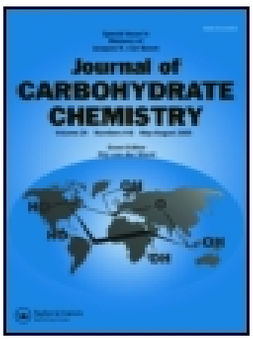


Journal of Carbohydrate Chemistry

ISSN: (Print) (Online) Journal homepage: https://www.tandfonline.com/loi/lcar20

$FeCl_3$/C as an efficient catalyst for Ferrier rearrangement of 3,4,6-tri-*O*-Benzyl-D-glucal

Yuling Mei , Youxian Dong , Juan Li , Bo Zhang , Guosheng Sun , Jiafen Zhou , Wenshuai Si , Yiwen Han , Zhenliang Wu & Jianbo Zhang

To cite this article: Yuling Mei , Youxian Dong , Juan Li , Bo Zhang , Guosheng Sun , Jiafen Zhou , Wenshuai Si , Yiwen Han , Zhenliang Wu & Jianbo Zhang (2020): $FeCl_3$/C as an efficient catalyst for Ferrier rearrangement of 3,4,6-tri-*O*-Benzyl-D-glucal, Journal of Carbohydrate Chemistry, DOI: 10.1080/07328303.2020.1788575

To link to this article: https://doi.org/10.1080/07328303.2020.1788575

Published online: 15 Jul 2020.

JOURNAL OF CARBOHYDRATE CHEMISTRY
https://doi.org/10.1080/07328303.2020.1788575

$FeCl_3$/C as an efficient catalyst for Ferrier rearrangement of 3,4,6-tri-*O*-Benzyl-D-glucal

Yuling Mei, Youxian Dong, Juan Li, Bo Zhang, Guosheng Sun, Jiafen Zhou, Wenshuai Si, Yiwen Han, Zhenliang Wu, and Jianbo Zhang

School of Chemistry and Molecular Engineering, East China Normal University, Shanghai, China

ABSTRACT

$FeCl_3$/C was used as an efficient and convenient promoter for glycosylation through Ferrier-type rearrangement of 3,4,6-tri-*O*-benzyl-D-glucal, which is a relatively unreactive substrate for this type of reaction. The method was applicable to a wide range of alcohols, especially phenols. A series of 2,3-unsaturated-*O*-glucosides were prepared efficiently (47–92%) by this method under mild conditions.

ARTICLE HISTORY
Received 6 May 2020
Accepted 24 June 2020

KEYWORDS
$FeCl_3$/C; Ferrier rearrangement; promoter; glycosylation; 346-tri-*O*-benzyl-D-glucal

Introduction

2,3-Unsaturated-*O*-glycosides are of great importance in organic synthesis and have been widely used as chiral intermediates in the preparation of various biologically active compounds,[1] such as nucleosides,[2] antibiotics,[3] glycopeptides,[4,5] oligosaccharides,[6] uronic acids,[7] and modified sugar derivatives.[8] The C2-C3 double bond of the pyranose ring can be further modified *via* several types of reactions, such as hydroxylation, hydrogenation, oxidation and aminohydroxylation, to generate structural complexity and diversity.[9–15] One of the most valuable methods to achieve 2,3-unsaturated-*O*-glycosides directly and efficiently is Ferrier rearrangement, in which glycal is reacted with nucleophiles under the promotion of various catalysts.[16] So far, many reagents have been developed to catalyze this reaction,[17–21] including Brönsted acid,[22–24] Lewis acid,[25–28] oxidant,[29] etc. However, most catalysts are difficult to be applied to the rearrangement of 3,4,6-tri-*O*-benzyl-D-glycal, mainly owing to the lower reactivity of *O*-benzyl sugar comparing to *O*-acetyl sugars in this reaction.[22] Previous methods reported for synthesis of 2,3-unsaturated glycosides from 3,4,6-tri-*O*-benzyl-D-glycal are shown in Figure 1. For instance, in 2001, Pachamuth and coworkers reported CAN-catalyzed synthesis of 2-deoxyglycosides. Meanwhile, 2,3-unsaturated glycoside product was also

CONTACT Jianbo Zhang jbzhang@chem.ecnu.edu.cn School of Chemistry and Molecular Engineering, East China Normal University, No 500, Dongchuan Road, Shanghai 200241, P. R. China

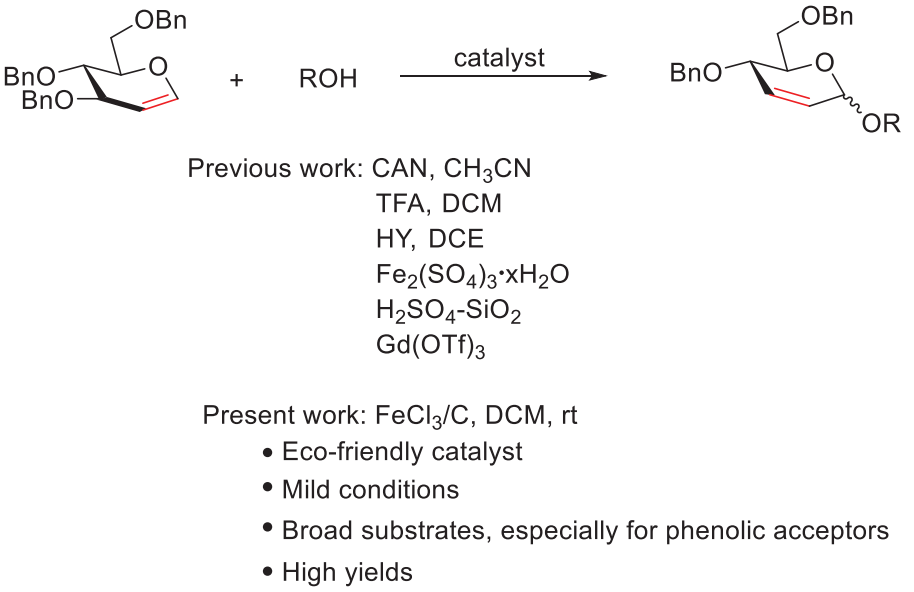


Figure 1. Methods for the synthesis of 2,3-unsaturated glycosides from 3,4,6-tri-*O*-benzyl-D-glycal.

obtained in low yields (18–44%).[30] Another approach was reported by the Lin group, using 10 equiv of TFA to catalyze the reaction of 3,4,6-tri-*O*-benzyl-D-galactal with cyclohexanol and the Ferrier rearrangment product was obtained in a yield of 24%.[31] Subsequently, Rauter and coworkers developed acid zeolite catalysts to prepare 2,3-unsaturated *O*- and *S*-glycosides at 85 °C with good α-selectivity, despite that only three acceptors were suitable to low yields (38–50%).[32] In 2008, $Fe_2(SO_4)_3{\cdot}\chi H_2O$ (1 mol%) was used as a catalyst to synthesize a benzyl protected 2,3-unsaturated glycoside by the Zhang group. The reaction was carried out at 60 °C or under microwave irradiation to give good yields (70–84%). Unfortunately, only four alcohol acceptors were suitable for this catalytic system.[33] Recently, our group used H_2SO_4/SiO_2 as a catalyst to promote the reaction of benzyl-protected glycal with a series of alcohol acceptors at room temperature. The reaction conditions were mild and the yields were good, but it was necessary to add nucleophilic acceptors after rearrangement.[24] More recently, Chen and co-workers developed $Gd(OTf)_3$ as a Lewis acid to catalyze the synthesis of benzyl protected 2,3-unsaturated glycosides at 60 °C.[26] Through the above reports, we can conclude that the current methods suffered from disadvantages including narrow scope of acceptors (none of the reaction systems are suitable for phenolic acceptors), low yields, long reaction time, harsh reaction conditions, or use of toxic agents.

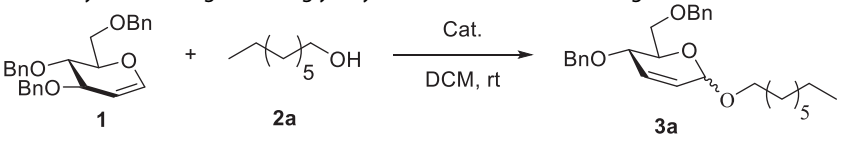
Iron catalysts have been extensively utilized as convenient and eco-friendly catalysts in synthetic chemistry.[34–37] It is noteworthy that $FeCl_3$ as a catalyst plays a more and more important role in carbohydrate

chemistry.[38–41] Based on our long-standing interest in iron catalysts, we have reported a series of glycosylation reactions catalyzed by ferric chloride.[42–44] Indeed, some of this type of catalysts such as $FeCl_3$,[45] $Fe_2(SO_4)_3$•xH_2O,[33] $Fe(OTf)_3$[46] and $FeCl_3$ immobilized in ionic liquids[47] have been utilized for the Ferrier rearrangement. In our previous reports, $FeCl_3$•6H_2O/C, Fe_3O_4@C@SO_3H and Fe_3O_4@C@Fe(III) were successfully used as the catalysts for 3,4,6-tri-*O*-acetyl-D-glucal Ferrier rearrangement with high yields and anomeric selectivity.[48–50] Recently, our group has successfully applied $FeCl_3$/C to catalyze β-stereoselective glycosylation of alcohols and phenolic acceptors for the synthesis of benzyl protecting propargyl glycosides.[51] In view that immobilized iron (III) catalysts have been successfully used in glycosylation, we expected that this mild approach would find more applications in glycoside synthesis, especially in Ferrier rearrangement of ether-protected glycals. This report describes the Ferrier rearrangement of 3,4,6-tri-*O*-benzyl-D-glucal under mild conditions using $FeCl_3$/C as an efficient catalyst.

Results and discussion

Initially, we conducted a model reaction between 3,4,6-tri-*O*-benzyl-D-glucal **1** and *n*-octanol **2a** in the presence of different iron catalysts in DCM at room temperature. The main reason for choosing *n*-octanol, instead of benzyl alcohol, as the model nucleophilic acceptor was due to the presence of the benzyl protecting group at the 3-*O*-position, which can easily form rearrangement by-products of 3,4,6-tri-*O*-benzyl-D-glucal.[24] First, we examined a series of iron (III) catalysts, $FeCl_3$, $FeCl_3$·6H_2O/C, $FeBr_3$, FeF_3, $Fe_2(SO_4)_3$ and $Fe(acac)_3$, for their ability to promote the glycosylation in CH_2Cl_2 at rt. As shown in Table 1, $FeCl_3$ showed the best catalytic activity (Entries 1–6). However, the glycosylation yield was not particularly high (∼67%). As a continuous work, we tried to substitute $FeCl_3$ for immobilized iron (III) catalysts. Then, reaction optimization was carried out by screening different carriers, including SiO_2, Al_2O_3, molecular sieves and carbon, to immobilize $FeCl_3$ according to the literature methods.[51–53] To our delight, we found that $FeCl_3$/C was the most promising, because other immobilized iron (III) catalysts, including $FeCl_3/SiO_2$, $FeCl_3/Al_2O_3$ and $FeCl_3$/4 Å MS, could only give the desired product either in longer time or poorer yields (Table 1, Entries 7–10). We also tried $FeCl_3$•6H_2O/C,[48] which had been utilized for Ferrier rearrangement of 3,4,6-tri-*O*-acetyl-D-glucal. Unfortunately, we did not get the desired result (Table 1, Entry 11). Then, the optimal mass ratio of $FeCl_3$/C was evaluated. When changing the mass ratio of $FeCl_3$/C to 3:5 or 1:10, product was obtained with lower yields (Entries 12 and 13). At the same time, to eliminate the possible

Table 1. Catalyst screening for the glycosylation of alcohol **2a** with glucal **1**[a]



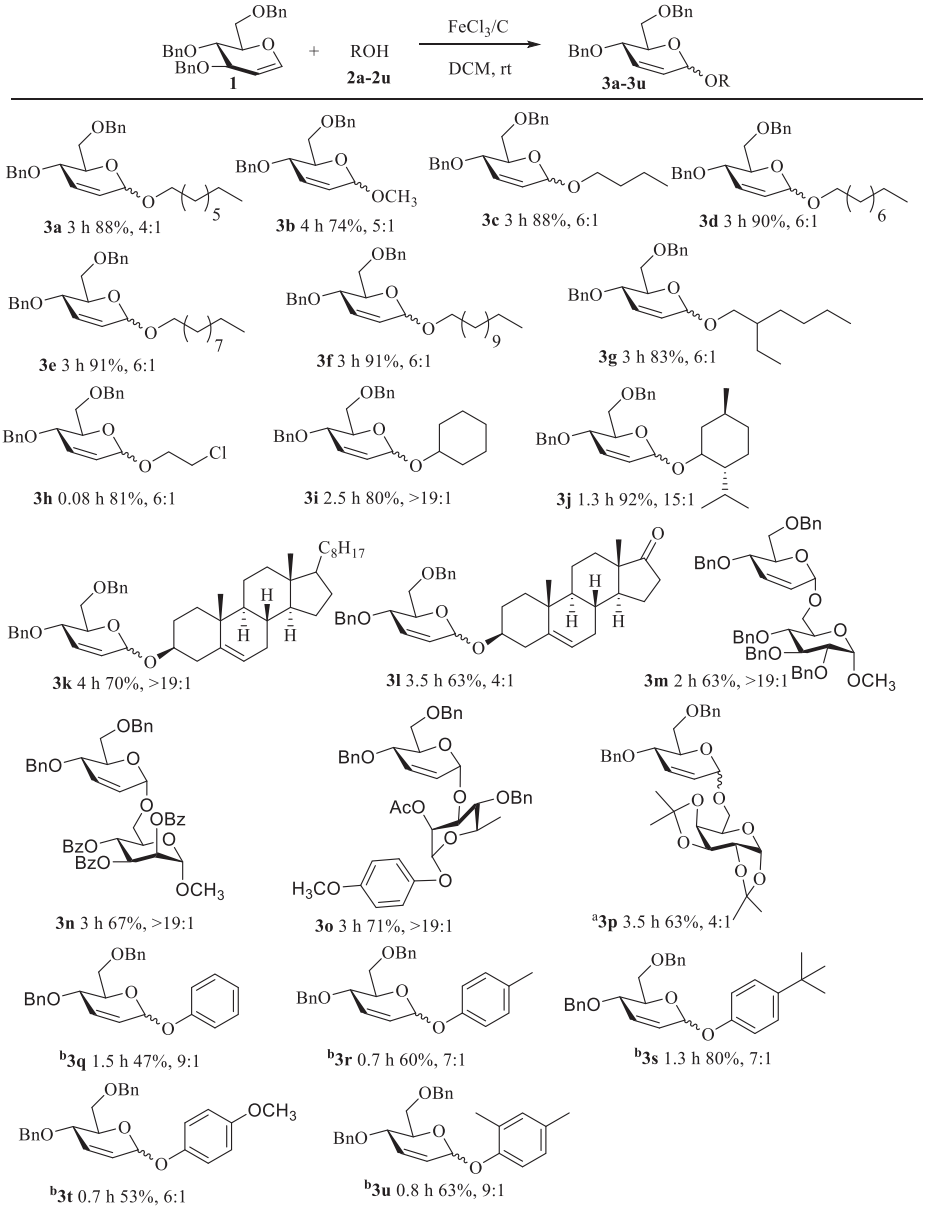
.

Entry	Catalyst	Mass ratio (Cat./C)	Eq. (Cat.)	Time (h)	Yield (%)[a]
1	$FeCl_3$	–	0.1	2	67
2	$FeCl_3•6H_2O$	–	0.1	2	57
3	$FeBr_3$	–	0.1	2	47
4	FeF_3	–	0.1	6	ND[b]
5	$Fe_2(SO_4)_3$	–	0.1	6	ND[b]
6	$Fe(acac)_3$	–	0.1	6	ND[b]
7	$FeCl_3/SiO_2$	1:5	0.1	2	78
8	$FeCl_3/Al_2O_3$	1:5	0.1	2	80
9	$FeCl_3$/4Å MS	1:5	0.1	20	ND[b]
10	$FeCl_3$/C	1:5	0.1	3	88
11	$FeCl_3•6H_2O$/C	1:5	0.1	4	69
12	$FeCl_3$/C	3:5	0.1	3	76
13	$FeCl_3$/C	1:10	0.1	4	72
14[c]	$FeCl_3$/C	1:5	0.1	3	78
15[d]	$FeCl_3$/C	1:5	0.1	3	89
16	$FeCl_3$/C	1:5	0.05	5	80
17	$FeCl_3$/C	1:5	0.2	2	83
18[e]	$FeCl_3$/C	1:5	0.1	5	78
19[f]	$FeCl_3$/C	1:5	0.1	24	ND[b]
20[g]	$FeCl_3$/C	1:5	0.1	24	65

[a]Isolated yields. [b]Not determined. [c]Three equivalents of **2a** were used. [d]Five equivalents of **2a** were used. [e]**2a** was added after the rearrangement occurred. [f]Et_2O was used as solvent. [g]CH_3CN was used as solvent, α:β = 7:1.

Ferrier rearrangement and other side reactions with benzyl alcohol generated *in situ*, more than one equivalent of the alcohol was tested, and we found that 4 equivalents of the alcohol were sufficient for this purpose (Entries 14–15). Moreover, we further optimized the use of $FeCl_3$/C, and found that reducing the amount of catalyst to 0.05 equivalent, the yield reduced to 80% and the reaction time was increased to 5 h (Entry 16). Increasing the catalyst equivalent to 0.2, the reaction time was shortened, but the yield was reduced to 83% (Entry 17). We also tested the two-step glycosylation as depicted in the reference.[24] After the system undergoing rearrangement reaction and then adding the acceptor, the reaction time required was longer while the yield was reduced (78%) with the generation of more rearranged by-products (Entry 18). Solvent effect was also evaluated, and we found that the reaction did not proceed in Et_2O (Entry 19).[50] When using CH_3CN as the solvent, desired product was obtained in poor yield (Entry 20),[28,50] although the α/β selectivity of product was slightly increased to 7:1. Considering the balance of reaction time and yields, we deemed DCM as the best solvent. Therefore, we have established the optimal reaction conditions as 1.0 equivalent of donor, 4.0 equivalents

Table 2. The Scope of Ferrier-rearrangement based glycosylation of various alcohols and phenols with glucal **1** under optimal conditions[a].



of acceptor, and 0.1 equivalent of $FeCl_3$/C (1:5) in DCM under room temperature.

Having established the optimal reaction conditions, we then turned our attention to exploring the scope of the acceptors using compounds **2a–2u** as shown in Table 2. In all cases, reactions proceeded smoothly and 2,3-unsaturated glycosides were obtained in good to excellent yields (47–92%),

demonstrating that the catalytic system tolerated the presence of alcoholic, saccharide, and phenolic nucleophiles, which was a significantly extended range of applicable nucleophilic acceptors compared to that reported in the literature. Structures of all compounds were confirmed by NMR and mass spectrometry, in accordance with literature reports.[30–33] In specific, the reactions with linear alcohols afforded products **3a–3f** in good to excellent yields (74–91%). When a branched alcohol was used as the nucleophile, the product **3g** was also obtained in 83% yield. Additionally, the reaction of chlorohydrin with 3,4,6-tri-*O*-benzyl-D-glucal afforded **3h** in a slightly lower yield (81%), probably due to the presence of an electron withdrawing group in the acceptor. For secondary alcohols such as cyclohexanol and menthol, the reaction system was also suitable to give **3i** and **3j**. Glycosylation with sterol also proceeded smoothly to afford **3k** and **3l**. Moreover, the catalytic system was suitable for saccharide acceptors. For example, the reactions with glucoside acceptor **2m**, mannoside **2n** and rhamnoside acceptor **2o** afforded the desired products **3m–3o** in good yields (63–71%) and high α-selectivity. It is worth noting that when galactoside acceptor **2p** was used to react with the donor under optimal conditions, the conversion rate of the donor was only 5% in 12 h, and after increasing the catalyst to 1 equivalent, the reaction could be completed in 3.5 h.

After the successful synthesis of various alcohol glycosides by the above method, we hoped to extend it to phenolic acceptors, considering the biological significance of many phenolic deoxyglycosides.[43,54–57] Although it is more difficult for phenols react with glycals as compared to alcohols, especially when $FeCl_3$ was utilized as the catalyst,[33,45] it should be noted that our method succeeded with phenols when 0.3 equivalent of $FeCl_3$/C (mass ratio of $FeCl_3$/C = 1:7) was used. As a result, a series of phenolic glycosides **3q–3u** were conveniently obtained in good yields (47–80%) and high anomeric selectivity (α:β > 6:1) in short reaction time (0.7–1.5 h).

In order to gain an insight into the reaction mechanism, we carried out the following control experiments (Fig. 2). Firstly, when 0.1 equivalent of DMAP was added in the system, the glycosylation reaction was quenched and no product was formed, leading to recovery of starting materials. However, addition of 0.1 equivalent of Cs_2CO_3 to the system, the reaction still occurred. Based on the above experimental results, we believed that

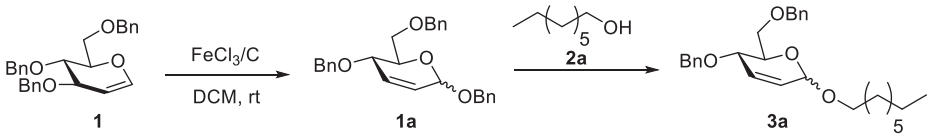


Figure 2. Two-step glycosylation of **2a** with **1** involving **1a** as an intermediate.

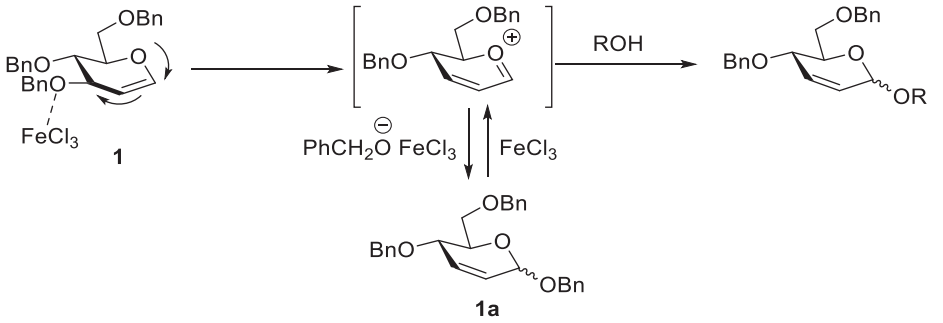


Figure 3. A plausible mechanism for Ferrier-rearrangement based glycosylation reactions of glucal **1**.

this was a Lewis acid-catalyzed process rather than a protic one. Secondly, when **1** was treated with the catalyst under the optimized reaction without adding a nucleophilic acceptor, **1a** was obtained after column chromatography and its structure was confirmed by ^{1}H-NMR data. Furthermore, after the isolated product **1a** was dissolved in dry DCM, treated with $FeCl_3$/C for 5 min and then mixed with acceptor **2a**, the desired product **3a** was formed in 78% isolated yield upon stirring at rt for 3 h. This result implied that rearrangement product **1a** was possibly an intermediate and could be further converted into product **3a** in the presence of nucleophiles under the optimized reaction conditions.

Based on the above observation and previous reports,[16,23,24,31,43] we proposed a reaction mechanism as depicted in Figure 3. First, 3,4,6-tri-*O*-benzyl-D-glucal was converted into an oxonium ion intermediate with the assistance of $FeCl_3$/C. Thereafter, this intermediate was transformed into glycosylation products *via* reaction with nucleophilic acceptors. At the same time, in the absence of proper nucleophiles the intermediate would also undergo rearrangement to result in 2,3-unsaturated benzyl glycoside **1a** as a by-product. However, the rearranged by-product **1a** could be further converted to an oxonium ion intermediate with the help of iron catalyst to react with nucleophiles to afford the desired products.

In conclusion, we have described herein a facile and efficient method for the synthesis of 2,3-unsaturated-*O*-glycosides from 3,4,6-tri-*O*-benzyl-D-glycal catalyzed by $FeCl_3$/C. The reaction is applicable to a wide range of acceptors including primary and secondary alcohols, sterols, sugars ad phenols, and the conditions are mild. The reaction proceeds with good to excellent yields. In addition, the catalyst $FeCl_3$/C has many advantages such as being affordable and safe, stable in the air, mild and efficient performance. Thus, we expect that this methodology will find widespread use in glycoside and oligosaccharide synthesis. Further applications of this

methodology to other ether-protected glycals are currently explored in our laboratory.

Experimental section

General procedures

To a stirred solution of 3, 4, 6-tri-*O*-benzyl-D-glucal (42 mg, 0.1 mmol) in DCM (1 mL) were added the corresponding acceptors (4 equiv.) and $FeCl_3$/C[44] (0.1 equiv.) at ambient temperature. After the reaction was completed (monitored by TLC), the reaction mixture was filtered and the catalyst was washed with dichloromethane. After evaporation of the solvent under vacuum, the crude products were purified by silica gel column chromatography. (Petroleum ether/EtOAc = 10/1). All compounds were fully characterized by NMR and MS.

Catalyst $FeCl_3$/C

Activated charcoal-supported $FeCl_3$ was prepared by the following method: To a mixture of $FeCl_3$ (0.1 g) and activated charcoal (0.5 g, 200–300 mesh) was added anhyd EtOH (5 mL) and the slurry was refluxed for 30 min.[51] The solvent was evaporated under reduced pressure resulting in free flowing $FeCl_3$/activated charcoal, which was dried at 120 °C for 2 h and used for the reactions directly.

Product characterization data

Octyl 4, 6-di-*O*-benzyl-2, 3-dideoxy-D-erythro-hex-2-enopyranoside (3a)[24]: α:β = 4:1 ^{1}H NMR (500 MHz, $CDCl_3$): **α-Anomer:** δ = 7.35 − 7.23 (m, 10H), 6.06 (d, J = 10.3 Hz, 1H), 5.78 (d, J = 10.3 Hz, 1H), 5.01(s, 1H), 4.65 (d, J = 12.2 Hz, 1H), 4.60 (d, J = 11.5 Hz, 1H), 4.51 (d, J = 12.2 Hz, 1H), 4.44 (d, J = 11.5 Hz, 1H), 4.17 (d, J = 9.4 Hz, 1H), 3.97 (d, J = 9.4 Hz, 1H), 3.80–3.70 (m, 3H), 3.50–3.46 (m, 1H), 1.62–1.56 (m, 2H), 1.26 (br, 10H), 0.89–0.86 (m, 3H). β-**Anomer:** δ = 7.35–7.23 (m, 10H), 6.03 (d, J = 12.5 Hz, 1H), 5.83 (d, J = 12.5 Hz, 1H), 5.11 (s, 1H), 4.59 (d, J = 12.2 Hz, 1H), 4.57 (d, J = 6.8 Hz, 1H), 4.52 (d, J = 6.8 Hz, 1H), 4.43 (d, J = 12.5 Hz, 1H), 4.17 (d, J = 2.0 Hz, 1H), 3.97 (d, J = 2.0 Hz, 1H), 3.97–3.95 (m, 3H), 3.50–3.46 (m, 1H), 1.62–1.56 (m, 2H), 1.26 (br, 10H), 0.89–0.86 (m, 3H). ESI-MS $[M + Na]^+$: calcd for $C_{28}H_{38}NaO_4$: 461.28, found: 461.33.

Methyl 4, 6-di-*O*-benzyl-2, 3-dideoxy-D-erythro-hex-2-enopyranoside (3 b):[24]α:β = 5:1 ^{1}H NMR (500 MHz, $CDCl_3$): **α-Anomer:** δ = 7.35 − 7.23 (m, 10H), 6.07 (d, J = 10.3 Hz, 1H), 5.77 (dt, J = 10.3, 2.1 Hz, 1H), 4.91 (s, 1H), 4.65 (d, J = 12.2 Hz, 1H), 4.59 (d, J = 11.6 Hz, 1H), 4.52 (d,

J = 12.2 Hz, 1H), 4.44 (d, J = 11.6 Hz, 1H), 4.17 (dd, J = 8.1 Hz, 1.4 Hz, 1H), 3.93 (dt, J = 9.4 Hz, 3.2 Hz, 1H), 3.74–3.69 (m, 2H), 3.44 (d, J = 13.3 Hz, 3H). β-**Anomer:** δ = 7.35 − 7.23 (m, 10H), 6.03 (d, J = 12.3 Hz, 1H), 5.78 (d, J = 12.3 Hz, 1H), 5.03(s, 1H), 4.65–4.44 (m, 4H), 3.98–3.94 (m, 2H), 3.74–3.69 (m, 2H), 3.44 (s, 3H). ESI-MS $[M + Na]^+$: calcd for $C_{21}H_{24}NaO_4$: 363.17, found: 363.17.

***n*-Butyl 4,6-Di-*O*-benzyl-2,3-dideoxy-a-D-erythro-hex-2-enopyranoside (3c)[24]: α:β = 6:1** ^{1}H NMR (500 MHz, $CDCl_3$): **α-Anomer:** δ = 7.35 − 7.24 (m, 10H), 6.07 (d, J = 10.2 Hz, 1H), 5.77 (d, J = 10.2, 1H), 5.01 (s, 1H), 4.65 (d, J = 12.1 Hz, 1H), 4.60 (d, J = 11.6 Hz, 1H), 4.51 (d, J = 12.1 Hz, 1H), 4.44 (d, J = 1.5 Hz, 1H), 4.17 (d, J = 9.4 Hz, 1H), 3.97 (d, J = 7.5 Hz, 1H), 3.85 − 3.70 (m, 3H), 3.51 − 3.47 (m, 1H), 1.60 − 1.56 (m, 2H), 1.40 − 1.35 (m, 2H), 0.93 − 0.89 (m, 3H). β-**Anomer:** δ = 7.35 − 7.24 (m, 10H), 6.02 (d, J = 12.2 Hz, 1H), 5.83 (d, J = 12.2 Hz, 1H), 5.10 (s, 1H), 4.65 − 4.30 (m, 4H), 3.96 (d, J = 2.0 Hz, 1H), 3.87 − 3.85 (m, 1H), 3.83 − 3.70 (m, 3H), 3.51 − 3.47 (m, 1H), 1.60 − 1.56 (m, 2H), 1.40 − 1.35 (m, 2H), 0.93–0.89 (m, 3H). ESI-MS $[M + Na]^+$: calcd for $C_{24}H_{30}NaO_4$: 405.21, found: 405.33.

Nonyl 4, 6-di-*O*-benzyl-2, 3-dideoxy-D-erythro-hex-2-enopyranoside (3d):[24] α:β = 6:1 ^{1}H NMR (500 MHz, $CDCl_3$): **α-Anomer:** δ = 7.35 − 7.23 (m, 10H), 6.06 (d, J = 10.3 Hz, 1H), 5.76 (d, J = 10.3 Hz, 1H), 5.01(s, 1H), 4.65 (d, J = 12.2 Hz, 1H), 4.59 (d, = 11.6 Hz, 1H), 4.51 (d, J = 12.2 Hz, 1H), 4.43 (d, J = 11.5 Hz, 1H), 4.17 (d, J = 9.4 Hz, 1H), 3.97 (d, J = 7.3 Hz, 1H), 3.80 − 3.68 (m, 3H), 3.50 − 3.46 (m, 1H), 1.60 − 1.55(m, 2H), 1.25 (br, 12H), 0.89 − 0.86 (m, 3H). β-**Anomer:** δ = 7.35 − 7.23 (m, 10H), 6.03 (d, J = 12.3 Hz, 1H), 5.80 (d, J = 12.3 Hz, 1H), 5.10(s, 1H), 4.65 − 4.43 (m, 4H), 3.97 (d, J = 7.6 Hz, 1H), 3.80 − 3.69 (m, 3H), 3.50–3.45 (m, 1H), 1.59 − 1.55 (m, 2H), 1.25 (br, 12H), 0.89 − 0.86 (m, 3H). ESI-MS: $[M + Na]^+$: calcd for $C_{29}H_{40}NaO_4$:475.29, found: 475.42.

Decyl 4, 6-di-*O*-benzyl-2, 3-dideoxy-D-erythro-hex-2-enopyranoside (3e):[24] α:β = 6:1 ^{1}H NMR (500 MHz, $CDCl_3$): **α-Anomer:** δ = 7.35 − 7.23 (m, 10H), 6.06 (d, J = 10.3 Hz, 1H), 5.78 (d, J = 10.3 Hz, 1H), 5.01(s, 1H), 4.65 (d, J = 12.2 Hz, 1H), 4.59 (d, J = 11.6 Hz, 1H), 4.51 (d, J = 12.2 Hz, 1H), 4.43 (d, J = 11.5 Hz, 1H), 4.17 (d, J = 9.4 Hz, 1H), 3.97 (d, J = 7.6 Hz, 1H), 3.80 − 3.69 (m, 3H), 3.50 − 3.45 (m, 1H), 1.59 − 1.55 (m, 2H), 1.30 − 1.25 (m, 14H), 0.89 − 0.86 (m, 3H) β-**Anomer:** δ = 7.35 − 7.23 (m, 10H), 6.02 (d, J = 12.3 Hz, 1H), 5.84 (d, J = 12.3 Hz, 1H), 5.10 (s, 1H), 4.65 − 4.43 (m, 4H), 3.97 (d, J = 7.6 Hz, 1H), 3.80 − 3.69 (m, 3H), 3.50 − 3.45 (m, 1H), 1.59 − 1.55 (m, 2H), 1.30 − 1.25 (m, 14H), 0.89 − 0.86 (m, 3H) ESI-MS: $[M + Na]^+$ calcd for $C_{30}H_{42}NaO_4$:489.31, found: 489.42.

Dodecanol 4, 6-di-*O*-benzyl-2, 3-dideoxy-D-erythro-hex-2-enopyranoside (3f):[24] α:β = 6:1 ^{1}H NMR (500 MHz, $CDCl_3$): **α-Anomer:** δ = 7.35–7.23 (m, 10H), 6.06 (d, J = 10.3 Hz, 1H), 5.77 (d, J = 10.3, 1H),

5.01(s, 1H), 4.65 (d, J = 12.2 Hz, 1H), 4.60 (d, J = 11.5 Hz, 1H), 4.51 (d, J = 12.2 Hz, 1H), 4.44 (d, J = 11.5 Hz, 1H), 4.17 (d, J = 9.4 Hz, 1H), 3.97 − 3.95 (m, 1H), 3.78 − 3.69 (m, 3H), 3.49 − 3.47 (m, 1H), 1.33 − 1.25 (m, 22H), 0.89 − 0.86 (m, 3H). β-**Anomer:** δ = 7.33–7.23 (m, 10H), 6.02 (d, J = 12.4 Hz, 1H), 5.81 (d, J = 12.4 Hz, 1H), 5.01 (s, 1H), 4.57 − 4.49 (m 4H), 3.97 − 3.95 (m, 1H), 3.87 − 3.83 (m, 1H), 3.78 − 3.69 (m, 3H), 3.49 − 3.47 (m, 1H), 1.33 − 1.25 (m, 22H), 0.89 − 0.86 (m, 3H) ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm): 138.21, 138.08, 130.45, 128.37, 128.32, 128.27, 127.91, 127.78, 127.68, 127.64, 127.53, 126.74, 94.55, 73.32, 70.99, 70.38, 69.09, 68.91, 68.65, 31.89, 29.78, 29.64, 29.60, 29.58, 29.40, 29.32, 26.19, 22.66, 14.09. ESI-MS: $[M + Na]^+$ calcd for $C_{32}H_{46}NaO_4$: 517.34, found: 517.42.

Isooctyl 4, 6-di-*O*-benzyl-2, 3-dideoxy-D-erythro-hex-2-enopyranoside (3g):[24] **α:β = 6:1** ^{1}H NMR (500 MHz, $CDCl_3$): **α-Anomer:** $\delta = 7.36 - 7.24$ (m, 10H), 6.06 (d, $J = 10.0$ Hz, 1H), 5.77 (d, $J = 10.0$ Hz, 1H), 4.99 (s, 1H), 4.67 (d, $J = 12.0$ Hz, 1H), 4.60 (d, $J = 11.5$ Hz, 1H), 4.51 (d, $J = 12.0$ Hz, 1H), 4.44 (d, $J = 11.5$ Hz, 1H), 4.18 (d, $J = 9.5$ Hz, 1H), 3.95 (d, $J = 9.0$ Hz, 1H), 3.77 − 3.69 (m, 3H), 3.38 − 3.34 (m, 1H),1.61 − 1.51(m, 1H), 1.36 − 1.27 (m, 8H), 0.89 − 0.84 (m, 6H). β-**Anomer:** $\delta = 7.36 - 7$ .24 (m, 10H), 6.02 (d, $J = 12.0$ Hz, 1H), 5.82 (d, $J = 12.0$ Hz, 1H), 5.09 (s, 1H), 4.68 − 4.43 (m, 4H), 3.98 − 3.97 (m, 1H), 3.78 − 3.70 (m, 2H), 3.38 − 3.34 (m, 1H), 1.61 − 1.51(m, 1H), 1.36 − 1.27 (m, 8H), 0.89 − 0.84 (m, 6H). ESI-MS: $[M + Na]^+$ calcd for $C_{28}H_{38}NaO_4$: 461.28, found: 461.25.

Chloroethanyl 4, 6-di-O-benzyl-2, 3-dideoxy-α, β-D-erythro-hex-2-enopyranoside (3h):[24] **α:β = 6:1** ^{1}H NMR (500 MHz, $CDCl_3$): **α-Anomer:** $\delta = 7.37 - 7.23$ (m, 10H), 6.10 (d, $J = 10.3$ Hz, 1H), 5.78 (dd, $J = 10.3$ Hz, $J = 2.0$ Hz, 1H), 5.07 (s, 1H), 4.65 (d, $J = 12.2$ Hz, 1H), 4.60 (d, $J = 11.5$ Hz, 1H), 4.50 (d, $J = 12.1$ Hz, 1H), 4.44 (d, $J = 11.5$ Hz, 1H), 4.17 (d, $J = 9.5$ Hz, 1H), 4.02 − 3.98(m, 2H), 3.82 − 3.77 (m, 1H), 3.75 − 3.64 (m, 3H). β-**Anomer:** $\delta = 7.37$–7.23 (m, 10H), 6.06 (d, $J = 12.3$ Hz, 1H), 5.82 (dd, $J = 12.3$ Hz, 1H), 5.19 (s, 1H), 4.65 − 4.42 (m, 4H), 4.01 − 3.98 (m, 2H), 3.82 − 3.78 (m, 1H), 3.75 − 3.64 (m, 3H). ESI-MS: $[M + Na]^+$ calcd for $C_{22}H_{25}ClNaO_4$: 411.14, found: 411.25.

Cyclohexyl 4, 6-di-*O*-benzyl-2, 3-dideoxy-D-erythro-hex-2-enopyranoside (3i):[24] **α:β > 19:1** ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.33 - 7.23$ (m, 10H), 6.06 (d, $J = 12.8$ Hz, 1H), 5.73 − 5.77 (m, 1H), 5.16 (s, 1H), 4.66 (d, $J = 14.9$ Hz, 1H), 4.60 (d, $J = 14.6$ Hz, 1H), 4.50 (d, $J = 15.3$ Hz, 1H), 4.44 (d, $J = 14.3$ Hz, 1H), 4.15 (d, $J = 11.9$ Hz, 1H), 4.03 − 4.00 (m, 1H), 3.76 − 3.66 (m, 3H), 1.91 − 1.71 (m, 2H), 1.61 − 1.60 (m, 2H), 1.57–1.53 (m, 4H), 1.36 − 1.25 (m, 2H). ESI-MS: $[M + Na]^+$ calcd for $C_{26}H_{32}NaO_4$: 431.23, found: 431.33.

Menthyl-4, 6-di-*O*-benzyl-2, 3-dideoxy-α,β-D-erythro-hex-2-enopyranoside (3j):[24] **α:β = 9:1** ^{1}H NMR (500 MHz, $CDCl_3$): **α-Anomer:**

$\delta = 7.35 - 7.22$ (m, 10H), 6.06 (d, $J = 10.3$ Hz, 1H), $5.80 - 5.78$ (m, 1H), 5.09 (s, 1H), 4.66 (d, $J = 12.1$ Hz, 1H), 4.59 (d, $J = 11.6$ Hz, 1H), 4.50 (d, $J = 12.2$ Hz, 1H), 4.41 (d, $J = 11.5$ Hz, 1H), 4.16 (d, $J = 9.4$ Hz, 1H), 4.02 (d, $J = 9.5$ Hz, 1H), $3.76 - 3.68$ (m, 2H), $3.45 - 3.40$ (m, 1H), $2.21 - 2.17$ (m, 1H), $2.12 - 2.06$ (m, 1H), $1.62 - 1.58$ (m, 2H), $1.40 - 1.25$ (m, 2H), $1.28 - 1.20$ (m, 1H), $1.01 - 0.76$ (m, 11H). **β-Anomer:** $\delta = 7.35 - 7.22$ (m, 10H), 6.01 (d, $J = 12.0$ Hz, 1H), 5.73 (d, $J = 12.0$ Hz, 1H), 5.25 (s, 1H), $4.61 - 4.54$ (m, 4H), 4.16 (m, 1H), 3.85 (m, 1H), $3.73 - 3.68$ (m, 1H), 3.54 (m, 1H), $2.21 - 2.17$ (m, 1H), $2.12 - 2.06$ (m, 1H), $1.62 - 1.58$ (m, 2H), $1.40 - 1.25$ (m, 2H), $1.28 - 1.20$ (m, 1H), $1.01 - 0.76$ (m, 11H). ESI-MS: $[M + Na]^+$ calcd for $C_{30}H_{40}NaO_4$: 487.29, found: 487.42.

Cholesteryl 4, 6-di-*O*-benzyl-2, 3-dideoxy-D-erythro-hex-2-enopyranoside (3k):[24] **α:β = 5:1** ^{1}H NMR (500 MHz, $CDCl_3$): **α-Anomer:** $\delta = 7.35 - 7.23$ (m, 10H), 6.06 (d, $J = 10.2$ Hz, 1H), 5.75 (d, $J = 10.2$ Hz, 1H), $5.25 - 5.24$ (m, 1H), 5.16 (s, 1H), 4.66 (d, $J = 12.2$ Hz, 1H), 4.60 (d, $J = 11.5$ Hz, 1H), 4.50 (d, $J = 12.1$ Hz, 1H), 4.44 (d, $J = 11.5$ Hz, 1H), 4.16 (d, $J = 9.3$ Hz, 1H), $4.03 - 4.01$(m, 1H), $3.75 - 3.68$ (m, 2H), $3.60 - 3.54$ (m, 1H), $2.42 - 2.31$ (m, 2H), $2.04 - 1.85$ (m, 5H), $1.56 - 1.47$ (m, 6H), $1.33 - 1.25$ (m, 5H), $1.11 - 1.09$ (m, 6H), $0.99 - 0.98$ (m, 5H), $0.92 - 0.90$ (m, 4H), $0.87 - 0.85$ (m, 7H), 0.67 (s, 3H). **β-Anomer:** $\delta = 7.35 - 7.23$ (m, 10H), 6.01 (d, $J = 12.2$ Hz, 1H), 5.81 (d, $J = 12.2$ Hz, 1H), $5.28 - 5.26$ (m, 2H), $4.66 - 4.42$ (m, 4H), 4.60 (d, $J = 11.5$ Hz, 1H), 4.50 (d, $J = 12.1$ Hz, 1H), 4.44 (d, $J = 11.5$ Hz, 1H), 4.16 (d, $J = 9.3$ Hz, 1H), $4.03 - 4.01$ (m, 1H), $3.75 - 3.68$ (m, 2H), $3.60 - 3.54$ (m, 1H), $2.42 - 2.31$ (m, 2H), $2.04 - 1.85$ (m, 5H), $1.56 - 1.47$ (m, 6H), $1.33 - 1.25$ (m, 5H), $1.11 - 1.09$ (m, 6H), $0.99 - 0.98$ (m, 5H), $0.92 - 0.90$ (m, 4H), $0.87 - 0.85$ (m, 7H), 0.67 (s, 3H). ESI-MS: $[M + Na]^+$ calcd for $C_{47}H_{66}NaO_4$: 717.50, found: 717.58.

Dehydroepiandrosteronyl 4, 6-di-*O*-benzyl-2, 3-dideoxy-D-erythro-hex-2-enopyranoside (3l):[24] **α:β > 19:1** ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.35 - 7.24$ (m, 10H), 6.07 (d, $J = 10.3$ Hz, 1H), 5.75 (d, $J = 10.2$ Hz, 1H), 5.27 (s, 1H), 5.17(s, 1H), 4.65 (d, $J = 12.1$ Hz, 1H), 4.60 (d, $J = 11.5$ Hz, 1H), 4.50 (d, $J = 12.1$ Hz, 1H), 4.44 (d, $J = 11.5$ Hz, 1H), 4.15 (d, $J = 9.5$ Hz, 1H), 4.03(d, $J = 9.5$ Hz, 1H), $3.73 - 3.72$ (m, 2H), $3.60 - 3.56$ (m, 1H), $2.45 - 2.43$ (m, 2H), $2.09 - 2.04$ (m, 1H), $1.87 - 1.83$ (m, 2H), $1.66 - 1.64$ (m, 4H), 1.59 (m, 4H), $1.51 - 1.49$ (m, 3H), $1.30 - 1.25$ (m, 2H), 1.02 (m, 1H), 1.00 (s, 3H), 0.88 (s, 3H). ESI-MS: $[M + Na]^+$ calcd for $C_{47}H_{66}NaO_4$: 619.35, found: 619.42.

4,6-Di-*O*-benzyl-2,3-dideoxy-α-D-hex-2-enopyranosyl-(1→6)-Methyl-2,3,4-tri-*O*-benzyl-α-D-glucopyranoside (3m):[58] **α:β > 19:1** ^{1}H NMR (500 MHz, $CDCl_3$): $\delta = 7.35 - 7.21$ (m, 25H), 6.05 (d, $J = 10.4$ Hz, 1H), 5.78 (d, $J = 10.2$ Hz, 1H), 5.10 (s, 1H), 4.97 (d, $J = 10.9$ Hz, 1H), 4.87 (d,

$J = 10.9$ Hz, 1H), 4.82 − 4.76 (m, 2H), 4.65 (t, $J = 11.8$ Hz, 2H), 4.61 (d, $J = 2.4$ Hz, 1H), 4.56 (d, $J = 12.0$ Hz, 2H), 4.41 (d, $J = 11.5$ Hz, 1H), 4.37 (d, $J = 12.2$ Hz, 1H), 4.18 (d, $J = 9.3$ Hz, 1H), 4.07 (dd, $J = 11.2$, 2.4 Hz, 1H), 3.98 (t, $J = 9.2$ Hz, 1H), 3.85 (d, $J = 9.2$ Hz, 1H), 3.76 (d, $J = 9.9$ Hz, 1H), 3.71 (d, $J = 11.3$ Hz, 1H), 3.63 − 3.58 (m, 2H), 3.55 − 3.47 (m, 2H), 3.37 (s, 3H).

4,6-Di-*O*-benzyl-2,3-dideoxy-α-D-hex-2-enopyranosyl-(1→6)-Methyl-2,3,4-tri-*O*-benzoyl-α-D-mannopyranoside (3n): α:β > 19:1 ^{1}H NMR (500 MHz, $CDCl_3$) δ = 8.12 (d, $J = 7.7$ Hz, 2H), 7.97 (d, $J = 7.8$ Hz, 2H), 7.86 (d, $J = 7.8$ Hz, 2H), 7.59 (d, $J = 7.0$ Hz, 1H), 7.55 − 7.47 (m, 3H), 7.44 (t, $J = 7.0$ Hz, 1H), 7.41 − 7.27 (m, 14H), 6.07 (t, $J = 9.2$ Hz, 2H), 5.86 (d, $J = 10.0$ Hz, 1H), 5.72 (dd, $J = 10.3$, 1.8 Hz, 1H), 5.68 (s, 1H), 5.11 (s, 1H), 5.00 (s, 1H), 4.62 (d, $J = 11.5$ Hz, 1H), 4.54 (d, $J = 12.2$ Hz, 1H), 4.47 (d, $J = 11.5$ Hz, 1H), 4.34 (d, $J = 12.2$ Hz, 1H), 4.25 (t, $J = 9.5$ Hz, 2H), 4.09 (d, $J = 11.0$ Hz, 1H), 3.98 (d, $J = 9.1$ Hz, 1H), 3.79 (d, $J = 10.8$ Hz, 1H), 3.67 (d, $J = 10.6$ Hz, 1H), 3.53 (s, 3H), 3.45 (d, $J = 10.7$ Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) 165.61, 165.60, 165.29, 138.32, 138.18, 133.48, 133.32, 133.13, 131.19, 130.05, 129.85, 129.50, 129.40, 129.29, 128.65, 128.46, 128.41, 128.34, 128.32, 127.91, 127.89, 127.75, 127.62, 126.14, 98.62, 94.90, 73.39, 71.17, 70.51, 70.41, 70.22, 69.72, 69.37, 68.57, 67.30, 66.74, 55.60. HRMS (ESI^+): m/z calcd. for $C_{48}H_{46}NaO_{12}$ $[M + Na]^+$ 837.2888, found 837.2881.

4,6-Di-*O*-benzyl-2,3-dideoxy-α-D-hex-2-enopyranosyl-(1→6)-4-Methoxyphenyl-2-*O*-acetyl-4-*O*-benzyl-α-L-rhamnopyranoside (3o): α:β > 19:1 ^{1}H NMR (500 MHz, $CDCl_3$) δ = 7.32 − 7.25 (m, 10H), 7.19 (d, $J = 9.1$ Hz, 5H), 6.98 (d, $J = 8.3$ Hz, 2H), 6.82 (d, $J = 8.2$ Hz, 2H), 6.09 (d, $J = 10.2$ Hz, 1H), 5.66 (d, $J = 10.2$ Hz, 1H), 5.48 (s, 1H), 5.30 (s, 1H), 5.26 (s, 1H), 4.84 (d, $J = 10.9$ Hz, 1H), 4.64 (d, $J = 10.9$ Hz, 1H), 4.59 (d, $J = 12.2$ Hz, 1H), 4.53 (d, $J = 11.5$ Hz, 1H), 4.48 (dd, $J = 9.5$, 3.0 Hz, 1H), 4.36 (d, $J = 11.4$ Hz, 1H), 4.27 (t, $J = 11.5$ Hz, 2H), 3.92 (dd, $J = 15.9$, 7.1 Hz, 2H), 3.77 (s, 3H), 3.42 (t, $J = 9.5$ Hz, 1H), 3.38 (s, 2H), 1.31 (d, $J = 6.2$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) 170.35, 154.99, 150.17, 138.30, 138.13, 138.11, 131.23, 128.27, 128.24, 128.22, 127.99, 127.86, 127.68, 127.61, 127.55, 127.52, 126.27, 117.64, 114.59, 96.84, 91.38, 79.10, 75.37, 73.59, 73.27, 71.32, 70.13, 69.53, 68.59, 68.54, 68.07, 55.65, 21.07, 17.97. HRMS (ESI^+): m/z calcd. for $C_{42}H_{46}NaO_{10}$ $[M + Na]^+$ 733.2990, found 733.2983.

4,6-Di-*O*-benzyl-2,3-dideoxy-α,β-D-hex-2-enopyranosyl-(1→6)-1,2;3,4-di-*O*-isopropylidene-α-D-galactopyranoside (3p):[24] **α:β = 4:1** ^{1}H NMR (500 MHz, $CDCl_3$): **α-Anomer:** $\delta = 7.34 - 7.23$ (m, 10H), 6.06 (d, $J = 10.3$ Hz, 1H), 5.78 (dt, $J = 10.3$ Hz, $J = 2.1$ Hz, 1H), 5.52 (d, $J = 5.0$ Hz,

1H), 5.09 (s, 1H), 4.66 (d, $J = 12.2$ Hz, 1H), 4.60 − 4.56 (m, 3H), 4.49 (d, $J = 12.3$ Hz, 1H), 4.43 (d, $J = 11.5$ Hz, 1H), 4.31 − 4.26 (m, 2H), 4.23 (d, $J = 9.4$ Hz, 1H), 4.02 − 4.00 (m, 3H), 3.85 − 3.84 (m, 1H), 3.80 − 3.75 (m, 2H), 3.74 − 3.70 (m, 1H), 1.52 (s, 3H), 1.44 (s, 3H),1.34 − 1.26 (m, 6H). **β-Anomer:** $\delta = 7.28 - 7.23$ (m, 10H), 6.01 (d, $J = 12.3$ Hz, 1H), 5.92 (dt, $J = 12.3$ Hz, 1H), 5.55 (d, $J = 5.0$ Hz, 1H), 5.20 (s, 1H,) , 4.66 − 4.42 (m, 6H), 4.31 − 4.26 (m, 2H), 4.23 (d, $J = 9.4$ Hz, 1H), 4.02 − 4.00 (m, 3H), 3.85 − 3.84 (m, 1H), 3.80 − 3.75 (m, 2H), 3.74 − 3.70 (m, 1H), 1.52 (s, 3H), 1.44 (s, 3H),1.34 − 1.26 (m, 6H). ESI-MS: $[M + Na]^+$ calcd for $C_{32}H_{40}NaO_9$: 591.27, found: 591.33.

Phenyl 4, 6-di-*O*-benzyl-2, 3-dideoxy-α, β-D-erythro-hex-2-enopyranoside (3q)[59]: α:β = 9:1 ^{1}H NMR (500 MHz, $CDCl_3$): **α-Anomer:** $\delta = 7.34 - 7.25$ (m, 12H), 7.13 − 7.11 (m, 2H), 7.02 − 7.01 (m, 1H), 6.20 (d, J = 10.1 Hz, 1H), 5.91 (d, J = 10.2 Hz, 1H), 5.70 (s, 1H), 4.65 − 4.45 (m, 4H), 4.29 (d, J = 9.5 Hz, 1H), 4.09 (d, J = 9.4 Hz, 1H), 3.76 − 3.66 (m, 2H). **β-Anomer:** $\delta = 7.34 - 7.25$ (m, 12H), 7.13 − 7.11 (m, 2H), 7.02 − 7.01 (m, 1H), 6.14 (d, J = 12.1 Hz, 1H), 6.03 (d, J = 12.2 Hz, 1H), 5.79 (s, 1H), 4.65 − 4.45 (m, 4H), 4.23 − 4.21 (m, 1H), 4.07 − 4.02 (m, 1H), 3.76 − 3.66 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ (ppm): 157.37, 138.08, 137.95, 131.68, 129.39, 129.36, 128.39, 128.26, 127.94, 127.87, 127.57, 125.70, 122.04, 117.02, 93.52, 73.28, 71.23, 70.06, 68.63, 20.55. ESI-MS: $[M + Na]^+$ calcd for $C_{26}H_{26}NaO_4$: 425.18, found: 425.25.

4-Methylphenyl 4, 6-di-*O*-benzyl-2, 3-dideoxy-α, β-D-erythro-hex-2-enopyranoside (3r):[60] α:β = 7:1 ^{1}H NMR (500 MHz, $CDCl_3$): **α-Anomer:** $\delta = 7.33 - 7.24$ (m, 10H), 7.07 − 7.05 (m, 2H), 7.02 − 6.98 (m, 2H), 6.19 (d, $J = 10.5$ Hz, 1H), 5.90 (d, $J = 10.5$ Hz, 1H), 5.65 (s, 1H), 4.64 − 4.45 (m, 4H), 4.26(d, $J = 9.0$ Hz, 1H), 4.08 (d, $J = 9.0$ Hz, 1H), 3.75–3.69 (m, 2H), 1.28 (s, 9H). **β-Anomer:** $\delta = 7.33 - 7.24$ (m, 10H), 7.07 − 7.05 (m, 2H), 7.02 − 6.98 (m, 2H), 6.13 (d, $J = 12.5$ Hz, 1H), 6.00 (d, $J = 12.5$ Hz, 1H), 5.73 (s, 1H), 4.64 − 4.45 (m, 4H), 4.19 − 4.18 (m, 1H), 4.02 − 4.00 (m, 1H), 3.75 − 3.69 (m, 2H), 2.29 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 155.24, 138.12, 137.98, 131.57, 131.41, 129.82, 128.37, 128.27, 127.82, 127.76, 127.60, 127.55, 125.85, 117.02, 93.52, 73.28, 71.23, 70.06, 68.63, 20.55. ESI-MS: $[M + Na]^+$ calcd for $C_{27}H_{28}NaO_4$: 439.20, found: 439.25.

***p-tert*-Butylphenyl 4, 6-di-*O*-benzyl-2, 3-dideoxy-α, β-D-erythro-hex-2-enopyranoside (3 s)[61]: α:β = 7:1** ^{1}H NMR (500 MHz, $CDCl_3$): **α-Anomer:** $\delta = 7.33$–7.26 (m, 12H), 7.06–7.05 (m, 2H), 6.19 (d, $J = 10.5$ Hz, 1H), 5.90 (d, $J = 10.0$ Hz, 1H), 5.66 (s, 1H), 4.65 − 4.46 (m, 4H), 4.27(d, $J = 9.0$ Hz, 1H), 4.07 (d, $J = 8.5$ Hz, 1H), 3.76 − 3.66 (m, 2H), 2.28 (s, 3H). **β-Anomer:** $\delta = 7.33$–7.26 (m, 12H), 7.06–7.05 (m, 2H), 6.09 (d, $J = 12.5$ Hz, 1H), 6.01 (d, $J = 12.5$ Hz, 1H), 5.76(s, 1H), 4.64 − 4.62(m, 2H), 4.48 − 4.61 (m, 2H), 4.25 − 4.21 (m, 1H), 4.05 − 4.03 (m, 1H), 3.76 − 3.66 (m, 2H), 2.25 (s, 9H).

^{13}C NMR (125 MHz, $CDCl_3$): 155.19, 144.79, 138.14, 137.98, 131.56, 128.37, 128.27, 127.84, 127.82, 127.76, 127.54, 126.15, 125.86, 116.54, 93.51, 73.31, 71.23, 70.10, 70.03, 68.65, 34.1 31.48. ESI-MS: $[M+Na]^+$ calcd for $C_{30}H_{34}NaO_4$: 481.25, found: 481.33.

Methoxyphenyl 4, 6-di-*O*-benzyl-2, 3-dideoxy-α, β-D-erythro-hex-2-enopyranoside (3t):[62] **α:β = 6:1** ^{1}H NMR (500 MHz, $CDCl_3$): **α-Anomer:** $\delta = 7.34-7.25$ (m, 10H), $7.06-7.04$ (m, 2H), $6.80-6.78$ (m, 2H), 6.19 (d, $J = 10.2$ Hz, 1H), 5.92 (d, $J = 10.2$ Hz, 1H), 5.56 (s, 1H), $4.65-4.46$ (m, 4H), 4.24 (d, $J = 9.5$ Hz, 1H), 4.11 (d, $J = 14.2$ Hz, 1H), $3.76-3.69$ (m, 5H). **β-Anomer:** $\delta = 7.34-7.25$ (m, 10H), $7.06-7.04$ (m, 2H), $6.80-6.78$ (m, 2H), 6.12 (d, $J = 12.2$ Hz, 1H), 6.01 (d, $J = 12.2$ Hz, 1H), 5.67 (s, 1H), $4.65-4.46$ (m, 4H), $4.18-4.15$ (m, 1H), $4.06-4.03$ (m, 1H), $3.74-3.68$ (m, 5H) ^{13}C NMR (125 MHz, $CDCl_3$): 154.93, 151.38, 138.13, 137.96, 131.50, 128.38, 128.27, 127.81, 127.77, 127.55, 125.94, 118.68, 117.94, 114.44, 94.30, 73.29, 71.18, 70.12, 69.96, 68.77, 55.60. ESI-MS: $[M+Na]^+$ calcd for $C_{27}H_{28}NaO_5$: 455.19, found: 455.25.

2,4-Dimethylphenyl 4, 6-di-*O*-benzyl-2, 3-dideoxy-α, β-D-erythro-hex-2-enopyranoside (3 u): α:β = 9:1 ^{1}H NMR (500 MHz, $CDCl_3$): **α-Anomer:** $\delta = 7.33-7.24$ (m, 10H), $7.11-7.09$ (m, 1H), $6.94-6.90$ (m, 2H), 6.18 (d, $J = 10.5$ Hz, 1H), 5.92 (d, $J = 10.0$ Hz, 1H), 5.61 (s, 1H), $4.65-4.46$ (m, 4H), 4.27 (d, $J = 9.5$ Hz, 1H), 4.09 (d, $J = 9.5$ Hz, 1H), $3.77-3.67$ (m, 2H), 2.25 (s, 3H), 2.17 (s, 3H). **β-Anomer:** $\delta = 7.31-7.24$ (m, 10H), $7.11-7.09$ (m, 1H), $6.92-6.90$ (m, 2H), 6.15 (d, $J = 12.5$ Hz, 1H), 6.02 (d, $J = 12.5$ Hz, 1H), 5.68 (s, 1H), $4.64-4.60$ (m, 2H), $4.50-4.46$ (m, 2H), $4.17-4.15$ (m, 1H), $4.07-4.05$ (m, 1H), $3.77-3.67$ (m, 2H), 2.25 (s, 3H), 2.17 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): 153.60, 138.14, 137.93, 131.35, 131.33, 128.39, 128.27, 127.90, 127.83, 127.80, 127.54, 127.10, 126.03, 115.64, 93.84, 73.32, 71.40, 70.15, 70.13, 68.65, 20.51, 16.25. ESI-MS: $[M+Na]^+$ calcd for $C_{28}H_{30}NaO_4$: 453.21, found: 453.33.

Acknowledgment

We sincerely thank the analytic center of East China Normal University for data measurements.

Funding

The project was supported by the Natural Science Foundation of Shanghai [11ZR1410400], large instruments Open Foundation of East China Normal University [20161043], DAXIA Science Research Foundation of East China Normal University [2011DX-288] and National Undergraduate Training Program for Innovation and Entrepreneurship [201710269030G].

References

[1] Liao, H.; Leng, W.; Hoang, K.; Yao, H.; He, J.; Voo, A.; Liu, X. Asymmetric syntheses of 8-oxabicyclo[3,2,1]octane and 11-oxatricyclo[5.3.1.0]undecane from glycals. *Chem. Sci*. **2017**, *8*(9), 6656–6661. doi: 10.1039/C7SC02625K.

[2] Park, Y.; Harper, K. C.; Kuhl, N.; Kwan, E. E.; Liu, R. Y.; Jacobsen, E. N. Macrocyclic bis-thioureas catalyze stereospecific glycosylation reactions. *Science*. **2017**, *355*(6321), 162–166. doi: 10.1126/science.aal1875.

[3] Kartika, R.; Frein, J. D.; Taylor, R. E. Electrophile-induced ether transfer: stereoselective synthesis of 2,6-disubstituted-3,4-dihydropyrans. *J. Org. Chem.* **2008**, *73*(14), 5592–5594. doi: 10.1021/jo800704d.

[4] Gu, Z.; Zhang, X.; Zhang, J.; Xing, G. Highly efficient α-C-sialylation promoted by $(p\text{-Tol})_2SO/Tf_2O$ with N-acetyl-5-N,4-O-oxazolidione protected thiosialoside as donor. *Org. Biomol. Chem.* **2013**, *11*(30), 5017–5022. doi: 10.1039/c3ob40876k.

[5] Li, C.; Wang, L. Chemoenzymatic methods for the synthesis of glycoproteins. *Chem. Rev.* **2018**, *118*(17), 8359–8413. doi: 10.1021/acs.chemrev.8b00238.

[6] Lowary, T. L. Twenty years of mycobacterial glycans: furanosides and beyond. *Acc. Chem. Res.* **2016**, *49*(7), 1379–1388. doi: 10.1021/acs.accounts.6b00164.

[7] Schmidt, R. R.; Angerbauer, R. A short synthesis of racemic uronic acids and 2,3-anhydrouronic acids. *Carbohydr. Res.* **1981**, *89*(1), 159–162. doi: 10.1016/S0008-6215(00)85239-8.

[8] Schmidt, R. R.; Angerbauer, R. Simplede-novo Synthesis of Reactive Pseudoglycals(Hex-2-enopyranosides)—Stereospecificα-Glycoside Coupling. *Angew. Chem. Int. Ed. Engl.* **1977**, *16*(11), 783–784. doi: 10.1002/anie.197707832.

[9] Gordon, D. M.; Danishefsky, S. J. Ritter-like reactions of 1,2-anhydropyranose derivatives. *J. Org. Chem.* **1991**, *56*(11), 3713–3715. doi: 10.1021/jo00011a050.

[10] Ernst, C.; Klaffke, W. Chemical synthesis of uridine diphospho-D-xylose and UDP-L-arabinose. *J. Org. Chem.* **2003**, *68*(14), 5780–5783. doi: 10.1021/jo034379u.

[11] Fernandes, A.; Dell'Olmo, M.; Tatibouët, A.; Imberty, A.; Philouze, C.; Rollin, P. Dramatic effect of PSE clamping on the behaviour of d-glucal under Ferrier I conditions. *Tetrahedron Lett.* **2008**, *49*(21), 3484–3488. doi: 10.1016/j.tetlet.2008.03.093.

[12] Tanmaya, P. Vinyl sulfone-modified carbohydrates: an inconspicuous group of chiral building blocks. *Tetrahedron* **2008**, *64*, 3605-3628. doi: 10.1016/j.tet.2008.01.069.

[13] Neyts, J.; De Clercq, E.; Singha, R.; Chang, Y. H.; Das, A. R.; Chakraborty, S. K.; Hong, S. C.; Tsay, S.-C.; Hsu, M.-H.; Hwu, J. R. Structure-activity relationship of new anti-hepatitis C virus agents: heterobicycle-coumarin conjugates. *J. Med. Chem.* **2009**, *52*(5), 1486–1490. doi: 10.1021/jm801240d.

[14] Leibeling, M.; Koester, D. C.; Pawliczek, M.; Schild, S. C.; Werz, D. B. Domino access to highly substituted chromans and isochromans from carbohydrates. *Nat. Chem. Biol.* **2010**, *6*(3), 199–201. doi: 10.1038/nchembio.302.

[15] Leibeling, M.; Milde, B.; Kratzert, D.; Stalke, D.; Werz, D. B. Intermolecular twofold carbopalladation/cyclization sequence to access chromans and isochromans from carbohydrates. *Chemistry* **2011**, *17*(36), 9888–9892. doi: 10.1002/chem.201101917.

[16] Ferrier, R. J.; Prasad, N. Unsaturated carbohydrates. Part IX. Synthesis of 2,3-dideoxy-α- D -erythro-hex-2-enopyranosides from tri-O-acetyl- D -glucal. *J. Chem. Soc. C.* **1969**, *0*(4), 570–575. doi: 10.1039/J39690000570.

[17] Ferrier, R.J.; Hoberg, J.O. Synthesis and reactions of unsaturated sugars. *Adv. Carbohydr. Chem. Biochem*. **2003**, *58*, 55–119. doi: 10.1016/s0065-2318(03)58003-9.

[18] Gomez, A. M.; Miranda, S.; Lopez, J. C. Ferrier rearrangement: an update on recent developments. *Carbohydr. Chem.* **2017**, *42*, 210–247. doi: 10.1039/9781782626657-00210.

[19] Gomez, A. M.; Lobo, F.; Uriel, C.; Lopez, J. C. Recent developments in the Ferrier rearrangement. *Eur. J. Org. Chem.* **2013**, *2013*(32), 7221–7262. doi: 10.1002/ejoc.201300798.

[20] Jiang, N.; Wu, Z.; Dong, Y.; Xu, X.; Liu, X.; Zhang, J. Progress in the synthesis of 2,3-unsaturated Glycosides. *Coc.* **2020**, *24*(2), 184–199. doi: 10.2174/1385272824666200130111142.

[21] Bihari, M. K.; Kandasamy, J. Tris(Pentafluorophenyl)Borane-Driven stereoselective O -glycosylation with glycal donors under mild condition. *Asian J. Org. Chem.* **2019**, *8*(4), 549–554. doi: 10.1002/ajoc.201900055.

[22] Zhou, J.; Zhang, B.; Yang, G.; Chen, X.; Wang, Q.; Wang, Z.; Zhang, J.; Tang, J. A facile H_2SO_4/4 Å molecular sieves catalyzed synthesis of 2,3-unsaturated O-glycosides *via* Ferrier-type rearrangement. *Synlett* **2010**, *2010*(06), 893–896. doi: 10.1055/s-0029-1219539.

[23] Zhou, J. F.; Chen, X.; Wang, Q. B.; Zhang, B.; Zhang, L. Y.; Yusulf, A.; Wang, Z. F.; Zhang, J. B.; Tang, J. H_2SO_4-SiO_2: highly efficient and novel catalyst for the Ferrier-type glycosylation. *Chin. Chem. Lett.* **2010**, *21*(8), 922–926. doi: 10.1016/j.cclet.2010.03.013.

[24] Zhang, J.; Zhang, B.; Zhou, J.; Chen, H.; Li, J.; Yang, G.; Wang, Z.; Tang, J. A Facile H_2SO_4-SiO_2–catalyzed ferrier rearrangement of 3,4,6-tri-O-benzyl-D-glucal. *J. Carbohydr. Chem.* **2013**, *32*(5–6), 380–391. doi: 10.1080/07328303.2013.809093.

[25] Sau, A.; Galan, M. C. Palladium-catalyzed α-stereoselective O-glycosylation of O(3)-acylated glycals. *Org. Lett.* **2017**, *19*(11), 2857–2860. doi: 10.1021/acs.orglett.7b01092.

[26] Chen, P.; Su, J. $Gd(OTf)_3$ catalyzed preparation of 2,3-unsaturated O-, S-, N-, and C-pyranosides from glycals by Ferrier rearrangement. *Tetrahedron* **2016**, *72*(1), 84–94. doi: 10.1016/j.tet.2015.11.002.

[27] Roy, R.; Rajasekaran, P.; Mallick, A.; Vankar, Y. D. Gold(III) chloride and phenylacetylene: a catalyst system for the ferrier rearrangement, and O-glycosylation of 1-O-acetyl sugars as glycosyl donors. *Eur. J. Org. Chem.* **2014**, *2014*(25), 5564–5573. doi: 10.1002/ejoc.201402606.

[28] Chen, H.; Luo, X.; Qiu, S.; Sun, G.; Zhang, J. TMSOTf mediated stereoselective synthesis of α-C-glycosides from unactivated aryl acetylenes. *Glycoconj. J.* **2017**, *34*(1), 13–20. doi: 10.1007/s10719-016-9718-7.

[29] Lopez, J. C.; Fraser-Reid, B. n-Pentenyl esters facilitate an oxidative alternative to the Ferrier rearrangement. An expeditious route to sucrose. *J. Chem. Soc. Chem. Commun.* **1992**, *0*(2), 94–96. doi: 10.1039/C39920000094.

[30] Pachamuthu, K.; Vankar, Y. D. Ceric ammonium nitrate-catalyzed tetrahydropyranylation of alcohols and synthesis of 2-deoxy-O-glycosides. *J. Org. Chem.* **2001**, *66*(22), 7511–7513. doi: 10.1021/jo0103322.

[31] Lin, H. C.; Du, W. P.; Chang, C. C.; Lin, C.H. Different reaction routes found in acid-catalyzed glycosylation of endo- and exo-glycals: competition between Ferrier rearrangement and protonation. *Tetrahedron Lett* **2005**, *46*(30), 5071–5076. doi: 10.1016/j.tetlet.2005.05.061.

[32] Rauter, A. P.; Almeida, T.; Xavier, N. M.; Siopa, F.; Vicente, A. I.; Lucas, S. D.; Marques, J. P.; Ramôa Ribeiro, F.; Guisnet, M.; Ferreira, M. J. Acid zeolites as efficient catalysts for O- and S-glycosylation. *J. Mol. Catal. A Chem.* **2007**, *275*(1–2), 206–213. doi: 10.1016/j.molcata.2007.06.002.

[33] Zhang, G.; Liu, Q.; Shi, L.; Wang, J. X. Ferric sulfate hydrate-catalyzed O-glycosylation using glycals with or without microwave irradiation. *Tetrahedron* **2008**, *64*(2), 339–344. doi: 10.1016/j.tet.2007.10.097.

[34] Enthaler, S.; Junge, K.; Beller, M. Sustainable metal catalysis with iron: from rust to a rising star? *Angew. Chem. Int. Ed. Engl.* **2008**, *47*(18), 3317–3321. doi: 10.1002/anie.200800012.

[35] Salunke, S. B.; Babu, N. S.; Chen, C.T. Iron(III) chloride as an efficient catalyst for stereoselective synthesis of glycosyl azides and a cocatalyst with Cu(0) for the subsequent click chemistry. *Chem. Commun. (Camb.)* **2011**, *47*(37), 10440–10442. doi: 10.1039/c1cc13370e.

[36] Ding, Y.; Zhang, S.-Y.; Chen, Y.-C.; Fan, S.-X.; Tian, J.-S.; Loh, T.-P. Regioselective C–H Amidation of (Alkyl)arenes by Iron(II) Catalysis. *Org. Lett.* **2019**, *21*(8), 2736–2739. doi: 10.1021/acs.orglett.9b00697.

[37] Piontek, A.; Bisz, E.; Szostak, M. Iron-catalyzed cross-couplings in the synthesis of pharmaceuticals: in pursuit of sustainability. *Angew. Chem. Int. Ed. Engl.* **2018**, *57*(35), 11116–11128. doi: 10.1002/anie.201800364.

[38] Jose, C. A.; Antonio, L. P.; Avelino, C. Iron-Catalysed Markovnikov Hydrothiolation of Styrenes. Adv. Synth. Catal. **2012**, *354*, 678–687. doi: 10.1002/adsc.201100731.

[39] Bauer, I.; Knölker, H.-J. Iron catalysis in organic synthesis. *Chem. Rev.* **2015**, *115*(9), 3170–3387. doi: 10.1021/cr500425u.

[40] Xolin, A.; Norsikian, S.; Boyer, F.; Beau, J. Iron(III)-triflate-catalyzed multiple glycosylations with peracetylated β-d-glucosamine. *Eur. J. Org. Chem.* **2016**, *2016*(20), 3408–3418. doi: 10.1002/ejoc.201600457.

[41] Mukherjee, M. M.; Basu, N.; Ghosh, R. Iron(III) chloride modulated selective 1,2-trans glycosylation based on glycosyl trichloroacetimidate donors and its application in orthogonal glycosylation. *RSC Adv.* **2016**, *6*(107), 105589–105605. doi: 10.1039/C6RA21859H.

[42] Qiu, S.; Zhang, W.; Sun, G.; Wang, Z.; Zhang, J. A facile and direct glycosidation method for the synthesis of 2-deoxy-α-rhamnosides catalyzed by ferric chloride. *ChemistrySelect* **2016**, *1*(15), 4840–4844. doi: 10.1002/slct.201600802.

[43] Qiu, S.; Sun, G.; Ding, Z.; Chen, H.; Zhang, J. Ferric chloride: an eco-friendly catalyst for the stereoselective synthesis of 2-deoxy aryl-O-rhamnosides. *Synlett.* **2017**, *28*(15), 2024–2029. doi: 10.1055/s-0036-1588864.

[44] Sun, G.; Wu, Y.; Liu, A.; Qiu, S.; Zhang, W.; Wang, Z.; Zhang, J. Substoichiometric $FeCl_3$ activation of propargyl glycosides for the synthesis of disaccharides and glycoconjugates. *Synlett* **2018**, *29*(5), 668–672. doi: 10.1055/s-0036-1591525.

[45] Masson, C.; Soto, J.; Bessodes, M. Ferric chloride: a new and very efficient catalyst for the ferrier glycosylation reaction. *Synlett* **2000**, *9*, 1281–1282. doi: 10.1055/s-2000-7138.

[46] Chen, P.; Wang, S. Iron(III) triflate, a new efficient catalyst for Type I Ferrier Rearrangement. *Tetrahedron* **2012**, *68*(27–28), 5356–5362. doi: 10.1016/j.tet.2012.04.115.

[47] Tilve, R. D.; Alexander, M. V.; Khandekar, A. C.; Samant, S. D.; Kanetkar, V. R. Synthesis of 2,3-unsaturated glycopyranosides by Ferrier rearrangement in $FeCl_3$ based ionic liquid. *J. Mol. Catal. A: Chem.* **2004**, *223*(1–2), 237–240. doi: 10.1016/j.molcata.2003.11.044.

[48] Zhou, J.; Chen, H.; Shan, J.; Li, J.; Yang, G.; Chen, X.; Xin, K.; Zhang, J.; Tang, J. $FeCl_3 \cdot 6H_2O$/C: an efficient and recyclable catalyst for the synthesis of 2,3-

unsaturated O- and S- glycosides. *J. Carbohydr. Chem* **2014**, *33*(6), 313–325. doi: 10.1080/07328303.2014.941995.

[49] Sun, G.; Qiu, S.; Ding, Z.; Chen, H.; Zhou, J.; Wang, Z.; Zhang, J. Magnetic Core-Shell Fe_3O_4@C-SO_3H as an Efficient and Renewable 'Green Catalyst' for the Synthesis of O-2,3-Unsaturated Glycopyranosides. *Synlett*. **2017**, *28*, 347–352. doi: 10.1055/s-0036-1588891.

[50] Dong, Y.; Ding, Z.; Guo, H.; Zhou, L.; Jiang, N.; Chen, H.; Qiu, S.; Xu, X.; Zhang, J. Transition-metal-catalyzed ketone α-alkylation and alkenylation with simple alkenes and alkynes through a dual activation strategy. *Synlett.* **2019**, *30*(6), 1419–1426. doi: 10.1055/s-0037-1611855.

[51] Guo, H.; Si, W.; Li, J.; Yang, G.; Tang, T.; Wang, Z.; Tang, J.; Zhang, J. An unexpected $FeCl_3$/C-catalyzed β-stereoselective glycosylation in the presence of the C(2)-benzyl group. *J. Synthesis.* **2019**, *51*(15), 2984–3000. doi: 10.1055/s-0037-1611801.

[52] Calleja, G.; Melero, J.A.; Martinez, F.; Molina, R. Activity and resistance of iron-containing amorphous, zeolitic and mesostructured materials for wet peroxide oxidation of phenol. *Water Res.* **2005**, *39*(9), 1741–1750. doi: 10.1016/j.watres.2005.02.013.

[53] He, L.; Du, G.; Gao, J.; Wang, X.; Wang, W., Dai, B., Synthesis of tributyl citrate catalyzed by active carbon supported solid acid Chem. *Res. Appli.* **2013**, *25*, 1628–1631. doi: 10.3969/j.issn.1004-1656.2013.12.003.

[54] Yang, Y.; Zhang, X.; Yu, B. O-Glycosylation methods in the total synthesis of complex natural glycosides. *Nat. Prod. Rep*. **2015**, *32*(9), 1331–1335. doi: 10.1039/c5np00033e.

[55] Cottreau, K.; Spencer, C.; Wentzell, J.; Graham, C. L.; Borissow, C. N.; Jakeman, D. L.; Mcfarland, S. A. Diverse DNA-cleaving capacities of the jadomycins through precursor-directed biosynthesis. *Org. Lett.* **2010**, *12*(6), 1172–1175. doi: 10.1021/ol902907r.

[56] Kusumi, S.; Sasaki, K.; Wang, S.; Watanabe, T.; Takahashi, D.; Toshima, K. Effective and chemoselective glycosylations using 2,3-unsaturated sugars. *Org. Biomol. Chem.* **2010**, *8*(14), 3164–3178. doi: 10.1039/c004204h.

[57] Sau, A.; Palo, C.; Galan, M. C. Substrate-controlled direct α-stereoselective synthesis of deoxyglycosides from glycals using $B(C_6F_5)_3$ as catalyst. *J. Org. Chem.* **2019**, *84*(5), 2415–2424. doi: 10.1021/acs.joc.8b02613.

[58] Ghosh, T.; Mukherji, A.; Kancharla, P. K. Sterically hindered 2,4,6-tri- tert-butylpyridinium salts as single hydrogen bond donors for highly stereoselective glycosylation reactions of glycals. *Org. Lett.* **2019**, *21*(10), 3490–3495. doi: 10.1021/acs.orglett.9b00626.

[59] Chen, P.; Li, S. $Y(OTf)_3$ as a highly efficient catalyst in Ferrier Rearrangement for the synthesis of O- and S-2,3-unsaturated glycopyranosides. *Tetrahedron Lett* **2014**, *55*(42), 5813–5816. doi: 10.1016/j.tetlet.2014.08.092.

[60] Kumaran, E.; Santhi, M.; Balasubramanian, K. K.; Bhagavathy, S. Montmorillonite K-10 clay-catalyzed Ferrier rearrangement of 2-C-hydroxymethyl-d-glycals, 3,4,6-tri-O-alkyl-d-glycals, and 3,4-(dihydro-2H-pyran-5-yl)methanol: a few unexpected domino transformations. *Carbohydr. Res.* **2011**, *346*(13), 1654–1661. doi: 10.1016/j.carres.2011.03.027.

[61] Wernicke, A.; Sinou, D. Synthesis of unsaturated C -glycosyl glycines. *J. Carbohydr. Chem.* **2001**, *20*(2), 181–190. doi: 10.1081/CAR-100103957.

[62] Nagaraj, P.; Ramesh, N. G. Direct Ferrier rearrangement on unactivated glycals catalyzed by indium(III) chloride. *Tetrahedron Lett.* **2009**, *50*(27), 3970–3973. doi: 10.1016/j.tetlet.2009.04.084.