

Acidic Brønsted Ionic Liquids Catalyzed the Preparation of 1-((Benzo[d]thiazol-2-ylamino)(aryl)-methyl)naphthalen-2-ol Derivatives 1-[(1,3-Benzothiazol-2-ylamino)(aryl)methyl]-2-naphthol

H.R. Shaterian* and M. Mohammadnia

Department of Chemistry, Faculty of Sciences, University of Sistan and Baluchestan, P.O. Box 98135-674, Zahedan, Iran.

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ABSTRACT

The acidic ionic liquids, triethylammonium hydrogen sulfate ($[\text{Et}_3\text{NH}][\text{HSO}_4]$), 2-pyrrolidonium hydrogen sulfate ($[\text{Hnhp}][\text{HSO}_4]$), 3-methyl-1-sulfonic acid imidazolium chloride ($[\text{Msim}]\text{Cl}$), and 1-methylimidazolium hydrogen sulfate ($[\text{Hmim}][\text{HSO}_4]$) catalyzed three-component condensation reaction of aromatic aldehydes, 2-aminobenzothiazole, and β -naphthol to afford corresponding 1-((benzo[d]thiazol-2-ylamino)(aryl)-methyl)naphthalen-2-ol derivatives. The inexpensive and non-toxic ionic liquids can be reused several times without noticeable loss of their activities.

KEYWORDS

Aldehyde, 2-aminobenzothiazole, β -naphthol, ionic liquids, catalyst, green chemistry.

1. Introduction

Ionic liquids (ILs), because of their low volatility, non-flammability, capability to dissolve various organic and inorganic compounds, and potentially recyclable properties, have attracted considerable attention as environmentally friendly reaction media in green organic synthesis.^{1,2}

The designs of multi-component reactions (MCRs) for the synthesis of diverse groups of compounds, especially the ones that are biologically active, have commanded great attention in green organic synthesis.^{3–5} As part of our continuing interest in the development of new synthetic methods in organic synthesis^{6,7} and multi-component reactions,⁸ in this paper we report applications of the acidic ionic liquids triethylammonium hydrogen sulfate ($[\text{Et}_3\text{NH}][\text{HSO}_4]$), 2-pyrrolidonium hydrogen sulfate ($[\text{Hnhp}][\text{HSO}_4]$), 3-methyl-1-sulfonic acid imidazolium chloride ($[\text{Msim}]\text{Cl}$), and 1-methylimidazolium hydrogen sulfate ($[\text{Hmim}][\text{HSO}_4]$) as catalysts (Fig. 1) in a three-component reaction for the synthesis of 1-((benzo[d]thiazol-2-ylamino)(aryl)-methyl)naphthalen-2-ol derivatives (Scheme 1).

Triethylammonium hydrogen sulfate⁹ has been used in the iodination of alcohols,¹⁰ 2-pyrrolidonium hydrogen sulfate¹¹ can catalyze the synthesis of benzoxanthene derivatives,¹¹ 3-methyl-1-sulfonic acid imidazolium chloride¹² has been used in the preparation of 1-amidoalkyl-2-naphthols,¹³ benzimidazoles,¹⁴ and 1-methylimidazolium hydrogen sulfate¹⁵ has been applied in the synthesis of 1,1-diacetates¹⁵ and 3,4-dihydropyrimidin-2-(1H)-ones.¹⁶

2. Results and Discussion

To study the effect of catalyst loading and temperature on the three component condensation reaction for the synthesis of 1-((benzo[d]thiazol-2-ylamino)(4-chloro-phenyl)methyl)naphthalen-2-ol, the reaction of 4-chlorobenzaldehyde, 2-aminobenzothiazole, and β -naphthol in the presence of the ionic liquid, triethylammonium hydrogen sulfate ($[\text{Et}_3\text{NH}][\text{HSO}_4]$), as catalyst

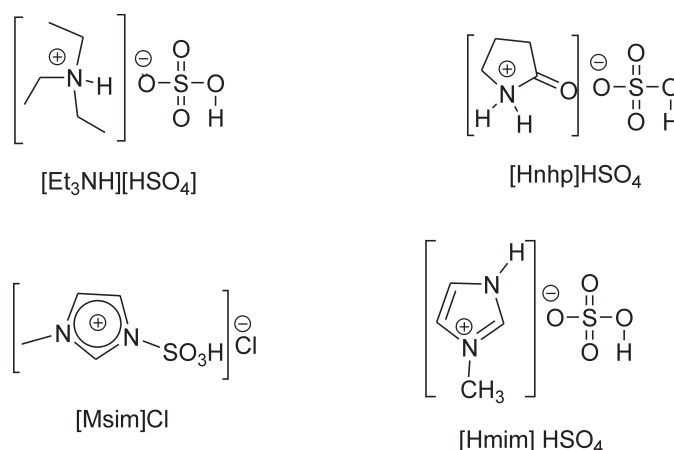
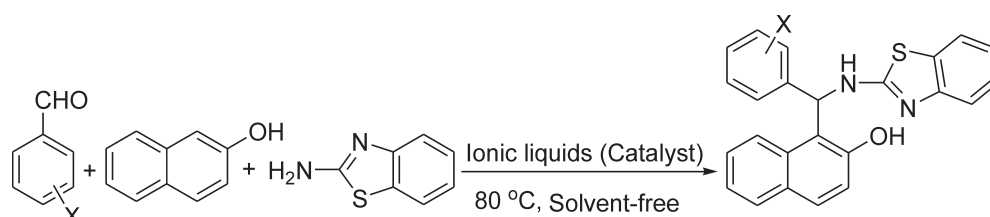


Figure 1 The structure of acidic Brønsted ionic liquids: $[\text{Et}_3\text{NH}][\text{HSO}_4]$, $[\text{Hnhp}][\text{HSO}_4]$, $[\text{Msim}]\text{Cl}$, and $[\text{Hmim}][\text{HSO}_4]$.

was selected as a model (Table 1). The reaction was carried out with different amounts of triethylammonium hydrogen sulfate as catalyst (0.05, 0.07, 0.1, 0.15, 0.2 mmol) and at various temperature (25, 50, 80 °C) (Table 1). As is shown in Table 1, 0.1 mmol of $[\text{Et}_3\text{NH}][\text{HSO}_4]$ as catalyst at 80 °C afforded the corresponding product in 6 min with 95% of yield. In continuation of our study, optimization conditions of ionic liquids, $[\text{Hnhp}][\text{HSO}_4]$, $[\text{Msim}]\text{Cl}$, and $[\text{Hmim}][\text{HSO}_4]$, as catalysts in the mentioned model were investigated. The best results were obtained using 0.06 mmol of $[\text{Hnhp}][\text{HSO}_4]$, 0.8 mmol of $[\text{Msim}]\text{Cl}$, and 0.08 mmol of $[\text{Hmim}][\text{HSO}_4]$ as catalysts at 80 °C (Table 1).

Next the three-component condensation reaction of aromatic aldehydes, 2-aminobenzothiazole, and β -naphthol, under optimized conditions, for preparation of 1-((benzo[d]thiazol-2-ylamino)(aryl)-methyl)naphthalen-2-ol derivatives was investigated (Table 2). A wide range of substituted and structurally diverse aldehydes was used to synthesize their

* To whom correspondence should be addressed. E-mail: hrshaterian@chem.usb.ac.ir



Ionic Liquids = $[\text{Et}_3\text{NH}][\text{HSO}_4]$, $[\text{Hnhp}]\text{HSO}_4$, $[\text{Msim}]\text{Cl}$, $[\text{Hmim}]\text{HSO}_4$

Scheme 1

The synthesis of 1-((benzo[d]thiazol-2-ylamino)(aryl)-methyl)naphthalen-2-ol derivatives.

Table 1 Optimization conditions for preparation of 1-((benzo[d]thiazol-2-ylamino)(4-chloro-phenyl)methyl)naphthalen-2-ol from 4-chloro-benzaldehyde, 2-aminobenzothiazole, and β -naphthol in the presence of different amount of ionic liquids, A: triethylammonium hydrogen sulfate, B: 2-pyrrolidonium hydrogen sulfate, C: 3-methyl-1-sulfonic acid imidazolium chloride, and D: 1-ethylimidazolium hydrogen sulfate, as catalysts under verities temperature

| Entry | Catalyst/mmol | | | | Temperature/ $^{\circ}\text{C}$ | Time/min | | | | Yield/% ^a | | | |
|-------|---------------|------|------|------|---------------------------------|----------|----|----|----|----------------------|-------|-------|-------|
| | A | B | C | D | | A | B | C | D | A | B | C | D |
| 1 | 0.2 | 0.2 | 0.21 | 0.24 | 25 | 30 | 30 | 29 | 30 | Trace | Trace | Trace | Trace |
| 2 | 0.07 | 0.16 | 0.1 | 0.1 | 50 | 16 | 16 | 16 | 16 | 40 | 40 | 41 | 44 |
| 3 | 0.15 | 0.19 | 0.15 | 0.14 | 50 | 13 | 12 | 13 | 13 | 50 | 53 | 52 | 50 |
| 4 | 0.05 | 0.03 | 0.04 | 0.04 | 80 | 9 | 7 | 8 | 7 | 80 | 80 | 80 | 82 |
| 5 | 0.1 | 0.06 | 0.08 | 0.08 | 80 | 6 | 6 | 6 | 6 | 95 | 96 | 95 | 95 |
| 6 | 0.15 | 0.11 | 0.14 | 0.13 | 80 | 7 | 6 | 7 | 6 | 92 | 93 | 93 | 93 |

^a Yields refer to pure isolated products.

corresponding products in high to excellent yields using the five Brønsted acidic ionic liquids as catalysts (Table 2).

Furthermore, the aliphatic aldehyde such as n-heptanal instead of benzaldehydes was examined in the reaction. All starting materials in the reaction were intact without formation of any desired product or side products after 10 h (Table 2, Entry 19). This observation is supported by reports on other catalysts in the literature.¹⁷

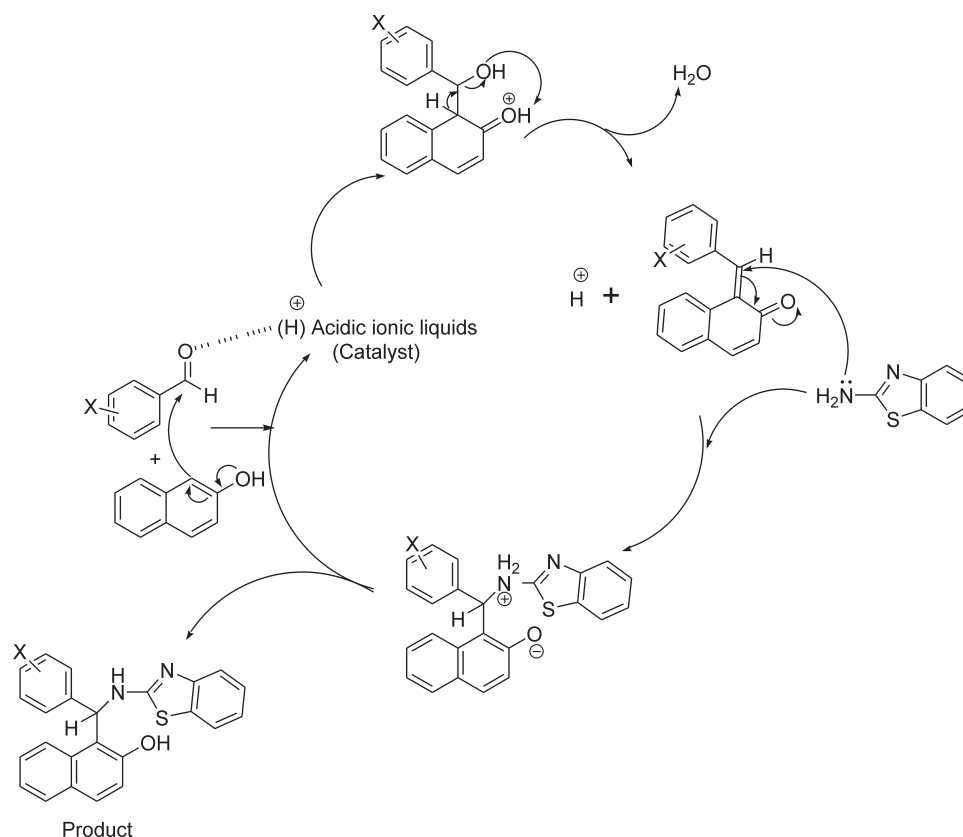
According to a literature survey,¹⁸ a suggested mechanism for the formation of the products is shown in Scheme 2.

The recycling of the ionic liquids under solvent-free conditions was also investigated using the model reaction of 4-chloro-benzaldehyde, 2-aminobenzothiazole, and β -naphthol in the presence of $[\text{Et}_3\text{NH}]\text{HSO}_4$ (0.1 mmol), $[\text{Hnhp}]\text{HSO}_4$ (0.06 mmol), $[\text{Msim}]\text{Cl}$ (0.08 mmol), and $[\text{Hmim}]\text{HSO}_4$ (0.08 mmol) (Table 2, Entry 2). After completion of the reaction, water was added and

Table 2 Three component synthesis of 1-((benzo[d]thiazol-2-ylamino)(aryl)-methyl)naphthalen-2-ol derivatives from the reaction of aromatic aldehydes (1 mmol), 2-aminobenzothiazole (1 mmol), and β -naphthol (1 mmol) in the presence of (A) $[\text{Et}_3\text{NH}]\text{HSO}_4$ (0.1 mmol), (B) $[\text{Hnhp}]\text{HSO}_4$ (0.06 mmol), (C) $[\text{Msim}]\text{Cl}$ (0.08 mmol) and (D) $[\text{Hmim}]\text{HSO}_4$ (0.08 mmol) as catalysts.

| Entry | Aldehydes | Time/min | | | | Yield/% ^a | | | | Melting point m.p/ $^{\circ}\text{C}$ (Lit. m.p/ $^{\circ}\text{C}$) ^[Ref] |
|-------|--|----------|---|---|---|----------------------|----|----|----|---|
| | | A | B | C | D | A | B | C | D | |
| 1 | C_6H_5 | 6 | 6 | 7 | 7 | 94 | 95 | 92 | 94 | 204 (202–203) ¹⁸ |
| 2 | 4- ClC_6H_4 | 6 | 6 | 6 | 6 | 95 | 96 | 95 | 95 | 209–211 (209–210) ¹⁸ |
| 3 | 4- $\text{CH}_3\text{OC}_6\text{H}_4$ | 7 | 7 | 8 | 7 | 92 | 93 | 92 | 91 | 176–177 (175–176) ¹⁹ |
| 4 | 3- $\text{NO}_2\text{C}_6\text{H}_4$ | 5 | 5 | 5 | 5 | 96 | 96 | 95 | 95 | 200 (198–199) ¹⁹ |
| 5 | 2- ClC_6H_4 | 6 | 6 | 7 | 8 | 91 | 91 | 91 | 91 | 188 (189–190) ¹⁸ |
| 6 | 4- FC_6H_4 | 8 | 6 | 7 | 7 | 92 | 92 | 92 | 92 | 189–190 (188–189) ¹⁸ |
| 7 | 4- MeC_6H_4 | 7 | 7 | 8 | 7 | 92 | 90 | 91 | 92 | 184 (182–183) ¹⁹ |
| 8 | 4- $\text{NO}_2\text{C}_6\text{H}_4$ | 5 | 5 | 5 | 6 | 96 | 96 | 95 | 96 | 190–191 (190–191) ¹⁸ |
| 9 | 3- BrC_6H_4 | 7 | 6 | 6 | 7 | 91 | 93 | 91 | 91 | 206 (205–206) ¹⁸ |
| 10 | 2- $\text{NO}_2\text{C}_6\text{H}_4$ | 7 | 6 | 6 | 5 | 92 | 93 | 92 | 93 | 216–217 (215–216) ¹⁸ |
| 11 | 2- HOC_6H_4 | 8 | 7 | 8 | 8 | 90 | 92 | 91 | 90 | 179 (177–178) ¹⁸ |
| 12 | 2,4- $\text{Cl}_2\text{C}_6\text{H}_3$ | 8 | 8 | 7 | 8 | 90 | 91 | 90 | 91 | 207–208 (206–207) ¹⁸ |
| 13 | 2,4- $(\text{CH}_3\text{O})_2\text{C}_6\text{H}_3$ | 9 | 8 | 8 | 9 | 89 | 90 | 89 | 89 | 160–162 (161–163) ²⁰ |
| 14 | 2- FC_6H_4 | 8 | 7 | 7 | 6 | 91 | 92 | 92 | 90 | 182 (181–183) ²⁰ |
| 15 | 3- ClC_6H_4 | 7 | 7 | 7 | 6 | 91 | 92 | 92 | 91 | 191–192 (192–194) ²⁰ |
| 16 | 2- $\text{CH}_3\text{OC}_6\text{H}_4$ | 8 | 8 | 8 | 7 | 90 | 91 | 91 | 91 | 166 (165–167) ²⁰ |
| 17 | 3- $\text{CH}_3\text{OC}_6\text{H}_4$ | 8 | 8 | 8 | 8 | 90 | 91 | 90 | 92 | 185–186 (184–186) ²⁰ |
| 18 | 4- CNC_6H_4 | 5 | 5 | 5 | 6 | 96 | 95 | 96 | 95 | 216 (214–215) ¹⁷ |
| 19 | Heptanal | 10 h | – | – | – | – | – | – | – | – |

^a Yield refers to the isolated pure products. The desired pure products were characterized by comparison of their physical data (melting points, IR, ^1H and ^{13}C -NMR) with those of known compounds.



Scheme 2

The suggested mechanism for the formation of 1-((benzo[d]thiazol-2-ylamino)(aryl)-methyl)naphthalen-2-ol derivatives.

the precipitated mixture was filtered off for separation of crude products. After washing the solid products with water completely, the water containing ionic liquid (IL is soluble in water) was evaporated under reduced pressure and ionic liquid was recovered and reused (Fig. 2). The recovered catalysts were reused for four runs without any significant loss of their activities. ¹HNMR spectroscopies showed that ionic liquids were not consumed or degraded.

In order to show the accessibility of the present work in comparison with four reported results in the literature, the results for the preparation of 1-((benzo[d]thiazol-2-ylamino)(aryl)-methyl)naphthalen-2-ol derivatives are summarized in Table 3. The results show that acidic ionic liquids such as [Et₃NH]HSO₄ (0.1 mmol), [Hnhp]HSO₄ (0.06 mmol), [Msim]Cl

(0.08 mmol), and [Hmim]HSO₄ (0.08 mmol) under solvent-free conditions relative to Wells-Dawson heteropolyacid (H₆P₂W₁₈O₆₂-24H₂O) (HPAs),¹⁷ *N*-methyl pyrrolidonium hydrogensulfate ([Hnmp]HSO₄),¹⁸ LiCl,¹⁹ sodium dodecyl sulfate (SDS)²⁰ are the most efficient catalysts with respect to the reaction time and the obtained yields.

In conclusion, we have shown that acidic ionic liquids, which can be prepared from commercially available and inexpensive starting materials, catalyzed efficiently synthesis of 1-((benzo[d]thiazol-2-ylamino)(aryl)-methyl)naphthalen-2-ol derivatives under solvent-free conditions. The simplicity of the procedure, eco-friendly, non-volatile, easy handling, safety and reusability of catalyst are the advantages of these methods. These methods not only afford the products in excellent yields but also avoid the

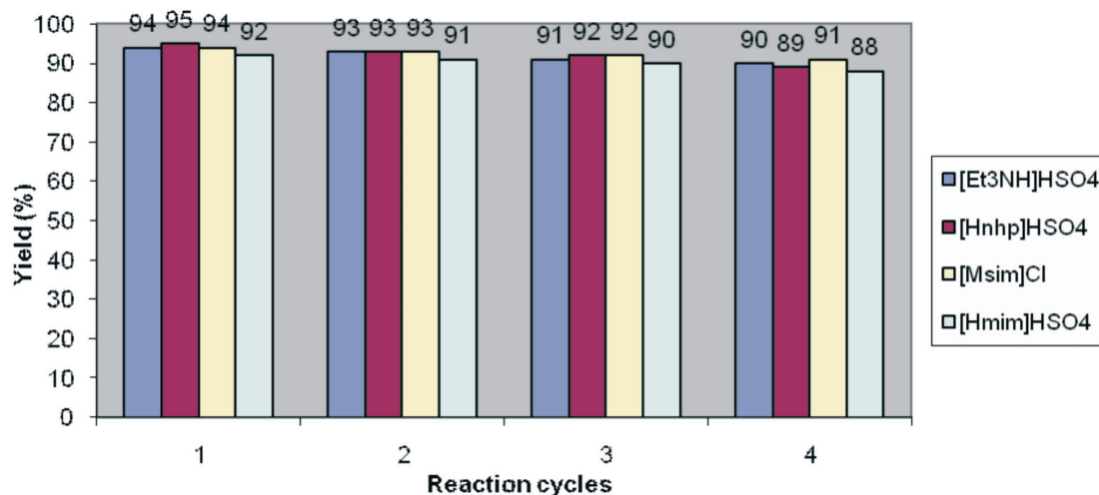


Figure 2 Recycling yields of the ionic liquids as catalyst.

Table 3 Comparison the results of [Et₃NH]HSO₄, [Hnhp]HSO₄, [Msim]Cl, and [Hmim]HSO₄ with [Hnmp]HSO₄, LiCl, sodium dodecyl sulfate (SDS), heteropolyacids (HPAs) in the synthesis of 1-((benzo[d]thiazol-2-ylamino)(aryl)-methyl)naphthalen-2-ol derivatives.

| Entry | Catalyst | Conditions | Time | Yield/% ^{Ref} |
|-------|---|---------------------------------|------------|------------------------|
| 1 | (HPAs) (0.09 g) | Ultrasound, water (3 mL), 45 °C | 80–120 min | 64–91 ¹⁷ |
| 2 | [Hnmp]HSO ₄ (0.1 mmol) | Solvent-free, 80 °C | 5–10 min | 92–96 ¹⁸ |
| 3 | LiCl (0.5 g, 71 mmol) | Water (5 ml), 90 °C | 5–7 h | 88–96 ¹⁹ |
| 4 | SDS (2 mmol) | Water (3 ml), 100 °C | 1–5 h | 71–93 ²⁰ |
| 6 | [Et ₃ NH]HSO ₄ (0.1 mmol) | Solvent-free, 80 °C | 5–9 min | 89–96 (Present work) |
| 7 | [Hnhp]HSO ₄ (0.06 mmol) | Solvent-free, 80 °C | 5–8 min | 90–96 (Present work) |
| 8 | [Msim]Cl (0.08 mmol) | Solvent-free, 80 °C | 5–8 min | 89–96 (Present work) |
| 9 | [Hmim]HSO ₄ (0.08 mmol) | Solvent-free, 80 °C | 5–9 min | 89–95 (Present work) |

problems associated with catalyst cost, and pollution. The mentioned ionic liquids show priority relative to other catalysts in the literature.

3. Experimental

3.1. General

All reagents were purchased from Merck and Aldrich and used without further purification. The acidic ionic liquids such as triethylammonium hydrogen sulfate,⁹ 2-pyrrolidonium hydrogen sulfate,¹¹ 3-methyl-1-sulfonic acid imidazolium chloride,¹² and 1-methylimidazolium hydrogen sulfate¹⁵ were prepared according to literature. All yields refer to isolated products after purification. The NMR spectra were recorded on a Bruker Avance DPX 300 MHz instrument. The spectra were measured in DMSO-*d*₆ relative to TMS (0.00 ppm). IR spectra were recorded on a JASCO FT-IR 460 plus spectrophotometer. Melting points were determined in open capillaries with a BUCHI 510 melting point apparatus. TLC was performed on silica-gel Poly Gram SIL G/UV 254 plates.

3.2 Synthesis of 1-((Benzo[d]thiazol-2-ylamino)(aryl)-methyl)naphthalen-2-ol derivatives under Solvent-free Conditions

The mixture of the aldehydes (10 mmol), 2-aminobenzothiazole (10 mmol), and β-naphthol (10 mmol) and ionic liquids containing [Et₃NH][HSO₄] (1 mmol), [Hnhp]HSO₄ (0.6 mmol), [Msim]Cl (0.8 mmol), or [Hmim]HSO₄ (0.8 mmol) as acidic catalysts was stirred at 80 °C for the specific time. After completion of the reaction, it was cooled to room temperature. Then, 5 mL of water was added to the mixture. The ionic liquid was dissolved in water, and filtered for separation of the crude product. The separated product was washed twice with water (2 × 5 mL). The crude products were purified by recrystallization from acetone. All of the desired product(s) were characterized by comparison of their physical data with those of known compounds. For recycling the catalysts, after washing mixture of the reaction with water completely, the water containing ionic liquid (IL is soluble in water) was evaporated under reduced pressure and ionic liquid was recovered and reused. The desired pure products were characterized by comparison of their physi-

cal data (melting points, IR, ¹H and ¹³C NMR spectra) with those of known compounds.^{17–20}

Acknowledgements

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