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Metal nitrates catalysed *O*-glucosylation using acetyl glucal in organic solvents and ionic liquids: A comparative investigation

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Abstract

The Ferrier glucosylation of alcohols with 3,4,6-tri-*O*-acetyl-D-glucal has been investigated with several metal nitrates and the optimal catalyst is bismuth nitrate pentahydrate (BNP). Good yields of pseudoglycals were also obtained with ferric nitrate nonahydrate (FNN), heightening the catalyst dosage (50 mol%) being required however. The BNP-mediated reactions showed remarkable solvent dependency and in the optimal protocol, the amount of BNP as low as 10 mol% was effective, furnishing excellent yields of *O*-glucosides with good anomeric selectivity in acetonitrile. A comparison of BNP and FNN in terms of yields and selectivity of the product has been made. In comparison to the reactions in acetonitrile, the catalytic ability of BNP was found to enhance drastically in the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF_6].

Keywords: 3,4,6-Tri-*O*-acetyl-D-glucal; Alcohols; Metal nitrates; Ferrier glucosylation; Ionic liquids

1. Introduction

The glycals, i.e. 1,2-unsaturated derivatives of pentoses and hexoses are amongst the most versatile chiral building blocks. These compounds have been a subject of considerable interest in carbohydrate chemistry [1]. The most investigated and exploited synthetic transformation used as a tool for the initial manipulation in glycal chemistry is the Ferrier rearrangement [2]. The Ferrier rearrangement is an allylic rearrangement of glycal esters in the presence of alcohols and phenols leading to alkyl and aryl 2,3-unsaturated *O*-glycosides, respectively, which are also termed as pseudoglycals. The pseudoglycals have further added to the diversity of unsaturated sugar derivatives. Alkyl and aryl 2,3-unsaturated glycosides are the versatile class of useful chiral precursors in the synthesis of a wide array of compounds, such as glucopeptides [3], modified carbohydrates [4], nucleosides [5,6] and biologically active natural products [7]. 2-Deoxy and 2,3-dideoxy sugars derived from 2,3-unsaturated sugars are structurally important building blocks for antibiotics [8]. Besides, the synthetic utility of the Ferrier rearrangement is not limited to the preparation of unsaturated *O*-glycosides, since the variation of nucleophiles can result in *S*- and *C*-glycosides. The catalysts commonly employed to effect the rearrangement are either Lewis acids, such as $BF_3{\cdot}Et_2O$ [9], $SnCl_4$ [10], $FeCl_3$ [11], $Sc(OTf)_3$ [12], $LiBF_4$ [13,14], $InCl_3$ [15], $Yb(OTf)_3$ [16], montmorillonite K10 [17], $BiCl_3$ [18], $InBr_3$ [19], $Dy(OTf)_3$ [20], $CeCl_3{\cdot}7H_2O$ [21], $ZnCl_2$ [22] and $ZrCl_4$ [23] or oxidizing agents, such as iodonium dicollidinium perchlorate [24], 2,3-dichloro-5,6-dicyano-1,4-quinone [25] and $Ce(NH_4)_2(NO_3)_6$ [26,27]. Very recently, $Et_2Zn/Pd(OAc)_2$ [28] and $HClO_4$–SiO_2 [29] have been reported to effect Ferrier glycosylation. The metal nitrates investigated for this reaction include $Bi(NO_3)_3{\cdot}5H_2O$ [30] and $Ce(NH_4)_2(NO_3)_6$ [26,27]. The former acts as a Lewis acid catalyst and the latter mediate the transposition as a redox reagent. The acid catalysts, which are usually employed in sub-stiochiometric amounts, generally provide good anomeric selectivity of the product under ambient conditions. On the other hand, they often suffer from the disadvantage of lack of generality of protocol as the acidic medium restricts the use of acid-labile

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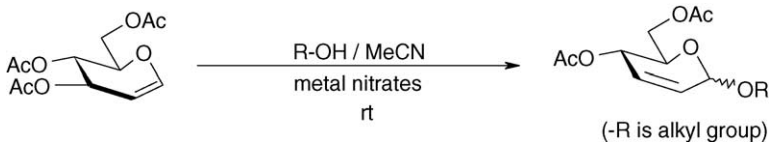


Scheme 1. Ferrier rearrangement of 3,4,6-tri-*O*-acetyl-D-glucal with alcohols mediated by metal nitrates.

glycal donors and acceptors. The oxidizing agents are often required in stiochiometric proportions and generally demand either longer reaction time or higher temperature and are known to offer low anomeric selectivity of the product.

Over the last couple of years, we have been engaged in understanding the chemistry revolving around the ionic liquids [31–36]. Besides the properties of the near ideal solvents, which have made them popular among the chemists, there is much more that these ideal solvents can offer. It is well known that at the molecular level, the ionic liquids can dramatically influence the course of reaction in certain cases by providing the ionic environment, thus stabilizing the ionic intermediates. In some of the examples reported recently, these solvents have displayed a dramatic influence on selectivity, rate and reactivity aspects of several reactions [37–41]. The interesting attributes that have resulted in widespread acceptability of the ionic liquids are diverse solvating ability, recyclability and environmentally benign nature. The fine-tuning or preselection of the structural architecture of ionic liquids (in terms of nature and size of organic cation, inorganic anion and the side chain tethered covalently to the organic cation) can result in the solvents possessing the broad spectrum/desired blend of properties that approach the functional 'ideal'. Thus, the conventional paradigm can be modified in the sense that instead of changing the solvent altogether, it can be designed to fit the process. This remarkable ensemble of properties has intensified the exploration of several reactions in these liquids. We also attempted to contemplate the influence of ionic liquids on the Ferrier rearrangement, so as to compare the reaction in the conventional solvents and ionic liquids.

2. Results and discussion

2.1. Screening of metal nitrates

We chose the metal nitrates of Fe, Cu, Cr, Ce, Bi, Co and Ni in their most stable oxidation states, as these catalysts are commercially available and are reported to be either Lewis acidic or are used for the redox reactions. In the preliminary experiment involving the reaction of 3,4,6-tri-*O*-acetyl-D-glucal with isobutyl alcohol using one equivalent of the metal nitrate (100 mol% catalyst) in acetonitrile, we observed that $Ce(NH_4)_2(NO_3)_6$, $Ni(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$ are inefficient for the rearrangement at room temperature. $Ce(NH_4)_2(NO_3)_6$ has been used at the reflux temperature of acetonitrile to efficiently mediate the glucosylation reaction [27]. $Cr(NO_3)_3{\cdot}9H_2O$ was relatively efficient for the reaction and good conversions were realised with $Bi(NO_3)_3{\cdot}5H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ as indicated by TLC. We had earlier investigated the regioselective biotransformations on 3,4,6-tri-*O*-acetyl-D-glucal, wherein the quantification of the product formed was achieved using high performance thin layer chromatography (HPTLC) [36]. The optimal conditions for the reaction were successfully established by HPTLC. Thus, for the similar system we employed the HPTLC as a tool (Scheme 1).

The reaction of 3,4,6-tri-*O*-acetyl-D-glucal with isobutyl alcohol in acetonitrile was chosen as a model. The reactions were carried out at room temperature with 100 mol% catalyst with respect to 3,4,6-tri-*O*-acetyl-D-glucal. The reactions were stopped after 10 min. The extracted organics were assayed on HPTLC. The conversions were monitored with respect to the formation of product, using 4,6-di-*O*-acetyl-D-glucal as an internal standard. The results revealed the excellent catalytic ability of $Bi(NO_3)_3{\cdot}5H_2O$ for the Ferrier glucosylation. As can be seen in Table 1, $Bi(NO_3)_3{\cdot}5H_2O$-mediated reaction indicated 88% conversion against 32%, and 12% conversions realised with $Fe(NO_3)_3{\cdot}9H_2O$ and $Cr(NO_3)_3{\cdot}9H_2O$, respectively. $Ce(NH_4)_2(NO_3)_6$, $Ni(NO_3)_2{\cdot}6H_2O$, $Co(NO_3)_2{\cdot}6H_2O$ and $Cu(NO_3)_2{\cdot}3H_2O$ were ineffective and they gave poor conversions even after the prolonged reaction times.

2.2. Optimisation of solvent and stiochiometry of $Bi(NO_3)_3{\cdot}5H_2O$

Bismuth has an electronic configuration of [Xe] $4f^{14}$, $5d^{10}$, $6s^2$, $6p^3$. Due to the weak shielding of the 4f electrons, i.e. lanthanide contraction, Bi(III) compounds exhibit Lewis acidity. Thus, in contrast to the conventional Lewis acids, Bi(III)

Table 1
Metal nitrates-mediated Ferrier *O*-glucosylation of isobutyl alcohol[a]

Metal nitrate	% Conversion[b]
$Ce(NH_4)_2(NO_3)_6$	2
$Ni(NO_3)_2{\cdot}6H_2O$	0
$Bi(NO_3)_3{\cdot}5H_2O$	88
$Co(NO_3)_2{\cdot}6H_2O$	3
$Cu(NO_3)_2{\cdot}3H_2O$	2
$Fe(NO_3)_3{\cdot}9H_2O$	32
$Cr(NO_3)_3{\cdot}9H_2O$	12

[a] 100 mol% catalyst used and reaction time was 10 min at room temperature.
[b] Monitored by HPTLC.

compounds are relatively non-corrosive, non-toxic, readily available at low cost and fairly insensitive to small amounts of water, and therefore require no special handling procedures. Above all, Bi(III) compounds demonstrate excellent catalytic competence in sub-stiochiometric quantities. Bismuth nitrate pentahydrate (BNP) possesses the optimum blend of all the above-said properties. The potential of BNP as a versatile and efficient catalyst for several reactions has already been explored [42–48].

Encouraged by the results obtained with BNP as a catalyst for Ferrier rearrangement, we planned a systematic study in which all the intricacies of the BNP-mediated reactions were probed. We attempted to investigate the influence of solvents on the rearrangement reaction. The reaction was conducted in acetonitrile, dichloromethane, 1,4-dioxane, THF, toluene, DMF and DMSO with 100 mol% BNP. Interestingly, the reaction occurred only in acetonitrile and THF and no reaction was observed in any other aforementioned solvents. To optimise solvent for the rearrangement, reactions were carried out in THF and acetonitrile with 100 mol% catalyst for 10 min. THF gave only 17% conversion against 88% conversions realised in acetonitrile. Probably, the solubility of BNP in acetonitrile was the contributing factor to the expeditious glucosylation. The earlier investigations on BNP promoted glucosylation in THF have indicated 68–75% yields of the glucoside with exclusive α-selectivity [30]. It is noteworthy that the authors have utilised excess of alcohol (1 mL for the reaction performed on 1.5 mmol scale), which being a good solvent, may be responsible for the enhanced rates of the reaction. This observation of solvent dependency in Bi(III)-mediated reactions is in line with what has been observed in earlier investigations [44]. Further, the solvent dependent nature of the reaction made us curious about carrying out the reaction in the newer reaction media, viz. ionic liquids (Scheme 2).

Excellent reactivity of alcohols was observed in glucosylation with 3,4,6-tri-*O*-acetyl-D-glucal using 100 mol% BNP. However, to justify the role of BNP as a catalyst for this reaction, we intended to determine the minimal amount of catalyst that gives fairly good reaction rate and conversion. So, the reactions were carried out at room temperature with the catalyst quantities such as 10–100 mol% with respect to 3,4,6-tri-*O*-acetyl-D-glucal. The results were encouraging as even 10 mol% BNP was capable of inducing 19% conversion after 10 min. This indicated the sub-stiochiometric nature of the catalyst. The detailed results of the investigation are presented in Fig. 1.

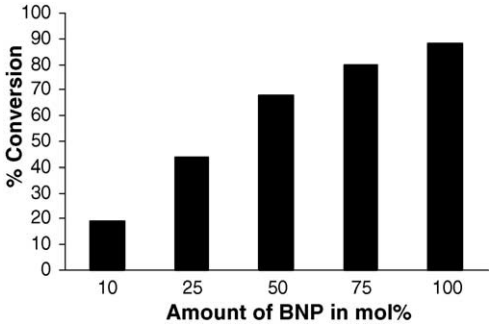


Fig. 1. The effect of amount of $Bi(NO_3)_3{\cdot}5H_2O$ on the % conversion in the Ferrier rearrangement of 3,4,6-tri-*O*-acetyl-D-glucal with isobutyl alcohol after 10 min.

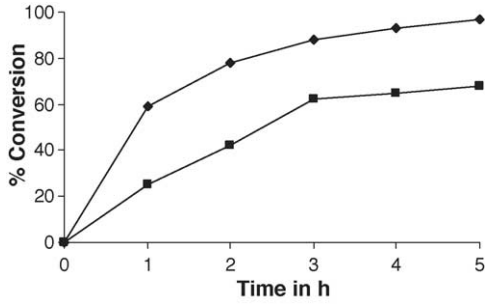
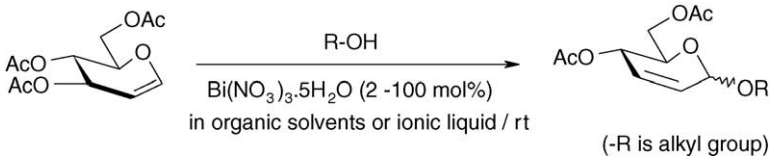


Fig. 2. The variation of % conversion with time in (♦) $Bi(NO_3)_3{\cdot}5H_2O$- and (■) $Fe(NO_3)_3{\cdot}9H_2O$-mediated Ferrier rearrangement of 3,4,6-tri-*O*-acetyl-D-glucal with isobutyl alcohol with 10 mol% catalyst.

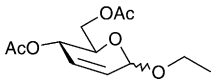
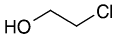
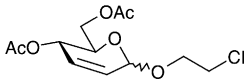
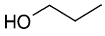
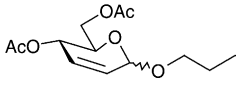
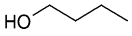
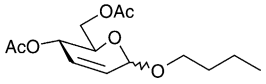
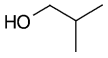
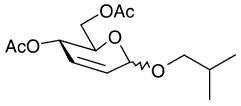
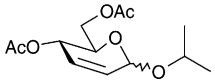
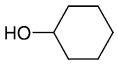
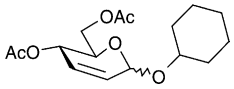
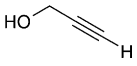
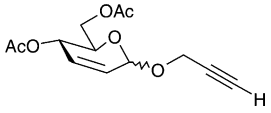
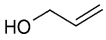
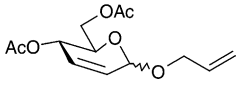
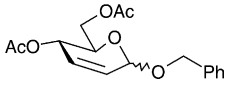
2.3. Optimisation of reaction time in $Bi(NO_3)_3{\cdot}5H_2O$- and $Fe(NO_3)_3{\cdot}9H_2O$-mediated reactions

From the viewpoint of the feasibility of the protocol, the yields of the product obtained are extremely important. It was necessary not only to make sure that 10 mol% BNP was capable of fetching good conversion, but also to ensure that the reaction time was sufficiently shorter or at least comparable to the existing protocols. To contemplate these points, the extent of conversion with 10 mol% catalyst was monitored at a fixed interval of time. The reactions were stopped at different time periods. As reflected from the results presented in Fig. 2, 10 mol% of the catalyst sufficed to give almost quantitative conversions (97%) after 5 h. No improvement in the conversion was realised with increase in time thereafter. However, further reduction in the catalyst quantity lengthened the reaction time enormously, so we compromised at 10 mol% catalyst for the reaction.



Scheme 2. $Bi(NO_3)_3{\cdot}5H_2O$-mediated Ferrier rearrangement of 3,4,6-tri-*O*-acetyl-D-glucal with alcohols.

Table 2
The scope of $Bi(NO_3)_3{\cdot}5H_2O$ mediated syntheses of 2,3-unsaturated glucopyranosides by Ferrier rearrangement of 3,4,6-tri-*O*-acetyl-D-glucal with alcohols in acetonitrile[a]

Entry	Acceptor	Ferrier product	Yield (%)[b]	α:β[c]
1			89	9:1
2			91	8:2
3			95	9:1
4			92	9:1
5			91	9:1
6			88	7:3
7			95	9:1
8			87	8:2
9			93	8:2
10			88	9:1

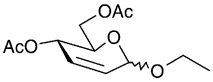
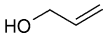
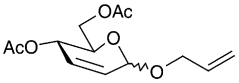
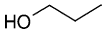
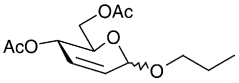
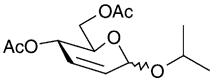
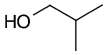
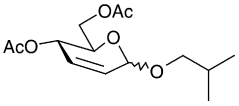
[a] 10 mol% BNP used and the reaction time was 5 h.
[b] Represents yields of the pure product isolated by column chromatography.
[c] Determined by ^{1}H NMR (300 MHz).

As already mentioned for the model reaction, amongst the metal nitrates investigated, only the nitrates of Bi, Fe and Cr attained positive results at room temperature. The reactions were performed with 10 mol% catalyst. $Cr(NO_3)_3{\cdot}9H_2O$ exhibited feeble catalytic ability, furnishing only 5% conversion after 5 h. However, the results with $Fe(NO_3)_3{\cdot}9H_2O$ were relatively impressive. These results prompted us to systematically investigate the catalytic ability of $Fe(NO_3)_3{\cdot}9H_2O$ for the Ferrier rearrangement. The reactions were carried out at room temperature with 10 mol% $Fe(NO_3)_3{\cdot}9H_2O$ for different time periods. The result of the study illustrated in Fig. 2 revealed that although $Fe(NO_3)_3{\cdot}9H_2O$ was reasonably effective in driving the reaction, the conversions were far from those realised with BNP. The maximum conversion realised with 10 mol% $Fe(NO_3)_3{\cdot}9H_2O$ was 68% after 5 h (Fig. 2). Higher amount of $Fe(NO_3)_3{\cdot}9H_2O$ was necessary for realising maximum conversions. Thus, 50 mol% $Fe(NO_3)_3{\cdot}9H_2O$ was required for maximum conversion (90%) after 5 h.

2.4. Generalisation of $Bi(NO_3)_3{\cdot}5H_2O$- and $Fe(NO_3)_3{\cdot}9H_2O$-mediated glucosylations

The BNP-mediated reactions with alcohols proceeded smoothly furnishing excellent yields of products with good α-selectivity at the anomeric carbon. The primary, secondary, benzylic, allylic and propargylic alcohols were put to test for the transformation and the results are summarised in Table 2. The reactions were also conducted with FNN as a catalyst and the results are summarised in Table 3. As expected, FNN-mediated reactions demanded more amount of catalyst. Thus, 50 mol% catalysts required 5 h to attain maximum conversions at room temperature. The reactions proceeded with relatively poor yields of products, but good anomeric selectivities were also realised in this case. The BNP-mediated glucosylation has been used for the synthesis of halogen functionalised novel *O*-glucoside (Table 2, entry 2), starting with the 2-chloroethanol as the glucal donor. The glucosides in all the

Table 3
The scope of $Fe(NO_3)_3{\cdot}9H_2O$ mediated syntheses of 2,3-unsaturated glucopyranosides by Ferrier rearrangement of 3,4,6-tri-*O*-acetyl-D-glucal with alcohols in acetonitrile[a]

Entry	Acceptor	Ferrier product	Yield (%)[b]	α:β[c]
1			77	9:1
2			80	8:2
3			79	9:1
4			76	8:2
5			81	8:2

[a] 50 mol% FNN used and the reaction time was 5 h.
[b] Represents yields of the pure product isolated by column chromatography.
[c] Determined by ^{1}H NMR (300 MHz).

cases were characterised by satisfactory elemental analysis, IR ^{1}H and ^{13}C NMR. The α:β ratios were determined by ^{1}H NMR.

2.5. $Bi(NO_3)_3{\cdot}5H_2O$-mediated glucosylation in ionic liquids

BNP as a catalyst displayed interesting solvent dependence for the Ferrier rearrangement. This feature made us inquisitive about the behavior of BNP in neoteric solvents, the ionic liquids. Several ionic liquids with hydrophobic and hydrophilic nature were prepared. The ionic liquids such as 1-butyl-3-methylimidazolium hexafluorophosphate, [bmim][PF_6]; 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF_4]; 1-butyl-3-methylimidazolium trifluoromethanesulphonate, [bmim][CF_3SO_3]; 1-butyl-3-methylimidazolium methanesulphonate, [bmim][CH_3SO_3] and 1-hexyl-3-methylimidazolium tetrafluoroborate, [hmim][BF_4] were investigated as the reaction media for the model reaction, with 10 mol% BNP. To ensure that the traces of protic and acidic impurities that might be present in the ionic liquids are not responsible for the reaction, all the ionic liquids were passed through basic alumina. Surprisingly, amongst the ionic liquids used, only the hydrophobic ionic liquids, viz. [bmim][PF_6] and [hmim][BF_4] showed competence as the reaction media and no reaction was observed in the other ionic liquids employed for the reaction. Only 7% conversion was observed in [hmim][BF_4] ionic liquid with 10 mol% BNP after 5 h. However, [bmim][PF_6] proved to be the most promising solvent for the reaction. It is worth noting that BNP has good solubility in acetonitrile, but it remains suspended in the ionic liquids. Therefore, the catalyst was finely ground when the ionic liquids were used as the reaction media.

Table 4
The variation of % conversion with time in the Ferrier rearrangement of 3,4,6-tri-*O*-acetyl-D-glucal with isobutyl alcohol in [bmim][PF_6] mediated by 10 mol% $Bi(NO_3)_3{\cdot}5H_2O$

Time (h)	% Conversion[a]
0.25	73
0.50	89
0.75	97
1.00	97

[a] Monitored by HPTLC.

We investigated the kinetics of reaction in [bmim][PF_6]. The HPTLC analysis revealed that the reactions were so expeditious in [bmim][PF_6] that as compared to 5 h reaction time in acetonitrile, merely 0.75 h was required for almost quantitative conversion (97%) in [bmim][PF_6]. The results are illustrated in Table 4. The observations clearly reflect the positive influence of the ionic liquid as the reaction media on the reaction. The excellent results obtained with [bmim][PF_6] as the solvent for the BNP-mediated glucosylation reaction made us curious to contemplate whether the ionic liquid was acting as a co-catalyst in the reaction. With this view, we performed a control experiment, wherein the reaction was carried out under similar conditions in the absence of BNP. No product formation was observed even after a prolonged reaction time of 12 h, indicating that the ionic liquid is not catalysing the reaction, but merely playing a role of a compatible solvent for the reaction. The higher extent of conversions with 10 mol% catalyst prompted us to further decrease the amount of catalyst employed in the reaction.

We conducted two different sets of experiments with 5 and 2 mol% of catalyst in [bmim][PF_6]. As seen in Fig. 3, amounts as low as 2 mol% of BNP in ionic liquid could drive the reaction to completion within 3.5 h. The 5 mol% of BNP fetched 95% conversion within 2 h. These results clearly indicated the critical role of ionic liquids making the protocol milder, cost effective, benign and efficient for the syntheses of 2,3-unsaturated *O*-glucosides. Further, the protocol was extended to several acceptors, and as can be seen from the results in Table 5, lower amount of catalyst was

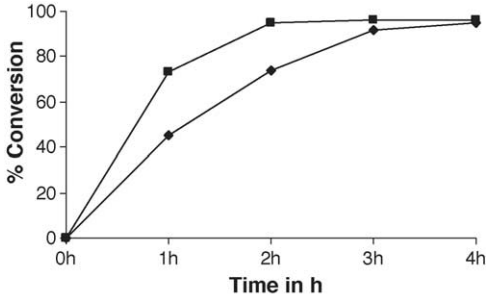
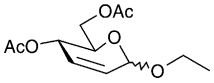
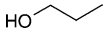
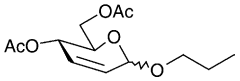
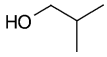
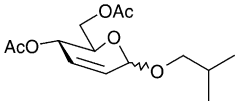
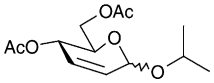
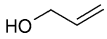
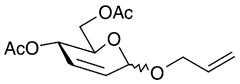


Fig. 3. The variation of % conversion with time in $Bi(NO_3)_3{\cdot}5H_2O$-mediated Ferrier rearrangement of 3,4,6-tri-*O*-acetyl-D-glucal with isobutyl alcohol using 2 mol% (♦) and 5 mol% (■) catalyst in [bmim][PF_6].

Table 5
Synthesis of 2,3-unsaturated glucopyranosides by the Ferrier rearrangement of 3,4,6-tri-*O*-acetyl-D-glucal with alcohols in [bmim][PF_6] mediated by 2 mol% $Bi(NO_3)_3{\cdot}5H_2O$[a]

Entry	Acceptor	Ferrier product	Yield (%)[b]	α:β[c]
1			91	8:2
2			89	8:2
3			92	9:1
4			87	9:1
5			88	8:2

[a] The reaction time is 3.5 h at room temperature as indicated by TLC in all the entries.
[b] Represents yields of the product isolated by column chromatography.
[c] Determined by ^{1}H NMR (300 MHz).

effective for mediating the rearrangement. This is the first report on the influence of ionic liquid on the catalytic Ferrier *O*-glucosylations.

The hydrophobic ionic liquid, [bmim][PF_6], possessing the PF_6^- anions exhibited good competence as the solvent for the reaction. So, we tried the reaction in more hydrophobic [hmim][PF_6] ionic liquid with the longer hexyl chain substituent at the cation, to check whether the hydrophobicity of the medium influences the course of reaction. It was observed that with 10 mol% BNP, the conversions increased from 70% after 0.25 h to 90% after 0.50 h, which further increased to the maximum of 96% after 0.75 h. These results are comparable to those observed with the BNP/[bmim][PF_6] system. Thus, the results are comparable and it appears that further increase in the hydrophobicity of the medium, i.e. the ionic liquid does not alter any further the catalytic behavior of BNP.

Fortunately, being hydrophobic, [bmim][PF_6] not only facilitated easy recovery of the products from the reaction medium by simple extraction with ether, but could be easily recycled without much pre-treatment before reuse. Thus, acetic acid formed as a byproduct during the reaction was easily neutralised by washing with aqueous sodium bicarbonate. Besides, no superfluous drying procedures were required for the reuse of the ionic liquid. Several experiments to adjudge the recyclability of the medium were carried out. It was found that [bmim][PF_6] could be effectively recycled for five runs without any influence on the efficacy of the reaction in terms of yield and selectivity of the product.

3. Experimental

3.1. Materials

3,4,6-Tri-*O*-acetyl-D-glucal was prepared by the method described earlier [49]. The ionic liquids [bmim][PF_6] [50], [bmim][BF_4] [51], [bmim][OTf] [52] and [hmim][BF_4] [52,53] were prepared by the methods reported earlier. [bmim][OMs] was prepared by the method used for the preparation of [bmim][OTf]. The purity of the ionic liquids was confirmed by satisfactory ^{1}H and ^{31}P NMR, wherever necessary.

3.2. High performance thin layer chromatography

3.2.1. Preparation of the internal standard, viz. 4,6-di-O-acetyl-D-glucal

The internal standard method was employed for the determination of isobutyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside. 4,6-Di-*O*-acetyl-D-glucal was an appropriate standard, because being a structural homologue of 3,4,6-tri-*O*-acetyl-D-glucal, it produces the same color upon derivatisation (λ_{max} 550 nm). Besides, the R_f values of 4,6-di-*O*-acetyl-D-glucal, 3,4,6-tri-*O*-acetyl-D-glucal and isobutyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside are distinguishingly different, viz. 0.22, 0.54 and 0.72, respectively. Thus, all the spots were well resolved on the TLC plate. The preparation of 4,6-di-*O*-acetyl-D-glucal was achieved by the enzymatic method developed by us earlier [36]. The product was characterised by ^{1}H and ^{13}C NMR, which were satisfactory when compared with the literature data [54]. All the solutions were 4.35×10^{-3} M with respect to 4,6-di-*O*-acetyl-D-glucal (each contained 0.0100 g of 4,6-di-*O*-acetyl-D-glucal in 10 mL solution), and the area ratio of isobutyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside to 4,6-di-*O*-acetyl-D-glucal was used for the product quantification.

3.2.2. Analytical and chromatographic conditions

The samples, including both the standards and the extracts of the reaction mixtures (after addition of standard and suitable dilution), were assayed employing the CAMAG Linomat IV sample applicator. Silica gel 60 F_{254} pre-coated plates were used in all the experiments. The 5 μL of the sample in CH_2Cl_2 was applied for each analysis. In all the cases, the plates were developed in a twin trough chamber using petroleum ether/ethyl acetate (7/3, v/v) as the mobile phase. The plates were derivatised by dipping in the methanolic solution, which contained 1% anisaldehyde (w/v), 1% concentration H_2SO_4 (w/v) and 1% glacial acetic acid (w/v). Subsequently, the plates were heated in an oven at 100 °C for 10 min. The plates were scanned on a CAMAG TLC Densitometric Scanner II, which was tuned at 550 nm and was equipped with the Cats 3.0 Version software to obtain the chromatograms. In all the cases, the absorbance and reflectance of the spots were the

parameters of the densitometric measurements. The calibration curve of isobutyl 4,6-di-*O*-acetyl-2,3-dideoxy-α-D-*erythro*-hex-2-enopyranoside was linear in the concentration range 0–26.27×10^{-3} M. The slope of this curve was used to compute the concentration of the product in the unknown solutions, as the same extent of dilution and concentration of the internal standard was maintained in all the solutions.

3.2.3. Experimental procedure

In all the experiments, to 3,4,6-tri-*O*-acetyl-D-glucal (0.0715 g, 0.2627 mmol) in 2 mL of the solvent (acetonitrile or ionic liquid) was added isobutyl alcohol (0.0583 g, 0.7881 mmol) and the catalyst ($Bi(NO_3)_3{\cdot}5H_2O$, $Fe(NO_3)_3{\cdot}9H_2O$, etc.) in the amount (2–100 mol% with respect to 3,4,6-tri-*O*-acetyl-D-glucal) specified in the text. The reaction mixture was stirred for the desired time period. The reaction was seized by the addition of aqueous saturated $NaHCO_3$ solution (10 mL) and extracted with Et_2O (5×20 mL). The resultant organics and washings were dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The contents were finally diluted to 10 mL with CH_2Cl_2 after addition of 4,6-di-*O*-acetyl-D-glucal (0.0100 g, 0.0435 mmol). Subsequently, the sample was assayed as per the general conditions specified above.

3.3. Experimental procedure for glucoside synthesis

To a mixture of 3,4,6-tri-*O*-acetyl-D-glucal (0.544 g, 2 mmol) and alcohol (6 mmol) in acetonitrile or [bmim][PF_6] (10 mL) was added $Bi(NO_3)_3{\cdot}5H_2O$ (0.2 mmol in acetonitrile or 0.04 mmol in [bmim][PF_6]) or $Fe(NO_3)_3{\cdot}9H_2O$ (1 mmol in acetonitrile) and stirred at room temperature for the appropriate time (as mentioned in the text, Tables 2, 3 and 5). The completion of reaction was indicated by TLC. In case of reactions in acetonitrile, the solvent was removed under reduced pressure; the reaction mixture was diluted with brine and subsequently, extracted with diethyl ether (3×15 mL). In case of reactions in [bmim][PF_6], the product was extracted directly in diethyl ether. The combined organic extracts were washed with aqueous saturated $NaHCO_3$ followed by water, dried over anhydrous Na_2SO_4 and concentrated under reduced pressure. The products were purified by silica gel column chromatography and characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy. The data for the products obtained from BNP-mediated reactions in acetonirile is presented below.

3.4. Characterisation of glucosides

All the glucosides were characterised by elemental analysis, IR, ^{1}H and ^{13}C NMR. The characterisation data of all the glucosides that appear in Table 2 is presented below.

3.4.1. Ethyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside

$[\alpha]_D^{31.7}$ + 113.1 (*c* 1.0, $CHCl_3$). Anal calcd. for $C_{12}H_{18}O_6$: C, 55.81; H, 6.98, found C, 55.84; H, 7.01. IR (CCl_4 film): ν_{max} 3054, 2977, 2895, 1747, 1445, 1371, 1233, 1185, 1108, 1048 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 1.25–1.30 (t, J = 7.2 Hz, 3H, –O–CH_2–CH_3), 2.11 (s, 3H, –CO–CH_3), 2.12 (s, 3H, –CO–CH_3), 3.58–3.63 (m, 1H, –O–*H*CH–CH_3), 3.83–3.88 (m, 1H, –O–*H*CH–CH_3), 4.12–4.31 (m, 3H, H-5, H_a-6, H_b-6), 5.07 (s, 1H, H-1), 5.33–5.36 (dd, J = 1.2, 9.6 Hz, 1H, H-4), 5.84–5.98 (m, 2H, H-2, H-3) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 15.50, 20.95, 21.15, 63.23, 64.47, 65.53, 67.05, 94.46, 128.21, 129.21, 170.46, 170.94 ppm.

3.4.2. Chloroethyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside

$[\alpha]_D^{31.7}$ + 98.84 (*c* 1.0, $CHCl_3$). Anal calcd. for $C_{12}H_{17}O_6Cl$: C, 49.23; H, 5.81, Cl, 12.14; found C, 49.20; H, 5.84, Cl; 12.12. IR (CCl_4 film): ν_{max} 3051, 2956, 2898, 1748, 1516, 1370, 1231, 1044 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.09 (s, 3H, –CO–CH_3), 2.10 (s, 3H, –CO–CH_3), 3.68–3.71 (t, J = 4.4 Hz, 2H, –O–CH_2–CH_2–Cl), 3.83–3.86 (m, 1H, –O–*H*CH–CH_2–Cl), 3.98–4.01 (m, 1H, –O–*H*CH–CH_2–Cl), 4.15–4.18 (m, 1H, H-5), 4.21–4.26 (m, 2H, H_a-6, H_b-6), 5.08 (s, 1H, H-1), 5.28–5.31(dd, J = 1.2, 9.5 Hz, 1H, H-4), 5.83–5.88 (m, 2H, H-2, H-3) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 20.75, 20.93, 42.97, 62.89, 65.10, 67.14, 68.88, 94.75, 127.19, 129.55, 170.24, 170.72 ppm.

3.4.3. n-Propyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside

$[\alpha]_D^{31.7}$ + 118.2 (*c* 1.0, $CHCl_3$). Anal calcd. for $C_{13}H_{20}O_6$: C, 57.35; H, 7.35; found C, 57.37; H, 7.38. IR (CCl_4 film): ν_{max} 3054, 2963, 2881, 1747, 1453, 1371, 1331, 1233, 1186, 1106, 1039 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.94–0.99 (t, J = 7.4 Hz, 3H, –O–CH_2–CH_2–CH_3), 1.62–1.69 (m, 2H, –O–CH_2–CH_2–CH_3), 2.10 (s, 3H, –CO–CH_3), 2.12 (s, 3H, –CO–CH_3), 3.45–3.54 (m, 1H, –O–*H*CH–CH_2–CH_3), 3.71–3.78 (m, 1H, –O–*H*CH–CH_2–CH_3), 4.05–4.17(m, 1H, H-5), 4.21–4.30 (m, 2H, H_a-6, H_b-6), 5.05 (s, 1H, H-1), 5.31–5.34 (dd, J = 1.3, 9.3 Hz, 1H, H-4), 5.84–5.97 (m, 2H, H-2, H-3) ppm. ^{13}C NMR (300 MHz, $CDCl_3$): δ 10.72, 20.81, 20.99, 22.99, 63.08, 65.35, 66.90, 70.62, 94.41, 128.00, 129.00, 170.32, 170.81 ppm.

3.4.4. n-Butyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside

$[\alpha]_D^{31.7}$ + 104.6 (*c* 2.0, $CHCl_3$). Anal calcd. for $C_{14}H_{22}O_6$: C, 58.74; H, 7.69; found C, 58.71; H, 7.66. IR (CCl_4 film): ν_{max} 3054, 2958, 2873, 1747, 1453, 1371, 1232, 1186, 1104, 1043 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.94–0.98 (t, J = 7.2 Hz, 3H, –O–CH_2–CH_2–CH_2–CH_3), 1.39–1.46 (m, 2H, –O–CH_2–CH_2–CH_2–CH_3), 1.58–1.65 (m, 2H, –O–CH_2–CH_2–CH_2–CH_3), 2.11 (s, 3H, –CO–CH_3),

2.13 (s, 3H, –CO–C*H*$_3$), 3.50–3.58 (m, 1H, –O–*H*CH–CH$_2$–CH$_2$–CH$_3$), 3.77–3.85 (m, 1H, –O–*H*CH–CH$_2$–CH$_2$–CH$_3$), 4.13–4.18 (m, 1H, H-5), 4.22–4.31 (m, 2H, H$_a$-6, H$_b$-6), 5.05 (s, 1H, H-1), 5.32–5.35 (dd, J = 1.2, 9.0 Hz, 1H, H-4), 5.84–5.98 (m, 2H, H-2, H-3) ppm. ^{13}C NMR (300 MHz, CDCl$_3$): δ 13.75, 19.32, 20.71, 20.89, 31.70, 63.01, 65.26, 66.81, 68.57, 94.32, 127.92, 128.89, 170.23, 170.72 ppm.

3.4.5. *Isobutyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside*

$[\alpha]_D^{31.7}$ + 113.5 (*c* 1.0, CHCl$_3$). Anal calcd. for C$_{14}$H$_{22}$O$_6$: C, 58.74; H, 7.69; found C, 58.76; H, 7.67. IR (CCl$_4$ film): ν_{max} 3054, 2958, 2904, 2129, 1747, 1463, 1371, 1333, 1234, 1186, 1104, 1045 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 0.92–0.93 (d, J = 2.4 Hz, 3H, –O–CH$_2$–CH(C*H*$_3$)CH$_3$), 0.94–0.95 (d, J = 2.4 Hz, 3H, –O–CH$_2$–CH(C*H*$_3$)CH$_3$), 1.86–1.93 (m, 1H, –O–CH$_2$–C*H*(CH$_3$)CH$_3$), 2.10 (s, 3H, –CO–C*H*$_3$), 2.11 (s, 3H, –CO–C*H*$_3$), 3.28–3.33 (m,1H, –O–*H*CH–CH(CH$_3$)CH$_3$), 3.52–3.57 (m,1H, –O–*H*CH–CH(CH$_3$) CH$_3$), 4.10–4.17(m, 1H, H-5), 4.21–4.26 (m, 2H, H$_a$-6, H$_b$-6), 5.02 (s, 1H, H-1), 5.30–5.33 (dd, J = 1.2, 9.6 Hz, 1H, H-4), 5.83–5.97 (m, 2H, H-2, H-3) ppm. ^{13}C NMR (300 MHz, CDCl$_3$): δ 19.23, 19.32, 20.65, 20.84, 28.33, 62.96, 65.24, 66.81, 75.54, 94.35, 127.87, 128.81, 170.17, 170.64 ppm.

3.4.6. *Isopropyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside*

$[\alpha]_D^{31.7}$ +115.3 (*c* 1.0, CHCl$_3$). Anal calcd. for C$_{13}$H$_{20}$O$_6$: C, 57.35; H, 7.35; found C, 57.32; H, 7.38. IR (CCl$_4$ film): ν_{max} 3054, 2973, 2901, 1747, 1450, 1371, 1317, 1233, 1184, 1127, 1102, 1036 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.19–1.21 (d, J = 6.0 Hz, 3H, –O–CH(C*H*$_3$)CH$_3$), 1.26–1.28 (d, J = 6.3 Hz, 3H, –O–CH(C*H*$_3$)CH$_3$), 2.09 (s, 3H, –CO–C*H*$_3$), 2.11 (s, 3H, –CO–C*H*$_3$), 3.98–4.16 (m,1H, –O–C*H*(CH$_3$)CH$_3$), 4.21–4.26 (m, 3H, H-5, H$_a$-6, H$_b$-6), 5.14 (s, 1H, H-1), 5.29–5.33 (dd, J = 1.3, 9.6 Hz, 1H, H-4), 5.80–5.90 (m, 2H, H-2, H-3) ppm. ^{13}C NMR (300 MHz, CDCl$_3$): δ 20.76, 20.97, 22.02, 23.53, 63.15, 65.43, 66.78, 70.76, 92.84, 128.49, 128.80, 170.32, 170.78 ppm.

3.4.7. *Cyclohexyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside*

$[\alpha]_D^{31.7}$ + 110.7 (*c* 1.0, CHCl$_3$). Anal calcd. for C$_{16}$H$_{24}$O$_6$: C, 61.54; H, 7.69; found: C, 61.56; H, 7.66. IR (CCl$_4$ film): ν_{max} 3054, 2934, 2858, 2659, 2133, 1747, 1450, 1370, 1233, 1187, 1101, 1036 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.17–1.43 (m, 5H, C$_h$ ring), 1.50–1.57 (m, 1H, C$_h$ ring), 1.67–1.80 (m, 2H, C$_h$ ring), 1.90–1.96 (m, 2H, C$_h$ ring), 2.08 (s, 3H, –CO–*CH*$_3$), 2.09 (s, 3H, –CO–*CH*$_3$), 3.61–3.68 (m, 1H, C$_h$ ring), 4.16–4.24 (m, 3H, H-5, H$_a$-6, H$_b$-6), 5.17 (s, 1H, H-1), 5.28–5.30 (dd, J = 1.3, 9.2 Hz, 1H, H-4), 5.78–5.87 (m, 2H, H-2, H-3) ppm. ^{13}C NMR (300 MHz, CDCl$_3$): δ 20.70, 20.93, 24.12, 24.35, 25.51, 32.10, 33.73, 63.12, 65.40, 66.71, 76.69, 92.75, 128.50, 128.70, 170.30, 170.74 ppm.

3.4.8. *Prop-2-ynyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside*

$[\alpha]_D^{31.7}$ + 156.4 (*c* 1.0, CHCl$_3$). Anal calcd. for C$_{13}$H$_{16}$O$_6$: C, 58.21; H, 5.97; found C, 58.23; H, 5.94. IR (CCl$_4$ film): ν_{max} 3310, 3054, 2954, 2916, 2123, 1748, 1517, 1446, 1370, 1232, 1188, 1139, 1101, 1041 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.11 (s, 3H, –CO–C*H*$_3$), 2.13 (s, 3H, –CO–C*H*$_3$), 2.49 (bs, 1H, H-3′), 4.12–4.29 (m, 3H, H-5, H$_a$-6, H$_b$-6), 4.34–4.38 (m, 2H, H$_a$-1′, H$_b$-1′), 5.26–5.27 (d, J = 1.2 Hz, 1H, H-1), 5.35–5.38 (dd, J = 1.2, 9.3 Hz, 1H, H-4), 5.85–5.88 (dd, J = 1.2, 1H, 10.2 Hz, H-2), 5.93–5.97 (dd, J = 1.2, 10.2 Hz, 1H, H-3) ppm. ^{13}C NMR (300 MHz, CDCl$_3$): δ 20.76, 20.93, 55.05, 62.76, 65.13, 67.18, 74.78, 79.06, 92.76, 127.21, 129.75, 170.22, 170.69 ppm.

3.4.9. *Allyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside*

$[\alpha]_D^{31.7}$ + 118.9 (*c* 1.0, CHCl$_3$). Anal calcd. for C$_{13}$H$_{18}$O$_6$: C, 57.77; H, 6.66; found C, 57.74; H, 6.68. IR (CCl$_4$ film): ν_{max} 3053, 2898, 1748, 1370, 1232, 1187, 1100, 1041 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.09 (s, 3H, –CO–C*H*$_3$), 2.11 (s, 3H, –CO–C*H*$_3$), 4.05–4.30 (m, 5H, H-5, H$_a$-6, H$_b$-6, H$_a$-1′, H$_b$-1′), 5.08 (s, 1H, H-1), 5.19–5.23 (dq, J = 1.3, 10.3 Hz, 1H, H$_a$-3′), 5.31–5.34 (m, 2H, H-4, H$_b$-3′), 5.83–6.01 (m, 3H, H-2, H-3, H-2′) ppm. ^{13}C NMR (300 MHz, CDCl$_3$): δ 20.81, 20.98, 62.98, 65.30, 66.98, 69.31, 93.67, 117.56, 127.77, 129.28, 134.11, 170.32, 170.81 ppm.

3.4.10. *Benzyl 4,6-di-O-acetyl-2,3-dideoxy-α-D-erythro-hex-2-enopyranoside*

$[\alpha]_D^{31.7}$ + 56.34 (*c* 1.0, CHCl$_3$). Anal calcd. for C$_{17}$H$_{20}$O$_6$: C, 63.75; H, 6.25; found C, 63.77; H, 6.24. IR (CCl$_4$ film): ν_{max} 3032, 2899, 1748, 1499, 1453, 1370, 1232, 1187, 1101, 1039 cm^{-1}. ^{1}H NMR (300 MHz, CDCl$_3$): δ 2.10 (s, 3H, –CO–C*H*$_3$), 2.12 (s, 3H, –CO–C*H*$_3$), 4.11–4.17 (m, 2H, H-5, H$_a$-6), 4.23–4.27 (dd, J = 5.4, 11.8 Hz, 1H, H$_b$-6), 4.59–4.62 (d, J = 12.0 Hz, 1H, –O–*H*CH–Ph), 4.79–4.82 (d, J = 12.0 Hz, 1H, –O–*H*CH–Ph), 5.12–5.13 (d, J = 1.1 Hz 1H, H-1), 5.32–5.35 (dd, J = 1.2, 9.4 Hz, 1H, H-4), 5.83–5.91 (m, 2H, H-2, H-3), 7.28–7.36 (m, 5H, aromatic) ppm. ^{13}C NMR (300 MHz, CDCl$_3$): δ 20.78, 20.93, 62.92, 65.29, 67.06, 70.28, 93.63, 127.73, 127.86, 128.02, 128.46, 129.28, 137.55, 170.29, 170.81 ppm.

4. Conclusion

In conclusion, Bi(NO$_3$)$_3$·5H$_2$O and Fe(NO$_3$)$_3$·9H$_2$O proved to be mild, non-corrosive and moisture-stable catalysts for the Ferrier rearrangement of 3,4,6-tri-*O*-acetyl-D-glucal in the presence of alcohols to yield synthetically important 2,3-unsaturated *O*-glucosides. The Bi(NO$_3$)$_3$·5H$_2$O-mediated glucosylation showed substantial

solvent dependency. $Bi(NO_3)_3{\cdot}5H_2O$ was superior to $Fe(NO_3)_3{\cdot}9H_2O$ in terms of yields, although good anomeric selectivities were attained with both catalysts. The catalytic efficiency of $Bi(NO_3)_3{\cdot}5H_2O$ was substantially enhanced in [bmim][PF_6] ionic liquid, reducing both the reaction time as well as the catalyst concentration. Thus, the present method serves as an improvement over certain protocols in terms of the ambient quality, eco-friendly nature and catalyst economy.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at 10.1016/j.molcata.2005.02.017.

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