small set of glycopyranosides with rigid or flexible linkers gave the corresponding α anomers as products in good yields. Further applications of some of the synthesized compounds in allylation reaction of aldehydes gave the corresponding homoallylic alcohols in good yields.

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1. Introduction

In addition to their role in energy metabolism, carbohydrates are also responsible for several functions in cells and organisms.[1] For instance, carbohydrates can be found in intra- and extracellular media bound to proteins and lipids.[2] They are also present as free polysaccharides on cell surfaces and in intercellular space, which are used by bacteria and virus as attachment sites.[3]

Pseudoglycosides can also be used as building blocks in the synthesis of natural products,[4] glycopeptides,[5] sugars,[6] oligosaccharides,[7] and nucleosides.[8] Besides, carbohydrates are present as units in several natural products such as salicin,[9] catalpol,[10] and macrolactin O[11] (Fig. 1), which present a wide range of biological activities.

2,3-Unsaturated-O-glycosides are useful intermediates in carbohydrate chemistry. They can be easily obtained from the glycosylation reaction or through a Ferrier rearrangement, which involves a nucleophilic substitution reaction combined with an allylic shift in a glycal.[12] The orientation of the formed glycoside bond, α or β depends on some combination of control elements, being the most important the 'kinetic anomeric effect'.[13]

A number of Lewis acids and oxidizing agents can promote this reaction[14] with some caveats in generality, yields, and selectivity. In addition, the use of strong acidic or oxidizing conditions, as well as the cost of the reagents led to a search for a milder procedure for the preparation of this class of compounds.

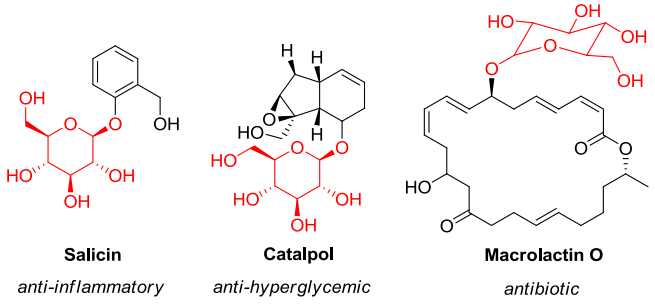

Fig. 1. Representative examples of natural products containing an *O*-glycosidic bond.

Tellurium tetrahalides ($TeCl_4$, $TeBr_4$, and TeI_4) are versatile compounds, since they can react with both Lewis bases and Lewis acids,[15] and this amphoteric behavior can be understood in terms of the partially ionic Te–X bonding, which can be controlled by the electronegativity of the halide.

Recently, we described the use of tellurium tetrabromide (IV) to promote the O-glycosylation of glycals to yield the corresponding 2,3-unsaturated-O-glycosides.[14b] We describe herein the results obtained by using tellurium tetrachloride, a less expensive and more electrophilic Lewis acid choice to promote the O-glycosylation of 3,4,6-tri-*O*-acetyl-D-glucal, **1**. The method may be useful as

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an alternative to the previously described ones, particularly for the synthesis of glycopyranosides with rigid or flexible linkers, compounds of great interest in chemistry and biology (Fig. 2).[16]

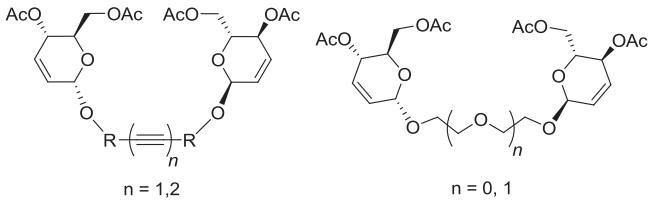
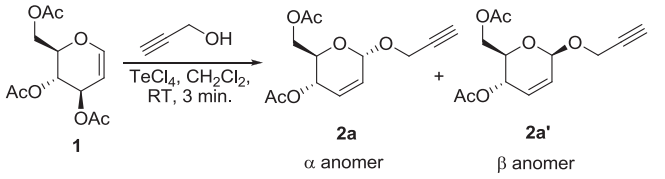


Fig. 2. Examples of pseudoglycosides with rigid or flexible linkers.

2. Results and discussion

For preliminary optimization of the reaction conditions, **1** (1.0 mmol) and propargyl alcohol (1.2 mmol) in dichloromethane (10 mL) were treated at room temperature with different amounts of $TeCl_4$ and the progress of the reaction was monitored by TLC. The results are depicted in Table 1.

Table 1
Influence of the amount of $TeCl_4$ in the synthesis of 2,3-unsaturated O-glycosides—**2a** and **2a'**[a]



Entry	$TeCl_4$ (equiv)	Ratio[a] (α:β)	Yield[b] (%)
1	0.4	88:12	90
2	0.2	88:12	91
3	0.08	89:11	92
4	0.05	89:11	92
5	0.02	88:12	92
6[c]	—	—	—

[a] The anomeric ratios were obtained by ^1H NMR and confirmed by gas chromatography for all reactions.
[b] Isolated yield.
[c] Product not observed after 360 min.

In all cases the reaction proceeded smoothly leading to the complete conversion of **1** into the corresponding 2,3-unsaturated O-glycoside **2a** in high yield and with excellent α selectivity (Table 1, entries 1–5). It is also interesting to note that when the amount of $TeCl_4$ was reduced from 0.4 to 0.02 equiv, no decrease in the yield and anomeric selectivity was observed (Table 1, entries 1 and 5). The stereochemistry of **2a** was supported by a NOESY experiment. The structure of the β anomer has the same stereochemistry at both $H_{1\beta}$ and H_5 whereas the α anomer has opposite stereochemistry. Thus, it is expected that the interaction between $H_{1\beta}$ and H_5 in the β anomer would produce a positive NOE effect. In our case, no NOE was observed after irradiation of the signal at δ 5.22 corresponding to the $H_{1\alpha}$ in the α anomer (Fig. 3).

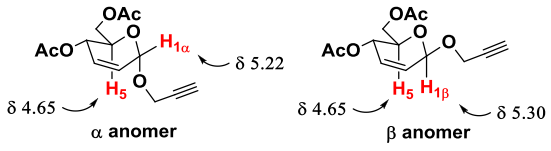


Fig. 3. NOE irradiation of **2a**.

In an attempt to broaden the scope of our methodology and to demonstrate its efficiency, we explored the generality of our method extending the conditions to other alcohols and the results are summarized in Table 2.

Inspection of Table 2 shows that the reaction worked well for a variety of alcohols. Both hindered and non-hindered alcohols gave the desired products in a short reaction time and α anomeric selectivity. The reaction with alkynols also gave the corresponding products after short reaction times with excellent α selectivity (Table 2, entries 1–3).

When allylic, homoallylic, and benzylic alcohols were used; the reaction times were slightly increased without any loss in the stereoselectivity (Table 2, entries 4–6). The same behavior was observed for aliphatic and cyclic alcohols (Table 2, entries 7–13). The reaction of glycal **1** with phenol derivatives is described to be difficult to proceed,[14c] but in our case, the product was obtained in moderate yield and anomeric selectivity (Table 2, entry 14).

The syntheses of molecules bearing multiple carbohydrate moieties are of great interest in chemistry and biology since these molecules can mimic ligand–receptor interactions increasing the affinities to an appropriate target.[17] This is particularly true for soluble proteins (lectins), which possess multiple and often homologous carbohydrate recognition domains (CRDs).[18]

Our strategy for the synthesis of analogs of this class of compounds was initially based on the use of alkynyl diols in order to obtain the corresponding alkynyl glycosides. Thus, the reaction of 3,4,6-tri-*O*-acetyl-D-glucal **1** with different alkynyl diols as nucleophiles using catalytic amounts of tellurium tetrachloride under the same conditions described in Table 2 gave the corresponding glycosides **2o**–**r** in good yields, selectivities, and short reaction times (Table 3).

In general, the reaction proceeded smoothly with good yield. In all cases the α,α isomer was observed as the major compound, with a slightly decrease in the selectivity when comparing Table 3 to Table 2. When but-2-yne-1,4-diol was used, compound **2o** was obtained in an excellent yield and moderate α selectivity (Table 3, entry 1).

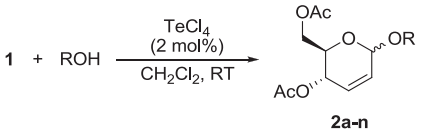
The distance between the two glycosidic units was increased when 1,3-diynes were used. In these cases, the yields were lower compared to the reaction using but-2-yne-1,4-diol (Table 3, entries 2–4). When a more hindered 1,3-diyne was used, compound **2q** was isolated in a similar yield with a slight increase in the selectivity (Table 3, entry 3). Finally, the use of a homopropargylic alkynyl alcohol gave the corresponding alkynyl glycoside **2r** in moderate yield and with α selectivity (Table 3, entry 4).

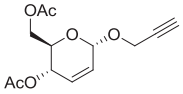
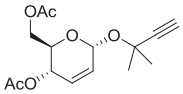
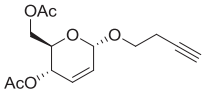
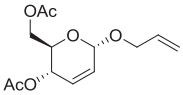
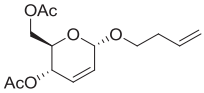
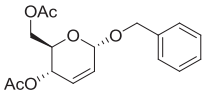
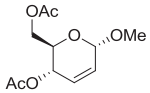
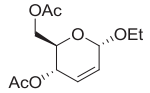
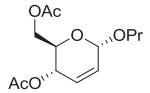
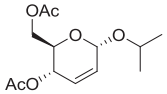
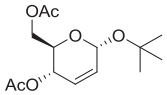
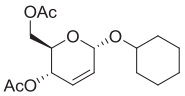
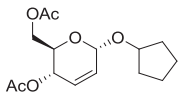
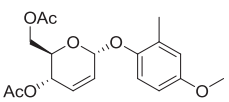
Given the yields and selectivities obtained when alkynyl diols were used we turned our attention to alternative procedures to prepare the alkynyl 2,3-unsaturated O-glycosides in a more selective way. So, compounds **2a**–**c** (Table 2, entries 1–3) were purified by column chromatography to give the corresponding pure α isomers, which were then submitted to a Ni-catalyzed aerobic oxidative coupling reaction[19] (Table 4). It is important to mention this oxidative coupling does not isomerizes the anomeric center, so α,α isomers were obtained exclusively.

From Table 3 it can also be observed that compound **2p** was obtained in 76% yield and 77% α,α selectivity (Table 3, entry 2). By comparison, using the Ni-catalyzed aerobic oxidative coupling reaction (Table 4, entry 1), the pure α,α isomer of **2p** was obtained in 70% overall yield after two steps starting from **2a** (Table 1, entry 1).

The synthesized compounds are useful intermediates for preparing aromatic cluster glycosides, through alkyne cyclotrimerization reaction,[20] which might conceivably serve as guests in host–guest chemistry. These systems contain a lipophilic core

Table 2
$TeCl_4$ promoted synthesis of 2,3-unsaturated O-glycosides **2a**–**n**



Entry	Product		Time (min)	Ratio[a] (α:β)	Yield[b] (%)
1		**2a**	3	88:12	92
2		**2b**	5	91:9	93
3		**2c**	3	89:11	94
4		**2d**	10	87:13	88
5		**2e**	15	92:8	89
6		**2f**	20	87:13	90
7		**2g**	20	87:13	90
8		**2h**	25	88:12	91
9		**2i**	10	88:12	88
10		**2j**	15	89:11	90
11		**2k**	15	91:9	87
12		**2l**	10	90:10	90
13		**2m**	15	87:13	87
14		**2n**	3	60:40	75

[a] The anomeric ratios were obtained by ^1H NMR and confirmed by gas chromatography for all reactions.
[b] Isolated yield.

surrounded by a hydrophilic shell, thus providing an ideal environment for inclusion compounds with amphiphilic guests.[21] In addition, compounds **2o**–**r** might be used in the formation of homogeneous cross-linked complexes with lectins for bioconjugations.[22]

Dimeric carbohydrates with flexible linkers were also shown to have higher affinities for some lectins having different kinetics and organization patterns of the cross-linked lattices.[23] Our strategy to synthesize these class of compounds was based on the glycosidation reaction of **1** with glycols catalyzed by tellurium tetrachloride. The corresponding products **2s**–**t** were obtained in good yields and α selectivities (Table 5).

Starting with ethylene glycol the method gave the corresponding product **2s** in good yield and selectivity in a very short reaction time (Table 5, entry 1). When the distance between the two glycosidic units was increased by the use of diethylene glycol the corresponding product **2t** was obtained in good yield and selectivity, demonstrating that other glycols could be used in the reaction (Table 5, entry 2).

Finally, the use of glycol ethers gave the corresponding products **2u**–**v** in moderate yields and selectivities (Table 6). Generally, analogs of these compounds are prepared by hydrogenolysis of the corresponding alkynyl derivatives, thus our method is complementary to the previous described strategies to prepare this class of compounds.[18c]

The development of methods focusing on environmentally benign reaction media has become particularly prominent.[24] Thus, advances in the development of aqueous biphasic catalysis[25] and the use of supercritical fluids,[26] ionic liquids,[27] and fluorous media[28] continue to be important areas of investigation. Study of organometallic reactions using water as (co)-solvent is still a challenge. However, the use of water as a solvent seems to be the best option due to its simplicity and very low cost.

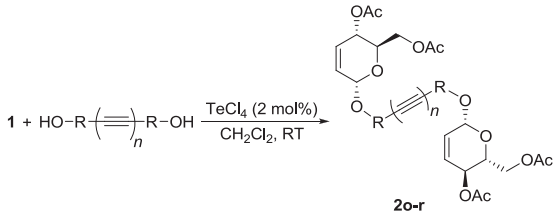
Despite the several existing methods for the allylation of carbonyl compounds in aqueous media based on In,[29] Sn,[30] Zn,[31] and Mg[32] derived reagents, organotrifluoroborates have proved to be very useful due to the good reactivity and excellent stereocontrol toward 1,2-additions. In this context, several methods for the allylation of carbonyl compounds using allylic trifluoroborates promoted by variety of Lewis acids[33] or palladium-catalysts[34] have been described.

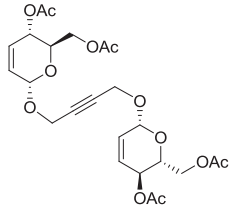
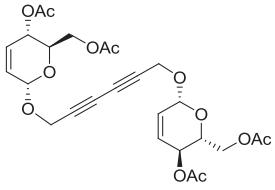
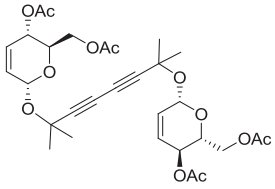
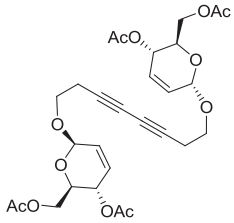
Thus we were interested in expanding the scope of these reactions to include the use of the synthesized compounds as catalysts in the allylation reaction of aldehydes. We first examined the viability of the reaction of 4-nitro-benzaldehyde **3** and potassium allyltrifluoroborate **4** in a biphasic reaction medium (CH_2Cl_2/H_2O) at room temperature using **2s**–**v** (10 mol %) as phase transfer catalysts to give the corresponding homoallylic alcohol **5**. These results are presented in Table 7.

In all cases, **5** was obtained in high yields and did not require further purification by chromatography. In the absence of a phase transfer catalyst, the product was obtained only in 7% yield after 15 min (Table 7, entry 5).

When **2s** and **2t** were used as promoters, the corresponding homoallylic alcohol **5** was obtained in excellent yield after only 10 min. Subsequent conversion of the obtained products of both reactions into their corresponding Mosher ester derivatives followed by ^{19}F analysis did not indicate any enantiomeric excess for the reaction. Compounds **2u**–**v** also gave the corresponding product in good yield; however when **2v** was used a longer reaction time was required for the reaction completion This fact may be explained by the role of cation solvation by the ligand in size match-selectivity phenomena, which is widely accepted as the most important factor in controlling metal ion selectivity for macrocyclic ligands.[35]

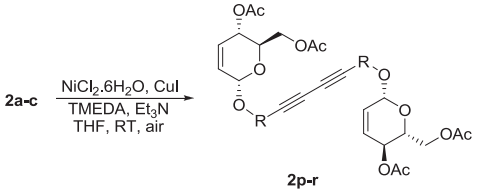
Table 3
$TeCl_4$ promoted synthesis of alkynyl 2,3-unsaturated O-glycosides **2o**–**r**



Entry	R	*n*	Product		Time (min)	Ratio (α:α/α:β/β:β)[a]	Yield[b] (%)
1	$-CH_2-$	1		**2o**	10	78:22:trace	89
2	$-CH_2-$	2		**2p**	10	77:23:trace	76
3	$-C(CH_3)_2$	2		**2q**	10	82:18:trace	71
4	$-CH_2CH_2-$	2		**2r**	10	80:20:trace	70

[a] The anomeric ratios were obtained by ^1H NMR and confirmed by gas chromatography for all reactions.
[b] Isolated yield.

Table 4
Synthesis of α,α conjugated diynes from the homocoupling reaction of alkynyl 2,3-unsaturated O-glycosides



Entry	Alkyne	Product	Time (h)	Ratio[a] (α:α/α:β/β:β)	Yield[b] (%)
1	**2a**	**2p**	10	100:0:0	75
2	**2b**	**2q**	12	100:0:0	76
3	**2c**	**2r**	10	100:0:0	72

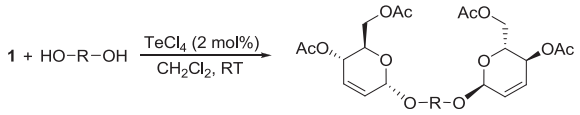
[a] The anomeric ratios were obtained by ^1H NMR and confirmed by gas chromatography for all reactions.
[b] Isolated yield.

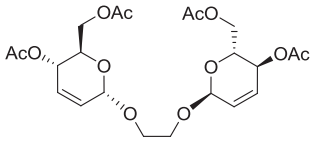
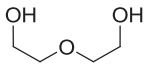
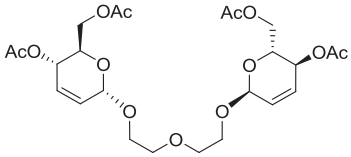
3. Conclusion

In summary, we have demonstrated that a catalytic amount of tellurium(IV) tetrachloride can efficiently promote the O-glycosylation of glycals. The approach is complementary to the previously described methods for the synthesis of O-glycosides and a comparison of the use of a catalytic amount of $TeCl_4$ with literature methods is described in Table 8. Although the available methods gave **2a** in good yields and selectivities in some cases, our method gave similar results using shorter reaction times and low catalyst loading under milder reaction conditions.

In addition, the application of the method in the synthesis of dimeric glycopyranosides having rigid or flexible linkers, gave the corresponding products in good yields and α anomeric selectivity. Further application of the synthesized compounds in the allylation reaction of aldehydes using potassium allyltrifluoroborate in aqueous conditions gave the corresponding homoallylic alcohols in good yields.

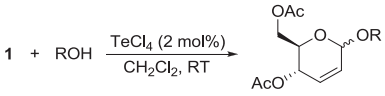
Table 5
$TeCl_4$ promoted the reaction of **1** with glycols

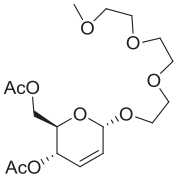
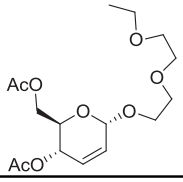


Entry	HO–R–OH	Product		Time (min)	Ratio[a] (α:α/α:β/β:β)	Yield[b] (%)
1			**2s**	15	86:14:Trace	70
2			**2t**	20	87:13:Trace	67

[a] The anomeric ratios were obtained by ^1H NMR and confirmed by gas chromatography for all reactions.
[b] Isolated yield.

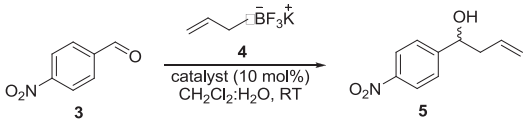
Table 6
$TeCl_4$ promoted the reaction of **1** with glycol ethers



Entry	Product		Time (min)	Ratio[a] (α:β)	Yield[b] (%)
1		**2u**	15	75:25	86
2		**2v**	20	76:24	88

[a] The anomeric ratios were obtained by ^1H NMR and confirmed by gas chromatography for all reactions.
[b] Isolated yield.

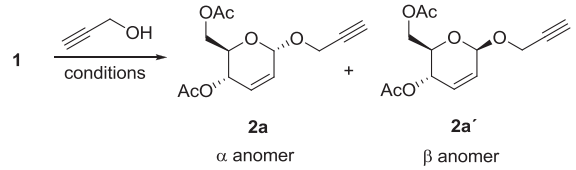
Table 7
2,3-unsaturated O-glycosides promote the allylation of aldehydes



Entry	Catalyst	Time (min)	Yield[a] (%)
1	**2s**	10	91
2	**2t**	10	90
3	**2u**	5	93
4	**2v**	90	92
5	—	15	7

[a] Isolated yield.

Table 8
Comparison between the use of $TeCl_4$ and other catalysts for the synthesis of **2a** and **2a′**



	Catalyst	Time (min)	Yield (%)	Ratio **2a**/**2a′**
1	*$TeCl_4$*	*3*	*92*	*88:12*
2	$TeBr_4$[14b]	5	92	87:13
3	$Er(OTf)_3$[14h]	20	80	68:32
4	HFIP[14g]	720	82	80:20
5	$ZnCl_2/Al_2O_3$[14d]	10	88	—[a]
6	H_3PO_4[14e]	10	86	91:9
7	$AuCl_3$[14c]	390	85	87:13
8	$CeCl_3 \cdot 7H_2O$[14n]	480	78	70:30
9	$InCl_3$[14o]	10	90	90:10
10	$Bi(OTf)_3$–SiO_2[14k]	150	76	88:12
11	$HClO_4$–SiO_2[14j]	60	76	91:9
12	$La(NO_3)_3 \cdot 6H_2O$[14f]	240	89	80:20
13	$FeCl_3$[14l]	69	78	60:40
14	K-10[14p]	60	97	86:14
15	$Mg(ClO_4)_2$[14i]	70	85	90:10
16	$Dy(OTf)_3$[14m]	90	93	90:10

[a] The ratio was not given.

4. Experimental section

4.1. Material

All reagents and solvents used were previously purified and dried in agreement with the literature.[36] Tellurium(IV) tetrachloride was purchased from Aldrich Chemical Co. and used as received. All other commercially available reagents and solvents were used as received. Reactions were monitored by thin-layer chromatography on 0.25 mm E. Merck silica gel 60 plates (F_{254}) using UV light, vanillin, and *p*-anisaldehyde as visualizing agents. Column chromatography purification was performed using Silica Gel 60 (230–400 mesh) unless indicated otherwise. All compounds

purified by chromatography were sufficiently pure for use in further experiments, unless indicated otherwise.

4.2. Instrumentation

^{1}H NMR and ^{13}C NMR data were recorded in $CDCl_3$ or DMSO-d_6. The chemical shifts are reported as delta (δ) units in parts per million (ppm) relative to the solvent residual peak as the internal reference. ^{11}B (128 MHz) and ^{19}F (376 MHz) NMR spectra were recorded in DMSO-d_6. Spectra were calibrated using $BF_3\cdot Et_2O$ (0.0 ppm) as external reference in the case of ^{11}B NMR and chemical shifts were referenced to external CF_3CO_2H (0.0 ppm) in the case of ^{19}F NMR. Coupling constants (J) for all spectra are reported in hertz (Hz). Further analysis by NOESY was performed to confirm the stereochemistry and peak assignments. High-resolution mass spectral analyses were performed on using ESI method. Infrared spectra were recorded using samples prepared as thin films on salt plates or as KBr pellets. The melting points (mp) are not corrected.

4.3. Typical procedure

*4.3.1. Synthesis of tri-O-acetyl-D-glucal (**1**).*[37] To a 100 mL round bottomed flask containing a suspension of D-glucose (1.0 g, 5.55 mmol) in acetic anhydride (3.60 g; 7.0 mol equiv) was added a solution of HBr/AcOH [hydrobromic acid 48% (0.5 mL) in acetic anhydride (2.0 mL)] at room temperature over 1 h period. An additional amount of HBr/AcOH [hydrobromic acid 48% (3.0 mL) in acetic anhydride (12.0 mL)] was added and the mixture was warmed up to room temperature and stirred overnight. Anhydrous sodium acetate (2.0 g, 24.4 mmol) was then added and after 0.5 h was added a suspension of $CuSO_4\cdot 5H_2O$ (0.315 g; 1.3 mmol) and zinc dust (12.6 g; 200 mmol) in water (10 mL) and acetic acid (15 mL) containing sodium acetate (9.45 g; 115 mmol). The mixture was stirred at room temperature for 1.5 h. The solid residue was filtered off and washed with ethyl acetate (100 mL) and water (100 mL). The organic phase was washed with a saturated solution of $NaHCO_3$ (100 mL) and brine (50 mL) before drying over $MgSO_4$. The organic phase was filtered and concentrated in vacuo. Silica gel chromatography using hexanes/EtOAc (9:1) provided 1.24 g (90%) of the title compound as a white solid; mp: 54–55 °C (lit.[37] 52–53 °C); $[\alpha]_D^{20}$ −10.4 (*c* 1.00, MeOH) [lit.[37] $[\alpha]_D^{25}$ −59.0 (*c* 1.00, EtOH)]; IR (KBr pellet) ν_{max} 2959, 1738, 1649, 1373, 1226, 1043 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.45 (d, J_{1-2}=6.0 Hz, 1H, H-1), 5.32 (br s, 1H, H-2), 5.20 (t, J_{3-2}=J_{3-4}=5.7 Hz, 1H, H-3), 4.84–4.81 (m, 1H, H-5), 4.38 (dd, J_{4-5}=12.0 Hz, J_{4-3}=5.7 Hz, 1H, H-4), 4.25–4.16 (m, 2H, H-6, H-6′), 2.07 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.02 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.4, 169.5, 145.6, 98.9, 73.8, 67.4, 67.1, 61.3, 20.9, 20.7, 20.7.

*4.3.2. General procedure for the synthesis of 2,3-unsaturated O-glycopyranosides (**2a**–**o**, **2v**, and **2w**).* To a 50 mL round bottomed flask containing a solution of **1** (272 mg, 1.0 mmol) and appropriate alcohol (1.2 mmol) in dichloromethane (10 mL) at 0 °C under argon was added $TeCl_4$ (5 mg, 2 mol %). The ice bath was removed and the mixture was stirred for the time indicated in Tables 2 and 6. A saturated solution of ammonium chloride (5 mL) was then added and the mixture was extracted with EtOAc (2×10 mL). The combined organic phases were dried over $MgSO_4$ and the solvents were removed under reduced pressure followed by purification by a flash column chromatography [hexanes/EtOAc (95:5)] to yield the corresponding 2,3-unsaturated O-glycopyranosides.

*4.3.2.1. Prop-2-yn-1-yl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2a**).*[14c] White solid; mp: 58–59 °C (lit.[14g] 57–58 °C); $[\alpha]_D^{20}$ +138.6 (*c* 1.00, MeOH) [lit.[14g] $[\alpha]_D$ +110.0 (*c* 0.80, MeOH)]; 0.25 g (92%); IR (KBr pellet) ν_{max} 3281, 2935, 2893, 2129, 1742, 1375, 1239, 1030 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.90 (br d, J_{3-2}=10.2 Hz, 1H, H-3), 5.82 (dt, J_{2-3}=10.2 Hz, J_{2-1}=J_{2-4}=1.5 Hz, 1H, H-2), 5.33 (ddd, J_{4-5}=9.6 Hz, J_{4-3}=3.0 Hz, J_{4-2}=1.5 Hz, 1H, H-4), 5.22 (br s, 1H, H-1), 4.29 (d, J=2.4 Hz, 2H, OCH_2), 4.25 (dd, $J_{6-6'}$=12.4 Hz, J_{6-5}=5.4 Hz, 1H, H-6), 4.16 (dd, $J_{6'-6}$=12.4 Hz, $J_{6'-5}$=2.4 Hz, 1H, H-6′), 4.07 (ddd, J_{5-4}=9.6 Hz, J_{5-6}=5.4 Hz, $J_{5-6'}$=2.4 Hz, 1H, H-5), 2.07 (t, J=2.4 Hz, 1H, C≡C−H), 2.09 (s, 3H, OAc), 2.07 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 170.2, 129.7, 127.1, 92.7, 78.9, 74.8, 67.1, 65.0, 62.7, 55.0, 20.9, 20.7.

*4.3.2.2. 2-Methyl but-3-yn-2-yl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2b**).*[38] Isolated as a colorless oil; 0.28 g (93%); $[\alpha]_D^{20}$ +51.7 (*c* 0.50, MeOH); IR (thin film) ν_{max} 3268, 2986, 1743, 1369, 1231, 1027, 887 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.85 (br d, J_{3-2}=10.2 Hz, 1H, H-3), 5.77 (ddd, J_{2-3}=10.2 Hz, J_{2-4}=2.7 Hz, J_{2-1}=1.8 Hz, 1H, H-2), 5.62 (br s, 1H, H-1), 5.26 (ddd, J_{4-5}=9.3 Hz, J_{4-2}=2.7 Hz, J_{4-3}=1.5 Hz, 1H, H-4), 4.29–4.02 (m, 3H, H-6, H-6′ and H-5), 2.51 (s, 1H, C≡C−H), 2.05 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.56 (s, 3H, OCH_3), 1.50 (s, 3H, OCH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.2. 170.7, 121.2, 128.9, 91.3, 85.6, 73.8, 72.0, 67.4, 65.4, 63.5, 30.9, 30.2, 21.7, 21.3.

*4.3.2.3. But-3-yn-1-yl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2c**).*[14m] Isolated as a colorless oil; 0.26 g; (94%); $[\alpha]_D^{20}$ +91.3 (*c* 1.00, MeOH) [lit.[39c] $[\alpha]_D^{25}$ +45.4 (*c* 2.50, $CHCl_3$)]; IR (KBr pellet) ν_{max} 3280, 2917, 1742, 1371, 1230, 1043, 974 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.87 (br d, J_{3-2}=10.2 Hz, 1H, H-3), 5.81 (ddd, J_{2-3}=10.2 Hz, J_{2-4}=2.7 Hz, J_{2-1}=1.5 Hz, 1H, H-2), 5.28 (ddd, J_{4-5}=9.6 Hz, J_{4-2}=2.7 Hz, J_{4-3}=1.8 Hz, 1H, H-4), 5.05 (br s, 1H, H-1), 4.25–4.17 (m, 2H, H-6 and H-6′), 4.11 (ddd, J_{5-4}=9.6 Hz, J_{5-6}=5.4 Hz, $J_{5-6'}$=3.0 Hz, 1H, H-5), 3.83 (dt, $J_{7-7'}$=16.5 Hz, J_{7-8}=6.6 Hz, 1H, OCH_2CH$_2$), 3.66 (dt, $J_{7'-7}$=16.5 Hz, $J_{7'-8}$=6.6 Hz, 1H, OCH_2CH$_2$), 2.50 (td, J_{8-7}=$J_{8-7'}$=6.6 Hz, J_{8-9}=2.7 Hz, 2H, OCH$_2$$CH_2$), 2.08 (s, 3H, OAc), 2.06 (s, 3H, OAc), 1.97 (t, J_{9-8}=2.7 Hz, 1H, C≡C−H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 170.2, 129.3, 127.4, 94.5, 80.9, 69.4, 66.9, 66.7, 65.1, 62.8, 20.9, 20.7, 20.0.

*4.3.2.4. Allyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2d**).*[14c] Isolated as a colorless oil; 0.24 g (88%); $[\alpha]_D^{20}$ +101.9 (*c* 1.00, MeOH) [lit.[14g] $[\alpha]_D$ +91.0 (*c* 0.80, MeOH)]; IR (thin film) ν_{max} 2920, 1743, 1642, 1371, 1235, 1039 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.98–5.83 (m, 3H, H-2,H-3 and −CH=CH$_2$), 5.30–5.13 (m, 3H, H-4 and −CH=CH_2), 5.05 (br s, 1H, H-1), 4.26–4.01 (m, 5H, H-5, H-6, H-6′ and OCH_2), 2.07 (s, 3H, OAc), 2.05 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 170.2, 134.0, 129.2, 127.6, 117.5, 93.5, 69.2, 66.8, 65.1, 62.8, 20.9, 20.7.

*4.3.2.5. But-3-en-1-yl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2e**).*[14f] Isolated as a colorless oil; 0.25 g (89%); $[\alpha]_D^{20}$ +83.5 (*c* 1.00, MeOH) [lit.[14f] $[\alpha]_D^{25}$ +80.9 (*c* 1.20, $CHCl_3$)]; IR (thin film) ν_{max} 2923, 1747, 1648, 1369, 1234, 1041 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.86 (br d, J_{3-2}=10.2 Hz, 1H, H-3), 5.83–5.76 (m, 2H, H-2 and −CH=CH$_2$), 5.31–5.26 (m, 1H, H-4), 5.11 (dd, J=3.0, 1.8 Hz, 1H, −CH=CH_2), 5.07–5.04 (m, 1H, −CH=CH_2), 5.02 (br s, 1H, H-1), 4.25 (dd, $J_{6-6'}$=12.4 Hz, J_{6-5}=5.4 Hz, 1H, H-6), 4.15 (dd, $J_{6'-6}$=12.4 Hz, $J_{6'-5}$=2.4 Hz, 1H, H-6′), 4.07 (ddd, J_{5-4}=9.6 Hz, J_{5-6}=5.4 Hz, $J_{5-6'}$=2.4 Hz, 1H, H-5), 3.80 (dt, J=9.6 Hz, J=6.9 Hz, 1H, OCH_2), 3.56 (dt, J=9.6 Hz, J=6.9 Hz, 1H, OCH_2), 2.38 (dt, J=6.9 Hz, J=1.5 Hz, 1H, −CH_2CH=C), 2.36 (dt, J=6.9 Hz, J=1.5 Hz, 1H, −CH_2CH=C), 2.08 (s, 3H, OAc), 2.06 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 170.2, 134.9, 129.0, 127.7, 116.5, 94.4, 68.0, 66.8, 65.1, 62.9, 34.1, 20.9, 20.7.

*4.3.2.6. Benzyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2f**).*[14c] Isolated as a colorless oil; 0.29 g (90%); $[\alpha]_D^{20}$ +62.1 (*c* 1.00, MeOH) [lit.[14g] $[\alpha]_D$ +150.0 (*c* 0.80, MeOH)]; IR

(thin film) ν_{max} 3030, 2899, 1745, 1656, 1490, 1451, 1371, 1234, 1042, 696 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 7.38–7.26 (m, 5H, H_{aryl}), 5.98–5.82 (m, 2H, H-2 and H-3), 5.35–5.31 (m, 1H, H-4), 5.13 (br s, 1H, H-1), 4.78 (d, J=11.4 Hz, 1H, $-OCH_2(C_6H_5)$), 4.56 (d, J=11.4 Hz, 1H, $-OCH_2(C_6H_5)$), 4.31–4.09 (m, 3H, H-5, H-6 and H-6′), 2.10 (s, 3H, OAc), 2.07 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 170.3, 137.6, 129.3, 128.5, 128.0, 127.9, 127.8, 93.6, 70.3, 67.1, 65.3, 62.9, 20.9, 20.8.

*4.3.2.7. Methyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2g**).*[14i] Isolated as a colorless oil; 0.22 g (90%); $[\alpha]_D^{20}$ +126.7 (*c* 1.00, MeOH) [lit.[14g] $[\alpha]_D$ +124.0 (*c* 1.20, MeOH)]; IR (thin film) ν_{max} 2969, 2893, 1747, 1443, 1370, 1232, 1182, 1106 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.91 (br d, J_{3-2}=10.8 Hz, 1H, H-3), 5.82 (dt, J_{2-3}=10.8 Hz, J_{2-1}=J_{2-4}=1.8 Hz, 1H, H-2), 5.32–5.28 (m, 1H, H-4), 4.92 (br s, 1H, H-1), 4.25 (dd, $J_{6-6'}$=12.3 Hz, J_{6-5}=5.4 Hz, 1H, H-6), 4.17 (dd, $J_{6'-6}$=12.3 Hz, $J_{6'-5}$=2.7 Hz, 1H, H-6′), 4.05 (ddd, J_{5-4}=9.9 Hz, J_{5-6}=5.4 Hz, $J_{5-6'}$=2.7 Hz, 1H, H-5), 3.44 (s, 3H, $-OCH_3$), 2.09 (s, 3H, OAc), 2.07 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 170.3, 129.2, 127.6, 95.4, 66.7, 65.1, 62.9, 55.9, 20.9, 20.8.

*4.3.2.8. Ethyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2h**).*[14i] Isolated as a colorless oil; 0.23 g (91%); $[\alpha]_D$ +78.7 (*c* 1.00, MeOH) [lit.[14g] $[\alpha]_D$ +120.0 (*c* 1.20, MeOH)]; IR (thin film) ν_{max} 2978, 2895, 1745, 1446, 1373, 1235, 1185, 1108 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.85 (br d, J_{3-2}=10.5 Hz, 1H, H-3), 5.80 (dt, J_{2-3}=10.5 Hz, J_{2-1}=J_{2-4}=1.5 Hz, 1H, H-2), 5.29–5.25 (m, 1H, H-4), 5.01 (br s, 1H, H-1), 4.22 (dd, $J_{6-6'}$=12.0 Hz, J_{6-5}=5.1 Hz, 1H, H-6), 4.14 (dd, $J_{6'-6}$=12.0 Hz, $J_{6'-5}$=2.4 Hz, 1H, H-6′), 4.07 (ddd, J_{5-4}=9.6 Hz, J_{5-6}=5.1 Hz, $J_{5-6'}$=2.4 Hz, 1H, H-5), 3.80 (q, J=7.2 Hz, 1H, $-CH_2CH_3$), 3.80 (q, J=7.2 Hz, 1H, $-CH_2CH_3$), 2.06 (s, 3H, OAc), 2.04 (s, 3H, OAc), 1.21 (t, J=7.2 Hz, 3H, $-CH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 170.2, 128.9, 127.8, 94.1, 66.7, 65.1, 64.1, 62.9, 20.9, 20.8, 15.1.

*4.3.2.9. n-Propyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2i**).*[39a] Isolated as a colorless oil; 0.24 g (88%); $[\alpha]_D^{20}$ +99.7 (*c* 1.00, MeOH) [lit.[39a] $[\alpha]_D^{31.7}$ +118.2 (*c* 1.00, $CHCl_3$)]; IR (thin film) ν_{max} 2964, 2881, 1747, 1450, 1371, 1234, 1182, 1105 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.92–5.78 (m, 2H, H-2 and H-3), 5.29–5.25 (m, 1H, H-4), 4.99 (br s, 1H, H-1), 4.21 (dd, $J_{6-6'}$=12.0 Hz, J_{6-5}=5.4 Hz, 1H, H-6), 4.14 (dd, $J_{6'-6}$=12.0 Hz, $J_{6'-5}$=2.1 Hz, 1H, H-6′), 4.08 (ddd, J_{5-4}=9.6 Hz, J_{5-6}=5.1 Hz, $J_{5-6'}$=2.1 Hz, 1H, H-5), 3.68 (dt, J=9.6, 7.5 Hz, 1H, $-CH_2CH_2CH_3$), 3.45 (dt, J=9.6, 7.5 Hz, 1H, $-CH_2CH_2CH_3$), 2.07 (s, 3H, OAc), 2.05 (s, 3H, OAc), 1.61 (qui, J=7.5 Hz, 2H, $-CH_2CH_2CH_3$), 0.91 (t, J=7.5 Hz, 3H, $-CH_2CH_2CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 170.2,128.9, 127.8, 94.2, 70.5, 66.7, 65.2, 62.9, 22.9, 20.9, 20.7, 10.6.

*4.3.2.10. iso-Propyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2j**).*[14d] Isolated as a colorless oil; 0.24 g (90%); $[\alpha]_D^{20}$ +96.5 (*c* 1.00, MeOH) [lit.[14g] $[\alpha]_D$ +97.0 (*c* 0.70, MeOH)]; IR (thin film) ν_{max} 2971, 2902, 1745, 1450, 1372, 1317, 1233, 1184, 1127 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.76 (br d, J=11.7 Hz, 1H, H-3), 5.69 (dt, J_{2-3}=11.7 Hz, J_{2-1}=J_{2-4}=1.8 Hz, 1H, H-2), 5.19–5.15 (m, 1H, H-4), 5.02 (br s, 1H, H-1), 4.17–4.01 (m, 3H, H-5, H-6 and H-6′), 3.98–3.84 (m, 1H, $-CH(CH_3)CH_3$), 1.98 (s, 3H, OAc), 1.97 (s, 3H, OAc), 1.14 (d, J=6.3 Hz, 3H, $-CH(CH_3)CH_3$), 1.07 (d, J=6.0 Hz, 3H, $-CH(CH_3)CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.4, 169.9, 128.5, 128.2, 92.5, 70.4, 66.5, 65.1, 62.8, 23.2, 21.7, 20.7, 20.5.

*4.3.2.11. tert-Butyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2k**).*[40] Isolated as a colorless oil; 0,25 g (87%); $[\alpha]_D^{20}$ +146.4 (*c* 1.00, MeOH) [lit.[40] $[\alpha]_D^{25}$ +100.0 (*c* 1.00, $CHCl_3$)]; IR (thin film) ν_{max} 2958, 2904, 2129, 1747, 1463, 1371, 1333, 1234, 1186, 1104 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5,82 (br d, J=10.2 Hz, 1H, H-3), 5.72 (dt, J_{2-3}=10.2 Hz, J_{2-1}=J_{2-4}=2.7 Hz, 1H, H-2), 5.31 (br s, 1H, H-1), 5.25 (br d, J_{4-5}=9.6 Hz, 1H, H-4), 4.26–4.10 (m, 3H, H-5, H-6 and H-6′), 2.07 (s, 3H, OAc), 2.05 (s, 3H, OAc), 1.27 (s, 9H, $-C(CH_3)_3$);^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 170.3, 129.5, 128.1, 88.9, 75.3, 66.4, 65.2, 63.2, 28.7, 20.9, 20.8.

*4.3.2.12. Cyclohexyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2l**).*[14b] Isolated as a colorless oil; 0.28 g (90%); $[\alpha]_D^{20}$ +86.9 (*c* 1.00, MeOH) [lit.[39b] $[\alpha]_D^{31.7}$ +110.7 (*c* 1.00, $CHCl_3$)]; IR (thin film) ν_{max} 2933, 2858, 2659, 2134, 1747, 1450, 1370, 1233, 1187, 1036 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.82 (br d, J=10.5 Hz, 1H, H-3), 5.76 (dt, J_{2-3}=10.5 Hz, J_{2-1}=J_{2-4}=1.5 Hz, 1H, H-2), 5.24 (dd, J_{4-5}=9.3 Hz, J_{4-3}=1.2 Hz, 1H, H-4), 5.12 (br s, 1H, H-1), 4.20 (m, 3H, H-5, H-6 and H-6′), 3.64–3.55 (m, 1H, $-OCH(CH_2)_5$), 2.04 (s, 3H, OAc), 2.03 (s, 3H, OAc), 1.92–1.82 (m, 2H, $-OCH(CH_2)_5$), 1.71–1.68 (m, 2H, $OCH(CH_2)_5$), 1.52–1.48 (m, 1H, $-OCH(CH_2)_5$), 1.37–1.15 (m, 5H, $-OCH(CH_2)_5$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 170.2, 128.6, 128.4, 92.6, 76.6, 66.5, 65.3, 63.0, 33.6, 32.0, 25.4, 24.3, 24.0, 20.9, 20.6.

*4.3.2.13. Cyclopentyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2m**).*[40] Isolated as a colorless oil; 0.26 g (87%); $[\alpha]_D^{20}$ +80.4 (*c* 1.00, MeOH) [lit.[40] $[\alpha]_D^{25}$ +99.0 (*c* 0.98, $CHCl_3$)]; IR (thin film) ν_{max} 2940, 2861, 2673, 2137, 1746, 1456, 1373, 1234, 1039 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.81 (br d, J=10.5 Hz, 1H, H-3), 5.74 (dt, J_{2-3}=10.5 Hz, J_{2-1}=J_{2-4}=2.4 Hz, 1H, H-2), 5.23 (dd, J_{4-5}=9.6 Hz, J_{4-3}=1.2 Hz, 1H, H-4), 5.04 (br s, 1H, H-1), 4.20 (dd, $J_{6-6'}$=12.0 Hz, J_{6-5}=5.4 Hz, 1H, H-6), 4.12 (dd, $J_{6'-6}$=12.0 Hz, $J_{6'-5}$=2.4 Hz, 1H, H-6′), 4.06 (ddd, J_{5-4}=9.6 Hz, J_{5-6}=5.4 Hz, $J_{5-6'}$=2.4 Hz, 1H, H-5), 2.04 (s, 3H, OAc), 2.02 (s, 3H, OAc), 1.76–1.47 (m, 9H, $-OCH(CH_2)_4$and $-OCH(CH_2)_4$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.6, 170.2, 128.5, 128.3, 93.5, 80.5, 66.6, 65.2, 62.9, 33.4, 32.2, 23.4, 23.0, 20.8, 20.7.

*4.3.2.14. 2-Methoxy-4-methyl-phenyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2n**).* Isolated as a colorless oil; 0.26 g (75%); $[\alpha]_D^{20}$ +81.7 (*c* 0.75, CH_2Cl_2); IR (thin film) ν_{max} 3056, 2955, 2936, 2852, 1741, 1514, 1370, 1237, 1098, 1048, 736 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) *glycal* α δ 6.91–6.64 (m, 3H, H_{aryl}), 6.08–5.79 (m, 2H, H-2 and H-3), 5.44–5.27 (m, 2H, H-1 and H-4), 4.14–4.27 (m, 2H, H-6 and H-6′), 4.12–4.06 (m, 1H, H-5), 3.84 (s, 3H, $ArOCH_3$), 2.31 (s, 3H, $ArCH_3$), 2.09 (s, 3H, OAc), 2.08 (s, 3H, OAc); GC–MS (EI, rel int. %) *m*/*z* 350 ($[M^+]$, 4), 290 (2), 275 (1), 230 (25), 217 (60), 187 (5), 165 (12), 138 (8), 111 (4), 91 (3), 43 (100); *glycal* β δ 6.91–6.64 (m, 3H, H_{aryl}), 6.08–5.79 (m, 2H, H-2 and H-3), 5.44–5.27 (m, 2H, H-1 and H-4), 4.14–4.27 (m, 2H, H-6 and H-6′), 3.95–3.88 (m, 1H, H-5), 3.87 (s, 3H, $ArOCH_3$), 2.36 (s, 3H, $ArCH_3$), 2.06 (s, 3H, OAc), 2.03 (s, 3H, OAc); GC–MS (EI, rel int. %) *m*/*z* 350 ($[M^+]$, 2), 311 (1), 290 (5), 279 (8), 262 (2), 230 (11), 217 (17), 167 (31), 149 (59), 138 (5), 71 (19), 57 (43), 43 (100); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.9, 170.5, 170.3, 170.2, 146.1, 143.6, 132.2, 131.8, 130.1, 129.6, 127.7, 127.3, 125.2, 125.1, 115.3, 114.0, 113.3, 113.0, 90.5, 74.8, 74.5, 70.9, 68.6, 67.3, 65.4, 65.0, 63.7, 62.8, 55.9, 21.0, 20.8, 20.7, 20.6, 18.6, 18.5; HRMS (ESI, MeOH/H_2O) calcd for $C_{18}H_{22}O_7Na$ $[M+Na]^+$ 373.1263, found 373.1279.

*4.3.2.15. 2-(2-(2-Methoxyethoxy)ethoxy)ethanyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2u**).* Isolated as a colorless oil; 0.32 g (86%); $[\alpha]_D^{20}$ +61.3 (*c* 1.00, MeOH); IR (KBr pellet) ν_{max} 2878, 1743, 1453, 1371, 1237, 1048 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 5.86 (br s, 2H, H-2, H-3), 5.31 (br d, J_{4-5}=9.6 Hz, 1H, H-4), 5.07 (br s, 1H, H-1), 4.25 (dd, $J_{6-6'}$=12.0 Hz, J_{6-5}=5.1 Hz, 1H, H-6), 4.16 (dd, $J_{6'-6}$=12.0 Hz, $J_{6'-5}$=2.1 Hz, 1H, H-6′), 4.10 (ddd, J_{5-4}=9.6 Hz, J_{5-6}=5.1 Hz, $J_{5-6'}$=2.1 Hz, 1H, H-5), 3.74–3.61 (m, 10H, OCH_2), 3.55–3.52 (m, 2H, OCH_2), 3.34 (s, 3H, OCH_3), 2.09 (s, 3H,

OAc), 2.07 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 170.3, 129.1, 127.7, 94.6, 71.9, 70.6, 70.5, 70.3, 67.8, 66.8, 65.2, 62.9, 58.9, 20.9, 20.8; ; HRMS (ESI, MeOH/H_2O) calcd for $C_{17}H_{28}NaO_9$ $[M+Na]^+$ 399,1631, found 399.1648.

*4.3.2.16. 2-(2-Ethoxyethoxy)ethanyl4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2v**).*[23c] Isolated as a colorless oil; 0.30 g (88%); $[\alpha]_D^{20}$ +48.4 (*c* 1.00, MeOH); IR (KBr pellet) ν_{max} 2973, 2872, 1743, 1445, 1235, 1110, 1048 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.85 (br s, 2H, H-2, H-3), 5.31 (br d, J_{4-5}=9.6 Hz, 1H, H-4), 5.07 (br s, 1H, H-1), 4.25 (dd, $J_{6-6'}$=13.5 Hz, J_{6-5}=5.4 Hz, 1H, H-6), 4.16 (dd, $J_{6'-6}$=13.5 Hz, $J_{6'-5}$=2.7 Hz, 1H, H-6′), 4.10 (ddd, J_{5-4}=9.6 Hz, J_{5-6}=5.4 Hz, $J_{5-6'}$=2.7 Hz, 1H, H-5), 3.55–3.69 (m, 8H, OCH_2), 3.51 (q, *J*=6.9 Hz, 2H, OCH_2CH$_3$),2.09 (s, 3H, OAc), 2.07 (s, 3H, OAc),1.19 (t, *J*=6.9 Hz, 3H, OCH$_2$CH_3); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 170.3, 129.1, 127.7, 94.6, 70.6, 70.4, 69.8, 67.8, 66.8, 66.6, 65.2, 62.9, 20.9, 20.8, 15.1.

*4.3.3. General procedure for the synthesis of 2,3-unsaturated O-glycopyranosides (**2o**–**r**).* To a 50 mL round bottomed flask containing a solution of **1** (326 mg, 1.2 mmol) and appropriate alcohol (0.5 mmol) in dichloromethane (10 mL) at 0 °C under argon was added $TeCl_4$ (5 mg, 2 mol %). The ice bath was removed and the mixture was stirred for the time indicated in Tables 3 and 5. A saturated solution of ammonium chloride (5 mL) was then added and the mixture was stirred until the change in the color. The mixture was extracted with EtOAc (2×10 mL) and the combined organic phases were dried over $MgSO_4$. The solvents were removed under reduced pressure followed by purification by a flash column chromatography [hexanes/EtOAc (95:5)] to yield the corresponding 2,3-unsaturated O-glycopyranosides.

*4.3.3.1. But-2-yne-1,4-diyl bis-4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2o**).*[41] Isolated as a colorless oil; 0.23 g (89%); $[\alpha]_D^{20}$ +95.9 (*c* 1.00, MeOH); IR (KBr pellet) ν_{max} 2924, 2861, 1744, 1375, 1235, 1036, 910, 838 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.91 (br d, J_{3-2}=10.2 Hz, 1H, H-3), 5.81 (dt, J_{2-3}=10.2 Hz, J_{2-1}=J_{2-4}=2.1 Hz, 1H, H-2), 5.43 (br s, 1H, H-1), 5.32 (br d, J_{4-5}=9.6 Hz, 1H, H-4), 4.24 (dd, $J_{6-6'}$=12.3 Hz, J_{6-5}=5.4 Hz, 1H, H-6), 4.17 (dd, $J_{6'-6}$=12.3 Hz, $J_{6'-5}$=2.4 Hz, 1H, H-6′), 4.12–4.05 (m, 1H, H-5), 2.09 (s, 2H, OCH_2C≡C), 2.08 (s, 3H, OAc), 2.07 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 170.2, 129.7, 127.1, 92.6, 82.0, 67.1, 65.0, 62.8, 55.2, 20.9, 20.7.

*4.3.3.2. Hexa-2,4-diyne-1,6-diyl bis-4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2p**).*[23b] Isolated as a colorless oil; 0.20 g (76%); $[\alpha]_D^{20}$ +123.8 (*c* 1.00, MeOH); IR (KBr pellet) ν_{max} 2912, 1742, 1233, 1035, 911 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.91 (br d, J_{3-2}=10.2 Hz, 1H, H-3), 5.81 (dt, J_{2-3}=10.2 Hz and J_{2-4}=J_{2-1}=2.1 Hz, 1H, H-2), 5.32 (br d, J_{4-5}=9.6 Hz, 1H, H-4), 5.19 (br s, 1H, H-1), 4.36 (s, 2H, OCH_2C≡C), 4.25 (dd, $J_{6-6'}$=12.3 Hz, J_{6-5}=5.1 Hz, 1H, H-6), 4.15 (dd, $J_{6'-6}$=12.3 Hz, $J_{6'-5}$=2.7 Hz, 1H, H-6′), 4.05 (ddd, J_{5-4}=9.6 Hz, J_{5-6}=5.1 Hz, $J_{5-6'}$=2.7 Hz, 1H, H-5), 2.08 (s, 3H, OAc), 2.07 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.7, 170.2, 129.9, 126.9, 92.9, 74.9, 70.4, 67.2, 64.9, 62.6, 55.4, 20.9, 20.7.

*4.3.3.3. 2,7-Dimethylocta-3,5-diyne-2,7-diyl bis-4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2q**).* Isolated as a colorless oil; 0.21 g (71%); $[\alpha]_D^{20}$ +175.1 (*c* 1.00, MeOH); IR (KBr pellet) ν_{max} 3055, 2987, 2917, 2848, 1742, 1369, 1229, 1025, 738 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.88 (br d, J_{3-2}=10.2 Hz, 1H, H-3), 5.80 (dt, J_{2-3}=10.2 Hz, J_{2-1}=J_{2-4}=1.8 Hz, 1H, H-2), 5.59 (br s, 1H, H-1), 5.28 (dd, J_{4-5}=9.6 Hz, J_{4-2}=1.8 Hz, 1H, H-4), 4.29–4.03 (m, 3H, H-5, H-6, H-6′), 2.07 (s, 6H, OAc), 1.59 (s, 3H, OCCH$_3$), 1.53 (3H, OCH$_3$); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 170.3, 128.7, 128.6, 91.2, 81.3, 72.0, 69.2, 67.0, 65.1, 63.0, 30.2, 29.7, 20.9, 20.7; HRMS (ESI, MeOH/H_2O) calcd for $C_{30}H_{38}O_{12}Na$ $[M+Na]^+$, 613.2261; found, 613.2257.

*4.3.3.4. Octa-3,5-diyne-1,8-diyl bis-4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2r**).* Isolated as a colorless oil; 0.19 g (70%); $[\alpha]_D^{20}$ +58.7 (*c* 1.00, MeOH); IR (KBr pellet) ν_{max} 2889, 1742, 1371, 1232, 1106, 1042 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.89 (br d, J_{3-2}=10.5 Hz, 1H, H-3), 5.82 (dt, J_{2-3}=10.5 Hz, J_{2-1}=J_{2-4}=2.1 Hz, 1H, H-2), 5.30 (br d, J_{4-5}=9.6 Hz, 1H, H-4), 5.05 (br s, 1H, H-1), 4.24 (dd, $J_{6-6'}$=12 Hz, J_{6-5}=5.4 Hz, 1H, H-6), 4.17 (dd, $J_{6'-6}$=12 Hz, $J_{6'-5}$=2.4 Hz, 1H, H-6′), 4.15–4.07 (m, 1H, H-5), 3.83(dt, $J_{7-7'}$=9.9 Hz, J_{7-8}=6.6 Hz, 1H, OCH_2CH$_2$), 3.70 (dt, $J_{7'-7}$=9.9 Hz, $J_{7'-8}$=6.6 Hz, 1H, OCH_2CH$_2$), 2.58 (t, J_{8-7}=$J_{8-7'}$=6.6 Hz, 2H, OCH$_2$CH_2), 2.10 (s, 3H, OAc), 2.08 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.8, 170.3, 129.4, 127.3, 94.6, 74.2, 67.0, 66.5, 66.2, 65.1, 62.8, 20.9, 20.8; HRMS (ESI, MeOH/H_2O) calcd for $C_{28}H_{34}O_{12}Na$ $[M+Na]^+$, 585.1948; found, 585.1959.

*4.3.3.5. Ethane-1,2-diyl bis-4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2s**).* Isolated as a colorless oil; 0.18 g (70%); $[\alpha]_D^{20}$ +72.8 (*c* 1.00, MeOH); IR (KBr pellet) ν_{max} 2938, 1742, 1371, 1235, 1041, 909 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.93–5.84 (m, 2H, H-2, H-3), 5.33 (br d, J_{4-5}=9.6 Hz, 1H, H-4), 5.10 (br s, 1H, H-1), 4.26 (dd, $J_{6'-6}$=12.0 Hz, $J_{6'-5}$=5.1 Hz, 1H, H-6′), 4.18 (dd, $J_{6-6'}$=12.0 Hz, J_{6-5}=2.4 Hz, 1H, H-6), 4.12 (ddd, J_{5-4}=9.6 Hz, J_{5-6}=5.1 Hz, $J_{5-6'}$=2.4 Hz, 1H, H-5), 3.94 (d, $J_{7'-7}$=12.3 Hz, 1H, OCH_2), 3.76 (d, $J_{7-7'}$=12.3 Hz, 1H, OCH_2), 2.11 (s, 3H, OAc), 2.10 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 170.5, 170.1, 129.6; 127.8; 94.9, 68.0, 67.2, 65.4, 63.2, 21.2, 21.0; HRMS (ESI, MeOH/H_2O) calcd for $C_{22}H_{30}O_{12}Na$ $[M+Na]^+$, 509.1635; found, 509.1634.

*4.3.3.6. 2,2′-Oxydiethanyl bis-4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**2t**).*[41] Isolated as a colorless oil; 0.18 g (67 %); $[\alpha]_D^{20}$ +83.5 (*c* 0.50, MeOH); IR (KBr pellet) ν_{max} 2961, 1737, 1369, 1260, 1019, 799 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.92–5.86 (m, 2H, H-2, H-3), 5.34 (br d, J_{4-5}=9.6 Hz, 1H, H-4), 5.10 (br s, 1H, H-1), 4.27 (dd, $J_{6'-6}$=12.0 Hz, $J_{6'-5}$=4.8 Hz, 1H, H-6′), 4.16 (dd, $J_{6-6'}$=12.0 Hz, J_{6-5}=2.4 Hz, 1H, H-6), 4.11 (ddd, J_{5-4}=9.6 Hz, $J_{5-6'}$=4.8 Hz, J_{5-6}=2.4 Hz, 1H, H-5), 3.94–3.89 (m, 1H, OCH_2CH$_2$), 3.89–3.68 (m, 3H, OCH_2CH_2), 2.11 (s, 3H, OAc), 2.09 (s, 3H, OAc); ^{13}C NMR (75 MHz, $CDCl_3$) δ 171.1, 170.6, 129.5, 127.9, 94.0, 70.7, 68.0, 67.1, 65.4, 63.1, 21.2, 21.1.

*4.3.4. General procedure for the homocoupling reaction of alkynyl 2,3-unsaturated O-glycopyranosides (**2a**–**c**).* In a flask containing a solution of the appropriate alkynes **2a**–**c** (1 mmol) in THF (4 mL) were added TMEDA (20 mol %), CuI (5 mol %), $NiCl_2 \cdot 6H_2O$ (5 mol %), and Et_3N (3 equiv). The mixture was stirred for the time indicated in Table 4 and then diluted using EtOAc (20 mL). The mixture was washed with water (5×50 mL) and the combined organic phases were dried over $MgSO_4$. The solvents were removed under reduced pressure and the crude product was purified using a flash column chromatography [hexanes/EtOAc (6:4)] to yield the corresponding 2,3-unsaturated O-glycopyranosides **2p**–**r**.

*4.3.5. General procedure for the potassium allyltrifluoroborate (**4**).*[42] To a solution of $B(OMe)_3$ (8.15 mL, 7.59 g, 73.2 mmol) in THF (40 mL) was added dropwise allylmagnesium chloride (30 mL, 60 mmol, 2.0 M in THF) at −78 °C. The mixture was stirred for 30 min. The ice bath was removed. The yellow solution with a white precipitate was allowed to reach the room temperature over a 1 h period. Then, it was cooled to 0 °C and KHF_2 (23.4 g, 300 mmol) was added in one portion. This was followed by the dropwise addition of H_2O (30 mL). The ice bath was removed. The mixture was stirred for 30 min and then concentrated under high vacuum. The white solid was extracted with hot acetone (4×100 mL). The extracts

were filtered through a Celite pad and the filtrate was concentrated to afford a white solid. The solid was purified by dissolving in the minimum amount of hot acetone, followed by cooling to room temperature and precipitation with Et_2O. The solution was allowed to stand for 20 min to complete precipitation. The precipitate was collected and dried under high vacuum to yield 3.37 g (38%) of a powdery white solid. ^{1}H NMR (300 MHz, DMSO-d_6) δ 5.85–5.74 (m, 1H, CH_2=CH), 4.56 (d, J=17.2 Hz, 1H, CH_2=CH), 4.49 (d, J=9.6 Hz, 1H, CH_2=CH), 0.92 (br s, 2H, CH_2BF_3K); ^{13}C NMR (75 MHz, DMSO-d_6) δ 142.9, 108.9; ^{11}B NMR (128 MHz, DMSO-d_6) δ 4.21 (q, $J_{11B,19F}$=61.3 Hz, BF_3K); ^{19}F NMR (376 MHz, DMSO-d_6) δ −136.4 ($J_{19F,11B}$=61.3 Hz, BF_3K).

*4.3.6. General procedure for the allylation of 4-NO_2–benzaldehyde (**3**) with potassium allyltrifluoroborate (**4**) using 2,3-unsaturated O-glycosides as catalysts.* To a solution of 4-NO_2–benzaldehyde **3** (151 mg, 1.0 mmol) and the appropriate 2,3-unsaturated O-glycosides **2s**–**v** (10 mol %) in CH_2Cl_2 (3 mL) was added potassium allyltrifluorborate **4** (163 mg, 1.10 mmol) followed by water (3 mL). The biphasic mixture was stirred for the time indicated in Table 7 and then diluted with CH_2Cl_2 (5 mL). The layers were separated and the aqueous layer was extracted with CH_2Cl_2 (3×5 mL) and dried over $MgSO_4$. The solvent was removed under reduced pressure to yield **5** without the need of further purification.

*4.3.6.1. 1-(4-Nitrophenyl)but-3-en-1-ol (**5**).*[30b] ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.21 (d, J=8.5 Hz, 2H, H_{Aryl}), 7.54 (d, J=8.5 Hz, 2H, H_{Aryl}), 5.86–5.72 (m, 1H, C*H*=CH_2), 5.22–5.16 (m, 2H, CH=CH_2), 4.87 (dd, J=8.0, 4.7 Hz, C*H*OH), 2.58–2.42 (m, 2H, CHCH_2), 2.31 (br s, 1H, OH); ^{13}C NMR (75 MHz, $CDCl_3$) δ 151.5, 147.5, 133.6, 126.9, 123.9, 119.9, 72.5, 44.2.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2012.07.070. These data include MOL files and InChiKeys of the most important compounds described in this article.

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