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Magnetically recyclable magnetite–ceria (Nanocat-Fe-Ce) nanocatalyst – applications in multicomponent reactions under benign conditions†

Manoj B. Gawande,*[a] Vasco D. B. Bonifácio,[a] Rajender S. Varma,[b] Isabel D. Nogueira,[c] Nenad Bundaleski,[d] C. Amjad A. Ghumman,[d] Orlando M. N. D. Teodoro[d] and Paula S. Branco*[a]

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A novel magnetite nanoparticle-supported ceria catalyst (Nanocat-Fe-Ce) has been successfully prepared by a simple impregnation method and was characterized by XRD, SIMS, FEG-SEM-EDS, and TEM. The exact nature of Nanocat-Fe-Ce was confirmed by X-ray photoelectron spectroscopy and it is noted that CeO_2 nanoparticles are supported on magnetite, with evidence of secondary ion mass spectrometry. Catalytic activity of the nano-catalyst was explored for the synthesis of dihydropyridines under benign conditions; a greener protocol is described that provides a simple and efficient method for the synthesis of functionalized 1,4-dihydropyridines using a recyclable nanocatalyst. Notably, 5.22 mol% of the catalyst is sufficient to catalyze the multicomponent reaction in ethanolic medium at room temperature. Importantly, the catalyst could be easily separated from the reaction mixture by using an external magnet and recycled several times without loss of activity.

Introduction

Green chemistry has made a major impact on several fronts encompassing various key features such as the use of sustainable magnetic nanomaterials, catalyst-free aqueous and solvent-free organic reactions, and the material consumption, preferably the use of bio-renewable resources, *etc.*[1] Additionally, various other alternative solvents such as polyethylene glycol (PEG), biodiesel byproduct, glycerol, and deep eutectic solvents (DESs) are now employed for greener reactions and other sustainable applications.[2] Environmentally benign and sustainably enhanced protocols for organic synthesis are being introduced with the improvement in atom economy. Among other factors, a major adverse effect on the environment is the consumption of energy for heating and cooling of reactions; the performance of reactions at ambient temperature or using alternative and selective energy systems may be a viable option.[3a]

In recent years, nano-catalysts have been introduced to address the sustainability issues[3b] and have emerged as an alternative approach for the improvement of many significant organic reactions.[4] These advances have opened the door for the design of novel nanocatalysts for specific applications in synthetic chemistry. These innovations led to the evolution of sustainable catalysts with excellent activity, selectivity, separation from the reaction mixture, and recyclability without losing their activity.[5–8] Magnetic nanoparticle-based materials (MNPs) are ideal supports for the immobilization of catalysts since they can be re-collected by using an external magnet. This enables convenient purification avoiding conventional filtration or centrifugation processes. Several metals have been successfully used for this purpose, including, ruthenium,[8] cobalt,[9] ruthenium–cobalt,[10] palladium,[11] and nickel.[12] Magnetic nanoparticles of Fe_3O_4 have recently emerged as a versatile support for immobilization, since they are inexpensive, non-toxic, chemically stable, and easily prepared from low-cost precursors.[13] Most importantly, Fe_3O_4–MNP-supported catalysts have been shown to be highly useful supports for asymmetric Michael addition in water,[14] enantioselective acylations,[15] Ullman-type,[16] Suzuki, Sonogashira, Stille,[17] and Suzuki–Miyaura[18] coupling reactions. In metal catalyze

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[a] *REQUIMTE, Department of Chemistry, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Lisbon, Portugal. E-mail: m.gawande@fct.unl.pt, mbgawande@yahoo.co.in, paula.branco@fct.unl.pt; Fax: +351 212948550; Tel: +351 212948300*

[b] *Sustainable Technology Division, National Risk Management Research Laboratory, US Environmental Protection Agency, MS 443, 26 West Martin Luther King Drive, Cincinnati, Ohio 45268, USA*

[c] *Instituto de Ciência e Engenharia de Materiais e Superfícies, IST, Lisbon, Portugal*

[d] *Centre for Physics and Technological Research (CeFITec), Department of Physics, Faculdade de Ciências e Tecnologia, Universidade Nova de Lisboa, 2829-516 Caparica, Portugal*

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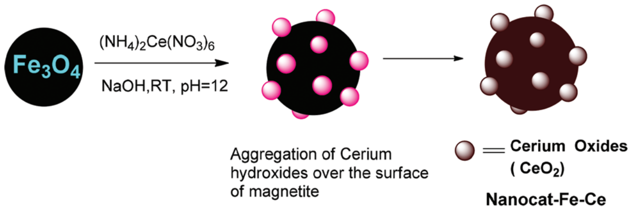
reactions, ceria is an important and promising material for catalysis and environmental and energy applications, due to its extraordinary thermal and chemical stability.[19] A few examples of mixed oxides (Fe_2O_3–CeO_2) have appeared, namely in dye degradation,[20] oxidations,[21] and synthesis of carbonyl compounds.[22] In view of the importance of this research area, reviews on nano-magnetite-supported catalysts and sustainable protocols are now available.[4g,13n,23] It is an important and urgent need to design magnetically recyclable nano-catalysts, to reduce their cost of preparation, and to show their efficacy in benign reaction media.

Multicomponent reactions (MCR) are the most powerful tool for the construction of complex structures in a single step.[24a] Despite the significant importance of MCR in the synthesis of biologically active Hantzsch 1,4-dihydropyridines,[24b,c] its synthesis using "free" nano-γ-Fe_2O_3 [25] and nano-CeO_2 [26] catalysts has been only recently reported. In continuation of our research on sustainable protocols, heterogeneous catalysis and nanomaterials,[27–29] herein, we report the multicomponent synthesis of di- and tetrahydropyridines using a facile, efficient, recyclable and reusable ferrite-CeO_2 nanocatalyst (Nanocat-Fe-Ce).

Results and discussion

Nanocat-Fe-Ce was synthesized using a simple wet impregnation protocol (Scheme 1) and fully characterized by X-ray diffraction (XRD), inductive coupled plasma-atomic emission spectroscopy (ICP-AES), transmission electron microscopy (TEM), secondary ion mass spectrometry (SIMS), X-ray photoelectron spectroscopy (XPS) and a field-emission gun scanning electron microscope-electron dispersive spectrometry (FEG-SEM-EDS). The XRD spectra of Fe_3O_4 and Nanocat-Fe-Ce nanoparticles are depicted in Fig. 1. The XRD spectrum of Fe_3O_4 clearly matches with the literature data from the Joint Committee on Powder Diffraction System (JCPDS 79-0419). The crystallite size of the Nanocat-Fe-Ce catalyst, determined by using the Debye–Scherrer equation, was found to be 21 nm. Due to the low percentage of Ce (7.41% by ICP-AES analysis) the peaks of CeO_2 are not detectable in the XRD spectrum.

The TEM and SEM images of Fe_3O_4 and Fe_3O_4–CeO_2 MNPs are shown in Fig. 2a–c. Notably, the particles are observed in the nano range sizes (20–35 nm). The clustering tendencies formerly observed (Fig. 2c) notwithstanding, small groups of equiaxial particles, almost entirely detached from each other, are discernible. EDS confirms the presence of Ce metal in the nanocatalyst (see the spectrum in Fig. 2d).



Scheme 1 Synthesis of Nanocat-Fe-Ce by wet impregnation.

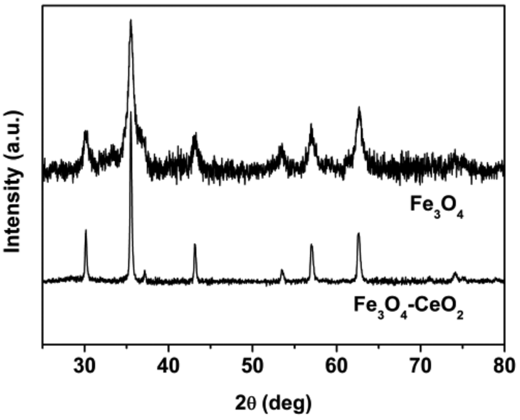


Fig. 1 XRD patterns of Fe_3O_4 and Nanocat-Fe-Ce MNPs.

TOF-SIMS analysis provides a highly efficient elemental and molecular composition of the top surfaces (<1 nm) with minimum surface damage. Therefore, TOF-SIMS in positive mode was used to confirm the presence of CeO_2 over the ferrite surface.

Fig. 3 shows the mass spectra in the m/z range of 0–150 (top) and 135–335 (bottom), with the characteristic ions of Fe_3O_4 and CeO_2 observed at m/z 56, 73, 140, 156, 157, 228, 312, 328, and 329, corresponding to Fe^+, $FeOH^+$, Ce^+, CeO^+, $CeOH^+$, $FeCeO_2^+$, $Ce_2O_2^+$, $Ce_2O_3^+$, and $Ce_2O_3H^+$, respectively. Sodium (Na^+, $m/z = 23$) is present in the spectrum as a contamination. The sodium adducts with CeO_2 are also observed at $m/z = 195$ ($NaCeO_2^+$) and at $m/z = 196$ ($NaCeO_2H^+$). The SIMS results clearly indicate that CeO_2 is present on the surface of the catalyst.

In order to know the exact nature of Ce metal in the catalyst, XPS measurements were performed (Fig. 4). Besides the signals corresponding to Fe, O and Ce, the signal for carbon was also observed, which is an expected impurity. The position of the carbon 1s line is shifted 0.6 eV towards higher binding energies with respect to the position characteristic of adventitious carbon (285.0 eV) due to charging effects. The binding energy axis was shifted accordingly in order to compensate the sample charging.

The characteristic XPS peak of Ce (Ce 3d doublet) is shown in the spectrum of Fig. 4. The position of the main Ce $3d_{5/2}$ line, its satellite peaks (S1 and S2), and the main Ce $3d_{3/2}$ line are assigned in the figure. The satellite S2 is particularly intense and partially overlaps with the $3d_{3/2}$ line. The two main oxide phases of Ce (CeO_2 and Ce_2O_3) can be clearly identified due to different positions and intensities of their shake up satellite peaks. The general shapes of the measured Ce 3d line, including the presence of two satellite peaks, indicate that Ce is present at the surface as Ce(IV) (CeO_2). Indeed, the main $3d_{5/2}$ line should be at 882.5 eV, its first satellite S1 is at 889.5 eV and the second one S2, which is more intense, is at 898.5 eV.[30] Additionally, Ce $3d_{3/2}$ should be at 901.3 eV.[31] The

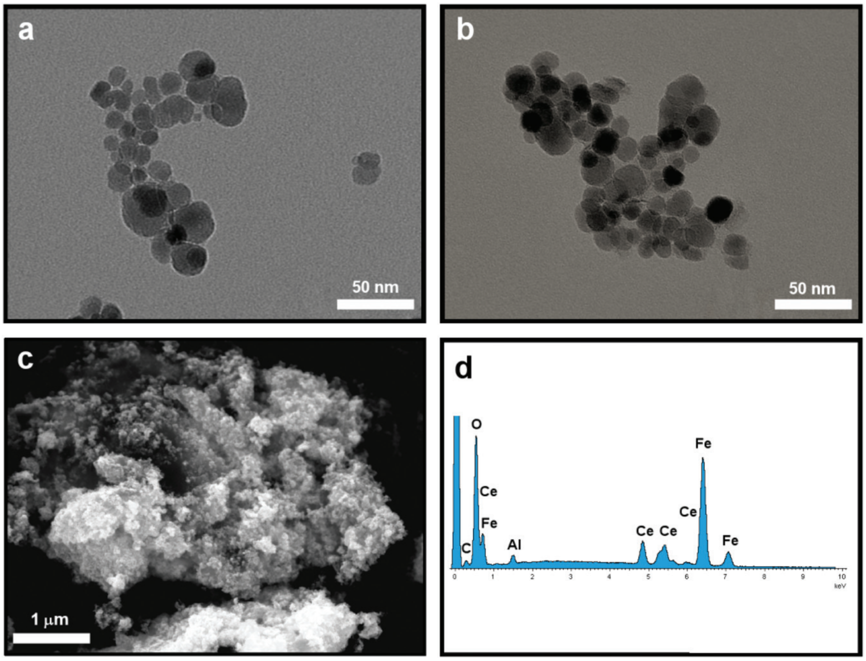


Fig. 2 Characterization of the MNPs: (a) TEM image of Fe_3O_4; (b) TEM image of Nanocat-Fe-Ce; (c) SEM image of Nanocat-Fe-Ce; (d) EDS profile of Nanocat-Fe-Ce.

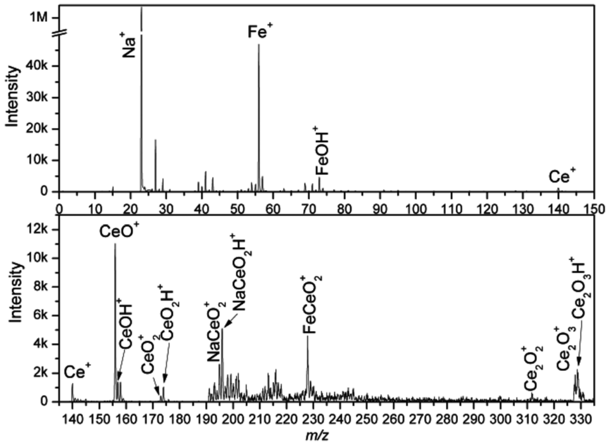


Fig. 3 TOF-SIMS spectra of Nanocat-Fe-Ce MNPs (positive mode): top spectrum *m*/*z* range 0–150, and bottom spectrum *m*/*z* range 135–355.

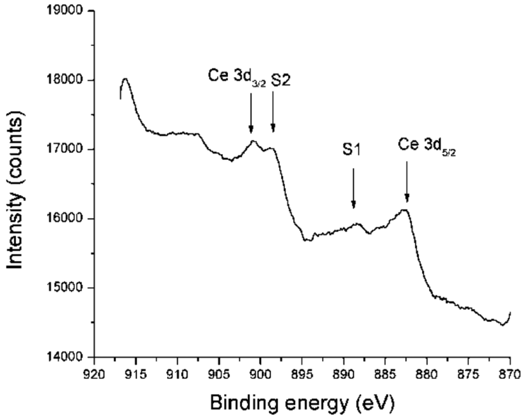


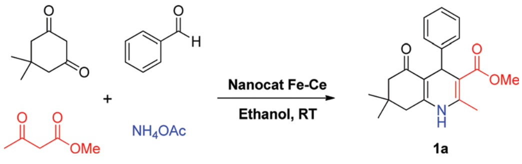
Fig. 4 The Ce 3d line taken from the Nanocat-Fe-Ce powder. The expected positions of the main Ce $3d_{5/2}$ line, its satellite peaks (S1 and S2) and the main Ce $3d_{3/2}$ line in the case of CeO_2 compound[30,31] are marked by arrows.

positions of peaks are in good agreement with the literature, which further supports the suggested phase identification.

The catalytic activity of Nanocat-Fe-Ce was investigated for the synthesis of di- and tetrahydropyridines using an MCR approach. For a model reaction, the reaction between benzaldehyde, methyl acetoacetate, and 5,5-dimethyl-1,3-cyclohexanedione was chosen at room temperature and in the presence of benign solvents (Table 1). Magnetite (Fe_3O_4) did not show any catalytic activity under the optimized conditions (Table 1, entry 2). When ceric ammonium nitrate (CAN) was used as a catalyst the Hantzsch product **1a** was obtained only in moderate yield (Table 1, entry 3). When water was used as a solvent, a side product was observed (bis-adduct **1a′**, 2,2′-(phenylmethylene)-bis(3-hydroxy-5,5-dimethylcyclohex-2-enone), see ESI†). The low yield of **1a** and the formation of **1a′** could be attributed to the low solubility of the reactants in water (Table 1, entry 5). When ethanol was used excellent selectivity and yield were obtained (Table 1, entry 6). Although not exactly the same, a related work for the synthesis of dihydropyridines has been described at elevated temperature.[32]

Further scope of the reaction for the synthesis of dihydropyridines (Table 2) was investigated using Nanocat-Fe-Ce and ethanol as the solvent. Notably, substrates having electron-donating or withdrawing groups led to the formation of products and the reactions proceeded smoothly in short reaction times with yields in the range of 83–95%. Moreover, Nanocat-Fe-Ce is highly robust and can be recycled and reused several times without any significant loss of the catalytic activity.

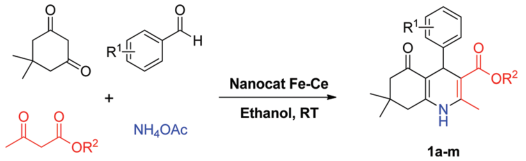
Table 1 Optimization of reaction conditions for the synthesis of 1,4-dihydropyridines[a]



Entry	Solvent	Catalyst	Time [h]	Yield [%]
1	EtOH	No-catalyst	2	Trace
2	EtOH	Fe_3O_4	2	Trace
3	EtOH	CAN	1.5	60
4	None	Fe_3O_4–CeO_2	2	45
5	H_2O	Fe_3O_4–CeO_2	2	45[b]
6	EtOH	Fe_3O_4–CeO_2	0.33	93

[a] Reaction conditions: benzaldehyde (1 mmol), methyl acetoacetate (1 mmol), ammonium acetate (1.5 mmol), 5,5-dimethyl-1,3-cyclohexanedione (1 mmol), solvent (2 mL), catalyst (100 mg, 5.22 mol % Ce). [b] A bis-adduct was isolated in 25% yield (see the Experimental section). CAN = ceric ammonium nitrate.

Table 2 Nanocat-Fe-Ce catalyze multicomponent synthesis of 1,4-dihydropyridines[a]



Entry	R^1	R^2	Compound	Time [min]	Yield [%]
1	H	Me	**1a**	20	93
2	H	Et	**1b**	20	95
3	4-CN	Et	**1c**	35	92
4	4-Br	Et	**1d**	35	90
5	3,4-$(OMe)_2$	Et	**1e**	20	92
6	3-OH	Et	**1f**	25	83
7	4-OMe	Et	**1g**	25	90
8	3-OH, 4-OMe	Et	**1h**	25	86
9	4-Br	Me	**1i**	35	92
10	3,4-$(OPh)_2$	Et	**1j**	25	85
11	4-CN	Me	**1l**	35	92
12	4-OMe	Me	**1m**	20	95

[a] Reaction conditions: aldehyde (1 mmol), acetoacetate (1 mmol), ammonium acetate (1.5 mmol), 5,5-dimethyl-1,3-cyclohexanedione (1 mmol), Nanocat-Fe-Ce (100 mg, 5.22 mol% Ce), ethanol (2 mL), room temperature.

The stability of Nanocat-Fe-Ce and its activity were investigated in recycling experiments for the reaction between benzaldehyde, methyl acetoacetate, and dimedone under the optimized conditions reported in Table 1 (entry 6). After each cycle, the catalyst was separated magnetically, washed with ethanol, dried at 50 °C under vacuum to remove residual solvents, and used for the next cycle. The yields of the reaction *vs.* the number of runs are shown in Fig. 5.

Using this procedure, Nanocat-Fe-Ce MNPs could be reused up to six times without any significant loss of the initial catalytic activity.

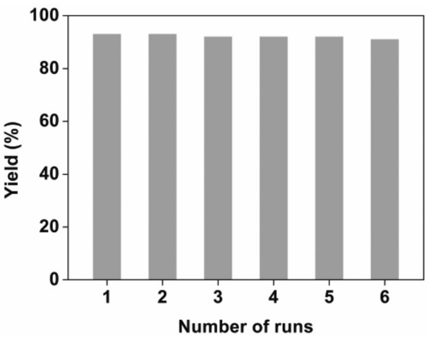
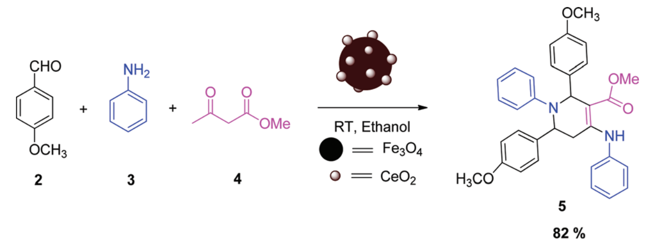


Fig. 5 Reusability of the magnetic catalyst Nanocat-Fe-Ce.

In order to prove that the reaction is heterogeneous, a standard leaching experiment was conducted by a hot filtration method. Benzaldehyde, methyl acetoacetate, and dimedone were allowed to react for 3–4 minutes in the presence of Nanocat-Fe-Ce at room temperature, in ethanol. The filtered reaction mixture was then stirred without a catalyst for 12 h; no formation of the corresponding product was observed, indicating that no homogeneous catalyst was involved. Inductively coupled plasma atomic emission spectra (ICP-AES) analysis of the filtrate (hot) revealed the absence of Fe and Ce species in the filtrate. The excellent catalytic activity and stability of Nanocat-Fe-Ce encouraged us to explore their catalytic activity for the functionalized tetrahydropyridines, as they are important building blocks for abundant natural products, pharmaceutical products, and a variety of biologically active compounds;[33] the development of methodologies for the synthesis of tetrahydropyridine derivatives under sustainable reaction conditions is a desirable pursuit and requires further attention.

The multicomponent reactions between 4-methoxybenzaldehyde, anilines, and methyl acetoacetate under benign conditions provided the desired compound **5** in 82% yield (Scheme 2).

In summary, a highly versatile magnetic nanocatalyst has been developed by coating magnetite with cerium oxide nanoparticles. The catalyst used in the multicomponent synthesis of functionalized 1,4 dihydropyridines was easily recovered from the reaction mixture by a simple and convenient magnetic separation of products using an external magnet. Functionalized tetrahydropyridines were synthesized in good yield



Scheme 2 Synthesis of methyl 2,6-bis(4-methoxyphenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (**5**).

under benign reaction conditions. This greener magnetic nanocatalyst could be used for other significant organic reactions and transformations. Further explorations of similar protocols are underway in our laboratory.

Experimental

Preparation of Fe_3O_4 MNPs[29a–d]

$FeCl_3·6H_2O$ (5.4 g) and urea (3.6 g) were dissolved in water (200 mL) at 85 to 90 °C for 2 h. The solution turned brown. To the resultant reaction mixture cooled to room temperature was added $FeSO_4·7H_2O$ (2.8 g) and then 0.1 M NaOH until pH 10. The molar ratio of Fe(III) to Fe(II) in the above system was nearly 2.00. The obtained hydroxides were treated by ultrasound in a sealed flask at 30 to 35 °C for 30 min. After ageing for 5 h, the obtained black powder (Fe_3O_4) was washed, and dried under vacuum.

Preparation of Nanocat-Fe-Ce[29a–d]

Magnetite nanoparticles Fe_3O_4 (2 g) and ceric ammonium nitrate (to obtain 8 wt% of Ce on ferrite) were stirred at room temperature in aqueous solution (50 mL) for 1 h. After impregnation, the suspension was adjusted to pH 12 by adding sodium hydroxide (1.0 M) and further stirred for 20 h. The solid was washed with distilled water (5 × 10 mL). The resulting Nanocat-Fe-Ce particles were sonicated for 10 min, washed with distilled water and subsequently with ethanol, and dried under vacuum at 60 °C for 24 h. The Ce content was determined by ICP-AES and it was found to be 7.41%.

Synthesis of 1,4-dihydropyridines catalyzed by Nanocat-Fe-Ce

In a typical reaction, the aldehyde (1 mmol), methyl/ethyl-acetoacetate (1 mmol), ammonium acetate (1.5 mmol), dimedone (1 mmol), and Nanocatalyst-Fe-Ce (100 mg, 5.22 mol% Ce) in ethanol (2 mL) were stirred at room temperature. After completion of the reaction (monitored by TLC), the magnetic nanocatalyst was separated from the products using an external magnet. The obtained reaction mixture was concentrated under vacuum and the crude 1,4-dihydropyridines (**1a–m**) purified by recrystallization from hot ethanol.

Synthesis of methyl 2,6-bis(4-methoxyphenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (5)[34]

To a 10 mL flask were sequentially added 4-methoxyaniline (1.0 mmol), methyl acetoacetate (0.5 mmol), Nanocat-Fe-Ce (100 mg, 5.22 mol% Ce), ethanol (4 mL), and benzaldehyde (1.0 mmol). After completion of the reaction (18 h, monitored by TLC), the magnetic nanocatalyst was separated from the products by an external magnet. The obtained reaction mixture was concentrated under vacuum and the residual reaction mixture was diluted with ethyl acetate, washed with brine, and dried over anhydrous sodium sulfate. Methyl 2,6-bis(4-methoxyphenyl)-1-phenyl-4-(phenylamino)-1,2,5,6-tetrahydropyridine-3-carboxylate (**5**) was obtained in 82% yield, which was purified by recrystallization from hot ethanol.

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