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$RuCl_3 \cdot 3H_2O$ as catalyst for Ferrier rearrangement: an efficient procedure for the preparation of pseudoglycosides

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ABSTRACT

By using $RuCl_3 \cdot 3H_2O$ as catalyst, an improved method for the synthesis of 2,3-unsaturated-glycosides has been established. A series of 2, 3-unsaturated-glucosides were obtained from 2,4,6-tri-*O*-acetyl-D-glucal or 3,4-di-*O*-acetyl-6-deoxy-L-glucal in good yield and high anomeric selectivity.

1. Introduction

2,3-Unsatureted-glycosides are of great importance in synthesis and have been widely used as chiral intermediates in the preparation of biologically active compounds[1] and functional materials[2] since they could provide the regio- and stereo-varieties for the subsequent reactions. One of the most useful procedures to achieve 2,3-unsaturated glycosides directly and efficiently is Type I Ferrier Rearrangement, in which glycal is reacted with nucleophile with the catalysis of various Lewis acid catalysts. This reaction is supposed to proceed through a highly resonance-stabilized cyclic allylic oxocarbonium intermediate, which is formed via removal of the leaving group at C-3 position of the glycal promoted by catalyst, followed by the attack of a nucleophile via quasi-equatorial orientation[3] (Scheme 1).

Besides some other type of catalysts, Lewis acids have been reported to be the major catalyst in Type I Ferrier Rearrangement. A wide range of Lewis acid catalysts, such as $BF_3 \cdot Et_2O$, $FeCl_3$, $Fe_2(SO_4)_3$, $Fe(NO_3)_3$, $InCl_3$, $BiCl_3$, $CeCl_3$, $ZnCl_2$, $Pd(OAc)_2$, $ZrCl_4$, $K_5CoW_{12}O_{40} \cdot 3H_2O$, $Bi(OTf)_3$, $Er(OTf)_3$, $Yb(OTf)_3$, $Fe(OTf)_3$, $TiCl_4$, $AuCl_3$, HBF_4–SiO_2, $ZnCl_2/Al_2O_3$, $TiCl_3(OTf)$ have been reported in the literature.[4] However, some of those reaction systems suffered from the drawbacks in terms of large excess of nucleophile, stoichiometric amount of catalyst, harsh reaction conditions, and low yields, which leading to extensive work up. We therefore have interest in finding new efficient catalyst for this reaction for milder and more efficient synthetic process with good anomeric selectivity and yield by using stoichiometric amount of nucleophile under low catalyst load.

In our previous investigation in the Type I Ferrier Rearrangement catalyzed by metal Lewis acid $Fe(OTf)_3$[4v] and $TiCl_3(OTf)$,[4x] a series of alcohols were reacted with 3,4,6-tri-*O*-acetyl-D-glucal affording 2,3-unsaturated *O*-glycosides in high yield and good anomeric selectivity. The influence of the inductive and the steric effects of the nucleophiles on the reaction results has also been examined. Following our previous work, now we report our results using $RuCl_3 \cdot 3H_2O$ as a new highly efficient catalyst for Type I Ferrier Rearrangement of various glucals with alcohols or thiols as nucleophiles.

2. Results and discussion

2.1. Role of the counter-ion in the metal chloride catalysts

For comparison of the catalytic activity of different metal chloride catalysts, a comparative study has been carried out by using tri-*O*-acetyl-D-glucal (**1**) and EtOH as the nucleophile in a model system catalyzed by $RuCl_3 \cdot 3H_2O$ and some other different chloride catalyst Lewis acid catalysts, including $FeCl_3$,[5a] $InCl_3$,[5b,c] $ZnCl_2$,[4s] and $TiCl_4$,[4w] which have been reported to be used in

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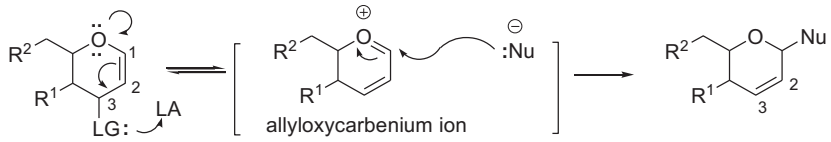


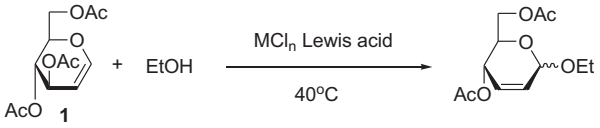
LG = leaving group

LA = Lewis acid catalyst

Scheme 1. Mechanism of Type I Ferrier Rearrangement proposed by R. J. Ferrier.[3b,f]

Type I Ferrier Rearrangement as catalysts. Results are shown in Table 1.

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	$TiCl_4$	24 h	Trace	/
2	$ZnCl_2$	24 h	N.R.	/
3	$SnCl_2$	24 h	Trace	/
4	$FeCl_3$	24 h	N.R.	/
5	$RuCl_3 \cdot 3H_2O$	18 h	44	4:1

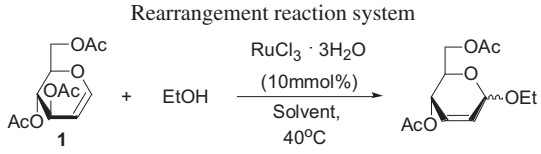
[a] Reaction conditions: tri-*O*-acetyl-D-glucal (**1**) (188 mg, 0.7 mmol), EtOH (5 mL), catalyst (10 mol %), 40 °C.
[b] Determined by analysis of the ^1H NMR spectra of the reaction mixture.
[c] The anomeric ratio was determined by integration of the anomeric hydrogen in the ^1H NMR spectra.

Results shown in Table 1 demonstrate the obviously different catalytic activity of the metal chloride catalysts with various counter-ions in this reaction. Among the tested metal chloride catalysts, $RuCl_3 \cdot 3H_2O$ is the most efficient one in terms of conversion and selectivity, which indicates that Ru(III) anion might attract the leaving group more effectively to form the intermediate allyloxycarbenium ion (Scheme 1).

2.2. Optimization of solvent

Solvent played an important role in the reaction. Therefore, optimization has been carried out. Table 2 shows the results.

Table 2
Optimization of solvent[a] for the $RuCl_3 \cdot 3H_2O$ catalyzed Ferrier Rearrangement reaction system



Entry	Solvent	Reaction time	Conversion (%)[b]	α:β[c]
1	Acetonitrile	30 min	89.5	7:1
2	DCM	40 min	77	6:1
3	THF	30 min	76	5:1
4	Toluene	50 min	77	7:1

[a] Reaction conditions: tri-*O*-acetyl-D-glucal (**1**) (188 mg, 0.7 mmol), EtOH (1.3 equiv), $RuCl_3 \cdot 3H_2O$ (10 mol %), solvent (5 mL), 40 °C.
[b] Determined by analysis of the ^1H NMR spectra of the reaction mixture.
[c] The anomeric ratio was determined by integration of the anomeric hydrogen in the ^1H NMR spectra.

By comparison of the results in entry 1 with the others in Table 2, acetonitrile appeared to be the most proper solvent. This might be attributed to its higher hydrophilic character than those of other tested solvents.

2.3. Type I Ferrier Rearrangement under the optimized conditions

After the optimization, we have established our reaction conditions: with $RuCl_3 \cdot 3H_2O$ (10 mol %) as the catalyst and acetonitrile as the solvent, the Ferrier Rearrangement was performed between 3,4,6-tri-*O*-acetyl-D-glucal (1 equiv) or 3,4-di-*O*-acetyl-6-deoxy-L-glucal (1 equiv) and various nucleophiles (1.5 equiv) at 40 °C. Results are summarized in Table 3. The structure and stereochemistry of all the glycosidation products were characterized by ^1H NMR, ^{13}C NMR, IR, and MS data.

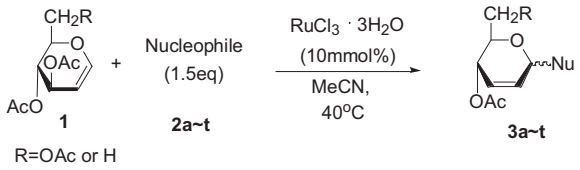
Generally, the reaction afforded 2,3-unsaturated glycosides in high yield with good anomeric selectivity. While using tri-*O*-acetyl-D-glucal as starting material, the simple alcohols (entries 1–3, Table 3) as the nucleophile gave the products with lower selectivity on the anomeric center, while those with higher steric hindrance (entries 4 and 5, Table 3) gave the products, which are good both in yield and in anomeric selectivity. Thiol (entry 6, Table 3) could be used as nucleophile in this reaction system and gives the product in satisfactory yield and selectivity. If 3,4-di-*O*-acetyl-6-deoxy-L-glucal was used, even those nucleophiles with relative low steric hindrance could give the products with high selectivity on the anomeric center (entries 14–17, Table 3).

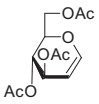
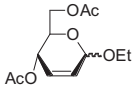
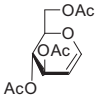
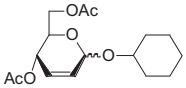
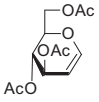
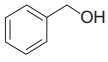
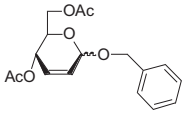
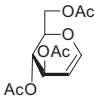
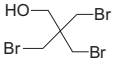
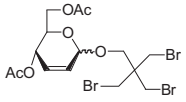
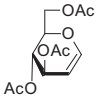
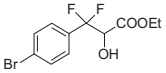
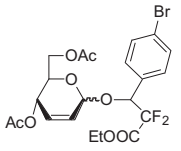
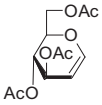
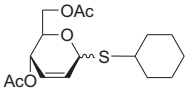
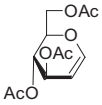
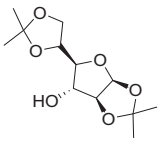
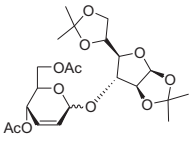
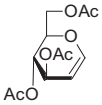
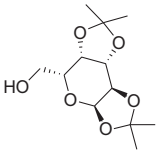
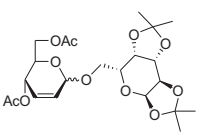
The scope of this procedure for the preparation of 2,3-unsaturated *O*-glycoside connected with various biologically important natural products has also been explored. Formation of two disaccharides (entries 7 and 8, Table 3), three steroid glycosides (entries 11–13, and 20, Table 3) and two other natural product (L-menthol and (1*R*)-*endo*-(+)-fenchol) glycosides (entries 9, 10, 18, and 19, Table 3) in good yield and high selectivity demonstrated the catalytic capability of $RuCl_3 \cdot 3H_2O$ in the synthesis of natural product analogs by the Ferrier Rearrangement.

3. Conclusion

We have established a practical procedure for Type I Ferrier Rearrangement with $RuCl_3 \cdot 3H_2O$ as the catalyst. Comparing with the metal Lewis acid $Fe(OTf)_3$[4v] and $TiCl_3(OTf)$,[4x] the reactions time of Ferrier Rearrangement promoted by $RuCl_3 \cdot 3H_2O$ could be reduced obviously. As an advantage, nucleophile other than alcohols, such as thiol, was used in this reaction system and gave satisfactory result. Besides tri-*O*-acetyl-D-glucal, 3,4-di-*O*-acetyl-6-deoxy-L-glucal was tested as another starting material and a series of corresponding 2,3-unsaturated glycosides were prepared with good yield and high selectivity, which meant that compared with our previous achievement, $RuCl_3 \cdot 3H_2O$, as the catalyst of Type I Ferrier Rearrangement, was applicable to more kinds of glucals.

Table 3
Type I Ferrier Rearrangement reaction of 3,4,6-tri-*O*-acetyl-D-glucal or 3,4-di-*O*-acetyl-6-deoxy-L-glucal (**1**) with various nucleophiles (**2a**–**t**) catalyzed by $RuCl_3 \cdot 3H_2O$[a]



Entry	Glycals (**1**)	Nucleophiles (**2**)	Time	Products (**3**)	Yield[b]/(α:β)[c]
1		EtOH	10 min	 **3a**	89% (7:1)
2			10 min	 **3b**	90% (10:1)
3			10 min	 **3c**	81% (7:1)
4			10 min	 **3d**	83% (17:1)
5			10 min	 **3e**	55% (12:1)
6[d]			5 h	 **3f**	65% (7:1)
7			30 min	 **3g**	50% (α only)
8			10 min	 **3h**	60% (5:1)

(*continued on next page*)

Table 3 (*continued*)

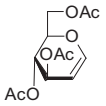
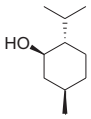
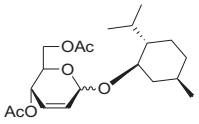
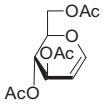
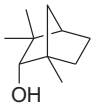
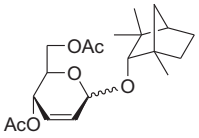
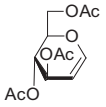
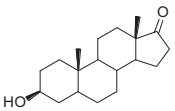
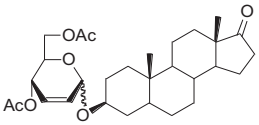
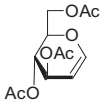
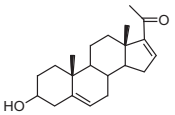
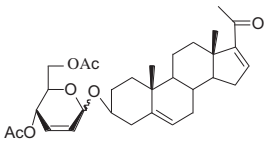
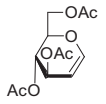
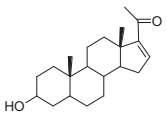
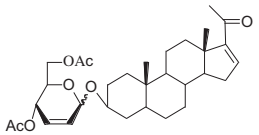
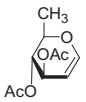
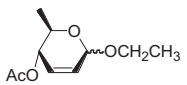
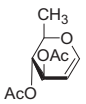
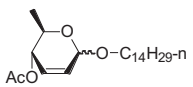
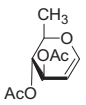
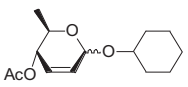
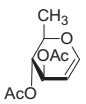
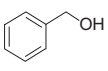
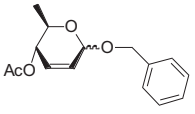
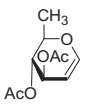
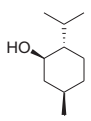
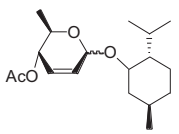
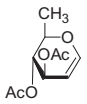
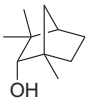
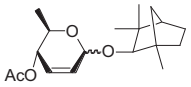
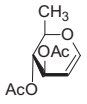
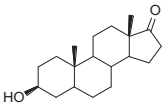
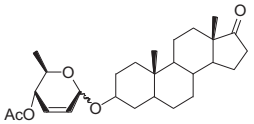
Entry	Glycals (**1**)	Nucleophiles (**2**)	Time	Products (**3**)	Yield[b]/(α:β)[c]
9			30 min	 **3i**	79% (α only)
10			5 min	 **3j**	75% (15:1)
11			20 min	 **3k**	70% (6:1)
12			20 min	 **3l**	52% (α only)
13			15 min	 **3m**	55% (10:1)
14		EtOH	10 min	 **3n**	78% (10:1)
15		*n*-$C_{14}H_{29}OH$	20 min	 **3o**	65% (12:1)
16			20 min	 **3p**	64% (α only)
17			10 min	 **3q**	71% (α only)
18			20 min	 **3r**	68% (α only)

Table 3 (*continued*)

Entry	Glycals (**1**)	Nucleophiles (**2**)	Time	Products (**3**)	Yield[b]/(α:β)[c]
19			10 min	 **3s**	75% (17:1)
20			10 min	 **3t**	40% (13:1)

[a] General reaction conditions: tri-*O*-acetyl-D-glucal (188 mg, 0.7 mmol) or 3,4-di-*O*-acetyl-6-deoxy-L-glucal (177 mg, 0.7 mmol), nucleophile (**2a**–**t**) (1.5 equiv), $RuCl_3 \cdot 3H_2O$ (20 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.
[d] The reaction temperature was −20 °C.

By using $RuCl_3 \cdot 3H_2O$ as catalyst, a series of alcohols and thiols were reacted with glucal donor affording 2,3-unsaturated glycosides in high yield and good anomeric selectivity. The influence of the inductive and the steric effects of the nucleophiles on the reaction results has also been examined. This reaction system has also demonstrated its applicability in the synthesis of natural product analogs of biological interest by the Ferrier Rearrangement.

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 M Hz) 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. Glucal, epiandrosterone, 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 2,4,6-tri-*O*-acetyl-D-glucal or 3,4-di-*O*-acetyl-6-deoxy-L-glucal catalyzed with $RuCl_3 \cdot 3H_2O$

To a stirred solution of tri-*O*-acetyl-D-glucal (188 mg, 0.7 mmol) or 3,4-di-*O*-acetyl-6-deoxy-L-glucal (177 mg, 0.7 mmol) and the corresponding nucleophile (1.5 equiv) in MeCN (5 mL) were added $RuCl_3 \cdot 3H_2O$ (10 mol %) at ambient temperature. The mixture was stirred under 40 °C for the appropriate amount of time (Table 3), 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 (3×20 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=8/1 while tri-*O*-acetyl-D-glucal as starting material or hexane/EtOAc=25/1 while 3,4-di-*O*-acetyl-6-deoxy-L-glucal as starting material).

*4.2.1. Ethyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3a**).* Colorless oil; $[\alpha]_D^{25}$ +112.5 (*c* 1.67, $CHCl_3$, α:β=7:1) {lit.[4x]: $[\alpha]_D^{25}$ +82.72 (*c* 0.83, $CHCl_3$, α:β=7:1)}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.89 (q, *J*=10.5 Hz, 2H), 5.34 (d, *J*=9.7 Hz, 1H), 5.07 (s, 1H), 4.37–4.11 (m, 3H), 3.92–3.80 (m, 1H), 3.68–3.54 (m, 1H), 2.12 (s, 3H), 2.10 (s, 3H), 1.28 (t, *J*=7.0 Hz, 3H) ppm; IR (film, cm^{-1}): 2978, 2896, 2896, 1738, 1642, 1378, 1235, 1142, 1044, 894, 731, MS (ESI) *m*/*z*: 280.9 ($[M+Na]^+$, 75), 212.9 (100), 153.0 (60).

*4.2.2. Cyclohexyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3b**).* Colorless oil; $[\alpha]_D^{25}$ +135.5 (*c* 1.60, $CHCl_3$, α:β=10:1) {lit.[4x]: $[\alpha]_D^{25}$ +65.3 (*c* 0.60, $CHCl_3$, α:β=8:1)}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.83 (q, *J*=10.3 Hz, 2H), 5.28 (d, *J*=9.4 Hz, 1H), 5.16 (s, 1H), 4.18 (dd, *J*=17.8, 8.2 Hz, 3H), 3.63 (dd, *J*=10.7, 7.2 Hz, 1H), 2.08 (s, 3H), 2.07 (s, 3H), 1.97–1.84 (m, 2H), 1.73 (d, *J*=4.4 Hz, 2H), 1.54 (d, *J*=10.3 Hz, 1H), 1.29 (ddd, *J*=28.0, 19.2, 11.1 Hz, 5H) ppm. IR (film, cm^{-1}):2933, 2851, 1744, 1637, 1372, 1234, 1037, 967. MS (ESI) *m*/*z*: 335.0 ($[M+Na]^+$, 55); 212.8 (100).

*4.2.3. Benzyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3c**).* Colorless oil; $[\alpha]_D^{25}$ +156.2 (*c* 1.43, $CHCl_3$, α:β=7:1) {lit.[4x]: $[\alpha]_D^{25}$ +46.6 (*c* 0.64, $CHCl_3$, α only)}; ^1H NMR (400 MHz, $CHCl_3$) δ 7.39 (d, *J*=3.9 Hz, 5H), 5.91 (q, *J*=10.7 Hz, 2H), 5.36 (d, *J*=9.5 Hz, 1H), 5.17 (s, 1H), 4.84 (d, *J*=11.7 Hz, 1H), 4.63 (d, *J*=11.6 Hz, 1H), 4.36–4.08 (m, 3H), 2.13 (s, 3H), 2.11 (s, 3H) ppm; IR (film, cm^{-1}):2880, 1743, 1650, 1450, 1143, 1039, 962, 833, 736, 699. MS (ESI) *m*/*z*: 338.0 ($[M+NH_4]^+$, 100); 212.9 (85).

*4.2.4. 2,2,2-Tribromomethyl ethoxyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3d**).* Colorless oil; $[\alpha]_D^{25}$ +88.7 (*c* 2.26, $CHCl_3$, α:β=17:1); {lit.[4x]: $[\alpha]_D^{25}$ +73 (*c* 0.65, $CHCl_3$, α:β=10:1); ^1H NMR (400 MHz, $CDCl_3$) δ 5.89 (dd, *J*=39.7, 10.2 Hz, 2H), 5.36 (d, *J*=9.7 Hz, 1H), 5.07 (s, 1H), 4.26 (t, *J*=3.8 Hz, 2H), 4.15–4.05 (m, 1H), 3.96 (d, *J*=9.4 Hz, 1H), 3.57 (s, 6H), 3.52 (d, *J*=9.4 Hz, 1H), 2.13 (s, 3H), 2.12 (s, 3H) ppm; IR (film, cm^{-1}):2957, 1743, 1645, 1424, 1375, 1231, 1043, 905, 853, 741, 665, 609. MS (ESI): *m*/*z* 555.8 ($[M+NH_4]^+$, 100).

*4.2.5. Ethyl 2,2-difluoro-3-O-(4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-3-(4-bromophenyl)propanoate (**3e**).* Colorless oil; $[\alpha]_D^{25}$ +182.4 (*c* 0.58, $CHCl_3$, α:β=12:1); ^1H NMR (400 MHz, $CDCl_3$) δ 7.55 (t, *J*=7.1 Hz, 2H), 7.41–7.30 (m, 2H), 5.95 (d, *J*=10.3 Hz, 1H), 5.80 (dd, *J*=21.4, 10.2 Hz, 1H), 5.44–5.25 (m, 2H), 5.14 (dd, *J*=15.4, 8.1 Hz, 1H), 4.88 (s, 1H), 4.40–4.22 (m, 3H), 4.09–3.99 (m, 1H), 2.16 (s, 3H), 2.12 (s, 3H), 1.34 (t, *J*=7.0 Hz, 3H); ^{13}C

NMR (101 MHz, $CDCl_3$): δ 170.87, 170.56, 170.21, 133.13, 131.88, 130.70, 129.82, 126.47, 124.08, 96.69, 91.21, 67.75, 64.85, 63.20, 62.42, 61.83, 20.96, 20.80, 13.95; ^{19}F NMR (377 MHz, $CDCl_3$) δ −119.20 (d, *J*=15.4 Hz), −119.47 (d, *J*=16.2 Hz) ppm; IR (film, cm^{-1}):2944, 1744, 1652, 1483, 1376, 1305, 1299, 908, 860, 741, 647, 609. MS (ESI): *m/z* 543.0 ($[M+Na]^+$, 100). HR-ESI $C_{21}H_{23}Br_1F_2Na_1O_8$ $[M+Na]^+$ calcd 543.0439, found 543.0437.

*4.2.6. Cyclohexyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-eno-1-thio-α-D-pyranoside (**3f**).* Colorless oil; $[\alpha]_D^{25}$ +101.3 (*c* 1.0, $CHCl_3$, α:β=7:1); {lit.[6a]: $[\alpha]_D^{25}$ +78 (*c* 0.80, $CHCl_3$, α only)}, ^1H NMR (400 MHz, $CDCl_3$) δ 5.95 (d, *J*=10.0 Hz, 1H), 5.78 (d, *J*=10.0 Hz, 1H), 5.69 (s, 1H), 5.37 (d, *J*=9.3 Hz, 1H), 4.43–4.15 (m, 3H), 2.92 (t, *J*=10.2 Hz, 1H), 2.12 (s, 3H), 2.11 (s, 3H), 2.04 (s, 2H), 1.77 (s, 2H), 1.62 (d, *J*=15.7 Hz, 1H), 1.50–1.25 (m, 5H); IR (film, cm^{-1}):2930, 2854, 1742, 1645, 1445, 1372, 1231, 1049, 966, 896, 832, 790, 648. MS (ESI): *m/z*346.0 ($[M+NH_4]^+$, 100).

*4.2.7. 3-O-(4,6-Di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-l,l2:5,6-di-O-isopropylidene-α-D-glucofuranose (**3g**).* Colorless oil; $[\alpha]_D^{25}$ +139.8 (*c* 0.51, $CHCl_3$, α only); {lit.[4x]: $[\alpha]_D^{25}$ +77 (*c* 0.56, $CHCl_3$, α:β=5:1)}; ^1H NMR (400 MHz, $CDCl_3$): δ 5.91 (d, *J*=3.2 Hz, 2H), 5.86 (d, *J*=10.0 Hz, 1H), 5.29 (s, 2H), 4.65 (d, *J*=3.0 Hz, 1H), 4.34 (d, *J*=2.0 Hz, 1H), 4.28–4.06 (m, 6H), 4.00 (dd, *J*=8.0, 4.9 Hz, 1H), 2.14 (s, 3H), 2.11 (s, 3H), 1.51 (s, 3H), 1.42 (s, 3H), 1.34 (s, 3H), 1.33 (s, 3H) ppm; IR (film, cm^{-1}): 2986, 1745, 1630, 1376, 1038, 845. MS (ESI) *m/z*: 490.1 ($[M+NH_4]^+$, 100); 472.1 (38).

*4.2.8. 6-O-(4,6-Di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-1,2:3,4-di-O-isopropylidene-α-D-galactopyranose (**3h**).* White solid; mp=132–134 °C; $[\alpha]_D^{25}$ +17.6 (*c* 0.83, $CHCl_3$, α:β=5:1); {lit.[4x]: $[\alpha]_D^{25}$ +24.2 (*c* 0.73, $CHCl_3$, α:β=6:1)}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.94–5.81 (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), 4.39–4.24 (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}):2996, 2930, 1741, 1638, 1450, 1378, 1226, 1172, 1051, 1004, 892, 645. MS (ESI): *m/z* 490.1 ($[M+NH_4]^+$, 100).

*4.2.9. L-Menthyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3i**).* Colorless oil; $[\alpha]_D^{25}$ 27.0 (*c* 0.50, $CHCl_3$, α only) {lit.[4x]: $[\alpha]_D^{25}$ +141 (*c* 0.53, $CHCl_3$, α only)}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.85 (s, 2H), 5.26 (d, *J*=8.9 Hz, 1H), 5.08 (s, 1H), 4.27–4.08 (m, 3H), 3.41 (td, *J*=10.4, 3.9 Hz, 1H), 2.19 (t, *J*=11.8 Hz, 1H), 2.09 (s, 3H), 2.06 (s, 3H), 1.61 (d, *J*=9.7 Hz, 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}): 2952, 2865, 1744, 1634, 1455, 1374, 1234, 1183, 1037, 911; MS (ESI) *m/z*: 391.0 ($[M+Na]^+$, 100), 212.9 (75).

*4.2.10. (+)-endo-Fenacholyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3j**).* White solid; mp=75–77 °C; $[\alpha]_D^{25}$ +132.3.6 (*c* 1.45, $CHCl_3$, α:β=15:1); {lit.[4x]: $[\alpha]_D^{25}$ +55.1 (*c* 0.54, $CHCl_3$, α only); mp=74–76 °C}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.89 (s, 2H), 5.32 (d, *J*=9.5 Hz, 1H), 5.01 (s, 1H), 4.34–4.12 (m, 3H), 3.48 (s, 1H), 2.12 (s, 6H), 1.67 (t, *J*=19.6 Hz, 4H), 1.54–1.26 (m, 3H), 1.14 (s, 3H), 1.07 (s, 3H), 0.90 (s, 3H) ppm; IR (film, cm^{-1}): 2956, 2876, 1743, 1644, 1461, 1373, 1329, 1228, 1040, 900, 832, 749. MS (ESI) *m/z*: 389.0 ($[M+Na]^+$, 70); 212.9 (100).

*4.2.11. Epiandrosteronyl-4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3k**).* White solid; mp=125–126 °C; $[\alpha]_D^{25}$ +112.7 (*c* 1.81, $CHCl_3$, α:β=6:1) {lit.[4x]: $[\alpha]_D^{25}$ +106 (*c* 0.61, $CHCl_3$, α:β=10:1); mp=124–126 °C}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.89 (t, *J*=12.2 Hz, 2H), 5.34 (d, *J*=9.7 Hz, 1H), 5.20 (s, 1H), 4.22 (dd, *J*=18.4, 8.2 Hz, 3H), 3.66 (s, 1H), 2.47 (dd, *J*=19.4, 9.0 Hz, 1H), 2.13 (s, 3H), 2.11 (s, 3H), 1.99–1.67 (m, 7H), 1.59–1.42 (m, 4H), 1.31 (d, *J*=20.3 Hz, 6H), 1.18 (d, *J*=11.6 Hz, 1H), 0.98 (t, *J*=11.9 Hz, 2H), 0.88 (s, 3H), 0.85 (s, 3H), 0.73 (d, *J*=10.0 Hz, 1H) ppm; IR (film, cm^{-1}): 2932, 2851, 1743, 1636, 1450, 1377, 1234, 1035; MS (ESI) *m/z*: 525.2 ($[M+Na]^+$, 100), 212.8 (8).

*4.2.12. 16-Dehydropregnenolonyl-4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3l**).* White solid; mp 72–73 °C; $[\alpha]_D^{25}$ +176.3 (*c* 1.38, $CHCl_3$, α only) {lit.[4x]: $[\alpha]_D^{25}$ +134 (*c* 0.51, $CHCl_3$, α only); 71–73 °C}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.74 (s, 1H), 5.88 (dd, *J*=23.8, 10.4 Hz, 2H), 5.39 (s, 1H), 5.33 (d, *J*=9.2 Hz, 1H), 5.20 (s, 1H), 4.25 (dt, *J*=20.5, 8.1 Hz, 3H), 3.66–3.49 (m, 1H), 2.51–2.35 (m, 3H), 2.29 (s, 3H), 2.13 (s, 3H), 2.11 (s, 3H), 2.05 (d, *J*=16.3 Hz, 2H), 1.95–1.86 (m, 2H), 1.73–1.26 (m, 10H), 1.06 (s, 3H), 0.94 (s, 3H) ppm; IR (film, cm^{-1}): 2939, 1745, 1664, 1439, 1372, 1233, 1037, 971. MS (ESI) *m/z*: 549.2 ($[M+Na]^+$, 100), 213.0 (8).

*4.2.13. (5,6-Dihydro-16-dehydropregnenolonyl)-4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3m**).* White solid; mp=127–129 °C; $[\alpha]_D^{25}$ +192.4 (*c* 1.63, $CHCl_3$, α:β=10:1) {lit.[4x]: $[\alpha]_D^{25}$ +76 (*c* 0.53, $CHCl_3$, α only); 124–126 °C}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.72 (s, 1H), 5.87 (dd, *J*=22.7, 10.3 Hz, 2H), 5.33 (d, *J*=9.4 Hz, 1H), 5.20 (s, 1H), 4.22 (dd, *J*=18.3, 7.9 Hz, 3H), 3.65 (t, *J*=10.8 Hz, 1H), 2.38 (dd, *J*=27.6, 15.3 Hz, 1H), 2.28 (s, 3H), 2.13 (s, 3H), 2.10 (s, 3H), 2.07–1.82 (m, 2H), 1.79–1.56 (m, 6H), 1.44 (d, *J*=11.5 Hz, 4H), 1.32 (d, *J*=8.6 Hz, 3H), 1.19–0.94 (m, 3H), 0.90 (s, 3H), 0.86 (s, 3H), 0.73 (t, *J*=9.3 Hz, 1H). IR (film, cm^{-1}): 2933, 2847, 1745, 1664, 1443, 1373, 1234, 1035, 910, 816, 743; MS (ESI) *m/z*: 551.2 ($[M+Na]^+$, 100), 213.0 (8).

*4.2.14. Ethyl 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3n**).*[6b] Colorless oil; $[\alpha]_D^{25}$ +21.9 (*c* 0.67, $CHCl_3$, α:β=10:1); ^1H NMR (400 MHz, $CDCl_3$) δ 5.87 (t, *J*=9.1 Hz, 2H), 5.08 (d, *J*=8.9 Hz, 1H), 5.00 (s, 1H), 4.01 (dq, *J*=12.6, 6.3 Hz, 1H), 3.85 (dq, *J*=14.5, 7.2 Hz, 1H), 3.71–3.42 (m, 1H), 2.11 (s, 3H), 1.28 (d, *J*=7.1 Hz, 3H), 1.26–1.24 (m, 3H) ppm; IR (film, cm^{-1}): 2979, 2889, 1742, 1690, 1474, 1474, 1382, 1309, 1237, 1045, 927, 640; MS (ESI) *m/z*: 222.9 ($[M+Na]^+$, 40); 212.4 (15).

*4.2.15. n-Tetradecyl 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3o**).* Colorless oil; $[\alpha]_D^{25}$ −140.8 (*c* 1.16, $CHCl_3$, α:β=12:1); ^1H NMR (400 MHz, $CDCl_3$) δ 5.94–5.79 (m, 2H), 5.07 (d, *J*=8.1 Hz, 1H), 4.97 (s, 1H), 4.09–3.94 (m, 1H), 3.77 (dd, *J*=11.5, 4.7 Hz, 1H), 3.55–3.46 (m, 1H), 2.10 (s, 3H), 1.61 (dd, *J*=13.5, 6.6 Hz, 3H), 1.26 (d, *J*=9.3 Hz, 24H), 0.90 (t, *J*=6.7 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 170.58, 129.52, 127.97, 94.36, 70.97, 68.78, 64.73, 31.94, 29.83, 29.68, 29.68, 29.68, 29.68, 29.68, 29.62, 29.42, 29.38, 26.19, 22.71, 21.11, 18.00, 14.14. IR (film, cm^{-1}):2925, 2857, 1744, 1637, 1460, 1375, 1235, 1099, 1044, 918, 724. MS (ESI): *m/z* 391.3 ($[M+Na]^+$, 100); HR-ESI:$C_{22}H_{40}Na_1O_4$ $[M+Na]^+$ calcd 391.2816, found 391.2819.

*4.2.16. Cyclohexyl 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3p**).* Colorless oil; $[\alpha]_D^{25}$ −191 (*c* 0.63, $CHCl_3$, α only) {lit.[6c]: α:β=6.2:1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.84 (t, *J*=11.0 Hz, 2H), 5.13 (s, 1H), 5.07 (d, *J*=9.3 Hz, 1H), 4.05 (dd, *J*=9.1, 6.3 Hz, 1H), 3.70–3.51 (m, 1H), 2.10 (s, 3H), 1.92 (d, *J*=4.3 Hz, 2H), 1.76 (d, *J*=4.0 Hz, 2H), 1.67–1.50 (m, 2H), 1.35 (s, 2H), 1.31 (s, 2H), 1.24 (d, *J*=6.3 Hz, 3H); IR (film, cm^{-1}):2931, 2856, 1744, 1636, 1450, 1375, 1236, 1096, 1038, 913, 737; MS (ESI): *m/z* 277.0 ($[M+Na]^+$, 100).

*4.2.17. Benzyl 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3q**).* Colorless oil; $[\alpha]_D^{25}$ −228 (*c* 0.51, $CHCl_3$, α only) {lit.[4q]: α:β=5:1}; ^1H NMR (400 MHz, $CDCl_3$): δ 7.41–7.30 (m, 5H), 5.87 (q, *J*=10.3 Hz, 2H), 5.09 (s, 2H), 4.81 (d, *J*=11.9 Hz, 1H), 4.63 (d, *J*=11.9 Hz, 1H), 4.04 (dq, *J*=12.7, 6.3 Hz, 1H), 2.11 (s, 3H), 1.22 (d,

J=6.2 Hz, 3H) ppm; IR (film, cm^{-1}): 2980, 2885, 1740, 1651, 1495, 1451, 1374, 1237, 1045, 927, 640. MS (ESI) m/z: 280.0 ($[M+NH_4]^+$, 100).

*4.2.18. L-Menthyl 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3r**).* Colorless oil; $[\alpha]_D^{25}$ −354 (*c* 1.15 $CHCl_3$, α only); ^1H NMR (400 MHz, $CDCl_3$) δ 5.80 (dd, J=47.3, 10.2 Hz, 2H), 5.16 (s, 1H), 5.05 (d, J=9.6 Hz, 1H), 4.09–3.88 (m, 1H), 3.55 (td, J=10.6, 4.0 Hz, 1H), 2.28 (dd, J=6.9, 5.1 Hz, 1H), 2.11 (s, 3H), 1.73–1.63 (m, 2H), 1.58–1.26 (m, 3H), 1.23 (d, J=6.2 Hz, 3H), 1.16–0.98 (m, 2H), 0.94 (s, 3H), 0.92 (s, 3H), 0.83 (d, J=6.9 Hz, 3H), 0.77 (t, J=6.5 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.57, 129.46, 128.38, 90.53, 75.84, 70.95, 65.01, 47.91, 40.29, 34.43, 31.43, 25.35, 22.84, 22.32, 21.15, 21.13, 18.02, 15.63; IR (film, cm^{-1}): 2924, 2864, 1745, 1455, 1374, 1325, 1098, 1032, 914, 837, 795; MS (ESI): m/z 333.2 ($[M+Na]^+$, 100); HR-ESI:$C_{18}H_{30}Na_1O_4$ $[M+Na]^+$ calcd 333.2033, found 333.2036.

*4.2.19. (+)-endo-Fenacholyl 4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3s**).* Colorless oil; $[\alpha]_D^{25}$ −203 (*c* 1.56, $CHCl_3$, α:β=17:1); ^1H NMR (400 MHz, $CDCl_3$) δ 5.85 (s, 2H), 5.04 (d, J=9.1 Hz, 1H), 4.92 (s, 1H), 4.00 (dq, J=12.6, 6.2 Hz, 1H), 3.24 (s, 1H), 2.12 (s, 3H), 1.71 (s, 3H), 1.51–1.30 (m, 3H), 1.25 (d, J=6.3 Hz, 3H), 1.12 (s, 1H), 1.09 (s, 3H), 1.06 (s, 3H), 0.90 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.58, 129.19, 128.00, 96.38, 92.97, 70.95, 64.91, 49.40, 48.07, 41.02, 38.99, 30.40, 26.17, 25.91, 21.66, 21.14, 19.76, 17.89; IR (film, cm^{-1}): 2927, 2864, 1730, 1638, 1458, 1384, 1233, 1097, 1042, 911, 805, 742; MS (ESI): m/z 331.2 ($[M+Na]^+$, 100); HR-ESI: $C_{18}H_{28}Na_1O_4$ $[M+Na]^+$ calcd 331.1875, found 331.1880.

*4.2.20. Epiandrosteronyl-4-O-acetyl-6-deoxy-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3t**).* Colorless oil; $[\alpha]_D^{25}$ −64 (*c* 0.52, $CHCl_3$, α:β=13:1); ^1H NMR (400 MHz, $CDCl_3$) δ 5.93–5.76 (m, 2H), 5.14 (s, 1H), 5.07 (d, J=9.1 Hz, 1H), 4.04 (dq, J=12.4, 6.2 Hz, 1H), 3.70–3.47 (m, 1H), 2.46 (dd, J=19.2, 8.8 Hz, 1H), 2.10 (s, 3H), 1.99–1.86 (m, 2H), 1.79 (dd, J=25.7, 12.8 Hz, 3H), 1.66 (s, 3H), 1.60–1.49 (m, 3H), 1.32 (dd, J=13.6, 8.8 Hz, 6H), 1.24 (d, J=6.3 Hz, 3H), 1.15 (d, J=11.8 Hz, 1H), 1.01 (dt, J=12.0, 9.2 Hz, 2H), 0.88 (s, 3H), 0.85 (s, 3H), 0.71 (dd, J=15.0, 7.3 Hz, 1H) ppm; ^{13}C NMR (101 MHz, $CDCl_3$): δ 170.60, 129.45, 128.36, 92.59, 71.00, 64.57, 54.45, 54.31, 51.42, 47.81, 44.83, 44.65, 37.12, 35.87, 35.80, 35.04, 34.61, 31.57, 30.91, 29.71, 28.51, 21.79, 21.11, 20.49, 18.02, 13.83, 12.23 ppm; IR (film, cm^{-1}): 2925, 2852, 1737, 1638, 1451, 1377, 1235, 1102, 1031, 918, 833, 748; MS (ESI) m/z: 467.3 ($[M+Na]^+$, 100); HR-ESI: $C_{27}H_{40}O_5Na_1$ $[M+Na]^+$ calcd 467.2761, found 467.2768.

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Supplementary data

Supplementary data include ^1H NMR, ^{19}F NMR spectra of all the products; ^{13}C NMR, HRMS of the new compounds are available. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.09.061.

References and notes

1. For examples, see: (a) Durham, T. B.; Miller, M. J. *Org. Lett.* **2002**, *4*, 135; (b) Williams, D. R.; Heidebrecht, R. W., Jr. *J. Am. Chem. Soc.* **2003**, *125*, 1843; (c) Domon, D.; Fujiwara, K.; Ohtaniuchi, Y.; Takezawa, A.; Takeda, S.; Kawasaki, H.; Murai, A.; Kawai, H.; Suzuki, T. *Tetrahedron Lett.* **2005**, *46*, 8279; (d) Panarese, J. D.; Waters, S. P. *Org. Lett.* **2009**, *11*, 5086; (e) Rusin, A.; Zawisza-Puchalka, J.; Kujawa, K.; Gogler-Piglowska, A.; Wietrzyk, J.; Switalska, M.; Glowala-Kosinska, M.; Gruca, A.; Szeja, W.; Krawczyk, Z.; Grynkiewicz, G. *Bioorg. Med. Chem.* **2011**, *19*, 295.
2. For example, see: Bozell, J. J.; Tice, N. C.; Sanyal, N.; Thompson, D.; Kim, J.-M.; Vidal, S. *J. Org. Chem.* **2008**, *73*, 8763.
3. (a) Ferrier, R. J.; Sankey, G. H. *J. Chem. Soc. C* **1966**, 2345; (b) Ferrier, R. J.; Prasad, N. *J. Chem. Soc. C* **1969**, 570; (c) Wieczorek, B.; Thiem, J. *J. Carbohydr. Chem.* **1998**, *17*, 785; (d) Csuk, R.; Shaad, M.; Krieger, C. *Tetrahedron* **1996**, *52*, 6397; (e) Ferrier, R. J. *Top. Curr. Chem.* **2001**, *215*, 153; (f) Ferrier, R. J. *Org. React.* **2003**, *62*, 174; (g) Ferrier, R. J.; Zubkov, O. A. *Org. React.* **2004**, *62*, 569.
4. (a) Babu, B. S.; Balasubramanian, K. K. *Tetrahedron Lett.* **2000**, *41*, 1271; (b) Masson, C.; Soto, J.; Bessodes, M. *Synlett* **2000**, 1281; (c) Takhi, M.; Rahman, A.; Adel, A. H.; Schmidt, R. R. *Tetrahedron Lett.* **2001**, *42*, 4053; (d) Swamy, N. R.; Venkateswarlu, Y. *Synthesis* **2002**, 598; (e) Yadav, J. S.; Reddy, B. V. S.; Reddy, K. B.; Satyanarayana, M. *Tetrahedron Lett.* **2002**, *43*, 7009; (f) Bettadaiah, B. K.; Srinivas, P. *Tetrahedron Lett.* **2003**, *44*, 7257; (g) Kim, H.; Men, H.; Lee, C. *J. Am. Chem. Soc.* **2004**, *126*, 1336; (h) Swamy, N. R.; Srinivasulu, M.; Reddy, T. S.; Goud, T. V.; Venkateswarlu, Y. *J. Carbohydr. Chem.* **2004**, *23*, 435; (i) Rafiee, E.; Tangestaninejad, S.; Habibi, M. H.; Mirkhani, V. *Bioorg. Med. Chem. Lett.* **2004**, *14*, 3611; (j) Babu, J. L.; Khare, A.; Vankar, Y. D. *Molecules* **2005**, *10*, 884; (k) Naik, P. U.; Nara, J. S.; Harjani, J. R.; Salunkhe, M. M. *J. Mol. Catal. A: Chem.* **2005**, *234*, 35; (l) Procopio, A.; Dalposso, R.; De Nino, A.; Nardi, M.; Oliverio, M.; Russo, B. *Synthesis* **2006**, 2608; (m) Procopio, A.; Dalpozzo, R.; Nino, A. D.; Maiuolo, L.; Nardi, M.; Oliverio, M.; Russo, B. *Carbohydr. Res.* **2007**, *342*, 2125; (n) Zhang, G.; Shi, L.; Liu, Q.; Wang, J.; Li, L.; Liu, X. *Tetrahedron* **2007**, *63*, 9705; (o) Zhang, G.; Liu, Q. *Synth. Commun.* **2007**, *37*, 3485; (p) Tayama, E.; Otoyama, S.; Isaka, W. *Chem. Commun.* **2008**, 4216; (q) Baramulugan, R.; Kopollu, S. R. *Tetrahedron* **2009**, *65*, 8139; (r) Rodriguez, O. M.; Colinas, P. A.; Bravo, R. D. *Synlett* **2009**, 1154; (s) Gorityala, B. K.; Lorpitthaya, R.; Bai, Y.; Liu, X.-W. *Tetrahedron* **2009**, *65*, 5844; (t) Nagaraj, P.; Ramesh, N. G. *Tetrahedron Lett.* **2009**, *50*, 3970; (u) Ding, F.; William, R.; Gorityala, B. K.; Ma, J.; Wang, S.; Liu, X.-W. *Tetrahedron Lett.* **2010**, *51*, 3146; (v) Chen, P.-R.; Wang, S.-S. *Tetrahedron* **2012**, *68*, 5356; (w) Deshpande, P. P.; Price, K. N.; Baker, D. C. *J. Org. Chem.* **1996**, *61*, 455; (x) Chen, P.-R.; Lin, L. *Tetrahedron* **2013**, *69*, 4524.
5. (a) Yadav, J. S.; Reddy, B. V. S.; Narasimha, C. D.; Madavi, C.; Kunwar, A. C. *Tetrahedron Lett.* **2009**, *50*, 81; (b) Mukherjee, D.; Yousuf, S. K.; Taneja, S. C. *Tetrahedron Lett.* **2008**, *49*, 4944; (c) Nagaraj, P.; Ramesh, N. G. *Tetrahedron* **2010**, *66*, 591.
6. (a) Chen, P.-R.; Wang, S.-S. *Tetrahedron* **2013**, *69*, 583; (b) Bhate, P.; Horton, D.; Priebe, W. *Carbohydr. Res.* **1985**, *144*, 331; (c) Toshima, K.; Ishizuka, T.; Matsuo, G.; Masaya Nakata, M.; Kinoshita, M. *J. Chem. Soc., Chem. Commun.* **1993**, 704.