

# Ionic liquid attached to colloidal silica nanoparticles: as high performance catalyst for the preparation of dihydrofurans under microwave irradiation

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**Abstract** The preparation of *trans*-dihydrofurans has been achieved by a one-pot condensation reaction of 4-bromophenacyl bromide, aromatic aldehydes and 5,5-dimethyl-1,3-cyclohexanedione using bis (1(3-trimethoxysilylpropyl)-3-methyl-imidazolium) copper tetrachloride tethered to colloidal silica nanoparticles under microwave irradiation. Ionic liquid tethered to colloidal silica nanoparticles have been characterized by H NMR spectroscopy, scanning electron microscope, energy dispersive spectroscopy, thermogravimetric analysis and dynamic light scattering.

**Keywords** Diastereoselective synthesis · Ionic liquid · Colloidal silica nanoparticles · Heterogeneous catalysts

## Introduction

Dihydrofurans exhibit biological activities including anti-influenza [1], anti-HSV-1 [2], analgesic [3], anticancer [4], and anti-Alzheimer's disease [5]. These features make dihydrofurans useful targets in organic synthesis. A number of methods have been developed for the synthesis of dihydrofurans in the presence of diverse catalysts, such as manganese(III) acetate [6], potassium carbonate [7], piperidine [8], cerium(IV) ammonium nitrate (CAN) [9],

copper(I) triflate [10], triphenylphosphine (Ph<sub>3</sub>P) [11], [BMIm]OH [12], *N*-methyl imidazole [13], NaOH [14], and Et<sub>3</sub>N [15]. Some of the reported procedures endure drawbacks such as long reaction times, and undesirable reaction conditions. Hence, to avoid these disadvantages, the finding of an effective method for the preparation of dihydrofurans is still favored.

In recent years, synthesis and immobilization of nanoparticles in ionic liquids (ILs) have been widely studied [16–22]. Ionic liquids can be considered as valuable key precursor compounds for catalysts [23–29]. The nature of cation–anion interactions in ambient temperature ionic liquids is an issue of increasing interest [30, 31]. The structures of 1-ethyl-3-methylimidazolium (Emim) and 1-butyl-3-methylimidazolium (Bmim) with transition metal chloride anions including NiCl<sub>4</sub><sup>2−</sup>, CoCl<sub>4</sub><sup>2−</sup>, and PdCl<sub>4</sub><sup>2−</sup> were investigated [32–35]. Herein, we report the use of bis (1(3-trimethoxysilylpropyl)-3-methyl-imidazolium) copper tetrachloride tethered to colloidal silica nanoparticles as an efficient catalyst for the diastereoselective synthesis of dihydrofurans by reaction of 4-bromophenacyl bromide, aromatic aldehydes and 5,5-dimethyl-1,3-cyclohexanedione under microwave irradiation (Scheme 1).

## Experimental

### Materials and characterization

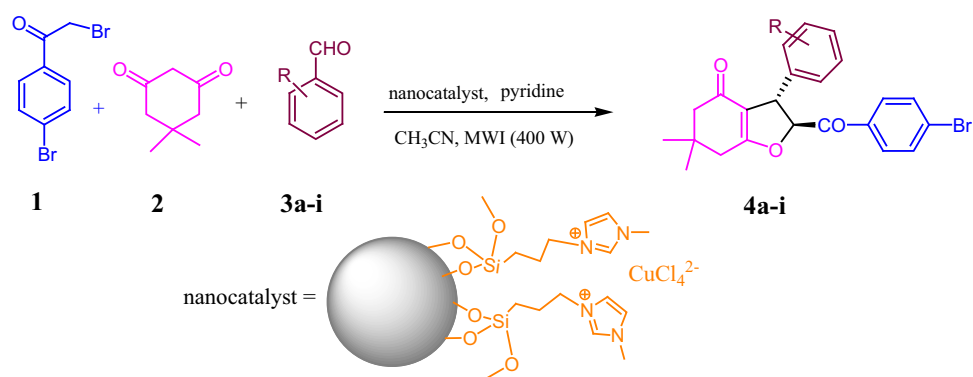
DLS was carried out using a Malvern Zetasizer Nano-S. The thermogravimetric analysis (TGA) curves are recorded using a V5.1A DUPONT 2000. To study the morphology and particle size of NPs, FE-SEM analysis and EDS spectrum of the products was visualized by a Sigma ZEISS.

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**Scheme 1** The preparation of dihydrofurans**Table 1** Optimization of reaction condition using different catalysts

Entry	Solvent (MWI)	Catalyst (amount)	Time (min)	Yield <sup>a</sup> (%)
1	$\text{CH}_3\text{CN}$ (500 W)	–	30	12
2	$\text{EtOH}$ (500 W)	Piperidine (10 mol %)	25	52
3	$\text{CH}_3\text{CN}$ (400 W)	Piperidine (10 mol %)	25	60
4	$\text{CH}_3\text{CN}$ (500 W)	$\text{ZrO}_2$ (3 mol %)	25	30
5	$\text{CH}_3\text{CN}$ (500 W)	<i>p</i> -TSA (10 mol %)	30	25
6	$\text{CH}_3\text{CN}$ (500 W)	$\text{InCl}_3$ (5 mol %)	30	20
7	$\text{CH}_3\text{CN}$ (400 W)	$\text{Et}_3\text{N}$ (10 mol %)	25	62
8	$\text{CH}_3\text{CN}$ (400 W)	Nano-ZnO (8)	25	38
9	$\text{CH}_3\text{CN}$ (400 W)	IL/nano-colloidal silica (12 mg)	15	86
10	$\text{CH}_3\text{CN}$ (400 W)	IL/nano-colloidal silica (14 mg)	15	90
11	$\text{CH}_3\text{CN}$ (400 W)	IL/nano-colloidal silica (16 mg)	15	90
12	$\text{CH}_3\text{CN}$ (300 W)	IL/nano-colloidal silica (14 mg)	15	84
13	$\text{CH}_3\text{CN}$ (500 W)	IL/nano-colloidal silica (14 mg)	15	90
14	$\text{EtOH}$ (400 W)	IL/nano-colloidal silica (16 mg)	15	74
15	$\text{DMF}$ (400 W)	IL/nano-colloidal silica (16 mg)	15	66
16	$\text{H}_2\text{O}$ (500 W)	IL/nano-colloidal silica (16 mg)	15	52
17	$\text{CH}_2\text{Cl}_2$ (500 W)	IL/nano-colloidal silica (16 mg)	15	35

Reaction conditions: a mixture of 4-bromophenacyl bromide (1 mmol), 5,5-dimethyl-1,3-cyclohexanedione (1 mmol), benzaldehyde **1** ( $\text{R}=\text{H}$ ) (1 mmol), in the presence of pyridine (1 mmol) and catalyst for various times

<sup>a</sup> Isolated yield

### Preparation of ionic liquid/nano-colloidal silica

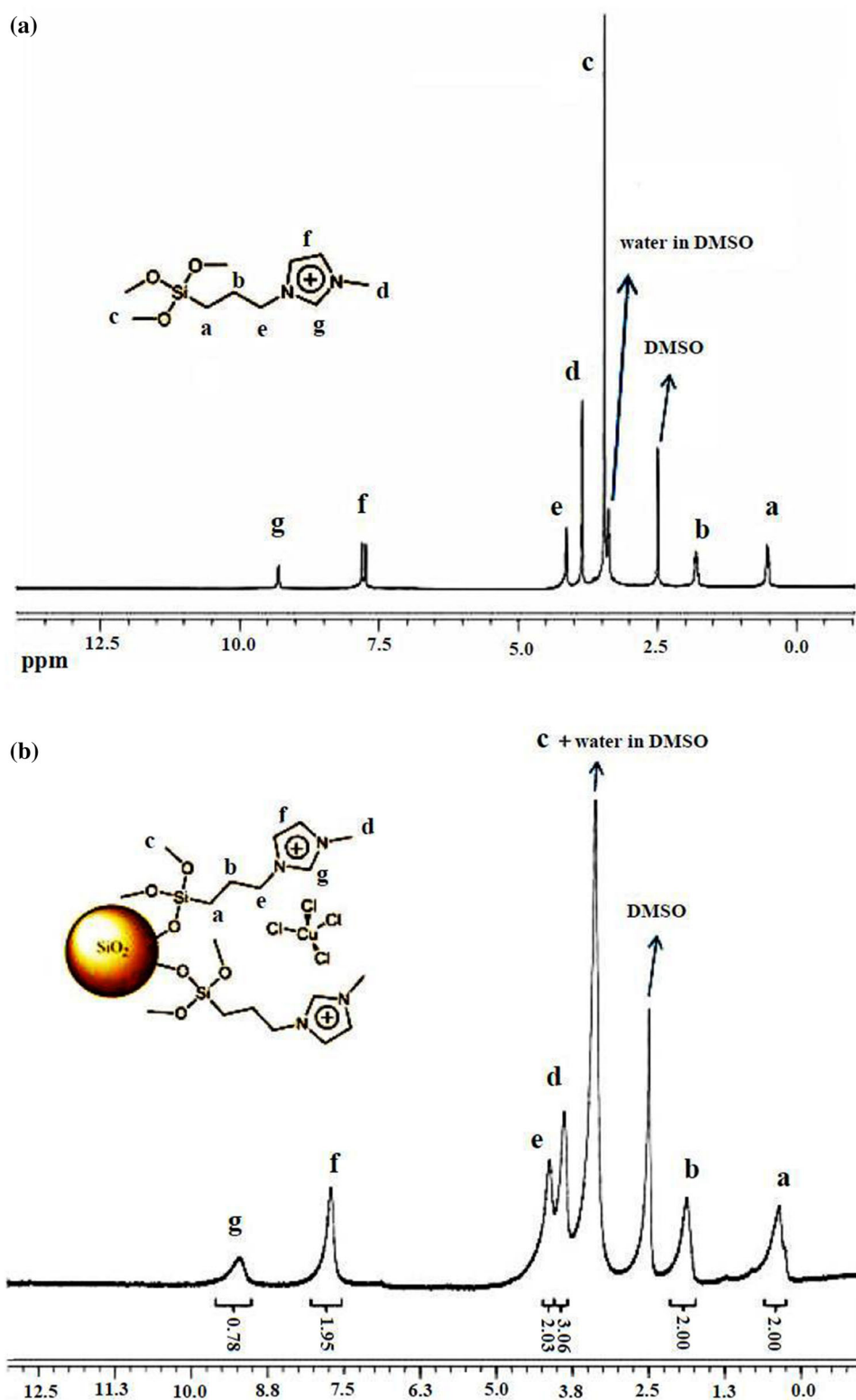
In a typical procedure, 0.098 mL of colloidal silica nanoparticles (LUDOX SM colloidal silica 30 wt% suspension in  $\text{H}_2\text{O}$ ) was diluted in 3 mL of deionized water, and 1.8 mmol of 1-(3-trimethoxysilylpropyl)-3-methylimidazolium chloride (IL) was added slowly with continuous stirring during 1 h. Then, 0.15 g of  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  was added and refluxed for 24 h. After 24 h, IL functionalized silica nanoparticles was separated by centrifugation and washed with acetone and methanol for four times, then IL/ $\text{Cu}^{2+}/\text{SiO}_2$  was dried by lyophilization/freezing-drying. The purity of the resultant IL/ $\text{Cu}^{2+}/\text{SiO}_2$  was confirmed using  $^1\text{H}$  NMR spectrum. The Cu loading was measured using XRF to be 4.7 wt%.

### General procedure for the preparation of *trans*-2,3-dihydrofuran (**4a-i**)

1 mmol of pyridine and 1 mmol of 4-bromophenacyl bromide were stirred for 2 min. Then, aldehyde (1 mmol), 5,5-dimethyl-1,3-cyclohexanedione (1 mmol) and bis (1-(3-trimethoxysilylpropyl)-3-methylimidazolium) copper tetrachloride tethered to silica nanoparticles (nanocatalyst) (14 mg) in 15 mL of acetonitrile were added and the mixture was irradiated in microwave oven at 50 °C and 400 W (Table 1). After ending of the reaction (TLC),  $\text{CHCl}_3$  was added. The catalyst was insoluble in  $\text{CHCl}_3$  and it could therefore be recycled by an easy filtration. The solvent was evaporated and the solid obtained recrystallized from ethanol to afford the *trans*-2,3-dihydrofuran.



**Fig. 1** **a**  $^1\text{H}$  NMR spectrum of 1(3-trimethoxysilylpropyl)-3-methyl-imidazolium chloride and **b** bis (1(3-trimethoxysilylpropyl)-3-methyl-imidazolium) copper tetrachloride tethered to silica nanoparticles (nanocatalyst) in dimethyl sulfoxide (DMSO)



*trans*-2-(4'-bromobenzoyl)-3-phenyl-6,6-dimethyl-3,5,6,7-tetrahydro-2H-benzofuran-4-one (**4a**): White solid, m.p. 152–154 °C, IR (KBr):  $\nu_{\text{max}}$  = 3056.2, 3032.5, 2966.7, 2894.2, 1697.5, 1634.6, 1586.3, 1224.7  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR

(400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.123 (s, 3H,  $\text{CH}_3$ ), 1.179 (s, 3H,  $\text{CH}_3$ ), 2.219 (ABq,  $J$  = 16.0 Hz, 2H), 2.338 (ABq,  $J$  = 18.0 Hz, 2H), 4.702 (d,  $J$  = 4.8 Hz, 1H), 5.625 (d,  $J$  = 4.8 Hz, 1H), 7.125 (m, 3H, ArH), 7.227 (m, 2H, ArH),



7.613 (d,  $J = 8.0$  Hz, 2H, ArH), 7.684 (d,  $J = 8.0$  Hz, 2H, ArH) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  28.9, 29.6, 34.8, 37.8, 49.4, 51.5, 91.5, 115.4, 126.5, 127.4, 127.7, 129.5, 133.6, 135.5, 136.6, 141.5, 176.7, 192.5, 194.4 ppm; Anal. Calcd. for  $\text{C}_{23}\text{H}_{21}\text{BrO}_3$ : C, 64.95; H, 4.98; Found C, 64.76; H, 4.82.

*trans*-2-(4'-bromobenzoyl)-3-(4-chloro-phenyl)-6,6-dimethyl-3,5,6,7-tetrahydro-2H-benzo furan-4-one (**4b**): White solid, m.p. 194–196 °C, IR (KBr):  $\nu_{\text{max}} = 3055.4$ , 3027.7, 2956.2, 2883.5, 1694.7, 1646.3, 1578.5, 1235.2  $\text{cm}^{-1}$ ;  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  1.163 (s, 3H,  $\text{CH}_3$ ), 1.247 (s, 3H,  $\text{CH}_3$ ), 2.235 (ABq,  $J = 18.0$  Hz, 2H), 2.254 (ABq,  $J = 20.0$  Hz, 2H), 4.406 (d,  $J = 4.4$  Hz, 1H), 5.765 (d,  $J = 4.4$  Hz, 1H), 7.173 (d,  $J = 8.4$  Hz, 2H), 7.327 (d,  $J = 8.4$  Hz, 2H), 7.614 (d,  $J = 8.0$  Hz, 2H), 7.685 (d,  $J = 8.0$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (100 MHz,  $\text{CDCl}_3$ ):  $\delta$  28.9, 29.6, 34.4, 37.8, 49.2, 51.5, 89.7, 115.8, 127.5, 128.3, 128.8, 130.2, 131.7, 133.5, 136.3, 137.5, 176.8, 193.3, 193.8 ppm; Anal. Calcd. for  $\text{C}_{23}\text{H}_{20}\text{BrClO}_3$ : C, 60.08; H, 4.38; Found: C, 59.85; H, 4.43.

## Results and discussion

Figure 1a, b exhibit the  $^1\text{H}$  NMR spectra for the 1(3-trimethoxysilylpropyl)-3-methyl-imidazolium chloride and bis (1(3-trimethoxysilylpropyl)-3-methyl-imidazolium) copper tetrachloride tethered to silica nanoparticles in dimethyl sulfoxide (DMSO), respectively. The NMR spectra of both materials are consistent with expected results for untethered and silica-tethered ionic liquids.

Figure 2 shows FE-SEM image of bis (1(3-trimethoxysilylpropyl)-3-methyl-imidazolium) copper tetrachloride tethered to silica nanoparticles (nanocatalyst). It is observed that the particles are strongly aggregated and glued with very large and continuous aggregates easily observed.

To investigate the size distribution of nanocatalysts [36, 37], dynamic light scattering (DLS) measurements of the nanoparticles were showed in Fig. 3. The size distribution is centered at a value of 43.8 nm. The dispersion for DLS analysis (2.5 g of nanocatalyst at 50 mL of ethanol) was performed using an ultrasonic bath (60 W) for 30 min. This analysis is in accordance with the previous SEM picture.

The elemental compositions of the nanocatalyst were studied by energy dispersive spectroscopy (EDS). EDS confirmed the attendance of Si, O, N, C, Cl and Cu in the compound (Fig. 4).

Thermogravimetric analysis (TGA) considers the thermal stability of the ionic liquid of untethered to  $\text{SiO}_2$  (pure ionic liquid) and silica-tethered ionic liquids. The curve shows a weight loss about 36.8% for ionic liquid@nano-

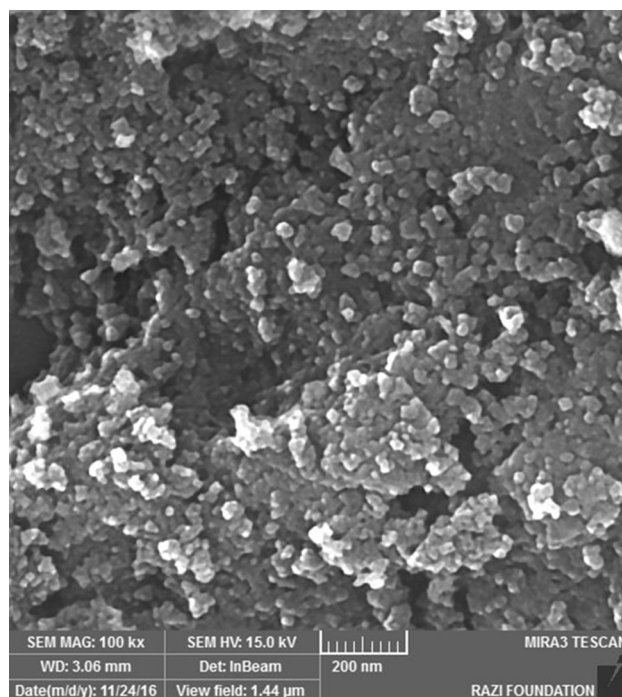


Fig. 2 FE-SEM image of nanocatalyst

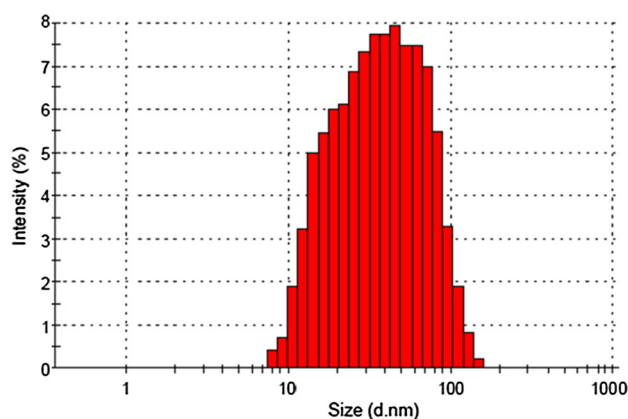
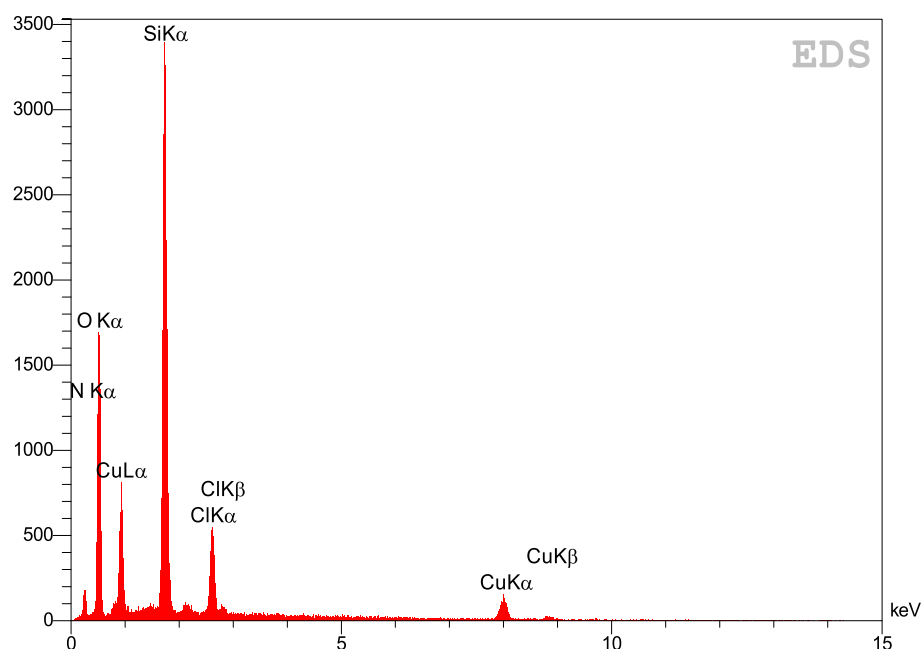
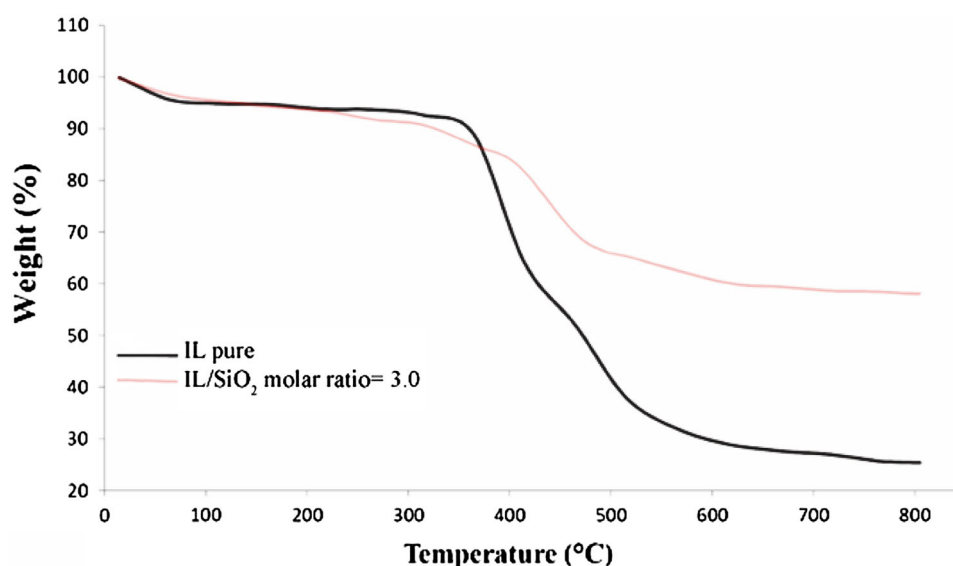


Fig. 3 DLS of nanocatalyst

colloidal silica from 240 to 550 °C, resulting from the destruction of organic spacer attaching to the nanoparticles. Hence, the nanocatalyst was stable up to 240 °C (Fig. 5).

We commenced our investigation by testing the reaction of 4-bromophenacyl bromide **1** (1 mmol), 5,5-dimethyl-1,3-cyclohexanedione **2** (1 mmol) benzaldehyde **3a** (R=H) (1 mmol) in the presence of pyridine (1 mmol) for the synthesis of dihydrofuran derivative **4a**. To obtain the ideal reaction conditions for the synthesis of compound **4a**, we studied some other catalysts, and solvents which are shown in Table 1. Screening of different catalysts such as piperidine,  $\text{ZrO}_2$ , *p*-TSA,  $\text{InCl}_3$ ,  $\text{Et}_3\text{N}$ , nano-ZnO and IL/nano-colloidal silica revealed IL/nano-colloidal silica (14 mg) as the most effective catalyst to perform this reaction under

**Fig. 4** EDS of nanocatalyst**Fig. 5** TGA of IL and nanocatalyst

microwave irradiation (400 W) (Table 1). In this study, microwave irradiation is utilized as a rapid procedure for the synthesis of dihydrofurans. The reaction is heated from the inside and the microwave energy is transmitted straightly to the substrates and catalyst [38, 39]. The nanocatalysts absorb microwave irradiation, hence they can utilize as an internal heat origin for the reactions.

We explored the feasibility of the reaction by choosing some representative substrates (Table 2). It has been considered that better yields are achieved with substrates having electron-withdrawing groups.

We also considered reusability of the IL/nano-colloidal silica as catalyst under microwave irradiation in

acetonitrile for the synthesis of product **4a** and it was found that product yields reduced to a small extent on each reuse (run 1, 90%; run 2, 90%; run 3, 89%; run 4, 89%; run 5, 88%).

A mechanism for the preparation of dihydrofurans **4a–i** using IL/nano-colloidal silica is proposed in Scheme 2. The reaction occurs via a Knoevenagel condensation between arylaldehydes **3a–i** and 5,5-dimethyl-1,3-cyclohexanedione **2**, forming the intermediate **I** on the active sites of IL/nano-colloidal silica. Afterwards, the Michael addition of pyridinium ylide with enone **I** affords the zwitterionic intermediate that undergoes cyclization to the title product. This mechanism is supported by literatures

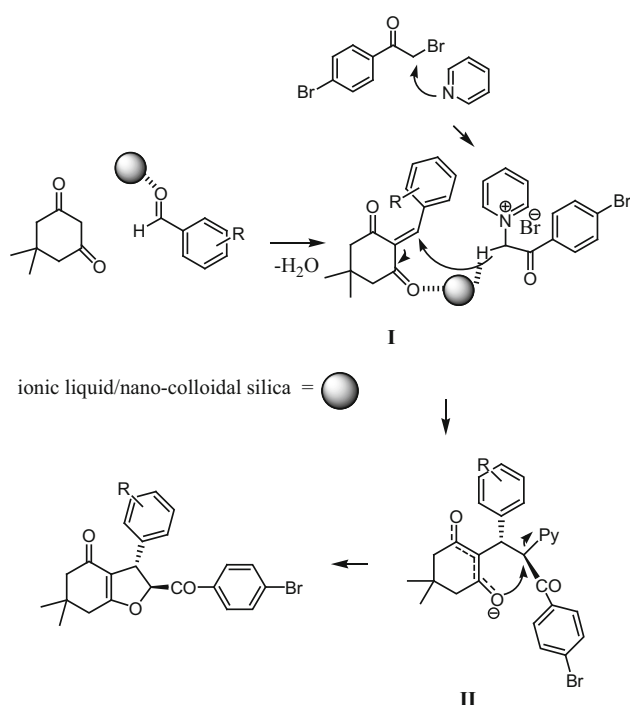


**Table 2** Yields of a series of dihydrofurans derivatives **4a–i** (R = various)

Entry	R	Product	Time (min)	Yield <sup>a</sup> (%)	m.p./°C found
1	H	<b>4a</b>	15	90	152–154
2	<i>p</i> -Cl	<b>4b</b>	15	94	194–196
3	<i>o</i> -Cl	<b>4c</b>	15	92	174–176
4	<i>m</i> -Cl	<b>4d</b>	15	91	155–157
5	<i>p</i> -CH <sub>3</sub>	<b>4e</b>	20	85	182–185
6	<i>p</i> -OCH <sub>3</sub>	<b>4f</b>	20	80	175–177
7	<i>m</i> -NO <sub>2</sub>	<b>4g</b>	15	92	204–206
8	<i>p</i> -NO <sub>2</sub>	<b>4h</b>	20	95	215–217
9	<i>p</i> -Br	<b>4i</b>	20	94	135–137

Reaction conditions: a mixture of 4-bromophenacyl bromide **1** (1 mmol), 5,5-dimethyl-1,3-cyclohexanedione **2** (1 mmol), arylaldehyde **3a–i** (R = various) (1 mmol), in the presence of pyridine (1 mmol), and IL/nano-colloidal silica (14 mg) under microwave irradiation (400 W) in acetonitrile (15 mL)

<sup>a</sup> Isolated yield

**Scheme 2** Possible mechanism for the synthesis of *trans*-2,3-dihydrofuran using IL/nano-colloidal silica

[12, 13, 15]. In this mechanism, the cation of ionic liquid activates the C=O group for better reaction with nucleophiles. Also, anion of ionic liquid acts as a weak base to promote removal of acidic protons.

## Conclusion

In this study, we described the preparation of *trans*-2,3-dihydrofuran using ionic liquid attached to colloidal silica nanoparticles as a reusable and efficient catalyst. The

advantages of this method are reusability of the catalyst, diastereoselective synthesis and utilizing of microwave as clean procedure.

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