

Indium trichloride catalyzed Ferrier rearrangement – facile synthesis of 2,3-unsaturated glycosides

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Dedicated to Professor P. T. Narasimhan on his 75th birthday

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Abstract

Treatment of tri-*O*-acetyl-D-glucal 1 with various alcohols and phenols in the presence of InCl₃ / CH₂Cl₂ at ambient temperature furnished the corresponding alkyl and aryl 2,3-unsaturated glycopyranosides in excellent yields in short reaction times and good anomeric selectivity.

Keywords: Glycal, glycosides, indium and compounds, Ferrier rearrangement

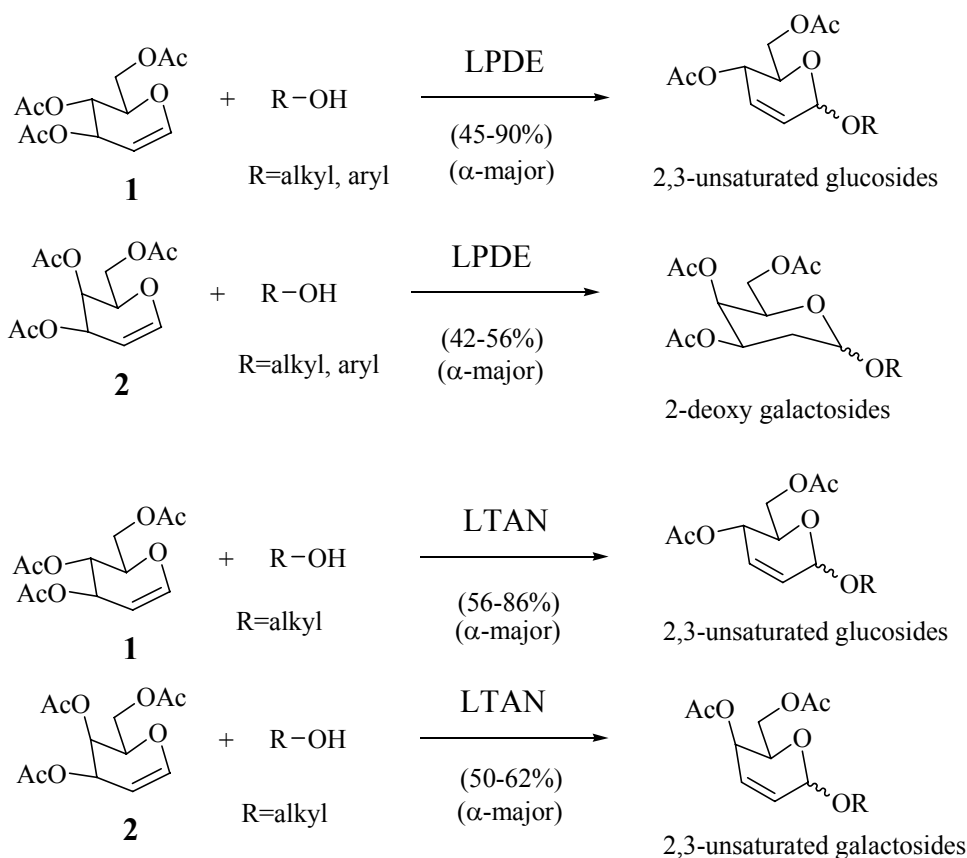
Introduction

2,3-Unsaturated glycosides have received wide attention in recent years particularly in the synthesis of several biologically active natural products and also as chiral synthons. Aryl and alkyl 2,3-unsaturated glucosides are accessible by acid catalyzed nucleophilic substitution with allylic rearrangement of tri-*O*-acetylglucal while it is not that easy to prepare the 2,3-unsaturated galactosides by this route. This reaction, often referred to as the "Ferrier rearrangement",¹ has found wide application. This reaction continues to receive wide attention and various glycosidation methodologies using it have been extensively reviewed.²

The requirement of an acid catalyst to bring about the Ferrier rearrangement precludes its applicability to substrates that are sensitive to acidic conditions. This has led to the development of essentially non-acidic alternative method *viz.*, iodonium reagents (NIS or iodonium dicollidinium perchlorate as promoter) by Fraser-Reid.³ Furthermore, Toshima *et al*⁴ reported a novel method for the glycosidation of glycals under neutral conditions by using a catalytic amount of 2,3-dichloro-5, 6-dicyano-*p*-benzoquinone (DDQ) to furnish 2,3-unsaturated glycosides in high yields. Mereyala *et al*⁵ described a general and efficient route to 1,6-anhydro-2,3-dideoxy- β -D-*erythro*-hex-2-enopyranoses *via* intramolecular Ferrier rearrangement catalyzed

by $\text{BF}_3 \cdot \text{Et}_2\text{O}$. Toshima *et al*⁶ came out with a practical method for the glycosidation of glycols using montmorillonite K-10 (a clay catalyst), an environmentally acceptable, inexpensive catalyst, and we successfully extended this method for the synthesis of 2,3-unsaturated galactosides under microwave irradiation conditions.⁷ Recently Lee *et al*⁸ reported an efficient and stereoselective palladium-catalyzed *O*-glycosylation using glycols. In contrast to the Lewis acid mediated Ferrier rearrangement, the anomeric stereochemistry of this reaction is controlled by the employed ligand.

As part of our ongoing research in carbohydrate chemistry⁹ and our continued interest in Ferrier rearrangement, we have explored the utility of various Lewis acid catalysts to effect this rearrangement. We observed 5*M* Lithium perchlorate in diethyl ether (LPDE) is a useful, neutral and mild medium for the synthesis of alkyl and aryl 2,3-unsaturated glucopyranosides and alkyl and aryl 2-deoxy galactopyranosides. An additional feature of interest, from the carbohydrate chemistry point of view, is the reactivity pattern difference between tri-*O*-acetyl-D-galactal **2** as compared to tri-*O*-acetyl-D-glucal **1** towards alcohols and phenols in (LPDE) medium (**Scheme 1**).¹⁰ A plausible mechanism to account for this difference in behavior is that the tri-*O*-acetylglucal, **1**, which exists in two different conformations ⁴H₅ and ⁵H₄ in equilibrium, undergoes Ferrier rearrangement in the ⁵H₄ conformation wherein anchimeric assistance is feasible, providing smoothly the 2,3-unsaturated glucosides. However, in the case of tri-*O*-acetylgalactal, **2**, the 3-OAc and 4-OAc are *cis* to each other and no anchimeric assistance is possible in either of the two conformations. Addition of the alcohol to the enol ether double bond takes a precedence, leading to 2-deoxy galactosides. However, LiBF_4 in CH_3CN (LTAN) was found to be an useful alternative catalyst to SnCl_4 ,^{1e,10c} providing a practical method for the synthesis of 2,3-unsaturated alkylglycosides, particularly for 2,3-unsaturated galactopyranosides in good yields.¹¹



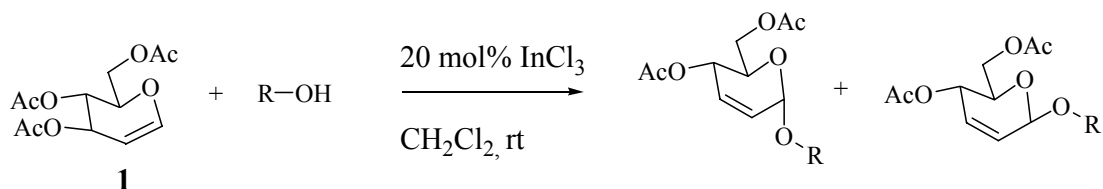
Scheme 1

Indium(III) chloride InCl_3 , which is a relatively strong Lewis acid, has been used as a catalyst for a wide variety of organic reactions.¹² However, Indium trichloride has hardly been used in the carbohydrate field. We have found an interesting application for InCl_3 as an efficient and versatile catalyst for the expeditious synthesis of alkyl and aryl 2,3-unsaturated glycopyranosides *via* Ferrier rearrangement.¹³ Recently a few papers have appeared on the InCl_3 catalyzed, microwave assisted Ferrier rearrangement of glycals leading to 2,3-unsaturated *O*- and *C*-glycosides in good to excellent yields.¹⁴

Results and Discussion

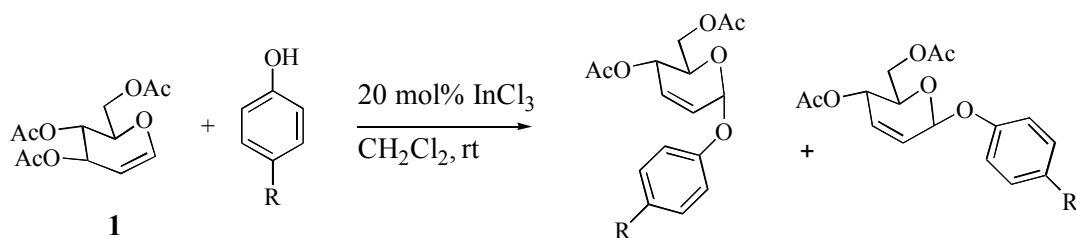
Synthesis of 2,3-unsaturated alkyl and aryl glycosides using InCl_3 . When 1 equiv. of tri-*O*-acetyl-D-glucal **1** was treated with 1.2 equiv. of benzyl alcohol and anhydrous InCl_3 in CH_2Cl_2 for 10 minutes at ambient temperature, a mixture of benzyl 2,3-unsaturated glucopyranosides **3a** and **3b** was obtained in 86% yield with the α -anomer as the major product. The product showed two close moving spots in TLC (almost identical R_f), corresponding to the α and β -anomers. The complete assignment of signals in the ^1H NMR spectrum was possible based on irradiation studies and the stereochemistry at the anomeric center was established unambiguously as α based

on our earlier NOE studies^{9c}. When the signal due to H-1 of the alpha anomer was irradiated, there was no significant enhancement in the intensity of the signal due to H-5, and vice versa. Based on the integration values of signals due to anomeric protons (α and β anomeric protons come without overlapping and can be integrated without difficulty) in the ¹H NMR (400 MHz) spectrum of the mixture, the ratio of the anomers was calculated. Likewise, a few other alcohols (**Scheme 2**) and phenols (**Scheme 3**) also underwent the Ferrier rearrangement catalyzed by InCl₃ in shorter reaction time furnishing the 2,3-unsaturated glycosides in excellent yields with high selectivity in favor of the α -anomer.

**Scheme 2**

Alcohol	Product	Yield (%)	$\alpha:\beta^*$
R = benzyl	3a + 3b	86	6.3:1
R = <i>o</i> -nitrobenzyl	4a + 4b	80	7:1
R = <i>o</i> -iodobenzyl ^a	5a + 5b	87	9:1
R = cyclohexyl ^b	6a + 6b	90	9:1
R = propargyl	7a + 6b	90	9:1
R = methyl	8a + 8b	90	7:1

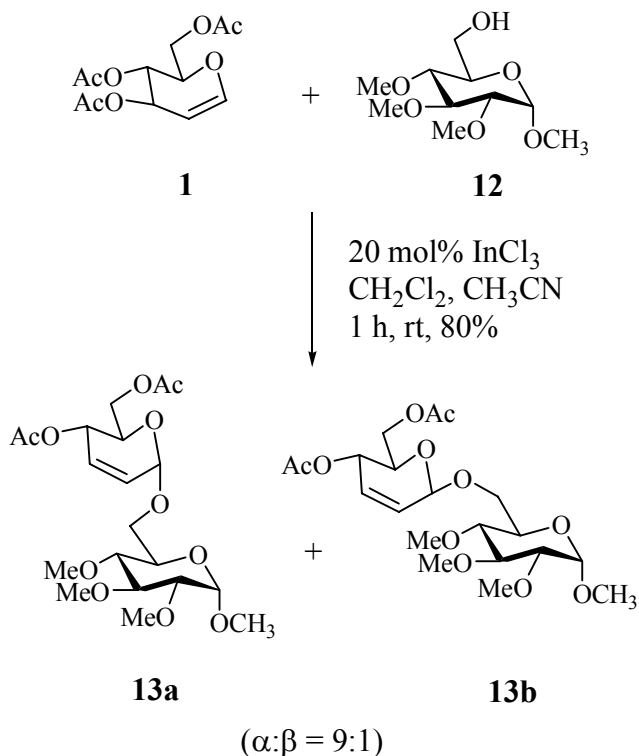
Time taken for the completion of the reaction is 10 min except ^a15 min and ^b30 min.

**Scheme 3**

Phenols	Product	Yield (%)	$\alpha:\beta^*$
<i>p</i> -methylphenol	9a + 9b	60	8:1
<i>p</i> -methoxyphenol	10a + 10b	65	7.5:1
<i>p</i> -chlorophenol ^a	11a + 11b	62	9:1

* Anomeric ratios were determined by ¹H and (300 & 400 MHz) spectroscopy
Time taken for the completion of the reaction is 10 min except ^a15 min.

This procedure worked equally well for the synthesis of a disaccharide *viz.* methyl 6-*O*- [4,6-di-*O*-acetyl-2,3-dideoxy-*D*-*erythro*-hex-2-enopyranosyl]-2,3,4-tri-*O*-methyl- α -*D*-glucopyranoside **13a** and β -anomer **13b** (Scheme 4). Thus, reaction of methyl 2,3,4-tri-*O*-methyl- α -*D*-glucopyranoside **12** with **1** in dichloromethane/acetonitrile in the presence of InCl_3 led to the known disaccharide^{6a} **13a** and **13b** in 80% yield with α -anomer as the major product (α : β = 9:1).



Scheme 4

Efficacy of various acid catalysts towards the Ferrier rearrangement of **1**

We have examined the efficacy of a few catalysts *viz.*, LiClO_4 , LiBF_4 , $\text{BF}_3 \cdot \text{Et}_2\text{O}$ and SnCl_4 for the Ferrier rearrangement of **1** with selected alcohols. We have observed that among all these catalysts, InCl_3 is found to be the best (Table 1).

Table 1. Study of various acid catalysts in the Ferrier rearrangement of **1** with alcohols

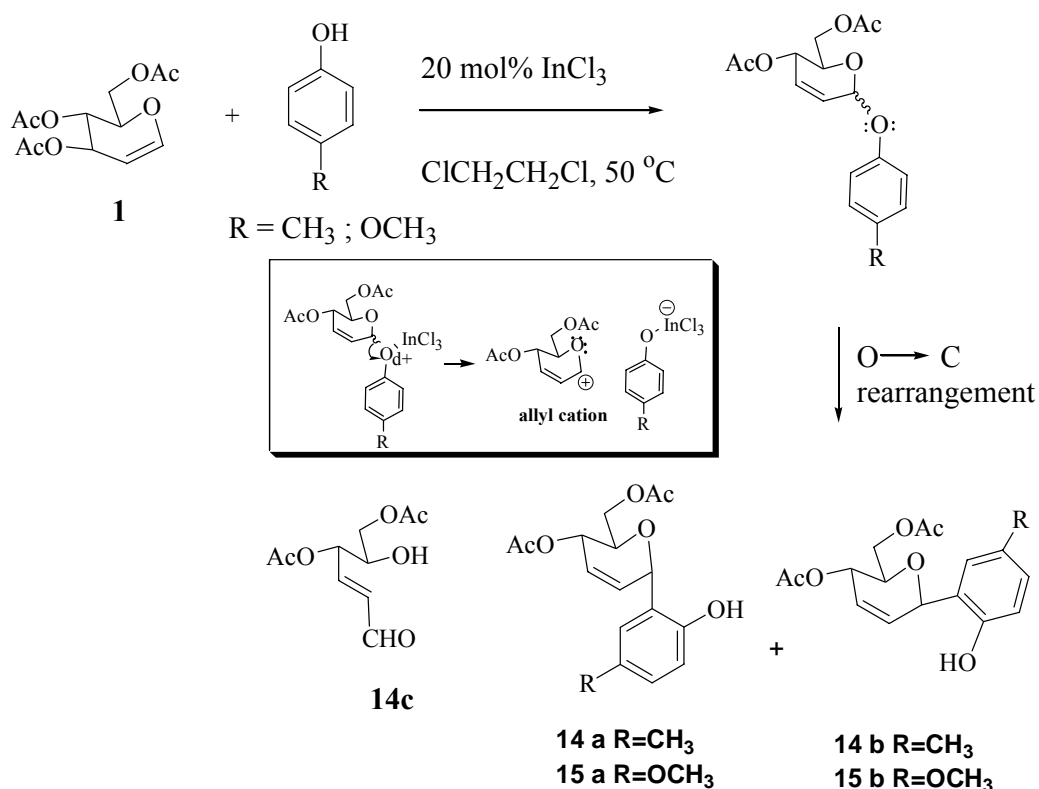
Alcohol	Products	Lewis acid catalyst (temp.)	Time	Yield (α : β)*
Benzyl alcohol	3a + 3b	LiClO ₄ / Et ₂ O (27 °C)	16 h	85% (5:1)
		LiBF ₄ / CH ₃ CN (27 °C)	4 h	86% (4:1)
		BF ₃ / Et ₂ O (0°C to 27 °C)	45 min	80% (4:1)
		SnCl ₄ /CH ₂ Cl ₂ (0°C to 27 °C)	45 min	85% (4.6:1)
		Montmorillonite K-10	-	-
		InCl ₃ / CH ₂ Cl ₂ (27 °C)	10 min	91% (6.3:1)
Cyclohexanol	6a + 6b	LiClO ₄ / Et ₂ O (27 °C)	18 h	90% (6:1)
		LiBF ₄ / CH ₃ CN (27 °C)	4 h	86% (8:1)
		BF ₃ / Et ₂ O (0°C to 27 °C)	45 min	70% (9:1)
		SnCl ₄ /CH ₂ Cl ₂ (0°C to 27 °C)	1 h	80% (6.5:1)
		Montmorillonite K-10 / CH ₂ Cl ₂	1 h	93% (7.3:1)
		InCl ₃ / CH ₂ Cl ₂ (27 °C)	10 min	90% (9:1)
Propargyl alcohol	7a + 7b	LiClO ₄ / Et ₂ O (27 °C)	18 h	90% (6:1)
		LiBF ₄ / CH ₃ CN (27 °C)	4 h	86% (8:1)
		BF ₃ / Et ₂ O (0° to 27 °C)	30 min	82% (6.3:1)
		SnCl ₄ /CH ₂ Cl ₂ (0°C to 27 °C)	45 min	80% (9:1)
		Montmorillonite K-10 / CH ₂ Cl ₂	1 h	97% (6.4:1)
		InCl ₃ / CH ₂ Cl ₂ (27 °C)	10 min	92% (9:1)

*Anomeric ratios were determined by ¹H NMR (200/400 MHz) spectroscopy.

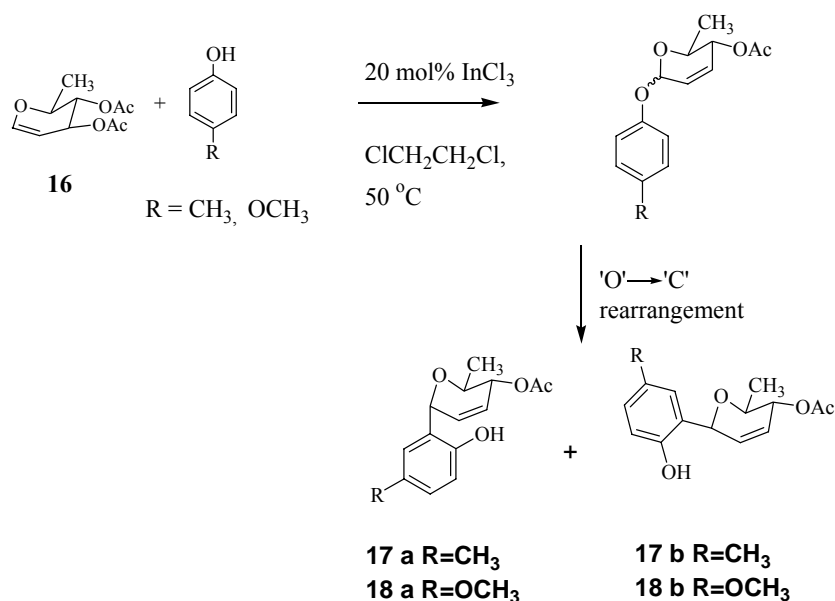
In all the cases studied, the reaction was fastest with InCl₃ as compared to other catalysts. It was observed that InCl₃ is better than SnCl₄. Besides anomeric selectivity; the yield was greatest with InCl₃. We have examined a few other catalysts such as TaCl₅, PsCl₃, and LnCl₃ also in dichloromethane. However, none of these Lewis acids was found to catalyze the Ferrier rearrangement.

The low yield of 2,3-unsaturated aryl glucopyranosides (**Scheme 3**) obtained in the case of phenols is due to further 'O' to 'C' rearrangement catalyzed by InCl₃. There is precedence for such a rearrangement from our own earlier work.^{9a}

One-pot synthesis of C-aryl glycosides using InCl₃. When the reaction between tri-*O*-acetyl-D-glucal **1** and *p*-cresol in the presence of anhyd. InCl₃ in CH₂Cl₂, was carefully monitored by TLC, formation of 4'-methylphenyl 4,6-di-*O*-acetyl-2, 3-dideoxy- α -D-*erythro*-hex-2-enopyranosides **9a** and **9b** was observed in the initial stages *viz.* first 10-15 min. Under longer reaction duration, TLC indicated consumption of the *O*-arylglycoside with the simultaneous formation of 2,3-unsaturated-C-arylglycosides **14a** and **14b**. It took about 10h for completion of this 'O' to 'C' rearrangement, but the reaction was accompanied by the formation of a substantial amount of an aldehyde product **14c** presumed to be (5*R*,6*R*)-5-(hydroxy)-4,6-di-*O*-acetyl-hex-2-ene-1-al, which was formed probably due to the presence of adventitious moisture (**Scheme 5**). This problem was overcome by employing ClCH₂CH₂Cl as the solvent and heating the reaction mixture at 50 °C for an hour, which led to completion of the reaction without the formation of any side products *viz.*, **14c**.



Scheme 5



Scheme 6

Glycal	Phenol	Products	Time (h)	Yield (%)	$\alpha:\beta^*$
1	R = CH ₃	14a + 14b	1	65	37:63
	R = OCH ₃	15a + 15b	1.5	63	34::66
16	R = CH ₃	17a + 17b	2	60	46:54
	R = OCH ₃	18a + 18b	2.5	65	46:54

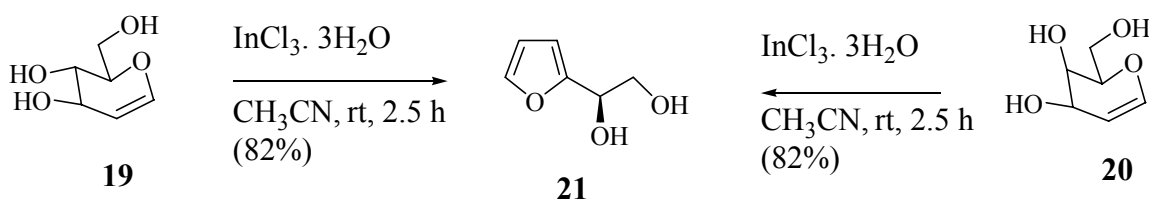
* Anomeric ratios were determined by ¹H and (200 & 400 MHz) spectroscopy.

The intermediate *O*-arylglycoside **9a** and **9b** could be isolated by quenching the reaction mixture with cold *aq.* NaOH at the end of 10 min. The 'O' to 'C' rearrangement pathway for the formation of **14a** and **14b** was confirmed by taking the pure *O*-arylglycosides **9a** and **9b** and subjecting them to the action of InCl₃ in dichloroethane which led to the *C*-arylglycoside **14a** and **14b**. This is an indication of a cleavage-recombination mechanism involving the intermediacy of highly stabilized allyl cation. It is worth mentioning that products of allylic attack at C-3 are not observed which is in agreement with the high electrophilic nature of the anomeric center in these glycols. While this method provides a convenient one-pot synthesis of *C*-aryl glycosides and also a rapid entry to 2,3-unsaturated-*C*-aryl glucopyranosides, it is not diastereoselective (**Scheme 5**). The reaction was successfully tested on *p*-methoxyphenol, which afforded a mixture of corresponding *C*-arylglycoside **15a** and **15b** in 63% yield *albeit* with poor anomeric selectivity. The diastereoselectivity observed however, was comparable to that reported with BF₃Et₂O as catalyst^{9a}.

The reaction underwent by 3,4-di-*O*-acetyl-*L*-rhamnal **16** also, which furnished the corresponding 2,3-unsaturated *C*-aryl rhamnosides in moderate yields but without any significant anomeric selectivity. **17-18** (**Scheme 6**). From this limited data, it appears that the presence of the substituent at C-6 does not have any influence on the anomeric selectivity in this reaction.

Strangely, under identical conditions tri-*O*-acetyl-D-galactal **2** yielded a complex mixture of products. All new compounds were thoroughly characterized by spectral means.

It should be emphasized that indium chloride has to be extremely anhydrous to effect the Ferrier rearrangement of **1** and **16** with various aglycons. Use of hydrated indium trichloride ($\text{InCl}_3 \cdot 3\text{H}_2\text{O}$) on **1** led to the formation of substantial amount of **14c** even in the presence of aglycon. Since anhydrous InCl_3 was found to be an efficient catalyst for Ferrier rearrangement it appeared worthwhile to examine its behavior towards free glycols. In the event, it led to a facile transformation affording the 2-(D-glycero-1', 2'-dihydroxyethyl) furan **21**, a very useful and important chiral intermediate in organic synthesis.¹⁸ Treatment of unprotected D-glucal **19** or D-galactal **20** with $\text{InCl}_3 \cdot 3\text{H}_2\text{O}$ (10 mol%) in acetonitrile at ambient temperature furnished 2-(D-glycero-1,2-dihydroxyethyl) furan **21**, an optically active furan diol in 82% yield (**Scheme 7**).



Scheme 7

Conclusions

- 1) Our study has revealed that anhydrous InCl_3 is the best catalyst among all the catalysts (LiClO_4 , LiBF_4 , $\text{BF}_3 \cdot \text{Et}_2\text{O}$, SnCl_4 , and Montmorillonite K-10) for the Ferrier rearrangement of tri-*O*-acetyl-D-glucal **1**. The reaction conditions are mild and reaction time is also relatively short. The reaction proceeded with good anomeric selectivity, furnishing high isolated yields of the products. The reaction is amenable for scale-up. The quantity of the nucleophile used for glycosylation by this method is only 1.2 equiv. as compared to 10 equiv. used in the conventional thermal Ferrier rearrangement. The medium is compatible with the ester group, thus avoiding the attendant problem of transesterification. The reaction has been extended to L-rhamnal also, but in the case of tri-*O*-acetyl-D-galactal, the reaction was not clean and led to a mixture of products.
- 2) A tandem Ferrier rearrangement and 'O' to 'C' rearrangement of tri-*O*-acetyl-D-glucal and di-*O*-acetyl-L-rhamnal with phenols to form the 2,3-unsaturated C-arylglucosides and C-arylrhamnosides respectively was achieved using anhyd. $\text{InCl}_3 / \text{ClCH}_2\text{CH}_2\text{Cl}$ at 50 °C.

Experimental Section

Tri-*O*-acetyl-D-glucal **1**, tri-*O*-acetyl-D-galactal **2** and 3,4-di-*O*-acetyl-L-rhamnol **16** were prepared according to the literature procedures.¹⁵

General Procedures. To a mixture of tri-*O*-acetyl-D-glucal **1** (1 mmol) and the aglycone (1.1 mmol), was added anhydrous InCl₃ (0.2mmol; 20 mol%) in dry CH₂Cl₂ (1-2 mL) (For *C*-aryl glycosides, ClCH₂CH₂Cl was used as the solvent and heated the reaction mixture at 50 °C for the required time) at ambient temperature. The contents were stirred for the required time and the reaction monitored by TLC. The reaction mixture was quenched by the addition of aqueous sodium hydrogen carbonate (10%, 25 mL), extracted with dichloromethane (3 x 25 mL), dried over anhydrous sodium sulphate, filtered and concentrated. The residue was purified by flash column chromatography on silica gel to obtain the products using hexane: EtOAc as eluents.

The product showed two close moving spots in TLC (almost identical *R_f*), corresponding to the α and β -anomers. The mixture of anomers was not separated but characterized as such by HRMS and NMR spectroscopy. Based on the integration values of signals due to anomeric protons in the ¹H NMR spectrum of mixture, the ratio of the anomers was calculated.

Benzyl 4,6-di-*O*-acetyl-2,3-dideoxy - α -D-erythro-hex-2-enopyranoside (3a) and β -anomer (3b).¹⁶ Nature: Viscous liquid. *R_f*: 0.5 (Hexane : EtOAc = 8 : 2). IR (CHCl₃) ν (cm⁻¹): 2944, 1734, 1644, 1599, 1446, 1382, 1260, 1193; ¹H NMR (300 MHz) δ (ppm): 2.07(s, 3H, -OCOCH₃), 2.09(s, 3H, -OCOCH₃) 4.09-4.31(m, 3H, H-5, H-6a, H-6b), 4.59(d, *J* = 11.65Hz, 1H, A of AB, PhCH_A), 4.80(d, *J* = 11.65Hz, 1H, B of AB PhCH_B), 5.13(bs, 1H, H-1 of α), 5.20(bs, H-1 of β), 5.33(d, *J*_{4,5} = 10.1Hz, 1H, H-4), 5.83-5.88(m, 2H, H-2, H-3), 7.28-7.36(m, 5H, Ar-H). ¹³C NMR (75MHz) δ (ppm): 20.70(q, -OCOCH₃), 20.86(q, -OCOCH₃), 62.81(t, C-6), 65.16(d, C-5), 66.94(d, C-4), 70.17(t, -OCH₂Ar), 93.52(d, C-1 of α), 93.61(d, C-1 of β), 127.65(d, Ar-CH), 127.84(d, Ar-CH), 127.78(d, C-2), 128.37(d, C-3), 137.46(s, Ar-C), 170.20(s, -OCOCH₃), 170.70(s, -OCOCH₃). MS (*m/z*): 380, 278, 242, 218, 213, 200, 176, 153, 111, 91; HRMS: Observed 261.129595 (M⁺-OCOCH₃) Calculated 261.13269 for C₁₅H₁₇O₄

2'-Nitrobenzyl 4,6-di-*O*-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (4a) and β -anomer (4b). Nature: Yellow gummy solid. *R_f*: 0.6 (Hexane : EtOAc = 7 : 3). IR (CHCl₃) ν (cm⁻¹): 3008, 2992, 1737, 1542, 1526, 1456, 1434, 1360, 1340, 1257, 1145, 1046, 966, 934, 834, 649, 633; ¹H NMR (400 MHz) δ (ppm): 2.07 (s, 3H, -OCOCH₃), 2.09 (s, 3H, -OCOCH₃), 4.11-4.29(m, 3H, H-5, H-6a, H-6b), 4.97(d, *J* = 14.3Hz, 1H, A of AB, PhCH_A), 5.20(d, *J* = 14.3Hz, 1H, B of AB, PhCH_B), 5.19(bs, 1H, H-1), 5.29(d, *J* = 8.3Hz, 1H, H-4), 5.91-5.93(m, 2H, H-2, H-3), 7.45(t, *J* = 7.23Hz, 1H, Ar-H), 7.63-7.76(m, 2H, Ar-H), 8.08(d, *J*=7.69Hz, 1H, Ar-H). ¹³C NMR (100MHz) δ (ppm): 20.73(q, -OCOCH₃), 20.96(q, -OCOCH₃), 62.81(t, C-6), 65.19(d, C-5), 67.12(t, -OCH₂-Ar), 67.27(d, C-4), 94.41(d, C-1), 124.71(d, -ArCH), 127.20(d, Ar-CH), 128.38(d, C-2), 129.15(d, Ar-CH), 129.73(d, C-3), 133.60(d, Ar-CH), 134.07(s, Ar-C), 147.52(s, Ar-C), 170.32(s, -OCOCH₃), 170.90(s, -OCOCH₃). MS (*m/z*): 306(M⁺-2 x OAc), , 263, 221,

213, 153, 136, 111, 78, 65, 51 HRMS: Observed 306.1250735($M^+ - 2 \times \text{OAc}$) Calculated 306.127765 for $\text{C}_{15}\text{H}_{16}\text{O}_6\text{N}$

2'-Iodobenzyl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (5a) and β -anomer (5b). Nature: Viscous liquid. *R_f*: 0.6 (hexane : EtOAc = 7 : 3). IR (CHCl_3) ν (cm^{-1}): 2948, 1740, 16539, 1433, 1408, 1363, 1260, 1260, 1142, 1097, 1046, 963, 934; ^1H NMR (300 MHz) δ (ppm): 2.08 (s, 3H, -OCOCH₃), 2.10 (s, 3H, -OCOCH₃), 4.14-4.30(m, 3H, H-5, H-6a, H-6b), 4.56(d, *J* = 12.53Hz, A of AB, PhCH_A), 4.83(d, B of AB, 1H, *J* = 12.53Hz, PhCH_B), 5.20(bs, 1H, H-1 of α) 5.28(bs, 1H, H-1 of β), 5.33(d, *J*_{4,5} = 9.24Hz, H-4), 5.92(bs, 2H, H-2, H-3 of α), 6.04(bs, 2H, H-2, H-3 of β), 6.99(t, *J* = 7.56Hz, 1H, Ar-H), 7.26-7.45(m, 2H, Ar-H), 7.84(d, *J* = 7.86Hz, 1H, Ar-H). ^{13}C NMR (75MHz) δ (ppm): 20.86(q, -OCOCH₃), 20.96(q, -OCOCH₃), 62.86(t, C-6), 65.20(d, C-5), 67.18(d, C-4), 74.26(t, -OCH₂-Ar), 94.20(d, C-1 of α), 98.15(d, C-1 of β), 98.15(s, Ar-Cl), 127.46(d, C-2), 128.26(d, Ar-CH), 129.30(d, Ar-CH), 129.46(d, C-3), 139.29(s, Ar-C), 139.85(s, Ar-C), 170.26(s, -OCOCH₃), 170.80(s, -OCOCH₃). HRMS: Observed 446.0195548; Calculated 446.022462 for $\text{C}_{17}\text{H}_{19}\text{O}_6\text{I}$

Cycohexyl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (6a) and β -anomer (6b). Nature: Viscous liquid. *R_f*: 0.7 (hexane : EtOAc = 7 : 3). IR (CHCl_3) ν (cm^{-1}): 2949, 1738, 1640, 1598, 1439, 1380, 1266, 1182, 1122, 1015; ^1H NMR (300 MHz) δ (ppm): 1.05-1.55(m, 6H), 1.62-1.75(m, 2H), 1.83-1.98(m, 2H), 2.09 (s, 3H, -OCOCH₃), 2.09 (s, 3H, -OCOCH₃), 3.58-3.69(m, 1H, -OCH(CH₂)₅), 4.05-4.33(m, 3H, H-5, H-6a, H-6b), 5.16(bs, 1H, H-1), 5.29(d, *J* = 8.28Hz, 1H, H-4), 5.77-5.94(m, 2H, H-2, H-3). ^{13}C NMR (75MHz) δ (ppm): 20.69(q, -OCOCH₃), 20.91(q, -OCOCH₃), 24.12(t), 24.34(t), 25.53(t), 32.10(t), 33.73(t), 63.14(t, C-6), 65.43(d, C-5), 66.74(d, C-4), 76.68(d, -OCH(CH₂)₅), 92.76(d, C-1), 128.53(d, C-2), 128.70(d, C-3), 170.28(s, -OCOCH₃), 170.72(s, -COCH₃).

HRMS: Observed 312.159426; Calculated 312.15729 for $\text{C}_{16}\text{H}_{24}\text{O}_6$

Propargyl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (7a) and β -anomer (7b).¹⁷ Nature: Viscous liquid. *R_f*: 0.7 (hexane : EtOAc = 7 : 3). IR (CHCl_3) ν (cm^{-1}): 2951, 2112, 1740, 1641, 1601, 1, 1380, 1266, 1182, 1122, 1015; ^1H NMR (400 MHz) δ (ppm): 2.08 (s, 3H, -OCOCH₃), 2.10 (s, 3H, -OCOCH₃), 2.47(t, *J*=2.42Hz, 1H, -OCH₂-C \equiv CH), 3.8-4.24(m, 3H, H-5, H-6a, H-6b), 4.31(d, *J* = 2.44Hz, 2H, -OCH₂-C \equiv CH), 5.24(bs, 1H, H-1), .5.34(d, *J*_{4,5} = 9.57Hz, H-4), 5.80-5.95(m, 2H, H-2, H-3). ^{13}C NMR (100MHz) δ (ppm): 20.68(q, -OCOCH₃), 20.84(q, -OCOCH₃), 54.98(d, -OCH₂-C \equiv CH), 62.71((t, C-6), 65.10(t, -OCH₂-C \equiv CH), 67.14(d, C-5), 74.75(d, C-4), 79.03(s, -OCH₂-C \equiv CH), 92.70(d, C-1 of α), 92.50(d, C-1 of β), 127.18(d, C-2), 129.69(d, C-3), 170.14(s, -OCOCH₃), 170.65(s, -OCOCH₃). MS (*m/z*): 268, 230, 213, 171, 153, 11, 83, 55

HRMS: Observed 268.09669; Calculated 268.09469 for $\text{C}_{13}\text{H}_{16}\text{O}_6$

Methyl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (8a) and β -anomer (8b).^{1c} Nature: Viscous liquid. *R_f*: 0.6 (hexane : EtOAc = 7 : 3). IR (CHCl_3) ν (cm^{-1}): 2928, 2816, 1734, 1593, 1449, 1369, 1264, 1180, 1136, 1107, 1065, 1014, 963, 905; ^1H NMR (200 MHz) δ (ppm): 2.08 (s, 6H, 2 x -OCOCH₃ of α), 2.09 (s, 6H, 2 x -OCOCH₃ of β), 3.45(s, 3H, OCH₃ of α), 3.46(s, 3H, OCH₃ of β), 3.99-4.31(m, 3H, H-5, H-6a, H-6b), 4.93(bs, 1H, H-1 of α), 5.04(d,

$J_{1,2} = 1.09\text{Hz}$, 1H, H-1 of β), 5.16-5.20(m, 1H, H-4 of β), 5.31(dd, $J_{4,5} = 9.67\text{Hz}$, $J_{3,4} = 1.09\text{Hz}$, 1H, H-4 of α), 5.79-5.87(m, 2H, H-2, H-3 of α), 5.90-6.03(m, 2H, H-2, H-3 of β). ^{13}C NMR (50MHz) δ (ppm): 20.59(q, -OCOCH₃), 20.76(q, -OCOCH₃), 55.11(q, OCH₃ of β), 55.73(q, OCH₃ of α), 63.20(t, C-6), 65.08(d, C-5), 66.69(d, C-4), 95.23(d, C-1 of α), 95.81(d, C-1 of β), 127.51(d, C-2), 129.04(d, C-3), 170.06(s, -OCOCH₃), 170.55(d, -OCOCH₃). HRMS: Observed 244.15920; Calculated 244.12469 for C₁₁H₁₆O₆

4'-Methylphenyl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (9a) and β -anomer (9b).^{1a,9c} Nature: Gummy solid. *R_f*: 0.7 (hexane : EtOAc = 7 : 3). IR (CHCl₃) ν (cm⁻¹): 2948, 1738, 1602, 1446, 1376, 1272, 1182, 1126; ^1H NMR (400 MHz) δ (ppm): 1.88(s, 3H, -OCOCH₃, of α), 2.10(s, 3H, -OCOCH₃, of α), 2.00(s, 3H, -OCOCH₃ of β), 2.10(s, 3H, -OCOCH₃ of β), 2.29(s, 3H, ArCH₃), 4.06-4.39(m, 3H, H-5, H-6_a, H-6_b), 5.16(bs, 1H, H-4 of β), 5.38(d, $J_{4,5} = 9.54\text{Hz}$, H-4 of α), 5.63(bs, 1H, H-1 of α), 5.75(bs, 1H, H-1 of β), 6.00(bs, 2H, H-2 and H-3 of α), 6.13(bs, 2H, H-2, H-3 of β), 7.01(d, 2H, $J = 8.48\text{Hz}$, Ar-H, H_A, H_{A'}), 7.09(d, 2H, $J = 8.48\text{Hz}$, Ar-H, H_B, H_{B'}). ^{13}C NMR (100MHz) δ (ppm): 20.56(q, -OCOCH₃), 20.67(q, -OCOCH₃), 20.94(q, Ar-CH₃), 62.73(t, C-6), 65.11(d, C-5), 67.69(d, C-4), 93.35(d, C-1), 117.18(d, Ar-CH), 127.25(d, C-2), 129.96(d, C-3), 131.86(s, Ar-C), 154.93(s, Ar-C), 170.15(s, -OCOCH₃), 170.60(s, -OCOCH₃). MS (m/z): 320(M⁺), 287, 258, 218, 213, 184, 173, 139, 128, 111, 97, 71, 57; HRMS: Observed 320.07048; Calculated 320.12599 for C₁₇H₂₀O₆. Elemental analysis: Observed C 62.99 H 6.50; Calculated C 63.71 H 6.29

4'-Methoxyphenyl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (10a) and β -anomer (10b).^{1a,9c} Nature: Gummy colourless solid. *R_f*: 0.7 (hexane : EtOAc = 6 : 4). IR (CHCl₃) ν (cm⁻¹): 2980, 1740, 1614, 1498, 1372, 1210, 1186, 1161; ^1H NMR (200 MHz) δ (ppm): 1.84(s, 3H, -OCOCH₃, of β), (2.01(s, 3H, -OCOCH₃ of α), 2.04(s, 3H, -OCOCH₃, of β), 2.10(s, 3H, -OCOCH₃ of α), 3.77(s, 3H, Ar-OCH₃), 4.14-4.29(m, 3H, H-5, H-6_a, H-6_b), 5.02(bs, 1H, H-4 of β), 5.37(d, $J = 9.27\text{Hz}$, H-4), 5.56(bs, 1H, H-1 of α), 5.57(bs, 1H, H-1 of β), 6.00(bs, 2H, H-2, H-3 of α), 6.06(bs, 2H, H-2, H-3 of β), 6.82(d, 2H, $J = 8.79\text{Hz}$, Ar-H, H_A, H_{A'}), 7.04(d, 2H, $J = 8.79\text{Hz}$, Ar-H, H_A, H_{B'}). ^{13}C NMR (50MHz) δ (ppm): 20.65(q, -OCOCH₃), 20.88(q, -OCOCH₃), 55.60(q, Ar-OCH₃), 62.76(t, C-6), 65.12(d, C-5), 67.61(d, C-4), 92.92(d, C-1 of β), 94.00(d, C-1 of α), 114.50(d, Ar-CH), 118.62(d, Ar-CH), 127.22(d, C-2), 129.62(d, C-3), 151.10(s, Ar-C), 155.20(s, Ar-C), 170.17(s, -OCOCH₃), 170.62(s, -OCOCH₃). MS (m/z): 336(M⁺), 203, 161, 147, 105, 91; HRMS: Observed 336.121885; Calculated 336.120905 for C₁₇H₂₀O₇; Elemental Analysis: Observed C 60.41 H 5.85; Calculated C 60.68 H 5.99

4'-Chlorophenyl 4,6-di-O-acetyl-2,3-dideoxy- α -D-erythro-hex-2-enopyranoside (11a) and β -anomer (11b).^{9c} Nature: Gummy colorless solid. *R_f*: 0.7 (hexane : EtOAc = 7 : 3). IR (CHCl₃) ν (cm⁻¹): 3020, 1737, 1594, 1484, 1459, 1366, 1312, 1091; ^1H NMR (400 MHz) δ (ppm): 1.86(s, 3H, -OCOCH₃, of β), 1.99(s, 3H, -OCOCH₃ of β), 2.04(s, 3H, -OCOCH₃, of α), 2.11(s, 3H, -OCOCH₃, of α), 4.11-4.29(m, 3H, H-5, H-6_a, H-6_b), 5.15(bs, 1H, H-4 of β), 5.38(d, $J_{4,5} = 9.76\text{Hz}$, 1H, H-4 α), 5.64(bs, 1H, H-1 of α), 5.75(bs, 1H, H-1 of β), 5.99(d, 1H, $J_{2,3} = 10.25\text{Hz}$, 1H, H-3), 6.03(d, $J_{2,3} = 10.75\text{Hz}$, 1H, H-2), 7.04(d, $J = 9.27\text{Hz}$, 2H, Ar-H, H_A, H_{A'}), 7.25(d, 2H, $J = 9.27\text{Hz}$, Ar-H, H_B, H_{B'}). ^{13}C NMR (100MHz) δ (ppm): 21.01(q, -OCOCH₃), 21.27(q, -OCOCH₃), 62.94(t,

C-6), 65.15(d, C-5), 68.10(d, C-4), 93.04(d, C-1 of α), 91.53(d, C-1 of β), 118.14(d, Ar-CH), 126.60(d, Ar-CH), 127.33(s, Ar-C), 129.42(d, Ar-CH), 130.42(d, Ar-CH), 155.65(s, Ar-C), 170.37(s, -OCOCH₃), 170.76(s, -OCOCH₃). MS (m/z): 356(M⁺), 213, 153, 111, 81; HRMS: Observed 305.1012985; Calculated 305.102515 for C₁₆H₁₇O₆Cl(-cl).

Methyl 6-O-[4',6'-di-O-acetyl-2',3'-dideoxy-D-erythro-hex-2'-enopyranosyl]-2,3,4-tri-O-methyl- α -D-glucopyranoside (13^a) and β -anomer (13b). Nature: Viscous liquid. *R_f*: 0.4 (hexane : EtOAc = 5 : 5). IR (CHCl₃) ν (cm⁻¹): 3008, 2912, 2848, 1737, 1596, 1539, 1491, 1462, 1369, 1260, 1148, 1100, 1049, 992, 899, 816; ¹H NMR (400 MHz) δ (ppm): 2.09(s, 3H, -OCOCH₃), 2.11(s, 3H, -OCOCH₃), 3.18-4.28(m, 9H, H-2, H-3, H-4, H-5, H-6a, H-6b, H-5', H-6'a, H-6'b), 3.40(s, 3H, -OCH₃), 3.54(s, 3H, -OCH₃), 3.62(s, 3H, -OCH₃), 3.68(s, 3H, -OCH₃), 4.81(d, *J*_{1,2} = 3.42Hz, 1H, H-1), 5.13(bs, 1H, H-1'), 5.20-5.21(m, 2H, H-4', H-1' of β), 5.32(d, *J*_{4',5'} = 9.76Hz, H-4'), 5.88(bs, 2H, H-2', H-3' of α), 5.97(bs, 2H, H-2', H-3', of β). ¹³C NMR (100MHz) δ (ppm): 20.81(q, -OCOCH₃), 20.99(q, -OCOCH₃), 55.15(q, -OCH₃), 58.97(q, -OCH₃), 60.39(q, -OCH₃), 60.88(q, -OCH₃), 62.85(t, C-6' of α), 63.43(t, C-6' of β), 65.19(d), 66.83(d), 66.98(t, C-6), 69.74(d), 79.14(d), 81.76(d), 83.54(d), 94.64(d, C-1), 97.38(d, C-1'), 127.68(d, C-2'), 129.08(d, C-2'), 170.29(s, -OCOCH₃), 170.82(d, -OCOCH₃). MS (m/z): 448, 392, 331, 301, 274, 246, 232, 189, 161, 147, 119, 105, 91, 57; HRMS: Observed 448.192065; Calculated 448.194465 for C₂₀H₃₂O₁₁.

2-(1',5'-Anhydro-4',6'-di-O-acetyl-2',3'-dideoxy- α -D-erythro-hex-2'-enopyranosyl)-4-methylphenol (14a) and β -anomer (14b).^{9a} Nature: Gummy solid. *R_f*: 0.4 (hexane : EtOAc = 7 : 3). IR (CHCl₃) ν (cm⁻¹): 3440, 2928, 2864, 1731, 1641, 1600, 1491, 1452, 1369, 1289, 1072, 972, 889, 825, 640; ¹H NMR (400 MHz) δ (ppm): 2.08(s, 3H, -OCOCH₃, of β), 2.09(s, 3H, -OCOCH₃ of β), 2.11(s, 6H, 2 x -OCOCH₃, of α), 2.25(s, 3H, -ArCH₃ of α), 2.26(s, 3H, -ArCH₃ of β), 3.90-4.35(m, 3H, H'-5, H-6'a, H-6'b), 5.25(dd, *J*_{4',5'} = 6.62Hz, *J*_{3',4'} = 3.32Hz, 1H, H-4' of α), 5.45(dd, *J*_{1',2'} = 3.50Hz, *J*_{1',3'} = 2.13Hz, 1H, H-1' of β), 5.47(bs, 1H, H-1' of α), 5.49(ddd, *J*_{4',5'} = 8.81Hz, *J*_{3',4'} = 1.84Hz, *J*_{2',4'} = 1.27Hz, 1H, H-4' of β), 5.82(dd, *J*_{2',3'} = 10.14Hz, *J*_{3',4'} = 1.74Hz, 1H, H-3' of β), 5.98(dd, *J*_{2',3'} = 10.42Hz, *J*_{3',4'} = 2.01Hz, 1H, H-2' of β), 6.04(dd, *J*_{2',3'} = 10.89Hz, *J*_{3',4'} = 2.01Hz, 1H, H-3' of α), 6.28(ddd, *J*_{2',3'} = 10.39Hz, *J*_{3',4'} = 2.99Hz, *J*_{2',4'} = 1.28Hz, 1H, H-2' of α), 6.76(d, *J*_{5,6} = 8.18Hz, 1H, H-6 of α), 6.79-7.10(m, 4H, Ar-H, Ar-OH). ¹³C NMR (100MHz) δ (ppm): 20.46(q, -OCOCH₃), 20.53(q, -OCOCH₃), 20.76(q, Ar-CH₃ of α), 21.00(q, Ar-CH₃ of β), 62.17(t, C-6' of α), 62.90(t, C-6' of β), 64.58(d, C-4' of β), 64.92(d, C-4' of α), 70.68(d, C-5' of α), 72.37(d, C-5' of β), 74.75(d, C-1' of α), 76.71(d, C-1' of β), 116.95(d, Ar-CH of α), 117.15(d, Ar-CH of β), 123.37(d), 124.83(d), 124.86(d), 127.71(d), 129.11(d), 129.21(s, s, Ar-C of α), 129.50(s, s, Ar-C of β), 130.14(d), 130.67(d), 130.90(d), 131.39(d), 152.77(s, Ar-C of α), 153.55(s, Ar-C of β), 170.24(s, -OCOCH₃), 170.88(s, -OCOCH₃). MS (m/z): 320(M⁺), 262, 187, 161, 145, 135; HRMS: Observed 320.12006; Calculated 320.12599 for ¹⁷H₂₀O₆

2-(1',5'-Anhydro-4',6'-di-O-acetyl-2',3'- dideoxy- α -D- erythro-hex-2'- enopyranosyl)-4-methoxyphenol (15a) and β -anomer (15b).^{9a} Nature: Viscous liquid. *R_f*: 0.4 (hexane : EtOAc = 7 : 3). IR (CHCl₃) ν (cm⁻¹): 3450, 2928, 2860, 1737, 1638, 1604, 1456, 1372, 1280, 1084; ¹H NMR (400 MHz) δ (ppm): 2.082(s, 3H, -OCOCH₃ of α), 2.089(s, 3H, -OCOCH₃ of α), 2.11(s,

6H, 2 x -OCOCH₃, of β), 3.74(s, 3H, -ArOCH₃ of β), 2.26(s, 3H, -ArCH₃ of α), 3.88-4.00(m, H-5' of α, H-5' of β), 4.10-4.35(m, H-6'a, H-6'b of α, H-6'a, H-6'b of β), 5.26(ddd, J_{4',5'} = 6.85Hz, J_{3',4'} = 3.75Hz, J_{2',4'} = 1.49Hz, 1H, H-4' of α), 5.43-5.52(m, 3H, H-1' of β, H-1' of α, H-4' of β), 5.83(dd, J_{2',3'} = 10.33Hz, J_{3',4'} = 1.73Hz, 1H, H-3' of β), 5.95-6.07(m, 2H, H-2' of β, H-3' of α), 6.24(ddd, J_{2',3'} = 10.36Hz, J_{1',2''} = 3.04Hz, J_{2',4'} = 1.27Hz, 1H, H-2' of α), 6.65-6.89(m, 4H, Ar-H, Ar-OH). ¹³C NMR (100MHz) δ (ppm): 20.66(q, -OCOCH₃), 20.91(q, -OCOCH₃), 55.74(q, Ar-OCH₃), 62.19(t, C-6' of α), 62.89(t, C-6' of β), 64.59(d, C-4' of β), 64.86(d, C-4' of α), 70.63(d, C-5' of α), 72.03(d, C-5' of β), 74.73(d, C-1' of α), 76.36(d, C-1' of β), 112.83(d), 114.59(d), 114.79(d), 117.61(d), 117.80(d), 124.59(d), 124.94(d), 125.17(d), 130.47(d), 131.11(d), 148.71(s, Ar-C of α), 149.55(s, Ar-C of β), 152.98(s, Ar-C of α), 153.26(s, Ar-C of β), 170.17(s, -OCOCH₃), 170.80(s, -OCOCH₃). MS (m/z): 336M⁺, 276, 216, 203, 161, 105, 91; HRMS: Observed 336.117857; Calculated 336.120905 for C₁₇H₂₀O₇

2-(1',5'-Anhydro-4'-O-acetyl-2',3',6'-trideoxy-L-threo-hex-2'-enopyranosyl)-4methylphenol (17a) and β-anomer (17b). Nature: Viscous liquid. R_f: 0.4 (hexane : EtOAc = 8 : 2). IR (CHCl₃) ν (cm⁻¹): 3450, 2980, 1740, 1640, 1598, 1438, 1362, 1257; ¹H NMR (200 MHz): δ (ppm): 1.31(d, J = 4.85Hz, 3H, 6'-CH₃ of α), 1.34(d, J = 4.85Hz, 3H, 6'-CH₃ of β), 2.04(s, 3H, -OCOCH₃, of α), 2.10(s, 3H, -OCOCH₃ of β), 2.24(s, 3H, -ArCH₃ of α), 2.25(s, 3H, -ArCH₃ of β), 3.62-3.90(m, 1H, H-5' of β), 3.98-4.10(m, 1H, H-5' of α), 4.55-5.40(m, 4H, H-1' of α, H-1' of β, H-4' of α, H-4' of β), 5.79(dd, J_{2',3'} = 10.25Hz, J_{3',4'} = 2.05Hz, 1H, H-3' of β), 5.86-6.02(m, 2H, H-2' of β, H-3' of α), 6.13(dd, J_{2',3'} = 10.25Hz, J_{1',2''} = 1.86Hz, 1H, H-2' of α), 6.69-6.91(m, 4H, Ar-H, Ar-OH). ¹³C NMR (50 MHz) δ (ppm): 16.06(q, C-6' of α), 18.74(q, C-6' of β), 20.40(q, -OCOCH₃), 21.01(q, -ArCH₃), 67.77(d), 68.83(d), 70.04(d), 70.46(d), 71.98(d), 73.68(d, C-1' of α), 76.36(d, C-1' of β), 115.06(d), 116.89(d), 123.46(d), 125.44(d), 127.84(d), 128.83(d), 129.05(d), 129.33(s, Ar-C), 129.96(s, Ar-C), 130.29(d), 130.44(d), 131.57(d), 132.02(d), 152.80(s, Ar-C), 153.57(s, Ar-C), 170.42(s, -OCOCH₃ of α), 170.54(s, -OCOCH₃ of β).

2-(1',5'-Anhydro-4'-O-acetyl-2',3',6'-trideoxy-L-threo-hex-2'-enopyranosyl)-4methoxyphenol (18a) and β-anomer (18b). Nature: Viscous liquid. R_f: 0.4 (hexane : EtOAc = 6 : 4). IR (CHCl₃) ν (cm⁻¹): 3452, 2987, 1737, 1638, 1602, 1439, 1364, 1237; ¹H NMR (200 MHz) δ (ppm): 1.31(d, J = 5.16Hz, 3H, 6'-CH₃ of α), 1.35(d, J = 4.85Hz, 3H, 6'-CH₃ of β), 2.10(s, 3H, -OCOCH₃, of β), 2.11(s, 3H, -OCOCH₃ of α), 3.74(s, 3H, -ArOCH₃ of α), 3.75(s, 3H, -ArCH₃ of β), 3.80-3.90(m, 1H, H-5' of β), 4.05(apparent qt, J = 6.52Hz, 1H, H-5' of α), 5.01(bs, 1H, H-4' of β), 5.22(dd, J_{4',5'} = 8.75Hz, J_{2',4'} = 1.36Hz, 1H, H-4' of α), 5.32(d, J_{1',2'} = 1.94Hz, 1H, H-1' of β), 5.35(bs, H-1' of α), 5.81(dd, J_{2',3'} = 10.29Hz, J_{3',4'} = 2.10Hz, 1H, H-3' of β), 5.85-6.04(m, 2H, H-2' of β, H-3' of α), 6.13(dd, J_{2',3'} = 10.34Hz, J_{3',4'} = 2.29Hz, 1H, H-2' of α), 6.63-6.93(m, 4H, Ar-H, Ar-OH). ¹³C NMR (50 MHz) δ (ppm): 16.13(q, C-6' of α), 18.45(q, C-6' of β), 21.02(q, -OCOCH₃), 55.78(q, -Ar-OCH₃), 68.76(d), 70.03(d), 70.36(d), 71.86(d), 73.65(d, C-1' of α), 76.36(d, C-1' of β), 113.00(d), 114.34(d), 114.58(d), 117.60(d), 117.69(d), 123.33(d), 124.48(d), 124.86(d), 125.64(d), 131.22(d), 131.58(d), 148.89(s, Ar-C), 149.69(s, Ar-C), 153.25(s, Ar-C), 170.40(s, -OCOCH₃). MS (m/z): 278(M⁺), 218, 192, 161, 124, 91

2-(D-Glycero-1',2'-dihydroxyethyl)furan (21).¹⁹ Nature: Viscous liquid. *R_f*: 0.6 (hexane : EtOAc = 7 : 3). [α]_D = + 34.5° (c 2.4, CHCl₃). IR (CHCl₃) ν (cm⁻¹): 3600, 3424, 2928, 1600, 1494, 1468, 1376, 1145, 1088, 1068, 998, 937, 873, 825, 652, 595; ¹H NMR (200 MHz) δ (ppm): 3.76(d, *J*_{1',2'}=5.7Hz, 2H, H-1'a, H-1'b), 4.73(t, *J*_{1',2'}=5.54Hz, 1H, H-2'), 6.23-6.30(m, 2H, H-3, H-4), 7.32-7.33(m, 1H, H-5); ¹³C NMR(50 MHz, CDCl₃, δ) 64.83(t, C-1'), 68.22(d, C-2'), 106.78(d, C-5), 110.17(d, C-3), 142.07(d, C-4), 153.58(s, C-2). MS (*m/z*): 128(M⁺), 97, 85, 83, 69, 47, 41; HRMS: Observed 128.0502322; Calculated 128.047345 for C₆H₈O₃.

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