

Natural base catalysis in the sustainable synthesis of functionalized 2-amino-4*H*-chromenes

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Original Research

Received:
26 December 2023
Revised:
23 February 2024
Accepted:
23 April 2024
Published online:
1 May 2024

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Abstract:

Functionalized 2-amino-4*H*-chromenes have been successfully synthesized via cyclization of C-H activated acids, aromatic aldehydes, and active methylene compounds using a natural base catalyst derived from waste snail shells (*Bellamya bengalensis*) in the water at ambient temperature. Freshwater snail shells are significant biological materials with diverse uses. As an economical and environmentally benign alternative to traditional stoichiometric reagents and expensive metal catalysts, the waste shells of snails worked well as a heterogeneous base catalyst in heterocyclization. The as-prepared catalyst was analyzed using FTIR, XRD, EDS, SEM, TEM, and TGA tools. The chemical analysis revealed the predominance of CaO, which in the water possibly provides an alkaline medium to the reaction through which the reaction accelerates efficiently and offers a quantitative yield of the desired product. Catalytic reusability showed slight leaching of the catalyst that could be recovered and reused.

Keywords: Sustainable chemistry; Heterogeneous catalysis; Waste snail shell; One-pot synthesis; 2-amino-4*H*-chromenes

1. Introduction

Waste from various sectors like agriculture, food, fruit, pulp, and animal or plant dead material is generated in tremendous quantities per day worldwide. Driven by fast urbanization and increasing population, worldwide annual waste generation is expected to reach 3.4 billion tonnes over the next 30 years [1]. The seafood industry discards around 7 million tonnes of mollusk shells. The vast majority of these shells are either thrown in landfills or dumped in water bodies, which can create environmental issues [2]. In addition, large quantities of waste natural shells of the mollusk are found at the river and sea sites. Mollusk shells consist of over 95% CaCO₃, which finds applications in agricultural and engineering sectors, wastewater treatment, pulp and paper, paint, fertilizer, filler in concrete, and many more [3]. Additionally, these materials can potentially serve as catalysts in several organic transformations [4]. Exploitation of waste materials to produce promising catalysts can appreciably reduce substantial waste disposal problems and mitigate potential environmental pollution [5].

4*H*-chromene moieties have attracted considerable interest due to their notable biological and pharmaceutical properties, such as antimicrobial, anti-HIV, antifungal, anti-tumour, and anti-neurodegenerative disorders [6–11]. Some synthesized bioactive 4*H*-chromenes have been shown in Figure 1 [12]. Literature reports revealed the successful synthesis of potent bioactive 2-amino-4*H*-chromenes via the cyclization of C-H activated acids, a diverse range of aromatic aldehydes, and either ethyl cyanoacetate or malononitrile. This synthetic achievement has been realized using various catalysts, such as Fe₃O₄-chitosan [13], K₂CO₃/cyanuric acid [14], TiO₂/Nano clinoptilolite [15], ZnO [16], ionic liquid-coated carbon nanotubes [17], potassium hydrogen phthalate (KHP) [18], triethylamine [19], Choline Chloride/Urea [20], Nano-[DMSPDE][Cl] [21], N,N-dimethylbenzylamine (DMBA) [22], sodium malonate [23], Potassium phthalimide (PPI) [24, 25], sodium benzoate [26] among others. Although certain approaches have proven effective, there is a growing demand for environmentally sustainable methods that employ cost-effective, easily accessible, and recyclable catalysts, green solvents,

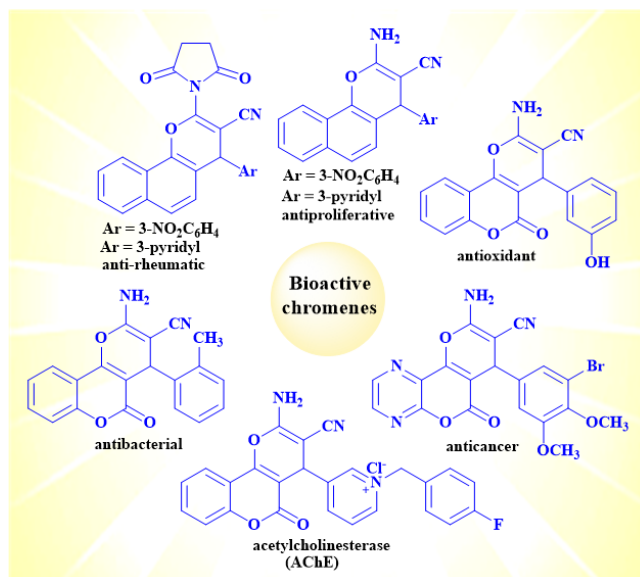


Figure 1. Glimpse of synthesized bioactive 4*H*-chromenes.

or solvent-free processes, and no or minimum energy investment.

In continuation of our ongoing research work on the implication of waste materials as catalysts in chemical transformations [27–30], here, we report a simple, clean, and efficient synthesis of 2-amino-4*H*-chromenes via multicomponent coupling of C-H activated acids, aromatic aldehydes, and malononitrile using a heterogeneous catalyst in the water at ambient temperature (Scheme 1). An inexpensive, innocuous, readily available, and biodegradable heterogeneous catalyst has been derived from waste shells of *Bellamyia bengalensis* via calcination, which has been abbreviated and referred to as CBS. This economical and green protocol offered a high yield of 2-amino-4*H*-chromene derivatives.

2. Experimental

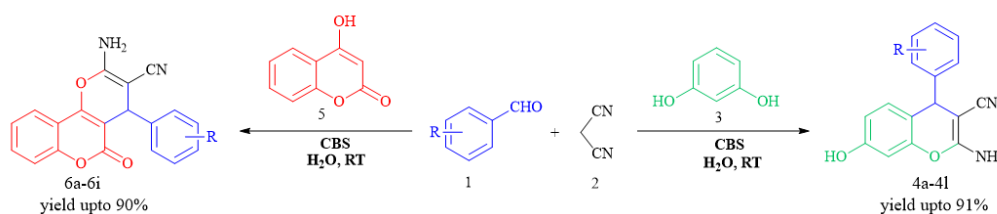
2.1 Material and methods

All the essential chemicals were procured from Loba Chemie, Sigma-Aldrich, and Merck and used as received. The waste snail shells were collected from the Bahe site of the Krishna River in Maharashtra, India, and authenticated by the Department of Life Sciences at KRP Kanya Mahavidyalaya, Islampur, MS, India. Physical constants were determined using the open-capillary method and are reported as uncorrected values. The FT-IR spectra were recorded using the Bruker (Alpha, 100508), and wave numbers ($\tilde{\nu}$) are reported in cm^{-1} . The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$

spectra of compounds were recorded using an AVANCE-300 spectrometer. The chemical shifts (δ) were given in parts per million (ppm) using the residue solvent peaks as a reference relative to TMS. For thin-layer chromatography (TLC), pre-coated plates of Silica gel 60 F254 were used. The Powder XRD measurement was recorded on XPERT-PRO X-Ray Powder Diffractometer (PANalytical, Pretoria, S.A.) using $\text{Cu K}\alpha$ radiation ($\lambda=1.5406\text{\AA}$) with scattering angle (2θ). The microscopic morphology was examined by JEOL 6380A (Japan), Scanning electron microscopy (SEM), and Transmission Electron Microscopy (TEM) by JEOL JEM-2100 Plus (USA). EDS analysis was performed using the Bruker XFlash 6—30 microscope with excellent energy resolution (123 eV at $\text{Mn K}\alpha$ and 453V at $\text{C K}\alpha$) and element detection range from 4 Be to 95Am. The XRF analysis was carried out using an X-ray Fluorescence spectrometer (PANalytical, USA).

2.2 Clean synthesis of CBS catalyst

The collected snail shells underwent a meticulous cleaning process involving multiple washes with tap water followed by rinsing with distilled water. Subsequently, the shells were dried in the oven at $100\text{ }^\circ\text{C}$ for 3 h. Once dried, shells were finely ground into a powder using mortar and pestle and then sieved through the mesh. The resulting powder was subjected to calcination ($900\text{ }^\circ\text{C}$) in a muffle furnace for 4 h. After the calcination, the powdered catalyst was



Scheme 1. Synthesis of 2-amino-4*H*-chromenes using CBS catalyst.

carefully stored in a sealed bottle to prevent moisture absorption and avoid reaction with CO₂. This method ensures the preservation of the catalyst's integrity for subsequent applications.

2.3 General procedure for the synthesis of 2-amino-4H-chromenes

In the experimental procedure, a reaction vessel was charged with a mixture comprising C-H activated acids, specifically resorcinol (1 mmol) or 4-hydroxycoumarin (1 mmol), an aromatic aldehyde (1 mmol), malononitrile (1.2 mmol), and CBS (50 mg) in water (3 mL). The reaction mixture was stirred at ambient temperature for a duration specified in Table 2. The progress of the reaction was monitored by thin-layer chromatography (TLC) using ethyl acetate: n-hexane (2:3) as the solvent system. Upon completion of the reaction, the mixture was subjected to filtration. The residual mass obtained was dissolved in hot ethanol and filtered. The resulting filtrate was then cooled to room temperature. The precipitated crude product was subsequently recrystallized from ethanol to yield the final pure product.

For the catalyst recovery, after the dissolution of the crude product in hot ethanol, the remaining solid was further treated with hot ethanol to remove residual reactants, by-products, or impurities that may be adsorbed on the surface of the catalyst. This step aims to improve the purity of the recovered catalyst. It was then dried in the furnace at 100 °C to eliminate any remaining solvent. The pure, free-flowing catalyst was collected and stored for further use.

3. Results and discussion

3.1 Catalyst characterization

Waste shells of *Bellamya bengalensis* were characterized by various analytical tools. The elemental concentration of natural (pre-calcined) and a calcined snail shell (CBS) was examined using the X-ray fluorescence (XRF) analysis (Table 1). XRF revealed that calcium is in a higher concentration than other components.

The FTIR spectra (Fig. 2) of CBS exhibited a weak absorp-

tion band at 1478 cm⁻¹, indicating the conversion of metal carbonates to oxides. The peaks assigned to organic components, which were observed in the natural snail shell (Fig. 1 ESI), disappeared in the CBS. The peak at 3641 cm⁻¹ was attributed to the hydroxyl functional group, which is assigned to metal hydroxides, while the peak at 1084 cm⁻¹ is ascribed to SiO₂. The XRD pattern of CBS was recorded and analyzed (Fig. 3), showing that the snail shell was composed of oxides and carbonates of metals. The intense peaks at 2θ = 23.52, 29.54, 31.60, 39.58, 43.28, 47.68, 48.66, and 66.06 assigned to the CaCO₃ (JCPDS File No. 41-1475 and 29-0306) (Fig. 2 ESI) shown by a natural snail shell. At the same time, CBS revealed the intense peaks at 2θ = 32.36, 37.56, 43.28, 53.94, 64.36, and 67.66 assigned to calcium oxide (JCPDS File Nos. 00-037-1497). The broad peaks observed in the CBS highlighted its crystalline nature. SEM images (Fig. 4) revealed that the CBS has particles with irregular cavities, a flower-like appearance, and agglomeration. SEM image also exhibited a porous surface, which may be due to the release of water and gaseous CO₂ during the decomposition of CaCO₃ to CaO. The catalytic activity of the CBS is possibly enhanced due to the presence of a porous surface.

The EDX analysis showed that natural snail shells (Fig. 3 ESI) constituted 45.80% of the calcium, while the CBS (Fig. 5) contained 49.97% of the calcium. The TGA curves (Fig. 6) exhibited that in the pre-calcined shell (curve b), below a temperature of 375 °C, the weight loss was about 2.78% because of the removal of moisture and organics. Excessive weight loss (40.61%) was observed in the 625 to 845 °C range, indicating the decomposition of CaCO₃ to CaO. Further, weight loss was not observed above 845 °C. The CBS (curve a) exhibited a slight loss in weight at the initial stage due to the removal of moisture, but after that, the weight of the CBS remained constant. TEM image (Fig. 7) revealed that CBS has large, closely packed, and agglomerated particles having spherical shapes with sizes ranging from roughly 85 to 190 nm.

Table 1. Elemental concentration in snail shell.

entry	inorganic components	concentration (%)	
		natural snail shell	calcined snail shell
1	CaO	97.11	98.09
2	SiO ₂	0.638	0.581
3	MgO	0.458	0.428
4	Fe ₂ O ₃	0.412	0.321
5	SrO	0.351	0.153
6	MnO	0.313	0.141
7	Na ₂ O	0.231	0.127
8	Al ₂ O ₃	0.187	0.121
9	K ₂ O	0.161	0.088
10	Cr ₂ O ₃	0.062	0.024
11	SO ₃	0.060	0.013
12	CuO	0.011	0.009
13	TiO ₂	0.004	0.003
14	P ₂ O ₅	0.002	0.001

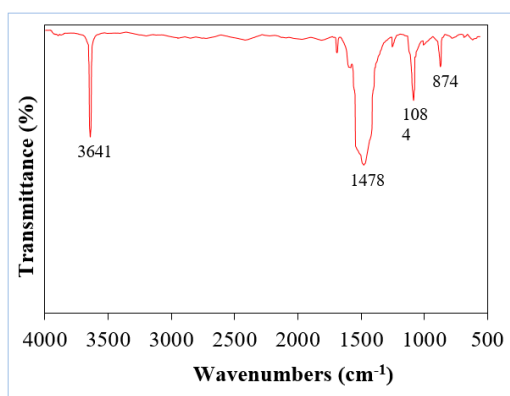


Figure 2. FTIR spectra of CBS.

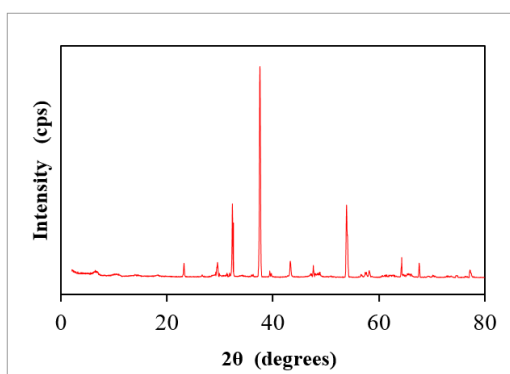


Figure 3. XRD pattern of CBS.

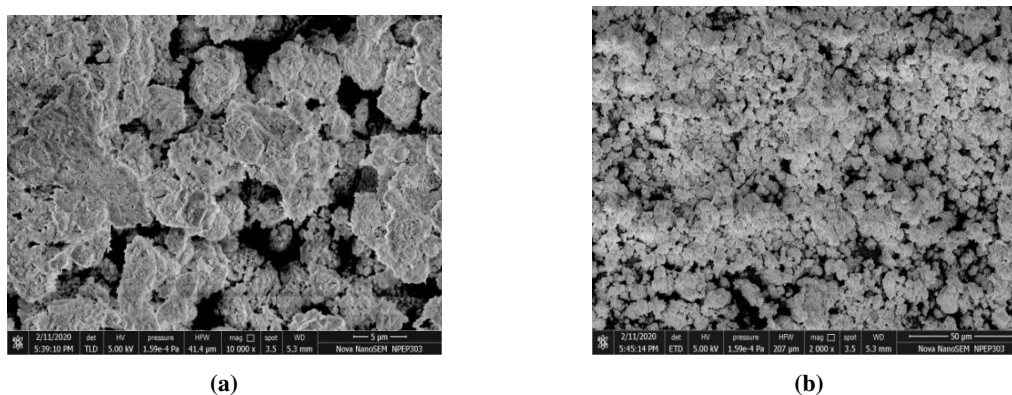


Figure 4. SEM micrograph (a, and b) of CBS.

3.2 Optimization of reaction conditions

At the outset, to evaluate the efficacy and catalytic activity of the CBS catalyst and to determine the optimal reaction conditions for synthesizing 2-amino-5-oxo-4-phenyl-4*H*,5*H*-pyrano[3,2-*c*] chromene-3-carbonitrile **4a** under different variables that affect the yield, we conducted a reaction between resorcinol **3**, benzaldehyde **1**, and malononitrile **2** (at a molar ratio of 1:1:1) as a model reaction. Despite conducting numerous trial reactions under various conditions, including the use of a CBS catalyst, the anticipated yield of **4a** was not achieved. Subsequently, we investigated the impact of the substrate, specifically malononitrile, on the **4a** yield. Employing a 1.1 mmol concentration of malonon-

itrile did not enhance the yield. Consequently, we increased the malononitrile concentration to 1.2 mmol, and the model reaction was executed under the following specified conditions.

The yield of **4a** was not detected under solvent and catalyst-free conditions at room temperature or even at 100 °C (Table 2, entries 1 and 2). Furthermore, under a catalyst-free state, only a trace amount of yield was detected at reflux temperature in water (Table 2, entries 3 and 4). The ideal reaction was carried out using a CBS catalyst under variable temperatures and in a solvent-free state to screen the efficacy of the catalyst. However, a low yield of **4a** was detected (Table 2, entries 5-7). Interestingly, the moderate target yield of **4a** was obtained in the water at room

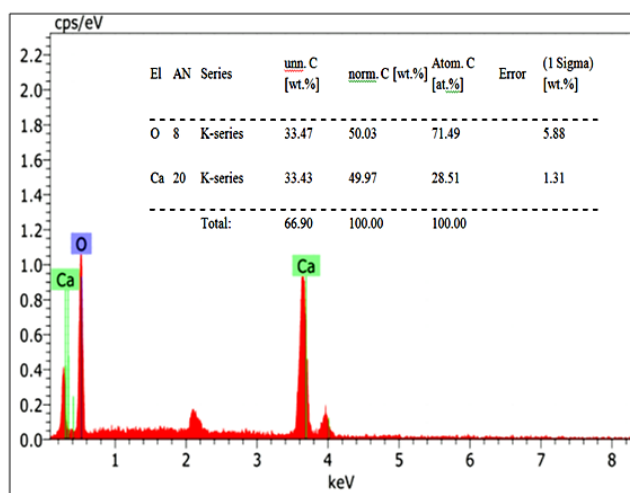


Figure 5. EDX analysis of CBS.

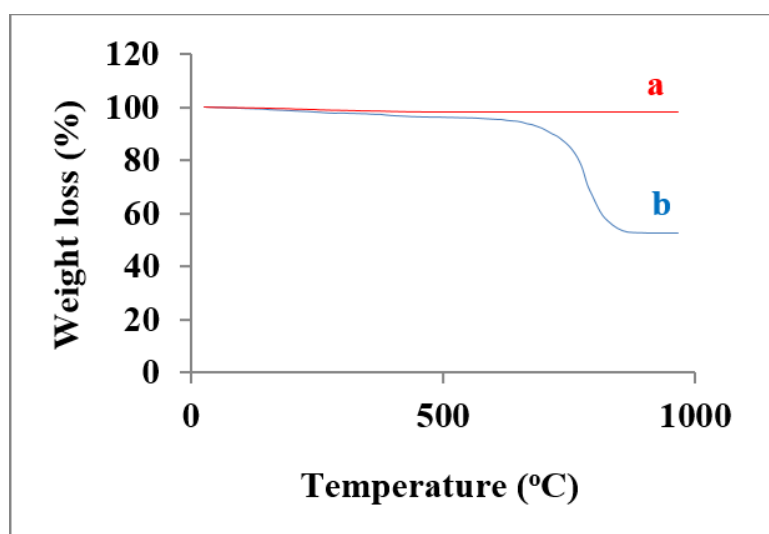


Figure 6. TGA of (a) CBS, and (b) pre-calcined snail shell.

Table 2. Optimization of reaction conditions^a.

entry	catalyst	catalyst loading (mg)	solvent	temp. (°C)	time (min)	yield (%) ^b
1	-	-	-	r.t.	60	-
2	-	-	-	100	60	-
3	-	-	water	r.t.	60	-
4	-	-	water	reflux	60	trace
5	CBS	25	-	r.t.	60	15
6	CBS	50	-	r.t.	60	27
7	CBS	50	-	reflux	60	49
8	CBS	25	water	r.t.	60	76
9	CBS	50	water	r.t.	20	93
10	CBS	75	water	r.t.	30	93
11	CBS	50	EtOH	r.t.	60	87
12	CBS	50	MeOH	r.t.	60	78
13	CBS	50	MeCN	r.t.	60	37
14	CBS	50	DCM	r.t.	60	26

^a Reaction conditions: resorcinol (1 mmol), benzaldehyde (1 mmol), malononitrile (1.2 mmol), solvent (3 mL).

^b Isolated yield.

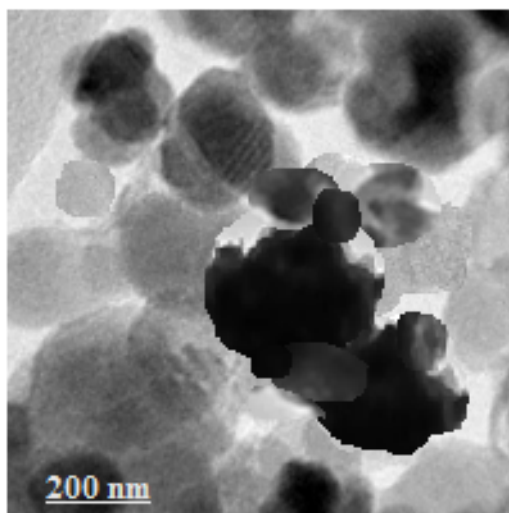


Figure 7. TEM image of CBS.

temperature (Table 2, entry 8). Excited by the results, we used different amounts of the catalyst, and the reaction was carried out in the water at room temperature conditions. It was found that 50 mg of the catalyst in an aqueous medium (3 mL) under room temperature conditions offered a good yield (93%) of **4a** (Table 2, entry 9). Further, increasing the amount of catalyst did not improve the yield of **4a** (Table 2, entry 10). Compared to other solvents, ethanol offered a good yield of **4a** (Table 2, entries 11 to 14).

Inorganic bases such as K_2CO_3 , NaOH, KOH, commercial CaO, and Na_2CO_3 were found to offer a yield in the range of 87%, 86%, 85%, 84%, and 92%, respectively, under various reaction conditions (Table 5). In comparison, a CBS offers a high yield (up to 93%) of the expected product. In order to assess the applicability of the present catalyst, a series of 2-amino-4*H*-chromene derivatives **4a-4l** were prepared under optimized reaction conditions. The results are summarised in Table 3.

The research revealed that elevating the malononitrile concentration from 1 to 1.2 mmol enhanced the reaction rate, leading to a high yield of the desired product in a short time. This observation aligns with earlier studies by Haas et al. [31] and Hruby's group [32], supporting the notion that increased malononitrile concentrations not only expedite the slow Michael addition step but also prevent the formation of side products.

The derivatives of 2-amino-4*H*-chromene were synthesized from resorcinol **3**, aromatic aldehydes **1**, and malononitrile **2** under optimized reaction conditions. Remarkably, resorcinol reacted at position-6 instead of position-2, which is presumably because of the steric hindrance between hydroxyl functional groups. From Table 3, it is clear that the reaction of resorcinol, malononitrile, and substituted benzaldehydes bearing electron-withdrawing groups completed within a short time with higher yields of corresponding products than its electron-donating counterparts. We performed all the reactions at room temperature. Fortunately, there was maximum conversion of the substrates into the products (up to 93%) without side reactions. Essentially, the resulting products were recrystallized from ethanol. All

synthesized compounds are known.

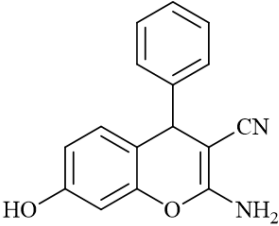
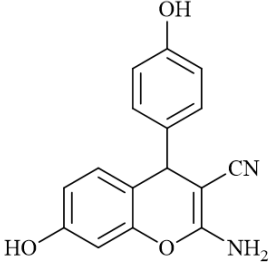
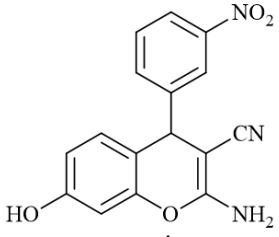
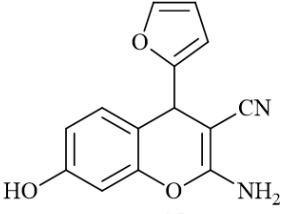
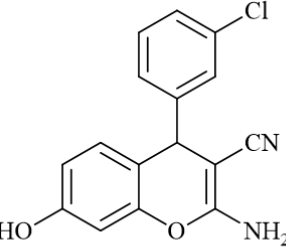
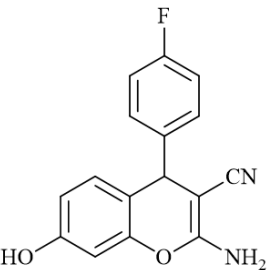
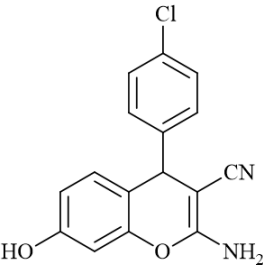
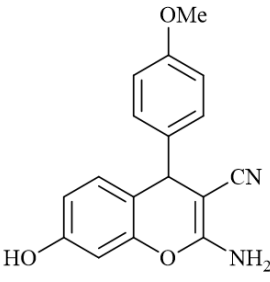
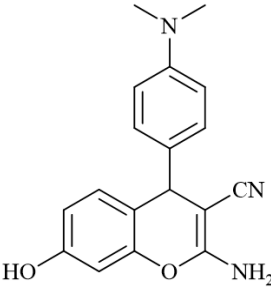
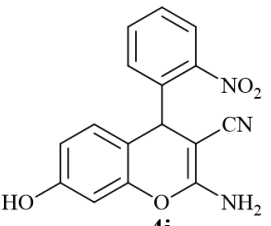
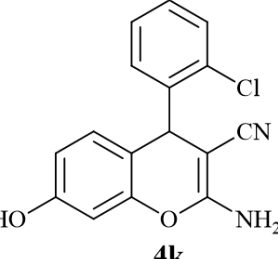
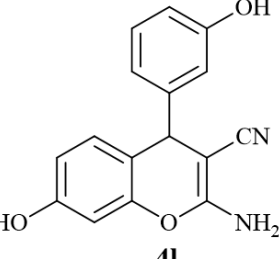
To broaden the scope of the CBS catalyst in the formation of various heterocyclic compounds, a set of 2-amino-5-oxo-4*H*,5*H*-pyrano[3,2-*c*] chromene-3-carbonitrile derivatives (**6a-6i**) was achieved successfully via the cyclization of 4-hydroxy coumarin **5**, appropriate aromatic aldehydes **1**, and malononitrile **2** under carefully optimized reaction conditions at room temperature as outlined in Table 4. From Table 4, it is clear that the reaction of 4-hydroxycoumarin with malononitrile and substituted benzaldehydes bearing electron-withdrawing groups completed in a short time with higher yields of corresponding products than its electron-donating counterparts. The position of substituent on benzaldehyde influences this reaction. *O*-substituted aldehydes offered lower yields of the products than *p*- and *m*-aldehydes.

4-hydroxycoumarin has both electrophilic and nucleophilic properties. Its reactivity is primarily linked to the nucleophilic carbon atom at position 3. In contrast to resorcinol, the formation of products from 4-hydroxycoumarin is comparatively time-consuming, which may be attributed to potential steric hindrance, electronic effects, and the complexity of its structure, that could influence the electrophilic or nucleophilic behaviour of specific atoms within 4-hydroxycoumarin [33].

3.3 Spectral characterization of representative product **4a**

The spectral characterization of compound **4a** is shown in Figure 8. FT-IR analysis (ESI) showed characteristic absorption bands at 3494 cm^{-1} due to the presence of the -OH functional group, absorption at 3322 , 2196 , and 1144 cm^{-1} attributed to the presence of NH_2 , CN, and C-O functional groups, respectively. 1H -NMR (ESI) signals in ppm appeared at δ 9.72, 6.81, and 4.66 ppm due to OH, primary amine NH_2 , and -CH protons, respectively. Triplet at δ 7.22, and a doublet at δ 7.32 ppm, 6.87, 6.78, 6.47, and 6.49 ppm, attributed to aromatic protons. The ^{13}C -NMR (ESI) signals at δ 161.0, 158.0, 149.0, 147.3, 130.1, 129.1, 128.2, 127.4, 121.0, 114.0, 113.4, 102.8, 58.4 ppm, and

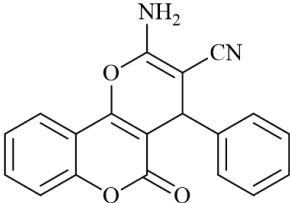
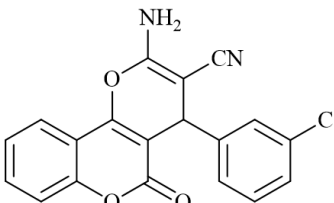
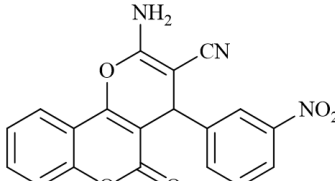
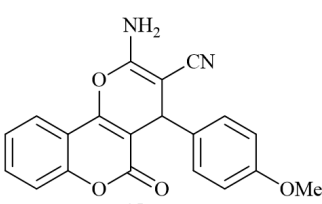
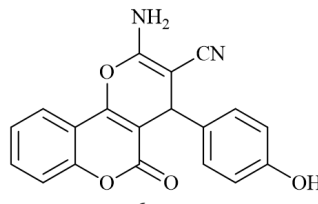
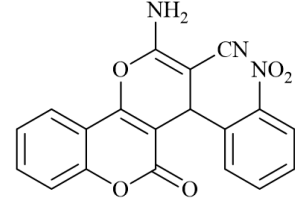
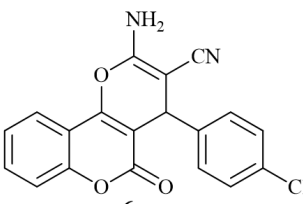
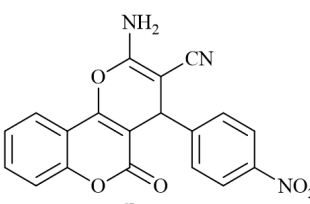
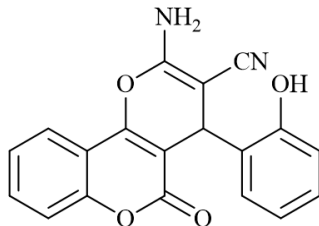
Table 3. Synthesis of 2-amino-3-cyano-7-hydroxy-4*H*-chromene derivatives (time in min., and yield in %).

 <p>4a 20 min., 93%</p>	 <p>4b 48 min., 87%</p>	 <p>4c 39 min., 86%</p>
 <p>4d 55 min., 86%</p>	 <p>4e 22 min., 91%</p>	 <p>4f 24 min., 89%</p>
 <p>4g 21 min., 90%</p>	 <p>4h 35 min., 86%</p>	 <p>4i 45 min., 84%</p>
 <p>4j 42 min., 86%</p>	 <p>4k 26 min., 90%</p>	 <p>4l 45 min., 87%</p>

physical constant 235 °C (Lit. 234-236 °C) [36] revealed the formation, and the confirmation of the compound **4a**. Drawing upon previous findings [37, 38] and the outcomes of our investigations, we present a comprehensive and plausible mechanism represented in scheme 2. A CBS catalyst is composed of many metal oxides; therefore, the active sites of the catalyst are unclear. Within the CBS catalyst, CaO emerges as the primary component, possibly responsible for the promotion of the reaction. The intermediate 2-arylidene malononitrile plays a crucial role in the synthe-

sis of 2-amino-4*H*-chromenes. A CBS catalyst, enriched with basic active sites, possibly abstracts proton, enhancing the reaction rate and facilitating the rapid development of the desired product. According to mechanistic insights from studies conducted by Calvino-Casilda et al. [39] and Khare et al. [40], the catalytic process involves multiple steps. These steps include the creation of a carbanion by proton abstraction, which attacks the carbonyl group of the aldehyde, forming a C-C bond adduct. This adduct then eliminates a hydroxide ion to form the Knoevenagel prod-

Table 4. Synthesis of 2-amino-5-oxo-4*H*,5*H*-pyrano[3,2-*c*] chromene-3-carbonitrile derivatives (time in min., and yield in %).

 <p>6a 72 min., 88%</p>	 <p>6b 65 min., 91%</p>	 <p>6c 88 min., 86%</p>
 <p>6d 84 min., 88%</p>	 <p>6e 97 min., 85%</p>	 <p>6f 92 min., 87%</p>
 <p>6g 60 min., 89%</p>	 <p>6h 85 min., 84%</p>	 <p>6i 94 min., 85%</p>

uct, 2-arylidinemalononitrile. Finally, a water molecule is produced, and the catalyst's active sites are restored. Subsequently, in the presence of a CBS catalyst, the Knoevenagel product reacts with resorcinol via Michael addition and, finally, an intramolecular cyclization and tautomerization of intermediates to provide the desired 2-amino-4*H*-chromenes.

3.4 Reusability of the catalyst

The assessment of catalytic reusability involved conducting the reaction with resorcinol **3**, benzaldehyde **1**, and malononitrile **2** under optimized conditions (Fig. 9). In the initial run, the fresh catalyst was introduced, and the reaction mixture was stirred at room temperature. Following the first run, the reaction mixture underwent filtration. The

resulting precipitate was dissolved in hot ethanol and filtered. The recovered catalyst was then dried in an oven at 100 °C for one hour, ready for the subsequent run. Over five consecutive cycles, a marginal reduction in yield was observed. This decline is likely attributable to impurities and the leaching of active metals from the catalyst. Across the five cycles, the yield of **4a** was 93%, 91%, 89%, 89%, and 87%, respectively. After the 5th run, the recovered catalyst was characterized by SEM and EDS analysis. The SEM image (Fig. 10) exhibited that the particles had a spherical shape and were agglomerated, while EDS analysis (Fig. 11) showed a slight reduction in Ca species (45.33%).

Table 5. Comparative study of various catalysts used for the synthesis of 2-amino-4*H*-chromenes.

entry	catalyst	reaction conditions	yield (%)	ref.
1	K ₂ CO ₃ (0.25 mmol)	70 °C, H ₂ O (5 mL), stirring, 25 min.	87	[34]
2	NaOH (10 mol%)	50 °C, grinding, 30 min.	86	[35]
3	KOH (10 mol%)	50 °C, grinding 30 min.	85	[35]
4	Commercial CaO (10 mol%)	room temperature, 60 min.	84	-
5	Na ₂ CO ₃ (10 mol%)	50 °C, grinding, 30 min.	92	[35]
6	CBS (50 mg)	room temperature, stirring, H ₂ O	93	this work

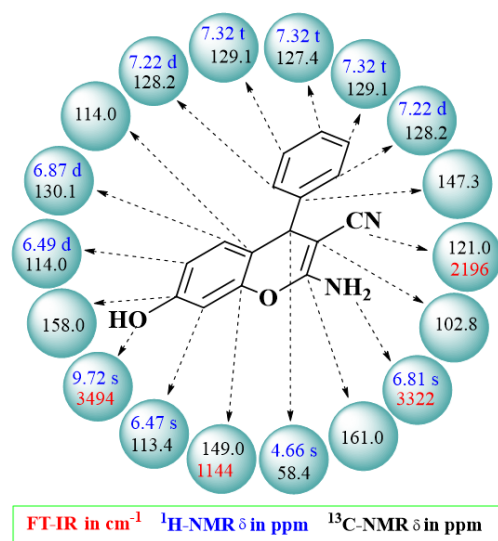


Figure 8. FT-IR, NMR characterization of representative product 4a.

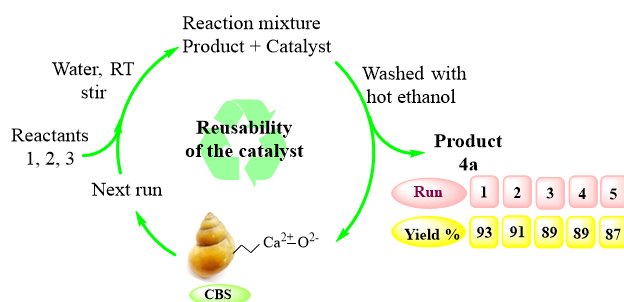


Figure 9. Reusability of the CBS catalyst.

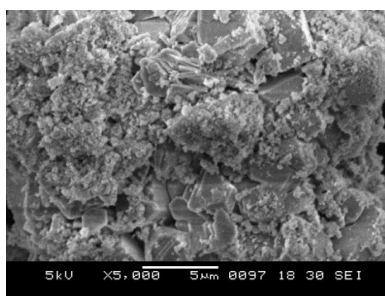


Figure 10. SEM image of CBS catalyst after the 5th run.

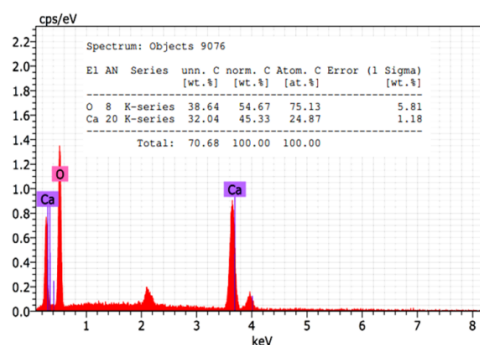
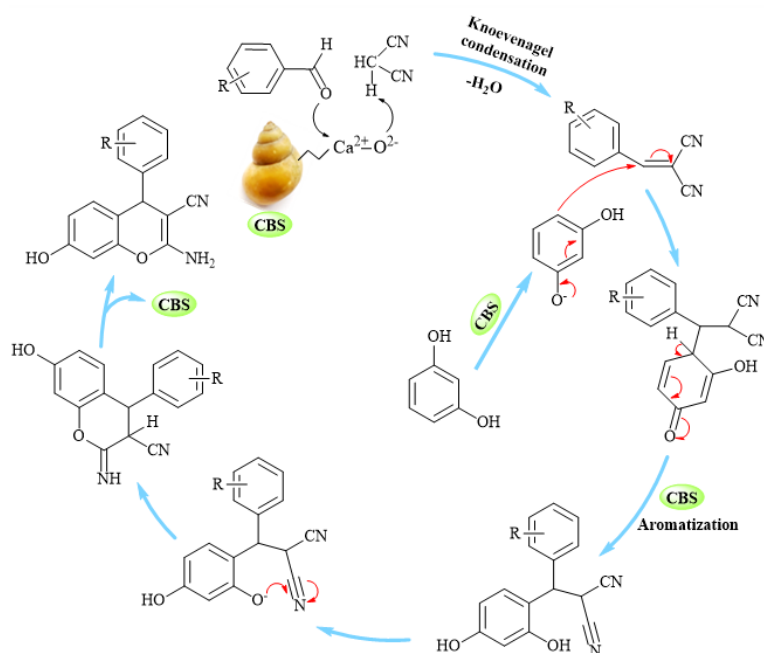


Figure 11. EDS analysis of CBS catalyst after the 5th run.



Scheme 2. Plausible mechanism for synthesis of 2-amino-4H-chromenes.

4. Conclusion

The calcined snail shell-derived heterogeneous catalyst has demonstrated remarkable catalytic efficacy in the synthesis of functionalized chromene derivatives within an aqueous medium at ambient temperature, yielding targeted products with quantitative efficiency. The enhanced catalytic activity can be attributed to the enrichment of CaO in the calcined snail shell, facilitating accelerated reaction kinetics and optimizing the efficiency of the desired reaction pathway. This investigation underscores the utilization of naturally abundant biowaste material as a catalyst, employing water as a green reaction medium and conducting reactions at ambient temperature, thereby establishing a green and economically viable protocol. Consequently, this approach aligns with environmentally friendly practices.

Acknowledgement

The authors express gratitude to Shivaji University, Kolhapur, ACS College, Palus, and KRP Kanya Mahavidyalaya, Islampur, for providing the essential facilities.

Authors Contributions

All authors have contributed equally to prepare the paper.

Availability of Data and Materials

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Conflict of Interests

The authors declare that they have no known com-

peting financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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