

# Magnetic BaFe<sub>12</sub>O<sub>19</sub>/Al<sub>2</sub>O<sub>3</sub>: An Efficient Heterogeneous Lewis Acid Catalyst for the Synthesis of $\alpha$ -Aminophosphonates (Kabachnik–Fields Reaction)

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Received: 14 March 2019 / Accepted: 20 July 2019 © Springer Science+Business Media, LLC, part of Springer Nature 2019

# Abstract

The design and application of environmentally friendly catalysts to reduce the quantity of toxic wastes is critical for improving the chemical synthesis process. Therefore,  $BaFe_{12}O_{19}/Al_2O_3$ , a magnetic mesoporous nanocomposites, were designed synthesized and characterized using different techniques such as energy dispersive X-ray (EDX) spectroscopy, X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), field emission scanning electron microscopy (FESEM), Brunauer–Emmett–Teller (BET) adsorption method, and vibrating sample magnetometry (VSM). The prepared  $BaFe_{12}O_{19}/Al_2O_3$  display a high surface area (1773.22 m<sup>2</sup>/g) with an average pore diameter of 3.946 nm from nitrogen sorption analysis. In addition, the synthesized nanocomposites prove to be an active heterogeneous Lewis acid catalyst for the solvent free synthesis of  $\alpha$ -aminophosphonates at ambient temperature, through three-component reaction of aldehydes/ketones, amines and triethyl phosphite. The use of this catalyst results in an effortless magnetic recoverability and recyclability, high yield and short reaction time under solvent-free conditions.

## **Graphic Abstract**



**Electronic supplementary material** The online version of this article (https://doi.org/10.1007/s10562-019-02910-8) contains supplementary material, which is available to authorized users.

Extended author information available on the last page of the article

Keywords Heterogeneous catalysis  $\cdot$  Amination  $\cdot$  Magnetic separation  $\cdot$  Mesoporous materials  $\cdot$  Lewis acid  $\cdot$  Kabachnik-fields reaction

# 1 Introduction

The synthesis of  $\alpha$ -aminophosphonates, known as bioisosteres of alpha-amino acids, has gained great interest because of their varied pharmacological properties like anticancer, antiviral, herbicides, fungicides, bactericides, peptide mimetic and enzyme inhibitor [1–4]. Considering their multipurpose pharmaceutical importance, various methods have been developed for the synthesis of  $\alpha$ -aminophosphonates [5]. Of these, the Kabachnik–Fields reaction of aldehydes/ketones, amines, and phosphites is of great interest [6–8]. Abundant protocols for this conventional synthesis include employment of various catalytic systems such as Lewis acids [9–11], Brønsted acids [12], heterogeneous catalysts [13], have been developed. Owing to their synthetic and biological values, there is still need to develop new accessible, environmentally benign and efficient protocol for the preparation of  $\alpha$ -aminophosphonates. In recent years, the use of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> as a support for catalytic applications has led to a new generation of heterogeneous "nanocatalyst." [14] Such catalysts are preferable to conventional catalysts because of numerous aspects such as greater surface area; higher activity; higher selectivity and longer life and thus, developing a newer type of sustainable environmentally friendly catalysts which may find a wide range of applications in the area of fine and bulk chemical industries, pharmaceuticals, and many other fields. Although the problem of their separation from the reaction medium is partly solved, but their separation and recycling involves the use of methods such as filtering or centrifugation which prolong the process. Also, these methods make part of the catalysts disappear and causes impurities to remain in the reaction environment.

In the current paper, magnetic nanoparticles of barium hexaferrite supported on gamma-aluminum oxide were prepared and used as heterogeneous Lewis acid catalyst in Kabachnik -Fields reaction. A very simple protocol was followed in the reaction process for the synthesis of  $\alpha$ -aminophosphonates via the addition of triethylphosphite to the double bond of imines, formed from the reaction between diverse aldehydes and aniline derivatives. The reaction proceeded smoothly at ambient temperature under solvent free conditions, at the same time the issues of separation and recycling of the catalyst is excluded due to its magnetic properties [15, 16].

# 2 Experimental

#### 2.1 Chemicals and Instruments

All of the reagents and solvents used in this work were achieved from Fluka or Merck and used without further purification. Fourier transform infrared spectroscopy (FT-IR) measurements were performed using KBr disk on a Shimazdu spectrometer. Ray X-ray analysis was performed by using Philips analyzer. Ultrasonic bath used for synthesis of catalyst from Elmasonic, Which produced 60 Hz frequency and maintained a temperature up to a maximum temperature of 80 °C. calcination of catalyst performed by Exciton oven. A vibrating-sample magnetometer (VSM) model MDKFD (Danesh Pajohan Kavir Co). Scanning electron microscope (SEM) used for analyses from Czech Republic. The <sup>1</sup>H- and <sup>13</sup>C-spectra were measured at 500 and 125 MHz, respectively, on a Bruker DRX 500-Avance FT-NMR instrument with CDCl<sub>3</sub> solvent. Melting point measured by Electro thermal 9100. The Brunauer-Emmett-Teller (BET) surface area measurements of the catalyst were carried out using ASAP 2020 instrument.

# 2.2 Synthesis of Barium Hexaferrite Magnetic Nanoparticles (BaFe<sub>12</sub>O<sub>19</sub>)

For the preparation of barium ferrite,  $Ba(NO_3)_2$  (0.52 g, 1.99 mmol) and of  $Fe(NO_3)_3 \cdot 9H_2O$  (9.6 g, 23.76 mmol) were poured into a 250 ml round-bottomed flask containing 100 ml of double-distilled water, followed by the addition of citric acid (4.5 g, 23.42 mmol). The mixture was then sonicated in an ultrasonic bath for 15 min to attain a homogenous dispersion. Then, aqueous ammonia solution (25%) was added to the dispersed solution until the pH value reached 8. After subsequent washing and drying, the product was calcined at 1000 °C for 2 h to obtain the desired magnetic nanoparticles of barium hexaferrite.

# 2.3 Synthesis of BaFe<sub>12</sub>O<sub>19</sub>/Al<sub>2</sub>O<sub>3</sub> Magnetic Nanocomposites

Aluminum nitrate (16.5 g, 77.93 mmol) and citric acid (9.2 g, 47.9 mmol) were dissolved in H<sub>2</sub>O/EtOH (2:1, 45 ml). Then, ammonia solution (25%) was added dropwise to the solution until pH 8 was reached and then barium ferrite (0.7 g, 0.63 mmol) was added under sonication conditions. In the next step, in order to utterly evaporate the

solvent, the mixture was stirred at 80 °C. The magnetic nanocomposites  $BaFe_{12}O_{19}/Al_2O_3$  were achieved after calcination treatment at 750 °C for 5 h.

# 2.4 General Procedure for the Synthesis of α-aminophosphonates (4a-4q)

For the synthesis of  $\alpha$ -aminophosphonates, triethylphosphite (0.199 mg, 1.2 mmol), aniline derivatives (1 mmol), aldehydes (or ketones) (1 mmol), and BaFe<sub>12</sub>O<sub>19</sub>/Al<sub>2</sub>O<sub>3</sub> magnetic nanocomposites (35 mg) were added into a test tube at room temperature under solvent-free condition. The mixture was stirred up to perform reaction at required time. The reaction was monitored by TLC (eluent: EtOAc/n-hexane, 1:3). At the end of the procedure the catalyst was removed from the reaction mixture by an external magnet, to be reused in the next cycle after being sufficiently washed with EtOH, n-hexane and ethyl acetate. The magnetic property of the catalyst was checked with magnet, which was desirable (Fig. 1).

# 3 Results and Discussion

The prepared  $BaFe_{12}O_{19}/Al_2O_3$  nanohybrid was characterized using Fourier transform infrared (FTIR), X-ray Diffraction XRD, vibrating sample magnetometer (VSM), scanning electron microscopy (SEM), energy dispersive X-ray (EDX) spectroscopy, and Brauner Emette Teller (BET) surface area analysis.

The FT-IR spectra of  $BaFe_{12}O_{19}/Al_2O_3$  was studied and shown in Fig. 2. The broad band at 3200–3700 cm<sup>-1</sup> was assigned to the OH stretching vibration and 1640 cm<sup>-1</sup> to the bending vibrations of H<sub>2</sub>O [15]. Peak at 880 cm<sup>-1</sup> attributed



Fig.1 Separation of magnetic  ${\rm BaFe_{12}O_{19}/Al_2O_3}$  catalyst by external magnet



Fig. 2 The FT-IR spectra of  $BaFe_{12}O_{19}$  and  $BaFe_{12}O_{19}/Al_2O_3$ 

to Al-O and peak at 550 cm<sup>-1</sup> was attributed to the bending vibration of the O–Al–O. One strong absorption band at 250–550 cm<sup>-1</sup> was attributed to vibrations of Fe–O in barium hexaferrite structure.

The XRD patterns of the BaFe<sub>12</sub>O<sub>19</sub> nanoparticles and BaFe<sub>12</sub>O<sub>19</sub>/Al<sub>2</sub>O<sub>3</sub> nanocomposite were shown in Fig. 2. As can be seen, the presence of all the crystal planes such as (110), (107), (114), (203), (217), (2011), and (220) ascribed to the crystal structure of hexaferrite of barium proves that BaFe<sub>12</sub>O<sub>19</sub> nanoparticles were synthesized and that its crystalline structure was maintained after its composition by Al<sub>2</sub>O<sub>3</sub> nanoparticles. The presence of diffraction peaks at 45.7° and 66.6° corresponding to (400) and (440) lattice planes related to the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> structure in the BaFe<sub>12</sub>O<sub>19</sub>/ Al<sub>2</sub>O<sub>3</sub> nanocomposite. The BaFe<sub>12</sub>O<sub>19</sub> and Al<sub>2</sub>O<sub>3</sub> nanoparticles were characterized by [01-072-0738] and [00-001-1308] standard carts, respectively.

Figure 3 shows VSM curves of BaFe<sub>12</sub>O<sub>19</sub> nanoparticles and BaFe<sub>12</sub>O<sub>19</sub>/Al<sub>2</sub>O<sub>3</sub>. The magnetic saturation ( $M_s$ ) remanent magnetization ( $M_r$ ) of M-type barium hexaferrite as a ferrimagnetic nanoparticles was 52.04 emu/g and 28.43 emu/g respectively, while  $M_s$  and  $M_r$  of BaFe<sub>12</sub>O<sub>19</sub>/Al<sub>2</sub>O<sub>3</sub> nanocomposite are shifted to 11.18 emu/g and 6.05 emu/g respectively (Fig. 4) due to the mass fraction of non-magnetic Al<sub>2</sub>O<sub>3</sub> nanoparticles in the nanocomposite. Both BaFe<sub>12</sub>O<sub>19</sub>/Al<sub>2</sub>O<sub>3</sub> and BaFe<sub>12</sub>O<sub>19</sub> nanomaterials show a hard-magnetic behavior conferring to their broad hysteresis loops. The increase in coercivity ( $H_c$ ) in BaFe<sub>12</sub>O<sub>19</sub>/Al<sub>2</sub>O<sub>3</sub> nanocomposite is due to the surface spin effect and the dipole–dipole interaction between BaFe<sub>12</sub>O<sub>19</sub> and Al<sub>2</sub>O<sub>3</sub>.

The morphologies of the BaFe<sub>12</sub>O<sub>19</sub> nanoparticles and BaFe<sub>12</sub>O<sub>19</sub>/Al<sub>2</sub>O<sub>3</sub> nanocomposite were investigated by SEM micrographs. As shown in Fig. 5a, BaFe<sub>12</sub>O<sub>19</sub> magnetic nanoparticles synthesized by sol–gel method had a hexagonal and uniform lace-like morphology. The SEM images of BaFe<sub>12</sub>O<sub>19</sub>/Al<sub>2</sub>O<sub>3</sub> nanocomposite illustrated in Fig. 4b show well that Al<sub>2</sub>O<sub>3</sub> sheets were almost uniformly covered by BaFe<sub>12</sub>O<sub>19</sub> nanoparticles.

Also, the EDX of  $BaFe_{12}O_{19}/Al_2O_3$  nanocomposites discloses the presence of O, Al, Fe and Ba in the structure of this material (Fig. 6).



**Fig.3** XRD patterns of **a** standard  $BaFe_{12}O_{19}$  nanoparticles and **b** synthesized  $BaFe_{12}O_{19}$  and  $BaFe_{12}O_{19}/Al_2O_3$  nanocomposites



Fig. 4 Magnetic hysteresis loops of the  $BaFe_{12}O_{19}$  nanoparticles and  $BaFe_{12}O_{19}/Al_2O_3$  nanocomposite

Figure 7 depicts an adsorption/desorption isotherm of  $BaFe_{12}O_{19}/Al_2O_3$  nanocomposites determined by BET method s at 77 K. The isotherm of the  $BaFe_{12}O_{19}/Al_2O_3$  sample was a typical mesoporous material with pore size between 2 and 50 nm. The BET surface area (SBET) was 1773.22 m<sup>2</sup>/g, average pore diameter was 3.946 nm, and the total volume of pore was 1.749 cm<sup>3</sup>/g.

# 3.1 Evaluation the Catalytic Activity of BaFe<sub>12</sub>O<sub>19</sub>/ Al<sub>2</sub>O<sub>3</sub> Magnetic Nanocomposites Through Synthesis of α-aminophosphonates

We studied the catalytic activity of heterogeneous Lewis acid  $BaFe_{12}O_{19}/Al_2O_3$  magnetic nanocomposites in onepot three-component synthesis of  $\alpha$ -aminophosphonates, through the reaction of aromatic aldehydes (and ketone), triethyl phosphite and aniline derivatives. In order to establish the optimum reaction conditions, we used 4-chlorobenzaldehyde, triethyl phosphite and aniline as model substrates. The reaction was studied under different conditions and the results of these comparative experiments are summarized in Table 1.

At the first, the reaction carried out in solvent-free and temperature (80 °C) in the presence of 10 mg of catalyst with 57% isolated yield. The reaction was carried out in various organic solvents such as Ethanol, Water, and Acetonitrile. The best yield achieved in solvent-free condition, thus the effect of various temperature checked out, while in room temperature yield of the reaction improved. By increasing the temperature (60, 80,100 °C) lower yields were observed. This is typical for any equilibrium where the direct reaction is exothermic. To probe the effect of the catalyst concentration, regular studies were carried out in the presence of different amounts of the catalyst (15, 25, 35 mg), giving  $\alpha$ -aminophosphonates with 73%, 79% and 90% isolated yields, individually. Thus, the best yield is accessible in the presence of just 35 mg catalyst, and use of higher amounts of the catalyst did not increase the result to a significant level. Therefore the best results appeared in solvent-free, at room temperature in the presence of 35 mg catalyst. In the absence of catalyst the reaction did not proceed even after 24 h at room temperature. Although in the presence of Nano BaFe<sub>12</sub>O<sub>19</sub> or Al<sub>2</sub>O<sub>3</sub> as catalyst the yield of reaction was improved, but high product yield was obtained using  $BaFe_{12}O_{19}/Al_2O_3$  magnetic nanocomposites. (Table 1, entry 11).

In the absence of the catalyst the reaction did not proceed even after 24 h at room temperature. Although in the presence of Nano  $BaFe_{12}O_{19}$  or  $Al_2O_3$  as catalyst the yield of reaction was improved, but high product yield was obtained using  $BaFe_{12}O_{19}/Al_2O_3$  magnetic nanocomposites (Table 2, entry 4).



Fig. 5 SEM images of a BaFe<sub>12</sub>O<sub>19</sub> nanoparticles and b BaFe<sub>12</sub>O<sub>19</sub>/Al<sub>2</sub>O<sub>3</sub> nanocomposite



Fig. 6 EDX spectrum of BaFe<sub>12</sub>O<sub>19</sub>/Al<sub>2</sub>O<sub>3</sub>

Under the optimal reaction conditions, a range of aldehydes were used with different anilines and triethyl phosphite in order to examine the three-component reaction. Several representative models are summarized in Table 3. Variety of functional groups present in the aryl aldehydes such as halogen, methoxy, hydroxyl groups were tolerated (see Table 3). It was found that most of the reactions proceeded smoothly to achieve the derivatives of  $\alpha$ -aminophosphonates in good yields (74–90%). Reaction with dialkyl phosphiste was also performed using dimethyl phosphite (DMP) as the P-component. The results shown that the reaction was slower, the yield is very low even after 1 day, and the condensation was not complete.



Fig. 7 Langmuir surface area plot for BaFe<sub>12</sub>O<sub>19</sub>/Al<sub>2</sub>O<sub>3</sub>

A conceivable mechanism for the synthesis of  $\alpha$ -aminophosphonates is suggested in Scheme 1. According to the mechanism, the catalyst activated the carbonyl group enabling the generation of the imine which is attacked by the triethyl phosphite to give the  $\alpha$ -aminophosphonates. Lewis acid catalyst is envisioned to activate the imine to nucleophilic attack. [32–36].

To survey the recyclability of the catalysts  $BaFe_{12}O_{19}/Al_2O_3$  magnetic nanocomposites was removed from the mixture of reaction by external magnet, washed plenty with ethanol, ethyl

Table 1 Optimization of catalyst loading and solvent for the synthesis of  $\alpha$ -aminophosphonates



Entry	Temperature(°C)	Solvent	Catalyst(mg)	Time(h)	Yield (%)
1	80	Ethanol	10	1	51
2	80	Water	10	1	Nil
3	80	Acetonitrile	10	1	43
4	80	-	10	1	57
5	r.t	_	10	1	65
6	60	-	10	1	60
7	100	-	10	1	55
8	r.t	-	15	1	73
9	r.t	-	25	1	79
10	r.t	_	35	1	90
11	r.t	-	50	1	92

Reaction conditions: 4-chlorobenzaldehyde (1 mmol), triethyl phosphite (1.2 mmol), aniline, catalyst (35 mg), room temperature

Table 2 Screening of catalyst conditions in synthesis of  $\alpha$ -aminophosphonates a

Entry	Catalyst	Catalyst(mg)	Time(h)	Yield (%)
1	_	_	24	Nil
2	Nano BaFe <sub>12</sub> O <sub>19</sub>	35	1	48
3	$Al_2O_3$	35	1	61
4	BaFe <sub>12</sub> O <sub>19</sub> /Al <sub>2</sub> O <sub>3</sub>	35	1	90

acetate and normal hexane. After drying at room temperature for several hours (or oven-dried at 50 °C for 10 min), the recycled catalyst was reused in the subsequent experiments. The results indicate that the catalyst is able to be used successfully in four sequential cycles without a significant change in catalytic activity (Fig. 8).

For comparison purposes, the catalytic performance of the present catalysts was compared with that of earlier reported catalysts used in Kabachnik–Fields reaction and exhibited in Table 4. BaFe<sub>12</sub>O<sub>19</sub>/Al<sub>2</sub>O<sub>3</sub> in comparison with other reported catalyst is exhibited in Table 4, interestingly, shows better catalytic performances in Kabachnik–Fields Reaction.

# 4 Conclusion

This study displays the potential for the synthesis and use of  $BaFe_{12}O_{19}/Al_2O_3$  mesoporous superparamagnetic nanocomposites as a novel heterogeneous Lewis acid catalyst. It has been proved to be highly active catalyst towards the synthesis of  $\alpha$ -aminophosphonates via one-pot three-component coupling reaction of carbonyl, triethylphosphite, and amine under solvent-free condition at room temperature. The prepared catalyst offers several advantages including high concentration of catalytically active sites with high surface area as well as ease of separation, and the recyclability of the catalyst as the environmental and economic requirements.

*Diethyl* ((5-*bromo 2-hydrox y phenyl*)(*phenylamino*) *methyl*)*phosphonate*, white crystalline solid, m.p. 136–138 °C. <sup>1</sup>HNMR (500 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$ =1.253–1.331 (m, 6H), 4.055–4.152 (m, 4H), 4.951–5.029 (d, <sup>2</sup>J<sub>PH</sub>=39, 1H), 6.694–6.843 (m, 4H), 7.153–7.276 (m, 3H), 7.361 (s, 1H).<sup>13</sup>CNMR (125 MHz, CDCl<sub>3</sub>, 25 °C):  $\delta$ =16.22–16.42 (t, J=0.061 Hz), 63.72–63.81 (d, J=0.092), 64.21–64.31 (d, J=0.098), 112.23 (s), 114.60 (s), 119.65 (s), 123.70 (s), 129.35 (s), 131.17 (s), 132.14 (s), 154.96 (s); <sup>31</sup>PNMR(200 MHz, 35); Anal. Calcd. For C<sub>17</sub>H<sub>21</sub>BrNO<sub>4</sub>P (413.039): C, 49.29; H, 5.11; N, 3.38; Fund C, 49.31; H, 5.08; N, 3.41.

*Diethyl ((4-chlorophenyl)((2-hydroxyphenyl)amino) methyl)phosphonate*, white crystalline solid, m.p. 146–148 °C.<sup>1</sup> HNMR (500 MHz, CDCl<sub>3</sub>):  $\delta$  = 1.18 (t, J = 7.5 Hz, 3H, OCH<sub>2</sub><u>CH<sub>3</sub></u>), 1.33 (t, J = 7.5 Hz, 3H, OCH<sub>2</sub><u>CH<sub>3</sub></u>), 3.74–3.79 (q, J = 6.25, 1H, OCH<sub>2</sub>), 3.98–4.02 (q, J = 5, 1H, OCH<sub>2</sub>), 4.26–4.32 (m, 2H), 4.86–4.91(d, <sup>2</sup>J<sub>PH</sub> = 25, 1H, PCH)), 5.69 (s, 1H, NH), 6.45–6.80 (m, 4H, Ar<u>H</u>)), 7.13–7.15 (m, 2H, Ar<u>H</u>), 7.36–7.38(m, 2H, Ar<u>H</u>), 9.10 (s, 1H, OH). <sup>13</sup>CNMR (125 MHz, CDCl<sub>3</sub>, 25 °C):  $\label{eq:action} \mbox{Table 3} \quad \mbox{One-pot solvent-free synthesis of $\alpha$-aminophosphonates using magnetic Lewis acid catalyst BaFe_{12}O_{19}/Al_2O_3$ at room temperature to the solvent-free synthesis of $\alpha$-aminophosphonates using magnetic Lewis acid catalyst BaFe_{12}O_{19}/Al_2O_3$ at room temperature to the solvent-free synthesis of $\alpha$-aminophosphonates using magnetic Lewis acid catalyst BaFe_{12}O_{19}/Al_2O_3$ at room temperature to the solvent-free synthesis of $\alpha$-aminophosphonates using magnetic Lewis acid catalyst BaFe_{12}O_{19}/Al_2O_3$ at room temperature to the solvent-free synthesis of $\alpha$-aminophosphonates using magnetic Lewis acid catalyst BaFe_{12}O_{19}/Al_2O_3$ at room temperature to the solvent-free synthesis of $\alpha$-aminophosphonates using magnetic Lewis acid catalyst BaFe_{12}O_{19}/Al_2O_3$ at room temperature to the solvent-free synthesis of $\alpha$-aminophosphonates using magnetic Lewis acid catalyst BaFe_{12}O_{19}/Al_2O_3$ at room temperature to the solvent-free synthesis of $\alpha$-aminophosphonates using magnetic Lewis acid catalyst BaFe_{12}O_{19}/Al_2O_3$ at room temperature to the solvent-free synthesis of $\alpha$-aminophosphonates using magnetic Lewis acid catalyst BaFe_{12}O_{19}/Al_2O_3$ at room temperature to the solvent-free synthesis of $\alpha$-aminophosphonates using magnetic Lewis acid catalyst BaFe_{12}O_{19}/Al_2O_3$ at room temperature to the solvent-free synthesis of $\alpha$-aminophosphonates using magnetic Lewis acid catalyst BaFe_{12}O_{19}/Al_2O_3$ at room temperature to the solvent-free synthesis of $\alpha$-aminophosphonates using magnetic Lewis acid catalyst BaFe_{12}O_{19}/Al_2O_3$ at room temperature to the solvent-free synthesis of $\alpha$-aminophosphonates using magnetic Lewis acid catalyst BaFe_{12}O_{19}/Al_2O_3$ at room temperature to the solvent-free synthesis of $\alpha$-aminophosphonates using magnetic Lewis acid catalyst BaFe_{10}/Al_2O_3$ at room temperature to the solvent-free synthesis of $\alpha$-aminophosphonates using magnetic Lewis acid catalyst BaFe_{10}/Al_2O_3$ at room t$ 

	ArCHO						
	or NH	l₂ EtO <sub>、P</sub> ∠C	Et BaFe <sub>12</sub> O <sub>19</sub> /Al <sub>2</sub> O <sub>3</sub> EtO		E Ft	tO, ,O O≖P ſ	
		+ ÖEt	Solvent Free, r.t. Ar	⊢ <sub>N</sub> ,/∽,∥	or		
	1m 2a-t	o 3		4a-q	L	4r	
		. ·	D. 1. (		<b>V</b> <sup>2</sup> 11 (01)		[ref ]
Entry			Product		rield (%)	m.p	m.p
1	C <sub>6</sub> H <sub>5</sub> -CHO	Aniline		45	86	88–89	87–89 [14]
2	2-Cl-C <sub>6</sub> H <sub>4</sub> -CHO	Aniline	Q, OEt	50	85	99–101	98–100 [15]
3	4-Cl-C <sub>6</sub> H <sub>4</sub> -CHO	Aniline	CI HN 4b	35	90	55–57	57–58 [17]
			NH EtO, Cl EtO <sup>, P</sup> O Cl <sub>4c</sub>				
4	2,4-(Cl) <sub>2</sub> -C <sub>6</sub> H <sub>3</sub> -CHO	Aniline		55	81	63–65	65–67 [18]
5	2-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -CHO	Aniline	O O O O O O O O O O O O O O	55	87	155–157	154–156 [19]
			4e				

## Table 3 (continued)

Entry	Carbonyl	Amine	Product	Time (min)	Yield (%)	m.p	m.p <sup>[ref.]</sup>
6	4-Me-C <sub>6</sub> H <sub>4</sub> -CHO	Aniline	HN EtO	50	85	60–62	61-62[20]
7	2-OMe-C <sub>6</sub> H <sub>4</sub> -CHO	Aniline	4f MeO HN EtO OEt	40	85	100–102	99–100 [21]
8	3-NO <sub>2</sub> -C <sub>6</sub> H <sub>4</sub> -CHO	Aniline	A g NO2 O O Et OEt	55	90	130–131	126–128 [3]
9	4-F-C <sub>6</sub> H <sub>4</sub> -CHO	Aniline	4 h F OEt OEt	50	87	84-85	78–79 [14]
10	3-OH-C <sub>6</sub> H <sub>4</sub> -CHO	Aniline	OH OH OEt OEt 4j	45	85	93	93[22]

Magnetic BaFe <sub>12</sub> O <sub>19</sub> /Al <sub>2</sub> O <sub>3</sub> : Ar	n Efficient Heterogeneous	Lewis Acid Catalyst for the
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### Table 3 (continued)

Entry	Carbonyl	Amine	Product	Time (min)	Yield (%)	m.p	m.p <sup>[ref.]</sup>
<sup>a</sup> 11	5-Br-2-OH-C <sub>6</sub> H <sub>4</sub> -CHO	Aniline	Br 人	45	85	136–138	_
			O H OEt				
			HO NH				
			4 k				
12	3-Br-C <sub>6</sub> H <sub>4</sub> -CHO	Aniline	O OEt	45	85	97–99	96–98[23]
			Br				
12		4 (Pr) Anilina		40	Q 1	125 127	124 126[24]
15	4-CI-C <sub>6</sub> II <sub>4</sub> -CIIO	4-(DI)-Ammic	O, OEt P <b>~</b> OEt	+0	01	125-127	124-120[24]
			NH				
			CI				
			Br 4 m				
14	C <sub>6</sub> H <sub>5</sub> CHO	4-(Br)-Aniline	O, OEt P∽	60	84	123–124	121–123[25]
			OEt NH				
15	Furfural	Aniline	Br <sub>40</sub>	60	83	51–52	53–55[ <mark>3</mark> ]
			NH				
			4p				
<sup>a</sup> 16		2-aminophenol		35	92	146–148	-
			HO				
			4q				

#### Table 3 (continued)

Entry	Carbonyl	Amine	Product	Time (min)	Yield (%)	m.p	m.p <sup>[ref.]</sup>
<sup>a</sup> 17	Cyclohexanone	Aniline		65	74	108	104 [26]

Reaction conditions: carbonyl (1 mmol), triethyl phosphite (1.2 mmol), amine (1 mmol),  $BaFe_{12}O_{19}/Al_2O_3$  (35 mg) <sup>a</sup>New compounds

Scheme 1 Plausible mechanism for the synthesis of  $\alpha$ -aminophosphonates





Fig. 8 Recyclability of catalyst

$$\begin{split} &\delta\!=\!16.07~(\text{d},\,^3\!\text{J}_{\text{PC}}\!=\!6.13),\,16.32(\text{d},\,^3\!\text{J}_{\text{PC}}\!=\!5.82),\,54.79,\,56.02,\\ &63.69~(\text{d},\,^2\!\text{J}_{\text{PC}}\!=\!7.5~\text{Hz},\,\text{OCH}_2),\,64.38~(\text{d},\,^2\!\text{J}_{\text{PC}}\!=\!10~\text{Hz},\\ &\text{OCH}_2),\,111.97,\,114.41,\,118.54,\,119.97,\,128.67,\,129.35 \end{split}$$

Table 4 Catalytic Performance of  $BaFe_{12}O_{19}\!/Al_2O_3$  in comparison with other reported catalyst

Entry	Catalyst	Temp (°C)	Time (min)	Yield	Ref.
1	Al <sub>2</sub> O <sub>3</sub> (10 mol%)	110	130	61	[27]
2	$\begin{array}{c} \text{TiO}_2 - \text{SiO}_2 \\ (15 \text{ mol}\%) \end{array}$	90	90	81	[28]
3	Al <sub>2</sub> O <sub>3</sub> / NH <sub>4</sub> HCO <sub>2</sub>	r.t.	240-480	59-80	[27]
4	γ-Fe <sub>2</sub> O <sub>3</sub> @SiO <sub>2</sub> - PA	80	120	86	[29]
5	Fe/SWCNTs	50	180	80-95	[30]
6	CeCl <sub>3</sub> .7H <sub>2</sub> O	r.t.	540	90	[31]
7	$\begin{array}{c} \text{BaFe}_{12}\text{O}_{19}\text{/}\\ \text{Al}_2\text{O}_3 \end{array}$	r.t.	35–65	74–92	This work

(d,  ${}^{2}J_{PC} = 6.25 \text{ Hz}$ , CHCAr), 134.37, 134.65, 145.10 (d,  ${}^{3}J_{PC} = 11.25 \text{ Hz}$ , NHCAr);  ${}^{31}$ PNMR (200 MHz, CDCl<sub>3</sub>):  $\delta = 35$ ; Anal. Calcd. For C<sub>17</sub>H<sub>21</sub>ClNO<sub>4</sub>P (369.08): C, 55.22; H, 5.72; N, 3.79. Found: C, 55.14; H, 5.63; N, 3.67.

Acknowledgements The authors gratefully acknowledge the support of the Research Council of the Iran University of Science and Technology, Tehran, IRAN.

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