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Research Article

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Aqueous Extract of *Acacia concinna* Pods: An Efficient Surfactant Type Catalyst for Synthesis of 3-Carboxycoumarins and Cinnamic Acids via Knoevenagel Condensation

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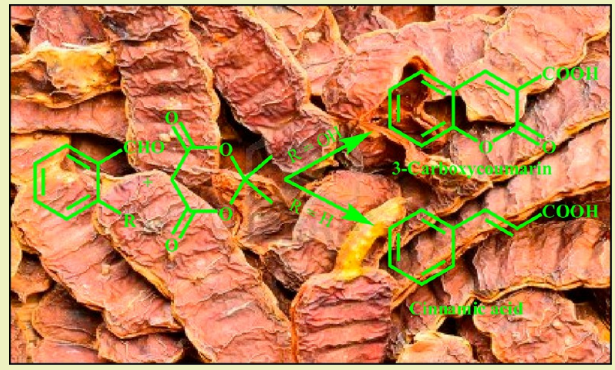
ABSTRACT: A simple, efficient, and environmentally benign protocol for the synthesis of 3-carboxycoumarins and cinnamic acids via Knoevenagel condensation has been achieved using aqueous extract of *Acacia concinna* pods as a naturally occurring surfactant type catalyst. We found for the first time that the aqueous extract of *Acacia concinna* pods could effectively catalyze the condensation of Meldrum's acid with salicylaldehyde/aromatic aldehyde to yield 3-carboxycoumarins and cinnamic acids in excellent yields under mild conditions. The low cost, easy availability of the catalyst, and simple reaction conditions suggest the possible use of the present method for large scale preparations.



KEYWORDS: *Green protocol, Acacia concinna, 3-Carboxycoumarins, Cinnamic acids, Knoevenagel condensation, Surfactant*

INTRODUCTION

New catalytic synthetic methods in organic chemistry that satisfy increasingly stringent environmental constraints are in great demand by the pharmaceutical and chemical industries. In addition, novel catalytic procedures are necessary to produce the emerging classes of organic compounds that are becoming the targets of molecular and biomedical research. Several types of substances such as enzymes, surfactants, ionic liquids, clays, and supercritical solvents are now widely recognized as practical alternatives to traditional organic synthesis and as convenient solutions to certain intractable synthetic problems. This is due to problems associated with prevailing catalysts, such as hazardous nature, expense, difficult handling, tedious workup, requirements of hazardous organic solvents, elevated temperature conditions, and above all, adverse effects on the environment. In an attempt to circumvent these disadvantages, we looked to nature for help. Nature provides a fantastic array of catalysts extremely well suited to supporting life such as intact plant systems that represent a unique class of potential biocatalysts for the reactions of various organic substrates.[1−3] The synthetic transformations using these materials are more efficient and generate less waste than the conventional chemical methods. More recently, the plant cell culture of *Daucus carota* root,[4−10] soaked *Phaseolus Aureus* (green grams),[11] and coconut juice (*Cocos Nucifera*)[12] were used as biocatalysts for selective reduction of ketones.

Coumarins are very well-known natural products that exhibit a broad range of applications in the pharmaceutical, perfume, and cosmetic industries.[13−15] Many well-known marketed drugs such as warfarin, novobiocin, and tioclomarol contain a coumarin nucleus as a basic scaffold, and recently, various ester and amide derivatives of coumarin-3-carboxylic acid were investigated as novel monamine oxidase (MAO-A and MAO-B) inhibitors,[16] antibacterial,[17] anti-AChE,[18] and anticancer agents[19−22] (Figure 1). They are also exploited as intermediates and building blocks in organic synthesis.[23,24] This has enthused us to search new and more convenient methods for the preparation of coumarin derivatives.

Numerous synthetic routes to 3-substituted coumarins from 2-hydroxyarylaldehydes or 2-hydroxyarylketones have been published[25−31] including syntheses requiring the use of noxious phosphorylating agents such as $POCl_3$, bases such as piperidine, or solvents such as DMF.[25] Recently a solid phase synthesis of substituted 3-carboxycoumarins utilizing ethyl malonate tethered to a Wang resin and suspended in pyridine has been described,[32] although reported yields are poor and often significantly less than 50%.

Various methods for 3-carboxycoumarin synthesis showed that very few simple, efficient, and green methodologies have been reported. Though we have reported one-pot, efficient, rapid microwave-mediated green synthesis of substituted 3-carboxycoumarins using a recyclable synthetic or natural acid catalyst, this method circumvents the use of noxious acid and solvent. It is not totally solvent-free as the product must be removed from the catalyst by dissolution in a volatile organic solvent, and product purification is deemed necessary.[33]

Scott et.al. have developed a one-pot green protocol for the synthesis of 3-carboxycoumarin from salicylaldehyde and

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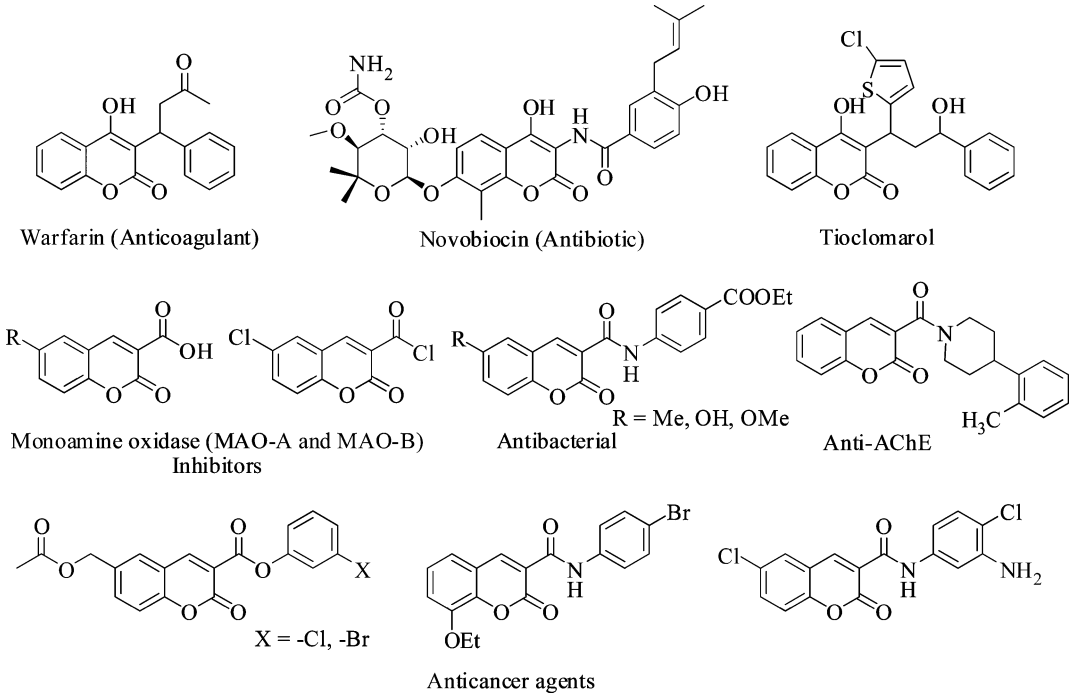


Figure 1. Biologically active coumarin derivatives.

Meldrum's acid using ammonium acetate as a catalyst under solvent-free grinding conditions or aqueous medium at room temperature.[34] A limited number of substrates (only two), laborious grinding, and long reaction time (overnight) are the limitations of this method, and it cannot be used for large scale preparation of 3-carboxycoumarin. 3-Carboxycoumarins were also prepared in high yields from Meldrum's acid and salicyaldehyde by carrying out the reaction in water at reflux for 10 h, avoiding the addition of any catalyst.[35] However, this method involves a long reaction time, elevated temperature, and unsatisfactory yields and worked very well for substituted o-hydroxyaldehydes and not with the salicylic aldehydes bearing lipophilic substituents.

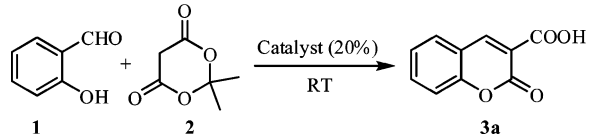
Cinnamic acids derivatives are naturally occurring substances found in fruits, vegetables, and flowers, and are consumed as dietary phenolic compounds. They play a vital role in the formation of commercially important intermediate molecules that are necessary for the production of different pharmaceutical ingredients. They possess a wide range of activities, such as antioxidant, hepatoprotective, anxiolytic, insect repellent, antidiabetic, anticholesterolemic, etc.[36−40] Various methods reported for the synthesis of cinnamic acids suffer from one or other drawbacks. To overcome limitations of the reported methods, there is a need to a develop mild, efficient, and eco-friendly method resulting in an excellent yield of product.

Acacia concinna is a medicinal plant (commonly known as Shikakai, Leguminosae family) that grows in the tropical rainforests of southern Asia. The fruit is known as "fruit for hair" in its use as a traditional shampoo. Various properties of *Acacia concinna* fruit are due to the presence of saponins in it, which are foaming agents. Saponins from the plant's pods have been traditionally used as a detergent. Specifically, they are amphipathic glycosides grouped phenomenologically by the soap-like foaming they produce when shaken in aqueous solutions and structurally by their composition of one or more hydrophilic glycoside moieties combined with a lipophilic triterpene derivative. The fruit is known to contain 10−11.5% saponins. The structures of different saponins present in the fruit has been recently established.[41,42] These saponins have surfactant properties similar to dodecyl benzene sulphonates.[43] The pods of *Acacia concinna* has been found to contain the saponin of acacic acid. Acacic acid was found to be a trihydroxy monocarboxylic triterpenic acid of either tetracyclic or α-amyrin group.[44] The aqueous extract of these pods of *Acacia concinna* shows acidic pH that is due to the presence of an acacic acid.[45] These interesting properties of aqueous extract of *Acacia concinna* pods allow us to use it as an eco-friendly acidic surfactant type catalyst for organic synthesis.

RESULTS AND DISCUSSION

In continuation of our work following the principles of green chemistry,[46−48] we have developed a simple, efficient, and green protocol for the preparation of 3-carboxycoumains using aqueous extract of pods of *Acacia concinna* as a green and inexpensive catalyst (Scheme 1). Our approach reduces the use of hazardous organic solvents and uses simple and mild conditions with inherently lower costs.

Scheme 1. Synthesis of 3-Carboxycoumarins



In the beginning, a test reaction using 2-hydroxy benzaldehyde **1** (1 mmol) and Meldrum's acid **2** (1 mmol) in 5 mL 10% (W/V) aqueous extract of *Acacia concinna* pods at room temperature was performed in order to establish the real effectiveness of the catalyst, and we are fortunate to get an excellent yield of product **3a** (92%) after 3 h. In order to optimize the reaction conditions, the same reaction was carried out using different concentrations of catalyst. It was found that

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20% of the catalyst shows maximum yield in minimum time (98%). Higher concentration of the catalyst (30%, 50%) neither increases the yield nor lowers the conversion time (Table 1). Thus, 20% (w/v) of 5 mL aqueous extract was found to be the optimal quantity and sufficient to push the reaction forward.

Table 1. Optimization of Concentration of Catalyst

entry	% conc. of aqueous extract (w/v)	time (min)	yield (%)[a]
1	5	300	NR[b]
2	10	180	92
3	20	60	98
4.	30	60	98
5	50	75	96

[a]Isolated yield. [b]No reaction.

In order to compare the strength of the aqueous extract of the *Acacia concinna* pods a catalyst with aqueous solutions of various cationic, anionic, and nonionic surfactants, a model reaction was carried out between 2-hydroxy benzaldehyde (**1**) and Meldrum's acid (**2**) using various surfactants as catalysts at room temperature, and the results are summarized in Table 2.

Table 2. Effect of Surfactant on Yield of 3-Carboxycoumarins

entry	surfactant[a]	time (min)	yield (%)[b]
1	none	720	NR[c]
2	DBSA	120	68
3	SDS	120	60
4	Triton X-100	120	52
5	CPB	120	40
6	CTAB	120	45
7	catalyst (20%)	60	98

[a]Reaction condition: Salicyaldehyde (1 mmol), Meldrum's acid (1 mmol), surfactant (10 mol %), rt. [b]Isolated yield. [c]No reaction.

The solutions in consideration were taken well above their critical micellar concentrations (CMC). In the presence of the acidic surfactant dodecylbenzene sulfonic acid (DBSA), the desired product was obtained in moderate yield (Table 2, entry 2). All other surfactants, sodium dodecyl sulfate (SDS), Triton X-100, cetyl pyridinium bromide (CPB), and cetyl trimethylammonium bromide (CTAB), afforded the desired product **3a** in low yields (Table 2, entries 3−6). However, in the presence of the aqueous extract of *Acacia concinna* pods (natural catalyst), the desired product was obtained in excellent yield within a short period of time (Table 2, entry 7). When the reaction was carried out in water, without any surfactant, no product formation was observed after 12 h (Table 2, entry 1). Thus, the aqueous extract of *Acacia concinna* pods was found to be the most obvious choice for further exploration of the methodology with other 2-hydroxy benzaldehyde derivatives.

The rate enhancement in the aqueous extract of *Acacia concinna* pods might be attributed due to its surfactant property and acidic pH. The probability of an enzyme-catalyzed reaction is ruled out because the plant extraction is carried out at 100 °C. The saponins, which are highly acidic, solubilize the reactant species strongly by hydrogen bond formation in aqueous medium. This increases the number of favorable collisions between the reactant species. Further encapsulation of the reactants in micellar cages may drive the equilibrium toward the product side by expelling the water molecule out of its hydrophobic interior that increases the speed as well as the yields of products (Figure 2).[49,50] This remarkable enhancement in reaction rate prompted us to explore the potential of this protocol for the synthesis of 3-carboxycoumarins.

The efficiency of this aqueous approach was studied for the synthesis of wide variety of 3-carboxycoumarin derivatives using similar reaction conditions, and the results are summarized in Table 3. The nature (electron withdrawing or electron donating) and position of the substituent on the aromatic ring did not show any marked difference in the yield of 3-carboxycoumarin derivatives. Mechanistically, the reaction proceeded via Knoevenagel condensation followed by cyclization to obtain 3-carboxycoumarins.

The Perkin reaction is the most frequently used method for the preparation of the cinnamic acids and its derivatives, but the main disadvantage of this reaction is that the presence of base leads to formation of unwanted side products. As well as in the presence of an electron-donating substituent, the yield of the target product markedly decreases. In such systems, the Perkin reaction is not employed for preparative purposes. For the electron-donating groups, Knoevenagel and Debner modification reactions lead to the final product in good yields. but the main drawback is that the reaction needs a long duration of time.

To further explore the potential of this aqueous approach, we have successfully applied this protocol for the synthesis of cinnamic acid derivatives by the condensation of various aromatic aldehydes other than salicyaldehydes with Meldrum's acid followed by ring-opening. Initially, when the reaction of benzaldehyde and Meldrum's acid was carried out at room temperature using the aqueous extract of *Acacia concinna* pods, only condensation product **5a** was observed. But, when the same reaction was carried out at 60 °C, formation of cinnamic acid **6a** was observed in excellent yield (Scheme 2). With the

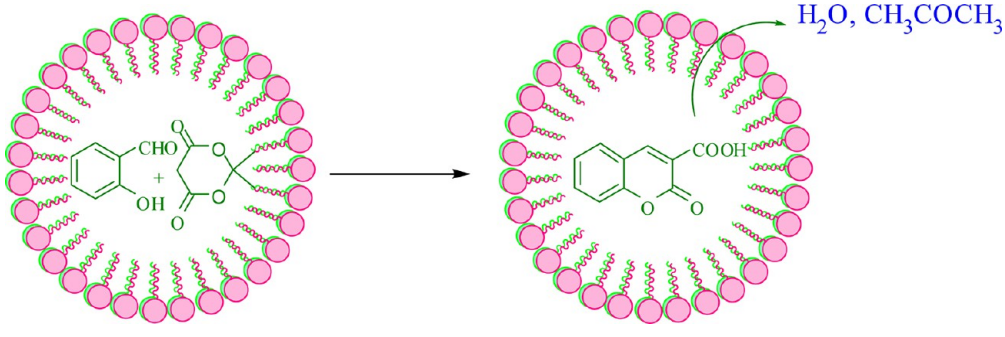

Figure 2. Micelle-promoted synthesis of 3-carboxycoumarins.

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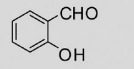
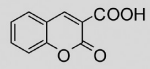
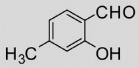
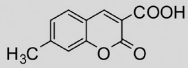
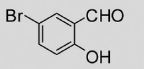
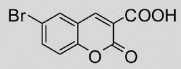
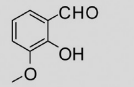
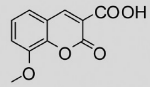
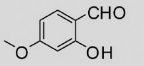
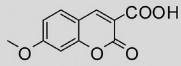
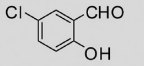
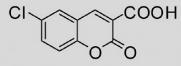
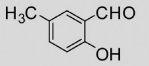
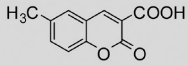
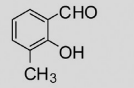
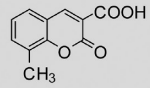
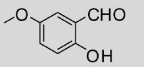
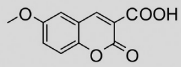
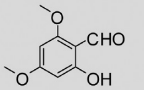
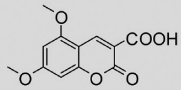
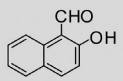
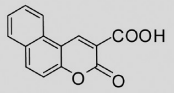
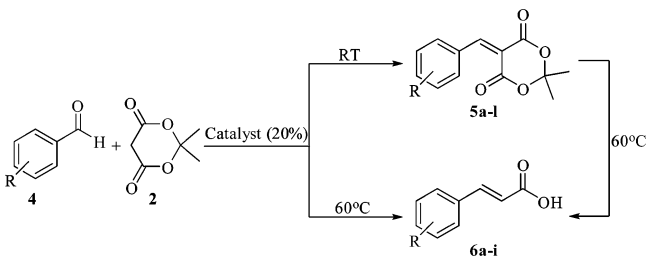
Table 3. Synthesis of 3-Carboxycoumarins

Entry	Aldehyde	Product		Time (min)	Yield[a] (%)	MP (°C)
1.			**3a**	60	98	188-190[11]
2.			**3b**	75	94	168-170[11]
3.			**3c**	60	96	196-194[11]
4.			**3d**	75	95	216-217[11]
5.			**3e**	75	96	193-195[11]
6.			**3f**	55	98	120-122[11]
7.			**3g**	70	95	167-168[11]
8.			**3h**	75	92	160-162[11]
9.			**3i**	65	96	192-194[11]
10.			**3j**	75	95	234-236[11]
11.			**3k**	55	98	216-218[11]

[a]Isolated yields.

optimized procedure in hand, an investigation into the scope of the methodology, using a range of aldehydes, was conducted (Tables 4 and 5).

Scheme 2. Synthesis of Cinnamic Acid Derivatives via Knoevenagel condensation



In recent years, various other methods have been reported for the preparation of cinnamic acid and its derivatives[51−53] such as microwave irradiation of aryl aldehydes and malonic acid with polyphosphate ester (PPE) as the mediator catalyst in solvent-free condition[54] and using $POCl_3$ as an acid catalyst.[55] However, major disadvantages of these methods include long reaction time, elevated temperature, unsatisfactory yields, and the fact that they only work very well for electron-donating substituents.

This aqueous protocol overcomes all these drawbacks and proceeds smoothly for substrates containing both electron-donating as well as electron-withdrawing groups within a very short period of time under mild condition resulting in excellent yields of substituted cinnamic acids.

In conclusion, we have found that the aqueous extract of *Acacia concinna* pods as an efficient, economical, and environmental friendly catalyst for the synthesis of 3-carboxycoumarins and cinnamic acids. The high yield of products in a short reaction time with high purity, mild reaction conditions, and a simple workup procedure makes this procedure attractive. The uses of water as a solvent and biodegradable catalyst are the attractive features of this protocol. Furnishing pure products by simple filtration makes an aqueous approach possible for large scale preparation of 3-carboxycoumarins and cinnamic acids.

EXPERIMENTAL SECTION

General Remarks. All chemicals were obtained from commercial suppliers and were used without further purification. Melting points were determined in open capillaries and were uncorrected. All reactions were monitored by thin layer chromatography (TLC) with 0.2 mm Merck silica gel F_{254} plates. NMR spectra were recorded on Bruker DRX FT NMR at 400 MHz spectrometer in DMSO-d_6 using

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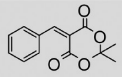
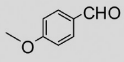
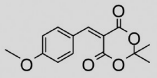
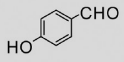
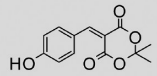
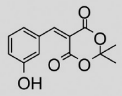
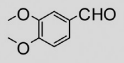
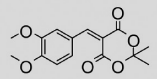
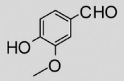
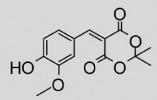
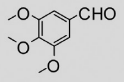
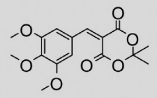
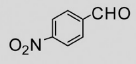
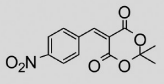
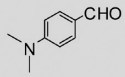
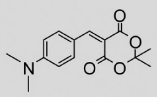
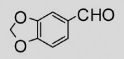
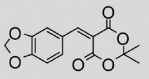
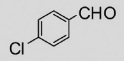
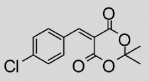
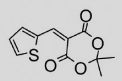
Table 4. Knoevenagel Condensation of Aromatic Aldehydes and Meldrum's Acid

Entry	Aldehyde	Product[a,b]		Time (min)	Yield (%)[c]	MP (°C)
1			**5a**	45	98	118-120[11]
2			**5b**	50	97	122-125[11]
3			**5c**	55	95	190-192[11]
4			**5d**	55	96	172-175[11]
5			**5e**	60	95	170-172[11]
6.			**5f**	55	94	1343-135[11]
7.			**5g**	75	94	152-154[11]
8.			**5h**	45	96	216-218[11]
9.			**5i**	50	95	170-172[11]
10.			**5j**	45	98	162-164[11]
11.			**5k**	40	98	158-160[11]
12.			**5l**	45	94	195-197[11]

[a]Reaction performed at rt. [b]All the compounds are reported in the literature. [c]Isolated yields.

TMS as internal standard (chemical shifts are expressed as δ values relative to TMS as internal standard). IR spectra were recorded on a Brüker VECTOR 22 FTIR spectrophotometer. ESI (positive) was recorded on an Esquire-LC-00075 spectrometer. Dry *Acacia concinna* pods were purchased from local market and authenticated from School of Life Sciences, SRTMU, Nanded, India.

General Procedure for the Preparation of Catalyst. Powdered pods of *Acacia concinna* fruit (20 g) and water (100 mL) in a 250 mL conical flask were boiled for 15 min. The material was then filtered off, and the aqueous extract was employed as a catalyst (20%, w/v) for the synthesis of 3-carboxycoumarins and cinnamic acids.

General Procedure for the Synthesis of 3-Carboxycoumarins (3a–k). A mixture of substituted 2-hydroxy benzaldehyde (2 mmol), Meldrum's acid (2 mmol), and catalyst (20%, 5 mL) were taken in a round-bottomed flask and stirred at room temperature for specified time period (Table 3). After completion of the reaction (TLC), a separated solid was filtered on Buchner funnel, washed well with water, and dried to obtain pure product.

General Procedure for the Synthesis of 5-Arylidene Meldrum's Acids (5a–l). A mixture of aldehyde (2 mmol), Meldrum's acid (2 mmol), and catalyst (20%, 5 mL) were taken in a round-bottomed flask and stirred at room temperature for a specified time period (Table 4). After completion of the reaction (TLC), a separated solid was filtered on Buchner funnel, washed well with water, and dried to obtain pure product.

General Procedure for the Synthesis of Cinnamic Acids (6a–i). A mixture of aldehyde (2 mmol), Meldrum's acid (2 mmol), and catalyst (20%, 5 mL) were taken in a round-bottomed flask and stirred at 60 °C for specified time period (Table 5). After completion of the reaction (TLC), the reaction mixture was cooled to room temperature, and a separated solid was filtered on Buchner funnel, washed well with water, and dried to obtain pure product.

Spectral Data. *2-Oxo-2H-chromene-3-carboxylic Acid (**3a**).* White solid, IR (KBr): 3056, 2932, 2780, 1744, 1681, 1608, 1567, 1452, 1243, cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 7.50 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 8.95 (s, 1H), 13.25 (bs, 1H). LCMS (ESI): m/z 190.90 ($M+H^+$).

*7-Methyl-2-oxo-2H-chromene-3-carboxylic Acid (**3b**).* IR (KBr): 3050–2700, 1743, 1678, 1626, 1558, 1428, 1223 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 2.45 (s, 3H), 7.25 (d, J = 8 Hz, 1H), 7.33 (s, 1H), 7.81 (d, J = 8 Hz, 1H), 8.85 (s, 1H), 13.15 (bs, 1H). LCMS (ESI): m/z 205 ($M+H^+$)

*6-Bromo-2-oxo-2H-chromene-3-carboxylic Acid (**3c**).* IR (KBr): 3500–3300, 3042, 1755, 1690, 1600, 1557, 1475, 1268 cm^{-1}. ^1H NMR

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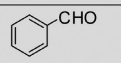
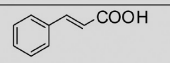
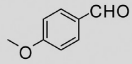
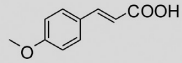
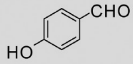
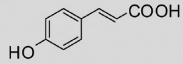
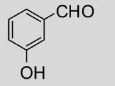
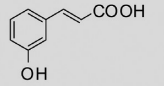
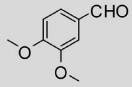
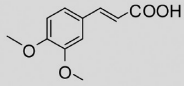
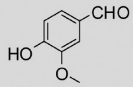
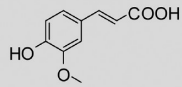
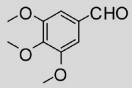
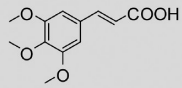
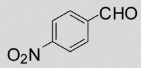
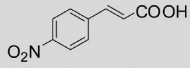
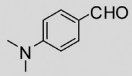
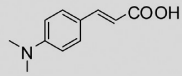
Table 5. Various Substituted Cinnamic Acids

Entry	Aldehyde	Product[a,b]		Time (min)	Yield (%)[c]	MP (°C)
1			**6a**	30	95	132-134[21]
2			**6b**	35	92	172-174[21]
3			**6c**	40	94	212-214[21]
4			**6d**	35	93	193-195[11]
5			**6e**	45	92	180-182[11]
6.			**6f**	40	92	168-170[11]
7.			**6g**	45	90	125-127[21]
8.			**6h**	30	95	198-200[21]
9.			**6i**	35	94	226-228[21]

[a]Reaction performed at 60 °C. [b]All the compounds are reported in the literature. [c]Isolated yields.

(400 MHz, DMSO-d_6): δ = 7.40, (d, J = 8 Hz, 1H), 7.72 (d, J = 8 Hz, 1H), 8.03 (s 1H), 8.68 (s, 1H), 13.30 (bs, 1H). LCMS (ESI): m/z 270.90 ($M+H^+$)

*8-Methoxy-2-oxo-2H-chromene-3-carboxylic Acid (**3d**).* IR (KBr): 3500−3250, 3027, 2994, 2946, 1757, 1681, 1607, 1584, 1479, 1264, 1195 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 3.92 (s, 3H), 6.90 (t, J = 8.4 Hz, 1H), 6.99 (d, J = 8.4 Hz, 1H), 7.53 (d, J = 8.4 Hz, 1H), 8.64 (s, 1H), 13.12 (bs, 1H). LCMS (ESI): m/z 221, 220.95 ($M+H^+$).

*7-Methoxy-2-oxo-2H-chromene-3-carboxylic Acid (**3e**).* IR (KBr): 3180−3200, 3045, 1748, 1690, 1612, 1560, 1478, 1260 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 4.05, (s, 3H), 7.07−7.18 (m, 2H), 7.92 (d, J = 8 Hz, 1 H), 8.91 (s, 1H), 13.22 (bs, 1H). LCMS (ESI): m/z 220 (M^+)

*6-Chloro-2-oxo-2H-chromene-3-carboxylic Acid (**3f**).* IR (KBr): 3500−3320, 3046, 1751, 1695, 1615, 1562, 1479, 1268 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 7.46 (d, J = 8 Hz, 1H), 7.76 (dd, J = 8, 1.8 Hz, 1H), 8.03 (d, J = 1.8 Hz, 1H), 8.68 (s, 1H), 13.44 (bs, 1H). LCMS (ESI): m/z 225 ($M+H^+$).

*6-Methyl-2-oxo-2H-chromene-3-carboxylic Acid (**3g**).* IR (KBr): 3500−3310, 3040, 1750, 1695, 1615, 1562, 1480, 1260 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 2.50 (s, 3H); 7.28 (dd, J = 8.2, 1.8 Hz, 1H), 7.40 (d, J = 8.2 Hz, 1H), 7.62 (d, J = 1.8 Hz, 1H), 8.65 (s, 1H), 13.42 (bs, 1H). LCMS (ESI): m/z 205 ($M+H^+$).

*8-Methyl-2-oxo-2H-chromene-3-carboxylic Acid (**3h**).* IR (KBr): 3500−3320, 3028, 2997, 2944, 1759, 1680, 1607, 1585, 1477, 1266 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 2.26 (s, 3H), 7.05 (t, J = 8 Hz, 1H), 7.22 (d, J = 8 Hz, 1H), 7.61 (d, J = 8 Hz, 1H), 8.69 (s, 1H) 13.15 (bs, 1H). LCMS (ESI): m/z 205 ($M+H^+$).

*6-Methoxy-2-oxo-2H-chromene-3-carboxylic Acid (**3i**).* IR (KBr): 3500−3250, 3045, 1752, 1695, 1618, 1565, 1480, 1265 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 3.82 (s, 3H); 6.95 (dd, J = 8, 1.6 Hz, 1H), 7.06 (d, J = 1.6 Hz, 1H), 7.45 (d, J = 8 Hz, 1H), 8.64 (s, 1H), 13.26 (bs, 1H). LCMS (ESI): m/z 221 ($M+H^+$).

*5,7-Dimethoxy-2-oxo-2H-chromene-3-carboxylic Acid (**3j**).* IR (KBr): 3500−3320, 3046, 1751, 1695, 1615, 1562, 1479, 1268 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ = 3.84 (s, 3H), 3.88 (s, 3H), 6.28 (6.28 (d, J = 2.1 Hz, 1H), 6.40 (d, J = 2.1 Hz, 1H), 8.31 (s, 1H), 13.30 (bs, 1H). LCMS (ESI): m/z 251 ($M+H^+$).

*3-Oxo-3H-benzo[f]chromene-2-carboxylic Acid (**3k**).* IR (KBr): 3070−2700, 1746, 1683, 1602, 1570, 1396, 1238 cm^{-1}.^1H NMR (400 MHz, DMSO-d_6): δ = 7.57 (d, J = 8 Hz, 1H), 7.69 (t, J = 8 Hz, 1H), 7.83 (t, J = 8 Hz, 1H), 7.97 (d, J = 8 Hz, 1H), 8.24 (d, J = 8 Hz, 1H), 8.43 (d, J = 8 Hz, 1H), 13.41 (bs, 1H). LCMS (ESI): m/z 240.95 ($M+H^+$)

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Notes

The authors declare no competing financial interest.

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