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L-Proline·H₂SO₄: a sustainable ionic liquid as a catalyst for the tetrahydropyranylation of alcohols in water

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A highly environmentally adaptable and green method is developed for the tetrahydropyranylation of alcohols in water, catalyzed by an ionic liquid, L-proline·H₂SO₄, derived from nature's chiral pool. The tetrahydropyranylation of primary, secondary, and tertiary alcohols was accomplished within an hour at room temperature. The catalyst was equally efficient for the deprotection of tetrahydropyranyl ethers in the presence of methanol to give the corresponding alcohols in quantitative yields. The method invites further attention due to the reusability of the L-proline·H₂SO₄ ionic liquid in water (as the reaction medium); it could be reused up to six times without any processing after each batch. The efficacy of the method was also established by carrying out the reaction at the multigram level, achieving excellent transformation without any loss of catalytic activity. Significantly low process mass intensity (2.99) and E-factor (1.97) in the synthesis of tetrahydropyranyl ether demonstrate the remarkable green compliance of the protocol.

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Although ionic liquids are being used as non-hazardous solvents and catalysts for organic synthesis and separation processes,¹ many common features of ionic liquids need critical analysis. Firstly, the ready availability of starting materials for ILs and their environmental compatibility remain as the primary requirements for the efficient use of ILs. An efficient ionic liquid synthesized from costly and bioincompatible starting materials through a series of steps involving hazardous processes including organic solvents belies their claim as a sustainable alternative to organic solvents. Secondly, to make the process sustainable, the ILs must be infinitely recyclable without any processing. However, the repeated use of ILs requires the separation of organic impurities after conducting the reactions. Generally, this is done by adding water to the IL-containing reaction mixture and extracting the reaction mixture with organic solvents. Finally, the IL is recovered by removing water at elevated temperature and reduced pressure. It may be noted that extraction with water is not a sustainable, energy-efficient measure because its removal from ILs requires distillation under high temperature and reduced pressure conditions. The use of high temperature and reduced pressure will invite green motion penalty points,² thereby making the process unsustainable. Nonetheless, washing with hazardous organic solvents increases the E-factor, thereby negating the benefits of using ILs as a reaction medium. Therefore, the choice of an ionic liquid as a catalyst or solvent should be based on (a) the

use of cheap, naturally and readily available, and biocompatible starting materials; (b) recyclability with minimal processing; (c) formation of biocompatible waste after use; and (d) the absence of bioaccumulation. Based on these assumptions, we recently developed an L-proline-based ionic liquid with a bisulfate counterion by stoichiometrically mixing L-proline with concentrated sulfuric acid. Considering that L-proline is naturally abundant and H₂SO₄ hardly poses any environmental risk upon dilution to pH 4.5 and above,³ we employed the L-proline·H₂SO₄ (prolinium bisulfate/PBS) ionic liquid as a catalyst for an acid-catalyzed Biginelli reaction of 4-hydroxycoumarin, isatin, and urea/thiourea.⁴ Given the ready availability of L-proline from nature's chiral pool and the ease of formation of IL with H₂SO₄, we planned to use PBS as an alternative to existing acid catalysts to develop new and sustainable reaction processes.

Many reagents and catalysts used in organic synthesis are not compatible with functionalities with ionizable and readily polarizable bonds. Protection deactivates such reactive functional groups, paving the way for the manipulation of another group present in the system. As protection and deprotection generally increase the number of steps, they are called necessary evils in organic synthesis, which practically do not conform to the green chemistry principles aimed at developing environmentally sustainable, atom-economic, energy-efficient, and safe methods. Therefore, the development of methodologies for the protection and deprotection of functional groups using recyclable catalysts and environmentally benign reusable solvents is of critical significance to overcome the challenges faced in the industries. Given the ease of manipulation of the hydroxy group

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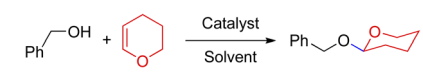


to obtain useful functionalities, a protected hydroxy group is often carried forward in the multi-step synthesis of complex molecules of industrial significance, such as active pharmaceutical ingredients,⁵ nucleotides,⁶ (glyco)peptides⁷ and oligosaccharides.⁸ Among the hydroxyl protecting groups, the tetrahydropyranyl (THP) moiety occupies the centre stage owing to the high stability of THP ethers in the presence of highly nucleophilic (*i.e.* organometallics), oxidizing (metal oxides, peroxides) or reducing (molecular hydrogen, hydrides) agents and under strongly basic reaction conditions.⁹ Additionally, for being 100% atom economic, the tetrahydropyranylation reaction of alcohol with 3,4-dihydro-2H-pyran (DHP) enjoys preference over other protective groups. THP protection is one of the simplest reactions in organic chemistry for installing one of the most robust protecting groups for alcohols. However, the development of a green solution for the THP protection of alcohols is paramount in making multistep synthesis sustainable. Most of the methods employ Brønsted acid catalysts for the protection of alcohols in volatile organic solvents, such as methylene chloride.¹⁰ Given the emphasis on green processes over the last two decades, recyclable heterogeneous catalysts, deep eutectic solvents (DES), and ionic liquids have been reported for the said transformation. While the acidic metal-containing IL-catalyzed protection of alcohol as a tetrahydropyranyl ether under solvent-free conditions has been reported, the green aspects, such as catalyst recovery and reuse, have not been evaluated.¹¹ Recently, Blangetti *et al.* reported a mild and sustainable method for the tetrahydropyranylation of alcohols using acidic, natural, deep eutectic solvents.¹² Despite being an excellent method, the method invites green motion penalty points due to the removal of water used in the extraction under reduced pressure from the aqueous layer to recover the ChCl/malonic acid eutectic mixture.

Given the environmentally docile characteristics of ILs, we explored the possibility of using L-proline · H₂SO₄ (PBS) both as an acidic catalyst and solvent for the tetrahydropyranylation of alcohols. Our study led to the development of an excellent, environmentally adaptable method for the protection of alcohols and phenols as their tetrahydropyranyl derivatives (Scheme 1).

To start with, a model reaction of benzyl alcohol (1 mmol) with 1.5 equivalents of 3,4-dihydropyran in neat PBS (1 mL) was stirred at room temperature (Table 1, entry 1). The reaction was completed within an hour. Since PBS is not soluble in organic solvents, the reaction was terminated by extracting the reaction mixture with cyclopentyl methyl ether (CPME) (3 × 3 mL). Since the solvent used in the extraction process contributes to a high E-factor, CPME was selected based on its stability in acidic environments, low volatility, high boiling point differential with DHP (106 °C *vs.* 86 °C), and the ease of recyclability of both CPME and DHP by fractional distillation. The crude product

Table 1 Screening of the reaction conditions^a

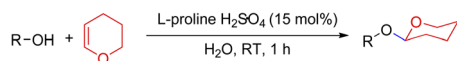
				
Entry	Cat. ^b (mol%)	Solvent ^c	t/h	%Yield ^d
1	—	PBS ^d	0.5	98
2	PBS (15)	CH ₂ Cl ₂	1	97
3	PBS (15)	Et ₂ O	1	98
4	PBS (15)	THF	1	94
5	PBS (15)	CPME	1	93
6	PBS (15)	1,4-Dioxane	1	95
7	PBS (15)	Water	1	98
8	PBS (20)	Water	1	98
9	PBS (10)	Water	1	82
10	PBS (10)	Water	2	89
11	H ₂ SO ₄ (15)	Water	1	37
12	L-Proline (15)	Water	1	Trace
13	L-Proline · HCl (15)	Water	1	48

^a The reaction was carried out at the 2 mmol level. ^b L-Proline · H₂SO₄ is abbreviated as PBS. ^c 1 mL of the solvent was used. ^d Yield of the pure product.

was isolated by distilling the solvent, along with excess DHP, and subsequently purified by passing the crude product through a short silica pad to achieve a near quantitative yield (98%). The residual organic solvent trapped in PBS was removed under reduced pressure and reused under similar conditions for two subsequent cycles. The colour of the IL developed a light-red color at the end of the 3rd cycle without losing any catalytic efficacy.

Interestingly, the residual DHP obtained after the fractional distillation of the combined CPME and DHP mixture collected over three cycles was found to be decomposed to a great extent, giving multiple spots on TLC. We suspected that the use of acidic PBS as the solvent might have induced the decomposition of DHP. Therefore, we checked the use of PBS as a catalyst in routinely used solvents, such as dichloromethane (1 mL), in the presence of 15 mol% of PBS. The reaction was completed within 1 h, affording a near quantitative yield. Since the use of dichloromethane has its share of disadvantages, especially its well-known toxicity towards the liver and nervous system, besides being environmentally persistent, we screen out a few more solvents, such as diethyl ether, THF, CPME, and 1,4-dioxane, to study their usefulness (entries 2–6). Interestingly, the reaction took longer in all the organic solvents, but complete conversion was achieved.

Since the reaction with organic solvents was terminated by adding water, the recovery of the catalyst, *i.e.* PBS, from water was not carried out, as the removal of water by distillation is a highly energy-consuming process. Therefore, we screened the model reaction in water itself with 15 mol% PBS so that the same water solution can be reused for multiple cycles of the same process (entry 7). We were pleasantly surprised to see that the tetrahydropyranylation of benzyl alcohol was completed in water within 1 h, giving an almost quantitative yield (98%). The screening of the catalyst loading (entries 7–10) confirmed that



Scheme 1 Tetrahydropyranylation of alcohols.



the reaction works at an optimum level with 15% PBS. The individual components of PBS were used separately to see if they could catalyze the reaction isolation (entries 11 and 12). While 15 mol% sulfuric acid catalyzed the reaction to give a 37% yield within 1 h, L-proline (15 mol%) hardly had any catalytic activity under our reaction conditions. We reasoned that two parameters might have affected the catalytic efficacy: (a) the hydrophobic elements of the pyrrolidine ring of L-proline that bring the reactant closure in the aqueous medium and (b) the bisulfate ion. The pK_a of L-proline might be insufficient to catalyze the reaction, leading to no conversion, while the absence of a hydrophobic environment in sulfuric acid might have resulted in the slow conversion. Another ionic liquid, *i.e.* prolinium hydrochloride, also catalyzed the reaction to give 48% yield in 1 h. L-Proline (15 mol%) hardly exhibited any catalytic activity under our reaction conditions. The observation suggests that while prolinium ion also catalyzes the reaction, the presence of the bisulfate counterion is critical to enhance the catalytic activity of the IL.

Having optimized the reaction conditions, a series of different alcohols was treated under similar reaction conditions to evaluate the substrate scope, compatibility of sensitive functional groups, and overall efficacy. Most of the benzylic alcohols (Chart 1, **1a–m**), including the ones with sensitive functional groups (such as OMe, CO₂Me, CN, and OCH₂O), gave complete conversion, affording excellent yields. Likewise, the tetrahydropyranylation of secondary alcohols (**2a–h**) was also equally effective. As for the aliphatic alcohols, the tetrahydropyranylation reaction worked extremely well for most of them with an alkyl chain length of up to 12 (Chart 2). Both secondary (**3i**) and tertiary alcohols (**4**) gave the corresponding THP ether in excellent yields. However, the protection of cholesterol with 15 mol% PBS in water was very slow, with hardly 10% conversion achieved in 1 h. Extending the reaction

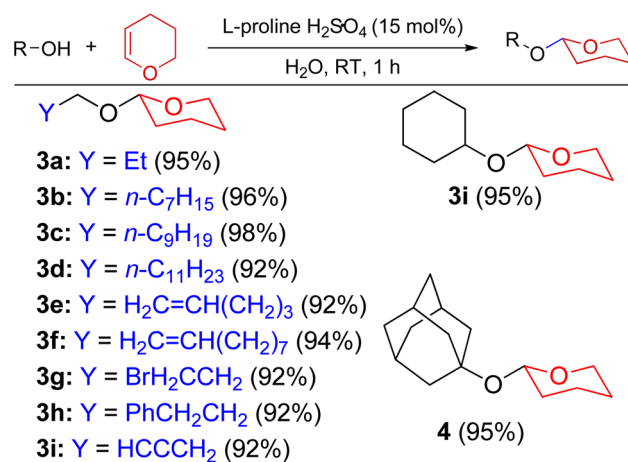


Chart 2 Tetrahydropyranylation of aliphatic alcohols.^{a,b} ^aAlcohol (1 mmol): DHP = 1:1.5. ^bYield of the pure product. ^cThe reaction was carried out using PBS as the solvent (1 mL).

time to 5 h did not have a proportionate improvement in the yield (38%). Varying the catalyst loading up to 30% and taking a 1:1 mixture of the IL and water were not effective as complete conversion was not achieved with up to 5 h of reaction (Table 1, SI). Ultimately, the complete conversion to tetrahydropyranyl ether of cholesterol (**5**) could be achieved with excellent yield upon stirring for 1 h at room temperature in PBS as the solvent.

The protocol was applied to phenols (Scheme 2) as well, and the observations are interesting. While phenol did not undergo tetrahydropyranylation under our catalytic conditions, 1-naphthol and 2-naphthol showed complete conversion into their corresponding tetrahydropyranyl ethers (**5a** and **5b**) in excellent yields. Conducting the reaction under neat conditions also did not help.

Reusability of the catalyst

The reusability of the catalyst is an important aspect of green and sustainable processes. Ordinarily, heterogeneous catalysis requires the processing of the catalyst through washing and drying. The reuse of the catalyst in the case of homogeneous catalysis is even more difficult, where the isolation of the catalyst from the solvent is highly energy demanding. Since we have used water as the solvent that dissolves the catalyst, no catalyst recovery using wasteful washing and energy-consuming drying was needed. Rather, we directly employed the aqueous layer containing PBS in the subsequent cycles. For that purpose, the model reaction of benzyl alcohol (2 mmol) with 1.5 mmol of 3,4-dihydropyran was chosen. The aqueous layer (1 mL) obtained

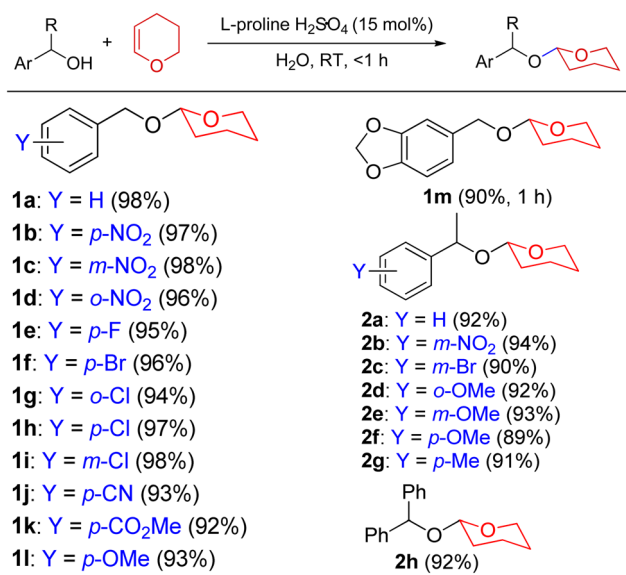
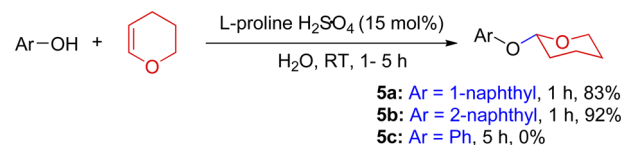


Chart 1 Tetrahydropyranylation of benzylic alcohols.^{a,b} ^aAlcohol (1 mmol): DHP = 1:1.5. ^bYield of the pure product.



Scheme 2 Tetrahydropyranylation of phenolic compounds.



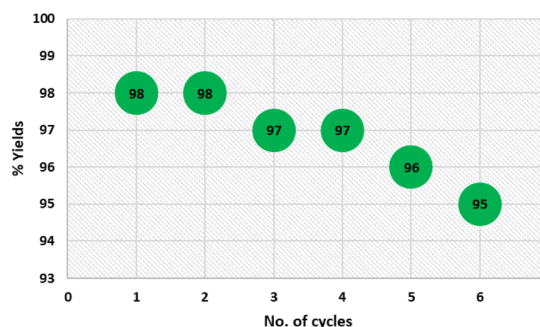


Fig. 1 Reusability of the catalyst.

after the completion of the 1st cycle was injected into the second batch, where a negligible loss in volume of the aqueous layer was observed. The same process was employed till the sixth cycle, where the volume of the aqueous layer containing PBS was found to be 0.8 mL. Given the proportionate loss of PBS in the aqueous solution, it was notable that conversion was completed within 1 h in each case. Moreover, no significant change in yield was observed up to the sixth cycle (Fig. 1).

Study of green matrices

The study of green chemistry metrics based on the twelve green chemistry principles is the hallmark of the evaluation of a sustainable chemical process.¹³ The metrics help in quantifying the efficiency of chemical processes and in improving the performance level to make the process environmentally sustainable. These quantifiable matrices may potentially facilitate a wider appreciation for green and sustainable technologies in large-scale production in industries. Therefore, in order to properly measure the environmental impact of our protocol, we conducted a model study to evaluate the greenness of our protocol by measuring the green matrices, such as atom economy, E-factor, reaction mass efficiency, and process mass

intensity,¹⁴ for the tetrahydropyranylation of benzyl alcohol. Keeping the industrial applications in mind, we studied these green matrices at the multigram level. While setting the model reaction on the gram scale, the use of CPME helped us recover both CPME and DHP. In the very first batch of the multigram reaction, the model reaction was conducted by proportionately increasing all the reactants and solvents, *viz.* 2.16 g (20 mmol) of benzyl alcohol with DHP (2.52 g, 30 mmol) with 15 mol% PBS (0.639 g, 3 mmol) in water (20 mL). Ironically, the reaction took almost 8 h to complete. Upon reducing the solvent volume, *i.e.*, water, to 10 mL, the reaction time decreased to 4 h for complete conversion. To our pleasant surprise, the reaction completed within 1 h upon reducing the volume of water further to 5 mL against 20 mmol of starting benzyl alcohol and gave a 99% yield. Any further volume reduction affected the recovery of excess DHP, which gave multiple spots at a high PBS concentration.

Therefore, the green matrices are studied for the protection of benzyl alcohol 2.16 g (20 mmol) with DHP (2.52 g, 30 mmol) in the presence of 15 mol% PBS (0.639 g, 3 mmol) in water (5 mL). Upon the completion of the reaction in the 1st cycle, the reaction mixture was extracted with 10 mL (8.63 g) of CPME, followed by washing of the PBS-H₂O solution with 10 mL (8.63 g) of CPME twice. Additionally, 5 mL (4.32 g) of CPME was used while washing the anhydrous sodium sulfate that was used to remove trace water in the organic layer. The recovered IL-H₂O was used for the next five successive cycles without any replenishment, and the CPME recovered through fractional distillation was repeatedly reemployed in the extraction process. In the recovery of CPME, a loss of approximately 2 mL (1.72 g) was observed in each batch. The sustainability of the protocol was measured up to six cycles by calculating the green matrices, as shown in Table 2. Interestingly, complete conversion was achieved in each cycle within an hour, and the overall yield remained almost similar irrespective of the cycles. Additionally, the reaction was completed under 1 h at room

Table 2 Assessment of green matrices^{a,b,c,d}

	Cycle					
	1	2	3	4	5	6
Green efficiency matrices						
%Yield	99	99	99	98	98	96
Atom economy	1	1	1	1	1	1
RME	0.812	0.813	0.812	0.809	0.809	0.805
E-factor with water	9.65	5.07	3.67	2.93	2.48	2.19
E-factor w/o water	8.33	4.5	3.23	2.6	2.22	1.97
PMI with water	10.65	6.17	4.68	3.99	3.49	3.2
PMI w/o water	9.34	5.51	4.24	3.61	3.23	2.99

^a The reaction was carried out with 20 mmol of benzyl alcohol. ^b Reaction mass efficiency (RME) = mass of the product/mass of the reactants. ^c E-factor = mass of (excess reagent + catalyst + solvent)/product mass. ^d Process mass intensity (PMI) = total mass of reactants, catalyst and solvents used in the process/product mass.

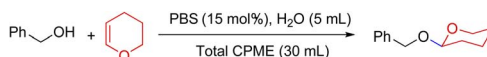


Table 3 Screening of the reaction conditions for tetrahydropyranylation^a

Entry	Cat. ^b (mol%)	Solvent ^c	t/h	%Yield ^d
1	PBS (15)	MeOH	2	93
2	PBS (20)	MeOH	2	94
3	PBS (10)	MeOH	2	93
4	PBS (5)	MeOH	8	95
5	PBS (10)	MeOH : H ₂ O (9 : 1)	4	94
6	PBS (10)	MeOH : H ₂ O (4 : 1)	5	93
7	PBS (10)	MeOH : H ₂ O (1 : 1)	6	90

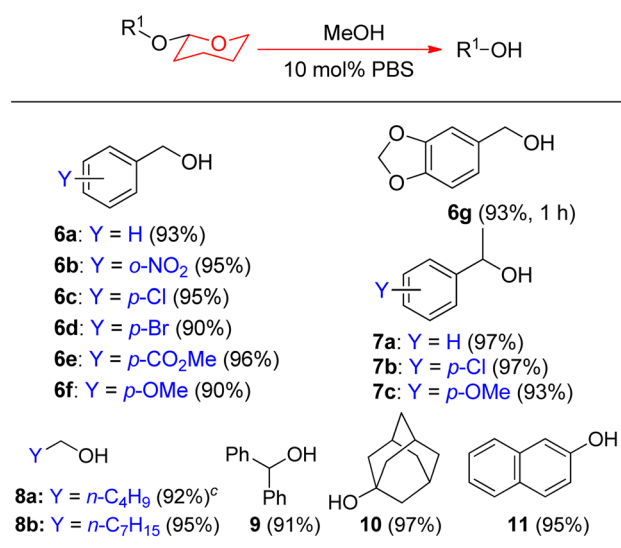
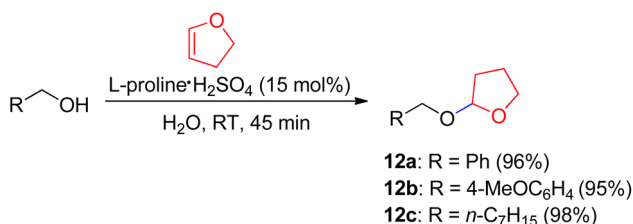
^a The reaction was carried out at the 2 mmol level. ^b L-Proline · H₂SO₄ is abbreviated as PBS. ^c 1 mL of the solvent was used. ^d Yield of the pure product.

temperature, resulting in no green motion penalty points given against high energy consumption due to the reaction being conducted for a long time under heating/high-pressure conditions.²

Since protection and deprotection are equally important components in organic synthesis, we explored the efficiency of PBS for the deprotection of THP ethers. Since the deprotection of THP ethers proceeds through transesterification with methanol in the presence of an acid catalyst, the deprotection of benzyl tetrahydropyranyl ether was initially tested in the presence of 15 mol% PBS in methanol (1 mL). The reaction took 2 h for complete conversion and gave a 93% purified yield (Table 3). The reaction took almost the same time in the presence of 20 mol% PBS as well. Interestingly, 10 mol% of PBS loading also took 2 h to generate benzyl alcohol in 93% yield. Upon further reduction of the catalyst loading to 5 mol%, the reaction took 8 h to complete. Keeping in mind the reusability of the catalyst, we checked the effect of water with methanol in the tetrahydropyranylation reaction. While 10% water in methanol (v/v) doubled the reaction time, complete conversion was achieved in 4 h. The time for complete conversion increased with the volume of water: 5 h in 20% water in methanol (v/v) and 6 h in 50% water in methanol (v/v).

Given the fact that the presence of water stymied the reaction, the reaction of tetrahydropyranyl ether with methanol in the presence of 10 mol% PBS was taken as the optimum condition to study the substrate scope of the reaction. While all the reactions achieved complete conversion within 2 h irrespective of the substitution in the phenyl ring, it is notable that acid-sensitive functional groups, such as CO₂Me, OMe, and methylenedioxy, were compatible in our reaction conditions (Chart 3). Likewise, secondary benzylic alcohol (**9**), tertiary alcohol (**10**), and β-naphthol (**11**) were achieved with their corresponding tetrahydropyranyl ethers with equal efficacy.

Given the fact that the protection of alcohols either as tetrahydropyranyl or tetrahydrofuranyl ethers is known to work under similar reaction conditions, a preliminary study was conducted for the reaction of alcohols with 2,3-dihydrofuran

**Chart 3** Deprotection of THP ethers.^a THP ether (1 mmol), 10 mol% PBS, MeOH (2 mL). ^bYield of the pure product.**Scheme 3** Synthesis of tetrahydrofuranyl ethers.

under our reaction conditions. We observed that the reactions took less than an hour to give their corresponding tetrahydrofuranyl ethers (Scheme 3).

In summary, a green process for the tetrahydropyranylation of alcohols catalyzed by an L-proline-derived acidic ionic liquid in water at room temperature is reported. This methodology is equally effective for the protection of primary, secondary and tertiary alcohols, and some phenolic compounds as their tetrahydropyranyl (THP) ethers. The nature-derived ionic liquid used as a catalyst, water used as a solvent, room temperature reaction conditions, short reaction time, and excellent compatibility of acid-labile functional groups (such as nitriles, esters, and ethers) make the method highly appealing. The catalyst could be reused without any processing, thereby negating the green motion penalty that accrues due to the use of high-temperature and pressure conditions. The high recyclability of the catalyst in H₂O with excellent yields over six cycles is worth noting. The reaction worked with equal efficiency on the multigram scale to give excellent yields. The study of the green matrices revealed an excellent process mass intensity (PMI 2.99) and E-factor (1.97), validating the environmental sustainability of our method for the tetrahydropyranylation of alcohols. The catalyst also affected the deprotection of tetrahydropyranyl ethers to give excellent yields of the corresponding alcohols



without needing any purification. Nonetheless, the protocol is equally effective for the tetrahydrofuranlation of alcohols under similar reaction conditions.

Conflicts of interest

There are no conflicts of interest to declare.

Data availability

The data supporting this article have been included as part of the supplementary information (SI). The supplementary information file contains the typical procedures for tetrahydropyranlation of alcohols and deprotection of THP ethers; calculations of green matrices such as E-factor, RME, and PMI; the analytical data; and ^1H NMR, ^{13}C NMR, and HRMS spectra. See DOI: <https://doi.org/10.1039/d5ra04126k>.

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