HETEROCYCLES, Vol. 91, No. 4, 2015, pp. 849 - 861. © 2015 The Japan Institute of Heterocyclic Chemistry
Received, 18th January, 2015, Accepted, 20th February, 2015, Published online, 4th March, 2015
DOI: 10.3987/COM-15-13174

IBr-CATALYZED *O*-GLYCOSYLATION OF D-GLUCALS: FACILE SYNTHESIS OF 2,3-UNSATURATED-*O*-GLYCOSIDES

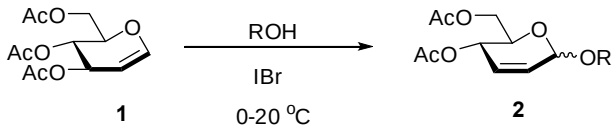
Rungnapha Saeeng, Onanong Siripru, and Uthaiwan Sirion*

Department of Chemistry and Center for Innovation in Chemistry, Faculty of Science, Burapha University, Sangsook, Chonburi 20131, Thailand; E-mail: uthaiwan@buu.ac.th

Abstract – Iodine monobromide (IBr) is explored as an alternative catalyst for the selective synthesis of 2,3-unsaturated glycosides from tri-*O*-acetyl-D-glucal **1** with several alcohols through Ferrier rearrangement. This reaction was shown to be a simple, efficient and cost-effective method, affords twenty examples of corresponding glycoside products in high yields with good α-selectivity.

2,3-Unsaturated-*O*-glycosides are useful chiral intermediates for the synthesis of building block of bioactive molecules. They could use to link with interesting scaffold for enhancing the pharmacological potential.[1,2] 2,3-Unsaturated-*O*-glycosides can be easily synthesized from Ferrier's rearrangement of glucal with various nucleophiles in the presence of a Lewis acid catalyst. Originally, $BF_3{\cdot}Et_2O$ was used.[3] In the past ten years, a large number of effective reagents to promote the Ferrier glycosylation reaction have been developed, including $InCl_3$,[4] $Sc(OTf)_3$,[5] Montmorillionite K-10,[6] $NbCl_5$,[7] $Bi(OTf)_3$,[8] $Er(OTf)_3$,[9] $Yb(OTf)_3$,[10] $ZnCl_2$-Al_2O_3,[11] $NaHSO_4$-SiO_2,[12] TMSOTf,[13] $Pd(OAc)_2$,[14] $FeCl_3$,[15] $CeCl_3{\cdot}7H_2O$,[16] $Fe_2(SO_4)_3$,[17] $Fe(OTf)_3$,[18] $TiCl_3(OTf)$,[19] and CF_3SO_3H-SiO_2.[20] In addition, oxidants also have been employed such as DDQ,[21] I_2,[22] and CAN.[23] Although these methods are available, new facile methods are still highly desirable due to the important of this transformation in glycoside synthesis. Iodine monobromide (IBr) is a highly polar interhalogen compound and can be used as a source of iodonium ion (I^+). IBr was early used as a catalyst for the electrophilic cyclization of homoallylic carbonates.[24] Recently, IBr was used to promote the iodocyclization for synthesis of 3-bromo-4-iodo-substituted furans, pyrroles and thiophenes in good to high yields.[25] In the field of glycoside chemistry, IBr can promote glycosylation of sugar alcohols by disarmed glycosyl bromide and thioglycosides.[26] Combination of IBr with $AgClO_4{\cdot}H_2O$ or AgOTf were used effectively as promoter in glycosylation of sialic acid[27] and Kdo-thioglycoside[28] respectively to obtain glycoside products in high yield. We have previously reported that iodine can be efficiently promoted the *O*-glycosylation of D-glucal.[29] In continuation of our efforts to develop new glycosylation methods, we

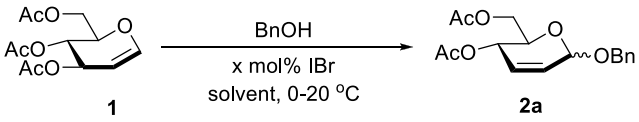
report herein the synthesis of 2,3-unsaturated-*O*-glycosides from D-glucal *via* Ferrier reaction by using IBr as a new catalyst for this reaction (Scheme 1).



Scheme 1

We optimized the reaction conditions for preparing 2,3-unsaturated glycosides from tri-*O*-acetyl-D-glucal **1** by using benzyl alcohol as nucleophile for the model reaction. First, the glycosylation was optimized using IBr 50 mol% as the I^+ source in various solvent (Table 1, entries 1-5). Employing MeCN or Et_2O as solvent, glycoside **2a** was obtained as a major product in fair yields (entries 1 and 4). Using THF as solvent resulted in low yield of product (entry 2). In the presence of CH_2Cl_2, the reaction turned out to be a complex mixture. Interestingly, when the non-polar solvent as toluene was used, glycoside **2a** was obtained as a major product in good yield, however the reaction was completed as long as 24 h (entry 5). Further evaluation of the IBr loading revealed that performing the reaction using IBr 20 mol%, the yield of product was improved and completed in short reaction time (entry 6). This result indicated that the use of 50 mol% IBr (entry 5) may lead to the formation of glycosyl-bromide which can be coupling with alcohol nucleophile at anomeric position to produce the desired product in longer reaction time than the direct glycosylation.[26] When the molecular sieve was used as desiccant, complex mixture was obtained without desired product (entry 7). Further experimental using a mixture of toluene and CH_2Cl_2 1:1 as solvents, the reaction proceeded smoothly and gave **2a** in 89% yield (entry 8). CH_2Cl_2 was used as co-solvent for enhancing the solubility of IBr in the reaction mixture.

Table 1. Optimization for the synthesis of 2,3-unsaturated glycosides



Entry[a]	Solvent	IBr (mol%)	Time (h)	Yield (%)[b]
1	MeCN	50	1.0	47
2	THF	50	4.0	20
3	CH_2Cl_2	50	1.0	–[c]
4	Et_2O	50	4.0	49
5	toluene	50	24.0	72
6	toluene	20	1.0	83
7	toluene/add 4 ÅMS	20	24.0	–[d]
8	toluene+CH_2Cl_2 (1:1)	20	1.0	89

[a] 0.184 mmol of tri-*O*-acetyl-D-glucal (**1**); [b]Isolated yields; [c]Complex mixtures
[d]The use of 4 AºMS resulted complex mixture and no desired product was obtained

To explore the efficacy of IBr catalyzed Ferrier reaction of glycal, we have studied the reactions of different alcohols with glycal. Under optimized condition in Table 1, entry 8, a series of glycosylation of tri-*O*-acetyl-D-glucal **1** with various alcohol nucleophiles were carried out using 20 mol% IBr in the mixture of toluene and CH_2Cl_2 (1:1) at 0-20 °C. As shown in Table 2, the versatile of IBr promoted glycosylation of tri-*O*-acetyl-D-glucal **1** *via* Ferrier reaction proved to be suitable for several types of alcohol nucleophiles leading to the corresponding glycosides **2b**-**2t** in good to excellent yields with α-anomeric selectivity.

The glycosylation reactions of tri-*O*-acetyl-D-glucal **1** were carried out with substituted benzyl alcohols to afford the desired 2,3-unsaturated-*O*-glycoside products **2a**-**2f** (Table 2, entries 1-6). Reaction of electron-rich 2-methoxybenzyl alcohol led to glycoside **2b** in high yield in 1 h (entry 2). Di- and trimethoxy benzyl alcohols are found to undergo glycosylation smoothly with glucal **1** using IBr (entries 5-6).

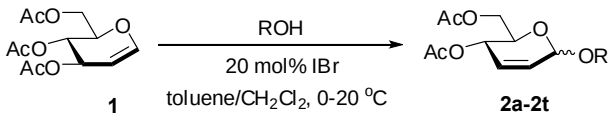
Reactions of phenyl-, di-phenyl ethanol and 1-phenyl-1-propanol resulted in the formation of the glycosides **2g**-**2i** in excellent yields (entries 7-9). Reaction of hindered diphenylmethanol required more time to complete the reaction to obtain glycoside **2j** with high α-stereoselective (entry 10). The high α-stereoselectivity was observed with the more hindered alcohol nucleophiles. The predominant formation of α-anomer may arise from a thermodynamic anomeric effect.

Moreover, the IBr-catalyzed Ferrier reaction of glycal was also tested employing diverse commercial available alcohols as octanol, 2-methyl-1-butanol, 2-propyn-1-ol, 2-bromoethanol, 2-butanol and cyclohexanol (entries 11-16) providing the corresponding glycosides in good yields. Glycosylation with 2-bromoethanol was completed within 30 min to obtain **2n** in 79% yield. Mild reaction conditions using IBr, allow alkyne- and halide-functional groups in compounds **2j** and **2n** to be tolerated in this reaction.

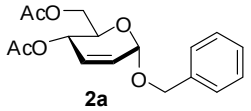
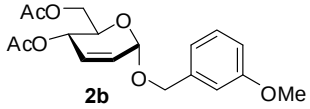
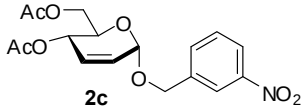
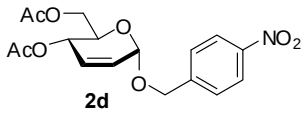
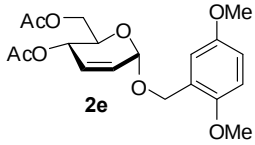
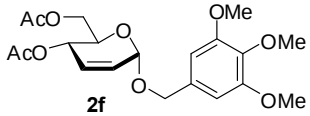
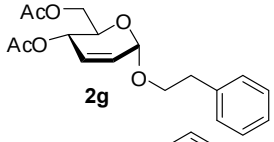
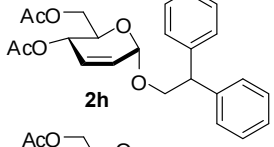
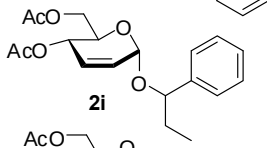
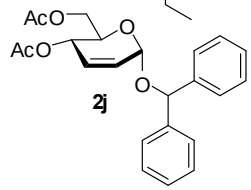
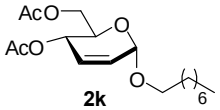
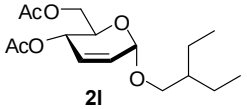
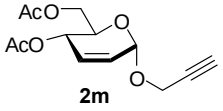
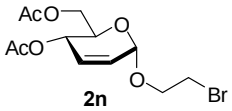
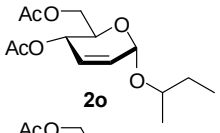
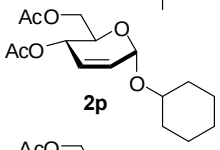
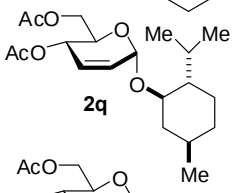
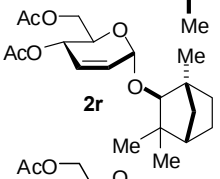
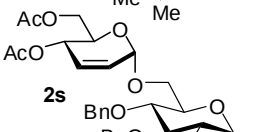
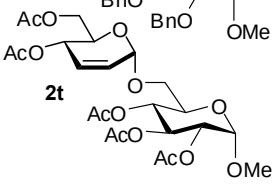
Interestingly, α-anomers were obtained exclusively in good yields when using natural product alcohols as (-)-menthol and fencyl alcohol (entries 17-18). Proving the generality of this methodology by addition of tri-benzyl and tri-acetyl-D-glucopyranoside as nucleophiles, disaccharides **2s** and **2t** were afforded in high yields (entries 17-18).

In summary, a new method of IBr-catalyzed *O*-glycosylation of D-glucal with various alcohols was developed. IBr an inexpensive, easily handle and readily available compound is found to be an efficient catalyst for *O*-glycosylation *via* Ferrier reaction. Using this catalyst, twenty examples of 2,3-unsaturated glycosides can be obtained in high yields with α-anomeric selectivity.

Table 2. Synthesis of 2,3-unsaturated glycoside derivatives



1 **2a-2t**

Entry	Major Product[c]	Time (h)	Yield (%)[a] (α:β)[b]
1	 **2a**	1.0	89 (4:1)
2	 **2b**	1.0	90 (5:1)
3	 **2c**	1.0	71 (5:1)
4	 **2d**	1.0	83 (4:1)
5	 **2e**	1.0	86 (8:1)
6	 **2f**	1.0	82 (6:1)
7	 **2g**	1.0	99 (4:1)
8	 **2h**	1.0	95 (7:1)
9	 **2i**	1.0	94 (4:1)
10	 **2j**	9.0	83 (15:1)
11	 **2k**	1.0	91 (6:1)
12	 **2l**	1.0	82 (4:1)
13	 **2m**	1.0	83 (7:1)
14	 **2n**	0.5	79 (5:1)
15	 **2o**	3.0	72 (4:1)
16	 **2p**	5.0	72 (10:1)
17	 **2q**	1.5	78 (α-only)
18	 **2r**	1.5	84 (α-only)
19	 **2s**	1.0	80 (4:1)
20	 **2t**	1.0	86 (5:1)

[a] Isolated yields were calculated from diastereomeric mixtures.
[b] The ratio of α- and β-isomers of **2** was determined by 1H NMR spectroscopy of the crude products.
[c] Major product can be separated by simple column chromatography.

EXPERIMENTAL

Proton NMR spectra were recorded on a BRUKER AVANC (400 MHz). All spectra were measured in $CDCl_3$ solvent and chemical shifts are reported as δ values in parts per million (ppm) relative to $CDCl_3$ (δ

7.26) as internal standard. Carbon NMR spectra were recorded on a BRUKER AVANC (100 MHz). All spectra were measured in $CDCl_3$ solvent and chemical shifts are reported as δ values in parts per million (ppm) relative to $CDCl_3$ (δ 77.0) as internal standard. High-resolution mass spectra (HRMS) were obtained with a Finnigan MAT 95. Infrared spectra were determined on a PERKIN ELMER FT/IR-2000S spectrophotometer and are reported in wave number (cm^{-1}). Optical rotation was determined with a JASCO P-1020 digital polarimeter. Analytical thin-layer chromatography (tlc) was conducted on precoated tlc plates; silica gel 60F-254 [E. Merck, Darmstadt, Germany]. Silica gel columns for open-column chromatography utilized silica gel 60 (0.040-0.063 mm) [E. Merck, Darmstadt, Germany]. Melting points were measured using a Melting point apparatus (Griffin) and are uncorrected.

General procedure for the synthesis of 2,3-unsaturated-*O*-glycosides. A mixture of 3,4,6-tri-*O*-acetyl-D-glucal **1** (50.0 mg, 0.184 mmol) and alcohol (0.193 mmol) was dissolved in dry-CH_2Cl_2 : dry-toluene (125 : 200 μL) under gas-nitrogen. The solution was cooled to 0 °C, then 0.5 M IBr in CH_2Cl_2 (20 mol%, 75 μL) was added slowly. The stirring was continued at 0-20 °C for 1-10 h. After TLC showed the completed conversion, the reaction mixture was quenched carefully with cooled aq. $Na_2S_2O_3$ (20 mL) and washed with satd aq. $NaHCO_3$ (20 mL), and extracted with EtOAc (3×20 mL). The combined organic layer was washed with brine (20 mL), dried over anhydrous Na_2SO_4, and then concentrated under reduced pressure. The residues were purified by silica gel column chromatography (EtOAc/*n*-hexane) to give the 2,3-unsaturated-*O*-glycoside products **2a-2t** in good to high yields (71-99%). In most cases, a mixture of α and β-anomers of glycoside **2** was obtained. The ratio of the isomers was determined by comparison of the integration values of the peaks in ^1H NMR analysis. The α-configuration was characterized from the position of anomeric proton which appears in an up field position compared to β-anomer in most cases. The β-isomers was not separated but characterized compared with the literature data of the mixture.[30] Spectral data of pure α-isomers are as followed.

Benzyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2a): a white solid; α-anomer R_f = 0.61 (30% EtOAc/*n*-hexane); mp 38-40 °C; $[\alpha]_D^{26}$ +82.22 (*c* 0.50, $CHCl_3$); IR ($CHCl_3$) 3025, 2929, 1745, 1497, 1455, 1370, 1231, 1039, 750, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.40-7.30 (m, 5H, Ph), 5.92 (brd, 1H, *J* = 10.0 Hz, H-3), 5.87 (ddd, 1H, *J* = 10.0, 2.5, 1.5 Hz, H-2), 5.36 (dm, 1H, *J* = 9.5 Hz, H-4), 5.16 (brs, 1H, H-1), 4.83 (d, 1H, *J* = 11.5 Hz, H-1'a), 4.62 (d, 1H, *J* = 11.5 Hz, H-1'b), 4.27 (dd, 1H, *J* = 11.5, 5.0 Hz, H-6a), 4.18 (ddd, 1H, *J* = 9.5, 5.0, 2.0 Hz, H-5), 4.14 (dd, 1H, *J* = 11.5, 2.0 Hz, H-6b), 2.13 (s, 3H, Ac), 2.10 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.81, 170.30, 137.61, 129.32, 128.49 (2×C), 128.05 (2×C), 127.90, 127.77, 93.67, 70.32, 67.11, 65.34, 62.96, 20.97, 20.81; HRMS (ESI) $C_{17}H_{20}O_6$ (M^++Na), Calcd 343.1158, Found 343.1192.

3-Methoxybenzyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2b): a colorless oil;

α-anomer R_f = 0.45 (30% EtOAc/*n*-hexane), $[\alpha]_D^{24}$ +67.13 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$) 2927, 1741, 1597, 1583, 1488, 1454, 1434, 1368, 1221, 1034, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.29 (t, 1H, *J* = 8.0 Hz, Ph), 6.96 (d, 1H, *J* = 8.0 Hz, Ph), 6.93 (d, 1H, *J* = 2.0 Hz, Ph), 6.86 (dd, 1H, *J* = 8.0, 2.0 Hz, Ph), 5.92 (brd, 1H, *J* = 10.0 Hz, H-3), 5.88 (ddd, 1H, *J* = 10.0, 2.5, 1.5 Hz, H-2), 5.36 (dm, 1H, *J* = 9.5 Hz, H-4), 5.15 (brs, 1H, H-1), 4.80 (d, 1H, *J* = 11.5 Hz, H-1'a), 4.60 (d, 1H, *J* = 11.5 Hz, H-1'b), 4.27 (dd, 1H, *J* = 11.5, 5.0 Hz, H-6a), 4.18 (ddd, 1H, *J* = 9.5, 5.0, 2.0 Hz, H-5), 4.16 (dd, 1H, *J* = 11.5, 2.0 Hz, H-6b), 3.84 (s, 3H, OC*H*$_3$), 2.13 (s, 3H, Ac), 2.11 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.84, 170.33, 159.76, 139.16, 129.55, 129.35, 127.74, 120.27, 113.60, 113.26, 93.62, 70.13, 67.11, 65.32, 62.95, 55.25, 21.00, 20.83; HRMS (ESI) $C_{18}H_{22}O_7$ (M^++Na) Calcd 373.1263, Found 373.1295.

3-Nitrobenzyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2c): a colorless oil; α-anomer R_f = 0.36 (30% EtOAc/*n*-hexane); $[\alpha]_D^{24}$ +52.78 (*c* 0.50, $CHCl_3$), IR ($CHCl_3$) 2922, 2852, 1741, 1530, 1456, 1367, 1350, 1256, 1226, 1036, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (brs, 1H, Ph), 8.19 (d, 1H, *J* = 8.0 Hz, Ph), 7.71 (d, 1H, *J* = 8.0 Hz, Ph), 7.56 (t, 1H, *J* = 8.0 Hz, Ph), 5.97 (brd, 1H, *J* = 10.0 Hz, H-3), 5.91 (ddd, 1H, *J* = 10.0, 2.5, 2.0 Hz, H-2), 5.37 (dm, 1H, *J* = 9.5 Hz, H-4), 5.18 (brs, 1H, H-1), 4.93 (d, 1H, *J* = 12.5 Hz, H-1'a), 4.71 (d, 1H, *J* = 12.5 Hz, H-1'b), 4.27 (dd, 1H, *J* = 12.0, 5.0 Hz, H-6a), 4.18 (dd, 1H, *J* = 12.0, 2.0 Hz, H-6b), 4.16 (ddd, 1H, *J* = 9.5, 5.0, 2.0 Hz, H-5), 2.12 (s, 3H, Ac), 2.11 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.73, 170.26, 148.42, 139.87, 133.61, 129.85, 129.46, 127.16, 122.82, 122.57, 94.10, 69.01, 67.33, 65.19, 62.87, 20.97, 20.78; HRMS (ESI) $C_{17}H_{19}NO_8$ (M^++Na) Calcd 388.1008, Found 388.1037.

4-Nitrobenzyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2d): a white solid; α-anomer R_f = 0.39 (30% EtOAc/*n*-hexane); mp 80-82 °C; $[\alpha]_D^{24}$ +44.38 (*c* 0.50, $CHCl_3$); IR ($CHCl_3$) 2924, 2852, 1740, 1606, 1520, 1365, 1346, 1260, 1220, 1034, 750 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.24 (d, 2H, *J* = 8.5 Hz, Ph), 7.55 (d, 2H, *J* = 8.5 Hz, Ph), 5.97 (brd, 1H, *J* = 10.0 Hz, H-3), 5.91 (ddd, 1H, *J* = 10.0, 2.5, 2.0 Hz, H-2), 5.37 (dm, 1H, *J* = 9.5 Hz, H-4), 5.17 (brs, 1H, H-1), 4.93 (d, 1H, *J* = 13.0 Hz, H-1'a), 4.72 (d, 1H, *J* = 13.0 Hz, H-1'b), 4.26 (dd, 1H, *J* = 12.0, 5.5 Hz, H-6a), 4.17 (dd, 1H, *J* = 12.0, 2.5 Hz, H-6b), 4.15 (ddd, 1H, *J* = 9.5, 5.5, 2.5 Hz, H-5), 2.12 (s, 3H, Ac), 2.10 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.66, 170.21, 147.53, 145.17, 129.89, 128.00 (2×C), 127.12, 123.71 (2×C), 94.13, 68.95, 67.36, 65.20, 62.84, 20.94, 20.75; HRMS (ESI) $C_{17}H_{19}NO_8$ (M^++Na) Calcd 388.1008, Found 388.1061.

2,5-Dimethoxybenzyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2e): a white solid; α-anomer R_f = 0.48 (30% EtOAc/*n*-hexane); mp 50-52 °C; $[\alpha]_D^{24}$ +58.43 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$) 2934, 2835, 1743, 1501, 1465, 1371, 1221, 1044 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.99 (brs, 1H, Ph), 6.83-6.81 (m, 2H, Ph), 5.92-5.89 (m, 2H, H-2, H-3), 5.37 (dm, 1H, *J* = 9.5 Hz, H-4), 5.19 (brs,

1H, H-1), 4.85 (d, 1H, *J* = 12.5 Hz, H-1'a), 4.62 (d, 1H, *J* = 12.5 Hz, H-1'b), 4.30 (dd, 1H, *J* = 12.0, 5.5 Hz, H-6a), 4.21 (ddd, 1H, *J* = 9.5, 5.5, 2.5 Hz, H-5), 4.18 (dd, 1H, *J* = 12.0, 2.5 Hz, H-6b), 3.81 (s, 3H, OC*H*$_3$), 3.80 (s, 3H, OC*H*$_3$), 2.12 (s, 3H, Ac), 2.10 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.87, 170.33, 153.57, 151.43, 129.20, 127.93, 127.20, 115.50, 113.04, 111.38, 93.99, 67.02, 65.39, 65.27, 62.94, 55.97, 55.78, 20.99, 20.77; HRMS (ESI) $C_{19}H_{24}O_8$ (M^++Na) Calcd 403.1369, Found 403.1363.

3,4,5-Trimethoxybenzyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2f): colorless oil; α-anomer R_f = 0.26 (30% EtOAc/*n*-hexane); $[\alpha]_D^{26}$ +62.41 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$) 2941, 2835, 1743, 1592, 1507, 1460, 1371, 1235, 1128, 1033, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.60 (s, 2H, Ph), 5.93 (brd, 1H, *J* = 10.0 Hz, H-3), 5.88 (ddd, 1H, *J* = 10.0, 2.5, 2.0 Hz, H-2), 5.37 (dm, 1H, *J* = 9.5 Hz, H-4), 5.15 (brs, 1H, H-1), 4.75 (d, 1H, *J* = 11.5 Hz, H-1'a), 4.54 (d, 1H, *J* = 11.5 Hz, H-1'b), 4.30 (dd, 1H, *J* = 12.0, 5.0 Hz, H-6a), 4.20 (dd, 1H, *J* = 12.0, 2.5 Hz, H-6b), 4.19 (ddd, 1H, *J* = 9.5, 5.0, 2.5 Hz, H-5), 3.89 (s, 6H, 2×OC*H*$_3$), 3.85 (s, 3H, OC*H*$_3$), 2.13 (s, 3H, Ac), 2.11 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.80, 170.32, 153.33, 137.67, 133.11 (2×C), 129.46, 127.67, 105.11 (2×C), 93.45, 70.41, 67.12, 65.31, 62.93, 60.86, 56.14 (2×C), 21.00, 20.85; HRMS (ESI) $C_{20}H_{26}O_9$ (M^++Na) Calcd 433.1475, Found 433.1469.

2-Phenylethyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2g): a colorless oil; α-anomer R_f = 0.36 (20% EtOAc/*n*-hexane); $[\alpha]_D^{24}$ +107.78 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$) 3028, 2927, 1744, 1604, 1497, 1454, 1370, 1237, 1040, 751, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35-7.21 (m, 5H, Ph), 5.89 (brd, 1H, *J* = 10.0 Hz, H-3), 5.83 (ddd, 1H, *J* = 10.0, 2.5, 2.0 Hz, H-2), 5.31 (dm, 1H, *J* = 9.5 Hz, H-4), 5.04 (brs, 1H, H-1), 4.20 (dd, 1H, *J* = 12.0, 5.0 Hz, H-6a), 4.06 (dd, 1H, *J* = 12.0, 2.5 Hz, H-6b), 4.00 (dt, 1H, *J* = 10.0, 7.0 Hz, H-1'a), 3.98 (ddd, 1H, *J* = 9.5, 5.0, 2.5 Hz, H-5), 3.78 (dt, 1H, *J* = 10.0, 7.0 Hz, H-1'b), 2.95 (t, 2H, *J* = 7.0 Hz, H-2'), 2.10 (s, 3H, Ac), 2.09 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.84, 170.34, 138.78, 129.13, 128.90 (2×C), 128.39 (2×C), 127.75, 126.33, 94.45, 69.55, 66.90, 65.20, 62.89, 36.35, 21.01, 20.81; HRMS (ESI) $C_{18}H_{22}O_6$ (M^+ +Na) Calcd 357.1314, Found 357.1330.

2,2-Diphenylethyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2h): a colorless oil; α-anomer R_f = 0.33 (20% EtOAc/*n*-hexane); $[\alpha]_D^{24}$ +64.62 (*c* 0.50, $CHCl_3$), IR ($CHCl_3$) 3028, 2925, 1744, 1495, 1451, 1370, 1231, 1040, 744, 701 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.20 (m, 10H, Ph), 5.84 (brd, 1H, *J* = 10.0 Hz, H-3), 5.75 (ddd, 1H, *J* = 10.0, 2.5, 2.0 Hz, H-2), 5.30 (dm, 1H, *J* = 9.5 Hz, H-4), 5.05 (brs, 1H, H-1), 4.39 (dd, 1H, *J* = 9.0, 8.0 Hz, H-1'a), 4.35 (dd, 1H, *J* = 8.0, 6.0 Hz, H-2'), 4.19 (dd, 1H, *J* = 12.5, 5.0 Hz, H-6a), 4.07 (dd, 1H, *J* = 9.0, 6.0 Hz, H-1'b), 4.05 (dd, 1H, *J* = 12.5, 2.5 Hz, H-6b), 3.83 (ddd, 1H, *J* = 9.5, 5.0, 2.5 Hz, H-5), 2.10 (s, 3H, Ac), 2.08 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.77, 170.23, 142.07, 141.99, 129.13, 128.47 (2×C), 128.42 (2×C), 128.30 (2×C), 128.24

(2×C), 127.59, 126.58, 126.56, 94.63, 71.83, 67.07, 65.14, 62.84, 50.98, 20.94, 20.78; HRMS (ESI) $C_{24}H_{26}O_6$ (M^+ + Na) Calcd 433.1627, Found 433.1657.

1-Phenylpropyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2i): a colorless oil; α-anomer R_f = 0.77 (30% EtOAc/*n*-hexane); $[\alpha]_D^{24}$ +201.20 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$) 3030, 2964, 2934, 1745, 1454, 1370, 1237, 1032, 757, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.39-7.29 (m, 5H, Ph), 5.90 (brd, 1H, *J* = 10.0 Hz, H-3), 5.77 (ddd, 1H, *J* = 10.0, 2.5, 2.0 Hz, H-2), 5.31 (dm, 1H, *J* = 8.0 Hz, H-4), 4.88 (brs, 1H, H-1), 4.64 (dd, 1H, *J* = 8.0, 5.0 Hz, H-1'), 4.30-4.23 (m, 3H, H-5, H-6), 2.15 (s, 3H, Ac), 2.12 (s, 3H, Ac), 1.93-1.81 (m, 1H, H-2'a), 1.77-1.67 (m, 1H, H-2'b), 1.00 (t, 3H, *J* = 7.0 Hz, H-3'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.84, 170.32, 141.87, 128.96, 128.46 (2×C), 128.21, 127.75, 126.86 (2×C), 91.59, 80.74, 67.35, 65.42, 63.23, 31.18, 20.99, 20.93, 10.84; HRMS (ESI) $C_{19}H_{24}O_6$ (M^++Na) Calcd 371.1471, Found 371.1469.

Benzhydryl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2j): a colorless oil; α-anomer R_f = 0.30 (20% EtOAc/*n*-hexane); $[\alpha]_D^{26}$ +97.82 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$) 3025, 2924, 2854, 1742, 1494, 1454, 1367, 1222, 1013, 744, 700 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42-7.24 (m, 10H, Ph), 5.93 (brd, 1H, *J* = 10.0 Hz, H-3), 5.89 (ddd, 1H, *J* = 10.0, 2.5, 2.0 Hz, H-2), 5.88 (s, 1H, H-1'), 5.35 (dm, 1H, *J* = 9.5 Hz, H-4), 5.16 (brs, 1H, H-1), 4.21 (dd, 1H, *J* = 11.5, 5.0 Hz, H-6a), 4.18 (ddd, 1H, *J* = 9.5, 5.0, 2.0 Hz, H-5), 4.03 (dd, 1H, *J* = 11.5, 2.0 Hz, H-6b), 2.10 (s, 3H, Ac), 2.09 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.77, 170.28, 142.29, 140.87, 129.34, 128.60 (2×C), 128.31 (2×C), 127.88 (2×C), 127.87, 127.45 (2×C), 127.08 (2×C), 92.59, 80.59, 67.37, 65.36, 62.86, 20.96, 20.76; HRMS (ESI) $C_{23}H_{24}O_6$ (M^++Na) Calcd 419.1471, Found 419.1465.

2-Octyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2k): a colorless oil; α-anomer R_f = 0.58 (20% EtOAc/*n*-hexane); $[\alpha]_D^{25}$ +77.70 (*c* 0.50, $CHCl_3$); IR ($CHCl_3$) 2927, 2856, 1748, 1457, 1370, 1234, 1042, 736, 604 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.90 (brd, 1H, *J* = 10.0 Hz, H-3), 5.86 (ddd, 1H, *J* = 10.0, 2.0, 1.0 Hz, H-2), 5.33 (dm, 1H, *J* = 9.5 Hz, H-4), 5.04 (brs, 1H, H-1), 4.27 (dd, 1H, *J* = 12.0, 5.5 Hz, H-6a), 4.19 (dd, 1H, *J* = 12.0, 2.5 Hz, H-6b), 4.13 (ddd, 1H, *J* = 9.5, 5.5, 2.5 Hz, H-5), 3.79 (dt, 1H, *J* = 9.5, 7.0 Hz, H-1'a), 3.52 (dt, 1H, *J* = 9.5, 7.0 Hz, H-1'b), 2.12 (s, 3H, Ac), 2.10 (s, 3H, Ac), 1.67-1.58 (m, 4H, 2×C*H*$_2$), 1.40-1.25 (m, 8H, 4×C*H*$_2$), 0.90 (t, 3H, C*H*$_3$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.79, 170.31, 128.87, 128.00, 94.40, 69.02, 66.90, 65.37, 63.07, 31.81, 29.73, 29.37, 29.24, 26.24, 22.63, 20.95, 20.77, 14.06; HRMS (ESI) $C_{18}H_{30}O_6$ (M^++Na), Calcd 365.1940, Found 365.1957.

2-Ethylbutyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2l): a colorless oil; α-anomer R_f = 0.52 (20% EtOAc/*n*-hexane); $[\alpha]_D^{26}$ +95.30 (*c* 0.50, $CHCl_3$); IR ($CHCl_3$) 2962, 2932, 2877, 1747, 1462, 1370, 1236, 1042, 742 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.89 (brd, 1H, *J* = 10.5 Hz, H-3), 5.85 (ddd, 1H, *J* = 10.0, 2.5, 2.0 Hz, H-2), 5.32 (dm, 1H, *J* = 9.5 Hz, H-4), 5.02 (brs, 1H, H-1), 4.25 (dd,

1H, *J* = 12.0, 5.5 Hz, H-6a), 4.20 (dd, 1H, *J* = 12.0, 2.5 Hz, H-6b), 4.11 (ddd, 1H, *J* = 9.5, 5.5, 2.5 Hz, H-5), 3.73 (dd, 1H, *J* = 9.5, 6.0 Hz, H-1'a), 3.40 (dd, 1H, *J* = 9.5, 5.5 Hz, H-1'b), 2.12 (s, 3H, Ac), 2.11 (s, 3H, Ac), 1.53-1.44 (m, 1H, H-2'), 1.44-1.32 (m, 4H, H-3', H-4'), 0.98 (t, 3H, *J* = 7.0 Hz, H-5'), 0.96 (t, 3H, *J* = 7.0 Hz, H- 6'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.82, 170.30, 128.83, 128.05, 94.59, 71.16, 66.97, 65.39, 63.15, 41.11, 23.36, 23.30, 20.97, 20.78, 11.05, 10.94; HRMS (ESI) $C_{16}H_{26}O_6$ (M^++Na) Calcd 337.1627, Found 337.1629.

1-Propynyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2m): a white solid; α-anomer R_f = 0.27 (20% EtOAc/*n*-hexane); mp 64-66 °C; $[\alpha]_D^{25}$ +164.07 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$) 3272, 2923, 2853, 2118, 1740, 1440, 1369, 1226, 1037, 749 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.95 (brd, 1H, *J* = 10.0 Hz, H-3), 5.86 (ddd, 1H, *J* = 10.0, 2.5, 2.0 Hz, H-2), 5.36 (dm, 1H, *J* = 9.5 Hz, H-4), 5.26 (brs, 1H, H-1), 4.33 (d, 2H, *J* = 2.5 Hz, H-1'), 4.28 (dd, 1H, *J* = 12.0, 5.0 Hz, H-6a), 4.20 (dd, 1H, *J* = 12.0, 2.5 Hz, H-6b), 4.11 (ddd, 1H, *J* = 9.5, 5.0, 2.5 Hz, H-5), 2.48 (t, 1H, *J* = 2.5 Hz, H-3'), 2.13 (s, 3H, Ac), 2.11 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.76, 170.24, 129.78, 127.24, 92.79, 79.09, 74.79, 67.22, 65.18, 62.80, 55.07, 20.93, 20.77; HRMS (ESI) $C_{13}H_{16}O_6$ (M^+ + Na) Calcd 291.0845, Found 291.0850.

2-Bromoethyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2n): a yellow oil; α-anomer R_f = 0.33 (20% EtOAc/*n*-hexane); $[\alpha]_D^{26}$ +83.93 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$) 2924, 2852, 1742, 1446, 1370, 1227, 1033, 750 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.94 (brd, 1H, *J* = 10.0 Hz, H-3), 5.87 (ddd, 1H, *J* = 10.0, 2.5, 2.0 Hz, H-2), 5.33 (dm, 1H, *J* = 9.5 Hz, H-4), 5.11 (brs, 1H, H-1), 4.26-4.16 (m, 3H, H-5, H-6), 4.07 (dt, 1H, *J* = 11.5, 6.0 Hz, H-1'a), 3.93 (dt, 1H, *J* = 11.5, 6.0 Hz, H-1'b), 3.56 (t, 2H, *J* = 6.0 Hz, H-2'), 2.13 (s, 3H, Ac), 2.11 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.76, 170.28, 129.62, 127.21, 94.78, 69.66, 67.24, 65.16, 62.95, 30.59, 20.96, 20.81; HRMS (ESI) $C_{12}H_{17}BrO_6$ (M^++Na) Calcd 359.0107, Found 359.0105.

1-Methylpropyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (2o): a mixture of isomers, colorless oil R_f = 0.42 (20% EtOAc/*n*-hexane); $[\alpha]_D^{26}$ +95.90 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$) 2963, 2930, 1745, 1457, 1371, 1230, 1036, 746 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90 (brd, 2H, *J* = 10.0 Hz, H-3 *isomer A,B*), 5.85 (ddd, 1H, *J* = 10.0, 2.5, 2.0 Hz, H-2 *isomer A*), 5.82 (ddd, 1H, *J* = 10.0, 2.5, 2.0 Hz, H-2 *isomer B*), 5.31 (dm, 2H, *J* = 9.5 Hz, H-4 *isomer A,B*), 5.15 (brs, 1H, H-1 *isomer B*), 5.14 (brs, 1H, H-1 *isomer A*), 4.29-4.14 (m, 6H, H-5, H-6 *isomer A,B*), 3.83-3.69 (m, 2H, H-1' *isomer A,B*), 2.11 (s, 6H, Ac *isomer A*), 2.10 (s, 3H, Ac *isomer B*), 2.09 (s, 3H, Ac *isomer B*), 1.65-1.43 (m, 4H, H-2' *isomer A,B*), 1.26 (d, 3H, *J* = 6.0 Hz, H-4' *isomer A*), 1.16 (d, 3H, *J* = 6.0 Hz, H-4' *isomer B*), 0.97 (t, 3H, *J* = 7.0 Hz, H-3' *isomer A*), 0.92 (t, 3H, *J* = 7.0 Hz, H-3' *isomer B*); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.81, 170.33, 128.83, 128.73, 128.44, 128.28, 94.33, 92.04, 77.15, 75.10, 66.97, 66.78, 65.45, 65.37, 63.19, 30.10,

29.51, 21.16, 20.97, 20.76, 19.24, 10.31, 9.79; HRMS (ESI) $C_{14}H_{22}O_6$ (M^++Na) Calcd 309.1314, Found 309.1300.

Cyclohexyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2p): a colorless oil; α-anomer R_f = 0.74 (30% EtOAc/*n*-hexane); $[\alpha]_D^{24}$ +111.72 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$) 2933, 2857, 1745, 1450, 1370, 1229, 1035, 744 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.89 (brd, 1H, *J* = 10.0 Hz, H-3), 5.83 (ddd, 1H, *J* = 10.0, 2.5, 2.0 Hz, H-2), 5.31 (ddd, 1H, *J* = 9.5, 2.5, 1.5 Hz, H-4), 5.19 (brs, 1H, H-1), 4.25 (dd, 1H, *J* = 12.0, 6.0 Hz, H-6a), 4.19 (dd, 1H, *J* = 12.0, 2.0 Hz, H-6b), 4.21-4.15 (m, 1H, H-5), 3.70-3.62 (m, 1H, H-1'), 2.11 (s, 3H, Ac), 2.10 (s, 3H, Ac), 2.01-1.88 (m, 2H, C*H*$_2$), 1.81-1.72 (m, 2H, C*H*$_2$), 1.60-1.16 (m, 6H, 3×C*H*$_2$); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.77, 170.32, 128.75, 128.58, 92.81, 76.73, 66.80, 65.49, 63.20, 33.78, 32.15, 25.57, 24.39, 24.17, 20.96, 20.74; HRMS (ESI) $C_{16}H_{24}O_6$ (M^++Na) Calcd 335.1471, Found 335.1460.

2-Isopropyl-5-methylcyclohexyl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2q): a colorless oil; α-anomer R_f = 0.58 (20% EtOAc/*n*-hexane); $[\alpha]_D^{26}$ +52.26 (*c* 1.00, $CHCl_3$); IR ($CHCl_3$) 2956, 2925, 2871, 1747, 1456, 1370, 1236, 1037, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.90-5.87 (m, 2H, H-2, H-3), 5.30 (dm, 1H, *J* = 9.0 Hz, H-4), 5.12 (brs, 1H, H-1), 4.25 (dd, 1H, *J* = 12.0, 6.0 Hz, H-6a), 4.22-4.19 (m, 1H, H-5), 4.20 (dd, 1H, *J* = 12.0, 2.0 Hz, H-6b), 3.44 (td, 1H, *J* = 10.0, 4.0 Hz, H-1'), 2.13 (s, 3H, Ac), 2.09 (s, 3H, Ac), 2.12-2.05 (m, 1H, H-2'), 1.70-1.60 (m, 2H, H-6'), 1.51-1.39 (m, 1H, H-7'), 1.31-1.22 (m, 1H, H-5'), 1.13-0.82 (m, 4H, H-3', H-4'), 0.93 (d, 3H, *J* = 6.5 Hz, H-8'), 0.92 (d, 3H, *J* = 7.0 Hz, H-9'), 0.79 (d, 3H, *J* = 7.0 Hz, H-10'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.85, 170.34, 128.57, 128.03, 96.15, 81.07, 66.70, 65.35, 63.35, 48.85, 43.34, 34.29, 31.73, 25.63, 23.18, 22.38, 21.15, 20.97, 20.84, 16.22; HRMS (ESI) $C_{20}H_{32}O_6$ (M^++Na) Calcd 391.2097, Found 391.2105.

1,3,3-Trimethylbicyclo[2.2.1]heptan-2-yl-4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside (2r): a white solid; α-anomer R_f = 0.61 (20% EtOAc/*n*-hexane); $[\alpha]_D^{26}$ +95.36 (*c* 0.50, $CHCl_3$); mp 64-66 °C; IR ($CHCl_3$) 2954, 2872, 1747, 1459, 1370, 1236, 1033, 745 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.89-5.86 (m, 2H, H-2, H-3), 5.31 (dm, 1H, *J* = 9.5 Hz, H-4), 5.00 (brs, 1H, H-1), 4.26 (dd, 1H, *J* = 12.5, 5.5 Hz, H-6a), 4.19-4.13 (m, 1H, H-5), 4.17 (dd, 1H, *J* = 12.5, 2.0 Hz, H-6b), 3.47 (s, 1H, H-1'), 2.11 (s, 3H, Ac), 2.10 (s, 3H, Ac), 1.79-1.63 (m, 2H, H-3'), 1.53-1.37 (m, 2H, H-4'), 1.15-0.96 (m, 3H, H-5', H-7'), 1.13 (s, 3H, H-8'), 1.06 (s, 3H, H-9'), 0.89 (s, 3H, H-10'); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.94, 170.32, 128.57, 127.99, 94.19, 90.18, 66.80, 65.29, 63.16, 48.86, 48.76, 41.37, 39.42, 31.85, 25.97 (2×C), 21.17, 21.03, 20.85, 19.75; HRMS (ESI) $C_{20}H_{30}O_6$ (M^++Na) Calcd 389.1940, Found 389.1952.

Methyl-2,3,4-tri-*O*-benzyl-6-*O*-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)-α-D-glucopyranoside (2s): a colorless oil; α-anomer R_f = 0.45 (40% EtOAc/*n*-hexane); $[\alpha]_D^{26}$ +55.36 (*c* 0.50, $CHCl_3$); IR ($CHCl_3$) 3025, 2932, 1743, 1453, 1369, 1240, 1096, 1029, 749, 712 cm^{-1}; ^1H NMR (400 MHz,

$CDCl_3$) δ 7.41-7.29 (m, 15H, Ph), 5.89-5.85 (m, 2H, H-2, H-3), 5.32 (d, 1H, *J* = 9.5 Hz, H-4), 5.13 (brs, 1H, H-1), 5.00 (d, 1H, *J* = 10.5 Hz, C*H*HPh), 4.95 (d, 1H, *J* = 11.5 Hz, C*H*HPh), 4.82 (d, 1H, *J* = 10.5 Hz, CH*H*Ph), 4.81 (d, 1H, *J* = 13.0 Hz, C*H*HPh), 4.69 (d, 1H, *J* = 13.0 Hz, CH*H*Ph), 4.66 (d, 1H, *J* = 11.5 Hz, CH*H*Ph), 4.63 (d, 1H, *J* = 3.5 Hz, H-6'), 4.18 (dd, 1H, *J* = 12.0, 5.0 Hz, H-6a), 4.07-3.99 (m, 4H, H-5, H-6b, H-1'a, H-4'), 3.79 (ddd, 1H, *J* = 10.0, 4.0, 1.5 Hz, H-2'), 3.74 (dd, 1H, *J* = 11.5, 1.5 Hz, H-1'b), 3.60 (t, 1H, *J* = 9.5 Hz, H-3'), 3.54 (dd, 1H, *J* = 9.5, 3.5 Hz, H-5'), 3.40 (s, 3H, OC*H*$_3$), 2.09 (s, 3H, Ac), 2.02 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.72, 170.23, 138.73, 138.37, 138.16, 128.99, 128.47 (2×C), 128.43 (2×C), 128.39 (2×C), 128.06 (2×C), 127.96 (2×C), 127.92, 127.74, 127.72, 127.61, 127.45 (2×C), 98.07, 94.80, 82.03, 80.02, 77.84, 75.75, 74.92, 73.34, 70.01, 67.09, 66.99, 65.20, 62.75, 55.19, 20.95, 20.69; HRMS (ESI) $C_{38}H_{44}O_{11}$ (M^+ + Na) Calcd 699.2781, Found 699.2772.

Methyl-2,3,4-tri-*O*-acetyl-6-*O*-(4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranosyl)-α-D-glucopyranoside (2t): a colorless oil; α-anomer R_f = 0.18 (40% EtOAc/*n*-hexane); $[\alpha]_D^{24}$ +163.14 (*c* 0.50, $CHCl_3$); IR ($CHCl_3$) 3031, 2924, 2854, 1745, 1454, 1228, 1029, 746, 697 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.92 (brd, 1H, *J* = 10.0 Hz, H-3), 5.85 (ddd, 1H, *J* = 10.0, 2.5, 2.0 Hz, H-2), 5.49 (t, 1H, *J* = 9.5 Hz, H-4'), 5.36 (dm, 1H, *J* = 9.5 Hz, H-4), 5.19 (t, 1H, *J* = 9.5 Hz, H-3'), 5.07 (brs, 1H, H-1), 4.96 (d, 1H, *J* = 3.5 Hz, H-6'), 4.90 (dd, 1H, *J* = 9.5, 3.5 Hz, H-5'), 4.29 (dd, 1H, *J* = 12.0, 4.5 Hz, H-6a), 4.11 (dd, 1H, *J* = 12.0, 2.5 Hz, H-6b), 4.09 (ddd, 1H, *J* = 9.5, 4.5, 2.5 Hz, H-5), 3.95 (ddd, 1H, *J* = 9.5, 4.0, 2.5 Hz, H-2'), 3.86 (dd, 1H, *J* = 11.0, 4.0 Hz, H-1'a), 3.65 (dd, 1H, *J* = 11.0, 2.5 Hz, H-1'b), 3.42 (s, 3H, OC*H*$_3$), 2.12 (s, 3H, Ac), 2.11 (s, 3H, Ac), 2.10 (s, 3H, Ac), 2.06 (s, 3H, Ac), 2.02 (s, 3H, Ac); ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.78, 170.32, 170.15 (2×C), 169.63, 129.53, 127.18, 96.73, 94.53, 70.81, 70.37, 69.02, 67.93, 66.93, 66.28, 65.05, 62.67, 55.43, 20.97, 20.79, 20.71 (2×C), 20.67; HRMS (ESI) $C_{23}H_{32}O_{14}$ (M^+ + Na), Calcd 555.1690, Found 555.1690.

ACKNOWLEDGEMENTS

This work was supported by the Thailand Research Fund (TRF) (Grant no. TRG5780298) and the Research Grant of Burapha University through National Research Council of Thailand and the Center of Excellence for Innovation in Chemistry (PERCH-CIC). Special thanks to Professor Apichart Suksamrarn (Ramkhamhaeng University) for specific rotation measurement.

REFERENCES

1. K. Polkowski, J. Popiołkiewicz, P. Krzeczyn´ski, J. Ramza, W. Pucko, S. S. Zegrocka, J. Boryskic, J. S. Skierski, P. A. Mazurek, and G. Grynkiewicz, *Cancer Lett.*, 2004, **203**, 59.
2. X. B. Meng, D. Han, S. N. Zhang, W. Guo, J. R. Cui, and Z. J. Li, *Carbohydr. Res.*, 2007, **342**, 1169.
3. R. J. Ferrier, W. G. Overend, and M. E. Ryan, *J. Chem. Soc.*, 1962, 3667; E. Wieczorek and J. Thiem,

Carbohydr. Res., 1998, **307**, 263.

4. B. S. Babu and K. K. Balasubramanian, *Tetrahedron Lett.*, 2000, **41**, 1271; S. K. Das, K. A. Reddy, and J. Roy, *Synlett*, 2003, 1607; P. Nagaraj and N. G. Ramesh, *Tetrahedron Lett.*, 2009, **50**, 3970.
5. J. S. Yadav, B. V. S. Reddy, and P. K. Chand, *Tetrahedron Lett.*, 2001, **42**, 4057.
6. B. Shanmugasundaram, A. K. Bose, and K. K. Balasubramanian, *Tetrahedron Lett.*, 2002, **43**, 6795.
7. S. Hotha and A. Tripathi, *Tetrahedron Lett.*, 2005, **46**, 4555.
8. J. L. Babu, A. Khare, and Y. D. Vankar, *Molecules*, 2005, **10**, 884.
9. A. Procopio, R. Dalpozzo, A. D. Nino, L. Maiuolo, M. Nardi, M. Oliverio, and B. Russo, *Carbohydr. Res.*, 2007, **342**, 2125.
10. P. Deelertpaiboon, V. Reutrakul, S. Jarussophon, P. Tuchinda, C. Kuhakarn, and M. Pohmakotr, *Tetrahedron Lett.*, 2009, **50**, 6233.
11. B. K. Gorityala, R. Lorpitthaya, Y. Bai, and X. W. Liu, *Tetrahedron*, 2009, **65**, 5844.
12. H. H. Kinfe, F. M. Mebrahtu, and K. Sithole, *Carbohydr. Res.*, 2011, **346**, 2528.
13. A. A.-H. Abdel-Rahman, G. A. Winterfeld, M. Takhi, and R. R. Schmidt, *Eur. J. Org. Chem.*, 2002, 713.
14. H. Kim and H. Men, C. Lee, *J. Am. Chem. Soc.*, 2004, **126**, 1336; N. de la Figuera, P. Forns, J. C. Fernndez, S. Fiol, F. D. Fernndez, and F. Albericio, *Tetrahedron Lett.*, 2005, **46**, 7271.
15. R. D. Tilve, M. V. Alexander, A. C. Khandekar, S. D. Samant, and V. R. Kanetkar, *J. Mol. Catal. A: Chem.*, 2004, **223**, 237.
16. J. S. Yadav, V. S. Reddy, K. B. Reddy, and M. Satyanarayana, *Tetrahedron Lett.*, 2002, **43**, 7009.
17. G. Zhang, Q. Liu, L. Shi, and J. Wang, *Tetrahedron*, 2008, **64**, 339.
18. P. Chen and S. Wang, *Tetrahedron*, 2012, **68**, 5356.
19. P. Chen and L. Lin, *Tetrahedron*, 2013, **69**, 4524.
20. P. Chen and S. Wang, *Tetrahedron*, 2013, **69**, 583.
21. K. Toshima, T. Ishizuka, G. Matsuo, M. Nakata, and M. Kinoshita, *J. Chem. Soc., Chem. Commun.*, 1993, 704.
22. M. Koreeda, T. D. Houston, B. K. Shull, E. Klemke, and J. Tuinman, *Synlett*, 1995, 90.
23. K. Pachamuthu and D. Vankar, *J. Org. Chem.*, 2001, **66**, 7511; J. S. Yadav, B. V. S. Reddy, and S. Pandey, *New J. Chem.*, 2001, **25**, 538; S. Paul and N. Jayaraman, *Carbohydr. Res.*, 2004, **339**, 2197.
24. J. J. W. Duan and A. B. Smith, *J. Org. Chem.*, 1993, **58**, 3703.
25. F. Yang, T. Jin, M. Bao, and Y. Yamamoto, *Tetrahedron*, 2011, **67**, 10147.
26. K. P. R. Kartha and R. A. Field, *Tetrahedron Lett.*, 1997, **38**, 8233.
27. H. Tanaka, H. Ando, H. Ishihara, and M. Koketsu, *Carbohydr. Res.*, 2008, **343**, 1585.
28. K. Mannerstedt, K. Ekelof, and S. Oscarson, *Carbohydr. Res.*, 2007, **342**, 631.

29. R. Saeeng, U. Sirion, Y. Sirichan, T. Trakulsujaritchok, and P. Sahakitpichan, *Heterocycles*, 2010, **81**, 2569; U. Sirion, S. Purintawarrakun, P. Sahakitpichan, and R. Saeeng, *Carbohydr. Res.*, 2010, **345**, 2401; W. Mangsang, U. Sirion, and R. Saeeng, *Carbohydr. Res.*, 2013, **375**, 79.
30. S. B. Boga and K. K. Balasubramanian, *ARKIVOC*, 2004, **viii**, 87.