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## Dramatic Rate Acceleration of Baylis-Hillman Reaction with Fe<sub>3</sub>O<sub>4</sub> Magnetic Nanoparticles and 1,8-diazabicyclo[5.4.0]undec-7-ene in Solvent Free Medium

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### ABSTRACT

The Baylis-Hillman reaction was greatly accelerated in the presence of Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles as an efficient and reusable co-catalyst and 1,8-diazabicyclo[5.4.0]undec-7-ene in a solvent free medium. A preliminary kinetic study revealed that the relative rate of the reaction using Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles was considerably faster than that of reaction without Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles. In this protocol the use of nanocatalyst provided a green, useful and rapid method to generate the Baylis-Hillman adducts in short reaction times and excellent yields (82-94 %).

### KEYWORDS

Baylis-Hillman reaction, Rate acceleration, Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles, 1,8-Diazabicyclo[5.4.0]undec-7-ene, Solvent free medium.

### INTRODUCTION

The Baylis-Hillman reaction, *i.e.*, the coupling of aldehydes and activated vinyl compounds, is one of the most important carbon-carbon bond forming reactions in organic synthesis [1,2]. This reaction has attracted the attention of many synthetic organic chemists because the resulting  $\beta$ -hydroxy- $\alpha$ -methylene adducts can be transformed into a variety of natural and unnatural compounds [3,4]. Several biologically natural and unnatural products such as (+)-mikanecic acid [5], sarcomycin ester [6], epopromycin B [7] and (-)-mycestericin E [8], have been synthesized using this reaction as a key step.

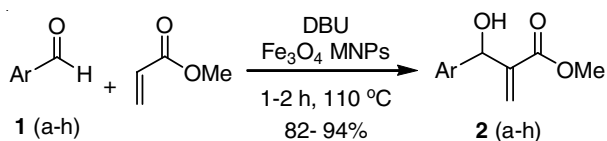
The Baylis-Hillman-Type C-C single bond formation is an exquisite reaction. The low-cost and readily available starting materials are converted, using a suitable catalyst, into functionalized products. However, the reaction suffers from poor reaction rates and many research groups have examined a variety of methods to accelerate the reaction [9].

Several attempts have been made to increase the rate of the reaction through either physical or chemical means, but there are disadvantages associated with most of the methods [10]. Various methods for the acceleration of Baylis-Hillman reaction have been developed with certain limitations [11-15]. One of the most important methods is the salt effect using Lewis acid as co-catalyst [9]. The combination of LiClO<sub>4</sub> and 1,4-diazabicyclo[2.2.2]octane (DABCO) in ether [16], use of

azoles as catalyst [17], Ionic liquid-immobilized quinuclidine [18], Lewis base effects including 4-(dimethylamino)pyridine (DMAP), N-Methylmorpholine and urotropine [19], N,N,N',N'-tetramethyl-1,3-propanediamine [20], LiBr and DBU in solvent free medium [21] in Baylis-Hillman reaction were examined.

Recently Aggarwal and co-workers [22] reported that 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) is in fact the optimum catalyst for the Baylis-Hillman reaction, providing adducts at much faster than using DABCO, 3-hydroxyquinoclidine (3-HDQ) and other catalysts.

In continuation of our interest for Baylis-Hillman adducts [23-26] and mechanistic studies of this reaction [21], herein we wish to report our novel methodology for the acceleration of Baylis-Hillman reaction with magnetic iron oxide nanoparticles (MNPs) and DBU in a solvent free medium (**Scheme-I**).



Ar = C<sub>6</sub>H<sub>5</sub>, 4-Py, 2-ClC<sub>6</sub>H<sub>4</sub>, 4-ClC<sub>6</sub>H<sub>4</sub>, 3-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>,  
4-MeC<sub>6</sub>H<sub>4</sub>, 4-MeOC<sub>6</sub>H<sub>4</sub>, 4-NMe<sub>2</sub>C<sub>6</sub>H<sub>4</sub>

**Scheme-I:** A schematic representation for the synthesis of different Baylis-Hillman adducts

## EXPERIMENTAL

All analytical grade reagents were purchased from the Merck and Aldrich chemical companies and used without further purification. IR spectra were determined on a Shimadzu IR-470 spectrometer. <sup>1</sup>H NMR spectra were recorded on a 500 MHz Bruker DRX-500 instrument in CDCl<sub>3</sub> as solvent and TMS as internal standard. The elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer. Magnetic separation was done by a super magnet with 1.4 T magnetic fields (10 × 5 × 4 cm). The morphology of particles was observed on a Philips XL30 scanning electron microscope (SEM). Specific surface areas were measured by the N<sub>2</sub> adsorption technique using a micrometris ASPS 2010 analyzer. The XRD were obtained on a STOE diffractometer with CuK<sub>α</sub> radiation.

**Preparation of Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles:** Briefly, FeCl<sub>3</sub>·6H<sub>2</sub>O (10.8 g, 40 mmol) and FeCl<sub>2</sub>·4H<sub>2</sub>O (4 g, 20 mmol) were dissolved in deionized water (100 mL), degassed with N<sub>2</sub> for 15 min and heated to 80 °C. A solution of NH<sub>4</sub>OH (32 %, 15 mL) was then added dropwise and the solid was separated after 15 min by a magnet and washed with NaCl solution (0.1 mol, 100 mL). The formation of Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles was confirmed by XRD, specific surface area measurements, SEM and EDAX microanalysis.

**Preparation of Baylis-Hillman adducts:** To a stirred mixture of methyl acrylate (0.45 mL, 5.0 mmol), aryl aldehyde (5.0 mmol) and Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (60 mg, 25 mmol) at 25 °C under nitrogen and solvent free condition was slowly added DBU (0.74 mL, 5.0 mmol) and the mixture was heated to 110 °C. After completion of the reaction, the catalyst was separated from the solution using a magnet. The reaction mixture was then separated by filtration, diluted with ether (25 mL) and washed with HCl (2 M, 15 mL) followed by

water (20 mL). The organic layer was dried over MgSO<sub>4</sub>, filtered and evaporated *in vacuo* to providing a crude mixture. The mixture was purified by column chromatography eluting with petroleum ether/diethyl ether (4:1) to give adducts **2a-h**. All products are known and were characterized by comparison of their physical and spectral data with authentic samples. Some data of selected compounds are listed below.

**Methyl 2-((4-chlorophenyl)(hydroxy)methyl) acrylate (2d):** Pale yellow solid; m.p. 42-43 °C (lit: 43-44 °C [22]); yield 93 %; IR (neat, ν<sub>max</sub>, cm<sup>-1</sup>): 3390, 2990, 2850, 1700, 1612, 1520, 1340, 1190, 810; Anal. calculated for C<sub>11</sub>H<sub>11</sub>ClO<sub>3</sub> (Found: C, 58.24; H, 4.87; requires C, 58.29; H, 4.89 %); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 4.63 (s, br, OH), 3.75 (s, 3H), 5.70 (s, 1H), 6.12 (s, 1H), 6.64 (s, 1H), 7.54 (d, 2H, J = 6.90 Hz), 7.85 (d, 2H, J = 6.90 Hz) ppm.

**Methyl 2-(hydroxy(3-nitrophenyl)methyl)acrylate (2e):** Yellow solid; m.p. 70-72 °C (lit: 71-73 °C [22]); yield 94 %; IR (neat, ν<sub>max</sub>, cm<sup>-1</sup>): 3400, 1680, 1662, 1573; Anal. calculated for C<sub>11</sub>H<sub>11</sub>NO<sub>5</sub> (Found: C, 55.63; H, 4.62; N, 5.58; requires C, 55.70; H, 4.67; N, 5.90 %); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 3.78 (s, 3H), 4.44 (s, br, OH), 5.57 (s, 1H), 5.93 (s, 1H), 6.42 (s, 1H), 7.81 (q, 1H, J = 7.20 Hz), 8.27 (d, 1H, J = 7.60 Hz), 8.51 (t, 1H, J = 7.30 Hz), 8.74 (s, 1H) ppm.

**Methyl 2-(hydroxy (p-tolyl) methyl) acrylate (2f):** Colourless solid, m.p. 40-41 °C (lit: 39-42 °C [22]); yield 88 %; IR (neat, ν<sub>max</sub>, cm<sup>-1</sup>): 3400, 3000, 2950, 1715, 1450; Anal. calculated for C<sub>12</sub>H<sub>14</sub>O<sub>3</sub> (Found: C, 69.84; H, 7.12; requires C, 69.88; H, 6.84 %); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 2.32 (s, 3H), 3.72 (s, 3H), 4.50 (s, br, OH), 5.75 (s, 1H), 5.99 (s, 1H), 6.43 (s, 1H), 7.21 (d, 2H, J = 7.43 Hz), 7.66 (d, 2H, J = 7.43 Hz) ppm.

**Methyl 2-(hydroxy (4-methoxyphenyl) methyl) acrylate (2g):** White solid, m.p. 44-46 °C (lit: 45-46 °C [21]); yield 87 %; IR (neat, ν<sub>max</sub>, cm<sup>-1</sup>): 3450, 3000, 2950, 1727, 1450; Anal. calculated for C<sub>12</sub>H<sub>14</sub>O<sub>4</sub> (Found: C, 64.81; H, 6.22; requires C, 64.86; H, 6.30 %); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 3.71 (s, 3H), 3.78 (s, 3H), 4.38 (s, br, OH), 5.57 (s, 1H), 5.92 (s, 1H), 6.42 (s, 1H), 6.94 (d, 2H, J = 6.93 Hz), 7.77 (d, 2H, J = 6.93 Hz) ppm.

**Methyl 2-((4-(dimethylamino)phenyl)(hydroxy)methyl)-acrylate (2h):** Pale green solid, m.p. 64-66 °C (lit: 65-67 °C [21]); yield 82 %; IR (neat, ν<sub>max</sub>, cm<sup>-1</sup>): 3436, 1725, 1614; Anal. calculated for C<sub>13</sub>H<sub>17</sub>NO<sub>3</sub> (Found: C, 66.32; H, 7.25; N, 5.91 requires C, 66.36; H, 7.28; N, 5.95 %); <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>): δ = 3.13 (s, 6H), 3.70 (s, 3H), 4.30 (s, br, OH), 5.43 (s, 1H), 5.75 (s, 1H), 6.43 (s, 1H), 6.74 (d, 2H, J = 8.75 Hz), 7.77 (d, 2H, J = 8.40 Hz) ppm.

## RESULTS AND DISCUSSION

Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles (MNPs) have attracted research interest because of their inherent properties such as large surface area (up to 400 m<sup>2</sup>/g) and fast response under applied external magnetic field, their super-paramagnetism, high coercivity and high thermal and mechanical stability [27-30]. Additionally, the magnetic properties make the recovery of the catalyst compete by mean of an external magnetic field [31]. These advantages even more attractive if such reactions can be conducted in aqueous media or a solvent free medium [32].

The  $\text{Fe}_3\text{O}_4$  MNPs were synthesized according to the previously reported procedure [27]. To investigate the phase of these MNPs as well as the purity, the XRD pattern of this catalyst was recorded (Fig. 1) and compared with the JCPDS (Joint Committee on Powder Diffraction Standards) card No. 851436. The pattern shows peaks at  $2\theta = 31^\circ, 35^\circ, 43^\circ, 54^\circ, 57^\circ$  and  $64^\circ$  that are attributed to (220), (311), (400), (422), (511) and (440) and confirm formation of the crystalline cubic spinel structure of the  $\text{Fe}_3\text{O}_4$  MNPs. Since no other phase peaks could be detected in the XRD pattern, this indicates high purity of the  $\text{Fe}_3\text{O}_4$  MNPs.

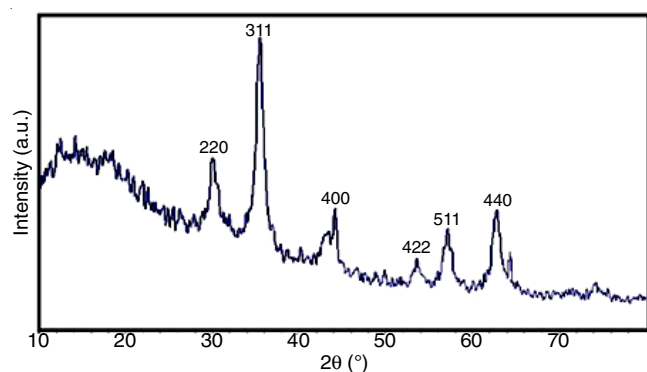


Fig. 1. XRD spectra of the  $\text{Fe}_3\text{O}_4$  MNPs

The purity of  $\text{Fe}_3\text{O}_4$  MNPs was further investigated by EDAX microanalysis (Fig. 2). It can be seen from the microanalysis that there are no impurities and only Fe and O are detected. Since the size and morphology of the  $\text{Fe}_3\text{O}_4$  MNPs are important in their catalytic efficiency, SEM micrograph images of these particles were recorded (Fig. 3). It can be seen that polyhedral MNPs (35-50 nm in diameter) were obtained under an ultrasound power.

For further investigation, the size distribution of the prepared nanoparticles was obtained using the Gaussian distribution curve, size distributions of nanoparticles have been examined by SEM and results are shown in Table-1. A total of 100 particles were measured per sample from SEM micrograph for each distribution of  $\text{Fe}_3\text{O}_4$  nanoparticles is shown in Fig. 4. The average size of  $\text{Fe}_3\text{O}_4$  MNPs produced by this method is 50-60 nm. The size of nanoparticles was calculated from the Scherrer equation and the average crystallite size was 15-19 nm.

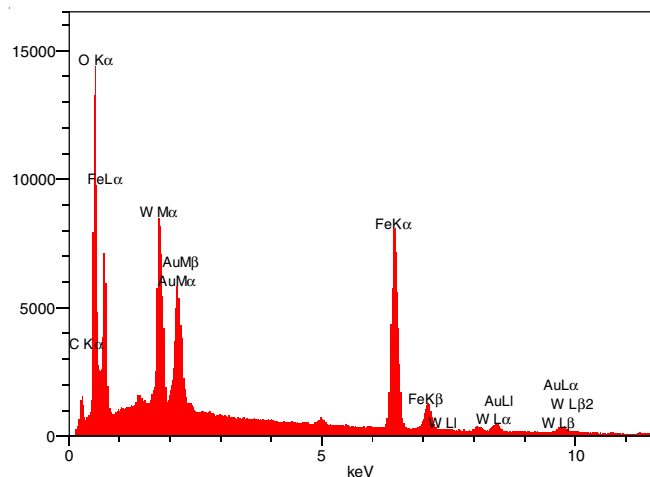


Fig. 2. EDAX analysis of the  $\text{Fe}_3\text{O}_4$  MNPs

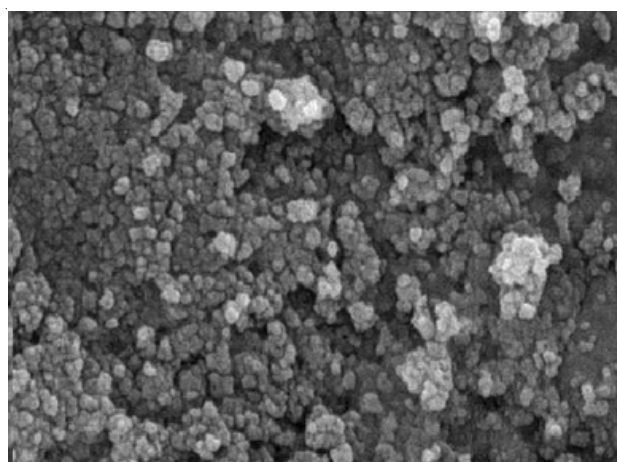


Fig. 3. SEM photographs of  $\text{Fe}_3\text{O}_4$  MNPs

TABLE-1 DISTRIBUTION MEAN AND SD	
$\text{Fe}_3\text{O}_4$ MNPs	
Mean	35 nm
S.D	17.5 nm

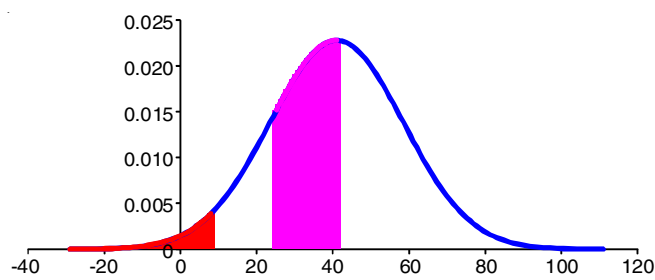


Fig. 4. Gaussian curve  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles

Another important parameter in catalytic performance is the specific surface area. The single point BET (Brunauer-Emmett-Teller) analysis showed a surface area of 342  $\text{m}^2/\text{g}$  for the  $\text{Fe}_3\text{O}_4$  MNPs.

To optimize the reaction conditions, the solvent free reaction of benzaldehyde with methyl acrylate and DBU were carried out at  $110^\circ\text{C}$  in the presence of  $\text{Fe}_3\text{O}_4$  MNPs under various conditions. Increasing the reaction time as well as the amount of co-catalyst did not improve the yield. Optimum conditions were achieved at 5 mol %  $\text{Fe}_3\text{O}_4$  MNPs and 1 h reaction time (Table-2, entry 2).

Baylis-Hillman adducts were prepared at the optimized reaction conditions by reacting methyl acrylate with different aryl aldehydes in the presence of DBU (as catalyst) and  $\text{Fe}_3\text{O}_4$

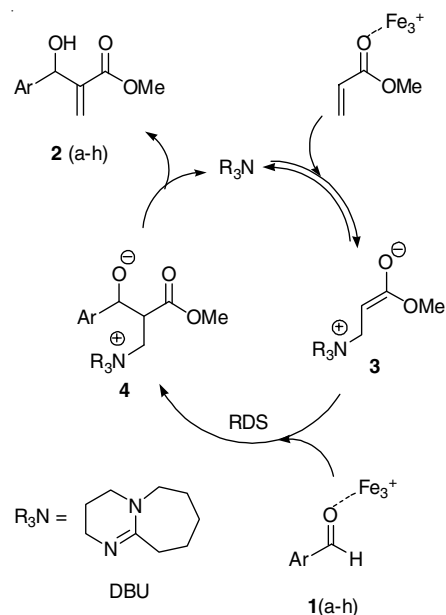
TABLE-2 OPTIMIZATION OF THE REACTION CONDITIONS AT $110^\circ\text{C}$			
Entry	Amount of MNPs (mol %)	Reaction time (min)	Yield (%) <sup>a</sup>
1	2.5	60	84
2	5	60	93
3	5	30	73
4	5	90	93
5	10	60	93

<sup>a</sup> All the reaction were carried out with benzaldehyde (1 mmol), methyl acrylate (1 mmol), DBU (1 mmol) and variable amount of MNPs in solvent free medium.

MNPs (5 mol %, as co-catalyst) under solventfree conditions for 1-2 h at 110 °C with good to excellent yields (Table-3).

A proposed mechanism of the catalyzed Baylis-Hillman reaction with DBU and Fe<sub>3</sub>O<sub>4</sub> MNPs is shown in **Scheme-II**. Mechanistic studies of this reaction show that the rate-determining step (RDS) of this reaction is the reaction of aldehyde (**1**) with the ammonium enolate (**3**). This enolate is formed by conjugate addition of the nucleophilic amine (DBU) to the methyl acrylate (a reversible process) and therefore to obtain faster rates, higher concentration of the enolate and stabilization of ammonium enolate (**3**) as intermediate are required. DBU and Fe<sub>3</sub>O<sub>4</sub> MNPs are a useful, efficient, low-cost and easily available system which can shift the equilibrium towards the generation of higher concentration of the enolate (**3**) by stabilizing this species and increases its equilibrium concentration and finally results in significant rate enhancement [22].

A preliminary kinetic study in the reaction of several aryl aldehydes with methyl acrylate revealed that relative rate of the reaction using Fe<sub>3</sub>O<sub>4</sub> MNPs was considerably faster than that of the reaction without Fe<sub>3</sub>O<sub>4</sub> MNPs (Table-4).



**Scheme-II:** Plausible mechanism for preparation of Baylis-Hillman adducts

TABLE-3  
SYNTHESIS OF BAYLIS-HILLMAN ADDUCTS

Entry	Aldehyde ( <b>1</b> )	Product ( <b>2</b> ) <sup>a</sup>	Time (min)	Yield (%) <sup>b</sup>
a	Benzaldehyde		60	93 <sup>c</sup> [22]
b	4-Pyridine carbaldehyde		60	93 <sup>c</sup> [21]
c	2-Chloro benzaldehyde		60	92 <sup>c</sup> [21]
d	4-Chloro benzaldehyde		60	93 <sup>c</sup> [22]
e	3-Nitro benzaldehyde		50	94 <sup>c</sup> [22]
f	4-Methyl benzaldehyde		75	88 <sup>c</sup> [22]
g	4-Methoxy benzaldehyde		90	87 <sup>c</sup> [21]
h	4- <i>N,N</i> -Dimethyl benzaldehyde		120	82 <sup>c</sup> [21]

<sup>a</sup>All compounds have been fully characterized spectroscopy by <sup>1</sup>H NMR, IR and elemental analyses; <sup>b</sup>Isolated yields; <sup>c</sup> Products were identified by comparison with authentic samples.

TABLE-4  
KINETIC STUDIES OF BAYLIS-HILLMAN REACTION IN THE PRESENCE OF Fe<sub>3</sub>O<sub>4</sub> MNPs

Entry	Co-catalyst	Time (h)	Yield <b>2</b> (%)	Rate (% per min)	K <sub>rel</sub>
a	None	6.00	89	0.247	6.27
	Fe <sub>3</sub> O <sub>4</sub> MNPs	1.00	93	1.550	
b	None	7.00	85	0.202	7.67
	Fe <sub>3</sub> O <sub>4</sub> MNPs	1.00	93	1.550	
c	None	10.00	84	0.140	10.95
	Fe <sub>3</sub> O <sub>4</sub> MNPs	1.00	92	1.533	
d	None	8.00	85	0.177	8.76
	Fe <sub>3</sub> O <sub>4</sub> MNPs	1.00	93	1.550	
e	None	6.00	80	0.222	8.47
	Fe <sub>3</sub> O <sub>4</sub> MNPs	0.83	94	1.880	
f	None	30.00	70	0.038	30.87
	Fe <sub>3</sub> O <sub>4</sub> MNPs	1.25	88	1.173	
g	None	48.00	62	0.021	46.03
	Fe <sub>3</sub> O <sub>4</sub> MNPs	1.50	87	0.966	
h	None	60.00	63	0.017	40.20
	Fe <sub>3</sub> O <sub>4</sub> MNPs	2.00	82	0.683	

As catalyst reusability is very important from both economic and environmental points of view, the catalytic reusability of Fe<sub>3</sub>O<sub>4</sub> MNPs was investigated in several subsequent runs. The nanocatalyst was separated from the reaction medium simply by an external magnetic field, washed with ethanol, dried under vacuum and reused for the subsequent reactions. After 10 successive runs the catalytic activity of Fe<sub>3</sub>O<sub>4</sub> MNPs was almost remained unchanged. The high reusability of the catalyst can be explained by its high thermal and mechanical stability and vast surface area owing to an extremely high porosity.

### Conclusion

In summary, for the first time we showed that Fe<sub>3</sub>O<sub>4</sub> MNPs was an effective heterogeneous co-catalyst for rate acceleration of Baylis-Hillman reaction in the presence of DBU and solvent-free conditions. The mild reaction conditions, green and cost-effective catalyst, excellent yields, easy work-up procedures, as well as high thermal and mechanical stability which avoid the use of large volumes of hazardous organic solvents, make it a useful alternative to previously applied procedures. Compared with nonmagnetic nanoparticle catalytic system, the present protocol combines the advantages of solid Lewis acid and magnetic nanoparticles and offers great potentials for the rapid synthesis of Baylis-Hillman adducts.

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