

## Recent advances in organo-nanocatalysis in the field of green organic synthesis

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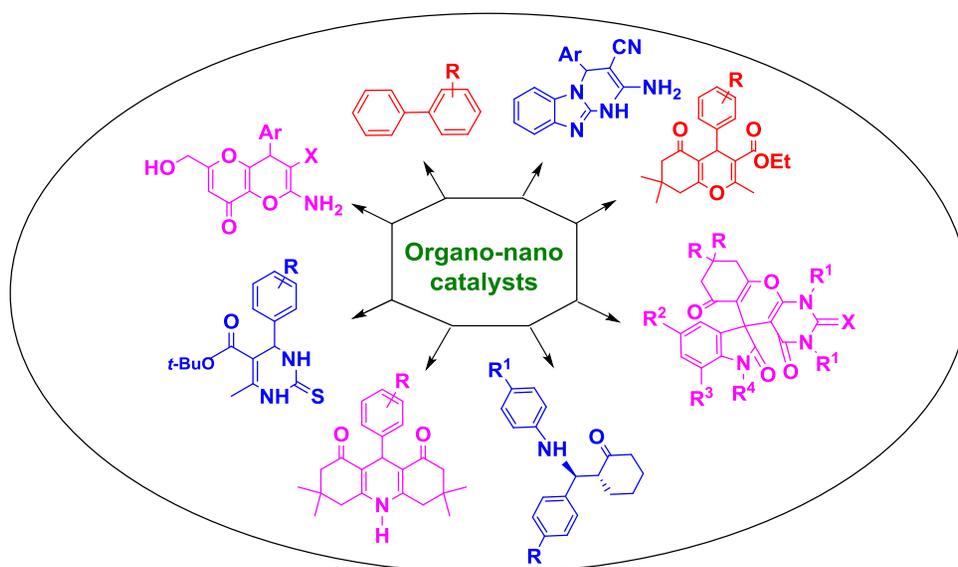
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### Abstract

This article presents a summary of the uses of the various organo-nanocatalysts in organic synthesis that have been reported in the literature. A key feature of the development of sustainable methodology in organic synthesis is the easy recovery of a valuable catalyst and its reuse in successive runs without appreciable loss in its efficiency. Progress in the synthetic approaches to magnetic organo-nanocatalysts and their applications in organic synthesis are covered.



**Keywords:** Organo-nanocatalysts, magnetic nanoparticles, recyclability, green chemistry, organic compounds

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## 1. Introduction

### 1.1 Historical note

Over the last 15 years, reactions carried out with organic molecules as catalysts (organo-catalysis) have been an active field of research in chemistry.<sup>1</sup> Around the year 2000, the term 'Organo-catalysis' first emerged from the seminal work of MacMillan.<sup>2</sup> However, Pracejus had already made the earliest report of an enantioselective reaction solely catalyzed by organic molecules in 1960, with the catalytic asymmetric reactions of ketenes using chinchona alkaloids.<sup>3</sup>

### 1.2 Homogeneous and heterogeneous catalysis

Homogeneous and heterogeneous catalysts are the two main classes of conventional catalysts which synthetic chemists have been using for over a century.<sup>4,5</sup>

Organo-catalysts are usually found to be homogeneous in nature, but when modified as nano-catalysts they are found to possess heterogeneous catalytic behaviour.<sup>6,7</sup> Individual applications of the mentioned catalysts are limited to certain extent, whereas the combination of both homogeneous and heterogeneous catalysts gives rise to a "super catalyst" having a wider scope of catalytic applications in the field of synthesis.<sup>8,9,10,11,12</sup>

Nano-catalysis, an emerging catalytic technique of the 21<sup>st</sup> century, has brought about a revolution in the field of catalysis as well as in "green" organic synthesis. They are attractive alternatives to conventional catalysts and can play a crucial role in organic synthesis as semi-heterogeneous catalysts because they possess a large surface to volume ratio, high selectivity, high catalytic activity, and often greater stability.<sup>13,14</sup>

They can be isolated easily from a reaction mixture by magnetic separation, filtration, or centrifugation. Although nano-catalysts possess several merits over conventional catalysts, their isolation and recovery from the reaction mixture is not always so easy. Due to the nanoscopic size of the catalyst, conventional filtration may not be suitable, which hampers the economic and sustainability aspects of nano-catalytic protocols. In order to overcome this issue, the use of magnetic nanoparticles or magnetic nano-supports, being insoluble in reaction mixture and paramagnetic in nature, has emerged to be one of the best solutions.<sup>15,16</sup> Thus, magnetic nanocatalysts offer a great advantage over other nanocatalysts as they offer easy isolation from the reaction vessel using an external magnetic stir bar, and thus the use of centrifugation and filtration methods can be avoided.<sup>16,17,18,19</sup> These nanoparticles can be prepared from metal salts of cobalt, nickel or iron. Although metal nanoparticles have been introduced as green catalysts, the catalytic applications of simple metal nanoparticles are limited to certain organic reactions only.<sup>20,21,22,23</sup>

Organo-catalysts like L-proline, glutathione, vitamin B<sub>1</sub>, meglumine *etc.* are non-toxic organic moieties which have been exploited in the regioselective and stereoselective synthesis of various biologically important organic compounds.<sup>24,25,26</sup>

They represent eco-friendly alternatives to toxic acid/basic catalysts. The activity and selectivity of homogenous catalysts are superior to those of heterogeneous catalysts due to the improved interaction between the reactants and the catalyst surface. However, owing to the difficulty of separation of homogenous catalysts from the reaction mixture, their industrial applicability (particularly in drug and pharmaceutical industries) is restricted due to the issue of metal contamination in the case of metal catalyzed synthetic protocols.

### 1.3 Green chemistry

By using catalytic reagents, one can reduce the temperature of a chemical transformation, reduce the amount

of reagent-based waste, and enhance the selectivity of a reaction that potentially avoids undesired side products, leading to a greener technology.<sup>27,28,29,30</sup> In 1998, Anastas *et al.* suggested a set of twelve principles on which are based the main philosophy of green chemistry, which is to reduce or eliminate chemicals and chemical processes that have harmful environmental impacts.<sup>31</sup> Designing and developing ideal catalysts is a very important aspect of green chemistry.

While catalysis is one of the key principles of “green chemistry”, researchers face a major challenge in the design and use of environmentally benign catalysts.<sup>32,33</sup> This requires that such a catalyst must have appreciable recyclability, efficient recovery, low cost in preparation, selectivity, good activity, and adequate chemical stability.

#### 1.4 Importance of organo-nanocatalysis

During the last few years, there is no doubt that organo-nanocatalysis has emerged as one of the more interesting and powerful tools in the field of catalysis in synthesizing organic compounds.<sup>8,34,35</sup> Greener fabrication of organo-nanocatalysts by the immobilization of the organo-catalyst onto magnetic solid supports and their eco-friendly applications in catalysis afford sustainable methods in synthesis in terms of cost-effectiveness and efficiency.<sup>36,37</sup> The advantages achieved by coating organo-catalysts onto the surface of a magnetic nanoscopic core are (i) extension of the catalytic utility of metal nanoparticles in organic synthesis, (ii) exploitation of the catalytic activity of organo-catalyst in heterogeneous catalysis, (iii) enabling the recycling of the organo-catalyst, (iv) reducing environmental hazards and (v) increasing the efficiency of the catalytic process.<sup>38,39</sup> Thus, heterogenization of the active molecules such as amino acids or organic moieties with a magnetic nano-solid support can be an eco-friendly and efficient strategy to achieve the easy recovery and recyclability of the catalyst.<sup>40,41,42</sup> Thus, the use of organo-nanocatalysts brings added benefits such as high TON/TOF, magnetically aided catalyst recyclability and reusability, and maximum utilization of the organo-catalyst by dispersing it over an increased surface area, thus providing increased efficiency of the overall catalytic process.<sup>43,44,45</sup>

#### 1.5 Scope

Over recent years, organo-nanocatalysis has been playing a prominent role in the field of green organic synthesis, as is evident from the dramatic increase in research publications in the various spheres of organic synthesis.<sup>46,47,48</sup> These catalysts are prepared from readily available starting materials and thus make organic synthetic protocols both environmentally and economically viable. Owing to the various advantages of using organo-nanocatalysts in organic synthesis, this field of catalysis requires more exploration of the utility of the catalysts. The catalytic efficiency of organo-nanocatalysts has been demonstrated in various realms of organic synthesis, particularly in reactions such as MCRs, cycloaddition reactions, sigmatropic rearrangements, C-C coupling reactions, asymmetric synthesis, photocatalytic reactions, oxidations, reductions, hydrogenation, and many others.<sup>49,51,50,51,52</sup>

#### 1.6 Highlights of the Review

A large number of magnetically recyclable supports such as magnetite ( $\text{Fe}_3\text{O}_4$ ), maghemite ( $\gamma\text{-Fe}_2\text{O}_3$ ), and iron metal (Fe) are employed in the synthesis of organo-nanocatalysts.<sup>53,54,55,56,57</sup> In this review, the various organo-catalysts immobilized on magnetically separable supports and their applications for a variety of catalytic processes, particularly in organic synthesis, are presented, including their preparative methods. The characterizations of the synthesized organo-nanocatalysts are not discussed in this review and no results of any spectroscopic or analytical techniques are presented, as they are adequately described in the cited papers

and are outside the scope of the present article. In this article, the preparation and silylation of ferrite nanoparticles are depicted diagrammatically but have not been explained in detail to avoid repetition of material in most of the methods of preparation of the nano-catalysts.<sup>58,59</sup>

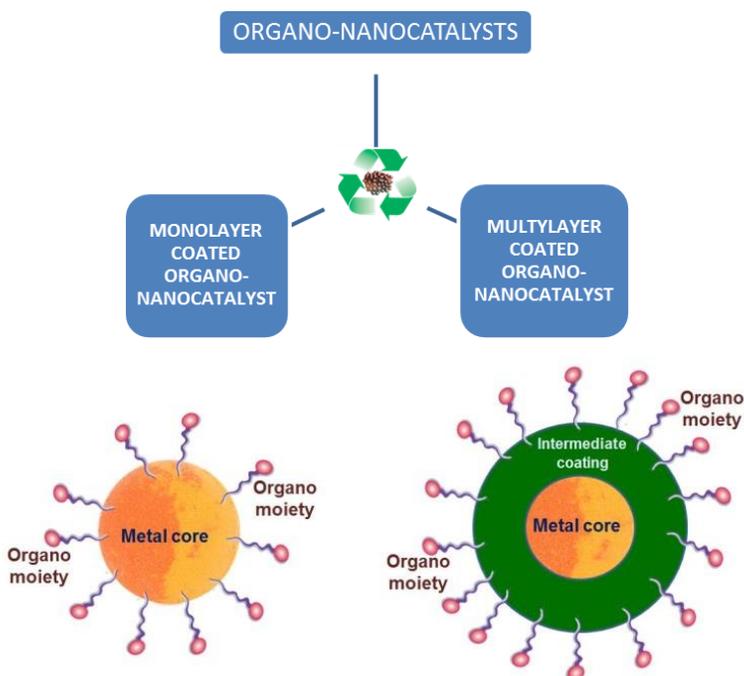
## 2. Ferrite as the Magnetic Core

There is always a need to develop efficient synthetic protocols/methodologies in order to maintain operational simplicity, to protect the environment, to avoid tedious product purification procedures, to separate the catalyst with ease, to make it recyclable and reusable, and to use it in minimal quantities. With these aims in view, iron-based magnetic nanocatalysts have been developed which address these requirements.<sup>60,61</sup>

Ferrite (iron oxide) nanoparticles are ferromagnetic in nature and hence can easily be separated simply by use of a clean magnetic stir bar.<sup>62</sup> Also, ferrite nanoparticles can easily be prepared from cheaply available starting materials like ferrous and ferric salts. Based on the nature of the magnetic core, these magnetic nanocatalysts can be further classified into two groups: one containing  $\text{Fe}_3\text{O}_4$  and the other bearing  $\text{Fe}_2\text{O}_3$ ; both have found applications in various coupling and oxidative reactions.<sup>63,64,65</sup> Encapsulation of the surfaces of the magnetic nanoparticles with an organic moiety provides a quasi-homogeneous phase in reaction media, thus acting as a bridge between homogenous and heterogeneous catalysis and mimicking the desirable merits of both of the catalytic systems.<sup>66</sup> This heterogenization of the catalyst as a magnetic nanocatalytic system allows them to be retrieved easily and facilitates their efficient reuse.

## 3. Types of Organo-nanocatalysts

Organo-catalysts can be broadly classified into two groups, namely (i) monolayer coated organo-nanocatalyst, and (ii) multilayer coated organo-nanocatalysts. These two classes of nanocatalysts differ only in the presence or absence of the intermediate coatings.



**Figure 1.** Two classes of organo-nanocatalyst.

## 4. Need for Intermediate Coating

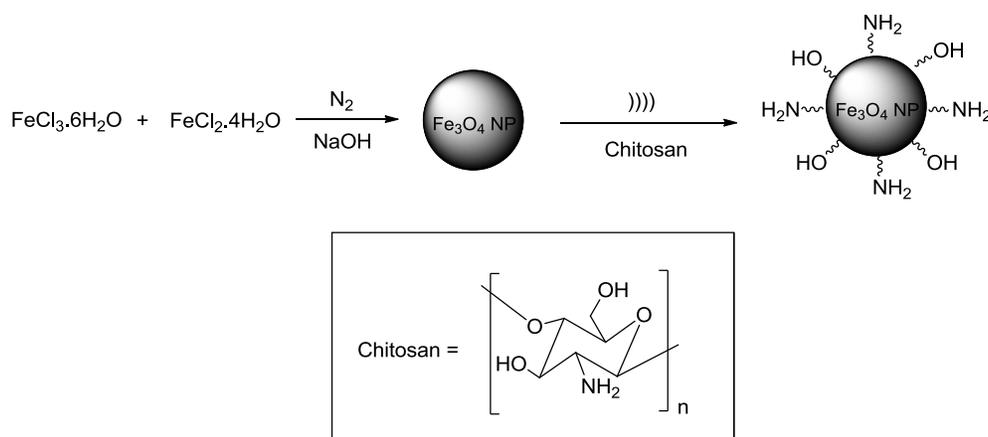
In monolayer organo-nanocatalysts, the organic moiety has a strong bonding affinity with the metal nano-surface, and hence there is no requirement for an intermediate coating.<sup>67,68,69</sup> In multilayer organo-nanocatalysts, the need for an intermediate coating arises due to weak bonding interaction between the organic moiety and the metal nanoparticles.<sup>70,47,8</sup> In order to ensure that the organic moiety is firmly attached to the surface of the nanoparticle, it is recommended to coat the nano-magnetic particles with an intermediate moiety which has strong bonding affinity with both the nano core and the organic moiety. In many such cases, silica ( $\text{SiO}_2$ ) is used as the intermediate.  $\text{SiO}_2$  shows strong bonding interaction with ferrite nanoparticles as well as with organocatalytic moieties bearing groups like  $-\text{OH}$ ,  $-\text{NH}_2$ , etc. Besides  $\text{SiO}_2$ , many other intermediate coatings have been reported, including L-proline, chitosan, glucose, etc.<sup>71,72,73</sup>

## 5. Synthesis and Applications of Organo-nanocatalysts

### 5.1 Synthesis and applications of monolayer coated organo-nanocatalysts

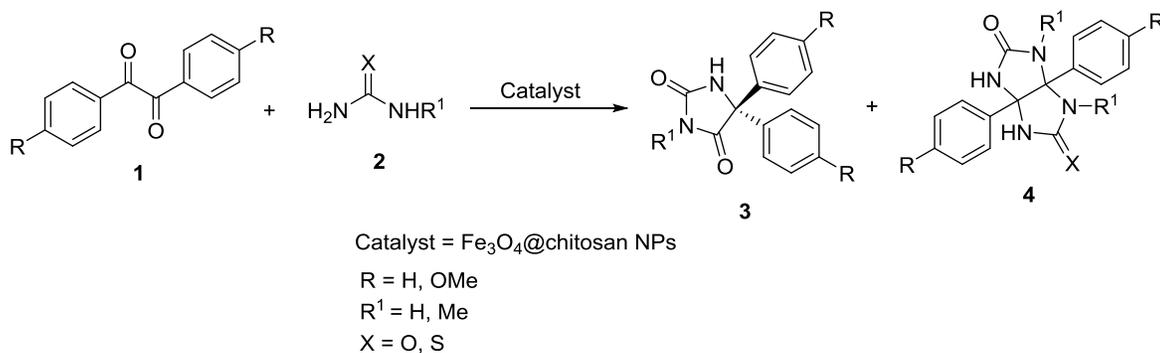
In this class of organo-nanocatalysts, the organo/enzyme moiety can be directly encapsulated onto the surface of the magnetic nano-core by covalent bonding. Recent research publications have reported some monolayer coated organo-nanocatalysts, such as  $\text{Fe}_3\text{O}_4$ @chitosan NPs,  $\text{Fe}_3\text{O}_4$ @L-proline NPs,  $\text{Fe}_3\text{O}_4$ @glutathione NPs,  $\text{Fe}_3\text{O}_4$ @L-cysteine NPs,  $\text{Fe}_3\text{O}_4$ @guanidine NPs,  $\text{Fe}_3\text{O}_4$ @cellulose NPs, and others. Their mode of preparation and applications in the field of organic synthesis are discussed below.

**5.1.1 Synthesis and applications of  $\text{Fe}_3\text{O}_4$ @chitosan NPs. Synthesis.**  $\text{Fe}_3\text{O}_4$ @chitosan NPs were prepared by many research groups as follows.<sup>74-84</sup> First,  $\text{Fe}_3\text{O}_4$  NPs were prepared using a chemical co-precipitation method. In a 250 mL round bottom flask, 5.2 g of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 2.0 g of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  were dissolved in 20 mL deionized water, to which 250 mL of 1.5 M NaOH was added dropwise with vigorous stirring. After the formation of black magnetic nanoparticles, the reaction mixture was cooled and the  $\text{Fe}_3\text{O}_4$  nanoparticles were isolated using a clean magnetic bar, and were washed several times with distilled water. Then 0.5 g of the  $\text{Fe}_3\text{O}_4$  nanoparticles were dispersed in 50 mL of distilled water under ultrasonic irradiation. 0.25 g of chitosan was added in 70 mL of 2.0 weight % aqueous acetic acid, and the resulting solution was slowly added to the mixture containing dispersed  $\text{Fe}_3\text{O}_4$  nanoparticles under vigorous stirring at 50 °C for 1 hour (Scheme 1). The  $\text{Fe}_3\text{O}_4$ @chitosan NPs were then isolated and utilized as catalysts.



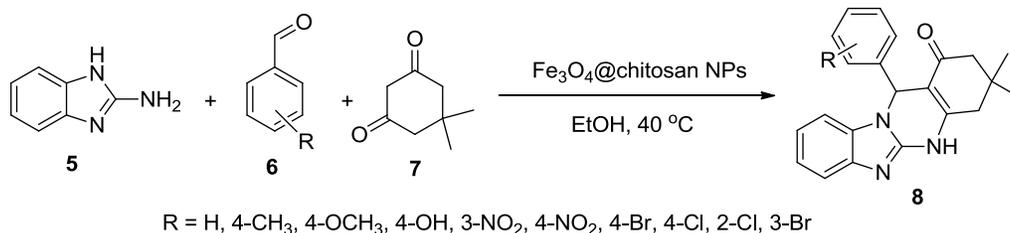
**Scheme 1.** Synthesis of  $\text{Fe}_3\text{O}_4$ @chitosan NPs.

**Applications.** Javed *et al.* reported the synthesis of 5,5-diphenylhydantoins (**3**; X = O), 5,5-diphenyl-2-thiohydantoins (**3**; X = S), and diarylglycolurils (**4**) from **1** and **2** using Fe<sub>3</sub>O<sub>4</sub>@chitosan NPs as a catalyst (Scheme 2). Since its development, this catalyst has been exploited as an efficient and recyclable organo-nanocatalyst in the synthesis of a number of heterocyclic compounds.<sup>74-84</sup>



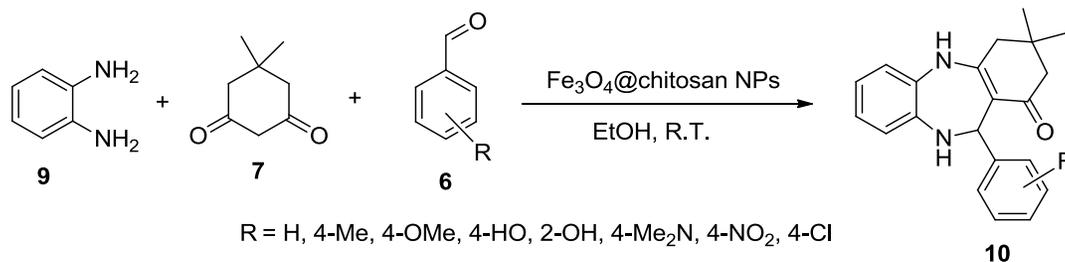
**Scheme 2.** Synthesis of 5,5-diarylhydantoins (**3**), diarylglycolurils (**4**) and their thio analogues.

In another paper, Maleki *et al.* reported the synthesis of benzimidazoloquinazolinone derivatives **8** from 2-aminobenzimidazole (**5**), aromatic aldehyde (**6**) and dimedone (**7**) at 40 °C in the presence of Fe<sub>3</sub>O<sub>4</sub>@chitosan NPs as a green and reusable catalyst (Scheme 3).<sup>75</sup>



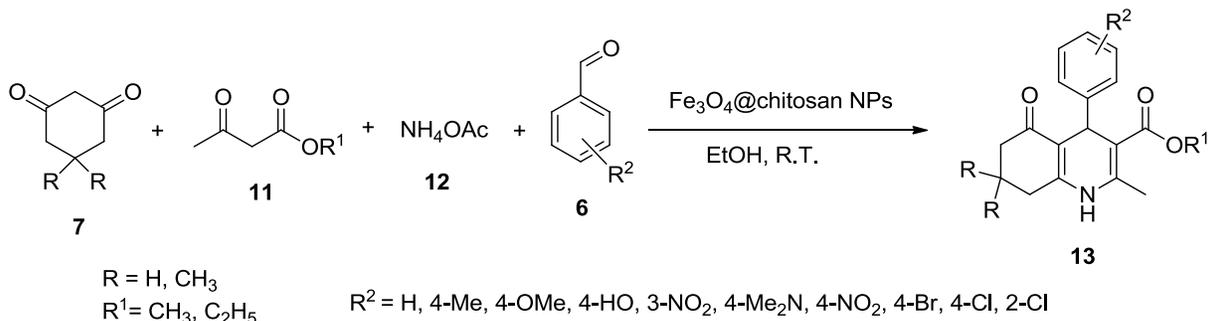
**Scheme 3.** Synthesis of benzimidazolo[2,3-*b*]quinazolinones.

Maleki *et al.* also reported the synthesis of benzodiazepine derivatives (**10**) starting from *o*-phenylenediamine (**9**), dimedone (**7**), and aromatic aldehydes (**6**) via a one-pot, three-component reaction at room temperature, exploiting the catalytic role of Fe<sub>3</sub>O<sub>4</sub>@chitosan NPs (Scheme 4).<sup>76</sup>

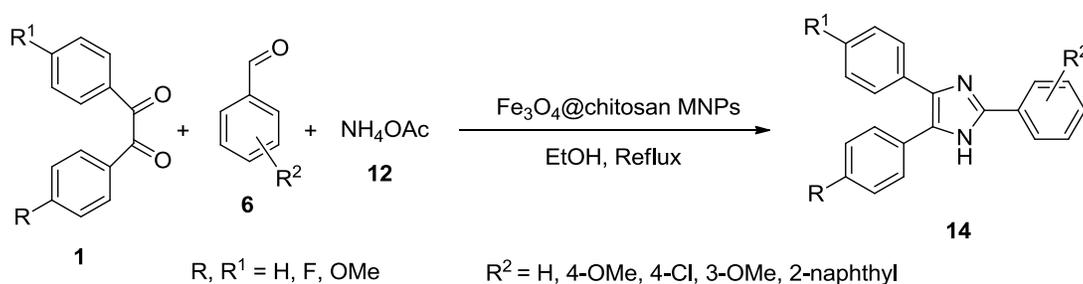


**Scheme 4.** Synthesis of benzodiazepines.

In 2015, Maleki *et al.* synthesized 1,4-dihydropyridines (**13**) from various aromatic aldehyde (**6**), dimedone or 1,3-cyclohexanedione (**7**), ethyl acetoacetate/methyl acetoacetate (**11**) and ammonium acetate using  $\text{Fe}_3\text{O}_4$ @chitosan NPs as a catalyst at room temperature under mild reaction conditions (Scheme 5).<sup>77</sup> Zarnegar and Safari used the same catalyst system to prepare 2,4,5-trisubstituted imidazoles (**14**) via a one-pot condensation of benzil (**1**), aryl aldehydes (**6**) and ammonium acetate (**12**) in EtOH (Scheme 6).<sup>78</sup>

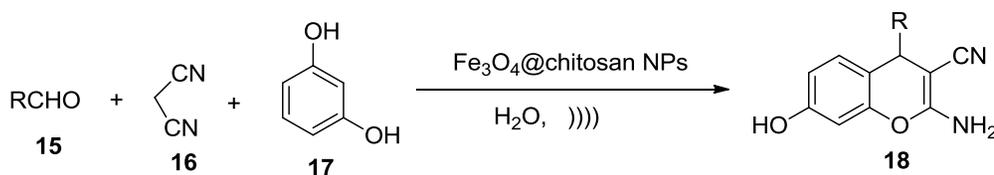


**Scheme 5.** Synthesis of 1,4-dihydropyridine derivatives.



**Scheme 6.** Synthesis of 2,4,5-trisubstituted imidazoles.

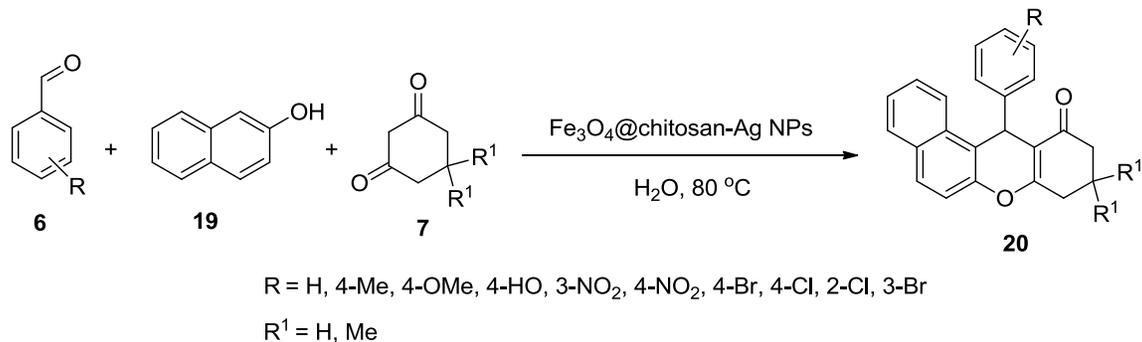
Safari *et al.* developed a one-pot and efficient synthetic protocol of 2-amino-4*H*-chromenes (**18**) by condensation of aldehydes (**15**) with malononitrile (**16**) and resorcinol (**17**) under ultrasonication using  $\text{Fe}_3\text{O}_4$ @chitosan NPs as an ecofriendly catalyst (Scheme 7).<sup>78</sup>



R = C<sub>6</sub>H<sub>5</sub>, 4-MeC<sub>6</sub>H<sub>4</sub>, 4-OMeC<sub>6</sub>H<sub>4</sub>, 3-ClC<sub>6</sub>H<sub>4</sub>, 3-HOC<sub>6</sub>H<sub>4</sub>, 2-FC<sub>6</sub>H<sub>4</sub>, 2-MeOC<sub>6</sub>H<sub>4</sub>, 2,4-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2,6-Cl<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 3,5-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>, 2-naphthyl, 2-furyl, 2-thienyl, 5-mefuryl, ethyl, propyl, heptyl, OHCC<sub>6</sub>H<sub>4</sub>

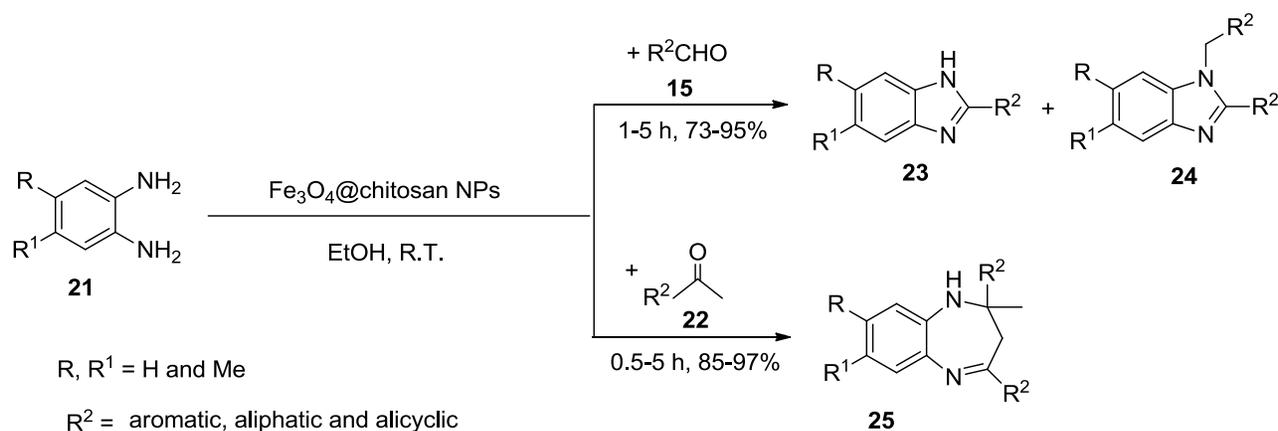
**Scheme 7.** Synthesis of 2-amino-4*H*-chromenes.

Mohammadi *et al.* synthesized 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-one derivatives (**20**) via a one-pot three-component condensation aromatic aldehydes (**6**), β-naphthol (**19**) and 1,3-diketones (**7**) in presence of  $\text{Fe}_3\text{O}_4$ @chitosan-Ag NPs as a catalyst (Scheme 8).<sup>79</sup>



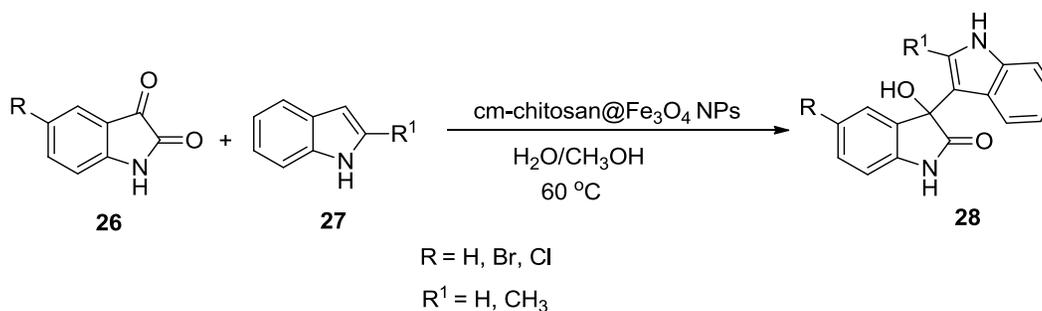
**Scheme 8.** Synthesis of 12-aryl-8,9,10,12-tetrahydrobenzo[*a*]xanthene-11-ones.

Maleki *et al.* prepared 1,2-disubstituted benzimidazole (**23**, **24**) and 1,5-benzodiazepine (**25**) derivatives using 1,2-diamines (**21**) and aldehydes (**15**) or ketones (**22**) in the presence of a catalytic amount of  $\text{Fe}_3\text{O}_4$ @chitosan NPs as a biodegradable nanocomposite (Scheme 9).<sup>80</sup>



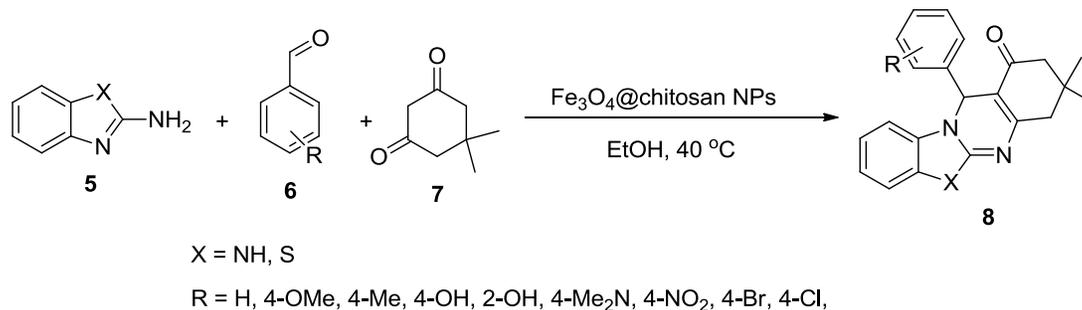
**Scheme 9.** Synthesis of benzimidazole and benzodiazepine derivatives.

Rad-Moghadam *et al.* developed a protocol for catalysis of Friedel–Crafts reaction between isatins (**26**) and indoles (**27**) using carboxymethyl(cm)-chitosan@ $\text{Fe}_3\text{O}_4$  NPs, giving selective synthesis of 3-hydroxy-3-indolylindolin-2-ones (**28**) (Scheme 10).<sup>81</sup>



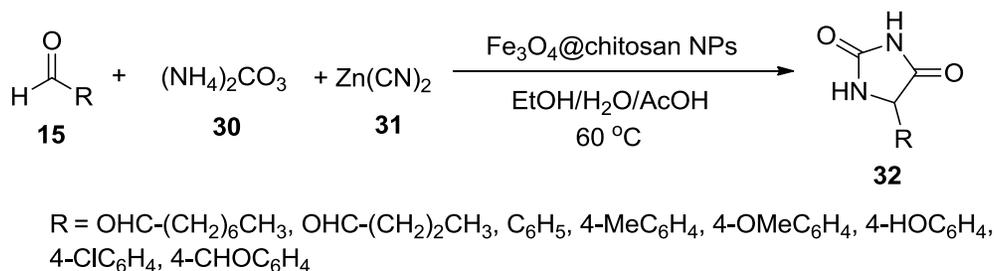
**Scheme 10.** Synthesis of 3-(indol-3-yl)-3-hydroxyindolin-2-ones.

Maleki *et al.* synthesized benzimidazolo[2,3-*b*]quinazolinone derivatives (**8**) via a one-pot multicomponent reaction of 2-aminobenzimidazoles (**5**), aromatic aldehydes (**6**) and dimedone (**7**) in ethanol at 40 °C promoted by a chitosan-based composite magnetic nanocatalyst (Scheme 11).<sup>82</sup>



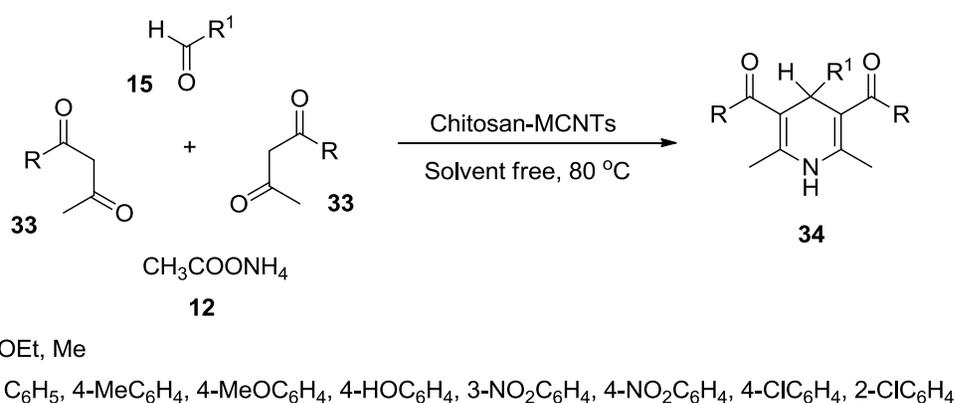
**Scheme 11.** Synthesis of benzimidazolo[2,3-*b*]quinazolinones.

Safari *et al.* recently developed a synthetic protocol for 5-substituted hydantoins (**33**) from aldehydes (**15**), ammonium carbonate (**30**) and zinc cyanide (**31**) in the presence of Fe<sub>3</sub>O<sub>4</sub>@chitosan MNPs (Scheme 12).<sup>83</sup>



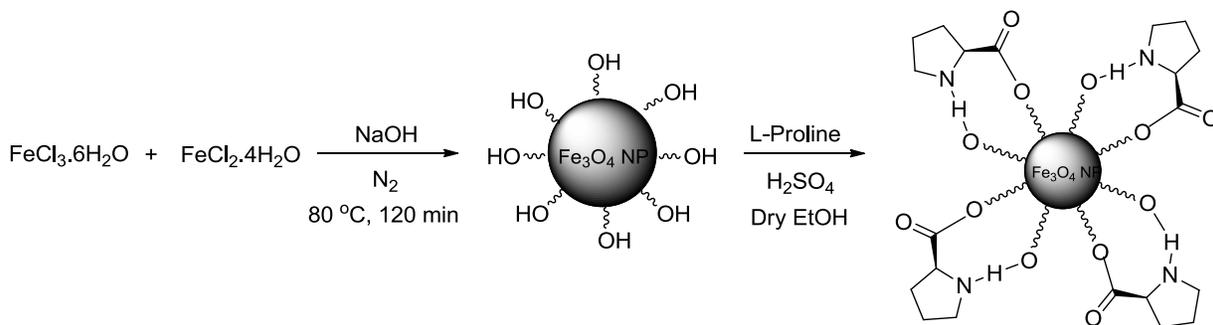
**Scheme 12.** Synthesis of 5-substituted hydantoins.

Zarnegar *et al.* developed a chitosan-MCNTs catalyst with carbon nanotubes, and used it in the synthesis of 1,4-dihydropyridines (**34**) from aromatic aldehydes (**15**), 1,3-dicarbonyls (**33**) and ammonium acetate (**25**) (Scheme 13).<sup>84</sup>



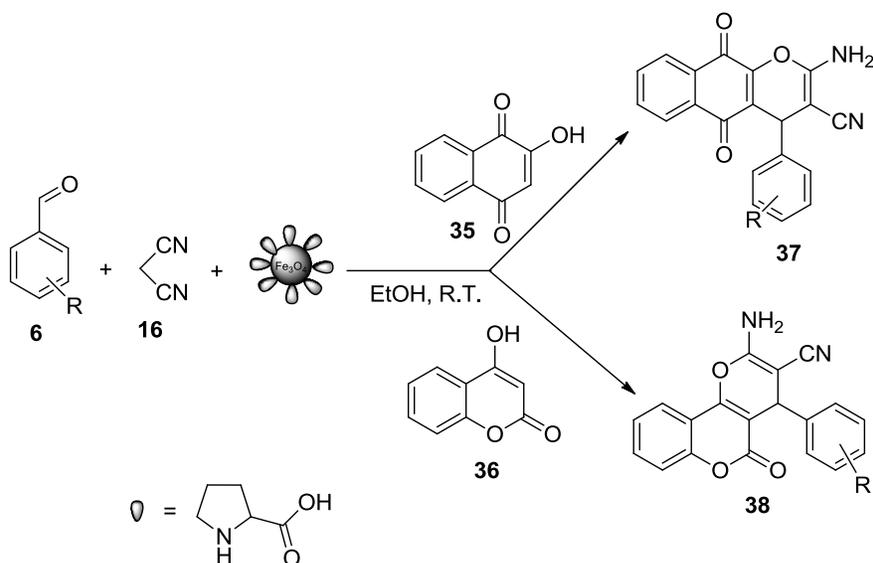
**Scheme 13.** Synthesis of 1,4-dihydropyridines.

**5.1.2 Synthesis and applications of Fe<sub>3</sub>O<sub>4</sub>@L-proline NPs. Synthesis.** L-Proline on magnetite nanoparticles was developed by Azizi *et al.* as an organo-nanocatalyst.<sup>21</sup> To prepare this, 5 mmol FeCl<sub>3</sub>·6H<sub>2</sub>O and 2.5 mmol FeCl<sub>2</sub>·4H<sub>2</sub>O salts were dissolved in 100 mL deionized water. Under vigorous stirring, 2 mmol of L-proline and 30 mL aqueous NH<sub>4</sub>OH (25%, w/w) were added until pH 11 and a black suspension was formed. This was refluxed for 6 hours with continued stirring. The Fe<sub>3</sub>O<sub>4</sub>@L-proline NPs thus formed were separated from the cooled aqueous solution by magnetic decantation, washed with methanol, water and ethanol several times and dried in an oven overnight (Scheme 14).



**Scheme 14.** Preparation of Fe<sub>3</sub>O<sub>4</sub>@L-proline NPs.

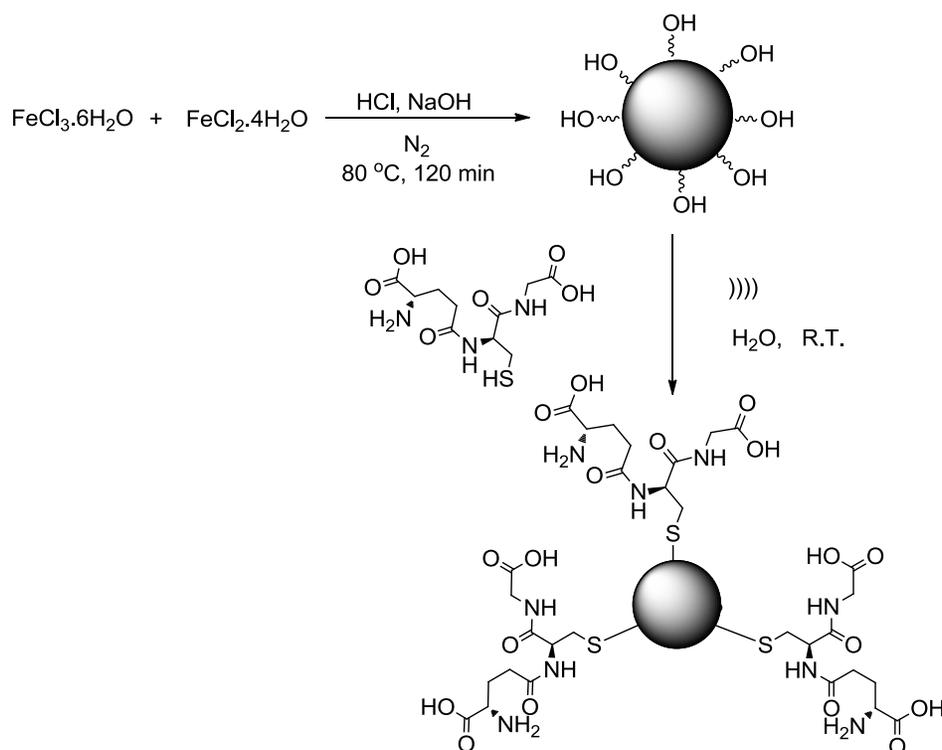
**Applications.** Azizi *et al.* synthesized functionalized chromene derivatives (**37**, **38**) via condensation and ring annulations of 2-hydroxynaphthalene-1,4-dione (**35**) or 4-hydroxycoumarin (**36**), aryl aldehyde (**6**) and malononitrile (**16**) in the presence of a catalytic amount of Fe<sub>3</sub>O<sub>4</sub>@L-proline NPs at room temperature in excellent yields (Scheme 15).<sup>85</sup>



**Scheme 15.** Synthesis of chromene derivatives using Fe<sub>3</sub>O<sub>4</sub>@L-proline NPs.

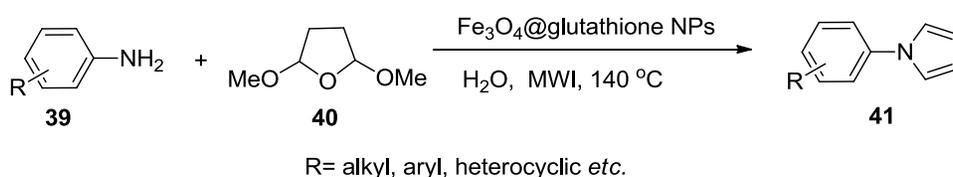
**5.1.3 Synthesis and applications of Fe<sub>3</sub>O<sub>4</sub>@glutathione NPs. Synthesis.** Fe<sub>3</sub>O<sub>4</sub>@glutathione NPs were synthesized by many research groups as follows.<sup>11,67,86,87,88</sup> A portion of 0.5 g of Fe<sub>3</sub>O<sub>4</sub> nanoparticles, prepared in the usual way, was dispersed in 20 mL of water-ethanol mixture (3:1) using ultrasonication. Glutathione (0.5 g in 5 mL water) was added, and the reaction mixture was ultrasonicated at room temperature for 2 hours.

Finally, the glutathione-coated nanoparticles were isolated by centrifugation, washed with water (5 mL x 2) followed by 5 mL methanol, and dried under vacuum at 30-40 °C (Scheme 16).

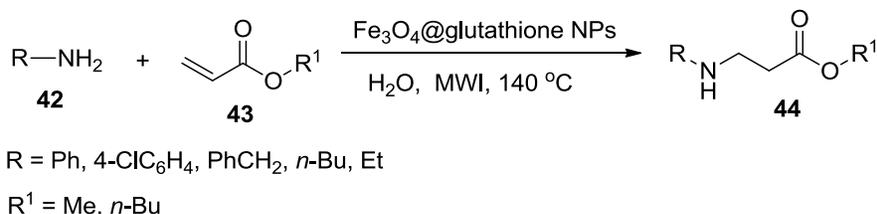


**Scheme 16.** Synthesis of Fe<sub>3</sub>O<sub>4</sub>@glutathione NPs.

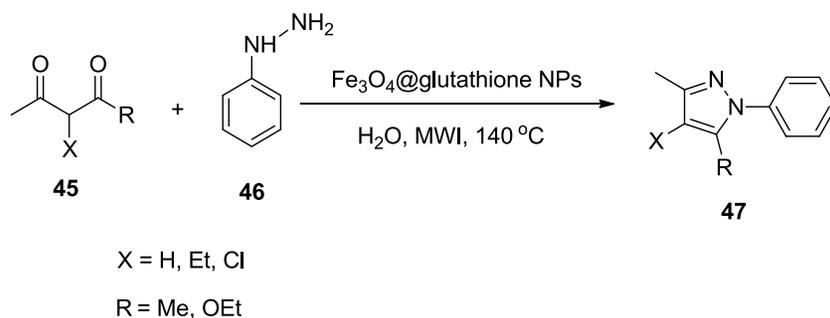
**Applications.** Polshettiwar and Varma utilized Fe<sub>3</sub>O<sub>4</sub>@glutathione NPs as an organo-nanocatalyst for microwave-assisted Paal–Knorr reaction for the synthesis of pyrrole derivatives (**41**) (Scheme 17), aza-Michael addition for the synthesis of 3-amino esters (**44**) (Scheme 18), and pyrazole derivatives (**47**) (Scheme 19).<sup>11</sup>



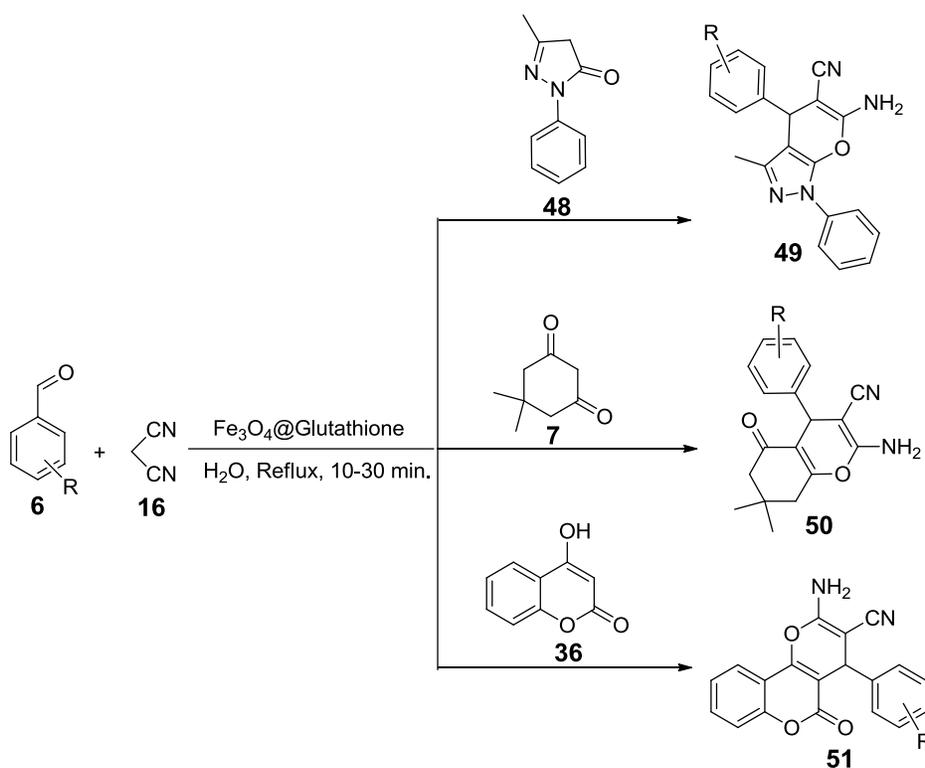
**Scheme 17.** Fe<sub>3</sub>O<sub>4</sub>@glutathione NPs promoted Paal–Knorr reactions.



**Scheme 18.** Fe<sub>3</sub>O<sub>4</sub>@glutathione NPs promoted aza-Michael reactions.



Scheme 19. Synthesis of pyrazole derivatives.

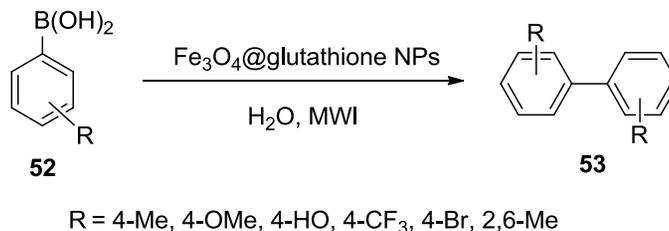


Scheme 20. Synthesis of 2-amino-4H-pyran derivatives.

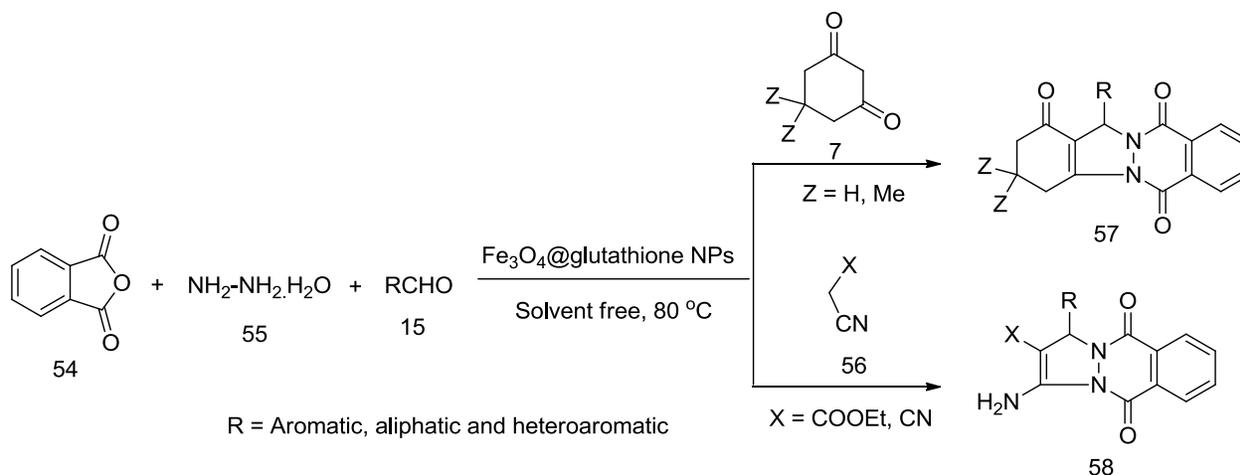
Gupta *et al.* synthesized various fused pyran derivatives (**49-51**) from aromatic aldehydes (**6**), malononitrile (**16**) and active methylene compounds (**48**, **7** and **36**) using  $\text{Fe}_3\text{O}_4$ @glutathione NPs as a heterogeneous catalyst (Scheme 20).<sup>86</sup>

Luque *et al.* developed a synthetic method of aqueous homocoupling of arylboronic acids under microwave irradiation using magnetically separable ferrite-anchored glutathione nanoparticles (Scheme 21).<sup>67</sup>

Dam *et al.* synthesized fused phthalazinetriones (**57**) and phthalazinediones (**58**) derivatives from phthalic anhydride (**54**), hydrazine hydrate (**55**), aldehydes (**15**) and active methylene compounds (**7** and **56**) under solvent free condition using nano- $\text{Fe}_3\text{O}_4$  supported glutathione as a catalyst (Scheme 23).<sup>87</sup>

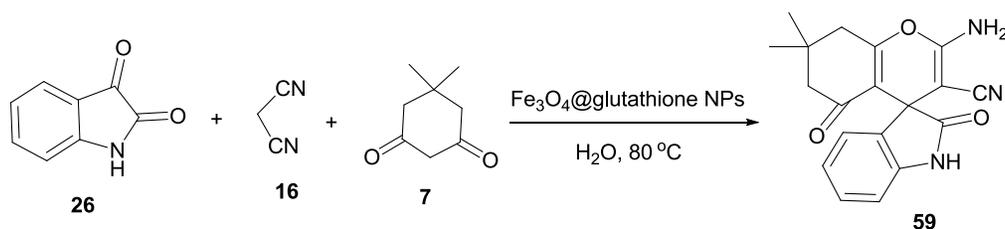


**Scheme 21.** Homocoupling of boronic acids in water.



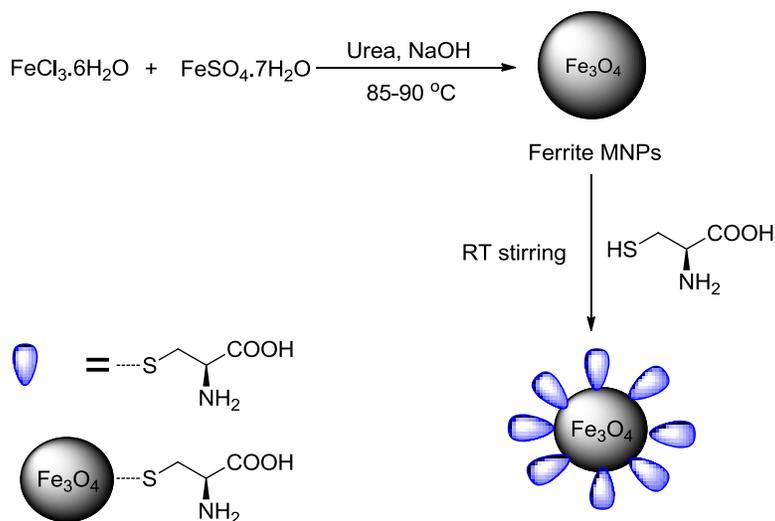
**Scheme 22.** Synthesis of fused phthalazine derivatives.

Jamatia *et al.* developed a synthetic protocol of spiroindoles (**59**) from isatin (**26**), malononitrile (**16**) and dimedone (**7**) in aqueous medium using Fe<sub>3</sub>O<sub>4</sub>@glutathione NPs as a heterogeneous catalyst (Scheme 22).<sup>88</sup>



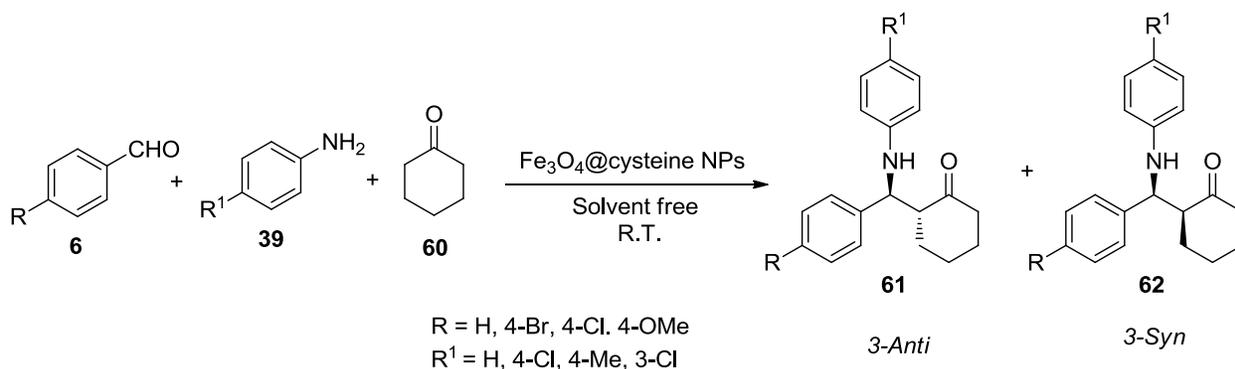
**Scheme 23.** Synthesis of spirooxindole derivatives.

**5.1.4 Synthesis and applications of Fe<sub>3</sub>O<sub>4</sub>@cysteine NPs. Synthesis.** Fe<sub>3</sub>O<sub>4</sub>@cysteine NPs, an organo-nanocatalyst, was first developed by Gawande *et al.* in 2012. At first, Fe<sub>3</sub>O<sub>4</sub> MNPs (1 g) were dispersed in 20 mL distilled water and L-cysteine (1 g) was dissolved in 40–50 mL methanol–water (1:1). Then both the solutions were mixed and the reaction mixture was stirred at room temperature for 24 hours (1200 RPM) using a magnetic stirrer. The Fe<sub>3</sub>O<sub>4</sub>@cysteine NPs were then isolated by simple magnetic decantation, washed with water and methanol and dried in vacuo at 60 °C for 2 hours (Scheme 24).<sup>37</sup>

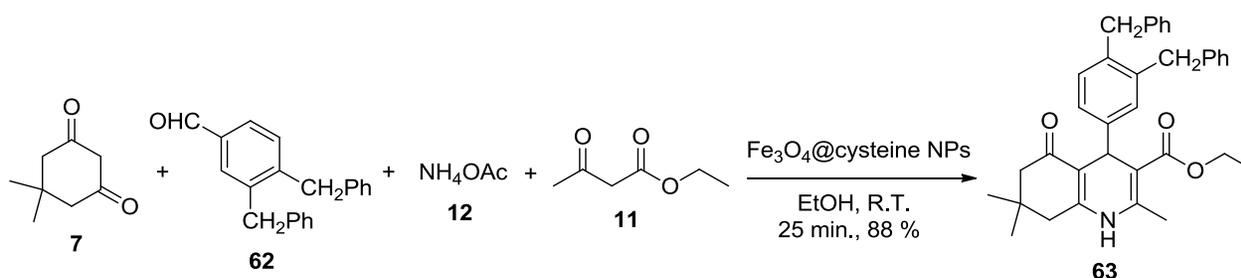


**Scheme 24.** Synthesis of  $\text{Fe}_3\text{O}_4$ @cysteine NPs.

**Applications.** Gawande *et al.* synthesized  $\beta$ -amino carbonyl compounds (Scheme 25) and hydroquinoline compounds (Scheme 26) using  $\text{Fe}_3\text{O}_4$ @cysteine NPs as a magnetic organo-nanocatalyst.<sup>89</sup>  $\beta$ -Amino carbonyl compounds (**61** and **62**) were synthesized from aromatic aldehydes (**6**), anilines (**39**) and cyclohexanone (**60**), while hydroquinoline compounds (**63**) were synthesized from dimedone (**7**), 3,4-dibenzylbenzaldehyde (**62**), ammonium acetate (**12**) and ethyl acetoacetate (**11**).

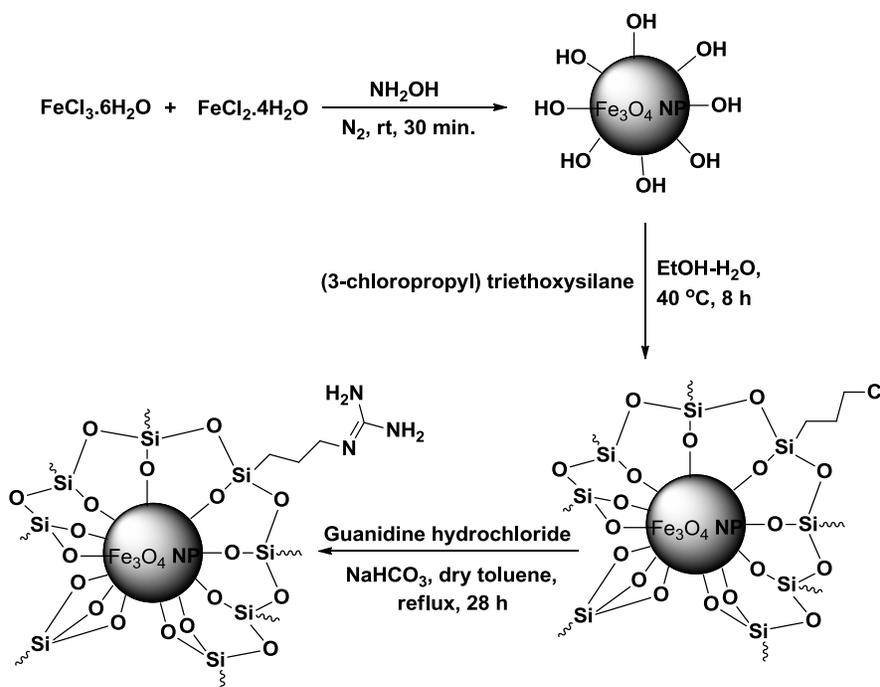


**Scheme 25.** Synthesis of  $\beta$ -amino carbonyl compounds.



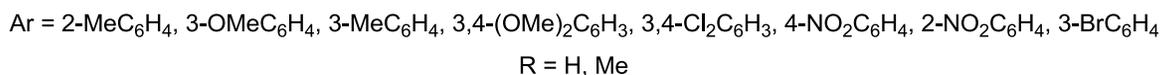
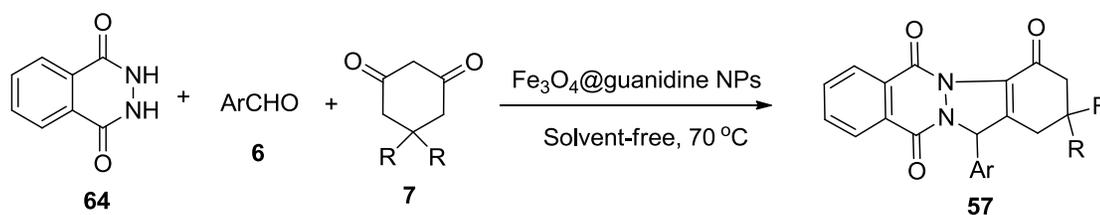
**Scheme 26.** Multicomponent reaction between 3,4-dibenzylbenzaldehyde, ammonium acetate, ethyl acetoacetate and 5,5-dimethylcyclohexane-1,3-dione.

**5.1.5 Synthesis and applications of Fe<sub>3</sub>O<sub>4</sub>@guanidine NPs. Synthesis.** Fe<sub>3</sub>O<sub>4</sub>@guanidine NPs, an organo-nanocatalyst, was developed by Atashkar *et al.* in 2013. It was prepared as shown in the following reaction sequence (Scheme 27).<sup>38</sup>



**Scheme 27.** Synthesis of Fe<sub>3</sub>O<sub>4</sub>@guanidine NPs.

**Applications.** Atashkar *et al.* used Fe<sub>3</sub>O<sub>4</sub>@guanidine NPs in the synthesis of 2*H*-indazolo[2,1-*b*]phthalazinetrione derivatives from a three-component, one-pot condensation of phthalhydrazide (**64**), cyclic 1,3-dicarbonyl compound (**7**), and aromatic aldehydes (**6**) under solvent-free conditions (Scheme 28).<sup>90</sup>



**Scheme 28.** Synthesis of 2*H*-indazolo[2,1-*b*]phthalazinetrione derivatives.

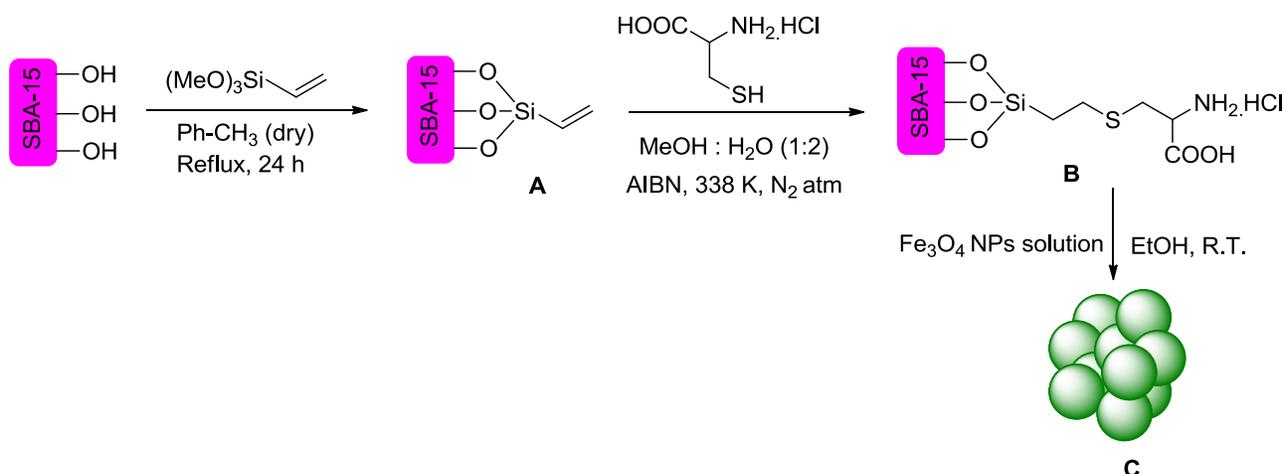
**5.1.6 Synthesis and applications of Ferrite@mesoporous SBA-15 nanoparticles. Synthesis.** Ferrite nanoparticles coated with SBA-15 (SBA-15 is a mesoporous ordered silica) were first prepared by Mondal *et al.* involving the following steps (**A-C**; Scheme 29).<sup>91</sup>

**(a) Synthesis of vinyl functionalized SBA-15 (A).** Calcined SBA-15 (0.1 g) in 10 mL of dry toluene was placed in a 25 mL round bottom flask equipped with a condenser. A solution of vinyl trimethoxysilane (0.81 mmol, 0.12 g) in 5 mL of dry toluene was added dropwise to the dispersed SBA-15 solution under continuous stirring.

After the complete addition of the organosilane precursor the reaction mixture was kept under refluxing conditions for about 12 hours under a nitrogen atmosphere. After the completion of the reaction, the reaction mixture was allowed to cool at room temperature. It was filtered through suction and washed thoroughly with toluene and dichloromethane and dried at room temperature.

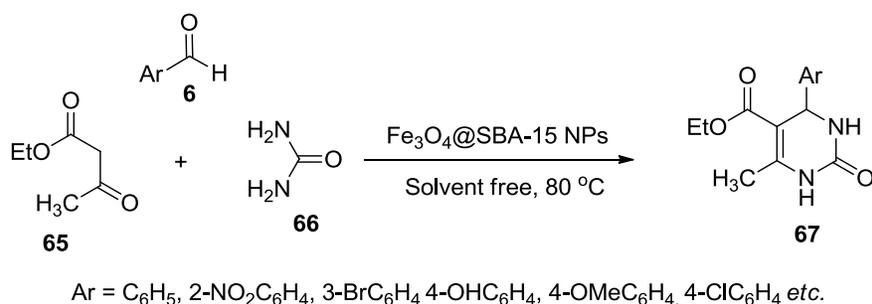
**(b) Synthesis of cysteine hydrochloride functionalized mesoporous SBA-15 (B).** A mixture of cysteine hydrochloride (142 mg, 0.00081 mol) in water (20 mL) and azobis(isobutyronitrile) (AIBN) (10 mg,  $6.3 \times 10^{-2}$  mmol) were added to the pre-prepared vinyl functionalized SBA-15 (A) dispersed in 10 mL methanol solution at room temperature. The mixture was heated to 338 K for 12 h under nitrogen atmosphere. The reaction mixture was allowed to cool at room temperature. Then the colorless white material (B) was collected by filtration after washing several times with water in order to remove unreacted cysteine hydrochloride.

**(c) Chemical conjugation of Fe<sub>3</sub>O<sub>4</sub> nanoparticles onto cysteine hydrochloride functionalized mesoporous SBA-15 (B) to form the Fe<sub>3</sub>O<sub>4</sub>@mesoporous SBA-15 nano-catalyst (C).** 0.1 g of cysteine hydrochloride functionalized SBA-15 material (B) was dispersed in 10 mL absolute ethanol. Then 1 mL of the Fe<sub>3</sub>O<sub>4</sub> nanoparticle suspension (32.2 mg mL<sup>-1</sup>) was added to the previous solution using a micropipette and the mixture was allowed to stir at room temperature for 12 hours. Then the reaction mixture was filtered and washed several times with water and ethanol. The black material (C) was dried at room temperature.



**Scheme 29.** Grafting of Fe<sub>3</sub>O<sub>4</sub> nanoparticles to cysteine immobilized SBA-15 using thiol-ene click reaction.

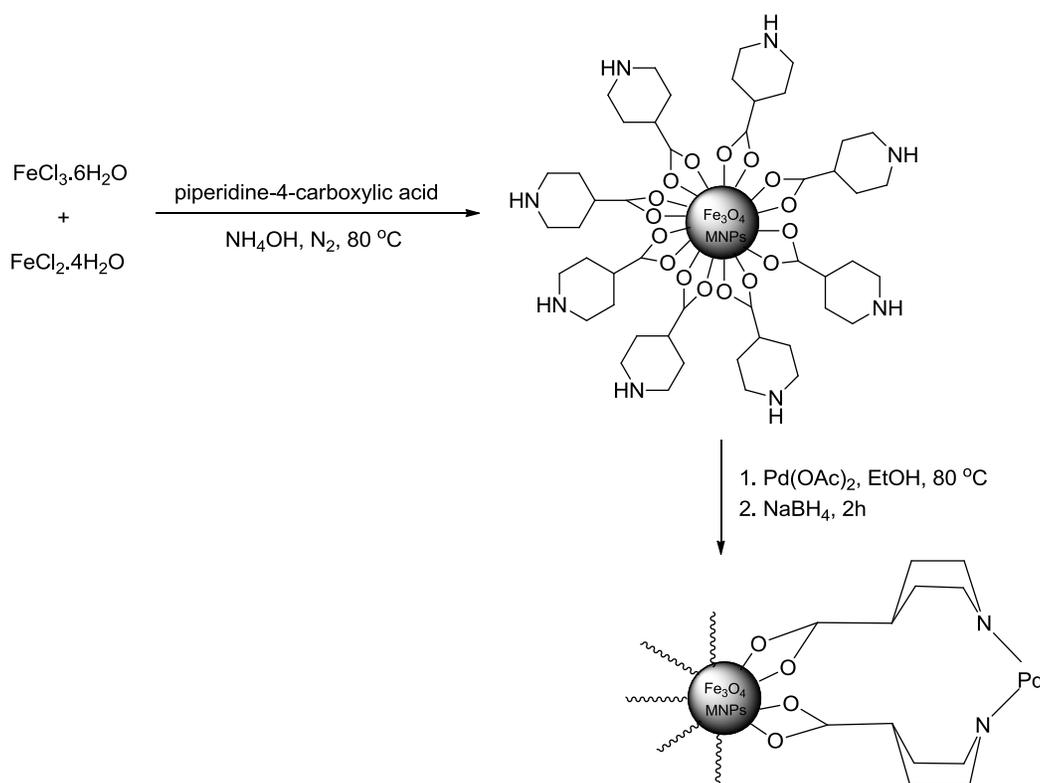
**Applications.** Mondal *et al.* developed a synthetic protocol of one-pot synthesis of 3,4 dihydropyrimidin-2(1H)-ones (**67**) via the Biginelli reaction using aromatic aldehydes (**6**), ethyl acetoacetate (**65**) and urea (**66**) in the presence of Fe<sub>3</sub>O<sub>4</sub>@mesoporous SBA-15 nanoparticles as a catalyst (Scheme 30).<sup>91</sup>



**Scheme 30.** Biginelli reaction.

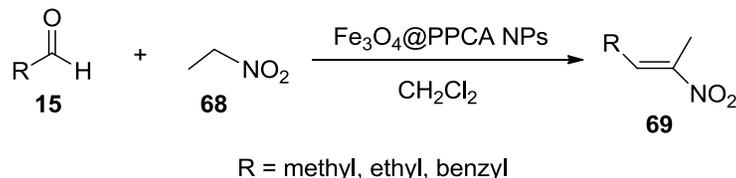
**5.1.7 Synthesis and applications of Fe<sub>3</sub>O<sub>4</sub>@PPCA NPs. Synthesis.** Magnetic Fe<sub>3</sub>O<sub>4</sub>@PPCA NPs were prepared using the following method.<sup>92</sup> Firstly, Fe(III) and Fe(II) salts (with the molar ratio of 2:1) were dissolved in 100 mL deionized water and kept at 40 °C for 15 minutes with vigorous stirring. Then PPCA and NH<sub>4</sub>OH solution were added to the mixture until the pH was raised to 11 when a black suspension was formed. This suspension was then refluxed at 100 °C for 6 hours, with vigorous stirring. Fe<sub>3</sub>O<sub>4</sub>@PPCA NPs were separated from the aqueous solution by magnetic decantation, washed with distilled water several times and then dried in an oven overnight.

Next, magnetic Fe<sub>3</sub>O<sub>4</sub>@PPCA@Pd(0) NPs were prepared using the following method. Fe<sub>3</sub>O<sub>4</sub>@PPCA nanoparticles (1000 mg) were added to a solution of Pd(OAc)<sub>2</sub> (500 mg) in 25 mL ethanol. This mixture was refluxed for 15 hours. Pd(II) ions were adsorbed onto the Fe<sub>3</sub>O<sub>4</sub>@PPCA nanoparticles and reduced by NaBH<sub>4</sub> to give Fe<sub>3</sub>O<sub>4</sub>@PPCA@Pd(0) nanoparticles. Subsequently, the reaction mixture was cooled to room temperature, and the solid was separated by magnetic decantation followed by washing with absolute ethanol and dried under vacuum at room temperature to produce the palladium-functionalized organo-nanocatalyst (Scheme 31).

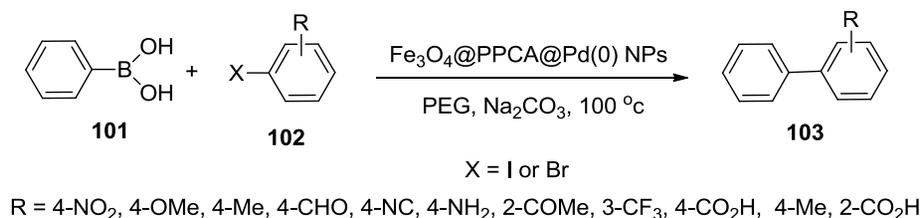
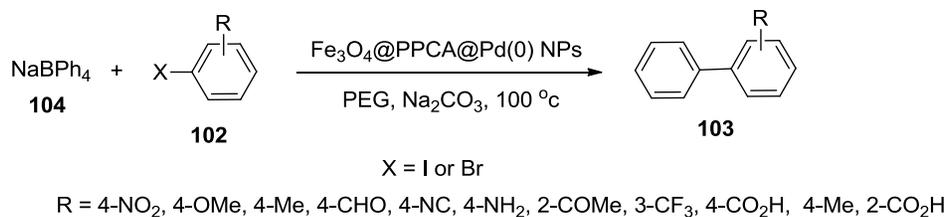


**Scheme 31.** Synthesis of Fe<sub>3</sub>O<sub>4</sub>@PPCA@Pd(0) NPs.

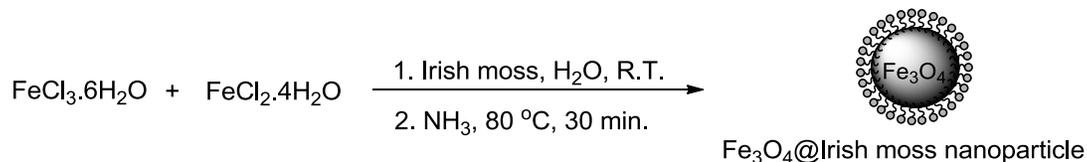
**Applications.** Karaoglu *et al.* developed this magnetic nano-catalyst for Knoevenagel reaction between aldehydes (**15**) and aliphatic nitro compounds (**68**) to produce nitro alkenes (**69**) (Scheme 32).<sup>92</sup>

**Scheme 32.** Nitro aldol condensation.

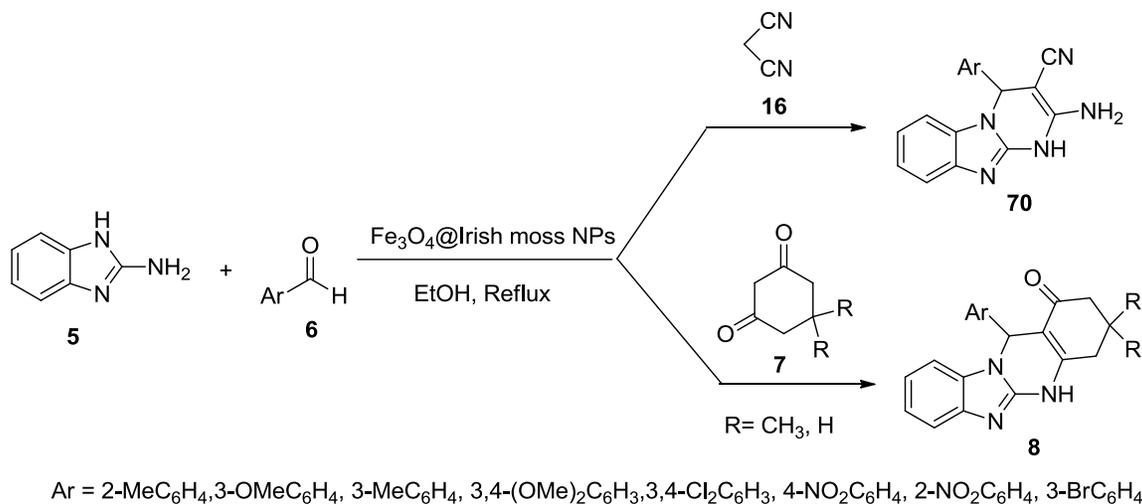
Azadi et al. developed  $\text{Fe}_3\text{O}_4@\text{PPCA}@\text{Pd}(0)$  NPs as an organo-nanocatalyst and exploited its catalytic roles in C–C coupling reactions using phenylboronic acid (101) and aryl halides (102) as starting materials in polyethylene glycol (PEG) solvent at 100 °C (Schemes 33 and 34).<sup>93</sup>

**Scheme 33.** Synthesis of biphenyls.**Scheme 34.** Synthesis of biphenyls.

**5.1.8 Synthesis and applications of  $\text{Fe}_3\text{O}_4@\text{Irish moss}$  NPs. Synthesis.** Initially, 2 g of Irish moss (Angel brand) was dissolved in 100 mL distilled water. Then,  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  (5g) and  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  (2 g) were slowly added into the mixture. The mixture was stirred vigorously at 80 °C to obtain a clear solution followed by addition of aqueous ammonia to the solution until the pH was raised to 12. The solution was kept at 80 °C under vigorous stirring for further 30 minutes. The precipitate was collected with an external magnet, washed several times with water methanol and dried in vacuum for 6 hours (Scheme 35).<sup>69</sup>

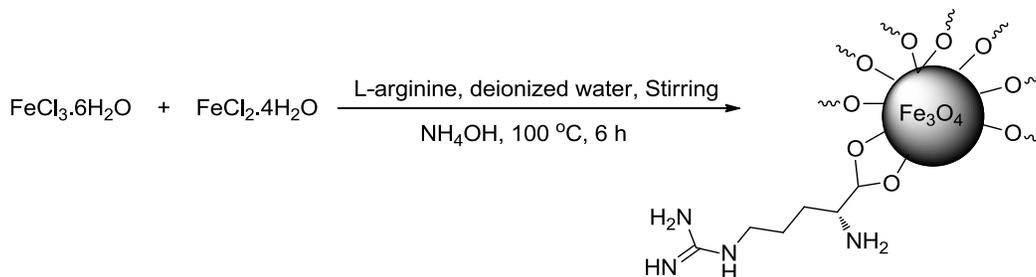
**Scheme 35.** Preparation of  $\text{Fe}_3\text{O}_4@\text{Irish moss}$  NPs.

**Applications.** Hemmati *et al.* synthesized  $\text{Fe}_3\text{O}_4$ @Irish moss NPs as an organo-nanocatalyst and utilized in the synthesis of imidazopyrimidine derivatives (**70**, **8**) via a three-component reaction of 2-aminobenzimidazole (**5**), aldehyde (**6**), and C–H acidic compounds (**16**, **7**) under reflux condition in ethanol (Scheme 36).<sup>69</sup>



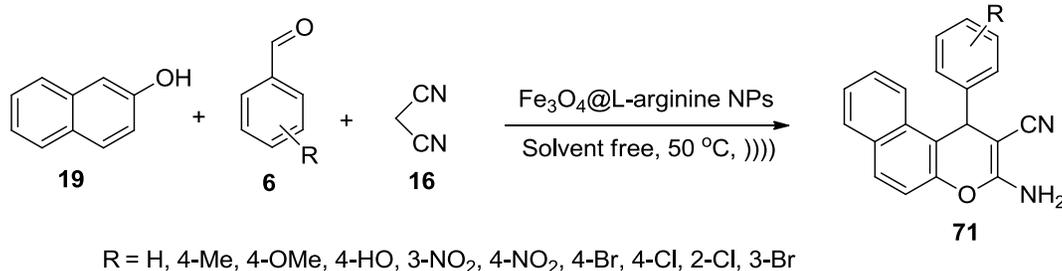
**Scheme 36.** Synthesis of imidazopyrimidine derivatives.

**5.1.9 Synthesis and applications of  $\text{Fe}_3\text{O}_4$ @L-arginine NPs. Synthesis.** In 2014 Azizi *et al.* developed  $\text{Fe}_3\text{O}_4$ @L-arginine NPs for the synthesis of chromene derivatives. The preparation method is given as follows. 5 mmol of  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  and 2.5 mmol of  $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$  were dissolved in 100 mL deionized water under vigorous stirring. 2 mmol of L-arginine and  $\text{NH}_4\text{OH}$  solution (25%, w/w, 30 mL) were added to the above mixture until the pH was raised to 11 at which a black suspension was formed. This suspension was then refluxed with vigorous stirring at 100 °C for 6 hours.  $\text{Fe}_3\text{O}_4$ @L-arginine NPs were separated from the aqueous solution by magnetic decantation, washed with water several times before being dried in an oven overnight (Scheme 37).<sup>94</sup>



**Scheme 37.** Synthesis of  $\text{Fe}_3\text{O}_4$ @L-arginine NPs.

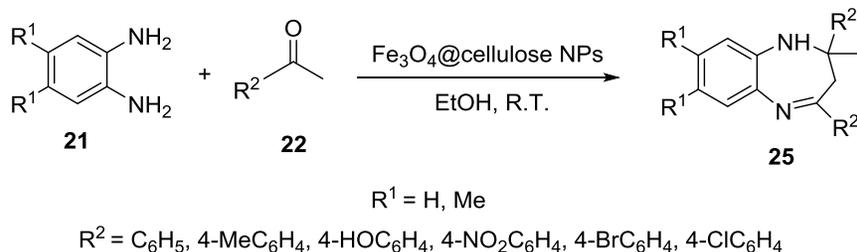
**Applications.** Azizi *et al.* utilized  $\text{Fe}_3\text{O}_4$ @L-arginine NPs as an organo-nanocatalyst in the development of synthetic protocol of chromenes (**71**) from  $\beta$ -naphthol (**19**), aromatic aldehydes (**6**) and malononitrile (**16**) in solvent-free condition at 50 °C (Scheme 38).<sup>94</sup>



**Scheme 38.** Synthesis of chromenes.

**5.1.10 Synthesis and applications of Fe<sub>3</sub>O<sub>4</sub>@cellulose NPs. Synthesis.** Maleki *et al.* reported the synthesis of Fe<sub>3</sub>O<sub>4</sub>@cellulose NPs as shown below. At the very outset, 4 g of cellulose was dissolved in 10 mL of NaOH-urea-H<sub>2</sub>O solution and was immediately pre-cooled to -8 °C to give a 4 weight% cellulose solution. The solution was centrifuged at 2000 rpm for 30 minutes. Then it was spread onto a glass plate to give a thickness of 0.5 mm and was then immersed in a 20 mL H<sub>2</sub>SO<sub>4</sub> (5 weight %) bath for 5 minutes. After acid ejection, the resulting product was washed with distilled water several times. The obtained wet films were immersed in 500 mL of a mixture of aqueous FeCl<sub>3</sub>·6H<sub>2</sub>O (0.1 M) for 24 hours. Then, the iron ions adsorbed on the surface of the composite were washed out with distilled water. After that, the composite was immersed in 500 mL of aqueous NaOH (4 mol/L) for 20 minutes and was washed with distilled water several times. Finally, the resulting product was dried at room temperature for 3 days to give Fe<sub>3</sub>O<sub>4</sub>@cellulose NPs.<sup>95</sup>

**Applications.** Maleki *et al.* developed a synthetic protocol for 1,5-benzodiazepines (**25**) starting from *o*-phenylenediamine (**21**) and two equivalents of aromatic ketones (**22**) in ethanol under room temperature stirring using Fe<sub>3</sub>O<sub>4</sub>@cellulose NPs as a catalyst (Scheme 39).<sup>95</sup>



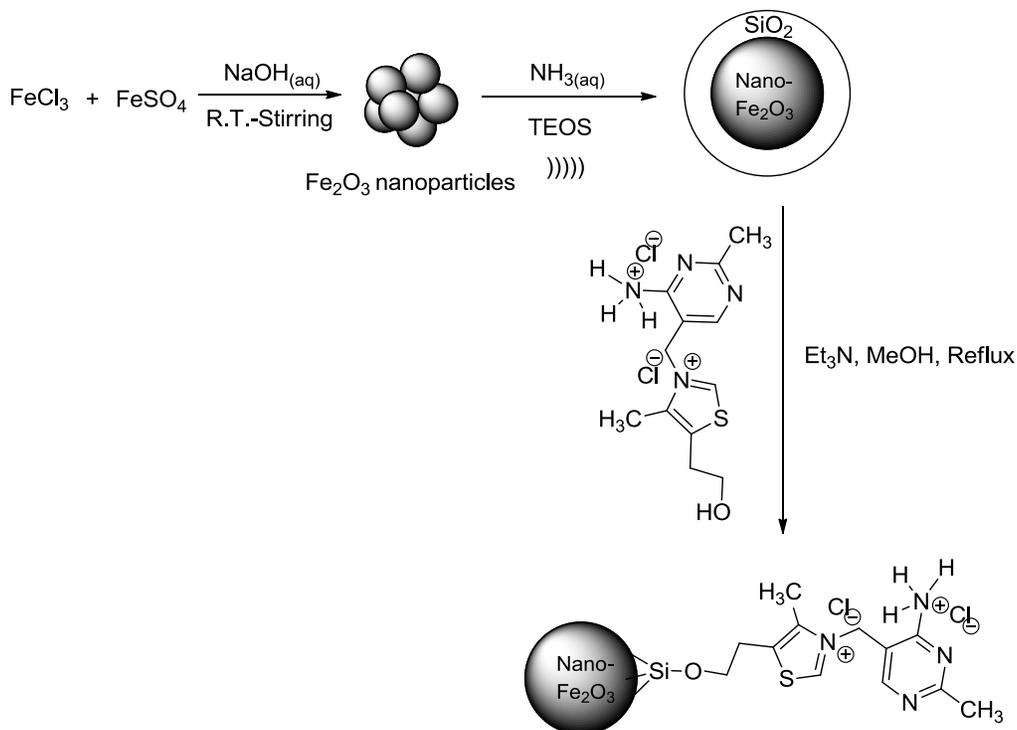
**Scheme 39.** Synthesis of 1,5-benzodiazepines.

## 5.2 Synthesis and applications of multilayer coated organo-nanocatalysts

In this class of organo-nanocatalysts, the organo/enzyme moieties are made to encapsulate onto the surface of the magnetic nano-core by formation of covalent bonding with an intermediate agent. Recent research publications report some multilayer-coated organo-nanocatalysts, including for instance Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>@vit. B<sub>1</sub> NPs, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@L-proline NPs, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@L-cysteine NPs, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@L-arginine NPs, Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@DDBSA NPs, Fe<sub>3</sub>O<sub>4</sub>@L-proline@SO<sub>3</sub>H NPs. Their mode of preparation and applications in the field of organic synthesis are discussed below.

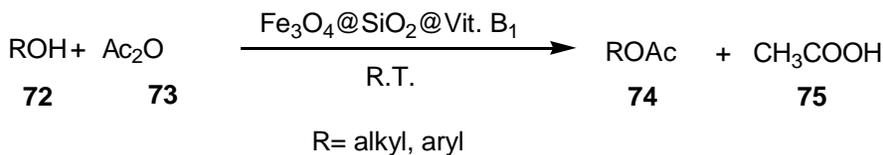
**5.2.1 Synthesis and applications of Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>@vit. B<sub>1</sub> NPs. Synthesis.** Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>@vit. B<sub>1</sub> NPs were synthesized as follows.<sup>96,97,98</sup> Firstly, an aqueous solution of Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> NPs (1 g) in methanol was ultrasonicated for 30 minutes in the presence of triethylamine (1.5 mL). Vitamin B<sub>1</sub> (0.6 g) was then added to

the solution, which was further ultrasonicated for 3 hours at 50 °C. On completion, the nanoparticles were filtered off and washed with water followed by diethyl ether. The nanoparticles were then acidified with HCl, in order to convert the alkaline  $\text{Fe}_2\text{O}_3@\text{SiO}_2@\text{thiamine}$  moiety into  $\text{Fe}_2\text{O}_3@\text{SiO}_2@\text{vit. B}_1$  (Scheme 40).



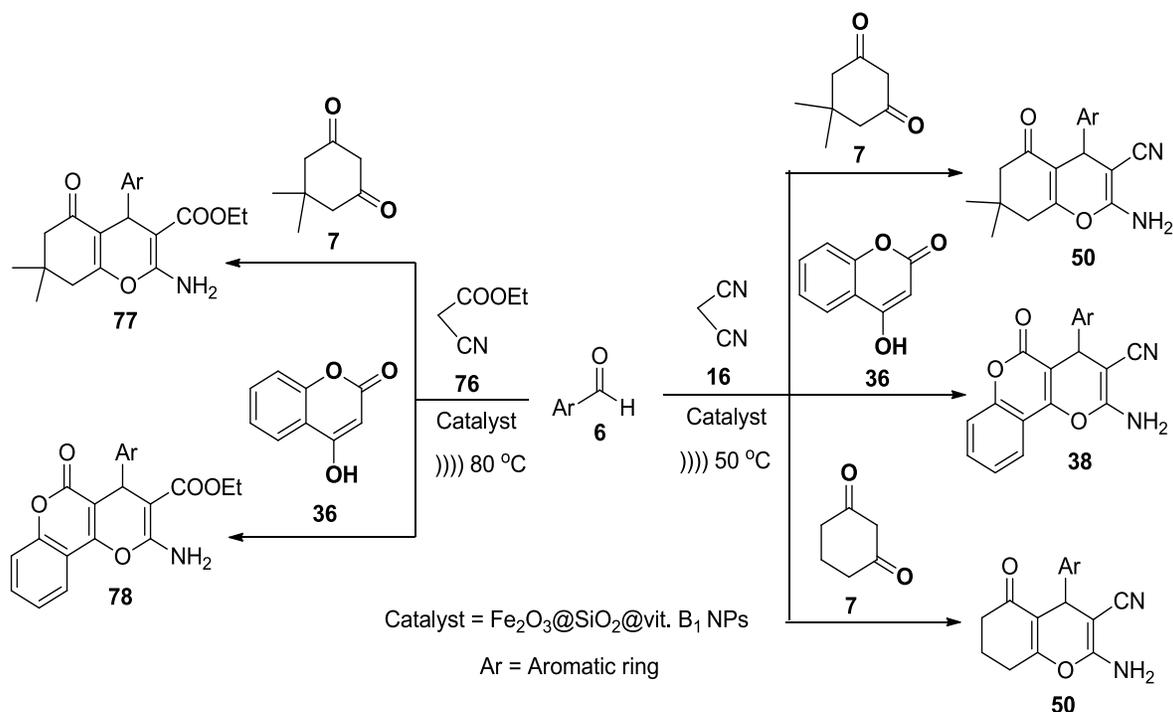
**Scheme 40.** Synthesis of  $\text{Fe}_2\text{O}_3@\text{SiO}_2@\text{vit. B}_1$  NPs.

**Applications.** Azizi *et al.* prepared  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{vit. B}_1$  NPs and exploited it as an organo-nanocatalyst in acylation of alcohols and phenols (**72**) using acetic anhydride (**73**) (Scheme 41).<sup>96</sup> The acetylation of phenol in the presence of various amounts of catalyst, in different solvents as well as under solvent-free conditions was optimized and the optimal conditions of the reaction were selected to be solvent-free at room temperature and in the presence of 10 mg catalyst.



**Scheme 41.** Acylation of alcohols and phenols.

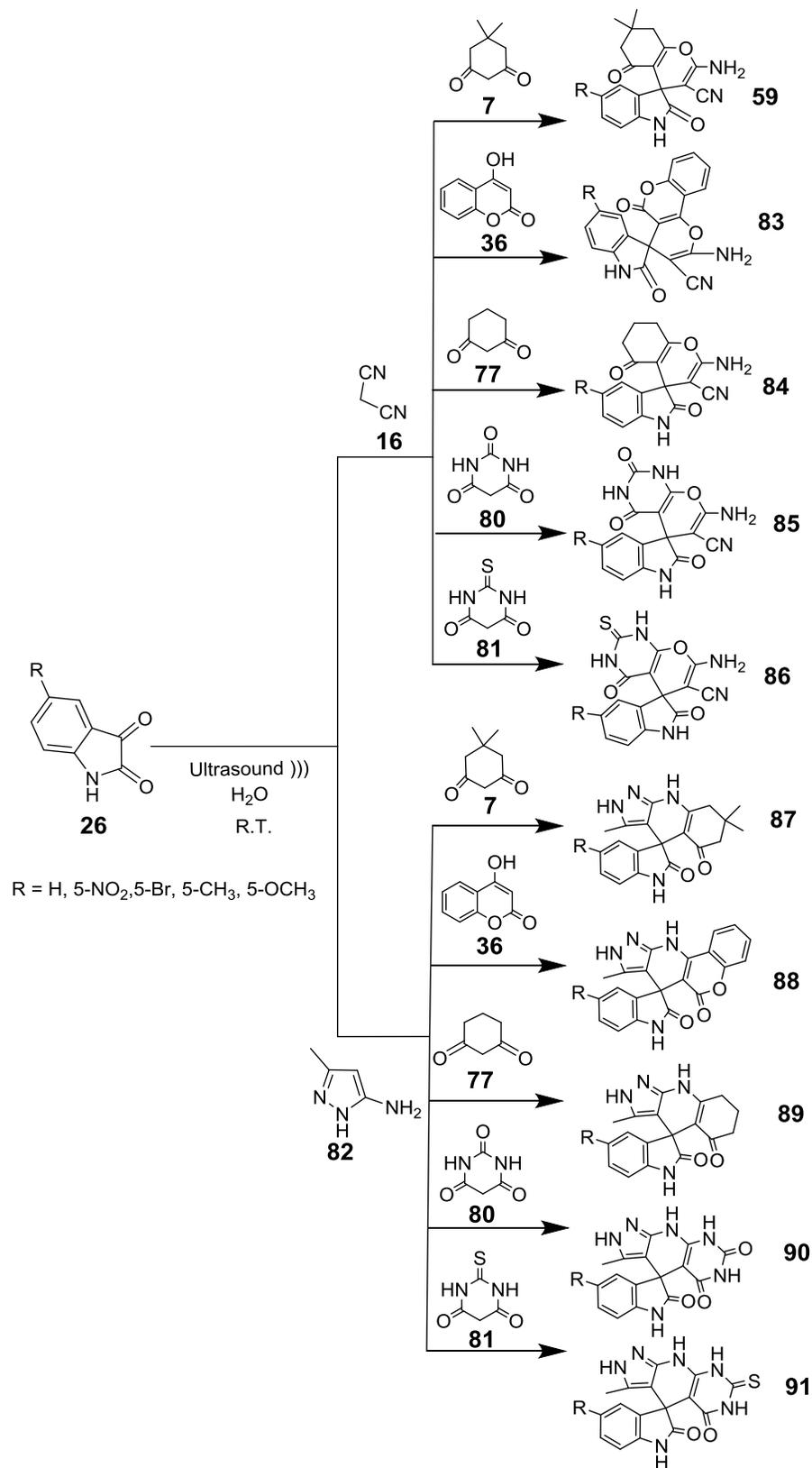
Recently, our group devised a similar protocol for the preparation of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{vit. B}_1$  NPs which was exploited in synthesizing various classes of organic compounds (Schemes 42 and 43). Various pyran derivatives were prepared using aromatic aldehydes (**6**), active methylene compounds (**16**, **76**) and 1,3-diketones (**7**)/coumarins (**36**) (Scheme 42).<sup>97</sup> A number of various spiro-derivatives of oxygen and nitrogen heterocycles were synthesized starting from isatin (**26**), malononitrile (**16**)/pyrazole (**42**) and various 1,3-diketones (**7**, **16**, **77**, **36**, **80**, **81**) under ultrasonication. The method was claimed to be a green approach in the use of water as an eco-friendly solvent and ultrasonication as the means of agitating the reaction mixture (Scheme 43).<sup>98</sup>



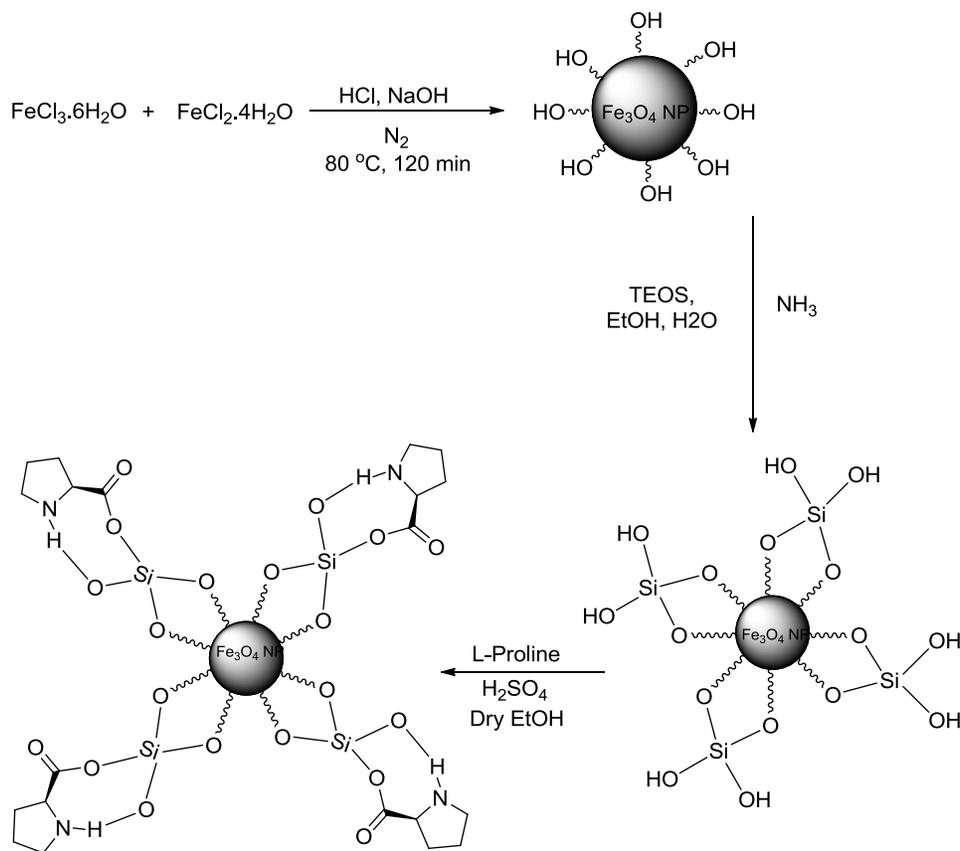
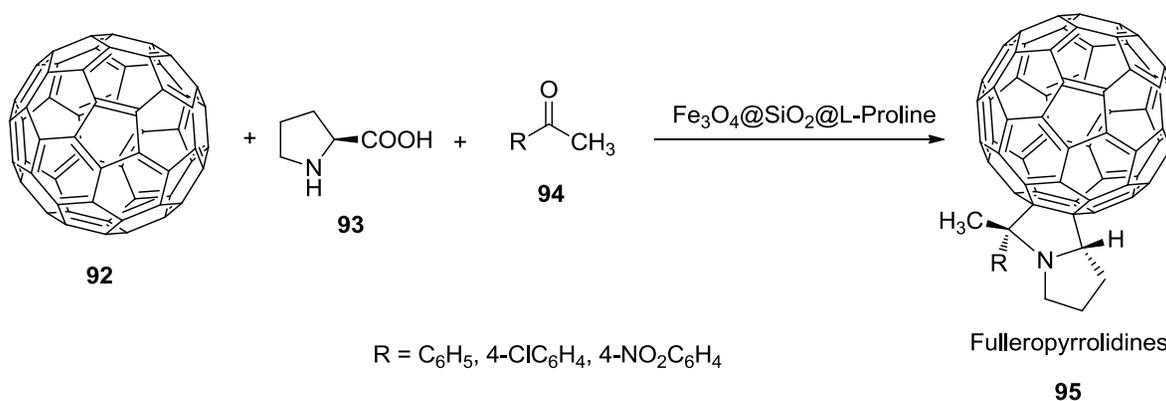
**Scheme 42.** Synthesis of benzo[*b*]pyran derivatives.

**5.2.2 Synthesis and applications of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{L-proline}$  NPs. Synthesis.**  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{L-proline}$  NPs were prepared as follows; firstly, 1 g of  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  NPs were dispersed in dry ethanol (10 mL) using an ultrasonic bath for 30 minutes. Then, 0.6 g of L-proline and 1 mL of  $\text{H}_2\text{SO}_4$  were added to the solution containing  $\text{Fe}_3\text{O}_4@\text{SiO}_2$  NPs and heated under reflux conditions. After completion of the reaction, the mixture was stirred for further 12 hours and the resulting MNPs were isolated using an external magnet and washed with ethanol and water before being dried in an oven at 70 °C to give  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{L-proline}$  NPs as a light brown powder (Scheme 44).<sup>8</sup>

**Applications.** Safaei *et al.* developed  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{L-proline}$  organo-nanocatalyst for the diastereoselective synthesis of fulleropyrrolidines (**95**) starting from fullerene (**92**), L-proline (**93**) and aromatic ketones (**94**) (Scheme 45).<sup>8</sup>

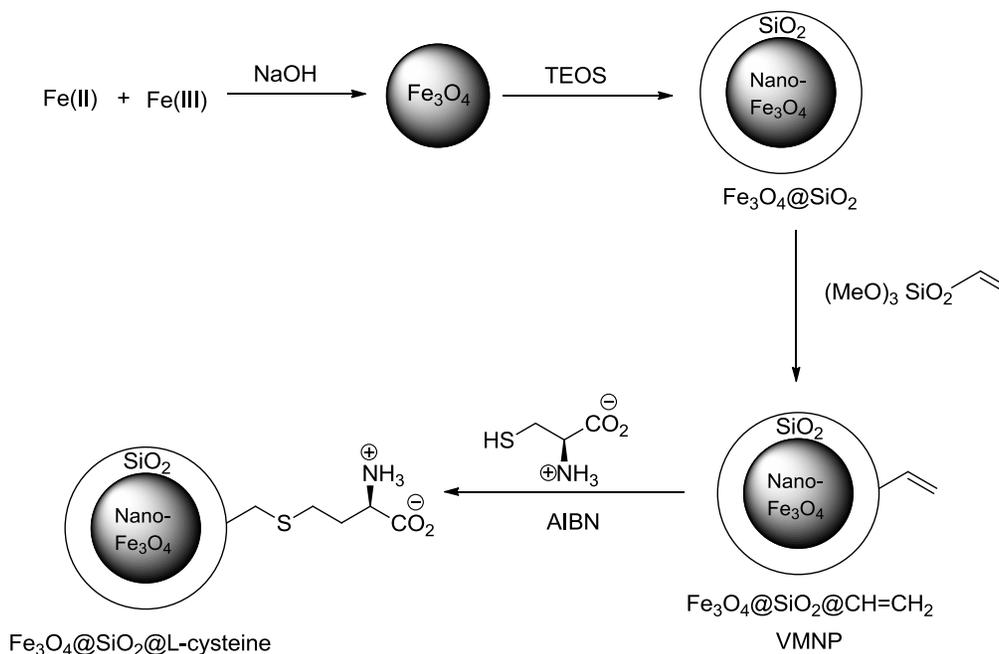


Scheme 43. Preparation of oxygen and nitrogen containing spiro compounds.

Scheme 44. Synthesis of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{L-proline}$  NPs.

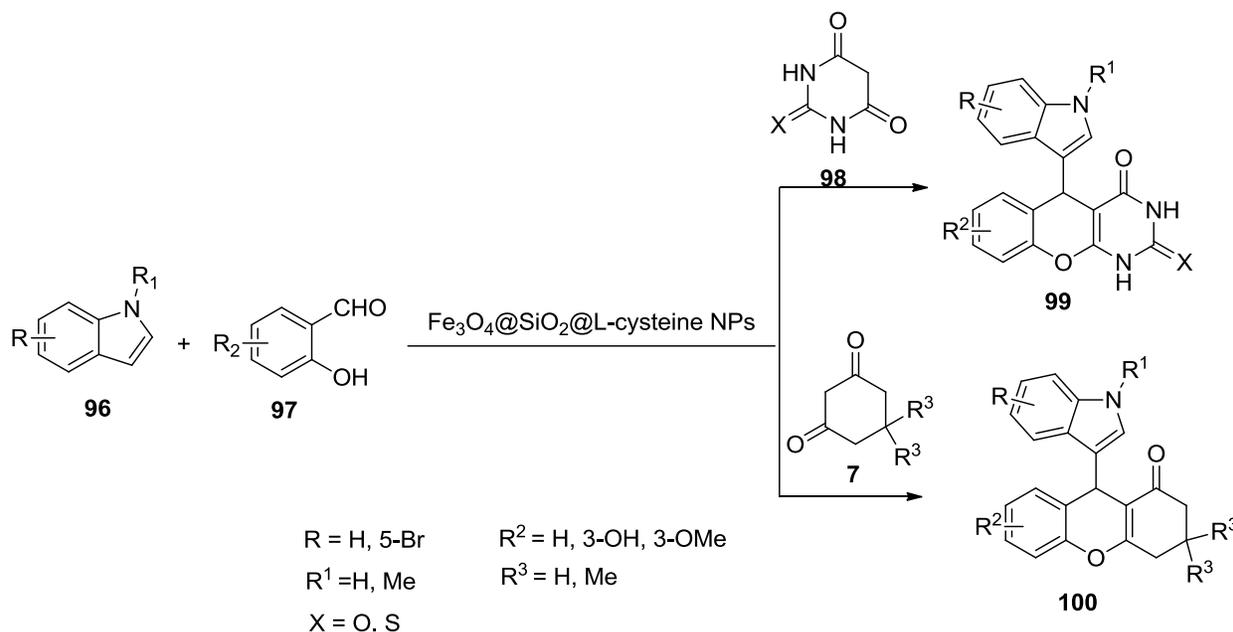
Scheme 45. Diastereoselective synthesis of fulleropyrrolidines.

**5.2.3 Synthesis and applications of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{L-cysteine}$  NPs. Synthesis.** Khalaf *et al.* synthesized  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{L-cysteine}$  NPs as follows. 1.1 g of L-cysteine was added to a prepared solution containing 5 g VMNP in 30 mL chloroform in the presence of AIBN (1.0 mmol). Then, the mixture was stirred for 12 hours at the refluxing temperature of chloroform. The resulting precipitate was filtered, washed with water, and dried in vacuo to afford the  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{L-cysteine}$  nanocatalyst (Scheme 46).<sup>49</sup>



**Scheme 46.** Preparation of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{L-cysteine}$  NPs.

**Applications.** Nourisfat *et al.* developed a synthetic protocol for the one-pot synthesis of 9-(1*H*-indol-3-yl)xanthen-4(9*H*)-one derivatives (**99-100**) from indoles or substituted indoles (**96**) and substituted salicyl aldehydes (**97**) using  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{L-cysteine}$  NPs as an efficient organo-nanocatalyst (Scheme 47).<sup>49</sup>

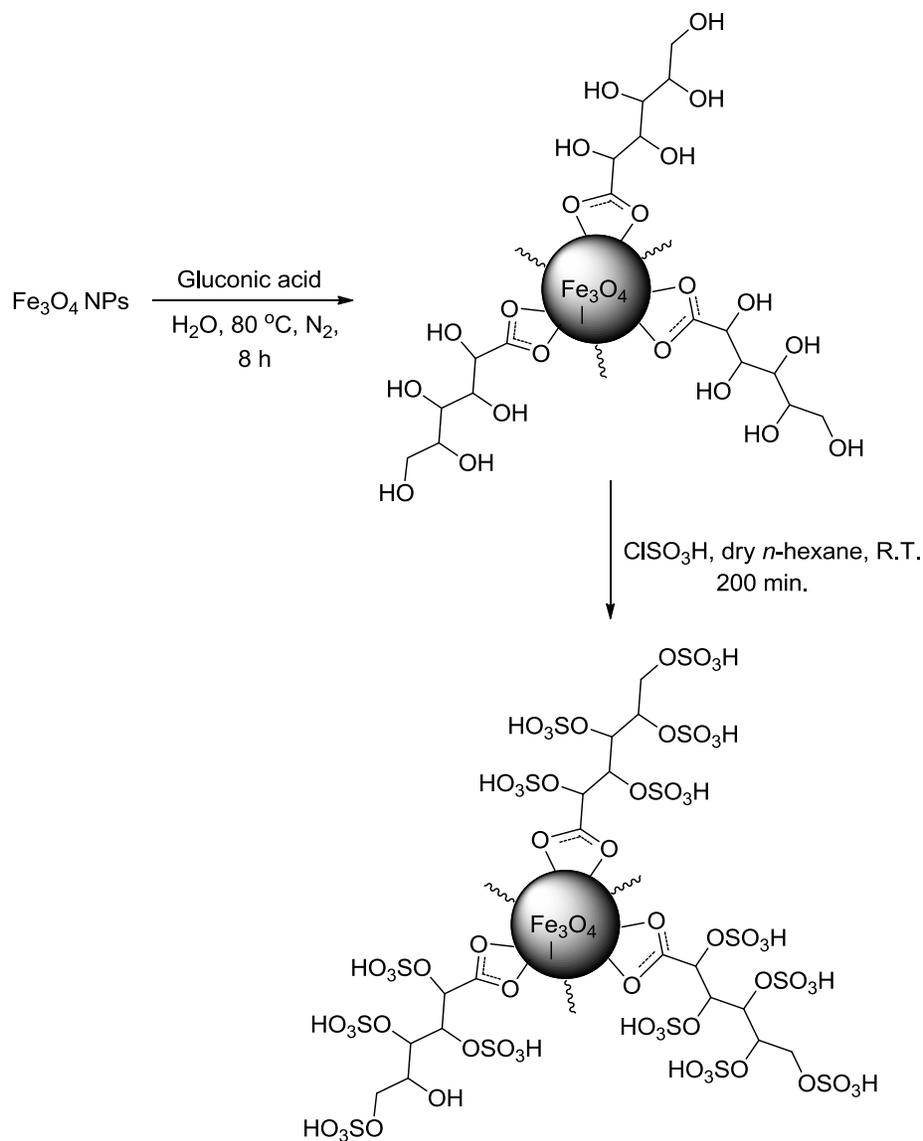


**Scheme 47.** Synthesis of 9-(1*H*-indol-3-yl)-2,2-dimethyl-2,3-dihydro-1*H*-xanthen-4(9*H*)-one.

**5.2.4 Synthesis and applications of  $\text{Fe}_3\text{O}_4@\text{GSA}$  NPs. Synthesis.** Glucosulfonic acid immobilized on  $\text{Fe}_3\text{O}_4$  magnetic nanoparticles were prepared as follows: 2 g of  $\text{Fe}_3\text{O}_4$  NPs was dispersed in 15 mL water and sonicated for 30 minutes, then gluconic acid solution (8 mL) was added to the reaction mixture followed by

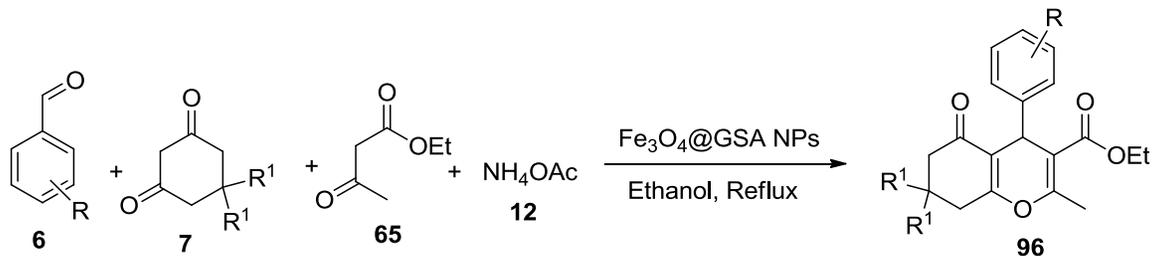
stirring under  $N_2$  atmosphere at  $80\text{ }^\circ\text{C}$  for 8 hours. The final product was separated by magnetic decantation and washed with ethanol to remove the unreacted substrates. Gluconic acid immobilized on  $Fe_3O_4$  magnetic nanoparticles ( $Fe_3O_4@GA$  NPs) thus formed were dried at room temperature.

The  $Fe_3O_4@GA$  NPs (0.5 g) were dispersed in dry *n*-hexane (5 mL) by ultrasonication for 20 minutes. Subsequently, chlorosulfonic acid (1.2 mL) was added drop wise over a period of 30 minutes and the mixture was stirred for 4 hours at room temperature. The final product ( $Fe_3O_4@GSA$  NPs) was separated by magnetic decantation and washed twice with ethanol and *n*-hexane to remove unreacted substrates (Scheme 48).<sup>99</sup>



**Scheme 48.** Synthesis of  $Fe_3O_4@GSA$  NPs.

**Applications.** Hajjami *et al.* developed  $Fe_3O_4@GSA$  NPs and utilized it for the synthesis of polyhydroquinoline and 2,3-dihydroquinazolin-4(1*H*)-one derivatives (**96**) from aromatic aldehydes (**6**), dimedone (**7**), ethyl acetoacetate (**65**) and ammonium acetate (**12**) (Scheme 49).<sup>99</sup>

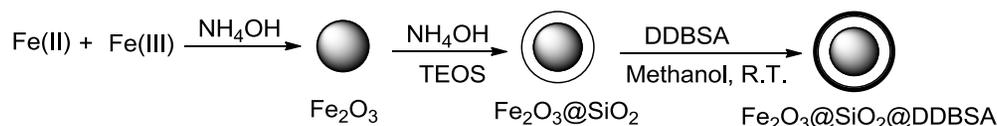


R = H, 4-Me, 4-OMe, 4-HO, 3-NO<sub>2</sub>, 4-NO<sub>2</sub>, 4-Br, 4-Cl, 2-Cl, 3-Br etc.

R<sup>1</sup> = H, Me

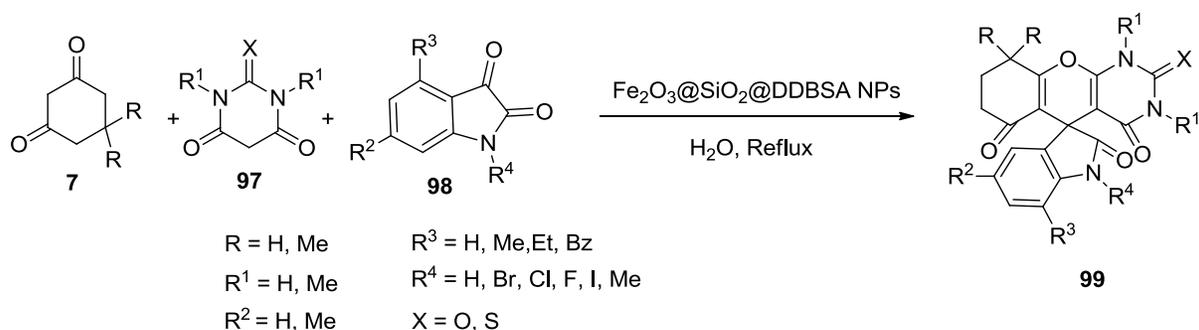
**Scheme 49.** Synthesis of polyhydroquinolines.

**5.2.5 Synthesis and applications of Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>@DDBSA NPs. Synthesis.** To a suspension of Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub> NPs (10.0 g) in 250 mL of dry methanol, dodecylbenzenesulfonic acid (DDBSA, 0.82 g, 2.5 mmol) was added. The mixture was sonicated for 60 minutes at room temperature. The methanol was removed under reduced pressure and the residue was dried at 110 °C for 2 hours to afford Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>-DDBSA (0.25 mmol/g, 10 mg = 0.0025 mmol of DDBSA) as a yellow powder (Scheme 50).<sup>100</sup>



**Scheme 50.** Synthesis of Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>@DDBSA NPs.

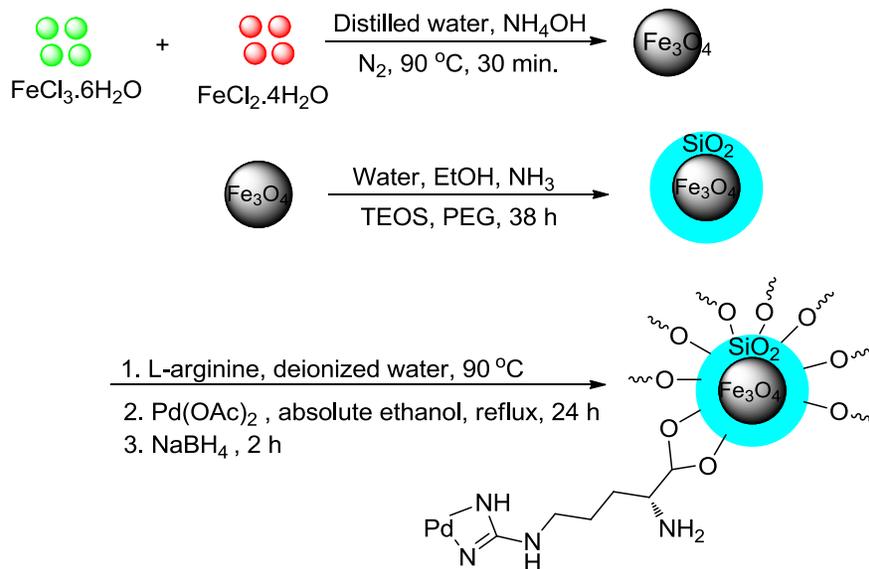
**Applications.** Deng *et al.* synthesized a library of spirooxindole-pyrimidines (**99**) from isatin (**8**), barbituric acid (**97**) and dimedone (**7**) catalyzed by magnetic nanoparticles with supported dodecylbenzenesulfonic acid in aqueous medium under reflux condition (Scheme 51).<sup>100</sup>



**Scheme 51.** Synthesis of spirooxindole-pyrimidines.

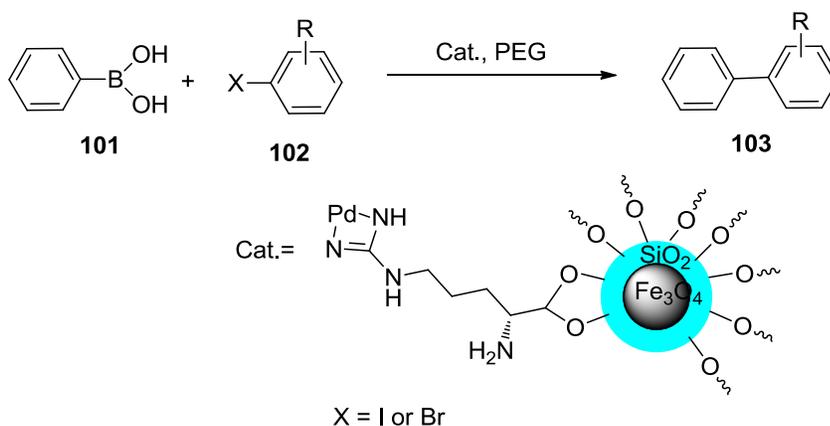
**5.2.6 Synthesis and applications of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@L-arginine@Pd(0) NPs. Synthesis.** 1 g of Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> NPs were suspended in deionized water (20 mL) and sonicated until they became fully dispersed. Then, 2 g of L-arginine were added and the mixture was stirred at 90 °C for 15 hours. Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@L-arginine NPs thus formed were separated from the aqueous solution by using an external magnet, washed with distilled water several times and then dried in an oven overnight. Then, incorporation of palladium onto the Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@L-

arginine nanocomposite was carried out by mixing the  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{L-arginine}$  NPs (0.5 g) and  $\text{Pd}(\text{OAc})_2$  (0.25 g) in 30 mL ethanol. The mixture was refluxed for 24 hours. Pd (II) ions were adsorbed onto the magnetic nanocarrier and reduced by  $\text{NaBH}_4$  to give  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{L-arginine}@\text{Pd}(0)$  NPs. Finally, the synthesized NPs were separated from the suspension using magnetic decantation, washed with ethanol and dried under vacuum at room temperature (Scheme 52).<sup>101</sup>



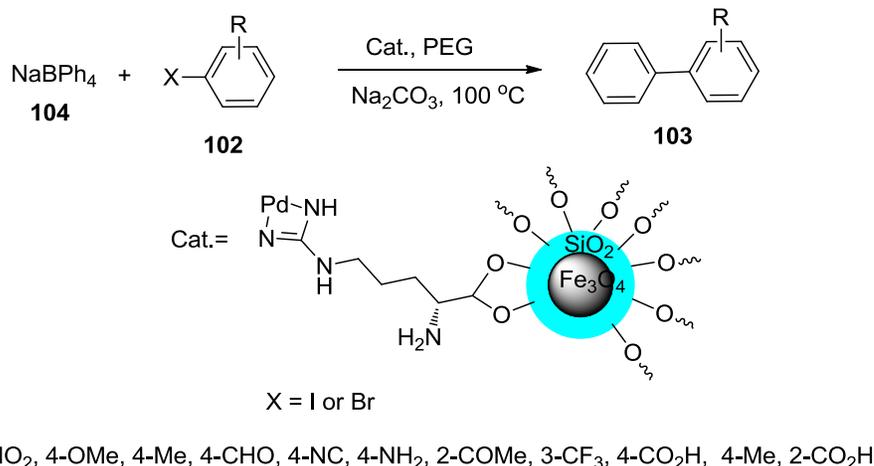
**Scheme 52.** General route for the fabrication of  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{L-arginine}@\text{Pd}(0)$  NPs.

**Applications.** Ghorbani-Choghamarani *et al.* developed  $\text{Fe}_3\text{O}_4@\text{SiO}_2@\text{L-arginine}@\text{Pd}(0)$  NPs as an organo-nanocatalyst and exploited its catalytic roles in C–C coupling reactions using phenylboronic acid (**101**) and aryl halides (**102**) as starting materials in polyethylene glycol (PEG) solvent (Schemes 53 and 54).<sup>101</sup>



R = 4- $\text{NO}_2$ , 4- $\text{OMe}$ , 4- $\text{Me}$ , 4- $\text{CHO}$ , 4- $\text{NC}$ , 4- $\text{NH}_2$ , 2- $\text{COMe}$ , 3- $\text{CF}_3$ , 4- $\text{CO}_2\text{H}$ , 4- $\text{Me}$ , 2- $\text{CO}_2\text{H}$

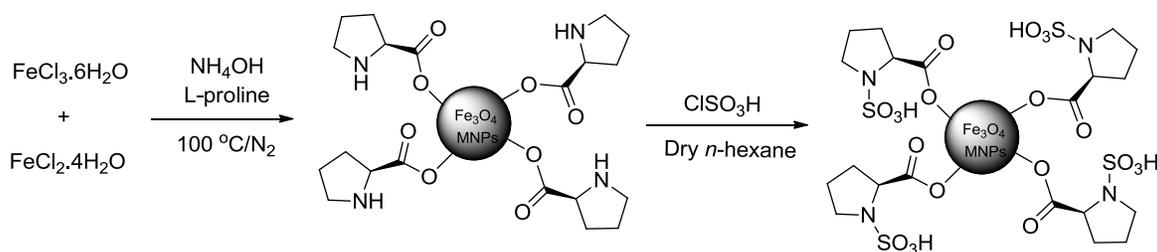
**Scheme 53.** General scheme for the Suzuki coupling reaction.



**Scheme 54.** Synthesis of biphenyl derivatives.

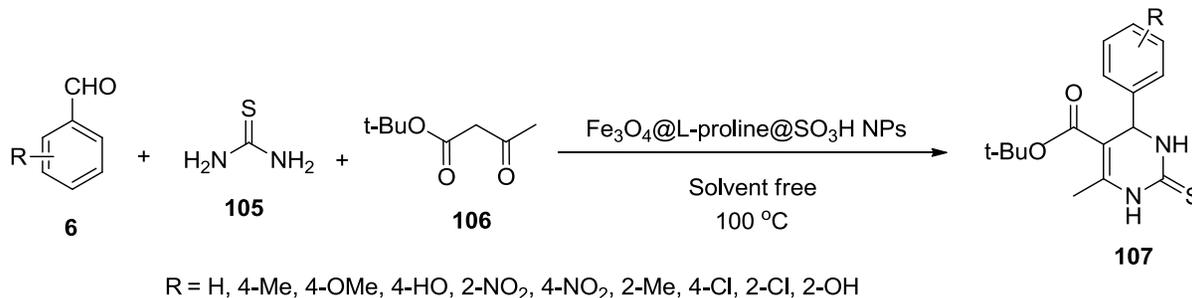
**5.2.7 Synthesis and applications of Fe<sub>3</sub>O<sub>4</sub>@L-proline@SO<sub>3</sub>H NPs. Synthesis.** Afradi *et al.* reported the synthesis of Fe<sub>3</sub>O<sub>4</sub>@L-proline@SO<sub>3</sub>H NPs as shown below.<sup>102</sup> An orange solution was obtained by mixing FeCl<sub>3</sub>·6H<sub>2</sub>O (4 mmol, 1.081 g) and FeCl<sub>2</sub>·4H<sub>2</sub>O (2 mmol, 0.398 g) in 150 mL of distilled water under N<sub>2</sub> atmosphere which was then stirred vigorously at 100 °C for 4 hours (approx.). Then, 0.8 g of L-proline and NH<sub>4</sub>OH (25 weight %, 15 mL) were added into the above solution until the pH was increased to 11 which formed a black suspension. The black solution was refluxed at 100 °C for 6 hours with vigorous stirring. Fe<sub>3</sub>O<sub>4</sub>@L-proline nanoparticles thus formed were isolated from the aqueous mixture using an external magnet, washed with distilled water until neutrality and eventually dried at 60 °C in vacuum for 24 hours.

A 250 mL suction flask was provided with a pressure-equalized dropping funnel. The gas vent was attached to a vacuum system via an adsorbing solution of alkali trap. Firstly, 1 g of Fe<sub>3</sub>O<sub>4</sub>@L-proline was placed into the flask and distributed in 10 mL of *n*-hexane by ultrasonic bath for 1 hour. Thereafter, 0.5 g of chlorosulfonic acid was added drop wise to a cooled (ice-bath) suspension of Fe<sub>3</sub>O<sub>4</sub>@L-proline NPs during an interval of time, approximately 30 minutes at room temperature. The resulting suspension was stirred for 90 minutes to eliminate the remaining HCl by suction. Finally, the L-proline *N*-sulfonic acid functionalized magnetic nanoparticles was isolated using an external magnet and washed with toluene (2 × 15 mL) and distilled water (2 × 10 mL) respectively, and dried in an vacuum oven at 60 °C (Scheme 55).



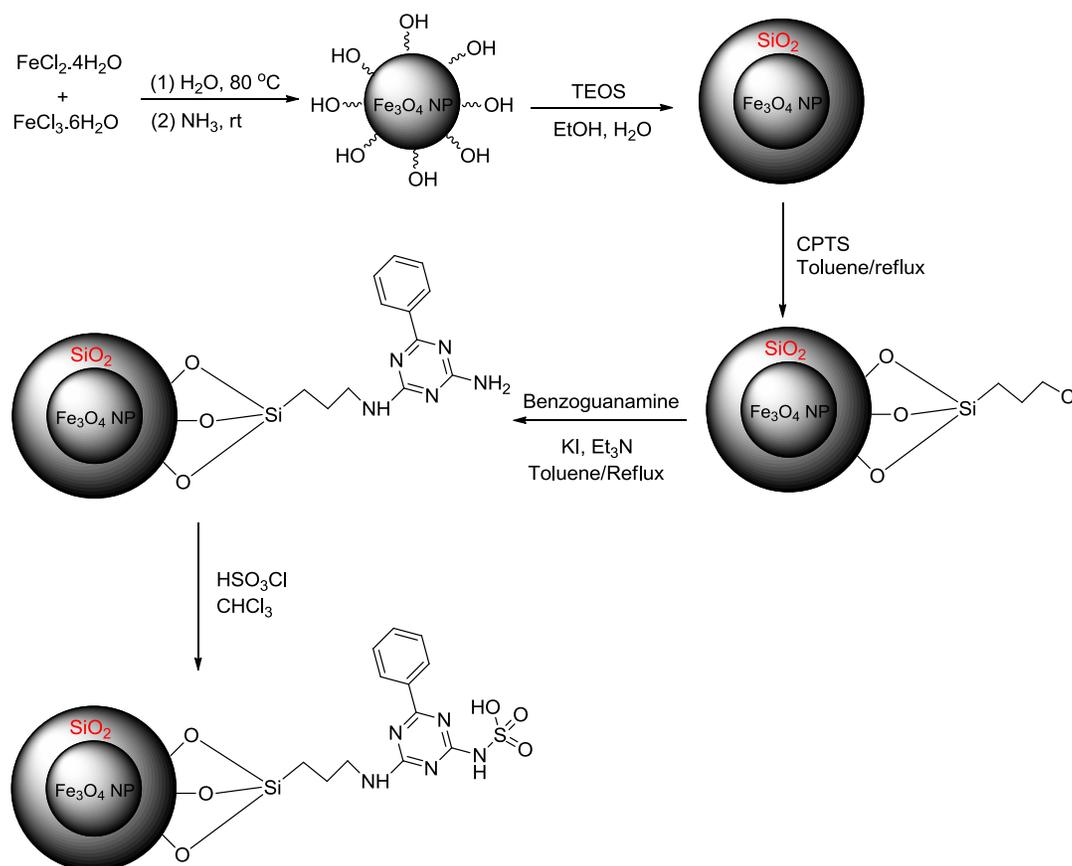
**Scheme 55.** Synthesis of Fe<sub>3</sub>O<sub>4</sub>@L-proline@SO<sub>3</sub>H NPs.

**Applications.** Using the prepared catalyst, he developed a synthetic protocol of 3,4-dihydropyrimidine-2(1*H*)-thiones (**107**) starting from aromatic aldehydes (**6**), thiourea (**105**) and *tert*-butyl 3-oxobutanoate (**106**) (Scheme 56).<sup>102</sup>



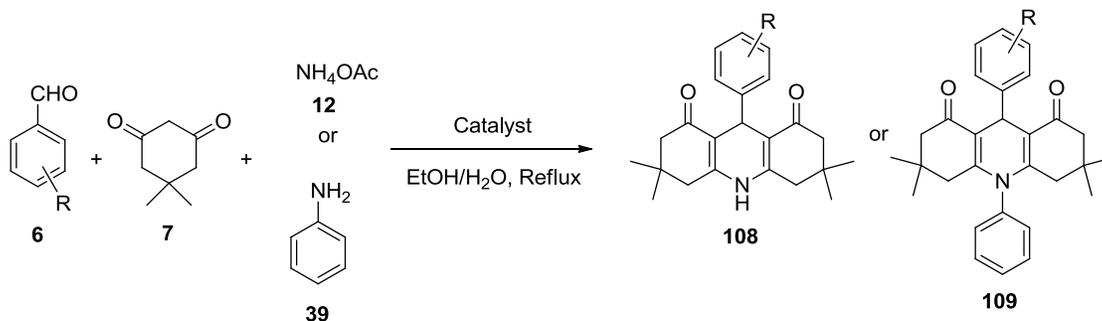
**Scheme 56.** Synthesis of 3,4-dihydropyrimidine-2(1*H*)-thiones.

**5.2.8 Synthesis and applications of Fe<sub>3</sub>O<sub>4</sub>@*N*-propyl-benzoguanamine-SO<sub>3</sub>H NPs. Synthesis.** The chloropropyl-modified silica-coated MNPs were prepared by Dehbalaei *et al.* according to a reported procedure.<sup>103</sup> To a magnetically stirred mixture of the prepared Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub> nanoparticles in toluene under reflux condition, CPTS (1 g) was added followed by benzoguanamine (10 mmol, 1.87 g) in presence of triethylamine (10 mmol, 1.39 mL) and the mixture was sonicated for 2 hours under N<sub>2</sub> atmosphere, and then stirred for 48 hours under reflux conditions. The obtained solid was magnetically collected from the solution and washed with water/ethanol (20:10 mL) three times and dried in vacuo for 5 hours. To a mixture of benzoguanamine-modified silica-coated Fe<sub>3</sub>O<sub>4</sub> MNPs (1 g) in dry CHCl<sub>3</sub> (3 mL), chlorosulfonic acid (ClSO<sub>3</sub>H, 1 mL) was added dropwise at 0 °C over 2 hours and then the mixture was filtered and washed with ethanol (5 mL) and dried at room temperature to afford Fe<sub>3</sub>O<sub>4</sub>@*N*-propyl-benzoguanamine-SO<sub>3</sub>H NPs (Scheme 57).



**Scheme 57.** Preparation of Fe<sub>3</sub>O<sub>4</sub>@*N*-propyl-benzoguanamine-SO<sub>3</sub>H NPs.

**Application.** Dehbalaei *et al.* investigated the use of the *N*-propyl-benzoguanamine-SO<sub>3</sub>H-stabilized magnetic nanoparticles in the synthesis of derivatives of 1,8-dioxodecahydroacridine (**109**) from aromatic aldehydes (**6**), dimedone (**7**) and ammonium acetate (**12**) or aniline (**39**) in ethanol-water medium under reflux (Scheme 58).<sup>103</sup>



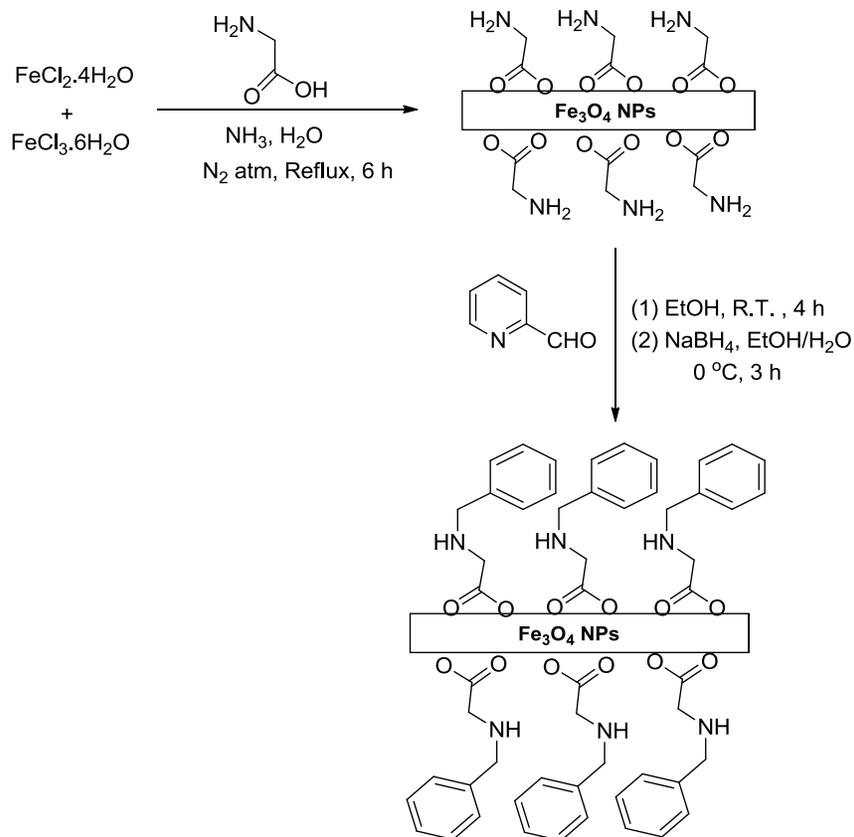
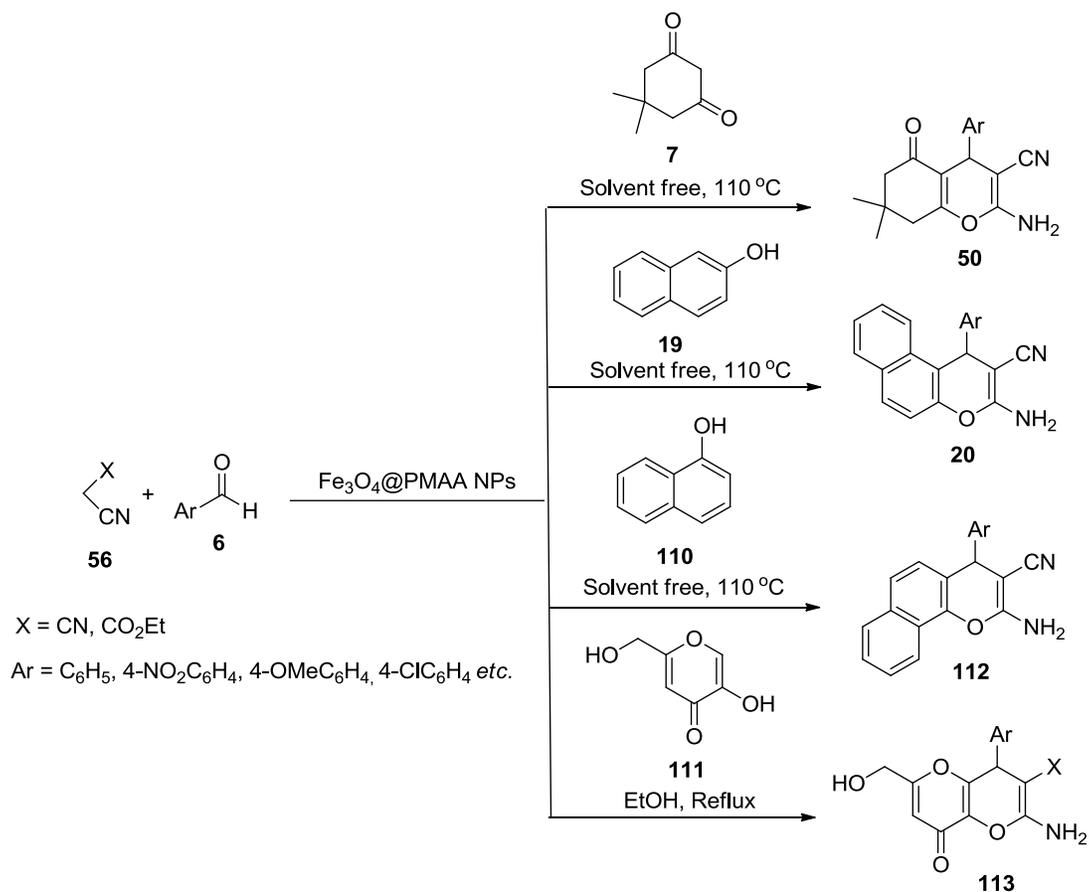
Catalyst = Fe<sub>3</sub>O<sub>4</sub>@*N*-propyl-benzoguanamine-SO<sub>3</sub>H NPs.

R = H, 4-Me, 4-CH(Me)<sub>2</sub>, 3-NO<sub>2</sub>, 4-NMe<sub>2</sub>, 3-OH, 2-NO<sub>2</sub>, 4-Cl, 2-Me, 3,4-(OMe)<sub>2</sub>

**Scheme 58.** Synthesis of derivatives of 1,8-dioxodecahydroacridine derivatives.

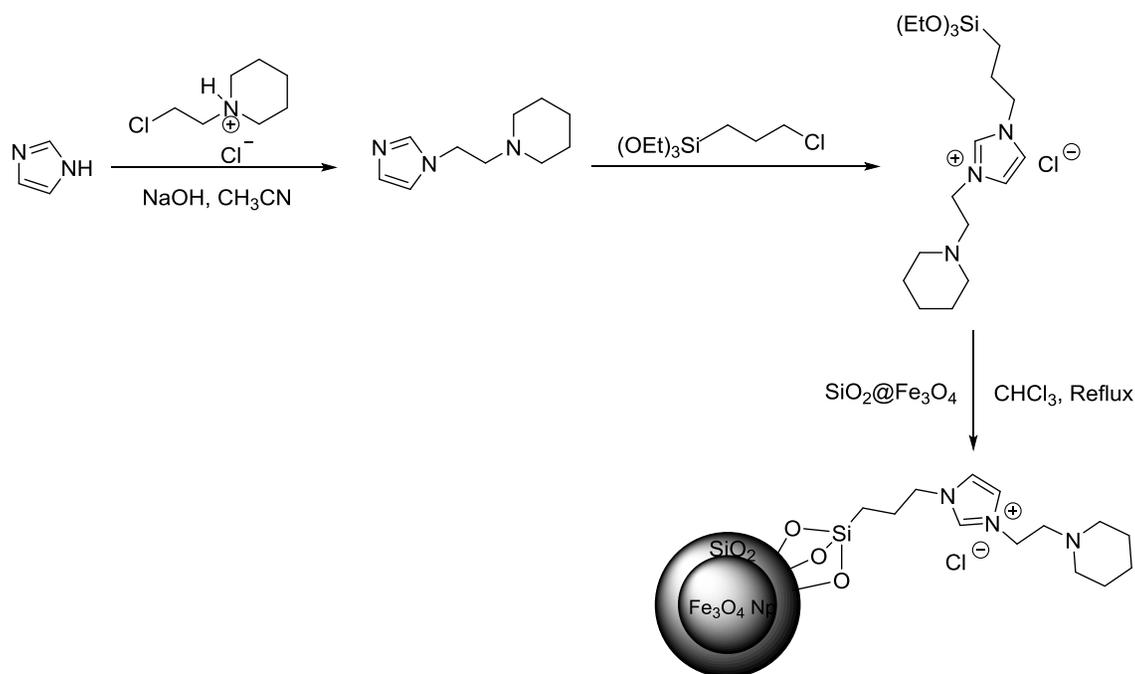
**5.2.9 Synthesis and applications of Fe<sub>3</sub>O<sub>4</sub>@PMAA NPs. Synthesis.** Eftekhari-Sis *et al.* developed Fe<sub>3</sub>O<sub>4</sub>@PMAA NPs for the first time.<sup>104</sup> To a pre-heated mixture of FeCl<sub>3</sub>·6H<sub>2</sub>O (4.8 mmol, 1.3 g) and FeCl<sub>2</sub>·4H<sub>2</sub>O (2.4 mmol, 0.48 g) in 20 mL of deionized water at 40 °C, glycine (6.1 mmol, 0.46 g) was added and the pH was adjusted to 11 using ammonia solution, and refluxed for 6 hours under N<sub>2</sub> atmosphere. By separation of the obtained precipitate using an external magnetic field and then washing with deionized water, and drying in oven at 60 °C for 3 hours, glycine grafted Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles were obtained. 0.25 g of glycine capped Fe<sub>3</sub>O<sub>4</sub> magnetic nanoparticles was dispersed in 10 mL EtOH using ultrasonic bath, and then pyridine-2-carbaldehyde (3.74 mmol, 0.4 g) was added and the mixture was stirred at room temperature for 4 hours. After cooling, the mixture to 0-4 °C using an ice bath, a solution of NaBH<sub>4</sub> (3.65 mmol, 0.138 g) in 5 mL water was added and was stirred for 3 hours at the same temperature. The obtained PMAA-Fe<sub>3</sub>O<sub>4</sub> NPs were separated using an external magnetic field and thoroughly washed with deionized water, and dried in oven at 60 °C for 3 hours (Scheme 59).

**Applications.** Eftekhari-Sis then developed an efficient protocol to synthesize a variety of chromene or pyran derivatives (**50**, **20**, **112**, **113**) using 2-[(2-pyridylmethyl)amino]acetic acid functionalized Fe<sub>3</sub>O<sub>4</sub> superparamagnetic nanorods as an efficient catalyst (Scheme 60).<sup>104</sup>

Scheme 59. Synthesis of  $\text{Fe}_3\text{O}_4$ @PMAA NPs.

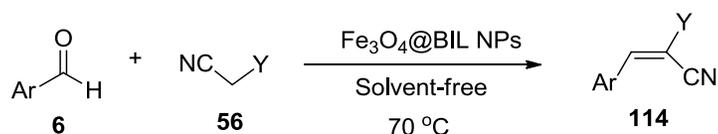
Scheme 60. Synthesis of a variety of chromene or pyran derivatives.

**5.2.10 Synthesis and applications of Fe<sub>3</sub>O<sub>4</sub>@BIL NPs. Synthesis.** Fe<sub>3</sub>O<sub>4</sub>@BIL (basic ionic liquid) NPs were prepared as follows. **Synthesis of BIL.** Imidazole (7.5 g, 110 mmol) was molten at 100 °C and then NaOH (4.0 g, 100 mmol) was added with vigorous stirring for 30 minutes. After removal of water under reduced pressure, a light yellow solid was obtained. Subsequently, 1-(2-chloroethyl)piperidine hydrochloride (9.2 g, 50 mmol) and acetonitrile (70 mL) were added. The mixture was then stirred at 80 °C for 10 hours and filtered. The filtrate was concentrated under reduced pressure, the obtained residue was dissolved in 100 mL of dichloromethane and extracted with water to remove inorganic salts and excess of imidazole. **Synthesis of BIL@MNPs.** 1.0 g of SiO<sub>2</sub>@Fe<sub>3</sub>O<sub>4</sub> nanoparticles were dispersed in 50 mL of chloroform by sonication. A chloroform solution of BIL (1.0 g/50 mL) was then added, and the mixture was refluxed for two days under nitrogen atmosphere. After cooling to room temperature, the target product BIL@MNPs were collected by a permanent magnet and rinsed thrice with chloroform (30 mL), and then dried under vacuum overnight (Scheme 61).<sup>105</sup>



**Scheme 61.** The synthetic route for Fe<sub>3</sub>O<sub>4</sub>@BIL NPs.

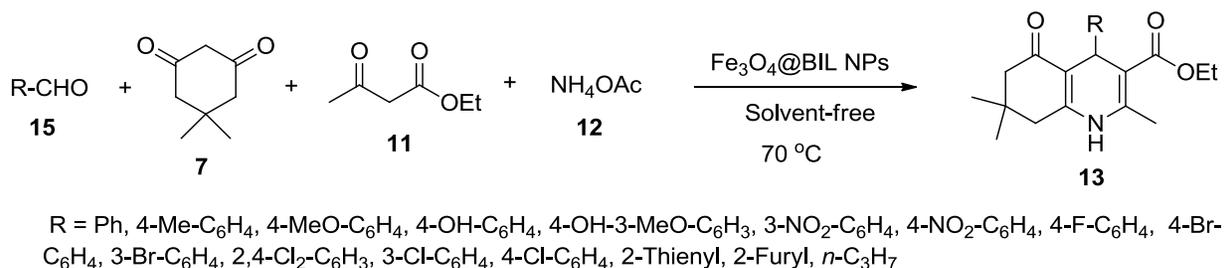
**Applications.** Zhang *et al.* reported the unsymmetrical Hantzsch reaction and Knoevenagel condensation in the presence of Fe<sub>3</sub>O<sub>4</sub>@BIL NPs as a reusable catalyst (Schemes 62 and 63). The Knoevenagel condensation involved a mixture of aromatic aldehyde (**6**) and activated methylene compounds (**56**) to afford the corresponding acrylate derivatives (**114**).<sup>105</sup>



Ar = 4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>, 3-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>, 4-Cl-C<sub>6</sub>H<sub>4</sub>, 4-F-C<sub>6</sub>H<sub>4</sub>, 4-Br-C<sub>6</sub>H<sub>4</sub>, 4-Me-C<sub>6</sub>H<sub>4</sub>, 4-OH-3-MeO-C<sub>6</sub>H<sub>3</sub>, 2-Furyl, Ph,  
3-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>, 4-MeO-C<sub>6</sub>H<sub>4</sub>  
Y = CN, CO<sub>2</sub>Et

**Scheme 62.** The Knoevenagel condensation by Fe<sub>3</sub>O<sub>4</sub>@BIL NPs.

Zhang *et al.* also reported the synthesis of polyhydroquinolines (**13**) from a mixture of aldehydes (**15**), dimedone (**7**), ethyl acetoacetate (**11**) and ammonium acetate using Fe<sub>3</sub>O<sub>4</sub>@BIL NPs as a catalyst (**12**).<sup>105</sup>



**Scheme 63.** Synthesis of tetrahydroquinolin-5(1*H*)-ones.

## 6. Conclusions

Over the past few years, ferrite-core organo-nanocatalysts have been exploited extensively in the synthesis of wide varieties of organic compounds, thus facilitating their easy magnetic separation and recyclability. Organo-nanocatalysis plays a central role in both the academic as well as industrial research and development. Industrial impact of nanocatalysis is clearly reflected by the increasing number of nanocatalysis related patents, technologies and products in the market. Size and shape controlled preparation of metal nanoparticles followed by coating with organic moieties are very promising for greener heterogeneous catalytic reactions. On the basis of better understanding of size and shape effects of the nanoparticles and their interactions with support materials or stabilizing agent, today it is very promising that scientists are able to solve current environmental, social and industrial problems. Thus, we hope this review will provide a brief information about organo-nanocatalysis and also inspire research and development in this field.

## 7. Acknowledgements

The author N. Rahman is grateful to the members of the research group of Dr. R. L. Nongkhaw, Associate Professor, Centre for Advanced Studies in Chemistry, Department of Chemistry, North-Eastern Hill University, Shillong, Meghalaya for stimulating discussions and suggestions.

## 8. Abbreviations

R.T. : room temperature

h : hour(s)

g : Gram(s)

mL : Millilitres

°C : Degree Celsius

Me : Methyl

Ph : Phenyl

Et : Ethyl

Bu : Butyl

Bz : Benzoyl

MCRs : Multi-component reactions

EtOH : Ethanol

TON : Turn over number

TEOS : Tetra ethyl ortho silicate

VMNP : Vinyl magnetic nanoparticles

TOF : Turn over frequency

)))) : Ultrasonication

MWI : Microwave irradiation

NPs : Nanoparticles

MNPs : Magnetic nanoparticles

Fe<sub>3</sub>O<sub>4</sub>@chitosan NPs : Chitosan functionalized ferrite nanoparticles

Fe<sub>3</sub>O<sub>4</sub>@chitosan-Ag NPs : Chitosan-Silver functionalized ferrite nanoparticles

cm-chitosan@Fe<sub>3</sub>O<sub>4</sub> NPs : Carboxymethyl chitosan functionalized ferrite nanoparticles

CNTs : Carbon nanotubes

chitosan-MCNTs : Chitosan-carbon nanotubes functionalized magnetic carbon nanotubes

Fe<sub>3</sub>O<sub>4</sub>@L-proline NPs: L-proline functionalized ferrite nanoparticles

Fe<sub>3</sub>O<sub>4</sub>@glutathione NPs : Glutathione functionalized ferrite nanoparticles

Fe<sub>3</sub>O<sub>4</sub>@L-cysteine NPs : L-cysteine functionalized ferrite nanoparticles

Fe<sub>3</sub>O<sub>4</sub>@guanidine NPs : Guanidine functionalized ferrite nanoparticles

Fe<sub>3</sub>O<sub>4</sub>@mesoporous SBA-15 NPs : Mesoporous SBA-15 functionalized magnetic nanoparticles

Fe<sub>3</sub>O<sub>4</sub>@PPCA NPs : Piperidine-4-carboxylic acid functionalized ferrite nanoparticles

Fe<sub>3</sub>O<sub>4</sub>@Irish moss NPs : Irish moss functionalized ferrite nanoparticles

Fe<sub>3</sub>O<sub>4</sub>@L-arginine NPs : L-arginine functionalized ferrite nanoparticles

Fe<sub>3</sub>O<sub>4</sub>@cellulose NPs : Cellulose functionalized ferrite nanoparticles

CPTS : (3-chloropropyl)trimethoxysilane

Fe<sub>2</sub>O<sub>3</sub>@SiO<sub>2</sub>@vit. B<sub>1</sub> NPs : Vitamin B<sub>1</sub> functionalized ferrite-silica nanoparticles

Fe<sub>3</sub>O<sub>4</sub>@L-arginine : L-arginine functionalized ferrite nanoparticles

Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@DDBSA NPs: Dodecyl benzenesulfonic acid functionalized ferrite-silica nanoparticles

Fe<sub>3</sub>O<sub>4</sub>@PPCA@Pd(0) : Palladium coated ferrite@piperidine-4-carboxylic acid nanoparticles

Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@L-proline NPs : L-proline functionalized Fe<sub>3</sub>O<sub>4</sub> nanoparticle

Fe<sub>3</sub>O<sub>4</sub>@GA NPs : Gluconic acid immobilized Fe<sub>3</sub>O<sub>4</sub> nanoparticles

Fe<sub>3</sub>O<sub>4</sub>@GSA NPs : Glucosulfonic acid functionalized ferrite nanoparticles

Fe<sub>3</sub>O<sub>4</sub>@PMAA : Ferrite@2-[(2-pyridylmethyl)amino]acetic acid functionalized ferrite nanoparticles

Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@L-cysteine NPs : L-Cysteine-functionalized ferrite-silica nanoparticles

Fe<sub>3</sub>O<sub>4</sub>@SiO<sub>2</sub>@L-arginine@Pd(0) : Palladium coated L-arginine functionalized ferrite-silica nanoparticles

Fe<sub>3</sub>O<sub>4</sub>@L-proline@SO<sub>3</sub>H NPs : L-proline-sulfonic acid-functionalized ferrite nanoparticles

Fe<sub>3</sub>O<sub>4</sub>@BIL NPs : Basic Ionic Liquid nanoparticles functionalized ferrite nanoparticles

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