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$Gd(OTf)_3$ catalyzed preparation of 2,3-unsaturated *O*-, *S*-, *N*-, and *C*-pyranosides from glycals by Ferrier Rearrangement

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2,3-Unsaturated glycosides

ABSTRACT

By using $Gd(OTf)_3$ as the catalyst, synthesis of 2,3-unsaturated-glycosides has been performed by Ferrier Rearrangement. A series of 2,3-unsaturated *O*-, *S*-, *N*-, and *C*-glycosides were obtained from 3,4,6-tri-*O*-acetyl-D-glucal, 3,4,6-tri-*O*-benzyl-D-glucal, and 3,4-di-*O*-acetyl-L-rhamnal under mild reaction conditions in good yields and high anomeric selectivities.

1. Introduction

2,3-Unsaturated glycosides are of great importance in the synthesis of biologically active molecules[1] and new functional materials[2] as chiral intermediates owing to their regio- and stereo-varieties that they provide for the subsequent transformations. As one of the most useful procedures to achieve 2,3-unsaturated glycosides directly and efficiently, Ferrier Rearrangement has been widely investigated[3] and a variety of reagents have been used to promote this reaction, including Bronsted acids,[4] Lewis acids,[5] as well as other reagents such as oxidants, etc.[6] Due to their unique properties and high catalytic activities, lanthanide salts as catalyst in Ferrier Rearrangement have recently gained more and more applications, among which there could be mentioned $Dy(OTf)_3$, $Er(OTf)_3$, $Yb(OTf)_3$, $Y(OTf)_3$, $Sm(OTf)_3$, and $Tm(OTf)_3$.[7] In our continuing efforts to search for more efficient catalysts for Ferrier Rearrangement, we found gadolinium triflate is a highly efficient catalyst for our purposes. Here we wish to report our results.

2. Results and discussion

2.1. Optimization of reaction conditions

Considering the effect of the counter anions of the salts on catalytic capacity,[5u,v] different gadolinium salts have been screened, including $Gd(OAc)_3 \cdot 6H_2O$, $GdBr_3 \cdot xH_2O$, GdB_6, $Gd(NO_3)_3$, and $Gd(OTf)_3$, among which $Gd(OTf)_3$ was found to be the best one. For the reaction solvent, we found acetonitrile gave the best result among acetone, acetonitrile, THF, dichloromethane, and toluene. Results are shown in Table 1 and Table 2.

2.2. Synthesis of 2,3-unsaturated glucosides with 3,4,6-tri-*O*-acetyl-D-glucal

Synthesis of 2,3-unsaturated glucosides with 3,4,6-tri-*O*-acetyl-D-glucal (**1**) was discussed in this section. Results are summarized in Table 3.

It could be seen that with tri-*O*-acetyl-D-glucal (**1**) as starting material, alcohols (including simple alcohols, chiral alcohols, and phenols) gave the corresponding 2,3-unsaturated glucosides in high yields with good anomeric selectivity. It was reported that when tri-*O*-acetyl-D-glucal was treated with *p*-methoxyphenol in

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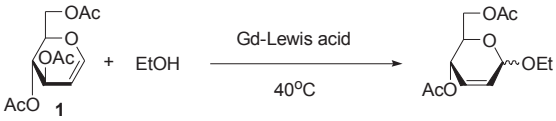
0040-4020/

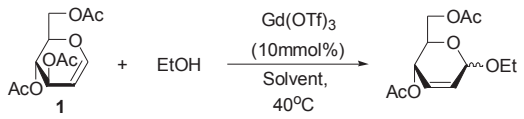
Table 1
A comparative study of the catalytic effect of different metal chloride Lewis acid catalysts in the Ferrier Rearrangement of glucal **1**[a]



Entry	Lewis acid catalyst	Reaction time	Conversion (%)[b]	α:β[c]
1	$Gd(OAc)_3 \cdot 6H_2O$	24 h	NR	/
2	$GdBr_3 \cdot xH_2O$	24 h	NR	/
3	GdB_6	24 h	NR	/
4	**$Gd(OTf)_3$**	**18 h**	**83**	**90:10**
5	$Gd(NO_3)_3$	24 h	NR	/

The bold represents the best reaction condition in the table.
[a] Reaction conditions: tri-*O*-acetyl-D-glucal (**1**) (190 mg, 0.7 mmol), EtOH(5 mL), catalyst (10 mol %), 40 °C.
[b] Determined by analysis of the ^{1}H NMR spectra of the reaction mixture.
[c] The anomeric ratio was determined by integration of the anomeric hydrogen in the ^{1}H NMR spectra.

Table 2
Optimization of solvent[a] for the $Gd(OTf)_3$ catalyzed Ferrier Rearrangement reaction system



Entry	Solvent	Reaction time	Conversion (%)[b]	α:β[c]
1	**Acetonitrile**	**30 min**	**91**	**89:11**
2	DCM	24 h	Trace	/
3	THF	24 h	NR	/
4	Acetone	24 h	NR	/
5	Toluene	24 h	NR	/

The bold represents the best reaction condition in the table.
[a] Reaction conditions: tri-*O*-acetyl-D-glucal (**1**) (190 mg, 0.7 mmol), EtOH(1.0 equiv), $Gd(OTf)_3$ (10 mol %), solvent (5 mL), 40 °C.
[b] Determined by analysis of the ^{1}H NMR spectra of the reaction mixture.
[c] The anomeric ratio was determined by integration of the anomeric hydrogen in the ^{1}H NMR spectra.

CH_2Cl_2 using $BF_3 \cdot OEt_2$ as the catalyst, *C*-glycoside was obtained exclusively.[8] However, in our case, no such phenomenon occurred. *p*-Methoxyphenol, 3-hydroxyl-benzaldehyde, and 2-naphthol gave the corresponding normal *O*-glycosides as sole products in good yield (entries 5, 6, and 7, Table 1), which could be confirmed by the two *ortho* aromatic signals in the ^{1}H NMR spectra of the products. When thiols were used as nucleophiles, the corresponding 2,3-unsaturaterd *S*-glycosides could also be obtained in high yields with good anomeric selectivities (entries 8–10, Table 3). Similarly, with TMS-activated *C*-donors, *C*-glucosides formed in high yields and good selectivity (entry 18–20, Table 1).

2.3. Synthesis of 2,3-unsaturated glycosides with 3,4-di-*O*-acetyl-L-rhamnal

Synthesis of 2,3-unsaturated glycosides with 3,4-di-*O*-acetyl-L-rhamnal (**4**) was summarized in Table 4. It could be seen that all of *O*-, *S*-, *N*-, *C*-donors gave good outcomes in terms of yields and selectivities.

2.4. Synthesis of 2,3-unsaturated glucosides with 3,4,6-tri-*O*-benzyl-D-glucal

Synthesis of 2,3-unsaturated glucosides with 3,4,6-tri-*O*-benzyl-D-glucal (**6**) was discussed in this section. Results are summarized in Table 5. By comparison of Table 3 with Table 5, it could be seen that relatively higher reactive temperature (60 °C) was necessary in Table 5, which meant that *O*-benzyl sugar was less reactive than *O*-acetyl sugar in the reactions. 3,4,6-Tri-*O*-benzyl-D-glucal (**6**) took longer time and gave lower yield in the reaction with the same nucleophiles (**2**) than 3,4,6-tri-*O*-acetyl-D-glucal (**1**) However, in our observation, even in the case of 3,4,6-tri-*O*-benzyl-D-glucal, $Gd(OTf)_3$ is a catalyst which appears to be efficient enough to afford satisfactory outcome in both yield and selectivity.

3. Conclusions

In summary, $Gd(OTf)_3$ has been demonstrated to be a highly efficient catalyst for the preparation of various 2,3-unsaturated glycosides in the Ferrier Rearrangement. Under our reaction conditions, 3,4,6-tri-*O*-acetyl-D-glucal, 3,4-di-*O*-acetyl-L-rhamnal, and 2,4,6-tri-*O*-benzyl-D-glucal afforded corresponding *O*-, *S*-, *N*-, and *C*-products in high to good yields with high anomeric selectivities.

4. Experimentals

4.1. Method and materials

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV-400 (400 MHz) spectrometer with Me_4Si as internal standard. ^{19}F NMR spectra were obtained on a Bruker AM-300 (282 MHz) spectrometer using $CFCl_3$ as an external standard; downfield shifts being designated as positive, all chemical shifts (δ) were expressed in ppm and coupling constants (J) are in Hz. Mass spectra were recorded on a Finnigan-MAT-8430 instrument using EI ionization at 70 eV. High-Resolution mass spectral (ESI) analyses were performed on a Finnigan MAT 8430 spectrometer. IR spectra were recorded on a Nicolet 380 spectrometer. Optical rotations were measured by WZZ-2 polarimeter. Melting points were measured on a WRS-2A melting point apparatus. The glycals, L-menthol, (1*R*)-*endo*-(+)-fenchol and the protected glucose were purchased from Energy-Chemical Company. All the solvents used in the reaction were purified by re-distillation.

4.2. General experimental procedure of Ferrier rearrangement of 3,4,6-tri-*O*-acetyl-D-glucal, 3,4-di-*O*-acetyl-L-rhamnal or 3,4,6-tri-*O*-benzyl-D-glucal catalyzed with $Gd(OTf)_3$

To a stirred solution of 3,4,6-tri-*O*-acetyl-D-glucal (190 mg, 0.7 mmol), 3,4-di-*O*-acetyl-L-rhamnal (150 mg, 0.7 mmol) or 3,4,6-tri-*O*-benzyl-D-glucal (292 mg, 0.7 mmol) and the corresponding nucleophile (1.0 equiv) in CH_3CN (5 mL) were added $Gd(OTf)_3$ (10 mol %) at ambient temperature. The mixture was stirred under 40 °C for the appropriate amount of time (Tables 3–5), and the extent of the reaction was monitored by TLC analysis. The reaction mixture was diluted with cooled sodium bicarbonate (satd, 20 mL) and extracted with DCM (3×10 mL). The combined organics were dried over anhydrous Na_2SO_4. The solvent was removed under vacuum. All the products were purified by silica gel column chromatography (hexane/EtOAc=6/1).

*4.2.1. Ethyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3a**).* White solid; mp=70–72 °C; $[\alpha]_D^{10}$=+87.2 (c 1.06, $CHCl_3$, α:β=89:11) {lit.:[5u] $[\alpha]_D^{25}$=+122.7 (c 0.88, $CHCl_3$, α:β=17:1)}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.90–5.80 (m, 2H), 5.31 (d, J=9.6 Hz, 1H), 5.04 (s, 1H), 4.28–4.08 (m, 3H), 3.83 (dq, J=9.6, 7.1 Hz, 1H), 3.57 (dq, J=9.5, 7.1 Hz, 1H), 2.09 (s, 3H), 2.07 (s, 3H), 1.24 (t,

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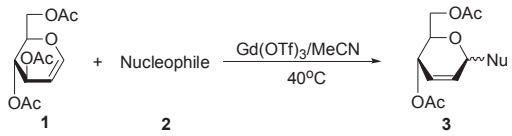
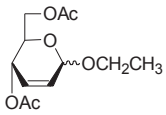
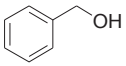
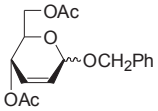
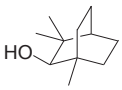
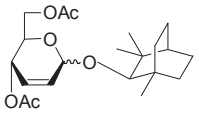
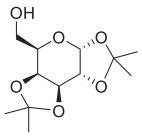
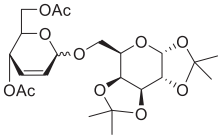
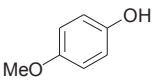
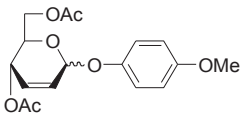
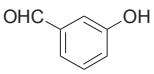
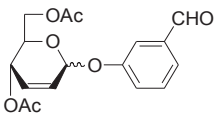
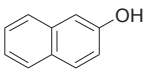
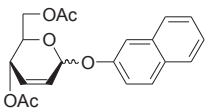
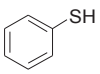
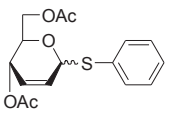
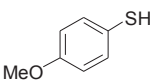
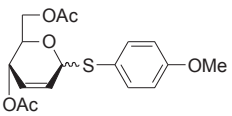
Table 3
$Gd(OTf)_3$ catalyzed synthesis of 2,3-unsaturated glucosides by Ferrier Rearrangement of 3,4,6-tri-*O*-acetyl-D-glucal (**1**) with nucleophiles (**2**)[a]



Entry	Nucleophile (**2**)	Reaction time	Product (**3**)	Yield[b]/(α:β)[c]
1		30 min	 **3a**	91% (89:11)
2		25 min	 **3b**	92% (α only)
3		15 min	 **3c**	92% (α only)
4		30 min	 **3d**	87% (88:12)
5		45 min	 **3e**	79% (α only)
6		30 min	 **3f**	70% (α only)
7		25 min	 **3g**	48% (89:11)
8		30 min	 **3h**	82% (α only)
9		20 min	 **3i**	74% (α only)

(*continued on next page*)

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Table 3 (*continued*)

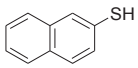
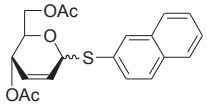
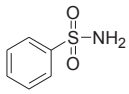
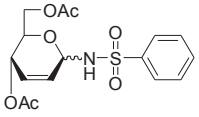
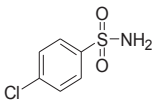
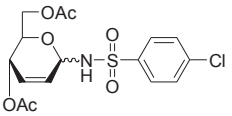
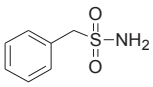
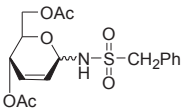
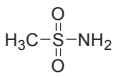
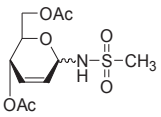
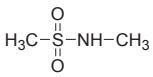
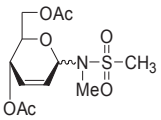
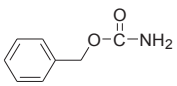
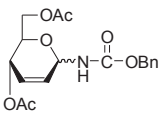
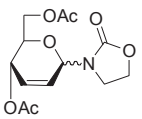
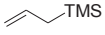
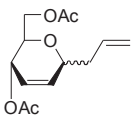
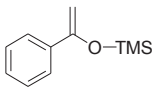
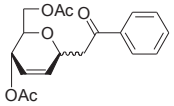
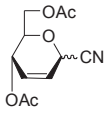
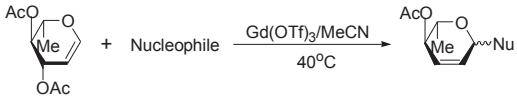
Entry	Nucleophile (**2**)	Reaction time	Product (**3**)	Yield[b]/(α:β)[c]
10		25 min	 **3j**	86% (α only)
11		30 min	 **3k**	74% (93:7)
12		20 min	 **3l**	72% (93:7)
13		50 min	 **3m**	71% (90:10)
14		20 min	 **3n**	84% (95:5)
15		20 min	 **3o**	76% (α only)
16		90 min	 **3p**	72% (α only)
17		5 h	 **3q**	71% (α only)
18		40 min	 **3r**	88% (α only)

Table 3 (*continued*)

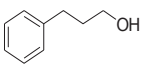
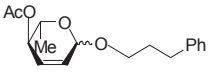
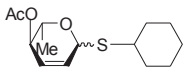
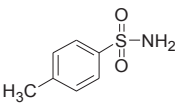
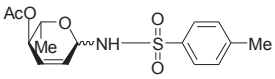
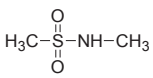
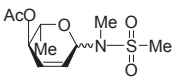
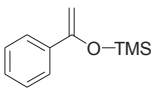
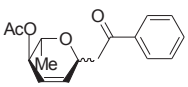
Entry	Nucleophile (**2**)	Reaction time	Product (**3**)	Yield[b]/(α:β)[c]
19		20 min	 **3s**	81% (α only)
20	TMSCN	90 min	 **3t**	85% (α only)

[a] General reaction conditions: tri-*O*-acetyl-D-glucal (**1**) (190 mg, 0.7 mmol), nucleophile (**2**) (1.0 equiv), $Gd(OTf)_3$ (10 mol %), MeCN (5 mL), 40 °C.
[b] Isolated yield.
[c] The anomeric ratio was determined by integration of the anomeric hydrogen in the ^1H NMR spectra.

Table 4
$Gd(OTf)_3$ catalyzed synthesis of 2,3-unsaturated glycosides by Ferrier Rearrangement of 3,4-di-*O*-acetyl-L-rhamnal (**4**) with nucleophiles (**2**)[a]



4 **2** **5**

Entry	Nucleophile (**2**)	Reaction time	Product (**5**)	Yield[b]/(α:β)[c]
1		30 min	 **5a**	85% (α only)
2		20 min	 **5b**	71% (α only)
3		30 min	 **5c**	87% (α only)
4		20 min	 **5d**	77% (α only)
5		20 min	 **5e**	65% (97:3)

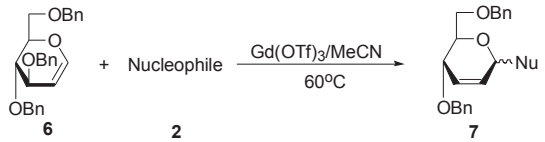
[a] General reaction conditions: 3,4-di-*O*-acetyl-L-rhamnal (**4**) (150 mg, 0.7 mmol), nucleophile (**2**) (1.0 equiv), $Gd(OTf)_3$ (10 mol %), MeCN (5 mL), 40 °C.
[b] Isolated yield.
[c] The anomeric ratio was determined by integration of the anomeric hydrogen in the ^1H NMR spectra.

J=7.1 Hz, 3H) ppm; IR (film, cm^{-1}): 2923, 2843, 1740, 1623, 1458, 1371, 1335, 1039, 979, 902; MS(ESI) *m*/*z*: 276.1 ($[M+NH_4]^+$,100).

*4.2.2. Benzyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3b**).* Colorless oil; $[\alpha]_D^{10}$=+58.5 (c 1.26, $CHCl_3$, α only) {lit.:[5x] $[\alpha]_D^{25}$=+68.3 (c 1.02, $CHCl_3$, α:β=9:1)}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.42–7.30 (m, 5H), 5.95–5.85 (m, 2H), 5.36 (d, *J*=9.4 Hz, 1H), 5.16 (s, 1H), 4.83 (d, *J*=11.7 Hz, 1H), 4.63 (d, *J*=11.7 Hz, 1H), 4.31–4.24 (m, 1H), 4.21–4.12 (m, 2H), 2.13 (s, 3H), 2.11 (s, 3H) ppm; IR (film, cm^{-1}): 3030, 2931, 1738, 1605, 1488, 1355, 1232, 1040, 907; MS(ESI) *m*/*z*: 338.2 ($[M+NH_4]^+$, 100).

*4.2.3. (+)-endo-Fenacholyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythrohex-2-enopyranoside (**3c**).* White solid; mp=75–76 °C; $[\alpha]_D^{10}$=+64.6 (c 1.12 $CHCl_3$, α only) {lit.:[5t] $[\alpha]_D^{24}$=+48.7 (c 0.5 $CHCl_3$, α only)}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.87 (s, 2H), 5.30 (d, *J*=9.5 Hz,

Table 5
$Gd(OTf)_3$ catalyzed synthesis of 2,3-unsaturated glucosides by Ferrier Rearrangement of 3,4,6-tri-*O*-benzyl-D-glucal (**6**) with nucleophiles (**2**)[a]



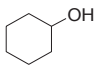
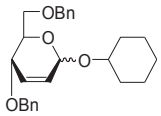
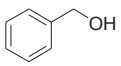
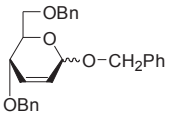
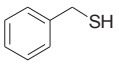
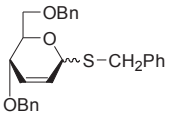
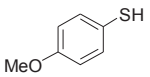
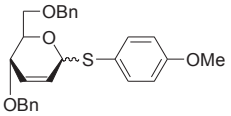
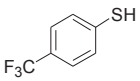
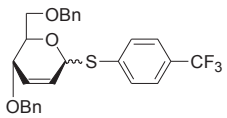
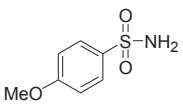
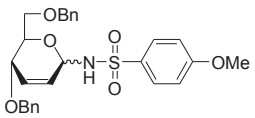
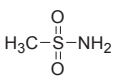
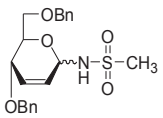
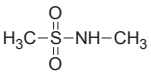
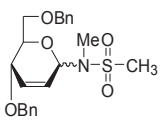
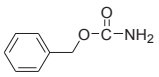
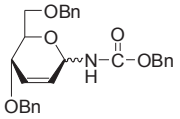
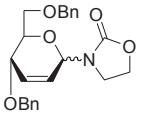
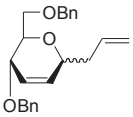
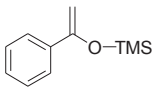
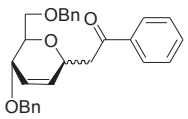
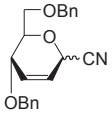
Entry	Nucleophile (**2**)	Reaction time	Product (**7**)	Yield[b]/(α:β)[c]
1		70 min	 **7a**	70% (α only)
2		60 min	 **7b**	91% (88:12)
3		60 min	 **7c**	69% (93:7)
4		30 min	 **7d**	46% (92:8)
5		40 min	 **7e**	57% (96:4)
6		90 min	 **7f**	73% (80:20)
7		90 min	 **7g**	70% (85:15)
8		60 min	 **7h**	68% (α only)

Table 5 (*continued*)

Entry	Nucleophile (**2**)	Reaction time	Product (**7**)	Yield[b]/(α:β)[c]
9		5 h	 **7i**	66% (89:11)
10		36 h	 **7j**	48% (α only)
11		25 min	 **7k**	68% (α only)
12		30 min	 **7l**	71% (α only)
13	TMSCN	130 min	 **7m**	67% (80:20)

[a] General reaction conditions: 2,4,6-tri-*O*-benzyl-D-glucal (**6**) (292 mg, 0.7 mmol), nucleophile (**2**) (1.0 equiv), $Gd(OTf)_3$ (10 mol %), MeCN (5 mL), 60 °C.
[b] Isolated yield.
[c] The anomeric ratio was determined by integration of the anomeric hydrogen in the ^1H NMR spectra.

1H), 5.00 (s, 1H), 4.29–4.22 (m, 1H), 4.19–4.12 (m, 2H), 3.47 (s, 1H), 2.10 (s, 6H), 1.79–1.63 (m, 3H), 1.53–1.36 (m, 2H), 1.13 (s, 3H), 1.12–1.07 (m, 1H), 1.06 (s, 3H), 1.04–0.95 (m, 1H), 0.89 (s, 3H) ppm; IR (film, cm^{-1}): 3036, 2927, 2853, 1737, 1443, 1377, 1045, 970, 908; MS(ESI) *m/z*: 389.0 ($[M+Na]^+$, 100).

*4.2.4. 6-O-(4,6-Di-O-acetyl-2,3-dideoxy-α-D-erythreo-hex-2-enopyranosyl)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (**3d**).* White solid; mp=131–132 °C; $[\alpha]_D^{10}$=+29.7 (c 1.12 $CHCl_3$, α:β=88:12) {lit.:[4b] $[\alpha]_D^{25}$=+16.8 (c 1.0, $CHCl_3$, α only)}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.88–5.79 (m, 2H), 5.50 (d, *J*=5.0 Hz, 1H), 5.30 (d, *J*=9.7 Hz, 1H), 5.07 (s, 1H), 4.61–4.57 (m, 1H), 4.32–4.29 (m, 1H), 4.27–4.21 (m, 2H), 4.16–4.07 (m, 2H), 3.97 (d, *J*=7.7 Hz, 1H), 3.85 (dd, *J*=10.2, 6.3 Hz, 1H), 3.73 (dd, *J*=10.2, 7.0 Hz, 1H), 2.08 (s, 3H), 2.06 (s, 3H), 1.51 (s, 3H), 1.42 (s, 3H), 1.32 (s, 3H), 1.31 (s, 3H) ppm; IR (film, cm^{-1}):2920, 2850, 1744, 1637, 1430, 1374, 1237, 1161, 783, 729, 671; MS(ESI) *m/z*: 495.1 ($[M+Na]^+$, 100).

*4.2.5. 4-Methoxyphenyl 4,6-di-O-acetyl-2,3-dideoxy-1-O-α-D-erythro-hex-2-enopyrano side (**3e**).* White solid; mp=77–78 °C, $[\alpha]_D^{10}$=+115.7 (c 1.08, $CHCl_3$, α only) {lit.: = +139.1 (c 0.66, $CHCl_3$, α only)}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.07 (d, *J*=8.9 Hz, 2H), 6.86 (d, *J*=8.9 Hz, 2H), 6.03 (s, 2H), 5.59 (s, 1H), 5.40 (d, *J*=9.2 Hz, 1H), 4.34–4.26 (m, 2H), 4.23–4.15 (m, 1H), 3.80 (s, 3H), 2.14 (s, 3H), 2.05 (s, 3H) ppm; IR (film, cm^{-1}): 2930, 1739, 1615, 1495, 1387, 1220, 1035, 970; MS (ESI) *m/z*: 359.0 ($[M+Na]^+$, 56).

*4.2.6. 3-Formylphenyl 4,6-di-O-acetyl-2,3-dideoxy-1-O-α-D-erythro-hex-2-enopyranoside (**3f**).* White solid; mp=72–74 °C, $[\alpha]_D^{10}$=+121.4 (c 0.93, $CHCl_3$, α only), {lit.:[7i] $[\alpha]_D^{10}$=+139.7 (c 0.85 $CHCl_3$, α:β=40:1)}; ^1H NMR (400 MHz, $CDCl_3$) δ 10.01 (s, 1H), 7.64 (s, 1H), 7.59 (d, *J*=7.5 Hz, 1H), 7.50 (t, *J*=7.8 Hz, 1H), 7.39 (d, *J*=8.0 Hz, 1H), 6.06 (dd, *J*=23.0, 10.3 Hz, 2H), 5.78 (s, 1H), 5.42 (d, *J*=9.3 Hz, 1H), 4.33–4.21 (m, 2H), 4.15 (d, *J*=11.1 Hz, 1H), 2.14 (s, 3H), 1.98 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.81, 170.69, 170.23, 157.61, 137.88, 130.58, 130.17, 126.55, 124.31, 123.40, 117.08, 92.98, 68.00, 64.94, 62.60, 20.97, 20.66; IR (film, cm^{-1}): 2927, 2838, 1737, 1624, 1477, 1365, 1230, 1035, 780, 739; MS(ESI) *m/z*: 357.1 ($[M+Na]^+$, 25). HR-ESI: $C_{17}H_{18}NaO_7$ $[M+Na]^+$ calcd 357.0945, found. 357.0942.

*4.2.7. 2-Naphenyl 4,6-di-O-acetyl-2,3-dideoxy-1-O-α-D-erythro-hex-2-enopyranoside (**3g**).* White solid; mp=72–74 °C; $[\alpha]_D^{10}$=+136.4 (c 1.13, $CHCl_3$, α:β=89:11) {lit.:[5o] $[\alpha]_D^{25}$=+153.9 (c 1.01, $CHCl_3$, α only)}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.81 (d, *J*=8.1 Hz, 1H), 7.76–7.68 (m, 2H), 7.51 (t, *J*=7.7 Hz, 1H), 7.37 (t, *J*=7.4 Hz, 1H), 7.13 (d, *J*=8.9 Hz, 1H), 6.34 (s, 1H), 6.02 (d, *J*=10.3 Hz, 1H), 5.92 (d, *J*=10.3 Hz, 1H), 5.69 (d, *J*=8.9 Hz, 1H), 4.43–4.35 (m, 2H), 4.17–4.09 (m, 1H), 2.19 (s, 3H), 2.17 (s, 3H) ppm; IR (film, cm^{-1}): 3095,1740,

1617, 1388, 1220, 1036, 820, 795; MS (ESI) *m/z*: 357.0 ([M+H]$^+$, 100).

*4.2.8. Phenyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-1-thio-hex-2-enopyranoside (**3h**).* White solid; mp=56–57 °C; $[\alpha]_D^{10}$=+144.2 (c 1.17, $CHCl_3$, α only) {lit.:[4b] $[\alpha]_D^{25}$=+28.2 (c 1.0, $CHCl_3$, *α:β*=12:1)}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.57 (d, *J*=6.2 Hz, 2H), 7.39–7.25 (m, 3H), 6.09 (d, *J*=9.2 Hz, 1H), 5.89 (d, *J*=9.9 Hz, 1H), 5.78 (s, 1H), 5.41 (d, *J*=7.8 Hz, 1H), 4.55–4.43 (m, 1H), 4.38–4.16 (m, 2H), 2.13 (s, 3H), 2.10 (s, 3H) ppm; IR (film, cm^{-1}): 2945, 2880, 1738, 1640, 1520, 1433, 1232, 1076, 904, 746, 712; MS(ESI) *m/z*: 345.0 ([M+Na]$^+$, 100).

*4.2.9. 4-Methoxylphenyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-1-thio-hex-2-enopyranoside (**3i**).* White solid; mp=75–76 °C; $[\alpha]_D^{10}$=+183.4 (c 1.09, $CHCl_3$, α only) {lit.:[4i], no rotation value reported, α only}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.52 (d, *J*=8.6 Hz, 2H), 6.88 (d, *J*=8.6 Hz, 2H), 6.08 (d, *J*=10.1 Hz, 1H), 5.87 (d, *J*=10.2 Hz, 1H), 5.62 (s, 1H), 5.39 (d, *J*=9.5 Hz, 1H), 4.57–4.47 (m, 1H), 4.33–4.23 (m, 2H), 3.83 (s, 3H), 2.14 (s, 6H) ppm; IR (film, cm^{-1}): 2932, 2844, 1740, 1628, 1520, 1452, 1233, 1064, 965, 812; MS(ESI) *m/z*: 375.1 ([M+Na]$^+$, 100).

*4.2.10. 2-Naphenyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-eno-1-thio-α-D-pyranoside (**3j**).* White solid; mp=97–98 °C; $[\alpha]_D^{10}$=133.8 (c 1.14,$CHCl_3$, α only) {lit.:[4i] no rotation value reported, *α:β*=9:1}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.07 (s, 1H), 7.87–7.77 (m, 3H), 7.64 (d, *J*=8.6 Hz, 1H), 7.56–7.45 (m, 2H), 6.17–6.10 (m, 1H), 5.92 (d, *J*=10.0 Hz, 2H), 5.43 (dd, *J*=9.5, 1.6 Hz, 1H), 4.60–4.50 (m, 1H), 4.39–4.24 (m, 2H), 2.15 (s, 3H), 2.06 (s, 3H) ppm; IR (film, cm^{-1}): 2925, 1740, 1624, 1520, 1428, 1231, 1036, 823; MS(ESI) *m/z*: 395.0 ([M+Na]$^+$, 100).

*4.2.11. 4,6-Di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl-phenylsulfonamide (**3k**).* Colorless oil; $[\alpha]_D^{10}$=+43.5 (c 0.96, $CHCl_3$, *α:β*=93:7) {lit.:[9b] *α:β*=5:1}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.97 (d, *J*=7.4 Hz, 2H), 7.63 (t, *J*=7.4 Hz, 1H), 7.55 (t, *J*=7.5 Hz, 2H), 5.96 (d, *J*=10.2 Hz, 1H), 5.85 (d, *J*=10.1 Hz, 1H), 5.74–5.63 (m, 2H), 5.29 (d, *J*=8.1 Hz, 1H), 3.93 (dd, *J*=12.2, 3.4 Hz, 1H), 3.55 (dt, *J*=9.2, 3.2 Hz, 1H), 3.36 (dd, *J*=12.2, 2.3 Hz, 1H), 2.06 (s, 3H), 2.04 (s, 3H) ppm; IR (film, cm^{-1}): 3267, 2940, 1741, 1638, 1580,1450, 1371, 1161, 1030, 746, 710; MS(ESI) *m/z*:391.9 ([M+Na]$^+$, 100).

*4.2.12. 4,6-Di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl-4′-chloro-phenylsulfonamide (**3l**).* Colorless oil; $[\alpha]_D^{10}$=+47.8 (c 0.89, $CHCl_3$,*α:β*=93:7) {lit.:[5r] no rotation value reported, *α:β*=85:15}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.90 (d, *J*=8.5 Hz, 2H), 7.52 (d, *J*=8.5 Hz, 2H), 5.95 (t, *J*=10.2 Hz, 2H), 5.84 (d, *J*=10.2 Hz, 1H), 5.64 (d, *J*=8.4 Hz, 1H), 5.27 (d, *J*=8.8 Hz, 1H), 3.96 (dd, *J*=12.8, 4.3 Hz, 1H), 3.64–3.55 (m, 2H), 2.06 (s, 3H), 2.04 (s, 3H) ppm; IR (film, cm^{-1}): 3325, 2938, 1739, 1590, 1427, 1340, 1208, 1124, 1034, 902, 789; MS(ESI) *m/z*: 426.0 ([M+Na]$^+$, 100).

*4.2.13. 4,6-Di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl-benzylsulfonamide (**3m**).* White solid; mp=137–138 °C; $[\alpha]_D^{10}$=+40.5 (c 1.04,$CHCl_3$, *α:β*=90:10) {lit.:[7i] $[\alpha]_D^{10}$=+44.9 (c 0.96, $CHCl_3$, *α:β*=10:1)}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.51–7.45 (m, 2H), 7.44–7.39 (m, 3H), 6.00 (dt, *J*=10.2, 1.9 Hz, 1H), 5.87–5.82 (m, 1H), 5.60 (d, *J*=7.7 Hz, 1H), 5.35 (d, *J*=8.8 Hz, 1H), 5.26 (dd, *J*=8.9, 1.8 Hz, 1H), 4.56 (d, *J*=13.7 Hz, 1H), 4.36–4.28 (m, 2H), 4.23 (dd, *J*=12.1, 6.4 Hz,1H), 4.05–3.99 (m, 1H), 2.13 (s, 3H), 2.04 (s, 3H) ppm; IR (film, cm^{-1}): 3310, 2938, 1739, 1590,1427, 1340, 1208, 1124, 1034, 902, 789; MS(ESI) *m/z*: 406.0 ([M+Na]$^+$, 100).

*4.2.14. 4,6-Di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl-methanesulfonamide (**3n**).* Colorless oil; $[\alpha]_D^{10}$=+98.7 (c 0.95, $CHCl_3$, *α:β*=95:5) {lit.:[9e] $[\alpha]_D^{25}$=+52 (c 0.5, $CHCl_3$), *α:β*=85:15, no rotation value reported}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 6.02 (d, *J*=10.1 Hz, 1H), 5.92–5.86 (m, 1H), 5.64–5.50 (m 2H), 5.26 (dd, *J*=9.1, 1.7 Hz, 1H), 4.29 (dd, *J*=12.1, 2.4 Hz, 1H), 4.16 (dd, *J*=12.0, 6.6 Hz, 1H), 4.02–3.95 (m, 1H), 3.16 (s, 3H), 2.13 (s, 3H), 2.09 (s, 3H) ppm; IR (film, cm^{-1}): 3284, 2919, 2833, 1740, 1445, 1132, 1040, 946; MS(ESI) *m/z*: 329.9 ([M+Na]$^+$, 100).

*4.2.15. 4,6-Di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl-N-methyl-methanesulfonamide (**3o**).* Colorless oil; $[\alpha]_D^{10}$=+73.4 (c 1.03, $CHCl_3$, α only) {lit.:[7i] $[\alpha]_D^{10}$=+66.9 (c 1.10, $CHCl_3$, α only)}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 5.97 (dt, *J*=10.3, 2.0 Hz, 1H), 5.81–5.78 (m, 1H), 5.72 (dt, *J*=10.4, 1.9 Hz, 1H), 5.26–5.20 (m, 1H), 4.23 (dd, *J*=12.1, 2.4 Hz, 1H), 4.10 (dd, *J*=12.1, 6.2 Hz, 1H), 3.87–3.80 (m, 1H), 2.91 (s, 3H), 2.74 (s, 3H), 2.06 (s, 3H), 2.03 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 170.53, 170.18, 131.22, 128.44, 82.76, 73.88, 64.38, 62.75, 38.29, 29.14, 20.90, 20.71; IR (film, cm^{-1}): 2979, 2865,1743, 1626, 1316, 1123, 904; MS(ESI) *m/z*: 344.1 ([M+Na]$^+$, 100); HR-ESI: $C_{12}H_{19}NNaO_7S$ [M+Na]$^+$, calcd 344.0774, found. 344.0762.

*4.2.16. 4,6-Di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl-benzylcarbamate (**3p**).* Colorless oil; $[\alpha]_D^{10}$=+45.6 (c 0.94, $CHCl_3$, α only) {lit.:[9d] $[\alpha]_D^{25}$=+52 (c 0.5, $CHCl_3$), *α:β*=3:1}; ^{1}H NMR (400 MHz, $CHCl_3$) *δ* 7.44–7.32 (m, 5H), 5.98 (d, *J*=10.2 Hz, 1H), 5.87–5.82 (m, 1H), 5.81–5.71 (m, 1H), 5.63 (s, 1H), 5.31 (dd, *J*=9.0, 1.8 Hz, 1H), 5.17 (s, 2H), 4.27 (dd, *J*=12.1, 5.0 Hz, 1H), 4.17 (dd, *J*=12.1, 2.4 Hz, 1H), 3.94–3.87 (m, 1H), 2.10 (s, 3H), 2.08 (s, 3H) ppm; IR (film, cm^{-1}): 3328, 2934, 2865, 1740, 1638, 1520, 1431, 1209, 890, 765, 712; MS(ESI) *m/z*: 386.0 ([M+Na]$^+$, 100).

*4.2.17. 2-(4,6-Di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl) oxazolidinone (**3q**).* White solid; mp=80–82 °C; $[\alpha]_D^{10}$=+96.4 (c 1.03, $CHCl_3$, α only) {lit.:[7i] $[\alpha]_D^{10}$=+111.6 (c 1.17, $CHCl_3$, *α:β*=10:1)}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 6.01 (d, *J*=10.2 Hz, 1H), 5.86 (s, 1H), 5.75 (d, *J*=10.3 Hz, 1H), 5.28 (d, *J*=9.1 Hz, 1H), 4.43–4.30 (m, 2H), 4.19 (d, *J*=4.1 Hz, 2H), 3.95–3.88 (m, 1H), 3.65 (q, *J*=8.6 Hz, 1H), 3.50–3.42 (m, 1H), 2.09 (s, 3H), 2.08 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 170.80, 170.28, 157.59, 131.26, 128.01, 78.53, 74.04, 64.46, 62.97, 62.42, 39.63, 20.93, 20.81. IR (film, cm^{-1}): 2930, 2842, 1740, 1623, 1425,1324, 1231, 1040, 966, 825; MS(ESI) *m/z*: 322.1 ([M+Na]$^+$,100). HR-ESI: $C_{13}H_{17}NNaO_7$ [M+Na]$^+$, calcd 322.0897, found. 322.0890.

*4.2.18. 3-(4′,6′-Di-O-acetyl-2′,3′-dideoxy-α-D-erythro-hex-2′-enopyranosyl)-1-propene (**3r**).* Colorless oil; $[\alpha]_D^{10}$=+97.5 (c 1.05, $CHCl_3$, α only) lit.:[7g] $[\alpha]_D^{26}$=+66.2 (c 1.0, $CHCl_3$, α only)}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 5.98–5.92 (m, 1H), 5.92–5.78 (m, 2H), 5.19–5.10 (m, 3H), 4.33–4.28 (m, 1H), 4.25 (dd, *J*=11.9, 6.6 Hz, 1H), 4.17 (dd, *J*=11.9, 3.5 Hz, 1H), 3.98 (td, *J*=6.5, 3.5 Hz, 1H), 2.53–2.44 (m, 1H), 2.39–2.30 (m, 1H), 2.11 (s, 6H) ppm; IR (film, cm^{-1}): 2931, 2843, 1738, 1630, 1332, 1220, 1040, 920, 831; MS(ESI) *m/z*: 277.0 ([M+Na]$^+$, 100).

*4.2.19. 2-(4′,6′-Di-O-acetyl-2′,3′-dideoxy-α-D-erythro-hex-2′-enopyranosyl)-acetophenone (**3s**).* Colorless oil; $[\alpha]_D^{10}$=+78.6 (c 0.92, $CHCl_3$, α only) {lit.:[9a] *α:β*=8:2, $[\alpha]_D^{23}$=+35.7 (c 0.99, $CHCl_3$) for α anomer, $[\alpha]_D^{23}$=+111.3 (c 0.574, $CHCl_3$) for β anomer}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 8.00–7.95 (m, 2H), 7.63–7.57 (m, 1H), 7.52–7.46 (m, 2H), 6.11–6.06 (m, 1H), 588–5.83 (m, 1H), 5.18–5.13 (m, 1H), 4.98–4.91 (m, 1H), 4.25 (dd, *J*=11.9, 6.6 Hz, 1H), 4.14 (dd, *J*=11.9, 3.6 Hz, 1H), 4.00 (td, *J*=6.4, 3.7 Hz, 1H), 3.48 (dd, *J*=16.4, 7.1 Hz, 1H), 3.15 (dd, *J*=16.4, 6.6 Hz, 1H), 2.10 (s, 3H), 2.03 (s, 3H) ppm; IR (film,cm^{-1}): 2930, 2838, 1741, 1590, 1325, 1224, 1030, 865, 710; MS(ESI) *m/z*: 355.0 ([M+Na]$^+$, 100).

*4.2.20. 4,6-Di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl cyanide (**3t**).* White solid; mp=86–87 °C;

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$[\alpha]_D^{10}$=−15.6 (c 1.10, $CHCl_3$, only) {lit.:[7i] $[\alpha]_D^{10}$=−19.8 (c 0.98, $CHCl_3$, α only)}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.06 (dt, *J*=10.2, 1.8 Hz, 1H), 5.92 (ddd, *J*=10.2, 3.5, 1.9 Hz, 1H), 5.40–5.34 (m, 1H), 5.12–5.08 (m, 1H), 4.29 (d, *J*=3.9 Hz, 2H), 4.10–4.04 (m, 1H), 2.15 (s, 3H), 2.14 (s, 3H) ppm; IR (film, cm^{-1}): 2935, 2840, 2212, 1741, 1565, 1350, 1221, 1032, 910, 721; MS(ESI) *m*/*z*: 261.9 ($[M+Na]^+$, 100).

*4.2.21. 3′-Phenylpropyl 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**5a**).* Colorless oil; $[\alpha]_D^{10}$=−56.8 (c 0.95, $CHCl_3$, α only); ^{1}H NMR (400 MHz, DMSO) δ 7.31–7.25 (m, 2H), 7.23–7.14 (m, 3H), 5.83 (q, *J*=10.4 Hz, 2H), 4.96 (s, 1H), 4.92 (d, *J*=9.2 Hz, 1H), 3.88–3.79 (m, 1H), 3.69–3.61 (m, 1H), 3.49–3.40 (m, 1H), 2.70–2.57 (m, 2H), 2.06 (s, 3H), 1.87–1.78 (m, 2H), 1.12 (d, *J*=6.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, DMSO) δ 170.53, 142.07, 129.33, 128.91, 128.76, 128.75, 126.20, 94.16, 70.61, 67.52, 64.79, 32.18, 31.49, 21.29, 18.23; IR (film, cm^{-1}): 2924, 1739, 1630, 1542, 1430, 1342, 1235, 1037, 923, 730; MS(ESI) *m*/*z*: 313.1 ($[M+Na]^+$, 100). HR-ESI: $C_{17}H_{22}NaO_4$ $[M+Na]^+$, calcd 313.1410, found. 313.1417.

*4.2.22. Cyclohexanethiol 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**5b**).* Colorless oil; $[\alpha]_D^{10}$=−117.5 (c 1.08, $CHCl_3$, α only) {lit.:[5v] $[\alpha]_D^{25}$=−156.9 (c 1.0, $CHCl_3$, α only)}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.91 (d, *J*=10.1 Hz, 1H), 5.74 (d, *J*=10.1 Hz, 1H), 5.61 (s, 1H), 5.12 (d, *J*=9.0 Hz, 1H), 4.23–4.14 (m, 1H), 2.96–2.86 (m, 1H), 2.10 (s, 3H), 2.08–1.99 (m, 2H), 1.82–1.73 (m, 2H), 1.64–1.57 (m, 1H), 1.46–1.29 (m, 5H), 1.24 (d, *J*=6.3 Hz, 3H) ppm; IR (film, cm^{-1}): 2932, 1741, 1630, 1423, 1235, 1042, 924, 833; MS(ESI) *m*/*z*: 293.0 ($[M+Na]^+$, 100).

*4.2.23. 4-Methylphenyl 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**5c**).* Colorless oil; $[\alpha]_D^{10}$=−118.6 (c 1.03, $CHCl_3$, α only); {lit.:[9c] α:β=9:1, no rotation value reported}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J*=8.3 Hz, 2H), 7.33 (d, *J*=8.1 Hz, 2H), 5.90 (d, *J*=10.1 Hz, 1H), 5.83–5.78 (m, 1H), 5.66 (d, *J*=9.1 Hz, 1H), 5.58–5.52 (m, 1H), 4.95–4.90 (m, 1H), 3.46–3.37 (m, 1H), 2.45 (s, 3H), 2.06 (s, 3H), 0.73 (d, *J*=6.2 Hz, 3H) ppm; IR (film, cm^{-1}): 3324, 2931, 2837, 1742, 1640, 1431, 1355, 1228, 1030, 910, 824, 732; MS(ESI) *m*/*z*: 343.1 ($[M+NH_4]^+$, 100).

*4.2.24. 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl-N-methyl-methanesulfonamide (**5d**).* Colorless oil; $[\alpha]_D^{10}$=−106.5 (c 1.17, $CHCl_3$, α only); ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.93 (d, *J*=10.3 Hz, 1H), 5.74 (s, 1H), 5.66 (d, *J*=10.3 Hz, 1H), 5.00 (d, *J*=7.1 Hz, 1H), 3.73–3.64 (m, 1H), 2.91 (s, 3H), 2.74 (s, 3H), 2.05 (s, 3H), 1.19 (d, *J*=6.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.37, 131.73, 128.34, 82.68, 71.99, 69.71, 38.32, 29.13, 20.98, 18.00; IR (film, cm^{-1}): 3078, 2920, 2853, 1740, 1641, 1336, 1223, 1040, 915, 816; MS(ESI) *m*/*z*: 286.1 ($[M+Na]^+$, 100). HR-ESI: $C_{10}H_{17}NNaO_5S$ $[M+Na]^+$, calcd 286.0720, found. 286.0714.

*4.2.25. 2-(4′-O-acetyl-6′-deoxy-2′,3′-dideoxy-α-D-erythro-hex-2′-enopyranosyl) acetophenone (**5e**).* Colorless oil; $[\alpha]_D^{10}$=−110.7 (c 1.09, $CHCl_3$, α:β=97:3) {lit.:[7i] $[\alpha]_D^{10}$=−110.7 (c 1.09, $CHCl_3$ α only)}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.97 (m, 2H), 7.63–7.57 (m, 1H), 7.53–7.46 (m, 2H), 6.09 (ddd, *J*=10.3, 2.1, 1.2 Hz, 1H), 5.85 (ddd, *J*=10.4, 3.6, 2.0 Hz, 1H), 4.95–4.85 (m, 2H), 4.01–3.92 (m, 1H), 3.47 (dd, *J*=16.5, 6.8 Hz, 1H), 3.16 (dd, *J*=16.5, 6.7 Hz, 1H), 2.11 (s, 3H), 1.27 (d, *J*=6.6 Hz, 3H) ppm; IR (film, cm^{-1}):2933, 2842, 1738, 1645, 1564, 1437, 1346, 1230, 1125, 1041, 814, 725; MS(ESI) *m*/*z*: 292.2 ($[M+NH_4]^+$, 24).

*4.2.26. Cyclohexyl-4,6-di-O-benzyl-2,3-dideoxy-D-erythro-1-thio-hex-2-enopyranoside (**7a**).* Colorless oil; $[\alpha]_D^{10}$=+68.7 (c 1.06, $CHCl_3$, α only) {lit.:[5v] $[\alpha]_D^{25}$=+53.6 (c 1.0 $CHCl_3$, α:β=10:1)}; ^{1}H NMR (400 MHz, DMSO) δ 7.38–7.24 (m, 10H), 6.09 (d, *J*=10.3 Hz, 1H), 5.74 (d, *J*=10.3 Hz, 1H), 5.11 (s, 1H), 4.65 (d, *J*=11.7 Hz, 1H), 4.56–4.43 (m, 3H), 3.92 (d, *J*=9.6 Hz, 1H), 3.89–3.82 (m, 1H), 3.66 (d, *J*=9.7 Hz, 1H), 3.63–3.54 (m, 2H), 1.92–1.78 (m, 2H), 1.71–1.55 (m, 2H), 1.50–1.40 (m, 1H), 1.34–1.08 (m, 5H) ppm; IR (film, cm^{-1}): 3064, 2941, 2832, 1625, 1518, 1423, 1330, 1231, 1120, 836, 744; MS(ESI) *m*/*z*: 426.3 ($[M+NH_4]^+$, 100).

*4.2.27. Benzyl-4,6-di-O-benzyl-2,3-dideoxy-D-erythro-1-thio-hex-2-enopyranoside (**7b**).* Colorless oil; $[\alpha]_D^{10}$=+86.7 (c 1.28, $CHCl_3$, α:β=88:12) {lit.:[5v] $[\alpha]_D^{23}$=+80.4 (c 1.4, $CHCl_3$, α:β=10:1)}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41–7.25 (m, 15H), 6.13 (d, *J*=10.3 Hz, 1H), 5.83 (dt, *J*=10.3, 2.3 Hz, 1H), 5.17 (s, 1H), 4.85 (d, *J*=11.8 Hz, 1H), 4.69 (d, *J*=12.2 Hz, 1H), 4.66–4.61 (m, 2H), 4.55 (d, *J*=12.2 Hz, 1H), 4.48 (d, *J*=11.5 Hz, 1H), 4.26–4.20 (m, 1H), 4.07–4.01 (m, 1H), 3.77 (dd, *J*=10.6, 4.1 Hz, 1H), 3.67 (dd, *J*=10.6, 1.8 Hz, 1H) ppm; IR (film, cm^{-1}): 2937, 1623, 1486, 1392, 1223, 1141, 1056, 809. MS(ESI) *m*/*z*: 434.2 ($[M+NH_4]^+$, 100).

*4.2.28. Benzyl 4,6-di-O-benzyl-2,3-dideoxy-α-D-erythro-hex-2-eno-1-thio-α-D-pyranoside (**7c**).* Colorless oil; $[\alpha]_D^{10}$=+76.5 (c 1.02, $CHCl_3$, α:β=93:7); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44–7.23 (m, 15H), 6.00 (d, *J*=10.2 Hz, 1H), 5.84–5.79 (m, 1H), 5.47 (s, 1H), 4.73–4.46 (m, 4H), 4.31–4.20 (m, 2H), 3.96 (d, *J*=13.4 Hz, 1H), 3.83–3.76 (m, 2H), 3.66 (dd, *J*=10.7, 1.6 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 138.49, 138.24, 138.08, 129.04, 128.78, 128.49, 128.41, 128.39, 127.91, 127.89, 127.79, 127.66, 127.44, 126.93, 79.28, 73.37, 71.14, 70.37, 69.26, 68.88, 35.68; IR (film, cm^{-1}): 3043, 2936, 2845, 1621, 1486, 1378, 1236, 1120, 1035, 912, 823, 755, 708; MS(ESI) *m*/*z*: 450.2 ($[M+NH_4]^+$, 100). HR-ESI: $C_{27}H_{29}O_3S$ $[M+H]^+$, calcd 433.1837, found. 433.1840.

*4.2.29. 4′-Methoxylphenyl 4,6-di-O-benzyl-2,3-dideoxy-α-D-erythro-1-thio-hex-2-enopyranoside (**7d**).* White solid; mp=46–48 °C; $[\alpha]_D^{10}$=+117.6 (c 0.92, $CHCl_3$, α:β=92:8); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J*=8.6 Hz, 2H), 7.40–7.30 (m, 10H), 6.77 (d, *J*=8.7 Hz, 2H), 6.08–5.99 (m, 2H), 5.63 (s, 1H), 4.71–4.64 (m, 2H), 4.58–4.49 (m, 2H), 4.47–4.41 (m, 1H), 4.23 (d, *J*=9.2 Hz, 1H), 3.85–3.81 (m, 2H), 3.79 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 159.63, 138.26, 138.02, 135.02, 128.77, 128.46, 128.35, 127.93, 127.90, 127.86, 127.60, 127.56, 125.49, 114.40, 84.85, 73.35, 71.10, 70.50, 69.36, 69.31, 55.32; IR (film, cm^{-1}): 2932, 2820, 1531, 1423, 1332, 1041, 945, 817; MS(ESI) *m*/*z*: 466.2 ($[M+NH_4]^+$, 100). HR-ESI: $C_{27}H_{32}O_4NS$ $[M+NH_4]^+$, calcd 466.2047, found. 466.2040.

*4.2.30. 4′-Trifluoromethoxylphenyl 4,6-di-O-benzyl-2,3-dideoxy-α-D-erythro-1-thio-hex-2-enopyranoside (**7e**).* White solid; mp=74–76 °C; $[\alpha]_D^{10}$=+121.5 (c 0.98, $CHCl_3$, α:β=96:4); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J*=8.1 Hz, 2H), 7.48 (d, *J*=8.2 Hz, 2H), 7.41–7.29 (m, 10H), 6.12 (d, *J*=10.2 Hz, 1H), 6.00 (d, *J*=10.2 Hz, 1H), 5.88 (s, 1H), 4.66 (d, *J*=12.5 Hz, 2H), 4.55–4.49 (m, 2H), 4.36–4.25 (m, 2H), 3.84–3.75 (m, 2H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 137.98, 137.82, 130.44, 129.86, 128.49, 128.38, 127.96, 127.91, 127.75, 126.61, 125.58 (q, *J*=4.0 Hz, 1C), 83.23, 73.36, 71.38, 70.15, 69.88, 68.91; ^{19}F NMR (377 MHz, $CDCl_3$) δ −62.56(s); IR (film, cm^{-1}): 2936, 2841, 1623, 1512, 1421, 1320, 1226, 1037, 915, 816; MS(ESI) *m*/*z*: 487.2 ([M+H]+, 100). HR-ESI: $C_{27}H_{26}O_3F_3S$ $[M+H]^+$, calcd 487.1549, found 487.1541.

*4.2.31. 4,6-Di-O-benzyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl-4′-methoxyl-phenylsulfonamide (**7f**).* Colorless oil; $[\alpha]_D^{10}$=+121.5 (c 1.12, $CHCl_3$, α:β=80:20); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J*=8.9 Hz, 2H), 7.41–7.25 (m, 10H), 6.82 (d, *J*=8.9 Hz, 2H), 6.11 (d, *J*=10.2 Hz, 1H), 5.79–5.73 (m, 1H), 5.67–5.61 (m, 1H), 5.58–5.51 (m, 1H), 4.57 (d, *J*=11.3 Hz, 1H), 4.51–4.35 (m, 3H), 4.19 (dd, *J*=9.1, 1.7 Hz, 1H), 3.79 (s, 3H), 3.44 (dd, *J*=10.7, 2.9 Hz, 1H), 3.30 (dt, *J*=9.0, 2.3 Hz, 1H), 2.80 (dd, *J*=10.7, 2.0 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) δ 162.77, 138.07, 137.62, 133.54, 131.97, 130.97, 129.63, 129.41, 128.46, 128.42, 127.99, 127.95, 127.74, 127.71, 125.51, 113.91, 79.39, 73.34, 71.83, 69.48, 69.26, 67.65, 55.59; IR (film,

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cm^{-1}):3341, 3076, 2964, 1634, 1517, 1418, 1334, 1225, 1078, 934, 817; MS(ESI) *m/z*: 513.2 ([M+NH$_4$]$^+$, 100). HR-ESI: $C_{27}H_{33}N_2O_6S$ [M+NH$_4$]$^+$, calcd 513.2054, found. 513.2047.

*4.2.32. 4,6-Di-O-benzyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl-methanesulfonamide (**7g**).* Colorless oil; $[\alpha]_D^{10}$=+94.6 (c 1.15, $CHCl_3$, *α:β*=85:15) {lit.:[9d] $[\alpha]_D^{25}$=+54 (c 0.7, $CHCl_3$, *α:β*=3:1)}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.41–7.26 (m, 10H), 6.16 (dt, *J*=10.2, 1.7 Hz, 1H), 5.80 (ddd, *J*=10.2, 3.0, 1.8 Hz, 1H), 5.58–5.53 (m, 1H), 5.39 (d, *J*=9.2 Hz, 1H), 4.68–4.46 (m, 4H), 4.00–3.95 (m, 1H), 3.85–3.79 (m, 1H), 3.75 (dd, *J*=10.3, 2.0 Hz, 1H), 3.64 (dd, *J*=10.3, 6.2 Hz, 1H), 3.06 (s, 3H) ppm; IR (film, cm^{-1}): 3289, 3035, 2921, 2857, 1372, 1233, 1020, 952, 724; MS(ESI) *m/z*: 421.2 ([M+NH$_4$]$^+$, 100).

*4.2.33. 4,6-Di-O-benzyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl-N-methyl-methanesulfonamide (**7h**).* Colorless oil; $[\alpha]_D^{10}$=+68.6 (c 1.10, $CHCl_3$, α only); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.41–7.29 (m, 10H), 6.21 (dt, *J*=10.3, 1.9 Hz, 1H), 5.82–5.79 (m, 1H), 5.70 (dt, *J*=10.3, 1.8 Hz, 1H), 4.67 (d, *J*=11.5 Hz, 1H), 4.61–4.51 (m, 3H), 4.13–4.07 (m, 1H), 3.80–3.74 (m, 1H), 3.73–3.68 (m, 2H), 2.97 (s, 3H), 2.81 (s, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 138.18, 137.71, 132.57, 128.51, 128.41, 127.99, 127.96, 127.72, 127.59, 127.21, 83.01, 76.53, 73.26, 71.57, 69.56, 69.33, 38.36, 29.29. IR (film,cm^{-1}): 3056, 2931, 2846, 1513, 1382, 1217, 1040, 843, 722; MS(ESI) *m/z*: 440.2 ([M+Na]$^+$, 100). HR-ESI: $C_{22}H_{27}NNaO_5S$ [M+Na]$^+$, calcd 440.1502, found. 440.1502.

*4.2.34. 4,6-Di-O-benzyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl-benzylcarbamate (**7i**).* Colorless oil; $[\alpha]_D^{10}$=+104.5 (c 1.11, $CHCl_3$, *α:β*=89:11) {lit.:[9d] $[\alpha]_D^{25}$=+29 (c 2.0, $CHCl_3$, *α:β*=7:3)}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.40–7.23 (m, 15H), 6.09 (dt, *J*=10.1, 1.9 Hz, 1H), 5.76 (d, *J*=9.4 Hz 1H), 5.71(d, *J*=10.2 Hz 1H), 5.40–5.31 (m, 1H), 5.22–5.07 (m, 2H), 4.70–4.41 (m, 4H), 4.27–4.19 (m, 1H), 3.80–3.67 (m, 3H) ppm; IR (film, cm^{-1}): 3048, 2940, 2841, 1520, 1410, 1221, 1032, 942, 825, 732; MS(ESI) *m/z*: 477.2 ([M+NH$_4$]$^+$, 100).

*4.2.35. 2-(4,6-Di-O-benzyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl) oxazolidinone (**7j**).* White solid; mp=54–56 °C; $[\alpha]_D^{10}$=+86.4 (c 0.96, $CHCl_3$, α only); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.41–7.25 (m, 10H), 6.20 (d, *J*=10.3 Hz, 1H), 5.85 (s, 1H), 5.68 (d, *J*=10.3 Hz, 1H), 4.68–4.60 (m, 2H), 4.56–4.49 (m, 2H), 4.42–4.29 (m, 2H), 4.20 (d, *J*=6.9 Hz, 1H), 3.83–3.73 (m, 3H), 3.71–3.63 (m, 1H), 3.50–3.42 (m, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 157.69, 138.20, 137.78, 132.66, 128.47, 128.36, 127.94, 127.81, 127.65, 126.57, 78.77, 76.99, 73.48, 71.70, 69.45, 68.91, 62.37, 39.78; IR (film, cm^{-1}): 2934, 2841, 1702, 1615, 1391, 1234, 1026, 840, 752; MS(ESI) *m/z*: 413.2 ([M+NH$_4$]$^+$, 100). HR-ESI: $C_{23}H_{29}O_5N_2$ [M+NH$_4$]$^+$, calcd 413. 2071, found. 413.2065.

*4.2.36. 3-(4′,6′-Di-O-benzyl-2′,3′-dideoxy-α-D-erythro-hex-2′-enopyranosyl)-1-propene (**7k**).* Colorless oil; $[\alpha]_D^{10}$=+88.4 (c 0.92, $CHCl_3$, α only) {lit.:[5x] $[\alpha]_D^{25}$=+73.529 (c 3.4, $CHCl_3$, α only)}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.39–7.24 (m, 10H), 5.97–5.82 (m, 3H), 5.17–5.06 (m, 2H), 4.66–4.46 (m, 4H), 4.30–4.23 (m, 1H), 4.04–3.98 (m, 1H), 3.87–3.81 (m, 1H), 3.74–3.64 (m, 2H), 2.55–2.45 (m, 1H), 2.38–2.28 (m, 1H) ppm; IR (film, cm^{-1}): 3058, 2921, 2853, 1642, 1372, 1233, 1040, 912, 732; MS(ESI) *m/z*:373.0 ([M+Na]$^+$, 100).

*4.2.37. 2-(4′,6′-Di-O-benzyl-2′,3′-dideoxy-α-D-erythro-hex-2′-enopyranosyl)-acetophenone (**7l**).* Colorless oil; $[\alpha]_D^{10}$=+112.6 (c 0.97, $CHCl_3$, α only); ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.97 (d, *J*=7.5 Hz, 2H), 7.62–7.56 (m, 1H), 7.52–7.44 (m, 2H), 7.36–7.27 (m, 10H), 6.00 (s, 2H), 4.94 (t, *J*=6.8 Hz, 1H), 4.67–4.48 (m, 4H), 4.03 (d, *J*=6.9 Hz, 1H), 3.91–3.85 (m, 1H), 3.73–3.61 (m, 2H), 3.51 (dd, *J*=16.3, 6.6 Hz, 1H), 3.19 (dd, *J*=16.3, 7.0 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$) *δ* 197.78, 138.18, 138.09, 136.99, 133.24, 131.08, 128.62, 128.41, 128.33, 128.21, 127.96, 127.81, 127.77, 127.58, 125.86, 73.43, 72.15, 71.11, 69.85, 69.18, 69.16, 42.38; IR (film, cm^{-1}): 2925, 2852, 1731, 1524, 1413, 1332, 1210, 1128, 1058, 755, 687; MS(ESI) *m/z*: 446.2 ([M+NH$_4$]$^+$, 100). HR-ESI: $C_{28}H_{29}O_4$ [M+H]$^+$, calcd 429.2066, found 429.2060.

*4.2.38. 4,6-Di-O-benzyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl cyanide (**7m**).* Colorless oil; $[\alpha]_D^{10}$=+72.8 (c 0.98, $CHCl_3$, *α:β*=80:20) {lit.:[5x] $[\alpha]_D^{25}$=+44.737 (c 3.8, $CHCl_3$, *α:β*=60:40)}; ^{1}H NMR (400 MHz, $CDCl_3$) *δ* 7.40–7.24 (m, 10H), 6.19 (d, *J*=10.2 Hz, 1H), 5.83–5.77 (m, 1H), 5.10–5.04 (m, 1H), 4.64 (dd, *J*=11.7, 6.7 Hz, 2H), 4.56–4.47 (m, 2H), 4.27 (dd, *J*=8.9, 1.8 Hz, 1H), 3.88 (dt, *J*=8.9, 2.7 Hz, 1H), 3.83–3.74 (m, 2H) ppm; IR (film, cm^{-1}): 3067, 2942, 2835, 2210, 1621, 1530, 1425, 1337, 1252, 1135, 1058, 945, 844, 753; MS(ESI) *m/z*: 453.2 ([M+NH$_4$]$^+$, 80).

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Supplementary data

Supplementary data (^{1}H and ^{13}C NMR spectra) associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.tet.2015.11.002.

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