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Tribromide ion immobilized on magnetic nanoparticle as new, efficient and reusable nanocatalyst in multicomponent reactions

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Tetraethyldiethylenetriamine tribromide magnetic nanoparticles, (MNPs-TEDETA tribromide) synthesise and characterize as an efficient, new, metal free and magnetically reusable nanocatalyst for synthesis of 2,3-dihydroquinazolin-4(1H)-one and polyhydroquinoline derivatives. The synthesized catalyst was characterized by FT-IR, TGA, XRD, EDX, VSM and SEM analyses.

1 Introduction

There are two main kinds of catalysis systems, heterogeneous and homogeneous, that each of them has advantages and drawbacks. For example benefits of heterogeneous catalysts are easy synthesis, easy separation, efficient recycling, product purification, and disadvantages including: insufficient catalytic surface, low activity and leaching. Meanwhile homogeneous catalysts have benefits such as high activity and high selectivity, but they have disadvantage such as laborious product purification, difficulty in recycling and recovery of the catalyst, deactivation of catalyst towards the end of the reaction [1-3]. Because of the catalysts are often expensive, the reusing and separation of them are very important. To overcome this afore mentioned drawbacks, magnetic nanoparticles which are often low cost, easy and clean separation from the reaction mixture with an external magnet [4-6], unique properties, potential applications in the variety of field [7], simple synthesis, high surface area, low toxicity and readily available are preferred [8].

Multicomponent reactions (MCRs) condensations are a chemical reaction where three or more simple substrates react to give highly selective products that retain majority of the atoms of the starting material [9]. MCRs are an important subclass of tandem reactions which has advantages such as convergent nature, milder reaction conditions, simplicity, high atom economy, facile execution, shorter reaction time, environment friendly, lower cost and energy conservation [10,11]. In the past decade the methodology of MCRs have emerged as a very efficient way to access heterocycles [12].

Polyhydroquinoline and 2,3-dihydroquinazolinone derivatives are very famous molecules that including six membered N-heterocyclic ring. These compounds have been reported to possess a vast range of biological properties and pharmaceutical activities [8, 13]. 2,3-Dihydroquinazolinones are a class of N-heterocycles that have attracted much attention because of their broad spectrum of pharmacological, biological [14] and medicinal activities such as antibacterial, antifertility, antitumor, antifibrilatory, vasodilatory, antifungal, and analgesic efficacy [15, 16]. In addition quinazolines are oxidized into quinazolin-4(3H)-ones analogs, which are known as important biologically active heterocyclic compounds [17]. 2,3-dihydroquinazolin-4(1H)-one analogues have been synthesized using several catalyst such as: $CuCl_2/Fe_3O_4$-TEDETA [4], GSA@MNPs [14], $BiBr_3$ [18], MES (2 morpholinoethanesulfonic acid) [19], SiO_2-$FeCl_3$ [20], Boehmite-SSA [21], Boehmite-Si-DSA[22].

some of these methodologies for the synthesis of 2,3-dihydroquinazolin-4(1H)-one was previously reported which suffered from expensive reagents, tedious work-up, high reaction temperature, harsh reaction conditions and low yields. Thus, development of a versatile and simple procedure is a highly desired goal in the synthesis of 2,3-dihydroquinazolin-4(1H)-ones [23,16]. Although some of the analogue nanoparticles prepared by other authors were previously reported [24, 25], the main novelty of this research is the first report of MNPs-TEDETA tribromide without any transition-metal, used as the catalyst for multicomponent reactions.

In this work with the aim to develop an efficient synthetic process, we develop the synthesis of 2,3-dihydroquinazolin-4(1H)-one derivative by one-pot two-component condensation of anthranilamide and aldehydes catalyst by MNPs-TEDETA tribromide in EtOH at reflux condition (Scheme 2) and synthesis of polyhydroquinoline by multi-component reactions of aldehyde, dimedon, ethylacetoacetate, ammonium acetate and MNPs-TEDETA tribromide as catalyst in PEG at 80 ºC (Scheme 4).

2 Results and discussion

2.1 Catalyst preparation

In this paper we report a new and efficient method for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones and polyhydroquinolines in the

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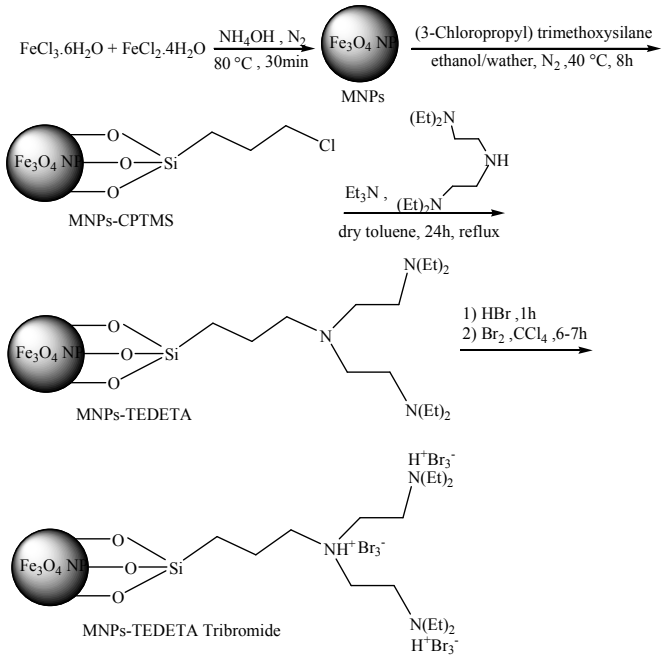
presence of catalytic amounts of MNPs-TEDETA tribromide. As shown in Scheme 1 the details synthesis procedure of catalyst is indicated. Initially the black precipitate of magnetic nano particles of Fe_3O_4 has been prepared by a mixture of $FeCl_3{\cdot}6H_2O$, $FeCl_2{\cdot}4H_2O$ in 30% NH_4OH under N_2 atmosphere at 80℃ [4, 13]. Then, Fe_3O_4 nanoparticles coated by 3-chloropropyltrimethoxysilane (CPTMS) solution. In the next step, the mixture of N, N, N′, N′-tetraethyldiethylenetriamine (TEDETA) and triethylamine was added to MNPs-CPTMS under reflux of dry toluene. Finally, the obtain TEDETA functionalized magnetic nanoparticles (MNPs-TEDETA) was reacted with HBr and Br_2 to afford MNPs-TEDETA tribromide.



Scheme 1. Synthesis of MNPs-TEDETA tribromide

2.2 Catalyst characterization

All reagents and solvents were purchased from Merck and Aldrich chemical companies. The synthesised catalyst was characterized by X-ray diffraction (XRD, GBC-Difftech MMA), Fourier transform infrared (FT-IR, Bruker, Germany) spectroscopy, scanning electron microscopy (SEM, FESEM-TESCAN MIRA3), energy dispersive X-ray (EDX, FESEM-TESCAN MIRA3), thermogravimetric analysis (TGA, PerkinElmer Pyris Diamond, U.K), and vibrating sample magnetometer (VSM, MDKFD) techniques.

As seen in Figure 1 the position of all peaks in the XRD pattern of MNPs-TEDETA tribromide and recovered catalyst were in agreement with standard XRD pattern of Fe_3O_4. As it is shown the catalyst and the recovered catalyst were identified from the peak positions at 2θ = 21.33, 35.20, 41.55, 50.65, 63.19, 67.52, 74.53 and 2θ = 21.32, 35.09, 41.45, 50.53, 63.27. 67.81, 74.58 respectively. These peaks with the corresponding reflections of (111), (220), (311), (400), (422), (511) and (440) indicated that the surface modification of the Fe_3O_4 nanoparticles does not lead to their phase change, even after recovery and they all match well with the data for the standard Fe_3O_4 sample [26]. Also this pattern indicated that the crystalline inverse cubic spinel structures are protecting during functionalization of MNPs.

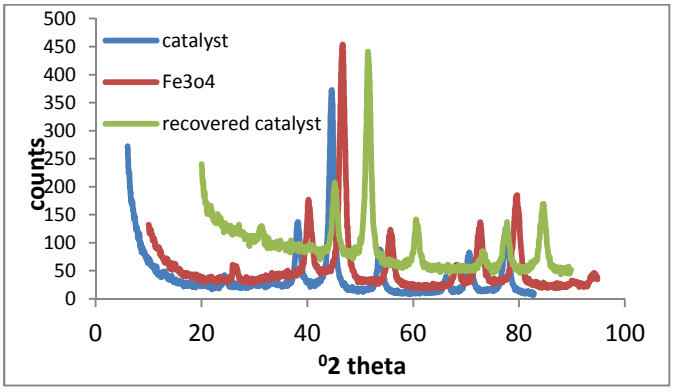


Figure 1. XRD pattern of MNPs-TEDETA tribromide and recovered catalyst

Figure 2 indicates FT-IR spectra for the MNPs, MNPs-CPTMS, MNPs-TEDETA, and MNPs-TEDETA tribromide**.** The IR spectrum of the Fe_3O_4 alone indicates the bond of stretching vibration at 3401 cm^{-1} belong to O-H bonds which are attached to the surface iron atoms and a peak appears at 1625 cm^{-1} belong to the stretching vibrational mode of an adsorbed water layer. Also the peak that appeared at 579 cm^{-1} comes from vibrations of Fe-O bonds [14, 27].

The IR spectrum of MNPs-CPTMS (Fig. 2(b)) shows the peak at 577cm^{-1} which assigned to the Fe-O vibration. The band formation between MNPs and 3-chloropropylsilica group is confirmed by Fe–O–Si absorption band that appears at near 999 cm^{-1} [28]. The peaks at 2880 cm^{-1} and 2972 cm^{-1} attribute to C-H stretching vibrations [27, 29].

As shown in Fig. 2(c), the presence of bands in 575 cm^{-1} and 997 cm^{-1} is assigned to the Fe-O vibration [14, 27] and Fe–O–Si absorption [28] respectively. The peaks 2947 cm^{-1} and 2999 cm^{-1} regions attribute to the C-H stretching vibrations [29].

The IR spectrum of the MNPs-TEDETA tribromide (Fig. 2(d)) indicates the bonds in 564 cm^{-1} and 627 cm^{-1} is assigned to vibrations of Fe-O bonds. The presences of band 1630 cm^{-1} belong to the stretching vibrations of C-N^+ [24]. This IR spectrum also shows the peaks at 1040 cm^{-1} and 1116 cm^{-1} which assigned to the SiO–H and Si–O–Si groups [30]. The presence of bands in 2923 cm^{-1} and 2981 cm^{-1} regions is assigned to the C-H stretching vibrations [27, 29]. For indicated the peak of Br_Br, which exhibits below 400 cm^{-1}, we captured another FT-IR spectra in region below 400 cm^{-1}. As shown in Figure 2 the peaks at 197 and 264 cm^{-1} assigned to the Br_3.

The scanning electron microscopic (SEM) image was investigated the morphological and size particle of the catalyst. It confirmed that the catalyst was made up of uniform-sized particle with an average diameter less than 10 nm also the shape of the MNPs-TEDETA tribromide is spherical (Figure 3).

The energy dispersive X-ray (EDX) spectrum of catalyst indicates the kinds of elements present (C, N, O, Si, Fe and Br) in the MNPs-TEDETA tribromide. As shown in Figure 4 (a) indicated the EDX spectrum of recovered catalyst and Figure 4 (b) indicated the EDX spectrum of recovered catalyst.

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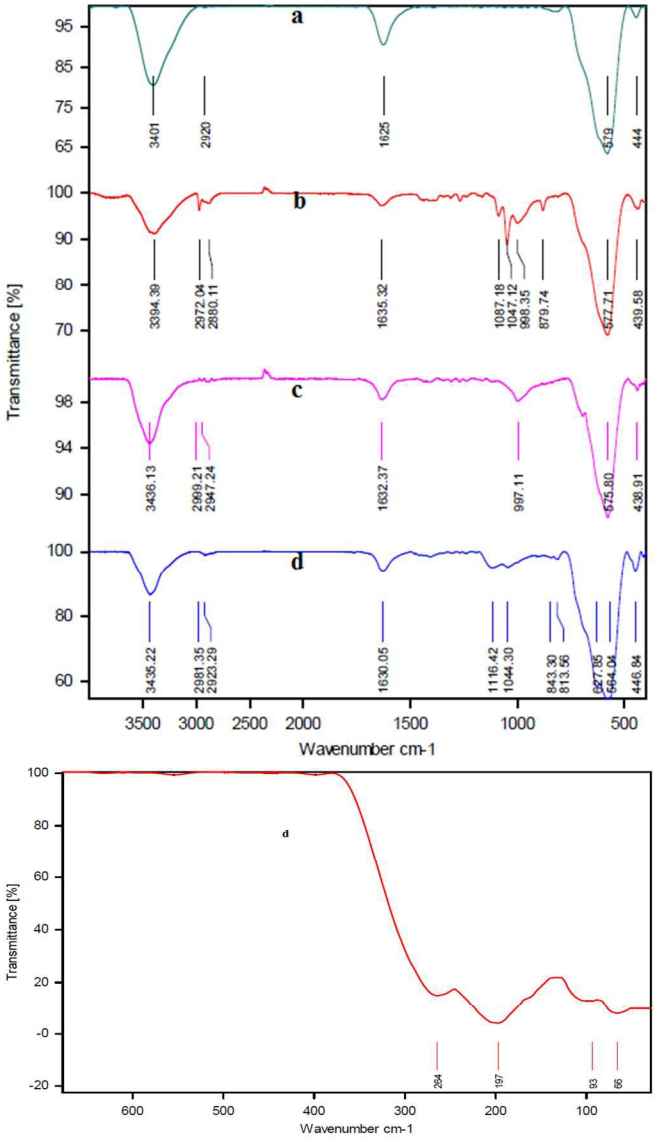
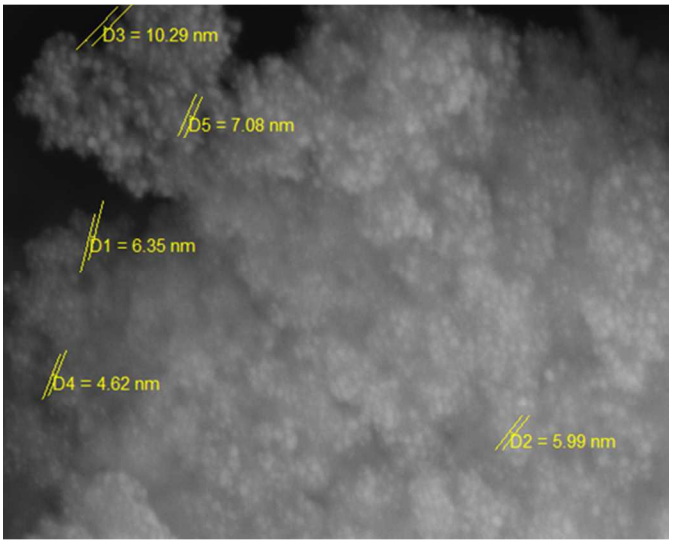


Figure 2. FT-IR spectra for the MNPs (a), MNPs-CPTMS (b), MNPs-TEDETA (c), and MNPs-TEDETA tribromide (d).



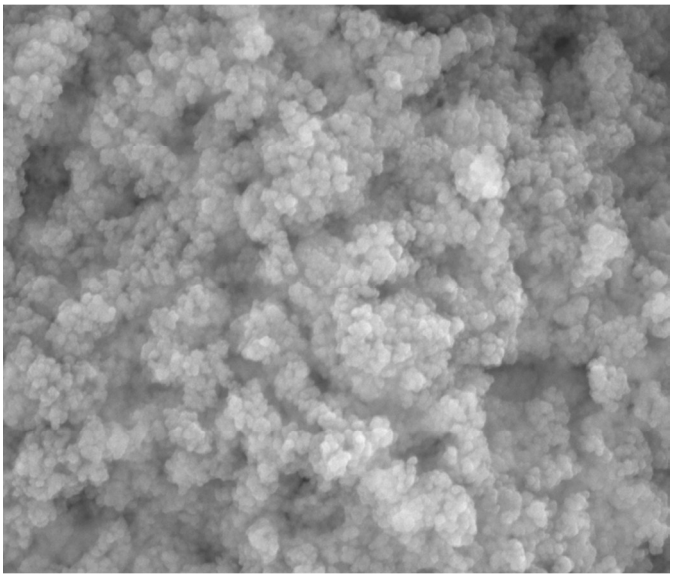
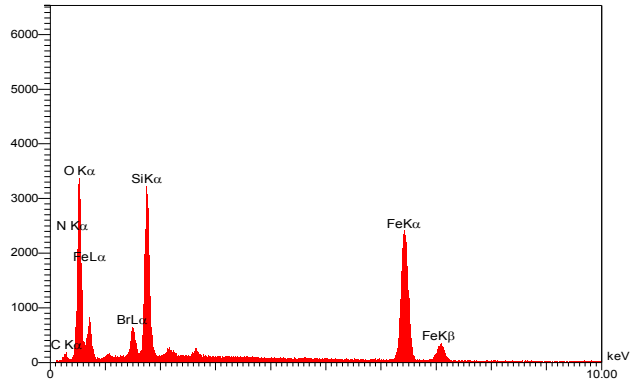
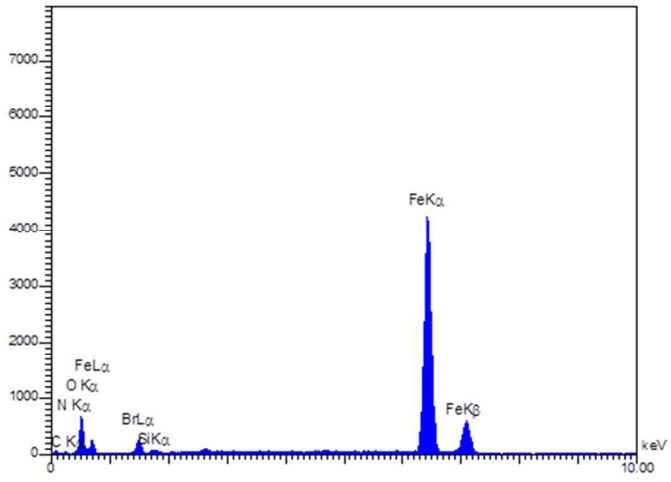


Figure 3. SEM images of the MNPs-TEDETA tribromide



a



b

Figure 4. EDX spectrum for MNPs-TEDETA tribromide (a), recovered catalyst (b)

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The bond formation between the nanoparticles and the catalyst can be inferred from the thermo gravimetric analysis (TGA). The TGA curves of the MNPs-TEDETA tribromide and bare Fe_3O_4 nanoparticles are showed in Figure 5. The mass loss at temperatures below 200 °C is due to the removal of physically adsorbed surface hydroxyl groups and solvent. The weight loss of 7% for MNPs-TEDETA tribromide between 205-636 °C associated to the thermal decomposition of organic groups grafted to Fe_3O_4.

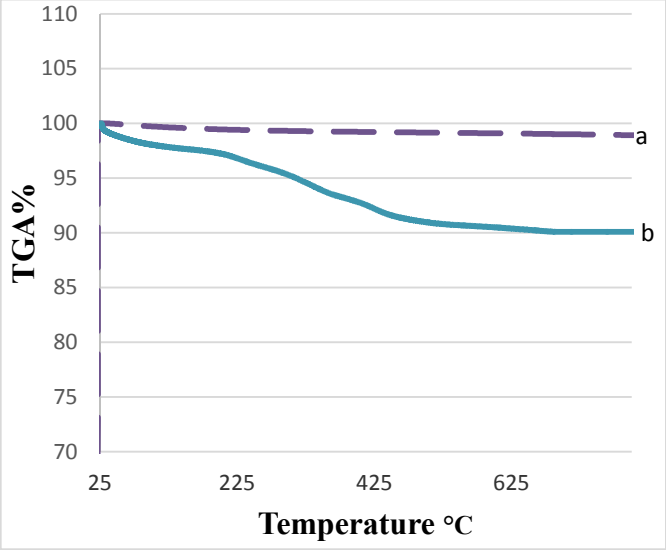


Figure 5. TGA profile of the Fe_3O_4 (a) and MNPs-TEDETA tribromide (b)

Vibrating sample magnetometer (VSM) analysis is employed for measurement of magnetic property of MNPs and MNPs- TEDETA tribromide. As shown in Figure 6, the bare MNPs and MNPs-TEDETA tribromide both present excellent paramagnetism but due to the coating of silica and the layer of the attached catalyst, the bare MNPs indicated the higher magnetic value in comparison with MNPs- TEDETA tribromide.

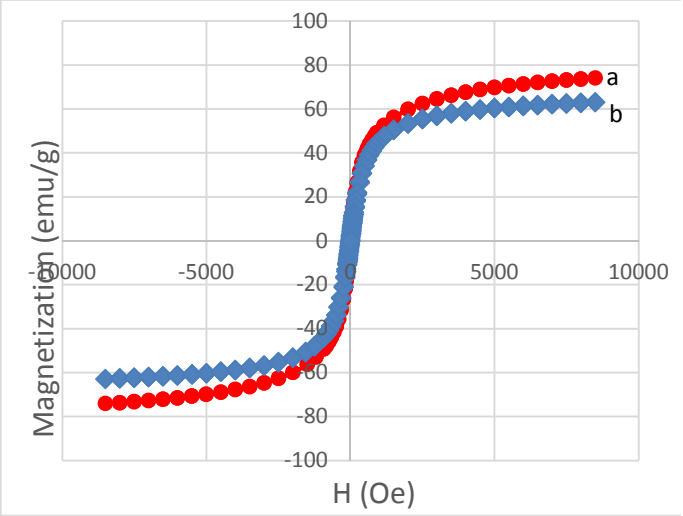
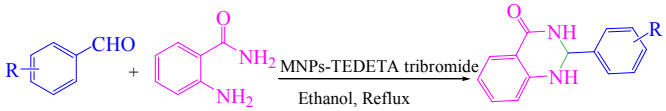


Figure 6. VSM analysis of the Fe_3O_4 (a) and MNPs-TEDETA tribromide (b)

2.3 Catalytic study

After characterizing MNPs- TEDETA tribromide, we investigated its efficiency as nanocatalyst in organic reactions such as synthesis of 2,3-dihydroquinazolin-4(1H)-one and polyhydroquinoline derivatives. First, to optimize the reaction condition for synthesis of 2,3-dihydroquinazolin-4(1H)-one, the condensation of 4-chlorobenzaldehyde (1 mmol) with 2-aminobenzamide and MNPs-TEDETA tribromide as catalyst was used as a model reaction (Scheme 2). The reactions were carried out in the presence of different amounts of catalyst and 2-aminobenzamide and various solvents. The best results were obtained with molar ratio of 1: 1.05 for aldehyde: 2-aminobenzamide and 0.05 g of MNPs-TEDETA tribromide in EtOH under reflux condition (Table1, entry 3).



Scheme 2. MNPs- TEDETA tribromide catalyzed the one-pot synthesis of 2,3-dihydroquinazolin-4(1H)-one derivatives.

In generality, the choice of solvent can have a significant effect on the performance of a reaction. Solvents can have an effect on solubility and reaction rates. In this light, we monitored the synthesis of 2,3-dihydroquinazolin-4(1H)-one using different solvent (polar and non-polar) such as: EtOH, H_2O, PEG, CH_2Cl_2, EtOAc, n-Hex, and aceton. The green solvent of H_2O applied but no product was obtained (no reaction). Also the yield of product with PEG was trace. Although CH_2Cl_2, EtOAc, n-Hex, and aceton are not safe solvents, we tested them for more investigation. As shown in Table 1, these solvents had low yield (15%-45%) and were not suitable for this multi component reaction. Among of several used solvent, EtOH is the best solvent because EtOH significantly improved the yield and it is safer than of CH_2Cl_2, EtOAc, n-Hex, and aceton. Also in several method that reported for the synthesis of 2,3-dihydroquinazolin-4(1H)-one, the solvent of reaction were EtOH [14, 19, 21, 31].

Table 1. Optimization condition for the condensation of 4-chlorobenzaldehyde (1mmol) and 2-aminobenzamide in EtOH[a]

Entry	2-aminobenzamide (mmol)	Catalyst (g)	Solvent	Temperature (ºC)	Yield (%)[b]
1	1.05	0.03	EtOH	80	63
2	1.05	0.04	EtOH	80	69
3	1.05	0.05	EtOH	80	95
4	1.05	0	EtOH	80	N.R[c]
5	1.05	0.06	EtOH	80	93
6	1.1	0.05	EtOH	80	88
7	1	0.05	EtOH	80	81
8	1.05	0.05	EtOH	70	70
9	1.05	0.05	H_2O	80	N.R
10	1.05	0.05	CH_2Cl_2	80	37
11	1.05	0.05	EtOAc	80	45
12	1.05	0.05	n-Hex	80	15
13	1.05	0.05	PEG	80	Trace
14	1.05	0.05	aceton	80	32

[a] 80 min
[b] Isolated yield.
[c] No Reaction

The reaction of the various benzaldehyde derivatives was then investigated. The 2,3-dihydroquinazolin-4(1H)-one derivatives were obtained in high yields. The results of this study are summarized in Table 2. As shown, a variety of benzaldehydes bearing electron-donation and electron-withdrawing substituents were successfully employed to prepare the corresponding 2,3-dihydroquinazolin-4(1H)-one derivatives in excellent yields.

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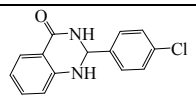
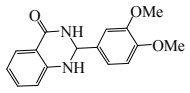
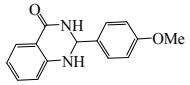
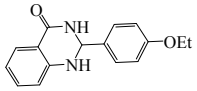
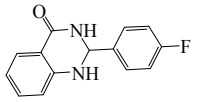
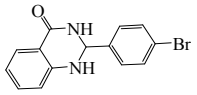
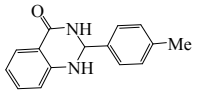
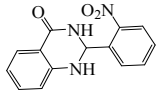
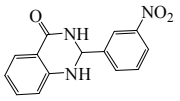
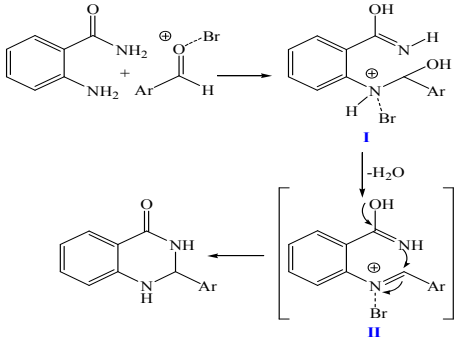
Table 2. Synthesis of 2,3-dihydroquinazolin-4(1H)-ones catalyzed by MNPs- TEDETA tribromide in ethanol and at 80 ºC.

Entry	Product	Time (min)	Yield (%)[a]	M. p (ºC)	Reference
1		80	95	198-200	[22]
2		35	99	210-211	[22]
3		60	70	174-177	[22]
4		120	92	170-172	[4]
5		65	95	204-206	[31]
6		90	82	189-191	[22]
7		60	96	226-227	[22]
8		130	80	187-190	[21]
9		90	99	192-193	[21]

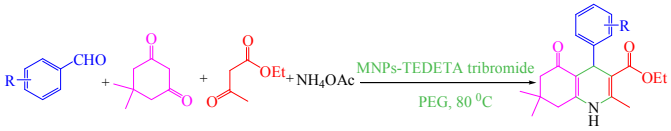
[a]Isolated yield.

The plausible mechanism for the formation of 2-aryl-2,3-dihydroquinazolinone-4(1H)-one was proposed and shown in Scheme 3. The carbonyl group in aldehyde activated with catalyst. Then the anthranilamide reacted with the activated aldehyde and the intermediate **I** is formed. After dehydration of intermediate **I**, the imine intermediate **II** is generated. Finally the intramolecular cyclization of imine intermediate **II** produced the final product [32].



Scheme 3. The proposed mechanism of synthesis 2-aryl-2,3-dihydroquinazolinone-4(1H)-one

In the second part of our work we were interested in finding a method for the one-pot synthesis of polyhydroquinoline derivatives using MNPs- TEDETA tribromide as a recoverable nanocatalyst in PEG as a green solvent (Scheme 3).



Scheme 4. Synthesis of polyhydroquinoline derivatives catalyzed by MNPs- TEDETA tribromide.

To optimize the reaction conditions for one-pot synthesis of polyhydroquinoline derivatives, 4-chlorobenzaldehyde with dimedone, ammonium acetate and ethylacetoacetate was used as a model reaction in the presence of different organic solvents and different amounts of catalyst and ammonium acetate in temperature condition (Table 3).

Table 3. Optimization the reaction condition for the synthesis of polyhydroquinoline using of 4-chlorobenzaldehyde, dimedone, ammonium acetate, ethylacetoacetate and catalyst as a model reaction.

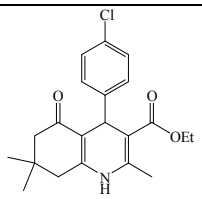
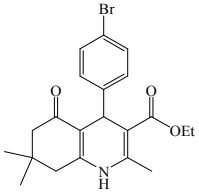
Entry	Catalyst (g)	Ammonium acetate (mmol)	Solvent	Temperature (ºC)	Time (min)	Yield (%)[a]
1	0.04	1.2	PEG	80	300	78
2	0.05	1.2	PEG	80	120	92
3	0.06	1.2	PEG	80	140	93
4	0	1.2	PEG	80	120	20
5	0.05	1.2	PEG	60	120	55
6	0.05	1.2	PEG	100	120	67
7	0.05	1.1	PEG	80	120	74
8	0.05	1	PEG	80	120	70
9	0.05	1.2	H_2O	80	120	trace
10	0.05	1.2	EtOH	80	120	61
11	0.05	1.2	EtOAc	80	120	50

[a] Isolated yield

As shown in entry 2 of Table 3 after the optimization of the reaction condition, 4-chlorobenzaldehyde (1 mmol), dimedon (1 mmol), ethylacetoacetate (1 mmol) and ammonium acetate (1.2 mmol) in the presence of 0.05 g MNPs- TEDETA tribromide in PEG was showed better results in terms of the reaction yield and rate.

In this reaction, the various benzaldehyde derivatives were employed. As shown in Table 4 the polyhydroquinoline derivatives were obtained in high yields.

Table 4. Synthesis of polyhydroquinoline catalyzed by MNPs-TEDETA tribromide in PEG and at 80 ºC.

Entry	Product	Time (min)	Yield (%)[a]	M. p. (ºC)	Reference
1		120	92	235-238	[14]
2		210	89	248-250	[14]

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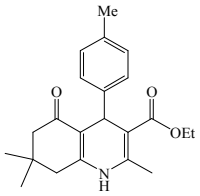
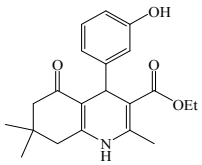
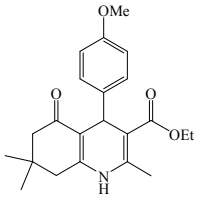
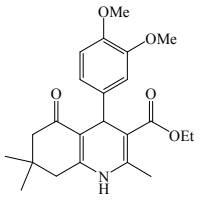
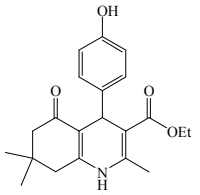
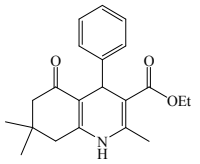
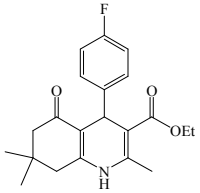
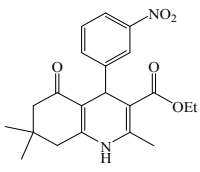
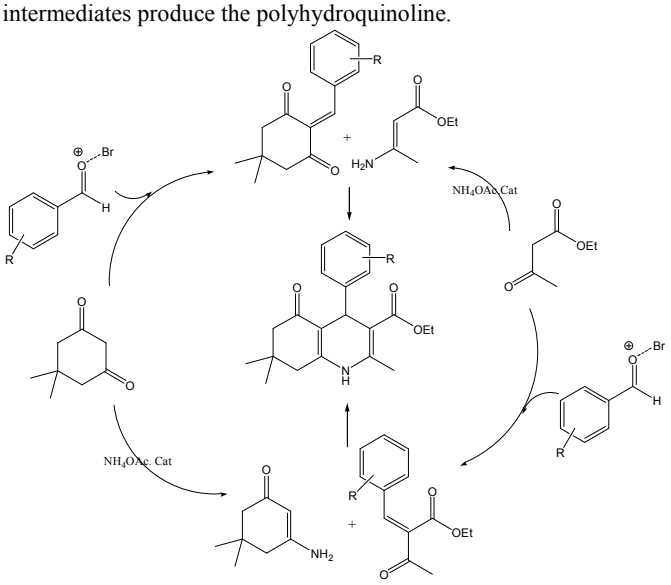
3		250	86	250-252	[14]
4		240	90	224-226	[14]
5		240	82	252-254	[14]
6		150	90	199-200	[29]
7		200	80	230-232	[29]
8		290	75	217-219	[29]
9		210	87	189-191	[14]
10		300	86	176-178	[14]

[a]Isolated yield.

As shown in Scheme 5 the mechanism of the synthesis of polyhydroquinoline derivatives was indicated [14]. The role of the catalyst comes in the condensation of aldehydes with the active methylene compounds (Knoevenagel Condensation) to afford α,β-unsaturated compound and the Michael-type addition of the intermediates produce the polyhydroquinoline.



Scheme 5. The proposed mechanism of synthesis polyhydroquinoline derivatives by MNPs-TEDETA tribromide

2.4 Recyclability of the catalyst

The recyclability of the catalyst was studied by using a model reaction between 2-aminobenzamide and 4-chlorobenzaldehyde in the presence of catalyst in reflux of EtOH under the optimization conditions. After completion of the reaction, the product was dissolved in hot ethanol. Then the catalyst was separated from the product by an external magnet. Then ethanol was removed by evaporation. Finally, the pure product was obtained by recrystallization in the EtOH. The recycled catalyst was dried and used for further runs and its activity did not show any significant decrease even after 6 runs (Figure 7).

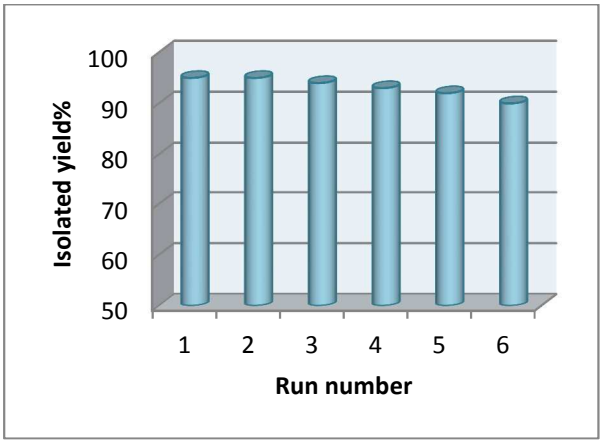


Figure 7. Recovery of the catalyst in the synthesis of 2,3-dihydroquinazolin-4(1H)-ones

2.5 Hot filtration

We were studied a hot filtration technique for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones. We investigated hot filtration technique for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones, by using of 4-chlorobenzaldehyde (1 mmol), 2-aminobenzamide (1.05 mmol) and MNPs-TEDETA tribromide (0.05 g) in refluxing of ethanol. This reaction carried out at 80 min and yield of product was 95%. We repeated the reaction and yield of product in half time of

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the reaction that it was 53%. In another reaction we repeat the reaction and after 40 min, catalyst was separated by an external magnet and washed with hot ethanol, then the solution was allowed to go for the remaining half stirring. After purification, yield of product was obtained 55%.

2.6 Comparison of the catalyst

To demonstrate the merit of MNPs-TEDETA tribromide, in comparison with other reported catalysts, we compared the results of the preparation of 2-(3,4-dimethoxyphenyl)-2,3-dihydoquinazolin-4(1H)-one from 3,4-dimethoxybenzaldehyde and anthranilamide with the previous reported in the literature. As shown in Table 5 these results indicated the efficiency of the proposed methodology in terms of the reaction yield and rate as compared to literature reports, also the prepared catalyst in this work is metal free catalyst.

Table 5. Comparison results of MNPs-TEDETA tribromide with other catalysts for the reaction of anthranilamide and 3,4-dimethoxybenzaldehyde

Entry	Condition	Time (min)	Yield %	Ref
1	CuCl2/Fe_3O_4-TEDETA (0.005 g), EtOH, Reflux	30	96	[4]
2	GSA@MNPs (0.01 g), EtOH, Reflux	25	98	[14]
3	$BiBr_3$ (5mol%), CH_3CN, R.T	30	84	[18]
4	2-Morpholino ethanesulfonic acid (10 mol%), Ethanol, 60 ^{0}C / MWI	180 /12	86 /88	[19]
5	SiO_2-$FeCl_3$ (0.005 g), solvent free, 80 ^{0}C	42h	90	[20]
6	Boehmite-SSA(0.03 g), EtOH, Reflux	130	88	[21]
7	Boehmite-Si-DSA (0.03 g), EtOH, Reflux	60	96	[22]
8	MNPs-TEDETA tribromide (0.05 g), EtOH, 80 ^{0}C	35	99	[a]

[a] this work

3 Conclusions

In summary, we have synthesized the MNPs-TEDETA tribromide as a new, reusable and efficient catalyst for the synthesis of 2,3-dihydroquinazolin-4(1H)-ones by the condensation between various aldehydes and anthranilamide in presence of MNPs-TEDETA tribromide and EtOH at 80 ºC and synthesis of polyhydroquinoline via a one-pot, multicomponent condensation reaction between of aldehyde, dimedon, ethylacetoacetate, ammonium acetate and MNPs-TEDETA tribromide as catalyst in PEG at 80 ºC. The benefits of the catalyst are the novelty, easy preparation, functionalization without tedious condition, easy separation by an external magnet, and low toxicity and price. Also the catalyst can be reused for 6 times without any significant loss of its activity.

4 Experimental

4.1 Preparation of the magnetic Fe_3O_4 nanoparticles (MNPs)

A mixture of $FeCl_3{\cdot}6H_2O$ (5.858 g) and $FeCl_2{\cdot}4H_2O$ (2.221 g) were dissolved in 100 mL deionized water until the salts dissolved completely. Then, 10 mL of 30% NH_4OH was added in to the reaction mixture under N_2 atmosphere about 30 min at 80℃ under vigorous mechanical stirring. Nanoparticles of Fe_3O_4 was collected and washed with doubly distilled water (five times) [13].

4.2 Preparation of MNPs coated by 3-chloropropyltrimethoxysilane (MNPs-CPTMS)

1.5 mL of 3-chloropropyltrimethoxysilane (CPTMS) was added to the obtained magnetic Fe_3O_4 nanoparticles (0.5 g) in 50 mL EtOH/H_2O (1:1) under N_2 atmosphere at 40℃ about 8 hours. Then, the final product was separated by external magnet. For remove the unattached substrates the product washed with ethanol and dried at room temperature.

4.3 Preparation of MNPs-TEDETA tribromide

2 mmol N, N, N′, N′-tetraethyldiethylenetriamine (TEDETA) was added to 4 mmol triethylamine at room temperature for 30 minutes. The obtained MNPs-CPTMS was added to the mixture in dry toluene under reflux conditions for 24 h. TEDETA functionalized magnetic nanoparticles (MNPs-TEDETA) prepared after washing with deionized water and ethanol and dried overnight. In the next step, HBr 47% was added to MNPs-TEDETA and stirred for an hour. Ultimately bromine in CCl_4 was added to the mixture and stirred for 6-7 h. Then the MNPs-TEDETA tribromide was collected by an external magnet and washed with doubly distilled water and ethanol.

4.4 General procedure for the synthesis of 2,3 dihydroquinazolin-4(1H)-ones derivatives

A stirred mixture of aldehyde (1 mmol), 2-aminobenzamide (1.05 mmol) and MNPs-TEDETA tribromide (0.05 g), was reacted in reflux of ethanol. After completion of the reaction, monitored by TLC, the product was dissolved in hot ethanol, and then catalyst was separated from the product by an external magnet. Then ethanol was removed by evaporation. Finally, pure products were obtained by recrystallization by EtOH.

4.5 General procedure for the synthesis of polyhydroquinoline derivatives

A mixture of aldehyde (1 mmol), dimedon (1 mmol), ethylacetoacetate (1 mmol), ammonium acetate (1.2 mmol) and MNPs-TEDETA tribromide (0.05 g) was stirred in PEG at 80 ºC. The progress of the reaction was monitored by TLC. After completion of the reaction, catalyst was separated by an external magnet then product extracted with ethylacetate. Finally, the solvent was evaporated and all products were recrystallized in ethanol, which the pure products were obtained in good to excellent yields.

4.6 Characterization data of all compounds

2-(4-Chlorophenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 1, Table 2). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 8.29 (s, 1H), 7.60–7.41 (m, 5H), 7.25–7.20 (t, J =7.5, 1H), 7.12 (s, 1H), 6.75–6.63 (m, 2H), 5.75 (s, 1H) ppm.

2-(3,4-Dimethoxyphenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 2, Table 2). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 8.21 (s, 1H), 7.64–7.61 (d, J = 1.6, 1H), 7.29–7.25 (t, J = 8, 1H), 7.15- 7.14 (d, J = 1.6, 1H), 7.03–6.97 (m, 2H), 6.95 (s, 1H), 6.78–6.76 (d, J = 8, 1H), 6.72–6.68 (t, J= 1.2, 1H), 5.71 (s, 1H), 3.77 (s, 3H), 3.76 (s, 3H) ppm.

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2-(4-Methoxyphenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 3, Table 2). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 8.22 (s, 1H), 7.66–7.63 (m, 1H), 7.46–7.44 (d, J = 8.8, 2H), 7.29- 7.24 (m, 1H), 7.04 (s, 1H), 6.99-6.69 (d, J=1.2, 2H), 6.78–6.76 (d, J = 8, 1H), 6.70–6.68 (t, J= 7.2, 1H), 5.74 (s, 1H), 3.77 (s, 3H) ppm.

2-(4-Ethoxyphenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 4, Table 2). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 7.95–7.94 (b, 1H), 7.51–7.50 (m, 2H), 7.34 (s, 1H), 7.27 (s, 1H), 6.94–6.90 (m, 3H), 6.68–6.67 (m, 1H), 5.85 (s, 1H), 5.75 (s, 1H), 4.08–4.06 (q, J ¼ 4, 2H), 1.46– 1.44 (s, 3H) ppm.

2-(4-Fluorophenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 5, Table 2). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 8.32 (s, 1H), 7.65–7.63 (m, 1H), 7.59–7.54 (m, 2H), 7.30- 7.23 (m, 3H), 7.13 (s, 1H), 6.79-6.77 (d, J=0.8, 1H), 6.69-6.67 (t, J=8, 1H) 5.80 (s, 1H) ppm.

2-(4-Bromophenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 6, Table 2). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 8.17–8.14 (m, 1H), 7.79–7.77 (m, 1H), 7.63–7.59 (m, 3H), 7.48–7.45 (m, 2H), 7.29–7.23 (m, 1H), 6.77–6.72 (d, J = 19.2, 1H), 6.70–6.67 (m, 1H), 5.76 (s, 1H) ppm.

2-(4-Methylphenyl)-2,3-dihydroquinazolin-4(1H)-one (entry 7, Table 2). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 8.21 (s, 1H), 7.63–7.60 (d, J = 7.5, 1H), 7.38–7.35 (d, J = 7.5, 2H), 7.25–7.13 (m, 3H), 7.03 (s, 1H), 6.74–6.63 (m, 2H), 5.71 (s, 1H), 2.49–2.42 (s, 3H) ppm.

2-(2-Nitrophenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 8, Table 2). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H :8.25 (s, 1H), 8.10–8.08 (d, J = 8, 1H), 7.90–7.87 (d, J = 8, 1H), 7.83–7.79 (t, J = 0.8, 1H), 7.69–7.63 (m, 2H), 7.30–7.26 (m, 1H), 7.04 (s, 1H), 6.81 (d, J = 1.2, 1H), 6.77–6.72 (m, 1H), 6.36 (m, 1H) ppm.

2-(3-Nitrrophenyl)-2,3-dihydoquinazolin-4(1H)-one (entry 9, Table 2). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 8.57 (s, 1H), 8.40–8.39 (t, J=1.6, 1H), 8.24–8.21 (m, 2H), 7.98- 7.96 (d, J=7.6, 1H), 7.74-7.70 (t, J=8, 1H), 7.66-7.64 (m, 1H), 7.38 (s, 1H), 7.32-7.28 (m, 1H), 6.83-6.81 (d, J=8, 1H), 6.74-6.70 (m, 1H), 5.98 (s, 1H) ppm.

Ethyl-4-(4-chlorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 1, Table 4). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 9.13 (s, 1H), 7.25–7.28 (m, 2H), 7.17–7.19 (m, 2H), 4.86 (s, 1H), 4.01–3.96 (q, J = 7.2, 2H), 2.46–2.41 (d, J = 16.8, 1H), 2.31–2.28 (m, 4H), 2.21–2.17 (d, J = 16, 1H), 2.01–1.97 (d, J = 16, 1H), 1.15–1.12 (t, J = 7.2, 3H), 1.02 (s, 3H), 0.85 (s, 3H) ppm.

Ethyl-4-(4-bromophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 2, Table 4). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 9.14 (s, 1H), 7.41–7.39 (d, J = 8.4, 2H), 7.13–7.11 (d, J = 8.4, 2H), 4.84 (s, 1H), 4.01–3.95 (q, J = 6.8, 2H), 2.52–2.46 (d, J = 26.4, 1H), 2.31–2.28 (m, 4H), 2.21–2.17 (d, J = 16, 1H), 2.01–1.97 (d, J = 16, 1H), 1.15–1.11 (t, J = 7.2, 3H), 1.02 (s, 3H), 0.84 (s, 3H) ppm.

Ethyl-4-(4-methylphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline- 3-carboxylate (entry 3, Table 4). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 9.04 (s, 1H), 7.05–7.03 (d, J = 8, 2H), 7.00–6.97 (d, J = 8, 2H), 4.81 (s, 1H), 4.01–3.95 (q, J = 6.8, 2H), 2.44–2.40 (d, J = 16, 1H), 2.30–2.26 (m, 4H), 2.21–2.15 (m, 4H), 2.10–1.96 (d, J = 16, 1H), 1.17–1.13 (t, J = 6.8, 3H), 1.02 (s, 3H), 0.86 (s, 3H) ppm.

Ethyl-4-(4-methoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 5, Table 4). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 9.04 (s, 1H), 7.08–7.06 (d, J = 8.4, 2H), 6.77–6.75 (d, J = 8.4, 2H), 4.81 (s, 1H), 4.01–3.96 (q, J = 7.2, 2H), 3.68 (s, 3H), 2.45–2.41 (d, J = 29.2, 1H), 2.31–2.29 (m, 4H), 2.20–2.16 (d, J = 16, 1H), 2.01–1.97 (d, J = 16.4, 1H), 1.17–1.14 (t, J = 7.2, 3H), 1.02 (s, 3H), 0.87 (s, 3H) ppm.

Ethyl-4-(3,4-dimethoxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 6, Table 4). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 9.05 (s, 1H), 6.79–6.76 (m, 2H), 6.65–6.63 (d, J = 8, 1H), 4.81(s, 1H), 4.04–3.99 (q, J = 7.2, 2H), 3.69–3.68 (d, J = 4.4, 5H), 2.47–2.42 (d, J = 17.2, 2H), 2.35–2.29 (m, 4H), 2.22–2.18 (d, J = 16, 1H), 2.03–1.99 (d, J = 16, 1H), 1.20–1.16 (t, J = 7.2, 3H), 1.03 (s, 3H), 0.90 (s, 3H) ppm.

Ethyl-4-(4-hydroxyphenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 7, Table 4). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 9.05 (s, 1H), 8.99 (s,1H), 6.95–6.93 (d, j=8.8, 2H), 6.58-6.55 (m, 2H), 4.75 (s, 1H), 4.02–3.98 (m, 2H), 2.44–2.40 (d, J = 16.8, 1H), 2.30–2.26 (m, 4H), 2.19–2.15 (d, J = 16, 1H), 2.00–1.96 (d, J = 16, 1H), 1.17–1.14 (t, J = 7.2, 3H), 1.02 (s, 3H), 0.87 (s, 3H) ppm.

Ethyl-4-(phenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8 hexahydroquinoline-3-carboxylate (entry 8, Table 4). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 9.08 (s, 1H), 7.22–7.17 (m, 4H), 7.10–7.06 (m, 1H), 4.88 (s, 1H), 4.02–3.97 (q, J = 7.2, 2H), 2.46–2.42(d, J = 17.2 1H), 2.33–2.29 (t, J=8.8, 4H), 2.21–2.17 (d, J = 16, 1H), 2.02–1.98 (d, J = 16, 1H), 1.16–1.13 (t, J = 7.2, 3H), 1.03 (s, 3H), 0.86 (s, 3H) ppm.

Ethyl-4-(4-fluorophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 9, Table 4). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 9.11 (s, 1H), 7.20–7.17 (m, 2H), 7.04–7.00 (t, J = 8.8, 2H), 4.87 (s, 1H), 4.02–3.96 (q, J = 7.2, 2H), 2.46–2.41 (d, J = 16.8, 1H), 2.32–2.28 (m, 4H), 2.21–2.17 (d, J = 16, 1H), 2.02–1.98 (d, J = 16, 1H), 1.15–1.12 (t, J = 7.2, 3H), 1.02 (s, 3H), 0.85 (s, 3H) ppm.

Ethyl-4-(3-nitrophenyl)-2,7,7-trimethyl-5-oxo-1,4,5,6,7,8-hexahydroquinoline-3-carboxylate (entry 10, Table 4). ^{1}H NMR (400 MHz, DMSO-d_6): δ_H : 9.25 (s, 1H), 8.12–8.10 (d, J = 8.4, 2H), 7.45–7.43 (d, J = 8.4, 2H), 4.99 (s, 1H), 4.01–3.95 (q, J = 7.2, 2H), 2.48–2.44 (d, J = 17.2, 1H), 2.34–2.30(d,J=16.8, 4H), 2.22–2.18 (d, J = 16, 1H), 2.02–1.98 (d, J = 16, 1H), 1.14–1.11 (t, J = 7.2, 3H), 1.02 (s, 3H), 0.84 (s, 3H) ppm.

Acknowledgements

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Graphical Abstract

Tribromide ion immobilized on magnetic nanoparticle as new, efficient and reusable nanocatalyst in multicomponent reactions

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