A review on convenient synthesis of substituted coumarins using reusable solid acid catalysts

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Due to growing concern about chemicals and their impact on the environment, cleaner reaction conditions are needed to be incorporated into chemical synthetic procedures. Recently, the use of heteropolyacid catalysts, mainly reusable solid acid catalysts, has gained a leading role in organic synthesis due to their environmental and economic considerations and industrial utilization. The high catalytic activity, moisture sensitivity, reusability and inexpensive makes solid supported reagents attractive substituents to conventional Lewis acids. Nowadays synthesis of coumarins and their derivatives has attracted considerable attention from organic and medicinal chemists for many years as a large number of natural products contain this heterocyclic nucleus. In continuation with our investigations into the synthesis of substituted coumarins and due to several advantages of heterogeneous catalysts viz. cost-effective, no side products, high yield of desired products and no toxic waste material, here we report a new approach for the synthesis of substituted coumarins using solid acid catalysts.

Introduction

Coumarins as a major class of natural and synthetic products exhibit a variety of pharmacological and biological activities. There is growing curiosity for coumarins and their derivatives due to their anti-HIV, anti-oxidant, anti-fungal, antihelminthic and antibacterial properties. They are used in food and cosmetic industries as additive and also found applications as insecticides, optical brighteners, fluorescent and laser dyes. Masesane et al. reported the synthesis of chromane derivatives through the reaction of salicylaldehyde and enolates and they found that the reactions of salicylaldehyde and enolates give nearly optically pure chromane derivatives. Coumarins can also be prepared by various methods viz. Pechmann condensation, Perkin, Knoevenagel and Reformatsky reactions. Pechmann condensation has been most popularly method for coumarin synthesis, since it proceeds from simple substrate viz. phenol and ß-ketoester and gives excellent yields of coumarins. Pechmann condensation utilizes various catalysts viz. sulphuric acid, trifluoroacetic acid, phosphorous pentaoxide, ZrCl₄, TiCl₄ and ionic liquids, which have many drawbacks such as long reaction time, use of hazardous solvents, creates side products and salt waste due to acid neutralization. There has been some effort to find alternative, eco-friendly synthetic methods. Nowadays, the use of heterogeneous solid acid catalysts has fascinated significant attention. These catalysts have some advantages such as ease of product work-up, recyclability, strong safety and tolerance for wide range of temperature and pressures. Naikwadi and his coworkers reported the catalytic reaction of active methylene compounds with cyclic enol ethers and aryl acetals through oxonium intermediate under solvent-free conditions using heterogeneous solid acid catalysts and they found that Amberlyst-15 gave excellent yields of alkylated products. Therefore, there is a propensity to replace the classic homogeneous catalysts by heterogeneous solid acid catalysts. Due to several benefits of heterogeneous catalysts, in this review we encapsulate synthesis of substituted coumarins using solid acid catalysis.

Synthesis of substituted coumarins using solid acid catalysts

An efficient and facile synthesis of novel class of coumarin-containing secondary benzamide derivatives (4) has been developed via one-pot condensation of 5,7-dihydroxy coumarins (1), substituted aldehydes (2) and benzamide (3) using tung state sulphuric acid by Karami and his coworkers (Scheme 1). To standardize the reaction conditions, a reaction between 5,7-dihydroxy-4-methylcoumarin, benzaldehyde and benzamide were chosen as a model reaction. The model reaction was screened under various conditions. After conducting several experiments, they found that the desired reaction took place efficiently using 1 mol% of tungstate sulphuric acid (TSA) at 120 °C under solvent-free conditions. The proposed mechanism of the formation of desired products is shown in Fig. 1. According to proposed mechanism, first there is formation of adduct (I) by the condensation reaction of substituted aldehyde and benzamide in the presence of TSA as an efficient proton source. Then C-8 of coumarin attacks on adduct (I) and gives
Finally, by tautomerization, the desired product is obtained. They also found that tungstate sulphuric acid is a reusable heterogeneous catalyst, which makes this procedure mild, convenient, and eco-friendly. Simplicity of procedure, use of safe and recyclable catalysts, high yields, and short reaction times are some beauties of the present methodology.

Khaligh et al. found that poly(4-vinylpyridinium) hydrogen sulfate solid acid was an efficient catalyst for the synthesis of substituted coumarins (7) via Pechmann condensation reaction between substituted phenols (5) and \( \beta \)-ketoester (6) using ultrasound irradiation at ambient temperature. Simplicity in operation, avoiding the use of toxic catalysts and solvents, excellent yield of desired products, reuse of catalyst are some merits of the present methodology. First, they standardized the reaction conditions by exploring a model reaction between resorcinol and ethylacetoacetate (Scheme 2) in the presence of different solvents.

**Scheme 1** TSA-catalyzed synthesis of coumarin-containing secondary benzamides.

**Fig. 1** Possible mechanism for synthesis of coumarin-containing secondary benzamides.
viz. toluene, methanol, ethanol and dichloromethane under reflux reaction conditions as well as solvent-free medium at variety of temperature with PVPHS as the catalyst. The results are presented in Table 1.

From Table 1 it was observed that resorcinol conversion increased with increase in temperature up to 80 °C. There was no significant difference in conversion between 70 and 80 °C (Table 1, entries 6–8). The yield of desired product decreased with decreasing of catalyst amount (Table 1, entry 9) and no reaction took place in the absence of catalyst after 6 h of reaction time (Table 1, entry 1).

Further, they also observed that PVPHS employed under ultrasonic irradiation showed a more effective catalytic activity in comparison with the stirring at room temperature in terms of yield and reaction time (Table 2, entries 2 and 3).

The plausible mechanism for the synthesis of substituted coumarins in the presence of 7-hydroxy-4-methylcoumarin in the presence of PVPHS as a promoter under ultrasound irradiation is shown in Fig. 2.

Akbari et al. reported the synthesis of bis-coumarin (9) in excellent yield via Knoevenagel condensation between substituted aldehydes (2) and 4-hydroxy coumarin (8) in water under microwave irradiation in the presence of Fe₃O₄@sulfosalicylic acid magnetic nanoparticles as solid acid catalyst (Scheme 3). Less reaction time, excellent yields of desired products, avoid the use of hazardous or toxic reagent and solvents, thermal durability, easy separation and high reusability are main attractive characteristics of current methodology. First, they explored the model reaction between benzaldehyde and 4-hydroxy coumarin and studied the effect of different reaction conditions. The results are summarized in Table 3. The results show that the highest yield and lowest time of reaction were obtained when the reaction was performed in the presence of 0.05 g of sulfosalicylic acid magnetic nanoparticles under microwave irradiation at 180 W in water as green solvent (Table 3, entry 9).

The possible reaction mechanism for the synthesis of bis-coumarin via Knoevenagel condensation is depicted in Fig. 3. First there is activation of substituted aldehyde by the acid catalyst and after that activated aldehyde react with 4-hydroxy coumarin to give an α,β-unsaturated intermediate. Then, there is Michael addition of the 4-hydroxy coumarin.
with an α,β-unsaturated intermediate to give the final pol-
hydroquinoline product. Finally, a tautomeric proton shift
produces the desired product. Table 4 presented the results
from the synthesis of bis-coumarin by reaction of benzal-
dehyde and 4 hydroxycoumarin in the presence of Fe₃O₄@sulfosalicylic acid magnetic nanoparticles which has

**Table 3** Optimization of the model reaction

| Entry | Catalyst (g)                          | Power | Time (min) | Yield (%) |
|-------|---------------------------------------|-------|------------|-----------|
| 1     | Sulfosalicylic acid (0.01)            | 180   | 15         | 75        |
| 2     | FeCl₃·6H₂O (0.05)                     | 180   | 15         | 43        |
| 3     | Bulk-Fe₃O₄ (0.05)                     | 180   | 15         | 50        |
| 4     | Nano-Fe₃O₄ (0.05)                     | 180   | 15         | 68        |
| 5     | Fe₃O₄@sulfosalicylic acid (0.03)      | 180   | 20         | 89        |
| 6     | Fe₃O₄@sulfosalicylic acid (0.03)      | 300   | 10         | 92        |
| 7     | Fe₃O₄@sulfosalicylic acid (0.05)      | 180   | 10         | 92        |
| 8     | Fe₃O₄@sulfosalicylic acid (0.05)      | 180   | 10         | 92        |
| 9     | Fe₃O₄@sulfosalicylic acid (0.08)      | 180   | 10         | 96        |
| 10    | Fe₃O₄@sulfosalicylic acid (0.015)     | 180   | 10         | 80        |
| 11    | —                                     | 180   | 20         | 30        |
been compared with the other methods reported in literature. The results show that the present method is preferable because of its reaction times and efficiency.

Samiei et al. reported the green synthesis coumarin derivatives (7) via Pechmann condensation reaction between substituted phenols (5) and β-ketoesters (6) in excellent yield under solvent-free conditions in presence of novel sulfonated carbon-coated magnetic nanoparticles (Scheme 4).

For optimization of reaction conditions, first the model reaction was explored between resorcinol and ethyl acetoacetate to produce 7-hydroxy-4-methylcoumarin. The reaction was also optimized with respect to various parameters viz. catalyst loading, different temperatures and various solvents as shown in Table 5. It was observed from Table 5 that lack of catalyst and also with a catalyst loading of Fe₃O₄ NPs, CCMNPs (Fe₃O₄@C) led to no product even after 6 h, while the use of SCCMNPs (Fe₃O₄@C@OSO₃H) could produce related 4H-coumarin in excellent yield.
a good yield during the short time. Hence, SCCMNPs with the sulfonylic acid moiety on the surface of MNP was introduced as an effective catalyst in the Pechmann condensation. They also found that 6.5 mol% catalyst loading was identified as an optimized concentration in the model reaction at 120 °C under solvent-free condition.

The comparison of catalytic activity of present catalyst with other catalysts reported in literature was shown in Table 6. Khan and his coworkers reported the synthesis of coumarins (7) via Pechmann condensation reaction between substituted phenols (5) and β-ketoesters (6) in presence of zirconia-based heterogeneous catalyst (Scheme 5).41 First of all model reaction was carried out between resorcinol and ethyl acetoacetate without a catalyst at 80 °C, but there will be no formation of product as shown in Table 7. They also observed that excellent yield of product was obtained when electron releasing group linked with substituted phenols, while poor yield of product was obtained when electron withdrawing group linked with substituted phenols. They also studied reaction between resorcinol and ethyl acetoacetate with 50 mg of the catalyst ZrO2–TiO2 in polar solvent viz. ethanol and non-polar solvent viz. toluene by varying the temperature condition as shown in Table 8. The plausible mechanism for the reaction is depicted in Fig. 4.
Kumbar and his coworkers developed efficient and facile methodology for synthesis of class of chromeno-3-substituted derivatives (10a–10l) in excellent yields in presence of solid-supported heterogeneous silica sulphuric acid as a reusable catalyst (Scheme 6).

They found that use of silica sulphuric acid as catalyst provide good to excellent yields of desired products as shown in Table 9. The reaction was also optimized with respect to polar protic and aprotic solvents viz. acetonitrile, ethanol, DMF, dioxane, THF and DMSO as summarized in Table 10. The plausible mechanism of reaction was presented in Fig. 5. First there is nucleophilic attack of aniline on the carbonyl carbon of coumarin. Then in next step protonation occurs from silica sulphuric acid, forming itself as a nucleophile in the reaction mixture. Then nucleophilic SSA abstracts protons from nitrogen and gains stability by the formation of double bond between C and N and subsequent dehydration give desired product.

Moghaddam and Hoda designed magnetic graphene oxide coated with cysteic acid as an efficient and reuseable catalyst for the synthesis of 4H-chromene derivatives (13) via one-pot...

![Plausible mechanism for the synthesis of substituted coumarins in presence of zirconia-based heterogeneous catalyst.](image-url)
multicomponent reaction between enolizable compound (11), malononitrile (12), substituted aldehydes (2) or isatin and a mixture of water–ethanol as a green solvent (Scheme 7). Excellent yield of desired products, less reaction time, mild reaction conditions and eco-friendly approach are some merits of present methodology.

An efficient and facile method for the one-pot synthesis of dihydropyrano[3,2-c]chromene derivatives (14) have been reported via reaction between substituted aldehydes (2), 4-hydroxycoumarin (8) and malononitrile (12) in presence of poly(4-vinyl-pyridine) as a cheap, efficient and recyclable catalyst (Scheme 8). They also reported the synthesis of biscoumarin derivatives (9) via one-pot reaction between substituted aldehydes (2) and 4-hydroxycoumarin (8) in presence of same catalyst (Scheme 9). To optimize the reaction conditions, a model reaction was explored between 4-chlorobenzaldehyde, malononitrile and 4-hydroxycoumarin in presence of different concentration of P4VPy. The effect of different solvents viz. CH3CN, CH2Cl2, H2O and EtOH and temperature in the synthesis of dihydropyrano[3,2-c] chromene derivatives in the presence of P4VPy summarized in Table 11. They found that best result was obtained using 20 mg of P4VPy at 70°C in a mixture of H2O and ethanol. They also observed that aldehydes containing electron-withdrawing as well as electron-donating groups such as Cl, Br, CH3, OCH3, NO2 and OH in the ortho, meta and para positions can be easily converted to the corresponding dihydropyrano[3,2-c] chromenes in less reaction times with excellent yield.

After most favourable results of P4VPy in the synthesis of dihydropyrano[3,2-c]chromene derivatives, they were interested to study the efficiency of this polymeric reagent in the synthesis

### Table 9 Physical and analytical data of synthesized coumarin derivatives

| Products | R       | Yield (%) | Time (min) | Melting point (°C) |
|----------|---------|-----------|------------|--------------------|
| 10a      | H       | 78        | 180        | 165–167            |
| 10b      | p-Cl    | 62        | 210        | 193–195            |
| 10c      | p-Br    | 61        | 190        | 182–184            |
| 10d      | p-OH    | 67        | 195        | 198–200            |
| 10e      | p-OCH3  | 62        | 210        | 205–208            |
| 10f      | p-CH3   | 71        | 240        | 202–204            |
| 10g      | 2,6-Dimethyl | 58   | 220        | 188–190            |
| 10h      | m-Cl    | 68        | 210        | 197–200            |
| 10i      | m-Br    | 69        | 190        | 178–181            |
| 10j      | m-OH    | 62        | 195        | 184–186            |
| 10k      | m-OCH3  | 59        | 200        | 208–210            |
| 10l      | m-CH3   | 73        | 225        | 212–214            |

### Table 10 Optimization of reaction conditions

| Entry | Solvent | SSA | Time (h) | Temperature (°C) | Yield (%) |
|-------|---------|-----|----------|------------------|-----------|
| 1     | Acetonitrile | 1.0 | 4        | 25               | 35        |
| 2     | Ethanol  | 1.0 | 3        | 25               | 78        |
| 3     | DMF      | 1.0 | 12       | 25               | Nil       |
| 4     | Dioxane  | 1.0 | 6        | 25               | 38        |
| 5     | THF      | 1.0 | 12       | 25               | Trace     |
| 6     | DMSO     | 1.0 | 12       | 25               | Nil       |
| 7     | Acetone  | 1.0 | 12       | 25               | Nil       |
| 8     | Acetonitrile | 2.0 | 12       | 40               | 42        |
| 9     | Ethanol  | 0.0 | 12       | 25               | Nil       |
| 10    | Ethanol  | Silica | 12   | 25               | 45        |
Fig. 5  Proposed reaction pathway for the synthesis of substituted coumarins.

Scheme 7  One-pot three-component reaction of enolizable compound, active methylene nitriles, and aldehydes catalyzed by MNPs-GO–CysA in water : ethanol.

Scheme 8  Synthesis of dihydropyrano[3,2-c] chromene derivatives.
of biscoumarins. For standardization of reaction conditions, first model reaction was carried out between 4-chlorobenzaldehyde and 4-hydroxycoumarin in the presence of P4VPy at different reaction conditions as shown in Table 12. They observed that best reaction conditions for the synthesis of the bisoumarin derivatives are use of 20 mg of the P4VPy in water at 90 °C. They also found that aldehydes containing electron-withdrawing or electron donating substituents converting to desired products in less time. The plausible mechanism for the synthesis of substituted pyrazoles given in Fig. 6. The comparison of catalytic activity and reaction conditions of present catalyst P4VPy for the synthesis of dihydropyrano[3,2-c] chromene derivatives and bisoumarin derivatives are summarized in Table 13 and Table 14. This comparison shows disadvantages of the other procedures such as long reaction times, toxic reagents, high temperature, organic solvents, excess reagents and low yields.

An efficient, green and inexpensive synthesis of benzylpyrazolyl coumarin (16) by one-pot multicomponent condensation of hydrazine hydrate or phenyl hydrazine (15), β-ketoester (6), substituted aldehydes (2) and 4-hydroxy coumarin (8) in the presence of Amberlite IR-120 as a catalyst in an aqueous medium has been reported by Katariya and his coworkers (Scheme 10).58

Kaur et al. reported the synthesis of 3,3′-(arylmethylen) bis(4-hydroxy-2H-chromen-2-ones) via one-pot reaction between substituted aldehydes (2) and 4-hydroxy coumarin (8) catalyzed by camphor sulfonic acid (Scheme 11).59 Mild reaction conditions, use of metal-free organocatalyst, excellent yields of desired products, high atom economy, eco-friendly, easy isolation of products and no need of column chromatography are some merits of present methodology. To standardize the reaction conditions they conducted a model reaction between 4-methylbenzaldehyde and 4-hydroxycoumarin. Firstly, they explored the reaction in the absence of catalyst as well as solvent at room temperature and they observed that trace amount of yield was obtained after 24 h. Then under catalyst-free conditions, the same reaction was give 22% yield of desired product (Scheme 10).59

A comparison of catalytic activity and reaction conditions of present catalyst P4VPy for the synthesis of dihydropyrano[3,2-c] chromene derivatives and bisoumarin derivatives are summarized in Table 13 and Table 14. This comparison shows disadvantages of the other procedures such as long reaction times, toxic reagents, high temperature, organic solvents, excess reagents and low yields.

Table 11 The effect of different reaction conditions for the synthesis of dihydropyrano[3,2-c] chromene derivatives in the presence of P4VPy

| Entry | Catalyst (mg) | Solvent | Temperature (°C) | Time (min) | Yield (%) |
|-------|---------------|---------|-----------------|------------|-----------|
| 1     | —             | No solvent | RT              | 120        | Nil       |
| 2     | —             | No solvent | 100             | 120        | Nil       |
| 3     | 20            | CH3CN    | RT              | 120        | Nil       |
| 4     | 20            | CH3CN    | Reflux          | 120        | Mixture of products |
| 5     | 20            | CH2Cl2   | RT              | 120        | Mixture of products |
| 6     | 20            | CH2Cl2   | Reflux          | 120        | Mixture of products |
| 7     | 20            | H2O      | 90              | 180        | 50        |
| 8     | 24            | H2O      | 90              | 120        | 50        |
| 9     | 24            | EtOH     | RT              | 150        | 60        |
| 10    | 20            | EtOH     | 50              | 120        | 60        |
| 11    | 20            | EtOH     | 70              | 120        | 60        |
| 12    | 20            | H2O      | 70              | 5          | 95        |
| 13    | 24            | H2O/ EtOH | 70             | 5          | 95        |

Table 12 Optimization of the reaction conditions for the synthesis of bisoumarin derivatives catalyzed by P4VPy

| Entry | Catalyst (mg) | Solvent | Temperature (°C) | Time (min) | Yield (%) |
|-------|---------------|---------|-----------------|------------|-----------|
| 1     | —             | No solvent | RT              | 120        | Nil       |
| 2     | —             | No solvent | 100             | 120        | Nil       |
| 3     | 20            | CH3CN    | RT              | 120        | Nil       |
| 4     | 20            | CH3CN    | Reflux          | 120        | Mixture of products |
| 5     | 20            | CH2Cl2   | RT              | 120        | Mixture of products |
| 6     | 20            | CH2Cl2   | Reflux          | 120        | Mixture of products |
| 7     | 20            | H2O      | 90              | 180        | 50        |
| 8     | 24            | H2O      | 90              | 120        | 50        |
| 9     | 24            | EtOH     | RT              | 150        | 60        |
| 10    | 20            | EtOH     | 50              | 120        | 60        |
| 11    | 20            | EtOH     | 70              | 120        | 60        |
| 12    | 20            | H2O      | 70              | 5          | 95        |
| 13    | 24            | H2O/ EtOH | 70             | 5          | 95        |
sulfonic acid as catalyst for this reaction. They observed that 20 mol% of camphor sulfonic acid in aqueous ethanol (1 : 1 v/v) at room temperature came out as the best suitable conditions for the synthesis of desired product in terms of reaction time as well as product yield as summarized in Table 15.

The plausible mechanism for the synthesis of 3,3-(aryl-methylene)-bis(4-hydroxy-2H-chromen-2-ones) is shown in Fig. 7. According to the mechanism, firstly camphor sulfonic acid activate the carbonyl group of aldehydes which enhance the attack from C-3 position of 4-hydroxycoumarin and generate

![Proposed mechanism](image-url)
the Knoevenagel intermediate. Then second molecule of 4-hydroxycoumarin attack on Knoevenagel intermediate followed by enolisation gives the desired product in excellent yield.

A novel heterogeneous catalytic method was developed for the synthesis of coumarin (7) via reaction between β-ketoesters (6) and substituted phenols (5) in presence of Zn_{0.925}Ti_{0.075}O as catalyst by Jadhav and his coworkers (Scheme 12). They also observed that this shows recycle activity up to seven cycles with very good stability. Firstly, they standardized the reaction conditions in order to verify the role of catalyst by conducting a model reaction between phloroglucinol and ethylacetoacetate under solvent-free conditions and the results are summarized in Table 16. They observed that Zn_{0.925}Ti_{0.075}O is best catalyst for optimization studies in the synthesis of coumarin by Pechmann condensation. The various solvents effect viz. DCM, ethylacetate, acetonitrile, water, ethanol, toluene and DMF also studied for optimizing the reaction conditions during the synthesis of coumarin and the results are summarized in Table

| Entry | Catalyst (mol%) | Reaction conditions | Time (min) | Yield (%) | References |
|-------|-----------------|---------------------|------------|-----------|------------|
| 1     | SDS             | Water/60 °C         | 150        | 88        | 48         |
| 2     | Nano ZnO       | Ethanol reflux      | 90         | 49        | 49         |
| 3     | Nano Al(OH)₃   | Ethanol reflux      | 120        | 48        | 49         |
| 4     | DAHP            | Ethanol-H₂O/25 °C   | 240        | 85        | 50         |
| 5     | (S)-proline     | Ethanol-H₂O/100 °C  | 180        | 78        | 50         |
| 6     | Nano Al₂O₃     | Ethanol reflux      | 120        | 71        | 51         |
| 7     | P₄VPy          | Ethanol-H₂O/70 °C   | 5          | 95        | 47         |

Table 13 Comparison of different catalysts for the synthesis of dihydropyrano[3,2-c]chromene derivatives

| Entry | Catalyst (mol%) | Reaction conditions | Time (min) | Yield (%) | References |
|-------|-----------------|---------------------|------------|-----------|------------|
| 1     | SDS             | Water/60 °C         | 150        | 93        | 48         |
| 2     | [bmim]BF₄       | Solvent-free/60–70 °C | 150    | 91        | 52         |
| 3     | I₂              | H₂O/100 °C          | 27         | 93        | 53         |
| 4     | CHOH            | Solvent-free/50 °C  | 120        | 99        | 54         |
| 5     | [P₄VPy-BuSO₃H]Cl-X(AlCl₃) | Toluene/90 °C  | 36         | 93        | 55         |
| 6     | PSA             | Solvent-free/100 °C | 240        | 96        | 56         |
| 7     | Piperidine      | EtOH/r.t            | 240        | 96        | 57         |
| 8     | P₄VPy          | H₂O/90 °C           | 5          | 96        | 47         |

Table 14 Comparison of different catalysts used for the synthesis of biscoumarins
They conclude that solvent-free conditions and temperature of 110 °C was suitable for the synthesis of desired products under the optimized reaction conditions. The effect of catalyst concentration was studied on model reaction and the results are presented in Table 18. They found that 10 mol% Zn_{0.925}Ti_{0.075}O catalyst was the most optimal for Pechmann condensation of ethylacetoacetate and phloroglucinol.

The reaction pathway for the synthesis of coumarin through Pechmann condensation is represented in Fig. 8. Initially,
The reaction proceeds with the nucleophilic attack of the hydroxyl group of phloroglucinol on the activated ethylacetoacetate, resulting in the formation of intermediate. The formed intermediate rapidly undergoes cyclization through Lewis acid-catalyzed intramolecular condensation and followed by removal of water molecule to give desired products.

A magnetic nanocatalyst of Fe$_3$O$_4$@SiO$_2$–ZnCl$_2$ has been used for the synthesis of coumarin derivatives (7) via Pechmann condensation reaction of substituted phenols (5) and β-ketoesters (6) in excellent yield under solvent-free conditions by Rahimi and Soleimani (Scheme 13). The advantages of this method are straightforward, easy work-up, catalyst reusability and leading to excellent yields.

Carrillo and his coworkers reported the synthesis of substituted coumarins (7) via one-pot reaction between substituted phenols (5) and β-ketoesters (6) in presence of propylsulfonic acid supported in FDU-5 (FDU-5-Pr–SO$_3$H) as a catalyst (Scheme 14). The catalytic activity of FDU-5-Pr–SO$_3$H for the synthesis of substituted coumarins under optimized conditions was compared with other organic and inorganic catalysts summarized in Table 19.

Saffarian et al. reported the synthesis of coumarin containing 1,4-dihydropyridines (18) via condensation reaction between substituted aldehydes (2), 4-hydroxycoumarin (8) and ammonium acetate (17) under solvent-free conditions.

| Table 17 | Solvent screening for synthesis of substituted coumarin by Pechmann condensation reaction |
|----------|------------------------------------------------------------------------------------------|
| Entry    | Solvent | Temperature (°C) | Time (h) | Yield (%) |
| 1        | DCM     | 40               | 8        | 24        |
| 2        | Ethyl acetate | 78               | 8        | 16        |
| 3        | Acetonitrile | 80               | 8        | 37        |
| 4        | Water   | 100              | 5        | 41        |
| 5        | Ethanol | 78               | 5        | 63        |
| 6        | Toluene | 110              | 10       | Nil       |
| 7        | DMF     | 150              | 10       | Nil       |
| 8        | Solvent-free | 110              | 3        | 88        |
| 9        | Solvent-free | 90               | 5        | 61        |
| 10       | Solvent-free | 130              | 3        | 80        |

| Table 18 | Effect of catalyst concentration for synthesis of substituted coumarin by Pechmann condensation reaction |
|----------|-----------------------------------------------------------------------------------------------------------|
| Entry    | Catalyst amount (mol%) | Time (h) | Yield (%) |
| 1        | 5                        | 5        | 67        |
| 2        | 10                       | 3        | 88        |
| 3        | 15                       | 3        | 88        |

Fig. 8 Plausible mechanism for Pechmann condensation using EAA and phloroglucinol promoted by Zn$_{0.925}$Ti$_{0.075}$O NPs.

Scheme 13 Direct synthesis of coumarin derivatives.
Simple protocol, simplicity of product isolation using water, decrease the temperature of reaction, reduce the use of hazardous solvents, excellent yield of products, eco-friendly conditions and less reaction times are some beauties of present methodology. Firstly, to optimize the reaction conditions they conducted a model reaction between 4-methyl benzaldehyde, 4-hydroxycoumarin and ammonium acetate. They observed that 10 mg of the Fe₃O₄@SiO₂@(CH₂)₃–urea–quinoline sulfonic acid chloride at 80°C under solvent free conditions supplied the best results as presented in Table 20.

They performed the model reaction also in the presence of different catalysts and obtained yields as presented in Table 21. They observed that 10 mg of the Fe₃O₄@SiO₂@(CH₂)₃–urea–quinoline sulfonic acid chloride under solvent free conditions supplied the best results as presented in Table 21.

| Entry | Solvent | Temperature (°C) | Catalyst (mg) | Time (min) | Yield (%) |
|-------|---------|------------------|---------------|------------|-----------|
| 1     | —       | 90               | —             | 90         | 30        |
| 2     | —       | 90               | 5             | 30         | 80        |
| 3     | —       | 90               | 10            | 20         | 86        |
| 4     | —       | 90               | 15            | 20         | 85        |
| 5     | —       | 100              | 10            | 20         | 81        |
| 6     | —       | 80               | 10            | 20         | 85        |
| 7     | —       | 60               | 10            | 30         | 70        |
| 8     | H₂O     | ReExx            | 10            | 30         | 85        |
| 9     | EtOH    | ReExx            | 10            | 45         | 70        |
| 10    | EtOAc   | ReExx            | 10            | 90         | 20        |
| 11    | CH₂Cl₂  | ReExx            | 10            | 90         | Nil       |
| 12    | n-      | ReExx            | 10            | 90         | Nil       |

Table 21 Screening the model reaction in the presence of desired catalyst

| Entry | Catalyst | Yield (%) |
|-------|----------|-----------|
| 1     | Fe₃O₄   | 40        |
| 2     | Fe₃O₄@SiO₂ | 40     |
| 3     | Fe₃O₄@SiO₂@(CH₂)₃–urea–quinoline | 65     |
| 4     | Fe₃O₄@SiO₂@(CH₂)₃–urea–quinoline sulfonic acid chloride | 85     |
related intermediates of the Fe₃O₄@SiO₂@(CH₂)₃–urea–quinoline sulfonic acid chloride at 80 °C under solvent free conditions for 20 min and results are summarized in Table 21.

A suitable protocol for synthesis of coumarins derivatives (7) was reported by Bouasla and his coworkers via one-pot reaction between substituted phenols (5) and β-ketoesters (6) in presence of heterogeneous solid acid catalyst viz. Amberlyst-15 in solvent-free medium under microwave irradiation (Scheme 16). Initially, they conducted a model reaction between resorcinol and ethylacetoacetate as model substrate. They observed that by changing the reaction time from 5 min to 20 min, a maximum yield of 97% was obtained and no reaction was observed in absence of catalyst as summarized in Table 22. The plausible mechanism for the reaction is shown in Fig. 9.

An efficient method for the synthesis of 3-carboxycoumarins (20) was reported via Knoevenagel condensation reaction between substituted aldehydes (2) and Meldrum’s acid (19) in presence of polymeric magnetic nanocatalyst by Maleki et al. (Scheme 17). This method has many advantages such as less reaction time, high yield and easy isolation of catalyst. The plausible mechanism for the reaction is shown in Fig. 10.

Suryawanshi and his coworkers reported the synthesis of coumarins (7) via Pechmann condensation reaction between substituted phenols (5) and β-ketoesters (6) in presence of reusable polymeric SO₂H-functionalized cation exchange resins viz. Amberlite IR-120, Dowex 50, X-8100 and Tulsion T-42 (Scheme 18). Excellent yield of products, short reaction time,
easy work-up and use of safe catalyst are some advantages of present methodology.

Rostami and Zare reported the synthesis of substituted coumarins (7) via one-pot reaction between substituted phenols (5) and β-ketoesters (6) in presence of carbonized sugarcane bagasse (CSCB) as a new and efficient solid acid catalyst (Scheme 19). Simple preparation of catalyst, safe handling, inexpensive, excellent yield of products, catalyst reuseability, solvent-free and easy work-up are some benefits of present methodology. Initially, model reaction was considered between

| Entry | Concentration of catalyst (mg) | Solvent    | Temperature (°C) | Time (min) | Yield (%) |
|-------|--------------------------------|------------|------------------|------------|-----------|
| 1     | None                           | H₂O        | Reflux           | 120        | 0         |
| 2     | 30                             | H₂O        | Reflux           | 60         | 50        |
| 3     | 30                             | EtOH       | Reflux           | 40         | 80        |
| 4     | 30                             | Solvent-free | 80              | 15         | 91        |
| 5     | 30                             | Solvent-free | 70              | 30         | 89        |
| 6     | 30                             | Solvent-free | 120             | 120        | 26        |
| 7     | 20                             | Solvent-free | 15              | 15         | 92        |
| 8     | 10                             | Solvent-free | 5               | 5          | 92        |
3-hydroxyphenol and ethylacetoacetate and the effect of different solvents, temperature and amount of catalyst was investigated and results were summarized in Table 23. The plausible mechanism for the reaction is shown in Fig. 11.

Sun and his coworkers reported the synthesis of substituted coumarins (7) via Pechmann condensation reaction between substituted phenols (5) and β-ketoesters (6) catalyzed from Wells–Dawson heteropolyacid (H₆P₂W₁₈O₆₂). This work provides a novel, cheaper and safer way to synthesize coumarins unsubstituted on the pyranic nucleus (Scheme 20). Initially, they optimized the reaction conditions by exploring a model reaction between 2-methyl-3-hydroxy-phenol and ethyl 3,3-diethoxypropionate. The effect of the temperature and reaction time were investigated and results were summarized in Table 24. The comparison of efficiencies of various catalysts used in the synthesis of 7-hydroxy-8-methylcoumarin was summarized in Table 25. The plausible mechanism for the reaction is shown in Fig. 12.

An efficient and facile synthesis of coumarins (7) was reported in excellent yields via Pechmann condensation reaction between substituted phenols (5) and β-ketoesters (6) under solvent-free medium using both conventional method and microwave irradiation in less reaction times in presence of

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**Table 24** Optimization of Pechmann condensation reaction for the synthesis of 7-hydroxy-8-methylcoumarin

| Entry | Catalyst concentration | Temperature (°C) | Time (h) | Yield (%) |
|-------|------------------------|------------------|----------|-----------|
| 1     | 0.10                   | 100              | 3        | 75        |
| 2     | 0.25                   | 100              | 3        | 87        |
| 3     | 0.50                   | 100              | 3        | 86        |
| 4     | 1.00                   | 100              | 3        | 84        |
| 5     | 0.25                   | 80               | 3        | 74        |
| 6     | 0.25                   | 90               | 3        | 90        |
| 7     | 0.25                   | 90               | 2        | 72        |
| 8     | 0.25                   | 90               | 4        | 89        |
| 9     | 0.25                   | 90               | 3        | 84        |
| 10    | 0.25                   | 90               | 3        | 90        |
| 11    | 0.25                   | 90               | 3        | 95        |
| 12    | 0.25                   | 90               | 3        | 95        |

**Table 25** Synthesis of 7-hydroxy-8-methylcoumarin mediated by different catalysts

| Entry | Catalyst | Time (h) | Yield (%) |
|-------|----------|----------|-----------|
| 1     | MeSO₃H   | 3        | 20        |
| 2     | MeSO₃H/basic Al₂O₃ | 3     | 30        |
| 3     | MeSO₃H/neutral Al₂O₃ | 3     | 34        |
| 4     | MeSO₃H/acidic Al₂O₃ | 3     | 80        |
| 5     | Acidic Al₂O₃ | 3        | 30        |
| 6     | Al₂O₃    | 2        | 10        |
| 7     | AlCl₃/MeSO₃H | 2     | 12        |
| 8     | ZnCl₂/MeSO₃H | 2     | 5         |
| 9     | Cu(CH₂CN)₄PF₆ | 2     | 10        |
| 10    | H₆P₂W₁₈O₆₂ | 2        | 82        |
| 11    | FeCl₃    | 3        | 8         |
| 12    | TiCl₄    | 3        | 5         |
The efficiency of the cellulose sulfuric acid compared with other catalysts is summarized in Table 26. It was found that cellulose sulfuric acid is a more efficient and superior catalyst over other acidic catalysts with respect to reaction time and yield.

| Entry | Catalyst                        | Yield (%) |
|-------|---------------------------------|-----------|
| 1     | Cellulose sulfuric acid         | 97        |
| 2     | Silica sulfuric acid            | 92        |
| 3     | p-Toluene sulfonic acid         | 85        |
| 4     | Sulfuric acid in acetic acid    | 55        |
| 5     | No catalyst                     | 15        |

cellulose sulfuric acid by Kuram et al. (Scheme 21). The efficiency of the cellulose sulfuric acid compared with other catalysts is summarized in Table 26. It was found that cellulose sulfuric acid is a more efficient and superior catalyst over other acidic catalysts with respect to reaction time and yield.

Palaniappan and John et al. reported the synthesis of substituted coumarins (7) via one-pot reaction between substituted phenols (5) and β-ketoesters (6) in presence of novel polyaniline–fluoroboric acid–dodecylhydrogensulfate (PANI-HBF₄–DHS) as reusable catalyst (Scheme 22).
Kolvari and his coworkers reported the synthesis of substituted coumarins (7) via one-pot reaction between substituted phenols (5) and β-ketoesters (6) in presence of perlite sulfonic acid (perlite-SO₃H (PeSA)) as heterogeneous reusable solid acid catalysts (Scheme 23). Inexpensive, ease of preparation, more stability and reusability, low toxicity and easy of handling are some advantages of present catalytic systems. To show the advantages of current protocol in comparison with reported results in literature was summarized in Table 27. They

![Scheme 23](image)

**Scheme 23** Synthesis of substituted coumarins catalyzed by PeSA.

| Entry | Catalyst | Condition | Yield (%) | Time (min) | References |
|-------|----------|-----------|-----------|------------|------------|
| 1     | PeSA     | 110 °C/Solvent-free | 97 | 15 | 80 |
| 2     | ASA      | 110 °C/Solvent-free | 85 | 30 | 81 |
| 3     | CMK-5-SO₃H | 110 °C/Solvent-free | 95 | 20 | 82 |

![Scheme 24](image)

**Scheme 24** W/ZrO₂ solid acid catalyzed synthesis of substituted coumarins.

![Scheme 25](image)

**Scheme 25** TfOH-mediated preparation of coumarins.

![Fig. 13](image)

**Fig. 13** Plausible mechanism for the synthesis of coumarins in the presence of TfOH as Brønsted acid catalyst.
found that PeSA showed greater activity than some other heterogeneous catalysts.

Reddy et al. reported the synthesis of substituted coumarins (7) via Pechmann condensation reaction between substituted phenols (5) and β-ketoesters (6) in presence of W/ZrO₂ solid acid catalyst (Scheme 24).⁸¹

Kim et al. reported the synthesis of substituted coumarins (22) via condensation reaction between substituted phenols (5) and allenes (21) in the presence of TFOH as Bronsted acid catalyst in excellent yield (Scheme 25).⁸⁴ The plausible mechanism for the reaction is shown in Fig. 13.

Maheswara and his coworkers synthesized substituted coumarins (7) via Pechmann condensation reaction between substituted phenols (5) and β-ketoesters (6) in presence of heterogeneous recyclable catalyst (HClO₄·SiO₂) under solvent-free medium (Scheme 26).⁸⁵ Cost-effective, less reaction time and operational simplicity are some benefits of present methodology.

Kuram et al. reported the synthesis of substituted coumarins (7) via Pechmann condensation reaction between substituted phenols (5) and β-ketoesters (6) in the presence of xanthan sulfuric acid as a solid acid catalyst under solvent-free conditions (Scheme 27).⁸⁶ They found that this method is very simple, inexpensive, less reaction time and catalyst could be reused. The effect of catalyst on the yield of products was summarized in Table 28. They also investigated the efficiency of the XSA compared to various sulphur analog acidic catalysts and results are summarized in Table 29.

Singh and his coworkers reported the synthesis of substituted coumarins (7) via Pechmann condensation reaction between substituted phenols (6) and β-ketoesters (5) in presence of sulphamic acid (Scheme 28).⁸⁷
Bose et al. reported the synthesis of substituted coumarins (7) via Pechmann condensation reaction between substituted phenols (6) and β-ketoesters (5) in presence of indium(III) chloride as an efficient catalyst (Scheme 29).

An efficient and facile synthesis of substituted coumarins (7) was reported by one-pot reaction between substituted phenols (5) and β-ketoesters (6) in presence of new magnetic nanocomposites of ZrO$_2$–Al$_2$O$_3$–Fe$_3$O$_4$ as green solid acid catalysts (Scheme 30).

Mesoporous zirconium phosphate (m-ZrP) is used as solid acid catalyst for the synthesis of substituted coumarins (7) via Pechmann condensation reaction between substituted phenols (5) and β-ketoesters (6) in both conventional heating as well as microwave heating (Scheme 31).

Table 30 Effect of different solvents on Pechmann condensation reaction for synthesis of substituted coumarins

| Solvent        | Time (h) | Temperature (°C) | Yield (%) |
|----------------|----------|------------------|-----------|
| Nitrobenzene   | 4        | 120              | 25        |
| Toluene        | 15       | 120              | 34        |
| Solvent-free   | 4        | 120              | 51        |
| Solvent-free   | 4        | 150              | 76        |

Table 31 Effect of SD-SO$_3$H catalyst concentration on the yield of product

| Entry | Catalyst (g) | Temperature (°C) | Time (min) | Yield (%) |
|-------|--------------|------------------|------------|-----------|
| 1     | —            | 90               | 120        | 0         |
| 2     | 0.025        | 90               | 120        | 40        |
| 3     | 0.05         | 90               | 75         | 72        |
| 4     | 0.075        | 90               | 120        | 70        |
| 5     | 0.10         | 90               | 120        | 60        |
| 6     | 0.15         | 90               | 120        | 60        |
assisted method by Sinhamahapatra and his coworkers (Scheme 31). The effect of solvent on reaction was summarized in Table 30.

Tahanpesar and Sarami reported the synthesis of substituted coumarins (7) via one-pot Pechmann condensation reaction between substituted phenols (5) and \(\beta\)-ketoesters (6) in presence of sulfonated sawdust (SD-SO\(_3\)H) as solid acid catalyst under solvent-free conditions (Scheme 32). Further, they observed the catalytic efficiency of SD-SO\(_3\)H on the yield of product and results were presented in Table 31. They also observed the effects of different solvents viz. CHCl\(_3\), CH\(_3\)CN, CH\(_2\)Cl\(_2\), THF, MeOH and H\(_2\)O and temperature on the synthesis of desired products and results were presented in Table 32.

The plausible mechanism for the synthesis of substituted coumarins was presented in Fig. 14. The comparison of catalytic activity of SD-SO\(_3\)H with other catalyst found in literature was presented in Table 33.

### Conclusion and future prospects

This review article summarized the synthesis of substituted coumarins using solid acid catalysts. Benefits of these methods include clean reaction profiles, minimization of side products,
efficient and facile experimental procedures and inexpensive.
This review is endeavouring to find potential future directions
in the development of more potent and specific analogs of
nitrogen and oxygen containing heterocyclic compounds for
the biological target by the use of heterogeneous catalysts.
The information illustrated in this review also encourage organic
chemist for the design of novel molecules to identify many more
biologically active heterocycles for the benefit of humanity.

Author contributions

Conceptualization: Susheel Gulati, Rajvir Singh, Suman Sangwan,
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Susheel Gulati, Rajvir Singh, Suman Sangwan, supervision:
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Conflicts of interest

Authors declared that there is no conflict of interest regarding
the publication of this paper.

Abbreviations

| Abbreviation | Meaning                                          |
|--------------|--------------------------------------------------|
| TSA          | Tungstate sulphuric acid                         |
| MW           | Microwave irradiation                           |
| PVPHS        | Poly(4-vinylpyridinium) hydrogen sulfate         |
| SCCMNs       | Sulfonated carbon-coated magnetic nanoparticles  |
| SSA          | Silica sulphuric acid                            |
| XSA          | Xanthan sulphuric acid                           |

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