



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



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## 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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## 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-2-naphthol 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, β-naphthols or β-naphthylamine, and amides/carbamates and/or urea under thermal and/or

heating or sonication conditions using various catalysts such as montmorillonite K10 clay [21], Ce(SO<sub>4</sub>)<sub>2</sub> [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 desired 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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to be effective and easily separated from the reaction media by applying an external magnetic field [39].

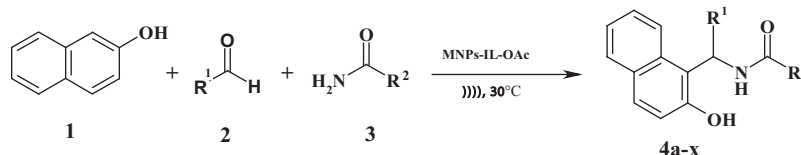
On the other hand, greener process involves mainly clean solvents, ultrasound irradiation and microwave irradiation. Ultrasound has increasingly been used in synthetic organic chemistry, because of its advantages including shorter reaction times, milder reaction conditions, higher yields, improved selectivity 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.  $^1\text{H}$  NMR and  $^{13}\text{C}$  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  $\text{cm}^{-1}$  with a Perkin-Elmer 550 spectrometer. Nanostructures were characterized using a Holland Philips Xpert X-ray powder diffraction (XRD) diffractometer (CuK $\alpha$  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 ( $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR) and physical data with those of authentic samples. All yields refer to isolated products after purification.



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

### 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  $80^\circ\text{C}$  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,  $\text{cm}^{-1}$ ): 1656, 1612, 1584.  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta_{\text{H}}$  (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,  $-\text{NCH}_2$ ), 3.86 (3H, s,  $-\text{NCH}_3$ ), 3.30 (9H, s,  $\text{OCH}_3$ ), 1.74 (2H, tt,  $J = 7.14$  Hz,  $-\text{CH}_2$ ), 0.37 (2H, t,  $J = 7.09$  Hz,  $\text{SiCH}_2$ ).  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ , TMS):  $\delta_{\text{C}} = 138.13$ , 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

$\text{Fe}_3\text{O}_4$ -MNPs were prepared using chemical coprecipitation described in the literature [39] and subsequently freshly prepared  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  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  $\text{Fe}_3\text{O}_4$  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  $100^\circ\text{C}$  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.

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