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

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

(received 19 Mar 04; accepted 08 Jan 05; published on the web 15 Jan 05)

Abstract

Treatment of tri-*O*-acetyl-D-glucal 1 with various alcohols and phenols in the presence of $InCl_3$ / CH_2Cl_2 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

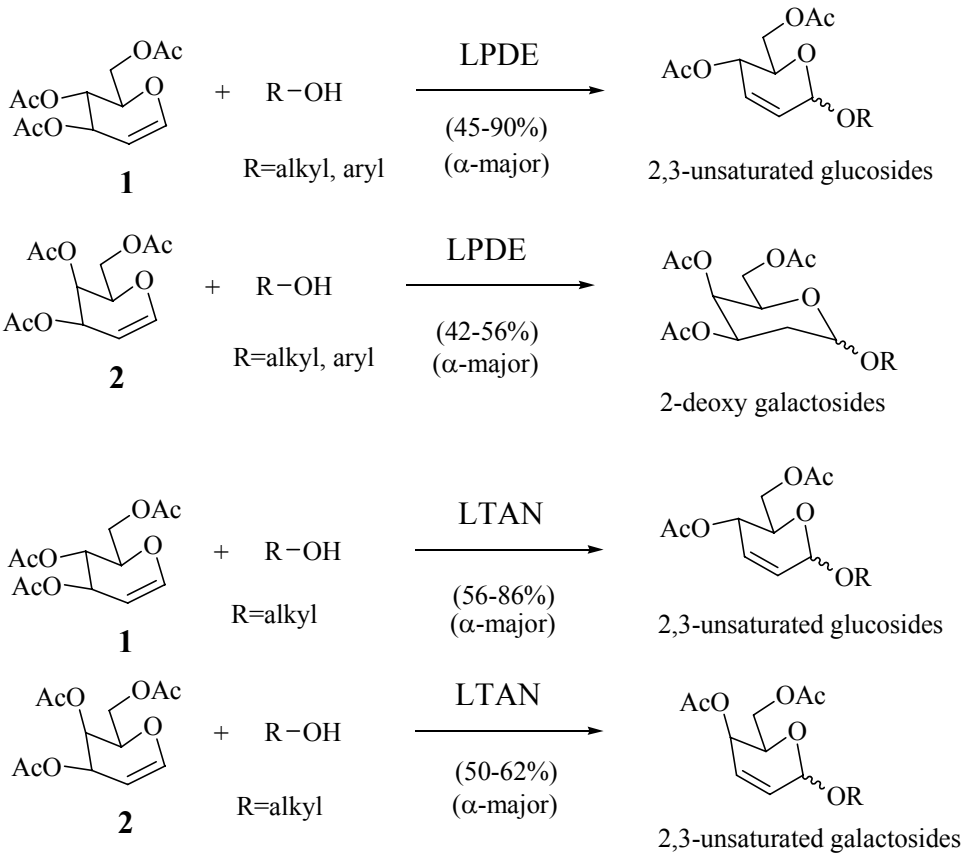
Introduction

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-unsaturatedglucosides 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 *etal*[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 *etal*[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 $BF_3.Et_2O$. Toshima *et al*[6] came out with a practical method for the glycosidation of glycals 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 *etal*[8] reported an efficient and streoselective palladium-catalyzed *O*-glycosylation using glycals. 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 chemistry[9] 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 diethtyl 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*-acetyglucal, **1**, which exists in two different conformations $^4H_5$ and $^5H_4$ in equilibrium, undergoes Ferrier rearrangement in the $^5H_4$ 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]



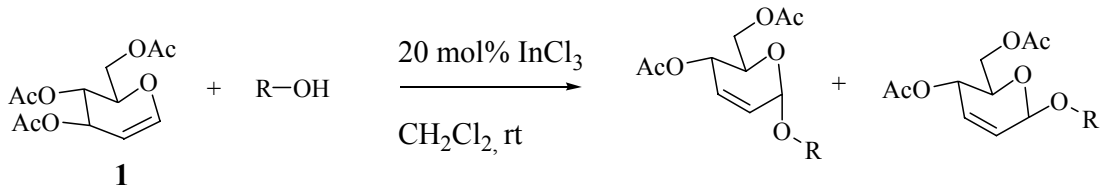
Scheme 1

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

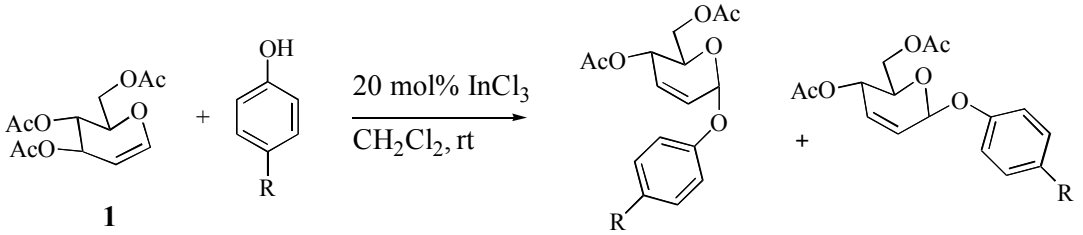
on our earlier NOE studies[9c]. When the signal due to H-1 of the alpha anomer was irradiated, there was no significant enhancement in the intensity of the signal due to H-5, and vice *versa*. Based on the integration values of signals due to anomeric protons (α and β anomeric protons come without overlapping and can be integrated without difficulty) in the ^{1}H 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 $InCl_3$ 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 (%)	α:β*
R = benzyl	3a + 3b	86	6.3:1
R = *o*-nitrobenzyl	4a + 4b	80	7:1
R = *o*-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 [a]15 min and [b]30 min.

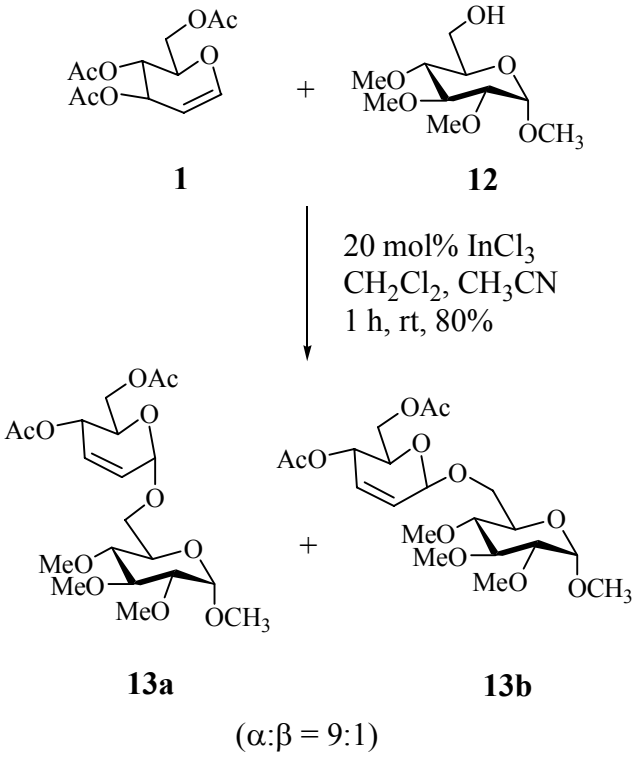


Scheme 3

Phenols	Product	Yield (%)	α:β*
p-methylphenol	**9a** + **9b**	60	8:1
p-methoxyphenol	**10a** + **10b**	65	7.5:1
p-chlorophenol[a]	**11a** + **11b**	62	9:1

* Anomeric ratios were determined by ^{1}H and (300 & 400 MHz) spectroscopy
Time taken for the completion of the reaction is 10 min except [a]15 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*., $LiClO_4$, $LiBF_4$, $BF_3.Et_2O$ 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

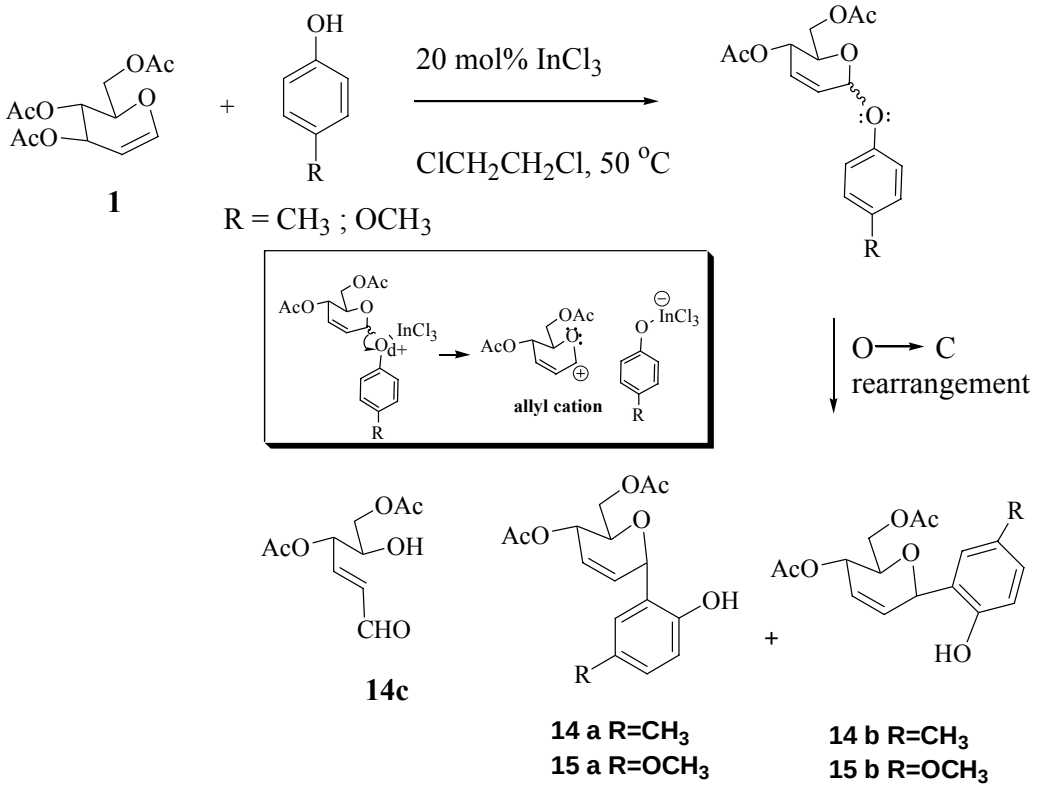
Alcohol	Products	Lewis acid catalyst (temp.)	Time	Yield (α:β)*
Benzyl alcohol	**3a + 3b**	$LiClO_4$/ Et_2O (27 ^oC)	16 h	85% (5:1)
		$LiBF_4$/ CH_3CN (27 ^oC)	4 h	86% (4:1)
		BF_3/ Et_2O (0^oC to 27 ^oC)	45 min	80% (4:1)
		$SnCl_4/CH_2Cl_2$ (0^oC to 27 ^oC)	45 min	85% (4.6:1)
		Montmorillonite K-10	-	-
		$InCl_3$/ CH_2Cl_2 (27 ^oC)	10 min	91% (6.3:1)
Cyclohexanol	**6a + 6b**	$LiClO_4$/ Et_2O (27 ^oC)	18 h	90% (6:1)
		$LiBF_4$/ CH_3CN (27 ^oC)	4 h	86% (8:1)
		BF_3/ Et_2O (0^oC to 27 ^oC)	45 min	70% (9:1)
		$SnCl_4/CH_2Cl_2$ (0^oC to 27 ^oC)	1 h	80% (6.5:1)
		Montmorillonite K-10 / CH_2Cl_2	1 h	93% (7.3:1)
		$InCl_3$/ CH_2Cl_2 (27 ^oC)	10 min	90% (9:1)
Propargyl alcohol	**7a +7b**	$LiClO_4$/ Et_2O (27 ^oC)	18 h	90% (6:1)
		$LiBF_4$/ CH_3CN (27 ^oC)	4 h	86% (8:1)
		BF_3/ Et_2O (0^o to 27 ^oC)	30 min	82% (6.3:1)
		$SnCl_4/CH_2Cl_2$ (0^oC to 27 ^oC)	45 min	80% (9:1)
		Montmorillonite K-10 / CH_2Cl_2	1 h	97% (6.4:1)
		$InCl_3$/ CH_2Cl_2 (27 ^oC)	10 min	92% (9:1)

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

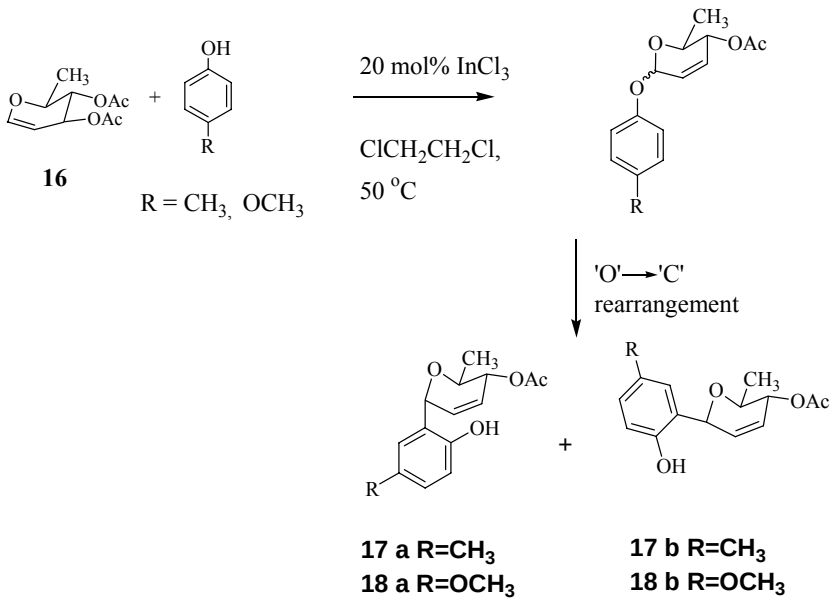
In all the cases studied, the reaction was fastest with $InCl_3$ as compared to other catalysts. It was observed that $InCl_3$ is better than $SnCl_4$. Besides anomeric selectivity; the yield was greatest with $InCl_3$. We have examined a few other catalysts such as $TaCl_5$, $PsCl_3$, and LnCl3 also 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 $InCl_3$. There is precedence for such a rearrangement from our own earlier work.[9a]

One-pot synthesis of *C*-aryl glycosides using $InCl_3$. When the reaction between tri-*O*-acetyl-D-glucal **1** and *p*-cresol in the presence of anhyd. $InCl_3$ in CH_2Cl_2, 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 $ClCH_2CH_2Cl$ as the solvent and heating the reaction mixture at 50 ^oC 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 (%)	α:β*
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

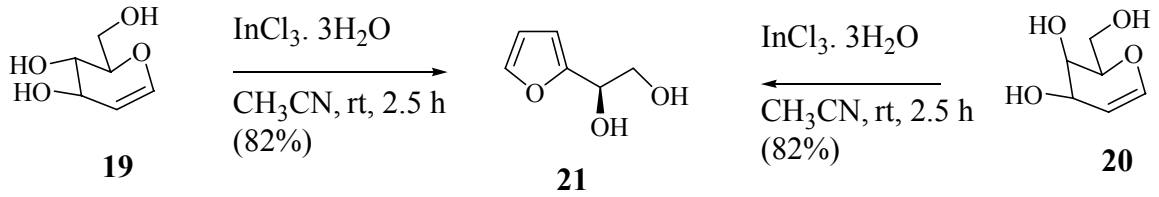
* Anomeric ratios were determined by ^{1}H and (200 & 400 MHz) spectroscopy.

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 $InCl_3$ 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 glycals. 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 $BF_3{\cdot}Et_2O$ as catalyst[9a].

The reaction underwent by 3,4-di-*O*-acetyl-*L*-rhamnal **16** also, which furnished the corresponding 2,3-unsaturated *C*-arylrhamnosides 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 ($InCl_3 \cdot 3H_2O$) 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 glycals. 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 $InCl_3 \cdot 3H_2O$ (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 ($LiClO_4$, $LiBF_4$, $BF_3 \cdot Et_2O$, $SnCl_4$, 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. $InCl_3$ / $ClCH_2CH_2Cl$ at 50 °C.

Experimental Section

Tri-*O*-acetyl-D-glucal **1**, tri-*O*-acetyl-D-galactal **2** and 3,4-di-*O*-acetyl-L-rhamnal **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 $InCl_3$ (0.2mmol; 20 mol%) in dry CH_2Cl_2 (1-2 mL) (For *C*-aryl glycosides, $ClCH_2CH_2Cl$ was used as the solvent and heated the reaction mixture at 50 ^oC 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 ($CHCl_3$) υ (cm^{-1}): 2944, 1734, 1644, 1599, 1446, 1382, 1260, 1193; ^1H NMR (300 MHz) δ (ppm): 2.07(s, 3H, -$OCOCH_3$), 2.09(s, 3H, -$OCOCH_3$) 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). ^{13}C NMR (75MHz) δ (ppm): 20.70(q, -$OCOCH_3$), 20.86(q, -$OCOCH_3$), 62.81(t, C-6), 65.16(d, C-5), 66.94(d, C-4), 70.17(t, -OCH_2Ar), 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, -$OCOCH_3$), 170.70(s, -$OCOCH_3$). MS (m/z): 380, 278, 242, 218, 213, 200, 176, 153, 111, 91; HRMS: Observed 261.129595 (M^+-$OCOCH_3$) Calculated 261.13269 for $C_{15}H_{17}O_4$

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 ($CHCl_3$) υ (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, - $OCOCH_3$), 2.09 (s, 3H, -$OCOCH_3$), 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). ^{13}C NMR (100MHz) δ (ppm): 20.73(q, -$OCOCH_3$), 20.96(q, -$OCOCH_3$), 62.81(t, C-6), 65.19(d, C-5), 67.12(t, -OCH_2-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, -$OCOCH_3$), 170.90(s, -$OCOCH_3$). MS (m/z): 306(M^+-2 x OAc), , 263, 221,

213, 153, 136, 111, 78, 65, 51 HRMS: Observed 306.1250735(M^+-2 x OAc) Calculated 306.127765 for $C_{15}H_{16}O_6N$

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 ($CHCl_3$) υ (cm^{-1}): 2948, 1740, 16539, 1433, 1408, 1363, 1260, 1260, 1142, 1097, 1046, 963, 934; ^{1}H NMR (300 MHz) δ (ppm): 2.08 (s, 3H, - $OCOCH_3$), 2.10 (s, 3H, -$OCOCH_3$), 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, -$OCOCH_3$), 20.96(q, -$OCOCH_3$), 62.86(t, C-6), 65.20(d, C-5), 67.18(d, C-4), 74.26(t, -OCH_2-Ar), 94.20(d, C-1 of α), 98.15(d, C-1 of β), 98.15(s, Ar-CI), 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, -$OCOCH_3$), 170.80(s, -$OCOCH_3$). HRMS: Observed 446.0195548; Calculated 446.022462 for $C_{17}H_{19}O_6I$

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 ($CHCl_3$) υ (cm^{-1}): 2949, 1738, 1640, 1598, 1439, 1380, 1266, 1182, 1122, 1015; ^{1}H 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, - $OCOCH_3$), 2.09 (s, 3H, -$OCOCH_3$), 3.58-3.69(m, 1H, -$OCH(CH_2)_5$), 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, -$OCOCH_3$), 20.91(q, -$OCOCH_3$), 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, -$OCH(CH_2)_5$), 92.76(d, C-1), 128.53(d, C-2), 128.70(d, C-3), 170.28(s, -$OCOCH_3$), 170.72(s, -$COCH_3$).

HRMS: Observed 312.159426; Calculated 312.15729 for $C_{16}H_{24}O_6$

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 ($CHCl_3$) υ (cm^{-1}): 2951, 2112, 1740, 1641, 1601, 1, 1380, 1266, 1182, 1122, 1015; ^{1}H NMR (400 MHz) δ (ppm): 2.08 (s, 3H, - $OCOCH_3$), 2.10 (s, 3H, -$OCOCH_3$), 2.47(t, J=2.42Hz, 1H, -OCH_2-C≡CH), 3.8-4.24(m, 3H, H-5, H-6a, H-6b), 4.31(d, J = 2.44Hz, 2H, -OCH_2-C≡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, -$OCOCH_3$), 20.84(q, -$OCOCH_3$), 54.98(d, -OCH_2-C≡CH), 62.71((t, C-6), 65.10(t, -OCH_2-C≡CH), 67.14(d, C-5), 74.75(d, C-4), 79.03(s, -OCH_2-C≡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, -$OCOCH_3$), 170.65(s, -$OCOCH_3$). MS (m/z): 268, 230, 213, 171, 153, 11, 83, 55

HRMS: Observed 268.09669; Calculated 268.09469 for $C_{13}H_{16}O_6$

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 ($CHCl_3$) υ (cm^{-1}): 2928, 2816, 1734, 1593, 1449, 1369, 1264, 1180, 1136, 1107, 1065, 1014, 963, 905; ^{1}H NMR (200 MHz) δ (ppm): 2.08 (s, 6H, 2 x - $OCOCH_3$ of α), 2.09 (s, 6H, 2 x -$OCOCH_3$ of β), 3.45(s, 3H, OCH_3 of α), 3.46(s, 3H, OCH_3 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,

$J_{1,2}$ = 1.09Hz, 1H, H-1 of β), 5.16-5.20(m, 1H, H-4 of β), 5.31(dd, $J_{4,5}$ = 9.67Hz, $J_{3,4}$ = 1.09Hz, 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, -OCOCH$_3$), 20.76(q, -OCOCH$_3$), 55.11(q, OCH$_3$ of β), 55.73(q, OCH$_3$ 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, -OCOCH$_3$), 170.55(d, -OCOCH$_3$). HRMS: Observed 244.15920; Calculated 244.12469 for $C_{11}H_{16}O_6$

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 ($CHCl_3$) υ (cm^{-1}): 2948, 1738, 1602, 1446, 1376, 1272, 1182, 1126; ^{1}H NMR (400 MHz) δ (ppm): 1.88(s, 3H, -OCOCH$_3$, of α), 2.10(s, 3H, -OCOCH$_3$, of α), 2.00(s, 3H, - OCOCH$_3$ of β), 2.10(s, 3H, -OCOCH$_3$ of β), 2.29(s, 3H, ArCH$_3$), 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, $J_{4,5}$ = 9.54Hz, 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= 8.48Hz, Ar-H, H_A, $H_{A'}$), 7.09(d, 2H, J=8.48Hz, Ar-H, H_B, $H_{B'}$). ^{13}C NMR (100MHz) δ (ppm): 20.56(q, -OCOCH$_3$), 20.67(q, -OCOCH$_3$), 20.94(q, Ar-CH$_3$), 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, -OCOCH$_3$), 170.60(s, -OCOCH$_3$). 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 $C_{17}H_{20}O_6$. Elemental anlaysis: 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 ($CHCl_3$) υ (cm^{-1}): 2980, 1740, 1614, 1498, 1372, 1210, 1186, 1161; ^{1}H NMR (200 MHz) δ (ppm): 1.84(s, 3H, - OCOCH$_3$, of β), (2.01(s, 3H, - OCOCH$_3$ of α), 2.04(s, 3H, - OCOCH$_3$, of β), 2.10(s, 3H, -OCOCH$_3$ of α), 3.77(s, 3H, Ar-OCH$_3$), 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 = 9.27Hz, 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 = 8.79Hz, Ar-H, H_A, $H_{A'}$), 7.04(d, 2H, J = 8.79Hz, Ar-H, H_A, $H_{B'}$). ^{13}C NMR (50MHz) δ (ppm): 20.65(q, -OCOCH$_3$), 20.88(q, -OCOCH$_3$), 55.60(q, Ar-OCH$_3$), 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, -OCOCH$_3$), 170.62(s, -OCOCH$_3$). MS (m/z): 336(M$^+$),203, 161, 147, 105, 91; HRMS: Observed 336.121885; Calculated 336.120905 for $C_{17}H_{20}O_7$; 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 ($CHCl_3$) υ (cm^{-1}): 3020, 1737, 1594, 1484, 1459, 1366, 1312, 1091; ^{1}H NMR (400 MHz) δ (ppm): 1.86(s, 3H, - OCOCH$_3$, of β), 1.99(s, 3H, -OCOCH$_3$ of β), 2.04(s, 3H, - OCOCH$_3$, of α), 2.11(s, 3H, -OCOCH$_3$, 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, $J_{4,5}$ = 9.76Hz, 1H, H-4 α), 5.64(bs, 1H, H-1 of α), 5.75(bs, 1H. H-1 of β) 5.99(d, 1H, $J_{2,3}$ = 10.25Hz, 1H, H-3), 6.03(d, $J_{2,3}$ = 10.75Hz, 1H, H-2), 7.04(d, J = 9.27Hz, 2H, Ar-H, H_A, $H_{A'}$), 7.25(d, 2H, J = 9.27Hz, Ar-H, H_B, $H_{B'}$). ^{13}C NMR (100MHz) δ (ppm): 21.01(q, -OCOCH$_3$), 21.27(q, -OCOCH$_3$), 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, -$OCOCH_3$), 170.76(s, -$OCOCH_3$). MS (m/z): 356(M^+), 213, 153, 111, 81; HRMS: Observed 305.1012985; Calculated 305.102515 for $C_{16}H_{17}O_6Cl$(-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 ($CHCl_3$) υ (cm^{-1}): 3008, 2912, 2848, 1737, 1596, 1539, 1491, 1462, 1369, 1260, 1148, 1100, 1049, 992, 899, 816; ^{1}H NMR (400 MHz) δ (ppm): 2.09(s, 3H, -$OCOCH_3$), 2.11(s, 3H, -$OCOCH_3$), 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, -OCH_3), 3.54(s, 3H, -OCH_3), 3.62(s, 3H, -OCH_3), 3.68(s, 3H, -OCH_3), 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). ^{13}C NMR (100MHz) δ (ppm): 20.81(q, -$OCOCH_3$), 20.99(q, -$OCOCH_3$), 55.15(q, -OCH_3), 58.97(q, -OCH_3), 60.39(q, -OCH_3), 60.88(q, -OCH_3), 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, -$OCOCH_3$), 170.82(d, -$OCOCH_3$). 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 $C_{20}H_{32}O_{11}$.

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 ($CHCl_3$) υ (cm^{-1}): 3440, 2928, 2864, 1731, 1641, 1600, 1491, 1452, 1369, 1289, 1072, 972, 889, 825, 640; ^{1}H NMR (400 MHz) δ (ppm): 2.08(s, 3H, - $OCOCH_3$, of β), 2.09(s, 3H, -$OCOCH_3$ of β), 2.11(s, 6H, 2 x -$OCOCH_3$, of α), 2.25(s, 3H, -$ArCH_3$ of α), 2.26(s, 3H, -$ArCH_3$ 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). ^{13}C NMR (100MHz) δ (ppm): 20.46(q, -$OCOCH_3$), 20.53(q, -$OCOCH_3$), 20.76(q, Ar-CH_3 of α), 21.00(q, Ar-CH_3 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, -$OCOCH_3$), 170.88(s, -$OCOCH_3$). MS (m/z): 320(M^+), 262, 187, 161, 145, 135; HRMS: Observed 320.12006; Calculated 320.12599 for $_{17}H_{20}O_6$

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 ($CHCl_3$) υ (cm^{-1}): 3450, 2928, 2860, 1737, 1638, 1604, 1456, 1372, 1280, 1084; ^{1}H NMR (400 MHz) δ (ppm): 2.082(s, 3H, -$OCOCH_3$ of α), 2.089(s, 3H, -$OCOCH_3$ of α), 2.11(s,

6H, 2 x -$OCOCH_3$, of β), 3.74(s, 3H, -$ArOCH_3$ of β), 2.26(s, 3H, -$ArCH_3$ 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). ^{13}C NMR (100MHz) δ (ppm): 20.66(q, -$OCOCH_3$), 20.91(q, -$OCOCH_3$), 55.74(q, Ar-OCH_3), 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, -$OCOCH_3$), 170.80(s, -$OCOCH_3$). MS (m/z): 336M^+), 276, 216. 203, 161, 105, 91; HRMS: Observed 336.117857; Calculated 336.120905 for $C_{17}H_{20}O_7$

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 ($CHCl_3$) υ (cm^{-1}): 3450, 2980, 1740, 1640. 1598, 1438, 1362, 1257; ^{1}H NMR (200 MHz): δ (ppm): 1.31(d, J = 4.85Hz, 3H, 6'-CH_3 of α), 1.34(d, J = 4.85Hz, 3H, 6'-CH_3 of β), 2.04(s, 3H, -$OCOCH_3$, of α), 2.10(s, 3H, -$OCOCH_3$ of β), 2.24(s, 3H, -$ArCH_3$ of α), 2.25(s, 3H, -$ArCH_3$ 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). ^{13}C NMR (50 MHz) δ (ppm): 16.06(q, C-6' of α), 18.74(q, C-6' of β), 20.40(q, -$OCOCH_3$), 21.01(q, -$ArCH_3$), 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, -$OCOCH_3$ of α), 170.54(s, -$OCOCH_3$ of β).

2-(1',5'-Anhydro-4'-*O*-acetyl-2',3',6'-trideoxy-L-*threo*-hex-2'-enopyranosyl)-4 methoxyphenol (18a) and β-anomer (18b). Nature: Viscous liquid. R_f: 0.4 (hexane : EtOAc = 6 : 4). IR ($CHCl_3$) υ (cm^{-1}): 3452, 2987, 1737, 1638, 1602, 1439, 1364, 1237; ^{1}H NMR (200 MHz) δ (ppm): 1.31(d, J = 5.16Hz, 3H, 6'-CH_3 of α), 1.35(d, J = 4.85Hz, 3H, 6'-CH_3 of β), 2.10(s, 3H, -$OCOCH_3$, of β), 2.11(s, 3H, -$OCOCH_3$ of α), 3.74(s, 3H, -$ArOCH_3$ of α), 3.75(s, 3H, -$ArCH_3$ 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). ^{13}C NMR (50 MHz) δ (ppm): 16.13(q, C-6' of α), 18.45(q, C-6' of β), 21.02(q, -$OCOCH_3$), 55.78(q, -Ar-OCH_3), 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, -$OCOCH_3$). 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). $[\alpha]_D$= + 34.5^o (c 2.4, $CHCl_3$). IR ($CHCl_3$) υ (cm^{-1}): 3600, 3424, 2928, 1600, 1494, 1468, 1376, 1145, 1088, 1068, 998, 937, 873, 825, 652, 595; ^{1}H 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); ^{13}C NMR(50 MHz, $CDCl_3$, 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 $C_6H_8O_3$.

Acknowledgments

The authors thank: Department of Science and Technology, India, for financial support, and RSIC, IIT, Chennai, SPIC Science Foundation, Chennai and Sun Pharmaceutical Advanced Research Center, Baroda for spectral data. One of us (BSB) also thanks Dr. K. Vijayakumaran, Director, R&D, Chimique Laboratories, Chennai, for useful discussions.

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