

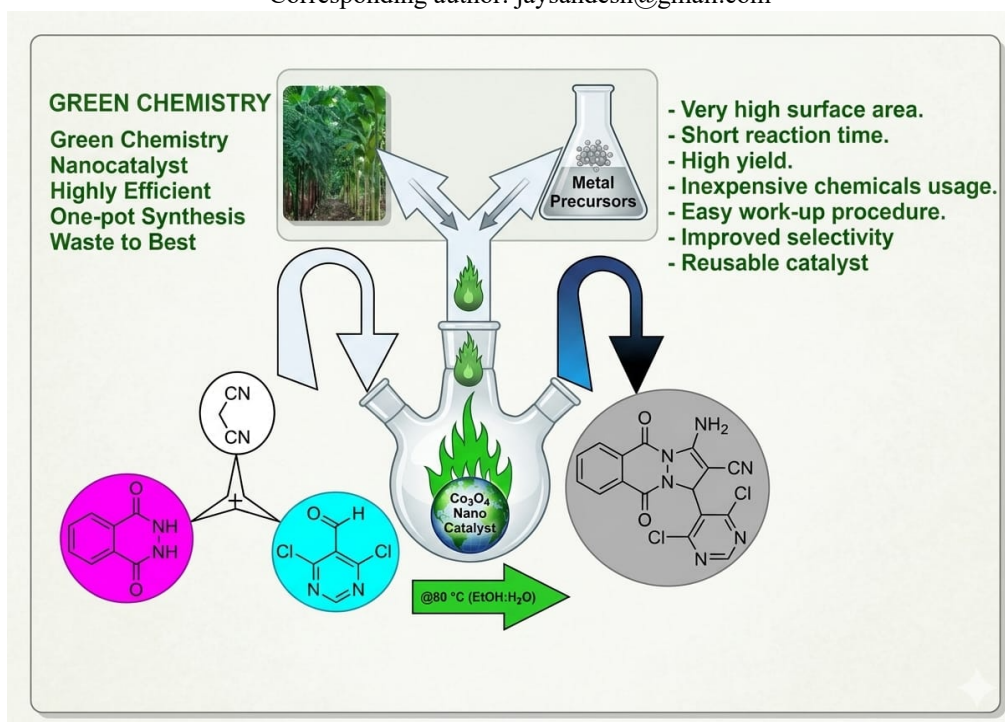
Green and Efficient Synthesis of 1H-Pyrazolo[1,2-b]phthalazine-5,10-diones Using Reusable Bioinspired Co₃O₄ Nanocatalysts Derived from *Musa paradisiaca* Stem Extract.

PATIL JAYESH ¹, BAVISKAR UDAY ² JAYBHAYE SANDESH ^{1*}

¹ Department of Chemistry, B K Birla College, Kalyan, Maharashtra, India

² Department of Chemistry, K M C College, Khopoli, Maharashtra, India

*Corresponding author: jaysandesh@gmail.com



ABSTRACT

The Fabrication of eco-friendly synthesis of bioactive 1H-pyrazolo[1,2-b]phthalazine-5,10-diones using green cobalt oxide nanocatalysts derived from *Musa paradisiaca* stem extracts. In the novel protocol, the robust cobalt oxide (Co₃O₄) nanocatalyst catalyzes the pseudo-three-component coupling and Sequential condensation of aromatic aldehydes with malononitrile and phthalhydrazide in a 1:1 ethanol–water mixture at 80°C. Intermolecular hydrogen bonding between the reactants and the Active surface of the catalyst facilitates the selective formation of pyrazolo-phthalazine diones in a sustainable medium with good to excellent yields. The methodology has numerous eco-friendly features including biocompatible starting materials, high yields, and short reaction times. Moreover, the magnetically retrievable catalyst exhibits robust reusability across cycles with negligible performance decline. The cobalt oxide nanocatalysts are thus valuable, economical, and efficient green agents for environmentally benign synthesis.

Keywords: Co₃O₄ nanocatalyst; Green chemistry; Heterocyclic synthesis; 1H-Pyrazolo[1,2-b]phthalazine-5,10-diones; Multicomponent reaction; Recyclable catalyst.

How to cite this article: PATIL JAYESH. Green and Efficient Synthesis of 1H-Pyrazolo[1,2-b]phthalazine-5,10-diones Using Reusable Bioinspired Co₃O₄ Nanocatalysts Derived from *Musa paradisiaca* Stem Extract.. *Int J Drug Deliv Technol.* 2026;16(87s):157-169. DOI: 10.25258/ijddt.16.87s.16.

1. INTRODUCTION

Nitrogen-containing fused heterocyclic ring systems have engaged notable research interest owing to the wide range of significant biological and pharmaceutical activities exhibited by these molecules [1,2]. Among these fused heterocycles,

pyrazolophthalazine derivatives represent one of the most interesting classes, particularly the 1H-pyrazolo[1,2-b]phthalazine-5,10-diones, which are well known for their significant antimicrobial, anti-inflammatory, analgesic, anticonvulsant,

antihypertensive (vasorelaxant), and anticancer activities [1–3]. Numerous of these biologically active molecules have served as lead compounds in medicinal chemistry and as important building blocks for sophisticated functional materials [2,3]. Consequently, the design of efficient and environmentally benign synthetic protocols for pyrazolophthalazine derivatives has become one of the most active research arena in modern organic and medicinal chemistry [1].

Conventionally, 1H-pyrazolo[1,2-b]phthalazine-5,10-dione scaffolds have been synthesized via multicomponent condensation reactions between aromatic aldehydes, malononitrile, and phthalhydrazide in the existence of homogeneous acid or base catalysts, typically requiring prolonged reaction times and relatively harsh conditions [1,4]. Multicomponent reactions (MCRs) are regarded as valuable synthetic tools, as they enable the rapid assembly of structurally complex molecules in a one-step process with high atom economy, operational simplicity, minimal purification requirements, and reduced by-product formation [4,5]. However, most presented synthetic protocols suffer from several limitations, including extended reaction times, the use of hazardous organic solvents, difficulty in catalyst recovery, poor catalyst reusability, and limited environmental compatibility [5]. Accordingly, the establishment of sustainable and green catalytic methodologies for such transformations has attracted considerable attention in recent years [5,6].

The past decade has witnessed remarkable advances in the application of nanotechnology to organic synthesis, as nanocatalysts comprise unique physicochemical properties such as elevated surface area, enhanced catalytic activity, tunable morphology, and facile separation from the reaction medium [7]. Among heterogeneous nanocatalysts, metal oxide nanocatalysts have been extensively studied for chemical transformations owing to their excellent catalytic efficiency, thermal stability, recyclability, and environmentally friendly nature [7,8]. Cobalt oxide nanoparticles (Co₃O₄ NPs) have attracted significant attention among metal oxide nanocatalysts because of these unique spinel crystal structure, which comprises both Co²⁺ and Co³⁺ oxidation states, imparting exceptional redox and catalytic behavior [8,9]. Furthermore, Co₃O₄ nanoparticles exhibit good catalytic activity, low toxicity, huge thermal stability, magnetic properties, and low cost, rendering them attractive and sustainable catalysts for a range of organic transformations [8,9].

Conventional methods for synthesizing cobalt oxide nanoparticles generally involve toxic reducing agents, hazardous chemicals, costly instrumentation, and high energy consumption [9]. Over the years, eco-friendly synthesis approaches utilizing biological resources have emerged as sustainable alternatives for the preparation of transition metal and metal oxide nanoparticles [9,10]. In plant-mediated green synthesis, phytochemicals present in plant extracts, such as flavonoids, alkaloids, terpenoids, tannins, phenolic compounds, carbohydrates, and proteins, act as reducing, stabilizing, and capping agents during nanoparticle formation, thereby eliminating the need for toxic chemicals and offering simple, economical, and environmentally benign synthetic routes [10,11].

Among the plant species investigated for green nanomaterial synthesis, *Musa paradisiaca* (banana plant) has attracted considerable interest owing to its rich phytochemical composition and abundant agricultural availability [11]. The stem extract of *Musa paradisiaca* contains polyphenols, antioxidant biomolecules, cellulose-derived macromolecules, amino acids, and reducing sugars, which facilitate the reduction of cobalt ions to stable cobalt oxide nanoparticles while simultaneously preventing nanoparticle aggregation [11,12]. Moreover, the utilization of banana stem waste for nanoparticle synthesis contributes to biomass valorization by transforming agricultural waste into valuable nanomaterials [12].

Green-synthesized Co₃O₄ nanoparticles have demonstrated promising applications in photocatalysis, antimicrobial studies, environmental remediation, sensing technologies, and heterogeneous catalytic organic synthesis [8,10]. Owing to their nanoscale dimensions and high surface-to-volume ratio, these nanoparticles provide a greater number of catalytically active sites, thereby accelerating organic transformations with enhanced selectivity and improved product yields [7,8]. Although several metal oxide nanocatalysts have been described for the synthesis of heterocyclic compounds, the application of green-synthesized cobalt oxide nanocatalysts derived from *Musa paradisiaca* stem extract for the synthesis of pyrazolophthalazine derivatives remains largely unexplored [1,9].

In continuation of our ongoing efforts toward the development of sustainable methodologies for heterocyclic synthesis, we herein report an efficient green catalytic protocol for the preparation of bioactive 1H-pyrazolo[1,2-b]phthalazine-5,10-diones using green-synthesized cobalt oxide (Co₃O₄) nanocatalysts

derived from *Musa paradisiaca* stem extract. The nanocatalyst was successfully employed to promote the pseudo-three-component coupling reaction of aromatic aldehydes, malononitrile, and phthalhydrazide in a 1:1 ethanol–water solvent system at 80 °C. The present protocol integrates agricultural waste valorization with green nanotechnology, affording the target heterocyclic derivatives in yields of up to 94% within a significantly reduced reaction time of approximately 60 minutes. Furthermore, the methodology exhibits broad substrate compatibility, accommodating aromatic aldehydes bearing both electron-donating and electron-withdrawing substituents, and led to the detection of a previously unreported derivative (compound 4a). The heterogeneous Co₃O₄ nanocatalyst also demonstrated excellent recyclability, maintaining its catalytic activity over multiple reaction cycles. Collectively, these features establish the present methodology as a sustainable, efficient, and environmentally responsible framework for the synthesis of pharmaceutically important pyrazolophthalazine derivatives, offering notable advantages over conventional synthetic approaches in terms of simplicity, mild reaction conditions, and green chemistry compliance [5,6].

2. MATERIALS AND METHODS

2.1 Chemicals and Reagents

Phthalic Hydrazine with 99.9% purity was sourced from Sisco Research Laboratories Pvt Ltd. Malononitrile (99% purity) and cobalt nitrate hexahydrate procured from sigma Aldrich Pvt Ltd, respectively. Ethanol LR grade was procured from National chemicals and HPLC grade water was used. The chemicals procured were used without any purification unless mentioned otherwise. Thin-layer chromatography-(TLC) was performed on Merck TLC Silicagel 60F₂₅₄ and visualized under UV light at 254nm for preliminary compound separation and analysis. The structural characterization of the synthesized compounds was meticulously conducted using nuclear magnetic resonance (NMR) spectroscopy, including both ¹H and ¹³C NMR spectroscopy. Solid-state NMR measurements were conducted out on a 500 MHz for ¹H NMR and 125 MHz for ¹³C NMR spectrometer at Indian Institute of Technology Bombay., with tetra-methylsilane (TMS) as an internal standard, and the recorded spectra were subjected using the evaluation version of MestReNova software ¹H NMR and ¹³C NMR ;DMSO-d₆ referenced at 2.50 ppm in ¹H NMR experiments.), Mass spectra (MS) were recorded on a Shimadzu 8040 LCMS/MS system(Japan) using electrospray ionization (ESI) mode, The morphological features of the synthesized nanoparticles was analyzed using a field-emission scanning electron microscope (FE-

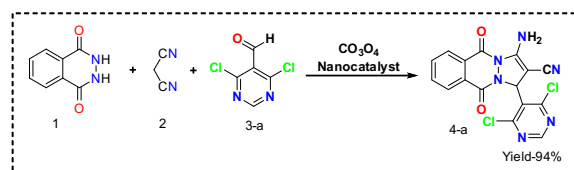
SEM, TESCAN CLARA-S8152). Elemental composition and purity were analyzed by energy-dispersive X-ray spectroscopy (EDS/EDAX) attached to the FE-SEM instrument. The crystalline structure and phase quality of the synthesized nanoparticles were characterized by X-ray diffraction (XRD) using a Bruker D2 PHASER diffractometer (Open designated in 2nd generation as A26-X1-A2B0B2B).

2.2 Preparation of Bioinspired Co₃O₄ Nanocatalyst

Fresh *Musa paradisiaca* (banana) stem extract was prepared by boiling chopped stem pieces in deionized water at 80–90 °C for 40 min, followed by filtration. An aqueous medium of cobalt nitrate hexahydrate (0.10 M) was sequentially added to the heated plant extract under continuous stirring. The pH of the reaction mixture was adjusted to 9–11 using 1.0 M NaOH, causing to the formation of a cobalt hydroxide precipitate. The reaction mixture was stirred for an additional 1-1.5 h, and the precipitate was isolated, washed thoroughly with deionized water and ethanol, and dried at 80 °C. The obtained parent compound was calcined at 400 °C for 3 h in a muffle furnace to afford Co₃O₄ nanocatalyst as a black powder.

2.3 General Procedure for Synthesis of 1H-Pyrazolo[1,2-b]phthalazine-5,10-diones

A mixture of aromatic aldehyde (1 mmol), malononitrile (1 mmol), phthalhydrazide (1 mmol), and Co₃O₄ nanocatalyst (15 wt%) was heated at 80 °C in an ethanol and water solvent system (10 mL). I monitored the reaction's progress using thin-layer chromatography (TLC) with n-hexane and ethyl acetate (6 and 4) as the mobile phase. Once the reaction finished, I added hot ethanol to the mixture and performed hot filtration to separate and recover the catalyst. I cooled the clear filtrate to 0-5 °C, resulting in the desired product precipitating as a solid. I filtered the obtained product, dried it, and characterized it using mass spectrometry, ¹H NMR, and ¹³C NMR spectroscopy. The spectral data aligned well with the values reported in the literature.



3. RESULTS AND DISCUSSION

3.1 FTIR Analysis of Co₃O₄ Nanocatalyst

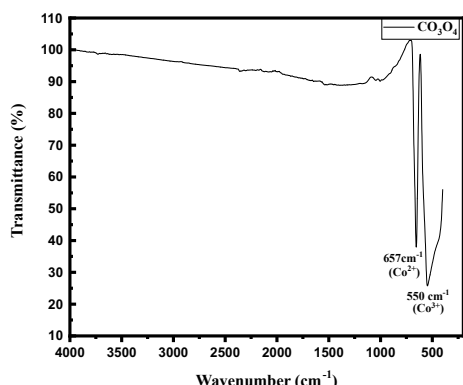


Fig. 1. Fourier-transform infrared (FTIR) spectrum of the Co₃O₄ nanocatalyst.

Fourier-transform infrared (FTIR) spectroscopy was performed to investigate the functional groups and chemical bonding characteristics of the synthesized chromium oxide (Cr₂O₃) nanoparticles. As shown in **Fig. 1** the FTIR spectrum exhibits prominent absorption bands in the low-wavenumber region, particularly at approximately **657 and 550 cm⁻¹**, which are characteristic of **Cr–O vibrational modes** in Cr₂O₃. The band observed around 550 cm⁻¹ can be assigned to the characteristic Cr–O lattice vibration of Cr³⁺ ions in the octahedral coordination environment, while the band near 657 cm⁻¹ is associated with additional Cr–O stretching vibrations within the chromium oxide lattice. Similar Cr–O vibrational bands in the region of approximately 540–650 cm⁻¹ have been reported for Cr₂O₃ nanoparticles. The existence of these characteristic Cr–O bands confirms the formation of chromium oxide and supports the successful conversion of the chromium precursor into Cr₂O₃ nanoparticles.

The FTIR spectrum of the biosynthesized Cr₂O₃ nanoparticles is displayed in Figure X. The spectrum shows specific absorption bands at approximately **657 and 550 cm⁻¹**, which can be assigned to the stretching vibrations of Cr–O bonds in the Cr₂O₃ lattice. The band near 550 cm⁻¹ is characteristic of Cr–O lattice vibrations associated with Cr³⁺ ions in octahedral coordination, while the band around 657 cm⁻¹ can be attributed to other Cr–O vibrational modes of the chromium oxide lattice [24].

The observed Cr–O vibrations are compatible with previously reported FTIR spectra of Cr₂O₃ nanoparticles, where characteristic Cr–O bands have been reported in the ~540–650 cm⁻¹ region. Thus, the FTIR results supply evidence for the successful formation of Cr₂O₃ nanoparticles [25].

3.2 XRD Analysis

The crystal structure, phase purity, and crystallite dimensions of the synthesized Co₃O₄ nanocatalyst were investigated using powder X-ray diffraction, as illustrated in **Fig. 2**.

The recorded diffractogram exhibits distinct, well-defined reflections at 2θ values of approximately 18.97°, 31.25°, 36.84°, 44.80°, 59.35° and 65.15°, which index precisely to the (111), (220), (311), (400), (511), and (440) crystallographic planes, respectively. All diffraction positions and relative intensities correspond to the pure face-centered cubic spinel phase of Co₃O₄ (JCPDS card no. 42-1467). No secondary diffraction signatures corresponding to cobalt hydroxides (Co(OH)₂), cobalt monoxide (CoO), or metallic cobalt phases were detected, corroborating the formation of a single-phase spinel lattice. The sharpness of the diffraction profiles signifies a high degree of crystallinity.

The average crystallite size (D) was evaluated using the classical Debye–Scherrer formulation:

$$D = k\lambda / B \cos \theta$$

where k is the shape factor (0.9), λ denotes the X-ray wavelength (0.15406 nm for Cu Kα), β represents the full width at half maximum (FWHM) of the deconvoluted peak in radians, and θ is the Bragg diffraction angle.

The molecular parameters and calculated crystallite sizes associated to the dominant diffraction planes are compiled in (**Table 1**). The individual crystallite sizes range between 36.00 nm and 52 nm, yielding an average crystallite size of **41.76 nm** (~42 nm). This calculated nanocrystalline dimension is in strong agreement with the primary particle size observed in high-magnification FE-SEM observations (38–60 nm), demonstrating that individual grains consist of coherent, single-domain nanocrystals.

Table 1. Structural parameters, peak fitting values, and crystallite sizes of the synthesized Co₃O₄ nanocatalyst calculated via the Debye–Scherrer relation.

Diffraction angle, 2θ (deg)	(hkl) Plane	FWHM, β (deg)	Crystallite size, D (nm)
36.84	(311)	0.2326	36.00
44.80	(400)	0.2091	41.09
59.35	(511)	0.2422	37.75
65.15	(440)	0.1805	52.22
Average	—	—	41.76

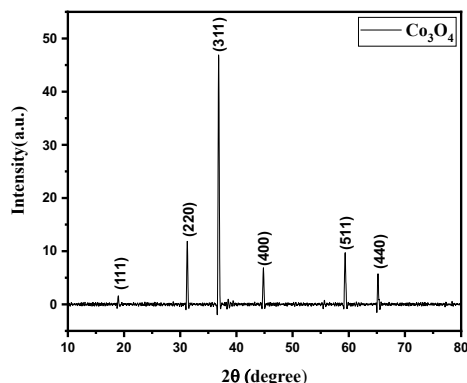


Fig. 2. Powder X-ray diffraction (XRD) pattern of the synthesized cubic spinel Co_3O_4 Nanocatalyst indexed with standard (hkl) miller planes.

3.3 SEM Scanning electron microscopy

The surface morphology, particle architecture, and textural characteristics of the synthesized Co_3O_4 nanocatalyst were characterized using Scanning Electron Microscopy (SEM) at both low and high magnifications, as illustrated in **Fig. 3a, b**.

The low-magnification micrograph (**Fig. 3a**) displays a three-dimensional, sponge-like network composed of randomly oriented and heavily agglomerated microclusters. The preparation of these secondary aggregates is primarily attributed to the high surface free energy correlated with nanoscale entities, thermal coalescence during calcination, and intrinsic magnetic dipole–dipole interactions characteristic of cobalt spinel oxides. Macroscopically, the particles demonstrate uniform spatial distribution with a rough, texturized surface profile. Closer inspection via high-magnification SEM (**Fig. 3b**) reveals that the dense clusters are constituted of interconnected, quasi-spherical primary nanoparticles. The measured dimensions of individual primary particles predominantly range between **38 and 60 nm**, exhibiting unique grain boundaries along with noticeable interparticle necking. These observed nanoscale dimensions show close alignment with the average crystallite size calculated from the X-ray diffraction (XRD) patterns via the Scherrer formulation, confirming the successful crystallization of nanoscale Co_3O_4 . Furthermore, the packing of these irregular nanoparticles gives rise to an open, porous inter-particle matrix. Even in the absence of templating agents, this rough surface architecture and accessible intergranular network facilitate effective contact between reactant molecules and active catalytic sites, thereby playing a essential role in enhancing mass-transfer kinetics during catalytic reactions.

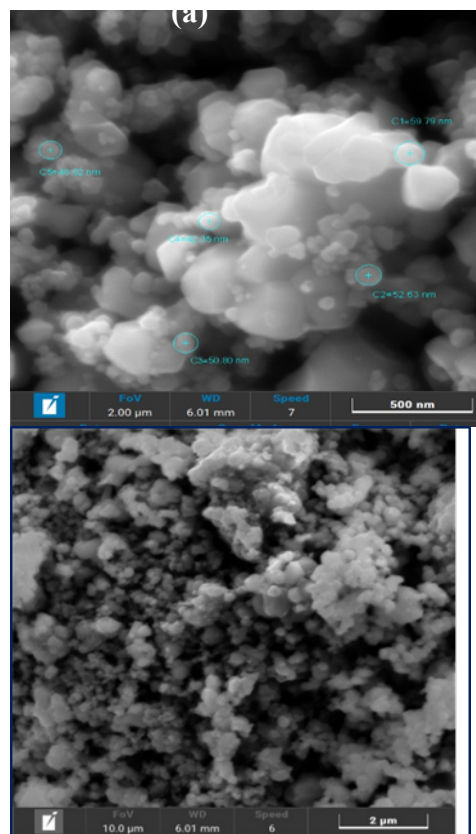


Fig. 3 Scanning electron microscopy (SEM) micrographs of the synthesized Co_3O_4 nanocatalyst: (a) low-magnification overview showing macroscopic agglomeration and porous surface distribution (scale bar = 2 μm), and (b) high-magnification image displaying quasi-spherical primary nanoparticles with intergranular voids (scale bar = 500 nm).

3.4 Compositional and Elemental Distribution Analysis

The elemental purity, chemical composition, and spatial distribution of the synthesized Co_3O_4 nanocatalysts were investigated using Energy-Dispersive X-ray Spectroscopy (EDX) coupled with elemental mapping, as displayed in **Fig. 4** and **Fig. 5**. The EDX spectrum (**Fig. 4**) confirms the presence of cobalt (Co) and oxygen (O) as the dominant constitutional elements. Distinct characteristic emission peaks corresponding to O K α (~ 0.52 keV) as well as Co L α (~ 0.78 keV) and Co K $\alpha/\text{K}\beta$ (~ 6.93 keV and ~ 7.65 keV) are prominently identified without any detectable signatures of elemental impurities. The minor signal observed for carbon (C) is attributed to the conductive carbon tape utilized for sample mounting during FESEM-EDX specimen preparation and ambient adventitious hydrocarbon adsorption. The stoichiometric ratio obtained from the spectral analysis closely reflects the theoretical

chemical formulation of the spinel Co₃O₄ phase, confirming high phase purity.

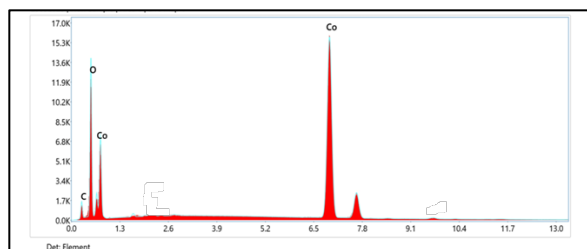


Fig. 4. EDX spectrum of the synthesized Co₃O₄ Nanocatalyst

Furthermore, elemental dot-mapping analysis (Fig. a-d) was conducted to evaluate the spatial homogeneity of the constituent elements across the sampled domain. The corresponding color-coded distribution maps demonstrate that Carbon (Fig.4b) oxygen (Fig.4c) and cobalt (Fig.4d) are well explained for with Co and O uniformly and homogeneously dispersed throughout the composite framework (Fig.4a) without local phase segregation or elemental accumulation. This homogeneous spatial configuration verifies the integrity of the crystal matrix and provides a well-dispersed distribution of catalytically effective redox sites, which is vital for achieving high catalytic efficiency in green organic transformations.

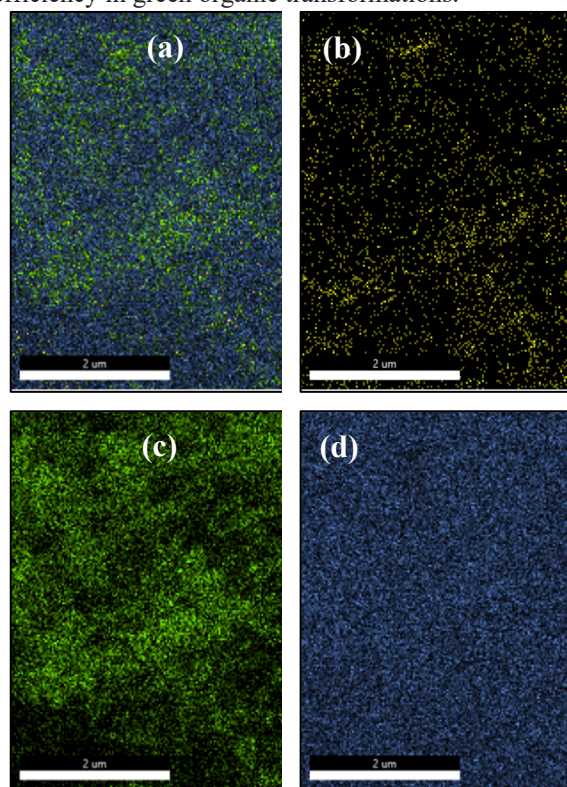


Fig. 5 Elemental mapping micrographs of the Co₃O₄ nanocatalyst showing the homogeneous spatial distribution of constituent elements: (a)

electron survey/overlay image, (b) carbon (C K) (c) oxygen (O K) and (d) cobalt (Co K).

3.5 Optimization of Reaction Conditions

To establish the optimal reaction conditions for the Co₃O₄ nanocatalyzed synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-dione derivatives, the impacts of solvent, catalyst loading, and reaction time were thoroughly investigated (Table 2). Initially, the reaction was examined in different solvent systems, revealing that no product formation occurred in water at room temperature even after 20 h, indicating that thermal activation is essential for the transformation. Under solvent-free conditions, the yield improved from 78% at 80 °C (2 h) to 84% at 100 °C (1.5 h), confirming that elevated temperature favorably influences the reaction rate. Among the solvents screened, ethanol and the ethanol-water (1:1) mixture proved most effective, affording the desired product in 94% yield within 1 h at 80 °C, while water alone at 80 °C also gave a comparable yield of 93% in 1.5 h. The ethanol-water (1:1) system was therefore selected as the optimal medium owing to its efficiency, low cost, and reduced environmental impact. The influence of catalyst loading was subsequently examined under these optimized solvent conditions. In the absence of catalyst, the reaction proceeded sluggishly, requiring 10 h to deliver only 38% yield, whereas increasing the Co₃O₄ loading to 5%, 10%, and 15% progressively enhanced the yield to 65%, 72%, and 94%, respectively, with a concomitant decrease in reaction time. A further increase in catalyst loading to 20% did not improve the yield, confirming that 15% is the optimum catalytic loading. Finally, the reaction time was optimized under the established solvent and catalyst conditions; the yield increased steadily from 44% at 15 min to 94% at 60 min, beyond which no further enhancement was observed even upon extending the reaction to 90 and 120 min. Based on these systematic investigations, the optimal reaction conditions were established as 15 mol% Co₃O₄ nanocatalyst in ethanol-water (1:1) at 80 °C for 60 min, affording the target pyrazolophthalazine derivatives in 94% yield.

Table 2. Optimization of solvent, catalyst loading, and reaction time for the Co₃O₄ nanocatalyzed synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-dione.^a

Entry	Catalyst Load	Solvent	Temperature (°C)	Time (h)	Yield (%)

	ing (%)	Syste m			
1	15	Water	RT	20	No reaction
2	15	Neat	80	2	78
3	15	Neat	100	1.5	84
4	15	Water	80	1.5	93
5	15	Ethanol	80	1	94
6	15	Ethanol-Water (1:1)	80	1	94
7	(No catalyst)	Ethanol-Water (1:1)	80	10	38
8	5	Ethanol-Water (1:1)	80	2.5	65
9	10	Ethanol-Water (1:1)	80	2	72
10	20	Ethanol-Water (1:1)	80	1	94

11 ^b	15	Ethanol-Water (1:1)	80	0.25	44
12 ^b	15	Ethanol-Water (1:1)	80	0.5	68
13 ^b	15	Ethanol-Water (1:1)	80	0.75	80
14 ^b	15	Ethanol-Water (1:1)	80	1.5	94
15 ^b	15	Ethanol-Water (1:1)	80	2	94

^a Reaction conditions: aromatic aldehyde (1 mmol), malononitrile (1 mmol), phthalhydrazide (1 mmol), Co₃O₄ nanocatalyst, solvent (3 mL). **Bold/optimized entry: Entry 6.**

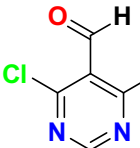
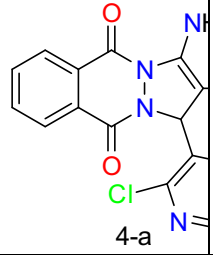
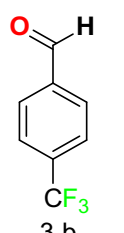
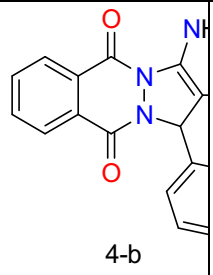
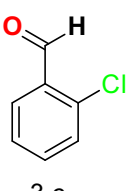
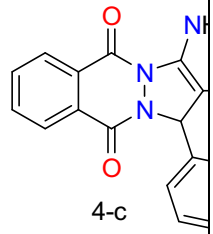
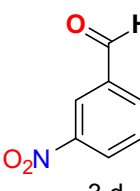
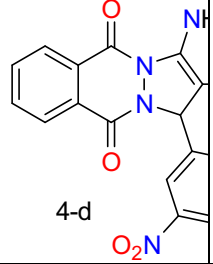
^b Time-course study conducted under the optimized solvent and catalyst conditions (Entry 6).

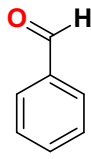
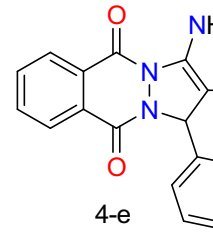
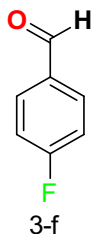
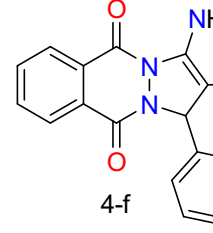
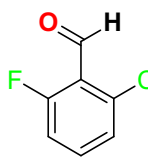
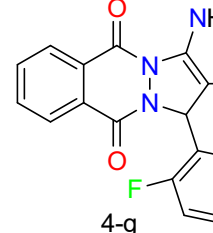
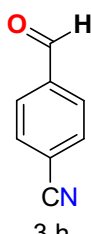
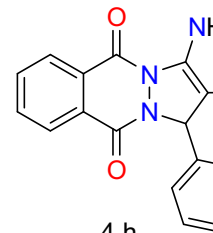
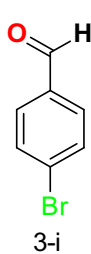
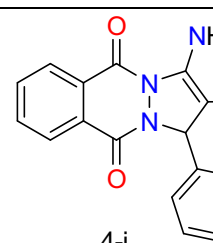
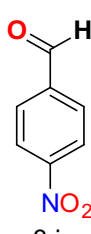
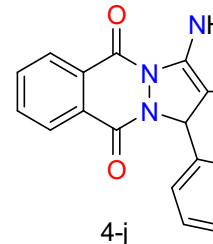
3.6 Catalytic Efficacy of Co₃O₄ in the Synthesis of Various derivatives of 1H-pyrazolo [1,2-b] phthalazine 5,10 diones:

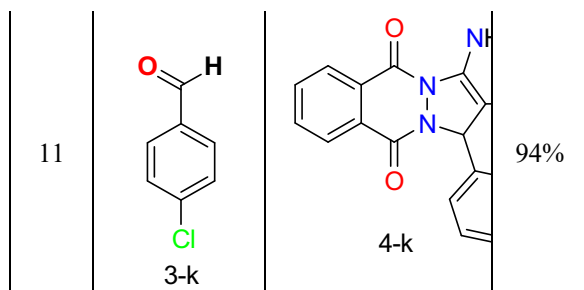
A sequence of substituted aromatic aldehydes were successfully applied for the synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-dione derivatives (**Table 3**) Upon the optimized reaction conditions. The reactions progressed smoothly with both electron-donating and electron-withdrawing substituents, affording the desired products in excellent yields ranging from 92.80% to 94.80%.

Halogen-, nitro-, trifluoromethyl-, and cyano-substituted aldehydes showed good compatibility with the reaction conditions, indicating broad substrate scope and high functional group tolerance. Among the synthesized derivatives, compound 4-a was found to be novel and has not been reported previously in the literature, whereas the remaining compounds were identified as known derivatives and characterized by comparison with reported spectral and physical data.

Table 3: Various derivatives of 1H-pyrazolo [1,2-b] phthalazine 5,10 diones

Sr. No	Aldehyde	Product	Yield
1	 3-a	 4-a	94%
2	 3-b	 4-b	93%
3	 3-c	 4-c	93.40%
4	 3-d	 4-d	94%

5	 3-e	 4-e	94.50%
6	 3-f	 4-f	92.80%
7	 3-g	 4-g	93%
8	 3-h	 4-h	94.70%
9	 3-i	 4-i	94.80%
10	 3-j	 4-j	93.20%



3.7 Characterization of the Synthesized Various derivatives of 1H-pyrazolo [1,2-b] phthalazine 5,10 diones:

All synthesized derivatives were successfully characterized using spectroscopic techniques including Mass spectrometry, ¹H NMR, and ¹³C NMR analysis. The obtained spectral data were in strong agreement with the proposed molecular structures of the synthesized compounds. In particular, the novel moiety **4-a** was further confirmed by LC–MS analysis, which established its molecular ion peak and structural integrity. Moreover, LC–MS purity analysis revealed that compound **4-a** exhibited 100% purity, indicating the successful generation of the target molecule without detectable impurities.

Spectral Deta

(4-a) 3-amino-1-(4,6-dichloropyrimidin-5-yl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile.

¹H-NMR (500 MHz, DMSO-*d*₆, δ ppm): 8.98 (s, 1H), 8.41 (bs, 2H), 8.30-8.32 (m, 1H), 8.12-8.14 (t, 1H), 8.02-8.04 (m, 2H), 6.81 (s, 1H).; ¹³C NMR (125 MHz, DMSO-*d*₆, δ ppm): 161.4, 159, 157.94, 156.47, 153.7, 152.39, 135.26, 134.43, 128.96, 128.89, 128.62, 128.38, 128.22, 127.71, 127.4, 126.9, 125.91, 114.96, 58.29, 54.37. MS Cal. [M] m/z (exact mass)= 386.01; Obs, m/z = 387.01 (M + H)⁺

(4-b) 3-amino-5,10-dioxo-1-(4-(trifluoromethyl)phenyl)-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile.

¹H-NMR (500 MHz, DMSO-*d*₆, δ ppm): 8.27-8.29 (m, 1H), 8.16 (bs, 2H), 8.08-8.10 (m, 1H), 7.97-7.99 (m, 2H), 7.74 (m, 4H), 6.25 (s, 1H).; ¹³C NMR (125 MHz, DMSO-*d*₆, δ ppm): 156.7, 153.76, 150.83, 143.16, 134.65, 133.82, 128.94, 128.88, 128.5, 127.61, 127.28, 127.4, 126.68, 125.52, 122.77, 115.88, 62.34, 60.86. MS Cal. [M] m/z (exact mass)=384.31, Obs, m/z = 383.05(M + H)⁺

(4-c) 3-amino-1-(2-chlorophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile

¹H-NMR (500 MHz, DMSO-*d*₆, δ ppm): 8.29 (t, 1H), 8.15 (bs, 2H), 8.09 (d, 1H), 7.99 (t, 2H), 7.59 (t, 1H), 7.49 (t, 1H), 7.35 (m, 2H), 6.47 (s, 1H).; ¹³C NMR (125 MHz, DMSO-*d*₆, δ ppm): 156.6, 153.53, 151.15, 134.75, 133.87, 131.23, 129.89, 129.73,

128.79, 128.36 127.82, 127.34, 126.69, 115.65, 62.34, 60.86 MS Cal. [M] m/z (exact mass)=350.76 Obs, m/z = 351.06 (M + H)⁺

(4-d) 3-amino-1-(3-nitrophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile

¹H-NMR (500 MHz, DMSO-*d*₆, δ ppm): 8.43 (s, 1H), 8.28 (t, 1H), 8.19 (bs, 2H), 8.07-8.10 (dd, 1H), 7.96-8.02 (m, 3H), 7.69 (t, 1H), 6.35 (s, 1H). ¹³C NMR (125 MHz, DMSO-*d*₆, δ ppm): 156.77, 153.89, 151.06, 147.98, 140.77, 134.58, 133.81, 130.16, 129.05, 128.46 127.21, 126.67, 123.35, 121.92, 62.11, 60.30 MS Cal. [M] m/z (exact mass)=361.31 Obs, m/z = 362.08 (M + H)⁺

(4-e) 3-amino-5,10-dioxo-1-phenyl-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile

¹H-NMR (500 MHz, DMSO-*d*₆, δ ppm): 8.27 (dd, 1H), 8.10 (s, 1H), 8.08 (bs, 2H), 7.96-7.98 (m, 2H), 7.46 (d, 2H), 7.32-7.39 (m, 3H), 6.13 (s, 1H). ¹³C NMR (125 MHz, DMSO-*d*₆, δ ppm): 156.64, 153.64, 150.61, 138.45, 134.65, 133.73, 128.80, 128.52, 127.28, 126.77 126.67, 116.06, 62.98, 61.41 MS Cal. [M] m/z (exact mass)= 316.31 Obs, m/z =317.10 (M + H)⁺

(4-f) 3-amino-1-(4-fluorophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile

¹H-NMR (500 MHz, DMSO-*d*₆, δ ppm): 7.27 (d, 1H), 8.11 (bs, 2H), 8.09 (t, 1H), 7.96-7.98 (dd, 2H), 7.55 (m, 2H), 7.19 (t, 2H), 6.16 (s, 1H). ¹³C NMR (125 MHz, DMSO-*d*₆, δ ppm): 163.14, 160.72, 158.54, 153.67, 150.68, 134.62, 133.72, 129.19, 128.83, 127.24 126.64, 116.01, 115.38, 115.17, 62.20, 61.10 MS Cal. [M] m/z (exact mass)=334.3 Obs, m/z =335.09 (M + H)⁺

(4-g) 3-amino-1-(2-chloro-6-fluorophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile

¹H-NMR (500 MHz, DMSO-*d*₆, δ ppm): 8.26-8.31 (m, 3H), 8.12 (dd, 1H), 7.99-8.02 (m, 2H), 7.44-7.46 (m, 3H), 6.66 (s, 1H). ¹³C NMR (125 MHz, DMSO-*d*₆, δ ppm): 162.18, 159.68, 158.45, 153.28, 151.5, 135.11, 134.15, 131.10, 128.28, 127.53 126.79, 125.94, 115.62, 57.50, 54.90. MS Cal. [M] m/z (exact mass)=368.75 Obs, m/z =369.05 (M + H)⁺

(4-h) 3-amino-1-(4-cyanophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile

¹H-NMR (500 MHz, DMSO-*d*₆, δ ppm): 8.28 (dd, 1H), 8.16 (bs, 2H), 8.10 (m, 1H), 7.98 (t, 2H), 7.85 (d, 2H), 7.72(d, 2H), 6.23 (s, 1H). ¹³C NMR (125 MHz, DMSO-*d*₆, δ ppm): 158.60, 153.74, 150.88, 143.94, 134.62, 133.82, 133.58, 128.99, 128.42, 127.60 126.68, 118.60, 115.81, 110.99, 62.34, 60.46.

MS Cal. [M] m/z (exact mass)=341.32 Obs, m/z=342.09 (M + H)⁺

(4-i) 3-amino-1-(4-bromophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile

¹H-NMR (500 MHz, DMSO-*d*₆, δ ppm): 6.53 (dd, 1H), 8.26 (bs, 2H), 8.13 (m, 1H), 7.97 (m, 2H), 7.56 (d, 2H), 7.46 (d, 2H), 6.14 (s, 1H). ¹³C NMR (125 MHz, DMSO-*d*₆, δ ppm): 158.62, 153.65, 150.71, 137.87, 134.61, 133.74, 131.41, 128.83, 127.24, 126.64, 121.43, 115.94, 62.35, 60.85. MS Cal. [M] m/z (exact mass)=395.21 Obs, m/z=395.01 (M + H)⁺

(4-j) 3-amino-1-(4-nitrophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile

¹H-NMR (500 MHz, DMSO-*d*₆, δ ppm): 8.29 (dd, 1H), 8.19-8.27 (m, 4H), 8.09 (d, 1H), 7.99 (m, 2H), 7.81 (d, 2H), 6.30 (s, 1H). ¹³C NMR (125 MHz, DMSO-*d*₆, δ ppm): 158.72, 153.80, 150.96, 147.38, 145.85, 134.68, 133.88, 128.99, 128.41, 127.31, 126.71, 123.81, 115.80, 62.08, 60.35. MS Cal. [M] m/z (exact mass)=361.31 Obs, m/z=362.09 (M + H)⁺

(4-k) 3-amino-1-(4-chlorophenyl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile

¹H-NMR (500 MHz, DMSO-*d*₆, δ ppm): 8.26 (dd, 1H), 8.13 (bs, 2H), 8.09 (t, 1H), 7.97 (t, 2H), 7.53 (d, 2H), 7.43 (d, 2H), 6.15 (s, 1H). ¹³C NMR (125 MHz, DMSO-*d*₆, δ ppm): 156.64, 153.67, 150.72, 137.47, 134.62, 133.75, 132.83, 128.83, 128.49, 127.25, 126.65, 115.96, 62.28, 60.9. MS Cal. [M] m/z (exact mass)=350.76 Obs, m/z=351.06 (M + H)⁺

3.8. Proposed Reaction Mechanism

Plausible Reaction Mechanism for the preparation of 1H-pyrazolo[1,2-b]phthalazine-5,10-dione

In view of the above observations, a plausible reaction mechanism for the construction of **3-amino-1-(4,6-dichloropyrimidin-5-yl)-5,10-dioxo-5,10-dihydro-1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (4-a)** is illustrated in Fig.6. Initially, the basic oxygen sites present on the Co₃O₄ nanoparticles activate the acidic C–H bond of malononitrile (2), facilitating its nucleophilic attack on the activated carbonyl carbon of aldehyde (3a). The Lewis acidic sites of Co₃O₄ NPs further promote this transformation, resulting to the formation of the Knoevenagel condensation intermediate (A). Subsequently, phthalhydrazide (1) undergoes a Michael-type addition with intermediate (A) to afford the iminomethylene intermediate (B). Finally, intramolecular cyclization followed by tautomerization in the presence of Co₃O₄ nanoparticles furnishes the desired **3-amino-1-(4,6-dichloropyrimidin-5-yl)-5,10-dioxo-5,10-dihydro-**

1H-pyrazolo[1,2-b]phthalazine-2-carbonitrile (4-a).

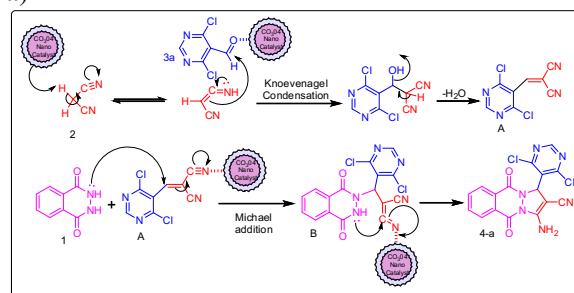


Fig. 6- Proposed Reaction Mechanism

3.9. Catalyst Reusability

The recyclability and reusability of the Co₃O₄ nanocatalyst under optimized reaction conditions. After reaction termination of the reaction, The reaction mass was filtered in hot condition, Due to the heterogeneous character of the Co₃O₄ nanocatalysts, the nanocatalysts was easily recovered by simple filtration/centrifugation, while the material was isolated from the filtrate medium. The recovered nanocatalysts was washed extensively with ethanol and distilled water, dried, and reused for subsequent catalytic cycles. The Co₃O₄ nanocatalyst was successfully reused for four consecutive cycles with only a marginal drops in catalytic activity, implying its excellent stability, robustness, and catalytic efficiency. The observed recyclability demonstrates the sustainable and cost-effective nature of the developed catalytic protocol for environmentally benign organic synthesis.

3.10. Comparison with Previously Reported Methods

A comparative evaluation of previously described catalytic systems for the synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-diones demonstrates the catalytic efficiency of the present Co₃O₄ nanoparticle catalyst (Table X). Various catalytic systems, including imidazole [26], β-cyclodextrin [27], ZnFe₂O₄ nanoparticles [28], Na₂ eosin Y [29], Et₃N [30], Al-KIT-6 [31], ZnO nanoparticles [32], *p*-toluenesulfonic acid [33], supported caesium carbonate [34], dicationic bipyridine–silica hybrid nanocomposite [35], and heteropolytungstate ionic liquid [36], have been reported with yields ranging from 86–96% under different reaction conditions. Although some catalysts afford slightly higher yields, several systems require elevated temperatures, prolonged reaction times, reflux, specialized supports, or solvent-free conditions. In comparison, the present Co₃O₄ NP catalyst affords **94% yield within 60 min at 80 °C in an H₂O–EtOH medium**, offering a favorable combination of high yield, short reaction time, and relatively mild reaction conditions. These results demonstrate the potential of Co₃O₄ nanoparticles as an effective heterogeneous

catalyst for the synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-diones.

Table. 4. Comparison of catalyst for the synthesis of 1H-pyrazolo [1,2-b] phthalazine 5,10 diones

Comparison of catalyst for the synthesis of 1H-pyrazolo [1,2-b] phthalazine 5,10 diones					
Entry	Catalyst	Solvent	Temp °C	Time	Yield %
1	Imidazole (20%)	H ₂ O-EtOH	80	0.5 hr	90 %
2	β-cyclodextrin	H ₂ O-EtOH	100	2.5 hr	86 %
3	ZnFe ₂ O ₄ NP	EtOH	Reflux	1 hr	90 %
4	Na ₂ eosin Y	H ₂ O-EtOH	white light	3 hr	96 %
5	Et ₃ N	EtOH	50	1 hr	90 %
6	Al-KIT-6	EtOH	60	240 min	93 %
7	ZnO NPs	Solvent free	100	1.5 hr	90 %
8	p-Toluenesulphonic acid	[bmim]Br	100 °C	180 min	94 %
9	Supported caesium carbonate (Ni _{0.5} Zn _{0.5} Fe ₂ O ₄ @HAP-Cs ₂ CO ₃)	Solvent-free,	110	15 hr	93 %
10	Dicationic 4,4'-bipyridine silica hybrid nanocomposite, SBA@BiPy ₂ +2Cl ⁻	Solvent-free,	100	4 hr	96 %
11	1-(Copperferrite siloxypropyl)-3-methyl imidazolium heteropolytungstate ionic liquid BW12-ILMNs	Solvent-free,	80	5 hr	94 %
12	Cobalt oxide nanoparticle [Present Work]	H ₂ O-EtOH	80	1 min	94 %

4. CONCLUSION

To sum up, we have developed a simple, efficient, and environmentally friendly method for the preparation of bioactive 1H-pyrazolo[1,2-b]phthalazine-5,10-dione derivatives using green-synthesized cobalt oxide (Co₃O₄) nanocatalysts derived from *Musa paradisiaca* stem extracts. The catalyst successfully facilitated the pseudo-three-component reaction of aromatic aldehydes, malononitrile, and phthalhydrazide in an ethanol–water medium, providing the target products in good to excellent yields within less reaction times. The excellent catalytic performance is likely due to favorable interactions between the reactants and the active surface of the nanocatalyst. The use of plant-based resources for catalyst preparation, combined with a green solvent system, operational simplicity, and high reaction efficiency, highlights the sustainable nature of this approach. Additionally, the catalyst could be easily recovered and reused several times with minimum loss in activity, demonstrating its stability and practical applicability. Overall, this work offers a cost-effective and eco-friendly strategy for the preparation of biologically important heterocyclic compounds and supports the growing emphasis on greener and more sustainable practices in organic synthesis.

ACKNOWLEDGEMENTS

We sincerely thank the Management of B. K. Birla College, Kalyan, for providing financial support and the necessary facilities to carry out my research work. I am deeply thankful to Dr. Naresh Chandra, Director, B. K. Birla College, Kalyan, and Dr. Avinash Patil, Principal, B. K. Birla College, Kalyan, for their valuable support, encouragement, and guidance throughout my research work. I also extend my sincere thanks to the Head, Department of Chemistry, and the laboratory staff for their cooperation and assistance during the course of this research. I am especially grateful to my research guide, Dr. Sandesh Jaybhaye, for his valuable guidance, constructive suggestions, continuous encouragement, and motivation throughout the research work. Finally, I express my heartfelt gratitude to my family for their constant encouragement, patience, understanding, and unwavering support, which have been a great source of motivation throughout my research journey.

REFERENCES

1. Safaei-Ghomi J, Shahbazi Alavi H, Badiei A, Teymuri R, Saberi MT. [Article title not provided]. *Chin Chem Lett.* 2014;25:401-405.
2. Shaterian M, Yarahmadi H, Ghashang M. [Article title not provided]. *Bioorg Med Chem Lett.* 2008;18:788-792.

3. Farag AM, Dawood KM. [Article title not provided]. *Eur J Med Chem.* 2010;45:5887-5896.
4. Dömling A, Ugi I. Multicomponent reactions with isocyanides. *Angew Chem Int Ed.* 2000;39:3168-3210.
5. Anastas PT, Warner JC. *Green Chemistry: Theory and Practice.* New York: Oxford University Press; 1998.
6. Kappe CO. 100 years of the multicomponent reaction. *Acc Chem Res.* 2000;33:879-888.
7. Rao CNR, Müller A, Cheetham AK. *The Chemistry of Nanomaterials.* Weinheim: Wiley-VCH; 2004.
8. Iravani S, Varma RS. Green synthesis, biomedical applications, and environmental implications of nanomaterials. *Green Chem.* 2020;22:2643-2661.
9. Annu, Ikram M, Ali J, et al. [Article title not provided]. *RSC Adv.* 2024;14:32733-32758.
10. Waris A, Din M, Ali A, et al. [Article title not provided]. *Open Life Sci.* 2021;16:14-30.
11. Samuel MS, Jose E, Selvarajan S, et al. [Article title not provided]. *J Photochem Photobiol B.* 2020;211:112011.
12. Baskar K, Rajeswari V. [Article title not provided]. *Mater Today Proc.* 2022;49:357-362.
13. Baviskar PD, Kale AD, Mahire VN, Dalal DS, Mahulikar PP. Imidazole as an organocatalyst for the rapid synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-diones in aqueous medium. *J Chem Sci.* 2024;136(4):94.
14. Tayade YA, Dalal DS. β -Cyclodextrin as a supramolecular catalyst for the synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-dione derivatives in water. *Catal Lett.* 2017;147(6):1411-1421.
15. Mhaske AK, Gadhave AG, Dholi AG, Uphade BK. One-pot, green synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-diones by ZnFe₂O₄ nanoparticles: an efficient nanocatalyst. *J Inorg Organomet Polym Mater.* 2024;34(3):999-1014.
16. Mohamadpour F. New role for photoexcited organic dye, Na₂eosin Y via the direct hydrogen atom transfer (HAT) process in photochemical visible-light-induced synthesis of spiroacenaphthylenes and 1H-pyrazolo[1,2-b]phthalazine-5,10-diones under air atmosphere. *Dyes Pigments.* 2021;194:109628.
17. Nabid MR, Rezaei SJT, Ghahremanzadeh R, Bazgir A. Ultrasound-assisted one-pot, three-component synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-diones. *Ultrason Sonochem.* 2010;17(1):159-161.
18. Karthikeyan G, Pandurangan A. Post synthesis alumination of KIT-6 materials with Ia3d symmetry and their catalytic efficiency towards multicomponent synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-dione carbonitriles and carboxylates. *J Mol Catal A Chem.* 2012;361:58-67.
19. Azarifar A, Nejat-Yami R, Azarifar D. Nano-ZnO: an efficient and reusable catalyst for one-pot synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-diones and pyrazolo[1,2-a][1,2,4]triazole-1,3-diones. *J Iran Chem Soc.* 2013;10(2):297-306.
20. Ghahremanzadeh R, Shakibaei GI, Bazgir A. An efficient one-pot synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-dione derivatives. *Synlett.* 2008;2008(8):1129-1132.
21. Maleki B, Barat Nam Chalaki S, Sedigh Ashrafi S, Rezaee Seresht E, Moeinpour F, Khojastehnezhad A, et al. Caesium carbonate supported on hydroxyapatite-encapsulated Ni_{0.5}Zn_{0.5}Fe₂O₄ nanocrystallites as a novel magnetically basic catalyst for the one-pot synthesis of pyrazolo[1,2-b]phthalazine-5,10-diones. *Appl Organomet Chem.* 2015;29(5):290-295.
22. Bashti A, Kiasat AR, Mokhtari B. Synthesis and characterization of dicationic 4,4'-bipyridinium dichloride ordered mesoporous silica nanocomposite and its application in the preparation of 1H-pyrazolo[1,2-b]phthalazine-5,10-dione derivatives. *RSC Adv.* 2015;5(33):25816-25823.
23. Saadati-Moshtaghin HR, Zonoz FM. Synthesis and characterization of magnetically recoverable 1-(copperferritesiloxypopyl)-3-methylimidazolium heteropolytungstate ionic liquid as a new nanocatalyst for the preparation of 1H-pyrazolo[1,2-b]phthalazine-5,10-diones. *J Nanostruct Chem.* 2017;7(4):317-325.
24. Larbi T, Ouni B, Gantassi A, Doll K, Amlouk M, Manoubi T. Structural, optical and vibrational properties of Cr₂O₃ with ferromagnetic and antiferromagnetic order: a combined experimental and density functional theory study. *J Magn Magn Mater.* 2017;444:16-22.
25. David SA, Doss A, Pole RP. Biosynthesis of chromium oxide nanoparticles by *Momordica charantia* leaf extract: characterization and

- their antibacterial activities. *Results Surf Interfaces*. 2023;11:100120.
26. Baviskar PD, Kale AD, Mahire VN, Dalal DS, Mahulikar PP. Imidazole as an organocatalyst for the rapid synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-diones in aqueous medium. *J Chem Sci*. 2024;136(4):94. doi:10.1007/s12039-024-02327-w.
 27. Tayade YA, Dalal DS. β -Cyclodextrin as a supramolecular catalyst for the synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-dione derivatives in water. *Catal Lett*. 2017;147(6):1411-1421. doi:10.1007/s10562-017-2032-6.
 28. Mhaske AK, Gadhave AG, Dholi AG, Uphade BK. One-pot, green synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-diones by ZnFe₂O₄ nanoparticles: an efficient nanocatalyst. *J Inorg Organomet Polym Mater*. 2024;34(3):999-1014. doi:10.1007/s10904-023-02875-7.
 29. Mohamadpour F. New role for photoexcited organic dye, Na₂eosin Y via the direct hydrogen atom transfer (HAT) process in photochemical visible-light-induced synthesis of spiroacenaphthylenes and 1H-pyrazolo[1,2-b]phthalazine-5,10-diones under air atmosphere. *Dyes Pigments*. 2021;194:109628.
 30. Nabid MR, Rezaei SJT, Ghahremanzadeh R, Bazgir A. Ultrasound-assisted one-pot, three-component synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-diones. *Ultrason Sonochem*. 2010;17(1):159-161.
 31. Karthikeyan G, Pandurangan A. Post synthesis alumination of KIT-6 materials with Ia_{3d} symmetry and their catalytic efficiency towards multicomponent synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-dione carbonitriles and carboxylates. *J Mol Catal A Chem*. 2012;361:58-67.
 32. Azarifar A, Nejat-Yami R, Azarifar D. Nano-ZnO: an efficient and reusable catalyst for one-pot synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-diones and pyrazolo[1,2-a][1,2,4]triazole-1,3-diones. *J Iran Chem Soc*. 2013;10(2):297-306.
 33. Ghahremanzadeh R, Shakibaei GI, Bazgir A. An efficient one-pot synthesis of 1H-pyrazolo[1,2-b]phthalazine-5,10-dione derivatives. *Synlett*. 2008;2008(8):1129-1132.
 34. Maleki B, Barat Nam Chalki S, Sedigh Ashrafi S, Rezaee Seresht E, Moeinpour F, Khojastehnezhad A, et al. Caesium carbonate supported on hydroxyapatite-encapsulated Ni_{0.5}Zn_{0.5}Fe₂O₄ nanocrystallites as a novel magnetically basic catalyst for the one-pot synthesis of pyrazolo[1,2-b]phthalazine-5,10-diones. *Appl Organomet Chem*. 2015;29(5):290-295.
 35. Bashti A, Kiasat AR, Mokhtari B. Synthesis and characterization of dicationic 4,4'-bipyridinium dichloride ordered mesoporous silica nanocomposite and its application in the preparation of 1H-pyrazolo[1,2-b]phthalazine-5,10-dione derivatives. *RSC Adv*. 2015;5(33):25816-25823.
 36. Saadati-Moshtaghin HR, Zonoz FM. Synthesis and characterization of magnetically recoverable 1-(copperferritesiloxypopyl)-3-methylimidazolium heteropolytungstate ionic liquid as a new nanocatalyst for the preparation of 1H-pyrazolo[1,2-b]phthalazine-5,10-diones. *J Nanostruct Chem*. 2017;7(4):317-325.