ISSN(PRINT) : 2320 -1967
ISSN(ONLINE) : 2320 -1975

GLOBAL SCIENTIFIC INC.

ChemXpress

ORIGINAL ARTICLE

CHEMXPRESS 8(3), 179-187, (2015)

An efficient and reusable catalyst for one-pot synthesis of dibenzoxanthene derivatives under solvent-free conditions based on p-sulfoanilino triazine

Meisam Shabanian[1]*, Hassan Moghanian[2]

[1]Faculty of Chemistry and Petrochemical Engineering, Standard Research Institute (SRI), P.O. Box 31745-139, Karaj, (IRAN)
[2]Department of Chemistry, Dezful Branch, Islamic Azad University, Dezful, (IRAN)
E-mail: m.shabanian@standard.ac.ir

Abstract : Tris(*p*-sulfoanilino)triazine (TSAT), readily prepared from the reaction of sulfanilic acid and cyanuric chloride, as a cheap and commercially available reagents, can be used as an easily reusable catalyst for one-pot condensation of 2-naphthol with aldehydes to construct dibenzoxanthene derivatives under solvent-free conditions. A variety of techniques including Fourier transform infrared spectroscopy (FTIR), nuclear magnetic resonance (NMR) and thermal gravimetric analysis (TGA) were used to characterize this solid acid catalyst. Simple and easy work-up, low cost, green process, short reaction times and excellent yields of the products are the advantages of this procedure. The catalyst was recovered by simple filtration and used several times with high catalytic activity.

Keywords : Tris(p-sulfoanilino)triazine; Zoxanthene; One-pot reaction; Solid acid; Solvent-free.

INTRODUCTION

Multi-bond-forming reactions, with three or more reactants combining in a one-pot procedure to give a new product, are an effective way for constructing different molecules. These reactions are finding increasing demands to be used as useful replacements for conventional linear-type syntheses in new technological applications, because of their high degree of atom economy, convergence, ease of execution and wide applications. One-pot/step strategies to access xanthenes and dibenzo[a,j]xanthenes, have attracted considerable attention over the years due to their diverse biological properties, such as antiviral[1], anti-inflammatory[2] and antibacterial activities[3], as well as their use as dyes and fluorescent materials[4-6]. In addition, xanthenes are found in a number of nature products, and most of them exhibit interesting biological activities. For example, blumeaxanthene *I* and 3-isopropyl-9amethyl-1,2,4a,9a-tetrahydroxanthene *II* have been isolated from compositae and fabaceae for use in traditional

ORIGINAL ARTICLE

Chinese and Indian medicine as a gynecological disorders[7] and antidote for all snake venoms[8] (Figure 1).

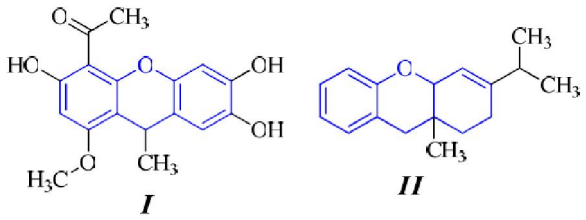


Figure 1 : Examples of natural xanthenes

According to these useful properties and related applications as above-mentioned, various methods are available for the construction of xanthenes and benzoxanthenes involving trapping of benzynes by phenols[9], cyclocondensation reaction between 2-hydroxyaromatic aldehydes and 2-tetralone[10], the reaction of aldehydes with 2-naphthol[11, 12], and intramolecular phenyl carbonyl coupling reactions of benzaldehydes and acetophenones[13]. Among them, condensation of 2-naphthol with alkyl or aryl aldehydes is the most important method. Xanthene synthesis by this procedure is catalyzed by many acidic catalysts, such as;*p*-toluenesulfonic acid[14], $HClO_4.SiO_2$[15], amberlyst-15[16], iodine[17], LiBr[18], silica sulfuric acid[19], $KAl(SO_4)_2.12H_2O$[20], $Yb(OTf)_3$[21], H_2SO_4/Ac_2O[13], montmorillonite K10[22], PEG-SO_3H[23], $K_5CoW_{12}O_{40}.3H_2O$[24], cyanuric chloride[25], sulfamic acid[26], cellulose sulfuric acid[27] and saccharin sulfonic acid[28]. Although these procedures provide an improvement, many of them suffer from disadvantages such as low yields, prolonged reaction times, harsh reaction conditions, need to excess amounts of the reagent and requirement of toxic solvents and catalysts. Another disadvantage of some of the existing methods is that the catalysts are destroyed during the work-up procedure and cannot be recovered and reused. Consequently, the introduction of efficient and green approaches using recoverable and reusable catalysts for the synthesis of these compounds is highly desirable.

Solvents are important in defining the environmental performance of industrial chemical processes and also have a significant impact on the associated costs and hazards. In recent times, exploration of solvent-free reactions has gained importance due to several advantages such as experimental simplicity, less energy requirement, and almost quantitative reactivity of the substrates due to intimacy of the reagents[29]. In continuation of our studies on the synthesis of various bioactive compounds herein[30-34], an efficient, facile, and convenient procedure for the synthesis of dibenzoxanthene derivatives was employed by the union of 2-naphthol and aldehydes in the presence of catalytic amount of tris(*p*-sulfoanilino)triazine (TSAT) as an environmentally benign and reusable organic catalyst under thermal solvent-free conditions.

EXPERIMENTAL

General

All chemicals were purchased from Merck or Fluka and used without further purification. Melting points were measured in capillary tubes on an electro thermal digital apparatus and are uncorrected. Known products were identified by comparison of their melting points and spectral data with those reported in the literature. The progress of reactions was monitored by thin-layer chromatography (TLC) using n-hexane/ EtOAc as an eluent. FTIR spectra were recorded on a Unicom Galaxy Series FT-IR 5000 spectrophotometer in the region 400-4000cm^{-1}, using pressed KBr discs. NMR spectra were recorded on Bruker Avance spectrophotometer (400 MHz), in $CDCl_3$ or DMSO-d_6, using TMS as internal standard. Thermal gravimetric analysis (TGA) and differential thermal gravimetric (DTG) data for TSAT were recorded on a Mettler TA4000 system under an N_2 atmosphere at a heating rate of 10 °C min^{-1}.

Preparation of the 2,4,6-tris(p-sulfoanilino) triazine (TSAT)

Cyanuric chloride (1.84 g, 10 mmol) dissolved in acetone (15 ml) was slowly added to a solution of sulfanilic acid (6.93 g, 40 mmol) dissolved in water (100 ml) at room temperature. The pH of the reaction mixture was maintained at 6 by the addition of aqueous Na_2CO_3 (2 M). Then, the reaction mixture was stirred under reflux conditions for 8 h.

ORIGINAL ARTICLE

After completion of the reaction, the mixture was cooled to room temperature. The pH of the reaction mixture was adjusted to 3 by the addition of HCl (2 M) and the mixture was stirred until the product precipitated. The resulting product was filtered, washed with water and dried at 60 °C under vacuum to give the title TSAT (5.06 g, 85%) as a white powder; FTIR (KBr): υ_{max}= 3392, 3298, 3017, 2821, 2592, 1709, 1576, 1501, 1441, 1353, 1289, 1115, 1076, 990, 789, 641 cm^{-1}; ^{1}H NMR (400 MHz, DMSO-d_6): δ= 9.53 (s, 3H, NH), 7.81 (d, *J*= 6.8 Hz, 6H, Ar-H), 7.61 (d, *J*= 7.0 Hz, 6H, Ar-H); ^{13}C NMR(100 MHz, DMSO-d_6): δ= 162.6, 142.6, 139.4, 125.9, 119.7; Anal. Calcd. For $C_{21}H_{18}N_6S_3O_9$: C, 42.42; H, 3.05; N, 14.13; S, 16.18. Found: C, 42.50; H, 3.09; N, 14.08; S, 16.25.

General procedure for synthesis of dibenzoxanthenes in the presence of TSAT catalyst

TSAT (0.03 g, 5 mol %) were added as a catalyst to a mixture of *β*-naphthol (2 mmol) and an aldehyde (1 mmol). The mixture was magnetically stirred under thermal solvent-free condition on a preheated oil bath at 120 °C for the appropriate time. After completion of the reaction, as indicated by TLC, the reaction mixture was cooled to room temperature. The crude product was heated in ethanol (30 mL) and the catalyst was removed by simple filtration. The pure product was obtained by cooling of the filtrate.

Compound 3n (TABLE 2, Entry 14): IR (KBr): υ_{max} = 3063, 2985, 2934, 2845, 1663, 1595, 1516, 1462, 1391, 1287, 1244, 1080, 804, 746 cm^{-1} ; ^{1}H NMR (400 MHz, $CDCl_3$): δ= 8.08 (d, *J* = 8.4 Hz, 2H), 7.91 (d, *J* = 8.2 Hz, 2H), 7.80 (d, *J* = 8.9 Hz, 2H), 7.67 (t, *J* = 7.1 Hz, 2H), 7.50 (t, *J* = 7.8 Hz, 2H), 7.35 (d, *J* = 8.9 Hz, 2H), 4.64 (s, 2H) ppm; ^{13}C NMR (75 MHz, $CDCl_3$): δ= 147.7, 132.3, 130.4, 128.9, 128.7, 127.4, 124.9, 123.5, 117.8, 111.7, 22.3 ppm; Anal. Calcd. For $C_{21}H_{14}O$: C, 89.34; H, 5.00. Found: C, 89.39; H, 5.05.

RESULTS AND DISCUSSION

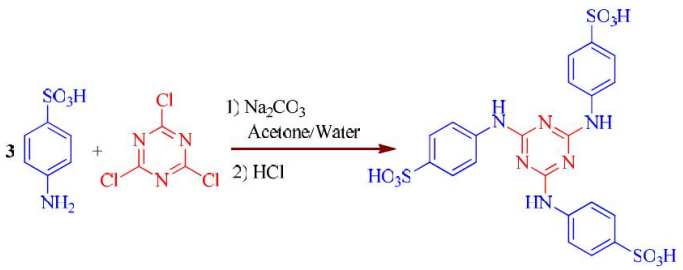
Preparation and characterization of the catalyst

TSAT was prepared by the reaction of cyanuric chloride (1 eq.) with sulfanilic acid (3 eq.) in the presence of sodium carbonate. Scheme 1 shows the preparation of the TSAT catalyst. The prepared catalyst was characterized by FTIR, elemental analysis, thermogravimetric analysis (TGA), ^{1}H and ^{13}CNMR.

FT-IR spectrum of TSAT is shown in Figure 2. Absorption bands appearing at 2600-3400 cm^{-1} (NH and OH stretching vibrations), 1576 cm^{-1} (C=N stretching vibrations of triazine ring), and 1501 cm^{-1} (stretching of aromatic C=C) confirmed the presence of amine, SO_3H and triazine groups in this compound. Furthermore, a strong bands at 1076 and 1115cm^{-1}in FT-IR is readily assigned to the SO_2 vibration of TSAT; which is normally observed in infrared spectra of sulfite derivatives as the strong bond.

The ^{1}H and ^{13}C NMR spectra of TSAT with peak assignments are shown in Figures 3 and 4. The resonance signals at 9.53 ppm and 7.61-7.81ppm in the ^{1}H NMR are ascribed to the protons of N-H groups (H_a) and aromatic carbon of benzene ring (H_b and H_c), respectively. Moreover, there are 5 peaks in the ^{13}C NMR spectrum for the proposed TSAT. The peaks at 162.6 ppm for the triazine ring (C_a in the ^{13}C NMR spectrum) and 142.6-119.7 ppm for the aromatic carbons of benzene ring clearly confirm that the TAST synthesized herein is consistent with the proposed structure.

The stability of the TSAT catalyst was deter-



Scheme 1 : Synthesis of the 2,4,6-tris(p-sulfoanilino)triazine (TSAT)

ORIGINAL ARTICLE

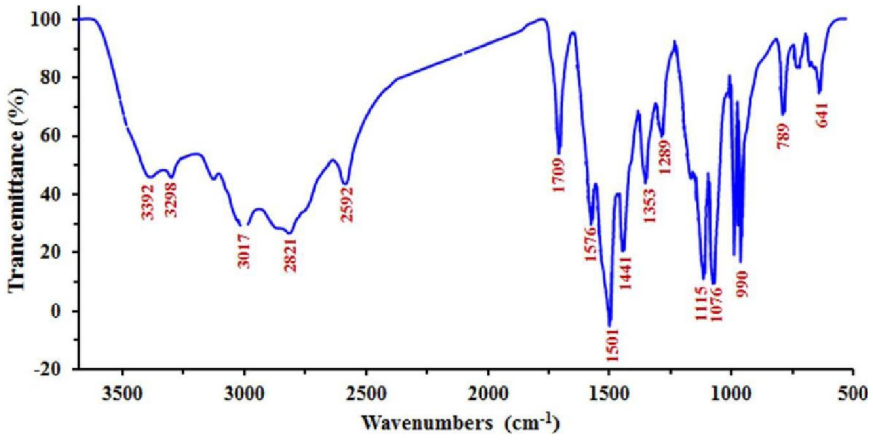


Figure 2 : FT-IR spectrum of the 2,4,6-tris(p-sulfoanilino)triazine (TSAT)

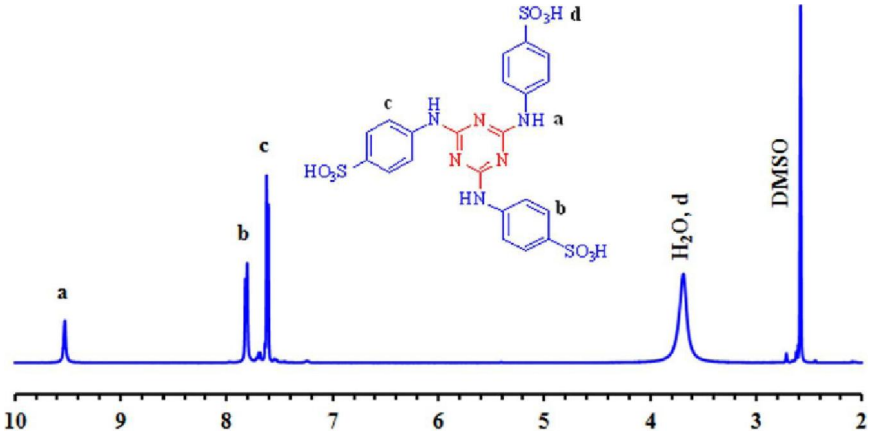


Figure 3 : ^{1}H-NMR spectrum of the 2,4,6-tris(p-sulfoanilino)triazine (TSAT)

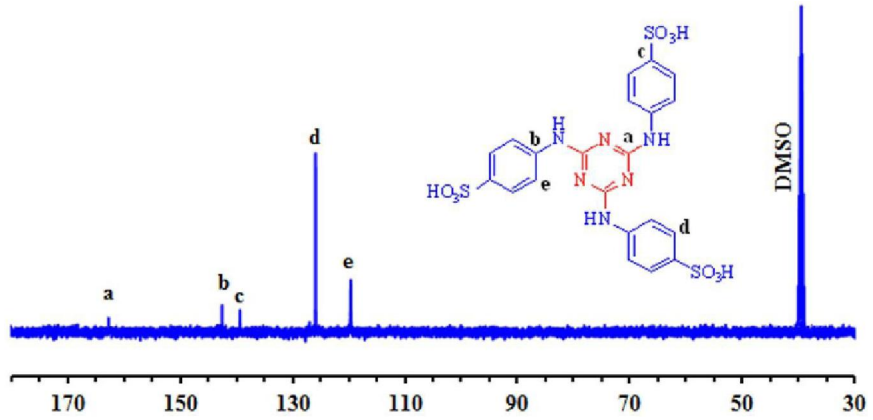


Figure 4 : ^{13}C-NMR spectrum of the 2,4,6-tris(p-sulfoanilino)triazine (TSAT)

mined by thermogravimetric analysis (TGA) and derivative thermo-gravimetry (DTG) (Figure 5). TGA thermogram was shown two weight loss steps. The first stage, including a low amount of weight loss at T < 350 °C, is due to the removal of physically adsorbed solvent and water, and the second step at about 350 °C to 550 °C is attributed to the decomposition of TSAT catalyst. The weight loss over the range 350–400 °C could be mainly attributed to the evaporation and subsequent decomposition of SO_3H groups. Furthermore, the DTG curve shows that the decomposition of the organic structure mainly occurred at 480 °C. Therefore, the TAST is stable around or below 350 °C.

Synthesis of 14-aryl or alkyl-14H-dibenzo[a,j]xanthene using TSAT

ORIGINAL ARTICLE

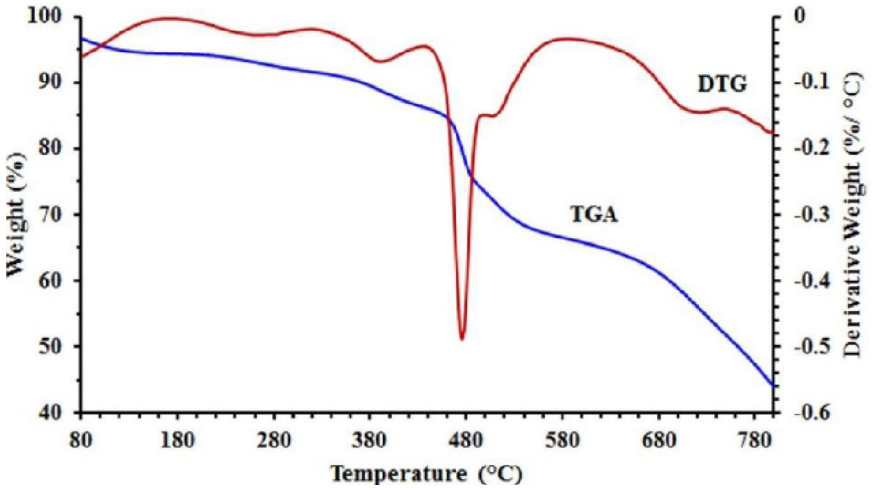
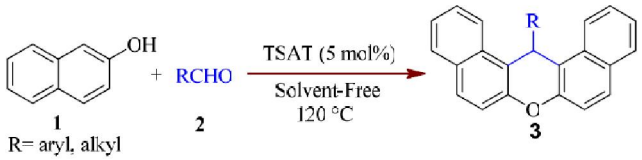


Figure 5 : TG-DTG analyses for 2,4,6-tris(p-sulfoanilino)triazine (TSAT)

On the basis of the information obtained from the above mentioned studies, we anticipated that 2,4,6-tris(p-sulfoanilino)triazine (TSAT) can be used as an efficient catalyst for the promotion of the reactions which need the use of an acidic catalyst to speed up. So we were interested to investigate the applicability of this reagent in the preparation of the dibenzoxanthene derivatives (Scheme 2).



Scheme 2 : Synthesis of dibenzoxanthene derivatives

Initially, in order to optimize the conditions for the synthesis of dibenzoxanthene derivatives, the reaction of benzaldehyde (1 mmol) with β-naphthol (2 mmol) was chosen as a model reaction and was conducted under different reaction parameters such as solvent and amount of catalyst. The model reaction was carried out in several solvents as well as under solvent-free conditions, to investigate the efficiency of the catalyst (TABLE 1). It was found that conventional heating at 120 °C under solvent-free conditions is more efficient than using organic solvents, with respect to reaction time and yield of the desired xanthene (TABLE 1, entry 8). Indeed in many cases, solid organic reactions occurred efficiently and more selectively than those of their solution counterparts. In addition, results indicated that when the reaction was done at room temperature in 24 h, the yield of the corresponding product was low (TABLE 1, entry 1).

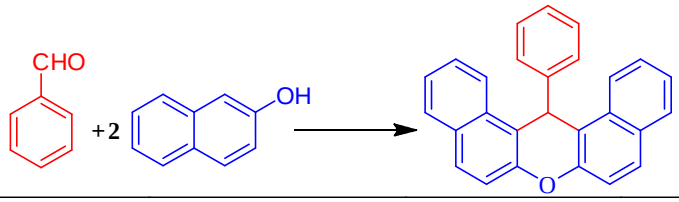
Effect of amount of the catalyst was also studied. Increasing the amount of catalyst did not show any improvement in the yield or reaction time (TABLE 1, entries 8-10). Moreover, the catalyst is essential and in the absence of the catalyst, only trace of the corresponding xanthene was produced even after prolonged reaction times (TABLE 1, entry 11). Finally, the efficiencies of different amount of sulfanilic acid as the catalyst towards the model reaction were compared and the results are depicted in TABLE 1. It was observed that TSAT was more efficient than the sulfanilic acid catalyst (entries 12, 13).

After optimization of the reaction conditions and in order to establish the effectiveness and the acceptability of the method, different substrates under the optimal conditions were synthesized. All reactions proceeded efficiently in the presence of catalytic amounts of TSAT at 120 °C and the desired products were obtained in good to excellent yields (40-95%) in relatively short reaction times, without formation of any side products.

As presented in TABLE 2, different aromatic aldehydes (containing electron withdrawing or electron-donating groups) were condensed with β-naphthol under the optimal conditions in high yields and very short reaction times. As can be seen, the nature of the substituents on the aromatic ring did not show strongly obvious effects in terms of yields and times under the selected reaction conditions. The aldehydes with Ortho or Meta substituents also deliv-

ORIGINAL ARTICLE

TABLE 1 : Optimization of the conditions for synthesis of 14-phenyl-14*H*-dibenzo[*a,j*]xanthene (TABLE 2, entry 1)[a]



Entry	Catalyst (mol%)	Solvent	Condition	Time	Yield (%)[b]
1	TSAT (5)	$ClCH_2CH_2Cl$	R.T.	24 h	15
2	TSAT (5)	$ClCH_2CH_2Cl$	Reflux	12 h	85
3	TSAT (5)	EtOH	Reflux	12 h	60
4	TSAT (5)	CH_3CN	Reflux	12 h	35
5	TSAT (5)	$CHCl_3$	Reflux	12 h	55
6	TSAT (5)	THF	Reflux	12 h	70
7	TSAT (5)	Solvent-Free	80 °C	30 min	47
8	TSAT (5)	Solvent-Free	120 °C	15 min	95
9	TSAT (2)	Solvent-Free	120 °C	30 min	77
10	TSAT (8)	Solvent-Free	120 °C	15 min	95
11	-	Solvent-Free	120 °C	4h	trace
12	SA (5) [c]	Solvent-Free	120 °C	15 min	38
13	SA (15)	Solvent-Free	120 °C	15 min	65

[a]Benzaldehyde (1 mmol), 2-naphthol (2 mmol); [b] Isolated yields; [c]SA = Sulfanilic Acid

TABLE 2 : Synthesis of dibenzoxanthene derivatives in presence of TSAT under solvent-free conditions

Entry	R (aldehyde)	Product	Time (min)	Yield (%)[a]	Mp (°C)	
					Found	Reported [lit.]
1	C_6H_5	3a	15	95	184-185	185[14]
2	2-ClC_6H_4	3b	20	88	214-215	214-216 [35]
3	4-$MeOC_6H_4$	3c	25	91	205-206	204-207[36]
4	4-BrC_6H_4	3d	20	92	294-296	295-296[37]
5	4-$NO_2C_6H_4$	3e	15	93	312-313	312-314[38]
6	4-FC_6H_4	3f	25	90	241-242	240-242 [37]
7	4-MeC_6H_4	3g	15	90	197-198	196-198 [39]
8	3-$MeOC_6H_4$	3h	25	92	203-204	204-205 [40]
9	3-$NO_2C_6H_4$	3i	20	91	210-212	211[14]
10	4-ClC_6H_4	3j	10	95	185-186	180-182 [39]
11	4-OHC_6H_4	3k	30	89	217-218	216-218 [41]
12	3,4,5-$(MeO)_3C_6H_2$	3l	25	87	193-194	192-193 [33]
13	Furfuryl	3m	20	84	201-202	198-200 [42]
14	2-OH-1-naphthyl	3n	35	40	204-206	-
15	CH_3CH_2	3o	30	80	153-154	150-152[43]
16	$(CH_3)_2CHCH_2$	3p	40	78	114-116	112-113[20]

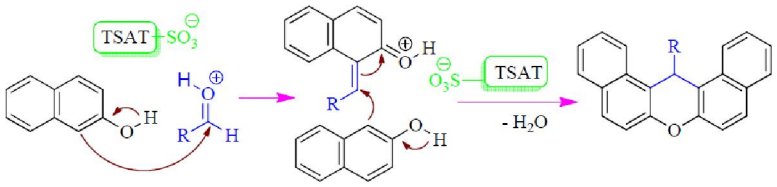
[a]Isolated yields.

ered the corresponding xanthenes in high yields (TABLE 2, entries 2, 8, 9, and 12). Similarly, aliphatic aldehydes such as propanal and 3-methylbutanal also were reacted under the same conditions and provided the desired products without any difficulties (TABLE 2, entries 15 and 16). In

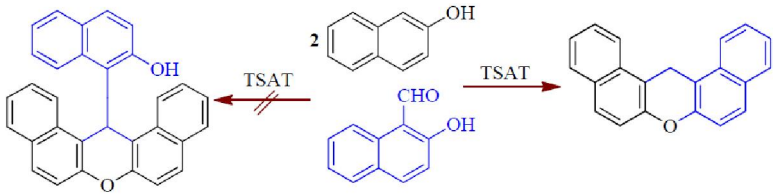
addition, the acid sensitive substrate thiophene-2-carbaldehyde gave the expected dibenzoxanthene 3m in good yield (TABLE 2, entry 13).

On the basis of the above observations and the literature reports, a plausible reaction pathway for the formation of dibenzoxanthene derivatives was depicted (Scheme 3). Phenol-aldehyde condensation in the presence of an acid catalyst was believed to proceed via a quinone methide (QM) intermediate[44], which has been used in many tandem processes[45] and[4+2] cyclo addition with a variety of dienophiles[46]. The reaction was done through the in situ formation of *ortho*-QM intermediates by nucleophilic addition of β-naphthol to the aldehyde. Aryl- or alkylmethane bisnaphthol was formed by the attack of 2-naphthol in second step. Elimination of water molecule take place from bisnaphthol to form final desired product 14-substituted-14*H*-dibenzo [*a,j*]xanthenes.

Among the condensation of aromatic aldehydes with 2-naphthol, 2-hydroxy-1-naphthaldehyde (TABLE 2, entry 14) was produced the 14*H*-dibenzo [*a,j*] xanthene instead of corresponding 14-(2-hydroxy-1-naphthyl)-14*H*-dibenzo [*a,j*] xanthene with 40% of yield. Probably, 2-hydroxy-1-naphthaldehyde condensed with 2-naphthol to produce the corre-



Scheme 3 : Proposed mechanism for the synthesis of dibenzoxanthene derivatives in the presence of TSAT under solvent-free conditions



Scheme 4 : Synthesis of 14*H*-dibenzo [*a,j*] xanthene

TABLE 3 : Comparison of TSAT with other catalysts reported in the literature for the synthesis of 14-phenyl-14*H*-dibenzo[*a,j*]xanthene.[a]

Entry	Catalyst (amount)	Condition	Time	Yield (%)[b]	Ref.
1	pTSA (10 mol%)	$ClCH_2CH_2Cl$ (r.t.)	20 h	91	[14]
2	DSIMHS (0.25 mmol)	Solvent-free, 90 °C	3 min	94	[47]
3	[Msim]BF_4 (10 mol%)	Solvent-free, 110 °C	8 min	88	[48]
4	[Et_3N-SO_3H]Cl (15 mol%)	Solvent-free, 120 °C	30 min	96	[38]
5	Sulfamic acid (10 mol%)	Solvent-free, 125 °C	8 h	93	[26]
6	Sulfuric acid (10 mol%)	CH_3COOH, 110-115 °C	1.5 h	91	[49]
7	Cellulose sulfuric acid (80 mg)	Solvent-free, 110-115 °C	1.5 h	81	[49]
8	Montmorillonitr K10 (300 mg)	Solvent-free, 120 °C	3 h	75	[50]
9	Amberlyst-15 (10 mg)	Solvent-free, 125 °C	2 h	94	[16]
10	Silica sulfuric acid (80 mg)	Solvent-free, 110-115 °C	1.5	89	[51]
11	Dowex-50W (100 mg)	Solvent-free, 100 °C	1.5	78	[52]
12	P(4-VPH)HSO_4 (10 mg)	Solvent-free, 100 °C	55 min	94	[35]
13	$HClO_4$–SiO_2 (20 mg)	Solvent-free, 125 °C	10 min	95	[15]
14	TSAT (5 mol%)	Solvent-free, 120 °C	15	95	This work

[a] **Reaction conditions: β-naphthol (2 mmol), benzaldehyde (1 mmol);** [b] **Isolated yields.**

ORIGINAL ARTICLE

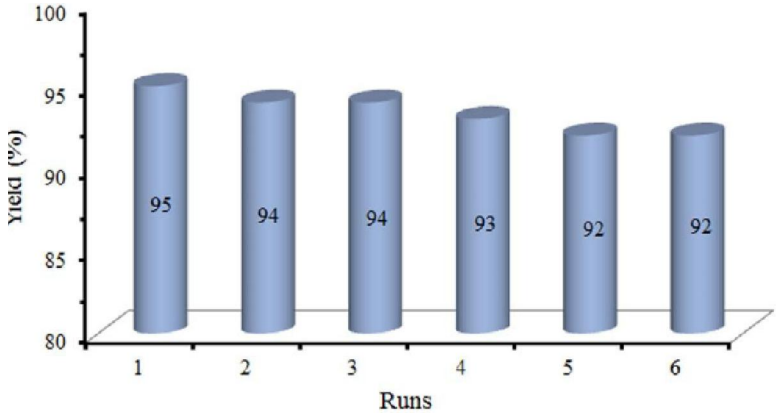


Figure 6 : Reusability of TSAT in the reaction of benzaldehdye (1 mmol), 2-naphthol (2 mmol), and catalyst (5 mol %) under solvent-free conditions

sponding *o*-QMs similar to other aromatic aldehydes through the suggested mechanism in Scheme 3. This intermediate furnished the 14*H*-dibenzo [*a,j*] xanthene upon an the intramolecular cyclization and oxidation-reduction reaction similar to Cannizzaro reaction (Scheme 4).

To compare the applicability and the efficiency of TSAT with the reported inorganic or organic catalysts for the synthesis of xanthenes, the results of these catalysts in the condensation reaction of benzaldehyde and β-naphthol under optimized conditions were tabulated (TABLE 3). It is clear that TSAT can act as an efficient and beneficial catalyst compared with the other mentioned reagents. For example, in TABLE 3, amount of the catalyst and reaction times in this work have been reduced relative to the other catalysts.

From the green chemistry point of view, efficient recovery and reuse of the catalyst are highly desirable, thus the recovery and reusability of TSAT was investigated in the sequential reaction of benzaldehdye (1 mmol) with 2-naphthol (2 mmol) under solvent-free conditions for 15 min at 120 °C. After completion of the reaction, the resulting solidified mixture was diluted with hot ethanol (30 mL). Then, the catalyst was easily separated using simple filtration, washed with hot ethanol, dried under vacuum and reused in a subsequent reaction. Nearly quantitative recovery of catalyst (up to 95%) could be obtained from each run. As seen in Figure 6, the recycled catalyst could be reused six times without any additional treatment or appreciable reduction in catalytic activity.

CONCLUSIONS

In conclusion, herein we described tris(*p*-sulfoanilino)triazineas an inexpensive, easily available, efficient, reusable and green catalyst for the synthesis of xanthenes in a simple one-pot protocol under solvent-free conditions with excellent yields. Several other advantages were found for using this catalyst such as: high reaction rates without by products; ease of catalyst synthesis; cost efficiency and effective recovery; reusability of the catalyst; synthesis of catalyst with very simple and cheap starting materials, low loading of catalyst and a simple experimental procedure.

REFERENCES

[1] J.M.Jamison, K.Krabill, A.Hatwalkar; *Cell.Biol.Int.Rep.*, **14**, 1075 **(1990)**.
[2] J.P.Poupelin et al.; *Eur.J.Med.Chem.*, **13**, 67 **(1978)**.
[3] J.P.Bacci, A.M.Kearney, D.L.V.Vranken; *J.Org.Chem.*, **70**, 9051 **(2005)**.
[4] M.Kamel, H.Shoeb; *Tetrahedron*, **20**, 491 **(1964)**.
[5] A.R.Katritzky, P.Czerney, J.R.Levell; *J.Org.Chem.*, **62**, 8198 **(1997)**.
[6] M.Nogradi; *Sci.Synth.*, **14**, 201 **(2003)**.
[7] L.Huang et al.; *Fitoterapia*, **81**, 389 **(2010)**.
[8] D.Thangadurai et al.; *Fitoterapia*, **72**, 92 **(2001)**.
[9] D.W.Knight, P.B.Little; *Synlett.*, 1141 **(1998)**.
[10] A.Jha, J.Beal; *Tetrahedron Lett.*, **45**, 8999 **(2004)**.
[11] J.A.Van Allan, D.D.Giannini, T.H.Whitesides; *J.Org.Chem.*, **47**, 820 **(1982)**.
[12] T.Ohishi et al.; *Tetrahedron Lett.*, **42**, 2493 **(2001)**.

[13] C.W.Kuo, J.M.Fang; *Synth.Commun.*, **31**, 877 **(2001)**.
[14] A.R.Khosropour, M.M.Khodaei, H.Moghannian; *Synlett*, 955 **(2005)**.
[15] M.A.Bigdeli, M.M.Heravi, G.H.Mahdavinia; *J.Mol.Catal.A: Chem.*, **275**, 25 **(2007)**.
[16] S.Ko, C.F.Yao; *Tedraherdon Lett.*, **47**, 8827 **(2006)**.
[17] B.Das et al.; *Journal of Molecular Catalysis A: Chemical*, **255**, 74 **(2006)**.
[18] A.Saini, S.Kumar, J.S.Sandhu; *Synlett.*, 1928 **(2006)**.
[19] M.Seyyedhamzeh, P.Mirzaei, A.Bazgir; *Dyes and Pigments*, **76**, 836 **(2008)**.
[20] M.Dabiri et al.; *Bioorg.Med.Chem.Lett.*, **18**, 436 **(2008)**.
[21] W.Su et al.; *Tetrahedron Letters*, **49**, 3391 **(2008)**.
[22] A.Sharifi et al.; *Synth.Commun.*, **38**, 2958 **(2008)**.
[23] M.N.K.Reddy et al.; *Molecules.*,**17**, 7543 **(2012)**.
[24] L.Nagarapu et al.; *Catalysis Communications*, **8**, 1173 **(2007)**.
[25] M.A.Bigdeli, M.M.Heravi, G.H.Mahdavinia; *Catal.Commun.*, **8**, 1595 **(2007)**.
[26] B.Rajitha et al.; *Tetrahedron Letters*, **46**, 8691 **(2005)**.
[27] J.Venu Madhav et al., *J.Mol.Catal.A: Chem.*, **304**, 85 **(2009)**.
[28] A.Zare et al.; *E-J.Chem.*, **9**, 1854 **(2012)**.
[29] P.J.Walsh, H.Li, C.A.De Parrodi; *Chem.Rev.*, **107**, 2503 **(2007)**.
[30] A.Mobinikhaledi, H.Moghanian, M.Deinavizadeh; *C.R.Chimie*, **16**, 1035 **(2013)**.
[31] H.Moghanian et al.; *RSC Adv.*, **4**, 28176 **(2014)**.
[32] H.Moghanian, M.Shabanian, H.Jafari; *C.R.Chimie*, **15(4)**, 346 **(2012)**.
[33] H.Moghanian, A.Mobinikhaledi, M.Deinavizadeh; *Res.Chem.Intermed.*, DOI: 10.1007/s11164, **(2014)**.
[34] N.Foroughifar, A.Mobinikhaledi, H.Moghanian; *Chemistry Letters*, **39**, 180 **(2010)**.
[35] N.Ghaffari Khaligh; *Ultrason.Sonochem.*, **19**, 736 **(2012)**.
[36] L.Khazdooz et al.; *Iran.J.Catal.*, **1**, 1 **(2011)**.
[37] J.Safaei-Ghomi, M.A.Ghasemzadeh; *Chin.Chem.Lett.*, **23**, 1225 **(2012)**.
[38] A.Zare et al.; *J.Mol.Liq.*, **167**, 69 **(2012)**.
[39] G.C.Nandi et al.; *Tetrahedron*, **65**, 7129 **(2009)**.
[40] M.M.Heravi et al.; *Mol.Divers.*, **14**, 621 **(2010)**.
[41] H.Moghanian, A.Mobinikhaledi, Z.Baharangiz; *J.Polym.Res.*, **21**, 513 **(2014)**.
[42] F.Shirini, N.G.Khaligh; *Dyes Pigm.*, **95**, 789 **(2012)**.
[43] M.Hong, C.Cai; *J.Fluorine Chem.*, **130**, 989 **(2009)**.
[44] A.Wolff et al.; *J.Org.Chem.*, **55**, 5665 **(1990)**.
[45] R.W.Van De Water, T.R.R.Pettus; *Tetrahedron*, **58**, 5367 **(2002)**.
[46] G.Desimoni, G.Tacconi; *Chem.Rev.*, **75**, 651 **(1975)**.
[47] F.Shirini, A.Yahyazadeh, K.Mohammadi; *Chin.Chem.Lett.*, **25**, 341 **(2014)**.
[48] M.A.Zolfigol, V.Khakyzadeh, A.R.Moosavi-Zare; *C.R.Chim.*, **15**, 719 **(2012)**.
[49] J.Venu Madhav et al.; *Journal of Molecular Catalysis A: Chemical*, **304**, 85 **(2009)**.
[50] M.Dabiri, S.C.Azimi, A.Bazgir; *Chem.Pap.*, **62**, 522 **(2008)**.
[51] M.Seyyedhamzeh, P.Mirzaei, A.Bazgir; *Dyes Pigm.*, **76**, 836 **(2008)**.
[52] G.Imani Shakibaei, P.Mirzaei, A.Bazgir; *Appl Catal A: Gen.*, **325**, 188 **(2007)**.