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An efficient procedure for the synthesis of 2,3-unsaturated-*O*-glycosides: $TiCl_3(OTf)$ as the catalyst for type I Ferrier rearrangement

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ABSTRACT

An efficient type I Ferrier rearrangement reaction system for the synthesis of 2,3-unsaturated-*O*-glycosides has been established by using $TiCl_3(OTf)$ as the catalyst. A series of 2,3-unsaturated-*O*-glucosides were prepared from 3,4,6-tri-*O*-acetyl-D-glucal in good yield and high anomeric selectivity.

1. Introduction

2,3-Unsaturated-*O*-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] because of the regio- and stereo-varieties that they could provide 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 under the promotion 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).

Lewis acids have been reported to be the major catalyst in type I Ferrier Rearrangement besides some other type of catalysts. 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, $ZnCl_2/Al_2O_3$ 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. In view of that Ti(IV) catalysts have been successfully used in many asymmetric synthesis,[5] we therefore have interest in investigating the catalytic behavior of other Ti(IV) catalysts than $TiCl_4$ 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.

Herein, we report our results using $TiCl_3(OTf)$ as a new highly efficient catalyst for type I Ferrier rearrangement.

2. Results and discussion

2.1. Role of the counter-ion in the Ti(IV) catalysts

$TiCl_4$ has been used as catalyst in type I Ferrier rearrangement to prepare *C*-linked 2,3-unsaturates glycosides.[4w] For comparison of the catalytic activity of different Ti(IV) catalysts, a comparative study has been carried out in a model system by using tri-*O*-acetyl-D-glucal (**1**) and EtOH as the nucleophile catalyzed by different Ti(IV) Lewis acid catalysts. Results are shown in Table 1.

Results shown in Table 1 demonstrate the remarkably different catalytic activity of the Ti(IV) catalysts with different counter-ions in this reaction. Among the tested Ti(IV) catalysts, $TiCl_3(OTf)$ is the most efficient one in terms of conversion and selectivity, which indicates that triflate anion might cause the Ti(IV) cation more active in attracting the leaving group to form the intermediate allyloxycarbenium ion (Scheme 1).

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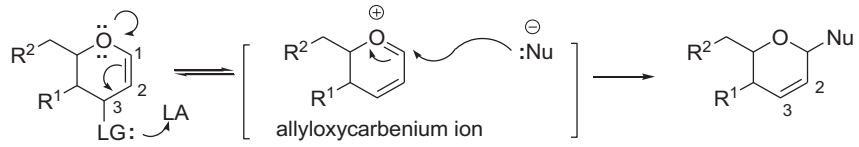
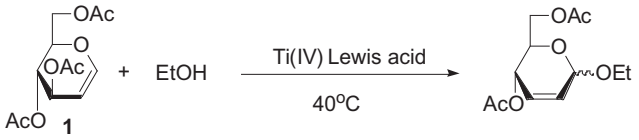


LG = leaving group

LA = Lewis acid catalyst

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

Table 1
A comparative study of the catalytic effect of different Ti(IV) Lewis acid catalysts in the Ferrier rearrangement of glucal **1**[a]



Entry	Lewis acid catalyst	Reaction time	Conversion (%)[b]	α:β[c]
1	$TiCl_4$	4 h	Trace	/
2	$Ti(O^iPr)_4$	24 h	N.R.	/
3	$TiCl_3(OTf)$	120 min	71	6:1
4	$Ti(O^iPr)_3(OTf)$	10 h	N.R.	/

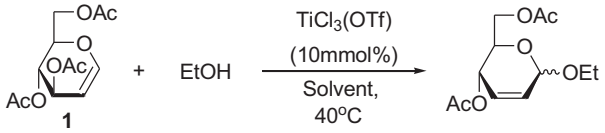
[a] Reaction conditions: tri-*O*-acetyl-D-glucal (**1**) (188 mg, 0.7 mmol), EtOH (5 mL), catalyst (10 mol %), 40 °C.
[b] Determined by analysis of the ^1H NMR spectra of the reaction mixture.
[c] The anomeric ratio was determined by integration of the anomeric hydrogen in the ^1H NMR spectra.

2.2. Optimization of solvent

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

By comparison of the results in entry 3 with the others in Table 2, DCM appeared to be the most proper solvent. When using THF, diethyl ether or toluene as solvent, no product was detected (entries 4–6, Table 2). The solvents with high polarity hydrophilic character, such as acetone or acetonitrile also led to relative low conversion and much longer reaction time (entries 1 and 2, Table 2).

Table 2
Optimization of solvent[a] for the $TiCl_3(OTf)$ catalyzed Ferrier rearrangement reaction system



Entry	Solvent	Reaction time	Conversion (%)[b]	α:β[c]
1	Acetone	120 min	77	7:1
2	Acetonitrile	60 min	73	6:1
3	DCM	10 min	88	7:1
4	THF	24 h	Trace	/
5	Diethyl ether	24 h	Trace	/
6	Toluene	24 h	Trace	/

[a] Reaction conditions: tri-*O*-acetyl-D-glucal (**1**) (188 mg, 0.7 mmol), EtOH (1.3 equiv), $TiCl_3(OTf)$ (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.

2.3. Type I Ferrier rearrangement under the optimized conditions

After the optimization, we have established our reaction conditions: with $TiCl_3(OTf)$ (10 mol %) as the catalyst and DCM as the solvent, the Ferrier rearrangement was performed between 3,4,6-tri-*O*-acetyl-D-glucal (1 equiv) and various nucleophiles (1.3 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, by using 3,4,6-tri-*O*-acetyl-D-glucal as the starting material, the reaction afforded 2,3-unsaturated-*O*-glycosides in high yield with good anomeric selectivity.

The simple aliphatic alcohols (entries 1–5, Table 3) as the nucleophile gave the products that were good both in yield and in anomeric selectivity, while those with halogen or small alkyl-ring substituents (entries 6–8, Table 3) gave the products with relatively low anomeric selectivity. In the series of benzylic alcohols (entries 9–11, Table 3), the nucleophiles gave satisfactory reaction outcomes. As relatively weak nucleophiles, benzylic alcohols with fluorine on the α-position (entries 12–14, Table 3) gave the corresponding 2,3-unsaturated *O*-glycoside with relatively low anomeric selectivity.

We have also explored the scope of this procedure for the preparation of 2,3-unsaturated *O*-glycoside connected with various biologically important natural products. Formation of two disaccharides (entries 17 and 18, Table 3), three steroid glycosides (entries 19, 20, and 21, Table 3) and two other natural product (L-menthol and (1*R*)-*endo*-(+)-fenchol) glycosides (entries 15 and 16, Table 3) in good yield and high selectivity demonstrated the catalytic capability of $TiCl_3(OTf)$ in the synthesis of natural product analogs by the Ferrier rearrangement.

3. Conclusion

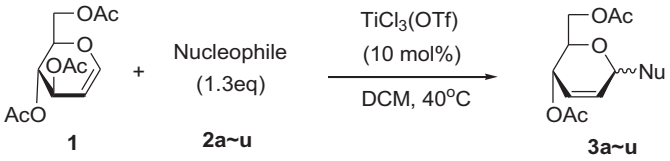
We have established a practical procedure for type I Ferrier rearrangement with $TiCl_3(OTf)$ as the catalyst. By using this catalyst, a series of alcohols were reacted with glucal donor affording 2,3-unsaturated *O*-glycosides in high yield and good anomeric selectivity. The influence of the inductive and the steric effects of the nucleophiles on the reaction results have 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

Table 3
Type I Ferrier rearrangement reaction of 3,4,6-tri-*O*-acetyl-D-glucal (**1**) with various nucleophiles (**2a**–**u**) catalyzed by $TiCl_3(OTf)$[a]



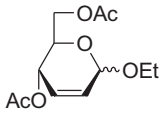
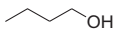
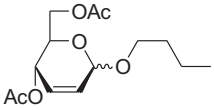
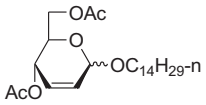
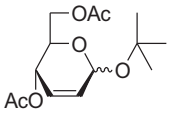
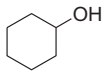
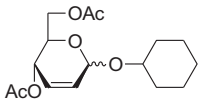
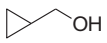
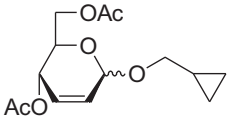
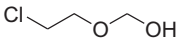
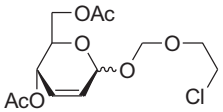
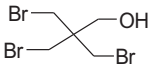
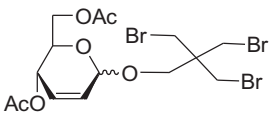
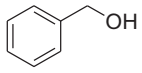
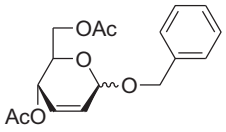
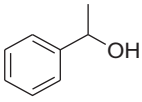
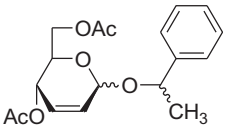
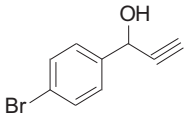
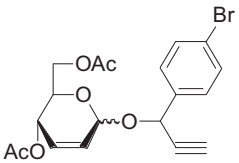
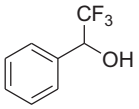
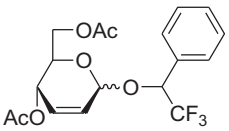
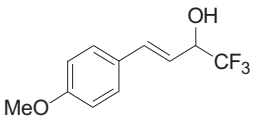
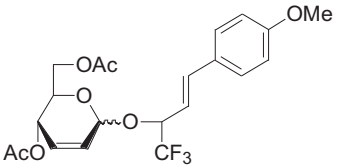
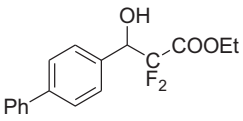
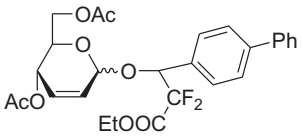
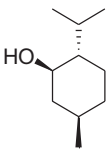
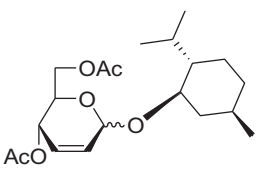
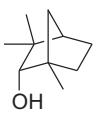
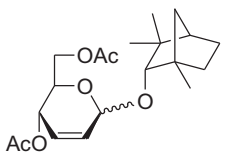
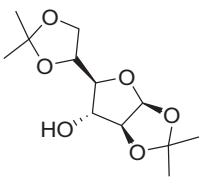
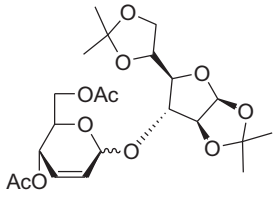
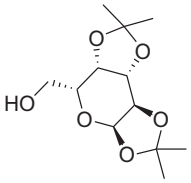
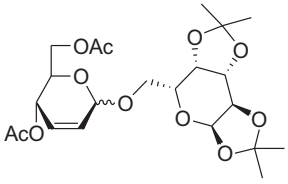
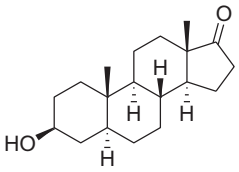
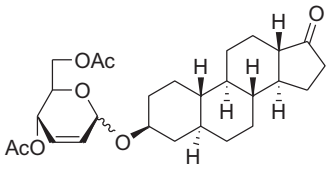
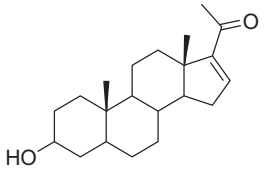
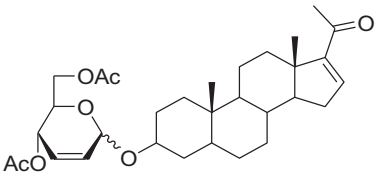
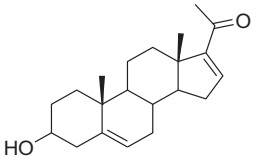
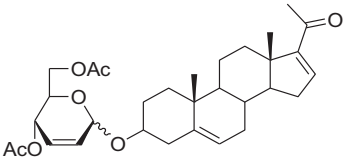
Entry	Nucleophile	Reaction time	Product	Yield[b] (%)	(α:β)[c]
1	EtOH **2a**	10 min	 **3a**	88	7:1
2	 **2b**	180 min	 **3b**	84	10:1
3	n-$C_{14}H_{29}OH$ **2c**	150 min	 **3c**	83	8:1
4	 **2d**	195 min	 **3d**	77	α only
5	 **2e**	45 min	 **3e**	90	8:1
6	 **2f**	230 min	 **3f**	81	4:1
7	 **2g**	80 min	 **3g**	86	3:1
8	 **2h**	85 min	 **3h**	81	5:1

Table 3 (*continued*)

Entry	Nucleophile	Reaction time	Product	Yield[b] (%)	(α:β)[c]
9	 **2i**	18 min	 **3i**	76	α only
10	 **2j**	40 min	 **3j**	72	8:1
11	 **2k**	130 min	 **3k**	61	10:1
12	 **2l**	20 min	 **3l**	83	3:1
14	 **2m**	30 min	 **2m**	54	2:1
13	 **2n**	360 min	 **3n**	50	3:1
15	 **2o**	125 min	 **3o**	61	α only
16	 **2p**	12 min	 **3p**	70	10:1

(*continued on next page*)

Table 3 (*continued*)

Entry	Nucleophile	Reaction time	Product	Yield[b] (%)	(α:β)[c]
17	 **2q**	115 min	 **3q**	42	α only
18	 **2r**	190 min	 **3r**	52	6:1
19	 **2s**	70 min	 **3s**	70	10:1
20	 **2t**	40 min	 **3t**	58	α only
21	 **2u**	100 min	 **3u**	72	α only

[a] Reaction conditions: tri-*O*-acetyl-D-glucal (**1**) (188 mg, 0.7 mmol), nucleophile (**2a**–**u**) (1.3 equiv), $TiCl_3(OTf)$ (10 mol %), DCM (5 mL), 40 °C.
[b] Isolated yield.
[c] The anomeric ratio was determined by integration of the anomeric hydrogen in the ^1H NMR 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, epiandrosteron, L-menthol, (1*R*)-*endo*-(+)-fenchol, and the protected glucose were purchased from Energy-Chemical Company. $TiCl_3(OTf)$ was prepared according to the known method.[6] All the solvents used in the reaction were purified by re-distillation.

4.2. General procedure for preparation of 2,3-unsaturated glycosides

To a stirred solution of tri-*O*-acetyl-D-glucal (188 mg, 0.7 mmol) and the corresponding alcohol (1.3 equiv) in DCM (5 mL) were added $TiCl_3(OTf)$ (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 (3×10 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**).* Colorless oil; $[\alpha]_D^{25}$ +82.72 (*c* 0.83, $CHCl_3$, α:β=7:1) {lit.:[4k] $[\alpha]_D^{31.7}$ +113.1 (*c* 1.0, $CHCl_3$, α:β=9:1)}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.05–5.63 (m, 2H), 5.24 (d, *J*=9.7 Hz, 1H), 4.97 (s, 1H), 4.28–4.12 (m, 2H), 4.10–4.01 (m, 1H), 3.76 (m, 1H), 3.58–3.45 (m, 1H), 2.03 (s, 3H), 2.01 (s, 3H), 1.18 (t, *J*=7.1 Hz, 3H) ppm; IR (film, cm^{-1}): 2980, 2901, 1736, 1416, 1383, 1239, 1119, 1052, 889, 832, 737; MS (EI 70 eV) *m*/*z*:257 ([M^+−1]), 213 ([M^+−OEt], 6),

199 (1), 185 (1), 213 (7), 171 (2), 153 (9), 114 (100), 111 (24), 86 (13), 81 (5), 57 (9).

*4.2.2. n-Butyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3b**).* Colorless oil; $[\alpha]_D^{25}$ +96.5 (*c* 0.73, $CHCl_3$, α:β=10:1) {lit.:[4k] $[\alpha]_D^{31.7}$ +113.1 (*c* 1.0, $CHCl_3$, α:β=9:1)}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.79 (q, *J*=10.4 Hz, 2H), 5.24 (d, *J*=9.7 Hz, 1H), 4.96 (s, 1H), 4.25–4.00 (m, 3H), 3.72 (dd, *J*=6.9, 2.6 Hz, 1H), 3.45 (dt, *J*=9.6, 6.4 Hz, 1H), 2.04 (s, 3H), 2.02 (s, 3H), 1.53 (dd, *J*=7.6, 4.6 Hz, 2H), 1.39–1.28 (m, 2H), 0.87 (t, *J*=7.3 Hz, 3H) ppm; IR (film, cm^{-1}): 2955, 2872, 1744, 1460, 1373, 1232, 1110, 1041, 904, 681, 607; MS (ESI) *m*/*z*; 304.1 ($[M+NH_4]^+$, 100), 305.1 (10), 212.9 (23).

*4.2.3. n-Tetradecyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3c**).* White solid; mp=37–38 °C, $[\alpha]_D^{25}$ +73 (*c* 0.64, $CHCl_3$, α:β=8:1) {lit.:[7a] $[\alpha]_D^{25}$ +59 (*c* 0.59, $CHCl_3$, α:β=20:1)}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.00–5.79 (m, 2H), 5.32 (d, *J*=9.5 Hz, 1H), 5.03 (s, 1H), 4.23 (dt, *J*=28.4, 8.7 Hz, 2H), 4.12 (d, *J*=8.1 Hz, 1H), 3.77 (dd, *J*=15.1, 7.4 Hz, 1H), 3.51 (dd, *J*=14.9, 7.4 Hz, 1H), 2.10 (s, 3H), 2.09 (s, 3H), 1.64–1.57 (m, 2H), 1.26 (m, 22H), 0.88 (t, *J*=6.1 Hz, 3H) ppm; IR (film, cm^{-1}): 2924, 2856, 1745, 1468, 1373, 1237, 1044, 899, 832, 730, 603; MS (ESI) *m*/*z*:449.2 ($[M+Na]^+$, 100), 450.2 (30), 213.0 (13).

*4.2.4. tert-Butyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3d**).* Colorless oil; $[\alpha]_D^{25}$ +98.8 (*c* 0.65, $CHCl_3$, α only) {lit.:[7b] $[\alpha]_D^{31.7}$ +100.69 (*c* 0.75, $CHCl_3$)}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.87–5.69 (m, 2H), 5.33–5.27 (m, 1H), 5.23 (dd, *J*=9.3, 1.3 Hz, 1H), 4.25–4.07 (m, 3H), 2.05 (s, 3H), 2.04 (s, 3H), 1.25 (s, 9H) ppm; IR (film, cm^{-1}): 3047, 2974, 2925, 1744, 1445, 1373, 1235, 1039, 897, 774, 608; MS (ESI) *m*/*z*: 309 ($[M+Na]^+$, 100), 212.9 (68), 153.0 (42).

*4.2.5. Cyclohexyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3e**).* Colorless oil; $[\alpha]_D^{25}$ +65.3 (*c* 0.60, $CHCl_3$, α:β=8:1) {lit.:[4k] $[\alpha]_D^{31.7}$ +110.7 (*c* 1.0, $CHCl_3$, α:β=9:1)}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.84–5.71 (m, 2H), 5.29–5.21 (m, 1H), 5.11 (s, 1H), 4.20–4.13 (m, 2H), 4.10 (t, *J*=4.5 Hz, 1H), 3.66–3.53 (m, 1H), 2.03 (s, 3H), 2.02 (s, 3H), 1.87 (dd, *J*=20.1, 11.2 Hz, 2H), 1.69 (d, *J*=5.1 Hz, 2H), 1.53–1.45 (m, 1H), 1.29 (d, *J*=2.6 Hz, 5H) ppm; IR (film, cm^{-1}): 3047, 2933, 2859, 1744, 1446, 1372, 1232, 1037, 739, 608; MS (ESI) *m*/*z*; 330.1 ($[M+NH_4]^+$, 100), 212.9 (65), 153 (27).

*4.2.6. Cyclopropylmethyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3f**).* Colorless oil; $[\alpha]_D^{25}$ +82.72 (*c* 0.83, $CHCl_3$, α:β=4:1) {lit.:[7c] $[\alpha]_D^{31.7}$ +113.1 (*c* 1.0, $CHCl_3$, α:β=9:1)}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.88 (d, *J*=38.3 Hz, 2H), 5.26 (d, *J*=9.7 Hz, 1H), 5.03 (s, 1H), 4.28–4.03 (m, 3H), 3.43 (ddd, *J*=31.0, 10.3, 7.2 Hz, 2H), 2.04 (s, 3H), 2.04 (s, 3H), 1.07 (s, 1H), 0.52 (d, *J*=7.9 Hz, 2H), 0.19 (t, *J*=5.5 Hz, 2H) ppm; IR (film, cm^{-1}): 2998, 2903, 1741, 1584, 1373, 1231, 1038, 907, 830, 736, 608; MS (ESI) *m*/*z*; 302.0 ($[M+NH_4]^+$, 100), 303.0 (20), 212.9 (23).

*4.2.7. 2-(2-Chloroethoxyl)-ethoxyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3g**).* Colorless oil; $[\alpha]_D^{25}$ +55.6 (*c* 0.56, $CHCl_3$, α:β=6:1) {lit.[7e] $[\alpha]_D^{25}$ +75.8 (*c* 0.86, $CHCl_3$, α:β=8:1)}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.90–5.78 (m, 2H), 5.29 (d, *J*=9.6 Hz, 1H), 5.06 (s, 1H), 4.24–4.07 (m, 3H), 3.97–3.83 (m, 1H), 3.75–3.67 (m, 5H), 3.61 (d, *J*=4.3 Hz, 2H), 2.07 (s, 3H), 2.05 (s, 3H) ppm; IR (film, cm^{-1}): 2883, 1741, 1442, 1372, 1232, 1122, 1044, 903, 832, 738, 663, 608, 485; MS (ESI) *m*/*z*: 354.1 ($[M+NH_4]^+$, 100), 213.0 (18), 153.1 (10).

*4.2.8. 2,2,2-Tribromomethyl ethoxyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3h**).* Colorless oil; $[\alpha]_D^{25}$ +73 (*c* 0.65, $CHCl_3$, α:β=10:1); {lit.:[7e] $[\alpha]_D^{25}$ +88 (*c* 0.75, $CHCl_3$, α only)}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.98–5.74 (m, 2H), 5.32 (d, *J*=9.7 Hz, 1H), 5.04 (s, 1H), 4.28–4.18 (m, 2H), 4.07 (ddd, *J*=9.3, 4.2, 2.6 Hz, 1H), 3.93 (d, *J*=9.4 Hz, 1H), 3.57–3.45 (m, 7H), 2.09 (s, 3H), 2.09 (s, 3H) ppm; IR (film, cm^{-1}): 2959, 1743, 1420, 1230, 1041, 902, 844, 661, 607; MS (ESI) *m*/*z*: 558.8 (100), 556.7 ($[M+Na]^+$, 40).

*4.2.9. Benzyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3i**).* Colorless oil; $[\alpha]_D^{25}$ +46.6 (*c* 0.64, $CHCl_3$, α only) {lit.:[4k] $[\alpha]_D^{31.7}$ +56.34 (*c* 1.0, $CHCl_3$, α:β=9:1)}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.37 (d, *J*=4.2 Hz, 5H), 5.88 (d, *J*=8.6 Hz, 2H), 5.34 (d, *J*=9.5 Hz, 1H), 5.14 (s, 1H), 4.81 (d, *J*=11.7 Hz, 1H), 4.61 (d, *J*=11.7 Hz, 1H), 4.26 (dd, *J*=11.6, 5.0 Hz, 1H), 4.15 (ddd, *J*=17.7, 10.3, 1.8 Hz, 2H), 2.10 (s, 3H), 2.08 (s, 3H) ppm; IR (film, cm^{-1}): 3031, 2877, 1740, 1494, 1450, 1374, 1236, 1094, 1036, 909, 821, 740, 693; MS (ESI) *m*/*z*; 338.0 ($[M+NH_4]^+$, 100), 339.0 (18), 213.0 (14).

*4.2.10. 1-Phenyl ethyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3j**).* Colorless oil; $[\alpha]_D^{25}$ +80.5 (*c* 1.67, $CHCl_3$, α:β=4:1) {lit.[7d]}; ^1H NMR (400 MHz, $CDCl_3$); ^1H NMR (400 MHz, $CDCl_3$): δ α-anomer 7.31 (t, *J*=13.6 Hz, 5H), 5.86 (s, 1H), 5.75 (dd, *J*=10.2, 1.4 Hz, 1H), 5.29 (d, *J*=9.9 Hz, 1H), 4.87 (d, *J*=6.8 Hz, 1H), 4.79 (q, *J*=6.2 Hz, 1H), 4.28 (dt, *J*=18.3, 10.0 Hz, 3H), 2.12 (s, 3H), 2.08 (s, 3H), 1.50 (d, *J*=6.1 Hz, 3H) ppm; β-anomer 7.37 (d, *J*=7.5 Hz, 1.5H), 5.91 (d, *J*=21.5 Hz, 0.3H), 5.18 (s, 0.3H), 4.79 (q, *J*=6.2 Hz, 0.3H), 4.00 (dd, *J*=11.8, 3.0 Hz, 0.3H), 3.83 (d, *J*=9.4 Hz, 0.3H), 3.41 (d, *J*=12.2 Hz, 0.3H), 2.03 (s, 1H), 1.97 (s, 1H); IR (film, cm^{-1}): 2924, 1746, 1494, 1374, 1234, 1132, 909, 858, 754, 701, 632, 609; MS (ESI) *m*/*z*: 357.0 ($[M+Na]^+$, 100), 212.9 (10).

*4.2.11. 1-(p-Bromo-phenyl)prop-2-ynyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3k**).* Colorless oil; $[\alpha]_D^{25}$ +3.5 (*c* 1.61, $CHCl_3$, α:β=10:1), ^1H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J*=8.2 Hz, 2H), 7.44 (d, *J*=8.2 Hz, 2H), 5.92 (dd, *J*=23.5, 10.3 Hz, 2H), 5.56 (s, 1H), 5.53 (s, 1H), 4.35–3.90 (m, 3H), 2.70 (s, 1H), 2.10 (s, 3H), 2.09 (s, 3H), ^{13}C NMR (101 MHz, $CDCl_3$): 170.85, 170.18, 136.67, 131.73, 129.75, 129.17, 128.28, 127.26, 122.76, 91.80, 80.16, 76.56, 67.46, 65.28, 63.06, 20.93, 20.78. IR (film, cm^{-1}): 3499, 2207, 1740, 1639, 1560, 1478, 1412, 1372, 1235, 1139, 1098, 1015, 642; MS (ESI) *m*/*z*: 445.0 ($[M+Na]^+$, 100). HR-ESI $C_{19}H_{19}O_6Br_1Na_1$ $[M+Na]^+$, calcd 445.02572, found 445.02605.

*4.2.12. 2,2,2-Trifluoro-1-phenyl ethyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3l**).* Colorless oil; $[\alpha]_D^{25}$ +72 (*c* 0.63, $CHCl_3$, α:β=3:1) {lit.:[7e] $[\alpha]_D^{25}$ +61 (*c* 0.58, $CHCl_3$, α:β=3:1); ^1H NMR (400 MHz, $CDCl_3$): δ α-anomer: 7.40 (d, *J*=5.4 Hz, 5H), 5.94 (s, 1H), 5.79 (d, *J*=10.2 Hz, 1H), 5.31 (dd, *J*=14.7, 9.8 Hz, 1H), 5.10 (q, *J*=6.9 Hz, 1H), 4.92 (s, 1H), 4.34–4.19 (m, 3H), 2.11 (s, 3H), 2.10 (s, 3H). β-anomer: 7.45 (d, *J*=7.7 Hz, 1.5H), 5.38 (s, 0.3H), 5.03–4.98 (m, 0.3H), 3.91 (dd, *J*=12.2, 3.4 Hz, 0.3H), 3.71 (d, *J*=8.3 Hz, 0.3H), 3.47 (d, *J*=12.3 Hz, 0.3H), 2.03 (s, 1H), 1.88 (s, 1H). ^{19}F NMR (377 MHz, $CDCl_3$) δ −76.35 (d, *J*=6.9 Hz), −76.72 (d, *J*=6.7 Hz); IR (film, cm^{-1}): 2924, 1746, 1447, 1374, 1234, 1132, 990, 909, 868, 754, 701, 602; MS (ESI) *m*/*z*; 406.0 ($[M+NH_4]^+$, 100), 213.0 (15).

*4.2.13. 1-Trifluoromethyl 3-(p-methoxy-phenyl) prop-2-enyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3m**).* Colorless oil; $[\alpha]_D^{25}$ 128.7 (*c* 1.52, $CHCl_3$, α:β=2:1), ^1H NMR (400 MHz, $CDCl_3$) δ 7.40–7.30 (m, 2H), 6.93–6.82 (m, 2H), 5.99–5.74 (m, 4H), 5.36–5.29 (m, 1H), 5.12 (s, 1H), 4.72–4.56 (m, 1H), 4.26–4.08 (m, 3H), 3.80 (s, 3H), 2.10 (s, 3H), 2.09 (s, 3H). ^{13}C NMR (101 MHz, $CDCl_3$): 170.72, 170.27, 160.25, 138.59, 135.87, 130.39, 128.34, 128.15, 127.72, 126.61, 115.91, 114.12, 90.95, 67.56, 65.04, 62.65, 55.30, 20.92, 20.68.^{19}F NMR (376 MHz, $CDCl_3$) δ −76.68 (d, *J*=6.7 Hz), −77.11 (d, *J*=6.6 Hz). IR (film, cm^{-1}): 2939, 1744, 1641, 1559, 1514, 1416, 1246, 1176, 1129, 1037; MS (ESI) *m*/*z*: 467.1 ($[M+Na]^+$, 100). HR-ESI $C_{21}H_{23}O_7F_3Na_1$ $[M+Na]^+$, calcd 467.12774, found 467.12652.

4.2.14. Ethyl 2,2-difluoro-3-O-(4,6-Di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-3-(4-phenylphenylpropanoate)

(**3n**). Colorless oil; $[\alpha]_D^{25}$ 0.6 (*c* 1.39, $CHCl_3$, α:β=3:1), ^1H NMR (400 MHz, $CDCl_3$): δ α-anomer 7.68–7.35 (m, 9H), 5.96 (d, *J*=10.2 Hz, 1H), 5.85 (t, *J*=13.3 Hz, 1H), 5.37 (dd, *J*=17.3, 9.6 Hz, 2H), 4.98 (s, 1H), 4.44–4.24 (m, 3H), 4.18–4.06 (m, 1H), 2.18 (s, 3H), 2.13 (s, 3H), 1.34 (t, *J*=6.9 Hz, 3H). β-anomer: 3.92 (dd, *J*=12.3, 3.7 Hz, 0.3H), 3.74 (d, *J*=9.7 Hz, 0.3H), 3.34 (d, *J*=12.1 Hz, 0.3H), 2.07 (s, 1H), 1.89 (s, 1H), 1.28 (t, *J*=7.0 Hz, 1H). ^{13}C NMR (101 MHz, $CDCl_3$): 170.86, 170.49, 170.20, 142.63, 141.98, 140.34, 130.12, 129.53, 128.85, 127.69, 127.33, 127.15, 126.96, 125.79, 96.72, 91.17, 67.72, 64.99, 63.66, 62.53, 20.95, 20.79, 13.44. ^{19}F NMR (376 MHz, $CDCl_3$) δ −118.56 (d, *J*=15.3 Hz), −118.94 (d, *J*=16.1 Hz). IR (film, cm^{-1}): 2985.66, 1744.81, 1437.30, 1372.86, 1302.43, 1228.20, 1044.41, 983.65, 751.96, 696.6; MS (ESI) *m*/*z*: 541.0 ($[M+Na]^+$, 100). HR-ESI $C_{27}H_{28}O_8F_2Na_1$ $[M+Na]^+$, calcd 541.16430, found 541.16445.

*4.2.15. L-Menthyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3o**).* Colorless oil; $[\alpha]_D^{25}$ +141 (*c* 0.53, $CHCl_3$, α only) {lit.:[4s] $[\alpha]_D^{25}$ +142.5 (*c* 0.5, $CHCl_3$, α only)}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.93–5.76 (m, 2H), 5.28 (t, *J*=8.0 Hz, 1H), 5.09 (s, 1H), 4.27–4.12 (m, 3H), 3.42 (td, *J*=10.6, 4.4 Hz, 1H), 2.20 (t, *J*=10.8 Hz, 1H), 2.10 (s, 3H), 2.07 (s, 3H), 1.68–1.58 (m, 2H), 1.41 (ddd, *J*=13.1, 12.4, 9.1 Hz, 1H), 1.33–0.94 (m, 5H), 0.91 (d, *J*=1.6 Hz, 3H), 0.90 (d, *J*=2.2 Hz, 3H), 0.77 (d, *J*=6.9 Hz, 3H). IR (film, cm^{-1}): 2952, 2921, 2865, 1745, 1580, 1455, 1373, 1233, 1098, 1037, 913, 844, 740; MS (ESI) *m*/*z*: 391.0 ($[M+Na]^+$, 100), 212.9 (8).

*4.2.16. (+)-endo-Fenacholyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3p**).* White solid; mp=74–76 °C; $[\alpha]_D^{25}$ +55.1 (*c* 0.54, $CHCl_3$, α only), {lit.:[4s] $[\alpha]_D^{24}$ +48.7 (*c* 0.5, $CHCl_3$, α only)}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.00–5.80 (m, 2H), 5.31 (d, *J*=9.4 Hz, 1H), 5.00 (s, 1H), 4.33–4.12 (m, 3H), 3.47 (s, 1H), 2.11 (s, 6H), 1.80–1.60 (m, 3H), 1.50 (d, *J*=10.4 Hz, 1H), 1.46–1.38 (m, 1H), 1.28 (s, 1H), 1.14 (s, 3H), 1.07 (s, 3H), 0.99 (d, *J*=11.0 Hz, 1H), 0.90 (s, 3H) ppm; IR (film, cm^{-1}): 3043, 2951, 2875, 1741, 1416, 1373, 1261, 1098, 972, 908, 832, 747, 611; MS (ESI) *m*/*z*: 389.0 ($[M+Na]^+$, 100), 212.9 (15).

*4.2.17. 3-O-(4,6-Di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranosyl)-1,2:5,6-di-O-isopropylidene-α-D-glucofuranose (**3q**).* Colorless oil; $[\alpha]_D^{25}$ +77 (*c* 0.56, $CHCl_3$, α:β=5:1), {lit.:[7g] $[\alpha]_D^{21}$ +47.0 (*c* 0.8, $CHCl_3$, α only)}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.94–5.87 (m, 2H), 5.83 (d, *J*=10.2 Hz, 1H), 5.27 (s, 1H), 4.63 (s, 1H), 4.32 (s, 1H), 4.25–4.05 (m, 6H), 3.98 (dd, *J*=8.3, 5.3 Hz, 1H), 2.12 (s, 3H), 2.09 (s, 3H), 1.49 (s, 3H), 1.40 (s, 3H), 1.32 (s, 6H) ppm; IR (film, cm^{-1}): 2991, 1746, 1638, 1555, 1379, 1232, 1066, 847, 599; MS (ESI) *m*/*z*: 495.0 ($[M+Na]^+$, 100), 511.0 (10).

*4.2.18. 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 (**3r**).* White solid; mp=132–133 °C; $[\alpha]_D^{25}$ +24.2 (*c* 0.73, $CHCl_3$, α:β=6:1), {lit.:[7f] $[\alpha]_D^{25}$ +16.8 (*c* 1.0, $CHCl_3$, α:β=5:1)}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.88 (q, *J*=10.7 Hz, 2H), 5.54 (d, *J*=5.0 Hz, 1H), 5.34 (d, *J*=9.6 Hz, 1H), 5.11 (s, 1H), 4.66–4.59 (m, 1H), 4.32 (ddd, *J*=20.3, 9.0, 5.1 Hz, 3H), 4.17 (d, *J*=10.2 Hz, 2H), 4.02 (t, *J*=6.7 Hz, 1H), 3.89 (dd, *J*=10.0, 6.4 Hz, 1H), 3.77 (dd, *J*=10.0, 7.2 Hz, 1H), 2.13 (s, 3H), 2.10 (s, 3H), 1.55 (s, 3H), 1.46 (s, 3H), 1.36 (s, 3H), 1.35 (s, 3H) ppm; IR (film, cm^{-1}): 2996, 1742, 1640, 1417, 1379, 1242, 1068, 1006, 902, 806, 687, 605; MS (ESI) *m*/*z*: 495.2 ($[M+Na]^+$, 72), 511.2 (8).

*4.2.19. Epiandrosteronyl-4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3s**).* White solid; mp=124–126 °C; $[\alpha]_D^{25}$ +106 (*c* 0.61, $CHCl_3$, α:β=10:1) {lit.:[4v] $[\alpha]_D^{25}$ +105 (*c* 0.53, $CHCl_3$, α:β=9:1), mp=124–126 °C}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.83 (ddd, *J*=13.2, 10.2, 6.4 Hz, 2H), 5.33–5.29 (m, 1H), 5.18 (s, 1H), 4.26–4.15 (m, 3H), 3.63 (td, *J*=11.2, 5.4 Hz, 1H), 2.44 (dd, *J*=19.1, 8.6 Hz, 1H), 2.10 (s, 3H), 2.08 (s, 3H), 1.97–1.78 (m, 4H), 1.67 (s, 2H), 1.57–1.40 (m, 6H), 1.37–1.24 (m, 5H), 1.16 (d, *J*=12.4 Hz, 1H), 0.96 (s, 2H), 0.86 (s, 3H), 0.83 (s, 3H), 0.73–0.65 (m, 1H) ppm. IR (film, cm^{-1}): 3048, 2933, 2851, 1744, 1641, 1373, 1229, 1037, 898, 828, 744, 600; MS (ESI) *m*/*z*: 525.2 ($[M+Na]^+$, 100), 213 (18).

*4.2.20. (5,6-Dihydro-16-dehydropregnenolonyl)-4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3t**).* White solid; mp=124–126 °C; $[\alpha]_D^{25}$ +76 (*c* 0.53, $CHCl_3$, α only); ^1H NMR (400 MHz, $CDCl_3$) δ 6.66 (s, 1H), 5.90–5.72 (m, 2H), 5.27 (d, *J*=9.1 Hz, 1H), 5.14 (s, 1H), 4.19 (ddd, *J*=18.5, 10.9, 5.0 Hz, 3H), 3.66–3.53 (m, 1H), 2.33 (d, *J*=11.8 Hz, 1H), 2.22 (s, 3H), 2.07 (s, 3H), 2.05 (s, 3H), 1.96–1.62 (m, 4H), 1.56 (d, *J*=11.2 Hz, 2H), 1.48–1.05 (m, 10H), 1.04–0.91 (m, 2H), 0.85 (s, 3H), 0.82 (s, 3H), 0.75–0.64 (m, 1H) ppm. ^{13}C NMR (101 MHz, $CDCl_3$): 196.66, 170.66, 170.21, 155.44, 144.32, 128.73, 128.47, 93.00, 77.84, 66.75, 65.36, 63.19, 56.27, 54.78, 46.27, 45.29, 36.72, 36.29, 35.75, 34.72, 33.73, 32.14, 31.90, 28.69, 28.09, 27.07, 20.98, 20.92, 20.75, 15.86, 12.17. IR (film, cm^{-1}): 2933, 2855, 1744, 1641, 1665, 1586, 1443, 1372, 1235, 1036, 913, 820, 735, 606; MS (ESI) *m*/*z*: 551.3 ($[M+Na]^+$, 100). HR-ESI $C_{31}H_{44}O_7Na_1$ $[M+Na]^+$, calcd 551.29792, found 551.29820.

*4.2.21. 16-Dehydropregnenolonyl-4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside (**3u**).* White solid; mp 71–73 °C; $[\alpha]_D^{25}$ +134 (*c* 0.51, $CHCl_3$, α only) {lit.:[4v] $[\alpha]_D^{25}$ +174 (*c* 0.60, $CHCl_3$, α only), 70–72 °C}; ^1H NMR (400 MHz, $CDCl_3$) δ 6.73 (s, 1H), 5.87 (dd, *J*=23.6, 10.4 Hz, 2H), 5.38 (s, 1H), 5.32 (d, *J*=10.2 Hz, 1H), 5.20 (s, 1H), 4.24 (dt, *J*=19.3, 8.1 Hz, 3H), 3.67–3.48 (m, 1H), 2.41 (dd, *J*=14.1, 10.3 Hz, 3H), 2.28 (s, 3H), 2.12 (s, 3H), 2.10 (s, 3H), 1.89 (d, *J*=9.9 Hz, 2H), 1.78–1.25 (m, 12H), 1.05 (d, *J*=8.9 Hz, 3H), 0.94 (s, 3H) ppm; IR (film, cm^{-1}): 2939, 2855, 1744, 1662, 1434, 1372, 1232, 1037, 904, 807, 747, 652; MS (ESI) *m*/*z*: 549.3 ($[M+Na]^+$, 100).

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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. Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2013.04.051.

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