Coconut endocarp shell ash (CESA): a non-conventional catalyst for green synthesis of 2-amino-4\(H\)-benzochromenes

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Received: 29 July 2022 / Accepted: 26 September 2022 / Published online: 18 October 2022
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Abstract
In the present research, the coconut endocarp shell as a natural waste was converted into a valuable non-conventional catalyst by a simple thermal treatment, namely coconut endocarp shell ash (CESA). The prepared CESA was characterized using several analytical techniques, including TGA, FT-IR, XRD, BET, SEM, and EDX. The catalytic property of the CESA was examined in the synthesis of pharmaceutically active 2-amino-4\(H\)-benzochromene derivatives via one-pot three-component condensation of aldehydes, malononitrile, and \(\alpha\) or \(\beta\)-naphthol in ethanol at room temperature. The most promising aspects of the presented approach are the high catalytic efficiency, short reaction time, excellent yield of products, operational simplicity, waste to wealth, and optimization with the design of experiment. Moreover, the CESA catalyst was recycled five times without any apparent loss of its catalytic activity.

Graphical abstract

Extended author information available on the last page of the article
Keywords  Coconut endocarp shell · Ash · Multi-component reaction · Naphthols · Green chemistry

Introduction

In the last few decades, green chemistry principles have played an important role in protecting the environment. Thus, modern synthetic chemists make continuous efforts to come up with green principles while conducting organic transformation with eco-friendly processes, especially eco-friendly catalyst [1–3]. In general, green chemistry principles focus on the design and application of clean and safe procedures in order to maximize efficiency and productivity, use renewable bio-degradable materials, minimize by-products and hazardous reagents, which reduce the use of hazardous chemicals that are risky to the environment and human beings. From this point of view, some aspects of green chemistry, such as multi-component reactions and reusable catalyst, can be combined, effectively following green chemistry protocols can be expected [4, 5].

Multi-component reaction (MCR) is an efficient, powerful technique that achieves a significant role in modern synthetic organic chemistry due to the fact that all the required reactants are incorporated into one pot to produce the desired products in a single step without isolation of any intermediate. Further, using a one-pot, multi-component reaction approach could result in several advantages such as operational simplicity, flexibility, shortage of synthetic routes, atom economy, decreased pollution, low cost, straightforward reaction design, and simple purification of target products. Moreover, MCRs with a heterocyclic moiety are particularly used in the construction of biologically active scaffolds and drug-like molecules, which have increased interest in the research community [6–9].

In addition, 2-amino-4H-benzochromene represents an important class of heterocyclic structural motifs. It is found in a number of natural products with remarkable biological active molecules [10] and varied pharmacological properties such as anti-tumour or tumour vascular disrupting agent [11, 12], anti-proliferative [13, 14], cytotoxic [15], anti-cancer and SRC kinase inhibitory action [16], anti-bacterial [17], anti-fungal [18], and anti-rheumatic actions [19]. Figure 1 represents some of the bioactive 2-amino-4H-benzochromene compounds that possess different types of pharmaceutical activities.

A literature survey revealed that, because of the biological activity of these compounds, by one-pot three-component reaction of aryl aldehyde, malononitrile, and β- or α-naphthol, several improved protocols have been investigated to synthesize 2-amino-4H-benzochromene by employing various catalysts, such as piperidine [20], TBABr [21], basic alumina [22], hexadecyl trimethyl ammonium bromide (HTMAB) [23], TiCl4 [24], NaOH [25], Amberlyst A-21 [26], KF-Al2O3 [27], 1,4-diazabicyclo[2.2.2]octane [28], Mg/Al hydrotalcite [29], Na2HPO4 [30], Fe(HSO4)3 [31], thiourea dioxide [32], p-dimethylaminopyridine [33], ionic liquids [34–37], nano-zeolite clinoptilolite [38], PANDMAPF [39], Ni–Al2O3 [40], SILLP [41], sodium malonate [42], potassium hydrogen phthalate [43], Potassium phthalimide [44], potassium 2-oxoimidazolidine-1,3-diide (POImD) [45];
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Also, some nanocatalyst or ionic liquid-supported nanocatalysts have been used for these transformations including Fe₃O₄@SiO₂@BenzIm-Fc[Cl]/BiOCl [46], CNT-Fe₃O₄ IL [47], SiO₂@Im-Fc[OAc] [48], Fe₃O₄@PS-Arg MNPs [49], γ-Fe₂O₃@HAp@CPTMS@AT [50], and GO Fc@Fe₃O₄ [51]. However, for the synthesis of 2-amino-4H-benzochromenes, many reported methods have effective and their own merits, but they suffer from some drawbacks such as harsh reaction conditions, prolonged reaction times, use of toxic and expensive solvents, difficult workup procedures, and furnishing the products in unsatisfactory yields. Also, the nanocatalyst plays an important role in organic transformation for selectivity and determining yield [52–64]. In recent years, the use of agro-food waste material as a catalyst has received significant attention in green protocols for multi-component synthesis. Therefore, natural feedstock as catalyst offers a promising alternative tool for organic processes due to their ability to act as catalysts with large surface area, biodegradability, low toxicity, low cost, and reusability properties [4, 65].

Therefore, the main goal of the current research work is to investigate the organic transformation through the utilization of naturally sourced catalysts. So, to avoid the

Fig. 1 Some examples of biologically active 2-amino-4H-benzochromene compounds
problem of disposal of solid waste biomass and to minimize possible environmental pollution, the naturally waste biomass used for the development of promising catalysts to make synthetic protocols cheap can be considerably reduced [66–68]. 

*Coconut nucifera* is a plant from the *Areceae* family (Palm family). On over 10 million hectares of land, coconuts are grown all over the world. India, Indonesia, and the Philippines account for over 75% of global coconut production [69, 70]. According to the literature, the coconut shell is rich in organic substance, having 33.61% cellulose, 36.51% lignin, 29.27% pentose, and 0.61% ash and inorganic matter [71].

In continuation of our present research, focusing on replacing inefficient traditional protocols with more efficient, cost-effective, and environmentally friendly alternatives [72–76], the present research work is to explore that naturally sourced catalytic system is a promising alternative tool in organic transformation. Herein, we report the first time a straightforward, cheap, and environmentally benign application of coconut endocarp shell ash (CESA) as a recoverable green catalyst, for synthesizing 2-amino-4*-H*-benzochromenes, from the condensation of β- or α-naphthol, aromatic aldehydes with malononitrile at room temperature in ethanol solvent (Scheme 1). This is a clean, efficient synthetic method, which preserves the simplicity as well as consistently gives good-to-excellent yields of corresponding products.

**Scheme 1** CESA-catalysed synthesis of 2-amino-4*-H*-benzochromenes

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**Experimental procedure**

**Materials and methods**

All chemicals and laboratory-grade reagents used for this study were obtained from Sigma-Aldrich and Merck chemical companies and were utilized without further purification. An analytical thin-layer chromatography (TLC) technique was used to check the purity of substances, and the progress of the reaction was performed using Merck 0.2 mm silica gel 60 F-254 Al-plates. The confirmation and characterization of the isolated pure form of products by spectroscopic data (IR, 1H NMR, 13C NMR, mass spectra). Infrared (FT-IR) spectra were obtained in KBr pellets on a Bruker ALPHA FT-IR spectrometer. Brucker-AC spectrometers in CDCl₃ and DMSO as solvent (for 1H NMR at 300 MHz and for 13C NMR at 75 MHz) are used to record 1H and 13C NMR spectral data. A Shimadzu QP2010 GCMS with an iron temperature of 280 °C was used to obtain the mass spectra. The melting points of purified...
derivatives were determined using the DBK programmable melting point as an open capillary method. Thermal gravimetric analysis (TGA) was measured using a TA SDT Q600 V20.9 Build instrument in the presence of air at a linear heating rate of 10 °C min⁻¹ from 25 to 1000 °C. For measurement of the scanning electron microscope (SEM), a JEOL (Tokyo, Japan) JSM-5200 was used. The N₂ adsorption–desorption isotherm for BET was recorded with a Micromeritics ASAP 2010 surface area and porosity analyser. An energy-dispersive X-ray spectroscopy analysis without oxygen was recorded with the Quanta 200 3D FEI scanning electron microscope.

**Preparation of coconut endocarp shell ash (CESA) catalyst**

To prepare the CESA catalyst, bio-waste endocarp shells of *Cocos nucifera* were collected from the local food market. The collected coconut endocarp shells (CESs) (Fig. 2a) were washed by using distilled water to remove dirt and sun-dried for two days. The dried CES (50 g) was broken into small pieces by using a mortar and pestle (Fig. 2b) and heated in a muffle furnace up to 800 °C for 2 h in a silica crucible. A fine soft ash (Fig. 2c) was obtained and was named as coconut endocarp shell ash (CESA) (Fig. 2c). Further, CESA was used as a catalyst for the synthesis of 2-amino-4H-benzochromenes.

**General procedure for the synthesis of 2-amino-4H-benzochromene derivatives**

In a clean and dry 25-mL round-bottom flask, a CESA catalyst (10 wt. %) was added to the mixture of aryl aldehyde 1 (1 mmol), malononitrile 2 (1 mmol), β-napthol 3a or α-naphthol 3b (1 mmol) and ethanol. Then, at room temperature, the reaction mixture was magnetically stirred for an appropriate time until the desired product was formed completely. The reaction progress was monitored by TLC (ethyl acetate: hexane 1:9). After the reaction was completed, the reaction mixture was treated for solvent extraction using ethyl acetate (4 × 10 mL). The combined organic phase was first washed with water and dried (Na₂SO₄), and the solvent was removed under reduced pressure to obtain a crude product. The further obtained crude products were purified by recrystallization using 96% ethanol. The identities of the synthesized products were established by FT-IR, ¹H NMR, and ¹³C NMR spectroscopic analysis.

![Fig. 2 Preparation of CESA catalyst](image-url)
methods. Additionally, the melting points of the synthesized products were measured, and they agree with values previously reported elsewhere in the literature.

**Results and discussion**

**Characterization of coconut endocarp shell ash (CESA) catalyst**

To identify the active sites of the CESA catalyst, it was characterized by using different analytical methods, including DSC-TGA, FT-IR, XRD, EDX, BET, and SEM.

**DSC-TGA analysis**

The thermal behaviour of coconut endocarp shell ash (CESA) was investigated by using thermogravimetric analysis (TGA) inflow of nitrogen atmosphere. The usual sample loading was 7–8 mg (Fig. 3). The TGA of CESA shows the temperatures at which it is decomposed when heated in a controlled environment. At temperatures that ranged from 0 to 1000 °C, four distinct stages of weight loss were observed. The results reveal that CESA showed the observed weight change below 100 °C. In the first step, minor weight loss at temperatures below 130.70 °C was 2.915 % (0.2519 mg), and in the second step, another weight loss...
that occurred between 130.70 °C and 177.70 °C was 2.509% (0.2168 mg) due to the loss of adsorbed moisture. In the third step, weight loss between temperature ranges of 177.70 °C and 627.76 °C was 5.910 % (0.5108 mg) due to the decomposition of organic compounds such as alkaloids, carotenoids, pectins, tannins, flavonoids, terpenoids, and chlorides. The decomposition of metal carbonates caused the 10.90% (0.9419 mg) weight loss in the fourth step between the temperatures of 627.76 °C and 740.23 °C, while metal oxides and silica were responsible for the 71.34% (6.166 mg) weight of residue remaining after the temperatures of 984.10 °C.

**FTIR analysis**

Fourier transform infrared (FT-IR) analysis was used to determine the active functional groups in the CESA catalyst. In the FTIR spectrum of CESA (Fig. 4), the strong absorption bands that occurred in the range of 2382 cm⁻¹, 2311 cm⁻¹, 1515 cm⁻¹, 1028 cm⁻¹, 628 cm⁻¹ clearly show that the presence of metal carbonates and the absorption band at 1695 cm⁻¹ indicate the presence of the C=O group of carbonate. Also, the weak absorption stretching band that appears at 3362 cm⁻¹ can be attributed to the presence of the OH group in the CESA catalyst that supports the formation of metal hydroxides due to the absorption of moisture from the environment.

![FTIR analysis of CESA catalyst](image-url)
XRD analysis

The phase composition of the synthesized CESA catalyst was analysed by X-ray diffraction (Fig. 5). Oxides and carbonates were the most dominant species after thermal treatment of CES as strong characteristic peaks of K\textsubscript{2}O and K\textsubscript{2}CO\textsubscript{3} were observed at 2\(\theta\) = 24.26, 28.27, 29.35, 31.52, 40.85, 50.09 (JCPDS reference file No—77-2176 and 87-0730). The XRD pattern shows that K\textsubscript{2}O has identical crystal structures to cubic type (space group Fm\textsubscript{3}m). The existence of CaO and CaCO\textsubscript{3} was also observed at 2\(\theta\) = 30.25, 39.33, 43.10, 47.43 (JCPDS reference file No: 82-1691 and 87-1863). In addition, several small peaks corresponding to KCl, MgO, SiO\textsubscript{2} (JCPDS card no 004-0587, 65-0476, 89-3609, respectively) were also seen. Thus, the increase in intensities of the peaks was noticed for potassium compounds after calcination of the CESA which had strong base sites [77]. The EDX analysis strongly complimented the findings of XRD and indicated that dominant elements in CESA were K (40.31%), Ca (33.72%) followed by Si (10.07%), Fe (5.81%), Na (5.37%), Cl (2.51%) and Mg (1.83%) and trace amount of Mn (0.38%) (Fig. 6). The K\textsubscript{2}O as major compound in CESA possesses basic surface sites, which make them highly efficient in catalytic process applications.

![Fig. 5 XRD Pattern of CESA catalyst](image-url)
EDX analysis

The type of elements in coconut endocarp shell ash (CESA) was investigated by recording EDX. It is shown in Fig. 6. The report reveals that this catalyst included the oxides of K, Na, Si, and Ca elements present with uniform distributions and moderate-to-less distributions of elements, including Mg, Mn, Fe and Cl. The carbonates, oxides, and hydroxides of corresponding metals give basicity to the CESA catalyst, which plays a crucial role in the catalyst.

BET analysis

Figure 7 indicates the data related to surface area, mean pore volume, and average pore radius for the activated CESA catalyst. The surface area and mean pore volume of the CESA catalyst were 168.92 m²/g and 0.093536 cm³/g⁻¹, respectively. The mean pore radius was 2.215 nm, respectively. In general, the smaller particle size of catalyst provides large contact area for catalysing the reaction [77].

SEM analysis

The synthesized CESA catalyst was analysed by employing scanning electron microscopy (SEM) to determine the surface morphology and particle shape as represented in Fig. 8. These SEM images clearly illustrate the CESA particles were observed with irregular sizes; they also have a porous nature [78], which provides more surface area for their catalytic activity.
Optimization of the reaction conditions

After this initial success, the efficiency of naturally sourced CESA catalyst was investigated by choosing the reaction of 4-chlorobenzaldehyde $1b$ (1 mmol), malononitrile $2$ (1 mmol), and β-naphthol $3a$ (1 mmol) as a model substrate for the synthesis of 3-amino-1-(4-chlorophenyl)-1$H$-benzo[f]chromene-2-carbonitrile $4b$. First, we concentrated on determining the optimal reaction conditions, which included a variety of solvents, amounts of synthesized CESA catalyst, and temperatures for
model reaction. These were examined for our proposed synthetic conversion, and those are summarized in Table 1.

Preliminary optimized reaction conditions indicated that in the absence of the catalyst and solvent, even under room temperature or at reflux conditions (Table 1, entry 1), only a trace amount of the desired product 4b was obtained (Table 1, entries 1, 2). However, the model reaction was examined in the absence of a catalyst, but in the presence of ethanol and water as solvents, only a small amount of the desired product 4b was obtained at room temperature (Table 1, entries 3, 4). This result reveals that a catalyst must be required for this transformation. We notice that, in the absence of solvents, the yield of desired product 4b is improved due to the addition of the CESA catalytic amount, but there is no further improvement in the yield of the desired product after adding the catalytic amount (Table 1, entry 5) and

Table 1  Optimization of reaction conditions for the synthesis of 4b

| Entry | CESA catalyst (wt%) | Solvent | Temp. (°C) | Time (min) | Yield (%)a |
|-------|---------------------|---------|------------|------------|------------|
| 1     | –                   | –       | RT         | 60         | Trace      |
| 2     | –                   | –       | Reflux     | 50         | Trace      |
| 3     | –                   | EtOH    | RT         | 40         | 35         |
| 4     | –                   | H2O     | RT         | 40         | 20         |
| 5     | 5                   | –       | RT         | 40         | 42         |
| 6     | 5                   | –       | Reflux     | 35         | 42         |
| 7     | 2                   | EtOH    | Reflux     | 05         | 85         |
| 8     | 5                   | EtOH    | RT         | 05         | 90         |
| 9     | 10                  | EtOH    | RT         | 05         | 98         |
| 10    | 12                  | EtOH    | RT         | 05         | 98         |
| 11    | 10                  | EtOH    | Reflux     | 15         | 88         |
| 12    | 10                  | MeOH    | RT         | 20         | 80         |
| 13    | 10                  | Toluene | RT         | 20         | 48         |
| 14    | 10                  | THF     | RT         | 20         | 42         |
| 15    | 10                  | H2O     | RT         | 20         | 84         |
| 16    | 10                  | CH3CN   | RT         | 24         | 64         |

Reaction conditions: 4-chlorobenzaldehyde 1b (1 mmol), malononitrile 2 (1 mmol), β-naphthol 3a (1 mmol) various amount of CESA catalyst with solvent (5 mL)

aIsolated yields
even at reflux conditions (Table 1, entry 6). The result indicates that there is a necessity of solvent to improve the yield of the desired product. Interestingly, when this model reaction was tested out in ethanol as a solvent with varying catalytic amounts (2, 5, 10, or 12 wt%) of CESA at room temperature, gave 85–98% corresponding product yield after 05 min (Table 1, entries 7–10).

Notably, it was found that the yield of the desired product drastically increased when increasing the catalytic amount from 2 to 10 wt% in the presence of EtOH (Table 1, entry 7–9). In contrast, with raising the catalytic amount, there were no improvements in the yield of desired product 4b (Table 1, entry 10). It was found that at reflux conditions, there were no improved effects on the product yield (Table 1, entry 11). Therefore, 10 wt% of CESA catalyst in 5 mL of ethanol solvent is sufficient to show the reactivity of the reactants (1 mmol each), and the corresponding product 4b was obtained at a 98% yield within 05 min. (Table 1, entry 9). Furthermore, the optimization of the model reaction was investigated by using MeOH, THF, CH3CN, and H2O as solvents, and the yield of the desired product was obtained from 42 to 84% (Table 1, entries 12–16). Thus, the best yield of the desired product was achieved in optimal ethanol solvent (5 mL) by using 10 wt. % of CESA catalyst at room temperature (Table 1, entry 9).

Therefore, to compare the catalytic activity of the CESA catalyst, the model reaction was carried out under optimized reaction conditions in the presence of analytical grade alkali metal carbonates and metal oxides (Table 2, entries 1–8). The result

| Entry | Catalyst   | Time (min) | Yield (%)b |
|-------|------------|------------|------------|
| 1     | K2CO3      | 110        | 60         |
| 2     | Na2CO3     | 110        | 58         |
| 3     | CaCO3      | 110        | 46         |
| 4     | MgCO3      | 110        | 50         |
| 5     | CaO        | 110        | 62         |
| 6     | MgO        | 110        | 62         |
| 7     | ZnO        | 110        | 58         |
| 8     | CESA       | 05         | 98         |

aReaction conditions: 4-chlorobenzaldehyde 1b (1 mmol), malononitrile 2 (1 mmol), β-naphthol 3a (1 mmol) various amount of CESA catalyst with solvent (5 mL).
bIsolated yields
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shows that only lower amounts of the product were observed on TLC after 110 min. (Table 2, entries 1–7), indicating that a synergetic effect of all alkali metal carbonates and oxides along with transition metals (Mn and Fe ions) in CESA provides a better catalytic activity for this transformation (Table 2, entry 8).

After finding the promising optimal reaction conditions for the model reaction, to extend the scope of catalytic activity of the CESA catalyst, to prepare 2-amino-4\textsubscript{H}-benzochromene using the reaction between various aryl aldehydes (1\textsubscript{a–p}), malononitrile (2) with β-naphthol (3\textsubscript{a}), were investigated under optimum conditions. The results are presented in Table 3. According to the results in Table 3, the presence of electron-withdrawing or electron-releasing groups on their aryl aldehyde ring was successfully participated in optimal reaction conditions and gave the products with excellent yields 4\textsubscript{a–m}. It was noticed that aryl aldehydes having inductively electron withdrawing groups increase the electrophilicity of the carbonyl group and have somewhat faster reaction rates than those with electron-releasing groups. It was also discovered that the yields of meta- and para-substituted aryl aldehydes were higher than those of ortho-substituted aryl aldehydes. Generally, this reaction is straightforward, and the desired product precipitates out of the reaction mixture. Isolation of the catalyst or evaporation of organic solvent from the reaction mixture affords pure products using simple filtration. All the desired products 4\textsubscript{a–m} of this reaction give good-to-excellent yields within short reaction times under the optimized reaction conditions. The structural confirmation of the isolated pure products 4\textsubscript{a–m} was investigated by melting point, IR, \textsuperscript{1}H NMR, and \textsuperscript{13}C NMR spectral data and is given in the supporting information.

The excellent performance of the synthesized CESA catalyst in the synthesis of biologically active 2-amino-4\textsubscript{H}-benzochromenes (4\textsubscript{a–m}) from various aldehydes, malononitrile and β-naphthol encouraged us to study its effect on the synthesis of 2-amino-4\textsubscript{H}-benzochromenes (5\textsubscript{a–l}) by replacement of the β-naphthol with α-naphthol. Several derivatives of the 2-amino-4\textsubscript{H}-benzochromenes have been synthesized, and the results are presented in Table 3. It was discovered that the CESA catalyst provides a good-to-excellent yield of the desired product in a shorter reaction time.

In terms of green chemistry, the recyclability of the catalyst with high efficiency of the product yield of the heterogeneous CESA catalyst is greatly desirable. Recyclability was the most important point for these catalysts. Therefore, to prove the recyclability of the CESA catalyst, it was checked in the synthesis of 2-amino-4\textsubscript{H}-benzochromene 4\textsubscript{b} using 4-chlorobenzaldehyde 1\textsubscript{b}, malononitrile 2 and β-naphthol 3\textsubscript{a} under the optimized reaction conditions.

After reaction completion, the reaction mixture was separated with ethyl acetate (4 × 20 mL) to obtain product 4\textsubscript{b} without the use of column purification. The remaining aqueous phase of the CESA catalyst was dried in an oven for 3 h at a temperature 120 °C and reused for the next run of the model reaction under the same reaction conditions (scheme 2). The result presented in Scheme 2 demonstrates that the yield of the desired product with each reuse of the catalyst is slightly reduced to a small extent. Scheme 2 shows that the isolated CESA catalyst from the reaction mixture was re-used for five successive runs without significantly losing catalytic efficiency.
### Table 3  Substrate scope of 2-amino-4H-benzochromene derivatives

| Entry | Aldehydes | Naphthols | Product \((4 \& 5)\) | Time (min.) | Yield \(\%\) | M.P. (°C) [Ref.] |
|-------|-----------|-----------|-----------------|-------------|-------------|-----------------|
| 1     | 1a        | β-naphthol | 4a              | 10          | 96          | 271–273 [38]    |
| 2     | 1b        | β-naphthol | 4b              | 05          | 98          | 205–206 [38]    |
| 3     | 1c        | β-naphthol | 4c              | 12          | 95          | 290–292 [50]    |
| 4     | 1d        | β-naphthol | 4d              | 18          | 96          | 192–194 [49]    |
| 5     | 1e        | β-naphthol | 4e              | 20          | 94          | 249–251 [49]    |
| No. | Reaction | Product | Yield | R.T. | Remarks |
|-----|----------|---------|-------|------|---------|
| 6   | 4f       | 1f      | 10    | 97   | 186–188 [38] |
| 7   | 4g       | 1g      | 18    | 94   | 259–260 [38] |
| 8   | 4h       | 1h      | 15    | 90   | 216–218 [28] |
| 9   | 4i       | 1i      | 10    | 96   | 240–242 [49] |
| 10  | 4j       | 1j      | 20    | 90   | 225–227 [48] |
| 11  | 4k       | 1k      | 22    | 88   | 246–248 [30] |
Table 3 (continued)

|   | Formula | Name   | R1  | R2  | R3  | R4  | R5  | R6  | R7  | R8  | R9  |   |
|---|---------|--------|-----|-----|-----|-----|-----|-----|-----|-----|-----|---|
|12 | CHO Cl  | β-naphthol | 18 | 92  |      |     | 256–258 [38] |
|13 | CHO Br  | β-naphthol | 10 | 96  |     |     | 229–231 [New] |
|14 | CHO     | α-naphthol | 12 | 96  | 176–177 [38] |
|15 | CHO Cl  | α-naphthol | 10 | 96  | 230–232 [38] |
|16 | CHO OH  | α-naphthol | 20 | 88  | 246–248 [38] |
|17 | CHO OCH3| α-naphthol | 15 | 95  | 188–190 [45] |
Table 3 (continued)

| No. | Reactant | Yield | T (°C) | Ref. |
|-----|----------|-------|--------|------|
| 18  | α-naphthol | 20    | 90     | 205–206 [38] |
| 19  | α-naphthol | 12    | 96     | 232–234 [38] |
| 20  | α-naphthol | 14    | 88     | 257–259 [28] |
| 21  | α-naphthol | 15    | 92     | 244–246 [28] |
| 22  | α-naphthol | 10    | 97     | 215–217 [28] |
Table 3 (continued)

| Reaction conditions: Aldehydes 1a–m (1 mmol), malononitrile 2 (1 mmol), β-naphthol 3a (1 mmol) or α-naphthol 3b (1 mmol), catalytic amount of CESA catalyst (10 wt%) in ethanol (5 mL) at room temperature |

| Run | Yield | Time |
|-----|-------|------|
| 1st | 98    | 5    |
| 2nd | 98    | 5    |
| 3rd | 98    | 5    |
| 4th | 97    | 5    |
| 5th | 96    | 5    |

*Yields refer to isolated products*

Scheme 2  Recyclability of CESA catalyst
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A hot filtration test was used to detect the heterogeneity of the recovered CESA catalyst. The results show that detectable methods with EDX (Fig. 6) have a similar composition, with K (40.21%), Ca (33.72%), Si (10.07%), Na (5.37%), Fe (5.81%), Mg (1.83%), Cl (2.51%), and Mn (0.38%).

The catalytic activity of the CESA after five runs was confirmed by characterizing XRD, SEM, and EDX. As shown in the XRD pattern of the CESA catalyst after 5th run (Fig. 9), the phase composition peaks of the CESA, after 5 times of recovery, observed at same 2θ angle but its intensity of peak decreased. It can be...
concluded that there is a slight decrease in the product yield due to the reduction of amount of metal carbonates, oxides, and hydroxides. Also, comparison to the SEM image results of recycled CESA catalyst shows that, without any major significant change, CESA particles have slightly decreased in sizes (Fig. 10). Moreover, the EDX spectra of the recycled CESA catalyst are displayed in Fig. 11. According to the EDX pattern of CESA after the recovery test, suggesting the CESA has almost the same phase composition of the elements in the catalyst, after consecutive 5 runs. The results shown in Figs. 9, 10, and 11 indicate that CESA has the characteristics of an excellent reusable catalyst.
### Table 4  Comparison of the activity of CESA catalyst with reported catalyst for the synthesis of 4b and 5b

| Naphthol | Entry | Reaction conditions | Time (min.) | Yield (%) | Ref. |
|----------|-------|---------------------|-------------|-----------|------|
| β-Naphthol | 1 | Hexadecyl trimethyl ammonium bromide (HTMAB) (10 mol%)/H₂O/Reflux | 360 | 82 | [23] |
|          | 2 | KF-Al₂O₃ (200 mg)/Grinding | 1440 | 84 | [27] |
|          | 3 | Diazabicyclo[2.2.2]octane (30 mol%)/EtOH(5 mL)/RT | 120–240 | 72 | [28] |
|          | 4 | Na₃HPO₄ (5 mol%)/120 °C | 60 | 92 | [30] |
|          | 5 | Fe(HSO₄)₃ (0.034 mg)/CH₃CN (10 mL)/Reflux | 240 | 85 | [31] |
|          | 6 | Thiourea dioxide (10 mol%)/H₂O(2 mL)/50 °C | 480 | 87 | [32] |
|          | 7 | Basic ionic liquid (20 mol%)/70 °C | 03 | 90 | [34] |
|          | 8 | Nano zeolite clinoptilolite (0.01 gm.)/H₂O (5 mL)/Reflux | 20 | 92 | [38] |
|          | 9 | SiO₂@Im-Fc[OAc] (10 mg)/90 °C | 20 | 92 | [48] |
|          | 10 | Fe₃O₄@PS-Arg MNPs (0.07 g)/EtOH (5 mL)/Reflux | 10 | 95 | [49] |
|          | 11 | γ-Fe₂O₃@HAp@CPTMS@AT (0.02 g)/EtOH (2 mL)/Reflux | 15 | 98 | [50] |
|          | 12 | GO-Fc@Fe₃O₄ (10 mg)/100 °C | 25 | 80 | [51] |
|          | 13 | CESA | 05 | 98 | [*] |
| α-Naphthol | 14 | Hexadecyl trimethyl ammonium bromide (HTMAB) (10 mol%)/H₂O/Reflux | 240 | 93 | [23] |
|          | 15 | TiCl₄ (10 mol%)/RT | 10 | 91 | [24] |
|          | 16 | KF-Al₂O₃ (200 mg)/Grinding | 960 | 90 | [27] |
|          | 17 | Diazabicyclo[2.2.2]octane (30 mol%)/EtOH(5 mL)/RT | 120–240 | 82 | [28] |
|          | 18 | Fe(HSO₄)₃ (0.034 mg)/CH₃CN (10 mL)/Reflux | 180 | 94 | [31] |
|          | 19 | Thiourea dioxide (10 mol%)/H₂O(2 mL)/50 °C | 480 | 88 | [32] |
|          | 20 | Basic ionic liquid (20 mol%)/70 °C | 03 | 92 | [34] |
|          | 21 | Nano zeolite clinoptilolite (0.01 gm.)/H₂O (5 mL)/Reflux | 20 | 95 | [38] |
|          | 22 | Potassium 2-oxoimidazolidine-1,3-diide (POImD) 90.08 g)/H₂O/MW (900 W) | 05 | 96 | [45] |
|          | 23 | γ-Fe₂O₃@HAp@CPTMS@AT (0.02 g)/EtOH (2 mL)/Reflux | 15 | 99 | [50] |
|          | 24 | CESA (10 wt. %)/EtOH/RT | 10 | 96 | [*] |

*Present work
According to the characteristics of the CESA catalyst and a literature survey, the proposed mechanism for the synthesis of biologically active 2-amino-4H-benzochromene derivatives from one-pot tandem Knoevenagel–Michael reaction of aryl aldehyde, malononitrile and diverse phenolic nucleophiles (β- naphthol or α-naphthol) by the CESA catalyst is illustrated in Scheme 3. At first, the Knoevenagel reaction occurs between aryl aldehyde and malononitrile; its methylene group is activated by the loss of an acidic proton in the presence of a CESA catalyst, followed by the removal of a water molecule, which affords the arylidinonitrile (I) as an intermediate. In the second step, this intermediate (I) reacts with phenolic nucleophiles, β-naphthol via Michael addition, affording intermediate (II). Finally, an intramolecular heterocyclization of the intermediate (III) followed by tautomerization afforded the formation of the desired 2-amino-4H-benzochromene derivative (4).

In order to show the efficiency and accessibility of the present work, we compared this method for the synthesis of the desired product of model reactions 4b and 5b with some previously reported catalysts (Table 4, entries 1 to 12 and 14 to 23). Each of the reported methodologies has its own merits, but some of them suffer from drawbacks like harsh reaction conditions, longer reaction times, low yields, and the use of expensive catalysts. The results summarized in Table 3 clearly show that the access of CESA catalyst in the present methodology is more effective than reported methods.

Conclusion

In conclusion, we have introduced an efficient one-pot multi-component procedure for the synthesis of pharmaceutically active 2-amino-4H-benzochromene derivatives in the presence of the CESA as a reusable natural catalyst in ethanol at room temperature. This method has the important advantages like simplicity in operation, excellent yields in a short reaction time, using ethanol as a green solvent, and avoids expensive catalyst. Moreover, the recovered catalyst can be successively reused in five runs without a significant loss in catalytic activity. These are the key benefits of the present method. Utilization of a natural waste material as a source of a catalyst not only provides an opportunity to catalyse organic reactions but also solves the problems of the waste generated. Thus, this CESA catalyst is a better and more practical alternative for green processes.

Acknowledgements The authors are grateful to the Indian Institute of Science (IISC), Bangalore, and Common Facility Center (CFC), Shivaji University Kolhapur for spectral analysis.

Author contributions SKS and SSP conceived the experiments and contributed equally. SPP and SKS performed the collection field material, characterization of the catalyst and molecular laboratory work. SKS and SSP designed and directed the study and also helped in drafting the manuscript. All authors gave the final approval for publication.

Funding Not applicable.
Declarations

Conflict of interest  The author’s declared that they have no conflict of interest.

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