#### Ultrasonics Sonochemistry 21 (2014) 1132-1139

Contents lists available at ScienceDirect

Ultrasonics Sonochemistry

journal homepage: www.elsevier.com/locate/ultson

### Ultrasound mediation for one-pot multi-component synthesis of amidoalkyl naphthols using new magnetic nanoparticles modified by ionic liquids

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#### ARTICLE INFO

Article history: Received 7 August 2013 Received in revised form 23 October 2013 Accepted 28 October 2013 Available online 13 November 2013

Keywords: Amidoalkyl naphthols Ultrasound irradiation Magnetic nanoparticles Multi-component reaction Supported ionic liquids

#### 1. Introduction

One-pot multicomponent reactions (MCRs) are of increasing importance in organic synthesis in recent years [1–5] as they can produce target products in a single operation without isolating the intermediates and therefore reducing the reaction times and energy input [6,7]. Particularly, in the last three decades a number of three and four-component MCRs have been developed, specially the Bignelli [8], Passerini [9], Ugi [10] and Mannich [11] reactions, which have further led to renaissance of MCRs. Therefore, great efforts have been and still are being made to find and develop new MCRs.

One of the classic MCRs is the synthesis of 1-aminoalkyl-2naphthol derivatives as they can be easily converted into biologically active derivatives by amide hydrolysis [12,13]. Also, these useful compounds can be also converted into 1,3-oxazines [14] with potentially different biological activities such as antibiotic [15], analgesic [16], antitumor [17], anticonvulsant [18], antihypertensive [19], and antirheumatic properties [20]. Owing to the biological and medicinal as well the pharmacological importance of 1-amidoalkyl-2-naphthols, efforts have been made by various researchers in developing MCRs for the preparation of 1-amidoalkyl-2-naphthols from aldehydes,  $\beta$ -naphthols or  $\beta$ -naphthylamine, and amides/carbamates and/or urea under thermal and/or

ABSTRACT

The ionic liquid 1-methyl-3-(3-trimethoxysilylpropyl) imidazolium acetate was immobilized on the Fe<sub>3</sub>O<sub>4</sub> nanoparticles (MNPs-IL-OAc) and used as an efficient new heterogeneous nanocatalyst for the one-pot multi-component synthesis of 1-amidoalkyl-2-naphthols under ultrasound irradiation. The advantages of present combined method are the use of a low scale catalyst, easier work-up procedure, waste-free, green and efficient synthetic entry to excellent yield of products in a high reusability and a short reaction time.

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heating or sonication conditions using various catalysts such as montmorillonite K10 clay [21],  $Ce(SO_4)_2$  [22], Iodine [23], p-TSA [24], Sulfamic acid [25] and cation-exchange resins [26], Ferric(III) hydrogensulfate [27], SiO<sub>2</sub>-HClO<sub>4</sub> [28], and silica sulfuric acid [29].

However, some of these methods are not environmentally friendly and suffer from one or more limitations, such as prolonged reaction times, high reaction temperature, lower yield of the desire product, tedious work-up, toxicity and recovery and reusability of the catalyst. Therefore, the development of the cleaning processes and utilizing eco-friendly and green catalysts is still challenging to develop a safe alternate method for the synthesis of amidoalkyl naphthols. The demand for environmentally benign procedure with heterogeneous and reusable catalyst, promoted us to develop a safe alternate method for the preparation of amidoalkyl naphthols [30].

In recent years, ionic liquids (ILs) based heterogeneous catalysis has attracted a considerable attention under the heading of "green chemistry" as they permit mutual advantages of both homogeneous as well as heterogeneous catalysts in organic synthesis [31–34]. In comparison to pure Lewis acidic ILs, Imidazolium-based ILs as heterogeneous catalyst offers more advantage like decrease in the amount of ILs used with ease of separation and efficient catalyst recovery [35,36]. Therefore, magnetic nanoparticles (MNPs), silica and polymer-supported ILs have been tested as catalysts in organic synthesis with variable results regarding activity and recycling [37–39]. Additionally, recent studies show that MNPs are excellent supports for ILs [39]. The supported catalysts proved





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<sup>1350-4177/\$ -</sup> see front matter @ 2013 Elsevier B.V. All rights reserved. http://dx.doi.org/10.1016/j.ultsonch.2013.10.024

to be effective and easily separated from the reaction media by applying an external magnetic field [39].

On the other hand, greener process involves mainly clean solvents, ultrasound irradiation and microwave irradiation. Ultrasound has increasingly been used in synthetic organic chemistry, because of its advantages including shorter reaction times, milder reaction conditions, higher yields, improved selectivity and clean reaction in comparison to classical methods [40–42]. Since in this green technique the reaction is carried out at lower external temperature relative to the usually thermal methods, the possibility of occurrence of undesired reactions is reduced, and as a result of cleaner reaction the workup is easier [43].

With the aim to develop a more efficient synthetic process, we herein describe a practical and effective method for the preparation 1-amidoalkyl-2-naphthol via the one-pot reaction of  $\beta$ -naphthol, aldehydes derivatives, amides or urea in the presence of magnetically MNPs-IL-OAc catalyst under ultrasound irradiation and ambient conditions (Scheme 1). To the best of our knowledge, there are no examples of the use magnetically heterogeneous nanocatalyst for the ultrasound assisted synthesis of amidoalkyl naphthols.

#### 2. Experimental

#### 2.1. Chemicals and apparatus

Chemical reagents in high purity were purchased from Merck and Aldrich and were used without further purification. Melting points were determined in open capillaries using an Electrothermal Mk3 apparatus and are uncorrected. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded with a Bruker DRX-400 spectrometer at 400 and 100 MHz respectively. FT-IR spectra were obtained with potassium bromide pellets in the range 400-4000 cm<sup>-1</sup> with a Perkin-Elmer 550 spectrometer. Nanostructures were characterized using a Holland Philips Xpert X-ray powder diffraction (XRD) diffractometer (CuK, radiation,  $\lambda = 0.154056$  nm), at a scanning speed of  $2^{\circ}/\text{min}$  from  $10^{\circ}$  to  $100^{\circ}$  (2 $\theta$ ). Scanning electron microscope (SEM) was performed on a FEI Quanta 200 SEM operated at a 20 kV accelerating voltage. The samples for SEM were prepared by spreading a small drop containing nanoparticles onto a silicon wafer and being dried almost completely in air at room temperature for 2 h, and then were transferred onto SEM conductive tapes. The transferred sample was coated with a thin layer of gold before measurement. Purity of the compounds synthesized was monitored by TLC, visualizing with ultraviolet light. A multiwave ultrasonic generator (Sonicator 3200; Bandelin, MS 73, Germany), equipped with a converter/transducer and titanium oscillator (horn), 12.5 mm in diameter, operating at 30 kHz with a maximum power output of 200 W, was used for the ultrasonic irradiation. The ultrasonic generator automatically adjusted the power level. A circulating water bath (DC2006, Shanghai Hengping Apparatus Factory) with an accuracy of 0.1 K was adopted to keep the reaction temperature at a constant. The known products were characterized by comparison of their spectral (<sup>1</sup>H NMR and <sup>13</sup>C NMR) and physical data with those of authentic samples. All yields refer to isolated products after purification.

#### 2.2. Preparation of catalyst

#### 2.2.1. Synthesis of 1-methyl-3-(3-trimethoxysilylpropyl)-1H-imidazol-3-ium Chloride (IL-Cl)

1-Methylimidazole (13.6 mL, 0.17 mol) and (3-chloropropyl) trimethoxysilane (31 mL, 0.17 mol) were refluxed at 80 °C for 3 days without solvent under Ar atmosphere. The unreacted materials were washed by diethyl ether ( $3 \times 8$  mL). The residue was evaporated under reduced pressure, to yield a yellowish viscous liquid isolated yield was 97% [44].

FT-IR (KBr, cm<sup>-1</sup>): 1656, 1612, 1584. <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>):  $\delta_{\rm H}$  (ppm): 10.22 (broad, 1H, Are-H), 7.59 (1H, dd, *J* = 7.89 and 2.86 Hz, Are-H), 7.26 (1H, dd, *J* = 7.89 and 2.79 Hz, Are-H), 4.06 (2H, t, *J* = 7.25 Hz, -NCH<sub>2</sub>), 3.86 (3H, s, -NCH<sub>3</sub>), 3.30 (9H, s, OCH<sub>3</sub>), 1.74 (2H, tt, *J* = 7.14 Hz, -CH<sub>2</sub>), 0.37 (2H, t, *J* = 7.09 Hz, SiCH<sub>2</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, TMS):  $\delta_{\rm C}$  = 138.13, 123.34, 121.58, 58.53, 51.66, 36.51, 24.32, 18.2, 7.03. Anal. Calcd.: C, 48.45; H, 8.39; N, 8.69. Found: C, 48.35; H, 8.32; N, 8.79.

## 2.2.2. Modification of magnetic nanoparticles with IL-Cl to obtain MNPs-IL-Cl

 $Fe_3O_4$ -MNPs were prepared using chemical coprecipitation described in the literature [39] and subsequently freshly prepared  $Fe_3O_4$  nanoparticles (2 g) were suspended in ethanol (95%, 250 mL), and sonicated for 30 min. The resulted suspension was mechanically stirred, followed by addition of a solution of ethanol (95%, 100 mL) containing IL (6 g, 18.5 mmol) and concentrated ammonia (28%, 1 mL). Stirring under Ar was continued for 36 h. The modified  $Fe_3O_4$  nanoparticles were magnetically separated and washed three times with ethanol (95%, 50 mL) and then dissolved in methanol (200 mL) and stirred mechanically for 30 min. Ether (50 mL) was added and the modified nanoparticles were magnetically separated, washed with ether (50 mL) and dried under a vacuum for 24 h and the nanoparticles of immobilized chloride ionic liquid was prepared [39].

### 2.2.3. Anion exchange in the immobilized chloride ionic liquid (MNPs-IL-OAc)

Immobilized chloride ionic liquid on MNPs and an excess amount of NaOAc were added into the deionized water and stirred for 24 h at room temperature. NaCl which was prepared during the exchange of chloride anion with OAc, was removed by washing with deionized water. Immobilized acetate ionic liquid on  $Fe_3O_4$ nanoparticles was obtained as a brownish black powder (Scheme 2).

#### 2.3. General procedure for the synthesis of amidoalkyl naphthols

#### 2.3.1. Typical heating method (method A)

A mixture of  $\beta$ -naphthol (5 mmol), aldehyde (5 mmol), amide/ urea (5.5 mmol) and MNPs-IL-OAc (0.04 g) were taken in round bottom flask and stirred and heated at 100 °C for appropriate times (monitored by TLC). Then, ethanol (20 mL) was added and the catalyst was separated by an external magnet. The reaction mixture was evaporated to remove solvent and the crystalline material left was taken up in ethanol:water (1:3) for recrystallization.



Scheme 1. One-pot synthesis of 1-amidoalkyl-2-naphthol catalyzed by MNPs-IL-OAc under ultrasound irradiation at ambient conditions.



Scheme 2. Preparation steps for fabricating 1-methyl-3-(3-trimethoxysilylpropyl)-1H-imidazol-3-ium acetar-functionalized magnetic Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

#### 2.3.2. Ultrasound irradiation method (method B)

A mixture of  $\beta$ -naphthol (5 mmol), a liquid aldehyde (5 mmol), an amide/urea (6 mmol), and MNPs-IL-OAc (0.04 g), taken in a flask (50 mL), was sonicated at 30 kHz frequency and 50 W power while pure argon was continuously purged in the reaction at 30 °C (by circulating water) for appropriate times. For solid aldehydes, dichloroethane (10 mL) was added to the mixture. After the TLC indicates the disappearance of starting materials, ethanol (20 mL) was added and the catalyst was separated by an external magnet and reused as such for the next experiment. The reaction mixture was concentrated on a rotary evaporator under reduced pressure and the crude residue was purified by crystallization in ethanol:water (1:3) to afford pure amidoalkyl naphthol.

#### 3. Results and discussion

#### 3.1. Characterization of MNPs-IL-OAc as catalyst

The magnetite nanoparticles of 20 nm were prepared by coprecipitation of iron(II) and iron(III) ions in basic solution at 85 °C using the method described by Massart [45]. For the surface modification, the MNPs coated with *N*-methyl-3-(3-trimethoxysilylpropyl) imidazolium acetate (Scheme 2).

Fig. 1 shows the Fourier transform infrared (FTIR) spectra of MNPs. The Fe–O stretching vibration near 580 cm<sup>-1</sup>, O–H stretching vibration near 3432 cm<sup>-1</sup> and O–H deformed vibration near 1625 cm<sup>-1</sup>were observed for both in Fig. 1(a) and (b). The significant features observed for Fig. 1(b) are the appearance of the peaks at 1010 cm<sup>-1</sup> (Si–O stretching), 2800 cm<sup>-1</sup> (–CH<sub>2</sub> stretching) and at 1575 (COO<sup>-</sup> stretching). These results provided the evidences that ILs were successfully attached to the surface of Fe<sub>3</sub>O<sub>4</sub> nanoparticles.

Fig. 2 presents the XRD-diffraction patterns of MNPs and MNPs-IL-OAc. The position and relative intensities of all peaks confirm well with standard XRD pattern of  $Fe_3O_4$  (JCPDS card No. 79-0417) indicating retention of the crystalline cubic spinel structure during functionalization of  $Fe_3O_4$  nanoparticles by imidazolium ionic liquid [39]. It is implied that the resultant nanoparticles are pure  $Fe_3O_4$  with a spinel structure and that the grafting process did not induced any phase change of  $Fe_3O_4$ .

The SEM image shows that magnetite nanoparticles have a mean diameter of about 20 nm and a nearly spherical shape in Fig. 3(a) and (b) shows that MNPs-IL-OAc nanoparticles still keep the morphological properties of  $Fe_3O_4$  except for a slightly larger particle size and smoother surface, which silica are uniform coated on the  $Fe_3O_4$  nanoparticles to form MNPs supported ILs.

Fig. 4 presents the magnetization curve for Fe<sub>3</sub>O<sub>4</sub> nanoparticles and MNPs-IL-OAc. Room temperature specific magnetization (*M*) versus applied magnetic field (*H*) curve measurements of the sample indicate a saturation magnetization value ( $M_s$ ) of 52.2 emu g<sup>-1</sup>, lower than that of bare MNPs (60.6 emu g<sup>-1</sup>) due to the coated shell [39].

# 3.2. Evaluation of the catalytic activity of MNPs-ILs through the synthesis of amidoalkyl naphthols

The concept of supported ionic liquid catalysis (SILC) was first developed by Mehnert's group in 2002 [46,47]. SILC, especially MNPs supported ILs, have emerged as a new class of pseudo-homogeneous-heterogeneous nanocatalyst. An important feature of these nanocatalysts is simple separation of them using an external magnet without filtration. Also, they have high catalytic activity owing to a uniform distribution of catalytic active species within. Therefore, we are reporting here an efficient MNPs-IL-OAc catalyzed and ultrasound induced much improved modification to synthesis of 1-aminoalkyl-2-naphthol derivatives. Moreover, the ultrasound technique represented a better procedure in terms of the higher yield, milder reaction conditions.

In order to consider the effects of this nanocatalyst under ultrasound irradiation; catalytic activity of same types of magnetic nanocatalyst such as MNPs, MNP-IL-Cl and MNP-IL-OAc were compared in the reaction of aldehyde,  $\beta$ -naphthol and acetamide as the model substrates at 30 °C (Scheme 3). Obtain results were indicated that in absence of catalyst, trace amount of product was generated but in presence of MNP-IL-OAc nanoparticles the reaction proceeds in high yield. Thereafter, the reaction was evaluated by varying the concentrations of catalyst (0.01–0.04 g). The resulting of Scheme 3 shows the optimum amount of the catalyst was (0.04) of MNP-IL-OAc nanoparticles which increasing of this amount did not show any significant change in yield.

Next, we carried out the reaction in presence of various solvents and the results are presented in Table 1. It was found that dichloroethane accelerated the reaction and therefore high yields were obtained for all solid aromatic aldehydes including 3-nitrobenzaldehyde. These solvents differ with respect to polarity and have significant cavitational intensity. Dichloroethane (DCE) was found to be the best solvent (Cav. Int. 39%) [25]. Different molar ratios of reagents were examined and the best result was obtained with 1:1:1.2:0.008 ratios of  $\beta$ -naphthol, aldehyde, amide/urea and MNP-IL-OAc.

After optimizing the reaction conditions, we have extended the procedure using different kinds of aldehyde carrying either



Fig. 1. The comparative FT-IR spectra for (a) MNPs, (b) MNP-IL-OAc.



Fig. 2. XRD patterns of (a) MNPs, (b) MNP-IL-OAc.



Fig. 3. The SEM image of (a) MNPs (b) MNPs-IL-OAc.



Fig. 4. Magnetization curves for the prepared MNPs and MNPs-IL-OAc at room temperature.



Scheme 3. Optimization of the model reaction using magnetic catalysts under ultrasonic irradiation.

#### Table 1

Reaction of 3-nitrobenzaldehyde (5 mmol),  $\beta$ -naphthol (5 mmol) and acetamide (6 mmol) to obtain in the presence of MNP-IL-OAc in different solvents and under solvent-free condition.

Entry	Solvent	Yield <sup>a</sup> (%)	Time (min)
1	CH <sub>3</sub> CH <sub>2</sub> OH	60	20
2	CH <sub>3</sub> OH	53	20
3	CH <sub>3</sub> CN	45	20
4	CHCl <sub>3</sub>	70	20
5	CH <sub>2</sub> Cl <sub>2</sub>	85	20
6	$C_2H_4Cl_2$	98	20
7	n-Hexane	No reaction	60
8	Solvent-free condition	65	60



<sup>a</sup> Isolated yield.

electron-donating or -withdrawing substituents. In all cases, aromatic aldehydes with substituent carrying either electron-donating or electron withdrawing groups reacted successfully and gave the products in excellent yields.

The study was extended to prepare various amidoalkyl naphthols using MNP-IL-OAc nanoparticles. For explain the efficiency and scope of the present process and to delineate the role of ultrasound, reactions were compared at heating conditions (method A) and ultrasonic irradiation (method B) in ambient conditions at

Fig. 5. Reusability and recycling of nanocatalyst for synthesis of **4a** under ultrasound irradiation.

30 °C in the presence of MNP-IL-OAc 0.04 g (Table 2). As illustrated in Table 2, method B in comparison with method A is better in both yields and especially in the reaction times. Once more, ultrasound enhanced the rate of a reaction and, consequently, reduced energy consumption. The driving force for the increased efficiency of formation of amidoalkyl naphthols by ultrasound is because of the increase in the temperature due to the formation of hot spots; and

#### Table 2

One-pot synthesis of amidoalkyl naphthols in the presence of MNPs-IL-OAc under heating conditions and sonication (method A and B).<sup>a</sup>

Entry	R <sup>1</sup>	R <sup>2</sup>	Product	Method B	Method A	Mp (lit. mp) [Ref.]
				Time (min)/yield <sup>b</sup> (%)	Time (min)/Yield <sup>b</sup> (%)	
1	C <sub>6</sub> H <sub>5</sub>	CH <sub>3</sub>	4a	10/95	90/90	242–244 [245–246] [7]
2	$4-CH_3C_6H_4$	CH <sub>3</sub>	4b	20/91	150/87	223-224 [222-223] [7]
3	$4-N(CH_3)_2C_6H_4$	CH <sub>3</sub>	4c	30/93	180/85	120-122 [123-125] [7]
4	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	4d	20/92	190/85	184–186 [183–185] [7]
5	$3-NO_2C_6H_4$	CH <sub>3</sub>	4e	20/98	60/97	253-254 [256-258] [51]
6	$2,4-Cl_2C_6H_3$	CH <sub>3</sub>	4g	20/93	180/93	202-203 [201-203] [7]
7	2-ClC <sub>6</sub> H <sub>4</sub>	CH <sub>3</sub>	<b>4i</b>	20/94	100/88	214-216 [213-215] [7]
8	$2-NO_2C_6H_4$	CH <sub>3</sub>	4j	15/95	80/92	217-219 [218-219] [50]
9	2,3-(CH <sub>3</sub> O) <sub>2</sub> C <sub>6</sub> H <sub>3</sub>	CH <sub>3</sub>	41	20/93	180/90	231-233 [231-233] [51]
10	C <sub>10</sub> H <sub>7</sub>	CH <sub>3</sub>	4m	20/92	150/90	229-230 [229-230] [51]
11	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	CH <sub>3</sub>	4n	20/90	150/87	222-223 [224-226] [52]
12	C <sub>6</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>5</sub>	40	15/95	100/85	238-240 [237-238] [52]
13	$3-NO_2C_6H_4$	C <sub>6</sub> H <sub>5</sub>	4p	25/97	90/92	230-233 [232-234] [52]
14	4-CH <sub>3</sub> OC <sub>6</sub> H <sub>4</sub>	C <sub>6</sub> H <sub>5</sub>	4q	25/92	210/80	209-211 [208-210] [52]
15	C <sub>6</sub> H <sub>5</sub>	$NH_2$	4r	10/90	90/82	177-178 [177-179] [52]
16	$3-NO_2C_6H_4$	NH <sub>2</sub>	4s	15/92	85/88	190–192 [193] [48]

<sup>a</sup> Reaction conditions: β-naphthol 5 mmol, aldehyde 5 mmol, amide 6 mmol and MNPs-IL-OAc 0.04 g.

<sup>b</sup> Isolated yields.



Scheme 4. Possible mechanism for the synthesis of amidoalkyl naphthol using MNP-IL-OAc.



Fig. 6. XRD patterns of recovered MNPs-IL-OAc after five recovery.

due to increase in the reactant contact surface area through cavitation phenomenon. Upon irradiation with ultrasound, the formation, growth, and implosive collapse of bubbles can create extreme chemical and physical conditions in solid/liquid systems, leading to short-lived localized hot-spots which produce relatively high temperature for this one-pot condensation reaction to occur, and the rate of the reaction got well accelerated under sonic condition [49]. Moreover, when cavitation phenomenon occurs near the solid catalyst surface, cavity collapse is non-spherical and as a result of this a liquid jet will be formed which is targeted at the surface and this effect is equivalent to high-pressure/highvelocity liquid. These jets activate the heterogeneous catalyst and increase the mass transfer to the surface by the disruption of the interfacial boundary layers as well as dislodging the material occupying the inactive sites [49c].

A proposed mechanism for this reaction was outlined in Scheme 4. The MNP-IL-OAc as a Lewis acid participate in the reaction which activate the aldehyde followed by nucleophilic addition of β-naphthol forming the intermediate ortho-quinone methides (o-QMs). On the basis of this mechanism, the implosive collapse of the cavitations period of the sound waves generates the bubbles at localized sites in the liquid phase. When these bubbles burst, it results in high temperature and high pressure which facilitate the intermediate o-QMs in the presence of solid catalyst. Then o-QMs reacted with amides or urea via a Michael addition to afford the expected amidoalkyl naphthols [48]. Ultrasound provides an unusual mechanism due to the immense temperatures and pressures and the extraordinary heating rate generated by cavitation bubble collapse. When the catalyst is a solid, the ultrasonic irradiation has several additional enhancement effects [49]. Since this system is a heterogeneous catalytic system, it seems that the main effect of US is due to its mechanical effect. On the other hand, during the sonication, break-up of the surface structure allows penetration of reactants and/or release of materials from surface and accelerated motion of suspended particles leads to better mass transfer [49].

The possibility of recycling the catalyst was examined after dilution with acetone and ethanol as such for subsequent experiments (up to five cycles) under similar reaction conditions without any further treatment. The results are presented in Fig. 5. As observed in Fig. 6 the XRD of the recovered nanocatalyst was indexed

according to the magnetite phase (JCPDS card No. 750449), and so there is no considerable change in its magnetic phase. Thus, the magnetite nanocatalyst is stable during synthesis of amidoalkyl naphthols under ultrasound irradiation.

Compared to other commonly employed methods for the preparation of amidoalkyl naphthols, the methodology presented herein also provided a novel, convenient and efficient access to a wide variety of amidoalkyl-2-naphthols in a one-pot manner under ultrasound irradiation. Ultrasound process as a synthetic green approach has gradually been used in this organic synthesis. Combining the advantages of ultrasonic irradiation and nanotechnology, this method provides an efficient and much improved modification of the multi-component synthesis of amidoalkyl naphthols.

#### 4. Conclusions

Simultaneously application of the ultrasonic and MNPs supported ILs as combined catalytic system in preparation of the some biologically interesting organic molecules via multicomponent reaction. Undoubtedly, as part of the continuing exploration of ultrasonic/magnetic nanocatalyst for the green organic reactions, these methods have great prospects of applications in organic syntheses, pharmacy and industrial processes that which this report opens an important field to the use of green strategy in organic process. At the outset of our studies, there was few literature precedent for the direct application of magnetically separable catalyst in combination with ultrasound.

#### Acknowledgments

We gratefully acknowledge the financial support from the Research Council of the University of Kashan for supporting this work by Grant NO. 256722/16.

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