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$Ni_{0.5}Zn_{0.5}Fe_2O_4$@HA-PRS NANOPARTICLE: A RECOVERABLE GREEN CATALYST FOR THE SYNTHESIS OF TETRAHYDROBENZO[b]PYRANS IN WATER

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ABSTRACT. A green, efficient and simple technique for the synthesize of tetrahydrobenzo[*b*]pyrans through one-pot three-component reaction of dimedone, aromatic aldehydes and malonitrile as active methylene compound using immobilization of Preyssler heteropoly acid on $Ni_{0.5}Zn_{0.5}Fe_2O_4$ magnetite nanoparticles (MNPs), coated with hydroxyapatite (HA) as a catalyst is described. Comparing with the previous studies on preparation of these compounds, the present methodology suggests some benefits which include high yields, short reaction times and green reaction conditions (room teperature in H_2O). More importantly, the magnetic catalyst was isolated from the reaction mixture using a simple magnet and efficiently reused at least five runs without any loss of catalytic activity. Thus, the developed separable catalysts are potentially beneficial for the economic production of organic compounds.

KEY WORDS: One-pot, Three-component, Tetrahydrobenzo[*b*]pyrans, Preyssler, Heteropoly acid, Magnetite nanocatalyst

INTRODUCTION

Designing and preparation of reusable catalysts are of great economic and environmental importance in the chemical and medicinal industries. Immobilization of homogeneous catalysts on various insoluble supports can lead to simplify the catalyst recycling process via different methods [1]. Recyclability and reusability are important features of heterogeneous catalysts, compared with homogeneous catalysts [2, 3]. Therefore, design of new heterogeneous catalysts is very important [4].

At present, nanoparticles (NPs) are used as solid supports for immobilizing homogeneous catalysts [5]. Because of their large surface area, which can carry a high amount of catalytically active species, these supported catalysts exhibit very high activity under mild conditions. Among these NPs, much attention has been directed towards the production of magnetic nanoparticles (MNPs), because these NPs can be well dispersed in the reaction mixtures without the magnetic field providing a large surface for ready access of substrate molecules. This point is important since at the end of the reactions, the MNP catalysts can be separated completely from the mixture using an appropriate external magnet [6]. There are several MNP oxides, for examples: Fe_3O_4, Fe_2O_3, $MnFe_2O_4$, $CoFe_2O_4$, $NiFe_2O_4$, $CuFe_2O_4$, etc. Nickel zinc ferrite ($Ni_{0.5}Zn_{0.5}Fe_2O_4$) is a type of MNP that has attracted attention because of its excellent thermal stability, moderate saturation magnetization, remarkable chemical stability, and mechanical hardness [7]. Coating of these nanoparticles with HA to obtain $Ni_{0.5}Zn_{0.5}Fe_2O_4$@HA composite can impart extra stabilization to such MNPs and retard their agglomeration in solutions [8]. The outer layer of HA makes it suitable for multifunctional surface modification, including catalyst immobilization [9, 10].

Preyssler ($H_{14}NaP_5W_{30}O_{120}$) is an important heteropoly acid (HPA) which has significant advantages, such as 14 acidic protons, high thermal stability, high hydrolytic stability ($0 < pH < 12$) and safety [11, 12]. Due to the low surface area (7–10 m^2/g) and high solubility of HPAs in polar solvents, it is usually preferred to use them in a supported form. These catalysts can be

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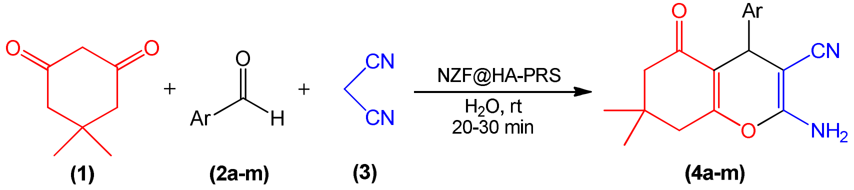
*Corresponding author. E-mail: alijavids@yahoo.com supported on acid-neutral solids, such as silica and alumina, hydroxyapatite (HA), activated carbons, zeolites and acidic ion-exchange resins [11-13].

4*H*-pyrans belong to a main group of heterocyclic compounds with essential biological roles [14]. They are reported to have several pharmaceutical properties such as antibacterial [15], antioxidant [16], antiallergic [17], potassium channel activator [18], and insulin-sensitizing activities [19]. They are also reported to serve as an important regulator for potassium cation channel [20] and photochemical activities [21].

Because of the intense interest in the biological activity of these compounds, several improved procedures for the synthesis of pyrans were reported [22]. One of the main approaches for synthesizing tetrahydrobenzo[*b*]pyrans is one-pot condensation of an aldehyde, dimedone and malononitrile. Most of these methods employ various catalysts such as $NH_4Al(SO_4)_2$ [23], magnetic Fe_3O_4/phenylsulfonic acid [24], magnetite-dihydrogen phosphate [25], ionic liquid [26, 27], magnetite supported heteropoly acid [28], mixed metal nano-oxides [29], molecular iodine [30], Ru(II) complexes [31], copper oxide nanoparticles [32], lithium bromide [33], sodium selenate [34], HPA-dendrimer functionalized magnetic nanoparticle [35], and nano α-Al_2O_3 supported ammonium dihydrogen phosphate [36]. However, despite these procedures are relatively useful, most of the methods encounter some limitations, such as expensive catalysts, long reaction times, toxic organic solvents and harsh reaction conditions. Thus, developing simple, efficient, clean, high yielding, and environmentally friendly approaches using new catalysts for synthesizing these compounds is a key role of organic chemists.

As a part of our program for investigating the use of reusable catalysts in organic reactions [37-42], the present article describes the results of an extended investigation into the activity of the Preyssler HPA supported onto the hydroxyapatite (HA) coated $Ni_{0.5}Zn_{0.5}Fe_2O_4$ MNPs ($Ni_{0.5}Zn_{0.5}Fe_2O_4$@hydroxyapatite-Preyssler, abbreviated NZF@HA-PRS) as an effective catalyst for synthesizing tetrahydrobenzo[*b*]pyran derivatives. Facile isolation of the catalyst using a magnetic field and the reusability of the catalyst (up to five cycles) is other main advantages of this system. According to our knowledge, there is no report on the application of NZF@HA-PRS as a novel nano magnetically-recoverable green catalyst for synthesizing tetrahydrobenzo[*b*]pyrans from the condensation of dimedone, aromatic aldehydes and malonitrile at ambient temperature in water. Therefore, we want to develop a simple, rapid and an efficient synthetic technique for synthesizing these compounds using NZF@HA-PRS as a heterogeneous nano acidic catalyst (Scheme 1).



Scheme 1. Synthesis of tetrahydrobenzo[*b*]pyran derivatives in the presence of NZF@HA-PRS as a nano acidic catalyst.

EXPERIMENTAL

All materials and chemicals were obtained from companies of Merck and Aldrich and utilized with no further purification. An Electrothermal model 9100 melting point apparatus was used to determine melting points. A Thermo Nicolet AVATAR-370 FT-IR spectrophotometer and a Bruker DRX400 spectrometer were used to provide FT-IR spectra and ^{1}H NMR spectra. NZF@HA-PRS was synthesized according to a previous report [42]. For synthesis of this catalyst, the Preyssler HPA was immobilized on the NZF@HA (the core-shell NZF@HA was synthesized based on our previous report [8]): To a suspension of NZF@HA (3 mmol; 1.0 g) in water (50 mL) was added a solution of the Preyssler HPA (0.1 mmol; 0.75 g) in water (5 mL) dropwise. The mixture was stirred for 12 h at ambient temperature under N_2 atmosphere. The solvent was evaporated and the supported catalyst was collected, dried under vacuum overnight and calcinated at 250 °C for 2 h.

*Synthesis of tetrahydrobenzo[b]pyran derivatives (**4a-m**)*

A combination of dimedone (1.0 mmol), aromatic aldehydes (1.0 mmol) malonitrile (1.0 mmol), and NZF@HA-PRS (2×10^{-3} mmol; 0.03 g) in water (10 mL) was stirred at room temperature for 20-30 min. Upon completion (TLC monitoring using *n*-hexane/ethyl acetate, 1:1 as an eluent), the nano-magnetic catalyst was isolated from the reaction mixture using a suitable magnet placed on the outside wall of the reaction vessel, washed with acetone (50 mL) and dried at 100 °C for 2 h, to be reused in the next run. Finally, the preconcentration of reaction mixture was performed under reduced pressure. The recrystallization of solid residue from ethanol was performed to produce compounds **4a-m.**

Spectral data for some selected tetrahydrobenzo[b]pyrans

*2-Amino-7,7-dimethyl-5-oxo-4-phenyl-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **(4a)***. Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.07 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 1.68 (s, 2H, CH_2), 2.41 (s, 2H, CH_2), 4.37 (s, 1H, CH), 4.73 (s, 2H, NH_2), 7.22-7.35 (m, 5H, Ph); IR (KBr) ν: 3391, 3335, 2179, 1682, 1216 cm^{-1}.

*2-Amino-7,7-dimethyl-4-(4-nitrophenyl)-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **(4c)***. Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.03 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 2.24 (s, 2H, CH_2), 2.51 (s, 2H, CH_2), 4.57 (s, 1H, CH), 4.61 (s, 2H, NH_2), 7.35 (d, J = 8.4 Hz, 2H, Ph), 8.23 (d, J = 8.8 Hz, 2H, Ph); IR (KBr) ν: 3394, 3329, 2172, 1683, 1221 cm^{-1}.

*2-Amino-4-(3-methoxyphenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **(4d)***. White solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.06 (s, 3H, CH_3), 1.14 (s, 3H, CH_3), 2.22 (s, 2H, CH_2), 2.51 (s, 2H, CH_2), 3.82 (s, 3H, OCH_3), 4.35 (s, 1H, CH), 4.61 (s, 2H, NH_2), 6.78-7.26 (m, 4H, Ph); IR (KBr) ν: 3390, 3328, 2177, 1685, 1213 cm^{-1}.

*2-Amino-4-(2-chlorophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile **(4f)***. Yellow solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ ppm: 1.09 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 2.19 (s, 2H, CH_2), 2.47 (s, 2H, CH_2), 4.60 (s, 2H, NH_2), 4.89 (s, 1H, CH), 7.11-7.29 (m, 4H, Ph); IR (KBr) ν: 3395, 3326, 2187, 1684, 1215 cm^{-1}.

RESULTS AND DISCUSSION

In order to evaluate the catalytic activity of immobilized Preyssler HPA on $Ni_{0.5}Zn_{0.5}Fe_2O_4$ MNPs coated with HA, at first, three-component facile synthesis of tetrahydrobenzo[*b*]pyran derivatives were performed in the presence of catalytic levels of NZF@HA-PRS. To establish the possibility of the strategy and optimize the conditions, the reaction of dimedone, benzaldehyde and malonitrile was chosen as a model reaction. The model reaction was examined in the diverse solvents such as CH_2Cl_2, EtOH, MeOH and H_2O as well as under solvent-free condition (Table 1). No product was achieved in the absence of the catalyst (entry 1). The reaction yield in the polar solvents, especially in the polar protic solvents was more than when using non-polar solvents and solvent-free condition (entries 6-12). We believe that because of the anionic structure generation and hydrogen bonding formation of HPAs in the polar solvents, the reaction could produce better yields (entries 10-12). Also, among these polar solvents, the use of water gave the best outcome (entry 12). Increasing the time of reaction and temperature did not improve the yield (entries 13). In addition, the model reaction was performed in the presence of Preyssler and others HPAs with Keggin structures, we observed which performance of the reaction under the same time and reaction conditions was lower than when we utilized NZF@HA-PRS as a catalyst (entries 14-16).

Table 1. Comparison of different catalysts and solvents in the preparation of tetrahydrobenzo[*b*]pyran derivative of benzaldehyde[a]

Entry	Catalyst	Solvent	Time (min)	Temperature	Yield (%)[b] [ref.]
1	None	H_2O	120	rt	No reaction
2	Na_2SeO_4	H_2O/EtOH	60	reflux	97 [34]
3	Fe_3O_4@SiO_2@NH-NH_2–PW	H_2O	30	reflux	93 [28]
4	$NH_4Al(SO_4)_2$	EtOH	120	reflux	92 [23]
5	Fe_3O_4@Ph-SO_3H	H_2O	30	rt	95 [24]
6	NZF@HA-PRS	solvent-free	30	rt	41 (this work)
7	NZF@HA-PRS	solvent-free	30	100°C	58 (this work)
8	NZF@HA-PRS	CH_2Cl_2	30	rt	Trace (this work)
9	NZF@HA-PRS	CH_3CN	30	rt	23 (this work)
10	NZF@HA-PRS	MeOH	30	rt	67 (this work)
11	NZF@HA-PRS	EtOH	30	rt	75 (this work)
12	NZF@HA-PRS	H_2O	20	rt	88 (this work)
13	NZF@HA-PRS	H_2O	60	reflux	89 (this work)
14	$H_{14}[NaP_5W_{30}O_{110}]$	H_2O	30	rt	80 (this work)
15	$H_3[PW_{12}O_{40}]$	H_2O	30	rt	74 (this work)
16	$H_4[SiW_{12}O_{40}]$	H_2O	30	rt	69 (this work)

[a]Dimedone (1 mmol), benzaldehyde (1 mmol) and malononitrile (1 mmol), in the present of different catalyst and different conditions. [b]Isolated yields.

To find the optimal amount of NZF@HA-PRS, the model reaction was performed under the earlier mentioned conditions with various amounts of catalyst (Table 2). No product was achieved without the presence of the catalyst (entry 1) demonstrating that the catalyst is necessary for this reaction. Increasing the amount of the catalyst enhanced the efficiency of the product **4a** (entries 2-5). The use of 0.03 g of catalyst produced the maximum efficiency in 20 min (entry 5). Enhancing the amount of the catalyst beyond this value did not increase the efficiency of the reaction noticeably (entries 6).

Table 2. Optimizing the level of NZF@HA-PRS in synthesis of tetrahydrobenzo[*b*]pyran derivative of benzaldehyde[a]

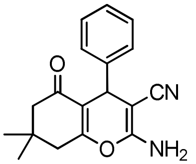
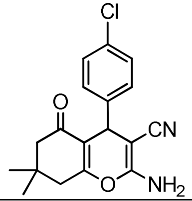
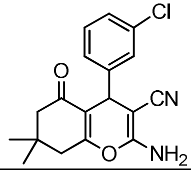
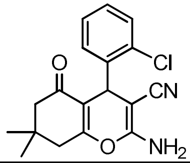
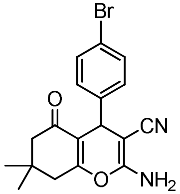
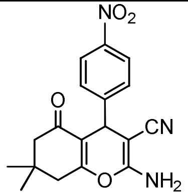
Entry	Catalyst amount (g)	Time (min)	Yield (%)[b]
1	None	120	No reaction
2	0.005	30	Trace
3	0.01	30	41
4	0.02	30	70
5	0.03	20	88
6	0.05	20	89

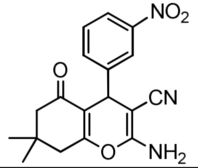
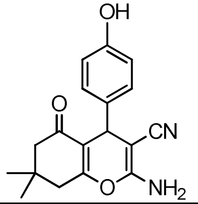
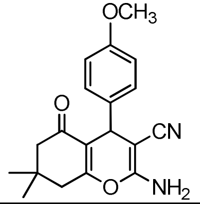
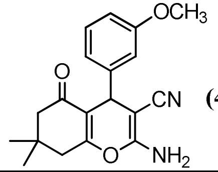
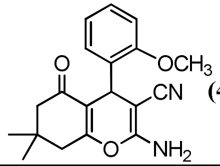
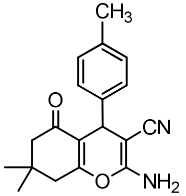
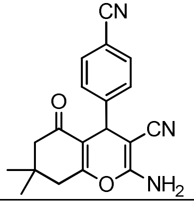
[a]Dimedone (1 mmol), benzaldehyde (1 mmol) malononitrile (1 mmol), and NZF@HA-PRS at room temperature in water. [b]Isolated yields.

Finally, under these optimal conditions, the scope and yield of the reaction were investigated when an extensive range of substituted 2-amino-4-aryl-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-

4*H*-chromene-3-carbonitriles were synthesized in the presence of NZF@HA-PRS. The results are presented in Table 3. Interestingly, a range of aryl aldehydes with electron-withdrawing or releasing substituents (ortho, meta, and para-substituted) participated well in this reaction and gave the desired product, 2-amino-4-aryl-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4*H*-chromene-3-carbonitriles in high yield (83-93%) confirming its efficiency.

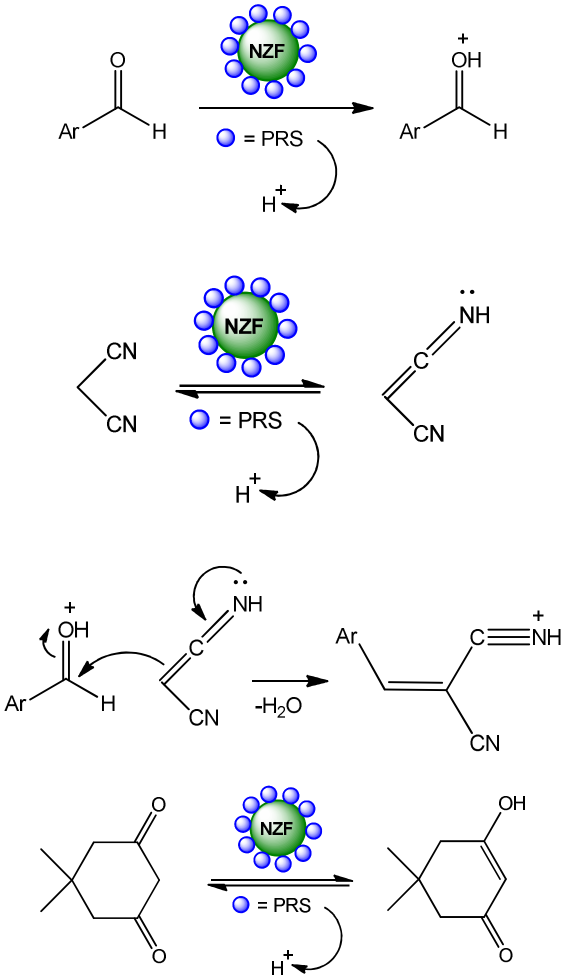
Table 3. Synthesis of tetrahydrobenzo[*b*]pyrans using of NZF@HA-PRS as a catalyst[a].

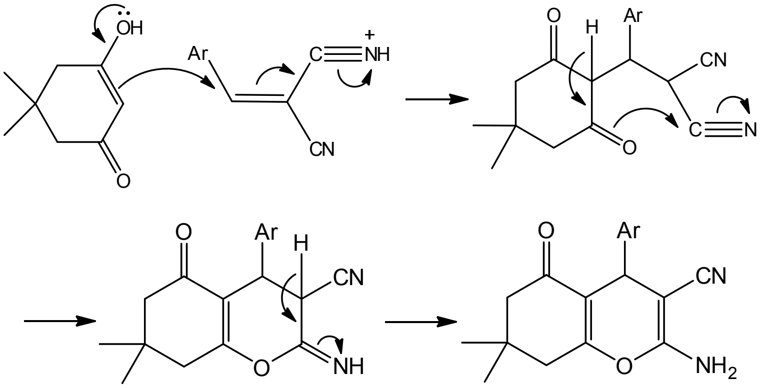
Entry	Aldehyde	Product	Yield (%)[b]	Mp (°C) Found	Mp (°C) Reported [ref.]
1	C_6H_5CHO	 **(4a)**	88	226-228	231-233[23]
2	$4\text{-}ClC_6H_4CHO$	 **(4b)**	90	211-213	217-219[23]
3	$3\text{-}ClC_6H_4CHO$	 **(4c)**	89	231-233	230-232[26]
4	$2\text{-}ClC_6H_4CHO$	 **(4d)**	87	216-218	213-215[26]
5	$4\text{-}BrC_6H_4CHO$	 **(4e)**	91	205-207	200-202[23]
6	$4\text{-}NO_2C_6H_4CHO$	 **(4f)**	93	178-180	182-184[25]

7	3-NO$_2$C$_6$H$_4$CHO	 **(4g)**	90	204-206	210-212[25]
8	4-OHC$_6$H$_4$CHO	 **(4h)**	86	212-214	207-209[23]
9	4-MeOC$_6$H$_4$CHO	 **(4i)**	88	198-200	203-205[25]
10	3-MeOC$_6$H$_4$CHO	 **(4j)**	86	204-206	208-210[25]
11	2-MeOC$_6$H$_4$CHO	 **(4k)**	83	202-204	200-202[25]
12	4-MeC$_6$H$_4$CHO	 **(4l)**	91	215-217	221-223[23]
13	4-CNC$_6$H$_4$CHO	 **(4m)**	92	215-217	220-223[26]

[a]Conditions: dimedone (1 mmol), aldehyde (1 mmol), malononitrile (1 mmol), and NZF@HA-PRS catalyst (0.03 g) at room temperature in water, after 20-30 min. [b]Isolated yields.

Using literature [28], we proposed the following mechanism for synthesizing tetrahydrobenzo[*b*]pyrans in the presence of nano acidic catalyst (Scheme 2). Initially, both aldehyde and active methylene compound (malonitrile) are activated in the presence of Preyssler HPA as a Bronsted acid. After Knoevenagel condensation and removal of a water molecule, the product reacts with 1,3-dicabonyl compound (dimedone) via Michael addition. Finally, an intramolecular cyclization and then, tautomerization of the intermediate afforded the desired tetrahydrobenzo[*b*]pyran derivative.





Scheme 2. Suggested mechanism for synthesis of tetrahydrobenzo[*b*]pyrans promoted by NZF@HA-PRS.

In terms of green chemistry, high efficiency and recyclability of the catalyst are greatly desirable. For this purpose, the similar model reaction was investigated under optimal conditions for a second time. At the end of the reaction, the nano-magnetic catalyst was isolated from the mixture using a simple external magnet and then washed with acetone, dried at 100 °C under vacuum for 2 h, and reused for a similar reaction. As shown in Figure 1, the catalyst could be reapplied at least five times without significant loss of its activity. In addition, there was no difference between the weight of the recovered catalyst and the fresh one that was used in the first cycle.

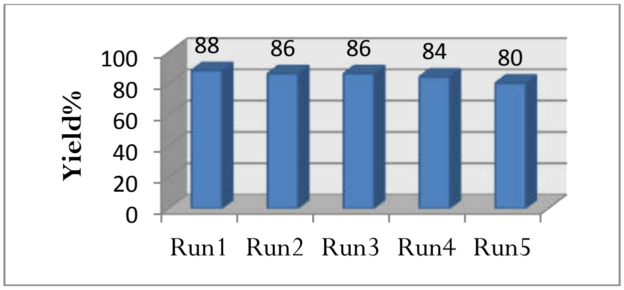


Figure 1. Reusability of NZF@HA-PRS for the model reaction.

CONCLUSION

In summary, we have used NZF@HA-PRS as an effective, and eco-friendly solid acid catalyst to synthesize tetrahydrobenzo[*b*]pyran derivatives which were prepared via a one-pot three component reaction system containing dimedone, aromatic aldehydes and malonitrile at ambient temperature in water as a green solvent. The catalyst could be recycled after a very simple workup (with the aid of an external magnet), and reused at least five runs with no considerable change in its catalytic activity. Excellent yields (up to 93%), enhanced reaction rates and short reaction times, simplicity of operations, and easy workup are some benefits of this technique. In addition to the use of synthesizing these products, the environmentally benign catalyst would be potentially promising for a range of other acid-catalyzed chemical reactions.

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