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Facile and efficient synthesis of benzo[*b*][1,5]diazepines by three-component coupling of aromatic diamines, Meldrum's acid, and isocyanides catalyzed by Fe_3O_4 nanoparticles

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Abstract Highly effective one-pot synthesis of benzo[*b*][1,5]diazepines has been achieved by three-component (or, in situ, including catalyst and solvent, five-component) reaction of aromatic diamines, Meldrum's acid, and isocyanides catalyzed by magnetite (Fe_3O_4) nanoparticles. Pharmaceutically and biologically active heterocyclic compounds including benzodiazepine derivatives were efficiently synthesized in excellent yields and short reaction times at room temperature. The significant features of the Fe_3O_4 nanoparticles are: easy preparation, cost-effectiveness, high stability, easy separation, low loading, and reusability of the catalyst. The heterogeneous nanoparticles were fully characterized by XRD, EDX, BET, SEM, TEM, and FT-IR analysis.

Keywords Fe_3O_4 · Nanoparticles · Benzo[*b*][1,5]diazepines · Multi-component reactions · Isocyanides

Introduction

Multi-component coupling reactions (MCRs) are valuable methods for producing compound libraries of small molecules for potential applications in medicinal and pharmaceutical chemistry [1]. MCRs often conform to the objectives of green chemistry in terms of economy of reaction steps and the many precise principles of desirable organic synthesis [2]. Because of their advantages, which include facile performance, environmentally benign nature, speed, and atom economy, MCRs have attracted much attention in combinatorial chemistry [3]. Among the different types of nitrogen-containing organic structures, benzodiazepine derivatives have a wide range of pharmaceutical and biological activity, including analgesic,

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anticonvulsant, anti-depressive, anti-anxiety, sedative, anti-inflammatory, and hypnotic [4–7]. They are also important drugs for treatment of diseases which include cardiovascular disorders, cancer, diabetes, and viral infections (e.g. HIV) [8–11]. Important 1,5-benzodiazepines with high medicinal activity include olanzapine, **1**, and clozapine, **2** (for treatment of schizophrenia) [12], clobazam, **3** (an anxiolytic agent) [13], and 3-carbamoyl-1,5-benzodiazepine, **4** (a selective CCK-B antagonist as potential anxiolytic drug) [14] (Fig. 1).

Synthesis of 1,5-benzodiazepines has therefore attracted much attention and many methods for synthesis of 1,5-benzodiazepines have been reported in the literature. Methods for synthesis of benzodiazepines mainly entail coupling of 1,2-phenylenediamines with a variety of ketones [15], chalcones [16], alkynes [17], 4,6-di-*O*-benzyl-2,3-dideoxyaldehydo-D-erythro-*trans*-hex-2-enose [18], 3-acetyl-4-hydroxy-6-methyl-2*H*-pyran-2-one [19], and alk-3-yn-1-ones [20]. Although many of these procedures have valuable advantages, some have specific disadvantages, for example hazardous reaction conditions, unsatisfactory yields, high cost of catalysts and solvents, complicated work-up and processing, production of side products, and long reaction times. Thus, development efficient, mild, simple, and environmentally benign methods for synthesis of benzodiazepine derivatives would be highly desirable.

In recent years, metal nanocatalysts have become an important alternative to traditional materials in the different fields of chemistry, and have attracted much interest among chemists [21]. The utility of heterogeneous catalysts in organic reactions can be enhanced by use of nano-sized materials, because of the very small size, and hence high surface area, of nanoparticles in comparison with the bulk form. Heterogeneous nanocatalysts have much potential for development of selective, efficient, and high-yielding procedures [22]. Recently, magnetite Fe_3O_4 nanoparticles (Fe_3O_4 NPs) have attracted much attention as nano-sized materials because of their wide range of uses in such fields as medical applications, drug delivery, and remediation, as catalysts, and in industry [23–26]. The salient and significant property of magnetite nanoparticles is the simple and facile separation of these catalysts from the reaction mixture by use of an external magnet. In the last decade Fe_3O_4 NPs have been used as an effective heterogeneous nanocatalyst in such organic reactions as synthesis of quinoxalines [27], α-aminonitriles [28], propargylic amines [29], sulfonamides [30], 3-[(2-chloroquinolin-3-yl)methyl]pyrimidin-4(3*H*)ones [31],

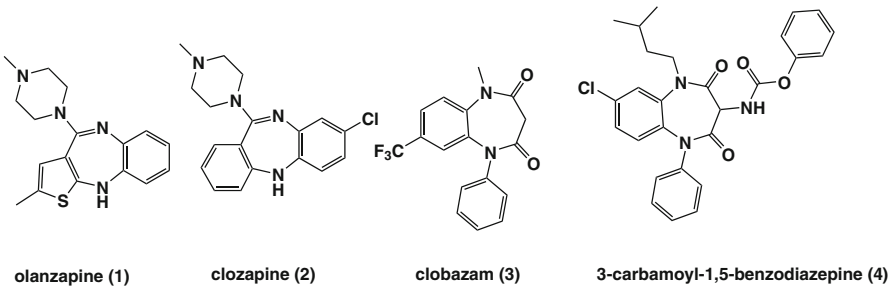
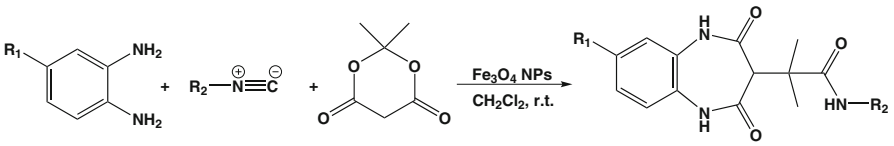


Fig. 1 Some biologically important benzodiazepines

1,8-dioxodecahydroacridine [32], coupling of phenols with aryl halides [33], the Suzuki reaction [34], the Sonogashira–Hagihara reaction [35], and the Paal–Knorr reaction, aza-Michael addition, and pyrazole synthesis [36]. Shaabani et al. have recently reported a novel and efficient method for synthesis of some tetrahydro-2, 4-dioxo-1*H*-benzo[*b*][1,5]diazepine-3-yl-2-methylpropanamide derivatives [37]. Although this method has valuable advantages, for example mild reaction conditions, good yields, and no undesirable byproducts, reaction times are long and yields are poor. So, despite its advantages, we decided to conduct research on this method, including increasing the reactivity of the substrates. In this context, and because of our interest in sustainable procedures for synthesis of heterocyclic compounds by use of multi-component reactions and nanocatalysts [38–42], we report herein a highly efficient and mild method for synthesis of tetrahydro-2,4-dioxo-1*H*-benzo[*b*][1,5]diazepine-3-yl-2-methylpropanamides by multi-component reaction of 1,2-phenylenediamines, isocyanides, and Meldrum's acid with Fe_3O_4 NPs as an environmentally benign, readily available, and economic nanocatalyst (Scheme 1).

Experimental

Chemicals of high purity were purchased from Merck and Fluka. IR spectra were recorded as KBr pellets on a Perkin–Elmer 781 spectrophotometer and an Impact 400 Nicolet FT-IR spectrophotometer. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker DRX-400 spectrometer (400 MHz) with TMS as internal reference and DMSO-d6 as solvent. All melting points are uncorrected and were determined in capillary tubes on a Boetius melting point microscope. TLC on silica gel polygram SILG/UV 254 plates was used for monitoring the purity of the reactants and the progress of reactions. Elemental analysis (C, H, N) was performed with a Carlo Erba model EA 1108 analyzer. Powder X-ray diffraction (XRD) was performed with a Philips X'pert diffractometer with monochromatic Cu Kα radiation ($\lambda = 1.5406$ Å). The microscopic morphology of products was studied by scanning electron microscopy (SEM; LEO 1455VP). Mass spectra were acquired by use of a Joel D-30 instrument at an electron energy of 70 eV. Transmission electron microscopy (TEM) was performed with a Jeol JEM-2100UHR, operated at 200 kV. N_2 adsorption/desorption analysis (BET) was performed at −196 °C by use of an automated gas adsorption analyzer (Tristar 3000, Micromeritics). Compositional analysis was performed by energy-dispersive X-ray analysis (EDAX, Kevex, Delta Class I).



Scheme 1 Preparation of tetrahydro-2,4-dioxo-1*H*-benzo[*b*][1,5]diazepine-3-yl-2methylpropanamides catalyzed by Fe_3O_4 NPs

Preparation of Fe_3O_4 nanoparticles

Fe_3O_4 nanoparticles were prepared by the procedure reported by Chen et al. [43]. $FeSO_4 \cdot 7H_2O$ (2.5 g) was dissolved in deionized water. Poly(ethylene glycol) 20,000 solution (50 g/l, 30 ml) was added, with stirring, followed by 10 ml dilute aqueous ammonia solution (2.5 %), again with stirring. H_2O_2 (0.27 ml) was then added slowly to the solution, followed by addition of 25 ml methanol. The mixture was stirred for 5 min to obtain a homogeneous solution. The solution was then transferred to a sealed 100-ml autoclave and heated at 160 °C for 7 h. The autoclave was then left to cool naturally to room temperature. The black product was centrifuged, isolated by filtration, washed several times with deionized water and alcohol, and finally dried at 80 °C for 8 h.

Typical procedure for synthesis of tetrahydro-2,4-dioxo-1*H*-benzo[*b*][1,5]diazepine-3-yl-2-methylpropanamides (**4a**–**4j**)

Fe_3O_4 nanoparticles (0.02 g, 0.1 mmol, 10 mol %) were added to a mixture of 1,2-phenylenediamines (1 mmol), Meldrum's acid (1 mmol), and isocyanide (1 mmol) in 5 ml dichloromethane. The reaction mixture was stirred for 3–4 h at room temperature. Progress of the reaction was continuously monitored by TLC. After completion of the reaction the residue was dissolved in methanol and the nanocatalyst was separated by use of an external magnet. The solvent was evaporated under vacuum and the solid obtained was washed several times with acetone to afford pure benzodiazepine.

All of the products were characterized and identified by determination of m.p. and by use of ^{1}H NMR, ^{13}C NMR, and FT-IR spectroscopy. Spectral data for new products are listed below.

*N-n-pentyl-2-(2,4-dioxo-2,3,4,5-tetrahydro-1H-benzo[b][1,5]diazepin-3-yl)-2-methylpropanamide (**4d**)*

White solid; mp = 286–288 °C; ^{1}H NMR (400 MHz, DMSO-d_6): 0.81–0.84 (t, 3H, CH_3 (pentyl)), 1.17–1.43 (m, 12H, 3 × CH_2 and 2 × CH_3), 2.96–2.97 (t, 2H, CH_2–NH), 3.39 (s, 1H, CH), 7.11–7.18 (m, 4H, ArH), 7.58 (bs, 1H, NH), 10.33 (bs, 2H, 2NH). ^{13}C NMR (100 MHz, DMSO-d_6): 14.4, 22.3, 28.9, 29.1, 29.8, 43.4, 48.1, 52.6, 112.4, 125.3, 130.4, 167.4, 177.1. FT-IR (KBr, cm^{-1}): 3,347 (NH), 1,700 (C=O), 1,660 (C=O), 1,546 (C=C). Anal. calcd for $C_{18}H_{25}N_3O_3$: C 65.23, H 7.60, N 12.58. Found C 65.09, H 7.71, N 12.69.; MS (EI) (*m*/*z*): 331 (M^+).

*N-(4-methoxyphenyl)-2-(2,4-dioxo-2,3,4,5-tetrahydro-1H-benzo[b][1,5]diazepin-3-yl)-2-methylpropanamide (**4e**)*

White solid; mp = 306–308 °C; ^{1}H NMR (400 MHz, DMSO-d_6): 1.48–1.53 (s, 6H, 2 × CH_3), 3.43 (s, 1H, CH), 3.69 (s, 3H, OCH_3), 6.82–6.82 (d, 2H, J = 8 Hz, ArH), 7.16–7.18 (m, 4H, ArH), 7.42–7.44 (d, 2H, J = 8 Hz, ArH), 9.53 (bs, 1H, NH), 10.47 (bs, 2H, 2NH). ^{13}C NMR (100 MHz, DMSO-d_6): 21.8, 43.1, 48.5, 56.1, 122.2, 125.5, 131.4, 133.6, 135.8, 136.2, 140.1, 167.8, 177.2. FT-IR (KBr, cm^{-1}): 3,424 (NH),

1,695, (C=O), 1,654 (C=O), 1,510 (C=C), 1,253 (C–O). Anal. calcd for $C_{20}H_{21}N_3O_4$: C 65.38, H 5.67, N 11.44. Found C 65.51, H 5.59, N 11.35.; MS (EI) (*m*/*z*): 367 (M^+).

*N-n-pentyl-2-methyl-2-(7-methyl-2,4-dioxo-2,3,4,5-tetrahydro-1H-benzo[b][1,5]diazepin-3-yl)propanamide (**4i**)*

White solid; mp = 246–248 °C; ^{1}H NMR (400 MHz, DMSO-d_6): 0.92–0.95 (t, 3H, CH_3 (pentyl)), 1.22–1.51 (m, 12H, 3 × CH_2 and 2 × CH_3), 2.22 (s, 3H, CH_3), 2.93 (t, 2H, CH_2–NH), 3.34 (s, 1H, CH), 7.09–7.16 (m, 3H, ArH), 8.11 (bs, 1H, NH), 10.43 (bs, 2H, 2NH). ^{13}C NMR (100 MHz, DMSO-d_6): 15.6, 19.8, 21.4, 22.8, 29.2, 29.7, 43.4, 48.2, 53.1, 112.4, 125.3, 126.7, 127.5, 128.4, 133.2, 167.2, 177.1. FT-IR (KBr, cm^{-1}): 3,339 (NH), 1,698 (C=O), 1,659 (C=O), 1,566 (C=C). Anal. calcd for $C_{19}H_{27}N_3O_3$: C 66.06, H 7.88, N 12.16. Found: C 66.18, H 7.79, N 12.04.; MS (EI) (*m*/*z*): 345 (M^+).

*N-(4-methoxyphenyl)-2-methyl-2-(7-methyl-2,4-dioxo-2,3,4,5-tetrahydro-1H-benzo[b][1,5]diazepin-3yl)propanamide (**4j**)*

White solid; mp = 283–285 °C; ^{1}H NMR (400 MHz, DMSO-d_6): 1.31–1.35 (s, 6H, 2 × CH_3), 2.22 (s, 3H, CH_3), 3.45 (s, 1H, CH), 3.81 (s, 3H, OCH_3), 6.91–6.93 (d, 2H, J = 7.9 Hz, ArH), 7.14–7.17 (m, 3H, ArH), 7.53–7.55 (d, 2H, J = 7.9 Hz, ArH), 9.66 (bs, 1H, NH), 10.44 (bs, 2H, 2NH). ^{13}C NMR (100 MHz, DMSO-d_6): 19.9, 42.8, 43.5, 55.1, 56.7, 122.6, 123.7, 125.6, 128.4, 130.7, 131.4, 135.2, 136.5, 138.3, 142.1, 167.6, 169.9. FT-IR (KBr, cm^{-1}): 3,448 (NH), 1,705 (C=O), 1,662 (C=O), 1,518 (C=C), 1,246 (C–O). Anal. calcd for $C_{21}H_{23}N_3O_4$: C 66.13, H 6.08, N 11.02. Found: C 66.24, H 5.99, N 10.93.; MS (EI) (*m*/*z*): 381 (M^+).

Recycling and reuse of the catalyst

The magnetite nanoparticles recovered by use of the external magnet were washed several times with methanol and acetone then dried at 80 °C for 8 h. To investigate the lifetime and reusability of the Fe_3O_4 NPs, they were reused several times. We observed that recovered magnetite nanoparticles could be used in six successive runs with slight reduction in activity, as indicated in Fig. 2.

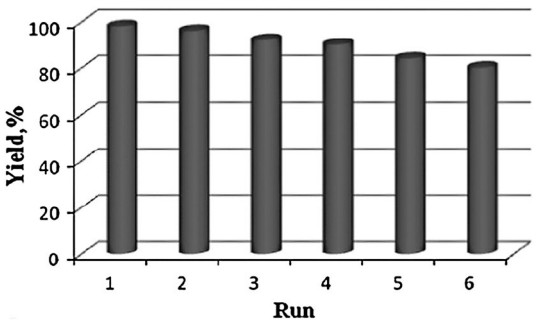


Fig. 2 Reusability of the Fe_3O_4 NPs

Results and discussion

In preliminary experiments magnetite nanoparticles were prepared and characterized by XRD, EDX, BET, SEM, TEM, and FT-IR analysis.

The crystalline nature of the synthesized Fe_3O_4 NPs was verified by XRD. The XRD pattern of the magnetite nanoparticles is shown in Fig. 3a. All reflection peaks in Fig. 3a can be readily indexed to those of the pure spherical phase of Fe_3O_4 with the P63mc group (JCDPS no. 75-0449). The crystallite size (D) of the nanocatalysts was calculated by use of the Debye–Scherrer equation ($D = K\lambda/\beta \cos \theta$), where β FWHM (full-width at half-maximum, or half-width) is in radians, θ is the position of the maximum of the diffraction peak, K is the so-called shape factor, which usually takes a value of approximately 0.9, and λ is the X-ray wavelength (1.5406 Å for Cu Kα). The crystallite size of Fe_3O_4 was 28 nm.

The chemical purity of the samples and their stoichiometry were studied by EDX. The EDX spectrum in Fig. 3b shows iron and oxygen are the only elements present.

The specific surface area was measured by nitrogen physisorption (the BET method); the specific surface area was approximately 98 m^2/g. The theoretical particle size calculated from the surface area and density of magnetite (5.18 g/cm^3) was 11.8 nm.

$$D_{BET} = \left(\frac{6,000}{\rho \times S}\right)$$

Figure 4 shows FT-IR spectrum of Fe_3O_4 NPs. The strong peak at approximately 570 cm^{-1} was ascribed to the Fe–O stretching frequency. In addition, the broad peaks at 3,452 and 1,637 cm^{-1} can be attributed to the ν (OH) stretching and bending vibrations, respectively. These peaks thus indicate the presence of a small amount of water physisorbed by the nanoparticles.

The morphology and particle size of Fe_3O_4 NPs were studied by SEM. The SEM image of Fe_3O_4 NPs in Fig. 5a shows the Fe_3O_4 to be a nanostructure with single-phase primary spherical particles of average diameter between 30 and 40 nm.

The size and morphology of the magnetite nanoparticles were analyzed by TEM (Fig. 5b). The results showed that the nanocatalyst consisted of spherical particles

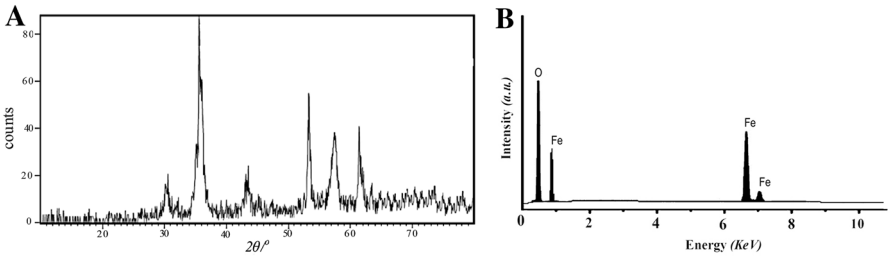


Fig. 3 XRD (**a**) and EDX (**b**) patterns of magnetite nanoparticles

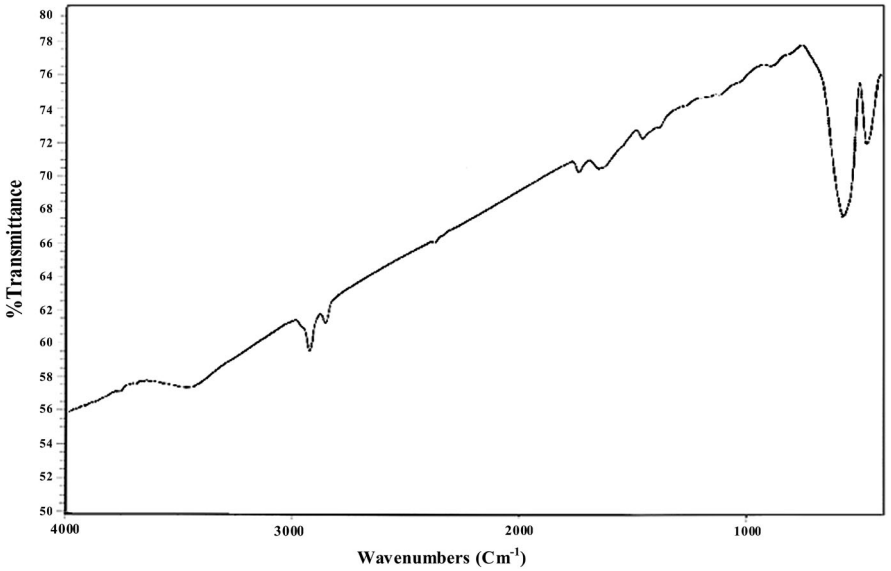


Fig. 4 FT-IR spectrum of Fe_3O_4 NPs

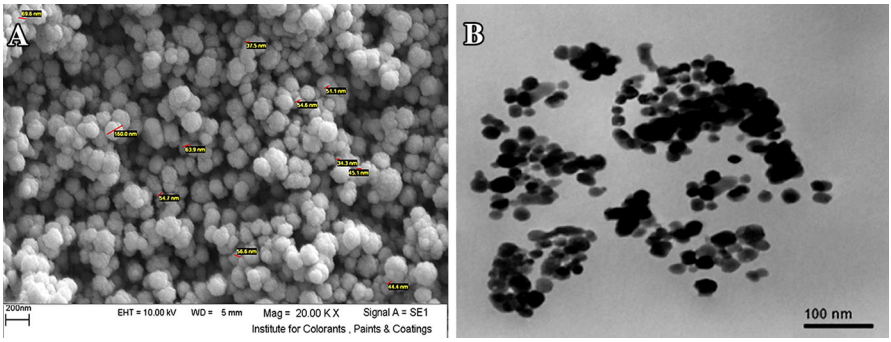
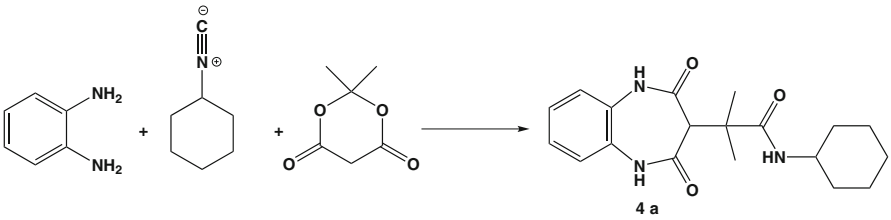


Fig. 5 SEM (**a**) and TEM (**b**) images of Fe_3O_4 NPs

with a crystallite size approximately 30 nm, in good agreement with the XRD crystal size.

In an initial study to find the optimum reaction conditions, preparation of *N*-cyclohexyl-2-(2,4-dioxo-2,3,4,5-tetrahydro-1*H*-benzo[*b*][1,5]diazepin-3-yl)-2-methylpropanamide **4a** was selected as model reaction (Scheme 2).

A mixture of *o*-phenylenediamine (1 mmol), Meldrum's acid (1 mmol), and cyclohexyl isocyanide (1 mmol) were reacted under different reaction conditions. When the reaction was conducted without Fe_3O_4 NPs as catalyst, a moderate yield of product was obtained after 9 h. We examined use of a variety of catalysts in this multi-component reaction. Many homogenous and heterogeneous catalysts



Scheme 2 Model reaction for synthesis of 1,5-benzodiazepin-2-one **4a**

Table 1 Synthesis of benzo[*b*][1,5]diazepin **4a** using various catalysts

Entry	Catalyst[a]	Time (h)	Yield (%)
1	None	9	62
2	SiO_2	6	65
3	CH_3COOH	4	62
4	$MgSO_4$	7	55
5	NaOH	9	Trace
6	MgO NPs	8	55
7	CaO NPs	8	51
8	CuO NPs	4	78
9	HCl	7	45
10	H_2SO_4	8	38
11	**Fe_3O_4 NPs**	**3**	**94**
12	Fe_3O_4 NPs (1 mol %)	6	75
13	Fe_3O_4 NPs (4 mol %)	4.5	82
14	Fe_3O_4 NPs (7 mol %)	3.5	90
15	Fe_3O_4 NPs (10 mol %)	3	94
16	Fe_3O_4 NPs (12 mol %)	3	94

Bold line refers to best result

[a] 20 mol % except where indicated

Reactions were performed in dichloromethane at room temperature

(including SiO_2, CH_3COOH, $MgSO_4$, NaOH, MgO NPs, CaO NPs, CuO NPs, HCl, H_2SO_4, and Fe_3O_4 NPs) were used to investigate the model reaction. Dichloromethane was used as solvent at room temperature and, initially, 20 mol % of each catalyst was used. The results summarized in Table 1 show that, although most of the Brønsted and Lewis acids could be used to perform the model reaction, the best results were obtained by use of Fe_3O_4 NPs.

The greater catalytic activity of magnetite Fe_3O_4 NPs compared with the other catalysts is because of their high surface area-to-volume ratio, which enables highly efficient diffusion. When the effect of using different amounts (1, 4, 7, 10, and 12 mol %) of Fe_3O_4 NPs was investigated, we observed that 10 mol % Fe_3O_4 NPs gave the best results and was sufficient to complete the reaction (Table 1).

In another experiment, we examined the effect of different solvents and of solvent-free conditions on synthesis of **4a**. As shown in Table 2, the results were highly dependent on the nature of the solvent. In each experiment the reactants were

Table 2 Model study catalyzed by Fe_3O_4 NPs in different solvents

Entry	Solvent	Time (h)	Yield (%)
1	No solvent	9	–
2	EtOH	9	Trace
3	DMF	5.5	55
4	$PhCH_3$	5	65
5	H_2O	9	Trace
6	**CH_2Cl_2**	**3**	**94**

Bold line refers to best result

Table 3 One-pot synthesis of benzo[*b*][1,5]diazepines catalyzed by Fe_3O_4 NPs

Entry	R_1	R_2	Product	Time (h)	Yield (%)
1	H	Cyclohexyl	**4a**	3	94
2	H	*tert*-Butyl	**4b**	2.5	95
3	H	Benzyl	**4c**	3.2	93
4	H	*n*-Pentyl	**4d**	3.5	91
5	H	4-Methoxyphenyl	**4e**	3.5	92
6	CH_3	Cyclohexyl	**4f**	2.5	95
7	CH_3	*tert*-Butyl	**4g**	2.2	97
8	CH_3	Benzyl	**4h**	3	95
9	CH_3	*n*-Pentyl	**4i**	3.2	94
10	CH_3	4-Methoxyphenyl	**4j**	3.5	93

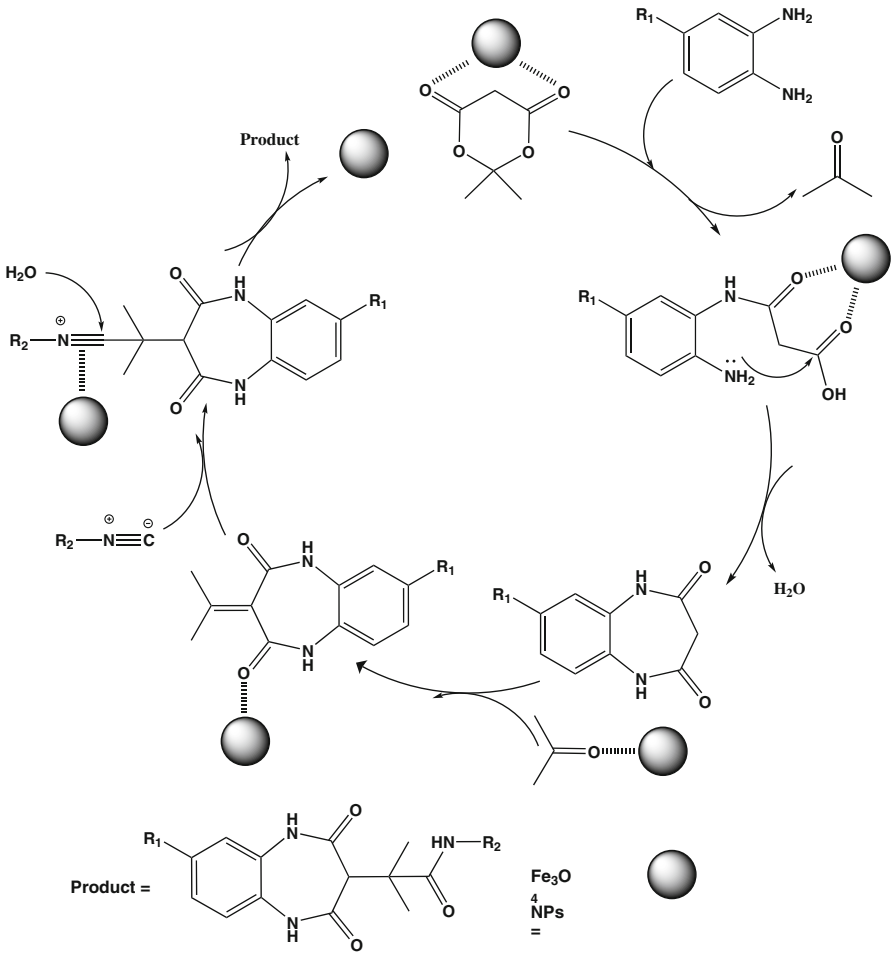
Reaction conditions: aromatic diamine (1 mmol), Meldrum's acid (1 mmol), isocyanide (1 mmol), Fe_3O_4 NPs (10 mol %), 5 ml CH_2Cl_2

mixed with 10 mol % Fe_3O_4 NPs in the presence of 5 ml solvent. Among the different solvents, it is apparent the best yield of **4a**, with a very short reaction time, was achieved by use of dichloromethane.

In the table dichloromethane is highlighted as the solvent of choice, because of facile and efficient synthesis of the product in a short reaction time and with satisfactory yield. In general, polar protic solvents, for example water and ethanol, give the lowest yields because the isocyanide nucleophiles are solvated in these solvents and, as a result, their nucleophilicity is reduced.

As shown in Table 3, we investigated the scope and limitations of multi-component synthesis of benzo[*b*][1,5]diazepine derivatives by using *o*-phenylenediamines and isocyanides with different structures under the optimized conditions. Three-component reactions of aromatic diamines, Meldrum's acid, and isocyanides were conducted very efficiently and cleanly in the presence of Fe_3O_4 NPs at room temperature, and no side products were observed.

In accordance with Table 3, we found that reaction of both mono and disubstituted aromatic diamines with isocyanides proceeded very smoothly, affording the corresponding 1,5-benzodiazepin-2-ones in excellent yields (91–97 %, entries 1–10, Table 3) and with short reaction times. To prove the generality of the method, we next used both aliphatic and aromatic isocyanides and, as a result, successfully synthesized a series of benzo[*b*][1,5]diazepines in high



Scheme 3 Proposed reaction pathway for synthesis of 1,5-benzodiazepin-2-ones with Fe_3O_4 NPs as catalyst

yields. The best results were obtained when *tert*-butyl isocyanide was used as substrate (95, 97 %, entries 2 and 7, Table 3).

The proposed reaction mechanism for synthesis of tetrahydro-2,4-dioxo-1*H*-benzo[*b*][1,5]diazepine-3-yl-2methylpropanamides is represented in Scheme 3. We suggest that Fe_3O_4 NPs behave as a Lewis acid and coordinate the oxygen atoms of Meldrum's acid and other intermediates and activate them for nucleophilic attack of 1,2-phenylenediamine and other nucleophiles. The high surface area-to-volume ratio of magnetite nanoparticles is mainly responsible for their catalytic properties. Finally the prepared benzo[*b*][1,5]diazepines could be isolated and the Fe_3O_4 NPs reused in further reactions.

Conclusions

In summary, we have described, for the first time, use of Fe_3O_4 NPs as an alternative to noble-metal-based catalysts for preparation of tetrahydro-2,4-dioxo-1*H*-benzo[*b*][1,5]diazepine-3-yl-2-methylpropanamides, which are pharmaceutically and biologically active heterocyclic compounds. This is a simple, efficient, and eco-friendly method for three-component (or, in situ, including catalyst and solvent, five-component) reaction of aromatic diamines, Meldrum's acid, and isocyanides using easily recoverable, environmentally benign, inexpensive, and nontoxic monodispersed magnetite nanoparticles (approx. 30 nm) as catalyst. The method is facile, avoids the use of high temperatures and expensive solvents and catalysts, and enables synthesis of the products in excellent yields and with short reaction times.

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References

1. L. Weber, Curr. Med. Chem. **9**, 2085 (2002)
2. G. Evano, N. Blanchard, M. Toumi, Chem. Rev. **108**, 3054 (2008)
3. M. Syamala, Org. Prep. Proced. Int. **1**, 41 (2009)
4. J.K. Landquist, in *Comprehensive Heterocyclic Chemistry*, vol. 1, ed. by A.R. Katritzky, C.W. Rees (Pergamon, Oxford, 1984), pp. 166–170
5. R.I. Fryer, Bicyclic diazepines, in *Comprehensive Heterocyclic Chemistry*, vol. 50, ed. by E.C. Taylor (Wiley, New York, 1991). Chapter II
6. H. Schutz, *Benzodiazepines* (Springer, Heidelberg, 1982)
7. R.K. Smalley, in *Comprehensive Organic Chemistry*, vol. 4, ed. by Barton, D. Ollis (Oxford, Pergamon, 1979)
8. K.S. Atwal, J.L. Bergey, A. Hedberg, S. Moreland, J. Med. Chem. **30**, 635 (1987)
9. M.D. Braccio, G. Grossi, G. Roma, L. Vargiu, M. Mura, M.E. Marongiu, Eur. J. Med. Chem. **36**, 935 (2001)
10. K.A. Parker, C.A. Coburn, J. Org. Chem. **57**, 97 (1992)
11. D.A. Claremon, N. Liverton, G.R. Smith, H.G. Selnick, U.S. Patent 5,726,171, 1998
12. A. Leyva-Pérez, J.R. Cabrero-Antonino, A. Corma, Tetrahedron **66**, 8203 (2010)
13. H. Kruse, Drug Dev. Res. **2**, 145 (1982)
14. M.E. Tranquillini, P.G. Cassara, M. Corsi, G. Curotto, D. Donati, G. Finizia, G. Pentassuglia, S. Polinelli, G. Tarzia, A. Ursini, F.T.M. Van Amsterdam, Arch. Pharm. (Weinhein, Ger.) **330**, 353 (1997)
15. B.M. Reddy, P.M. Sreekanth, Tetrahedron Lett. **44**, 4447 (2003)
16. S.R. Sardaa, W.N. Jadhavb, N.B. Kolheb, M.G. Landgec, R.P. Paward, J. Iran. Chem. Soc. **6**, 477 (2009)
17. J. Qian, Y. Liu, J. Cui, Z. Xu, J. Org. Chem. **77**, 4484 (2012)
18. J.S. Yadav, B.V.S. Reddy, G. Satheesh, G. Srinivasulu, A.C. Kunwar, Arkivoc **3**, 221 (2005)
19. R. Kaoua, N. Bennamane, S. Bakhta, S. Benadji, C. Rabia, B. Nedjar-Kolli, Molecules **16**, 92 (2011)
20. A. Solan, B. Nişanci, M. Belcher, J. Young, C. Schäfer, K.A. Wheeler, B. Török, R. Dembinski, Green Chem. **16**, 1120 (2014)
21. B. Morak-Miodawska, K. Pluta, Heterocycles **78**, 1289 (2009)
22. E. Moreno-Manas, R. Pleixats, Acc. Chem. Res. **36**, 638 (2003)
23. A.R. Kiasat, J. Davarpanah, Res. Chem. Intermed. (2011). doi:10.1007/s11164-013-1407-6
24. A.-H. Lu, E.L. Salabas, F. Schuth, Angew. Chem. Int. Ed. **46**, 1222 (2007)
25. J. Perez, M. Nat, Nanotechnology **2**, 535 (2007)
26. S.H. Sun, C.B. Murray, D. Weller, L. Folks, A. Moser, Science **287**, 1989 (2000)

27. H.Y. Lü, S.H. Yang, J. Deng, Z.H. Zhang, Aust. J. Chem. **63**, 1290 (2010)
28. M.M. Mojtahedi, M. Abaee, T. Alishiri, Tetrahedron Lett. **50**, 2322 (2009)
29. T. Zeng, W. Chen, C.M. Cirtiu, A. Moores, G. Song, C. Li, Green Chem. **12**, 570 (2010)
30. F. Shi, M.K. Tse, S. Zhou, M.-M. Pohl, J. Radnik, S. Hübner, K. Jähnisch, A. Brückner, M. Beller, J. Am. Chem. Soc. **131**, 1775 (2009)
31. S.M. Roopan, F.R. Nawaz-Khan, B.K. Mandal, Tetrahedron Lett. **51**, 2309 (2010)
32. M.A. Ghasemzadeh, J. Safaei-Ghomi, H. Molaei, C. R. Chimie **15**, 969 (2012)
33. R. Zhang, J. Liu, S. Wang, J. Niu, C. Xia, W. Sun, Chem. Cat. Chem.**3**, 146 (2011)
34. A. Taher, J.-B. Kim, J.-Y. Jung, W.-S. Ahn, M.-J. Jin, Synlett. **15**, 2477 (2009)
35. H. Firouzabadi, N. Iranpoor, M. Gholinejad, J. Hoseini, Adv. Synth. Catal. **353**, 125 (2011)
36. V. Polshettiwar, R.S. Varma, Tetrahedron **66**, 1091 (2010)
37. A. Shaabani, A.H. Rezayan, S. Keshipour, A. Sarvary, S. Weng, Org. Lett. **11**, 3342 (2009)
38. M.A. Ghasemzadeh, J. Safaei-Ghomi, J. Chem. Res. **38**, 313 (2014)
39. J. Safaei-Ghomi, M.A. Ghasemzadeh, J. Sulfur Chem. **34**, 233 (2013)
40. M.A. Ghasemzadeh, J. Safaei-Ghomi, S. Zahedi, J. Serb. Chem. Soc. **78**, 769 (2013)
41. J. Safaei-Ghomi, M.A. Ghasemzadeh, Acta Chim. Slov. **59**, 697 (2012)
42. J. Safaei-Ghomi, M.A. Ghasemzadeh, Chin. Chem. Lett. **23**, 1225 (2012)
43. J. Chen, F. Wang, K. Huang, Y. Liu, S. Liu, J. Alloy. Compd. **475**, 898 (2009)