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### Preparation, characterization, and catalytic application of nano Ag/ZnO in the oxidation of benzylic C-H bonds in sustainable media<sup>+</sup>

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Nano Ag/ZnO is successfully synthesized by a new simple and low cost method employing  $Zn(NO_3)_2 \cdot 6H_2O$ , AqNO<sub>3</sub>, and urea. X-ray diffraction (XRD), transmission electron microscopy (TEM), adsorption/desorption porosimetry (BET) and X-ray photoelectron spectroscopy (XPS) were used to characterize the structure and morphology of the catalyst. The amount of Ag loading on ZnO (9.276  $\times$  10<sup>-5</sup>, 7.391  $\times$  10<sup>-5</sup>, 3.632  $\times$  $10^{-5}$ , and 3.286  $\times$   $10^{-5}$  mol%) was determined by induced coupled plasma (ICP). The resulting ZnOsupported Ag nanoparticles efficiently catalyzed the oxidation reactions of alkyl-substituted benzenes with hydrogen peroxide  $(H_2O_2)$  as a cheap and environmentally friendly oxidant under solvent-free conditions. This catalytic reaction gave good to excellent yield of products by using mild reaction conditions and no additives were employed during the reaction.

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#### Introduction

Catalytic oxidation by inexpensive, safe, and environmentally friendly oxidants, such as oxygen, hydrogen peroxide or *t*-butyl hydro peroxide is a feasible method for the synthesis of many commodity chemicals as well as perfumes, drugs and pharmaceuticals.1-4 Among all oxidation reactions, direct benzylic oxidation of alkylarenes via C-H bond abstraction using an inexpensive and safe oxidant under mild conditions for the synthesis of ketones attracts considerable attention.<sup>5</sup> Ketones are important intermediates for the assembly or synthesis of complex organic molecules as well as for the manufacture of high-value and high-tonnage chemicals, agrochemicals, and pharmaceuticals.<sup>6,7</sup> Due to the great importance of these compounds in industry, many reports have been published for the synthesis of ketones.8-10 Classical benzylic C-H bond oxidations are accomplished with a large excess of metal based oxidants (chromium and manganese reagents) which have suffered from drawbacks such as exhausting of toxic metal residues, tedious work-up procedures, and waste disposal.5 To overcome these drawbacks active catalysts mainly for liquid phase oxidations have also been reported.11 Most catalytic systems based on Co,<sup>12-15</sup> Pt,<sup>16</sup> Cu,<sup>17,18</sup> Ag,<sup>19</sup> and Au,<sup>20</sup> are also known. Moreover, zinc salts as inexpensive and environmentally friendly catalysts and also as a non-redox metal have been reported for the redox reactions.21 Unfortunately by using most of these catalytic systems the reactions are often performed at

high pressure, high temperature, using an additional solvent, and also lack of selectivity. For instance, cobalt(II) oxideimmobilized mesoporous silica (Co/SBA-15) was reported to catalyse the oxidation of ethyl benzene; however, the catalytic reaction was shown to work only at relatively high temperatures (120-150 °C) and give only moderate % conversion of ethyl benzene. Furthermore, the catalyst was reported to form mixed uncontrolled oxidation products such as 1-phenylethyl hydro peroxide, benzoic acid, acetophenone and 1-phenylethanol.<sup>14</sup> Therefore, development of eco-friendly and cheap catalysts for efficient oxidation of C-H bonds under mild reaction conditions (avoiding elevated pressure and working under neat condition) in combination with appropriate stoichiometry oxidant is currently remain to be among major research efforts in catalysis.

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ZnO, a functional n-type semiconductor, both in bulk and nano size, is attracting significant attention. ZnO can act as a potential candidate for applications in energy generators, sensors, lasers, optoelectronics, light-emitting diodes, and catalysts.<sup>22-26</sup> In particular, ZnO has been proven to exhibit better photo catalytic proficiency for the degradation of some organic compounds than that of the TiO<sub>2</sub>, which is currently the most extensively studied photo catalysis. ZnO is also biodegradable, nontoxic and biocompatible for environmental applications, making it more competitive than those other metal oxides. For the above mentioned diverse applications, various shapes, and doping with metals of ZnO in nano dimensions have been synthesized. Recent researches revealed that modification with noble metals, such as Au, Ag, or Pt is an effective way to prohibit the recombination of charge carriers and to raise the photo catalytic performance of ZnO photo catalysts for degrading toxic organic pollutants.<sup>27-30</sup> Especially,

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Ag/ZnO nanostructures with various morphologies have been obtained with different synthesis strategies, and it was shown activities as electron sinks, improving the separation of photo generated electrons and holes, increasing the surface hydroxyl contents of ZnO, facilitating trapping the photo induced electrons and holes to form more active hydroxyl radicals and therefore, enhancing the photo catalytic proficiency of ZnO.<sup>31-37</sup>

In this paper, we would like to report the preparation of nano Ag/ZnO by a new and cheap method with various loadings of Ag on ZnO. This new catalyst (Ag/ZnO) was fully characterized by various methods such as TEM, XPS, BET, ICP and XRD. Then to show the efficiency of this catalyst, its application in benzylic C–H bond oxidation under solvent-free condition was studied.

#### **Results and discussion**

#### Characterization of the catalyst

**Catalyst preparation.** As described in the Experimental section, Ag/ZnO nanoparticles were prepared in high yield by precipitation method. Based on related literature,  $^{38-43}$  a possible mechanism is proposed, as schematically in eqn (1)–(9).

$$CO(NH_2)_2 + 3H_2O \rightarrow 2NH_4^+ + CO_2 + 2OH^-$$
 (1)

$$Zn(NO_3)_2 \cdot 6H_2O + H_2O \rightarrow Zn^{2+} + 2NO_3^{-}$$
 (2)

$$AgNO_3 + H_2O \rightarrow Ag^+ + NO_3^-$$
(3)

$$\operatorname{Zn}^{2+} + 2\operatorname{OH}^{-} \to \operatorname{Zn}(\operatorname{OH})_2 \downarrow$$
 (4)

$$Ag^+ + OH^- \rightarrow AgOH \downarrow$$
 (5)

$$Zn(OH)_2 + 2OH^- \rightarrow Zn(OH)_4^{2-}$$
(6)

$$AgOH + OH^{-} \rightarrow Ag(OH)_{2}^{-}$$
<sup>(7)</sup>

$$Zn(OH)_4^{2-} + 2Ag(OH)_2^{-} \rightarrow Ag_2O/ZnO + 2H_2O + 4OH^{-}$$
 (8)

$$Ag_2O/ZnO + NH_4^+ \rightarrow Ag/ZnO$$
 (9)

At first,  $Zn(NO_3)_2$  and  $AgNO_3$  were reacted with  $H_2O$ , and corresponding  $Zn^{2+}$  and  $Ag^+$  ions were formed. By the addition of urea,  $Zn(OH)_2$  and AgOH was formed (eqn (4) and (5)). When the amount of urea increased (addition of 10%) more than stoichiometric amount,  $Zn(OH)_2$  and AgOH will be gradually dissolved into  $Zn(OH)_4^{2-}$  and  $Ag(OH)_2^-$ , respectively (eqn (6) and (7)). Under the alkaline thermal condition, intermolecular dehydrolysis between  $Zn(OH)_4^{2-}$  and  $Ag(OH)_2^-$  may occur, and  $Ag_2O/ZnO$  was formed (eqn (8)). Urea here plays a dual role, acting not only as a co-solvent but also as a reducing agent to reduce  $Ag^+$  into Ag. Finally, Ag/ZnO nanoparticles would be produced.

According to this method, four kinds of Ag/ZnO nanoparticles were prepared. The content of Ag in Ag/ZnO nanoparticles was varied from  $9.276 \times 10^{-5}$  (Ag/ZnO (1)),  $7.391 \times 10^{-5}$  (Ag/ZnO (2)),  $3.632 \times 10^{-5}$  (Ag/ZnO (3)), and  $3.286 \times 10^{-5}$  mol% (Ag/ZnO (4)), which the molar ratio of AgNO<sub>3</sub> : Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was 1 : 1, 1 : 2, 1 : 4, and 1 : 8, respectively. The physical appearance of these

catalysts can be seen in Fig. 1. The natural color of ZnO is white. By increasing the amount of Ag doped on ZnO, the colors of the catalysts were changed from white to dark-brown.

Catalyst characterization. XRD patterns of nano Ag, nano ZnO and nano Ag/ZnO with various amounts of Ag doped on ZnO, are shown in Fig. 2. The diffraction peaks could be categorized into two sets. Those marked with "#" are the diffraction peaks at  $2\theta = 32^{\circ}$ ,  $34^{\circ}$ , and  $36^{\circ}$  and are indexed to (100), (002), and (101) diffractions of hexagonal structured ZnO (wurtzite) (JCPD no. 36-1451) respectively, while the others marked with "\*" and located at  $2\theta = 38^{\circ}$  and  $44^{\circ}$  are characteristic of (111) and (200) diffractions of FCC structured Ag (JCPDS no. 04-0783), respectively. The sharp diffraction peaks indicates that the nano Ag/ZnO are highly crystallized. Besides, the diffraction peaks corresponding to silver oxide species, for example Ag<sub>2</sub>O at 32.97° are not detected, so it can be concluded that there is no silver oxide species in the samples as well.44 Furthermore, from (a) to (f) a consistent decrease in the intensity of silver peaks can be noted with the decrease in concentration of Ag from 9.276  $\times$  10<sup>-5</sup>,  $7.391 \times 10^{-5}$ ,  $3.632 \times 10^{-5}$  and  $3.286 \times 10^{-5}$  mol%, respectively. Additionally, the average sizes of the ZnO and Ag nanoparticles, calculated by the Scherrer formula<sup>45</sup> applied to the major peaks  $(2\theta = 34^{\circ} \text{ for ZnO})$  were estimated to be approximately 36.28, 36.02, 39.6, 30.13 and 65.04 nm for Ag/ZnO (1), Ag/ZnO (2), Ag/ZnO (3), Ag/ZnO (4) and nano ZnO, respectively, and  $(2\theta = 38^{\circ})$ for Ag) were estimated to be approximately 45.83 nm, 43.79 nm, 53.31 nm, 31.55 nm and 25.57 nm for Ag/ZnO (1), Ag/ZnO (2), Ag/ZnO (3), Ag/ZnO (4) and nano Ag, respectively. With the obtained XRD results, indicated that the present catalyst (Ag/ZnO) shows the presence of Ag only, and not any peaks for silver oxides (AgO, or Ag<sub>2</sub>O) were observed. In subsequent paragraphs, we will prove this by XPS method.

By comparing the XRD pattern of pure hexagonal ZnO and nano Ag/ZnO (Fig. 3), there is a shift with the peak position of ZnO for the prepared Ag/ZnO samples ( $\sim$ 0.15°). Generally this shift in peak position value is observed when a doping element having a larger ionic radius than Zn<sup>2+</sup> is replaced at the substitutional sites of the ZnO crystal lattice. Zn<sup>2+</sup> ions (0.71 Å)



Fig. 1 Physical appearance of various Ag/ZnO nanoparticles.



Fig. 2 The XRD patterns of the Ag/ZnO nanoparticles with various Ag content, nano ZnO and nano Ag.



Fig. 3 X-ray diffraction patterns of nano ZnO (red curve) and Ag/ZnO (2) (blue curve) for comparison.

have lower ionic size than  $Ag^+$  (1.22 Å). So, this shift in the XRD peak position can be suggested that Ag ion has occupied the interstitial sites of ZnO.<sup>46</sup>

The surface structure of the Ag/ZnO sample with Ag content of 7.391  $\times 10^{-5}$ % was investigated by using XPS analysis and the results are shown in Fig. 4. All the peaks on the curve can be ascribed to Ag, Zn, O, and C elements, while C 1s at 285 eV is due to the hydrocarbon from the XPS instrument itself.<sup>47</sup> It is clear that all the peaks are ascribed to Zn, O, and Ag, and no peaks characteristic of impurities are observed. Fig. 4b shows the Zn 2p XPS spectra of the catalyst. Because of strong spin–orbit coupling, the Zn 2p peak split into Zn 2p<sub>3/2</sub> and Zn 2p<sub>1/2</sub> with a doublet peak energy separation of ~23 eV. The peak positions at 1022.8 and 1045.7 eV corresponds to the Zn 2p<sub>3/2</sub>, and Zn 2p<sub>1/2</sub>, respectively, which confirm that the Zn in the catalyst mainly exists in the form of Zn<sup>2+</sup>.<sup>48</sup>

Fig. 4c provides the XPS spectra of Ag. The Ag  $3d_{5/2}$  and  $3d_{3/2}$  peaks appear at a binding energy of 367.5 and 373.1 eV,



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Fig. 4 XPS spectra of the sample with a Ag content of  $7.391 \times 10^{-5}$  mol%: (a) XPS full spectrum of the sample; (b) Zn 2p spectrum; (c) Ag 3d; (d) O 1s spectrum spectra.

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Fig. 5 Transmission electron microscopic (TEM) image of Ag/ZnO (2).

respectively. Here, interestingly, the peaks of Ag in our work were found to shift to the lower binding energy compared with the standard value (about 368.2, and 374.1 eV). This confirms the interaction between Ag and ZnO nanocrystals. When the Ag and ZnO nanoparticles attach together, they adjust the position of their corresponding Fermi energy levels to the same value. Thus, there are many free electrons above the new Fermi level of metallic Ag nanoparticles. Because the conduction band (CB) of ZnO nanoparticles is vacant, the free electrons could tunnel into the CB, resulting in the higher valence of Ag.<sup>49,50</sup> This is in consistent than the results from XRD.

Fig. 4d shows the O 1s peaks of Ag/ZnO catalyst. The O 1s peak can be divided into two peaks at about 530 and 532 eV, corresponding to the lattice oxygen and surface hydroxyl oxygen, respectively.

The BET surface areas of Ag/ZnO (2) catalyst synthesized in this work are measured about 4.204 m<sup>2</sup> g<sup>-1</sup>. Results of BET surface area measurements for nano Ag/ZnO (2) are shown in Table 1.

The morphology of nano Ag/ZnO (2) obtained from TEM analysis was displayed in Fig. 5. The size of Ag/ZnO nanoparticle that was seen from TEM image was about in the range of 34 nm.

Table 1         Results of BET surface area measurements for Ag/ZnO (2)			
Surface area	BET surface	4.20	
	area (m <sup>2</sup> g <sup><math>-1</math></sup> )		
	BJH adsorption	4.86	
	cumulative surface		
	area of pores $(m^2 g^{-1})$		
Pore volume	Single point adsorption	0.03	
	total pore volume of		
	pores (cm <sup>3</sup> g <sup><math>-1</math></sup> )		
	BJH adsorption cumulative	0.03	
	volume of pores (cm <sup>3</sup> g <sup><math>-1</math></sup> )		
Pore size	Mean pore diameter (nm)	31.27	
	Pore size distribution (nm)	2.74	

**Catalytic activity of nano Ag/ZnO for oxidation of benzylic C-H bonds.** The catalytic activities of the synthesized Ag/ZnO nanoparticles with different amounts of Ag loading were then investigated in ethyl benzene oxidation reaction. Initially, the catalytic activity of various Ag/ZnO nanoparticles catalysts for the oxidation of ethylbenzene to acetophenone was investigated and the results are shown in Table 2, which reveals that the conversion of ethylbenzene is >90% on Ag/ZnO (1) and (2). The lower conversion of product with Ag/ZnO (3) and (4) may be due to the insufficient amount of Ag. Then we tried to optimize the solvent, temperature, and amount of the catalyst. The results are summarized in Table 3.

According to Table 3, the impact of reaction temperature in the oxidation of ethylbenzene can be also seen from entries 1–4. At room temperature, the conversion of ethylbenzene was around 50%, which has been rising up to 90% when the reaction temperature was increased to 80 °C. Then the amount of catalyst was investigated, and 0.005 g of Ag/ZnO (2) was found to be fitful for the catalysis (Table 3, entries 2, 5–7). The best result was obtained with 0.005 g of nano Ag/ZnO (2) (Table 3, entry 5). The elevated amount of the catalyst did not give any improvement in the yield. In the absence of catalyst the reaction did not proceed well even after extending the time (Table 3, entry 7).

A wide range of literature shows that the selective production of acetophenone from ethylbenzene is a challenge on heterogeneous catalysts. High selectivity towards acetophenone is mainly hindered due to the formation other oxygenates *via* different oxidation sites depending upon the type of catalyst used.<sup>51</sup> Benzaldehyde, benzoic acid, phenylacetic acid, styrene, 1-phenylethane-1,2-diol *p*-acetophenone, *m*-acetophenone *etc.* are the<sup>52,53</sup> other products that are generally formed from ethylbenzene oxidation. As evidenced from the results obtained during the oxidation of ethyl benzene using nano Ag/ZnO (2), the major product was acetophenone with high selectivity and other by products were not observed.

After optimization of the reaction conditions, a number of methylene compounds were submitted to equivalent reaction conditions to examine the scope and the generality of the nano Ag/ZnO (2) to form ketones. The results are summarized in Table 4.

Table 4, showing that not only monoarylated methylene groups (entries 1–3), but also diactivated (diarylated) methylene positions (entries 4 and 5) can be efficiently oxidized to the corresponding ketones. The extension of the scope of this advantageous oxidation methodology to other substrates is currently under investigation.

The heterogeneity of the catalyst was evaluated to study whether the reaction using solid catalysts or was catalyzed by Ag/ZnO species in the liquid phase. To address this issue, two separate experiments were conducted with ethyl benzene. In the first experiment, the reaction was terminated after two hours; at this juncture, the catalyst was separated from the reaction mixture, and the reaction was continued with the filtrate for an additional three hours. In the second experiment, the reaction was terminated after two hours. In both cases, the desired Table 2 Effect of Ag loading on ZnO in the oxidation of ethyl benzene to acetophenone<sup>a</sup>



Entry	Catalyst	Time (h)	Yield (%)
1	$Ag/ZnO(1)^b$	7	90
2	$Ag/ZnO(2)^{c}$	7	90
3	$Ag/ZnO(3)^d$	7	80
4	$Ag/ZnO(4)^{e}$	7	75

<sup>*a*</sup> Reaction condition: ethyl benzene (1 mmol), catalyst (0.005 g),  $\rm H_2O_2$  (1 mmol), solvent-free, 80 °C. <sup>*b*</sup> The amount of Ag is 9.276 × 10<sup>-5</sup> mol%. <sup>*c*</sup> 7.391 × 10<sup>-5</sup> mol%. <sup>*d*</sup> 3.632 × 10<sup>-5</sup> mol%. <sup>*e*</sup> 3.286 × 10<sup>-5</sup> mol%.

Table 3Effect of solvent, amount of catalyst, and temperature for the<br/>oxidation of ethyl benzene $^{a}$ 

Entry	Solvent	Cat. (g)	$T(^{\circ}C)$	Time (h)	Yield (%)
1	None	0.01	100	11	52
2	None	0.01	80	10	83
3	None	0.01	50	8	70
4	None	0.01	r.t.	8	53
5	None	0.005	80	7	90
6	None	0.0025	80	9	80
7	None	None	80	11	10
8	THF	0.005	80	9	20
9	DMF	0.005	80	9	30
10	DMSO	0.005	80	8	40
11	$H_2O$	0.005	80	9	50
12	EtOH	0.005	80	8	50
13	CH <sub>3</sub> CN	0.005	80	8	60
14	None	$0.01^{b}$	80	11	0
15	None	$0.01^{c}$	80	11	0

 $^a$  Reaction condition: ethyl benzene (1 mmol), nano Ag/ZnO (2), H<sub>2</sub>O<sub>2</sub> and solvent (1 mL).  $^b$  Only nano ZnO was used as catalyst.  $^c$  Only nano Ag was used as catalyst.

product was obtained in the same yield (45%). Ag was not detected in the filtrate in either experiment by ICP analyzer. These studies demonstrate that only the Ag bound to ZnO during the reaction is active, and the reaction proceeds on the heterogeneous surface. We also confirmed that no leaching of Ag from the Ag/ZnO catalyst occurred during the oxidation of ethyl benzene no Ag can be detected in the filtrate after the reaction.

Recycling of the nano Ag/ZnO catalyst was also examined. For this, the oxidation reaction of ethyl benzene in the presence of nano Ag/ZnO (2) was studied. When the reaction was completed, the reaction mixture was diluted by EtOAc and the catalyst was easily separated by centrifugation, dried under vacuum and reused in a subsequent reaction. The recycled catalyst was used for five times (Table 5).



<sup>*a*</sup> Reaction condition: substrate (1 mmol),  $H_2O_2$  (1 mmol), nano Ag/ZnO (2) (0.005 g), 80 °C. <sup>*b*</sup> Large scale test: ethylbenzene (50 mmol),  $H_2O_2$  (50 mmol) in the presence of 0.005 g of nano Ag/ZnO (2).

 Table 5
 Reuse-ability of the recovered catalyst<sup>a</sup>

Recycle number	Yield (%)
1	90
2	87
3	87
4	85
5	85

 $^a$  Reaction condition: ethylbenzene (1 mmol), solvent-free, 1 mmol $\rm H_2O_2,$  80 °C, nano Ag/ZnO (2) (0.005 g), for 7 h.



In order to investigate the stability of nano Ag/ZnO (2) during the 5 consecutive cycles, the XRD pattern of the catalyst after 5 times recycling was analyzed. As shown in Fig. 6, no

notable change were detected, which is indicative of catalyst stability for at least 5 times reuses. The X-ray diffraction patterns of the reuse catalyst were found to be similar to the fresh sample.

### Conclusions

In conclusion, four different silver doped on zinc oxide catalysts have been prepared and used as catalysts for oxidation reactions in the atmospheric pressure in solvent-free condition. Good yields have been observed in oxidation of methylene compounds, heading to aromatic ketones. Moreover, this catalyst is an active heterogeneous catalyst in the oxidation of benzylic C–H bonds.

#### **Experimental section**

All the reagents and materials, including, zinc nitrate  $(\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O})$ , silver nitrate  $(\text{AgNO}_3)$  and urea were obtained from Fluka or Merck and used as received without further purification. The catalyst was characterized using XRD, XPS, ICP, TEM and BET. The catalyst was characterized by X-ray diffraction technique using Bruker D8-advance X-ray diffractometer with Cu Ka ( $\lambda = 1.54178$  Å) radiation. The size of nanoparticles was confirmed by Zeiss – EM10C – 80 KV TEM instrument. The specific surface areas (SSABET; (m<sup>2</sup> g<sup>-1</sup>)) of the nanopowders were determined with the nitrogen adsorption measurement applying the BET method at 77 K (BELsorp-mini II). X-ray photoelectron spectroscopy (XPS) measurements were conducted with a XR3E2 (VG Microtech) twin anode X-ray source using AlK $\alpha = 1486.6$  eV. Silver content (wt%) were determined by ICP.

#### General procedure for the synthesis of catalyst

 $Zn(NO_3)_2 \cdot 6H_2O$ , AgNO<sub>3</sub> and  $CO(NH_2)_2$  (molar ratio of AgNO<sub>3</sub> :  $Zn(NO_3)_2 \cdot 6H_2O$  :  $CO(NH_2)_2 = 1 : 1 : 1$ , 1 : 2 : 1, 1 : 4 : 1, 1 : 8 : 1) were dissolved in a minimum quantity of deionized water to form a transparent solution. The mixture was refluxed for 6 h at 100 °C. The powder was centrifuged and washed with deionized water and absolute ethanol and was allowed to dry at 80 °C in an oven. Then the catalyst was prepared after annealed at 500 °C in air atmosphere for 3 h in a high-temperature furnace.

#### General procedure for the oxidation of benzylic C-H

A mixture of alkyl benzene (1 mmol),  $H_2O_2$  (30% in water, 2 mmol) and nano Ag/ZnO (2) (0.005 g, which contains 7.391 × 10<sup>-5</sup> mol% Ag) was stirred at 80 °C in an oil bath. After the reaction was completed, EtOAc (10 mL) was added to the reaction mixture, and nano Ag/ZnO was removed by centrifuge. The organic solvent was then washed with  $H_2O$  (2 × 10 mL) and a saturated solution of NaHCO<sub>3</sub> (10 mL) and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After removal of the solvent, the pure product was obtained. This was further purified by column chromatography. The structure of the products was confirmed by <sup>1</sup>H NMR, <sup>13</sup>C NMR and comparison with authentic samples obtained commercially or prepared by reported methods.

All compounds are known and were characterized by comparison of their physical and spectroscopic data with the already described in the literatures.

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