Review Article

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Inorganic nanoparticles promoted synthesis of oxygen-containing heterocycles

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Abstract: Since many of the U.S. Food and Drug Administration (FDA)-approved medications contain oxygen-containing heterocyclic molecules, they have been discovered to be quite important. Moreover, over the past 10 years, the field of reusable nanocatalysts has expanded quickly. Therefore, the development of nanotechnology has led to a wide range of applications for nanocatalysis in the synthesis of heterocyclic molecules. The domains of organic chemistry and pharmaceuticals have recently shown a great deal of interest in nanocatalyzed organic processes. Such nanocatalysts enable non-toxic, simpler, environmentally friendly, and more affordable synthetic processes that give only the most desirable compounds in higher quantities and provide simple catalyst separation. As a result of their efficient methods for separating catalysts and products, nanocatalysts were chosen over other catalysts for the synthesis of heterocyclic compounds. This review emphasized the preparation of nanocatalysts, synthetic approaches, and recycling studies of highly excited catalytic systems employed for the synthesis of oxygen-containing heterocyclic compounds.

Keywords: catalyst, benign, furan, recycle, efficient

1 Introduction

In this modern day, the need to provide environmentally acceptable methods for the synthesis and use of various types of catalysts is growing to prevent pollution [1]. Magnetic material-based nanocatalysts can be readily recovered from obtained products and reused. Therefore, all of the functionalized organic materials grafted to magnetic nanoparticles (MNPs) might be taken into consideration for their basic magnetic properties, excellent biodegradability, and bio-environment suitability [2]. Materials that have at least one dimension in the nanometer range (1–100 nm) are referred to as nanomaterials. With the recent significant advancement, nanotechnology has found wide-ranging applications in fields such as biotechnology, biology and medicine, carbon nanotubes, therapeutics, automobiles, wastewater management, food and nutraceuticals, environmental applications, fabrics, and textiles [3–11]. The development of both complex and straightforward spectrophotometric and robotic instrumentation has also made a large range of approaches available for the characterization of nanomaterials. Nuclear magnetic resonance (NMR), UV–visible spectroscopy, X-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM), etc., can be used to characterize the size of nanoparticles (NPs). Vibrating sample magnetometry and Mossbauer spectroscopy can be used to assess the magnetic behavior of NPs. The liquid NMR and the Brunauer, Emmett, and Teller approach can be used to measure the NPs’ surface properties. XRD, X-ray photoelectron spectroscopy, inductively coupled plasma mass spectrometry, and NMR can be used to determine the chemical composition of NPs and TEM, high-resolution TEM, and atomic force microscopy can be used to characterize their shape [12]. Because of their extremely small size and high surface-to-volume ratio, which cause changes in their chemical and physical properties when compared to bulk materials with similar chemical composition, such as mechanical and biological properties, optical absorption, superior catalytic activity, melting point, and thermal and electrical conductivity, nanostructure catalysts have been crucial in the synthesis of organic materials [13–15]. In this review, we are systematically presenting the synthesis of different oxygen-containing heterocyclic compounds using recyclable inorganic NPs.

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2 Multicomponent synthesis of heterocycles of different sizes and ring system containing an oxygen atom

2.1 Three-membered rings

In 2020, Mohamed and his co-workers designed a novel and efficient nanocatalyst, Nitmtaa@N-Thiourea dioxide (TUD)-1, for the epoxidation of cyclohexene **1** to cyclohexene oxide **2** under ambient conditions [16]. The reaction is carried out in the presence of *meta*-chloroperoxybenzoic acid (*m*-CPBA) as an oxidant and CH_2Cl_2/CH_3CN (1:1 v/v) as a solvent. In addition, the catalyst Nitmtaa@N-TUD-1 demonstrated great stability over the course of four cycles, maintaining a strong quasi-constant catalytic activity. Atomic absorption spectroscopy (AAS) measurements of leaching supported the highly stable nature of the synthesized nanocatalyst. Mechanistically, the rapid adsorption of *m*-CPBA onto the catalyst Nitmtaa@N-TUD-1 initiates the reaction. Furthermore, *m*-CPBA is deprotonated and nickel-bonded activated-*m*-CPBA (Ni^{II}-OOAr, **A**) is generated. The bond O–O in the intermediate Ni^{II}-OOAr would heterotically cleave to generate the active Ni^{IV}oxo (**B**), with the change in color from brown to yellow along with a proton transfer that would help the formation of bi-product *meta*-chlorobenzoic acid. Following this interaction with cyclohexene, the electrophilic nickel-oxo intermediate Ni^{IV}-oxo transfers the oxygen atom to the cyclohexene double bond. The desired product, cyclohexene oxide **2**, is generated by the cleavage of the intermediate (**C**), the oxygen atom transfer from Ni^{IV}-oxo to the cyclohexene occurs via a concerted transition state (**D**), and the catalyst Nitmtaa@N-TUD-1 is recovered (Scheme 1).

2.2 Five-membered rings

2.2.1 Two-component reactions

CuO NPs catalyzed the synthesis of poly-substituted furans **5** via oxidative C–H/C–H functionalization was developed in 2016 [17]. In this reaction, CuO NPs were used as reusable catalysts in direct functionalization of α,β-unsaturated carbonyl compounds **3** through conjugate addition in aqueous ethanol. Through the oxidative reaction of 1,3-diphenylprop-2-ene-1-one **3** and acetylacetone **4** in aqueous ethanol, Payra et al. explored a 3,4-dicabonyl-substituted furan derivative **5** using CuO NPs as a catalyst and tertiary butyl hydroperoxide (TBHP) as an oxidizing agent. This method afforded the products in greater isolated yields (70–91%) with faster reaction time. Moreover, the recyclability and homogenous nature of CuO NP catalyst and use of aqueous ethanol as a green solvent made the protocol environment benign (Scheme 2).

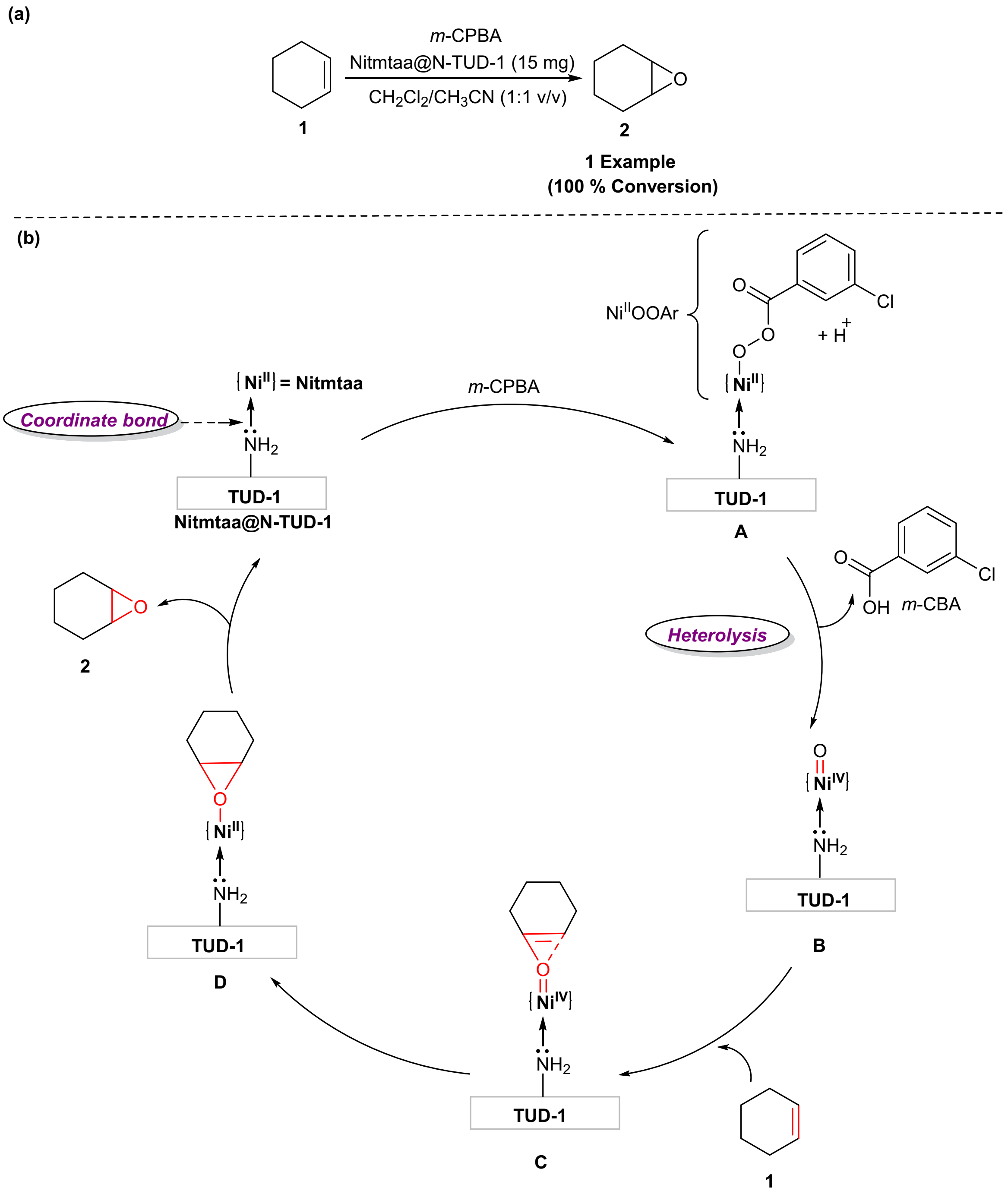
Ji et al. reported a highly efficient protocol for the synthesis of benzofurans **8** via one-pot two-component reaction of *o*-iodophenols **6** with phenylacetylene **7**. The reaction occurs in the presence of palladium NPs supported on *N*,*O*-dual-doped hierarchical porous carbon through Sonogashira cross-coupling followed by cyclization of *o*-halogenated phenols **6** with terminal alkynes **7** under copper- and ligand-free conditions (Scheme 3). The catalyst has great stability and is simple to recover for further usage. The approach is an environmentally friendly way to create biologically useful heterocyclic compounds [18].

2.2.2 Three-component reactions

A one-pot three-component reaction between isocyanides **11**, secondary amines **9**, and an electron-poor 2-hydroxybenzaldehyde derivative **10** for the synthesis of benzo[*b*]furan derivatives **12** using silica NPs from rice husk ash as a green catalyst at ambient temperature was reported in 2014 [19]. Due to greater electrophilicity of the carbonyl groups of electron-withdrawing 2-hydroxybenzaldehyde derivatives relative to carbonyl groups of electron-releasing 2-hydroxybenzaldehyde derivatives, the electron-withdrawing 2-hydroxybenzaldehyde derivatives have more preference as a suitable starting material over electron-releasing derivatives (Scheme 4).

According to the possible mechanism of this reaction (Scheme 5), the intermediate **A** would be produced by the condensation of 2-hydroxybenzaldehyde derivative **10** and secondary amine **9**, which would then react with the alkyl isocyanide **11** to produce intermediate **B**. The cyclization of the ionic intermediate **B** would produce benzofuran, followed by tautomerization of intermediate **C** afforded the desired product, benzo[*b*]furan derivatives **12**.

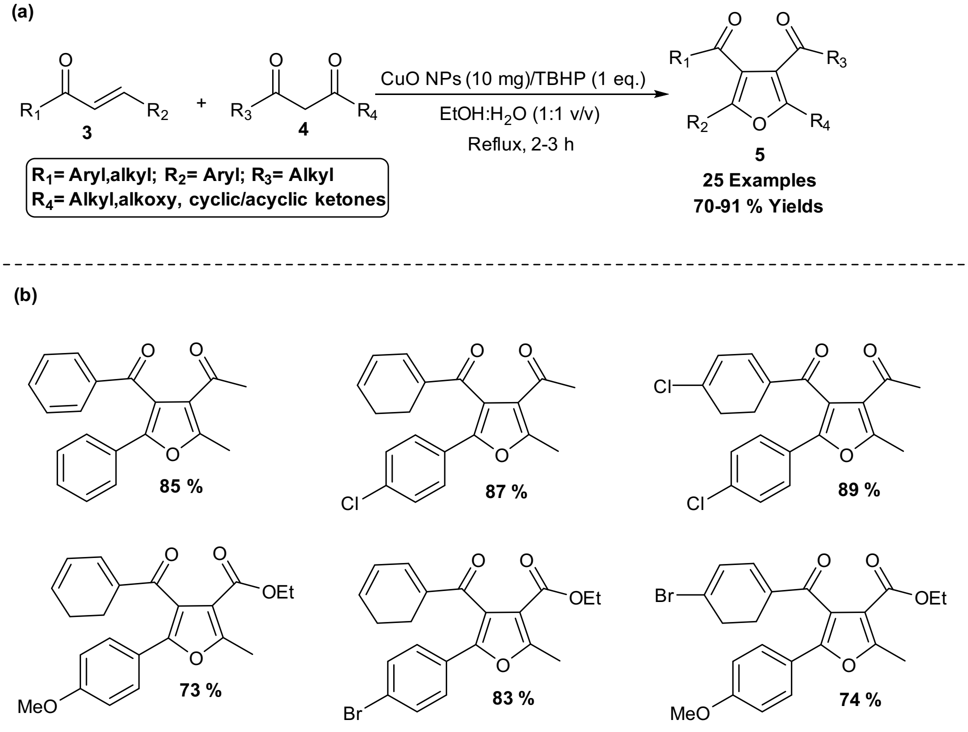
In 2018, a facile synthesis of *trans*-dihydroindeno[1,2-*b*] furans **16** was developed via one-pot three-component reaction between *N*-[2-(aryl)-2-oxoethyl)]pyridinium bromide **13** with 1,3-indandione **14** and an aryl glyoxal **15** in the presence of nano-γ-Fe_2O_3-quinuclidine based as a catalyst in an aqueous medium [20]. The advantages of this approach include fast setup, avoidance of toxic catalysts and organic solvents, reusability of the catalyst, little



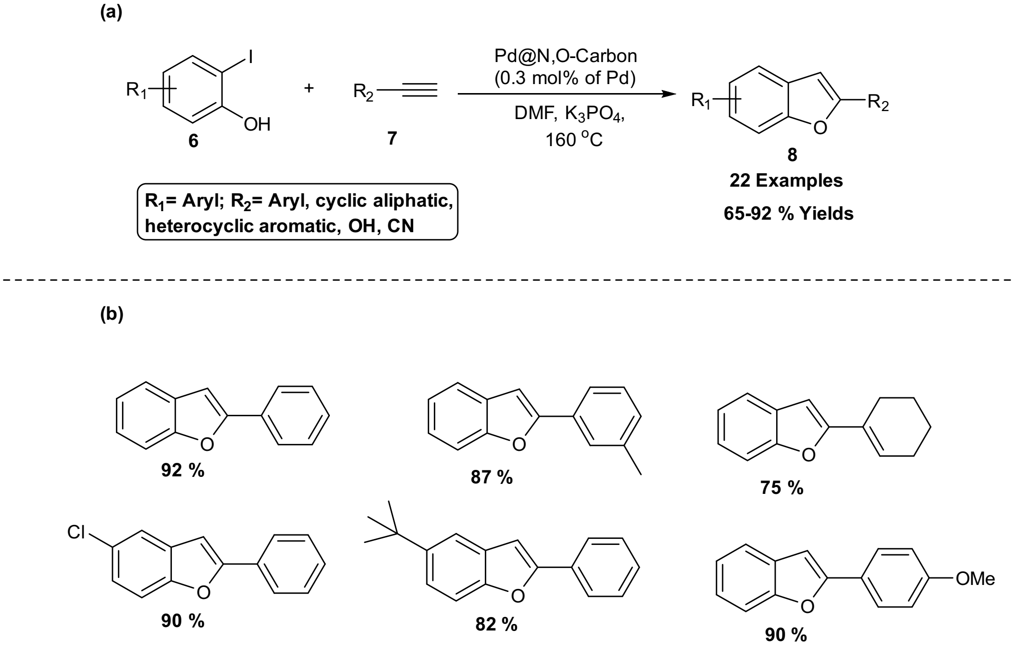
Scheme 1: The epoxidation of cyclohexene employing Nitmtaa@N-TUD-1 nanocatalyst. (a) Method review; (b) Plausible Mechanism.

catalyst loading, quick reaction times, and simple product separation (Scheme 6).

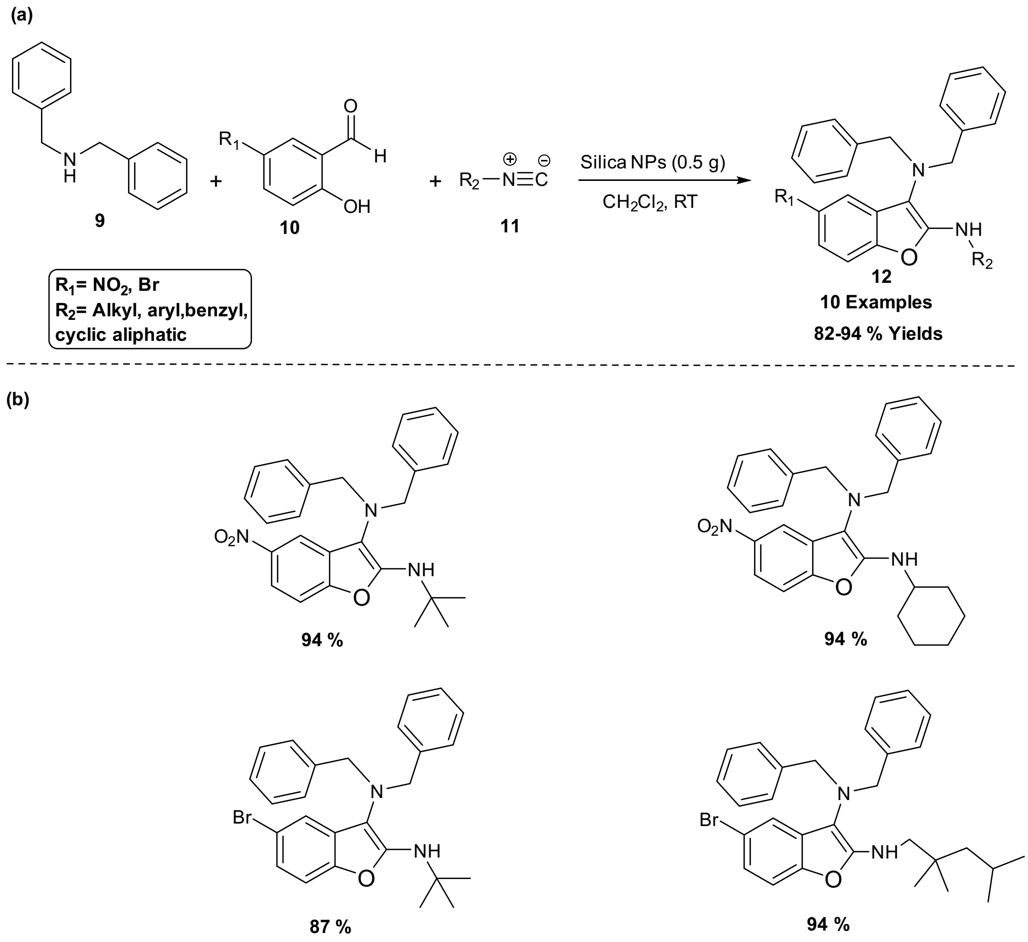
Shirzaei et al. reported a green approach for the synthesis of furan derivatives using thiocarbohydrazide doped iron nanoparticles as catalyst. This three components reaction of dialkyl acetylenedicarboxylate **18** with aromatic aldehydes **10** and aromatic amines **17** in the presence of the catalyst was carried out in EtOH giving high yields of the product (Scheme 7). The general route for the preparation of nanocatalyst, Fe_3O_4@SiO_2@ionic liquid (IL) as a heterogeneous acidic catalyst, is shown in Scheme 8. The catalyst's capacity to be reused up to five times without experiencing any desired decrease in efficacy is by far its most notable attribute. As a result, this catalyst offers several advantages over additional non-magnetic catalysts [1].



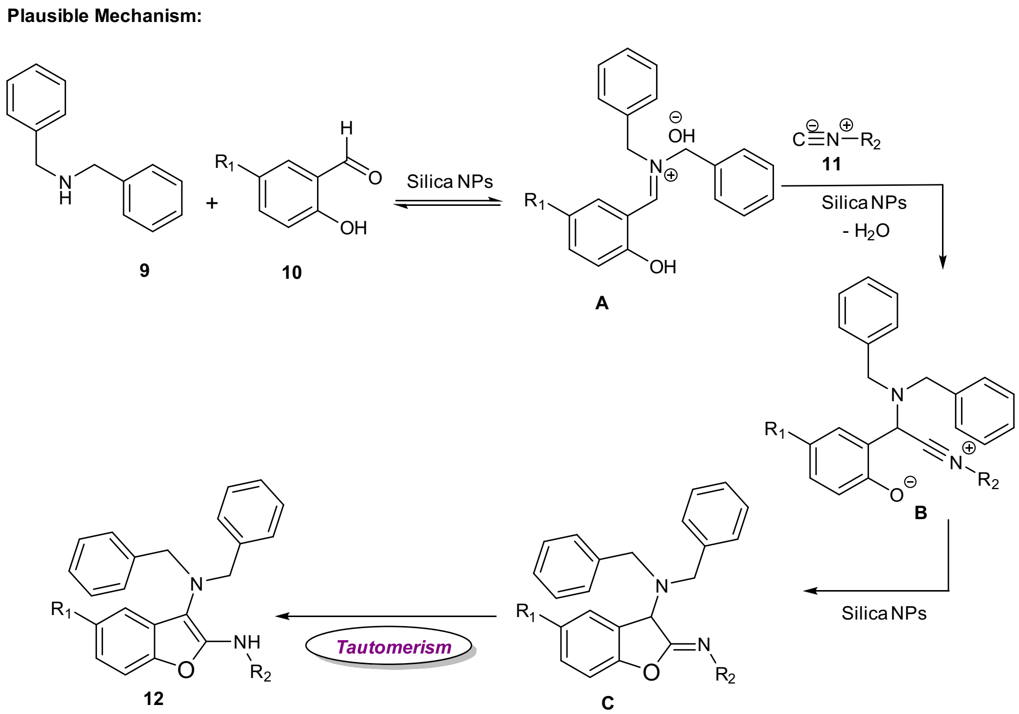
Scheme 2: CuO NPs catalyzed the synthesis of poly-substituted furans. a) Method overview; (b) representative examples.



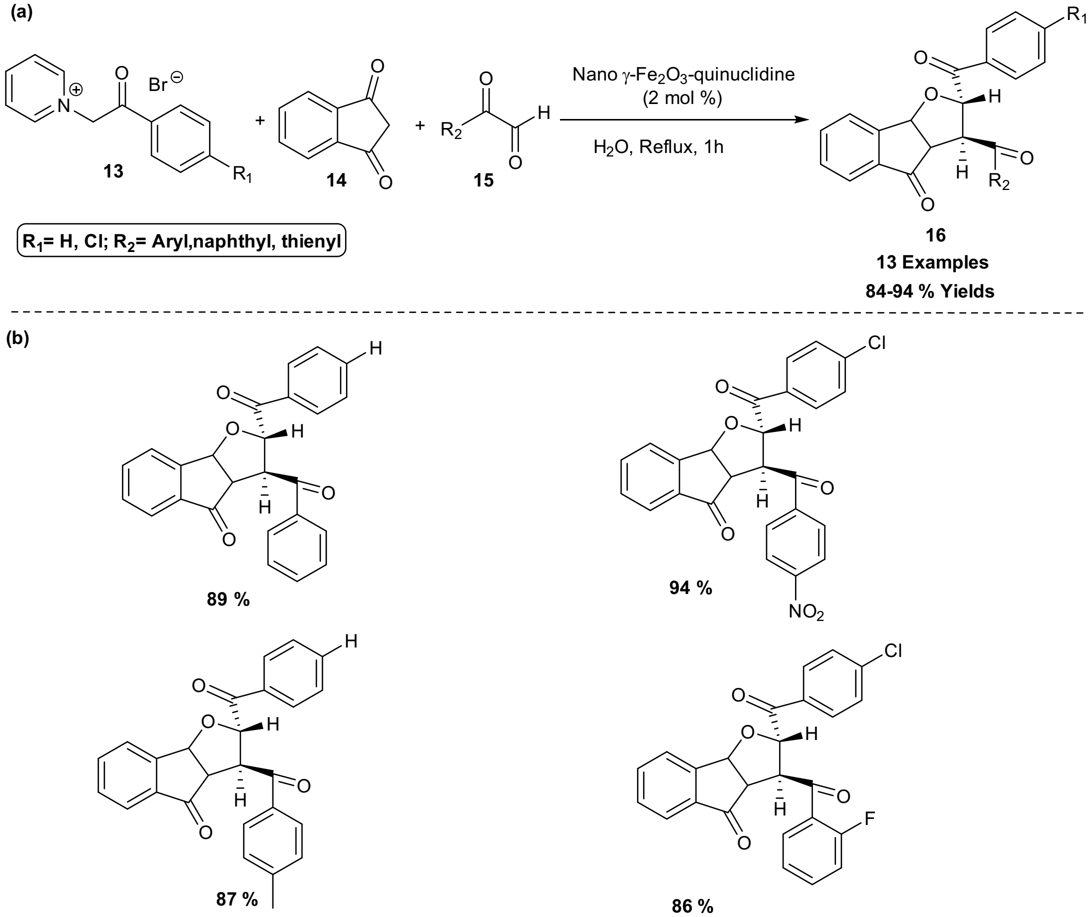
Scheme 3: Synthesis of benzofurans employing Pd@N,O-carbon. (a) Method overview; (b) representative examples.



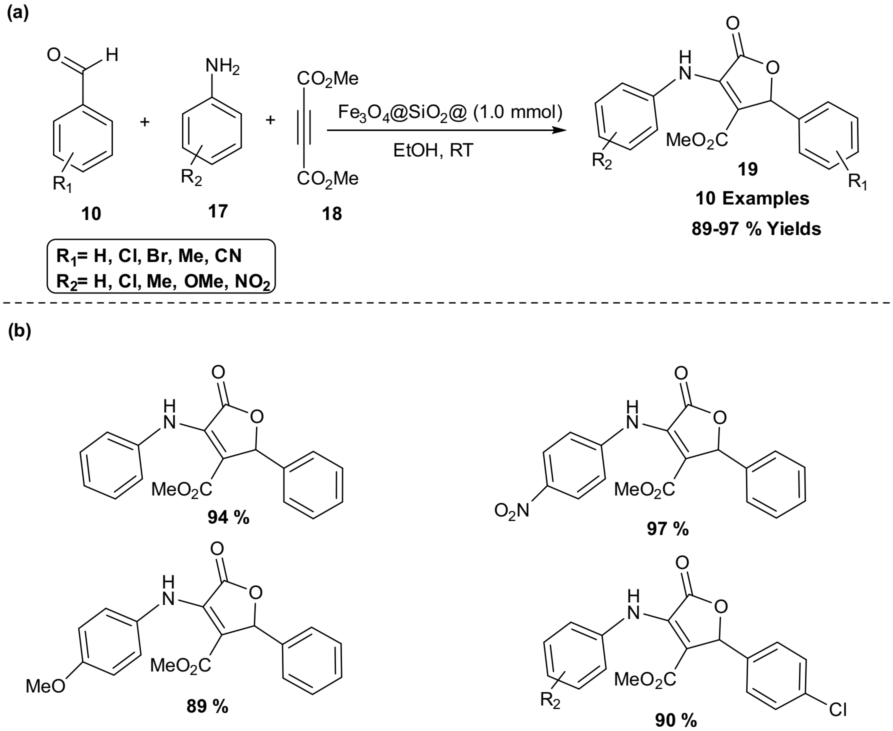
Scheme 4: Three-component synthesis of benzo[*b*]furan derivatives using silica NPs. (a) Method overview; (b) representative examples.



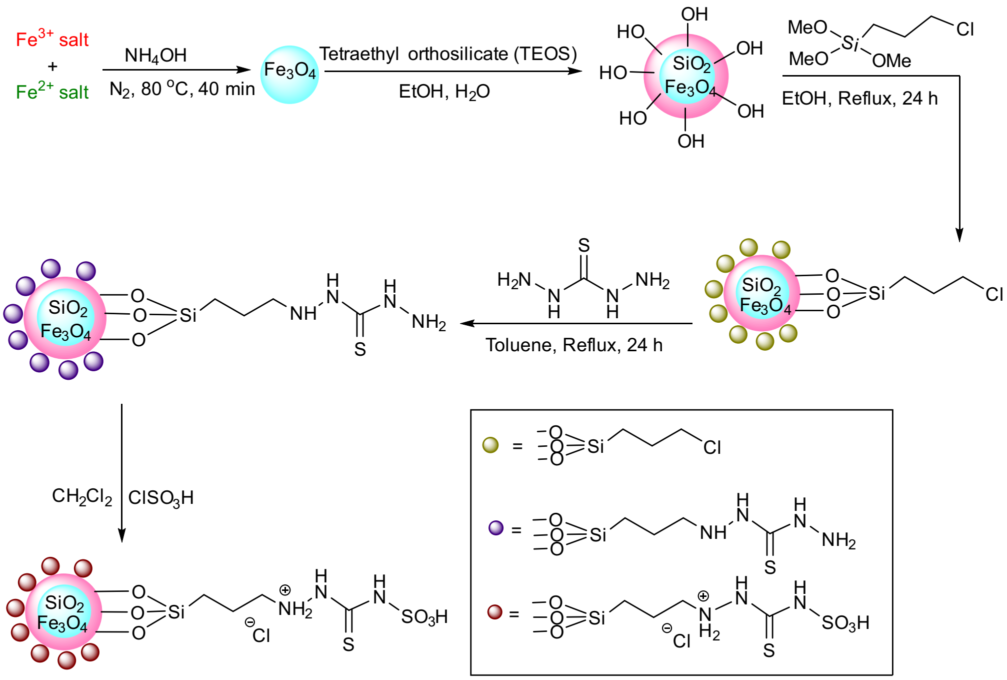
Scheme 5: Mechanism for the formation of benzo[*b*]furan derivatives using silica NPs.



Scheme 6: Synthesis of *trans*-dihydroindeno[1,2-*b*]furans with γ-Fe_2O_3-quinuclidine NPs. (a) Method overview; (b) representative examples.



Scheme 7: Synthesis of furan derivatives catalyzed by Fe_3O_4@SiO_2@IL. (a) Method overview; (b) representative examples.



Scheme 8: General route for the synthesis of $Fe_3O_4@SiO_2@IL$.

According to the plausible mechanism of the reaction, MNP catalyst promotes the condensation of the carbonyl group between intermediates **A** and **B** to produce the intermediate **C**. The catalyst further activates the carbonyl group of intermediate **C**, followed by nucleophilic attack through Michael addition, producing intermediate **D**. Finally, the removal of H^+ terminated the reaction, generating the desired product **19** (Scheme 9). In another study, 4-carboxybenzyl sulfamic acid-functionalized Fe_3O_4 NPs were also used as a novel catalyst in this reaction [2].

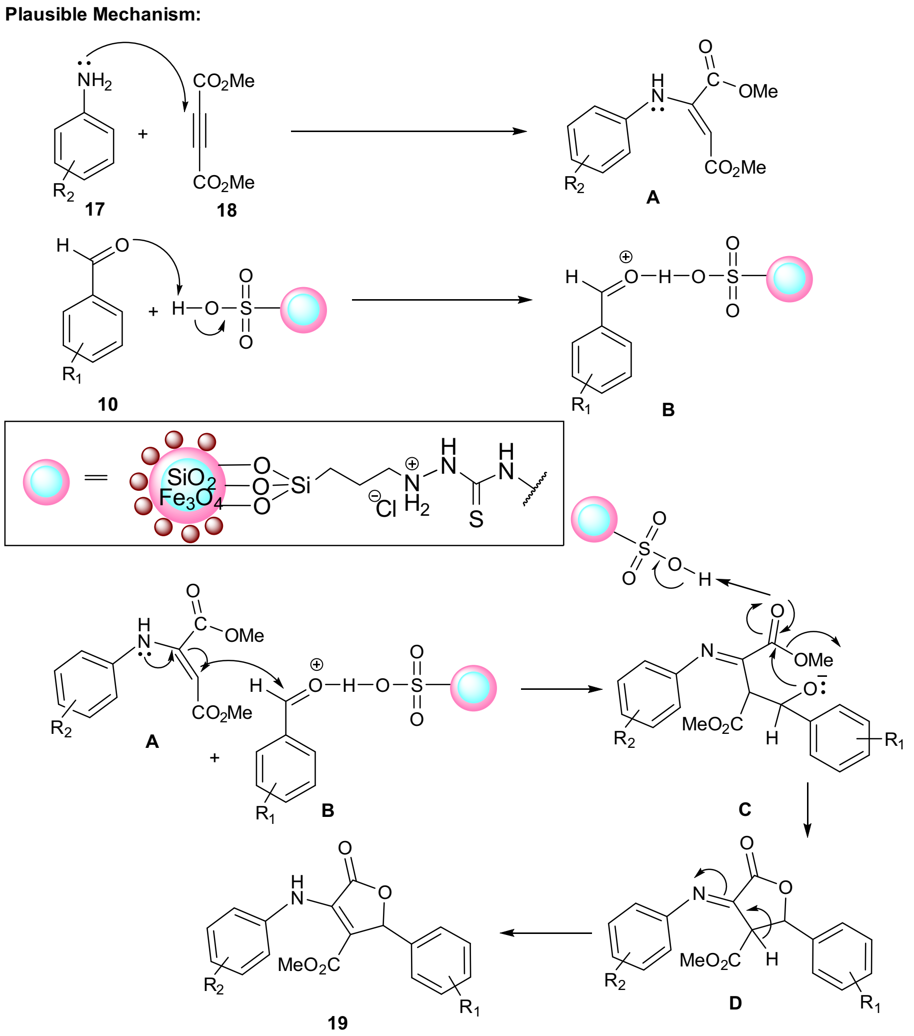
Feng and his co-workers, in 2021, slightly modified the previous work in Scheme 7 for the synthesis of furan derivatives [21]. In this work, they used sulfamic acid 2-aminobenzothiazole-6-carboxylic acid (SA-ABTCA)-functionalized Fe_3O_4 as nanocatalyst for the synthesis of novel 3,4,5-trisubstituted furan-2(5*H*)-ones derivatives **21** via one-pot reaction of aryl aldehydes **10**, 4-amino pyridine **20**, and dimethylacetylenedicarboxylate **18**. The average particle diameter determined by the Scherrer equation afforded the crystalline size for SA-ABTCA Fe_3O_4 NPs to be about 21 nm. Moreover, some compounds also exhibited good antibacterial activity and can be further promoted as powerful antibacterial agents. The antibacterial active compounds have higher effectiveness against *Bacillus subtilis* but exert moderate activity against both gram-positive and gram-negative bacteria. This green nanocatalytic protocol for the synthesis of the desired compound offers clean production in a brief amount of time and has strong reversibility, making the strategy more feasible and affordable for researchers (Scheme 10).

Wang et al. developed an effective carbonylation of cinnamyl chloride **22** and phenylacetylene **11** with CO_2 **23** to afford 4-dihydronaphtho[2,3-*c*]furan-1(3*H*)-one **24** using α-cyclodextrin (α-CD) doping dendritic fibrous nano-silica (DFNS)-supported gold NPs as a catalyst [22]. It was discovered that the DFNS/α-CD/Au nanostructures could be nominated because of their efficient and distinctive catalytic behavior during the synthesis of the desired compound (Scheme 11).

2.3 Six-membered rings

2.3.1 Two-component reactions

A high atom economy and efficient approach to synthesize a xanthone **25** skeleton via highly efficient copper-based magnetically recoverable nanocatalyzed coupling of 2-substituted benzaldehydes **10** with phenol derivatives **6** was developed by Cintia and his co-workers [23]. The catalyst is easily recovered by means of an external magnet and reused again as a catalyst for further reaction without significant loss of catalytic activity. Moreover, the technology offers an interesting protocol for the production of a small library of xanthones **25** in very good yield and is compatible with a number of functional groups. Better yields of



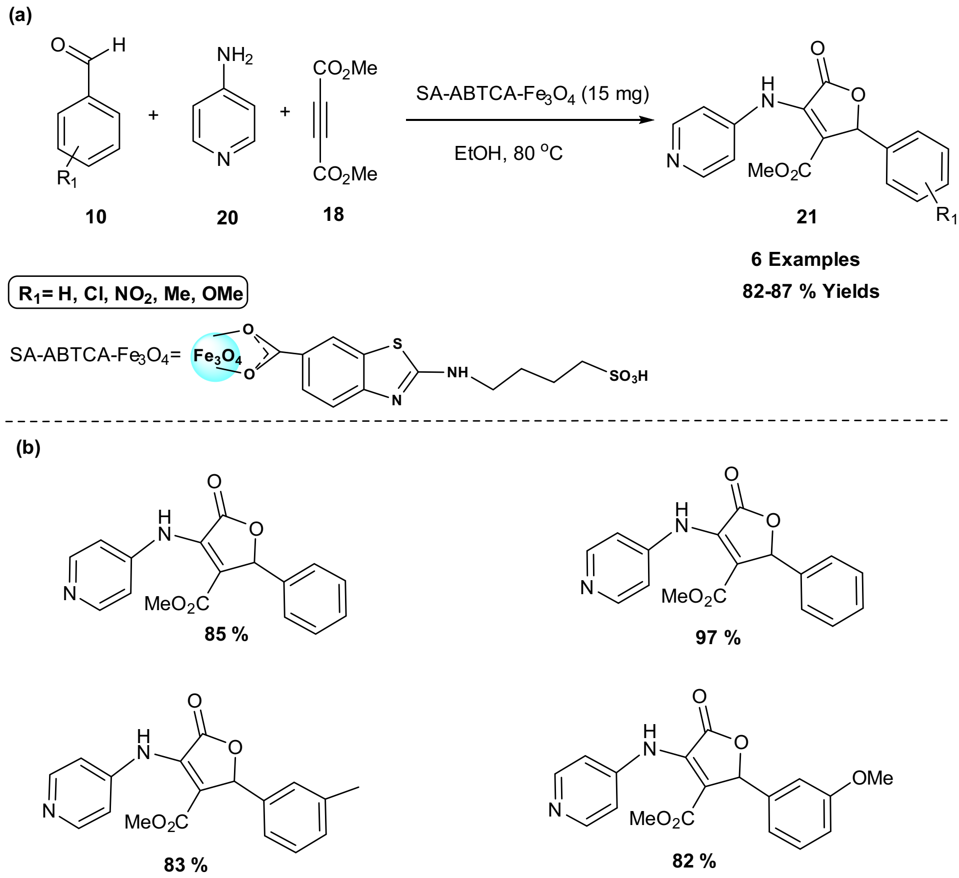
Scheme 9: Proposed mechanism for the synthesis of furans catalyzed by {Fe_3O_4@SiO_2@IL}.

the cyclization products were obtained with regard to the electronic characteristics of the substituents when electron-donating groups were present on the aromatic ring of the phenols (Scheme 12).

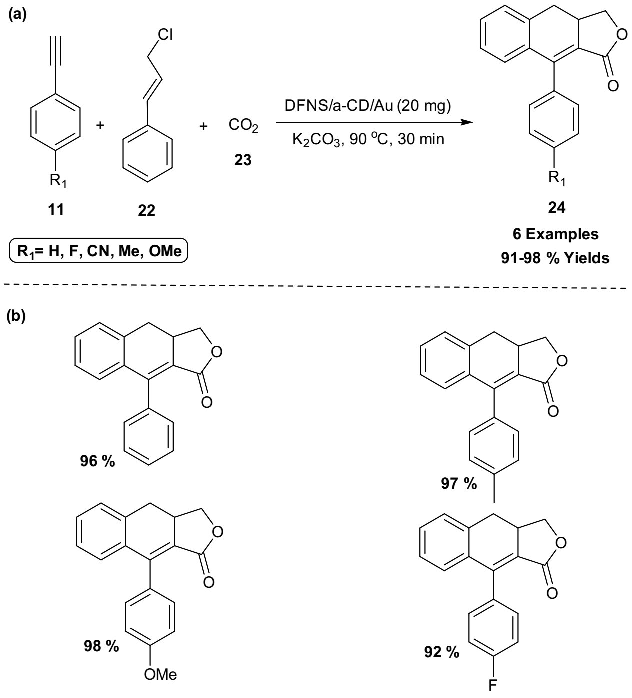
Anshu and his co-workers reported a highly efficient, chemoselective synthesis of pyrano[2,3-*c*:6,5-*c*′]dipyrazol]-2-ones **28** in water via one-pot reaction of carbonyl compounds **26** with 3-methyl-1-phenyl-1*H*-pyrazol-5(4*H*)-one **27** (1:2 ratio) in the presence of Ag NPs decked graphene oxide (GO) composite as a catalyst (Scheme 13). This technique demonstrates the high selectivity of pyranodipyrazolones **28** over arylmethylene bispyrazolols and arylmethylene-pyrazolones. Due to the loss of two water molecules, the method has a high atom economy and is environmentally friendly. Furthermore, the catalyst was easily recoverable and could be recycled at least seven times without suffering a significant reduction in catalytic activity [24].

The mechanism of this reaction involves electrophilic activation of benzaldehyde **26** by coordinating with the Lewis acid sites of Ag NPs/GO (Ag NPs/GO) composite. Then, Knoevenagel condensation of activated benzaldehyde **A** with pyrazolone **27** formed Knoevenagel adduct **B**. Furthermore, activation of adduct **B** by the catalyst through coordination with oxygen facilitates the Michael addition of a second pyrazolone **27** unit forming hydroxyl derivate **C**. Finally, successive cyclization afforded the desired product **28** with the loss of water molecule and released the catalyst for the next cycle (Scheme 14).

A highly efficient and recyclable CoNP@SBA-15 (Co nanoparticles@santa barbara amorphous-15) nanocatalyst supported an aqueous and environmentally friendly approach for the synthesis of 1,8-dioxo-octahydroxanthenes **30** through the reaction of dimedone **29** with aromatic aldehydes **10** (2:1 ratio) was developed by Rajabi et al. [25]. In this



Scheme 10: SA-ABTCA-Fe_3O_4 catalyzed synthesis of novel 3,4,5-trisubstituted furans. (a) Method overview; (b) representative examples.

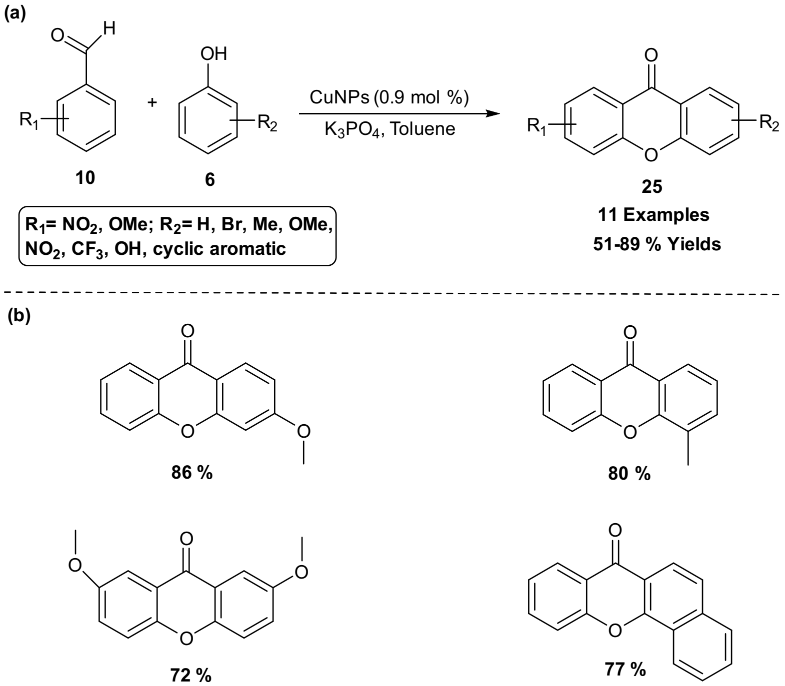


Scheme 11: Synthesis of 4-dihydronaphtho[2,3-*c*]furan-1(3*H*)-ones in the presence of DFNS/α-CD/Au NPs. (a) Method overview; (b) representative examples.

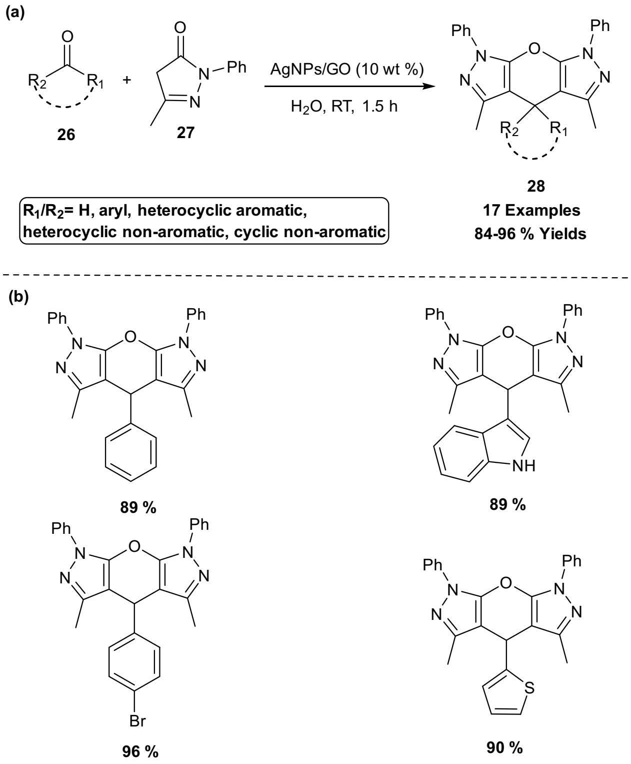
protocol, high yields, minimal catalyst loading, quick reaction times, and simple workup offered the benefits of employing this heterogeneous catalytic system. Additionally, the catalyst was successfully reused 10 times in a row without significantly losing any catalytic activity. The catalyst with a pore size of 3.6 nm had a surface area of 448 m^2 g^{-1} and 0.77 mL g^{-1} mesoporous pore volume (Scheme 15).

An efficient, selective, rapid, and eco-friendly microwave-assisted direct synthesis of xanthones **32** via intermolecular catalytic coupling of salicylaldehydes **10** and 1,2-dihaloarenes **31** using green nanopalladium-supported catalyst (PdNPs) was developed in 2019 (Scheme 16). The reaction proceeds with high regioselectivity and excellent yields, and the catalyst can be recycled up to four times without significant loss of its catalytic activity [26].

Mechanistically, the oxidative addition of 1,2-dihaloarene **31** with palladium (o) catalyst formed aryl-palladium(ii) intermediate **A**. Then, salicylate **10**, generated under basic conditions by displacing the halide, reacts with intermediate **A** to form aryl(aryloxy) palladium(ii) intermediate **B**. Consequently, intermediate **B** undergoes a C–H activation through the C–H bond of the aldehyde to



Scheme 12: Synthesis of xanthone skeleton using Cu nanoparticle (CuNP) catalyst. (a) Method overview; (b) representative examples.



Scheme 13: The chemo-selective synthesis of pyrano[2,3-*c*:6,5-*c′*]dipyrazol]-2-ones. (a) Method overview; (b) representative examples.

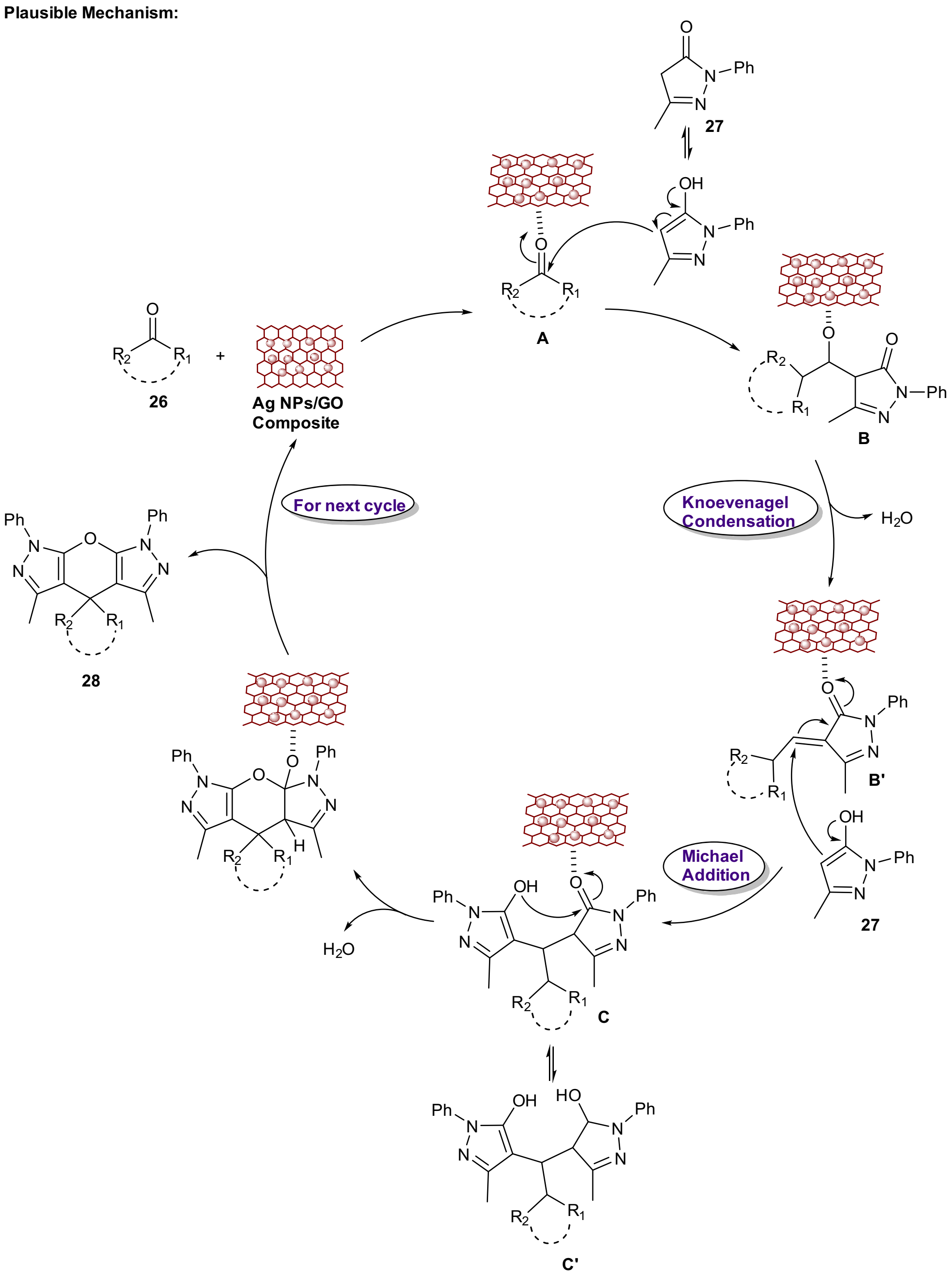
afford cyclic palladium intermediate **C**. Finally, the desired xanthone **32** is formed by the β-elimination of **C** and an intramolecular nucleophilic substitution (Scheme 17).

2.3.2 Three-component reactions

Nezhad et al. [27] explored a silica-coated $Fe_3O_4@SiO_2$ MNP-catalyzed synthesis of 2-amino-4*H*-chromene-3-carbonitrile derivatives **35** under mild, green, and heterogeneous conditions through one-pot three-component coupling reaction between indole derivatives **33**, salicylaldehyde **10**, and malononitrile **34** (Scheme 18). The synthesis of MNPs supported L-cysteine (LCMNP) is shown in Scheme 19.

The designed technique allowed for the reuse of this magnetic recyclable organ catalyst system seven times without the need for any modifications to its catalytic activity. These NPs have an average size of 10 nm according to dynamic light scattering analysis, with a spherical shape displayed in TEM images of the NPs.

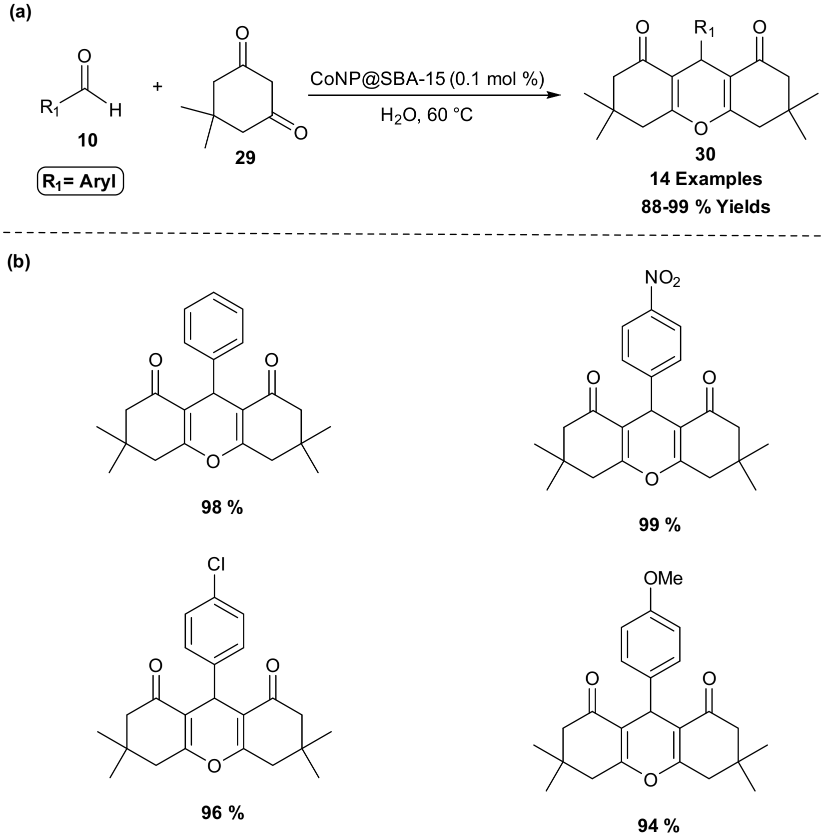
A facile one-pot ultrasound-assisted efficient synthesis of benzo[*g*]chromenes 37 using Fe_3O_4/polyethylene glycol (PEG) core/shell NP was developed in 2016 [28]. The reaction proceeds through one-pot three-component condensation of aldehyde **10** (1 mmol), malononitrile **34** (1.5 mmol),



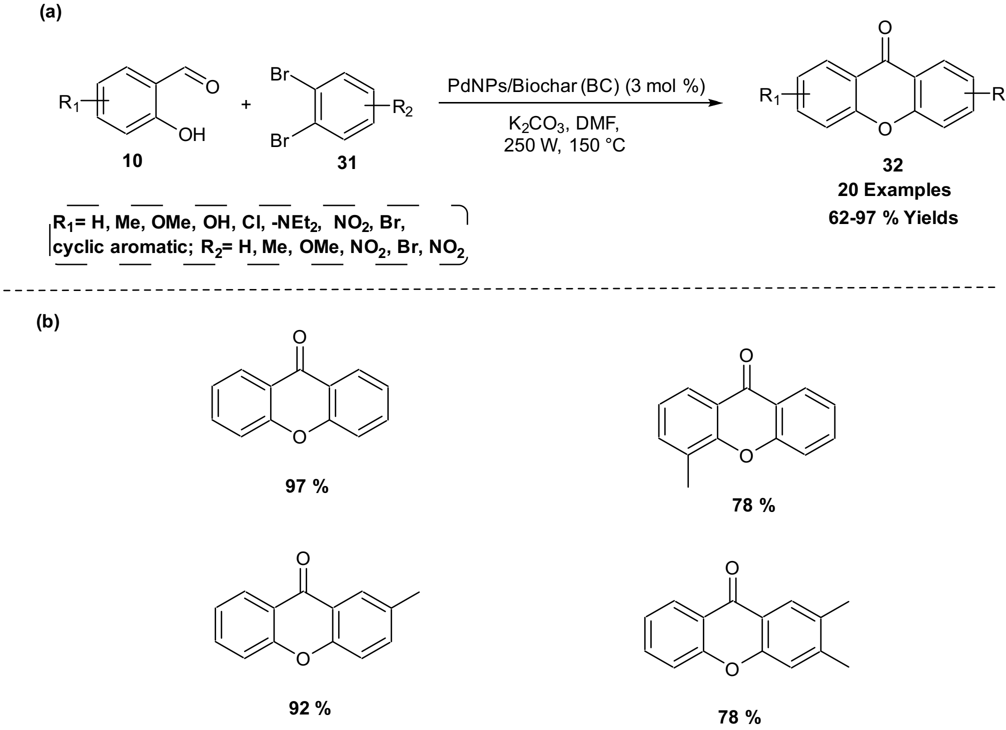
Scheme 14: Plausible mechanism for synthesis of pyrano[2,3-*c*:6,5-*c'*]dipyrazol]-2-ones.

and 2-hydroxy-1,4-naphthoquinone **36** (1 mmol) in ethanol with 12 mg of nano-Fe_3O_4/PEG. The significant benefits of this protocol include simple setup, rapid reaction times, easy workup, catalyst recycling, little catalyst loading, and the effective and efficient use of ultrasonic irradiation (Scheme 20). After completion of the reaction, the catalyst was separated by an external magnetic field and can be reused five times with a slight reduction in the product yields on each reuse (run 1, 95%; run 2, 95%; run 3, 94%; run 4, 94%; run 5, 93%).

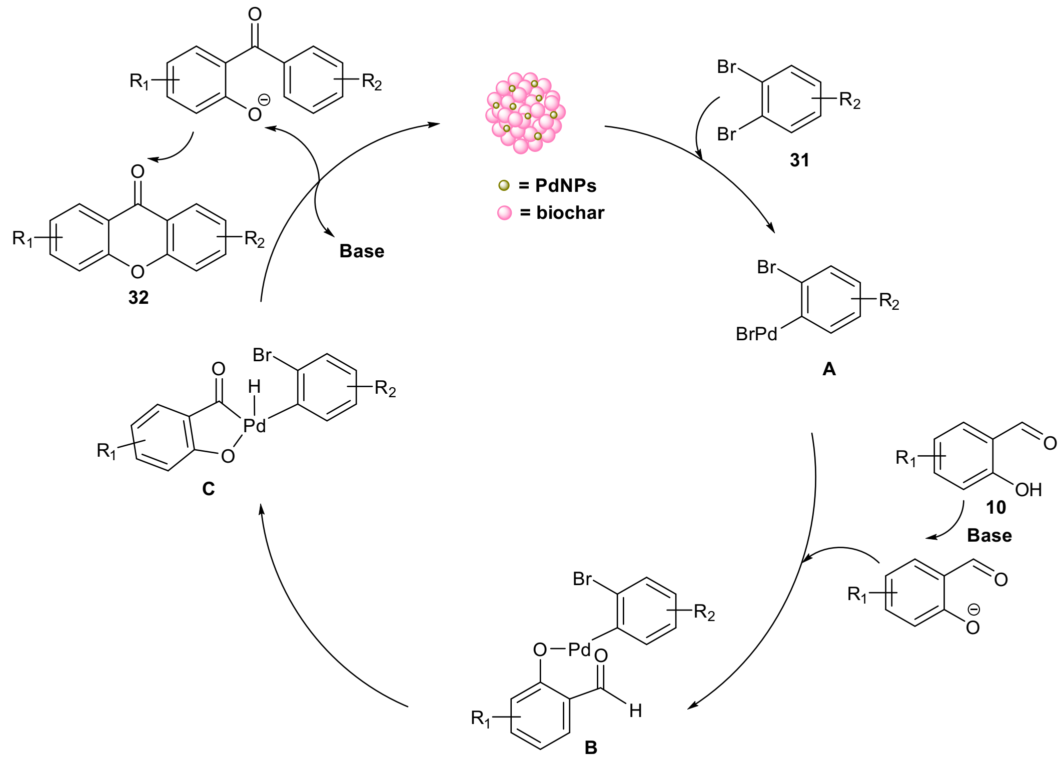
Davood and Masoumeh developed an efficient, green, and reusable thiourea dioxide-grafted γ-Fe_2O_3/hydroxyapatite



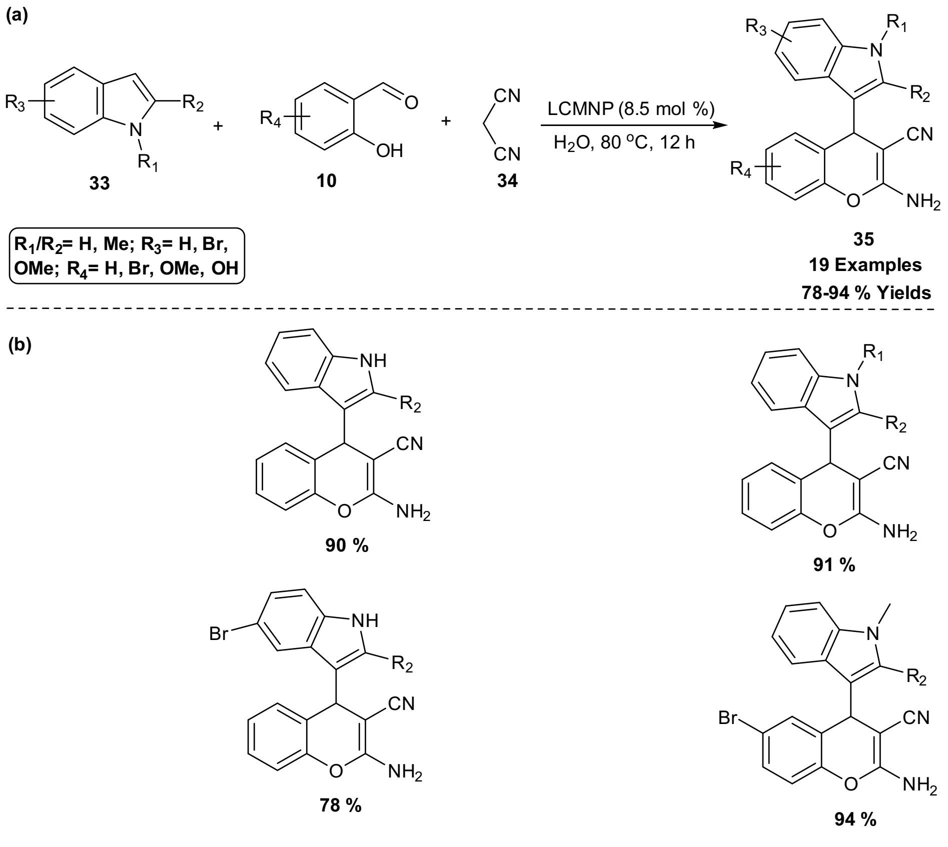
Scheme 15: Synthesis of 1,8-dioxo-octahydroxanthenes in the presence of CoNP@SBA-15. (a) Method overview; (b) representative examples.



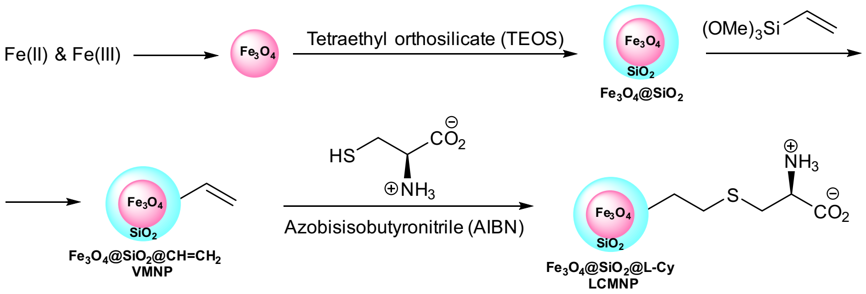
Scheme 16: Microwave-assisted synthesis of xanthones using a green nanopalladium-supported catalyst. (a) Method overview; (b) representative examples.



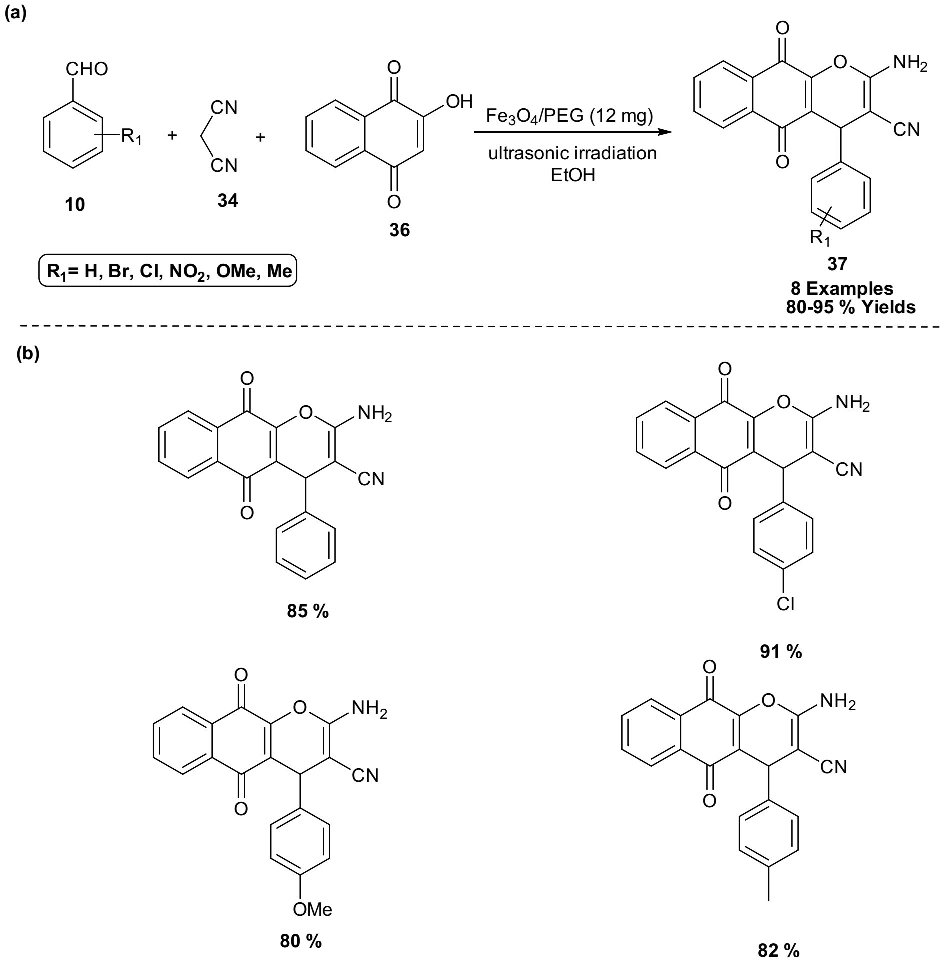
Scheme 17: Proposed catalytic cycle for the PdNP-catalyzed direct synthesis of xanthones.



Scheme 18: Synthesis of 2-amino-4*H*-chromene-3-carbonitriles using LCMNP. (a) Method overview; (b) representative examples.



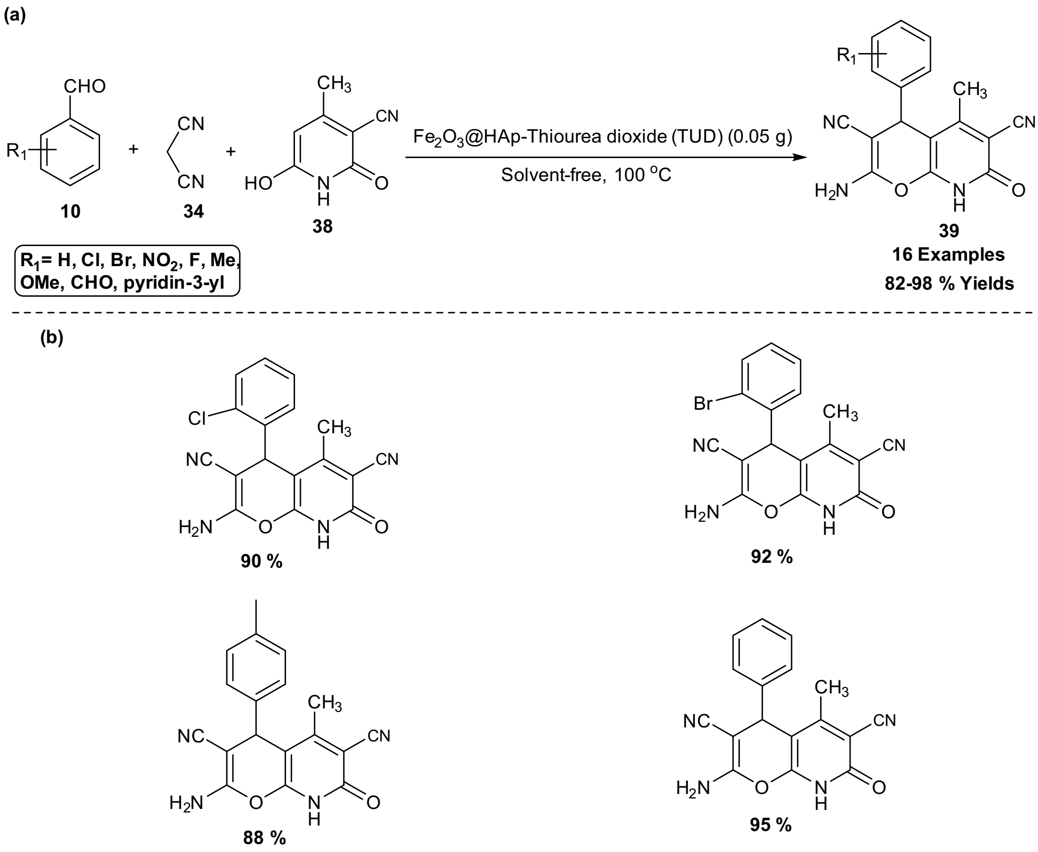
Scheme 19: Synthesis of MNPs supported L-cysteine.



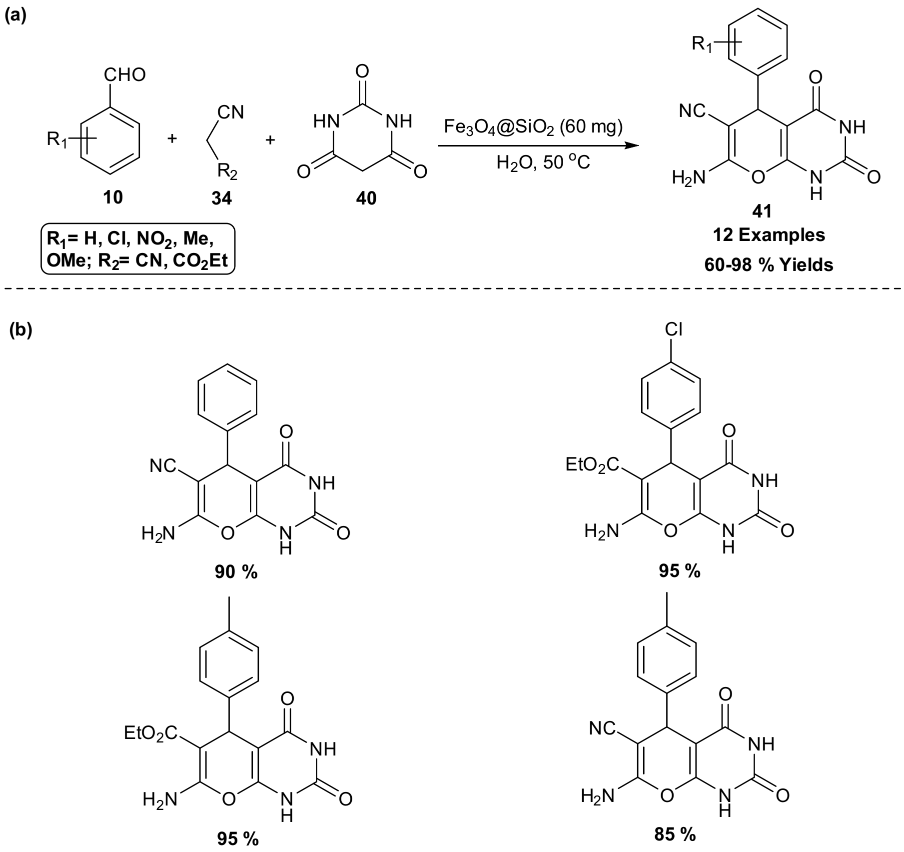
Scheme 20: Fe_3O_4/PEG core/shell catalyzed synthesis of benzo[*g*]chromenes. (a) Method overview; (b) representative examples.

(HAp) MNP for the synthesis of pyranopyridine derivatives **39** in high yields. The reaction proceeds through one-pot three-component reactions between aldehydes **10**, malononitrile **34**, and 3-cyano-6-hydroxy-4-methyl-pyridin-2(1*H*)-one **38** under mild and solvent-free conditions (Scheme 21). The catalyst is easily recyclable in a magnetic field and can be used five times in a row without noticeably losing any substantial catalytic activity. From the study of field-emission (FE-SEM) and TEM, the NPs display a regularly spherical morphology with an average diameter of about 80 nm [29].

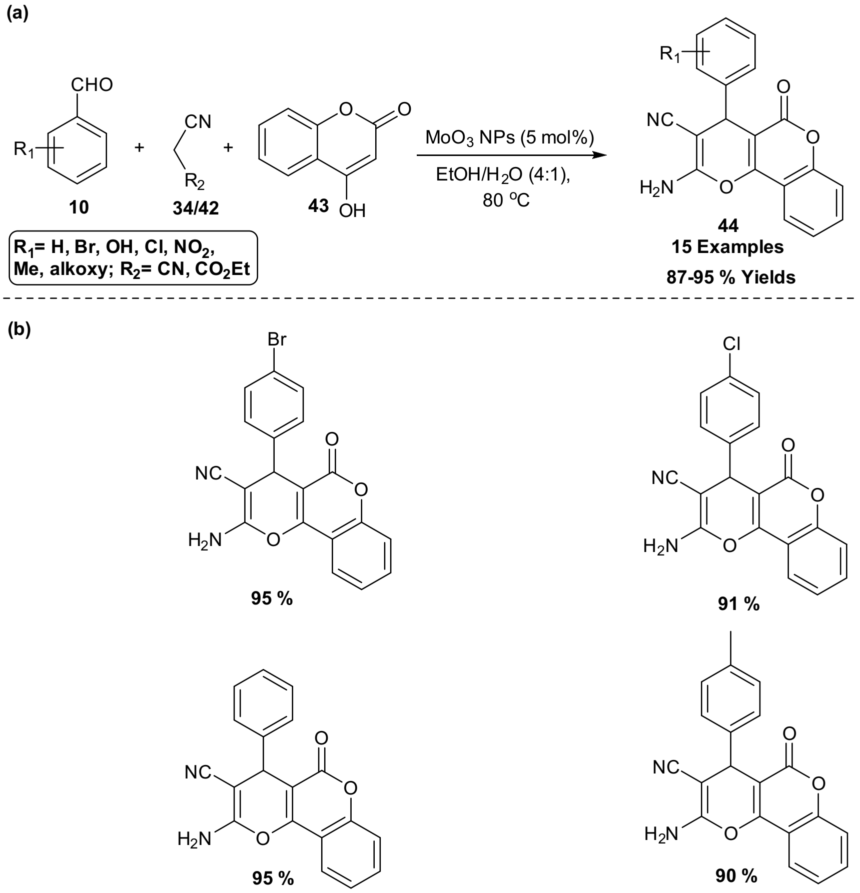
Green and magnetic recyclable formamidine sulfonic acid-functionalized $Fe_3O_4@SiO_2$ as an efficient and hydrogen bonding catalyst for the synthesis of pyrano[2,3-*d*]



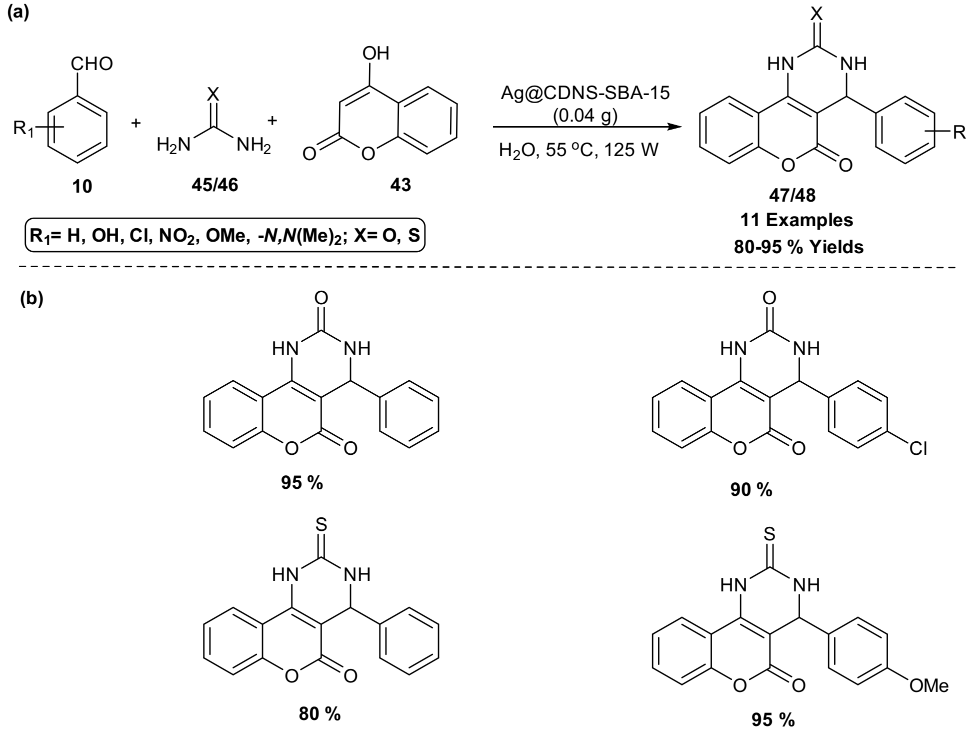
Scheme 21: Thiourea dioxide-grafted γ-Fe_2O_3/HAp catalyzed synthesis of pyranopyridine derivatives. (a) Method overview; (b) representative examples.



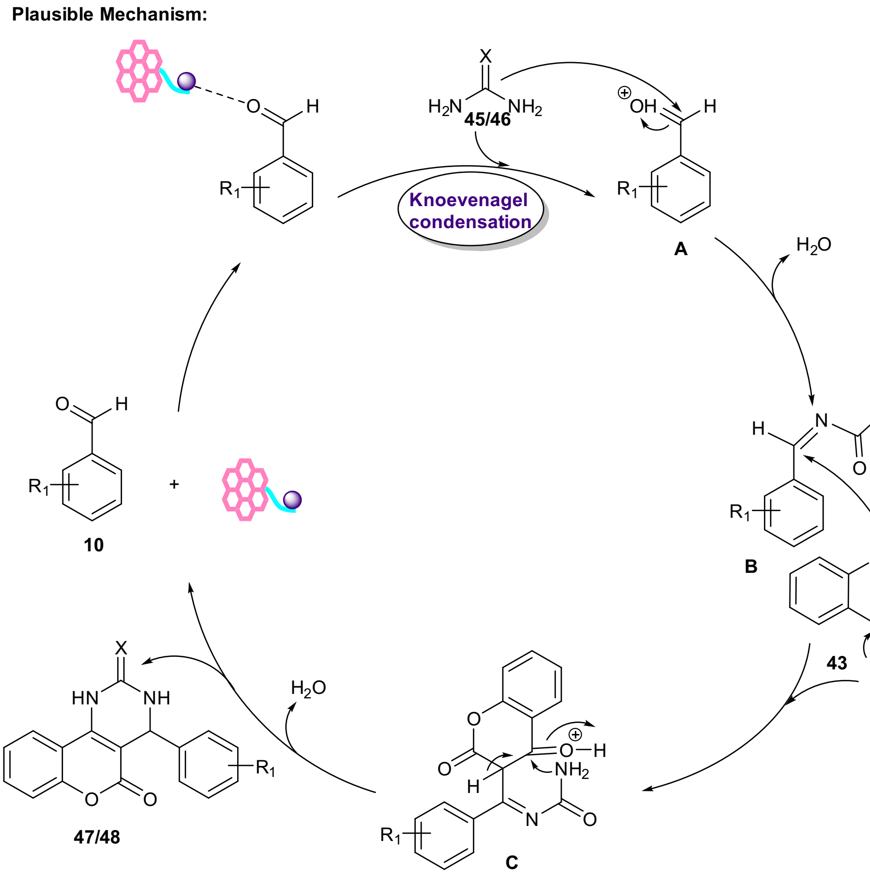
Scheme 22: One-pot three-component synthesis of pyrano[2,3-*d*] pyrimidinone derivatives. (a) Method overview; (b) representative examples.



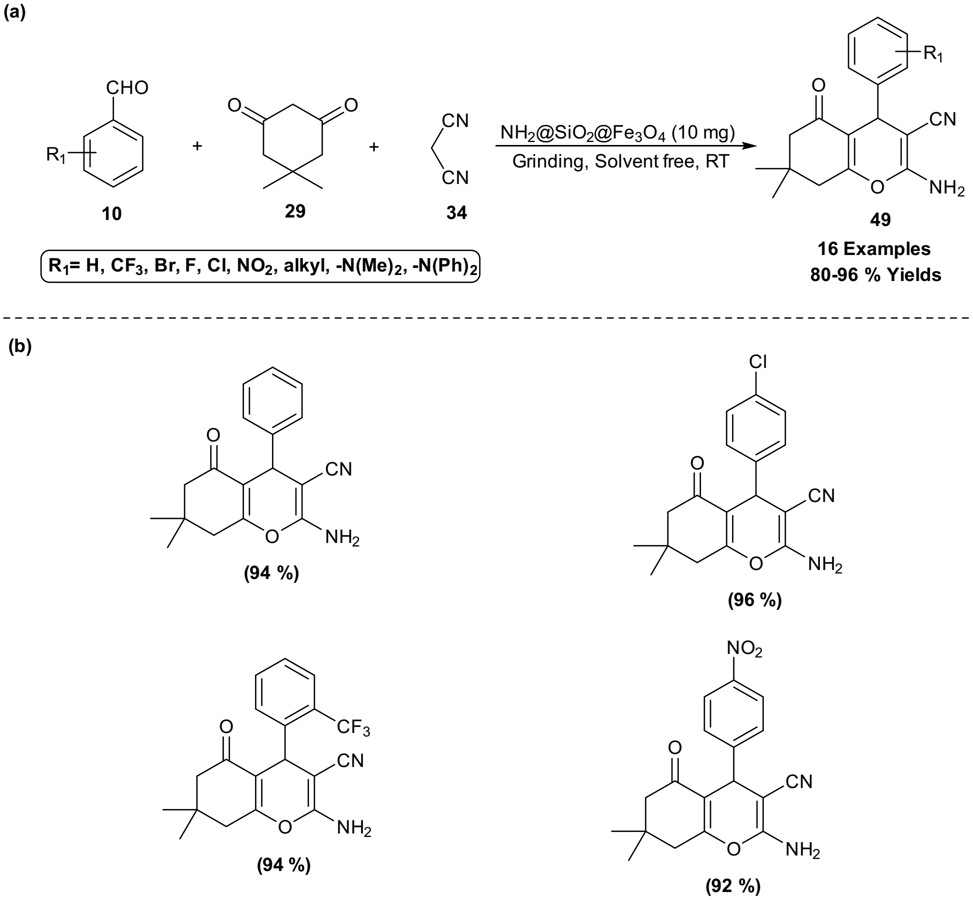
Scheme 23: MoO_3 NPs catalyzed the synthesis of 4-aryl-substituted pyranofuzed coumarins. (a) Method overview; (b) representative examples.



Scheme 24: Ag@CDNS-SBA-15 promoted the synthesis of benzopyranopyrimidines. (a) Method overview; (b) representative examples.



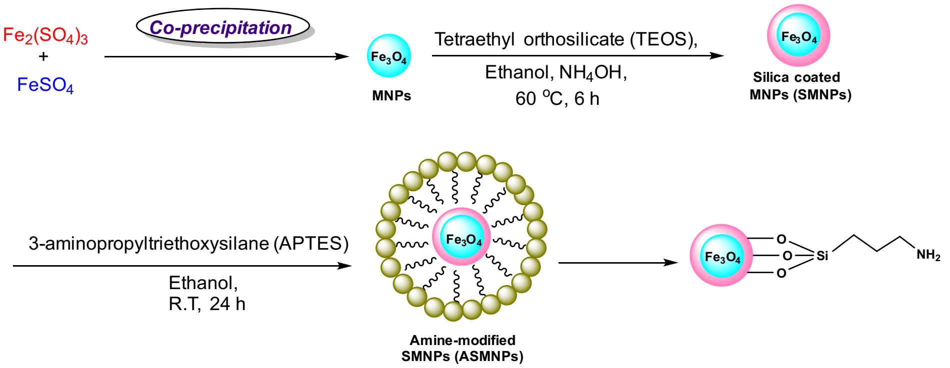
Scheme 25: Plausible mechanism for synthesis of benzopyranopyrimidines.



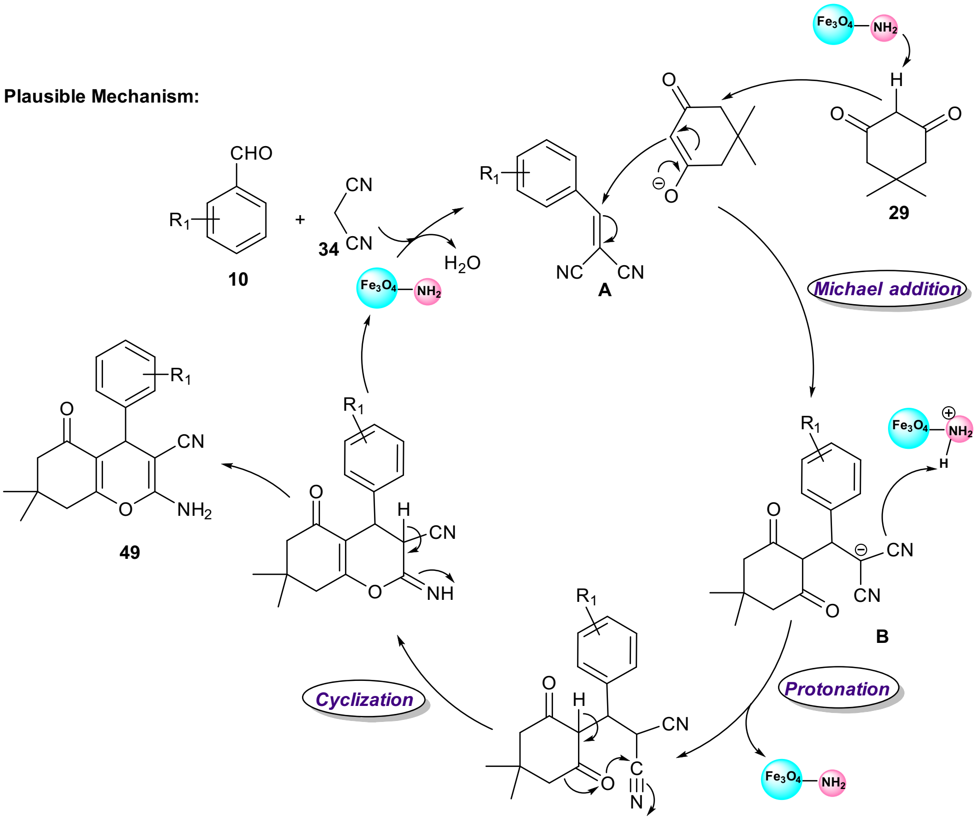
Scheme 26: $SiO_2@Fe_3O_4$ catalyzed synthesis of 2-amino-4*H*-benzo[*b*]pyrans. (a) Method overview; (b) representative examples.

pyrimidinone derivatives **41** via one-pot three-component condensation reaction of benzaldehyde **10** (1 mmol), malononitrile **34** (1.2 mmol), and barbituric acid **40** (1 mmol) in water at room temperature was employed by Ghandi et al. [30]. The catalyst could be employed repeatedly without a noticeable decrease in its activity, and Fourier transform infrared (FT-IR) observations show no substantial changes in the structure of the catalyst before and after the reaction. This reaction protocol has a short reaction time, high yield, simplicity of product isolation, clean reaction profile, and environmental benignity (Scheme 22).

A practical three-component reaction between 4-hydroxycoumarin **43**, malononitrile 34/ethylcyanoacetate **42** and arylaldehydes **10** for the synthesis of 4-aryl-substituted pyranofuzed coumarins **44** using recyclable molybdenum oxide nanocatalyst (MoO_3 NPs) was described by Yaghoub and his co-workers (Scheme 23). The SEM image analysis of MoO_3 NPs shows a diameter of about 40 nm of the



Scheme 27: Synthesis of $NH_2@SiO_2@Fe_3O_4$ MNPs.



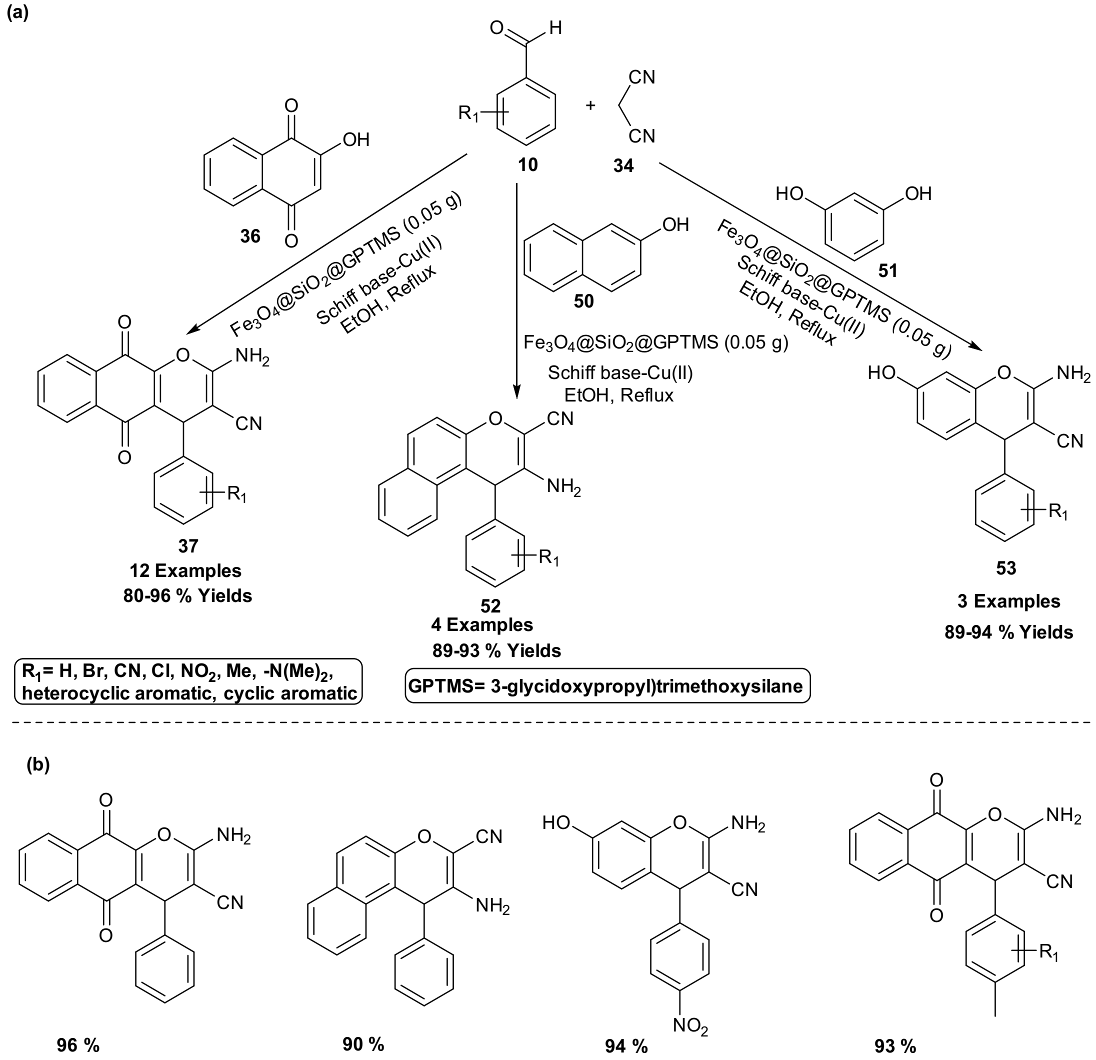
Scheme 28: Mechanism of synthesis of 2-amino-4*H*-benzo[*b*]pyrans.

nanocatalyst without any amorphous or other kinds of crystallized phase particles. The catalyst can be recovered and reused over six successive runs in comparable yields with that obtained from freshly prepared catalysts. The TEM and XRD patterns of the reused catalyst clearly displayed that no notable agglomeration or changes in the crystalline phase had taken place through each run [31].

Sadjadi et al. [32] reported a heterogeneous nanocatalyst Ag@cyclodextrin nanosponge (CDNS)-santa barbara amorphous-15 (SBA-15) promoted three-component reaction of benzaldehydes **10**, 4-hydroxycoumarin **43**, and urea **44** or thiourea **45** under ultrasonic irradiation to afford benzopyranopyrimidines **46**. The catalyst can be recovered after the reaction and reused for up to four reaction runs with slight Ag (0) leaching and loss of catalytic activity (Scheme 24).

According to the proposed mechanism (Scheme 25), activation of aldehyde **10** by the catalyst (compound **A**) followed by Knoevenagel condensation reaction with urea **45**/thiourea **46** formed intermediate **B**. Then, the reaction of intermediate **B** with 4-hydroxycumarin **43** afforded intermediate **C**. Finally, the cyclization of intermediate **C** with the loss of a water molecule formed the desired final product **47/48**.

Highly efficient and magnetically retrievable amine-functionalized $SiO_2@Fe_3O_4$ NP-catalyzed green and mechanochemical one-pot multicomponent synthesis of bioactive 2-amino-4*H*-benzo[*b*]pyrans **49** was explored in 2020 (Scheme 26). The reaction is an environmentally benign reaction achieved by simply grinding substituted aromatic aldehydes **10**, dimedone **29**, and malononitrile **34** at room temperature under solvent and waste-free conditions with



Scheme 29: $Fe_3O_4@SiO_2$ MNPs catalyzed the synthesis of chromene-annulated heterocycles. (a) Method overview; (b) representative examples.

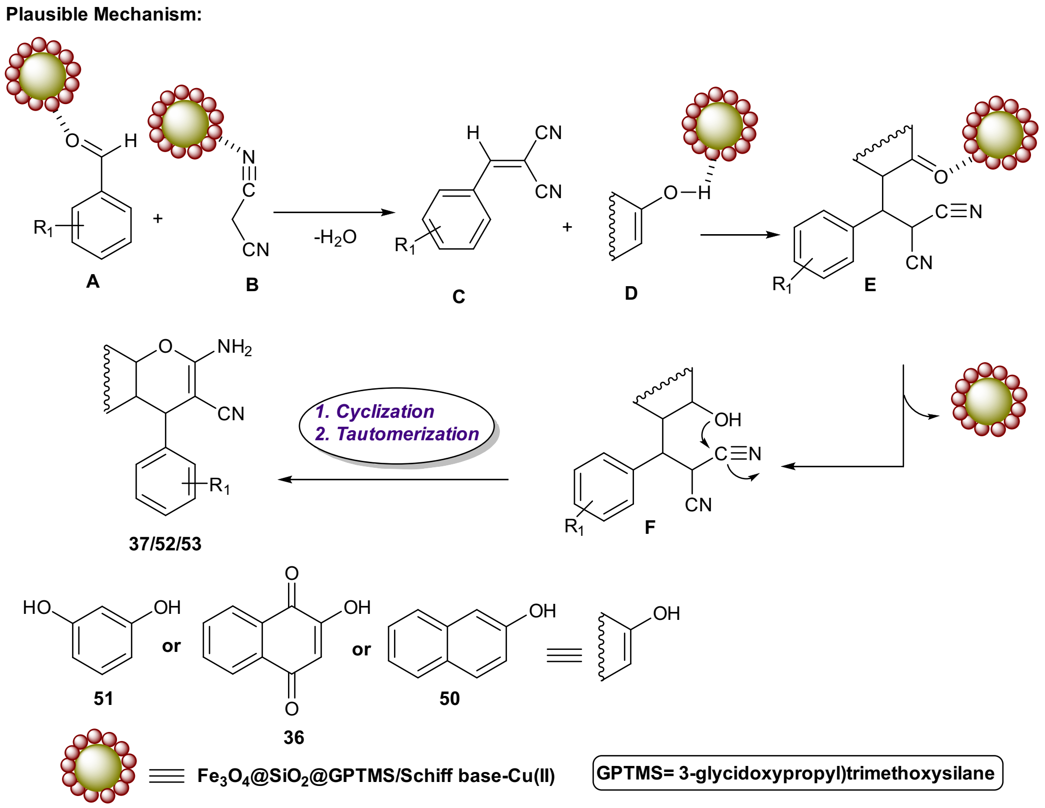
good yields, high purity, milder reaction conditions, and short reaction time.

Furthermore, the proposed catalyst has a number of significant properties, including broad functional group tolerance, enhanced yield, and recyclability [33]. A schematic illustration for the formation of $NH_2@SiO_2@Fe_3O_4$ MNPs is shown in Scheme 27.

The mechanism of the reaction is driven specifically by the basic amino sites of the catalyst. Initially, Knoevenagel condensation between malononitrile **34** and aromatic aldehyde **10** formed the arylidiene malononitrile **A**, followed by Michael's addition of dimedone **29** to arylidiene malononitrile **A** to form the intermediate **B**. Finally, intramolecular cyclization and protonation to the intermediate **B** results in the formation of the desired products **49**, and the catalyst is regenerated in the reaction mixture (Scheme 28). In another study, a magnetic nanocatalyst $Fe_3O_4@SiO_2$-imidazole (imid)-$H_3PMo_{12}O_4$ NPs (PMA^n) was used for this reaction under ultrasonic irradiation or reflux conditions by Preeti and his co-workers [34].

An eco-friendly novel Schiff base complex of copper coated on epoxy-modified $Fe_3O_4@SiO_2$ MNPs nanocatalyst for the synthesis of chromene-annulated heterocycles via one-pot three-component reaction of aromatic aldehydes **10**, various phenols (2-hydroxynaphthalene-1,4-dione **36**/resorcinol **51**/β-naphthol **50**), and malononitrile **34** in ethanol under reflux conditions was explored in 2021. This method represents a novel and significant advancement in the synthesis of several chromene-annulated heterocycles with no usage of column chromatography, simple techniques, good yields, and magnetic recoverability of the catalyst (Scheme 29). The higher activity of this nanocatalyst due to its small size between 26 and 45 nm leads to the dispersion and diffusion of the nanocatalyst in the reaction mixture and can be rapidly taken out from the mixture with an external magnet. Furthermore, it can be reused directly in seven sequential runs without any loss in activity after washing with ethanol and drying it (Scheme 29) [35].

According to the plausible mechanism of this reaction, Knoevenagel condensation reaction between aldehydes **10** and malononitrile **34** in the presence of the Schiff base complex of copper coated on epoxy modified $Fe_3O_4@SiO_2$ MNPs nanocatalyst as a Lewis acid formed Knoevenagel product **C**. Then, the intermediate **E** is produced through Michael's addition of 2-hydroxynaphthalene-1,4-dionein **D** with Knoevenagel product **C**. Finally, intramolecular nucleophilic cyclization of intermediate **F**, formed by enolization of intermediate **E** afforded the 2-amino-4*H*-chromene derivatives



Scheme 30: Plausible mechanism for the synthesis of chromene-annulated heterocycles.

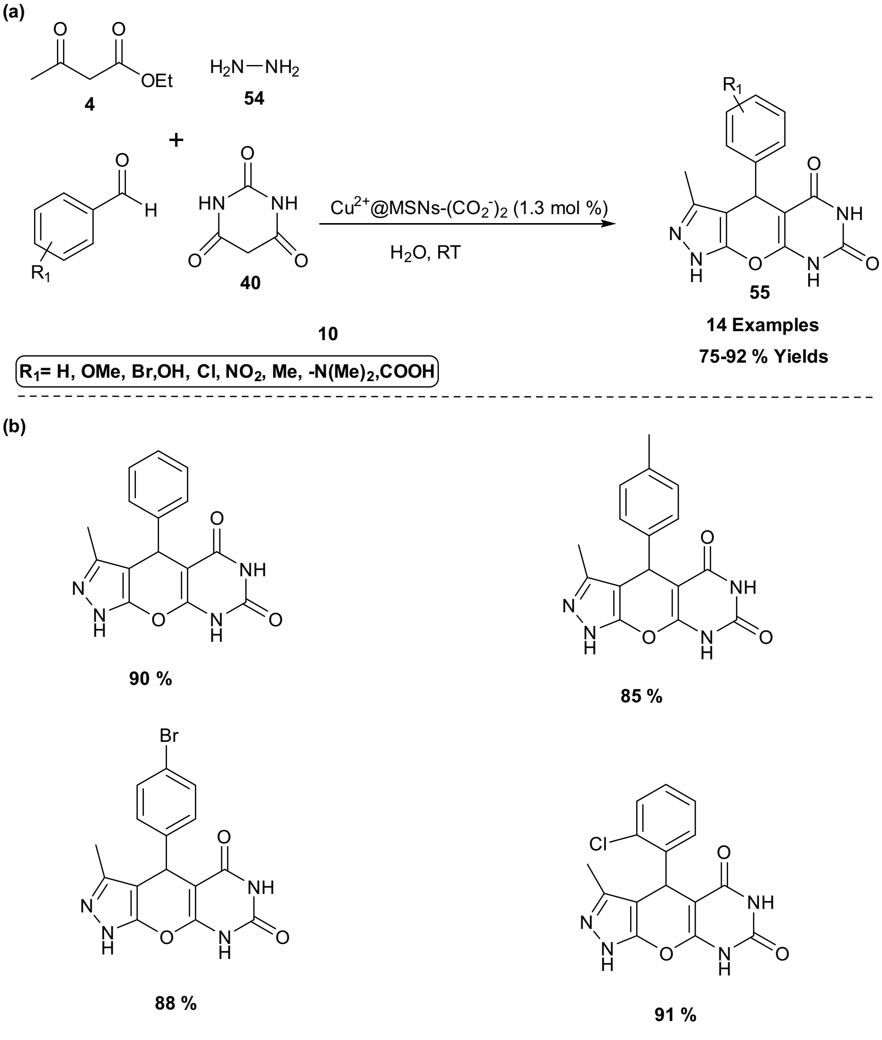
37/**52**/**53**. Then, the nanocatalyst was removed by a magnetic field from the reaction mixture for further use (Scheme 30).

2.3.3 Four-component reactions

Zahra and Mohammad explored a facile one-pot, four-component condensation reaction of ethyl-3-oxobutanoate **4**, hydrazine hydrate **54**, aromatic aldehydes **10**, and barbituric acid **40** employing an efficient Cu-immobilized mesoporous silica NP, [Cu^{2+} @MSNs-$(CO_2^-)_2$] as a catalyst for the synthesis of pyrazolopyranopyrimidines **55** in water. The catalyst was characterized by using nitrogen adsorption–desorption analysis, SEM, small angle powder XRD, thermal analyses (TGA and DTA), FT-IR studies, SEM, TEM, and EDX. The catalyst can be easily recovered from the reaction mixture at the end and reused numerous times without any loss in its catalytic activity (Scheme 31). The present protocol offered a relatively short reaction time, ease of product isolation, efficiency, generality, and high yield of products [36].

3 Conclusion

The present review focuses on the synthesis of oxygen-containing heterocyclic compounds employing recyclable nanocatalysts for the past ten years. Various non-toxic, simpler, environmentally friendly, and more affordable multicomponent synthetic approaches have successfully synthesized heterocycles of different sizes and ring systems containing oxygen atoms using various recyclable reusable nanocatalysts. The oxygen-containing heterocycles are a significant family of molecules in organic chemistry, mostly due to their wide range of biological roles and natural abundance. Well-known examples of



Scheme 31: Cu-immobilized mesoporous silica NP synthesis of pyrazolopyranopyrimidines. (a) Method overview; (b) representative examples.

promising medicinal substances are natural and semi-synthetic oxygen heterocyclic compounds, such as lovastatin (hypolipidemic), digoxin (treating CHF), cyclosporine-A (immunosuppressive), and taxol.

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Conflict of interest: Authors state no conflict of interest.

Data availability statement: The datasets generated during and/or analyzed during the current study are available from the corresponding author on reasonable request.

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