

# Sodium Alginate as a Reusable Biopolymeric Macromolecule Catalyzed Metal-Free Green Synthesis of 2-Amino-4H-Chromene Scaffolds

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**Abstract:** A simple method for producing 2-amino-4H-chromene scaffolds by cyclo condensation of aryl aldehydes, malononitrile, and resorcinol is reported via sodium alginate as a bifunctional biopolymeric heterogeneous catalyst under reflux conditions in EtOH. Distinguishing advantages of existing protocols are energy-efficient reusable catalysts using commercially available and cheap precursors, ease of operation, environmentally friendly solvents, high yields, and atomic economy. It fulfills several properties of sustainable and environmentally friendly chemistry. Also, the catalyst was so stable that it could be used four consecutive times with no significant structural change or activity loss.

**Keywords:** sodium alginate; natural macromolecule; reusable biopolymeric catalyst; green procedure; 2-amino-4H-chromene scaffolds.

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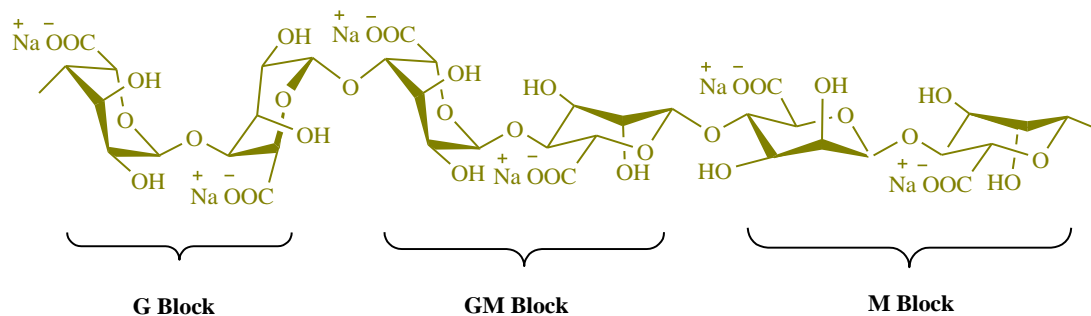
## 1. Introduction

In green chemistry, the most notable objectives of atomic saving include the reduction of byproducts, the number of stages of organic synthesis, energy costs, waste generated, and the use of non-hazardous reagents in catalytic protocols. The green catalyst is one of the important factors of green chemistry in recent organic synthetic pathways. Our recent research has focused on developing green catalysts in organic synthesis [1,2].

Natural biodegradable and renewable feedstocks are the best substitutes for traditional reagents that are synthesized chemically. Biopolymers in heterogeneous catalytic systems have been increasingly considered a substitute for synthetic organic polymers. Alginates as natural polysaccharides are extensively distributed in matrix and brown algae cell walls. It is possible to extract them naturally from various species of brown seaweed, such as *Laminaria spp*, *Ascophyllum nodosum*, *Lessonia nigrescens*, *Cystoseirabarbata*, *Sargassum turbinarioides*, etc. Specific telluric bacteria, like the genus *Pseudomonas* and *Azotobacter* species, excrete acetylated alginates [3].

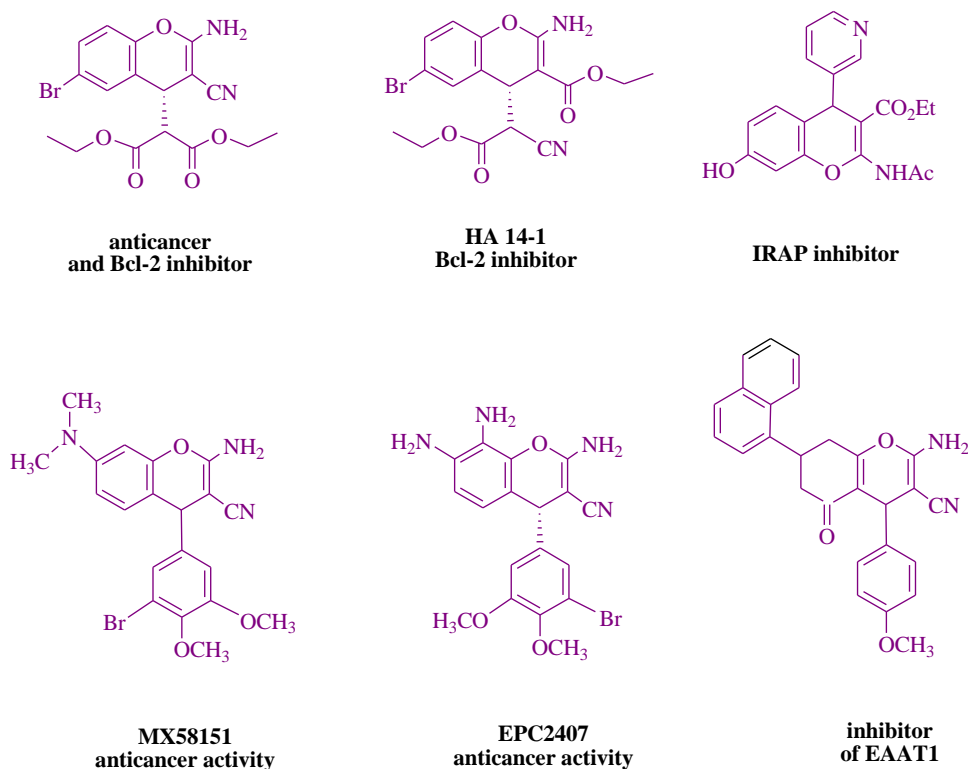
Sodium alginate (Scheme 1) is considered a safe material that is notably used in the food industries as an emulsifying, gel-forming [4], and thickening ingredient. Besides, the cosmetic industry uses it to dress wounds and encapsulate active ingredients in personal care goods [5]. Sodium alginate also possesses outstanding antioxidant features [6]. It is a homogeneous sequence established by G (G-blocks) and M units (Mblocks) alternate mixed

sequences (MG-blocks) with varying lengths (Scheme 1). Because of its stable status in many organic solvents, it is a good catalyst option for organic synthesis [7]. The monomeric units of sodium alginate include two hydroxyl groups and one carboxylate. Thus, sodium alginate could be a bifunctional organocatalyst with the capability of activating the electrophilic and nucleophilic reaction sites through its hydrogen bonding and carboxylate groups simultaneously. In cases where water is the reaction byproduct, it even has a more conspicuous catalytic activity since sodium alginate can absorb water 200-300 times its weight [4]. Recently, its usage for organic synthesis has been reported [8-10]. Here, we attempt to extend its catalytic scope to synthesizing 2-amino 4H-chromenes through condensation of resorcinol, aryl aldehydes, and malononitrile.



**Scheme 1.** Chemical structure of sodium alginate.

Chromenes and their analogs have attracted attention to them because of their biological activities, such as antiallergenic [11], antimicrobial [12], antifungal [13], anti-inflammatory [14], antibacterial [15], antioxidant [16], antileishmanial [17], anti-HIV [18,19], and anticancer [20,21]. In addition, some of these compounds could also be used as inhibitors [22]. Some of them are shown with biological characteristics in Figure 1.



**Figure 1.** Medical compounds with chromene motifs.

Numerous approaches for synthesizing 2-amino-4H-chromene scaffolds using MCRs have been reported with different opposite catalysts such as per-6-NH<sub>2</sub>- $\beta$ -CD [23], mesolite [24], potassium phthalimide [25], MgFe<sub>2</sub>O<sub>4</sub>NPs [26], POM@Dy-PDA [27], P4VPy-CuI [28], nano zeolite clinoptilolite [29], Water Extract of Lemon Fruit Shell Ash (WELFSA) [30], tungstic acid functionalized SBA-15 [31], MIL-101(Cr)-SO<sub>3</sub>H [32], [Et<sub>2</sub>NH(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>H][AcO] [33], {[4,4'-BPyH][C(CN)<sub>3</sub>]<sub>2</sub>} [34], DBU [35], hydrotalcite [36], and Fe<sub>3</sub>O<sub>4</sub>MNPs [37]. These procedures resulted in numerous cases. However, some synthesis policies also have limitations related to metal catalysts, harsh reaction conditions, monotonous processing procedures, unacceptable yields, long response times, and using a homogeneous catalyst that is problematically detached from the mixture of reactions.

Due to the above considerations and our interest in the development synthesis of multicomponent reactions [38-55], the study of eco-safe and reusable natural catalysts under green circumstances for the proper synthesis of 2-amino-4H-chromenes has been an important goal. Here, sodium alginate as a renewable bifunctional biopolymeric heterogeneous catalyst [56] produced 4a-w. The phenomenal yields and short reaction times were procured by anticipated products, which might solve some expense issues in the industry. However, the sodium alginate macromolecule can be recycled a minimum of four times with no crucial decline in catalytic activity.

## 2. Materials and Methods

### 2.1. General procedure.

Combination reactants and sodium alginate as a biopolymeric macromolecule catalyst (10 mol %) in EtOH were refluxed for the appropriate time (Scheme 2). TLC conducted monitoring of reaction progress (ethyl acetate-*n*-hexane (7:3)). When the reaction is finished, the catalyst is removed by simple filtration. Finally, the recrystallization occurred in the mixer from ethanol to bring the pure products (**4a-w**) with no need for further purification.

After comparing spectroscopic information, the merchandise was categorized. In this paper, the following spectroscopic data were obtained:

#### **2-Amino-3-cyano-7-hydroxy-4-(4-methoxyphenyl)-4H-chromene (4t)**

Yield: 91%; M.p. 208-210 °C; <sup>1</sup>HNMR (300 MHz, DMSO-d<sub>6</sub>): 3.71 (3H, s, OCH<sub>3</sub>), 4.53 (1H, s, CHAr), 6.18 (1H, d, J=8.8 Hz, ArH), 6.45 (1H, dd, J=7.2, 2.4 Hz, ArH), 6.77 (1H, d, J=8.4 Hz, ArH), 6.84 (2H, s, NH<sub>2</sub>), 7.25 (2H, d, J=8.4 Hz, ArH), 7.83 (2H, d, J=9.2 Hz, ArH), 9.78 (1H, s, OH).

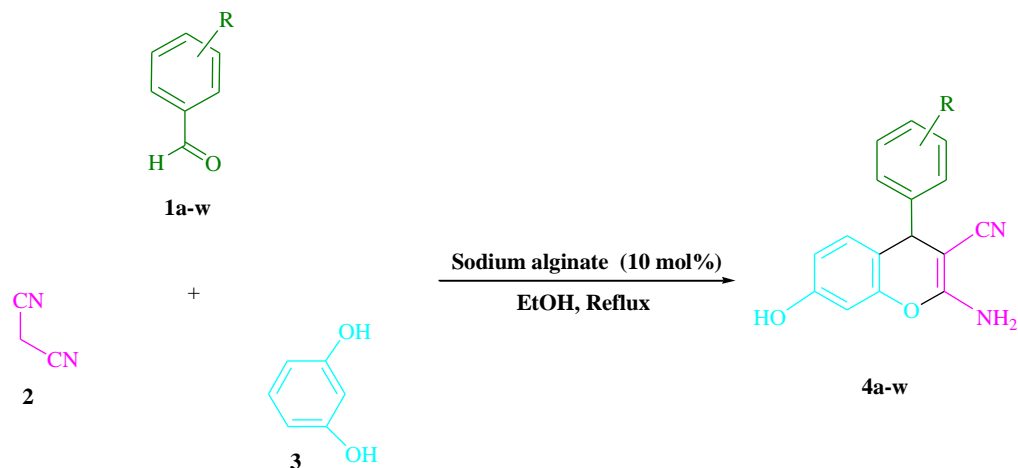
#### **2-Amino-3-cyano-7-hydroxy-4-(3-nitrophenyl)-4H-chromene (4v)**

Yield: 92%; M.p. 170-172 °C; <sup>1</sup>HNMR (300 MHz, DMSO-d<sub>6</sub>): 4.82 (1H, s, CHAr), 6.19 (1H, d, J=8.8 Hz, ArH), 6.59 (1H, d, J=9.6 Hz, ArH), 6.77 (1H, d, J=9.6 Hz, ArH), 6.97 (2H, s, NH<sub>2</sub>), 7.33 (2H, d, J=9.6 Hz, ArH), 7.86 (2H, d, J=9.6 Hz, ArH), 9.69 (1H, s, OH).

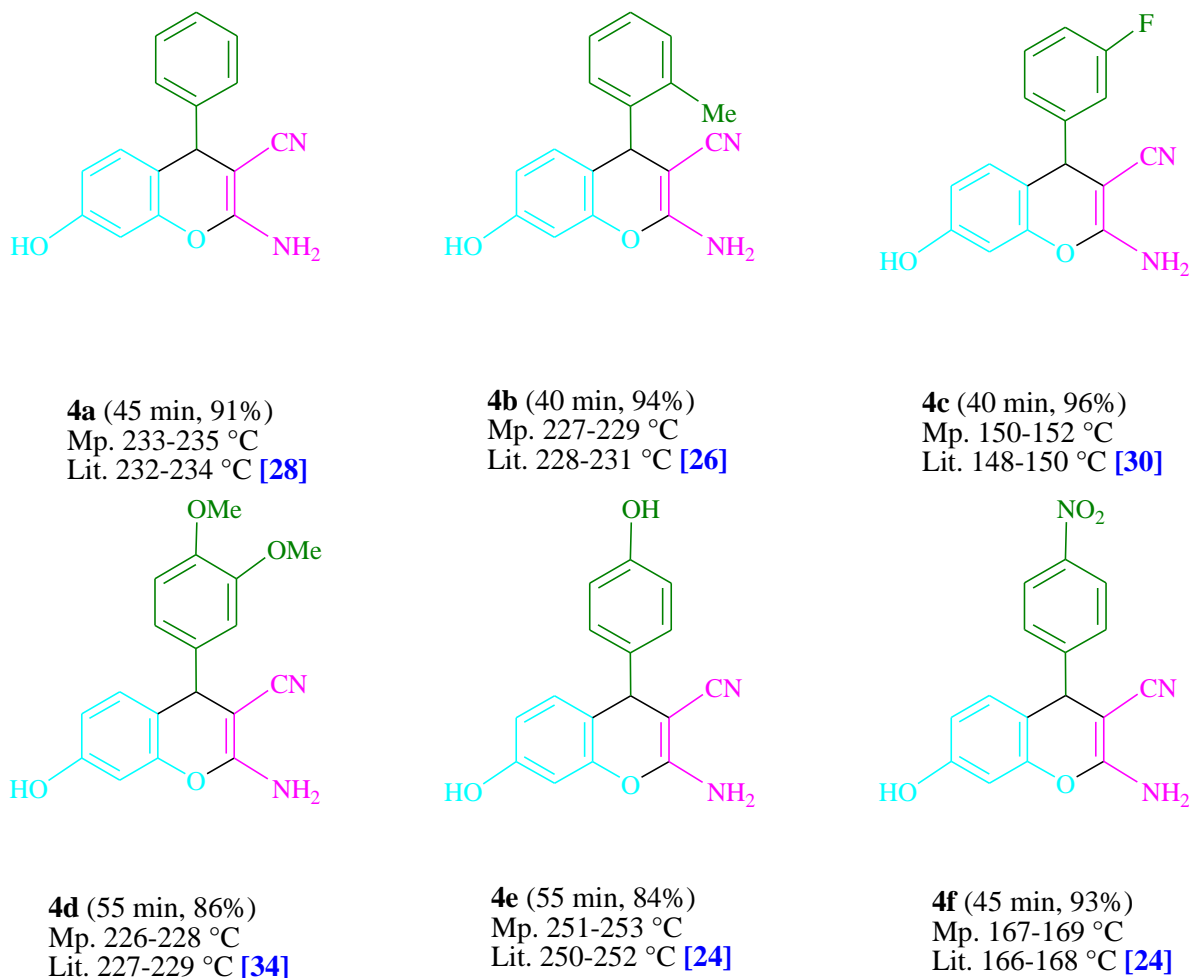
## 3. Results and Discussion

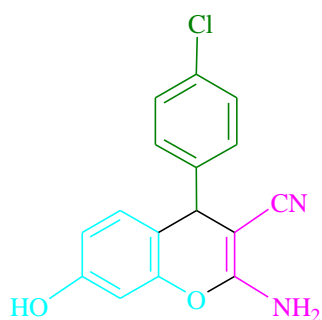
The preparation of 4a was studied in various solvents opposite different molars of sodium alginate. Table 1 illustrates the results. Without sodium alginate, 12 % and trace amount 4a was seen at reflux and rt in EtOH for 120 min. This table shows that products were produced in H<sub>2</sub>O, H<sub>2</sub>O/EtOH (1:1), CH<sub>3</sub>CN, MeOH, solvent-free, DMF, THF, DMSO, CH<sub>2</sub>Cl<sub>2</sub>, and CHCl<sub>3</sub> solvents at higher reaction times and lower yields and a great enhancement in EtOH as solvent (Table 1). Also, the optimization conditions are determined by different temperatures

(rt, 40 °C, 60 °C, and reflux). The best outcomes were found in the presence of sodium alginate (10 mol %) at reflux in EtOH (Table 1, entry 4). We recognized the optimized conditions by different molar of catalyst (5, 10, and 15 mol %). Also, the best results were opposite sodium alginate (10 mol %) (Table 1, entry 4). No important change in reaction time and yield was observed with the increase in the amount of catalyst to 15 mol % (Table 1, entry 18). Schemes 2 and 3 show that this technique can function in diverse substrates.

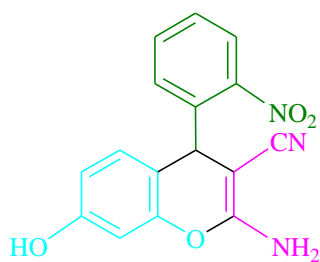


**Scheme 3.** Sodium alginate as a reusable biopolymeric catalyst for the synthesis of 2-amino-4*H*-chromene scaffolds.

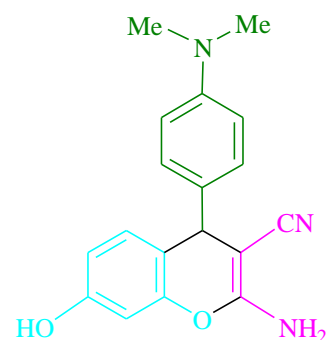




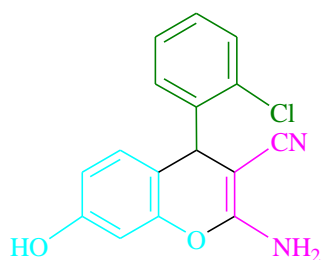
**4g** (60 min, 84%)  
Mp. 163-165 °C  
Lit. 162-163 °C [28]



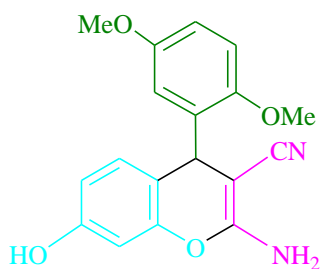
**4h** (40 min, 90%)  
Mp. 161-163 °C  
Lit. 162-163 °C [35]



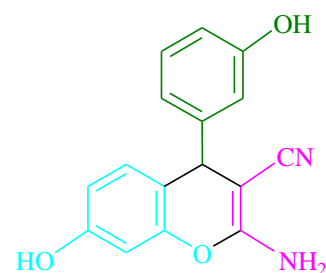
**4i** (45 min, 89%)  
Mp. 193-195 °C  
Lit. 194-196 °C [25]



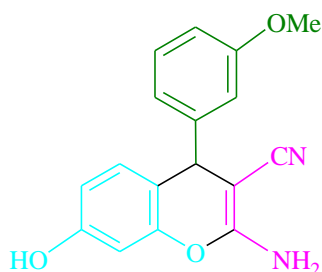
**4j** (55 min, 82%)  
Mp. 191-193 °C  
Lit. 189-191 °C [28]



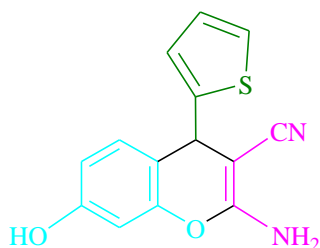
**4k** (55 min, 84%)  
Mp. 196-198 °C  
Lit. 198-200 °C [36]



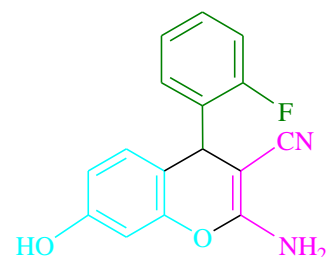
**4l** (55 min, 82%)  
Mp. 221-223 °C  
Lit. 219-221 °C [34]



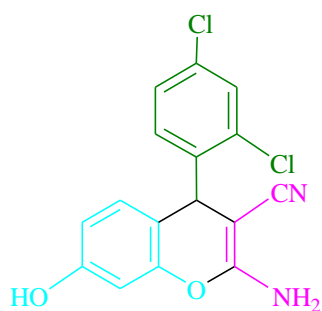
**4m** (50 min, 89%)  
Mp. 179-181 °C  
Lit. 180-182 °C [34]



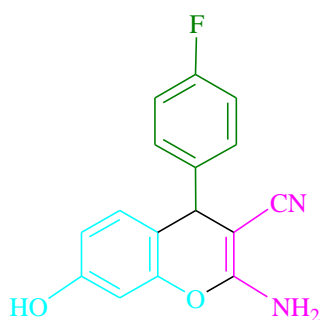
**4n** (40 min, 92%)  
Mp. 211-213 °C  
Lit. 210-212 °C [25]



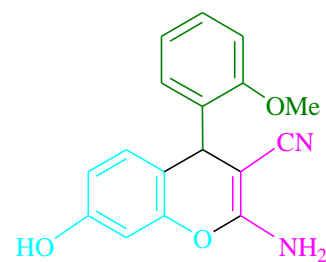
**4o** (35 min, 97%)  
Mp. 199-201 °C  
Lit. 200-202 °C [35]



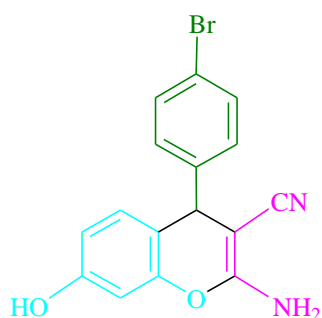
**4p** (60 min, 81%)  
Mp. 259-261 °C  
Lit. 257-259 °C [28]



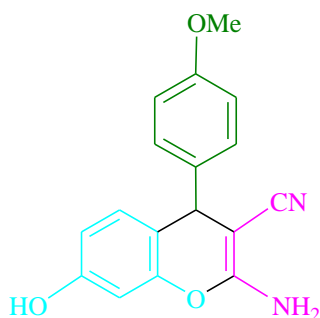
**4q** (40 min, 93%)  
Mp. 186-188 °C  
Lit. 188-190 °C [28]



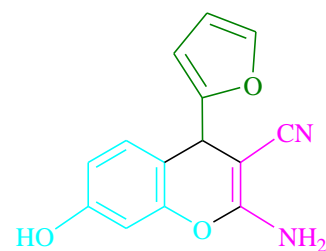
**4r** (45 min, 86%)  
Mp. 223-225 °C  
Lit. 222-224 °C [37]



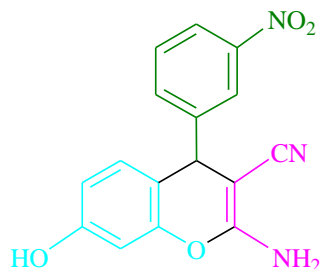
**4s** (60 min, 82%)  
Mp. 221-223 °C  
Lit. 222-224 °C [25]



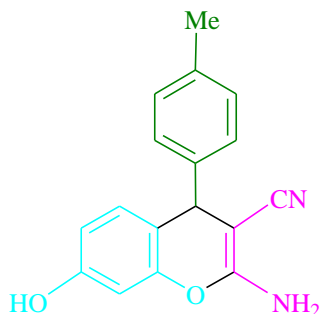
**4t** (50 min, 91%)  
Mp. 208-210 °C  
Lit. 210-212 °C [30]



**4u** (40 min, 96%)  
Mp. 188-190 °C  
Lit. 190-192 °C [33]



**4v** (40 min, 92%)  
Mp. 170-172 °C  
Lit. 168-170 °C [33]



**4w** (40 min, 92%)  
Mp. 188-190 °C  
Lit. 186-188 °C [29]

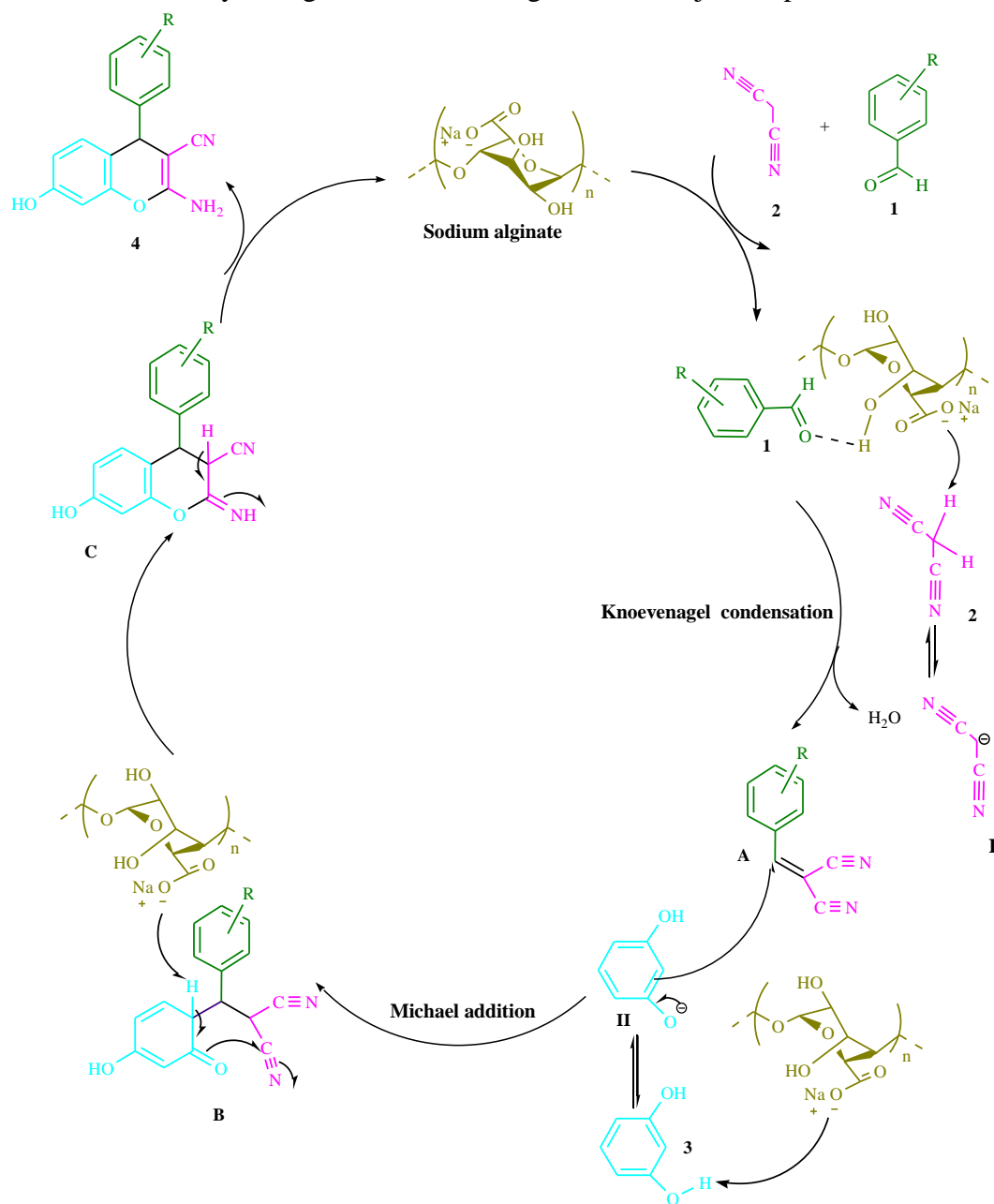
**Table 1.** Optimization table for the synthesis of **4a<sup>a</sup>**.

Entry	Sodium alginate (mol %)	Solvent/Temperature (°C)	Time (min)	Isolated Yields (%)
1	Catalyst free	EtOH/Reflux	120	12
2	Catalyst free	EtOH/rt	120	trace
3	5	Reflux/ EtOH	50	76
4	10	Reflux/ EtOH	45	91
5	10	EtOH/rt	100	68
6	10	EtOH/40°C	75	79
7	10	EtOH/60°C	65	84
8	10	H <sub>2</sub> O/Reflux	65	63
9	10	H <sub>2</sub> O/EtOH (1:1)/Reflux	55	71
10	10	CH <sub>3</sub> CN/Reflux	50	64
11	10	MeOH/Reflux	60	67
12	10	Solvent free/100°C	50	58
13	10	DMF/Reflux	70	54

Entry	Sodium alginate (mol %)	Solvent/Temperature (°C)	Time (min)	Isolated Yields (%)
14	10	THF/Reflux	70	59
15	10	DMSO/Reflux	65	51
16	10	CH <sub>2</sub> Cl <sub>2</sub> /Reflux	75	45
17	10	CHCl <sub>3</sub> /Reflux	75	38
18	15	EtOH/Reflux	45	92

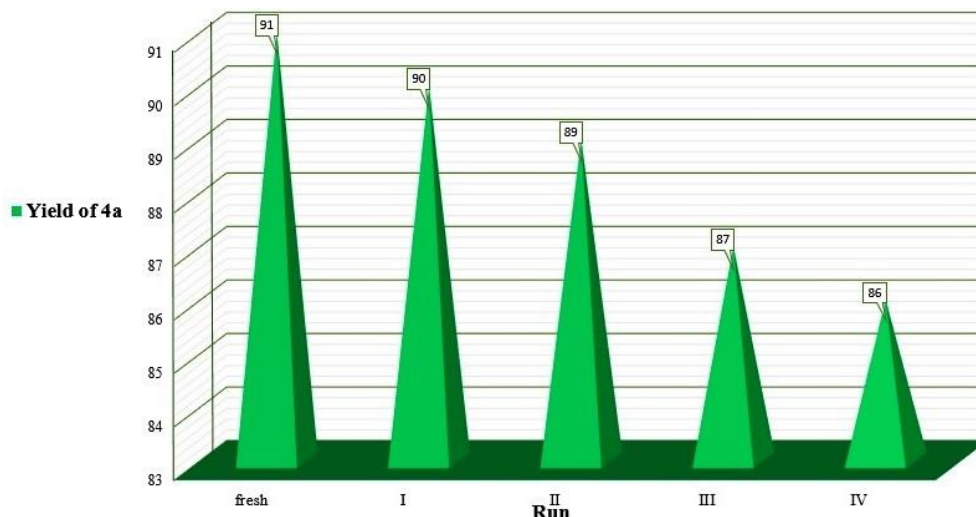
<sup>a</sup> Reaction condition: benzaldehyde (1 mmol), malononitrile (1 mmol), resorcinol (1 mmol) under various temperatures, solvents, and molar catalysts.

Scheme 4 indicates recommended mechanism. We provoked the reaction by devising an inclusion in the intermediate A changed into devised in situ from Knoevenagel condensation among 2 and arylaldehyde 1 by sodium alginate through hydrogen bonding and anion formation. We can show this via the aryl aldehydes' steric impacts on the reaction (Table 2). Sodium alginate also catalyzed the resorcinol 3 attack on intermediate A as Michael acceptor to give B, which after cyclizing and tautomerizing, aims the objective products 4.



**Scheme 4.** Mechanistic route.

Reusability of the catalyst: since the catalyst reusability is economically and environmentally important, the sodium alginate catalyst reusability has been investigated over the next few periods. Recovery and reuse of the catalyst to prepare 4a were examined. At the end of the reaction, EtOH is used for filtering and washing the catalyst to separate the unreacted initial materials from the products through anion formation and hydrogen bonding. The sodium alginate was reused for four rounds of recycling, while the detached product had sufficient potential to be affordable. In the first, second, third, and fourth reactions, there were very low reductions in yield (90%, 89%, 87%, and 86%, respectively) (Figure 2).



**Figure 2.** Very low reductions in yield.

#### 4. Conclusions

The current survey revealed that reusable and bifunctional biopolymeric heterogeneous catalysts can be employed for synthesizing chromene scaffolds in EtOH under reflux conditions. Utilizing great yields, efficient sides of the reaction, reusable natural macromolecule catalyst, secure reaction circumstances, appropriate and expedient procedure, green solvent, and cheap substances are the most conspicuous pros of this green protocol. These characteristics have caused this procedure to be highly beneficial in facing environmental worries and industrial needs.

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#### Acknowledgments

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#### Conflicts of Interest

The authors declare no conflict of interest.

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