Full paper

Applied Organometallic Chemistry

Received: 27 February 2015 Revised: 23 April 2015 Accepted: 26 April 2015 Published online in Wiley Online Library: 11 June 2015

(wileyonlinelibrary.com) DOI 10.1002/aoc.3333

L-Proline-functionalized Fe_3O_4 nanoparticles as a novel magnetic chiral catalyst for the direct asymmetric Mannich reaction

Javad Safaei-Ghomi* and Safura Zahedi

L-Proline has been successfully anchored on the surface of magnetic nanoparticles and characterized using powder X-ray diffraction, scanning electron microscopy, vibrating sample magnetometry and Fourier transform infrared spectroscopy. These nanoparticles as a chiral catalyst have been employed to promote the direct asymmetric Mannich reaction. The corresponding products are obtained in high yields with high level of diastereoselectivity (up to 99:1 dr) in the presence of Fe_3O_4–L-proline. Also this heterogeneous catalyst can be recovered easily and reused many times without significant loss of its catalytic activity.

Keywords: magnetic materials; asymmetric catalysis; Mannich reaction; L-proline; Fe_3O_4 nanoparticles

Introduction

Recently, magnetic nanoparticles (MNPs) have been widely employed as alternative catalyst supports. Most importantly, these MNP-supported catalysts show not only high catalyst recycling but also high surface area resulting in high catalyst loading capacity, high dispersion and good stability.[1–3] Magnetic separation offers a very expedient approach for removing and recycling particles/composites by applying external magnetic fields.[4–6] Fe_3O_4 nanoparticles have plentiful hydroxyl groups on their surfaces, and hence they are naturally hydrophilic. The surface coating or modification of iron oxide nanoparticles is very important in many applications, because of their aggregation and difficulty in dispersion in organic media. Conventionally, heterogeneous catalysis is favoured over homogeneous catalysis due to ease of handling and regenerability.[7–12] Proline as an important chiral small-molecule organocatalyst has attracted much attention since it is easily accessible, environmentally safe and available in both enantiomeric forms.[13–15] L-Proline is not very expensive, and studies of supported proline and its derivatives still have important significance. Immobilization and recycling of L-proline have received considerable attention in recent years. Supported proline catalysts can be easily recovered from a reaction mixture and retain stable catalytic activity and selectivity after being reused many times, which is meaningful for environmental protection and energy conservation. Several types of supports, such as polymers,[16–19] silica,[20–24] ionic liquids,[25,26] β-cyclodextrin,[27] Merrifield resin[28] and magnetite,[29] are usually considered for the immobilizations of proline and its derivatives.

The catalytic asymmetric Mannich reaction has proven to be a powerful tool to access optically active nitrogen-containing compounds such as β-amino carbonyl compounds, which are important synthetic intermediates for various pharmaceuticals and natural products.[30–32] Hence, the synthesis of these compounds is an important and useful task in organic chemistry. Recently, the three-component condensation of aldehydes, amines and ketones has gained popularity. A variety of catalysts such as $Zn(OTf)_2$,[33] $H_3PW_{12}O_{40}$,[34] $ZrOCl_2{\cdot}8H_2O$,[35] (*S*)-serine,[36] dodecylbenzenesulfonic acid,[37] 1,1,3,3-tetramethylguanidine,[38] proline–thiourea,[39] $HClO_4$–SiO_2[40] and silica sulfuric acid[41] have been utilized for three-component synthesis of β-amino carbonyl compounds. A powerful way of catalysing the direct asymmetric Mannich reaction is the use of proline and proline derivatives as catalysts.[42] On the basis of these observations, herein we report the Mannich reaction between aldehydes, amines and cyclohexanone using magnetic chiral organocatalytic nanoparticles (Fe_3O_4–L-proline) under mild conditions (Scheme 1).

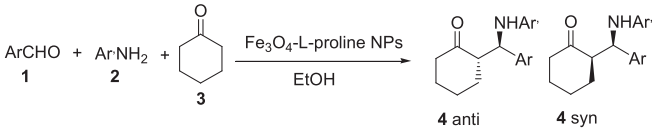
Experimental

Materials and physical measurements

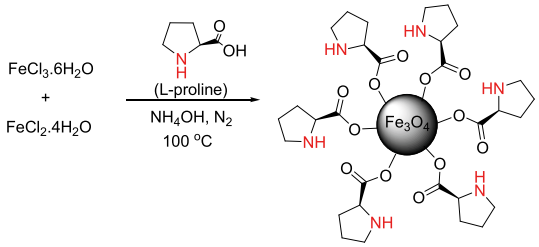
All the chemicals reagents used in our experiments were of analytical grade and were used as received without further purification. Powder X-ray diffraction (XRD) was carried out using a Philips X'pert diffractometer with monochromatized Cu Kα radiation (k = 1.5406 Å). ^{1}H NMR and ^{13}C NMR spectra were measured, respectively, at 400 and 100 MHz. The solvent used for NMR spectroscopy was $CDCl_3$, using tetramethylsilane as the internal reference. FT-IR spectra of all compounds were recorded with an FT-IR Magna 550 apparatus using KBr plates. Elemental analyses (C, H, N) were conducted using a Carlo Erba model EA1108 analyser. Melting points were determined with an Electro Thermal 9200, and are not corrected. Microscopic morphology of products was visualized using SEM (LEO 1455VP).

* *Correspondence to: Javad Safaei-Ghomi, Department of Organic Chemistry, Faculty of Chemistry, University of Kashan, Kashan 87317, IR Iran. E-mail: safaei@kashanu.ac.ir*

Department of Organic Chemistry, Faculty of Chemistry, University of Kashan, Kashan 87317, IR Iran



Scheme 1. One-pot, three-component Mannich reaction catalysed by Fe_3O_4–L-proline nanoparticles (NPs).



Scheme 2. Schematic procedure for the preparation of Fe_3O_4–L-proline nanoparticles.

Preparation of Fe_3O_4–L-Proline nanoparticles

The overall procedure used to synthesize the magnetic catalyst is illustrated in Scheme 2. The detailed procedure was as follows. $FeCl_3{\cdot}6H_2O$ (0.54 g) and $FeCl_2{\cdot}4H_2O$ (0.2 g) salts (with molar ratio of 2:1) were dissolved in 100 ml of deionized water and kept at a constant temperature of 40°C for 15 min with vigorous stirring. Then, 0.3 g of L-proline and NH_4OH solution (25 wt%) were added to the mixture until the pH was raised to 11 at which point a black suspension was formed. This suspension was then refluxed at 100°C for 6 h, with vigorous stirring. Fe_3O_4–L-proline nanoparticles were separated from the aqueous solution by magnetic decantation, washed with distilled water several times and then dried in an oven overnight. The whole synthesis was done under nitrogen atmosphere. The L-proline content in the Fe_3O_4–L-proline nanoparticles was 4.68 mmol g^{-1}, which was determined according to the content of nitrogen element in Fe_3O_4–L-proline nanoparticles from elemental analyses.

General procedure for Mannich reaction catalysed by Fe_3O_4–L-proline nanoparticles

In a typical Mannich reaction, the novel Fe_3O_4–L-proline nanoparticles catalyst (0.03 g), aromatic aldehyde (2.5 mmol), aromatic amine (2.5 mmol), cyclohexanone (3 mmol) and ethanol were added into a round-bottomed flask and stirred at 100°C. After completion of the reaction, the mixture was cooled to room temperature, the catalyst was recovered using an external magnet and the reaction mixture was purified by flash column chromatography to give pure β-amino ketone derivatives. Products **4d** and **4i** (Fig. 1) were completely characterized from spectroscopic data as follows.

2-((2-Chlorophenyl)(phenylamino)methyl)cyclohexanone (**4d**). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.61 (d, J = 8.0 Hz, 1H, HC-19), 7.53 (m, 1H, HC-17), 7.24 (m, 1H, HC-18), 7.05–7.13 (m, 3H, HC-11,12,13), 6.66 (d, J = 7.2 Hz, 1H, HC-16), 6.54 (d, J = 8.0 Hz, 2H, HC-10,14) 4.91 (br s, 1H, NH), 4.81 (d, J = 6.4 Hz, 1H, HC-7), 2.95–2.99 (m, 1H, HC-6), 2.30–2.41 (m, 2H, CH-2), 1.95–2.14 (m, 4H, HC-4,5), 1.59–1.85 (m, 2H, HC-3). FT-IR (KBr, ν, cm^{-1}): 3396.45, 1697.69, 1601.76, 1502.64, 809.08. ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 212.89 (C-1), 146.69 (C-9), 140.43 (C-15), 132.31 (C20), 129.01 (C-11,13), 128.90 (C-16), 128.28 (C-19), 127.34 (C-18), 123.61 (C-17), 117.23 (C-12), 113.11 (C-10,14), 57.59 (C-6), 54.99 (C-7), 42.80 (C-2), 32.74 (C-3), 27.85 (C-4), 24.80 (C-5). Anal. Calcd for $C_{19}H_{20}ClNO$ (%): C, 72.72; H, 6.42; N, 4.46. Found (%): C, 72.69; H, 6.35; N, 4.41.

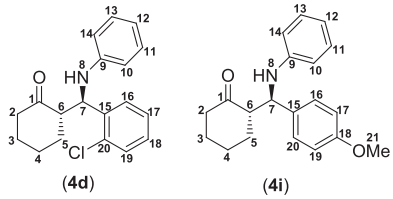


Figure 1. Structures of products 4d and 4i.

2-((4-Methoxyphenyl)(phenylamino)methyl)cyclohexanone (**4i**). ^{1}H NMR (400 MHz, $CDCl_3$, δ, ppm): 7.25 (d, J = 8.4 Hz, 2H, HC-16,20), 7.14 (d, J = 7.6 Hz, 2H, HC-10,14), 7.10–7.07 (m, 2H, HC-11,13), 6.63 (t, J = 7.2 Hz, 1H, HC-12), 6.66 (d, J = 8.4 Hz, 2H, HC-17,19), 4.71 (br s, 1H, NH), 4.62 (d, J = 7.2 Hz, 1H, HC-7), 2.72–2.76 (m, 1H, HC-6), 2.34–2.38 (m, 2H, HC-2), 1.83–1.93 (m, 4H, HC-4,5), 1.68–1.75 (m, 3H, HC-3). FT-IR (KBr, ν, cm^{-1}): 3332.42, 1707.26, 1600.92, 1532.21, 800.33. ^{13}C NMR (100 MHz, $CDCl_3$, δ, ppm): 212.73 (C-1), 147.01 (C-18), 138.38 (C-9), 136.47 (C-15), 129.21 (C-11,13), 128.77 (C-16,20), 126.96 (C-12), 117.16 (C-17,19), 113.34 (C-10,14), 57.39 (C-21), 57.30 (C-6), 41.43 (C-7), 30.92 (C-2), 27.92 (C-3), 23.28 (C-4), 20.81 (C-5). Anal. Calcd for $C_{20}H_{23}NO_2$ (%): C, 77.64; H, 7.49; N, 4.53. Found (%): C, 77.43; H, 7.56; N, 4.54.

Results and discussion

The asymmetric Mannich reaction is a well-known and widely used synthetic pathway for carbon–carbon bond formation in organic synthesis. The catalytic performance of the Fe_3O_4–L-proline nanoparticles was evaluated in the synthesis of β-amino ketones in the Mannich reaction.

Characterization of catalyst

Initially, in order to investigate the structure of the catalyst, we characterized the Fe_3O_4–L-proline nanoparticles using XRD, FT-IR spectroscopy, vibrating sample megnetometry (VSM) and SEM. Phase investigation of the crystalline Fe_3O_4 and Fe_3O_4–L-proline nanoparticles was performed using XRD and the diffraction pattern is presented in Fig. 2. The same peaks are observed in both the Fe_3O_4 and Fe_3O_4-L-proline patterns, indicating retention of the crystalline spinel ferrite core structure during the immobilization of L-proline. The XRD pattern indicates diffraction peaks at 2θ of 30.4°, 35.8°, 43.5°, 53.7°, 57.2° and 62.9° corresponding to the spinel structure of Fe_3O_4, which can be assigned to the diffractions of the (220), (311), (400), (422), (511) and (440) faces of the crystals, respectively. All of the observed diffraction peaks are indexed to the cubic structure of Fe_3O_4 (JCPDS no. 79-0417) revealing a high phase purity of magnetite.

The FT-IR spectra of L-proline and Fe_3O_4–L-proline nanoparticles are shown in Fig. 3. In the spectrum of Fe_3O_4–L-proline the intense peak at 1632 cm^{-1} is derived from C=O stretching. The absorption peak at 589 cm^{-1} is characteristic of Fe–O bond which confirms the presence of Fe_3O_4 nanoparticles. It is worth noting that the C=O stretch band of the carboxyl group is present at 1621 cm^{-1} in the spectrum of L-proline, but is absent in the spectrum of Fe_3O_4–L-proline. Two new bands appear at 1632 and 1400 cm^{-1}, which are

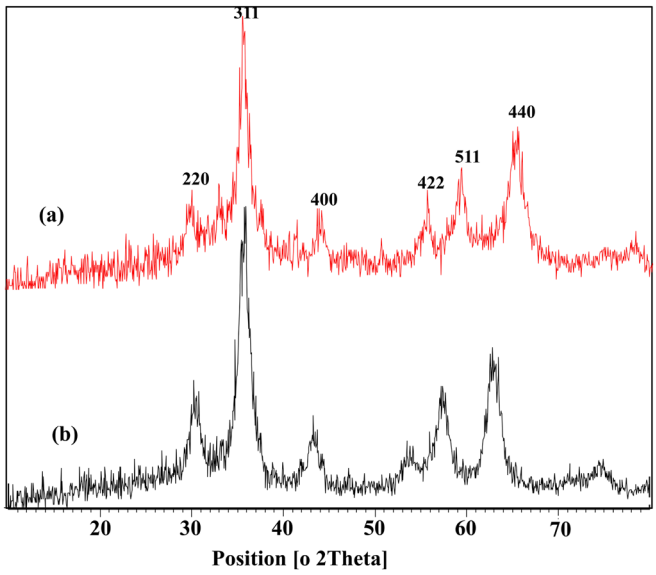


Figure 2. XRD patterns of (a) naked Fe_3O_4 and (b) Fe_3O_4–L-proline nanoparticles.

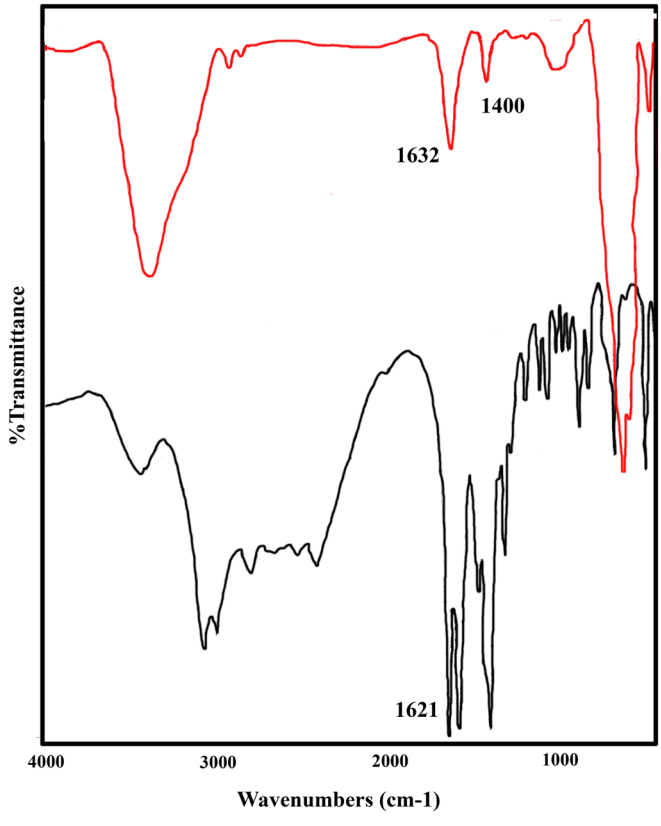


Figure 3. FT-IR spectra of Fe_3O_4–L-proline nanoparticles (top) and L-proline (bottom).

ascribed to asymmetric $\nu_{as}(COO^-)$ and symmetric $\nu_s(COO^-)$ stretching of carboxyl group. These results reveal that L-proline is chemisorbed onto the Fe_3O_4 nanoparticles in a monodentate manner. According to Zhang *et al.* the wavenumber separation, *D*, between the $\nu_{as}(COO^-)$ and $\nu_s(COO^-)$ FT-IR bands can be used to distinguish the type of interaction between the carboxylate head and the metal atom. The largest *D* (200–320 cm^{-1}) corresponds to monodentate interaction and the smallest *D* (<110 cm^{-1}) corresponds to chelating bidentate interaction. Intermediate *D* (140–190 cm^{-1}) corresponds to bridging bidentate.[43] In the present study, *D* (1632 − 1400 = 232 cm^{-1}) corresponds to monodentate interaction.

SEM imaging provides more accurate information on the particle size and morphology of the functionalized MNPs (Fig. 4). These images show that the nanoparticles have a uniform size and a spherical shape. It can be seen from Fig. 4(a) that magnetite Fe_3O_4 particles have a mean diameter of about 40–50 nm and a nearly spherical shape. The SEM image shown in Fig. 4(b) demonstrates that most of the Fe_3O_4–L-proline nanoparticles are spherical with the same particle size.

The magnetic properties of Fe_3O_4 and Fe_3O_4–L-proline nanoparticles were measured via VSM at room temperature (Fig. 5). It can be seen that the saturation magnetization values of the samples are 34.5 and 26.3 emu g^{-1} for Fe_3O_4 and Fe_3O_4–L-proline nanoparticles, respectively. Thus, our catalyst can be recovered using an external magnetic field.

Catalytic behaviour of Fe_3O_4–L-Proline nanoparticles

The catalytic activity of the Fe_3O_4–L-proline nanoparticles in the asymmetric Mannich reaction was investigated by performing a model reaction of benzaldehyde, aniline and cyclohexanone. In order to determine the optimal catalyst loading, the three-component model Mannich reaction was carried out using 0.01–0.04 g of Fe_3O_4–L-proline nanoparticles. The best result in terms of yield (90%) for the formation of β-amino ketone is achieved within 1.5 h with a catalyst loading of 0.03 g (Table 1). Interestingly, the Mannich reaction shows an intriguing solvent effect; therefore, Table 1 also summarizes the results obtained using various solvents. High yield and good anti selectivity of the reaction are observed for EtOH compared with MeOH, CH_2Cl_2 and H_2O.

Further, we investigated the general applicability of Fe_3O_4–L-proline in the coupling of various aldehyde and aniline derivatives with cyclohexanone under the optimized conditions. As evident from Table 2, the reactions of various aromatic aldehydes, anilines and cyclohexanone give the β-amino ketone adduct in good to high yield with good to excellent anti selectivity at 100°C.

Mechanistic aspects

In order to explain the observed stereoselectivities, it is proposed that the reaction occurs via the transition state shown in Scheme 3. The proposed mechanism of the Mannich reaction catalysed by the Fe_3O_4–L-proline nanoparticles is depicted in this scheme: the nucleophilic attack of the proline moiety on cyclohexanone (a), the dehydration of the carbinol amine to give an enamine (b), carbon–carbon bond forming between imine and enamine in the transition state (c) and, after hydrolysis, reaction to give the diastereoselective Mannich product (d and e). Typically, Mannich products are formed via si-face attack on an imine. Accordingly, in the Mannich transition state we assume that the configurations of both the proline enamine and the imine are in E form.[44] The si-face of the imine is selectively attacked by the re-face of enamine to allow for protonation of the lone pair and compensation of vnegative charge formation. Attack of the imine re-face would result in unfavourable steric interactions between the pyrrolidine and the aromatic ring.

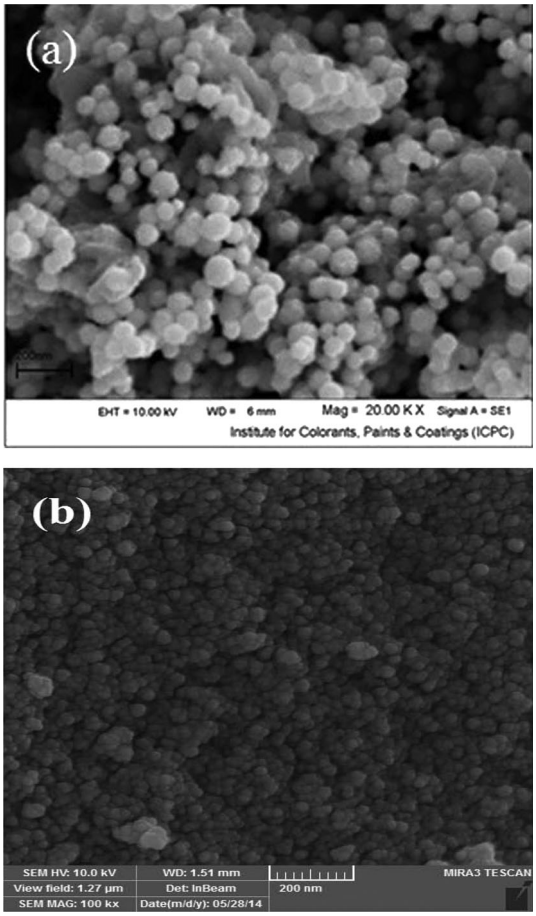


Figure 4. SEM images of (a) naked Fe_3O_4 and (b) Fe_3O_4–L-proline nanoparticles.

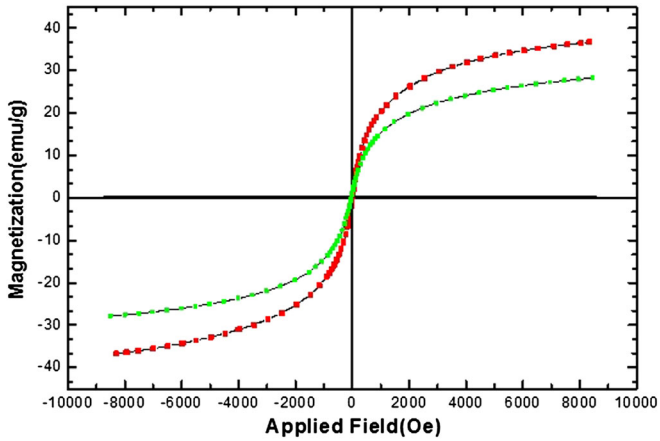
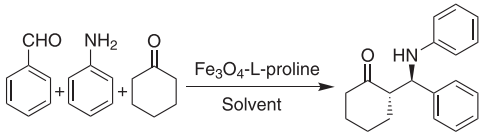


Figure 5. Magnetization curves for the prepared Fe_3O_4 MNPs (red curve) and Fe_3O_4–L-proline (green curve) at room temperature.

The anti/syn ratio was identified using ^{1}H NMR analysis, according to the values of the coupling constants between the vicinal protons α and β to C=O. It has been reported that the *J* values of anti isomers (*ca* 7.5 Hz) are higher than those of syn isomers (*ca* 4.5 Hz) in these types of systems.[45] The isomers were determined from the relative areas under the absorption peaks for H_β.

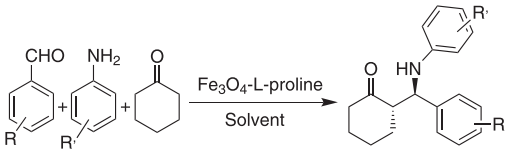
Table 1. Solvent screening and effect of catalyst loading on three-component Mannich reaction



Entry	Catalyst (g)	Solvent	Temperature (°C)	Yield (%)[a]
1	0.03	H_2O	50	Trace
2	0.03	MeOH	50	45
3	0.03	CH_2Cl_2	50	35
4	0.01	EtOH	50	57
5	0.01	EtOH	70	66
6	0.02	EtOH	90	75
7	0.03	EtOH	100	90
8	0.04	EtOH	100	90

[a]Isolated yield.

Table 2. Direct asymmetric Mannich reaction catalysed by Fe_3O_4–L-proline nanoparticles[a]

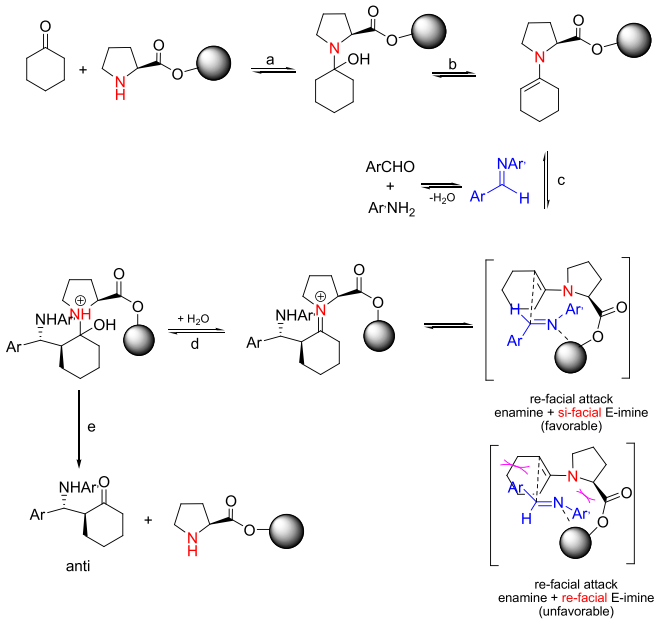


Entry	R	R′	Product	Time (h)	Yield (%)[b]	Anti/syn[c]
1	H	H	**4a**	1.5	90	99:1
2	H	4-Cl	**4b**	2	86	98:2
3	H	3-Me	**4c**	2	85	97:3
4	2-Cl	H	**4d**	1.5	90	97:3
5	4-Me	H	**4e**	2	85	99:1
6	4-Cl	H	**4f**	1.5	89	99:1
7	4-Br	H	**4g**	1.5	90	99:1
8	4-Cl	4-Me	**4h**	2	85	98:2
9	4-OMe	H	**4i**	2	85	98:2
10	H	4-Me	**4j**	2	85	99:1
11	H	4-Cl	**4k**	2	89	98:2
12	2-OMe	H	**4l**	2	85	99:1
13	2-Br	H	**4m**	1.5	90	99:1
14	2,3-OMe	H	**4n**	2	85	98:2
15	2,5-OMeC_6H_3	Ph	**4o**	2	85	98:2

[a]Reaction conditions: aromatic aldehyde (2.5 mmol), aromatic amine (2.5 mmol), cyclohexanone (3 mmol), Fe_3O_4–L-proline nanoparticle (0.03 g).
[b]Isolated yield.
[c]Anti/syn ratio determined using ^{1}H NMR analysis.

Recycling of catalyst

The recycling and recovery of catalysts are key from both practical and environmental points of view. Therefore, we explored the



Scheme 3. Proposed mechanism of Mannich reaction catalysed by Fe_3O_4–L-proline.

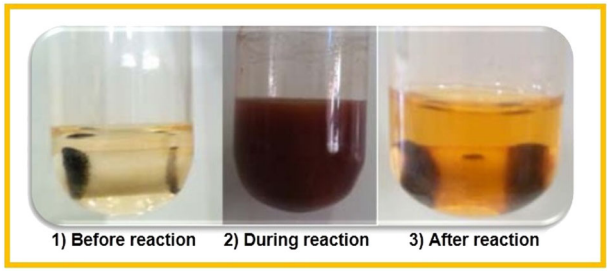


Figure 6. Easy separation of Fe_3O_4–L-proline nanoparticles using an external magnet.

reusability of the catalyst in the model reaction between benzaldehyde, aniline and cyclohexanone in the presence of 0.03 g of catalyst at 100°C. The MNP-supported chiral catalyst is easily and completely separated from the mixture reaction using an external magnetic field. As shown in Fig. 6, the Fe_3O_4–L-proline nanoparticles have a good dispersion in the ethanol solvent, and an excellent magnetic separation capability appears when a magnet is applied to the vessel. After the separation from the reaction mixture using a magnet, the catalyst was reused in the model reaction for five reaction cycles. It is found that product yields decrease to a small extent on each reuse (run 1, 90%; run 2, 90%; run 3, 89%; run 4, 89%; run 5, 88%).

Conclusions

In summary, we demonstrated the preparation of novel MNPs by anchoring L-proline on the surface of iron oxide nanoparticles as a chiral magnetically separable catalyst for the asymmetric Mannich reaction. This protocol is compatible with various aldehydes and anilines, thus affording β-amino ketones with high yields and excellent diastereoselectivities (up to 99:1 dr). Also, the resultant catalyst combines many advantages such as low cost, long-term stability, high catalytic activity and easy recovery for this reaction. Furthermore, it can be used repeatedly five times with minor variation of catalytic activity.

Acknowledgment

The authors are grateful to the University of Kashan for supporting this work under grant no. 159148/XII.

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