

Synthesis of coumarin-based derivatives from different starting materials: A review of ongoing developments

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ABSTRACT

Objective: This brief review highlights the recent advances in the synthesis of coumarin-based derivatives from phenols, aldehydes, ketones, and various other functional group-containing starting compounds. Also, the recent developments in the conditions of several original synthetic methods involving Pechmann and Knoevenagel reactions are being revised.

Conclusion: It is critical to decreasing energy consumption, prevent hazardous chemicals, and get pure molecules in high yields during synthesis. Scientists working in this sector will be able to utilize this comparison of reaction conditions and compound yields to create new efficient procedures.

Keywords: Coumarin, Synthesis, Pechmann and Knoevenagel reactions

الغاية من الدراسة: تحضير المركبات التي تحتوي على الكومارين من الفينولات والألدهيدات والكيوتونات ومختلف المركبات الوظيفية الأخرى التي تحتوي على مجموعة بدائية. أيضاً، تتم مراجعة التطورات الأخيرة في ظروف العديد من الأساليب الاصطناعية التقليدية التي تتضمن تفاعلات بجمان ونوفينايجل. **الاستنتاج:** تقليل أو منع انبعاث الطاقة، ومنع المواد الكيميائية الخطرة، والحصول على مركبات ذات نقاوة عالية بنسبة ناتج عالي جداً خلال عملية التشييد. سيتمكن العلماء العاملون في هذا القطاع من الاستفادة من هذه المقارنة لظروف التفاعل والعوائد المركبة لطرق جديدة فعالة. **الكلمات المفتاحية:** الكومارين، التوليف، تفاعلات بجمان ونوفينايجل.

INTRODUCTION

Coumarins are abundantly expressed in nature and may be found as secondary metabolites in many plant sections involving the seeds, roots, leaves, peels, flowers, and fruits¹. Because the majority of recovered coumarins exhibit various biological activities²⁻⁴, coumarin derivatives are increasingly being synthesized. As the extraction of coumarins from the plants is time-

consuming and unprofitable (several processing steps to the last product)⁵.

Coumarin derivatives can be synthesized via a range of methodologies, including the Baylis-Hillman, Perkin condensation, Vilsmeier-Haack, Knoevenagel condensation, Claisen rearrangement, Pechmann condensation, Wittig-reaction, and Suzuki cross-coupling reaction⁶.

Their findings on the coumarins' therapeutic potentials⁷. Some of these

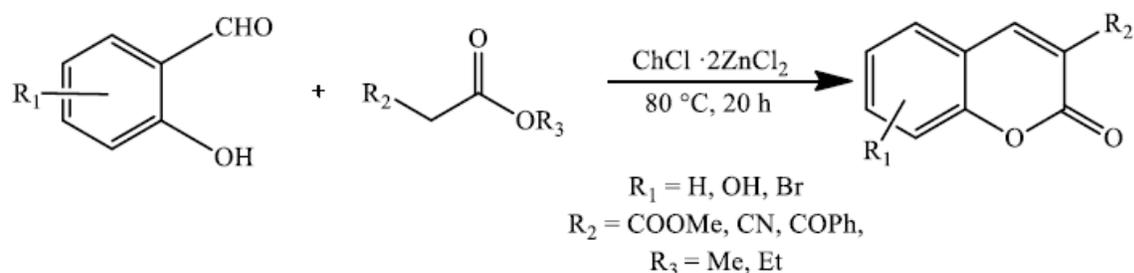
results indicated that many synthetic coumarins have antimicrobial properties, including anti-HIV, antiviral, anti-tuberculosis, antibacterial, and antifungal impacts ⁸. Also, several coumarin compounds were shown to have strong antioxidant properties and some of them are being evaluated as acetyl cholinesterase (AChE) inhibitors, with the potential to be used as medications for treating Alzheimer's disease ^{9,10}. Additionally, other coumarin derivatives have a variety of biological effects, such as anti-hyperglycemic, anticancer, anti-inflammatory, and anticoagulant actions ¹¹.

Since the coumarin chemical nucleus has been established as a functional pharmacophore, the demand for synthesizing compounds derived from this backbone is increasingly grown ¹². Many coumarin synthetic methods have been employed using starting materials with various functional groups and reaction experimental parameters ¹³. The present brief review article summarizes

the results of the recently reported research papers regarding the synthesis of coumarin derivatives from various precursors via various experimental methods.

Synthesis of coumarin derivatives from aldehyde functionalized compounds

Keshavarzipour and Tavakol reported the facile green synthesis of coumarin derivatives via the Knoevenagel condensation reaction phenotype using a deep eutectic solvent. This dissolving agent that also acts as a catalyst was prepared by mixing, at 100°C, one mole of choline chloride and two moles of zinc chloride. The starting materials utilized in this synthesis, as shown in Scheme 1, included simple or functionalized salicylaldehydes and methylene involving compounds, such as ethyl 3-oxo-3-phenylpropanoate, ethyl cyanoacetate, and dimethyl malonate. The incomes were significant ranged between 61% and 96% ¹⁴.



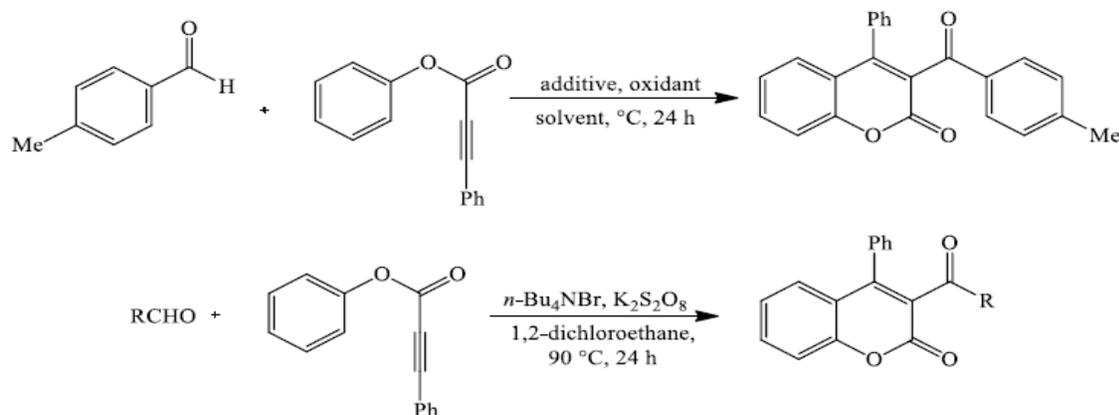
Scheme 1. Synthesis of coumarin derivatives from various aldehydes and active methylenes as described by Keshavarzipour and Tavakol.

Mi and colleagues administrated the metal-free tandem oxidative acylation and cyclization, as shown in Scheme 2, various 3-acyl-4-aryl coumarin derivatives were synthesized by coupling alkynoates with aldehydes. For optimizing the reaction conditions, the condensation between diethyl-*p*-

tolualdehyde and phenyl 3-phenylpropionate was performed as a reaction model in the locked environment under nitrogen gas using an oil bath for one day. Through the optimization process, the incoming factors have been modulated: catalyst (Et₄NBr, n-Bu₄NI, n-Bu₄NBr, n-

Bu₄NCl, n-Bu₄NF, and pivalic acid), oxidizing agent ((NH₄)₂S₂O₈, Na₂S₂O₈, K₂S₂O₈, and *tert*-butyl hydroperoxide), solvent (H₂O, ACN, CH₃CH₂Cl₂, dioxane, and toluene), and activating temperature (80, 90 and

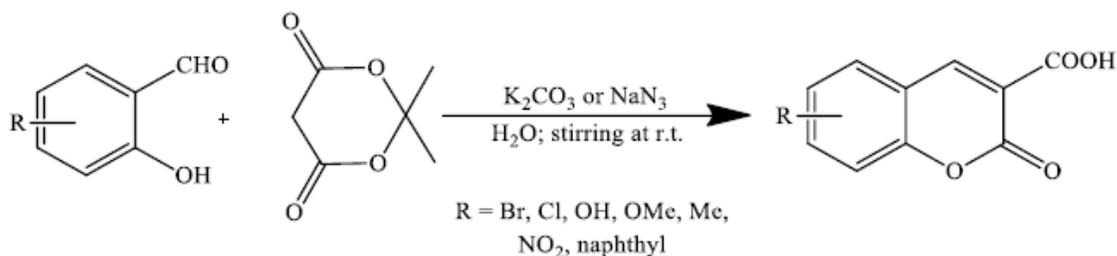
100°C). Based on the acquired results, the authors concluded that the best reaction factors are the K₂S₂O₈ as an oxidizing agent, n-Bu₄NBr as a catalyst, ClCH₂CH₂Cl as a solvent, and 90°C as an activating temperature ¹⁵



Scheme 2. Metal-free tandem oxidative acylation and cyclization for the synthesis of various 3-acyl-4-aryl coumarin derivatives, as demonstrated by Mi and colleagues.

Brahmachari recorded the synthesis of various coumarin-3-carboxylic acid derivatives at room temperature in an aqueous medium using a one-pot Knoevenagel condensation reaction. To recognize the catalytic agent afforded the best yield, a model reaction between Meldrum's acid and salicylaldehyde was conducted. The results reported that the best catalytic agents were NaN₃ and K₂CO₃ indicated the reaction yields of 99% and 92%, respectively. Subsequently, the condensations

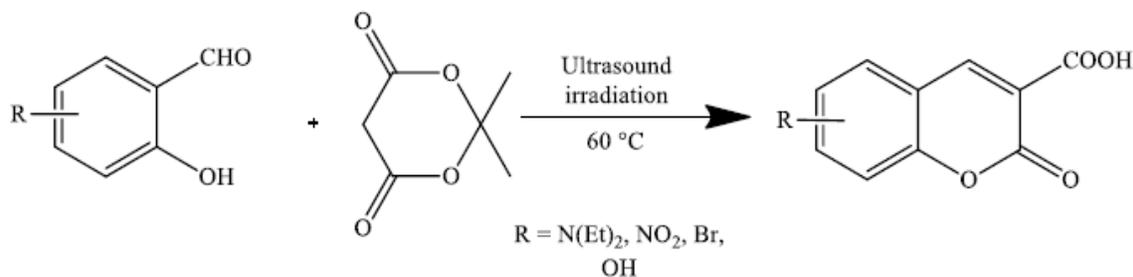
between different functionalized salicylaldehydes and Meldrum's acid were conducted using the detected catalytic agents resulting in different functionalized coumarin-3-carboxylic acid derivatives, as shown in Scheme 3, in the yields ranged between 73% and 99%. Since the NaN₃ is a highly toxic reagent especially at the employed concentration (50 mol%), the author recommended the utilization of K₂CO₃ in the concentration of 20 mol% as a preferred catalytic agent ¹⁶.



Scheme 3. Synthesis of various coumarin-3-carboxylic acid derivatives via a one-pot Knoevenagel condensation reaction as described by Brahmachari.

Fiorito *et al.* developed a new advancement in the synthesis of coumarin-3-carboxylic acid derivatives by applying a green version of the Knoevenagel condensation reaction. This advance, as shown in Scheme 4, involved the sonication of various functionalized salicylaldehydes with Meldrum's acid at 60°C. The innovation involved in this method was the

utilization of vegetable juice like liqueur limoncello or aqueous-based liquid acquired from the processing of olive or buttermilk as a dissolving medium. The technique afforded products with high yield percentages ranged between 91 to 99. From the obtained results, the authors concluded that the best outcome was related to the use of lemon juice as a dissolving medium ¹⁷.

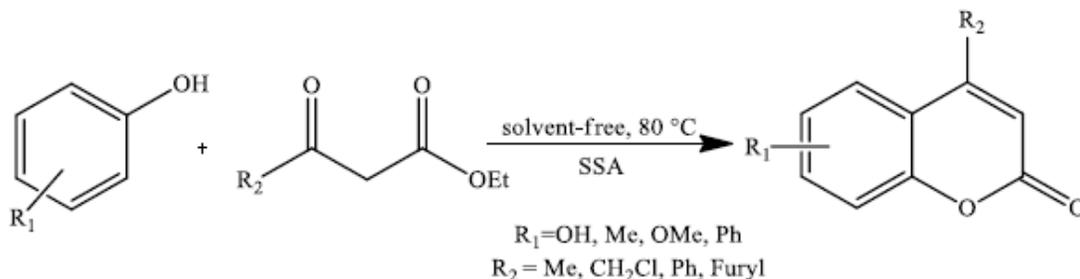


Scheme 4. Sonication-assisted synthesis of coumarin-3-carboxylic acid derivatives as described by Fiorito *et al.*

Synthesis of coumarin derivatives from phenol functionalized compounds

Rezaei *et al.* prepared several coumarin derivatives via a solvent-free version of the Von-Pechmann reaction. Through this, different phenolic- and β-ketoester-containing compounds were coupled in

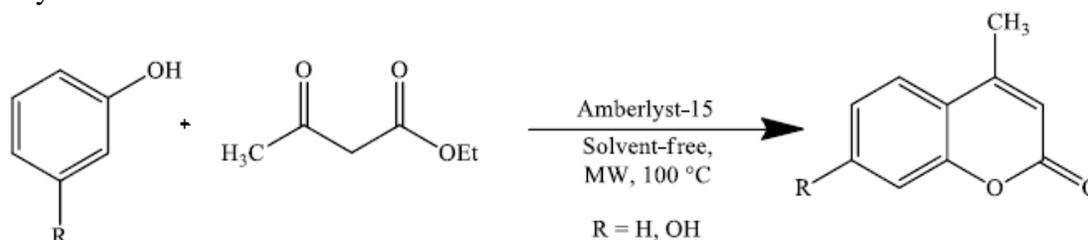
the presence of starch sulfuric acid as a catalyst, as shown in Scheme 5. To optimize the reaction conditions, including the mixing period, activating temperature, and catalyst concentration, a model reaction was initiated by coupling 3-hydroxyphenol and ethyl acetoacetate at 80°C ¹⁸.



Scheme 5. Von-Pechmann reaction catalyst by SSA (starch sulfuric acid) as reported by Rezaei *et al.*

Bouasla *et al.* investigated the green synthesis of hymecromone and 4-methylumbelliferyl using the solvent-free version of Pechmann reaction, as depicted in Scheme 6. This synthesis was promoted by microwave irradiation and catalyzed by a solid heterogeneous catalyst like sulfonic acid functionalized

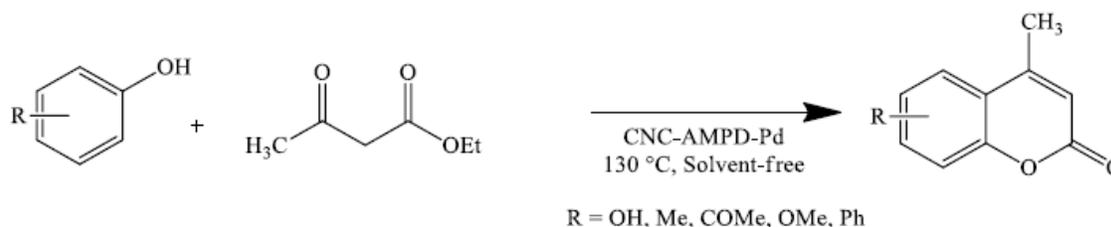
hybrid silica, zeolite β , or Amberlyst-15. The authors concluded from the acquired results that the latter catalyst afforded the best catalytic effect in comparison with the others, with yields for hymecromone and 4-methylumbelliferyl were 97% and 43% respectively ¹⁹.



Scheme 6. Green synthesis of hymecromone and 4-methylumbelliferyl as reported by Bouasla *et al.*

Mirosanloo *et al.* prepared a novel bioproped nanocatalyst, named Palladium nanoparticle supported with 2-aminopyrimidine nanocellulose (CNC-AMPD-Pd), to catalyze the solvent-free synthesis of coumarin derivatives via a Pechmann condensation, as shown in Scheme 7. The condensation reaction between resorcinol and ethyl-acetoacetate was selected as a model for studying the impacts of various reaction conditions on the yield. The results

indicated that the preferred reaction conditions that afforded the 96% yield of 7-hydroxy-4-methylcoumarin solvent-free reaction at 130°C. The author documented that the prepared catalyst can be reused and recycled multiple times before losing its catalytic performance. This advantage paired with the solvent-free environment result in low pollution, quick access to products, no pd leaking into the environment, safe operation, and simple workup ²⁰.



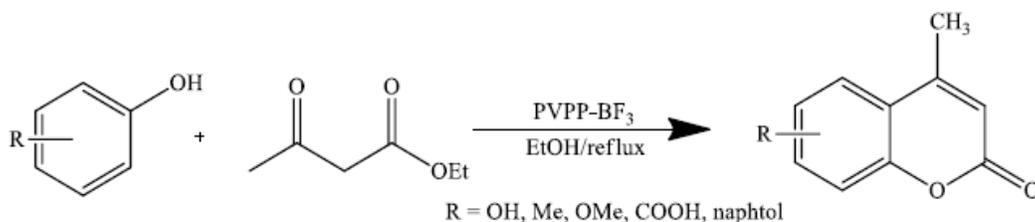
Scheme 7. Green synthesis of different 4-methylumbelliferyl derivatives using the solid catalyst prepared by Mirosanloo *et al.*

Mokhtary and Najafzadeh investigated the utility of the solid heterogeneous catalyst, which is the boron trifluoride loaded on polyvinylpyrrolidone (PVPP-BF₃), to promote Pechmann

condensation. This reaction, as shown in Scheme 8, was run perfectly in the synthesis of 4-methylcoumarin based derivatives through the condensation of various phenolic compounds with ethyl

acetoacetate in EtOH at refluxing conditions. Besides the high yields, the catalytic agent offered two benefits

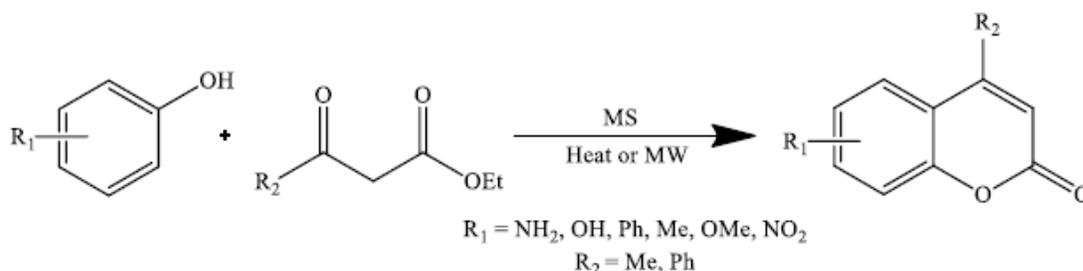
including the non-corrosive nature and heightened Lewis acid character²¹.



Scheme 8. Synthesis of different 4-methylcoumarin derivatives using the solid catalyst symbolized as PVPP-BF₃.

To develop a benign Pechmann condensation reaction, Moradi and co-workers introduced the employment of meglumine sulfate (MS) as a promoting agent, as shown in Scheme 9. As a model reaction, the coupling of resorcinol and ethyl acetoacetate was proceeded to identify the optimal reaction conditions. Time of mixing,

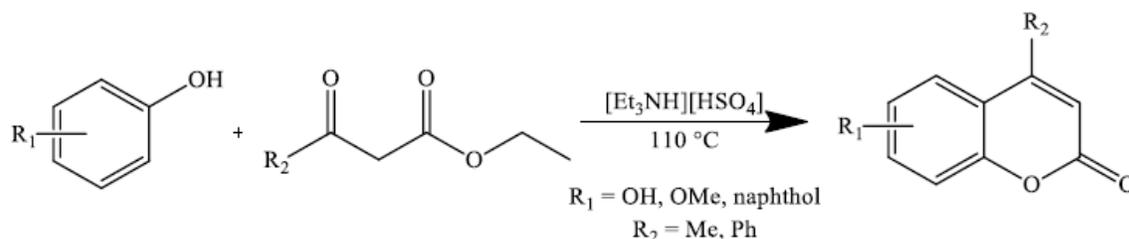
activating energy, and quantity of the catalytic agent were among the studied parameters. From the acquired outcomes, the authors concluded that the solvent-free reaction promoted by microwave irradiation and catalyzed by MS represented an efficient green protocol for synthesis of coumarins via a Pechmann condensation reaction²².



Scheme 9. Synthesis of different coumarin derivatives using the protocol introduced by Moradi and co-workers.

To improve the production of potent pharmacologically active coumarinic compounds, Karimi-Jabei *et al.* investigated the employment of an ionic-liquid catalyst named hydrogen sulfate salt of triethylamine and symbolized chemically as [Et₃NH][HSO₄]. During the optimization protocol, two reaction parameters were manipulated using the condensation of resorcinol with ethyl acetoacetate as a model reaction. The variables included the solvent (MeOH,

EtOH, ACN, CHCl₃, and solvent-free) and activating temperature (25, 50, 110, and 130°C). The results revealed that the best outcomes were acquired by applying the activating temperature of 110°C under a solvent-free reaction environment. By utilizing this protocol, different 4-substituted coumarin derivatives, as shown in Scheme 10, have resulted from condensing various functionalized β-keto esters in good to excellent outcomes (83-95%)²³.

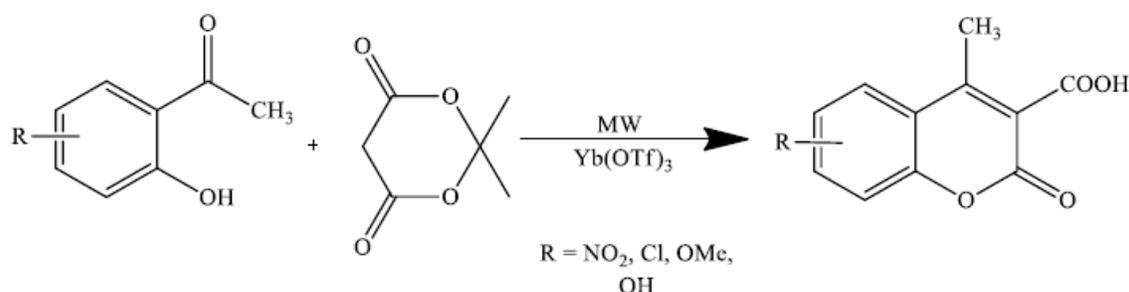


Scheme 10. Utilization of hydrogen sulfate salt of triethylamine in the synthesis of different 4-substituted coumarin derivatives.

Synthesis of coumarin derivatives from ketone functionalized compounds

To improve and optimize the synthesis of an interested group of semi-synthetic coumarins named coumarin-3-carboxylic acid, Fiorito *et al.* investigated a new synthetic protocol. In which, derivatives of the titled group were synthesized by condensing Meldrum's acid with different *ortho*-hydroxy acetophenones, as shown in Scheme 11. The reaction

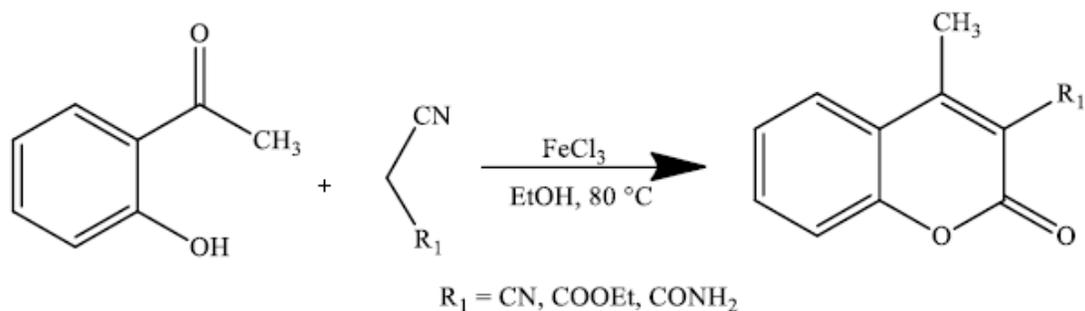
parameters included the use of microwave irradiation as activating energy, solvent-free conditions as a reaction milieu, and ytterbium triflate as a catalytic agent. The authors proposed that the latter, which is symbolized as $(\text{Yb}(\text{OTf})_3)$, can increase the reaction outcome to the maximum extend (98%)²⁴.



Scheme 11. Microwave-assisted synthesis of different coumarin-3-carboxylic acid derivatives as proposed by Fiorito *et al.*

An efficient and green synthesis of 3-functionalized-4-methylcoumarin derivatives was developed by He *et al.* The target compounds were prepared, as shown in Scheme 12, by coupling *ortho*-hydroxy acetophenone with each of the following compounds containing

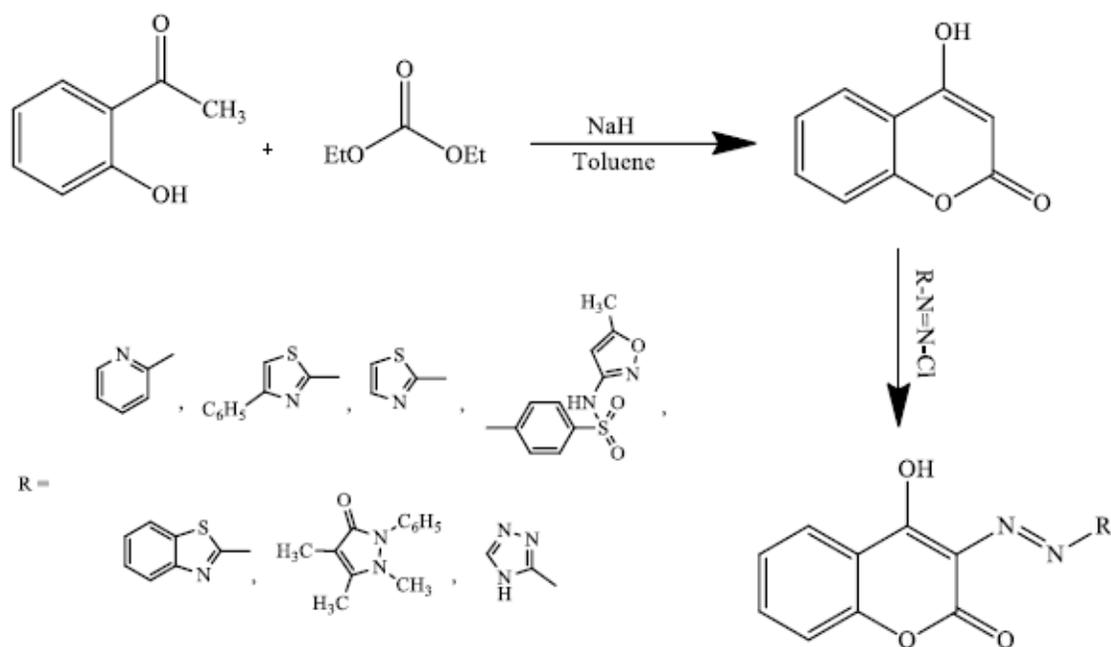
activated methylene moiety: ethyl 2-cyanoacetate, malononitrile, and 2-cyanoacetamide. The authors proposed that the positive impact of this environmentally benign protocol was the utilized catalyst, FeCl_3 , that shifted the yields percentage from 41 to 63²⁵.



Scheme 12. Environmentally benign synthetic protocol for synthesizing 3-functionalized-4-methylcoumarin derivatives as developed by He *et al.*

Sahoo *et al.* demonstrated the synthesis of various 3-heteroarylazo derivatives of 4-coumarinol, as shown in Scheme 13. In the first step of this synthesis, Claisen condensation in toluene was utilized to prepare 4-coumarinol by coupling *ortho*-hydroxy acetophenone with eufin

(diethyl carbonate) using NaH as a base. The target derivatives were obtained in the second synthetic step by coupling the diazonium salts of different heterocyclic amines. The acquired % yields ranged between 55% and 82%²⁶.



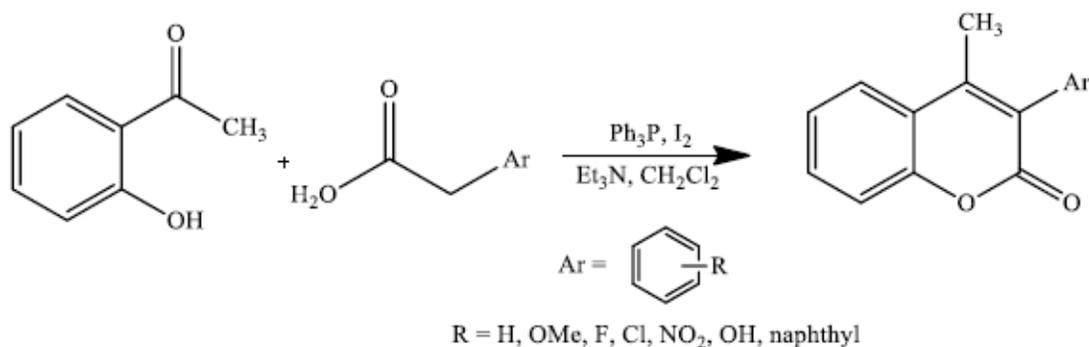
Scheme 13. Two-step synthesis of various 3-heteroarylazo derivatives of 4-coumarinol as described by Sahoo *et al.*

A two-step one-pot synthesis of 3-aryl 4-methylcoumarin compounds substituted at 3-position with various aryl moieties was described by Phakhodee *et al.* This

synthesis, as shown in Scheme 14, was performed at room temperature and mediated by a specific catalytic mixture consists of Ph_3P , I_2 , and Et_3N . The

condensation of 2-hydroxybenzaldehyde and 4-methoxy phenylacetic acid was used as a model reaction. The optimization protocol involved the variation in the base type (NNM, DABCO, imidazole, DMAP, and Et₃N) and solvent (ACN, DMF, toluene, and DCM). From the afforded results, the authors concluded that the best outcomes

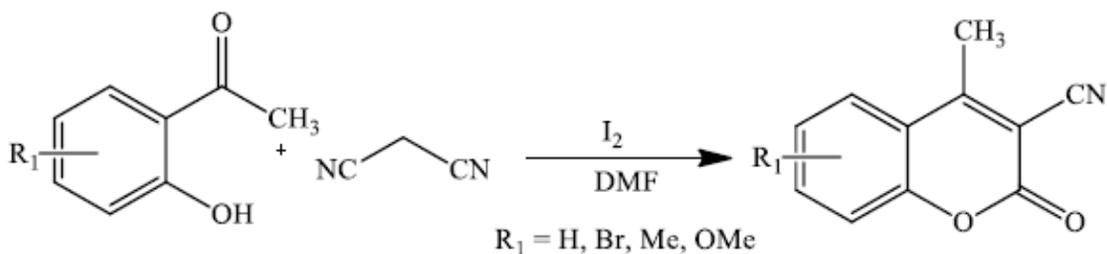
were arisen by using Et₃N and DCM as base and solvent, respectively. Based on this conclusion, 20 congeners were prepared from the condensation of various hydroxy acetophenone compounds with aryl acetic acids under the detected optimized reaction conditions affording good to excellent yields ranged between 52% to 89%²⁷.



Scheme 14. A two-step one-pot synthesis of 4-methylcoumarin based derivatives substituted at 3-position with various aryl moieties as described by Phakhodee *et al.*

Sharma and Makrandi described the one-pot synthesis of 3-cyano-4-methylcoumarin compounds under conventional heating and microwave irradiation. This synthesis, as depicted in Scheme 15, proceeded in DMF by condensing malononitrile with various *ortho*-hydroxy acetophenone derivatives employing iodine as a catalytic agent.

From the obtained results, the authors concluded that there are no significant differences in the %yields among the utilized activating energy sources. Despite this, the basic merit of using microwave irradiation as activating energy was the reduction in the reaction interval²⁸.

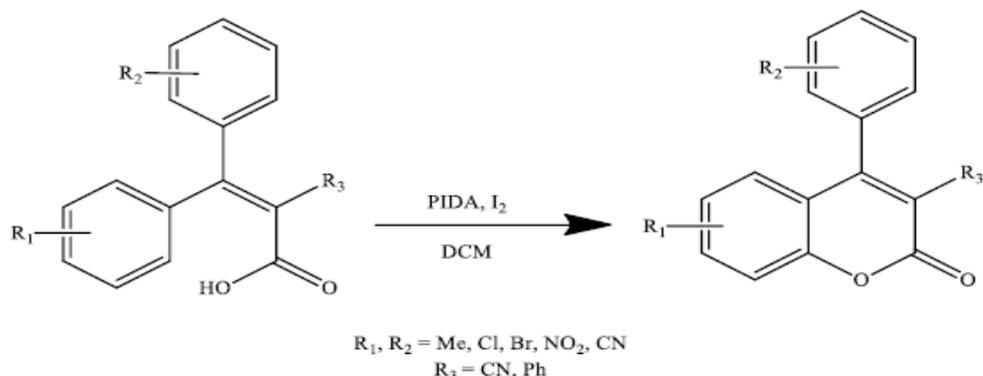


Scheme 15. A one-pot synthesis of 3-cyano-4-methylcoumarin compounds as described by Sharma and Makrandi.

Synthesis of coumarin derivatives from carboxylic acid functionalized compounds

Li *et al.* demonstrated a specific method for synthesizing various 4-phenylcoumarins from carboxylic acid-functionalized compounds under microwave irradiation conditions, as shown in Scheme 16. During the course of the reaction, the optimization process was conducted using various phenyl acrylic acid-based derivatives, solvents (EtOH, ACN, DMF, toluene, DCM, and

TFA), catalysts (I₂, LiBr, BF₃.Et₂O, and TFA), and oxidants (phenyliodine diacetate that symbolized as PIDA and bistrifluoroacetate that symbolized as PIFA). From the obtained outcomes, the authors identified the best reaction parameters that were DCM, I₂, and PIDA as a solvent, catalyst, and oxidizing agent, respectively. By applying the aforementioned reaction parameters, a series of neoflavonoids (4-phenylcoumarins) was prepared in good-to-excellent outcomes ranged between 41% to 92% ²⁹.



Scheme 16. Microwave-aided synthesis of 4-phenylcoumarin as described by Li *et al.*

Yan *et al.* developed a novel and practical method for the synthesis of trisubstituted coumarin derivatives. This silver-promoted radical cyclization method involved the coupling between various alkynoates and α -ketoacids, as shown in Scheme 17. The coupling between phenylglyoxylic acid and 3-phenylpropiolate was used as a model reaction and accomplished in varied conditions. The variables included the change in the solubilizing agent

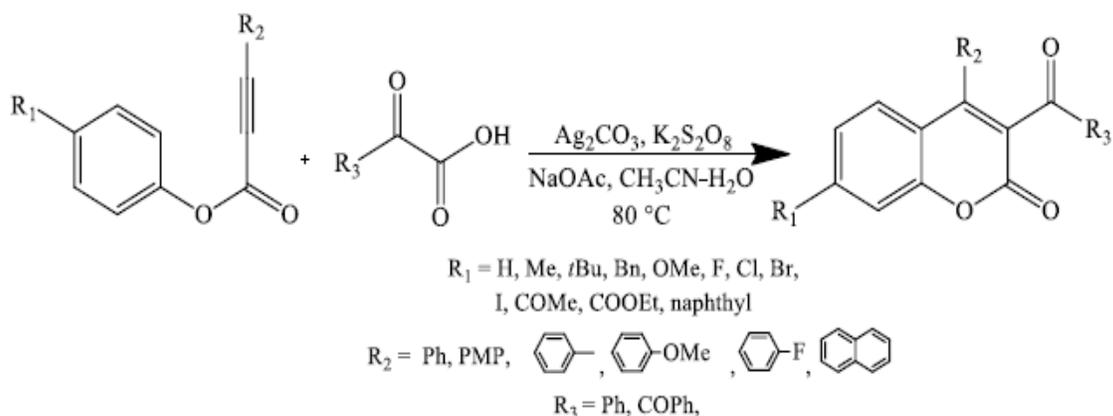
(DMF:H₂O, H₂O, and ACN:H₂O), oxidant (K₂S₂O₈, O₂, TBHP, (NH₄)₂S₂O₈, and Na₂S₂O₈), and catalyst (AgOAc, Ag₂CO₃, Ag₂O, AgNO₃, and catalyst-free). From the afforded results, the researchers reported that the best outcome (75%) was arisen from applying the following reaction parameters: ACN:H₂O, K₂S₂O₈, and AgNO₃ as a solvent mixture, oxidant, and catalyst, respectively ³⁰.



Scheme 17. Silver-promoted radical cyclization method for the synthesis of trisubstituted coumarin derivatives as described by Yan *et al.*

Liu *et al.* demonstrated the novel and efficient synthesis of 4,7-disubstituted-3-acylcoumarins, as shown in Scheme 18, by silver-activated decarboxylative annulation. The coupling between 2-phenyl-2-oxoacetic acid and alkynoate was utilized as a model reaction and performed in diverse conditions. The variables included the change in the catalytic- (AgNO_3 and Ag_2CO_3), oxidizing- (TBHP, $\text{PhI}(\text{OAc})_2$, oxone,

$(\text{NH}_4)_2\text{S}_2\text{O}_8$, and $\text{K}_2\text{S}_2\text{O}_8$), solubilizing- ($\text{ACN-H}_2\text{O}$, $\text{DMF-H}_2\text{O}$, ACN , and DMF), and neutralizing- (KOH , KHCO_3 , NaOAc , and Na_2CO_3) agents. The researcher concluded from the afforded results that the highest outcome (74%) was arisen from applying the following reaction parameters: $\text{ACN:H}_2\text{O}$, $\text{K}_2\text{S}_2\text{O}_8$, Ag_2CO_3 , and NaOAc as a solvent mixture, oxidant, catalyst, and base, respectively³¹.



Scheme 18. Silver-activated decarboxylative annulation method for the synthesis of 4,7-disubstituted-3-acylcoumarins as described by Liu *et al.*

CONCLUSION

Coumarin derivatives have a variety of biological functions and are beneficial to human health management. Extraction of coumarin-based products from such

plants is time-consuming and costly. Synthesis using green methods has greater yields than the derivatives acquired by traditional methods.

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