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Graphical Abstract

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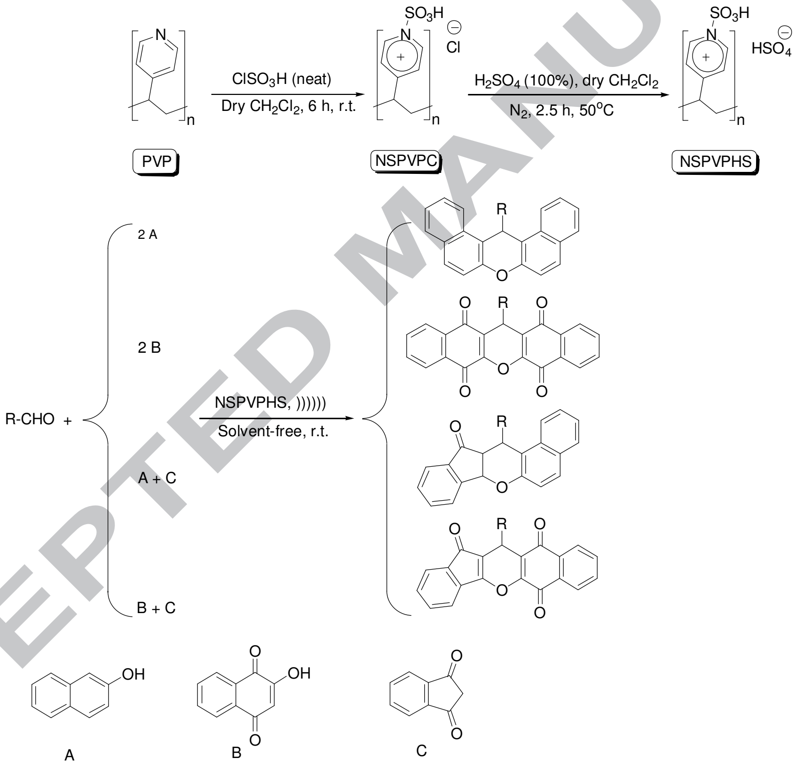

N-sulfonic acid poly(4-vinylpyridinium) hydrogen sulfate as an efficient and reusable solid acid catalyst for one-pot synthesis of xanthene derivatives in dry media under ultrasound irradiation

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ABSTRACT

N-sulfonic acid poly(4-vinylpyridinium) hydrogen sulfate catalyzed efficiently the synthesis of xanthene derivatives under ultrasonic irradiation at room temperature, which has prompted various concerns involving cost and environmental persistence. This methodology shows the effect of presence of anion hydrogen sulfate as an important and effective factor on the promotion of the one-pot muti-components and condensation reactions. The catalyst can be recovered by simple filtration and used for several times without a significant loss of catalytic activity.

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1. Introduction

Due to the spectroscopic properties, xanthene derivatives were used as dyes [1-3], in laser technologies [4], and in fluorescent materials for visualization of biomolecules [5]. Also a variety of natural and synthetic xanthene and benzoxanthene derivatives have the potential biological and pharmaceutical properties [6-11]. Because of these significant features there has been a continuous interest in the synthesis of these types of compounds and consequently numerous approaches have been reported for their synthesis [12-24]. The main synthetic method for the preparation of xanthenes is based on the three-component condensation in the presence of a *Brönsted* or *Lewis* acid. Even though various procedures were reported, some of them suffer from the disadvantages including low yields, prolonged reaction times, use of very expensive catalysts, the formation of by-products, use of an excess of reagents/catalysts, corrosion as well as waste acid pollution problems and use of toxic organic solvents. Therefore, there is still scope for development of a safer, more convenient and efficient method.

Ultrasound as an eco-environmental technology in green chemistry has advantageous over the traditional thermal methods as enhanced reaction rates, formation of purer products, improved yields, suppression of side products, increased selectivities, easier experimental procedures, and use of milder conditions [25-28]. A survey of the literature reveales that a number of researchers have demonstrated the efficacy of sonication under solvent-free conditions but at least one of the phases of the reaction mixture was a liquid [29-31]. In addition, the use of heterogeneous catalysts in dry media can contribute to improve the production process, eliminating or transforming unwanted and/or toxic byproducts avoiding the need for tedious separation.

Supported reagents have been the subject of increasing levels of attention in organic chemistry [32,33]. They can be readily recovered from the reaction mixture and reused. Among the various supports available for synthetic reagents, poly(4-vinylpyridine) cross-link with divinylbenzen P(4-VP) is one of the most commonly used heterogeneous polymeric supports in organic chemistry. Recently, it was used as a support for the preparation of solid acid catalysts [34-40].

2. Experimental Section

2.1. Materials

Unless specified, all chemicals were analytical grade and purchased from Merck, Aldrich and Fluka Chemical Companies and used without further purification. Products were characterized by their physical constant and comparison with authentic samples. The purity determination of the substrates and reaction monitoring were accompanied by TLC using silica gel SIL G/UV 254 plates.

2.2. Instrumentation

The purity determination of the products was accomplished by TLC and GC-MS on an Agilent GC-Mass-6890 instrument under 70 eV conditions. The FT-IR spectra were recorded on a Perkin Elmer 781 Spectrophotometer using KBr pellets for solid and neat for liquid samples in the range of 4000-400 cm^{-1}. In all the cases the ^{1}H and ^{13}C NMR spectra were recorded with Bruker Avance 300 MHz instrument. All chemical shifts are quoted in parts per million (ppm) relative to TMS using deuterated solvent. Microanalyses were performed on a Perkin- Elmer 240-B microanalyzer. Melting points were recorded on a Büchi B-545 apparatus in open capillary tubes.

Sonication was performed in Bandelin Sonorex reactor with a frequency of 35 kHz and a nominal power of 200 W, built-in heating, 30-80 ºC thermostatically adjustable. The reaction vessel placed inside the ultrasonic bath containing water.

2.3. A General procedure for the synthesis of xanthene derivatives by grinding and heating method

A mixture of aldehyde (1 mmol) and the desired substrates {2-naphthol (2 mmol), 2-hydroxynaphthalene-1,4-dione (2 mmol), mixture of 2-naphthol (1 mmol) and indane-1,3-dione(1 mmol) or 2-hydroxynaphthalene-1,4-dione (1 mmol) and indane-1,3-dione(1 mmol); according to Scheme 1} was heated and mixed in the presence of NSPVPHS (10 mg) [40] at 60 °C by grinding under solvent-free conditions. The progress of the reaction was monitored by TLC. After completion of the reaction, the product was extracted with Et_2O (3 × 5 mL) and the catalyst was recovered and was dried at 65°C under vacuum to remove moisture, and then was reused. The combined ethereal solution was concentrated under vacuum to afford the crude product. The highly pure product was obtained by recrystallization from EtOH. The products were characterized by IR, NMR spectroscopic data and elemental analysis. The melting point of known compounds is compared with reported values [36-38 and 41-46].

2.4. A General procedure for the synthesis of xanthene derivatives by sonochemical method

A mixture of aldehyde (1 mmol) and the desired substrates {2-naphthol (2 mmol), 2-hydroxynaphthalene-1,4-dione (2 mmol), mixture of 2-naphthol (1 mmol) and indane-1,3-dione (1 mmol) or 2-hydroxynaphthalene-1,4-dione (1 mmol) and indane-1,3-dione (1 mmol); according to Scheme 1} were mixed in the presence of NSPVPHS (10 mg) at room temperature under ultrasound irradiation. The progress of the reaction was monitored by TLC. After completion of the reaction, the product was extracted with Et_2O (3 × 5 mL) and the catalyst was recovered and was dried at 65°C under vacuum to remove moisture, and then was reused. The combined ethereal solution was concentrated under vacuum to afford the crude product. The highly pure product was obtained by recrystallization from EtOH.

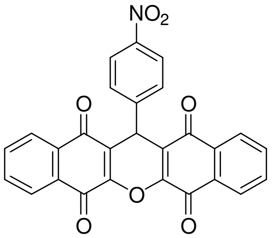
2.5. Hydrolysis of catalyst in aqueous media

The reaction of NSPVPHS with water is important because water was produced as a by-product through the condensation reaction and also moisture was observed about 12% due to absorption of physisorbed water molecules before drying. After drying, the content of water of NSPVPHS was 1.2% using Karl–Fischer titration method. On the other hand, analysis showed one equivalent point for neutralization in curve of titration, therefore it seems that the slow hydrolysis of catalyst in aqueous solution may be presented by the following equation (Scheme 2).

2.6. Acivation procedure for the recycled catalyst

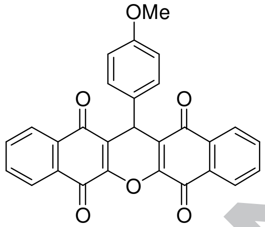
The recovered catalyst collected from different experiments was washed successively with Et_2O and acetone. Then catalyst was dried in vacuum at room temperature and it was stirred with chlorosulfonic acid and then sulfuric acid in dry CH_2Cl_2 to recover its activity.

2.7. Spectral data for new compounds



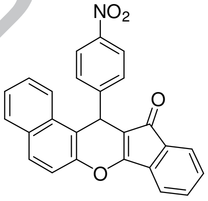
13-(4-Nitrophenyl)-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraone

Orange powder, m.p. >320 °C; IR (KBr) ν_{max} = 3030, 1660,1600 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-*d6*): δ = 5.45 (s, 1H, CH), 7.14–8.16 (m, 12H, ArH) ppm; MS (m/z, %): 463 (M$^+$, 25), 418 (M$^+$-NO$_2$, 40), 313 (M$^+$- NO$_2$-C$_6$H$_4$-CHO, 100); Anal. Calcd (%) for $C_{27}H_{13}NO_7$: C, 69.98; H, 2.83; N, 3.02. Found: C, 69.93; H, 2.80; N, 3.06.



13-(4-methoxyphenyl)-5H-dibenzo[b,i]xanthene-5,7,12,14(13H)-tetraone

Brown-redish powder, m.p. >320 °C; IR (KBr) ν_{max} = 3080, 1660, 1605, 1230, 1020 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-*d6*): δ = 3.81 (s, 3H, CH$_3$), 5.11 (s, 1H, CH), 7.15-7.67 (m, 10H, ArH), 8.02-8.10 (m, 2H, ArH) ppm; MS (m/z, %): 448 (M$^+$, 35), 420 (M$^+$-CHO, 100), 313 (M$^+$-MeO-C$_6$H$_4$-CHO, 65); Anal. Calcd (%) for $C_{28}H_{16}O_6$: C, 75.00; H, 3.57. Found: C, 74.92; H, 3.52.



13-(4-Nitrophenyl)-indeno[1,2-b]naphtho[1,2-e]pyran-12(13H)-one

Yellow solid, mp 262-264 °C. IR (KBr) ν_{max} = 3035, 1665,1608 cm^{-1}; ^{1}H NMR (300 MHz, DMSO-*d6*): δ = 5.57 (s, 1H, CH), 7.31-7.87 (m, 11H, ArH), 7.93-8.07 (m, 3H, ArH) ppm; MS (m/z, %): 405 (M$^+$, 30), 360 (M$^+$-NO$_2$, 45), 255 (M$^+$- NO$_2$-C$_6$H$_4$-CHO, 100); Anal. calcd for $C_{26}H_{15}NO_4$: C, 77.03; H, 3.73; N, 3.46. found: C, 76.88; H, 3.69; N, 3.52.

3. Results and discussion

Part of our research is aiming to show the potential ability of the ultrasound irradiation as a green source of energy for organic synthesis under solvent-free conditions [25-28]. Poly(4-vinylpyridinium) hydrogen sulfate was prepared and used in the variety of organic transformations [36 and 38]. Very recently, The synthesis of *N*-sulfonic acid poly(4-vinylpyridinium) chloride [NSPVPC] and its applications in the chemoselective 1,1-diacetate protection and deprotection of aldehydes [34] and *N*-Boc protection of amines [35] was described. Herein, and in continuation of these studies, we wish to report the application of another analogue of Solid Acid Functionalized Poly(4-vinylpyridine) [SAFPVP], namely, *N*-sulfonic acid poly(4-vinylpyridinium) hydrogen sulfate (NSPVPHS) [40] as a reusable heterogeneous catalyst in the promotion of the synthesis of xanthene derivatives in dry media at significantly milder reaction conditions than those known in literature (Scheme 1). For that purpose, eco-efficient methodology as ultrasound irradiation that allows decreasing the amount of waste and a better use of energy is proposed.

The reaction of 4-chloro-benzaldehyde (1 mmol) with 2-naphthol (A, 2 mmol) was taken as model and treated with NSPVPHS (10 mg) under different conditions including various solvents such as phMe, MeCN, EtOH, Et_2O, THF, DCM, and water at room temperature or reflux conditions; and also the model reaction was done at different temperatures in the absence of solvent (Scheme 3). The reaction was not completed in the presence of solvents at reflux after 2 h and two products (I) and (II) were observed (IR and GCMS) and the yield of the product (II) was low (32%). The significant increase was not observed in the yield of product (II) with longer reaction times. The reaction was completed after 15 minutes under solvent-free conditions at 60 °C and 14-(4-chlorophenyl)-14*H*-dibenzo[*a,j*]xanthene was obtained with yield 94%. The better catalytic activity of NSPVPHS under neat conditions compared to that in solvents may be explained due to the better electrostatic effect of the ionic aggregates in the solid state to activate the substrates. The poor results obtained in solvents may be reasonably included due to the competitive interaction of the solvent molecules with the active sites of the catalyst and also the decreased diffusion of the substrates in the presence of the solvent.

In order to optimization, the model reaction was carried out in the presence of different amounts of NSPVPHS at 60 °C under grinding and solvent-free conditions. The results showed that the reaction was not possible in the absence of the catalyst. Increasing the amount of solid acid catalyst to 20 mg showed no significantly improvement in the yield (95%) and only the reaction time was decreased slightly (12 min). It should be noted that when the reaction proceeded in solvent the reaction time became longer.

To survey the effect of ultrasonic irradiation, the model reaction was performed using NSPVPHS at room temperature under ultrasonic irradiation. In general, ultrasound has chemical and mechanical effects. The majority of the advantages of the uses of ultrasound in the processing of liquids can be directly related to the physical effects of acoustic cavitation: the formation, growth and implosive collapse of bubbles in liquids irradiated with high-intensity ultrasound [47]. Since this work is a heterogeneous catalytic system in dry media, it seems that the main effect of ultrasound can be due to its mechanical effect. The mechanical effects of ultrasound allows penetration of reactants and/or release of materials from surface, degradation of large solid particles due to shear forces induced by shock waves and microstreaming leads to reduction of particle size and increase of surface area and accelerated motion of suspended particles leads to better mass transfer [48]. Frequencies below 50 kHz are generally preferred for the heterogeneous systems due to the more intense mechanical effects [49]; hence, we selected 35 kHz for maximum sonication. Control experiments showed the effect of a possible simultaneous thermal activation. 14-(4-Chlorophenyl)-14*H*-dibenzo[*a,j*]xanthene was obtained in the presence of NSPVPHS (10 mg) at room temperature and 60 ºC under grinding method in 28% and 94% yield, respectively, after 15 min (Table 1, entry 2). The reaction was subjected to ultrasonic irradiation initially for 2 min, but no product was detected (TLC monitoring), sonication was then continued, product formation was noticed, and after 5 min the percentage of the product formation was found 95% yield. Continuation of sonication for 15 min, did not affect the yield (Table 1, entry 2). It was apparent that the ultrasound irradiation could accelerate the reaction. The need of just one third of reaction time (5 min vs. 15 min) and the lower temperature (ca. 25 ℃ vs. 60 ℃) showed that ultrasonic chemical activation clearly affected the course of the reaction increasing its energy efficiency.

For exploring of the scope and efficiency of the NSPVPHS, 2-naphthol (A), 2-hydroxynaphthalene-1,4-dione (B) and indane-1,3-dione (C) were condensed with a variety of aldehydes under the optimized reaction conditions. The results are summarized in Table 1. The results showed that presence of the electron-withdrawing and electron-donating substituents on the aromatic ring of aldehydes have influence on the reaction times and the yields. With electron releasing groups (-OMe) in the *para*-position of the aromatic aldehydes, rate and yield of the reaction was decreased due to the electrophilic character of the carbonyl carbon became less for the electrophilic attack (Table 1, entry 4). In the presence of electron-withdrawing groups (-NO_2) in the *para*-position, electrophicity of the carbonyl carbon is enhancing (Table 1, entry 5). The presence of a –NO_2 group in the *ortho* position decreased both the rate and the yield of 14-(2-nitrophenyl)-14*H*-dibenzo [*a,j*]xanthene. It seems be due to intramolecular interaction and steric interference (Table 1, entry 6). Moreover, the presence of halogen on the aromatic ring of the aldehydes had a negligible effect on the reaction results (Table 1, entries 2,3). After the successful synthesis of the 14-aryl-14*H*-dibenzo[*a,j*]xanthenes, we decided to explore the synthesis of 13-aryl-5*H*-dibenzo[*b,i*]xanthene-5,7,12,14(13*H*)-tetraone, 13-aryl-indeno[*1,2-b*]naphtho[*1,2-e*]pyran-12(13*H*)-one and 12-aryl-12*H*-indeno[*1,2-b*]naphtho[*3,2-e*]pyran-5,11,13-trione derivatives using NSPVPHS as a versatile solid acid catalyst under similar conditions. When 2-hydroxynaphthalene-1,4-dione (B) was applied in the reaction, the desired xanthenes were obtained in short reaction time and high yields (Table 1, entries 8-13).

A search of the literature indicated that only few methods were available for the synthesis of indeno[*1,2-b*]naphtho[*e*]pyrans. It was possible to prepare 13-aryl-indeno[1,2-*b*]-naphtha[1,2-e]pyran-12(13*H*)-ones employing silica chloride [44a], sulfamic acid [44b], ionic liquids [45] and poly(4-vinylpyridinium) hydrogen sulfate [46] as a catalyst under thermal solvent-free conditions. However, there were several limitations to these procedures, such as high temperature, unsatisfactory yields and long reaction time.

In addition, synthesis of 12-aryl-12*H*-indeno[1,2-*b*]naphtho[3,2-*e*]pyran-5,11,13-triones by the three component reaction of 2-hydroxynaphthalene-1,4-dione, aldehydes, and 2*H*-indene-1,3-dione under thermal solvent-free conditions in the presence of poly(4-vinylpyridinium) hydrogen sulfate as a soild acid [38] and acidic ionic liquids was reported [45].

Interestingly, ultrasound irradiation of a mixture of 2-naphthol (1mmol) and indane-1,3-dione (1 mmol) (A+C) or 2-hydroxynaphthalene-1,4-dione (1 mmol) and indane-1,3-dione (1 mmol) (B+C) in presence of NSPVPHS at room temperature yielded the asymmetric xanthenes (Table 1, entries 14-18 and 19-24). Therefore both symmetric and asymmetric derivatives of xanthenes can be produced using this procedure (Scheme 1).

On the other hand, when comparing the results obtained using conventional heating method in the absence of solvent, with those obtained by means of the ultrasonic method, we can conclude that both methods afford the respective xanthenes in a shorter time, with good yields and with minimal environmental impact. In both cases the work-up method is relatively simple. In addition, ultrasonic equipments are common in organic synthetic laboratories.

In order to assess the efficiency of the present method in comparison with the reported methods for the preparation of xanthene derivatives, compound 14-(phenyl)-14*H*-dibenzo[*a,j*] xanthene was synthesized applying the reported methods (Table 2). Compared with data presented in the literature (Table 2), the systems reported here demand milder operation conditions (temperature and time) and simpler experimental conditions (dry media) to reach much higher conversion for 14-(phenyl)-14*H*-dibenzo[*a,j*] xanthene. Madhav et al. run this reaction at high temeprature (110-115 ºC) reaching of 91% and 81% yield in 1.5 h using sulfuric acid and cellulose sulfuric acid, respectively, as catalyst (Table 2) [48]. In this work, the reaction was performed at room temperature and 60 ºC, with a heterogeneous catalyst, in dry media needing significantly less time: 5-15 min vs. 90 min. These changes lead to remarkable process intensification through a much more efficient use of energy and materials. In addition to use milder reaction conditions, room temperature, solvent-free and dry media, we report an economic heterogeneous catalyst that can be easily prepared.

To examine the feasibility of a relatively large-scale synthesis, a mixture containing 10 mmol of each of the reactants was subjected to the reaction conditions for 20 min leading to isolation of more than 90% of 14-(phenyl)-14*H*-dibenzo[*a,j*] xanthene.

The probable mechanism of the reaction is not fully established, but the formation of dibenzoxanthenes could be described by a reaction sequence similar to the literature report [54]. NSPVPHS activates the aldehyde towards electrophilic attack of 2-naphthol (A), 2-hydroxynaphthalene-1,4-dione (B). Such activation through acid sites of catalyst, as depicted in the Scheme 4, along with simultaneous sonication can provide the required activation energy for the reactants to overcome the transition state barrier at room temperature, giving rise to Knoevenagel intermediate in shorter times (1 or 2 in Scheme 4). The reaction then is followed by nucleophilic addition of the second of these fragments onto the Knoevenagel intermediate, which undergoes intramoleular cyclization to produce the xanthene derivatives. Also under ultrasound irradiation, the increase in reaction rate might be due to an increase in the rate of the breaking of C-OH and C-H bonds and elimination of H_2O that is critical in this type of multi-component reactions.

The recycling of the catalyst is a valuable advantage of our method. The excellent yields was obtained for the synthesis of 14-(4-chlorophenyl)-14*H*-dibenzo[*a,j*]xanthenes in the presence of recycled catalyst even after five cycles. It implied that NSPVPHS can be reused without significant loss of activity (Fig. 1). In the other process, after completion of the reaction, the product was separated and new substrates were added to the reaction vessel. The progress of the reaction was monitored by TLC at optimized reaction conditions and this process was repeated for five runs. The results showed that the activity of catalyst was not decreased and the yields ranged from 95% to 92% in an average reaction time approximately 5 min.

The sulfuric acid leakage from the matrix was studied in the optimized reaction conditions. Any measurable leakage was not observed under the optimized conditions. An activity loss of 3% was observed within the 5th use (in this case, a small amount of sulfuric acid leakage was detected in the reaction medium and wash solutions). However, after 10 cycle repeated uses, the catalyst retained about 92% of its initial activity (data not shown), attributed to strong interactions between the pyridyl units of poly(4-vinylpyridine) and acid sites. When the yield drops, the catalyst can be activated to recover its activity by simple activation procedure.

4. Conclusions

This work presents the research to intensify the synthesis of xanthene derivatives using a catalytic amount of NSPVPHS solid acid in dry media under ultrasound irradiation, which results in a more efficient use of energy and materials (no solvent, heterogeneous catalyst). Thus, this work offers a practical alternative to conventional heating in traditional catalysis and brings important improvements in the search of new routes to synthesis of xanthene and its derivatives in high added value chemicals and less environmental impact. Compared with traditional methods, the present methodology has exhibited several advantages such as: the accelerated reaction rate and excellent yields, minimizing the energy consumption, no side reactions, ease of preparation and handling of the catalyst, cost efficiency (use of inexpensive catalyst with lower loading) and simple experimental procedure, mild conditions. Recovery and reuse of NSPVPHS is also satisfactory, which demonstrates the green aspect of the methodology.

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Table captions

Table 1. Synthesis of the xanthenes derivatives are catalyzed in the presence of NSPVPHS under grinding and solvent-free conditions.

Table 2. Comparison of our results with the results obtained by other groups in the synthesis of 14-(phenyl)-14*H*-dibenzo[*a,j*] xanthene.

Table 1. Synthesis of the xanthenes derivatives are catalyzed in the presence of NSPVPHS.[a]

Entry	Aldehyde	Grinding and heating method[b]		Ultrasound method[c]		Melting point (°C)	
		Time (min)	Yield (%)[d]	Time (min)	Yield (%)[d]	Found	Reported [Ref.]
1	C_6H_5-CHO	15	95	5	97	185-186	183-185 [36,41]
2	4-Cl-C_6H_4-CHO	15	94	5	95	293-295	290-292 [36,41]
3	4-Br-C_6H_4-CHO	15	93	5	96	297-298	296-298 [36,41]
4	4-MeO-C_6H_4-CHO	20	88	8	90	206-208	203-206 [36,41]
5	4-NO_2-C_6H_4-CHO	10	92	8	95	310-312	312-313 [36,41]
6	2-NO_2-C_6H_4-CHO	15	86	5	88	296-298	293 [36,41]
7	Furfural	15	89	5	91	202-204	198-200 [37]
8	C_6H_5-CHO	22	92	10	95	301-304	305-307 [42,43]
9	4-Cl-C_6H_4-CHO	15	95	5	95	>320	330-332 [42,43]
10	4-Me-C_6H_4-CHO	22	94	10	95	301-303	304-307 [42,43]
11	4-Br-C_6H_4-CHO	15	90	5	93	>320	333-335 [42,43]
12	4-MeO-C_6H_4-CHO	18	88	8	90	>320	-
13	4-NO_2-C_6H_4-CHO	12	92	6	95	>320	-
14	C_6H_5-CHO	15	88	5	90	208-210	202-203 [44]
15	4-Cl-C_6H_4-CHO	18	91	8	94	229-231	225-226 [44]
16	4-Me-C_6H_4-CHO	15	91	5	94	195-197	192-193 [44]
17	4-MeO-C_6H_4-CHO	20	85	8	89	230-232	225-226 [44]
18	4-NO_2-C_6H_4-CHO	10	93	5	95	262-264	-
19	C_6H_5-CHO	15	90	5	92	311-314	311-314 [38]
20	4-Cl-C_6H_4-CHO	15	91	5	94	230-232	>330 [38]
21	4-Br-C_6H_4-CHO	15	90	5	92	>320	>330 [38]
22	4-Me-C_6H_4-CHO	18	88	8	91	198-200	314-316 [38]
23	4-MeO-C_6H_4-CHO	25	78	12	88	311-313	309-311 [38]
24	4-NO_2-C_6H_4-CHO	12	94	5	95	>320	>330 [38]

[a] Products were characterized by ^{1}H NMR, IR and melting point and also by comparison with the reported in literature data.

[b] Reaction conditions: aldehyde, 1.0 mmol; substrate {2-naphthol (2 mmol), 2-hydroxynaphthalene-1,4-dione (2 mmol), mixture of 2-naphthol (1 mmol) and indane-1,3-dione(1 mmol) or 2-hydroxynaphthalene-1,4-dione (1 mmol) and indane-1,3-dione(1 mmol); according to Scheme 1}; NSPVPHS, 10 mg; 60 °C, grinding under solvent-free conditions.

[c] Reaction conditions: aldehyde, 1.0 mmol; substrate {2-naphthol (2 mmol), 2-hydroxynaphthalene-1,4-dione (2 mmol), mixture of 2-naphthol (1 mmol) and indane-1,3-dione(1 mmol) or 2-hydroxynaphthalene-1,4-dione (1 mmol) and indane-1,3-dione(1 mmol); according to Scheme 1}; NSPVPHS, 10 mg; room temperature and under ultrasound irradiation.

[d] Isolated yields.

Table 2. Comparison of our results with the results obtained by other groups in the synthesis of 14-(phenyl)-14*H*-dibenzo[*a,j*] xanthene.

Entry	Catalyst	Amount of catalyst (mg)	Temp. (°C)	Time (h)	Yield (%)[a]	Ref.
1	*p*-TSA	17.2	125	4	89	14
2	Sulfamic acid	9.7	125	8	93	24
3	Poly(4-vinylpyridinium) hydrogen sulfate	10	100	55 min	94	36
4	Succinimide-*N*-sulfonic acid	10	80	35 min	94	38
5	Sulfuric acid	10	110-115[b]	1.5	91	50
6	Cellulose sulfuric acid	80	110-115	1.5	81	50
7	Montmorillonitr K10	300	120	3	75	51
8	Amberlyst-15	10	125	2	94	52
9	Silica sulfuric acid	80	110-115	1.5	89	53
10	Dowex-50W	100	100	1.5	78	54
11	NSPVPHS	10	60	15 min	94	This work
12	NSPVPHS	10	Utrasonic method at r.t.	5 min	95	This work

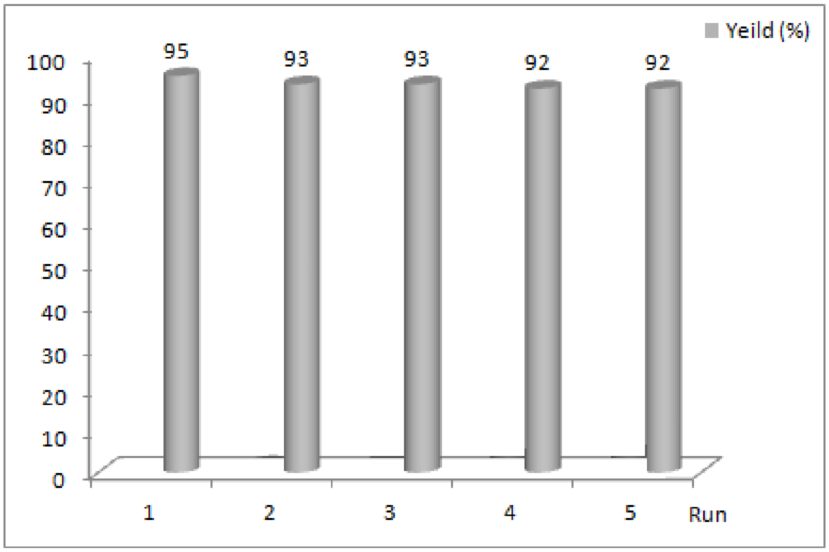
[a] Isolated yields.

[b] Solvent: acetic acid.

Figure captions

Fig. 1. Synthesis of 14-(4-chlorophenyl)-14*H*-dibenzo[*a*,*j*]xanthenes under ultrasound irradiation in presence of recycled NSPVPHS within 5 min under ultrasound irradiation.

Fig. 1. Synthesis of 14-(4-chlorophenyl)-14*H*-dibenzo[*a*,*j*]xanthenes under ultrasound irradiation in presence of recycled NSPVPHS within 5 min under ultrasound irradiation.



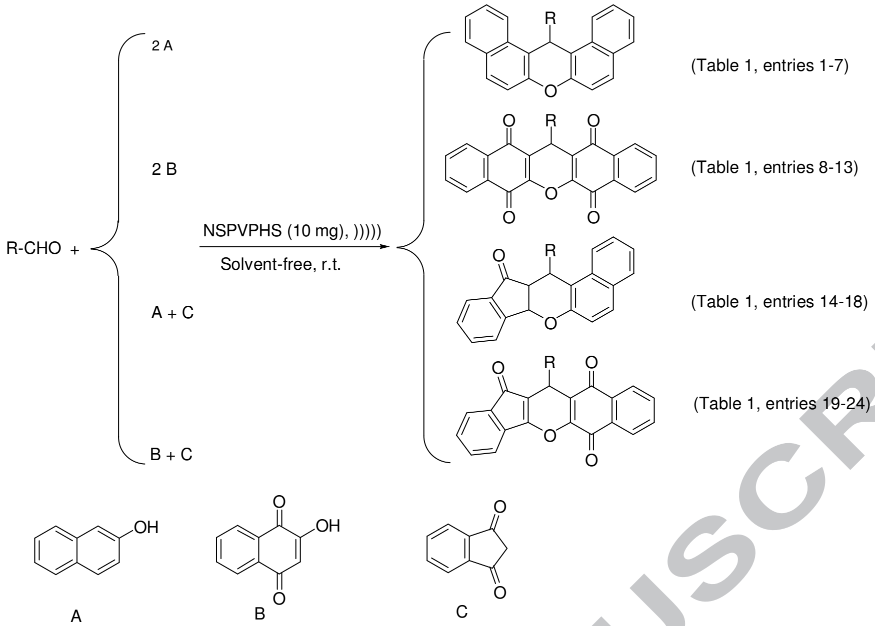
Scheme captions

Scheme 1. NSPVPHS catalyzed synthesis of xanthenes under grinding and solvent-free conditions.

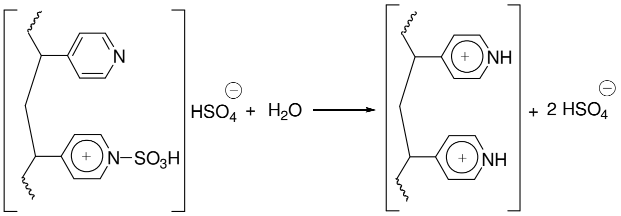
Scheme 2. The proposed equation for the slow hydrolysis of catalyst in aqueous media.

Scheme 3. The Elucidation of catalytic activity of *N*-sulfonic acid poly(4-vinylpyridinium) hydrogen sulfate (NSPVPHS).

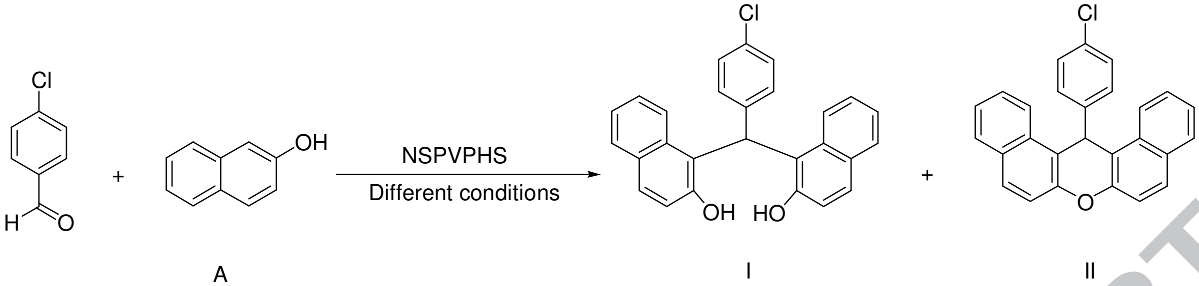
Scheme 4. A plausible mechanism for synthesis of xanthene derivatives in the presence of NSPVPHS under solvent free conditions.



Scheme 1. NSPVPHS catalyzed synthesis of xanthenes under grinding and solvent-free conditions.

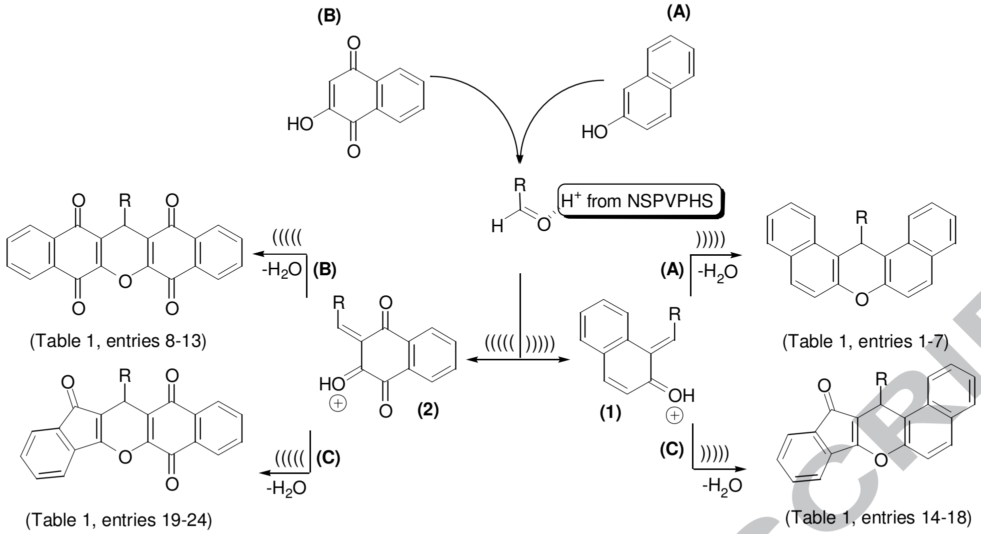


Scheme 2. The proposed equation for the slow hydrolysis of catalyst in aqueous media.



A I II

Scheme 3. The Elucidation of catalytic activity of *N*-sulfonic acid poly(4-vinylpyridinium) hydrogen sulfate (NSPVPHS).



Scheme 4. A plausible mechanism for synthesis of xanthene derivatives in the presence of NSPVPHS under solvent free conditions.

Highlights

- Introducing new solid acid catalyst for organic transformations
- Showing the important supporting role of anion hydrogen sulfate on selectivity of the products of xanthene derivatvies
- Application of ultrasonic method as a green source of energy
- Generality of the method, high yields and high reaction rates
- Recoverability and reusability solid acid catalyst