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Green in water sonochemical synthesis of tetrazolopyrimidine derivatives by a novel core-shell magnetic nanostructure catalyst

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ABSTRACT

A green approach for the one-pot four-component sonochemical synthesis of 5-methyl-7-aryl-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-6-carboxylic esters from the reaction of 2-cyano-guanidine, sodium azide, various aromatic aldehydes and methyl or ethyl acetoacetate in the presence of a catalytic amount of Fe_2O_3@SiO_2-$(CH_2)_3NHC(O)(CH_2)_2PPh_2$ as a new hybrid organic–inorganic core–shell nanomagnetic catalyst is described. This is the first design, preparation, characterization and application of the present nanomaterial and also the first ultrasound irradiated synthesis of the biologically and pharmaceutically important heterocyclic compounds in water as a green solvent. This novel sonocatalysis/nanocatalysis protocol offers several advantages such as high yields, short reaction times, environmentally-friendly reaction media, easily isolation of the products, simple preparation, full characterization and recoverability of the nanocatalyst by an external magnet and re-using several times without significant loss of activity.

1. Introduction

Multicomponent reactions (MCRs) are one of the most useful synthetic strategies as well as green chemistry protocols to construct diverse molecular scaffolds starting from a few available starting materials or intermediates. MCRs include various potentials such as complexity-generating power, resource and energy effectivity, intrinsic convergence, operational simplicity, atom-economy and sustainable technology and large chemical libraries of drug-like compounds [1]. Aza-heterocycles as an important class of organic chemicals have various properties such as antitumor, anticancer, anti-inflammatory and antibacterial agents, calcium channel blockers and antagonists, etc. In the literature, a few traditional stepwise and one-pot MCR procedures have been reported for the synthesis of substituted tetrazolo[1,5-*a*]pyrimidine heterocyclic compounds [2–13].

Due to its importance, ultrasonic irradiation has been the core of scientific and industrial investigations. Sonochemistry as a useful and green technique can be applied in various organic synthetic reactions. It has some superiorities such as convenience, short times, simplicity and controllability vs. traditional heating methods which generally require longer reaction times, high temperatures and expensive reagents. Therefore, a large number of organic reactions can be carried out under ultrasonic irradiation in higher yields, shorter reaction times or milder conditions in accordance with the green chemistry principles. A

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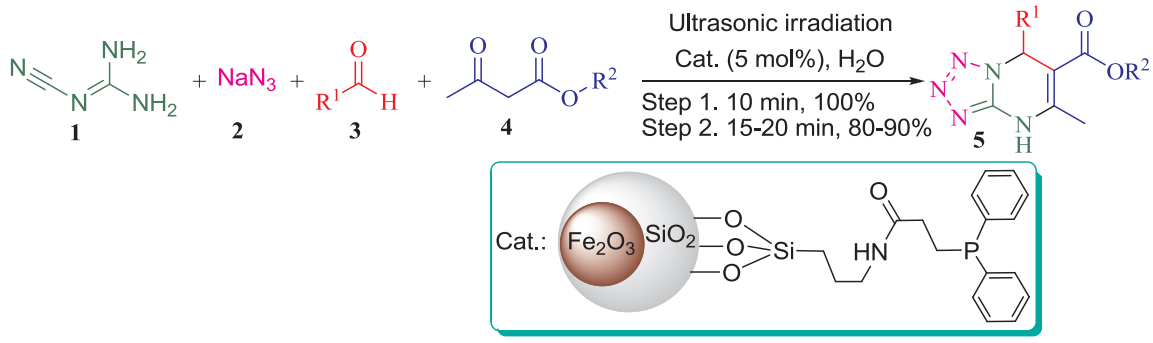


Scheme 1. Synthesis of tetrazolo[1,5-*a*]pyrimidine derivatives **5a-o** in the presence of MNPs@NHC(O)$CH_2CH_2PPh_2$ via a green 4-CR conditions.

justification to the rate enhancement of organic reactions under ultrasonic irradiation conditions can be explained by the acoustic cavitation theory that explains by the generation of high microscopic pressures and energies within a few seconds and leading to increase the reaction rate [14–16].

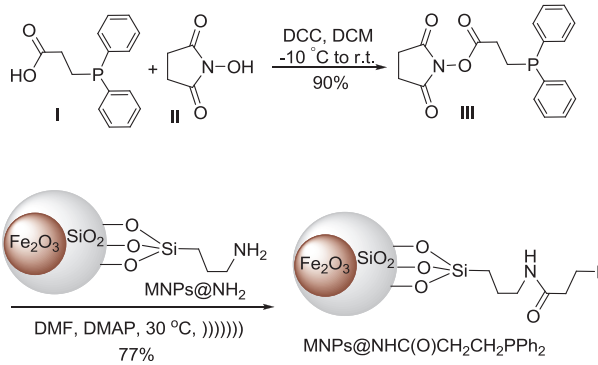
In recent years, surface-modified metal oxide magnetic nanoparticles (MNPs) have attracted much attention because of their diverse roles in chemistry, biology, optoelectronic, environmental and materials science and technology. Additionally, the magnetic nanocatalysts (MNCs) have a lot of benefits such as ease of isolation from the reactions mixtures, recyclablity, excellent activity and suitable chemical stability under various conditions [17].

In connection with our interest in design and development of MNCs and MCRs [18-27], herein, we wish to report the sonochemical synthesis of tetrazolo[1,5-*a*]pyrimidines **5** via an one-pot 4-CR of 2-cyanoguanidine **1**, sodium azide (NaN_3) **2**, various aromatic aldehydes **3** and methyl or ethyl acetoacetate **4** in the presence of a catalytic amount of modified magnetic iron oxide nanoparticles (MNPs@NHC(O)$CH_2CH_2PPh_2$) (Scheme 1).

2. Results and discussion

At first, stepwise linker immobilization and diphenylphosphine functionalization of the silica-coated Fe_2O_3 nanoparticles (MNPs@NHC(O)$CH_2CH_2PPh_2$) as a heterogeneous MNC was readily prepared according to the previous literature and our procedures.

The synthesis of bare MNPs was performed according to the modified Massart method [28], and MNPs coated with siloxane shell MNPs@NH_2 were performed according previously reported procedures [29,30]. The total amount of amino group was measured by acid-base titration as 0.48 mmol per 1 g of NPs. To evaluate the possibility of the functionalisation MNPs@NH_2 was subjected to the reaction with 4-nitrobenzaldehyde run in benzene at ambient temperature under the ultrasonication conditions (Scheme 2).



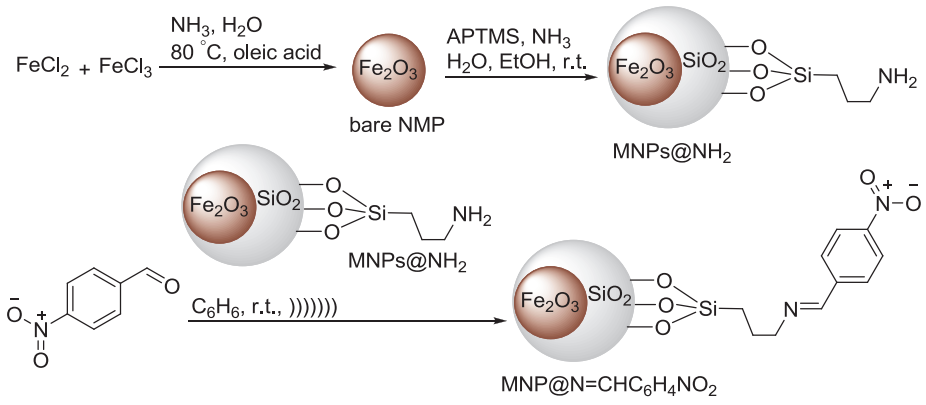
Scheme 3. Synthesis of MNPs@NHC(O)$CH_2CH_2PPh_2$.

Then, the phosphine functionality was introduced in reaction of activated 3-(dipohenylphosphine)propionic acid (**I**) (Scheme 3). We chose the classical peptide coupling activation conditions [31,32], according to which the 3-(dipohenylphosphino)propionic acid was converted to the corresponding ester in reaction with *N*—hydroxysuccinimide (**II**) and DCC run in dichloromethane (DCM), and next obtained 1-{[3-(diphenylphosphino)propanoyl]oxy}pyrrolidine-2,5-dione (**III**) was used in the reaction with MNPs@NH_2 in DMF catalyzed by DMAP under the sonication conditions and room temperature to furnish MNPs@NHC(O)$CH_2CH_2PPh_2$ nanoparticles.

The particle size was studied by field emission scanning electron microscopy (FE-SEM) and the identification of MNPs@NHC(O)$CH_2CH_2PPh_2$ was based on the analysis of SEM images that clearly showed a monodispersed spherical shape of the nanoparticles (Fig. 1).

In addition, energy-dispersive X-ray spectroscopy (EDX) spectra of the MNC indicated the presence of Fe, Si, P, C, N and O elements in the MNPs@NHC(O)$CH_2CH_2PPh_2$ composite MNC (Fig. 2).

The TEM-based techniques were used to evaluate the size and the



Scheme 2. Synthesis and evaluation of MNPs@NH_2 and MNPs@N = $CC_6H_4NO_2$.

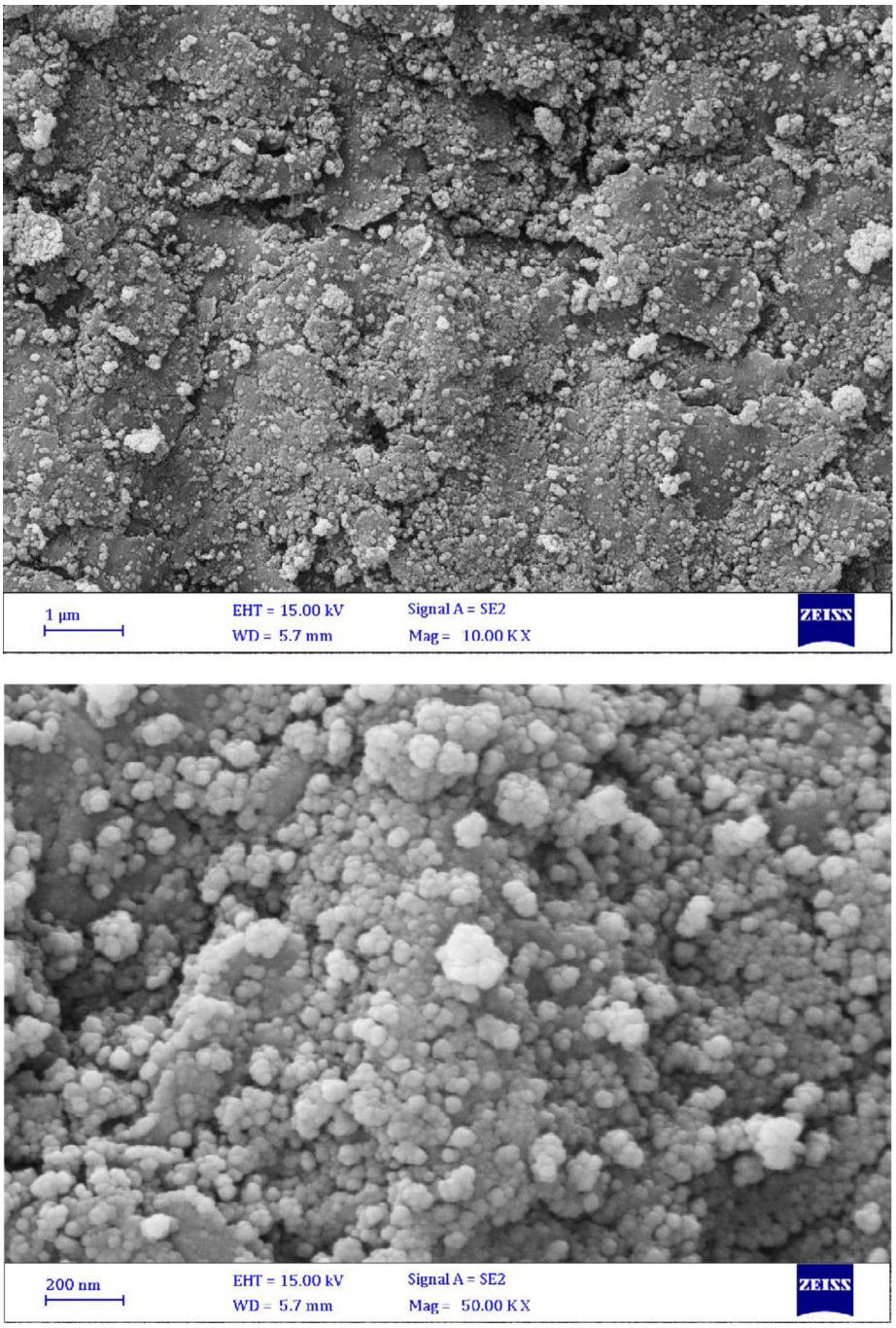


Fig. 1. FE-SEM images of MNPs@NHC(O)$CH_2CH_2PPh_2$ with different magnifications.

shape of the nanoparticles. The TEM images were measured at high-magnification. The particles were found to be spherical and an average size was estimated at 10 ± 2 nm (MNPs@NH_2). TEM image and histogram of the size distribution of diameters for magnetic nanoparticles were presented on Fig. 3.

Thermogravimetric analysis (TGA) studies were carried out of bare (MNPs) and aminosiloxane coated nanoparticles (MNPs@NH_2). TG curve refers to the temperature-dependent mass change in percent. The TG curve of MNPs shows a small weight loss (about 5%) in the entire temperature range, most likely due to removal of adsorbed water. In the thermogram of MNPs@NH_2 sample a broad degradation region between 300 and 500 °C, typical for APTMS, is observed Fig. 4.

The modifications of MNPs surface were confirmed by FT-IR spectroscopy. Figs. 5 and 6 show ATR spectra of MNPs, MNPs@NH_2 and MNPs@N = $CHC_6H_4NO_2$. The existence of magnetite core in all samples is indicated by band at about ~ 550 cm^{-1} which corresponds to the Fe—O stretching mode of Fe_3O_4. MNPs@NH_2 spectrum shows new bands at around 1000–1150 cm^{-1} which can be ascribed to the Si—O, Si—O—Si and Fe—O—Si vibrations. The corresponding NO_2 stretching vibrations were appeared at 1346 and 1522 cm^{-1}.

To optimize the reaction conditions, a pilot experiment was carried out with **1**, **2**, benzaldehyde **3** and ethyl acetoacetate **4** in the presence of a catalytic amount of MNPs@NHC(O)$CH_2CH_2PPh_2$ (5 mol%) in water under ultrasonic irradiation with a frequency of 40 kHz and power of 250 W to afford tetrazolo[1,5-*a*]pyrimidine derivatives **5a** in 90% yield after 10 + 1 min. It was found that the efficiency and the yield of the pilot experiment in water was higher than other solvents such as MeCN, MeOH, CH_2Cl_2, EtOH, and toluene, and also under

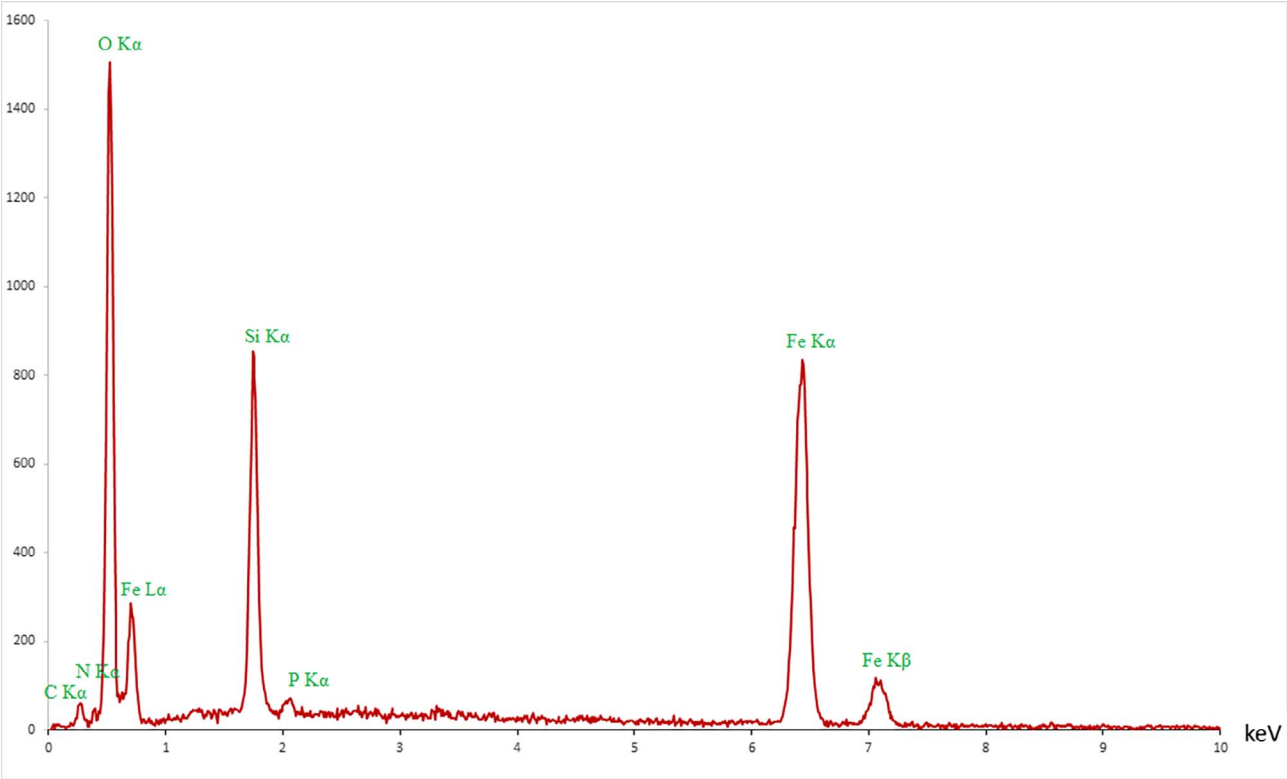


Fig. 2. EDX of the MNPs@NHC(O)$CH_2CH_2PPh_2$ MNC.

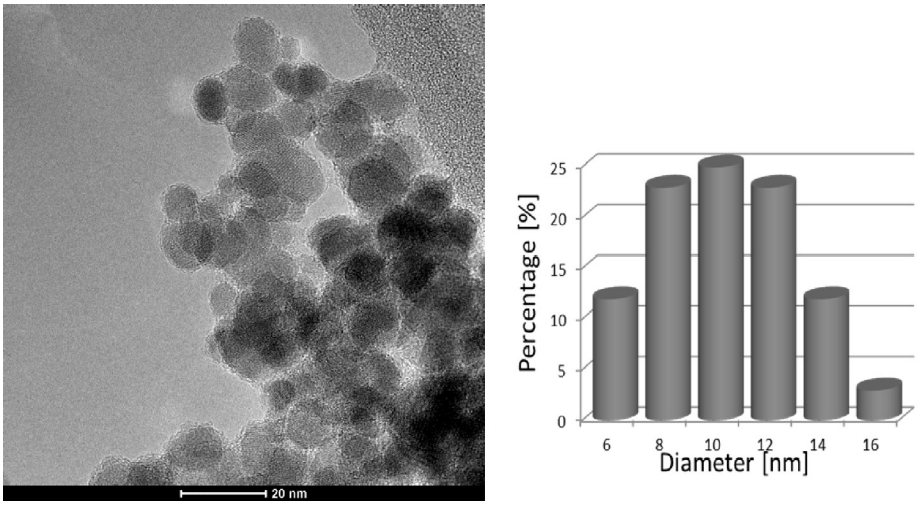


Fig. 3. TEM image of modified with aminosiloxane magnetic nanoparticles and histogram of the diameter distribution for MNPs@NH_2 (iron oxide core of 10 ± 2 nm).

solvent-free conditions.

To illustrate the need of the present MNC for the MCR, and in order to compare its catalytic activity with some other convenient catalysts, the model reaction was carried out through ultrasonic irradiation with a frequency of 40 kHz and power of 250 W in the presence of various catalysts such as protic solid acids (Montmorillonite-K_{10} and Amberlyst-21), liquid acids (HCl and H_2SO_4), Lewis acids ($AlCl_3$ and $FeCl_3$), SiO_2, Fe_2O_3 and PPh_3 (Table 1, entries 2–10) and our previously reported catalyst Fe_3O_4@SiO_2–OSO_3H [18] (Table 1, entry 11). The results showed that the efficiency and the yield of the reaction in the presence of the core/shell catalyst was the best (Table 1, entry 1). The yield in the rest of cases was detect or very low. Furthermore, an experiment was conducted in the absence of any catalyst (Table 1, entry 12). The yield in this case was trace after 40 min. Therefore, MNPs@NHC(O)$CH_2CH_2PPh_2$ was essential for the reaction. Additionally, the experimental result has been provided for the reaction using the catalyst prepared without ultrasonic irradiation (Table 1, entry 13). As a result, it was confirmed that the synergistic effect of the sonocatalysis/nanocatalysis has increased the reaction yield up to 30%.

To study the generality of the present protocol, diverse substituted aldehydes **3** and β-keto-esters **4** were reacted with **1** and **2** in an one-pot 4-CR operation to give the corresponding products **5b-o** in high yields within 25–30 min. Almost all used benzaldehydes including various substituents were readily used in this reaction to give the target compounds under clean, mild conditions, and no undesirable side reactions or byproducts were observed under ultrasonic irradiation with a frequency of 40 kHz and power of 250 W. As compiled in the Table 2, the reaction proceeded efficiently in all of the investigated cases in the

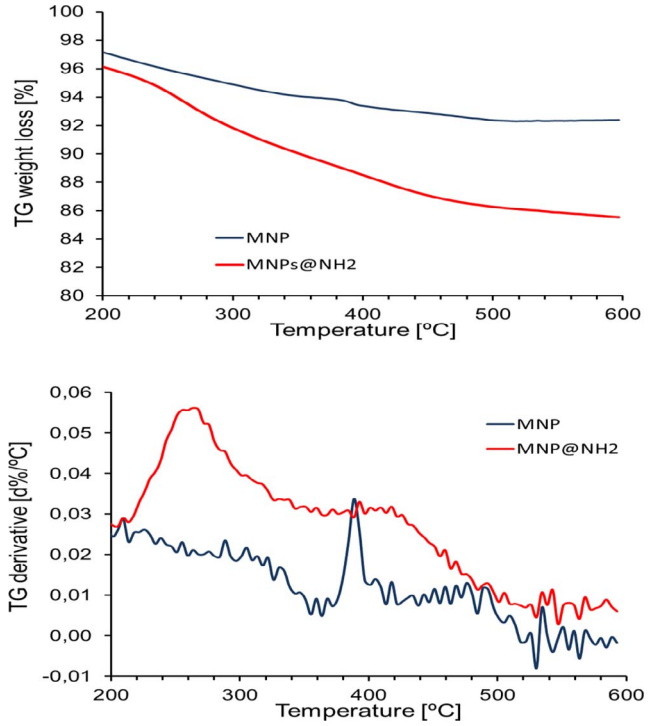


Fig. 4. TGA (a) and DTG (b) curves of the bare MNPs and MNPs@NH_2.

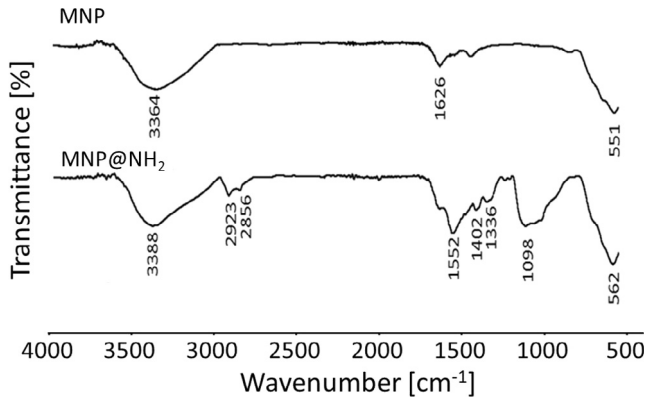


Fig. 5. ATR FT-IR spectra of the bare (MNPs) and modified (MNPs@NH_2) magnetic nanoparticles.

presence of MNPs@NHC(O)$CH_2CH_2PPh_2$ (MNC).

It should be mentioned that the MNPs@NHC(O)$CH_2CH_2PPh_2$ MNC is very active, stable to air and moisture, and nontoxic. In addition, it can be quantitatively recovered by simple separation using an external magnet and reused in subsequent reactions at least six times (Table 2, entry 1). Another advantage of this heterogeneous MNC was its high selectivity, and undesired side products were not observed. In addition, no extra care should be taken in order to storage or handle the catalyst in recovery process; because, it does not have any air or moisture sensitive nature.

On the other hand, ultrasonic either assisted to maximize the simultaneous increasing of the catalyst efficiency and frequency of molecular interactions (higher yields) or decreasing activation energy of rate determining step (lower times).

A plausible mechanism for the formation of the products **5a-o** is outlined in Scheme 4. It is conceivable that the initial event is the formation of 5-aminotetrazole **6** by condensation of cyanamide (*in situ* generated from its stable chemical equivalent **1**) [33] and **2** under ultrasonic irradiation in the presence of MNPs@NHC(O)$CH_2CH_2PPh_2$ and α,β-unsaturated Michael acceptor **7** from another parallel reaction of **3** and **4** through a Knoevenagel condensation. Then, intermediate **8** was formed from a nucleophilic Michael addition of **6** to **7**. Finally, it was followed by an intramolecular nucleophilic addition of the NH_2 group of the enamine tautomer of **8** to the second keto C═O group to give compound **9** which after releasing an H_2O molecule yield the target products **5a-o**.

3. Conclusions

In summary, tetrazolo[1,5-*a*]pyrimidine derivatives were synthesized by using 2-cyano-guanidine, sodium azide, various aromatic aldehydes and methyl or ethyl acetoacetate under ultrasonic irradiation with a frequency of 40 kHz and power of 250 W in the presence of a catalytic amount of MNPs@NHC(O)$CH_2CH_2PPh_2$. The results indicated the scope and generality of the one-pot strategy with respect to various starting materials. This new, green and efficient MCR protocol for the preparation of synthetically, biologically, and pharmaceutically relevant tetrazolopyrimidine derivatives presents some important advantages such as simple and readily available precursors, easy workup procedure, reusability of the heterogeneous MNC, high atom economy, excellent yields and mild reaction conditions.

4. Experimental

4.1. General

All solvents, chemicals, and reagents were purchased from Merck, Fluka, and Sigma-Aldrich and used without purification. Melting points were determined by an Electrothermal 9100 apparatus and are uncorrected. IR Spectra were recorded on a Shimadzu FT-IR 8400 s spectrometer. Attenuated total reflection (ATR) FT-IR spectra were recorded using Thermo Scientific Nicolet 6700 FT-IR spectrophotometer. A thin layer of sample was placed in direct contact with an infrared ATR diamond crystal. ^1H and ^{13}C NMR spectra were provided on Bruker DRX-300 Avance spectrometer relative to Me_4Si as an internal standard at 300 and 75 MHz fields, respectively. MS was recoded on a Finnigan-MAT 8430 mass spectrometer operating at an ionization potential of 70 eV. TEM image was done on Tecnai G2 X-TWIN transmission electron microscope. Thermogravimetric analyses (TGA) were performed on a Mettler Toledo Star TGA/DSC unit. Argon was used as a purge gas (10 mL·min^{-1}). Samples between 2 and 5 mg were placed in aluminium pans and heated from 25 °C to 600 °C with a heating rate of 10 °C/min. FE-SEM image was obtained from Zeiss-DSM 960A microscope. Magnetic measurement of the solid samples were performed using Megnetic Daghigh Daneshpajouh Co., Iran vibrating sample magnetometer (VSM). EDX spectra were recorded on Numerix DXP–X10P. Elemental analyses were provided by Elementar Analysensysteme GmbH VarioEL. Ultrasonic irradiation was performed in an ultrasound cleaning bath KQ-250 DE with a frequency of 40 kHz and power of 250 W.

4.2. Preparation of MNPs@NHC(O)$CH_2CH_2PPh_2$ MNC

The present heterogeneous MNC was prepared according to our previous reported procedures, as follows:

4.3. Preparation of bare Fe_2O_3 nanoparticles (MNPs)

Iron oxide nanoparticles were synthesized according to the modified Massart method [28]. The water solutions of $FeCl_3$ (0.07 M) and $FeCl_2$ (0.04 M) were purge under the argon gas for 15 min. and were vigorously stirred at 80 °C. Then, the ammonia aqueous solution (25%) was dropped until the pH of the suspension gained 11. After 30 min of stirring at 80 °C oleic acid was added to the reaction mixture. The precipitate was isolated by magnetic decantation in the presence of neodymium magnet. Finally, it was washed twice with deionized water

Fig. 6. ATR FT-IR spectra of MNPs@N = $CHC_6H_4NO_2$ nanoparticles.

Table 1
Monitoring of the catalyst effect on the model reaction.[a]

Entry	Catalyst (5 mol%)	Time (min)	Yield[b] (%)
1	MNPs@NHC(O)$CH_2CH_2PPh_2$	25	90
2	Montmorillonite-K_{10}	30	30
3	Amberlyst-21	30	28
4	HCl	30	35
5	H_2SO_4	30	48
6	$AlCl_3$	35	40
7	$FeCl_3$	35	35
8	SiO_2	35	25
9	Fe_2O_3	35	30
10	PPh_3	35	18
11	Fe_3O_4@SiO_2–OSO_3H	35	72
12	–	40	Trace
13	MNPs@NHC(O)$CH_2CH_2PPh_2$	25	60[c]

[a] Cyano-guanidine (1 mmol), sodium azide (1.1 mmol), benzaldehyde (1 mmol), ethyl acetoacetate (1 mmol), H_2O (10 mL), ultrasonic irradiation with a frequency of 40 kHz and power of 250 W, 10 min was required for the pre-reaction of **1** and **2**.
[b] Isolated yield.
[c] Without ultrasonic irradiation.

and dried into powder 60 °C.

MNPs (ATR FT-IR): ν = 3500–3200 (s; ν(O—H)), 552 (s; ν(Fe-O)) cm^{-1}.

4.4. Preparation of MNPs coated with siloxane shell (MNPs@NH_2)

The MNPs (1.026 g) were ultrasonically re-dispersed in ethanol (800 mL), and after 1.5 h 400 mL of ethanol was added. The suspension was placed in Radley's reactor and stirred for 15 min under argon atmosphere. Then, concentrated 4 mL of ammonia and APTMS (0.513 g) was added dropwise to the particle suspension. Vigorous stirring was continued for 4 to 5 h at room temperature. The MNPs@NH_2 were separated by magnetic decantation, washed and dried as above.

Acid-base titration was done to estimate the amount of NH_2 groups on the MNPs@NH_2 surface. APTMS modified magnetic nanoparticles (100 mg) were sonicated in 0.01 M HCl (standard solution) till good dispersion. 5 mL of this mixture was titrated with 0.005 M sodium hydroxide (standard solution). We estimated that the number of amino groups was 0.48 mmol per 1 g of nanoparticles. The determination of the titration endpoint was based on second derivative's chart.

MNPs@NH_2 (ATR FT-IR): ν = 3500–3200 (s; ν_{as}(N—H)), 2925 (m; ν_{as}(C—H)), 2870 (w, ν_s(C—H)), 1115 (s; ν_{as}(Si-O)), 1025 (s; ν_{as}(Si—O—Si)), 552 (s; ν(Fe-O)) cm^{-1}.

CHN analysis: C 8.64, H 1.99, N 2.85.

4.5. Preparation of functionalised MNPs (MNPs@N=$CHC_6H_4NO_2$)

The MNPs (0.05 g) were ultrasonically redispersed in dry benzene (10 mL), and after 0.5 h solution of 4-nitrobenzaldehyde (0.05 g) in 2 mL of benzene was added. The reaction was argonated and heated under reflux for 16 h. The nanoparticles were separated with strong magnet, washed 3 times with warm benzene and dry under the reduced pressure to furnish 30 mg of MNPs@N=$CHC_6H_4NO_2$.

MNPs@N=C—$C_6H_4NO_2$ (ATR FT-IR): ν = 2924 (m; ν_{as}(C—H)), 2847 (w, ν_s(C—H)), 1634,1602 (s; ν_s and ν_{as}(C—H-Ar)), 1522 and 1346 (s; ν_s and ν_{as}(NO_2)), 1191 (s; ν_{as}(Si-O)), 1108 (s; ν_{as}(Si—O-Si)), 630 (s; ν(Fe-O)) cm^{-1}.

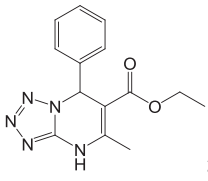
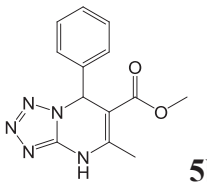
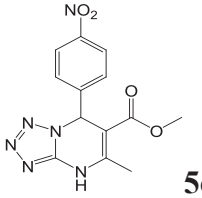
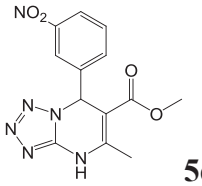
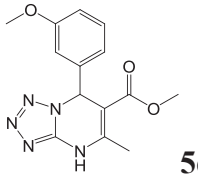
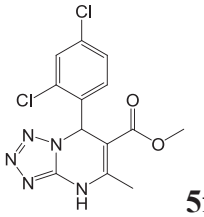
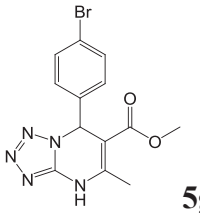
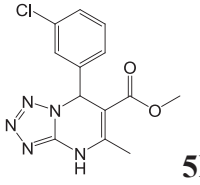
CHN analysis: C 16.62, H 1.98, N 3.96.

4.6. Synthesis of 1-{[3-(diphenylphosphino)propanoyl]oxy}pyrrolidine-2,5-dione

The 50 mL flask was charged with 3-(dipohenylphosphino)propionic acid (500 mg) and *N*—hydroxysuccinimide (500 mg) and argonated in usual sequence vacuum/argon refilling and 10 mL of DCM was added to dissolved the reagents. The reaction mixture was cooled down to -10 °C and dicyclohexylcarbodiimide (500 mg) was added at once. The stirring reaction mixture was allowed to warm to room temperature for a period of 3 h, and the stirring was continued for next 16 h at that temperature. After that the formed dicyclohexylurea was filtered all and the product was isolated after the column chromatography eluted with hexane/ethyl acetate (3/1) mixture to yield 620 mg (90%) of 1-{[3-(diphenylphosphino)propanoyl]oxy}pyrrolidine-2,5-dione with consistent to literature spectral data [34].

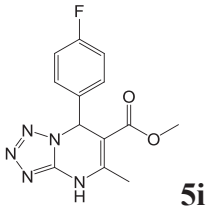
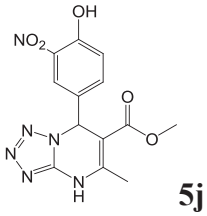
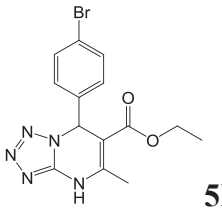
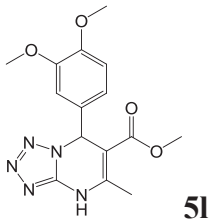
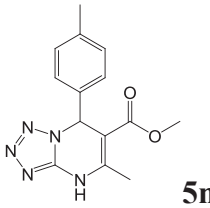
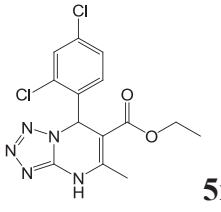
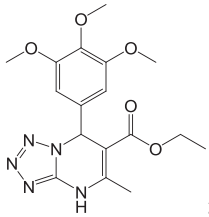
^{1}H NMR (500.13 MHz, $CDCl_3$): δ = 7.5–7.3 (m, 10*H*, Ar), 2.8 (s, 4H), 2.7 (m, 2H), 2.4 (m, 2H). ^{31}P NMR (202.45 MHz, $CDCl_3$) δ = –15.3.

Table 2
Green synthesis of 5-methyl-7-aryl-4,7-dihydrotetrazolo[1,5-*a*]pyrimidine-6-carboxylic ester derivatives **5a-o** in the presence of 5 mol% of MNPs@NHC(O)$CH_2CH_2PPh_2$ MNC in water via ultrasonic irradiation.

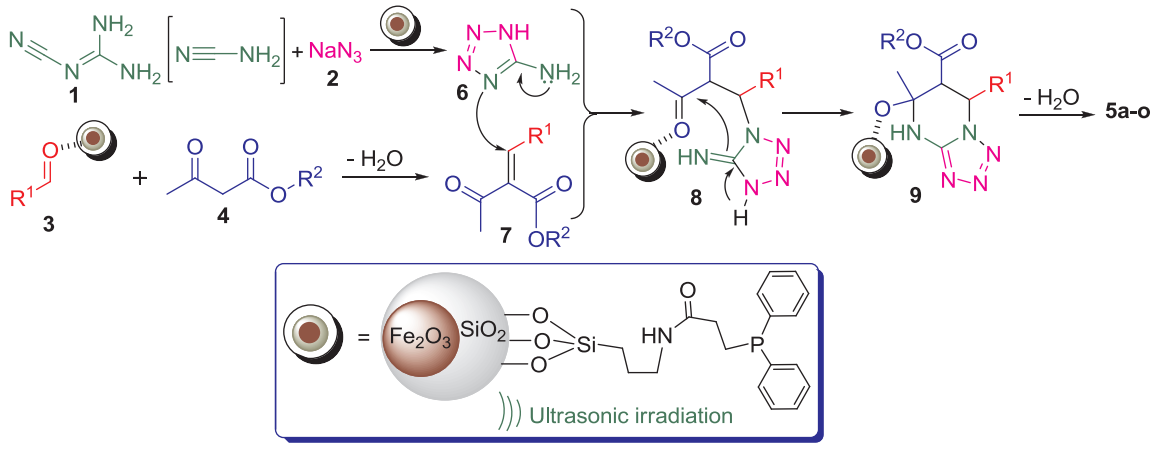
Entry	Product	Time (min)	Yield[a] (%)	Mp (°C)	
				Found	Reported
1	 **5a**	25	90[b]	202–204	204–205 [11]
2	 **5b**	25	89	190–191	189–191 [11]
3	 **5c**	30	82	230–231	230–232 [11]
4	 **5d**	25	84	225–227	226–228 [11]
5	 **5e**	30	80	201–202	200–202 [12]
6	 **5f**	30	83	252–254	253–255 [11]
7	 **5 g**	30	82	221–223	220–222 [11]
8	 **5 h**	25	90	184–185	184–186 [11]

(*continued on next page*)

Table 2 (*continued*)

Entry	Product	Time (min)	Yield[a] (%)	Mp (°C)	
				Found	Reported
9	 **5i**	25	88	196–198	197–198 [11]
10	 **5j**	25	86	248–249	247–249 [11]
11	 **5 k**	25	90	238–240	237–238 [11]
12	 **5 L**	30	85	219–220	218–220 [11]
13	 ***5 m***	25	88	192–195	194–196 [12]
14	 ***5n***	25	89	256–258	257–259 [11]
15	 **5o**	30	81	200–202	199–201 [11]

[a] Isolated yields.
[b] Yields of the six subsequent runs by using the same recovered catalyst were 90, 88, 87, 86, 83 and 82%, respectively.



Scheme 4. Proposed mechanism for the green synthesis of the products **5a-o**.

4.7. Preparation of MNPs@NHC(O)$CH_2CH_2PPh_2$ (MNC)

The MNPs@NH_2 (200 mg), DMAP (30 mg), DMF (4 mL), and compound **III** were placed into a reaction tube, argonated by usual vacuum/argon refilling sequence, and sealed with a glass stopper. The reaction mixture was subjected to ultrasound redispersion for 2 h at 25–30 °C, and next it was stirred for additional 72 h at ambient temperature. The nanoparticles were separated with strong magnet, washed 2 × 4 mL DMF, 2 × 4 mL DCM, 2 × 4 mL EtOH and dry under the reduced pressure to furnish 95 mg of MNPs@NHC(O)$CH_2CH_2PPh_2$.

CHN analysis: C 13.07, H 2.12, N 2.31.

4.8. General procedure for the synthesis of tetrazolo[1,5-a]pyrimidine derivatives (5a-o)

Initially, 5-aminotetrazole was prepared *in-situ* as follows: briefly, a mixture of 2-cyano-guanidine (1 mmol, 0.084 g) and NaN_3 (1.1 mmol, 0.072 g) were dissolved in 10 mL of distilled water in the presence of MNPs@NHC(O)$CH_2CH_2PPh_2$ (5 mol%, 0.1 g). Then, the mixture was sonicated for 10 min at 50 °C to give 5-aminotetrazole in approximately 100% yield. After that, an aryl aldehyde **1** (1 mmol) and an acetoacetate ester **2** (1 mmol) were added to the reaction pot. Next, the mixture was irradiated in the water bath of the ultrasonic cleaner at 40 kHz and 250 W for appropriate times (15–20 min). The progress of the reaction was monitored by TLC (EtOAc/*n*-hexane 4:1). After completion of the reaction, the MNC was simply separated by using an external magnet and the rest of the reaction mixture was filtered, washed with further water, dried and purified by recrystallization from ethanol to yield target products **5a-o**. It was observed that the MNC can be washed with ethanol, dried and reused in next reactions at least six times without any significant reduction in yield.

All the products were known compounds that were confirmed by comparison of their melting points with their literature authentic samples (As indicated in Table 2).

4.9. Selected spectral data of methyl-7-(4-bromophenyl)-5-methyl-4,7-dihydrotetrazolo-[1,5-a]pyrimidine-6-carboxylate (5g)

^{1}H NMR (DMSO-d_6): 2.54 (s, 3H, CH_3), 3.61 (s, 3H, OCH_3), 6.64 (s, 1H, CH), 7.24 (d, J = 7.5 Hz, 2H, ArH), 7.48 (d, J = 7.5 Hz, 2H, ArH), 11.19 (s, 1H, NH). ^{13}C NMR (DMSO-d_6) δ: 170.1, 153.4, 152.3, 144.4, 136.5, 136.3, 127.2, 102.1, 60.6, 56.1, 30.5. FT-IR (KBr): 3255, 3058, 2949, 1710, 1648, 1574, 1488, 1432, 1413, 1385, 1302, 1278, 1227, 1190, 1153, 1103, 1072, 1012, 839, 813, 772, 725, 686 cm^{-1}. Anal. calcd for $C_{13}H_{12}BrN_5O_2$: C, 44.59; H, 3.45; N, 20.00; Found: C, 44.55; H, 3.40; N, 20.12.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.ultsonch.2017.12.047. These data include MOL files and InChiKeys of the most important compounds described in this article.

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