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ADVANCES AND PERSPECTIVES OF FE METAL NANOPARTICLES SYNTHESIZED IN IONIC LIQUID AND THEIR APPLICATIONS

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ABSTRACT:

Green chemistry and Sustainable development in the field of synthetic organic chemistry is central in the advancement of environmentally friendly strategies towards the synthesis of molecules of commercial and biological relevance. There are large numbers of efficient methodologies have already been disclosed under the guidelines of green and sustainable chemistry. However, as a novel catalytic system i.e metal nano-particles in ionic liquids have recently been gaining popularity as a state-of-the-art solution for organic transformations. Metal nano-particles in ionic liquids offers miraculous promises as it is an exceptional catalytic system that have a potential to replace the conventional methods of organic synthesis, and besides that are found labile in the field of pharmaceutics, biochemistry, molecular biology, and process and technology as well. In this review, our aim is to investigate the recent developments in the synthesis of fe metal nanoparticles synthesized in ionic liquid which refers to the catalytic system, of choice, and offers exceptional functional group tolerance as well as delivers highly specific organic transformations which provides considerably improved eco-friendly, cost effective and sustainable alternatives to the conventional catalytic processes.

Keywords: Metal nanoparticles, ionic liquids, green and sustainable development, catalytic system.

1. INTRODUCTION

The myriad applications of nanomaterials have led to increasing demand in the chemical industry. Hence, quite a large number of chemicals, for instance solvents, raw materials, reagents, and template materials, have successfully been utilized for the production of nanomaterials. In addition, it has been evidenced that the creation of toxic or hazardous intermediates and products, as well as chemical wastes has increased through the chemical transformation which are aiming to prepare desirable chemicals. In order to control or reduce or eliminate the generation of undesirable products and to minimize the use of hazardous materials in chemical processes, the concept of green and sustainable development in chemistry was introduced to chemical science and industry. [i-ii]

In this context, catalysis is considered as a foundation pillar of green chemistry, playing, for instance, a central role in biological and industrial processes. Initially, catalysis has been divided into homogeneous and heterogeneous reactions, and scientific communities have been glazed around these aspects of catalysis. The introduction of nanosciences has now boosts the efficacy of the organic transformations by altering conventional catalytic strategies with nano-catalysis. Nanocatalyst of size one to only a few nanometers offer the best catalytic efficiency[iii]. In his comprehensive book entitled Inorganic Chemistry by Atkins and Shriver have an excellent account of the development in the field of nanoscience. In accordance with the Atkins classic Nature discloses the original version of nanotechnology very elegantly, she tuned organisms in such a way that they can developed an ability to build up molecular devices by integrating light and matter on an atomic scale for specific life governing functions, such as reproduction, storing information, and moving about. DNA the primary metabolite associated with the key life governing processes is an ultimate nanomaterial, it having its own mechanism to store information as sequence of base pairs. In the next, the process of photosynthesis is another crucial example of Nature’s biological nanotechnology, where nanostructural machines are very aptly exploited to absorb appropriate wavelength of radiation, easily separates an electrical charge for the conversion of solar energy into chemical energy for the biological transformations. Noticeably, human beings have been practiced nanotechnology for centuries as a science of colloids, and utilize gold and silver salts have to colour the glass[iv].

In this context, the use of transition-metal nanoparticles in catalysis[iii-v-xviii] have widely been exploited in the organic transformations where high selectivity is required, mechanistically nanoparticles in catalysis offers activation of metal surface and emerges high efficiency to the heterogeneous catalysis. Transition-metal nanoparticles are the clusters which comprises of few tens to several thousand metal atoms, have been stabilized by ligand surroundings, additionally, additives like surfactants, polymers or dendrimers provides a protective shield to their surfaces. This approach is also pertinent to homogeneous catalysis, because in homogeneous catalysis there is a full continuum in between small and large metal clusters, and the latter is referred as colloids, sols or nanoparticles. Nanoparticles can be tuned as catalysts in homogeneous systems or can be heterogenized by coating them onto a heterogeneous support such as silica, alumina, other oxides or carbon. Thus, the field of nanoparticle catalysis bridges both the homogeneous and heterogeneous catalysis, and sometimes referred as “semi-heterogeneous”. The field of nanoparticle catalysis has been attracted a substantial attention in recent times, as confirmed by the rapidly increasing number of publications in the form of reviews, research articles, books and monographs. Nanoparticle catalysis, there selectivity, efficiency, and recyclability is responsible for their exploration as green catalysts in number of catalytic transformations.

Recently, modern transition-metal nanoparticles have been differentiated from classical colloids on the basis of their size and stability in the solution and several other respects[iii-xix]. Generally, in number of cases transition-metal nanoparticles are found in 1-10 nm in diameter and exhibit quite a narrow size compared with the classical colloids, which are typically > 10 nm in diameter. Metal nanoparticle of such a small size exhibits unique set of properties that are primarily grounds on their characteristic large surface-to-volume ratio and quantum size effect[iii,xx-xxi]. Additionally, the well-defined compositions of transition-metal NPs have had a significant impact on their isolation, stability and re-producibility, and in fact, are the key points that separated them from classical colloids. It is to be noted that the transition-metal nanoparticles are kinetically stable species and the reason behind this is the formation of bulk metal is thermodynamically favorable. It is also anticipated that the process of agglomeration of metal nanoparticle is solvent dependent phenomenon have played a crucial role in the formation of stable and uniform sized metal nanoparticles. In this regards, the use of water -

soluble polymers, quaternary ammonium salts, surfactants, or polyoxoanions is highly appreciated for the stabilization of nanoparticles in the solution via electrostatic and/or steric protection[iii,xxii-xxv].

One of the most widely studied stabilizing agents is belonging from the family of quaternary ammonium salts for soluble transition-metal nanoparticle catalysts[xxvi-xxxiii]. In the 1975 Osteryoung and his co-workers pioneered the field of ionic liquids by synthesizing first ionic liquid i.e. N-butylpyridinium chloride for their electrochemical applications[xxxiv]. Thereafter, Yves Chauvin in the 1990s for the first time introduced ionic liquids in catalytic applications [xxxv] and have received considerable attention in this field[xxxvi-xxxvii]. Ionic liquids are very precisely defined by Wilkes as a salt, having melting point at or below 100^0C [xxxviii]. In addition to that, the physicochemical properties of ionic liquids are highly tunable and are depending upon the composition[xxxix]. It is also noticeable that ionic liquids are considered as supramolecular material after water, these innovative fluids offers an exceptional set of structure related properties, primarily, for instance, their relatively low or negligible vapour pressure, non-inflammability, non-combustibility, high thermal stability, relatively low viscosity, wide temperature range for the liquid state and appreciable ionic conductivity as well[xl-xlii]. These characteristic features of ionic liquid are the key reason for their exploitation in every domain of modern day science, for instance, in organic transformations as solvent[xliii-xlvi], in polymer formulations as stabilizer or plasticizer[xlvii-xlix], in pharmaceuticals[l], in petroleum[li], and many more as environment friendly alternatives to the volatile organic solvents. In addition to that, ionic liquids in the field of organometallics are considered as a favorable media for the electrostatic stabilization of pre-formed metal nanoparticles at room temperature[lii-lxii]. Work in the combined areas of nanoscience or nanotechnology and ionic liquids has thus been multidisciplinary as well as diverse in scope.

LITERATURE REVIEW

This review aims to introduce this broad field, highlighting the importance of organic chemistry in the multidisciplinary research directed towards understanding the nature of nanomaterials in ionic liquids.

Synthesis of Fe Nanoparticles in Ionic Liquids:

Nanoparticles of iron oxide opened up a wide range of striking potentials in the field of science of materials as well as biomedicine. It has been evident that due to the miniscule size, nanomaterials exhibit different set of physical, chemical, and biological properties when compared with their larger, microscale, and macroscale counterparts. As the global nano revolution is taking in consideration, the nanoparticles of iron oxide have exploited for the treatment of polluted waters. These nanoparticles exhibit remarkable magnetic properties and are considered as magnetic nanoparticles, and magnetic iron oxide nanoparticles can also be effectively actuated by external magnetic fields and are promising for their further exploitations. It is therefore of great interest for the scientists to explore the solvent properties of ionic liquids to access these privileged nanomaterials.

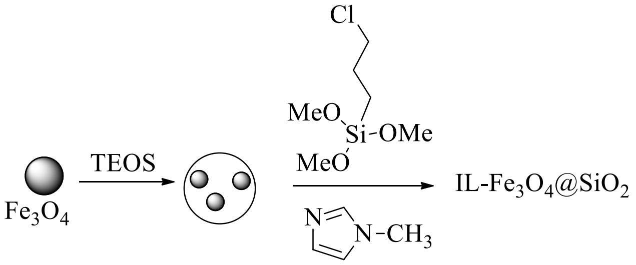
To address this issue, Sundrarajan *et al.* developed method for the synthesis Fe_3O_4 nanoparticles by coprecipitation technique using [BMIM][TfO] ionic liquid and ferrous sulfate heptahydrate as a metal precursor in alkaline solution of NaOH at pH 11[lxiii].

[BMIM][TfO] ionic liquid was used as the solvent and stabilizer to efficiently tune the particle formation, to prevent the inter-particle aggregation and to regulate the shape of the iron oxide nanoparticles. dispersive nanoparticles with the average size about 35nm. These nanoparticles are moderately uniform and appear as cubic structure. The shape and size controlled product is able to synthesize using the [BMIM][TfO] ionic liquid owing to its large surface activity, and the reactants could disperse in ionic liquid which forms a lot of petite reactors. Room temperature ionic liquids have high polarity and interfacial tension which made the inorganic species to higher nucleation rate, which thrusted the formation of the nanoparticles.

$$FeSO_4 . 7\,H_2O \xrightarrow[\text{NaOH, }70^0\text{ C, pH 11}]{[BMIm][OTf]} Fe_3O_4$$

Scheme (1): Synthesis of magnetite nanoparticles using 1-n-butyl-3-methylimidazolium trifluoromethane sulfonate [BMIM][TfO] ionic liquid

A novel method for pathogenic bacteria identification directly from blood samples by cationic ionic liquid-modified magnetic nanoparticle (CILMS) was reported[lxiv]. The magnetic nanoparticles were prepared by co-precipitation and the core-shell $Fe_3O_4@SiO_2$ nanoparticles were prepared by the sol-gel process, followed by the grafting of 3-chloropropyltrimethoxysilane that was reacted further with N-methylimidazole to form cationic ionic liquid-modified $Fe_3O_4@SiO_2$ magnetic nanoparticles (CILMS).



Scheme (2): Synthesis of the cationic ionic liquid-modified $Fe_3O_4@SiO_2$ magnetic nanoparticle (CILMS)

Liu *et al.* (2013) fabricated a novel and effective IL-assisted solvothermal method for the synthesis of nanoparticle assembled Fe_3O_4 nanoflakes using $[C_{16}mim]Cl$ (1-hexadecyl-3-methylimidazolium chloride) as a template[lxv]. Moreover, it is found that the morphology of the product exerts a remarkable effect on its magnetic property. Nanoparticle-assembled Fe_3O_4 nano-flakes with a uniform morphology and good dispersity have been synthesized. $[C_{16}mim]Cl$ plays an important part in controlling the shape of the Fe_3O_4 nanoflakes. The product has a special magnetic property, which may be beneficial for overcoming the ‘‘superparamagnetic limit’’ of Fe_3O_4 nanostructures.

$$\begin{array}{c} FeCl_2 . 4\,H_2O \\ + \\ N_2H_4 . H_2O \end{array} \xrightarrow[\substack{\text{Water - glycerol,} \\ 180^0\text{ C, 24h}}]{[C_{16}MIm]Cl} Fe_3O_4$$

Scheme (3): Schematic illustration of the formation process of the Fe_3O_4 nanoflakes.

Liu *et al.* modified the surface of Fe_3O_4 silica magnetic nanoparticles using ionic liquid 1-octadecyl-3-methylimidazoliumbromide ($C_{18}mimBr$) and methyl orange (MO) by hydrothermal method[lxvi]. Ionic liquid 1-hexadecyl-3-methylimidazolium chloride ($[C_{16}mim]Cl$) stabilized Fe_3O_4 nanoparticles. The saturation magnetization of the particles (Ms = 67.69 emu/g) is lower than that of bulk magnetite (92 emu/g), which can be explained by a larger number of lattice defects in the NPs with smaller sizes. Compared with some other superparamagnetic Fe_3O_4 NPs, the $[C_{16}mim]$ Cl-stabilized Fe_3O_4 NPs possess relatively high saturation magnetization, which is benefit for their application. Finally, the Fe_3O_4 NPs retain no permanent magnetism once the field is removed.

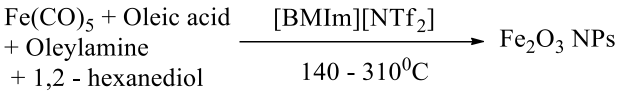
$$\begin{array}{c} FeCl_2 .4H_2O \\ + \\ N_2H_4 .H_2O \end{array} \xrightarrow[\substack{C_6H_5Na_3O_7 .2H_2O \\ 150^0\text{C,12h}}]{[C_{16}MIm]Cl} Fe_3O_4$$

Scheme (4): Synthesis of the ionic liquid-modified Fe_3O_4 nanoparticles.

Absalan *et al.* developed route for synthesis of iron nanoparticle using ionic liquid BTDABCOCl[lxvii]. To estimate the amount of ionic liquid deposited onto the surface of Fe_3O_4, the thermogravimetric analysis (TGA) of Fe_3O_4 and IL-Fe_3O_4 was conducted. In the lower temperature range (up to 201^0 C), the initial weight loss was not observed. The weight loss of IL-Fe_3O_4 nanoparticles occurred in the temperature range of 201–261^0C was due to the decomposition of ionic liquid. At temperatures above 261^0C, the ionic liquid was completely decomposed. The residual weight should be the weight of Fe_3O_4. According to the TGA curves, the ionic liquid content of IL-Fe_3O_4 nanoparticles was evaluated to be 5.82% by weight.

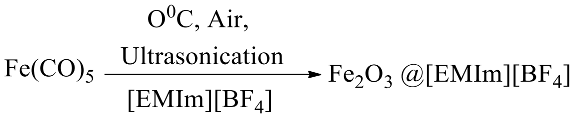
Scheme (5): Synthesis of Fe_3O_4 magnetic nanoparticles using ionic liquid as modifier

Wang *et al.* utilized 1-butyl-3-methylimidazolium bis(triflylmethyl-sulfonyl) imide ([BMIM][Tf_2N]) ionic liquids as solvents for controlling the size and shape of nanomaterials[lxviii].



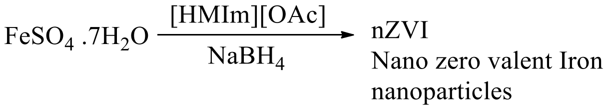
Scheme (6): Synthesis of Fe_3O_4 magnetic nanoparticles in 1-butyl-3-methylimidazolium bis(triflylmethyl-sulfonyl) imide ([BMIM][Tf2N]) ionic liquid.

Zhang *et al.* demonstrated synthesis of Fe_2O_3@[EMIm][BF4]) in IL in air by ultrasonic decomposition method[lxix]. Ionic liquids (ILs)-stabilized iron oxide (Fe_2O_3) nanoparticles were synthesized by the ultrasonic decomposition of iron carbonyl precursors in [EMIm][BF4] without any stabilizing or capping agents.



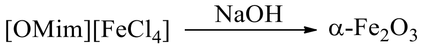
Scheme (7): Synthesis of iron oxide nanoparticles in [EMIm][BF4].

Zarif *et al.* attempted to produce Fe (0) nanoparticles by reduction of $FeSO_4$ .7 H_2O using $NaBH_4$[lxx]. And modified by mechanically grinding for 30 min adding the protic IL 1-H-3-Methylimidazolium acetate [HMIM][OAc] in the pestle-mortar. A similar procedure was employed for synthesis of ionic liquid coated bismuth doped nano Zero-valent Iron (BinZVI). Resulted nanoparticles were used for optical determination of H_2O_2.



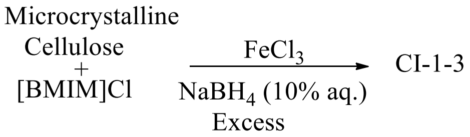
Scheme (8):Synthesis of Nano zero valent Iron nanoparticles (nZVI)

Xu *et al.* designed synthesis of α-Fe_2O_3 hollow microspheres in presence of metal ion-containing reactable ionic liquid 1-octyl-3-methylimidazolium tetrachlorideferrate(III) ([Omim]$FeCl_4$) under the solvothermal condition[lxxi].



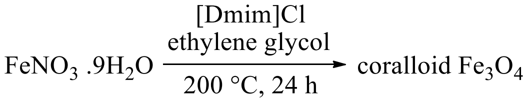
Scheme (9): α-Fe_2O_3 hollow microspheres in the presence of metal ion-containing
reactable ionic liquid 1-octyl-3-methylimidazolium tetrachlorideferrate(III) ([Omim]FeCl4)

Sharma *et al.* reported method of reductive coprecipitation of cellulose from ionic liquid ([BMIM]Cl)-water binary mixture and $FeCl_3$ to form Microcrystalline cellulose immobilized zerovalent iron nanoparticles (CI-1-3)[lxii]. The iron content of the CI-1-3 were analyzed using phenanthroline method. The size of the nZVI particles lie in the range of 20–100 nm and were spherical in shape.



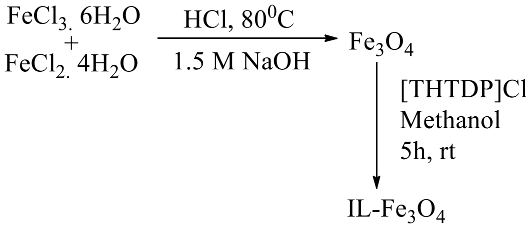
Scheme (10): Synthesis of microcrystalline cellulose immobilized nZVI.

Sun *et al.* grafted Coralloid Fe_3O_4 nanoclusters ionic liquid 1-n-decyl-3-methylimidazolium chloride ([DMim]Cl by solvothermal method[lxiii].



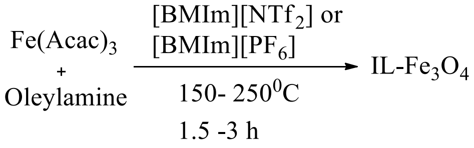
Scheme (11): Synthesis of coralloid Fe_3O_4 nanoclusters stabilized by 1-n-decyl-3-methylimidazolium chloride ([Dmim]Cl) ionic liquid.

Pillai *et al.* developed an efficient trihexyltetradecylphosphonium chloride ionic liquid modified Fe_3O_4 NPs by coprecipitation method[lxxiv]. And further used for fluoride removal from groundwater.



Scheme (12): Synthesis of iron oxide nanoparticles

Oliveira *et al.* synthesized magnetic nanoparticles by thermal decomposition of $Fe(Acac)_3/M(Acac)_2$ using (1-n-butyl-3-methyl imidazolium bis (trifluromethyl sulfonyl) imide, BMI.NTf_2 & (1-n-butyl-3-methyl imidazolium hexafluorophosphate) BMI.PF_6 ionic liquids and oleylamine[lxxv]. Due to monolayer coating by oleylamine, nanoparticles generate stable dispersions in non-polar solvents. By adjusting the reaction temperature and time using ionic liquid growth of nanoparticles controlled.



Scheme (13): Synthesis of magnetic nanoparticles using [BMI]NTf_2 (1-n-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) or [BMI]PF_6 (1-n-butyl-3-methylimidazolium hexafluorophosphate) ionic liquids

Hu *et al.* reported facile process for preparation of monodisperse magnetite nanoparticles using [Bmim][BF_4] as MW absorber, stabilizing agent and as recycling solvent in reaction[lxxvi]. In their work, Fe_3O_4 obtained by two methods. In first method by using $Fe(Acac)_3$ + 1,2-hexane diol in presence of oleic acid using under MW heating & in second method using $Fe(Acac)_3$ +1,2-hexane diol in presence of oleic acid using dibenzyl ether under oil bath. Both these experiment resulted in a viscous red brown mixture which was difficult to purify & characterize. Fe_3O_4 obtained from reaction mixture of Fe $(Acac)_3$ +1,2-hexane diol in presence of oleic acid and oleylamine by controlled MW heating. The reaction produces upper black & lower red –brown ppt. in the vial, precipitation was difficult to purify and characterize. Only upper black portion produces small quantity of Fe_3O_4 nanoparticles. Dibenzyl ether with lower dielectric const. (Ɛ=3.86) and non-polar solvent so addition of [Bmim] [BF_4] makes the non-polar solvent suitable for MW heating.

$$\begin{array}{l}\text{Fe(acac)}_3 + \text{1,2-hexanediol in} \\ \text{dibenzyl ether + Oleic acid} \\ \text{+ Oleyamine + BMim.BF}_4\end{array} \xrightarrow[25^0\text{C, 5 min}]{\text{MW Heating}} \text{Fe}_3\text{O}_4 \text{ NPs}$$

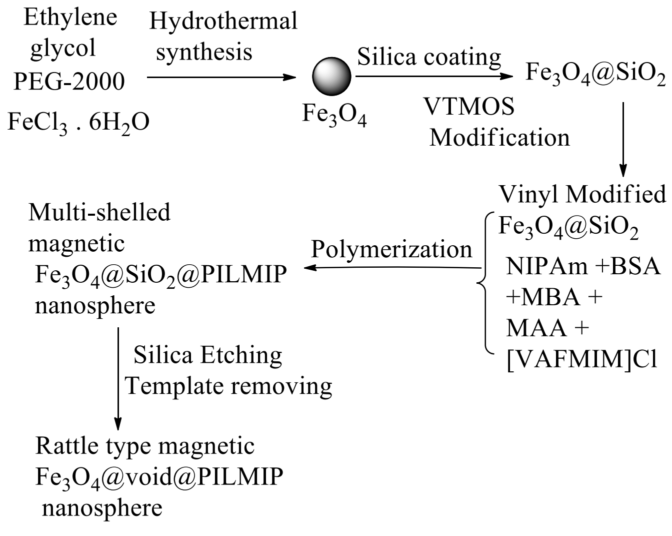
Scheme (14): microwave-assisted synthesis of monodisperse magnetite nanoparticles in ionic liquid [Bmim] [BF_4].

Lee *et al.* in their work fabricated IL coated iron oxide nanoparticles by the thermal decomposition of $Fe(CO)_5$ in an IL/DMF mixture solvent system[lxxvii]. To investigate the role of IL, they carried out synthesis of M-NPs by taking different proportions of [omim] [BF_4] and DMF solvent. They conclude that, both solvents were essential to form nanoparticles and no nanoparticles were formed in ionic liquid alone or DMF. In 1:3 proportion of IL/DMF anisotropic wire like nanoparticles were formed. The IL [Omim][BF_4] acts as stabilizer and shape regulator. Afterward they studied effect of chain length on shape of nanoparticles. On changing the alkyl chain length different shape nanoparticles were formed. The resulted nanoparticles showed a good super magnetic behavior.

$$\text{Fe(CO)}_5 \xrightarrow[\text{[OMim][BF}_4\text{]/DMF}]{90^0\text{C, 1h}} \text{Fe}_2\text{O}_3\text{@[OMim][BF}_4\text{]}$$

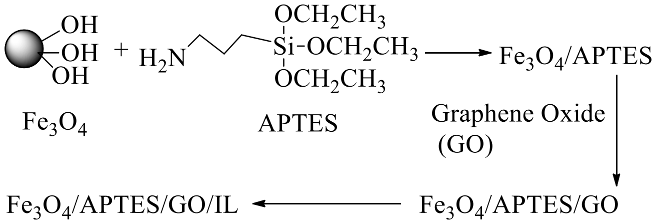
Scheme (15): Synthesis of Ionic-Liquid-Coated Iron Oxide Nanoparticles Fe_2O_3@[Omim][BF_4]

Fan *et al.* developed Fe_3O_4 magnetic nanospheres were prepared by the solvothermal reaction and then silica was coated on the outer surface of the Fe_3O_4 core to form a core-shell structure ($Fe_3O_4@SiO_2$). silica surface of the $Fe_3O_4@SiO_2$ magnetic nanospheres was functionalized with carbon–carbon double bonds after VTMOS modification[lxxviii]. PILMIP shell was coated on the surface of the modified $Fe_3O_4@SiO_2$ nanospheres to form multi-shelled magnetic $Fe_3O_4@SiO_2$ @PILMIP nanospheres. Then the silica shell of the multi-shelled magnetic $Fe_3O_4@SiO_2$@PILMIP nanospheres was etched to form the rattle-type magnetic Fe_3O_4@void@PILMIP nanospheres further used for specific recognition of protein.



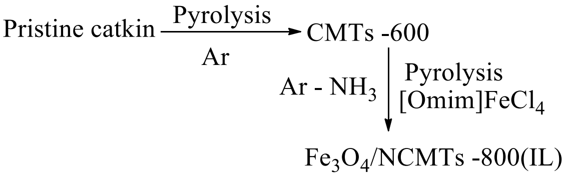
Scheme (16):The schematic illustration of the preparation of the rattle-type magnetic Fe_3O_4@void@PILMIP nanospheres.

Huang *et al.* 2015 applied solid-phase extraction (MSPE) technique to obtain betaine-based ionic liquid (IL) coated 3-aminopropyltriethoxysilane (APTES)-Fe_3O_4 grafted graphene oxide (GO) nanocomposite, (Fe_3O_4 /APTES/GO/IL) which could be implemented as magnetic adsorbent for protein extraction[lxxix]. Betaine is a common name for 1-carboxy-N,N,N-trimethymethanaminium hydroxide, and it is an inner salt since it has a zwitterionic structure. The synthesis of Fe_3O_4 nanoparticles was carried out by the modified co-precipitation method. 0.04mol of $FeCl_3 .6H_2O$ was dissolved in 60mL of water, then 0.02 mol of $FeSO_4.7H_2O$ was added to the solution. After being completely dissolved, 2mL of hydrazine hydrate was added into the mixture quickly with violent stirring. In a short while, ammonium hydroxide was gradually added until pH=9. The reaction was kept at room temperature for 30min, followed by 2h at 60℃ in water bath. Afterwards amino-silane modified Fe_3O_4 nanoparticles (Fe_3O_4/APTES) were synthesized. The preparation of Fe_3O_4/APTES/GO/IL was carried out by sonicating the mixture of 0.4g of IL dissolved in 8mL of methanol and 0.1g of Fe_3O_4/APTES/GO. Further it was applied in MSPE of protein. They showed that, these coverings on the surface of Fe_3O_4 nanoparticles are non-magnetic, and their shielding effect resulted in the reduction of the magnetic property of Fe_3O_4 nanoparticles but still resulted nanocatalyst possesses sufficient magnetism to ensure rapid separation.



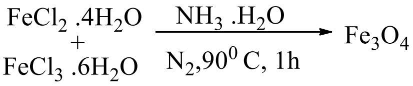
Scheme (17): Synthesis of Fe_3O_4/APTES/GO/IL

Liu *et al.* designed Fe_3O_4 nanoparticles decorated N-doped 3D hollow porous carbon microtubes multifunctional electrocatalyst (Fe_3O_4/NCMTs-800(IL)[lxxx]. Size of Fe_3O_4 nanoparticles controlled by ionic liquid [Omim][$FeCl_4$], due to which uniform nanoparticles on hollow carbon microtubes were formed.



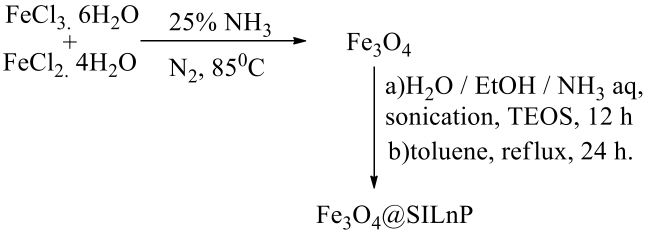
Scheme (18): Synthesis of Fe_3O_4/NCMTs-800(IL).

Davarpanah *et al.* of bis(n-propyl trimethoxysilane)-1,4-diazoniabicycle [2.2.2] octane chloride, BPTDABCOCl[lxxxi].



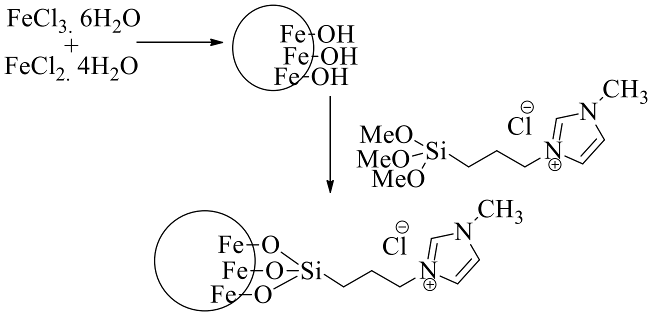
Scheme (19): Synthesis of Fe_3O_4@SiO_2/DABCO.

Supported catalysts are effective and get easily separated from reaction media on application with external magnetic field so, Isaad *et al.* developed method for new class of supported ionic liquid catalysts (SILC), acidic Fe_3O_4 @ SILnP nanoparticles for diazotization iodination of aromatic amines in presence of N-propyl – 2 - pyrrolidonium hydrogen sulfate supported on nano sized silica coated magnetic (Fe_3O_4@SILnP) as acid cat under solvent free conditions in good to excellent yields[lxxxii].



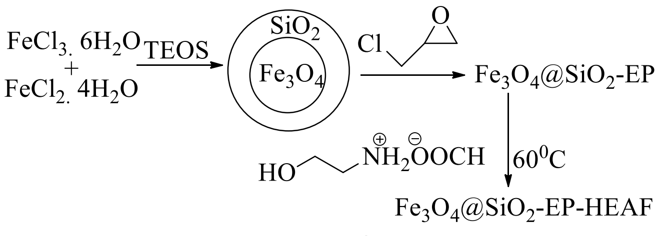
Scheme (20): Synthesis of the supported ionic liquid catalysts (Fe3O4@SILnP) based on N-propyl-2-pyrrolidonium hydrogen sulfate ([HNPP]HSO4) bonded to nano-sized silica-coated magnetite.

Safari *et al.* In the first step, the magnetite nanoparticles of 18–20 nm were prepared by coprecipitation of iron(II) and iron(III) ions in basic solution at 85^0C[lxxxiii]. Then, 1-methyl-3-(3-trimethoxysilylpropyl)imidazolium chloride (IL) was prepared from the reaction of N-methylimidazole with (3-chloropropyl)trimethoxysilane at 80^0 C. In the second step, the external surface of MNPs was coated with IL to obtain IL-MNPs. Fourier transform infrared (FTIR) spectra of both the unfunctionalized and functionalized magnetic nanoparticles. The Fe–O stretching vibration near 580 cm-1, O–H stretching vibration near 3,432 cm-1, and O–H deformed vibration near 1,625 cm-1 were observed for both. The obtained magnetic nanoparticles had an excellent magnetic responsivity, which prevents composite nanoparticles from aggregation and enables them to redisperse rapidly when the magnetic field is removed. Magnetite Fe_3O_4 nanoparticles have a mean diameter of about 18 nm and a nearly spherical shape.



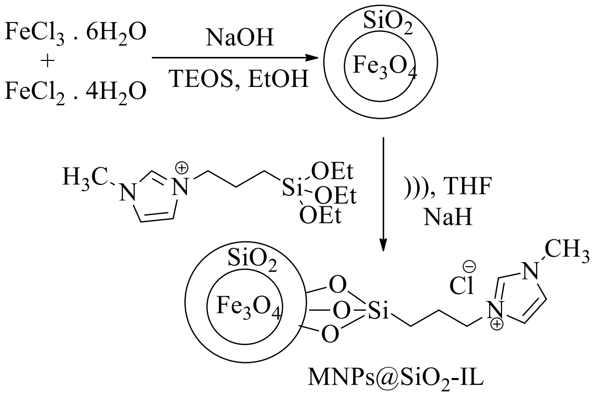
Scheme (21): Synthesis of IL-Fe_3O_4 nanoparticles

Rajabzadeh *et al.* designed 2-hydroxyethylammonium formate ionic liquid grafted magnetic nanoparticle for synthesis of substituted imidazoles[lxxxiv]. In the first step, the Fe_3O_4@SiO_2 magnetic nanoparticles were synthesized using the stober method. In the next step, the substitution reaction of epichlorohydrin species was accomplished with hydroxyl groups of silica coated magnetic nanoparticles. Finally, Fe_3O_4@SiO_2-EP-HEAF was obtained by simple mixing of Fe_3O_4@SiO_2 -EP and 2-hydroxyethylammonium formate in 60°C. FTIR spectra of the final catalyst which was synthesized in 4 step. The characteristic absorption peak of Fe3O4 magnetic nanoparticles is found at 585 cm−1 is attributed to Fe–O vibrations Fe_3O_4@SiO_2 MNPs were synthesized by the conventional stober method. To a solution of epichlorohydrin (10 mmol, 1.36 g) in ethanol (3 ml), Fe_3O_4@SiO_2 MNPs (0.5 g) was added and the resulting mixture was stirred for 5 h at 60°C. The precipitate was separated by a magnet and washed with ethanol several times. The formed Fe_3O_4@SiO_2-EP (0.5 g) was dispersed in 3 ml 2-hydroxy ethyl ammonium formate with ultrasonic for 120 min, then the mixture was vigorously stirred for 6 h at 60°C. The precipitate was separated with using an external magnet and washed with distilled water and with ethanol for three times, then dried at 60 °C for 6 h.



Scheme (22): Preparation of Fe_3O_4@SiO_2-EP-HEAF catalyst

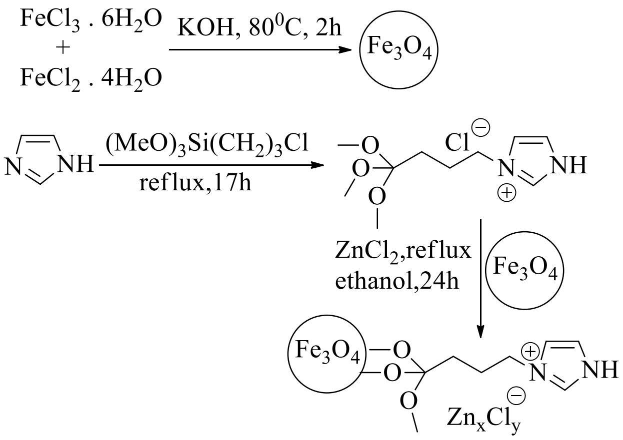
Azgomi *et al.* in 2015 reported synthesis of magnetically supported ionic liquid on Fe_3O_4@SiO_2 nanoparticles (MNPs@ SiO_2-IL) by co-precipitation of fe precursors in basic medium[lxxxv]. The external surface of MNPs was coated with 1-methyl-3-(3-trimethoxysilylpropyl) imidazolium chloride (IL) to form MNPs@SiO_2-IL. And they proved that the MNPs@SiO_2-IL is super-paramagnetic by studying magnetization curve. Saturation magnetization of MNPs was 58.9emu/g and saturation magnetization of MNPs@SiO_2-IL was 23.7 emu/g. Compared with the uncoated Fe_3O_4particles, the saturation magnetization of the MNPs@SiO_2-ILobviously decreased because the diamagnetic contribution of the thick SiO_2 and organic matter resulted in a low mass fraction of the Fe_3O_4 magnetic substance. Even with this reduction in the saturation magnetization, the solid could still be efficiently separated from solution with a permanent magnet.



Scheme (23). Preparation steps for synthesis of 1-methyl-3-(3-trimethoxysilylpropyl)-1H-imidazol-3-ium chloride supported nano-Fe_3O_4@SiO_2.

Nguyen *et al.* performed a synthesis of 3-(3-(trimethoxysilyl)propyl)-1H-imidazol-3-ium chlorozincate (II) ionic liquid immobilized Fe_3O_4 nanoparticles LAIL@MNP[lxxxvi].

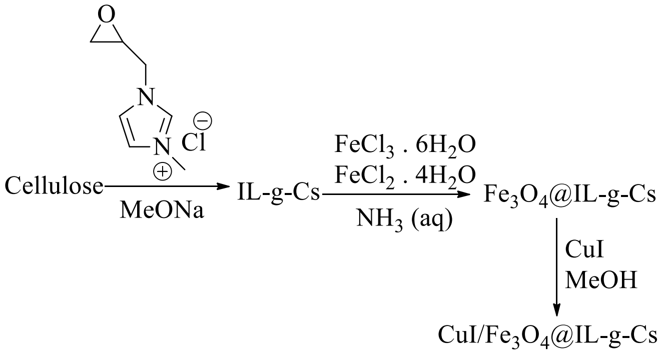
Initially, magnetite ferrite nanoparticle was formed via a co-precipitation method while the precursor ionic liquid was independently synthesized by the treatment of (3-chloropropyl)triethoxysilane with imidazole. Then the outermost surface of MNP was coated with the prepared ionic liquid. Finally, $ZnCl_2$ was added and the resulting mixture was heated under reflux for 24 h to form LAIL@MNP. They showed that the morphology of LAIL@MNP as uniform spherical particles which was depicted in SEM. Transmission electron microscopy (TEM) confirmed that dark Fe_3O_4 core coated by grey silica shell has the average diameter of 10–15 nm. The thermo-stability of the LAIL@MNP was studied by thermogravimetric analysis (TGA). The entire loss of the grafted LAIL was detected in the region from 220^0C to 400^0C.



Scheme (24): Synthesis of LAIL@MNP.

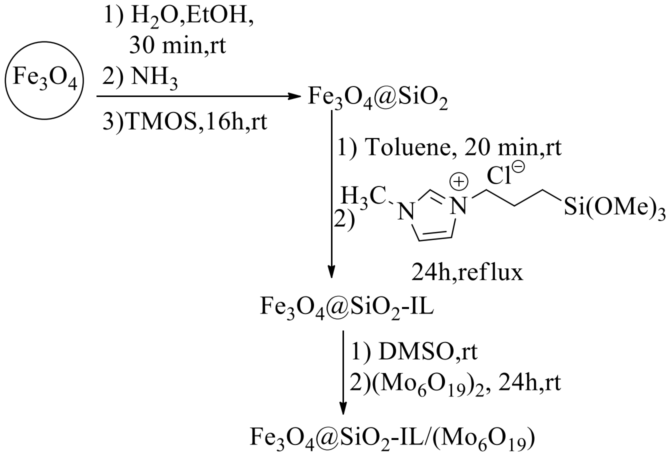
Shojaei *et al.* designed synthetic route for CuI/Fe_3O_4 nanoparticles supported on ionic liquid 1-methyl-3-(oxiran-2-ylmethyl)-1H–imidazol-3-ium chloride-grafted cellulose Fe_3O_4NPs@IL-g-Cs[lxxxvii]. They conclude that the amount of ionic liquid supported on cellulose is about 27 wt% by studying thermogravimetric analysis (TGA) of sample. This technique considered as a powerful technique for measurement and calculation of the percentage of a connected polymer.

The nanocatalyst was also characterized using Fourier transform infrared (FT-IR) spectroscopy. The FT-IR spectrum of ionic liquid-grafted cellulose, peaks at 1647 and 1428 cm−1 are due to the stretching vibrations of C═N and C═C in the imidazolium rings, respectively. Comparison of the three spectra shows that the band at 594 cm−1 in the spectrum of CuI/Fe_3O_4NPs@IL-g-Cs can be assigned to the vibration of Fe─O in Fe_3O_4. Scanning electron microscopy (SEM) images show good dispersity of CuI and Fe_3O_4 nanoparticles on the cellulose support and also verify the presence of CuI and Fe_3O_4 with average particle size of 35–40 nm. Saturation magnetization value of Fe_3O_4NPs@IL-g-Cs and CuI/Fe3O4NPs@IL-g-Cs is 7.75 and 6.45 emu g−.



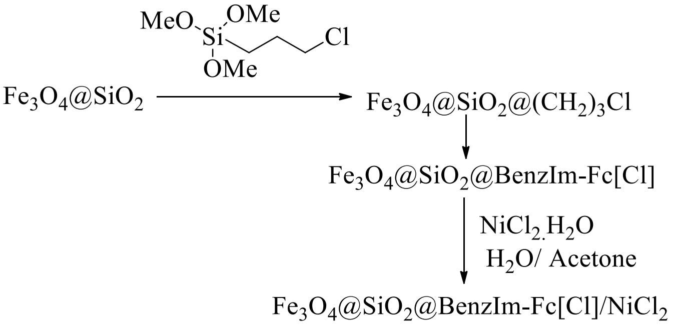
Scheme (25): Synthesis of CuI/ Fe_3O_4 nanoparticles supported on ionic liquid-grafted cellulose.

Kargar *et al.* in their work designed method for Fe_3O_4@SiO_2-IL/[Mo6O19] nanocatalyst[lxxxviii]. Fe_3O_4@SiO_2 NPs were synthesized by a chemical co-precipitation method. Silica shell was first coated on the Fe_3O_4 surface through a sol–gel process. To prepare Fe_3O_4@SiO_2-IL, Fe_3O_4@SiO_2 NPs reacted with 1-Methyl-3-(3-trimethoxysilylpropyl)imidazolium Chloride. Further tetrabutylammonium hexamolybdate ($(n\text{-}Bu_4N)_2[Mo_6O_{19}]$) used to immobilize $[Mo_6O_{19}]2-$ on the Fe_3O_4@SiO_2-IL nanomaterial.



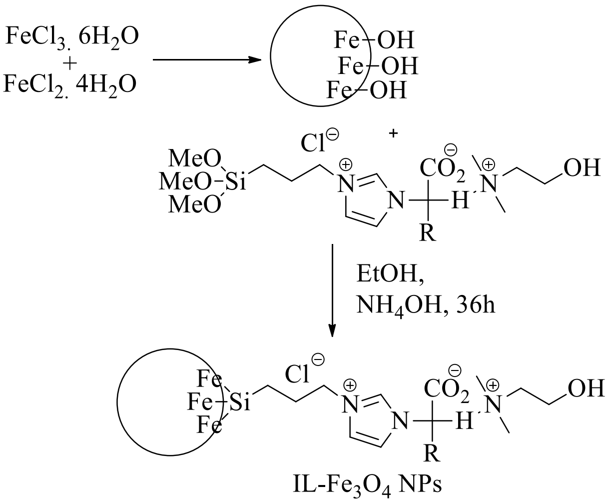
Scheme (26): Preparation of Fe_3O_4@SiO_2-IL/[Mo6O19] nanocatalyst.

Mohammadi *et al.* developed method for synthesis of Fe_3O_4@SiO_2 @BenzIm-Fc[Cl]/NiCl2 nanoparticle 1-(4-ferrocenylbutyl)-1*H*benzimidazole added to the mixture of Fe_3O_4@SiO_2-propylchloride and heated at 80 °C for 72 h to form Fe3O4@SiO2@BenzIm-Fc[Cl] nano-particles[lxxxix]. Modified by adding NiCl2·6H2O to synthesized nanoparticles. a number of aromatic aldehydes with electron-with drawing groups and electron-donating groups were reacted with different C-H acid derivatives (4-hydroxycoumarin, dimedone and resorcinol) and malononitrile in the presence of catalytic amount of Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/$NiCl_2$ nanoparticle under ultrasonic irradiation. In all cases, the corresponding products were afforded within 10-20 min in good to excellent yields.



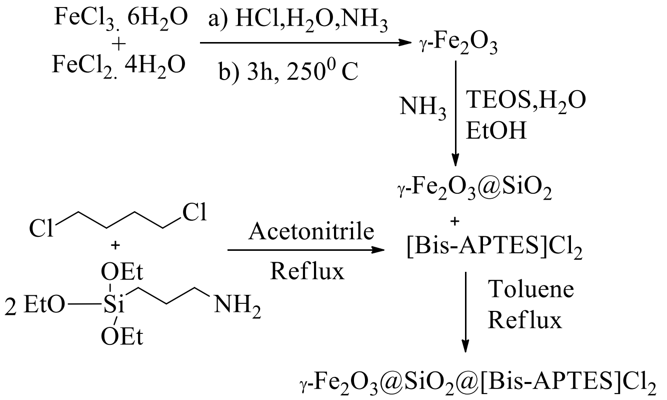
Scheme (27): Synthesis of $Fe_3O_4@SiO_2@BenzIm\text{-}Fc[Cl]/NiCl_2$ nanoparticle.

Safaei-Ghomi *et al.* utilized ionic liquid (IL) with L-alanine and choline chloride or synthesis of IL supported on Fe_3O_4 NPs (IL- Fe_3O_4 NPs)[xc]. Chemical co-precipitation applied for nanoparticle synthesis using fe precursors in a molar ratio of 1.75:1 under nitrogen. Aqueous ammonia solution added to form black ppt of Fe_3O_4 nanoparticles at pH 9.0. Afterwards, formed nanoparticles were modified with ionic liquid under sonication.



Scheme (28): Synthesis of IL- Fe_3O_4 nanoparticles.

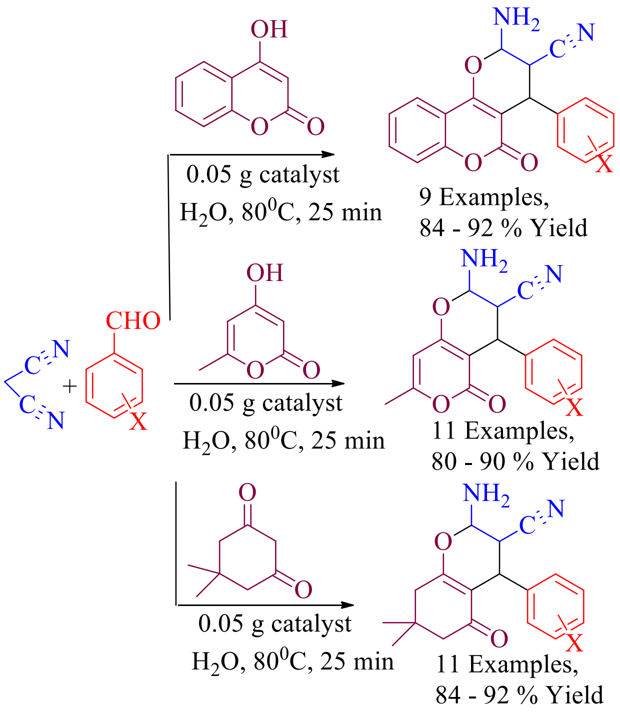
In 2019, Karimi-Chayjani *et al.* developed novel nanocatalyst g-$Fe_2O_3@SiO_2@N_1,N_4$-bis(3-(triethoxysilyl)propyl)butane-1,4-diaminium dichloride, γ-$Fe_2O_3@SiO_2@$[Bis-APTES]Cl_2 nano particles immobilized by bis-dicationic ionic liquid N_1,N_4-bis(3-(triethoxysilyl)propyl)butane-1,4-diaminium dichloride, [Bis-APTES]Cl_2[xci]. In first step, γ-Fe_2O_3 nano particles were formed by co-precipitation method. A solution of $FeCl_2.4H_2O$, $FeCl_3.6H_2O$ and HCl in deionized water stirred under an argon atmosphere at room temperature then ammonia solution added to reach to pH 11. In second step, nano γ-Fe_2O_3 coated by silica. Then formed γ-$Fe_2O_3@SiO2$ was utilized to form $Fe_2O_3@SiO_2@N_1,N_4$-bis(3-(triethoxysilyl)propyl)butane-1,4-diaminium dichloride, γ-$Fe_2O_3@SiO_2@$[Bis-APTES]Cl_2 nano particles.

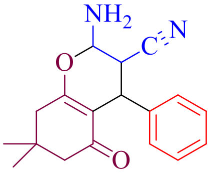


Scheme (29): Preparation of γ-$Fe_2O_3@SiO_2@[Bis\text{-}APTES]Cl_2$ nano particles.

Applications of Fe Nanoparticles in Catalysis:

Davarpanah *et al.* reported method of preparation of pyran annulated heterocyclic compounds in water using bis(n-propyltrimethoxysilane)-1,4-diazonia bicyclo [2.2.2] octane chloride, BPTDABCOCl ionic liquid supported magnetic double-charged diazonia bicyclo [2.2.2] octane dichloride silica hybrid,Fe3O4@SiO2/DABCO nanocatalyst[lxxxi].





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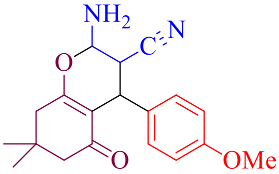

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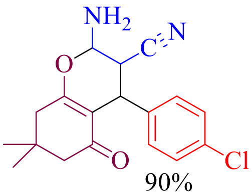

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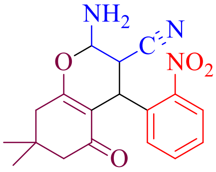

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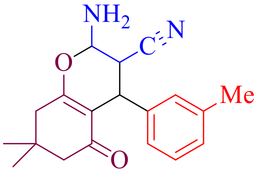

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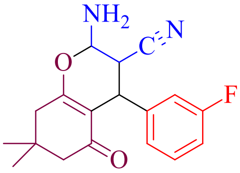

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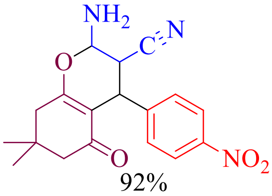

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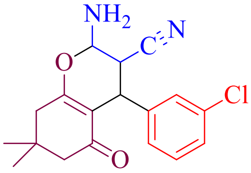

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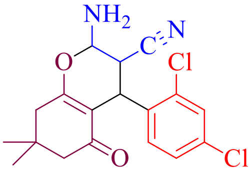

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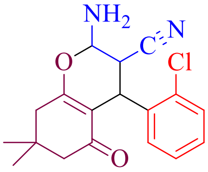

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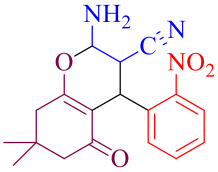

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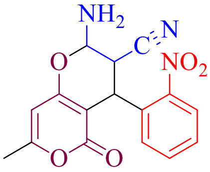

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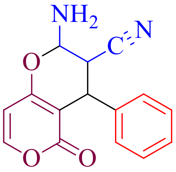

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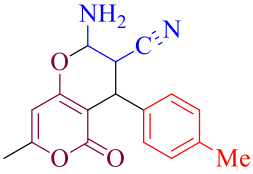

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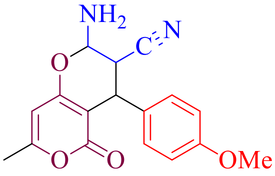

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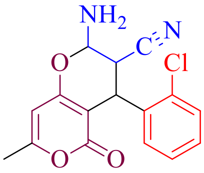

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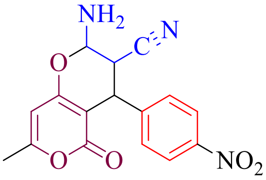

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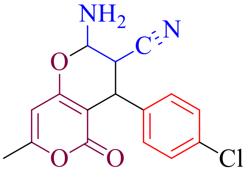

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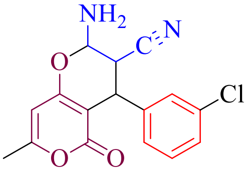

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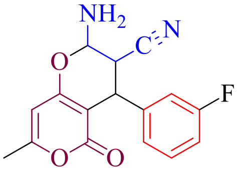

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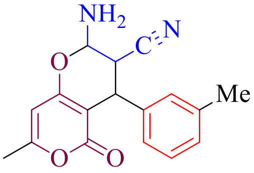

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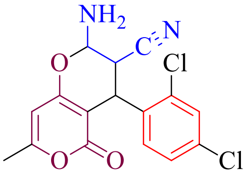

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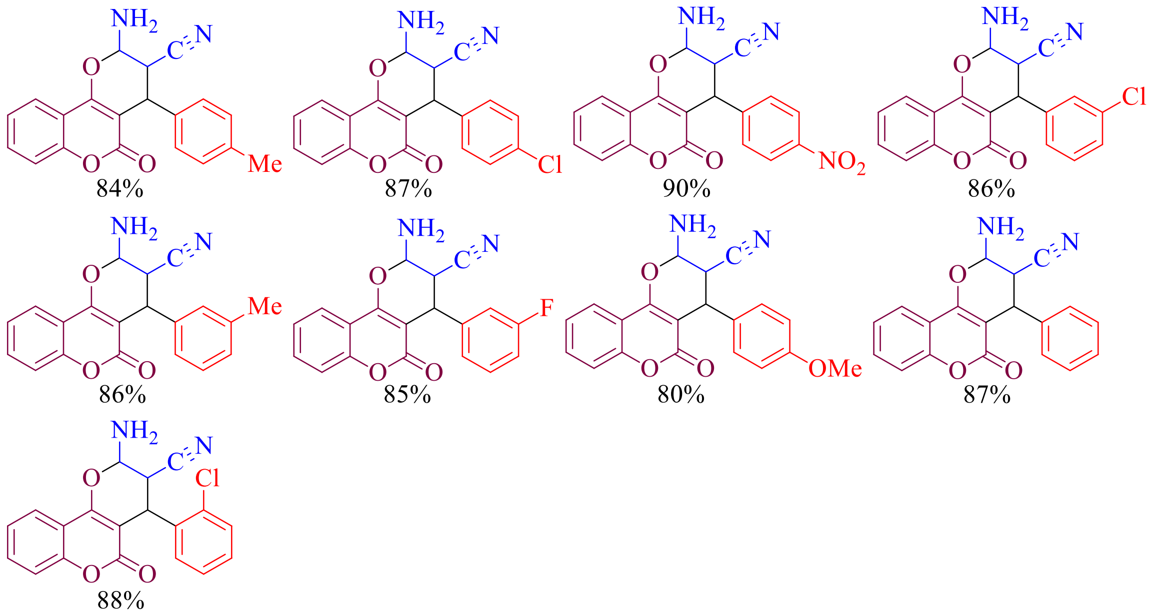
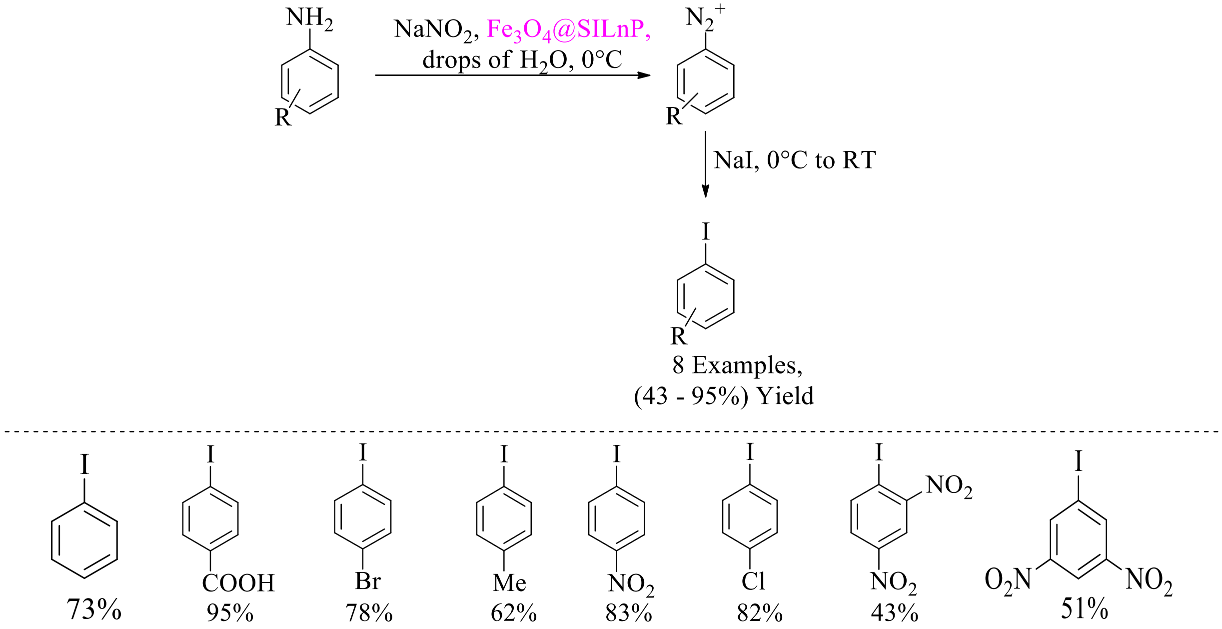


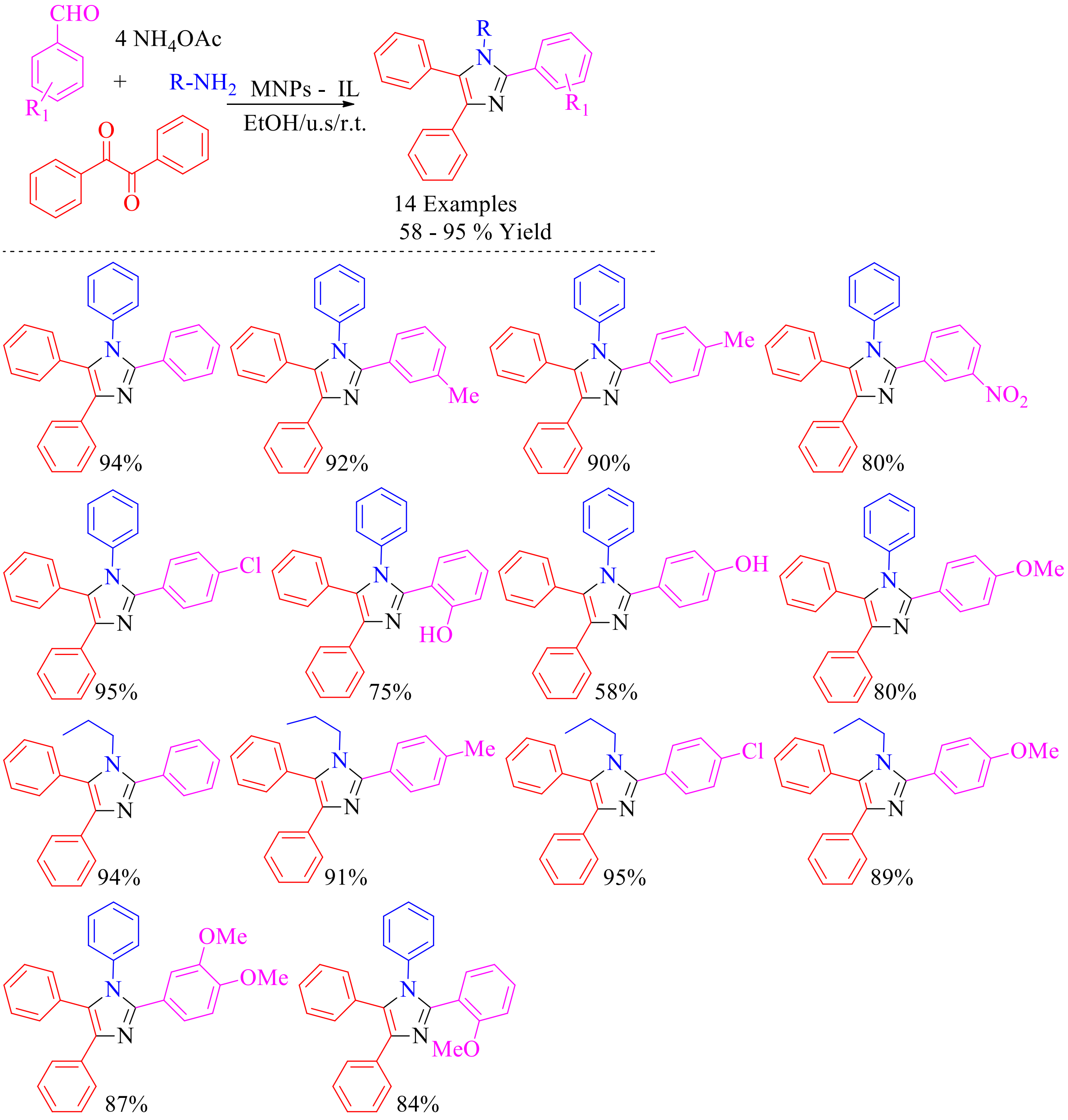
Scheme (19): Synthesis of 4H-benzo[b]pyran derivatives through multicomponent reaction promoted by $Fe_3O_4@SiO_2$/DABCO.

Supported catalysts are effective and get easily separated from reaction media on application with external magnetic field so, Jalal Isaad et al developed method for new class of supported ionic liquid catalysts (SILC), acidic Fe_3O_4 @ SILnP nanoparticles for diazotization iodination of aromatic amines in presence of N-propyl – 2 - pyrrolidonium hydrogen sulfate supported on nano sized silica coated magnetic (Fe_3O_4@SILnP) as acid catalyst under solvent free conditions in good to excellent yields[lxxxii].



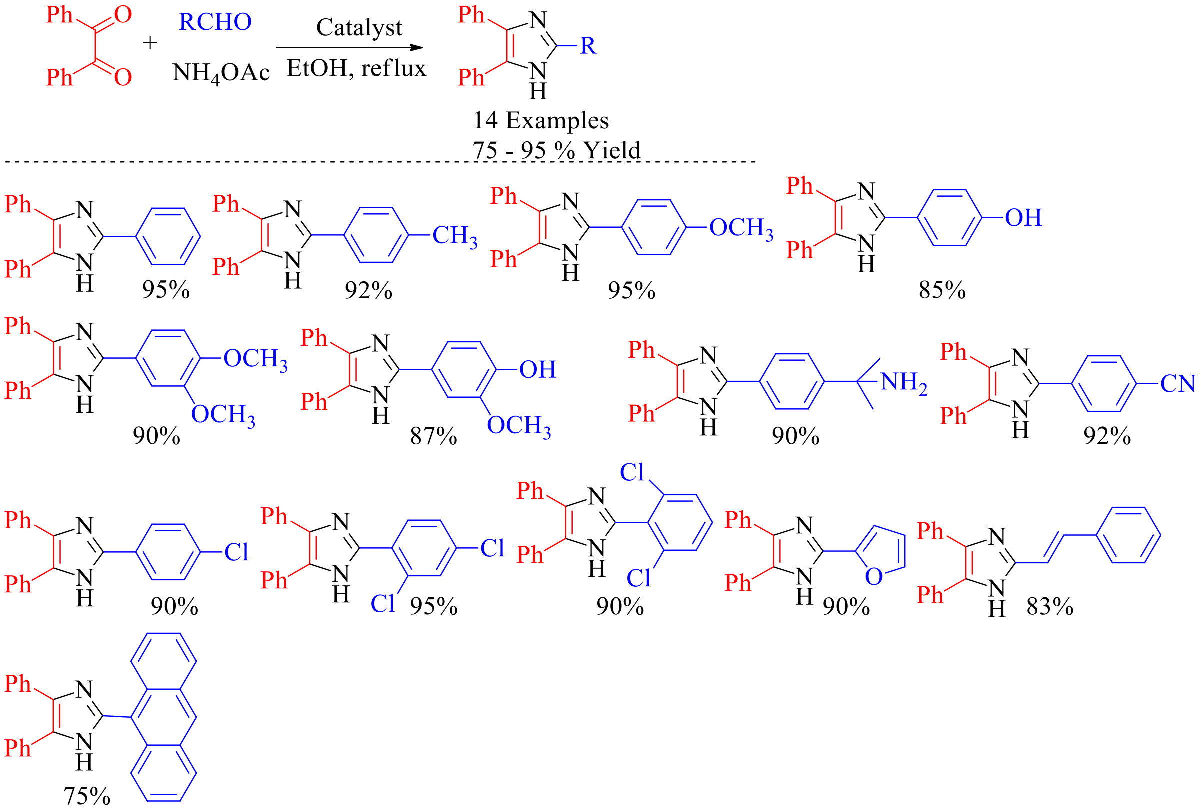
Scheme (20): Synthesis of the aryl iodide by using Fe_3O_4@SILnP as catalyst.

Safari *et al*. fabricated efficient route for synthesis of magnetic nanoparticles supported on ionic liquid. The prepared nanocatalyst was successfully used for accessing substituted imidazoles derivative from multicomponent reactions of aromatic aldehyde, benzyl, primary aliphatic or aromatic amine and ammonium acetate under ultrasonic irradiation at room temperature[lxxxiii]. In order to evaluate catalytic activity of IL/MNPs through the synthesis of 1,2,4,5-tetrasubstituted imidazoles, they developed green, facile, and efficient method for the synthesis of 1,2,4,5-tetrasubstituted imidazoles catalyzed by IL-MNPs under ultrasonic irradiation at room temperature. To optimize amount of IL-MNPs as a catalyst they performed reaction of benzil (1 m mol), benzaldehyde (1 m mol), aniline (1 m mol), and ammonium acetate (5 m mol) at 40 kHz under sonication. They found that, use of 0.15 g of IL-MNPs in ethanol afforded an 87 % yield of the desired product. Upon completion, the catalyst was separated by an external magnet and was washed with acetone, and the recycled catalyst was saved for the next reaction. The recycled catalyst could be reused six times without any further treatment.



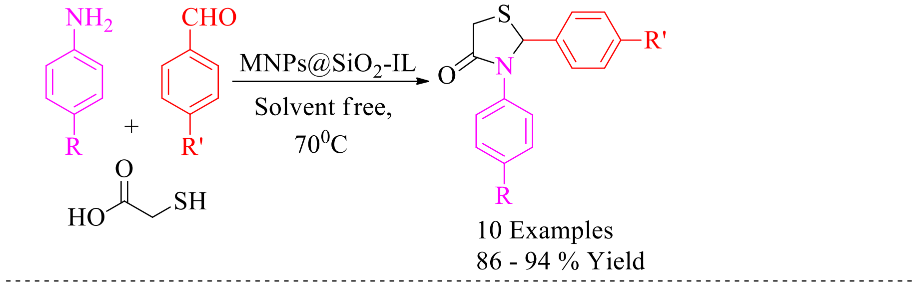
Scheme (21): Synthesis of substituted imidazoles under ultrasonic irradiation.

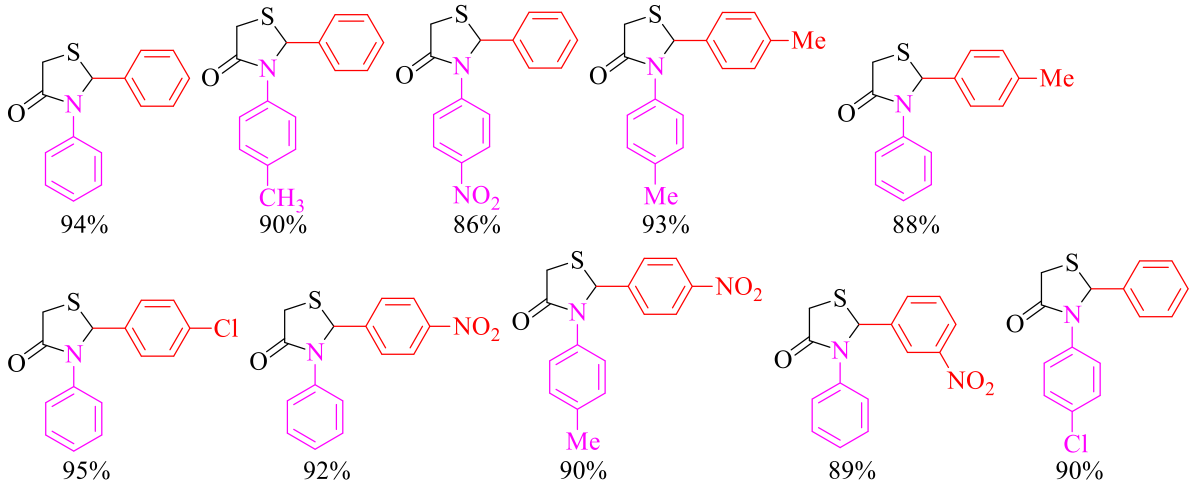
Rajabzadeh *et al.*[lxxxiv] in their work carried out one-pot condensation of benzil and ammonium acetate with a variety of aldehydes in the presence of 2-hydroxyethylammonium formate (HEAF) grafted on a magnetic nanoparticles as a new heterogeneous catalyst Fe_3O_4@SiO2-EP-HEAF to achieve the intended products. The results indicate that the excellent yields were achieved in the reaction at the presence of 0.02 g catalyst Fe_3O_4@SiO2-EP-HEAF is superior with respect to reported catalysts in terms of reaction time, yield and conditions. There was no product formation without catalyst. The products were obtained in excellent yields with both electron rich and electron deficient aromatic aldehydes.



Scheme (22): One pot catalytic Synthesis of 2,4,5-trisubstituted -1H-imidazole.

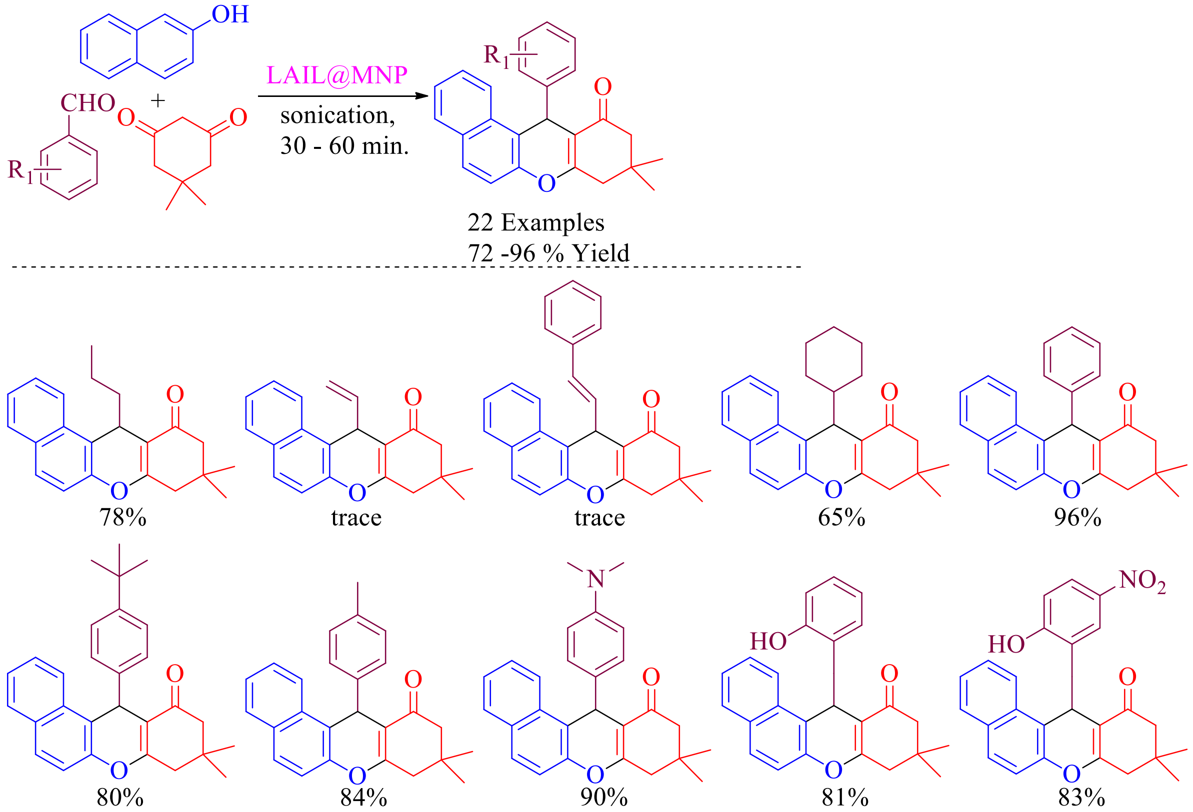
Thiazolidinones have emerged as an important class of compound because of their biological importance and have shown interesting biological activity profiles such as anti-histaminic, anti-inflammatory, antioxidant, anti-tubercular, anti HIV, anti-bacterial and anticancer agents. Previous work requires longer reaction time, corrosive, hazardous reaction condition, tedious work-up procedures, unsatisfactory yields, and non-recyclable reagents. Therefore, it seems that a major task of current research is to replace less efficient and traditional catalysis procedures with more acceptable methods based on improved, stable, and recoverable catalysts. Azgomi *et al.* used nano – $Fe_3O_4@SiO_2$ supported ionic liquid as a catalyst for synthesis of 1,3- thiazolidin-4-ones in 86–95% yields[lxxxv]. They conclude that conventional heating at 70°C under solvent-free conditions is more efficient than using organic solvents, with respect to reaction time and yield of the desired 1,3-thiazolidin-4-ones. To investigate the effect of catalyst loading, the model reaction was carried out in the presence of different amounts of catalyst. It was observed that the variation for MNPs@SiO_2-IL had an effective influence. The best amount of MNPs@SiO_2-IL is 0.0007 g which afforded the desired product in 94% yields.

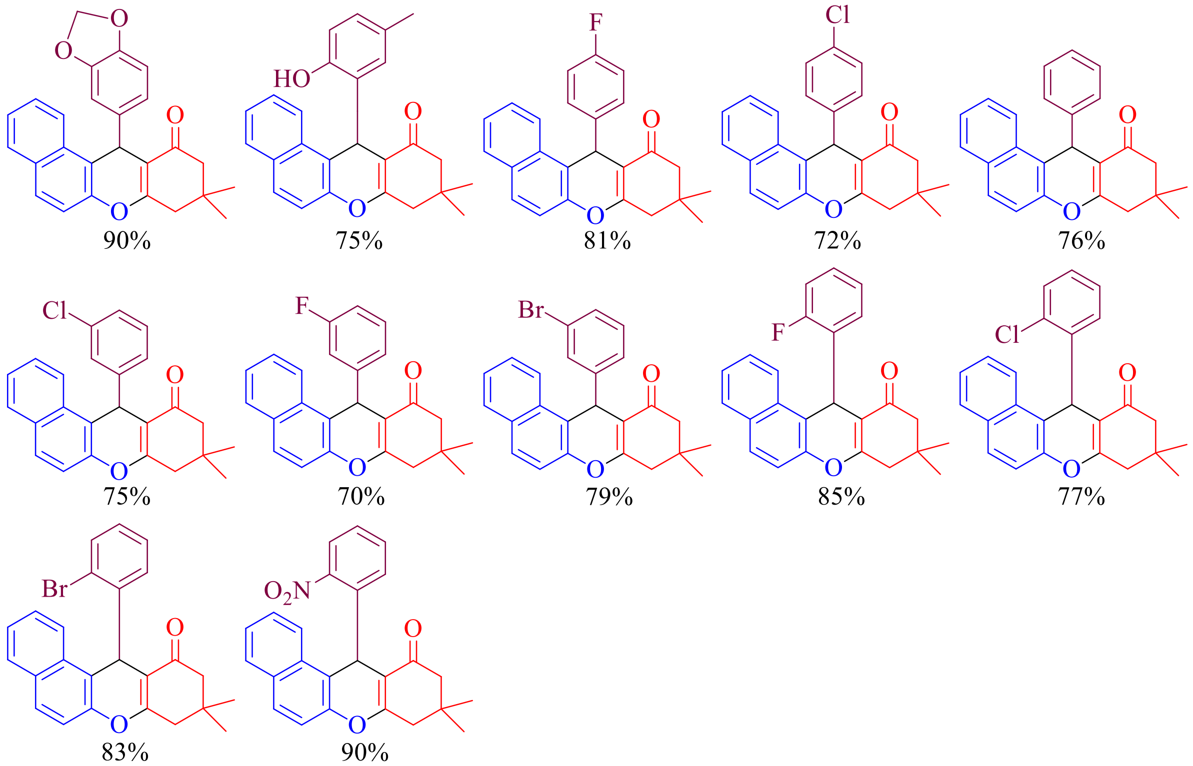




Scheme (23): Synthesis of 1,3- thiazolidin-4-ones catalyzed by MNPs@SiO_2-IL.

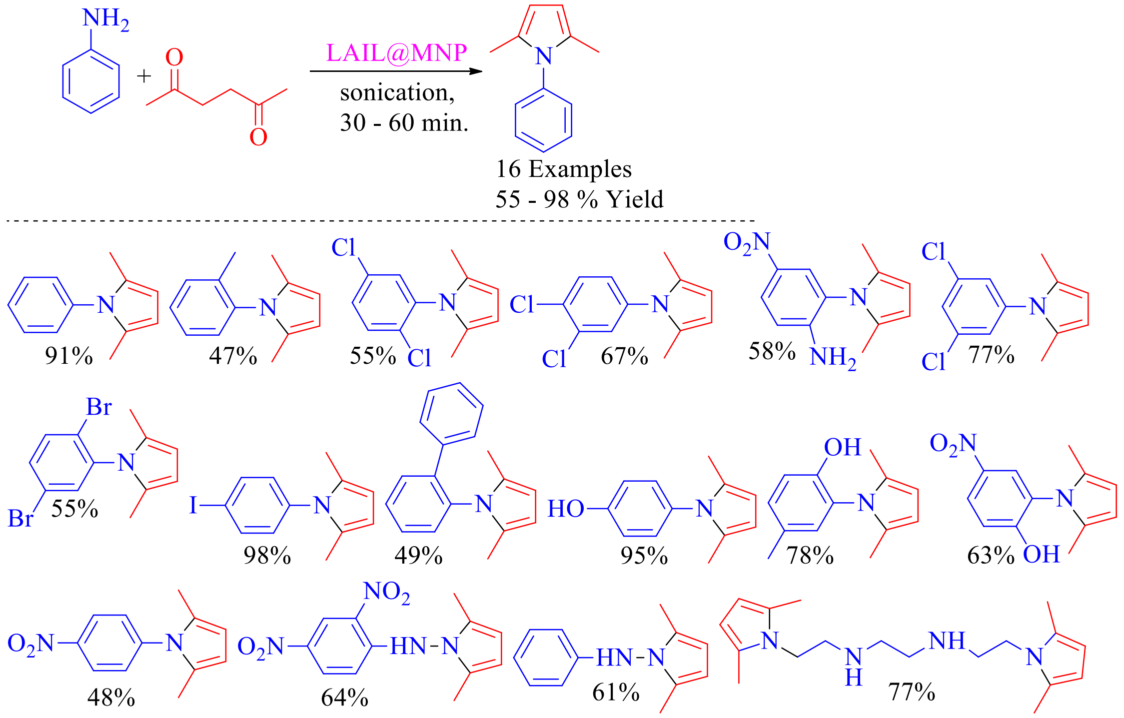
Nguyen *et al.* reported the application of Fe_3O_4 nano-catalyst that had been successfully supported with Lewis acidic IL and used in synthesis of benzoxanthenes and pyrroles[lxxxvi]. Magnetic Fe_3O_4 nanoparticles were synthesized by simple co-precipitation of $FeCl_3.6H_2O$ and $FeSO_4.7H_2O$ in basic condition at 80^0C. The resulted magnetic Fe_3O_4 nanoparticles were further modified by IL. A mixture of 3-chloroethoxy propyl silane and imidazole was stirred and reflux for 17 hr. freshly prepared Fe_3O_4 nanoparticle suspension in 100 ml of 1:1 EtOH - H_2O was added to the above IL solution and the mixture was sonicated at 40^0 C for 4 hr. The resultant IL@MNP was washed with CH_2Cl_2 and dried at 70^0C. A mixture of IL@MNP and $ZnCl_2$ in EtOH was further refluxed for 24 hr. to synthesize LA IL@MNP. The nanocatalyst used for one pot, multicomponent reaction of β -Naphthol, aromatic aldehyde and substituted dimedone under solvent free sonication at 80^0 C for 30 min. to synthesize benzoxanthenes derivative.





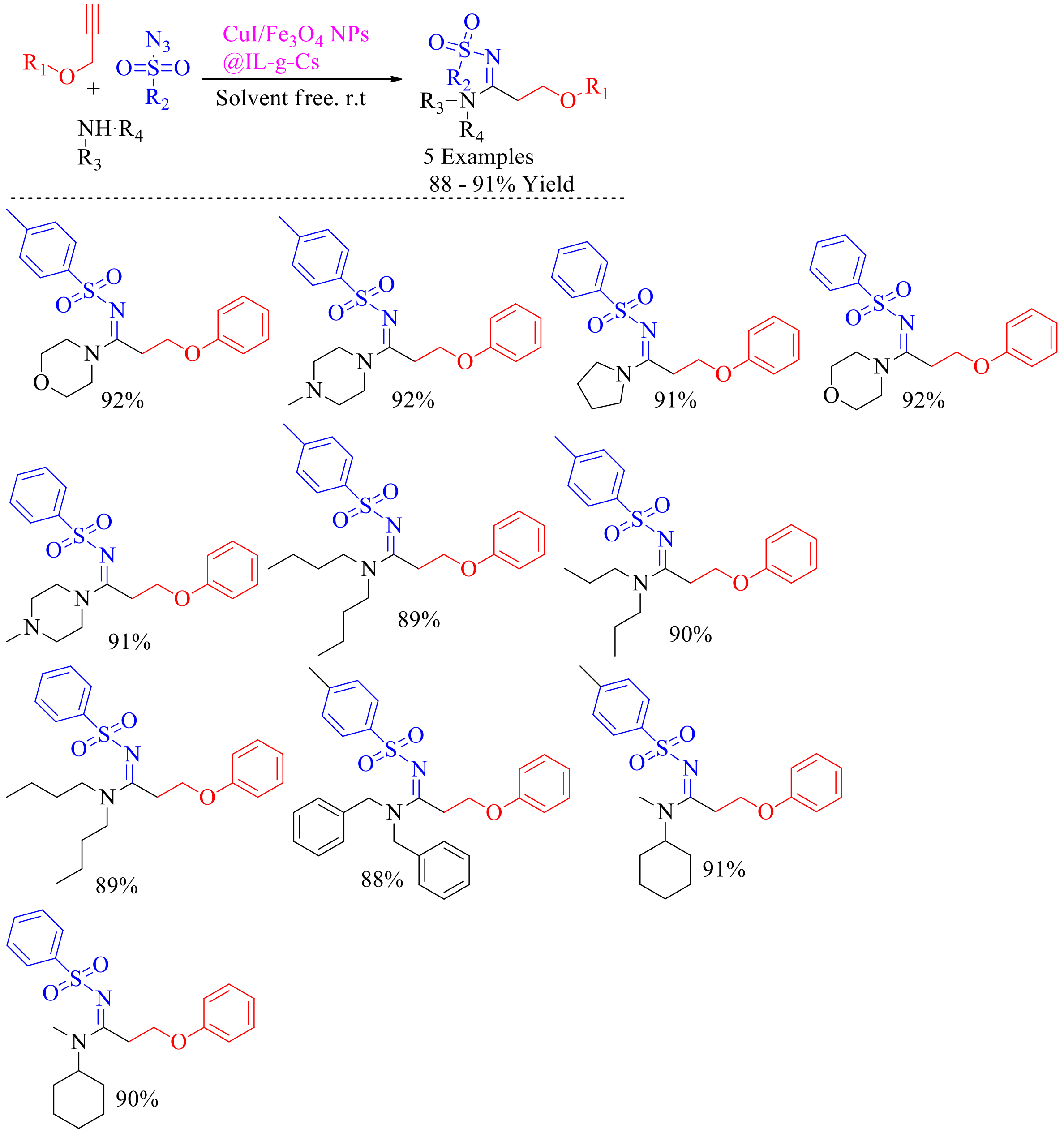
Scheme (24): Synthesis of Benzoxanthenes catalyzed by Fe_3O_4 NPs supported by IL.

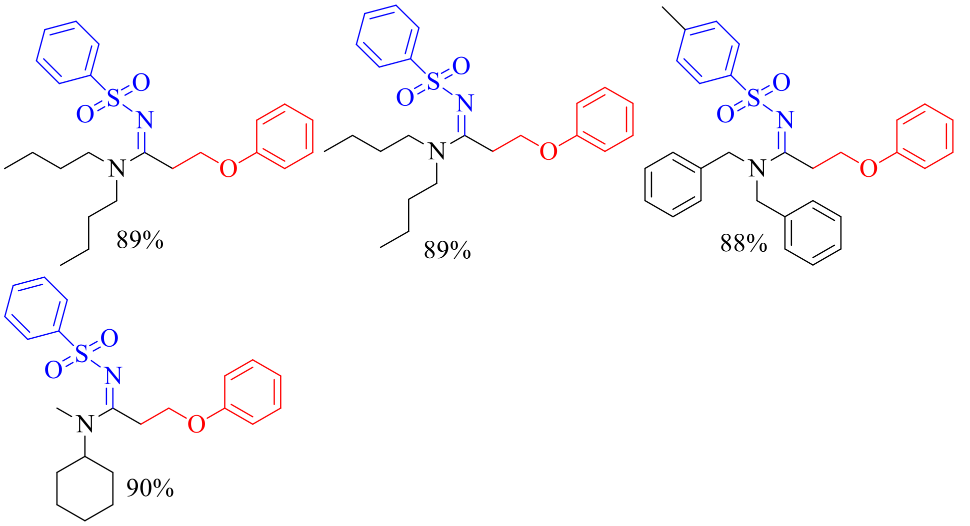
Synthesis of pyrrole derivative was achieved by one pot reaction of aniline (1.0 m mol), acetonyl acetone and LAIL@MNP under solvent free sonication. After completion of reaction the resulting mixture was diluted by ethyl acetate and the solid catalyst was separated and then reused for next cycles.



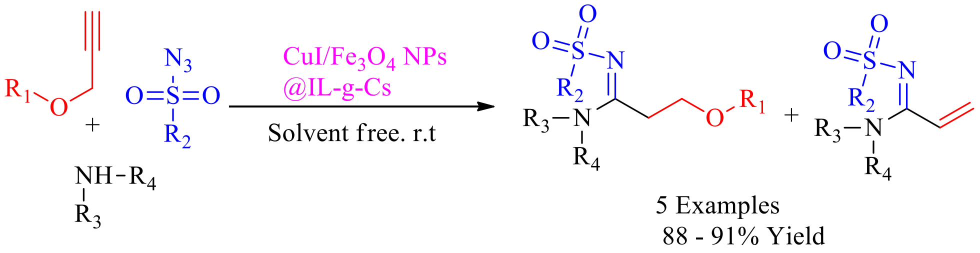
Scheme (25): Synthesis of Pyrroles catalyzed by Fe_3O_4 NPs supported by IL.

N-Sulfonylamidines, which are important privileged scaffolds in bioactive and natural products N-Sulfonylamidines have been identified as essential parts of important neonicotinoid pharmacophores osteoclast differentiation inhibitors, anti-proliferative, antiresorptive, antitumour and anticancer agents, and also dopamine transporter inhibitors. Shojaei *et al*. reported synthesis of green nanocatalyst supported on imidazolium based ionic liquid grafted cellulose and used for synthesis of N-sulfonyl amidines, N-sulfonyl acrylamidines by multicomponent reaction of sulfonyl azides, aryl propargyl ethers and secondary amines under solvent free condition[lxxxvii]. Simple methodology, eco-friendliness, excellent yields, short reaction times, superior catalytic activity as well as simple recovery and recyclability of the heterogeneous catalyst nanocatalyst without any marked change in the overall yield are important advantages.

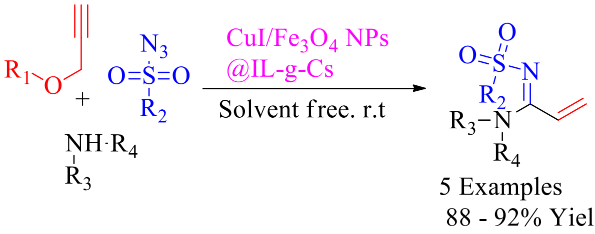




Scheme (26): Synthesis of N-sulfonylamidine derivatives in presence of CuI/Fe3O4NPs@IL-g-Cs.

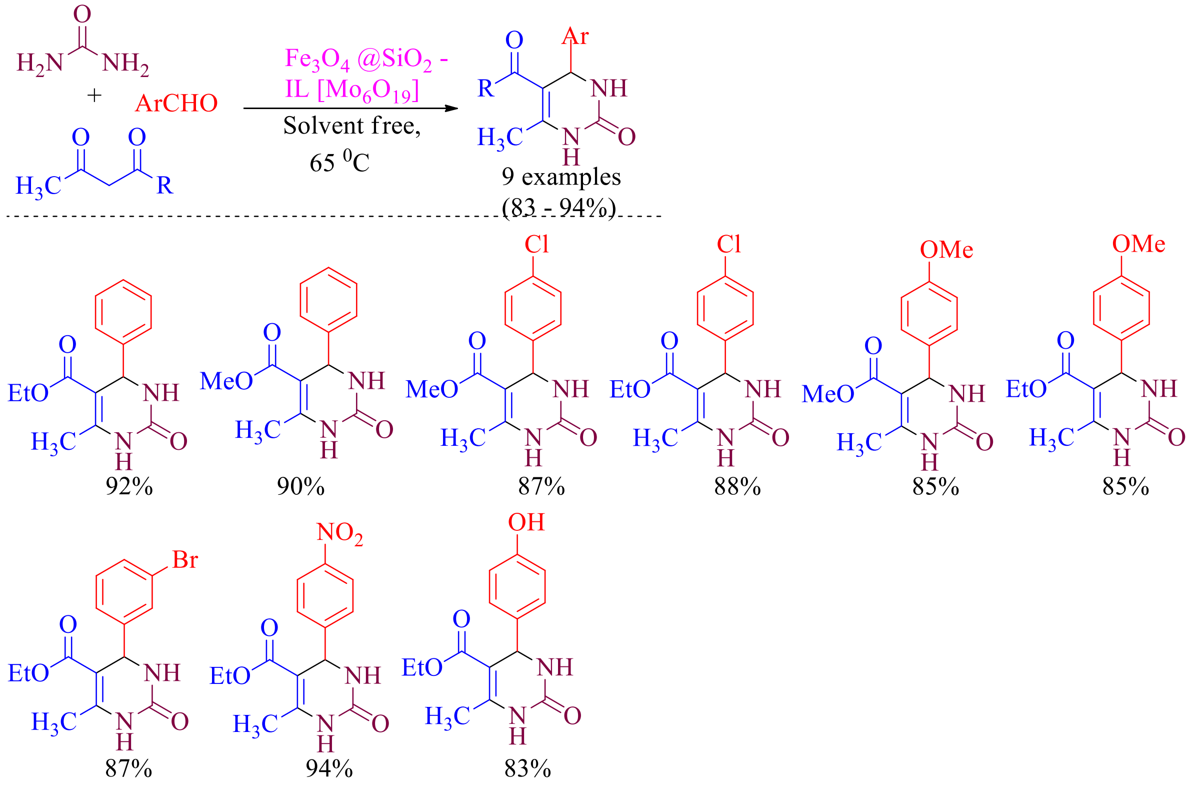


Scheme (27): Synthesis of N-sulfonylamidine and N-sulfonylacrylamidine derivatives in presence of sterically hindered secondary amines using CuI/Fe_3O_4NPs@IL-g-Cs.



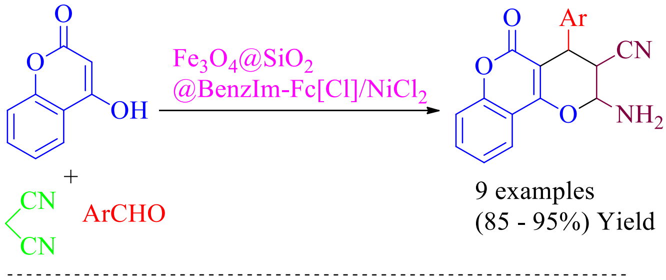
Scheme (28): Synthesis of N-sulfonylacrylamidine as sole product in presence of sterically hindered secondary amines.

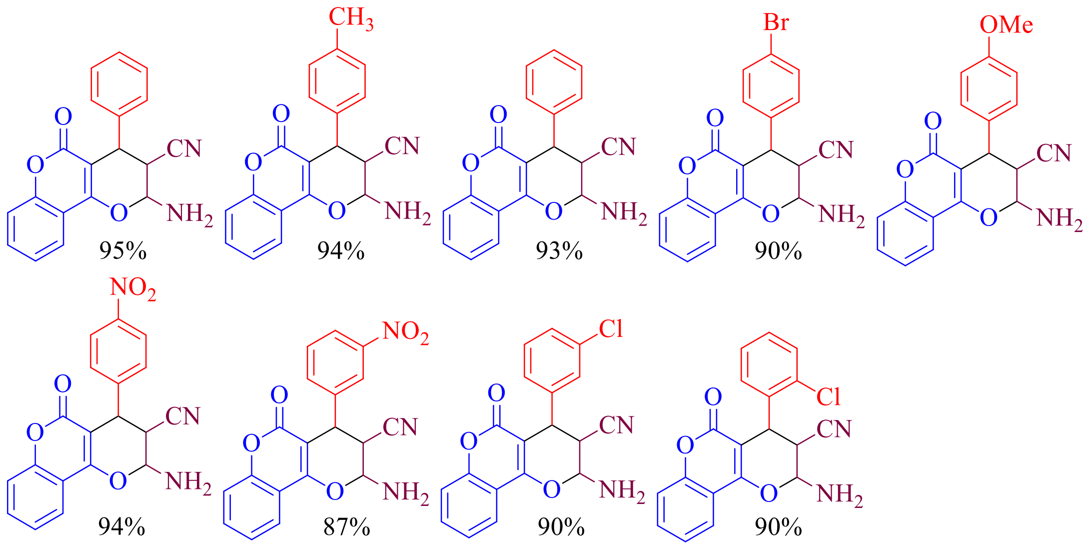
Kargar *et al.* have developed novel magnetic silica-nanomaterial supported ionic liquid/hexamolybdate (Fe_3O_4@SiO_2-IL/[Mo_6O_{19}]) nanoparticles synthesized by sol–gel method[lxxxviii]. Dihydropyrimidinone derivatives were prepared by the condensation of benzaldehyde with ethyl acetoacetate and urea under ultrasonication with solvent free reaction condition. They found that electrostatic interaction between the imidazolium cation and the hexamolybdate anions helps in stabilization of nanoparticle and supported hexamolybdate resist the formation agglomerates or inactive dimers in homogeneous solution which thereby increases the catalytic activity compared with Fe_3O_4@SiO_2/IL. Under optimized reaction conditions, aldehydes bearing both electron-donating and electron-accepting substituents enhance yields. Catalyst recycled for next consecutive six runs with no significant reduction in efficiency which indicates high stability and durability of this nanocatalyst.



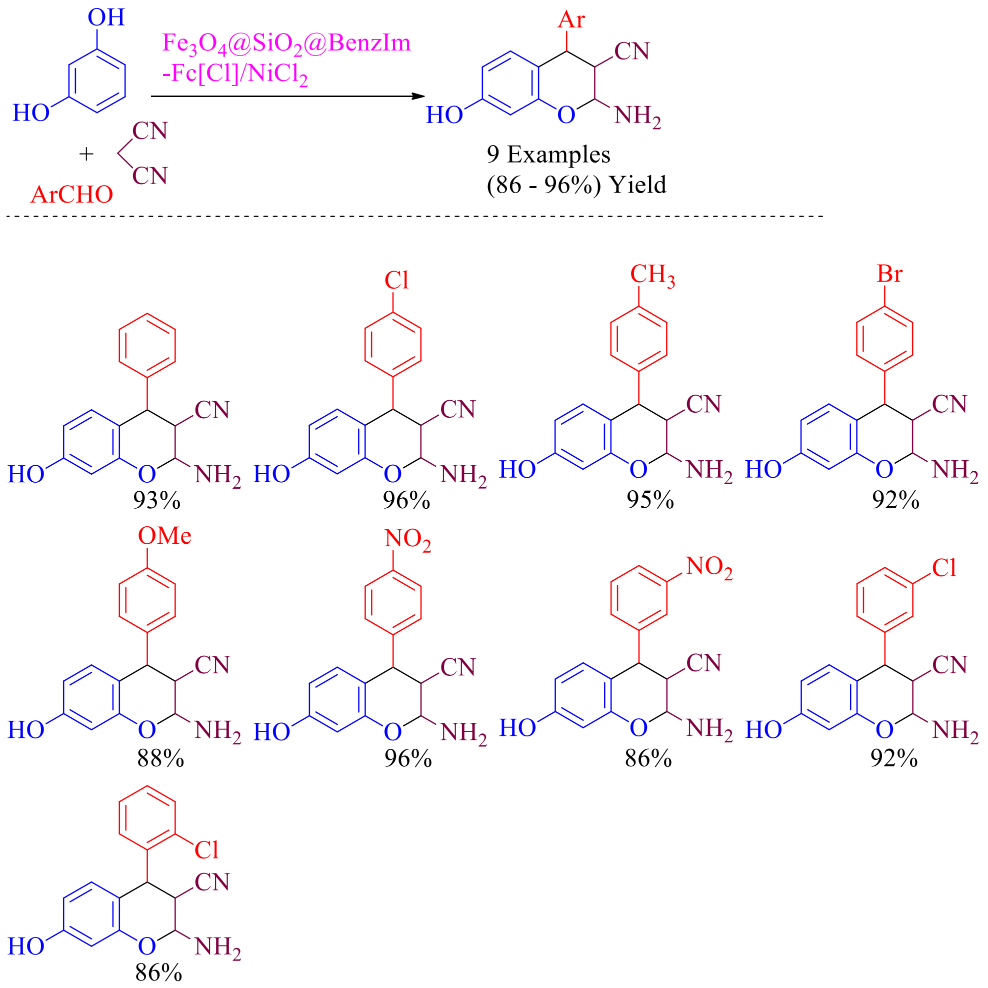
Scheme (29): Synthesis of dihydropyrimidinones via Biginelli reaction catalyzed by Fe_3O_4@SiO_2-IL/[Mo_6O_{19}] Nanocatalyst.

Pyran annulated heterocyclic compounds have been attracted considerable attention because of their various useful biological and pharmaceutical activities. Mohammadi *et al.* (2018) designed a novel Fe_3O_4@SiO_2-BenzIm-Fc[Cl]/$NiCl_2$ nanoparticle synthesized using a simple chemical coprecipitation approach[lxxxix]. The catalytic activities of the novel magnetically recoverable Fe_3O_4@SiO_2-BenzIm-Fc[Cl]/$NiCl_2$ nanoparticle were evaluated in the synthesis of pyrano [3,2-c]chromene derivatives and compared with products formed using [BuMeIm][Cl], [FcBuMeBenzIm][I] ionic liquids, Fe_3O_4@SiO_2@BenzIm-Fc[Cl] catalyst. Under optimized reaction conditions they conclude that supported ionic liquid [FcBuMeBenzIm][I] is better than conventional [BuMeIm][Cl] ionic liquid. While Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/$NiCl_2$ gives excellent results. Then series of pyrano[3,2-c]chromene, pyrano[3,2-b]pyran and pyrano[2,3-d]pyrimidine derivatives were synthesized using novel nanocatalyst. One-pot three-component reaction of 4-chlorobenzaldehyde, malononitrile and 4-hydroxycoumarin catalyzed by Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/$NiCl_2$ was investigated in various solvents. Out of which ethanol-water (4:2, v/v) found to be better solvent in which excellent yield obtained. Nano-catalyst reused for six runs without significant loss in catalytic activity.

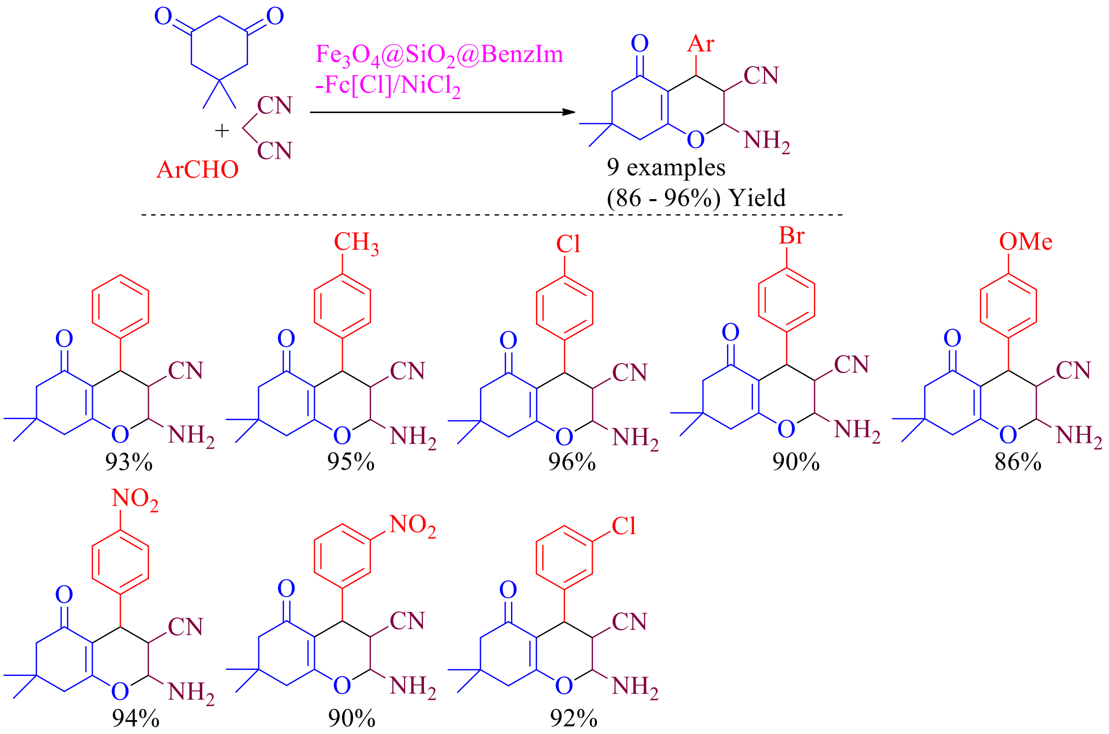




Scheme(30): Synthesis of Pyran derivatives using $Fe_3O_4@SiO_2@BenzIm\text{-}Fc[Cl]/NiCl_2$ Nanocatalyst.

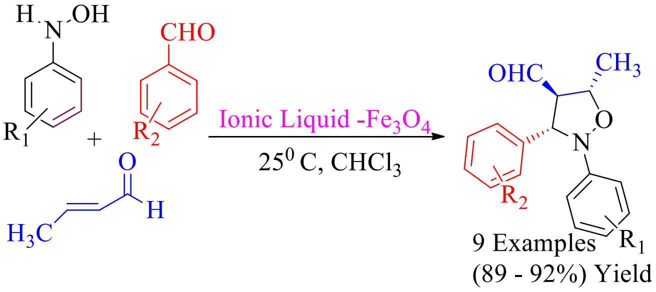


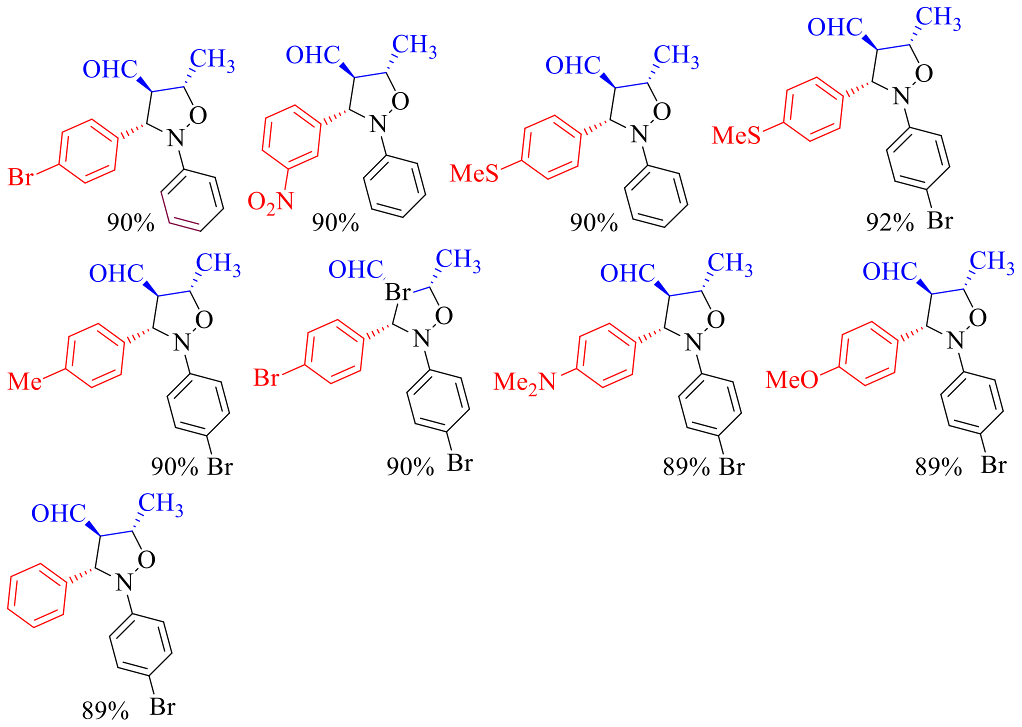
Scheme (31): Synthesis of Pyran derivatives using $Fe_3O_4@SiO_2@BenzIm\text{-}Fc[Cl]/NiCl_2$ Nanocatalyst.



Scheme (32): Synthesis of Pyran derivatives using $Fe_3O_4@SiO_2@BenzIm-Fc[Cl]/NiCl_2$ Nanocatalyst.

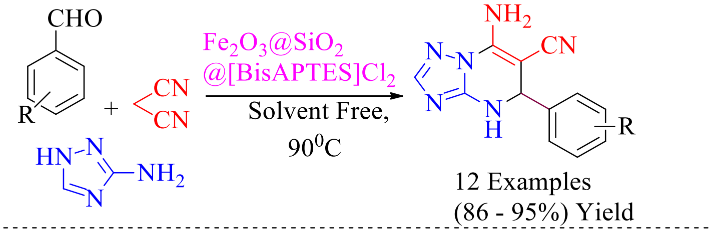
Javad Safaei-Ghomi et al developed Fe_3O_4 NPs supported novel ionic liquid (IL) with L-alanine and choline chloride[xc] nanocatalyst for synthesis of isoxazolidines. Mixture of N-arylhydroxylamine, aromatic aldehyde, α, β-unsaturated aldehyde, and $CHCl_3$ stirred at rt. external magnet the catalyst. Benzaldehyde, N-phenylhydroxylamine, and crotonaldehyde were chosen as model substrates for the synthesis of representative isoxazolidines, and the reaction was performed at room temperature. Among THF, $CHCl_3$, Methanol and CH_3CN, best solvent in terms of yield was $CHCl_3$. MNPs was recovered by and the reaction mixture was purified by flash column chromatography to yield pure products.

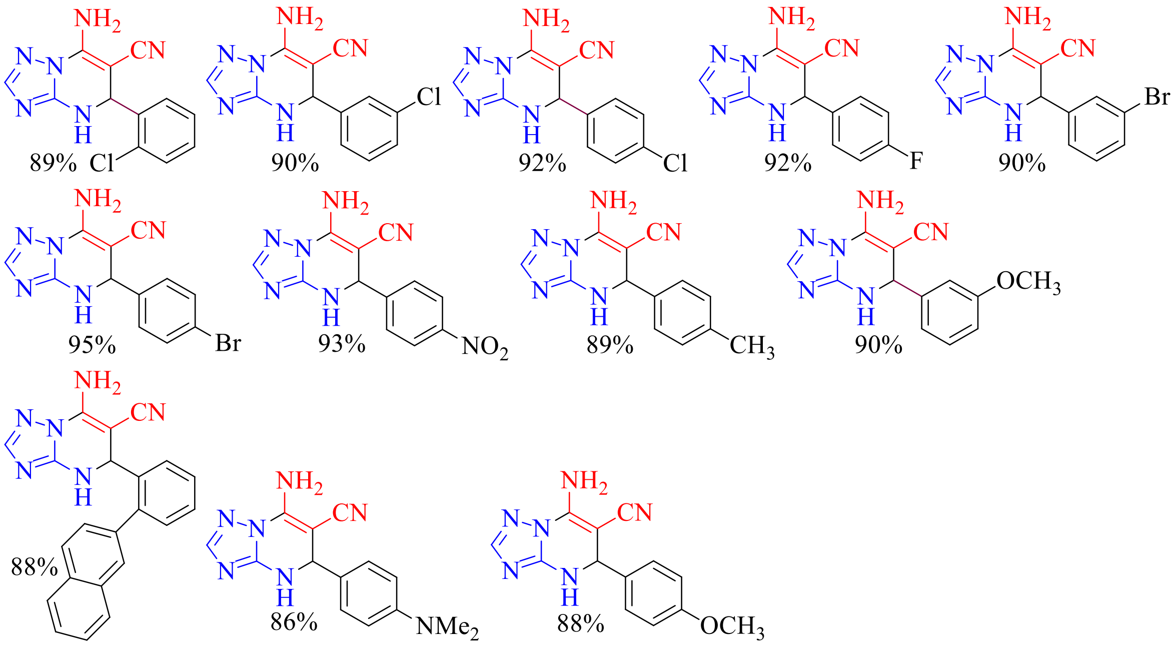




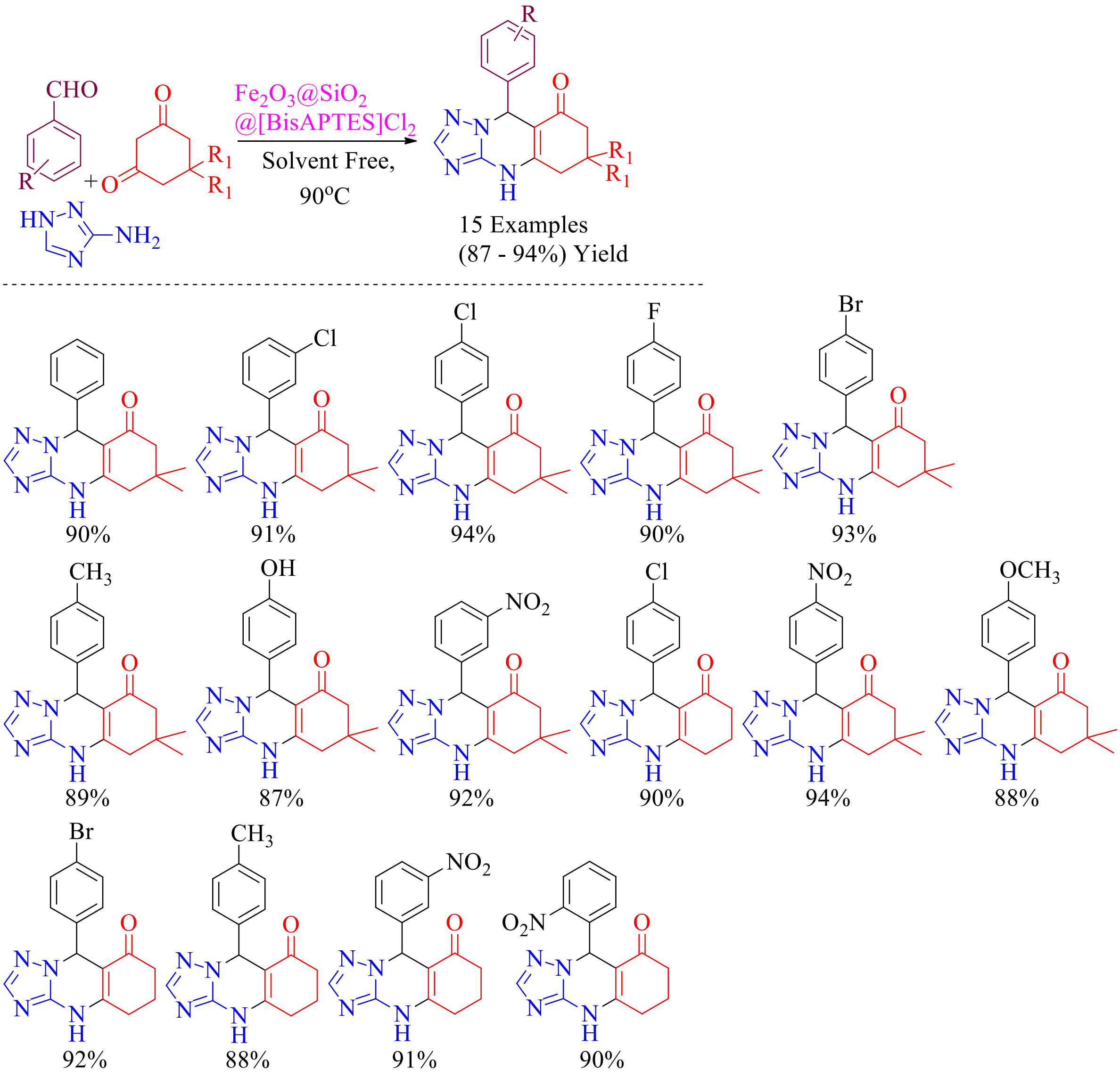
Scheme (33): 1,3- dipolar cycloaddition catalyzed by IL-MNPs.

Karimi-Chayjani *et al.* reported synthesis bis-[(3-aminopropyl)triethoxysilane] dichloride immobilized on magnetic nano g-Fe_2O_3@SiO_2 g-Fe_2O_3@SiO_2@N1,N4-bis(3-(triethoxysilyl) propyl)butane-1,4-diaminium dichloride i.e [g-Fe_2O_3@SiO_2@[Bis-APTES]Cl_2] nano particles[xci]. In order to assess the generality and efficacy of catalyst for the production of 5-amino-7-aryl-7,8-dihydro- [1,2,4] triazolo [4,3-a]-pyrimidine-6-carbonitrile/[1,2,4]triazolo [5,1-b] quinazolin-8-ones, arylaldehydes (with various substituents) were reacted with 3-amino-1,2,4-triazole, malononitrile or dimedone and 10 mg catalyst under the optimal reaction conditions. Aldehydes with electron-donating and electron-withdrawing groups lead to excellent yields. But use of dimedone in place of malononitrile increases rate of reaction.



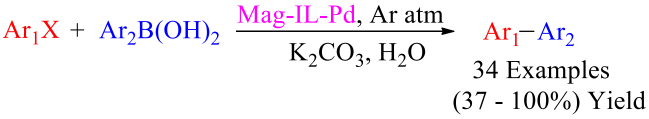


Scheme (34): Synthesis of 1,2,4’ triazolopyrimidine/ quinazolinone derivative.



Scheme (35): Synthesis of 1,2,4’ triazolopyrimidine/ quinazolinone derivative.

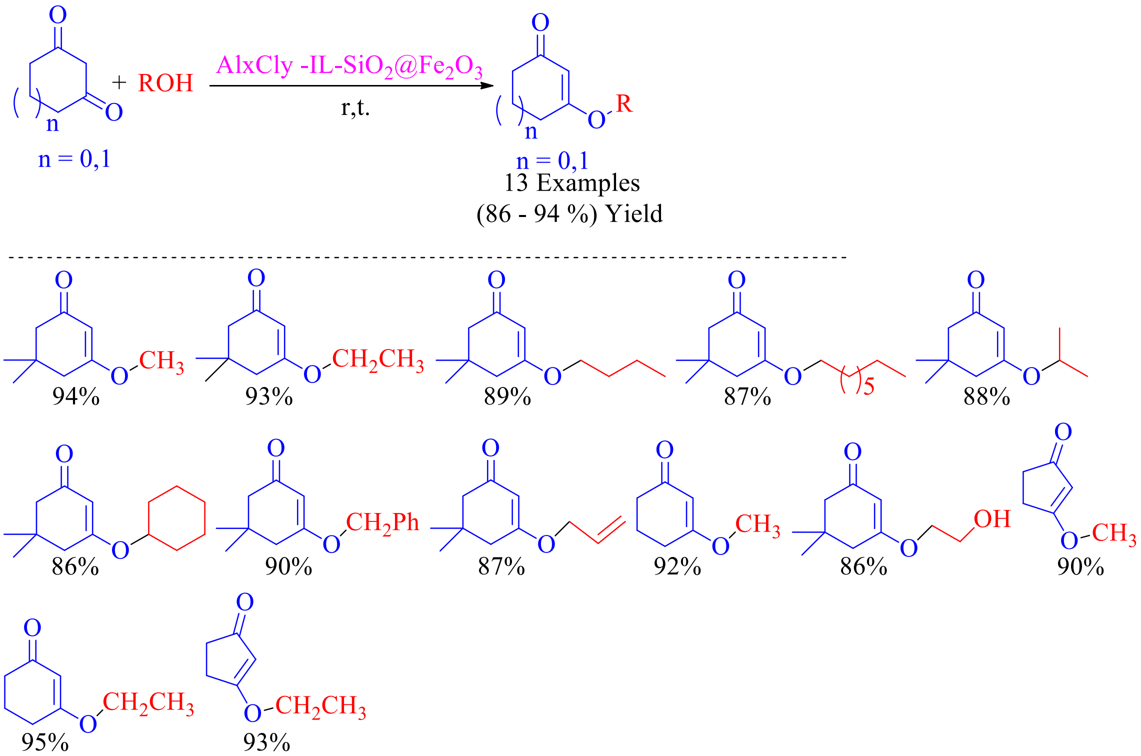
To investigate catalytic activity of prepared nanocatalyst Karimi *et al.* carried out suzuki reaction of various aryl halides and boronic acids in the presence of Mag-IL-Pd catalyst[xcii]. Optimization of the Suzuki coupling reaction of 4-bromoanisole and phenyl boronic acid in the presence of Mag-IL-Pd was carried out. The magnetic properties of the $Fe_3O_4@SiO_2$, Mag-IL and Mag-IL-Pd catalysts were investigated using a vibrating sample magnetometer at room temperature. The presence of a hydrophilic ionic liquid in the surface of magnetic nanoparticles provides a means of complete dispersion of the catalyst into the aqueous phase and they found the catalyst had no affinity to the organic phase and exposes the active Pd sites to substrates like homogeneous systems. Catalyst recycled ten times. Mag-IL-Pd was used as an eco-friendly and economic catalyst to perform this transformation.



$$Ar_1X + Ar_2B(OH)_2 \xrightarrow[K_2CO_3,\ H_2O]{\text{Mag-IL-Pd, Ar atm}} Ar_1{-}Ar_2$$

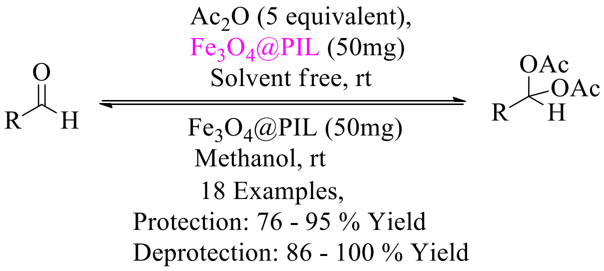
Scheme (36): Suzuki Miyaura coupling reaction catalyzed by Mag- IL- Pd Nanocatalyst

Li *et al.* designed magnetically ionic liquid supported on γ-Fe_2O_3 nano catalyst (AlxCly-IL-$SiO_2@\gamma$-Fe_2O_3) for synthesis of β-keto enol ethers[xciii]. The model reaction was carried out of 5,5-dimethylcyclohexane-1,3-dione and ethanol at room temperature using AlxCly-IL-SiO2@γ-Fe_2O_3 Nanocatalyst. Under optimized reaction conditions 5,5-dimethylcyclohexane-1,3-dione were treated with alcohols such as methanol, ethanol, butan-1-ol, heptan-1-ol, propan-2-ol, cyclohexanol, benzyl alcohol as well as allyl alcohols to form β-keto enol ethers.



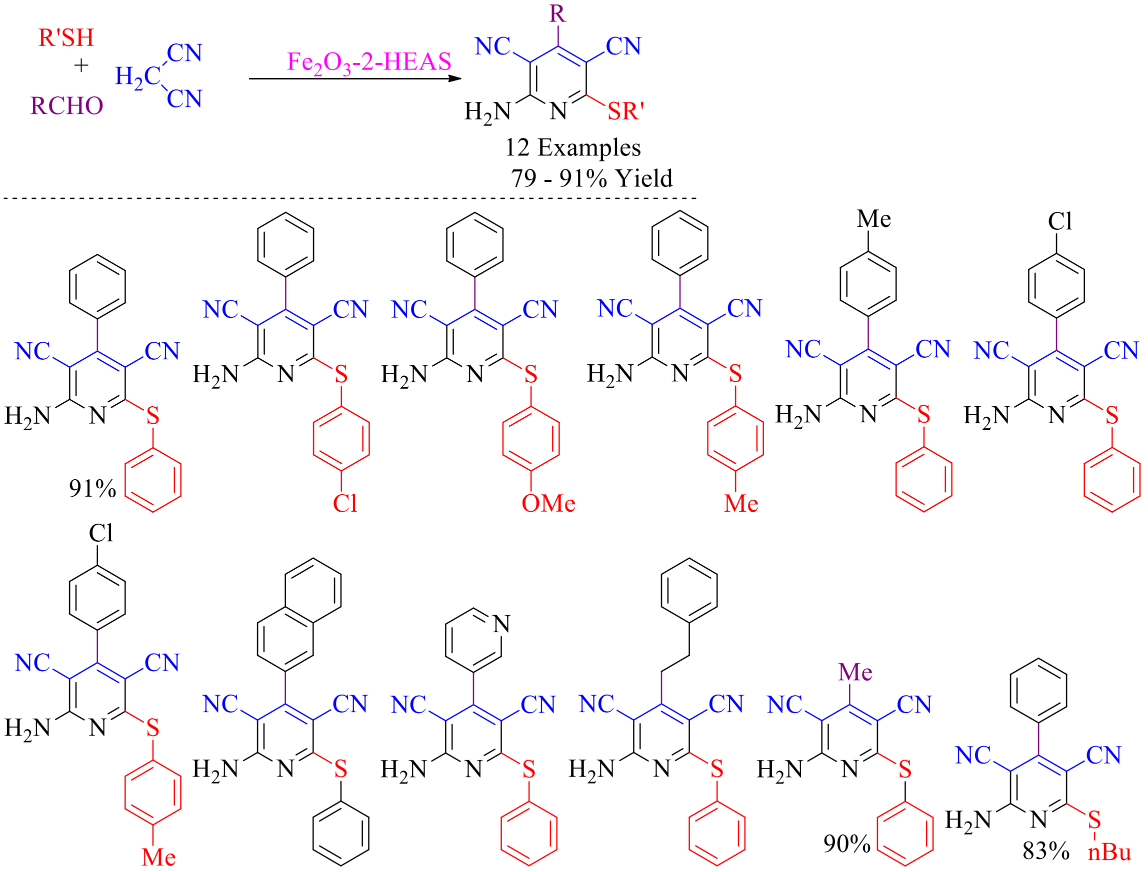
Scheme (37): Synthesis of beta-keto enol ethers

Pourjavadi *et al.* reported synthesis of functionalized poly(ionic liquid) coated magnetic nanoparticle (Fe_3O_4@PIL) catalyst[xciv]. To check catalytic activity of synthesized nanocatalyst, synthesis of 1,1-diacetyl using the reaction between aldehydes and acetic anhydride at room temperature was carried out. They found that Fe_3O_4@PIL worked well in diacetylation of hindered aldehydes and highly deactivated aldehydes .

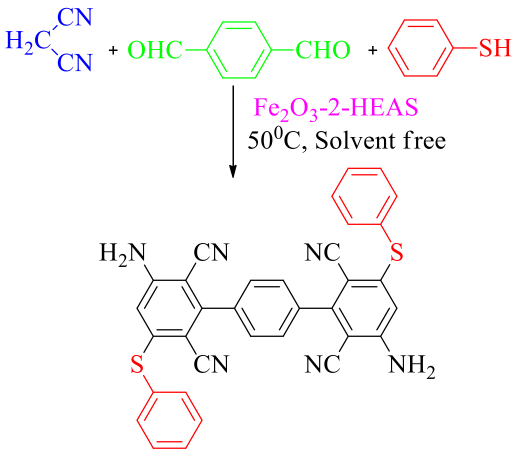


Scheme (38): Acetylation of Aldehyde using Ac_2O and their deprotection in presence of Fe_3O_4@PIL as catalyst

Sobhani *et al.* developed method for heterocycles containing 2-amino-3,5-dicarbonitrile-6-thiopyridine ring system which are known as interesting compounds in the pharmaceutical industry due to their various therapeutic applications[xcv]. The catalytic activity of 2-Hydroxyethylammonium sulphonate immobilized on Fe_2O_3 nanoparticles (Fe_2O_3-2-HEAS) was studied in the synthesis of three-component synthesis of 2-amino-3,5-dicarbonitrile-6-thio-pyridines. After the reaction was completed, EtOAc was added to the reaction mixture and the whole amount of Fe_2O_3-2-HEAS simply separated from the product by an external magnet. The magnetic property of Fe_2O_3-2-HEAS facilitates the efficient recovery of the catalyst.

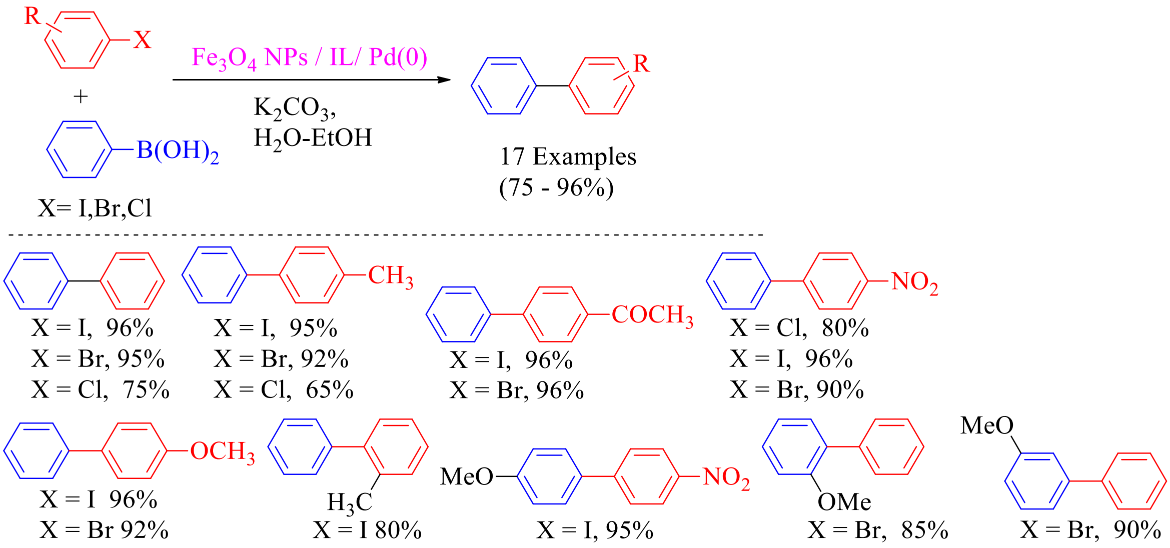


Scheme (39): Synthesis of 2-amino-3,5-dicarbonitrile-6-thio-pyridines catalyzed by Fe_2O_3-2-HEAS catalyst.



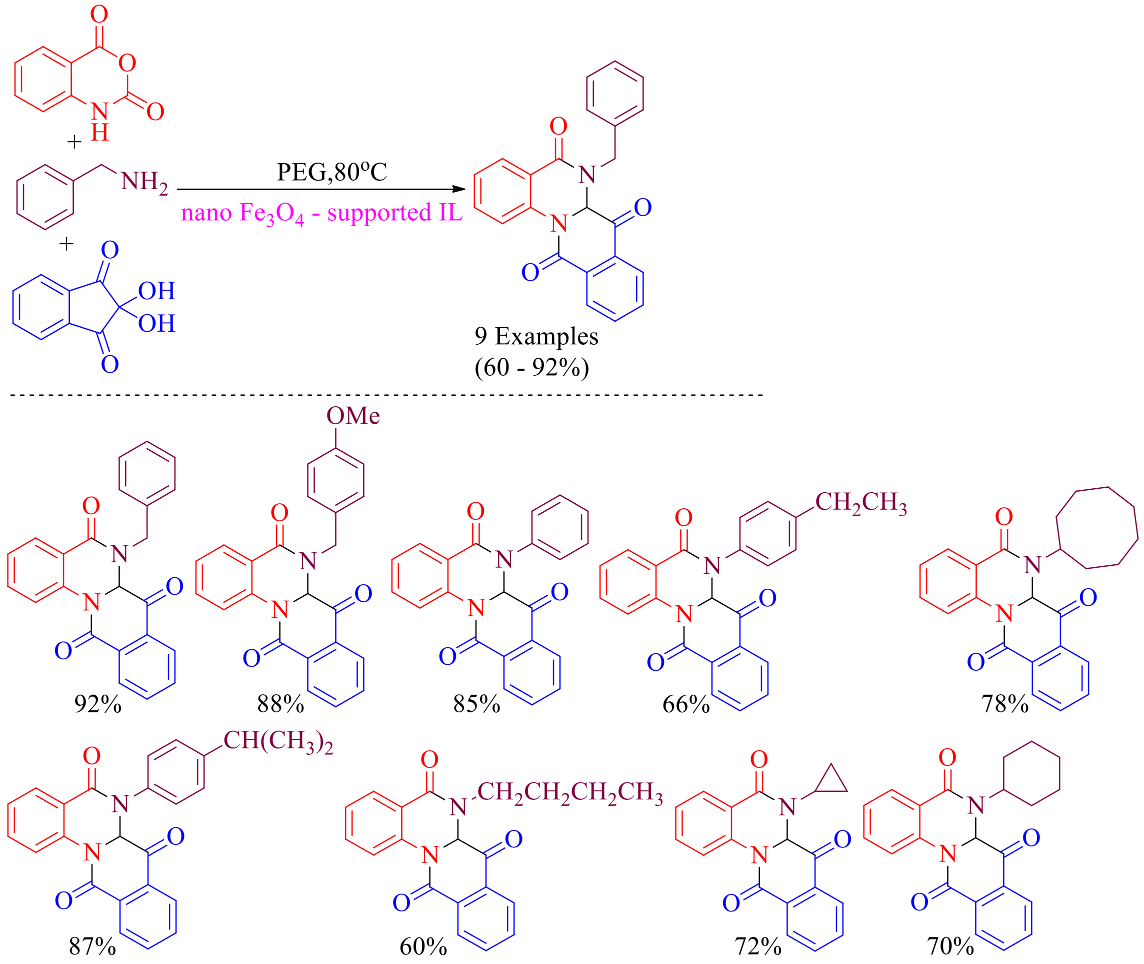
Scheme (40): Synthesis of 1,4-bis(2-amino-6-phenyl sulfanyl -4-pyridyl-3,5-dicarbonitrile) benzene catalyzed by Fe_2O_3-2-HEAS.

Veisi *et al.* designed a new hybrid magnetic Nano composite with ionic nature and lipophilic featured Pd nanoparticles immobilized on triethanolamine- functionalized magnetic nanoparticles [Fe_3O_4/IL/Pd] [xcvi]. Resulted nanocatalyst characterized by (HR-TEM, XRD, FT-IR, TGA, EDX, FE-SEM, ICP, XPS and VSM techniques. In order to check its utility Suzuki–Miyaura coupling reaction of different aryl halides with phenylboronic acid was carried out. Electron rich aryl boronic acids provided coupling products in good yields, 17(75-96%). After completion of the reaction, the catalyst was recovered with the help of a magnet, washed with distilled water (to remove excess base) and ethanol and dried in an oven at 50^0C.



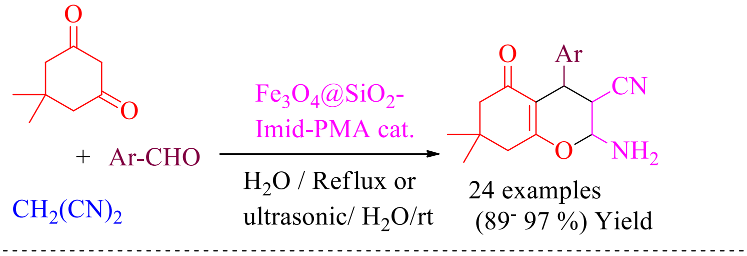
Scheme (41): Suzuki-Miyaura Cross coupling reaction catalyzed by Fe_3O_4/IL/Pd Nanocatalyst.

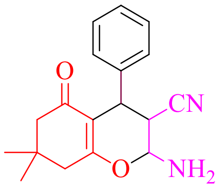
Ghorbani-Choghamarani *et al.* reported method for synthesis series of tetracyclic quinazoline compounds using nano-Fe_3O_4- supported ionic liquid[xcvii].



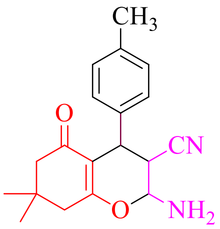
Scheme (42): Magnetic ionic liquid catalyzed one pot synthesis of tetracyclic quinazoline.

Due to nano size and strong interactions between each other magnetic nanoparticles have tendency to agglomerate, hence to overcome this problem nanoparticles are coated with silica layer and for increasing the catalytic activity heteropolyacids supported on materials like carbon, silica, acidic ion exchange resins. Mohan Emaeilpour et al developed Fe_3O_4@ SiO_2-imid-PMA NPs as efficient green catalyst for the synthesis of tetrahydrobenzo [b] pyran & dihydro pyrano [3,2-C] chromene derivatives under ultrasonic irradiation or reflux conditions in water[xcviii]. The model reaction was refluxed in the presence of 0.02 g of Fe_3O_4@SiO2-imid-PMA it is showed that the reaction proceed efficiently in refluxing H_2O and resulted in high yields of the desired product. This three-component condensation was accomplished in protic solvents under reflux and the corresponding products were obtained in 79-87% yield, Aprotic solvents afforded the desired product in lower yields and longer reaction times.

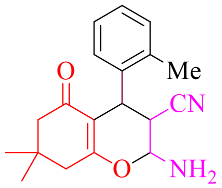




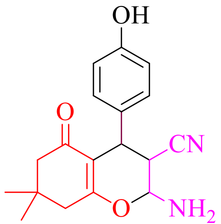
H_2O/Reflux : 94%
Ultrasonic/H_2O/r.t : 96%



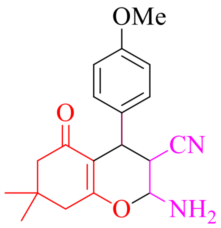
H_2O/Reflux : 85%
Ultrasonic/H_2O/r.t : 91%



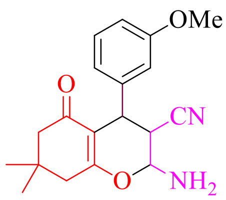
H_2O/Reflux : 82%
Ultrasonic/H_2O/r.t : 92%



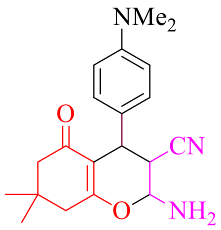
H_2O/Reflux : 92%
Ultrasonic/H_2O/r.t : 96%



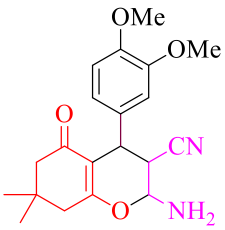
H_2O/Reflux : 87%
Ultrasonic/H_2O/r.t : 94%



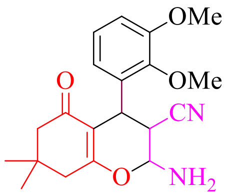
H_2O/Reflux : 88%
Ultrasonic/H_2O/r.t : 92%



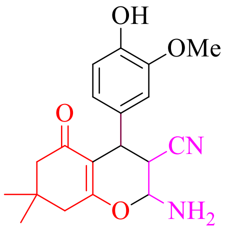
H_2O/Reflux : 90%
Ultrasonic/H_2O/r.t : 95%



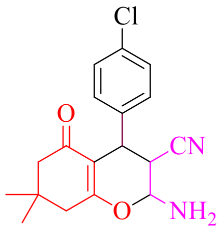
H_2O/Reflux : 84%
Ultrasonic/H_2O/r.t : 93%



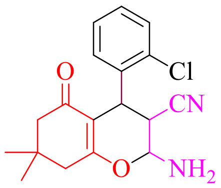
H_2O/Reflux : 85%
Ultrasonic/H_2O/r.t : 90%



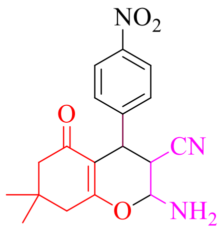
H_2O/Reflux : 88%
Ultrasonic/H_2O/r.t : 91%



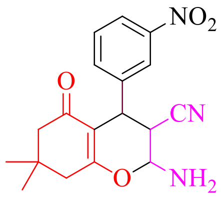
H_2O/Reflux : 95%
Ultrasonic/H_2O/r.t : 97%



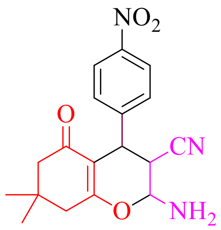
H_2O/Reflux : 90%
Ultrasonic/H_2O/r.t : 93%



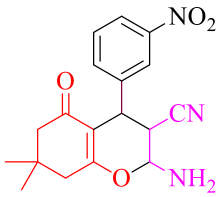
H_2O/Reflux : 96%
Ultrasonic/H_2O/r.t : 97%



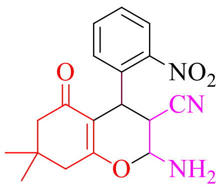
H_2O/Reflux : 93%
Ultrasonic/H_2O/r.t : 95%



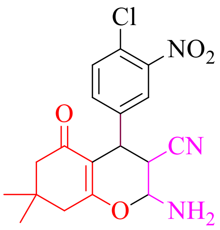
H_2O/Reflux : 96%
Ultrasonic/H_2O/r.t : 97%



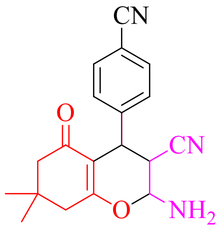
H_2O/Reflux : 93%
Ultrasonic/H_2O/r.t : 95%



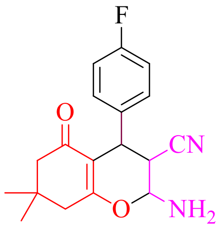
H_2O/Reflux : 93%
Ultrasonic/H_2O/r.t : 92%



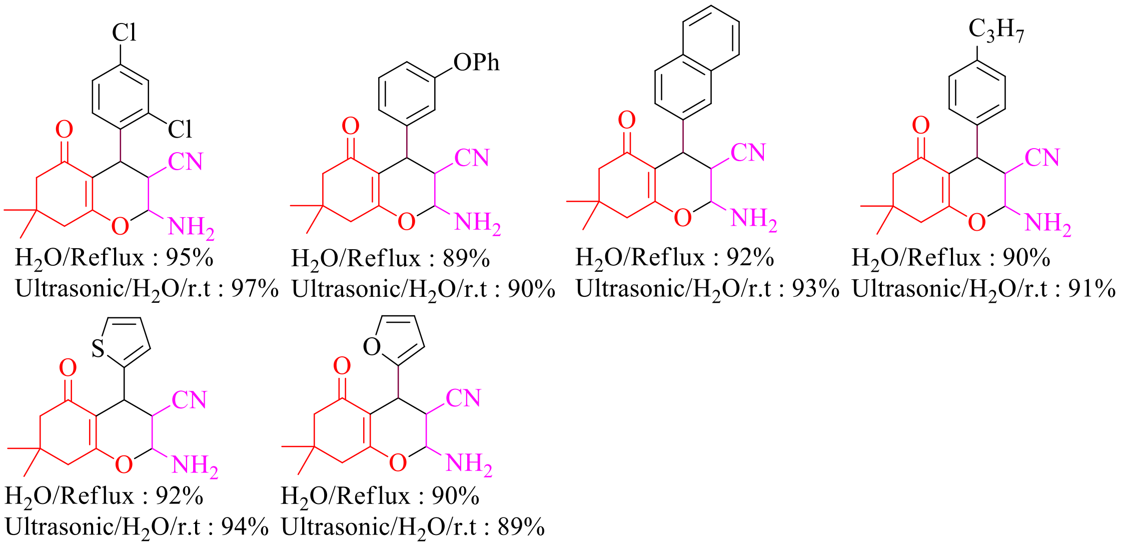
H_2O/Reflux : 97%
Ultrasonic/H_2O/r.t : 96%



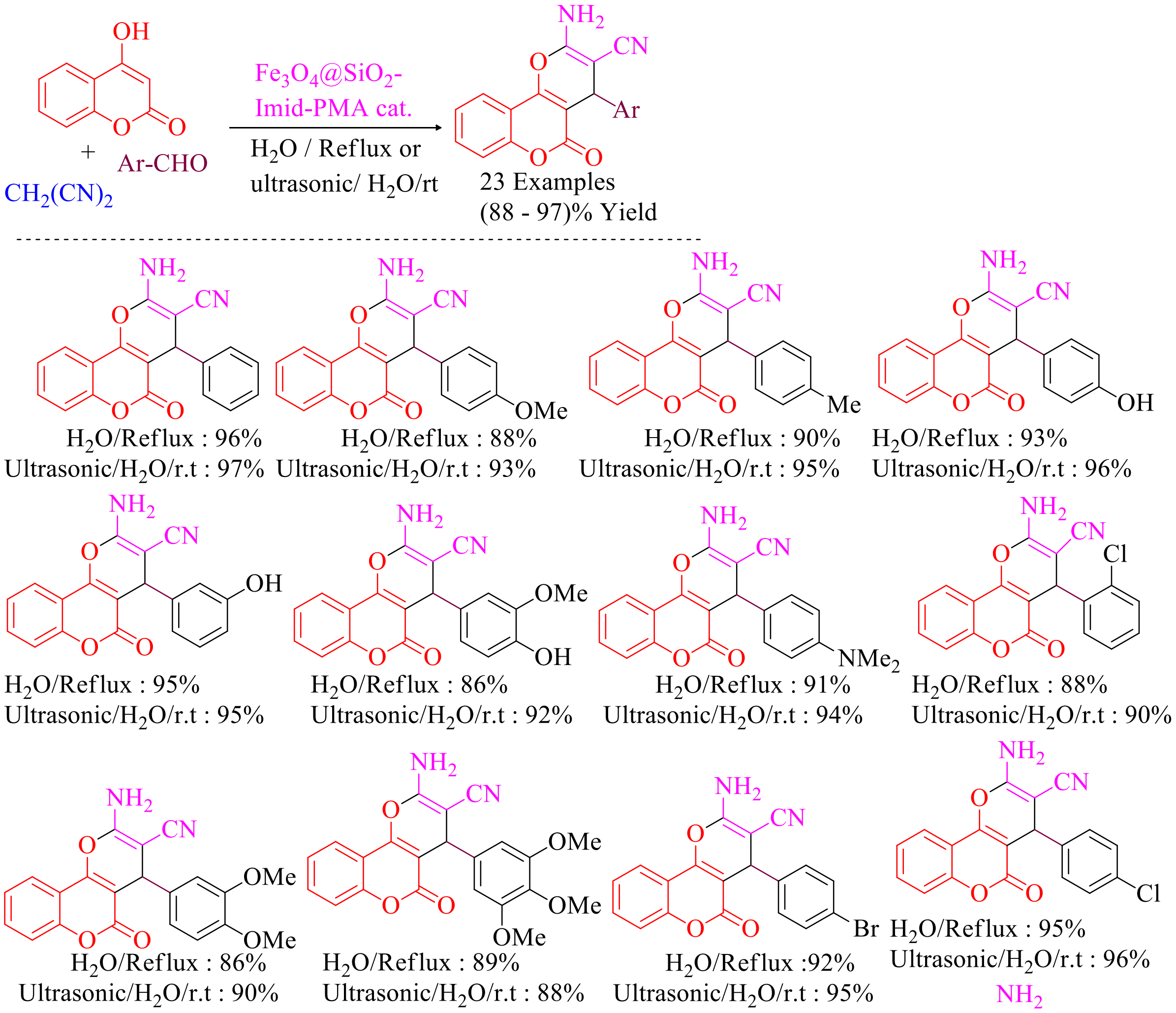
H_2O/Reflux : 89%
Ultrasonic/H_2O/r.t : 96%

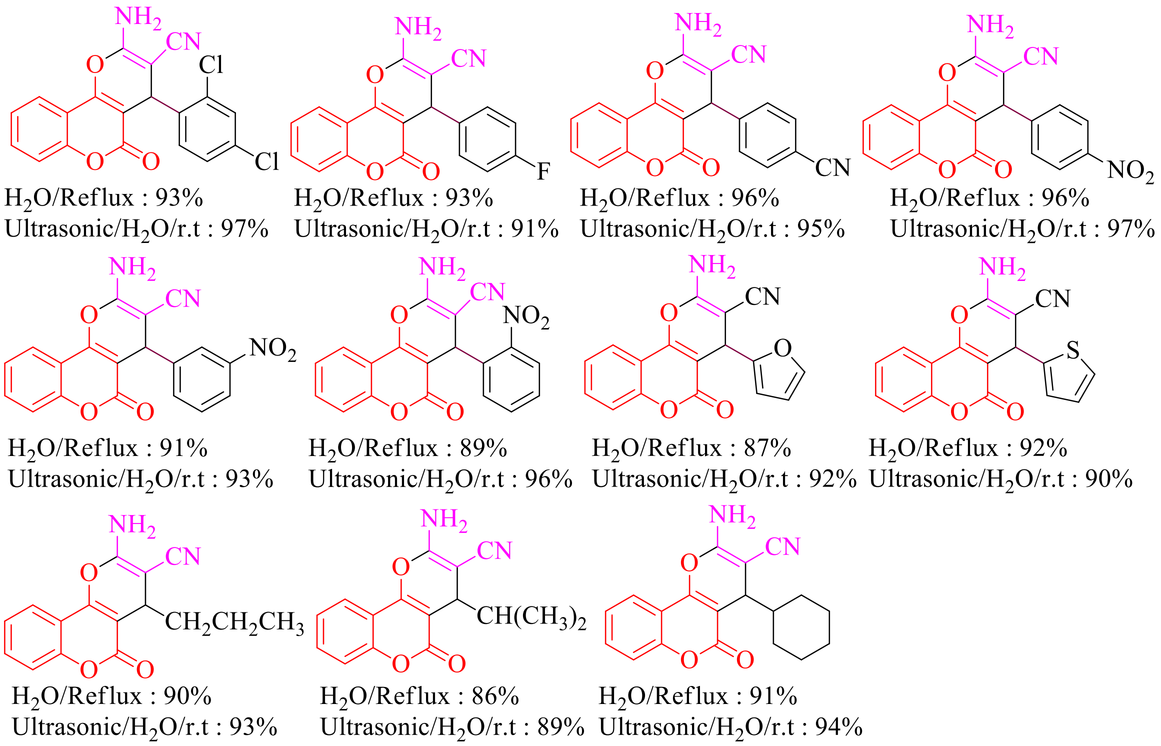


H_2O/Reflux : 96%
Ultrasonic/H_2O/r.t : 95%



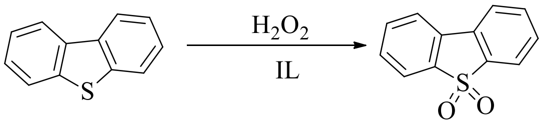
Scheme (43): Synthesis of derivatives of 2-amino-5-oxo-5,6,7,8-tetrahydro-4H-benzo{b] pyran in the presence of $Fe_3O_4@SiO_2$-Imid-PMA cat.





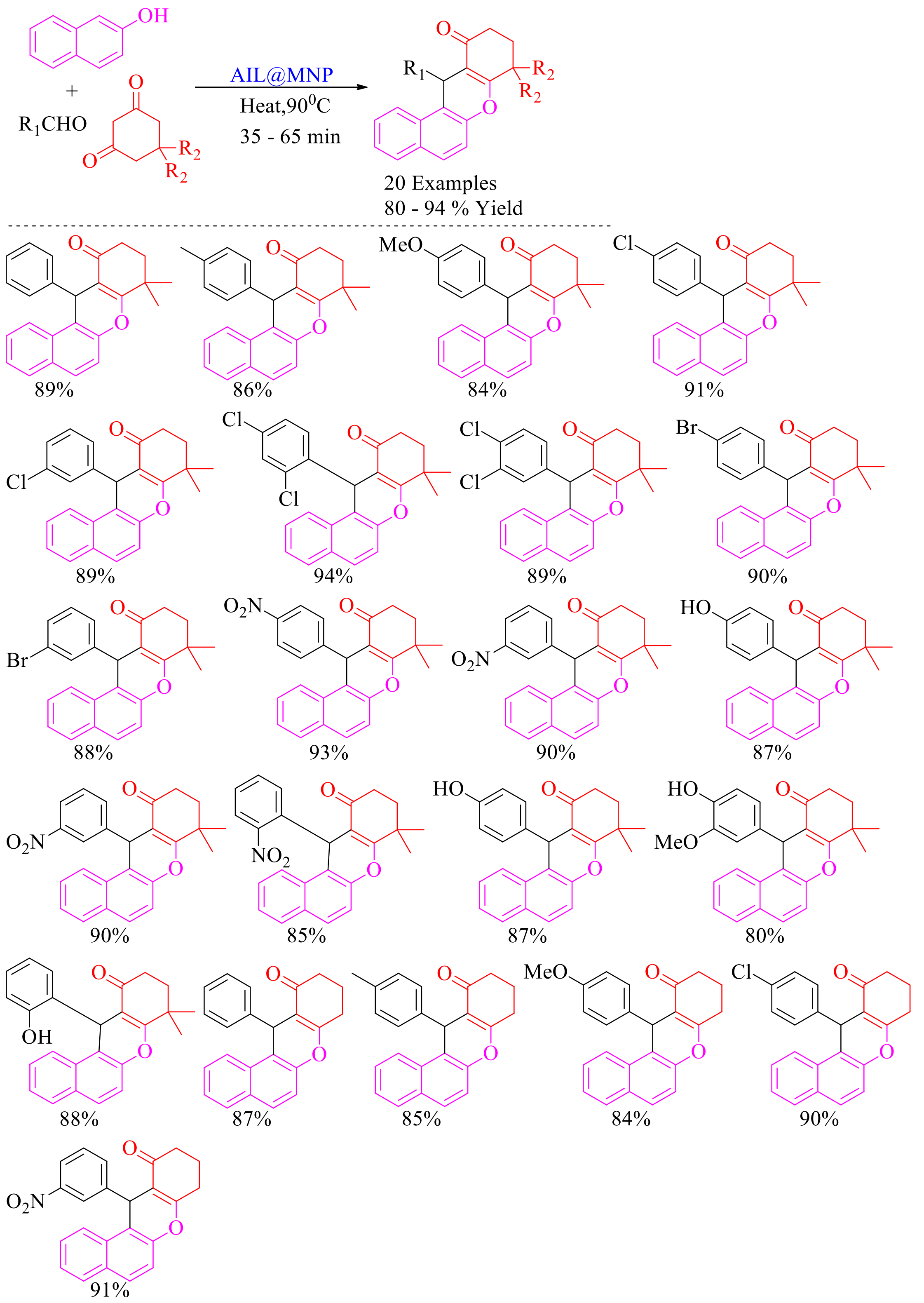
Scheme (44): Synthesis of dihydropyrano [3,2-C] chromene derivatives in the presence of $Fe_3O_4@SiO_2$-Imid-PMA cat.

Alizadeh *et al.* have reported a facile process of synthesis of $Fe_3O_4@ SiO_2$-ionic liquid catalyst and used as heterogeneous catalyst for di benzo thiophene oxidation in biphasic system[xcix]. Conversion of dibenzothiophene to dibenzothiophene sulfone was not observed. These observations were contributed to this fact that on the surfaces of $Fe_3O_4@ SiO_2$, $Fe_3O_4@ SiO_2$–Cl and $Fe_3O_4@ SiO_2$ methyl imidazolium chloride nanoparticles does not exist necessary sites for activation of H_2O_2. The presence of the ionic liquid moieties on the surface of magnetic nanoparticles leading to high polarity of the catalyst surface and the polar catalyst could be easily dispersed in acetonitrile phase. H_2O_2 as an oxidant could be easily adsorbed to the polar surface of the catalyst and then the oxidation process continues.



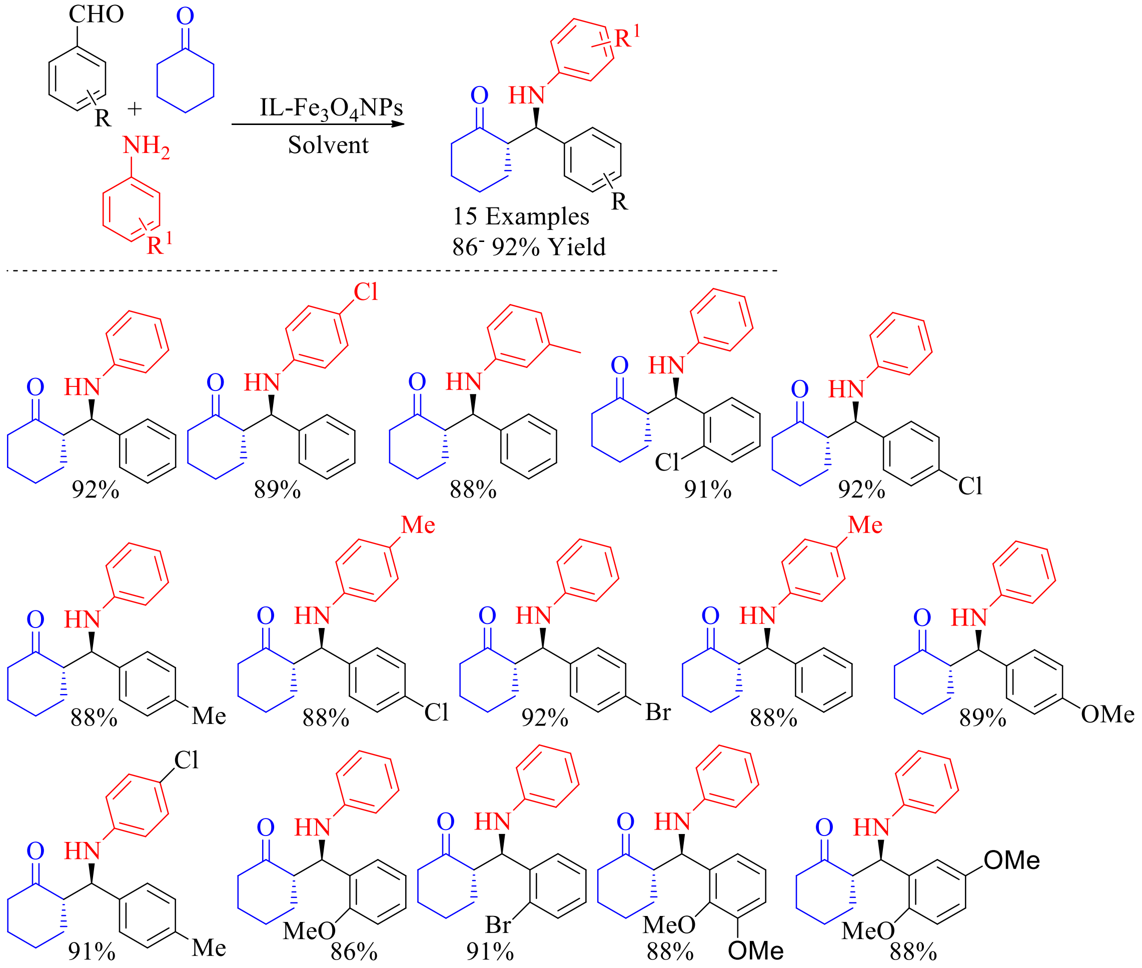
Scheme (45): The oxidation of DBT to sulfone catalyzed by $Fe_3O_4@SiO_2$–methylimidazolium ionic liquid

Zhang *et al.* reported one pot synthesis of benzoxanthenes using one-pot three-component condensation of dimedone with 4-chlorobenzaldehyde and 2-naphthol catalyzed by magnetic nanoparticle supported dual acidic ionic liquid as model substrates at 90^0C under solvent-free conditions[c]. Without the addition of catalyst, only trace amounts of product were detected. Under the optimized reaction conditions, a variety of electron withdrawing and electron donating substituent on aromatic aldehyde provided good to excellent product yields.



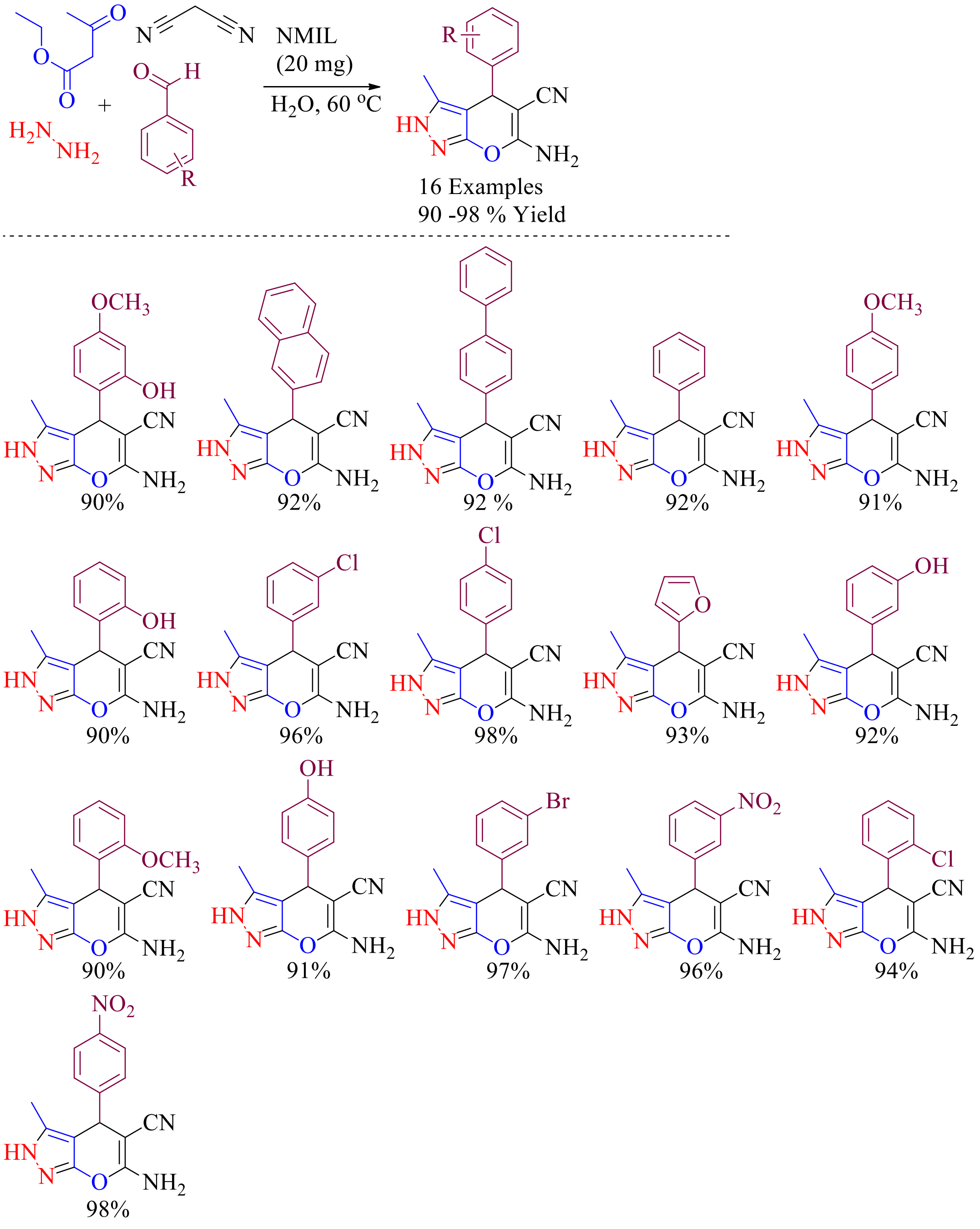
Scheme (46): Synthesis of bezoxanthenes derivatives in the presence of magnetic nanoparticles supported by IL.

Ghomi *et al.* reported synthesis of Ionic liquid derived from L-alanine and choline chloride and used effectively for stabilization of magnetic Fe_3O_4 nanoparticles[ci]. Magnetic Fe_3O_4 nanoparticle stabilized by ionic liquid used for highly anti selective three component Mannich reaction. In a typical Mannich reaction, aryl aldehyde (2.5mol), arylamine (2.5mol), cyclohexanone (3mol) and EtOH (20 mL) were added to the IL-MNPs (0.001 g) in a 50mL flask equipped with a heating arrangement and a stirrer and the temperature was set at reflux condition. After the reaction was completed, the catalyst was separated by an external magnet. The reaction mixture was purified by flash column chromatography to give the pure β-amino ketone derivatives. Also they used ultrasonic radiation method. The aromatic aldehyde (2.5 mmol), aromatic amine (2.5 mmol), cyclohexanone (3.0 mmol), IL-MNPs (0.001 g) and EtOH (20 mL) were added into a 25 mL round bottomed flask. The reaction mixture was sonicated under 75 W for the period of time.



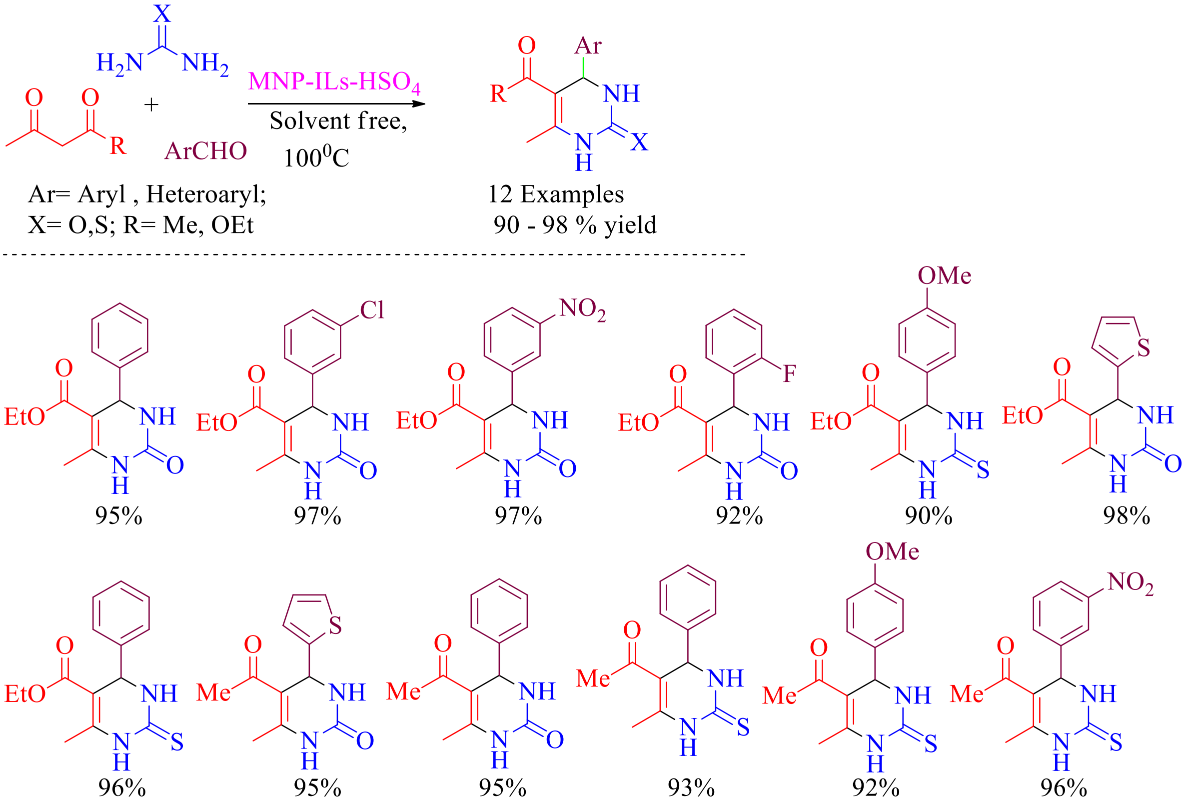
Scheme (47): Direct asymmetric mannich reaction catalyzed by IL-Fe3O4 NPs under ultrasonic irradiation

Pyrano [2, 3-c] pyrazole are joined to heterocyclic compounds that possess many biological properties such as fungicidal, bactericidal, vasodilator activities and acts as anticancer agents. Ramin Ghorbani-Vaghei *et al.* fabricated a novel, org-inorganic hybrid heterogeneous catalystFe$_3$O$_4$ @SiO$_2$@piperidinium benzene-1, 3-disulfonate for the synthesis of 6-amino-3-methyl-4-phenyl-2,4-dihydropyrano[2,3-c] pyrazole derivatives[cii]. Condensation reaction between ethyl acetoacetate, aryl aldehydes, malononitrile and hydrazine hydrate in water solvent at 60^{0}C was employed for synthesis of pyrano [2, 3-c] pyrazole derivatives. Good results were obtained when reaction was carried out using 20 mg of nano magnetic catalyst. They investigated that water is best solvent among ethanol, acetonitrile, CH_3CO_2Et, CH_2Cl_2 and toluene at 60^{0}C. Aromatic aldehydes with electron withdrawing groups reacted faster than aromatic aldehydes with electron donating groups. Ortho substituted aromatic aldehydes gives low yield due to steric reasons but meta and para substituted aromatic aldehydes reacted with excellent yields. Use of MNP catalyst increased the yield with reduced reaction time.



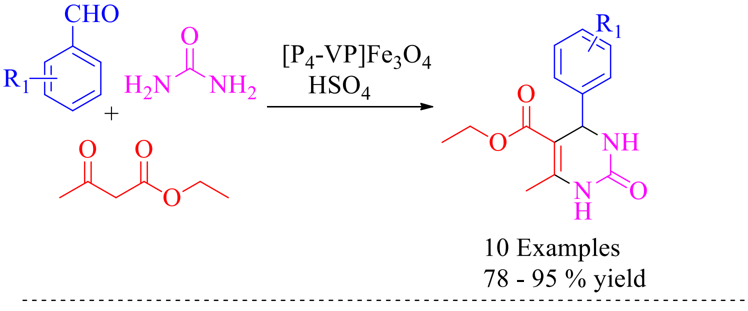
Scheme (48): synthesis of 6-amino-4-(4-methoxyphenyl)-5-cyano-3-methyl-1- phenyl-1,4-dihydropyarno[2,3-c]pyrazolesderivative using\ Fe_3O_4@SiO_2@piperidinium benzene-1,3-disulfonaate (Fe_3O_4@SiO_2 nanoparticle supported IL.

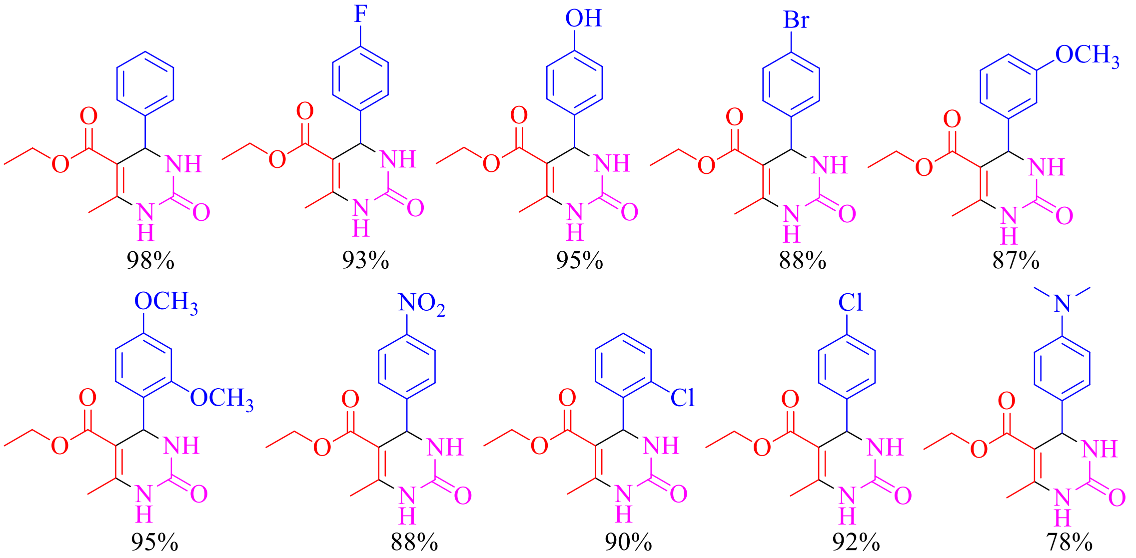
As the Dihydropyrimidones scaffolds shows wide biological applications, Zarnegar *et al.* developed novel synthetic route for modified Fe_3O_4 nanoparticles supported on imidazolium ionic liquids[ciii]. 1-methyl-3-(3-trimethylsilylpropyl)imidazolium hydrogen sulfate (MNPs-IIL-HSO4) , 1-methyl-3-(3-trimethylsilylpropyl)imidazolium hydrogen acetate (MNPs-IIL-OAc), 1-methyl-3-(3-trimethylsilylpropyl)imidazolium hydrogen chloride (MNPs-IIL-Cl) were used as the efficient catalyst for Bigenilli reaction in the synthesis of substituted Dihydropyrimidones.



Scheme (49): Synthesis of 3,4-dihydropyrimidin-2(1H)-ones and thiones catalyzed by MNPs-IL-HSO4.

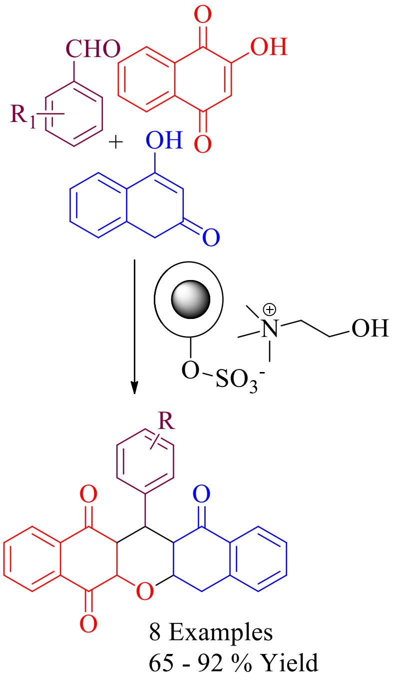
Zarchi *et al.* have described an efficient nanocatalyst based on [P4-VP]-Fe_3O_4 nanoparticles supported on Bronsted acid ionic liquid & effectively used for the synthesis of 3,4-dihydropyrimidin-2(1H)-ones derivative by Biginelli Reaction[civ]. In order to investigate catalytic amount they carried out model reaction of Benzaldehyde, urea & ethyl acetoacetate using various amounts of [P4-VP]-Fe_3O_4 HSO_4. They found that only 75 mg was considered to be optimum amount of catalyst to catalyze the reaction with good yields. Also they studied effect of temp. on reaction in presence of 75 mg of catalyst. They conclude that according to catalyst selectivity and yield of products, the best reaction conditions for pure Biginelli products are provided at 80⁰ C.

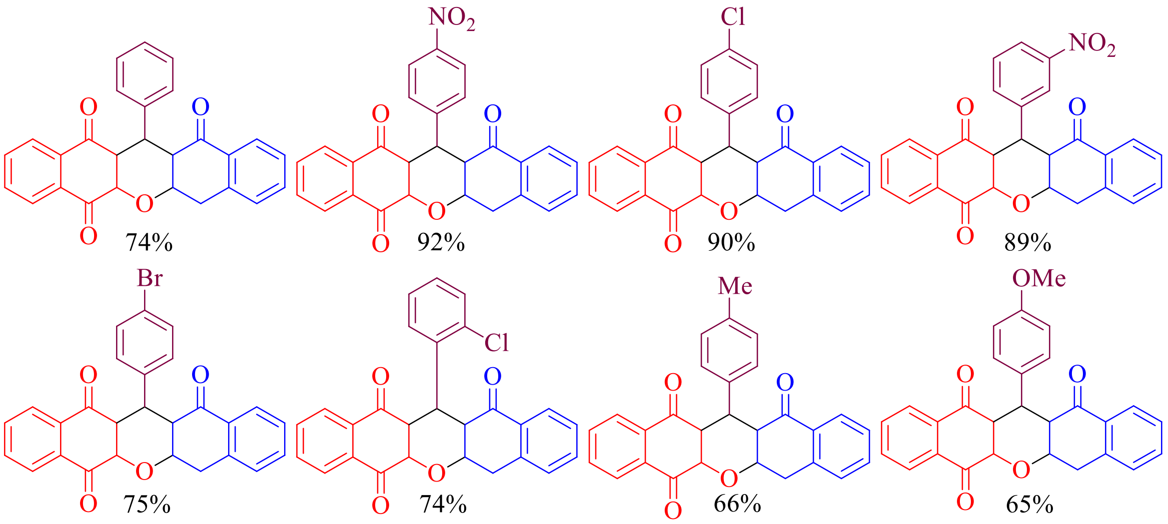




Scheme (50) : Synthesis of substituted dihydropyrimidones by Biginelli reaction.

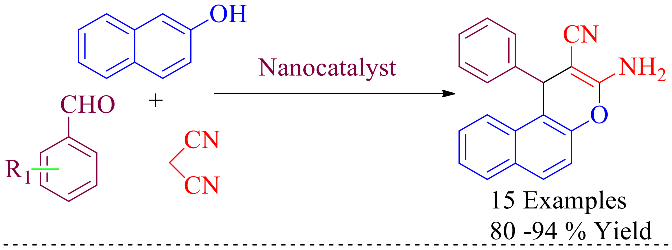
Chromenes exhibit important biological properties including anticancer, anti-inflammatory, antibacterial, antioxidant and anti-HIV activities. Therefore, the improvement of simple methods for the development of chromenes is still necessary and in demand. The preparation of chromenes has been reported in the presence of diverse catalysts Safaei-Ghomi *et al.* reported the preparation of new chromene by the reaction of aldehydes, 4-hydroxycoumarin and 2-hydroxynaphthalene-1,4-dionein the presence of an IL supported on Fe_3O_4 nanoparticles (nano- Fe_3O_4-IL) in ethanol–water at 50 °C^{cv}. With optimized reaction condition they demonstrated the influence of the catalyst on the model reaction. It was found that good yield obtained when catalyst was 20 mg. And catalyst was recyclable for six times.

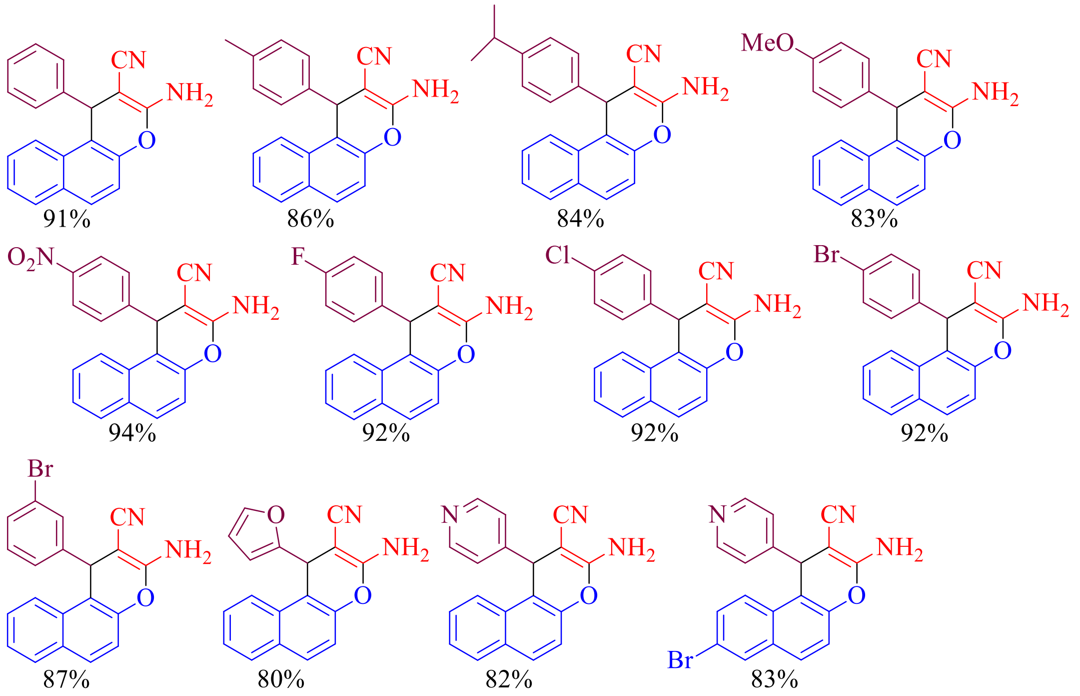




Scheme (51): Synthesis of chromenes using Fe_3O_4 -IL MNPs.

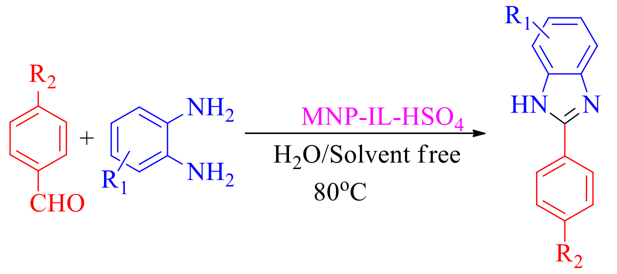
Teimuri-Mofrad *et al.* described solvent-free reaction between aldehydes, β- Naphthol and malononitrile in 2-amino-3-cyano-4H-pyran derivatives preparation using a ferrocene-containing imidazole-based IL stabilized on silica-coated Fe_3O_4 MNPs i.e. [Fe_3O_4@SiO_2@Im-Fc][OAc] as an efficient catalyst[cvi]. Reaction between benzaldehyde, β- naphthol and malononitrile was conducted in order to obtain optimized reaction condition. During reaction optimization, following parameters has been changed: catalyst {([BuMeIm][Cl]), ([BuMeIm][BF_4]), ([BuMeIm][PF_6]), ([BuMeIm][HSO_4]), ([BuMeIm][HCOO]), ([BuMeIm][OAc]), ([FcBuMeIm][Cl]), ([FcBuMeIm][OAc])}, Solvent: (EtOH, $CHCl_3$, CH_2Cl_2,H_2O and solvent free condition) and temperature: (r.t., 40^0-110^0C). All reactions were carried out at 90°C under solvent-free conditions in an oil bath. At solvent free condition, temperature 90°C and 10 mg amount of the nanocatalyst were found to be the best reaction conditions. Condensation reactions of 2-naphthols with a series of aromatic aldehydes and malononitrile was carried out in optimized conditions.



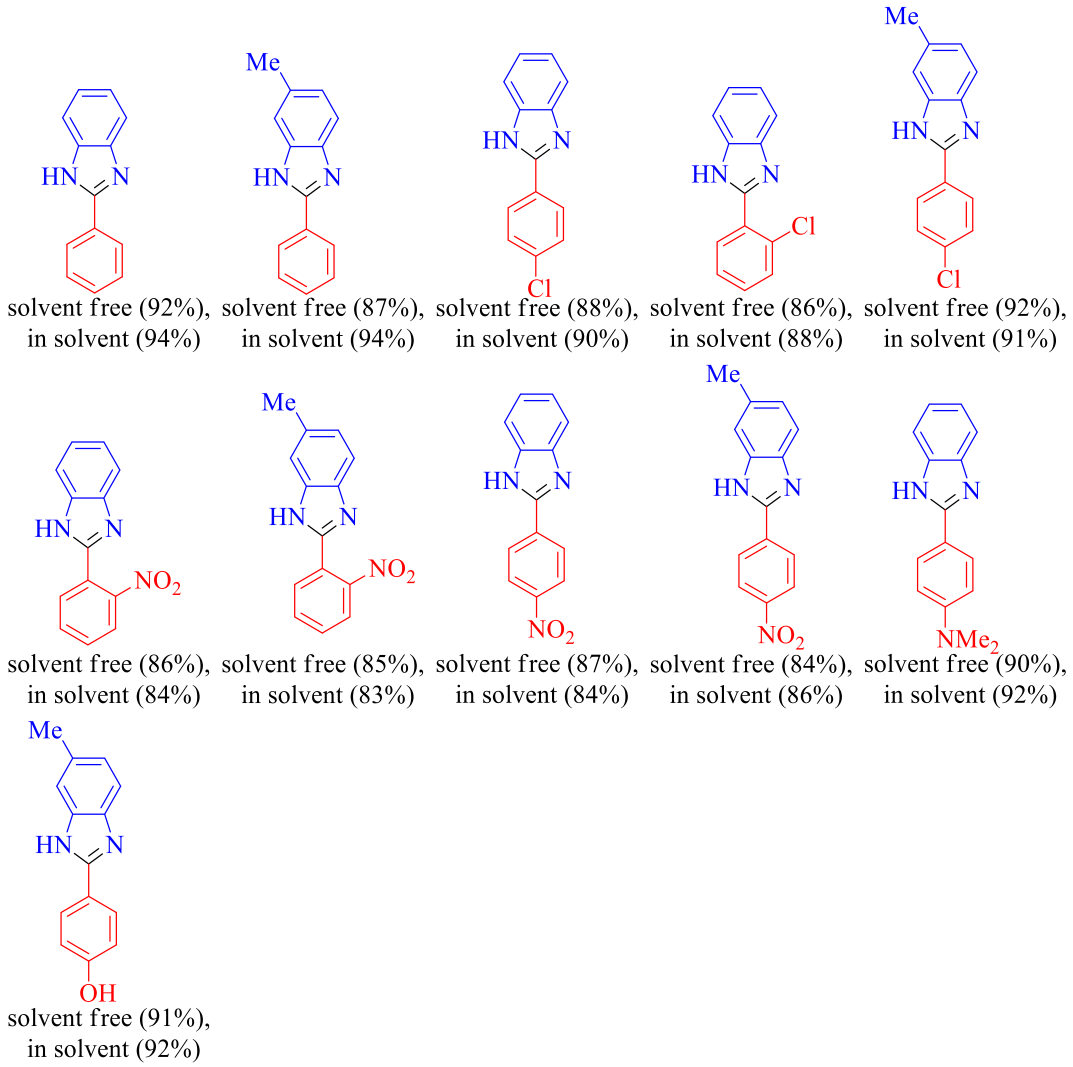


Scheme (52): Synthesis of 2-amino-3-cyano-4H-pyran derivatives catalyzed by Fe3O4 NPs supported IL.

Eshagh Rezaee Nezhad (2019) *et al.* developed simple route for the synthesis of benzimidazoles using Si-Im-HSO4 MNPs[cvii]. Aromatic aldehydes, carrying strong electron-withdrawing substituents gives lower yield requisite longer reaction time, whereas aryl aldehydes, with electron-donating groups produce excellent yield of the benzimidazole derivatives. Nanocatalyst separated by magnet and recycled for seven consecutive runs.

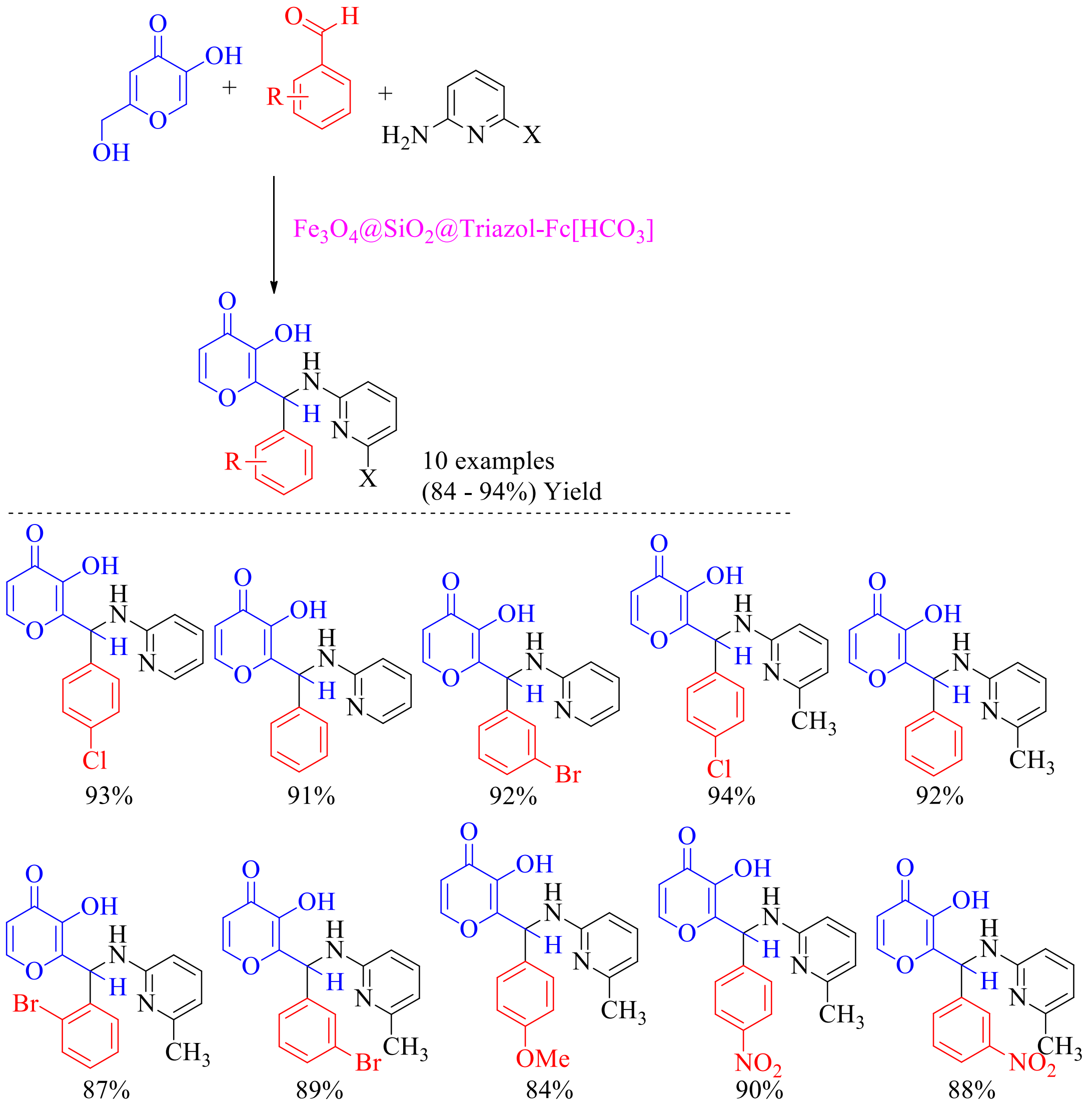


11 Examples
solvent free (84-92%),
in solvent (83-94%)

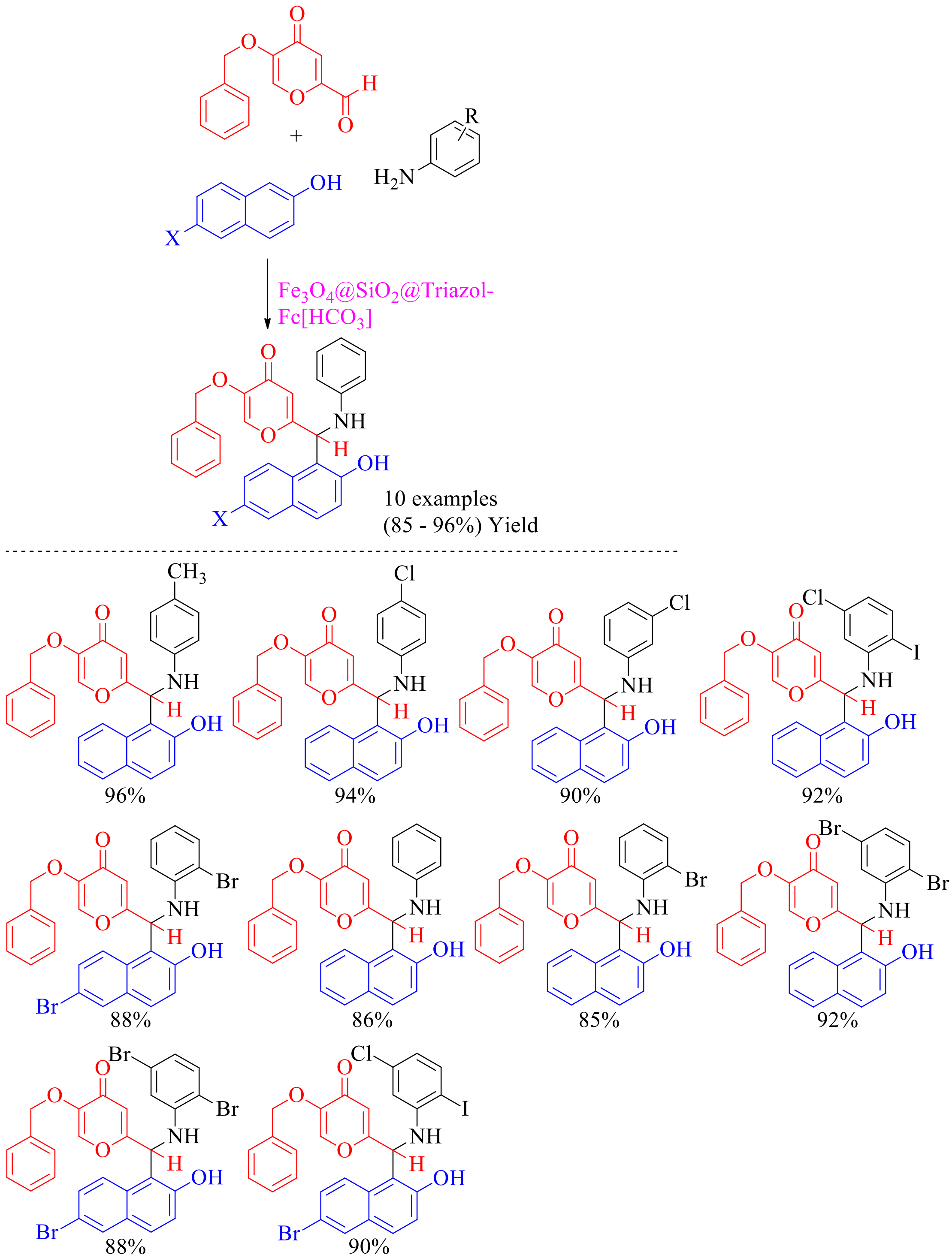


Scheme (53): Synthesis of benzimidazoles by using MNP-IL.

Nazari *et al.* developed a methodology for ferrocene-labelled ionic liquid based on triazolium, [Fe_3O_4@SiO_2@Triazol-Fc][HCO3] nanocatalyst that would satisfy the requirements of mild reaction conditions and would exhibit an efficient catalytic cativity in Synthesis of 2-hydroxynaphthalenyl(arylamino)methyl-4H-pyran-4-one derivatives and aryl(pyridinylamino)methyl-4H-pyran-4-one derivatives[cviii]. To investigate catalytic activity of prepared nanocatalyst one-pot three-component reaction of kojic aldehyde, 2-naphthol and 4-methylaniline was carried out to form kojic acid-containing Betti bases. Under optimized reaction conditions results showed that [Fe_3O_4@SiO_2@Triazol-Fc][HCO_3] is more efficient than [BuMeIm][Cl], [BuMeIm][BF_4], [BuMeIm][PF_6], [BuMeIm][HCO_3] ionic liquid catalysts. The novel synthesized [Fe_3O_4@SiO_2@Triazol-Fc] [HCO_3] nanocatalyst has several basic and acidic active sites which could help the promotion of the reaction. HCO_3 is a Brønsted base site of the nanocatalyst which could activate nucleophiles. Consequently, acidic sites of the nanocatalyst increase the electrophilicity of the aldehydes and activate them to the nucleophilic attack.

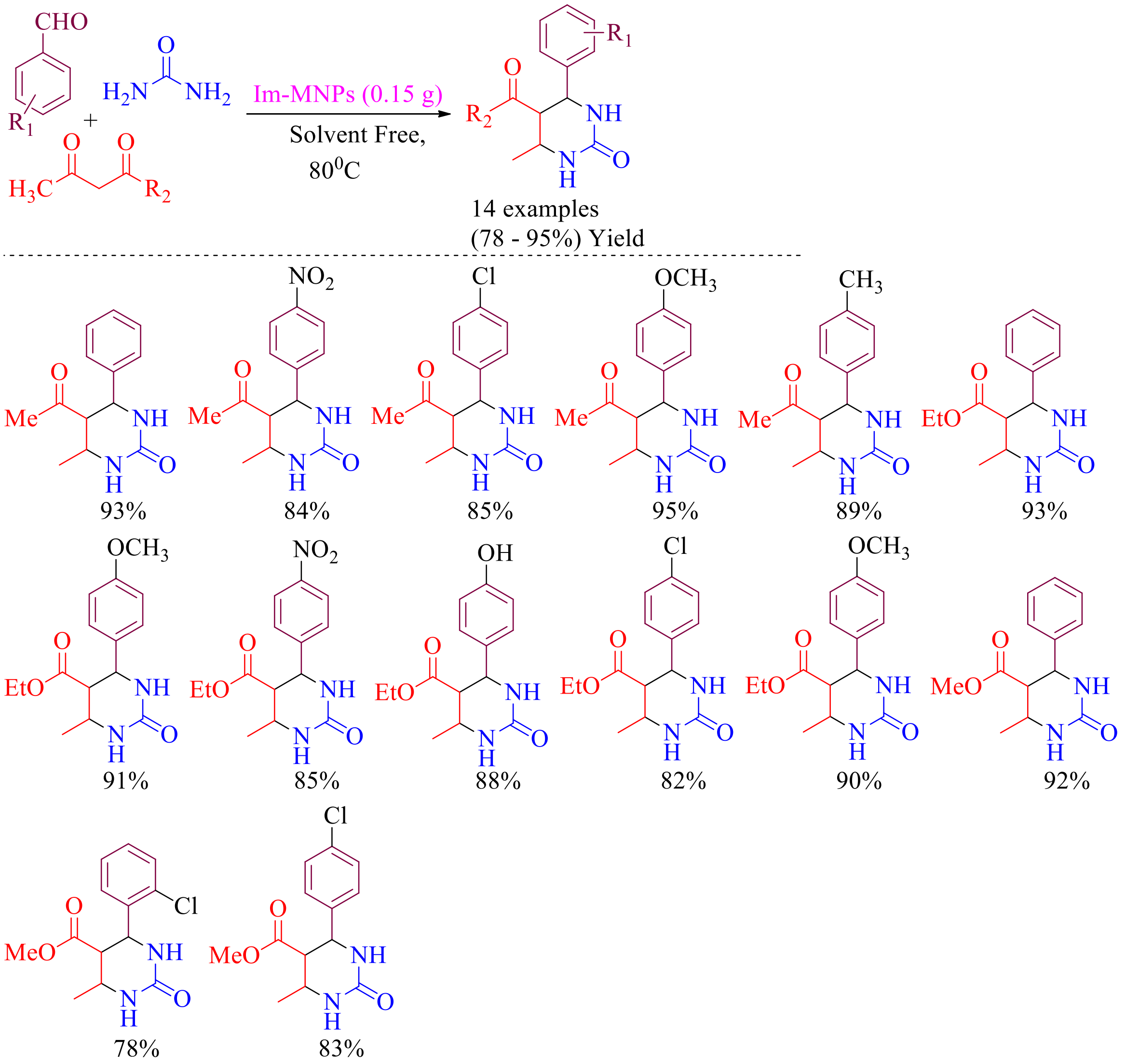


Scheme (54): Synthesis of aryl (pyridinyl amino) methyl -4H-pyran -4-one derivatives using $Fe_3O_4@SiO_2@$Triazol-Fc[HCO_3] Nanocatalyst.



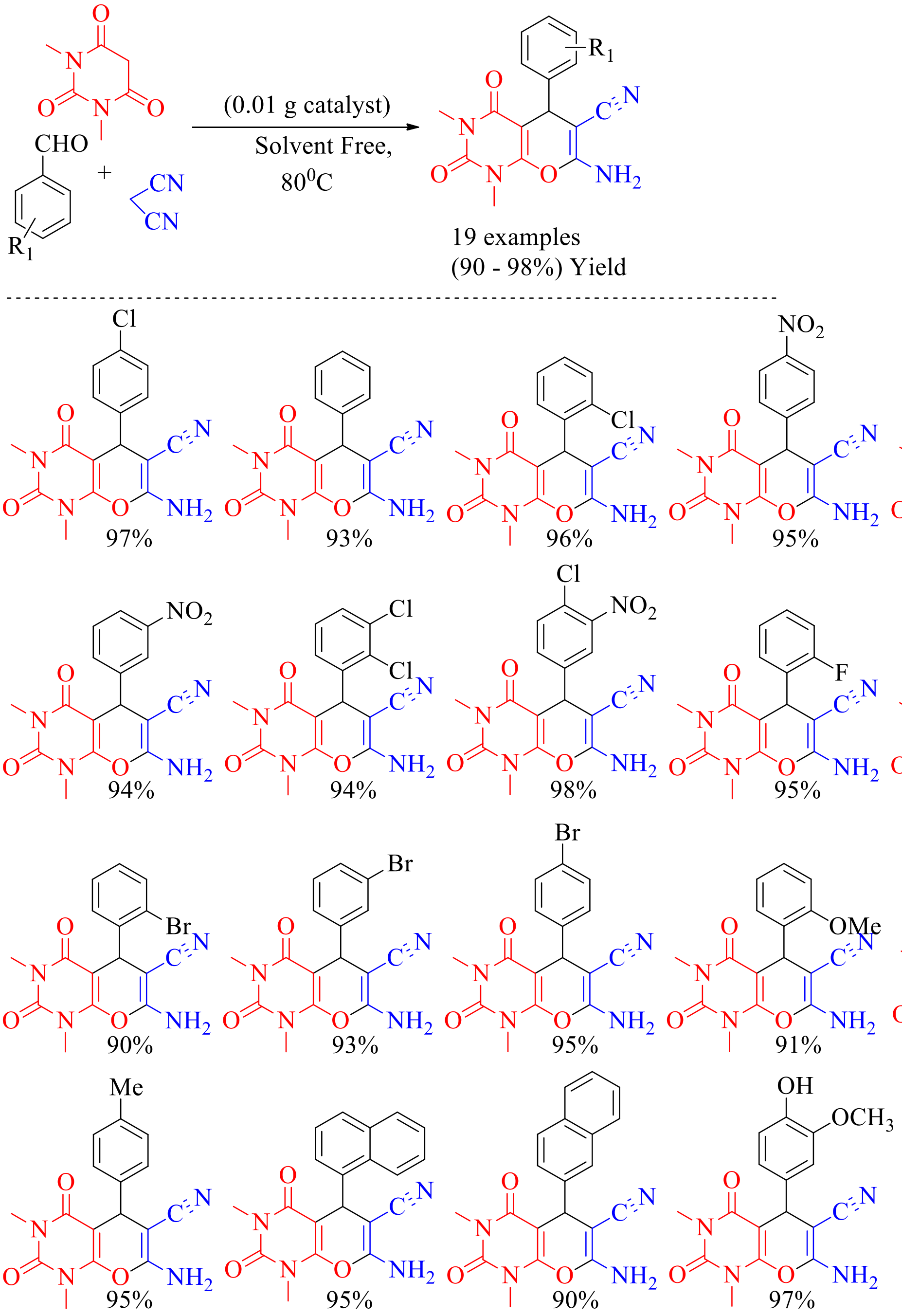
Scheme (55): Synthesis of 2-hydroxynaphthalenyl (aryl amino) methyl-4H-pyran-4-one derivatives using Fe_3O_4@SiO_2@Triazol-Fc[HCO_3] Nanocatalyst.

Nazari *et al.* fabricated imidazole functionalized magnetic Fe_3O_4 nanoparticles (Im-MNPs) for synthesis of Dihydropyrimidinone derivatives by Biginelli reaction[cix]. The obtained result showed that in the absence of imidazole support, the reaction proceeded sluggishly, and after a prolonged reaction time, a considerable amount of starting material remained. Therefore, the imidazole groups were strong promoters of the reaction. All the building block combinations reacted very well, giving moderate to excellent yields with high purity of the desired products under optimized reaction conditions. Im-MNPs promoted this heterocyclization reaction by virtue of their inherent Brønsted acidity conferred by the most acidic N–H hydrogen. This makes the Im-MNPs capable of bonding with the carbonyl oxygen, increasing the reactivities of the parent carbonyl compounds. Then nucleophilic attack of the nitrogen of urea on the activated carbonyl group resulted in the formation of acylimine, followed by the addition of β-ketoester to the imine bond, and consequently the ring was closed by the nucleophilic attack by the amine on the carbonyl group were quantitatively recovered simply by adding ethanol to the stirred reaction mixture followed by application of an external magnet and washing with water and acetone. Catalyst reused for four successive runs.



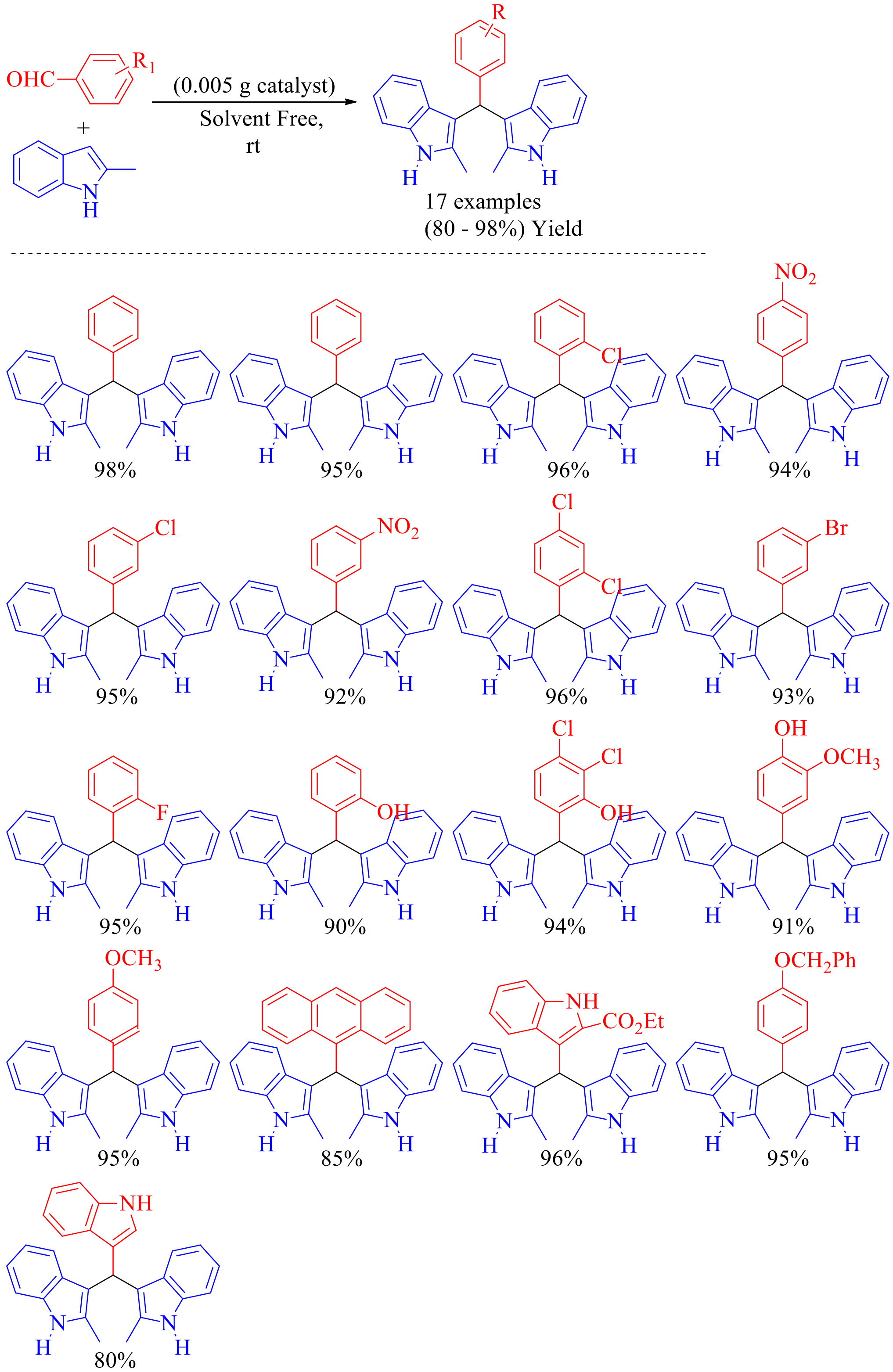
Scheme (56): Synthesis of dihydropyrimidinone derivatives in presence of Im-MNPs.

Zolfigol *et al.* (2016) applied {$Fe_3O_4@SiO_2@(CH_2)_3$-Urea-SO_3H/HCl} catalyst to form bis(indolyl)methane derivatives and pyrano[2,3-d] pyrimidinone derivatives which could be implemented as biological scaffolds for drug synthesis[cx].



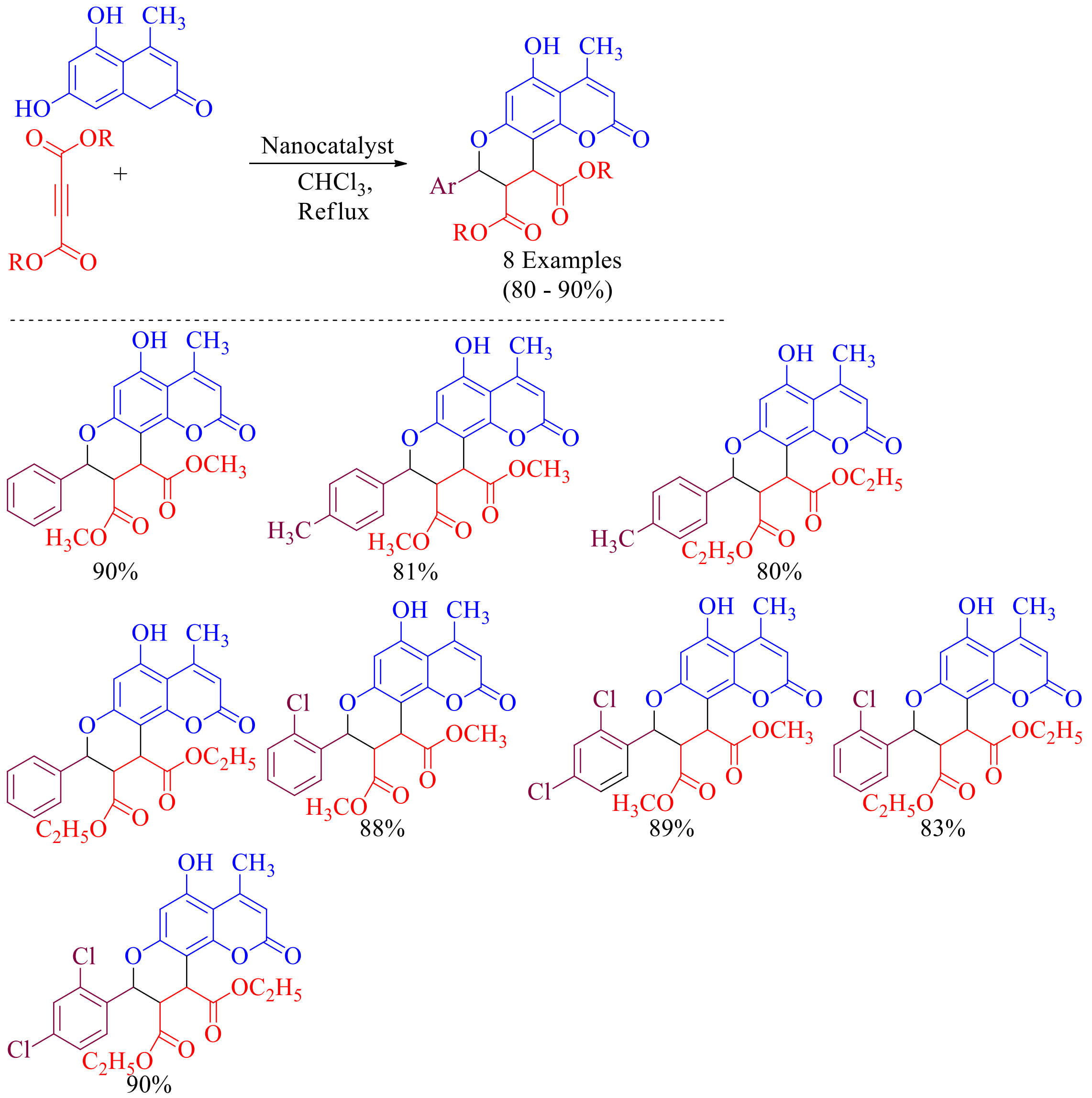
Scheme (57): Synthesis of Pyrano[2,3-d] pyrimidinone derivative using $\{Fe_3O_4@SiO_2@(CH_2)_3\text{-Urea-}SO_3H/HCl\}$ nanocatalyst.

Synthesis of pyrano[2,3-d]pyrimidinone derivatives using $\{Fe_3O_4@SiO_2@(CH_2)_3\text{-Urea-}SO_3H/HCl\}$ MNP catalyst. The reaction times of aromatic aldehydes having electron-withdrawing groups are rather faster than those having electron-donating groups. Furthermore, recyclability and reusability of the catalyst were also considered Inductively coupled plasma (ICP) spectroscopy was applied for the determination of the amount of Fe(III) in the recycled catalyst.



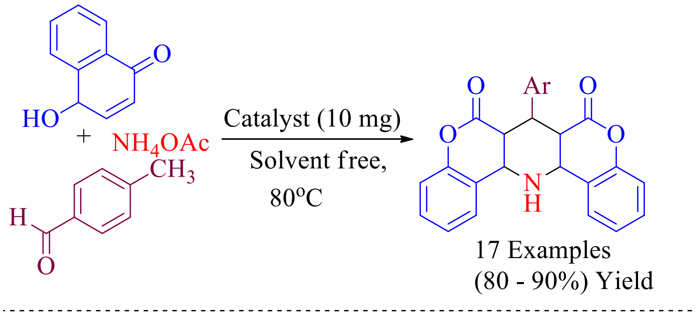
Scheme (58): Synthesis of Bis(Indolyl) methane derivatives using {Fe_3O_4@SiO_2@$(CH_2)_3$-Urea-SO_3H/HCl}Nanocatalyst.

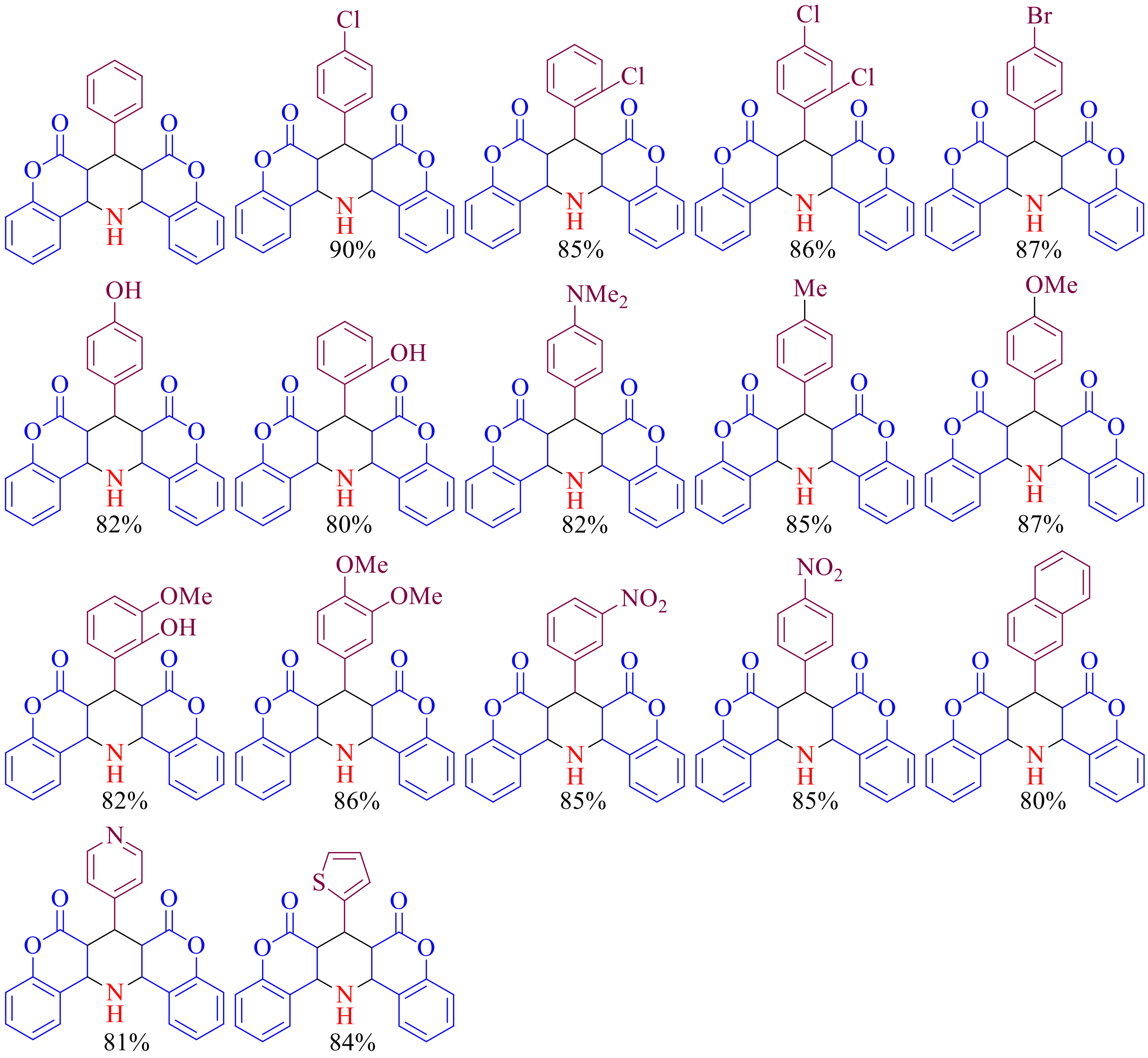
Tanuraghaj *et al.* (2019) developed sodium carbonate functionalized silica coated-iron oxide nanoparticles (Fe_3O_4@SiO_2@$(CH_2)_3OCO_2Na$)[cxi]. The catalytic activity of synthesized (Fe_3O_4@SiO_2@$(CH_2)_3OCO_2Na$) was assessed for synthesis of pyrano[2,3-h]coumarin derivatives. Catalyst recycled at least ten times without any noticeable loss in its activity.



Scheme (59): Synthesis of Pyrano [2,3-h] Coumarins by $Fe_3O_4@SiO_2@(CH_2)_3OCO_2Na$ Catalyst.

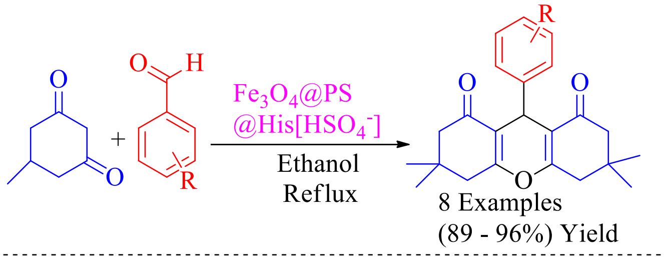
Saffarian *et al.* reported method for coumarin containing 1,4-dihydropyridines (DHPs), through a condensation reaction of aromatic aldehydes, 4-hydroxycoumarin, and ammonium acetate under solvent-free conditions using $Fe_3O_4@SiO_2@(CH_2)_3$ -urea-quinoline sulfonic acid chloride[cxii].

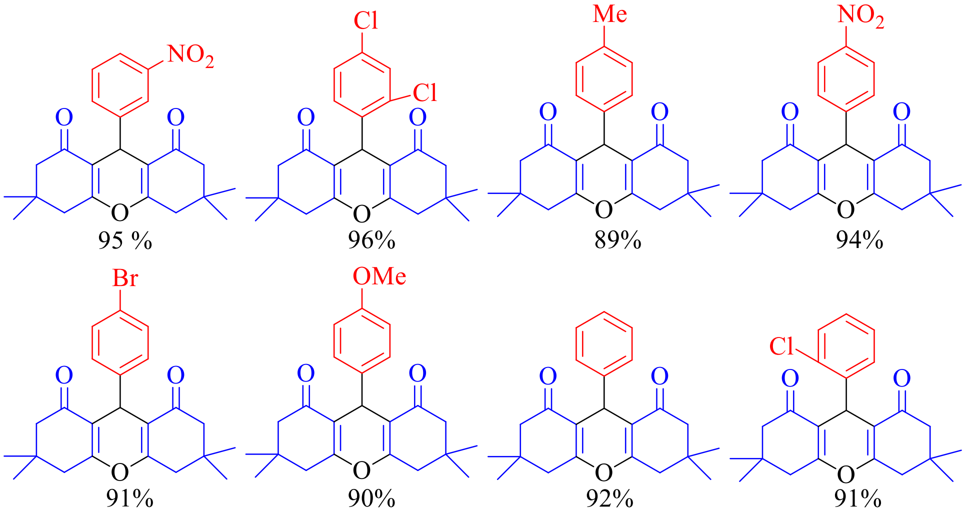




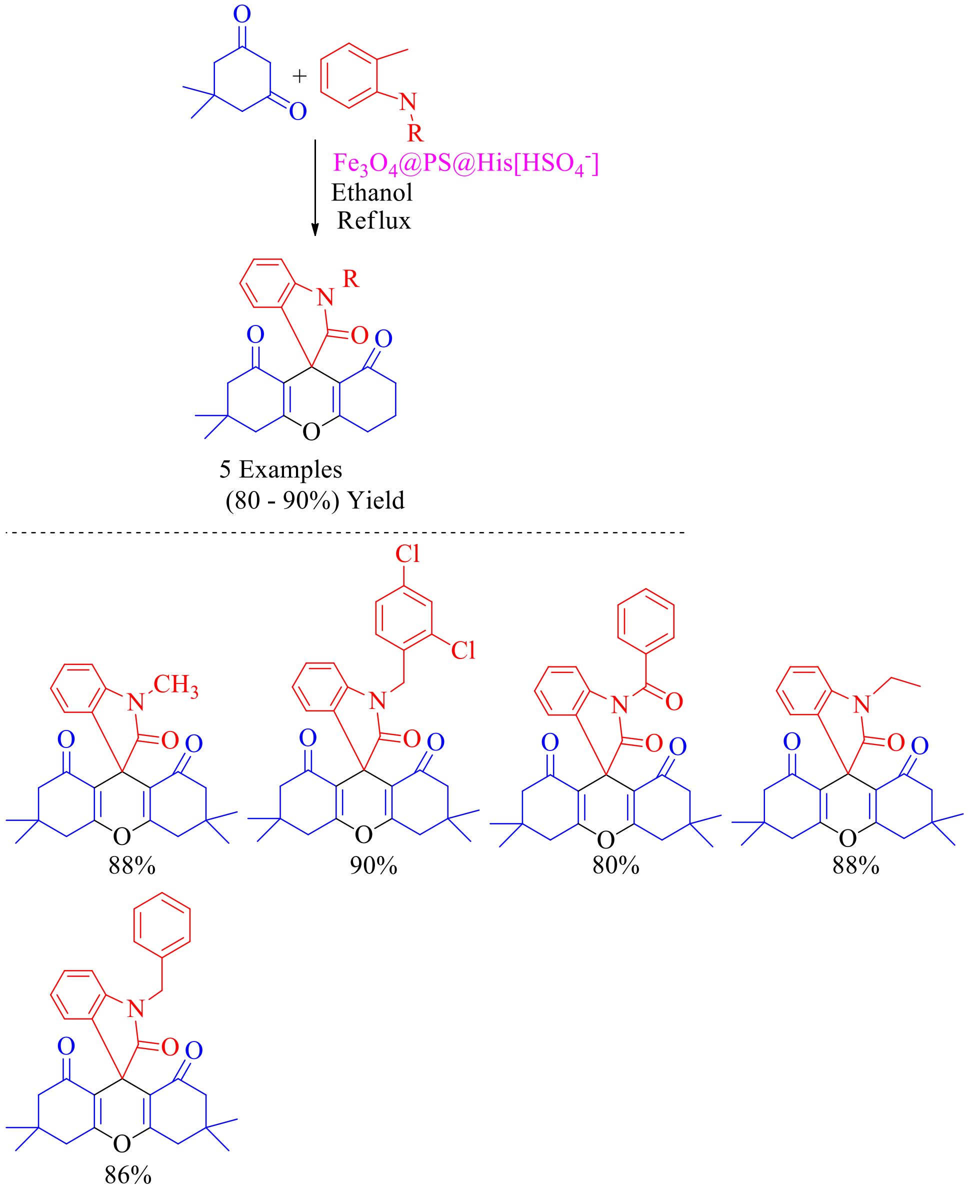
Scheme (60): Synthesis of coumarin containing DHPs moieties under solvent free conditions in presence of $Fe_3O_4@SiO_2@(CH_2)_3$-urea-quinoline sulfonic acid chloride.

Mousavifar *et al.* applied Fe_3O_4@Propylsilane@Histidine [HSO_4-] as a novel environmentally friendly ionic liquid/ magnetite nanocatalyst for synthesis of 9-aryl-1,8-dioxooctahydroxanthene and spiro[indoline-3,9′-xanthene] trione derivatives[cxiii]. The catalytic activity of synthesized HILMNPs was appraised for the mixture of an aromatic aldehyde or isatin derivatives, dimedone, Fe_3O_4@PS@His[HSO4-] and ethanol was refluxed. HILMNPs gave the corresponding products in better yields, and shorter times. Nanocatalyst was separated with a magnet.





Scheme (61): Synthesis of spiro[indoline-3,9′-xanthene]triones and 9-aryl-1,8-dioxooctahydro xanthenes usng Fe_3O_4@PS@His[$HSO4^-$].



Scheme (62): Synthesis of spiro[indoline-3,9′-xanthene]triones and 9-aryl-1,8-dioxooctahydro xanthenes usng Fe_3O_4@PS@His[$HSO4^-$].

Conclusion: There are numerous advantages in the use of metal nano-particles in ionic liquids as a catalytic system, such as it reduces the catalytic loading in organometallic transformations, enhances chemo, regio, and stereoselectivity of the process, and improves atom economy of the process. This catalytic system not only plays the role of solvent but also working as a catalyst for the organic transformations to achieve maximum efficacy of the reactants under the optimized reaction conditions.

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