



Sharif University of Technology

Scientia Iranica

Transactions C: Chemistry and Chemical Engineering

www.sciencedirect.com

Sulfonic acid functionalized imidazolium salts/ FeCl_3 as novel and highly efficient catalytic systems for the synthesis of benzimidazoles at room temperature

A. Khazaei^{a,*}, M.A. Zolfigol^{a,*}, A.R. Moosavi-Zare^a, A. Zare^b, E. Ghaemi^a, V. Khakyzadeh^a, Zh. Asgari^a, A. Hasaninejad^c

^a Faculty of Chemistry, Bu-Ali Sina University, Hamedan, P.O. Box 6517838683, Islamic Republic of Iran

^b Chemistry Department, Payame Noor University, 19395-4697 Tehran, Islamic Republic of Iran

^c Department of Chemistry, Faculty of Sciences, Persian Gulf University, Bushehr, P.O. Box 75169, Islamic Republic of Iran

Received 18 April 2011; accepted 14 August 2011

KEYWORDS

Sulfonic acid functionalized imidazolium salt;
Ionic liquid;
 FeCl_3 ;
Benzimidazole;
Benzene-1, 2-diamine;
Aldehyde.

Abstract Ionic liquid 3-methyl-1-sulfonic acid imidazolium chloride/ FeCl_3 , as well as ionic liquid 1, 3-disulfonic acid imidazolium chloride/ FeCl_3 catalytic systems, efficiently catalyze the condensation of benzene-1, 2-diamine with aromatic aldehydes in the presence of atmospheric air as a green oxidant in ethyl acetate at room temperature to afford benzimidazole derivatives in high yields and in short reaction times. The reaction is also efficiently performed when carboxylic acids are used instead of aldehydes.

© 2012 Sharif University of Technology. Production and hosting by Elsevier B.V.

Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/4.0/).

1. Introduction

Benzo-fused heterocyclic systems like benzimidazole are well-known due to possessing a wide range of biological properties and clinical applications [1–3]. These heterocyclic ring systems are present in numerous antiparasitic, fungicidal, anthelmintic and anti-inflammatory drugs [4–7]. Antibacterial and antifungal activity was observed for benzimidazole derivatives [8]. 2-Aryl and 2-alkyl benzimidazoles exhibit activity against HIV [9]. Thus, the synthesis of these compounds has received considerable attention in diverse areas of chemistry. A

number of synthetic methods have been developed to uncover a variety of new reagents for the preparation of benzimidazoles [10–27]. The most commonly-used synthetic approaches typically entail the condensation of o-arylenediamines with carbonyl compounds, such as aldehydes, carboxylic acids and their derivatives [16–22]. In addition, there are several reports on benzimidazoles synthesis *via* the reductive cyclization of o-nitroanilines with aldehydes [23], cyclization of o-nitroaniline derivatives with aryl isothiocyanates [24,25], and Baker's yeast reduction of 2, 4-dinitroacyl anilines [26]. Recently, Salehi et al. reported that the reaction of benzene-1, 2-diamine with aldehydes in the presence of silica sulfuric acid produce 2-aryl-1-arylmethyl-1H-1, 3-benzimidazoles [27]. However, most of the reported methods have several drawbacks including low yield, long reaction time, the use of expensive reagents, harsh reaction conditions, tedious workup procedures, involving more than one step in their synthesis, and co-occurrence of several side reactions.

Ionic liquids (based imidazolium or other organic cations) have found wide usage in catalytic and non-catalytic reactions, besides the application of these compounds as green solvent [28–32]. Moreover, the synthesis of task-specific ionic liquids, which have a functional group in their framework, may expand the application of ionic liquids in organic chemistry [33,34]. Acidic ionic liquids have been also successfully used

* Corresponding authors.

E-mail addresses: Khazaei_1326@yahoo.com (A. Khazaei), zolfi@basu.ac.ir (M.A. Zolfigol).

1026-3098 © 2012 Sharif University of Technology. Production and hosting by Elsevier B.V. Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/4.0/).

Peer review under responsibility of Sharif University of Technology.

doi:10.1016/j.scient.2011.09.016



Production and hosting by Elsevier

ELSEVIER

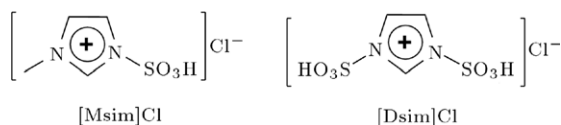
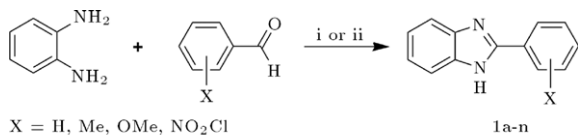
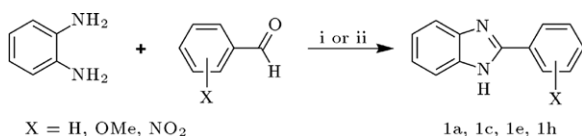


Figure 1: The structures of 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl} and 1,3-disulfonic acid imidazolium chloride {[Dsim]Cl}.



- i: [Msim]Cl (10 mol%)/FeCl₃ (10 mol%), EtOAc, r.t.
 ii: [Dsim]Cl (10 mol%)/FeCl₃ (10 mol%), EtOAc, r.t.

Figure 2: The synthesis of benzimidazoles from benzene-1, 2-diamine and aldehydes.



- i: [Msim]Cl (10 mol%)/FeCl₃ (10 mol%), EtOAc, 60 °C
 ii: [Dsim]Cl (10 mol%)/FeCl₃ (10 mol%), EtOAc, 60 °C

Figure 3: The synthesis of benzimidazoles from benzene-1, 2-diamine and carboxylic acids.

in many organic transformations [33–38]. More recently, the high importance of ionic liquids based imidazolium salts, with Brønsted acidic property, encouraged us to prepare ionic liquid 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl} [35–38] and 1,3-disulfonic acid imidazolium chloride {[Dsim]Cl} (Figure 1) [38].

Herein, we report the synthesis of benzimidazole derivatives from benzene-1, 2-diamine and aromatic aldehydes (or carboxylic acids) in the presence of catalytic amounts of functionalized sulfonic acid imidazolium salts {[Msim]Cl or [Dsim]Cl} and FeCl₃ as efficient and mild catalytic systems, beside air as a green oxidant in ethyl acetate (Figures 2 and 3). Interestingly, this method has none of the above-mentioned drawbacks for the preparation of benzimidazoles at all.

2. Results and discussion

In our previous work [35], we produced ionic liquid 3-methyl-1-sulfonic acid imidazolium chloride {[Msim]Cl} (Figure 4) and used it, beside NaNO₂, for the efficient nitration of phenols. The synthesis of bis(indolyl)methans [36] and N-Sulfonyl imines were also successfully catalyzed by [Msim]Cl [37]. Furthermore, more recently, we synthesized another sulfonic acid functionalized imidazolium salt, [Dsim]Cl, as an ionic liquid, *via* the reaction of imidazole with chlorosulfonic acid (Figure 5), and applied it as catalyst in the preparation of 1-amidoalkyl-2-naphthols [38]. In this presented work, we wish to use [Msim]Cl/FeCl₃ or [Dsim]Cl/FeCl₃ as mild catalytic systems in the presence of air for the preparation of benzimidazole derivatives. For this purpose, as a model, the condensation of benzene-1, 2-diamine (2 mmol) with benzaldehyde (2 mmol) was examined in the presence of different molar ratios of [Msim]Cl/FeCl₃ as well as [Dsim]Cl/FeCl₃ catalytic systems in different solvents and under solvent-free conditions at

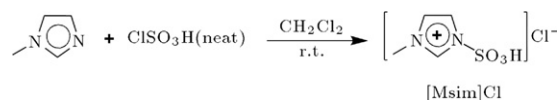


Figure 4: The preparation of [Msim]Cl.

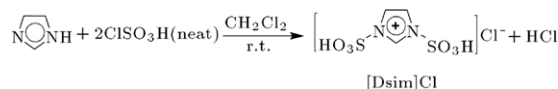


Figure 5: The preparation of [Dsim]Cl.

room temperature. Higher yields of the product and shorter reaction times were obtained when 10 mol% of the ionic liquids, beside 10 mol% of FeCl₃ in ethyl acetate, were utilized. In these conditions, [Msim]Cl/FeCl₃ afforded the product in 88% yield within 15 min, and [Dsim]Cl/FeCl₃ gave the product in 91% within 12 min.

To assess efficacy and generality of [Msim]Cl/FeCl₃ and [Dsim]Cl/FeCl₃ catalytic systems, benzene-1, 2-diamine was reacted with various aromatic aldehydes under the optimized reaction conditions to furnish the corresponding benzimidazoles in high yields and in short reaction times (Table 1). The effect of electron-releasing and electron-withdrawing substituents on the aromatic ring of aldehydes was also studied, using [Msim]Cl/FeCl₃ and [Dsim]Cl/FeCl₃ as catalysts. As seen in Table 1, the electron-releasing groups slightly decreased the yields and increased the reaction times (Table 1, compounds 1b–d); however, the electron-withdrawing substituents increased the yields and decreased the reaction times (Table 1, compounds 1e and 1f). Moreover, the results showed that the presence of halogens on the aromatic ring of aldehydes had negligible influence on the yields, but slightly decreased the reaction times (Table 1, compounds 1g–i). The reaction was also efficiently progressed when aromatic aldehydes containing hydroxyl group or hetero-aromatic aldehydes were applied (Table 1, compounds 1j–n).

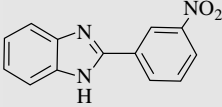
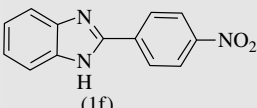
The method was also applied successfully for the condensation of benzene-1, 2-diamine with carboxylic acids to afford benzimidazoles in high yields and in short reaction times (Figure 2 and Table 2); nevertheless, in this case, the reaction was performed at 60 °C.

In a plausible mechanism which is confirmed with the literature [39], benzene-1, 2-diamine attacks aldehyde, which is activated with the sulfonic acid imidazolium salt {[Dsim]Cl} to give I by exiting one mole of H₂O. Then, II is produced *via* intra-molecular condensation of I and proton transfer of the intermediate. High-valent oxidoiron(IV), as a key intermediate in these oxidation conditions, can be formed by treatment between Fe(III) and oxidant. Afterward, Fe(IV) oxidizes II to III and IV, respectively, in two steps, and converts to Fe(II). Finally, O₂ of air, as a green oxidant, oxidizes Fe(II) to high-valent oxidoiron(IV), and this cycle continues until completion of the reaction. Mechanistically, we observed that iron(III)chloride, beside the sulfonic acid imidazolium salts, successfully catalyzed the production of benzimidazoles. The proposed mechanism is displayed in Figure 6.

3. Conclusion

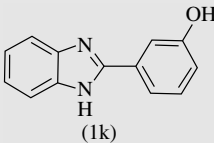
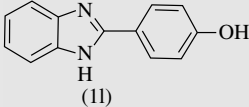
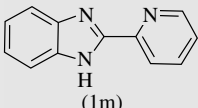
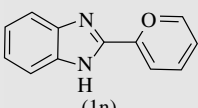
In summary, we have introduced [Msim]Cl/FeCl₃ and [Dsim]Cl/FeCl₃, in the presence of atmospheric air, as efficient, green and mild catalytic systems for the synthesis of benzimidazole derivatives at room temperature. The promising points of

Table 1: The preparation of benzimidazole derivatives from benzene-1, 2-diamine and aldehydes using [Msim]Cl/FeCl₃ as well as [Dsim]Cl/FeCl₃ at 60 °C.

Product	[Msim]Cl		[Dsim]Cl		M.p. °C (Lit.)
	Time (min)	Yield ^a (%)	Time (min)	Yield ^a (%)	
 (1a)	15	88	12	91	289–293 (292–294) [16]
 (1b)	20	86	16	89	268–270 (270) [17]
 (1c)	25	84	20	86	225–227 (226) [17]
 (1d)	25	86	18	88	203–205 (201–204) [16]
 (1e)	12	95	9	95	200–203 (204–207) [16]
 (1f)	10	97	6	97	315–317 (316) [39]
 (1g)	15	90	10	92	231–233 (234) [11]
 (1h)	13	89	8	93	290–292 (292) [39]
 (1i)	14	86	8	87	277–279 (279) [39]
 (1j)	18	87	10	90	239–241 (242) [39]

(continued on next page)

Table 1 (continued)

Product	[Msim]Cl		[Dsim]Cl		M.p. °C (Lit.)
	Time (min)	Yield ^a (%)	Time (min)	Yield ^a (%)	
 (1k)	13	90	9	95	183–186 (181–184) [39]
 (1l)	20	85	15	88	253–255 (254–255) [39]
 (1m)	24	82	15	84	216–218 (218) [39]
 (1n)	22	78	15	79	284–286 (287–288) [39]

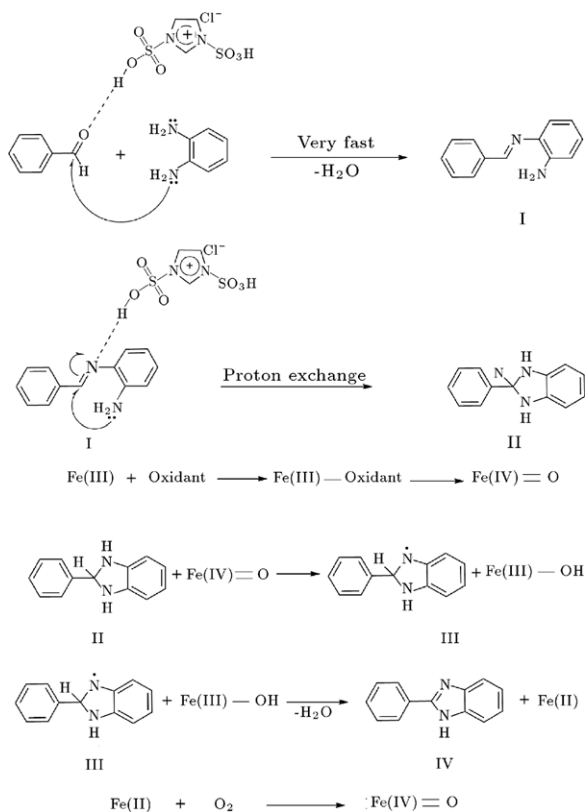
^a Isolated yield.

Figure 6: The proposed mechanism for the synthesis of benzimidazole derivatives.

this method are simple experimental procedure, mild reaction conditions, safety, high yields, short reaction times and mini-

mization of chemical wastes, as compared to the other method counterparts.

4. Experimental

All Chemicals were purchased from Merck or Fluka Chemical Company. The products were identified by comparison of their ¹H NMR, TLC and melting points, with those in the authentic samples. Progress of the reactions was monitored by TLC, using silica gel SIL G/UV 254 plates. The ¹H NMR (250 MHz) and ¹³C NMR (62.5 MHz) were run on a Bruker Avance DPX-250 FT-NMR spectrometer (δ in ppm). Melting points were recorded on a Stuart Scientific Apparatus SMP3 (UK) in open capillary tubes.

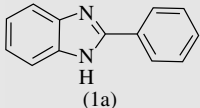
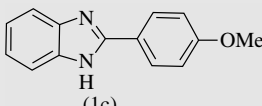
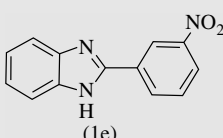
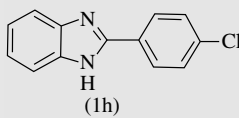
4.1. Procedure for the preparation of ionic liquid [Msim]Cl

A round-bottomed flask (100 mL) was charged with 1-methylimidazole (0.410 g, 5 mmol) in dry CH₂Cl₂ (50 mL), and then chlorosulfonic acid (0.605 g, 5.2 mmol) was added dropwise over a period of 5 min at room temperature. After the addition was completed, the reaction mixture was stirred for 20 min, left to stand for 5 min, and the CH₂Cl₂ was decanted. The residue was washed with dry CH₂Cl₂ (3 × 50 mL) and dried under vacuum to give [Msim]Cl as a viscous colorless oil in 92% yield, 0.912 g (Figure 4) [35–38].

4.2. Procedure for the preparation of ionic liquid [Dsim]Cl

To a round-bottomed flask (100 mL) containing imidazole (0.340 g, 5 mmol) in dry CH₂Cl₂ (50 mL), chlorosulfonic acid (1.1885 g, 10.2 mmol) dropwise over a period of 20 min at room temperature was added. After the addition was completed, the reaction mixture was stirred for 12 h under the pressure of nitrogen (to remove the produced HCl), left to stand for 5 min, and the CH₂Cl₂ was decanted. The residue was washed with dry CH₂Cl₂ (3 × 50 mL) and dried under vacuum to give [Dsim]Cl as a viscous pale yellow oil in 95% yield, 1.257 g (Figure 5) [38].

Table 2: The preparation of benzimidazole derivatives from benzene-1, 2-diamine and carboxylic acids using [Msim]Cl/FeCl₃ as well as [Dsim]Cl/FeCl₃ at 60 °C.

Product	[Msim]Cl		[Dsim]Cl		M.p. °C (Lit.)
	Time (min)	Yield ^a (%)	Time (min)	Yield ^a (%)	
 (1a)	30	86	25	88	289–293 (292–294) [16]
 (1c)	40	80	35	84	225–227 (226) [17]
 (1e)	25	89	18	93	200–203 (204–207) [16]
 (1h)	25	88	20	89	290–292 (292) [39]

^a Isolation yield.

4.3. General procedure for the synthesis of benzimidazoles via the condensation of benzene-1, 2-diamine with aldehydes or carboxylic acids (Figures 2 and 3)

To a mixture of benzene-1, 2-diamine (0.22 g, 2 m mol), aldehyde or carboxylic acid (2 m mol), the sulfonic acid imidazolium salt (0.2 m mol) and FeCl₃ (0.032 g, 0.2 m mol) in a 10 mL round-bottomed flask was added EtOAc (10 mL), and the resulting mixture was stirred at room temperature for the appropriate time (Tables 1 and 2). (Note: When carboxylic acids were utilized instead of aldehydes, the reaction was carried out at 60 °C). Afterward, warm EtOAc (60 mL) was added to the reaction mixture, filtered, and the filtrate was washed with saturated solution of NaHCO₃ (2 × 40 mL) and H₂O (2 × 40 mL). After drying and evaporation of the solvent, the resulting solid was recrystallized from EtOH to give the pure product.

4.4. Selected spectral data of the products

2-Phenyl-1H-benzimidazole (1a): ¹H NMR (DMSO-d₆): δ 7.12–7.19 (m, 2H), 7.49–7.55 (m, 5H), 7.98 (m, 2H), 12.56 (s, 1H); ¹³C NMR (DMSO-d₆): δ 114.2, 121.6, 125.3, 126.2, 130.6, 131.2, 134.7, 148.8.

2-(4-Methoxyphenyl)-1H-benzimidazole (1c): ¹H NMR (DMSO-d₆): δ 3.75 (s, 3H), 7.14 (d, *J* = 8.7 Hz, 2H), 7.19 (m, 2H), 7.47 (m, 2H), 8.09 (d, *J* = 8.7 Hz, 2H), 12.69 (s, 1H); ¹³C NMR (DMSO-d₆): δ 55.8, 112.2, 115.1, 121.2, 123.1, 128.2, 134.1, 151.8, 160.3.

2-(3-Nitrophenyl)-1 H-benzimidazole (1e): ¹H NMR (DMSO-d₆): δ 7.18 (m, 2H), 7.56 (m, 2H), 7.69–7.78 (m, 1H), 8.29 (m, 1H), 8.58 (m, 1H), 8.91 (s, 1H), 13.12 (s, 1H); ¹³C NMR (DMSO-d₆): δ 115.7, 120.2, 121.9, 124.3, 130.2, 131.9, 133.0, 137.2, 148.7, 150.1.

Acknowledgments

The authors gratefully acknowledge the partial support of this work by the Research Affairs Office of Bu-Ali Sina University (Grant number 32-1716 entitled development of chemical methods, reagent and molecules), and the Center of Excellence in Development of Chemical Method (CEDCM), Hamedan, I.R. Iran.

References

- [1] Spasov, A.A., Yozhitsa, I.N., Bugaeva, L.I. and Anisimova, V.A. "Benzimidazole derivatives: spectrum of pharmacological activity and toxicological properties", *Pharm. Chem. J.*, 33, pp. 232–243 (1999).
- [2] Perston, P.N. *The Chemistry of Heterocyclic Compounds, Benzimidazoles and Congeneric Tricyclic Compounds*, 40, Part 2, (Chapter 10), John Wiley & Sons, New York (1980).
- [3] Sheehan, D.J., Hitchcock, C.A. and Sibley, C.M. "Current and emerging azole antifungal agents", *Clin. Microbiol. Rev.*, 12, pp. 40–79 (1999).
- [4] Habib, N.S., Soliman, R., Ashour, F.A. and el-Taiebi, M. "Synthesis and antimicrobial testing of novel oxadiazolylbenzimidazole derivatives", *Pharmazie*, 52, pp. 746–749 (1997).
- [5] Tuncbilek, M., Goker, H., Ertan, R., Eryigit, R., Kendi, E. and Altanlar, E. "Synthesis and antimicrobial activity of some new anilino benzimidazoles", *Arch. Pharm.*, 330, pp. 372–376 (1997).
- [6] Pedini, M., Alunni Bistochi, G., Ricci, A., Bastianini, L. and Lepri, E. "New heterocyclic derivatives of benzimidazole with germicidal activity – XII – Synthesis of N1-glycosyl-2-furyl benzimidazoles", *Farmaco*, 49, pp. 823–827 (1994).
- [7] Lackner, T.E. and Clisshold, S.P. "Bifonazole. A review of its antimicrobial activity and therapeutic use in superficial mycoses", *Drugs*, 38, pp. 204–225 (1989).
- [8] Stefan'ska, J.Z., Gralewska, R., Staros'ciak, B.J. and Kazimierczuk, Z. "Antimicrobial activity of substituted azoles and their nucleosides", *Pharmazie*, 54, pp. 879–884 (1999).
- [9] Porcari, A.R., Devivar, R.V., Kucera, L.S., Drach, J.C. and Townsend, L.B. "Design, synthesis, and antiviral evaluations of 1-(substituted benzyl)-2-substituted-5,6-dichlorobenzimidazoles as nonnucleoside analogues of 2, 5, 6-trichloro-1-(β-D-ribofuranosyl)benzimidazole", *J. Med. Chem.*, 41, pp. 1252–1262 (1998).
- [10] Bourgin, K., Loupy, A. and Soufiaoui, M. "Three new ways to synthesize 1, 3-azole derivatives by microwaves, Trois nouvelles voies de synthese des derives 1, 3-azoliques sous micro-ondes", *Tetrahedron*, 54, pp. 8055–8064 (1998).

- [11] Rope, M., Isensee, R.W. and Joseph, L. "Derivatives of 2-phenylbenzimidazole", *J. Am. Chem. Soc.*, 74, pp. 1095–1096 (1952).
- [12] Addison, A.W. and Burke, P.J., *J. Heterocycl. Chem.*, 18, p. 803 (1981).
- [13] Tempest, P., Ma, V., Thomas, S., Hua, Z., Kelly, M.G. and Hulme, C. "Two-step solution-phase synthesis of novel benzimidazoles utilizing a UDC (Ugi/de-Boc/cyclize) strategy", *Tetrahedron Lett.*, 42, pp. 4959–4962 (2001).
- [14] Boido, C., Boido, V., Novelli, F. and Paratore, S. "Formation of basic compounds during the indole cyclization of ketone phenylhydrazones", *J. Heterocycl. Chem.*, 35, pp. 853–858 (1998).
- [15] Ramsden, C.A. and Rose, H.L. "Oxidative rearrangement and cyclisation of N-substituted amidines using iodine(III) reagents and the influence of leaving group on mode of reaction", *J. Chem. Soc., Perkin Trans.*, 1(16), pp. 2319–2327 (1997).
- [16] Heravi, M.M., Tajbakhsh, M., Ahmadi, A.N. and Mohajerani, B. "Zeolites. Efficient and eco-friendly catalysts for the synthesis of benzimidazoles", *Monatsh. Chem.*, 137, pp. 175–179 (2006).
- [17] Allouma, A.B., Bougrin, K. and Soufiaoui, M. "The synthesis of azo compounds from nitro compounds using lead and triethylammonium formate [Synthèse chimiosélective des benzimidazoles sur silice traité par le chlorure du thionyle]", *Tetrahedron Lett.*, 44, pp. 5935–5937 (2003).
- [18] Trivedi, R., De, S.K. and Gibbs, R.A. "A convenient one-pot synthesis of 2-substituted benzimidazoles", *J. Mol. Catal. A: Chem.*, 245, pp. 8–11 (2006).
- [19] Niknam, K. and Fatehi-Raviz, A. "Synthesis of 2-substituted benzimidazoles and bis-benzimidazoles by microwave in the presence of alumina-methanesulfonic acid", *J. Iran. Chem. Soc.*, 4, pp. 438–443 (2007).
- [20] Nadaf, R.N., Siddiqui, S.A., Daniel, T., Lahoti, R.J. and Srinivasan, K.V. "Room temperature ionic liquid promoted regioselective synthesis of 2-aryl benzimidazoles, benzoxazoles and benzthiazoles under ambient conditions", *J. Mol. Catal. A: Chem.*, 214, pp. 155–160 (2004).
- [21] Preston, P.N. "Synthesis, reactions, and spectroscopic properties of benzimidazoles", *Chem. Rev.*, 74, pp. 279–314 (1974).
- [22] Lin, S. and Yang, L. "A simple and efficient procedure for the synthesis of benzimidazoles using air as the oxidant", *Tetrahedron Lett.*, 46, pp. 4315–4319 (2005).
- [23] Yang, D., Fokas, D., Li, J., Yu, L. and Baldino, C.M. "A versatile method for the synthesis of benzimidazoles from o-nitroanilines and aldehydes in one step via a reductive cyclization", *Synthesis*, pp. 47–56 (2005).
- [24] Su, Y.-S. and Sun, C.-M. "Microwave-assisted benzimidazole cyclization by bismuth chloride", *Synlett*, pp. 1243–1264 (2005).
- [25] Su, Y.-S., Lin, M.-J. and Sun, M.C. "Mercury chloride assisted cyclization toward benzimidazoles by focused microwave irradiation", *Tetrahedron Lett.*, 46, pp. 177–180 (2004).
- [26] Olguin, L.F., Jiménez-Estrada, M., Bárzana, E. and Navarro-Ocana, A. "Baker's yeast-mediated regioselective reduction of 2, 4-dinitroacylanilines: synthesis of 2-substituted 6-nitrobenzimidazoles", *Synlett*, pp. 340–342 (2005).
- [27] Salehi, P., Dabiri, M., Zolfigol, M.A., Otokesh, S. and Baghbzadeh, M. "Selective synthesis of 2-aryl-1-arylmethyl-1H-1, 3-benzimidazoles in water at ambient temperature", *Tetrahedron Lett.*, 47, pp. 2557–2560 (2006).
- [28] Zare, A., Moosavi-Zare, A.R., Hasaninejad, A., Parhami, A., Khalafi-Nezhad, A. and Beyzavi, M.H. "Green, catalyst-free protocol for the efficient synthesis of N-sulfonyl aldimines and ketimines in ionic liquid [bmim]Br", *Synth. Commun.*, 39, pp. 3156–3165 (2009).
- [29] Zare, A., Parhami, A., Moosavi-Zare, A.R., Hasaninejad, A., Khalafi-Nezhad, A. and Beyzavi, M.H. "A catalyst-free protocol for the green and efficient condensation of indoles with aldehydes in ionic liquids", *Can. J. Chem.*, 87, pp. 416–421 (2009).
- [30] Zare, A., Hasaninejad, A., Khalafi-Nezhad, A., Moosavi Zare, A.R. and Parhami, A. "Organic reactions in ionic liquids: MgO as efficient and reusable catalyst for the Michael addition of sulfonamides to α , β -unsaturated esters under microwave irradiation", *ARKIVOC*, 13, pp. 105–115 (2007).
- [31] Zare, A., Hasaninejad, A., Moosavi Zare, A.R., Parhami, A., Sharghi, H. and Khalafi-Nezhad, A. "Zinc oxide as a new, highly efficient, green, and reusable catalyst for microwave-assisted Michael addition of sulfonamides to α , β -unsaturated esters in ionic liquids", *Can. J. Chem.*, 85, pp. 438–444 (2007).
- [32] Zare, A., Hasaninejad, A., Safinejad, R., Moosavi-Zare, A.R., Beyzavi, M.H., Khalafi-Nezhad, A., Miralaei-Moreddi, M., Dehghani, E. and Kazerooni-Mojarrad, P. "Ionic liquid-accelerated Michael addition of pyrimidine and purine nucleobases to α , β -unsaturated esters: a rapid approach to carboacyclic nucleosides synthesis", *ARKIVOC*, 16, pp. 51–64 (2008).
- [33] Fraga-Dubreuil, J., Bourahla, K., Rahmouni, M., Bazureau, J.P. and Hamelin, J. "Catalyzed esterifications in room temperature ionic liquids with acidic counter anion as recyclable reaction media", *Catal. Commun.*, 3, pp. 185–190 (2002).
- [34] Gu, D.-G., Ji, S.-J., Jiang, Z.-Q., Zhou, M.-F. and Loh, T.-P. "An efficient synthesis of bis(indolyl)methanes catalyzed by recycled acidic ionic liquid", *Synlett*, pp. 959–962 (2005).
- [35] Khazaei, A., Zolfigol, M.A., Moosavi-Zare, A.R. and Zare, A. "New Brønsted acidic ionic liquid 3-methyl-1-sulfonic acid imidazolium chloride/NaNO₂: a novel and efficient system for the nitration of phenols under mild conditions", *Scientia Iranica, Trans. C: Chem. Chem. Eng.*, 17, pp. 31–36 (2010).
- [36] Zolfigol, M.A., Khazaei, A., Moosavi-Zare, A.R. and Zare, A. "3-Methyl-1-sulfonic acid imidazolium chloride [(Msim)Cl] as a new, efficient and recyclable catalyst and solvent for the preparation of N-sulfonyl imines at room temperature", *J. Iran. Chem. Soc.*, 7, pp. 646–651 (2010).
- [37] Zolfigol, M.A., Khazaei, A., Moosavi-Zare, A.R. and Zare, A. "Ionic liquid 3-methyl-1-sulfonic acid imidazolium chloride as a novel and highly efficient catalyst for the very rapid synthesis of bis(indolyl)methanes under solvent-free conditions", *Org. Prep. Proceed. Int.*, 42, pp. 95–102 (2010).
- [38] Zolfigol, M.A., Khazaei, A., Moosavi-Zare, A.R., Zare, A. and Khakyzadeh, V. "Rapid synthesis of 1-amidoalkyl-2-naphthols over sulfonic acid functionalized imidazolium salts", *Applied Catal. A. Gen.*, 400, pp. 70–81 (2011).
- [39] Sharghi, H., Beyzavi, M.H. and Droodmand, M.M. "Reusable porphyrinatoiron(III) complex supported on activated silica as an efficient heterogeneous catalyst for a facile, one-pot, selective synthesis of 2-arylbenzimidazole derivatives in the presence of atmospheric air as a green oxidant at ambient temperature", *Eur. J. Org. Chem.*, pp. 4126–4138 (2008).

Ardeshir Khazaei was born in 1948 in Nahavand, Iran. He obtained the B.S. and M.S. degrees from Pittsburgh University, USA, in 1975, and with Professor John Crendel, in 1977, respectively. He received his Ph.D. from Manchester University, UK, with Professor Ronald Erick Bank, in 1990. He became a faculty member of Bu-Ali Sina University, Iran, a Professor in 2003, and a national outstanding Professor in 2006. His research includes discovery and development of polymer supported reagent, synthesis and application of new N-halo compounds such as N-halo sulfonamides.

Mohammad Ali Zolfigol was born in 1966 in Salehabad (Ashtian), Iran. He obtained the B.S. degree from Arak University, Iran, the M.S. degree from Isfahan University of Technology, with Professor Shadpour Mallakpour, and the Ph.D. degree from Shiraz University, with Professor Nasser Iranpoor. He became a faculty member of Bu-Ali Sina University in 1997, and a Professor in 2005. In 2003, he was selected as distinguished researcher by the Ministry of Science, Research and Technology of Iran. He was also awarded at the Khwarizmi International Festival and at COM.S.TEC in 2008. His research interests include discovery and development of new synthetic methods by the synthesis and application of new solid-supported reagents, especially silica-based resins.

Ahmad Reza Moosavi-Zare was born in Shiraz, Iran, in 1974. He received the B.S. degree in Chemistry from Yazd University, Iran, in 1998, and the M.S. degree in Organic Chemistry from Mohagheghe Ardebili University (Iran) in 2006 with Dr. Gholam Hasan Imanzadeh. He is currently working on his Ph.D. in Organic Chemistry under the supervision of Professor Mohammad Ali Zolfigol and Professor Ardeshir Khazaei in the Organic Chemistry Department at Bu-Ali Sina University, Hamedan, Iran. His research interests include applications of ionic liquids, solvent-free conditions and microwave irradiation in organic synthesis and green chemistry.

Abdolkarim Zare was born in Bushehr, Iran, in 1977. He received the B.S. degree in Chemistry from Yazd University, Iran, in 1998, and the M.S. and Ph.D. degrees in Organic Chemistry from Shiraz University, Iran, with Professor Hashem Sharghi, in 2002, and with Professor Ali Khalafi-Nezhad, in 2006, respectively. He is faculty member of Payame Noor University (PNU). His research field includes applications of solvent-free conditions, ionic liquids and microwave irradiation in organic synthesis, and study of methodology in organic chemistry.

Ezat Ghaemi was born in Hamedan, Iran, in 1959. She received the B.S. degree in Chemistry from Razi University, Iran, in 1986, and the M.S. degree in Organic Chemistry from Birjand University, Iran, with Professor Davood Habibi in 1998. She is a faculty member of Bu-Ali Sina University, Hamedan, Iran. Her research fields include synthesis of nitro aromatic compounds, oxidation of organic compounds, and application of solid acids, such as silica sulfuric acid in organic synthesis.

Vahid Khakyzadeh was born in Hamedan, Iran, in 1984. He received his B.S. degree in Chemistry in 2008, and his M.S. degree in Organic Chemistry from Bu-Ali Sina University, Hamedan, Iran, in 2010 with Professor Mohammad Ali Zolfigol. He was introduced as outstanding M.S. student in Bu-Ali Sina University

in 2009. He is currently working on his Ph.D. in Organic Chemistry under the supervision of Professor Mohammad Ali Zolfgol in the Organic Chemistry Department at Bu-Ali Sina University, Hamedan, Iran. His research interests include applications of ionic liquids, solvent-free conditions in organic synthesis and green chemistry.

Zhila Asgari was born in Kangaavar, Iran, in 1978. She received her B.S. degree in Chemistry in 1995 and her M.S. degrees in Organic Chemistry from the Bu-Ali Sina University, Hamedan, Iran, in 2007, with Professor Davood Habibi. Her research fields include electro synthesis of organic compounds, application of

ionic liquids and solid acids in organic synthesis, and study of methodology in organic chemistry.

Alireza Hasaninejad was born in Dehbid, Iran, in 1973. He received his B.S. degree in Chemistry from Sistan and Baluchestan University, Iran, in 1997, and his M.S. and Ph.D. degrees in Organic Chemistry from Shiraz University, Iran, with Professor Hashem Sharghi in 2001 and 2005, respectively. He is now a faculty member of the Persian Gulf University in Iran. His research fields include applications of solvent-free conditions, ionic liquids and microwave irradiation in organic synthesis, and study of methodology in organic chemistry.