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ORIGINAL PAPER

Phospho sulfonic acid as efficient heterogeneous Brønsted acidic catalyst for one-pot synthesis of 14*H*-dibenzo[*a*,*j*]xanthenes and 1,8-dioxo-octahydro-xanthenes

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A simple, efficient procedure for the preparation of phospho sulfonic acid $PO(OSO_3H)_3$ as a Brønsted acidic and recoverable heterogeneous catalyst is described, used for the one-pot synthesis of aryl-14*H*-dibenzo[*a*,*j*]xanthenes and 1,8-dioxo-octahydro-xanthenes. A cost-effective, simple and convenient procedure for the synthesis of aryl-14*H*-dibenzo[*a*,*j*]xanthenes was developed via a one-pot condensation from substituted benzaldehydes and β-naphthol under solvent-free conditions. The one-pot condensation of substituted benzaldehydes and 5,5-dimethyl-1,3-cyclohexanedione (dimedone) under solvent-free conditions leads to 1,8-dioxo-octahydro-xanthenes. These protocols afford a number of advantages, such as: excellent yields, very short reaction times, easy procedure, simple methodology and ease of preparation and regeneration of the catalyst.

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Keywords: phospho sulfonic acid, Brønsted acidic catalyst, aryl-14*H*-dibenzo[*a*,*j*]xanthenes, 1,8-dioxo-octahydro-xanthenes, solvent-free conditions, reuse of catalyst.

Introduction

Xanthenes and benzoxanthenes are an important category of organic compounds which have recently received a great deal of attention from organic and medical chemists due to their wide range of therapeutic and biological properties, including their antiviral (Lambert et al., 1997), antibacterial (Takeshiba & Jiyoujima, 1981) and anti-inflammatory activities (Poupelin et al., 1978). Furthermore, these compounds are used in laser technologies (Ahmad et al., 2002), fluorescent material in the visualisation of biomolecules (Knight & Stephens, 1989), as well as being widely used as dyes (Kitahara & Tanaka, 2002).

Many methods using the synthesis of xanthene and benzoxanthene have been reported in the literature, including cyclodehydration (Bigdeli et al., 2007; Nagarapu et al., 2007; Pasha & Jayashankara, 2007; Patil et al., 2007), cyclisation of polyclic aryl triflate esters (Wang & Harvey, 2002), trapping benzynes by phenols (Knight & Little, 1998), intermolecular phenyl carbonyl-coupling reactions of benzaldehydes and acetophenones (Kuo & Fang, 2001) and cyclocondensation between 2-hydroxy aromatic aldehydes and 2-tetralone (Jha & Beal, 2004). Different reagents have been employed for the synthesis of xanthenes and benzoxanthenes, such as $Al(HSO_4)_3$ (Shaterian et al., 2007), ZnO-NPs (Rao et al., 2012), PVPP-BF_3 (Mokhtary & Refahati, 2013), $H_5PW_{10}V_2O_{40}$ (Tayebee & Tizabi, 2012), imidazol-1-yl-acetic acid (Nazari et al., 2014), succinimide-*N*-sulfonic acid (Shirini & Khaligh, 2012), ceric ammonium nitrate (CAN) (Sivaguru & Lalitha, 2014), sulfonic acid functionalized imidazolium salts (SAFIS) (Zolfigol et al., 2012) and 1,3-disulfonic acid imidazolium hydrogen sulphate (Shirini et al., 2014) as catalysts. However, these methods suffer from certain drawbacks including longer reaction times (Khosropour et al., 2005; Dabiri et al., 2008; Tisseh et al., 2008), unsatisfactory yields (Khosropour et al., 2005; Saini et al., 2006; Dabiri et al., 2008; Tisseh et al., 2008), harsh reaction conditions and the use of toxic catalysts (Das et al., 2006).

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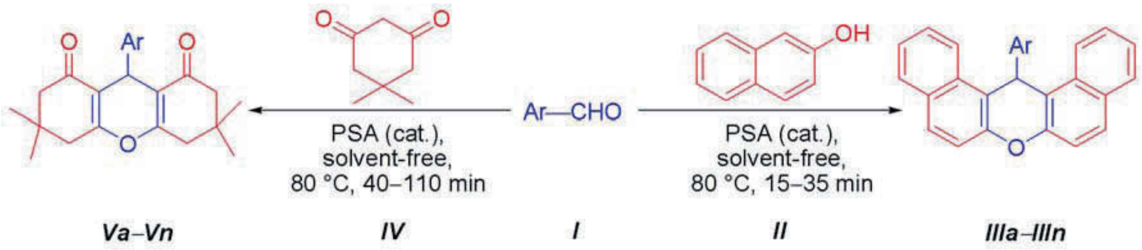


Fig. 1. One-pot synthesis of xanthene derivatives using PSA.

Hence, the development of a new catalyst for the synthesis of xanthenes and benzoxanthenes would be highly desirable. In the past, researchers have shown increasing interest in applying ionic liquids (ILs) to organic reactions, because ILs are excellent candidates as replacements for toxic and volatile organic compounds. The important features of these ILs include their tunable polarity, high thermal stability, immiscibility with a number of organic solvents, insignificant vapour pressure and ease of recyclability (Dupont et al., 2002; Sarkar et al., 2011; Zolfigol et al., 2011).

In organic synthesis, the use of solid acidic catalysts and solid-state reactions (or solvent-free reactions) has many advantages. For example, high efficiency and selectivity, operational simplicity, environmental compatibility, non-toxicity, reusability, low cost, ease of isolation and benefits for industry as well as the environment (Carrigan et al., 2001; Hajipour et al., 2008; Kiasat & Fallah-Mehrjardi, 2008; Hajinasiri & Rezayati, 2013; Karami et al., 2013; Zareyee et al., 2013; Rezayati et al., 2014; Sajjadifar & Rezayati, 2014; Zareyee & Serehneh, 2014).

The present work reports a new and simple method for the synthesis of aryl-14*H*-dibenzo[*a*,*j*]xanthenes *IIIa–IIIn* and 1,8-dioxo-octahydro-xanthene *V* using phospho sulfonic acid as a new, environmentally benign, heterogeneous, solid acid catalyst under solvent-free conditions (Fig. 1).

Experimental

General

All reagents were purchased from Aldrich (USA) or Merck Fine Chemicals (Germany) and were used without further purification. The IR spectra of the compounds were obtained using a Perkin-Elmer spectrometer (USA), version 10.03.06 using a KBr disk. ^{1}H NMR spectra were recorded on a Bruker DRX-300 AVANCE (Germany) spectrometer in $CDCl_3$ as a solvent and chemical shift values are given as parts per million (δ) relative to TMS as an internal standard. Thin-layer chromatography (TLC) was performed on pre-coated aluminium plates (silica gel 60 F254, Merck, Germany). The chromatographic spots on the plates were visualised under UV light and iodine vapour. Melting points were recorded on an electrothermal capillary melting point apparatus (UK) and are uncorrected.

Preparation of phospho-sulfonic acid

A 100 mL suction flask was equipped with a constant-pressure dropping funnel. The gas outlet was connected to a vacuum system through an adsorbing solution (water) and alkali trap. The flask was charged with diammonium hydrogen phosphate (4 g, 30 mmol) and chlorosulfonic acid (10.48 g, 90 mmol) in CH_2Cl_2 (10 mL) was added dropwise over a period of 45–60 min at ambient temperature. After completion of the addition, the mixture was shaken for 2 h, while the residual HCl was eliminated by suction. Next, the mixture was washed with CH_2Cl_2 (2 × 5 mL) to remove the unreacted chlorosulfonic acid (Fig. 2). Finally, phospho sulfonic acid was obtained as a solid white powder (8.50 g, 83 %); free-flowing powder could be stored at ambient temperature for several months without losing its catalytic potentiality.

Typical procedure for preparation of aryl-14H-dibenzo[a,j]xanthenes

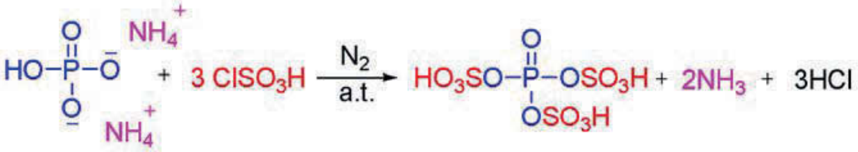
A mixture of β-naphthol (2.0 mmol), various aldehydes (1.0 mmol) and PSA (0.05 g, 7.0 mole %) was added and the mixture was kept in an oil bath at 80 °C for a certain time (Table 4). The progress of the reaction was monitored by TLC. After completion of the reaction (hexane : ethyl acetate, 8 : 2, vol.), the mixture was cooled to ambient temperature, and the reaction mixture was washed with $CHCl_3$ (10 mL) and filtered to recover the catalyst. Chloroform was evaporated from the reaction mixture. The solid product was purified by a recrystallisation procedure in aqueous ethanol. The structures of the products were identified from their spectral (IR, ^{1}H NMR and ^{13}C NMR) data.

Typical procedure for preparation of 1,8-dioxo-octahydro-xanthenes

The procedure was similar to that described for *III*, with the exception that β-naphthol was replaced with 5,5-dimethyl-1,3-cyclohexanedione.

Table 1. Spectral data of prepared compounds

Compound	Spectral data
IIIa	IR, $\tilde{\nu}/\text{cm}^{-1}$: 805, 1248, 1518, 1591, 1625, 3056 ^{1}HNMR ($CDCl_3$), δ: 5.39 (1H, s, CH), 7.30 (d, 2H, $J = 8.5$ Hz, ArH), 6.68–6.74 (4H, m, ArH), 5.89–6.80 (11H, m, ArH) ^{13}CNMR($CDCl_3$), δ: 38.03, 117.31, 118.01, 122.68, 124.23, 126.37, 126.78, 128.25, 128.47, 128.79, 128.85, 131.04, 131.44, 144.98, 148.71
IIIb	IR, $\tilde{\nu}/\text{cm}^{-1}$: 680, 744, 813, 1590, 1243, 1625, 3321 ^{1}HNMR ($CDCl_3$), δ: 5.34 (1H, s, CH), 6.16–6.48 (10H, m, ArH), 6.68–6.75 (4H, m, ArH), 7.19–7.22 (2H, m, ArH) ^{13}CNMR($CDCl_3$), δ: 37.46, 116.65, 118.01, 120.21, 122.39, 124.37, 126.92, 128.91, 129.11, 129.88, 131.04, 131.24, 131.58, 143.98, 148.67
IIIc	IR, $\tilde{\nu}/\text{cm}^{-1}$: 744, 810, 1242, 1513, 1592, 3065 ^{1}HNMR ($CDCl_3$), δ: 5.44 (1H, s, CH), 6.33–6.57 (8H, m, ArH), 6.71–6.76 (4H, m, ArH), 6.85–6.89 (2H, d, ArH), 7.16 (2H, d, $J = 8.3$ Hz, ArH) ^{13}CNMR($CDCl_3$), δ: 37.88, 115.75, 118.06, 122.04, 123.86, 124.58, 127.19, 128.96, 129.06, 129.59, 131.07, 146.27, 148.75, 152.01
IIIf	IR, $\tilde{\nu}/\text{cm}^{-1}$: 810, 1230, 1250, 1570, 1640, 3053 ^{1}HNMR ($CDCl_3$), δ: 2.49 (3H, s, OMe), 5.36 (1H, s, CH), 5. 60 (2H, d, $J = 8.66$ Hz, ArH), 6.32–6.45 (6H, m, ArH), 6.49–6.55 (2H, m, ArH), 6.69–6.76 (4H, m, ArH), 7.32 (2H, d, $J = 8.48$ Hz, ArH) ^{13}CNMR ($CDCl_3$), δ: 37.17, 55.05, 113.89, 117.58, 118.06, 122.77, 124.28, 126.81, 128.80, 128.87, 129.23, 131.13, 131.47, 137.45, 148.69, 157.89
IIIh	IR, $\tilde{\nu}/\text{cm}^{-1}$: 742, 836, 1240, 1450, 1510, 1580, 1625, 3044 ^{1}HNMR ($CDCl_3$), δ: 5.57 (1H, s, CH), 5.63 (1H, s, ArH), 5.78 (2H, d, $J = 8.56$ Hz, ArH), 6.16–6.21 (4H, m, ArH), 6.52 (2H, d, $J = 8.20$ Hz, ArH), 6.55–6.74 (4H, m, ArH), 7.55 (2H, d, $J = 8.54$ Hz, ArH) ^{13}CNMR ($CDCl_3$), δ: 34.2, 117.4, 118.0, 123.1, 124.5, 127.0, 128.4, 128.7, 129.1, 129.2, 130.5, 130.9, 131.5, 132.7, 132.8, 142.2, 148.9.
IIIk	IR, $\tilde{\nu}/\text{cm}^{-1}$: 748, 812, 1256, 1592, 1625, 3055 ^{1}HNMR ($CDCl_3$), δ: 5.69 (1H, s, CH), 5.82 (2H, d, $J = 5.19$, ArH), 6.27–6.40 (5H, m, ArH), 6.50 (2H, d, $J =$ 7.15 Hz, ArH), 6.55–6.67 (4H, m, ArH), 7.65 (2H, d, $J = 8.5$ Hz, d, ArH) ^{13}CNMR ($CDCl_3$), δ: 34.63, 118.02, 118.11, 123.46, 124.44, 126.93, 127.87-127.94, 128.66, 129.08, 129.60, 130.13, 130.89, 131.76, 131.81, 143.57, 148.95
Vb	^{1}H NMR ($CDCl_3$), δ: 0.98 (s, 6H, 2Me), 1.10 (s, 6H, 2Me), 2.14–2.46 (m, 8H,), 4.70 (s, 1H, CH), 7.17–7.26 (m, 4H, ArH) ^{13}C NMR ($CDCl_3$), δ: 27.2, 29.2, 31.4, 32.9, 40.7, 50.6, 115.1, 115.2, 128.1, 129.7, 131.9, 142.7, 162.5, 196.4
Vc	^{1}H NMR ($CDCl_3$), δ: 1.00 (s, 6H, 2Me), 1.09 (s, 6H, 2Me), 2.13–2.46 (m, 8H), 5.50 (s, 1H, CH), 7.22–7.26 (m, 1H, ArH), 7.37–7.45 (m, 2H, ArH), 7.75 (d, $J = 8$ 1 Hz, ArH) ^{13}C NMR ($CDCl_3$), δ: 27.5, 28.4, 28.9, 32, 40.7, 50.5, 114.1, 124.5, 127.1, 132, 138.1, 149.7, 163, 196.3



$$(NH_4)_2HPO_4 + 3\,ClSO_3H \xrightarrow[\text{a.t.}]{N_2} P(O)(OSO_3H)_3 + 2NH_3 + 3HCl$$

Fig. 2. Scheme of phospho sulfonic acid preparation.

Results and discussion

Phospho sulfonic acid as a new solid acid catalyst was reported by Kiasat et al. (2013) and it was used for the regioselective conversion of indazolo[1,2-*b*]-phthalazinetriones under solvent-free condition. Phospho sulfonic acid was readily prepared. This reaction included the addition of chlorosulfonic acid to diammonium hydrogen phosphate in CH_2Cl_2 under N_2 atmosphere at ambient temperature. This reaction was clean and easily performed, because HCl and NH_3 gases evolved instantly in the reaction vessel (Fig. 2).

First, the effect of catalyst-loading on the condensation between benzaldehyde (*I*) and β-naphthol (*II*) was investigated to afford *IIIa* under solvent-free conditions in order to better determine the role of PSA, as can be seen in Table 2. When reactions were carried out in the absence of a catalyst for long periods of time (180 min under solvent-free conditions), the yields of products were low (< 5 %) (Table 2, Entry 1). Better yields and shorter reaction times were obtained when the reaction was carried out in the presence of 0.05 g of the catalyst under solvent-free conditions (Table 2, Entry 4). It is worth noting that, when 0.1 g of the catalyst was used, the yield did not increase nor did the conversion time shorten (Table 2, Entry 5). It was observed that the reaction did not proceed at ambient temperature. Raising the reaction temperature proved

Table 2. Optimisation of PSA amount

Entry	Loading of catalyst/g	Time/min	Yield/%[a]
1	–	180	< 5
2	0.01	120	58
3	0.03	50	62
4	0.05	25	74
5	0.07	35	70
6	0.1	45	68

a) Yield of isolated products.

Table 3. Effect of temperature on synthesis of *IIIa*[a]

Entry	Temperature/ °C	Yield/%
1	60	78
2	80	84
3	100	76
4	120	68

a) Benzaldehyde (1 mmol) and β-naphthol (2 mmol) in presence of 0.05 g catalyst, under different thermal and solvent-free conditions.

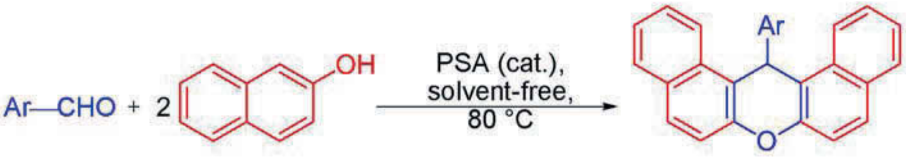
helpful, and the yield of the desired product increased considerably. The reaction proceeded smoothly and an almost complete conversion to the product was observed at 80 °C, affording 14*H*-dibenzo[*a*,*j*]xanthenes with 84 % yield within a short time (Table 3, Entry 2).

As anticipated, both aromatic aldehydes containing electron-donating as well as electron-withdrawing groups were used in the present case to form the corresponding benzoxanthenes *IIIa*–*IIIn* with high yields. In addition, as shown in Table 4, the reaction was performed with benzaldehyde containing electron-withdrawing as well as electron-donating groups, but benzaldehyde with electron-donating groups is generally more reactive than its equivalent with electron-withdrawing groups and affords the desired product in a short reaction time with an excellent yield (Table 4). This observation clearly shows that the preparation of benzoxanthenes is more strongly affected by electronic factors. This method was general and efficient; all reactions were successfully performed to furnish the corresponding 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes with high to excellent yields and in relatively short reaction times.

However, the reaction conducted by α-naphthol instead of β-naphthol did not afford any product. In Table 5, the results are compared with the results of some other procedures for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes. Table 5 clearly shows the current method for the synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthene derivatives to be simpler, more efficient and less time-consuming. The data show a comparison of the promising features of this method in terms of molar ratio of the catalyst, reaction time and yield of the product with those reported in the literature.

It was found that the catalyst could be reused a number of times without any appreciable loss of activity. This was demonstrated using benzaldehyde and β-naphthol under solvent-free conditions as a model reaction. After completion of the reaction, the reaction mixture was washed with $CHCl_3$ (10 mL) and filtered to recover the catalyst (Table 4, Entry 1 and Table 6, Entry 1). The proposed mechanism for the phos-

Table 4. PSA-catalysed efficient synthesis of aryl-14*H*-dibenzo[*a*,*j*]xanthenes[a]



Entry	Ar	Product	Time/min	Yield/%[b]	M.p./ °C	Reference
1	C_6H_5	*IIIa*	15	84 (83, 82, 80)[c]	178–179	Kumar et al. (2010)
2	4-BrC_6H_4	*IIIb*	20	78	291–293	Kumar et al. (2010)
3	4-$NO_2C_6H_4$	*IIIc*	25	76	307–308	Kumar et al. (2010)
4	3-$NO_2C_6H_4$	*IIId*	30	85	207–208	Kumar et al. (2010)
5	4-ClC_6H_4	*IIIe*	15	80	288–291	Kumar et al. (2010)
6	4-$OMeC_6H_4$	*IIIf*	15	81	204–205	Kumar et al. (2010)
7	4-OHC_6H_4	*IIIg*	30	74	141–143	Madhav et al. (2008)
8	2,4-ClC_6H_4	*IIIh*	20	76	255–256	Mahdavinia et al. (2009)
9	2-$NO_2C_6H_4$	*IIIi*	35	85	290–291	Rajitha et al. (2005)
10	3-BrC_6H_4	*IIIj*	30	81	186–187	Khosropour et al. (2005)
11	2-ClC_6H_4	*IIIk*	30	86	212–213	Khosropour et al. (2005)

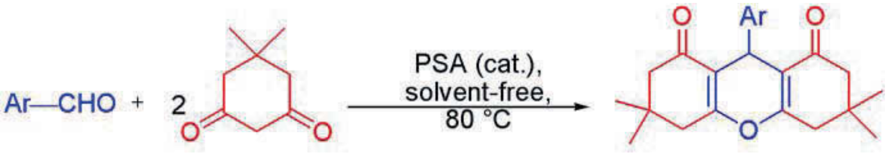
a) Reaction conditions: β-naphthol (2 mmol), aldehyde (1 mmol) in the presence of PSA under solvent-free condition at 80 °C; *b*) yield of isolated products; *c*) yield of isolated products after the catalyst recycling.

Table 5. Comparison of efficiency of various catalysts in synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes

Entry	Catalyst	Temperature/°C	Time/h	Yield/%^{a}	Reference
1	Sulphamic acid	125	6–12	90–95	Rajitha et al. (2005)
2	Selectfluor	125	6–12	90–95	Kumar et al. (2006)
3	Amberlyst-15	125	0.5–2	80–94	Ko and Yao (2006)
4	I_2	90	2–5	85–95	Das et al. (2006)
5	*p*-TSA	125	2.5–6	80–96	Khosropour et al. (2005)
6	*p*-TSA^b	80	15–24	85–95	Khosropour et al. (2005)
7	LiBr	130	1–1.2	80–84	Saini et al. (2006)
8	Silica sulfuric acid	80	0.5–2	80–96	Seyyedhamzeh et al. (2008)
9	Dowex-50W	100	1–2	78–91	Shakibaei et al. (2007)
10	This work	80	15–35 min	76–86^c	–
11	This work	80	40–110 min	75–89^d	–

a) Yield of isolated products; *b*) in CH_2Cl_2; *c*) reaction conditions: β-naphthol (2 mmol), aldehyde (1 mmol) in the presence of PSA under solvent-free condition at 80 °C; *d*) reaction conditions: dimedone (2 mmol), aldehyde (1 mmol) in the presence of PSA under solvent-free condition at 80 °C.

Table 6. PSA-catalysed efficient synthesis of 1,8-dioxo-octahydro-xanthenes



Entry	Ar	Product	Time/min	Yield/%^{a}	M.p./°C	Reference
1	C_6H_5	*Va*	50	86 (85, 84, 82)^b	202–203	Hasaninejad et al. (2012)
2	$\text{4-ClC}_6\text{H}_5$	*Vb*	90	89	228–229	Jin et al. (2004)
3	$\text{2-NO}_2\text{C}_6\text{H}_4$	*Vc*	100	84	172–174	Jin et al. (2004)
4	$\text{4-HOC}_6\text{H}_4$	*Vd*	90	85	242–243	Jin et al. (2005)
5	$\text{4-OCH}_3\text{-C}_6\text{H}_4$	*Ve*	40	78	239–240	Jin et al. (2004)
6	$\text{4-NO}_2\text{C}_6\text{H}_4$	*Vf*	90	79	221–223	Jin et al. (2005)
7	$\text{2,4-Cl}_2\text{-C}_6\text{H}_4$	*Vg*	110	81	250–251	Jin et al. (2004)
8	$\text{4-Me}_2\text{NC}_6\text{H}_4$	*Vh*	110	75	223–225	Horning and Horning (1964)
9	$\text{4-BrC}_6\text{H}_5$	*Vi*	100	86	233–234	Song et al. (2007)
10	$\text{2-ClC}_6\text{H}_4$	*Vj*	85	80	227–228	Zhang and Liu (2008)

a) Yield of isolated products; *b*) yield of isolated products after the catalyst recycling.

pho sulfonic acid-catalysed transformation is shown in Fig. 3. Concerning the reaction mechanism, it is suggested that, initially, a carbocation be formed (structure *VI*) and then aryl-methanebisnaphthols prepared (structure *VII*), which then undergo dehydration to afford the final product (structure *VIII*).

In another study, the reaction of 5,5-dimethyl-1,3-cyclohexanedione (*IV*) instead of β-naphthol (*II*) was carried out using various aromatic aldehydes such as those bearing electron-donating substituents, electron-withdrawing substituents or halogens on their aromatic rings under solvent-free conditions at 80 °C, which afforded 1,8-dioxo-octahydro-xanthene derivatives *Va*–*Vj* (Fig. 1, Table 6). The various aromatic aldehydes containing both electron-donating and electron-withdrawing groups and halogens on their aromatic rings afforded the corresponding products with good to high yields and in short reaction times (Table 6). Hence, the protocol was efficient and general.

Conclusions

In summary, a facile and economical method for the synthesis of aryl-14*H*-dibenzo[*a*,*j*]xanthenes and 1,8-dioxo-octahydro-xanthenes under solvent-free conditions using phospho sulfonic acid as an efficient, heterogeneous, solid acid catalyst. This simple method is important from both environmental and economical perspectives as it produces little waste. The present method possesses the advantages of, short reaction times, simplicity of reaction and reusability of the catalyst and non-chromatographic purification of products, i.e. simple recrystallisation from ethanol, as well as eliminating the use of corrosive liquid acids. The catalyst is readily available, inexpensive and can be conveniently handled and removed from the reaction mixture. This protocol could serve as a valuable alternative to the recognised reaction systems.

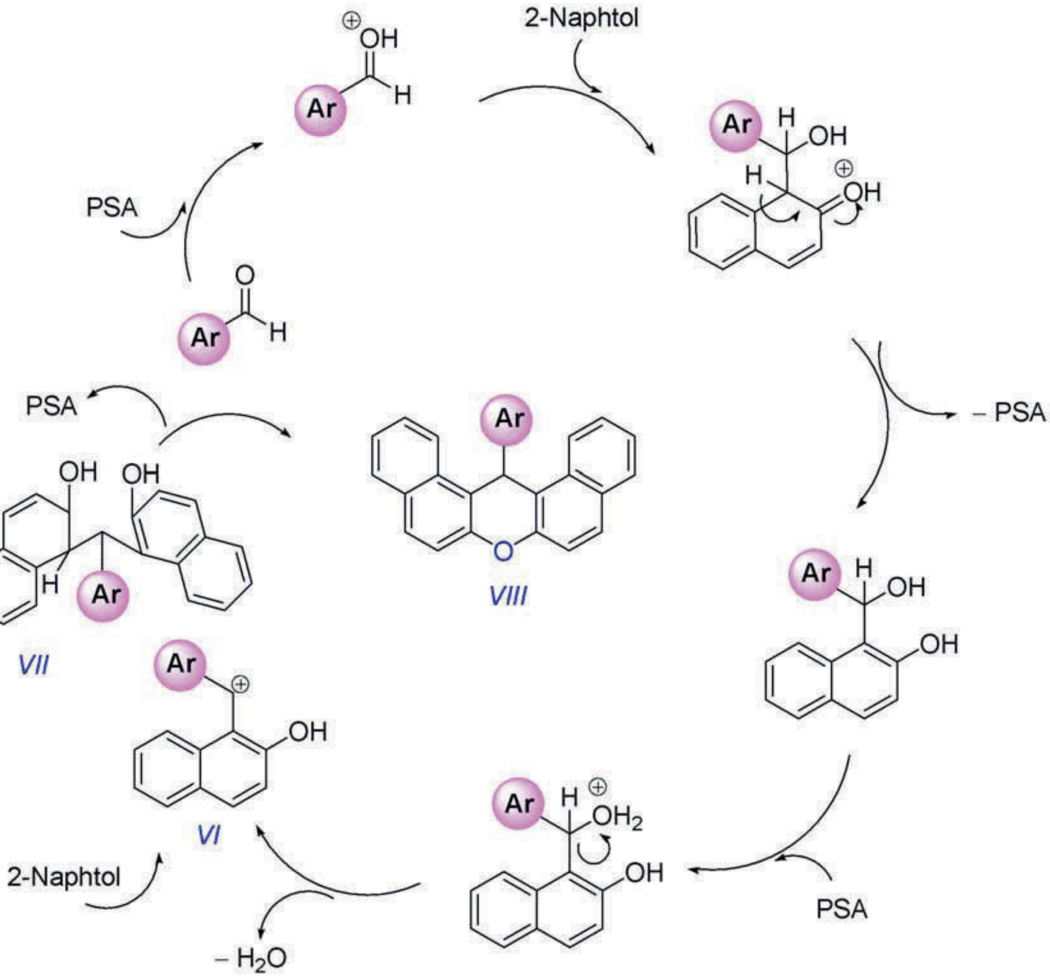


Fig. 3. Proposed mechanism for preparation of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthenes.

References

Ahmad, M., King, T. A., Ko, D. K., Cha, B. H., & Lee, J. M. (2002). Performance and photostability of xanthene and pyrromethene laser dyes in sol–gel phases. *Journal of Physics D: Applied Physics*, *35*, 1473–1476. DOI: 10.1088/0022-3727/35/13/303.

Bigdeli, M. A., Heravi, M. M., & Mahdavinia, G. H. (2007). Silica supported perchloric acid ($HClO_4$-SiO_2): A mild, reusable and highly efficient heterogeneous catalyst for the synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a*,*j*]xanthenes. *Journal of Molecular Catalysis A: Chemical*, *275*, 25–29. DOI: 10.1016/j.molcata.2007.05.007.

Carrigan, M. D., Eash, K. J., Oswald, M. C., & Mohan, R. S. (2001). An efficient method for the chemoselective synthesis of from aromatic aldehydes using bismuth triflate. *Tetrahedron Letters*, *42*, 8133–8135. DOI: 10.1016/s0040-4039(01)01756-7.

Dabiri, M., Azimi, S. C., & Bazgir, A. (2008). One-pot synthesis of xanthene derivatives under solvent-free conditions. *Chemical Papers*, *62*, 522–526. DOI: 10.2478/s11696-008-0050-y.

Das, B., Ravikanth, B., Ramu, R., Laxminarayana, K., & Rao, B. V. (2006). Iodine catalyzed simple and efficient synthesis of 14-aryl or alkyl-14*H*-dibenzo[*a*,*j*]xanthenes. *Journal of Molecular Catalysis A: Chemical*, *255*, 74–77. DOI: 10.1016/j.molcata.2006.04.007.

Dupont, J., de Souza, R. F., & Suarez, P. A. Z. (2002). Ionic liquid (molten salt) phase organometallic catalysis. *Chemical Reviews*, *102*, 3667–3692. DOI: 10.1021/cr010338r.

Hajipour, A. R., Khazdooz, L., & Ruoho, A. E. (2008). Brønsted acidic ionic liquid as an efficient catalyst for chemoselective synthesis of 1,1-diacetates under solvent-free conditions. *Catalysis Communications*, *9*, 89–96. DOI: 10.1016/j.catcom.2007.05.003.

Hajinasiri, R., & Rezayati, S. (2013). Solvent-free synthesis of 1,2-disubstituted derivatives of 1,2- dihydroisoquinoline, 1,2 dihydroquinoline and 1,2-dihydropyridine. *Zeitschrift für Naturforschung B*, *68*, 818–822. DOI: 10.5560/znb.2013-3095.

Hasaninejad, A., Dadar, M., & Zare, A. (2012). Silica-supported phosphorus containing catalysts efficiently promoted synthesis of 1,8-dioxo-octahydro-xanthenes under solvent-free conditions. *Chemical Science Transactions*, *1*, 233–238. DOI: 10.7598/cst2012.107.

Horning, E. C., & Horning, M. G. (1964). Methone derivatives of aldehydes. *The Journal of Organic Chemistry*, *11*, 95–99. DOI: 10.1021/jo01171a014.

Jha, A., & Beal, J. (2004). Convenient synthesis of 12*H*-benzo[*a*]xanthenes from 2-tetralone. *Tetrahedron Letters*, *45*, 8999–9001. DOI: 10.1016/j.tetlet.2004.10.046.

Jin, T. S., Zhang, J. S., Xiao, J. C., Wang, A. Q., & Li, T. S. (2004). Clean synthesis of 1,8-dioxo-octahydroxanthene derivatives catalyzed by *p*-dodecylbenezenesulfonic acid in aqueous media. *Synlett*, *5*, 866–870. DOI: 10.1055/s-2004-820022.

Jin, T. S., Zhang, J. S., Wang, A. Q., & Li, T. S. (2005). Solid-state condensation reactions between aldehydes and 5,5-dimethyl-1,3-cyclohexanedione by grinding at room temperature. *Synthetic Communications*, *35*, 2339–2345. DOI: 10.1080/00397910500187282.

Karami, B., Zare, Z., & Eskandari, K. (2013). Molybdate sulfonic acid: Preparation, characterization and application as an effective and reusable catalyst for octahydroxanthene-1,8-dione synthesis. *Chemical Papers*, *67*, 145–154. DOI: 10.2478/s11696-012-0263-y.

Khosropour, A. R., Khodaei, M. M., & Moghannian, H. (2005). A facile, simple and convenient method for the synthesis of 14-alkyl or aryl-14*H*-dibenzo[*a,j*]xanthenes catalyzed by pTSA in solution and solvent-free conditions. *Synlett*, *6*, 955–958. DOI: 10.1055/s-2005-864837.

Kiasat, A. R., & Fallah-Mehrjardi, M. (2008). $B(HSO_4)_3$: A novel and efficient solid acid catalyst for the regioselective conversion of epoxides to thiocyanohydrins under solvent-free conditions. *Journal of the Brazilian Chemical Society*, *19*, 1595–1599. DOI: 10.1590/s0103-50532008000800020.

Kiasat, A. R., Mouradzadegun, A., & Saghanezhad, S. J. (2013). Phospho sulfonic acid: A novel and efficient solid acid catalyst for the one-pot preparation of indazolo[1,2-*b*]-phthalazinetriones. *Journal of the Serbian Chemical Society*, *78*, 469–476. DOI: 10.2298/jsc120508088k.

Kitahara, Y., & Tanaka, K. (2002). Synthesis, crystal structure and properties of thiaheterohelicenes containing phenolic hydroxy functions. *Chemical Communications*, *2002*, 932–933. DOI: 10.1039/b110514k.

Knight, C. G., & Stephens, T. (1989). Xanthene-dye-labelled phosphatidylethanolamines as probes of interfacial pH. Studies in phospholipid vesicles. *Biochemical Journal*, *258*, 683–687.

Knignt, D. W., & Little, P. B. (1998). The first high-yielding benzyne cyclization using a phenolic nucleophile: A new route to xanthenes. *Synlett*, *1998*, 1141–1143. DOI: 10.1055/s-1998-1878.

Ko, S. K., & Yao, C. F. (2006). Heterogeneous catalyst: Amberlyst-15 catalyzes the synthesis of 14-substituted-14*H*-dibenzo[*a,j*]xanthenes under solvent-free conditions. *Tetrahedron Letters*, *47*, 8827–8829. DOI: 10.1016/j.tetlet.2006.10.072.

Kumar, P. S., Sunil Kumar, B., Rajitha, B., Narsimha Reddy, P., Sreenivasulu, N., & Thirupathi Reddy, Y. (2006). A novel one pot synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes catalyzed by selectfluor$^{\mathrm{TM}}$ under solvent free conditions. *Arkivoc*, *2006*, 46–50. DOI: 10.3998/ark.5550190.0007.c05.

Kumar, R., Nandi, G. C., Verma, R. K., & Singh, M. S. (2010). A facile approach for the synthesis of 14-aryl- or alkyl-14*H*-dibenzo[*a,j*]xanthenes under solvent-free condition. *Tetrahedron Letters*, *51*, 442–445. DOI: 10.1016/j.tetlet.2009.11.064.

Kuo, C. W., & Fang, J. M. (2001). Synthsis of xanthnes, indanes and tetrahydronaphthalenes via intramolecular phenyl-carbonyl coupling reactions. *Synthetic Communications*, *31*, 877–892. DOI: 10.1081/scc-100103323.

Lambert, R. W., Martin, J. A., Merrett, J. H., Parkes, K. E. B., & Thomas, G. J. (1997). International Patent No. WO9706178. The International Patent System.

Mokhtary, M., & Refahati, S. (2013). Polyvinylpolypyrrolidone-supported boron trifluoride (PVPP-BF_3): Mild and efficient catalyst for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*] xanthenes and bis(naphthalen-2-yl-sulfane) derivatives. *Dyes and Pigments*, 99, 378–381. DOI: 10.1016/j.dyepig.2013.05.023.

Madhav, J. V., Kuarm, B. S., & Rajitha, B. (2008). Dipyridine cobalt chloride: A novel and efficient catalyst for the synthesis of 14-aryl-14*H*-dibenzo[*a,j*]xanthenes under solvent-free conditions. *Arkivoc*, *2008*, 204–209. DOI: 10.3998/ark.5550190.0009.222.

Mahdavinia, G. H., Rostamizadeh, S., Amani, A. M., & Emdadi, Z. (2009). Ultrasound-promoted greener synthesis of aryl-14*H*-dibenzo[*a,j*]xanthenes catalyzed by $NH_4H_2PO_4$/SiO_2 in water. *Ultrasonics sonochemistry*, *16*, 7–10. DOI: 10.1016/j.ultsonch.2008.05.010.

Nagarapu, L., Kantevari, S., Mahankhali, V. C., & Apuri, S. (2007). Potassium dodecatungsto cobaltate trihydrate ($K_5CoW_{12}O_{40} \cdot 3H_2O$): A mild and efficient reusable catalyst for the synthesis of aryl-14*H*-dibenzo[*a,j*]xanthenes under conventional heating and microwave irradiation. *Catalysis Communications*, *8*, 1173–1177. DOI: 10.1016/j.catcom.2006.11.003.

Nazari, S., Keshavarz, M., Karami, B., Iravani, N., & Vafaee-Nezhad, M. (2014). Imidazol-1-yl-acetic acid as a novel green bifunctional organocatalyst for the synthesis of 1,8-dioxooctahydroxanthenes under solvent-free conditions. *Chinese Chemical Letters*, *25*, 317–320. DOI: 10.1016/j.cclet.2013.12.011.

Pasha, M. A., & Jayashankara, V. P. (2007). Molecular iodine catalyzed synthesis of aryl-14*H*-dibenzo[*a,j*]xanthenes under solvent-free condition. *Bioorganic & Medicinal Chemistry Letters*, *17*, 621–623. DOI: 10.1016/j.bmcl.2006.11.009.

Patil, S. B., Bhat, R. P., & Samant, S. D. (2006). Cation exchange resins: Efficient heterogeneous catalysts for facile synthesis of dibenzoxanthene from β-naphthol and aldehydes. *Synthetic Communications*, *36*, 2163–2168. DOI: 10.1080/00397910600639372.

Poupelin, J. P., Saint-Ruf, G., Foussard-Blanpin, O., Narcisse, G., Uchida-Ernouf, G., & Lacroix, R. (1978). Synthesis and anti inflammatory properties of bis (2-hydroxy-1-naphthyl)methane derivatives. *European Journal of Medicinal Chemistry*, *13*, 67–71.

Rajitha, B., Kumar, B. S., Reddy, Y. T., Reddy, P. N., & Sreenivasulu, N. (2005). Sulfamic acid: A novel and efficient catalyst for the synthesis of aryl-14*H*-dibenzo[*a,j*]xanthenes under conventional heating and microwave irradiation. *Tetrahedron Letters*, *46*, 8691–8693. DOI: 10.1016/j.tetlet.2005.10.057.

Rao, G. B. D., Kaushik, M. P., & Halve, A. K. (2012). An efficient synthesis of naphtha[1,2-*e*]oxazinone and 14-substituted-14*H*-dibenzo[*a,j*]xanthene derivatives promoted by zinc oxide nanoparticle under thermal and solvent-free conditions. *Tetrahedron Letters*, *53*, 2741–2744. DOI: 10.1016/j.tetlet.2012.03.085.

Rezayati, S., Hajinasiri, R., Erfani, Z., Rezayati, S., & Afshari-Sharifabad, S. (2014). Boric acid as a highly efficient and reusable catalyst for the one-pot synthesis of 1,8-dioxo-octahydroxanthenes under solvent-free conditions. *Iranian Journal of Catalysis*, *4*, 157–162.

Saini, A., Kumar, S., & Sandhu, J. S. (2006). A new LiBr-catalyzed, facile and efficient method for the synthesis of 14-alkyl or aryl-14*H*-dibenzo[*a,j*]xanthenes and tetrahydrobenzo[*b*]pyrans under solvent-free conventional and microwave heating. *Synlett*, *2006*, 1928–1932. DOI: 10.1055/s-2006-947339.

Sajjadifar, S., & Rezayati, S. (2014). Synthesis of 1,1-diacetates catalysed by silica-supported boron sulfonic acid under solvent-free conditions and ambient temperature. *Chemical Papers*, *68*, 531–539. DOI: 10.2478/s11696-013-0480-z.

Sarkar, A., Roy, S. R., Parikh, N., & Chakraborti, A. K. (2011). Nonsolvent application of ionic liquids: organo-catalysis by 1-alkyl-3-methylimidazolium cation based room-temperature ionic liquids for chemoselective *N-tert*-butyloxycarbonylation of amines and the influence of the C-2 hydrogen on catalytic efficiency. *The Journal of Organic Chemistry*, *76*, 7132–7140. DOI: 10.1021/jo201102q.

Seyyedhamzeh, M., Mirzaei, P., & Bazgir, A. (2008). Solvent-free synthesis of aryl-14*H*-dibenzo[*a*,*j*]xanthenes and 1,8-dioxo-octahydro-xanthenes using silica sulfuric acid as catalyst. *Dyes and Pigments*, *76*, 836–839. DOI: 10.1016/j.dyepig.2007.02.001.

Shakibaei, G. I., Mirzaei, P., & Bazgir, A. (2007). Dowex-50W promoted synthesis of 14-aryl-14*H*-dibenzo[*a*,*j*]xanthene and 1,8-dioxo-octahydroxanthene derivatives under solvent-free conditions. *Applied Catalalysis A: General*, *325*, 188–192. DOI: 10.1016/j.apcata.2007.03.008.

Shaterian, H. R., Ghashang, M., & Mir, N. (2007). Aluminium hydrogensulfate as an efficient and heterogeneous catalyst for preparation of aryl 14*H*-dibenzo[*a*,*j*]xanthene derivatives under thermal and solvent-free conditions. *Arkivoc*, *2007*, 1–10. DOI: 10.3998/ark.5550190.0008.f01.

Shirini, F., & Khaligh, N. G. (2012). Succinimide-*N*-sulfonic acid: An efficient catalyst for the synthesis of xanthene derivatives under solvent-free conditions. *Dyes and Pigments*, *95*, 789–794. DOI: 10.1016/j.dyepig.2012.06.022.

Shirini, F., Yahyazadeh, A., & Mohammadi, K. (2014). One-pot synthesis of various xanthene derivatives using ionic liquid 1,3-disulfonic acid imidazolium hydrogen sulfate as an efficient and reusable catalyst under solvent-free conditions. *Chinese Chemical Letters*, *25*, 341–347. DOI: 10.1016/j.cclet.2013.11.016.

Sivaguru, P., & Lalitha, A. (2014). Ceric ammonium nitrate supported HY-zeolite: An efficient catalyst for the synthesis of 1,8-dioxo-octahydroxanthenes. *Chinese Chemical Letters*, *25*, 321–323. DOI: 10.1016/j.cclet.2013.11.043.

Song, G. Y., Wang, B., Luo, H. T., & Yang, L. M. (2007). Fe^{3+}-montmorillonite as a cost effective and recyclable solid acidic catalyst for the synthesis of xanthenediones. *Catalysis Communications*, *8*, 673–676. DOI: 10.1016/j.catcom.2005.12.018.

Takeshiba, H., & Jiyoujima, T. (1981). Japan Patent No. 56005480. Tokyo, Japan: Japan Patent Office.

Tayebee, R., & Tizabi, S. (2012) Highly efficient and environmentally friendly preparation of 14-aryl-14*H* dibenzo[*a*,*j*]xanthenes catalyzed by tungsto-divanado-phosphoric acid. *Chinese Journal of Catalysis*, *33*, 962–969.

Tisseh, Z. N., Azimi, S. C., Mirzaei, P., & Bazgir, A. (2008). The efficient synthesis of aryl-5*H*-dibenzo[*b*,*i*]xanthene-5,7,12,14(13*H*)-tetraone leuco-dye derivatives. *Dyes and Pigments*, *79*, 273–275. DOI: 10.1016/j.dyepig.2008.04.001.

Wang J. Q., & Harvey, G. R. (2002). Synthesis of polycyclic xanthenes and furans via palladium catalyzed cyclization of polycyclic aryltriflate esters. *Tetrahedron*, *58*, 5927–5931. DOI: 10.1016/s1872-2067(11)60387-2.

Zareyee, D., Alizadeh, P., Ghandali, M. S., & Khalilzadeh, M. A. (2013). Solvent-free acetylation and tetrahydropyranylation of alcohols catalyzed by recyclable sulfonated ordered nanostructured carbon. *Chemical Papers*, *67*, 713–721. DOI: 10.2478/s11696-013-0369-x.

Zareyee, D., & Serehneh, M. (2014). Recyclable CMK-5 supported sulfonic acid as an environmentally benign catalyst for solvent-free one-pot construction of coumarin through Pechmann condensation. *Journal of Molecular Catalysis A: Chemical*, *391*, 88–91. DOI: 10.1016/j.molcata.2014.04.013.

Zhang, Z. H., & Liu, Y. H. (2008). Antimony trichloride/SiO_2 promoted synthesis of 9-ary-3,4,5,6,7,9-hexahydroxanthene-1,8-diones. *Catalysis Communications*, *9*, 1715–1719. DOI: 10.1016/j.catcom.2008.01.031.

Zolfigol, M. A., Vahedi, H., Massoudi, A., Sajjadifar, S., Louie, O., & Javaherneshan, N. (2011). Mild and efficient one pot synthesis of benzimidazoles from aldehydes by using BSA as a new catalyst. *Clinical Biochemistry*, *44*, S219. DOI: 10.1016/j.clinbiochem.2011.08.973.

Zolfigol, M. A., Khakyzadeh, V., Moosavi-Zare, A. R., Zare, A., Azimi, S. B., Asgari, Z., & Hasaninejad, A. (2012). Preparation of various xanthene derivatives over sulfonic acid functionalized imidazolium salts (SAFIS) as novel, highly efficient and reusable catalysts. *Comptes Rendus Chimie*, *15*, 719–736. DOI: 10.1016/j.crci.2012.05.003.