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Nano-[SiO_2@R-Im-SO_3H][CF_3COO]: an effectual catalyst for the production of bis-coumarins and *N,N′*-alkylidene bisamides

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ABSTRACT

A novel organic-inorganic hybrid nanomaterial namely nano-[SiO_2@R-Im-SO_3H][CF_3COO] (NSRISC) was synthesized, and characterized using FT-IR, EDS, FE-SEM, TGA and XRD analyses. Thereafter, the solvent-free production of bis-coumarins (from aryl aldehydes and 4-hydroxycoumarin) and *N,N′*-alkylidene bisamides (from aryl aldehydes and benzamide) was catalyzed by NSRISC. Bis-coumarins were produced in 86-97% at 100 ºC, and bisamides were obtained in 87-97% at 105 ºC. The reaction times were 15-30 min for both kinds of compounds.

***Keywords**: Nano-[SiO*$_2$*@R-Im-SO*$_3$*H][CF*$_3$*COO] (NSRISC), Organic-inorganic hybrid nanomaterial, Solvent-free, Bis-coumarin, N,N′-Alkylidene bisamide.*

1. Introduction

The materials having at least one dimension in the range of 1-100 nm are nominated as nanomaterials; various industries can use them for numerous applications [1]. Organic-inorganic hybrid nanomaterials are a significant category of them that were constructed from at least two organic and inorganic parts grafting together and this synergetic effect improves their properties; some benefits of these materials are thermal and chemical durability, eco-friendly nature, easy functionalization, simple separation and large specific surface area [2-5]. Utilization of the hybrid nanomaterials in biosensors [5], supercapacitives [6], lasers [7] and photodetectors [7], and for electrocatalytic CO2 reduction [8] and drug release [9] has been reported. Absorbance of dye effluents [10] and catalyzing organic reactions [11-17] are also their important applications. Coumarin is found in many plants, such as bison grass, tonka bean, and woodruff [18]. Coumarin derivatives represent a number of biological properties, e.g. inhibition of growing hepatoprotective [19], antitumor activity [20], protecting rat tissues against isoproterenol toxicity [21], and anti-quorum sensing [22]. Application of them in two-photon fluorescence microscopy [23], live cell imaging [24] and dye sensitized solar cells [25] has been also reported. Bis-coumarins can be produced through reacting aryl aldehydes (1 eq.) and 4-hydroxycoumarin (2 eq.); progress of this reaction needs a catalyst [26-33].

Bisamide exists in the framework of many biological and industrial materials [34-40]. For instance, antitumor [35], antimicrobial [36] and anti-inflammatory [37] activities have been reported for bisamide-containing materials. Additionally, bisamide derivatives have been used for electrochemical sensing of H_2O_2 [38], MRI blood-pool contrasting [39], and isolation of organic dyes [40]. The reaction of aryl aldehydes (1 eq.) with primary amides (2 eq.) is a useful procedure for the construction of N,N′-alkylidene bisamides in the presence of a catalyst [41-46].

We have reported here the production of nano-[SiO_2@R-Im-SO_3H][CF_3COO] (NSRISC) as a novel organic-inorganic hybrid nanomaterial, characterizing it by FT-IR, EDS (energy-dispersive X-ray spectroscopy), FE-SEM (field emission scanning electron microscopy), TG (thermogravimetric), DTG (differential thermal

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gravimetric) and XRD (X-ray diffraction) analyses, and utilizing it as a highly effective nanocatalyst for the construction of bis-coumarins and N,N′-alkylidene bisamides without the need of using solvent as reaction medium.

2.Experimental

2.1. Materials and instruments

Supplementary file contains information on materials and instruments.

2.2. Synthesis of NSRISC

Imidazole (0.34 g, 5 mmol) and (3-chloropropyl)trimethoxysilane (0.99 g, 5 mmol) were stirred in reflexed toluene (15 mL) for 12 h; the solvent was distilled at 100 ºC under vacuum to provide **I**. Then, **I** was reacted with nano-SiO_2 (0.6 g, 10 mmol) in refluxed EtOAc (15 mL) for 18 h to produce **II**. In continue, **II** was gradually added to a stirring solution of $ClSO_3H$ (0.34 mL, 5 mmol) in dry CH_2Cl_2 (15 mL) at 10 ºC (ice-water bath), and stirred for 4 h at ambient temperature to generate **III**. In the final step, a solution of CF_3CO_2H (0.46 mL, 6 mmol) in dry CH_2Cl_2 (15 mL) was gradually added to **III** at ambient temperature, and stirred for 9 h at that temperature, and 3 h under reflux conditions to give NSRISC. The compounds produced in second to fourth stages (i.e. **II**, **III** and NSRISC) were separated by centrifugation and decanting, washed by the used solvent in the related step, and dried (**Scheme 1**).

2.3. The production of bis-coumarins

Aldehyde (1 mmol), 4-hydroxycoumarin (2 mmol) and NSRISC (0.04 g) were stirred by a rod at 100 ºC. When TLC showed completing the reaction, the mixture was cooled to ambient temperature, EtOAc (30 mL) was added, and stirred accompanied with refluxing for 2 min; centrifugation and decanting were utilized to separate the unsolvable. Thereafter, the EtOAc resulting from the decanting was distilled, and the remaining precipitate (the raw product) was purified by recrystallization in ethanol (95%).

2.4. The construction of N,N′-alkylidene bisamides

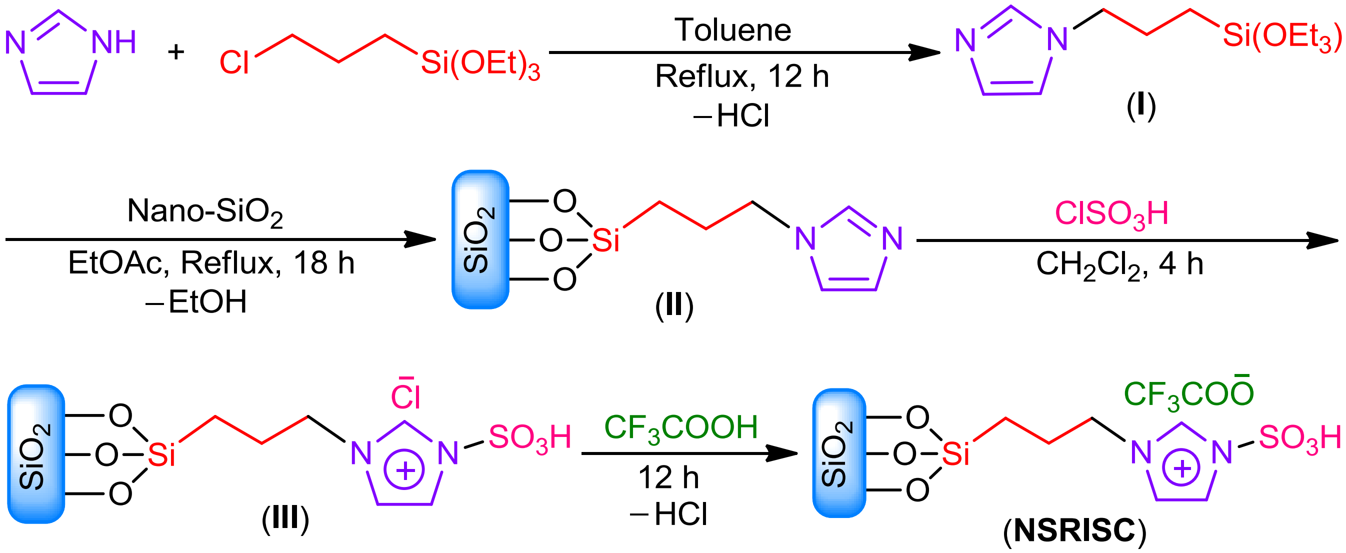
Benzamide (2 mmol), aldehyde (1 mmol) and NSRISC (0.052 g) were stirred by a rod at 105 ºC. After confirming completion of the reaction by TLC, and cooling the mixture to ambient temperature, EtOAc (30 mL) was added, and stirred accompanied with refluxing for 2 min; centrifugation and decanting were used to isolate the unsolvable nanocatalyst. Thereinafter, EtOAc resulted from the decanting was distilled, and purification of the raw product was performed by recrystallization in ethanol (95%).

3. Results and Discussion

3.1. Characterization of the nanocatalyst

FT-IR, EDS, FE-SEM, TG, DTG and XRD analyses were utilized to characterize NSRISC.

Fig. 1 and **Table 1** illustrate the FT-IR spectrum and data of NSRISC, respectively. The peaks related to the bonds and functional groups in the structure of NSRISC were observed in the spectrum [47,48].



Scheme 1. The synthesis of NSRISC.

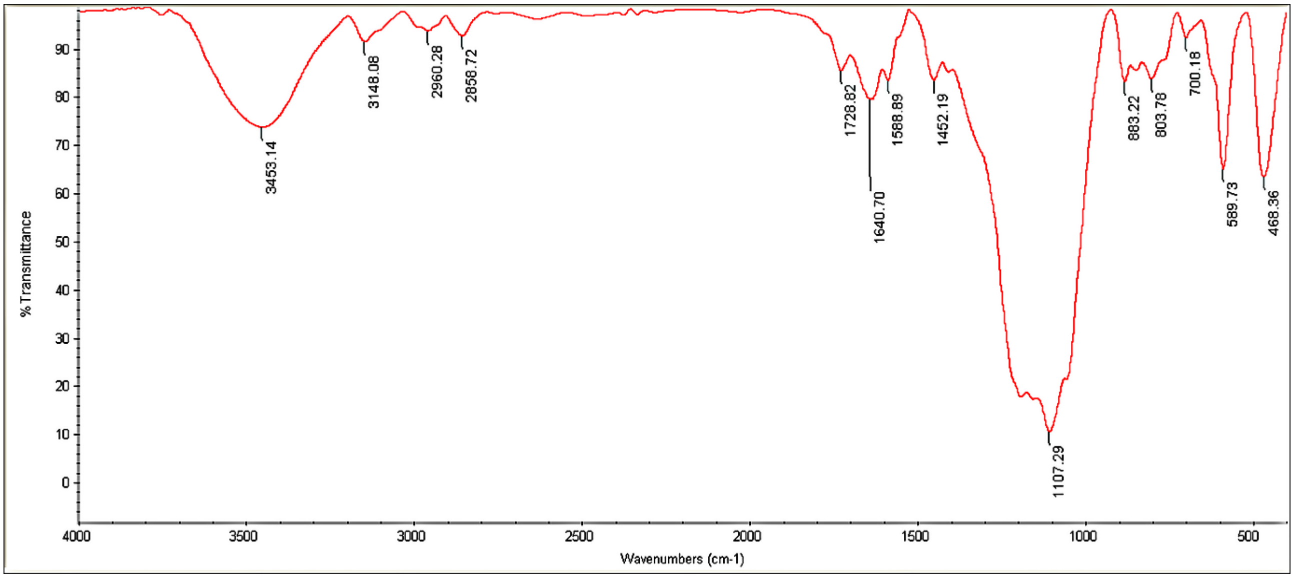


Fig. 1. The FT-IR spectrum of NSRISC.

Table 1. The FT-IR data of NSRISC

Peak (cm^{-1})	Bond or functional group
468	Rocking of Si–O
590	Bending of –SO_2–
883	Stretching of N–S
1107	Symmetric stretching of –SO_2–
~1194	Asymmetric stretching of –SO_2–
1452	Bending of aliphatic C–H
1641	Stretching of C=N
2960	Symmetric stretching of aliphatic C–H
3148	Stretching of aromatic C–H
3200-3736	Stretching of OH group of the SO_3H and OH groups on SiO_2 surface

The EDS spectrum (**Fig. 2**) confirmed all elements existed in the structure of NSRISC, i.e. carbon, nitrogen, oxygen, fluorine, silicon and sulfur.

Fig. 3 exhibits the FE-SEM image of NSRISC, and verifies that the particles sizes are in nanoscale; e.g., the sizes of some particles are 13.9, 22.9, 24.7, 27.7 and 30.9 nm.

Fig. 4 represents the TG and DTG diagrams of NSRISC, and confirms that weight losing has occurred in 3 stages. In first stage (less than ~200 ºC), the weight loss may be pertinent to evaporation of the absorbed solvents on the SiO_2 surface. In second stage (~200-300 ºC), the weight loss may be because of decomposition of the organic components grafted with the SiO_2 surface, and the removal of SO_2 and CO_2 gases. In third stage (~300-600 ºC), the weight loss is attributed to the decomposition of the organic components grafted with the SiO_2 surface, and the condensation of silanol groups [12].

In the XRD pattern of NSRISC (**Fig. 5**), the broad peak (at 2θ ≈ 16-34º) is related to the amorphous structure of SiO_2. The sharp peaks (at 2θ ≈ 12.0, 13.1, 22.4, 26.1, 31.9, 41.6, 45.5, 47.4, 49.3 and 61.1º) belong to the crystalline forms of the nanocatalyst [11,12].

3.2. Examining catalytic activity of NSRISC for the construction of bis-coumarins and N,N′-alkylidene bisamides

At the outset, the following model reactions were selected: (i) the solvent-free reaction of 4-chlorobenzaldehyde (1 mmol) with 4-hydroxycoumarin (2 mmol) for the construction of bis-coumarin (**Scheme 2**), and (ii) the solvent-free reaction of 4-chlorobenzaldehyde (1 mmol) with benzamide (2 mmol) for the construction of *N*,*N′*-alkylidene bisamides (**Scheme 2**). To acquire the optimum conditions, the model reactions were investigated in the presence of diverse amounts of NSRISC at a range of 90-110 ºC; **Table 2** demonstrates the summarized results. Considering the results, the optimum catalyst amount and temperature for the production of bis-coumarins were 0.040 g and 100 ºC, respectively (entry 2 of **Table 2**); furthermore, the optimum catalyst amount and temperature for the construction of *N*,*N′*-alkylidene bisamides were 0.052 g and 105 ºC, respectively (entry 9 of **Table 2**).

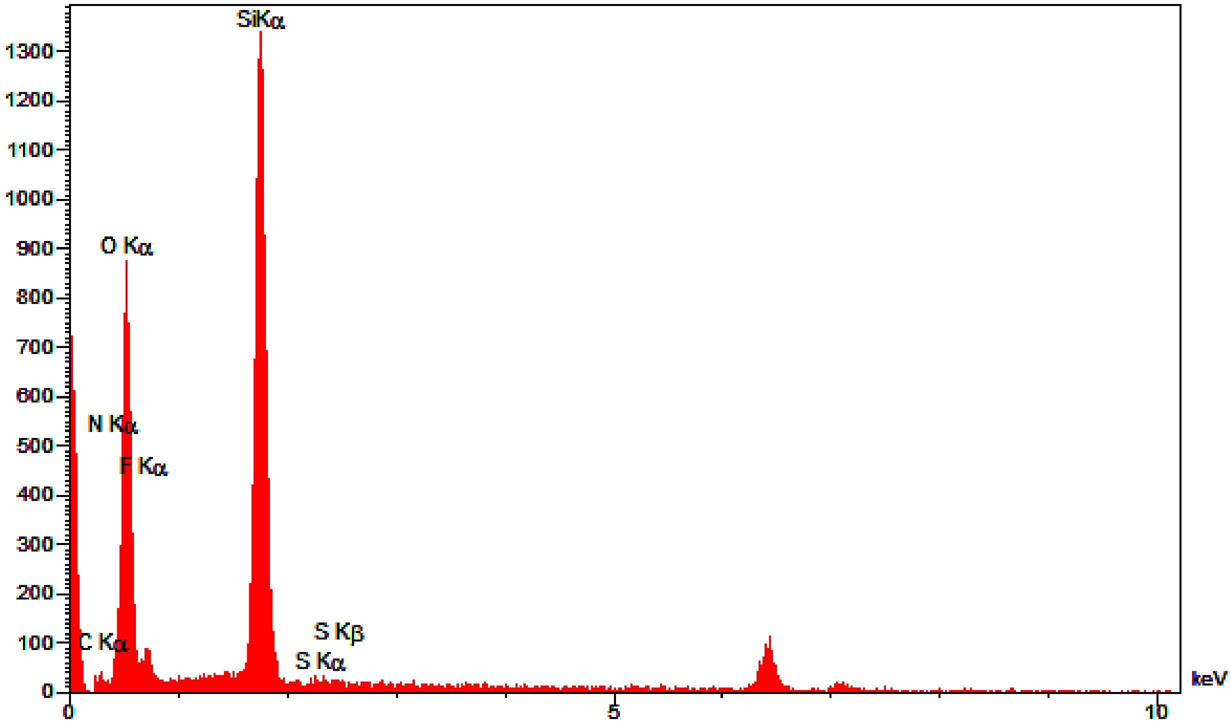


Fig. 2. The EDS spectrum of NSRISC.

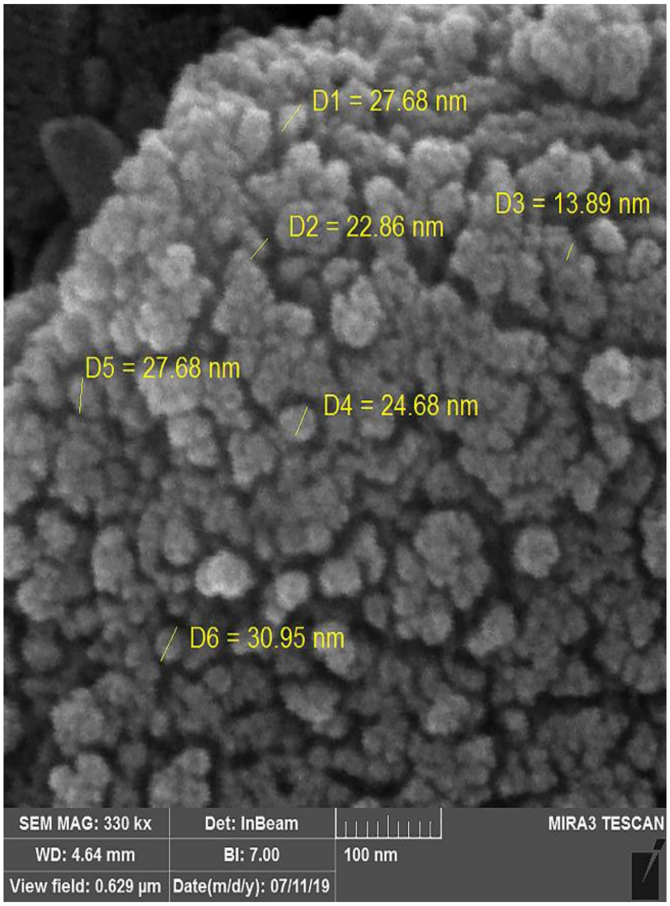


Fig. 3. The FE-SEM image of NSRISC.

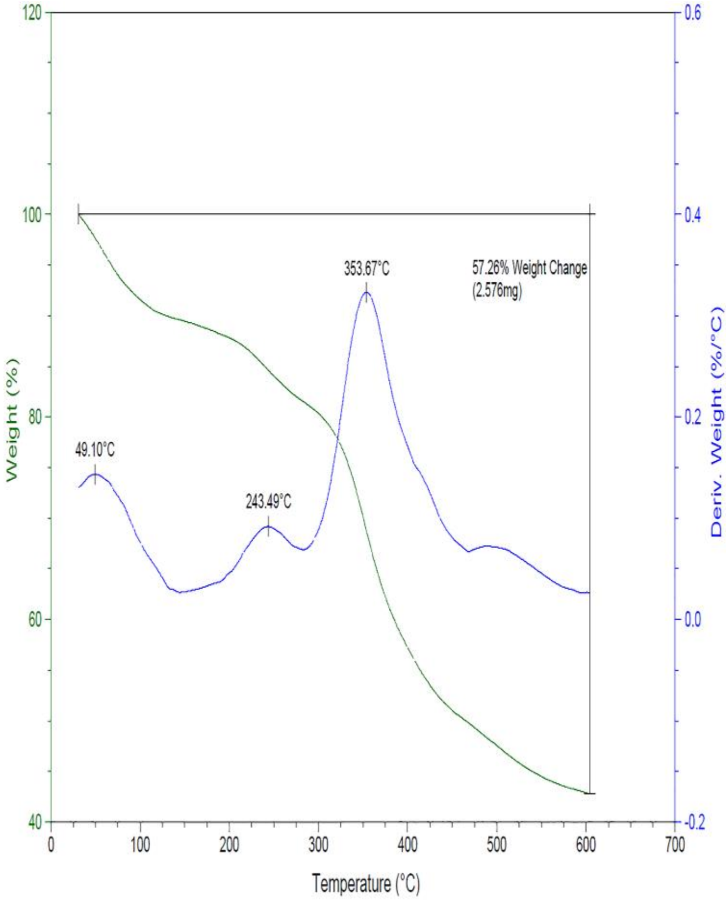


Fig. 4. The TG and DTG diagrams of NSRISC.

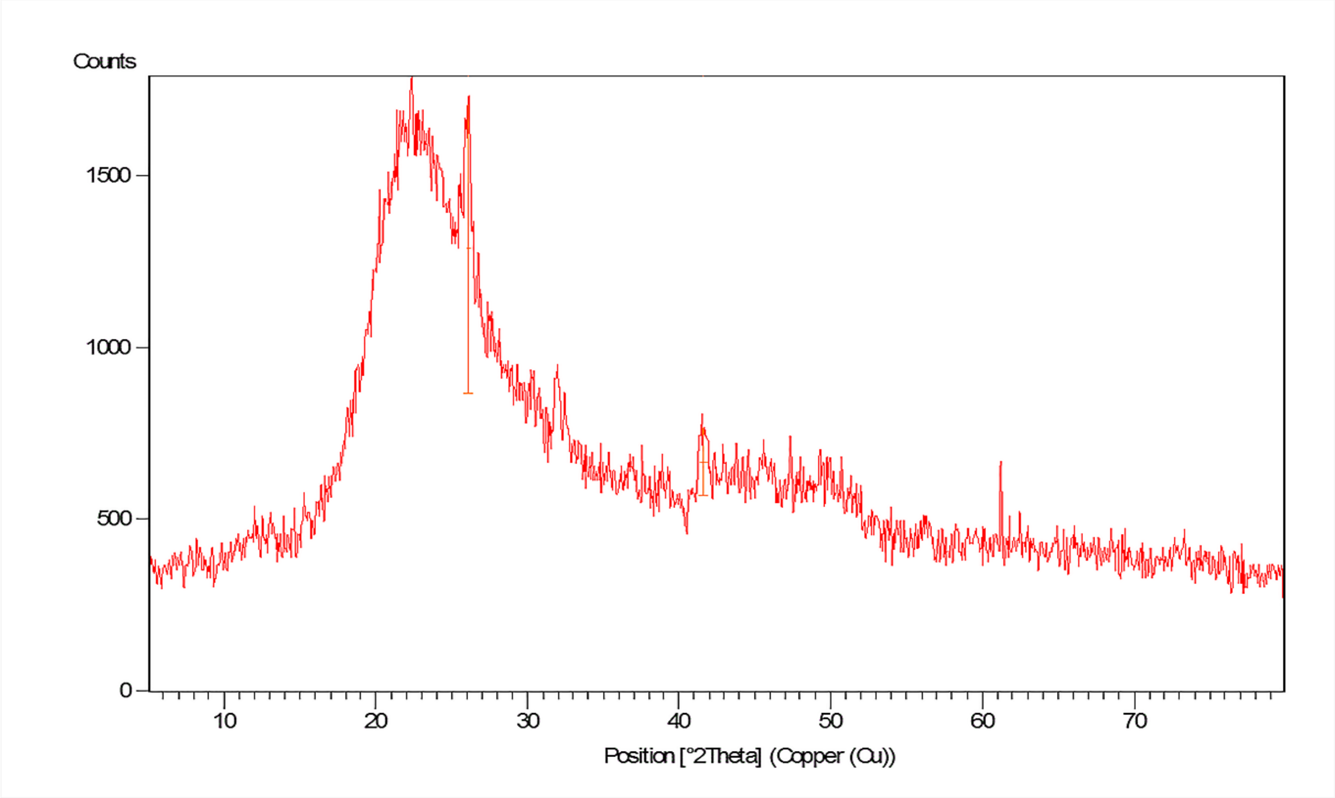
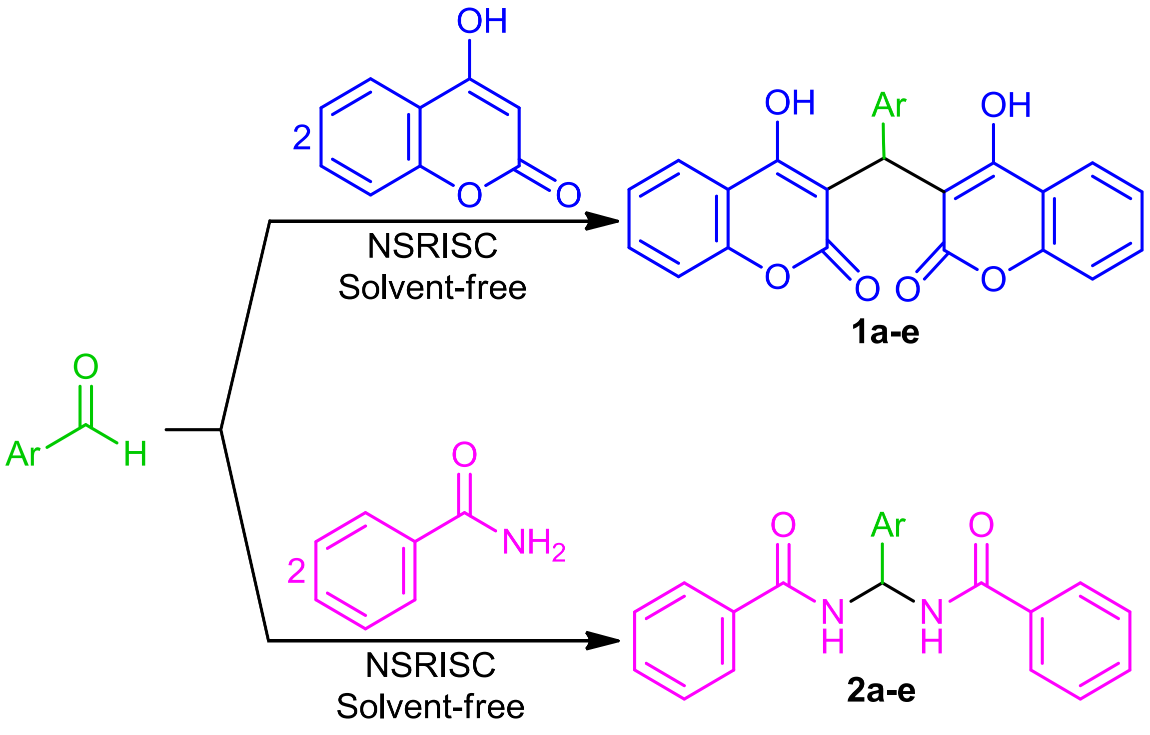


Fig. 5. The XRD pattern of NSRISC.



Scheme 2. The production of bis-coumarins (**1a-e**) and *N*,*N′*-alkylidene bisamides (**2a-e**).

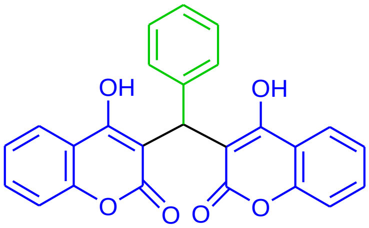
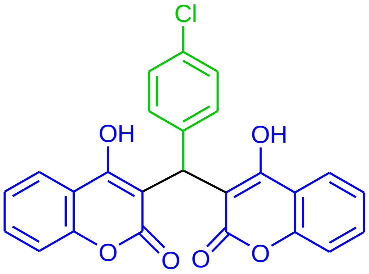
Table 2. Effect of the catalyst amount and temperature on the model reactions.

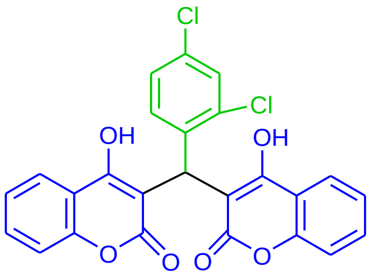
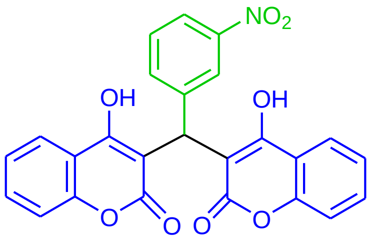
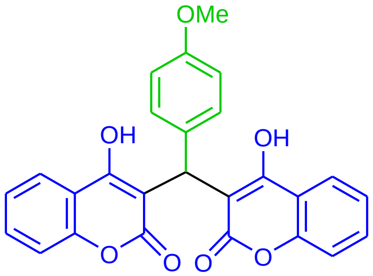
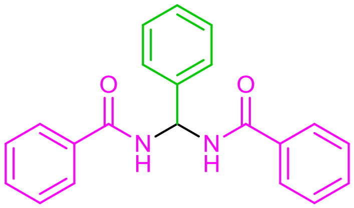
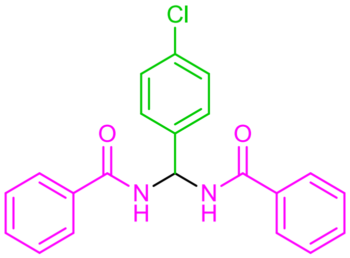
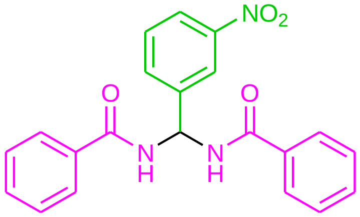
Entry	Product	The catalyst amount (g)	Temp. (ºC)	Time (min)	Yield (%)
1	**1b**	0.032	110	15	91
2	**1b**	0.040	100	15	96
3	**1b**	0.040	90	30	87
4	**1b**	0.052	100	15	96
5	**2b**	0.040	90	30	78
6	**2b**	0.052	90	15	82
7	**2b**	0.040	100	30	85
8	**2b**	0.052	100	15	93
9	**2b**	0.052	105	15	97
10	**2b**	0.060	105	15	97

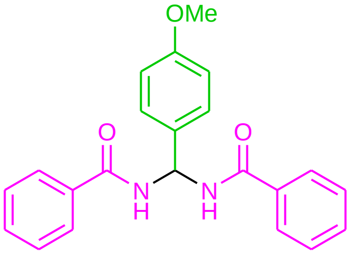
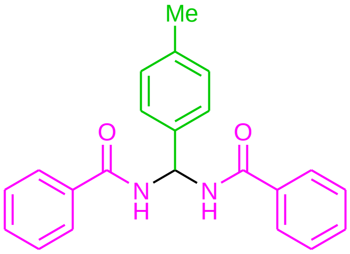
In continue, several derivatives of bis-coumarins and *N*,*N′*-alkylidene bisamides were constructed through the reaction of aryl aldehydes with 4-hydroxycoumarin (or benzamide) under the optimum conditions (**Table 3**). As **Table 3** demonstrates that the desired bis-coumarins and *N*,*N′*-alkylidene bisamides were prepared with high yields in short times using aryl aldehydes bearing electron-withdrawing, electron-donating and halogens substituents. The results approved high effectuality and wide scope of NSRISC to catalyze the reactions.

The tasks of NSRISC in the reactions consist of: (i) activation of the electrophiles by its SO$_3$H to accept the nucleophiles (**Scheme 3:** steps 1 and 3; **Scheme 4:** steps 1′ and 3′), (ii) helping removal of a H$_2$O molecule (**Scheme 3:** step 2; **Scheme 4**: step 2′), and (iii) acceleration of tautomerization (**Scheme 3**: step 4; **Scheme 4**: step 4′). The mechanisms are suggested considering the literature reports [46,53].

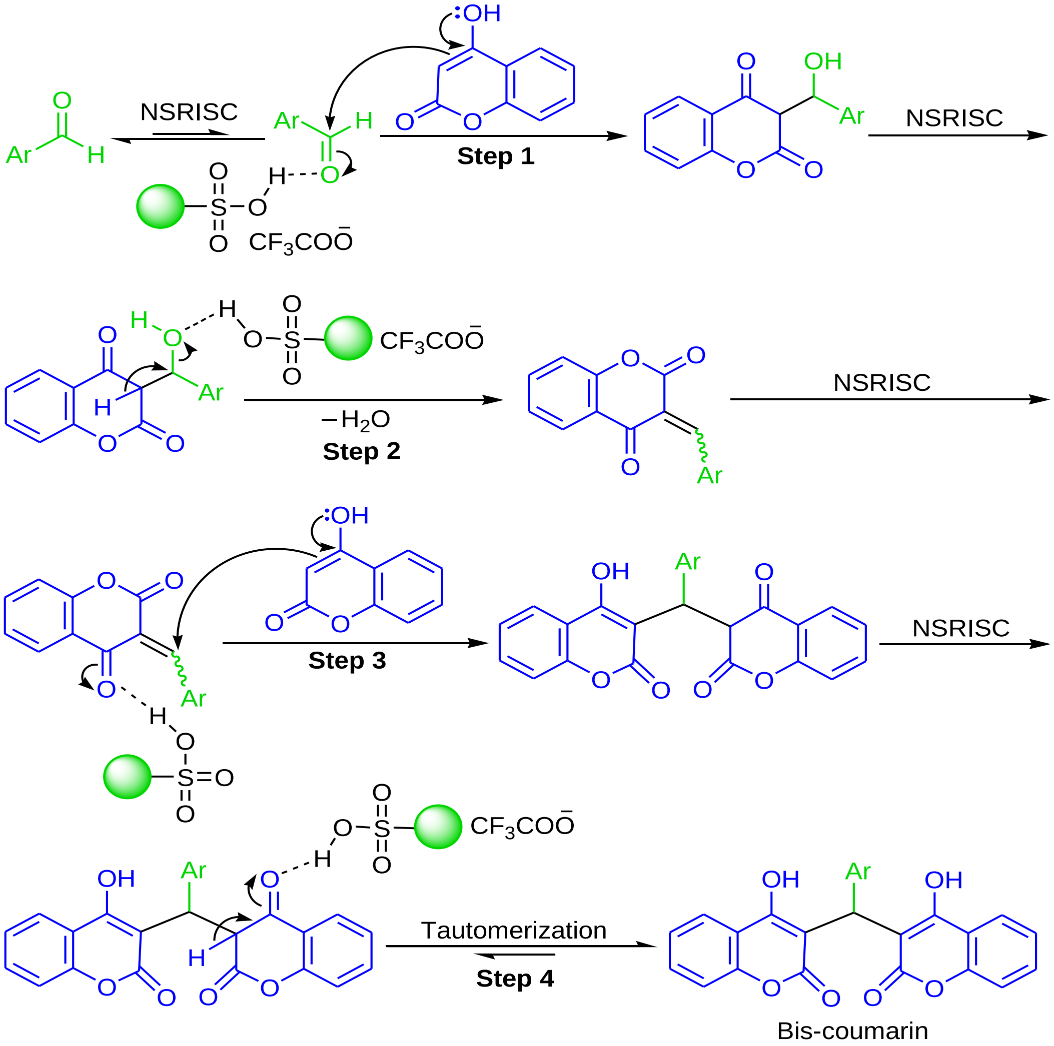
Table 3. The construction of bis-coumarins (**1a-e**) and *N*,*N′*-alkylidene bisamides (**2a-e**) using NSRISC.

Product No.	Product	Time (min)	Yield^a (%)	M.p. (ºC) [lit.]
1a		15	94	229-230(228-230) [29]
1b		15	96	254-256 (256-258) [26]

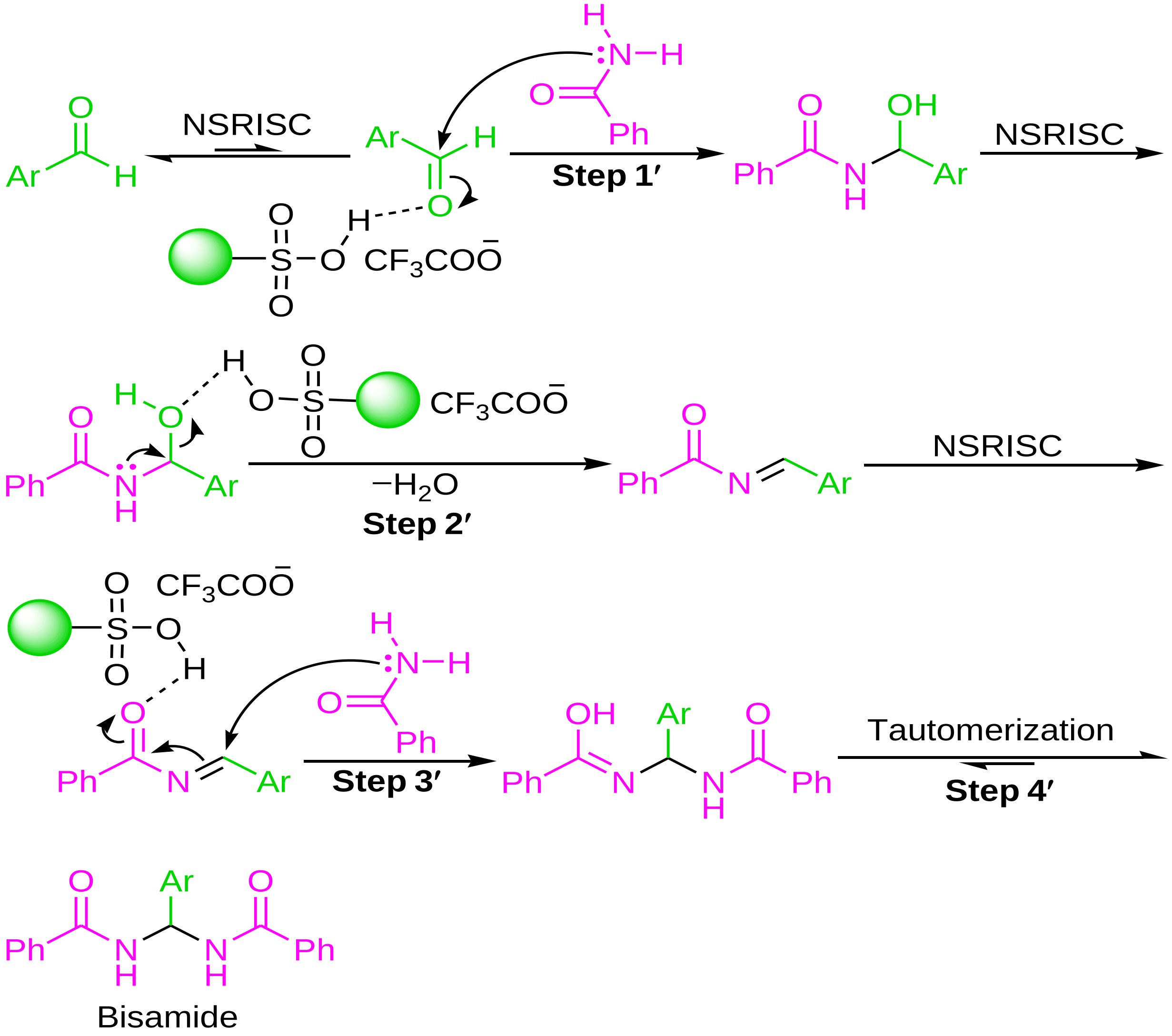
1c		30	86	264-265 (262-264) [49]
1d		30	97	229-234 (229-231) [50]
1e		30	88	247-249 (248-250) [51]
2a		15	95	224-226 (222-224) [52]
2b		15	97	256-258 (252-254) [45]
2c		30	94	233-235 (230-232) [41]

2d		30	93	226-228 (228-230) [53]
2e		30	87	264-266 (267-269) [54]

[a]Isolated yield.



Scheme 3. The proposed mechanism for the construction of bis-coumarins



Scheme 4. The proposed mechanism for the construction of *N*,*N*′-alkylidene bisamides

We compared NSRISC with some reported catalysts for the production of bis-coumarins and *N*,*N*′-alkylidene bisamides derivatives in **Tables 4** and **5**. NSRISC is superior than the others in terms of the reaction time, yield and/or the reaction conditions (solvent-free versus utilization of toxic organic solvents).

Table 4. Comparison of NSRISC with some reported catalysts for the production of bis-coumarins

Catalyst	Conditions	Time range (min)	Yield range (%)	Ref.
NSRISC	Solvent- free, 100 ºC	15-30	86-97	-
Sodium dodecyl sulfate	H_2O, 60 ºC	150-180	84-98	[26]
$RuCl_3.nH_2O$	H_2O, 80 ºC	25-60	75-95	[28]
I_2	H_2O, 100 ºC	20-34	91-99	[29]
Melamine trisulfonic acid	H_2O, 80 ºC	12-46	75-97	[30]
W-ZnO	H_2O, 80 ºC	15-120	90-98	[53]

Table 5. Comparing NSRISC with some reported catalysts for the construction of *N*,*N′*-alkylidene bisamides

Catalyst	Conditions	Time range (min)	Yield range (%)	Ref.
NSRISC	Solvent-free, 105 ºC	15-30	87-97	-
$NiFe_2O_4@SiO_2$-PPA	CH_3OH, reflux	40-130	52-93	[41]
$Ca_5(PO_4)_3(OH)$	CH_3CN, reflux	180	87-95	[42]
$H_{14}[NaP_5W_{29}MoO_{110}]$	CH_3OH, reflux	50-150	42-95	[45]
Nano-$[TSPSED][Cl]_2$	Solvent- free, 90 ºC	15-55	83-98	[54]
p-Toluene sulfonic acid	Solvent- free, 100 ºC	60	85-99	[56]

4. Conclusions

We have reported the construction and characterization of NSRISC; it can promote organic reactions which need acidic catalysts. Application of NSRISC to catalyze the construction of bis-coumarins and *N*,*N′*-alkylidene bisamides in this work is associated the advantages of high effectuality, high yields, short reaction times, solvent-free conditions, compatible with principles of green chemistry and easy procedures to purify the products.

Acknowledgements

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