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Synthesis and applications of $CoFe_2O_4$ nanoparticles for multicomponent reactions

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An efficient, simple, green protocol is developed for the synthesis of 2-amino-4-(phenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile derivatives and 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) derivatives in the presence of $CoFe_2O_4$ nanoparticles in aqueous ethanol medium. $CoFe_2O_4$ nanoparticles have been synthesised by a co-precipitation method followed by ultrasonication. The synthesised $CoFe_2O_4$ nanoparticles have high surface area (140.9 m^2 g^{-1}) and small size (2–8 nm). The present catalytic process provides sustainability as aqueous medium is used, the reaction proceeded in short reaction times by providing high yields of products and is economical as the catalyst is inexpensive and can be recovered from the reaction mixture. The recovered catalyst can be used for multiple cycles without much loss of its activity. The protocol is green as no chromatographic technique is used, thus eliminating the use of hazardous organic solvents. $CoFe_2O_4$ emerged as an efficient, sustainable, stable and recyclable catalyst.

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Introduction

In recent years, use of sustainable catalysts and benign solvents are considered as key points from a green chemistry point of view for the development of sustainable protocols.[1] From this aspect, nanocatalysts have emerged with good catalytic activity due to their small size, large surface area, selectivity, recovery from reaction mixtures and reusability.[2,3] Moreover, the magnetic nanoparticles (MNPs) have gained a significant place among nanocatalysts because of their applications in a variety of disciplines such as biotechnology/biomedicine,[4] magnetic resonance imaging,[5] data storage[6] and especially in catalysis as a magnetically separable catalyst.[7] The separation of magnetic nanoparticles from reaction mixtures is driven by an external magnet, which make the recovery and reusability of the catalyst easier and avoids loss of catalyst associated with traditional filtration and centrifugation methods, therefore supporting the green chemistry principles in terms of eco-benign and economical needs for sustainability.[8] In addition to these points, the magnetic properties of nanoparticles are stable and can tolerate the chemical environment except those that are acidic/corrosive.[9] Among the various MNPs, Fe_3O_4 is used widely as a catalyst,[10] but is reactive to acidic and oxidative environments as Fe^{2+} present in Fe_3O_4 is oxidised easily and the magnetic properties of Fe_3O_4 are vulnerable to loss of magnetism,[11] while Fe_2O_3 nanoparticles are not thermally stable.[12]

The aqueous mediated reactions have gained intensive attention in organic synthesis for the design of environmentally benign and low impact protocols.[13] Thus water is chosen as a green solvent, which addresses several features of green chemistry such as being cheap, easily available, non-toxic and non-flammable.[14] Further, the hydrophobic nature of water enhances the rate of reaction and influences the selectivity of reaction.[15]

In organic chemistry the synthesis of biologically and pharmaceutically active heterocycles are considered as a pivotal theme. Among various heterocycles, 2-amino-4-(phenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile derivatives have gained a strong place in drug research due to their pharmaceutical, biological and medicinal properties such as antifungal, antioxidant, antiviral, hypotensive and antitumor activities.[16] Further these derivatives have applications in various fields such as pigments, cosmetics,[17] agrochemicals,[18] optical brighteners,[19] laser dyes,[20] and fluorescence makers.[21] The 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) derivatives are also considered as important biologically active compounds possessing tyrosinase inhibitor properties.[22] These compounds are used as key intermediates for the preparation of heterocyclic compounds such as xanthenediones which show a wide range of biological, therapeutic[23] and spectroscopic properties as used in laser technology,[24] and acridindione derivatives,[25] which have been used as electron donors,[26] electron acceptors and in the photoinitiated polymerisation of acrylates and methacrylates.[27] 2,2′-Arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) derivatives have a phenolic functionality so they can couple with diazonium compounds to afford dyestuffs.[28] The synthesis of 2-amino-4-(phenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile derivatives has

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been carried out by the reaction of aldehydes, active methylene compounds and enolizable C–H activated compounds with the variety of reagents. On the other hand 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) derivatives can be prepared by condensation of aromatic aldehydes with 1,3-cyclic diketones using catalyst and catalyst free conditions. However, many of the reported methods are not effective for the synthesis of the desired compounds and suffer from drawbacks such as toxic solvents, long reaction times, use of excessive catalysts, low yields, tedious workup procedures, complex reaction pathways, harsh reaction conditions, cost effective reagents/catalysts, unrecyclable catalyst and formation of side products.

So in continuation of our work on green catalysis,[29] we synthesised $CoFe_2O_4$ nanoparticles and applied them as a catalyst for the preparation of 2-amino-4-(phenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile derivatives and 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) derivatives. $CoFe_2O_4$ nanoparticles have a spinel structure with high thermal stability, moderate magnetisation, chemical stability, high surface area and mechanical hardness.[30,31]

Results and discussion

In this paper we present the synthesis of 2-amino-4-(phenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile derivatives and 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) derivatives using $CoFe_2O_4$ nanoparticles as a catalyst. The $CoFe_2O_4$ nanoparticles were prepared by a previously reported method[29b] involving co-precipitation along with ultrasonication under basic conditions resulting in small sized (2–8 nm) nanoparticles with high surface area (140.9 $m^2\ g^{-1}$) and good thermal stability. The formation of $CoFe_2O_4$ nanoparticles was confirmed from XRD data. The synthesised $CoFe_2O_4$ nanoparticles have a cubic structure. Fig. 1 represents the XRD diffraction pattern. The size of particles was determined by transmission electron microscopy (TEM). TEM images showed the spherical shaped nanoparticles (Fig. 2).

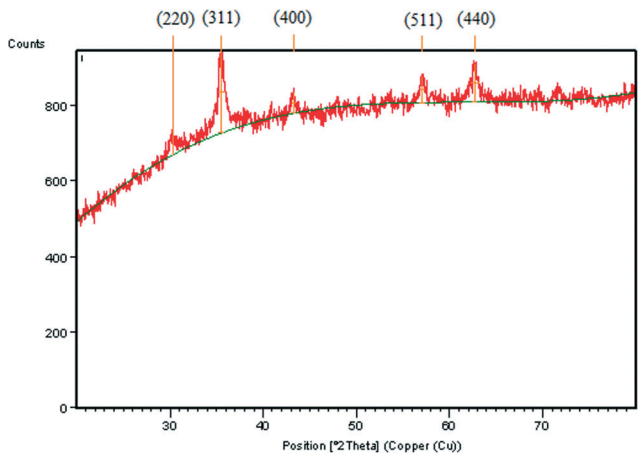


Fig. 1 XRD pattern of $CoFe_2O_4$ nanoparticles.

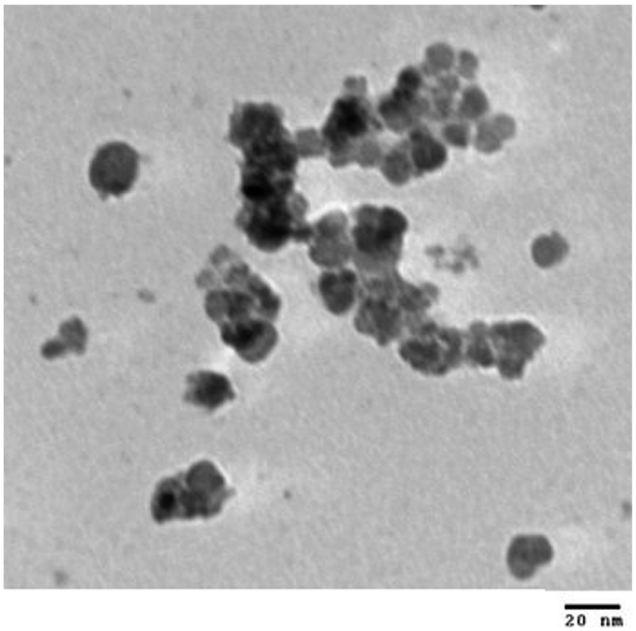


Fig. 2 TEM image of $CoFe_2O_4$ nanoparticles.

The $CoFe_2O_4$ nanoparticles were recovered from the reaction product using an external magnet due to their magnetic character, which was established by a vibrating sample magnetometer (VSM) showing saturation magnetization to be 1.77 emu g^{-1} (Fig. 3).

To establish the scope of catalytic activity of $CoFe_2O_4$ nanoparticles, we synthesised different products using $CoFe_2O_4$ nanoparticles.

Synthesis of 2-amino-4-(phenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile derivatives using $CoFe_2O_4$ nanoparticles as catalyst

Firstly the study was carried out by choosing the reaction of 4-Cl benzaldehyde (**1a**), 1,3-cyclohexanedione (**2a**) and malononitrile

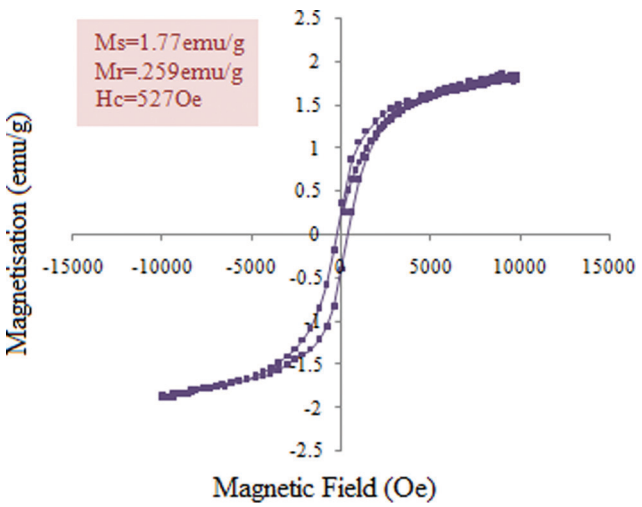
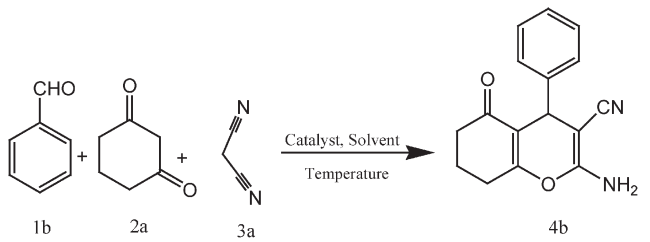


Fig. 3 VSM plot of $CoFe_2O_4$ nanoparticles.

(**3a**) in equimolar ratio as the model reaction (Scheme 1) without using catalyst providing low yield of product 58% after 60 min of reaction (Table 1, entry 1) but the addition of $CoFe_2O_4$ (0.05 mmol) to the reaction mixture increased the yield of product to 68% by decreasing the reaction time to 15 min (Table 1, entry 2), which showed the role of catalyst in the present protocol. Encouraged by these results we studied the various parameters such as different reaction temperatures, various solvents and amount of catalyst to find the optimised reaction conditions. The investigation was started by carrying out the reaction of **1a**, **2a** and **3a** at different temperatures starting from stirring at room temperature to 80 °C in EtOH using $CoFe_2O_4$ (0.05 mmol) (Table 1, entries 3–6). The reaction at 60 °C was chosen as the best temperature in terms of yield and time. After this, the effect of different solvents was examined at 60 °C (Table 1, entries 7–15). The H_2O : EtOH (1 : 3) system was considered as the optimum solvent. It is mentioned here that polar solvents gave better results as compared to non-polar solvents. However the yield of product in water was lower in comparison to other polar solvents because of lesser solubility of reactants. Generally the choice of solvent is explained on the basis of the fact that the solvent affects the transition state in the synthesis, as the transition state is better solvated by polar solvents and increases the reaction rate, which increases the product yield.[32] The reaction in H_2O : EtOH (1 : 3) gave the best yield of product (89%) in a shorter time, which was further explained as higher dispersability of the magnetic nanoparticles in the water–ethanol mixture making the system quasi-homogenous, which increases the interaction of the nanoparticles with the reactants, resulting in increased reaction rate.[33] 0.025 mmol of catalyst $CoFe_2O_4$ was taken as standard from various amounts of catalyst (Table 1, entries 16–19). The reaction was also carried out using bulk $CoFe_2O_4$ but the yield and reaction time were not impressive as compared to our synthesised $CoFe_2O_4$ nanoparticles (Table 1, entry 20). This can be attributed to the higher surface area and smaller size of $CoFe_2O_4$ nanoparticles, which increases the catalytic activity and interaction with the reacting species. All the results are shown in Table 1. The $CoFe_2O_4$ (0.025 mmol) with H_2O : EtOH (1 : 3) mixture at 60 °C was considered as the optimum reaction conditions (Table 1, entry 17) for the preparation of the desired product to obtain the best yield in shorter reaction time. We also investigated the reaction with synthesised Fe_3O_4, ZnO nanoparticles, but the yield was very low as compared to $CoFe_2O_4$ nanocatalyst, which showed the superiority of present catalytic system (Table 1, entries 20, 21).



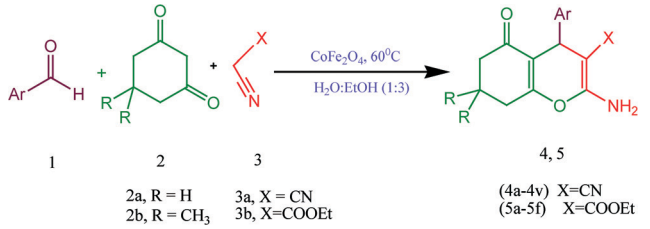
Scheme 1

The efficiency of these optimised parameters were examined for the synthesis of 2-amino-4-(phenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile derivatives, which were prepared by carrying out a one pot three component reaction of 1,3-cyclic diketones (**2a** and **2b**), active methylene compounds (**3a** and **3b**) and a wide range of aldehydes in the presence of $CoFe_2O_4$ (0.025 mmol) in H_2O–EtOH (1 : 3) mixture at 60 °C (Scheme 2 and Table 2, entries 1–28). All the aldehydes including aromatic, heterocyclic and unsaturated were employed for the present synthesis and reacted smoothly. The reactions of aldehydes bearing electron withdrawing groups (–Cl, $–NO_2$) and electron releasing

Table 1 Optimization of various reaction conditions for the synthesis of **4b**

Entry	Catalyst (mmol)	Solvents	Time (min)	Temperature (°C)	Yield[a] (%)
1	—	EtOH	60	RT (35 °C)	58
2	$CoFe_2O_4$ (0.05)	EtOH	15	RT (35 °C)	68
3	$CoFe_2O_4$ (0.05)	EtOH	5	Stirring (35 °C)	69
4	$CoFe_2O_4$ (0.05)	EtOH	7	45	70
5	$CoFe_2O_4$ (0.05)	EtOH	6	60	83
6	$CoFe_2O_4$ (0.05)	EtOH	4	80	75
7	$CoFe_2O_4$ (0.05)	H_2O	7	60	76
8	$CoFe_2O_4$ (0.05)	MeOH	8	60	82
9	$CoFe_2O_4$ (0.05)	CH_3CN	20	60	80
10	$CoFe_2O_4$ (0.05)	EtOAc	23	60	79
11	$CoFe_2O_4$ (0.05)	Toluene	25	60	70
12	$CoFe_2O_4$ (0.05)	H_2O : EtOH (1 : 1)	6	60	84
13	$CoFe_2O_4$ (0.05)	H_2O : EtOH (1 : 2)	6	60	86
14	$CoFe_2O_4$ (0.05)	H_2O : EtOH (1 : 3)	5	60	87
15	$CoFe_2O_4$ (0.05)	H_2O : EtOH (1 : 4)	5	60	85
16	$CoFe_2O_4$ (0.01)	H_2O : EtOH (1 : 3)	7	60	85
17	$CoFe_2O_4$ (0.025)	H_2O : EtOH (1 : 3)	4	60	89
18	$CoFe_2O_4$ (0.07)	H_2O : EtOH (1 : 3)	5	60	87
19	$CoFe_2O_4$ (0.1)	H_2O : EtOH (1 : 3)	5	60	84
20	$CoFe_2O_4$[b] (0.025)	H_2O : EtOH (1 : 3)	20	60	65
21	Fe_3O_4 (0.025)	H_2O : EtOH (1 : 3)	18	60	65
23	ZnO (0.025)	H_2O : EtOH (1 : 3)	16	60	71

[a] Isolated yield. [b] Bulk $CoFe_2O_4$.



Scheme 2

groups (–OH, $–OCH_3$) proceeded well in the given time under optimised reaction conditions. The results are tabulated in Table 2. It was demonstrated that a variety of 2-amino-4-(phenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile derivatives were synthesised in good to high yields (60–96%). The reactions were clean and completion of reaction was identified by precipitation of product along with TLC. The catalyst was separated out from reaction product without any tedious work-up by just attaching the external magnet to the walls of reaction flask and reused after drying. It was found that the reaction proceeded with ethyl cyanoacetate (Table 2, entries 23–28) took longer time as compared to malononitrile (Table 2, entries 11–14, 16, 17). The reason may be because the cyanide group attached to malononitrile, which has a greater capability to stabilize the intermediate as compared to the ester group of ethyl cyanoacetate.[34] All the products were formed with good chemoselectivities without the formation of any previously reported unwanted side products, such as hydrolysis of cyano group[35] and formation of polymerised product[36] in the case of cinnamaldehyde, which is an acid sensitive aldehyde.

The catalyst played the role of base to afford the product by the Knoevenagel condensation followed by a Michael addition. The Lewis basic sites originate from electrons trapped in the intrinsic defects or from surface hydroxyl groups[41] or from co-ordinatively unsaturated oxide ion associated with neighbouring hydroxyl groups.[42]

Synthesis of 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) derivatives using $CoFe_2O_4$ nanoparticles as catalyst

Encouraged from the above results we also tried to synthesise 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) derivatives by the reaction of aromatic aldehydes and 1,3-cyclic diketones (dimedone and 1,3-cyclohexanedione) in a 1 : 2 molar ratio to investigate the scope of our catalytic system. The initial study started with the reaction of 4-methoxy benzaldehyde (**1d**) with dimedone (**2a**) in the presence of $CoFe_2O_4$ (0.025 mmol) in H_2O : EtOH (1 : 1) mixture at room temperature to afford the desired product, which is obtained in 72% yield (Table 3, entry 1). To check further the role of catalyst, a blank reaction was studied under similar reaction conditions and gave the product with 48% yield after 48 min (Table 1, entry 2). From these observations we carried out further work to obtain the standardised reaction conditions for

Table 2 Scope of catalytic activity of $CoFe_2O_4$ nanoparticles for synthesis 2-amino-4-(phenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile derivatives[a]

Entry	Ar	X	R	Product	Time (min)	Yield[b] (%)	M.P. obs.	M.P. lit.
1	4-Cl C_6H_4	CN	H	**4a**	4	89	230–232	226–229[37]
2	C_6H_5	CN	H	**4b**	6	85	228–230	234–235[37]
3	2-Cl C_6H_4	CN	H	**4c**	9	83	200–202	213–215[37]
4	3-NO_2 C_6H_4	CN	H	**4d**	6	86	200–202	198–200[37]
5	4-Br C_6H_4	CN	H	**4e**	3	91	235–238	—
6	4-OCH_3 C_6H_4	CN	H	**4f**	10	80	188–190	186–189[38]
7	4-OH C_6H_4	CN	H	**4g**	12	87	240–242	—
8	3,4-OCH_3 C_6H_3	CN	H	**4h**	20	84	192–194	—
9	C_6H_5CH═CH	CN	H	**4i**	15	88	195–198	—
10	-$N(CH_3)_2$ C_6H_4	CN	H	**4j**	10	89	171–174	—
11	4-Cl C_6H_4	CN	CH_3	**4k**	4	96	210–212	215–217[34]
12	C_6H_5	CN	CH_3	**4l**	7	93	224–226	234–235[34]
13	2-Cl C_6H_4	CN	CH_3	**4m**	12	90	198–200	215–216[34]
14	3-NO_2 C_6H_4	CN	CH_3	**4n**	7	94	210–212	213–214[34]
15	3-Cl C_6H_4	CN	CH_3	**4o**	5	93	210–212	224–225[37]
16	-$N(CH_3)_2$ C_6H_4	CN	CH_3	**4p**	10	91	206–208	210–212[34]
17	4-OCH_3 C_6H_4	CN	CH_3	**4q**	9	85	190–192	196–198[34]
18	4-OH C_6H_4	CN	CH_3	**4r**	15	87	212–215	224–226[34]
19	3,4-OCH_3 C_6H_3	CN	CH_3	**4s**	18	89	170–172	171–173[39]
20	C_6H_5CH═CH	CN	CH_3	**4t**	12	86	185–188	182–184[34]
21	4-OH-3,5-OCH_3 C_6H_2	CN	CH_3	**4u**	14	80	190–192	—
22	Furyl	CN	CH_3	**4v**	6	84	200–204	220–223[34]
23	C_6H_5	COOEt	CH_3	**5a**	10	80	150–152	151–153[40]
24	3-NO_2 C_6H_4	COOEt	CH_3	**5b**	15	71	148–150	154–156[40]
25	-$N(CH_3)_2$ C_6H_4	COOEt	CH_3	**5c**	18	69	170–172	—
26	2-Cl C_6H_4	COOEt	CH_3	**5d**	16	60	200–202	209–212[40]
27	4-OCH_3 C_6H_4	COOEt	CH_3	**5e**	20	70	140–141	131–134[40]
28	4-Cl C_6H_4	COOEt	CH_3	**5f**	14	77	130–133	139–142[40]

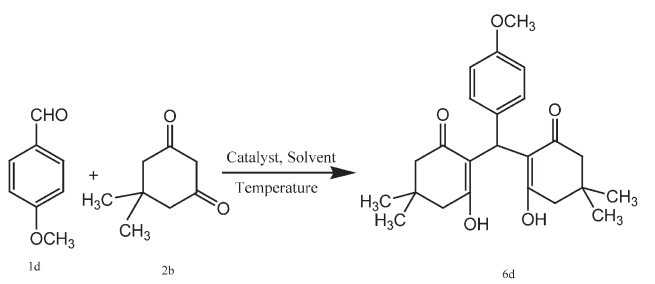
[a] Reaction conditions: aldehyde (2.5 mmol), dimedone (or 1,3-cyclohexanedione) (2.5 mmol), malononitrile (or ethylcyanoacetate) (2.5 mmol), $CoFe_2O_4$ (0.025 mmol), H_2O : EtOH (1 : 3) 3 ml. [b] Isolated yield.

Table 3 Optimisation of different reaction conditions for the synthesis of 6d

Entry	Catalyst (mmol)	Different optimization conditions	Solvents	Yield[a] (%)
1	$CoFe_2O_4$ (0.025)	RT (35–40 °C)	H_2O : EtOH (1 : 1)	72
2	—	RT (35–40 °C)	H_2O : EtOH (1 : 1)	48
3	$CoFe_2O_4$ (0.025)	Stirring at RT (35–40 °C)	H_2O : EtOH (1 : 1)	76
4	$CoFe_2O_4$ (0.025)	50 °C	H_2O : EtOH (1 : 1)	85
5	$CoFe_2O_4$ (0.025)	60 °C	H_2O : EtOH (1 : 1)	93
6	$CoFe_2O_4$ (0.025)	70 °C	H_2O : EtOH (1 : 1)	89
7	$CoFe_2O_4$ (0.025)	Refluxing	H_2O : EtOH (1 : 1)	90
8	$CoFe_2O_4$ (0.01)	60 °C	H_2O : EtOH (1 : 1)	87
9	$CoFe_2O_4$ (0.05)	60 °C	H_2O : EtOH (1 : 1)	95
10	$CoFe_2O_4$ (0.07)	60 °C	H_2O : EtOH (1 : 1)	88
11	$CoFe_2O_4$ (0.1)	60 °C	H_2O : EtOH (1 : 1)	86
12	$CoFe_2O_4$ (0.05)	60 °C	H_2O : EtOH (1 : 2)	90
13	$CoFe_2O_4$ (0.05)	60 °C	H_2O : EtOH (1 : 3)	88
14	$CoFe_2O_4$ (0.05)	60 °C	H_2O : EtOH (1 : 4)	83
15	$CoFe_2O_4$ (0.05)	60 °C	EtOH	80
16	$CoFe_2O_4$ (0.05)	60 °C	H_2O	70
17	$CoFe_2O_4$ (0.05)	60 °C	MeOH	75
18	$CoFe_2O_4$ (0.05)	60 °C	CH_3CN	78
19	$CoFe_2O_4$[b] (0.05)	60 °C	H_2O : EtOH (1 : 1)	68
20	Fe_3O_4 (0.05)	60 °C	H_2O : EtOH (1 : 1)	62
21	ZnO (0.05)	60 °C	H_2O : EtOH (1 : 1)	80

[a] Isolated yield. [b] Bulk $CoFe_2O_4$.

the synthetic protocol. Various parameters were studied, such as temperature, catalyst loading and effect of solvents (Scheme 3). First the effect of temperature was investigated (Table 3, entries 3–7). The reactions were studied at different temperatures, refluxing and stirring conditions using $CoFe_2O_4$ (0.025 mmol) in H_2O : EtOH (1 : 1) mixture. Of various temperature conditions, reaction at 60 °C provided the best results. Next we moved our consideration towards the influence of the amount of catalyst on the synthesis of the desired compounds. The reactions were carried out with model reactants (**1d**) and (**2a**) in the presence of H_2O : EtOH (1 : 1) mixture at 60 °C, starting from 0.01 mmol to 0.1 mmol (Table 3 entries 5, 8–10). We observed that the reaction proceeded smoothly with 0.05 mmol of catalyst providing an excellent yield. Last, to evaluate the effect of solvent on the synthesis of desired products, various solvents were studied, including H_2O, EtOH, MeOH, CH_3CN, H_2O : EtOH (1 : 1), H_2O : EtOH (1 : 2), H_2O : EtOH (1 : 3) and H_2O : EtOH (1 : 4) using $CoFe_2O_4$ (0.05 mmol) nanoparticles at 60 °C (Table 3, entries 9, 12–18). The H_2O : EtOH (1 : 1) solvent system gave a good result (Table 3, entry 4). Hence the standardised reaction conditions were found to be 0.05 mmol of catalyst at 60 °C using H_2O : EtOH (1 : 1) mixture as solvent (Table 3, entry 9).



Scheme 3

To explore the versatility of the present protocol, different substituted aldehydes were taken to react with dimedone (**2b**)/1,3-cyclohexanedione (**2a**) using $CoFe_2O_4$ (0.05 mmol) at 60 °C to give the corresponding desired products in good to excellent yields (76–95%) in H_2O : EtOH (1 : 1) (Table 4, Scheme 4).

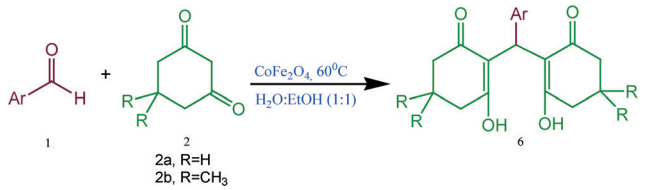
The reactions proceeded smoothly with aldehydes having electron donating groups like –OH, $–OCH_3$, –3,4-OCH_3, $–N(CH_3)_2$ and electron withdrawing groups like –Cl, $–NO_2$. The reactions were simple, clean and completion of the reaction was monitored by TLC. After that, the catalyst was separated out from the reaction mixture using an external magnet. The products were purified during the separation of catalyst from reaction product and characterized by FT-IR, ^{1}H-NMR and ^{13}C-NMR spectroscopy. The aldehydes such as heteroatomic aldehydes and unsaturated aldehydes were well reacted to afford the corresponding products. All the products have good chemoselectivity.

To present the merits and capability of our protocols, they were compared with other reported methods/catalysts. Pd nanoparticles[46] (0.04 mmol) and potassium phthalimide-*N*-oxyl (POPINO)[34] (0.5 mmol) afforded **4k** in 88% yield after 4.2 h in CH_3CN and 95% after 15 min in H_2O under refluxing conditions, respectively. Amberlyst A21[47] (30 mg $mmol^{-1}$) gave 84% yield in H_2O after 1 h at room temperature. But $CoFe_2O_4$ (0.025 mmol) nanoparticles afforded 96% yield of compound **4k** after 4 min in H_2O : EtOH (1 : 3) at 60 °C. On the other hand compound **6d** was obtained in 95% yield after 5 min in H_2O : EtOH (1 : 1) at 60 °C using $CoFe_2O_4$ (11.7 mg) nanoparticles, while Fe_3O_4@SiO_2–SO_3H[44] (10 mg), $CaCl_2$[43] (22 mg) and urea[48] (15 mg) afforded 95% yield after 90 min at room temperature in H_2O, 85% yield after 15 h at room

Table 4 Synthesis of 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) derivatives *via* condensation of various substituted aldehydes and dimedone or 1,3-cyclohexanedione in the presence of $CoFe_2O_4$ nanoparticles[a]

Entry	Ar	R	Product	Time (min.)	Yield (%)[b]	M.P. Obs.	M.P. Lit.
1	C_6H_5	CH_3	**6a**	3	91	188–190	192–194[43]
2	4-Cl C_6H_4	CH_3	**6b**	4	89	143–144	145–147[43]
3	2-Cl C_6H_4	CH_3	**6c**	2	86	200–202	202–204[43]
4	4-OCH_3 C_6H_4	CH_3	**6d**	5	95	142–145	146–148[43]
5	4-OH C_6H_4	CH_3	**6e**	8	94	194–196	201–203[43]
6	4-$(CH_3)_2N$ C_6H_4	CH_3	**6f**	5	89	190–192	194–195[44]
7	$C_6H_5CH{=}CH$	CH_3	**6g**	3	76	210–212	215–216[43]
8	Furyl	CH_3	**6h**	4	79	140–142	142–144[43]
9	3,4-(OCH_3) C_6H_4	CH_3	**6i**	9	92	178–181	187–189[43]
10	3-NO_2 C_6H_4	CH_3	**6j**	3	91	189–191	197–198[43]
11	4-OH-3,5-(OCH_3) C_6H_3	CH_3	**6k**	5	92	192–194	—
12	C_6H_5	H	**6l**	5	87	207–209	208–210[45]
13	4-Cl C_6H_4	H	**6m**	5	84	204–206	202–204[45]
14	2-Cl C_6H_4	H	**6n**	4	80	229–231	—
15	4-$OCH_3C_6H_4$	H	**6o**	7	85	193–195	195–197[45]
16	4-OH C_6H_4	H	**6p**	9	90	192–194	197–199[45]
17	3,4-(OCH_3) C_6H_4	H	**6r**	10	89	170–172	—
18	3-NO_2 C_6H_4	H	**6s**	4	92	205–207	207–209[45]

[a] Reaction conditions: aldehyde (1.25 mmol), dimedone (or 1,3-cyclohexanedione) (2.5 mmol), $CoFe_2O_4$ (0.05 mmol), H_2O : EtOH (1 : 1) 3 ml. [b] Isolated yield.



Scheme 4

temperature in CH_3CN and 93% yield after 100 min using ultrasound at 50 °C in H_2O, respectively. The results are tabulated in Table 5 and Table 6, from which it is clear that both the present protocols are superior to other reported protocols and the catalyst is an excellent catalyst as it is required in smaller quantity, it is cheap and efficient, no loading/coating/functionalisation is needed and moreover it is recyclable.

Reusability of $CoFe_2O_4$ nanoparticles

Finally recyclability and reusability of $CoFe_2O_4$ nanoparticles was investigated for the synthesis of desired products **4k** and **6d**. The investigation was carried out in following steps.

1) After completion of reaction, solvent EtOH (3 ml) was added to the reaction flask and flask was stirred to completely dissolve the product.

2) The catalyst was recovered by attaching the external magnet to the walls of reaction flask, providing the clear solution which was extracted by micro syringe to another flask. The whole process was repeated twice and combined layers of product were concentrated under vacuum to obtain the pure form of product. The recovered catalyst was dried in same reaction flask at 70 °C for 1 h and reused for up to seven cycles. The recycled $CoFe_2O_4$ nanoparticles can be reused without much loss of activity. The results are summarised in Fig. 4.

Further the morphology of reused catalyst was checked by TEM analysis (Fig. 5 (a) and (b)) which showed not much change in morphology and size but showed agglomeration, which can be the reason for slight decrease in yield of the products **4k** and **6d**.

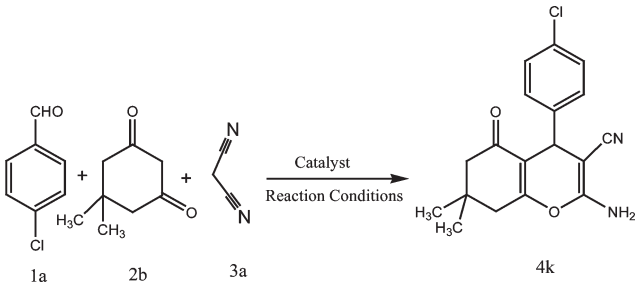
Experimental

All the solvents and reagents were obtained from local suppliers. Products were analyzed and characterized by using BRUKER AVANCE II 400 NMR spectrometer using $CDCl_3$ as a solvent and tetramethyl silane (TMS) as an internal standard for ^{1}H-NMR and ^{13}C-NMR measurements. FT-IR spectra were recorded on a Perkin Elmer spectrometer. Melting points were determined by Gallenkamp apparatus and were uncorrected. Thin layer chromatography (TLC) was carried out on silica gel 60 precoated on aluminium sheets with layer thickness 0.2 mm (SD-fine chemicals). The visualization of spots was performed in an I_2 chamber.

General procedure for the synthesis of 2-amino-4-(phenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile derivatives (4a–4v and 5a–5f)

The dimedone (2.5 mmol) (or 1,3-cyclohexanedione), an aromatic aldehyde (2.5 mmol), malononitrile (2.5 mmol) (or ethyl cyanoacetate) was dissolved in H_2O : EtOH (1 : 3) mixture (3 ml) followed by addition of $CoFe_2O_4$ (0.025 mmol, 0.0058 g). The reaction mixture was heated for the appropriate time (Table 2). The completion of reaction was identified by precipitation of product formed and along with TLC. The solid product formed was dissolved in EtOH. The catalyst was separated from the resulting clear solution of product by the use of an external magnet, washed with ethanol, dried and reused. The solution of product was concentrated under vacuum to

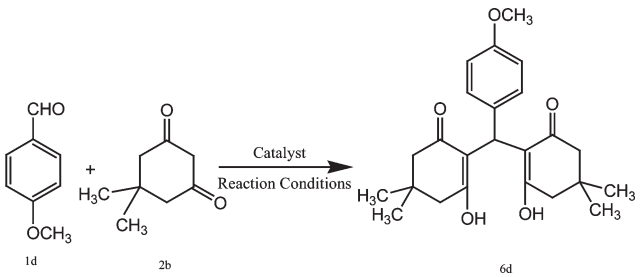
Table 5 Comparison of synthesis of 2-amino-4-(phenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile derivatives with reported protocols for compound **4k**



1a 2b 3a 4k

S. no.	Catalyst	Reaction conditions (temp./solvent/time)	Yield (%)	Catalyst loading
1	$Ni(NO_3)_2{\cdot}6H_2O$[49]	Refluxing/H_2O/20 min	88	0.1 mmol
2	*N*-Methylimidazole[50]	RT/H_2O/90 min	90	0.2 mmol
3	DMAP[40]	Refluxing/EtOH/15 min	94	0.2 mmol
4	MgO[51]	RT/Neat/25 min	86	0.5 mmol
5	POPINO[34]	Refluxing/H_2O/15 min	95	0.5 mmol
6	SB-DABCO[52]	RT/EtOH/25 min	95	0.06 mmol
7	HDMBAB[37]	80–90 °C/H_2O/7.5 h	90	0.12 mmol
8	Amberlyst A21[47]	RT/EtOH/1 h	84	30 mg $mmol^{-1}$
9	PPA-SiO_2[53]	Refluxing/H_2O/10 min	93	0.05 mmol
10	Pd nanoparticles[46]	Refluxing/CH_3CN/4.2 h	88	0.04 mmol
12	$CoFe_2O_4$ [present work]	60 °C/H_2O : EtOH (1 : 3)/4 min	96	0.025 mmol

Table 6 Comparative study of synthesis of 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) derivatives with reported protocols for compound **6d**



1d 2b 6d

S. no.	Catalyst	Reaction conditions (temp./solvent/time)	Yield (%)	Catalyst amount
1	Ni nanoparticles[54]	RT/E.G./10 min	90	100 mg
2	Fe_3O_4@SiO_2–SO_3H[44]	RT/H_2O/90 min	95	10 mg
3	$Yb(OTf)_3$-SiO_2[45]	Grinding/neat/2 min	83	300 mg
4	$CaCl_2$[43]	RT/$CHCl_3$/15 h	85	22 mg
5	Urea[48]	Ultrasound at 50 °C/H_2O/100 min	93	15 mg
6	$HClO_4{\cdot}SiO_2$[55]	100 °C/H_2O/48 min	74.2	16 mg
7	EDDA[56]	Refluxing/THF/4 h	94	54 mg
8	Catalyst free[57]	Stirring at RT/H_2O/4 h	93	—
9	Neutral alumina[58]	MW/neat/8 min	81	—
10	L-Histidine[59]	60 °C/ionic liquid/45 min	85	31 mg
14	$CoFe_2O_4$ [present work]	60 °C/H_2O : EtOH(1 : 1)/5 min	95	11.7 mg

give the product. The product obtained was pure without recrystallisation. The products were characterised based on their melting point and FT-IR, ^{1}H-NMR and ^{13}C-NMR spectra.

Spectral data. Table 2, entry 2: m.p 228–230 °C; ^{1}H-NMR (400 Hz, $CDCl_3$) δ (ppm):1.90–2.05 (m, 2H, CH_2), 2.25–2.36 (m, 2H, CH_2), 2.53–2.66 (m, 2H, CH_2), 4.22 (s, 1H, CH), 6.79 (s, 2H, NH_2), 7.14–7.28 (m, 5H, Ar–H).

Table 2, entry 19: m.p 170–172 °C; FT-IR(KBr) (ν_{max}, cm^{-1}): 3390, 1602, 1415, 1245; ^{1}H-NMR (400 Hz, $CDCl_3$) δ (ppm): 1.05 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 2.23 (d, 2H, J = 3.72 Hz, CH_2), 2.44 (s, 2H, CH_2), 3.83 (s, 3H, CH_3), 3.86 (s, 3H, CH_3), 4.35 (s, 1H, CH), 4.56 (s, 2H, NH_2), 6.73–6.80 (m, 3H, Ar–H); ^{13}C-NMR (400 Hz, $CDCl_3$) δ (ppm): 27.5, 29.0, 32.1, 35.0, 50.6, 55.8, 63.6, 111, 111.2, 114.1, 119.4, 135.9, 148.0, 148.8, 157.3, 161.3, 196.0.

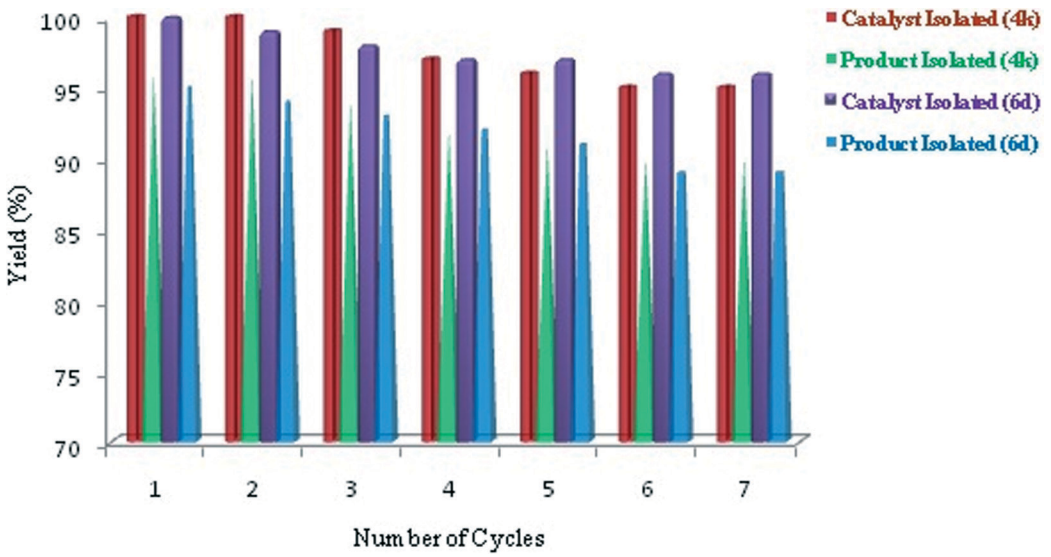


Fig. 4 Reusability of $CoFe_2O_4$ nanoparticles for synthesis of **4k** and **6d** up to seven cycles.

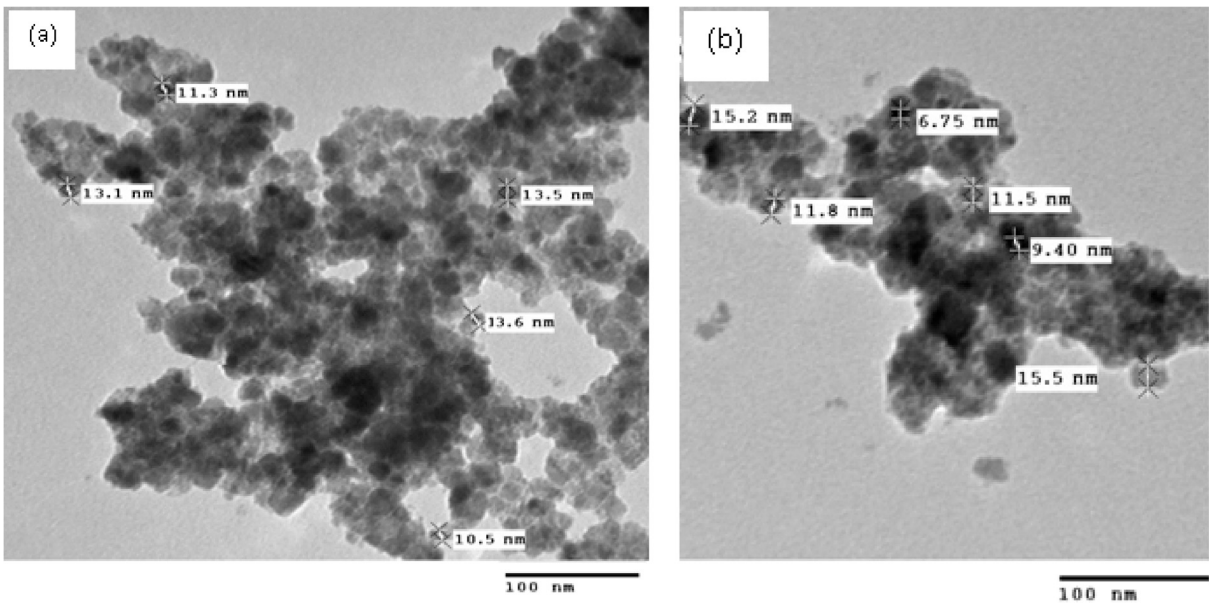


Fig. 5 TEM images of reused $CoFe_2O_4$ nanoparticles: (a) after catalytic reaction of **4k** (b) after catalytic reaction of **6d** after 5th run.

Table 2, entry 21: m.p. 190–192 °C; ^{1}H-NMR (400 Hz, $CDCl_3$) δ (ppm):1.06 (s, 3H, CH_3), 1.12 (s, 3H, CH_3), 2.24 (d, 2H, J = 2.88 Hz, CH_2), 2.45 (d, 2H, J = 3.48 Hz, CH_2), 3.85 (s, 6H, OCH_3), 4.32 (s, 1H, CH), 4.64 (s, 2H, NH_2), 5.47 (s, 1H, OH), 6.44 (s, 2H, Ar–H).

General procedure for the synthesis of 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) derivatives (6a–6s)

The dimedone (2.5 mmol) (or 1,3-cyclohexanedione) was dissolved in H_2O : EtOH (1 : 1) mixture (3 ml) followed by addition of an aromatic aldehyde (1.25 mmol). The catalyst $CoFe_2O_4$ (0.05 mmol, 0.0117 g) was added to the reaction mixture. The mixture was heated at 60 °C until the completion of the reaction, monitored by TLC. The completion of the reaction resulted in the separation of solid product. The product was dissolved in EtOH and catalyst was separated from reaction product using an external magnet, washed with ethanol, dried and reused. The organic layer was concentrated under vacuum to give the product, which was characterized by its melting point and FT-IR and ^{1}H-NMR spectra.

Spectral data. Table 4, entry 1: m.p 188–190 °C; ^{1}H-NMR (400 Hz, $CDCl_3$) δ (ppm): 1.09 (s, 6H, CH_3), 1.23 (s, 6H, CH_3), 2.28–2.48 (m, 8H, CH_2), 5.54 (s, 1H, CH), 7.09 (d, 2H, J = 7.6 Hz, Ar-H), 7.16 (t, 1H, J = 7.1 Hz, Ar–H), 7.26 (d, 2H, J = 7.4 Hz, Ar–H), 11.44 (s, 1H, OH), 11.90 (s, 1H, OH).

Table 4, entry 11: m.p 192–194 °C; ^{1}H-NMR (400 Hz, $CDCl_3$) δ (ppm): 1.11 (s, 6H, CH_3), 1.24 (s, 6H, CH_3), 2.35–2.47 (m, 8H, CH_2), 3.77 (s, 6H, CH_3), 5.43 (s, 1H, OH), 5.49 (s, 1H, CH), 6.34 (s, 2H, Ar–H), 11.5(s, 1H, OH), 12.0(s, 1H, OH).

Conclusion

In conclusion, we developed an efficient, simple, green method for the synthesis of 2-amino-4-(phenyl)-5,6,7,8-tetrahydro-7,7-dimethyl-5-oxo-4*H*-chromene-3-carbonitrile derivatives and 2,2′-arylmethylene bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one) derivatives using $CoFe_2O_4$ nanoparticles as a catalyst. The merits of the present work are as follows: 1) high efficiency, clean reaction, simplicity, short reaction time, versatility, high yields, chemoselectivity, non-chromatography technique. 2) Separation and recrystallisation of product occurs simultaneously, which reduces the use of organic solvents. 3) The catalyst is efficient, sustainable, stable and recyclable. 4) The catalyst is cheap and formed in single step, no coating/loading material or functionalisation is used. 5) The catalyst has small size, high surface area and magnetic properties. These features make the present work useful from industrial, economical and environmental points of view.

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References

1 (*a*) M. B. Gawande, P. S. Brancoa and R. S. Varma, *Chem. Soc. Rev.*, 2013, **42**, 3371–3393; (*b*) K. V. S. Ranganath and F. Glorius, *Catal. Sci. Technol.*, 2011, **1**, 13–22.

2 (*a*) R. J. White, R. Luque, V. L. Budarin, J. H. Clark and D. J. Macquarrie, *Chem. Soc. Rev.*, 2009, **38**, 481–494; (*b*) A. Schatz, T. R. Long, R. N. Grass, W. J. Stark, P. R. Hanson and O. Reiser, *Adv. Funct. Mater.*, 2010, **20**, 4323–4328.

3 (*a*) M. B. Gawande, A. K. Rathi, P. S. Branco, T. M. Potewar, A. Velhinho, I. D. Nogueira, A. Tolstogouzov, C. Amjad, A. Ghumman and O. M. N. D. Teodoro, *RSC Adv.*, 2013, **3**, 3611–3617; (*b*) M. B. Gawande, S. N. Shelke, A. Rathi, P. S. Branco and R. K. Pandey, *Appl. Organomet. Chem.*, 2012, **26**, 395–400; (*c*) M. B. Gawande, V. D. B. Bonifácio, R. S. Varma, I. D. Nogueira, N. Bundaleski, C. Amjad, A. Ghumman, O. M. N. D. Teodoro and P. S. Branco, *Green Chem.*, 2013, **15**, 1226–1231.

4 A. K. Gupta and M. Gupta, *Biomaterials*, 2005, **26**, 3995–4021.

5 (*a*) S. Mornet, S. Vasseur, F. Grasset, P. Veverka, G. Goglio, A. Demourgues, J. Portier, E. Pollert and E. Duguet, *Prog. Solid State Chem.*, 2006, **34**, 237–247; (*b*) Z. Li, L. Wei, M. Y. Gao and H. Lei, *Adv. Mater.*, 2005, **17**, 1001–1005.

6 T. Hyeon, *Chem. Commun.*, 2003, 927–934.

7 (*a*) M. B. Gawande, P. S. Branco, I. D. Nogueira, C. A. A. Ghumman, N. Bundaleski, A. Santos, O. M. N. D. Teodoro and R. Luqued, *Green Chem.*, 2013, **15**, 682–689; (*b*) M. B. Gawande, A. K. Rathi, I. D. Nogueira, R. S. Varma and P. S. Branco, *Green Chem.*, 2013, **15**, 1895–1899; (*c*) R. Cano, D. J. Ramón and M. Yus, *J. Org. Chem.*, 2010, **75**, 3458–3460; (*d*) V. Polshettiwar and R. S. Varma, *Tetrahedron*, 2010, **66**, 1091–1097; (*e*) M. B. Gawande, A. K. Rathi, I. D. Nogueira, C. A. A. Ghumman, N. Bundaleski, O. M. N. D. Teodoro and P. S. Branco, *ChemPlusChem*, 2012, **77**, 865–871; (*f*) J. Feng, L. Sua, Y. Maa, C. Ren, Q. Guo and X. Chen, *Chem. Eng. J.*, 2013, **221**, 16–24; (*g*) J. Mondal, T. Sen and A. Bhaumik, *Dalton Trans.*, 2012, **41**, 6173–6181; (*h*) F. Shi, M. K. Tse, M. M. Pohl, A. Bruckner, S. Zhang and M. Beller, *Angew. Chem., Int. Ed.*, 2007, **46**, 8866–8868; (*i*) S. R. Kale, S. S. Kahandal, M. B. Gawande and R. V. Jayaram, *RSC Adv.*, 2013, **3**, 8184–8192.

8 (*a*) A. H. Lu, E. L. Salabas and F. Schuth, *Angew. Chem., Int. Ed.*, 2007, **46**, 1222–1244; (*b*) S. Shylesh, V. Schunemann and W. R. Thiel, *Angew. Chem., Int. Ed.*, 2010, **49**, 3428–3459; (*c*) C. W. Lim and I. Su Lee, *Nano Today*, 2010, **5**, 412–434.

9 A. Rostami, B. Atashkar and H. Gholami, *Catal. Commun.*, 2013, **37**, 69–74.

10 (*a*) P. D. Stevens, G. Li, J. Fan, M. Yen and Y. Gao, *Chem. Commun.*, 2005, 4435–4437; (*b*) H. Yoon, S. Ko and J. Jang, *Chem. Commun.*, 2007, 1468–1470; (*c*) D. Guin, B. Baruwati and S. V. Manorama, *Org. Lett.*, 2007, **9**, 1419–1421; (*d*) V. Polshettiwar, B. Baruwati and R. S. Varma, *Green Chem.*, 2009, **11**, 127–131.

11 Z. Wang, P. Xiao, B. Shen and N. He, *Colloids Surf., A*, 2006, **276**, 116–121.

12 P. W. Sellwood, *Magnetochemistry*, Interscience, London 1956.

13 M. B. Gawande, V. D. B. Bonifacio, R. Luque, P. S. Branco and R. S. Varma, *Chem. Soc. Rev.*, 2013, **42**, 5522–5551.

14 D. Kumar, N. M. Kumar, G. Patel, S. Gupta and R. S. Varma, *Tetrahedron Lett.*, 2011, **52**, 1983–1986.

15 C. J. Li and L. Chen, *Chem. Soc. Rev.*, 2006, **35**, 68–82.

16 (*a*) L. Alvey, S. Prado, V. Huteau, B. Saint-Joanis, S. Michel, M. Koch, S. T. Cole, F. Tillequin and Y. L. Janin, *Bioorg. Med. Chem.*, 2008, **16**, 8264–8272; (*b*) T. Narender, Shweta and S. Gupta, *Bioorg. Med. Chem. Lett.*, 2004, **14**, 3913–3916; (*c*) V. Lakshmi, K. Pandey, A. Kapil, N. Singh, M. Samant and A. Dube, *Phytomedicine*, 2007, **14**, 36–42; (*d*) D. Kumar, V. B. Reddy, S. Sharad, U. Dube and S. Kapur, *Eur. J. Med. Chem.*, 2009, **44**, 3805–3809; (*e*) M. C. Yimdjo, A. G. Azebaze, A. E. Nkengfack, A. M. Meyer, B. Bodo and Z. T. Fomum, *Phytochemistry*, 2004, **65**, 2789–2795; (*f*) Z. Q. Xu, K. Pupek, W. J. Suling, L. Enache and M. T. Flavin, *Bioorg. Med. Chem.*, 2006, **14**, 4610–4626; (*g*) L. Alvey, S. Prado, B. Saint-Joanis, S. Michel, M. Koch, S. T. Cole, F. Tillequin and Y. L. Janin, *Eur. J. Med. Chem.*, 2009, **44**, 2497–2505.

17 G. P. Ellis, *In the Chemistry of Heterocyclic of Compounds. Chromenes, Harmones and Chromones*, John Wiley, New York, NY, 1977, chapter II, pp. 1113.

18 (*a*) E. A. A. Hafez, M. H. Elnagdi, A. G. A. Elagamey and F. M. A. A. El-Taweel, *Heterocycles*, 1987, **26**, 903–907; (*b*)

F. M. A. Galil, B. Y. Riad, S. M. Sherif and M. H. Elnagdi, *Chem. Lett.*, 1982, 1123–1126.
19 H. Zollinger, *Color Chemistry*, Verlag Helvetica Chimica Acta: Zurikh and Wiley-VCH, Weinheim, 3rd edn., 2003.
20 G. A. Reynolds and K. H. Drexhage, *Opt. Commun.*, 1975, **13**, 222–225.
21 E. R. Bissell, A. R. Mitchell and R. E. Smith, *J. Org. Chem.*, 1980, **45**, 2283–2287.
22 K. M. Khan, G. M. Maharvi, M. T. H. Khan, A. J. Shaikh, S. Perveen, S. Begum and M. I. Choudhary, *Bioorg. Med. Chem.*, 2006, **14**, 344–351.
23 G. M. Maharvi, S. Ali, N. Riaz, N. Afza, A. Malik, M. Ashraf, L. Iqbal and M. Lateef, *J. Enzyme Inhib. Med. Chem.*, 2008, **23**, 62–69.
24 O. Sirkecioglu, N. Talinli and A. Akar, *J. Chem. Res.*, 1995, 502–506.
25 (*a*) P. Shanmugasundaram, K. J. Prabahar and V. T. Ramakrishnan, *J. Heterocycl. Chem.*, 1993, **30**, 1003–1007; (*b*) N. Srividya, P. Ramamurthy, P. Shanmugasundaram and V. T. Ramakrishnan, *J. Org. Chem.*, 1996, **61**, 5083–5091.
26 (*a*) H. J. Timpe, S. Ulrich and S. Ali, *J. Photochem. Photobiol., A*, 1991, **61**, 77–89; (*b*) H. J. Timpe, S. Ulrich and J. P. Fouassier, *J. Photochem. Photobiol., A*, 1993, **73**, 139–150; (*c*) S. Ulrich, H. J. Timpe, J. P. Fouassier and F. M. Savary, *J. Photochem. Photobiol., A*, 1993, **74**, 165–170.
27 H. J. Timpe, S. Ulrich, C. Decker and J. P. Fouassier, *Macromolecules*, 1993, **26**, 4560–4566.
28 M. V. Kowjalgi and B. H. Iyer, *Curr. Sci.*, 1950, **19**, 210.
29 (*a*) J. K. Rajput and G. Kaur, *Tetrahedron Lett.*, 2012, **53**, 646–649; (*b*) J. K. Rajput and G. Kaur, *Chin. J. Catal.*, 2013, **34**, 1697–1704.
30 R. S. Turtelli, G. V. Duong, W. Nunes, R. Grossinger and M. Knobel, *J. Magn. Magn. Mater.*, 2008, **320**, e339–e342.
31 C. Cannas, A. Ardu, A. Musinu, D. Peddis and G. Piccaluga, *Chem. Mater.*, 2008, **20**, 6364–6371.
32 (*a*) J. Gascon, U. Aktay, M. D. Hernandez-Alonso, G. P. M. V. Klink and F. Kapteijn, *J. Catal.*, 2009, **261**, 75–87; (*b*) A. Corma, S. Iborra, I. Rodriguez and F. Sanchez, *J. Catal.*, 2002, **211**, 208–215.
33 I. Rodriguez, G. Sastre, A. Corma and S. Iborra, *J. Catal.*, 1999, **183**, 14–23.
34 M. G. Dekamin, M. Eslami and A. Maleki, *Tetrahedron*, 2013, **69**, 1074–1085.
35 (*a*) M. M. Heravi, K. Bakhtiari, V. Zadsirjan, F. F. Bamoharram and O. M. Heravi, *Bioorg. Med. Chem. Lett.*, 2007, **17**, 4262–4265; (*b*) B. S. Kumar, N. Shrinvasulu, R. H. Udupi, B. Rajitha, Y. T. Reddy, P. N. Reddy and P. S. Kumar, *J. Heterocycl. Chem.*, 2006, **43**, 1691–1693; (*c*) M. M. Heravi, B. Baghernejad and H. A. Oskooie, *J. Chin. Chem. Soc.*, 2008, **55**, 659–662.
36 (*a*) M. G. Dekamin and Z. Mokhtari, *Tetrahedron*, 2012, **68**, 922–930; (*b*) M. G. Dekamin, Z. Mokhtari and Z. Karimi, *Sci. Iran., Trans. C*, 2011, **18**, 1356–1364.
37 T. S. Jin, A. Q. Wang, F. Shi, L. S. Han, L. B. Liu and T. S. Li, *ARKIVOC*, 2006, **XIV**, 78–86.
38 J. Zheng and Y. Li, *Mendeleev Commun.*, 2011, **21**, 280–281.
39 G. Sabitha, K. Arundhathi, K. Sudhakar, B. S. Sastry and J. S. Yadav, *Synth. Commun.*, 2009, **39**, 433–442.
40 A. T. Khan, M. Lal, S. Ali and M. M. Khan, *Tetrahedron Lett.*, 2011, **52**, 5327–5332.
41 K. Meguro and K. Esumi, *J. Adhes. Sci. Technol.*, 1990, **4**, 393–410.
42 D. Cordischi and V. Indovina, *J. Chem. Soc., Faraday Trans. 1*, 1976, **72**, 2341–2347.
43 A. Ilangovan, S. Muralidharan, P. Sakthivel, S. Malayappasamy, S. Karuppusamy and M. P. Kaushik, *Tetrahedron Lett.*, 2013, **54**, 491–494.
44 F. Nemati, M. M. Heravi and R. S. Rad, *Chin. J. Catal.*, 2012, **33**, 1825–1831.
45 V. K. Rao, M. K. Muthyala and A. Kumar, *Indian J. Chem.*, 2011, **50B**, 1128–1135.
46 M. Saha and A. K. Pal, *Advances in Nanoparticles*, 2012, **1**, 61–70.
47 M. Bihani, P. P. Bora, G. Bez and H. Askari, *C. R. Chim.*, 2013, **16**, 419–426.
48 J. T. Li, Y. W. Li, Y. L. Song and G. F. Chen, *Ultrason. Sonochem.*, 2012, **19**, 1–4.
49 B. Boumoud, A. A. Yahiaoui, T. Boumoud and A. Debache, *J. Chem. Pharm. Res.*, 2012, **4**, 795–799.
50 X. Z. Lian, Y. Huang, Y. Q. Li and W. J. Zheng, *Monatsh. Chem.*, 2008, **139**, 129–131.
51 D. Kumar, V. B. Reddy, S. Sharad, U. Dube and S. Kapur, *Eur. J. Med. Chem.*, 2009, **44**, 3805–3809.
52 A. Hasaninejad, M. Shekouhy, N. Golzar, A. Zare and M. M. Doroodmand, *Appl. Catal., A*, 2011, **402**, 11–22.
53 A. Davoodnia, S. Allameh, S. Fazli and N. T. Hoseini, *Chem. Pap.*, 2011, **65**, 714–720.
54 J. M. Khurana and K. Vij, *J. Chem. Sci.*, 2012, **124**, 907–912.
55 S. Kantevari, R. Bantu and L. Nagarapu, *J. Mol. Catal. A: Chem.*, 2007, **269**, 53–57.
56 D. H. Jung, Y. R. Lee, S. H. Kim and W. S. Lyoo, *Bull. Korean Chem. Soc.*, 2009, **30**, 1989–1995.
57 J. J. Yu, L. M. Wang, J. Q. Liu, F. L. Guo, Y. Liu and N. Jiao, *Green Chem.*, 2010, **12**, 216–219.
58 M. Saha and A. K. Pal, *Iran. J. Org. Chem.*, 2010, **2**, 423–429.
59 Y. Zhang and Z. Shang, *Chin. J. Chem.*, 2010, **28**, 1184–1188.