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A review on convenient synthesis of substituted coumarins using reuseable 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 reuseable 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.[1–3] There is growing curiosity for coumarins and their derivatives due to their anti-HIV, anti-oxidant, anti-fungal, antihelmintic and antibacterial properties.[4–8] They are used in food and cosmetic industries as additive and also found applications as insecticides, optical brighteners, fluorescent and laser dyes.[9–13] Masesane *et al.*[14] reported the synthesis of chromane derivatives through the reaction of salicylaldehyde and enolates and they found that 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.[15] Pechmann condensation has been most popularly method for coumarin synthesis, since it proceeds from simple substrate *viz.* phenol and β-ketoester and gives excellent yields of coumarins. Pechmann condensation utilizes various catalysts *viz.* sulphuric acid, trifluoroacetic acid, phosphorous pentaoxide, $ZrCl_4$, $TiCl_4$ 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.[16] 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.[17–21] Naikwadi and his coworkers[22] 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 catalyst.

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 tungstate sulphuric acid by Karami and his coworkers (Scheme 1).[23] 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

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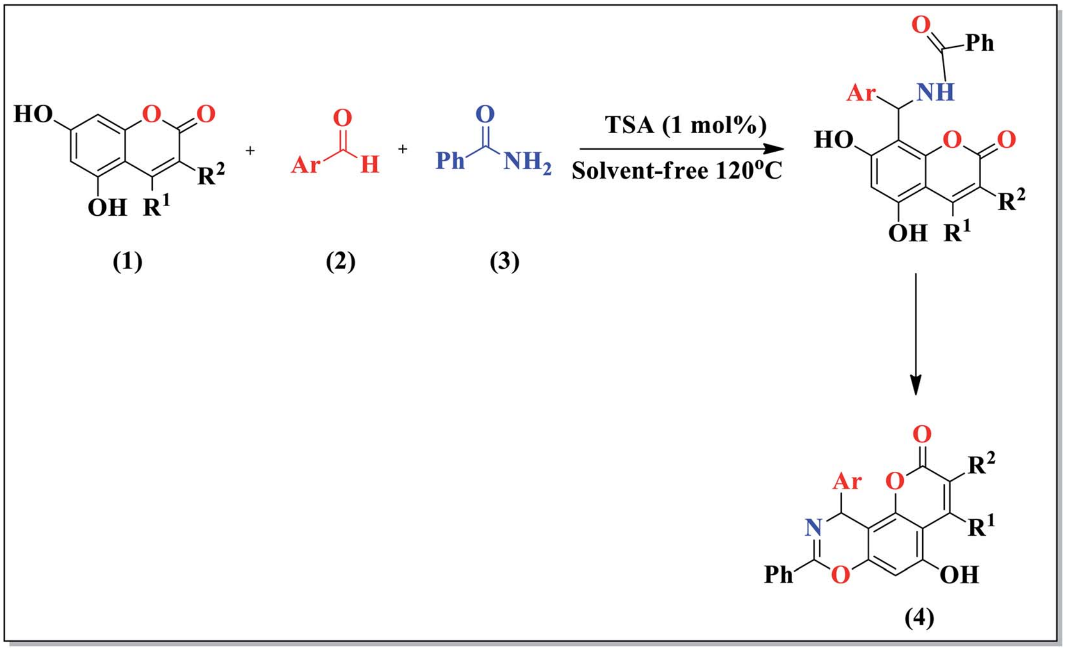


Scheme 1 TSA-catalyzed synthesis of coumarin-containing secondary benzamides.

intermediate **(II)**. Finally by tautomerization desired product obtained. They also found that tungstate sulphuric acid is reuseable heterogeneous catalyst, which make 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 present methodology.

Khaligh *et al.* found that poly(4-vinylpyridinium) hydrogen sulfate solid acid was efficient catalyst for the synthesis of substituted coumarins **(7)** *via* Pechmann condensation reaction between substituted phenols **(5)** and β-ketoester **(6)** using ultrasound irradiation at ambient temperature. Simplicity in operation, avoid use of toxic catalysts and solvents, excellent yield of desired products, reuse of catalyst are some merits of present methodology. First they standardized the reaction conditions by exploring model reaction between resorcinol and ethylacetoacetate (Scheme 2)[24] in presence of different solvents

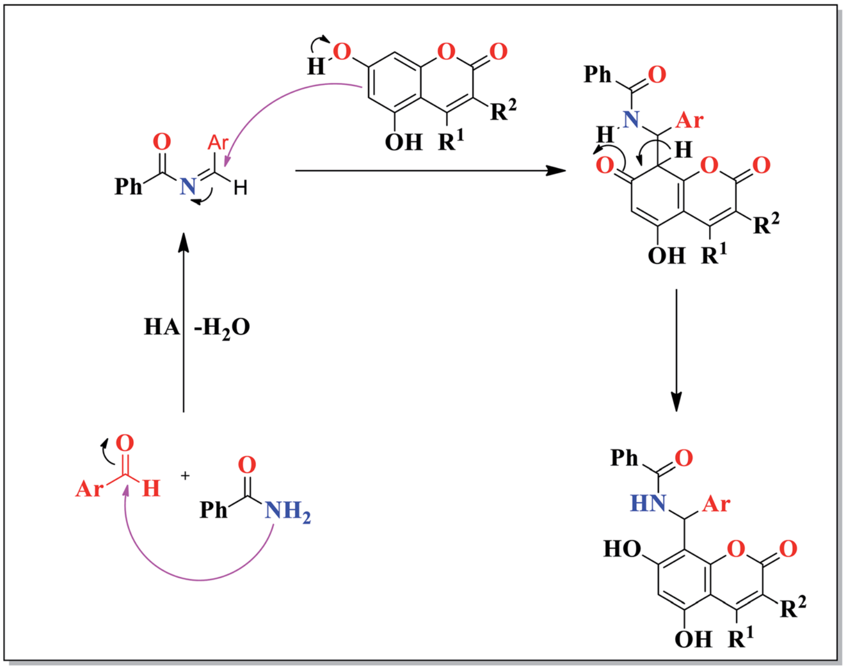
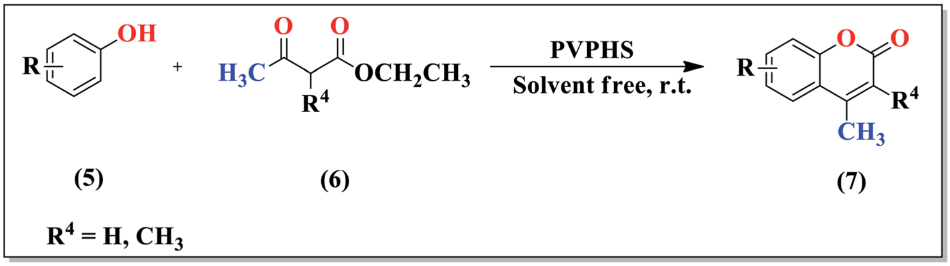


Fig. 1 Possible mechanism for synthesis of coumarin-containing secondary benzamides.



Scheme 2 The synthesis of substituted coumarins in presence PVPHS at room temperature under ultrasound irradiation and solvent-free conditions.

Table 1 Effect of temperature, solvent, amount of catalyst on the synthesis of substituted coumarins

Entry	Amount of catalyst (mg)	Temperature (°C)	Solvent	Time (min)	Yield (%)
1	—	60	Clean	360	Nil
2	10	Reflux	$C_6H_5CH_3$	60	72
3	10	Reflux	CH_3OH	60	66
4	10	Reflux	C_2H_5OH	60	68
5	10	Reflux	CH_2Cl_2	60	70
6	10	60	Clean	60	88
7	10	70	Clean	60	92
8	10	80	Clean	60	94
9	5	70	Clean	60	69

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* reaction between substituted aldehydes **(2)** and 4-hydroxycoumarin **(8)** in water under microwave irradiation in the presence of Fe_3O_4@sulfosalicylic acid magnetic nanoparticles as solid acid catalyst (Scheme 3).[25] 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-hydroxycoumarin 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-hydroxycoumarin to give an α,β-unsaturated intermediate. Then, there is Michael addition of the 4-hydroxycoumarin

Table 2 Reaction of resorcinol and ethylacetoacetate in the presence of different amount of PVPHS

		Room temperature		Ultrasonic irradiation	
Entry	Amount of catalyst (mg)	Time (h)	Yield (%)	Time (min)	Yield (%)
1	—	6 Trace		60 44	
2	5	2 32		15 86	
3	10	2 48		5 96	

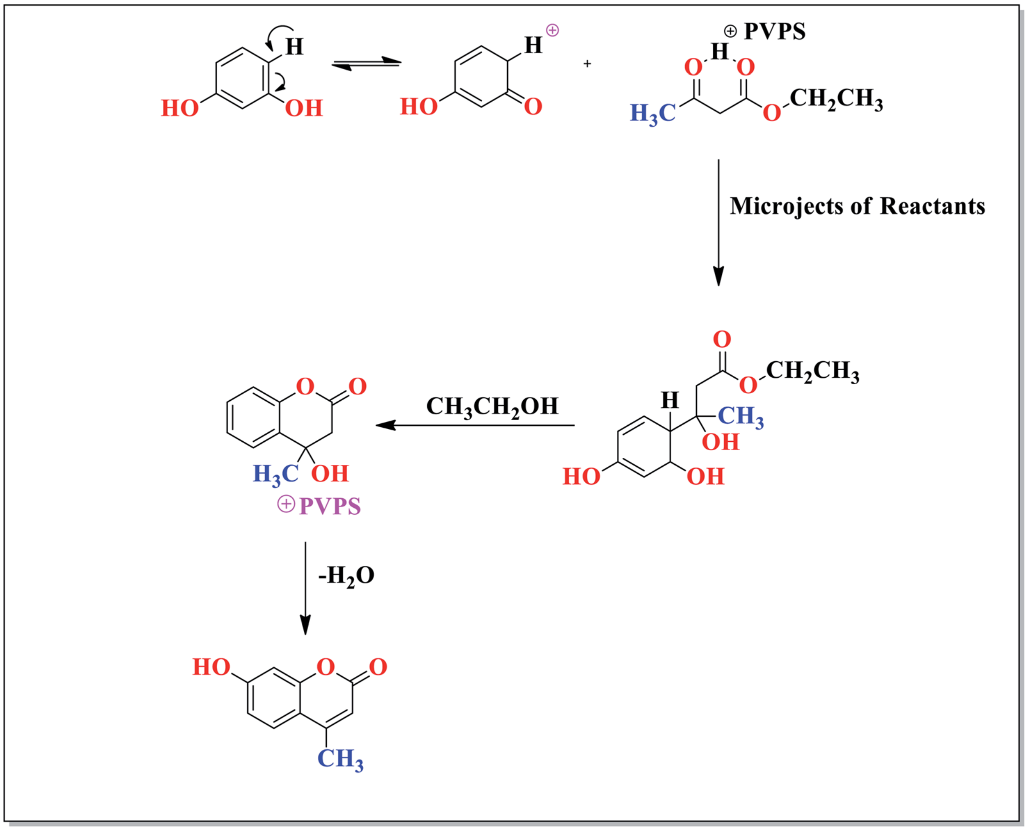
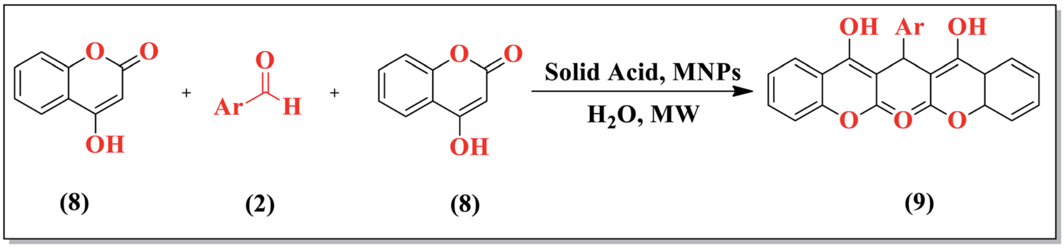


Fig. 2 Proposed mechanism for Pechmann reaction of resorcinol with ethyl acetoacetate at room temperature under ultrasonic irradiation.



Scheme 3 Synthesis of bis-coumarin derivatives in Fe_3O_4 @sulfosalicylic acid MNPs as catalyst under microwave irradiation in water.

with an α,β-unsaturated intermediate to give the final polyhydroquinoline product. Finally, a tautomeric proton shift produces the desired product. Table 4 presented the results from the synthesis of bis-coumarin by reaction of benzaldehyde and 4 hydroxycoumarin in the presence of Fe_3O_4@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	$FeCl_3 \cdot 6H_2O$ (0.05)	180	15	43
3	Bulk-Fe_3O_4 (0.05)	180	15	50
4	Nano-Fe_3O_4 (0.05)	180	15	68
5	Fe_3O_4@sulfosalicylic acid (0.03)	180	20	89
6	Fe_3O_4@sulfosalicylic acid (0.03)	300	10	92
7	Fe_3O_4@sulfosalicylic acid (0.05)	100	10	89
8	Fe_3O_4@sulfosalicylic acid (0.05)	180	10	96
9	Fe_3O_4@sulfosalicylic acid (0.08)	180	10	96
10	Fe_3O_4@sulfosalicylic acid (0.015)	180	10	80
11	—	180	20	30

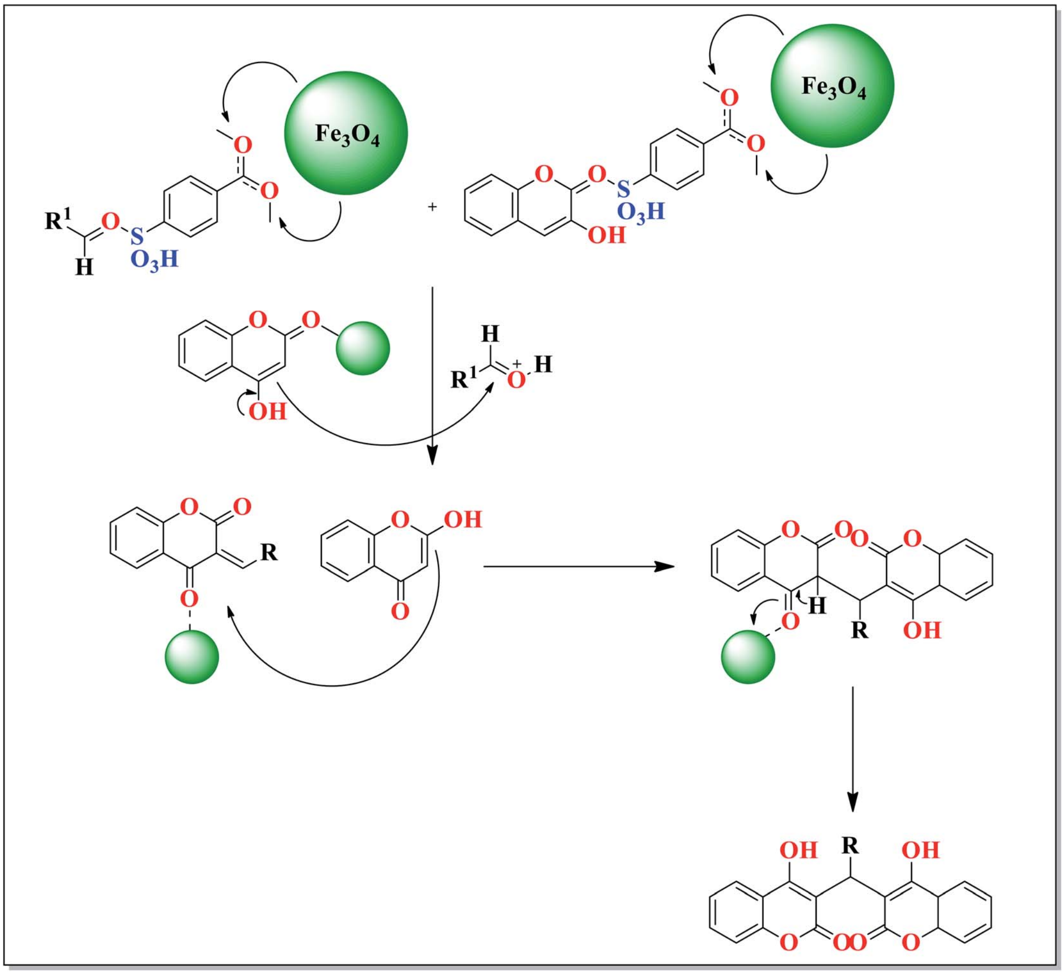


Fig. 3 Proposed mechanism for the synthesis of biscoumarin derivatives in the presence of Fe_3O_4@sulfosalicylic acid magnetic nanoparticles.

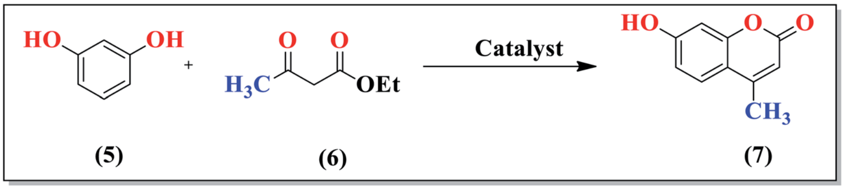
Table 4 Comparison of efficiency of present catalyst with other catalysts reported in literature

Entry	Catalyst/condition	Time (min)	Yield	References
1	Ionic liquids, reflux	260	84	26
2	Choline hydroxide, reflux	240	86	27
3	No catalyst/trifluoroethanol, reflux	360	80	28
4	**Fe_3O_4@sulfosalicylic acid/H_2O, M_W**	**10**	**96**	25

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).[29]

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 Fe_3O_4 NPs, CCMNPs (Fe_3O_4@C) led to no product even after 6 h, while the use of SCCMNPs (Fe_3O_4@C@OSO_3H) could produce related 4*H*-coumarin in



Scheme 4 Synthesis of substituted coumarins.

Table 5 The effect of various solvents, temperature and catalyst loadings for the synthesis of substituted coumarins through Pechmann condensation

Entry	Catalyst loading	Solvent	T (°C)	Time (min)	Yield (%)
1	—	—	120	360	No reaction
2	Fe_3O_4 NPs (6.5 mol%)	—	120	360	No reaction
3	CCMNPs (Fe_3O_4@C) (6.5 mol%)	—	120	360	No reaction
4	SCCMNPs (Fe_3O_4@C@OSO_3H) (3.25 mol%)	—	120	30	86
5	**SCCMNPs (Fe_3O_4@C@OSO_3H) (6.5 mol%)**	**—**	**120**	**20**	**98**
6	SCCMNPs (Fe_3O_4@C@OSO_3H) (13 mol%)	—	120	20	98
7	SCCMNPs (Fe_3O_4@C@OSO_3H) (6.5 mol%)	—	100	30	87
8	SCCMNPs (Fe_3O_4@C@OSO_3H) (6.5 mol%)	—	90	40	83
9	SCCMNPs (Fe_3O_4@C@OSO_3H) (6.5 mol%)	H_2O	Reflux	360	Trace
10	SCCMNPs (Fe_3O_4@C@OSO_3H) (6.5 mol%)	Toluene	Reflux	360	No reaction
11	SCCMNPs (Fe_3O_4@C@OSO_3H) (6.5 mol%)	CH_2Cl_2	Reflux	360	No reaction
12	SCCMNPs (Fe_3O_4@C@OSO_3H) (6.5 mol%)	EtOH	Reflux	360	No reaction
13	SCCMNPs (Fe_3O_4@C@OSO_3H) (6.5 mol%)	CH_3CN	Reflux	360	No reaction

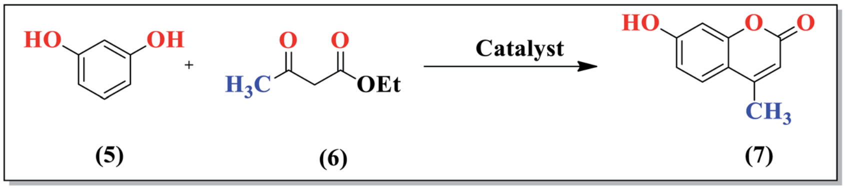
Table 6 Comparison of activity of some heterogeneous solid acid catalysts for the synthesis of substituted coumarins

Entry	Catalyst	Catalyst (mol%)	T (°C)	Time (min)	Yield (%)	References
1	Fe_3O_4-DABCO	1	100	40	93	30
2	γ-Fe_3O_4@HAp–Ag	10	80	20	95	31
3	Fe_3O_4@SiO_2@$PrSO_3H$	2	130	25	96	32
4	CMK-15-SO_3H	3	130	20	95	33
5	Random pore carbon-SO_3H	7	130	60	90	34
6	Fe_3O_4@SiO_2@$EtSO_3H$	75	90	90	93	35
7	$SnCl_x$–SiO_2	5	120	35	90	36
8	SBA-15-Ph-Pr–SO_3H	7	130	60	90	36
9	ZrW_2	20	12	120	94	37
10	SnW_2	20	120	120	88	37
11	Nanosponge MFI zeolite	0.5	130	120	94	38
12	TiZnO	10	110	180	85	39
13	Fe_3O_4@Boehmite–NH_2–CoII	6.6	90	30	95	40
14	**SCCMNPs**	**6.5**	**120**	**20**	**98**	29

a good yield during the short time. Hence, SCCMNP with the sulfonic 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 ZrO_2–TiO_2 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.



Scheme 5 Synthesis of substituted coumarins.

Table 7 The reaction for synthesis of substituted coumarins in solvent-free condition at room temperature

Entry	Reactant	Catalyst	Temperature (°C)	Time (min)	%Yield
1	Resorcinol + ethylacetoacetate	ZrO_2–TiO_2	RT	180	97
2	Resorcinol + ethylacetoacetate	ZrO_2–ZnO	RT	240	63
3	Resorcinol + ethylacetoacetate	ZrO_2/cellulose	RT	180	Nil
4	Catechol + ethylacetoacetate	ZrO_2–TiO_2	80	240	55
5	*o*-Nitrophenol + ethylacetoacetate	ZrO_2–TiO_2	80	240	Nil
6	**Resorcinol + ethylacetoacetate**	**Without catalyst**	**80**	**240**	**Nil**

Table 8 Comparison of efficiency ZrO_2–TiO_2 with reported catalysts

Entry	Catalyst	Time (min)	Temperature (°C)	Solvent	Yield	References
1	Zeolite BEA	240	130	$PhNO_2$	63	42
2	PFPAT	180	110	Toluene	90	43
3	MFRH	50	80	Solvent-free	65	43
4	Nanoreactors	60	130	Solvent-free	30	43
5	CMK-5-SO_3H	20	130	Solvent-free	95	44
6	CMK-5	60	130	Solvent-free	10	44
7	**ZrO_2–TiO_2**	**180**	**RT**	**Solvent-free**	**97**	41
8	**ZrO_2–TiO_2**	**110**	**60**	**Toluene**	**95**	41
9	**ZrO_2–TiO_2**	**150**	**60**	**Ethanol**	**92**	41

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 reuseable catalyst (Scheme 6).[45]

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 4*H*-chromene derivatives (**13**) *via* one-pot

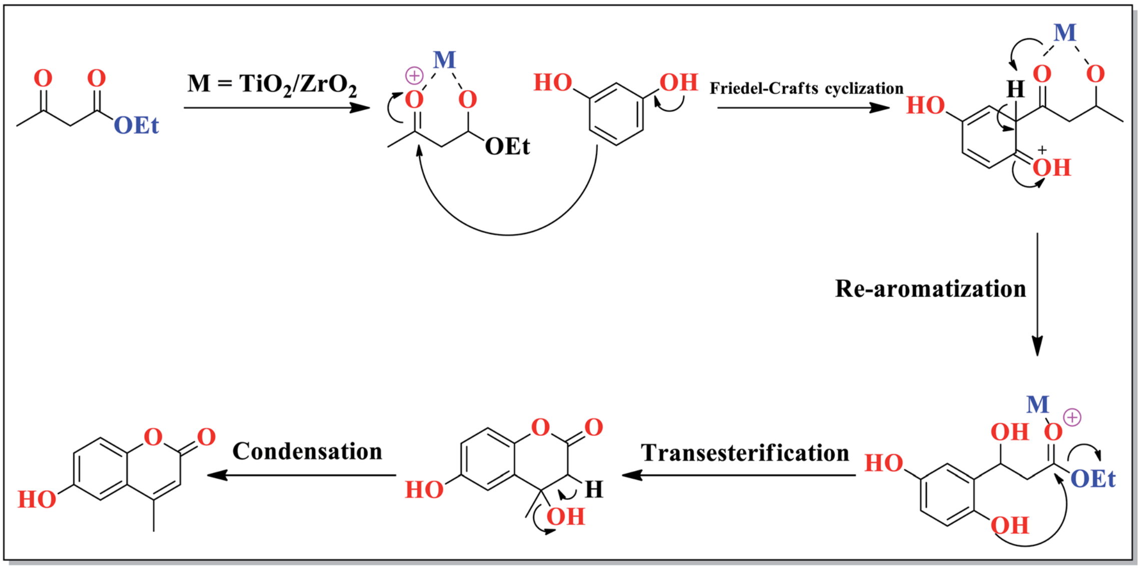
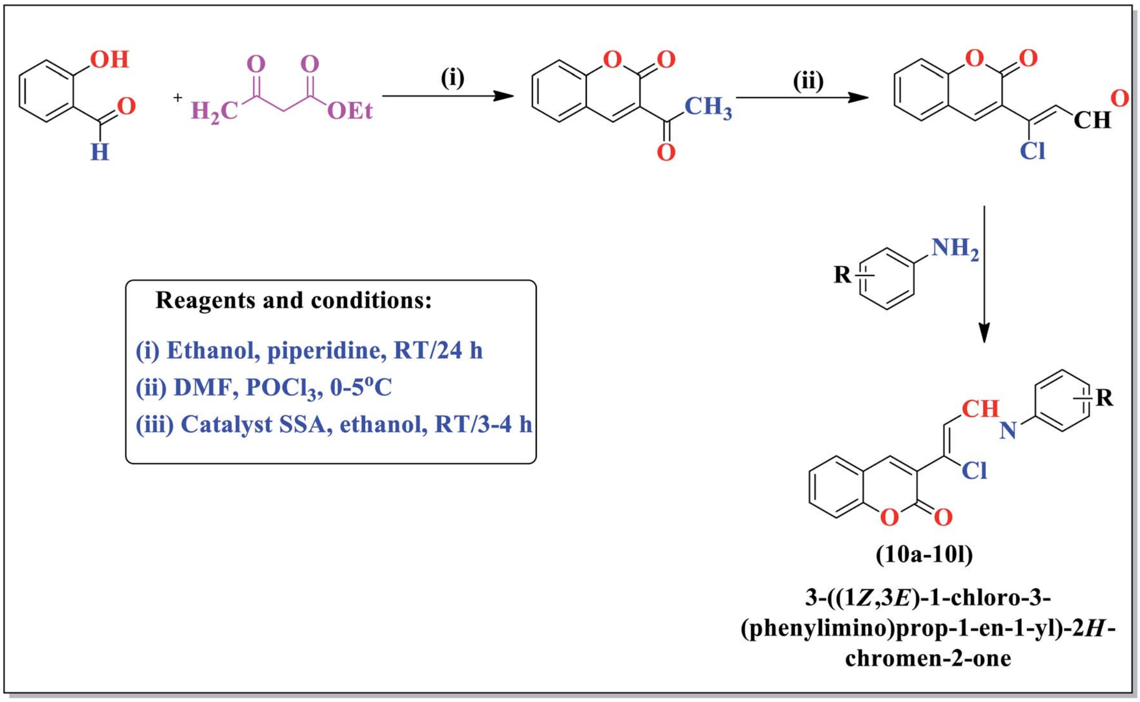


Fig. 4 Plausible mechanism for the synthesis of substituted coumarins in presence of zirconia-based heterogeneous catalyst.



Scheme 6 Synthesis of novel coumarin Schiff bases in presence of silica sulphuric acid as reuseable catalyst.

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).[46] 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).[47]

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*-OCH_3	62	210	205–208
10f	*p*-CH_3	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*-OCH_3	59	200	208–210
10l	*m*-CH_3	73	225	212–214

To optimize the reaction conditions, a model reaction was explored between 4-chlorobenzaldehyde, malononitrile and 4-hydroxycoumarin in presence of different concentration of P_4VPy. The effect of different solvents *viz.* CH_3CN, CH_2Cl_2, H_2O and EtOH and temperature in the synthesis of dihydropyrano[3,2-*c*] chromene derivatives in the presence of P_4VPy summarized in Table 11. They found that best result was obtained using 20 mg of P_4VPy at 70 °C in a mixture of H_2O and ethanol. They also observed that aldehydes containing electron-withdrawing as well as electron-donating groups such as Cl, Br, CH_3, OCH_3, NO_2 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 P_4VPy 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 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

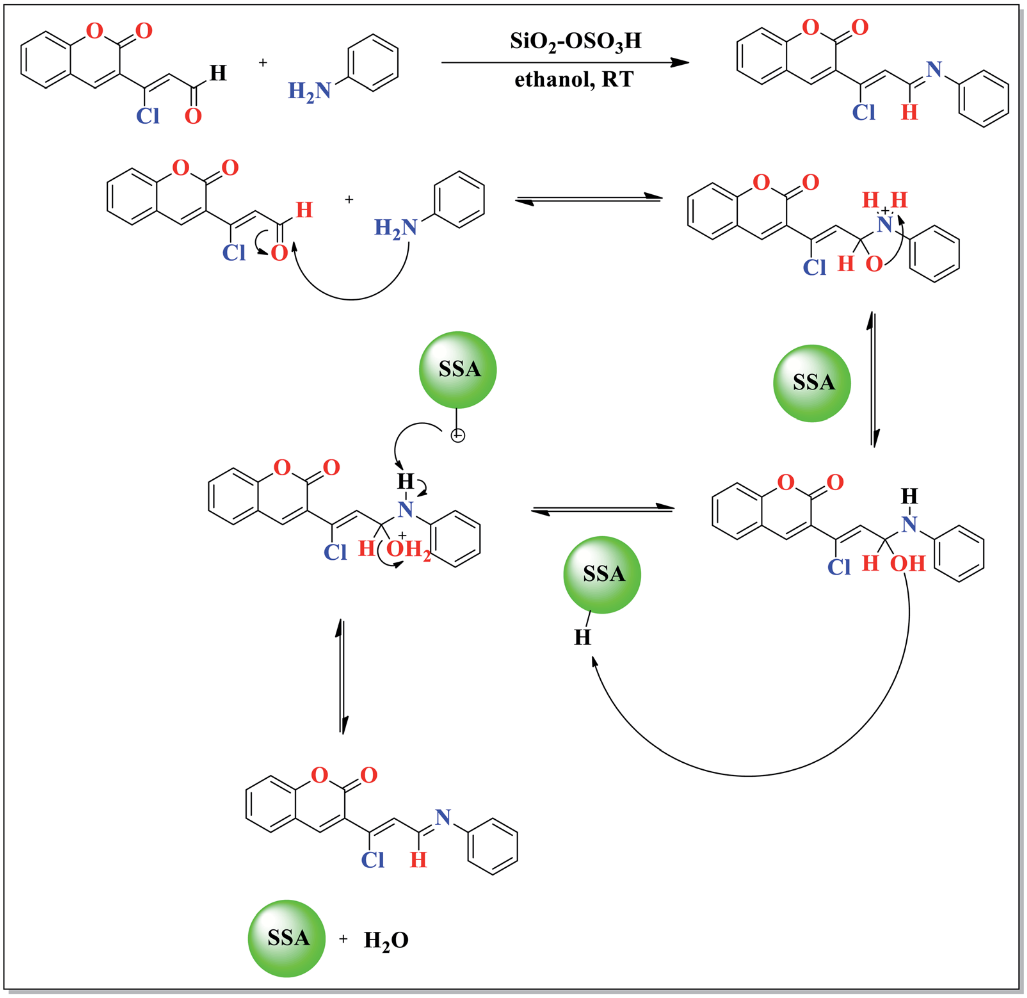
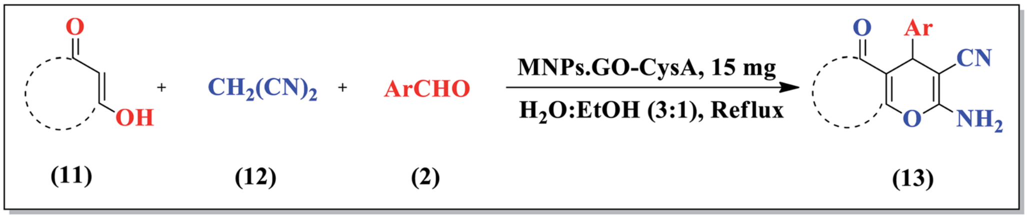
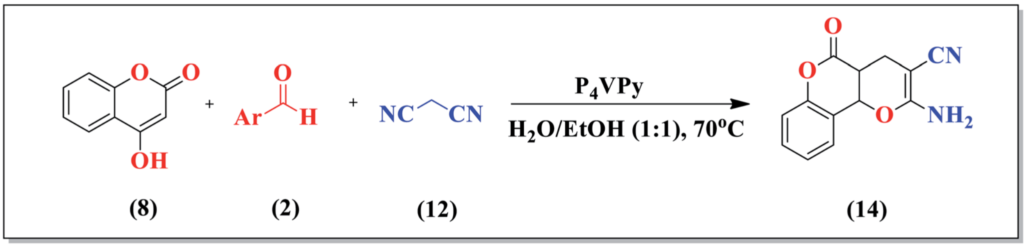


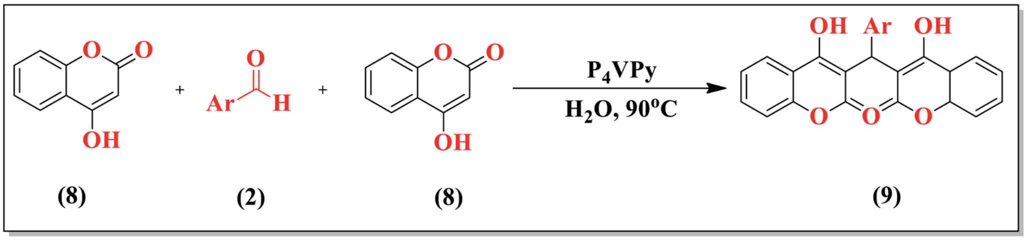
Fig. 5 Proposed reaction pathway for the synthesis of substituted coumarins.



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.



Scheme 9 Synthesis of biscoumarin derivatives.

of biscoumarins. For standardization of reaction conditions, first model reaction was carried out between 4-chlorobenzaldehyde and 4-hydroxycoumarin in the presence of P_4VPy at different reaction conditions as shown in Table 12. They observed that best reaction conditions for the synthesis of the biscoumarin derivatives are use of 20 mg of the P_4VPy 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 P_4VPy for the synthesis of dihydropyrano[3,2-*c*] chromene derivatives and biscoumarin 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-hydroxycoumarin **(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′-(arylmethylene) bis(4-hydroxy-2*H*-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 in ethanol. After getting the poor yields of desired product, they were interested to check the catalytic activity of camphor

Table 11 The effect of different reaction conditions for the synthesis of dihydropyrano[3,2-*c*] chromene derivatives in the presence of P_4VPy

Entry	Catalyst (mg)	Solvent	Temperature (°C)	Time (min)	Yield (%)
1	—	No solvent	RT	120	Nil
2	—	No solvent	100	120	Nil
3	20	CH_3CN	RT	120	Nil
4	20	CH_3CN	Reflux	120	Mixture of products
5	20	CH_2Cl_2	RT	120	Nil
6	20	CH_2Cl_2	Reflux	120	Mixture of products
7	20	H_2O	90	180	50
8	24	H_2O	90	120	50
9	24	EtOH	RT	150	60
10	20	EtOH	50	120	60
11	20	EtOH	70	120	60
12	20	H_2O/EtOH	70	5	95
13	24	H_2O/EtOH	70	5	95

Table 12 Optimization of the reaction conditions for the synthesis of biscoumarin derivatives catalyzed by P_4VPy

Entry	Catalyst (mg)	Solvent	Temperature (°C)	Time (min)	Yield (%)
1	—	No solvent	RT	120	Nil
2	—	No solvent	100	120	Nil
3	20	CH_3CN	RT	120	Nil
4	20	CH_3CN	Reflux	120	Mixture of products
5	20	CH_2Cl_2	RT	120	Nil
6	20	CH_2Cl_2	Reflux	120	Mixture of products
7	20	EtOH	RT	120	30
8	20	EtOH	Reflux	120	60
9	10	H_2O	RT	90	40
10	15	H_2O	RT	90	50
11	20	H_2O	RT	90	75
12	20	H_2O	90	5	96
13	24	H_2O/EtOH	90	5	96

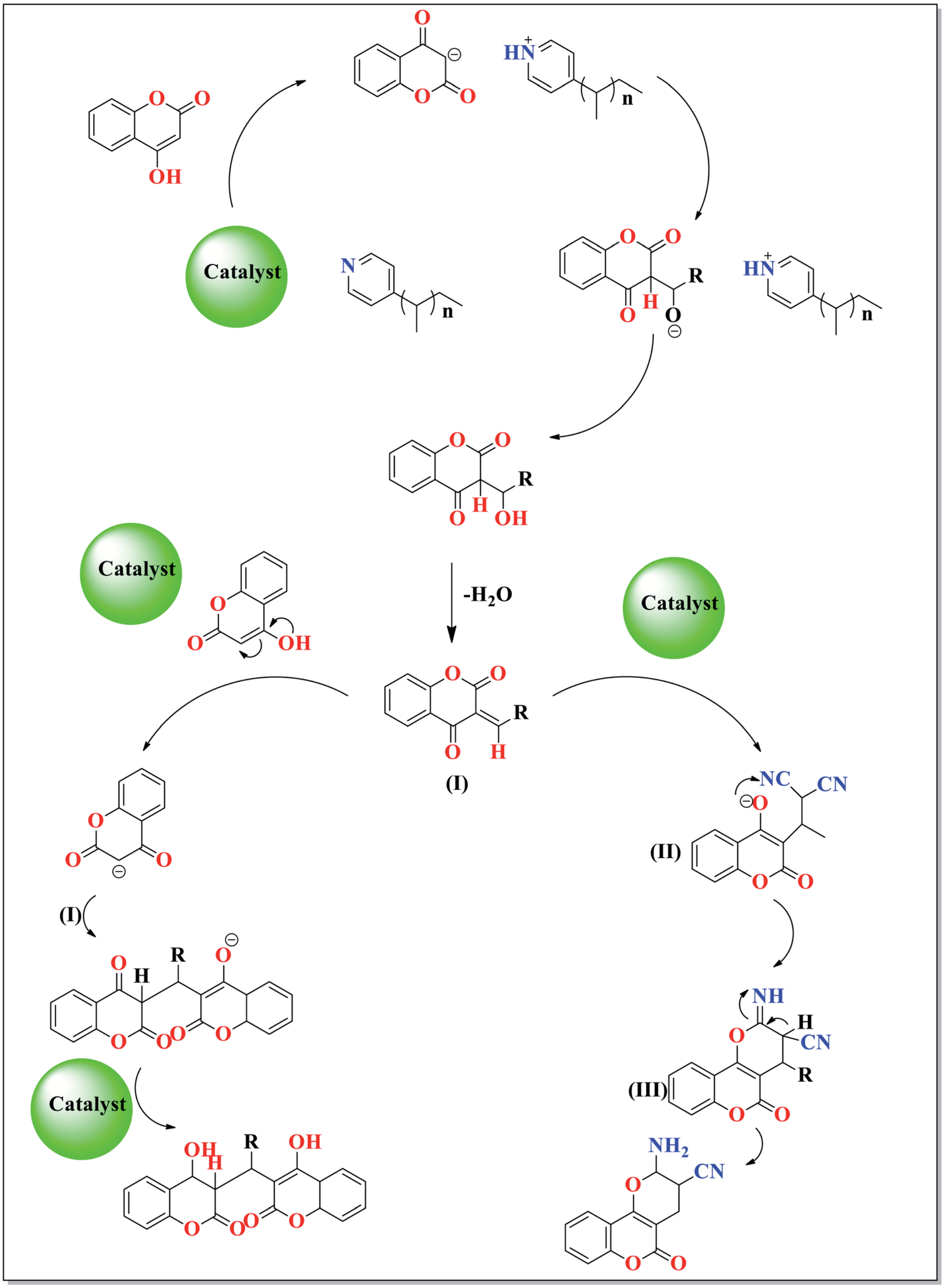


Fig. 6 Proposed mechanism for the synthesis of dihydropyrano[3,2-c]chromene and biscoumarin derivatives in the presence of P_4VPy as catalyst.

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.

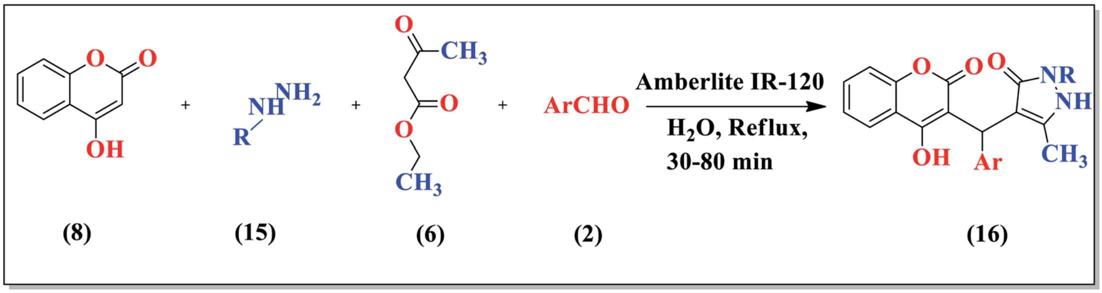
The plausible mechanism for the synthesis of 3,3-(arylmethylene)-bis(4-hydroxy-2*H*-chromen-2-ones) is shown in Fig. 7. According to the mechanism, firstly camphor sulfonic acid activate the carbonyl group of aldehydes which enhance the attack from C-3 position of 4-hydroxycoumarin and generate

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

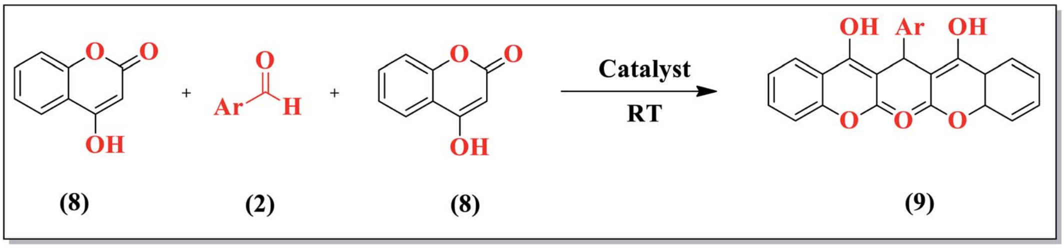
Entry	Catalyst (mol%)	Reaction conditions	Time (min)	Yield (%)	References
1	SDS	Water/60 °C	150	88	48
2	Nano ZnO	Ethanol reflux	90	49	49
3	Nano $Al(OH)_3$	Ethanol reflux	120	48	49
4	DAHP	Ethanol–H_2O/25 °C	240	85	50
5	(*S*)-proline	Ethanol–H_2O/100 °C	180	78	50
6	Nano Al_2O_3	Ethanol reflux	120	71	51
7	**P_4VPy**	**Ethanol–H_2O/70 °C**	**5**	**95**	47

Table 14 Comparison of different catalysts used for the synthesis of biscoumarins

Entry	Catalyst (mol%)	Reaction conditions	Time (min)	Yield (%)	References
1	SDS	Water/60 °C	150	93	48
2	[bmim]BF_4	Solvent-free/60–70 °C	150	91	52
3	I_2	H_2O/100 °C	27	93	53
4	CHOH	Solvent-free/50 °C	120	99	54
5	[P_4VPy-BuSO_3H]Cl–X($AlCl_3$)	Toluene/90 °C	36	93	55
6	PSA	Solvent-free/100 °C	240	96	56
7	Piperidine	EtOH/r.t	240	96	57
8	**P_4VPy**	**H_2O/90 °C**	**5**	**96**	47



Scheme 10 General scheme for the synthesis of benzlypyrazolyl coumarin.



Scheme 11 Reported protocols for the synthesis of biscoumarin.

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).[60] 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

Table 15 Standardization of reaction conditions for the synthesis of 3,3′-(arylmethylene)bis(4-hydroxy-2*H*-chromen-2-ones)

Entry	Catalyst (mol%)	Solvent	Time (h)	Yield (%)
1	No catalyst	Solvent-free	24	Nil
2	No catalyst	EtOH	6	22
3	Camphor sulfonic acid (20 mol%)	EtOH	6	78
4	Camphor sulfonic acid (20 mol%)	MeOH	6	72
5	Camphor sulfonic acid (20 mol%)	H_2O	6	61
6	**Camphor sulfonic acid (20 mol%)**	**EtOH : H_2O (1 : 1 v/v)**	**2**	**94**
7	Camphor sulfonic acid (15 mol%)	EtOH : H_2O (1 : 1 v/v)	2	86
8	Camphor sulfonic acid (20 mol%)	EtOH : H_2O (1 : 1 v/v)	2	94

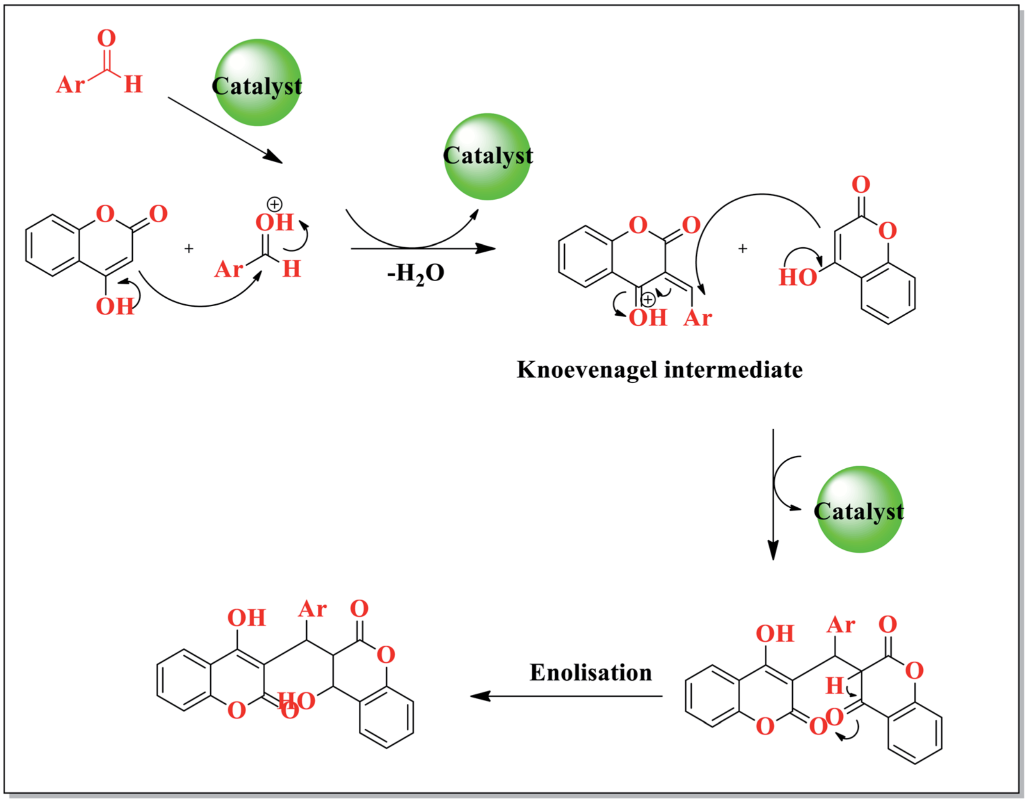
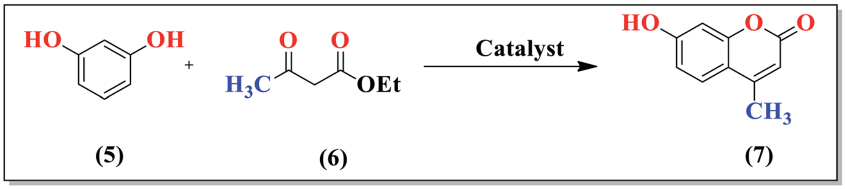


Fig. 7 Proposed mechanism for the synthesis of biscoumarin catalyzed by camphor sulfonic acid.



Scheme 12 Coumarin synthesis by Pechmann condensation.

17. They conclude that solvent-free conditions and temperature 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,

Table 16 Catalytic screening for synthesis of substituted coumarin by Pechmann condensation reaction

Entry	Catalyst	Time (h)	Yield (%)
1	No catalyst	24	Nil
2	ZnO	5	Nil
3	$Zn_{0.975}Ti_{0.025}O$	3	37
4	$Zn_{0.950}Ti_{0.050}O$	4	60
5	**$Zn_{0.925}Ti_{0.075}O$**	**3**	**88**
6	$Zn_{0.900}Ti_{0.100}O$	3	88

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

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 give desired products.

A magnetic nanocatalyst of Fe_3O_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).[61] The advantages of this method are straightforward, easy work-up, catalyst reuseability 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_3H) as a catalyst (Scheme 14).[62] The catalytic activity of FDU-5-Pr–SO_3H 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

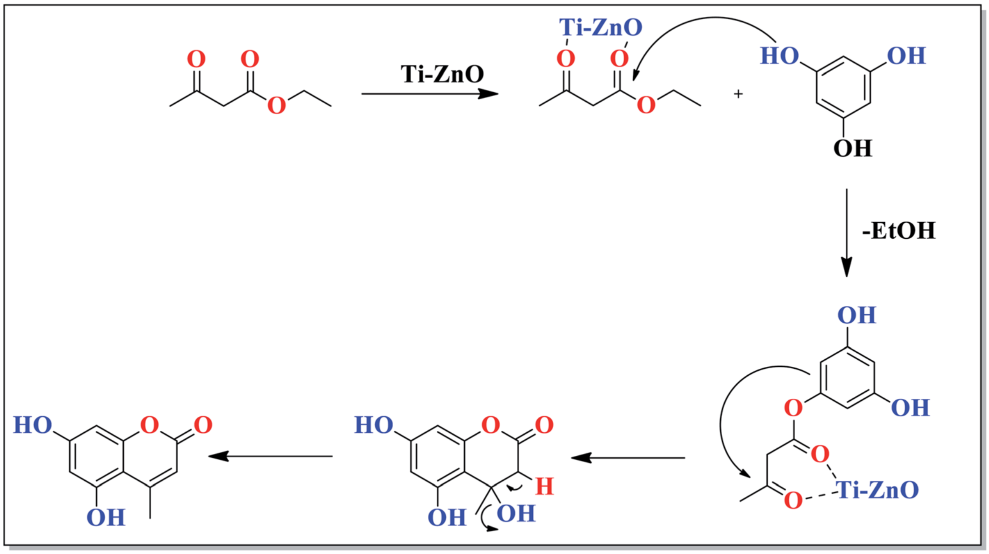
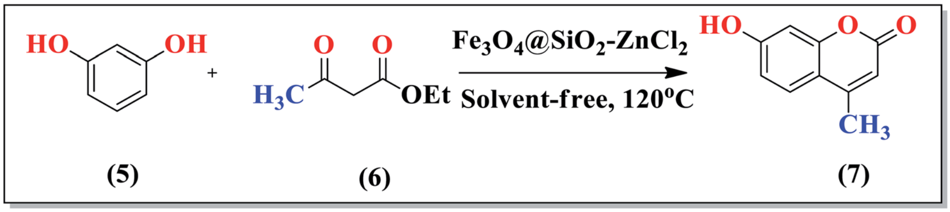
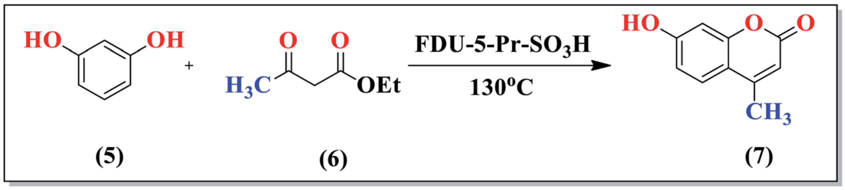


Fig. 8 Plausible mechanism for Pechmann condensation using EAA and phloroglucinol promoted by $Zn_{0.925}Ti_{0.075}O$ NPs.



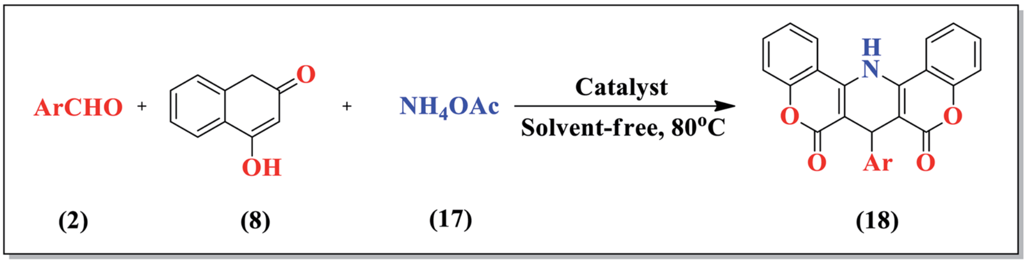
Scheme 13 Direct synthesis of coumarin derivatives.



Scheme 14 Synthesis of coumarin derivatives *via* Pechmann condensation of phenols with β-keto-ester catalyzed by FDU-5-Pr–SO_3H.

Table 19 Comparison of different catalysts used for the synthesis of substituted coumarins

Catalyst	Catalyst amount (mol%)	Reaction time (min)	Temperature (°C)	Yield (%)	References
FDU-5	1.65	120	130	NR	62
FDU-5-Pr–SO_3H	1.65	60	130	97	62
MCM-41–10SO_3H	3.6	120	120	99	63
SBA-15–10SO_3H	2.0	120	120	88	63
C@TiO_2–SO_3–$SbCl_2$	100.0	35	120	94	64
m-ZrP	2.0	240	160	76	65
SiO_2–$SnCl_3$	5.0	35	120	64	66
$FeCl_3$ (ultrasound)	10.0	20	100	97	67
Fe_3O_4@SiO_2@Et-PhSO_3H	0.3	120	120	93	68
CMK-5-SO_3H	3.0	130	130	95	69
SBA-15-Ph-Pr–SO_3H	7.0	130	130	90	70
p-TsOH	7.0	130	130	65	70
Zr-TMS-BSA-10	10 wt%	150	150	81.4	71



Scheme 15 Catalytic synthesis of coumarin containing 1,4-DHPs.

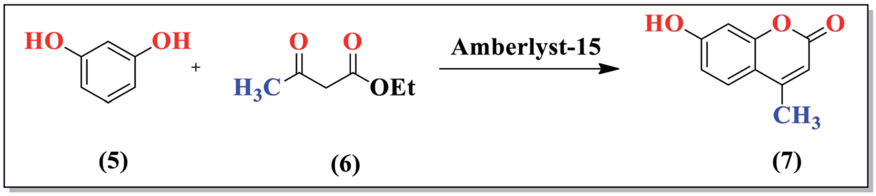
(Scheme 15).[72] Simple protocol, simplicity of product isolation using water, decrease the temperature of reaction, reduce the use of hazardous solvents, excellent yield of products, eco-friendly conditions and less reaction times are some beauties of present methodology. Firstly, to optimize the reaction conditions they conducted a model reaction between 4-methyl benzaldehyde, 4-hydroxycoumarin and ammonium acetate. They observed that 10 mg of the Fe_3O_4@SiO_2@$(CH_2)_3$–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

Table 20 Optimization of reaction conditions

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	H_2O	Reflux	10	30	85
9	EtOH	Reflux	10	45	70
10	EtOAc	Reflux	10	90	20
11	CH_2Cl_2	Reflux	10	90	Nil
12	*n*-Hexane	Reflux	10	90	Nil

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

Entry	Catalyst	Yield (%)
1	Fe_3O_4	40
2	Fe_3O_4@SiO_2	40
3	Fe_3O_4@SiO_2@$(CH_2)_3$–urea–quinoline	65
4	**Fe_3O_4@SiO_2@$(CH_2)_3$–urea–quinoline sulfonic acid chloride**	**85**



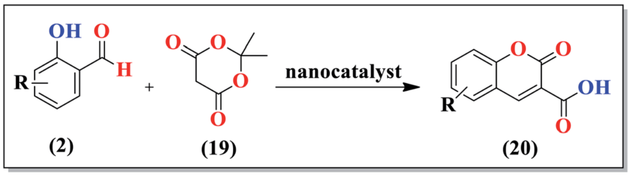
Scheme 16 Pechmann reaction of resorcinol with ethylacetoacetate to produce 7-hydroxy-4-methylcoumarin.

Table 22 Condensation reaction of resorcinol with ethyl acetoacetate using various heterogeneous solid acids catalysts

Catalyst	Acidity	Yield (%)
Amberlyst-15	4.30	97
H-β	1.01	21
TS–OS–SO_3H	1.24	44

related intermediates of the $Fe_3O_4@SiO_2@(CH_2)_3$–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).[73] 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.



Scheme 17 Synthesis of substituted coumarins.

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).[74] 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 reuseable polymeric SO_3H-functionalized cation exchange resins *viz.* Amberlite IR-120, Dowex 50, X-8100 and Tulsion T-42 (Scheme 18).[75] Excellent yield of products, short reaction time,

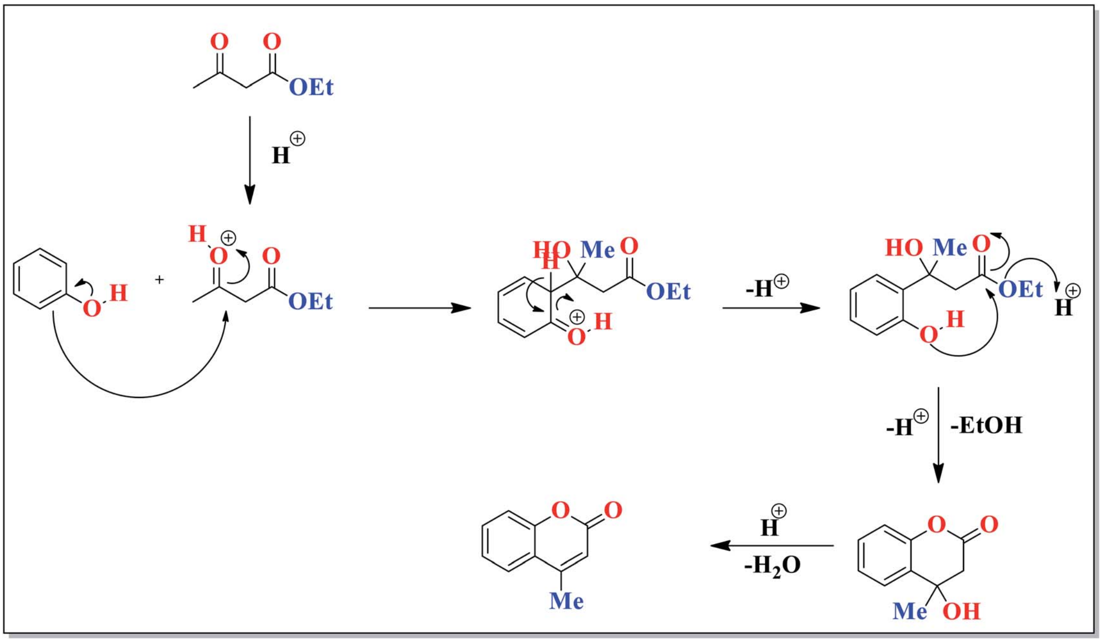


Fig. 9 A plausible mechanism for the Pechmann condensation of phenol and ethylacetoacetate in presence of Amberlyst-15.

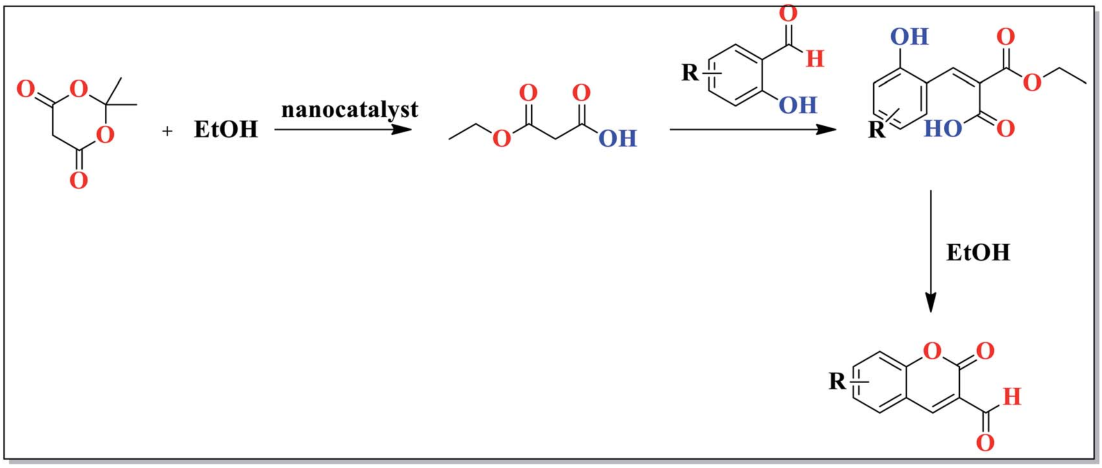
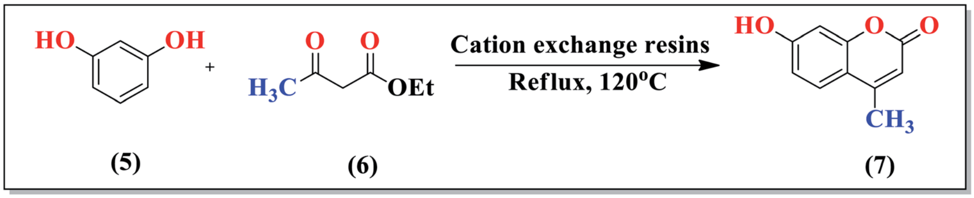
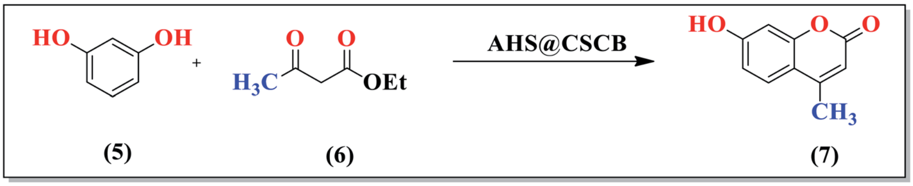


Fig. 10 Proposed mechanism for the synthesis of 3-carboxy coumarins in presence of polymeric magnetic nanocatalyst.



Scheme 18 The Pechmann condensation between resorcinol and ethyl acetoacetate catalyzed by different cation exchange resins.



Scheme 19 Synthesis of substituted coumarins.

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).[76] 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

Table 23 Optimization of reaction conditions for AHS@CSCB catalyzed Pechmann condensation between 1,3 dihydroxy phenol and ethyl acetoacetate

Entry	Concentration of catalyst (mg)	Solvent	Temperature (°C)	Time (min)	Yield (%)
1	None	H_2O	Reflux	120	0
2	30	H_2O	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**

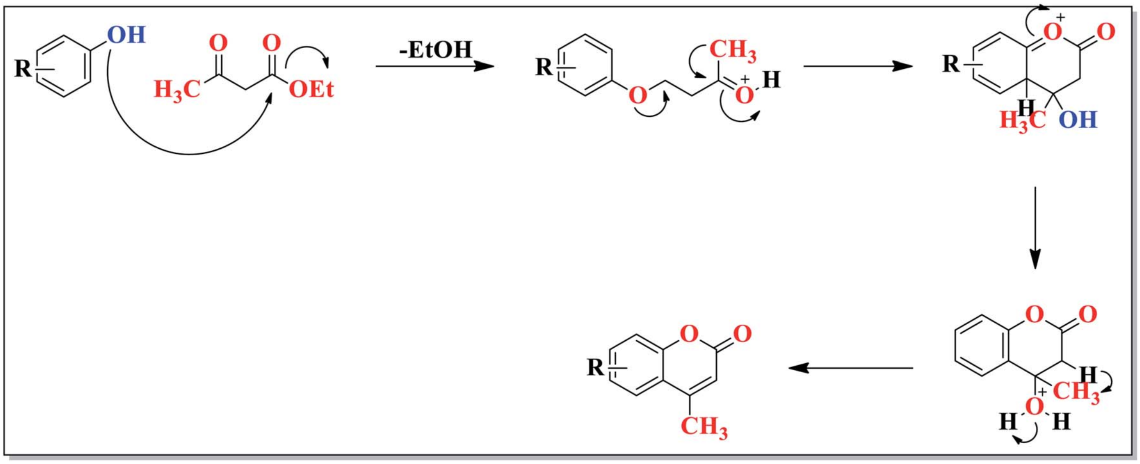
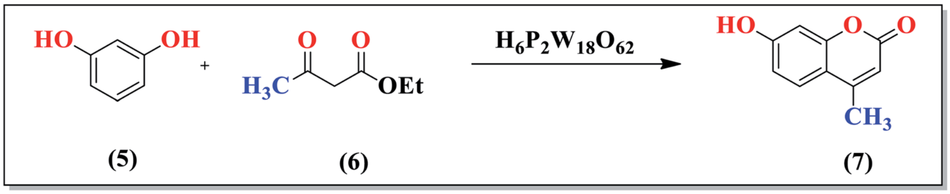


Fig. 11 Plausible mechanism for the synthesis of coumarins, biscoumarins and benzoxanthenes in the presence of AHS@CSCB.



Scheme 20 Synthesis of substituted coumarins.

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 ($H_6P_2W_{18}O_{62}$). This work provides a novel, cheaper and safer way to synthesize coumarins unsubstituted on the pyranic nucleus (Scheme 20).[77] 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

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	$MeSO_3H$	3	20
2	$MeSO_3H$/basic Al_2O_3	3	30
3	$MeSO_3H$/neutral Al_2O_3	3	34
4	$MeSO_3H$/acidic Al_2O_3	3	80
5	Acidic Al_2O_3	3	30
6	Al_2O_3	2	10
7	$AlCl_3/MeSO_3H$	2	12
8	$ZnCl_3/MeSO_3H$	2	5
9	$Cu(CH_3CN)4PF_6$	2	10
10	$H_6P_2W_{18}O_{62}$	2	82
11	$FeCl_3$	3	8
12	$TiCl_4$	3	5

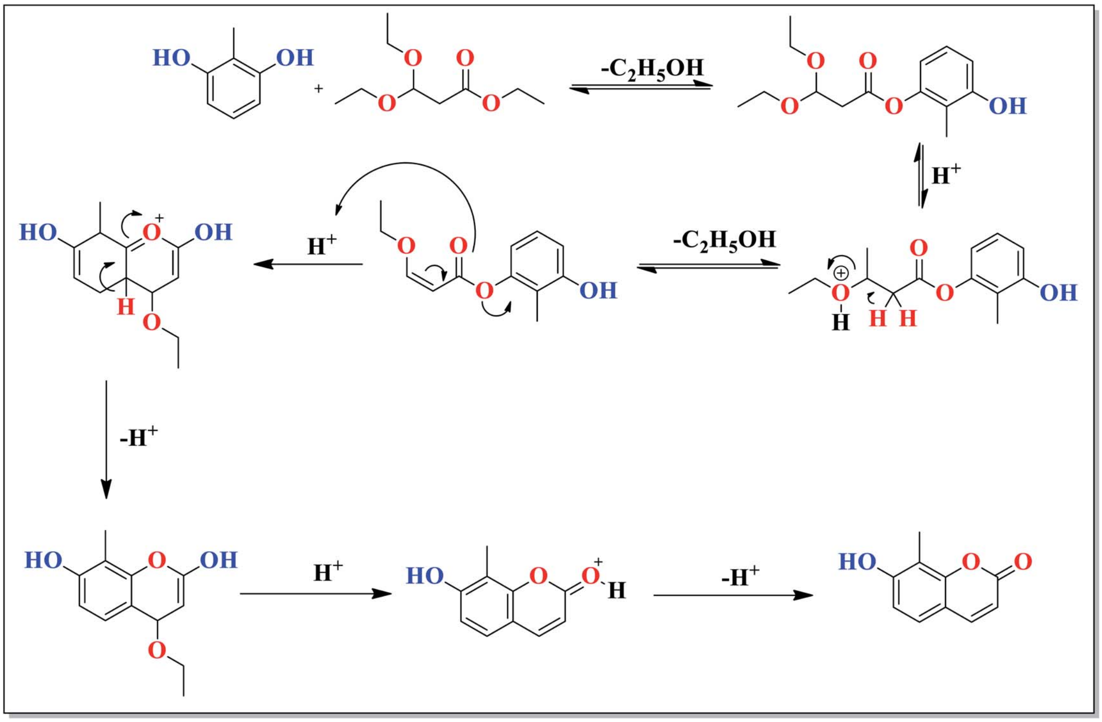
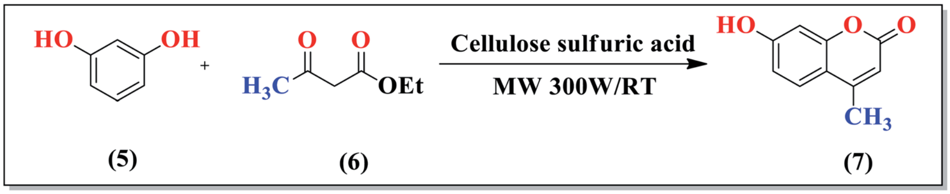


Fig. 12 Possible mechanism for the synthesis of coumarins catalyzed from Wells–Dawson heteropolyacid ($H_6P_2W_{18}O_{62}$).



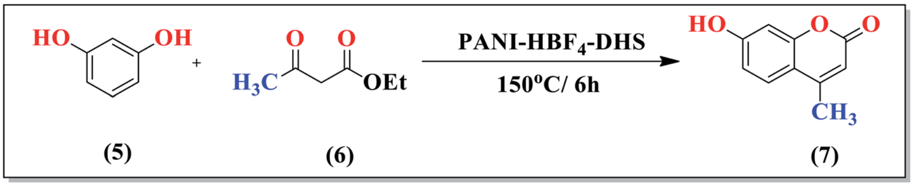
Scheme 21 Synthesis of coumarins by using cellulose sulfuric acid as a solid acid catalyst.

Table 26 Comparison of efficiency of cellulose sulfuric acid with reported catalysts

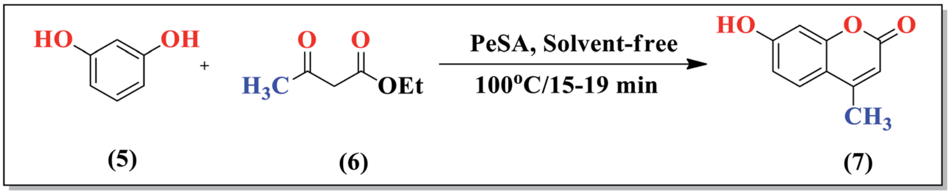
Entry	Catalyst	Yield (%)
1	Cellulose sulfuric acid	97
2	Silica sulfuric acid	92
3	*p*-Toluene sulfonic acid	85
4	Sulfuric acid in acetic acid	55
5	No catalyst	15

cellulose sulfuric acid by Kuram *et al.* (Scheme 21).[78] 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–HBF_4–DHS) as reuseable catalyst (Scheme 22).[79]



Scheme 22 Synthesis of substituted coumarins.

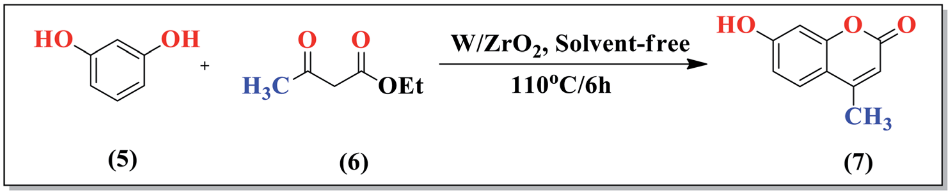


Scheme 23 Synthesis of substituted coumarins catalyzed by PeSA.

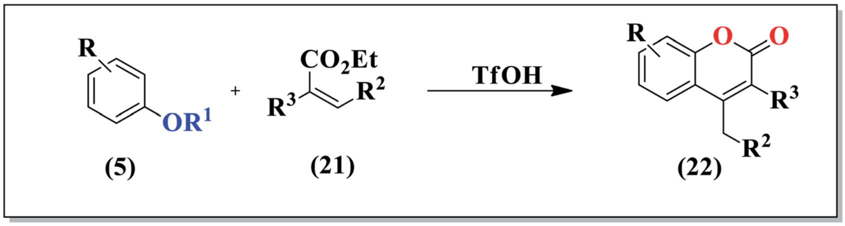
Table 27 Comparison of activity of the PeSA catalyst with some other reported catalysts

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-SO_3H	110 °C/Solvent-free	95	20	82

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-SO_3H (PeSA)) as heterogeneous reuseable solid acid catalysts (Scheme 23).[80] 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 24 W/ZrO_2 solid acid catalyzed synthesis of substituted coumarins.



Scheme 25 TfOH-mediated preparation of coumarins.

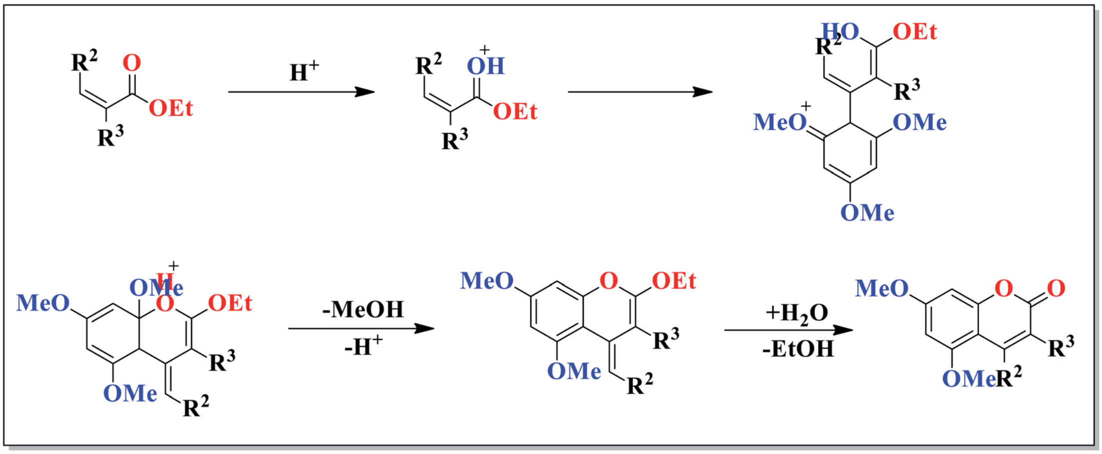
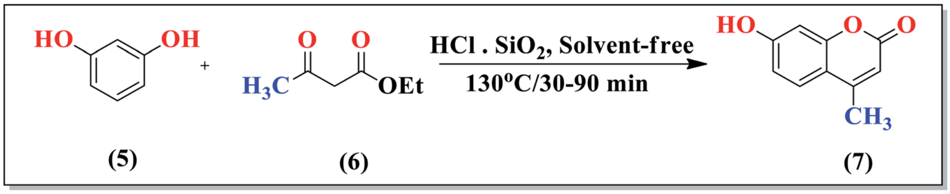
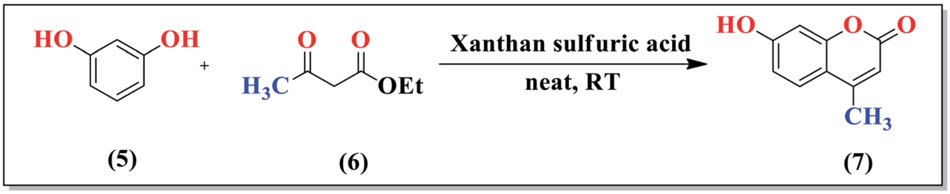


Fig. 13 Plausible mechanism for the synthesis of coumarins in the presence of TfOH as Brønsted acid catalyst.



Scheme 26 Synthesis of coumarins using $HClO_4.SiO_2$ under solvent-free conditions.



Scheme 27 Synthesis of coumarin by xanthan sulfuric acid as a solid acid catalyst.

Table 28 Effect of catalysts on yield of synthesis of substituted coumarins

Entry	Catalyst	Quantity	Yield (%)
1	Xanthan sulfuric acid	0.08 g	96
2	Silica sulfuric acid	0.08 g	92
3	Methane sulfonic acid	0.1 mmol	86
4	Sulfuric acid in acetic acid	0.1 mmol	56
5	No catalyst	None	10

Table 29 Influence of the catalytic amounts of xanthan sulfuric acid for synthesis of substituted coumarins

Entry	Catalyst (g)	Time (min)	Yield (%)
1	None	60	Nil
2	0.01	20	28
3	0.03	20	51
4	0.05	20	79
5	0.08	40	96
6	0.08	20	96

found that PeSA showed greater activity than some other than some other heterogeneous catalysts.

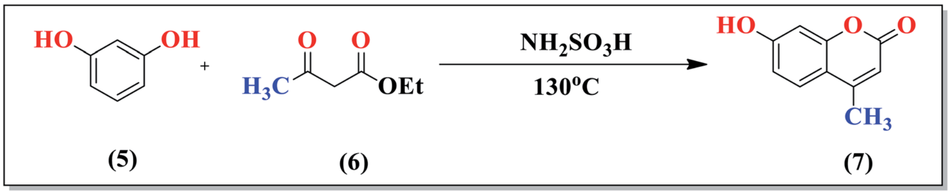
Reddy *et al.* reported the synthesis of substituted coumarins (**7**) *via* Pechmann condensation reaction between substituted phenols (**5**) and β-ketoesters (**6**) in presence of W/ZrO_2 solid acid catalyst (Scheme 24).[83]

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.

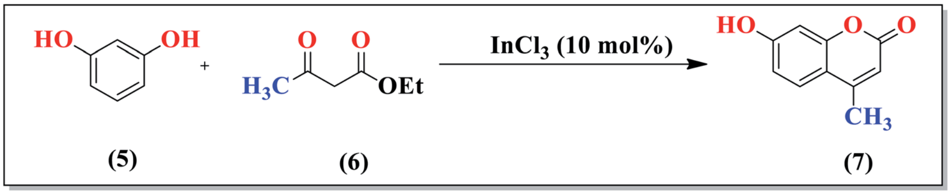
Maheswara and his coworkers synthesized substituted coumarins (**7**) *via* Pechmann condensation reaction between substituted phenols (**5**) and β-ketoesters (**6**) in presence of heterogeneous recyclable catalyst ($HClO_4.SiO_2$) under solvent-free medium (Scheme 26).[85] Cost-effective, less reaction 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.

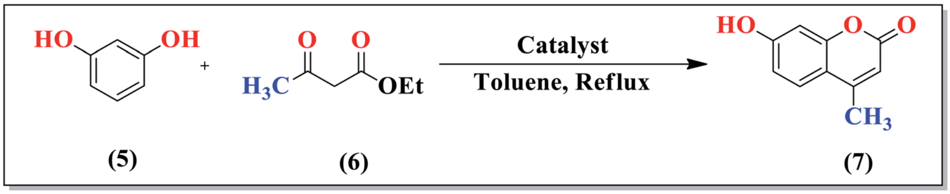
Singh and his coworkers reported the synthesis of substituted coumarins (**7**) *via* Pechmann condensation reaction between substituted phenols (**6**) and β-ketoesters (**5**) in presence of sulphamic acid (Scheme 28).[87]



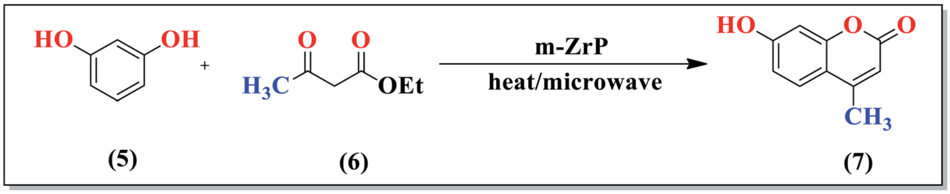
Scheme 28 Pechmann condensation using sulphamic acid (SA) as catalyst.



Scheme 29 Synthesis of coumarins *via* von Pechmann condensation of phenols with β-ketoesters induced by In(III)Cl_3.



Scheme 30 Synthesis of 7-hydroxyl-4-methyl coumarin.



Scheme 31 Synthesis of substituted coumarins.

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

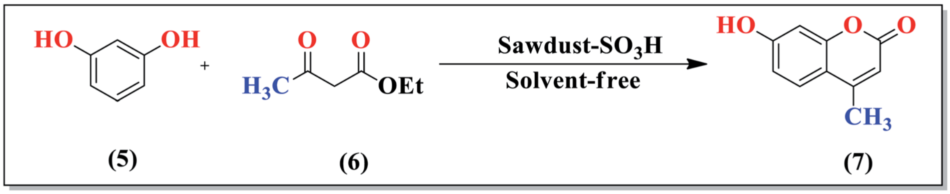
Table 31 Effect of SD-SO_3H catalyst concentration on the yield of product

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

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).[88]

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_2O_3–Fe_3O_4 as green solid acid catalysts (Scheme 30).[89]

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



Scheme 32 Synthesis of coumarins catalyzed by SD-SO_3H under solvent-free conditions.

Table 32 Effect of solvents and temperature on the synthesis of substituted coumarins

Entry	Solvent	Temperature (°C)	Time (min)	Yield (%)
1	—	90	75	72
2	$CHCl_3$	Reflux	200	35
3	CH_3CN	Reflux	200	10
4	CH_2Cl_2	Reflux	200	20
5	THF	Reflux	200	0
6	MeOH	Reflux	200	0
7	H_2O	Reflux	200	0
8	—	70	120	70
9	—	110	25	91
10	—	130	25	92

assisted method by Sinhamahapatra and his coworkers (Scheme 31).[90] 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 β-ketoesters (**6**) in presence of sulfonated sawdust (SD-SO_3H) as solid acid catalyst under solvent-free conditions (Scheme 32).[91] Further, they observed the catalytic efficiency of SD-SO_3H on the yield of product and results were presented in Table 31. They also observed the effects of different solvents *viz.* $CHCl_3$, CH_3CN, CH_2Cl_2, THF, MeOH and H_2O 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_3H 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,

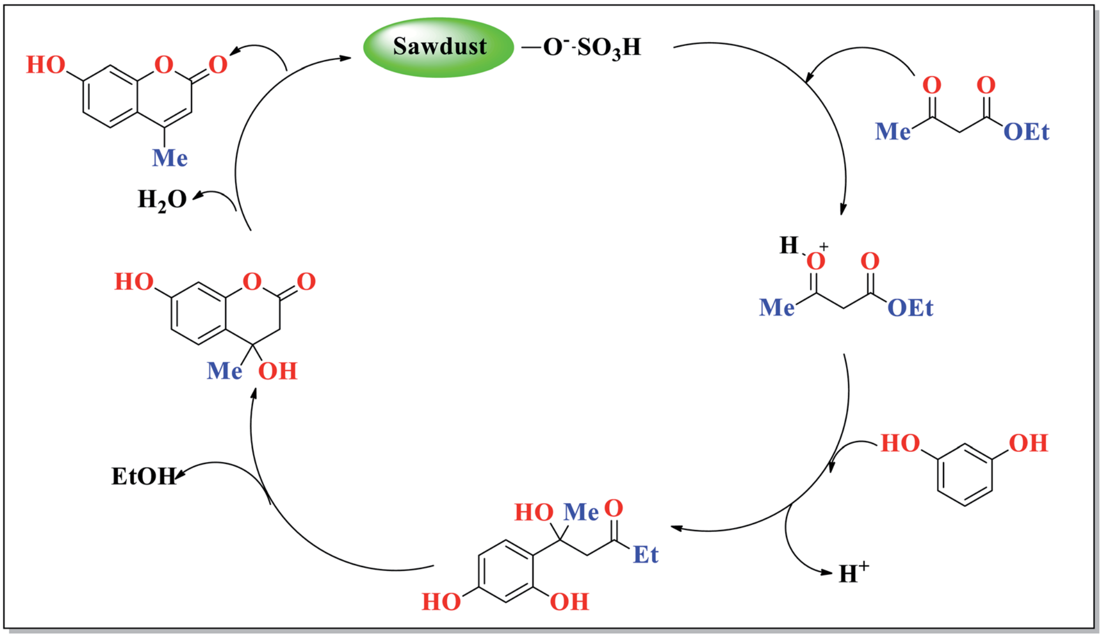


Fig. 14 The plausible mechanism of formation of 7-hydroxy-4-methylcoumarin in presence of sulfonated sawdust (SD-SO_3H) as solid acid catalyst.

Table 33 Comparison of catalytic activity of SD-SO_3H with some other catalysts

Entry	Catalyst	Temperature (°C)	Time (min)	Yield (%)	References
1	SD-SO_3H	110	9	98	91
2	*m*-ZrP	160	240	94	92
3	SCZ	120	143	87	93
4	ASA	100	30	98	94
5	CMK-5-SO_3H	130	20	95	95
6	$H_6P_2W_{18}O_{62}\cdot 24H_2O$	130	42	87	96
7	Zeolite-E4a	110	180	97	97
8	$HClO_4\cdot SiO_2$	130	35	95	98

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, formal analysis: Susheel Gulati, Suman Sangwan, investigation: Susheel Gulati, Rajvir Singh, Suman Sangwan, supervision: Susheel Gulati, Rajvir Singh, validation: Susheel Gulati, Suman Sangwan, writing-original draft: Susheel Gulati, writing-review & editing: Susheel Gulati, Rajvir Singh, Suman Sangwan.

Conflicts of interest

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

Abbreviations

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

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