

# An efficient, high yielding, and eco-friendly method for the synthesis of 14-aryl- or 14-alkyl-14*H*-dibenzo[*a,j*]xanthenes using polyvinylsulfonic acid as a recyclable Brønsted acid catalyst

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**Abstract** Aryl or alkyl-14*H*-dibenzo[*a,j*]xanthene derivatives were synthesized efficiently by the reaction of 2-naphthol and aromatic or aliphatic aldehydes in the presence of polyvinylsulfonic acid (PVSA) as a reusable Brønsted acid catalyst under aqueous conditions at 90 °C. This reaction was studied under different conditions, and several solvents were examined. In terms of reaction yield and time, water was found to be the optimum solvent. The catalytic performance of PVSA was then compared with various acidic catalysts under optimized reaction conditions. The catalyst is well characterized using IR and DSC techniques.

**Keywords** Condensation · Heterocycles · Polyvinylsulfonic acid · Brønsted acid catalyst · Functional polymers

## Introduction

In recent years, there has been growing interest in the catalytic application of functional polymers in organic synthesis. Many typical acid- or base-catalyzed reactions using functional polymers having acidic or basic properties as catalysts, such as polyanilines [1–3], poly(vinylamine) and poly(allylamine) [4], polyacrylamide [5], polyvinylpyridine [6], polyvinylpyrrolidone [7], and cation and anion exchange resins [8–11], have been investigated so far. The most important advantage in using a functionalized polymer as a

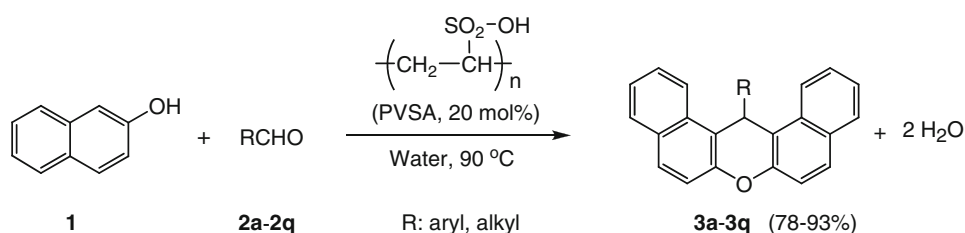
catalyst is the simplification of product workup, separation, and isolation. In the case of linear polymers, techniques such as precipitation, sedimentation, and ultrafiltration can be employed for isolation and washing, although these are by no means as convenient and readily available in all laboratories [12]. However, these solid catalysts suffer from disadvantages such as undesirable by-product formation because of their very high acidity or basicity, and often require a high degree of agitation, which causes rupture of the polymeric matrix. Hence, the development of a homogeneous and active acid functionalized polymer catalyst in organic transformations seems highly desirable.

Performing organic reactions in aqueous media without the use of harmful organic solvents has attracted much attention in recent years, because water would be considerably safe, non-toxic, environmentally friendly, and cheap compared to organic solvents. Moreover, when a water soluble catalyst is used, the insoluble products can be separated by simple filtration, and the catalyst system can be recycled. Therefore, development of a polymeric Brønsted acid catalyst that is not only stable in water but also completely soluble in it is highly desirable [13–15].

Xanthenes, especially benzoxanthenes, are an important and very useful class of intermediates in organic synthesis because of their wide range of biological and pharmaceutical properties, such as antibacterial [16], antiviral [17], and anti-inflammatory activities [18], and being sensitizers in photodynamic therapy for destroying tumor cells [19]. Also these heterocyclic compounds are widely used as leuco-dyes [20], pH-sensitive fluorescent materials for visualization of biomolecules [21], and in laser technology [22]. The reported methods for the synthesis of 14-aryl- or 14-alkyl-14*H*-dibenzo[*a,j*]xanthenes involve the mixing of 2-naphthol with aldehydes in the presence of an acidic catalyst such as AcOH-H<sub>2</sub>SO<sub>4</sub> [23], *p*-TSA [24], sulfamic

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Scheme 1



acid [25], molecular iodine [26, 27], LiBr [28], Amberlyst-15 [29], silica sulfuric acid [30–32], silica perchloric acid [31, 32], heteropolyacid [33, 34], wet cyanuric chloride [35],  $\text{BF}_3 \cdot \text{SiO}_2$  [36],  $\text{Yb}(\text{OTf})_3$  [37], alum [38], montmorillonite K-10 [39],  $\text{P}_2\text{O}_5/\text{Al}_2\text{O}_3$  [40], and ionic liquids [41–43]. In spite of the potential utility of the aforementioned routes for the synthesis of benzoxanthene derivatives, some of these methods suffer from at least one or more disadvantages, such as a long reaction time, relatively expensive reagents, use of toxic solvents and catalysts, requirement of excess of reagents/catalysts, harsh reaction conditions, unsatisfactory yield, and tedious workup procedures. Thus, the development of simple, convenient, and environmentally friendly approaches for the preparation of these pharmaceutically important compounds is still demanding.

In continuation of our interest in the synthesis of organic compounds from condensation of phenols with dialdehydes [44–50], we herein report an efficient and green procedure for the synthesis of aryl- or alkyl-14*H*-dibenzo[*a,j*]xanthenes using polyvinylsulfonic acid (PVSA) as a novel Brønsted acid catalyst in aqueous media (Scheme 1). To the best of our knowledge, synthesis of the title compounds in water is relatively sparse, and there is only one report on the application of PVSA catalyst for the Michael addition reaction in the literature [51]. PVSA has been a known compound for several decades; however, its catalytic activities have not been studied in more detail so far. PVSA is a strong aliphatic polymeric sulfonic acid and has high solubility in water and lower alcohols [52–54]. PVSA is a semi-solid material; however, it can be handled easily by preparing aqueous solutions. This polymeric catalyst is easily recovered from the reaction mixture, owing to its complete solubility in water, and it is ready to be used in further reactions with economic and ecological advantages.

## Results and discussion

Polymeric sulfonic acid is a strong polybasic acid comparable to sulfuric acid, and protons are considered to be localized along the polymer chain. Hence, the proton density in solutions may be locally concentrated, unlike in mineral acid. PVSA was prepared in two steps according to the known literature procedure with slight modification

[55, 56]. The key intermediate for its preparation is the sodium salt of polyvinylsulfonic acid (Na-PVSA), which can be prepared from the polymerization of sodium vinylsulfonate monomer using potassium persulfate and sodium bisulfite as an initiator system (number average molecular weight 53,000). The free acid (PVSA) was prepared by ion exchange technique. The DSC thermogram of Na-PVSA showed thermal stability up to 350 °C. The FT-IR spectrum of Na-PVSA showed two absorption peaks at 724 and 1,189  $\text{cm}^{-1}$ , which are assigned to the methylene groups ( $-\text{CH}_2-$ ) in polymer backbone and sulfonate groups, respectively. The absorption bands at 1,448 and 2,924  $\text{cm}^{-1}$  are attributed to  $-\text{CH}_2-$  bond deformation and stretching vibration, respectively.

The synthetic utility of PVSA catalyst was explored by examining the reaction of 2-naphthol (2 mmol) and 4-chlorobenzaldehyde (1 mmol) as a model substrate in different solvents, and the results are presented in Table 1. Initial screening studies identified water at 90 °C and 20 mol% of PVSA catalyst loading as the optimal solvent for this reaction, and the desired product was obtained in high yield (93%) within 1 h of reaction time. To show the

**Table 1** The effect of solvent on the reaction of 2-naphthol and 4-chlorobenzaldehyde (**2d**) in the presence of 20 mol% of PVSA at 90 °C

Entry	Solvent <sup>a</sup>	Time/h	Yield/% <sup>d</sup>
1	EtOH	8	41
2	MeOH	8	35
3	DMSO	8	29
4	DMF	8	26
5	<i>i</i> -PrOH	8	33
6	$\text{CH}_3\text{CN}$	8	25
7	$\text{H}_2\text{O}$	1	93
8	– <sup>b</sup>	4	60
9	$\text{H}_2\text{O}^c$	10	0

<sup>a</sup> 3  $\text{cm}^3$  solvent

<sup>b</sup> The reaction was run under solvent-free conditions at 90 °C

<sup>c</sup> The reaction was run in the absence of PVSA under reflux conditions

<sup>d</sup> Isolated yield

effect of polyvinyl sulfonic acid, the reaction of 2-naphthol and 4-chlorobenzaldehyde (molar ratio 2:1) was examined in the absence of the catalyst. However, this reaction did not proceed, and hardly any product was detected after 10 h under reflux conditions in water (Table 1, entry 9).

Based on the optimized conditions in the reaction of 2-naphthol and 4-chlorobenzaldehyde using PVSA as catalyst, we also tested the catalytic activity of different acidic catalysts for comparing the efficiency of PVSA, and we

**Table 2** Effect of acidic catalyst (20 mol%) on the reaction of 2-naphthol (**1**, 2 mmol) and 4-chlorobenzaldehyde (**2d**, 1 mmol) in water

Entry	Catalyst	Time/h	Yield/%
1	NH <sub>4</sub> Cl	8	22
2	NaHSO <sub>3</sub>	8	18
3	NaHSO <sub>4</sub>	8	21
4	(NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>	8	Trace
5	Fe(HSO <sub>4</sub> ) <sub>3</sub>	8	Trace
6	KAl(SO <sub>4</sub> ) <sub>2</sub> ·12H <sub>2</sub> O <sup>a</sup>	4	90
7	<i>p</i> -TsOH	8	51
8	Silica sulfuric acid	6	64
9	I <sub>2</sub>	8	Trace
10	Montmorillonite K-10	8	35
11	H <sub>2</sub> SO <sub>4</sub>	8	20
12	PVSA	1	93

<sup>a</sup> 50 mol% was used

obtained low to moderate yields in water (Table 2). All the reactions were run in the same reaction conditions, and similar amounts of catalysts (20 mol%) were used. As can be seen in Table 2, PVSA catalyzes the reaction better than other catalysts, and satisfactory results were obtained only with PVSA (entry 12). The reason is that a huge excess of acidic groups is present along the polymer chain of PVSA, and the proton density in solution is locally concentrated; as a result, the reaction takes place only in the neighborhood of the polymer molecule.

Encouraged by the remarkable results obtained with the above reaction conditions, and in order to show the generality and scope of this new protocol, we used several aromatic and aliphatic aldehydes and 2-naphthol in the presence of PVSA in water. The results obtained are summarized in Table 3. Aromatic aldehydes carrying different functional groups were subjected to the reaction, and in all cases the desired product was synthesized in high yields and short reaction times (Table 3, entries 1–13). Another advantage of this method is its efficiency for the high yield synthesis of 14-alkyl-14*H*-dibenzo[*a,j*]xanthenes from aliphatic and cycloaliphatic aldehydes (Table 3, entries 14–17). The workup procedure is simple and includes filtration of the mixture to separate the product, and the aqueous solution was saved for the next reaction. Compared with traditional homogeneous Brønsted acid catalysts, it is easy for PVSA to be reused, which is prior to the conventional homogeneous acid catalysts. Hence, we

**Table 3** Synthesis of 14-aryl- or 14-alkyl-14*H*-dibenzo[*a,j*]xanthenes **3a–3q** catalyzed by PVSA using different aldehydes **2** and 2-naphthol (**1**)

Entry	R	Time/h	Prod.	Yield/% <sup>a</sup>	M.p./°C	Lit. m.p./°C
1	C <sub>6</sub> H <sub>5</sub>	1.5	<b>3a</b>	91	184–185	185 [33]
2	4-MeC <sub>6</sub> H <sub>4</sub>	2	<b>3b</b>	90	228	229 [33]
3	4-MeOC <sub>6</sub> H <sub>4</sub>	1.5	<b>3c</b>	90	203–204	204 [33]
4	4-ClC <sub>6</sub> H <sub>4</sub>	1	<b>3d</b>	93	289–290	289 [33]
5	2-ClC <sub>6</sub> H <sub>4</sub>	1.5	<b>3e</b>	90	214–216	215 [33]
6	4-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	2	<b>3f</b>	92	310–311	310 [33]
7	2-O <sub>2</sub> NC <sub>6</sub> H <sub>4</sub>	2.5	<b>3g</b>	90	213–214	213 [33]
8	4-BrC <sub>6</sub> H <sub>4</sub>	2	<b>3h</b>	90	297–298	297 [33]
9	4-HOC <sub>6</sub> H <sub>4</sub>	1.5	<b>3i</b>	91	261–262	263 [28]
10	4-NCC <sub>6</sub> H <sub>4</sub>	1.5	<b>3j</b>	88	293–294	291–292 [37]
11	4-OHCC <sub>6</sub> H <sub>4</sub>	2	<b>3k</b>	86	309–310	309–312 [39]
12	4-MeO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub>	1.5	<b>3l</b>	91	249–250	249–250 [42]
13	4-FC <sub>6</sub> H <sub>4</sub>	1.5	<b>3m</b>	90	238–239	238–240 [38]
14	CH <sub>3</sub> CH <sub>2</sub>	2.5	<b>3n</b>	83	149–150	152 [43]
15	CH <sub>3</sub> CH <sub>2</sub> CH <sub>2</sub>	3	<b>3o</b>	82	154–155	155–157 [36]
16	(CH <sub>3</sub> ) <sub>2</sub> CH	3	<b>3p</b>	79	152–153	152–154 [36]
17	C <sub>6</sub> H <sub>11</sub>	4.5	<b>3q</b>	78	173–174	174–175 [57]

Reaction conditions: aldehyde **2** (1 mmol), 2-naphthol (**1**, 2 mmol), PVSA (20 mol%), 3 cm<sup>3</sup> water, 90 °C

<sup>a</sup> Isolated yields

**Table 4** Reuse of PVSA for synthesis of **3d**

Run	1	2	3	4	5
Yield/% <sup>a</sup>	93	91	89	87	84

Reaction conditions: **2d** (1 mmol), 2-naphthol (**1**, 2 mmol), and PVSA (20 mol%) in 3 cm<sup>3</sup> water at 90 °C

<sup>a</sup> Isolated yield

decided to study the catalytic activity of recycled Brønsted-acidic PVSA for the synthesis of **3d**. After the separation of product, the filtrate containing catalyst was evaporated to remove water, and the resulting catalyst was reused directly for the next run. As shown in Table 4, the Brønsted-acidic PVSA can be recycled at least five times without any treatment and without a significant decrease in catalytic activity. The yields ranged from 93 to 84%.

We also studied the reaction between terephthalaldehyde (1 mmol) and excess amounts of 2-naphthol (4 mmol); we expected that both of the formyl groups on the aromatic ring of terephthalaldehyde would react with 2-naphthol. However, we observed that one of the formyl groups was condensed with 2-naphthol and another group was intact because of steric effects between *o*-hydrogens of the benzene ring and the xanthene ring (Scheme 2).

Based on the experimental results and by referring to the literature [24, 25, 30], the mechanism of the dibenzoxanthene formation proceeds by the usual pathway proposed using acidic catalysts.

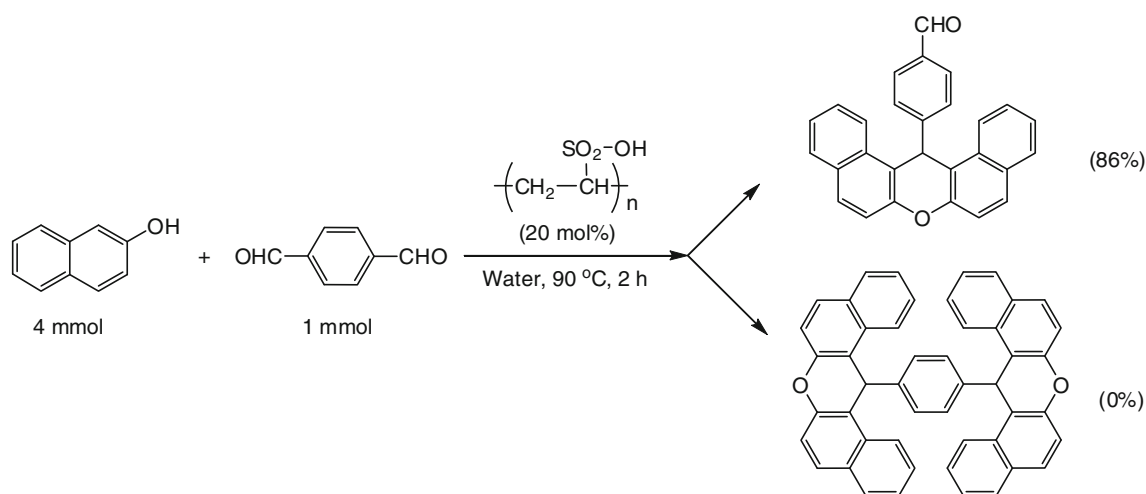
## Conclusion

In conclusion, we successfully developed a new, efficient, and eco-friendly method for the preparation of 14-aryl- or

14-alkyl-14*H*-dibenzo[*a,j*]xanthene derivatives using PVSA that can be prepared by a simple operation from commercially available and relatively cheap starting monomer. The notable advantages of this methodology are short reaction times, the easy purification of the products by simple filtration and crystallization, generality, and the use of water as solvent. The unique acid properties, easy handling, and catalytic performance of PVSA as a Brønsted polymeric acid catalyst will allow the development of methods for a variety of organic transformations. To the best of our knowledge, this protocol is the first report on the synthesis of the title compounds using polymeric Brønsted acid catalyst in aqueous media. Recovery and reuse of PVSA catalyst are also satisfactory, demonstrating the cost effectiveness and green aspect of our methodology.

## Experimental

The monomer and starting materials were purchased from Fluka and Merck chemical companies and used without purification. PVSA was prepared according to the reported procedure with slight modification [55, 56]. Viscosity measurements were carried out using an Ubbelohde viscometer. Differential scanning calorimetry (DSC) was performed on a Stanton STA-625 instrument. FT-IR spectra were run on a Shimadzu FTIR-8300 spectrophotometer. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded on a Bruker Avance DPX instrument (250 MHz) using TMS as internal standard. The progress of the reactions was followed by TLC on silica gel Polygram SIL/UV 254 plates. Elemental analyses were performed using a Heraeus CHN-O-Rapid analyzer, and the results agreed favorably with calculated values.



**Scheme 2**

### Preparation of sodium salt of polyvinylsulfonic acid (Na-PVSA)

A mixture of 20 g sodium vinylsulfonate solution (50% w/w, 10 g of sodium vinylsulfonate), 0.088 g potassium persulfate, and 0.033 g sodium bisulfite was made in a Teflon vessel. The vessel was evacuated and pressured repeatedly with nitrogen, and then sealed. The sealed Teflon vessel was rotated in a bath at 15 °C for 48 h. The resulting viscous oil was dissolved in 45 cm<sup>3</sup> water and precipitated with 60 cm<sup>3</sup> methanol. Na-PVSA (7.54 g) was obtained after drying in vacuo over P<sub>2</sub>O<sub>5</sub>.

### General experimental procedure for the synthesis of 14-aryl- or 14-alkyl-14H-dibenzo[a,j]xanthenes

A mixture of 2-naphthol (2 mmol), aldehyde (1 mmol), and 43.2 mg PVSA (50% w/w, 20 mol%, 0.2 mmol) in 3 cm<sup>3</sup> water was heated at 90 °C with stirring for the time shown in Table 3. The progress of the reaction was monitored by TLC (*n*-hexane/ethyl acetate, 3/1). After completion of the reaction, the reaction mixture was cooled to room temperature, and the precipitated product was filtered and finally washed with 2 × 20 cm<sup>3</sup> of cold and hot water, respectively. The xanthene product obtained was recrystallized from ethanol. The filtrate containing the polymeric catalyst was further evaporated to dryness, and the resulting catalyst was reused directly for the next run. The reactions using the recycled catalyst were conducted in a similar manner. All of the products are known compounds and were characterized by IR and NMR spectroscopy, and their melting points agreed with reported values.

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