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A green and eco-friendly method for the synthesis of xanthene derivatives using cellulose sulfuric acid under solvent-free conditions

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Abstract

A green and convenient method for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*i*]xanthene-8,13-diones and spiro[dibenzo[*a*,*i*]-xanthene-14,3'-indoline]-2',8,13-triones is described in the presence of a catalytic amount of cellulose sulfuric acid (CSA) as an efficient biopolymer-based catalyst under solvent-free conditions at 100 °C. The condensation reactions of *β*-naphtol, 2-hydroxynaphthalene-1,4-dione with aldehydes or isatins afforded the corresponding xanthenes in good to excellent yields. To the best of our knowledge, it is the first example of a multicomponent reaction to the synthesis of these compounds using cellulose sulfuric acid. The present approach offers several advantages such as shorter reaction times, simple work-up, excellent yields, non-toxicity of the catalyst, and solvent-free conditions. Moreover, cellulose sulfuric acid is successfully reused for four cycles without significant loss of activity.

Keywords: Xanthenes; cellulose sulfuric acid; 2-hydroxynaphthalene-1,4-dione; *β*-naphtol; solvent-free.

Introduction

Designing for more impressive processes which allow for the rapid generation of molecular complexity and variety from simple and readily accessible starting materials have attracted much attention of organic chemists [1]. Among them, multicomponent reactions (MCRs) are

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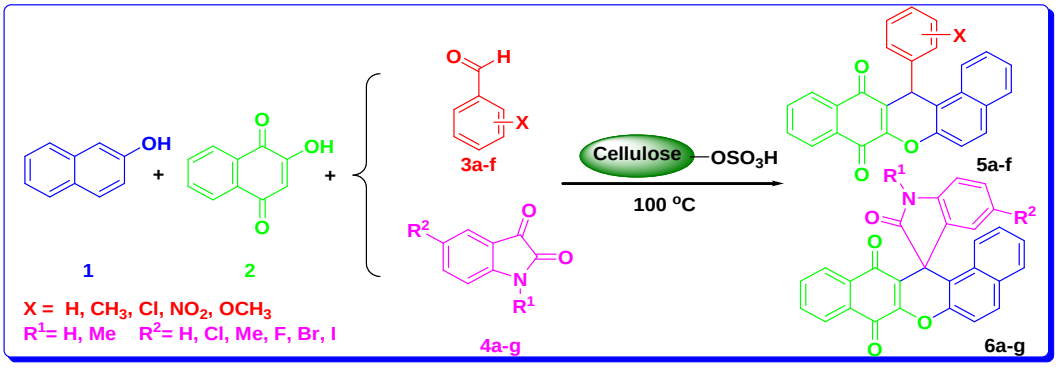
effictive methods in heterocyclic scaffolds for the formation of different chemical libraries of drug-like advanced compounds. In analogy to the convergent synthesis and in contrast to a divergent multi-step synthesis, MCRs are convergent. They allow the creation of several bonds in a single operation rather than multiple steps which minimize the tedious work-up procedures and environmental hazardous wastes. They also have considerable advantages in terms of user and environmental friendliness because of the step reduction and atom economy associated to their use [2]. The developing of new MCRs and improving the known MCRs are an area of considerable current interest in organic and medicinal chemistry [3].

Xanthenes and benzoxanthene derivatives are the parent skeleton found in a large number of naturally products as well as synthetic products possessing prominent positions in medicinal chemistry [4]. Because of their wide range of synthetic, industrial and pharmacological application, many methods for the preparation of xanthenes are reported in the literature [5]. Xanthene derivatives occupy an important position among different families of dyes, owing to a number of reasons related to their photochemical and photophysical properties [6]. Furthermore, xanthenes and benzoxanthenes have recently received great attention because of their wide range of therapeutic and biological properties, such as antibacterial [7], antiviral [8], and anti-inflammatory activities [9] as well as in photodynamic therapy [10] and for antagonism of the paralyzing action of zoxazolamine [11]. The other useful applications of these heterocycles are as leucodyes [12], in laser technologies [13] and in fluorescent materials for visualization of biomolecules [14]. The spirocyclic systems containing one carbon atom common to two rings are the core structure of many pharmacological agents and natural alkaloids [15]. Therefore, a number of methods have been reported for the preparation of spirooxindole fused heterocycles [16].

Recently, the emphasis of science and technology are shifting more towards sustainable resources and processes. In this regard, biopolymers are noteworthy candidates to explore for supported catalysis. Cellulose is one of the most abundant natural biopolymers in the world and has been widely studied during the past several decades because it is a biodegradable material and a renewable resource [17]. In the recent years, cellulose sulfuric acid has emerged as a promising biopolymeric solid-support acid catalyst for acid-catalyzed

reactions, such as the synthesis of aryl-14*H*-dibenzo[*a.j*]xanthenes [18], 1,4-dihydropyridines [19], quinoxaline [20], α-amino nitriles [17], Pechmann condensation [21], thiadiazolo benzimidazoles [22], imidazoazines [23], quinolines [24], 3,3'-indolyloxindoles [25], 3,4-dihydropyrimidine-2(1*H*)-ones [26], 2,4,5-triarylimidazoles [27], *β*-acetamido carbonyl derivatives [28], Knoevenagel condensation [29], oxazolines, imidazolines and thiazolines [30].

In continuation of our ongoing program in developing environmentally friendly methodologies for the preparation of heterocyclic compounds [31], herein we have reported a green and facile methodology for the synthesis of xanthene derivatives in the presence of CSA as an inexpensive and biodegradable solid acid catalysts at 100 °C (Scheme 1).



Scheme 1. Synthesis of xanthene derivatives in the presence of CSA

Experimental

General

All of the solvents and reagents were purchased from Fluka or Merck chemical companies. Melting points were measured with an Electrothermal apparatus and are uncorrected. IR spectra were obtained in KBr discs on a Shimadzu IR-470 spectrometer. ^{1}H NMR spectra were determined on a BRUKER DRX-400 AVANCE spectrometer at 400.13 MHz.

Procedure for the preparation of cellulose sulfuric acid

To a magnetically stirred mixture of cellulose (5.00 g, DEAE for column chromatography, Merck) in $CHCl_3$ (20 mL), chloro sulfonic acid (1.00 g, 9 mmol) was added drop wise at 0 °C during 2 h. After the addition was complete, the mixture was stirred for 2 h

until HCl was removed from reaction vessel. Then, the mixture was filtered and washed with methanol (30 mL) and dried at room temperature to obtain cellulose sulfuric acid as white powder (5.13 g) [17].

IR analysis of Catalyst

Figure 1 presents the FT-IR spectra of cellulose sulfuric acid. The broad band, at 3000-3600 cm^{-1}, can be typically seen in the spectra of catalyst due to OH stretching. The SO_2 asymmetric vibration is found to be at 1325 cm^{-1} as a medium band in the IR spectrum and the symmetric SO_2 stretching vibration appears around 1172 cm^{-1} in IR [32a]. By comparison with SOH bending frequencies in sulfuric acid and other sulfonic acids, the band at 1071 cm^{-1} is assigned to SOH bend [32b]. Also, appearing band at 1040 cm^{-1} can be assigned to the (C-O) group in cellulose.

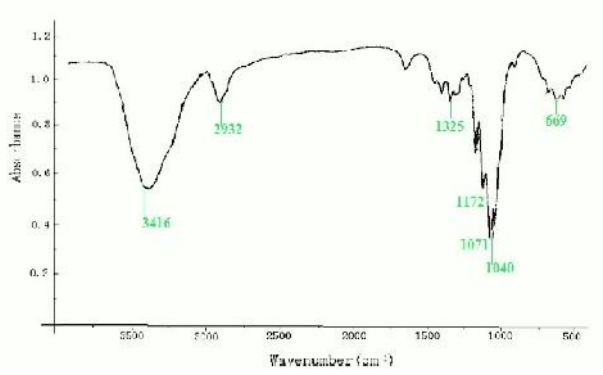


Figure 1. FT-IR spectra of CSA

General procedure for the synthesis of 14-aryl-14*H*-dibenzo[*a,i*]xanthene-8,13-dione (5a) and spiro[dibenzo[*a,i*]-xanthene-14,3'-indoline]-2',8,13-trione (6a)

A mixture of *β*-naphthol (1 mmol), 2-hydroxynaphthalene-1,4-dione (1 mmol), bezaldehyde or isatin (1 mmol), and cellulose sulfuric acid (0.07 g) was heated at 100 ^oC for an appropriate time. After completion of the reaction, as indicated by TLC, the reaction mixture was allowed to cool to room temperature. The solid obtained was filtered and washed with CH_2Cl_2 (10 mL) to separate the catalyst. Then, the filtrate's solvent was evaporated under reduced pressure and recrystallized from ethanol to afford the pure product **(5a)** or **(6a)**. The same procedure was also used for the other products listed in Table 2**.**

The selected spectral data

14-(2-Nitrophenyl)-14H-dibenzo[a,i]xanthene-8,13-dione (5f):

Yellow powder, Yield 93%; mp 298-300 °C; IR 3067, 1665, 1637, 1592, 1576, 1362, 1287, 1238, 1214 cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz): δ 8.24-8.23 (2H, m, 2CH), 8.13 (1H, d, *J* = 7.2 Hz, CH), 7.88-7.82 (3H, m, 3CH), 7.64-7.28 (6H, m, 6CH), 7.07-7.03 (2H, m, 2CH), 6.23 (1H, s, CH). ^{13}C NMR ($CDCl_3$, 100 MHz): δ 35.21, 115.18, 115.28, 116.95, 122.16, 123.25, 123.34, 124.91, 125.87,

127.83, 128.85, 129.42, 129.61, 130.10, 130.34, 130.45, 130.62, 131.67, 132.05, 135.05, 135.32, 145.07, 147.35, 148.57, 157.72, 178.04, 178.15. MS (EI, 70 eV) *m/z*: 433 (M^+, 20), 387 (17), 368 (45), 311 (35), 285 (21), 264 (33), 245 (49), 167 (22), 149 (58), 83 (65), 57 (100).

5'-Iodospiro[dibenzo[*a,i*]-xanthene-14,3'-indoline]-2',8,13-trione (6g):

Red powder; Yield 89%; mp 396-398 ^oC; IR 3281, 1803, 1676, 1631, 1560, 1503, 1356, 1297, 1246, 1120, 981, 813, 715 cm^{-1}; ^1H NMR (DMSO-d_6, 400 MHz): δ 11.05 (1H, s, CH), 8.12-7.98 (3H, m, 3CH), 7.82-7.69 (5H, m, 5CH), 7.43-7.38 (4H, m, 4CH), 6.67 (1H, s, CH). MS (EI, 70 eV) *m/z*: 555 (M^+, 19), 428 (12), 394 (23), 368 (70), 313 (45), 236 (56), 135 (25), 83 (74), 57 (100).

Due to very low solubility of the product **6g**, we cannot report the ^{13}C NMR data for this product.

Results and discussion

In this paper, the three component condensation of *β*-naphthol, 2-hydroxynaphthalene-1,4-dione, and aldehyde or isatin have been studied in the presence of a heterogeneous solid acid catalyst of CSA for the preparation of 14-aryl-14*H*-dibenzo[*a,i*]xanthene-8,13-diones and spiro[dibenzo[*a,i*]-xanthene-14,3'-indoline]-2',8,13-triones (Scheme 1). We first considered a reaction between *β*-naphthol **1**, 2-hydroxynaphthalene-1,4-dione **2**, and isatin **4a** by screening the reaction conditions. To determine the optimum conditions, we examined the effect of the amount of catalyst, the choice of solvent and the reaction temperature (Table 1). Initially, 0.04 g CSA was used to perform the reaction. But it requires slightly long reaction time. Therefore, the loading of the catalyst was gradually increased from 0.04 g to 0.07 g. It was found that 0.07 g of CSA is optimal to carry out the reactions in 50 min. The use of excess of catalyst did not alter either reaction time or yield of the product (Table 1, Entry 9). Subsequently, the effect of solvent in this reaction was studied. The experiment was performed in various solvents including water, ethanol, acetonitrile, dimethylformamide, dichloromethane, and a solvent-free system in the presence of 0.07 g CSA. The best result was obtained under solvent-free conditions. Thus, the use of 0.07 g CSA at 100 °C is ideal to achieve the desired product **6a** in good yields 96% (Table 1, Entry 8).

Under the optimized reaction conditions, the generality of the reaction was fully investigated with *β*-naphthol, 2-hydroxynaphthalene-1,4-dione, different aldehydes, or isatins to produce 14-aryl-14*H*-

dibenzo[*a,i*]xanthene-8,13-dione **5a-f** and spiro[dibenzo[*a,i*]-xanthene-14,3'-indoline]-2',8,13-trione derivatives **6a-g**. The results are summarized in Table 2. These results show the effects of electron-withdrawing and electron-donating groups on the time required and the yield of the reactions. It is noteworthy that the presence of electron-donating and electron-accepting as well as steric desired substituents on the reacting aldehydes do not affect the overal yield and rate of the reactions advisable. The results represented that the reactions were performed within 20-90 min of heating, and the favorable products were provided in good yields (Table 2). Short reaction times, recyclability of the catalyst with no loss in its activity, easy work-up procedures, the use of green solvent, the use of nontoxic, noncorrosive and an inexpensive solid acid catalyst are important features of this new protocol to prepare xanthene derivatives.

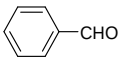
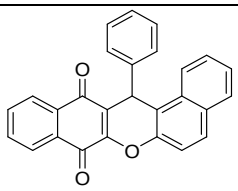
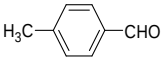
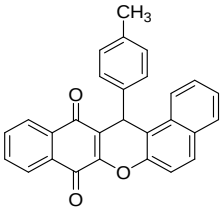
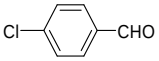
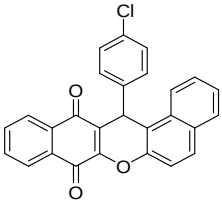
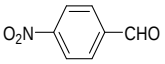
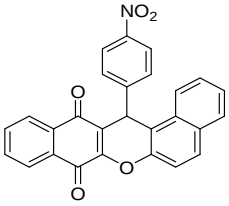
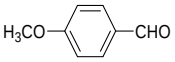
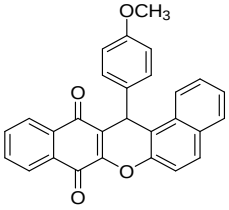
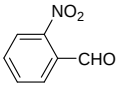
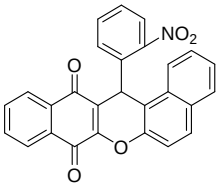
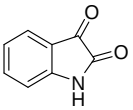
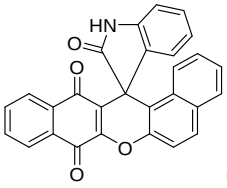
We also investigated the reusability of the catalyst. For this purpose, after completion of the model reaction, the cellulose sulfuric acid was separated from the reaction mixture by simple filtration, washing with CH_2Cl_2, and drying in a vacuum oven at 60 °C for 5 h prior to reuse in subsequent reactions. The recovered catalyst can be reused at least four additional times in subsequent reactions without significant loss in product yield (Figure 2).

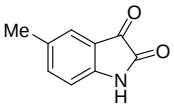
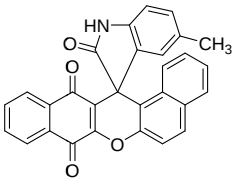
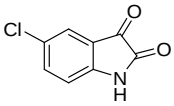
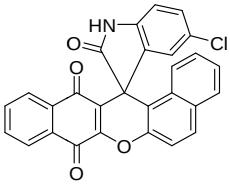
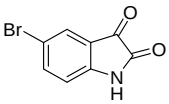
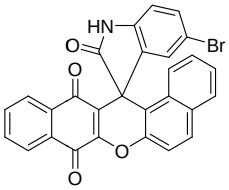
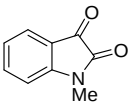
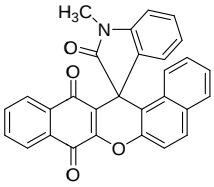
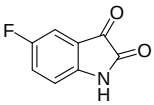
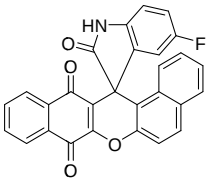
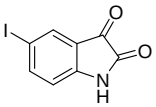
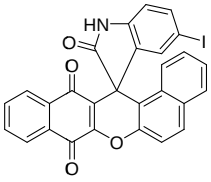
Table 1. Optimization of the reaction conditions for the synthesis of compound **6a**[a]

Entry	Catalyst	Conditions	Time (min)	Yield(%)[b]
1	-	Solvent-free/ 25 °C	600	-
2	-	Solvent-free/ 100 °C	300	-
3	CSA (0.07)	H_2O/ reflux	150	83
4	CSA (0.07)	EtOH/ reflux	180	79
5	CSA (0.07)	CH_3CN / reflux	240	65
6	CSA (0.07)	DMF / reflux	300	45
7	CSA (0.07)	CH_2Cl_2 / reflux	240	63
8	CSA (0.07)	Solvent-free/ 100 °C	50	96
9	CSA (0.08)	Solvent-free/ 100 °C	50	94
10	CSA (0.06)	Solvent-free/ 100 °C	50	89
11	CSA (0.05)	Solvent-free/ 100 °C	100	68
12	CSA (0.04)	Solvent-free/ 100 °C	120	56
13	$H_4SiW_{12}O_{40}$	Solvent-free/ 110 °C	60	89[c]
14	$[HMIm]HSO_4$	Solvent-free/ 100 °C	90	91[d]
15	CSA (0.07)	Solvent-free/ 25 °C	100	35
16	CSA (0.07)	Solvent-free/ 80 °C	70	88

[a]Reaction Condition: *β*-naphthol **1** (1 mmol), 2-hydroxynaphthalene-1,4-dione **2** (1 mmol), and isatin **4a** (1 mmol)
[b]Isolated yield
[c,d] Ref. 5a,b

Table 2. Synthesis of xanthene derivatives in the presence of CSA at 100 ˚C

Entry	Aldehyde or Isatin	Product[a]	Time (min)	Yield (%)[b]	Mp (°C) (Found)	Mp (°C) (Reported)
1	 **3a**	 **5a**	30	96	319-320	320 [16e]
2	 **3b**	 **5b**	20	94	255-257	256-258 [16e]
3	 **3c**	 **5c**	30	95	304-306	305-306 [16f]
4	 **3d**	 **5d**	20	96	331-333	332-333 [16f]
5	 **3e**	 **5e**	20	94	278-279	279-280 [16f]
6	 **3f**	 **5f**	30	93	298-300	-
7	 **4a**	 **6a**	50	96	364-365	365-366 [5b]

8	 **4b**	 **6b**	50	95	380-382	382-383 [5b]
9	 **4c**	 **6c**	60	94	391-393	392-393 [5b]
10	 **4d**	 **6d**	60	93	378-380	379-380 [5b]
11	 **4e**	 **6e**	90	91	386-388	388-389 [5b]
12	 **4f**	 **6f**	60	94	388-390	389-390 [5b]
13	 **4g**	 **6g**	60	89	396-398	-

[a]All the products were characterized by comparison of their spectroscopic and physical data with those reported in literature
[b]Isolated yield

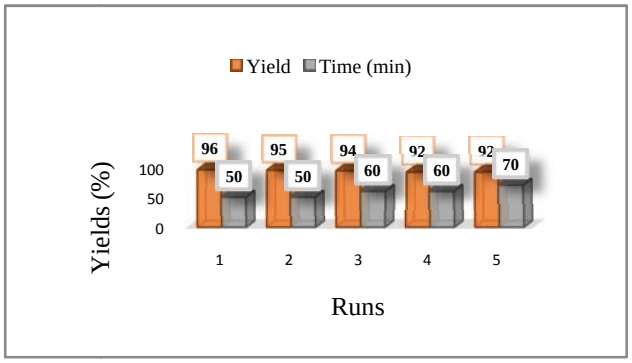
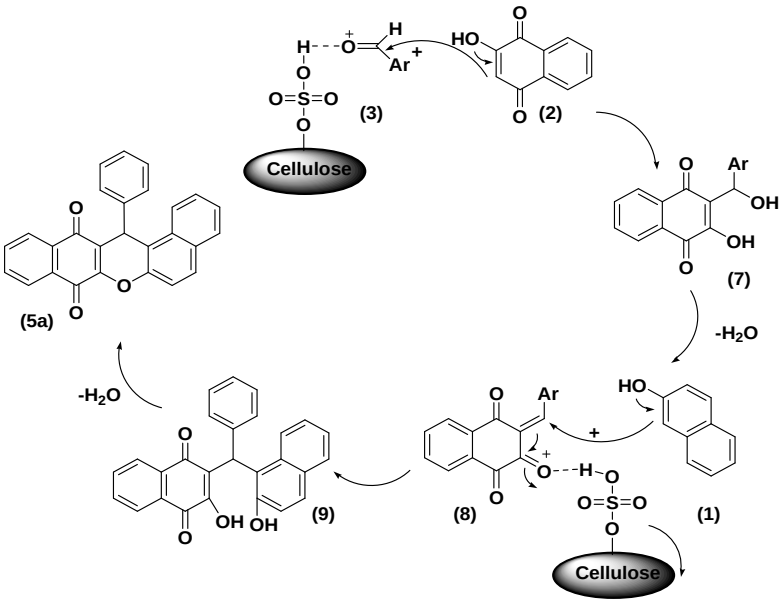


Figure 2. Reusability of the catalyst in product **6a**

A plausible mechanism for the formation of 14-aryl-14*H*-dibenzo[*a*,*i*]xanthene-8,13-diones is shown in Scheme 2. The dibenzo[*a*,*i*]xanthene synthesis presumably is initiated by nuleophilic addition of the substrate 2-hydroxynaphthalene-1,4-dione **2** on the reactant aldehyde **3** activated by CSA. The resulting adduct **7** undergoes dehydration to give the key enone intermediate **8** which is likely activated by CSA to follow a Michael type addition by the *β*-naphthol **1**. Cyclization of the intermediate **9** and subsequent loss of H_2O leads to the xanthene **5a**.



Scheme 2. A plausible mechanism for the synthesis of xanthene derivatives **5a-f** in the presence of CSA

Conclusion

In this paper, we have introduced a straightforward, green and eco-friendly method for the synthesis of xanthene derivatives in the presence of cellulose sulfuric acid under solvent-free conditions. Simple experimental procedure, excellent yields of the products, recyclability of the catalyst with no loss in its activity, and easy work-up procedure are the major advantages of the present method.

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