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Nano-catalyzed Synthetic Methods for Benzimidazoles

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Abstract: Benzimidazole derivatives being the nitrogen heterocycles showed diverse applications in medicinal, pharmaceutical, and agricultural fields. Recent studies have developed efficient, sustainable, and green synthetic routes. Recently, nano-catalyzed approaches have emerged as promising route for the expeditious synthesis of benzimidazoles. This review covers recent progress in metal oxide, magnetic, and hybrid nanocomposite as nanocatalyst-assisted synthesis. These methods achieve high yields, shorter reaction times, and less environmental impact. The review also highlights green chemistry approaches, such as solvent-free processes and non-toxic reagents. Overall, Nano catalytic methods offer an efficient and sustainable way to synthesize benzimidazole derivatives.

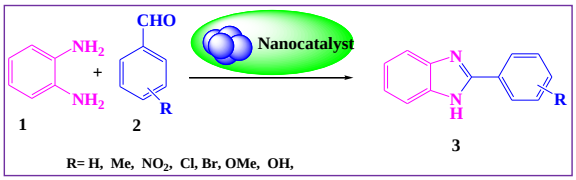
Keywords: heterocycles, benzimidazoles, green methods, nano-catalyst.

INTRODUCTION

THE advance literature has extensive reports for the synthesis of heterocyclic scaffolds using polymer-supported catalysts,[1] with nanocatalyst's receiving particular attention for their efficiency, stability, and eco-friendly application.[2] Benzimidazoles are bicyclic heteroaromatic organic molecules made of fused benzene with imidazole rings, joined at the 4 and 5 positions.[3,4] The first benzimidazole was synthesized by Hoebrecker in 1872 through the reduction of 2-nitro-*p*-acetotoluidide. Since then, numerous researchers have reported various approaches for the preparation of 1-substituted and 1, 2-disubstituted benzimidazoles under diverse reaction conditions, employing different functional groups. Typically, monosubstituted and disubstituted benz-imidazoles can be obtained by condensing 1,2-phenylenediamine with ketonic groups of aliphatic or aromatic aldehydes, benzylic alcohols, or benzyl amines, often in the presence of different nanocatalyst's to enhance efficiency and selectivity.[4,5] Although new methods offer improved yields, they are less effective with aldehydes bearing bulky substituents.[6]

Numerous synthetic strategies for benzimidazole and its derivatives have been documented in the scientific literature. Typically, *o*-phenylenediamine reacts with various carbonyl compounds through cyclo-condensation under different reaction conditions-varying in solvents, catalysts, and modes of activation to produce benzimidazoles.[7] In medicinal chemistry, benzimidazoles are important heterocyclic nuclei that are widely utilized. The benzimidazole moiety is a component of vitamin B_{12} and is structurally related to both the stimulant caffeine and the purine bases of DNA. Benzimidazoles also play a significant role in the healthcare sector. Several derivatives, including omeprazole, esomeprazole, pantoprazole, lansoprazole, and rabeprazole, are employed as active pharmaceutical ingredients.[8] Benzimidazole derivatives exhibit significant antiviral activity against a variety of viruses, such as HIV,[9] HSV-1,[10] influenza,[11] and HCMV.[12] Moreover, benzimidazole derivatives demonstrate several biological functions, like as anticancer agents.[13] antiulcer,[14] antihypertensive, antiviral, antitumor,[15] antibacterial, antifungal,[16] and anti-inflammatory.[17] Multicomponent reactions (MCRs) are essential in organic synthesis and provide an efficient means of generating

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Scheme 1. Nanocatalyst-assisted synthesis of benzimidazole derivatives.

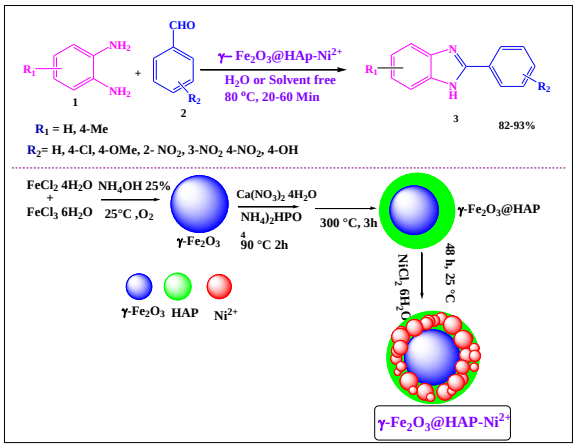
molecular complexity. Although several traditional methods for synthesizing benzimidazoles and their derivatives have been reported,[18] they often involve harsh conditions, low yields, lengthy work-up procedures, and multiple side reactions. To overcome these drawbacks, recent studies have developed cost-effective, safe, and environmentally friendly strategies for benzimidazole synthesis, particularly using a variety of nanocatalyst.[19] In the recent years, numerous reports were added to the scientific literature focused on polymers and nanocatalyst for the synthesis of benzimidazole derivatives.[18,20]

INORGANIC NANOCATALYST

Magnetic Nanocatalyst Synthesis of Benzimidazole Derivatives

Zolfigo Ali et al. (2012) reported a green, efficient, heterogeneous, and reusable catalytic system using magnetic Fe_3O_4 nanoparticles (Table 1, Entry 1) for synthesizing benzimidazoles from *o*-phenylenediamine and aromatic aldehydes in water under ambient air, achieving excellent yields of 85–97 %. Characterization of the nanocatalyst was performed by FTIR, XRD, TEM, and VSM. FTIR spectra showed a peak at 582 cm^{-1} corresponding to Fe-O-Fe stretching vibrations, and TEM images indicated an average nanoparticle diameter of ~9 nm. The method offers several advantages, including low cost, safety, simple catalyst recovery and reuse, no chemical waste, mild reaction conditions, high yields, rapid reactions, easy experimental setup, and compliance with green chemistry principles.[21]

Guoyi et al. (2014) developed a safe, one-pot synthesis of 2-benzimidazoles from 1,2-diaminobenzene and aldehydes in ethanol at room temperature using H_2O_2 and a magnetic Fe_3O_4@SiO_2@$(NH_4)_6Mo_7O_{24}$ (Table 1, Entry 2) catalyst, which could be easily recovered with an external magnet. While unsupported ammonium molybdate, no catalyst, or Fe_3O_4@SiO_2 gave low selectivity for 2-phenylbenzimidazole (11.6–18.3 %), the Fe_3O_4@SiO_2@$(NH_4)_6Mo_7O_{24}$ catalyst achieved 94 % selectivity within 30 minutes. TEM and HRTEM analyses revealed spherical nanoparticles of roughly 62 nm average size. The major advantages of this catalytic system include mild reaction

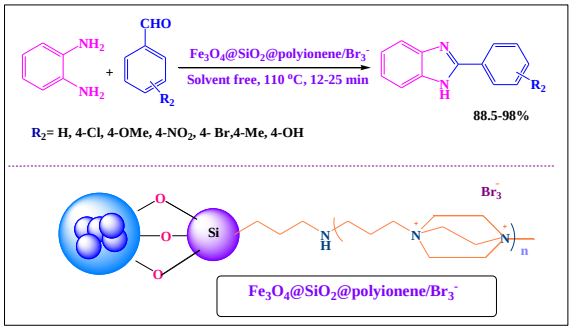


Scheme 2. Construction of benzimidazoles by used of nano γ-Fe_2O_3@HApNi^{2+} catalyst.

conditions (room temperature), the use of ethanol as a green solvent, a short reaction time, high catalytic efficiency and selectivity, facile magnetic separation, and excellent catalyst recyclability.[22]

Saaid Karimian et al. (2015) reported Ni^{2+} supported on hydroxyapatite-core@shell γ-Fe_2O_3 (Table 1, Entry 3) nanoparticles as a reusable catalyst for synthesizing benzimidazole (3) derivatives from *o*-phenylenediamine (1) and aromatic aldehyde (2) under solvent and solvent-free conditions. The catalyst was characterized by TEM, SEM, VSM, XRD and FT-IR techniques, which confirmed its structural features and magnetic properties. The method is characterized by many advantages such as high yields of product, short reaction times, easy magnetic separation, very good reusability and green chemistry compatibility (Scheme 2).[23]

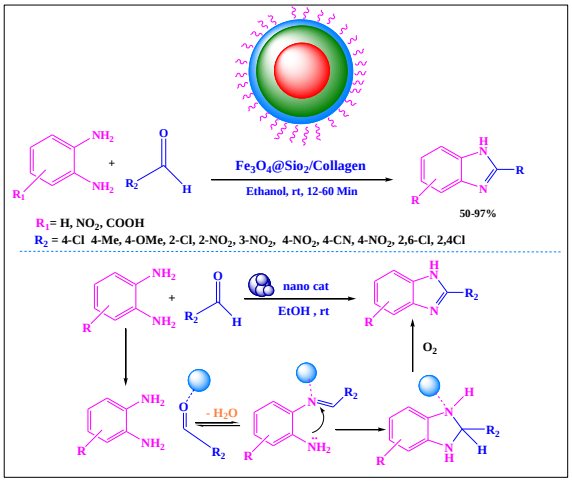
Elham et al. (2016) developed a green and efficient method for the synthesis of benzimidazole derivatives by condensation of o-phenylenediamine with different aryl aldehydes under solvent free conditions in the presence of Fe_3O_4@SiO_2@polyionene/Br_3^- (Table 1, Entry 4) magnetic nanoparticles as a reusable heterogeneous catalyst. The protocol gave the target benzimidazole derivatives in excellent yields in a short time of 12–25 min, which is indicative of high catalytic activity of the magnetic nanocatalyst. The solvent-free reaction conditions minimized the use of hazardous solvents and were in a good accordance with the principles of sustainable and environmentally friendly synthesis. Also, the catalyst was easily separated from the reaction mixture by magnetic separation which avoids tedious filtration steps and simplifies the isolation of the product. The recovered catalyst showed excellent reusability and operational stability and maintained its catalytic performance over several reaction cycles (Scheme 3).[24]



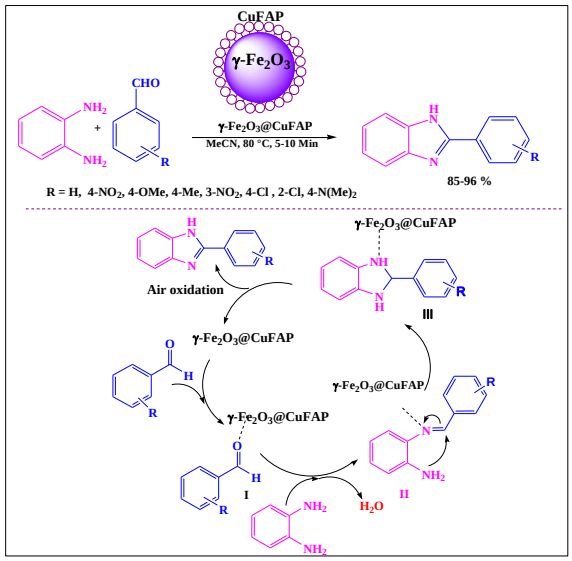
Scheme 3. Preparation of benzimidazoles catalyzed by Fe_3O_4@SiO_2@polyionene/Br_3– MNPs.

Ghafuri et al. (2016) reported Fe_3O_4@SiO_2/collagen (Table 1, Entry 5) as an efficient and environmentally benign magnetic nanocatalyst for the synthesis of benzimidazole derivatives via the condensation of *o*-phenylenediamine with various aryl aldehydes. The protocol was carried out under mild reaction conditions giving the desired products in excellent yields in short reaction times. SEM analysis revealed that the spherical core-shell had a uniform morphology with particle sizes mostly in the range of 26-53 nm, with a Fe_3O_4 core (16–25 nm) uniformly covered by a SiO_2/collagen shell (9–14 nm). The catalyst showed high catalytic efficiency, simple product isolation, easy magnetic separation and good recyclability, making the process operationally simple and cost-effective. The sustainability of this approach is also due to the use of a collagen-coated magnetic support, through the improved stability of the catalyst (Scheme 4).[25]

Mirfarjood et al. (2017) that established a green and effective technique for synthesizing aryl-substituted benzimidazoles by reacting *o*-phenylenediamine with aromatic aldehydes using γ-Fe_2O_3@CuFAP magnetic



Scheme 4. The proposed paths for the synthesis of benzimidazole derivatives using Fe_3O_4@SiO_2/collagen.

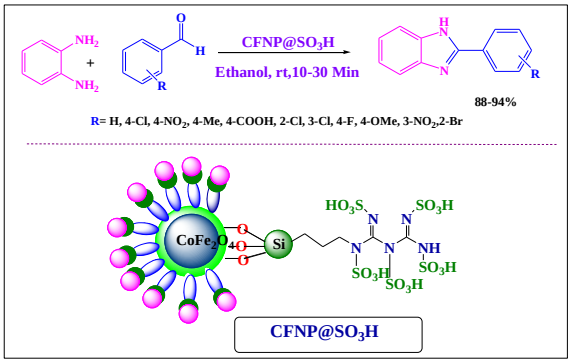


Scheme 5. Proposed mechanism for the γ-Fe_2O_3@CuFAp-catalyzed synthesis of benzimidazole derivatives.

nanoparticles (MNPs) (Table 1, Entry 6) in acetonitrile at 80°C. The catalyst was analysed by TEM, SEM, ICP, XRD, FT-IR, and other methods. TEM images showed that the nanoparticles had an average size of 60nm and were spherical in morphology, which was also confirmed by SEM. The copper content was 0.28 mmol Cu per gram of γ-Fe_2O_3@CuFAP as determined by ICP-AES analysis. The γ-Fe_2O_3@CuFAp catalyst showed excellent reusability and retained catalytic activity for twelve consecutive cycles with no significant loss of efficiency. The catalyst was recovered after each run, washed with CH_2Cl_2, dried at room temperature and properly reused (Scheme 5).[26]

Kommula et al. (2017) demonstrated an efficient use of a nano-Fe_2O_3 catalyst (Table 1, Entry 7) for synthesizing benzimidazoles from 1, 2-diaminobenzenes and substituted benzaldehyde. The procedure offers several advantages, including the use of an aqueous medium, short reaction times, high yields, and catalyst recyclability. This sustainable approach avoids toxic, moisture-sensitive, or hazardous reagents, employs mild reaction conditions, and utilizes an economical and readily available catalyst. The nano-Fe_2O_3 catalyst maintained its activity over four consecutive recycling and reuse cycles.[27]

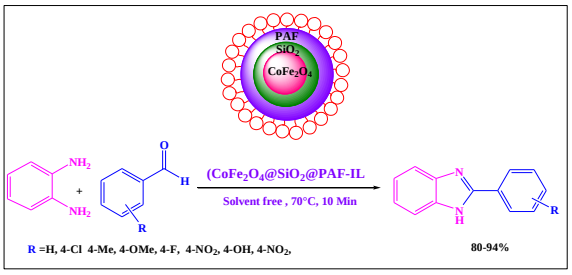
Shojaee Sara et al. (2018) synthesized benzimidazole derivatives from *o*-phenylenediamine and 4-chlorobenzaldehyde using Wt-Fe_2O_4 magnetic nanoparticles (MNPs) as a catalyst (Table 1, Entry 8) in acetonitrile under reflux at 80 °C, achieving high yields within brief reaction periods. After the reaction, the catalyst was easily recovered with a magnet, and the product was purified by recrystallization. The Wt-Fe_3O_4 MNPs were cleaned with ethanol and reused up to four times, maintaining yields of up to 95 %.[28]



Scheme 6. Magnetic cobalt ferrite nanoparticles fabricated with sulfonic acid used for synthesis of benzimidazole compounds.

Yadav and collaborators (2021) utilized a sulfonic acid functionalized cobalt ferrite magnetic nanocatalyst CFNP@SO_3H (Table 1, Entry 9) for green and facile synthesis of benzimidazoles. The catalyst was highly efficient under mild reaction conditions, gave good yields and had a broad substrate scope. The magnetic recovery of the catalyst with maintained activity for several cycles was found to be remarkable. On the negative side, the study could be enhanced with more mechanistic details (e.g. nature of active site, rate-limiting step) and quantitative comparisons (TON/TOF) with existing catalysts. Overall, it is a significant step further in sustainable benzimidazole synthesis (Scheme 6).[29]

Bodaghifard and his team (2021) of researchers presented the synthesis, characterization, and function of an innovative ionic liquid–silica-coated cobalt-ferrite nanocomposite, $CoFe_2O_4$@SiO_2@PAF-IL (Table 1, Entry 10), (PAF-IL) porous aromatic framework ionic liquid as a hybrid catalyst for the solvent-free multicomponent reaction of *o*-phenylenediamine with benzaldehyde to produce benzimidazole derivatives. The hybrid nanocatalyst was prepared by sonication it with K_2CO_3 and MeI in DMF for ten minutes. This method offered high to excellent yields, rapid reactions, and environmentally friendly conditions, no solvent use, and easy work-up. The catalyst was reused six times with little loss (Scheme 7).[30]



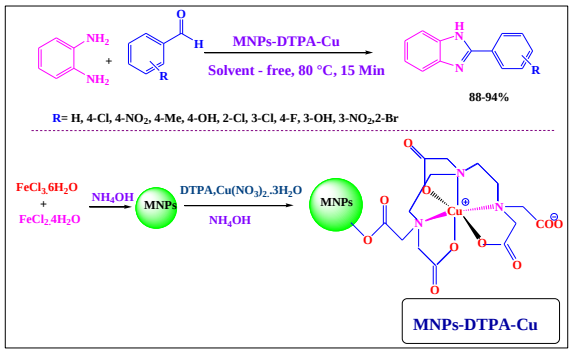
Scheme 7. Preparation of benzimidazole utilizing $CoFe_2O_4$@SiO_2@PAF-IL catalyst.

R. Mohammadi et al. (2022) synthesized various benzimidazoles using o-phenylenediamine and benzaldehyde using $CuFe_2O_4$ nano-catalyst (Table 1, Entry 11) in water under reflux for 25 minutes, achieving an excellent yield of 96 %. The catalyst was easily recovered magnetically and reused with minimal activity loss. Notable advantages of this approach include thermal stability, ease of preparation and separation, heterogeneous nature, excellent catalytic performance, high yield, easy and simple work up.[31]

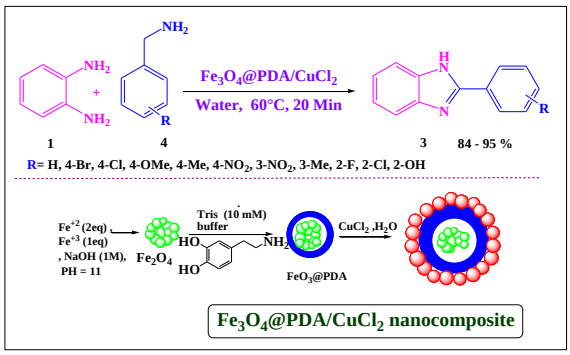
Shinde et al. (2022) developed a simple, magnetically separable Ag@Fe_2O_3 core–shell nanocatalyst using a sol–gel method (Table 1, Entry 12). This catalyst efficiently promoted the one-pot production of benzimidazoles using *o*-phenylenediamine and aryl aldehydes under ambient conditions. The process offered high yields, green conditions, easy set-up, and outstanding ability for reusing, with the catalyst retaining its activity over multiple cycles. TEM analysis revealed an average crystallite size of 73.7 nm, while HRTEM confirmed nearly spherical core–shell nanoparticles with a Fe_2O_3 shell of 5–5.5 nm encasing a ~80 nm Ag core. EDS mapping further validated the distinct Fe_2O_3 shell structure.[32]

Moghanian et al. (2023) introduced a novel magnetically heterogeneous nanocatalyst, MNPs-DTPA-Cu (Table 1, Entry 13), consisting of Fe_3O_4 nanoparticles functionalized with a copper complex of diethylenetriaminepentaacetic acid (DTPA). This catalyst efficiently promoted solvent-free, single pot condensation of aldehydes with 1,2-phenylenediamine affording benzimidazole derivatives in better yields of up to 96 %. FE-SEM analysis revealed nearly spherical nanoparticles under 75 nm in size. The system offered notable benefits, including shorter reaction times, mild conditions, simplicity, and non-toxicity. Furthermore, the catalyst can be magnetically separated and reused up to six times without any significant loss in activity (Scheme 8).[33]

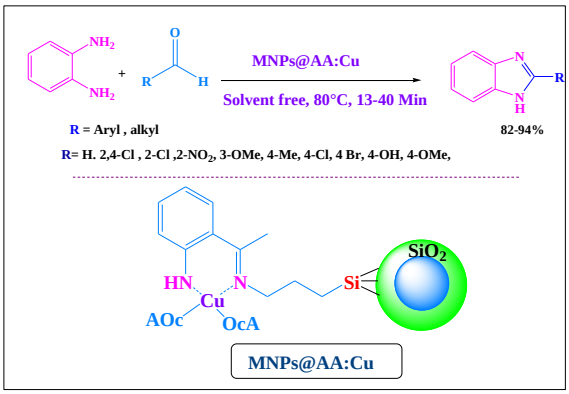
Mehran et al. (2023) developed Fe_3O_4@PDA/$CuCl_2$ magnetite dopamine-supported copper nanoparticles (Table 1, and Entry 14) as an efficient heterogeneous catalyst for the one-pot synthesis of 2-substituted



Scheme 8. Preparation of benzimidazole derivatives using nano MNPs-DTPA-Cu nanoparticles.



Scheme 9. Synthesize of benzimidazole used for Fe_3O_4 @PDA/$CuCl_2$ nanoparticle.



Scheme 10. Synthesis of 2-substitutedbenzimidazole derivatives by using MNPs@AA : Cu.

benzimidazoles (3) from *o*-phenylenediamine (1) and benzyl amine (4). Heterogeneous copper catalysts, being cost-effective and sustainable, are considered highly promising for catalytic applications. The Fe_3O_4@PDA/$CuCl_2$ nanocatalyst offers several advantages, including excellent selectivity, rapid reaction rates, non-toxicity, and recyclability. It can be magnetically separated and reused for five cycles without efficiency loss. The nanocomposite was synthesized through a simple three-step procedure, ensuring both practicality and sustainability (Scheme 9).[34]

Balali et al. (2025) reported an efficient and sustainable protocol for the synthesis of benzimidazole derivatives via the condensation of *o*-phenylenediamine with a variety of substituted aromatic aldehydes using the MNPs@AA : Cu nanocatalyst (Table 1, Entry 15) under solvent-free conditions at 80 °C. The catalytic system afforded the desired benzimidazoles in excellent yields (82–96 %) within short reaction times using a low catalyst loading, without the formation of undesirable imine intermediates. The catalyst exhibited broad substrate compatibility, as both electron-donating and electron-withdrawing aromatic aldehydes provided high yields with minimal influence of substituent effects on reaction efficiency. In addition, heterocyclic aldehydes, including thiophene-2-carbaldehyde, furan-2-carbaldehyde, and pyridine-2-carbaldehyde, were successfully converted into the corresponding benzimidazole derivatives in good yields (83–91 %). The magnetic nanocatalyst also demonstrated excellent catalytic activity, facile magnetic separation, high stability, and reusability for up to six consecutive cycles without significant loss of activity, as confirmed by the nearly identical FT-IR spectra of the fresh and recycled catalyst (Scheme 10).[35]

Zizhao et al. (2025) reported a novel Fe_3O_4/WO_3 heterojunction catalyst (Table 1, Entry 16), synthesized using plantain peel extract, for the single-pot creation of products of benzimidazole using ethanol at 65 °C and 1,2-phenylenediamine with substituted aryl aldehydes. The catalyst achieved excellent yields, up to 98 % under optimal conditions, with aldehydes containing electron-withdrawing groups performing better than those with electron-donating substituents. SEM analysis revealed uniform nanoparticles (~75 nm) with semi-elliptical morphology. Compared to Fe_3O_4 and WO_3 individually, the composite catalyst showed superior efficiency, operating under mild, eco-friendly conditions, and remained reusable for five cycles without significant loss of activity, making it both cost-effective and sustainable.[36]

The nanocatalysts discussed for benzimidazole synthesis exhibit significant improvements in catalytic efficiency, green chemistry, and recyclability compared with conventional catalysts. Most of the reported systems, including Fe_3O_4, Fe_3O_4@SiO_2@$(NH_4)_6Mo_7O_{24}$, γ-Fe_2O_3@HAp-Ni^{2+}, Fe_3O_4@SiO_2/collagen, $CuFe_2O_4$, MNPs-DTPA-Cu, Fe_3O_4@PDA/$CuCl_2$, and MNPs@AA, are magnetically recoverable, enabling rapid catalyst separation and reuse while minimizing waste. Functionalized magnetic nanocatalysts generally outperform simple metal oxides by providing higher yields, shorter reaction times, broader substrate compatibility, and enhanced stability. Among them, γ-Fe_2O_3@CuFAp exhibits exceptional durability, retaining its catalytic activity for twelve recycling cycles, whereas Ag@Fe_2O_3 and CFNP@SO_3H offer excellent catalytic performance under mild or ambient conditions. Green reaction media such as water, ethanol, and solvent-free conditions are frequently employed, demonstrating strong adherence to sustainable chemistry principles. However, several catalysts require multistep synthesis, specialized functionalization, or elevated temperatures, increasing preparation cost and complexity. In addition, some systems are limited mainly to aromatic substrates or have relatively short recycling lifetimes. Overall, magnetic heterogeneous nanocatalysts provide an excellent balance of catalytic activity, environmental sustainability, and operational simplicity, making them highly promising for the efficient synthesis of benzimidazole derivatives.

Table 1. Magnetic nano-catalysts' employed synthesis of benzimidazole derivatives (rt = room temperature).

Entry	Catalyst	Solvent	Energy medium	*t* / °C	Time/ min	Substituents on Aldehyde/ Benzyl amine/Benzyl alcohol	Yields/ %
1.	Nano Fe_3O_4[21] Pros: Aqueous medium Cons: High temperature	H_2O	heat	85	30–100	H, 2-Cl, 3-Cl, 4-Cl +12 derivatives	85–97
2.	Fe_3O_4@SiO_2@ $(NH_4)_6Mo_7O_{24}$[22] Pros: High catalytic activity at rt Cons: Hydrogen peroxide is required	Ethanol	–	rt	30–65	H, 4-Cl, 3-Cl, 2-Cl +4 derivatives	87.3–95.2
3.	γ-Fe_2O_3@HAp Ni^{2+}[23] Pros: Both solvent-free and aqueous conditions Cons: Multistep preparation of catalyst	Water	heat	80	20–60	H, 4-Cl, 2-Cl,4-Me + 7 derivatives	82–95
4.	Fe_3O_4@SiO_2@polyionene/Br_3^-[24] Pros: Simple work-up Cons: Electron-withdrawing substituted aldehydes	–	heat	110	12–90	H, 4-OMe, 2-Cl, 4-Me, 4-Cl+3 derivatives	67–98
5.	Fe_3O_4@SiO_2/collagen[25] Pros: Green and mild reaction conditions, using ethanol Cons: Hydrothermal treatment, and drying	Ethanol	–	rt	12–60	4-NO_2, 4-CN, 4-Cl, 4-OMe +11 derivatives	50–97
6.	γ-Fe_2O_3@CuFAp MNPs[26] Pros: Outstanding reusability at least 12 consecutive cycles Cons: Requires acetonitrile	Acetonitrile	heat	80	5–10	H,3-NO_2, 4-Cl, 2-Me +11 derivatives	85–96
7.	Nano Fe_2O_3[27] Pros: Inexpensive, and suitable for green chemistry applications Cons: Lower yields	Water	reflux	80	120	H,4-NO_2,4-Cl, 4-OMe, + 4 derivatives	70–84
8.	WtFe$_3$O$_4$MNPs[28] Pros: Green synthesis: prepared using white tea (Camellia sinensis) Cons: Uses acetonitrile as solvent	Acetonitrile	heat	80	120	4-Cl Only one derivative	96
9.	CFNP@SO_3H[29] Pros: High catalytic efficiency Cons: Uses chlorosulfonic acid	Ethanol	-	rt	10–30	H,4-Br, 4-Cl, 4-Me, 4-COOH, 4-F + 14 derivatives	78–98
10.	$CoFe_2O_4$@SiO_2@PAF-IL[30] Pros: Short reaction time Cons: Used methyl iodide (MeI) and DMF	Solvent free	heat	70	10	H,4-Me, 4-OMe, 4-Cl, 4-F, 4-NO_2 + 5 derivatives	80–94
11.	$CuFe_2O_4$NPs[31] Pros: Thermally stable Cons: Requires reflux heating in water	Water	heat	reflux	25–60	4-NO_2, 4-Me, 4-Cl, 4-CN +5 derivatives	86–96
12.	Ag@Fe_2O_3 [32] Pros: rt reaction proceed Cons: Silver (Ag), a noble metal that increases catalyst cost compared	Ethanol	-	rt	7–22	H, 4-OH,4-Cl, 4Me +9 derivatives	80–98
13.	MMPs-DTPA-Cu[33] Pros: Broad substrate scope Cons: Potential copper leaching	n-Hexane	heat	80	12–40	H, 4-Me, 2-Br, 4-F, 4-OH +17 derivatives	83–96
14.	Fe_3O_4@PDA/$CuCl_2$[34] Pros: Green reaction used water Cons: Reaction is oxygen-dependent	Water	heat	40	20	4-NO_2, 4-OH, 2-Cl, 4-OMe +16 derivatives	69–95
15.	MNPs@AA:Cu[35] Pros: Negligible copper leaching Cons: Multistep catalyst synthesis	-	heat	80	13–120	H, 4-NO_2, 4-OH, 4-Br, 4-OMe +20 derivatives	13–96
16.	Fe_3O_4/WO_3[36] Pros: Green synthesis used plantain peel extract for catalyst preparation Cons: Catalyst preparation is complex	Ethanol	heat	65	50–100	H,4-Br, 4-OH +8 derivatives	97–98

Non-Magnetic Nanocatalyst-Mediated Synthesis of Benzimidazole Derivatives

Rathod et al. (2011) revealed an efficient and sustainable technique for the synthesis of benzimidazole derivatives through solvent free condensation of aromatic aldehydes with o-phenylenediamine using MoO_3/CeO_2-ZrO_2 (Table 2, Entry 1) as heterogeneous nano catalyst. The catalyst was characterized by XRD, EDS, IR and SEM analyses. The successful formation of nanoparticles was confirmed with an average size of 33.17 nm for the 20 % MoO_3 /CeO_2 -ZrO_2 catalyst. This methodology has several advantages that include very short reaction time (3–5 min), solvent free conditions, cheap and easily available starting materials, high purity of products and recyclability of catalyst for up to three successive cycles without significant loss of catalytic activity.[37]

Hajihakimi Mohammad and team (2013) employed Nano scale sulphated zirconia (SO_4^{2-}-ZrO_2) (Table 2, Entry 2) as a heterogeneous catalyst for the condensation of *o*-phenylenediamine with aromatic aldehydes in ethanol as a green reaction medium and obtained benzimidazole derivatives in excellent yields. The catalyst was characterized by XRD, FT-IR, and SEM analyses. Features high catalytic activity, ethanol as a green solvent, mild reaction conditions and easy recycling and reuse from the catalyst and drawbacks the multiple washings with ethanol in catalyst recovery result in excess amount of solvent usage and treatment time required.[38]

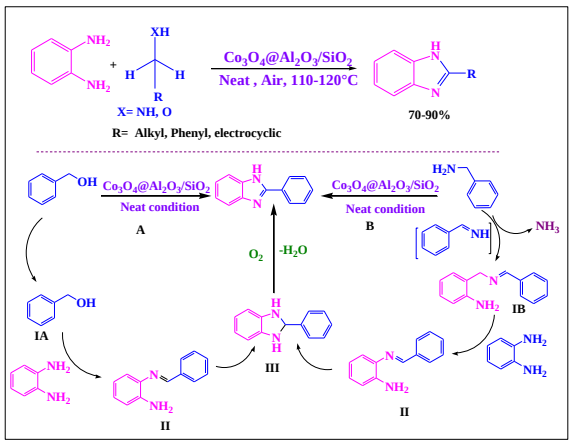
The study by Sharma et al. (2014) used recyclable ZnO nanoparticles to create benzimidazole derivatives in a sustainable, solvent-free manner (Table 2, Entry 3) via ball milling. As demonstrated by a low E-factor and high ecoscale score, this mechanochemical technique delivers excellent efficiency, even on a multi-gram scale, with simple product isolation and no environmental impact. The advantages of this method are solvent free reaction conditions, high catalytic efficiency, easy product isolation, catalyst recyclability and less environmental impact thus this method is a sustainable green protocol.[39]

Wade Anil and co-workers (2015) reported a visible-light-responsive CdSe/MMT nanocomposite (Table 2, Entry 4) for the synthesis of 2-substituted benzimidazoles from *o*-phenylenediamine and aliphatic or aromatic aldehydes in ethanol at ambient temperature, achieving up to 68-94% conversion**.** The catalyst promoted imine formation followed by photocyclization and remained active for four consecutive recycling cycles. The CdSe-MMT nanocomposite facilitated condensation to form an imine intermediate, which underwent photocyclization on the catalytic surface. The advantages of this catalyst are mild reaction conditions, use of ethanol as green solvent and high catalytic efficiency. However, its use in daily life is limited by the toxicity of cadmium, the need for visible-light irradiation, and relatively limited recyclability.[40]

Naeimi et al. (2016) reported aqueous ethanol mediated ultrasonicated method for preparations of 2-substituted benzimidazoles using MnO_2 nanoparticles (Table 2, Entry 5). The method gave high yields of the desired compounds. The catalyst was characterized by SEM and FTIR spectra recorded feature absorption at 527 cm^{-1}, attributed to Mn-O stretching vibrations within the MnO_6 hexagonal framework. The protocol afforded high yields under mild conditions. Its advantages include the use of an aqueous ethanol medium, a low-cost MnO_2 catalyst, rapid reaction, operational simplicity, and high catalytic efficiency.[41]

Rajabi et al. (2015) disclosed an efficient solvent-free method for the synthesis of benzimidazole derivatives by oxidative condensation of aromatic aldehydes with o-phenylenediamine using SBA-15 supported cobalt(II) nanocatalyst (Table 2, Entry 6). The mesoporous structure of SBA-15 provided good accessibility of the substrates and resulted in high catalytic activity. The protocol offers several advantages such as solvent-free reaction conditions, excellent catalyst reusability up to seven cycles without significant loss of activity and good alignment with the principles of green chemistry. However, the use of cobalt, a potentially toxic transition metal, and the need for catalyst preparation and immobilization on SBA-15, may add to the overall cost and complexity of the technique.[42]

Reddy and colleagues (2017) characterized Co_3O_4@Al_2O_3/SiO_2 (Table 2, Entry 7) as an efficient heterogeneous nanocatalyst used for the synthesis of benzimidazole derivatives through oxidative coupling of primary amines or benzyl alcohols with o-phenylenediamine. HR-TEM analysis revealed spherical nanoparticles with sizes of 2.0–3.5 nm, distributed uniformly. The catalyst showed high catalytic efficiency, broad substrate scope, good product yields and excellent recyclability for up to six successive cycle's minimal loss of



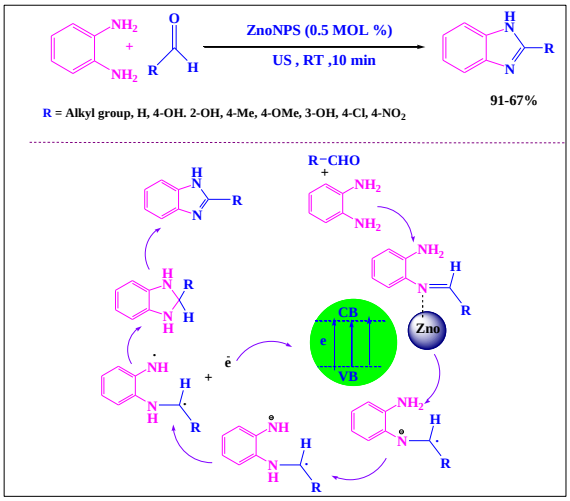
Scheme 11. Mechanism of Co_3O_4@Al_2O_3/SiO_2-catalyzed oxidative synthesis of 2-substituted benzimidazoles.

activity. However, catalyst recovery was performed by centrifugation, not magnetic separation. Sterically hindered ortho-substituted benzyl alcohols were less reactive, producing lower yields (Scheme 11).[43]

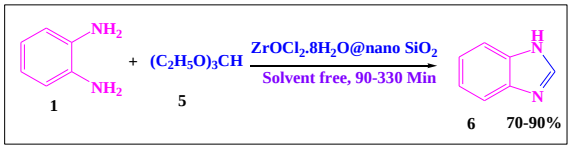
Mohammadi et al. (2017) reported one-pot synthesis of benzimidazoles from 1,2-diaminobenzenes and aryl aldehydes in the absence of solvent using BiOCl/FeOCl/SiO_2 nanocomposite catalyst (Table 2, Entry 8) at 70 °C to give excellent yields within 17 min. TEM and SEM analysis showed the formation of rod like crystalline structures with particle size of 10 to 15 nm. The catalyst has numerous benefits like fast reaction, high yields, solvent free condition, mild operating temperature, low cost and easy handling.[44]

Paul et al. (2017) synthesized benzimidazole derivatives using green synthesized ZnO nanoparticles (Table 2, Entry 9) by reaction of o-phenylenediamine with aromatic aldehydes under ultrasonic irradiation. Parkia roxburghii seed extract leading to stable hexagonal nanoparticles. The ZnO nanoparticles were synthesized by a simple and eco-friendly single-pot method using. The protocol provided good yields under mild conditions and showed catalyst recyclability. Advantages include synthesis of green catalysts, simple reactions, beneficial catalytic efficiency and catalyst reusability (Scheme 12).[45]

Sheikh et al. (2018) reported an environment friendly method to synthesize CuO nanoparticles using aqueous lemon juice. The CuO nanoparticles (Table 2, Entry 10) were used in the synthesis of 2-arylbenzimidazoles via solvent-free cyclocondensation of 1,2-diaminobenzene with aldehydes at 80 °C for 20–90 min in 76–97 % yields. FE-SEM images with high resolution revealed uniform, Nano sized CuO particles of ~100 nm. The catalyst was found to be highly efficient and could be reused for up to eight cycles with little loss of activity.[46]



Scheme 12. Mechanistic pathway for ZnO nanocomposite catalyzed preparation of benzimidazole derivatives.



Scheme 13. Synthesis of benzimidazole by utilization of $ZrOCl_2{\cdot}8H_2O$@nanoSiO_2.

The Nikoofar et al. (2018) studied $ZrOCl_2.8H_2O$@nanoSiO_2 as a catalyst for the synthesis of benzimidazole derivatives (6). This catalyst was used to obtain compounds by a one-pot reaction of orthoesters (5) with *o*-phenylenediamine (1) in a solvent-free system at 60°C (Table 2, Entry 11). The SEM analysis showed the average size of the nanoparticles was 30–40 nm, which was slightly higher than that for commercial nano SiO_2 (20–30 nm). The method has several advantages including solvent free condition, operational simplicity, low cost, safe reaction conditions and reusability of the catalyst for four consecutive cycles without significant loss of activity (Scheme 13).[47]

Wang et al. (2019) reported an efficient and environmentally friendly method for the synthesis of benzimidazole derivatives via the direct condensation of *o*-phenylenediamine with various aldehydes using CoOx@NC-800 (Table 2, Entry 12). The protocol afforded excellent yields and demonstrated good catalytic activity, stability, and recyclability. Its advantages include high catalytic efficiency, additive- and oxidant-free reaction conditions, broad substrate applicability, and an environmentally benign, cost-effective synthetic approach.[48]

Tzani et al. (2020) reported gold nanoparticles-AuNPs, (Table 2, Entry 13) as catalysts for the selective synthesis of 2-substituted benzimidazoles. Among various gold nanoparticle platforms, the Au/TiO_2 system efficiently produced 2-aryl and 2-alkyl benzimidazoles at room temperature without additives, using chloroform: methanol (3 : 1) solvent mixture. This heterogeneous method requires no external oxidants or additives, accommodates a wide substrate scope, and provides a practical approach for C–N bond formation with mild circumstances. The AuNPs measured 4.4–9.4 nm and retained high activity over five cycles with minimal loss. The procedure has a few advantages, including mild reaction conditions, broad substrate scope, good catalytic efficiency and recyclability.[49]

In 2021, Rao et al. reported work a mixture of *o*-phenylenediamine and the corresponding aryl aldehyde in dry ethanol was treated with nano-ZrO_2 (Table 2, Entry 14) and stirred at 60 °C and best yield was achieved. The study reports an effective and eco-friendly method for the synthesis of benzimidazole derivatives using reusable nano-zirconia (Nano-ZrO_2) as a catalyst. The protocol offers benefit such as minimal reaction conditions, superb yields,

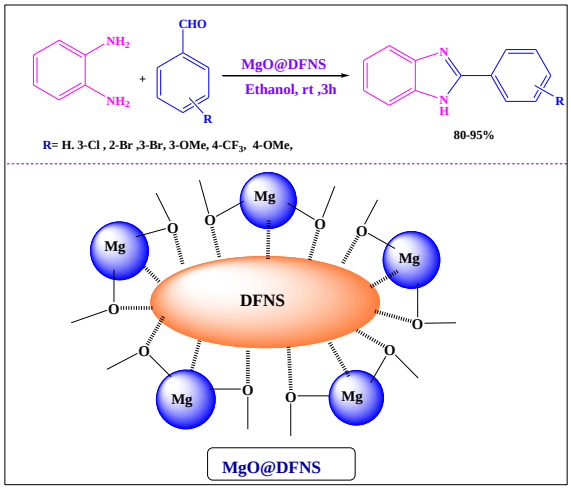
eases workup, and catalyst recyclability. Furthermore, the synthesized benzimidazole compounds were evaluated for their biological activities and exhibited promising antifungal and antibacterial properties. These results demonstrate the potential of benzimidazole derivatives as useful options for the development of antibacterial drugs and nano-zirconia as a sustainable catalyst.[50]

Mahalingam et al. (2022) introduced a (Zn-BNT) Zinc-loaded bentonite catalyst (Table 2, Entry 15) for the synthesis of benzimidazole analogues via the condensation of 1,2-phenylenediamine with various aldehydes in acetonitrile under microwave irradiation at 140 °C. The method provided excellent yields, ranging from 82 % to 97 %. The catalyst was thoroughly analyzed by SEM, XRD, EDX, FT-IR DSC-TGA, and BET analyses. SEM images revealed rod-like zinc particles with a width of about 16 nm and lengths of 50–150 nm, displaying a long, needle-like morphology. Compared to other systems, Zn-BNT showed superior catalytic activity and may be utilized again up to eight times with even a minor loss of efficiency. Key advantages of this approach include environmentally friendly circumstances, ease of use, wide range of substrates, and excellent yields easy product isolation, and catalyst recyclability.[51]

Valvi et al. (2023) reported to making of benzimidazoles by condensing aromatic aldehydes and o-phenylenediamine under sonication by utilizing of zinc sulfide nanoparticles (Table 2, Entry 16). The method proved efficient for producing benzimidazoles and their derivatives, offering advantages such as solvent-free conditions, short reaction times, mild processes, easy work-up, catalyst reusability, and the use of plant waste stems as a resource. XRD analysis confirmed that the ZnS nanoparticles exhibited a cubic zinc blende crystalline structure, while SEM revealed well-defined grains composed of ZnS crystallites.[52]

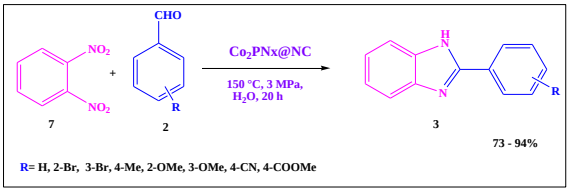
Britto (2023) reported a green and sustainable strategy for the synthesis of 2-aryl benzimidazole derivatives using nanocrystalline $ZnAl_2O_4$ (Table 2, Entry 17) prepared via a plant-mediated route using Cymbopogon citratus (lemongrass) extract as a capping and stabilizing agent. The catalyst was found to be very efficient for the condensation of *o*-phenylenediamine with aromatic aldehydes in ethanol at room temperature to give benzimidazole derivatives in high yields (88–94 %) in only 10 min. The formation of crystalline $ZnAl_2O_4$ nanoparticles having sizes in the range of 1–11 nm was confirmed by XRD, FT-IR, SEM, EDX and UV-DRS techniques. Moreover, the catalyst maintained the catalytic activity after recycling, which showed the good stability, reusability and prospect for green synthesis of benzimidazoles.[53]

Kusuma et al. (2023) developed a green and efficient method for synthesizing benzimidazoles by condensing *o*-phenylenediamine with aromatic aldehydes using MgO-supported dendritic fibrous nano-silica MgO@DFNS as a catalyst (Table 2, Entry 18). Under mild reaction conditions, MgO@DFNS achieved 100 % conversion, 90 % selectivity, and 90 % yield. The method proved versatile with aryl and aliphatic aldehydes, offering advantages such as environmental safety, simple work-up and rapid recovery, and reusability for six cycles without loss of activity or morphological changes (Scheme 14).[54]



Scheme 14. By using nano MgO@DFNS catalyst for synthesis of benzimidazoles.

Luis et al. (2024) disclosed the in aqueous medium formation of benzimidazoles (3) using a non-noble metal catalyst (Table 2, Entry 19). The reaction was conducted by reductively combining aromatic aldehydes (2) with *o*-dinitrobenzene (7) in water at 150 °C for 20 hours. The study showed that the preparation of supported heteroatom-doped Co nanoparticles required both phosphorus and nitrogen ligands to achieve the desired benzimidazoles. The $Co_2PNx@NC$ catalyst showed an excellent catalytic activity and could be successfully recycled five repeated reaction cycles with high product yields. The major advantages of this strategy are water as a green solvent, replacement of noble metal catalysts by a cobalt-based catalyst, high product yields, excellent catalyst recyclability and an environmentally benign catalytic system. However, this method has several

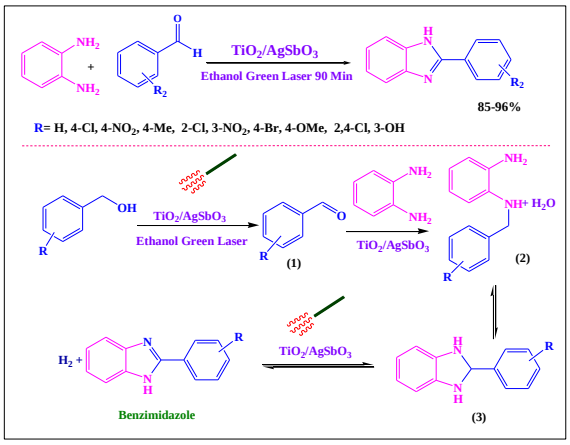


Scheme 15. Manufacture of benzimidazole by using $Co_2PNx@NC$.

drawbacks. The reaction requires a relatively high temperature (150 °C) and a long reaction time (20 h), which increases energy consumption and makes the process time-consuming (Scheme 15).[55]

Abdi et al. (2025) reported a multicomponent reaction of benzyl alcohols (4) with o-phenylenediamine (1) under photocatalytic conditions using $TiO_2/AgSbO_3$ nanoparticles in ethanol with a 25 W light source, yielding substituted benzimidazoles (3) in 96 % (Table 2, Entry 20). Alternative solvents afforded lower yields (61 % in a green solvent and 55 % in toluene). The catalyst, consisting of uniform and nearly spherical nanoparticles, was thoroughly characterized using DRS, FT-IR, XRD, EDX, and FE-SEM techniques, confirming its structural and morphological properties. The most significant advantages of this photocatalytic system are high catalytic efficiency, excellent product yields, and mild reaction conditions, use of ethanol as an environmentally friendly solvent, non-toxicity, cost-effective and good recyclability of the catalyst. Visible-light-driven photo catalysis is an energy-efficient and sustainable approach compared with the conventional thermal methods. Disadvantage the reaction needs an external light source, which can complicate scale-up because of issues of uniform exposure to light and consistent irradiation requirements in larger reactors (Scheme 16).[56]

Kadam et al. (2025) presented a new technique for creating compounds with benzimidazole from *o*-phenylenediamine and aryl aldehydes utilizing $Zn_{0.5}Cu_{0.5}Al_2O_4$ nanoparticles as the catalyst (Table 2, Entry 21) in water at room temperature and atmospheric pressure. The catalyst, made of copper-substituted zinc aluminate magnetic nanoparticles, was prepared through a sol-gel method and characterized using various spectroscopic techniques. The major advantages of this catalytic system include the use of water as a green reaction medium, mild



Scheme 16. Synthesis of benzimidazole by using $TiO_2/AgSbO_3$.

reaction conditions, high catalytic efficiency, magnetic recoverability, simple catalyst separation, and good recyclability. The magnetic nature of $Zn_{0.5}Cu_{0.5}Al_2O_4$ nanoparticles enables easy recovery using an external magnet, reducing catalyst loss and waste generation. However, the sol-gel preparation method involves multiple steps and controlled conditions, which may increase the complexity of large-scale catalyst production.[57]

Venkatesan et al. reported (2026) that the oxidative condensation of substituted o-phenylenediamine with benzaldehyde employing the nano catalyst α-$MnMoO_4$ (Table 2, Entry 22) in ethanol at 60 °C yields a good yield of 2-substituted benzimidazoles. Most of the solvents assessed (DMF, DMSO, EtOH), ACN, H_2O and ethanol was shown to be the most effective solvent. Hydrogen peroxide (H_2O_2) served as the oxidant; however, operations carried out in its absence yielded very little of the outcome. The nanoparticle's durability, reuse, and visibility significantly increased their suitability for practical application in wastewater treatment and environmentally friendly fine-chemical production. Future studies may enhance the benefits of α-$MnMoO_4$-based nanocatalysts as low-cost, environmentally benign, and versatile materials for various applications in sustainable chemical chemistry and sustainability.

The key advantages of the present catalytic system are the use of ethanol as a relatively green solvent, efficient oxidative conversion, good catalytic activity, and stability of the nanoparticles and reusability of the catalyst. The α-$MnMoO_4$ nanocatalyst provides an economical and eco-friendly pathway for the synthesis of benzimidazole. However, this method also has some drawbacks. The reaction needs the presence of an external oxidant (H_2O_2) which increases the number of components in the reaction and can lead to the formation of additional waste.[58]

The nanocatalysts described in Table 2 exhibit diverse structural features and catalytic performances for the green synthesis of benzimidazole derivatives. Most heterogeneous nanocatalysts, including MoO_3/CeO_2-ZrO_2, SO_4^{2-}-ZrO_2, ZnO, Co/SBA-15, BiOCl/FeOCl/SiO_2, ZnS, and MgO@DFNS, provide high catalytic efficiency under solvent-free or environmentally benign conditions, highlighting their compatibility with green chemistry principles. Catalysts supported on mesoporous materials such as Co/SBA-15 and MgO@DFNS exhibit enhanced dispersion of active sites, resulting in improved catalytic activity and broad substrate tolerance. Photocatalytic systems, including CdSe/MMT and $TiO_2/AgSbO_3$, operate under visible-light irradiation and offer high product yields under mild conditions, although their dependence on an external light source may limit large-scale applications. Mechanochemical (ZnO ball milling), ultrasonic (MnO_2, green ZnO, ZnS), and microwave-assisted (Zn-BNT) methods significantly

Table 2. Non-magnetic nano-catalysts' employed synthesis of benzimidazole derivatives (rt = room temperature).

Entry	Catalyst	Solvent	Energy medium	*t* / °C	Time/ min	Substituents on Aldehyde/ Benzyl amine/Benzyl alcohol	Yields/ %
1.	20%MoO_3/CeO_2 ZrO_2[37] Pros: Short reaction time Cons: Multiple steps, synthesis of Catalyst	–	MW	450 W	3–5	H, 4-Cl, 4-Me,4-OH + 6 derivatives	92–94
2.	SO_4^{2-}-ZrO_2[38] Pros: Non-toxic, non- corrosive solid catalyst Cons: Relatively long reaction times	Ethanol	reflux	50	40–150	H, 4-Cl, 4-Me, 4-OH + 9 derivatives	68–97
3.	ZnO-NPs[39] Pros: Low catalyst loading, requiring only 0.5 mol% Cons: Catalyst activity Decreases in re-runs	–	Ball mill	rt	30	H, 4-OH, 2-OH + 3 derivatives	85–94
4.	CdSe/MMT[40] Pros: Photocatalytic performance reaction Cons: Contains toxic Cd, posing environmental and health concerns despite minimized leaching	Ethanol	UV	rt	90–180	H, 4-NO_2 + 4 derivatives	68–94
5.	MnO_2[41] Pros: Green reaction medium used a water/ethanol Cons: No catalyst recyclability	Ethanol / Water	US	55 W	3–5	H, 4-Cl, 4-Me, 3-OH + 10 derivatives	82–87
6.	Co/SBA-15[42] Pros: Good thermal and chemical stability Cons: High cost of SBA-15 preparation	Ethanol	heat	60	240	H, 4-Cl, 4-F, 4-Br + 7 derivatives	85–98
7.	Co_3O_4@Al_2O_3/SiO_2[43] Pros: Negligible cobalt leaching Cons: Requires high temperatures 140 °C for aliphatic alcohols	–	heat	110–120	120	H, 4-Cl, 2-Me, 3-OMe + 5 derivatives	82–98
8.	BiOCl/FeOCl/SiO_2[44] Pros: Mild aerobic conditions Cons: Catalyst recovery requires centrifugation	–	heat	70	17–50	H, 4-Cl, 4-F, 4-OH + 9 derivatives	80–96
9.	ZnO NPs[45] Pros: Biosynthesized and avoiding hazardous reducing agents Cons: Catalytic performance is solvent-dependent, with lower yields obtained in water, acetonitrile, or tert-butanol than in ethanol	Ethanol	US	rt	10	H, 4-Cl, 4-Me, 4-OH + 5 derivatives	91–97
10.	CuO NPs[46] Pros: Avoiding hazardous reagents during catalyst preparation Cons: Requires hydrogen peroxide	–	heat	80	20–120	H, 4-Cl, 3,4,5-OMe, 4-F, 4-OH + 8 derivatives	76–97
11.	$ZrOCl_2.8H_2O$ @nano SiO_2[47] Pros: Inexpensive, non-toxic, and easy-to-handle catalyst Cons: Possible zirconium leaching during repeated use	Water/ Ethanol	heat	60	78–318	orthoester 6 derivatives	70–90
12.	CoOx@NC-800[48] Pros: Broad substrate scope Cons: Uses THF solvent	Tetrahydro-furan	heat	100	480	H, 4-Cl, 4-CN, 4-OH,4- NO_2 + 27 derivatives	35–98
13.	Au/TiO_2[49] Pros: High catalytic efficiency Cons: Contains gold nanoparticles increasing cost	Acetonitrile/ Methanol	–	rt	120	4-Cl, 4-Me, 4-CN 4-OMe + 35 derivatives	51–99
14.	nano-ZrO_2[50] Pros: Green dry ethanol solvent Cons: Moderate catalytic activity	Dry ethanol	heat	60	180	H, 3-Cl, 4-Me, 4-OMe, 3-Br + 5 derivatives	82–95
15.	ZN/BNT[51] Pros: Good thermal stability Cons: Microwave irradiation at high temperature	Acetonitrile	MW	140	15	H, 4-Cl, 2-Me,4-F + 4 examples	82–97

Table 2. Non-magnetic nano-catalysts' employed synthesis of benzimidazole derivatives (rt = room temperature).

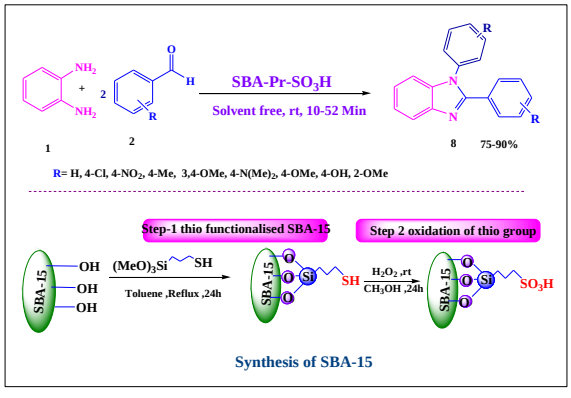
Entry	Catalyst	Solvent	Energy medium	*t* / °C	Time/ min	Substituents on Aldehyde/ Benzyl amine/Benzyl alcohol	Yields/ %
16.	ZnS (2023) [52] Pros: Simple and inexpensive catalyst, based on low-cost Cons: Reaction time remains moderate	Ethanol	heat	70	60	2-OH,4-NO_2, 4-Cl, 4-OH + 6 derivatives	81–98
17.	$ZnAl_2O_4$[53] Pros: Green catalyst synthesis Cons: Lengthy catalyst Fabrication	Ethanol	–	rt	10	H, 4-Me, 4-F, 4-OH + 2 derivatives	88–94
18.	MgO@DFNS[54] Pros: Highly stable catalyst Cons: MgO loading decreases the specific surface area	Ethanol	–	rt	180	H, 3-Cl, 3-OMe, 4-F, 4-CF_3 + 10 derivatives	80–94
19.	Co_2PNx@NC[55] Pros: Green solvent used Cons: High temperature, pressure and longer reaction time	Water	heat	150	1200	H + 7 derivatives	54–98
20	$TiO_2/AgSbO_3$[56] Pros: Cost-effective and non-toxic photocatalyst Cons: Ag is costly metal	Ethanol	green laser	25	90	H, 4-Me, 4-Br, 3-OH, 2-NO_2 + 4 derivatives	85–96
21	$Zn_{0.5}Cu_{0.5}Al_2O_4$[57] Pros: Green reaction medium, using water Cons: Catalytic activity gradually decreases	Water	–	rt	5–30	H, 4-Cl, 4-OMe, 4-OH + 5 derivatives	78–93
22	α-$MnMoO_4$[58] Pros: Multifunctional nanomaterial Cons: Moderate product yields	Ethanol	heat	60	360	H, 4-Cl, 4-Me, 4-OH, 4-NO_2 + 5 derivatives	47–85

reduce reaction times but require specialized equipment. Zn-BNT and CuO nanoparticles demonstrate excellent recyclability of up to eight cycles, whereas Co/SBA-15, MgO@DFNS, and Co_3O_4@Al_2O_3/SiO_2 also retain high activity after repeated reuse. In contrast, some catalysts require elevated temperatures, external oxidants (H_2O_2), or involve potentially toxic metals such as cadmium and cobalt, while others require multistep preparation procedures. Overall, mesoporous-supported, magnetic, and green-synthesized nanocatalysts provide the best balance of catalytic activity, sustainability, substrate scope, and reusability, making them promising alternatives to conventional catalysts for benzimidazole synthesis.

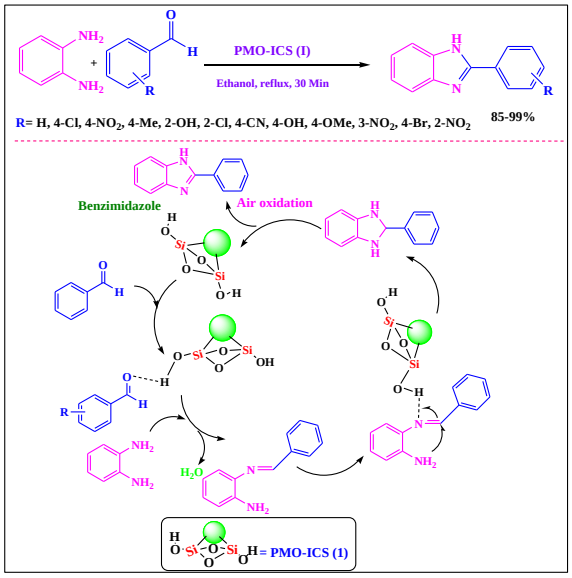
Hybrid (Organic and Inorganic Based) Nanocatalyst for the Synthesis of Benzimidazole Derivatives

Ziarani Mohammadi and associates (2012) demonstrated the synthesis of substituted benzimidazole derivatives (8) by a one-pot, multi-component condensation of *o*-phenylenediamine (1) and aromatic aldehydes (2) under solvent-free conditions with microwave irradiation and SBA-Pr-SO_3H as a nanocatalyst in good to excellent yields (Table 3, Entry 1). The catalyst was found to be highly efficient, simple to prepare, easy to isolate the product and the reaction conditions are eco-friendly. It was also easily recoverable and could be reused several times without significant loss in catalytic activity, which is indicative of its sustainability. But the technique demands specialized microwave irradiation equipment which may restrict its practical use in laboratories not provided with such equipment (Scheme 17).[59]

Mohammad G. et al. (2016) revealed the synthesis of benzimidazole derivatives by a single-pot multi-component reaction of o-phenylenediamine with aldehydes catalyzed by PMO-ICS in ethanol (Table 3, Entry 2). The products were obtained in crystalline yield of 99 % after refluxing for 35 min. The catalyst was characterized by means of TGA,



Scheme 17. Synthesis of 1,2-disubstituted benzimidazoles using SBA-Pr-SO_3H.



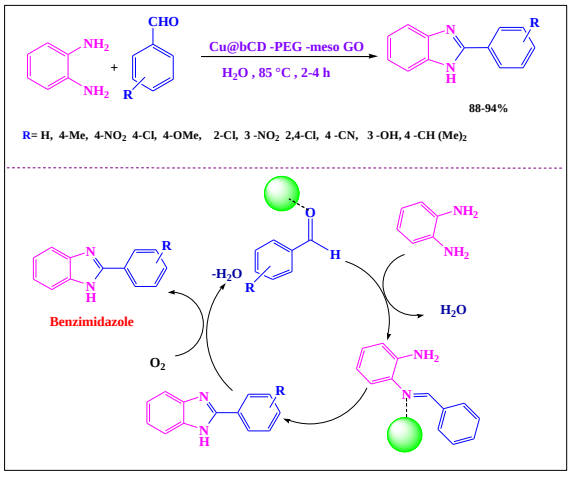
Scheme 18. PMO-ICS (I) catalyzed the synthesis of benzimidazoles.

XRD, FTIR and TEM. TEM displayed a well-ordered hexagonal mesostructure, FTIR bands at 2935–2850 cm^{-1} were assigned to C-H stretching and isocyanurate vibrations, and bands at 1120, 1070, and 935 cm^{-1} were attributed to Si-O-Si modes.

TGA revealed thermal stability of the isocyanurate bridges up to ~470 °C. PMO-ICS exhibited a simple procedure, short reaction time, high yield, excellent reusability, and strong catalytic performance. The PMO-ICS nanocatalyst can be easily recovered and reused without appreciable loss of catalytic activity. The use of ethanol as green solvent, simple work-up procedure and good thermal stability further increase the sustainability and practical application. However, the synthesis of PMO-ICS is rather laborious and may require expensive organosilica precursors and various steps in preparation (Scheme 18).[60]

Zakeri and team (2018) presented the synthesis of benzimidazole derivatives by reaction of benzaldehyde with 1,2-phenylenediamine in the presence of Cu (II)–TD@nSiO_2 as catalyst (Table 3, Entry 3) at ambient temperature for 15 min without any solvent. The method gave high yields with a novel heterogeneous catalyst consisting of copper (II) particles supported on thiolated nano-silica triazine dendrimer (Cu (II)–TD@nSiO_2). SEM images showed uniform round nSiO_2 particles of 50–70 nm in diameter, while TEM images showed matrix sizes of 15–30 nm. Preliminary catalyst is reused for five runs with marginal activity loss, providing simple reaction set up and excellent product yield.[61]

Saeed et al. (2018) synthesized a mesoporous silica–graphene oxide hybrid catalyst, β-cyclodextrin-modified

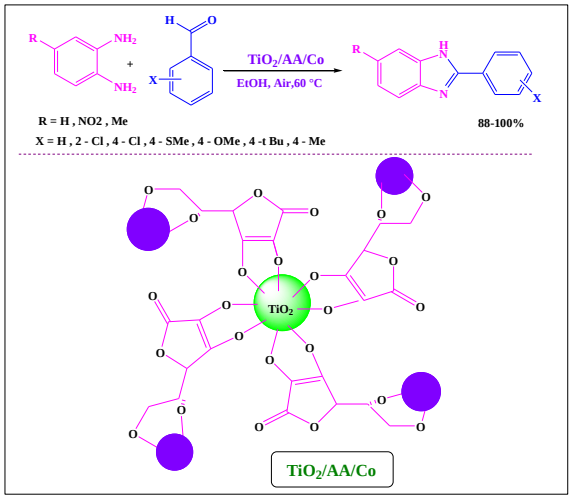


Scheme 19. Schematic possible way of benzimidazole.

copper Cu@βCD-PEG-mesoGO, (Table 3, Entry 4,) which was water-tolerant, recyclable, and effective for C–N bond oxidation and cyclization. This catalyst was used to synthesize a series of 2-substituted benzimidazoles from 2-aminobenzene and aromatic aldehydes in water at 85 °C for 2–4 h in good yields. The mesoporous graphene oxide exhibits high surface area and SEM/TEM images showed nano sheet structures with an ordered hexagonal pore network with an average pore size of 6.8 nm. Water was used as an environmentally benign solvent, open air was used as the oxidant, no toxic reagents were used and purification was minimal. The catalyst exhibited good reusability for ten cycles with excellent activity (Scheme 19).[62]

Feizpour et al. (2018) developed a green approach for the synthesis of benzimidazole derivatives. Benzaldehyde and *o*-phenylenediamine were aerobically oxidatively cyclocondensed in ethanol at 60 °C under oxygen to give the product in 96 % yield within 30 min using a TiO_2/ascorbic acid/cobalt (TiO_2/AA/Co) nanohybrid catalyst (Table 3, and Entry 5). The catalyst showed good absorption around 493 nm in the range of 450–550 nm indicating its high catalytic efficiency. It could be easily separated by centrifugation and recovered for four cycles with sustained performance (Scheme 20).[63]

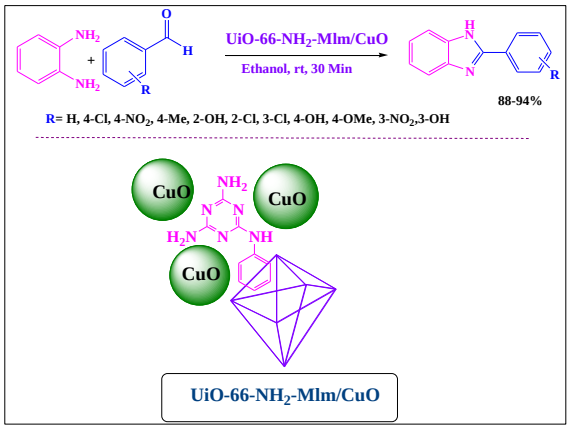
Zahra et al. (2018) reported ZnO@SiO_2-TTIP (Table 3, Entry 6) for the synthesis of 2-substituted benzimidazoles. The performance of the catalyst was improved by doping with Titanium isopropoxide (TTIP) to minimize the recombination of electrons and holes. This catalyst efficiently synthesized benzimidazoles from *o*-phenylenediamine and aryl aldehydes in alcohol at room temperature in 10–25 min. SEM analysis showed the ZnO@SiO_2 nanoparticles of size 59–91 nm and the pore size measurement showed the maximum depth of 2.1 nm. The method gives high yields, fast reactions, mild conditions and the catalyst can be recycled.[64]



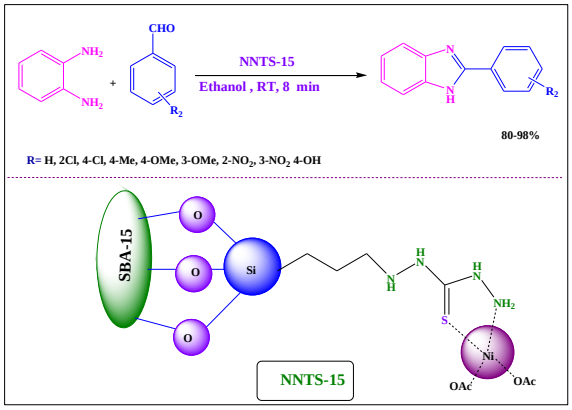
Scheme 20. TiO_2/AA/Co-catalyzed condensation of substituted *o*-phenylenediamine and aldehydes for benzimidazole synthesis.

Ziarati et al. (2018) reported the synthesis of benzimidazole derivatives from benzyl alcohol and *o*-phenylenediamine using BHC-TiO_2 benzene hex chloride (BHC) (Table 3, Entry 7) under visible light irradiation at room temperature, with yields of 77–86 %. The surface Ti^{3+} species of the catalyst reduced the band gap of TiO_2 and accelerated the separation of electrons and holes, whereas the ultrathin shell promoted molecular diffusion and the exposure of active sites. The hollow cubic structure also enhanced light absorption by scattering and refractive effects. The photocatalyst was easily recovered and reused after washing with hot ethanol and chloroform.[65]

Najari et al. (2019) synthesized the CuO nanomaterials on melamine-modified UiO-66-NH2 (UiO-66-NH_2-Mlm/CuO NPs), (Table 3, and Entry 8) which guaranteed the uniform dispersion and minimized leaching. This catalyst



Scheme 21. Support for copper oxide nanoparticles UiO-66-NH_2-Mlm/CuO.



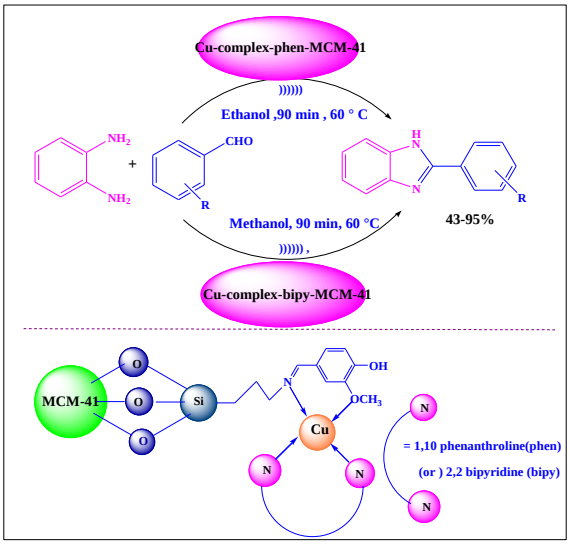
Scheme 22. Synthesis of benzimidazole derivatives from o-phenyldiamine and aromatic aldehyde with used of Ni/TCH@SBA-15 (NNTS-15).

was effective in the efficient synthesis of 2-substituted benzimidazoles from aryl aldehydes with *o*-phenylenediamine in ethanol at room temperature without oxidants. SEM images revealed particles in the range of 100–200 nm and FTIR peaks at 865–950 cm^{-1} were attributed to Cu–O–Cu vibrations. The catalyst as reusable with only minor loss in yield (Scheme 21).[66]

Kalhor et al.[67] (2019) reported a nickel-based nanocomposite Ni/TCH@SBA-15 (NNTS-15) as an efficient heterogeneous catalyst for the synthesis of benzimidazole derivatives at ambient temperature (Table 3, and Entry 9). SEM analysis revealed the formation of spherical nanoparticles of NNTS-15 with particle sizes in the range of 27–40 nm. The method presented several advantages such as high yields in short reaction times, mild conditions, simple work-up, clean and non-toxic reactions and ease of catalyst handling. Moreover, the Ni(II) species supported on SBA-15 was stable throughout the process, which allowed its efficient recycling and reuse for five cycles (Scheme 22).

Bharathi et al. (2020) prepared benzimidazole derivatives by a green method using ultrasound-assisted method in the presence of Cu-Schiff base complexes supported on MCM-41 (Table 3, Entry 10). The system offered high yields, short reaction times and mild conditions and the catalyst could be reused up to three times. Although the study offers an efficient and green approach, it gives very little mechanistic insight into the role of ultrasound in improving catalytic activity (Scheme 23).[68]

Esmael et al. (2021) reported an efficient and eco-friendly polyethylene-graphene oxide composite functionalized with 2-aminothiazole moieties by trifluoroacetate-bonded. The catalyst, PE@GO-DETA-Thiazole-TFA (Table 3, Entry 11), was successfully applied for solvent-free synthesis of benzimidazoles from 1,2-phenylenediamine and benzaldehyde at 75 °C for 1 h with



Scheme 23. Synthesis benzimidazole by used of Cu-complex-bipy-MCM-41and Cu-complex-phen-MCM-41.

an excellent yield of 75 %. The catalyst was recovered by addition of hot ethanol and filtration of the mixture and was active in five consecutive runs which indicates its reusability and environment friendly nature. The thermal analysis showed that the composite was thermally stable up to 450 °C and the use of low-cost graphene and polyethylene makes it more useful in practice. The without catalyzed reaction was very slow and after six hours gave only 11 % yield.[69]

Kohli et al. (2021) reported a new, reusable and efficient heterogeneous nanocatalyst, Al_2O_3/CuI/PANI (Table 3, Entry 12), for the one-pot synthesis of 2-substituted benzimidazoles in ethanol as a green solvent. The catalyst was prepared by a simple self-growth process where aniline is oxidized to PANI (Polyaniline) and serves as a reductant in the presence of KI. The catalyst was characterized by FT-IR, EDX, BET, XRD, SEM, and TEM. The method provides high yields, fast reaction times and does not require bases or additives. It also showed better green parameters such as low E-factor (0.17), better chemical performance (85.34 %), high process mass intensity (1.17) and high reaction mass efficiency (85.34 %).TEM analysis indicated the sizes of nanoparticles in the range of 25–40 nm and the catalyst exhibited good catalytic activity for five successive reaction cycles with simple recovery and reuse.

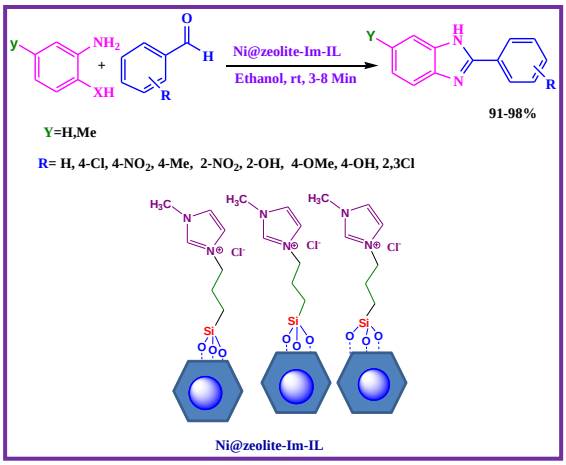
The main advantages of this catalyst are environmentally friendly reaction conditions, use of ethanol as a green solvent, high catalytic efficiency, easy preparation and good recyclability. The main disadvantages of the Al_2O_3/Its drawbacks include the assessment over only five recycling cycles, limited substrate scope, potential catalyst deactivation due to Cu(I) leaching or oxidation, and the necessity of advanced characterization techniques. In addition, the reaction efficiency might be reduced for sterically hindered or less reactive aldehydes due to the slower Schiff base formation and possible active site blocking during catalyst reuse.[70]

Shukla and co-workers (2021) reported the synthesis of surfactant-free metallovesicles, CuNPs@vesicles (Table 3, Entry 13), loaded with Cu nanoparticles. These vesicles efficiently catalyzed the synthesis of benzimidazoles from 1,2-diaminobenzenes with aryl aldehydes, achieving yields up to 85 %. HR-TEM and FEG-SEM analyses confirmed spherical vesicles with sizes ranging from 130 to 160 nm, while AFM measurements indicated a height of 20 nm, smaller than the 140 nm diameter, supporting their spherical morphology. The nanocatalyst maintained its activity over five consecutive reaction cycles without affecting product yields.[71]

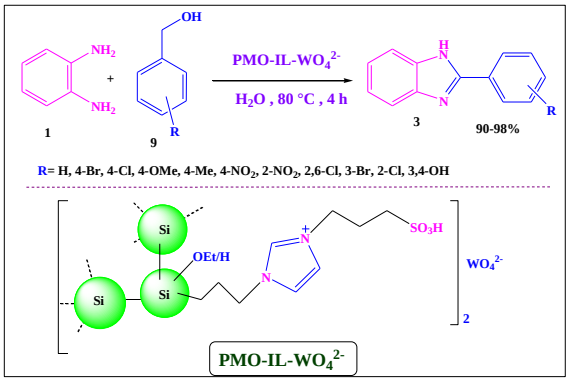
In 2022, F. Feizpour et al. reported a new single-pot method for the benzimidazoles synthesis from benzylic alcohols and aryl diamines. It consisted of aerobic photo-oxidation of benzyl alcohols and oxidative coupling of the resulting benzaldehyde with o-phenylenediamine. The reaction was catalyzed by a Co–g-C_3N_4-imine/TiO_2 nanohybrid (Table 3, entry 14) which functions as a heterojunction photocatalyst. SEM analysis revealed the formation of spherical nanoparticles with diameters of 19–23 nm. The synergistic interaction between cobalt–carbon nitride and TiO_2 causes the enhanced photocatalytic activity. Synergistic interaction of cobalt–carbon nitride with TiO_2 leads to enhanced photocatalytic activity. This system exhibits high thermal stability, low-cost materials, air as a green oxidant, UV light as a sustainable energy source and excellent catalyst durability. The catalyst also exhibited structural integrity and efficiency even after five cycles indicating its potential as a promising solution according to the principles of green chemistry.[72]

Zohre Zarnegar et al. (2022) synthesized a new Ni@zeolite-Y (Table 3, Entry 15) nanocatalyst based on 1-methylimidazolium ionic liquid and evaluated its catalytic efficiency in the one-pot synthesis of 2-aminothiazoles and 2-arylbenzimidazoles. The multifunctional nanocatalyst efficiently catalyzed the condensation reactions under mild and green conditions to afford the target products in good to excellent yields. The catalyst was very active, compatible with a broad range of substrates, easily isolated, and recyclable. Moreover, this protocol is attractive and sustainable due to its heterogeneous nature, simplicity in operation and reusability of this method for the synthesis of biologically important heterocyclic compounds (Scheme 24).[73]

Fatemeh et al. (2024) reported a green and sustainable synthesis of benzimidazoles (3) via reaction of phenyl methanol (9) with *o*-phenylenediamine, (1) in a single pot over periodic mesoporous organosilica–ionic liquid (PMO-



Scheme 24. The synthesis of products using Ni@zeolite-Im-IL.



Scheme 25. Synthesis of 2-substituted benzimidazole by use of PMO-IL-WO_4^{2-}.

IL-WO_4^{2-}) nanoparticles (Table 3, and Entry 16). Mild and sustainable conditions were employed to achieve the reaction in water at room temperature with > 90 % yield, without the requirement of organic solvents and additives. This reaction has several advantages such as efficient performance in water as green and environment benign solvent at room temperature. The catalyst was prepared using *N*-(3-propyltriethoxysilane) imidazole, with tungstic acid (H_2WO_4) incorporated through treatment in acetonitrile after the addition of 1-sulfonate, followed by stirring for three hours at ambient temperature. The produced yellow solid was filtered, washed by using acetonitrile and air dry (Scheme 25).[74]

The nanocatalysts described in Table 3 demonstrate significant advances in the sustainable synthesis of benzimidazole derivatives through improved catalytic efficiency, green reaction conditions, and enhanced reusability. Mesoporous silica-supported catalysts such as SBA-Pr-SO_3H, PMO-ICS, Ni/TCH@SBA-15, and Cu@βCD-PEG-mesoGO benefit from high surface area and well-dispersed active sites, resulting in excellent yields, short reaction times, and efficient catalyst recycling. PMO-ICS and PMO-IL-WO_4^{2-} further stand out because they combine high thermal stability with the use of environmentally benign solvents such as ethanol and water. Photocatalytic systems including TiO_2/AA/Co, BHC-TiO_2, and Co–g-C_3N_4-imine/TiO_2 utilize light-driven oxidation to achieve high catalytic activity while reducing the need for harsh oxidants. Green-supported catalysts such as UiO-66-NH_2-Mlm/CuO, Al_2O_3/CuI/PANI, PE@GO-DETA-Thiazole-TFA, and Ni@zeolite-Y exhibit broad substrate compatibility, operational simplicity, and good recyclability, making them attractive heterogeneous catalysts. However, several catalysts require multistep preparation, expensive supports, or specialized equipment such as microwave irradiation, ultrasound, or UV/visible-light sources, increasing the complexity of large-scale applications. Some systems also require elevated temperatures, prolonged reaction times, or repeated washing during catalyst recovery, while metal-based catalysts may experience gradual deactivation or leaching after repeated use. Overall, mesoporous and hybrid nanocatalysts offer the best balance of catalytic activity, stability, sustainability, and recyclability, making them highly promising candidates for environmentally friendly benzimidazole synthesis.

CONCLUSION

Nanocatalyst-supported synthesis has revolutionized the preparation of benzimidazole derivatives by providing efficient, sustainable, and environmentally benign synthetic routes. The studies discussed in this review show that the magnetic, non-magnetic and hybrid nanocatalysts have important advantages such as high yields of products, shorter reaction times, mild reaction conditions, broad substrate scope and excellent recyclability of the catalyst. The rising interest in green chemistry and sustainable organic chemical synthesis can be observed by the increasing use of green solvents, solvent-free protocols, microwave and ultrasonic irradiation and magnetically recoverable catalysts. Such developments demonstrate the promise of nanocatalysts as general platforms for the synthesis of biologically important benzimidazole derivatives.

Despite these advances, some challenges remain. Many nanocatalysts have complex synthesis routes, expensive precursors and limited long term stability studies. Moreover, the issue of catalyst leaching, mechanistic insight, scalability, and industrial applicability need to be explored in more detail. In the future, the focus should be on the development of cost effective, robust and environmentally benign nanocatalysts from renewable resources and improving catalyst durability and recyclability.

Table 3. Hybrid (organic and inorganic based) nano-catalysts' employed synthesis of benzimidazole derivatives (rt = room temperature).

Entry	Catalyst	Solvent	Energy medium	*t* / °C	Time/ min	Substituents on Aldehyde/ Benzyl amine/Benzyl alcohol	Yields/ %
1.	$SBA\text{-}Pr\text{-}SO_3H$[59] Pros: High efficiency, green, reusable, versatile, rapid Cons: Complex, limited, laborious, moderate, expensive	–	–	rt	10–52	H, 4-Cl, 4-OH, 4-NO_2, 4-Me + 12 derivatives	75–90
2.	PMO ICS[60] Pros: Metal-free catalyst non-toxic Cons: Laborious catalyst recovery	Ethanol	heat	reflux	30–70	H, 4-Cl, 2-Cl, 2-NO_2, 4-CN, 4-Br + 12 derivatives	85–99
3.	$Cu(II)TD@n\text{-}SiO_2$[61] Pros: Excellent catalytic efficiency Cons: Complex synthesis solvent requirement	Ethyl acetate	heat	50	15–80	H, 4-Cl, 4-Me, 4-Br + 4 derivatives	88–100
4.	Cu@βCD-PEG-mesoGO[62] Pros: Green aqueous oxidation process Cons: Laborious catalyst recovery	Water	heat	85	120–220	H, 4-HO, 4-OMe, 4-CN + 11 derivatives	85–94
5.	$TiO_2/AA/Co$[63] Pros: Visible-light-driven photo catalysis Cons: Requires appropriate light source and photocatalytic setup	Ethanol	UV, air	60	25–180	H, 4-Me, 4-Cl, 4-OMe + 13 derivatives	42–96
6.	$ZnO@SiO_2$.TTIP[64] Pros: High surface area Cons: Requires H_2O_2 as an oxidant.	Ethanol	–	rt	5–60	H, 4-Cl, 4-Me, 2-OH	90–97
7.	$BHC\text{-}TiO_2$[65] Pros: Eco-friendly oxidation using O_2 Cons: Uses chloroform during regeneration	Ethanol/ Acetonitrile	Uv	rt	420	H, 4-Cl, 4-Me, 3-Me, 4-OMe, 4-NO_2, 2-Cl	77–86
8.	$UiO\text{-}66\text{-}NH_2$ MIm/CuO NPs[66] Pros: One-pot tandem synthesis Cons: Possible Cu leaching after reuse	Ethanol	–	rt	30–80	H, 4-Cl, 2 OMe, 4-OH + 6 derivatives	64–95
9.	Ni/TCH@SBA-15 (NNTS-15)[67] Pros: Reusable and stable Cons: Possible Ni leaching after repeated reuse	Ethanol	–	rt	5–25	H, 4-Cl, 4-Me, 4-NO_2 2,3-Cl, 2-OH,4-OH + 30 derivatives	79–98
10.	Cu-complex –phen-MCM-41[68] Pros: Reusable with low Cu leaching. Cons: Requires ultrasonic irradiation.	Ethanol	US	60	90	H, 4-NO_2, 4-OMe, 4-Cl + 6 derivatives	43–95
	Cu-complex-bipy-MCM-41[68] Pros: Simple catalyst recovery Cons: Used methanol and lowyields	Methanol	US	60	90	H, 4-NO_2, 4-OMe, 4-Cl + 6 derivatives	29–67
11.	PE@GO-DETA-Thiazole-TFA[69] Pros: Metal-free and cost-effective. High thermal stability Cons: Complex catalyst preparation	–	heat	75	60–80	H, 4-Br, 4-OMe, 4-Cl, 2-OH + 8 derivatives	87–97
12.	$Al_2O_3/CuI/PANI$[70] Pros: Low E-factor and high efficiency Cons: Contains copper iodide (CuI) catalytic cost may increase	Ethanol	–	rt	60	4-Cl, 4-Me, 4-Br, 4-F + 9 derivatives	87–95
13.	CuNPs@vesicls[71] Pros: Green reaction medium Cons: High-temperature catalyst synthesis.	Water	–	rt	30–70	4-Cl, 4-Me,4-Br, 4-NO_2 3-NO_2, 2-OH,4-OCH_2-CH_3	87–95
14.	Co-g-C_3N_3-Imine/ TiO_2[72] Pros: High chemical and thermal stability Cons: Requires visible-light irradiation	Ethanol	air CFC lamp	60	45–140	H, 4-Cl, 4-OMe, 4-Me, 4-OH +5 derivatives	20–98
15.	Ni@zeolite-Im-IL.[73] Pros: Low-cost and non-toxic catalyst Cons: Ethanol, a green solvent	Ethanol	–	rt	3	H, 4-Cl, 4-Me, 4-OH +6 derivatives	90–98
16.	$PMO\text{-}IL\text{-}WO_4{}^{2}$[74] Pros: Green process water solvent, air oxidant Cons: Long reaction time	Water	heat	80	240	H, 4-Cl, 4-OMe, 4-Me, 2,6- Cl +7 derivatives	90–98

Combining continuous-flow synthesis, photo catalysis, mechanochemistry and computational approaches, including artificial intelligence-assisted catalyst design, could accelerate catalyst discovery and process optimization. To summarize, on-going innovations in the area of nanocatalyst development will facilitate the sustainable, scalable, and industrial production of benzimidazole derivatives for applications in the pharmaceutical, medicinal, and fine chemical fields.

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