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$Sm(OTf)_3$ as a highly efficient catalyst for the synthesis of 2,3-unsaturated *O*- and *S*-pyranosides from glycals and the temperature-dependent formation of 4-*O*-acetyl-6-deoxy-2,3-unsaturated *S*-pyranosides and 4-*O*-acetyl-6-deoxy-3-alkylthio glycals

Peiran Chen [a,b,*], Dalin Zhang [a]

[a] Key Lab of Eco-Textile, The Ministry of Education, Donghua University, 2999 Renmin Road North, Songjiang District, Shanghai 201620, China
[b] Key Laboratory of Synthetic Chemistry of Natural Substances, Shanghai Institute of Organic Chemistry, CAS, Shanghai 200032, China

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ABSTRACT

By using $Sm(OTf)_3$ as the catalyst, synthesis of 2,3-unsaturated-glycosides has been performed. A series of 2,3-unsaturated glycosides were obtained from 3,4,6-tri-*O*-acetyl-D-glucal or 3,4-di-*O*-acetyl-L-rhamnal under mild reaction conditions in good yield and high anomeric selectivity. It was found that under certain conditions, reaction of 3,4-di-*O*-acetyl-L-rhamnal with thiol leads to temperature-dependent formation of C-1-S and C-3-S product. A temperature-dependent profile of the yield of these two products is given.

1. Introduction

Alkyl and aryl 2,3-unsaturated glycosides are capable of versatile chemical transformations, therefore they are important chiral intermediates in the synthesis of biologically active molecules[1] and new functional materials.[2] Ferrier rearrangement is an efficient and facile reaction for the synthesis of 2,3-unsaturated glycopyranosides.[3] A variety of reagents have been used to promote this reaction, including Bronsted acids, such as H_2SO_4, H_3PO_4, $HClO_4$–SiO_2, TfOH–SiO_2, etc.[4] Lewis acids, such as $BF_3{\cdot}OEt_2$, $FeCl_3$, $Fe_2(SO_4)_3$, $Fe(NO_3)_3$, $InCl_3$, $BiCl_3$, $CeCl_3$, $ZnCl_2$, $Pd(OAc)_2$, $ZrCl_4$, $K_5CoW_{12}O_{40}{\cdot}3H_2O$, $Bi(OTf)_3$, $Sc(OTf)_3$, $Fe(OTf)_3$, $TiCl_4$, $AuCl_3$, HBF_4–SiO_2, $ZnCl_2/Al_2O_3$, $TiCl_3(OTf)$, $RuCl_3$[5] as well as oxidants, such as I_2, IDCP, NIS, and DDQ, etc.[6] In recent years, due to their special properties and high catalytic activities, lanthanide elements as catalyst have got more and more application. Among lanthanides, which have been employed as the catalysts in Ferrier Rearrangement, there can be mentioned $Dy(OTf)_3$, $Er(OTf)_3$, and $Yb(OTf)_3$, etc.[7] Most of those researches concentrated on using 3,4,6-tri-*O*-acetyl-D-glucal as substrate and the reactions had to promoted by ionic solvent.[7c,7f–i] In our continuing efforts to search for more efficient catalyst for Ferrier Rearrangement, we found $Sm(OTf)_3$ was a highly efficient catalyst for our purposes. Here we wish to report our result.

2. Results and discussion

2.1. Optimization of reaction conditions

Considering the effect of anions in the salts on the catalytic capacity,[5u,5v] we screened several samarium salts, including $SmCl_3$, $Sm(NO_3)_3$, SmI_2, and $Sm(OTf)_3$ and found $Sm(OTf)_3$ was the best one. For the reaction solvent, we found acetonitrile gave the best result among acetone, acetonitrile, THF, diethyl ether, and toluene.

2.2. Synthesis of *O*-2,3-unsaturated glucosides

This section discusses the synthesis of *O*-alkyl and *O*-aryl 2,3-unsaturated glycosides. The reaction was carried out under mild conditions. The substrate alcohols included simple alcohol and

* Corresponding author. Tel.: +86 21 67792594; e-mail address: prchen@dhu.edu.cn (P. Chen).

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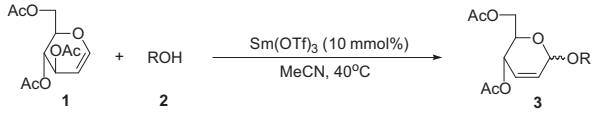
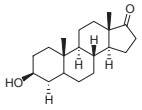
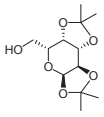
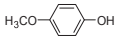
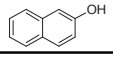
chiral alcohols. The reaction time was short and the yield was good for two types of the examined glycals: 3,4,6-tri-*O*-acetyl D-glucal and 3,4-di-*O*-acetyl-L-rhamnal. (Table 1 and Table 2) Similar results were gained for the phenol substrates. A report mentioned that when tri-*O*-acetyl-D-glucal was treated with *p*-methoxyphenol in CH_2Cl_2 with $BF_3\cdot OEt_2$ as the catalyst, *C*-glucoside was obtained exclusively.[8] However, in our case, no such phenomenon occurred. *p*-Methoxyphenol gave the normal product *O*-glucoside in good yield (entry 7), which could be confirmed by the two *ortho* aromatic signals in the product ^1H NMR.

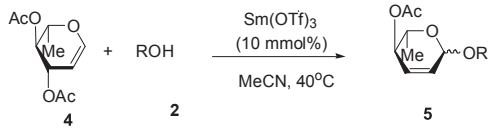
Table 1
Synthesis of *O*-alkyl and *O*-aryl 2,3-unsaturated glucosides from tri-*O*-acetyl-D-glucal



Entry	ROH	Reaction time (min)	Product yield (%)[a](α:β)[b]
1	EtOH	10	**3a**: 88 (33:1)
2		10	**3b**: 85 (10:1)
3		10	**3c**: 78 (α only)
4		40	**3d**: 72 (7:1)
5		10	**3e**: 69 (7:1)
6		30	**3f**: 67 (α only)
7		20	**3g**: 75 (α only)
8		30	**3h**: 73 (α only)

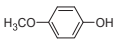
[a] Isolated yield.
[b] The anomeric ratio was determined by integration of the anomeric hydrogen in the ^1H NMR spectra.

Table 2
Synthesis of *O*-alkyl and *O*-aryl 2,3-unsaturated glycosides from 3,4-di-*O*-acetyl-L-rhamnal



Entry	ROH	Reaction time (min)	Product yield (%)[a](α:β)[b]
1	EtOH	10	**5a**: 77 (9:1)
2		10	**5b**: 65 (α only)
3		10	**5c**: 72 (α only)
4		10	**5d**: 70 (6:1)

Table 2 (*continued*)

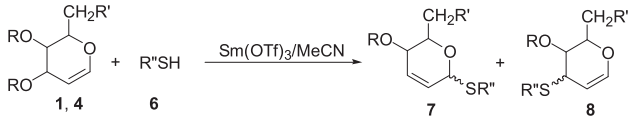
Entry	ROH	Reaction time (min)	Product yield (%)[a](α:β)[b]
5		20	**5e**: 71 (α only)
6		30	**5f**: 62 (α only)
7		20	**5g**: 64 (α only)

[a] Isolated yield.
[b] The anomeric ratio was determined by integration of the anomeric hydrogen in the ^1H NMR spectra.

2.3. Synthesis of *S*-alkyl 2,3-unsaturated glycosides

This section discusses the reaction of 3,4,6-tri-*O*-acetyl-D-glucal and 3,4-di-*O*-acetyl-L-rhamnal with thiols. As showed in Table 3, similar to the case of *O*-glycosidation, the reaction was carried out under mild conditions in short reaction time with good yield.

Table 3
Synthesis of *S*-alkyl 2,3-unsaturated glycosides from 3,4,6-tri-*O*-acetyl-D-glucal and 3,4-di-*O*-acetyl-L-rhamnal

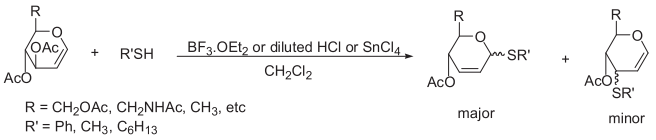


1: R = R' = OAc
4: R = OAc, R' = H

Entry	Starting material	R'SH	Reaction time (min)	Product yield (%)[a](α:β)[b]
1	**1**	EtSH	10	**7a**: 86 (α only)
2	**1**	n-$C_{12}H_{25}SH$	20	**7b**: 83 (α only)
3	**1**		20	**7c**: 81 (α only)
4	**4**	EtSH	20	**7d** (C-1-S product): **8d** (C-3-S product) See Table 4
5	4	n-$C_{12}H_{25}SH$	20	**7e** (C-1-S product): **8e** (C-3-S product) See Table 4
6	4		20	**7f**: 73 (17:1)

[a] Isolated yield.
[b] The anomeric ratio was determined by integration of the anomeric hydrogen in the ^1H NMR spectra.

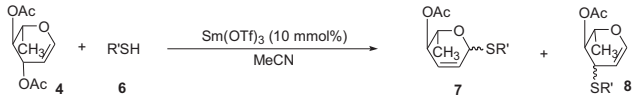
It was reported that reaction of some kind of glucals with thiols in the presence of $BF_3\cdot OEt_2$,[9a,b] diluted hydrochloric acid[9c] or $SnCl_4$[3] in CH_2Cl_2 gave 1-*S* glucoside as the major product and 3-*S* glucal as the minor product (Scheme 1).



Scheme 1. Literature reported reaction of glucal with thiol giving 1-*S*-glucoside and 3-*S*-glucal.

This was also true in our case. When 3,4-di-*O*-acetyl-L-rhamnal was reacted with EtSH or n-$C_{12}H_{25}SH$, two products formed. It was found that C-1-S products (**7e, 7f**) were the major products at lower reaction temperature, while C-3-S products (**8e, 8f**) increased as the reaction temperature elevated. Table 4 collected the yields changing at varying reaction temperature. However, in the case of 3,4,6-tri-*O*-acetyl-D-glucal, formation of C-3-S product was not detected

Table 4
Reaction of 3,4-di-*O*-acetyl-L-rhamnal with two alkythiols



R' = CH_3CH_2- and n-$C_{12}H_{25}$-

Entry	R′SH	Reaction temperature (°C)	Reaction time (min)	Product yield[a] C-1-S (**7**)/C-3-S(**8**)	Total yield (%)/C-1-S(**7**): (α:β)[b]
1	EtSH	−20	90	76.5(**7e**)/2.5(**8e**)	79(14:1)
2	EtSH	−5	60	67.4(**7e**)/5.6(**8e**)	73(14:1)
3	EtSH	0	40	40.9(**7e**)/24.1(**8e**)	65(14:1)
4	EtSH	25	20	10.1(**7e**)/60.9(**8e**)	71(14:1)
5	EtSH	40	10	6.4(**7e**)/70.6(**8e**)	77(14:1)
6	n-$C_{12}H_{25}SH$	−5	70	72.1(**7f**)/2.9(**8f**)	75(10:1)
7	n-$C_{12}H_{25}SH$	0	50	38.1(**7f**)/23.8(**8f**)	62(10:1)
8	n-$C_{12}H_{25}SH$	25	30	8.8(**7f**)/57.2(**8f**)	66(10:1)
9	n-$C_{12}H_{25}SH$	40	10	6(**7f**)/66(**8f**)	72(10:1)

[a] Yield is determined by analysis of the ^1H NMR spectra of the product mixture.
[b] The anomeric ratio was determined by integration of the anomeric hydrogen in the ^1H NMR spectra.

even under reflux in acetonitrile. We also noticed that in a work by Schmidt and co-worker, 3,4,6-tri-*O*-acetyl-D-glucal reacted with n-$C_8H_{17}SH$ or PhSH in CH_2Cl_2 promoted by $Yb(OTf)_3$ at room temperature, no C-3-product formation was reported.[7d]

Data in Table 3 are presented as curves in Fig. 1, which clearly showed the formation of C-1-S and C-3-S products is reaction temperature-dependent. It implies that the C-3-S product is thermodynamically more stable.

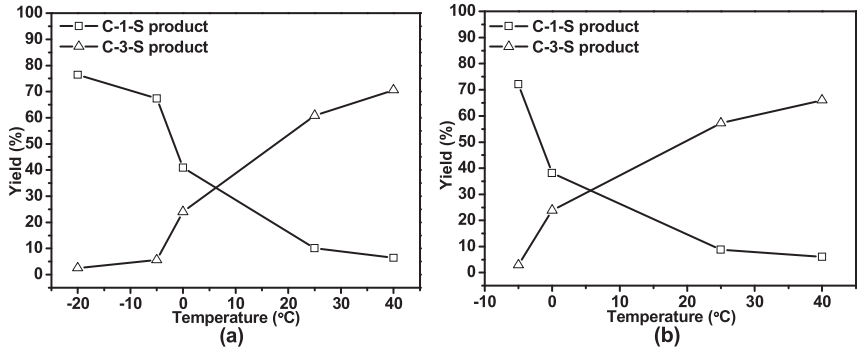


Fig. 1. Reaction temperature-dependent formation of 1-*S*-alkyl glucosides and 3-*S*-alkyl glucals. (a) *S*-ethyl and (b) *S*-*n*-dodecyl.

3. Conclusion

Samarium(III) triflate was a highly efficient catalyst for Ferrier Rearrangement to yield *O*- and *S*-2,3-unsaturated glycosides. This catalyst allowed the reaction proceeding under mild conditions to give the desired products with good yields and high anomeric selectivities in short time. Under certain conditions, reaction of 3,4-di-*O*-acetyl-L-rhamnal with EtSH or n-$C_{12}H_{25}SH$ led to temperature-dependent formation of C-1-S and C-3-S product. A temperature-dependent profile of the yield of these two products was given.

4. Experimental

4.1. Method and materials

^1H 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 parts per million and coupling constants (J) are in Hertz. 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, epiandrosteron, 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 and 3,4-di-*O*-acetyl-L-rhamnal catalyzed with $Sm(OTf)_3$

To a stirred solution of 3,4,6-tri-*O*-acetyl-D-glucal (163 mg, 0.6 mmol) or 3,4-di-*O*-acetyl-L-rhamnal (128 mg, 0.6 mmol) and the corresponding alcohol (1.2 equiv) in acetonitrile (5 mL) were added $Sm(OTf)_3$ (10 mol %) at ambient temperature. The mixture was stirred under 40 °C for the appropriate amount of time, 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=20/1 in the case of 3,4,6-tri-*O*-acetyl-D-glucal as the starting material, or hexane/EtOAc=60/1 in the case of 3,4-di-*O*-acetyl-L-rhamnal as the starting material).

*4.2.1. Ethyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3a**).* Colorless oil; $[\alpha]_D^{25}$ +106.1 (*c* 0.98, $CHCl_3$, α:β=33:1){lit[5x]: $[\alpha]_D^{25}$ +112.5 (*c* 1.67, $CHCl_3$, α:β=7:1)}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.91–5.80 (m, 2H), 5.32 (d, J=9.6 Hz, 1H), 5.05

(s, 1H), 4.30–4.08 (m, 3H), 3.87–3.79 (m, 1H), 3.62–3.54 (m, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 1.25 (t, *J*=7.1 Hz, 3H) ppm; IR (film, cm^{-1}): 2986, 2931, 2842, 1738, 1636, 1504, 1373, 1218, 1095, 1034, 997, 830, 723; MS(ESI) *m/z*: 280.9([M+Na]$^+$55), 212.9(100), 152.9(45).

*4.2.2. Cyclohexyl 4, 6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside(**3b**).* Colorless oil; $[\alpha]_D^{25}$ +112.9 (*c* 0.92, $CHCl_3$, α:β=10:1){lit[5x]: $[\alpha]_D^{25}$ +135.5 (*c* 1.60, $CHCl_3$, α:β=10:1)}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.87–5.79 (m, 2H), 5.28 (d, *J*=9.4 Hz, 1H), 5.16 (s, 1H), 4.24–4.15 (m, 3H), 3.63 (s, 1H), 2.08 (s, 3H), 2.07 (s, 3H), 1.98–1.85 (m, 2H), 1.72 (s, 2H), 1.54 (d, *J*=10.3 Hz, 1H), 1.42–1.19 (m, 5H) ppm; IR (film, cm^{-1}):2925, 2885, 1744, 1656, 1466, 1371, 1232, 1037, 998, 907, 740, 605; MS (ESI) *m/z*:335.0 ([M+Na]$^+$95), 212.8(100).

*4.2.3. L-Menthyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3c**).* Colorless oil; $[\alpha]_D^{25}$ +140.4 (*c* 0.54, $CHCl_3$, α only){lit[4i]: $[\alpha]_D^{25}$ +151 (*c* 1.63, $CHCl_3$, α only)}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.90–5.80 (m, 2H), 5.26 (d, *J*=8.9 Hz, 1H), 5.08 (s, 1H), 4.23–4.13 (m, 3H), 3.44–3.38 (m, 1H), 2.19 (d, *J*=11.7 Hz, 1H), 2.09 (s, 3H), 2.06 (s, 3H), 1.62 (s, 3H), 1.46–0.93 (m, 5H), 0.90 (s, 3H), 0.88 (s, 3H), 0.76 (d, *J*=6.9 Hz, 3H) ppm; IR (film, cm^{-1}): 2955, 2924, 2870, 1747, 1454, 1370, 1230, 1102, 1035, 907, 739; MS (ESI) *m/z*: 391.0 ([M+Na]$^+$100), 212.9(65).

*4.2.4. Epiandrosteronyl-4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3d**).* White solid; mp=124–126 °C; $[\alpha]_D^{25}$ +101.9 (*c* 0.97, $CHCl_3$, α:β=7:1){lit[5x]: $[\alpha]_D^{25}$ +112.7 (*c* 1.81, $CHCl_3$, α:β=6:1); mp=125–126 °C}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.90–5.81 (m, 2H), 5.30 (d, *J*=9.5 Hz, 1H), 5.17 (s, 1H), 4.24–4.15 (m, 3H), 3.63 (m, 1H), 2.43 (dd, *J*=19.2, 8.7 Hz, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 1.98–1.70 (m, 7H), 1.57–1.42 (m, 4H), 1.30 (d, *J*=27.3 Hz, 6H), 1.15 (t, *J*=11.5 Hz, 1H), 1.00–0.93 (m, 2H), 0.86 (s, 3H), 0.83 (s, 3H), 0.71 (d, *J*=11.3 Hz, 1H)ppm; IR (film, cm^{-1}): 2931, 2858, 1746, 1648, 1450, 1372, 1222, 1041, 749, 605; MS (ESI) *m/z*: 520.3 ([M+NH_4]$^+$100).

*4.2.5. 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 (**3e**).* White solid; mp=132–133 °C; $[\alpha]_D^{25}$ +16.4 (*c* 0.73, $CHCl_3$, α:β=7:1){lit[5x]: $[\alpha]_D^{25}$ +17.6 (*c* 0.83, $CHCl_3$, α:β=5:1); mp=132–134 °C}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.93–5.86 (m, 2H), 5.55 (d, *J*=5.0 Hz, 1H), 5.35 (d, *J*=12.9 Hz, 1H), 5.12 (s, 1H), 4.64 (d, *J*=6.4 Hz, 1H), 4.35–4.27 (m, 3H), 4.17 (d, *J*=11.4 Hz, 2H), 4.02 (d, *J*=7.1 Hz, 1H), 3.90 (dd, *J*=10.2, 6.3 Hz, 1H), 3.78 (dd, *J*=9.9, 7.4 Hz, 1H), 2.14 (s, 3H), 2.11 (s, 3H), 1.56 (s, 3H), 1.47 (s, 3H), 1.37 (s, 3H), 1.36 (s, 3H) ppm; IR (film, cm^{-1}): 2994, 2927, 1741, 1576, 1378, 1226, 1051, 1003, 895, 646; MS (ESI) *m/z*: 490.2 ([M+NH_4]$^+$100).

*4.2.6. Phenyl 4,6-di-O-acetyl-2,3-dideoxy-a-D-erythro-hex-2-enopyranoside (**3f**).* White solid; mp=47–48 °C; $[\alpha]_D^{25}$ +133.75 (*c* 1.05, $CHCl_3$, α only){lit:[7c] $[\alpha]_D^{25}$ +165.5 (*c* 1.45, C_2H_5OH, α:β=10:1); mp=47–48 °C}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.31 (m, 2H), 7.13 (d, *J*=8.0 Hz, 2H), 7.08–7.04 (m, 1H), 6.12–5.96 (m, 2H), 5.73 (s, 1H), 5.41 (d, *J*=9.3 Hz, 1H), 4.31 (dd, *J*=11.7, 5.6 Hz, 1H), 4.29–4.22 (m, 1H), 4.16 (d, *J*=11.7 Hz, 1H), 2.13 (s, 3H), 2.00 (s, 3H) ppm; IR (film, cm^{-1}):2929, 2853, 1745, 1645, 1447, 1370, 1232, 1051, 975, 792, 604; MS(ESI) *m/z*: 329.0 ([M+Na]$^+$65), 212.8(100).

*4.2.7. p-Methoxyphenyl 4,6-di-O-acetyl-2,3-dideoxy-a-D-erythro-hex-2-enopyranoside (**3g**).* White solid; mp=69–70 °C; $[\alpha]_D^{25}$ +113.5 (*c* 1.45, $CHCl_3$, α only){lit:[7c] $[\alpha]_D^{25}$ +123 (*c* 1.5, $CHCl_3$, α:β=15:1); mp=69–70 °C}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.07 (d, *J*=9.1 Hz, 2H), 6.86 (d, *J*=9.1 Hz, 2H), 6.06–6.00 (m, 2H), 5.59 (s, 1H), 5.40 (d, *J*=9.3 Hz, 1H), 4.31–4.17 (m, 3H), 3.80 (s, 3H), 2.14 (s, 3H), 2.05 (s, 3H) ppm; IR (film, cm^{-1}):2941, 2841, 1746, 1507, 1450, 1374, 1226, 1035, 988, 830, 765, 605; MS (ESI) *m/z*: 358.9 ([M+Na]$^+$100), 212.9(95).

*4.2.8. 2-Naphthyl 4,6-di-O-acetyl-2,3-dideoxy-a-D-erythro-hex-2-enopyranoside (**3h**).* White solid; mp=108–110 °C; $[\alpha]_D^{25}$ +125.7 (*c* 0.83, $CHCl_3$, α only){lit[4g]: $[\alpha]_D^{25}$ +151.5 (*c* 1.0,$CHCl_3$, α only)}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58 (s, 1H), 7.81 (d, *J*=8.0 Hz, 1H), 7.75–7.69 (m, 2H), 7.52 (m, 1H), 7.37 (t, *J*=7.4 Hz, 1H), 7.14 (t, *J*=7.6 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*=8.2 Hz, 1H), 4.44–4.32 (m, 2H), 4.13 (dt, *J*=9.1, 2.9 Hz, 1H), 2.19 (s, 3H), 2.17 (s, 3H) ppm; IR (film, cm^{-1}):2945, 2925, 2889, 1742, 1491, 1370, 1242, 1044, 811, 781; MS(ESI) *m/z*: 378.9([M+Na]$^+$100).

*4.2.9. Ethyl 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**5a**).* Colorless oil; $[\alpha]_D^{25}$ +37.23 (*c* 1.14, $CHCl_3$, α:β=9:1) {lit[5x]: $[\alpha]_D^{25}$ +21.9 (*c* 0.67, $CHCl_3$, α:β=10:1)}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.95–5.74 (m, 2H), 5.06 (d, *J*=10.4 Hz, 1H), 4.98 (s, 1H), 3.99 (dq, *J*=9.2, 6.2 Hz, 1H), 3.83 (dq, *J*=9.6, 7.1 Hz, 1H), 3.56 (m, 1H), 2.09 (s, 3H), 1.30–1.24 (m, 3H), 1.23 (d, *J*=3.7 Hz, 3H) ppm; IR (film, cm^{-1}): 2977, 2933, 2857, 1742, 1449, 1372, 1231, 1029, 910, 772, 604; MS(ESI) *m/z*: 222.8 ([M+Na]$^+$50), 212.9(20).

*4.2.10. Cyclohexyl 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**5b**).* Colorless oil; $[\alpha]_D^{25}$ −162.35 (*c* 0.54, $CHCl_3$, α only) {lit[5x]: $[\alpha]_D^{25}$ −191 (*c* 0.63, $CHCl_3$, α only)}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.84–5.72 (m, 2H), 5.08 (s, 1H), 5.02 (d, *J*=10.4 Hz, 1H), 4.00 (dq, *J*=12.6, 6.3 Hz, 1H), 3.63–3.57 (m, 1H), 2.05 (s, 3H), 1.92–1.84 (m, 2H), 1.76–1.68 (m, 2H), 1.60–1.37 (m, 2H), 1.36–1.27 (m, 2H), 1.27–1.20 (m, 2H), 1.19 (d, *J*=6.3 Hz, 3H) ppm; IR (film, cm^{-1}): 2930, 2859, 1743, 1641, 1448, 1373, 1233, 1099, 1033, 912, 733; MS(ESI) *m/z*: 272.2([M+NH_4]$^+$100).

*4.2.11. L-Menthyl 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**5c**).* Colorless oil; $[\alpha]_D^{25}$ −279.66 (*c* 0.91, $CHCl_3$, α only) {lit[5x]: $[\alpha]_D^{25}$ −354 (*c* 1.15, $CHCl_3$, α only)}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.75 (dd, *J*=47.2, 10.2 Hz, 2H), 5.12 (s, 1H), 5.00 (d, *J*=8.7 Hz, 1H), 3.96–3.89 (m, 1H), 3.51 (td, *J*=10.6, 4.0 Hz, 1H), 2.26–2.23 (m, 1H), 2.06 (s, 3H), 1.65–1.61 (m, 2H), 1.36–1.23 (m, 3H), 1.18 (d, *J*=6.2 Hz, 3H), 1.07–0.96 (m, 2H), 0.90 (s, 3H), 0.88 (s, 3H), 0.79 (d, *J*=6.9 Hz, 3H), 0.73 (t, *J*=6.3 Hz, 1H) ppm; IR (film, cm^{-1}): 2925, 2866, 1745, 1453, 1374, 1233, 1095, 1030, 915, 810, 733; MS(ESI) *m/z*: 328.2([M+NH_4]$^+$100).

*4.2.12. (+)-endo-Fenacholyl 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**5d**).* Colorless oil; $[\alpha]_D^{25}$ −113.68 (*c* 0.87, $CHCl_3$, α:β=6:1) {lit[5x]: $[\alpha]_D^{25}$ −203 (*c* 1.56, $CHCl_3$, α:β=17:1)}; ^{1}H NMR (400 MHz, $CDCl_3$): δ5.85–5.79 (m, 2H), 4.98 (d, *J*=9.2 Hz, 1H), 4.85 (s, 1H), 3.97–3.90 (m, 1H), 3.18 (s, 1H), 2.05 (s, 3H), 1.69–1.62 (m, 3H), 1.46–1.24 (m, 3H), 1.19 (d, *J*=6.3 Hz, 3H), 1.07 (d, *J*=2.5 Hz, 1H), 1.03 (s, 3H), 1.00 (s, 3H), 0.84 (s, 3H) ppm; IR (film, cm^{-1}): 2965, 2929, 2870, 1746, 1644, 1451, 1371, 1231, 1083, 1049, 884, 761; MS(ESI) *m/z*: 331.1([M+Na]$^+$100).

*4.2.13. 2,2,2-Tribromomethyl ethoxyl 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**5e**).*[8] Colorless oil; $[\alpha]_D^{25}$ −186 (*c* 0.72, $CHCl_3$, α only); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.82 (d, *J*=10.2 Hz, 1H), 5.73 (d, *J*=10.2 Hz, 1H), 5.00 (d, *J*=9.3 Hz, 1H), 4.92 (s, 1H), 3.88 (m, 2H), 3.49 (s, 6H), 3.42–3.40 (m, 1H), 2.04 (s, 3H), 1.19 (d, *J*=6.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.15, 130.20, 127.07, 94.24, 70.56, 66.83, 65.23, 43.39, 34.60, 21.09, 17.91; IR (film, cm^{-1}): 2975, 2925, 2889, 1742, 1424, 1373, 1234, 1042, 994, 917, 852, 735, 670, 610; MS (ESI) *m/z*: 439.9([M+NH_4]$^+$30); HR-ESI: $C_{13}H_{23}O_4NBr_3$ [M+NH_4]$^+$ Calcd 493.9164, found 493.9172.

*4.2.14. Phenyl 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**5f**).* Yellow oil; $[\alpha]_D^{25}$ −174 (*c* 0.65, $CHCl_3$, α only);

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35–7.31 (m, 2H), 7.14–7.11 (m, 2H), 7.05 (t, *J*=7.3 Hz, 1H), 6.05–5.97 (m, 2H), 5.69 (s, 1H), 5.18–5.12 (m, 1H), 4.13 (qd, *J*=9.4, 6.3 Hz, 1H), 2.14 (s, 3H), 1.25 (d, *J*=6.3 Hz, 3H) ppm; IR (film, cm^{-1}): 2966, 2929, 2870, 1747, 1642, 1453, 1374, 1227, 1144, 1099, 1055, 921, 801, 760; MS(ESI) *m*/*z*: 266.1 ($[M+NH_4]^+$100).

*4.2.15. p-Methoxyphenyl 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**5g**).*[8] White solid; mp=112–114 °C; $[\alpha]_D^{25}$ −151 (*c* 1.5, $CHCl_3$, α only); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.06 (d, *J*=9.0 Hz, 2H), 6.86 (d, *J*=9.0 Hz, 2H), 6.04–5.95 (m, 2H), 5.55 (s, 1H), 5.14 (d, *J*=9.3 Hz, 1H), 4.14 (qd, *J*=12.5, 6.2 Hz, 1H), 3.80 (s, 3H), 2.13 (s, 3H), 1.25 (d, *J*=6.3 Hz, 3H) ppm; IR (film, cm^{-1}): 2955, 2929, 2873, 1743, 1640, 1458, 1373, 1235, 1106, 1035, 917, 740; MS(ESI) *m*/*z*: 296.1 ($[M+NH_4]^+$100).

*4.2.16. Ethyl 4,6-di-O-acetyl-2,3-dideoxy-a-D-erythro-1-thio-hex-2-enopyranoside (**7a**).* Yellow oil; $[\alpha]_D^{25}$ +132.1 (*c* 0.68, $CHCl_3$, α only) {lit[5g]: α:β=7:1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.88 (dd, *J*=10.1, 4.9 Hz, 1H), 5.72 (d, *J*=10.2 Hz, 1H), 5.53 (s, 1H), 5.30 (dd, *J*=9.2, 1.8 Hz, 1H),4.29–4.24 (m, 1H), 4.21 (dd, *J*=11.9, 5.4 Hz, 1H), 4.11 (dd, *J*=11.8, 1.9 Hz, 1H), 2.72–2.56 (m, 2H), 2.03 (s, 6H), 1.26 (t, *J*=7.4 Hz, 3H) ppm; IR (film, cm^{-1}):2978, 2931, 2873, 1744, 1664, 1448, 1374, 1236, 1105, 1055, 917, 727, 609; MS(ESI) *m*/*z*: 296.9 ($[M+Na]^+$80), 212.9(100).

*4.2.17. Dodecanyl 4,6-di-O-acetyl-2,3-dideoxy-a-D-erythro-1-thio-hex-2-enopyranoside (**7b**).* Yellowish oil; $[\alpha]_D^{25}$ +66 (*c* 0.62, $CHCl_3$, α only){lit[5g]: α:β=9:1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.96 (d, *J*=10.2 Hz, 1H), 5.79 (d, *J*=10.1 Hz, 1H), 5.57 (s, 1H), 5.39 (dd, *J*=9.1, 1.8 Hz, 1H), 4.37–4.27 (m, 2H), 4.18 (d, *J*=10.1 Hz, 1H), 2.79–2.70 (m, 1H), 2.69–2.59 (m, 1H), 2.12 (s, 3H), 2.11 (s, 3H), 1.70–1.62 (m, 3H), 1.40–1.27 (m, 17H), 0.90 (t, *J*=6.8 Hz, 3H) ppm; IR (film, cm^{-1}): 2925, 2856, 1747, 1638, 1570, 1453, 1372, 1232, 1049, 959, 788, 605; MS(ESI)*m*/*z*: 432.3 ($[M+NH_4]^+$100).

*4.2.18. Cyclohexyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-eno-1-thio-α-D-pyranoside (**7c**).* Colorless oil:$[\alpha]_D^{25}$ +90.15 (c 0.9, $CHCl_3$, α only) {lit[5x]: $[\alpha]_D^{25}$ +101.3 (*c* 1.0,$CHCl_3$, α:β=7:1)}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.92 (d, *J*=11.2 Hz, 1H), 5.75 (d, *J*=10.1 Hz, 1H), 5.65 (s, 1H), 5.34 (d, *J*=11.1 Hz, 1H), 4.36–4.14 (m, 3H), 2.93–2.85 (m, 1H), 2.09 (s, 3H), 2.08 (s, 3H), 2.03 (d, *J*=16.4 Hz, 2H), 1.76 (d, *J*=15.8 Hz, 2H), 1.60 (d, *J*=10.5 Hz, 1H), 1.46–1.29 (m, 5H) ppm; IR (film, cm^{-1}): 2932, 2874, 1738, 1652, 1447, 1373, 1236, 1050, 965, 833, 738, 608; MS (ESI) *m*/*z*:350.9 ($[M+Na]^+$85), 212.9 (100).

*4.2.19. Cyclohexyl 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-1-thio-hex-2-enopyranoside (**7f**).* Colorless oil:$[\alpha]_D^{25}$ −149.54 (*c* 0.81, $CHCl_3$, α only); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.91 (dd, *J*=12.5, 2.4 Hz, 1H), 5.74 (d, *J*=10.1 Hz, 1H), 5.61 (s, 1H), 5.11 (dd, *J*=9.0, 1.8 Hz, 1H), 4.18 (dq, *J*=12.5, 6.3 Hz, 1H), 2.95–2.86 (m, 1H), 2.10 (s, 3H), 2.03 (d, *J*=13.7 Hz, 2H), 1.77 (d, *J*=11.0 Hz, 2H), 1.66–1.60 (m, 1H), 1.36 (m, 5H), 1.24 (d, *J*=6.3 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.56, 129.45, 126.98, 79.18, 70.85, 64.76, 44.56, 34.37, 34.00, 26.05, 25.72, 21.12, 18.00; IR (film, cm^{-1}): 2927, 2854, 1742, 1638, 1572, 1415, 1374, 1232, 1092, 1048, 786, 646; MS (ESI) *m*/*z*: 288.2 ($[M+NH_4]^+$100); HR-ESI: $C_{14}H_{26}O_3NS$ $[M+NH_4]^+$ Calcd 288.1625, found 288.1628.

*4.2.20. Ethyl 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-1-thio-hex-2-enopyranoside (**7d**).* Colorless oil; $[\alpha]_D^{25}$ +15.33 (*c* 0.47, $CHCl_3$, α:β=14:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.90 (d, *J*=10.1 Hz, 1H), 5.74 (d, *J*=10.1 Hz, 1H), 5.51 (s, 1H), 5.10 (dd, *J*=8.9, 1.5 Hz, 1H), 4.14 (dq, *J*=12.6, 6.2 Hz, 1H), 2.79–2.59 (m, 2H), 2.09 (s, 3H), 1.31 (t, *J*=7.4 Hz, 3H), 1.23 (d, *J*=6.2 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.51, 129.17, 127.18, 79.82, 70.81, 64.83, 26.03, 21.10, 17.97, 15.37; IR (film, cm^{-1}): 2924, 2846, 1743, 1637, 1574, 1414, 1109, 1010, 923, 648; MS (ESI) *m*/*z*: 234.1 ($[M+NH_4]^+$100); HR-ESI: $C_{10}H_{20}O_3NS$ $[M+NH_4]^+$ Calcd 234.1156, found 234.1158.

*4.2.21. Dodecanyl 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-1-thio-hex-2- enopyranoside (**7e**).* Colorless oil; $[\alpha]_D^{25}$ −126.72 (*c* 1.04, $CHCl_3$, α:β=10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.96–5.89 (m, 1H), 5.75 (d, *J*=10.1 Hz, 1H), 5.50 (s, 1H), 5.13 (dd, *J*=8.9, 1.7 Hz, 1H), 4.16 (dq, *J*=12.6, 6.2 Hz, 1H), 2.78–2.59 (m, 2H), 2.11 (s, 3H), 1.80–1.51 (m, 3H), 1.40–1.26 (m, 20H), 0.90 (t, *J*=6.7 Hz, 3H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 129.25, 127.10, 80.25, 70.86, 64.85, 32.16, 31.92, 30.13, 29.76, 29.13, 28.83, 22.70, 21.13, 18.00, 14.13; IR (film, cm^{-1}): 2925, 2865, 1744, 1637, 1572, 1417, 1371, 1233, 1043, 911, 784; MS (ESI) *m*/*z*: 374.3 ($[M+NH_4]^+$100); HR-ESI: $C_{20}H_{40}O_3NS$ $[M+NH_4]^+$ Calcd 374.2718, found 374.2723.

*4.2.22. Ethyl 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-3-thio-hex-2-enopyranoside (**8d**).* Colorless oil:$[\alpha]_D^{25}$ +58.5 (*c* 1.1, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.39 (dd, *J*=6.0, 2.1 Hz, 1H, H-1), 4.95 (t, *J*=8.3 Hz, 1H, H-4), 4.75 (dd, *J*=6.0, 2.5 Hz, 1H, H-2), 3.92 (dq, *J*=12.9, 6.4 Hz, 1H, H-5), 3.34 (dt, *J*=8.0, 2.3 Hz, 1H, H-3), 2.62–2.48 (m, 2H, $-CH_2-$), 2.13 (s, 3H, $-COCH_3$), 1.29 (d, *J*=6.4 Hz, 3H, C_5-CH_3), 1.22 (t, *J*=7.5 Hz, 3H, $-CH_2-CH_3$) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.01, 144.45, 102.04, 73.73, 72.47, 42.51, 22.91, 20.96, 17.28, 14.64; IR (film, cm^{-1}): 2977, 2929, 2891, 1742, 1648, 1426, 1366, 1231, 1033, 993, 910, 728, 610; MS (ESI) *m*/*z*: 234.1 ($[M+NH_4]^+$50); HR-ESI: $C_{10}H_{20}O_3NS$ $[M+NH_4]^+$ Calcd 7234.1156, found 234.1158.

*4.2.23. Dodecanyl 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-3-thio-hex-2-enopyranoside (**8e**).* Colorless oil: $[\alpha]_D^{25}$ +81.6 (*c* 1.32, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.42 (dd, *J*=6.0, 2.0 Hz, 1H, H-1), 4.97 (t, *J*=8.3 Hz, 1H, H-4), 4.77 (dd, *J*=6.0, 2.5 Hz, 1H, H-2), 3.95 (dq, *J*=13.0, 6.4 Hz, 1H, H-5), 3.36 (dt, *J*=7.9, 2.2 Hz, 1H, H-3), 2.55 (dd, *J*=16.3, 7.5 Hz, 2H, $-SCH_2-$), 2.15 (s, 3H, $-COCH_3$), 1.59 (d, *J*=5.7 Hz, 3H, C_5-CH_3), 1.33–1.28 (m, 20H, 10-CH_2-), 0.90 (s, 3H, $-CH_2-CH_3$) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.02, 144.50, 102.11, 73.77, 72.50, 42.61, 31.92, 29.45, 28.89, 22.68, 20.98, 17.30, 14.11; IR (film, cm^{-1}): 2925, 2846, 1745, 1633, 1574, 1416, 1223, 1097, 1007, 914, 815, 649; MS (ESI) *m*/*z*: 374.3 ($[M+NH_4]^+$100); HR-ESI: $C_{20}H_{40}O_3NS$ $[M+NH_4]^+$ Calcd 374.2720, found 374.2723.

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Supplementary data

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