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ORIGINAL PAPER

# Preparation of Lewis acid ionic liquids for one-pot synthesis of benzofuranol from pyrocatechol and 3-chloro-2-methylpropene

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Several Lewis acid ionic liquids (LAILs) with different acidic scales were synthesised and used as catalysts for the synthesis of benzofuranol by condensation of pyrocatechol and 3-chloro-2-methylpropene in one pot. The catalytic activity of these ionic liquids was correlated with their Lewis acidity. Low to moderate conversion with excellent selectivity to benzofuranol was obtained in the presence of the appropriate LAILs. Compared to the two-step synthetic method currently used in industry, a higher yield plateau (81.1 %) of benzofuranol was achieved in the presence of [BMIm][$AlCl_4$] IL as catalyst at 418 K after 4 h. Furthermore, the catalyst is readily separated from the resultant products via decantation and could be reused after treatment in vacuum.

**Keywords:** benzofuranol, condensation, Lewis acid ionic liquid, acidity

## Introduction

Benzofuranol (2,2-dimethyl-2,3-dihydrobenzofuran-7-ol) and its derivatives, which are important intermediates of drugs and agrochemicals, have been extensively applied in pharmaceutical synthesis and pesticide production (Engler et al., 1993; Kossakowski et al., 2006, 2009). For example, 4,6-di-*tert*-butyl-2,2-dipentyl-2,3-dihydrobenzofuran-5-ol, an important derivative of benzofuranol, which performs a more effective inhibition of the peroxidation of low-density lipoprotein in vivo than natural antioxidants such as vitamin E, has been used as an antiatherogenic agent (Murakata & Kimura, 2010). Similarly, as the derivatives of benzofuranol, spirocyclicbenzofuranones are the main components of antimycotics such as griseofulvin and aromatase inhibitors due to their herbicidal and anti-inflammatory activities (Yang et al., 2006) and pterocarpans, which contain a benzofuran moiety, exhibit antiviral and antibacterial properties (Seo et al., 2011). Apart from its application in drugs, benzofuranol is also the direct source of some agrochemicals such as arbofuran, carbosulphan and furathiocab (Tamura et al., 2003). Hence benzofuranol plays an important role in the manufacture of drugs and agrochemicals. The current pathway for the production of benzofuranol in industry is shown in Fig. 1; this pathway entails two separate steps. In the first step, the etherification of pyrocatechol (*I*) and 3-chloro-3-methylpropene (*II*) is performed in the presence of alkali metal carbonate or hydroxide as catalysts to form 2-(2-methylallyloxy)phenol (*III*). Subsequently, benzofuranol (*V*) is prepared by the consecutive rearrangement and cyclisation of *III* catalysed by acidic

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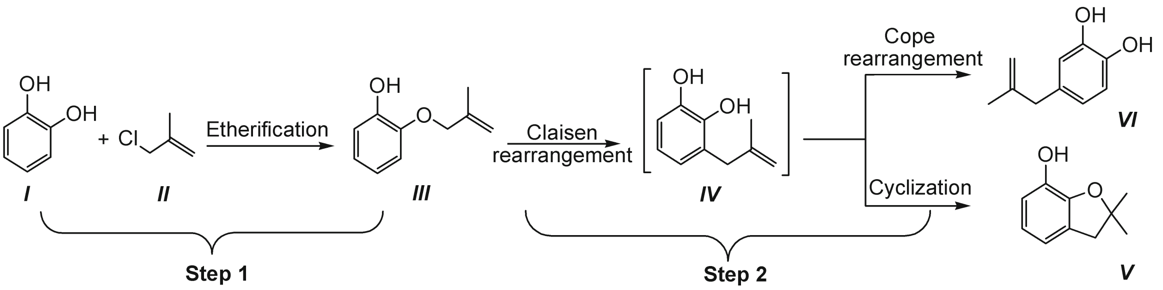

**Fig. 1.** Route for synthesis of benzofuranol ($V$) from pyrocatechol ($I$) and 3-chloro-2-methylpropene ($II$).

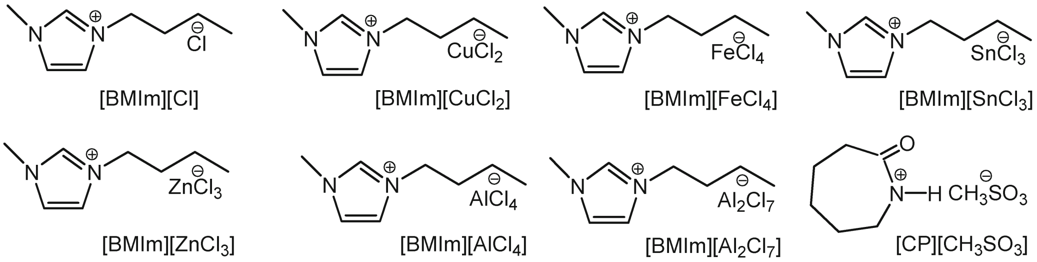

**Fig. 2.** Structures of ionic liquids synthesised.

substances such as $ZnCl_2$, $SiO_2$-$Al_2O_3$ or $\gamma$-$Al_2O_3$ in the second step. Clearly, this process possesses some drawbacks. For example, a large amount of salts is produced as a by-product in the firststep. The separation of these salts prolongs the production time and inevitably increases the overall cost. In addition, there are problems with corrosion and the tedious separation of the product-catalyst caused by using acidic substances as catalysts in the second step. Accordingly, the development of an efficient and eco-friendly method for the synthesis of $V$ is highly desirable.

Ionic liquids (ILs), owing to their negligible vapour pressure, high thermal stability, wide electrochemistry window and selective solubility, have gained recognition as environmentally benign media and catalysts and have been reported in a number of applications (Handy, 2011; Welton, 1999; Greaves & Drummond, 2008). Lewis acid ILs (LAILs), an interesting subset of ILs, have been successfully applied in several organic reactions (MacFarlance et al., 2006). For instance, in 2002, Harjani et al. (2002) reported that 1-butyl-3-methylimidazolium chloroaluminate LAIL functioned well as catalyst and solvent in the Knoevenagel condensation of benzaldehyde and substituted benzaldehydes with diethyl malonate to afford benzylidenemalonate, whereas it was not a suitable solvent for the linear dimerisation of 1-butene in the presence of a nickel complex as catalyst (Chauvin et al., 1997). Zhao et al. (2007) described 1-ethyl-3-methylimidazolium chlorochrominate IL as an efficient catalyst in converting sugars to 5-hydroxymethylfurfural. Recently, Yue et al. (2013) used [BMIm][$ZnCl_3$] LAIL as catalyst for the degradation of poly(ethylene terephthalate); the conversion achieved 100 % and the yield of the corresponding product was 83.8 %. Also, Srivastava et al. found that the bi-functional acidic IL [$MImC_3SO_3H$][$ZnCl_3$] is an effective catalyst for the Beckmann rearrangement of acetophenoneoxime (Kore & Srivastava, 2013). Clearly, in comparison with inorganic acid catalysts, the use of LAILs in organic synthesis not only enhances the yields, but reduces the pollution and also simplifies the product separation.

In effect, Lewis acids play an important role as catalysts in the second step of the process for producing benzofuranol (Fig. 1). However, to the best of our knowledge, to date there have been few attempts to use LAILs as catalysts for the synthesis of $V$. The present work sought an efficient and environmentally friendly synthesis of $V$ from $I$ and $II$ in one pot using LAILs as catalysts, with the highest plateau achieved in the presence of [BMIm][$AlCl_4$] IL.

## Experimental

Pyrocatechol (99 mass %) and 3-chloro-2-methylpropene (99 mass %) were acquired from Alfa Aesar (China), 1-methylimidazole (AR), 1-chlorobutane (AR), acetonitrile (AR), anhydrous aluminium chloride (AR) and other chemicals (AR) were purchased from Sinopharm Chemical Reagent (China). 1-Methylimidazole and 1-chlorobutane were double-distilled immediately prior to use. All other chemicals were used as received.

### *General preparation of Lewis acid ILs*

These LAILs were synthesised following the procedures described in the literature (Fig. 2) (Chauvin et al., 1997; Harjani et al., 2002; Zhao et al., 2007; Olivier-Bourbigou et al., 2010; Yue et al., 2013). The structures were confirmed by $^1$H and $^{13}$C NMR studies and thermal gravimetric analysis (TGA). The NMR spectroscopy was performed on a Brüker AV-400 Fourier transform NMR spectrometer using an inner capillary filled with $CDCl_3$. Chemical shifts were reported in parts per million (ppm, $\delta$). Thermal gravimetric analysis (TGA) was performed using asimultaneous thermal analysis-STA 409EP. The thermal decomposition temperature ($T_d$) was recorded with 10 % of mass loss of LAILs with a scan-rate of 10 K $min^{-1}$ under $N_2$ atmosphere.

### *Acidity measurement*

Measurement of the acidic scale of LAILs was conducted on a Jasco 610 instrument using KBr technique following the procedures previously reported in the literature (Yang & Kou, 2004; Chen et al., 2010). The specific band stretches of IR spectra recorded the relative acidities of these LAILs.

### *Synthesis ofbenzofuranol*

3.0 mmolof pyrocatechol, calculated amounts of 3-chloro-2-methylpropene and ILs were added to a 100 mL Parr reactor with 23 mL of toluene. The reaction mixture was heated to 418 K and held constant for the desired time. The resultant mixture formed two layers after cooling to ambient temperature, and the upper phase was separated and analysed using a capillary GC (SGE BPX5: 30 m × 0.25 mm × 0.25 µm) equipped with a flame ionisation detector and *o*-xylene as an internal standard. The toluene in the separated upper phase was removed by distillation and the yield of benzofuranol was obtained.

## Results and discussion

### *Characterisation of LAILs*

The LAILs were synthesised with yields of 93–98 %. Most of them were miscible with polarorganic solvents such as butane-1-ol, acetonitrile and alcohol, but insoluble or partly soluble in non-polar organic solvents such as benzene and diethyl ether. The single decomposition peak in the TGA profiles (see S3 in Supporting Information) implies that the synthesised LAILs were not mixed compounds, which accords with the NMR data (see S4–S5 in Supporting Information). The thermal stability of these LAILs was characterised by the thermal decomposition temperature ($T_d$), ranging from 238 ℃ to 410 ℃.

### *Acidity of LAILs*

The relative acidity of these LAILs was characterised by IR. Fig. 3A shows that two IR bands at 2250 $cm^{-1}$ and 2291 $cm^{-1}$, due to C≡N stretching vibrations, can be observed in pure acetonitrile (curve a). After different LAILs were added in acetonitrile, the IR bands of C≡N shifted to the higher wavenumbers due to the strong interaction between acetonitrile and LAILs. The stronger the acidity, the stronger the interaction and the larger blue shift induced. Accordingly, the relative acid strength of these LAILs has the following order, from the right: $[BMIm][Al_2Cl_7]$; $[BMIm][AlCl_4]$; $[BMIm][ZnCl_3]$; $[BMIm][SnCl_3]$; $[BMIm][FeCl_4]$; $[BMIm][CuCl_2]$ (Chen et al., 2010). Clearly, the anions play a crucial role in determining the acidity of these LAILs. The change in the anions leads to the great difference in acidity.

### *Catalytic test of LAILs*

Prior to investigating the performance of different LAILs in the catalysed condensation of *I* and *II*, $[BMIm][AlCl_4]$ IL was selected due to its immiscibility with toluene and higher apparent viscosity, as catalyst in the biphasic catalysis to optimise the reaction conditions including the molar ratio of reactants, reaction temperature, timeand mediumprofile.The results are listed in Table 1. It can be seen that the higher temperature promptedthe conversion of *I*, but too high a temperature decreased the selectivity of *V* (Table 1, entries 1–3 and 4). For instance, a 76.2 % conversion of *I* with 95.6 % selectivity to *V* could be obtained with a 5 % molar ratio of the catalyst to substrates at 418 K for 4 h (Table 1, entry 3) whereas, when the reaction temperature was increased to 433 K, a higher conversion of *I* (86.0 %) was obtained at the cost of the selectivity to *V* (Table1, entry 4). Furthermore, better results/yields were obtained by increasing the ratio of either *II* or $[BMIm][AlCl_4]$ IL to the totalsubstrates. For example, a 79.4 % conversion of *I* accompanied with 99.1 % selectivity to *V* (Table 1, entry 5) was obtained as a result of the enhancement of the ratio of *II*. In comparison with the results for entry 5, there is no significant effect to further enhance the ratio of *II* (Table 1, entry 6). Similarly, the highest yield of *V* (81.1 %) was achieved by increasing the catalysts-to-substrate molar ratio from 5 % to 8 % (Table 1, entries 5 and 7). Further increase in the amount of catalysts led to a reduction in the selectivity of *V*, although the conversion ratio of *I*was increased slightly (Table 1, entry 8). It is also worthnoting that no significant increase either in the conversion of *I* or selectivity to *V* occurred as a result of the reaction time being prolonged from 4 h to 6 h or even 8 h (Table 1, entries 7, 9 and 10). Hence, optimisation of the reaction conditions for the$[BMIm][AlCl_4]$ catalyst revealed that themaximum yield of *V* was obtained at 418 K for 4 h, with a molar ratio of $I : II :$ ILs = 50 : 60 : 8, and the isolated yield was 76.2 %.

**Table 1.** Synthesis of (*V*) from (*I*) and (*II*) catalysed by [BMIm][$AlCl_4$] under different conditions[a]

| Entry | *I* : *II* : IL (molar ratio) | Temperature/K | Time/h | Conversion/%[c] | Selectivity/%[c] | | |
|---|---|---|---|---|---|---|---|
| | | | | | *III* | *V* | Others[b] |
| 1 | 50 : 50 : 5 | 373 | 4 | 6.0 | 99.1 | 0.7 | 0.2 |
| 2 | 50 : 50 : 5 | 393 | 4 | 25.1 | 92.6 | 5.8 | 1.6 |
| 3 | 50 : 50 : 5 | 418 | 4 | 76.2 | 1.3 | 95.6 | 3.1 |
| 4 | 50 : 50 : 5 | 433 | 4 | 86.0 | 0 | 91.4 | 8.6 |
| 5 | 50 : 60 : 5 | 418 | 4 | 79.4 | 0.6 | 99.1 | 0.3 |
| 6 | 50 : 80 : 5 | 418 | 4 | 80.1 | 0.3 | 99.4 | 0.3 |
| 7 | 50 : 60 : 8 | 418 | 4 | 82.4 | 0 | 98.9 | 1.1 |
| 8 | 50 : 60 : 10 | 418 | 4 | 82.9 | 0 | 98.1 | 1.9 |
| 9 | 50 : 60 : 8 | 418 | 6 | 83.2 | 0 | 99.2 | 0.8 |
| 10 | 50 : 60 : 8 | 418 | 8 | 84.0 | 0 | 99.1 | 0.9 |

*a*) Reaction conditions: 3.0 mmol (0.33 g) of *I*, calculated amounts of *II* and catalyst in 23 mL toluene under different conditions; *b*) others include *IV*, *VI* and polymer of *III*; *c*) data from GC.

**Table 2.** Synthesis of (*V*) from (*I*) and (*II*) catalysed by different acidic catalysts[a]

| Entry | Catalyst | Conversion/%[d] | Selectivity/%[d] | | |
|---|---|---|---|---|---|
| | | | *III* | *V* | Others[c] |
| 1 | [BMIm][Cl] | 0 | 0 | 0 | 0 |
| 2 | [BMIm][$CuCl_2$] | 53.2 | 13.2 | 83.5 | 3.3 |
| 3 | [BMIm][$FeCl_4$] | 52.5 | 11.5 | 85.6 | 2.9 |
| 4 | [BMIm][$SnCl_3$] | 76.1 | 5.1 | 94.5 | 1.4 |
| 5 | [BMIm][$ZnCl_3$] | 77.6 | 3.8 | 95.1 | 1.1 |
| 6 | [MMIm][$AlCl_4$] | 81.9 | 0.3 | 98.8 | 0.9 |
| 7 | [BMIm][$Al2Cl_7$] | 82.7 | 0 | 96.1 | 3.9 |
| 8 | [CP][$CH_3SO_3$]b | 5.8 | 7.9 | 91.4 | 0.7 |
| 9 | $AlCl_3$ | 9.2 | 3.9 | 93.7 | 0.2 |

*a*) Reaction conditions: 3.0 mmol (0.33 g) of *I*, 3.6 mmol (0.33 g) of *II* and 0.24 mmol catalyst in 23 mL toluene at 418 K for 4 h; *b*) CP = caprolactam; *c*) others include *IV*, *VI* and polymer of *III*; *d*)data from GC.

Table 2 compares the performance of different acidic ILs as catalysts for the one-pot synthesis of *V* from *I* and *II* in toluene as the medium under the same conditions. It can be seen that these catalysts exhibited low to high catalytic activities in the condensation of *I* and *II* to produce *V* in onepot. Combined with the acidity order of these LAILs given above, it was evident that the relative acid strength affected the catalytic performance in the process of the synthesis of *V* (Fig. 3B). For example, in the presence of pure [BMIm][Cl] IL, the relative acid strength of which was at the weakest level out of the catalysts investigated, there was no significant conversion of *I* (Table 2, entry 1). The catalysts with Lewis acidity, either [BMIm][$CuCl_2$] or [BMIm][$FeCl_4$], exhibited improved activity, affording conversions of *I* of 53.2 % and 52.5 %, respectively (Table 2, entries 2 and 3). When the reaction for the synthesis of *V* was catalysed by [BMIm][$SnCl_3$] or [BMIm][$ZnCl_3$] IL, the conversion of *I* attained 76.1 % (Table 2, entry 4) and 77.6 % (Table 2, entry 5), respectively, and the selectivity to *V* was at an equal level because of their similar relative acid strengths. For comparison, the Brønsted acid IL [CP][$CH_3SO_3$] and $AlCl_3$ were also tested in this reaction. The conversion of *I* was lower than 10.0 % although the selectivity to *V* was maintained > 90.0 % (Table 2, entries 8 and 9). Furthermore, the catalytic performance of the homologues of [BMIm][$AlCl_4$] and [BMIm][$Al_2Cl_7$], which have higher relative acidity than the LAILs referred to above, were tested under the same conditions. A lower selectivity of *V* (96.1 %) was also obtained in the presence of [BMIm][$Al_2Cl_7$] IL as catalyst, although the conversion of *I* increased from 82.4 % to 82.7 % when the [BMIm][$AlCl_4$] was replaced by the stronger acidic [BMIm][$Al_2Cl_7$] IL (Table 1, entry 7 and Table 2, entry 8). Similarly, the [MMIm][$AlCl_4$] was chosen to test the influence of the LAIL's cation on the catalytic performance. Clearly, the influence is negligible provided that the anions are same. Accordingly, the [BMIm][$AlCl_4$] catalyst exhibited the best catalytic activity, giving a conversion of 82.4 % of *I* accompanied with a 98.9 % selectivity to *V* at 418 K for 4 h, out of the tested ILs. This is better than the highest yield obtained in the two-step synthesis of benzofuranol currently adopted in industry, as detailed previously (Fig. 1) (Wang et al., 2011). It is also worthnoting the negative correlation of the yield of intermediate *III* and the relative acid strength

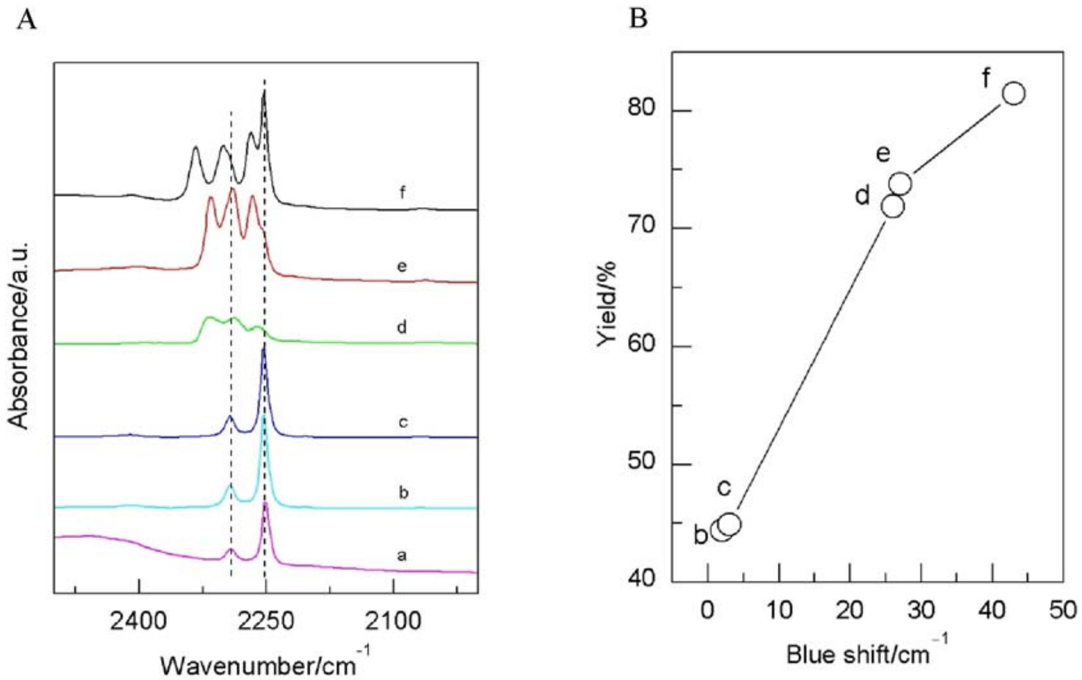

**Fig. 3.** FT-IR spectra of pure acetonitrile (a), [BMIm][CuCl$_2$] + acetonitrile (b), [BMIm][FeCl$_4$] + acetonitrile (c), [BMIm][SnCl$_3$] + acetonitrile (d), [BMIm][ZnCl$_3$] + acetonitrile (e), [BMIm][AlCl$_4$] + acetonitrile (f) (A). Relationship of blue shift wavenumber and yield of *V* (B).

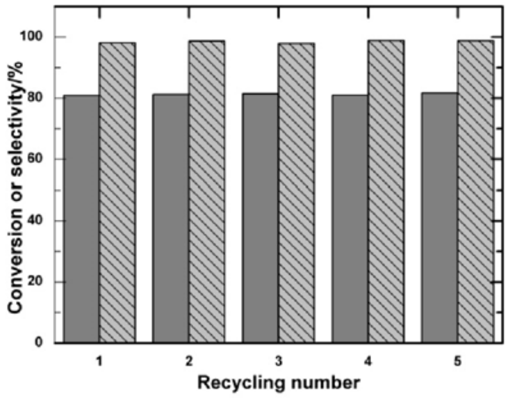

**Fig. 4.** Recycling of [BMIm][AlCl$_4$] IL in one-pot synthesis of *V* from *I* and *III*. Reaction conditions: 3.0 mmol (0.33 g) of *I*, 3.6 mmol (0.33 g) of *II* and 0.24 mmol of catalyst in 23 mL toluene at 418 K for 4 h. Data from GC. Legend: conversion (full) and selectivity (patterned).

of catalysts. This may be explained by the fact that the cyclisation is the rate-controlling step catalysed by Lewis acid catalysts in the synthesis of *V* (Mathewet al., 2005). The above results revealed that the one-pot synthesis of benzofuranol was largely dependent on the acidity of LAILs.

### *Reusability of [BMIm][AlCl$_4$] IL*

In order to evaluate the reusability, after the upper phase was separated from the reaction mixture, the bottom residues from the Parr reactor were collected and treated in vacuum (667–1340 Pa) for reuse.The reusability of the [BMIm][AlCl$_4$] catalyst is shown in Fig. 4. It can be seen that there was no obvious loss of catalytic activity in one-pot synthesis of benzofuranol from pyrocatechol and 3-chloro-2-methylpropene after five consecutive recycling procedures provided that the catalyst was treated simply in vacuum after each recycling procedure. The conversion of *I* remained $> 80.0$ % and the selectivity to *V*remained at $> 95.0$ %. The results indicate that LAILs having an aluminium chlorate anion are a class of robust and reusable catalysts for the direct synthesis of benzofuranol from *I* and *II*. In comparison with Lewis acid catalysts, these ILs are not only readily separated and can be reused directly without obvious decrease in catalytic activity, but they also cause little corrosion to the equipment and have a negligible effect on the environment.

## Conclusions

One-pot synthesis of *V* from *I* and *II* was achieved using LAILs as catalysts. In comparison with the two-step industrial process for the production of *V*, this method is more economical and environmentally friendly, and the yield of *V* is slightly higher than in the current industrial process. Furthermore, the catalytic performance of these acidic ILs is closely related to their acidity. The IL [BMIm][AlCl$_4$] catalyst exhibited a markedly higher activity for the *V* formation than the other acidic ILs tested; an 82.4 % conversion of *I* accompanied with selectivity to *V* as high as 98.9 % was obtained when the reaction was carried out in a sealed reactor at 418 K for 4 h. In addition, the use of LAILs as catalysts reduces environmental pollution and corrosion of equipment. Nonetheless, acidic ILs with the proper ratio of Lewis/Brønsted acidic sites may be the optimal candidates for catalysing the synthesis of *V* from *I* and *II* in one-pot. Further investigation of this issue is currently under way.

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## Supplementary data

Supplementary data associated with this article (Preparation of Lewis acid ionic liquids for one-pot synthesis of benzofuranol from pyrocatechol and 3-chloro-2-methylpropene) can be found in the online version of this paper (DOI: 10.1515/chempap-2015-0145).

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