
Atish Roy, Anil Kumar Bahe, Aayushi Chanderiya, Hemlata Dangi, Pratibha Mishra, Arunesh K. Mishra, and Ratnesh Das*

Department of Chemistry, Dr. Hari Singh Gour University, Sagar, M.P. India.

Abstract: In organic synthesis, nanocatalysts play a significant role. Nitrogen- and oxygen-containing based heterocyclic atoms are the substantial and essential primary units available in different organically dynamic characteristic items, industrial and pharmaceutical, and agrochemicals. Nanoparticles (NPs) or nanoclusters (NCs) have high synergist action; the maintainable and financial advantages of the convention are the exceptional returns of items, short response time, primary stir-up method, and utilization of a non-poisonous and reusable impetus the response. The current review looks at the various forms of nanocatalysts used to form heterocyclic compound synthesis and some other important ring functionalization.

Keywords: Heterocyclic atoms, nanoclusters, pharmaceutical, agrochemicals, nanoparticle (NPs), green chemistry.

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*Corresponding author. E-mail: ratneshdas1@gmail.com.

INTRODUCTION

The carbon-nitrogen bond arrangement is a significant manufactured advance in natural combination for creating N-heterocyclic particles, which assume a real job in the union of modern polymers, agrochemical, besides organically dynamic drug products (1). The 2,3-benzopyrrole core is one of the most seriously considered primary examples by manufactured just as organic scientific experts (2) because of the natural organic exercises. Nanoparticles (NPs) are great impetuses for the natural union, and however, during the movement of a synthetic response, they show the extraordinary inclination to total and misshape. Thus, they need help to achieve their synthetic and actual security as catalysts. Nitrogen-containing heterocyclic compounds are vital applications because of their abundance in nature. Several nitrogen-containing heterocyclic compounds exhibit many biological activities like antibacterial, antiarthritis, antiasthmatic, and many other types of biological activities (3–5).

Nitrogen-containing heterocycles also show their essential role as ligands, explosives, stabilizers in photography (6–8). The synthesis of such compounds by eco-friendly methods is of great interest to the research community. Oxygen-containing heterocycles have displayed a very wide range of biological and therapeutic properties (9). This chromene moiety, which belongs to a naturally occurring oxygen-heterocylic class, shows a wide range of biological activity. These compounds can be used as antioxidant agents, antifungal agents, anticancer agents etc. (10).

Heterocyclic compounds are structural units present in various biologically active natural products and pharmaceuticals (11). However, due
to a lack of substrate, the extent and generality of a particular 2,3-benzopyrrole's synthesis have sometimes been reduced. As a result, developing reliable and cost-effective methods for synthesizing 2,3-benzopyroles from readily available starting materials is still challenging (12). One of the most pressing issues and problems in recent decades has been the use of nanoscience in the advancement of ecology, drug, and most notably, catalysts. Nanoscience and green chemistry have unique compatibility and accuracy due to the efficient implementation of nanotechnology in manufacturing greener goods, making nanoscience a savior in environmental and energy challenges (13). Due to their high reactivity, sustainability, ease of recapture, and opportunity to recycle, metallic nanoparticles have recently been widely used as alternative catalysts in organic synthesis. Metal nanoparticle catalyzed reactions have many advantages over traditional metal-catalyzed reactions, including low catalyst loading, low cost, strong atom efficiency, higher yields, shorter reaction time, and the opportunity to recycle catalysts (14).

**Figure 1:** The structures of cyprodinil and imatinib.

**Formation of 3-Substituted 2,3-Benzopyrrole in Water Using Polymer-Attached ZnO NPs as a Eco-Friendly Catalyst**

3-Amino alkylated 2,3-benzopyroles were synthesized by Tauhid Shaikh et al. in the presence of ZnO nanoparticles. 2,3-Benzopyroles react with benzaldehyde and aniline to form 3-amino alkylated 2,3-benzopyroles. Polylactic acid (PLA) includes a hydrophobic region around ZnO, which is naturally hydrophilic. PLA can absorb organic molecules, as shown by its use in the drug delivery framework; thus, this nanocomposite can serve as an amphiphilic catalyst. By absorbing substrate molecules, PLA may improve the accessibility of the catalyst (ZnO) (15). To investigate the effect of solvent on reaction results, a model reaction was carried out in various solvents, such as N,N-dimethylformamide (DMF), p-dioxane, dimethyl sulfoxide ((CH₃)₂SO), acetonitrile, oxolane, acetone, and H₂O. The best result is found in the presence of water.

**Scheme 1:** Synthesis of 3-amino-alkylated 2,3-benzopyrrole. Adapted from (15).

**Larock’s 2,3-Benzopyrrole Synthesis Using N, N-Dimethylformamide-Stabilized Pd Nanocluster**

In the presence of a Pd nanocluster, Kaito Onishi et al. synthesized 2-idoanilines with alkynes to produce 2,3-disubstituted 2,3-benzopyroles. This reaction took place in the absence of ligands and with low catalyst loadings. The most effective solvent was DMF, which created an isolated yield of 88%. Then there were mixed solvents like DMF/H₂O (1:1) and N-methyl pyrrolidone (NMP)/H₂O (1:1). A trace amount of product was obtained when DMF/H₂O (1:1) was used. When NMP/H₂O (1:1) was used, the product was obtained in 28% yield, and various additives are used, but NaCl was the best additive; product yield was 69 percent without the addition of NaCl. As reported in the palladium complex-catalyzed Larock 2,3-benzopyrrole synthesis, salts such as NaCl increased the catalytic activity by synthesizing a chloride-ligated zerovalent palladium species (16).
Synthesis of Bis(indolyl)methanes Using an Efficient and Versatile Reagent, Ag NPs
Aromatic aldehyde and 2,3-benzopyrrole react to form bis(indolyl)methanes in the presence of Ag nanoparticles. This is an outline of a modest, mild, and effective method to the fusion of bis(indolyl)methane and its derivatives because the most active cruciferous compounds for promoting healthy estrogen metabolism and inducing apoptosis in human cancer cells are bis(indolyl)methanes, at 25 °C, an optimized number of nano-Ag arranged the reaction of benzaldehyde and 2,3-benzopyrrole. When Ag nanoparticles take less than 0.001 mol, the yield of the product also decreases. Several Lewis acids catalyzed a mixture of products in EtOH at 25 °C, but the best synthesis formed is in the presence of Ag NPs. Some solvents yielded like CHCl₃ (55%), CH₃CN (42%), H₂O (20%), but EtOH gave 94% yield (17).

Synthesis of 2,3-Benzopyrrole of 2-Nitrobenzyl Cyanide in the Presence of Co−Rh Heterobimetallic NPs
Reductive cyclization of two 2-Nitrobenzyl Cyanide in the presence of heterobimetallic Cobalt-Rhodium NPs yields 2,3-Benzopyrrole (14). They have higher catalytic efficiency compared to monometallic NPs. Heterobimetallic NPs have recently been concerned with much consideration as catalysts (18).

Synthesis of N-arylation of 2,3-Benzopyrrole and Imidazole with Aryl Halide in the Presence of CuFe₂O₄ Magnetic NPs
2,3-Benzopyrrole and imidazole N-arylation reactions with various aryl halides in the presence of CuFe₂O₄ nanoparticles. In the below ligand-free
circumstances, the reaction yields well to excellent with CuFe$_2$O$_4$ nanoparticles as the catalyst. Furthermore, CuFe$_2$O$_4$ NPs could be recycled six times, lacking down their operation (19). Optimization of reaction taken in different solvents and bases such as 1. NMP 97%, 2. DMF 82%, 3. CH$_3$CN 22%, 4. CH$_2$Cl$_2$ 26%, 5. Toluene 15%, and 6. K$_3$PO$_4$ 97% 7. Et$_3$N 35%, 8. K$_2$CO$_3$ 71%, 9. KOH 64%, 10. Na$_3$PO$_4$.12H$_2$O 58% 11. Cs$_2$CO$_3$ 78%.

![Scheme 5](image)

**Scheme 5:** Synthesis of N-Arylindole and N-Arylimidazole. Adapted from (19).

**Synthesis of 1,1,3-tris(1H-indol-3-yl) Alkanes in Attendance of Silica-Coated Magnetic Nanoparticle**

Proposed a straightforward and worthy system for the amalgamation of 1,1,3-tris(1H-indol-3-yl) alkanes catalyzed with MNPs-TUD-SO$_3$H. As per the response pathway to start with, the carbonyl gathering of α β-unsaturated compound will be initiated within sight of MNPs-TUD-SO$_3$H impetus and shaped the dynamic halfway. 2,3-Benzopyrrole effectively assaulted to this insecure halfway, and the item relating gives due to the 1,4- and 1,2-increments. Subsequent stage followed by initiation of existing moderate through attractive nanoparticles MNPs-TUD-SO$_3$H and a nucleophilic response of the third atom of 2,3-benzopyrrole with this halfway that in the end this synergistic cycle finished by eliminating a water atom and the ideal item 1,1,3-tris(1H-indol-3-yl) alkane was created at present of the novel nanostructured impetus. The authors related that the reaction between crotonaldehyde and 2,3-benzopyrrole was considered under the same reaction condition in the presence of 10 mol% thiourea dioxide as a catalyst. The corresponding 1,1,3-tri(1H-indol-3-yl) alkane was synthesized in 40% yield (20).

![Scheme 6](image)

**Scheme 6:** Synthesis of 1,1,3-tris(1H-indol-3-yl)alkanes. Adapted from (20).

**One-Pot Synthesis of Benzofurans under Aqueous Conditions Using Silver Iodide NPs**

In the existence of a silver iodide nanocatalyst, the reaction of salicylaldehyde, morpholine, and phenylacetylene produce 2,3-disubstituted benzofuran in aqueous media. First, in this condensation reaction, reagents, such as copper iodide, copper chloride, silver bromide, and silver iodide, were used to test the efficiency of the catalytic activity. We discovered that silver iodide is the best catalyst for this reaction, so we ran the model reaction with silver iodide nanoparticles. Furthermore, compared to bulk AgI, silver iodide NPs produced outstanding yields in quicker response times (21).
Synthesis of Poly-Substituted Furans Catalyzed CuO NPs in an Aqueous Medium

MnO2 interceded ZnCl2 and helped blend of 3,4-dicarbonylfuran subsidiaries in corrosive acidic medium, according to Zhuo et al. The Zhuo technique had a few limitations, such as the use of an abundance measure of ZnCl2/MnO2 as an impetus that was not reusable, unforgiving reaction conditions (refluxing in a corrosive acidic medium at 130 °C), and a longer response time (24 h). It lowered segregated yields of items (15-80%). The addition of 2-methylpropane-2-peroxol as an oxidizing agent (1 eq.) increases the yield and decreases the reaction time significantly (3 h). After 12 hours of refluxing a mixture of A (1 millimole), B (5 mmol), and CuONPs (10 milligrams) in the presence of Cu nanoparticles (10 milligrams), 40% of the required furan derivative was obtained. The addition of 2-methylpropane-2-peroxol as an oxidizing agent (1 eq.) increases product amount and decreases response time significantly (3 h) (22).

Synthesis of Naphthopyran Derivatives, Using Novel Ferrocene-Based Ionic Liquid Supported on Silica Nanoparticles

The model reactions were 2-naphthol, benzaldehyde, and malononitrile. For this reason, the efficiency of (SiO2@Im-Fc [OAc]) was investigated employing a change of solvents, temperatures, and quantities of synthesized nanocatalyst to find a more efficient, convenient, and rapid method for the synthesis of naphthopyran derivatives. The findings are summarized in this report. For the model reaction at room temperature in the presence of 30 mg nanocatalyst, a variety of traditional organic solvents such as EtOH, CH2Cl2, CHCl3, CH3CN, and H2O, as well as solvent-free conditions, were screened. At ordinary temperatures, various traditional solvents provided low to moderate yields. Surprisingly, the best results were obtained without the use of any solvents. The model reaction was then performed in varying amounts of nanocatalyst (5 to 50 mg) and at different temperatures (23).
Synthesis of 3,4,5-Trisubstituted Furan-2(5H)-one Derivative Using 4-carboxybenzylsulfamic Acid Supported on Magnetic NPs

In the presence of magnetic NPs aided by 4-carboxybenzylsulfamic acid, the combination of trisubstituted furan derivatives from aryl aldehydes, various anilines, and dimethyl acetylene dicarboxylate. Designing heterogeneous hybrid catalysts to synthesize furans, such as 4-carboxybenzylsulfamic acid-functionalized Fe$_3$O$_4$ nanoparticles (SA-AMBA-MNPs) as a new green and magnetically simple distinguishable catalyst (24). The reaction was carried out using various solvents and amounts of catalyst, with the best results obtained using ethanol catalyst at 20 mg at 70 °C for two hours and a yield of 92%.

Amine-Functionalized SiO$_2$@Fe$_3$O$_4$ NPs are Used in a One-Pot Multi-Component Synthesis of Bioactive 2-Amino-4H-Benz[b]Pyrans

Formation of 2-amino-4-(4-bromophenyl)-7,7-dimethyl-5-oxo-5,6,7,8-tetrahydro-4H-chromene-3-carbonitrile required the use of amine-functionalized SiO$_2$@Fe$_3$O$_4$ NPs from p-bromobenzaldehyde, propanedinitrile, and dimedone. The lack of a catalytic product led to an absence of 2-amino-4H-benzo[b]pyrans. Rising the quantity of catalyst by 2 to 10 mg resulted in a higher percentage yield of the formula (25).

Synthesis of Benzofurans from Terminal Alkynes and Indophenols using Recyclable Palladium NPs under the Ligand-Free Condition

The authors developed highly efficient and robust heterogeneous reaction supported by Pd nanoparticles on N,O-dual-doped hierarchical porous carbon using a one-pot tandem reaction of o-iodophenols with terminal alkynes. The catalyst allowed for sequential intermolecular Sonogashira cross-coupling followed by cyclization of o-iodophenols with terminal alkynes to synthesize a variety of 2-benzofurans under copper- and ligand-free conditions (26). The reagent allowed successive intermolecular Sonogashira reactions after recirculating o-iodophenols with terminal alkynes to produce a variety of 2-benzofuran derivatives under copper- and ligand-free conditions with a selectivity of 60%. Various bases were used in the reaction, including Na$_2$CO$_3$, K$_2$CO$_3$, Cs$_2$CO$_3$, K$_3$PO$_4$, NaO'Bu, KOH, DBU (1,8-diazabicyclo[5.4.0]undec-7-ene), and TEA (triethylamine). Under similar conditions, it was discovered that K$_3$PO$_4$ with two equivalents to the reactant was the best option for superior catalytic efficiency in terms of equal operation and selectivity (a full conversion with up to 96% selectivity).
A One-Pot Three-Component Reaction Catalyzed by Zinc Oxide NPs: A Simple Synthesis of 4-ArylNH1,2,3 Triazoles

Synthesis of NH-triazoles in the presence of ZnO nanoparticles using 4-bromobenzaldehyde, nitromethane, and sodium azide as model substrates. A wide variety of solvents, both organic and aqueous, were studied. Surprisingly, the yield of the desired items varies significantly in each case. It can be shown that when PEG-400 was used as a solvent at 100 °C, the best results were obtained. The reaction can also proceed when aqueous was also carried out in the water, but the product yield was meager.

Following that, several solvents were investigated, including dichloromethane (DCM), DMF, dimethylsulfoxide (DMSO), ethylene glycol, and toluene, but the yields of NH-triazoles were inferior. The cycloaddition reaction of 4-bromobenzaldehyde, nitromethane, and sodium azide was also performed in PEG-400 solvent at 80 °C to optimize the temperature. Notably, at this temperature, the product's yield decreased (27).

ZnO NPs are Used to Synthesize 3,4-Dihydropyrimidin-2(1H)-(thio)one Derivatives

It’s a Biginelli reaction in which aldehyde, diketones, and urea were used as starting materials. As a solvent, H2O was used. The response took place at 50 °C. ZnO nanoparticles catalyze this reaction. These types of responses are not able to proceed without the use of catalysts. It is observed that this reaction produces a small yield of desired products without catalyst after straining the reaction mixture for 28 hours. However, when catalysts were used, the result of the desired outcome was good to excellent. Moreover, the time for the completion of the reaction was about half an hour at mild temperature (28).

Synthesis of Furan Derivatives using Highly Efficient Silica-Coated Magnetic NPs by Multi-Component Reaction

The derivatives of furan are formed when aniline, aromatic aldehyde, and dialkylacetylenedicarboxylate react. This reaction proceeds at room temperature, and the catalyst used for this process was silica-coated magnetic NPs. Only 0.004 g of catalyst was used for the response. Observations have shown that as the catalyst volume increases from 0.004 to 0.006, the product yields do not change. So it can be concluded that the best quantity of catalyst was 0.004 g. A trace amount of product was obtained in the catalyst shortage (29). At room temperature, 4 mg of catalyst was measured in different solvents such as aqueous medium, ethyl alcohol, methyl alcohol, and acetonitrile. As can be shown, ethyl alcohol is the perfect solvent designed for this conversion, yielding 93% of the time.
Scheme 15: Synthesis of methyl-oxo-2,4-diphenyl-2,5-dihydrofuran-3-carboxylate. Adapted from (29).

Synthesis of Trans-dihydroindeno[1,2-b]furans in the Presence of a Nano-Fe$_3$O$_4$-Quinuclidine-based Catalyst
When N-arylpyridinium bromide, 1,3-diketohydrindene, and arylglyoxal were reacted in the equimolar condition in the presence of nano-Fe$_3$O$_4$-quinuclidine in aqueous media for 1.5 hours, the best product will come from the Ar group 4-NO$_2$C$_6$H$_4$ and the X group Cl, with a 94% overall yield (30).

Scheme 16: Synthesis of trans-dihydroindeno[1,2-b]furans. Adapted from (30).

Synthesis of Novel Furan-2(5H)-One's Derivatives Utilize Magnetic Nanoparticle and their Antibacterial Activities
Fe$_3$O$_4$ nanoparticles functionalized with 2-amino-1,3-benzothiazole-6-carboxylic acid (SA-ABTCA-Fe$_3$O$_4$) were synthesized as a new heterogeneous catalyst containing inorganic and organic parts. The product shows antimicrobial action. This synthesis was carried out at different temperatures (25, 80 °C), varying the quantity of SA-ABTCAFe$_3$O$_4$ as catalyst (5, 10, 15 mg). The results showed that 15 mg of SA-ABTCA-Fe$_3$O$_4$ at 80°C was the best condition (31).

Scheme 17: Synthesis of novel furan-2(5H)-one derivatives. Adapted from (31).
One-pot Multi-Constiuent Synthesis of Tetrahydrobenzo[b]pyran Using Heterogeneous Nanoparticle

The one-pot multi-component reaction of aldehydes, active methylene groups such as malononitrile, and dimedone in the presence of Fe₃O₄@SiO₂-imid-PM have been developed to synthesize various derivatives of tetrahydrobenzo[b]pyran and 3,4dihydropyrano[c]chromene under different conditions such as reflux in water, ultrasonic irradiations nanoparticles behave as a magnetic catalyst. Because of their magnetic property, these catalysts can quickly be recovered from the reaction mixture. H₂O, EtOH, MeOH, EtOAc, CHCl₃, and CH₃CN were used as solvents to complete the reaction using 20 mg Fe₃O₄@SiO₂-imid-PM. The data showed that the response went smoothly in refluxing H₂O, producing the desired product’s high yields. Under reflux, this multi-component condensation can also be achieved in solvents such as ethanol and methanol as they are protic solvents. These solvents yield 87% and 79% of desired product, respectively. However, this reaction can take more time and produce less yield of desired outcomes in the presence of aprotic solvents like CHCl₃, EtOAc, and CH₃CN (32).

Scheme 18: Synthesis of tetrahydrobenzo[b]pyran derivatives. Adapted from (32).

Synthesis of Benzo[b]furan and its Derivatives Using Green Nanocatalyst

Isocyanides, 2° amines, and 2-hydroxybenzaldehyde derivative form benzo[b]furan derivatives by utilizing silica NPs in a one-pot multi-component reaction (33). The best results and yield (95%) were obtained, when R₁=(1,3,3-tetramethylbutyl), R(Benzyl) X, (NO₂)

Scheme 19: Synthesis of benzo[b]furan derivatives. Adapted from (33).

Interpolation of CO₂ into Aryl Alkynes Followed by Allylic Chlorides using Nanocatalyst

Heterocyclic compounds were synthesized by utilizing catalyzed carbonylation cinnamyl chloride and the derivative of phenylacetylene in the presence of CO₂ gas. The reactions were done in the presence of DFNS/-CD/Au NPs. Approximately 98% of the product is obtained (34).
Porous CuO Catalyzed Green Synthesis of Some Novel 3-Alkylated Indoles

The green synthesis of some novel 3-alkylated indoles as active antitubercular agents was catalyzed by porous CuO. In 10 mL of water, a solution of indole (1 millimole), dimedone (1 millimole), and substituted aldehyde (1 millimole) were stirred at room temperature until the reaction was completed in the presence of 0.04 mmol mpCuO as a heterogeneous catalyst. The solid compound that resulted was filtered out and then treated with DMF. To recover mpCuO particles, the mixture was centrifuged for a long time at 2500 rpm. After that, the organic solution was poured into water, purified, and recrystallized from ethanol before being dried under a vacuum to obtain the pure product (35).

CONCLUSION

The most commonly used strategies and mechanistic descriptions of various nanoparticles and some nitrogen oxygen-containing heterocyclic compounds were discussed. The effect of solvent role in the reaction was investigated. From a mechanical standpoint, the catalyst's most notable characteristic is its ability to be reused up to three times or more without losing its efficacy. As a result, this catalyst outperforms other non-magnetic catalysts in several respects. Easy process, smoother reaction, adequate recovery, and reversibility of the nanocatalysts are appealing and exciting features of this procedure.

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