

EFFICIENT SYNTHESIS OF *BIS*-(4-HYDROXYCOUMARIN) USING SULFANILIC ACID AS RECYCLABLE CATALYST IN WATER

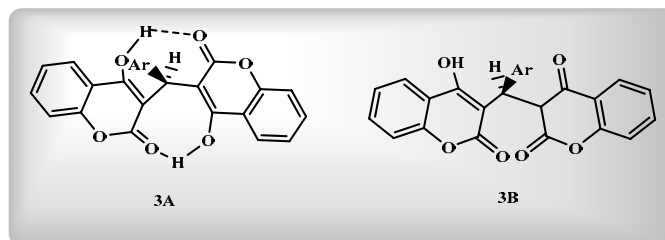
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Received January 23, 2020

A catalytic reaction between aromatic aldehydes and 4-hydroxycoumarin has been developed to form a decent range of functionalized biscoumarin skeletons in excellent yields using sulfanilic acid as reusable catalyst in aqueous media. The catalytic reaction shows good generality and was compatible with aldehydes bearing electron-withdrawing and electron-releasing substituents. This method avoids the use of tedious work-up and column chromatographic purification of products, making the method expedient and superior. The efficient and cost-effective catalyst could be recovered and reused several times.



INTRODUCTION

Heterocyclic compounds are broadly found in nature and are vital to lifespan.¹ Coumarins are an important class of heterocycles with diverse and interesting biological activities.² This significance could be recognized to their broad scope of pharmaceutical and biological properties like anticoagulant,³ antibacterial,⁴ anti-Hepatitis C virus,⁵ antitumor,⁶ anticancer,⁷ anti-inflammatory,⁸ antioxidative,⁹ as well as antiviral,¹⁰ activities. Based on these findings, the synthesis of heterocycles bearing biscoumarin as motif will be valuable from the synthetic chemistry and biological point of view.

Numerous approaches have been recently described for the synthesis of biscoumarin derivatives with catalytic reactions based on usage of molecular iodine,¹¹ tetrabutylammonium bromide (TBAB),¹² sulfated titania,¹³ Sodium dodecyl sulfate (SDS),¹⁴ SO₃H functionalized ionic liquids,¹⁵ Zn(Proline)₂,¹⁶

[bmim][BF₄],¹⁷ RuCl₃·nH₂O,¹⁸ SiO₂-OSO₃H NPs,¹⁹ NaHSO₄/SiO₂/indion190 resin,²⁰ choline hydroxide²¹ CuO-CeO₂ nanocomposite,²² HY zeolite,²³ Phthalimide-N-sulfonic,²⁴ and ionic liquid [Et₃NH][HSO₄]²⁵ as catalyst being among the most proficient procedures.

Though these actions provide a development in the synthesis of the above stated bis-heterocyclic mixtures and their importance could not be overstated, some of them suffer from the limitations such as long reaction times, harsh reaction conditions, low yields, costly reagents, usage of organic solvents, tedious workup, and non-recoverability of the catalyst. Consequently, the introduction of novel catalysts and approaches regarding the potential simplicity, high activity, low cost, high yields, and short reaction times, is still in request.

Based on the above literature and in continuation of our interest in the applications of reusable catalysts in organic synthesis we report

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herein a green approach for the synthesis of some biscoumarin derivatives from a reaction involving aldehydes and 4-hydroxycoumarin catalysis in sulfanilic acid (SA) in water for the first time. Water is a readily available solvent which have the advantages of being green. This solvent has been utilized as an environmentally attractive medium for some chemical transformations.

RESULTS AND DISCUSSION

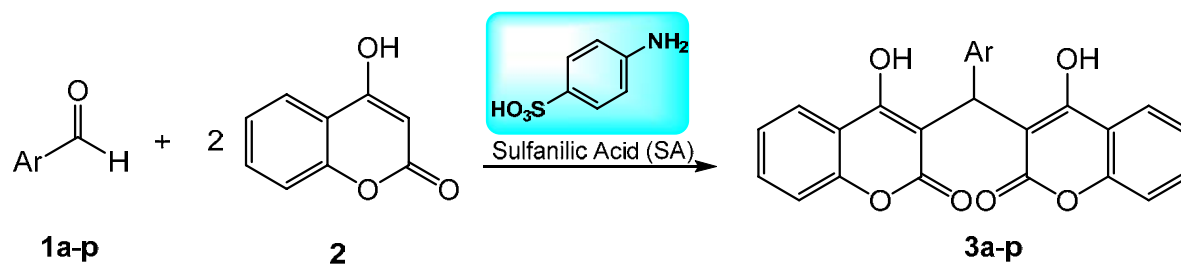
The Knoevenagel–Michael type reaction for the synthesis of biscoumarins was conducted with aromatic aldehydes and 4-hydroxycoumarin in the presence of SA as catalyst (Scheme 1). SA was utilized based on its good solubility in aqueous media, offering the advantage of simple purification of the desired products from the reaction medium and additionally, found to be a good catalyst for the synthesis of biscoumarin skeletons.

The efficiency of the proposed catalytic reaction was examined with 3-nitro-benzaldehyde (**1e**) (1.0 mmol) and 4-hydroxycoumarin (**2**) (2.0 mmol) under different reaction parameters and our selected results are summarized in Table 1. At the outset of our study, the reaction was examined with different amount of the catalyst (Table 1, entries 1-5). A tiny increase in yield occurred in similar reaction periods upon increasing the catalyst loading (Table 1, entry 1 *vs.* 2). Additionally, further increase in amounts of the catalyst resulted in completion of the desired reaction in shorter reaction times likely due to the presence of more active electrophilic species for the desired condensation reaction (Table 1, entries 3-5). However, a variation of catalyst loading of 20 mol% to 25 mol% did not affect the reaction outcome in appreciable manner (Table 1, entry 4 *vs.* 5). Accordingly, the 10 mol% catalyst loading was selected as the optimum choice based on the efficiency and cost of the catalyst (Table 1, entry 2). It is worth mentioning that the presence of catalyst is necessary for success of the transformation as in the absence of the catalyst, only traces amount of the desired product was detected in crude reaction mixture analysis even after prolonged reaction times (not shown in Table 1).

Afterwards, the effect of the reaction temperature on the reaction outcome was examined (Table 1, entries 6-12). The study indicated that decreasing the reaction temperature adversely affected the yields of the targeted product (Table 1, entries 6-10). Additionally, these reactions required longer reaction times to afford the targeted product

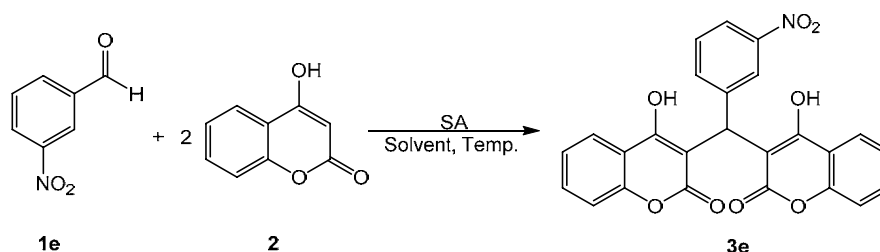
in acceptable yields. An outcome we attributed to the lower solubility of substrates in water and the leaving group ability of H_2O^+ at lower temperatures. Finally, the prototype reaction was conducted in various solvents as well as under solvent-free conditions (Table 1, entries 13-19). As shown in Table 1, the reaction was also productive in common organic solvents even at lower temperature. Additionally, the presence of solvent is vital for carrying out the transformation (Table 1, entry 19). Based on these findings, the optimal reaction conditions for this methodology were developed with a 1:2 mol ratio of benzaldehyde and 4-hydroxycoumarin in the presence of 10 mol% of SA as the catalyst in water at 80 °C (Entry 2).

The generality of the transformation was then examined under the optimum conditions developed above (Table 2). 2-Chloro benzaldehyde (**1a**) gave the targeted product in slightly lower yields than that of 2-nitro substituted aldehyde (**1b**) likely due to the resonance donation nature of chloride group. It could also be deduced that the steric hindrance of substrates did not effect on the reaction outcome (Table 2, entries 1–2). Highly electron-rich substrates **1c-1d** were also tolerated and afford the corresponding product in 87% and 83% yield, respectively (Table 2, entries 3–4) likely due to the electrophilicity of the substrates. 3-Nitro and 4-nitrobenzaldehydes **1e-1f** reacted efficiently to afford the desired compounds **3e-3f** in excellent yields and short times (Table 2, entries 5–6). 4-Chlorobenzaldehyde (**1g**) afforded a good yield (Table 2, entry 7). The tolerance for chloride offers an opportunity for subsequent cross-coupling reaction to for highly functionalized biscoumarin skeletons. As noticed, electron-rich substrates like 4-methoxybenzaldehyde (**1h**) or hydroxyl-substituted benzaldehydes (**1i-1k**) required longer reaction times to furnish the transformation with good yields (Table 2, entries 8–11). The tolerance of hydroxyl motif adds further advantage to current procedure. A modest decrease in yield occurred upon using of 2,4-dichlorobenzaldehyde (**1l**) (Table 2, entry 12). *p*-Tolylaldehyde (**1m**) afforded an excellent yield (Table 2, entry 13). Benzaldehyde (**1n**) was also good substrate in this transformation (Table 2, entry 14). By comparison, 3-methoxybenzaldehyde (**1p**) reacted more efficiently than that of 2-methoxybenzaldehyde (**1o**) (Table 2, entry 16 *vs.* 15). Generally speaking, aromatic aldehydes bearing electron-withdrawing groups were more reactive than those of electron-neutral or electron-rich substrates. The presence of nitrile, ketone, and ester groups on aldehyde structure were not compatible with this transformation.



Scheme 1 – Synthesis of biscoumarin.

Table 1

Optimization of the reaction conditions **3e**^a

Entry	Solvent	Catalyst (mol%)	Temp.(°C)	Time ^b	Yield ^c
1	H ₂ O	5	80	35 min	93
2	H₂O	10	80	25 min	98
3	H ₂ O	15	80	24 min	95
4	H ₂ O	20	80	22 min	97
5	H ₂ O	25	80	21 min	98
6	H ₂ O	10	RT	24 h	51
7	H ₂ O	10	40	1 h	63
8	H ₂ O	10	50	1 h	67
9	H ₂ O	10	60	1 h	81
10	H ₂ O	10	70	1 h	93
11	H ₂ O	10	90	17 min	87
12	H ₂ O	10	100	14 min	96
13	EtOH	10	60	1 h	83
14	EtOH	10	80	1 h	92
15	Ethyl acetate	10	80	1 h	83
16	CH ₂ Cl ₂	10	80	1 h	85
17	THF	10	80	1 h	57
18	Toluene	10	80	1 h	81
19	Solvent-Free	10	80	24 h	-

^a Reaction conditions: **1e** (1.0 mmol), **2** (2.0 mmol), solvent (5.0 mL), and catalyst (5-25 mol%) at 25-100 °C.^b Progress of the reaction was monitored with TLC analysis. ^c Isolated yields.

Based on ¹H NMR spectra and according to the literature,²⁴ the two coumarin fragments in **3a-p** can be depicted as two-different enolic forms (Figure 1). For example, in the ¹H NMR spectrum of compound **3d**, two singlet appeared at $\delta=11.37$ and 11.59 ppm attributed to OH protons. The emergence of two distinct peaks in two separate areas suggests that the two hydroxyl groups are not equivalent, which can be attributed to two different hydrogens indicating the presence of intramolecular hydrogen bonding in the conformation 3A. Accordingly, it can be considered that the molecule adopts conformation 3A. This result is supported

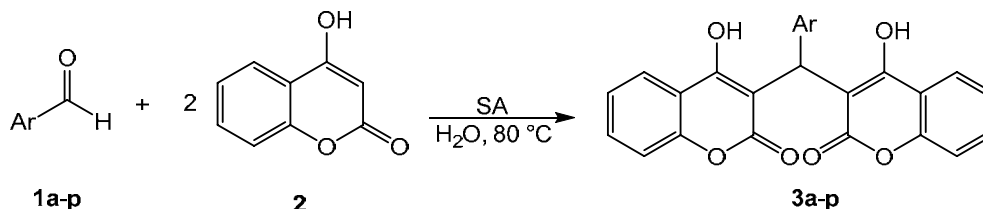
by X-ray crystallographic studies reported in the literature.

The recycling and reusability of the catalyst are very important for scale-up the reaction and industrial applications therefore, the recovery and reusability of SA was investigated in the reaction of 4-Nitro-benzaldehyde and 4-hydroxycoumarin under the optimum condition described in Table 1 (Table 3). Upon completion of the reaction, the catalyst was recovered after each run (see experimental section) and reused for subsequent run. The model reaction was conducted with recovered catalyst and the results indicated that the

catalyst could be recycled five times with only a modest loss of activity. This indicated that the SA was an efficient and recyclable catalyst for the preparation of biscoumarins. It is worth mention-

ing that almost all the catalyst (up to 96%) could be recovered from each run. After the reaction has been ended, the reaction mixture was cooled to room temperature.

Table 2

Scope of the reaction with different aromatic aldehydes^a

Entry	1	Ar	Time (min.)	Product, Yield (%)	Melting point	
					Found	Reported
1	a	2-Cl-C ₆ H ₄	40	3a , 90	198-200	201-203 ²
2	b	2-NO ₂ -C ₆ H ₄	6	3b , 97	200-202	198-200 ²
3	c	4-Me ₂ N-C ₆ H ₄	23	3c , 87	217-218	221-222 ²⁸
4	d	3,4-(MeO) ₂ -C ₆ H ₃	38	3d , 83	265-266	271-273 ²⁸
5	e	3-NO ₂ -C ₆ H ₄	25	3e , 98	216-217	214-215 ²
6	f	4-NO ₂ -C ₆ H ₄	11	3f , 96	233-235	233-235 ²
7	g	4-Cl-C ₆ H ₄	25	3g , 92	258-260	261-263 ²
8	h	4-MeO-C ₆ H ₄	25	3h , 90	253-257	250-252 ²
9	i	2-OH-C ₆ H ₄	28	3i , 81	252-252	254-256 ²
10	j	3-OH-C ₆ H ₄	12	3j , 94	260-262	268-269 ²⁸
11	k	4-OH-C ₆ H ₄	33	3k , 88	227-228	228-231 ²⁸
12	l	2,4-(Cl) ₂ -C ₆ H ₃	22	3l , 84	198-199	190-195 ⁴
13	m	4-Tolyl	20	3m , 96	269-270	266-270 ²
14	n	Ph	16	3n , 94	230-232	229-231 ²
15	o	2-MeO-C ₆ H ₄	25	3o , 83	212-213	213-215 ¹⁴
16	p	3-MeO-C ₆ H ₄	22	3p , 96	259-260	252-254 ²⁸

^a Conditions: **1** (1.0 mmol), **2** (2.0 mmol), H₂O (5.0 mL), and catalyst (10 mol%) at 80 °C. ^b All the products were characterized by ¹H-NMR, ¹³C-NMR, and IR analysis. ^c Isolated yield.

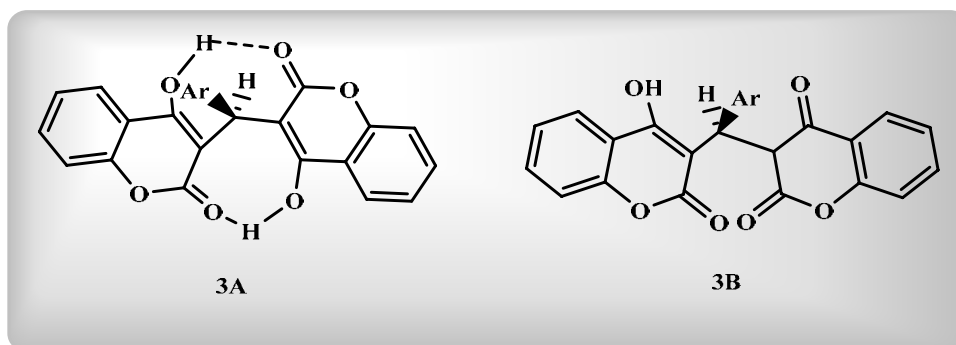
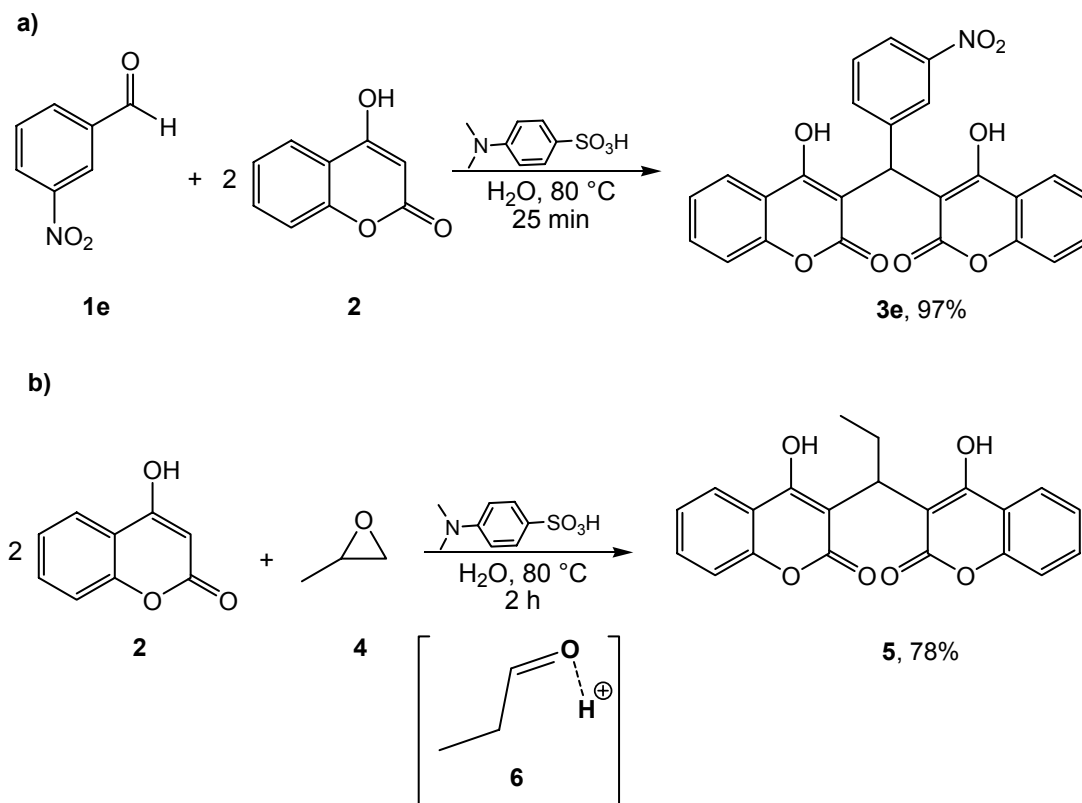
Fig. 1 – Two conformations of **3**.

Table 3

Reusability of SA in **3e**^a

Catalyst recycle	Fresh	Run1	Run2	Run3	Run4
Time/min	25	30	40	55	80
Isolated yield%	98	93	87	80	70

^aThe reaction conditions are similar to the optimized conditions described in Table 1.



Scheme 2 – Control experiment.

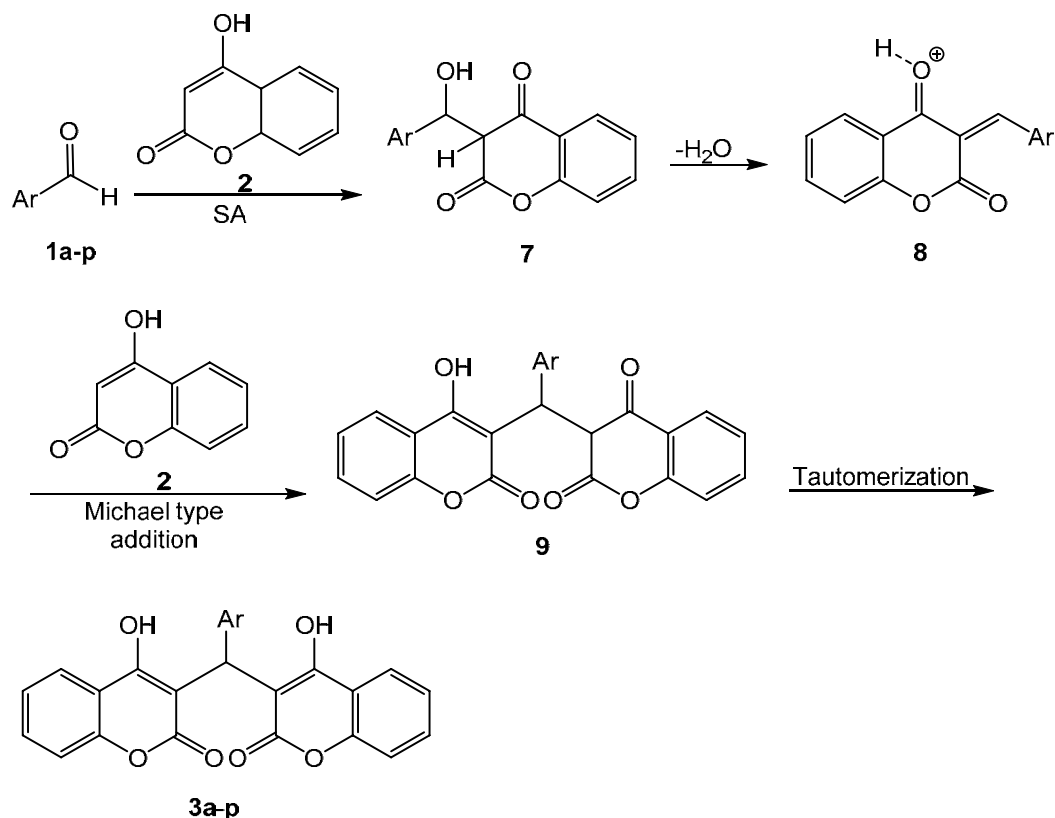
In all cases, the biscoumarin synthons were isolated with a high degree of purity. If necessary, crude products can be recrystallized from the aqueous ethanol or a mixture of hexane and ethanol. The products were characterized with ^1H NMR, ^{13}C NMR, and physical constant. Physical and spectral data of recognized mixtures are in line with those described in the earlier studies.

To get a better insight on reaction mechanism, some control experiment were conducted (Scheme 2). To examine if the amine motif in SA is involved in reaction progress through formation of corresponding iminium salt of aldehyde, the reaction was conducted with 4-(dimethylamino)benzenesulfonic acid. As shown in Scheme 2 (part a), the reaction afforded the desired product **3e** in almost similar yield of that SA. It could be deduced that the reaction did not proceed through an iminium salt. It should be noted that the reaction was not productive using aliphatic aldehyde like acetaldehyde and propionaldehyde as aldehyde source. The reaction was also conducted with methyl oxirane (**4**) to explore the reactivity of oxirane source in this transformation (Scheme 2, part b). The reaction afforded the desired product **5** in 78% yield. It could be deduced that the reaction proceeded through the attack of **2** on intermediate

6 which is probably formed *via* Meinwald rearrangement in the presence of SA.²⁶

A reasonable mechanism supported by literature^{27,28} can be suggested for the formation of 3,3'-arylmethylene-*bis*(4-hydroxycoumarins) (Scheme 3). Initially, 4-hydroxycoumarin (**2**) attacks on activated aldehyde **2** by the action of SA to form intermediate **7** which is then converted to the unsaturated intermediate **8** through elimination of water. Subsequently, the second molecule of 4-hydroxycoumarin reacted with **8** through a Michael type reaction to give species **9** which is further tautomerizes to the desired product **3** in the presence of SA.

In order to show the merit of the present work in comparison with recently published procedures, we compared the results of the reaction of 3-nitrobenzaldehydes (1.0 mmol), 4-hydroxycoumarin (2.0 mmol) in the presence of various catalysts (Table 4). As revealed in Table 4, SA might function as an efficient catalyst with respect to the reaction time and yield. The important benefits of this approach are shorter reaction times, simple work-up process, cheap and non-toxic catalysis, easy preparation and handling of the catalyst, environmental benignity, reprocessing of the catalyst and outstanding yields.



Scheme 3 – A proposed mechanism for the formation of biscoumarins.

Table 4

Comparison of the catalytic performance of SA catalyst for the synthesis of 3e with those obtained by reported catalysts

Entry	Catalyst (mol%)	Solvent/Temp	Time (min)	% Yield ^{ref.}
1	sulfanilic acid (SA) (10)	H ₂ O/80 °C	25 min	98 ^[this work]
2	[P ₄ VPy-BuSO ₃ H]HSO ₄ (10)	Toluene/90 °C	42 min	95 ²⁸
3	sulfosalicylic acid (15)	H ₂ O/80 °C	28 min	95 ²⁹
4	Nano-MgO (3)	None/100 °C	21 min	88 ³⁰
5	Sodium dodecyl sulfate(SDS) (20)	H ₂ O/60 °C	147 min	95 ¹⁴
6	SiO ₂ Cl (75)	CH ₂ Cl ₂ /40 °C	210 min	90 ³¹
7	PISA (10)	H ₂ O:EtOH(1:1)/80 °C	30 min	96 ²⁴
8	Poly(4-vinylpyridinium)perchlorate (30)	H ₂ O/80 °C	15 min	91 ²⁶

^a Reaction conditions: 3-Nitro-benzaldehyde (1.0 mmol), 4-hydroxycoumarin (2.0 mmol). ^b Isolated yields

EXPERIMENTAL

Materials

All the reagents and chemicals were commercially available and used without further purification. All yields refer to the isolated products. The known products were identified by comparison of their melting points and spectral data with those reported in the literature.

Equipment

The progress of the reactions was monitored by TLC on Merck pre-coated silica gel 60 F254 aluminum sheets, visualized by UV light. IR spectra were recorded on a Shimadzu FT-IR 8300 Spectrophotometer using the KBr pellets technique. ¹H NMR and ¹³C NMR spectra were recorded at ambient temperature on a BRUKER AVANCE

DRX-500 MHz spectrophotometer using DMSO-d₆ as the solvent and TMS as an internal standard.

Procedure

A mixture of 4-hydroxycoumarin (2.0 mmol), aldehyde (1.0 mmol), SA (0.017 gr, 10 mol%), and water (5.0 mL) in a round bottom flask was heated at 80 °C for the appropriate time as mentioned in Table 2. After the completion of the reaction (monitored by TLC), the reaction mixture was cooled to room temperature. Then, the precipitated product was filtered, washed with water (20 mL) and ether (10 mL), and dried in vacuum to give the pure targeted compounds **3a-p** in high yields. The catalyst was recovered from the filtrate by evaporation of the water *in vacuo*. The residue was then washed with ethyl acetate (3 times, 3.0 mL), dried, and reused for the next runs. The catalyst was successfully reused up to five runs without significant decrease of the yields. All

products were characterized by IR, ^1H and ^{13}C NMR spectral data and by comparison with melting points of the reported compounds.

Spectral data of some selected products:

3, 3'-((4-Methoxyphenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3h)

IR (KBr): 3440, 3072, 3002, 1668, 1604, 1565, 1510, 1454, 1353, 1258, 1180, 1094, 907, 828, 768 cm^{-1} ; ^1H NMR (500 MHz, DMSO- d_6): δ 3.81 (s, 3H), 6.05 (s, 1H), 6.89 (d, $J = 8.7$ Hz, 2H), 7.14 (d, $J = 8.7$ Hz, 2H), 7.31-7.42 (m, 4H), 7.65 (t, $J = 8.2$ Hz, 2H), 8.02 (dd, $J = 8.4$ Hz, 2H), 11.31 (s, 1H), 11.53 (s, 1H); Anal. Calcd. For $\text{C}_{26}\text{H}_{18}\text{O}_7$: C, 70.58; H, 4.10%; found C, 70.48; H, 4.21%.

3, 3'-((4-Chlorophenyl)methylene)bis(4-hydroxy-2H-chromen-2-one) (3f)

IR (KBr): 3352, 3069, 2680, 2610, 1669, 1619, 1600, 1491, 1455, 1353, 1310, 1267, 1185, 1096, 922, 910, 822, 790 cm^{-1} ; ^1H NMR (500 MHz, DMSO- d_6): δ 6.08 (s, 1H), 7.19 (dd, $J = 0.9, 8.5$ Hz, 2H), 7.32 (d, $J = 8.6$ Hz, 2H), 7.41-7.46 (m, 4H), 7.66-7.69 (m, 2H), 8.03 (d, $J = 7.8$ Hz, 1H), 8.11 (d, $J = 7.74$ Hz, 1H), 11.37 (s, 1H), 11.59 (s, 1H); ^{13}C NMR (125MHz, DMSO- d_6): δ 36.2, 104.1, 105.7, 116.8, 117.0, 117.1, 117.2, 124.8, 125.4, 128.4, 129.2, 133.1, 133.5, 134.3, 152.7, 152.9, 165.1, 166.4, 167.3, 169.6; Anal. Calcd. For $\text{C}_{25}\text{H}_{15}\text{ClO}_6$: C, 67.20; H, 3.38%; found C, 67.18; H, 3.42%.

3,3'-(propane-1,1-diyl)bis(4-hydroxy-2H-chromen-2-one) (5)

IR (KBr): 3373, 3066, 2621, 1673, 1626, 1605, 1467, 1323, 1311, 1266, 1175 1096, 1034 cm^{-1} ; ^1H NMR (500 MHz, DMSO- d_6): δ 0.89 (t, $J = 6.1$, 3H), 1.55 (qd, $J = 6.1, 5.4$, 2H), 4.39 (t, $J = 5.4$ Hz, 2H), 7.23-7.28 (m, 2H), 7.35-7.43 (m, 4H), 7.56-7.61 (m, 2H), 7.93 (d, $J = 7.5$ Hz, 1H), 8.17 (d, $J = 7.9$ Hz, 1H), 11.78 (s, 1H), 12.27 (s, 1H); ^{13}C NMR (125MHz, DMSO- d_6): δ 10.8, 17.6, 30.3, 101.1, 103.5, 118.3, 119.5, 120.1, 121.7, 122.8, 124.0, 126.7, 127.1, 130.1, 130.9, 149.8, 151.1, 152.9, 166.8, 167.2, 169.1, 171.4; Anal. Calcd. For $\text{C}_{21}\text{H}_{16}\text{O}_6$: C, 69.23; H, 4.43%; found C, 69.37; H, 4.29%.

CONCLUSIONS

In conclusion, SA was found to be as a novel and efficient catalyst for the synthesis of biscoumarine derivatives under aqueous media. We have developed an environmentally benign catalytic method for the synthesis of biscoumarins through the reaction of various aldehydes with 4-hydroxycoumarin. This method offers several advantages, including high yield of products, short reaction time, low cost, cleaner reaction profile, ease of preparation of catalyst, and ease of work up. Additionally, the catalyst was successfully recovered and recycled for at least five runs without significant loss in activity.

Acknowledgment: Financial support of Islamic Azad University, South Tehran Branch is acknowledged.

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